Supporting Information

Synthesis of 2-Fluorinated Pyrazolo[1,5-*a*]pyridines via Base-Mediated [3+2] Cycloaddition of *N*-Aminopyridinium Salts with *gem*-Difluorostyrenes

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Table of Contents

1. Materials and Methods

All chemicals were purchased from Energy Chemical Reagent, Ltd, Zane Chemical Technology company, Aladdin Ltd, Crystal pure bio-tech company and so forth. Unless otherwise stated, all experiments were conducted in a seal tube under argon atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

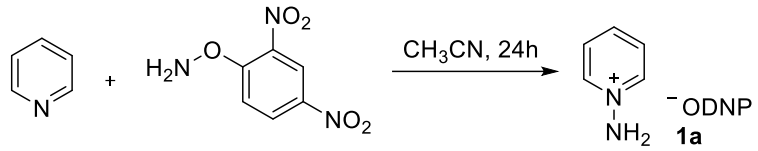
^{1}H-NMR, ^{13}C-NMR and ^{19}F-NMR spectra were recorded in $CDCl_3$ on Nuclear Magnetic Resonance spectrometer (400 MHz for ^{1}H or 600 MHz for ^{1}H, 151 MHz for ^{13}C, 376 MHz for ^{19}F) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H NMR, δ = 77.00 for ^{13}C NMR) as an internal reference. High resolution mass spectra were recorded using ZAB-HS Bifocal high resolution mass spectrometer. Coupling constants (J) were reported in Hertz (Hz).

2. Experimental procedures and characterization data

2.1. The synthesis of compounds **1** according to the following procedure

The substrates **1** were prepared according to the procedures in the literature[1].

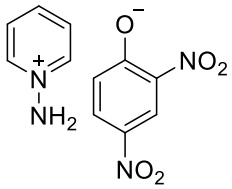
As exemplified for **1a**:



To a solution of pyridine (0.47 g, 6.0 mmol) in acetonitrile (25 mL) was added *O*-(2,4-dinitrophenyl) hydroxylamine (1.3 g, 6.6 mmol). The reaction flask was sealed with rubber plug, and the reaction mixture was stirred for 24 h at room temperature, then upon filtering off the solvent. The orange solid was obtained, which was used in the next step without further purification.

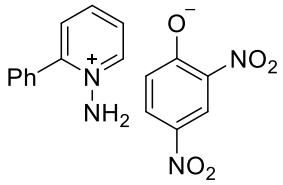
2.2 Characterization data of some starting materials **1**

All characterization data of compounds **1** are consistent with literature after contrast. As known compounds, we herein list the melting point, ^{1}H NMR and ^{13}C NMR data of some compounds **1**.



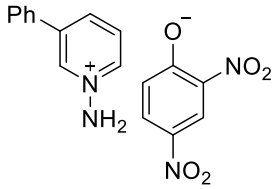
1-Aminopyridin-1-ium ylide (1a)

Yellow solid; Yield =1.25 g (75%); mp 149 - 151 °C. **^{1}H NMR** (600 MHz, CD_3SOCD_3), δ: 8.85 (s, 2H), 8.74 - 8.59 (m, 3H), 8.30 (t, J = 7.8 Hz, 1H), 8.05 (t, J = 7.2 Hz, 2H), 7.85 - 7.83 (m, 1H), 6.42 (d, J = 9.6 Hz, 1H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 170.9, 139.9, 138.6, 136.5, 128.6, 128.6, 128.0, 127.0, 125.4.



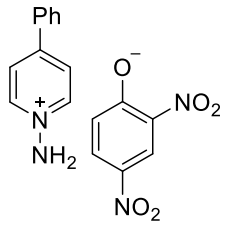
1-Amino-2-phenylpyridin-1-ium ylide (1c)

Yellow solid; Yield = 1.32 g (62%); mp 134-136 °C. **^{1}H NMR** (400 MHz, CD_3SOCD_3), δ: 9.04 (s, 1H), 8.67 (s, 1H), 8.40 (t, J = 7.2 Hz, 1H), 8.13 - 8.03 (m, 4H), 7.86 - 7.78 (m, 3H), 7.64 (s, 3H), 6.41 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 170.6, 150.1, 141.3, 141.2, 136.4, 131.4, 130.8, 130.4, 130.1, 129.2, 128.1, 127.4, 126.8, 125.4.



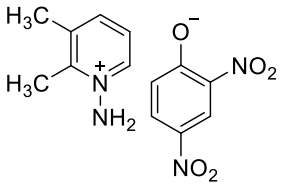
1-Amino-3-phenylpyridin-1-ium ylide (1e)

Yellow solid; Yield = 1.49 g (70%); mp 118 - 120 °C. **^{1}H NMR** (400 MHz, CD_3SOCD_3), δ: 9.18 (s, 1H), 8.81 (s, 1H), 8.76 - 8.53 (m, 4H), 8.09 (t, J = 8.0 Hz, 1H), 7.88 - 7.75 (m, 3H), 7.67 - 7.50 (m, 3H), 6.40 (d, J = 10.0 Hz, 1H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 170.9, 140.1, 137.2, 136.7, 136.4, 136.2, 133.6, 130.5, 129.9, 128.4, 128.0, 127.6, 127.0, 125.4.



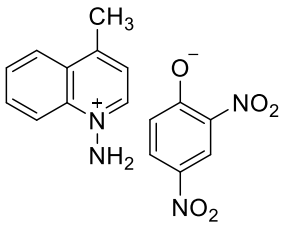
1-Amino-4-phenylpyridin-1-ium ylide (1i)

Yellow solid; Yield = 1.70 g (80%); mp 164 - 166 °C. **^{1}H NMR** (400 MHz, CD_3SOCD_3), δ: 8.82 (d, J = 7.2 Hz, 2H), 8.62 (d, J = 3.2 Hz, 1H), 8.47 (s, 2H), 8.37 (d, J = 7.2 Hz, 2H), 7.99 - 7.97 (m, 2H), 7.84 (dd, J = 10.0, 3.2 Hz, 1H), 7.67 - 7.57 (m, 3H), 6.43 (d, J = 10.0 Hz, 1H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 169.7, 149.9, 139.0, 136.5, 134.2, 131.8, 130.0, 128.7, 128.1, 128.0, 126.4, 125.2, 125.1.



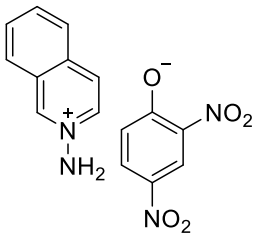
1-Amino-2,3-dimethylpyridin-1-ium ylide (1j)

Yellow solid; Yield =1.54 g (84%); mp 101 - 103 °C. **^{1}H NMR** (400 MHz, CD_3SOCD_3), δ: 8.72 (d, J = 6.4 Hz, 1H), 8.61 (d, J = 3.2 Hz, 1H), 8.12 - 8.10 (m, 3H), 7.80 (dd, J = 9.6, 3.2 Hz, 1H), 7.76 (t, J = 7.2 Hz, 1H), 6.36 (d, J = 10.0 Hz, 1H), 2.66 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 175.4, 154.9, 145.7 (d, J = 9.4 Hz), 143.1, 142.7 (d, J = 39.4 Hz), 141.2, 132.7, 131.7, 130.1 (d, J = 30.3 Hz), 129.6, 24.2, 20.4.



1-Amino-4-methylquinolin-1-ium ylide (1o)

Yellow solid; Yield = 1.48 g (72%); mp 164 - 166 °C. **^{1}H NMR** (600 MHz, CD_3SOCD_3), δ: 9.28 (d, J = 3.0 Hz, 1H), 8.64 - 8.55 (m, 2H), 8.47 - 8.31 (m, 3H), 8.27 - 8.19 (t, J = 7.8 Hz, 1H), 8.05 - 7.92 (m, 2H), 7.77 (dd, J = 9.6, 3.0 Hz, 1H), 6.34 (d, J = 9.6 Hz, 1H), 2.93 (s, 3H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 170.8, 154.1, 143.2, 136.8, 136.4, 134.6, 130.2, 129.2, 127.9, 127.0, 126.7, 125.4, 122.7, 119.1, 19.5.

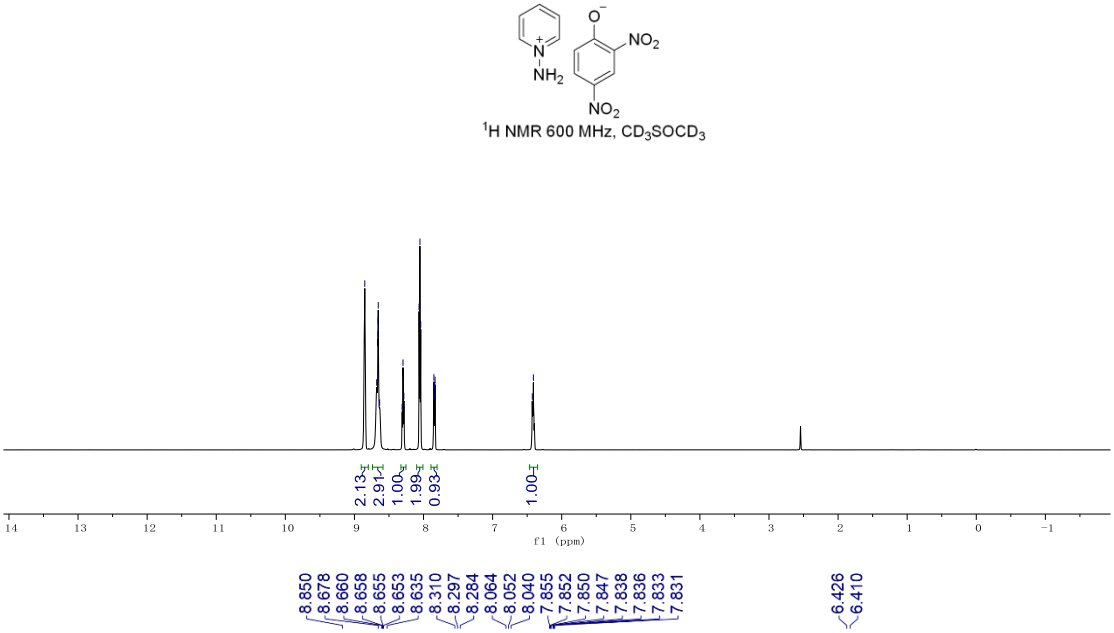


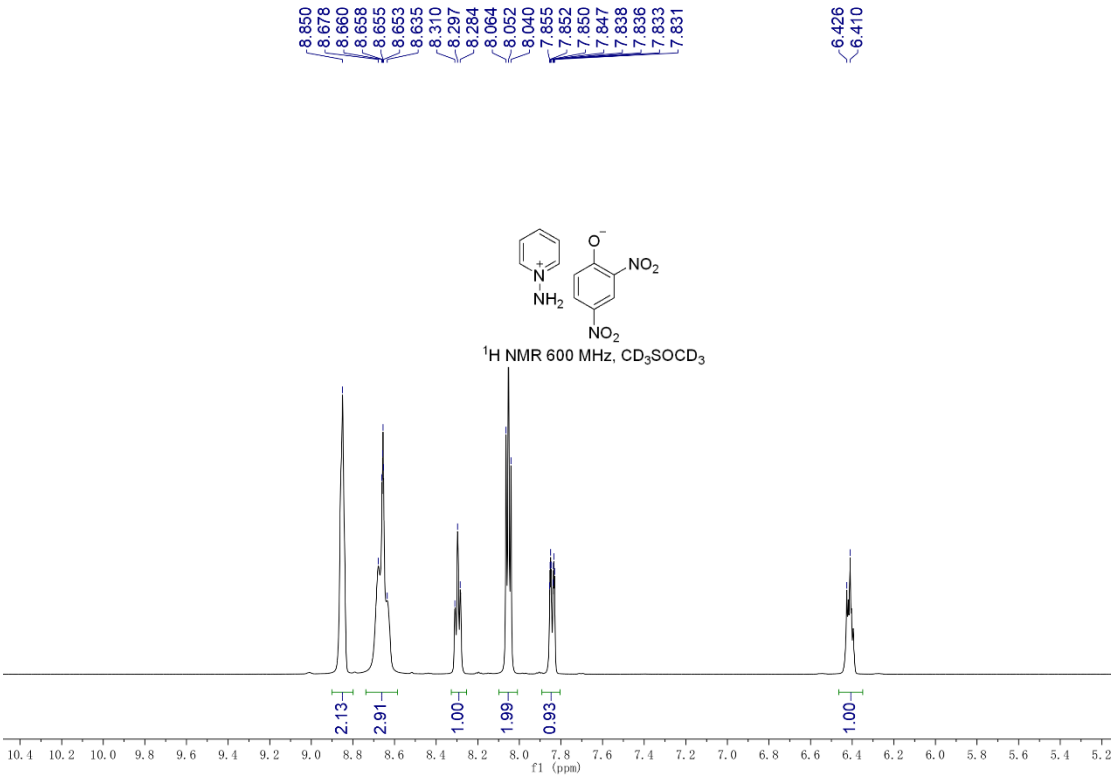
1-Aminoisoquinolin-2-ium ylide (1q)

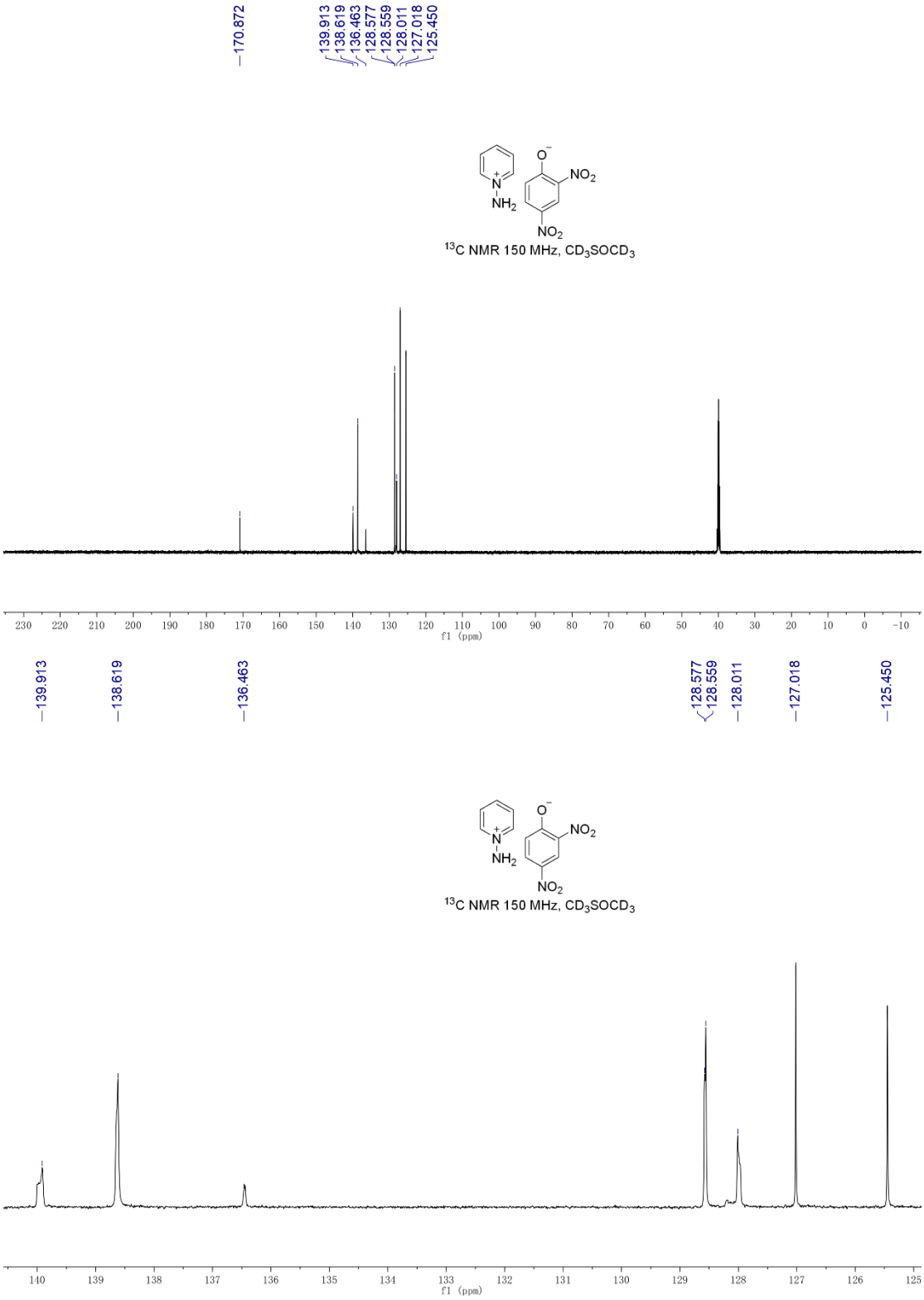
Yellow solid; Yield =1.34 g (68%); mp 160 - 162 °C. **^{1}H NMR** (400 MHz, CD_3SOCD_3), δ: 9.76 (s, 1H), 8.88 - 8.58 (m, 4H), 8.57 - 8.48 (m, 1H), 8.47 - 8.28 (m, 2H), 8.19 - 7.94 (m, 2H), 7.83 (dd, J = 9.6, 3.2 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (150 MHz, CD_3SOCD_3), δ: 170.7, 140.9, 136.4, 135.0, 134.3, 132.1, 131.4, 129.3, 128.0, 127.8, 127.6, 126.9, 126.7, 125.4.

2.3. NMR spectra for some starting materials **1**

NMR copies of compound **1a**:



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139.913
138.619
136.463
128.577
128.559
128.011
127.018
125.450
NO2
NO2
NH2
13C NMR 150 MHz, CD3SOCD3
f1 (ppm)
139.913
138.619
136.463
128.577
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128.011
127.018
125.450
NO2
NO2
NH2
13C NMR 150 MHz, CD3SOCD3
f1 (ppm)

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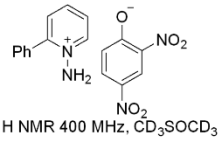

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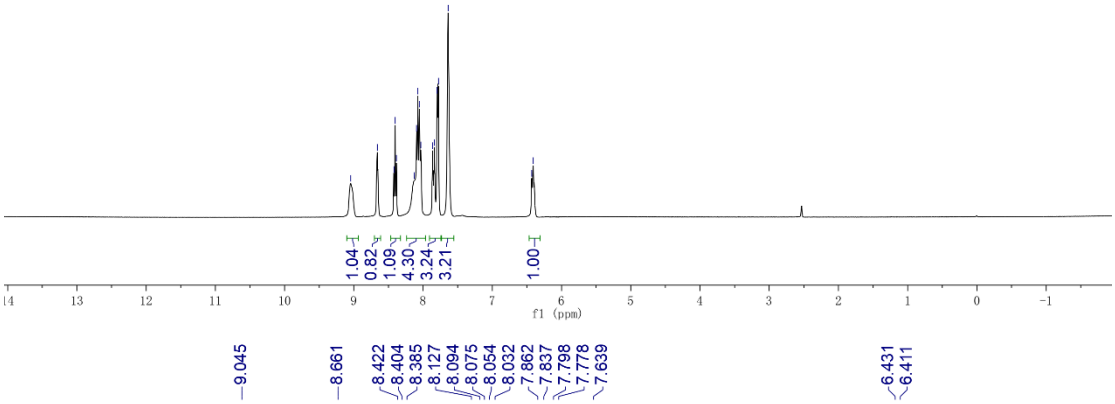

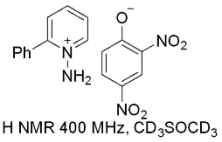

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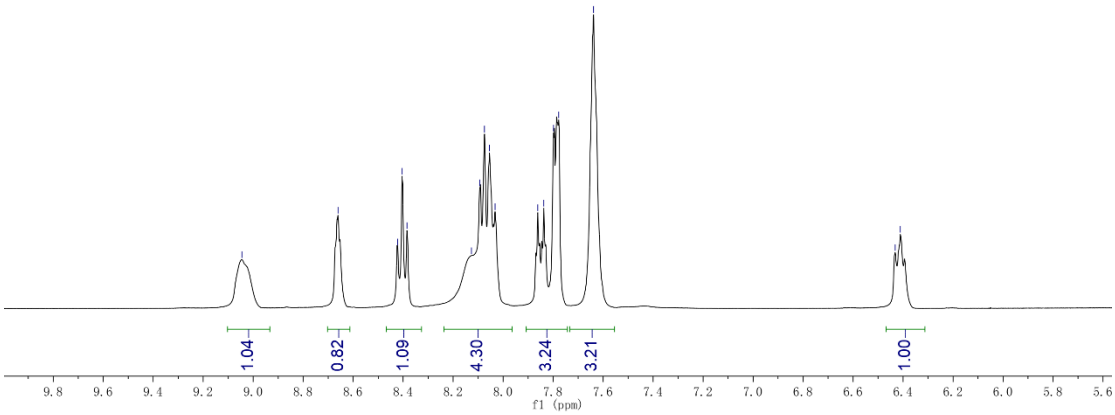

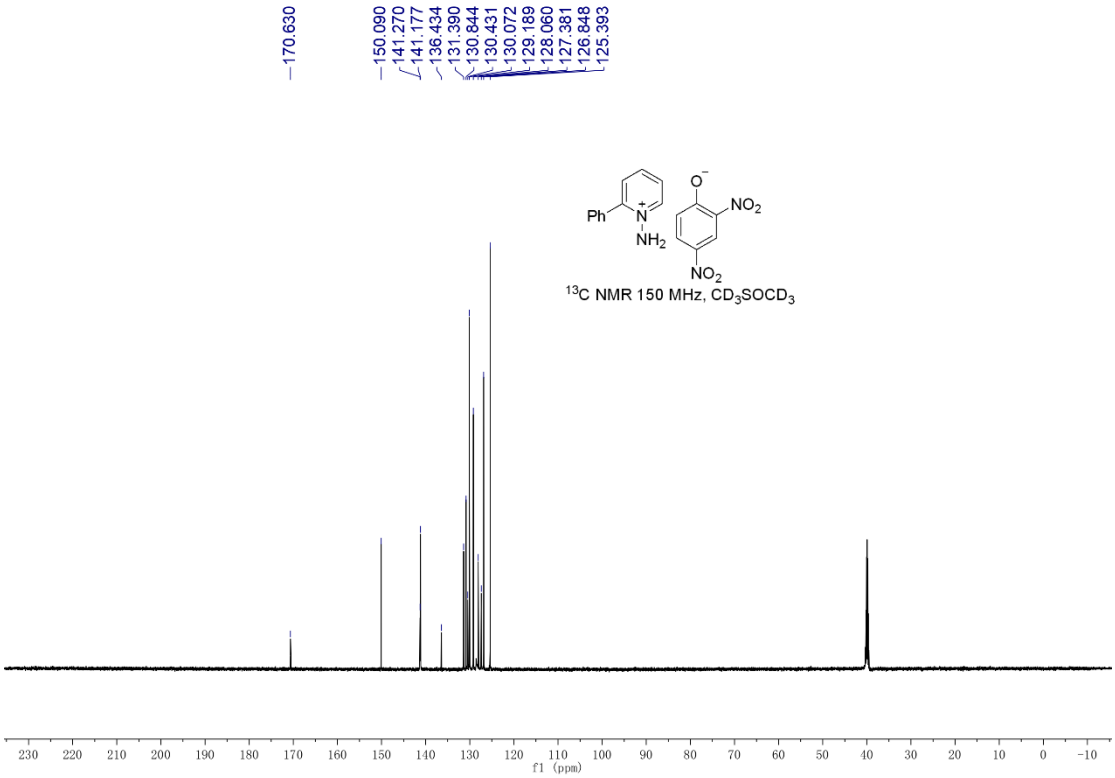
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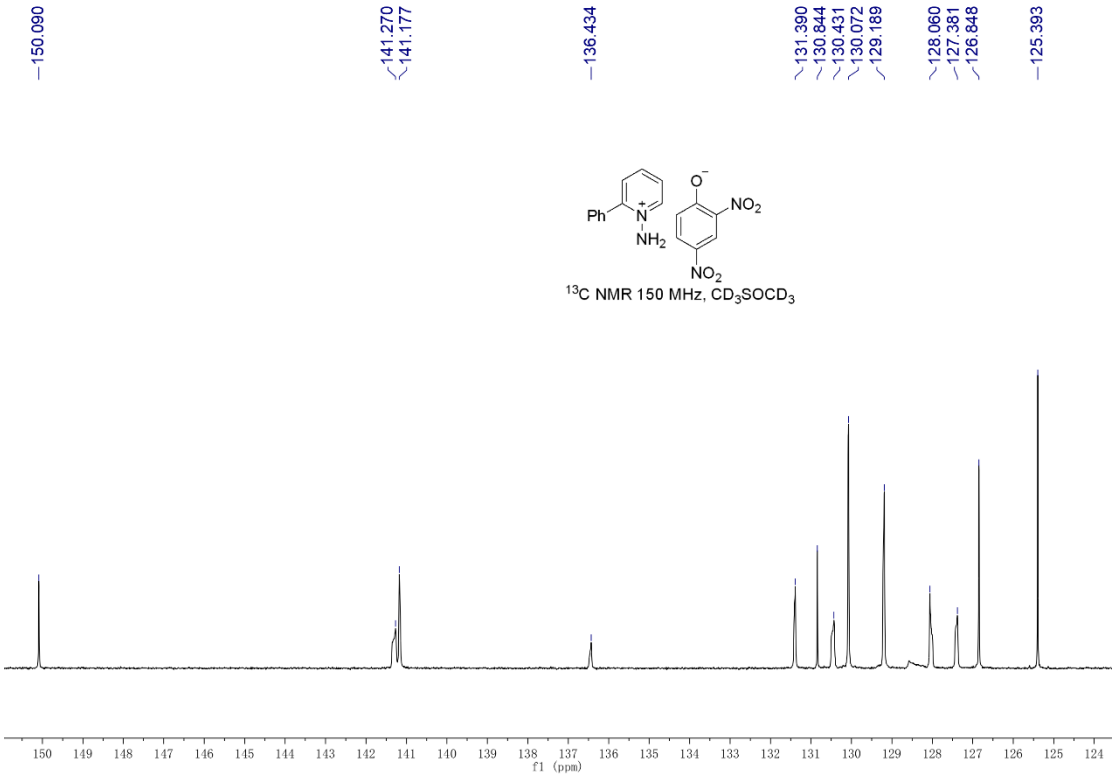
141.177
136.434
131.390
130.844
130.431
130.072
129.189
128.060
127.381
126.848
125.393
Ph
N
NH2
O
NO2
NO2
13C NMR 150 MHz, CD3SOCD3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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141.270
141.177
136.434
131.390
130.844
130.431
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129.189
128.060
127.381
126.848
125.393
Ph
N
NH2
O
NO2
NO2
13C NMR 150 MHz, CD3SOCD3
150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)

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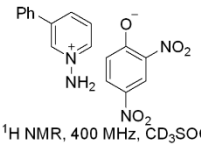

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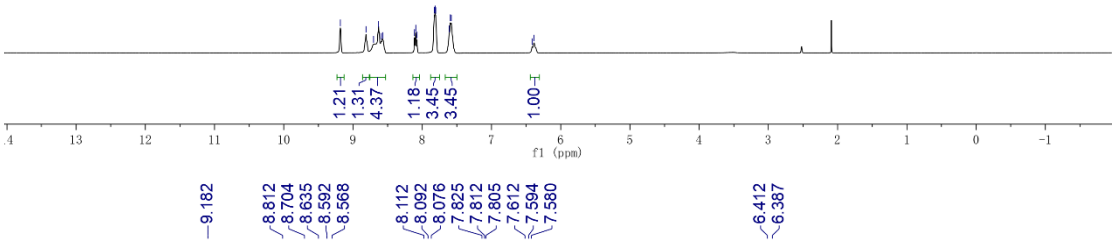

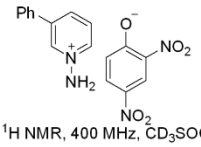

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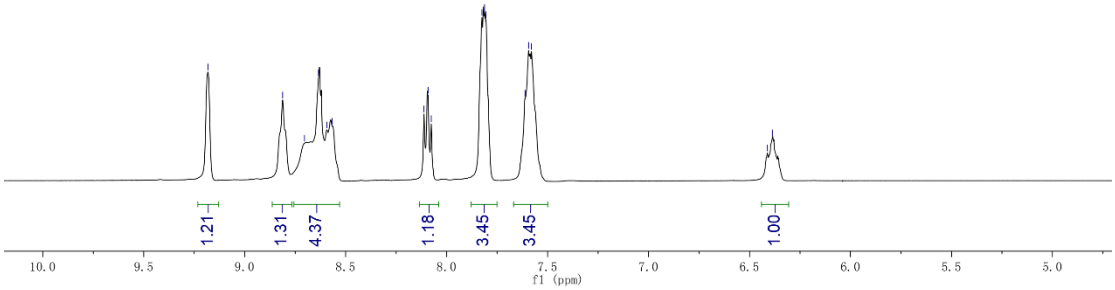

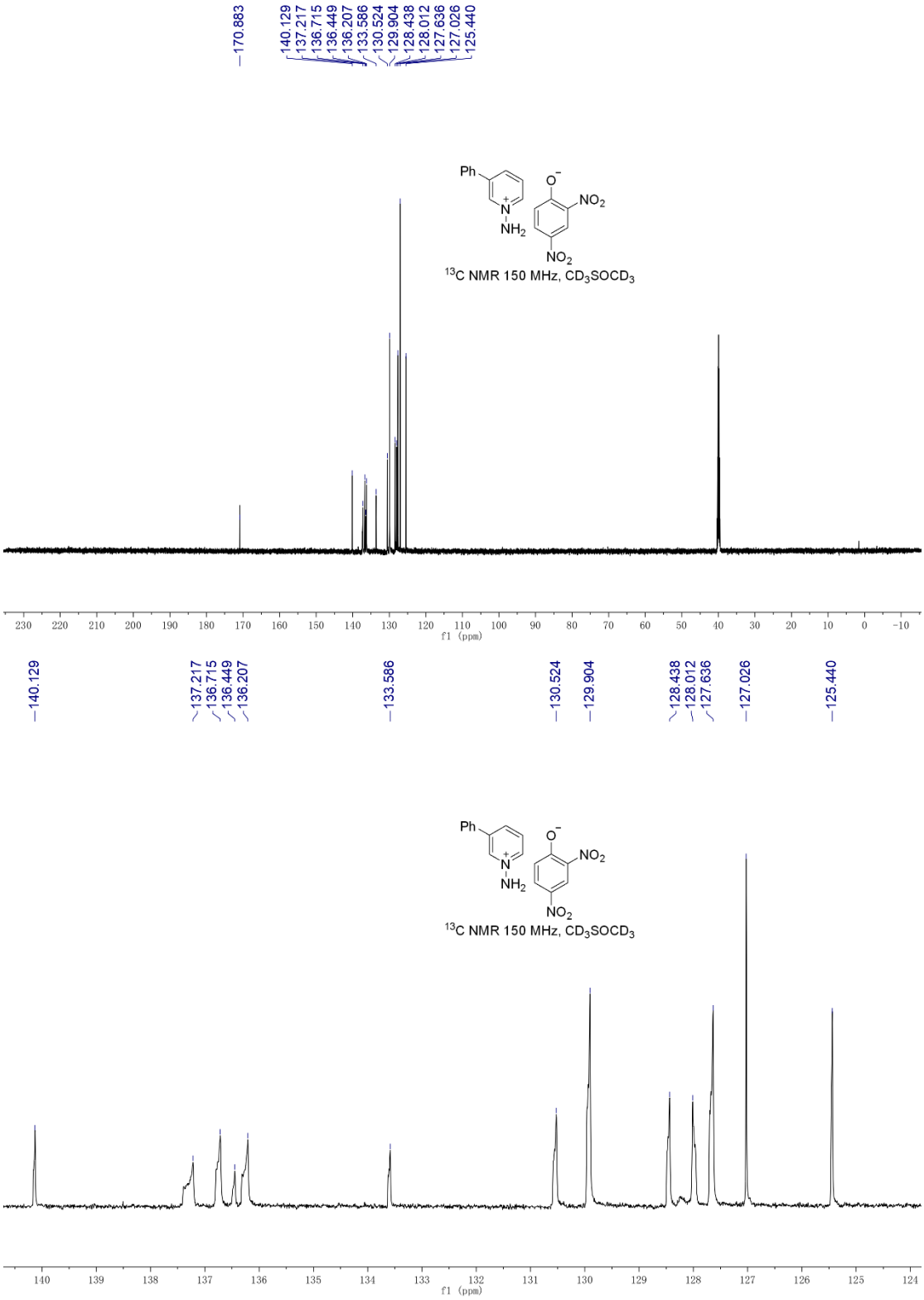
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Ph
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13C NMR 150 MHz, CD3SOCD3
f1 (ppm)

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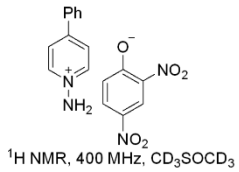

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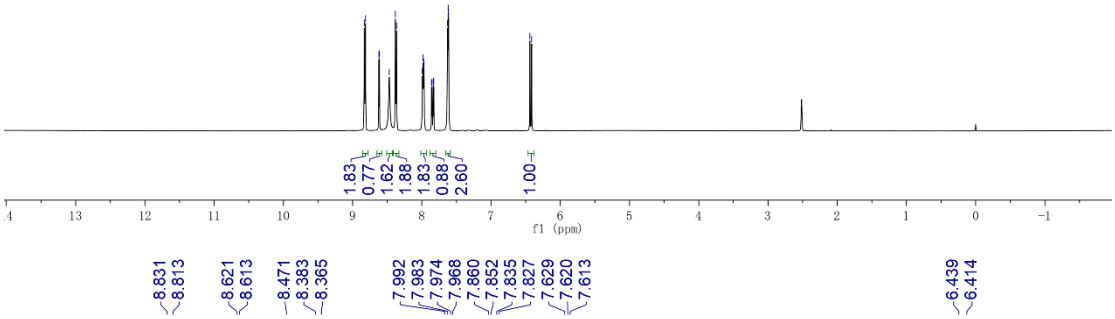

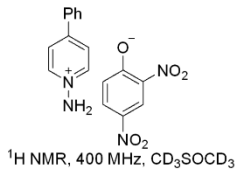

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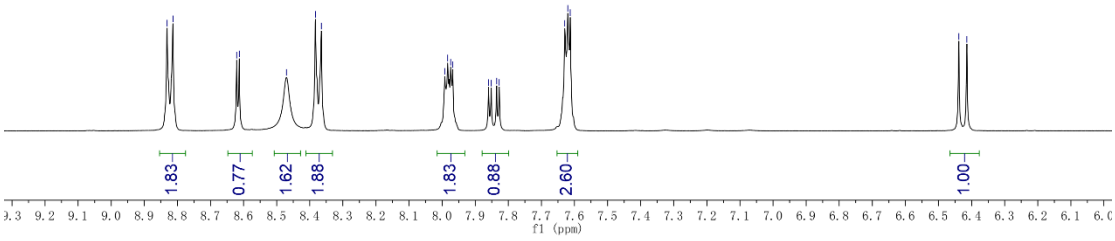

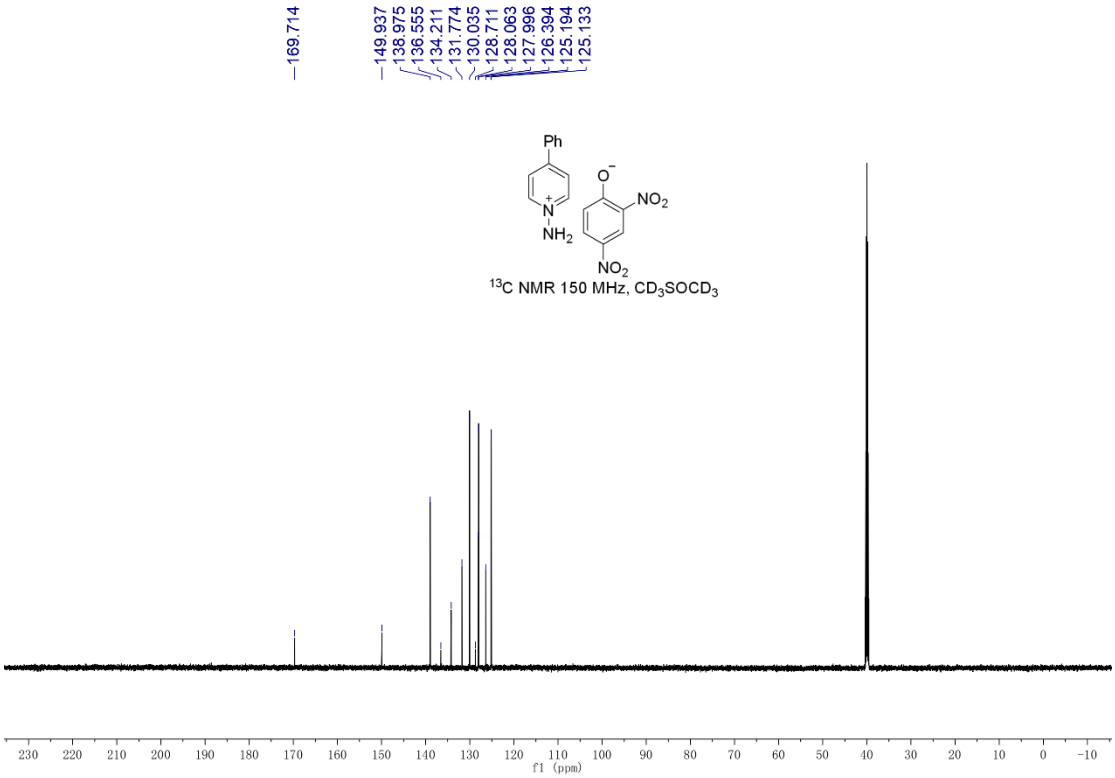
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Ph
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N+
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NO2
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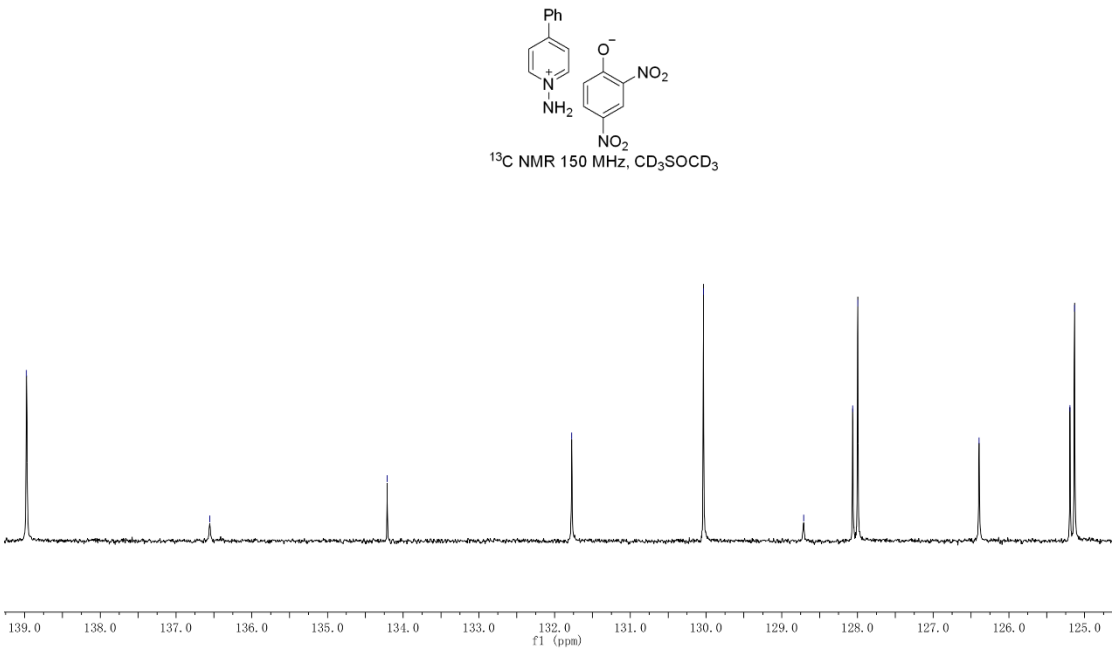
f1 (ppm)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136.555
134.211
131.774
130.035
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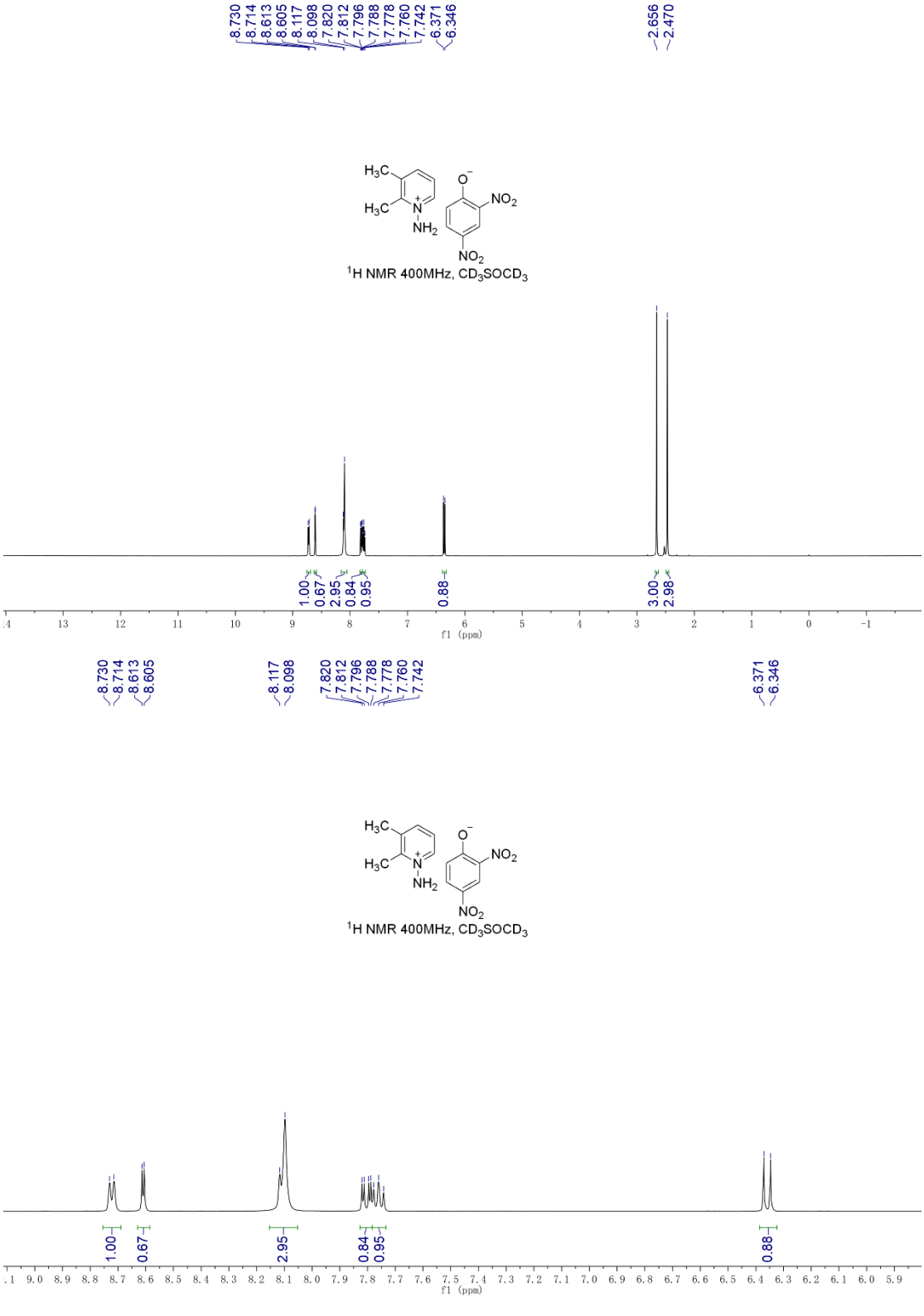
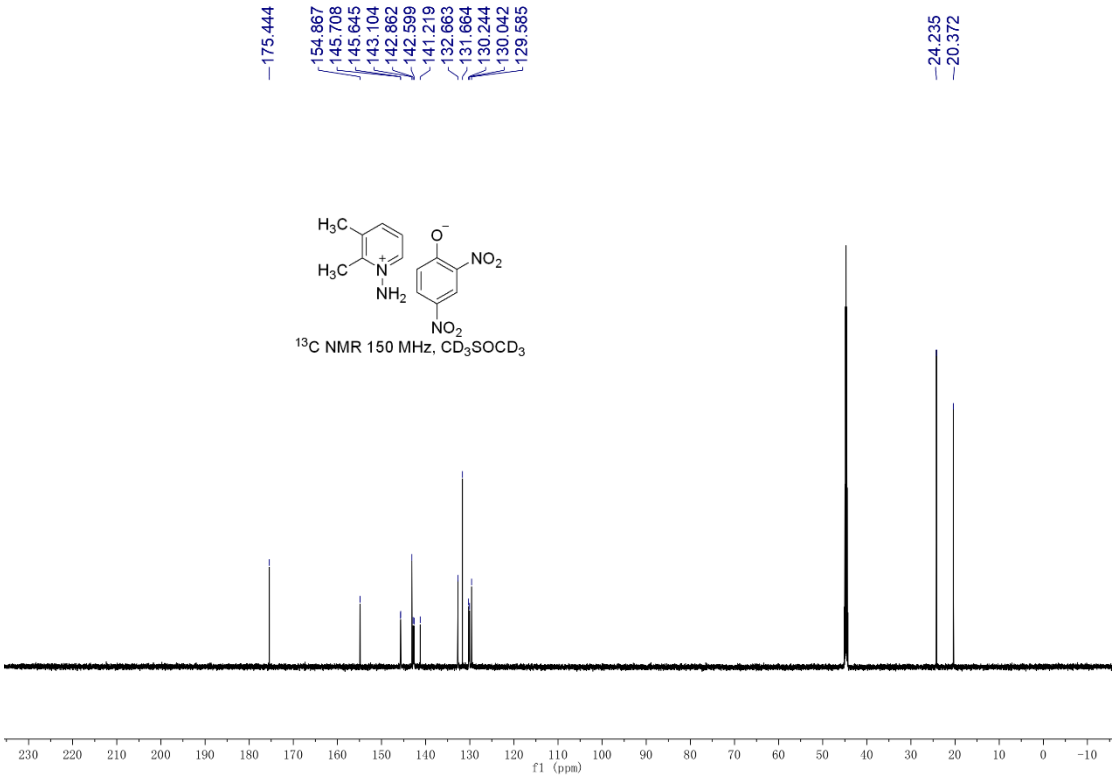
NO2
N+
NH2
NO2
13C NMR 150 MHz, CD3SOCD3
f1 (ppm)

NMR copies of compound **1j**:

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145.645
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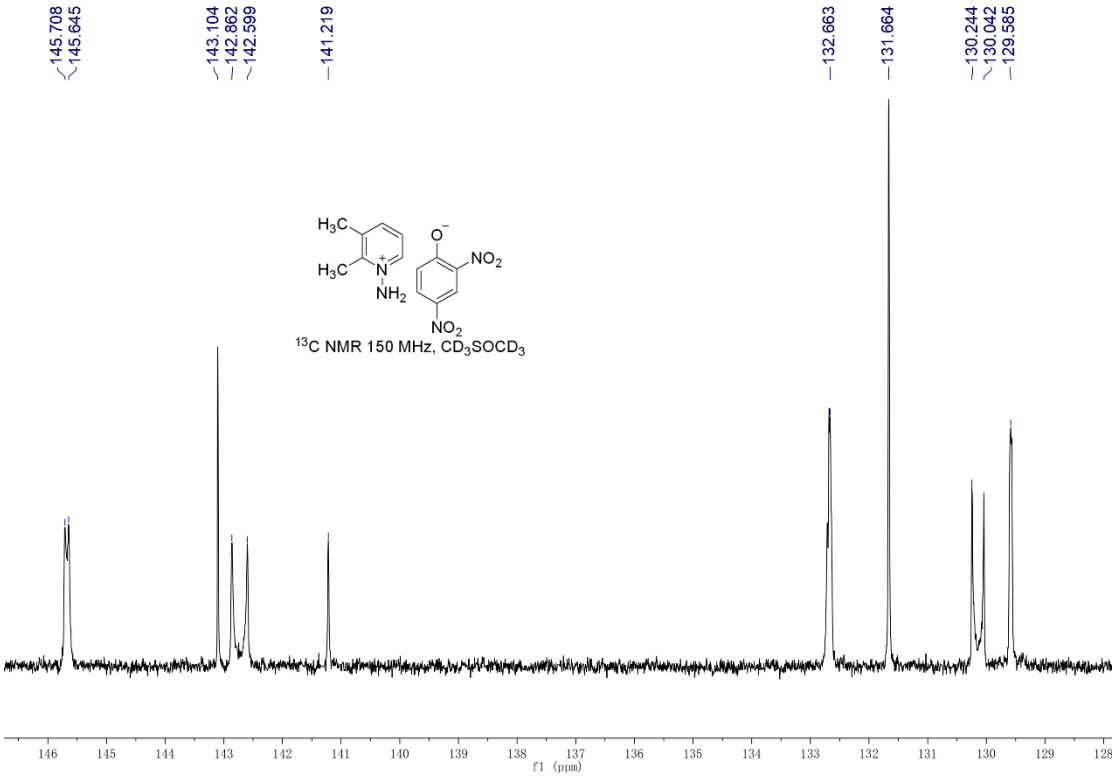
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145.645
143.104
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142.599
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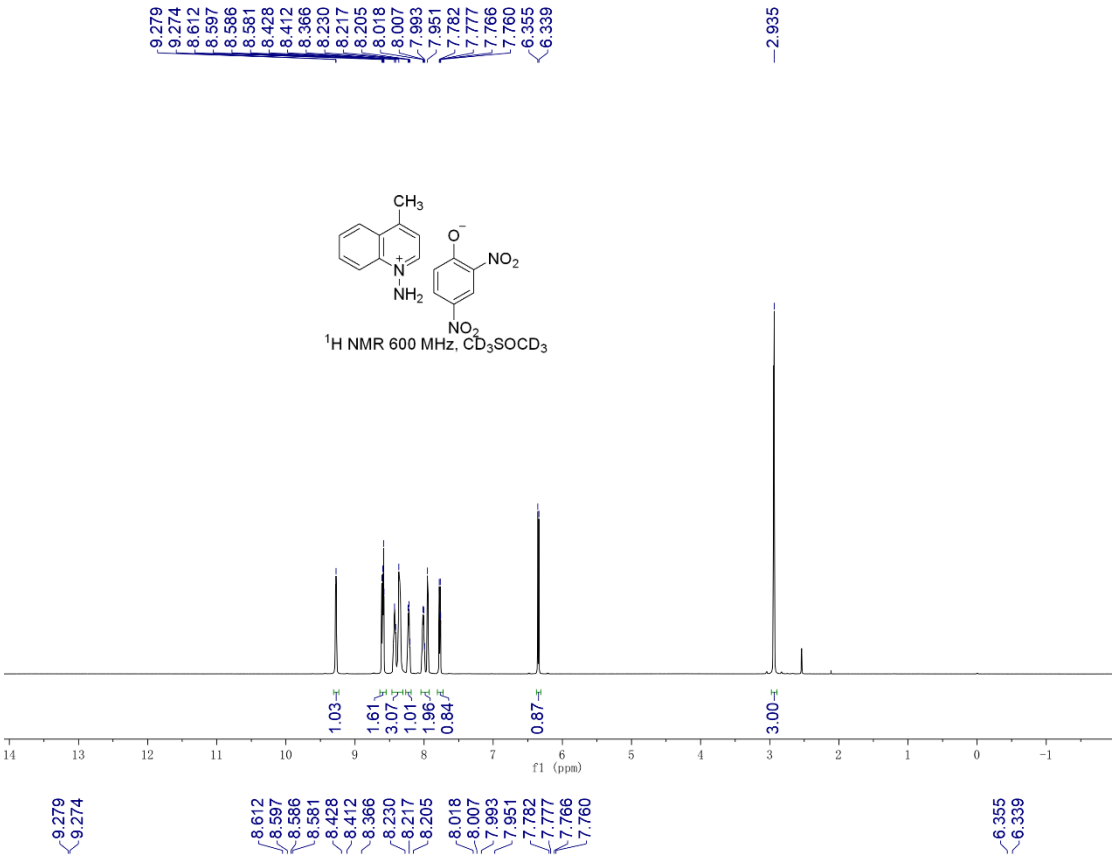
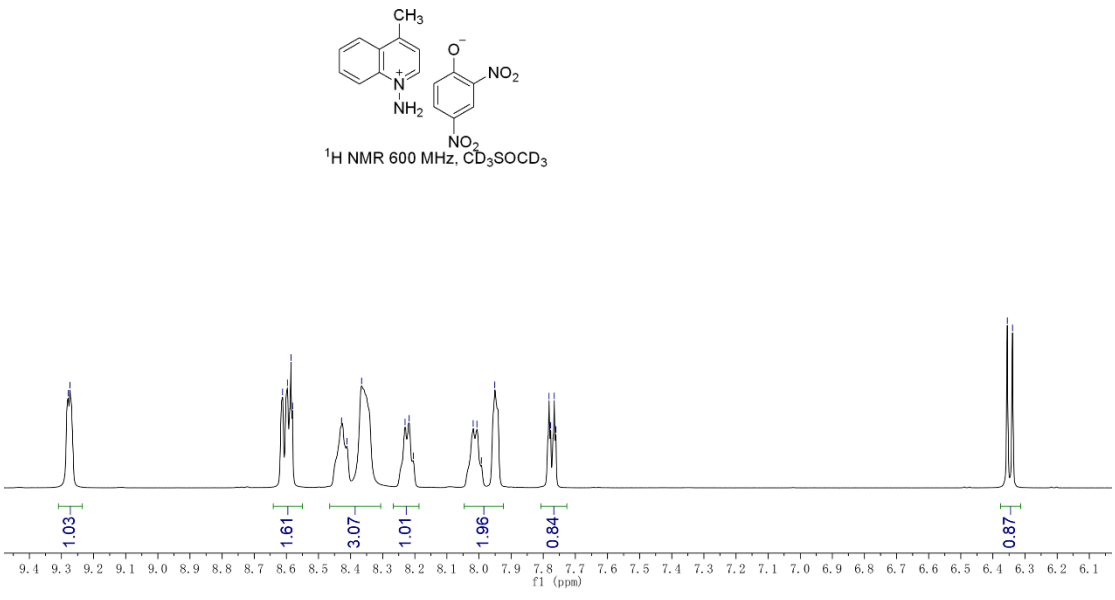
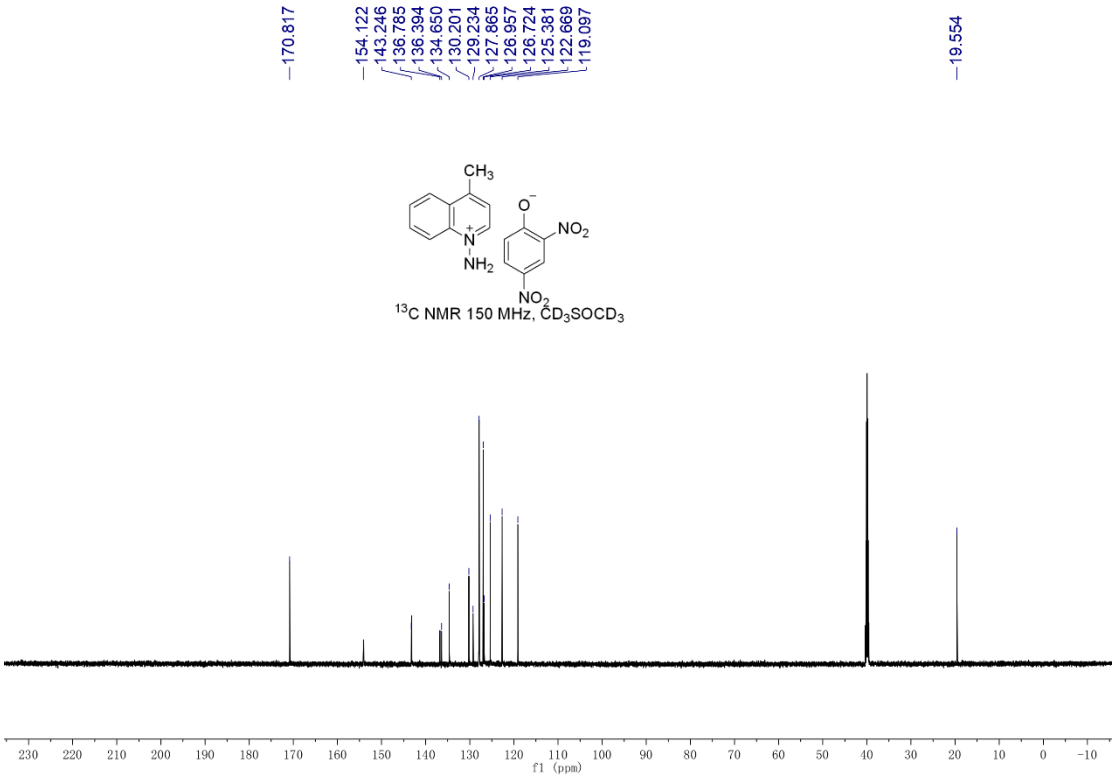
f1 (ppm)

