

## ***Supporting Information for***

### **Stereoselective synthesis of $\alpha$ -fluoroacrylonitriles through organocatalytic cyanation of *gem*-difluoroalkenes and TMSCN**

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## 1. General methods and typical experimental procedures

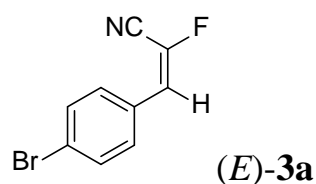
### 1.1 General methods

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 (δ). Gem-difluoroalkenes were prepared according to literature procedure.<sup>[1]</sup> 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. DMF, DMSO CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN were distilled from calcium hydride. Petroleum ether, where used, has a boiling point range of 60–90 °C.

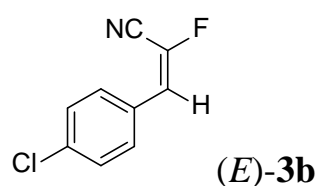
**1.2 General procedure for DBU-catalyzed nucleophilic substitution reaction of gem-difluoroalkenes and trimethylsilyl cyanide:** To a solution of *gem*-difluoroalkene **1a** (0.2 mmol, 44mg) and trimethylsilyl cyanide **2** (0.4 mmol, 52 μL) in 2.0 mL anhydrous DMSO was DBU (3.0 mg, 10 mol%). The mixture was stirred at room temperature until full consumption of **1a** 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 Na<sub>2</sub>SO<sub>4</sub> 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**.

## 2. Spectroscopic data for all products

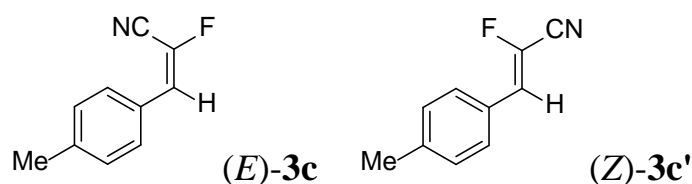


*(E)*-3-(4-bromophenyl)-2-fluoroacrylonitrile (**3a**)<sup>[2]</sup>: yield: 84%, 38 mg; yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 16.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 132.5, 131.4 (d, *J* = 240.0 Hz), 129.8 (d, *J* = 3.3 Hz), 127.1 (d, *J* = 6.6 Hz), 125.1 (d, *J* = 24.0 Hz), 125.0 (d, *J* = 2.2 Hz), 112.2 (d, *J* = 46.8 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -120.7.

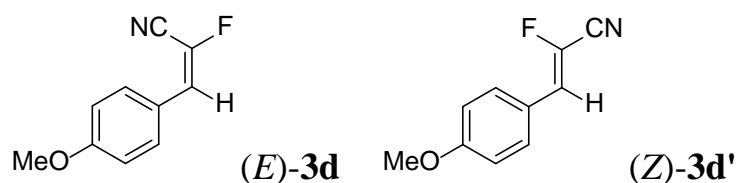


*(E)*-3-(4-chlorophenyl)-2-fluoroacrylonitrile (**3b**)<sup>[3]</sup>: yield: 75%, 27 mg; yellow liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 16.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.7 (d, *J* = 2.2 Hz), 131.4 (d, *J* = 240.6 Hz), 129.6 (d, *J* = 3.2

Hz), 129.5, 126.6 (d,  $J = 6.6$  Hz), 124.9 (d,  $J = 24.9$  Hz), 112.3 (d,  $J = 46.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -121.0.

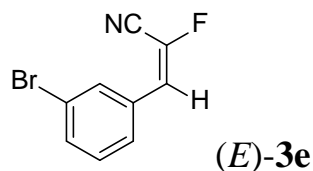


(*E*)-2-fluoro-3-(*p*-tolyl)acrylonitrile (**3c**)<sup>[3]</sup> and  
(*Z*)-2-fluoro-3-(*p*-tolyl)acrylonitrile (**3c'**), a mixture of inseparable regioisomers, **3c/3c'** > 20:1; yield: 59%, 19 mg; colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.48 (d,  $J = 8.2$  Hz, 2H), 7.24 (d,  $J = 8.1$  Hz, 2H), 7.03 (d,  $J = 17.0$  Hz, 1H), 2.39 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  141.1 (d,  $J = 2.2$  Hz), 130.6 (d,  $J = 236.0$  Hz), 129.9, 128.4 (d,  $J = 3.3$  Hz), 126.1 (d,  $J = 24.0$  Hz), 125.2 (d,  $J = 6.3$  Hz), 112.6 (d,  $J = 46.6$  Hz), 21.5;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.1; Representative peak of (**3c'**)  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.90.

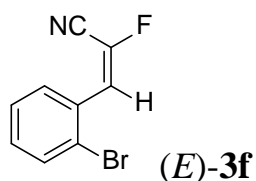


(*E*)-2-fluoro-3-(4-methoxyphenyl)acrylonitrile (**3d**)<sup>[3]</sup> and  
(*Z*)-2-fluoro-3-(4-methoxyphenyl)acrylonitrile (**3d'**), a mixture of inseparable regioisomers, **3d/3d'** > 20:1; yield: 52%, 18 mg; yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 4.0$  Hz, 2H), 7.00 (d,  $J = 17.2$  Hz, 1H), 6.94 (d,  $J = 4.0$  Hz, 2H), 3.85 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4 (d,  $J = 2.1$  Hz), 130.1 (d,  $J = 3.2$  Hz), 129.8 (d,  $J =$

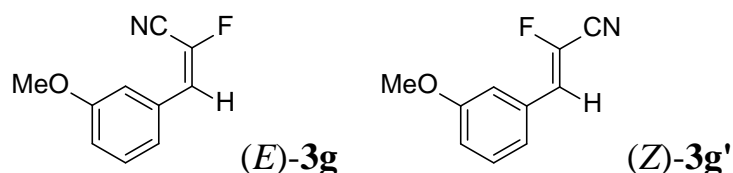
234.0 Hz), 125.8 (d,  $J = 24.4$  Hz), 120.4 (d,  $J = 6.3$  Hz), 114.7, 113.0 (d,  $J = 46.8$  Hz), 55.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.1; Representative peak of (**3d'**)  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.72.



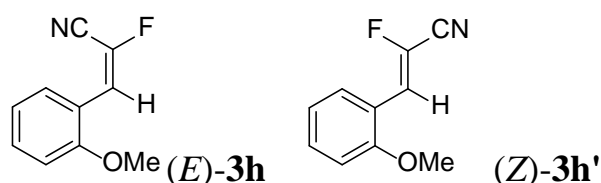
(*E*)-3-(3-bromophenyl)-2-fluoroacrylonitrile (**3e**)<sup>[3]</sup>: yield: 77%, 35 mg; yellow liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (s, 1H), 7.57-7.55 (m, 2H), 7.33-7.30 (m, 1H), 6.99 (d,  $J = 16.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.5 (d,  $J = 2.0$  Hz), 131.9 (d,  $J = 240.0$  Hz) 131.5 (d,  $J = 3.4$  Hz), 130.7, 130.2 (d,  $J = 6.7$  Hz), 126.6 (d,  $J = 3.0$  Hz), 124.5 (d,  $J = 24.9$  Hz), 123.2, 112.0 (d,  $J = 46.7$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -119.3.



(*E*)-3-(2-bromophenyl)-2-fluoroacrylonitrile (**3f**): yield: 65%, 30 mg; colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.73-7.71 (m, 1H), 7.66 (d,  $J = 7.2$  Hz, 1H), 7.43-7.38 (m, 1H), 7.36 (d,  $J = 15.1$  Hz, 1H), 7.32-7.28 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.4, 132.5 (d,  $J = 242.0$  Hz), 131.7 (d,  $J = 1.0$  Hz), 129.1 (d,  $J = 1.0$  Hz), 128.9 (d,  $J = 8.0$  Hz), 128.1, 125.4 (d,  $J = 24.0$  Hz), 124.7 (d,  $J = 5.0$  Hz), 111.8 (d,  $J = 46.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.9.

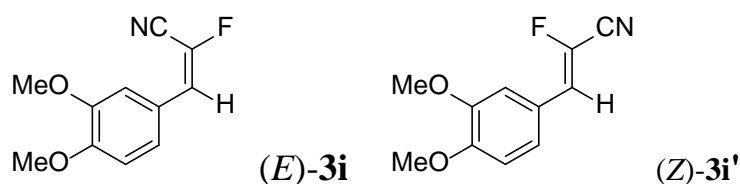


**(E)-2-fluoro-3-(3-methoxyphenyl)acrylonitrile** (**3g**)<sup>[4]</sup> and **(Z)-2-fluoro-3-(3-methoxyphenyl)acrylonitrile** (**3g'**), a mixture of inseparable regioisomers, **3g/3g'** > 20:1; yield: 87%, 31 mg; colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 – 7.31 (m, 1H), 7.17 – 7.12 (m, 2H), 7.03 (d, *J* = 16.7 Hz, 1H), 7.00 – 6.95 (m, 1H), 3.84 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.0, 131.3 (d, *J* = 238.0 Hz), 130.2, 129.3 (d, *J* = 6.5 Hz), 126.0 (d, *J* = 24.1 Hz), 121.1 (d, *J* = 3.3 Hz), 116.7 (d, *J* = 1.9 Hz), 113.1 (d, *J* = 3.0 Hz), 112.5 (d, *J* = 46.9 Hz), 55.4; <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -122.0; Representative peak of (**3g'**) <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -120.84.

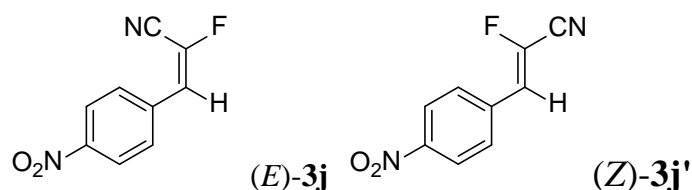


**(E)-2-fluoro-3-(2-methoxyphenyl)acrylonitrile** (**3h**)<sup>[5]</sup> and **(Z)-2-fluoro-3-(2-methoxyphenyl)acrylonitrile** (**3h'**), a mixture of inseparable regioisomers, **3h/3h'** > 20:1; yield: 81%, 29 mg; colorless liquid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.71-7.69 (m, 1H), 7.41 – 7.37 (m, 2H), 7.03 – 7.01 (m, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 3.87 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 157.4 (d, *J* = 3.8 Hz), 131.3 (d, *J* = 236.0 Hz), 132.0 (d, *J* = 1.7 Hz), 128.1 (d, *J* = 1.8 Hz), 121.4 (d, *J* = 25.5 Hz), 120.9, 117.3 (d, *J* = 6.4 Hz), 112.7 (d, *J* = 47.4 Hz), 110.9, 55.5; <sup>19</sup>F NMR (376 MHz,

$\text{CDCl}_3$ )  $\delta$  -121.7; Representative peak of (**3h'**)  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -121.78.

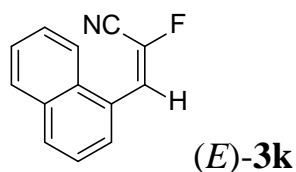


(*E*)-3-(3,4-dimethoxyphenyl)-2-fluoroacrylonitrile (**3i**)<sup>[6]</sup> and (*Z*)-3-(3,4-dimethoxyphenyl)-2-fluoroacrylonitrile (**3i'**), a mixture of inseparable regioisomers, **3i/3i'** = 13:1; yield: 50%, 21 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3i**:  $\delta$  7.23 (d,  $J$  = 2.1 Hz, 1H), 7.13-7.09 (m, 1H), 7.00(d,  $J$  = 17.2 Hz, 1H), 6.89 (d,  $J$  = 8.3 Hz, 1H), 3.92 (d,  $J$  = 1.6 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3i**:  $\delta$  151.10 (d,  $J$  = 2.2 Hz), 149.3, 129.9 (d,  $J$  = 235.2 Hz), 126.2 (d,  $J$  = 24.6 Hz), 123.0 (d,  $J$  = 4.0 Hz), 120.6 (d,  $J$  = 6.2 Hz), 113.2 (d,  $J$  = 46.8 Hz), 111.3, 109.9 (d,  $J$  = 2.4 Hz), 56.0, 55.9;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3i**:  $\delta$  -126.8. Representative peak of (**3i'**)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3i'**:  $\delta$  6.38 (d,  $J$  = 32.0Hz, 1H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.65.

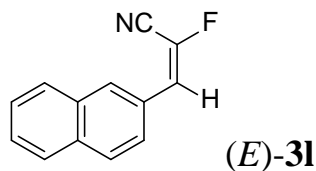


(*E*)-2-fluoro-3-(4-nitrophenyl)acrylonitrile (**3j**)<sup>[5]</sup> and (*Z*)-2-fluoro-3-(4-nitrophenyl)acrylonitrile (**3j'**), a mixture of inseparable regioisomers, **3j/3j'** = 1:5; yield: 84%, 32 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3j'**:  $\delta$  8.28 (d,  $J$  = 8.0 Hz, 2H), 7.75 (d,  $J$  = 8.0Hz, 2H),

6.56 (d,  $J = 33.1$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of **3j'**:  $\delta$  135.6 (d,  $J = 5.0$  Hz), 133.2 (d,  $J = 260.4$  Hz), 130.9 (d,  $J = 8.3$  Hz), 124.2, 123.8 (d,  $J = 25.6$  Hz), 121.2 (d,  $J = 6.4$  Hz), 112.2 (d,  $J = 46.3$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of **3j'**:  $\delta$  -115.2; Representative peak of (**3j**)  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of **3j**: 8.31(d,  $J = 8.0\text{Hz}$ , 2H), 7.76 (d,  $J = 8.0\text{Hz}$ , 2H), 7.14 (d,  $J = 16.0\text{Hz}$ );  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of (**3j**):  $\delta$  129.31 (d,  $J = 3.0\text{Hz}$ ), 124.40;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.8.



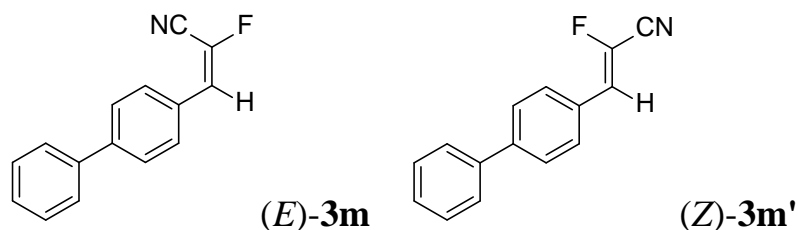
(*E*)-2-fluoro-3-(naphthalen-1-yl)acrylonitrile (**3k**): yield: 70%, 28 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 – 7.83(m, 3H), 7.77 (d,  $J = 7.2\text{Hz}$ , 1H), 7.72 (d,  $J = 14.2\text{Hz}$ , 1H), 7.62 – 7.49 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  133.6, 132.7 (d,  $J = 243.0\text{Hz}$ ), 131.3 (d,  $J = 3.1$  Hz), 131.0, 129.0, 127.2, 126.8 (d,  $J = 1.9$  Hz), 126.7, 125.5, 125.3 (d,  $J = 6.0$  Hz), 123.9 (d,  $J = 22.6$  Hz), 123.2, 112.1 (d,  $J = 46.9$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.8.



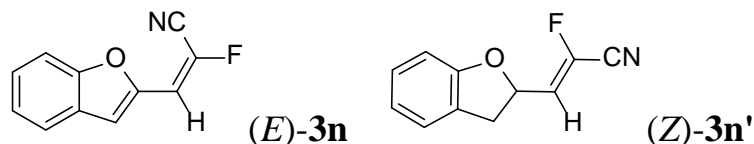
(*E*)-2-fluoro-3-(naphthalen-2-yl)acrylonitrile (**3l**)<sup>[51]</sup>: yield: 77%, 30 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (s, 1H), 7.87-7.82 (m, 3H), 7.71 (dd,  $J = 8.6, 1.9$  Hz, 1H), 7.61 – 7.46 (m, 2H), 7.17 (d,  $J = 16.9$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.0 (d,  $J = 1.4$  Hz), 133.1,



131.2 (d,  $J = 238.5$  Hz), 129.5 (d,  $J = 4.6$  Hz), 129.1, 128.5, 127.8, 127.7, 127.1, 126.2 (d,  $J = 24.4$  Hz), 125.5 (d,  $J = 6.3$  Hz), 124.1 (d,  $J = 2.1$  Hz), 112.7 (d,  $J = 46.6$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -121.9.

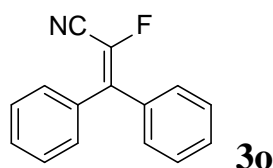


(*E*)-3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylonitrile (**3m**)<sup>[3]</sup> and (*Z*)-3-([1,1'-biphenyl]-4-yl)-2-fluoroacrylonitrile (**3m'**), a mixture of inseparable regioisomers, **3m/3m'** > 20:1; yield: 85%, 38 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (s, 4H), 7.62 – 7.57 (m, 2H), 7.49 – 7.43 (m, 2H), 7.42 – 7.35 (m, 1H), 7.08 (d,  $J = 16.8$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4 (d,  $J = 2.2$  Hz), 139.8, 131.0 (d,  $J = 237.0$  Hz), 129.0, 128.9 (d,  $J = 3.2$  Hz), 128.1, 127.8, 127.1, 127.0 (d,  $J = 6.4$  Hz), 125.7 (d,  $J = 24.4$  Hz), 112.7 (d,  $J = 46.8$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.4; Representative peak of (**3m'**)  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -121.54.

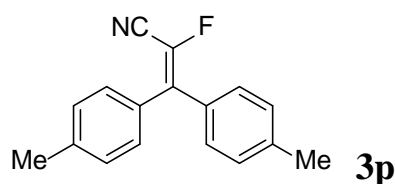


(*E*)-3-(benzofuran-2-yl)-2-fluoroacrylonitrile (**3n**) and (*Z*)-3-(benzofuran-2-yl)-2-fluoroacrylonitrile (**3n'**), a mixture of inseparable regioisomers, **3n/3n'** > 20:1; yield: 83%, 31 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.62-7.58 (m, 1H), 7.55-7.51 (m, 1H),

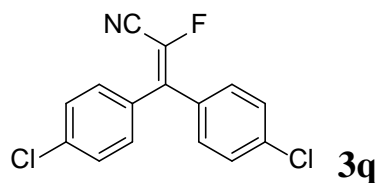
7.42-7.36 (m, 1.3 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.08 (s, 1H), 6.98 (d,  $J = 14.0$  Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.4(d,  $J = 2.3$  Hz), 145.3 (d,  $J = 7.6$  Hz), 131.5 (d,  $J = 242.8$  Hz), 127.7, 126.9 (d,  $J = 1.5$  Hz), 123.8, 121.7, 114.8 (d,  $J = 30.0$  Hz), 112.1 (d,  $J = 45.1$  Hz), 111.7, 111.5 (d,  $J = 9.4$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -122.6; Representative peak of (**3n'**)  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -116.90.



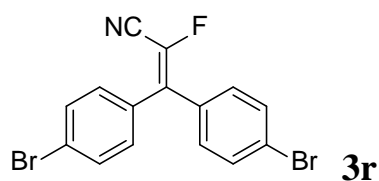
2-fluoro-3,3-diphenylacrylonitrile (**3o**)<sup>[31]</sup>: yield: 96%, 43 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 – 7.40(m, 3H), 7.40 – 7.33 (m, 5H), 7.33 – 7.29 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.7 (d,  $J = 10.9$  Hz), 134.0, 133.9, 133.8, 133.7, 130.2 (d,  $J = 5.6$  Hz), 130.1 (d,  $J = 3.0$  Hz), 130.0, 129.1 (d,  $J = 247.7$  Hz), 128.7 (d,  $J = 36.9$  Hz), 113.2 (d,  $J = 46.1$  Hz);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -124.1.



2-fluoro-3,3-di-p-tolylacrylonitrile (**3p**)<sup>[31]</sup>: yield: 93%, 47 mg; white solid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.3 – 7.2 (m, 8H), 2.4 (s, 3H), 2.4 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.4, 140.3, 140.2, 138.7 (d,  $J = 10.8$  Hz), 131.1 (d,  $J = 4.4$  Hz), 131.0 (d,  $J = 3.0$  Hz), 130.2 (d,  $J = 5.7$  Hz), 130.1 (d,  $J = 2.9$  Hz), 129.4 (d,  $J = 35.9$  Hz), 128.6 (d,  $J = 246.0$  Hz), 113.6 (d,  $J = 46.5$  Hz), 21.5, 21.4;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -125.7.



3,3-bis(4-chlorophenyl)-2-fluoroacrylonitrile (**3q**)<sup>[3]</sup>: yield: 98%, 57 mg; white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.46 – 7.41 (m, 2H), 7.40 – 7.35 (m, 2H), 7.32 – 7.27 (m, 2H), 7.26 – 7.22 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 136.6, 136.5 (d, *J* = 1.8 Hz), 136.5 (d, *J* = 2.0 Hz), 136.4, 131.8, 131.7 (d, *J* = 5.0 Hz), 131.5, 131.4, 129.4 (d, *J* = 250.0 Hz), 129.2 (d, *J* = 42.0 Hz), 112.8 (d, *J* = 45.9 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -122.2 .



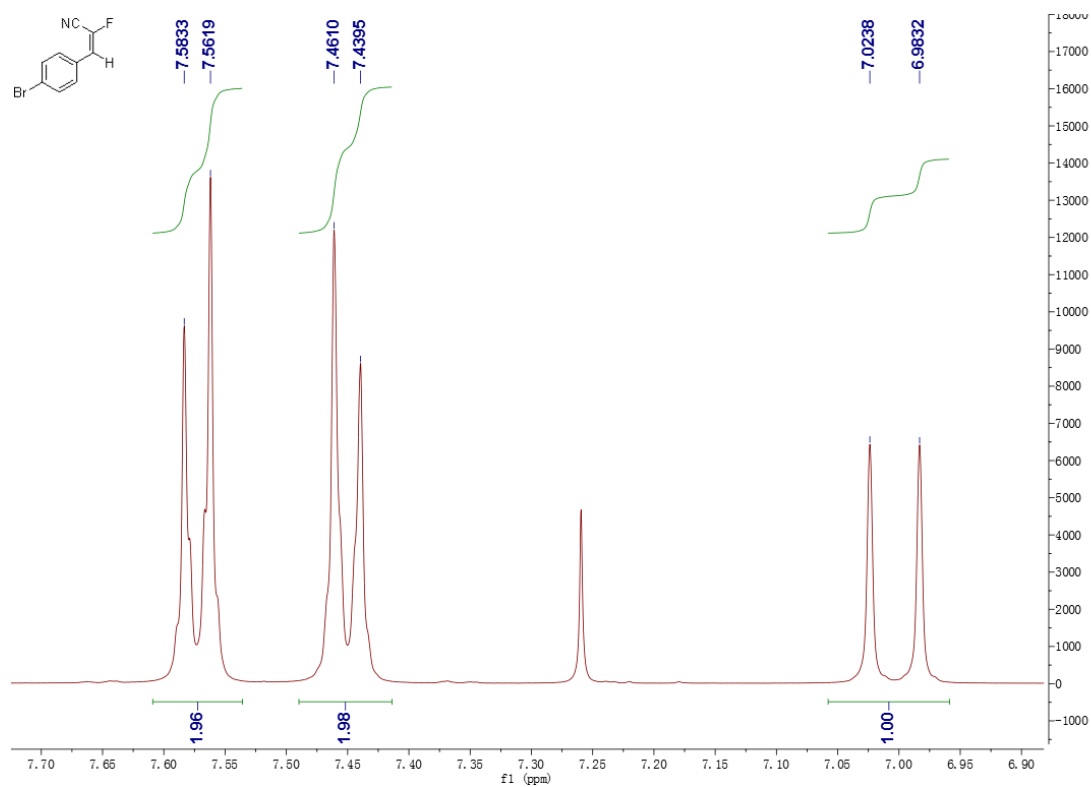
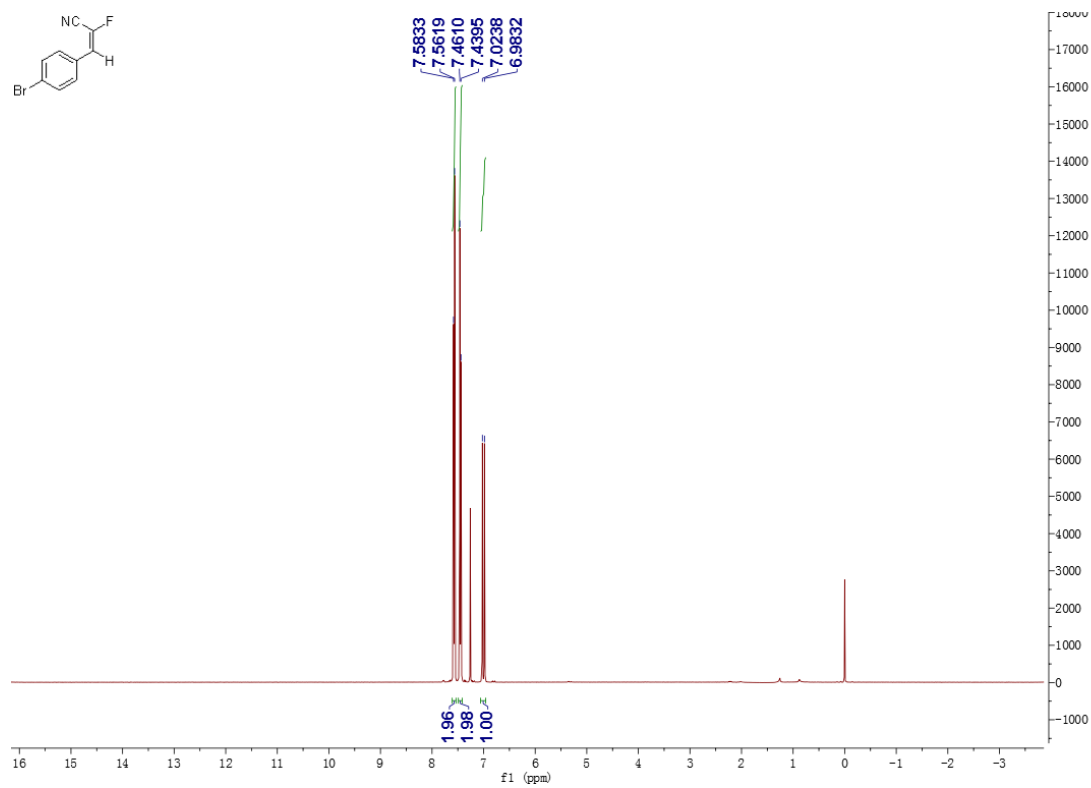
3,3-bis(4-bromophenyl)-2-fluoroacrylonitrile (**3r**)<sup>[3]</sup>: yield: 95%, 72 mg; White solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.6 – 7.6 (m, 2H), 7.6 – 7.5 (m, 2H), 7.2 – 7.2 (m, 2H), 7.2 – 7.1 (m, 2H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.7, 136.5, 132.2 (d, *J* = 4.0 Hz), 132.1 (d, *J* = 3.1 Hz), 132.1 (d, *J* = 4.4 Hz), 131.6 (d, *J* = 2.1 Hz), 131.5, 129.3 (d, *J* = 251.6 Hz), 125.0, 124.9 (d, *J* = 1.8 Hz), 112.7 (d, *J* = 46.2 Hz); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -122.0.

### 3. Reference

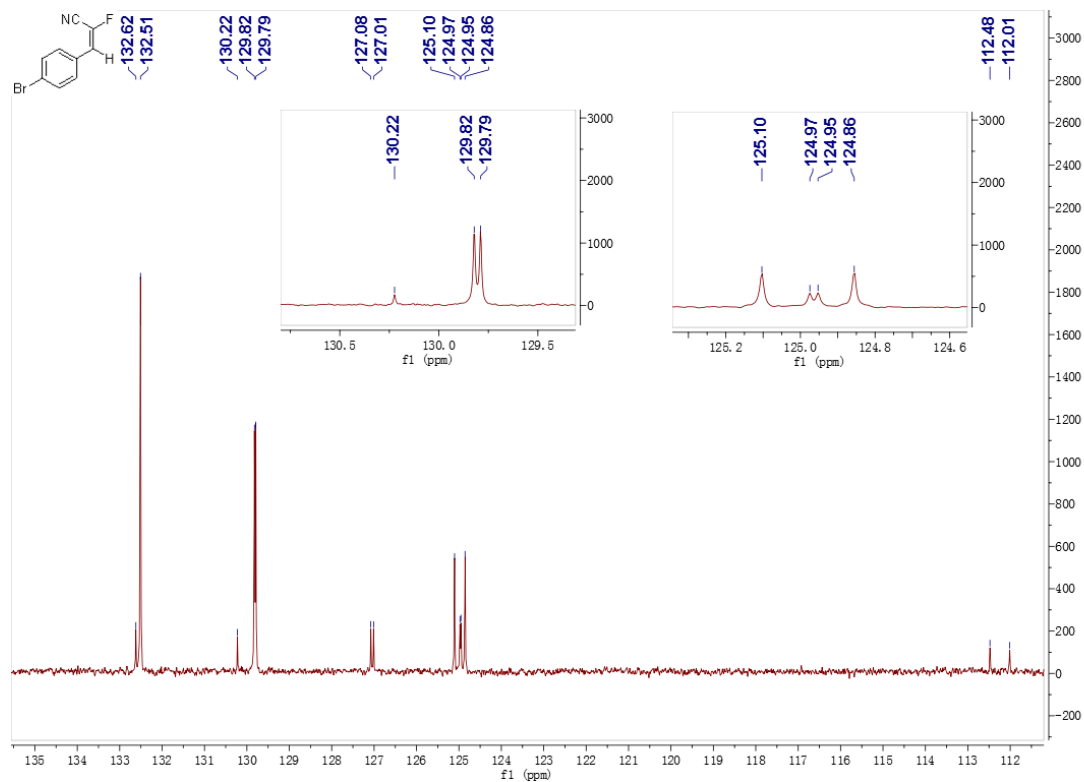
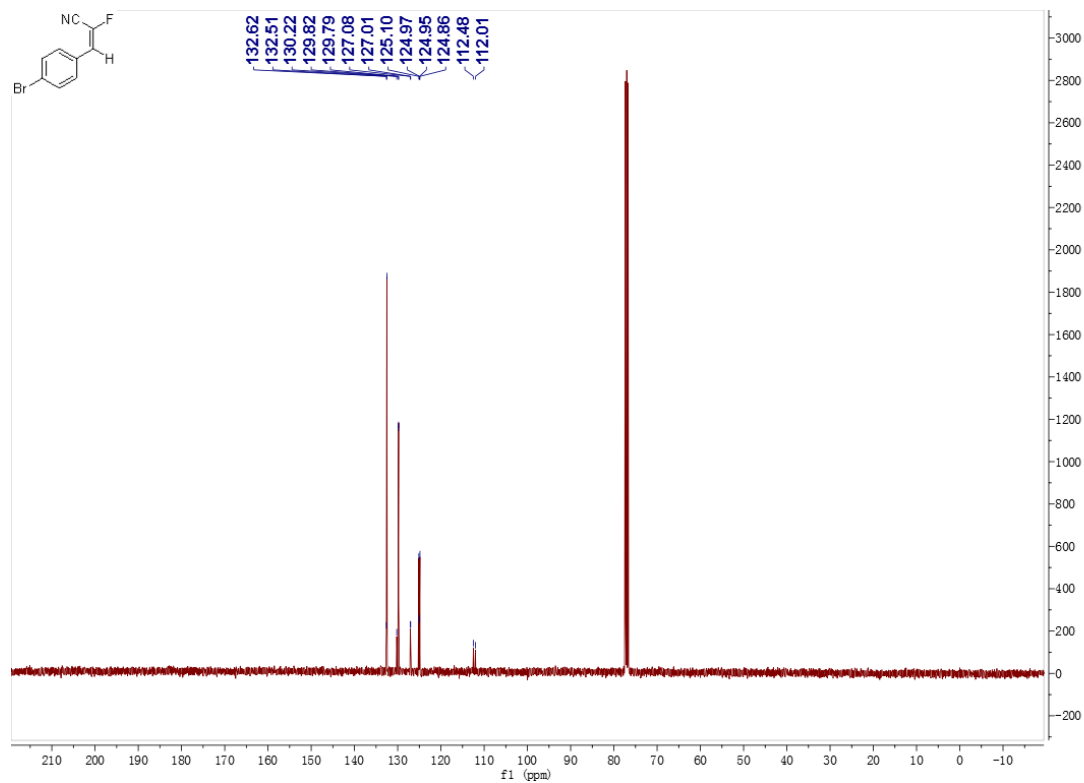
- [1] C. S. Thomason, H. Martinez, W. R. Dolbier Jr. *J. Fluorine Chem.*, 2013, **150**, 53.
- [2] S. Eddarir, M. Kadjout, C. Rolando. *Tetrahedron.*, 2012, **68**, 603.
- [3] J. Zhang, C. Xu, W. Wu, S. Cao. *Chem. Eur. J.*, 2016, **22**, 9902.
- [4] CAS number: 2122856-63-5
- [5] M. del Solar, A. K. Ghosh, B. Zajc. *J. Org. Chem.*, 2008, **73**, 8206
- [6] V.G. Nenajdenko, V. M. Muzalevskiy, A. V. Shastin, E. S. Balenkova, G. Haufe, *J. Fluorine Chem.*, 2007, **128**, 818

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

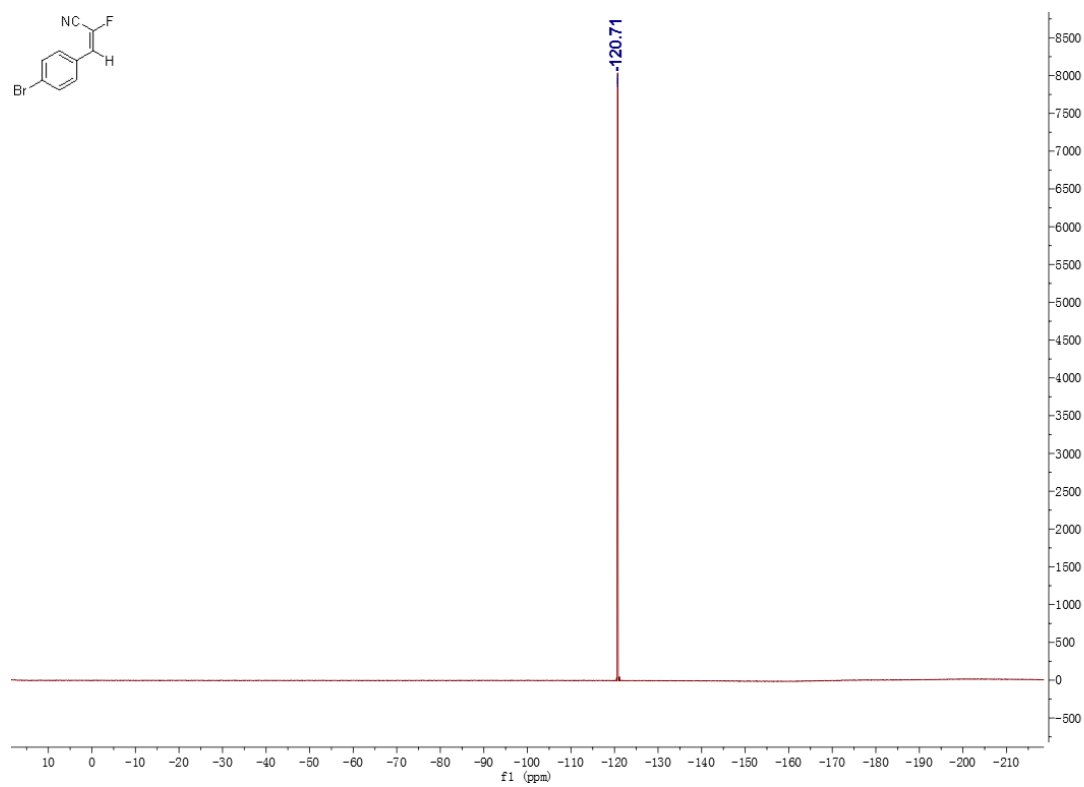
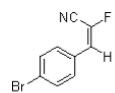
$^1\text{H}$  NMR spectrum of (*E*)-**3a**



