

## ***Supporting Information for***

N-Heterocyclic carbene-catalyzed switchable reaction of 9-(trimethylsilyl)fluorene and aldehydes: chemoselective synthesis of dibenzofulvenes and fluorenyl alcohols

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## 1.1 General experimental methods

Unless otherwise indicated, all reactions were conducted under nitrogen atmosphere in oven-dried glassware with magnetic stirring bar. Column chromatograph was performed with silica gel (200~300 mesh) and analytical TLC on silica gel 60-F<sub>254</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) spectra were recorded on a Bruker-DMX 400 spectrometer in CDCl<sub>3</sub>, with tetramethylsilane as an internal standard and reported in ppm ( $\delta$ ). 9-(Trimethylsilyl)fluorene **1a** and all other chemicals were obtained from commercial supplies and used as received without any further purification. Anhydrous THF and toluene were distilled from sodium and benzophenone. DMSO, DMF, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and CH<sub>3</sub>CN were distilled from calcium hydride. 1, 2-dichloroethane was distilled from calcium chloride. Petroleum ether, where used, has a boiling point range of 60–90 °C.

## 1.2 Typical Procedure for the Synthesis of Compound **3a**

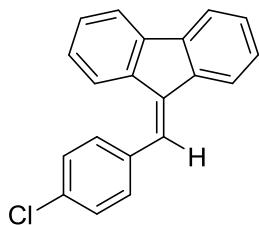
To a mixture of 9-(trimethylsilyl)fluorene **1a** (0.1 mmol, 23.8mg), *p*-chlorobenzaldehyde **2a** (0.1 mmol, 14 mg) and 4 Å MS (0.1g) in 1.0 mL anhydrous DMSO was added NHC **A** (10 mol%). The mixture was stirred at room temperature until full consumption of **2a** that was indicated by TLC (12 h). Then, the mixture was diluted with 15.0 ml EtOAc and washed with water (2.0 ml × 3). The organic layer was separated, dried

over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was then removed under reduced pressure and the crude material was purified by flash column chromatography (silica gel, PE/EtOAc ( $v : v$ ) = 100:1) to give the desired product **3a**.

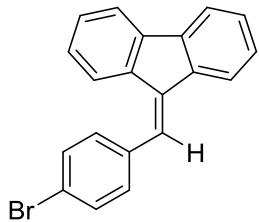
### **1.3 Typical Procedure for the Synthesis of Compound 4a**

To a mixture of 9-(trimethylsilyl)fluorene **1a** (0.1 mmol, 23.8mg), *p*-chlorobenzaldehyde **2a** (0.1 mmol, 14 mg) and  $\text{H}_2\text{O}$  (100  $\mu\text{l}$ ) in 1.0 mL anhydrous DMSO was added NHC **A** (1 mol%). The mixture was stirred at 10 °C until full consumption of **2a** that was indicated by TLC (12 h). Then, the mixture was diluted with 15.0 ml EtOAc and washed with water (2.0 ml  $\times$  3). The organic layer was separated, dried over  $\text{Na}_2\text{SO}_4$  and filtered. The solvent was then removed under reduced pressure and the crude material was purified by flash column chromatography (silica gel, PE/EtOAc ( $v : v$ ) = 20:1) to give the desired product **4a**.

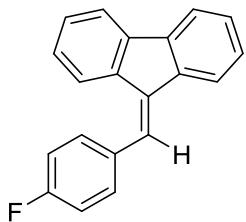
## 2. Spectroscopic data for all products



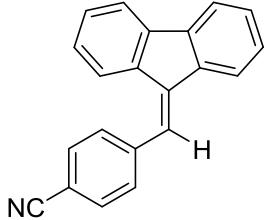
9-(4-chlorobenzylidene)-9H-fluorene (**3a**)<sup>[1]</sup> : yield: 88%, 25 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 2H), 7.59 (s, 1H), 7.55 – 7.48 (m, 3H), 7.46 – 7.28 (m, 5H), 7.07 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.38, 139.26, 139.24, 137.08, 136.28, 135.33, 133.88, 130.68, 128.80, 128.79, 128.44, 127.07, 126.76, 125.66, 124.33, 120.27, 119.84, 119.65.



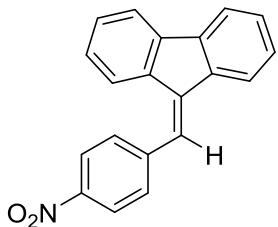
9-(4-bromobenzylidene)-9H-fluorene (**3b**)<sup>[2]</sup> : yield: 79%, 26 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.60 – 7.53 (m, 3H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.37 (td, *J* = 7.4, 1.2 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.07 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.39, 139.26, 139.25, 137.08, 136.28, 135.80, 131.75, 130.97, 128.82, 128.46, 127.09, 126.78, 125.65, 124.35, 122.08, 120.29, 119.86, 119.66.



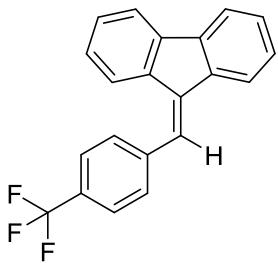
9-(4-fluorobenzylidene)-9H-fluorene (**3c**)<sup>[3]</sup> : yield: 98%, 26 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 7.3 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.61 (s, 1H), 7.54 (m, 2H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.27 (m, 3H), 7.14 (t, *J* = 8.7 Hz, 2H), 7.06 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.49 (d, *J* = 247.9 Hz), 141.32, 139.33, 139.19, 136.75, 136.38, 132.82 (d, *J* = 3.5 Hz), 131.07 (d, *J* = 8.0 Hz), 128.67, 128.32, 127.04, 126.71, 126.01, 124.24, 120.22, 119.82, 119.63, 115.62 (d, *J* = 21.5 Hz).; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -113.23 (s, 1F).



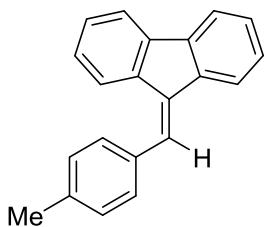
4-((9H-fluoren-9-ylidene)methyl)benzonitrile (**3d**)<sup>[1]</sup> : yield: 79%, 22 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 – 7.64 (m, 7H), 7.56 (s, 1H), 7.43 – 7.30 (m, 4H), 7.06 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.91, 141.69, 139.48, 138.92, 138.51, 135.88, 132.34, 130.05, 129.35, 128.99, 127.27, 126.91, 124.33, 124.29, 120.49, 120.05, 119.79, 118.81, 111.51.



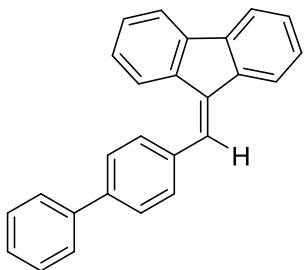
9-(4-nitrobenzylidene)-9H-fluorene (**3e**) <sup>[4]</sup>: yield: 80%, 24 mg, yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.32 (d, *J* = 8.7 Hz, 2H), 7.82 – 7.66 (m, 5H), 7.60 (s, 1H), 7.43 – 7.33 (m, 4H), 7.06 (td, *J* = 7.7, 1.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.27, 139.55, 139.14, 138.99, 136.62, 136.20, 129.30, 128.78, 128.28, 127.62, 127.36, 127.03, 126.87, 124.42, 120.20, 119.80, 119.64, 119.02.



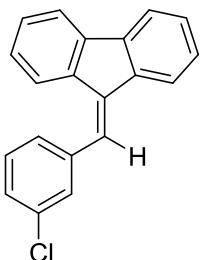
9-(4-(trifluoromethyl)benzylidene)-9H-fluorene (**3f**) <sup>[3]</sup>: yield: 83%, 27 mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (d, *J* = 7.4 Hz, 1H), 7.73 – 7.65 (m, 6H), 7.61 (s, 1H), 7.45 – 7.28 (m, 4H), 7.06 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.55, 140.72, 139.40, 139.09, 137.91, 136.11, 129.91 (q, *J* = 32.6 Hz), 129.60, 129.08, 128.74, 127.18, 126.86, 125.52 (q, *J* = 3.8 Hz), 125.02, 124.35, 124.18 (q, *J* = 272.0 Hz), 120.40, 119.93, 119.72; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.47 (s, 3F).



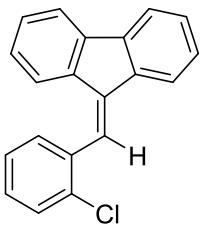
9-(4-methylbenzylidene)-9H-fluorene (**3g**)<sup>[1]</sup>: yield: 60%, 16 mg; yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 – 7.61 (m, 5H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.44 – 7.23 (m, 5H), 7.07 (t, *J* = 7.6 Hz, 1H), 2.44 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.04, 139.31, 139.18, 136.89, 136.70, 136.68, 136.26, 130.20, 129.36, 128.39, 128.20, 126.97, 126.80, 126.56, 125.87, 124.45, 120.34, 119.63, 20.13.



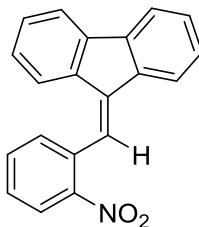
9-([1,1'-biphenyl]-4-ylmethylene)-9H-fluorene (**3h**) : yield: 77%, 26 mg, white solid; mp 176-178 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 7.1 Hz, 1H), 7.75 – 7.63 (m, 10H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.40 – 7.28 (m, 4H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.31, 140.79, 140.55, 139.57, 139.18, 136.56, 136.55, 135.85, 129.91, 128.91, 128.61, 128.23, 127.59, 127.14, 127.06, 127.02, 126.95, 126.71, 124.46, 120.28, 119.78, 119.62; HRMS (EI) m/z calcd for C<sub>26</sub>H<sub>18</sub><sup>+</sup> (M)<sup>+</sup> 330.1403, found 330.1404.



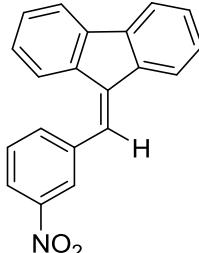
9-(3-chlorobenzylidene)-9H-fluorene (**3i**)<sup>[1]</sup>: yield: 57%, 16 mg; yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 7.4 Hz, 1H), 7.70 (dd, *J* = 7.4, 0.6 Hz, 2H), 7.57 (s, 1H), 7.56 – 7.55 (m, 1H), 7.48 – 7.42 (m, 2H), 7.40 – 7.28 (m, 5H), 7.07 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.43, 139.34, 139.16, 138.78, 137.48, 136.21, 134.48, 129.84, 129.17, 128.89, 128.57, 128.05, 127.44, 127.11, 126.84, 125.24, 124.43, 120.34, 119.85, 119.67.



9-(2-chlorobenzylidene)-9H-fluorene (**3j**) : yield: 65%, 19 mg; colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 7.1 Hz, 1H), 7.75 – 7.64 (m, 3H), 7.61 (s, 1H), 7.52 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.43 – 7.27 (m, 6H), 7.03 (td, *J* = 7.6, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.42, 139.39, 139.10, 137.49, 136.38, 135.41, 134.07, 131.46, 129.75, 129.52, 128.82, 128.56, 127.13, 126.77, 126.61, 124.40, 123.94, 120.64, 119.81, 119.64; HRMS (EI) m/z calcd for C<sub>20</sub>H<sub>13</sub>Cl<sup>+</sup> (M)<sup>+</sup> 288.0700, found 288.0702.

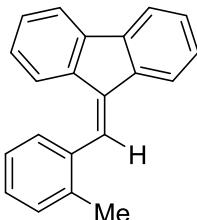


**9-(2-nitrobenzylidene)-9H-fluorene (3k)** : yield: 88%, 26 mg, yellow solid; mp 125-127 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.27 (dd,  $J = 8.2, 1.1$  Hz, 1H), 7.90 – 7.80 (m, 2H), 7.79 – 7.57 (m, 5H), 7.42 – 7.33 (m, 2H), 7.29 (td,  $J = 7.4, 1.3$  Hz, 1H), 7.03 – 6.86 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.70, 141.60, 139.35, 138.91, 137.08, 136.09, 133.45, 133.03, 132.75, 129.18, 128.93, 128.78, 127.28, 126.68, 125.11, 124.16, 122.91, 120.80, 120.00, 119.69; HRMS (EI) m/z calcd for  $\text{C}_{20}\text{H}_{13}\text{NO}_2^+$  (M)<sup>+</sup> 299.0941, found 299.0944.

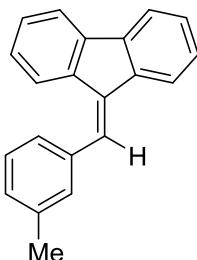


**9-(3-nitrobenzylidene)-9H-fluorene (3l)** : yield: 89%, 27 mg, yellow solid; mp 120-121 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (s, 1H), 8.24 (dd,  $J = 8.2, 2.1$  Hz, 1H), 7.90 (d,  $J = 7.6$  Hz, 1H), 7.76 (d,  $J = 7.5$  Hz, 1H), 7.70 (d,  $J = 7.3$  Hz, 2H), 7.66 – 7.56 (m, 2H), 7.40 (t,  $J = 7.8$  Hz, 1H), 7.36 – 7.29 (m, 3H), 7.05 (td,  $J = 7.6, 0.9$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.46, 141.70, 139.48, 138.87, 138.69, 138.61, 135.84, 135.40, 129.56, 129.35, 128.98, 127.29, 126.97, 124.19, 124.11, 123.57, 122.77, 120.47,

120.08, 119.78; HRMS (EI) m/z calcd for  $C_{20}H_{13}NO_2^+$  ( $M$ )<sup>+</sup> 299.0941, found 299.0944.

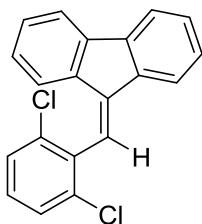


**9-(2-methylbenzylidene)-9H-fluorene (3m)**<sup>[5]</sup>: yield: 53%, 14 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 6.8 Hz, 1H), 7.75 – 7.68 (m, 2H), 7.67 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.25 (m, 6H), 7.16 (d, *J* = 7.8 Hz, 1H), 7.01 (td, *J* = 7.7, 1.1 Hz, 1H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.17, 139.62, 139.07, 138.01, 136.63, 135.98, 133.86, 129.28, 129.23, 128.39, 128.03, 127.55, 126.93, 126.60, 124.38, 120.16, 119.68, 119.55, 21.46.

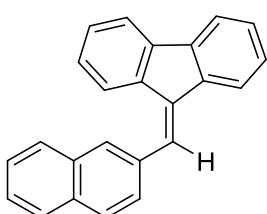


**9-(3-methylbenzylidene)-9H-fluorene (3n)**<sup>[3]</sup> : yield: 52%, 14 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78 (d, *J* = 7.1 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.67 (s, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.26 (m, 6H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.06 (td, *J* = 7.7, 1.1 Hz, 1H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.21, 139.54, 139.15, 138.17, 136.81,

136.63, 136.30, 129.85, 128.78, 128.45, 128.43, 128.13, 127.53, 126.96, 126.65, 126.33, 124.45, 120.20, 119.69, 119.57, 21.44.

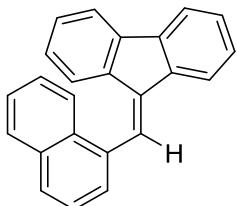


**9-(2,6-dichlorobenzylidene)-9H-fluorene (3o)** : yield: 89%, 29 mg, white solid; mp 129-130 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (dt, *J* = 7.2, 0.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.45 (s, 1H), 7.43 (s, 1H), 7.41 – 7.26 (m, 5H), 7.04 (td, *J* = 7.6, 1.1 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.21, 139.84, 139.49, 138.44, 136.64, 135.16, 134.69, 129.53, 129.04, 128.85, 128.22, 127.25, 124.12, 120.87, 119.89, 119.76, 119.75; HRMS (EI) m/z calcd for C<sub>20</sub>H<sub>12</sub>Cl<sub>2</sub><sup>+</sup> (M)<sup>+</sup> 322.0311, found 322.0311.

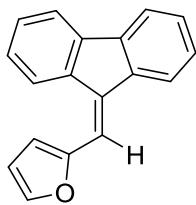


**9-(naphthalen-2-ylmethylene)-9H-fluorene (3p)** : yield: 87%, 26 mg, white solid; mp 99-102 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (s, 1H), 7.95 – 7.78 (m, 5H), 7.75 – 7.66 (m, 3H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.42 – 7.25 (m, 3H), 7.00 (td, *J* = 7.7, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.19, 139.41, 139.18, 138.00, 136.73,

134.30, 133.68, 131.69, 128.54, 128.51, 128.48, 128.39, 127.16, 127.06, 126.71, 126.39, 126.28, 125.49, 125.30, 125.18, 124.73, 120.48, 119.69, 119.64; HRMS (EI) m/z calcd for  $C_{24}H_{16}^+$  ( $M$ )<sup>+</sup> 304.1247, found 304.1246.

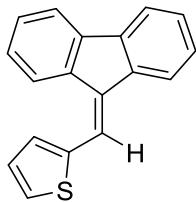


9-(naphthalen-1-ylmethylene)-9H-fluorene (**3q**)<sup>[2]</sup> : yield: 77%, 24 mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 6.2 Hz, 2H), 7.98 – 7.88 (m, 3H), 7.79 – 7.65 (m, 3H), 7.60 – 7.50 (m, 2H), 7.49 – 7.34 (m, 3H), 7.24 (td, *J* = 7.2, 1.0 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.88 (td, *J* = 7.8, 1.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.19, 139.41, 139.18, 138.00, 136.73, 134.30, 133.68, 131.69, 128.54, 128.51, 128.48, 128.39, 127.16, 127.06, 126.71, 126.39, 126.28, 125.49, 125.30, 125.18, 124.73, 120.48, 119.69, 119.64.

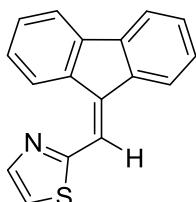


2-((9H-fluoren-9-ylidene)methyl)furan (**3r**)<sup>[1]</sup> : yield: 47%, 11 mg, yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.76 (d, *J* = 7.2 Hz, 1H), 7.79 – 7.66 (m, 4H), 7.43 – 7.27 (m, 5H), 6.77 (d, *J* = 3.4 Hz, 1H), 6.59 (dd, *J* = 3.4, 1.8 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.16, 143.85,

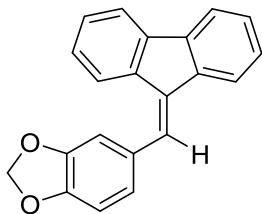
141.04, 140.26, 138.96, 136.12, 132.72, 128.48, 127.86, 127.11, 126.82, 125.68, 119.82, 119.59, 119.55, 115.54, 112.65, 112.45.



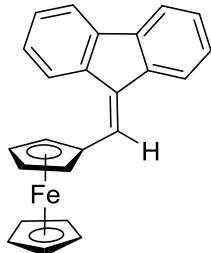
2-((9H-fluoren-9-ylidene)methyl)thiophene (**3s**)<sup>[6]</sup> : yield: 82%, 21 mg, yellow; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.72 (q, *J* = 7.6 Hz, 3H), 7.61 (s, 1H), 7.49 – 7.41 (m, 2H), 7.38 – 7.28 (m, 3H), 7.21 – 7.11 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.27, 139.55, 139.14, 138.99, 136.62, 136.20, 129.30, 128.78, 128.28, 127.62, 127.36, 127.03, 126.87, 124.42, 120.20, 119.80, 119.64, 119.02.



2-((9H-fluoren-9-ylidene)methyl)thiazole (**3t**) : yield: 99%, 26 mg, yellow solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.38 (d, *J* = 7.8 Hz, 1H), 8.08 (d, *J* = 3.2 Hz, 1H), 7.76 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 2H), 7.56 (s, 1H), 7.48 (d, *J* = 3.3 Hz, 1H), 7.46 – 7.28 (m, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.33, 144.63, 141.59, 140.06, 139.69, 139.05, 135.94, 129.91, 129.13, 127.69, 127.66, 127.11, 121.02, 120.47, 119.79, 119.49, 115.86.

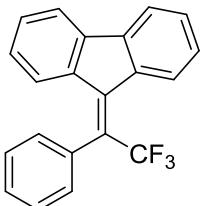


5-((9H-fluoren-9-ylidene)methyl)benzo[d][1,3]dioxole (**3u**) : yield: 50%, 15 mg, yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (dd,  $J = 17.1, 7.7$  Hz, 4H), 7.59 (s, 1H), 7.34 (dt,  $J = 20.7, 7.1$  Hz, 3H), 7.14 – 7.04 (m, 3H), 6.90 (d,  $J = 7.9$  Hz, 1H), 6.04 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.79, 147.53, 141.19, 139.56, 139.01, 136.43, 135.89, 130.59, 128.42, 128.06, 127.13, 126.94, 126.67, 124.37, 123.46, 120.11, 119.73, 119.56, 109.61, 108.52, 101.27; HRMS (EI) m/z calcd for  $\text{C}_{21}\text{H}_{14}\text{O}_2^+$  ( $\text{M}^+$ ) 298.0988, found 299.0992.

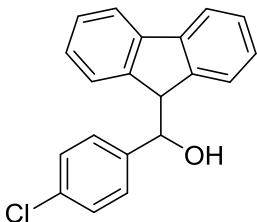


2-((9H-fluoren-9-ylidene)methyl)Ferrocene (**3v**) : yield: 43.3%, 16 mg, red solid; mp 148-149 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J = 7.8$  Hz, 1H), 7.79 (dd,  $J = 6.5, 1.5$  Hz, 1H), 7.74 – 7.71 (m, 2H), 7.47 (s, 1H), 7.37 – 7.30 (m, 3H), 7.18 (td,  $J = 7.7, 1.1$  Hz, 1H), 4.71 (t,  $J = 1.8$  Hz, 2H), 4.46 (t,  $J = 1.8$  Hz, 2H), 4.20 (s, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  140.57, 139.92, 138.22, 136.84, 133.70, 127.69, 127.31, 126.74, 126.47, 126.28, 124.24, 119.64, 119.59, 119.53, 81.35, 70.71, 69.76, 69.51;

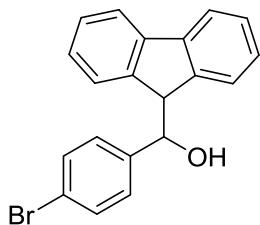
HRMS (ESI) m/z calcd for  $C_{24}H_{18}Fe^+$  ( $M$ )<sup>+</sup> 362.0752, found 362.0757; IR (KBr, thin film): 3085, 3055, 3008, 1622, 1600, 1446, 1433, 1350, 1249, 1105, 1028, 825, 775, 727, 617, 499, 484 cm<sup>-1</sup>.



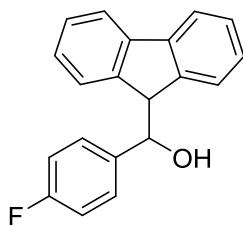
**9-(2,2,2-trifluoro-1-phenylethylidene)-9H-fluorene (3x)** : yield: 78%, 25mg, yellow solid; mp 95-97 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 7.5, 0.6 Hz, 1H), 7.57 (d, *J* = 7.3 Hz, 1H), 7.52 (qd, *J* = 4.3, 1.6 Hz, 3H), 7.45 – 7.28 (m, 4H), 7.21 (td, *J* = 7.5, 0.7 Hz, 1H), 6.79 (td, *J* = 8.1, 1.2 Hz, 1H), 5.88 (d, *J* = 8.0 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 142.27 (q, *J* = 3.2 Hz), 141.85, 141.26, 137.73, 135.39 (q, *J* = 2.9 Hz), 134.80, 130.17, 129.68, 129.63, 129.29, 129.13, 128.84 (q, *J* = 33.2 Hz), 127.71, 127.11, 127.00 (q, *J* = 8.1 Hz), 126.74, 123.43 (q, *J* = 273.0 Hz), 119.46, 119.26. HRMS (EI) m/z calcd for C<sub>21</sub>H<sub>13</sub>F<sub>3</sub> ( $M$ )<sup>+</sup> 322.0968, found 322.0965; IR (KBr thin film): 3053, 2925, 2848, 1598, 1446, 1315, 1276, 1224, 1163, 1136, 1110, 972, 854, 790, 765, 736, 717, 700, 644 cm<sup>-1</sup>.



(4-chlorophenyl)(9H-fluoren-9-yl)methanol (**4a**)<sup>[7]</sup>: yield: 74%, 23 mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 7.7, 2.5 Hz, 2H), 7.39 – 7.31 (m, 2H), 7.31 – 7.15 (m, 8H), 5.13 (dd, *J* = 5.7, 3.6 Hz, 1H), 4.36 (d, *J* = 5.6 Hz, 1H), 1.98 (d, *J* = 3.7 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.05, 142.95, 141.86, 141.77, 140.30, 133.40, 128.20, 128.11, 127.75, 127.74, 126.80, 126.72, 125.96, 125.52, 119.95, 119.87, 75.65, 54.63.

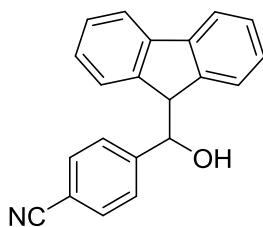


(4-bromophenyl)(9H-fluoren-9-yl)methanol (**4b**)<sup>[7]</sup>: yield: 65%, 23 mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.67 (m, 2H), 7.43 – 7.32 (m, 4H), 7.27 (d, *J* = 7.7 Hz, 1H), 7.24 – 7.19 (m, 3H), 7.16 – 7.11 (m, 2H), 5.13 (dd, *J* = 5.5, 3.7 Hz, 1H), 4.36 (d, *J* = 5.6 Hz, 1H), 1.97 (d, *J* = 3.7 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.00, 142.94, 141.85, 141.78, 140.82, 131.15, 128.46, 127.77, 127.75, 126.82, 126.72, 125.95, 125.50, 121.57, 119.96, 119.89, 75.67, 54.57.

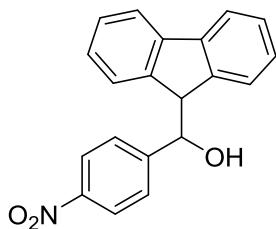


(9H-fluoren-9-yl)(4-fluorophenyl)methanol (**4c**)<sup>[7]</sup>: yield: 80%, 23 mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 7.6, 3.5 Hz, 2H),

7.40 – 7.31 (m, 3H), 7.25 – 7.13 (m, 5H), 6.97 (t,  $J$  = 8.7 Hz, 2H), 5.10 (d,  $J$  = 5.8 Hz, 1H), 4.36 (d,  $J$  = 5.9 Hz, 1H), 1.99 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  162.27 (d,  $J$  = 245.9 Hz), 143.36, 143.04, 141.87, 141.73, 137.63 (d,  $J$  = 3.1 Hz), 128.43, 128.35, 127.70, 127.68, 126.73, 126.70, 126.03, 125.61, 119.87 (d,  $J$  = 8.4 Hz), 114.91 (d,  $J$  = 21.3 Hz), 75.76, 54.78;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.63 (s, 1F).