NMR copies of compound **1o**:



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134.650
130.201
129.234
127.865
126.957
126.724
125.381
122.669
119.097
19.554
CH3
O−
NO2
N+
NH2
NO2
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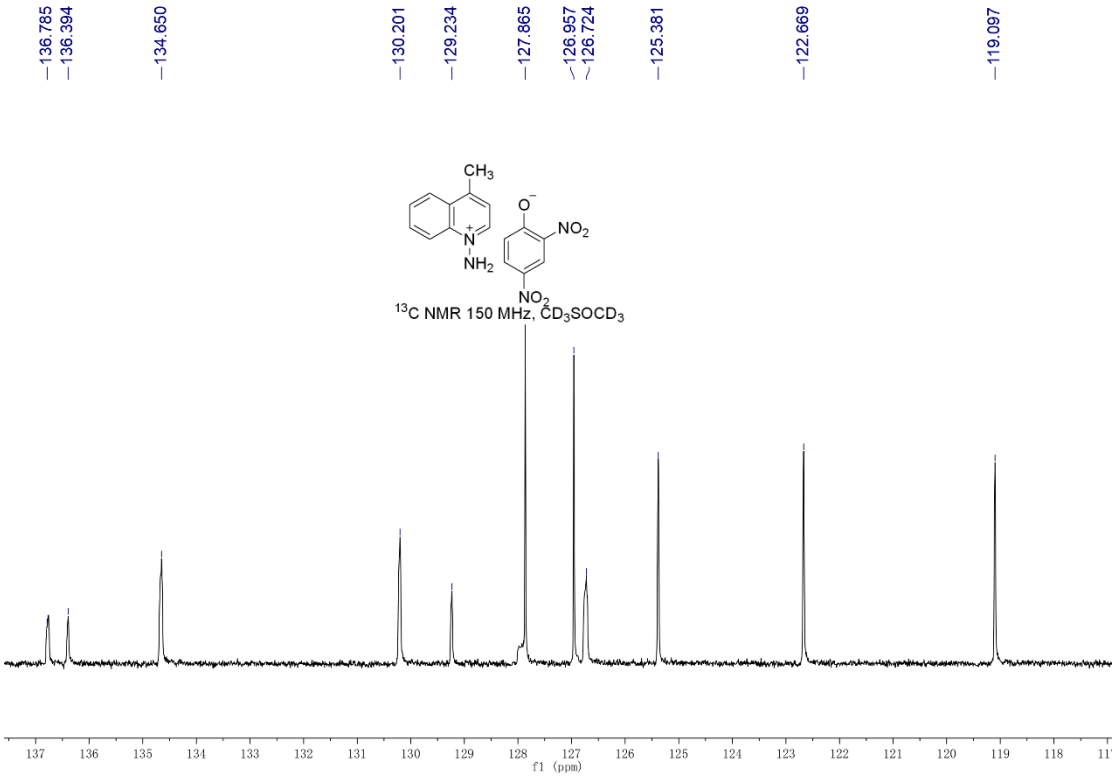
f1 (ppm)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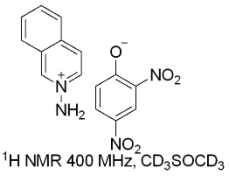
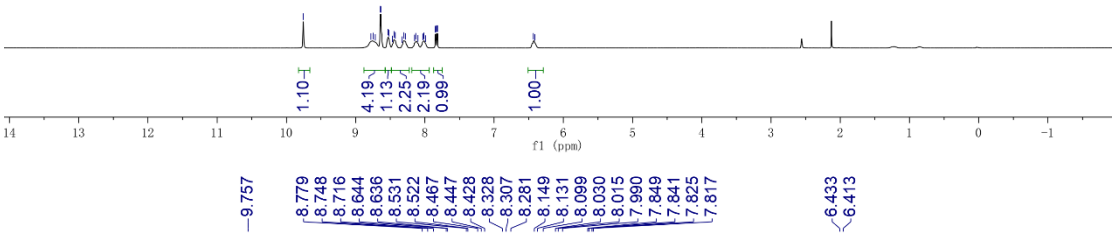
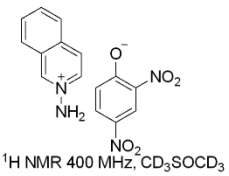
136.394
134.650
130.201
129.234
127.865
126.957
126.724
125.381
122.669
119.097
CH3
O−
NO2
N+
NH2
NO2
13C NMR 150 MHz, CD3SOCD3
137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118
f1 (ppm)

NMR copies of compound **1q**:

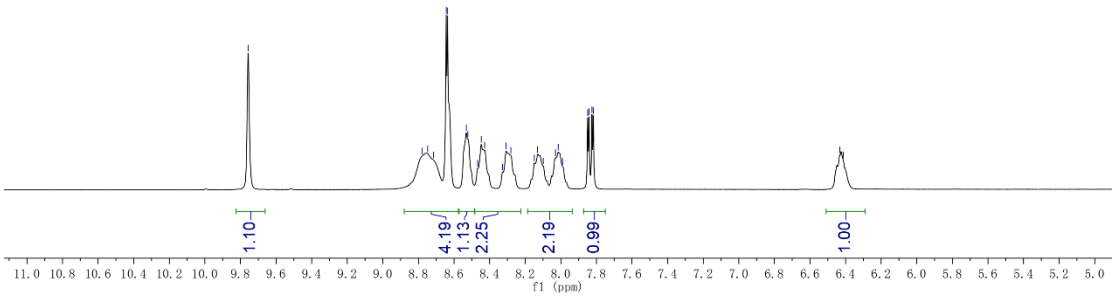


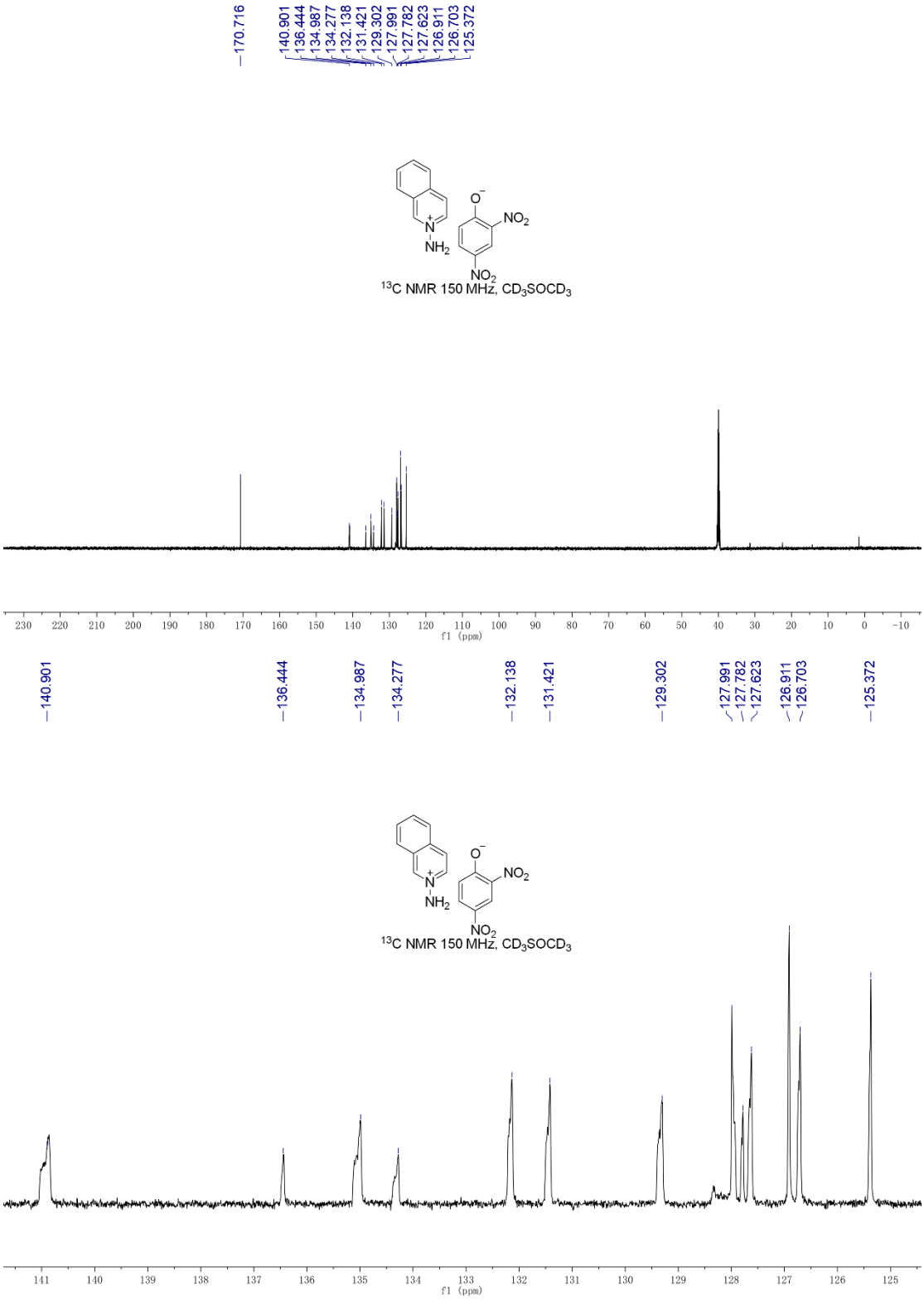
^{1}H NMR 400 MHz, CD_3SOCD_3



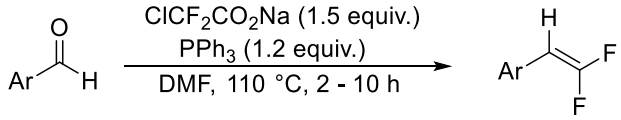


^{1}H NMR 400 MHz, CD_3SOCD_3



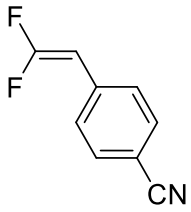

170.716
140.901
136.444
134.987
134.277
132.138
131.421
129.302
127.991
127.782
127.623
126.911
126.703
125.372
O⁻
NO2
N+
NH2
NO2
13C NMR 150 MHz, CD3SOCD3
f1 (ppm)
140.901
136.444
134.987
134.277
132.138
131.421
129.302
127.991
127.782
127.623
126.911
126.703
125.372
O⁻
NO2
N+
NH2
NO2
13C NMR 150 MHz, CD3SOCD3
f1 (ppm)

2.4. The synthesis of compounds **2** according to the following procedure **2**



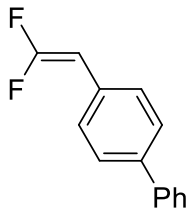
$ClCF_2CO_2Na$ (1.2 equiv., 12.0 mmol) in 50 mL DMF was added slowly to the mixture of corresponding aldehyde (10.0 mmol) and PPh_3 (1.5 equiv., 15.0 mmol) in DMF (40 mL) at 110 ℃, the reaction was heated at 110 ℃ and kept at this temperature until no further evolution of CO_2 was observed. The reaction mixture was cool to room temperature then water (50 mL) was added to the reaction slowly and the mixture was extracted with EtOAc (3 × 15 mL). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography to afford the difluoroalkenes.

2.5. Characterization data of some starting materials **2**



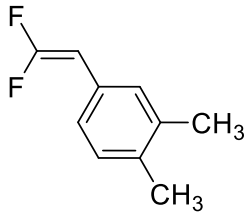
4-(2,2-difluorovinyl)benzonitrile (2a)

Purification by flash column chromatography on silica gel (EA/n-hexane = 1:50), white solid; Yield = 1.04 g (63%); mp 56 - 58 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.62 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 5.34 (dd, J = 25.6, 3.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -77.90 (dd, J = 25.2, 21.4 Hz), -79.55 (d, J = 20.3 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 157.0 (dd, J = 299.5, 290.5 Hz), 135.3 (dd, J = 7.5, 6.6 Hz), 132.4, 128.0 (dd, J = 6.9, 3.6 Hz), 118.6, 110.5, 81.8 (dd, J = 30.3, 12.7 Hz). **HRMS** (ESI): Calcd for $C_9H_6F_2N^+$ m/z 166.0463 $[M+H]^+$, found 166.0464.



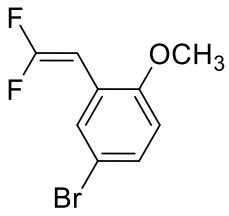
4-(2,2-difluorovinyl)-1,1'-biphenyl (2f)

Purification by flash column chromatography on silica gel (n-hexane), white solid; Yield =1.64 g (76%); mp 77 - 79 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.59 - 7.55 (m, 4H), 7.48 - 7.29 (m, 5H), 5.29 (dd, J = 26.4, 3.6 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -81.89 (dd, J = 30.8, 26.3 Hz), -83.81 (dd, J = 30.4, 3.4 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 156.4 (dd, J = 296.7, 286.9 Hz), 140.5, 139.8 (t, J = 2.1 Hz), 129.4 (t, J = 6.4 Hz), 128.8, 128.0 (dd, J = 6.3, 3.6 Hz), 127.4, 127.3, 127.0, 81.9 (dd, J = 28.9, 13.3 Hz). **HRMS** (ESI): Calcd for $C_{14}H_{11}F_2^+$ m/z 217.0823 $[M+H]^+$, found 217.0827.



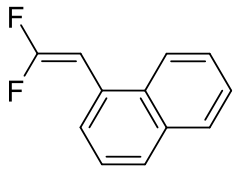
4-(2,2-difluorovinyl)-1,2-dimethylbenzene (2m)

Purification by flash column chromatography on silica gel (n-hexane), Colorless oil; Yield = 1.39 g (83%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.14 - 6.98 (m, 3H), 5.18 (dd, J = 26.4, 4.0 Hz, 1H), 2.23 (s, 6H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -83.24 (dd, J = 34.2, 26.7 Hz), -83.39 (dd, J = 34.2, 3.8 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 156.1 (dd, J = 295.9, 285.6 Hz), 136.8, 135.5 (t, J = 1.8 Hz), 129.9, 128.8 (dd, J = 5.2, 3.6 Hz), 127.8 (t, J = 6.4 Hz), 125.0 (dd, J = 5.8, 2.8 Hz), 81.9 (dd, J = 28.6, 13.8 Hz), 19.7, 19.4. **HRMS** (ESI): Calcd for $C_{10}H_{11}F_2^+$ m/z 169.0823 $[M+H]^+$, found 169.0825.



4-bromo-2-(2,2-difluorovinyl)-1-methoxybenzene (2o)

Purification by flash column chromatography on silica gel (n-hexane), Colorless oil; Yield = 1.93 g (78%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.54 (s, 1H), 7.27 (d, J = 8.4 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 5.59 (d, J = 26.4 Hz, 1H), 3.78 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -81.28 (d, J = 27.8 Hz), -81.52 (t, J = 26.7 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 156.4 (dd, J = 296.5, 286.8 Hz), 155.2 (dd, J = 4.6, 1.5 Hz), 130.7 (dd, J = 2.7, 1.3 Hz), 130.7, 121.3, 112.9, 112.1, 75.6 (dd, J = 31.8, 12.1 Hz), 55.7. **HRMS** (ESI): Calcd for $C_9H_8F_2OBr^+$ m/z 248.9721 $[M+H]^+$, found 248.9721.

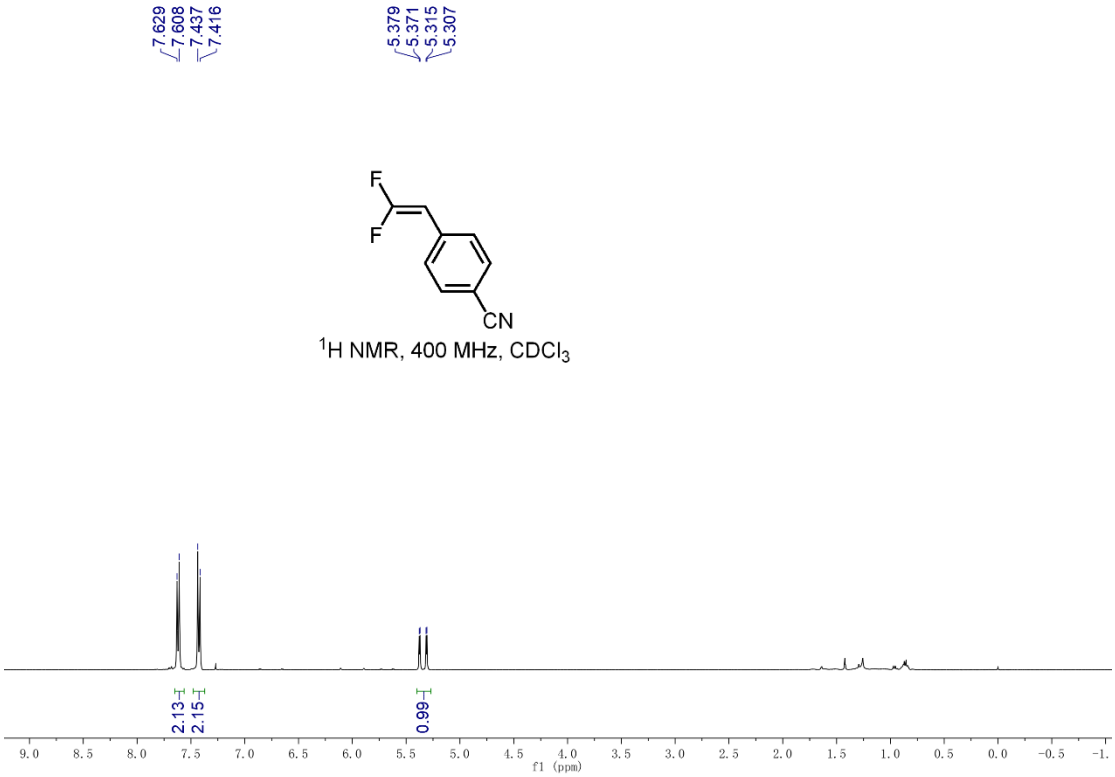


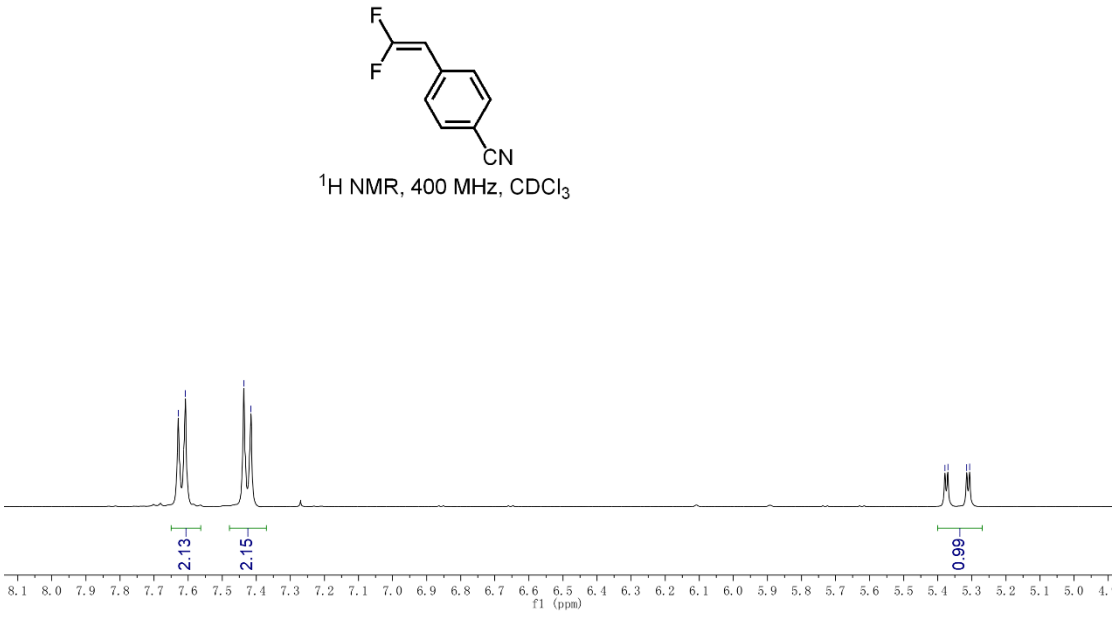
1-(2,2-difluorovinyl)naphthalene (2q)

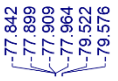
Purification by flash column chromatography on silica gel (n-hexane), Colorless oil; Yield =1.25 g (66%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.08 - 6.96 (m, 7H), 5.74 (d, J = 21.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -82.78 (d, J = 29.3 Hz), -84.62 (t, J = 27.4 Hz). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 156.9 (dd, J = 294.6, 286.8 Hz), 133.8, 131.6 (d, J = 3.4 Hz), 128.8, 128.1, 126.7, 126.6 (dd, J = 6.6, 1.6 Hz), 126.5, 126.1, 125.6, 123.8, 78.8 (dd, J = 28.9, 15.4 Hz). **HRMS** (ESI): Calcd for $C_{12}H_9F_2^+$ m/z 191.0667 $[M+H]^+$, found 191.0666.

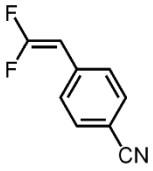
2.6. NMR and HRMS spectra copies of some starting materials **2**

NMR copies of compound **2a**:

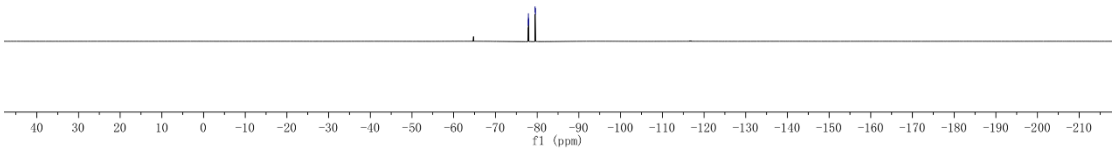


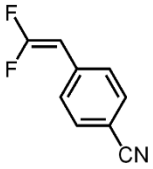




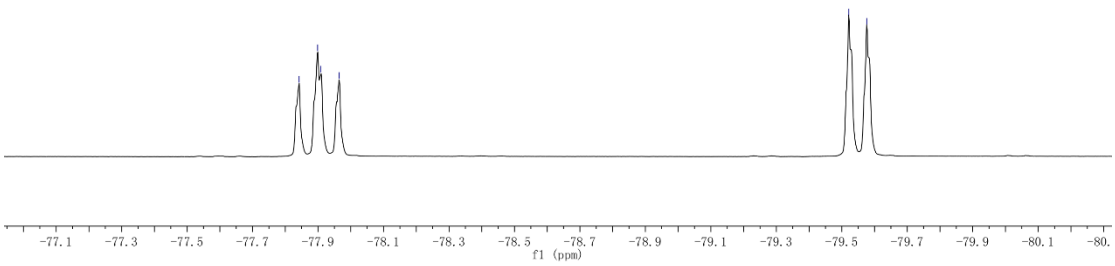


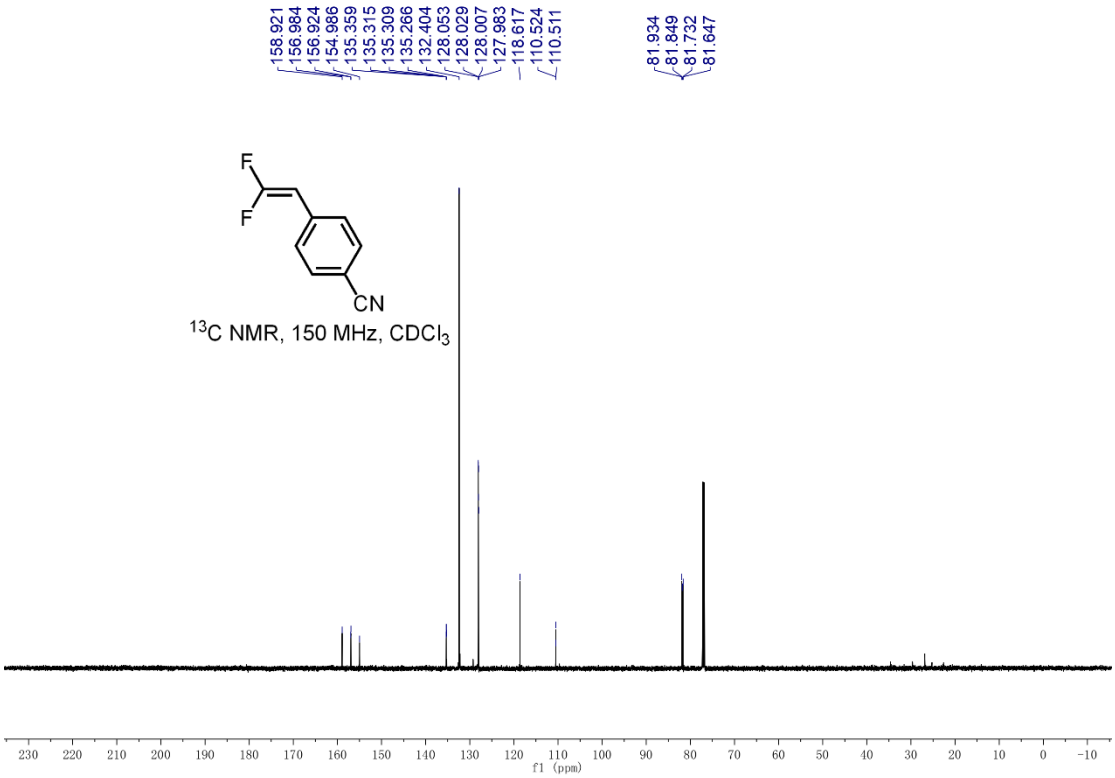
^{19}F NMR, 376 MHz, $CDCl_3$

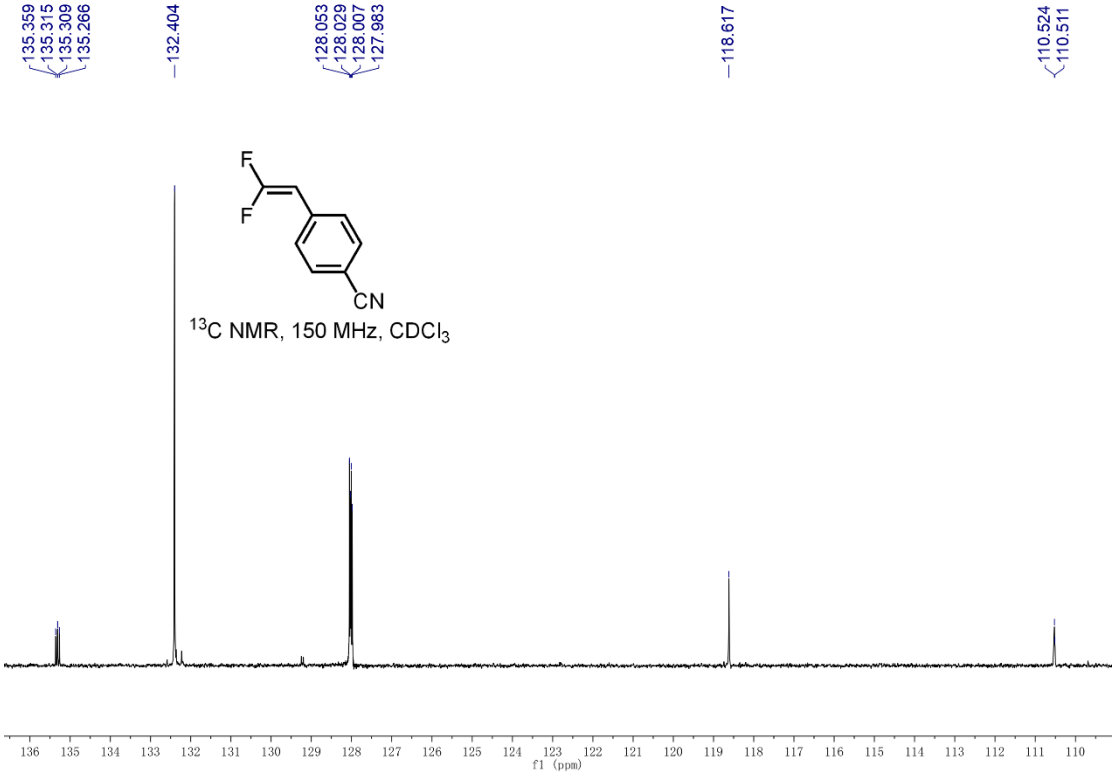


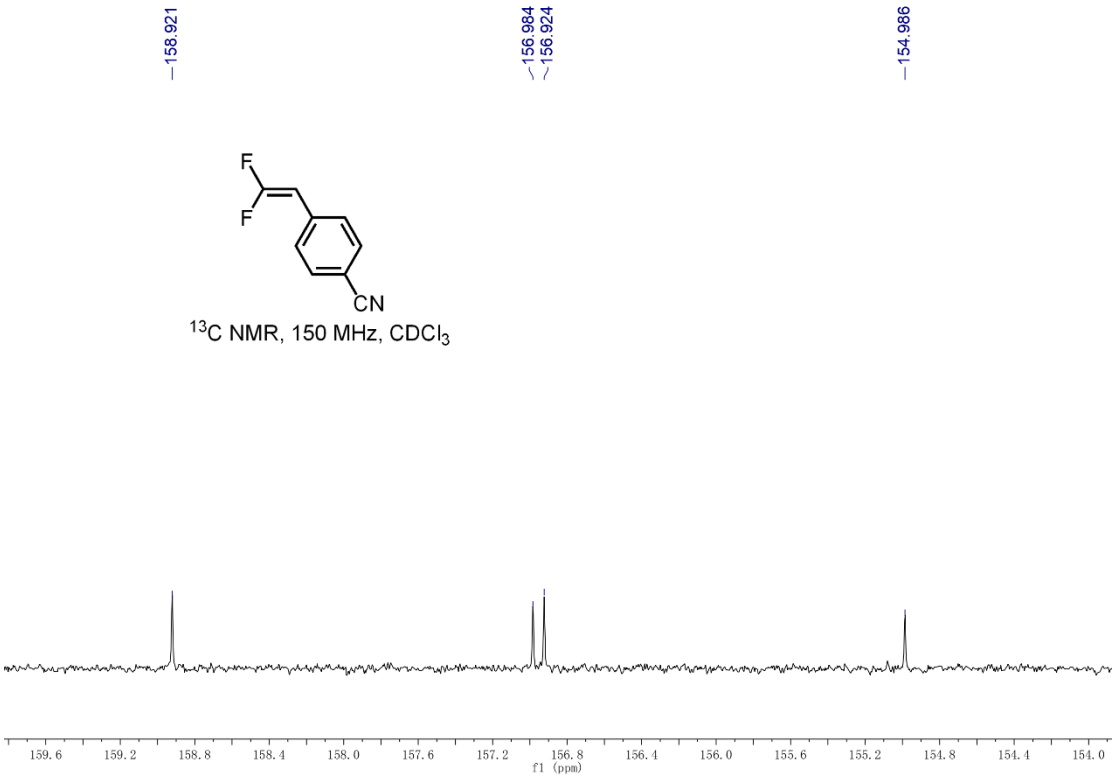


^{19}F NMR, 376 MHz, $CDCl_3$

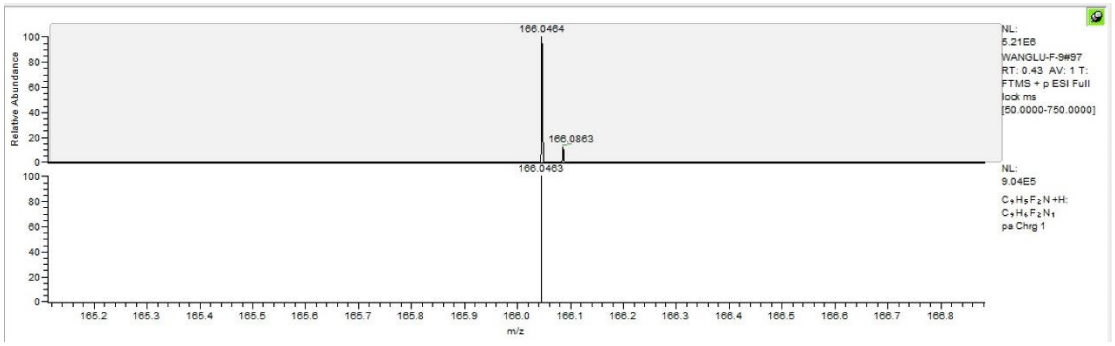



158.921
156.984
156.924
154.986
135.359
135.315
135.309
135.266
132.404
128.053
128.029
128.007
127.983
118.617
110.524
110.511
81.934
81.849
81.732
81.647
F
F
CN
13C NMR, 150 MHz, CDCl3
f1 (ppm)

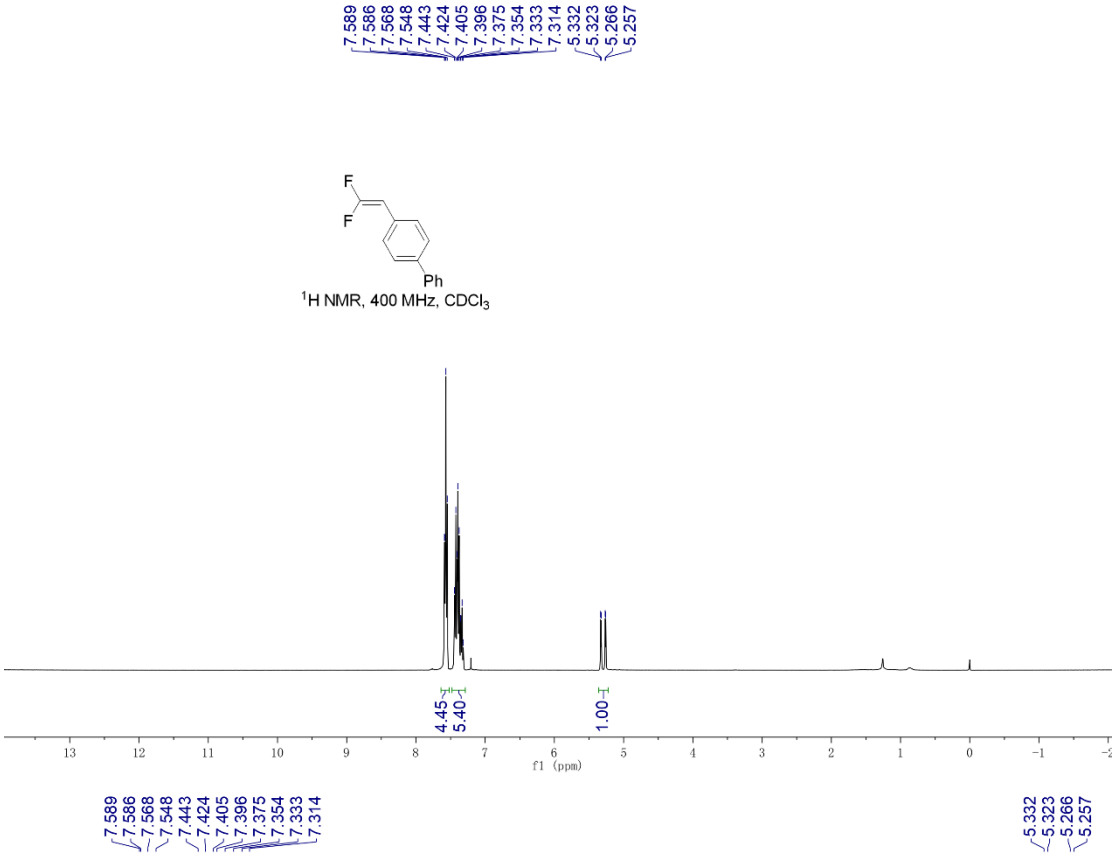

135.359
135.315
135.309
135.266
132.404
128.053
128.029
128.007
127.983
118.617
110.524
110.511
F
F
CN
13C NMR, 150 MHz, CDCl3
f1 (ppm)

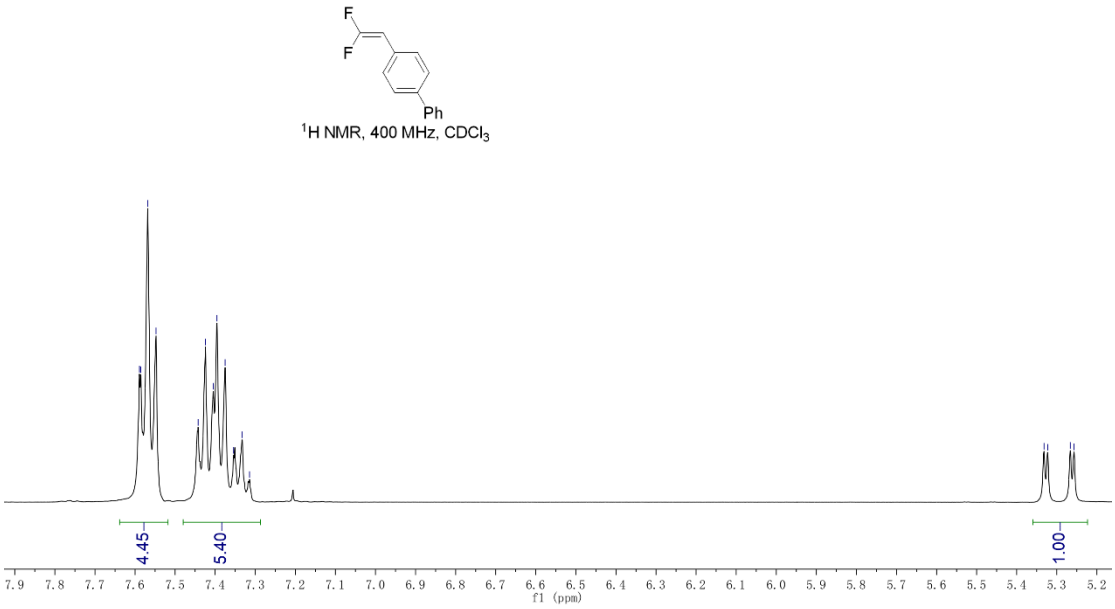


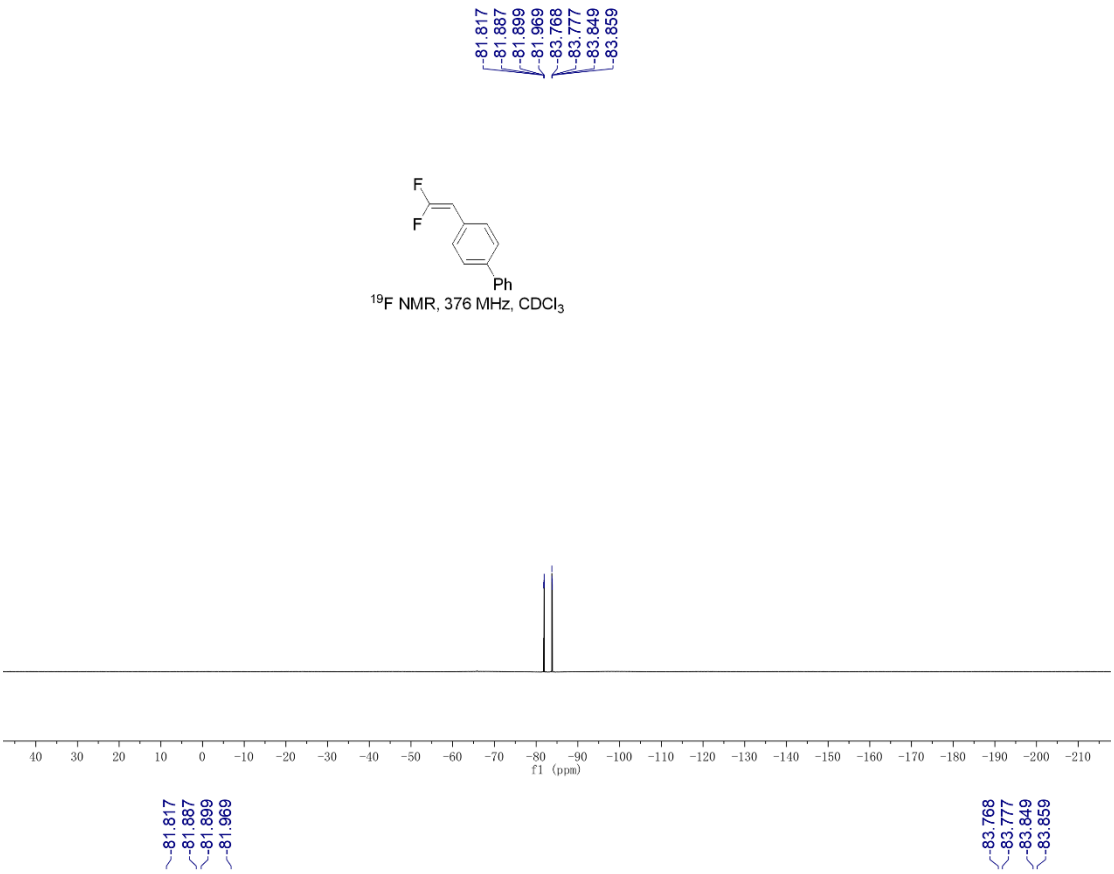
HRMS (ESI) copy of compound **2a**:



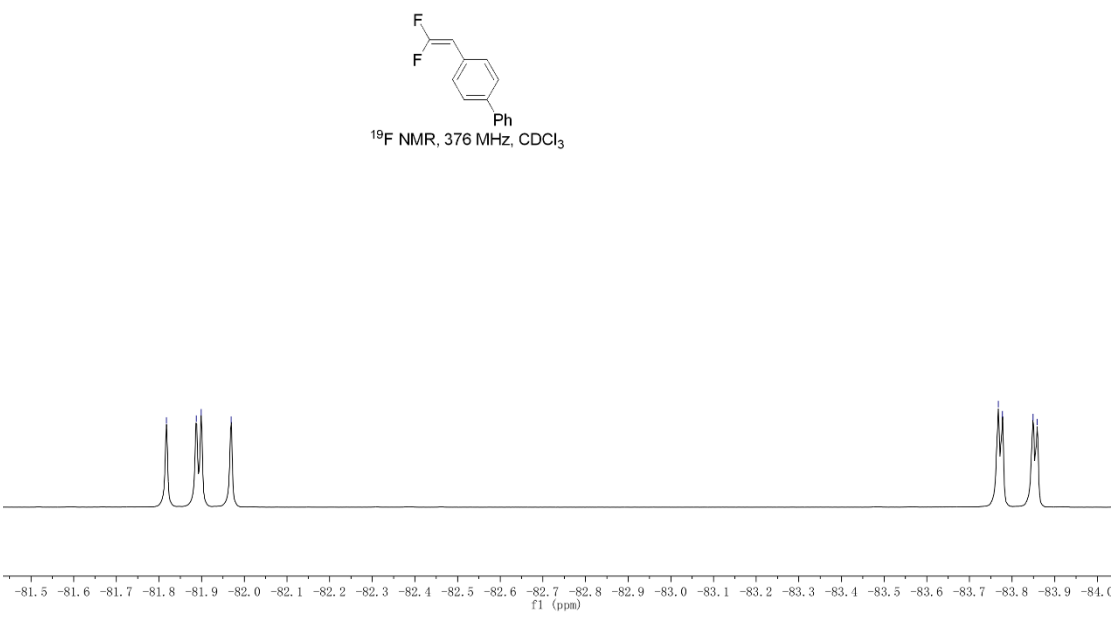
NMR copies of compound **2f**:



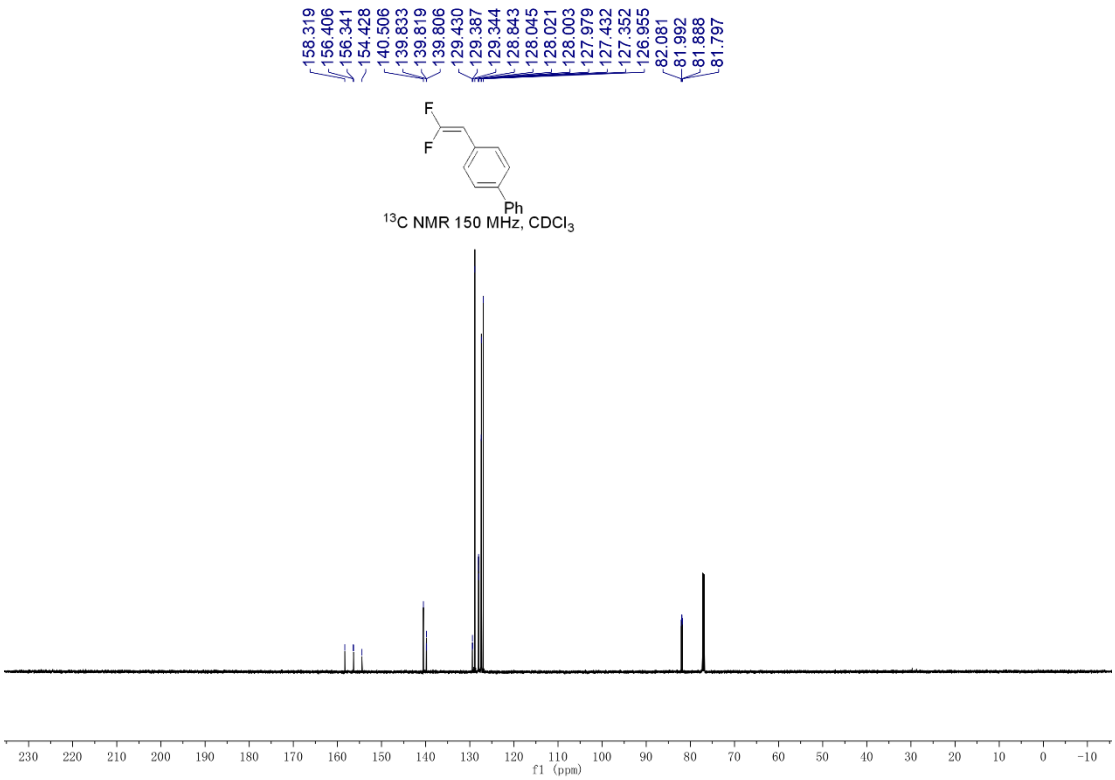


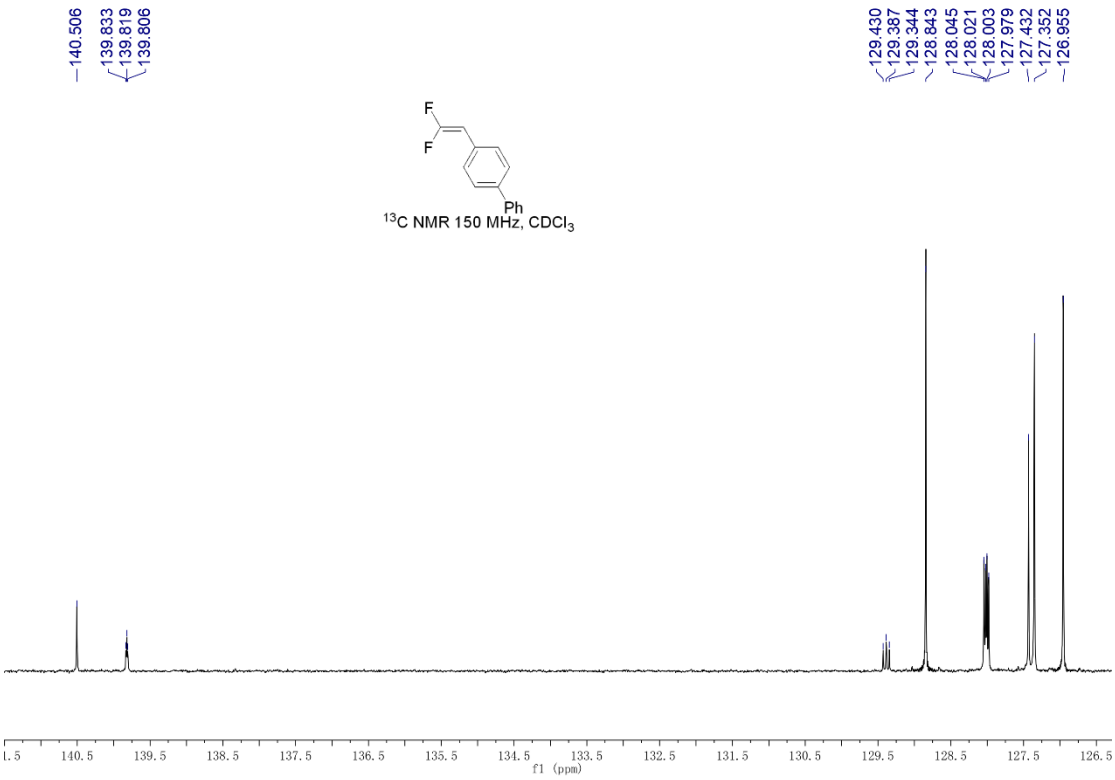


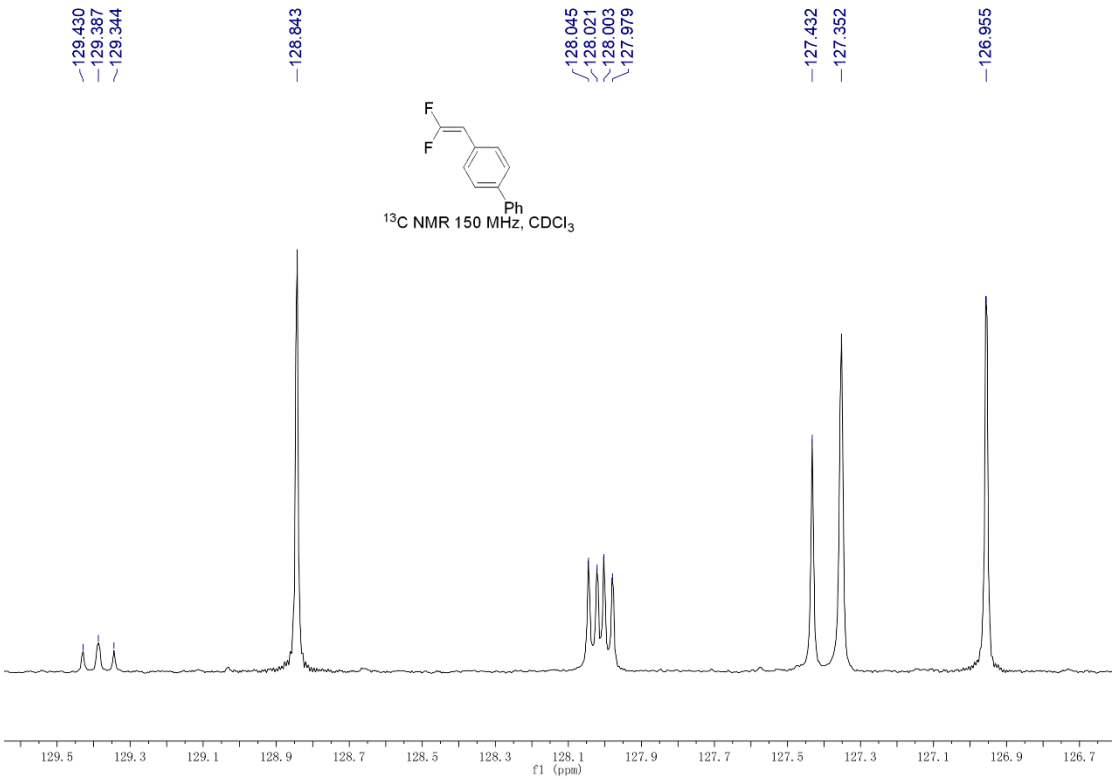
^{19}F NMR, 376 MHz, $CDCl_3$



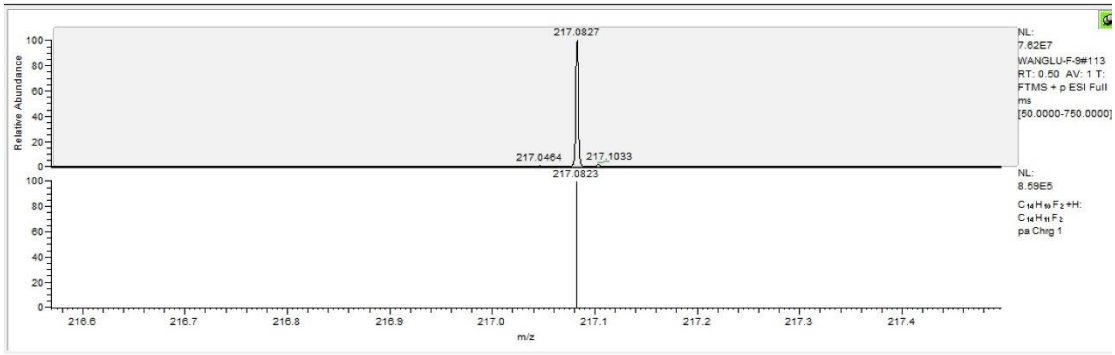
^{19}F NMR, 376 MHz, $CDCl_3$


158.319
156.406
156.341
154.428
140.506
139.833
139.819
139.806
129.430
129.387
129.344
128.843
128.045
128.021
128.003
127.979
127.432
127.352
126.955
82.081
81.992
81.888
81.797
F
F
Ph
13C NMR 150 MHz, CDCl3
f1 (ppm)

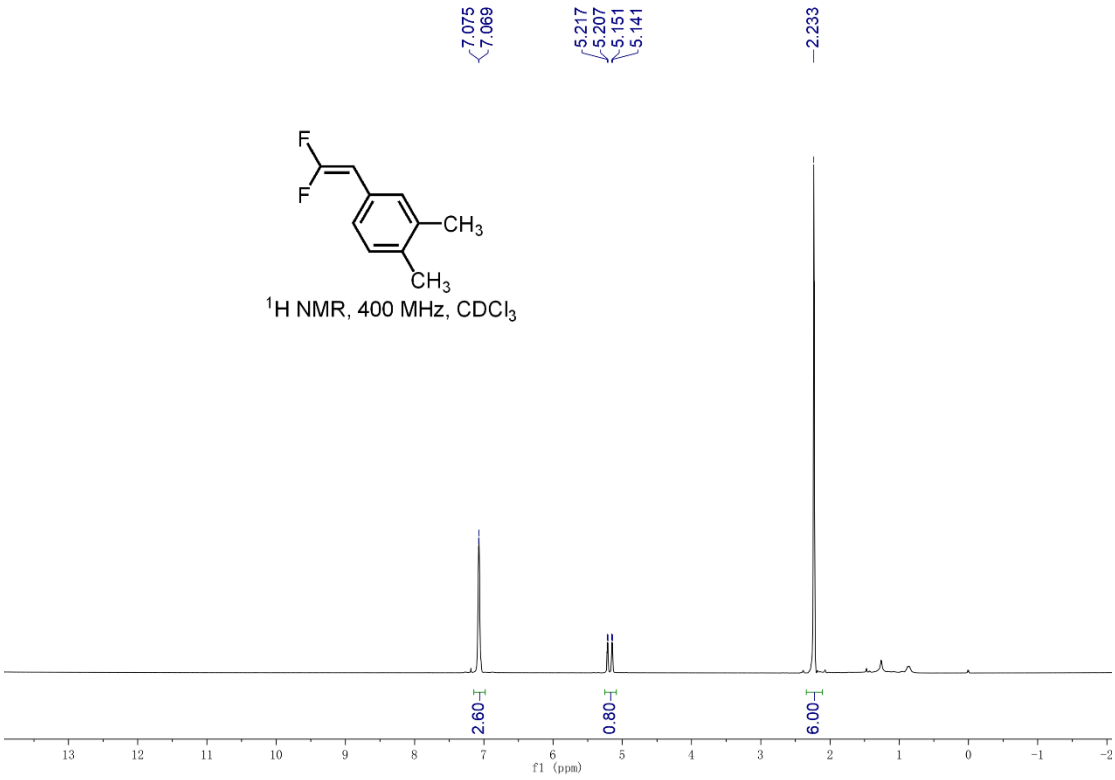

140.506
139.833
139.819
139.806
129.430
129.387
129.344
128.843
128.045
128.021
128.003
127.979
127.432
127.352
126.955
F
F
Ph
13C NMR 150 MHz, CDCl3
f1 (ppm)

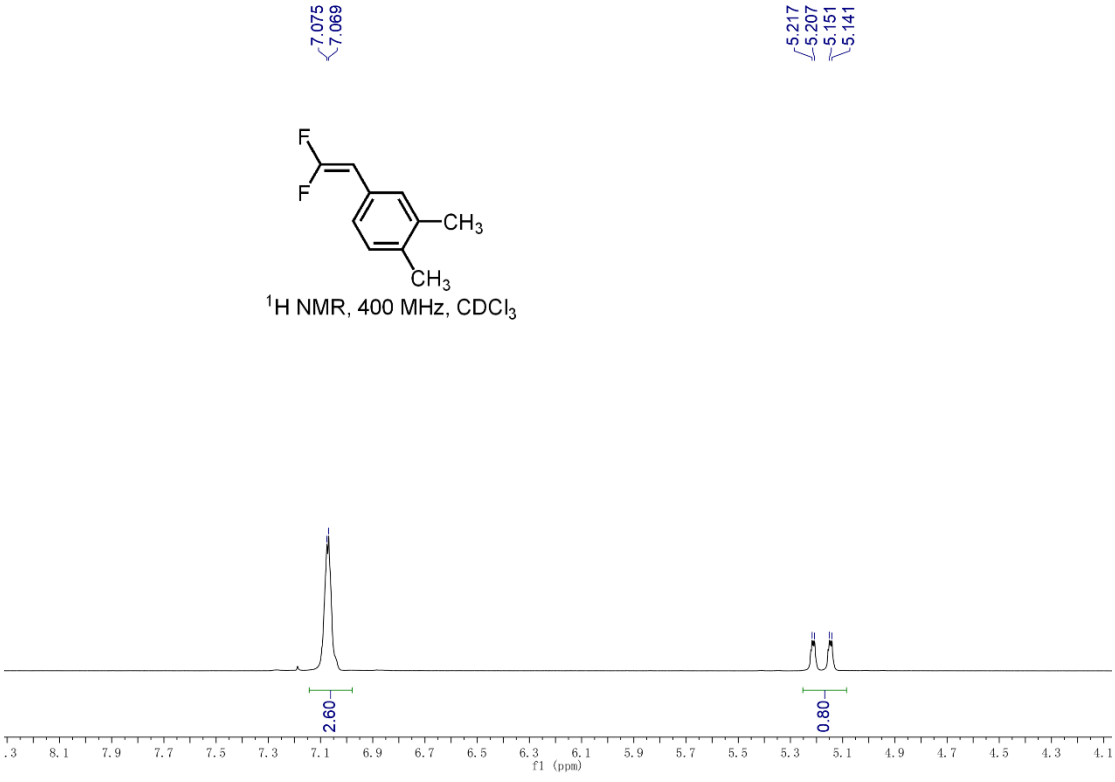


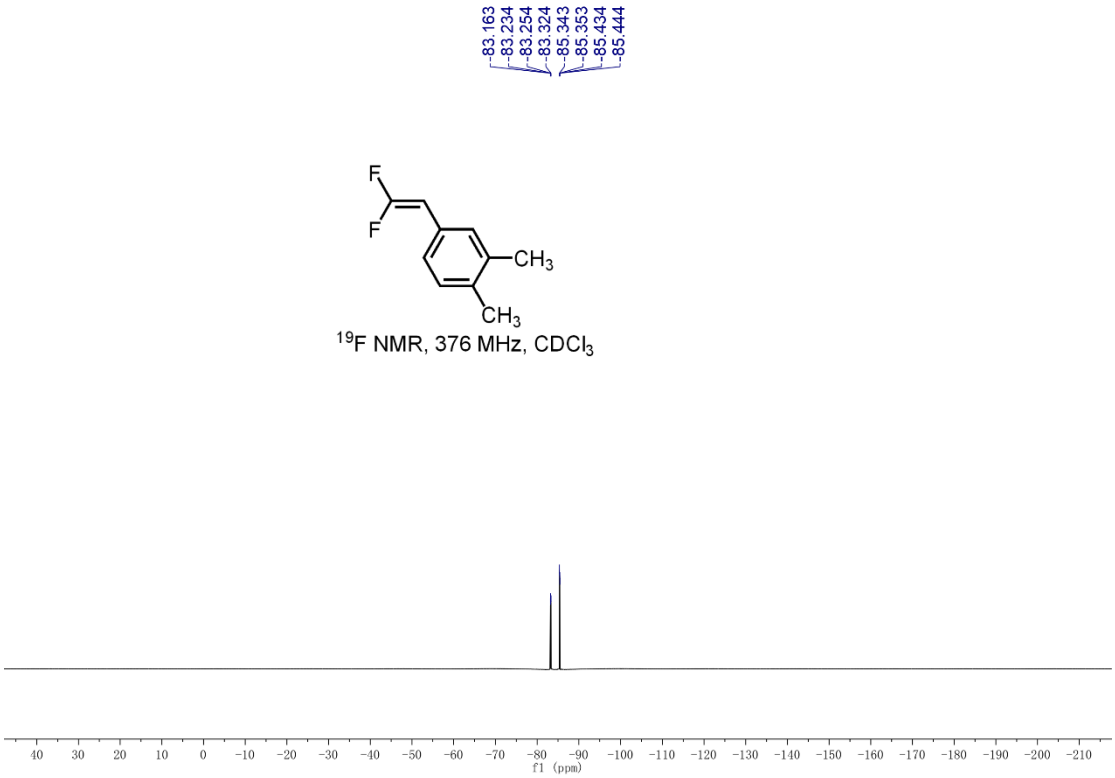
HRMS (ESI) copy of compound **2f**:

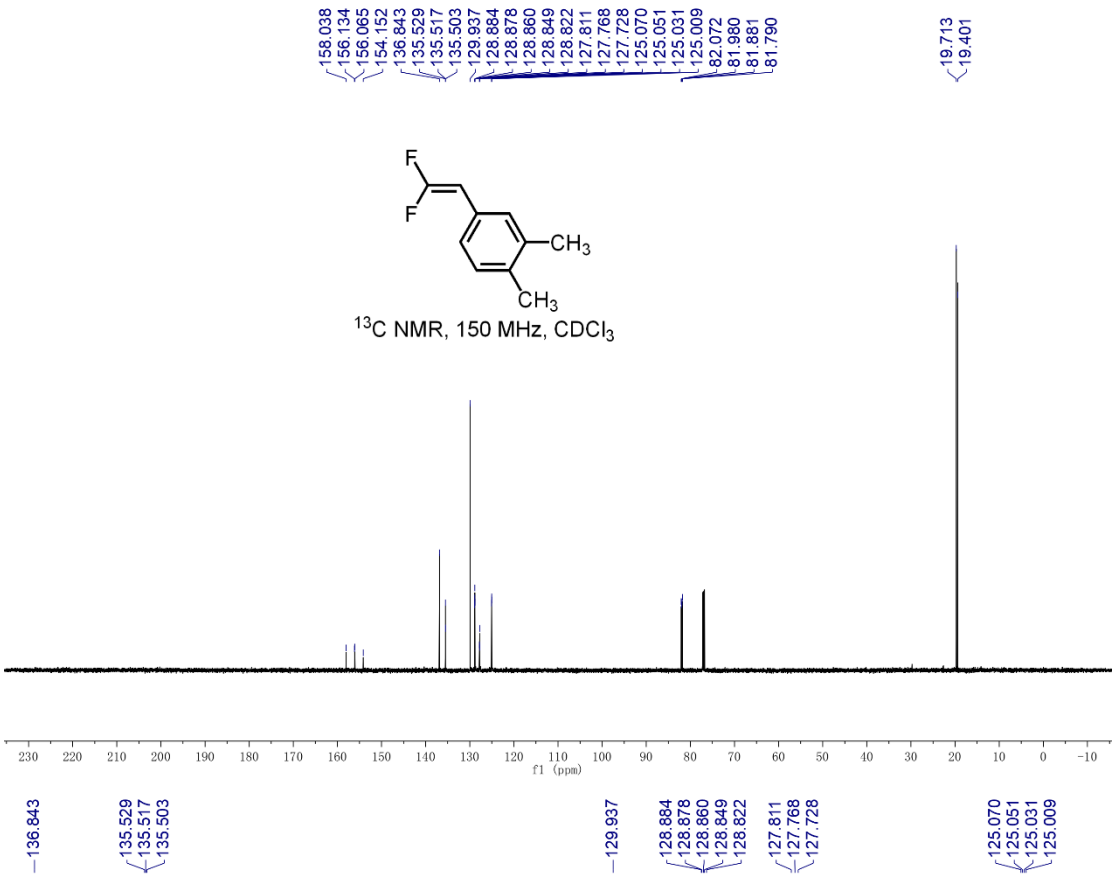


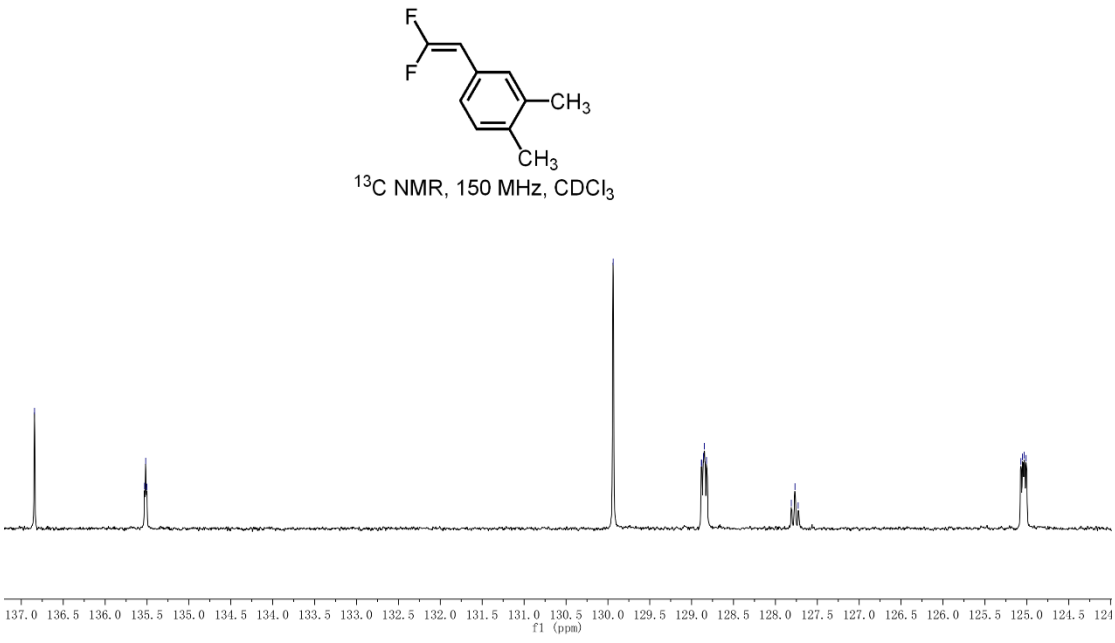
NMR copies of compound **2m**:

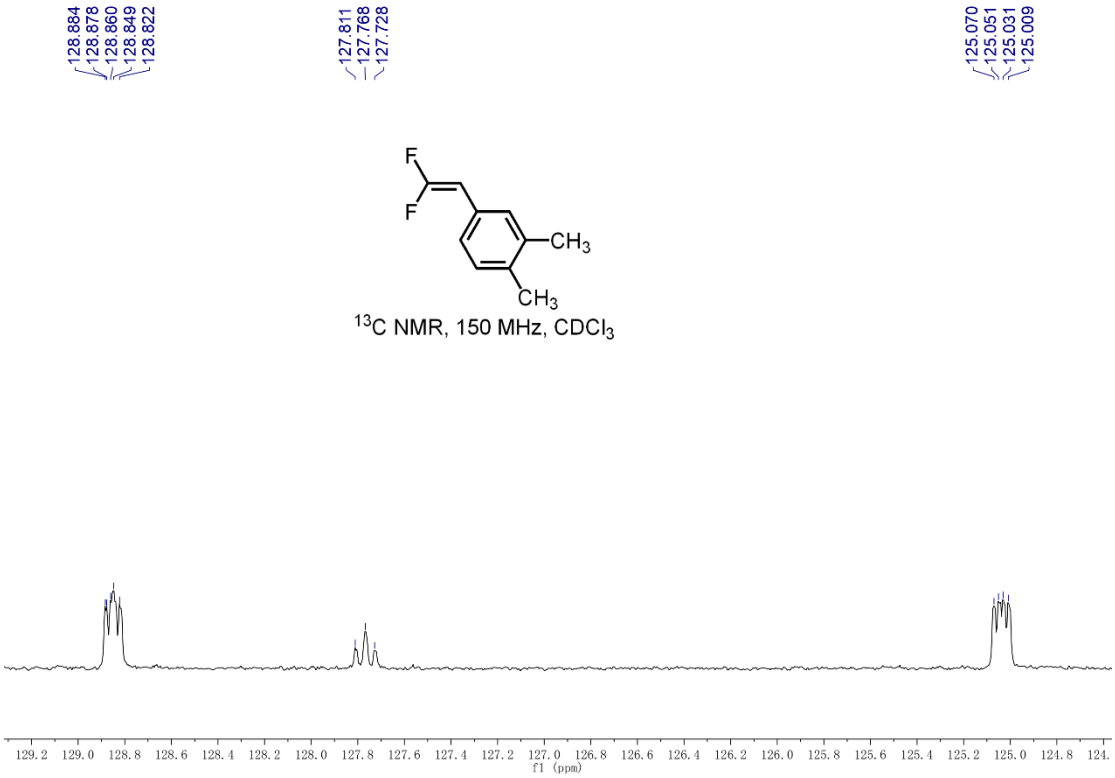




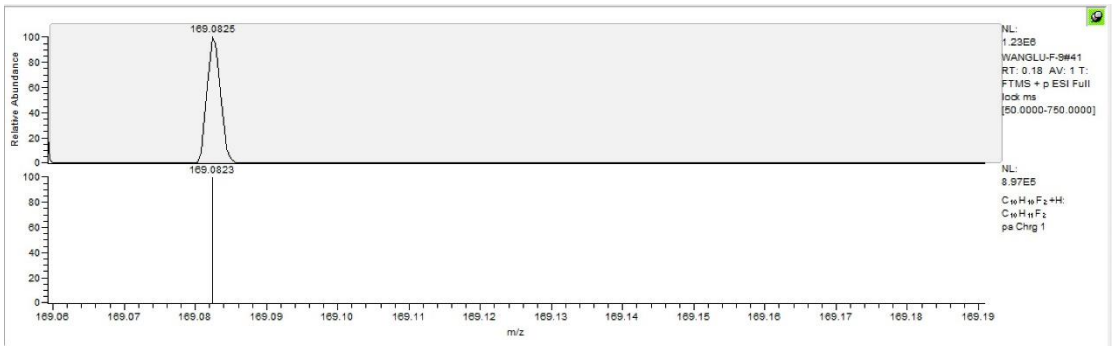

-83.163
-83.234
-83.254
-83.324
-85.343
-85.353
-85.434
-85.444
F
F
CH3
CH3
19F NMR, 376 MHz, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
-83.163
-83.234
-83.254
-83.324
-85.343
-85.353
-85.434
-85.444
F
F
CH3
CH3
19F NMR, 376 MHz, CDCl3
-82.5 -82.7 -82.9 -83.1 -83.3 -83.5 -83.7 -83.9 -84.1 -84.3 -84.5 -84.7 -84.9 -85.1 -85.3 -85.5 -85.7 -85.9 -86.1
f1 (ppm)


158.038
156.134
156.065
154.152
136.843
135.529
135.517
135.503
129.937
128.884
128.878
128.860
128.849
128.822
127.811
127.768
127.728
125.070
125.051
125.031
125.009
82.072
81.980
81.881
81.790
19.713
19.401
F
F
CH3
CH3
13C NMR, 150 MHz, CDCl3
f1 (ppm)

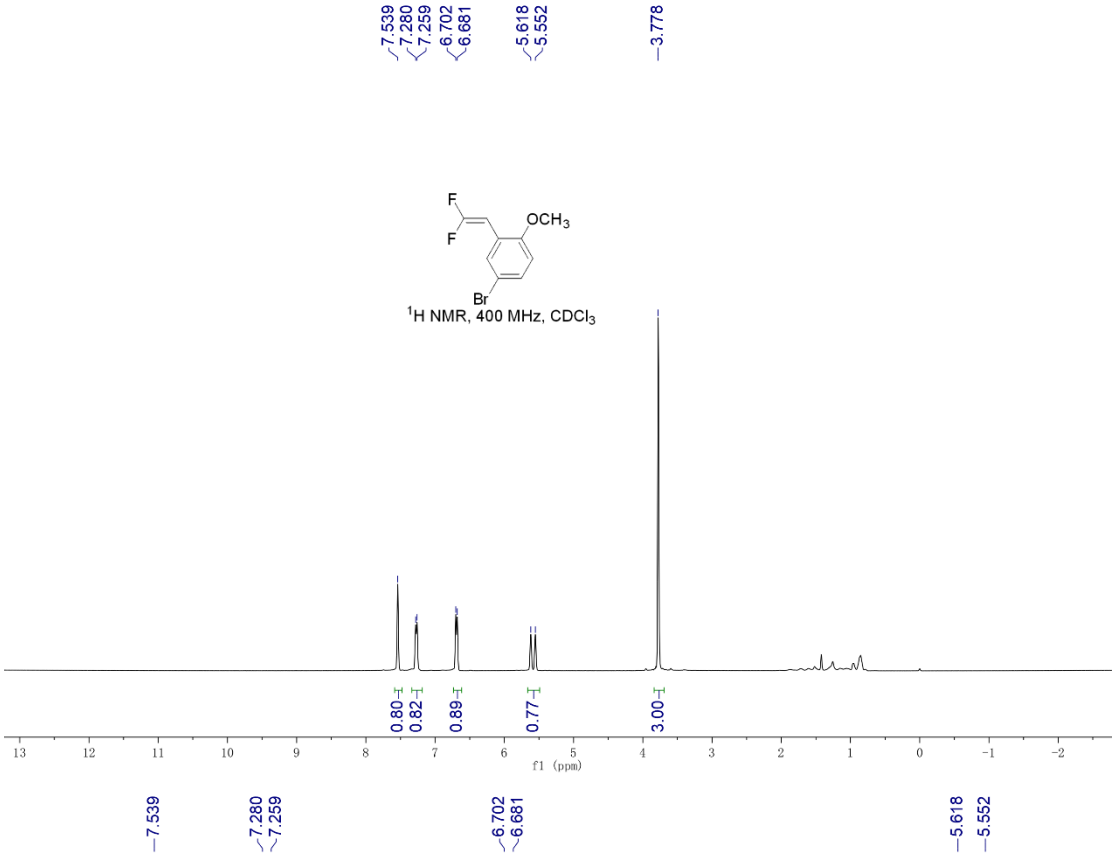

136.843
135.529
135.517
135.503
129.937
128.884
128.878
128.860
128.849
128.822
127.811
127.768
127.728
125.070
125.051
125.031
125.009
F
F
CH3
CH3
13C NMR, 150 MHz, CDCl3
f1 (ppm)

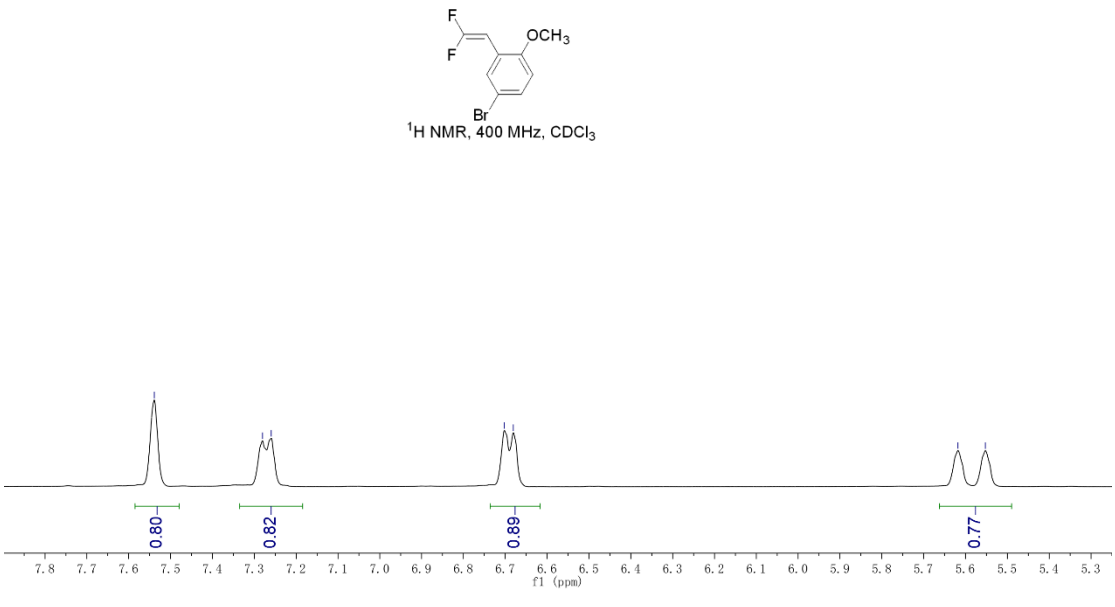


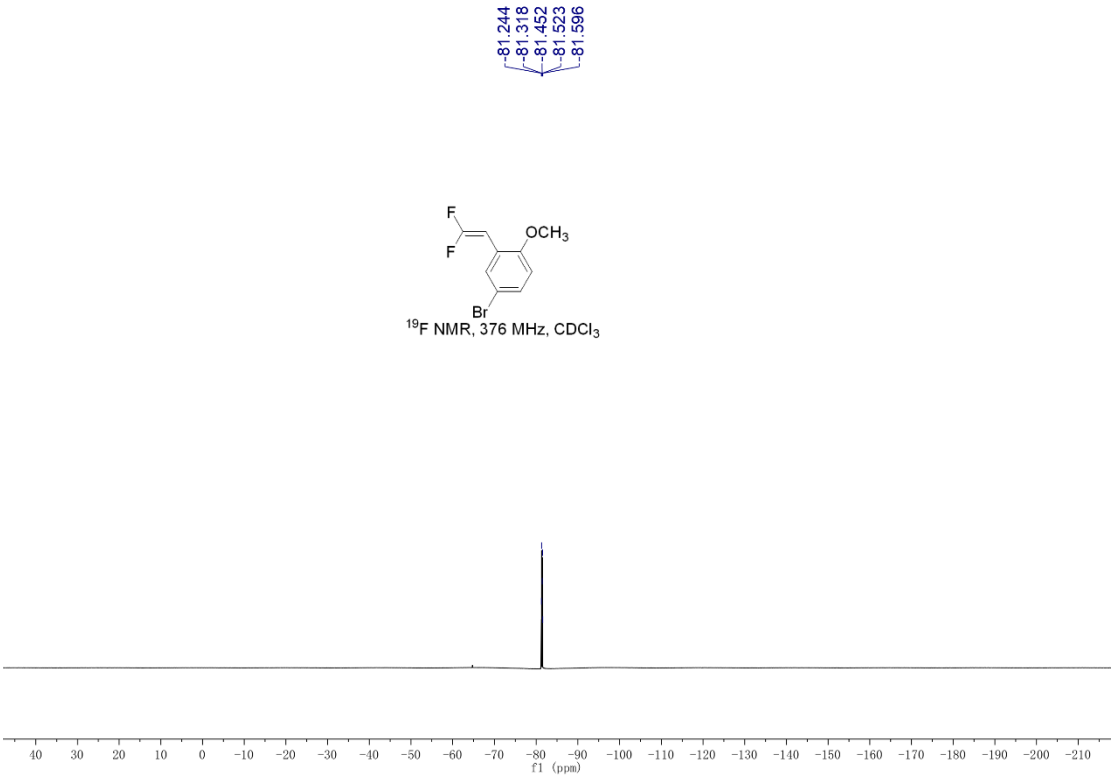
HRMS (ESI) copy of compound **2m**:



NMR copies of compound **2o**:



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-81.452
-81.523
-81.596
F
F
OCH3
Br
19F NMR, 376 MHz, CDCl3
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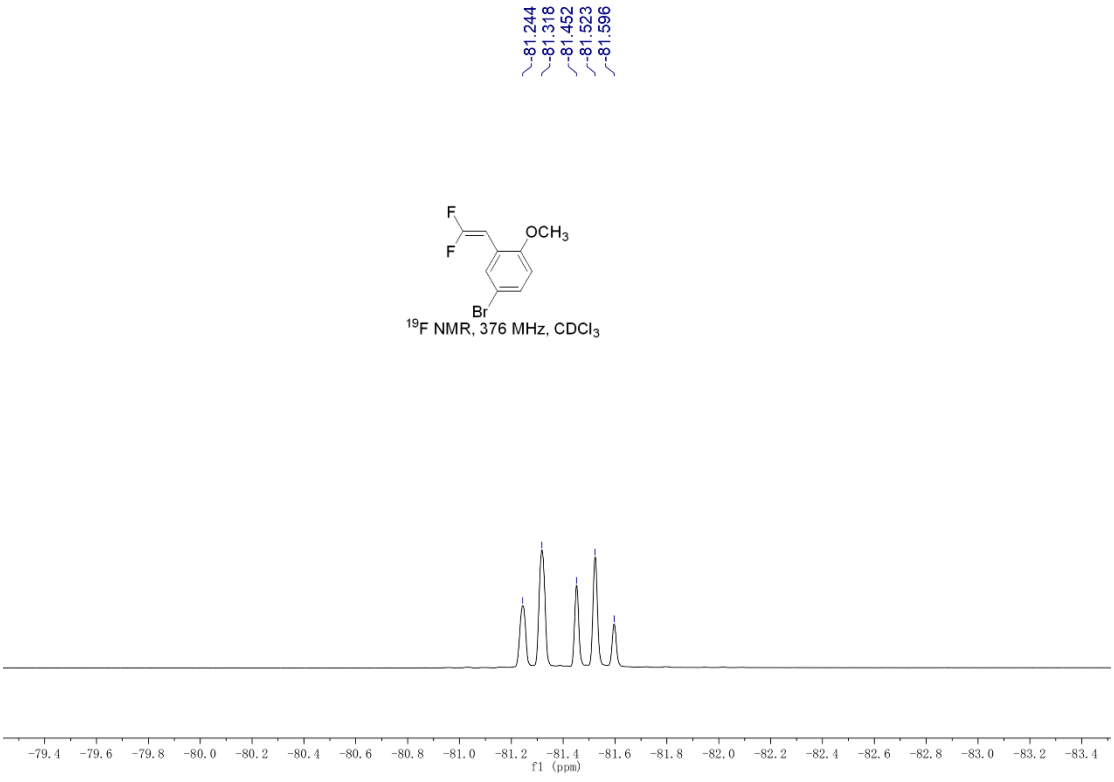
f1 (ppm)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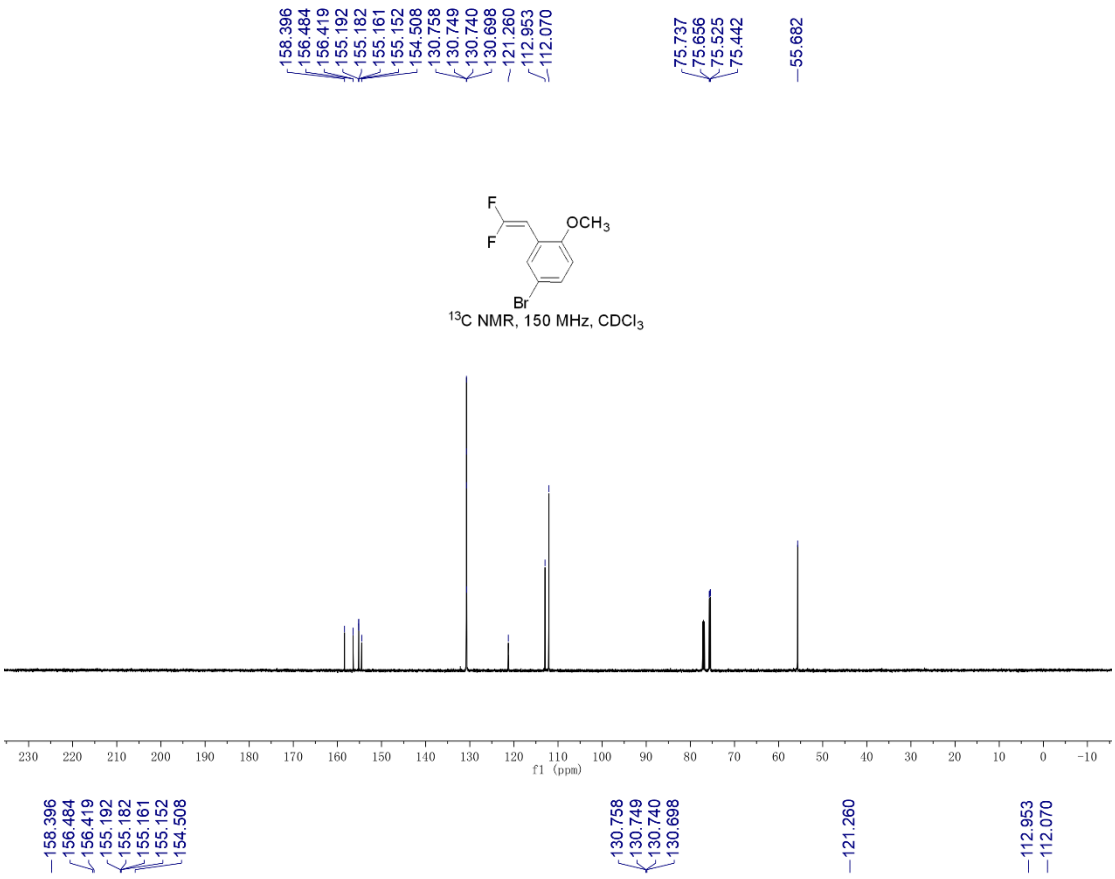
F
F
OCH3
Br
19F NMR, 376 MHz, CDCl3
-79.4 -79.6 -79.8 -80.0 -80.2 -80.4 -80.6 -80.8 -81.0 -81.2 -81.4 -81.6 -81.8 -82.0 -82.2 -82.4 -82.6 -82.8 -83.0 -83.2 -83.4
f1 (ppm)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155.192
155.182
155.161
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154.508
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130.749
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130.698
121.260
112.953
112.070
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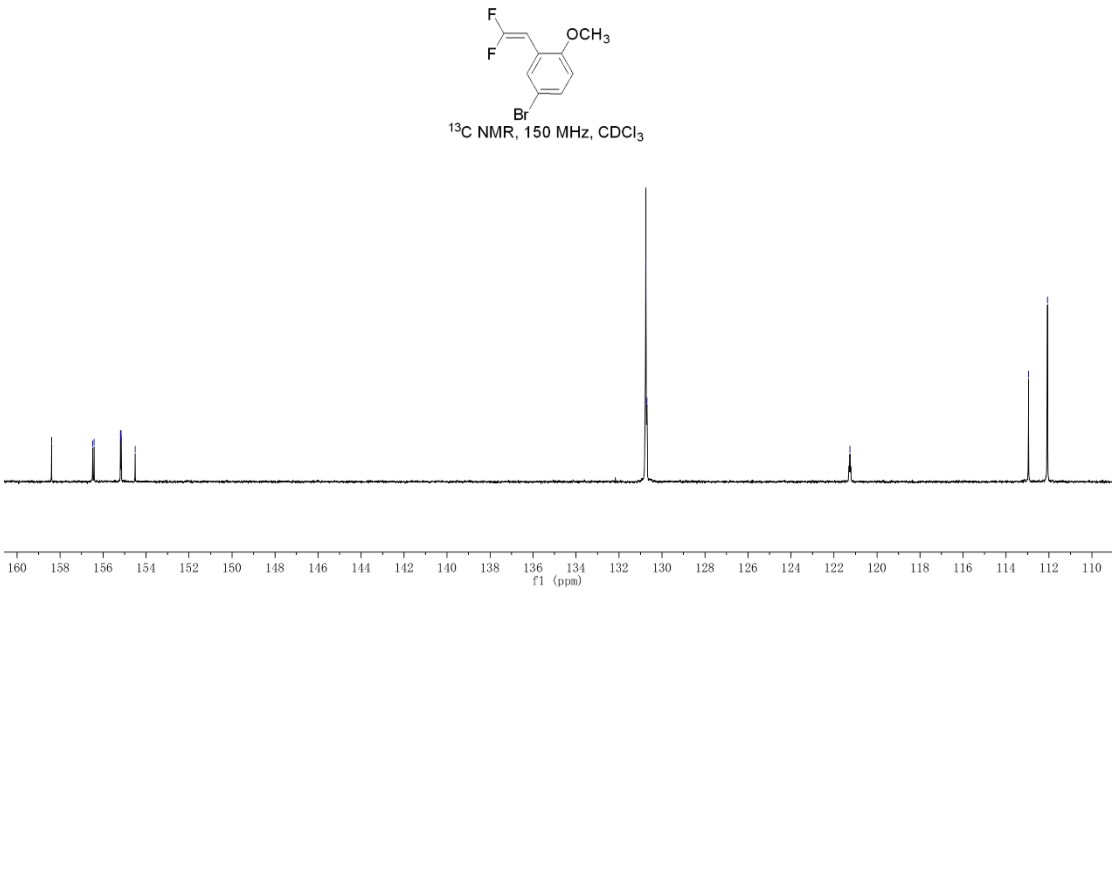
75.525
75.442
55.682
F
F
OCH3
Br
13C NMR, 150 MHz, CDCl3
f1 (ppm)


158.396
156.484
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154.508
130.758
130.749
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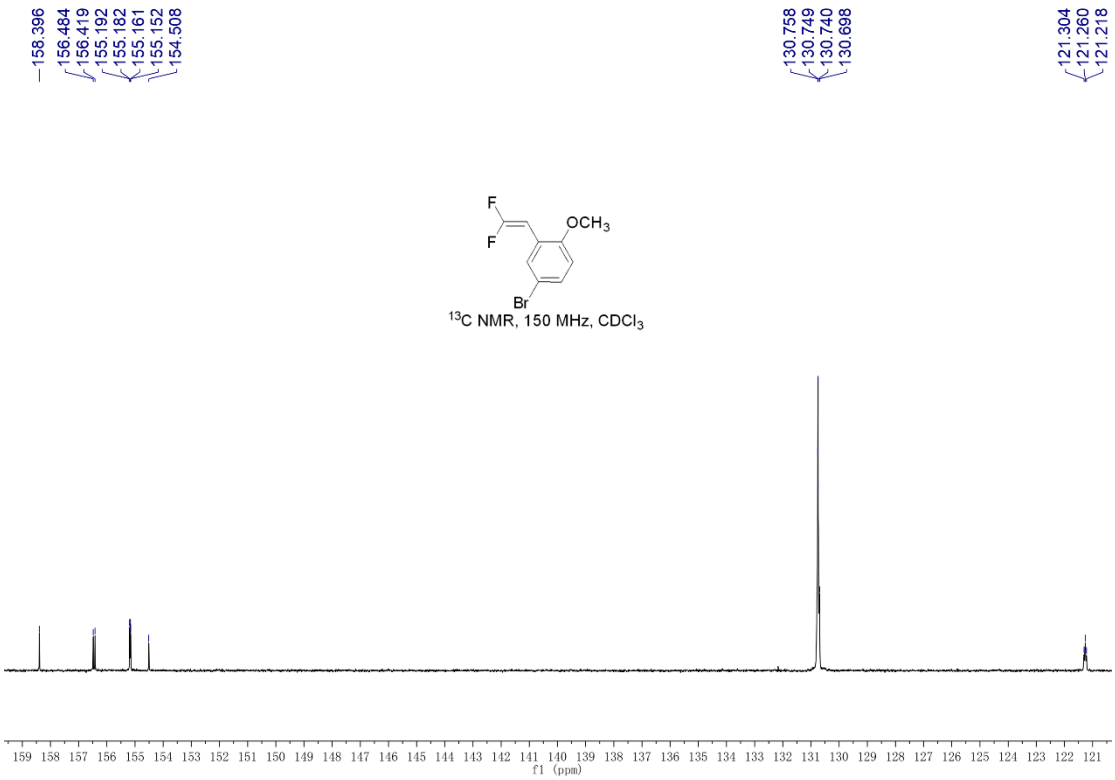
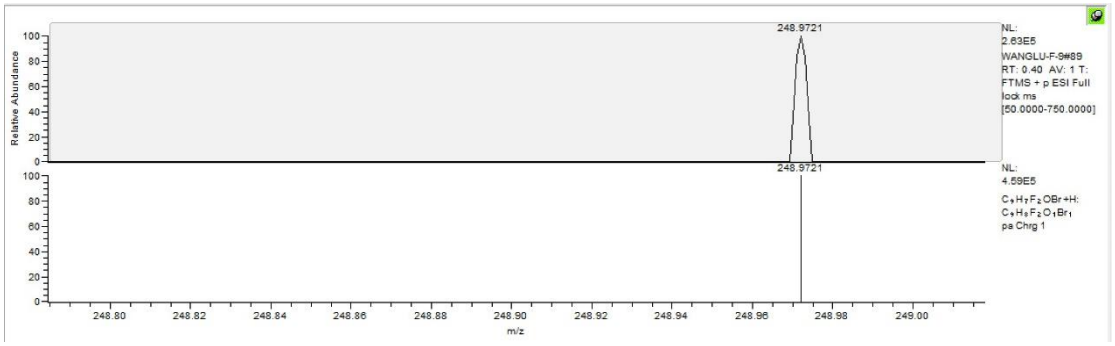
121.260
112.953
112.070
F
F
OCH3
Br
13C NMR, 150 MHz, CDCl3
f1 (ppm)



HRMS (ESI) copy of compound **2o**:



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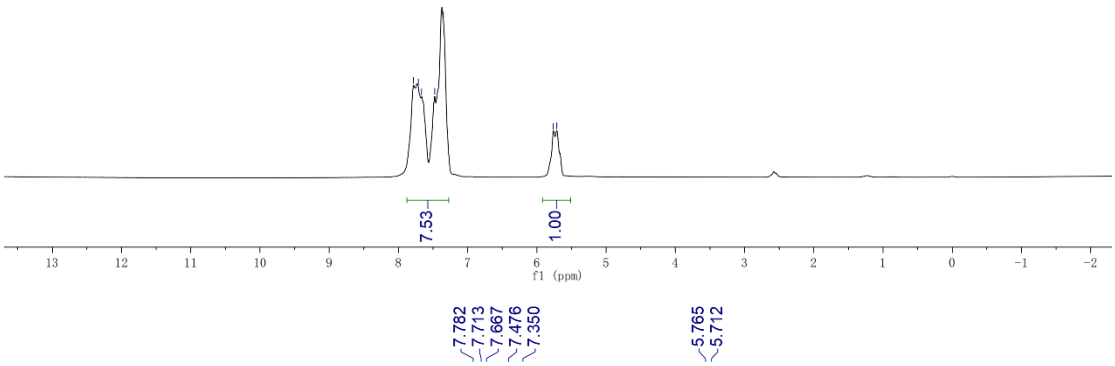
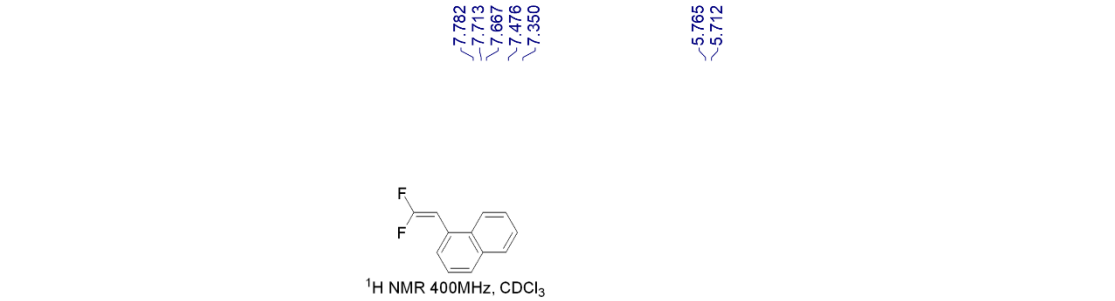
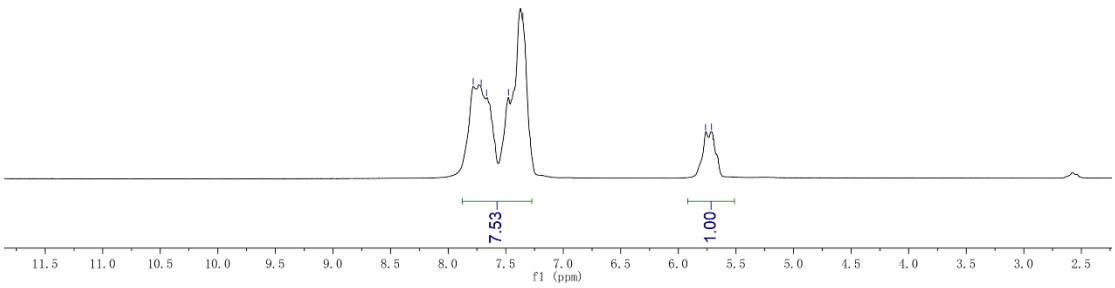
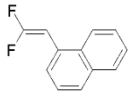
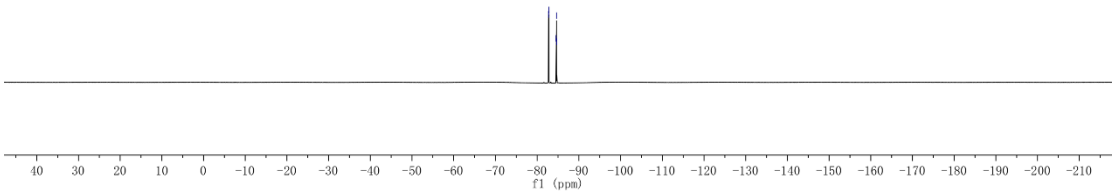


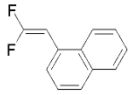




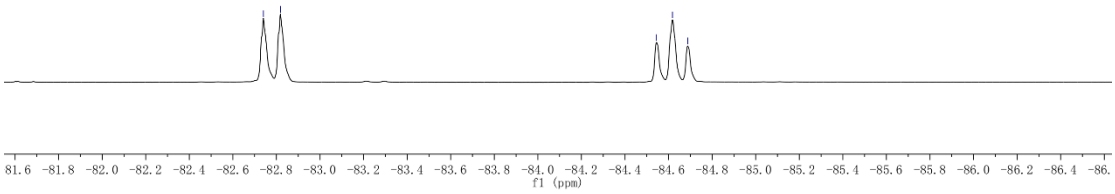


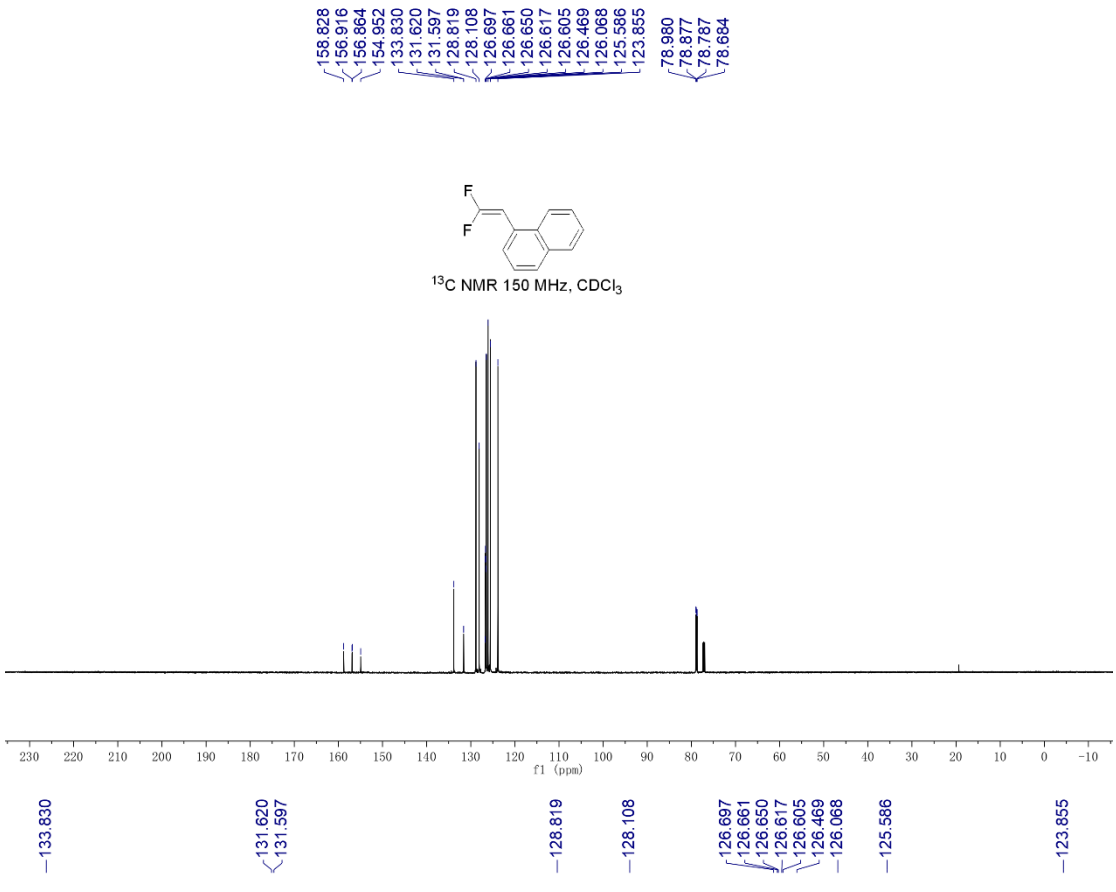
^{1}H NMR 376 MHz, $CDCl_3$





^{1}H NMR 376 MHz, $CDCl_3$

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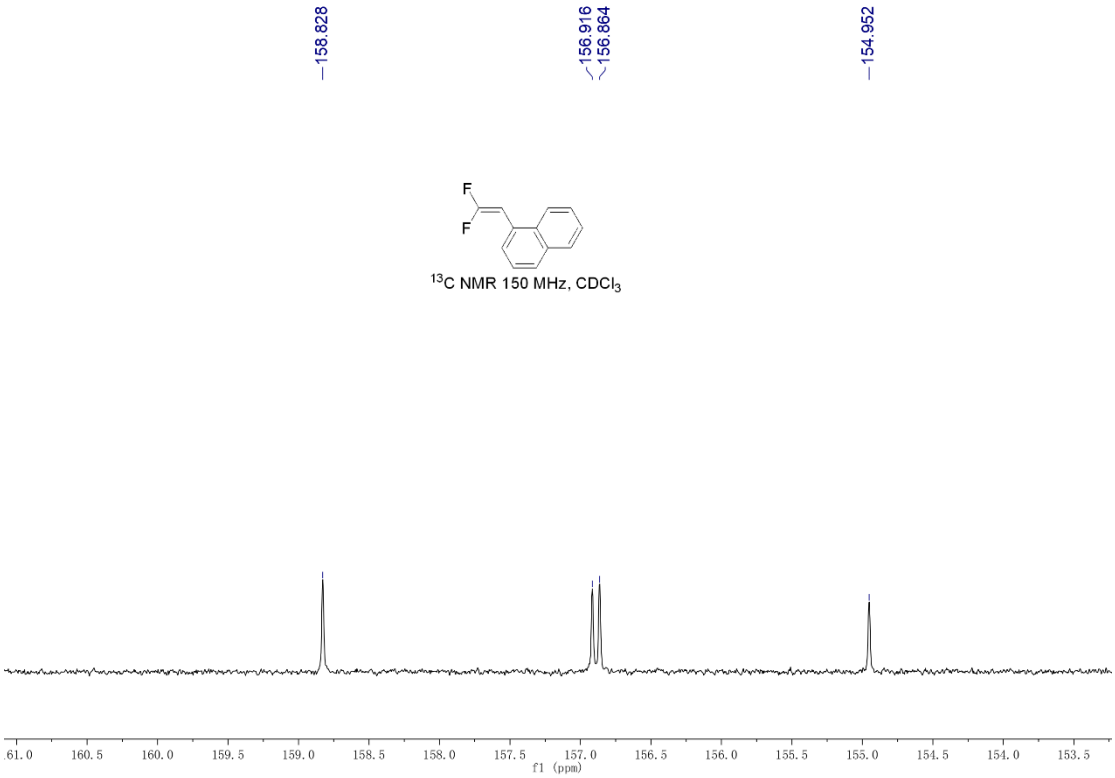
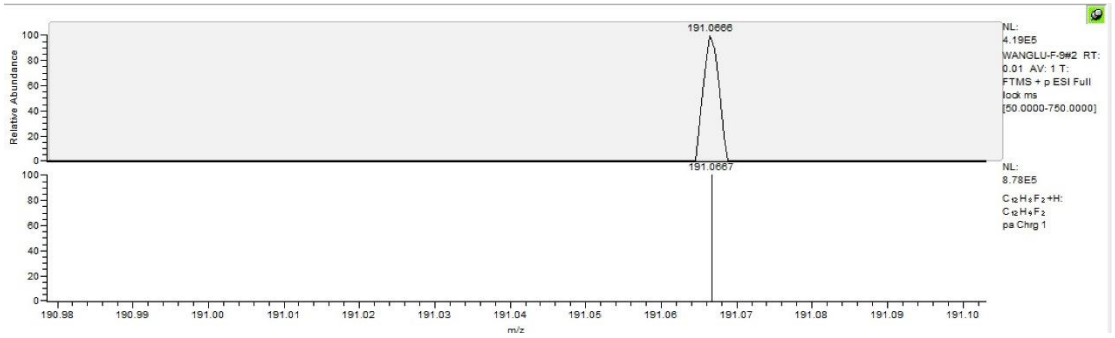
126.617
126.605
126.469
126.068
125.586
123.855
78.980
78.877
78.787
78.684
F
F
13C NMR 150 MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
133.830
131.620
131.597
128.819
128.108
126.697
126.661
126.650
126.617
126.605
126.469
126.068
125.586
123.855
F
F
13C NMR 150 MHz, CDCl3
134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0
f1 (ppm)



HRMS (ESI) copy of compound **2q**:



3. General procedure for the synthesis of compounds 3 or 4:

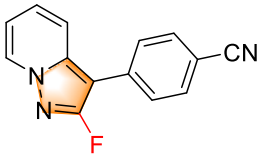
A mixture of 1 (0.6 mmol, 1.2 equiv), 2 (0.5 mmol, 1.0 equiv), and Cs_2CO_3 (0.6 mmol, 1.2 equiv) in DMF (3 ml) were charged into a reaction tube (10 mL). The reaction mixture was stirred for 12 h at 100°. The progress of the reaction was monitored by TLC. After the complete consumption of starting materials, the reaction mixture was quenched with water and the product was extracted with EtOAc (3 × 15 mL), the combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the corresponding compounds **3** or **4**.

