Supporting Information

Metal-Free carbenoid C–H insertion: A versatile strategy for constructing fluorenes with quaternary carbon centres

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General Methods and Materials

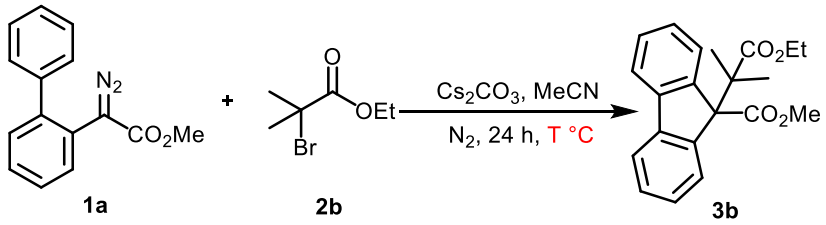
Unless specified, all reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. For reactions that require heating, the heat source is SCILOGEX (type: MS-H-Pro+) magnetic stirrer with metal heating module. Diazo compounds [1-3] were synthesized according to previous literatures. $KHCO_3$ (purity: 99%) was purchased from *Bidepharm*; MeCN (super dry, 99.7%) was purchased from *J&K*; all other reagents were purchased and used without further purification unless specified otherwise. Solvents for chromatography were technical grade and distilled prior to use.

Flash chromatography was performed using 200-300 mesh silica gel with the indicated solvent system according to standard techniques. Analytical thin-layer chromatography (TLC) was performed on pre-coated, glass-backed silica gel plates. Visualization of the developed chromatogram was performed by UV absorbance (254 nm).

^1H NMR and ^{13}C NMR data were recorded on Bruker 300 M nuclear resonance spectrometers unless otherwise specified, respectively. Chemical shifts (δ) are given in parts per million relatively to the solvent peak, and coupling constants (*J*) are given in hertz (Hz). The peaks around δ 7.26 (^1H NMR) and 77.16 (^{13}C NMR) correspond to $CDCl_3$. ^{13}C NMR spectra were recorded with total proton decoupling. Multiplicities are given as: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet). High resolution mass spectrometry (HRMS) analysis was performed using electrospray ionization (ESI) with a quadrupole-time of flight (QTOF) mass analyzer. HRMS (ESI) analysis was performed by The Analytical Instrumentation Center at College of Chemistry and Materials Science, Jinan University, and (HRMS) data were reported with ion mass/charge (m/z) ratios as values in atomic mass units.

Conditions Screening

Table 1 Temperature optimizations [a]

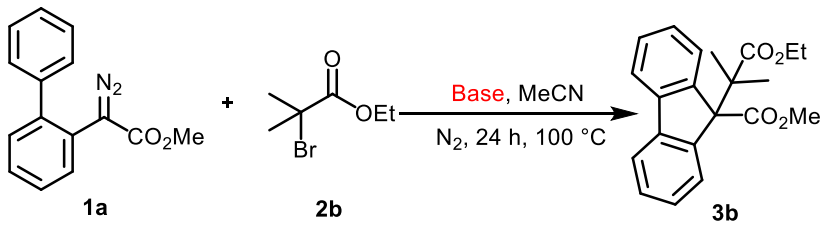


1a 2b 3b

Entry	Temperature (℃)	Yield of **3b**
1	80	18%
2	90	50%
3	**100**	**56%**
4	110	55%
5	120	50%

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (2.0 equiv.), Cs_2CO_3 (1.0 equiv.), MeCN (1.0 mL), under N_2, 24 h, and ^1H NMR yield.

Table 2 Base optimizations [a]

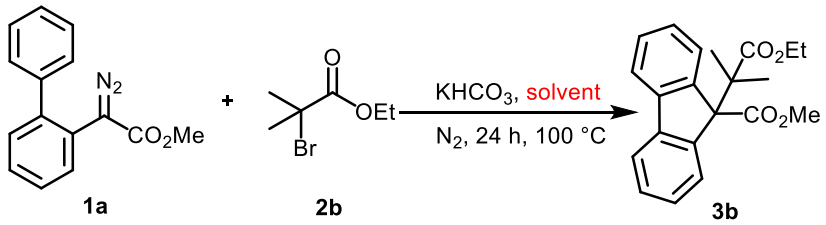


1a 2b 3b

Entry	Base	Yield of **3b**
1	**$KHCO_3$**	**71%**
2	Na_2CO_3	27%
3	K_2CO_3	70%
4	Cs_2CO_3	56%
5	^{t}BuONa	14%
6	K_3PO_4	40%
7	DIPEA	62%
8	DBU	18%

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (2.0 equiv.), base (1.0 equiv.), MeCN (1.0 mL), under N_2, 24 h, and ^1H NMR yield.

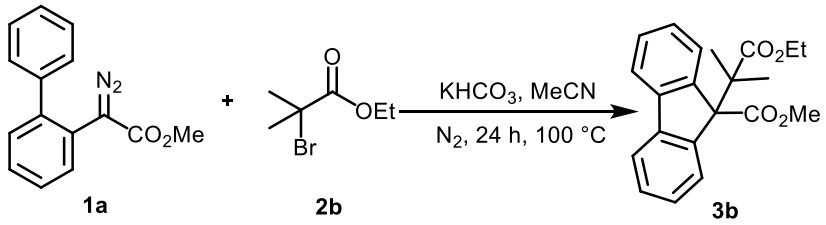
Table 3 Solvent optimizations [a]



Entry	Solvent	Yield of **3b**
1	1,4-dioxane	12%
2	**MeCN**	**71%**
3	DMSO	46%
5	PhMe	67%
6	DMF	69%
7	DME	45%

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (2.0 equiv.), $KHCO_3$ (1.0 equiv.), solvent (1.0 mL), under N_2, 24 h, and ^1H NMR yield.

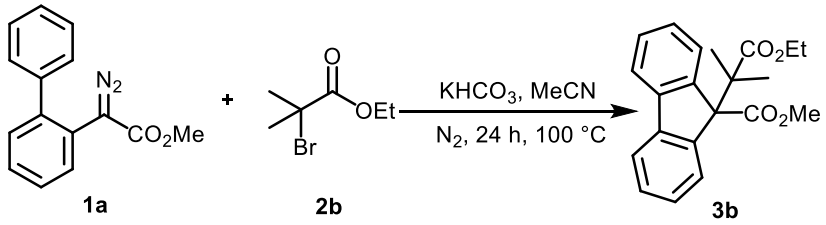
Table 4 Amounts of $KHCO_3$ [a]



Entry	Amounts of $KHCO_3$ (equiv.)	Yield of **3b**
1	0.5	41%
2	**1.0**	**71%**
3	1.5	71%
4	2.0	71%

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (2.0 equiv.), $KHCO_3$ (X equiv.), MeCN (1.0 mL), under N_2, 24 h, and ^1H NMR yield.

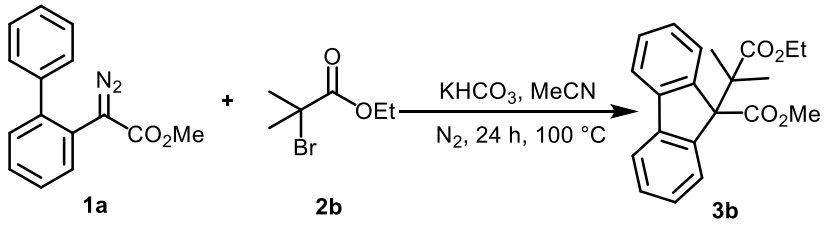
Table 5 Concentration optimizations [a]



Entry	Concentration (M)	Yield of **3b**
1	0.1	71%
2	0.2	66%
3	0.3	74%
4	**0.5**	**77%**
5	1.0	59%

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (2.0 equiv.), $KHCO_3$ (1.0 equiv.), MeCN, under N_2, 24 h, and ^1H NMR yield.

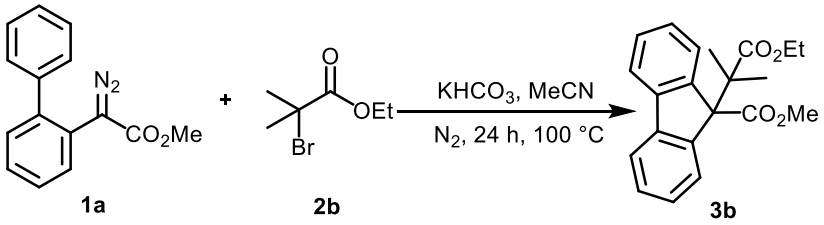
Table 6 Amounts of **1a** and **2b** [a]



Entry	Amounts of **1a** (equiv.)	Amounts of **2b** (equiv.)	Yield of **3b**
1	1.0	1.0	54%
2	1.0	1.2	61%
3	**1.0**	**1.5**	**79%**
4	1.0	2.0	77%
6	1.5	1.0	65%

[a] Reaction on a 0.1 mmol scale, using **1a** (X equiv.), **2b** (Y equiv.), $KHCO_3$ (1.0 equiv.), MeCN (0.2 mL), under N_2, 24 h, and ^1H NMR yield.

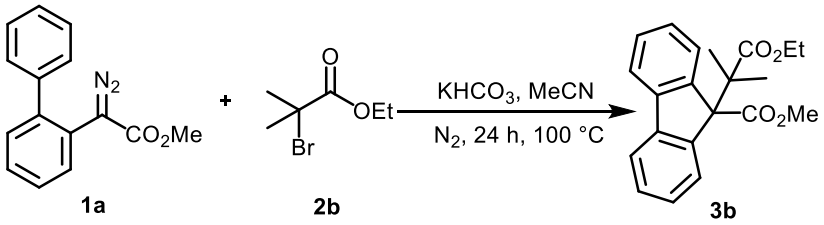
Table 7 Reaction time optimizations [a]



Entry	Time (h)	Yield of **3b**
1	8	49%
2	16	63%
3	**24**	**79%**
4	30	65%
5	48	64%

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (1.5 equiv.), $KHCO_3$ (1.0 equiv.), MeCN (0.2 mL), under N_2, and ^1H NMR yield.

Table 8 Control experiments [a]



Entry	Variation from standard conditions	Yield of **3b**
1	Without $KHCO_3$	N.D.
2	**None**	**79%**

[a] Reaction on a 0.1 mmol scale, using **1a** (1.0 equiv.), **2b** (1.5 equiv.), $KHCO_3$ (1.0 equiv.), MeCN (0.2 mL), under N_2, 24 h, and ^1H NMR yield.

Note:

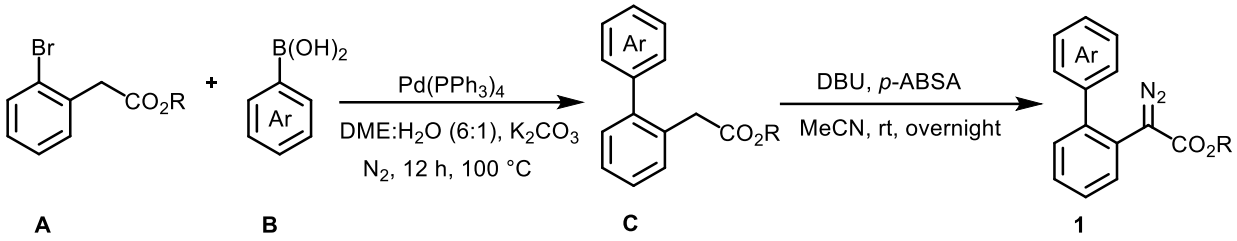
DBU = 1,8-diazabicyclo[5,4,0]undec-7-ene; DME = 1,2-dimethoxyethane;

DIPEA = N,N-diisopropylethylamine;

N.D. = not detected.

General Procedure

(I) Preparation of alkyl 2-(biaryl-2-yl)diazoacetates[2-3]

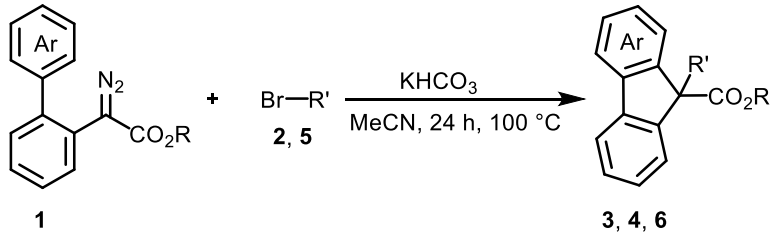


A **B** **C** **1**

To a solution of alkyl 2-(2-bromophenyl)acetate **A** (10 mmol, 1.0 equiv.) and $Pd(PPh_3)_4$ (0.1 mmol) dissolved in 40 mL DME (dimethoxyethane), K_2CO_3 (30 mmol, 3.0 equiv) in 17 mL of distilled water was added under argon atmosphere. After stirring for 5 min, the corresponding boronic acid **B** (15 mmol, 1.5 equiv.) in 60 mL of DME was added, and the resulting mixture was heated to 100 °C for 12 h. After cooling, DME was evaporated under reduced pressure, and the residual was dissolved in DCM. The organic phase was washed with 1.0 M HCl solution and saturated $NaHCO_3$ solution, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel by using a mixtures of petroleum ether/EtOAc (50:1) to provide alkyl 2-(biaryl-2-yl)acetates **C**.

To a dried 250 mL round bottom flask, **C** (12 mmol, 1.0 equiv.) and *p*-ABSA (*p*-acetamidobenzenesulfonyl azide) (36 mmol, 3.0 equiv.) were dissolved in MeCN (77 mL). After stirring for 5 min, DBU (120 mmol, 10 equiv.) was added. The reaction mixture was stirred for 12 h at room temperature. After reaction, water (50 mL) was added to the above solution, and the mixture was extracted with EtOAc (30 mL × 3). The organic layer was washed with saturated brine (30 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting residue was purified by column chromatography on silica gel by using a mixtures of petroleum ether/EtOAc (50:1) as an eluent to provide the corresponding alkyl 2-(biaryl-2-yl)diazoacetate **1**.

(II) Preparation of fluorene products

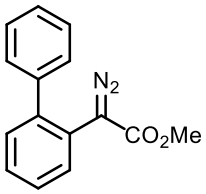


1 **3**, **4**, **6**

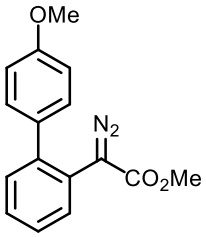
$KHCO_3$ (0.02 mmol, 1.0 equiv.) was weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then alkyl 2-(biaryl-2-yl)diazoacetate **1** (0.2 mmol, 1.0 equiv.) and **2**/**5** (0.3 mmol, 1.5 equiv.) in MeCN (0.4 mL) were added through the side-arm by syringe. The reaction was stirred

under nitrogen at 100 °C for 24 h. After reaction, the mixture was cooled to room temperature. Water (10 mL) was added to the above solution, and the mixture was extracted with EtOAc (10 mL × 3). The organic layer was washed with saturated brine (10 mL) and dried over Na_2SO_4. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (100:1 to 5:1) to afford the desired fluorene products **3**-**4**, **6**.

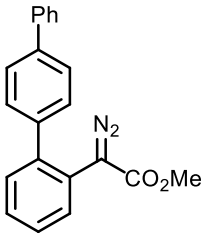
Characterization of Starting Materials



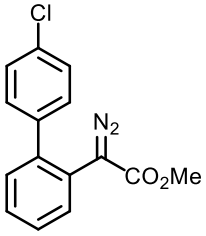
methyl 2-([1,1'-biphenyl]-2-yl)-2-diazoacetate (1a). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.0 Hz, 1H), 7.46-7.32 (m, 8H), 3.75 (s, 3H). The ^{1}H NMR data was in accordance with previous report.[1]



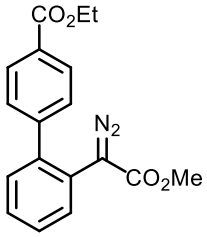
methyl 2-diazo-2-(4'-methoxy-[1,1'-biphenyl]-2-yl)acetate (1b). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 1H), 7.42-7.24 (m, 6H), 7.00-6.93 (m, 2H), 3.85 (s, 3H), 3.77 (s, 2H). The ^{1}H NMR data was in accordance with previous report.[1]



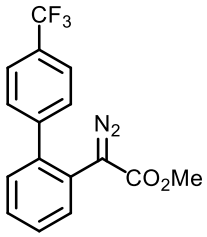
methyl 2-([1,1':4',1''-terphenyl]-2-yl)-2-diazoacetate (1c). Following the *General Procedure (I)*, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.60 (m, 5H), 7.50-7.34 (m, 8H), 3.77 (s, 3H). The ^{1}H NMR data was in accordance with previous report.[1]



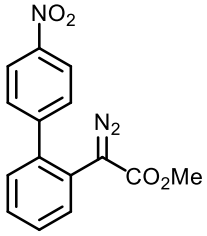
methyl 2-(4'-chloro-[1,1'-biphenyl]-2-yl)-2-diazoacetate (1d). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 1H), 7.46-7.37 (m, 4H), 7.34-7.26 (m, 3H), 3.76 (s, 3H). The ^{1}H NMR data was in accordance with previous report.[1]



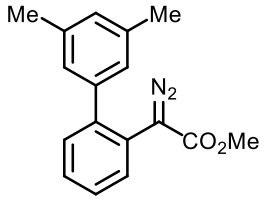
ethyl 2'-(1-diazo-2-methoxy-2-oxoethyl)-[1,1'-biphenyl]-4-carboxylate (1e). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 2H), 7.62 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.49-7.34 (m, 5H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H). The ^{1}H NMR data was in accordance with previous report.[1]



methyl 2-diazo-2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)acetate (1f). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.50-7.41 (m, 4H), 7.36 (td, *J* = 7.9, 7.4, 1.6 Hz, 1H), 3.74 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.53 (s, 3F). The ^{1}H NMR data was in accordance with previous report.[1]

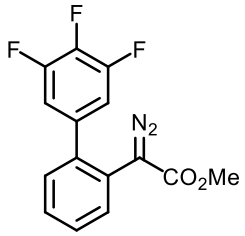


methyl 2-diazo-2-(4'-nitro-[1,1'-biphenyl]-2-yl)acetate (1g). Following the *General Procedure (I)*, yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34-8.29 (m, 2H), 7.64 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.56-7.43 (m, 4H), 7.37 (dd, *J* = 7.7, 1.5 Hz, 1H), 3.75 (s, 3H). The ^{1}H NMR data was in accordance with previous report.[1]

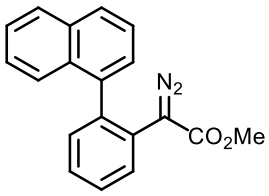


methyl 2-diazo-2-(3',5'-dimethyl-[1,1'-biphenyl]-2-yl)acetate (1h). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.43-7.30

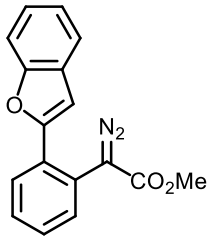
(m, 3H), 6.99 (s, 1H), 6.94 (s, 2H), 3.77 (s, 3H), 2.35 (s, 6H). The ^{1}H NMR data was in accordance with previous report.[1]



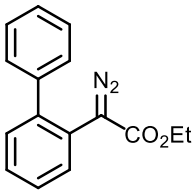
methyl 2-diazo-2-(3',4',5'-trifluoro-[1,1'-biphenyl]-2-yl)acetate (1i). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.49-7.38 (m, 2H), 7.29 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.04-6.94 (m, 2H), 3.79 (s, 3H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -133.44 (s, 1F), -133.49 (s, 1F), -161.51 (s, 1F). The ^{1}H NMR data was in accordance with previous report.[2]



methyl 2-diazo-2-(2-(naphthalen-1-yl)phenyl)acetate (1j). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.3, 4.2 Hz, 2H), 7.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.56-7.41 (m, 5H), 7.40-7.33 (m, 3H), 3.63 (s, 3H). The ^{1}H NMR data was in accordance with previous report.[1]

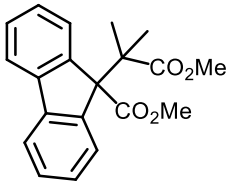


methyl 2-(2-(benzofuran-2-yl)phenyl)-2-diazoacetate (1k). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1H), 7.64-7.57 (m, 2H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.47-7.42 (m, 2H), 7.33-7.25 (m, 2H), 6.92 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.8, 153.9, 132.1, 129.1, 129.1, 128.9, 128.9, 124.7, 123.1, 122.5, 121.3, 111.2, 104.8, 52.3. IR (ATR): 3063, 2952, 2089, 1698, 1434, 1256, 743 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{12}N_2NaO_3$ 315.0740; Found 315.0742.

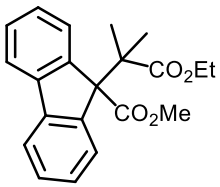


ethyl 2-([1,1'-biphenyl]-2-yl)-2-diazoacetate (1l). Following the *General Procedure (I)*, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63-7.58 (m, 1H), 7.46-7.34 (m, 8H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H). The ^{1}H NMR data was in accordance with previous report.[3]

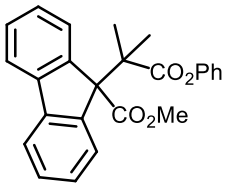
Characterization of Products



methyl 9-(1-methoxy-2-methyl-1-oxopropan-2-yl)-9H-fluorene-9-carboxylate (3a). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 19.6 mg, yield: 31%, white solid, melting point: 110-113 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 3.76 (s, 3H), 3.66 (s, 3H), 1.14 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 172.4, 143.2, 141.4, 128.3, 127.14, 127.10, 119.6, 65.3, 52.4, 52.2, 50.2, 22.9. IR (ATR): 2951, 1715, 1430, 1241, 751 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}NaO_4$ 347.1254; Found 347.1262.

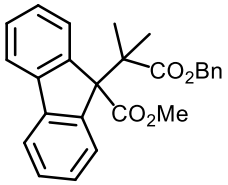


methyl 9-(1-ethoxy-2-methyl-1-oxopropan-2-yl)-9H-fluorene-9-carboxylate (3b). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 40.7 mg, yield: 60%, white solid, melting point: 98-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 8.7 Hz, 4H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.65 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.14 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 172.5, 143.4, 141.4, 128.3, 127.2, 127.1, 119.6, 65.3, 61.1, 52.4, 50.0, 22.9, 14.1. IR (ATR): 2985, 1712, 1238, 1137, 750 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{22}NaO_4$ 361.1410; Found 361.1399.

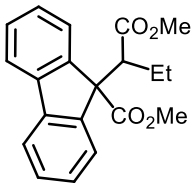


methyl 9-(2-methyl-1-oxo-1-phenoxypropan-2-yl)-9H-fluorene-9-carboxylate (3c). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1 to 70:1), 41 mg, yield: 71%, white solid, melting point: 132-134 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.44-7.37 (m, 4H), 7.32 (td, *J* = 7.6, 1.3 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 3.62 (s, 3H), 1.33 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 172.3, 150.8, 143.2, 141.5, 129.6, 128.5, 127.3, 127.2, 126.0, 121.4, 119.7, 65.3, 52.6, 50.3, 23.2.

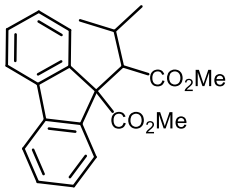
IR (ATR): 2945, 1718, 1448, 1109, 747 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}NaO_4$ 409.1410; Found 409.1422.



methyl 9-(1-(benzyloxy)-2-methyl-1-oxopropan-2-yl)-9H-fluorene-9-carboxylate (3d). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 60:1 to 40:1), 47.9 mg, yield: 80%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.40-7.32 (m, 7H), 7.24 (td, *J* = 7.6, 1.2 Hz, 2H), 5.19 (s, 2H), 3.49 (s, 3H), 1.17 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 172.4, 143.3, 141.4, 135.6, 128.6, 128.4, 128.33, 128.31, 127.14, 127.12, 119.6, 67.0, 52.3, 50.2, 23.0. IR (ATR): 2949, 1724, 1236, 1129, 746 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{24}NaO_4$ 423.1567; Found 423.1573.

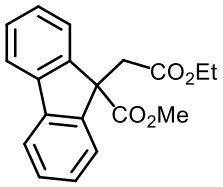


methyl 9-(1-methoxy-1-oxobutan-2-yl)-9*H*-fluorene-9-carboxylate (3e). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1 to 60:1), 36.5 mg, yield: 75%, white solid, melting point: 120-123 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 1H), 7.71 (dd, *J* = 7.7, 2.2 Hz, 2H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.2 Hz, 2H), 7.35-7.30 (m, 2H), 3.70 (s, 3H), 3.59 (s, 3H), 3.54 (dd, *J* = 10.5, 3.5 Hz, 1H), 1.22-1.12 (m, 1H), 0.87 – 0.75 (m, 1H), 0.67 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 173.3, 144.1, 142.8, 141.6, 141.3, 128.7, 128.4, 127.64, 127.62, 127.5, 124.4, 119.8, 119.7, 63.3, 53.9, 52.8, 51.7, 20.8, 12.7. IR (ATR): 2952, 1721, 1434, 1241, 752 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}NaO_3$ 347.1254; Found 347.1263.

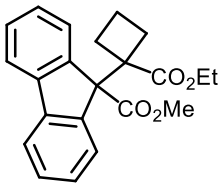


methyl 9-(1-methoxy-3-methyl-1-oxobutan-2-yl)-9H-fluorene-9-carboxylate (3f). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 38.4 mg, yield: 76%,

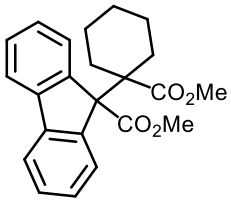
white solid, melting point: 122-124 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.7 Hz, 1H), 7.72 (dd, *J* = 7.6, 4.4 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.44-7.38 (m, 2H), 7.32 (q, *J* = 6.8 Hz, 2H), 3.71 (s, 3H), 3.69 (d, *J* = 3.9 Hz, 1H), 3.53 (s, 3H), 1.15-1.05 (m, 1H), 0.72 (d, *J* = 6.9 Hz, 3H), 0.45 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.5, 174.0, 144.3, 142.9, 142.1, 141.4, 129.0, 128.7, 128.4, 127.6, 127.4, 124.0, 119.9, 119.7, 63.0, 58.0, 52.8, 51.4, 26.5, 24.0, 19.8. IR (ATR): 2951, 1726, 1236, 1193, 749 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{22}NaO_4$ 361.1410; Found 361.1419.



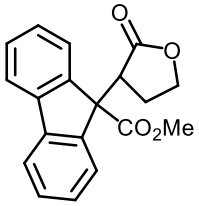
methyl 9-(2-ethoxy-2-oxoethyl)-9*H*-fluorene-9-carboxylate (3g). Following the *General Procedure (II)*, using **1a** (0.3 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 65.7 mg, yield: 71%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 11.4, 7.5 Hz, 4H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 3.13 (s, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 170.8, 144.7, 140.6, 128.6, 127.8, 125.2, 120.1, 60.8, 58.2, 52.9, 43.0, 14.1. IR (ATR): 2982, 1727, 1449, 1241, 739 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}NaO_4$ 333.1097; Found 333.1096.



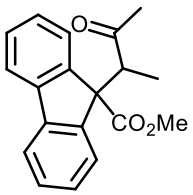
methyl 9-(1-(ethoxycarbonyl)cyclobutyl)-9*H*-fluorene-9-carboxylate (3h). Following the *General Procedure (II)*, using **1a** (0.3 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 60.1 mg, yield: 57%, white solid, melting point: 95-98 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.69 (s, 3H), 2.27-2.15 (m, 4H), 1.89-1.77 (m, 1H), 1.43-1.31 (m, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 172.6, 142.8, 141.4, 128.5, 127.4, 126.5, 119.7, 63.9, 61.1, 54.4, 52.3, 27.7, 15.9, 14.0. IR (ATR): 2950, 1708, 1444, 1240, 749 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}NaO_4$ 373.1410; Found 373.1407.



methyl 9-(1-(methoxycarbonyl)cyclohexyl)-9*H*-fluorene-9-carboxylate (3i). Following the *General Procedure (II)*, using **1a** (0.3 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1 to 60:1), 30 mg, yield: 27%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 2H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.38 (td, *J* = 7.5, 1.1 Hz, 2H), 7.29 (td, *J* = 7.6, 1.3 Hz, 2H), 3.69 (s, 3H), 3.62 (s, 3H), 2.11 (d, *J* = 12.4 Hz, 2H), 1.57-1.44 (m, 3H), 1.37-1.15 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 171.0, 142.3, 141.3, 128.3, 126.6 119.2, 67.1, 55.2, 52.4, 51.5, 30.2, 25.1, 23.6. IR (ATR): 2947, 1727, 1219, 745 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{24}NaO_4$ 387.1567; Found 387.1558.

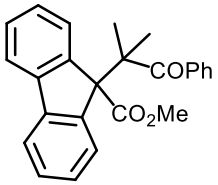


methyl 9-(2-oxotetrahydrofuran-3-yl)-9*H*-fluorene-9-carboxylate (3j). Following the *General Procedure (II)*, using **1a** (0.3 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 30:1 to 10:1), 72.7 mg, yield: 79%, white solid, melting point: 158-161 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.66 (m, 3H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.47-7.38 (m, 2H), 7.37-7.30 (m, 2H), 4.14 (dd, *J* = 11.4, 9.0 Hz, 1H), 4.05-3.97 (m, 1H), 3.88 (td, *J* = 9.0, 2.2 Hz, 1H), 3.71 (s, 3H), 1.69-1.59 (m, 1H), 1.13-0.99 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 172.2, 143.4, 141.9, 141.4, 140.4, 129.02, 128.96, 128.3, 128.2, 126.7, 123.9, 120.2, 120.1, 66.4, 60.6, 53.1, 47.1, 23.5. IR (ATR): 2956, 1764, 1726, 1449, 1374, 1240, 748 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{16}NaO_4$ 331.0941; Found 331.0942.

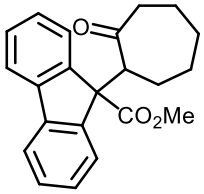


methyl 9-(3-oxobutan-2-yl)-9*H*-fluorene-9-carboxylate (3k). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 20:1), 30.5 mg, yield: 69%, white solid, melting point: 119-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 6.9 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 3.87 (q, *J* = 7.6 Hz, 1H), 3.57 (s, 3H), 2.24 (s, 3H), 0.52 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 174.1, 144.4, 142.9, 142.0, 141.2, 128.7, 128.5, 128.1, 127.7, 127.6, 123.6, 119.8, 119.7, 63.06, 54.8, 52.7,

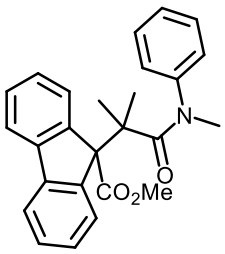
28.6, 10.9. IR (ATR): 2970, 1704, 1429, 1248, 750 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}NaO_3$ 317.1148; Found 317.1162.



methyl 9-(2-methyl-1-oxo-1-phenylpropan-2-yl)-9H-fluorene-9-carboxylate (3l). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1 to 60:1), 39.1 mg, yield: 70%, white solid, melting point: 154-156 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 4H), 7.45-7.27 (m, 9H), 3.68 (s, 3H), 1.24 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.5, 173.4, 144.2, 141.6, 139.6, 130.5, 128.3, 128.1, 127.5, 127.23, 127.16, 119.7, 65.6, 56.7, 52.4, 23.8. IR (ATR): 2947, 1712, 1239, 747 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{22}NaO_3$ 393.1461; Found 393.1477.

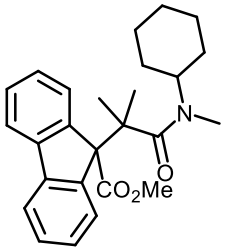


methyl 9-(2-oxocycloheptyl)-9H-fluorene-9-carboxylate (3m). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 25 mg, yield: 50%, colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.74-7.68 (m, 2H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.43-7.37 (m, 2H), 7.34-7.28 (m, 2H), 3.98-3.91 (m, 1H), 3.56 (s, 3H), 2.83-2.74 (m, 1H), 2.52-2.41 (m, 1H), 1.89-1.75 (m, 3H), 1.52-1.43 (m, 1H), 1.20-1.07 (m, 2H), 0.75-0.66 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 214.2, 174.2, 144.5, 143.3, 142.1, 141.4, 128.8, 128.7, 128.1, 127.7, 127.6, 123.7, 119.8, 119.6, 63.1, 59.6, 52.6, 44.0, 30.1, 29.7, 25.2, 23.8. IR (ATR): 2927, 1720, 1449, 1241, 738 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{22}NaO_3$ 357.1461; Found 357.1471.

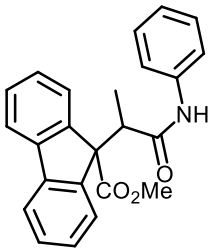


methyl 9-(2-methyl-1-(methyl(phenyl)amino)-1-oxopropan-2-yl)-9*H*-fluorene-9-

carboxylate (3n). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 20:1), 23.6 mg, yield: 30%, yellow solid, melting point: 163-165 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.36 (td, *J* = 7.4, 1.2 Hz, 2H), 7.29 (td, *J* = 7.5, 1.3 Hz, 2H), 7.23-7.18 (m, 3H), 7.02 (dd, *J* = 7.9, 1.8 Hz, 2H), 3.67 (s, 3H), 3.35 (s, 3H), 0.79 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.1, 173.5, 144.7, 144.4, 141.6, 129.3, 128.5, 128.0, 127.9, 127.4, 127.1, 119.4, 67.5, 60.4, 53.8, 52.3, 42.2, 24.1. IR (ATR): 2983, 2946, 1720, 1629, 1235, 747 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{25}NNaO_3$ 422.1727; Found 422.1740.

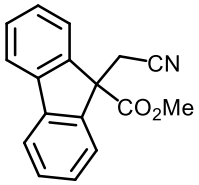


methyl 9-(1-(cyclohexyl(methyl)amino)-2-methyl-1-oxopropan-2-yl)-9*H*-fluorene-9-carboxylate (3o). Following the *General Procedure (II)*, using **1a** (0.3 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 20:1), 11 mg, yield: 14%, white solid, melting point: 195-197 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.39 (td, *J* = 7.5, 1.1 Hz, 2H), 7.29 (dd, *J* = 7.5, 1.2 Hz, 2H), 3.67 (s, 3H), 1.97-1.88 (m, 2H), 1.74-1.58 (m, 5H), 1.46-1.32 (m, 3H), 1.27 (dd, *J* = 9.7, 2.5 Hz, 1H), 1.11 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 172.6, 143.6, 141.3, 128.2, 127.4, 127.1, 119.5, 65.4, 52.5, 49.8, 48.2, 33.1, 25.5, 24.8, 23.1. IR (ATR): 3279, 2927, 1725, 1621, 1241, 746 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{31}NNaO_3$ 414.2040; Found 414.2054.

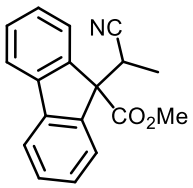


methyl 9-(1-oxo-1-(phenylamino)propan-2-yl)-9H-fluorene-9-carboxylate (3p). Following the *General Procedure (II)*, using **1a** (0.3 mmol), The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 20:1), 11.2 mg, yield: 15%, colorless oil, melting point: 233-235 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.61 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.46-7.40 (m, 2H), 7.37-7.31 (m, 4H), 7.11 (t, *J* = 7.3 Hz, 1H), 3.60 (s, 3H), 0.69 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.4, 171.4, 143.9, 142.1, 141.7, 141.3, 137.8, 129.1, 128.8, 128.5, 127.8, 127.7, 127.5, 124.3, 124.1, 120.1, 119.9, 119.8, 63.7, 53.0, 48.0, 12.1. IR (ATR): 3362, 2982, 1715,

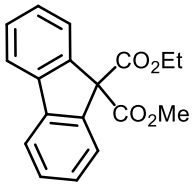
1539, 1245, 748 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{21}NNaO_3$ 394.1414; Found 394.1416.



methyl 9-(cyanomethyl)-9*H*-fluorene-9-carboxylate (3q). Following the *General Procedure (II)*, using **1a** (0.3 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 54.3 mg, yield: 68%, white solid, melting point: 130-132 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 7.6 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 3.63 (s, 3H), 3.15 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 143.0, 140.9, 129.5, 128.3, 123.9, 120.7, 116.9, 57.4, 53.4, 26.3. IR (ATR): 2924, 2251, 1730, 1244, 749 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{13}NaO_2$ 286.0838; Found 286.0833.

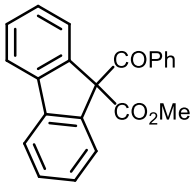


methyl 9-(1-cyanoethyl)-9*H*-fluorene-9-carboxylate (3r). Following the *General Procedure (II)*, using **1a** (0.15 mmol), the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 33.9 mg, yield: 81%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.75 (t, *J* = 7.1 Hz, 2H), 7.52 -7.38 (m, 4H), 7.34 (td, *J* = 7.6, 1.2 Hz, 1H), 3.88 (q, *J* = 7.2 Hz, 1H), 3.66 (s, 3H), 0.71 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 141.7, 141.53, 141.47, 141.2, 129.4, 129.3, 128.3, 128.1, 125.3, 123.6, 121.3, 120.5, 120.4, 62.0, 53.3, 32.4, 12.4. IR (ATR): 2952, 2243, 1723, 1241, 747 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{15}NNaO_2$ 300.0995; Found 300.1004.

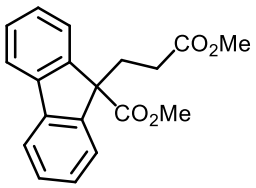


ethyl 9-methyl 9*H*-fluorene-9,9-dicarboxylate (3s). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 22.1 mg, yield: 37%, white solid. melting point: 113-115 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.44 (td, *J* = 7.5, 1.2 Hz, 2H), 7.36 (td, *J* = 7.5, 1.2 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz,

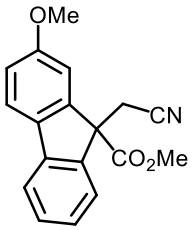
$CDCl_3$) δ 169.2, 168.4, 141.3, 140.1, 129.2, 127.8, 126.8, 120.1, 68.3, 62.4, 53.3, 14.0. IR (ATR): 3435, 2956, 1728, 1234, 1053, 748 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}NaO_4$ 319.0941; Found 319.0947.



methyl 9-benzoyl-9*H*-fluorene-9-carboxylate (3t). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1), 11 mg, yield: 18%, white solid, melting point: 98-100 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.40 (td, *J* = 7.6, 1.1 Hz, 2H), 7.27-7.21 (m, 3H), 7.12-7.05 (m, 2H), 7.04-6.96 (m, 2H), 3.74 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 169.3, 141.3, 141.1, 135.3, 132.6, 129.3, 128.6, 128.2, 128.1, 127.4, 120.5, 53.3. IR (ATR): 2922, 1739, 1448, 1234, 743 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{16}NaO_3$ 351.0992; Found 351.1004.

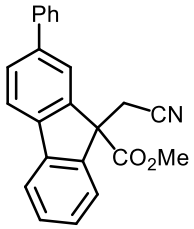


methyl 9-(3-methoxy-3-oxopropyl)-9*H*-fluorene-9-carboxylate (3u). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 30:1), 47 mg, yield: 76%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.40 (td, *J* = 7.5, 1.2 Hz, 2H), 7.33 (td, *J* = 7.5, 1.3 Hz, 2H), 3.58 (s, 3H), 3.48 (s, 3H), 2.79-2.71 (m, 2H), 1.70-1.62 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.4, 144.2, 141.2, 128.5, 127.8, 124.5, 120.2, 60.5, 52.7, 51.5, 31.8, 28.6. IR (ATR): 2952, 1728, 1238, 728 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}NaO_4$ 333.1097; Found 333.1110.

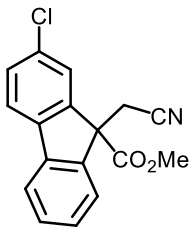


methyl 9-(cyanomethyl)-2-methoxy-9H-fluorene-9-carboxylate (4a). Following the *General Procedure (II)*, using **1b** (0.17 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 30:1 to 20:1), 28.7 mg, yield: 58%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 1H), 7.44

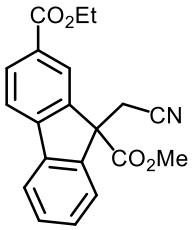
(t, *J* = 7.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.14 (d, *J* = 2.3 Hz, 1H), 7.01 (dd, *J* = 8.4, 2.4 Hz, 1H), 3.87 (s, 3H), 3.63 (s, 3H), 3.12 (d, *J* = 3.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 160.1, 144.7, 142.6, 140.8, 133.5, 129.5, 127.0, 123.8, 121.6, 119.9, 116.9, 115.3, 109.6, 57.3, 55.7, 53.4, 26.4. IR (ATR): 2955, 2252, 1728, 1241, 730 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{15}NNaO_3$ 316.0944; Found 316.0961.



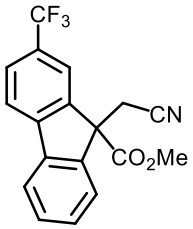
methyl 9-(cyanomethyl)-2-phenyl-9*H*-fluorene-9-carboxylate (4b). Following the *General Procedure (II)*, using **1c** (0.26 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 20:1), 31.0 mg, yield: 35%, white solid, melting point: 161-164 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.77 (m, 3H), 7.72 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.68-7.60 (m, 3H), 7.52-7.44 (m, 3H), 7.41-7.34 (m, 2H), 3.64 (s, 3H), 3.19 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 143.8, 143.3, 141.5, 140.5, 139.9, 129.6, 129.0, 128.5, 128.2, 127.7, 127.2, 124.0, 122.6, 121.0, 120.8, 117.0, 57.4, 53.4, 26.4. IR (ATR): 2955, 2252, 1731, 1238, 761 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{17}NNaO_2$ 362.1151; Found 362.1157.



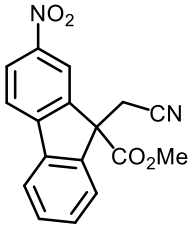
methyl 2-chloro-9-(cyanomethyl)-9H-fluorene-9-carboxylate (4c). Following the *General Procedure (II)*, using **1d** (0.12 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 14.8 mg, yield: 42%, white solid, melting point: 171-173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 1H), 7.62-7.57 (m, 2H), 7.52-7.44 (m, 2H), 7.40 (td, *J* = 7.5, 1.2 Hz, 1H), 3.65 (s, 3H), 3.17 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 144.5, 139.8, 139.5, 133.9, 129.9, 129.7, 128.6, 124.5, 124.0, 121.7, 120.8, 116.5, 57.5, 53.6, 26.2. IR (ATR): 2966, 2251, 1718, 1248, 747 cm^{-1}. HRMS (ESI) m/z: $[M_{Cl}{}^{35}+Na]^+$ Calcd for $C_{17}H_{12}ClNNaO_2$ 320.0449, Found 320.0449; $[M_{Cl}{}^{37}+Na]^+$ Calcd for $C_{17}H_{12}ClNNaO_2$ 322.0419, Found 322.0425.



2-ethyl 9-methyl 9-(cyanomethyl)-9H-fluorene-2,9-dicarboxylate (4d). Following the *General Procedure (II)*, using **1e** (0.16 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 41.5 mg, yield: 77%, white solid, melting point: 127-129 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.17 (m, 2H), 7.84 (dd, *J* = 7.6, 2.8 Hz, 2H), 7.65 (d, *J* = 7.4 Hz, 1H), 7.52 (td, *J* = 7.5, 1.2 Hz, 1H), 7.45 (td, *J* = 7.6, 1.2 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 3.36 (d, *J* = 16.6 Hz, 1H), 3.16 (d, *J* = 16.6 Hz, 1H), 1.43 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 166.1, 145.3, 143.9, 143.1, 139.8, 131.3, 130.3, 129.7, 129.4, 125.0, 124.2, 121.6, 120.5, 116.4, 61.3, 57.4, 53.5, 26.0, 14.4. IR (ATR): 2983, 2254, 1731, 1240, 731 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{17}NNaO_4$ 358.1050; Found 358.1061.

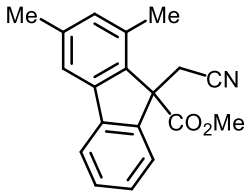


methyl 9-(cyanomethyl)-2-(trifluoromethyl)-9H-fluorene-9-carboxylate (4e). Following the *General Procedure (II)*, using **1f** (0.16 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 20:1), 48.5 mg, yield: 92%, white solid, melting point: 153-155 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.81 (m, 3H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.53 (td, *J* = 7.5, 1.2 Hz, 1H), 7.46 (td, *J* = 7.5, 1.2 Hz, 1H), 3.66 (s, 3H), 3.29-3.15 (m, 2H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -61.90 (s, 3F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 144.4, 143.5, 143.4, 139.3, 130.2 (q, *J* = 33.3 Hz), 129.8, 129.5, 127.0 (q, *J* = 4.0 Hz), 124.2, 124.0 (q, *J* = 273.7 Hz), 121.5, 121.03 (q, *J* = 4.0 Hz), 121.0, 116.3, 57.5, 53.6, 26.2. IR (ATR): 2923, 1728, 1329, 1245, 734 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{12}F_3NNaO_2$ 354.0712; Found 354.0707.

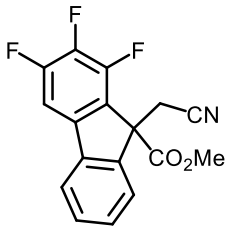


methyl 9-(cyanomethyl)-2-nitro-9*H*-fluorene-9-carboxylate (4f). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum

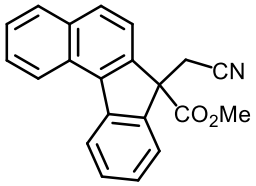
ether/EtOAc, 10:1), 48 mg, yield: 78%, white solid, melting point: 201-203 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 2.1 Hz, 1H), 8.41 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 7.89 (d, *J* = 7.4 Hz, 1H), 7.69 (d, *J* = 7.4 Hz, 1H), 7.60-7.50 (m, 2H), 3.68 (s, 3H), 3.39-3.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 147.6, 147.3, 144.3, 143.9, 138.5, 130.4, 130.2, 125.7, 124.4, 122.2, 121.0, 119.8, 116.0, 57.6, 53.8, 26.0. IR (ATR): 2963, 2250, 1728, 1518, 1339, 1244, 741 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{12}N_2NaO_4$ 333.0689; Found 333.0693.