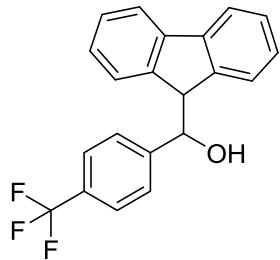


4-((9H-fluoren-9-yl)(hydroxy)methyl)benzonitrile (**4d**)<sup>[7]</sup>: yield: 62% 18 mg, white;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (dd,  $J$  = 7.6, 2.8 Hz, 2H), 7.51 (d,  $J$  = 8.4 Hz, 2H), 7.40 – 7.33 (m, 3H), 7.30 (d,  $J$  = 8.1 Hz, 2H), 7.28 – 7.20 (m, 2H), 7.17 (d,  $J$  = 7.5 Hz, 1H), 5.37 – 5.32 (m, 1H), 4.40 (d,  $J$  = 5.0 Hz, 1H), 2.07 (d,  $J$  = 3.7 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  146.65, 142.50, 142.29, 141.83, 141.80, 131.66, 127.98, 127.96, 127.33, 126.96, 126.82, 125.56, 125.45, 120.10, 120.00, 118.80, 111.34, 75.50, 54.50.

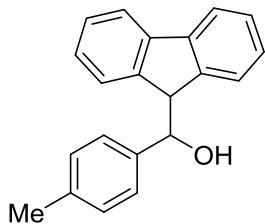


(9H-fluoren-9-yl)(4-nitrophenyl)methanol (**4e**) : yield: 91%, 29 mg, yellow solid; mp 169-171 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J$  =

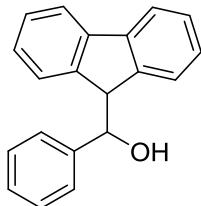
8.8 Hz, 2H), 7.65 (dd,  $J = 7.6$ , 3.8 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.39 – 7.30 (m, 4H), 7.27 (dd,  $J = 7.5$ , 1.1 Hz, 1H), 7.25 – 7.16 (m, 2H), 5.53 – 5.30 (m, 1H), 4.42 (d,  $J = 4.9$  Hz, 1H), 2.14 (d,  $J = 3.6$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  148.55, 147.26, 142.43, 142.15, 141.84, 141.78, 128.03, 128.01, 127.42, 127.01, 126.86, 125.50, 122.99, 120.15, 120.03, 75.35, 54.52; HRMS (ESI) m/z calcd for  $\text{C}_{20}\text{H}_{16}\text{NO}_3^+$  ( $\text{M} + \text{H}$ ) $^+$  318.1125, found 318.1127; IR (KBr, thin film): 3178, 2894, 1502, 1475, 1444, 1294, 1176, 1143, 1078, 1051, 958, 881, 740, 622  $\text{cm}^{-1}$ .



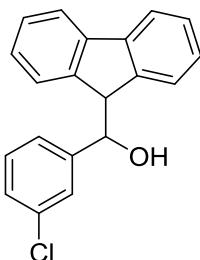
(9H-fluoren-9-yl)(4-(trifluoromethyl)phenyl)methanol (**4f**)<sup>[7]</sup>: yield: 89%, 30 mg, yellow solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 – 7.67 (m, 2H), 7.54 (d,  $J = 8.2$  Hz, 2H), 7.39 – 7.34 (m, 4H), 7.30 – 7.25 (m, 1H), 7.24 – 7.16 (m, 3H), 5.31 – 5.24 (m, 1H), 4.40 (d,  $J = 5.3$  Hz, 1H), 1.98 (d,  $J = 3.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.67, 142.82, 142.61, 141.85, 129.81 (q,  $J = 32.3$  Hz), 127.88, 127.86, 127.01, 126.92, 126.77, 125.82, 125.35, 124.97 (q,  $J = 3.7$  Hz), 124.14 (q,  $J = 270.0$  Hz), 120.03, 119.96, 75.58, 54.59;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.38 (s, 3F).



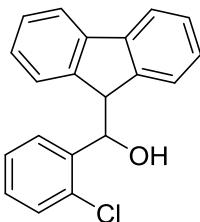
(9H-fluoren-9-yl)(p-tolyl)methanol (**4g**)<sup>[7]</sup> : yield: 40%, 11mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (dd, *J* = 7.5, 4.8 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.24 – 7.11 (m, 6H), 7.06 – 7.02 (m, 1H), 4.99 (d, *J* = 6.3 Hz, 1H), 4.37 (d, *J* = 6.3 Hz, 1H), 2.36 (s, 3H), 1.92 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.79, 143.42, 141.86, 141.73, 139.27, 137.48, 128.91, 127.56, 127.51, 126.75, 126.63, 126.35, 125.60, 119.79, 119.71, 76.26, 54.72, 21.23.



(9H-fluoren-9-yl)(phenyl)methanol (**4h**)<sup>[7]</sup> : yield: 55%, 15mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (dd, *J* = 7.6, 4.5 Hz, 2H), 7.39 – 7.27 (m, 8H), 7.23 – 7.13 (m, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 5.04 (d, *J* = 6.1 Hz, 1H), 4.37 (d, *J* = 6.1 Hz, 1H), 1.97 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.61, 143.32, 142.17, 141.88, 141.76, 128.20, 127.84, 127.64, 127.59, 126.83, 126.69, 126.67, 126.29, 125.55, 119.83, 119.76, 76.33, 54.78.

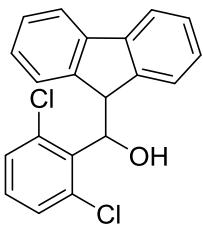


(3-chlorophenyl)(9H-fluoren-9-yl)methanol (**4i**) : yield: 64%, 20 mg white solid; mp 159-161°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 – 7.68 (m, 2H), 7.39 – 7.31 (m, 3H), 7.28 – 7.26 (m, 1H), 7.25 – 7.14 (m, 6H), 5.12 (dd, *J* = 5.4, 4.0 Hz, 1H), 4.36 (d, *J* = 5.6 Hz, 1H), 1.94 (d, *J* = 3.9 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.04, 142.92, 142.88, 141.86, 141.82, 134.14, 129.35, 127.87, 127.82, 127.80, 126.94, 126.87, 126.76, 126.03, 125.37, 124.90, 119.94, 119.89, 75.56, 54.61; HRMS (ESI) m/z calcd for C<sub>20</sub>H<sub>14</sub>Cl<sup>+</sup> (M - OH)<sup>+</sup> 289.0779, found 289.0773; IR (KBr thin film): 3450, 3060, 3024, 1571, 1473, 1442, 1386, 1294, 1193, 1078, 794, 750, 744, 738, 692, 624, 559 cm<sup>-1</sup>.

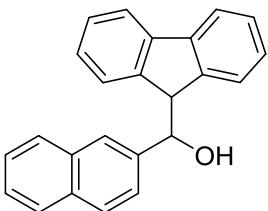


(2-chlorophenyl)(9H-fluoren-9-yl)methanol (**4j**) : yield: 78%, 24 mg, white solid; mp 124-125 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.76 (dd, *J* = 7.9, 2.2 Hz, 2H), 7.53 (dd, *J* = 7.2, 2.1 Hz, 1H), 7.48 – 7.26 (m, 7H), 7.14 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 5.66 (s, 1H), 4.56 (d, *J* = 4.1 Hz, 1H), 1.70 (s, 1H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.93, 142.31,

142.25, 141.91, 139.73, 132.14, 129.54, 128.91, 128.64, 127.84, 127.73, 127.26, 126.79, 126.47, 126.45, 124.46, 119.97, 119.96, 72.47, 52.48; HRMS (ESI) m/z calcd for  $C_{20}H_{14}Cl^+$  ( $M - OH$ )<sup>+</sup> 289.0779, found 289.0774; IR (KBr thin film): 3548, 3446, 3064, 2898, 1473, 1446, 1390, 1307, 1234, 1182, 1033, 771, 748, 696, 678  $\text{cm}^{-1}$ .

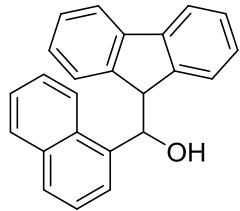


(2,6-dichlorophenyl)(9H-fluoren-9-yl)methanol (**4k**): yield: 89%, 30 mg, white solid; mp 58-59 °C; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 7.2$  Hz, 1H), 7.79 (d,  $J = 7.5$  Hz, 1H), 7.73 (d,  $J = 7.6$  Hz, 1H), 7.44 (t,  $J = 7.2$  Hz, 1H), 7.40 – 7.23 (m, 5H), 6.95 (td,  $J = 7.6, 1.1$  Hz, 1H), 6.25 – 6.14 (m, 1H), 5.08 (t,  $J = 9.5$  Hz, 1H), 4.87 (d,  $J = 10.1$  Hz, 1H), 3.27 (d,  $J = 9.2$  Hz, 1H); <sup>13</sup>C NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  145.48, 141.82, 141.81, 141.19, 136.74, 129.56, 129.43, 127.72, 127.50, 126.96, 126.91, 126.51, 125.10, 119.85, 119.73, 74.55, 51.47; HRMS (EI) m/z calcd for  $C_{20}H_{14}Cl_2O^+$  ( $M$ )<sup>+</sup> 340.0416, found 340.0412.



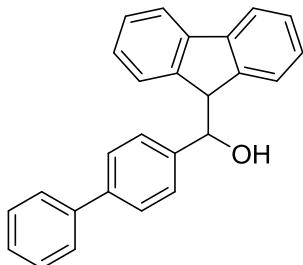
(9H-fluoren-9-yl)(naphthalen-2-yl)methanol (**4l**) : yield: 59%, 19mg; white solid; mp 133-134 °C; <sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (dd,  $J =$

9.0, 4.9 Hz, 2H), 7.80 – 7.75 (m, 1H), 7.75 – 7.66 (m, 3H), 7.53 (dd,  $J$  = 8.5, 1.7 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.34 (q,  $J$  = 7.0 Hz, 2H), 7.27 (d,  $J$  = 7.4 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.08 (d,  $J$  = 7.3 Hz, 1H), 5.23 (d,  $J$  = 5.9 Hz, 1H), 4.50 (d,  $J$  = 5.9 Hz, 1H), 2.01 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.43, 143.34, 141.90, 141.81, 139.63, 133.09, 133.04, 128.20, 128.05, 127.72, 127.68, 127.64, 126.78, 126.70, 126.34, 126.17, 126.01, 125.83, 125.44, 124.72, 119.87, 119.82, 76.35, 54.56; HRMS (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{17}^+$  ( $\text{M}-\text{OH}$ ) $^+$  305.1325, found 305.1328; IR (KBr thin film): 3450, 3057, 2921, 2854, 1448, 1367, 1296, 1271, 1012, 825, 746, 557, 478, 428  $\text{cm}^{-1}$ .

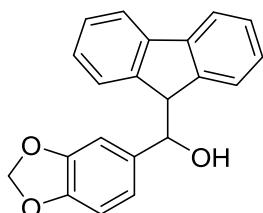


(9H-fluoren-9-yl)(naphthalen-1-yl)methanol (**4m**) : yield: 73%, 23mg, white solid; mp 137-138 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 – 8.23 (m, 1H), 7.99 – 7.93 (m, 1H), 7.90 (d,  $J$  = 8.0 Hz, 1H), 7.76 (d,  $J$  = 7.6 Hz, 2H), 7.62 – 7.49 (m, 4H), 7.36 (td,  $J$  = 7.5, 4.0 Hz, 2H), 7.20 – 7.08 (m, 3H), 6.96 (d,  $J$  = 7.5 Hz, 1H), 5.84 (d,  $J$  = 5.2 Hz, 1H), 4.62 (d,  $J$  = 5.2 Hz, 1H), 1.86 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.88, 143.01, 142.03, 141.93, 137.76, 133.90, 130.40, 129.22, 128.54, 127.73, 127.68, 126.96, 126.86, 126.50, 126.24, 125.67, 125.25, 124.90, 124.75, 123.06, 119.91, 119.85, 73.27, 53.69. HRMS (ESI) m/z calcd for  $\text{C}_{24}\text{H}_{17}^+$  ( $\text{M} +$

$\text{H}^+$  305.1325, found 305.1325; IR (KBr thin film): 3556, 3055, 3012, 2921, 1450, 1082, 808, 783, 740, 683  $\text{cm}^{-1}$ .

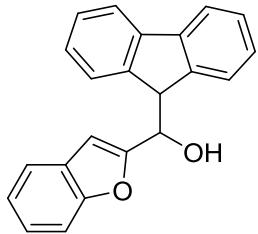


[1,1'-biphenyl]-4-yl(9H-fluoren-9-yl)methanol (**4n**) : yield: 83%, 29mg, white solid; mp 153-154 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 – 7.68 (m, 2H), 7.65 – 7.59 (m, 2H), 7.56 (d,  $J$  = 8.3 Hz, 2H), 7.44 (t,  $J$  = 7.5 Hz, 2H), 7.41 – 7.31 (m, 6H), 7.26 – 7.11 (m, 3H), 5.11 (d,  $J$  = 5.8 Hz, 1H), 4.42 (d,  $J$  = 6.0 Hz, 1H), 1.99 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.51, 143.29, 141.90, 141.79, 141.21, 140.65, 140.52, 128.81, 127.67, 127.63, 127.38, 127.26, 127.05, 126.83, 126.74, 126.69, 126.28, 125.54, 119.87, 119.81, 76.11, 54.73; HRMS (ESI) m/z calcd for  $\text{C}_{26}\text{H}_{19}^+$  ( $\text{M}-\text{OH}$ )<sup>+</sup> 331.1481, found 331.1484; IR (KBr thin film): 3462, 3057, 3028, 2925, 1487, 1444, 1035, 1004, 846, 746, 696, 555  $\text{cm}^{-1}$ .

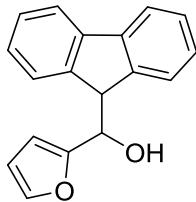


benzo[d][1,3]dioxol-5-yl(9H-fluoren-9-yl)methanol (**4o**) : yield: 40%, 13 mg white solid; mp 149-150 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.71 (dd,  $J$  = 7.5, 5.0 Hz, 2H), 7.44 (d,  $J$  = 6.9 Hz, 1H), 7.36 (dt,  $J$  = 10.0, 7.4 Hz,

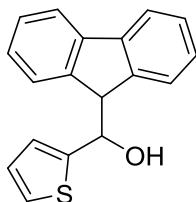
2H), 7.24 (td,  $J = 7.5, 1.1$  Hz, 1H), 7.18 (td,  $J = 7.5, 1.1$  Hz, 1H), 7.06 (d,  $J = 7.0$  Hz, 1H), 6.87 (s, 1H), 6.76 – 6.70 (m, 2H), 5.99 – 5.94 (m, 2H), 4.92 (d,  $J = 6.3$  Hz, 1H), 4.33 (d,  $J = 6.4$  Hz, 1H), 1.95 (d,  $J = 1.9$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  147.60, 147.09, 143.71, 143.15, 141.82, 141.65, 136.28, 127.61, 127.57, 126.68, 126.66, 126.28, 125.65, 120.40, 119.81, 119.73, 107.81, 107.27, 101.04, 76.29, 54.74; HRMS (EI) m/z calcd for  $\text{C}_{21}\text{H}_{16}\text{O}_3^+$  ( $\text{M}^+$ ) 316.1094, found 316.1091.



benzofuran-2-yl(9H-fluoren-9-yl)methanol (**4p**) : yield: 95% 30 mg, white solid; mp 141–143 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 7.6$  Hz, 2H), 7.57 – 7.51 (m, 2H), 7.41 – 7.14 (m, 8H), 6.52 (s, 1H), 5.23 (t,  $J = 4.9$  Hz, 1H), 4.67 (d,  $J = 5.5$  Hz, 1H), 2.01 (d,  $J = 5.5$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  157.60, 154.71, 143.03, 142.29, 142.05, 141.85, 128.19, 127.94, 127.86, 127.17, 126.97, 126.02, 124.82, 124.34, 123.02, 121.31, 120.00, 119.96, 111.44, 104.26, 70.71, 52.08; HRMS (ESI) m/z calcd for  $\text{C}_{22}\text{H}_{15}\text{O}^+$  ( $\text{M-OH}^+$ ) 295.1117, found 295.1113, IR (KBr, thin film): 3390, 3064, 3035, 2920, 1450, 1257, 1170, 1047, 1004, 939, 817, 738, 565  $\text{cm}^{-1}$ .

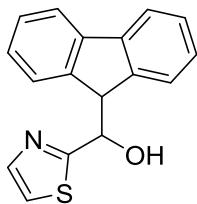


(9H-fluoren-9-yl)(furan-2-yl)methanol (**4q**)<sup>[7]</sup>: yield: 47%, 12 mg, white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.74 (dd, *J* = 7.6, 3.1 Hz, 2H), 7.48 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.26 – 7.19 (m, 2H), 7.07 – 7.03 (m, 1H), 6.38 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.12 (d, *J* = 3.2 Hz, 1H), 5.02 (t, *J* = 5.3 Hz, 1H), 4.55 (d, *J* = 6.3 Hz, 1H), 1.97 (d, *J* = 5.0 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.94, 143.14, 142.99, 141.83, 141.79, 141.75, 127.75, 127.68, 126.95, 126.88, 126.05, 124.95, 119.85, 119.78, 110.61, 107.51, 70.42, 52.51.



(9H-fluoren-9-yl)(thiophen-2-yl)methanol (**4r**) : yield: 45%, 13 mg white solid; mp 117-118 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.42 (m, 1H), 7.40 – 7.33 (m, 2H), 7.28 – 7.21 (m, 3H), 7.20 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.82 (dt, *J* = 3.5, 1.0 Hz, 1H), 5.42 – 5.36 (m, 1H), 4.44 (d, *J* = 5.9 Hz, 1H), 2.18 (d, *J* = 4.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.77, 143.01, 142.99, 141.91, 141.81, 127.76, 127.74, 126.84, 126.83, 126.37, 125.87, 125.71, 124.95, 124.85, 119.85, 119.73, 72.93, 54.88; HRMS (ESI) m/z calcd for

$C_{18}H_{13}S^+$  ( $M + H$ )<sup>+</sup> 261.0733, found 261.0732; IR (KBr thin film): 3544, 3066, 2904, 1444, 1236, 1029, 854, 752, 744, 694, 545 cm<sup>-1</sup>.



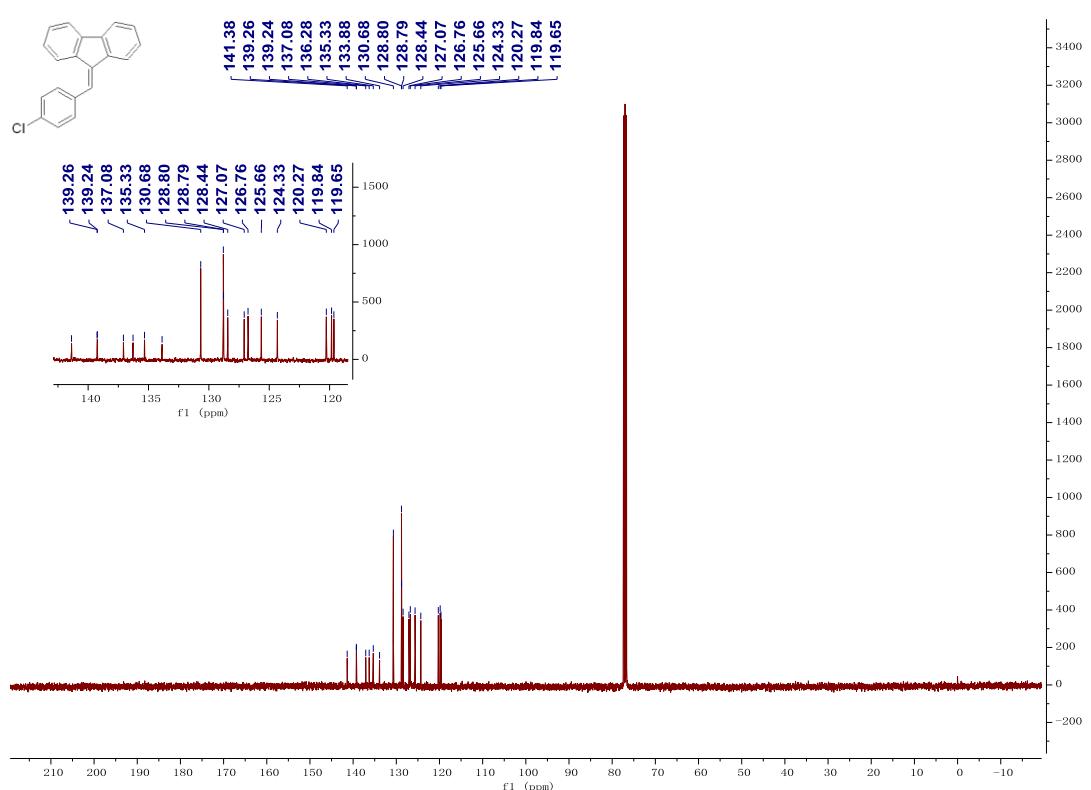
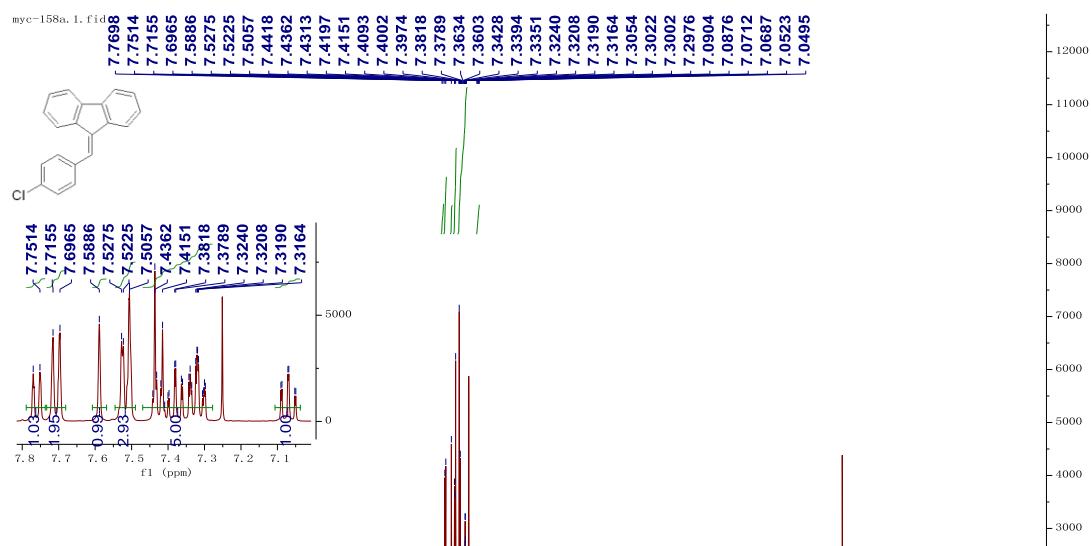
(9H-fluoren-9-yl)(thiazol-2-yl)methanol (**4s**) : yield: 88%, 25 mg, white solid; mp 132-133 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 – 7.67 (m, 3H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.37 (td, *J* = 7.4, 3.0 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 1H), 7.24 – 7.15 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.71 (d, *J* = 3.8 Hz, 1H), 4.80 (d, *J* = 3.6 Hz, 1H), 3.08 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.38, 143.00, 142.49, 141.87, 141.36, 128.09, 127.89, 127.24, 127.01, 125.36, 125.03, 120.06, 119.92, 119.51, 73.82, 53.57; HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>14</sub>NOS<sup>+</sup> ( $M + H$ )<sup>+</sup> 280.0791, found 280.0790; IR (KBr thin film): 3178, 2894, 1502, 1475, 1444, 1294, 1176, 1143, 1078, 1051, 958, 881, 740, 622 cm<sup>-1</sup>.

### 3. References

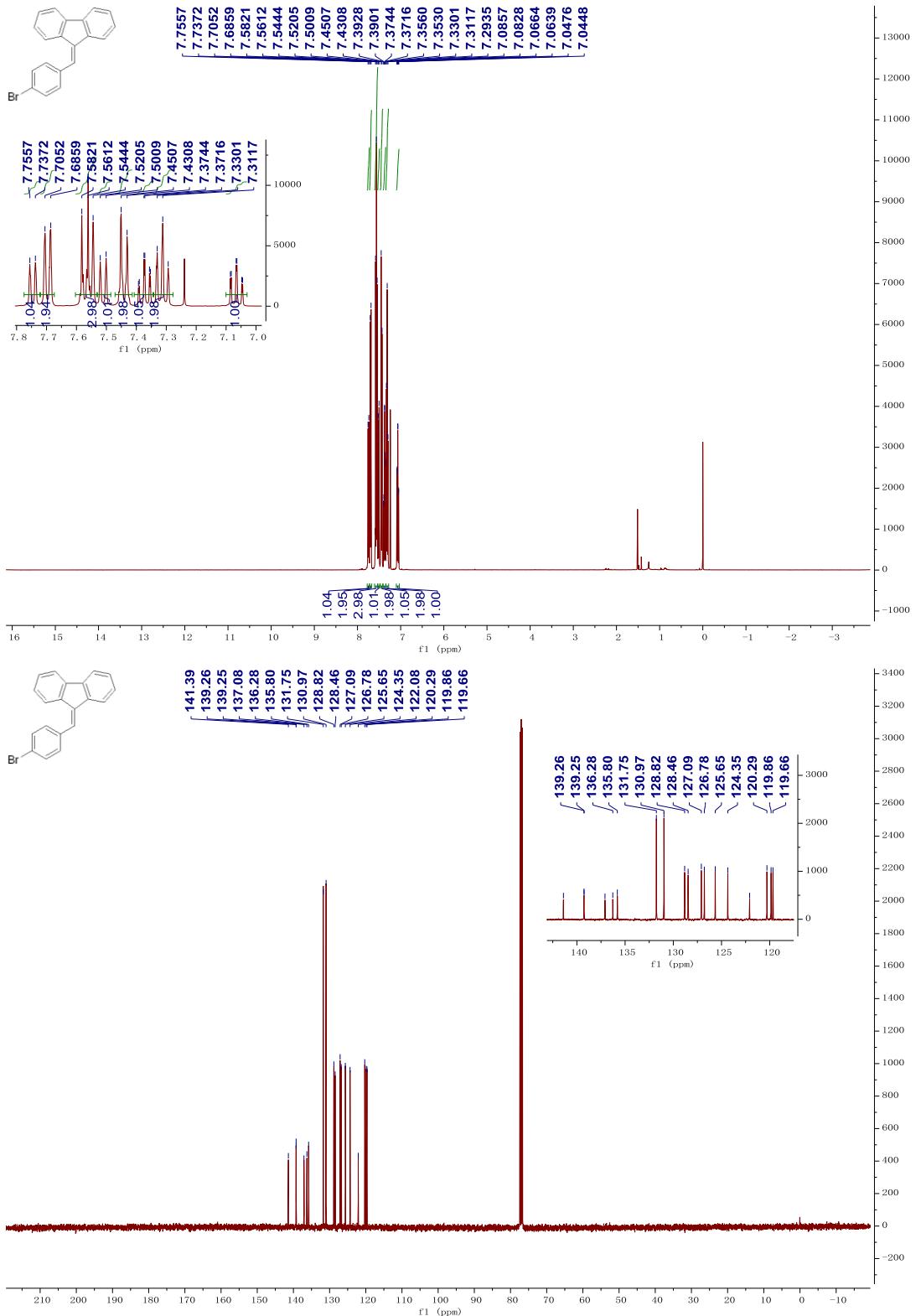
- [1] M. Paraja, C. Valdés, *Organic Letters* **2017**, *19*, 2034-2037.
- [2] T. Amaya, H. Fujimoto, *Tetrahedron Letters* **2018**, *59*, 2657-2660.
- [3] C. Do, J. Hatfield, S. Patel, D. Vasudevan, C. Tirla, N. S. Mills, *The Journal of Organic Chemistry* **2011**, *76*, 181-187.
- [4] N. Chernyak, V. Gevorgyan, *Advanced Synthesis & Catalysis* **2009**, *351*, 1101-1114.
- [5] D. Casarini, L. Lunazzi, A. Mazzanti, *The Journal of Organic Chemistry* **2008**, *73*, 2811-2818.
- [6] M. Michalík, A. A. Eckstein, E. Kozma, F. Galeotti, V. Lukeš, P. Hrdlovič, D. Végh, *Monatshefte für Chemie - Chemical Monthly* **2016**, *147*, 2103-2112.
- [7] A. G. Giuglio-Tonolo, T. Terme, P. Vanelle, *Molecules* **2016**, *21*, 1408.