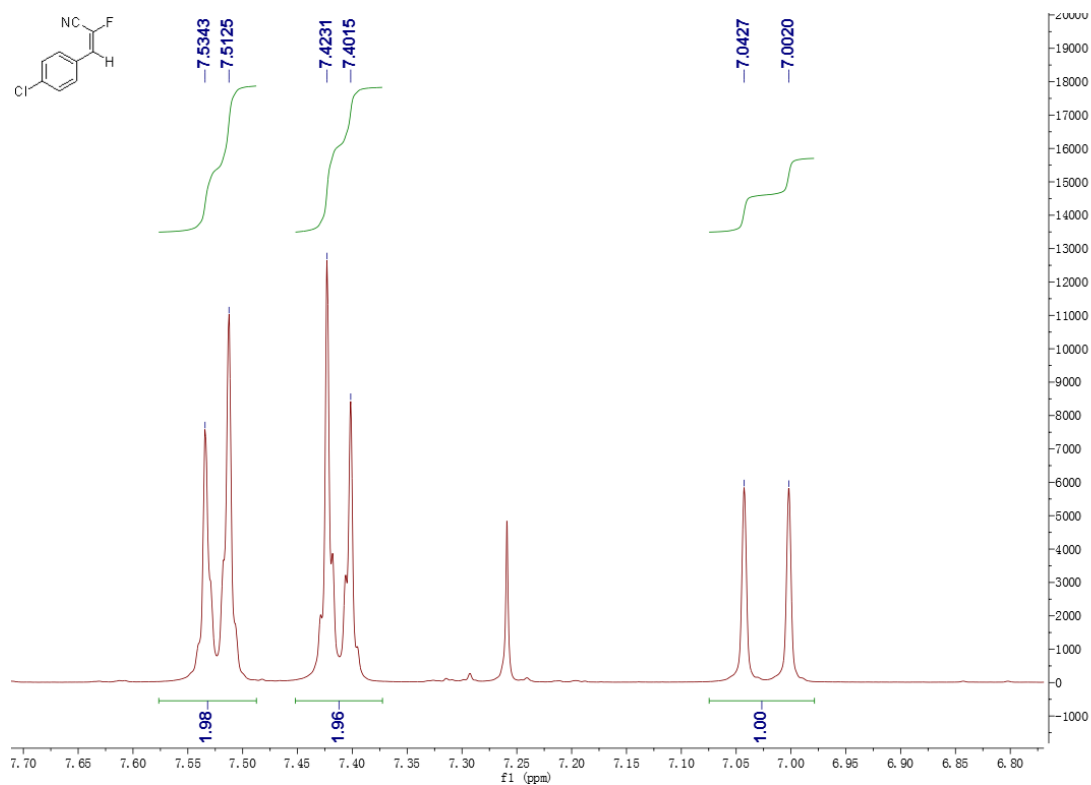
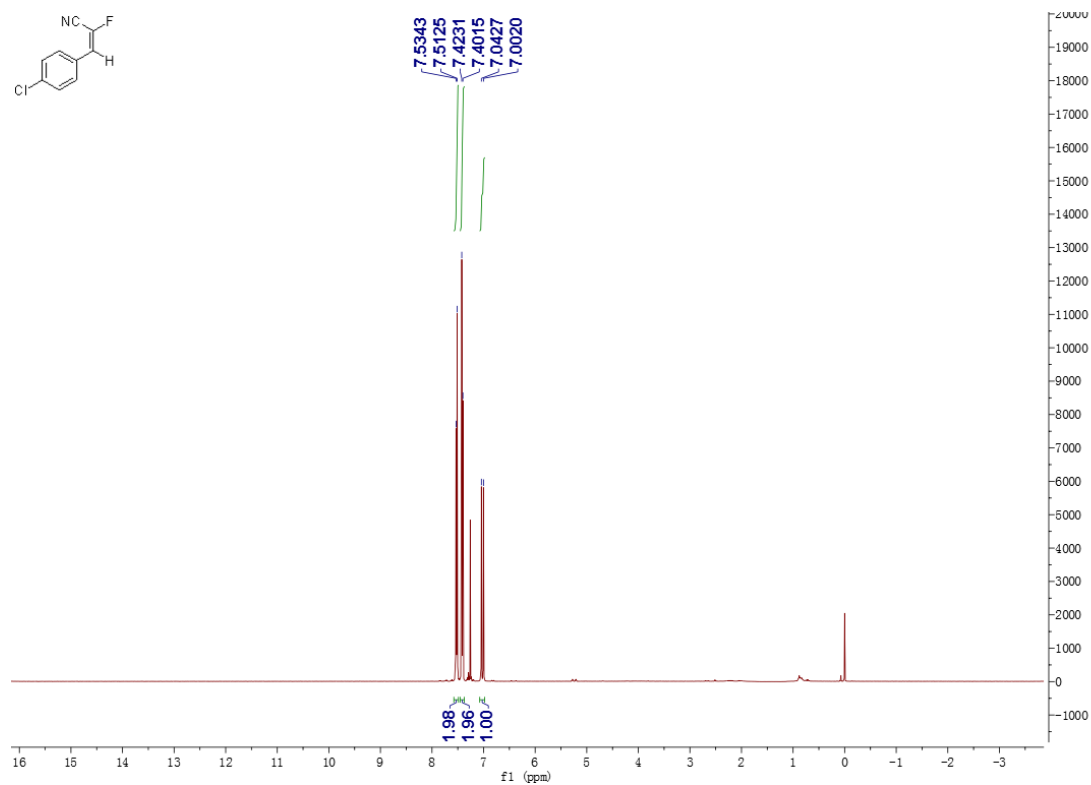
<sup>13</sup>C NMR spectrum of (*E*)-**3a**



$^{19}\text{F}$  NMR spectrum of (*E*)-**3a**

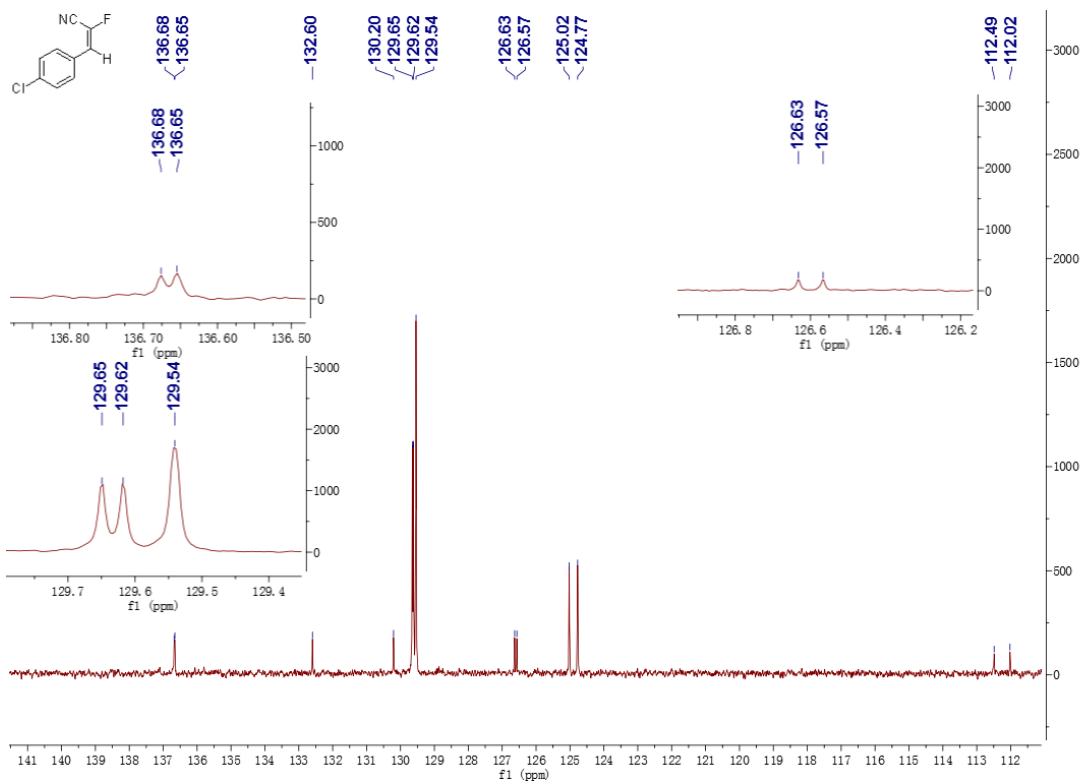
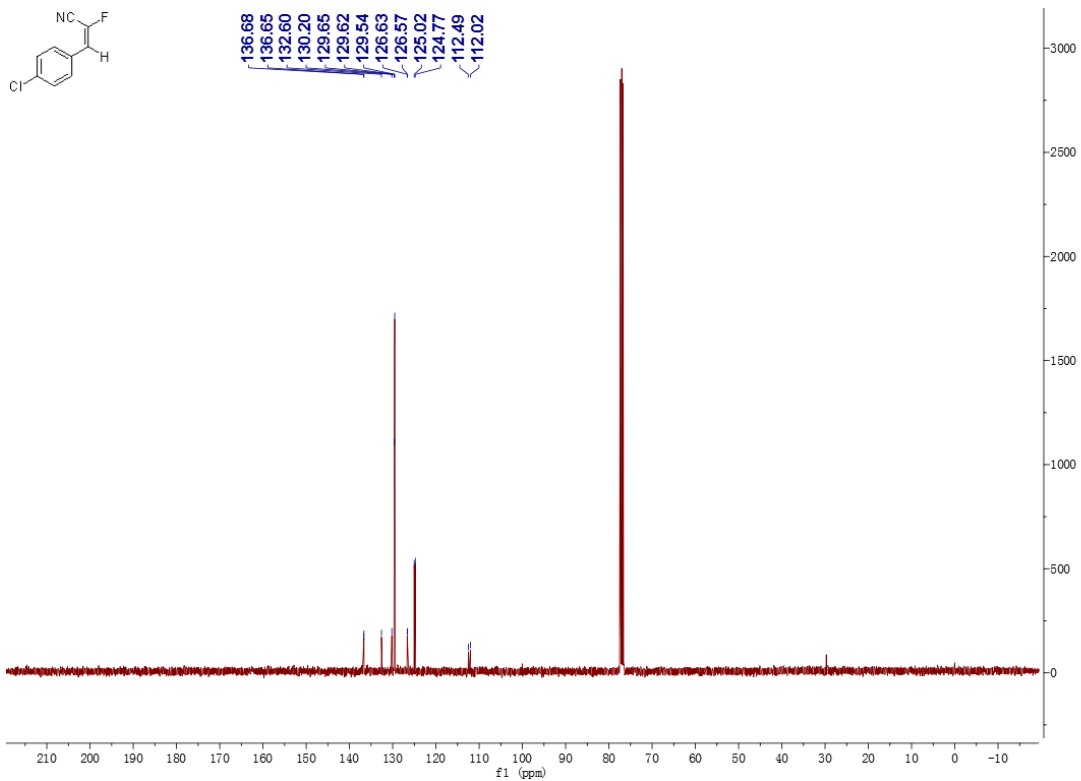


# <sup>1</sup>H NMR spectrum of (*E*)-**3b**

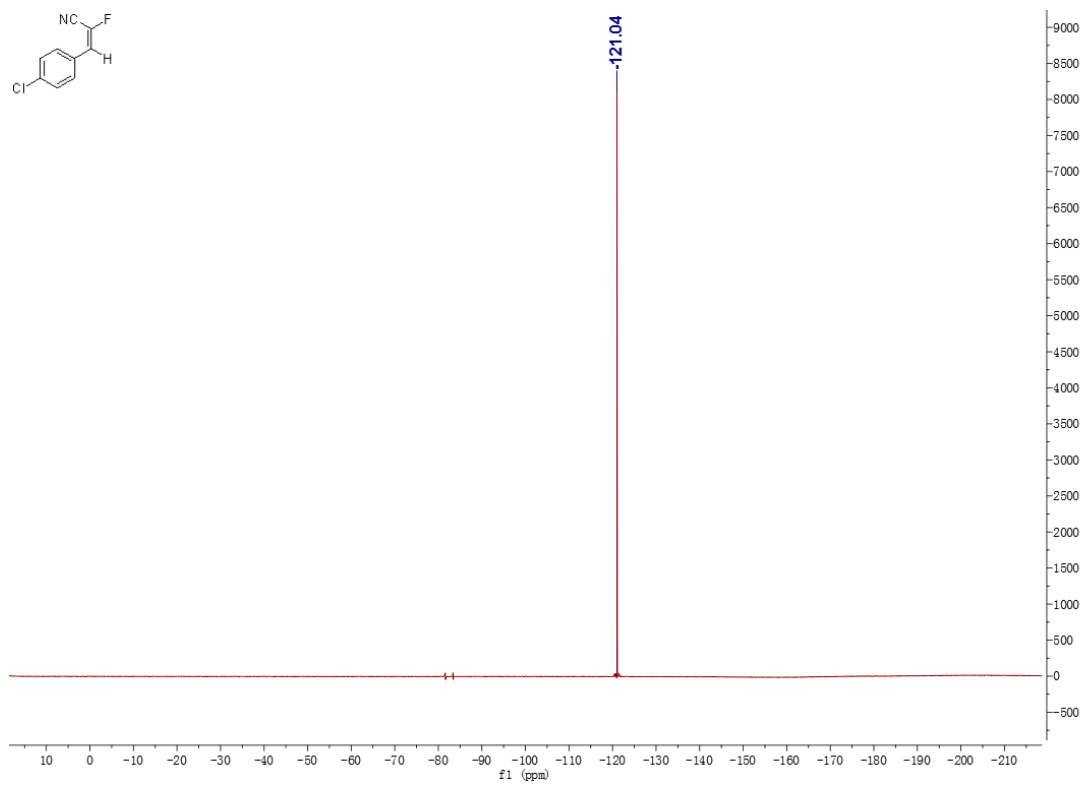




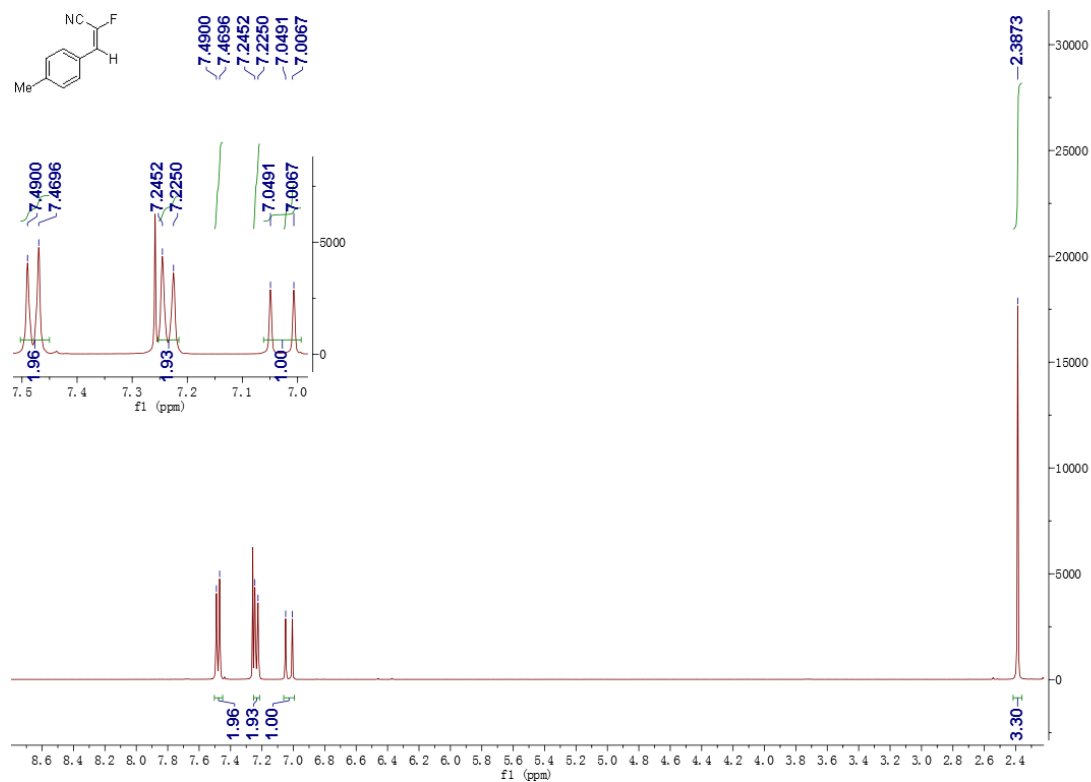
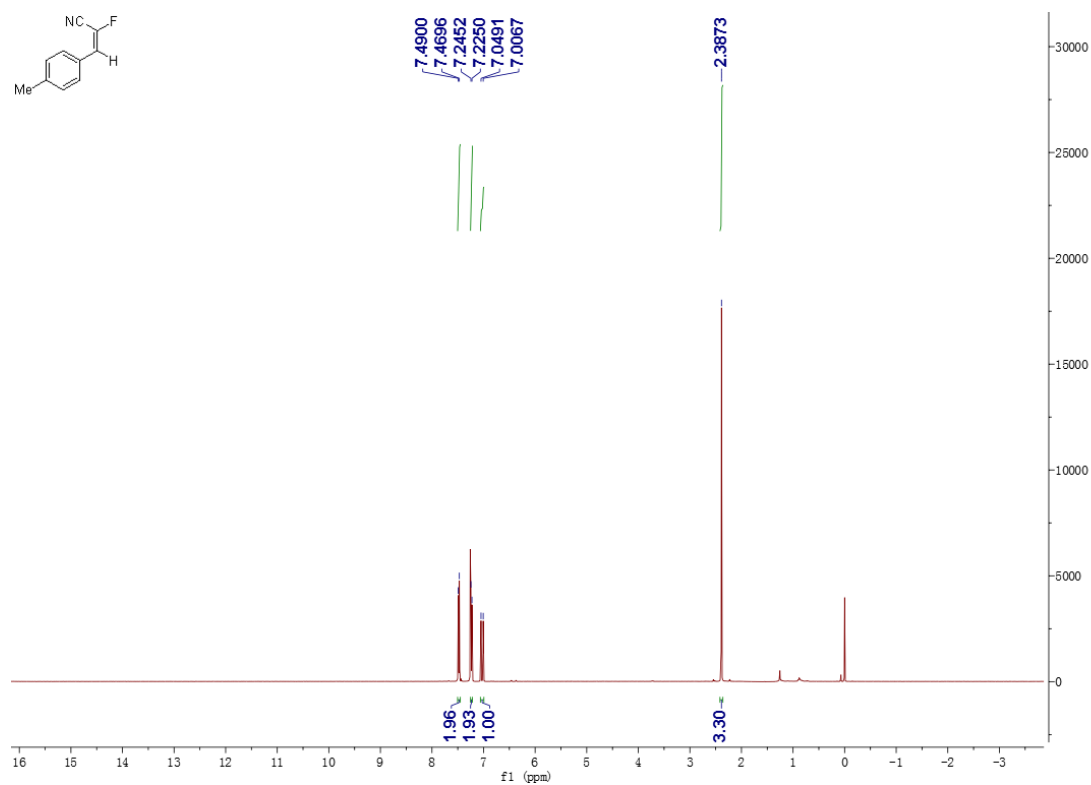
# <sup>13</sup>C NMR spectrum of (*E*)-**3b**



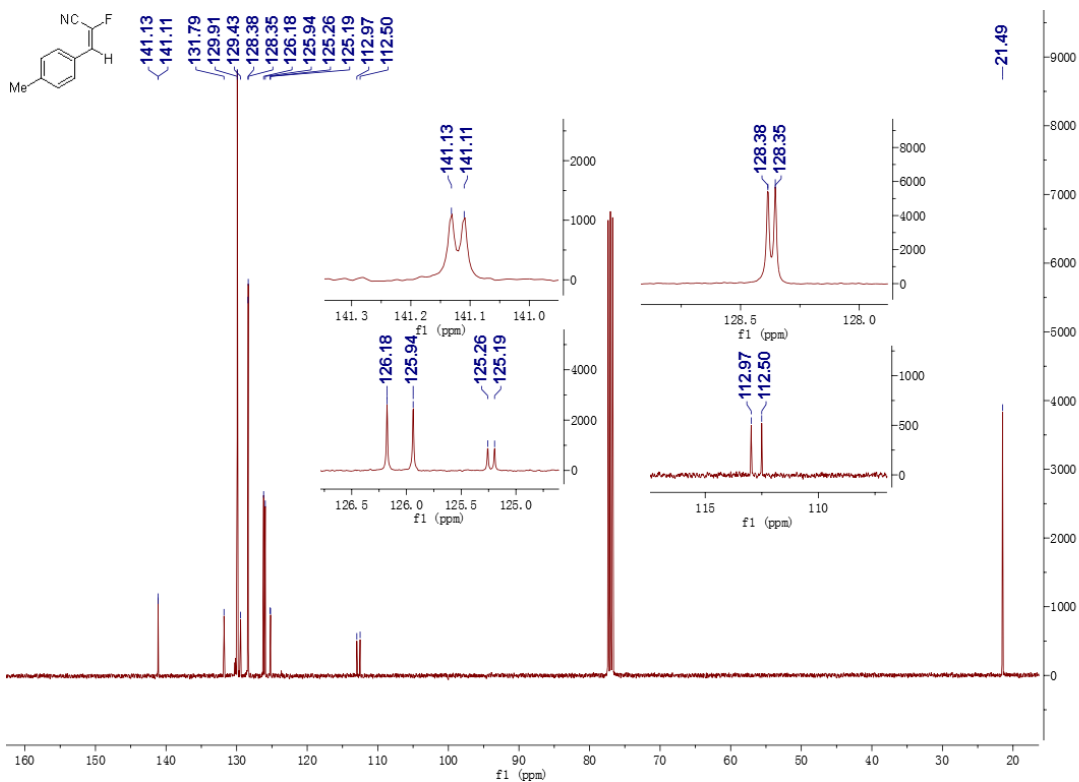
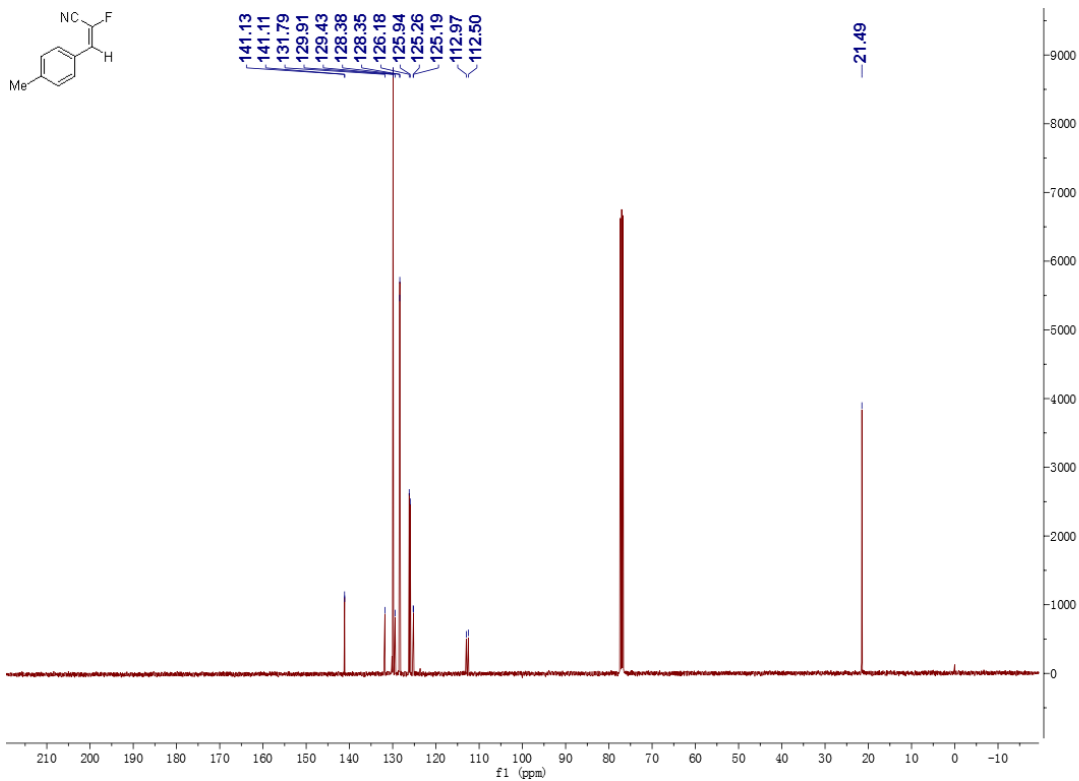
$^{19}\text{F}$  NMR spectrum of (*E*)-**3b**



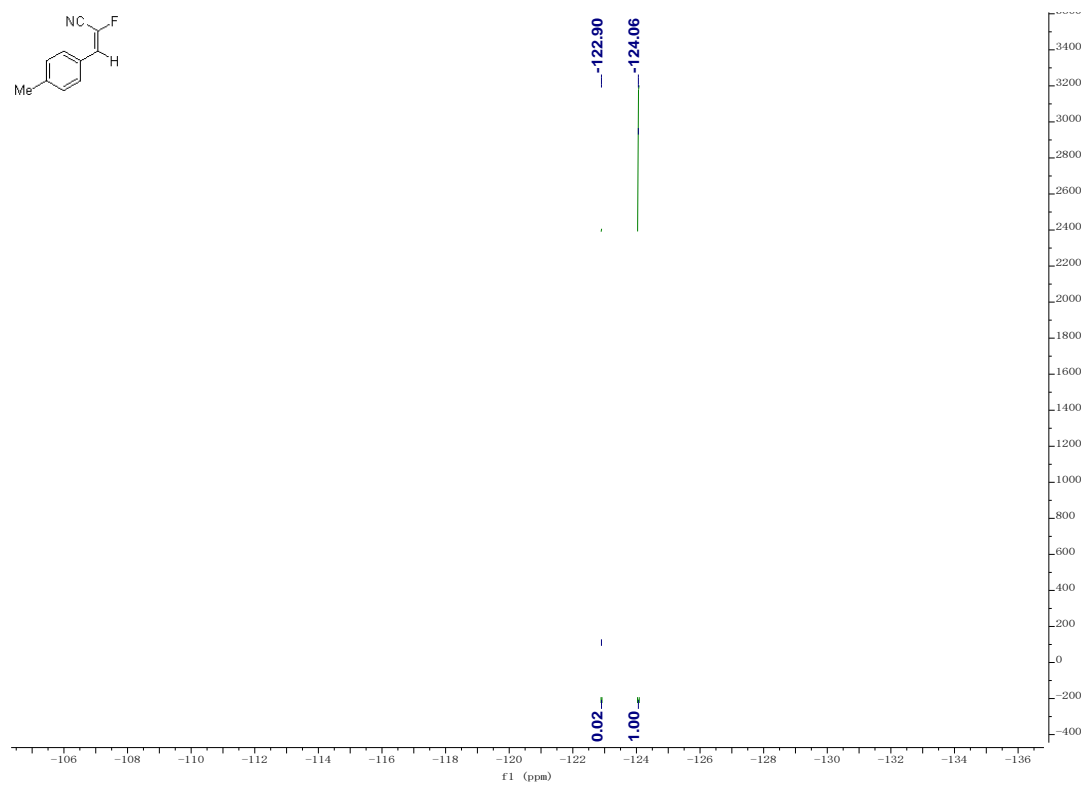
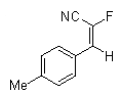
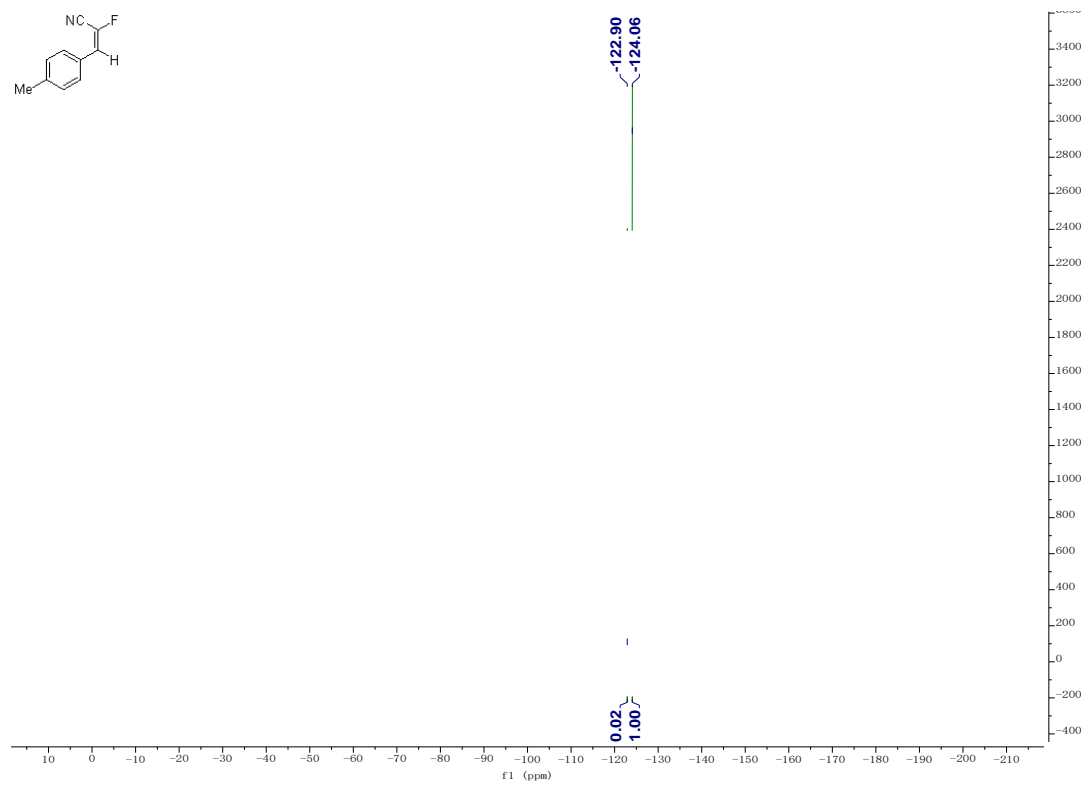
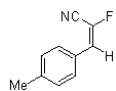
# <sup>1</sup>H NMR spectrum of (*E*)-3c



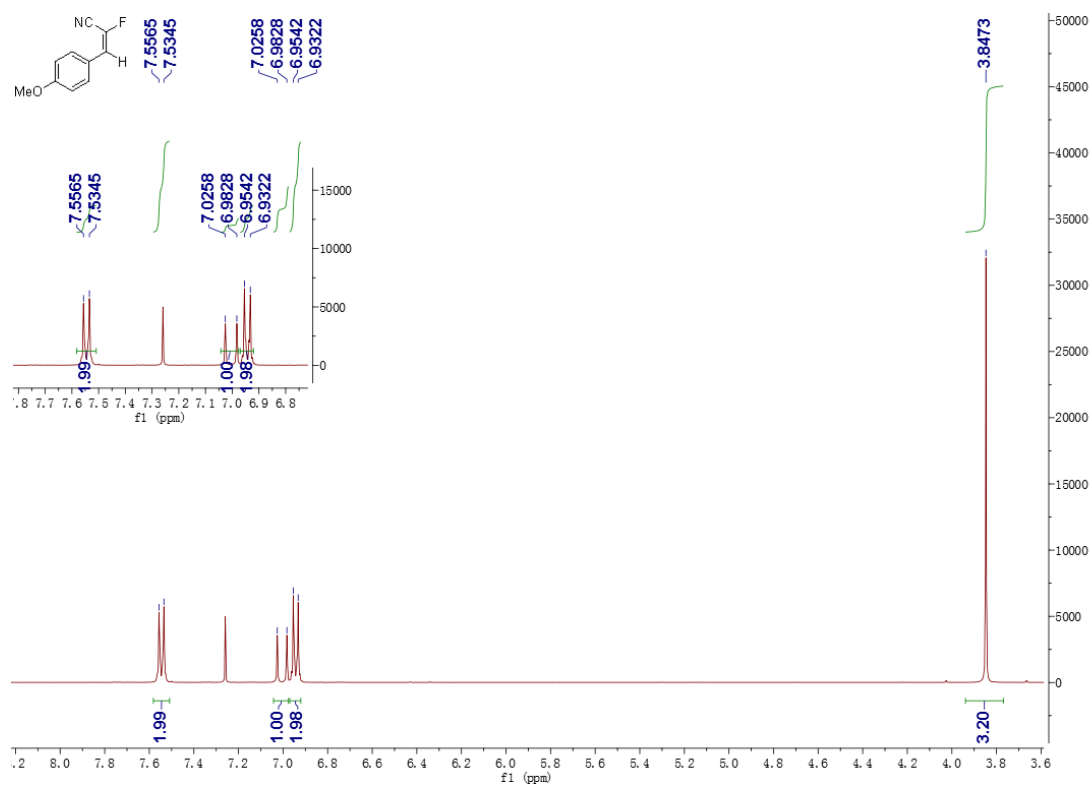
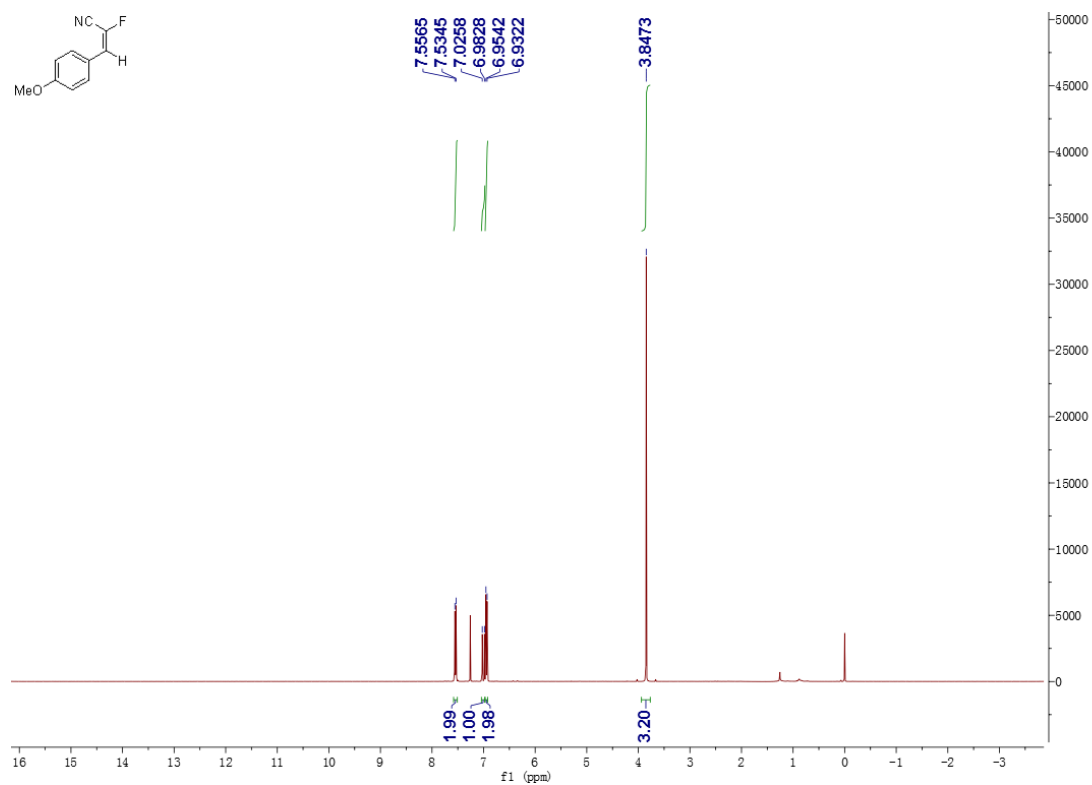
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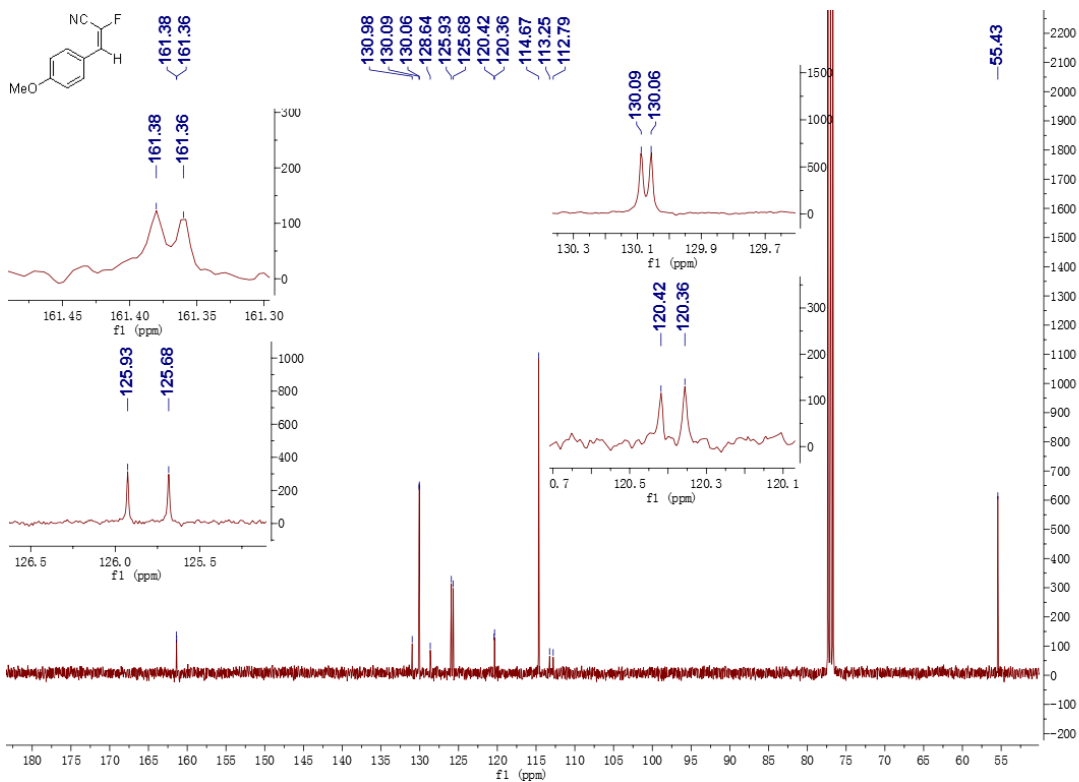
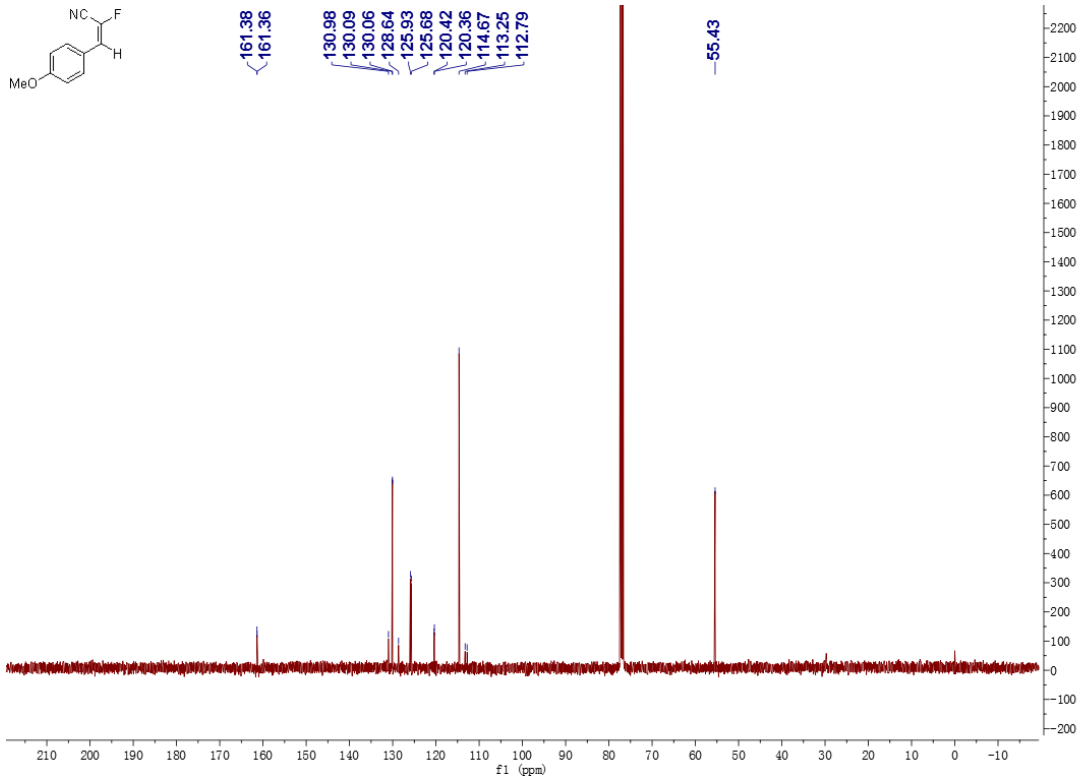
<sup>19</sup>F NMR spectrum of (*E*)-**3c**