4. References

[1] (a) Shi, X. T., Wang, Q., Tang, Z. Q., Huang, H. L., Cao, H., Liu, X. *Org. Lett*. **2024**, *26*, 1255−1260; (b) Shi, X. T., Lin, Y., Wei, J. H., Zhao, L. M., Guo, P. F., Cao, H., Liu, X. *Org. Chem. Front.* **2023**, *10*, 2892; (c) Li, W., Zhang, M. - Q., Yan, J., Ni, L.Y., Cao, H., Liu, X. *Org. Chem. Front.* **2022**, *9*, 2529; (d) Dai, W.; Li, C.; Liu, Y.; Han, X.; Li, X.; Chen, K.; Liu, H. *Org. Chem. Front*. **2020**, *7*, 2612; (e) Li, Y.; Cui, M.; Sha, F.; Li, Q.; Wu, X. *Org. Biomol. Chem*. **2019**, *17*, 8963; (f) Fang, L.; Chen, L.; Yu, J.; Wang, L. *Eur. J. Org. Chem*. **2015**, *9*, 1910.

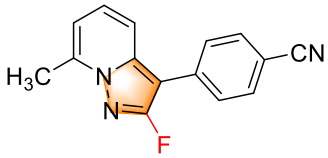
[2] (a) Liu, J., Yu, L. H., Zheng, C. W., Zhao, G. *Angew. Chem. Int. Ed*. **2021**, *60*, 23641; (b) Yan, S.-S.; Wu, D.-S.; Ye, J.-H.; Gong, L.; Zeng, X.; Ran, C.-K.; Gui, Y.-Y.; Li, J.; Yu, D.-G. *ACS. Catal*. **2019**, *9*, 6987-6992; (c) Sakaguchi, H.; Uetake, Y.; Ohashi, M.; Niwa, T.; Ogoshi, S.; Hosoya, T. *J. Am. Chem. Soc*. **2017**, *139*, 12855-12862.

5. Characterization data of compounds 3 and 4:



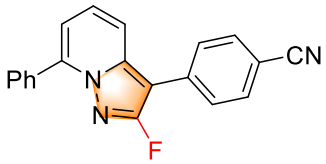
4-(2-fluoropyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3a)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Yellow solid; Yield = 98 mg (83%); mp 221 - 223 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.36 (d, J = 7.2 Hz, 1H), 7.76 - 7.71 (m, 5H), 7.35 (t, J = 8.0 Hz, 1H), 6.91 (t, J = 7.4 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.89 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.2 (d, J = 249.1 Hz), 138.6, 135.2 (d, J = 4.3 Hz), 132.7, 129.5, 127.4 (d, J = 2.8 Hz), 126.5, 118.9, 116.5 (d, J = 3.4 Hz), 112.7 (d, J = 2.5 Hz), 109.5, 93.0 (d, J = 16.9 Hz). **HRMS** (ESI): Calcd for $C_{14}H_9FN_3^+$ m/z 238.0775 $[M+H]^+$, found 238.0776.



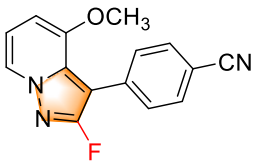
4-(2-fluoro-7-methylpyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3b)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 78 mg (62%); mp 204 - 206 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.73 (s, 4H), 7.64 (d, J = 8.8 Hz, 1H), 7.31 (dd, J = 7.2 Hz, J = 8.8 Hz,1H), 6.78 (d, J = 7.2 Hz, 1H), 2.72 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -128.34 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.0 (d, J = 248.2 Hz), 139.4, 139.0, 135.6 (d, J = 4.5 Hz), 132.7, 127.4 (d, J = 2.8 Hz), 126.7, 119.0, 113.9 (d, J = 3.4 Hz), 112.3 (d, J = 2.8 Hz), 109.3, 92.9 (d, J = 16.9 Hz), 17.7. **HRMS** (ESI): Calcd for $C_{15}H_{11}FN_3^+$ m/z 252.0932 $[M+H]^+$, found 252.0932.



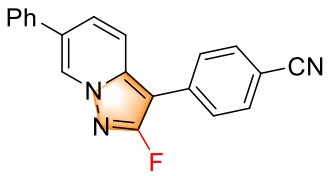
4-(2-fluoro-7-phenylpyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3c)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 113 mg (72%); mp 196 - 198 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.84 (dd, J = 2.0 Hz, J = 8.0 Hz, 2H), 7.71 (s, 4H), 7.68 (s, 1H), 7.54 - 7.51 (m, 3H), 7.39 (dd, J = 7.2 Hz, J = 8.8 Hz, 1H), 6.94 (dd, J = 1.2 Hz, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.79 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 247.8 Hz), 141.4, 139.7, 135.4 (d, J = 4.5 Hz), 132.7, 132.4, 130.0, 129.2, 128.5, 127.5 (d, J = 2.5 Hz), 126.9, 119.0, 115.1 (d, J = 3.1 Hz), 113.6 (d, J = 2.7 Hz), 109.5, 93.3 (d, J = 17.2 Hz). **HRMS** (ESI): Calcd for $C_{20}H_{13}FN_3^+$ m/z 314.1088 $[M+H]^+$, found 314.1088.



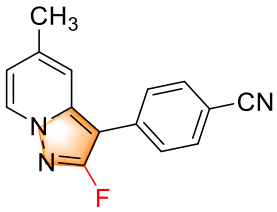
4-(2-fluoro-4-methoxypyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3d)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 71 mg (53%); mp 165 - 167 °C. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 7.99 (d, J = 7.6 Hz, 1H), 7.70 - 7.59 (m, 4H), 6.80 - 6.72 (m, 1H), 6.58 (d, J = 7.6 Hz, 1H), 3.87 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -130.99 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.3 (d, J = 247.5 Hz), 151.1 (d, J = 3.1 Hz), 134.7 (d, J = 3.9 Hz), 132.1, 131.4, 130.7 (d, J = 1.8 Hz), 122.3, 119.2, 111.7 (d, J = 2.5 Hz), 109.6, 102.3, 94.4 (d, J = 17.2 Hz), 55.6. **HRMS** (ESI): Calcd for $C_{15}H_{11}FN_3O^+$ m/z 268.0881 $[M+H]^+$, found 268.0883.



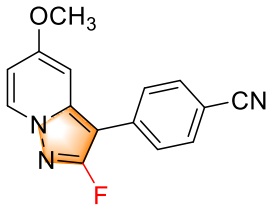
4-(2-fluoro-6-phenylpyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3e)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 86 mg (55%); mp 135 - 137 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.53 (s, 1H), 7.78 (d, J = 9.2 Hz, 1H), 7.74 – 7.69 (m, 4H), 7.63 – 7.53 (m, 3H), 7.50 (t, J = 7.2 Hz, 2H), 7.43 (d, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -126.76 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.3 (d, J = 249.9 Hz), 137.4, 136.2, 135.1 (d, J = 4.3 Hz), 132.8, 129.3, 128.3, 127.2 (d, J = 2.8 Hz), 126.9, 126.7 (d, J = 6.9 Hz), 119.0, 116.4 (d, J = 3.3 Hz), 109.5, 93.1 (d, J = 16.5 Hz). **HRMS** (ESI): Calcd for $C_{20}H_{13}FN_3^+$ m/z 314.1088 $[M+H]^+$, found 314.10877.



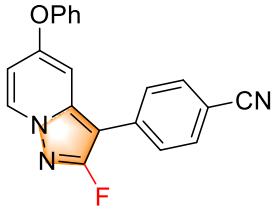
4-(2-fluoro-5-methylpyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3f)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 100 mg (80%); mp 188 - 190 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.21 (d, J = 7.2 Hz, 1H), 7.74 -7.69 (m, 4H), 7.48 (s, 1H), 6.65 (dd, J = 1.6 Hz, J = 7.2 Hz, 1H), 2.45 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.81 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.4 (d, J = 249.0 Hz), 138.7 (d, J = 1.0 Hz), 137.9, 135.6 (d, J = 4.5 Hz), 132.7, 128.7, 127.2 (d, J = 2.8 Hz), 119.0, 115.2 (d, J = 2.7 Hz), 114.9 (d, J = 3.3 Hz), 109.1, 92.0 (d, J = 16.8 Hz), 21.6. **HRMS** (ESI): Calcd for $C_{15}H_{11}FN_3^+$ m/z 252.0932 $[M+H]^+$, found 252.0932.



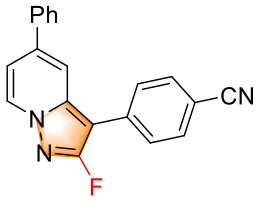
4-(2-fluoro-5-methoxypyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (**3g)**

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 113 mg (85%); mp 218 - 220 °C. **^{1}H NMR** (600 MHz, $CDCl_3$), δ: 8.16 (d, J = 7.8 Hz, 1H), 7.73 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 7.8 Hz, 2H), 6.90 (d, J = 2.4 Hz, 1H), 6.57 (dd, J = 3.0 Hz, J = 7.8 Hz, 1H), 3.91 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.21 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.8 (d, J = 248.8 Hz), 158.9, 139.7, 135.7 (d, J = 4.5 Hz), 132.7, 130.4, 127.0 (d, J = 2.7 Hz), 119.1, 109.0, 107.0 (d, J = 2.5 Hz), 93.8 (d, J = 2.7 Hz), 92.3 (d, J = 18.9 Hz), 55.8. **HRMS** (ESI): Calcd for $C_{15}H_{11}FN_3O^+$ m/z 268.0881 $[M+H]^+$, found 268.0881.



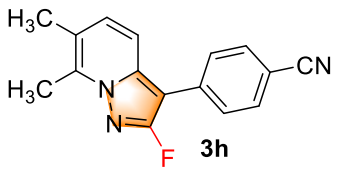
4-(2-fluoro-5-phenoxypyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (**3h)**

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 146 mg (89%); mp 142 - 144 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.25 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 7.12 (d, J = 7.6 Hz, 2H), 7.03 (d, J = 2.4 Hz, 1H), 6.67 (dd, J = 2.8 Hz, J = 7.6 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -126.39 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.9 (d, J = 249.3 Hz), 157.2, 154.6, 139.5, 135.2 (d, J = 4.3 Hz), 132.7, 131.0, 130.3, 126.9, 125.4, 120.1, 118.9, 109.2, 107.0 (d, J = 2.5 Hz), 100.5 (d, J = 2.7 Hz), 92.8 (d, J = 17.4 Hz). **HRMS** (ESI): Calcd for $C_{20}H_{13}FN_3O^+$ m/z 330.1037 $[M+H]^+$, found 330.1037.



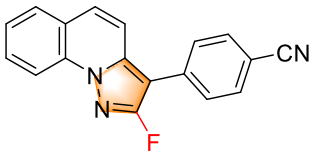
4-(2-fluoro-5-phenylpyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3i)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 122 mg (78%); mp 167 - 169 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.38 (d, J = 7.2 Hz, 1H), 7.84 (s, 1H), 7.74 (s, 4H), 7.64 (d, J = 6.8 Hz, 2H), 7.53 - 7.44 (m, 3H), 7.14 (dd, J = 2.0 Hz, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.14 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.5 (d, J = 249.7 Hz), 139.9, 138.7, 138.1, 135.3 (d, J = 4.3 Hz), 132.8, 129.4, 129.2, 129.0, 127.4 (d, J = 2.8 Hz), 126.9, 119.0, 113.3 (d, J = 3.4 Hz), 112.6 (d, J = 2.5 Hz), 109.5, 93.4 (d, J = 16.8 Hz). **HRMS** (ESI): Calcd for $C_{20}H_{13}FN_3^+$ m/z 314.1088 $[M+H]^+$, found 314.1089.



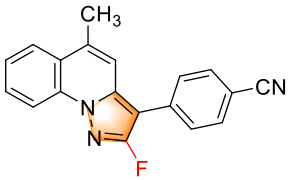
4-(2-fluoro-6,7-dimethylpyrazolo[1,5-*a*]pyridin-3-yl)benzonitrile (3j)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 99 mg (75%); mp 166 - 169 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 7.70 (s, 4H), 7.53 (d, J = 8.8 Hz, 1H), 7.20 (d, J = 9.2 Hz, 1H), 2.68 (s, 3H), 2.38 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -128.82 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.7 (d, J = 247.0 Hz), 137.6, 136.7, 135.8 (d, J = 4.5 Hz), 132.6, 130.0, 127.1 (d, J = 3.0 Hz), 119.8 (d, J = 2.8 Hz), 119.1, 112.9 (d, J = 3.3 Hz), 108.9, 92.3 (d, J = 16.9 Hz), 17.9, 14.0. **HRMS** (ESI): Calcd for $C_{16}H_{13}FN_3^+$ m/z 266.1088 $[M+H]^+$, found 266.1088.



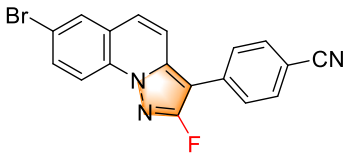
4-(2-fluoropyrazolo[1,5-*a*]quinolin-3-yl)benzonitrile (**3n**)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 108 mg (75%); mp 199 - 201 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.45 (d, J = 8.4 Hz, 1H), 7.82 - 7.72 (m, 6H), 7.65 (d, J = 9.6 Hz, 1H), 7.61 (d, J = 9.2 Hz, 1H), 7.52 - 7.48 (m, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -128.56 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.6 (d, J = 249.4 Hz), 141.2, 136.3, 135.0 (d, J = 4.5 Hz), 134.4, 132.7, 130.5, 128.6, 127.8 (d, J = 2.2 Hz), 127.6, 125.2, 123.0, 118.9, 115.3, 114.5 (d, J = 2.1 Hz), 110.0, 96.4 (d, J = 17.4 Hz). **HRMS** (ESI): Calcd for $C_{18}H_{11}FN_3^+$ m/z 288.0932 $[M+H]^+$, found 288.0930.



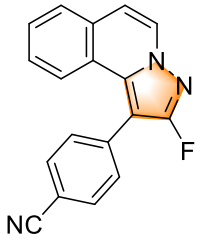
4-(2-fluoro-5-methylpyrazolo[1,5-*a*]quinolin-3-yl)benzonitrile (3o)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 126 mg (84%); mp 202 - 204 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.46 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.77 - 7.71 (m, 5H), 7.54 - 7.51 (m, 1H), 7.43 (s, 1H), 2.67 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.01 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.7 (d, J = 248.7 Hz), 136.2, 135.3 (d, J = 4.3 Hz), 135.3, 134.1, 132.7, 130.2, 127.7 (d, J = 2.7 Hz), 125.3, 125.0, 123.5 (d, J = 2.1 Hz), 119.0, 115.6, 113.8 (d, J = 2.1 Hz), 109.7, 95.4 (d, J = 17.8 Hz), 19.5. **HRMS** (ESI): Calcd for $C_{19}H_{13}FN_3^+$ m/z 302.1088 $[M+H]^+$, found 302.1087.



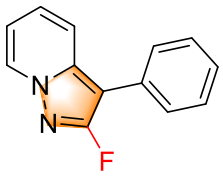
4-(7-bromo-2-fluoropyrazolo[1,5-*a*]quinolin-3-yl)benzonitrile (3p)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 131 mg (72%); mp 244 - 246 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.32 (d, J = 8.8 Hz, 1H), 7.94 (d, J = 2.0 Hz, 1H), 7.80 (dd, J = 2.0, J = 8.8, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 9.6 Hz, 1H), 7.54 (d, J = 9.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.99 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.7 (d, J = 249.4 Hz), 136.1, 134.6 (d, J = 4.5 Hz), 133.4, 133.2, 132.8, 130.8, 127.9 (d, J = 2.4 Hz), 126.4, 124.5 (d, J = 1.6 Hz), 118.8, 118.5, 117.2, 115.8 (d, J = 2.4 Hz), 110.3, 97.1 (d, J = 17.8 Hz). **HRMS** (ESI): Calcd for $C_{18}H_{10}BrFN_3^+$ m/z 366.0037 $[M+H]^+$, found 366.0034.



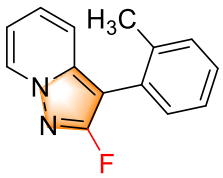
4-(2-fluoropyrazolo[5,1-*a*]isoquinolin-1-yl)benzonitrile (3q)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 92 mg (64%); mp 148 - 150 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.10 (d, J = 7.2 Hz, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 8.0 Hz, 1H), 7.41 (t, J = 7.2 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -131.81 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.5 (d, J = 247.0 Hz), 135.4 (d, J = 3.3 Hz), 135.3, 132.6, 131.0, 129.7, 128.9, 127.9, 127.6, 126.2, 123.9 (d, J = 2.5 Hz), 123.1, 118.7, 112.6 (d, J = 2.4 Hz), 111.5, 97.5 (d, J = 20.1 Hz). **HRMS** (ESI): Calcd for $C_{18}H_{10}BrFN_3^+$ m/z 288.0932 $[M+H]^+$, found 288.0935.



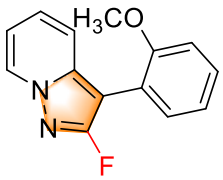
2-fluoro-3-phenylpyrazolo[1,5-*a*]pyridine (4a)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Orange oil; Yield = 61 mg (58%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.30 (d, J = 6.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 7.2 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.80 (t, J = 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -130.22 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.0 (d, J = 247.6 Hz), 138.5 (d, J = 1.6 Hz), 130.1 (d, J = 4.1 Hz), 129.0, 128.9, 127.5 (d, J = 2.1 Hz), 126.5, 125.17, 116.8 (d, J = 3.7 Hz), 111.9 (d, J = 2.8 Hz), 94.5 (d, J = 17.5 Hz). **HRMS** (ESI): Calcd for $C_{13}H_{10}FN_2^+$ m/z 213.0823 $[M+H]^+$, found 213.0822.



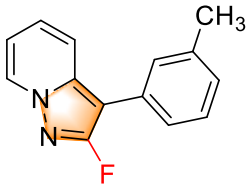
2-fluoro-3-(o-tolyl)pyrazolo[1,5-*a*]pyridine (4b)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Orange oil; Yield = 34 mg (30%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.32 (d, J = 7.2 Hz, 1H), 7.32 - 7.29 (m, 5H), 7.18 - 7.14 (m, 1H), 6.80 (t, J = 8.4 Hz, 1H), 2.29 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.51 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.8 (d, J = 247.0 Hz), 139.4 (d, J = 2.7 Hz), 137.7, 130.8, 130.6, 128.7, 128.5 (d, J = 3.0 Hz), 127.8, 125.8, 124.6, 116.8 (d, J = 3.9 Hz), 111.7 (d, J = 3.0 Hz), 94.1 (d, J = 21.0 Hz), 20.0. **HRMS** (ESI): Calcd for $C_{14}H_{12}FN_2^+$ m/z 227.0979 $[M+H]^+$, found 227.0978.



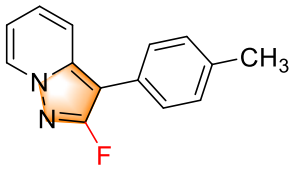
2-fluoro-3-(2-methoxyphenyl)pyrazolo[1,5-*a*]pyridine (4c)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Orange oil; Yield = 43 mg (36%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.27 (d, J = 7.2 Hz, 1H), 7.43 - 7.39 (m, 2H), 7.37 - 7.33 (m, 1H), 7.14 (t, J = 7.2 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.76 (t, J = 6.8 Hz, 1H), 3.84 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -128.31 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.2 (d, J = 247.6 Hz), 156.8, 139.3 (d, J = 2.1 Hz), 131.1 (d, J = 1.0 Hz), 128.7, 128.6, 124.2, 120.8, 118.5 (d, J = 3.7 Hz), 118.0 (d, J = 3.6 Hz), 111.5 (d, J = 2.7 Hz), 111.3, 91.1 (d, J = 19.2 Hz), 55.4. **HRMS** (ESI): Calcd for $C_{14}H_{12}FN_2O^+$ m/z 243.0928 $[M+H]^+$, found 243.0929.



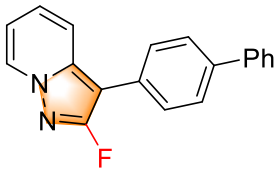
2-fluoro-3-(m-tolyl)pyrazolo[1,5-*a*]pyridine (4d)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Orange oil; Yield = 72 mg (64%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.30 (d, J = 7.2 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.42- 7.34 (m, 3H), 7.24 -7.20 (m, 1H), 7.13 (d, J = 7.2 Hz, 1H), 6.80 (t, J = 6.8 Hz, 1H), 2.43 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -130.17 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.0 (d, J = 247.8 Hz), 138.6, 138.5 (d, J = 1.8 Hz), 130.0 (d, J = 4.2 Hz), 129.0, 128.9, 128.3 (d, J = 1.9 Hz), 127.3, 125.0, 124.6 (d, J = 2.1 Hz), 116.9 (d, J = 3.6 Hz), 111.8 (d, J = 2.7 Hz), 94.6 (d, J = 17.4 Hz), 21.5. **HRMS** (ESI): Calcd for $C_{14}H_{12}FN_2^+$ m/z 227.0979 $[M+H]^+$, found 227.0979.



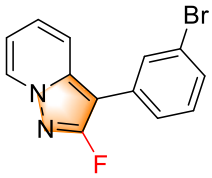
2-fluoro-3-(p-tolyl)pyrazolo[1,5-*a*]pyridine (4e)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Orange oil; Yield = 96 mg (85%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.29 (d, J = 7.2 Hz, 1H), 7.68 (d, J = 9.2 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.20 (t, J = 8.0 Hz, 1H), 6.79 (t, J = 7.2 Hz, 1H), 2.40 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -130.47 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 247.6 Hz), 138.4 (d, J = 1.6 Hz), 136.3, 129.6, 128.9, 127.5 (d, J = 1.9 Hz), 127.1 (d, J = 4.2 Hz), 124.9, 116.8 (d, J = 3.7 Hz), 111.8 (d, J = 2.8 Hz), 94.5 (d, J = 17.7 Hz), 21.2. **HRMS** (ESI): Calcd for $C_{14}H_{12}FN_2^+$ m/z 227.0979 $[M+H]^+$, found 227.0979.



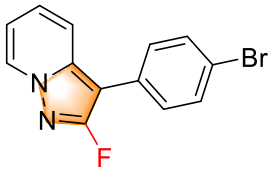
3-([1,1'-biphenyl]-4-yl)-2-fluoropyrazolo[1,5-*a*]pyridine (4f)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 127 mg (88%); mp 114 - 116 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.30 (d, J = 7.2 Hz, 1H), 7.74 -7.63 (m, 7H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 8.0 Hz, 1H), 6.80 (t, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.74 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 247.8 Hz), 141.4, 139.7, 135.4 (d, J = 4.5 Hz), 132.7, 132.4, 130.0, 129.2, 128.5, 127.5 (d, J = 2.5 Hz), 126.9, 119.0, 115.1 (d, J = 3.1 Hz), 113.6 (d, J = 2.7 Hz), 109.5, 93.3 (d, J = 17.2 Hz). **HRMS** (ESI): Calcd for $C_{19}H_{14}FN_2^+$ m/z 289.1136 $[M+H]^+$, found 289.1136.



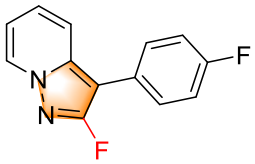
3-(3-bromophenyl)-2-fluoropyrazolo[1,5-*a*]pyridine (4h)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Orange oil; Yield = 75 mg (52%). **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.31 (d, J = 7.2 Hz, 1H), 7.74 (s, 1H), 7.69 (d, J = 9.2 Hz, 1H), 7.53 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.31 - 7.24 (m, 1H), 6.84 (t, J = 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.38 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 248.4 Hz), 138.5 (d, J = 1.2 Hz), 132.2 (d, J = 4.2 Hz), 130.4, 130.1 (d, J = 2.4 Hz), 129.4, 129.1, 126.0 (d, J = 2.2 Hz), 125.7, 123.0, 116.5 (d, J = 3.4 Hz), 112.2 (d, J = 2.7 Hz), 93.2 (d, J = 17.2 Hz). **HRMS** (ESI): Calcd for $C_{13}H_9BrFN_2^+$ m/z 290.9928 $[M+H]^+$, found 290.9918.



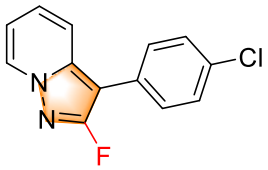
3-(4-bromophenyl)-2-fluoropyrazolo[1,5-*a*]pyridine (4i)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 99 mg (68%); mp 129 - 131 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.31 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.26 (t, J = 7.2 Hz, 1H), 6.83 (t, J = 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.75 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 247.9 Hz), 138.4 (d, J = 1.5 Hz), 132.1, 129.1 (d, J = 2.2 Hz), 129.1, 128.9 (d, J = 2.2 Hz), 125.6, 120.2, 116.5 (d, J = 3.4 Hz), 112.1 (d, J = 2.8 Hz), 93.5 (d, J = 17.4 Hz). **HRMS** (ESI): Calcd for $C_{13}H_9BrFN_2^+$ m/z 290.9928 [M+H] +, found 290.9928.



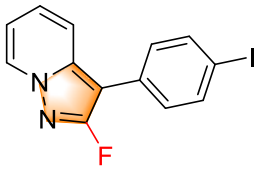
2-fluoro-3-(4-fluorophenyl)pyrazolo[1,5-*a*]pyridine (4j)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 83 mg (72%); mp 87 - 89 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.31 (d, J = 6.8 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.56 (d, J = 5.2 Hz, 1H), 7.54 (d, J = 5.2 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 8.8 Hz, 2H), 6.82 (t, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -115.35 (m), -130.72 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.8 (d, J = 247.3 Hz), 161.5 (d, J = 245.0 Hz), 138.4 (d, J = 1.5 Hz), 129.2 (dd, J = 1.9 Hz, J = 7.8 Hz), 129.0, 126.1 (t, J = 3.7 Hz), 125.3, 116.5 (d, J = 3.6 Hz), 115.9 (d, J = 21.3 Hz), 112.0 (d, J = 2.7 Hz), 93.6 (d, J = 17.7 Hz). **HRMS** (ESI): Calcd for $C_{13}H_9F_2N_2^+$ m/z 231.0728 $[M+H]^+$, found 231.0729.



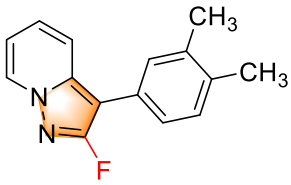
3-(4-chlorophenyl)-2-fluoropyrazolo[1,5-a]pyridine (4k)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 86 mg (70%); mp 133 - 135 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.30 (d, J = 6.8 Hz, 1H), 7.64 (d, J = 9.2 Hz, 1H), 7.52 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.26 - 7.22 (m, 1H), 6.82 (t, J = 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.88 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 247.9 Hz), 138.4 (d, J = 0.9 Hz), 132.2, 129.1, 129.1, 128.6, 128.6, 125.5, 116.5 (d, J = 3.6 Hz), 112.1 (d, J = 2.7 Hz), 93.4 (d, J = 17.5 Hz). **HRMS** (ESI): Calcd for $C_{13}H_9ClFN_2^+$ m/z 247.0433 $[M+H]^+$, found 247.0436.



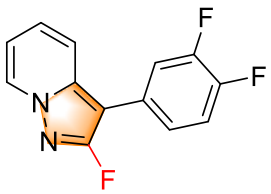
2-fluoro-3-(4-iodophenyl)pyrazolo[1,5-*a*]pyridine (4l)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 84 mg (50%); mp 90 - 92 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.30 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 9.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 6.82 (t, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.54 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 248.1 Hz), 138.3 (d, J = 1.3 Hz), 138.0, 129.7 (d, J = 4.2 Hz), 129.1 (d, J = 2.1 Hz), 125.6, 116.5 (d, J = 3.6 Hz), 112.2 (d, J = 2.7 Hz), 93.5 (d, J = 17.4 Hz), 91.4. **HRMS** (ESI): Calcd for $C_{13}H_9FIN_2^+$ m/z 338.9789 $[M+H]^+$, found 338.9789.



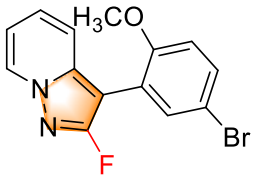
3-(3,4-dimethylphenyl)-2-fluoropyrazolo[1,5-*a*]pyridine (4m)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 96 mg (80%); mp 61 - 62 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.28 (d, J = 7.2 Hz, 1H), 7.67 (d, J = 9.2 Hz, 1H), 7.37 (s, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.25 - 7.17 (m, 2H), 6.78 (t, J = 7.2 Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -130.45 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.9 (d, J = 247.5 Hz), 138.5 (d, J = 1.8 Hz), 137.2, 135.0, 130.2, 128.9, 128.8 (d, J = 2.1 Hz), 127.5 (d, J = 4.0 Hz), 125.0 (d, J = 1.9 Hz), 124.8, 116.9 (d, J = 3.7 Hz), 111.7 (d, J = 2.8 Hz), 94.5 (d, J = 17.7 Hz), 19.9, 19.5. **HRMS** (ESI): Calcd for $C_{15}H_{14}FN_2^+$ m/z 241.1136 $[M+H]^+$, found 241.1136.



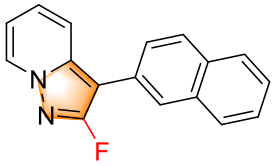
3-(3,4-difluorophenyl)-2-fluoropyrazolo[1,5-*a*]pyridine (4n)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 68 mg (55%); mp 87 - 89 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.32 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.8 Hz, 1H), 7.42 - 7.40 (m, 1H), 7.34 - 7.20 (m, 3H), 6.85 (t, J = 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.99 (s), -137.08 (m), -140.19 (m). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.8 (d, J = 247.6 Hz), 151.4 (d, J = 12.9 Hz), 149.7 (dd, J = 2.5 Hz, J = 12.6 Hz), 148.2 (d, J = 12.7 Hz), 138.4, 129.2, 127.1 (d, J = 6.9 Hz), 125.8, 123.5 - 123.4 (m), 117.8 (d, J = 17.4 Hz), 116.3 (t, J = 7.8 Hz), 112.2 (d, J = 2.8 Hz), 92.7 (d, J = 17.4 Hz). **HRMS** (ESI): Calcd for $C_{13}H_8F_3N_2^+$ m/z 249.0634 $[M+H]^+$, found 249.0625.



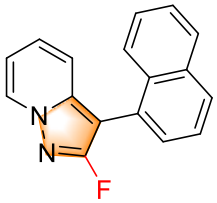
3-(5-bromo-2-methoxyphenyl)-2-fluoropyrazolo[1,5-*a*]pyridine (4o)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 120 mg (75%); mp 81 - 83 °C. **^{1}H NMR** (600 MHz, $CDCl_3$), δ: 8.28 (d, J = 6.6 Hz, 1H), 7.52 (d, J = 3.0 Hz, 1H), 7.42 (dd, J = 2.4, J = 9.0 Hz, 1H), 7.38 (d, J = 9.0 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 6.88 (d, J = 9.0 Hz, 1H), 6.78 (t, J = 7.2 Hz, 1H), 3.82 (s, 3H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.55 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.0 (d, J = 248.1 Hz), 156.0, 139.3 (d, J = 1.8 Hz), 133.4 (d, J = 1.0 Hz), 131.2, 128.7, 124.7, 120.7 (d, J = 3.9 Hz), 117.7 (d, J = 3.6 Hz), 112.9, 112.8, 111.8 (d, J = 2.7 Hz), 89.9 (d, J = 19.2 Hz), 55.7. **HRMS** (ESI): Calcd for $C_{14}H_{10}BrFN_2ONa^+$ m/z 344.9832 $[M+Na]^+$, found 344.9830.



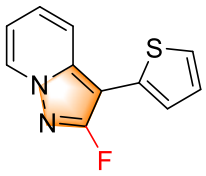
2-fluoro-3-(naphthalen-2-yl)pyrazolo[1,5-*a*]pyridine (4p)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Yellow oil; Yield = 94 mg (72%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ: 8.35 (d, J = 6.8 Hz, 1H), 7.92 - 7.80 (m, 3H), 7.61 - 7.41 (m, 4H), 7.25 (d, J = 8.8 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H), 6.79 (t, J = 6.8 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -128.55 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.3 (d, J = 247.5 Hz), 140.0 (d, J = 2.1 Hz), 134.0, 132.0, 128.8, 128.5, 128.5, 128.3, 126.3, 126.0, 125.7 (d, J = 1.0 Hz), 125.5, 124.9, 122.4, 117.1 (d, J = 3.7 Hz), 111.9 (d, J = 2.8 Hz), 92.9 (d, J = 20.2 Hz). **HRMS** (ESI): Calcd for $C_{17}H_{12}FN_2^+$ m/z 263.0979 $[M+H]^+$, found 263.0980.



2-fluoro-3-(naphthalen-1-yl)pyrazolo[1,5-*a*]pyridine (4q)

Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), White solid; Yield = 84 mg (64%); mp 98 - 100 °C. **^{1}H NMR** (400 MHz, $CDCl_3$), δ: 8.32 (d, J = 7.2 Hz, 1H), 8.02 (s, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 6.0 Hz, 2H), 7.78 (d, J = 8.8 Hz, 1H), 7.73 (d, J = 8.8 Hz, 1H), 7.52 - 7.45 (m, 2H), 7.26 - 7.22 (m, 1H), 6.81 (t, J = 7.2 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -129.76 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 163.2 (d, J = 247.9 Hz), 138.7 (d, J = 1.6 Hz), 133.7, 132.0, 129.1, 128.6, 127.8, 127.7, 127.6 (d, J = 4.0 Hz), 126.4, 125.9 (d, J = 1.9 Hz), 125.8 (d, J = 2.1 Hz), 125.8, 125.3, 116.8 (d, J = 3.6 Hz), 112.0 (d, J = 2.8 Hz), 94.6 (d, J = 17.4 Hz). **HRMS** (ESI): Calcd for $C_{17}H_{12}FN_2^+$ m/z 263.0979 $[M+H]^+$, found 263.0980.

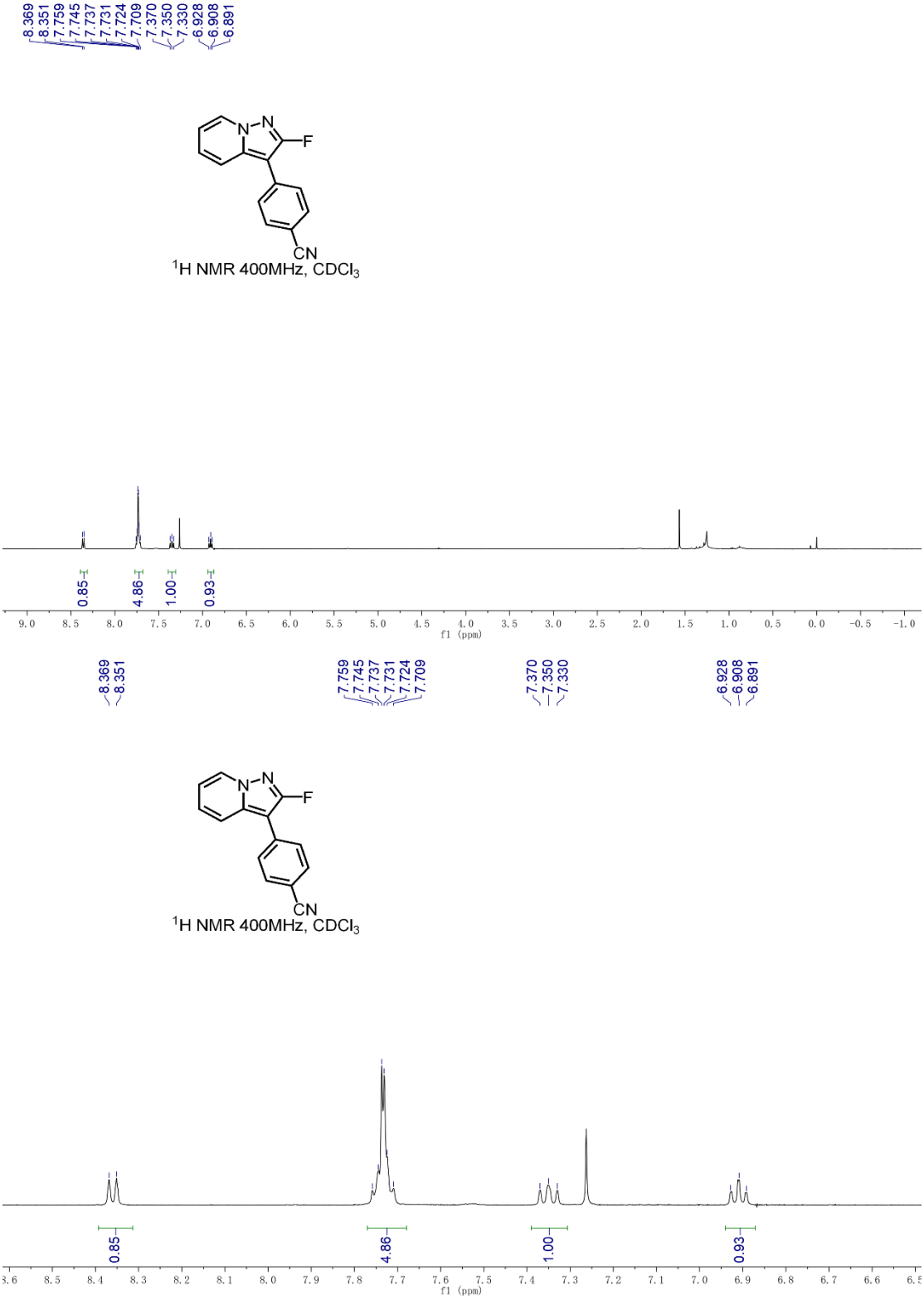


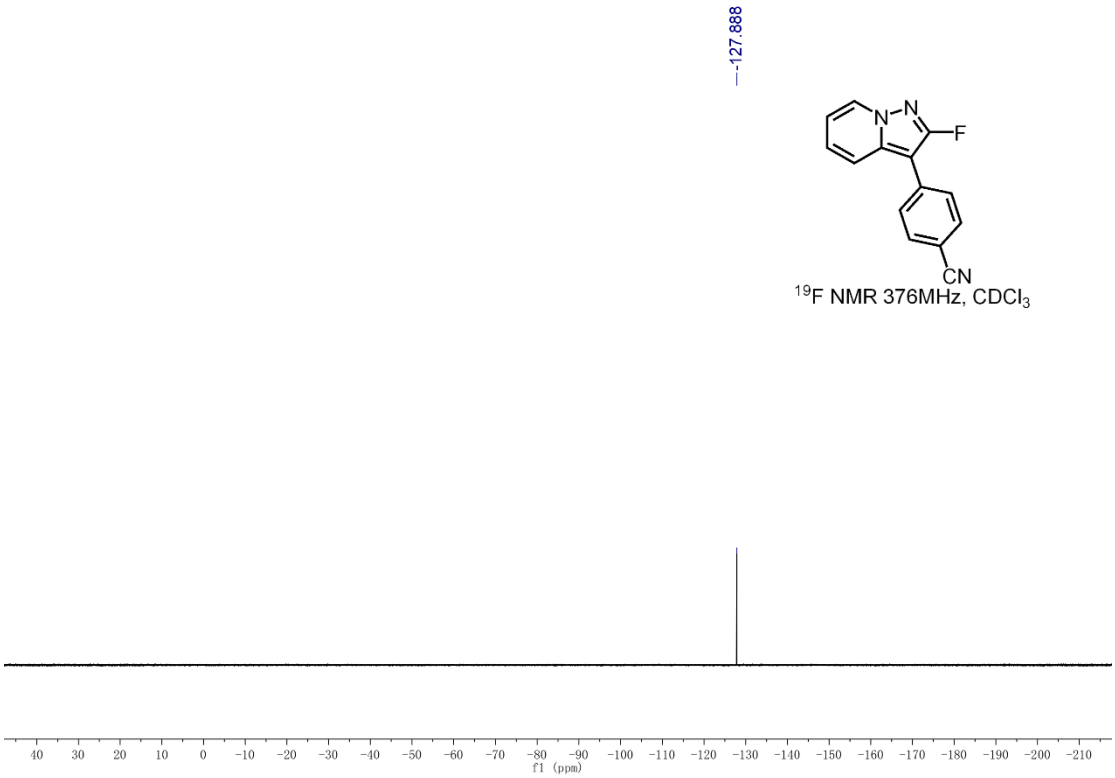
2-fluoro-3-(thiophen-2-yl)pyrazolo[1,5-*a*]pyridine (4r)

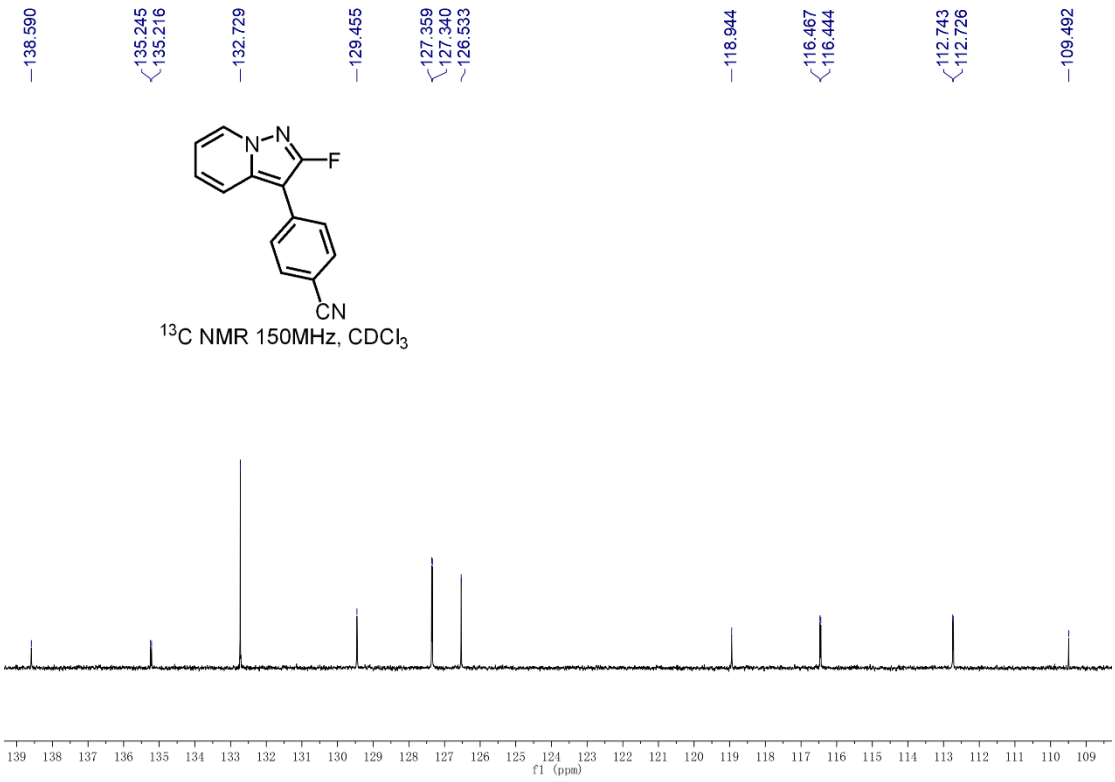
Purification by flash column chromatography on silica gel (EA/petroleum ether = 1:4), Yellow oil; Yield = 57 mg (52%). **^{1}H NMR** (600 MHz, $CDCl_3$), δ: 8.27 (d, J = 7.2 Hz, 1H), 7.77 (d, J = 9.0 Hz, 1H), 7.29 -7.28 (m, 2H), 7.26 (t, J = 8.4 Hz, 1H), 7.13 (t, J = 4.2 Hz, 1H), 6.81 (t, J = 6.6 Hz, 1H). **^{19}F NMR** (376 MHz, $CDCl_3$), δ: -127.40 (s). **^{13}C NMR** (150 MHz, $CDCl_3$), δ: 162.5 (d, J = 248.5 Hz), 137.9 (d, J = 1.3 Hz), 131.1 (d, J = 5.4 Hz), 128.9, 127.5, 125.4, 123.9 (d, J = 3.3 Hz), 123.1 (d, J = 1.5 Hz), 117.1 (d, J = 3.6 Hz), 112.1 (d, J = 2.7 Hz), 89.6 (d, J = 18.6 Hz). **HRMS** (ESI): Calcd for $C_{11}H_8FN_2S^+$ m/z 219.0387 $[M+H]^+$, found 219.0390.