#### 4. Copies of $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

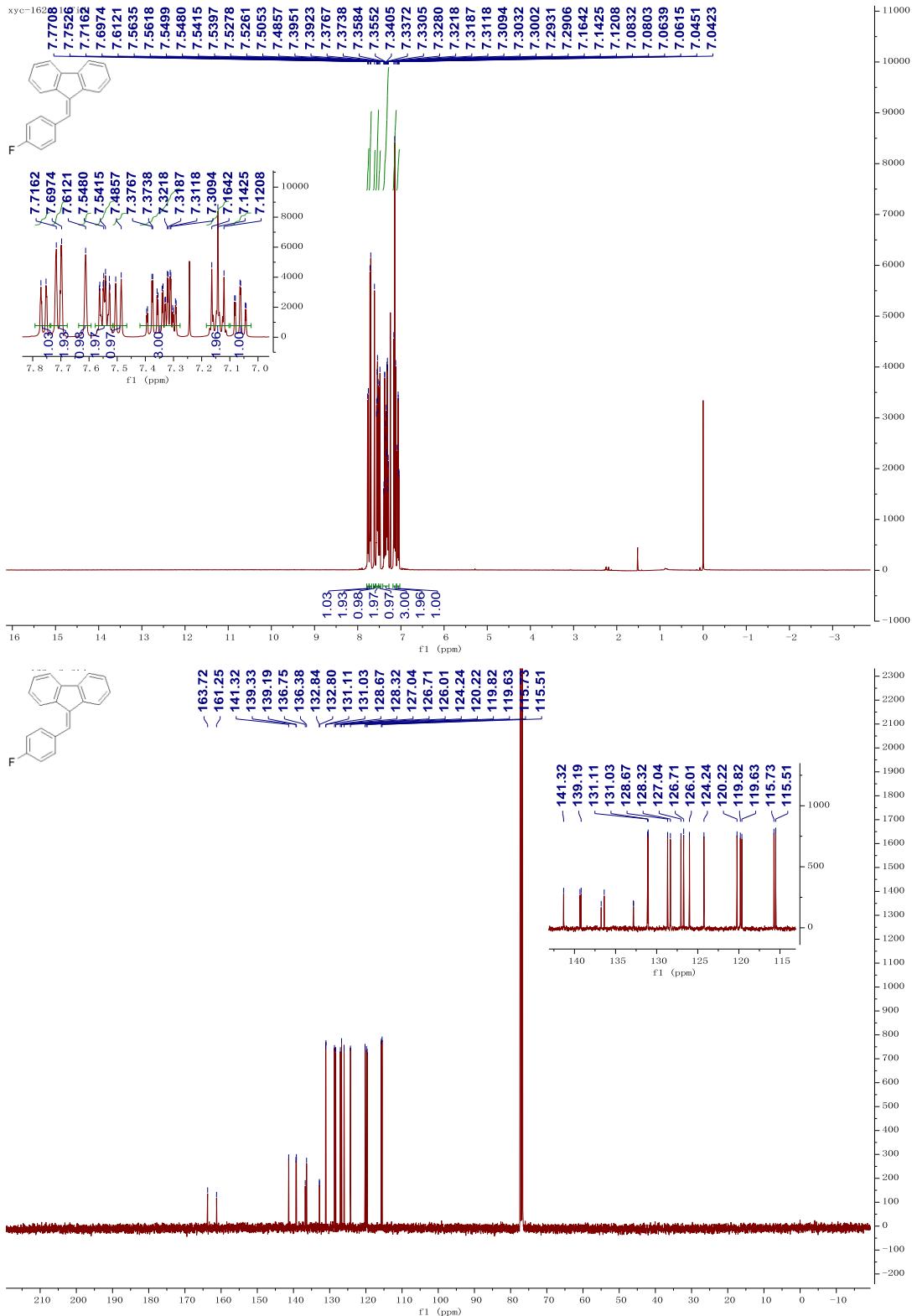
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3a**

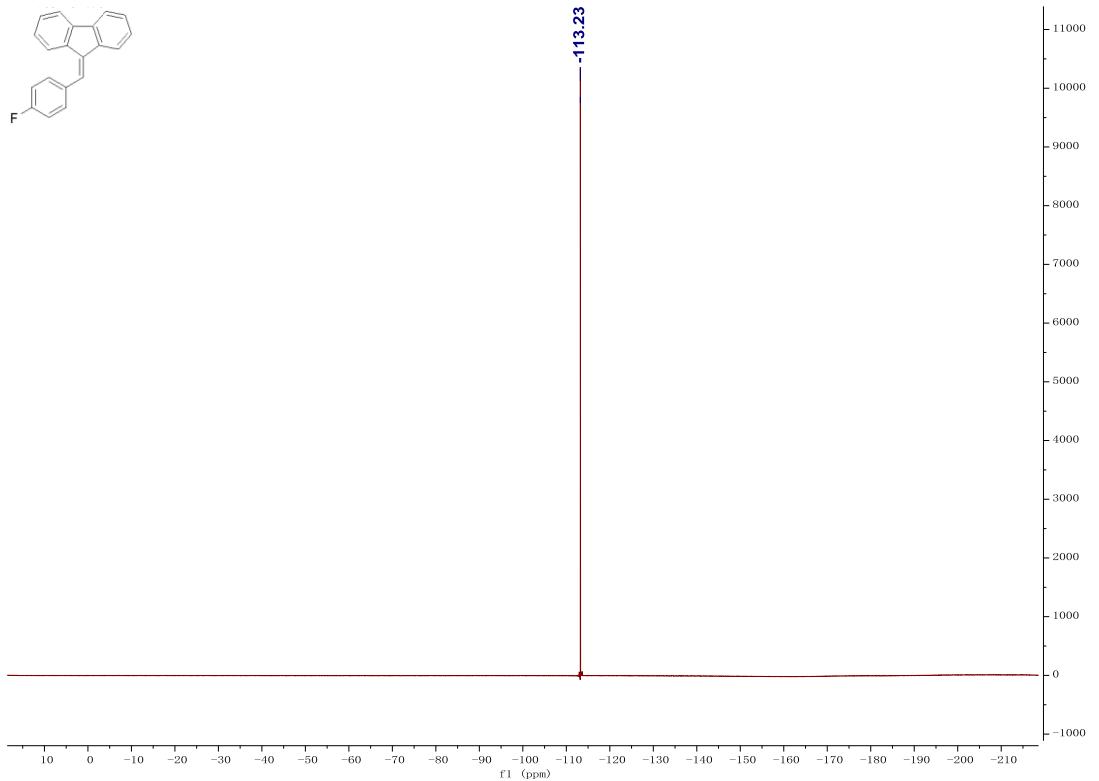


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3b**

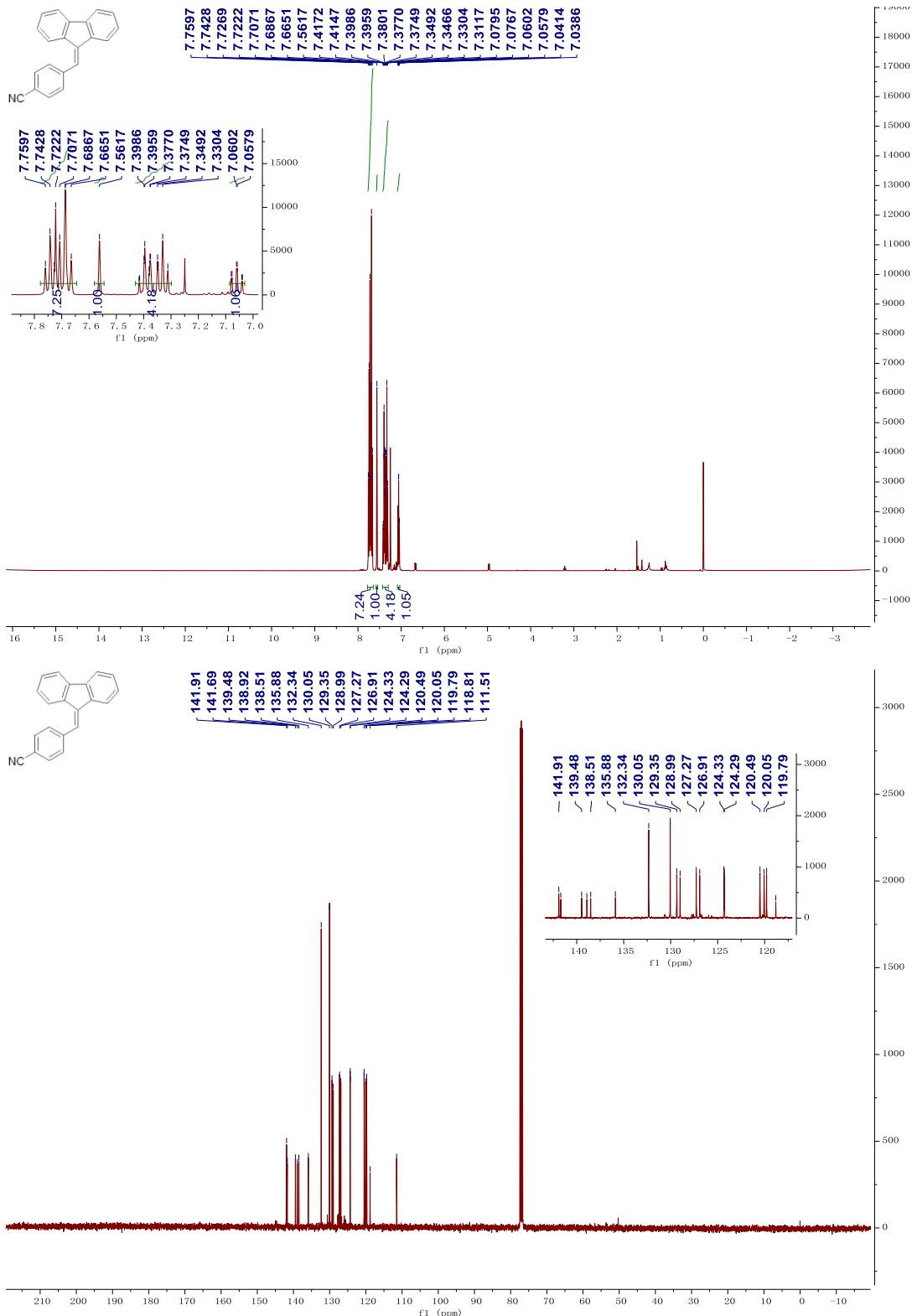


<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR spectrum of **3c**

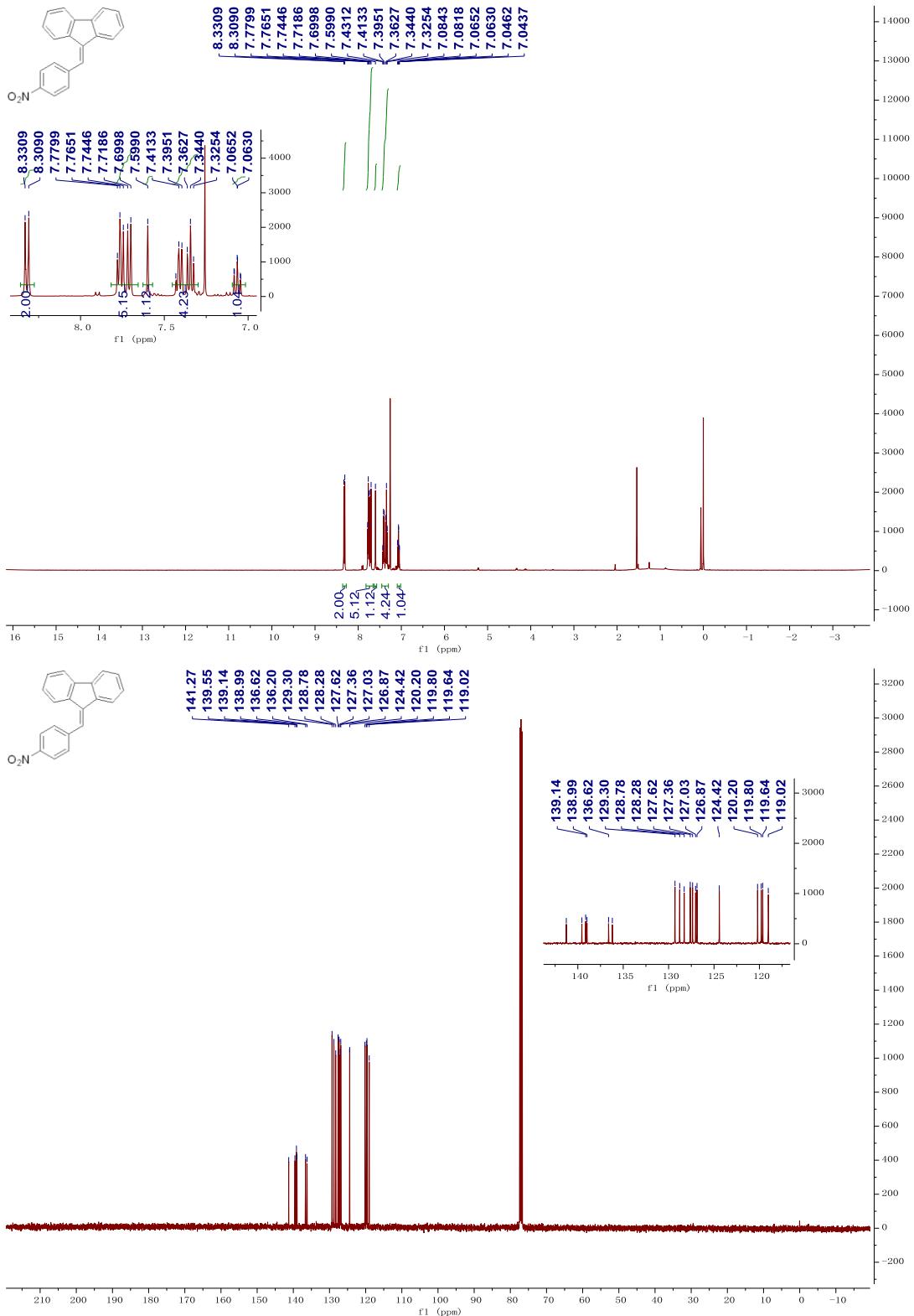




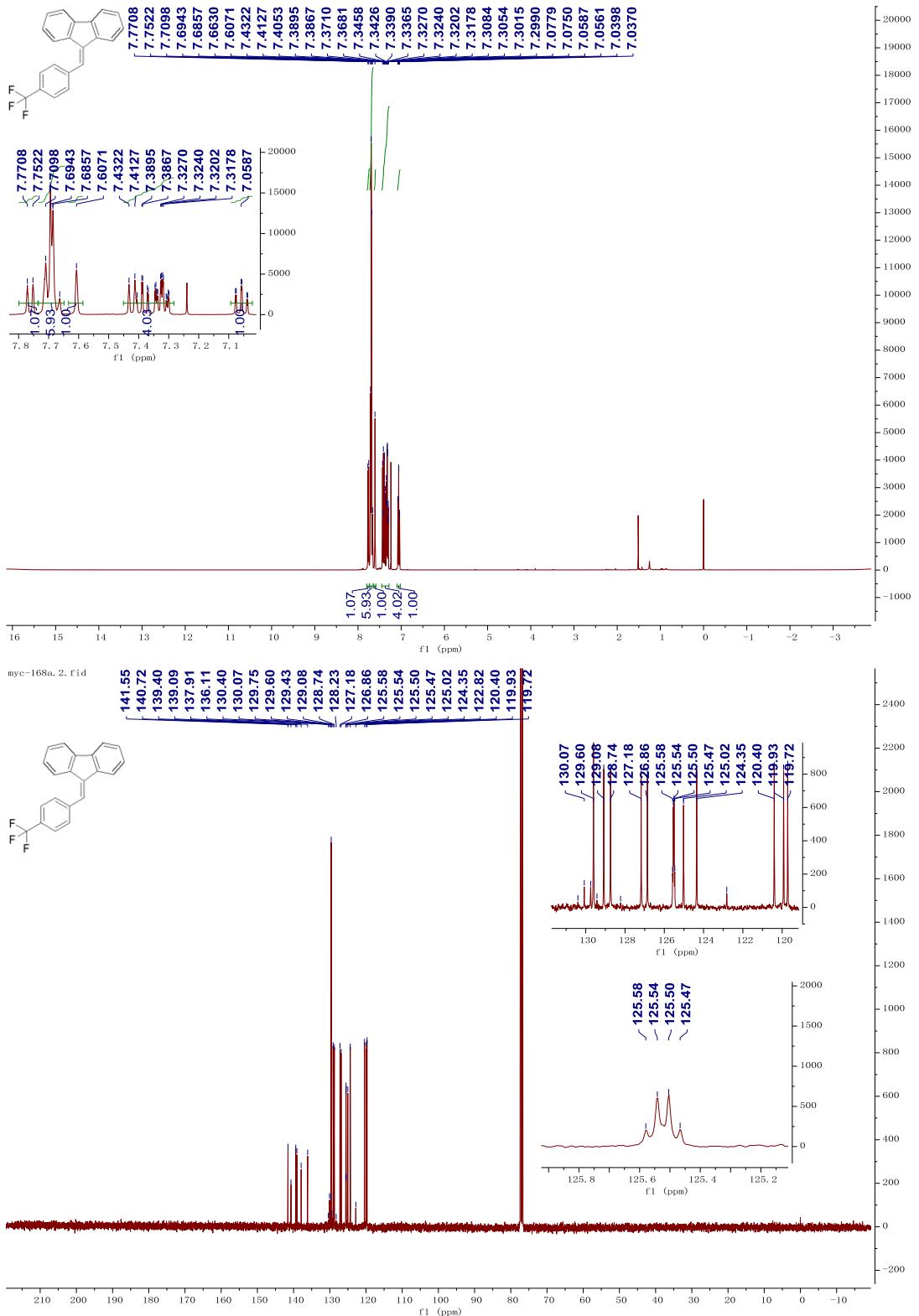
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3d**

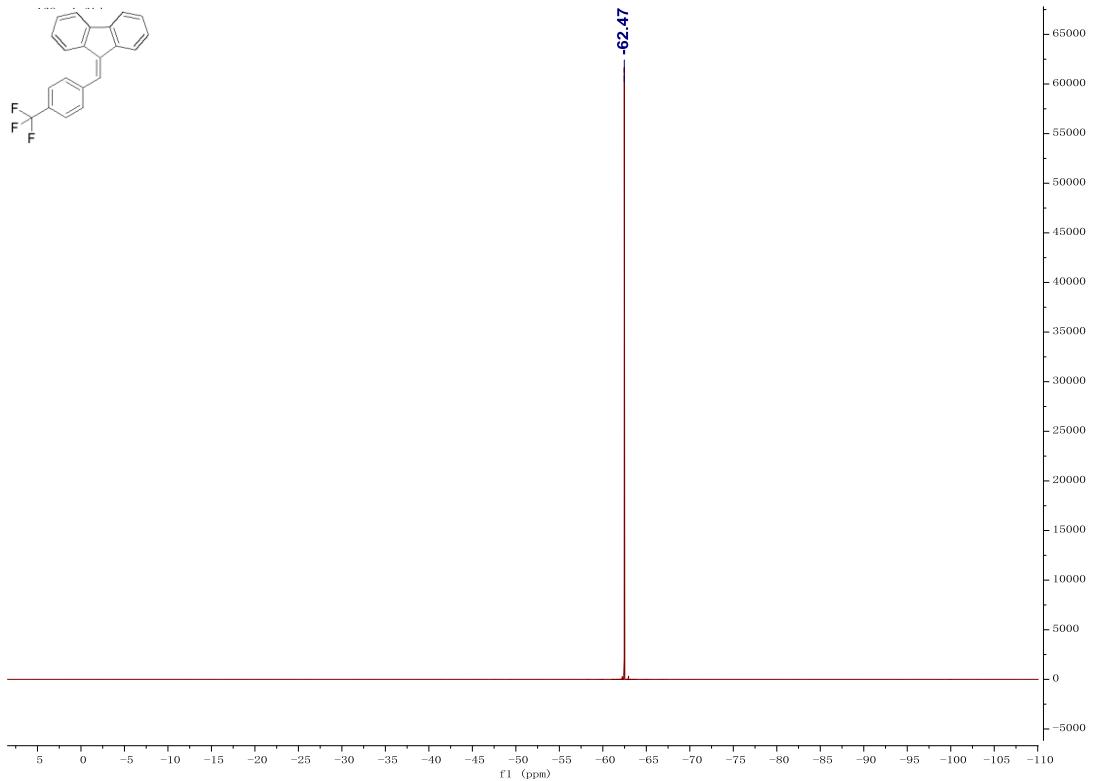


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3e**



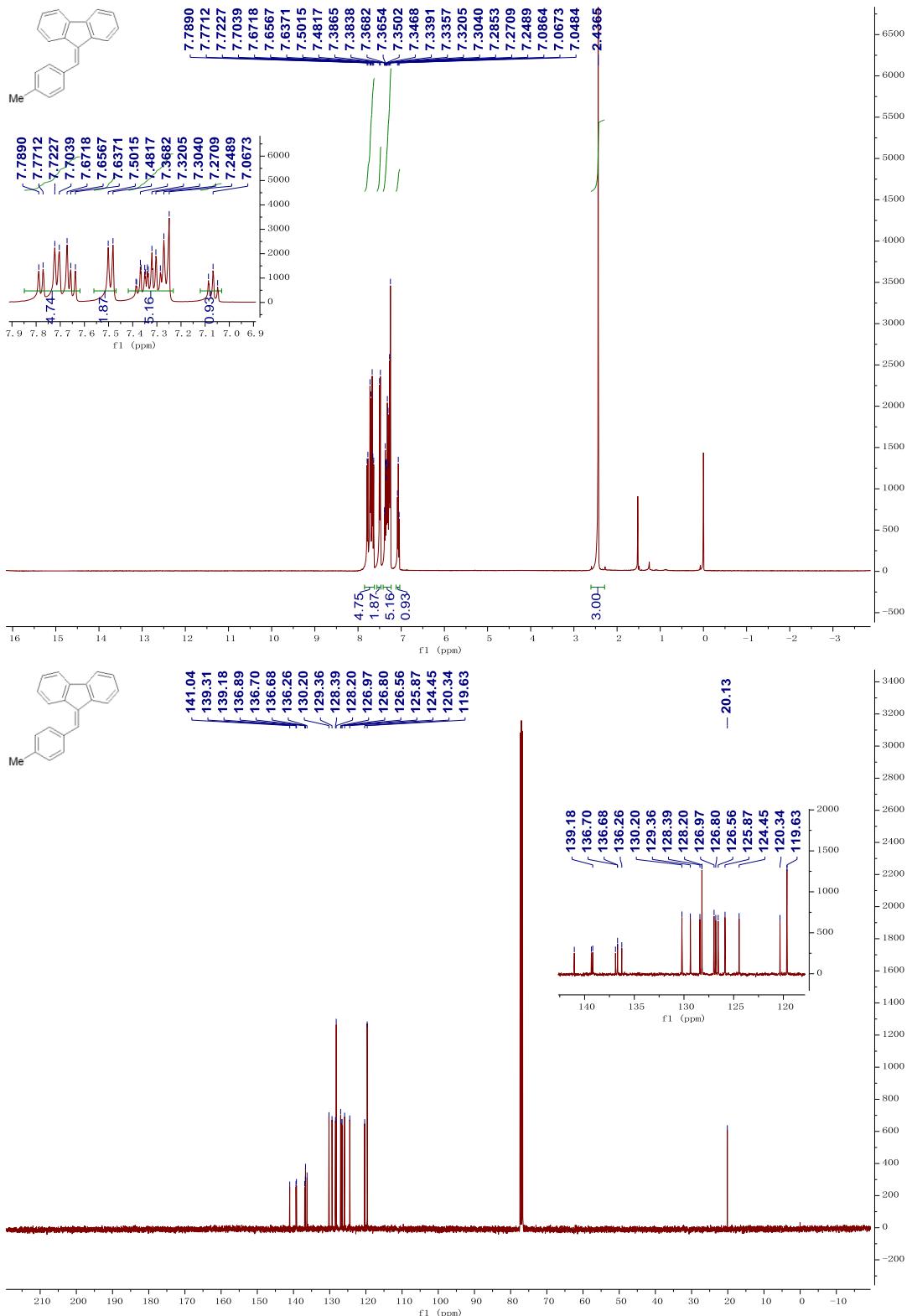
<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>FNMR spectrum of **3f**