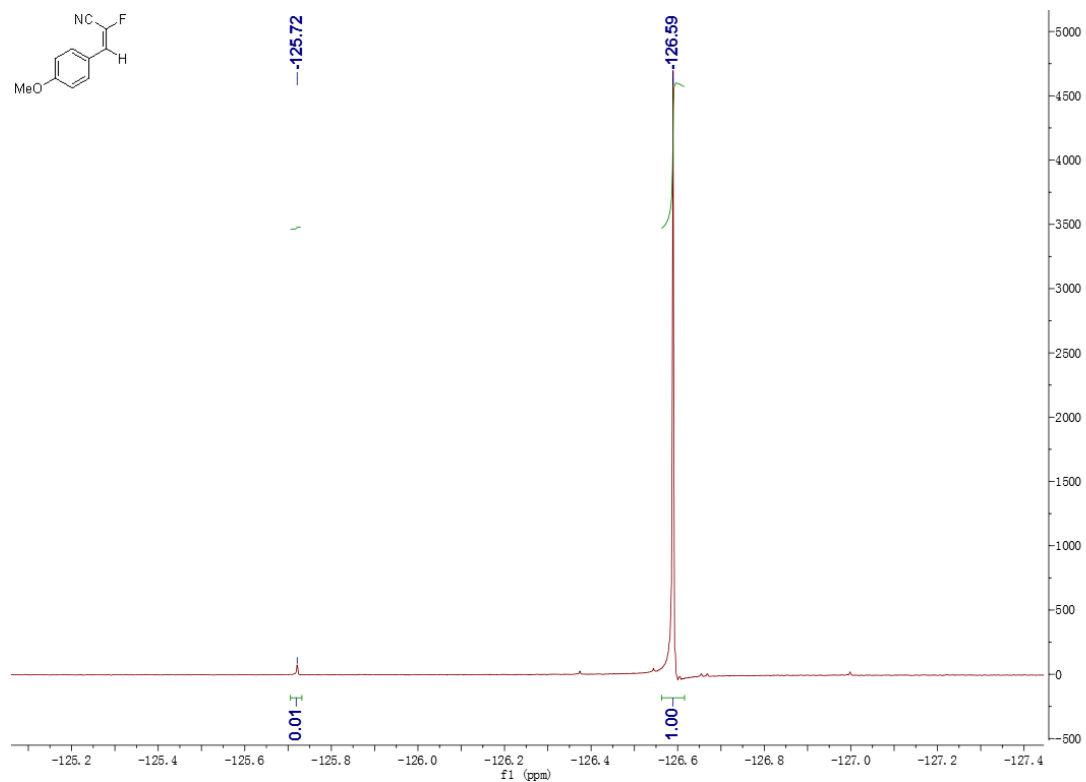
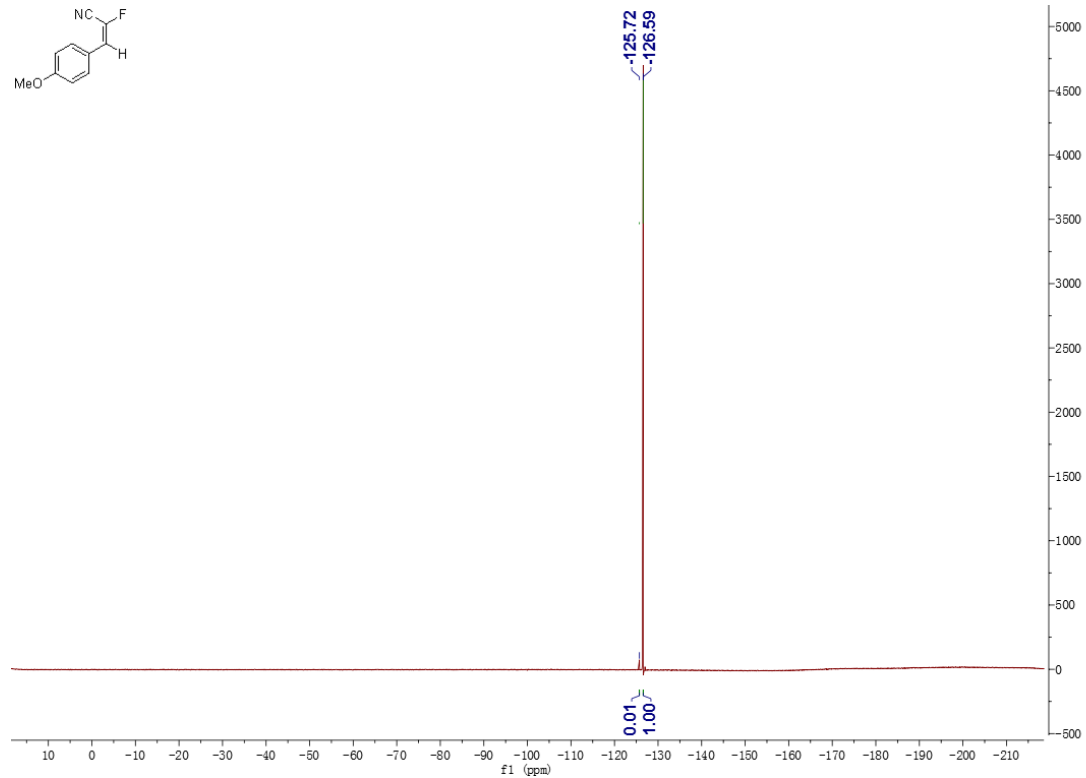
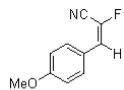
# <sup>1</sup>H NMR spectrum of (*E*)-3d



# <sup>13</sup>C NMR spectrum of (*E*)-3d

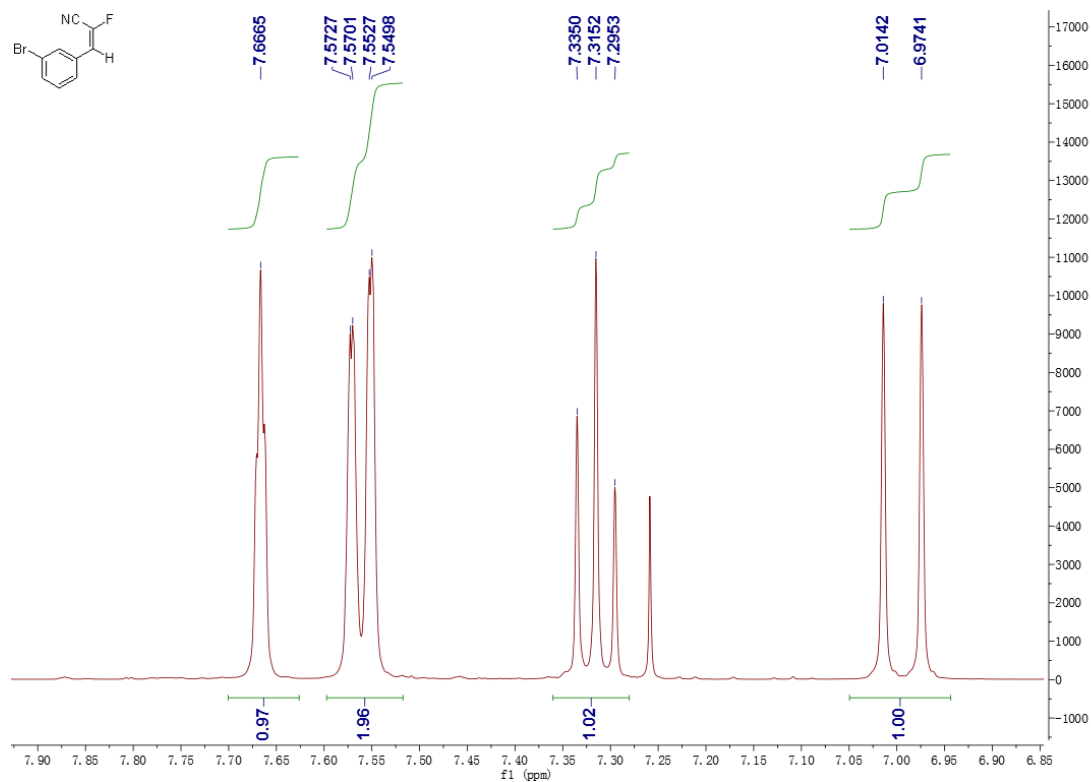
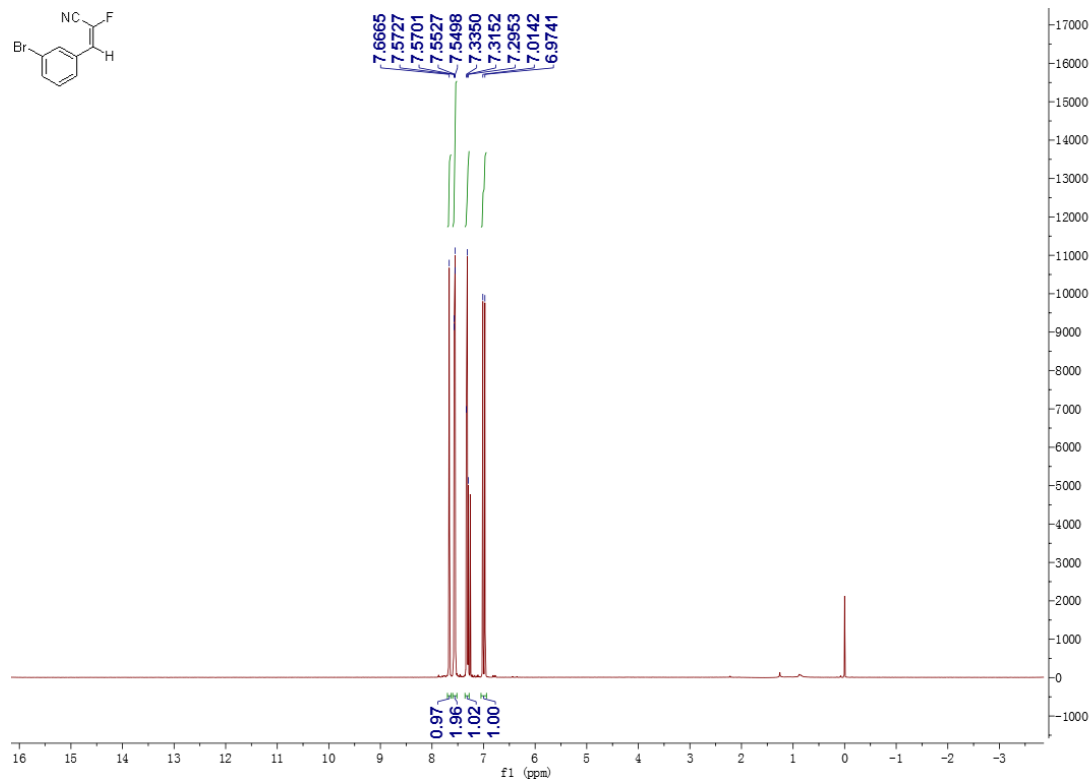


<sup>19</sup>F NMR spectrum of (*E*)-**3d**

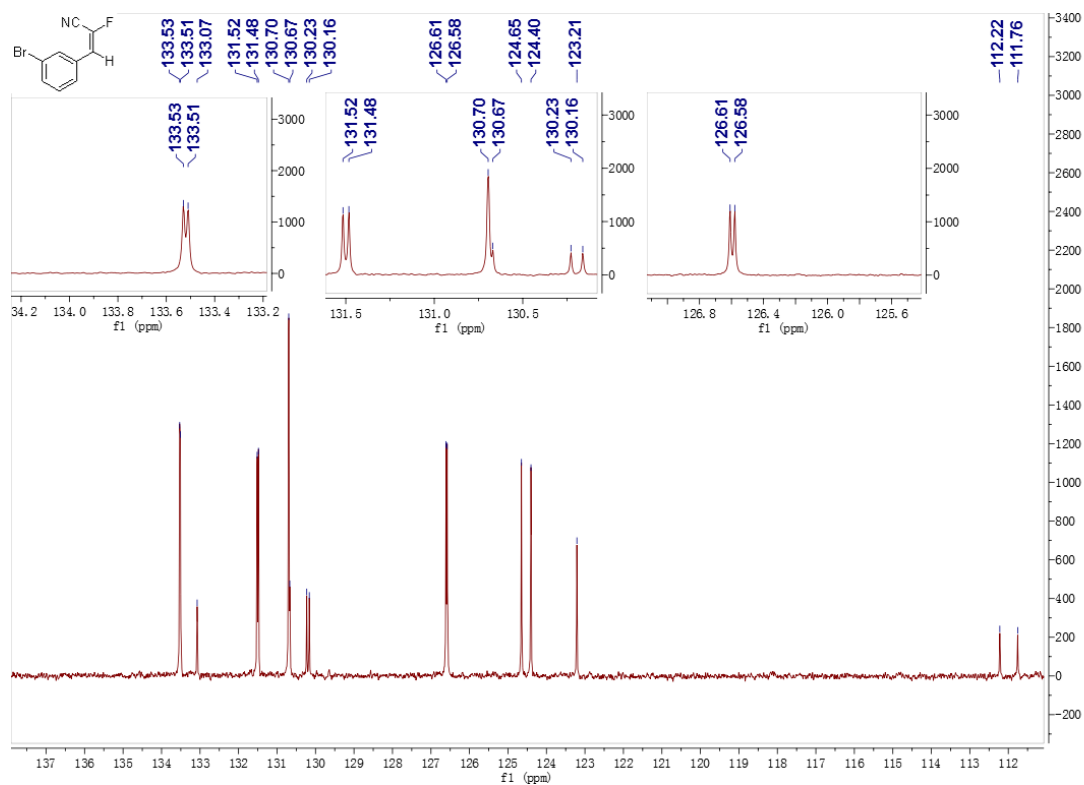
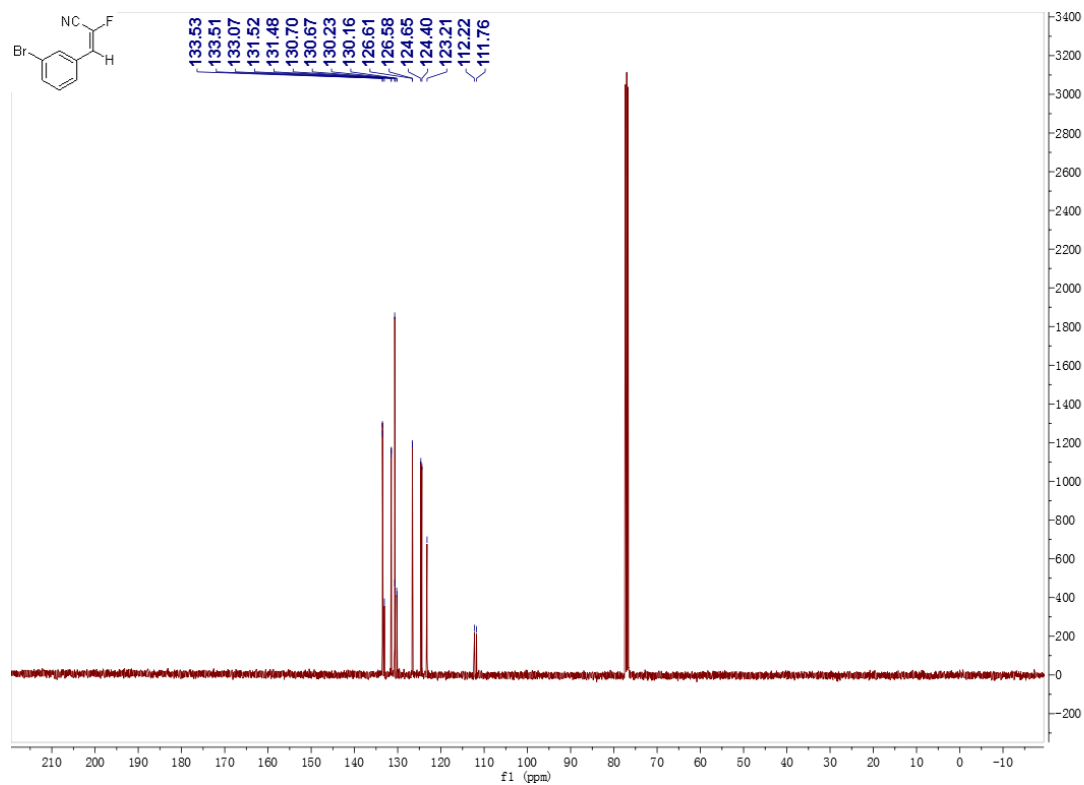




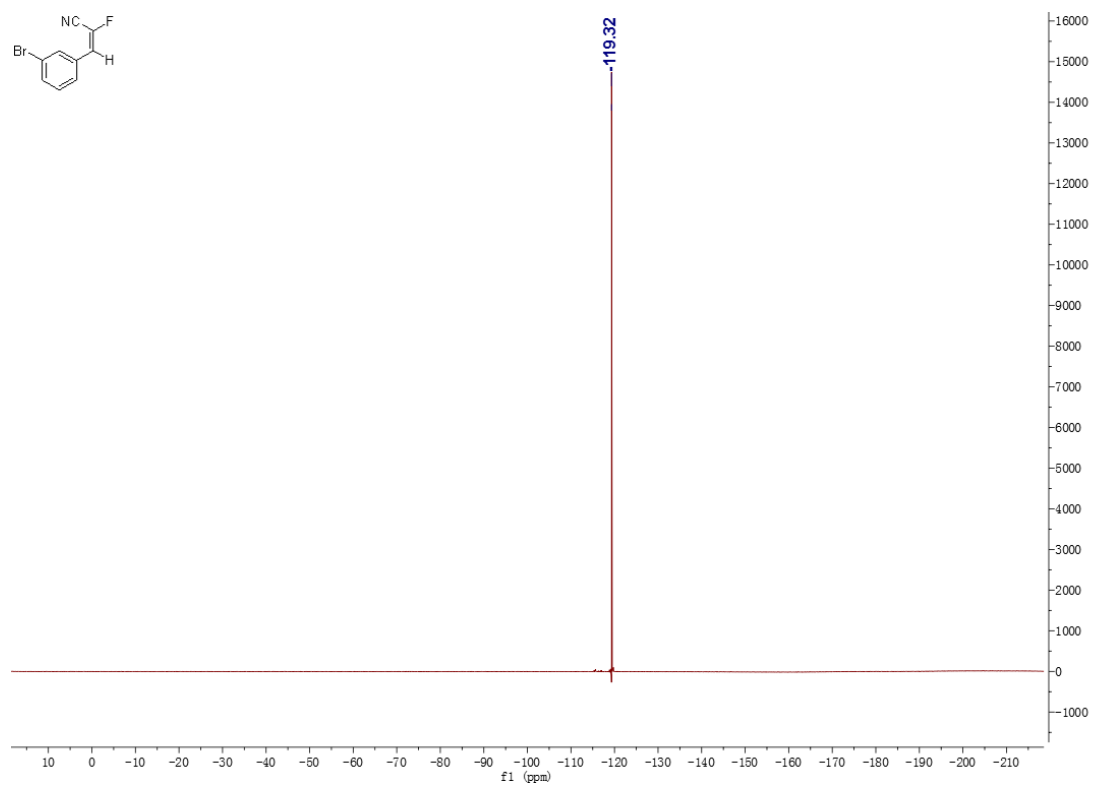
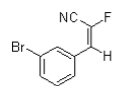
# $^1\text{H}$ NMR spectrum of (*E*)-3e



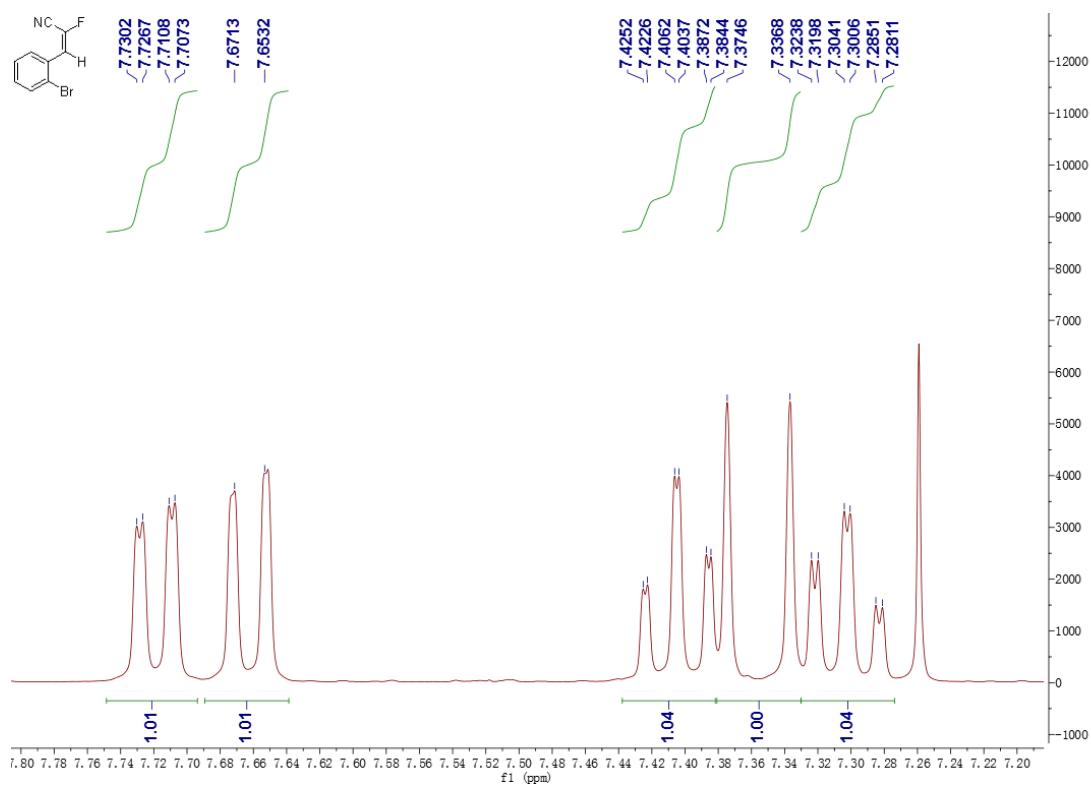
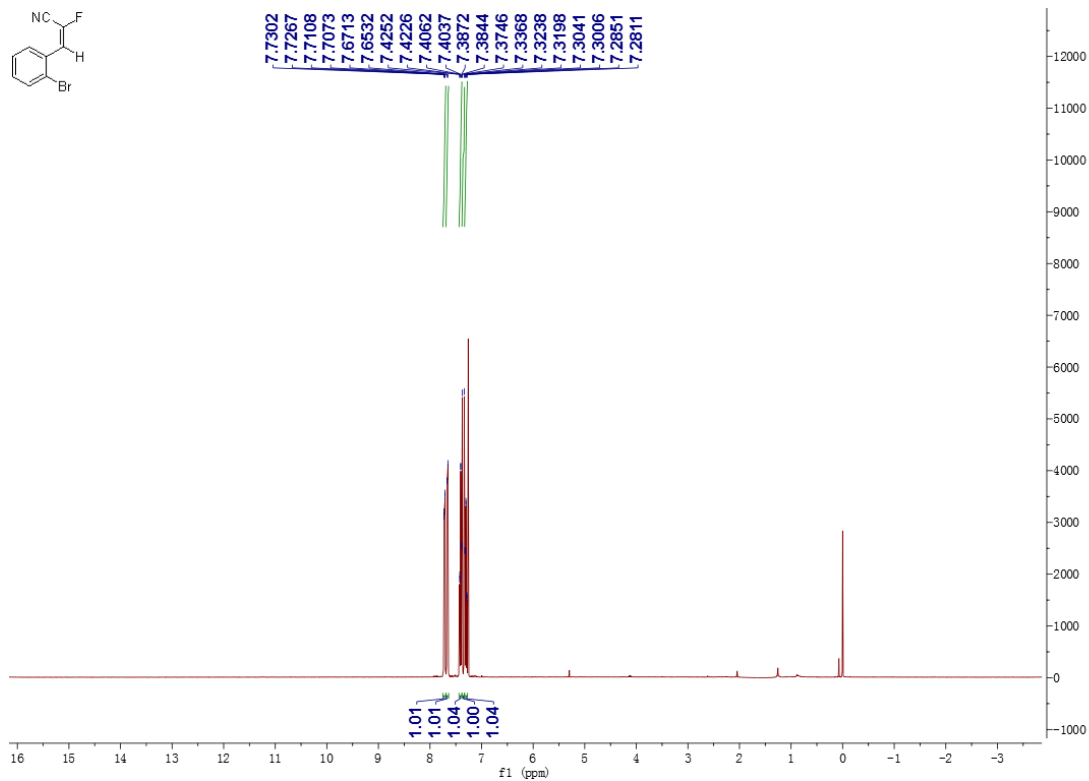
# <sup>13</sup>C NMR spectrum of (*E*)-**3e**



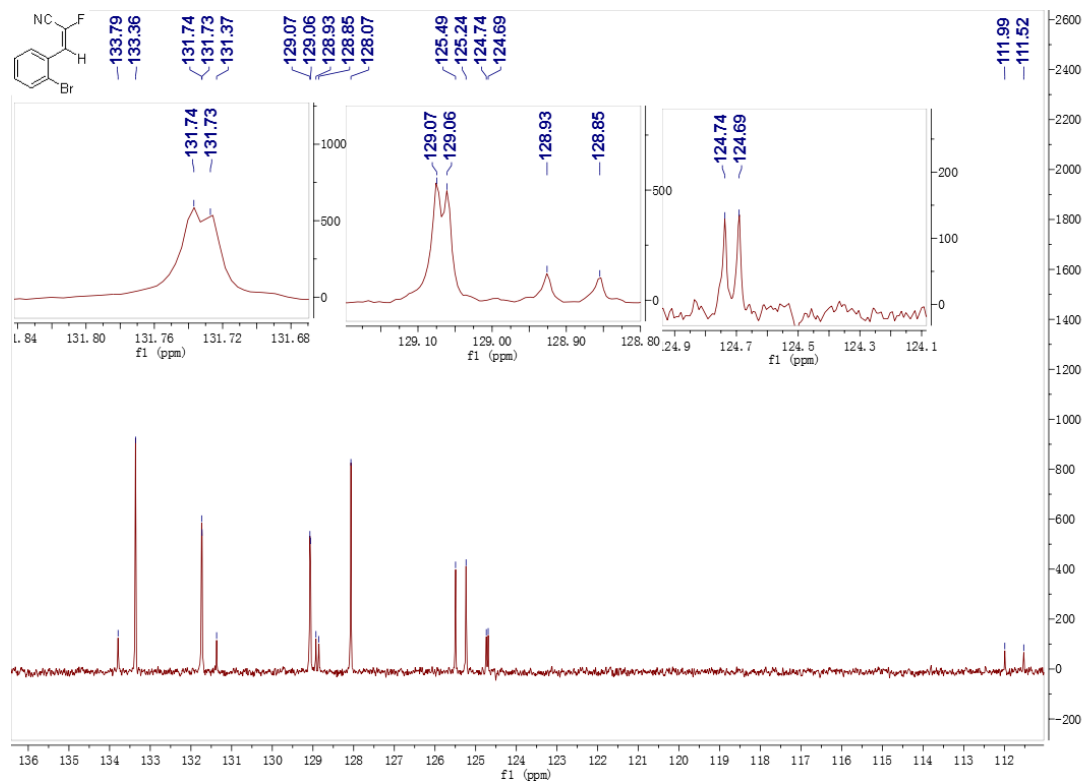
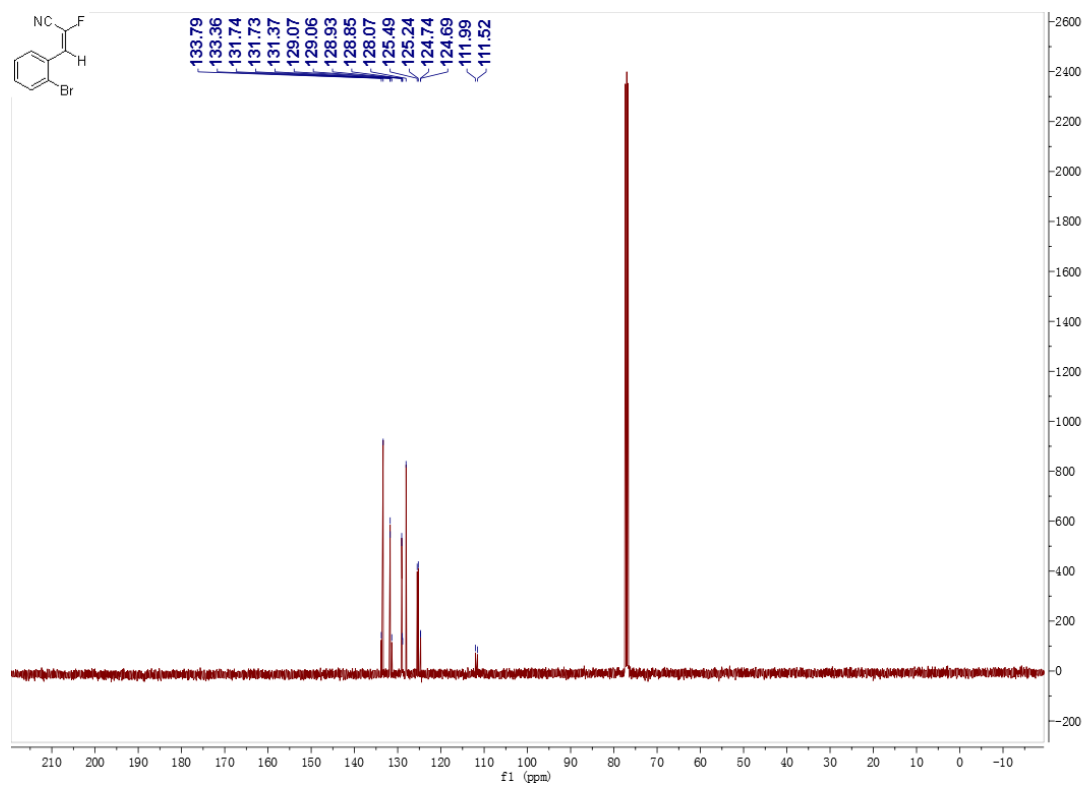
$^{19}\text{F}$  NMR spectrum of (*E*)-**3e**