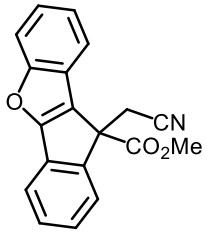
methyl 9-(cyanomethyl)-1,3-dimethyl-9H-fluorene-9-carboxylate (4g). Following the *General Procedure (II)*, using **1h** (0.16 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 19.5 mg, yield: 42%, white solid, melting point: 203-205 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.6 Hz, 1H), 7.51-7.43 (m, 3H), 7.35 (td, *J* = 7.5, 1.2 Hz, 1H), 6.96 (s, 1H), 3.58 (s, 3H), 3.56 (d, *J* = 17.4 Hz, 1H), 3.24 (d, *J* = 16.9 Hz, 1H), 2.41 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 143.5, 141.8, 141.3, 139.5, 138.2, 133.7, 131.3, 129.5, 128.1, 122.9, 120.7, 119.2, 116.3, 57.2, 53.2, 24.2, 21.5, 18.4. IR (ATR): 2955, 2248, 1720, 1435, 1248, 757 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{17}NNaO_2$ 314.1151; Found 314.1159.



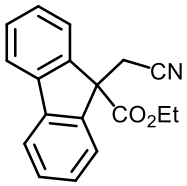
methyl 9-(cyanomethyl)-1,2,3-trifluoro-9*H*-fluorene-9-carboxylate (4h). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 20:1), 42.7 mg, yield: 67%, white solid, melting point: 172-174 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.43-7.35 (m, 1H), 3.66 (s, 3H), 3.63-3.33 (m, 2H); ^{19}F NMR (377 MHz, $CDCl_3$) δ -130.73 (dd, J = 19.3, 8.2 Hz, 1F), -137.93 (dd, J = 20.8, 8.2 Hz, 1F), -160.03 (t, *J* = 18.9 Hz, 1F); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 152.9 (ddd, *J* = 252.5, 11.1, 2.0), 148.2 (ddd, *J* = 253.5, 12.1, 4.0), 142.6, 139.6 (dt, *J* = 253.5, 14.1), 139.0-138.9 (m), 137.6-137.4 (m), 130.2, 129.3, 125.3 (dd, *J* = 12.1, 3.0), 123.4, 121.2, 115.5, 105.0 (dd, *J* = 20.2, 4.0 Hz), 56.8, 53.7, 24.3. IR (ATR): 2925, 2257, 1738, 1246, 746 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{10}F_3NNaO_2$ 340.0556; Found 340.0556.



methyl 7-(cyanomethyl)-7*H*-benzo[*c*]fluorene-7-carboxylate (4i). Following the *General Procedure (II)*, using **1j** (0.14 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 20:1), 33.7 mg, yield: 77%, white solid, melting point: 171-173 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.5 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.72-7.65 (m, 3H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.1 Hz, 1H), 3.59 (s, 3H), 3.24 (d, *J* = 2.0 Hz, 2H); ^{13}C NMR(101 MHz, $CDCl_3$) δ 172.0, 143.9, 142.0, 141.5, 136.3, 134.6, 129.64, 129.57, 129.5, 129.4, 127.5, 127.4, 126.4, 124.1, 123.8, 123.7, 120.8, 116.8, 57.5, 53.4, 26.0. IR (ATR): 2920, 2255, 1735, 1242, 755 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{15}NNaO_2$ 336.0995; Found 336.1004.

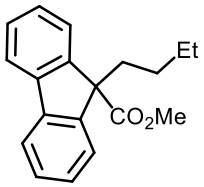


Methyl 10-(cyanomethyl)-10*H*-indeno[1,2-*b*]benzofuran-10-carboxylate (4j). Following the *General Procedure (II)*, using **1k** (0.1 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 23 mg, yield: 76%, yellow solid, melting point: 106-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 1H), 7.66-7.58 (m, 3H), 7.47 (t, *J* = 7.7 Hz,1H),7.38-7.31 (m, 3H), 3.69 (s, 3H), 3.43 (d, *J* = 16.5 Hz, 1H), 2.92 (d, *J* = 16.4 Hz, 1H); ^{13}C NMR(101 MHz, $CDCl_3$) δ 170.9, 161.5, 159.9, 146.6, 131.9, 129.6, 127.4, 124.6, 124.3, 124.24, 124.20, 124.15, 120.3, 118.8, 117.0, 112.6, 53.6, 53.4, 25.2. IR (ATR): 2956, 2253, 1732, 1239, 746 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{13}NNaO_3$ 326.0788; Found 326.0796.

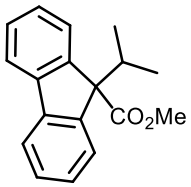


ethyl 9-(cyanomethyl)-9*H*-fluorene-9-carboxylate (4k). Following the *General Procedure (II)*, using **1l** (0.18 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 40:1 to 20:1), 29.3 mg, yield: 59%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.3 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.13 (s, 2H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 143.2, 140.8, 129.4, 128.2, 124.0, 120.7, 117.0, 62.3, 57.4, 26.4, 13.9. IR (ATR): 2982,

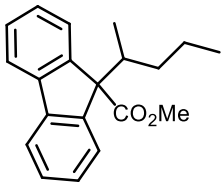
2254, 1725, 1240, 737 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{15}NNaO_2$ 300.0995; Found 300.1009.



methyl 9-butyl-9*H*-fluorene-9-carboxylate (6a). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 35.5 mg, yield: 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.38 (td, *J* = 7.4, 1.2 Hz, 2H), 7.32 (td, *J* = 7.5, 1.3 Hz, 2H), 3.58 (s, 3H), 2.37-2.27 (m, 2H), 1.21-1.09 (m, 2H), 0.71 (t, *J* = 7.4 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.3, 145.5, 141.0, 128.0, 127.5, 124.6, 120.0, 61.5, 52.6, 37.3, 25.8, 22.8, 13.8. IR (ATR): 2954, 1726, 1448, 1233, 741 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{20}NaO_2$ 303.1356; Found 303.1363.

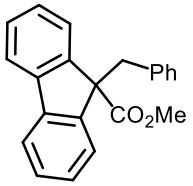


methyl 9-isopropyl-9*H*-fluorene-9-carboxylate (6b). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 21.7 mg, yield: 41%, white solid, melting point: 83-85 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 2H), 7.39 (td, *J* = 7.4, 1.2 Hz, 2H), 7.32 (td, *J* = 7.5, 1.3 Hz, 2H), 3.67 (s, 3H), 2.99-2.88 (m, 1H), 0.72 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 144.2, 141.2, 128.0, 127.2, 125.7, 119.7, 66.1, 52.4, 36.9, 17.8. IR (ATR): 2971, 1720, 1240, 741 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{18}NaO_2$ 289.1199; Found 289.1211.

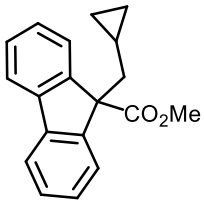


methyl 9-(pentan-2-yl)-9*H*-fluorene-9-carboxylate (6c). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 23.1 mg, yield: 52%, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 2H), 7.39 (tt, *J* = 7.5, 1.3 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 3.66 (s, 3H), 2.78-2.68 (m, 1H), 1.39 -1.30 (m, 1H), 1.20-1.06 (m, 2H), 1.00-0.89 (m, 1H), 0.79 (t, *J* = 7.1 Hz, 3H), 0.66 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 144.6,

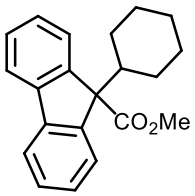
144.1, 141.4, 141.2, 127.9, 127.23, 127.16, 125.9, 125.6, 119.7, 119.6, 66.5, 52.4, 41.3, 34.3, 20.9, 14.6, 14.1. IR (ATR): 2957, 1725, 1448, 1233, 743 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{22}NaO_2$ 317.1512; Found 317.1527.



methyl 9-benzyl-9*H*-fluorene-9-carboxylate (6d). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 35.4 mg, yield: 75%, white solid, melting point: 103-106 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.4 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.33 (td, *J* = 7.4, 1.3 Hz, 2H), 7.28 (td, *J* = 7.4, 1.3 Hz, 2H), 7.07-6.95 (m, 3H), 6.75-6.69 (m, 2H), 3.63 (s, 3H), 3.53 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 144.6, 140.8, 136.2, 130.3, 128.1, 127.4, 127.1, 126.5, 125.6, 119.9, 62.4, 52.7, 43.9. IR (ATR): 2954, 2925, 2102, 1724, 1449, 1236, 742 ,699 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{22}H_{18}NaO_2$ 337.1199; Found 337.1206.

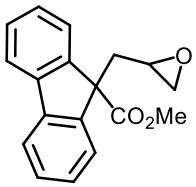


methyl 9-(cyclopropylmethyl)-9*H*-fluorene-9-carboxylate (6e). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 37.1 mg, yield: 67%, yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.2 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.55 (td, *J* = 7.5, 1.3 Hz, 2H), 7.47 (td, *J* = 7.5, 1.2 Hz, 2H), 3.76 (s, 3H), 2.40 (d, *J* = 6.8 Hz, 2H), 0.50-0.39 (m, 1H), 0.30-0.25 (m, 2H), 0.02-0.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 145.6, 140.9, 128.0, 127.2, 125.2, 119.9, 61.8, 52.5, 42.9, 6.6, 4.4. IR (ATR): 2999, 1725, 1448, 1235, 741 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{18}NaO_2$ 301.1199; Found 301.1216.

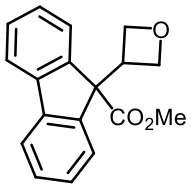


methyl 9-cyclohexyl-9*H*-fluorene-9-carboxylate (6f). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 43.7 mg, yield: 71%, yellow solid, melting point: 129-131 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.68 (t, *J* = 7.3 Hz, 4H), 7.38 (td, *J* = 7.4, 1.3 Hz, 2H), 7.32 (td, *J* = 7.4, 1.4 Hz, 2H), 3.66 (s, 3H),

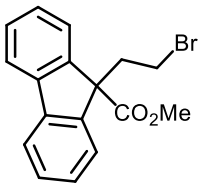
2.53 (tt, *J* = 12.0, 2.9 Hz, 1H), 1.65-1.52 (m, 3H), 1.34 (d, *J* = 11.4 Hz, 2H), 1.26-1.12 (m, 2H), 1.03-0.81 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 144.4, 141.2, 128.0, 127.2, 126.0, 119.6, 66.1, 52.4, 47.5, 28.0, 26.7, 26.3. IR (ATR): 2923, 1716, 1446, 1234, 738 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{21}H_{22}NaO_2$ 329.1512; Found 329.1522.



methyl 9-(oxiran-2-ylmethyl)-9*H*-fluorene-9-carboxylate (6g). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 20:1), 34.4 mg, yield: 61%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.5, 2.8 Hz, 2H), 7.58 (dd, *J* = 16.4, 7.5 Hz, 2H), 7.43 (tdd, *J* = 7.5, 4.2, 1.2 Hz, 2H), 7.39-7.31 (m, 2H), 3.60 (s, 3H), 2.74-2.65 (m, 1H), 2.47-2.35 (m, 3H), 2.19 (dd, *J* = 5.0, 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 144.7, 144.6, 141.0, 140.8, 128.5, 127.7, 127.6, 124.9, 124.6, 120.27, 120.25, 59.8, 52.8, 48.5, 47.0, 40.2. IR (ATR): 2995, 1727, 1449, 1238, 741 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}NaO_3$ 303.0992; Found 303.1007.

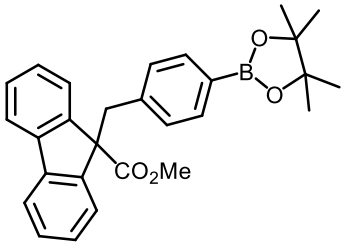


methyl 9-(oxetan-3-yl)-9*H*-fluorene-9-carboxylate (6h). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 30:1), 32.2 mg, yield: 57%, white solid, melting point: 125-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.45 (td, *J* = 7.4, 1.2 Hz, 2H), 7.36 (td, *J* = 7.5, 1.2 Hz, 2H), 4.62 (dd, *J* = 8.3, 6.6 Hz, 2H), 4.31 (t, *J* = 6.7 Hz, 2H), 4.15-4.05 (m, 1H), 3.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 143.0, 141.3, 128.8, 127.9, 125.0, 120.3, 73.4, 61.2, 52.7, 41.2. IR (ATR): 2952, 1721, 1432, 1241, 745 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}NaO_3$ 303.0992; Found 303.1001.

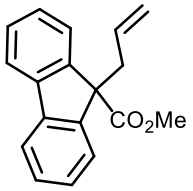


methyl 9-(2-bromoethyl)-9*H*-fluorene-9-carboxylate (6i). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 50:1 to 10:1), 32.4 mg, yield: 49%, yellow solid, melting point: 87-89 ℃. ^{1}H NMR

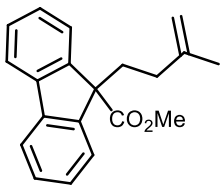
(400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.43 (td, *J* = 7.5, 1.2 Hz, 2H), 7.35 (td, *J* = 7.4, 1.2 Hz, 2H), 3.60 (s, 3H), 2.99-2.91 (m, 2H), 2.75-2.67 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 143.7, 141.0, 128.7, 128.0, 124.4, 120.4, 61.3, 52.9, 40.2, 27.2. IR (ATR): 2951, 1727, 1449, 1240, 742 cm^{-1}. HRMS (ESI) m/z: $[M_{Br}{}^{79}+Na]^+$ Calcd for $C_{17}H_{15}BrNaO_2$ 353.0148, Found 353.0150; $[M_{Br}{}^{81}+Na]^+$ Calcd for $C_{17}H_{15}BrNaO_2$ 355.0127, Found 355.0134.



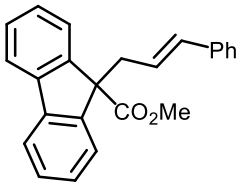
methyl 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)-9*H*-fluorene-9-carboxylate (6j). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1 to 50:1), 44.1 mg, yield: 50%, white solid, melting point: 141-143 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.47-7.42 (m, 4H), 7.33 (td, *J* = 7.4, 1.3 Hz, 2H), 7.27 (td, *J* = 7.5, 1.3 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 3.62 (s, 3H), 3.54 (s, 2H), 1.29 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 144.5, 140.7, 139.5, 134.0, 129.7, 128.1, 127.1, 125.6, 120.0, 83.7, 62.3, 52.7, 44.0, 24.9. IR (ATR): 2980, 1733, 1357, 1230, 731 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{28}H_{29}BNaO_4$ 463.2051; Found 463.2054.



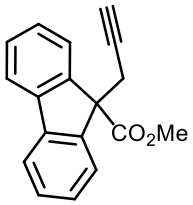
methyl 9-allyl-9*H*-fluorene-9-carboxylate (6k). Following the *General Procedure (II)*, using **1a** (0.15 mmol). The product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 36.9 mg, yield: 93%, white solid, melting point: 75-77 ℃. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.39 (td, *J* = 7.5, 1.3 Hz, 2H), 7.32 (td, *J* = 7.5, 1.3 Hz, 2H), 5.35-5.23 (m, 1H), 4.92 -4.79 (m, 2H), 3.59 (s, 3H), 3.03 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 144.9, 140.9, 132.6, 128.2, 127.4, 124.9, 120.0, 118.8, 61.0, 52.6, 41.9. IR (ATR): 2952, 2923, 1721, 1448, 1237, 743 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}NaO_2$ 287.1043; Found 287.1055.



methyl 9-(3-methylbut-3-en-1-yl)-9*H*-fluorene-9-carboxylate (6l). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 10.7 mg, yield: 18%, yellow solid, melting point: 84-87 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.41 (td, *J* = 7.5, 1.2 Hz, 2H), 7.34 (td, *J* = 7.5, 1.2 Hz, 2H), 4.59 (s, 1H), 4.53 (s, 1H), 3.60 (s, 3H), 2.53-2.46 (m, 2H), 1.55 (s, 3H), 1.42-1.35 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.2, 145.1, 141.1, 128.1, 127.6, 124.5, 120.0, 109.7, 61.2, 52.6, 35.4, 31.5, 22.6. IR (ATR): 2951, 1723, 1448, 1233, 735 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}NaO_2$ 315.1356; Found 315.1366.

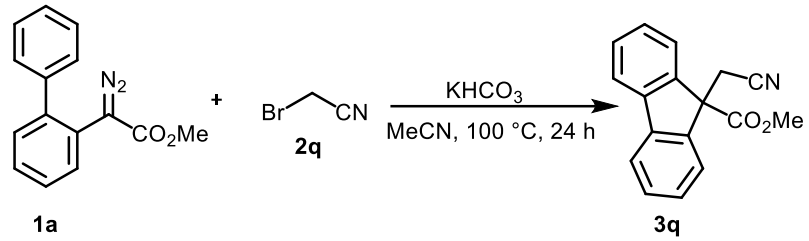


methyl 9-cinnamyl-9*H*-fluorene-9-carboxylate (6m). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 100:1), 48.9 mg, yield: 72%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.5 Hz, 2H), 7.58 (d, *J* = 7.5 Hz, 2H), 7.37 (td, *J* = 7.4, 1.2 Hz, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 2H), 7.23-7.10 (m, 5H), 6.23 (d, *J* = 15.8 Hz, 1H), 5.89-5.80 (m, 1H), 3.60 (s, 3H), 3.11 (dd, *J* = 7.5, 1.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 145.0, 140.8, 137.3, 133.9, 128.5, 128.3, 127.5, 127.2, 126.2, 125.1, 124.7, 120.1, 61.4, 52.7, 41.5. IR (ATR): 2949, 1723, 1448, 1237, 745 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{20}NaO_2$ 363.1356; Found 363.1368.



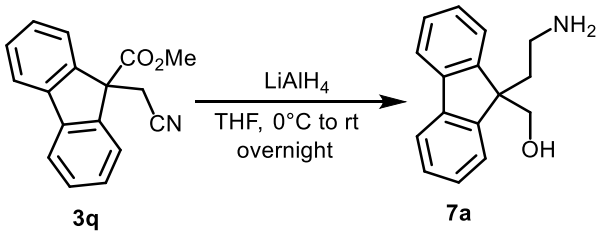
methyl 9-(prop-2-yn-1-yl)-9*H*-fluorene-9-carboxylate (6n). Following the *General Procedure (II)*, the product was purified by flash chromatography on silica gel (petroleum ether/EtOAc, 80:1), 19.4 mg, yield: 37%, white solid, melting point: 119-121 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.43 (td, *J* = 7.5, 1.2 Hz, 2H), 7.34 (td, *J* = 7.5, 1.2 Hz, 2H), 3.63 (s, 3H), 3.03 (d, *J* = 2.7 Hz, 2H), 1.93 (t, *J* = 2.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.7, 144.5, 140.8, 128.7, 127.7, 124.7, 120.1, 80.3, 70.6, 59.5, 52.9, 28.1. IR (ATR): 3283, 2996, 1715, 1247, 746 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{14}NaO_2$ 285.0886; Found 285.0894.

Procedure for Scale-Up Reaction

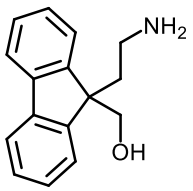


$KHCO_3$ (4.0 mmol, 400 mg) was weighed into a Schlenk tube. The reaction vessel was capped and subjected to three vacuum-purge/nitrogen-flush cycles. Then methyl 2-([1,1'-biphenyl]-2-yl)-2-diazoacetate **1a** (4.0 mmol, 1.0 g) and 2-bromoacetonitrile **2q** (6.0 mmol, 708 mg) in MeCN (8 mL) were added through the side-arm by syringe. The reaction was stirred under nitrogen at 100 °C for 24 h. After reaction, the mixture was cooled to room temperature. Water (50 mL) was added to the above solution, and the mixture was extracted with EtOAc (50 mL × 3). The organic layer was washed with saturated brine (30 mL) and dried over Na_2SO_4. Volatile solvent and reagents were removed by rotary evaporation and the residue was purified by silica gel flash chromatography using petroleum ether/EtOAc (50:1 to 20:1) to afford the desired product **3q,** 870.8 mg, 75% yield.

Reduction with $LiAlH_4$



Methyl 9-(cyanomethyl)-9*H*-fluorene-9-carboxylate **3a** (0.7 mmol, 200 mg) and $LiAlH_4$ (2.1 mmol, 78 mg) were weighed into a Schlenk tube, then THF was added through the side-arm by syringe at 0 ℃ under N_2. The mixture was stirred at room temperature overnight. After reaction, water (5 mL) was added, and it was extracted with EtOAc (10 mL × 3), washed with saturated brine (20 mL), and dried over anhydrous Na_2SO_4. After filtration, the filtrate was concentrated under reduced pressure and the residue was purified by silica gel flash chromatography using CH_2Cl_2/MeOH (10:1) to afford the desired product **7a**, 131.0 mg, yield: 78%.



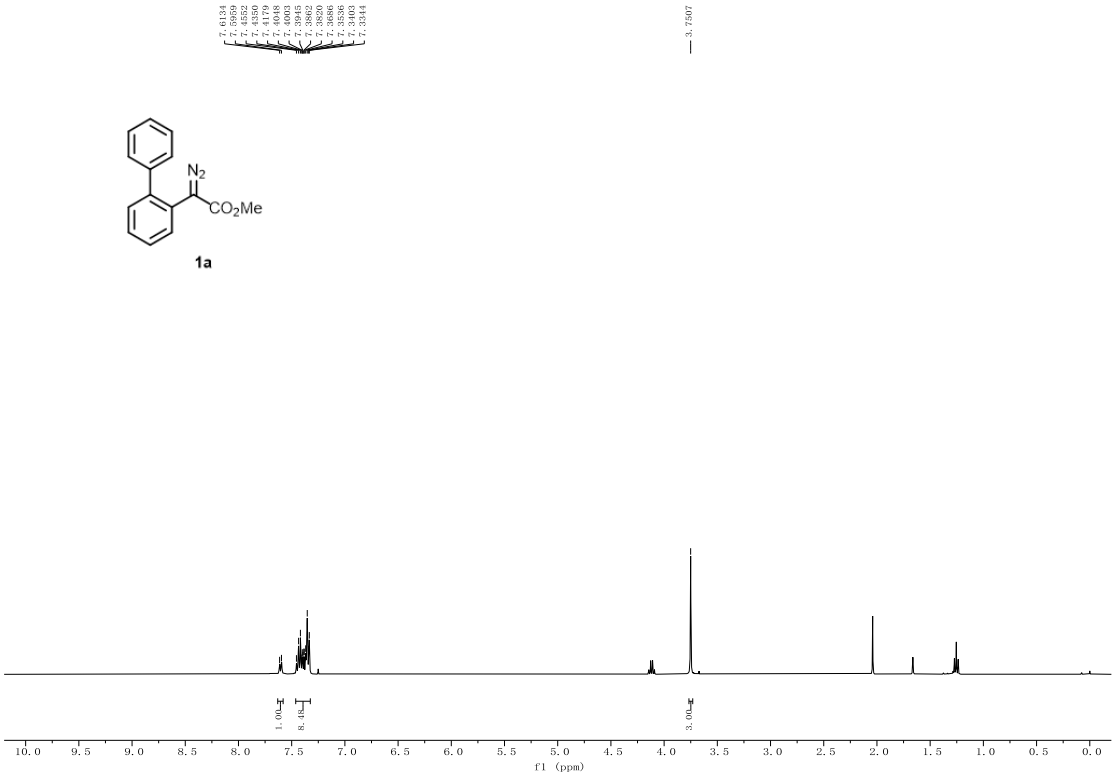
(9-(2-aminoethyl)-9*H*-fluoren-9-yl)methanol (7a). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.5 Hz, 2H), 7.52 (d, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 2H), 3.73 (s, 2H), 2.91 (s, 3H), 2.47 (t, *J* = 6.9 Hz, 2H), 2.19 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.0, 140.6, 127.8, 127.3, 124.1, 120.2, 69.0, 55.6, 37.6. IR (ATR): 3288, 2924, 1447, 735 cm^{-1}. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{16}H_{18}NO$ 240.1383; Found 240.1396.

References

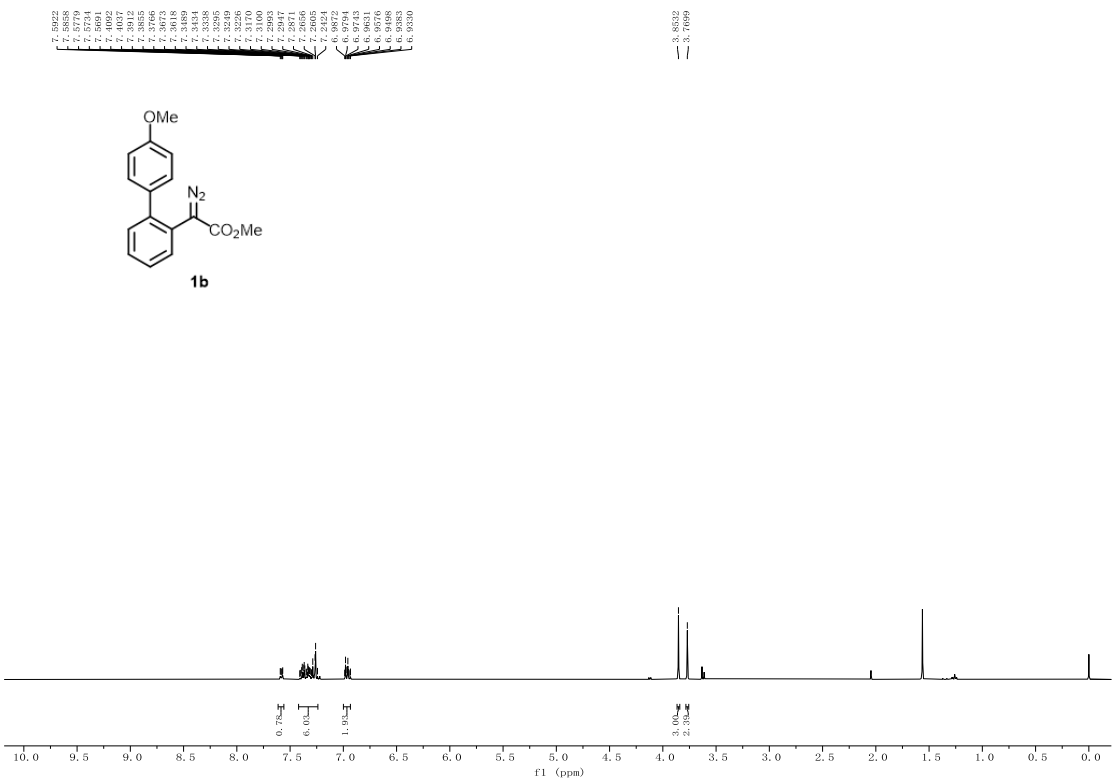
1. Kim, J.; Ohk, Y.; Park, S. H.; Jung, Y.; Chang, S. *Chem. Asian J.* **2011**, *6*, 2040.
2. Zeng, T.; Zhang, H.-Y.; Xie, Z.-B.; Dong, Y.-Y. Gong, S.-S; Sun, Q. *Asian. J. Org. Chem*. **2023**, *12*, e202200638.
3. Lu, L.; Chen, C.; Jiang H.; Yin B. *J. Org. Chem.* **2018,** *83*, 14385.

NMR Spectra Images of Starting Materials and Products

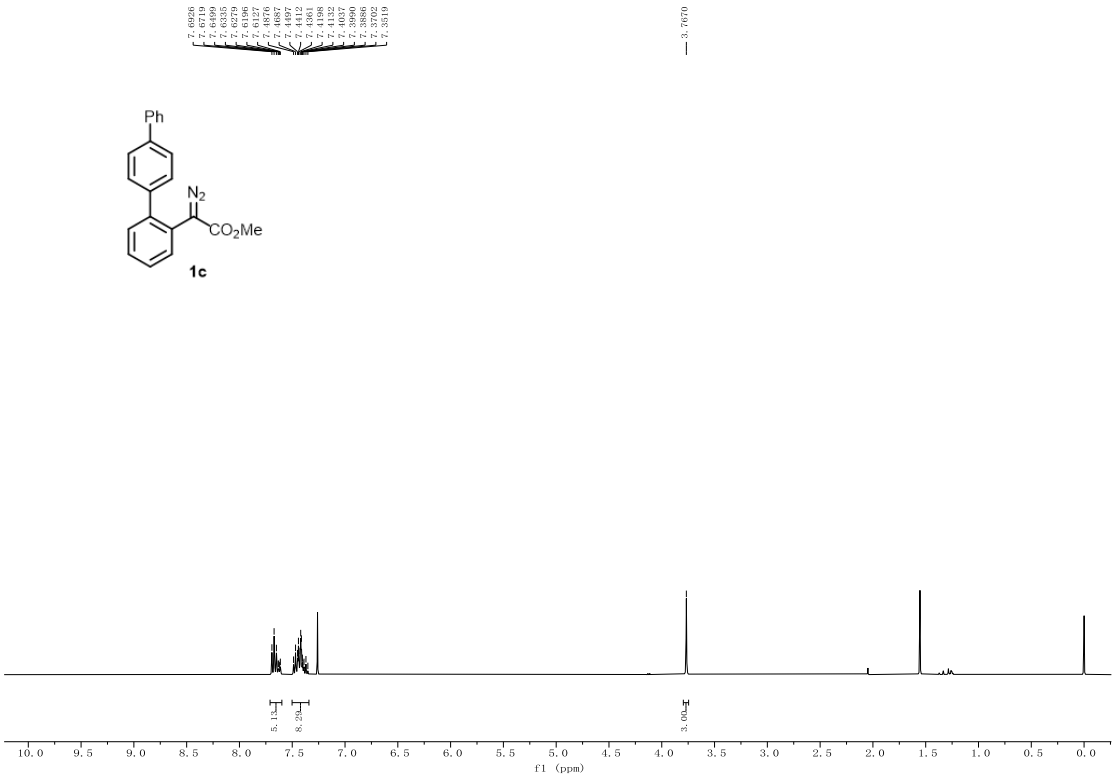
^{1}H NMR of compound **1a** (400 MHz in $CDCl_3$)



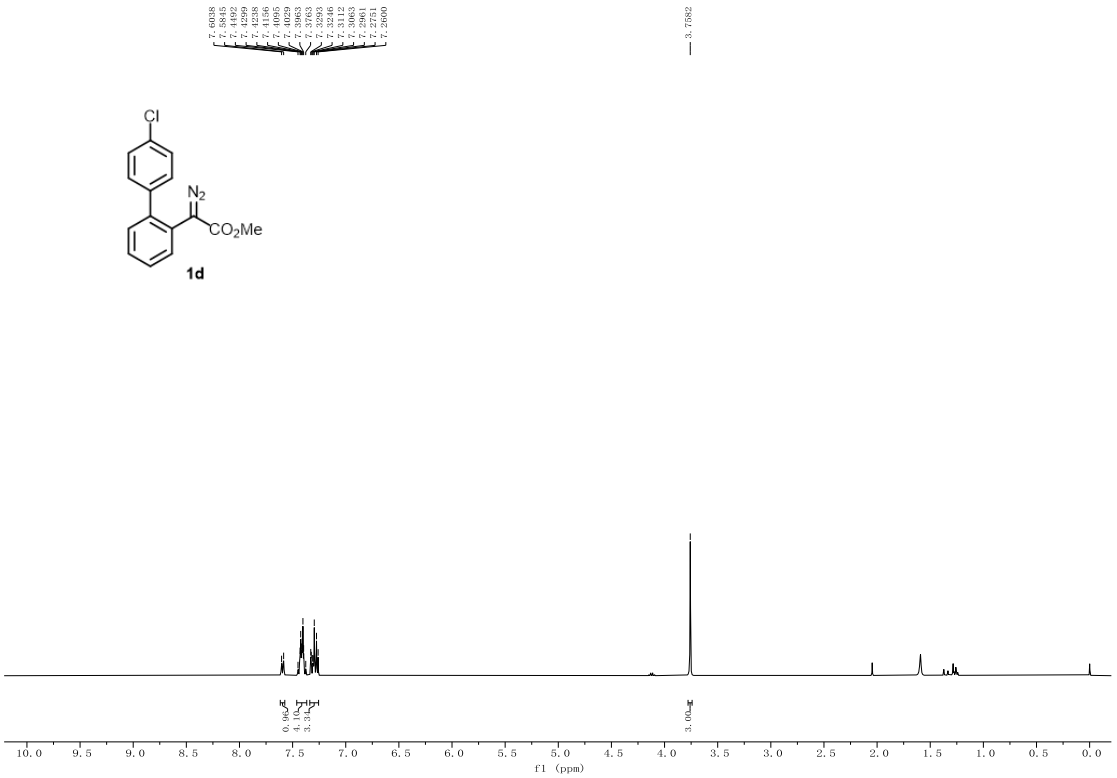
^{1}H NMR of compound **1b** (400 MHz in $CDCl_3$)



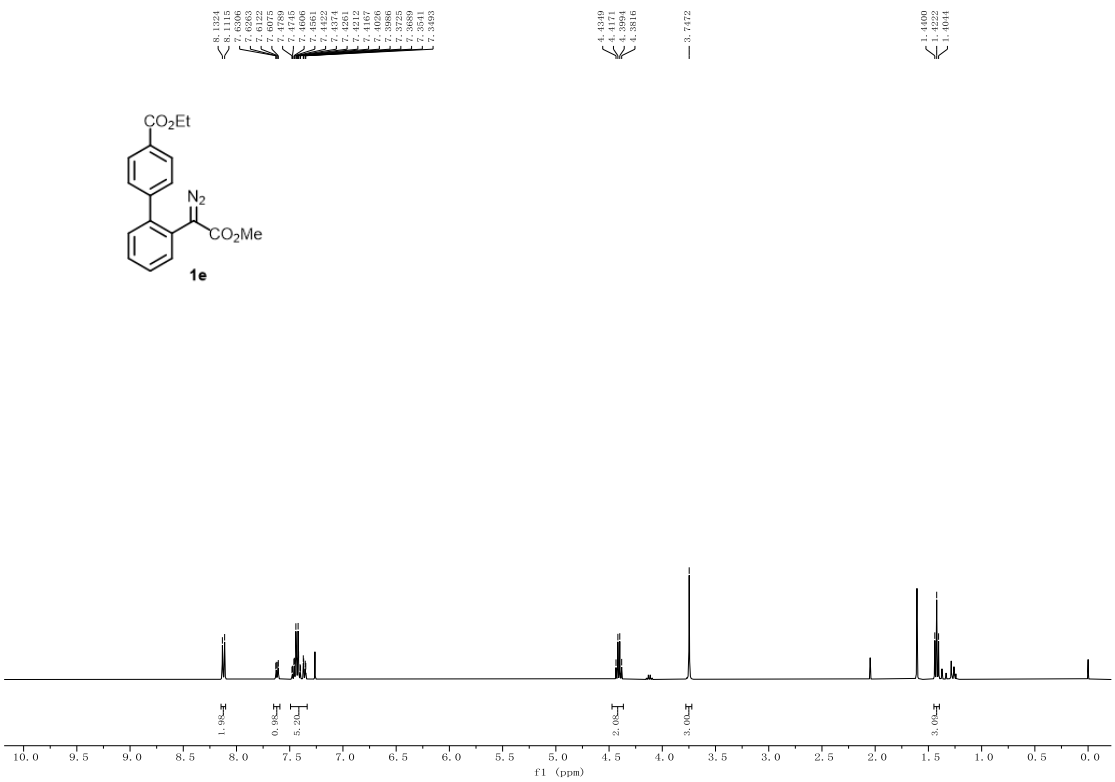
^{1}H NMR of compound **1c** (400 MHz in $CDCl_3$)



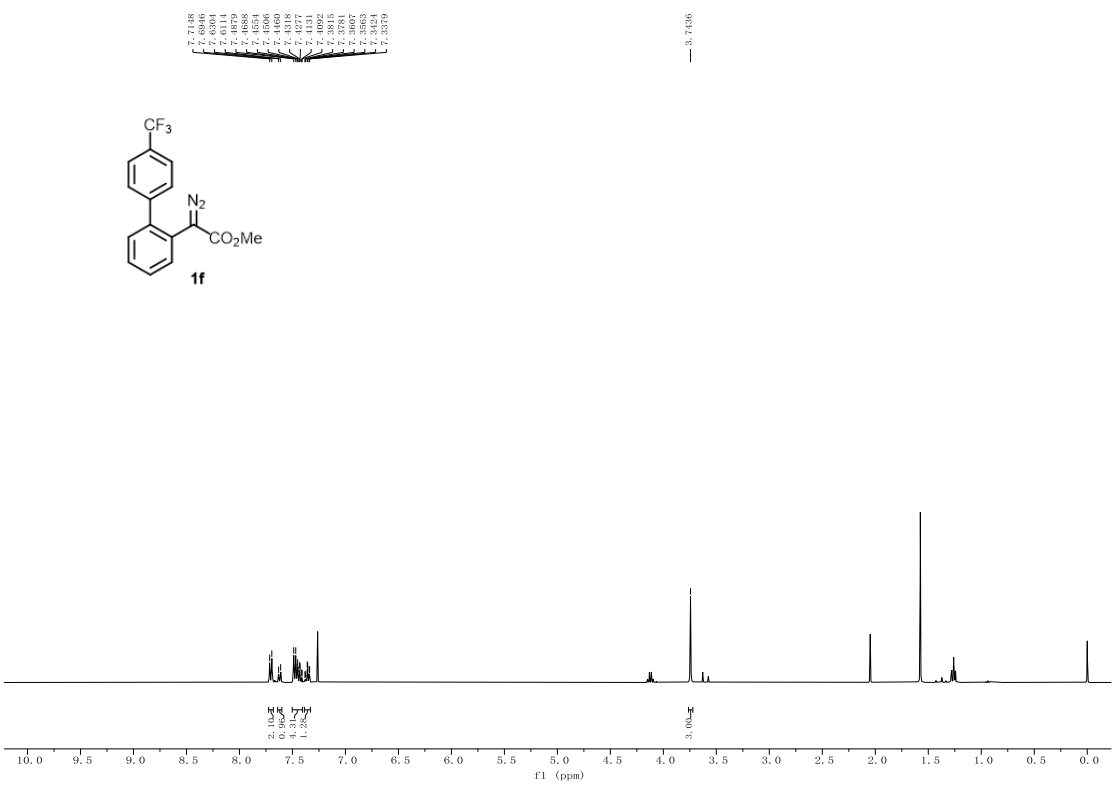
^{1}H NMR of compound **1d** (400 MHz in $CDCl_3$)



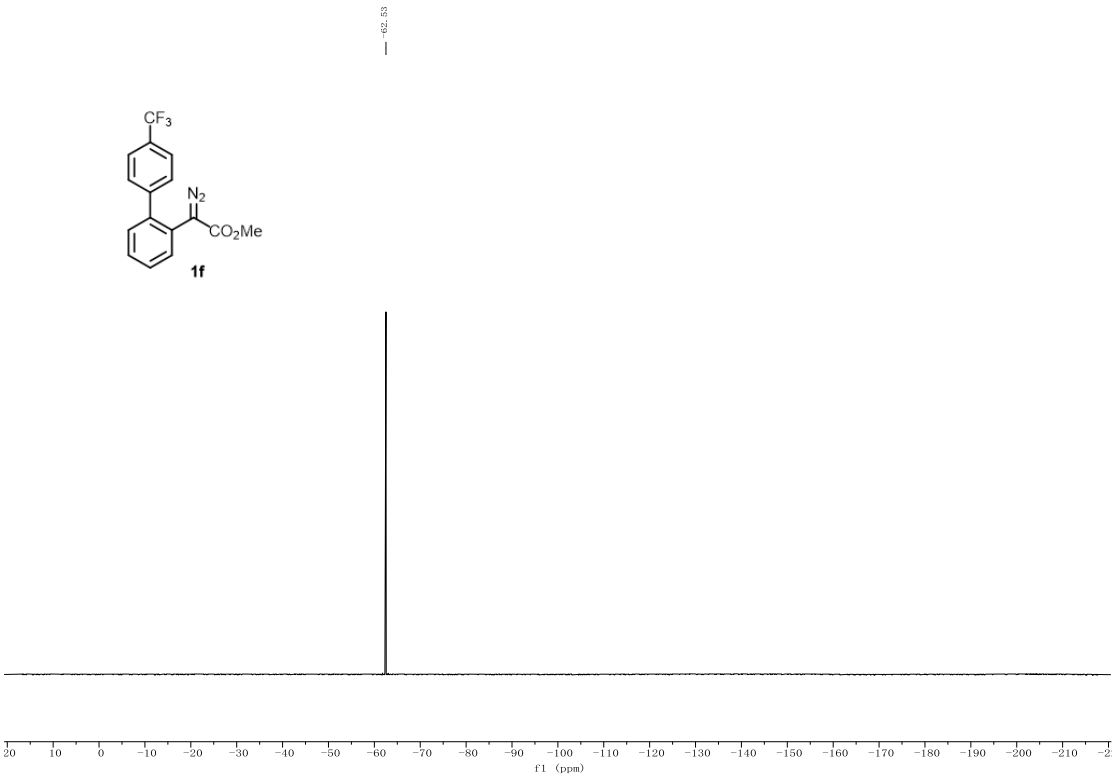
^{1}H NMR of compound **1e** (400 MHz in $CDCl_3$)



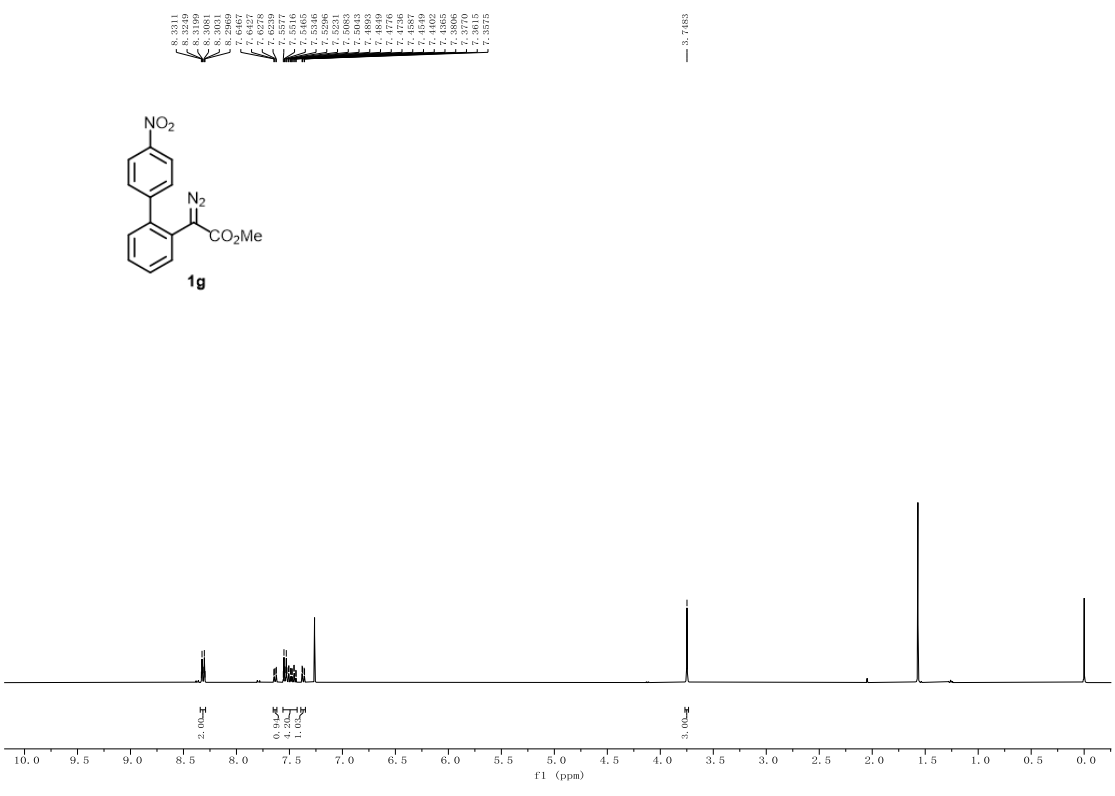
^{1}H NMR of compound **1f** (400 MHz in $CDCl_3$)



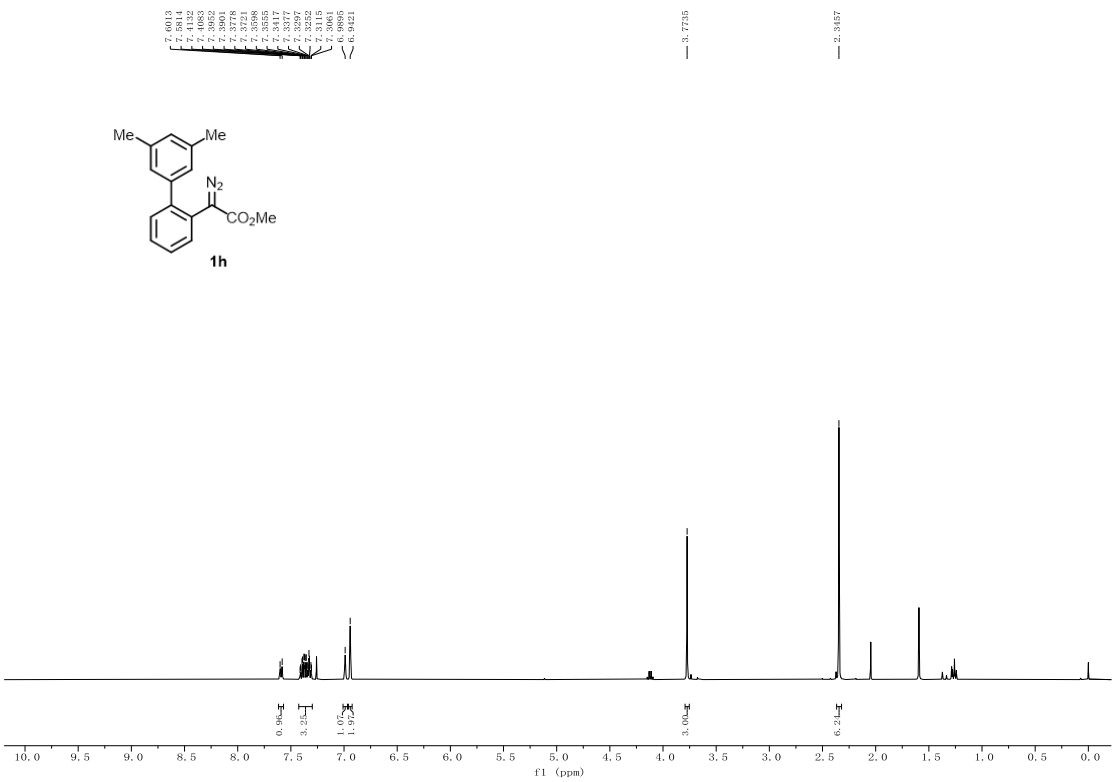
^{19}F NMR of compound **1f** (377 MHz in $CDCl_3$)