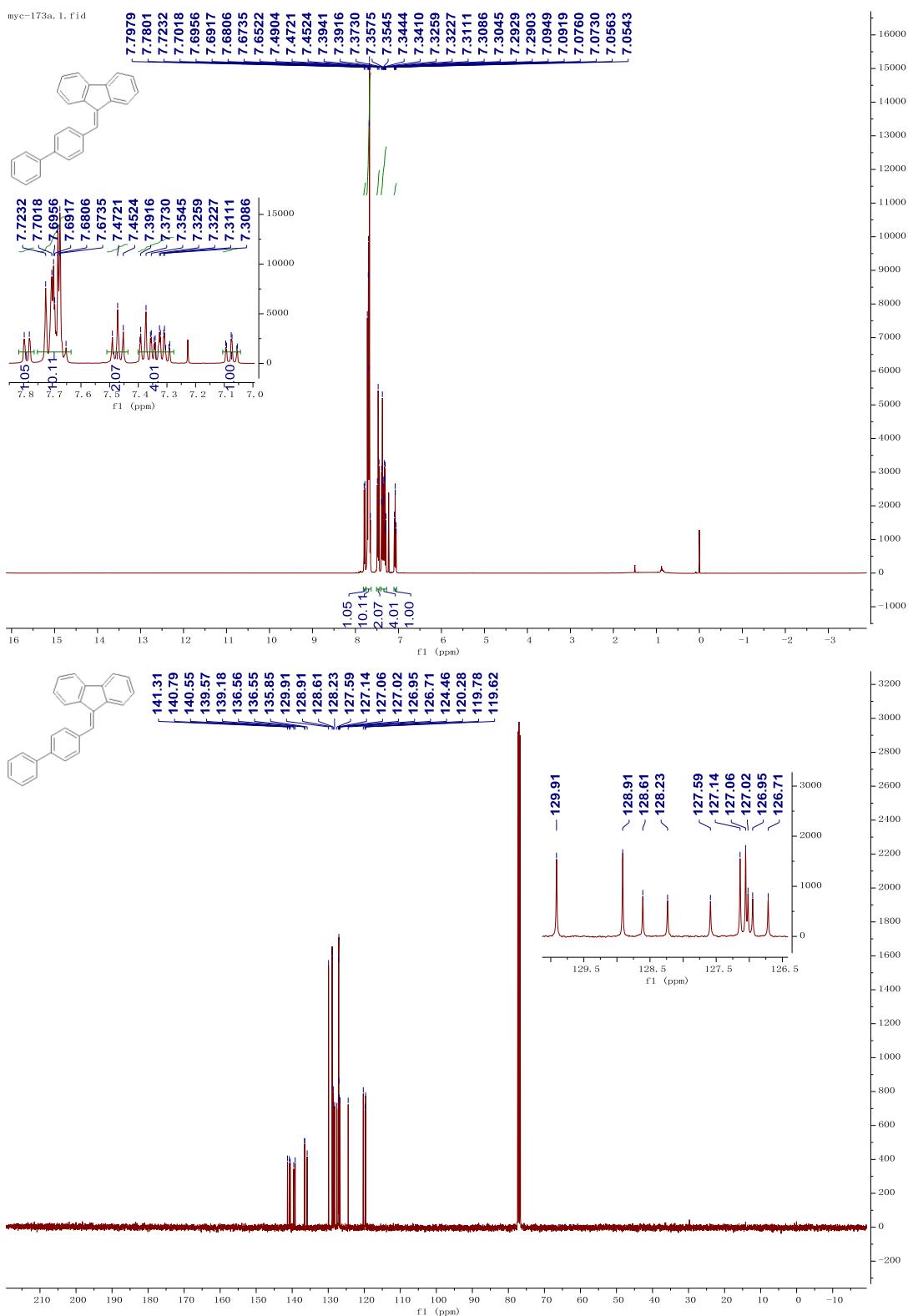


**S34**

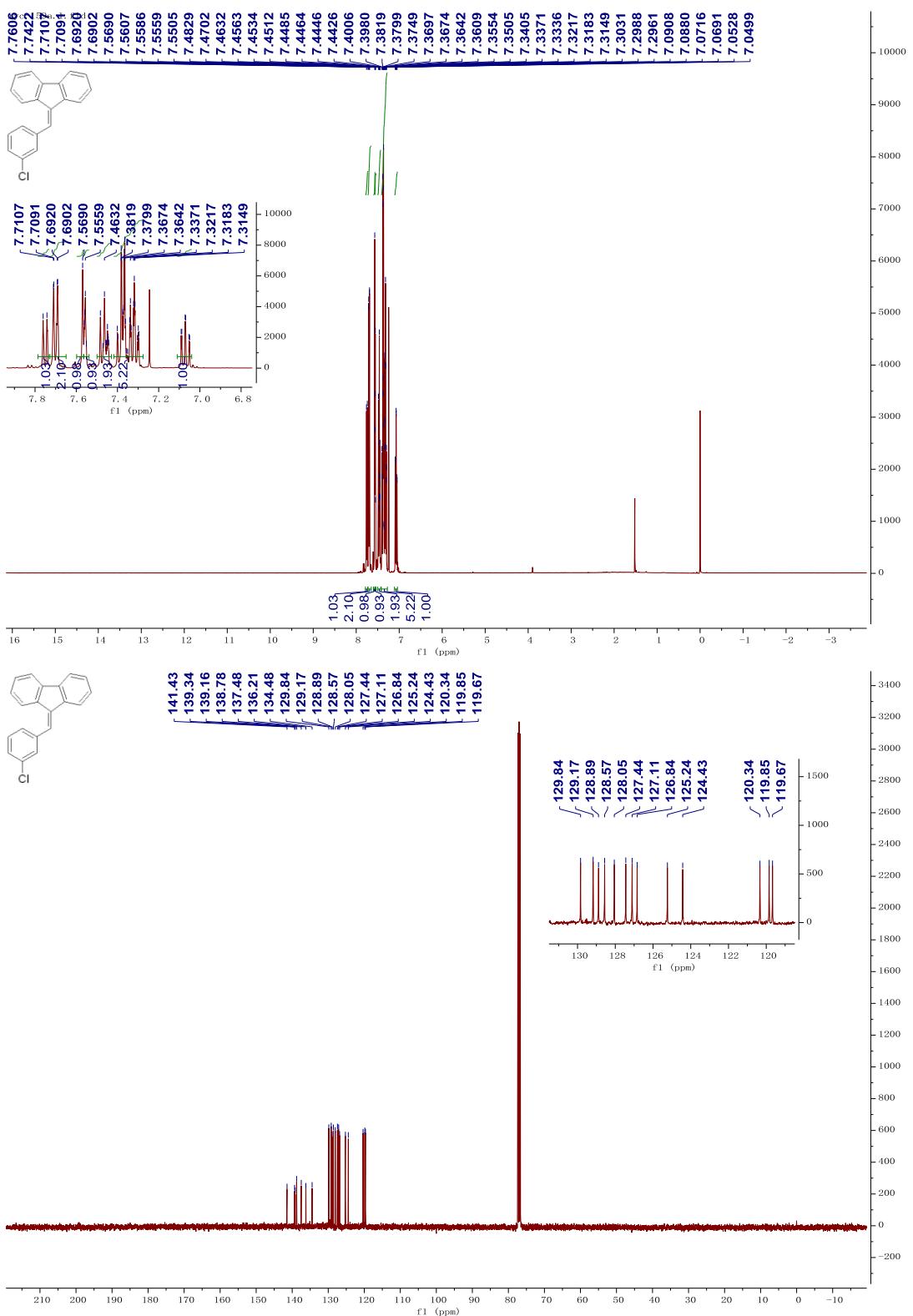
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3g**



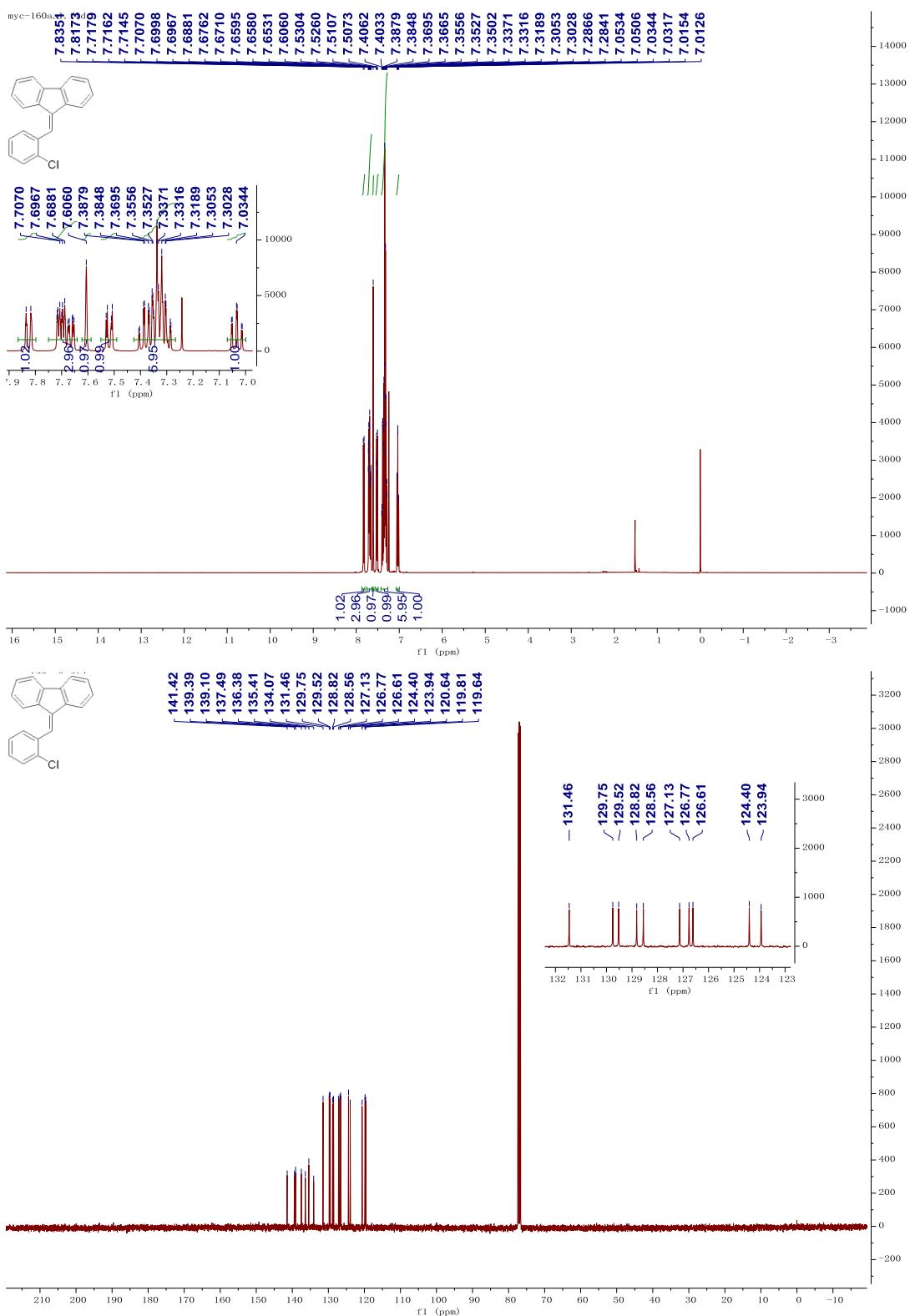
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3h**



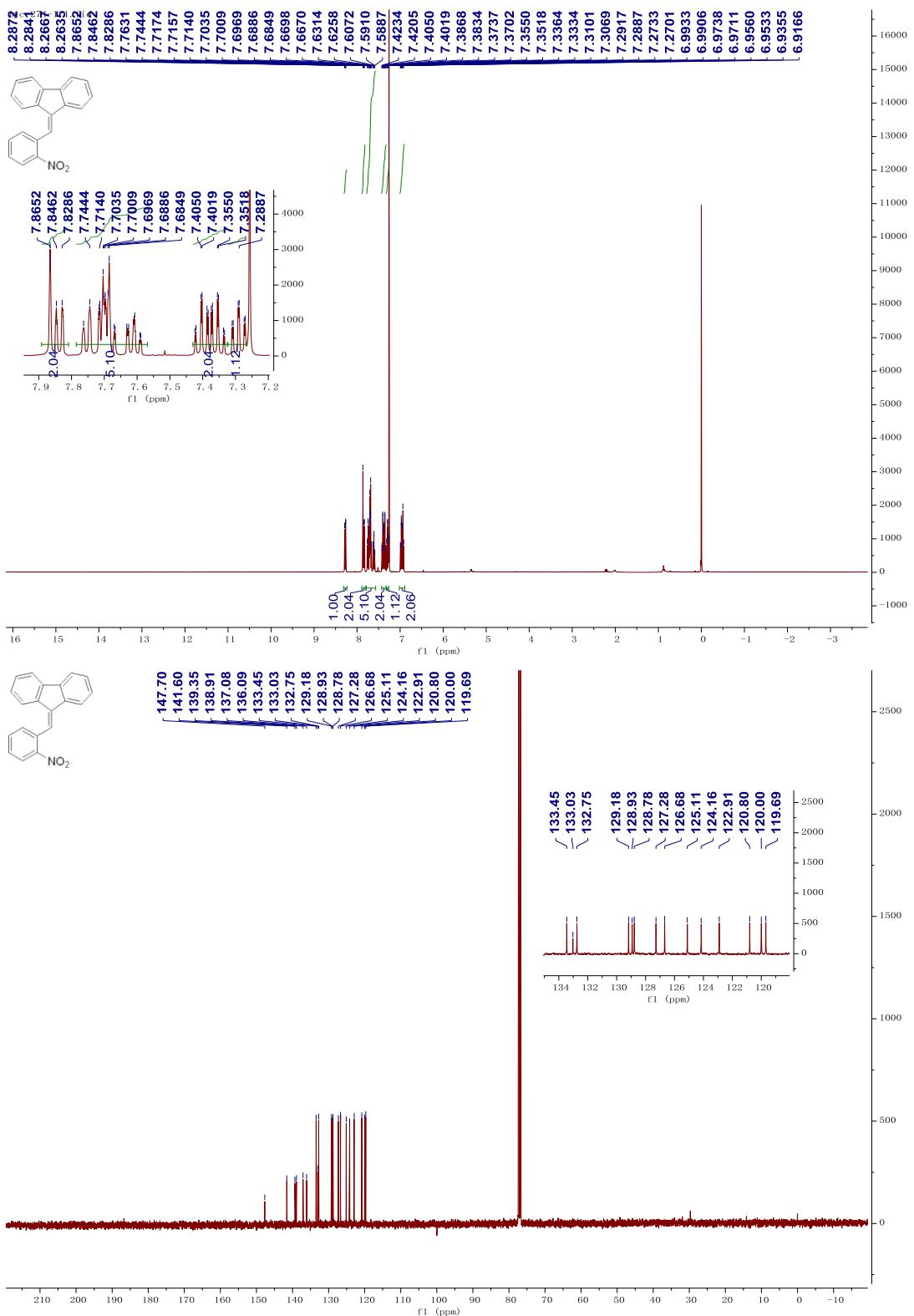
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3i**



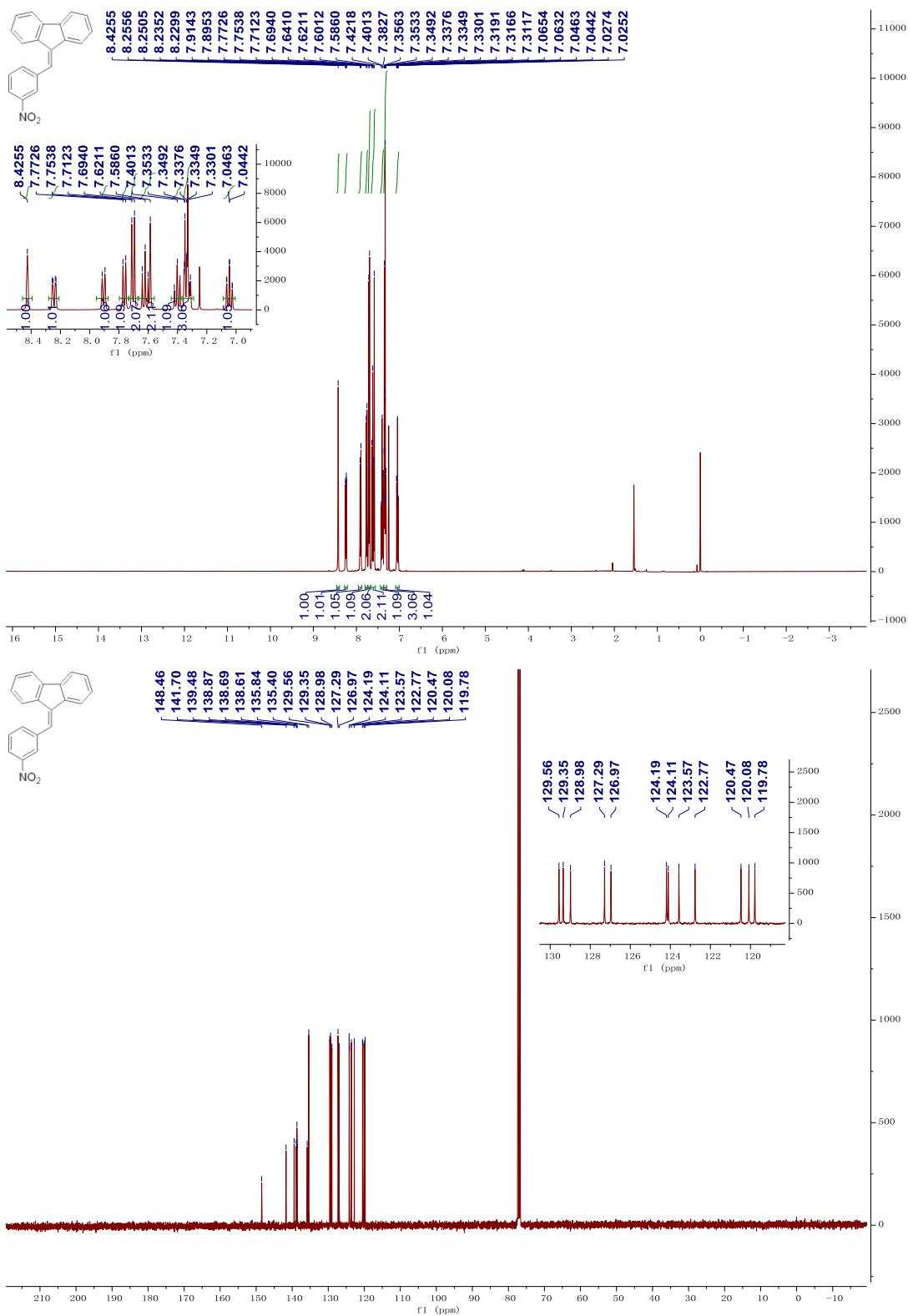
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3j**



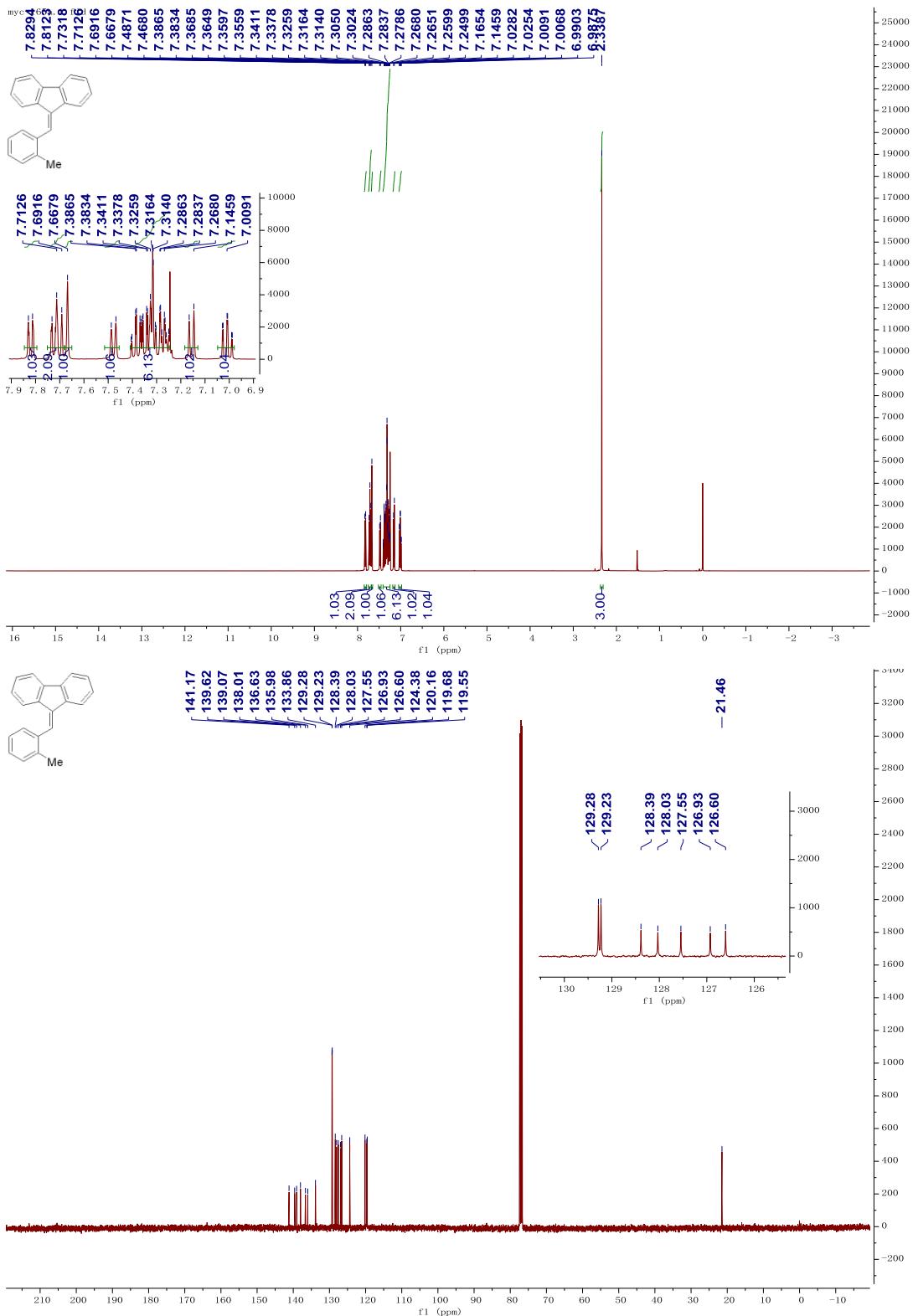
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3k**



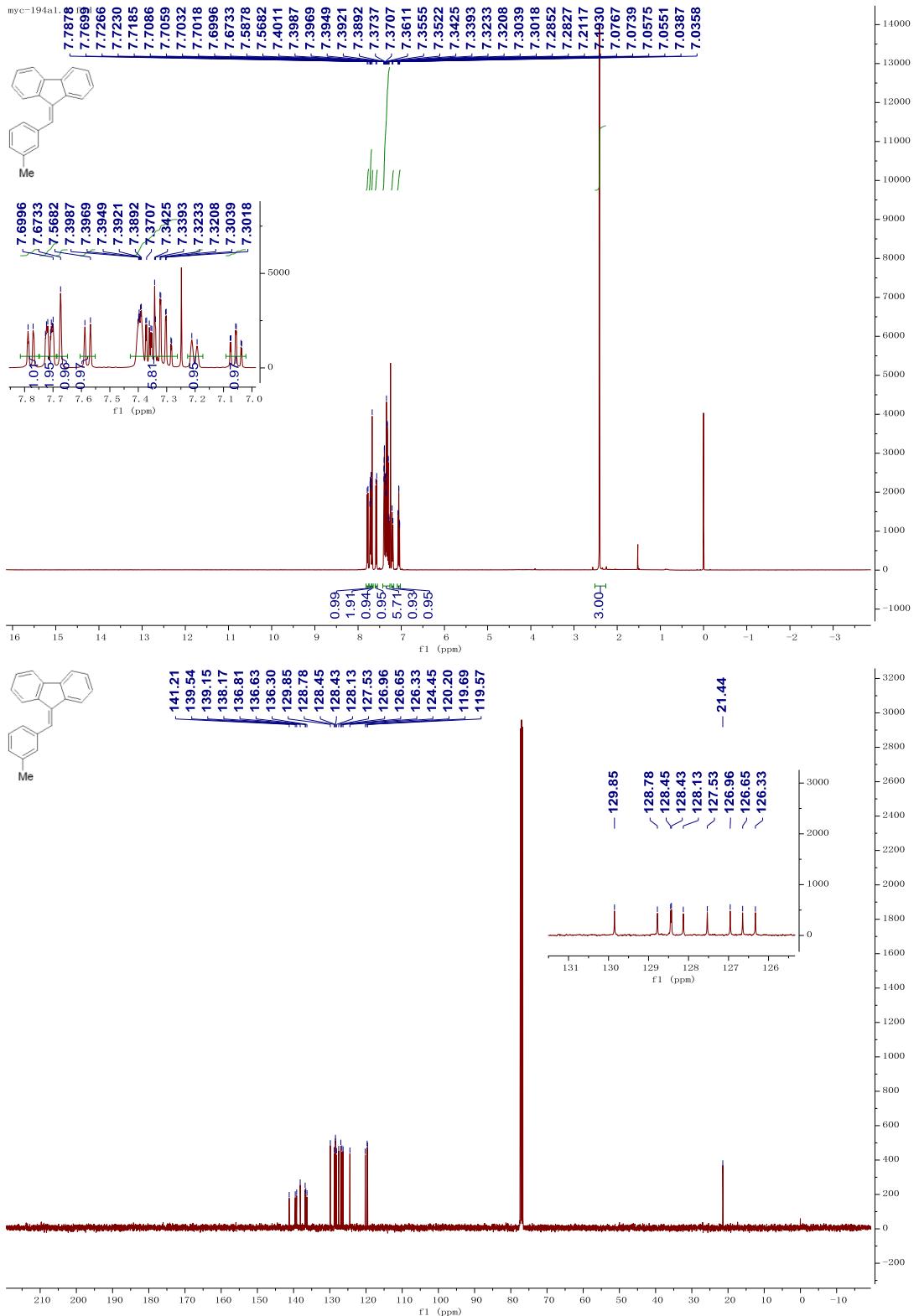
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3l**



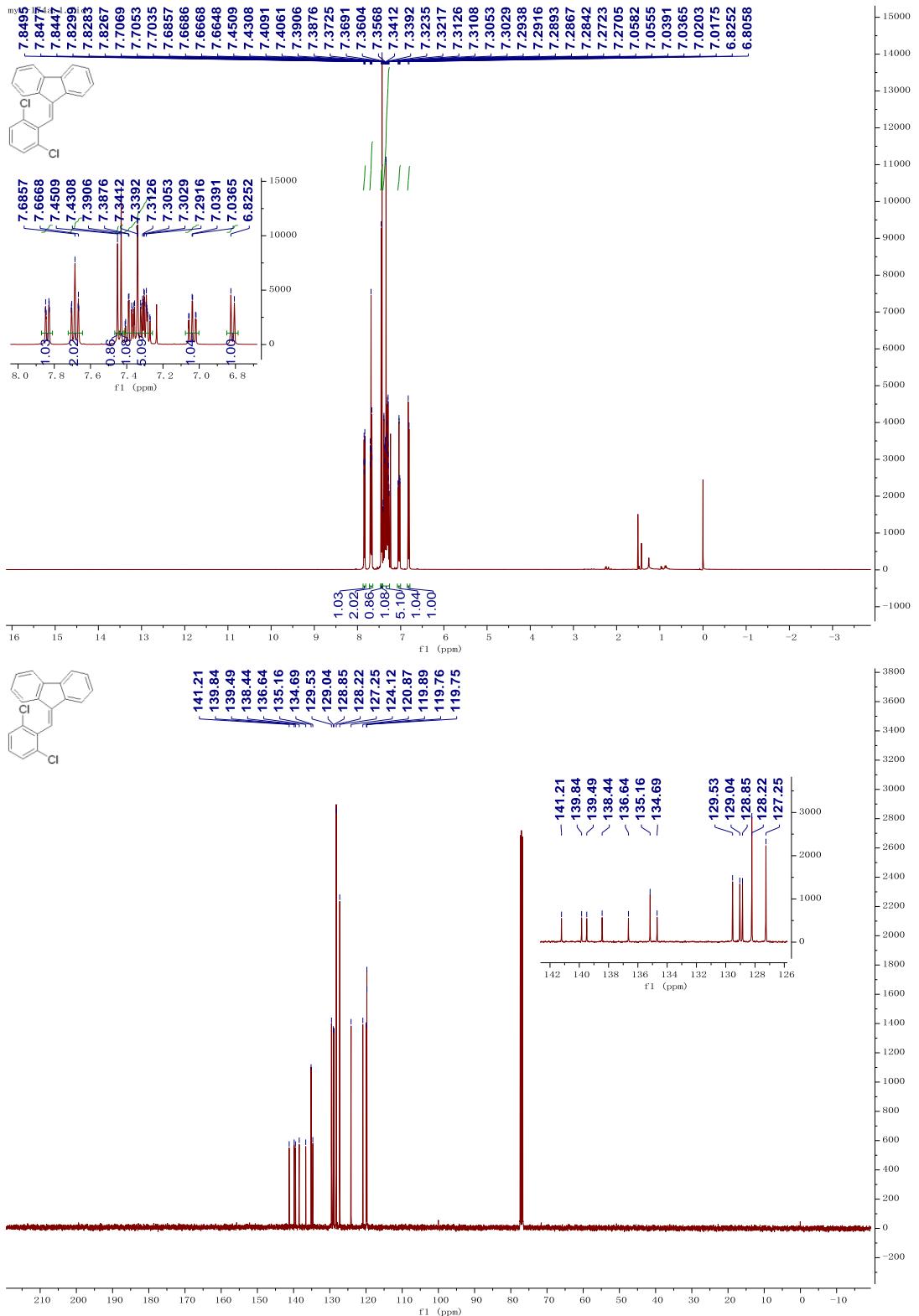
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3m**