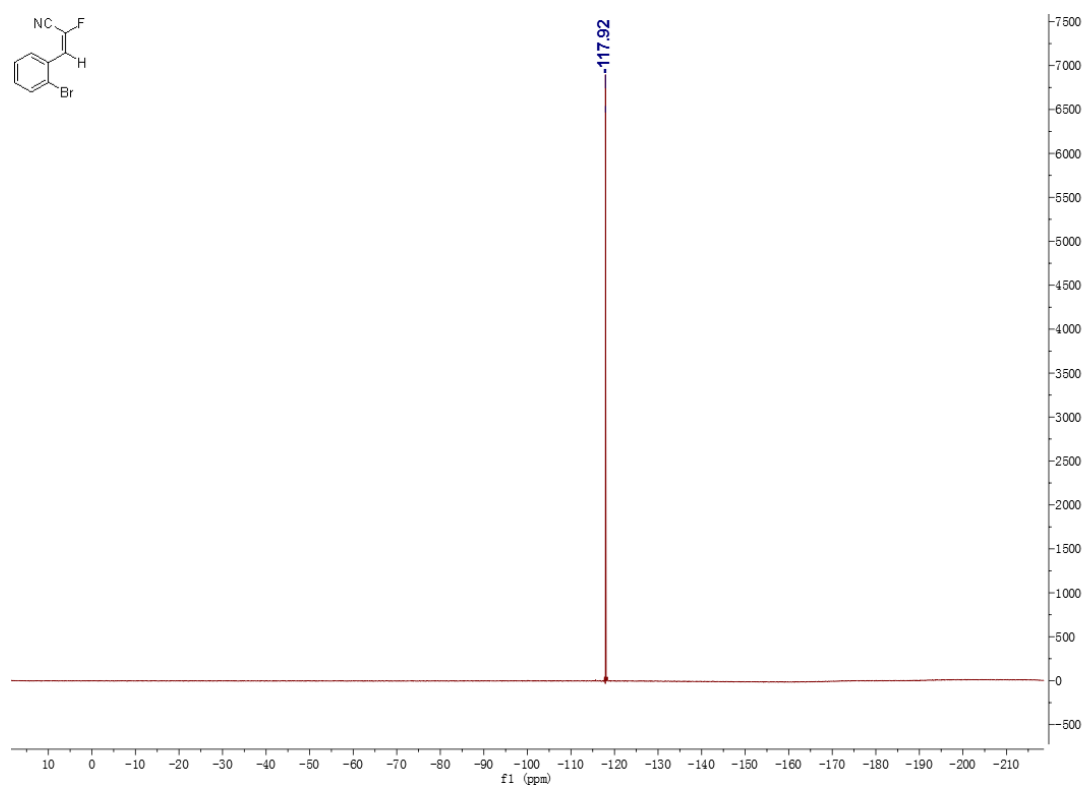
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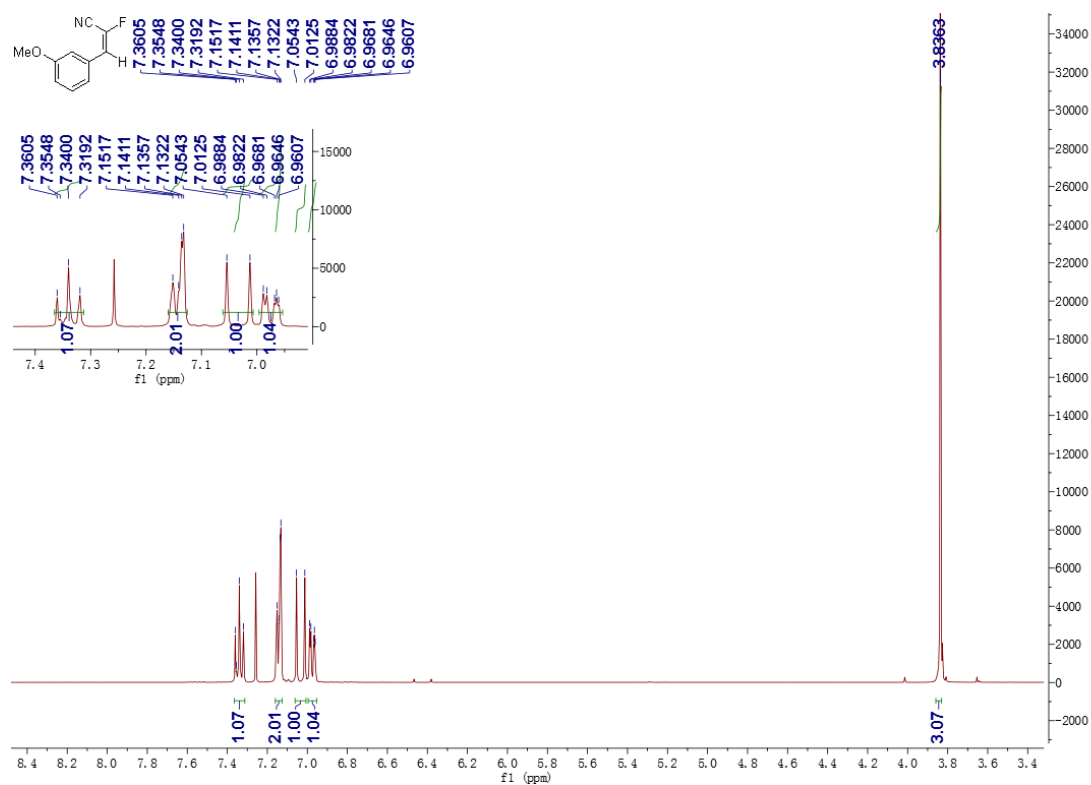
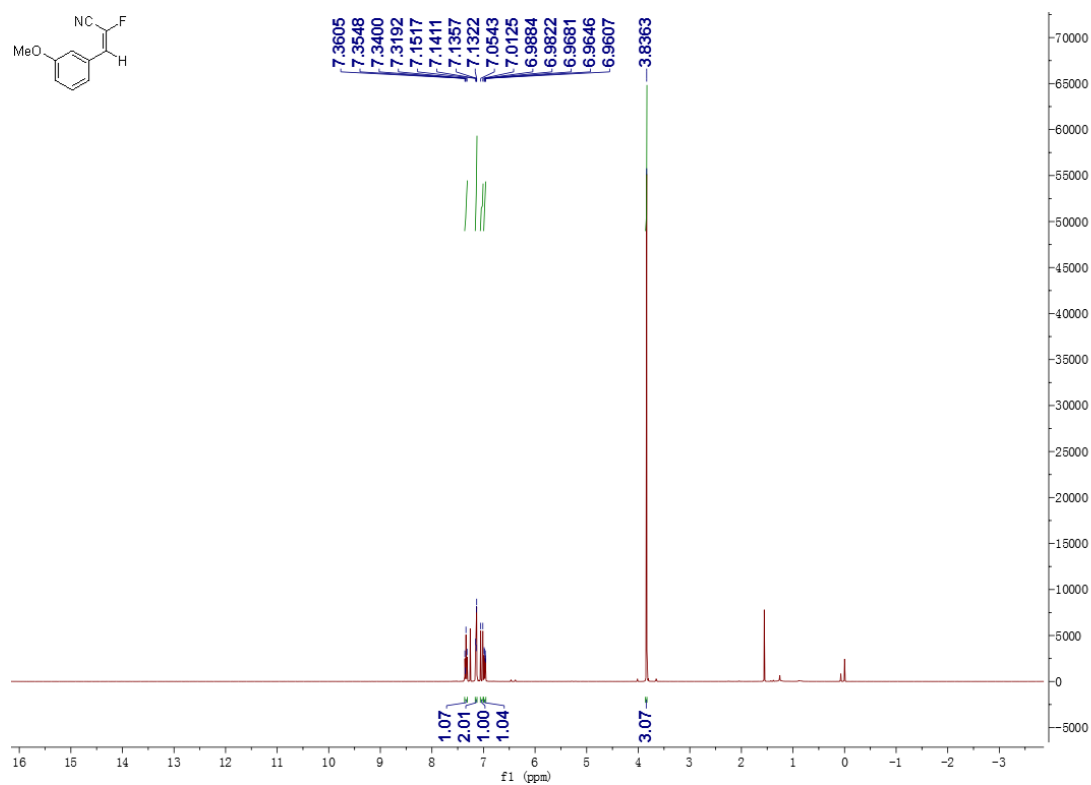
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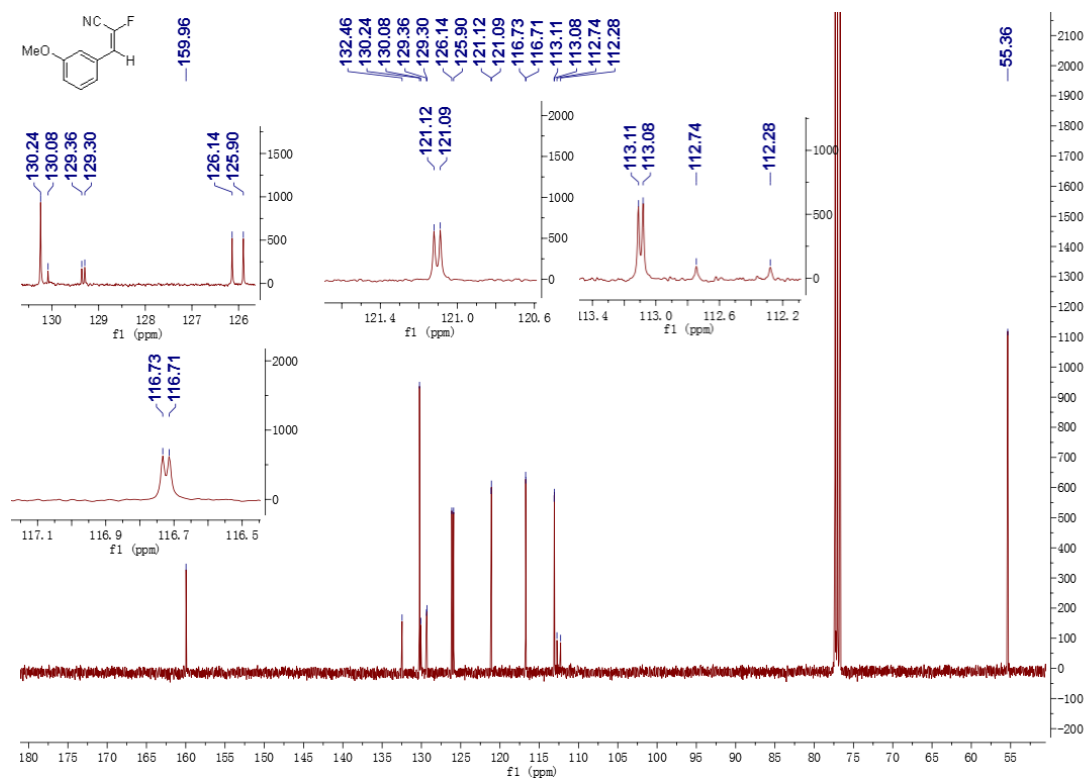
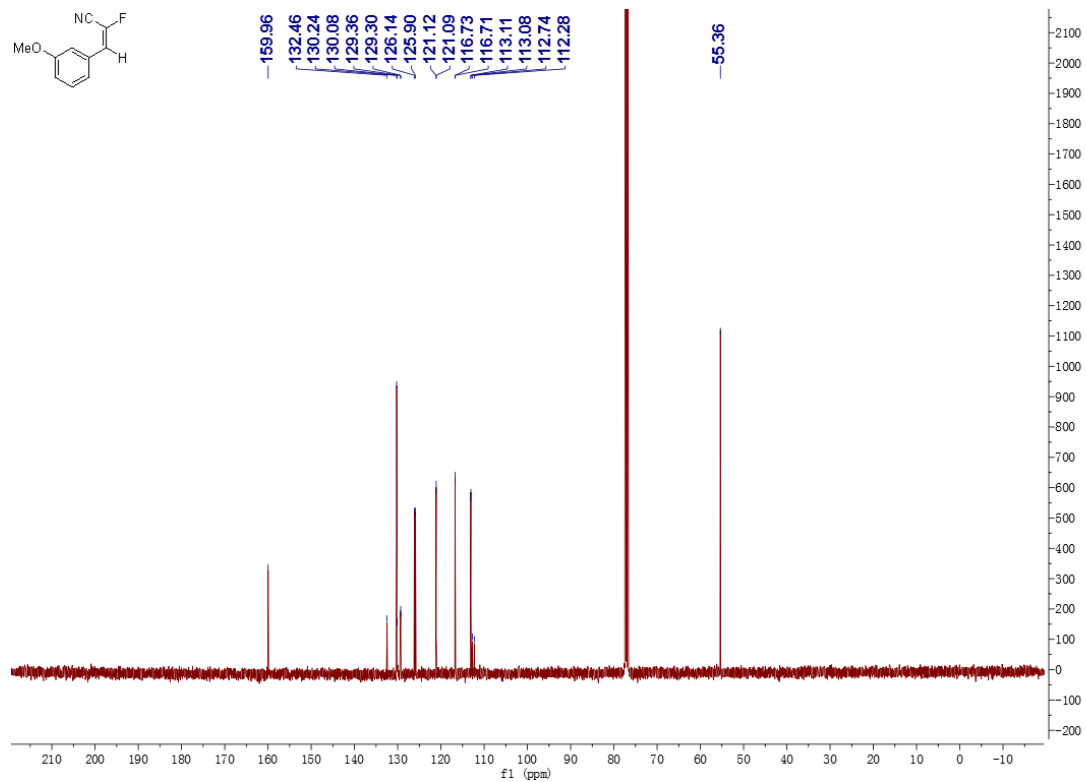
$^{19}\text{F}$  NMR spectrum of (*E*)-**3f**



# <sup>1</sup>H NMR spectrum of (E)-3g

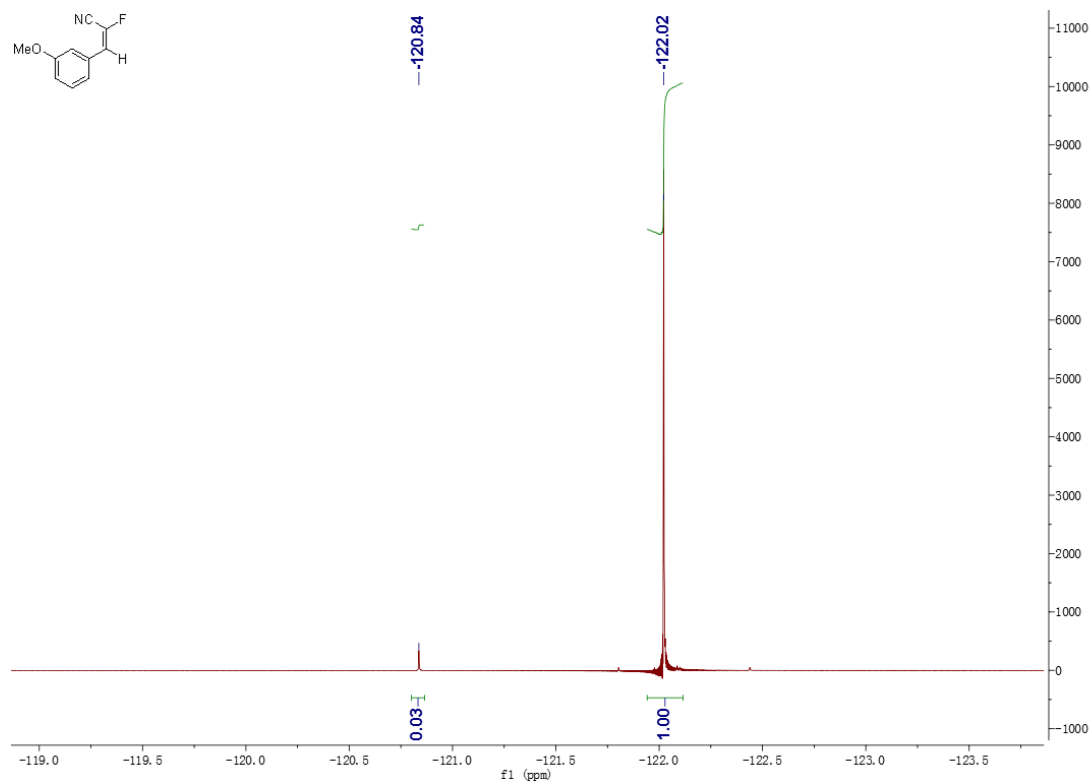
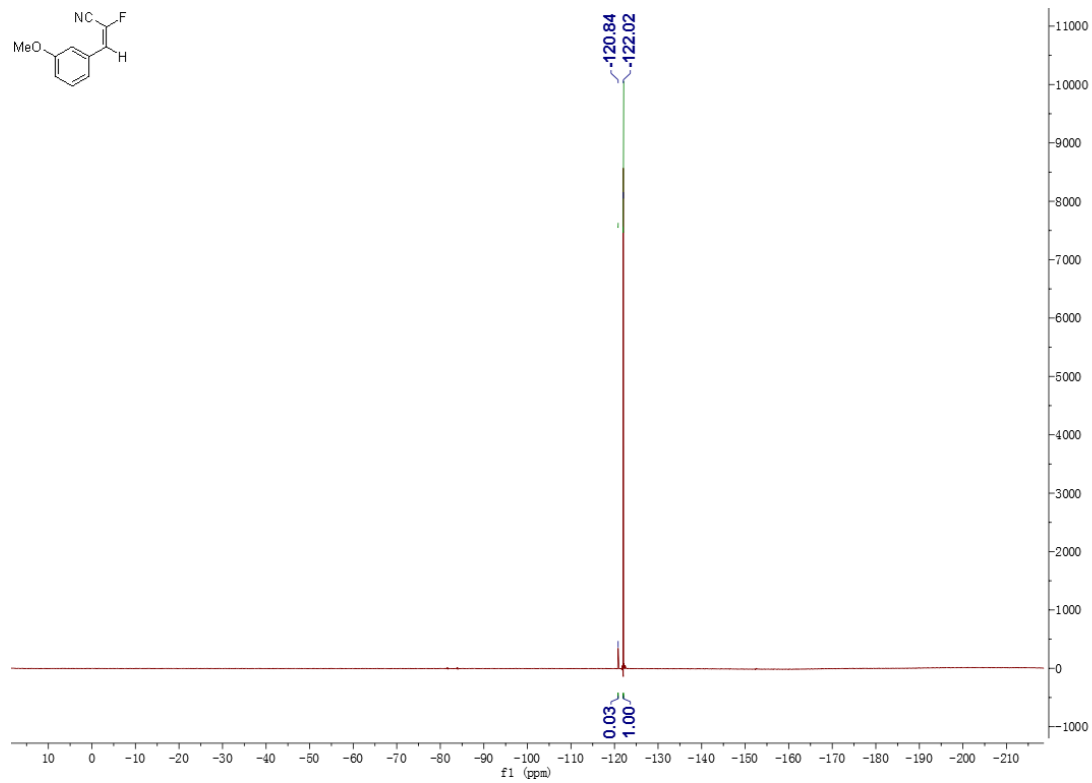
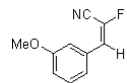


# $^{13}\text{C}$ NMR spectrum of (*E*)-3g

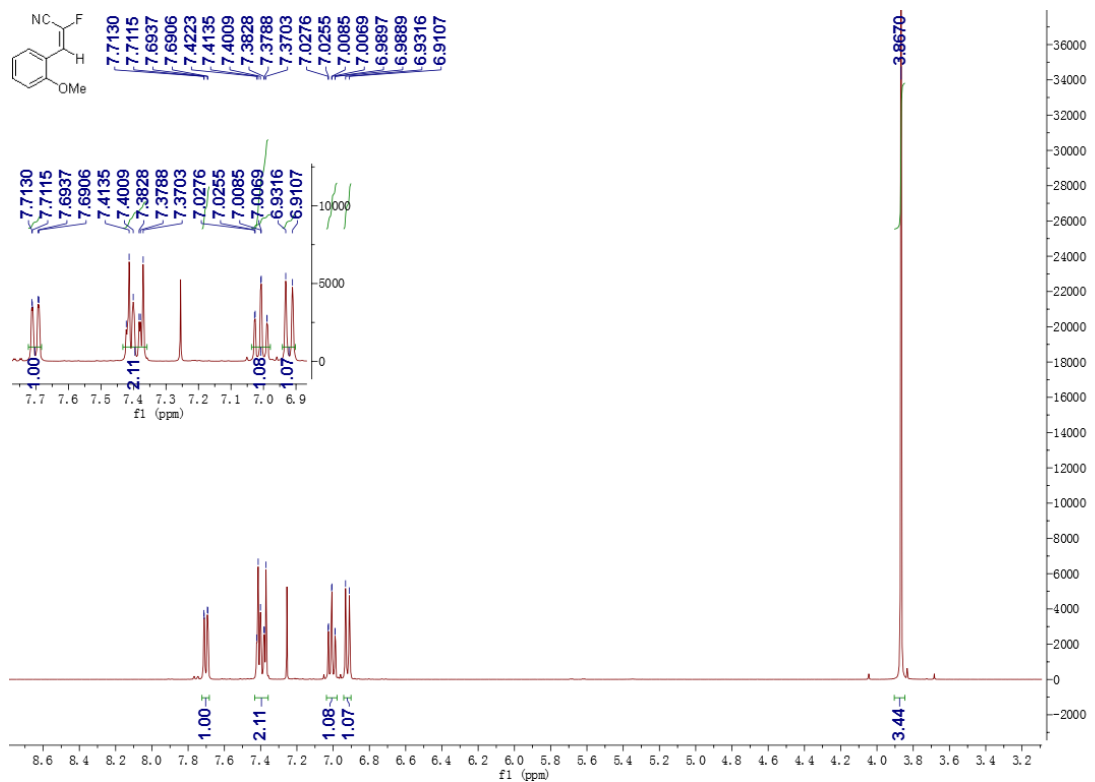
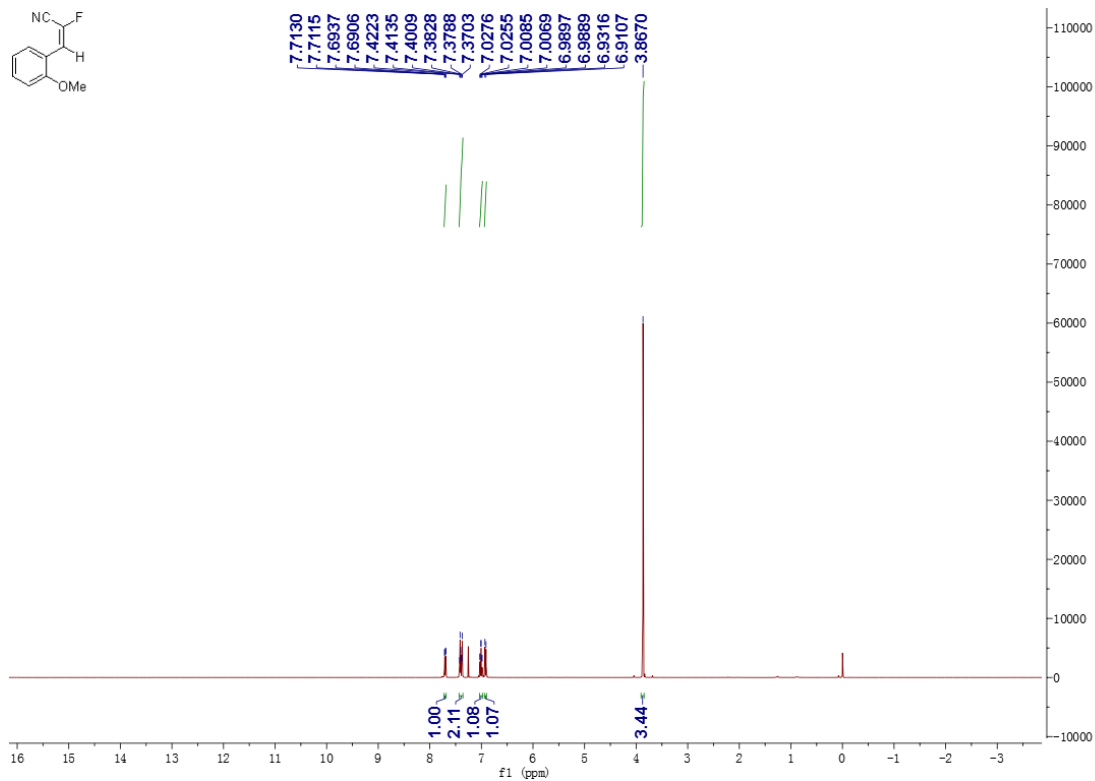




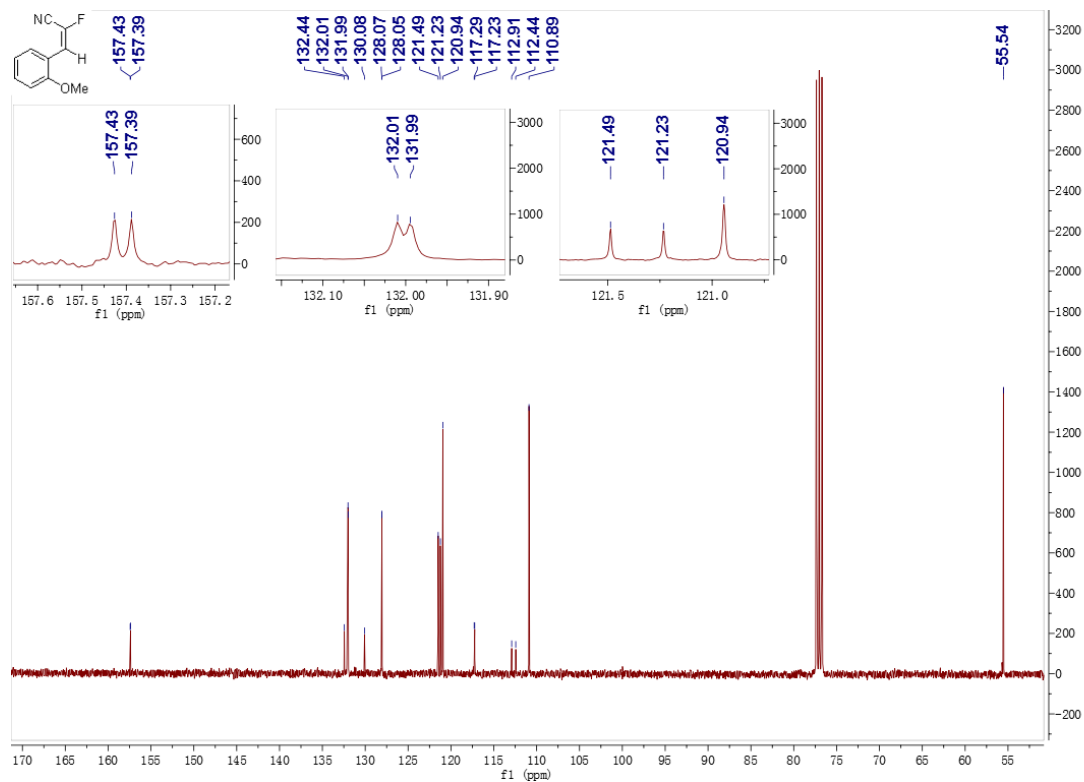
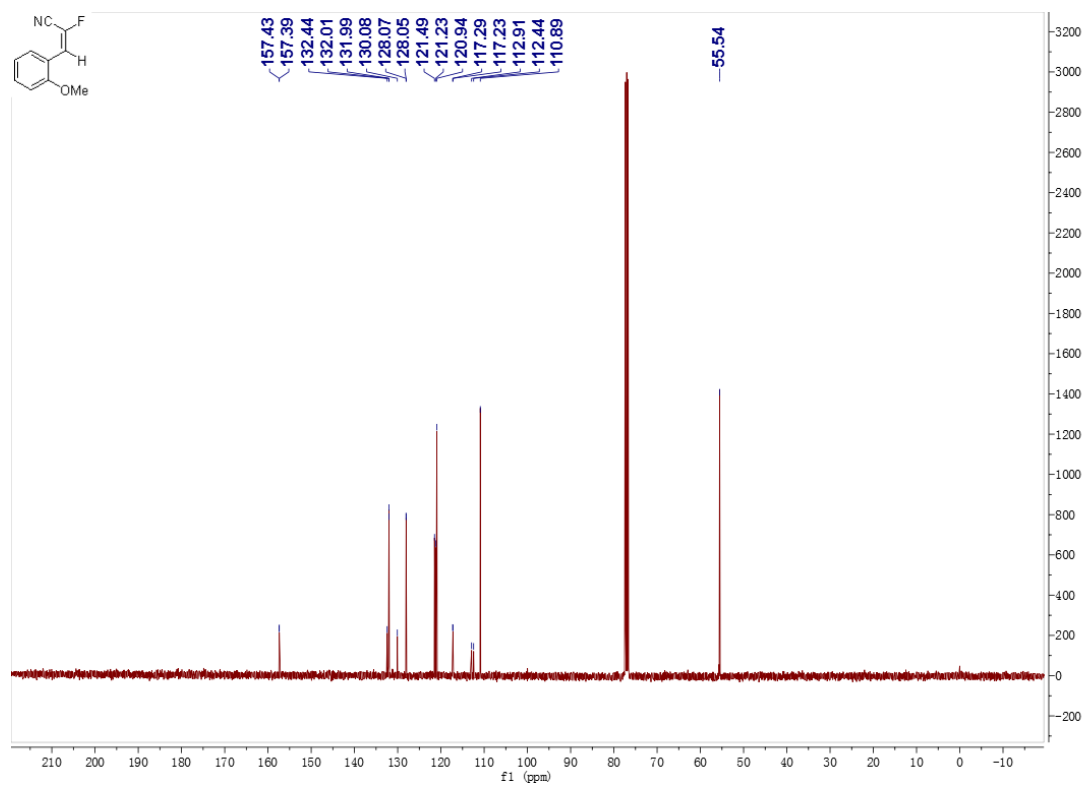
# $^{19}\text{F}$ NMR spectrum of (*E*)-**3g**



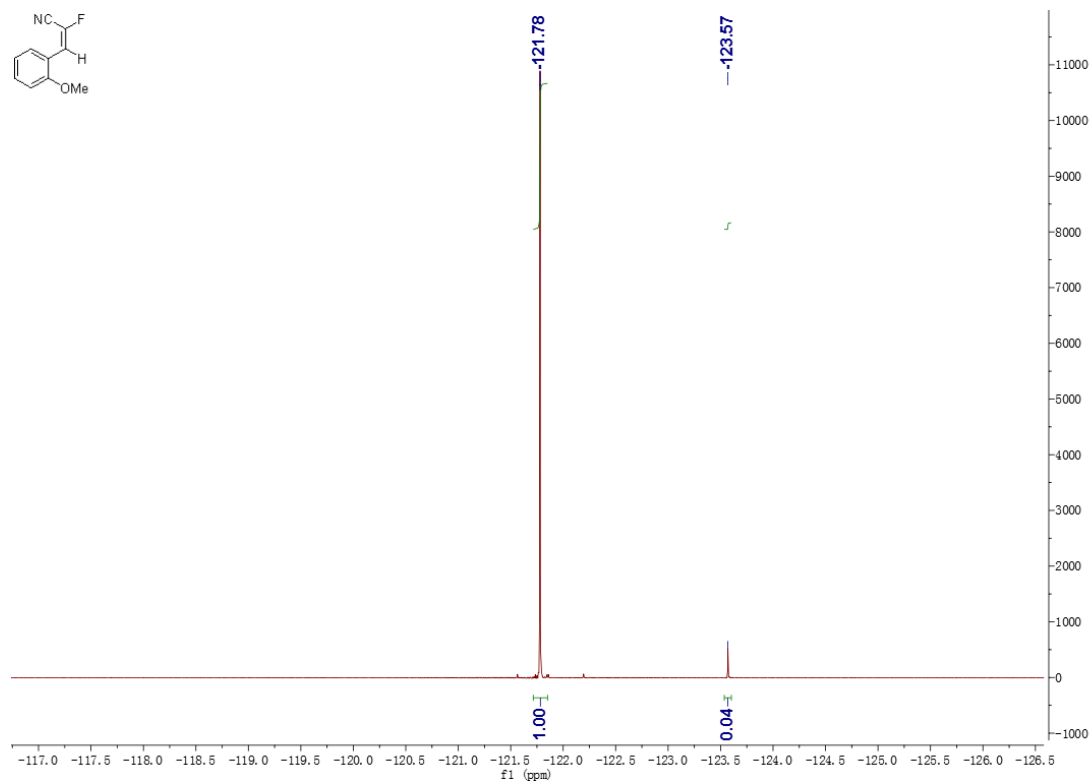
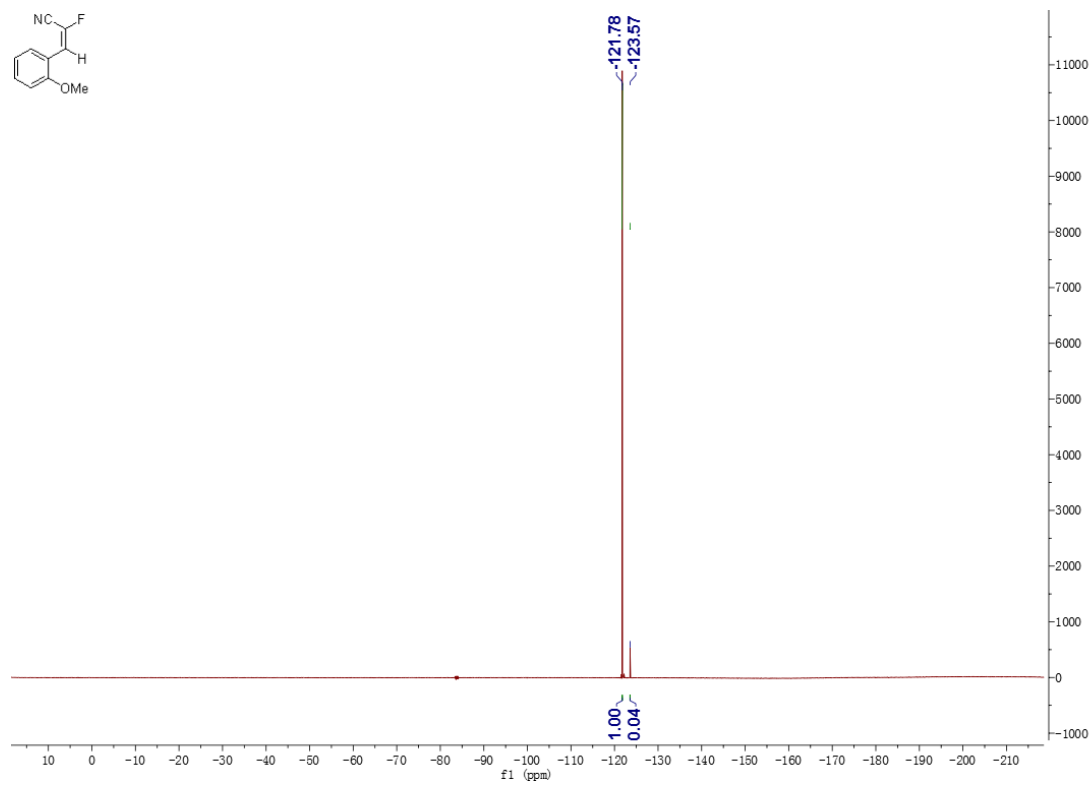
<sup>1</sup>H NMR spectrum of (*E*)-**3h**