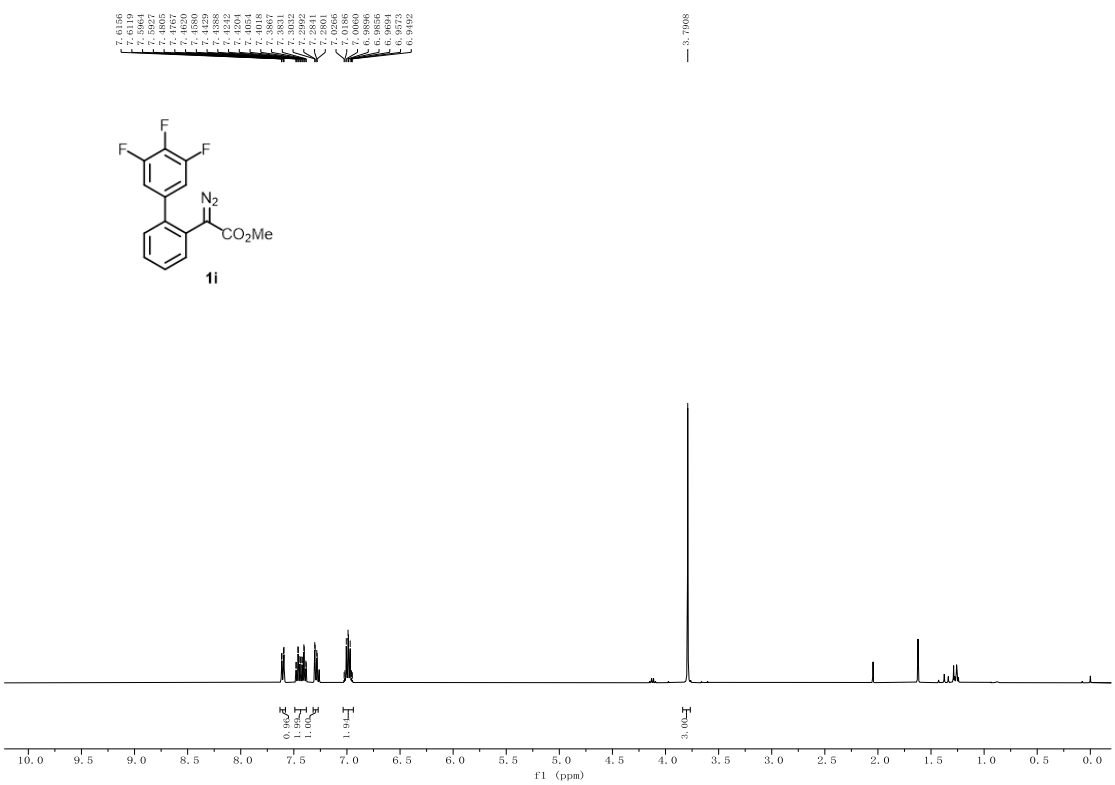
^{1}H NMR of compound **1g** (400 MHz in $CDCl_3$)



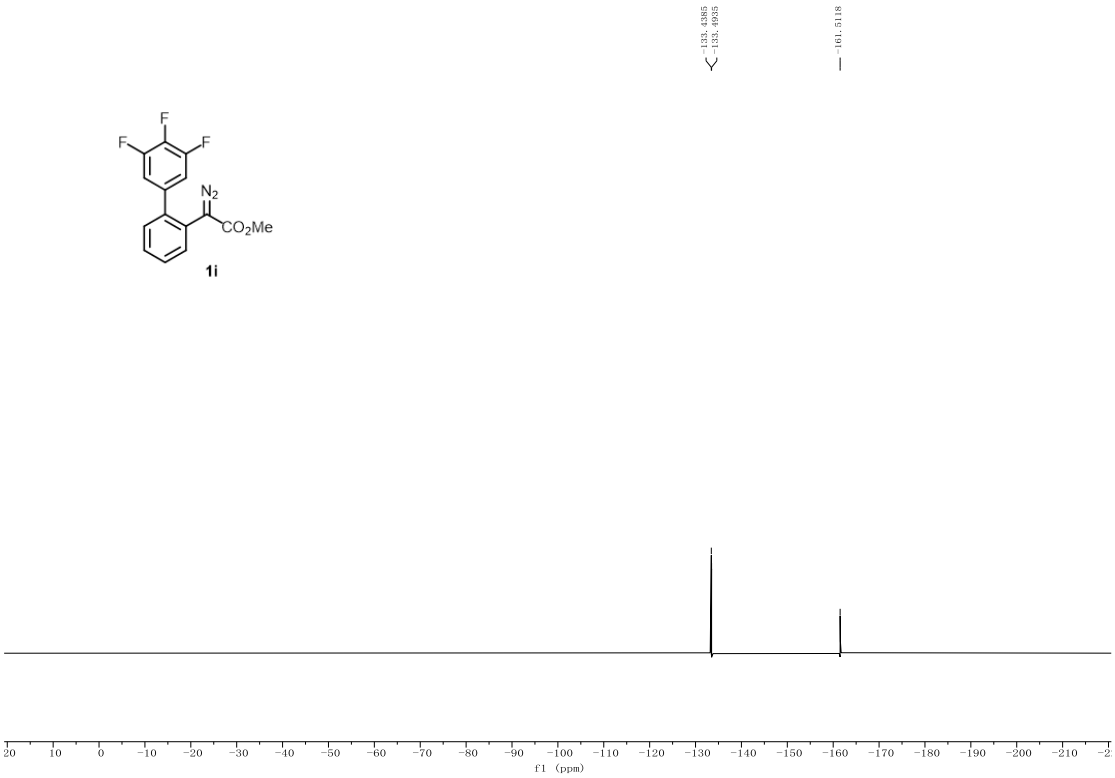
^{1}H NMR of compound **1h** (400 MHz in $CDCl_3$)



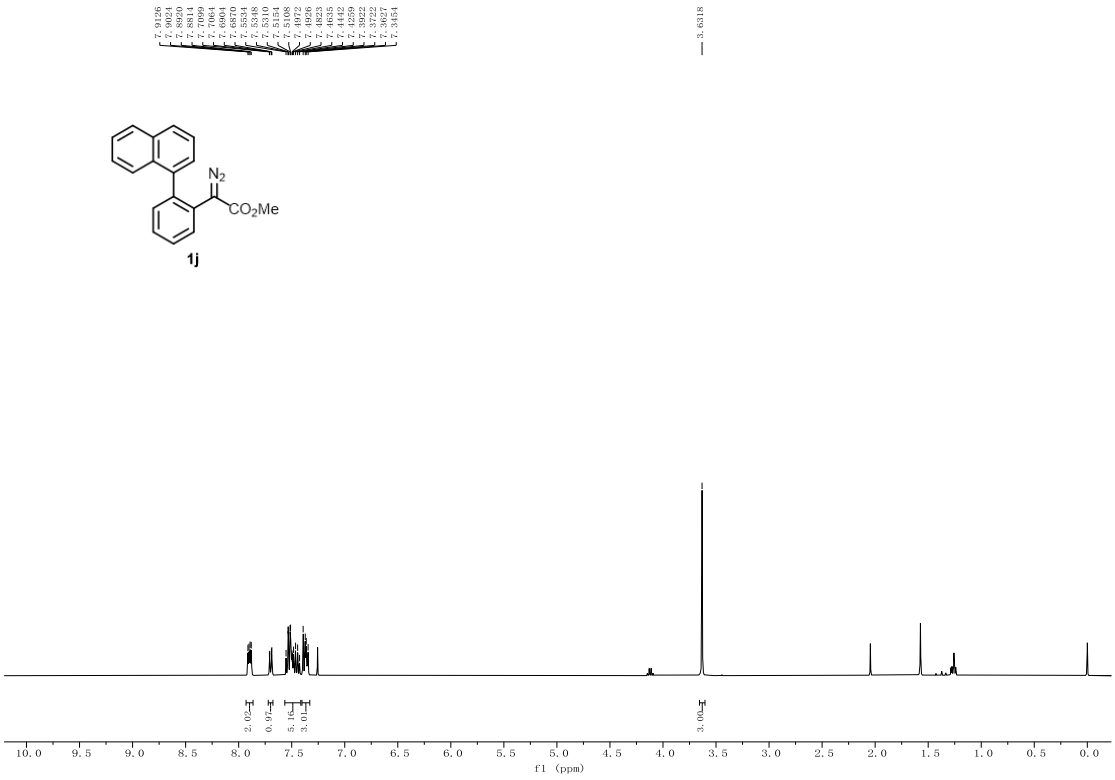
^{1}H NMR of compound **1i** (400 MHz in $CDCl_3$)



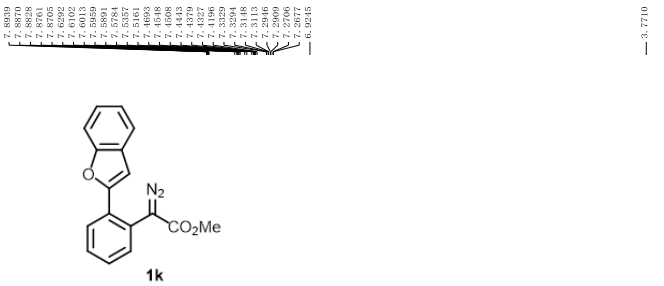
^{19}F NMR of compound **1i** (377 MHz in $CDCl_3$)



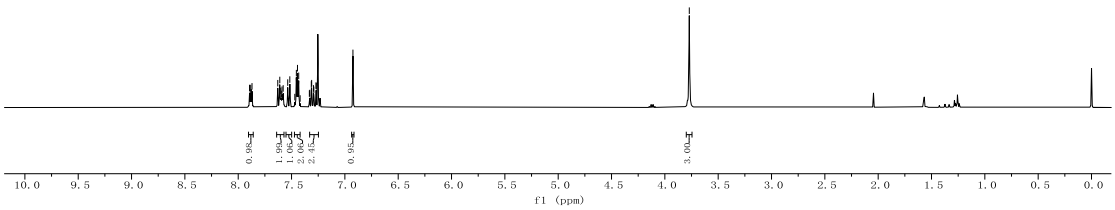
^{1}H NMR of compound **1j** (400 MHz in $CDCl_3$)



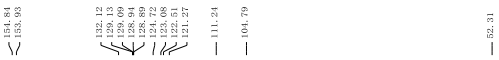
^{1}H NMR of compound **1k** (400 MHz in $CDCl_3$)

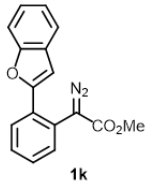


1k

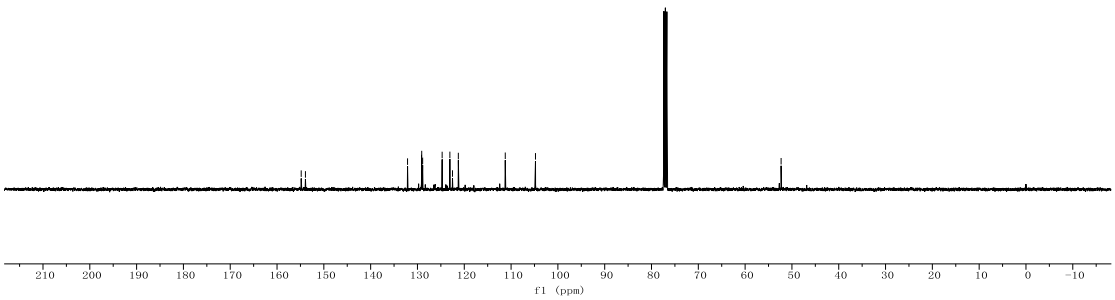


^{13}C NMR of compound **1k** (101 MHz in $CDCl_3$)

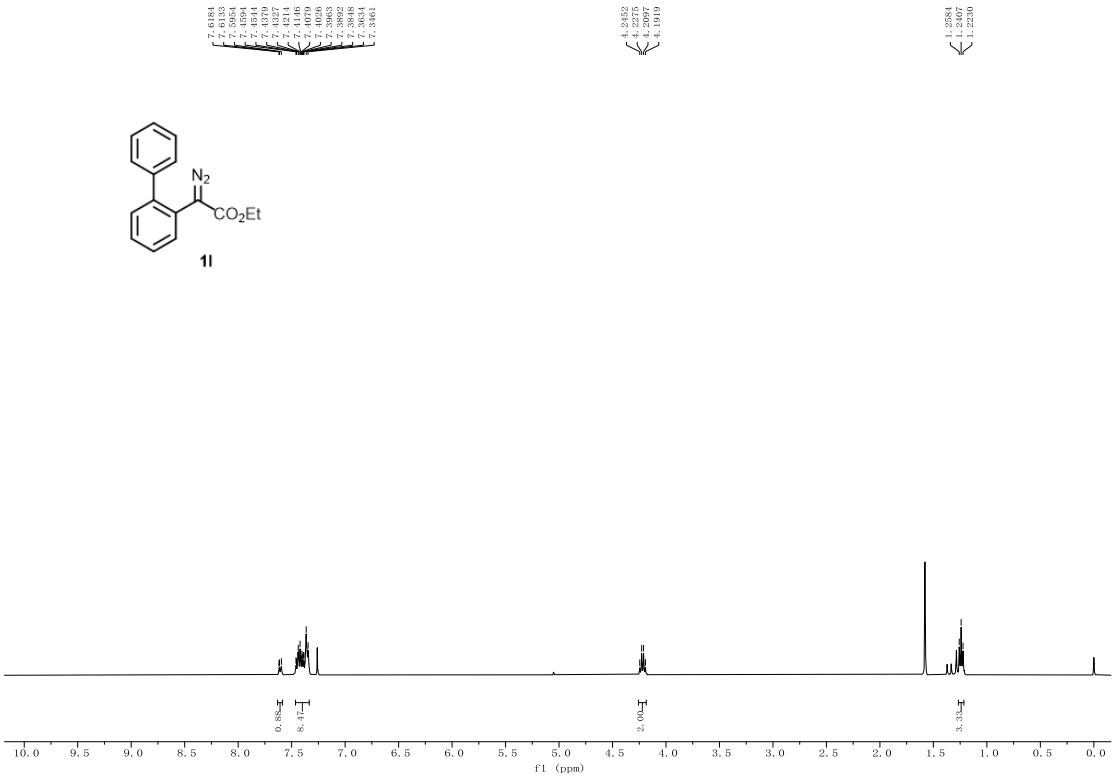




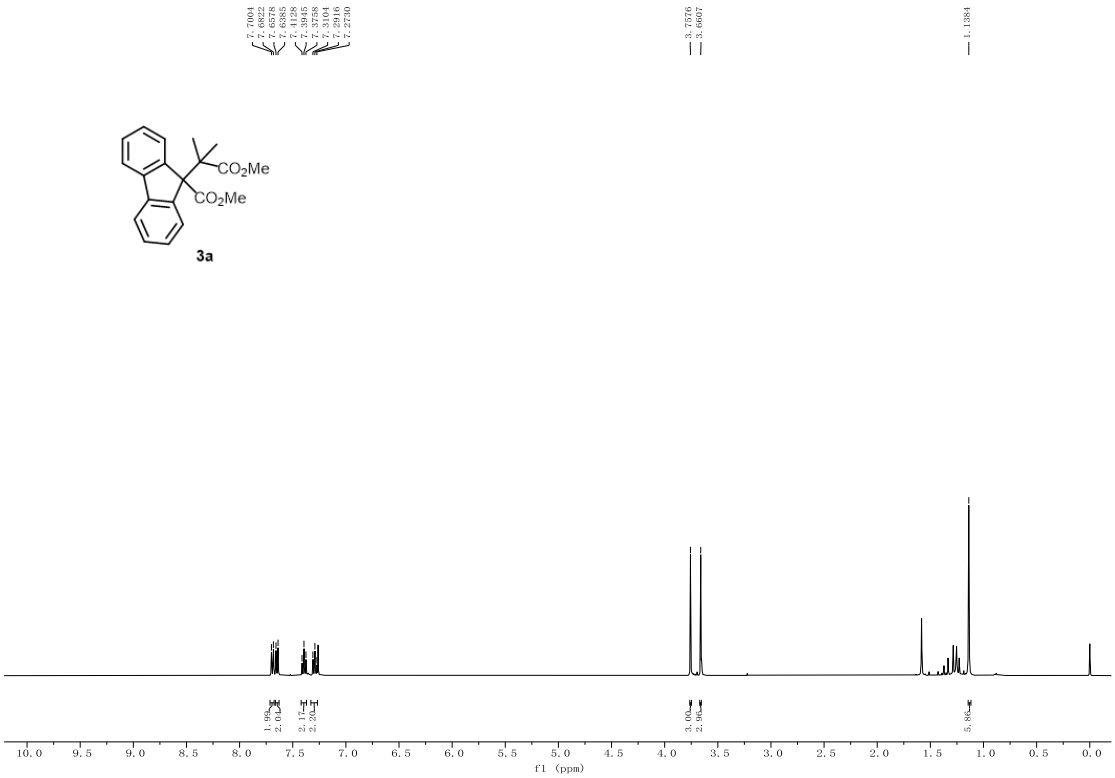
1k



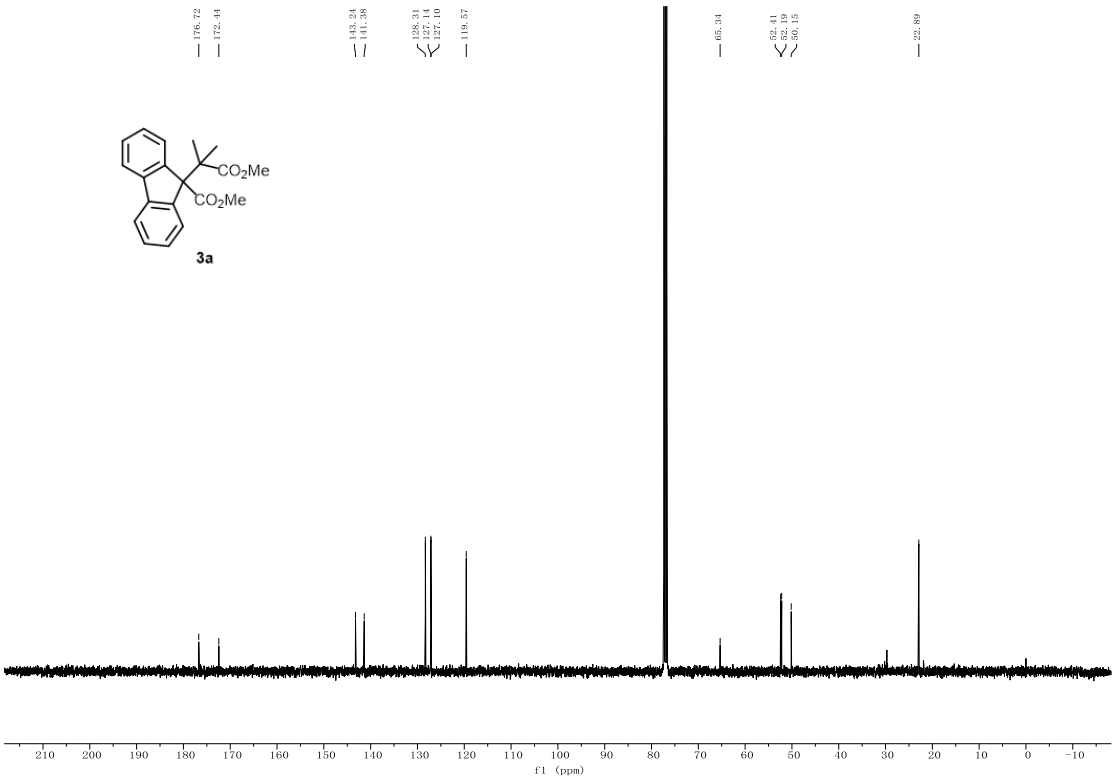
^{1}H NMR of compound **1l** (400 MHz in $CDCl_3$)



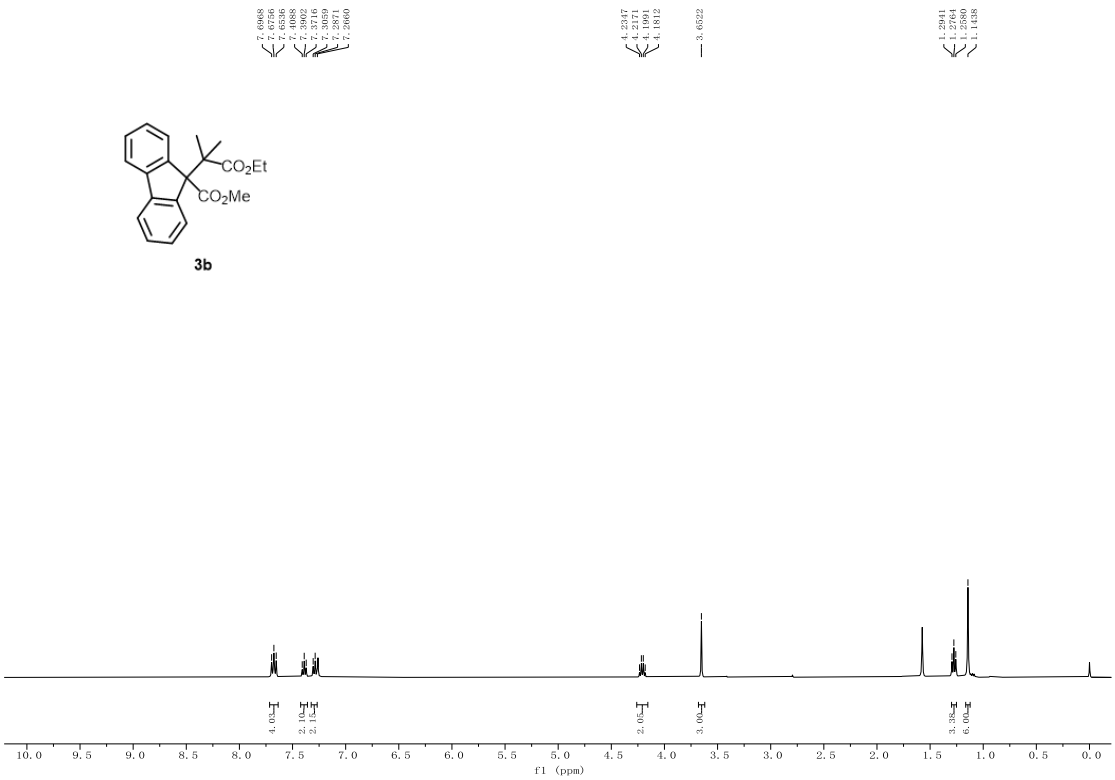
^{1}H NMR of compound **3a** (400 MHz in $CDCl_3$)



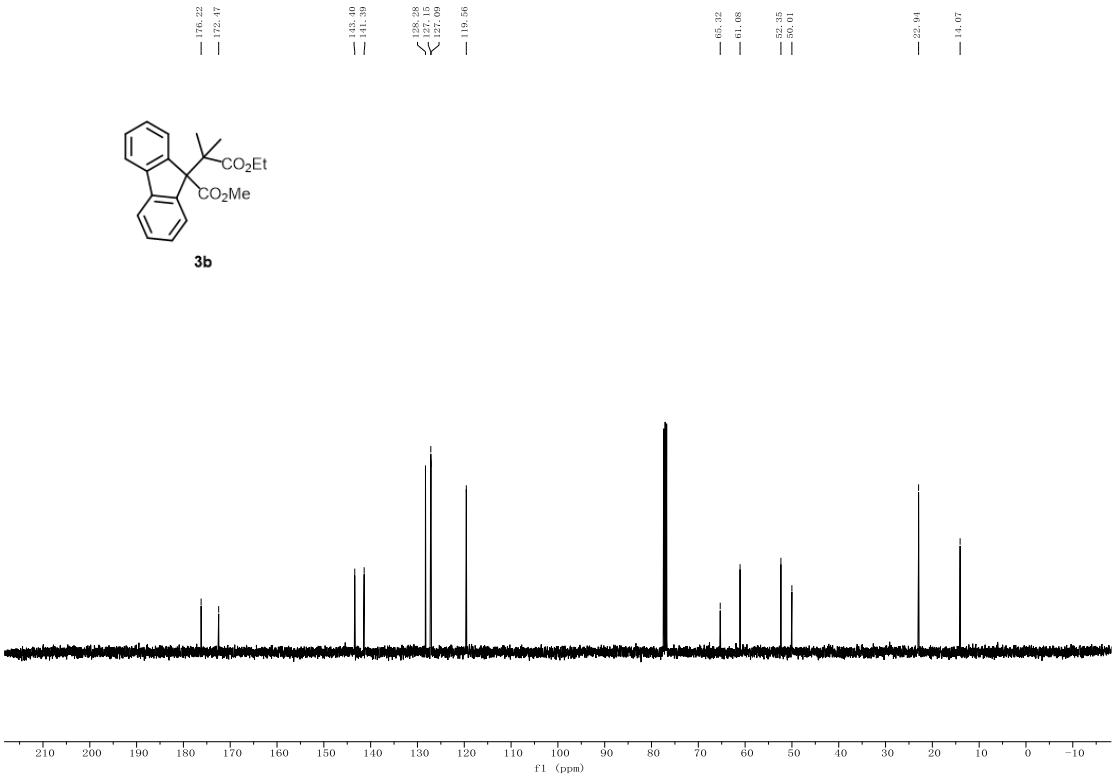
^{13}C NMR of compound **3a** (101 MHz in $CDCl_3$)



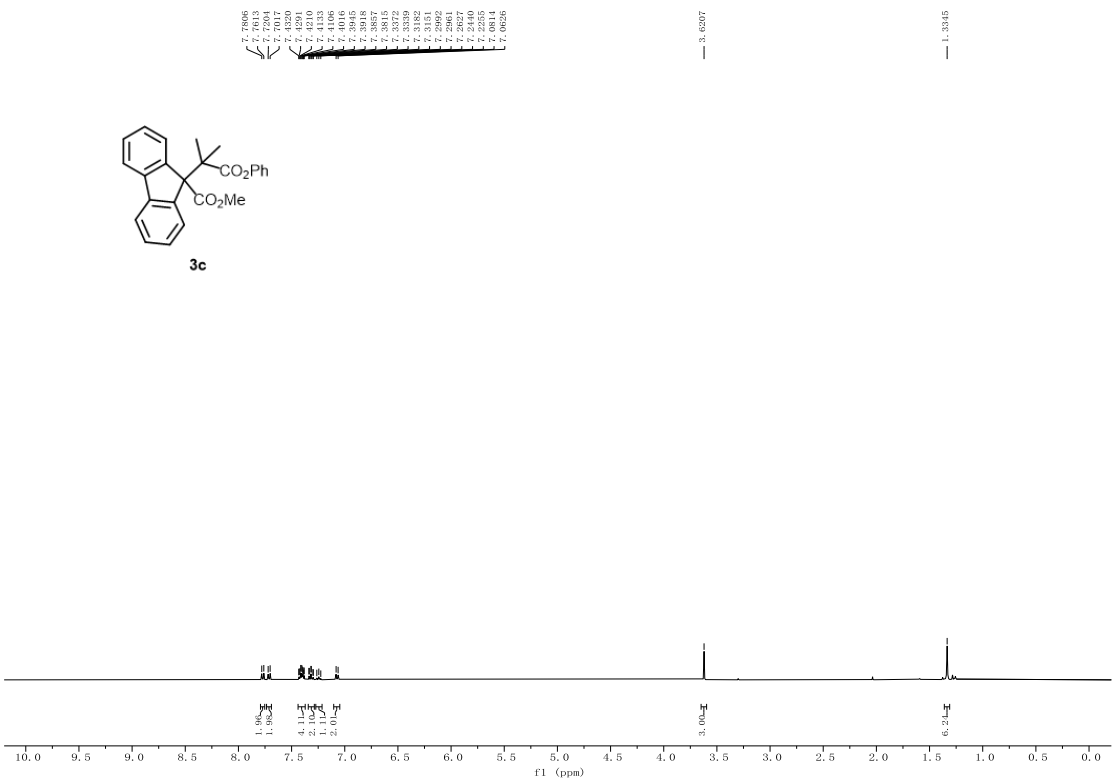
^{1}H NMR of compound **3b** (400 MHz in $CDCl_3$)



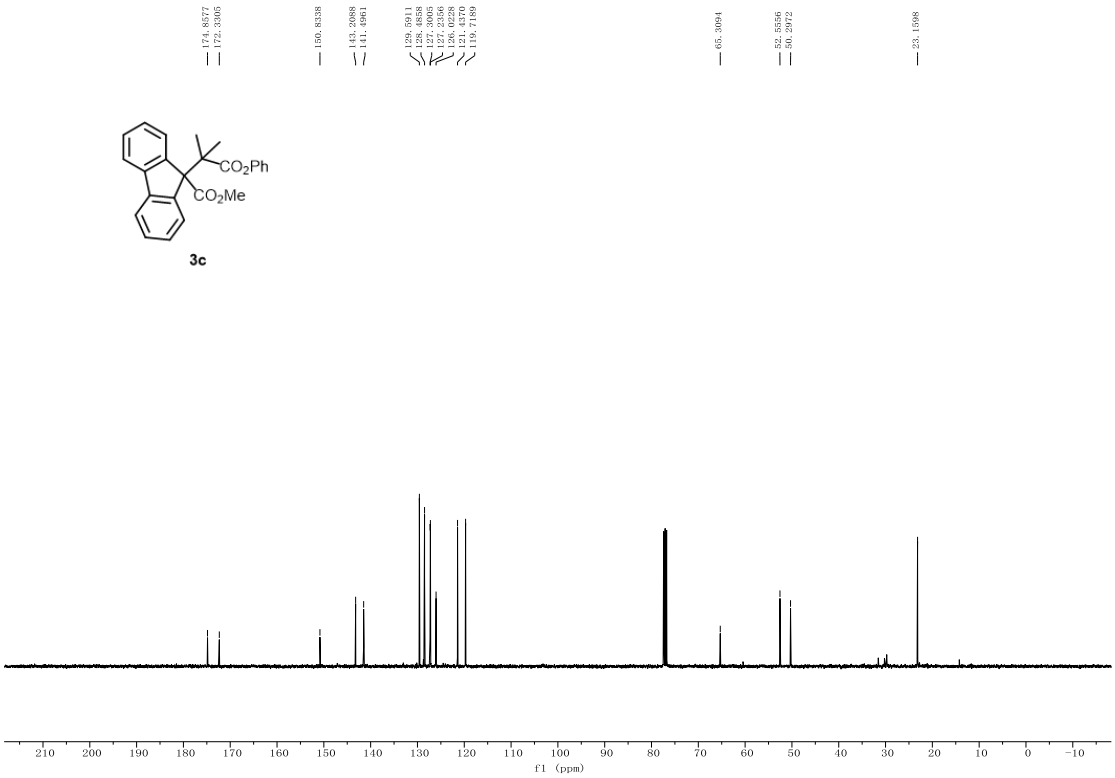
^{13}C NMR of compound **3b** (101 MHz in $CDCl_3$)



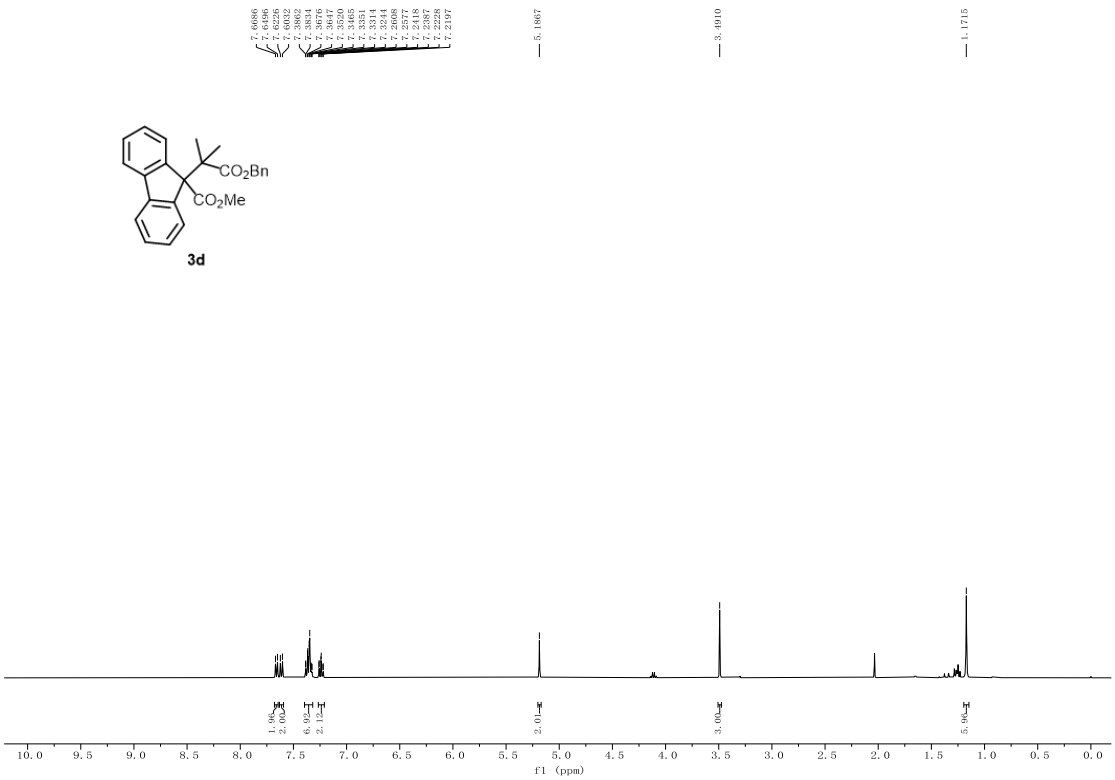
^{1}H NMR of compound **3c** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **3c** (101 MHz in $CDCl_3$)



^{1}H NMR of compound **3d** (400 MHz in $CDCl_3$)



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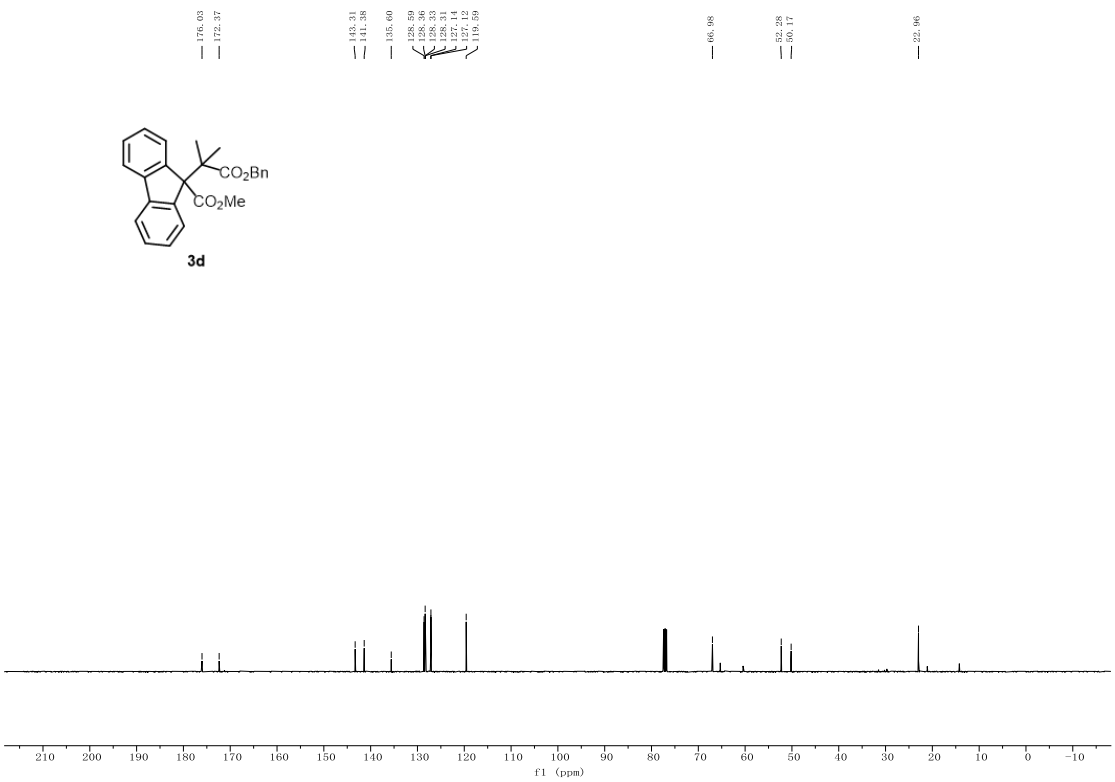

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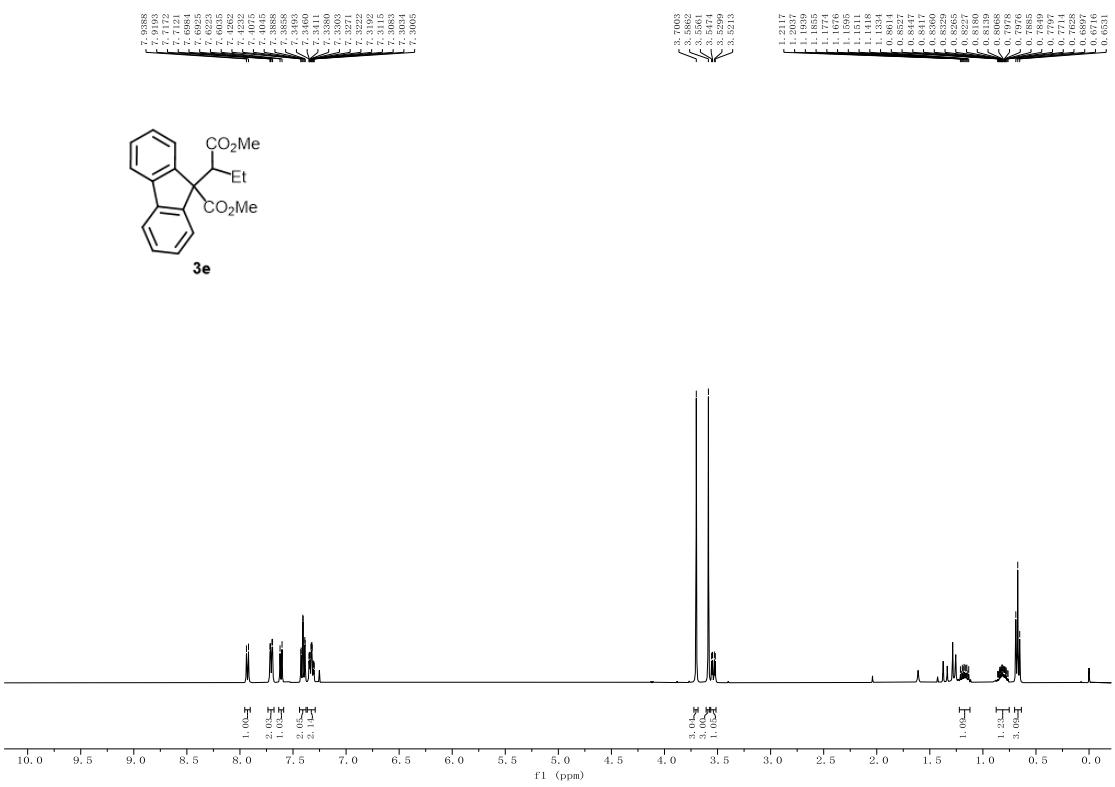

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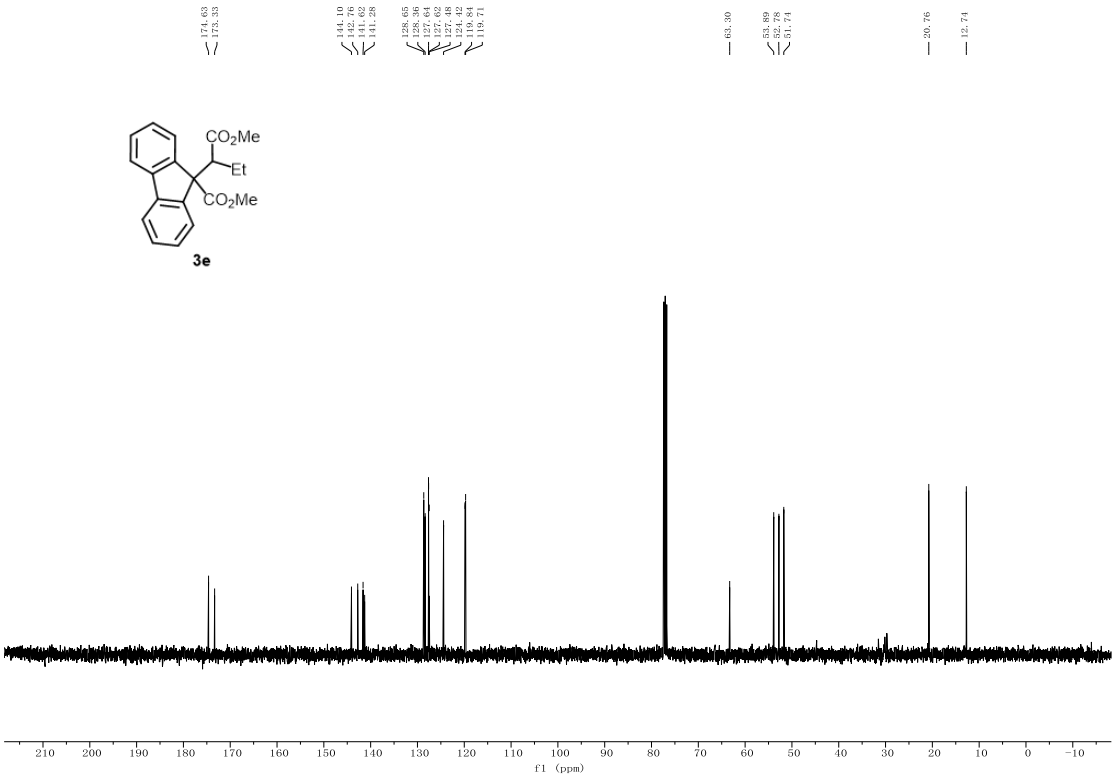
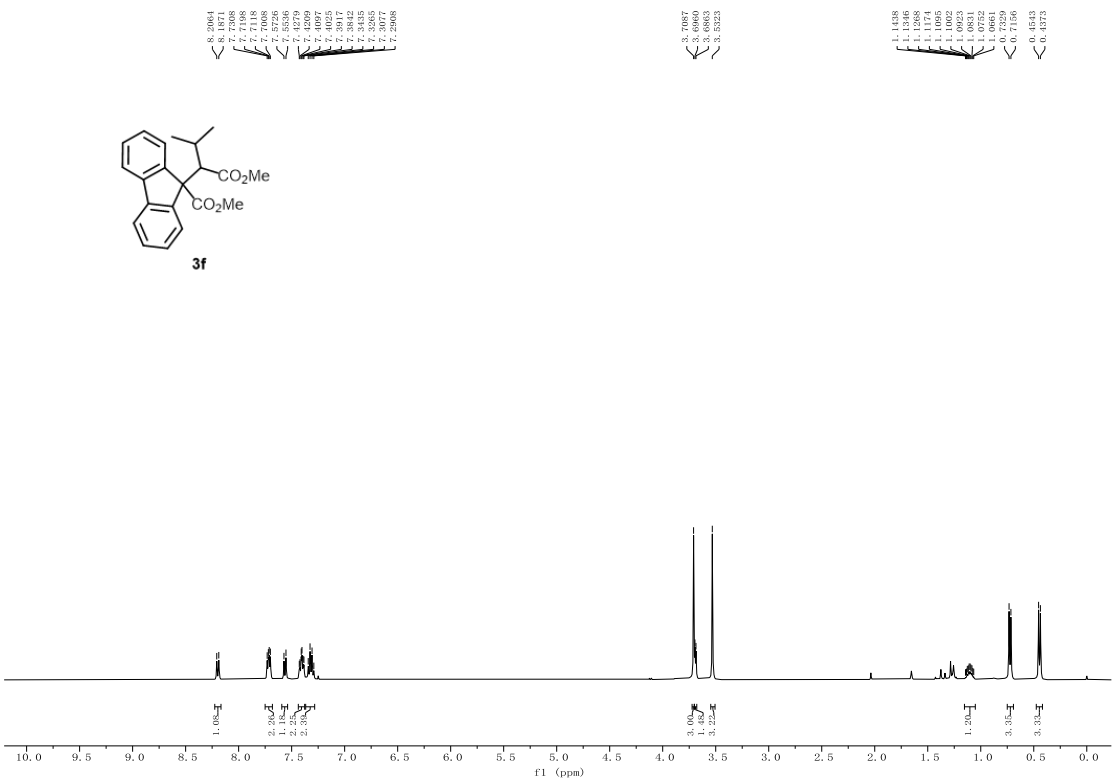


^{1}H NMR of compound **3f** (400 MHz in $CDCl_3$)