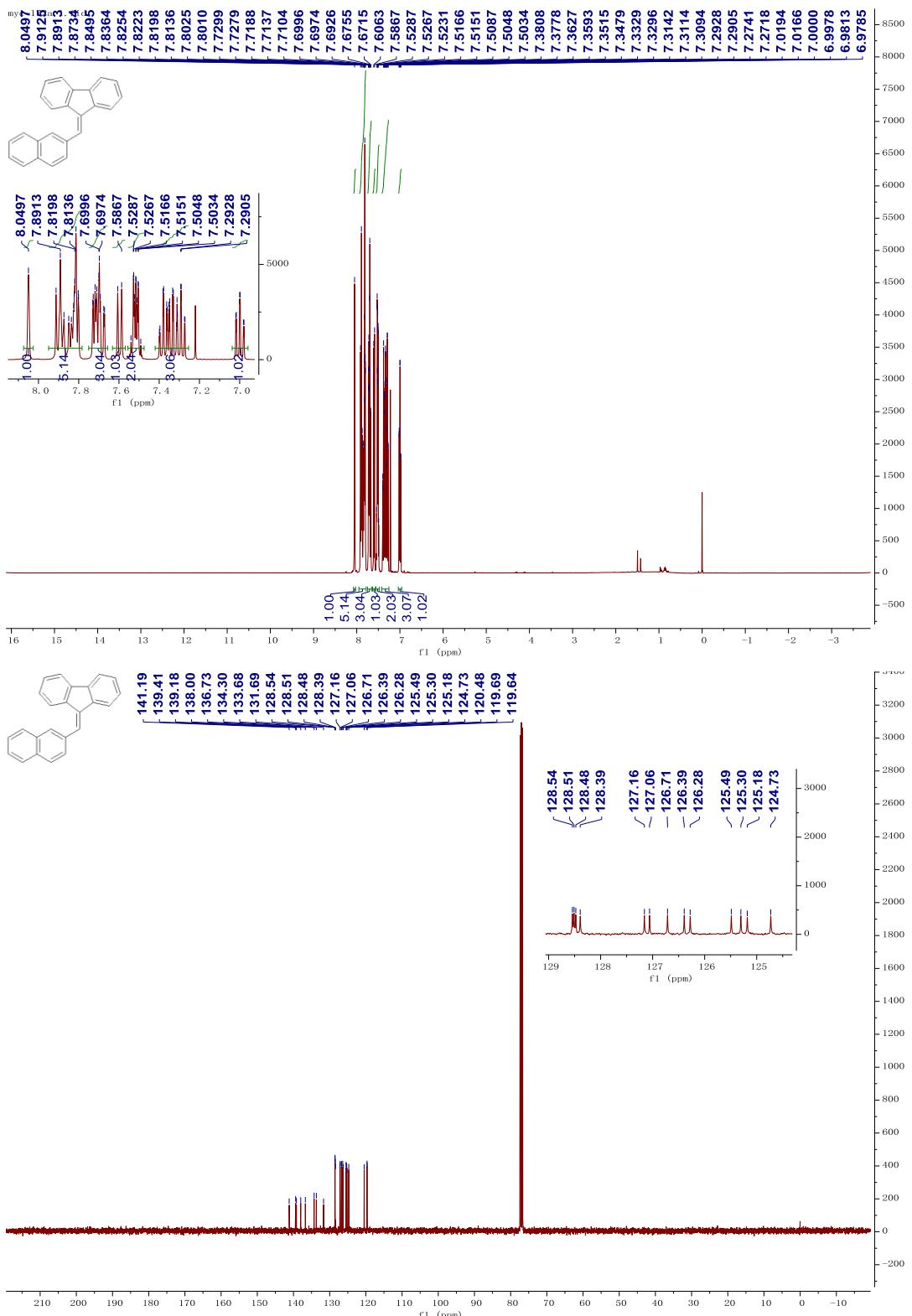
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3n**



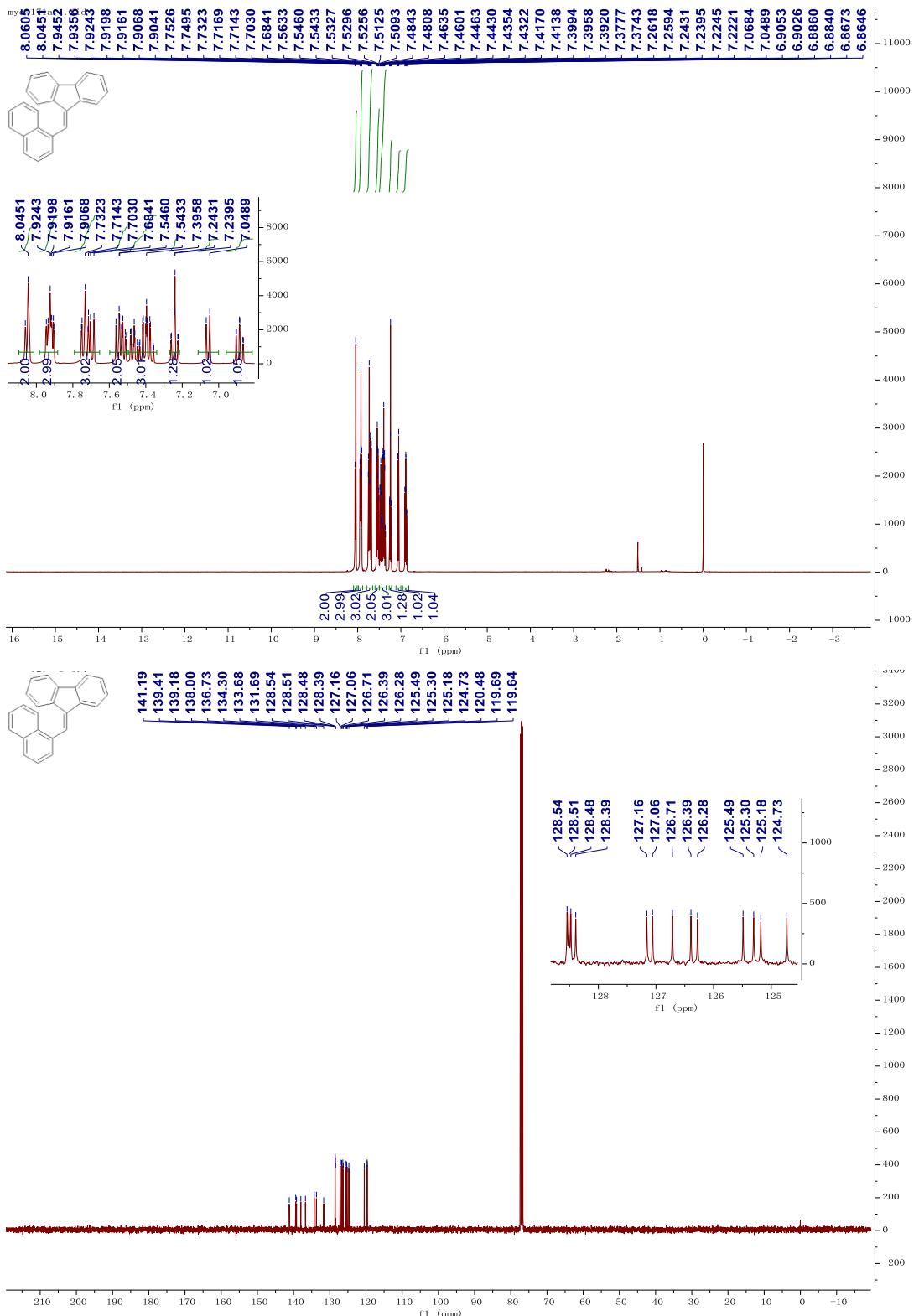
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3o**



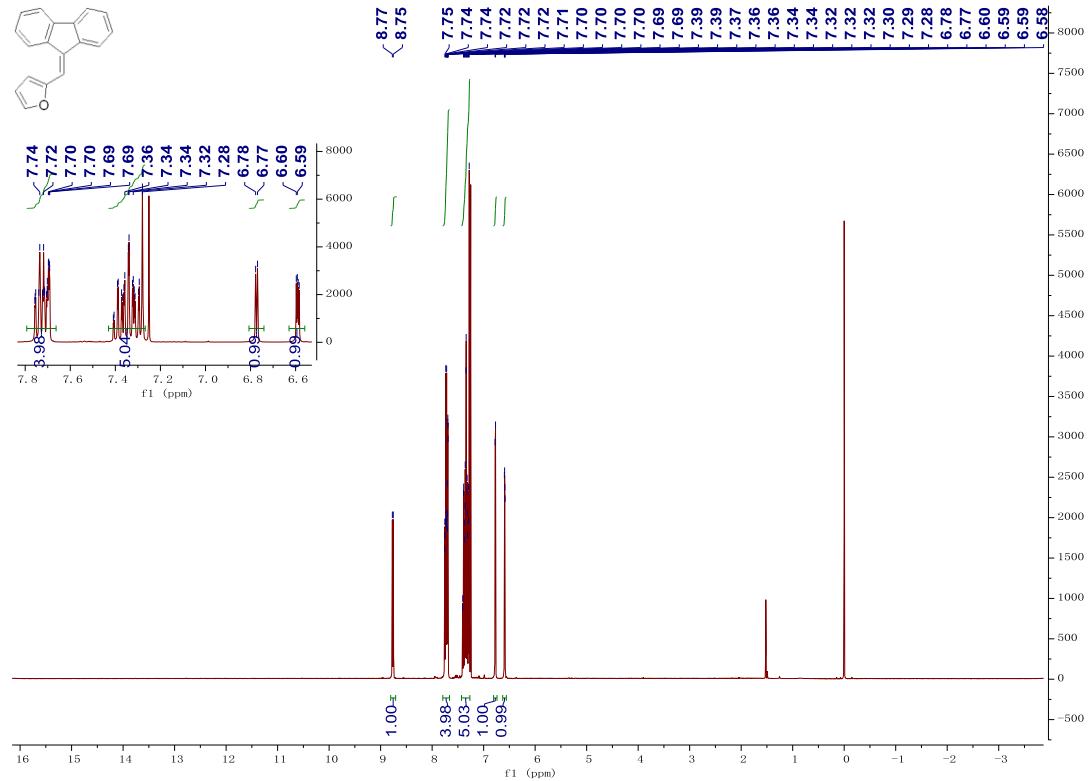
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectrum of **3p**

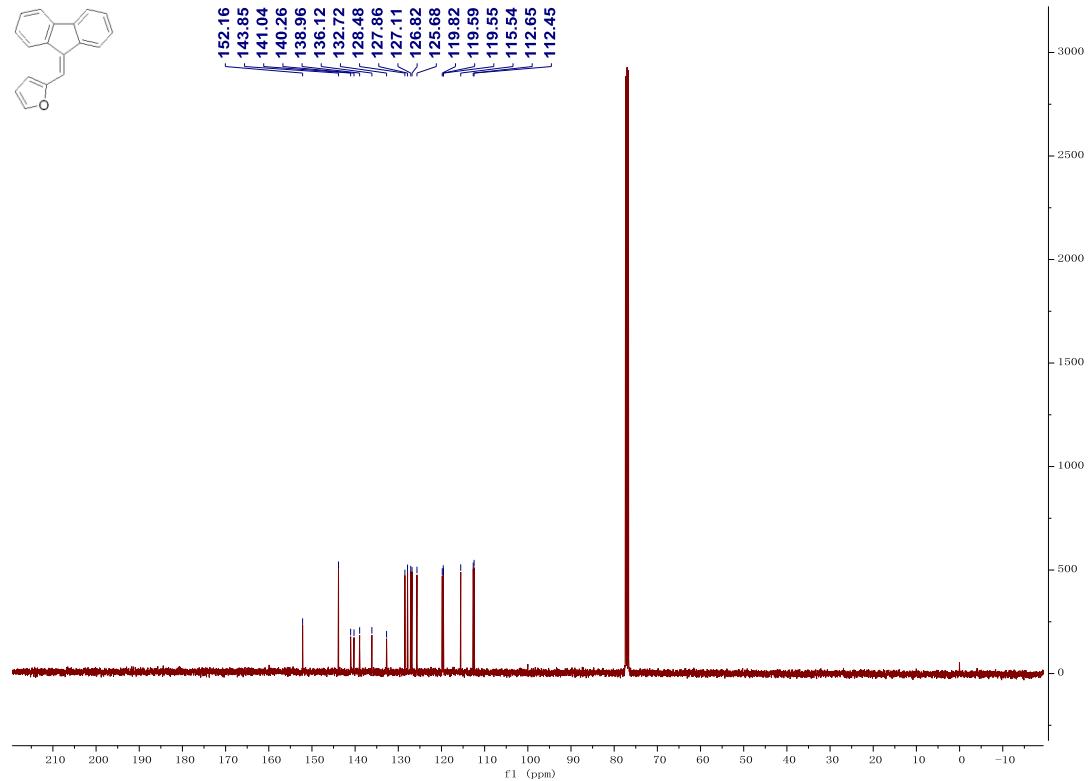


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3q**

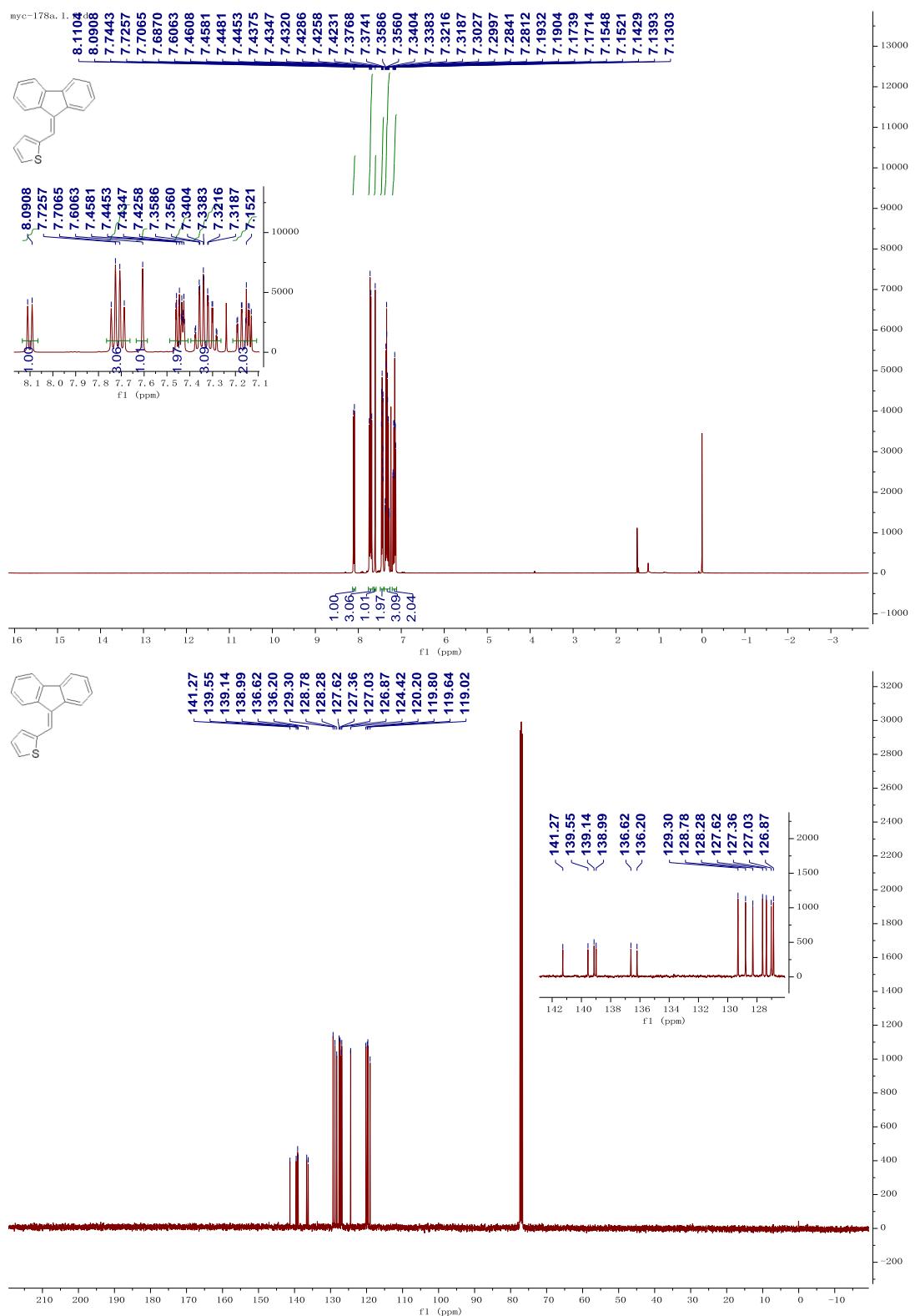


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3r**

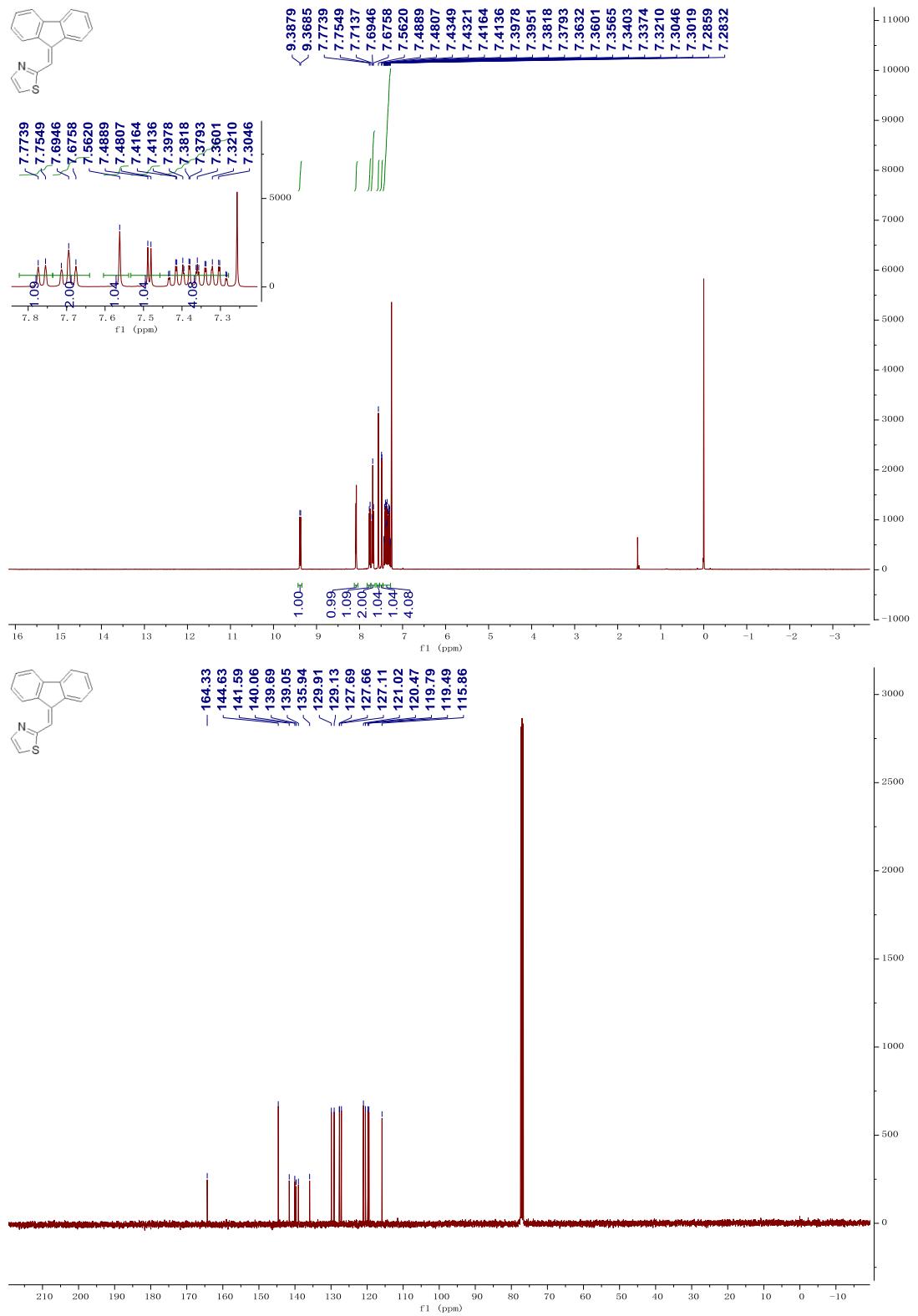




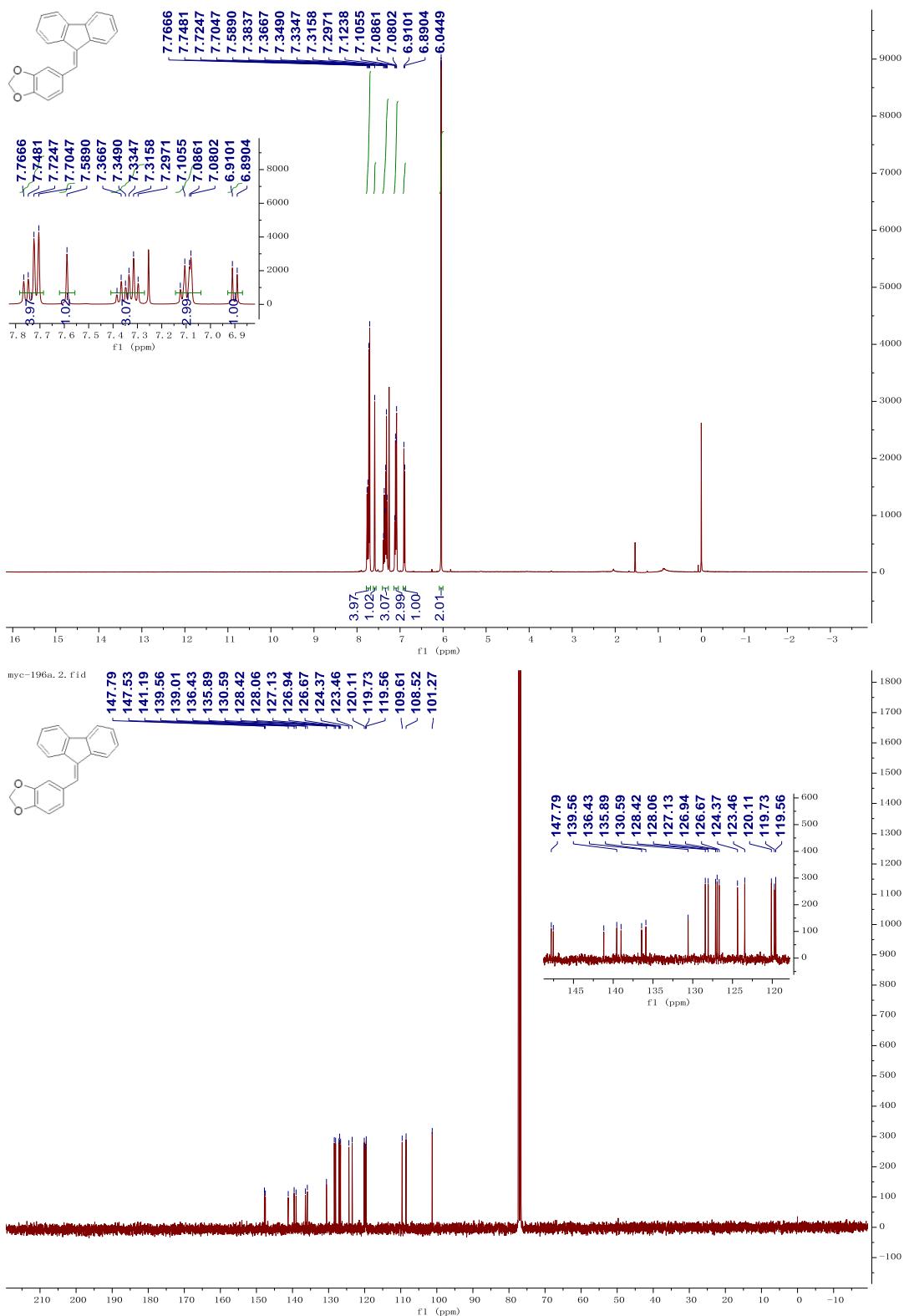
$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR spectrum of **3s**



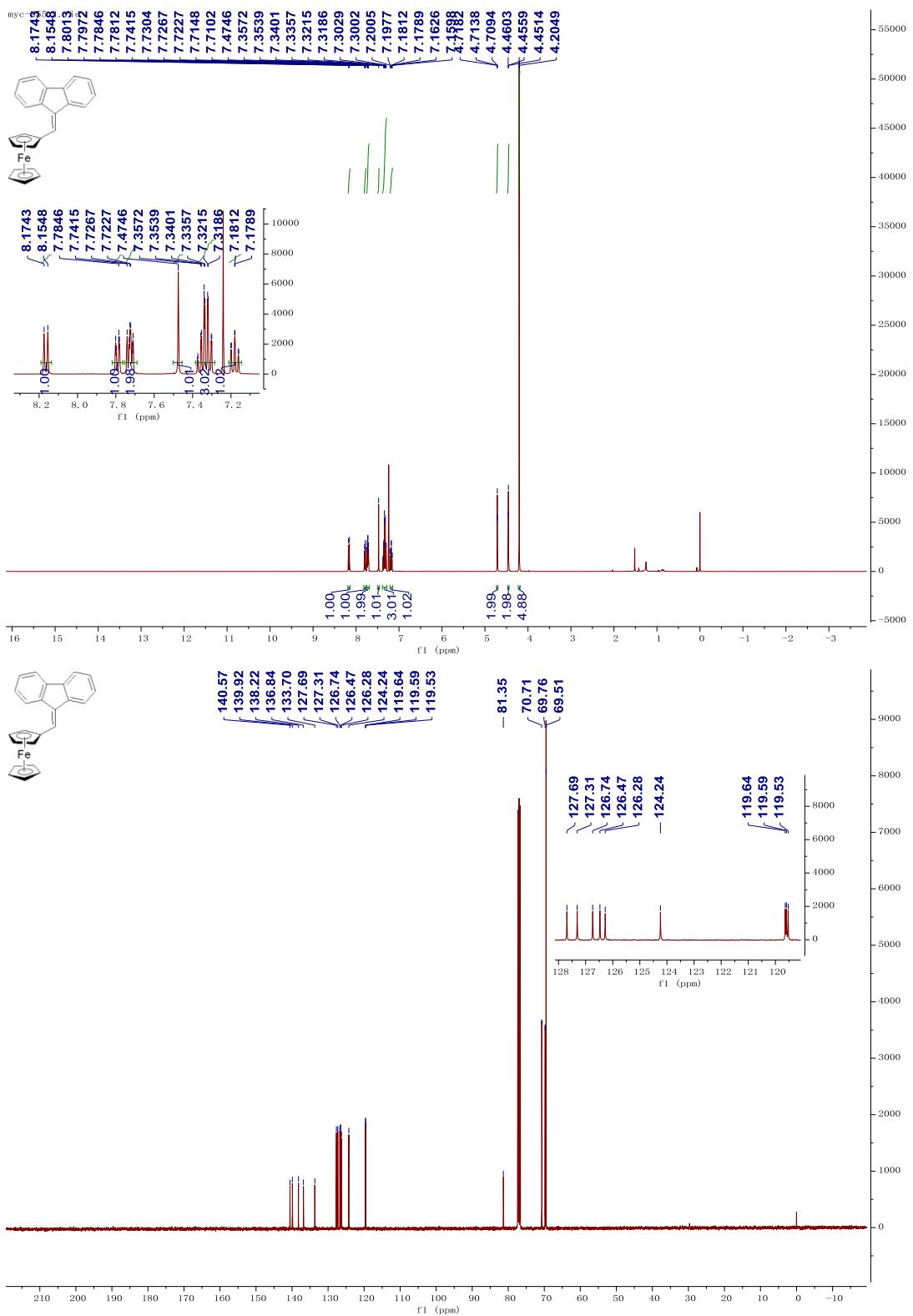
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3t**