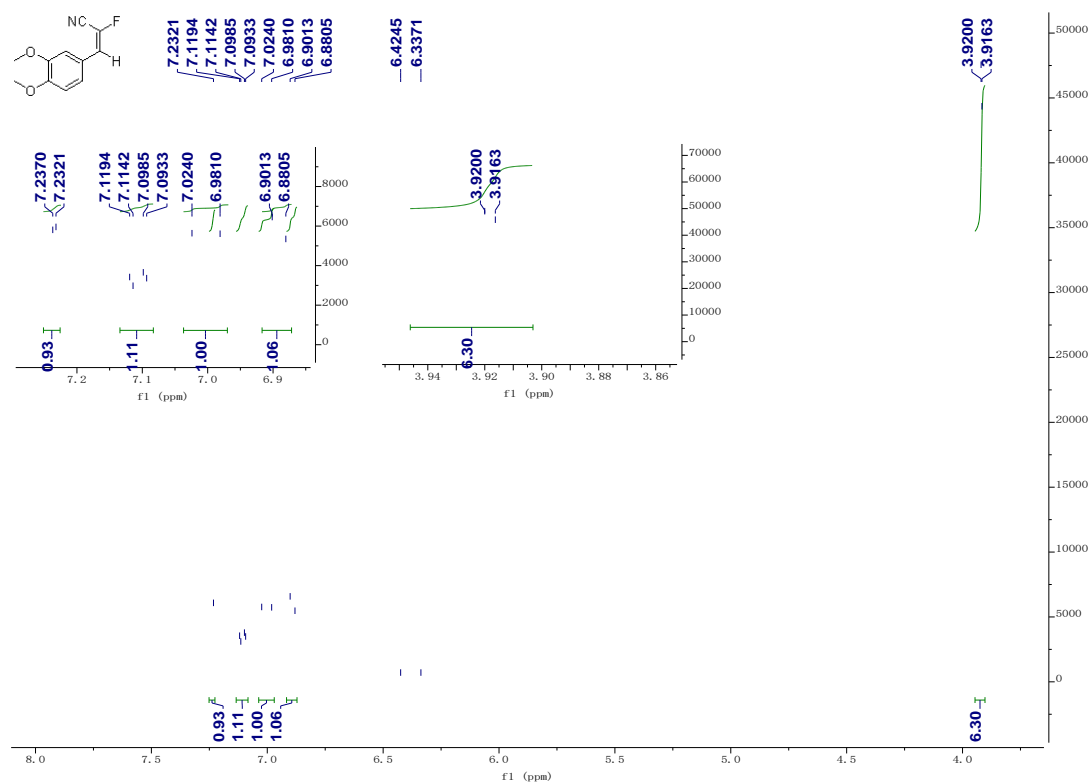
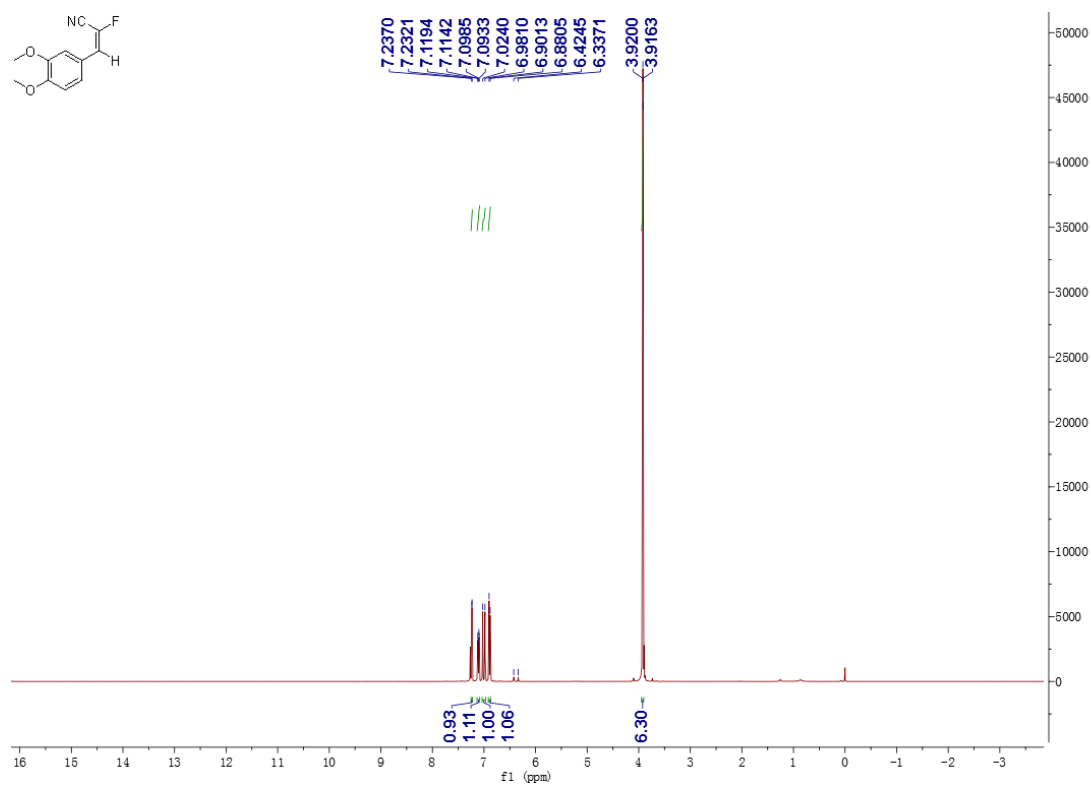
# <sup>13</sup>C NMR spectrum of (*E*)-**3h**



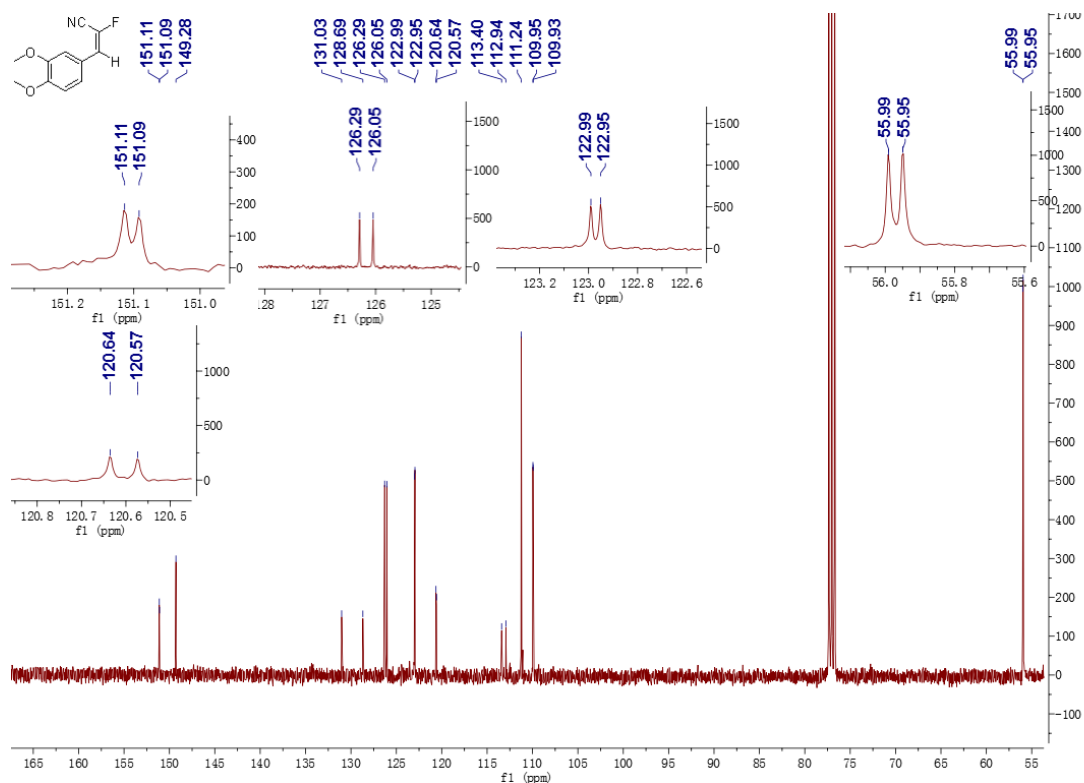
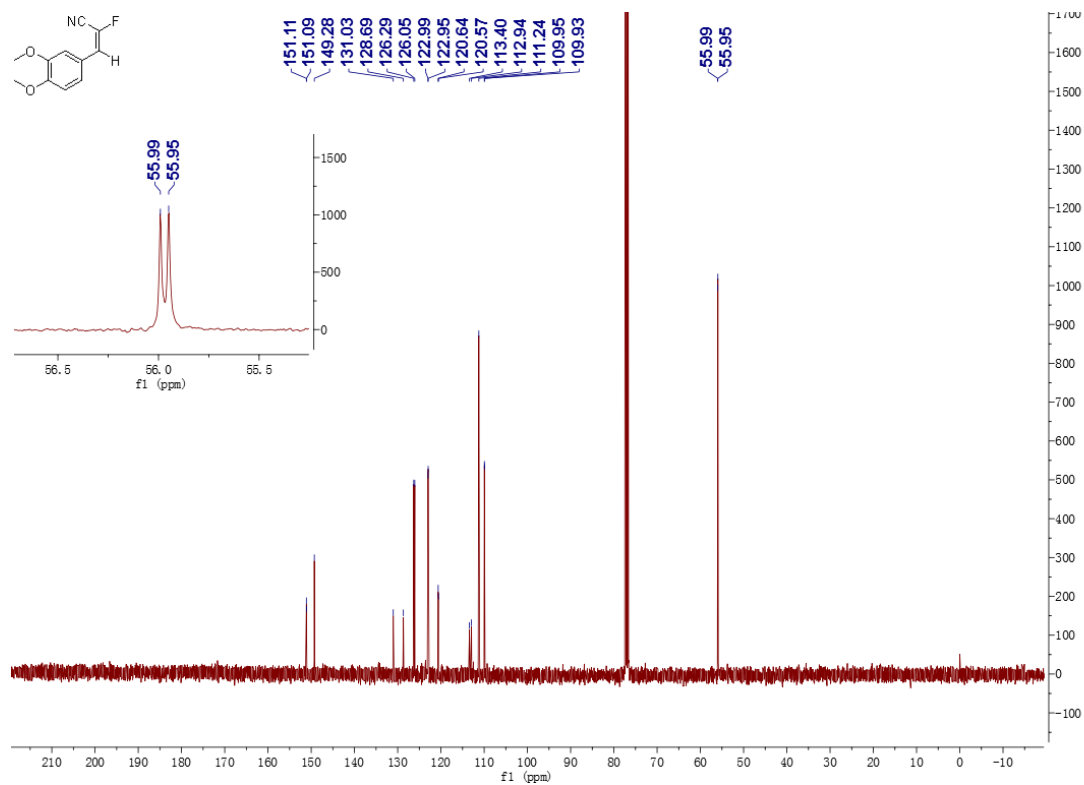
<sup>19</sup>F NMR spectrum of (*E*)-**3h**



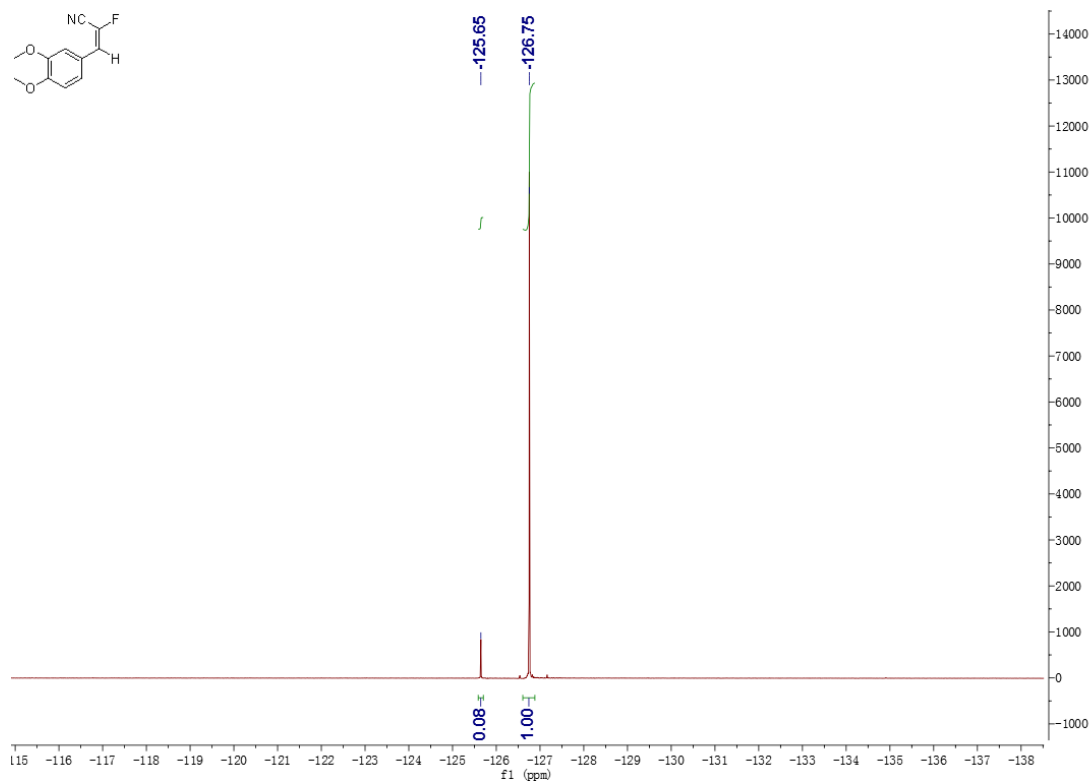
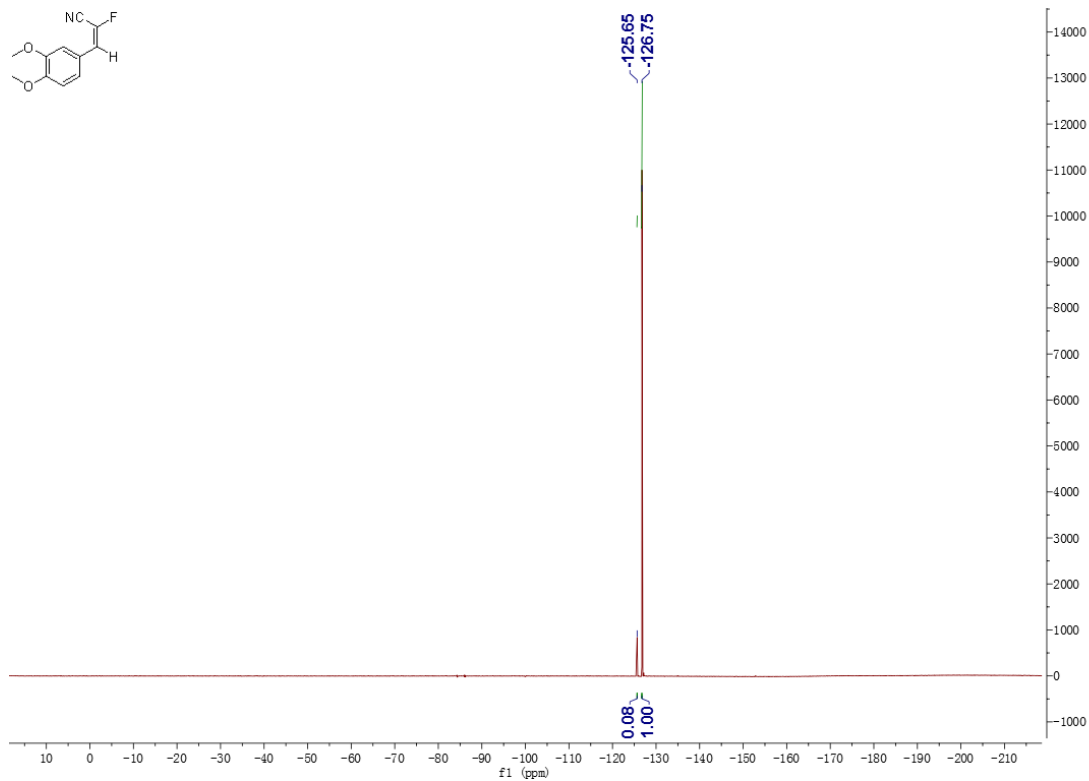
# $^1\text{H}$ NMR spectrum of (*E*)-**3i**



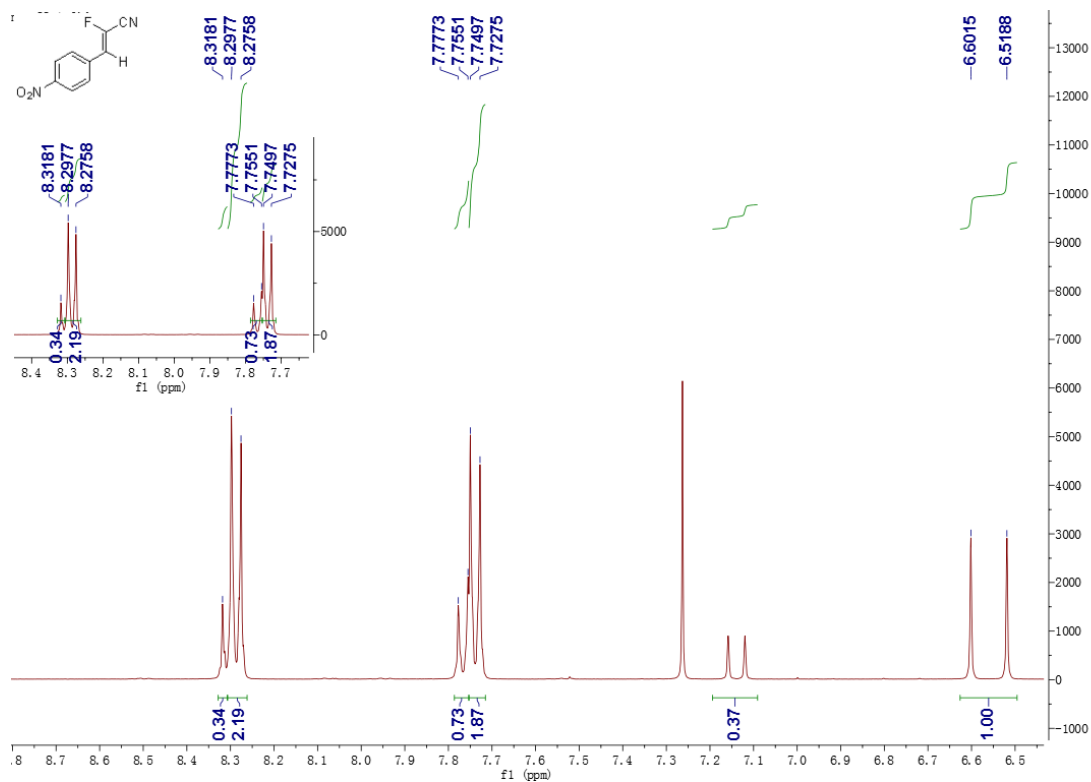
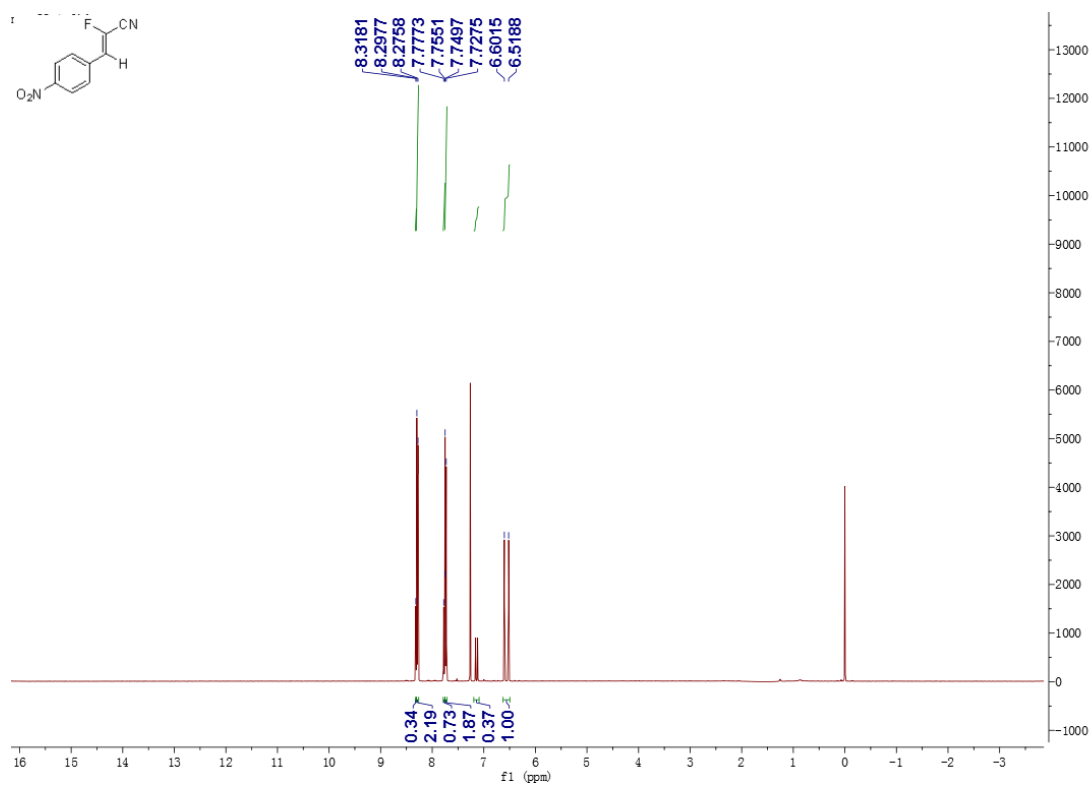
# $^{13}\text{C}$ NMR spectrum of (*E*)-3i



<sup>19</sup>F NMR spectrum of (*E*)-**3i**

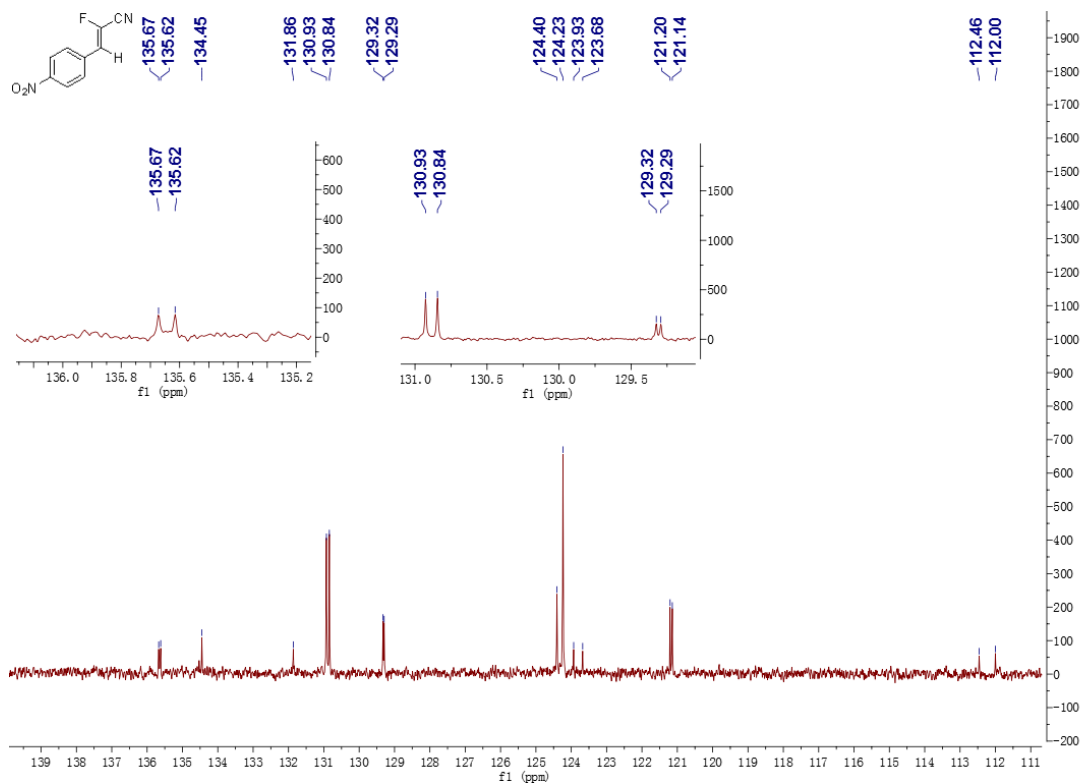
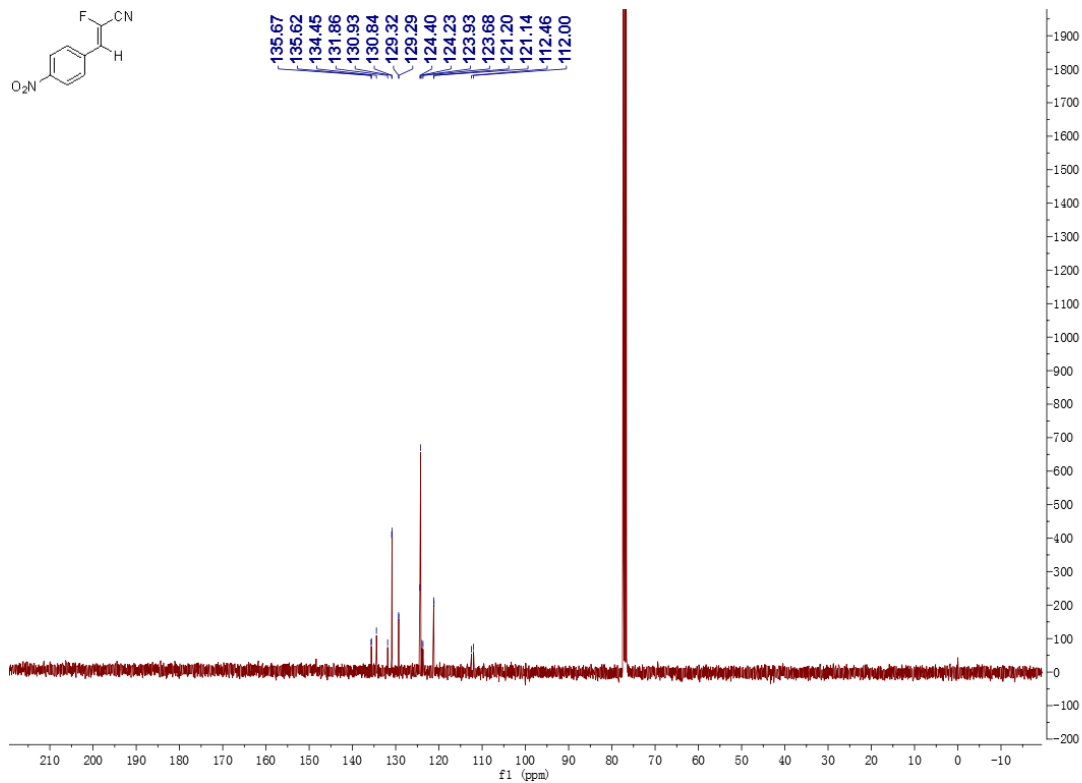


# <sup>1</sup>H NMR spectrum of (Z)-3j

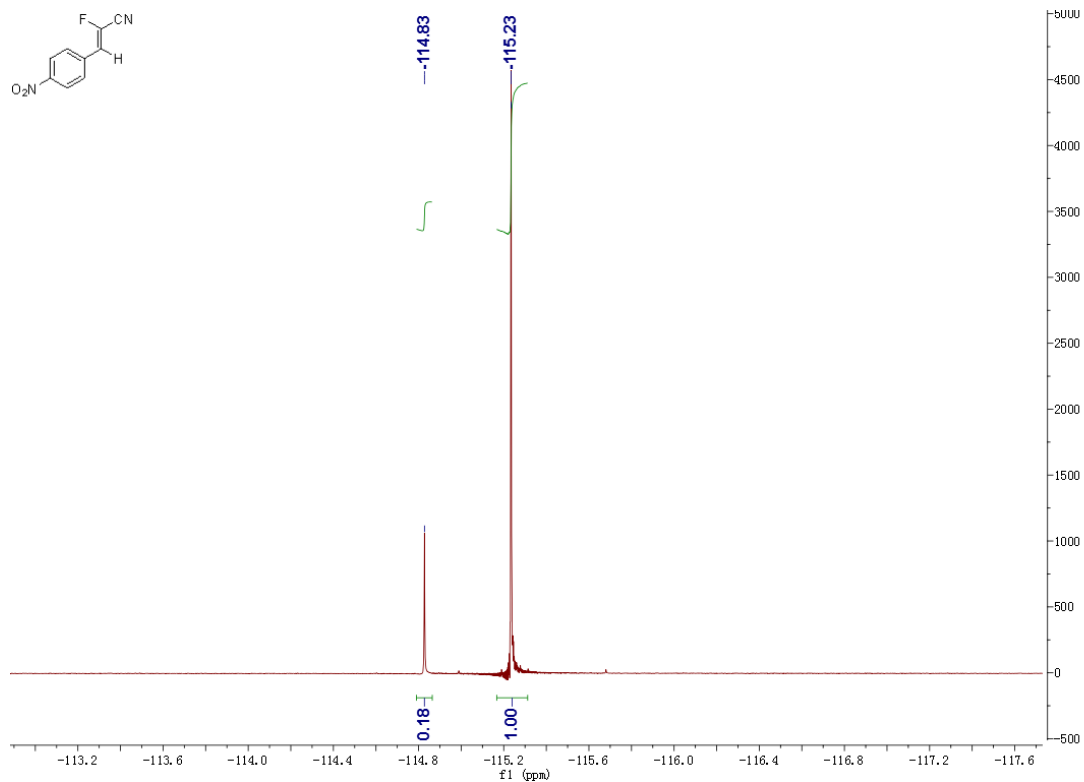
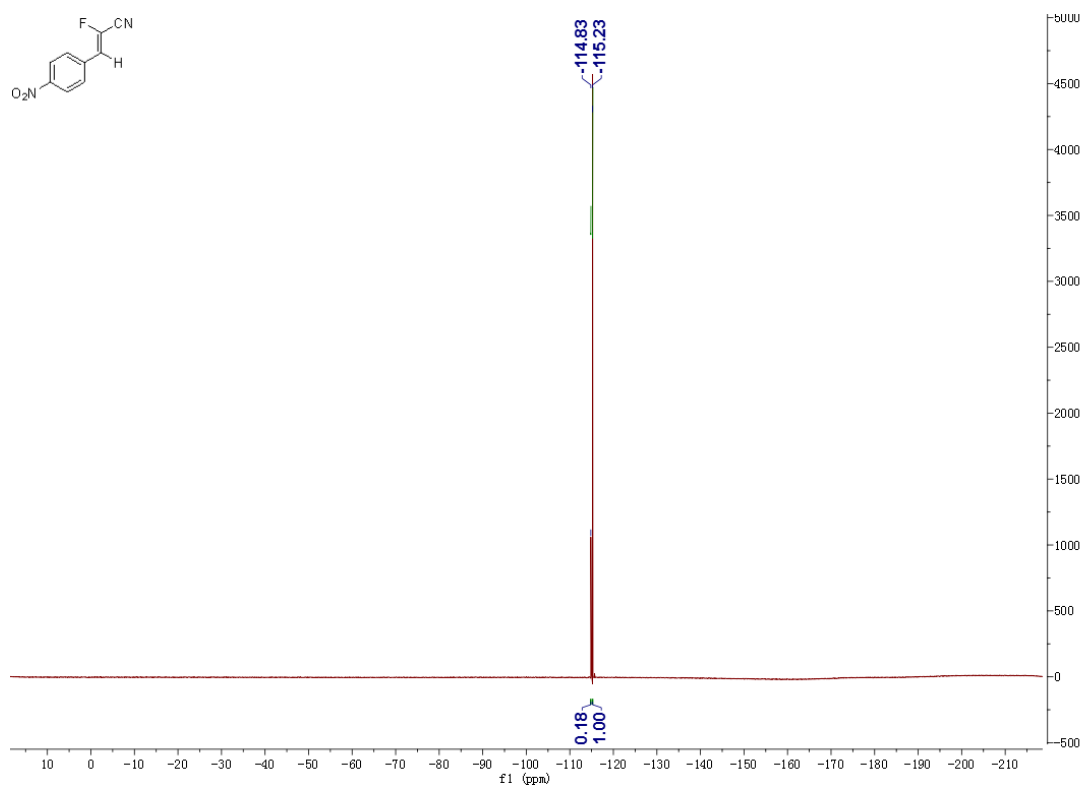
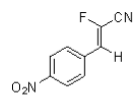




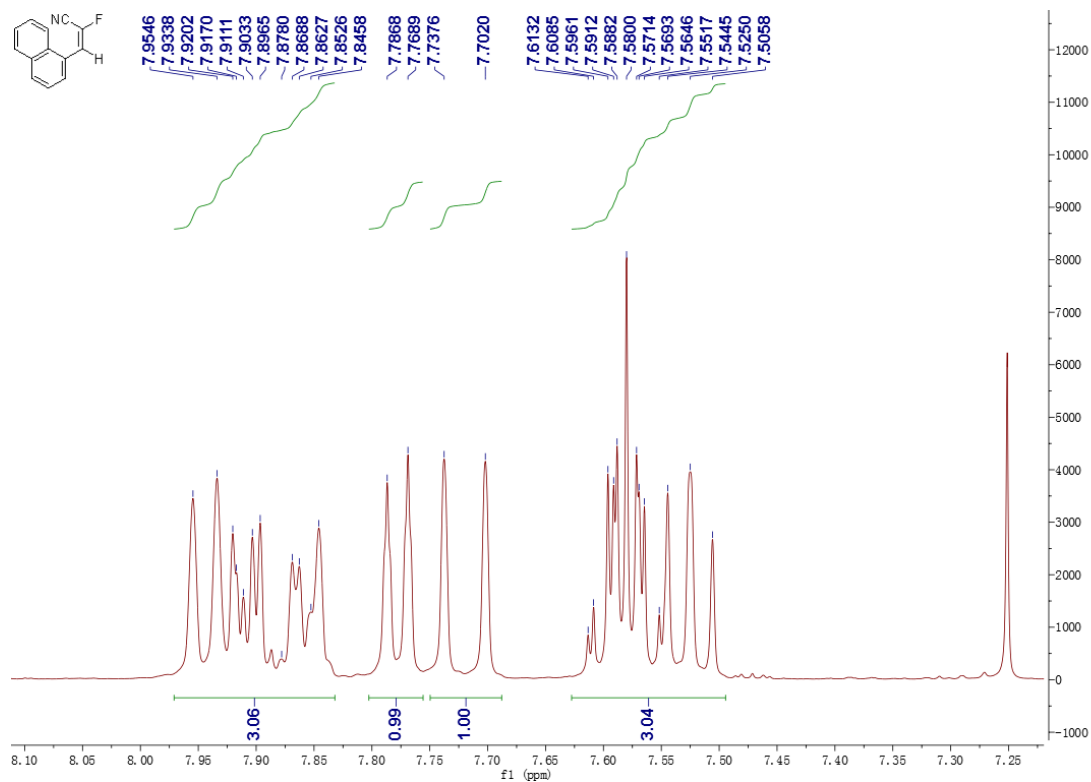
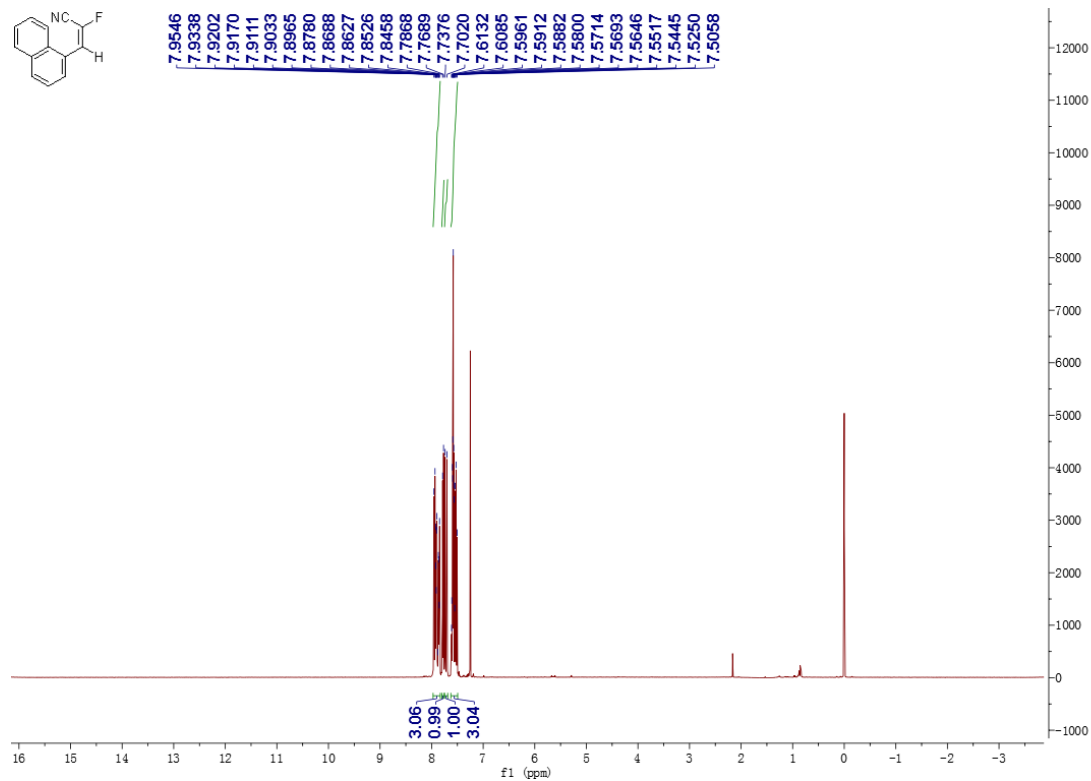
# <sup>13</sup>C NMR spectrum of (Z)-3j