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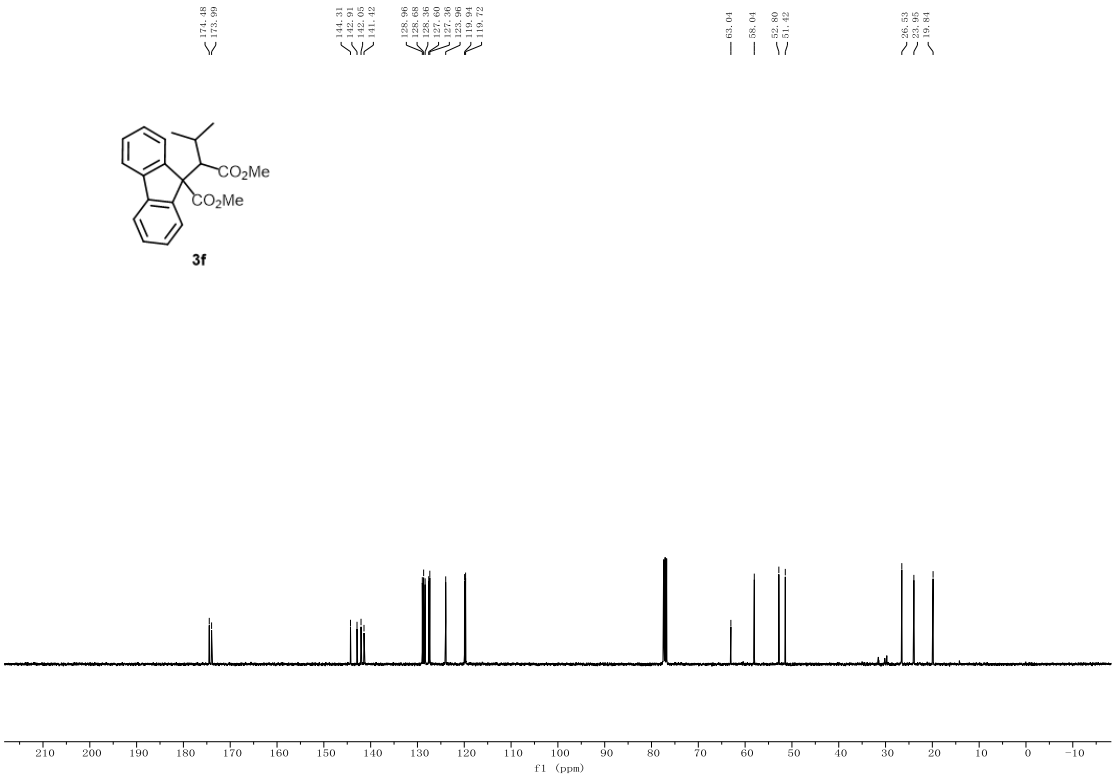
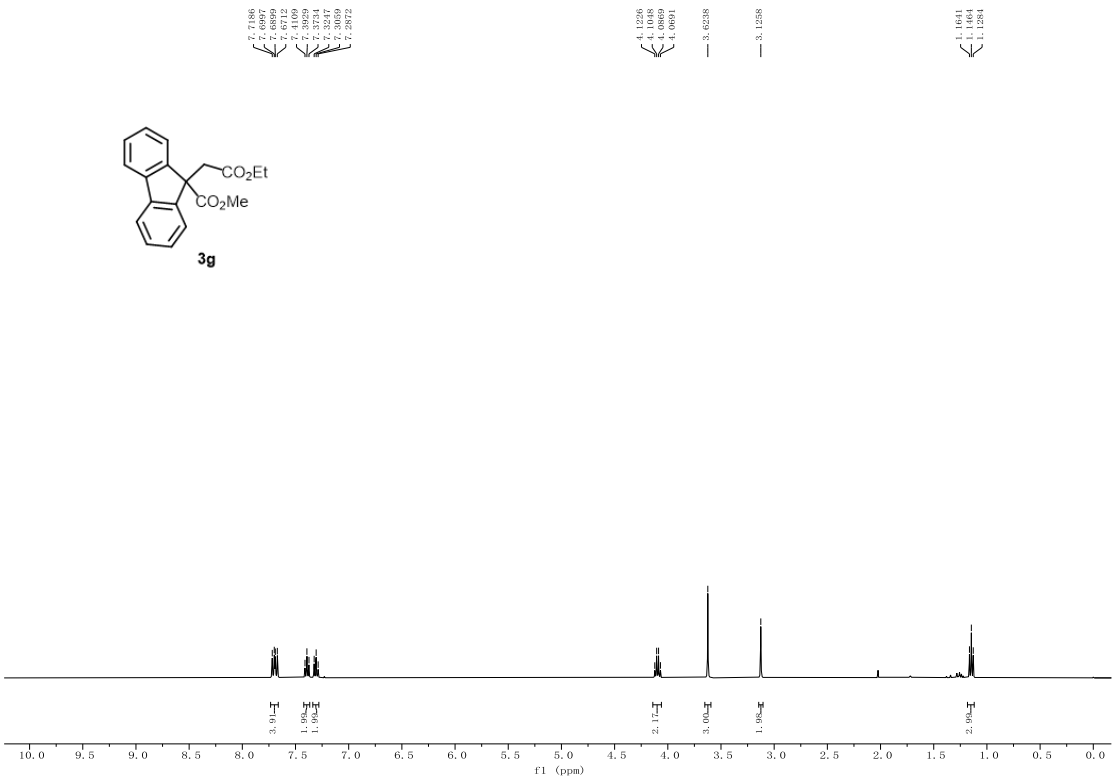


^{1}H NMR of compound **3g** (400 MHz in $CDCl_3$)



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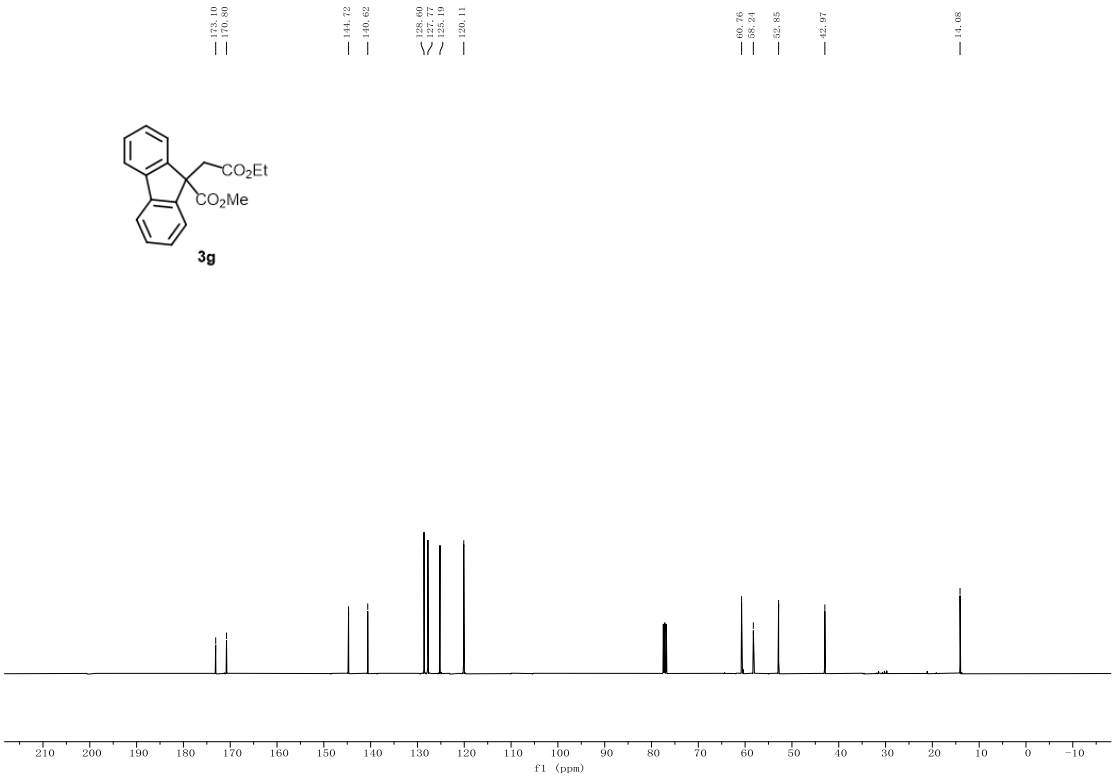
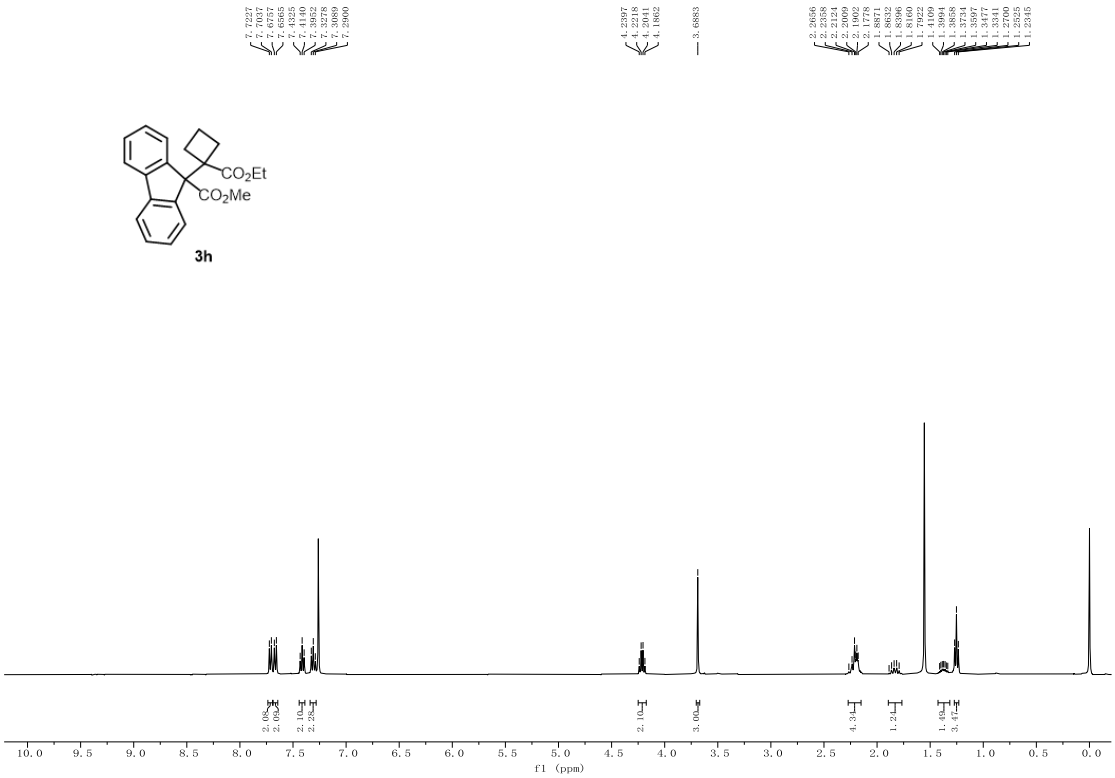
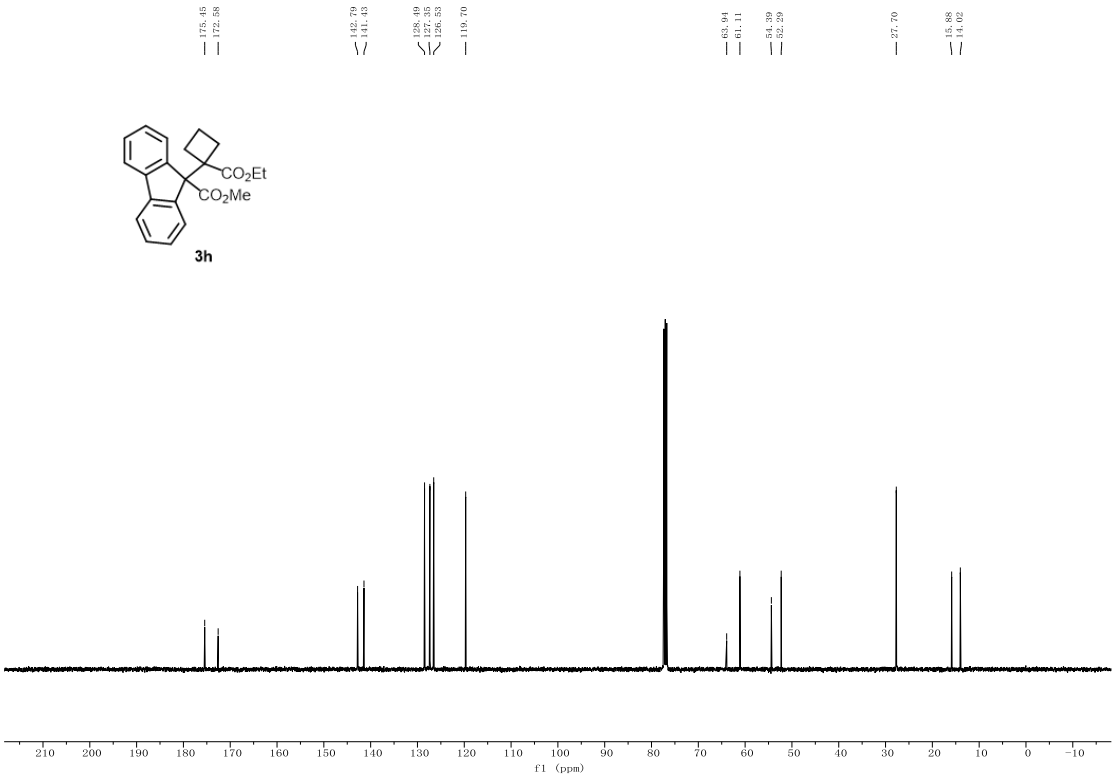


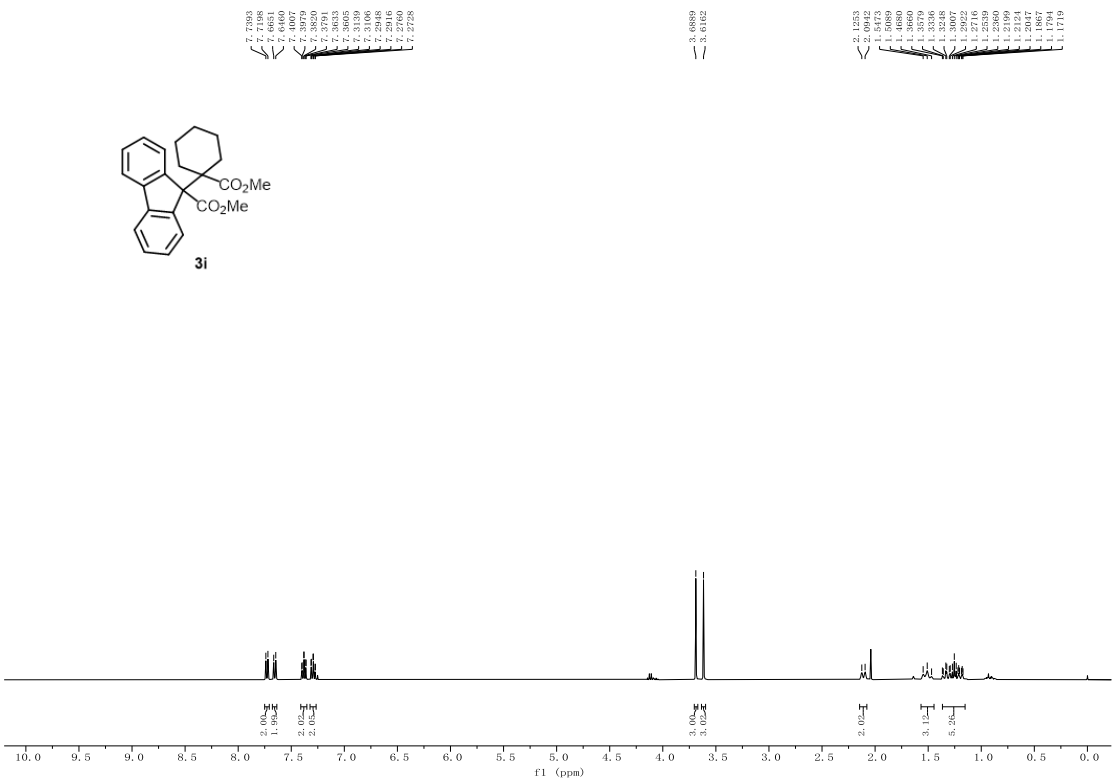
^{1}H NMR of compound **3h** (400 MHz in $CDCl_3$)



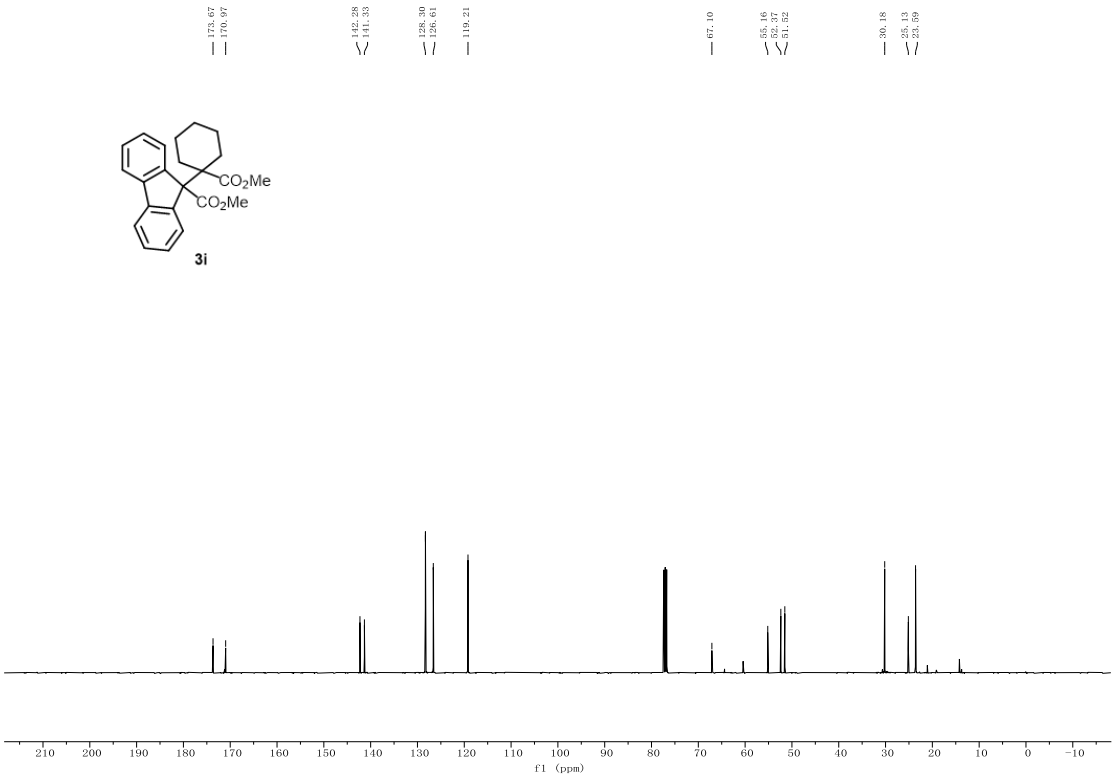
^{13}C NMR of compound **3h** (101 MHz in $CDCl_3$)



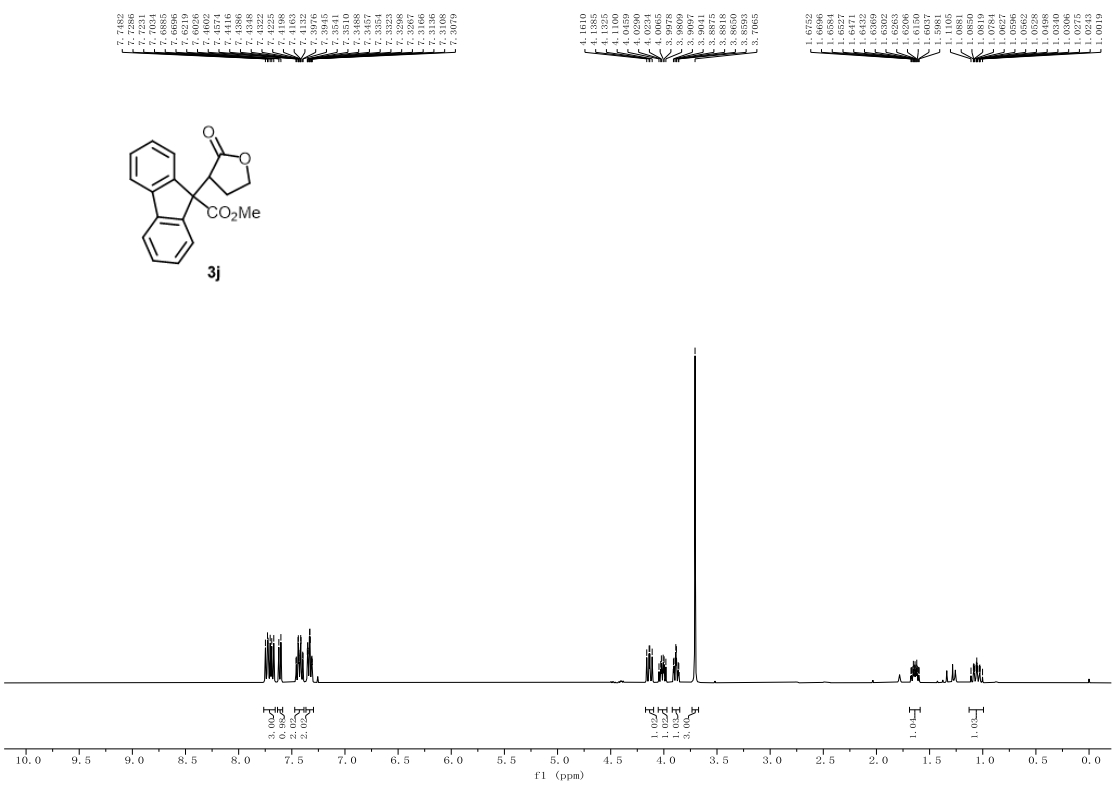
^{1}H NMR of compound **3i** (400 MHz in $CDCl_3$)



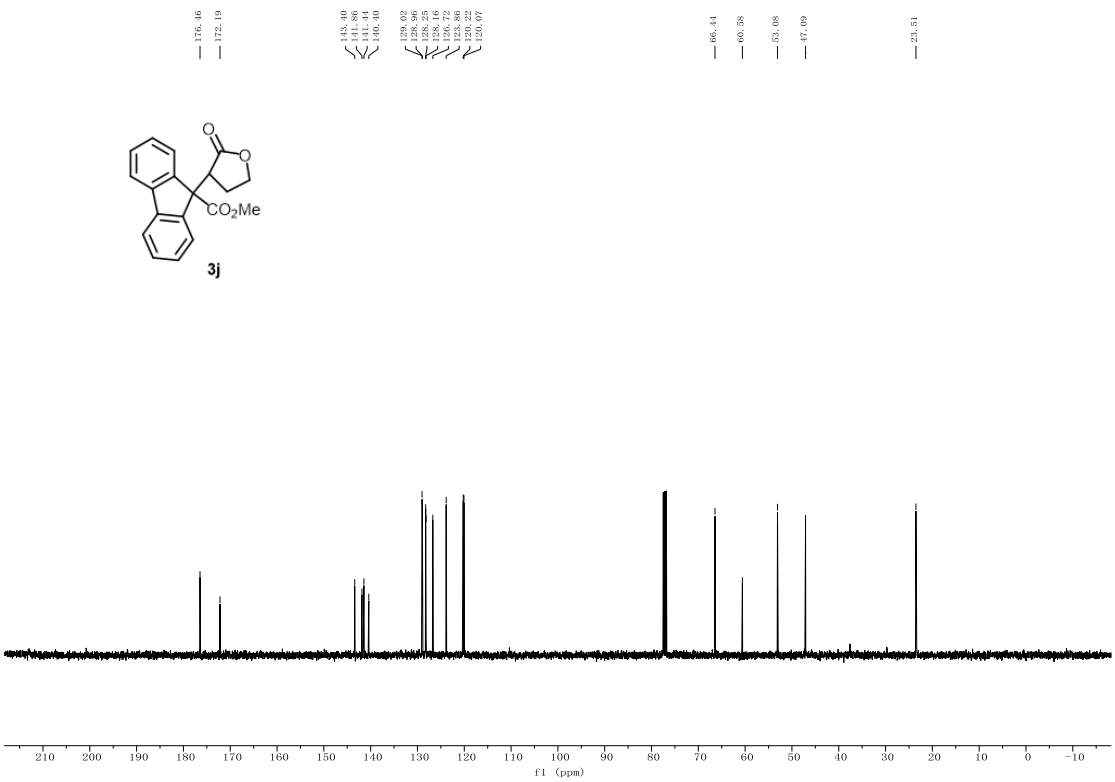
^{13}C NMR of compound **3i** (101 MHz in $CDCl_3$)



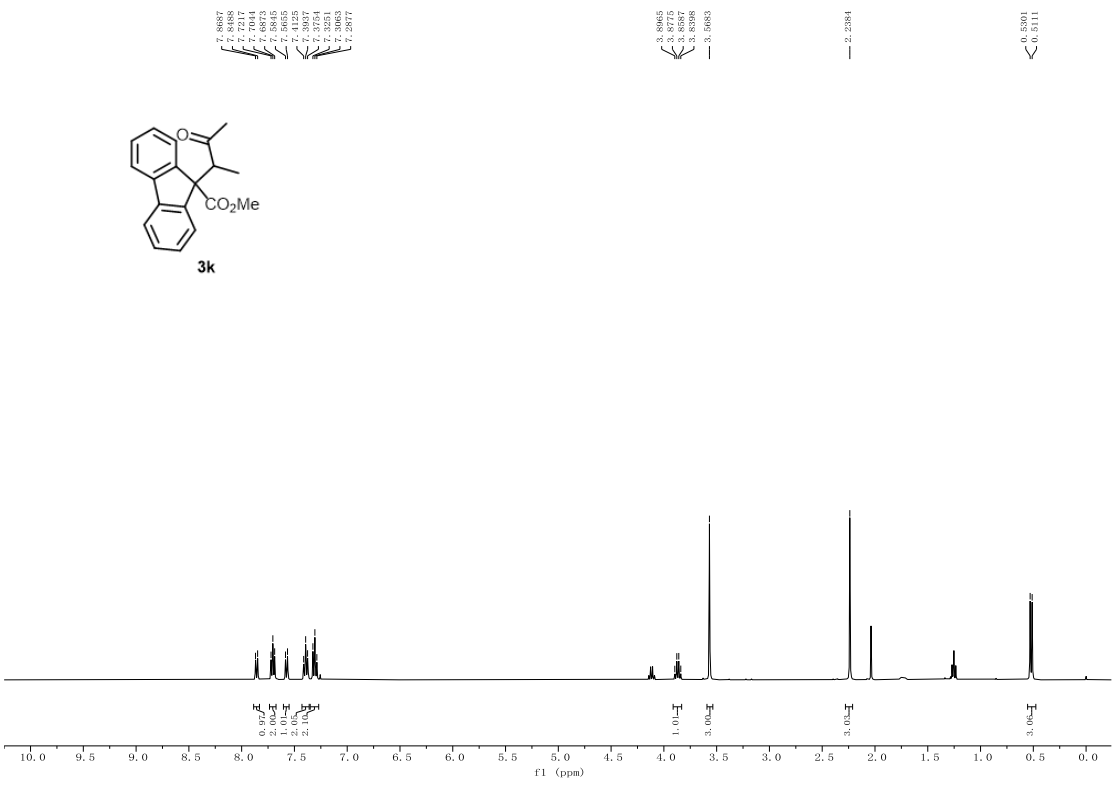
^{1}H NMR of compound **3j** (400 MHz in $CDCl_3$)



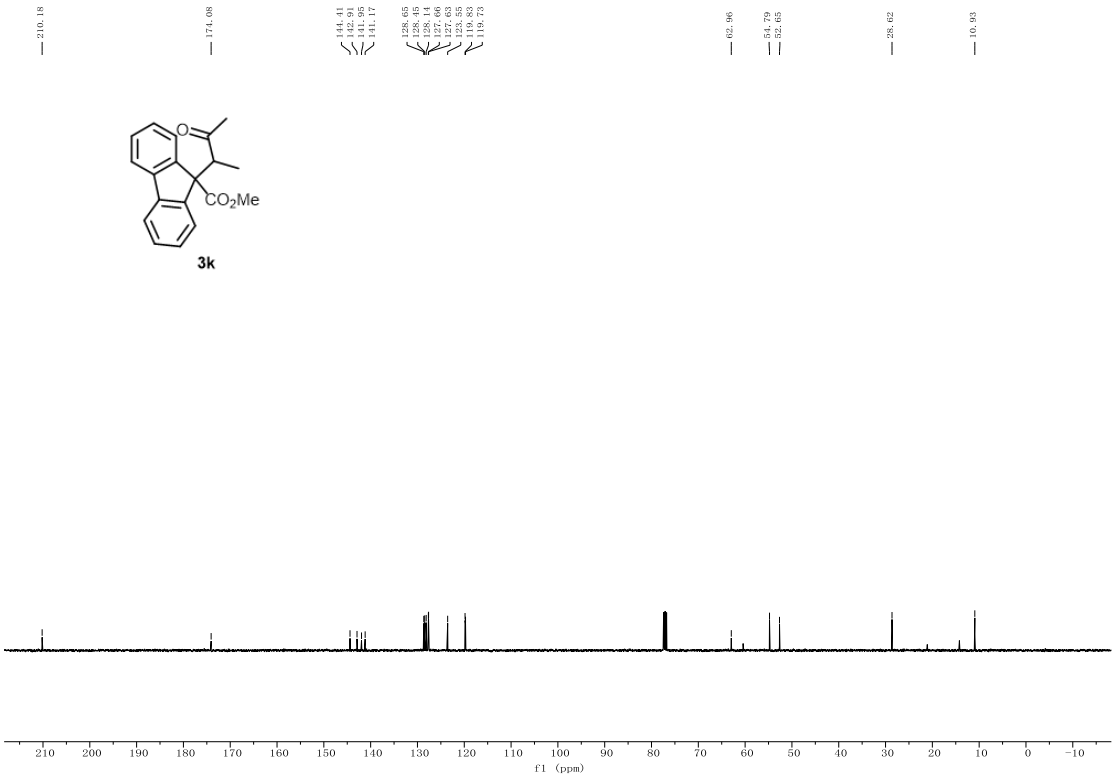
^{13}C NMR of compound **3j** (101 MHz in $CDCl_3$)



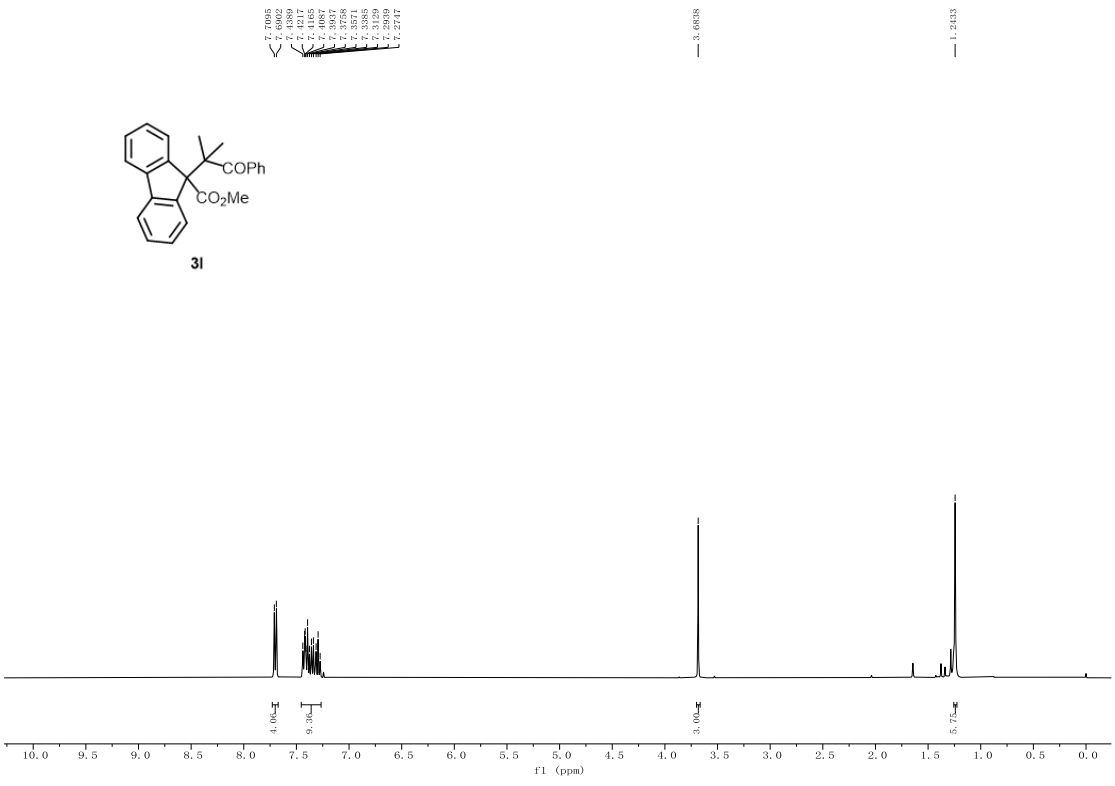
^{1}H NMR of compound **3k** (400 MHz in $CDCl_3$)



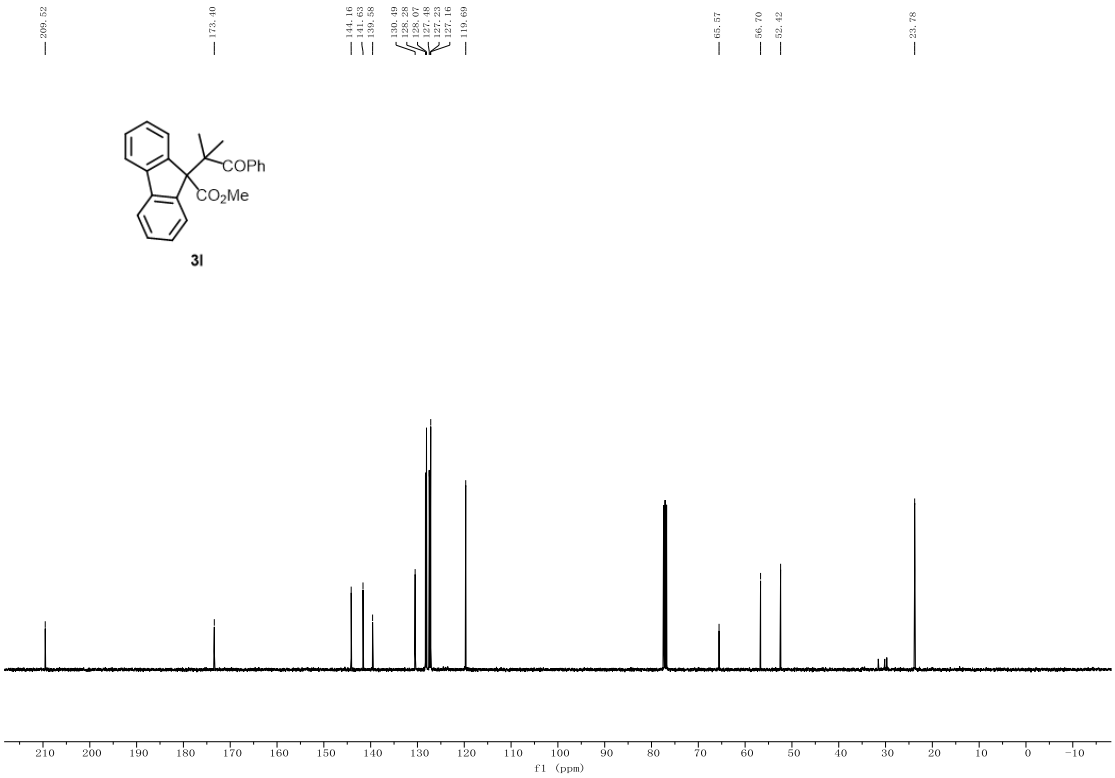
^{13}C NMR of compound **3k** (101 MHz in $CDCl_3$)



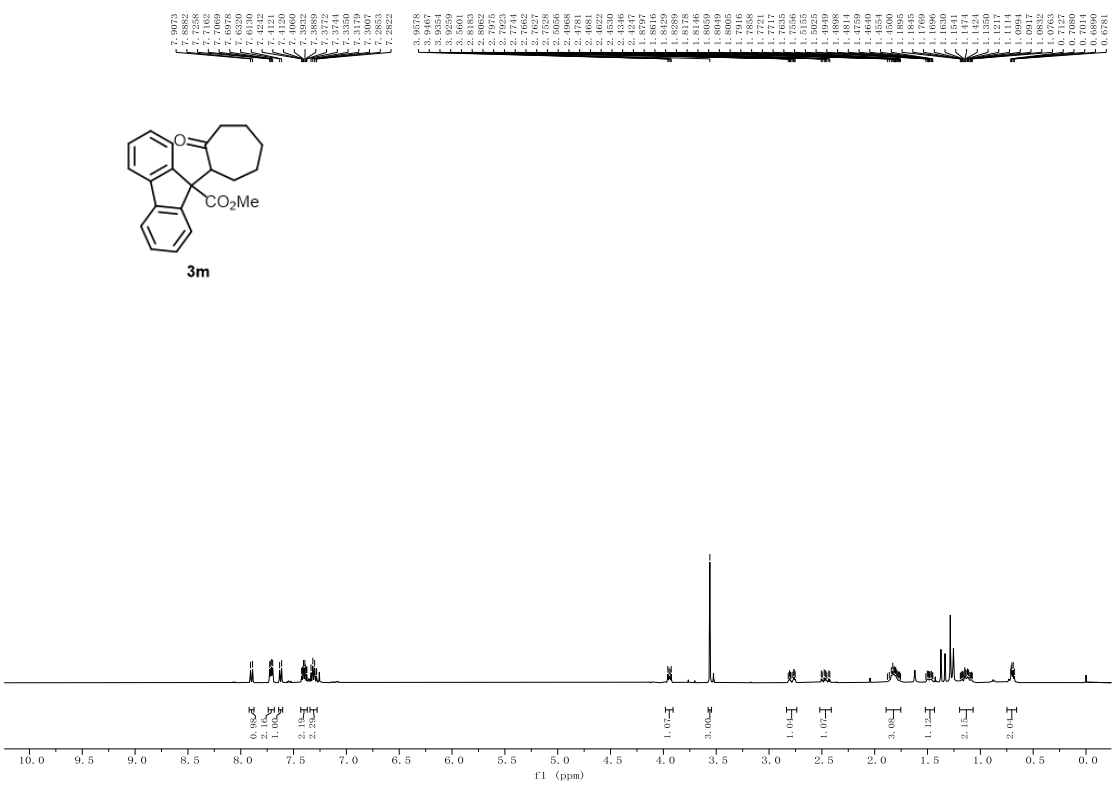
^{1}H NMR of compound **3l** (400 MHz in $CDCl_3$)



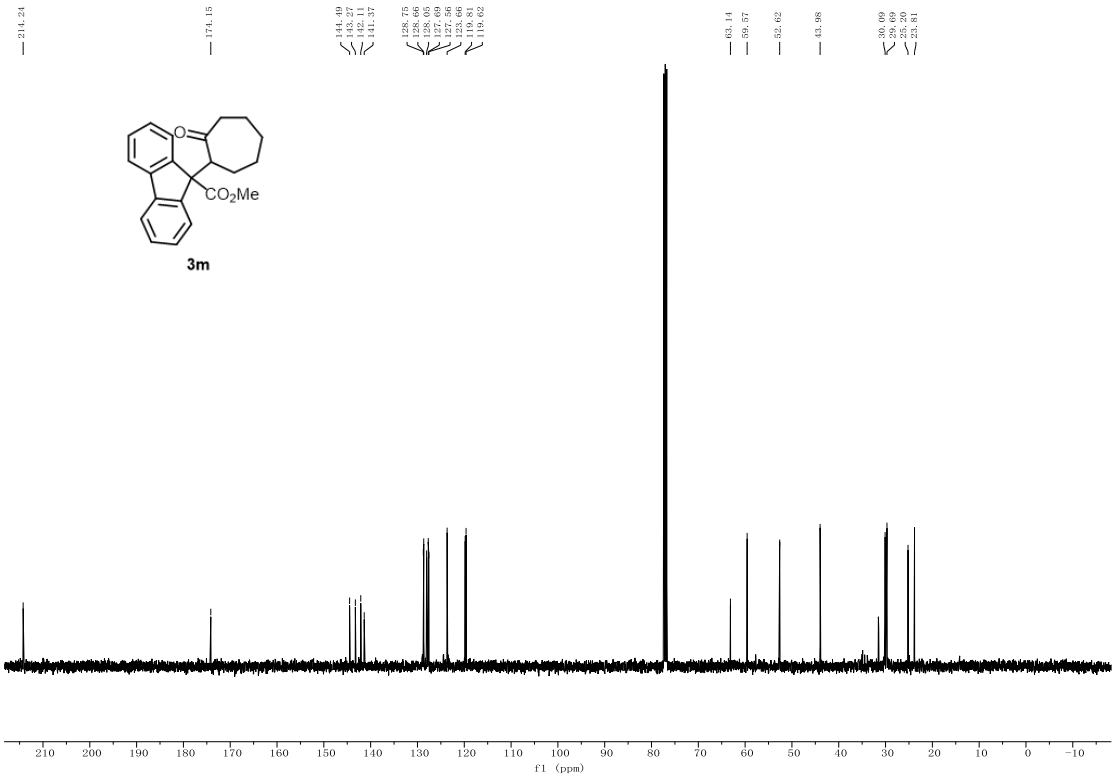
^{13}C NMR of compound **3l** (101 MHz in $CDCl_3$)



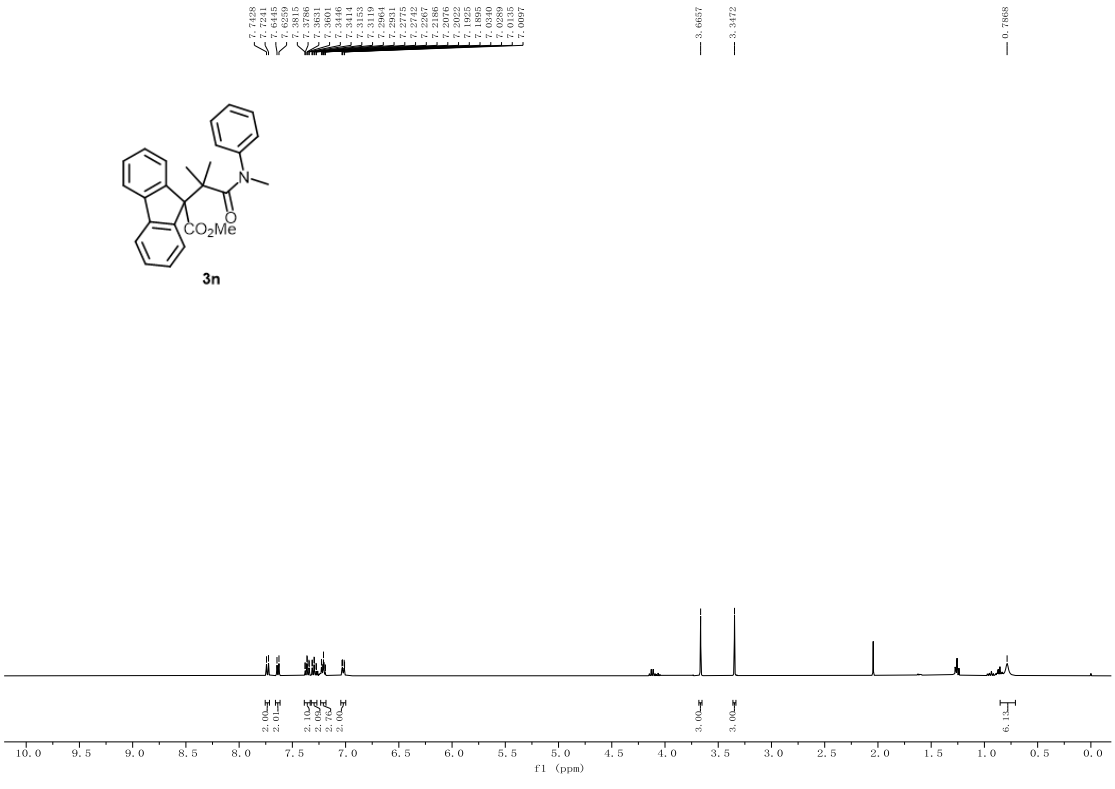
^{1}H NMR of compound **3m** (400 MHz in $CDCl_3$)



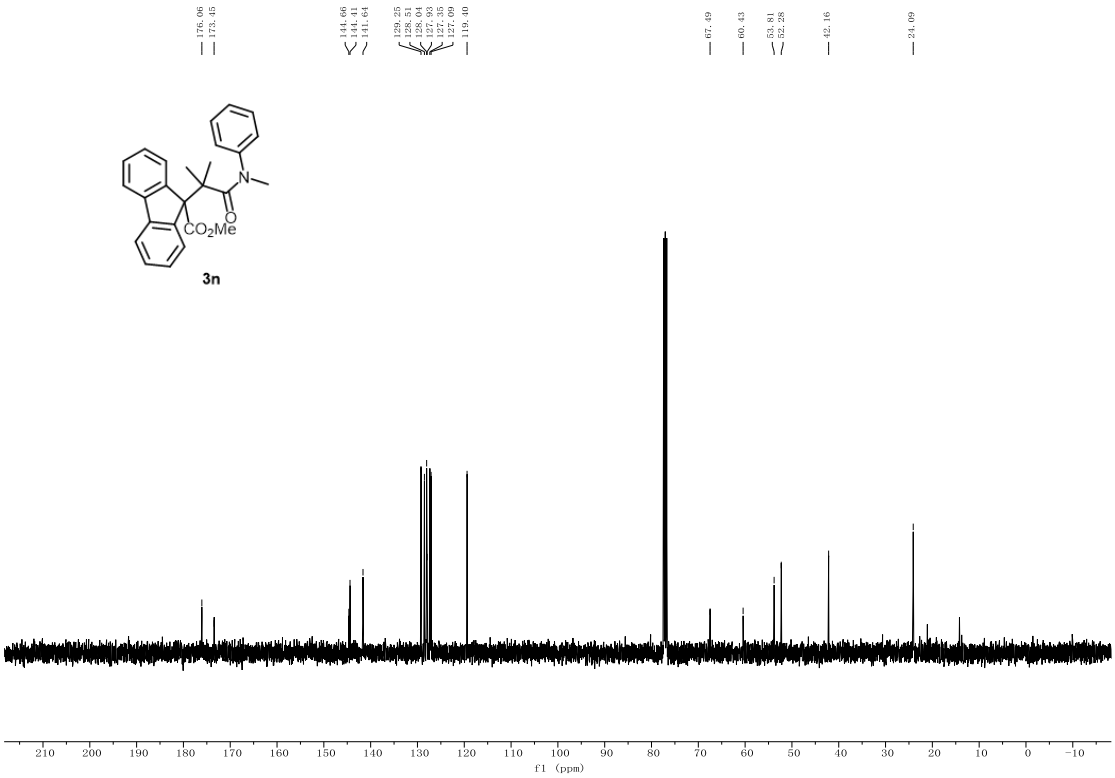
^{13}C NMR of compound **3m** (101 MHz in $CDCl_3$)



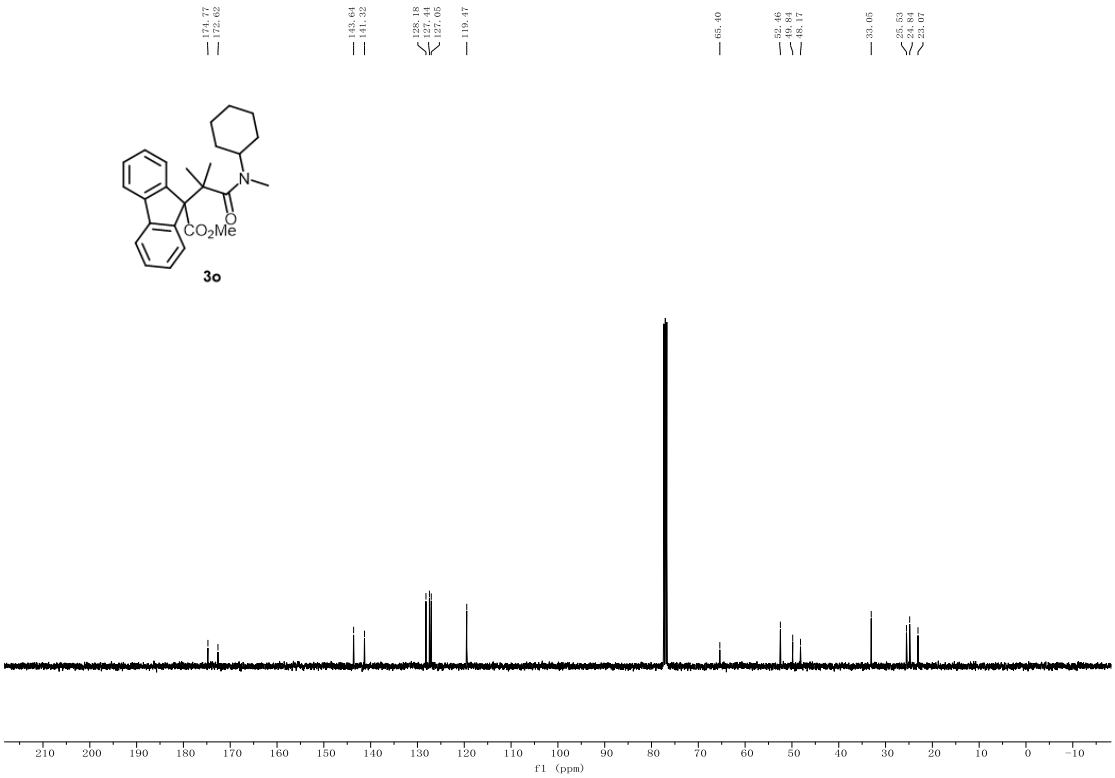
^{1}H NMR of compound **3n** (400 MHz in $CDCl_3$)