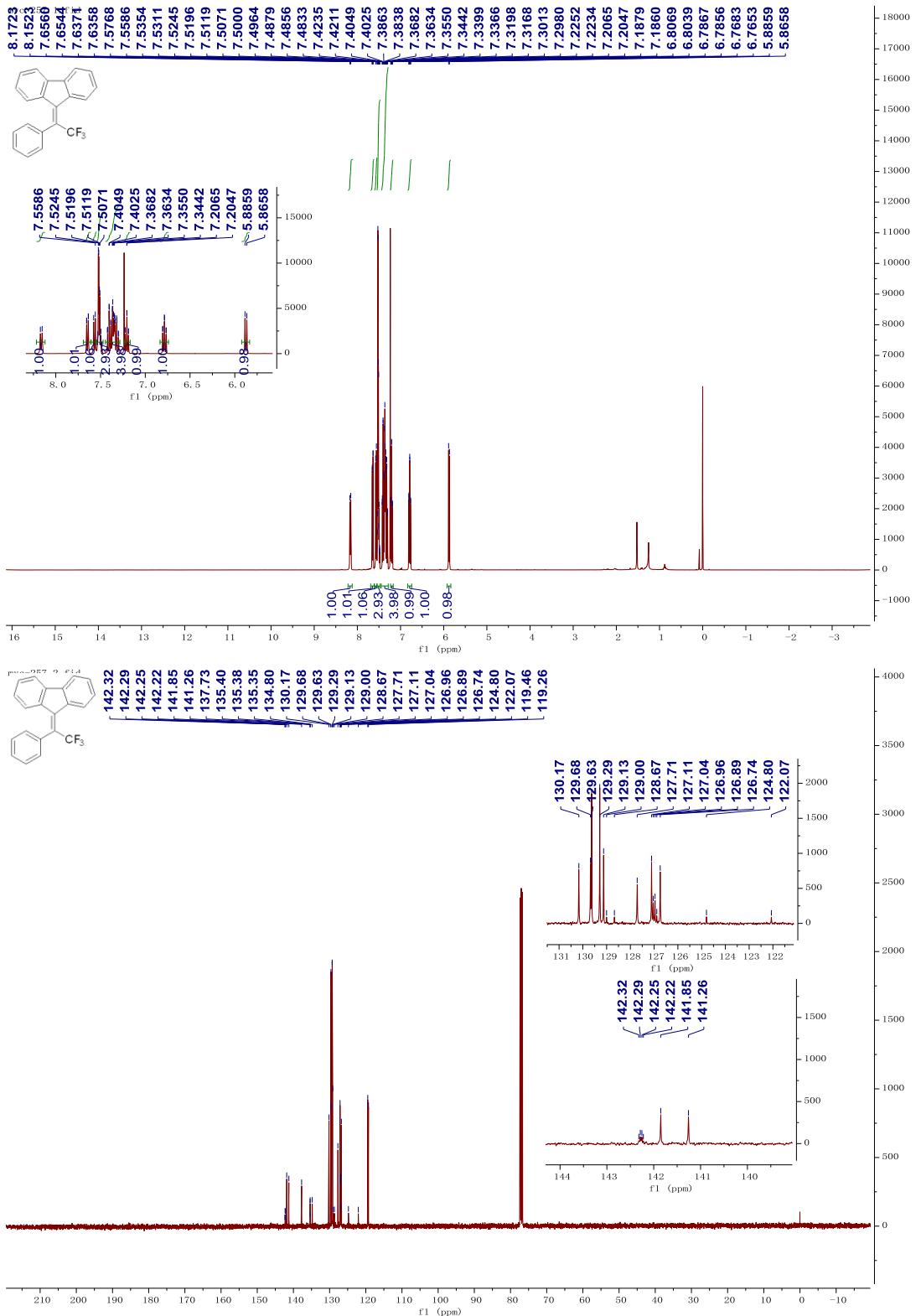
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3u**

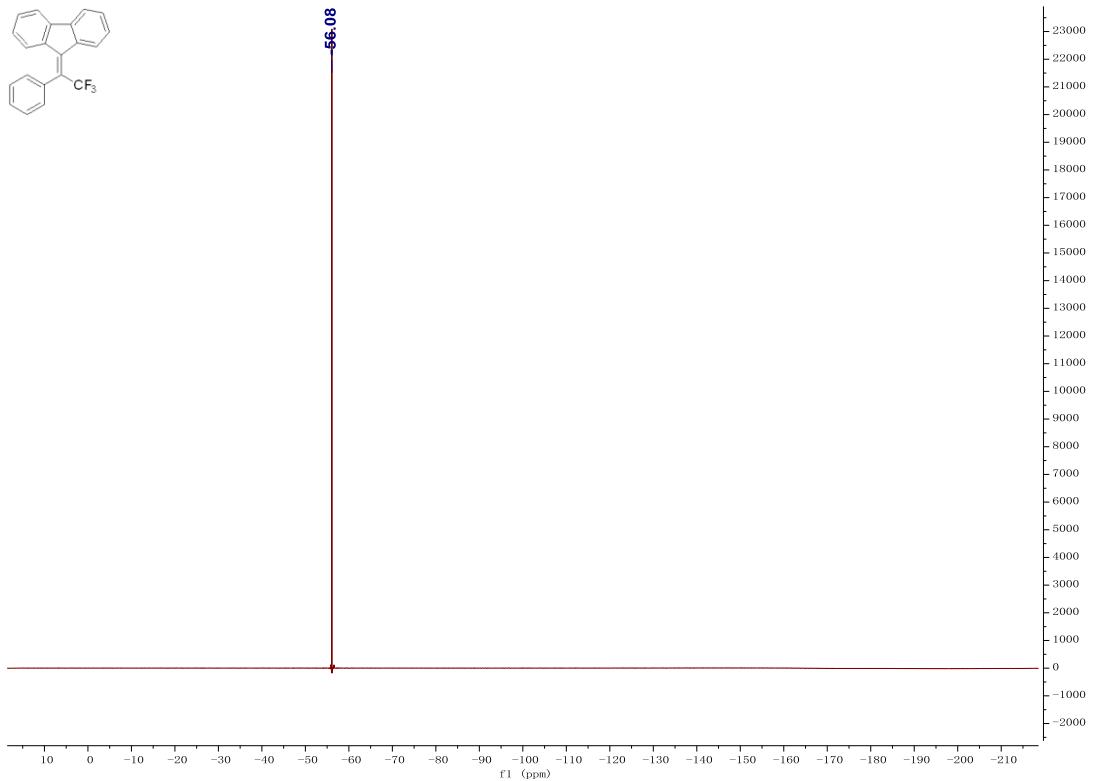


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **3v**

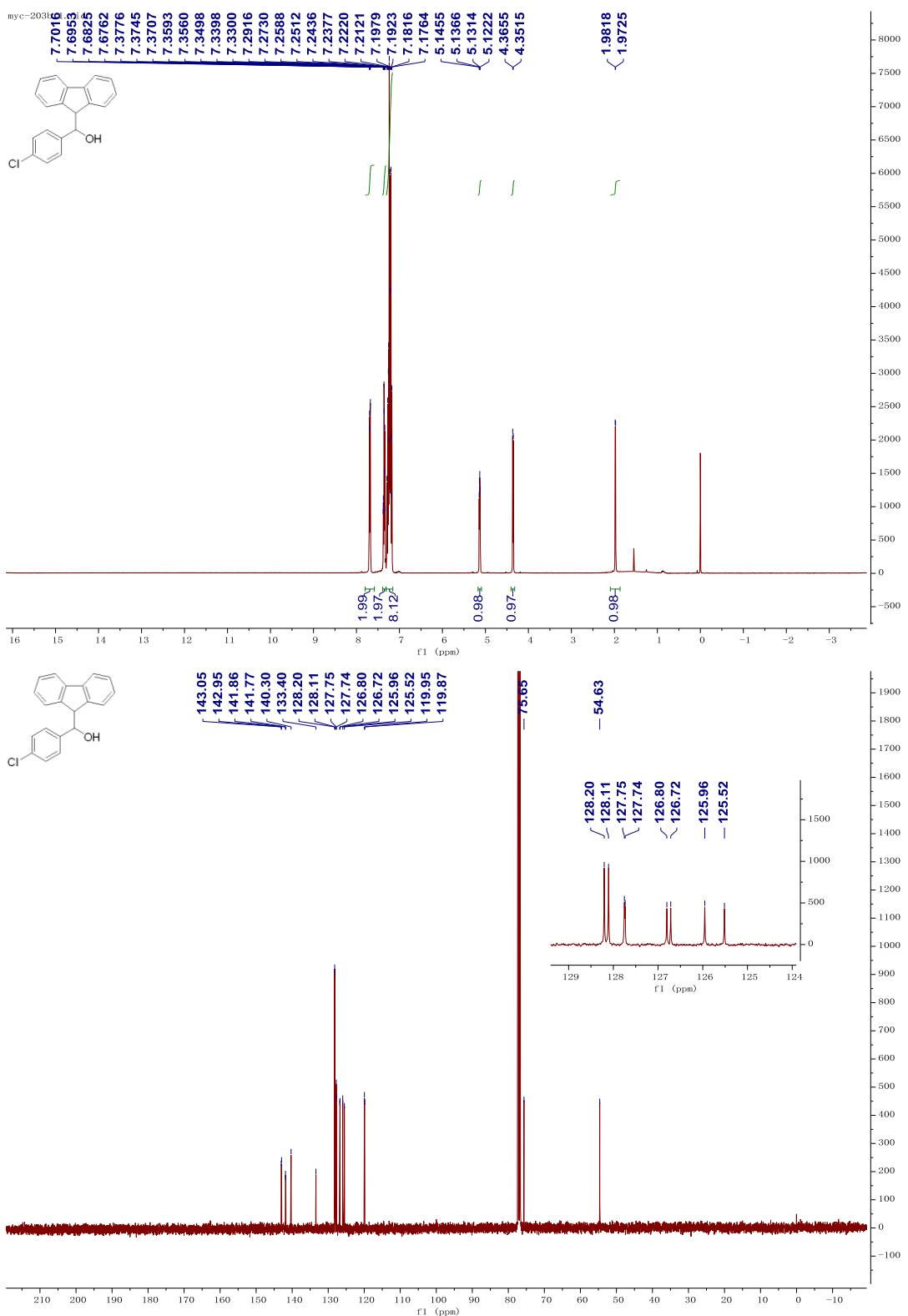


<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR spectrum of **3x**

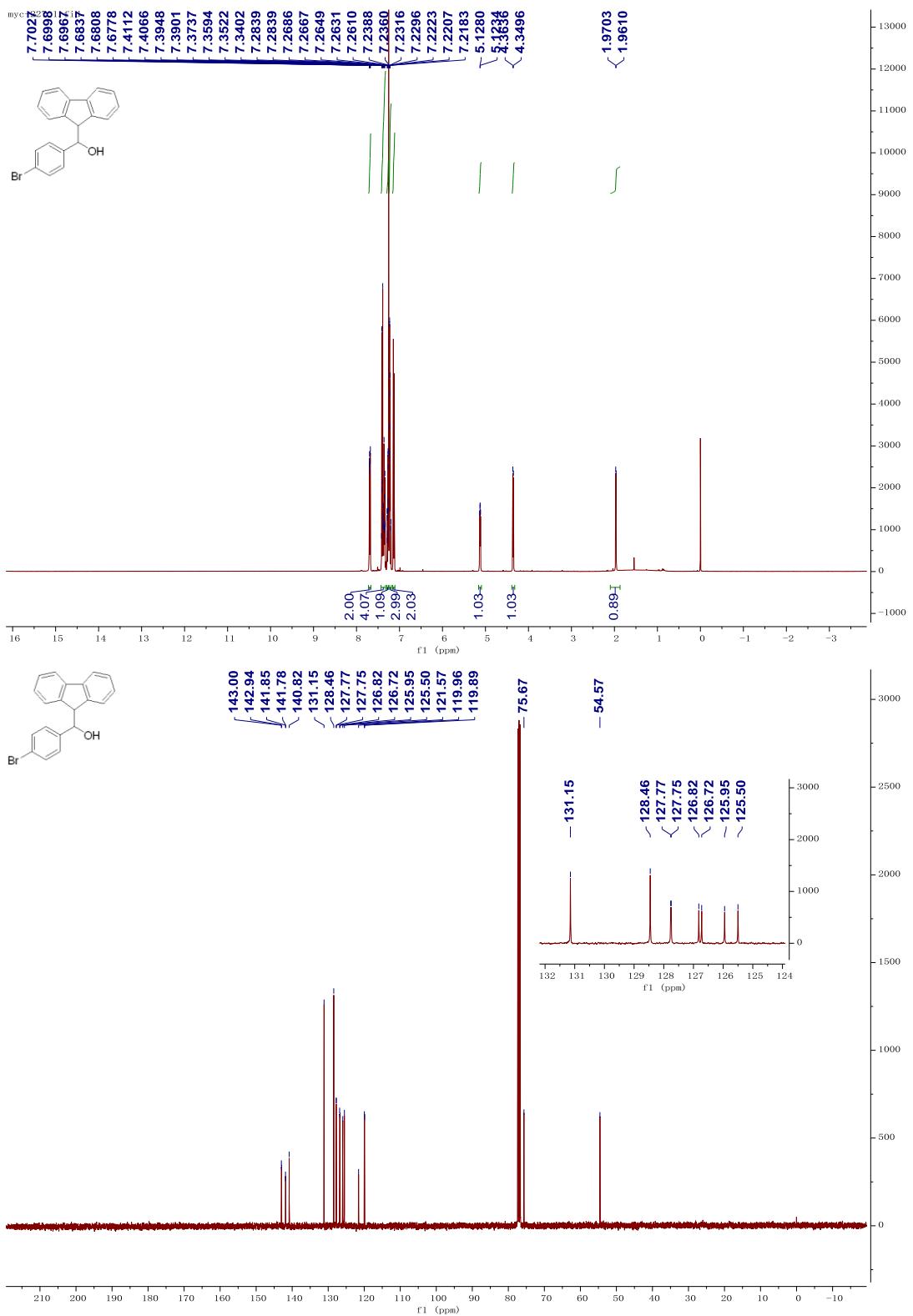




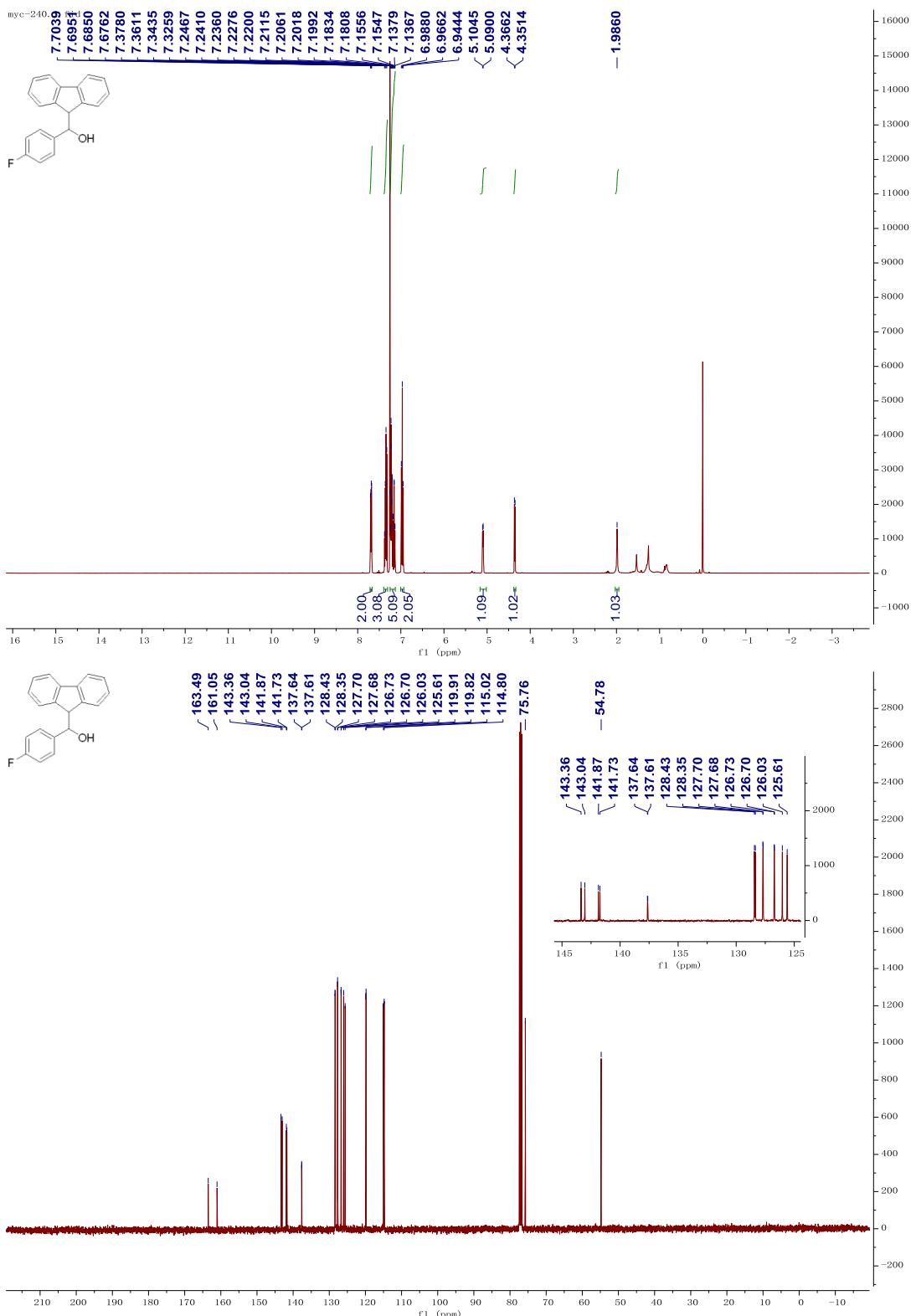
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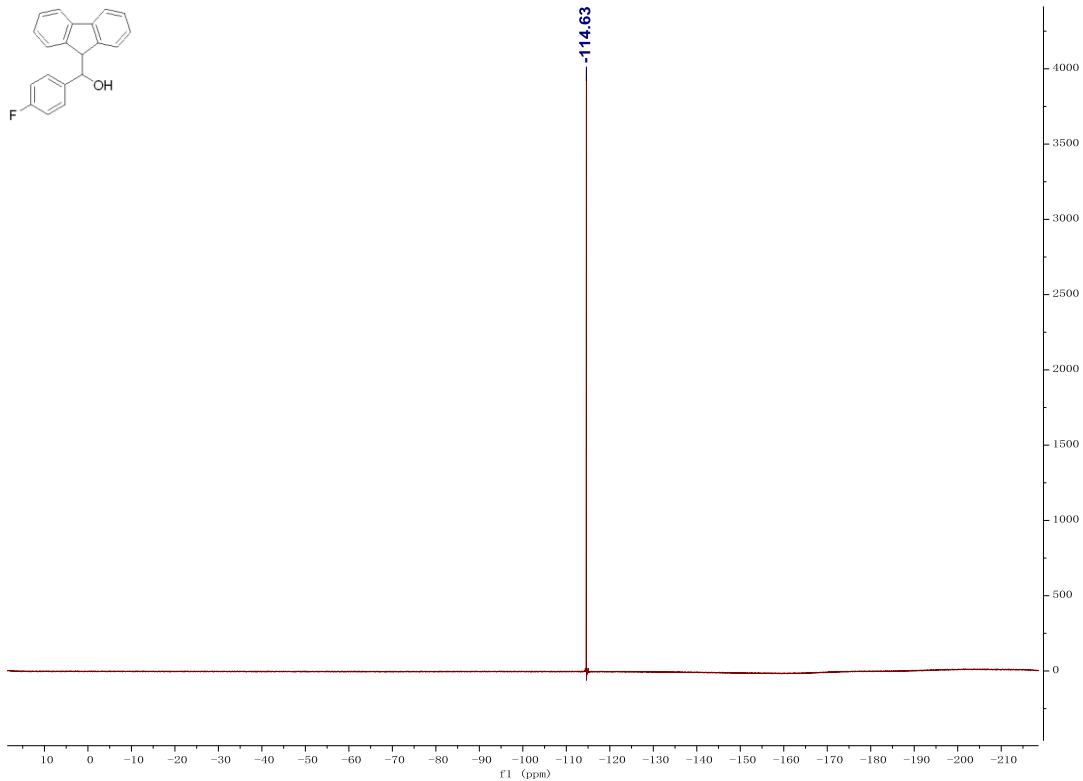