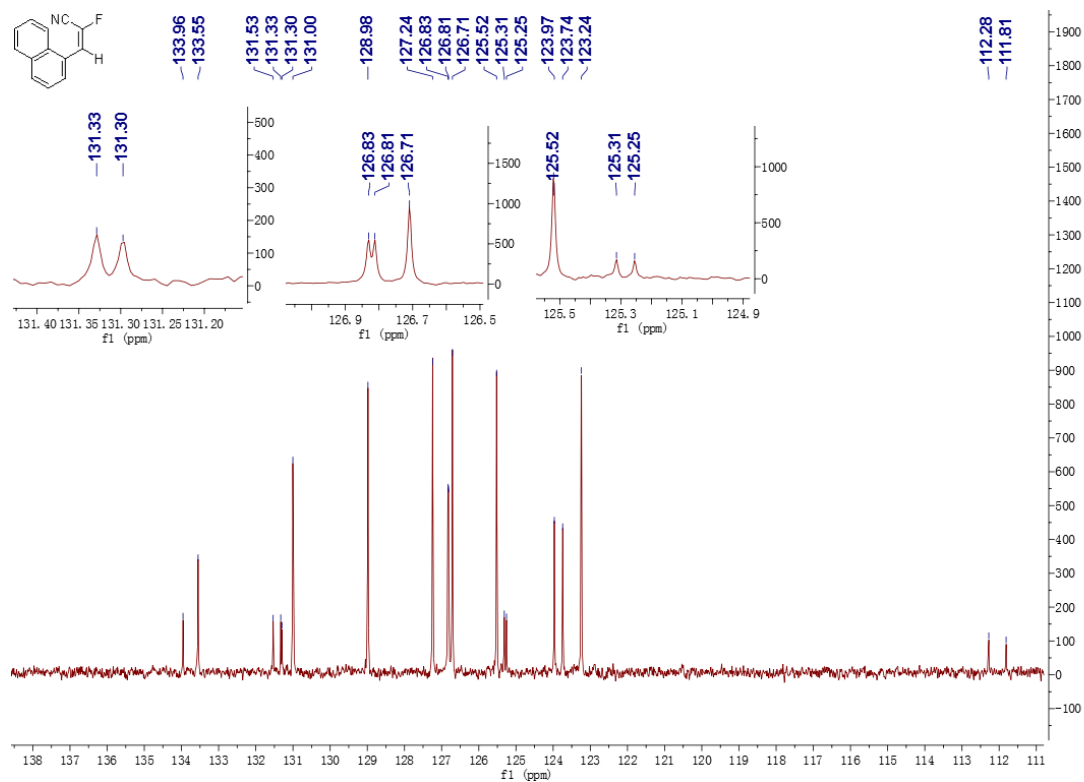
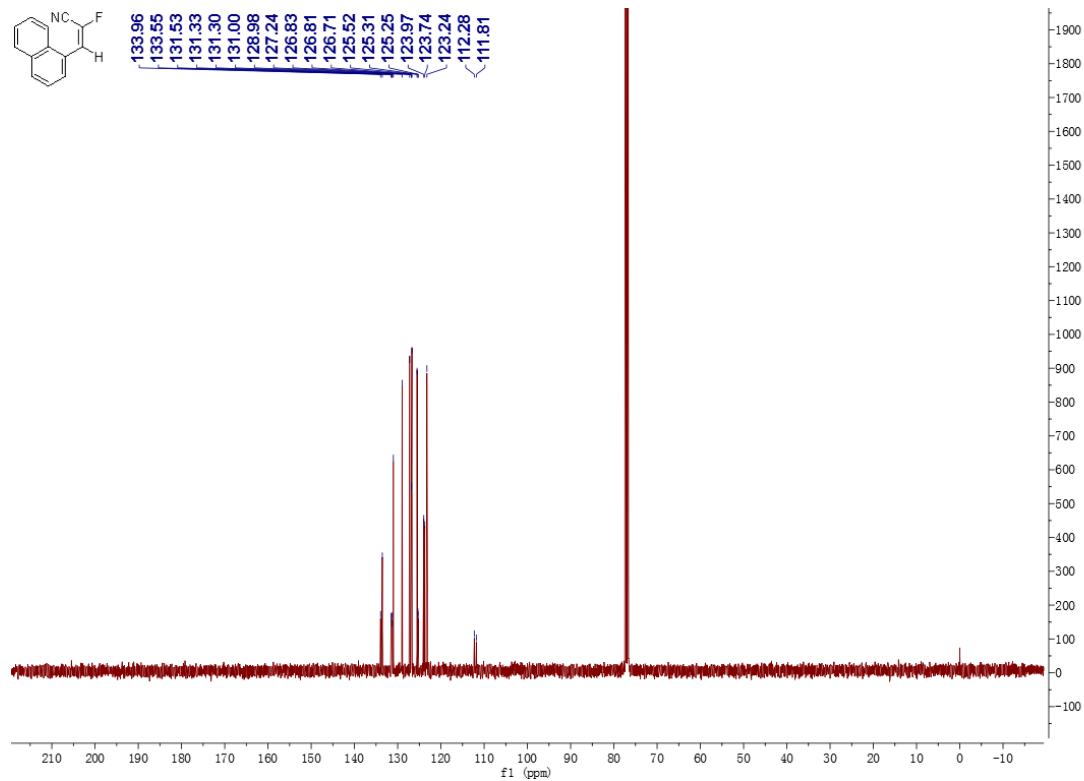
<sup>19</sup>F NMR spectrum of (Z)-3j



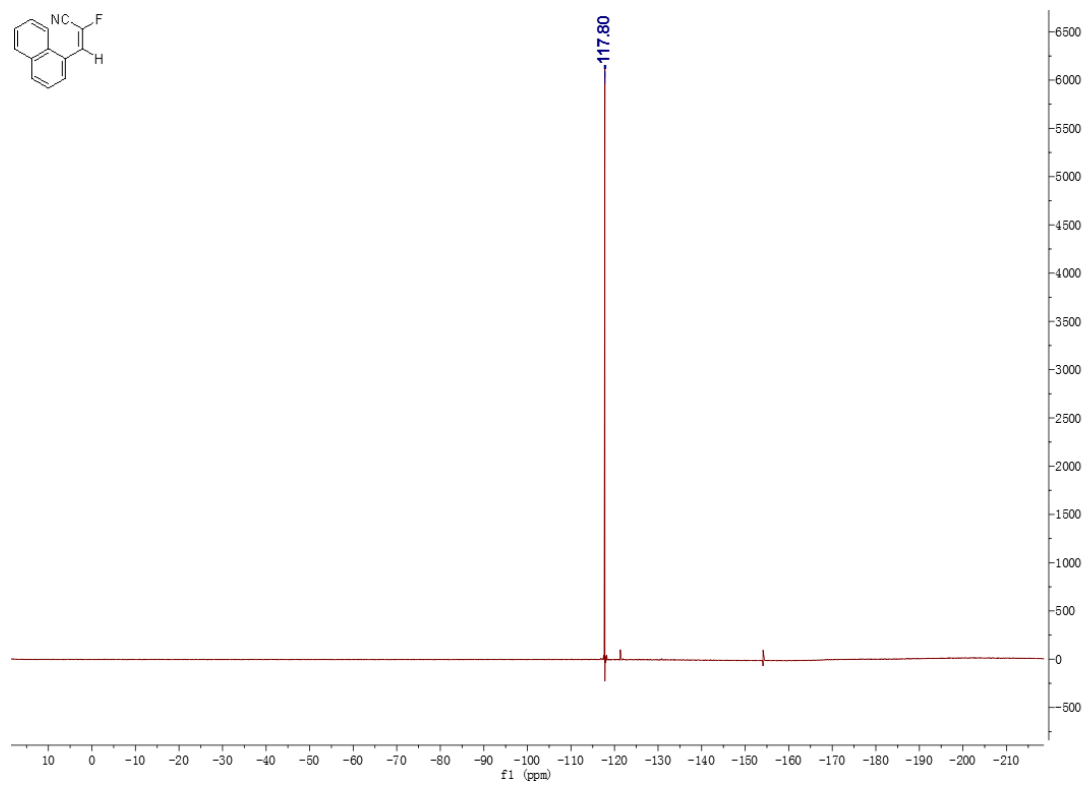
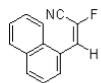
# <sup>1</sup>H NMR spectrum of (*E*)-**3k**



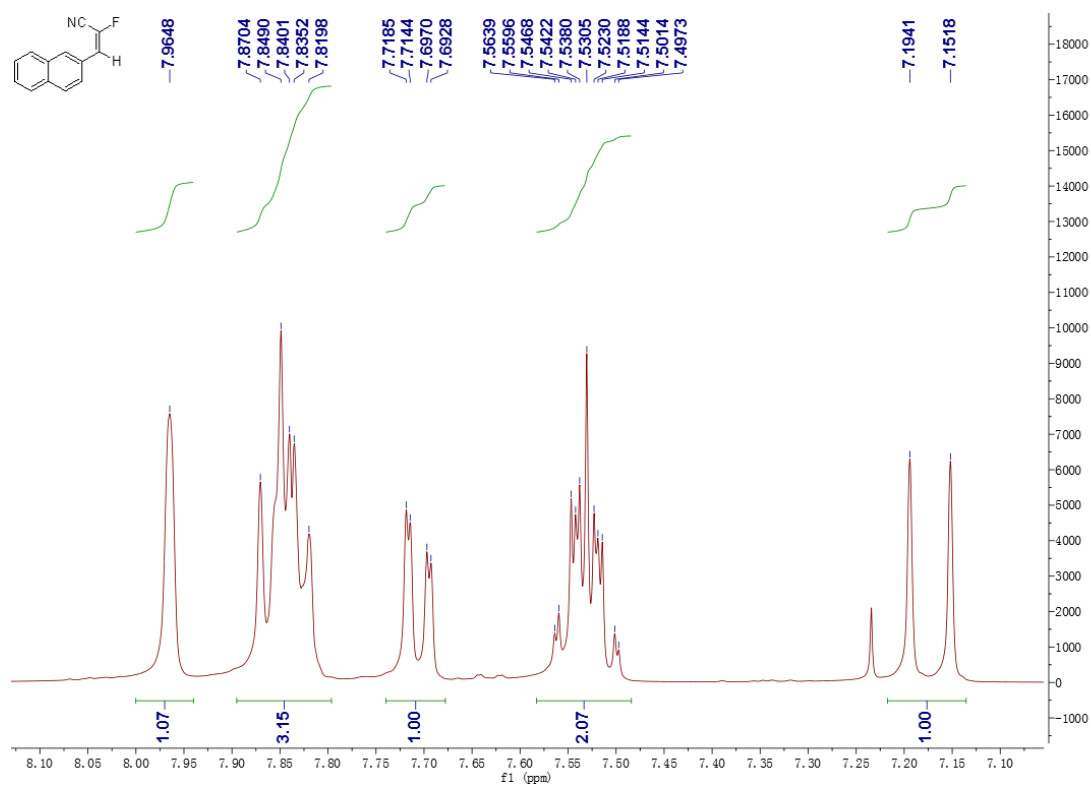
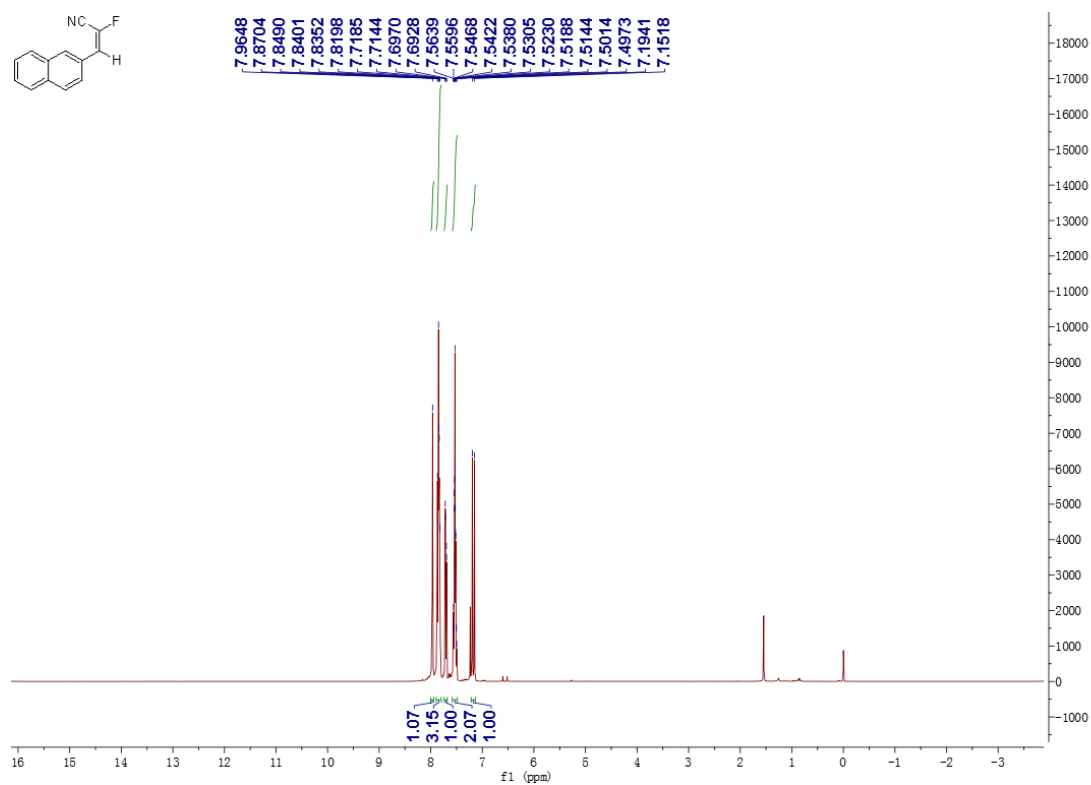
# <sup>13</sup>C NMR spectrum of (*E*)-**3k**



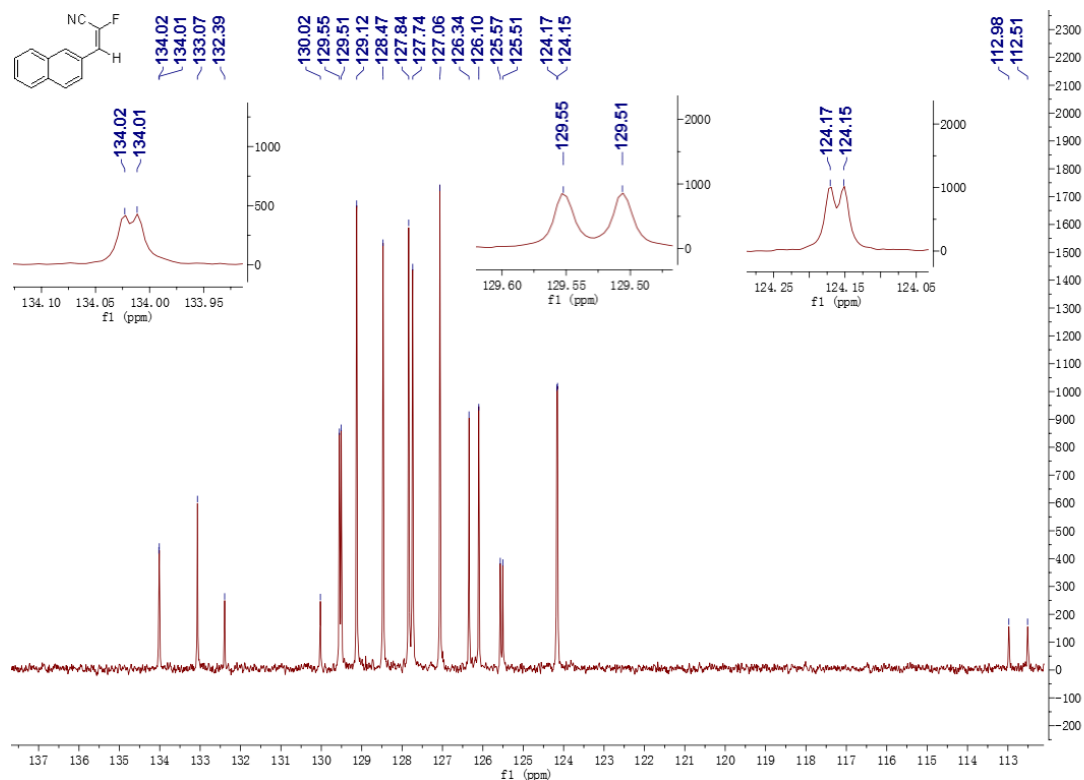
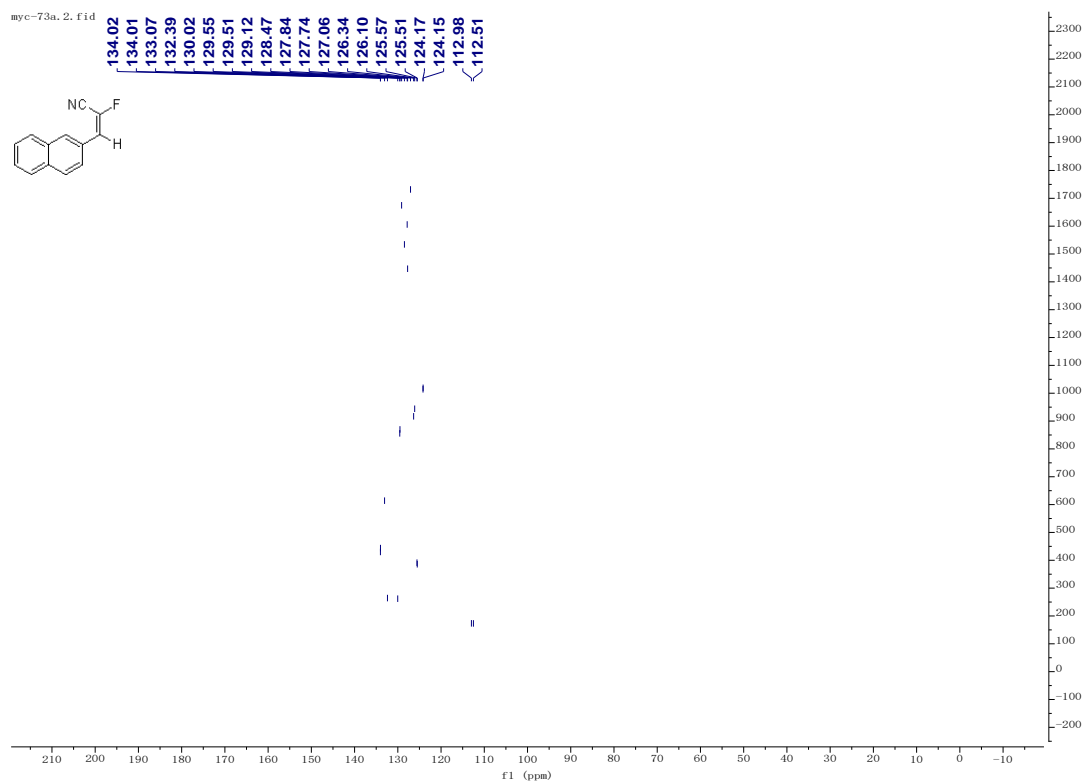
$^{19}\text{F}$  NMR spectrum of (*E*)-**3k**



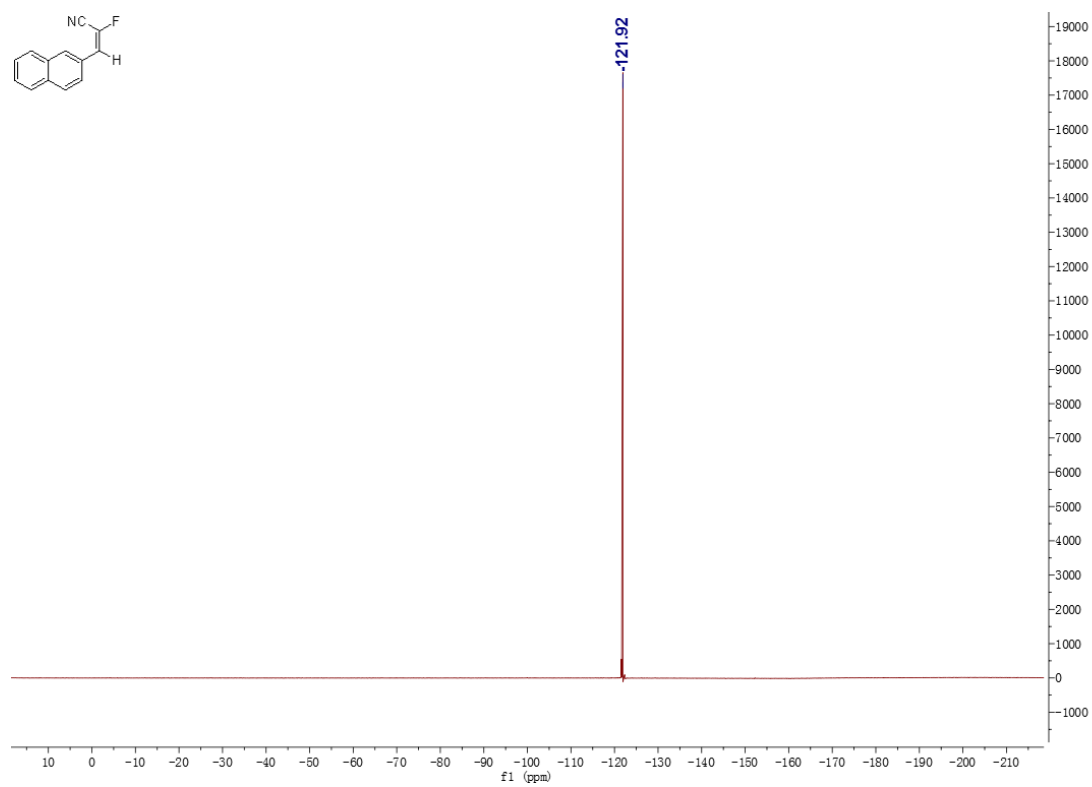
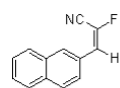
# <sup>1</sup>H NMR spectrum of (*E*)-31



# $^{13}\text{C}$ NMR spectrum of (*E*)-**31**

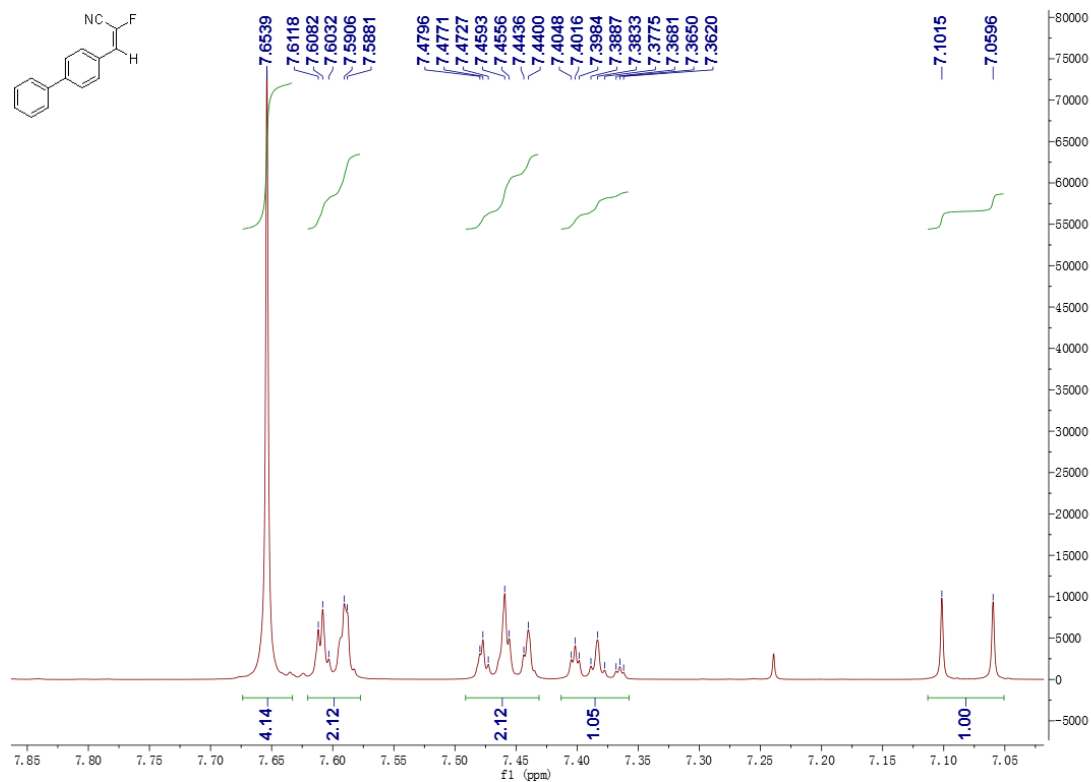
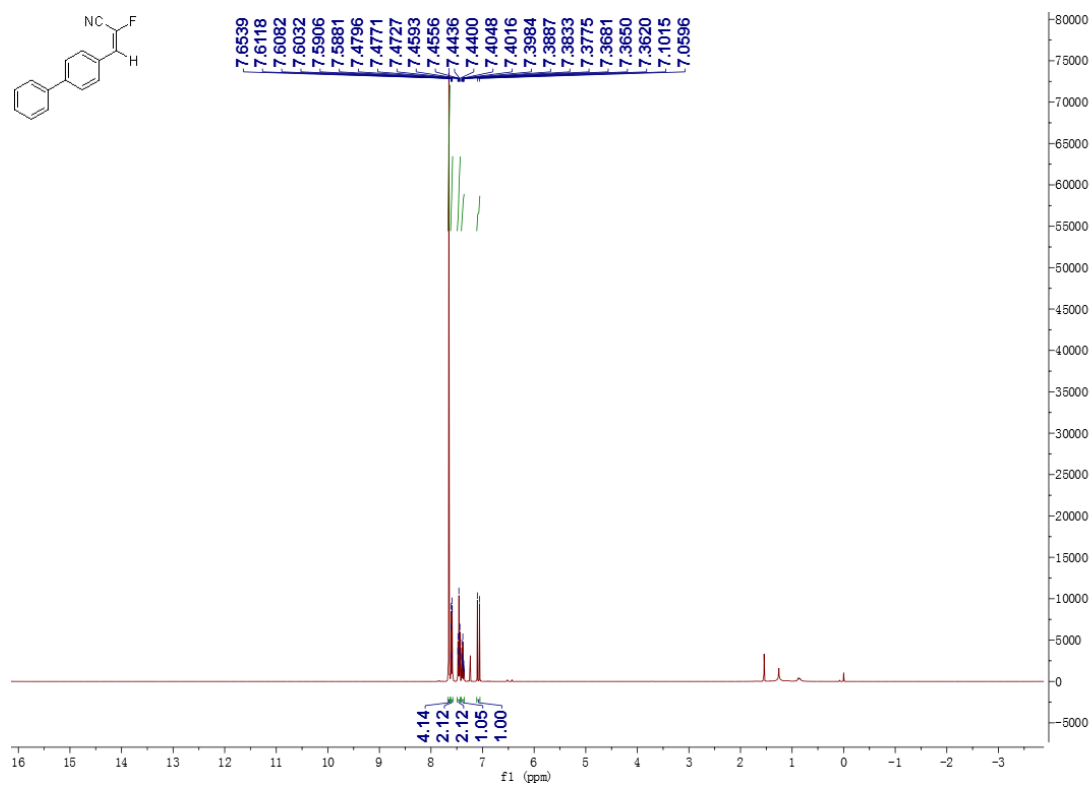


$^{19}\text{F}$  NMR spectrum of (*E*)-**3I**

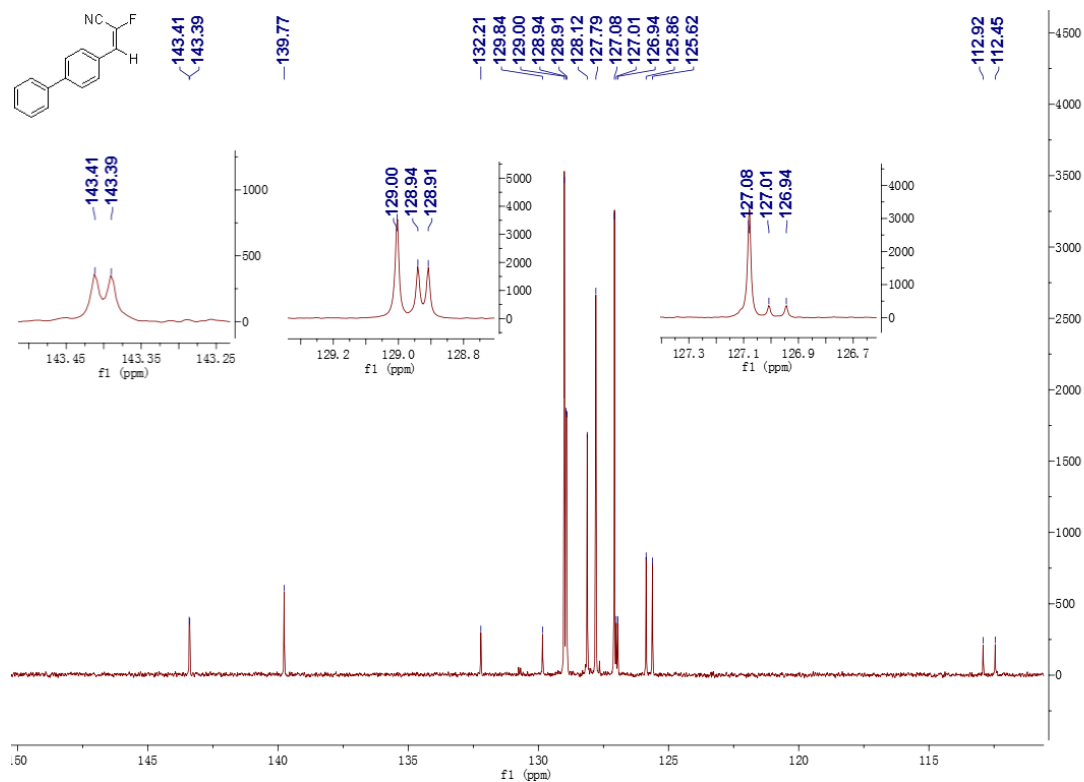
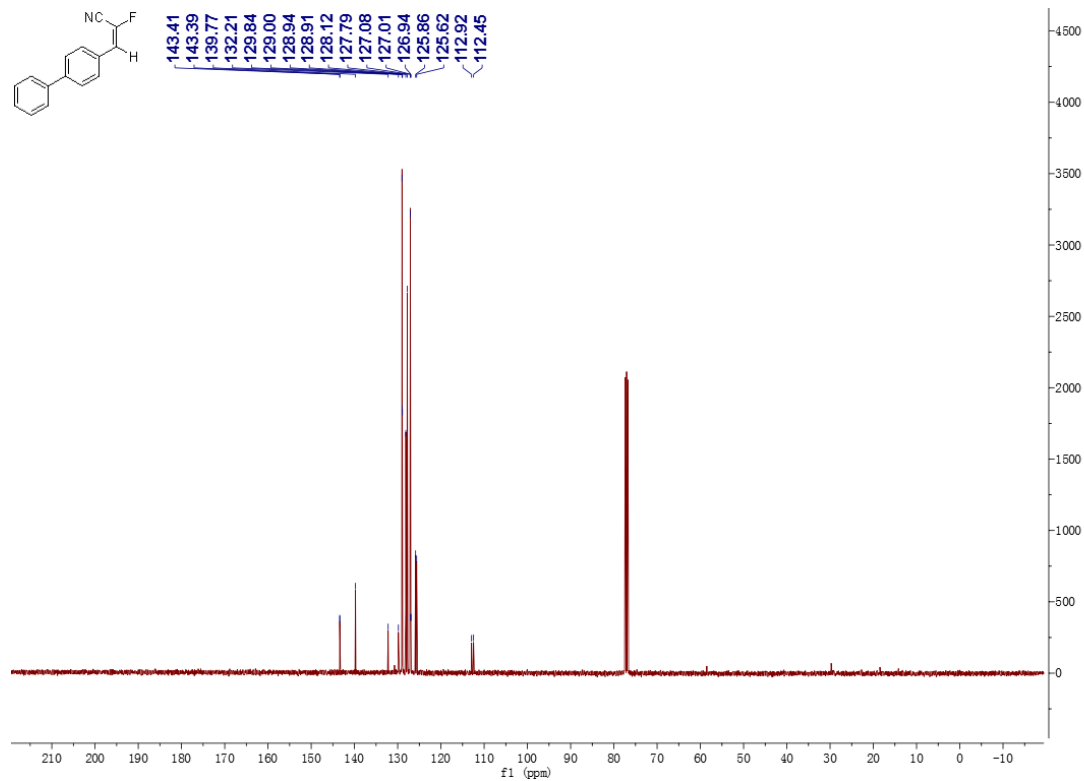