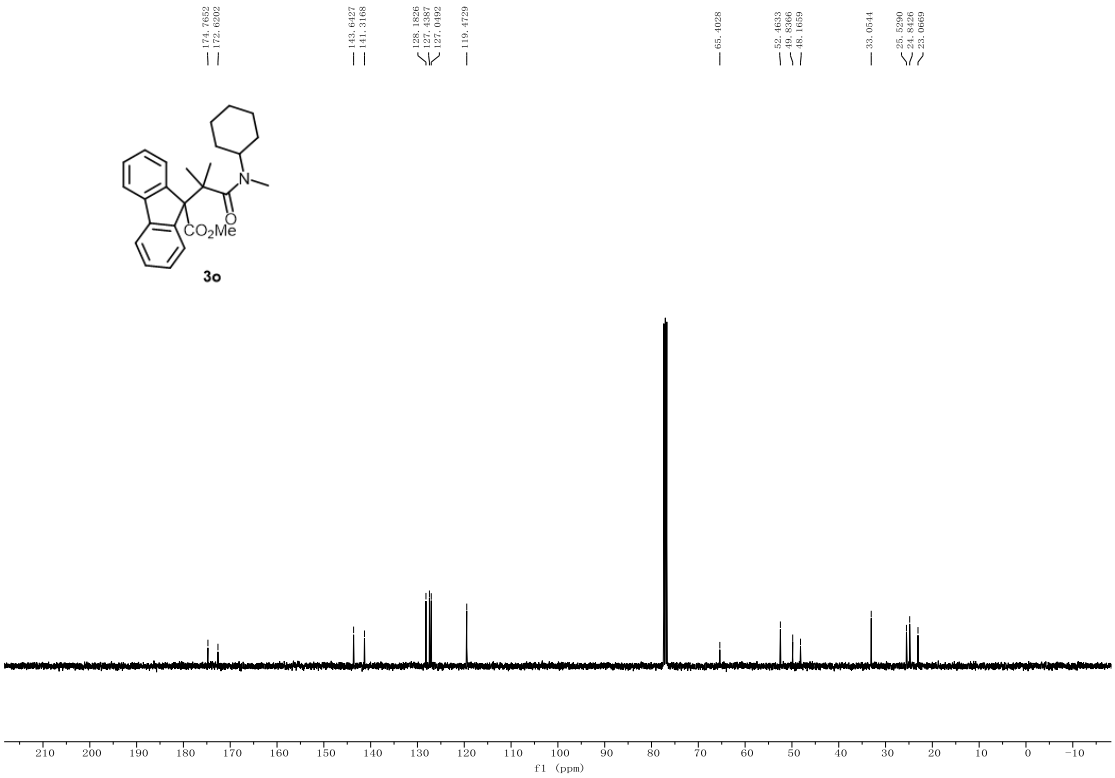
^{13}C NMR of compound **3n** (101 MHz in $CDCl_3$)



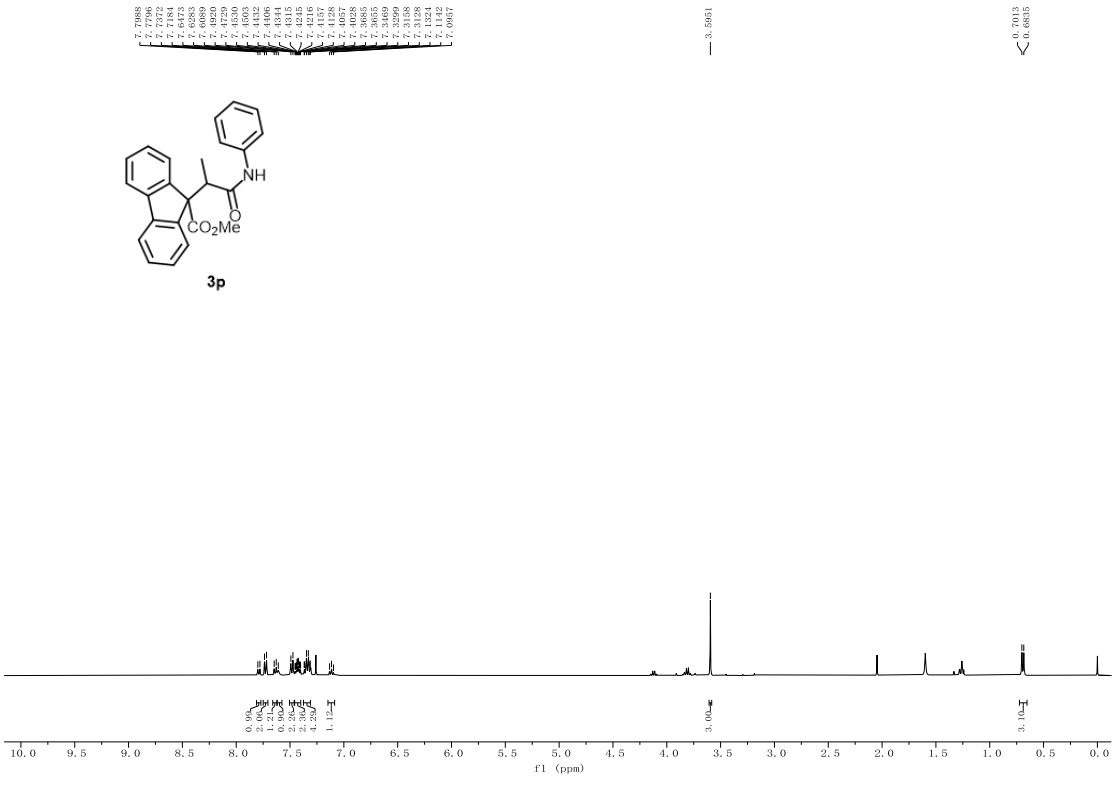
^{1}H NMR of compound **3o** (400 MHz in $CDCl_3$)



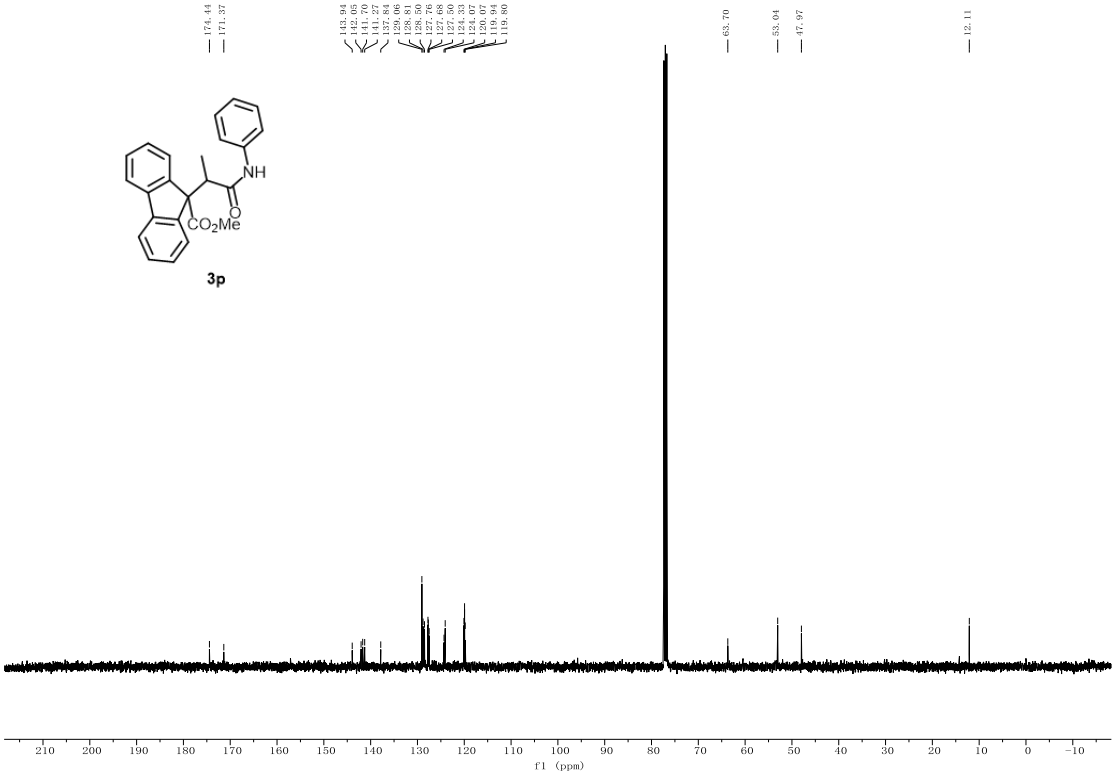
^{13}C NMR of compound **3o** (101 MHz in $CDCl_3$)



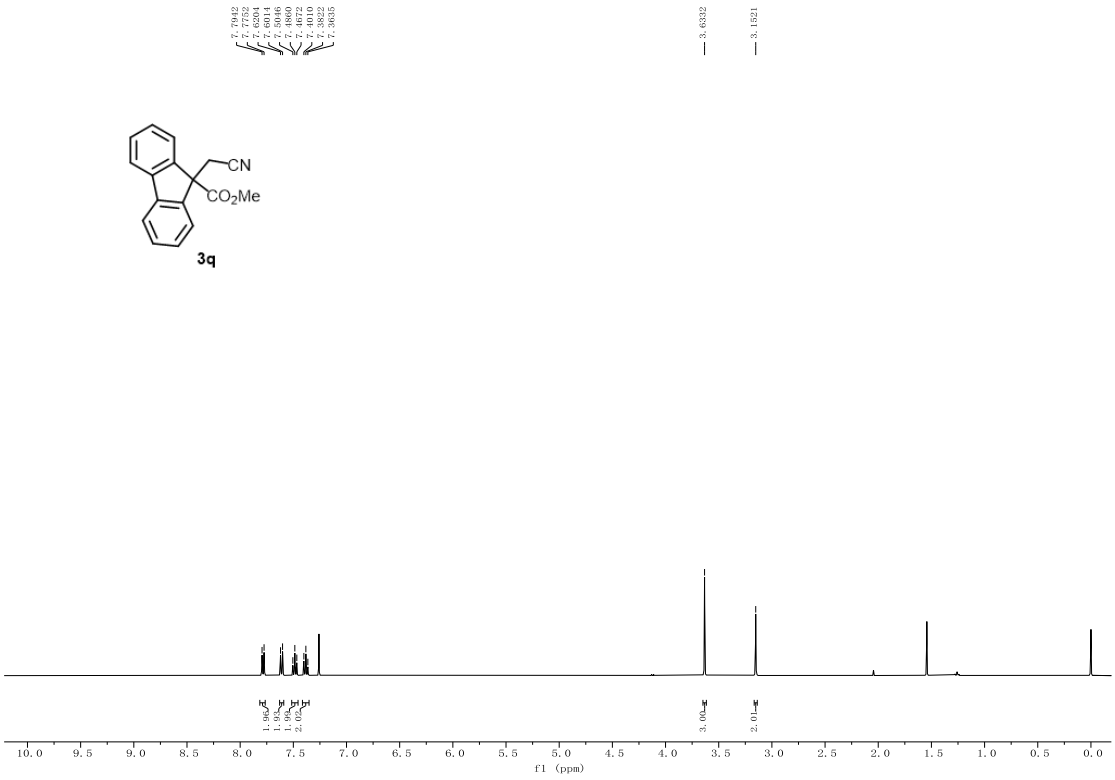
^{1}H NMR of compound **3p** (400 MHz in $CDCl_3$)



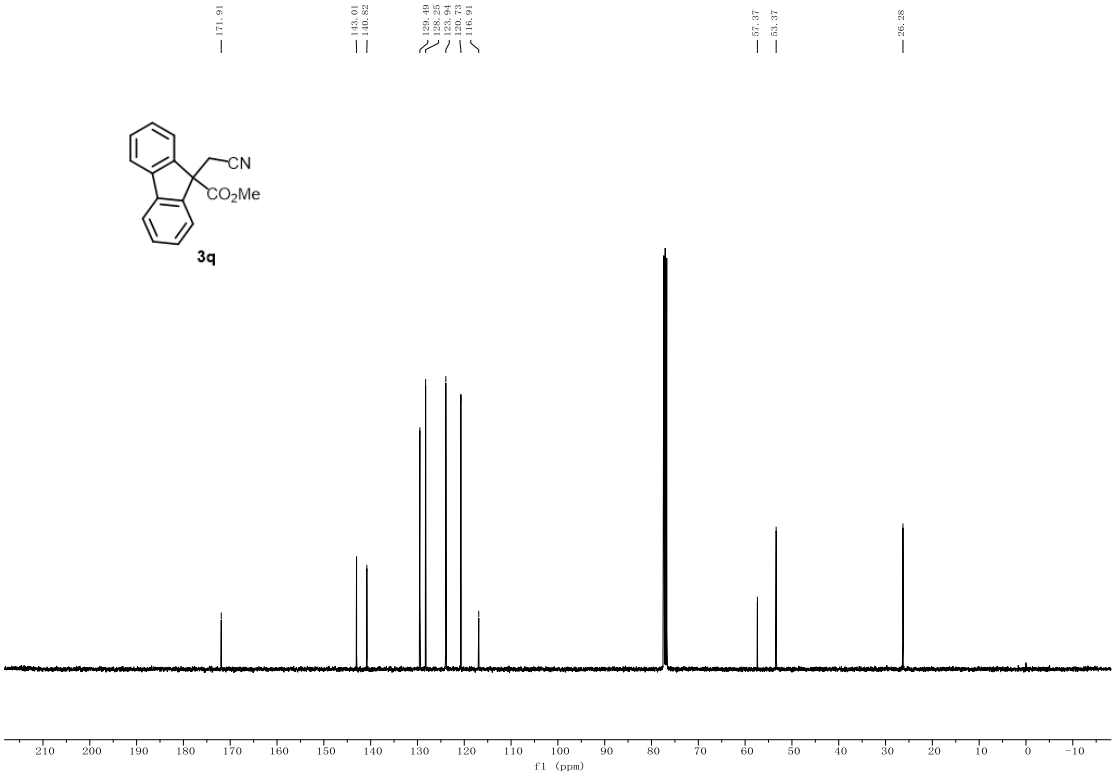
^{13}C NMR of compound **3p** (101 MHz in $CDCl_3$)



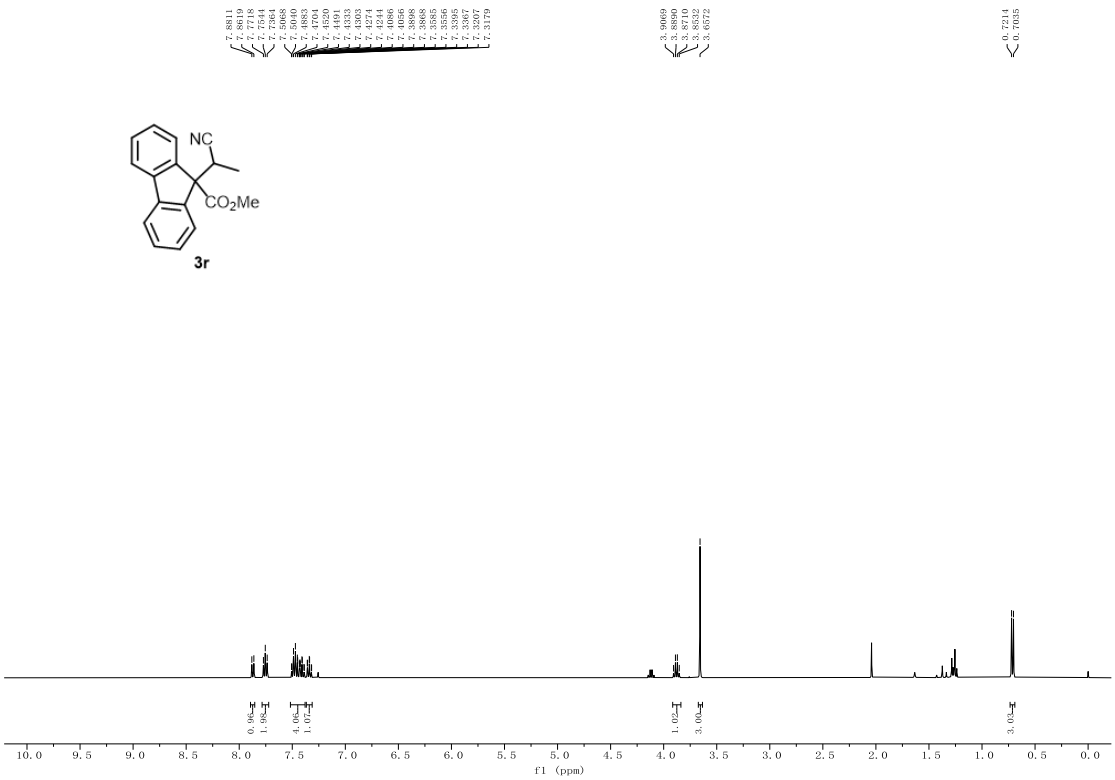
^{1}H NMR of compound **3q** (400 MHz in $CDCl_3$)



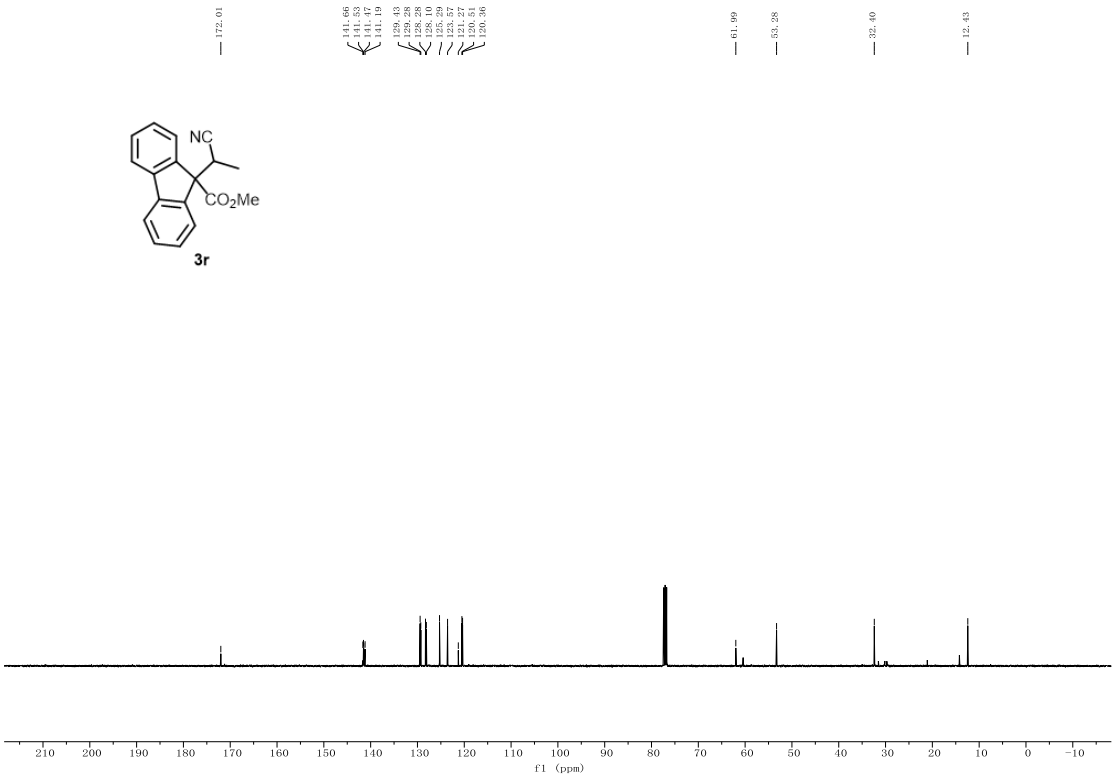
^{13}C NMR of compound **3q** (101 MHz in $CDCl_3$)



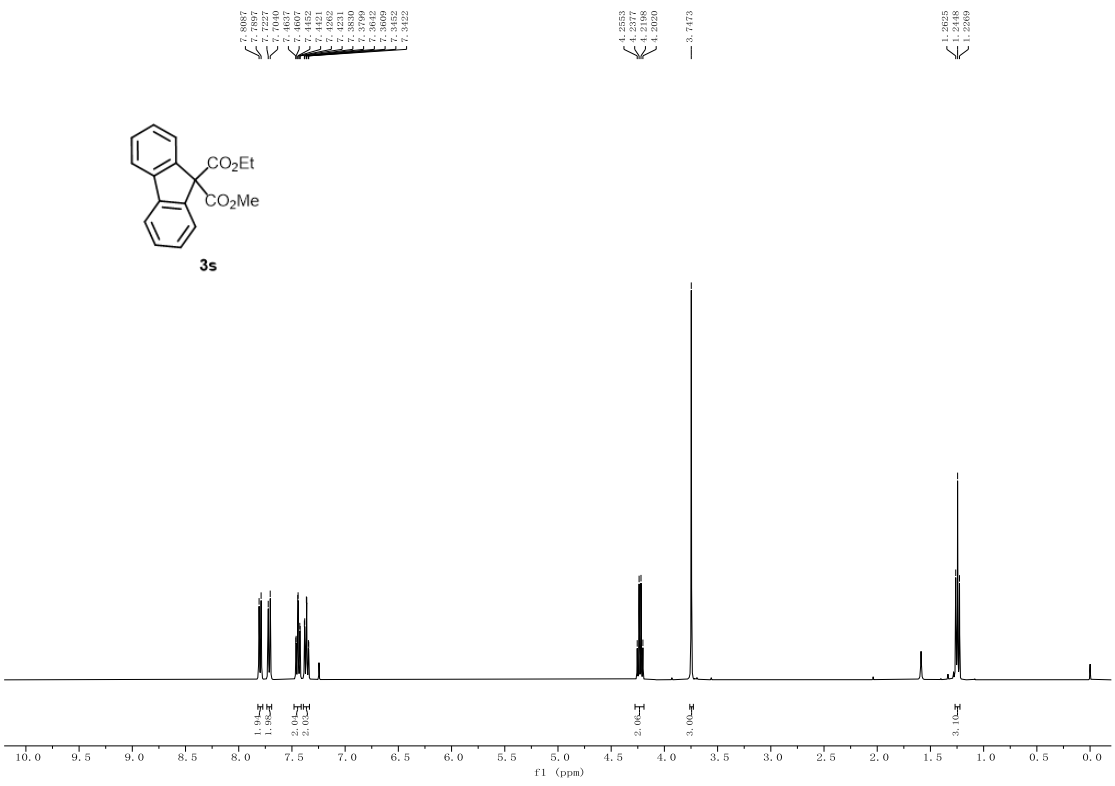
^{1}H NMR of compound **3r** (400 MHz in $CDCl_3$)



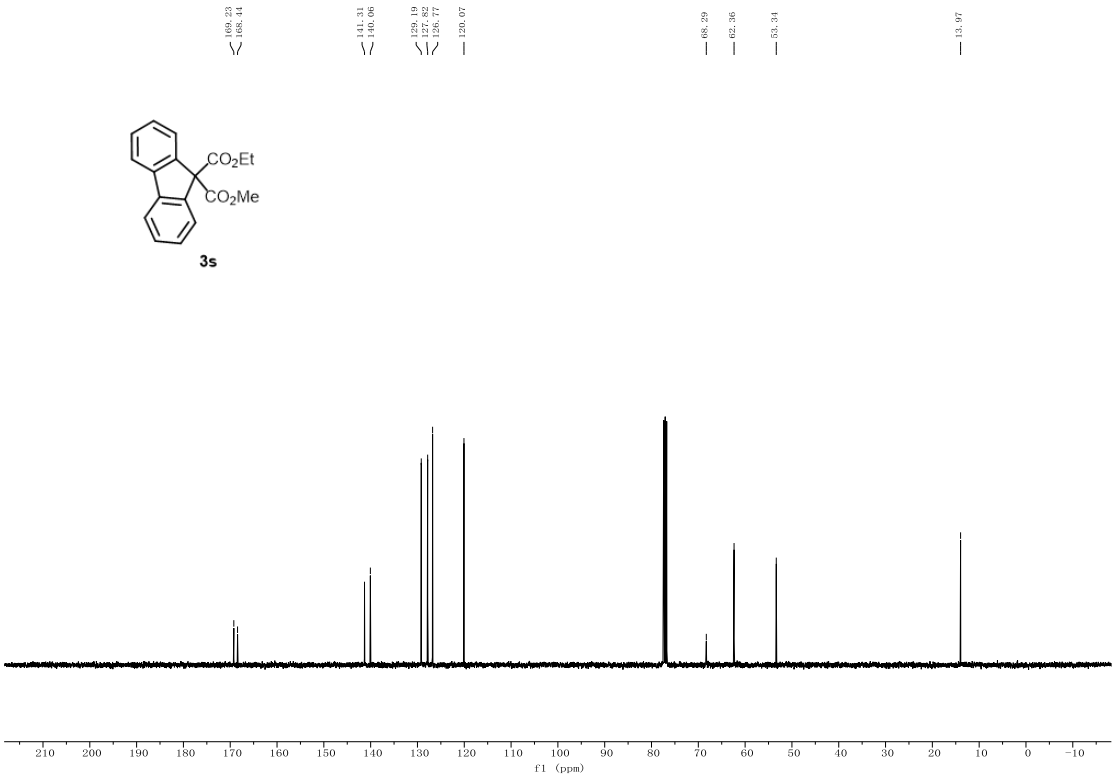
^{13}C NMR of compound **3r** (101 MHz in $CDCl_3$)



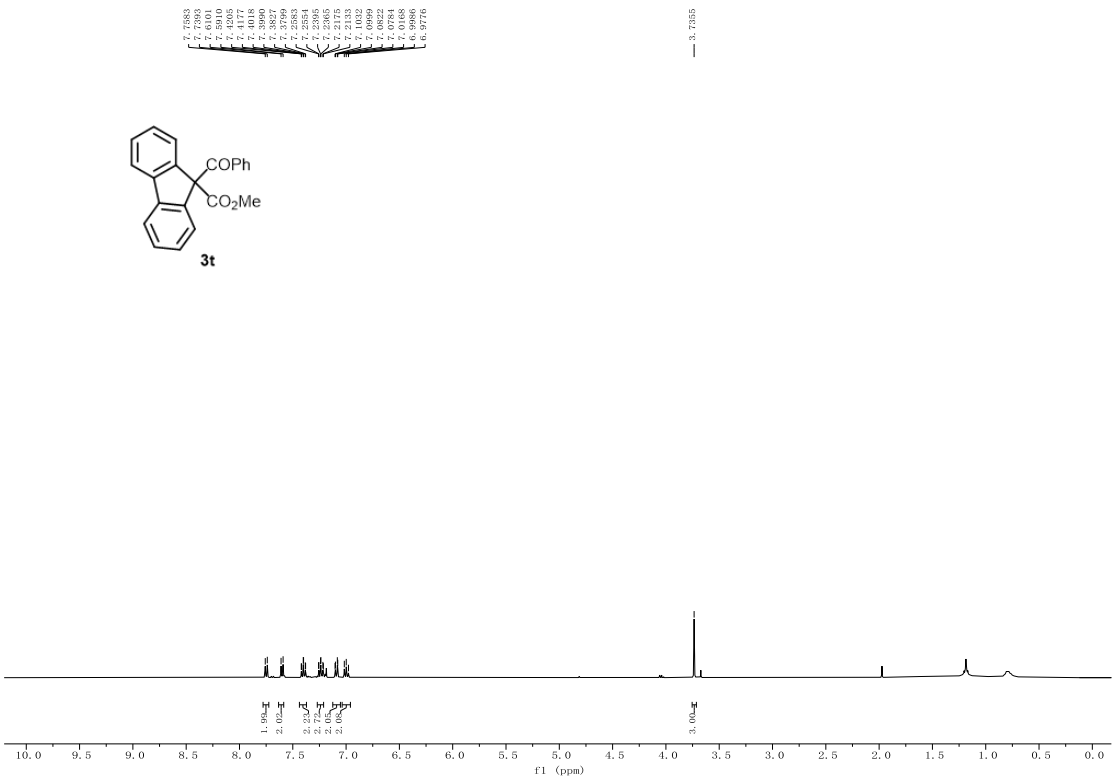
^{1}H NMR of compound **3s** (400 MHz in $CDCl_3$)



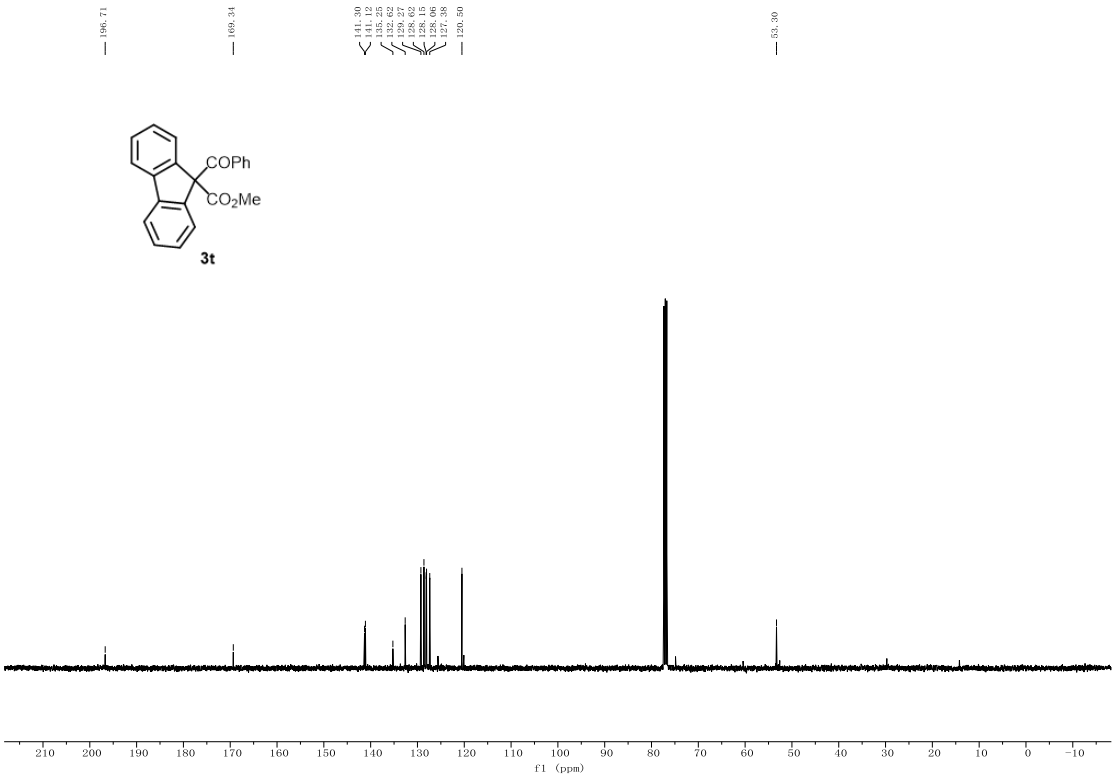
^{13}C NMR of compound **3s** (101 MHz in $CDCl_3$)



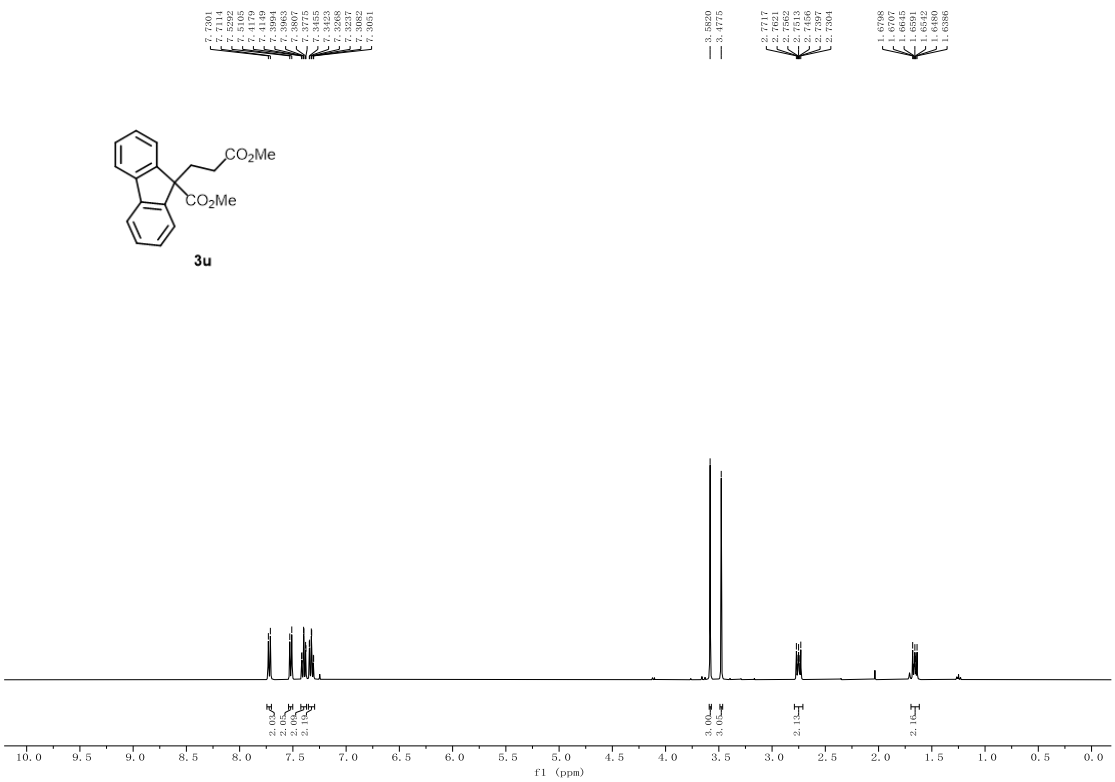
^{1}H NMR of compound **3t** (400 MHz in $CDCl_3$)



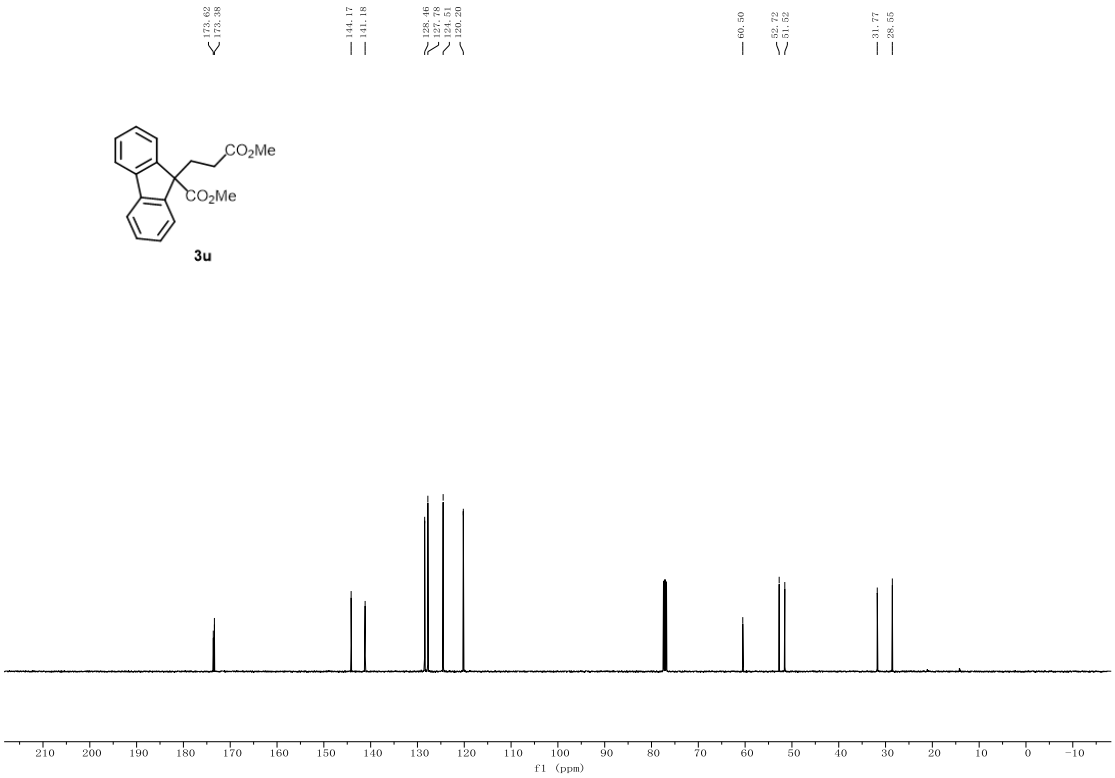
^{13}C NMR of compound **3t** (101 MHz in $CDCl_3$)



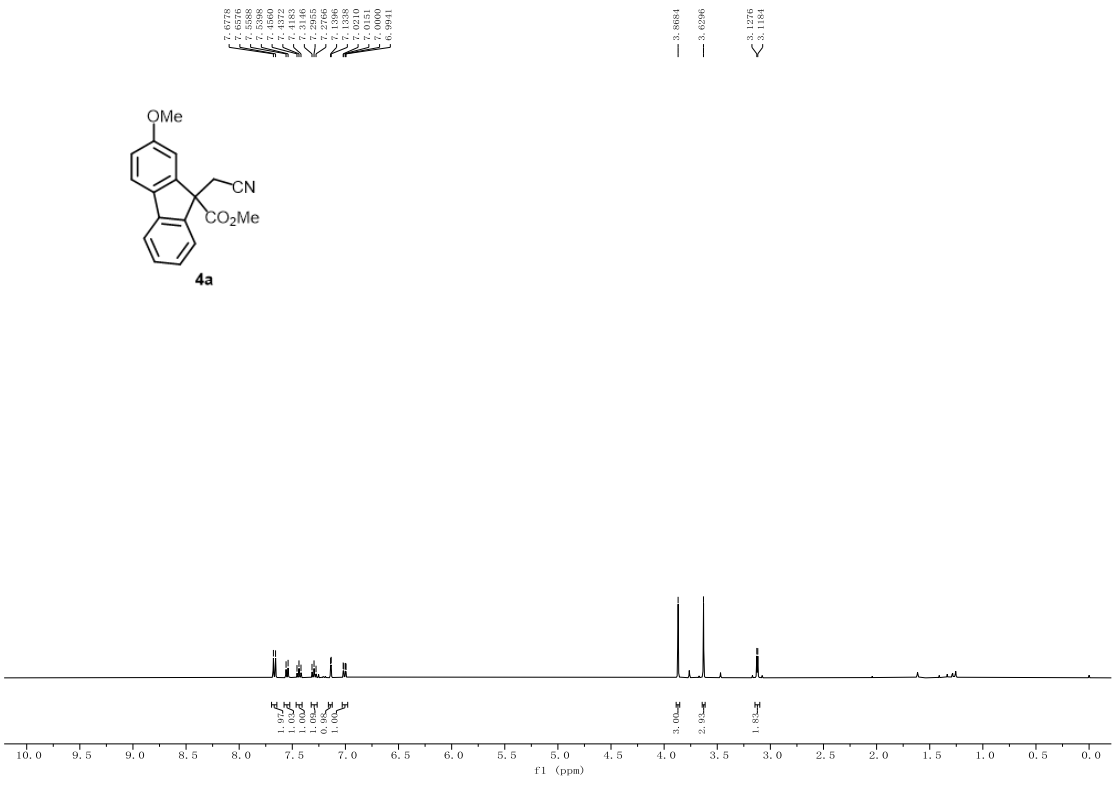
^{1}H NMR of compound **3u** (400 MHz in $CDCl_3$)



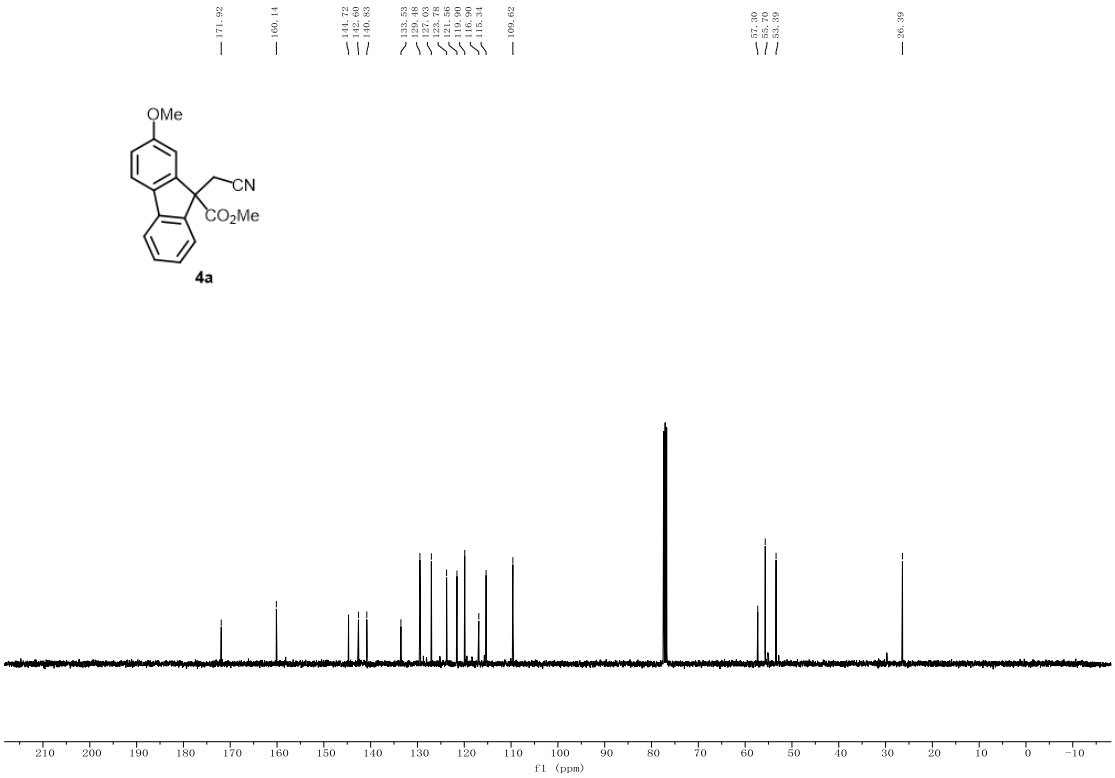
^{13}C NMR of compound **3u** (101 MHz in $CDCl_3$)



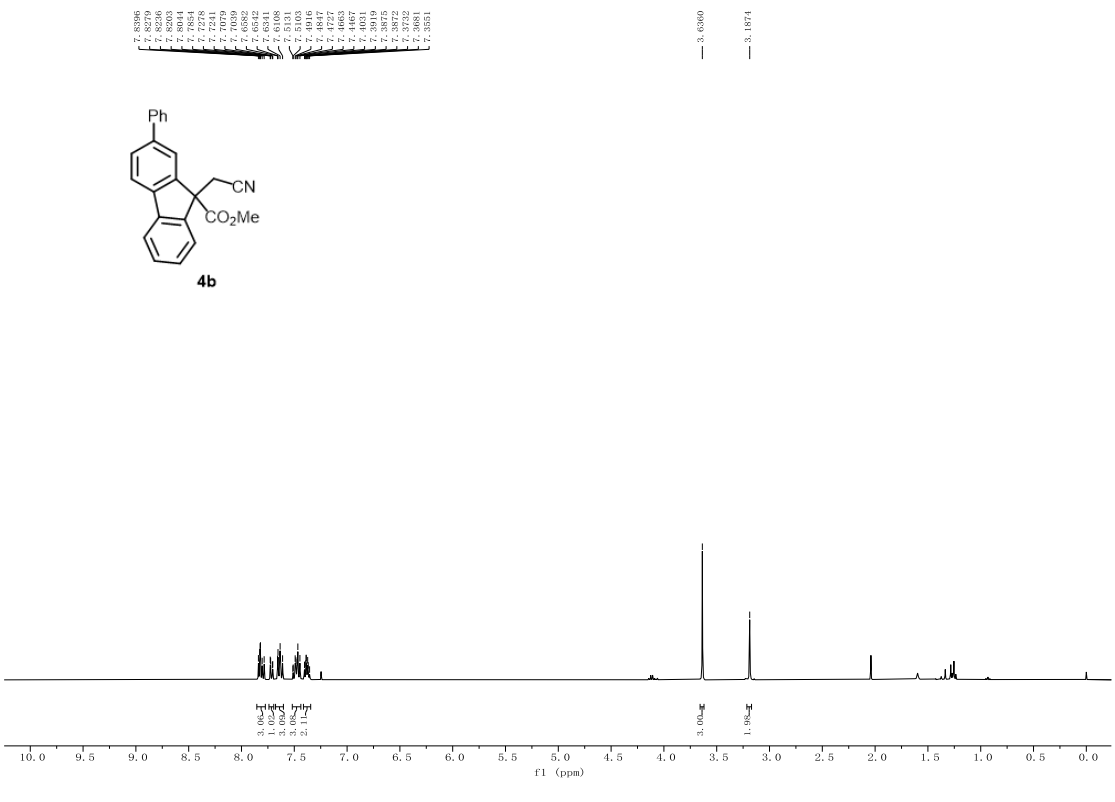
^{1}H NMR of compound **4a** (400 MHz in $CDCl_3$)