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4b**

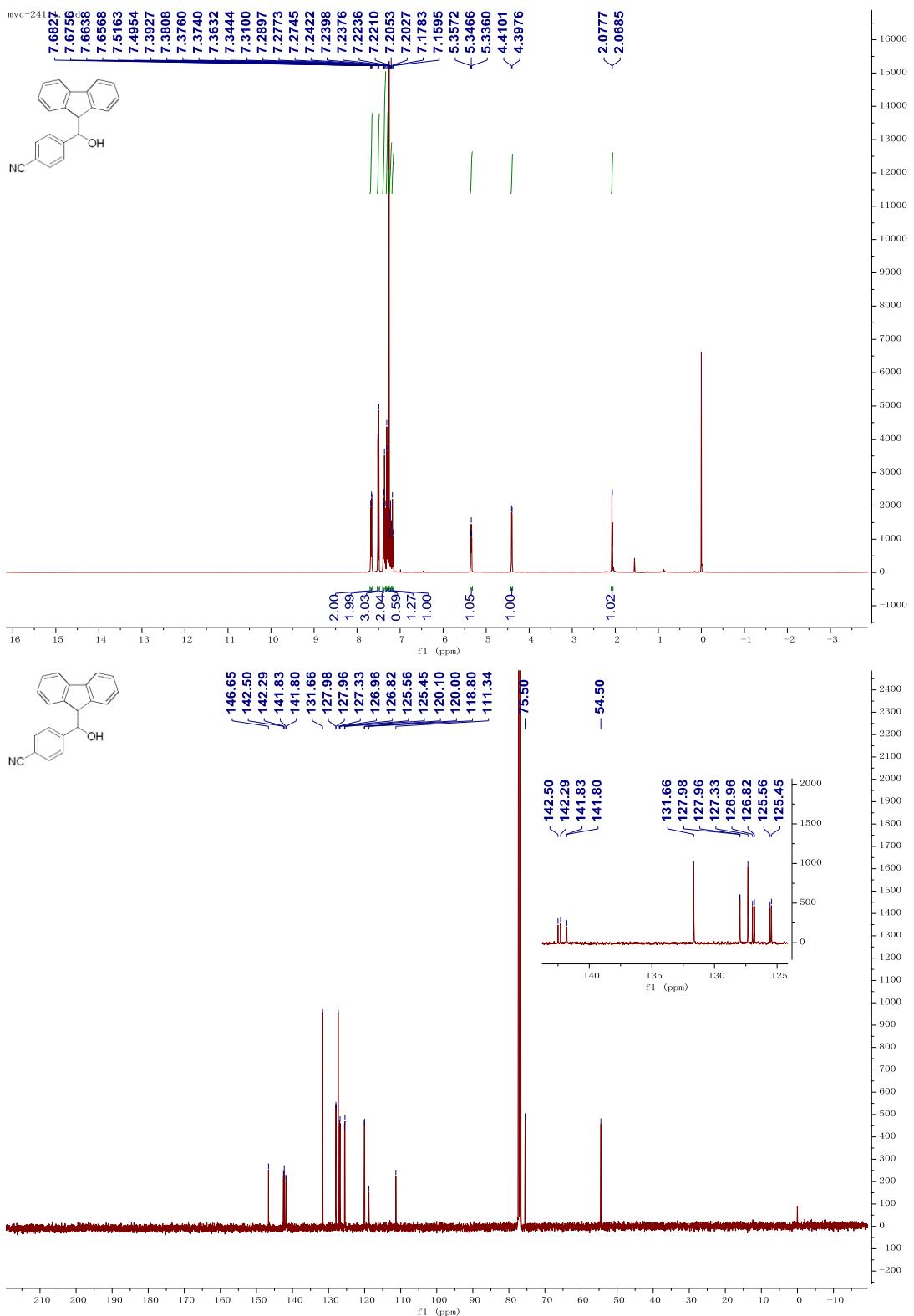


<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR spectrum of 4c

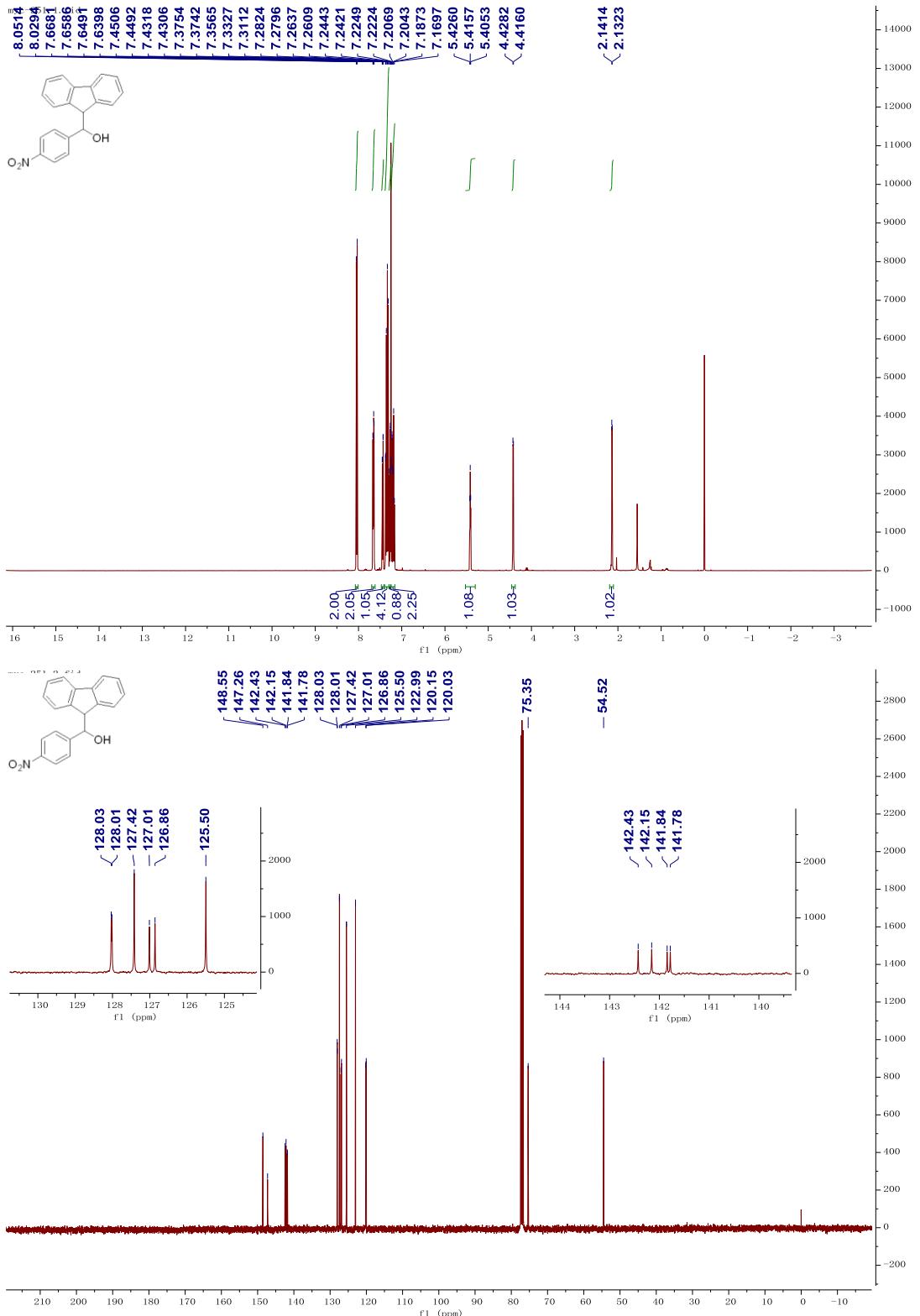




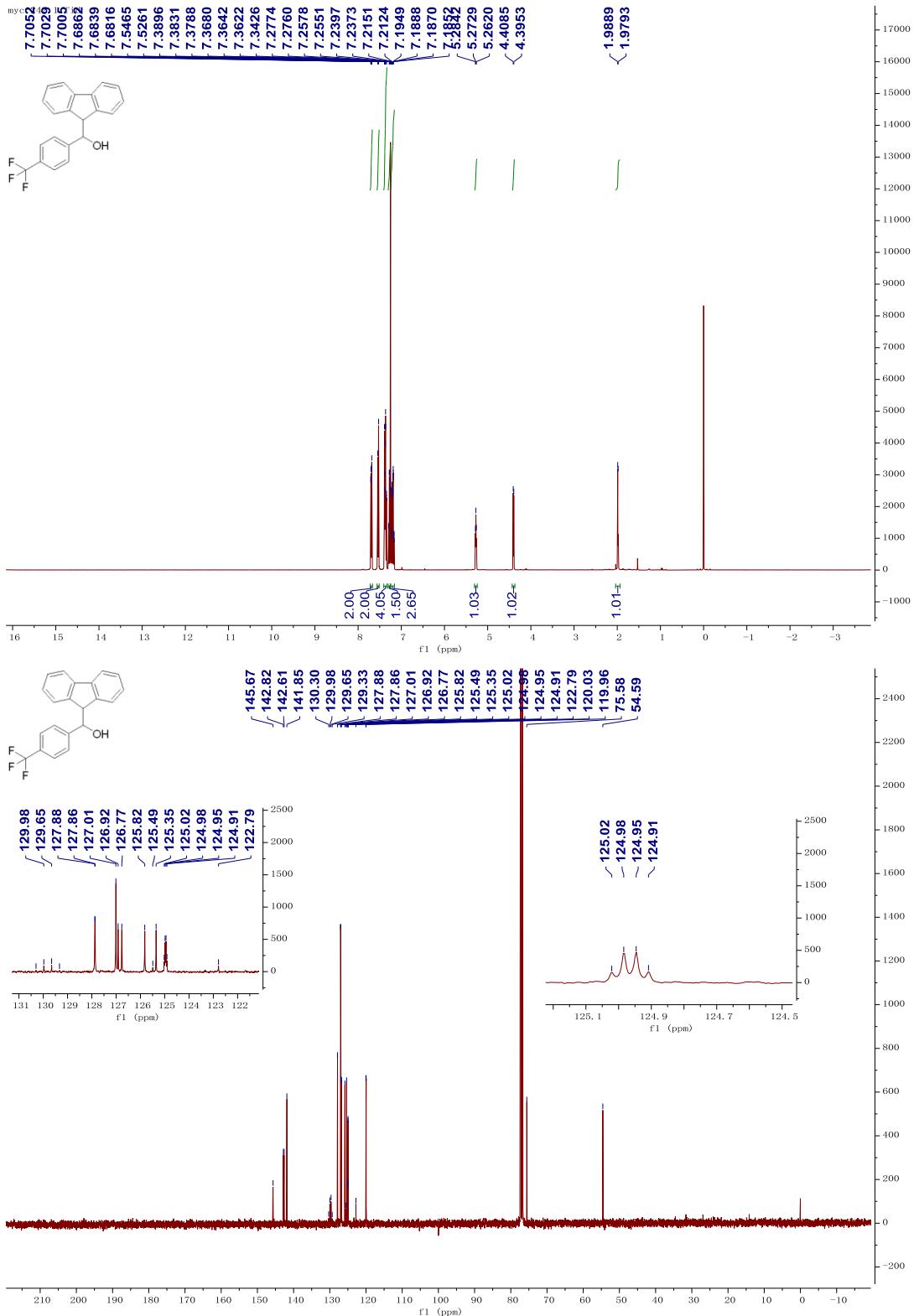
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4d**

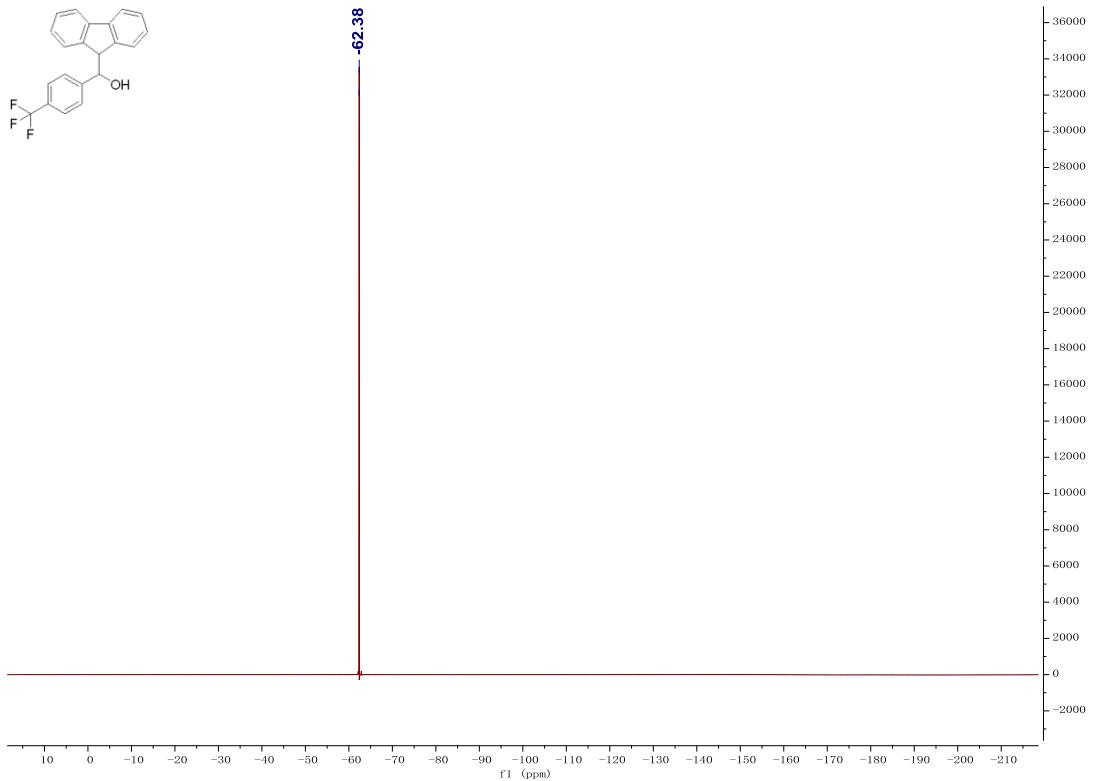


<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4e**

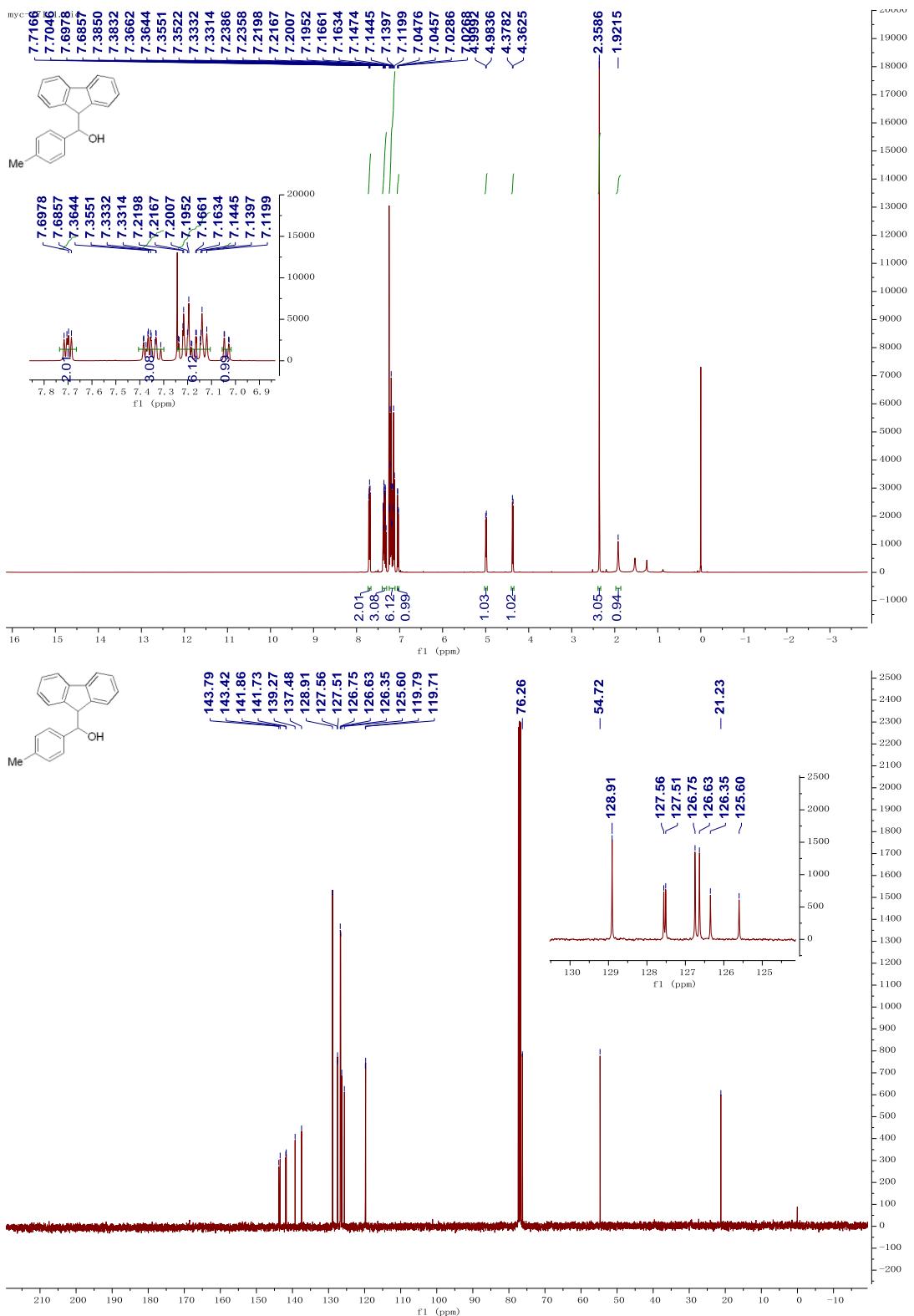


<sup>1</sup>H NMR, <sup>13</sup>C NMR, <sup>19</sup>F NMR spectrum of **4f**

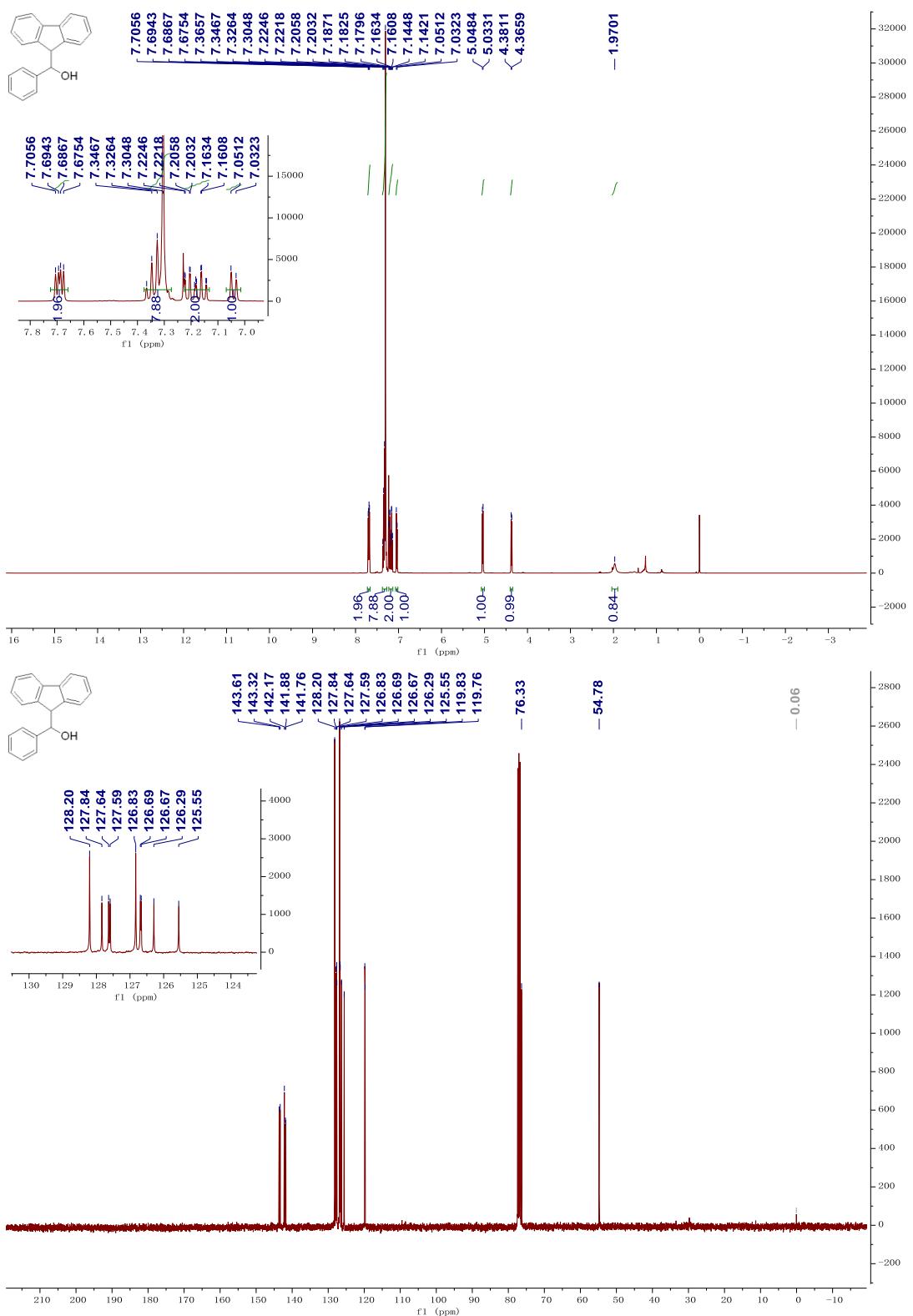




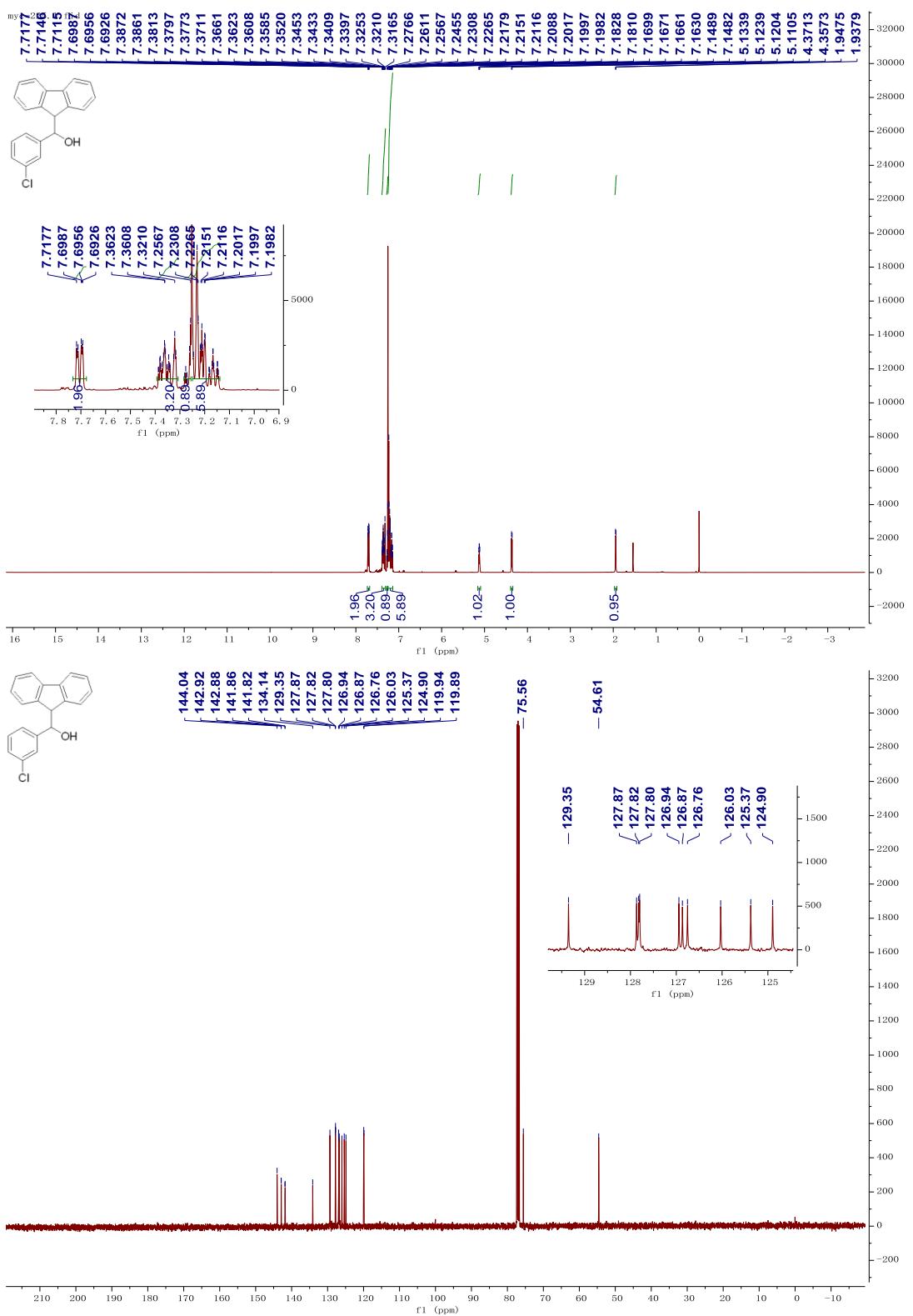
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4g**



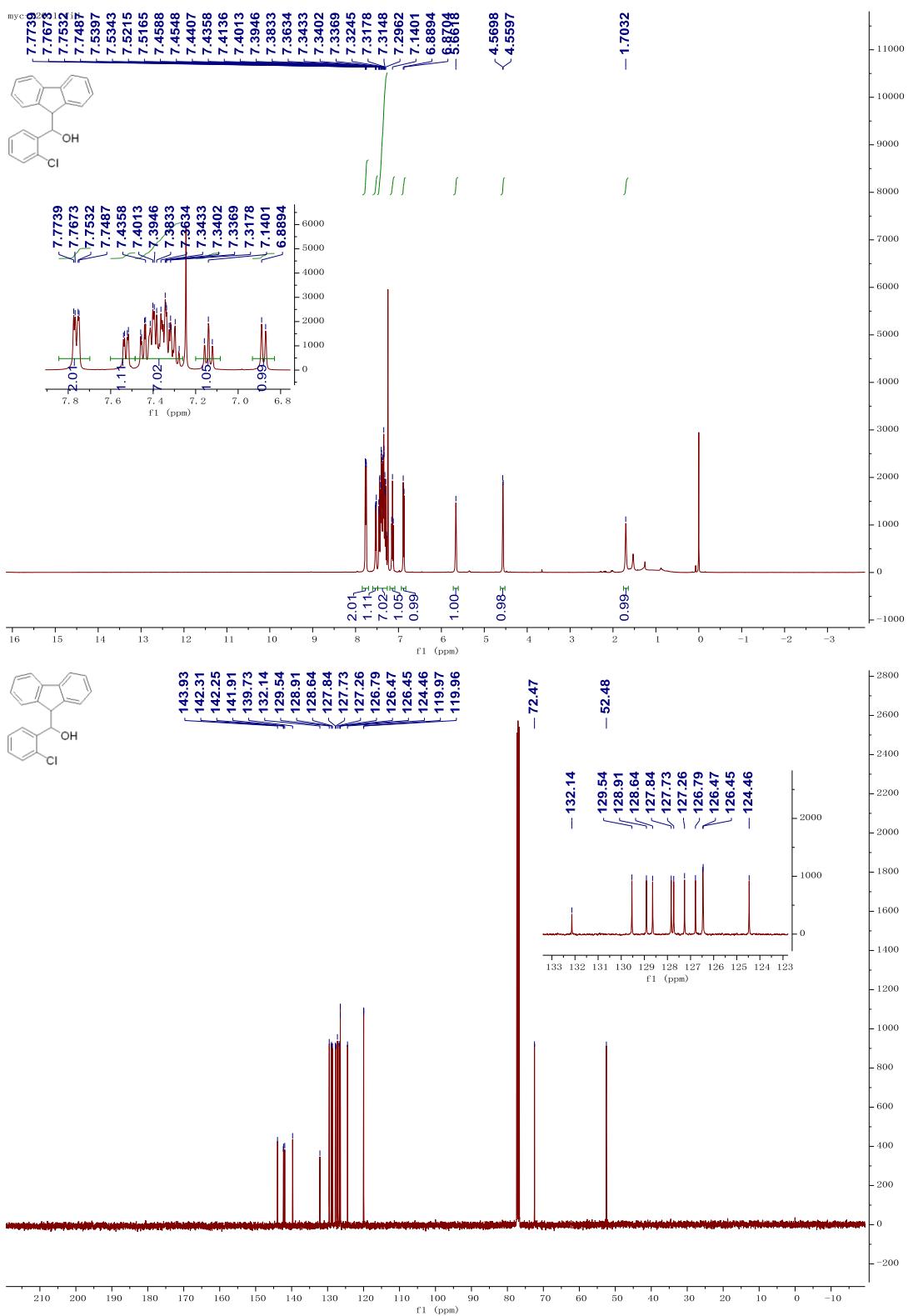
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4h**



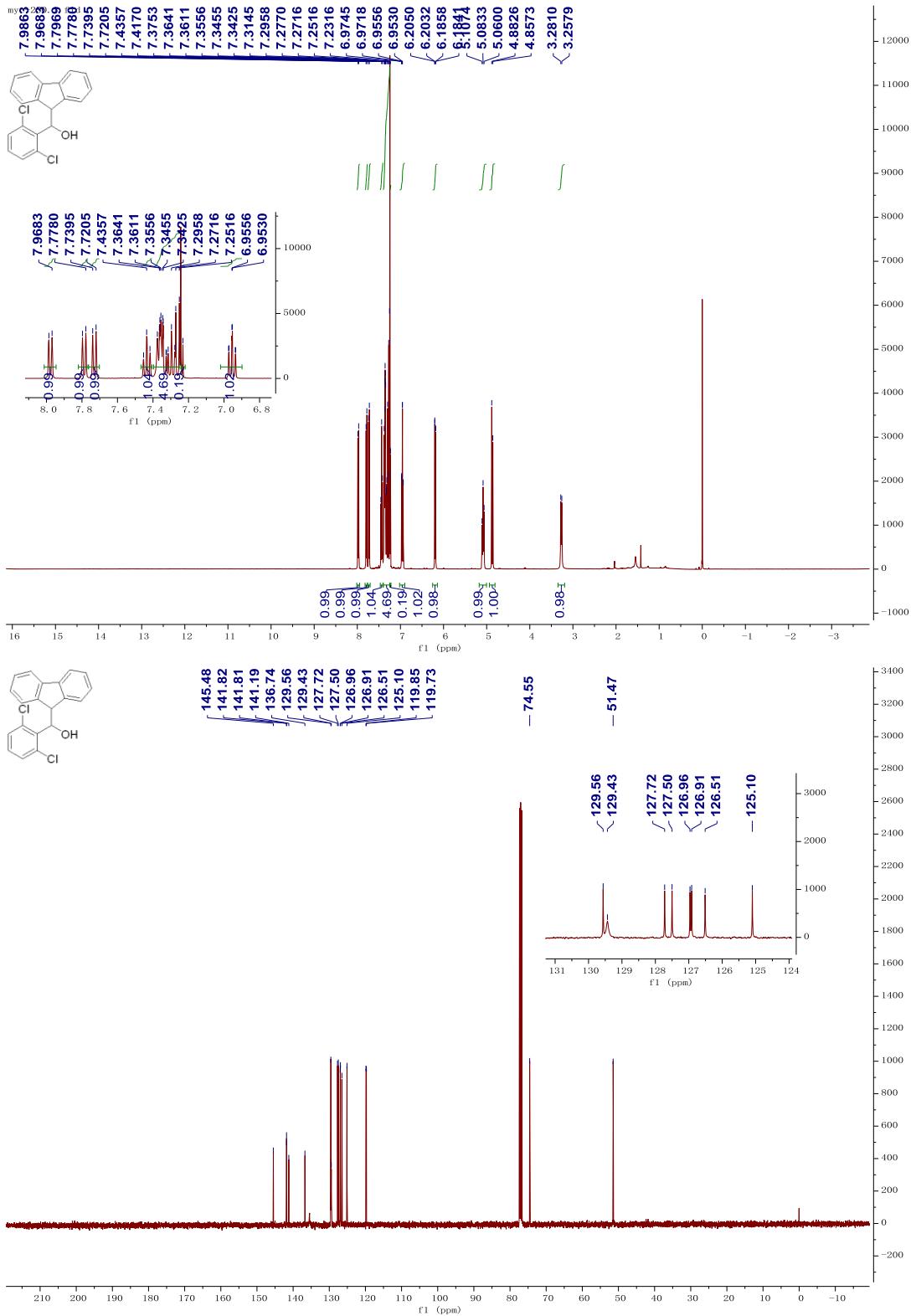
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4i**