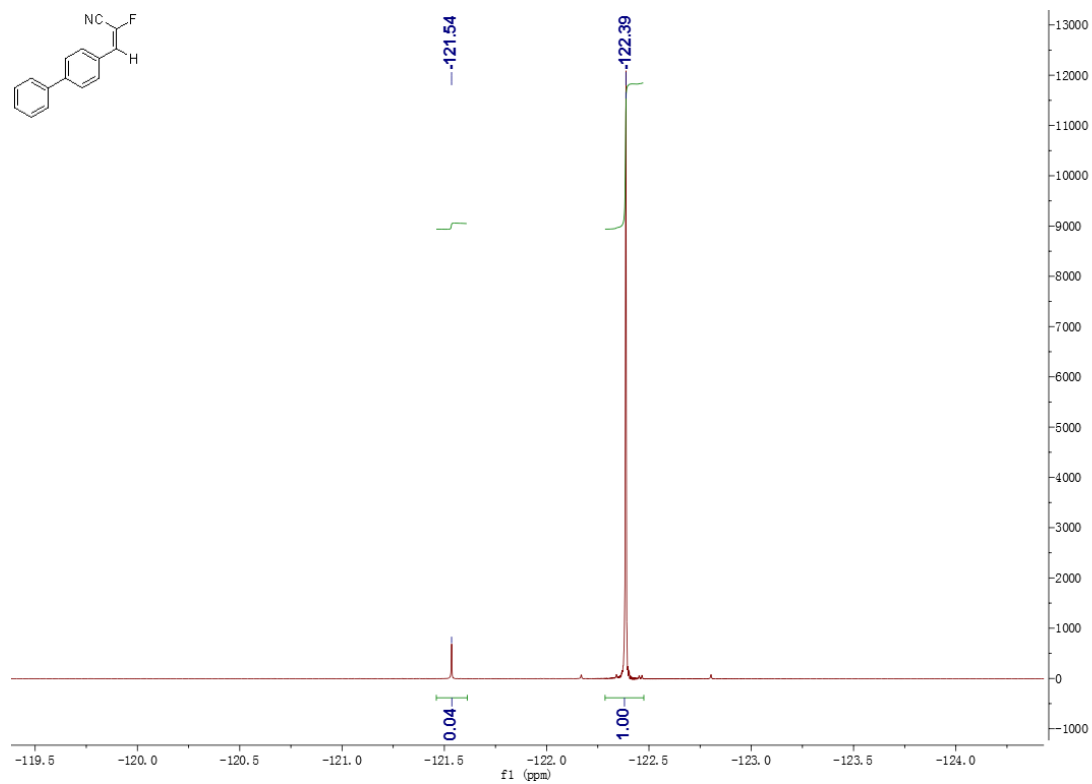
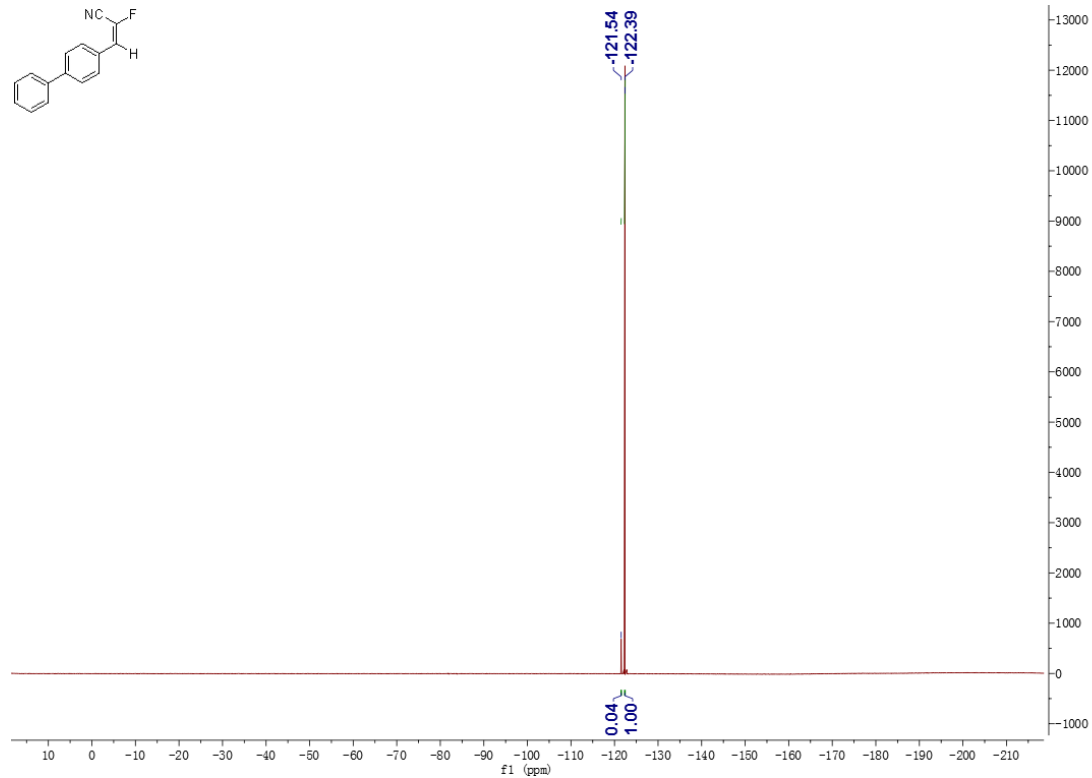
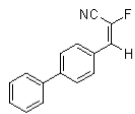
# <sup>1</sup>H NMR spectrum of (E)-3m



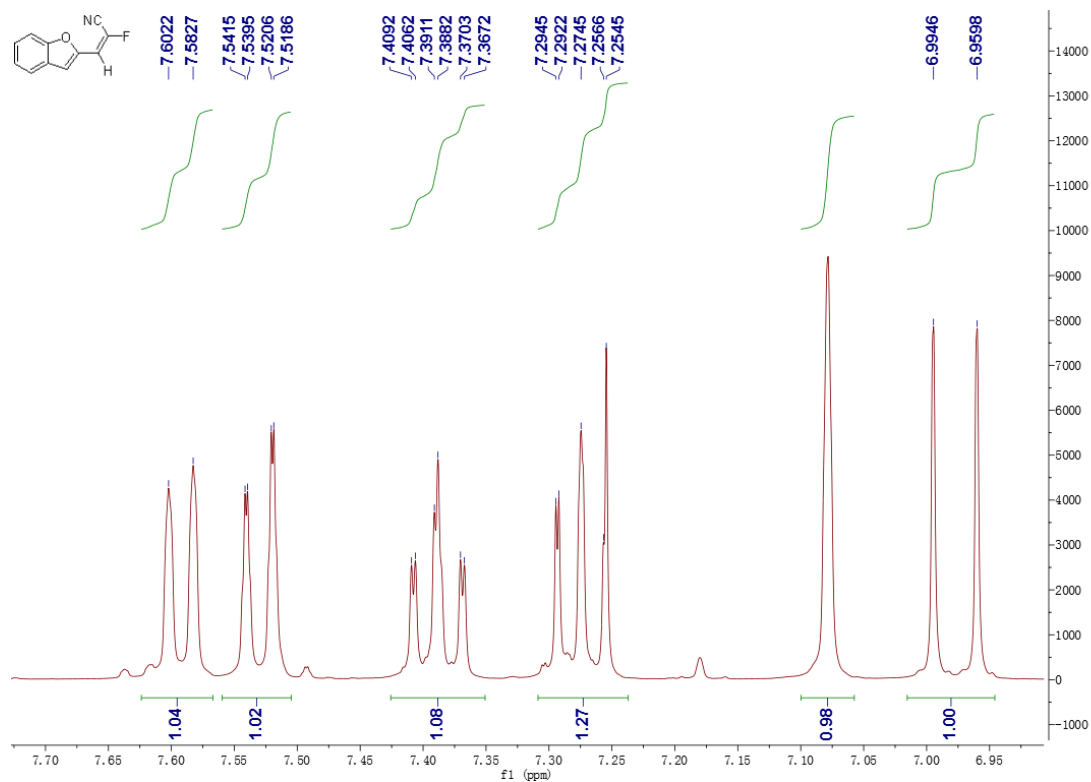
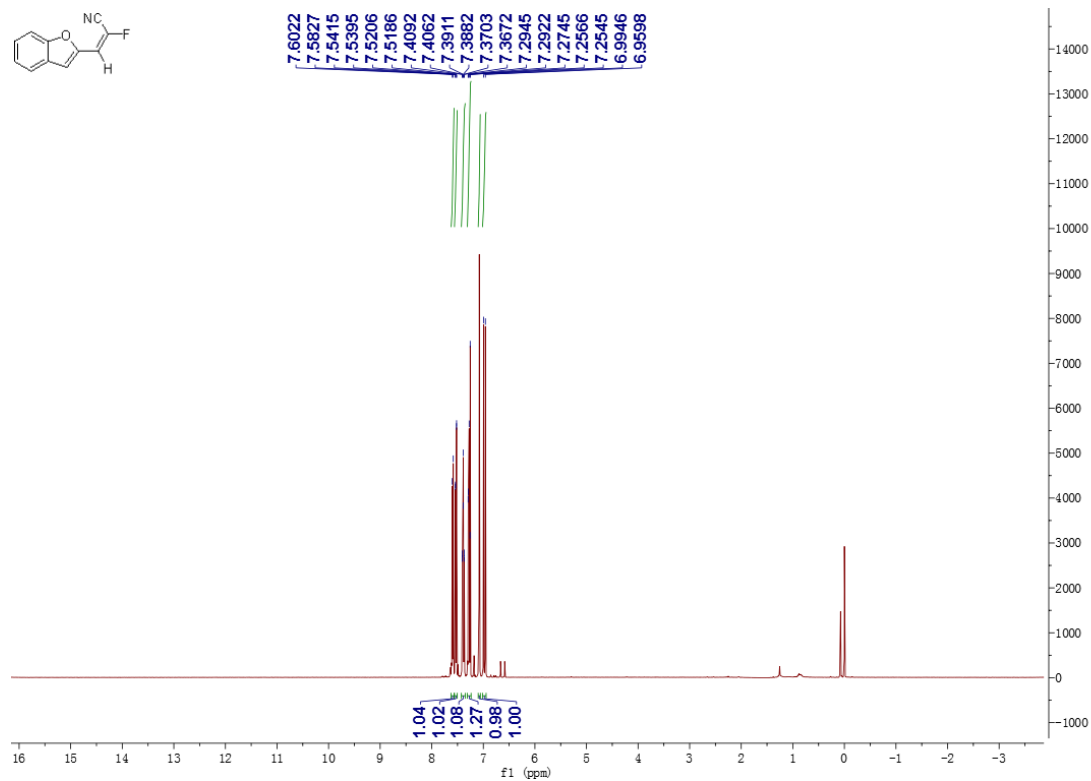
# <sup>13</sup>C NMR spectrum of (*E*)-**3m**



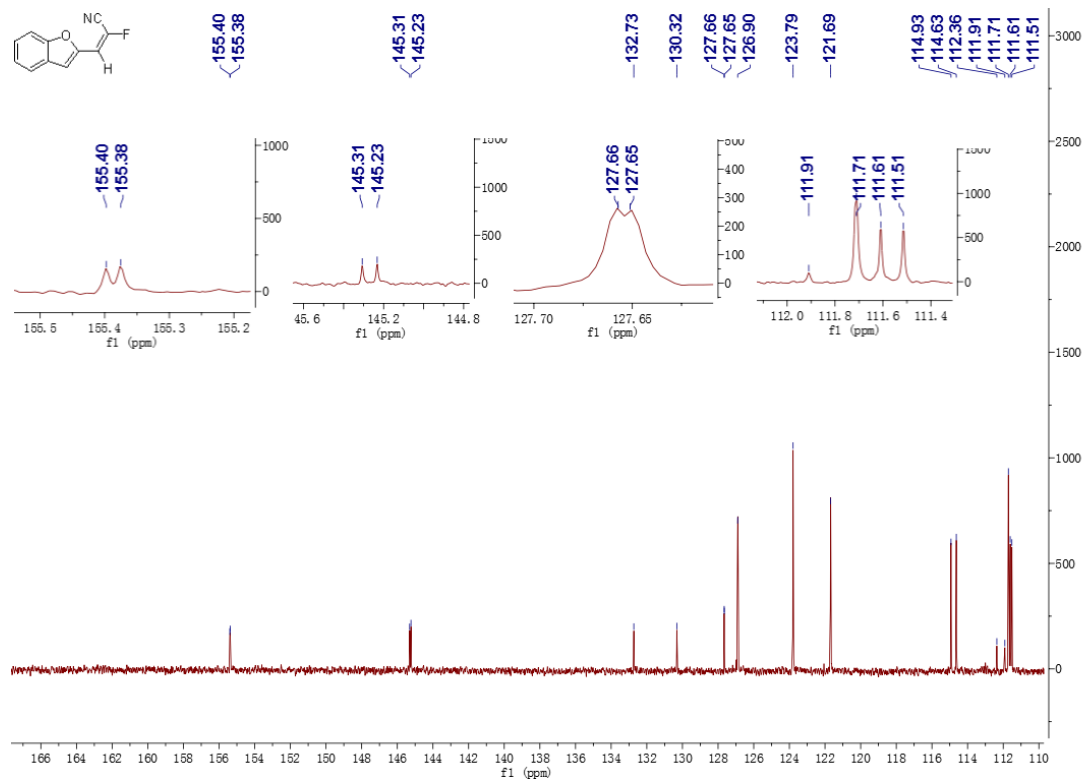
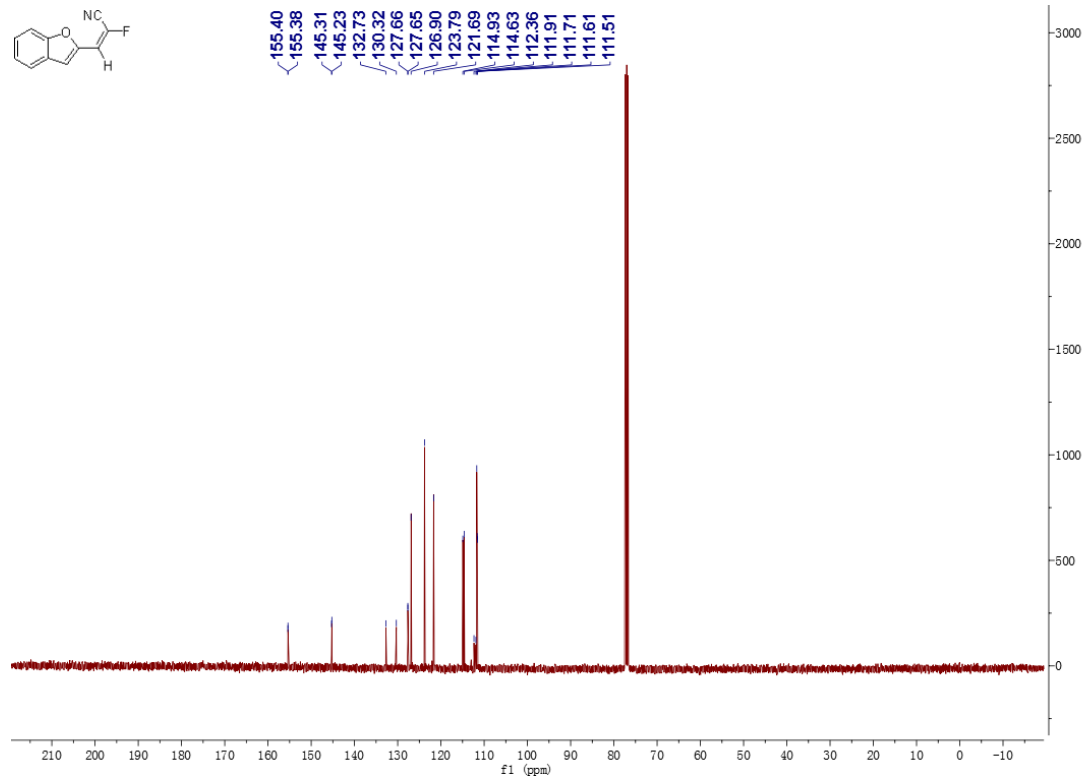
# <sup>19</sup>F NMR spectrum of (*E*)-**3m**



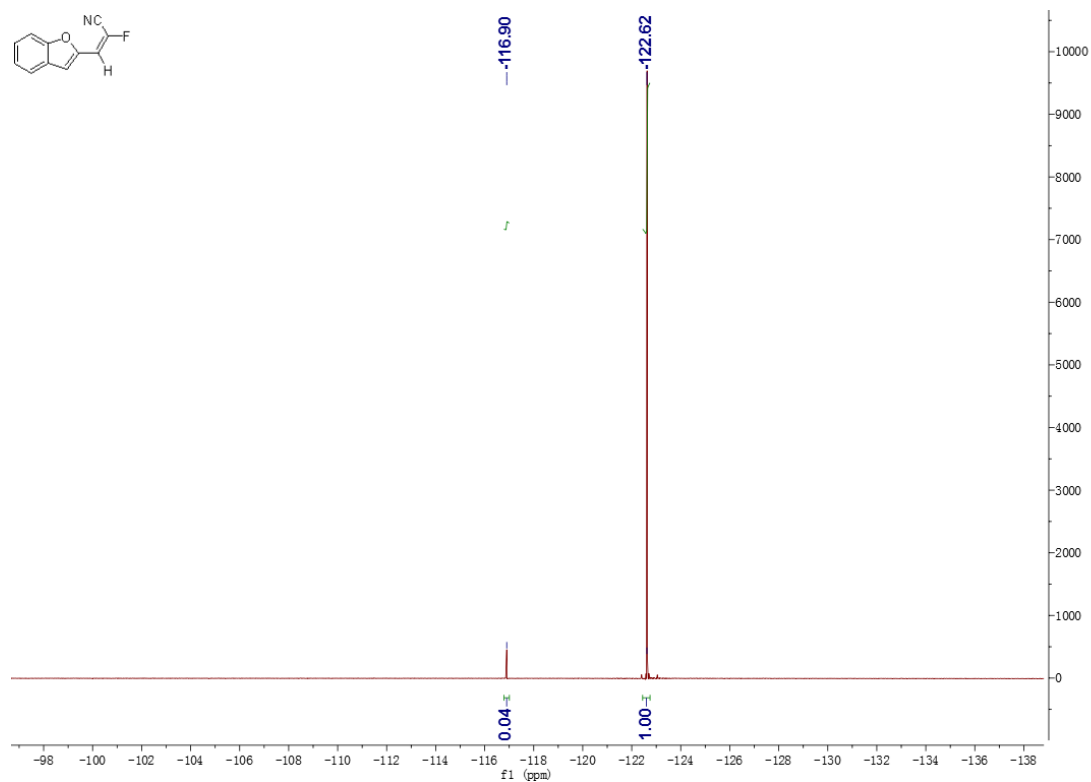
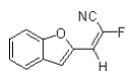
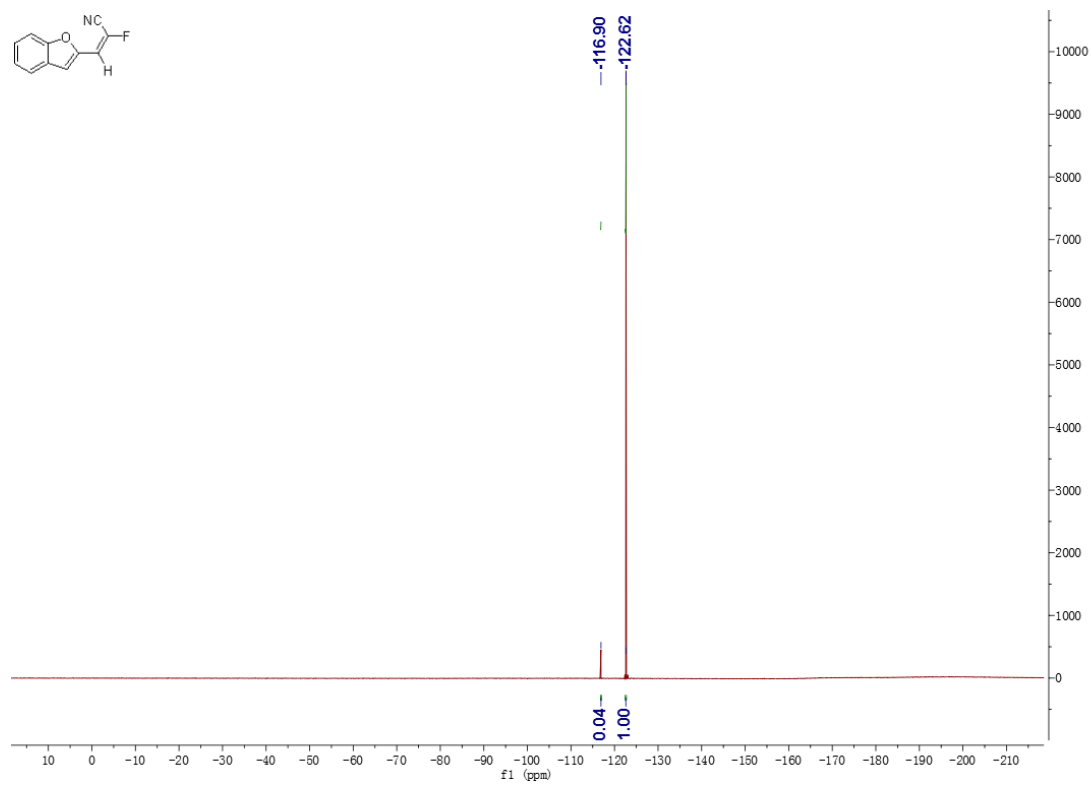
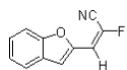
# <sup>1</sup>H NMR spectrum of (*E*)-3n



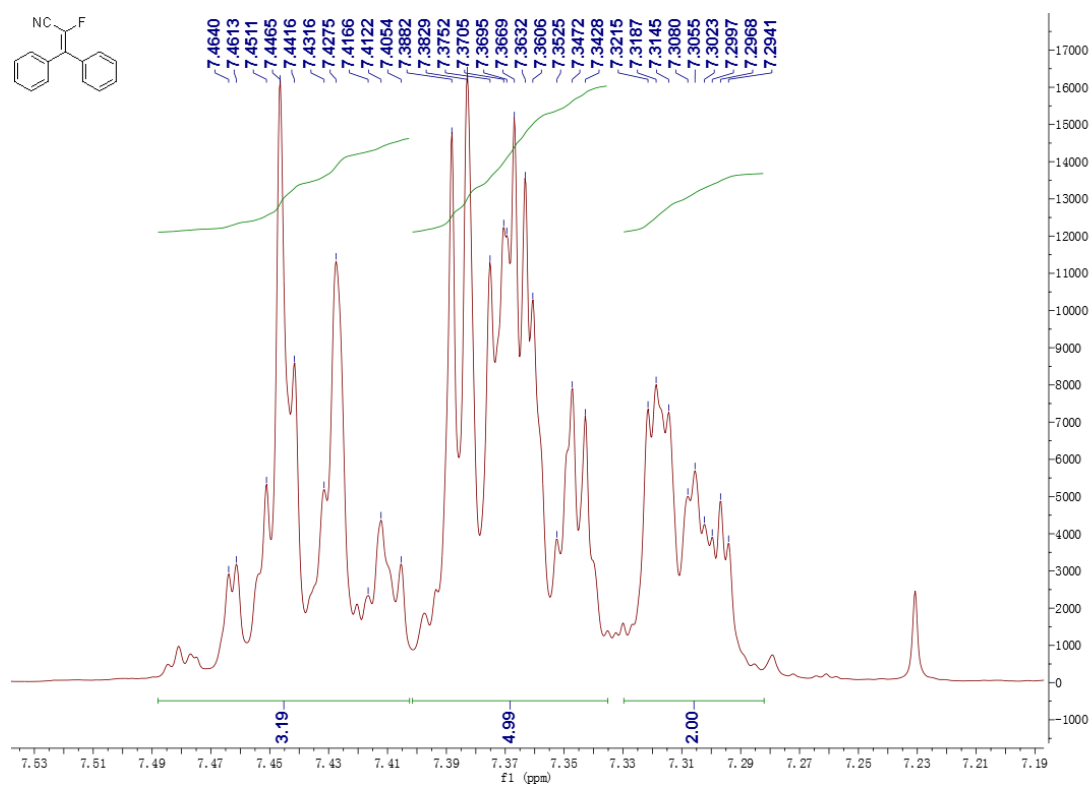
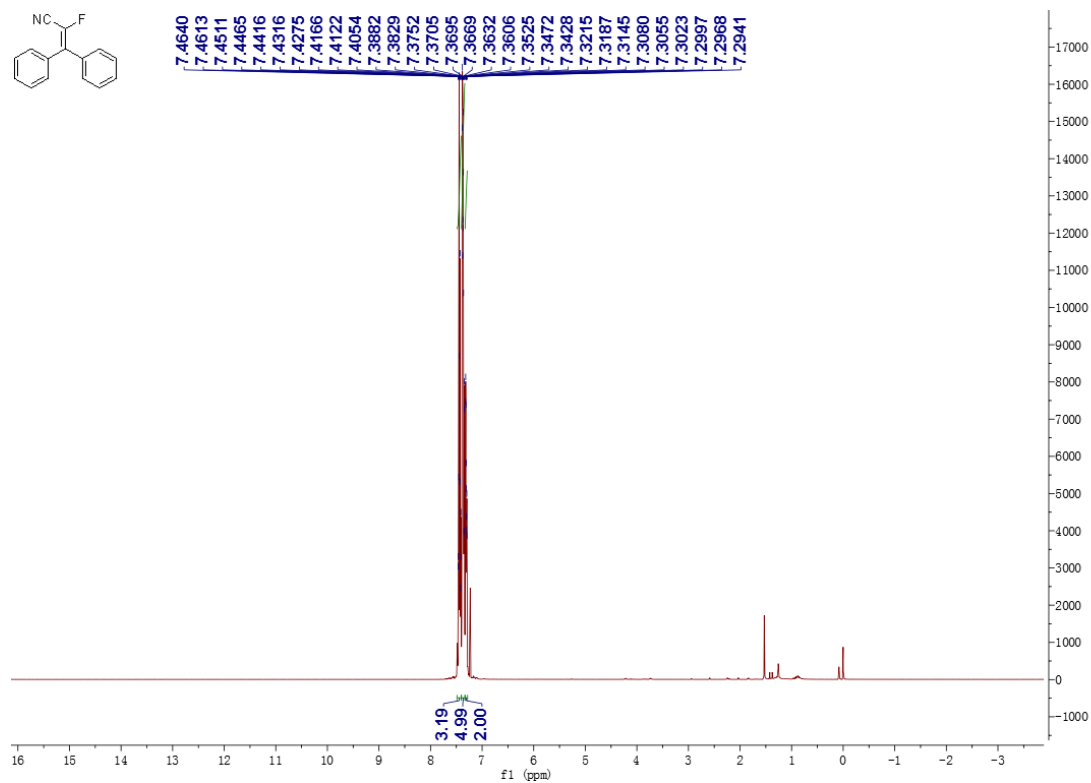
# $^{13}\text{C}$ NMR spectrum of (*E*)-**3n**



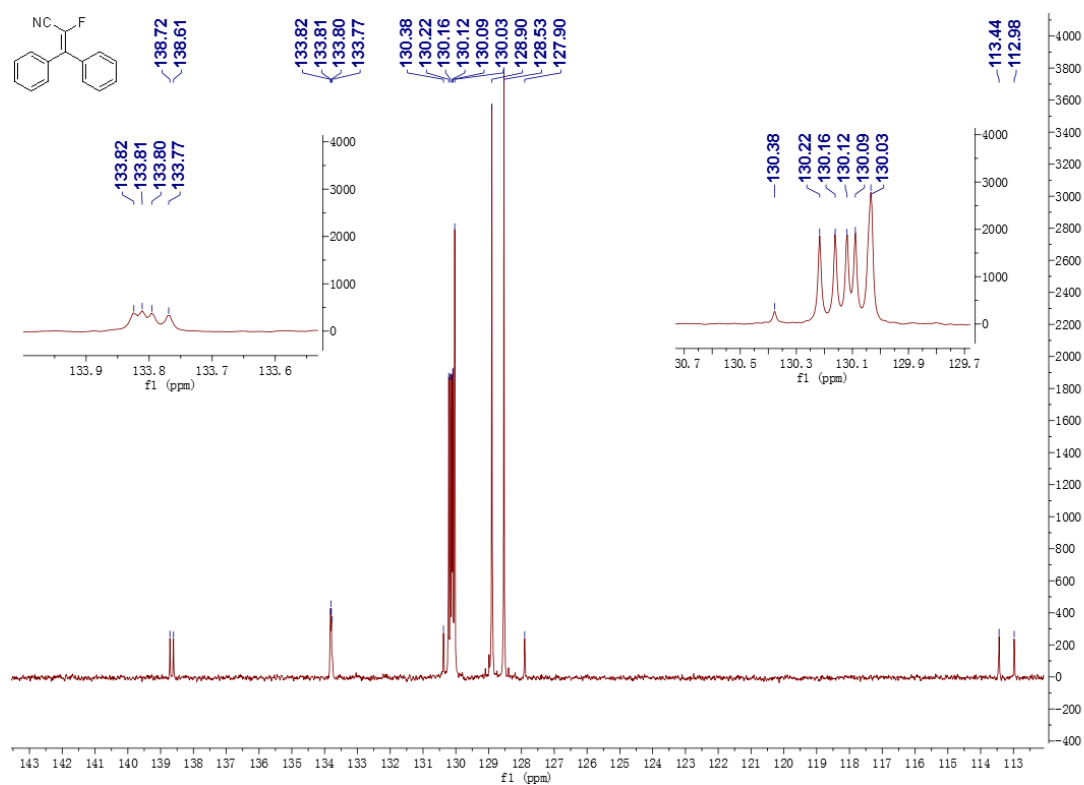
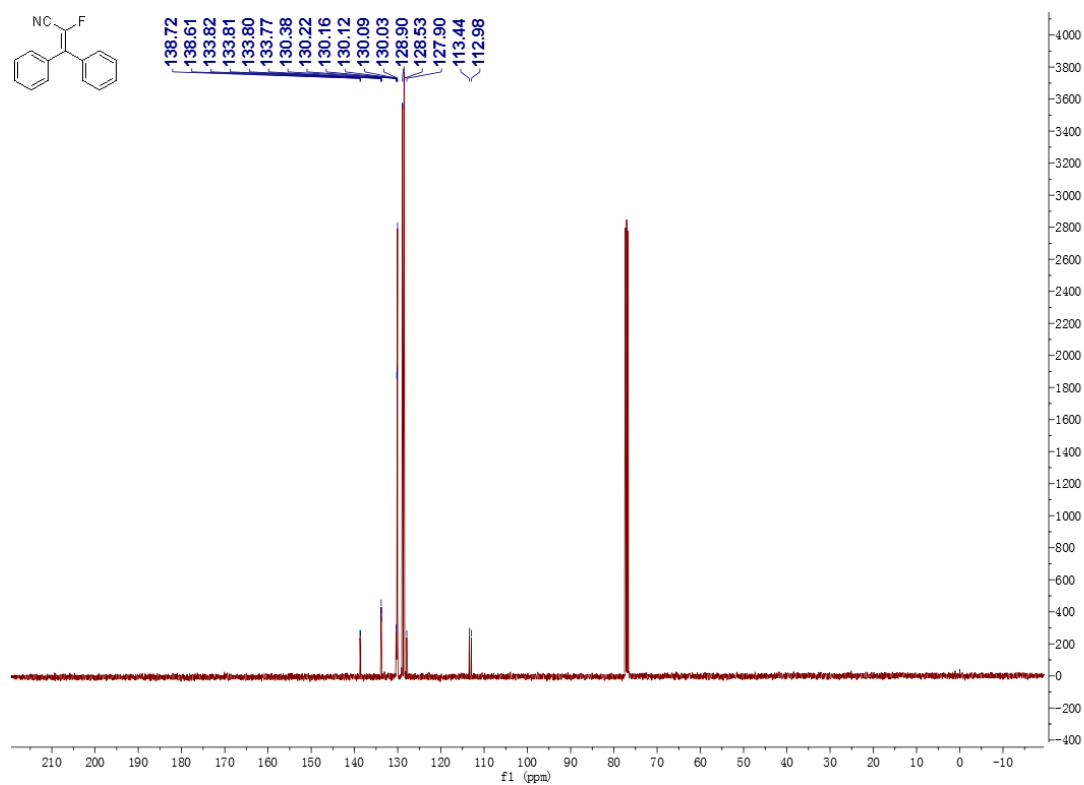
# <sup>19</sup>F NMR spectrum of (E)-3n



# <sup>1</sup>H NMR spectrum of (*E*)-**3o**

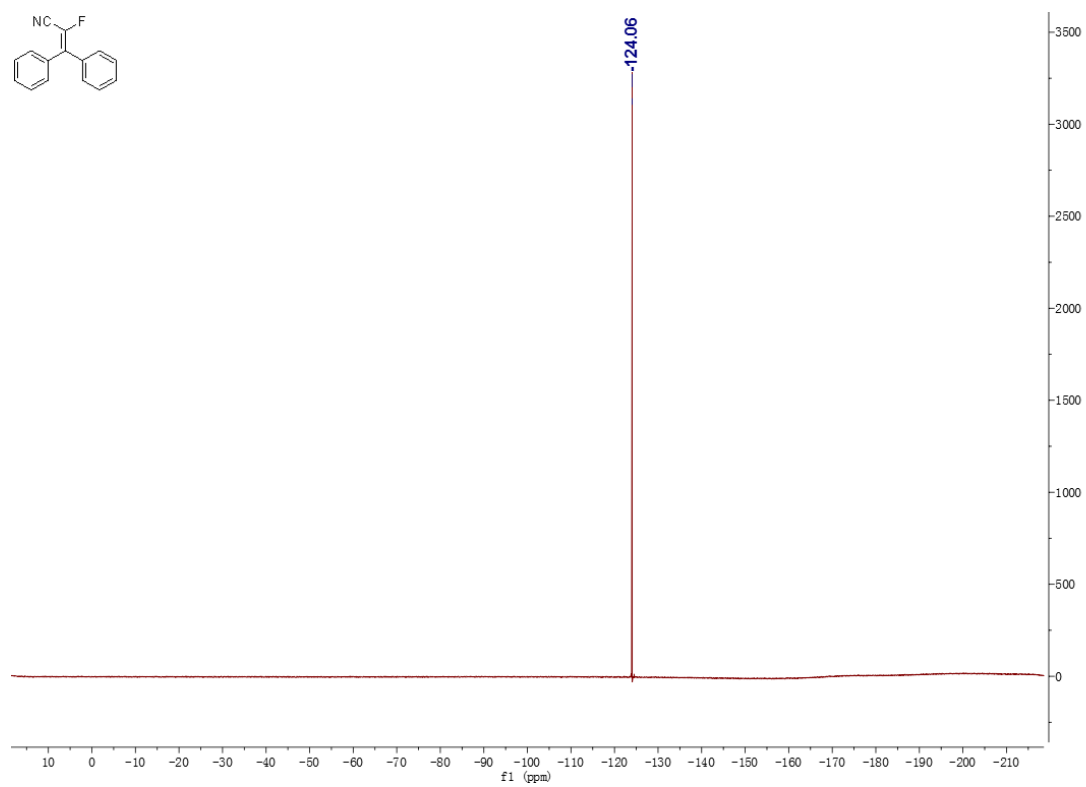
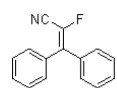


# <sup>13</sup>C NMR spectrum of (*E*)-**3o**

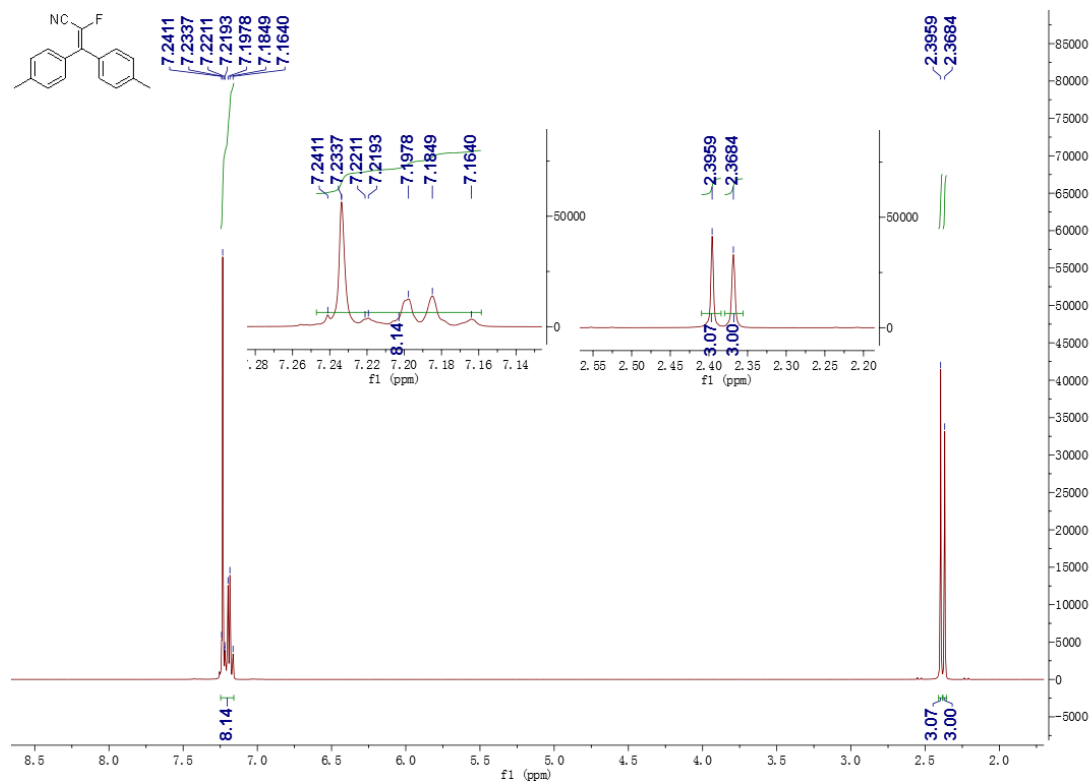
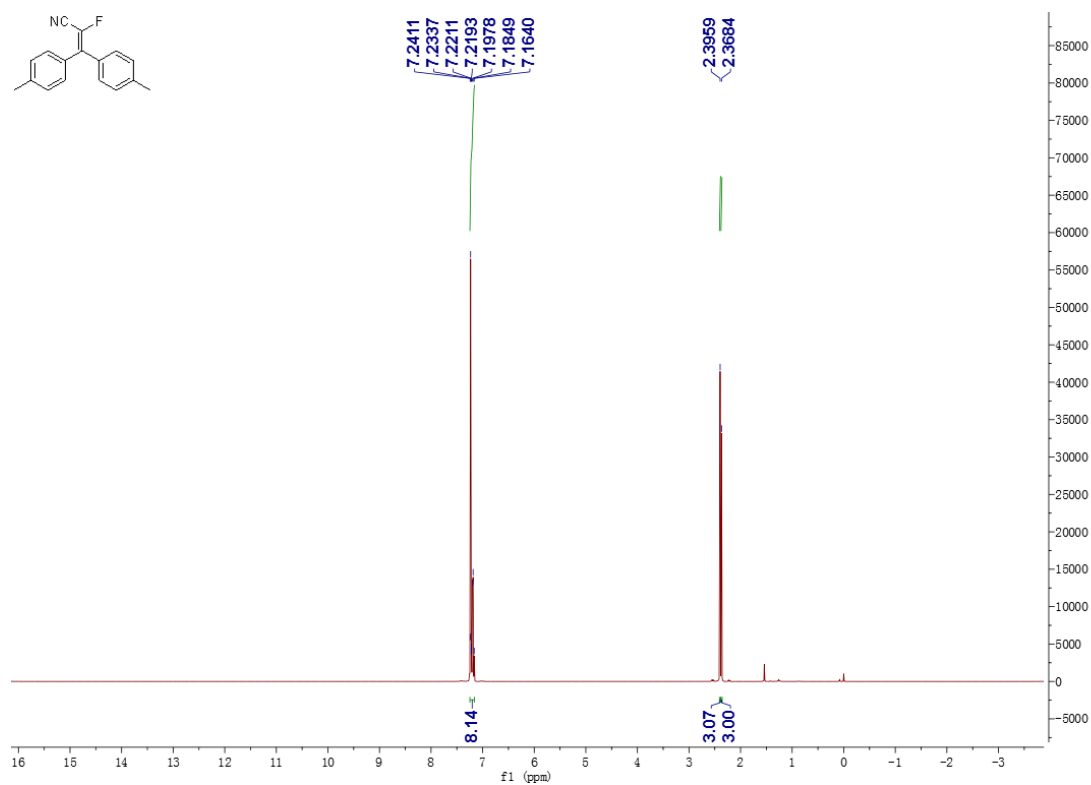