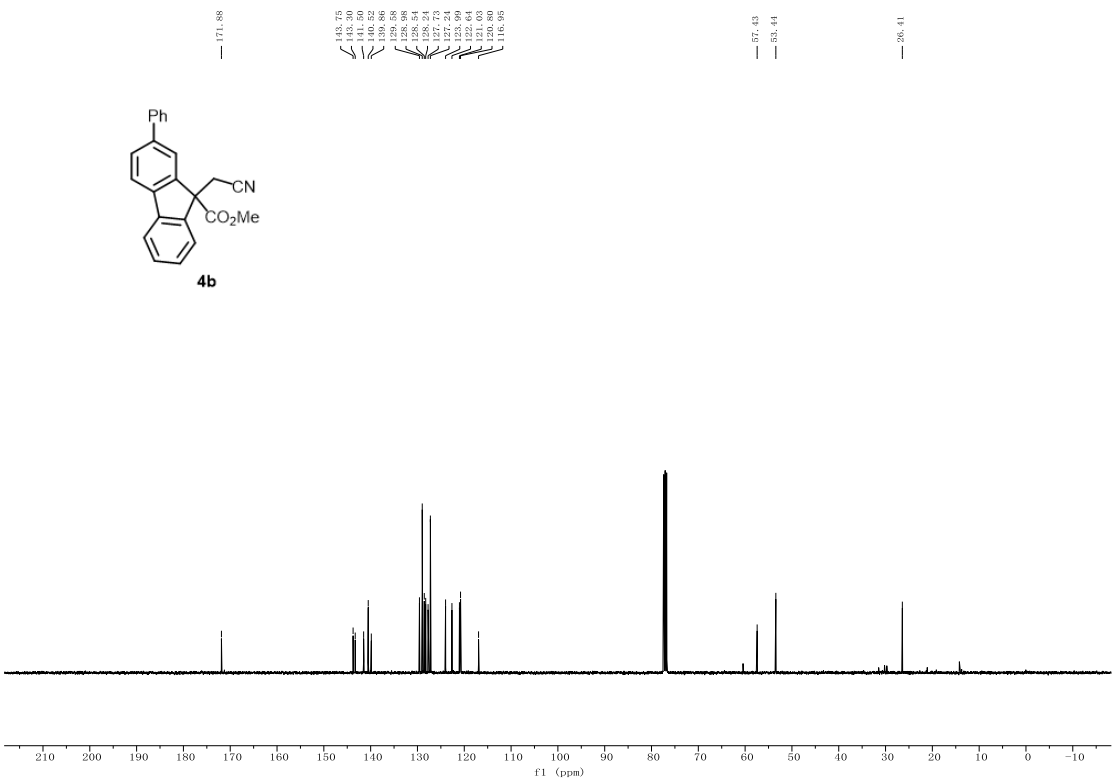
^{13}C NMR of compound **4a** (101 MHz in $CDCl_3$)



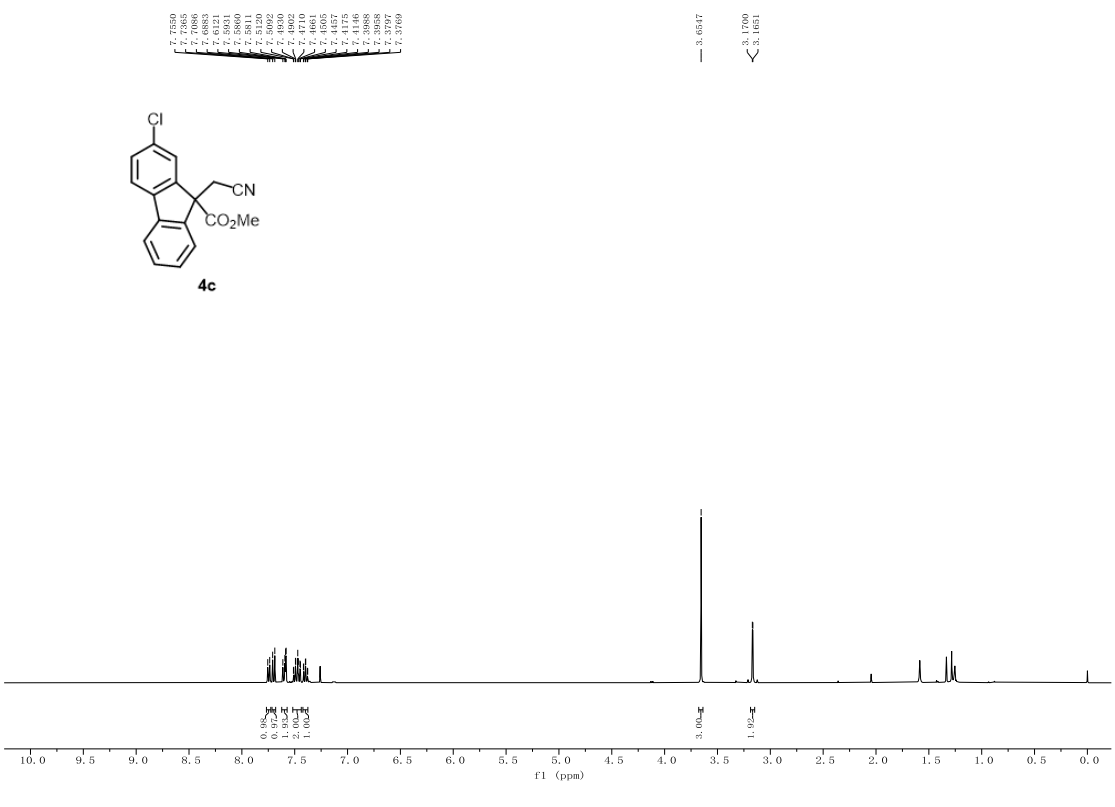
^{1}H NMR of compound **4b** (400 MHz in $CDCl_3$)



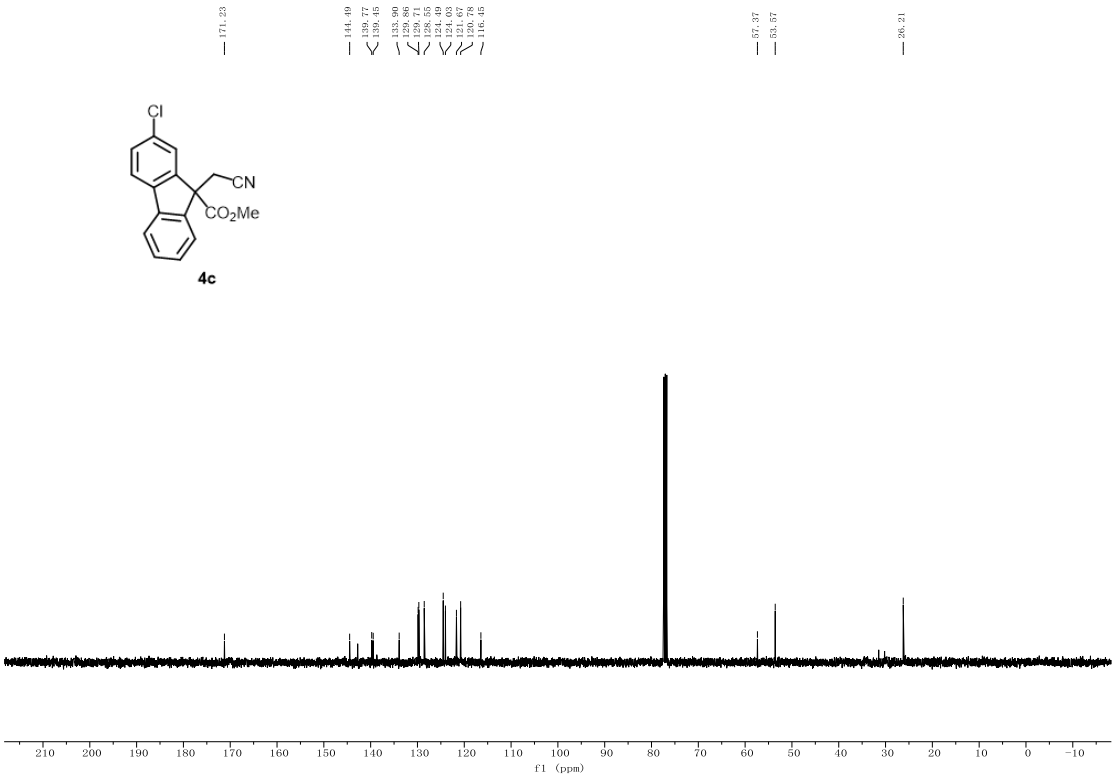
^{13}C NMR of compound **4b** (101 MHz in $CDCl_3$)



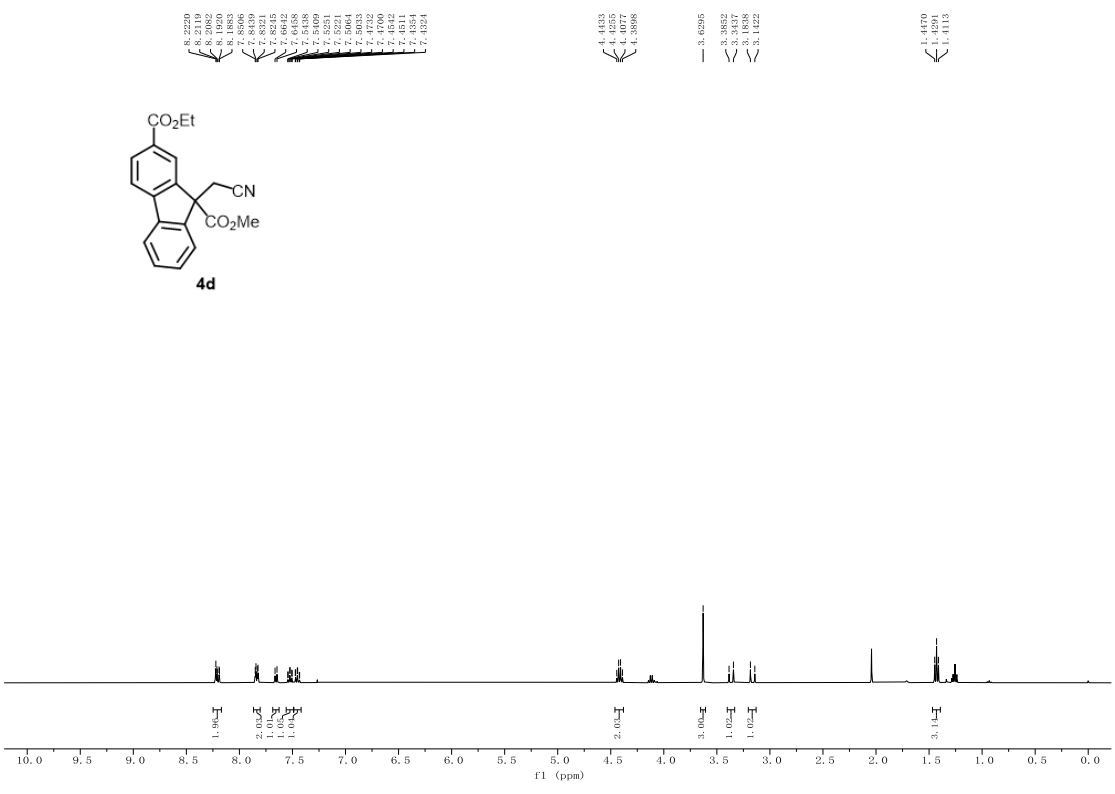
^{1}H NMR of compound **4c** (400 MHz in $CDCl_3$)



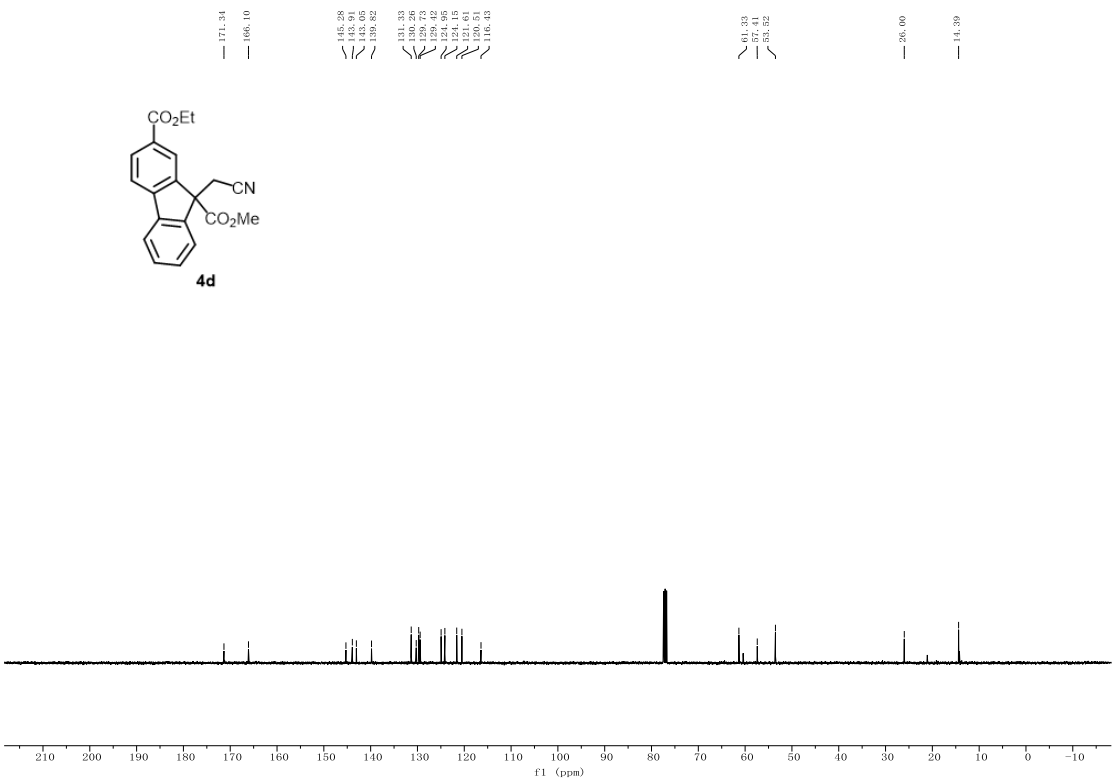
^{13}C NMR of compound **4c** (101 MHz in $CDCl_3$)



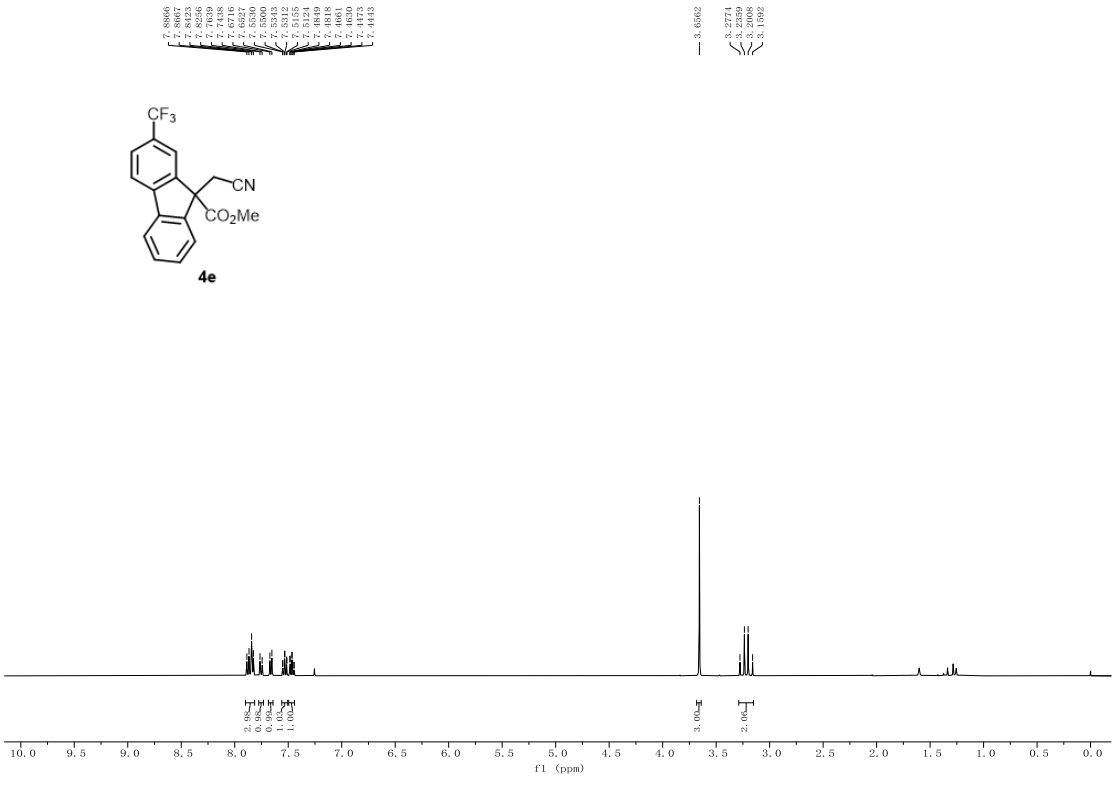
^{1}H NMR of compound **4d** (400 MHz in $CDCl_3$)



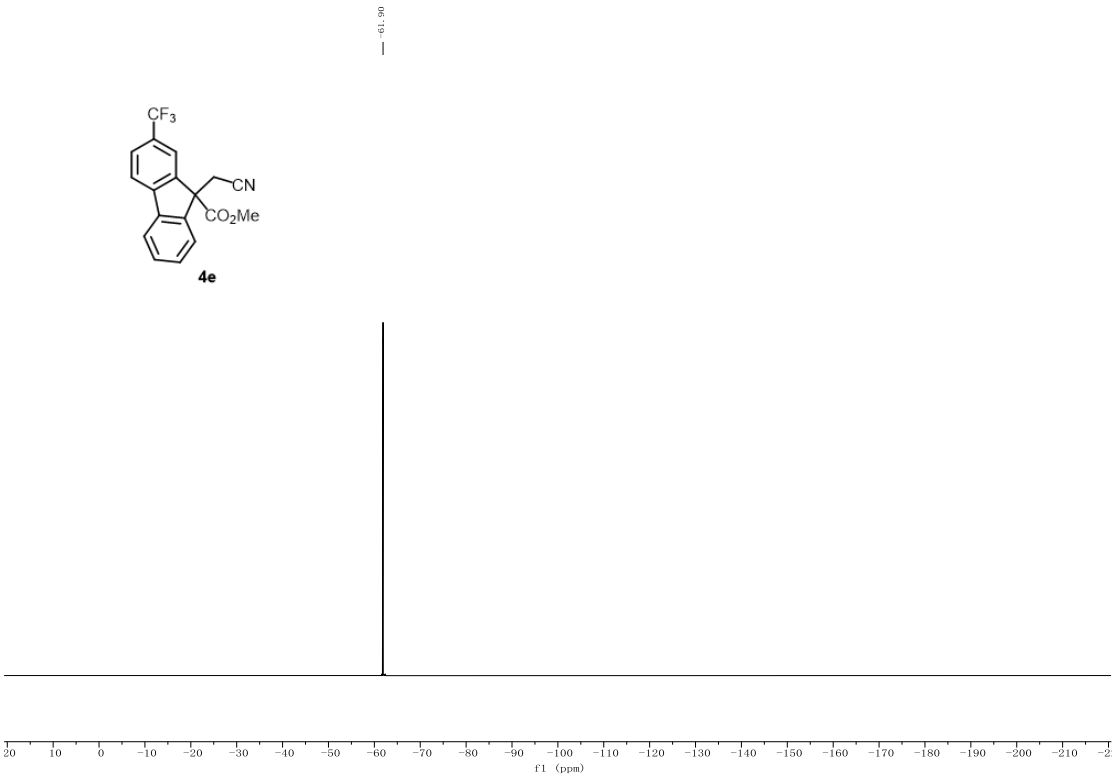
^{13}C NMR of compound **4d** (101 MHz in $CDCl_3$)



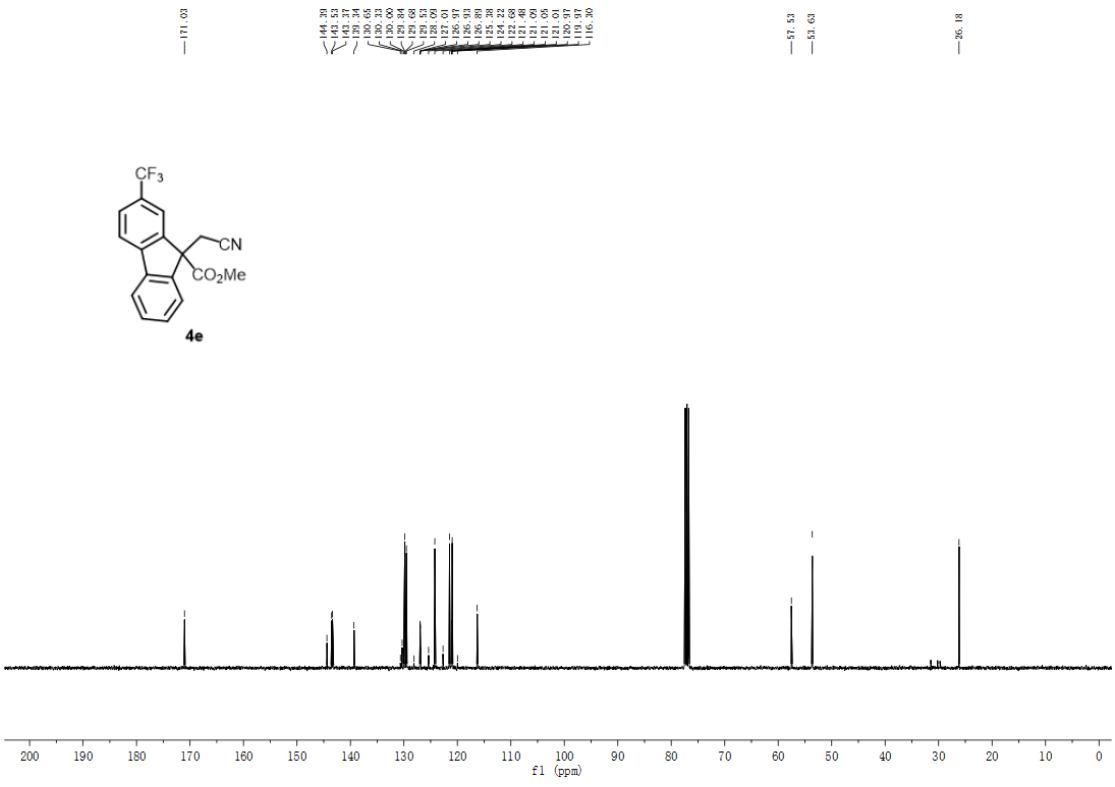
^{1}H NMR of compound **4e** (400 MHz in $CDCl_3$)



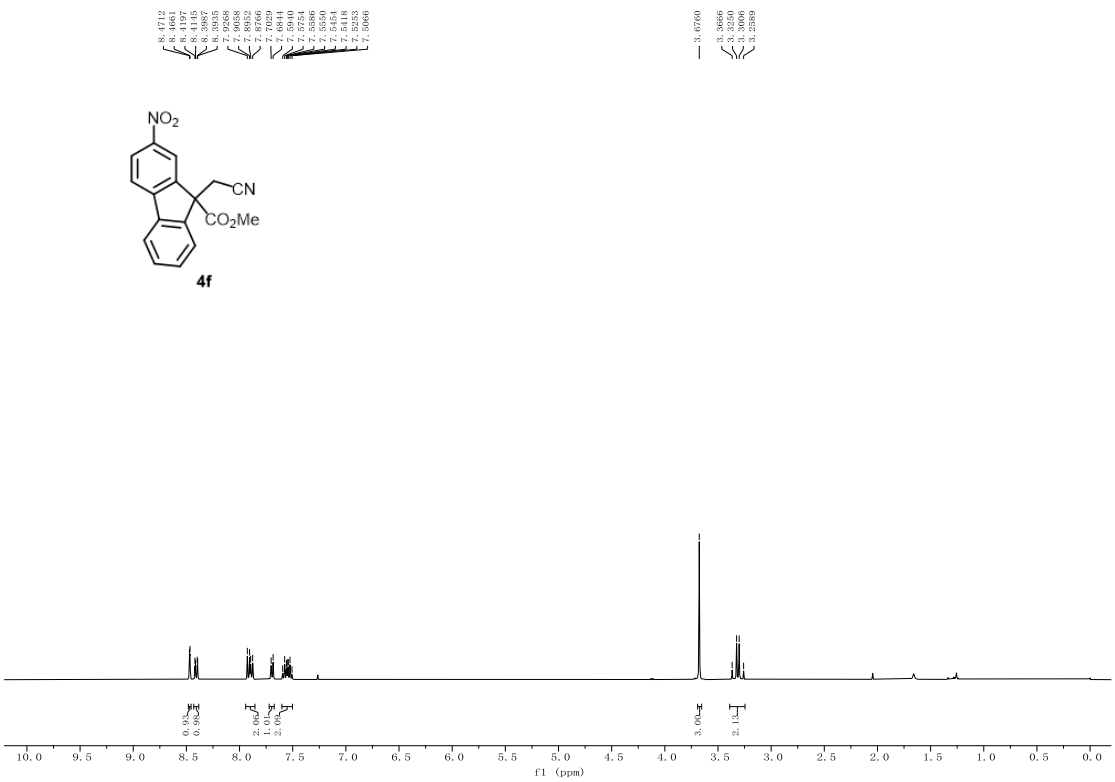
^{19}F NMR of compound **4e** (377 MHz in $CDCl_3$)



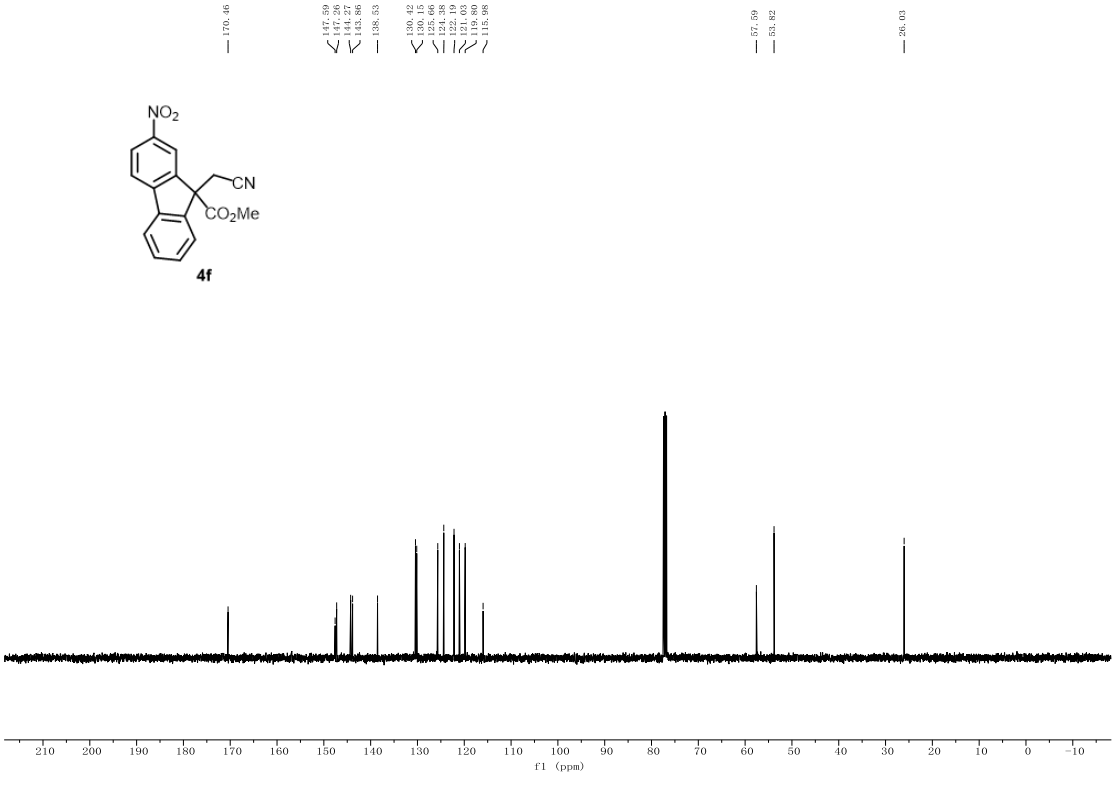
^{13}C NMR of compound **4e** (101 MHz in $CDCl_3$)



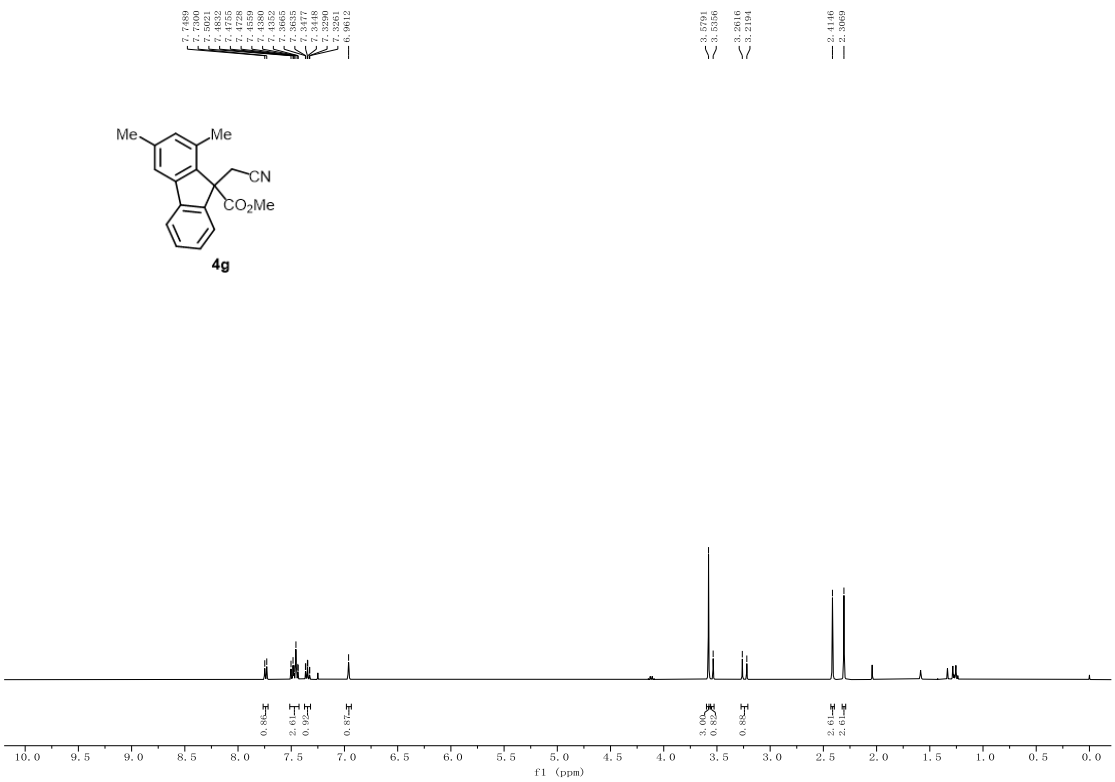
^{1}H NMR of compound **4f** (400 MHz in $CDCl_3$)



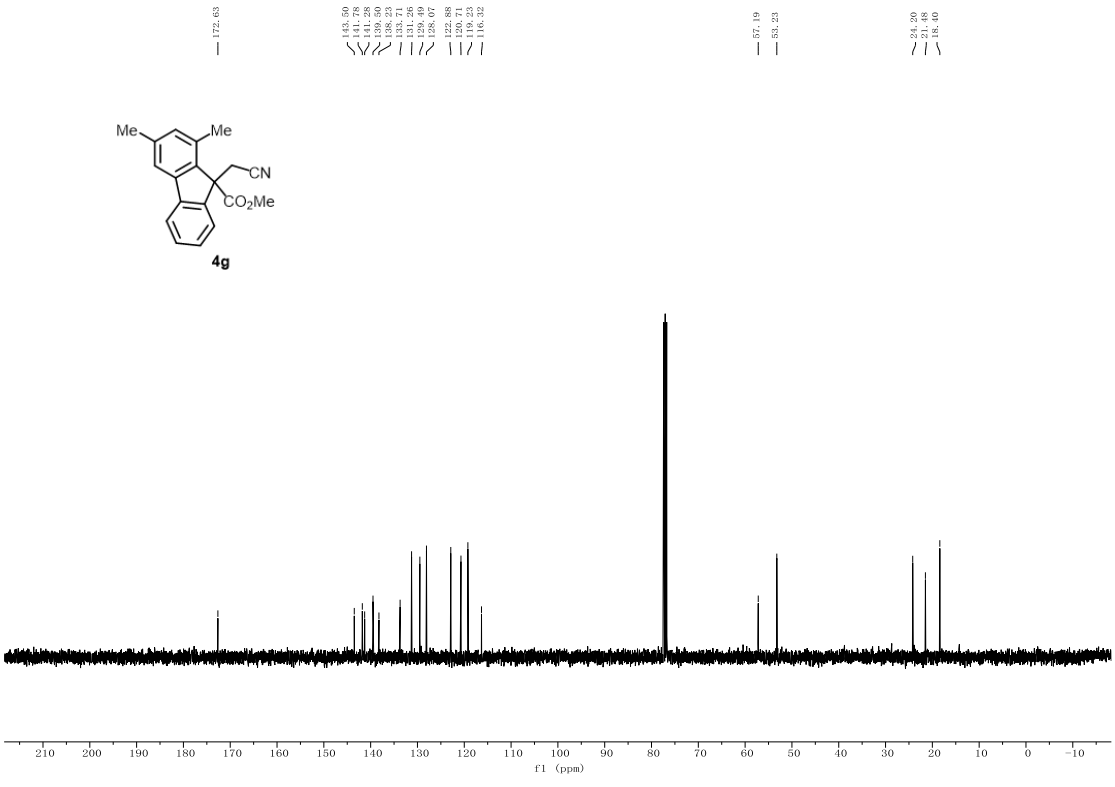
^{13}C NMR of compound **4f** (101 MHz in $CDCl_3$)



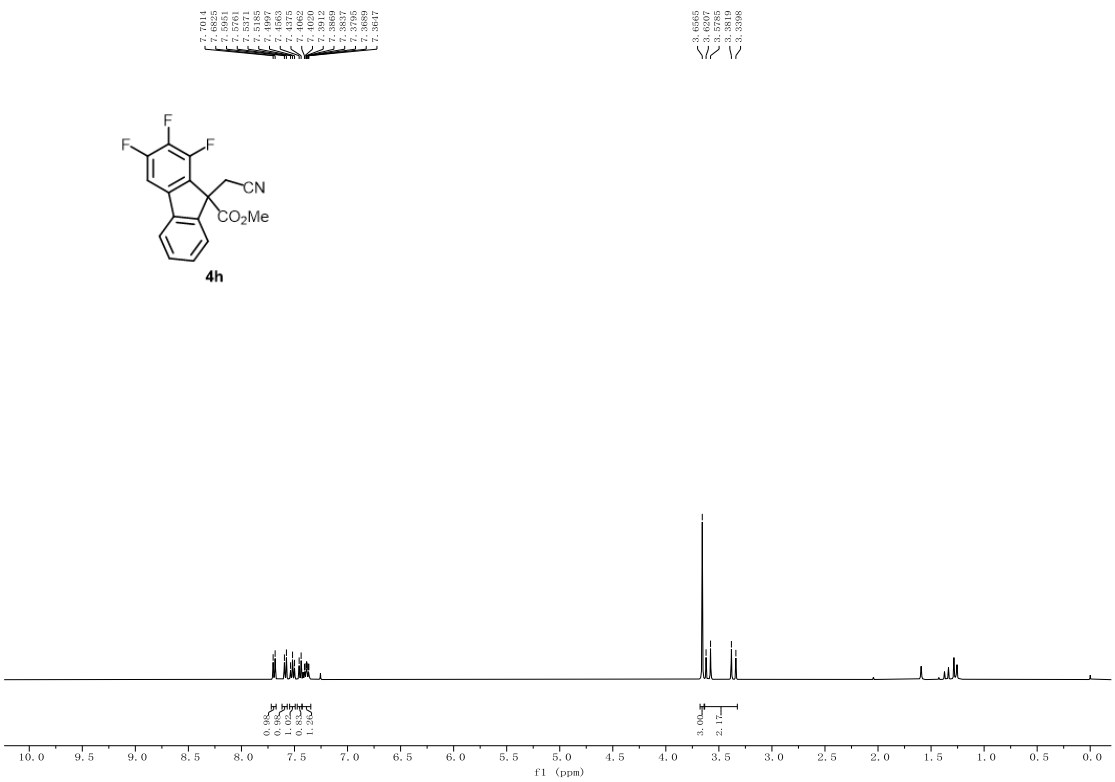
^{1}H NMR of compound **4g** (400 MHz in $CDCl_3$)



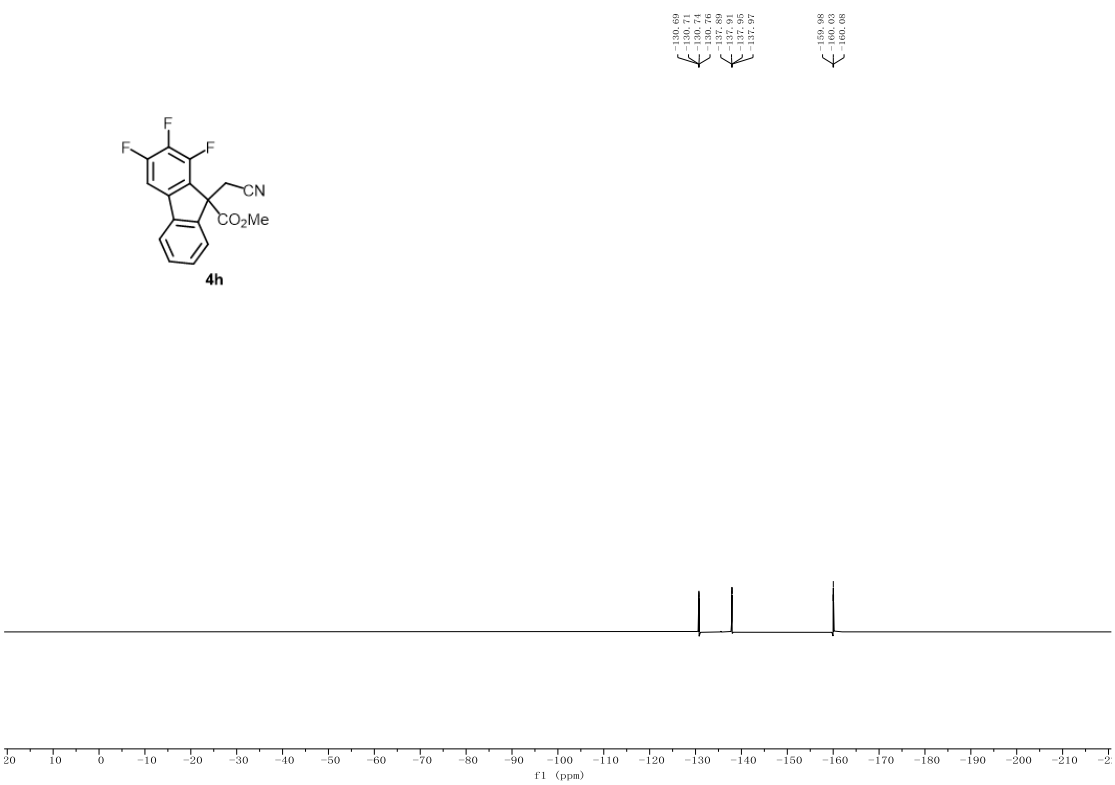
^{13}C NMR of compound **4g** (101 MHz in $CDCl_3$)



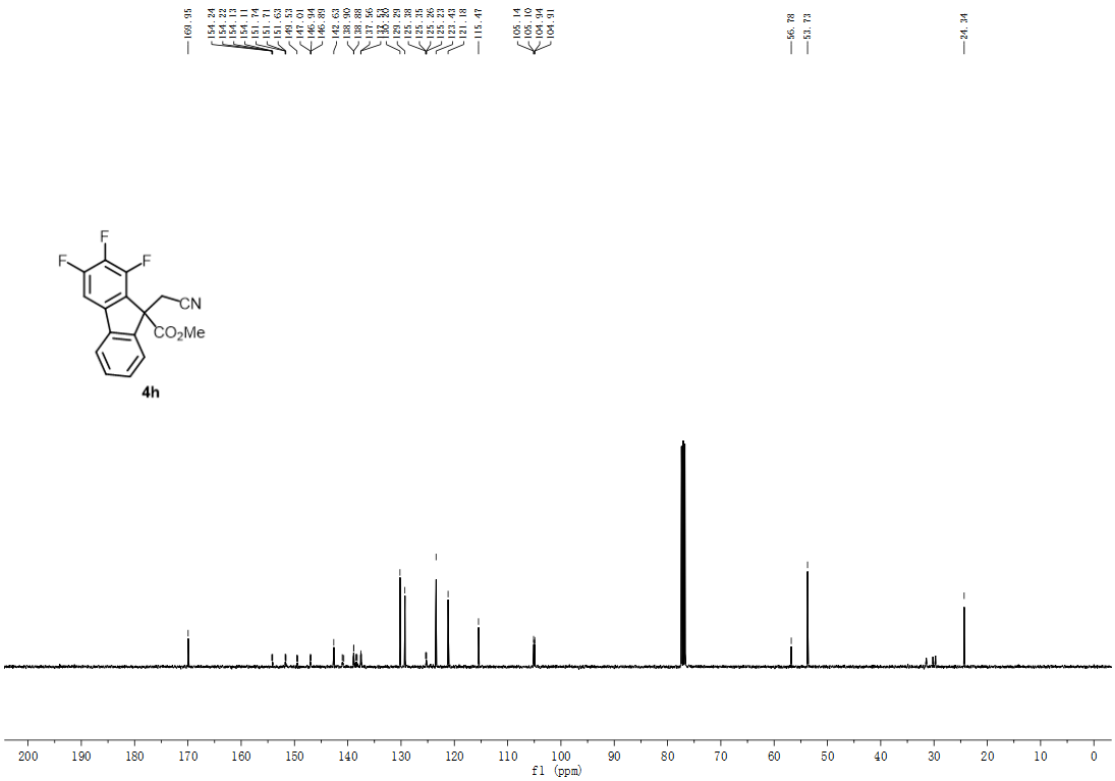
^{1}H NMR of compound **4h** (400 MHz in $CDCl_3$)



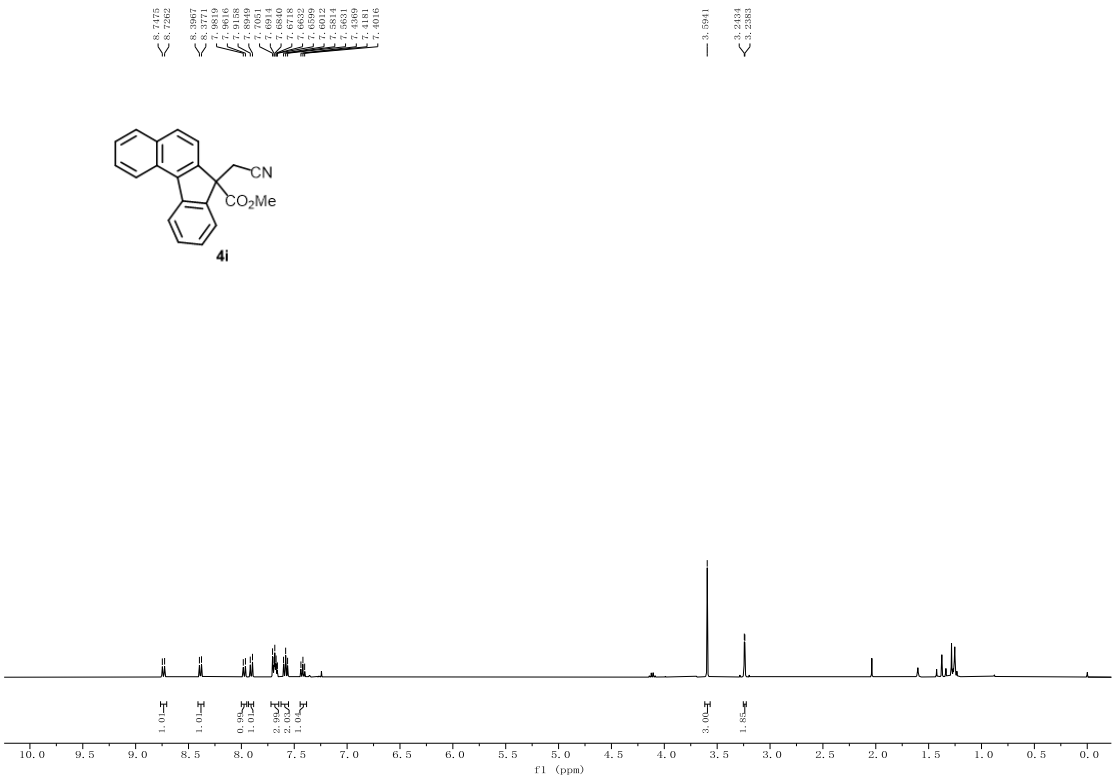
^{19}F NMR of compound **4h** (377 MHz in $CDCl_3$)



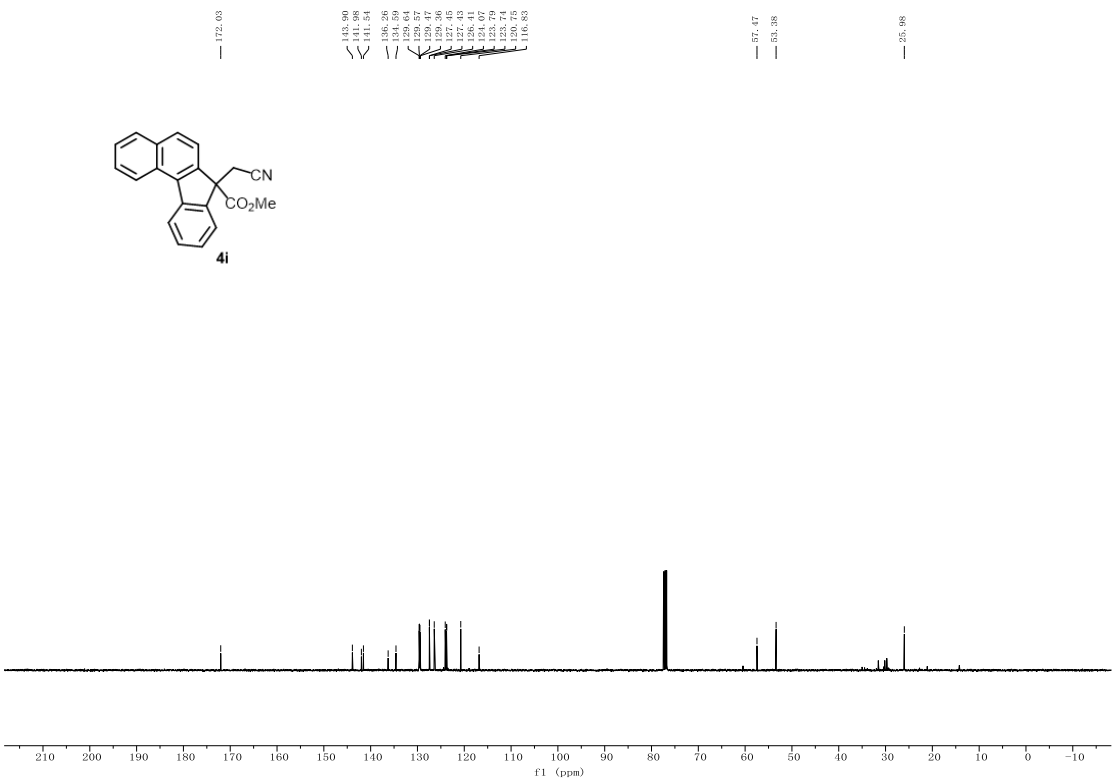
^{13}C NMR of compound **4h** (101 MHz in $CDCl_3$)