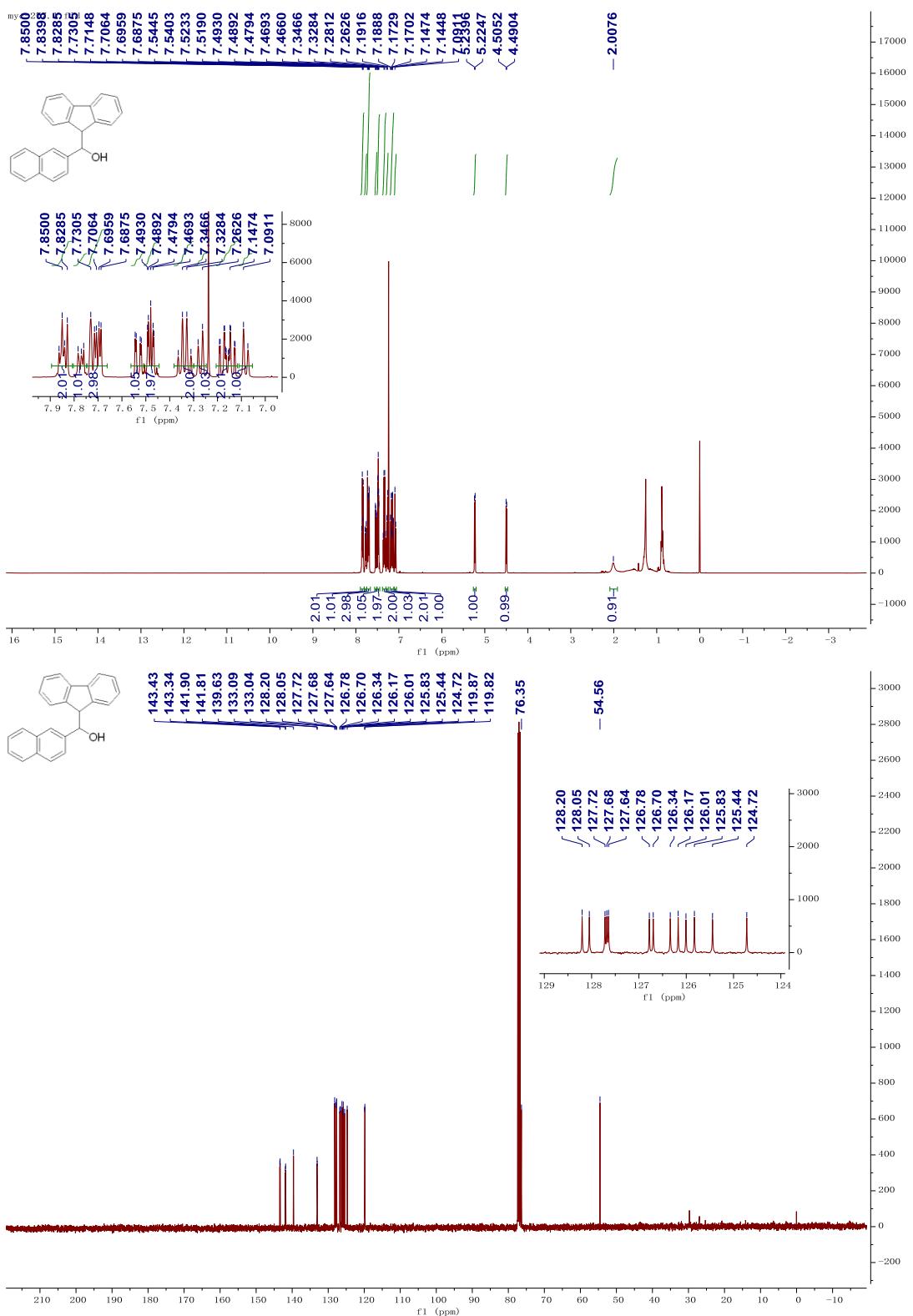
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4j**



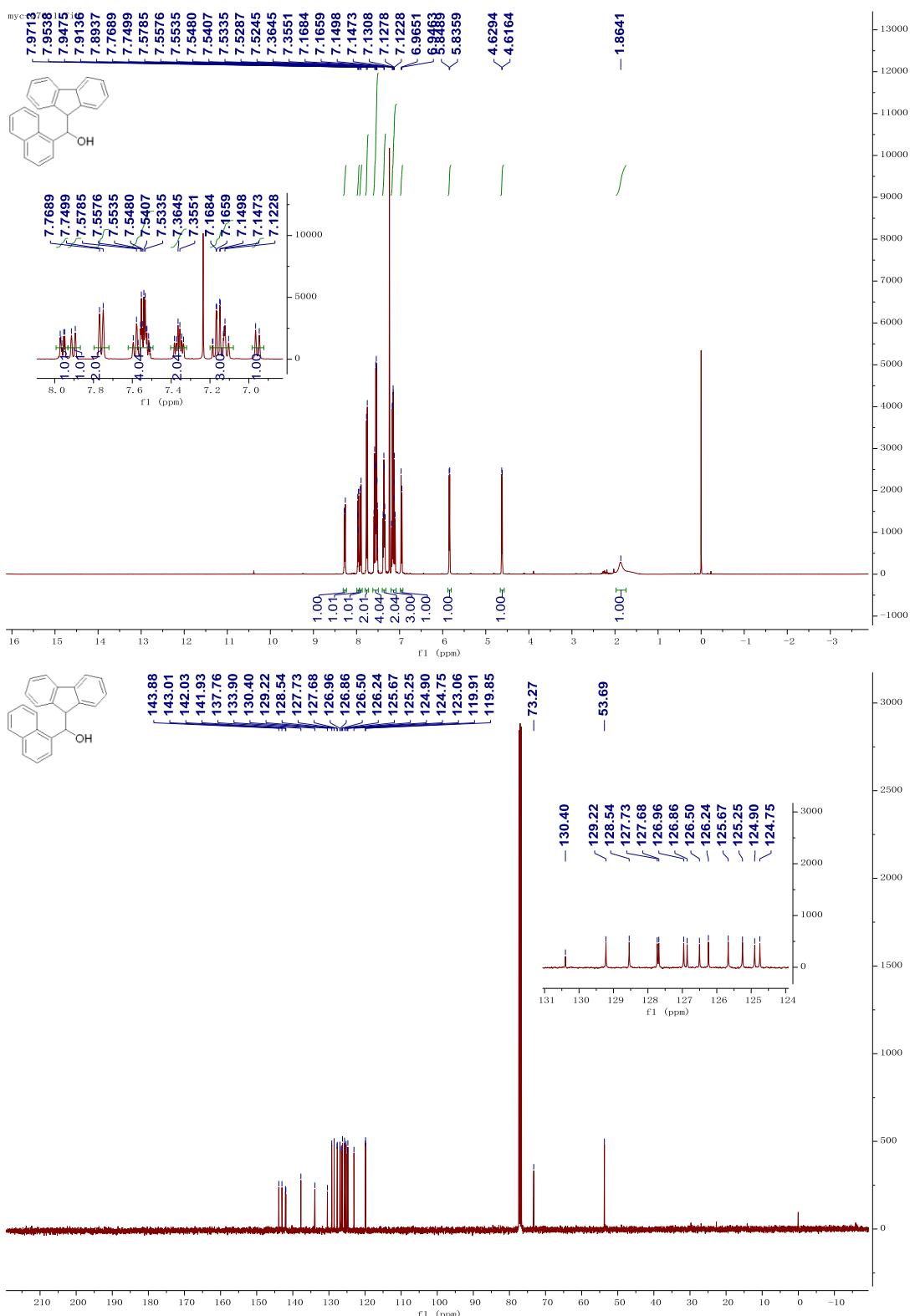
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4k**



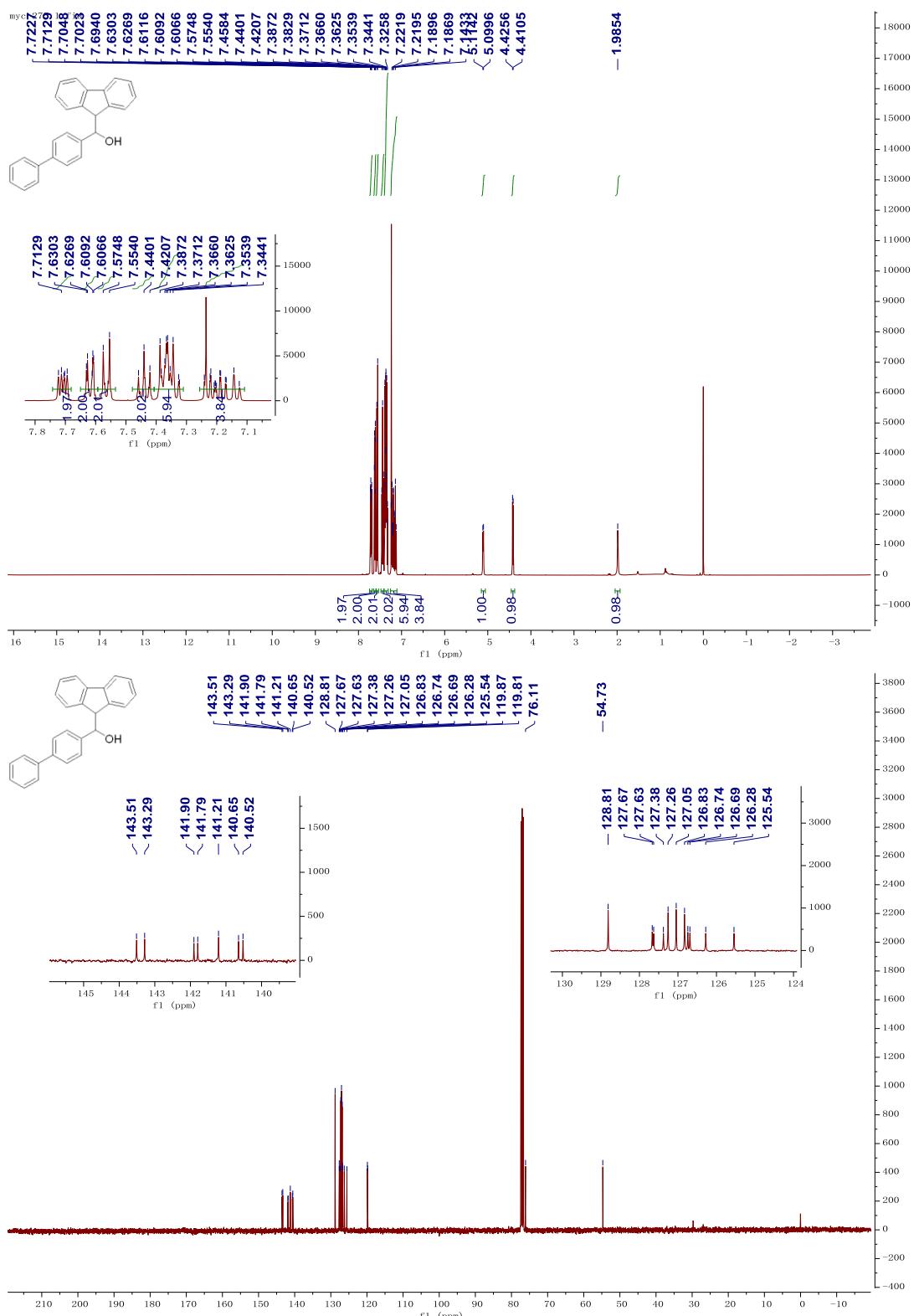
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4I**



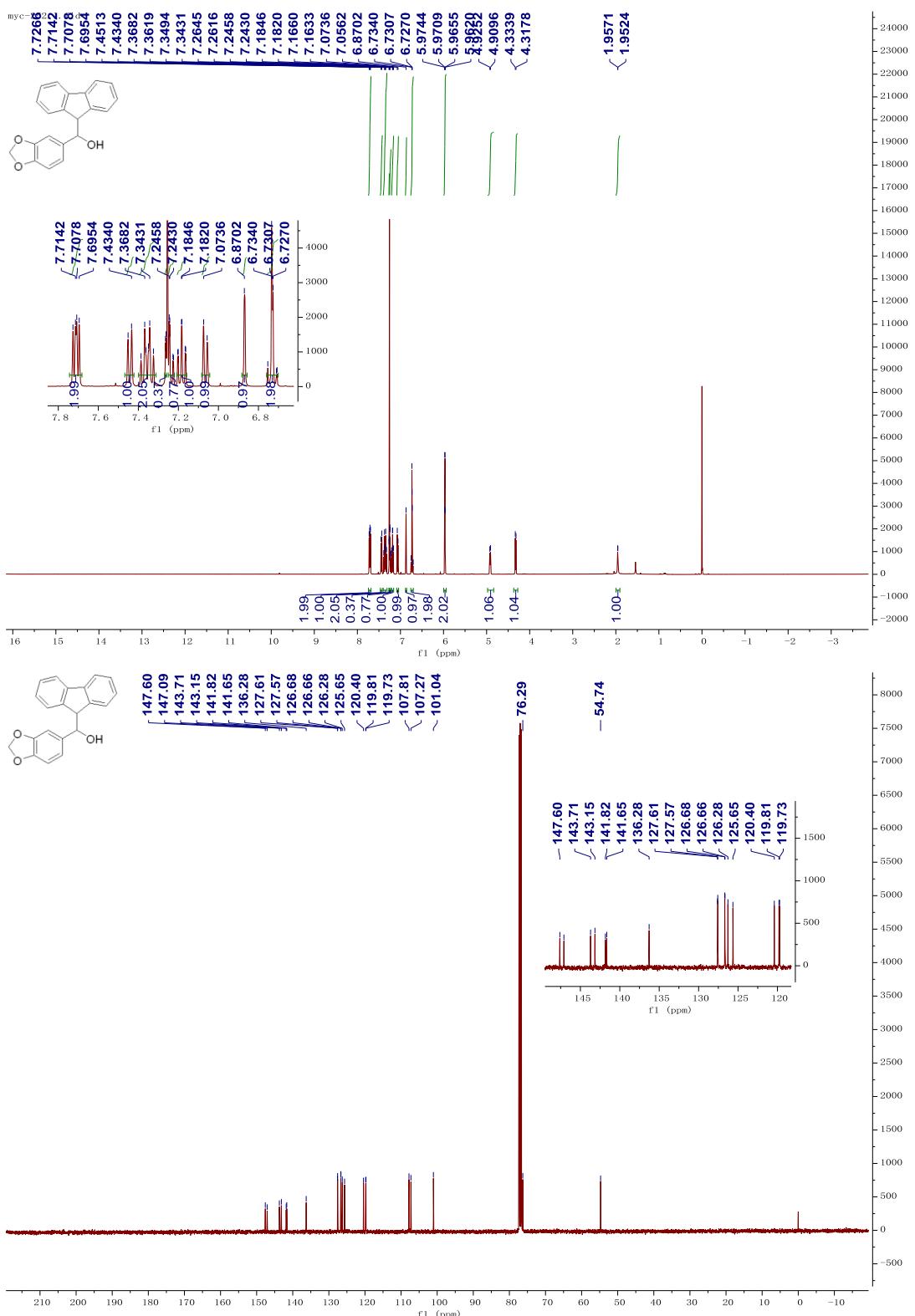
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4m**



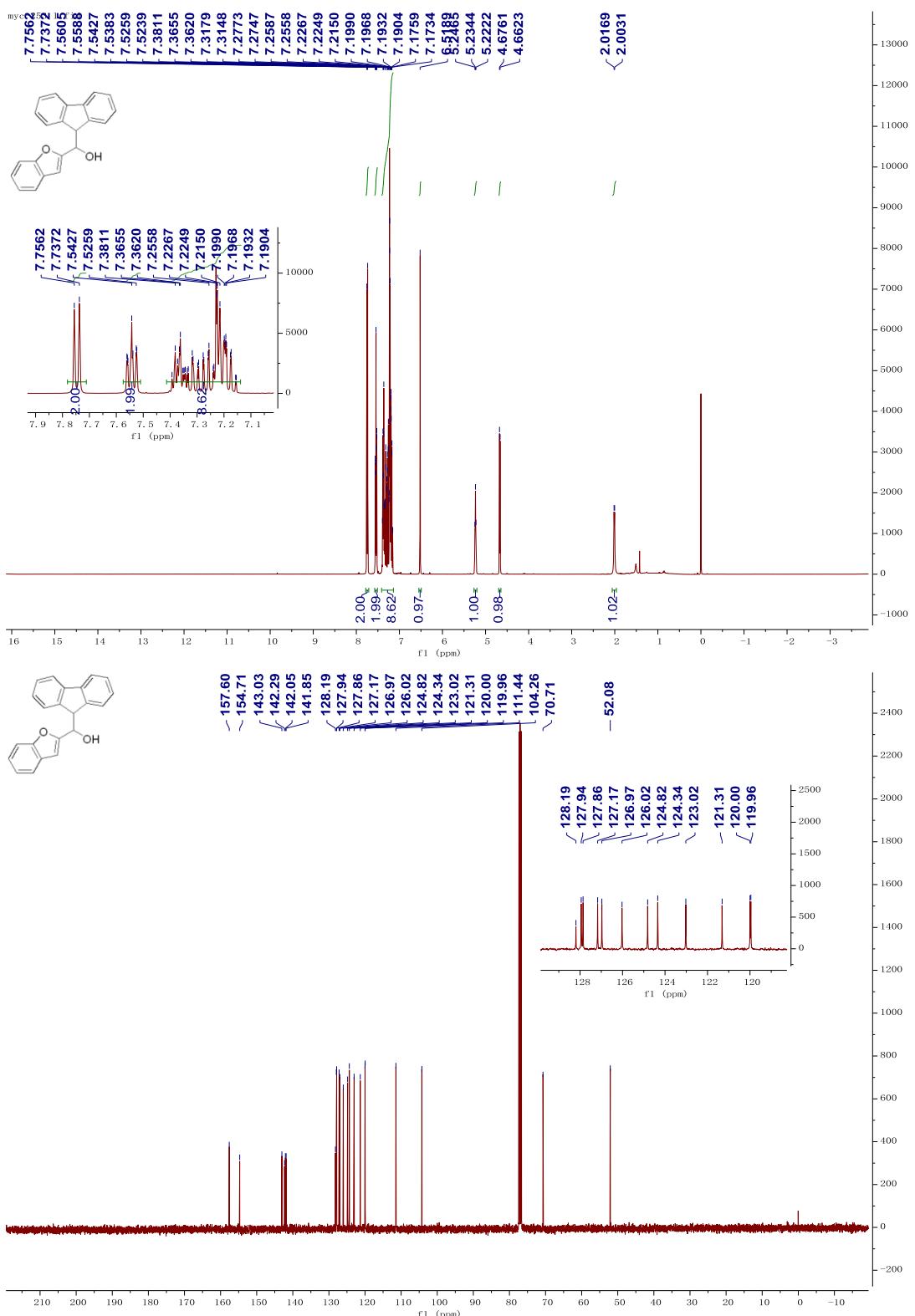
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4n**



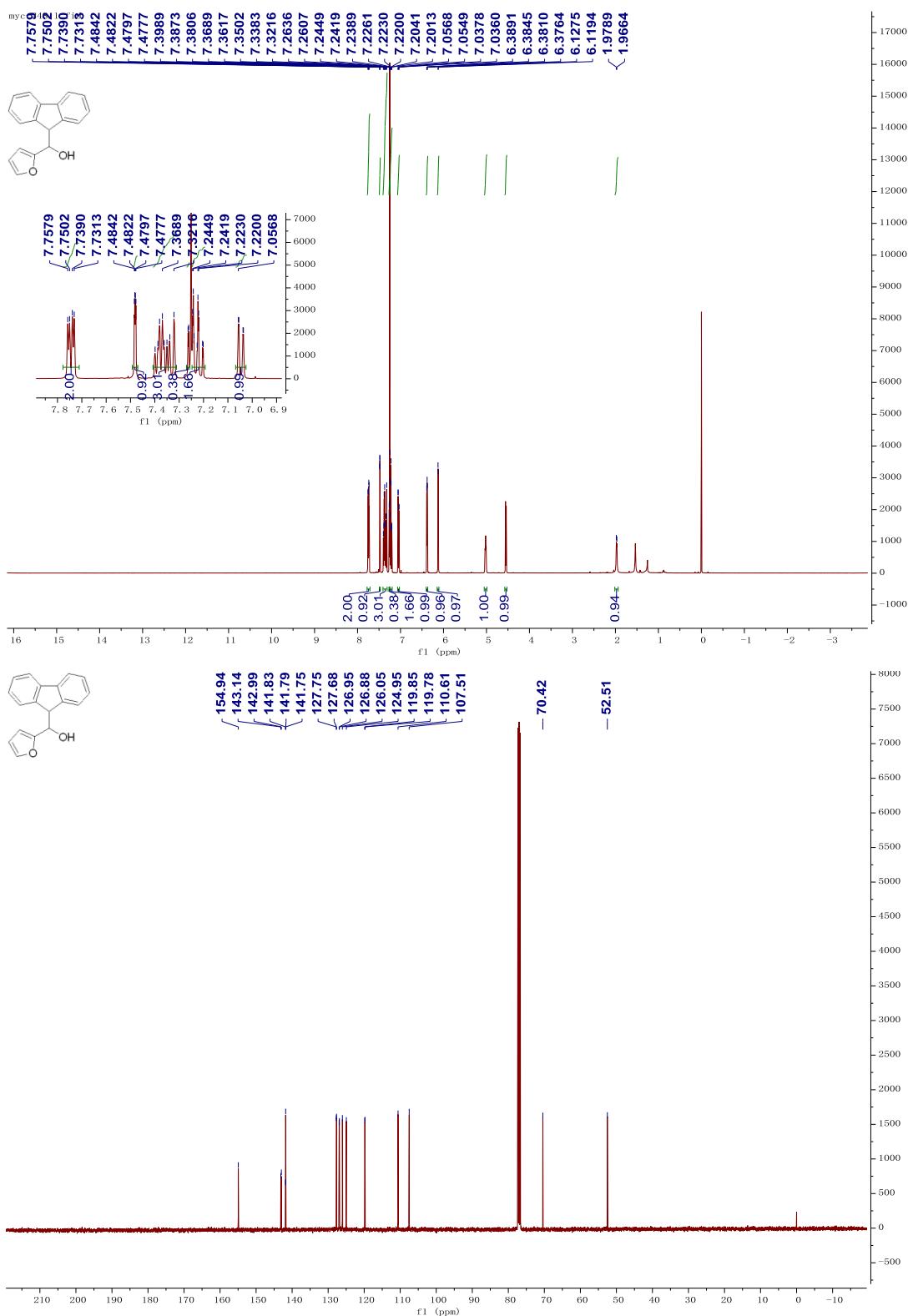
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4o**



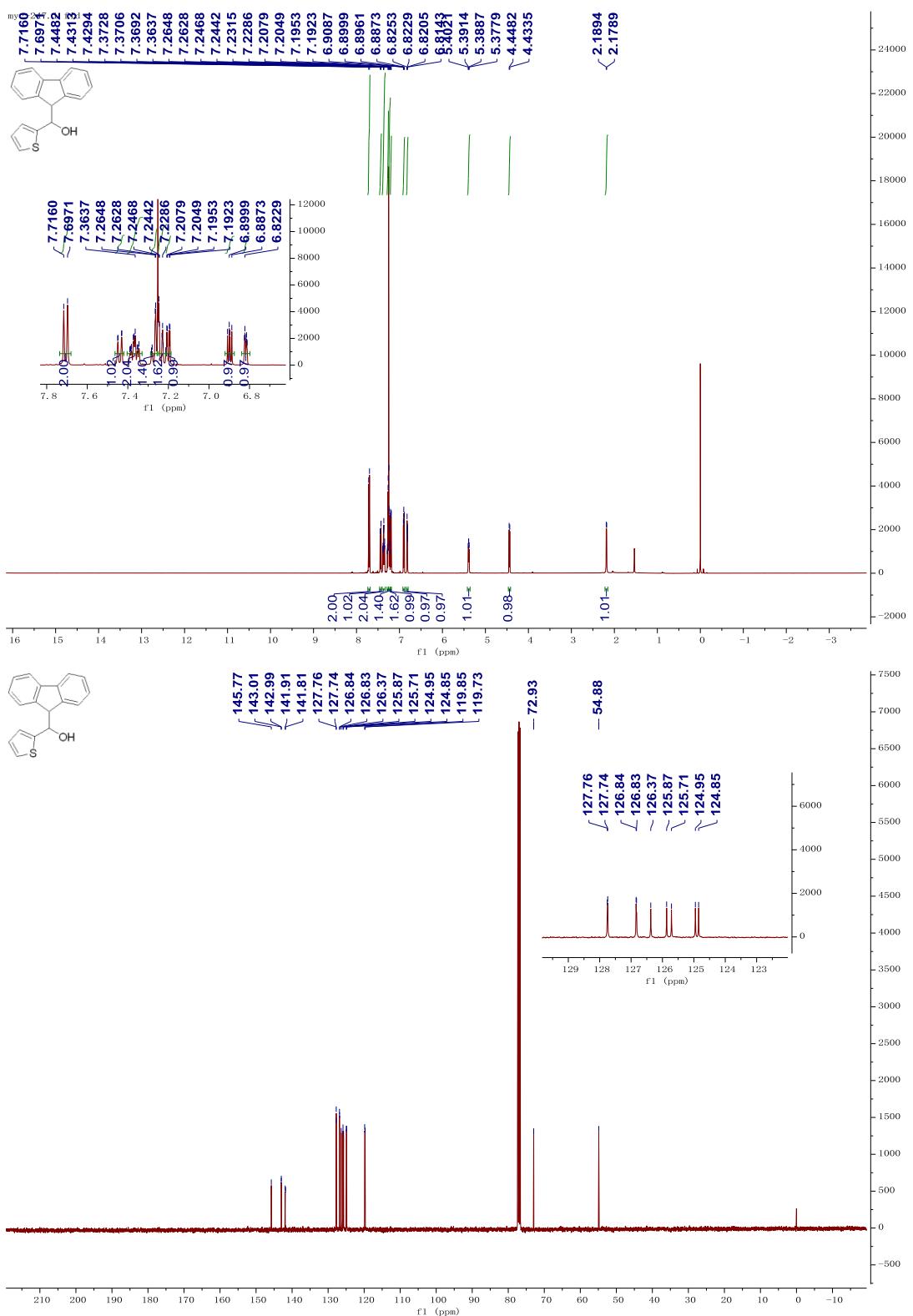
<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4p**



<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4q**



<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4r**



<sup>1</sup>H NMR, <sup>13</sup>C NMR spectrum of **4s**