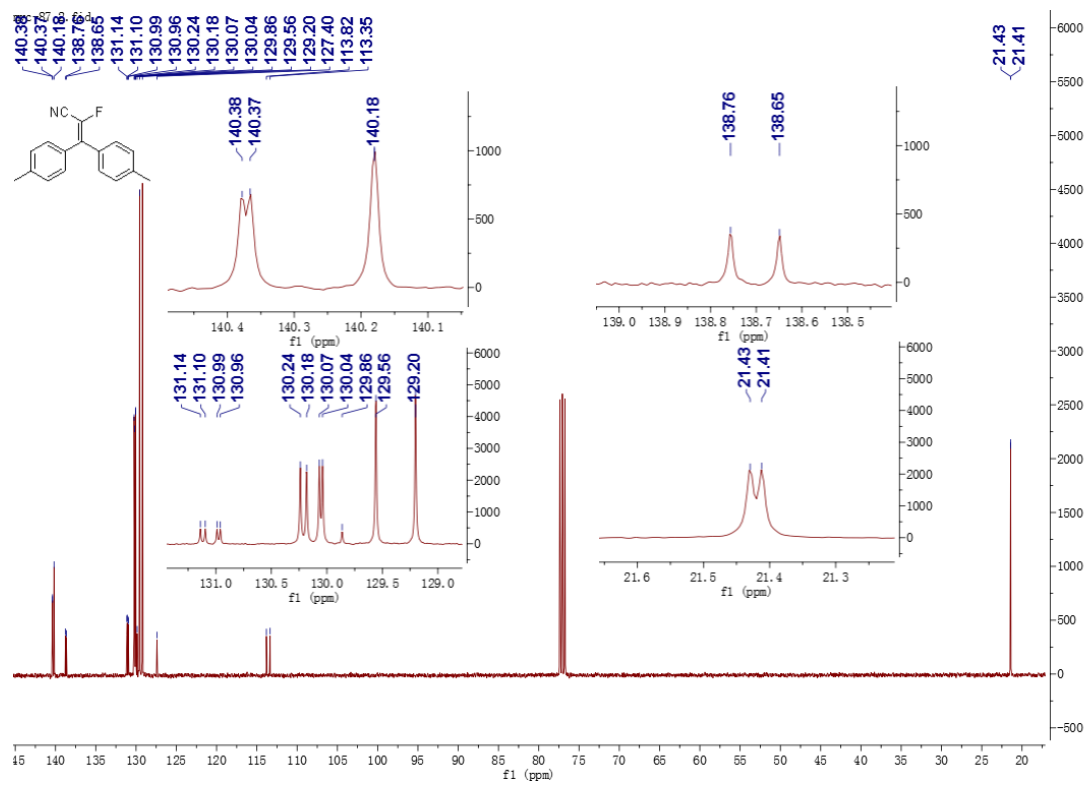
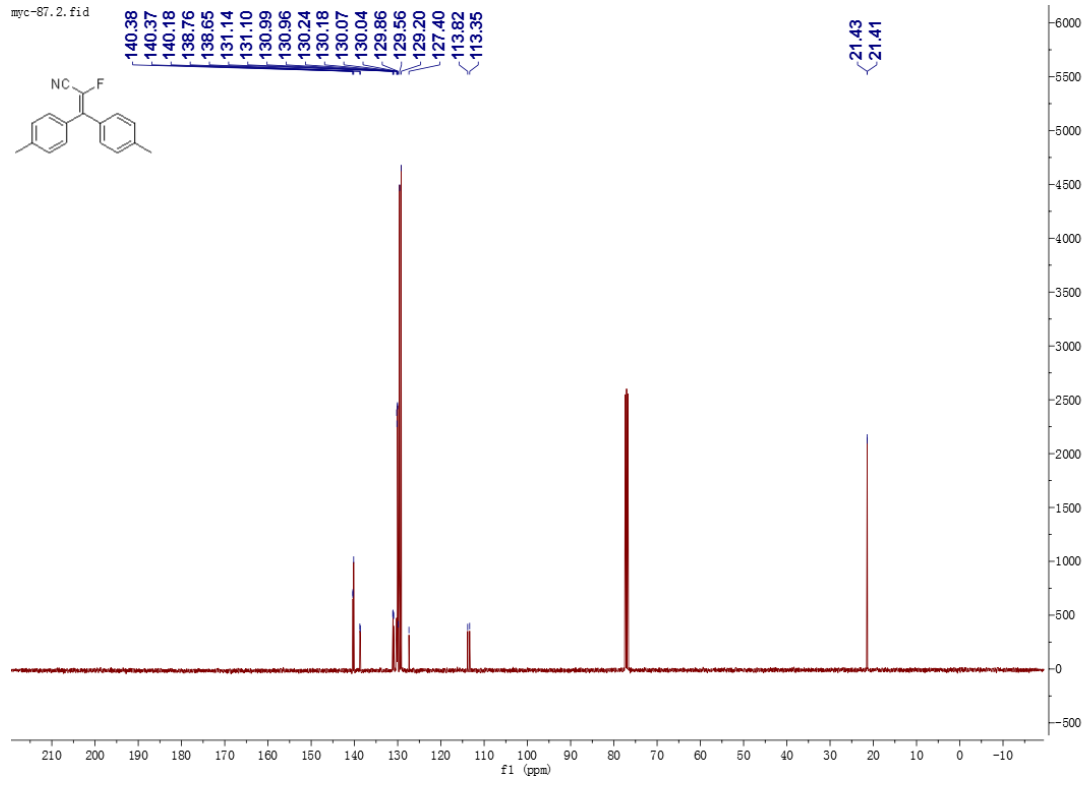
<sup>19</sup>F NMR spectrum of (E)-**3o**



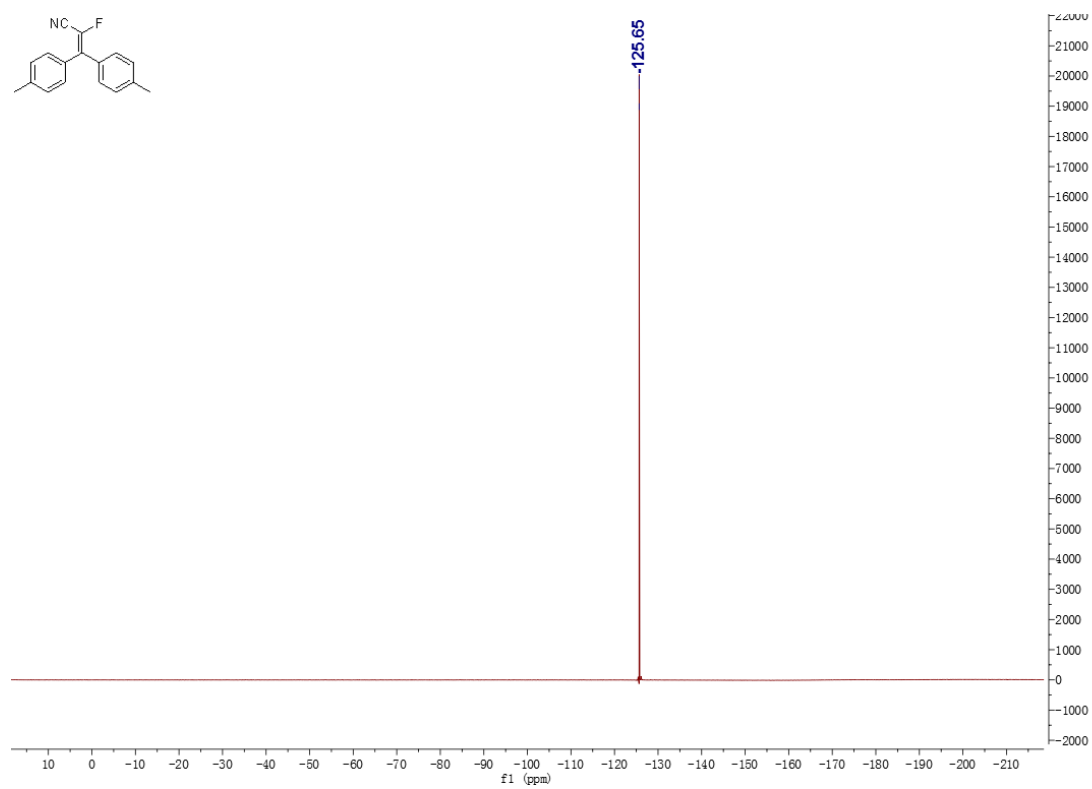
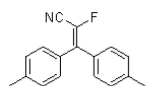
# <sup>1</sup>H NMR spectrum of (*E*)-3p



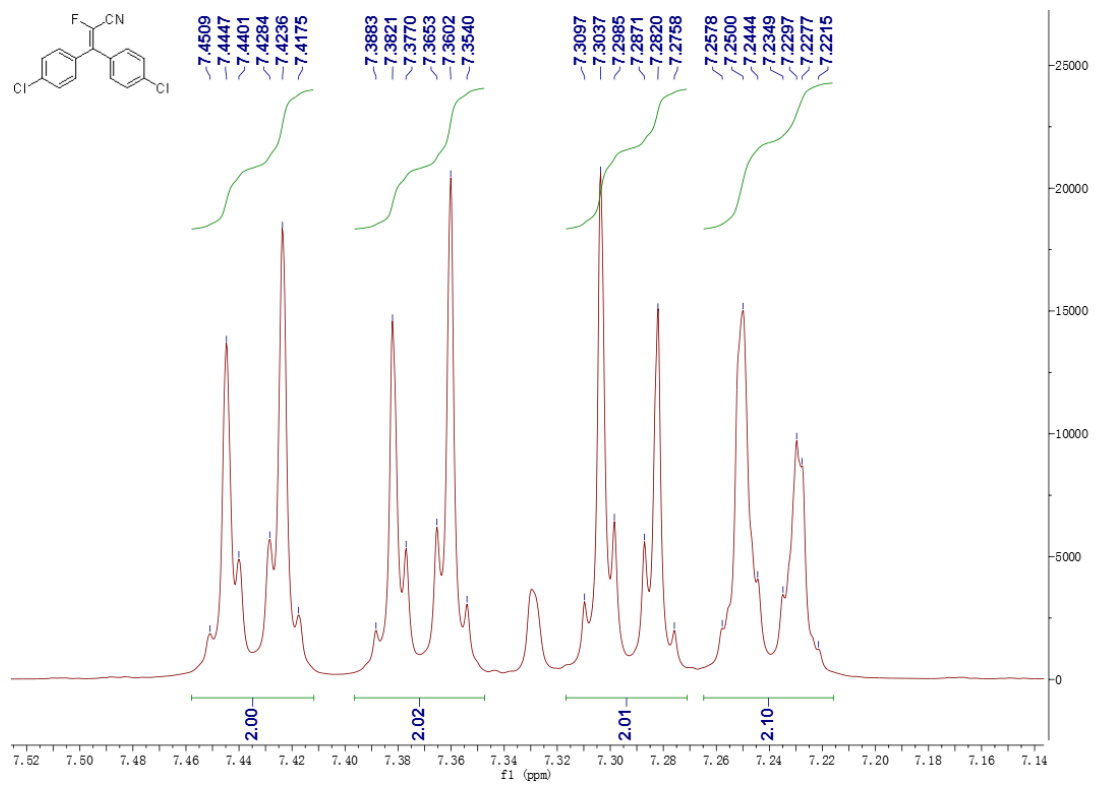
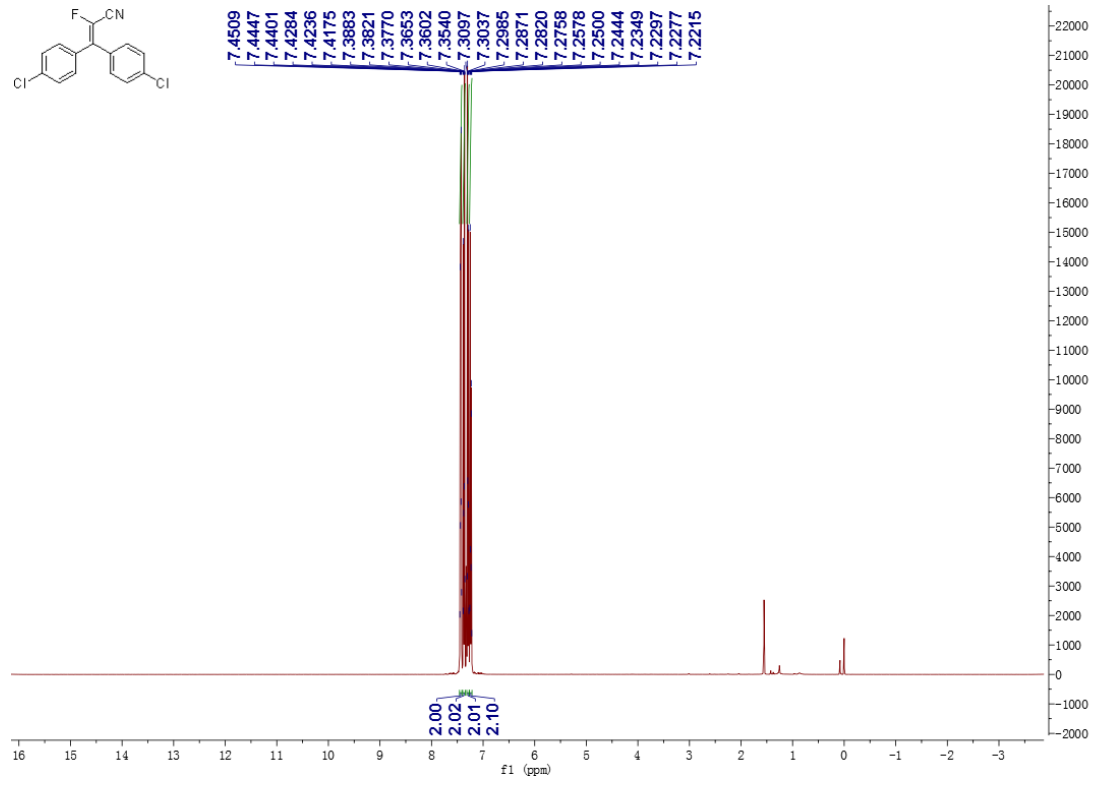
# <sup>13</sup>C NMR spectrum of (*E*)-3p



# $^{19}\text{F}$ NMR spectrum of (E)-**3p**

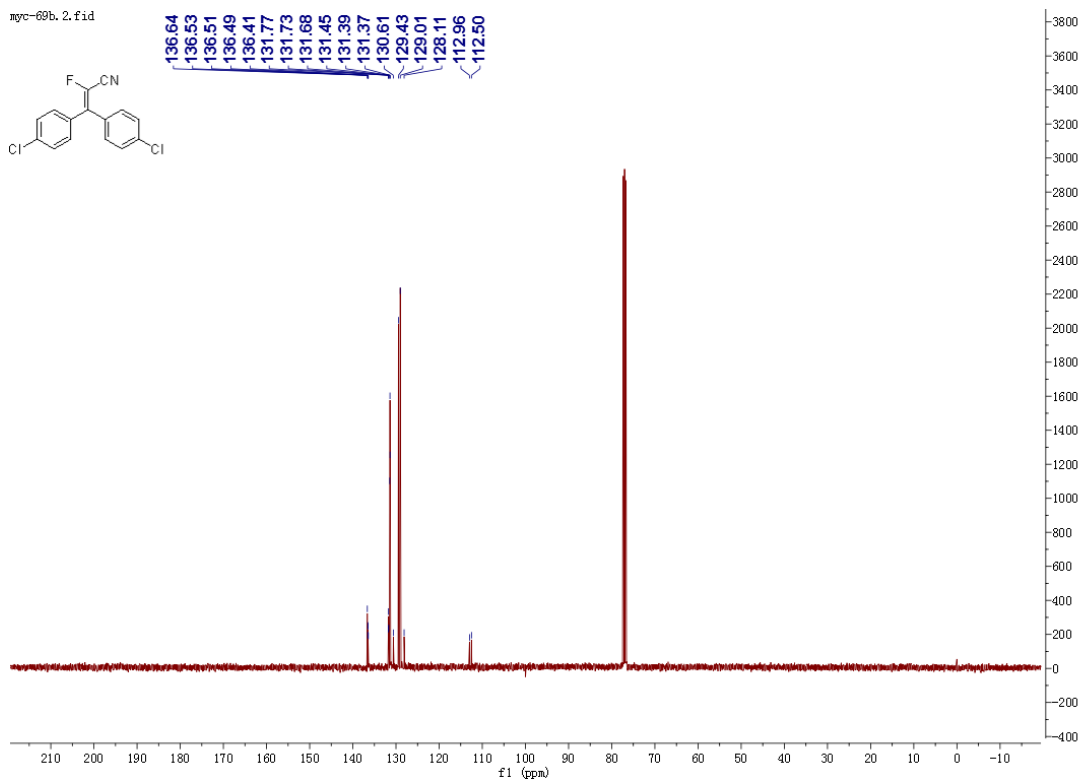
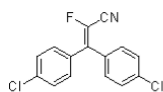


# <sup>1</sup>H NMR spectrum of (E)-3q

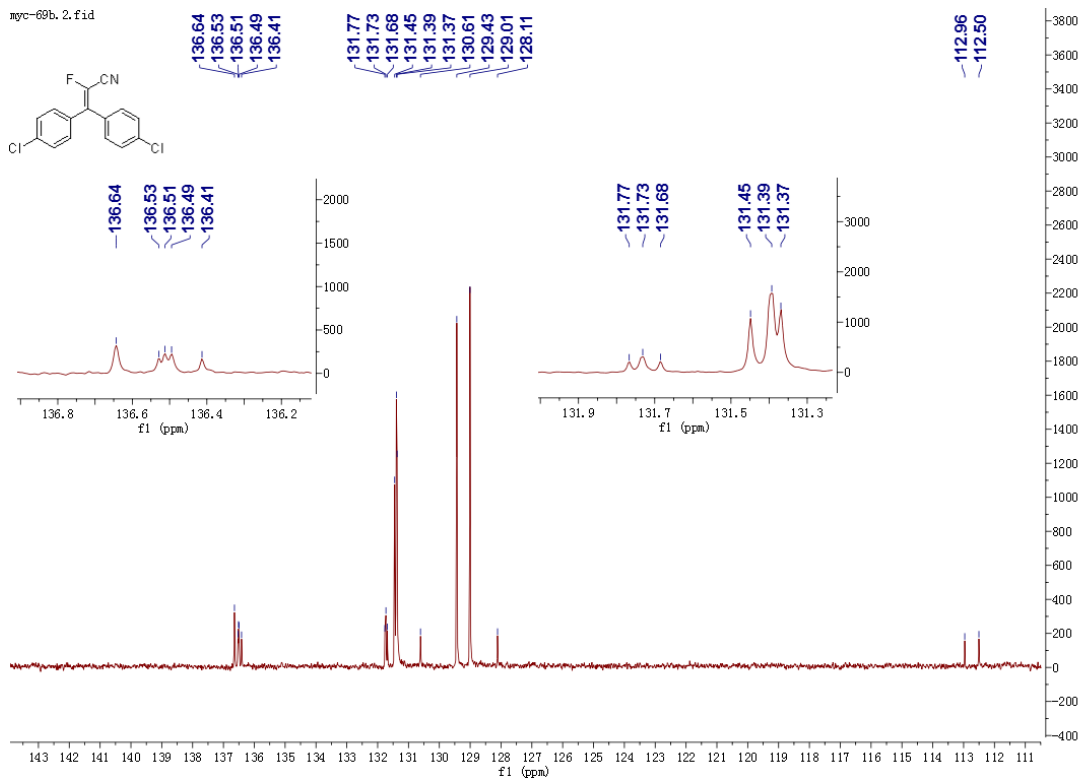
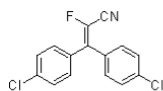


# <sup>13</sup>C NMR spectrum of (*E*)-**3q**

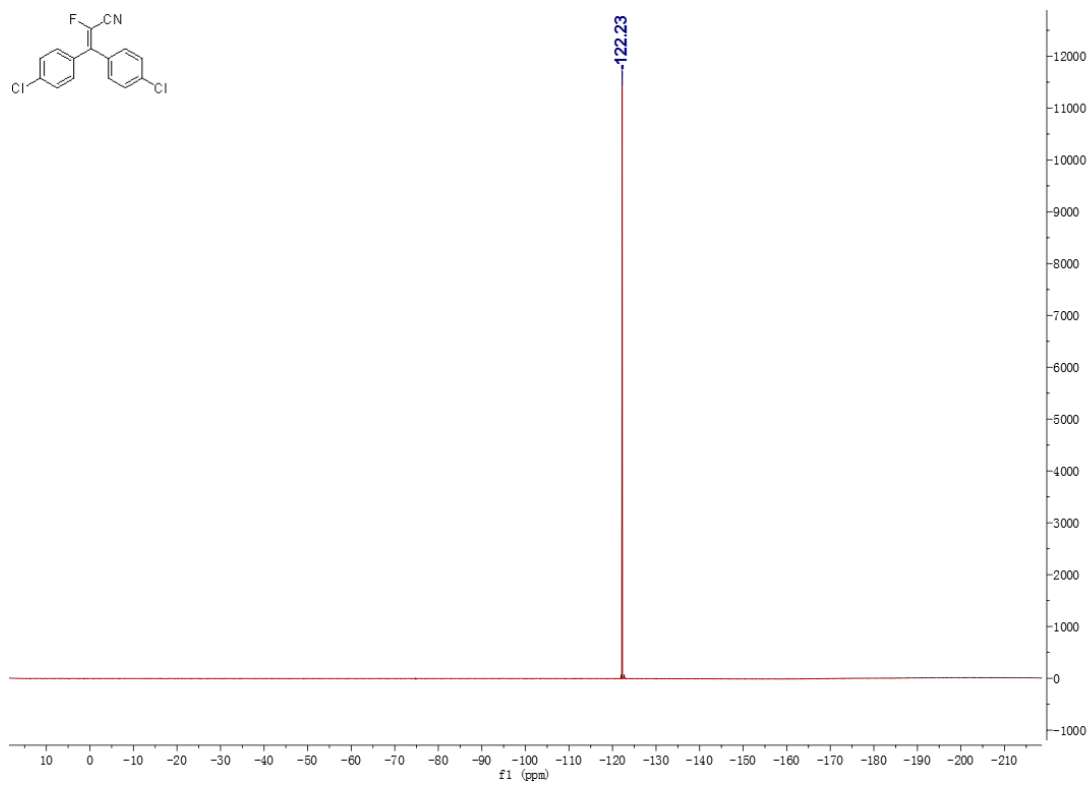
mpc-69b, 2.fid



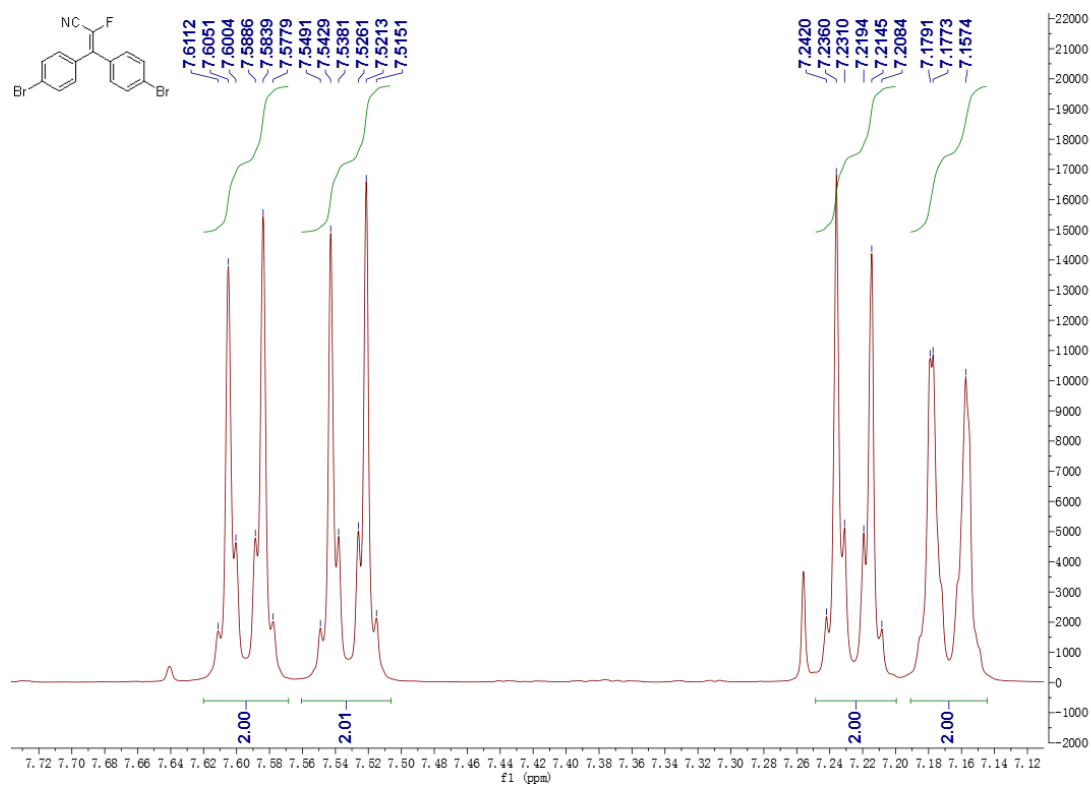
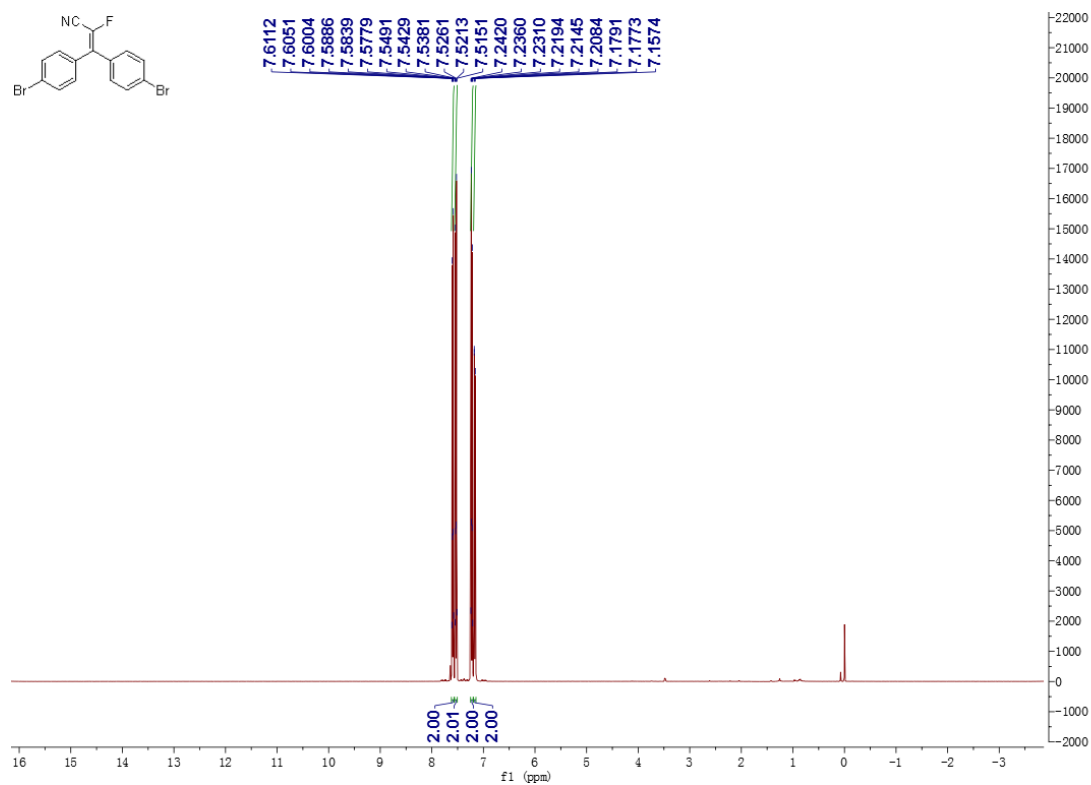
mpc-69b, 2.fid



<sup>19</sup>F NMR spectrum of (E)-**3q**

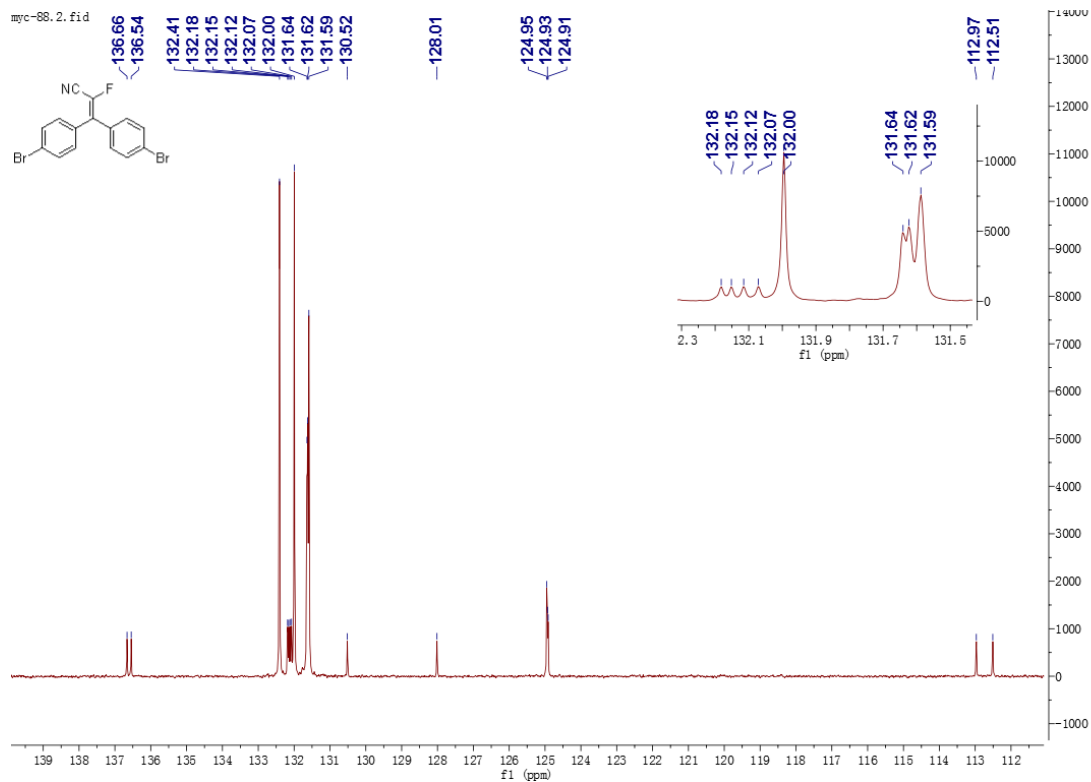
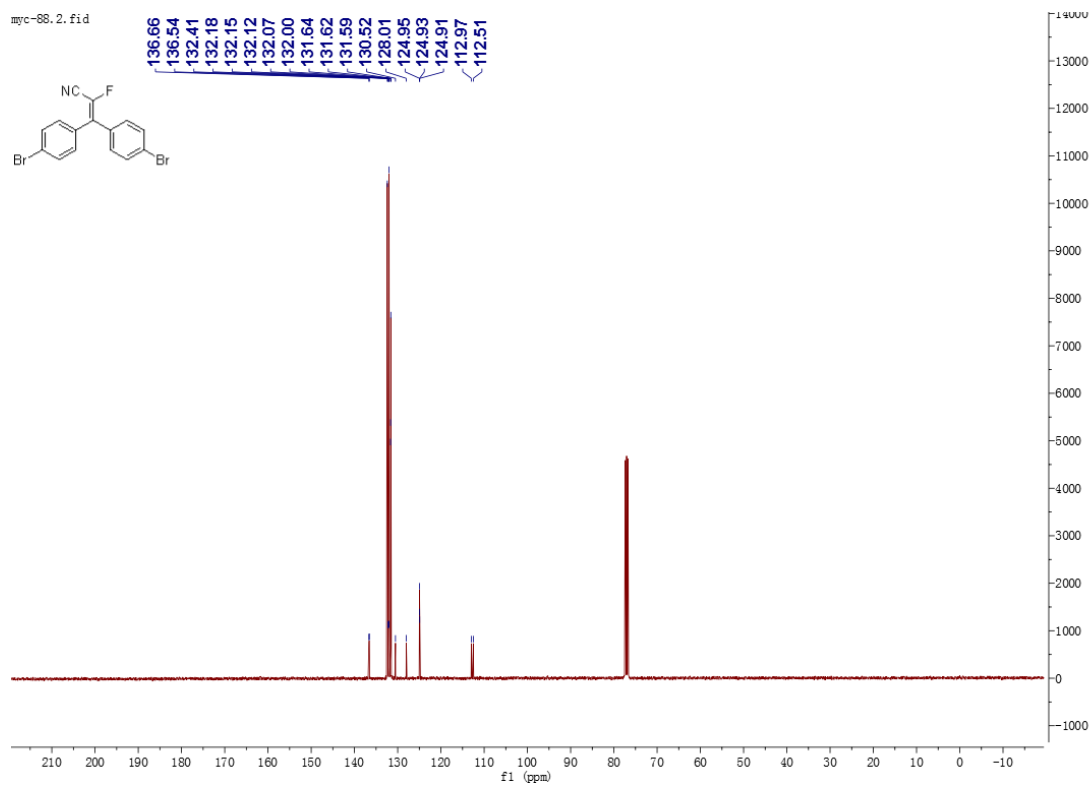


# <sup>1</sup>H NMR spectrum of (*E*)-**3r**





# <sup>13</sup>C NMR spectrum of (*E*)-**3r**



<sup>19</sup>F NMR spectrum of (E)-**3r**