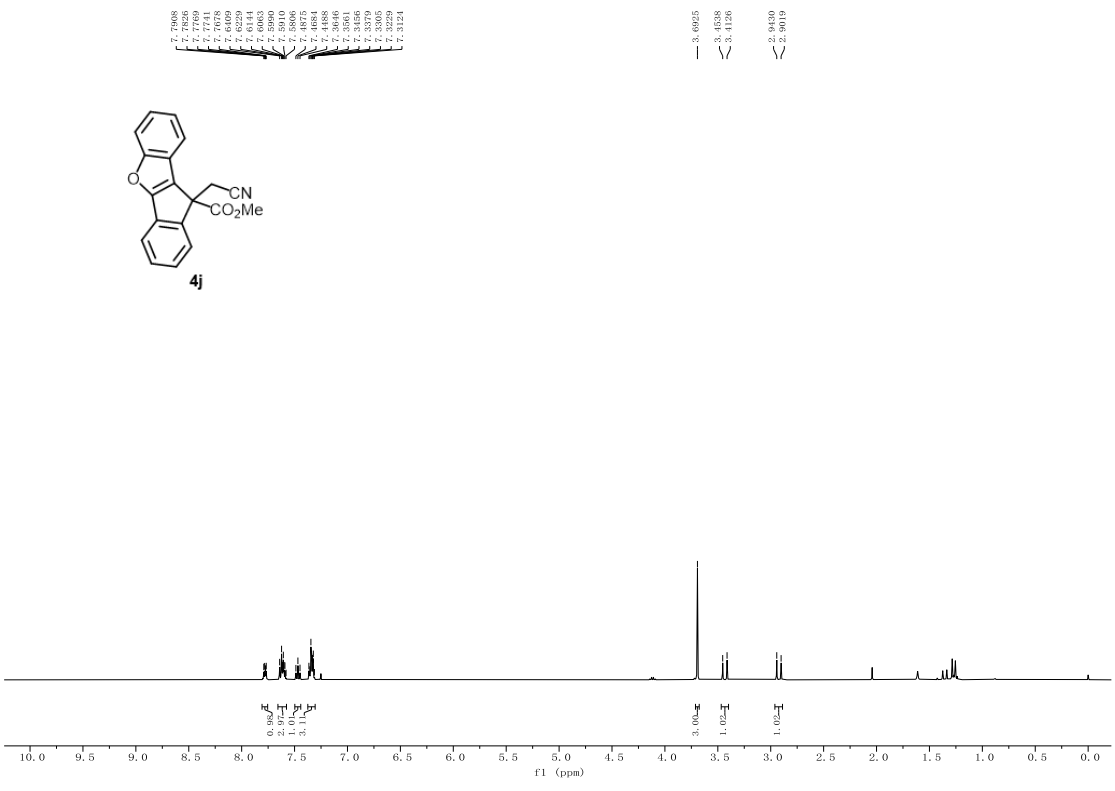
^{1}H NMR of compound **4i** (400 MHz in $CDCl_3$)



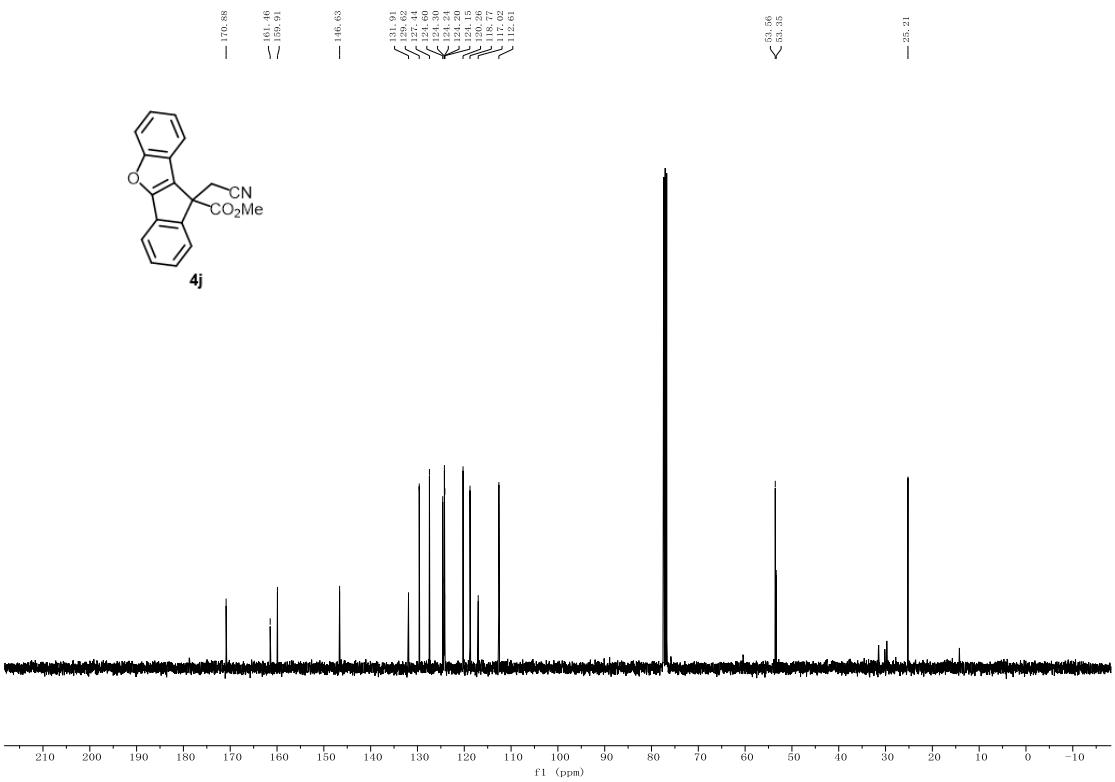
^{13}C NMR of compound **4i** (101 MHz in $CDCl_3$)



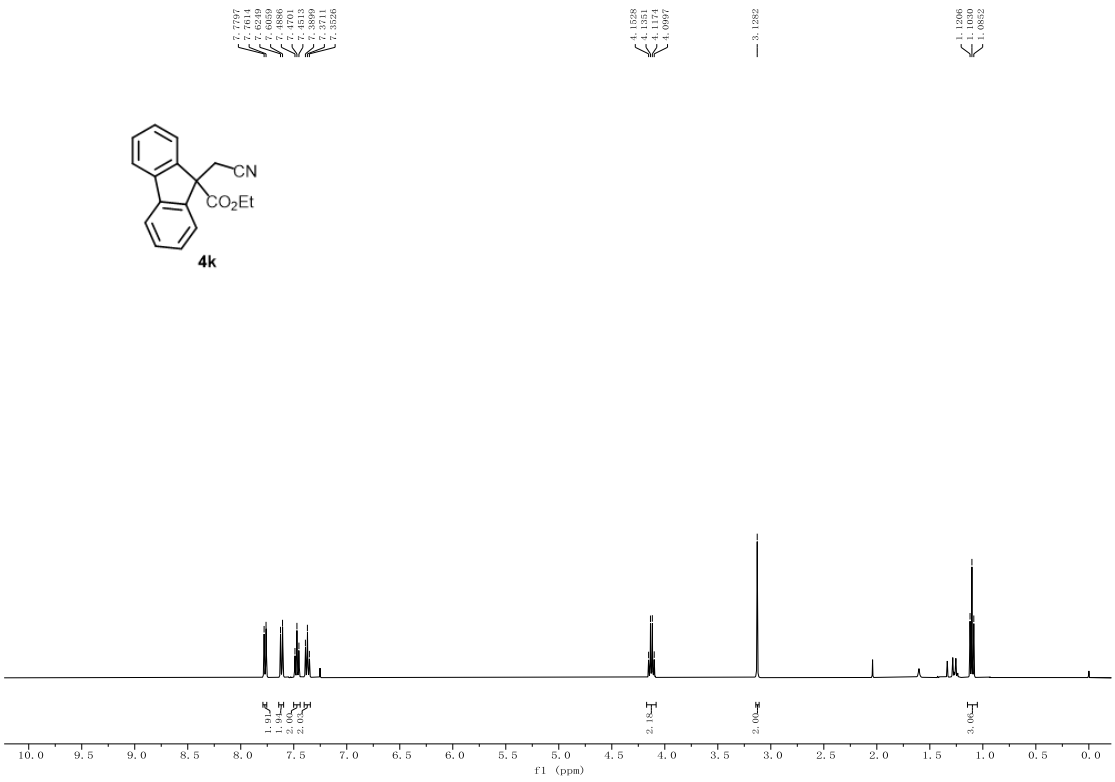
^{1}H NMR of compound **4j** (400 MHz in $CDCl_3$)



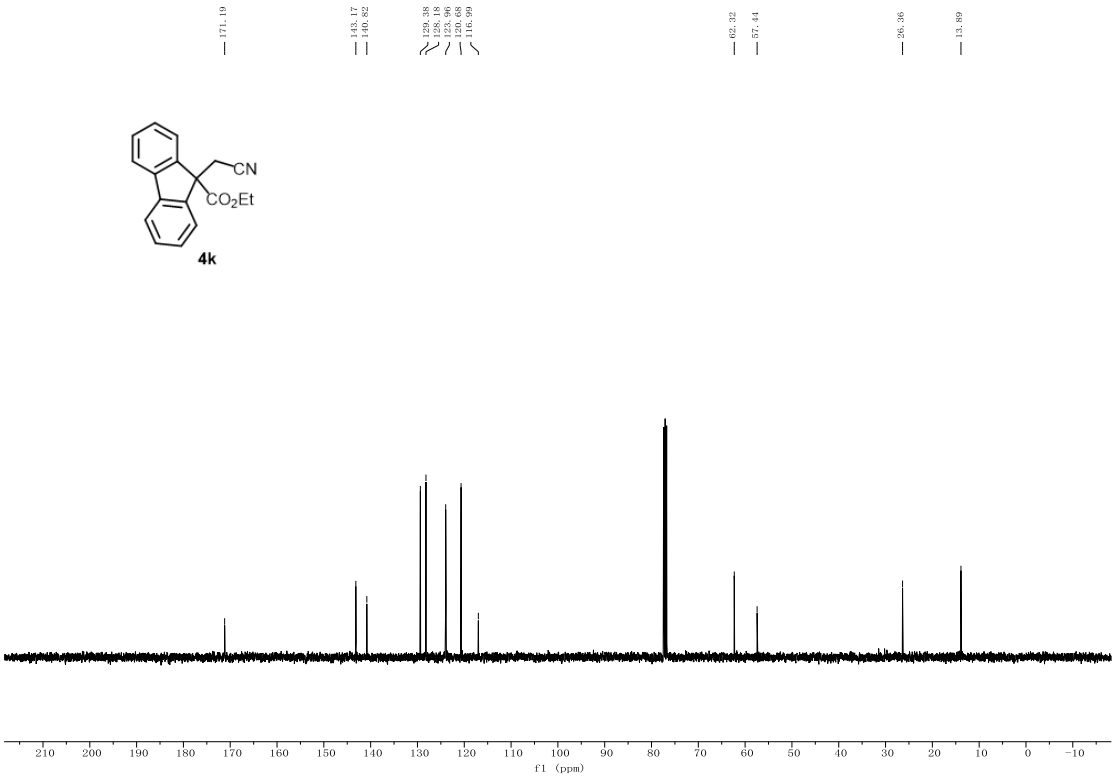
^{13}C NMR of compound **4j** (101 MHz in $CDCl_3$)



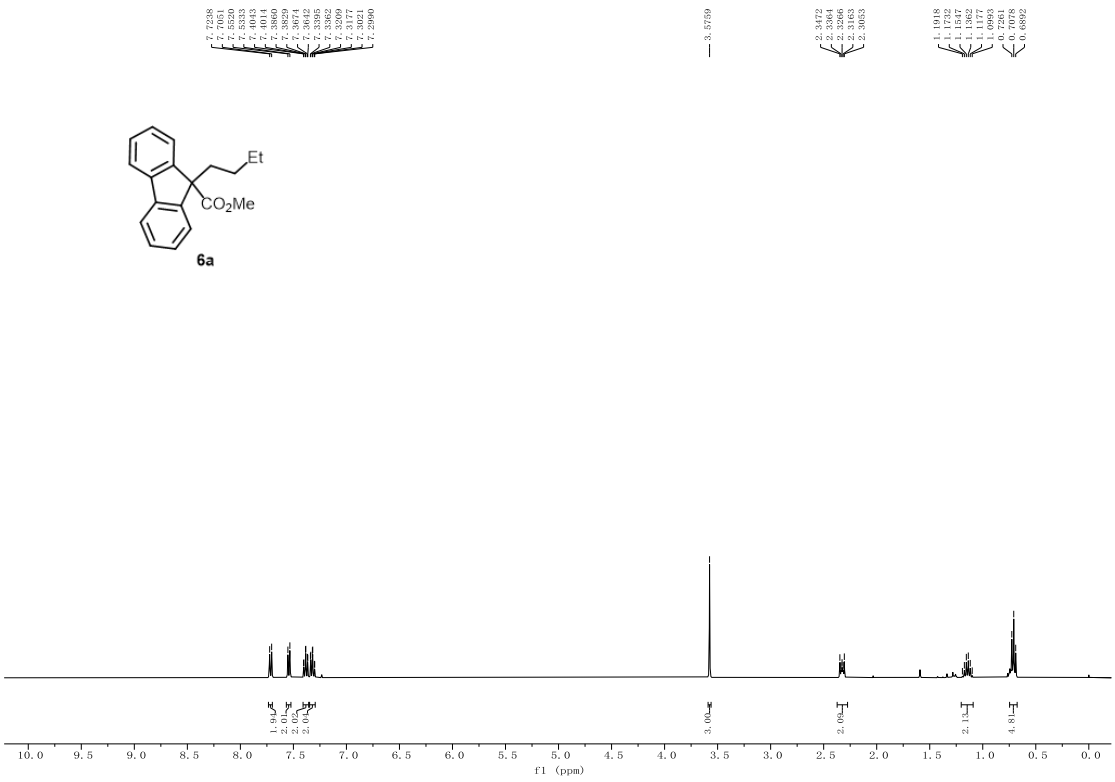
^{1}H NMR of compound **4k** (400 MHz in $CDCl_3$)



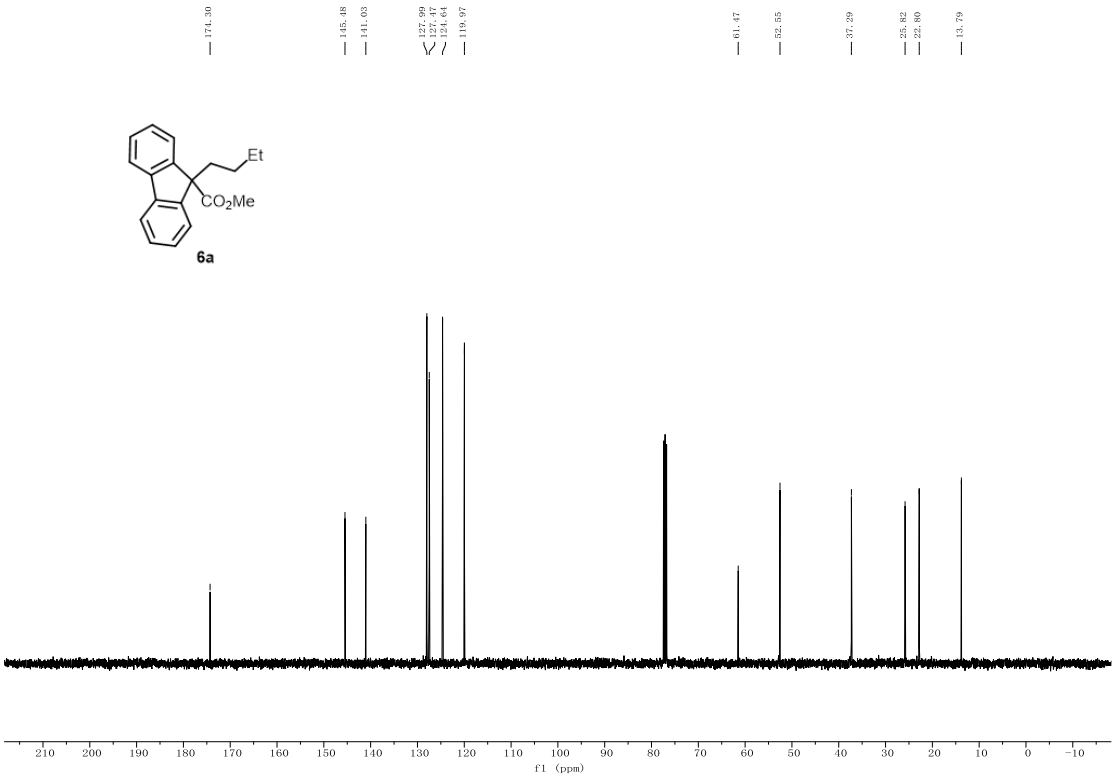
^{13}C NMR of compound **4k** (101 MHz in $CDCl_3$)



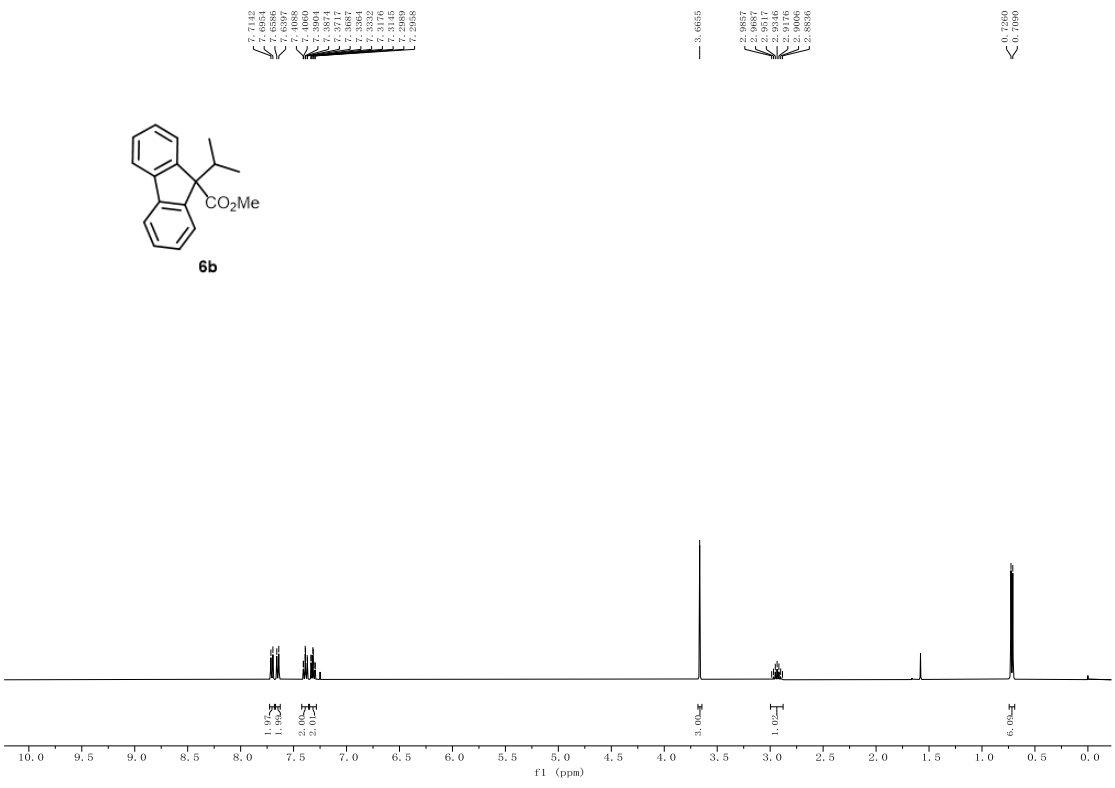
^{1}H NMR of compound **6a** (400 MHz in $CDCl_3$)



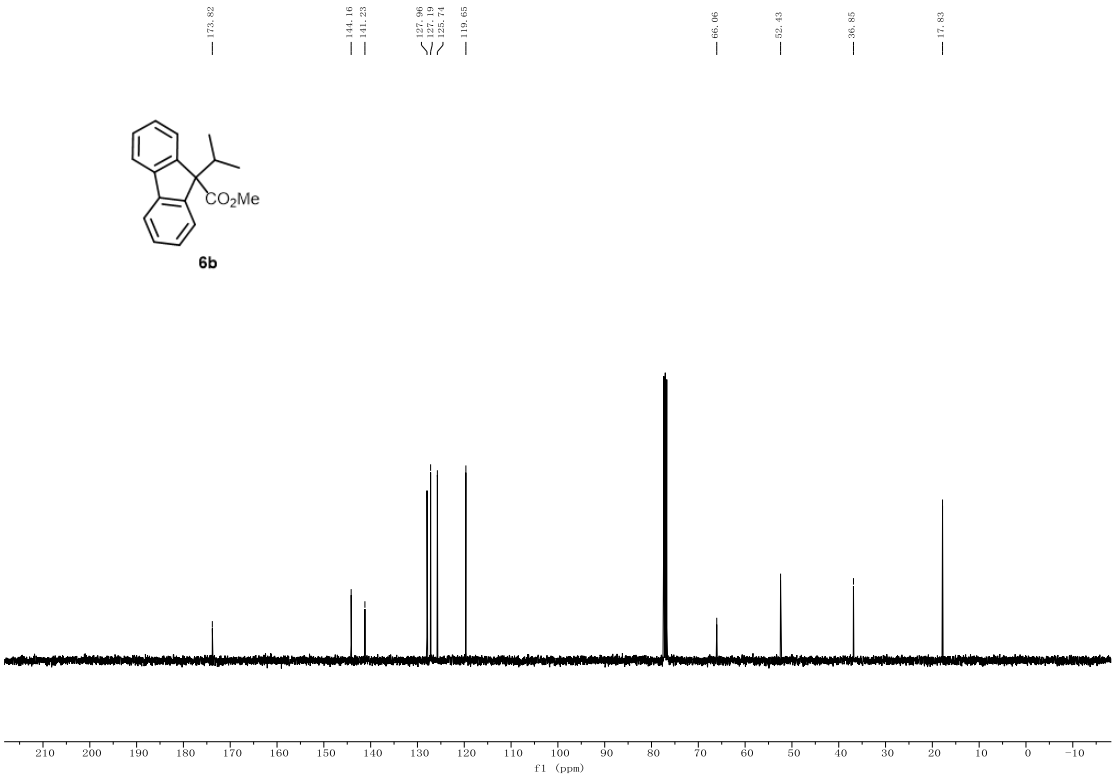
^{13}C NMR of compound **6a** (101 MHz in $CDCl_3$)



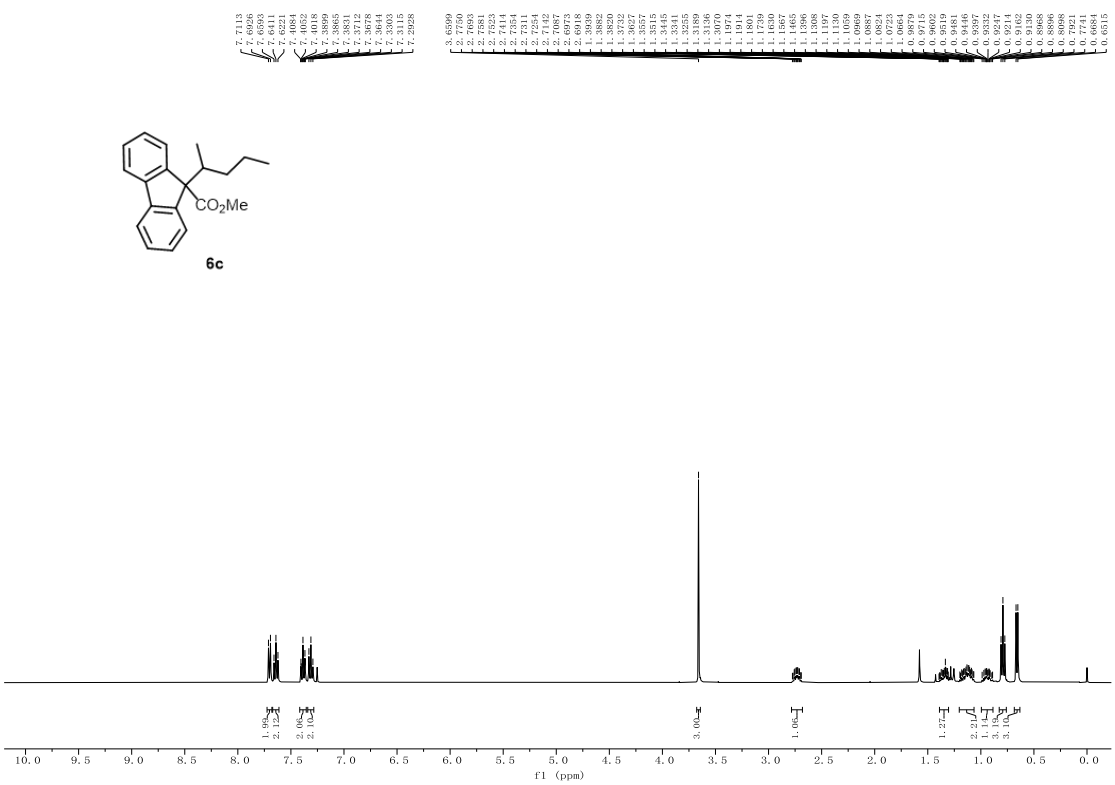
^{1}H NMR of compound **6b** (400 MHz in $CDCl_3$)



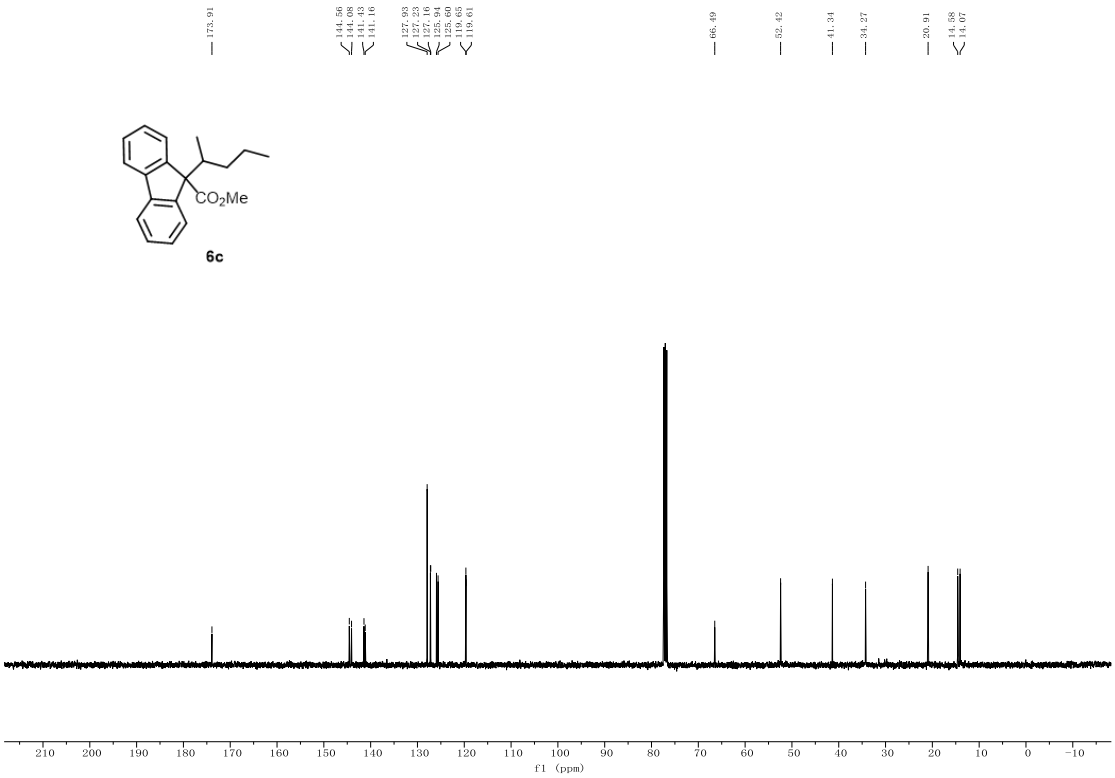
^{13}C NMR of compound **6b** (101 MHz in $CDCl_3$)



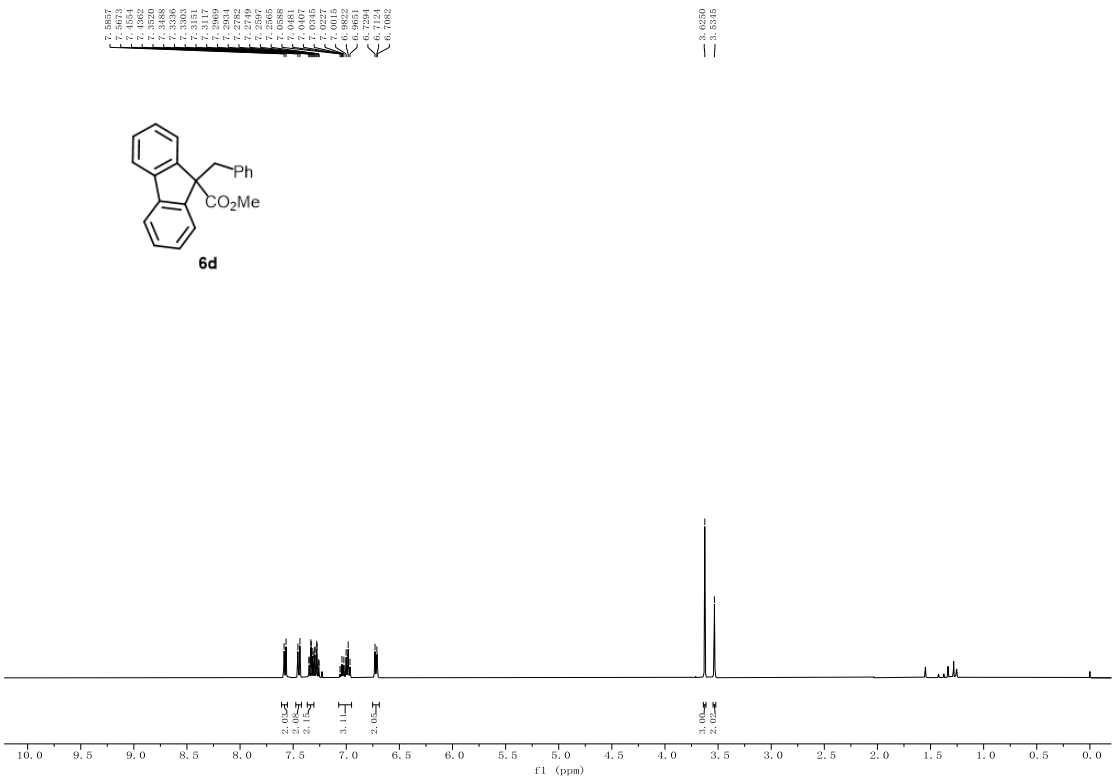
^{1}H NMR of compound **6c** (400 MHz in $CDCl_3$)



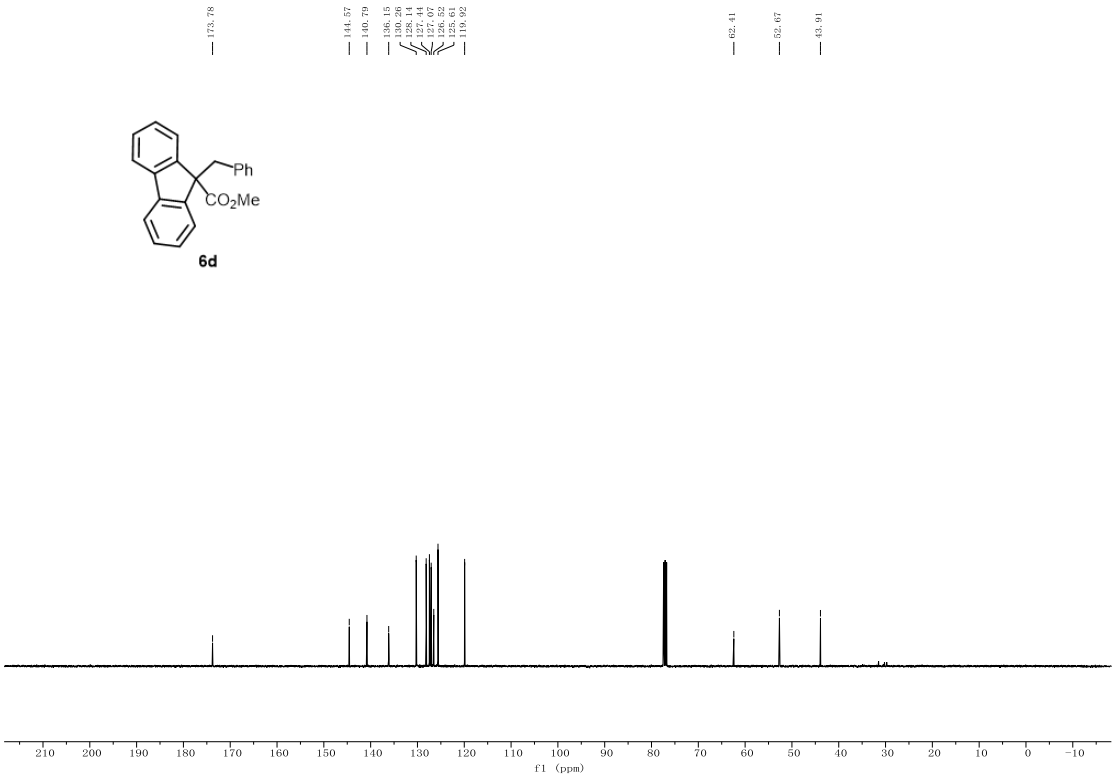
^{13}C NMR of compound **6c** (101 MHz in $CDCl_3$)



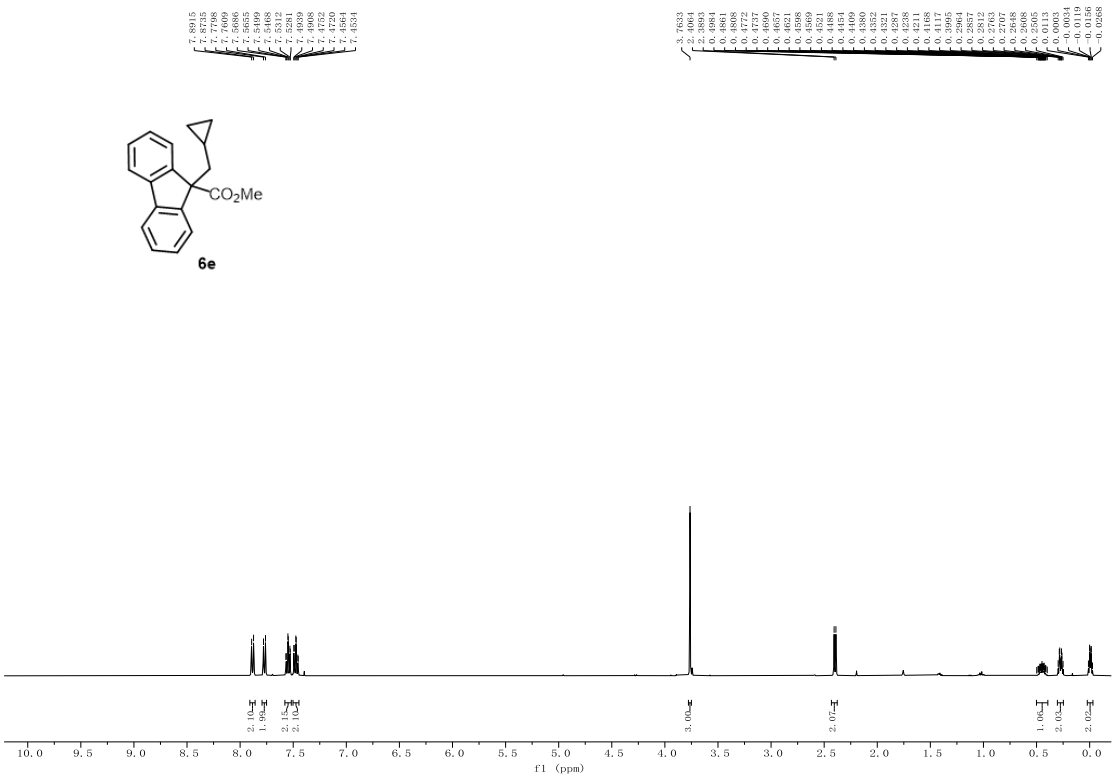
^{1}H NMR of compound **6d** (400 MHz in $CDCl_3$)



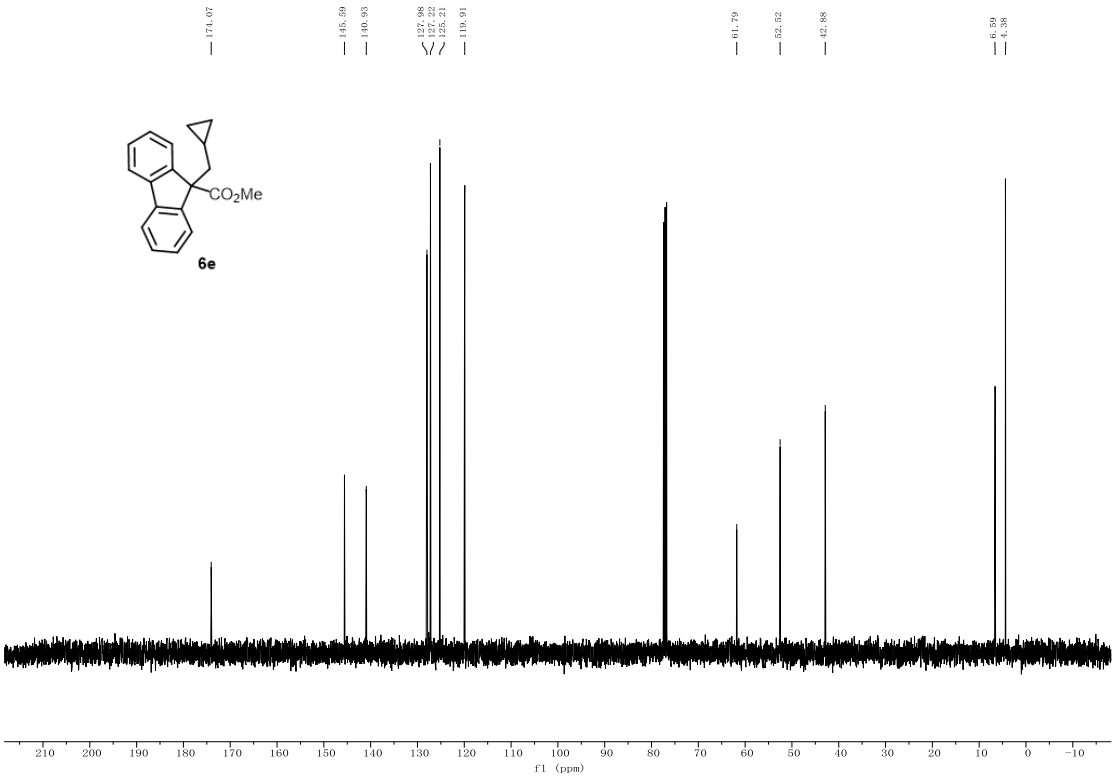
^{13}C NMR of compound **6d** (101 MHz in $CDCl_3$)



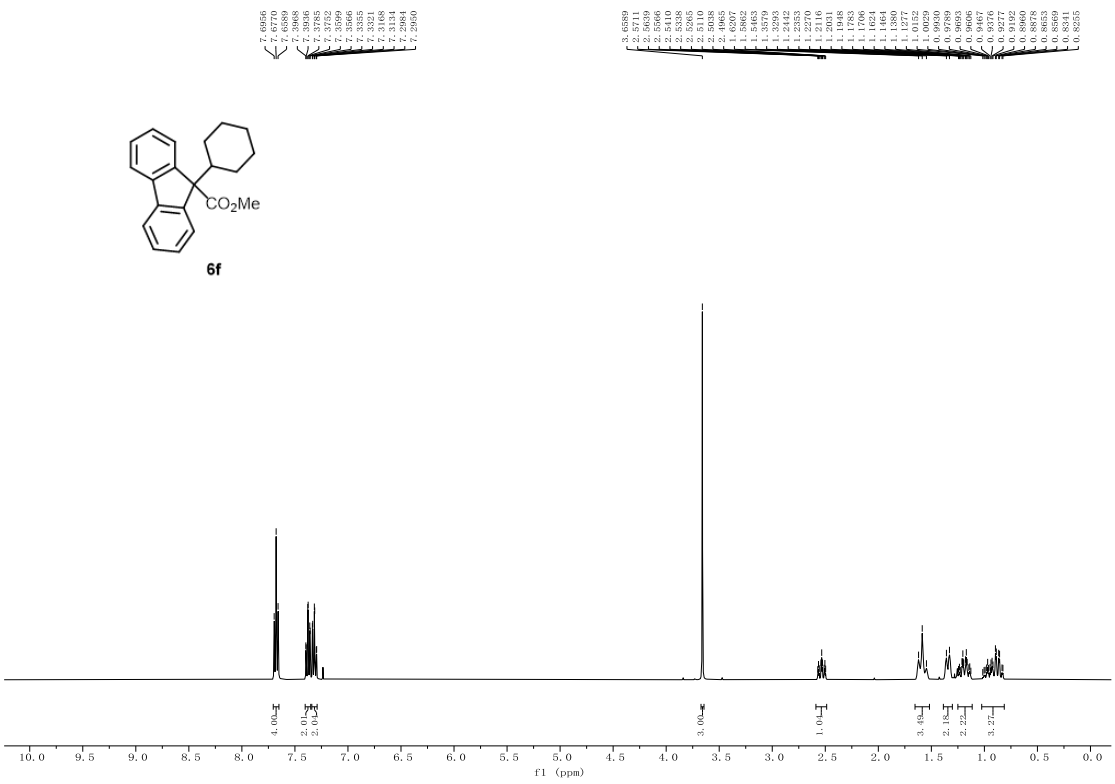
^{1}H NMR of compound **6e** (400 MHz in $CDCl_3$)



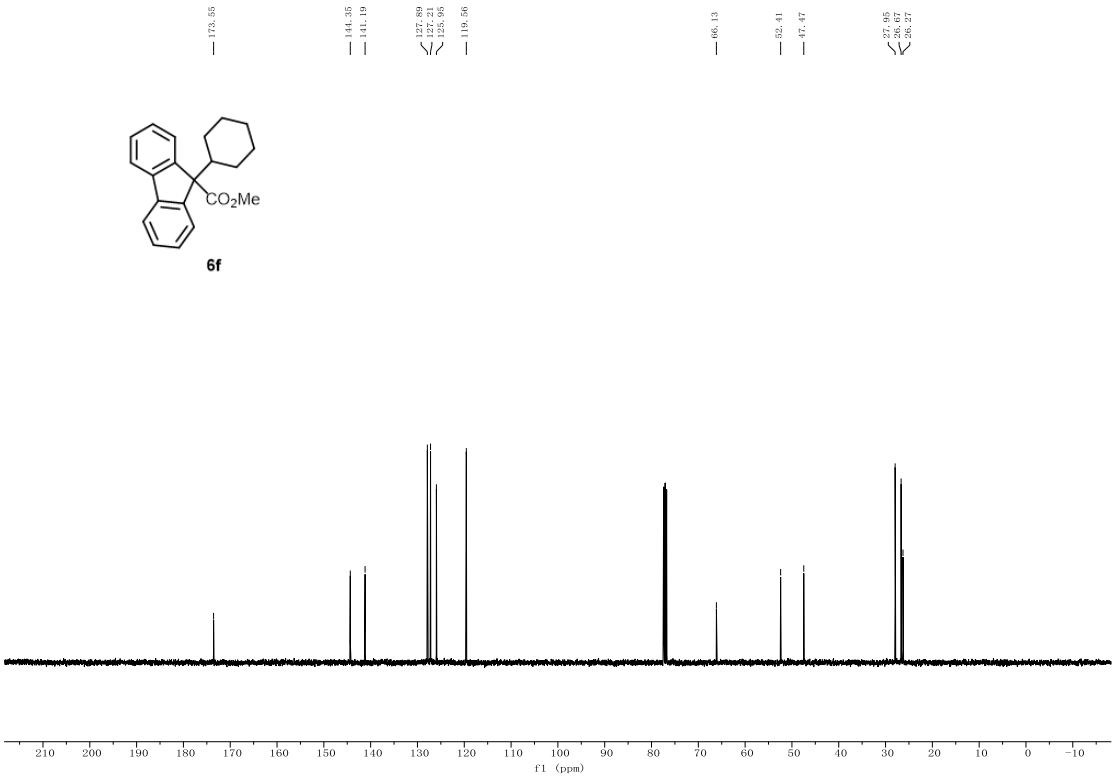
^{13}C NMR of compound **6e** (101 MHz in $CDCl_3$)



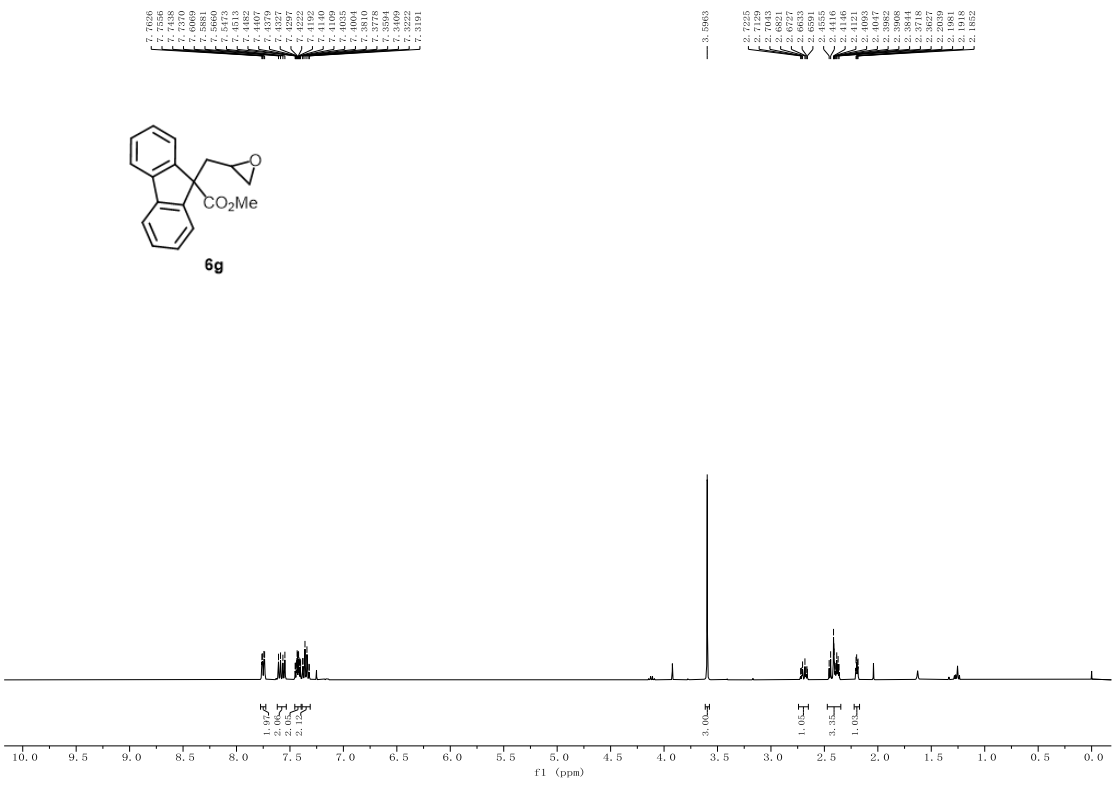
^{1}H NMR of compound **6f** (400 MHz in $CDCl_3$)



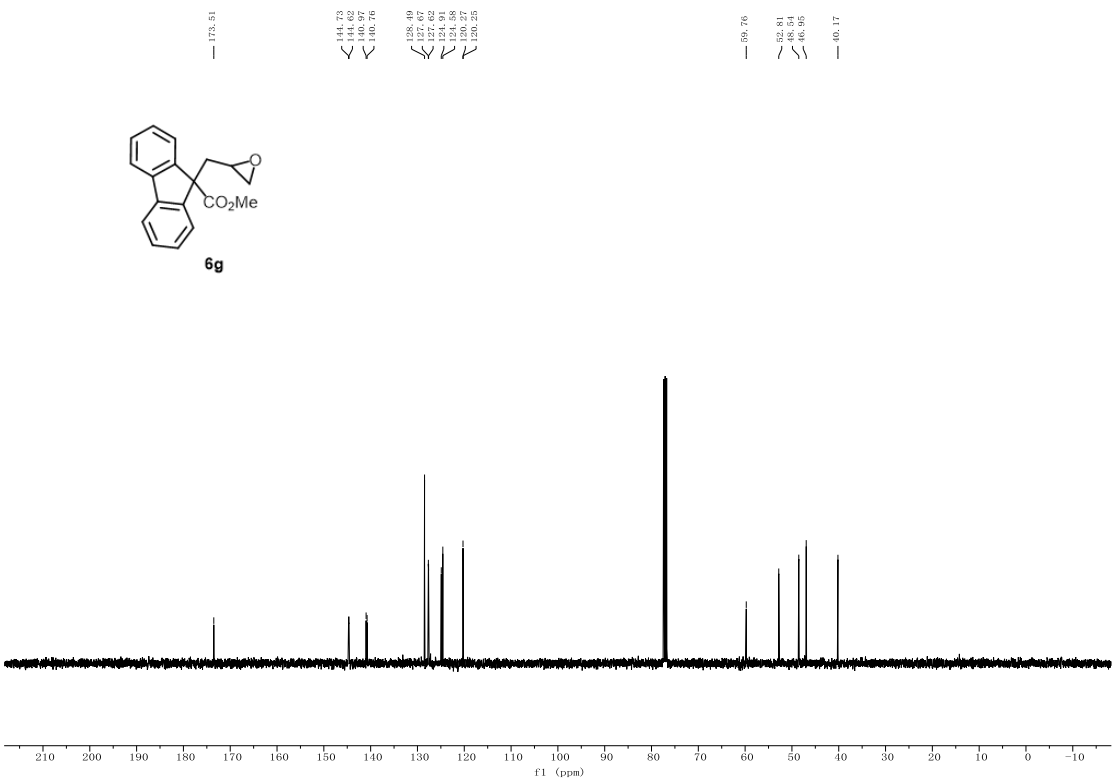
^{13}C NMR of compound **6f** (101 MHz in $CDCl_3$)



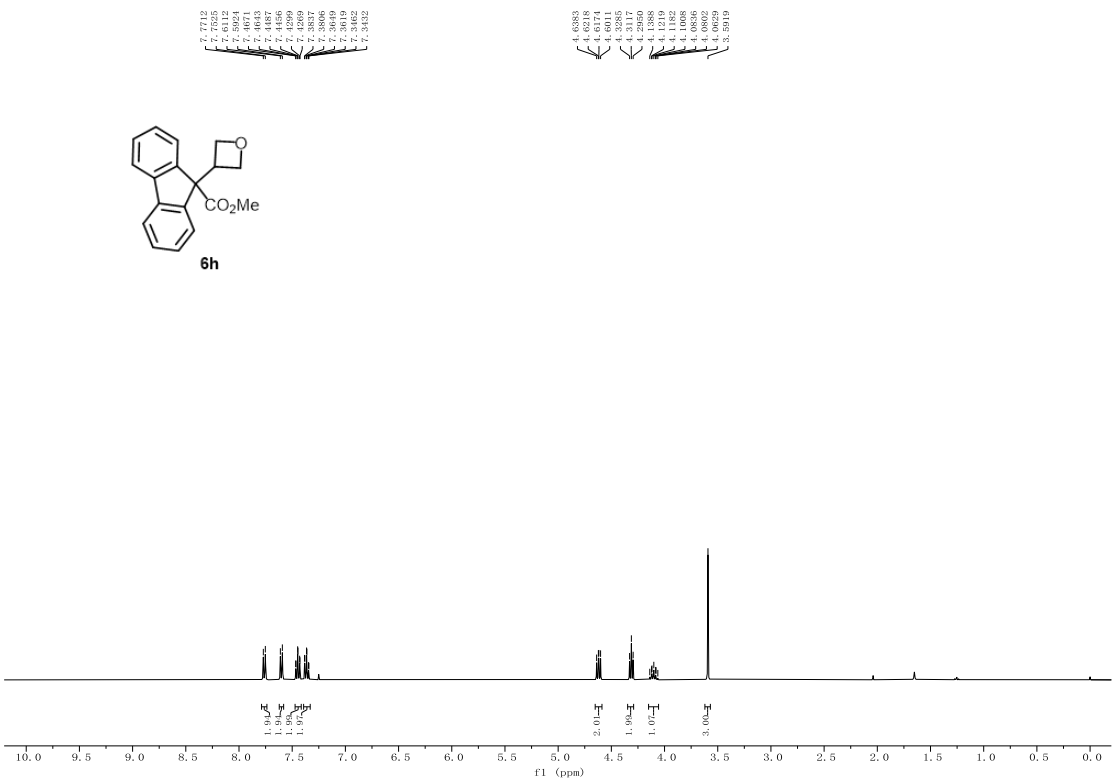
^{1}H NMR of compound **6g** (400 MHz in $CDCl_3$)



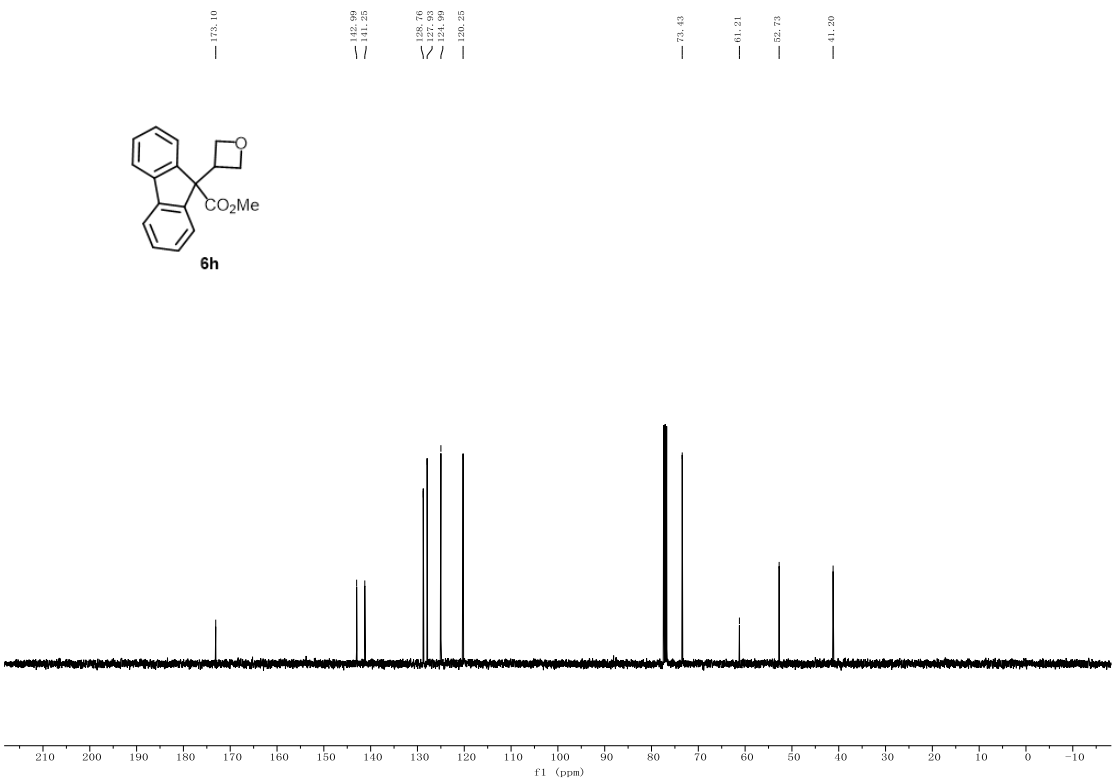
^{13}C NMR of compound **6g** (101 MHz in $CDCl_3$)



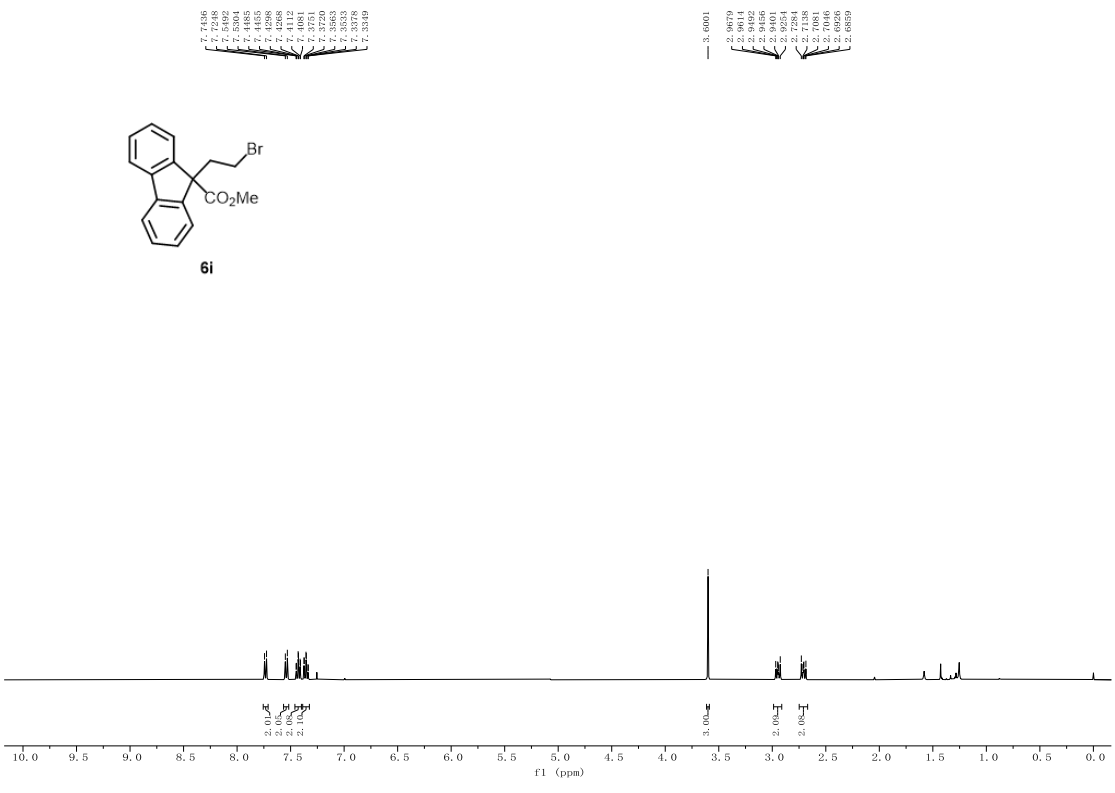
^{1}H NMR of compound **6h** (400 MHz in $CDCl_3$)



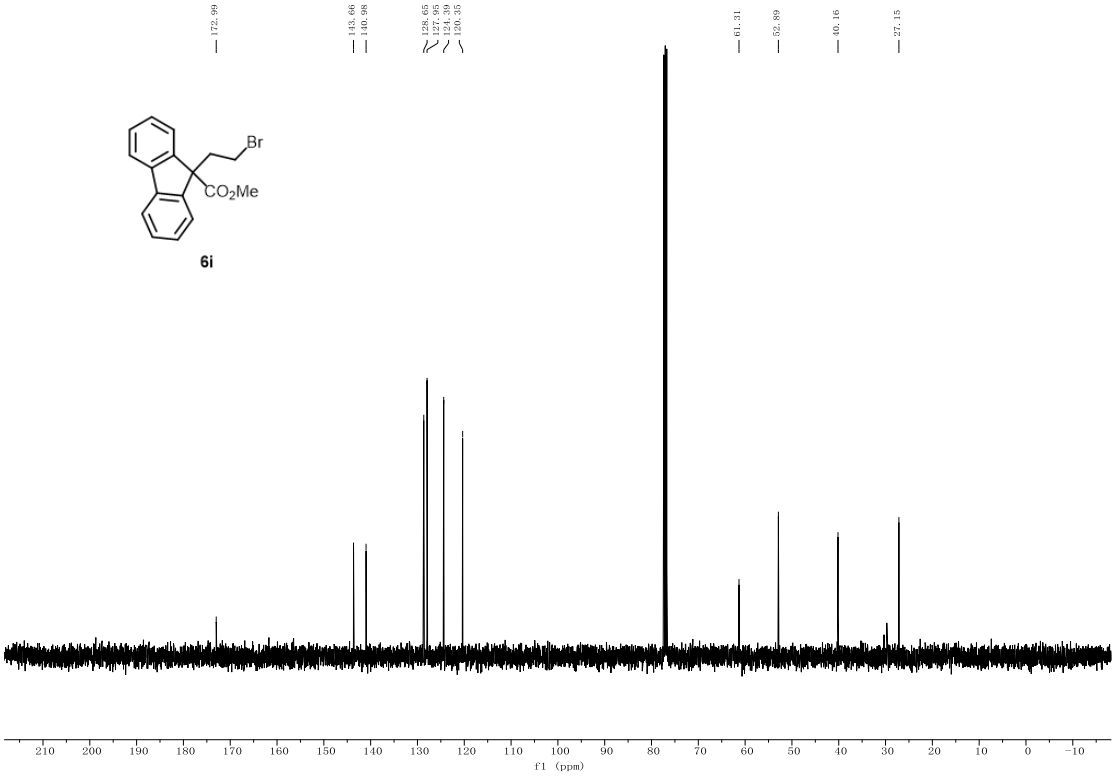
^{13}C NMR of compound **6h** (101 MHz in $CDCl_3$)



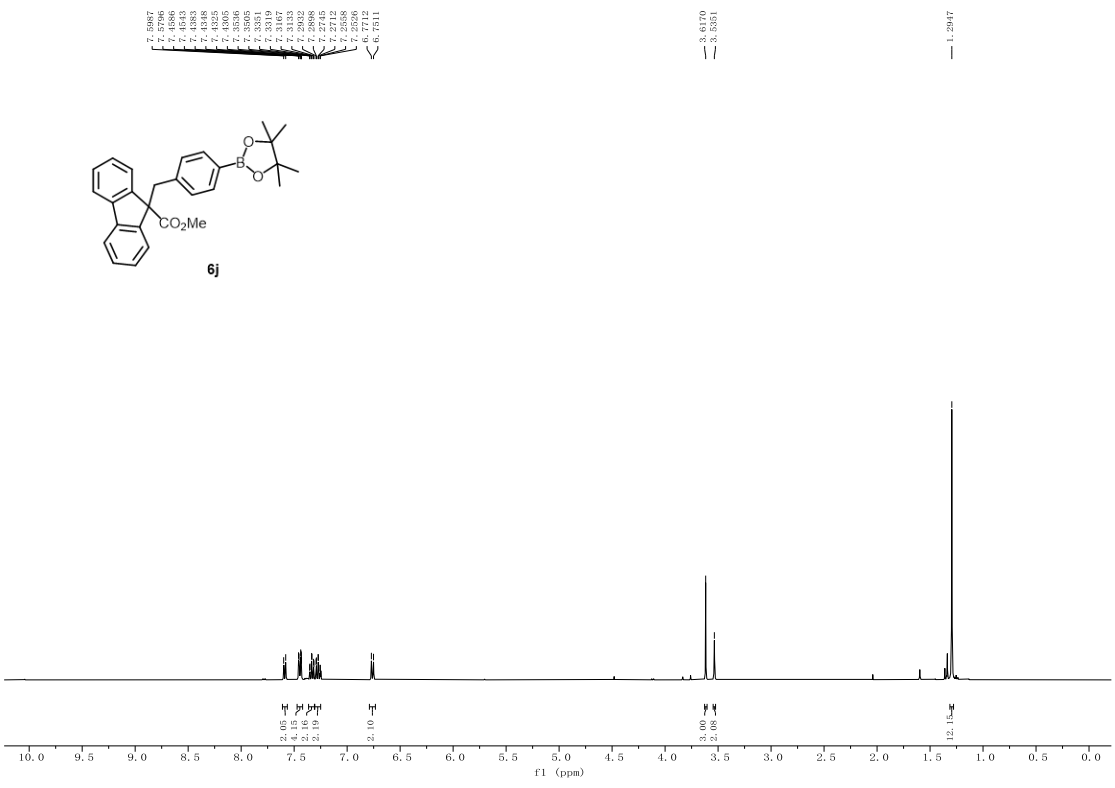
^{1}H NMR of compound **6i** (400 MHz in $CDCl_3$)



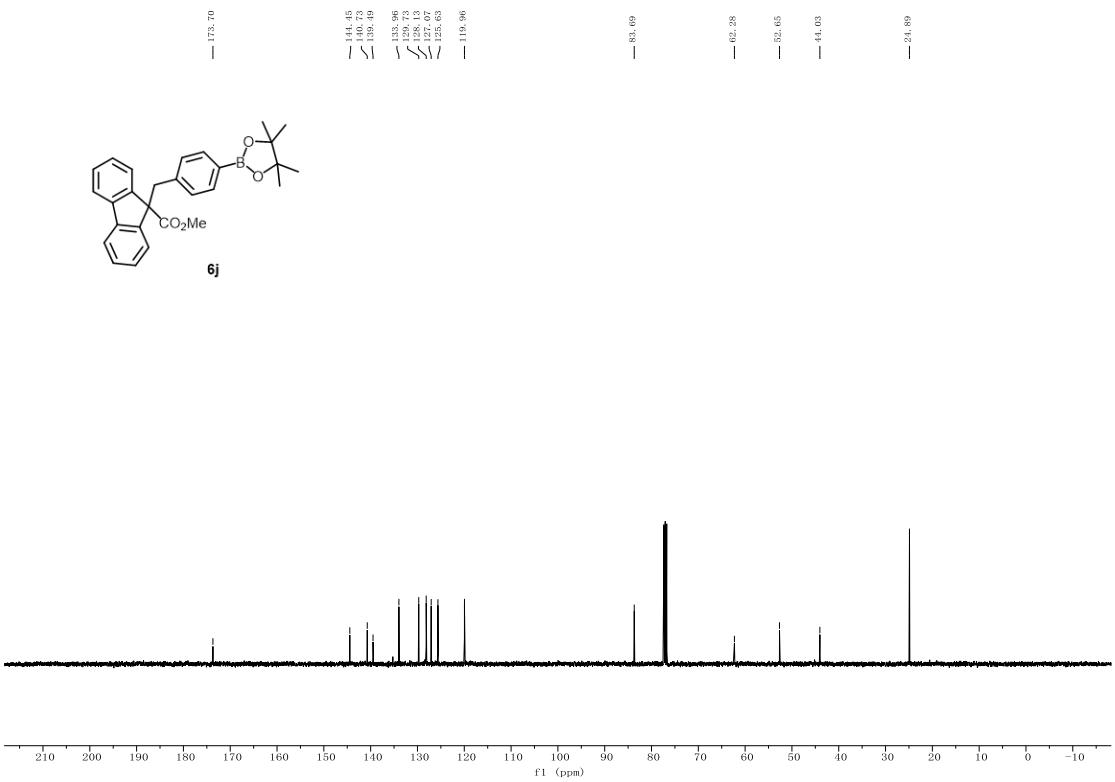
^{13}C NMR of compound **6i** (101 MHz in $CDCl_3$)



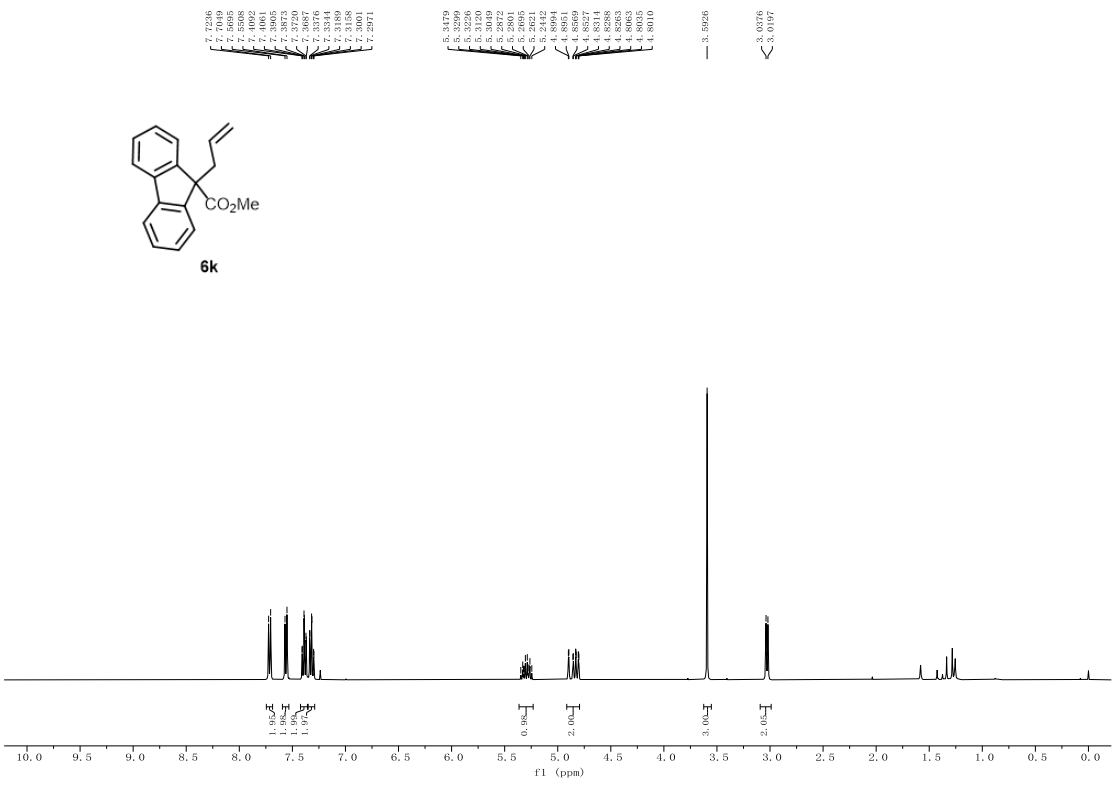
^{1}H NMR of compound **6j** (400 MHz in $CDCl_3$)



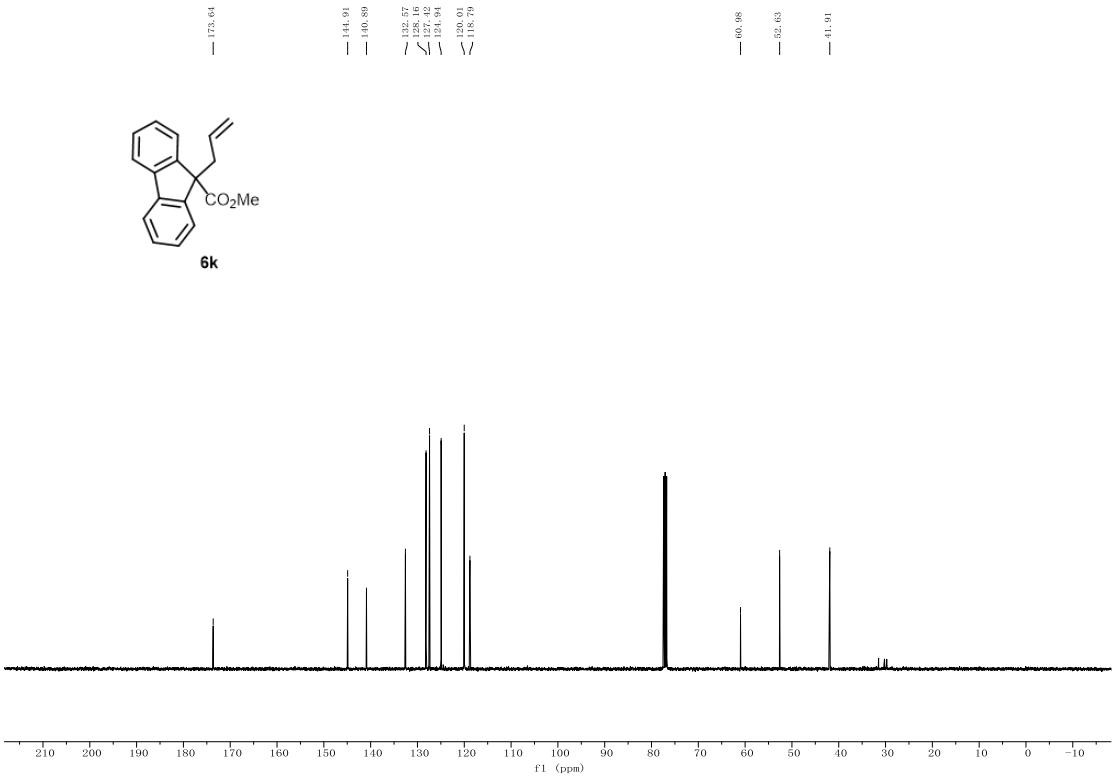
^{13}C NMR of compound **6j** (101 MHz in $CDCl_3$)



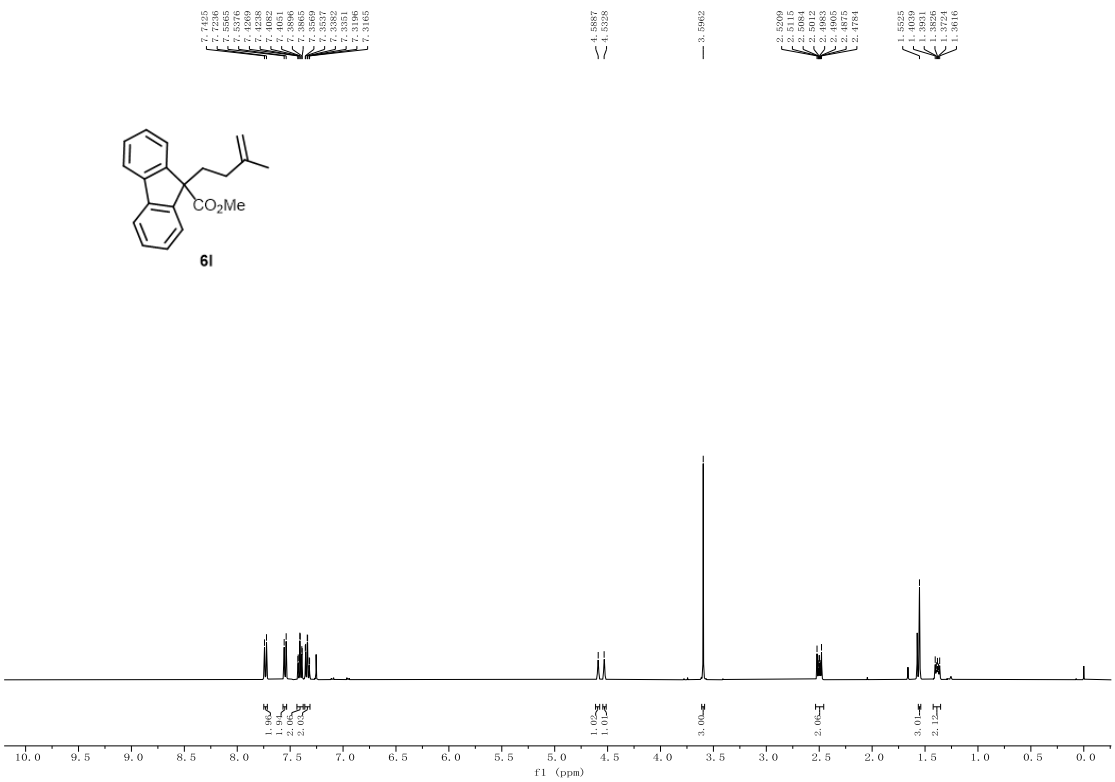
^{1}H NMR of compound **6k** (400 MHz in $CDCl_3$)



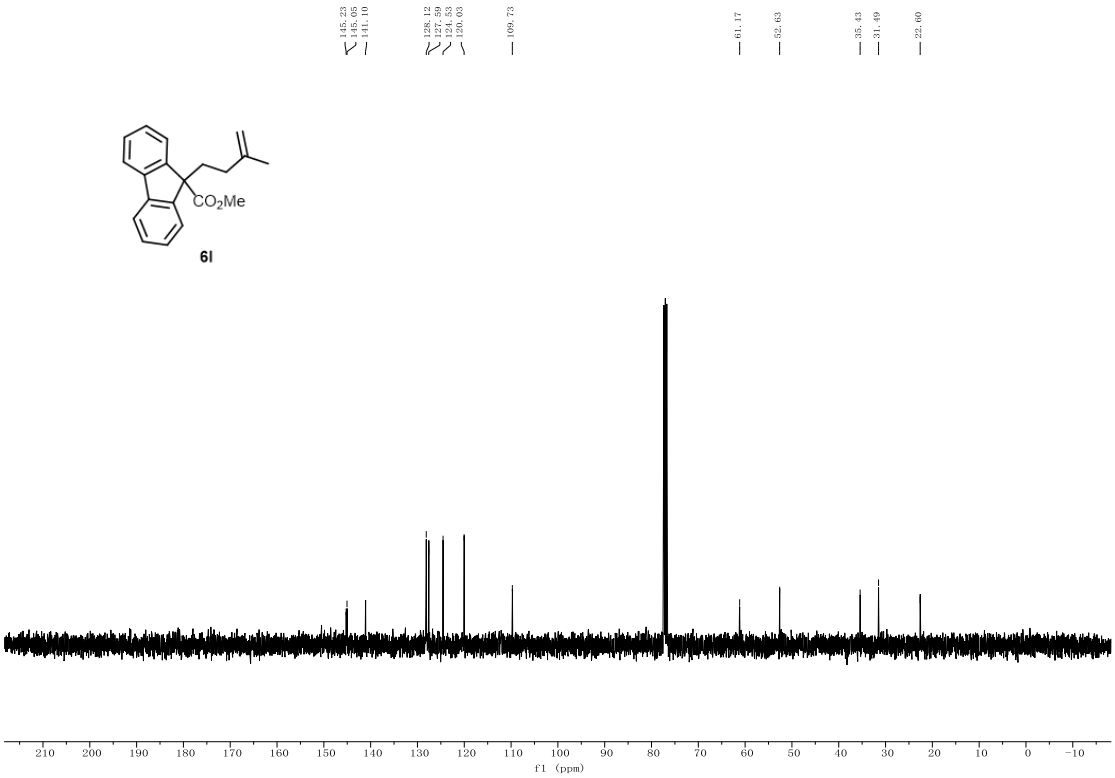
^{13}C NMR of compound **6k** (101 MHz in $CDCl_3$)



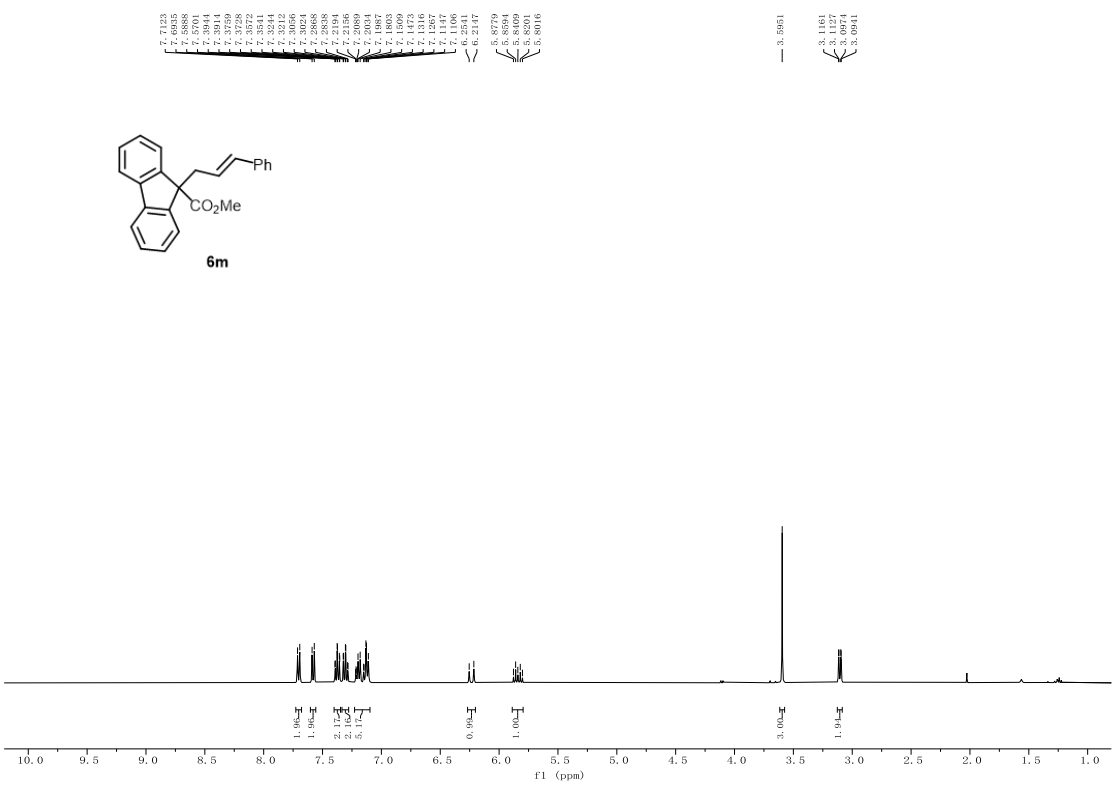
^{1}H NMR of compound **6l** (400 MHz in $CDCl_3$)



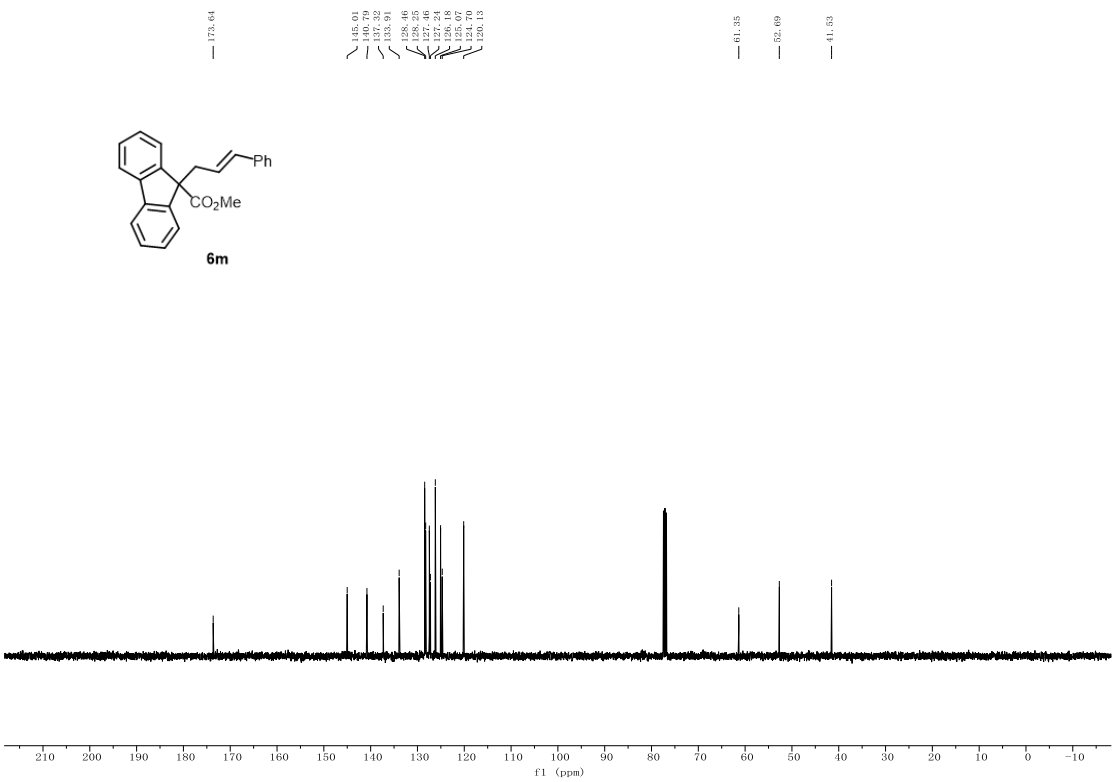
^{13}C NMR of compound **6l** (101 MHz in $CDCl_3$)



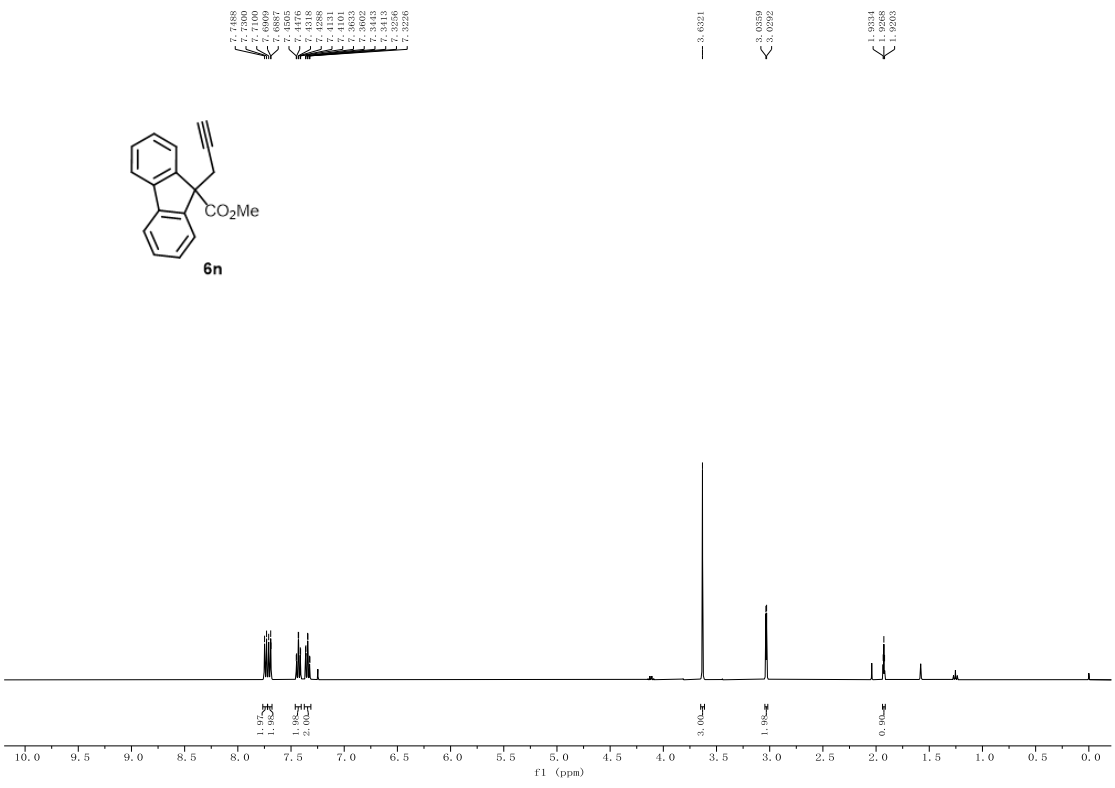
^{1}H NMR of compound **6m** (400 MHz in $CDCl_3$)



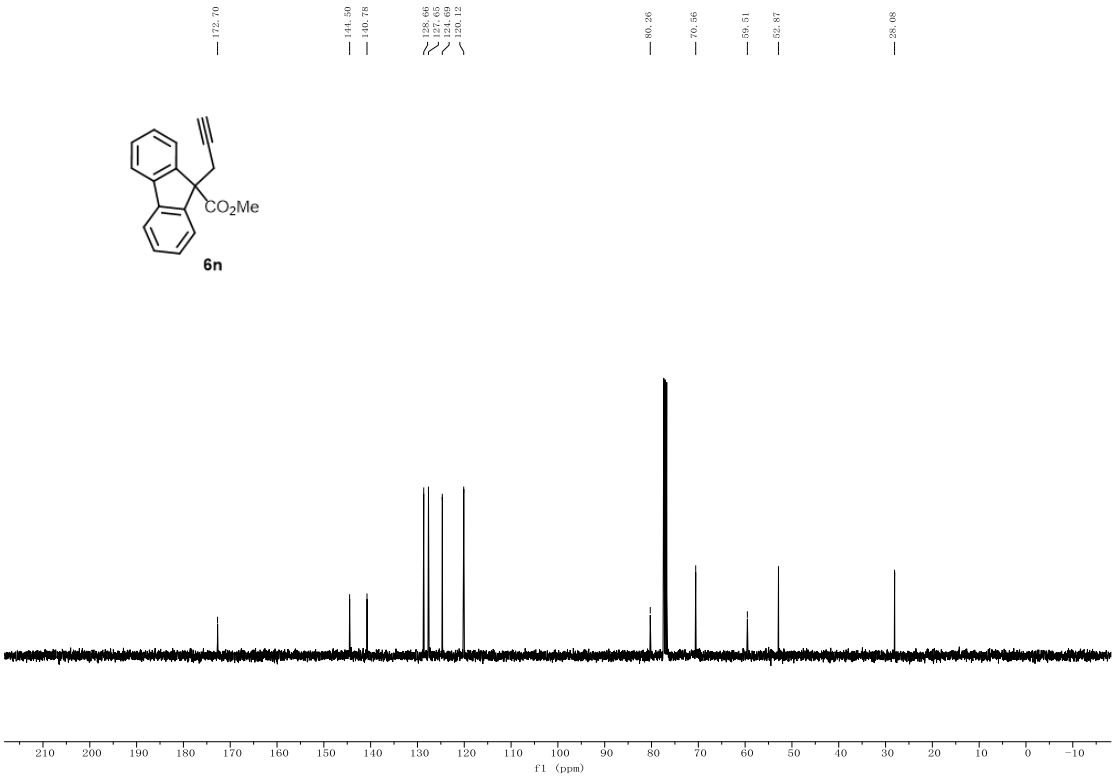
^{13}C NMR of compound **6m** (101 MHz in $CDCl_3$)



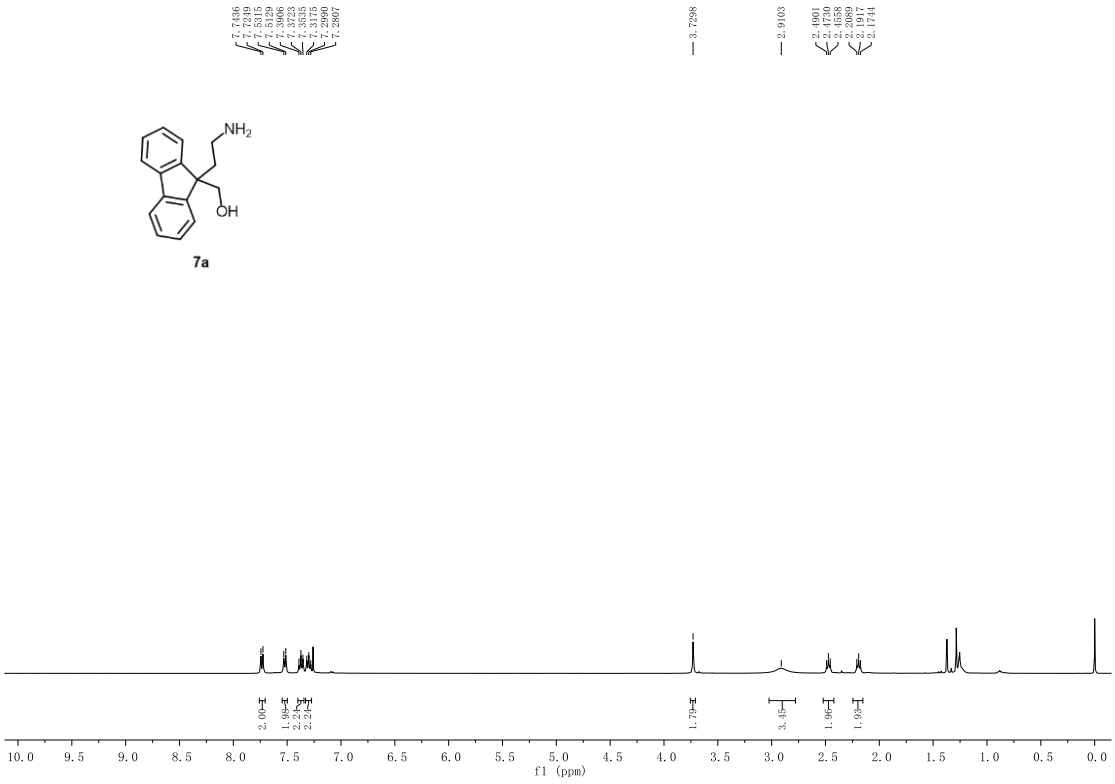
^{1}H NMR of compound **6n** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **6n** (101 MHz in $CDCl_3$)



^{1}H NMR of compound **7a** (400 MHz in $CDCl_3$)



^{13}C NMR of compound **7a** (101 MHz in $CDCl_3$)