6. NMR and HRMS spectra copies of compounds 3 and 4

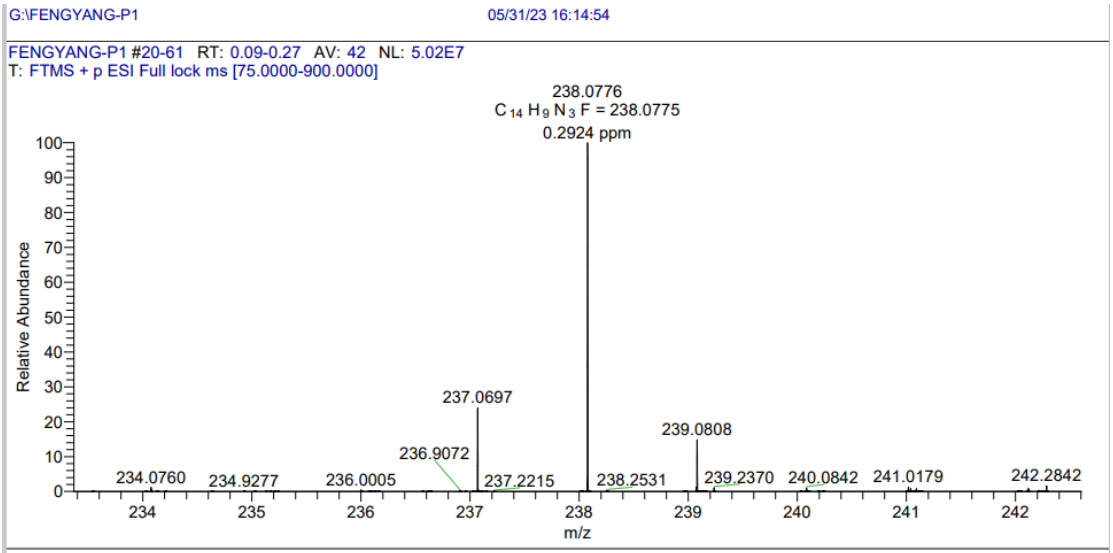
NMR copies of compound **3a**:




-127.888
F
CN
^{19}F NMR 376MHz, CDCl$_3$
f1 (ppm)
164.018
162.357
138.590
135.245
135.216
132.729
129.455
127.359
127.340
126.533
118.944
116.467
116.444
112.743
112.726
109.492
93.099
92.986
F
CN
^{13}C NMR 150MHz, CDCl$_3$
f1 (ppm)

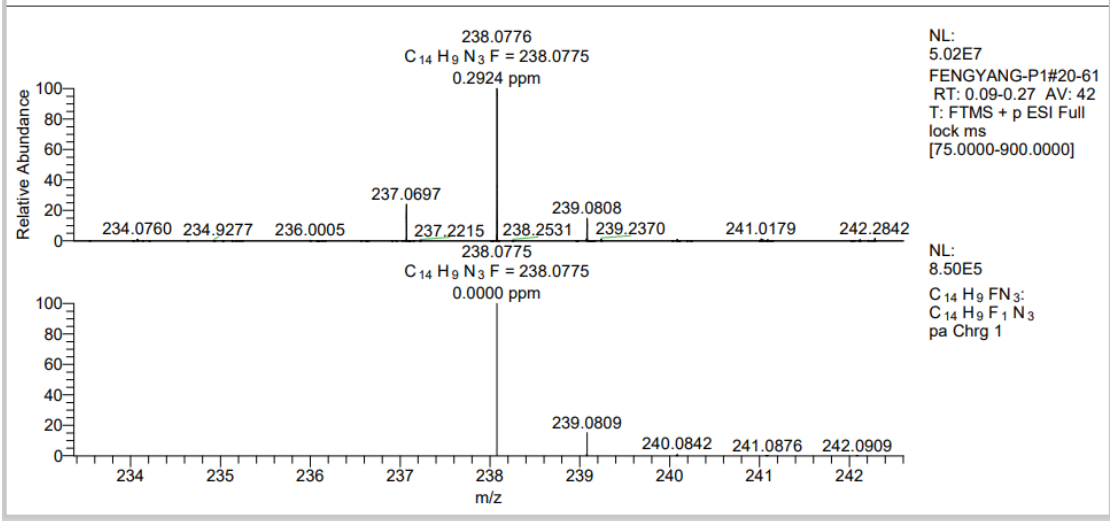

138.590
135.245
135.216
132.729
129.455
127.359
127.340
126.533
118.944
116.467
116.444
112.743
112.726
109.492
N
N
F
CN
13C NMR 150MHz, CDCl3
139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111 110 109
f1 (ppm)

HRMS (ESI) copy of compound **3a**:

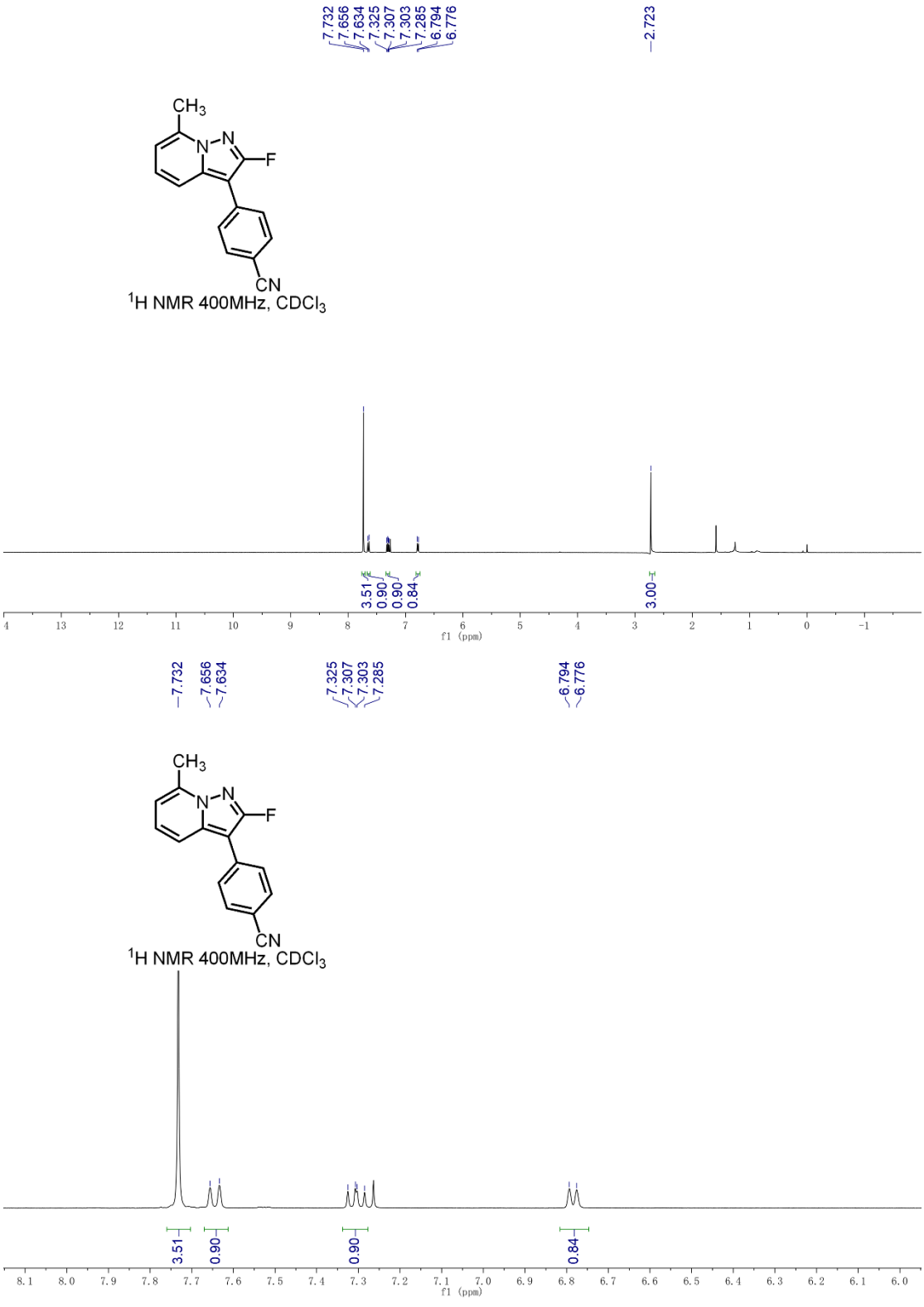


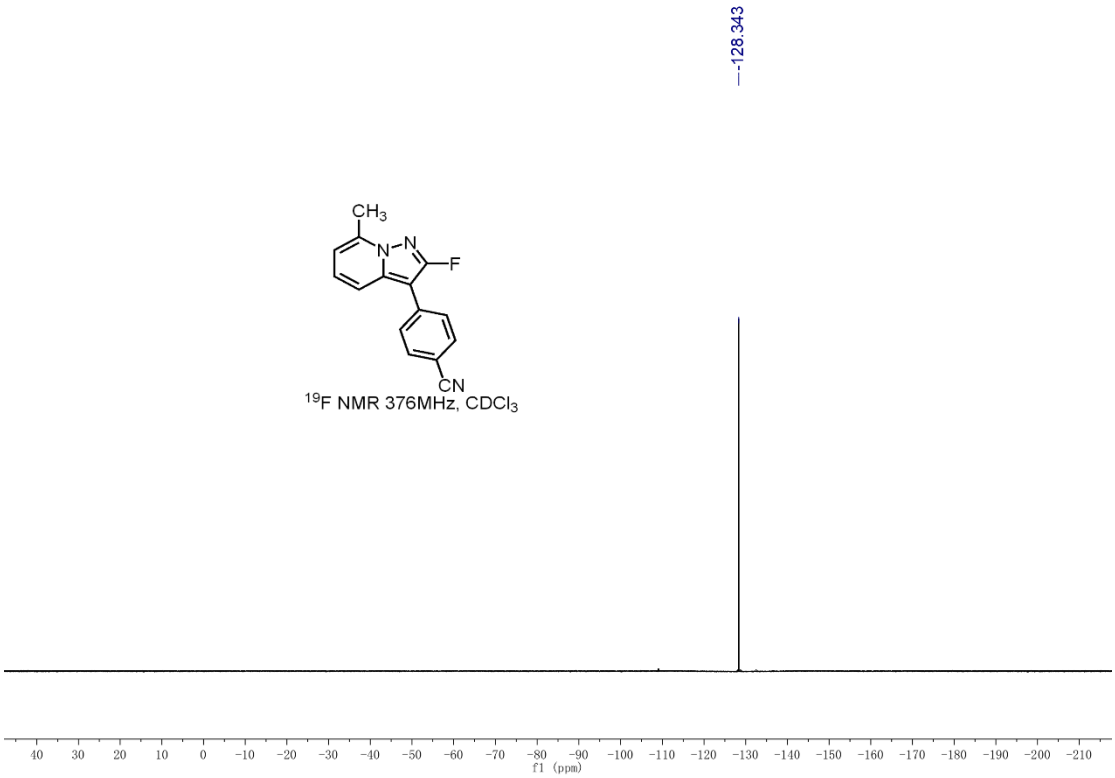
FENGYANG-P1#20-61 RT: 0.09-0.27 AV: 42
T: FTMS + p ESI Full lock ms [75.0000-900.0000]
m/z= 233.3671-242.6008

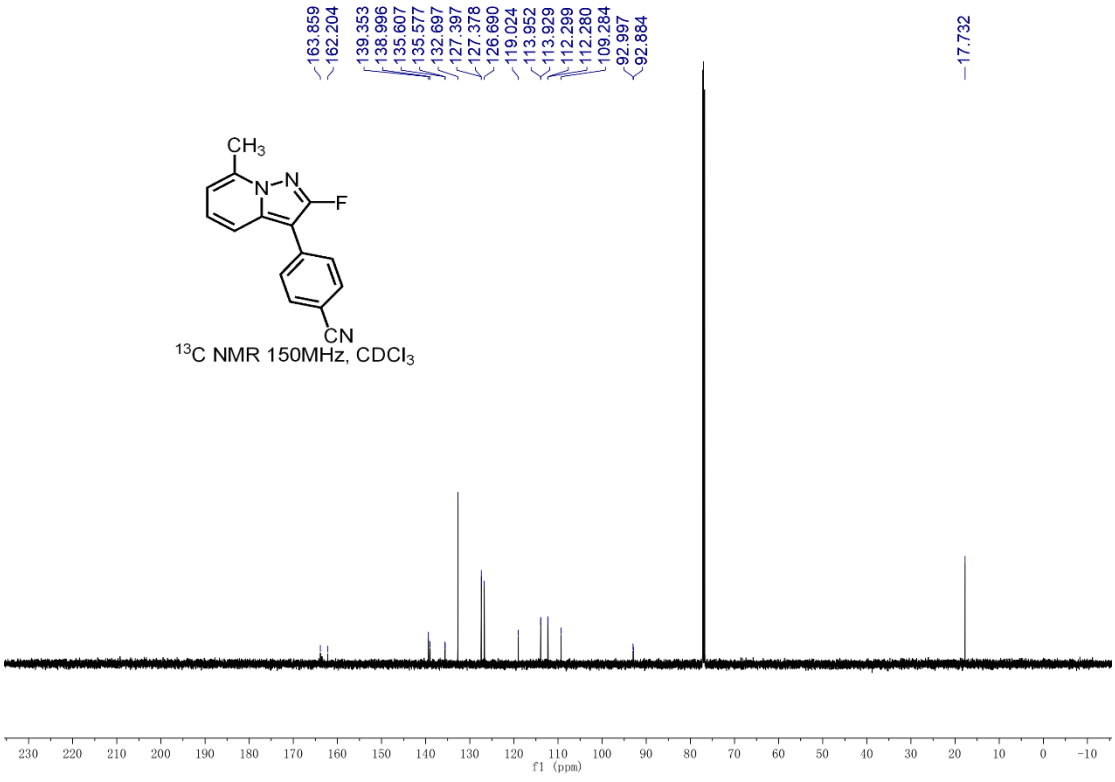
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
237.0697	12341680.0	24.01			
238.0776	51411800.0	100.00	238.0775	0.07	$C_{14}H_9N_3F$
239.0808	7644389.5	14.87			
242.2842	817317.1	1.59			

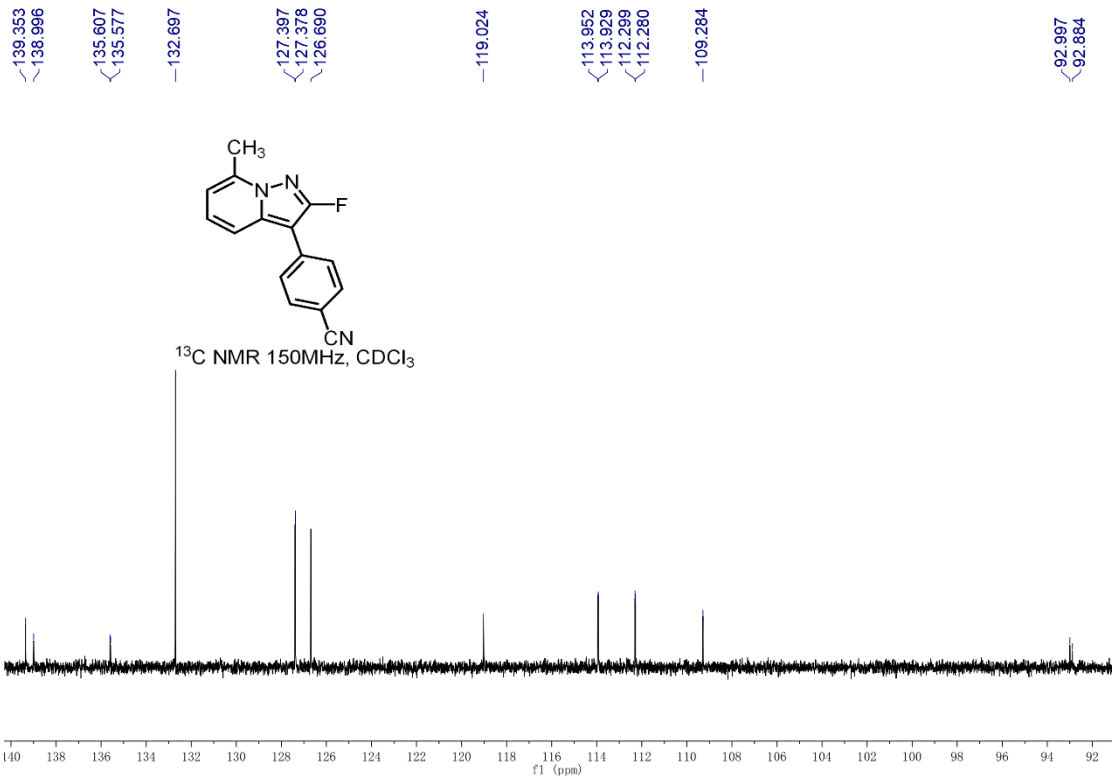


NMR copies of compound **3b:**

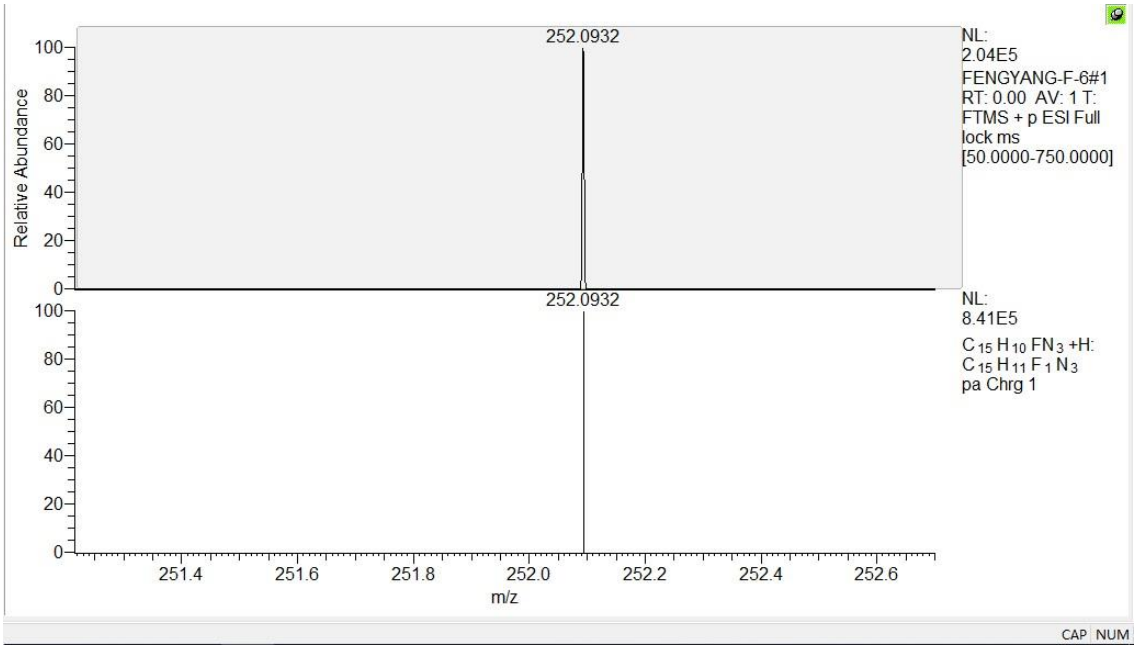



-128.343
CH3
N
N
F
CN
19F NMR 376MHz, CDCl3
f1 (ppm)

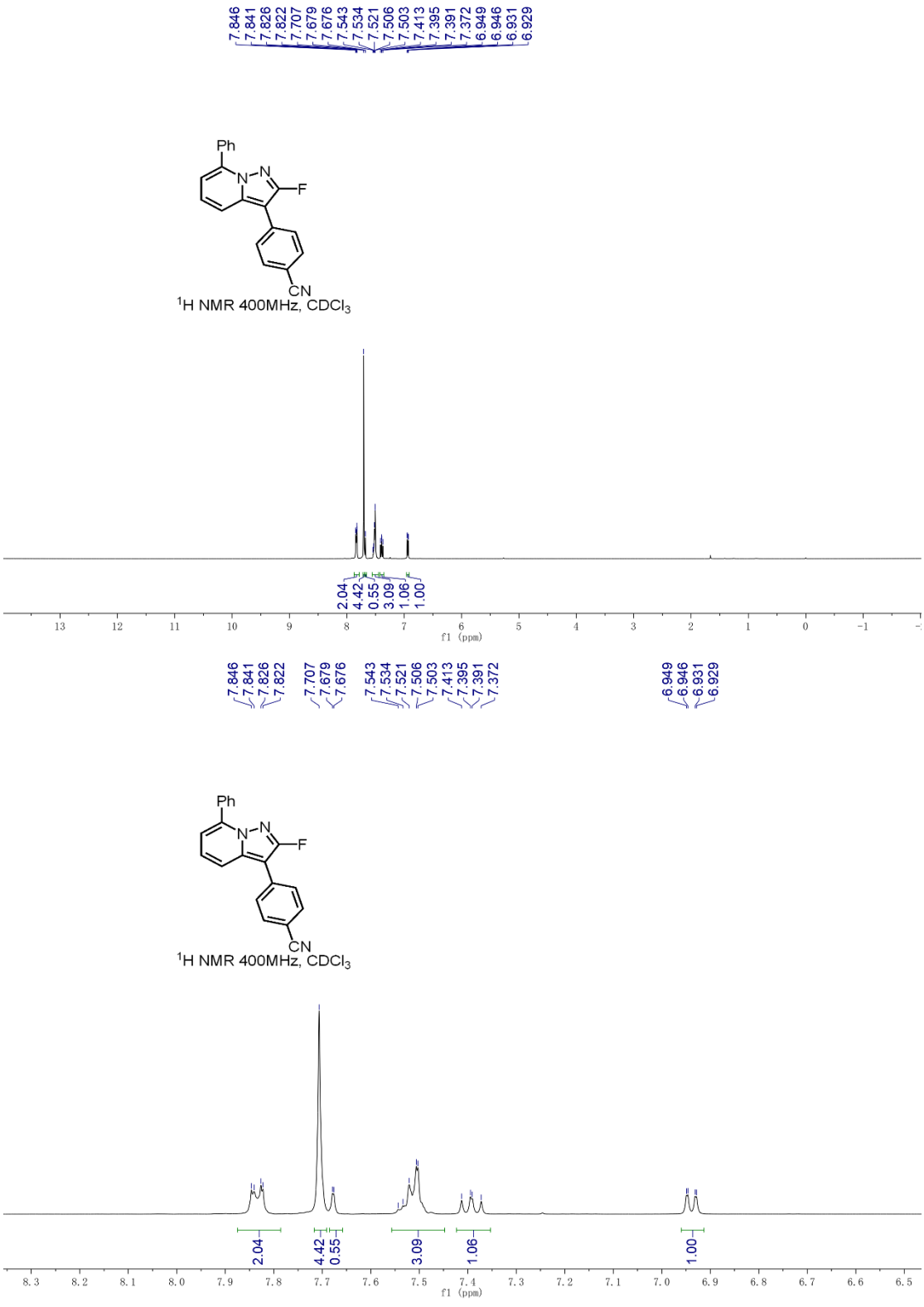

163.859
162.204
139.353
138.996
135.607
135.577
132.697
127.397
127.378
126.690
119.024
113.952
113.929
112.299
112.280
109.284
92.997
92.884
17.732
CH3
N
N
F
CN
13C NMR 150MHz, CDCl3
f1 (ppm)

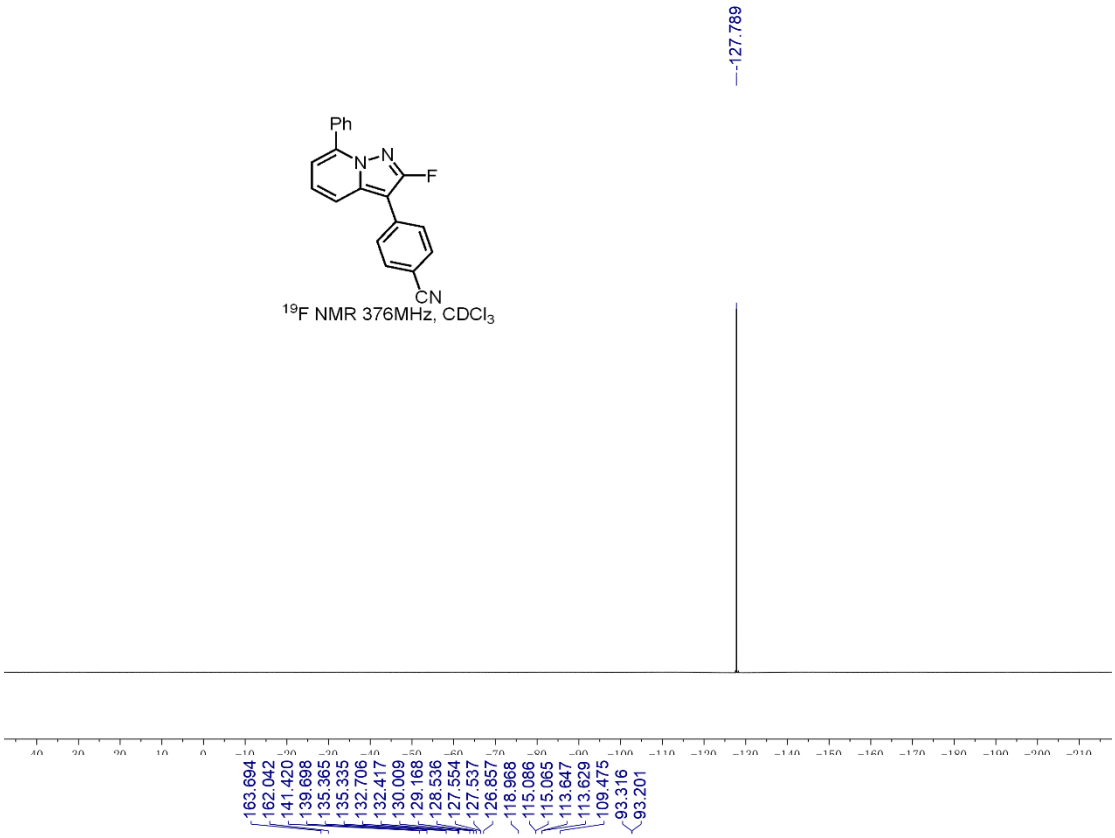


HRMS (ESI) copy of compound **3b**:

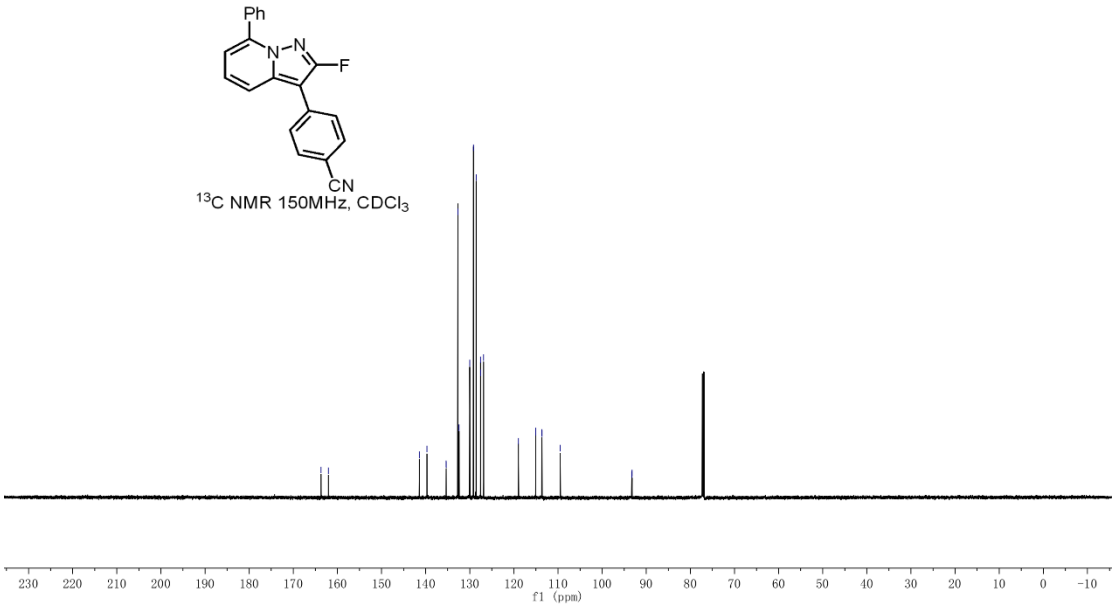


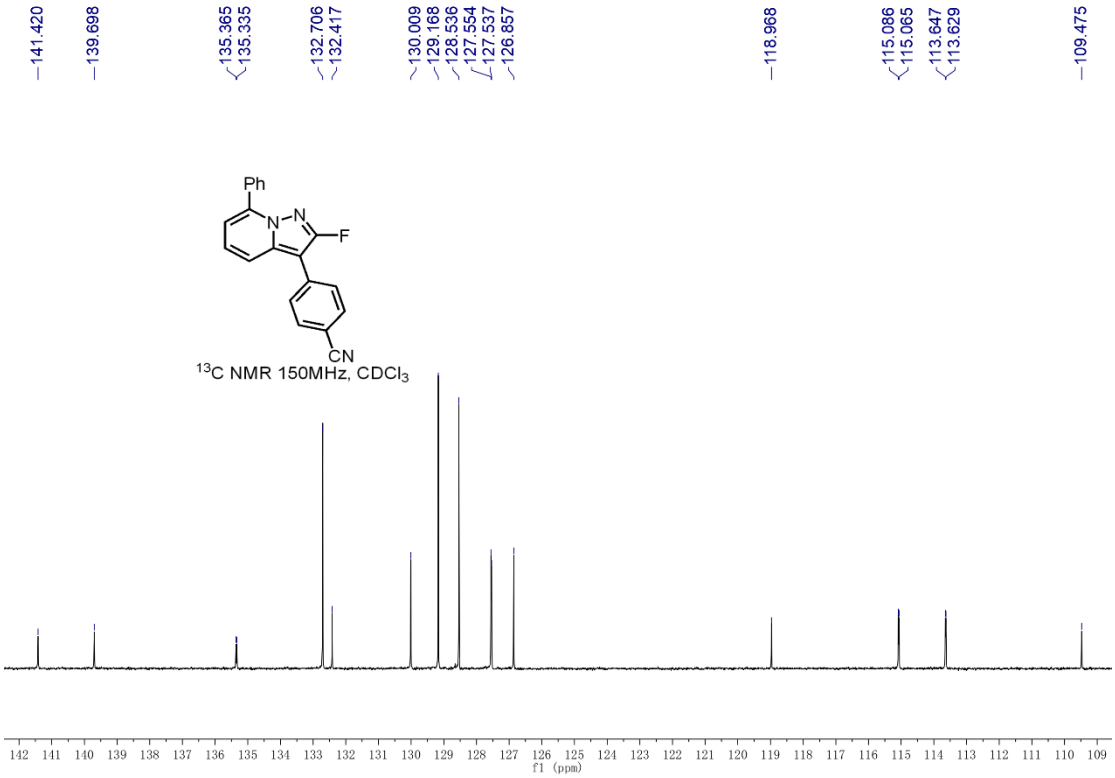
NMR copies of compound **3c**:



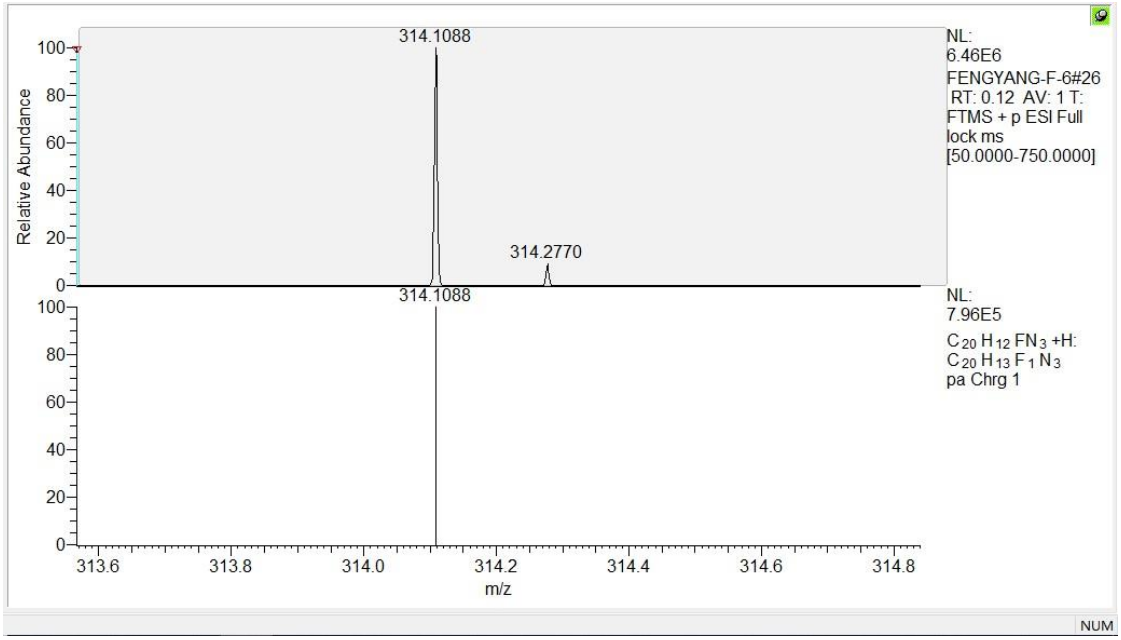

Ph
N
N
F
CN
^{19}F NMR 376MHz, CDCl$_3$
-127.789

163.694
162.042
141.420
139.698
135.365
135.335
132.706
132.417
130.009
129.168
128.536
127.554
127.537
126.857
118.968
115.086
115.065
113.647
113.629
109.475
93.316
93.201

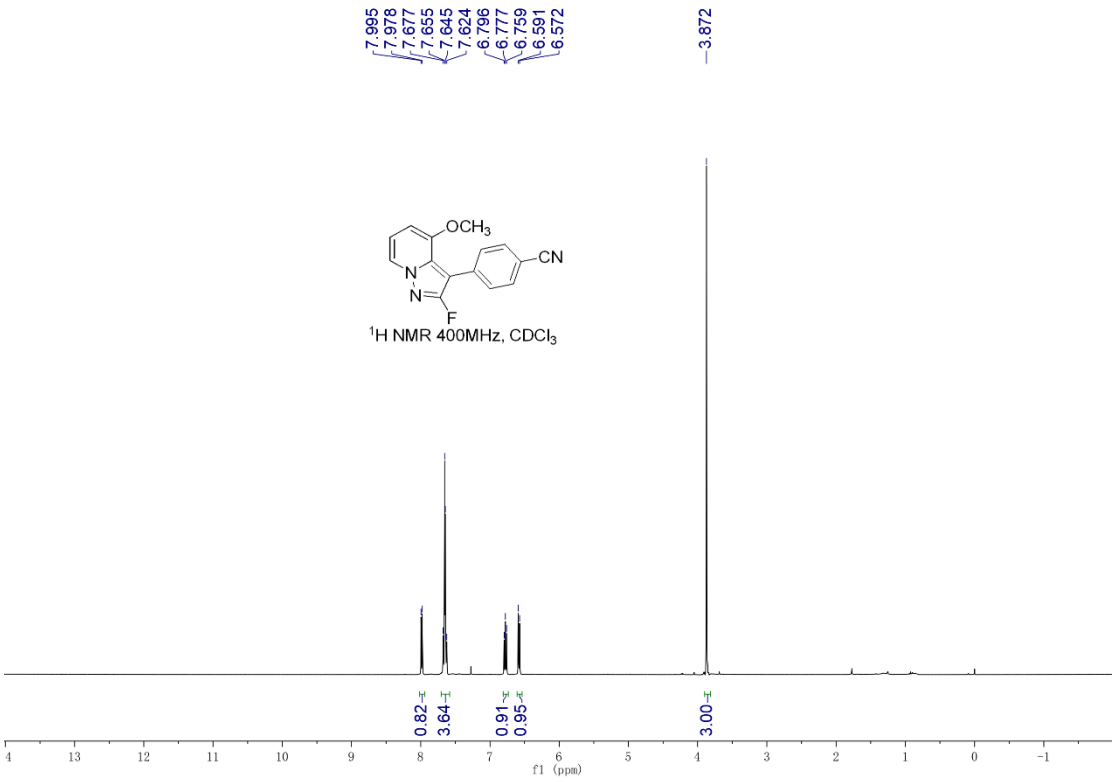

Ph
N
N
F
CN
^{13}C NMR 150MHz, CDCl$_3$
f1 (ppm)

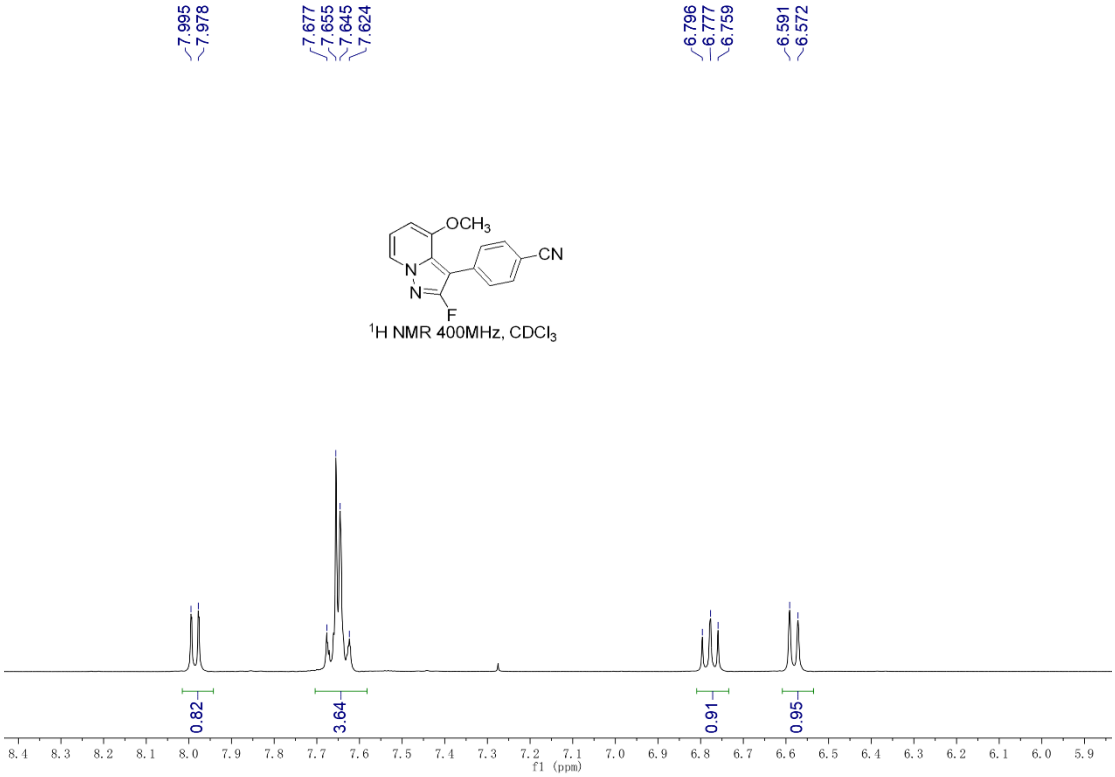


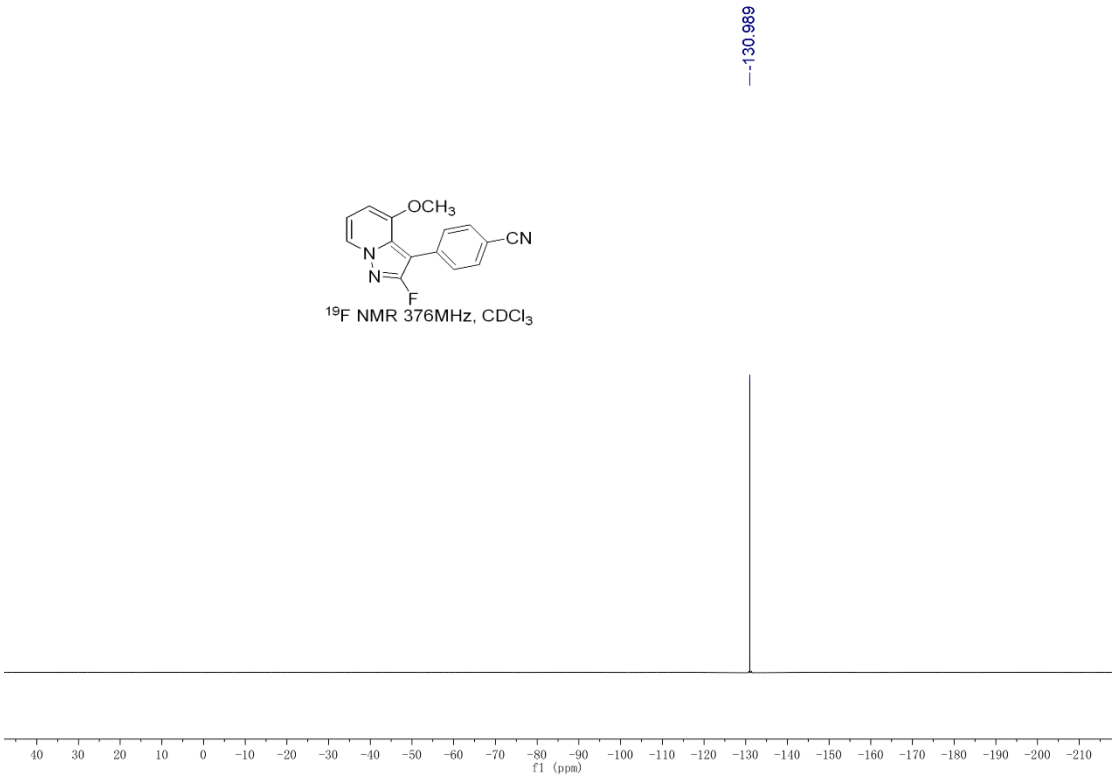
HRMS (ESI) copy of compound **3c**:

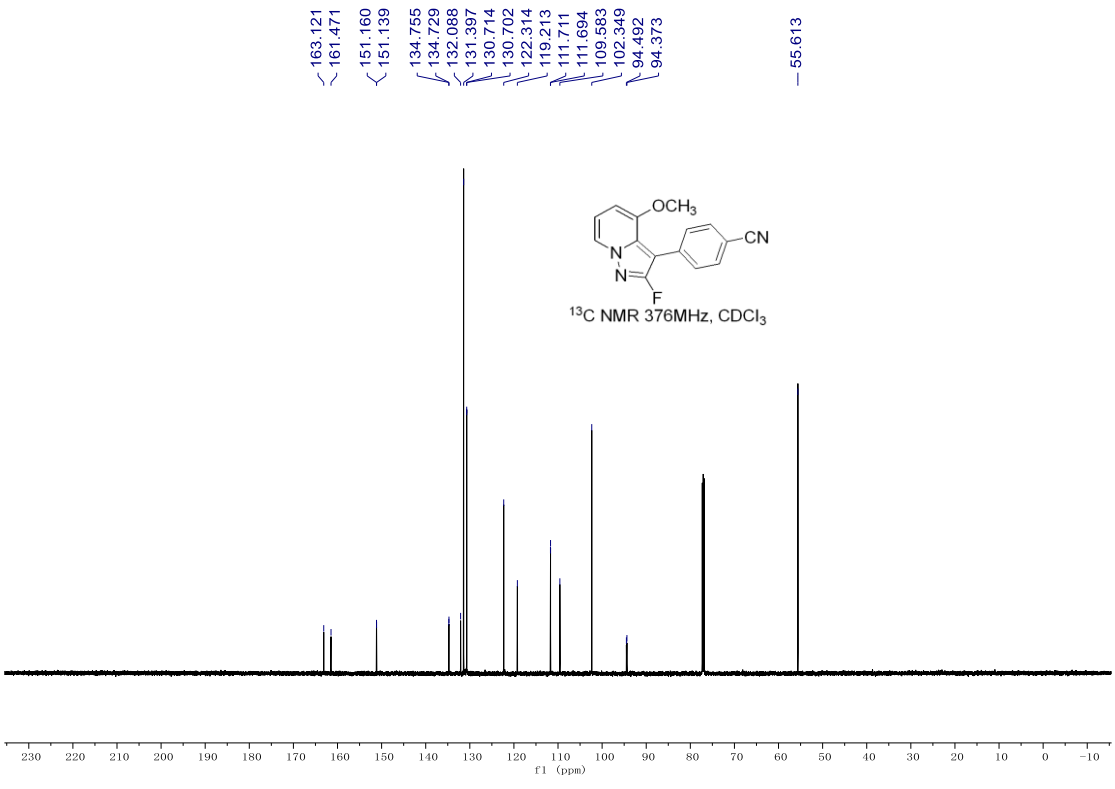


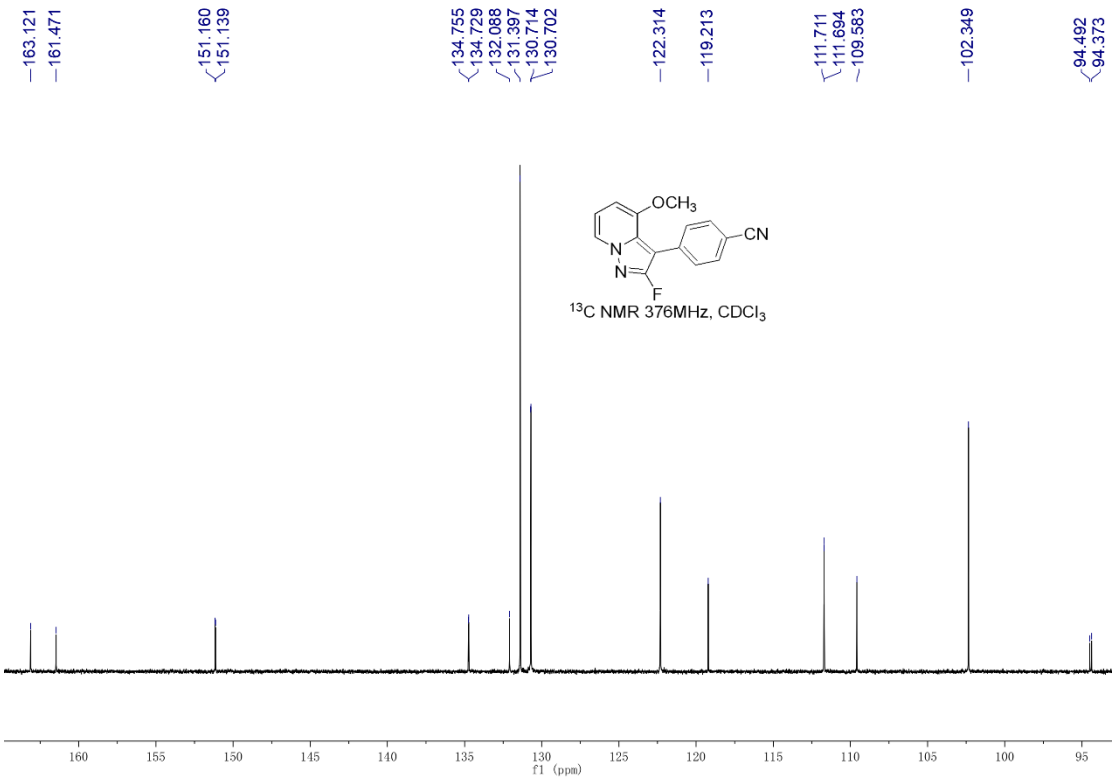
NMR copies of compound **3d:**



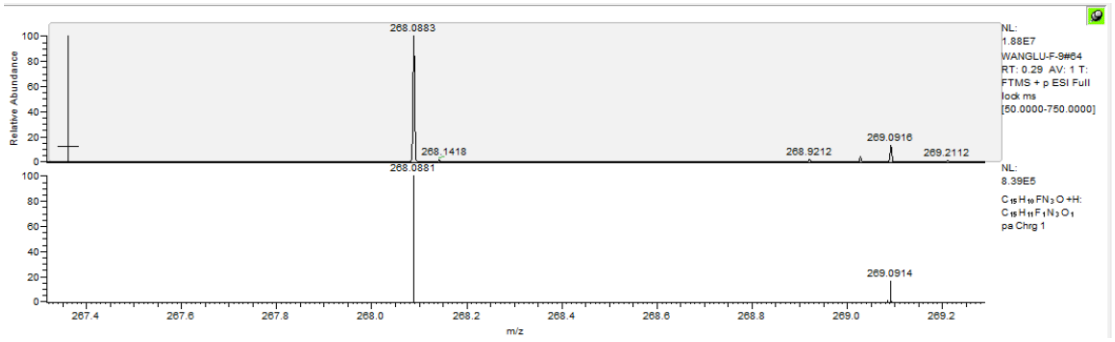



-130.989
OCH3
CN
N
N
F
19F NMR 376MHz, CDCl3
f1 (ppm)

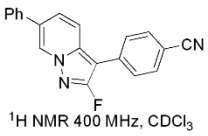

163.121
161.471
151.160
151.139
134.755
134.729
132.088
131.397
130.714
130.702
122.314
119.213
111.711
111.694
109.583
102.349
94.492
94.373
55.613
OCH3
CN
N
N
F
13C NMR 376MHz, CDCl3
f1 (ppm)



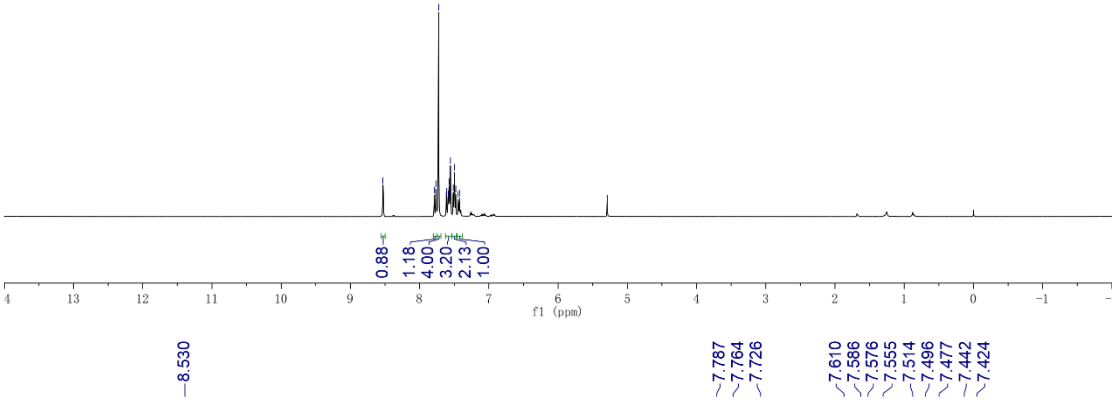
HRMS (ESI) copy of compound **3d**:

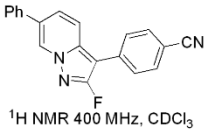


NMR copies of compound **3e:**

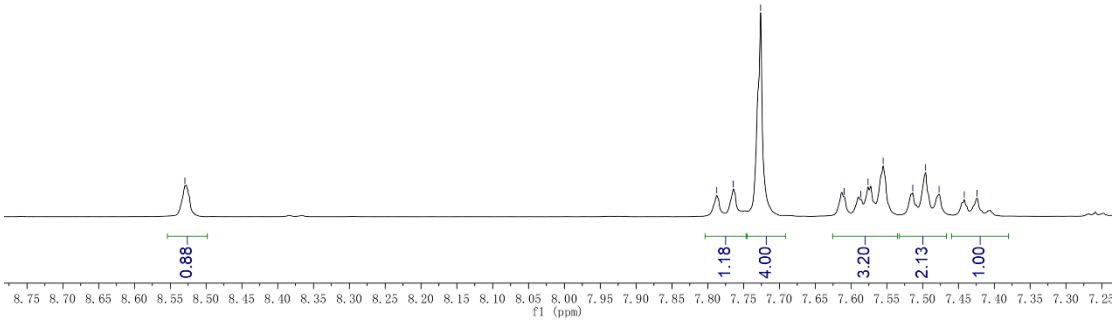


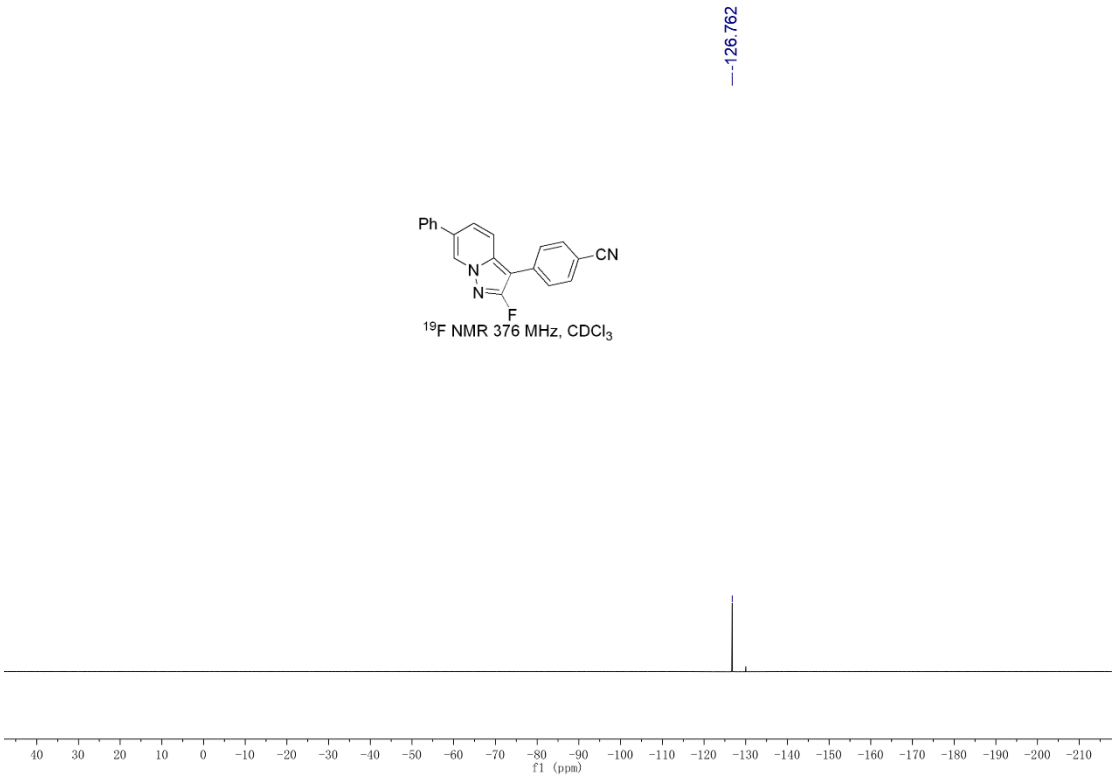
^{1}H NMR 400 MHz, $CDCl_3$



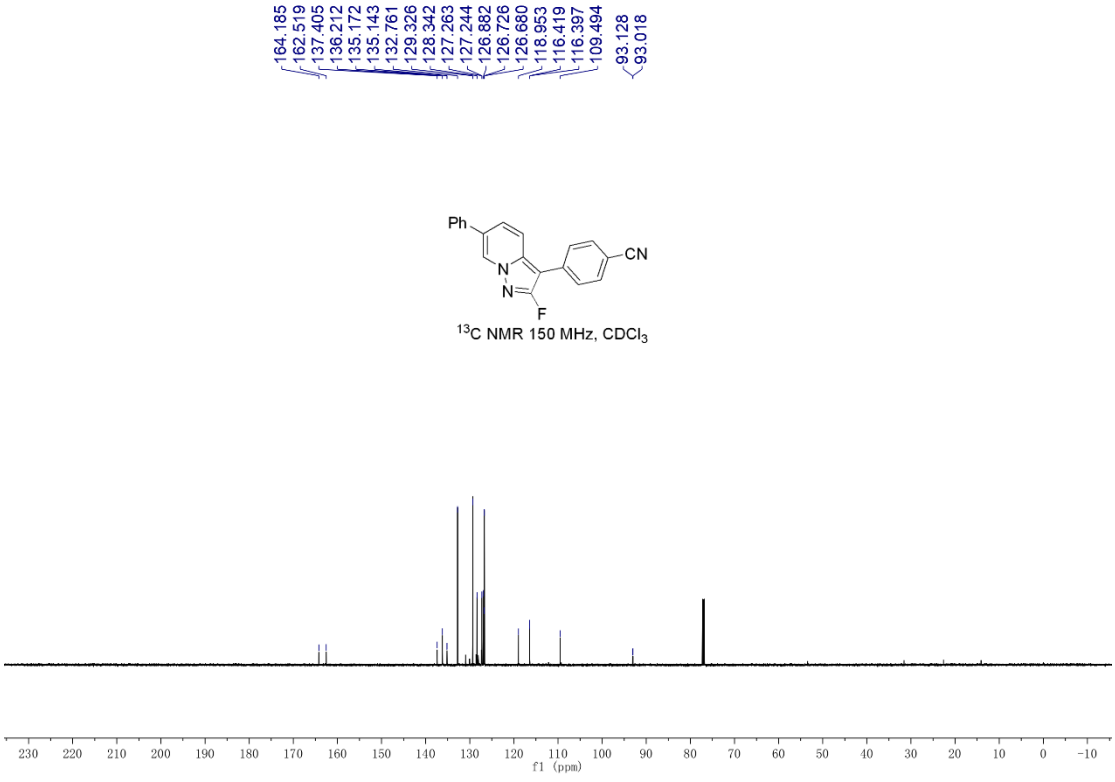


^{1}H NMR 400 MHz, $CDCl_3$

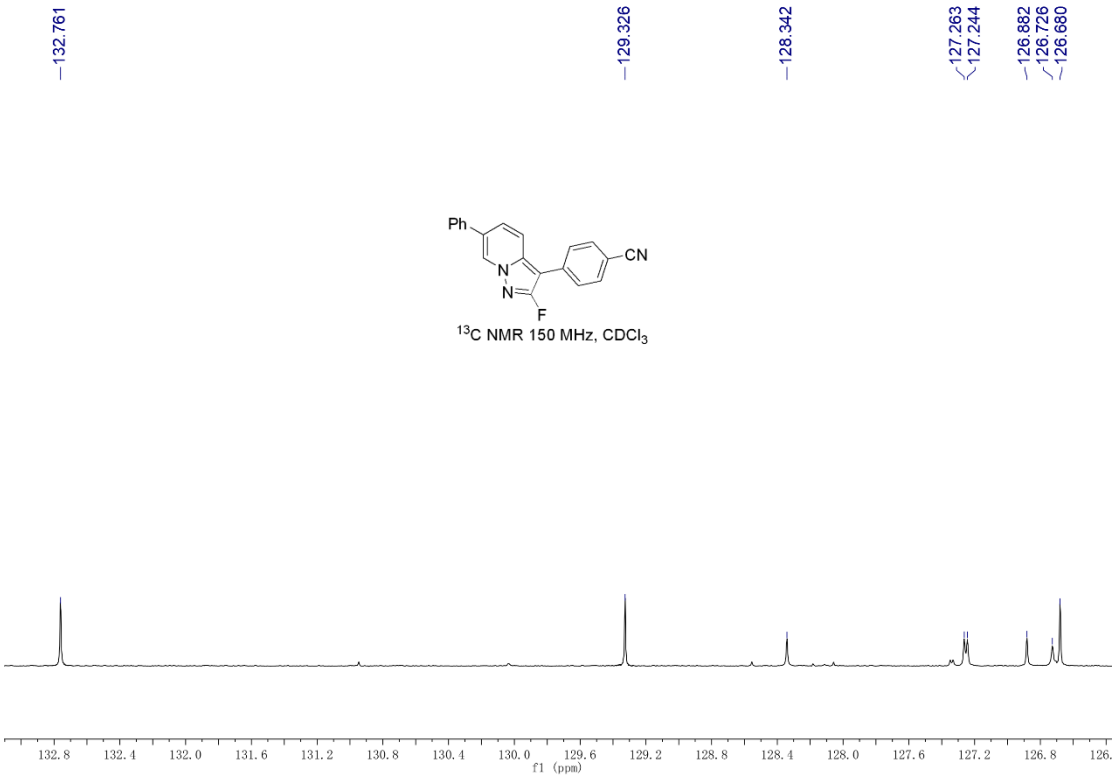




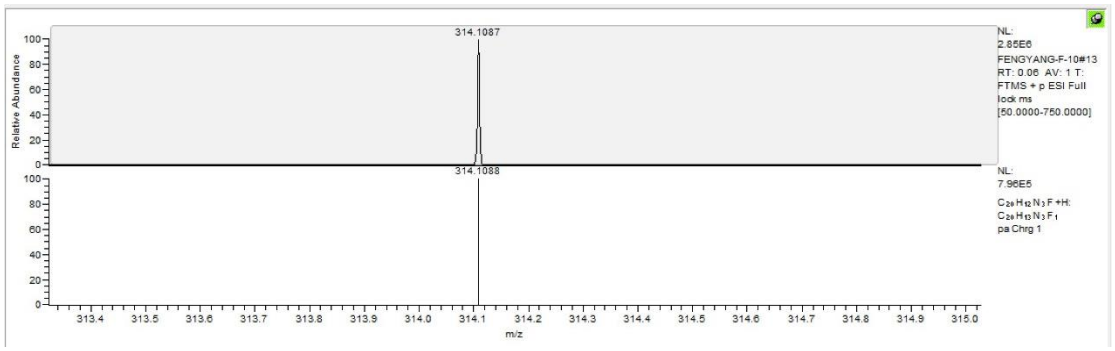
^{19}F NMR 376 MHz, $CDCl_3$



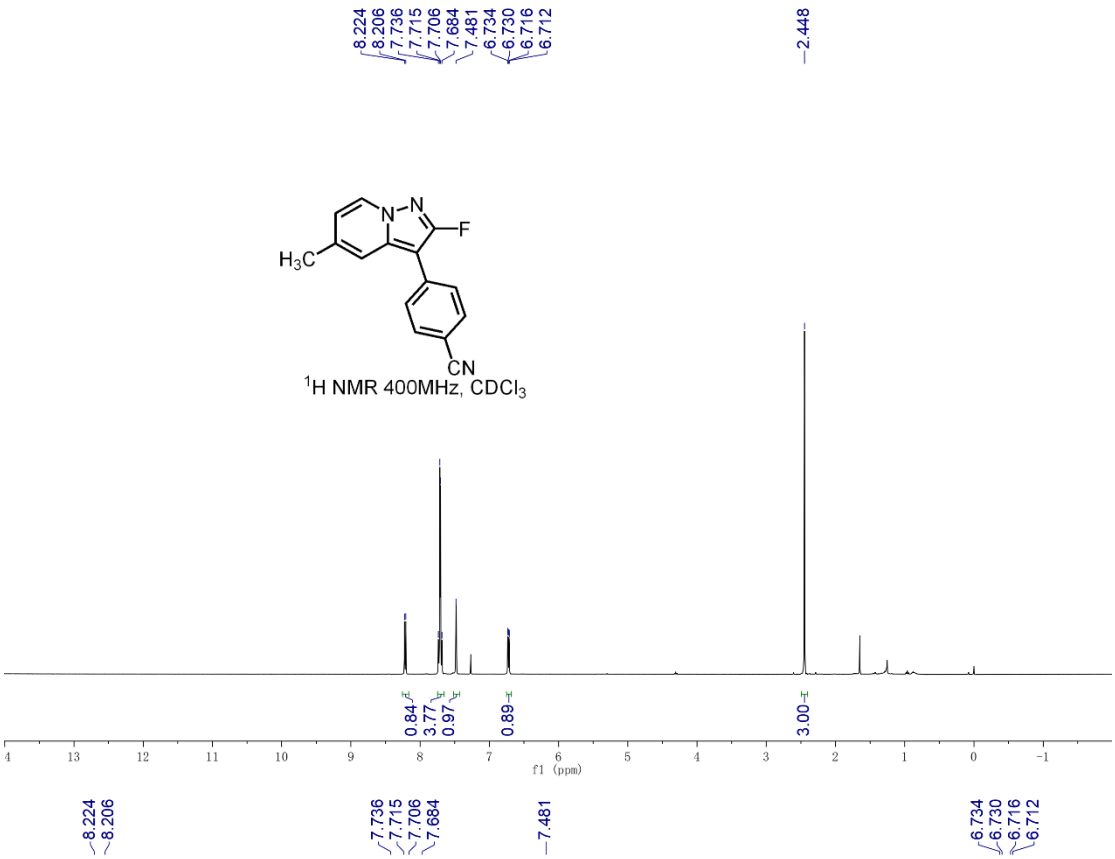
^{13}C NMR 150 MHz, $CDCl_3$

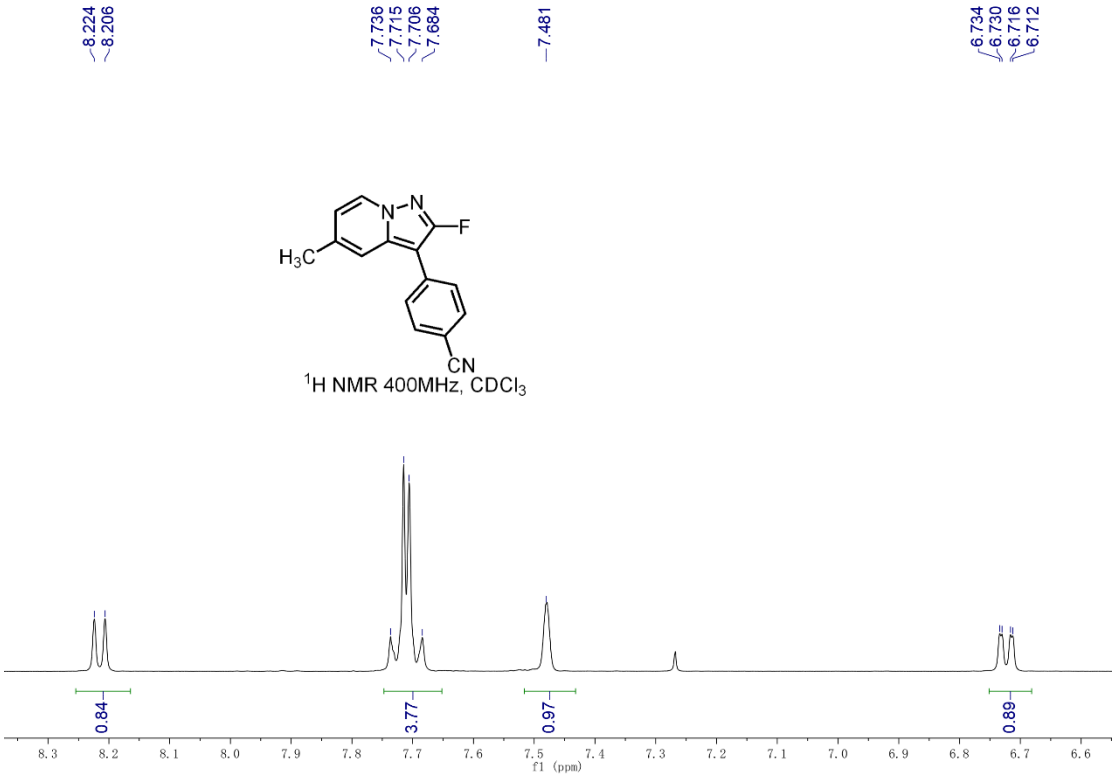


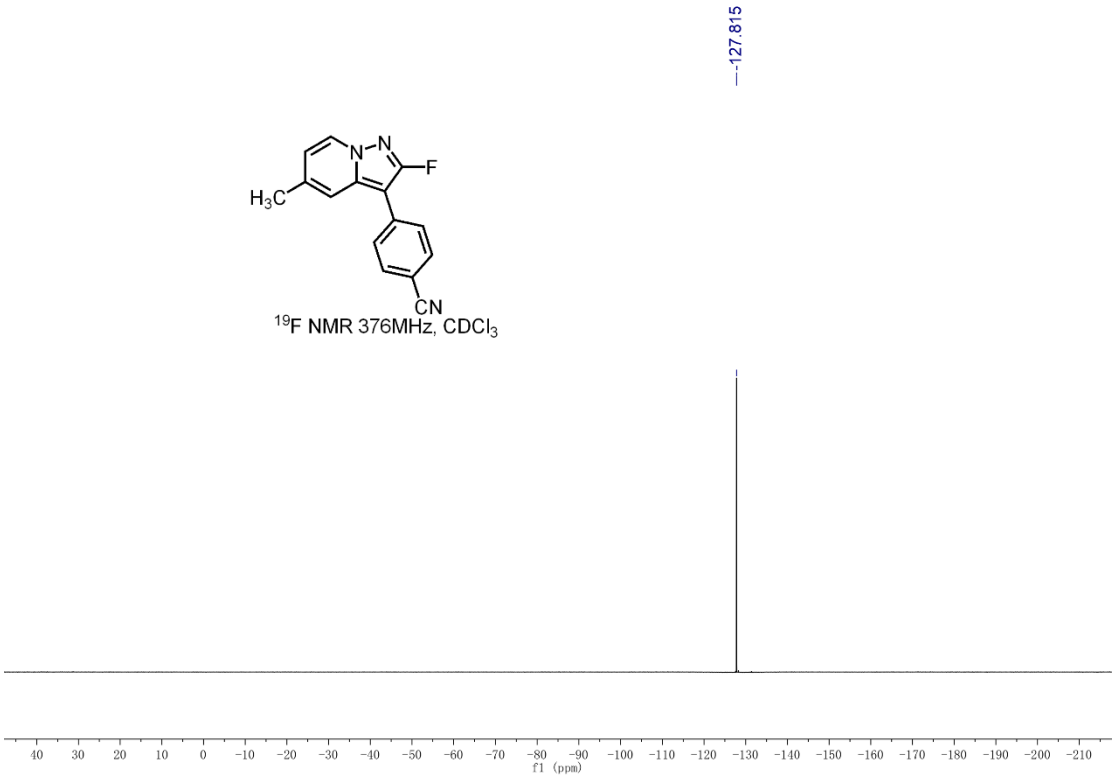
HRMS (ESI) copy of compound **3e**:

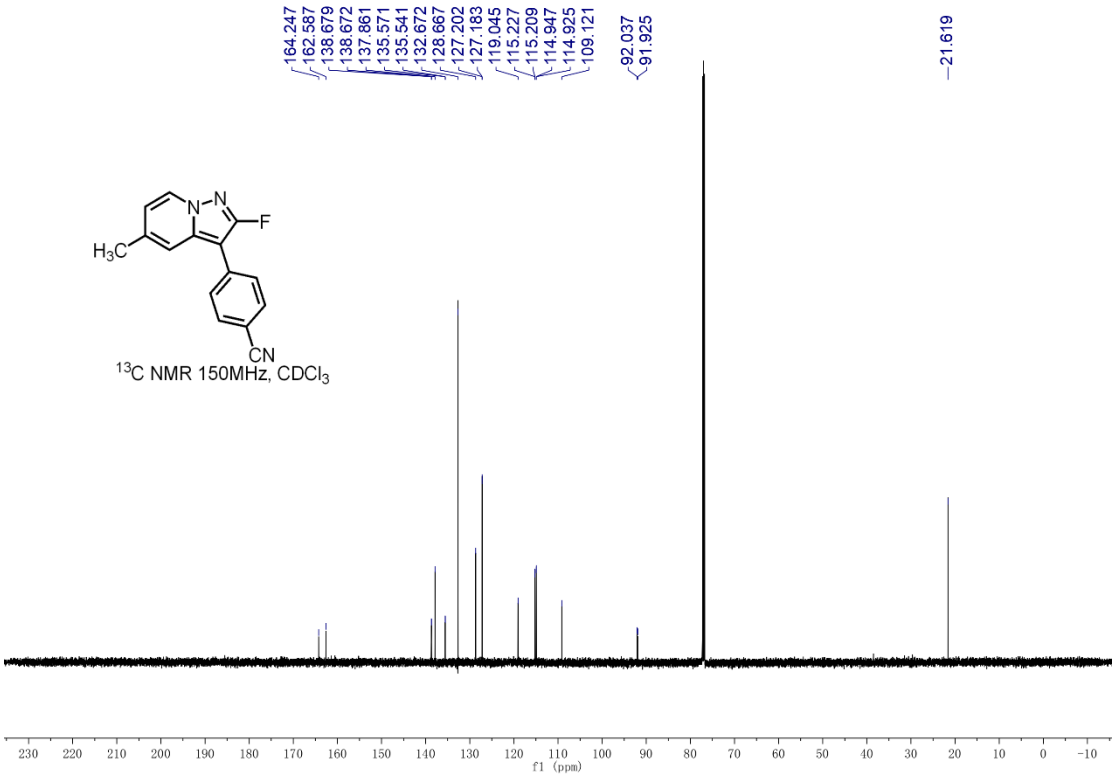


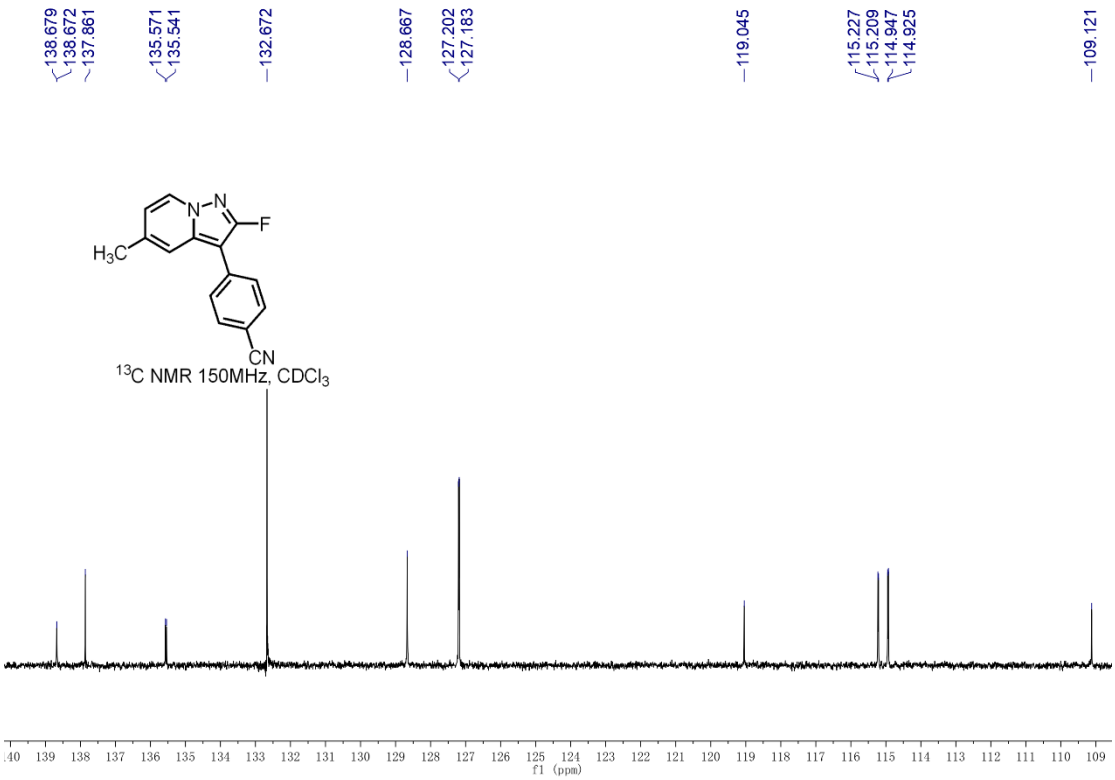
NMR copies of compound **3f:**



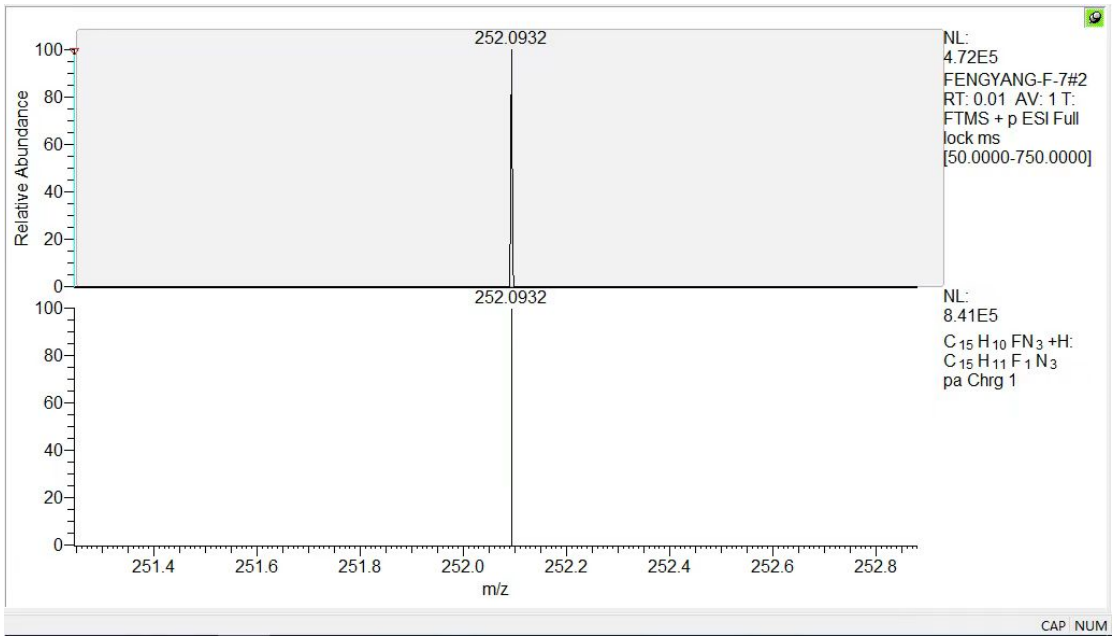



-127.815
F
H_3C
CN
^{19}F NMR 376MHz, $CDCl_3$
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

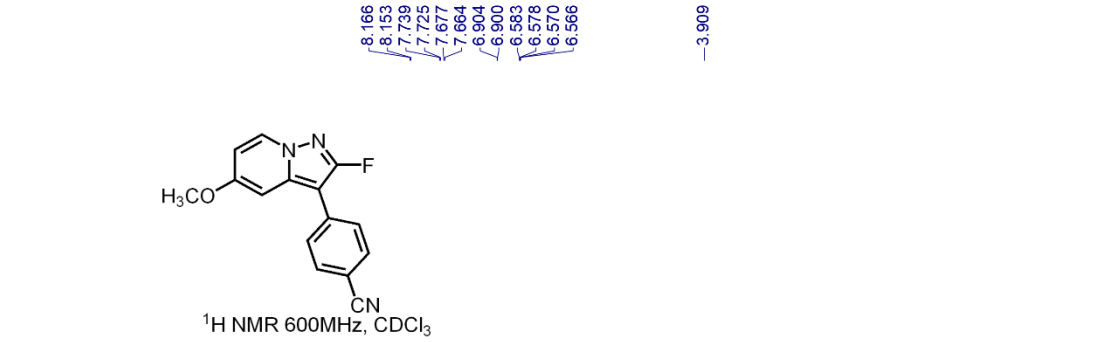

164.247
162.587
138.679
138.672
137.861
135.571
135.541
132.672
128.667
127.202
127.183
119.045
115.227
115.209
114.947
114.925
109.121
92.037
91.925
-21.619
F
H_3C
CN
^{13}C NMR 150MHz, $CDCl_3$
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



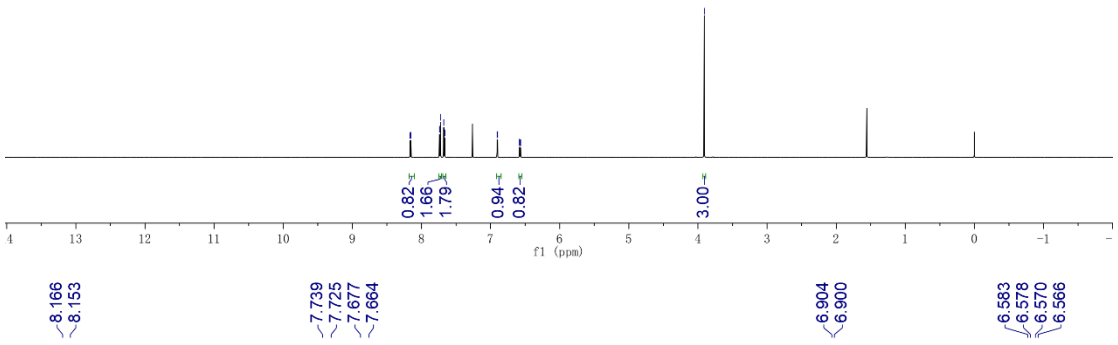
HRMS (ESI) copy of compound **3f**:

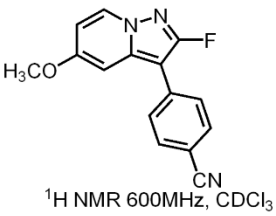


NMR copies of compound **3g:**

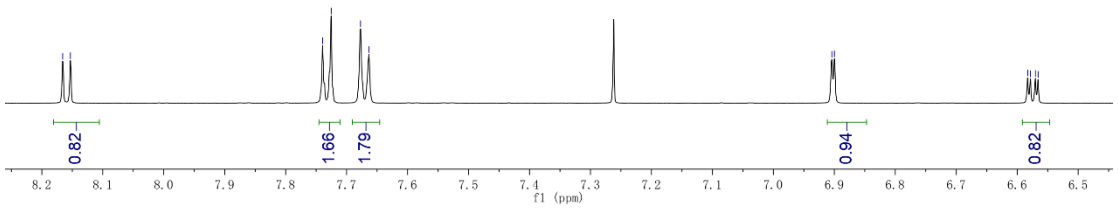


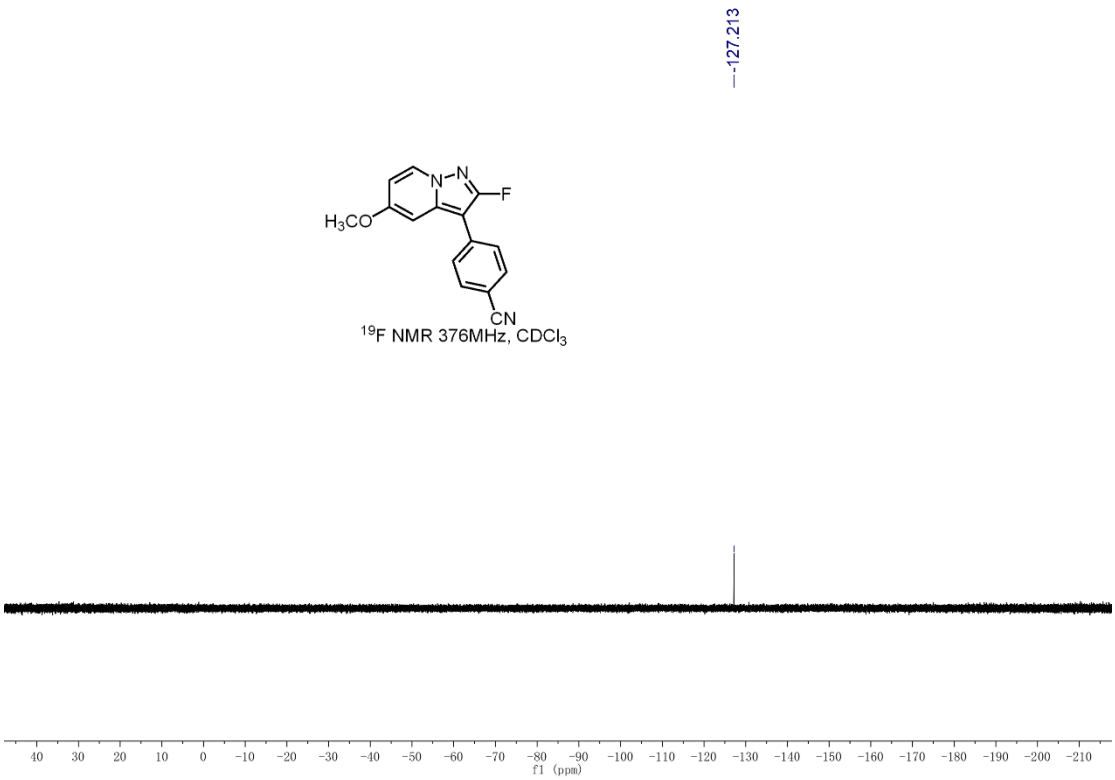
^{1}H NMR 600MHz, $CDCl_3$

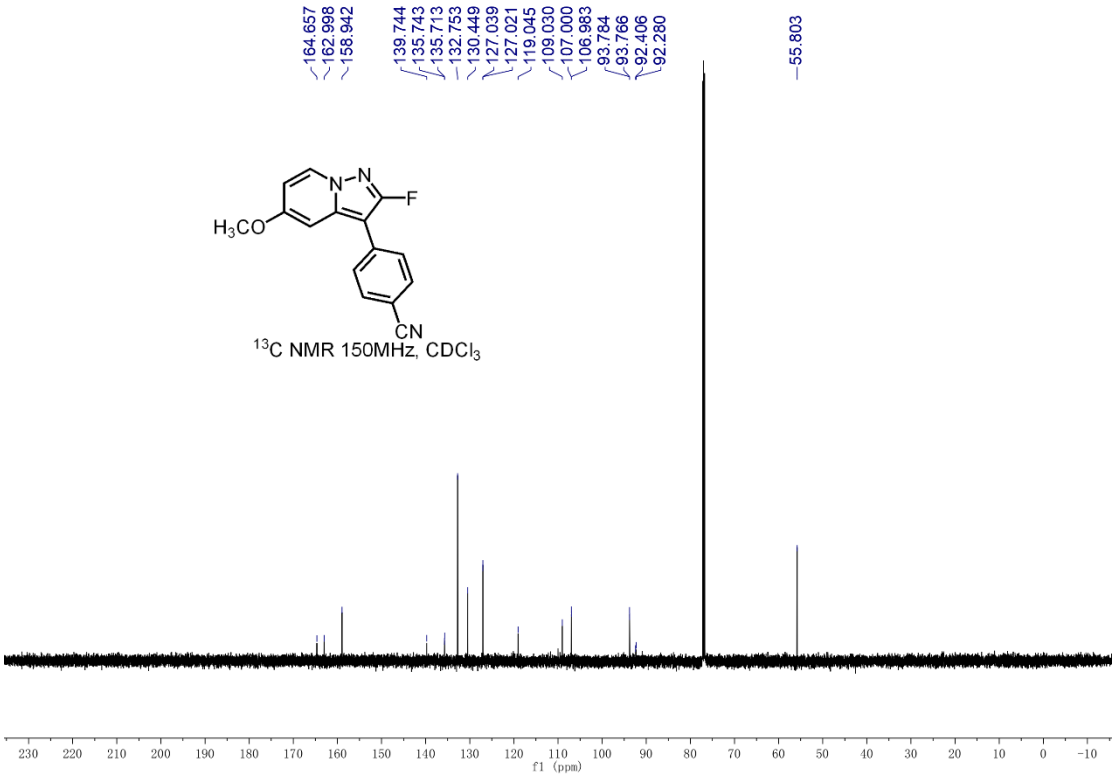


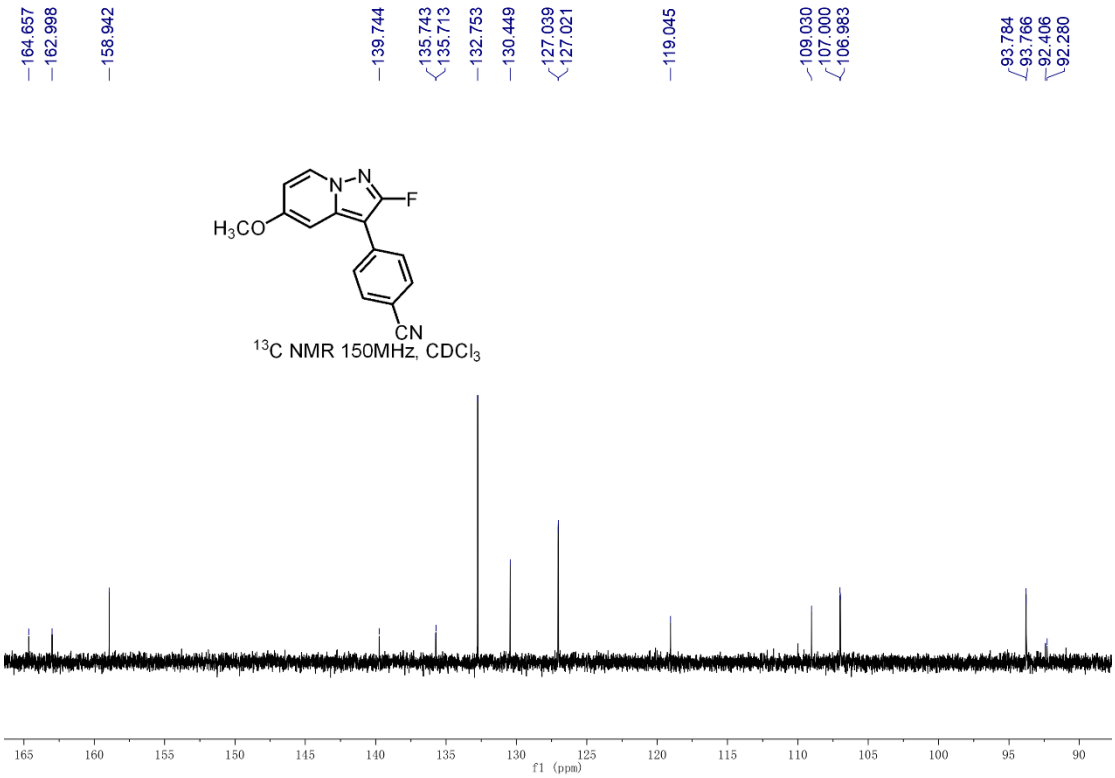


^{1}H NMR 600MHz, $CDCl_3$

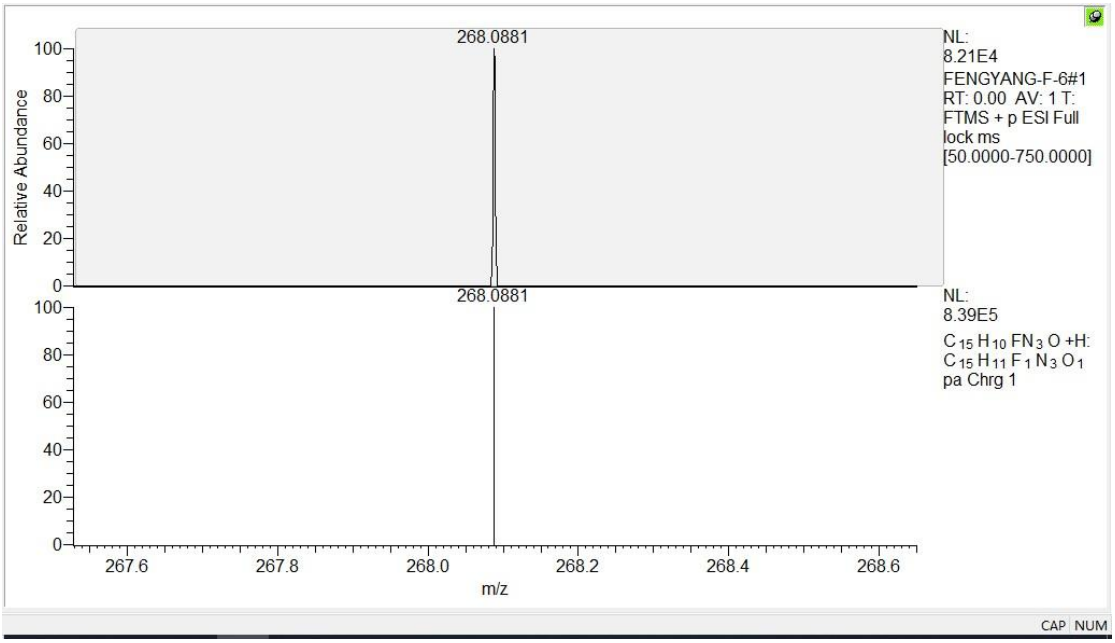



-127.213
H3CO
F
CN
19F NMR 376MHz, CDCl3
f1 (ppm)

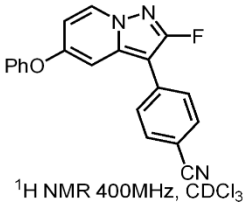

164.657
162.998
158.942
139.744
135.743
135.713
132.753
130.449
127.039
127.021
119.045
109.030
107.000
106.983
93.784
93.766
92.406
92.280
55.803
H3CO
F
CN
13C NMR 150MHz, CDCl3
f1 (ppm)

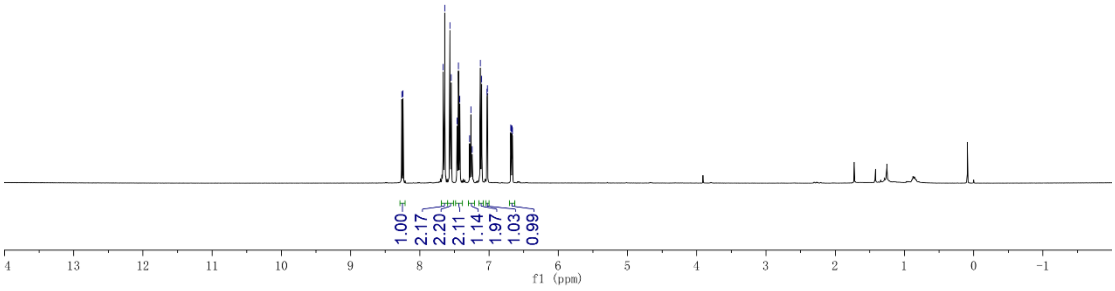


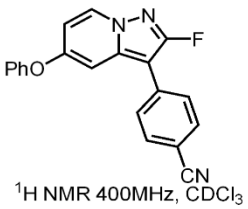
HRMS (ESI) copy of compound **3g**:

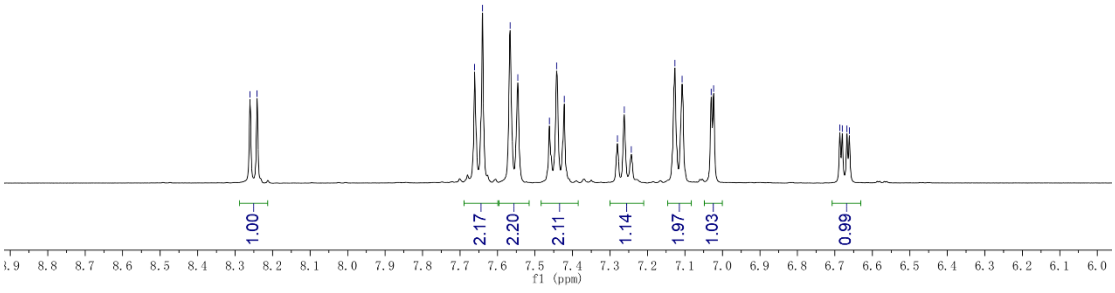


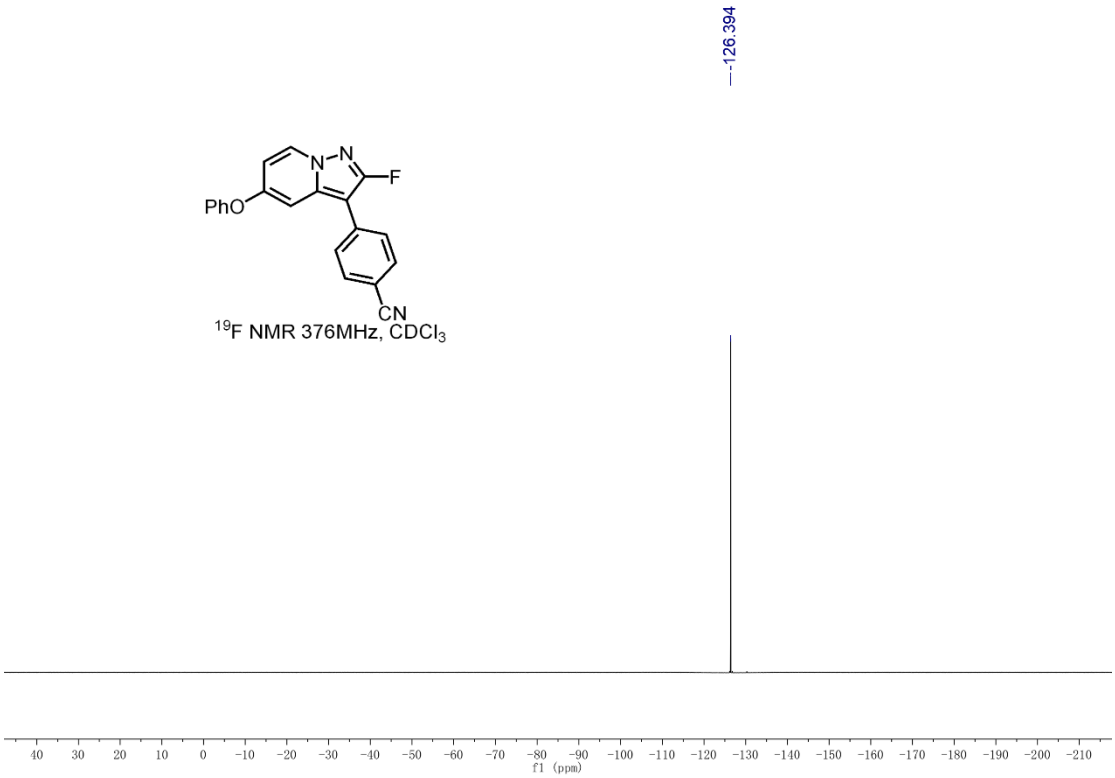
NMR copies of compound **3h:**



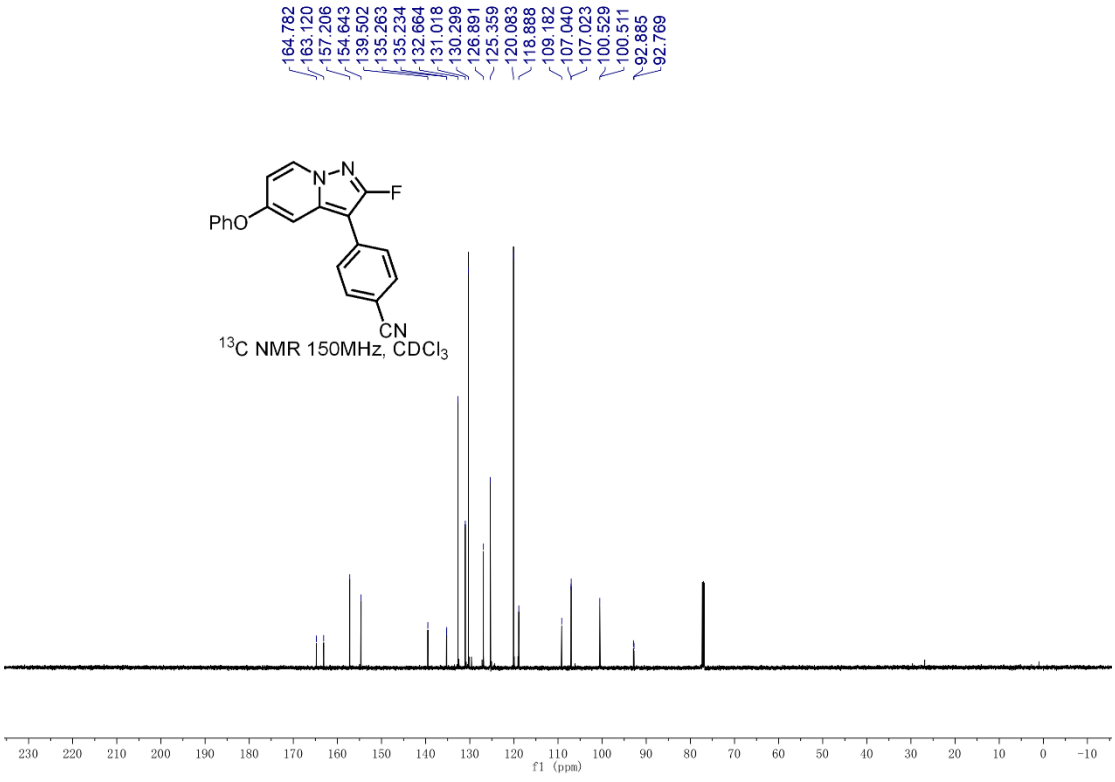




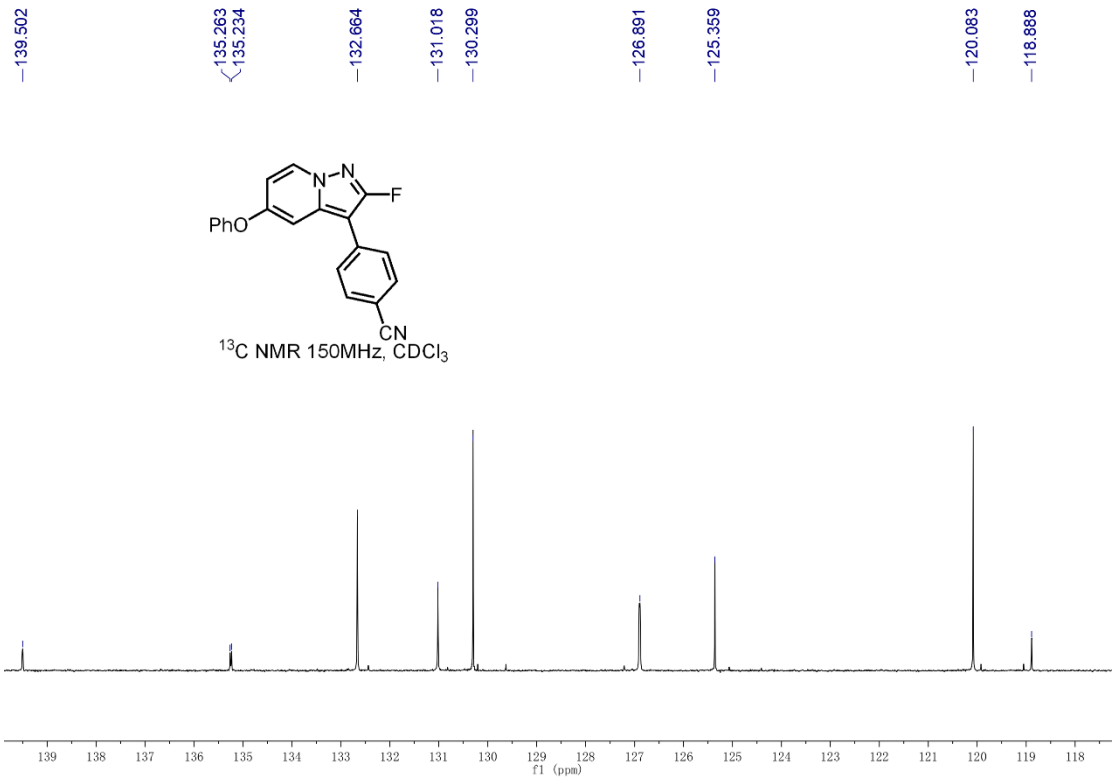




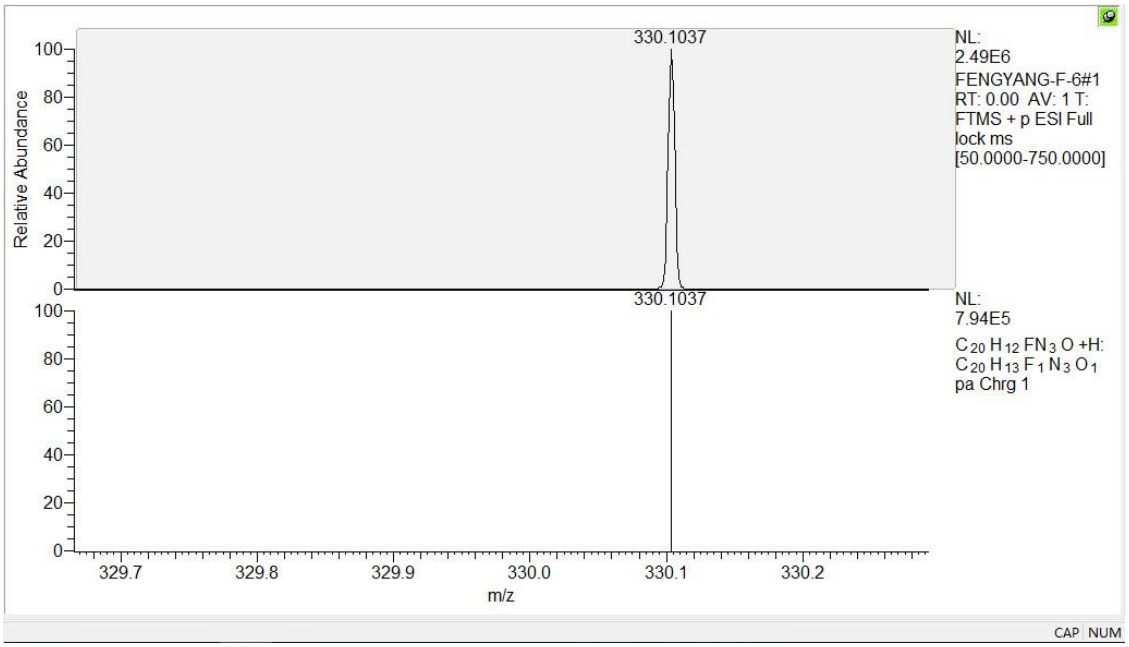
^{19}F NMR 376MHz, $CDCl_3$



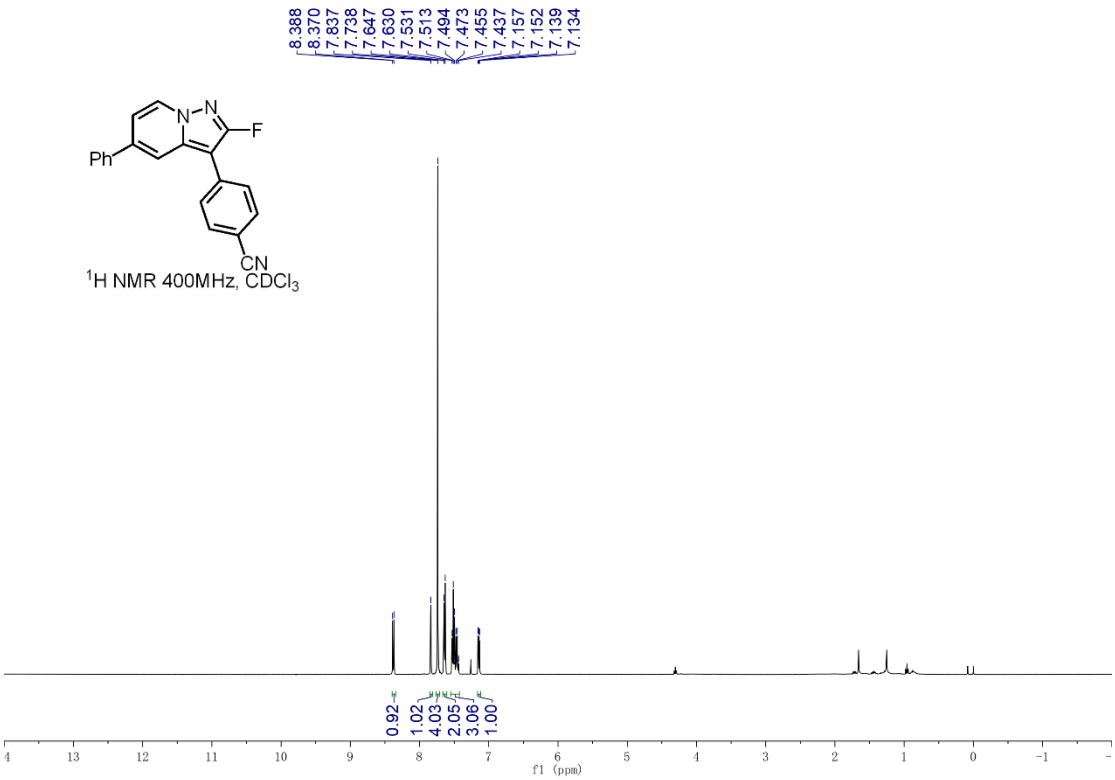
^{13}C NMR 150MHz, $CDCl_3$

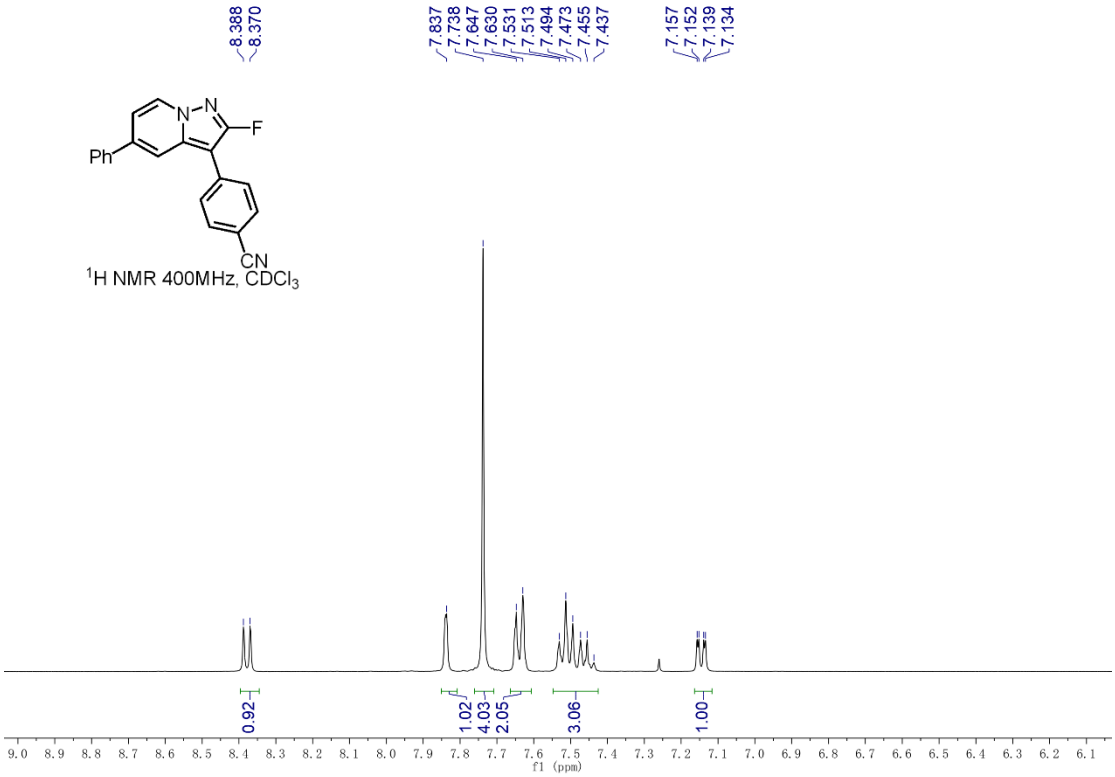


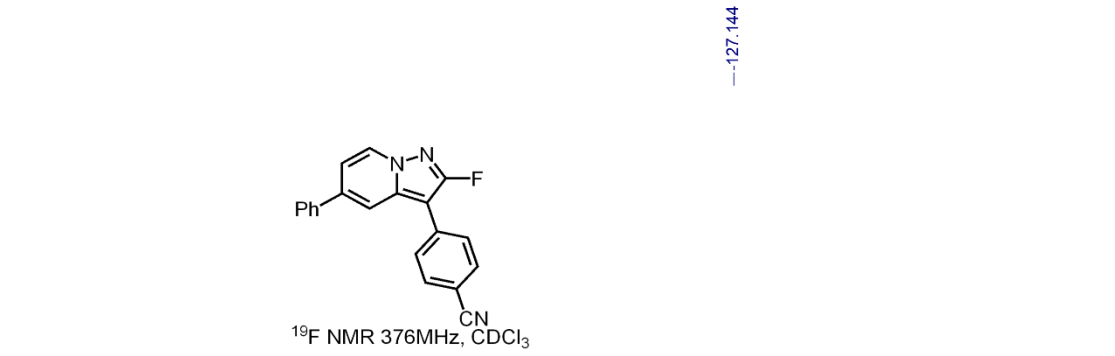
HRMS (ESI) copy of compound **3h**:



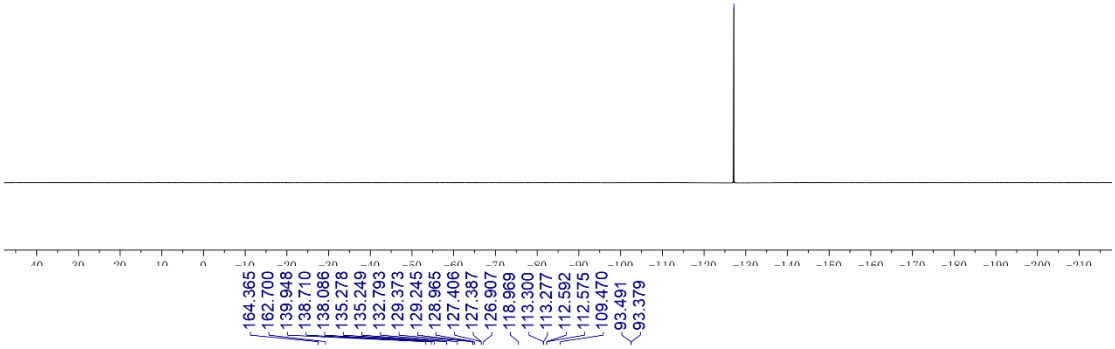
NMR copies of compound **3i:**

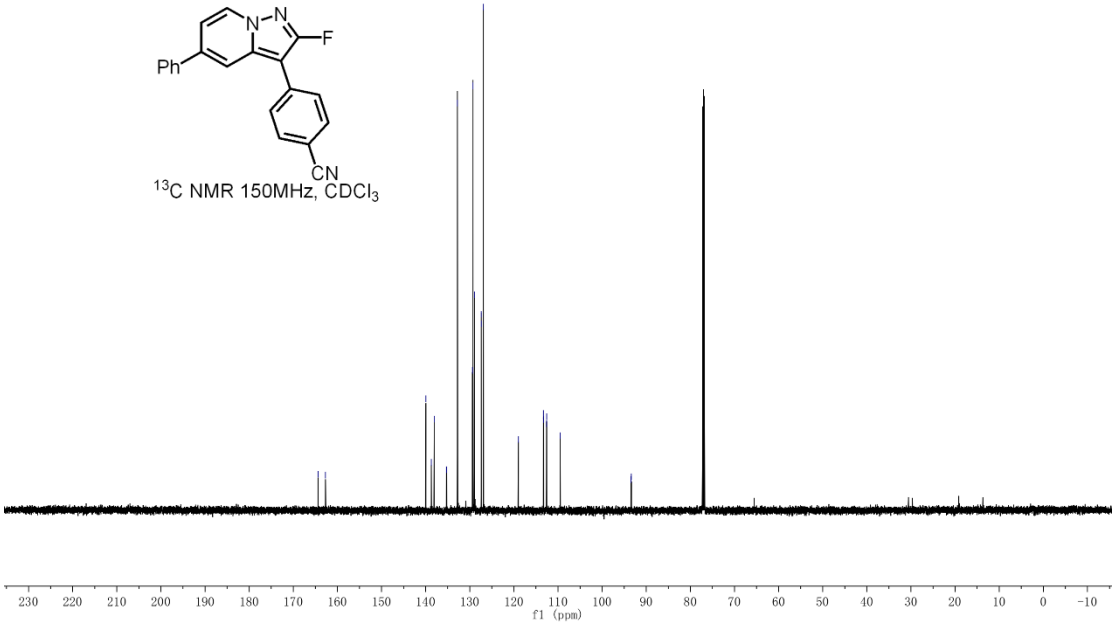




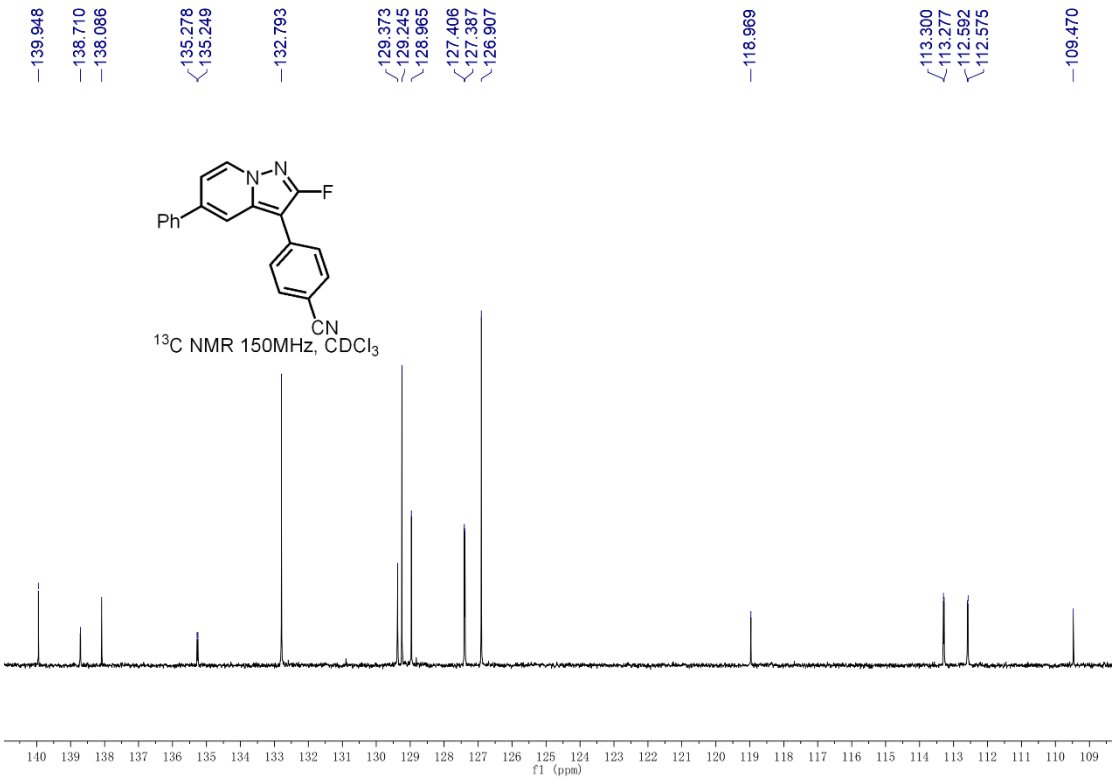


^{19}F NMR 376MHz, $CDCl_3$

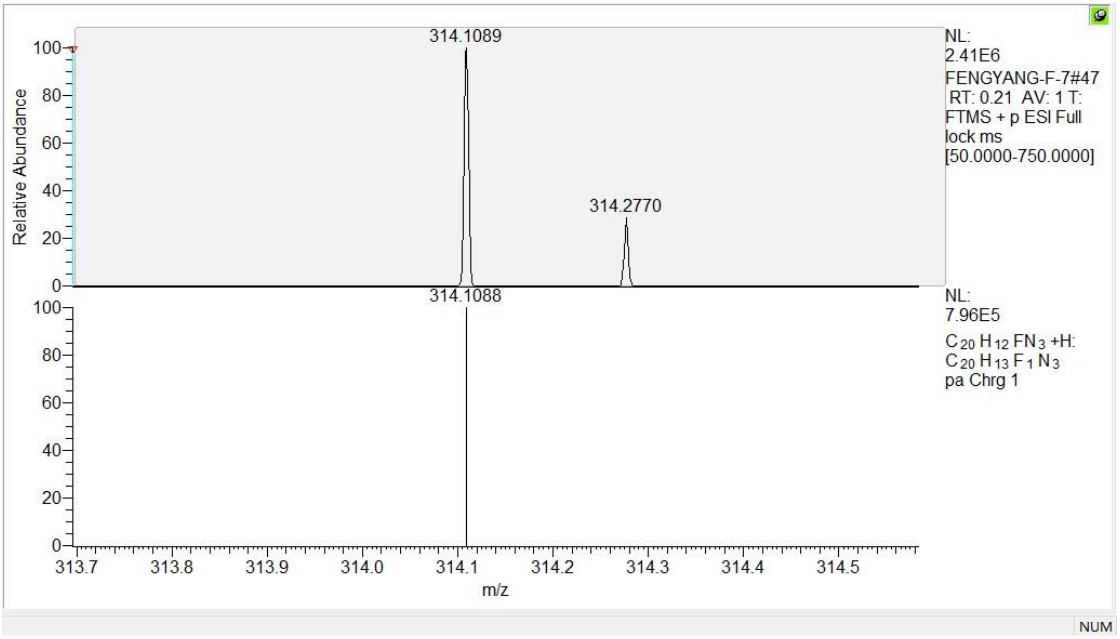




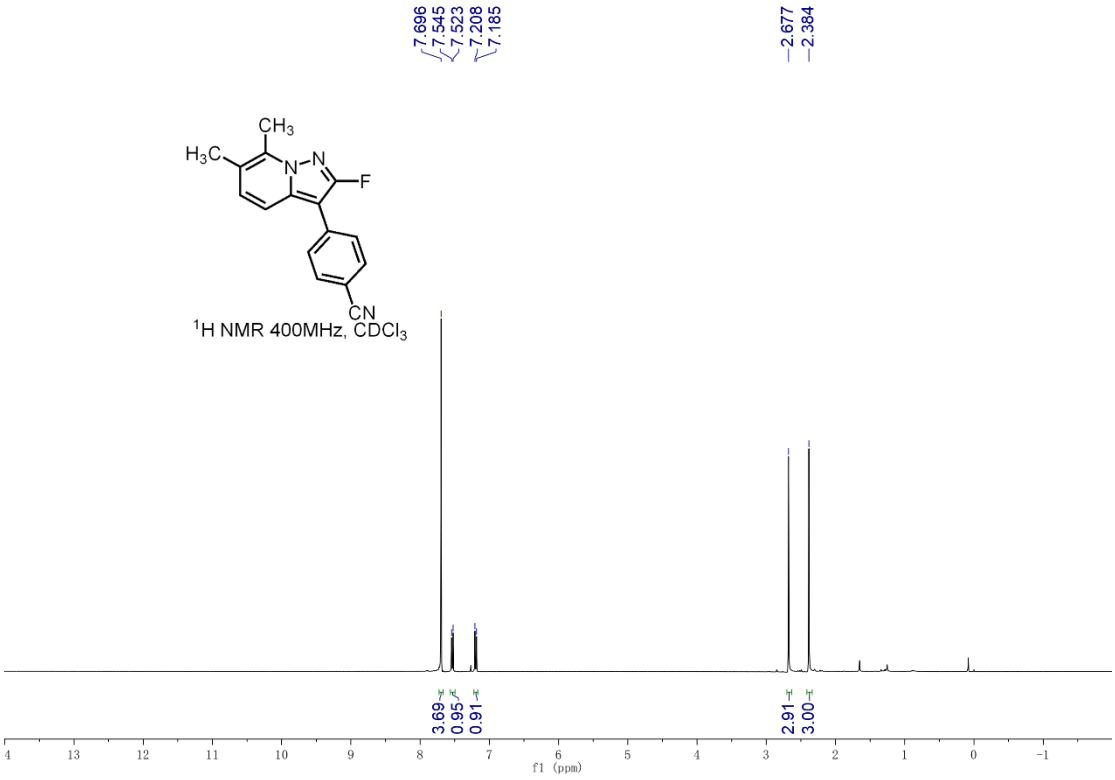
^{13}C NMR 150MHz, $CDCl_3$

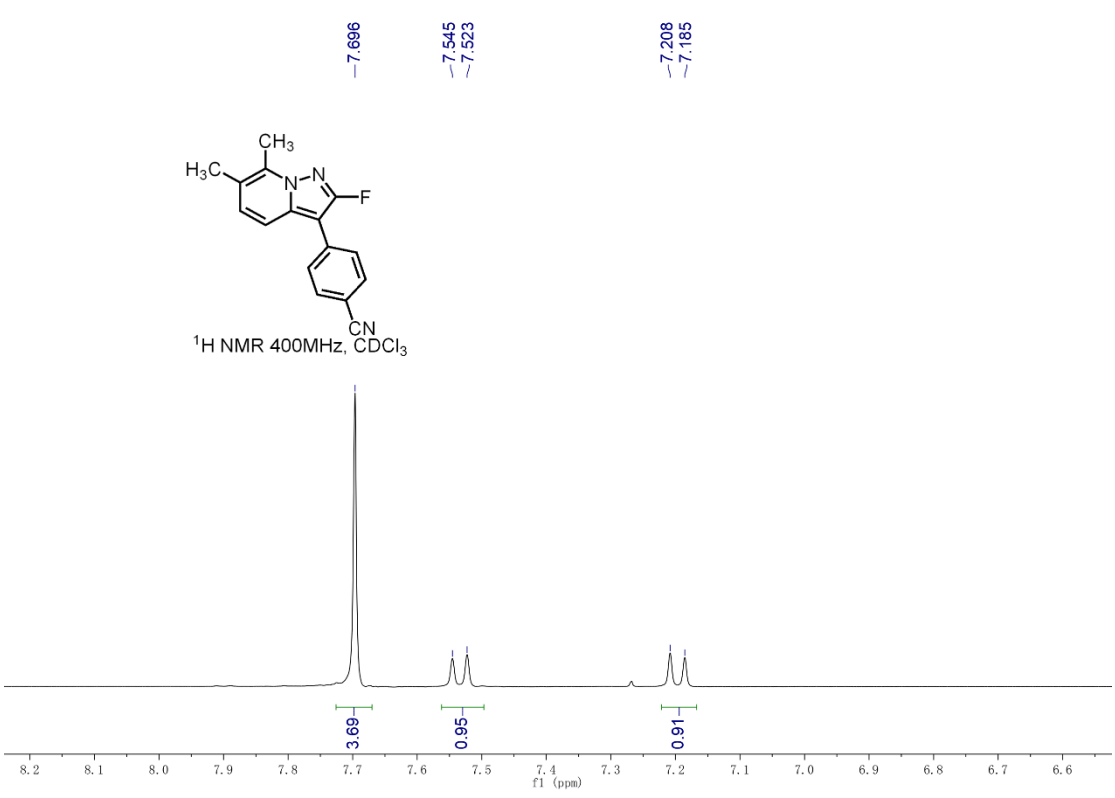


HRMS (ESI) copy of compound **3i**:

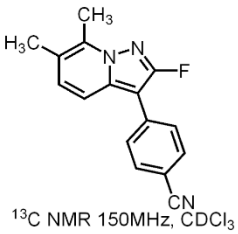


NMR copies of compound **3j:**

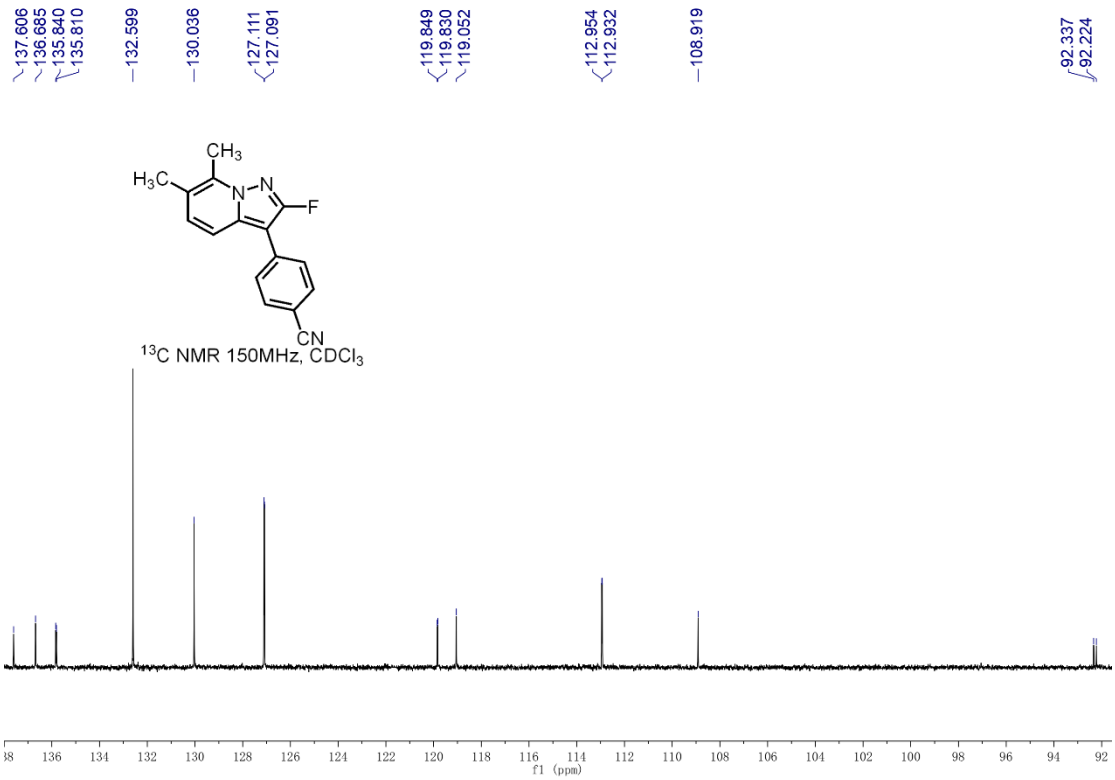




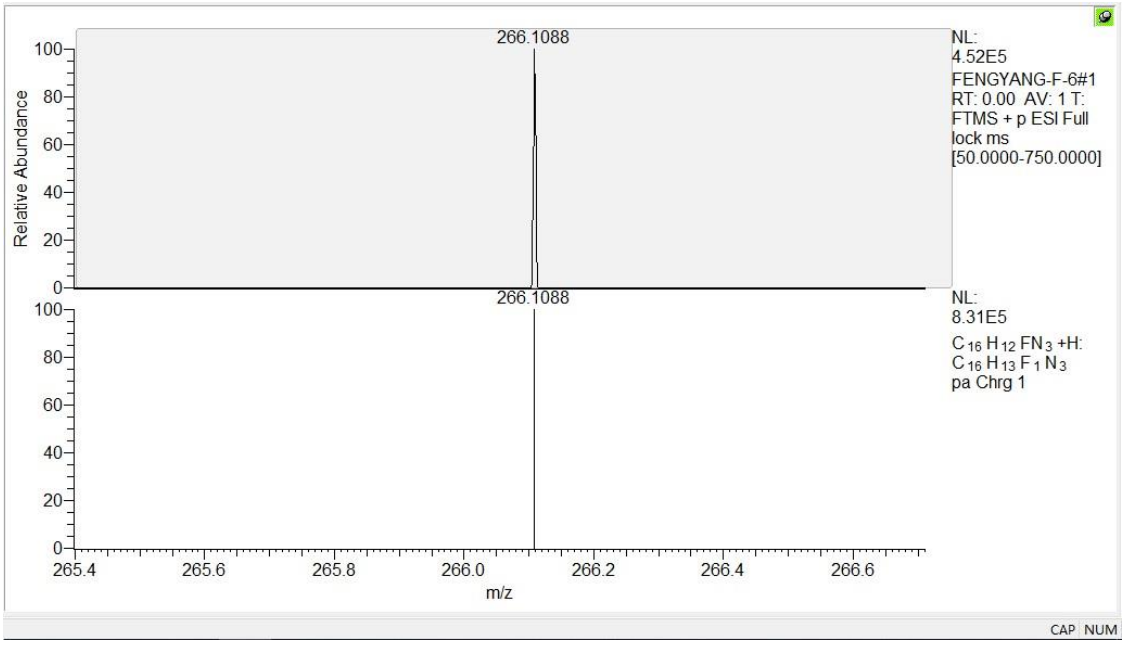
^{19}F NMR 376MHz, $CDCl_3$



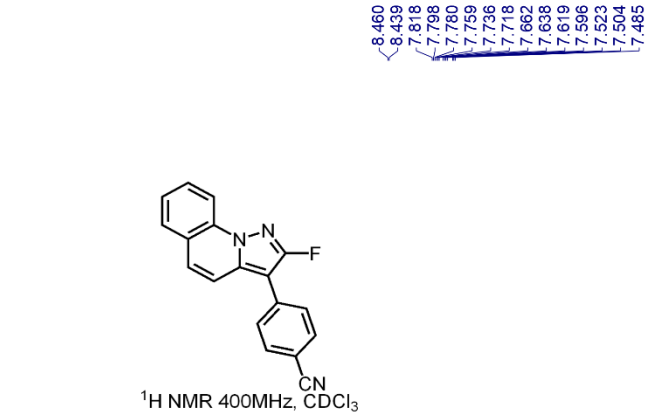
^{13}C NMR 150MHz, $CDCl_3$

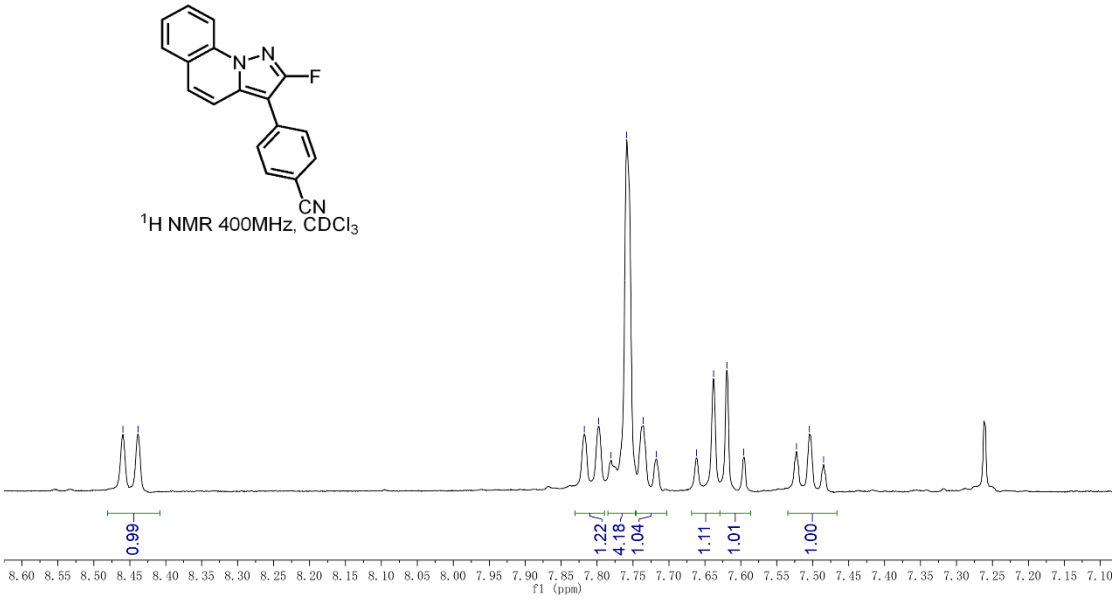


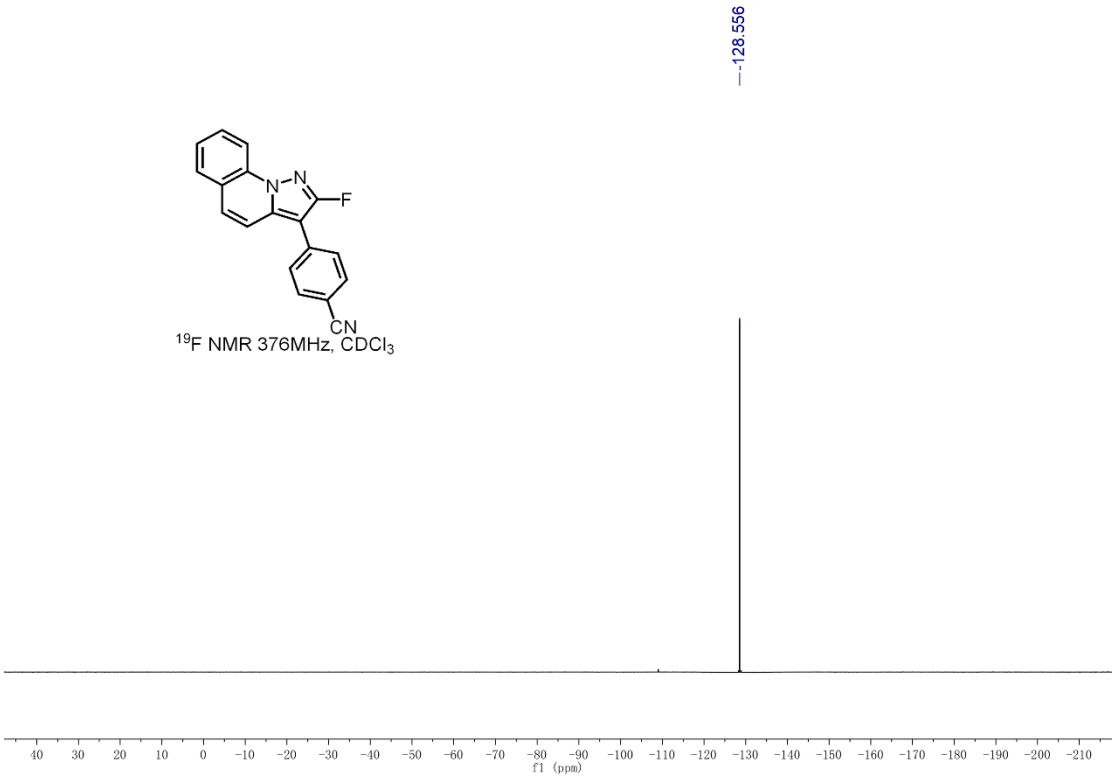
HRMS (ESI) copy of compound **3j**:



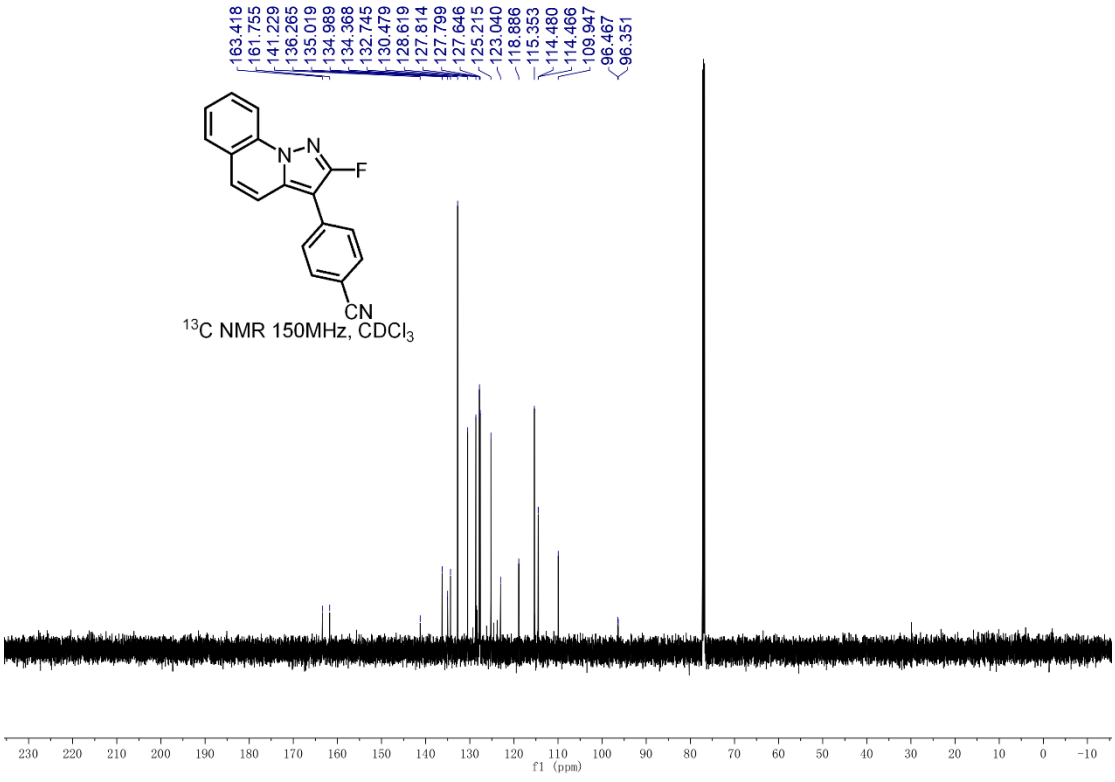
NMR copies of compound **3n:**



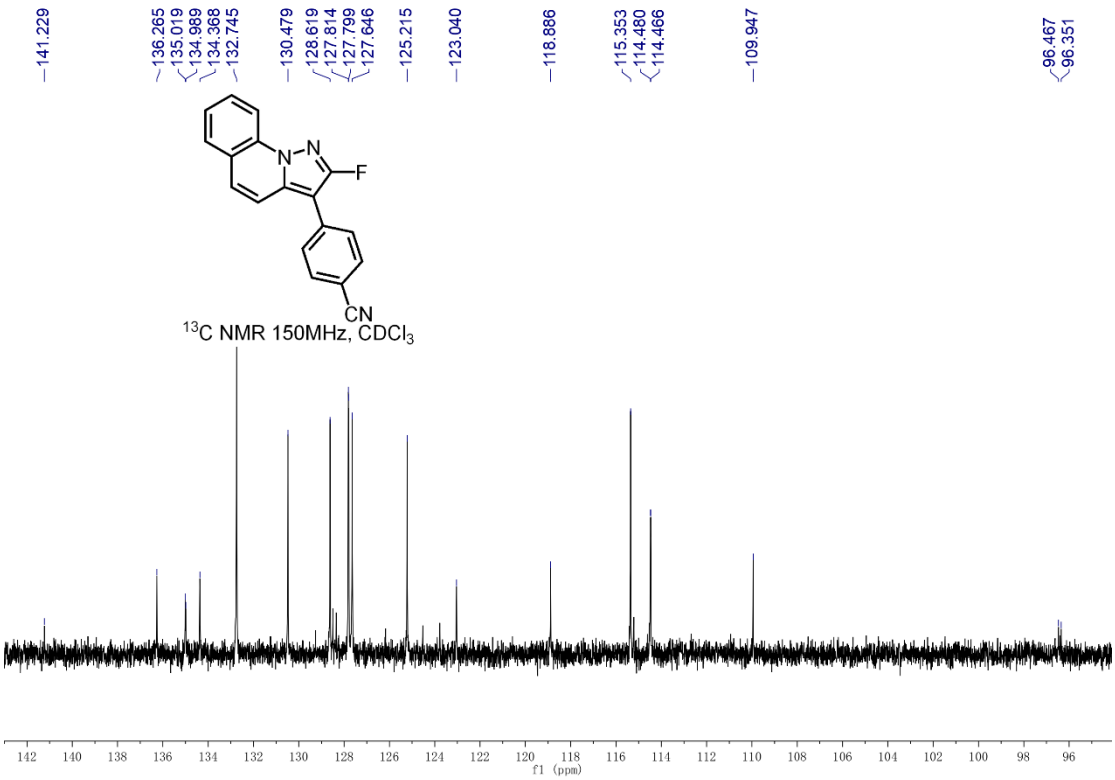




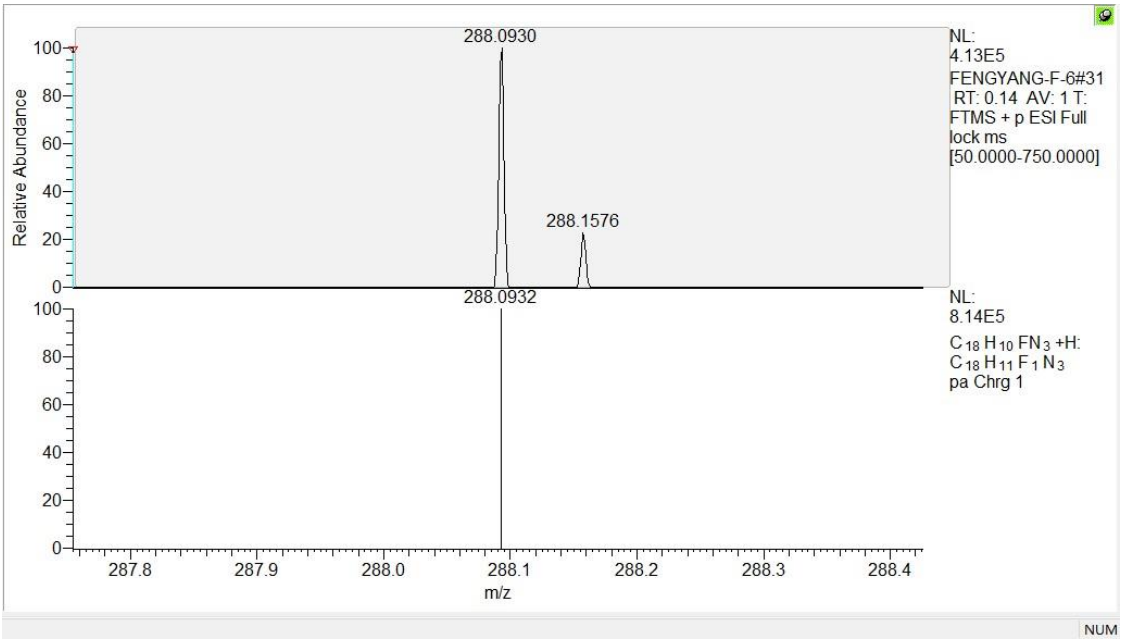
^{19}F NMR 376MHz, $CDCl_3$



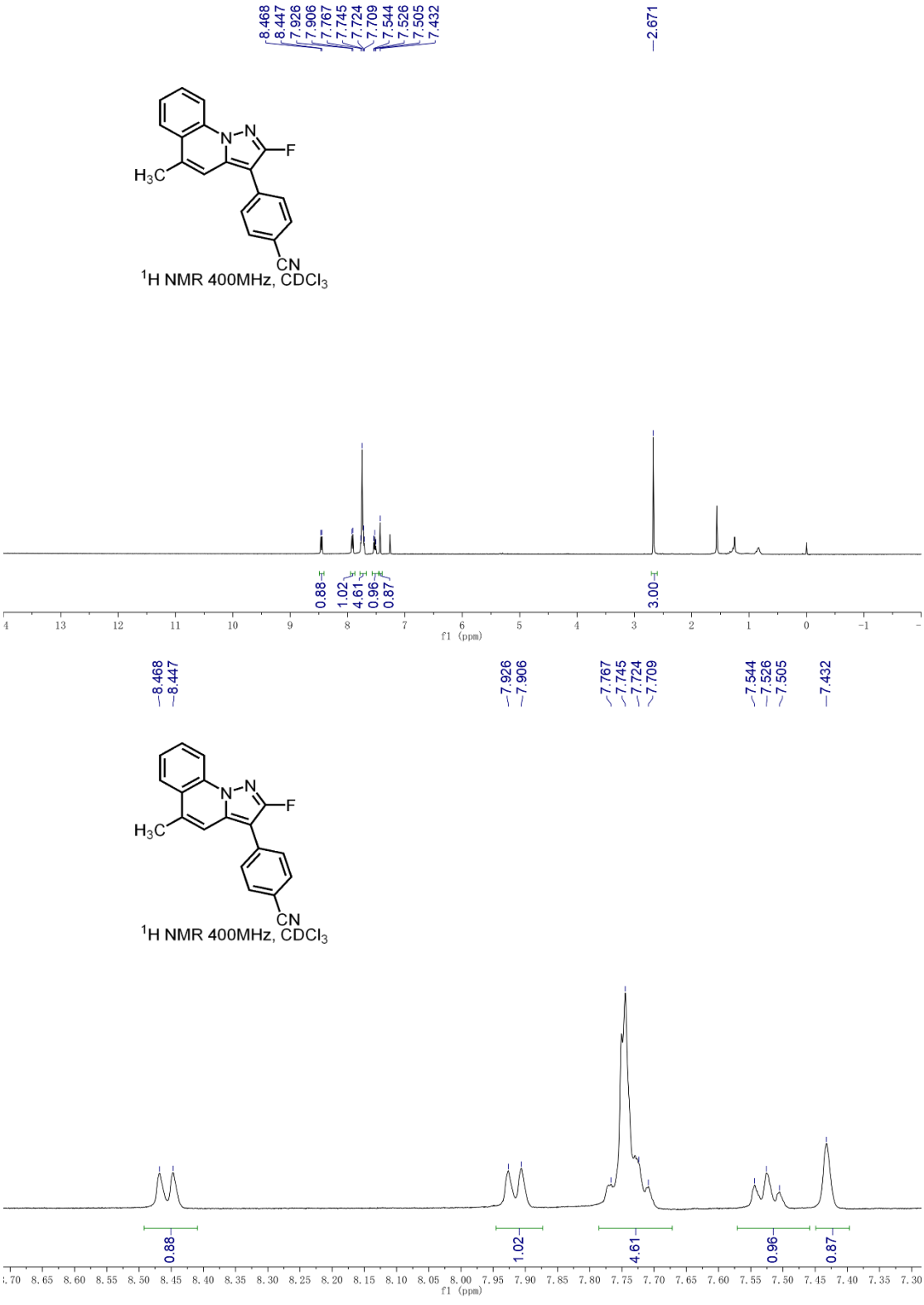
^{13}C NMR 150MHz, $CDCl_3$

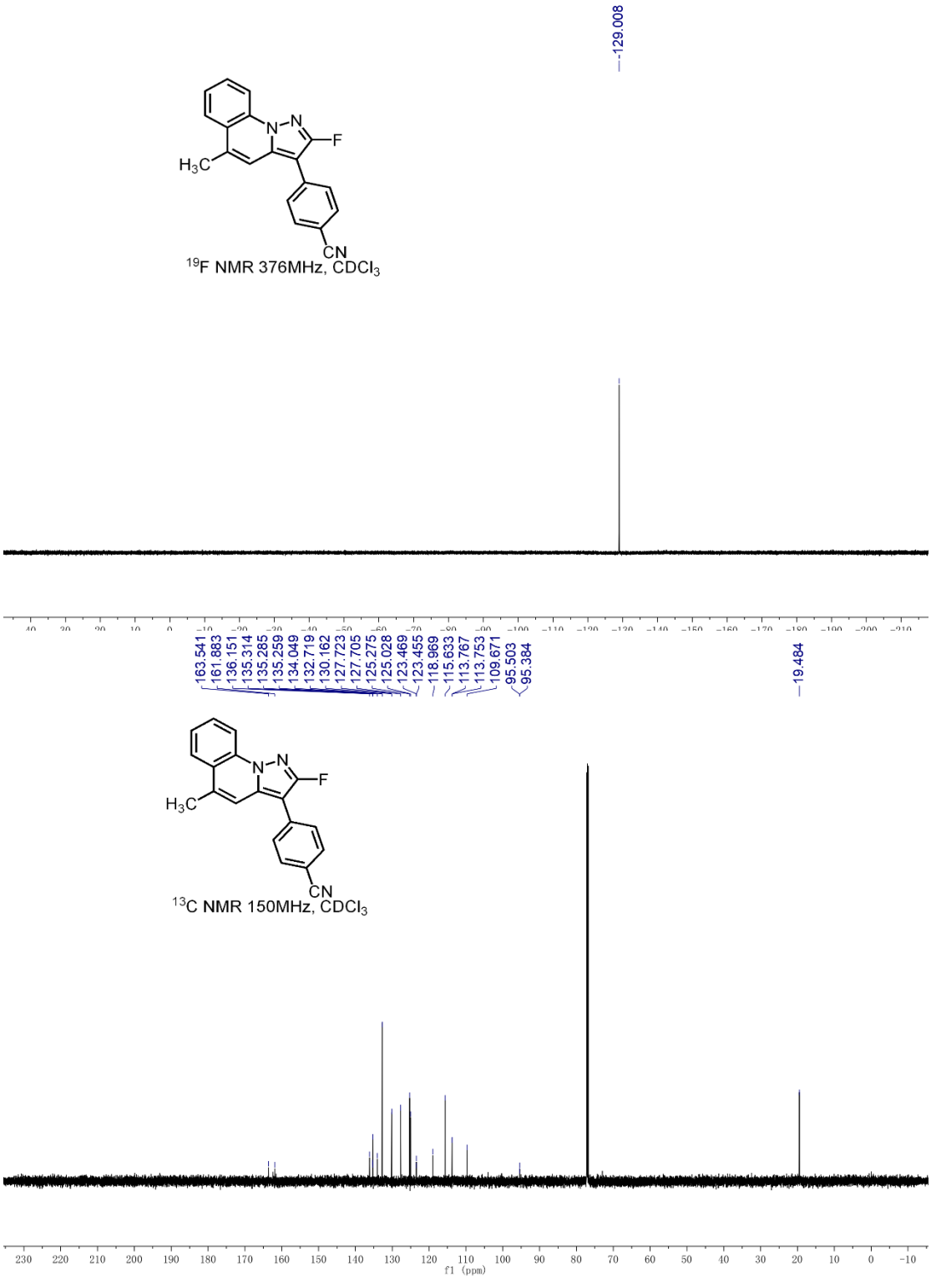


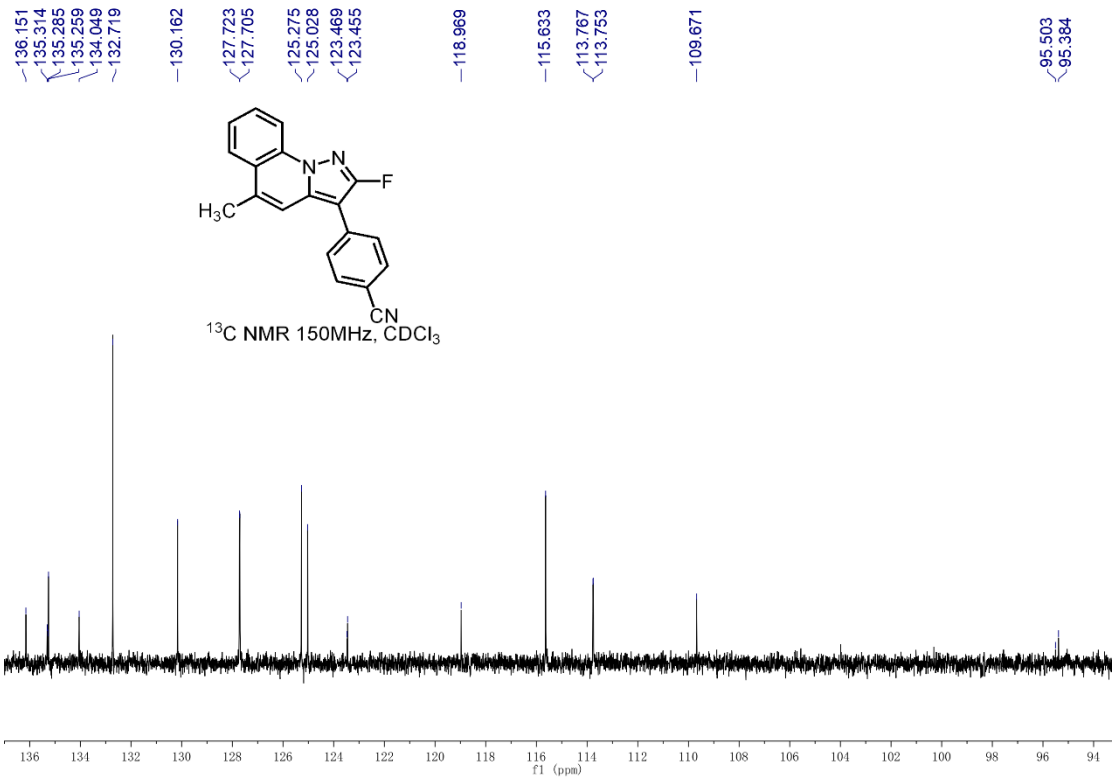
HRMS (ESI) copy of compound **3n**:



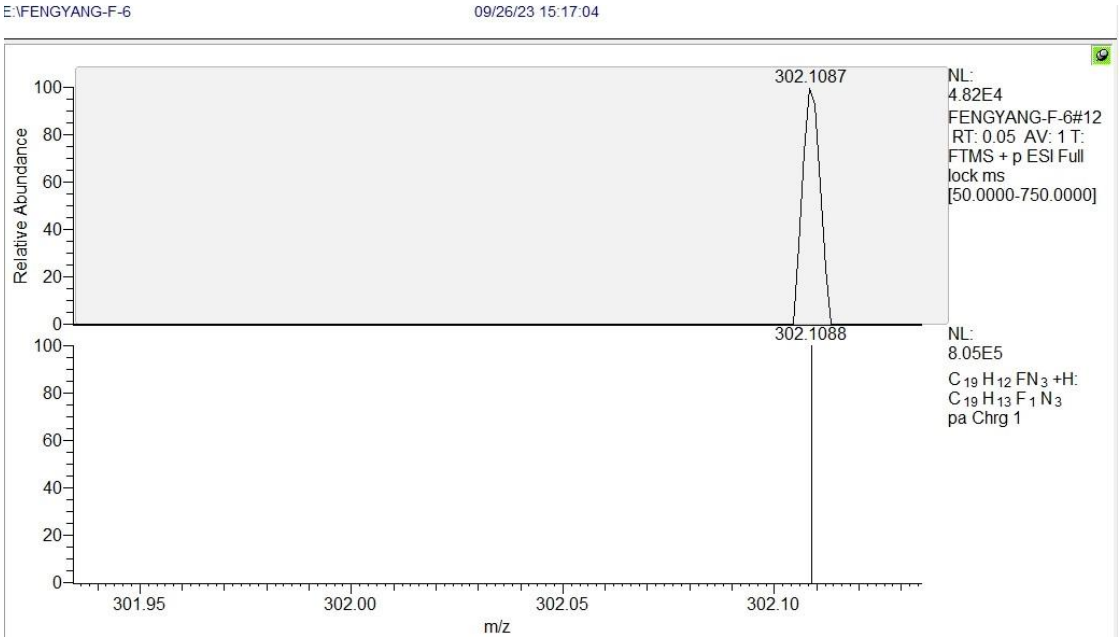
NMR copies of compound **3o**:



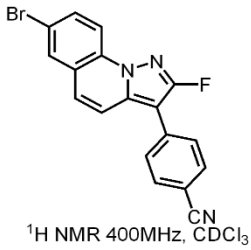

-129.008
H3C
F
N
N
CN
19F NMR 376MHz, CDCl3
163.541
161.883
136.151
135.314
135.285
135.259
134.049
132.719
130.162
127.723
127.705
125.275
125.028
123.469
123.455
118.969
115.633
113.767
113.753
109.671
95.503
95.384
19.484
H3C
F
N
N
CN
13C NMR 150MHz, CDCl3
f1 (ppm)



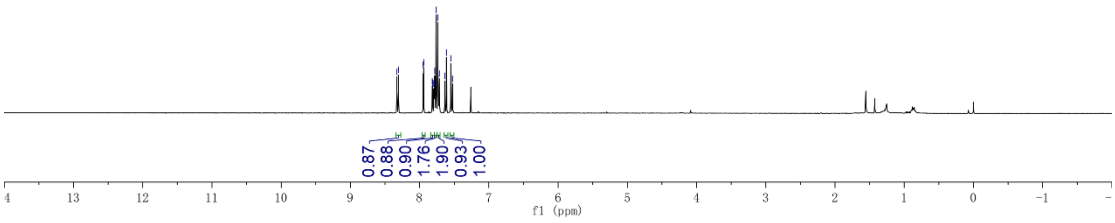
HRMS (ESI) copy of compound **3o**:

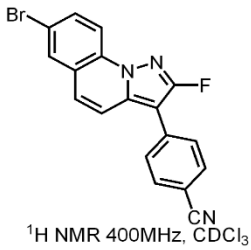


NMR copies of compound **3p**:

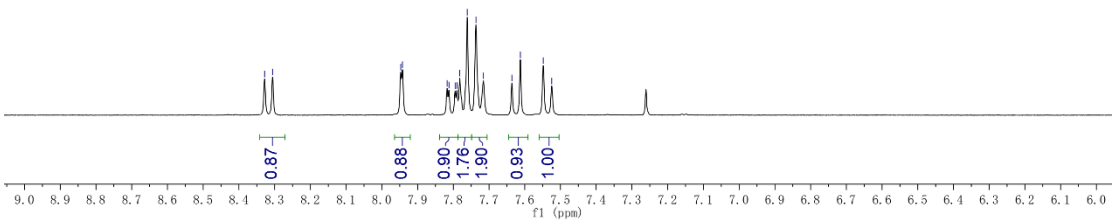


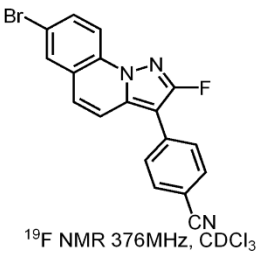
^{1}H NMR 400MHz, $CDCl_3$



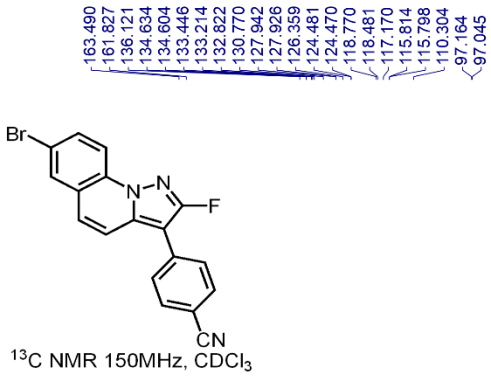


^{1}H NMR 400MHz, $CDCl_3$

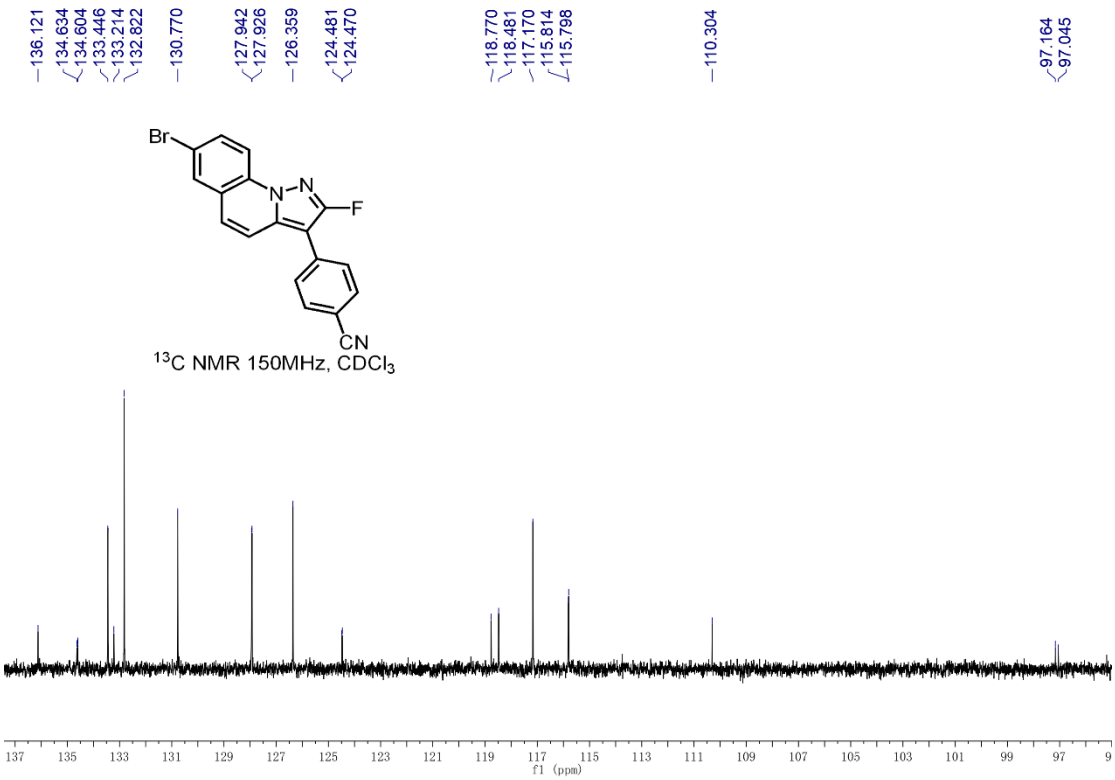




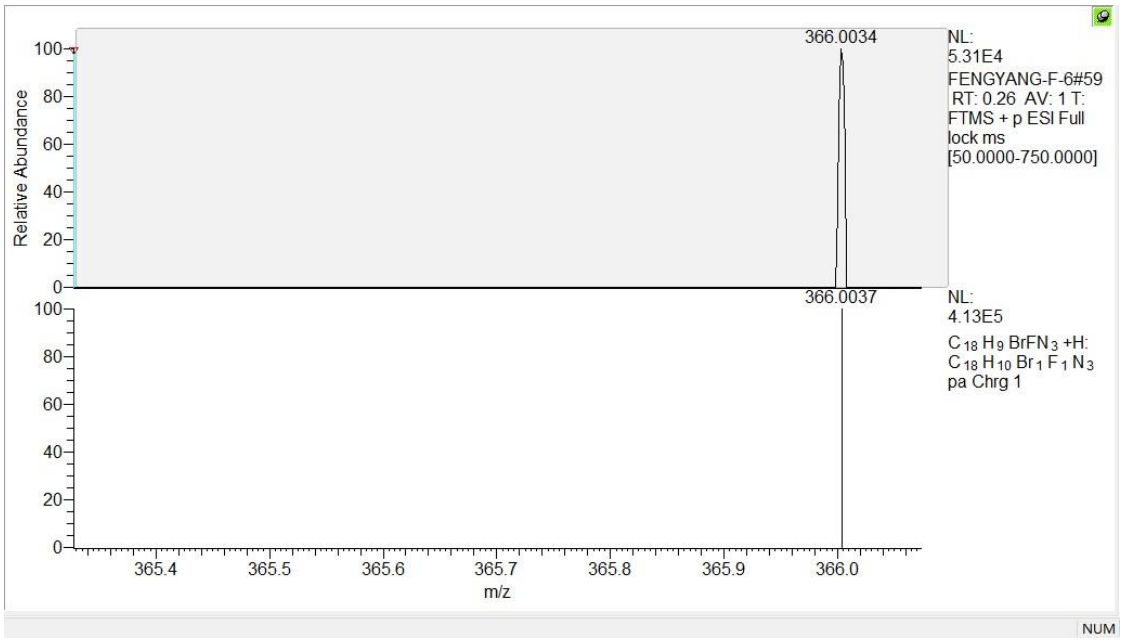
^{19}F NMR 376MHz, $CDCl_3$



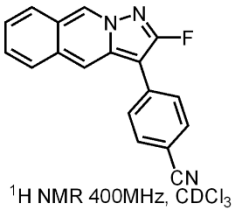
^{13}C NMR 150MHz, $CDCl_3$



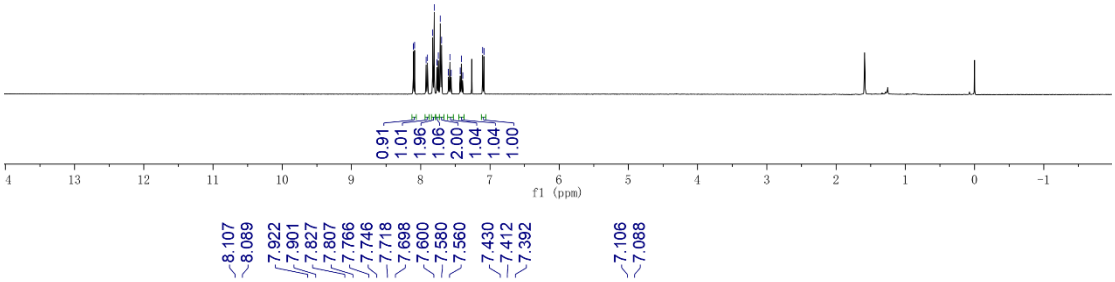
HRMS (ESI) copy of compound **3p**:

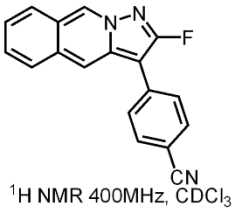


NMR copies of compound **3q:**

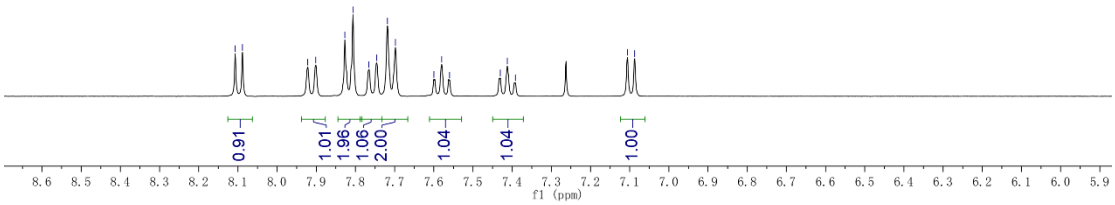


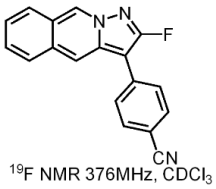
^{1}H NMR 400MHz, $CDCl_3$



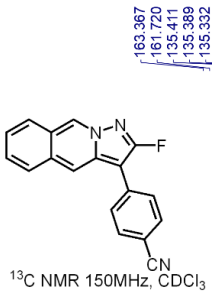


^{1}H NMR 400MHz, $CDCl_3$

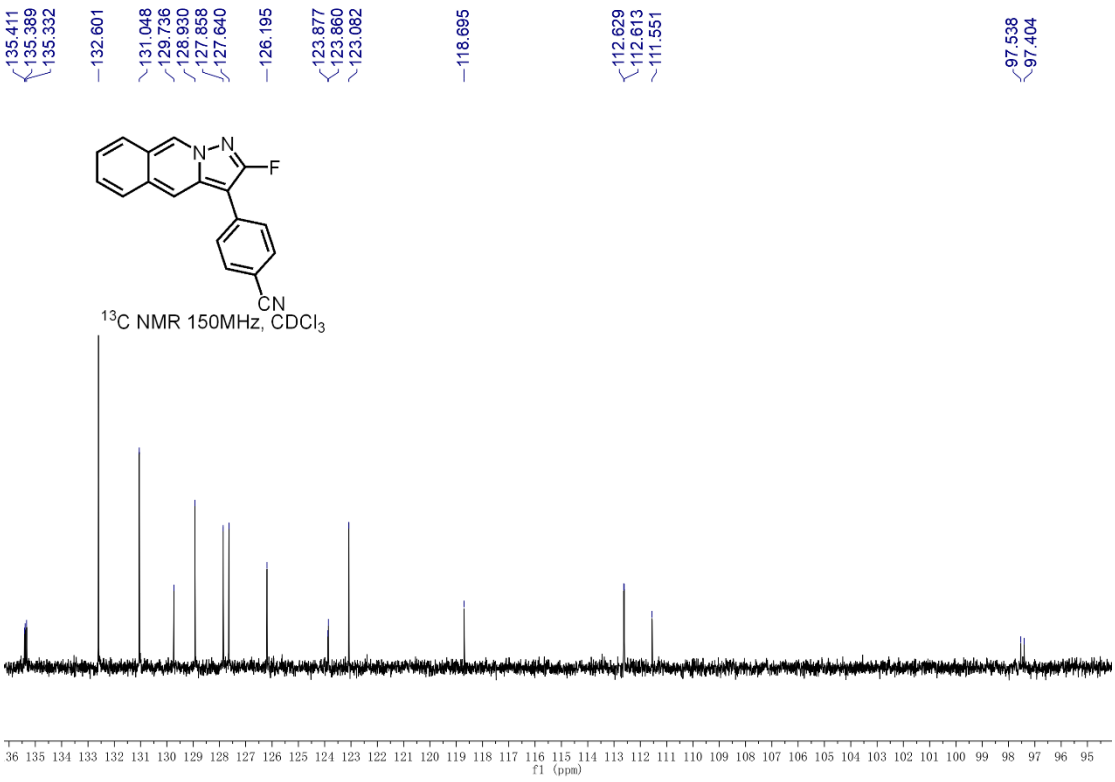




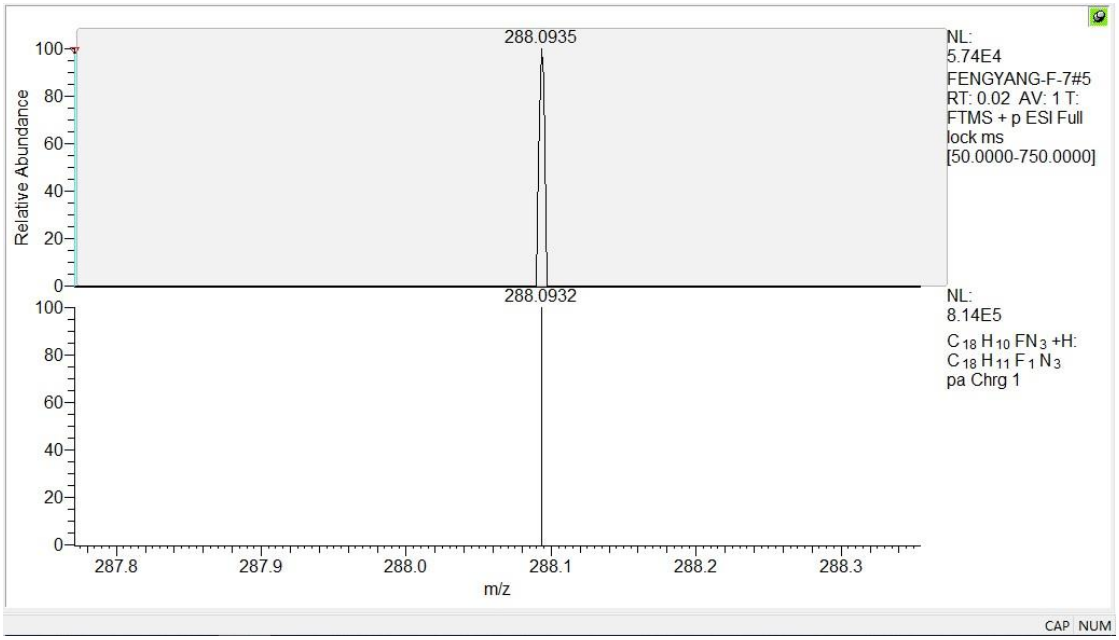
^{19}F NMR 376MHz, $CDCl_3$



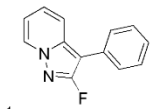
^{13}C NMR 150MHz, $CDCl_3$



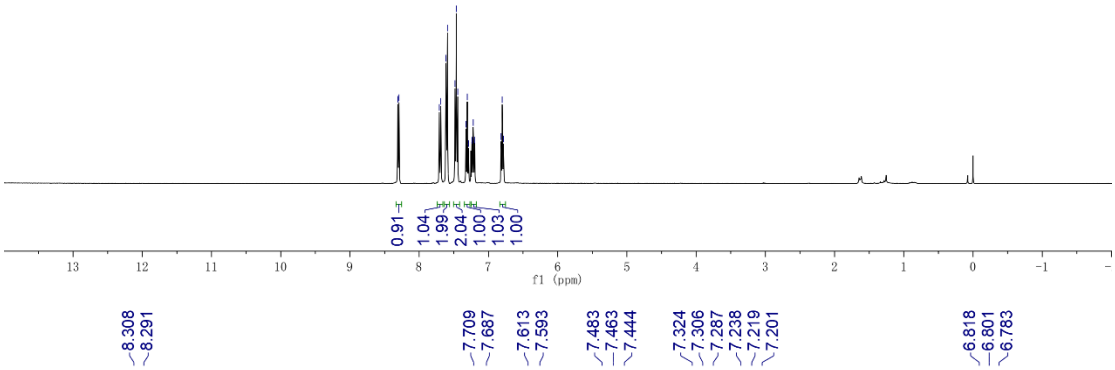
HRMS (ESI) copy of compound **3q**:



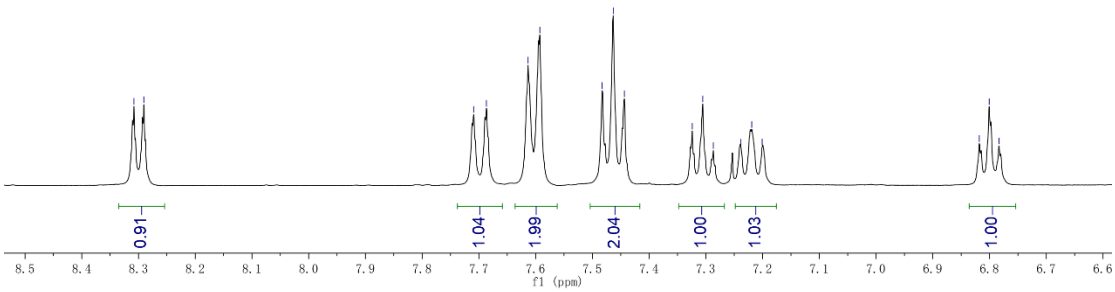
NMR copies of compound **4a:**

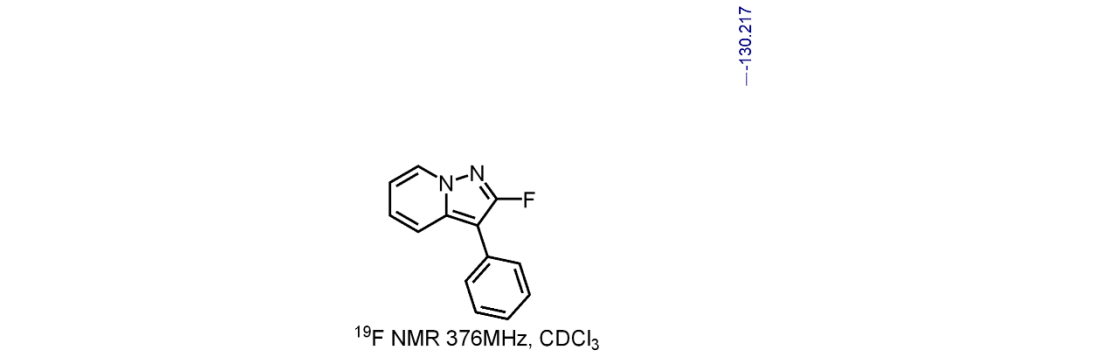


^{1}H NMR, 400 MHz, $CDCl_3$

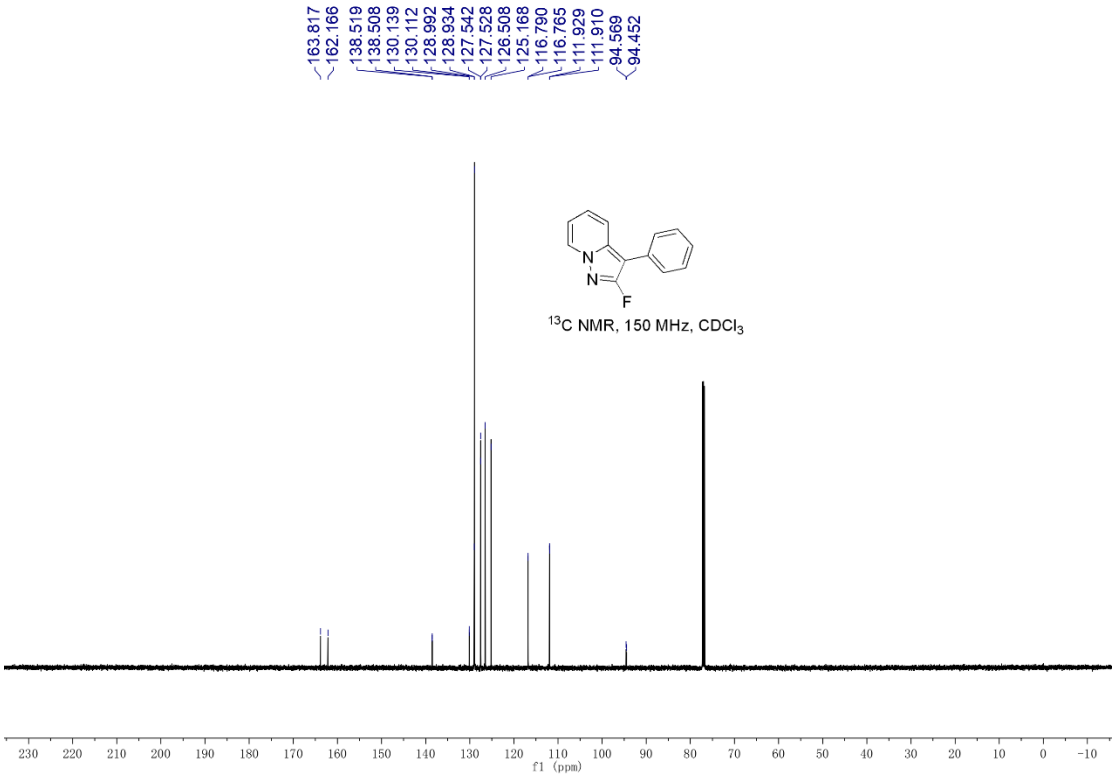


^{1}H NMR, 400 MHz, $CDCl_3$

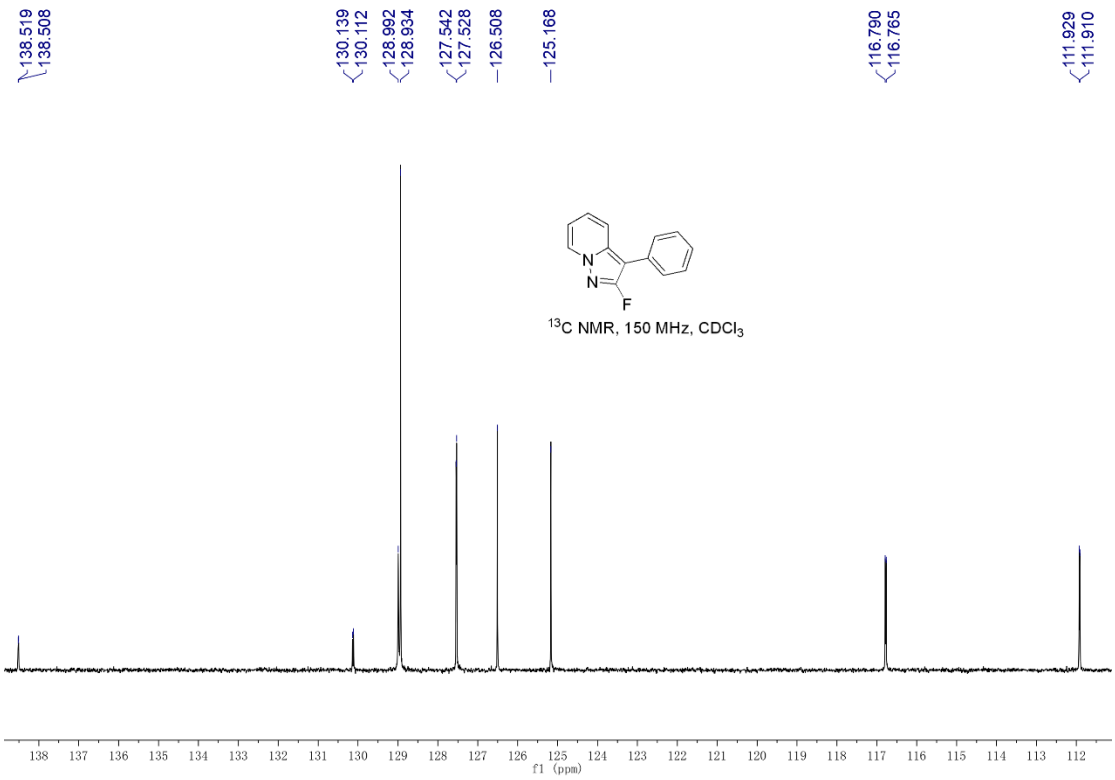




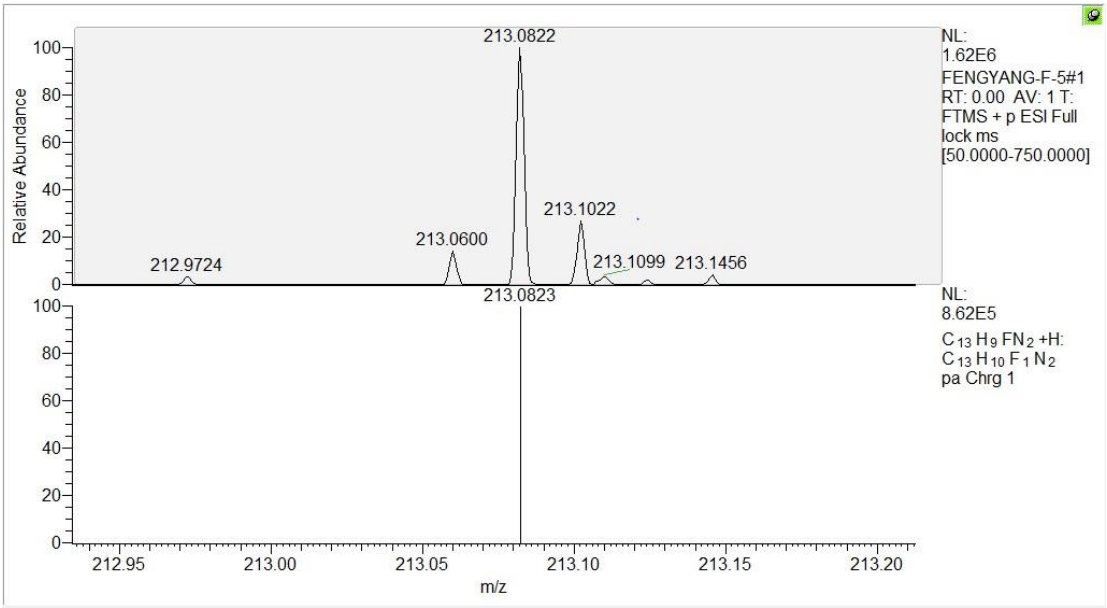
^{19}F NMR 376MHz, $CDCl_3$



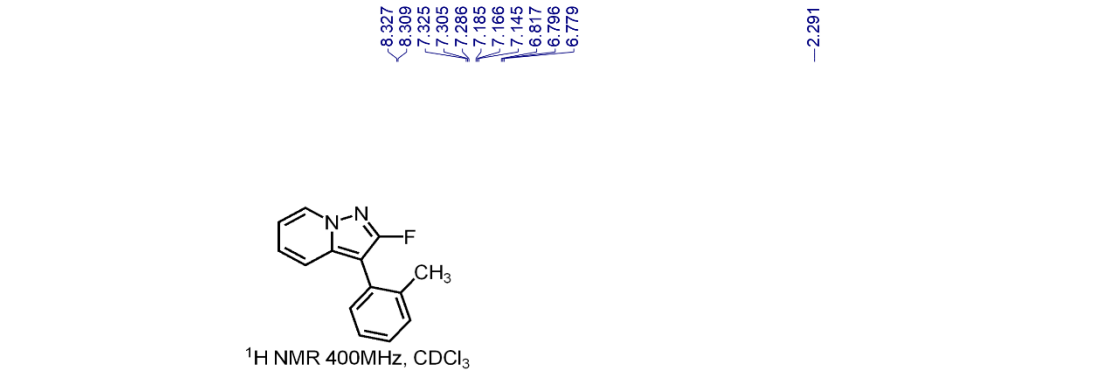
^{13}C NMR, 150 MHz, $CDCl_3$



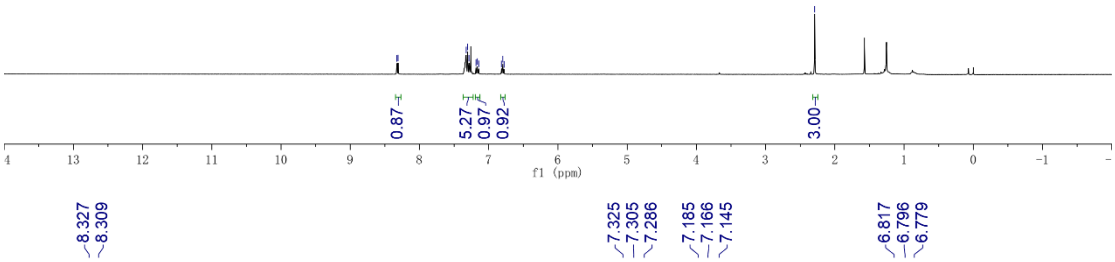
HRMS (ESI) copy of compound **4a**:

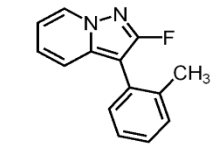


NMR copies of compound **4b:**

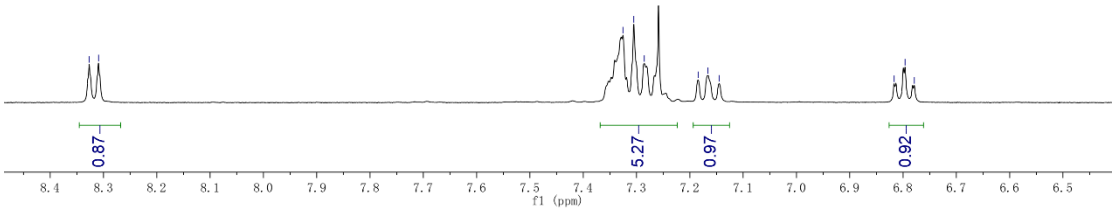


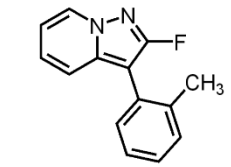
^{1}H NMR 400MHz, $CDCl_3$



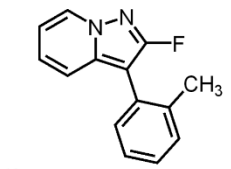


^{1}H NMR 400MHz, $CDCl_3$

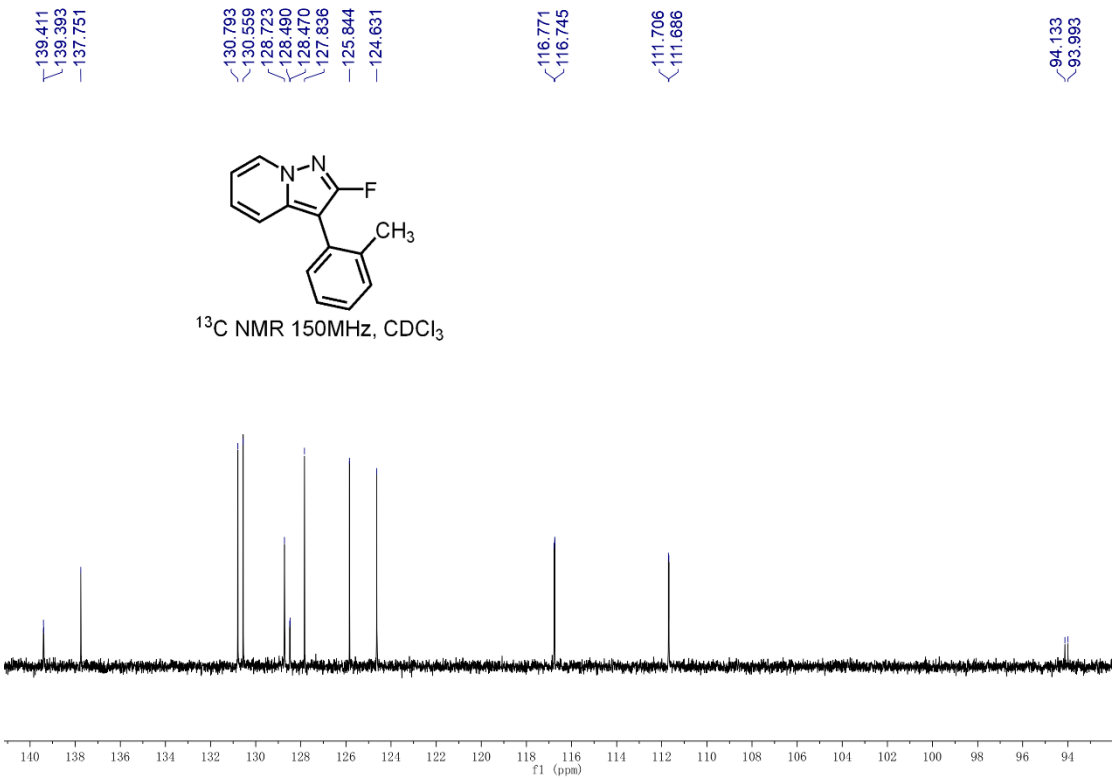




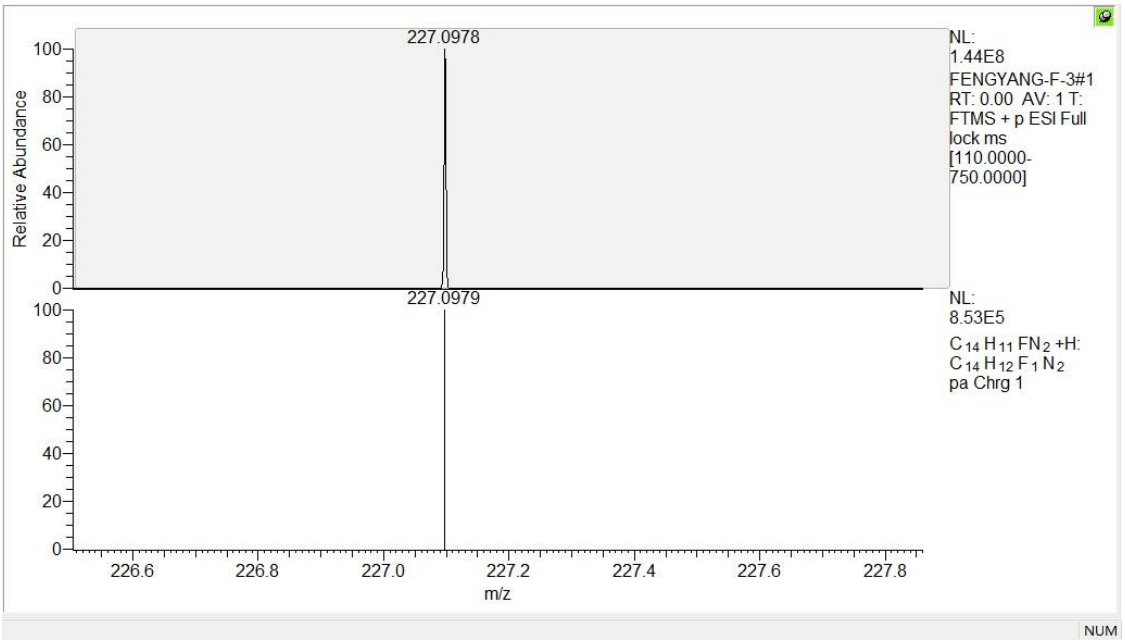
^{19}F NMR 376MHz, $CDCl_3$



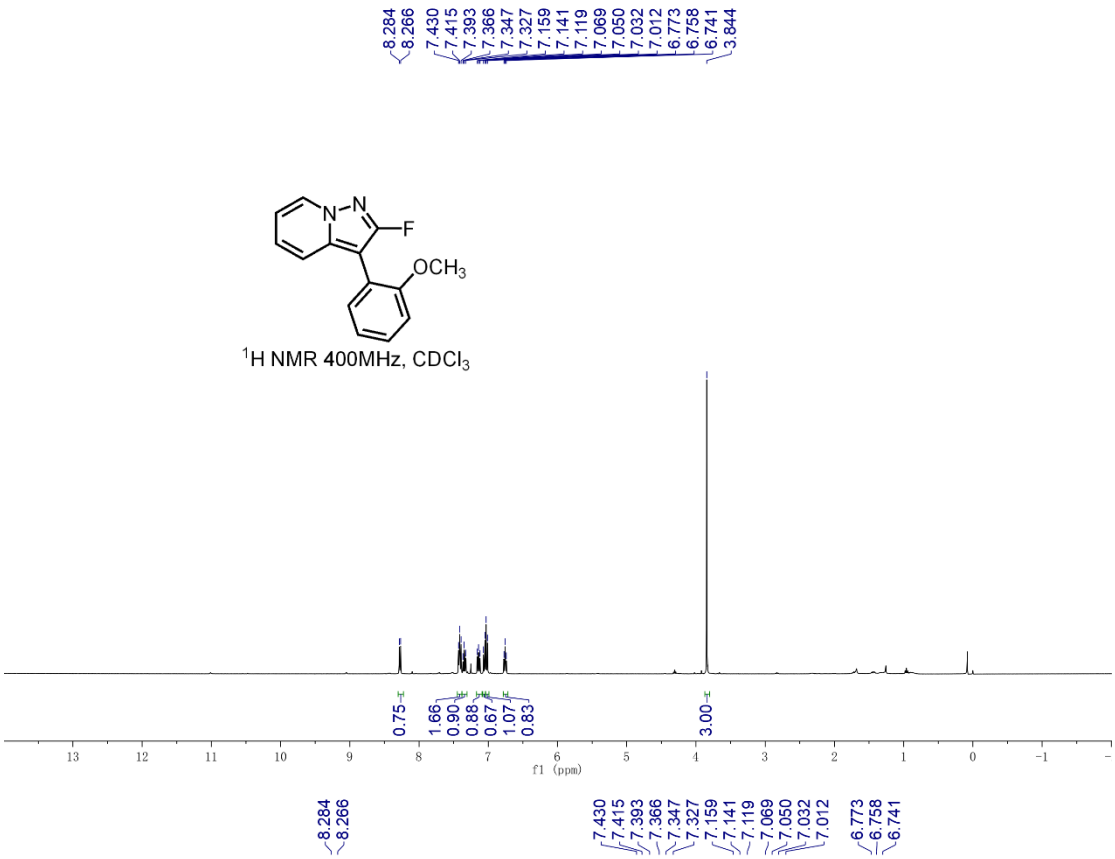
^{13}C NMR 150MHz, $CDCl_3$

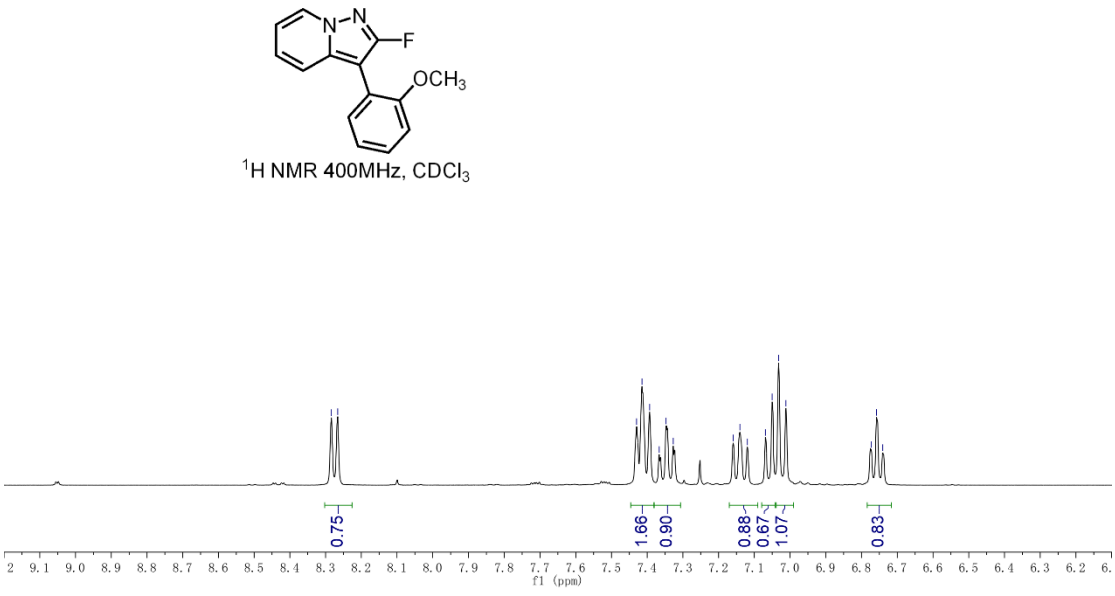


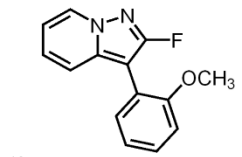
HRMS (ESI) copy of compound **4b**:



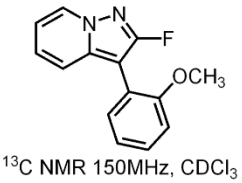
NMR copies of compound **4c:**



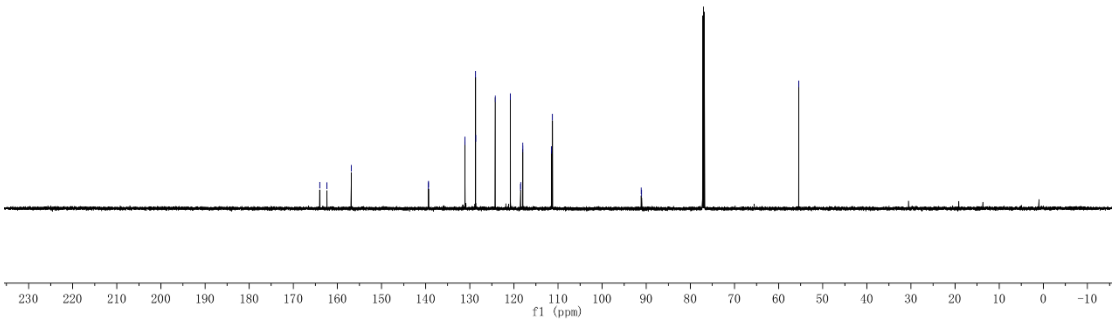


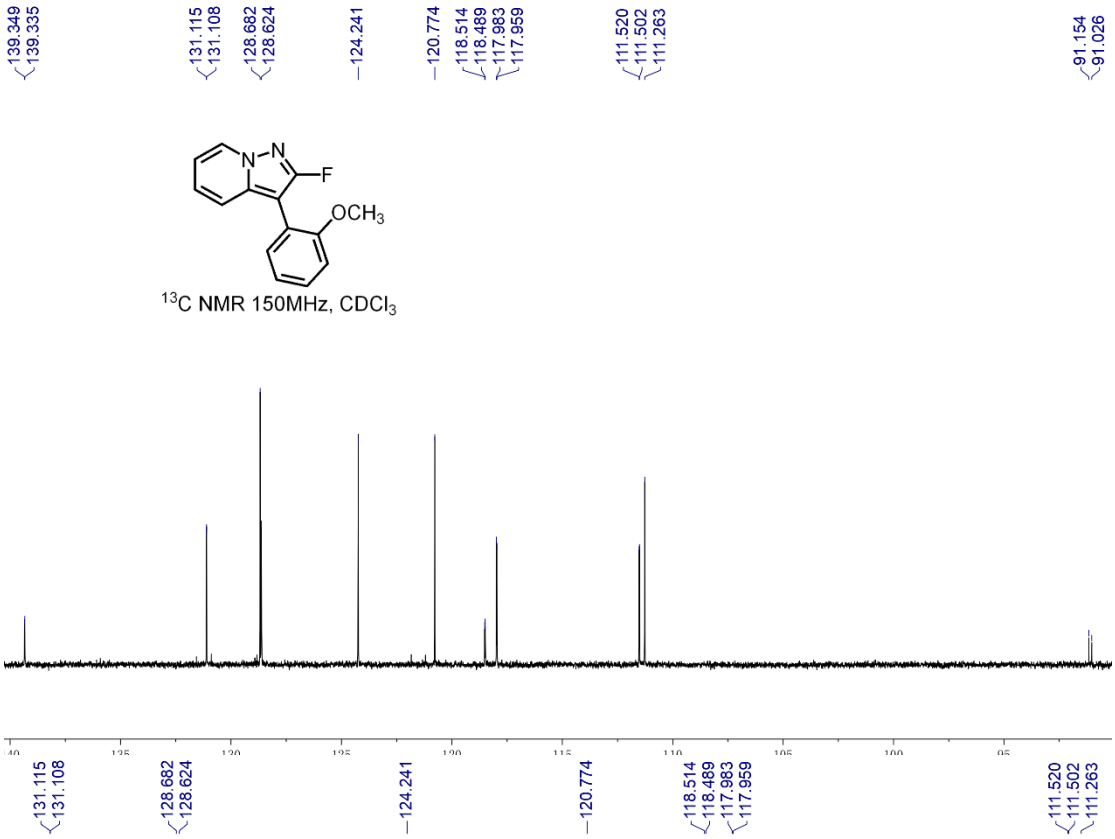


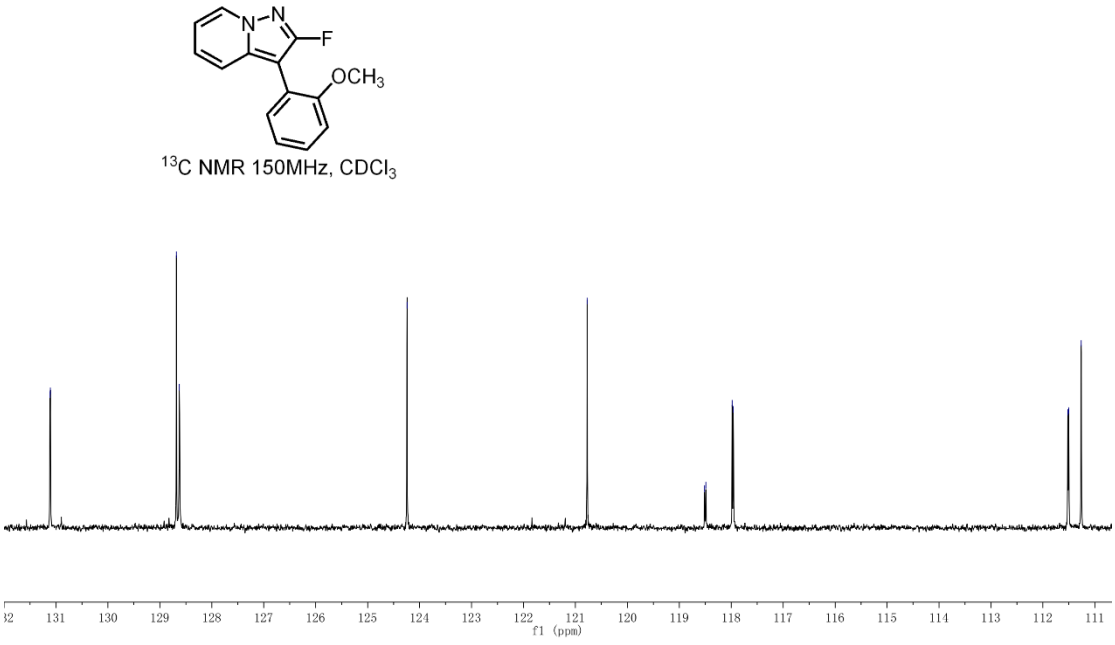
^{19}F NMR 376MHz, $CDCl_3$



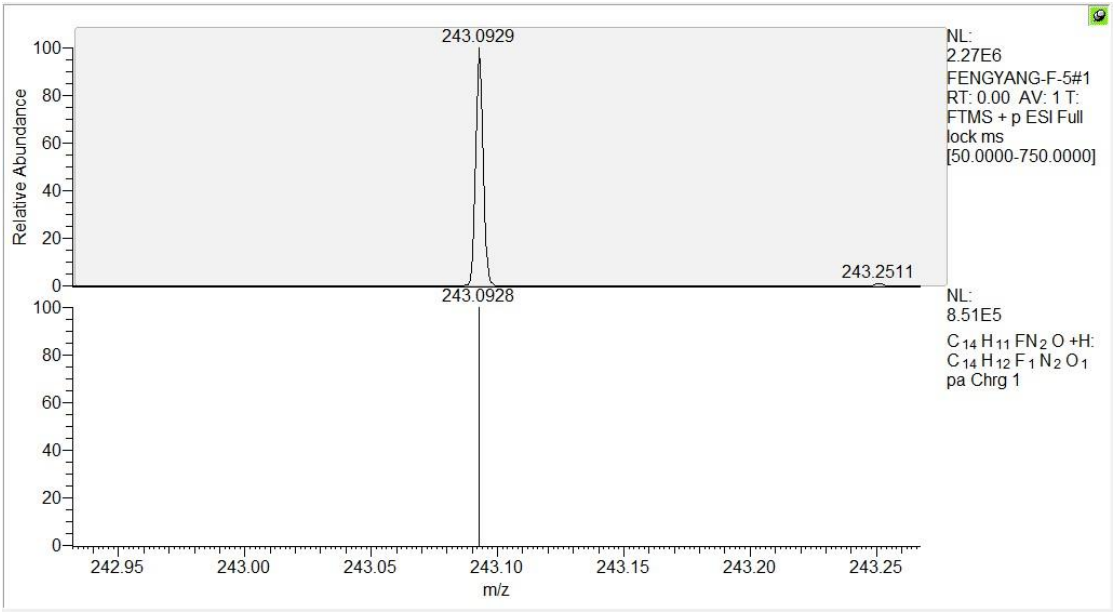
^{13}C NMR 150MHz, $CDCl_3$



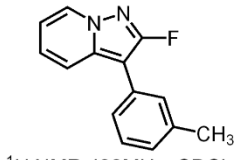

139.349
139.335
131.115
131.108
128.682
128.624
124.241
120.774
118.514
118.489
117.983
117.959
111.520
111.502
111.263
91.154
91.026
F
OCH3
13C NMR 150MHz, CDCl3


131.115
131.108
128.682
128.624
124.241
120.774
118.514
118.489
117.983
117.959
111.520
111.502
111.263
F
OCH3
13C NMR 150MHz, CDCl3
f1 (ppm)

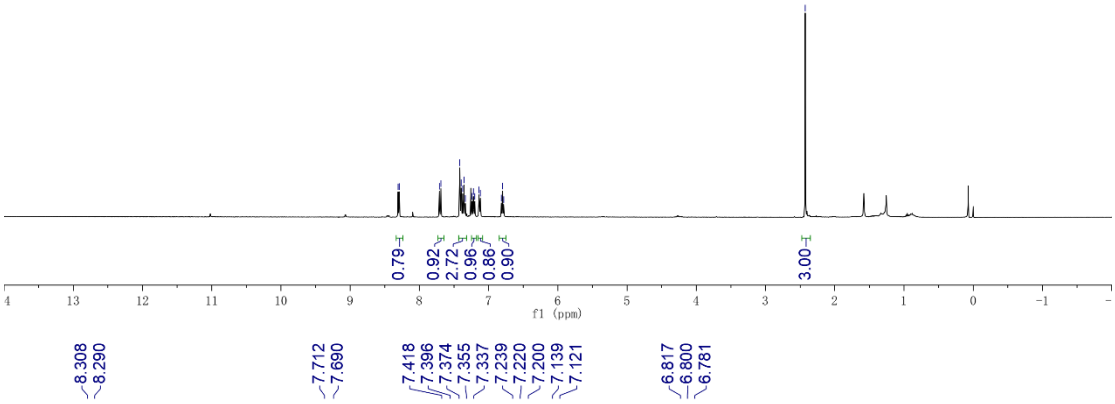
HRMS (ESI) copy of compound **4c**:

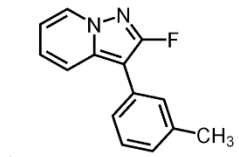


NMR copies of compound **4d:**

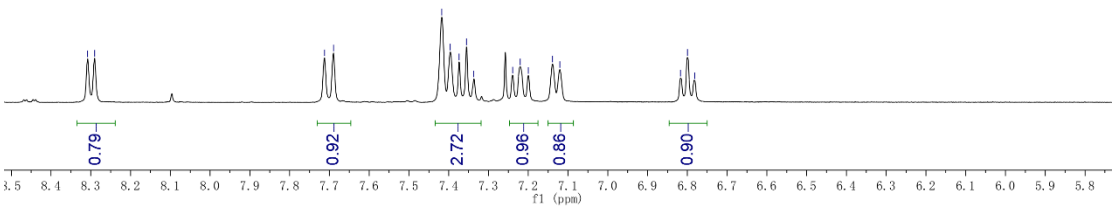


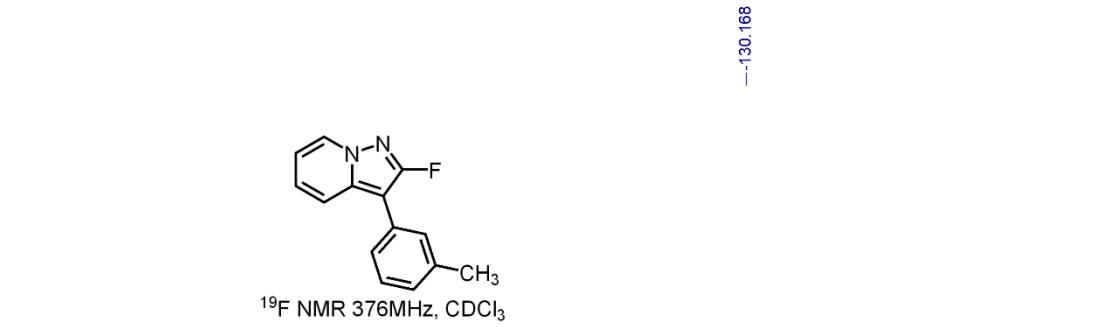
^{1}H NMR 400MHz, $CDCl_3$



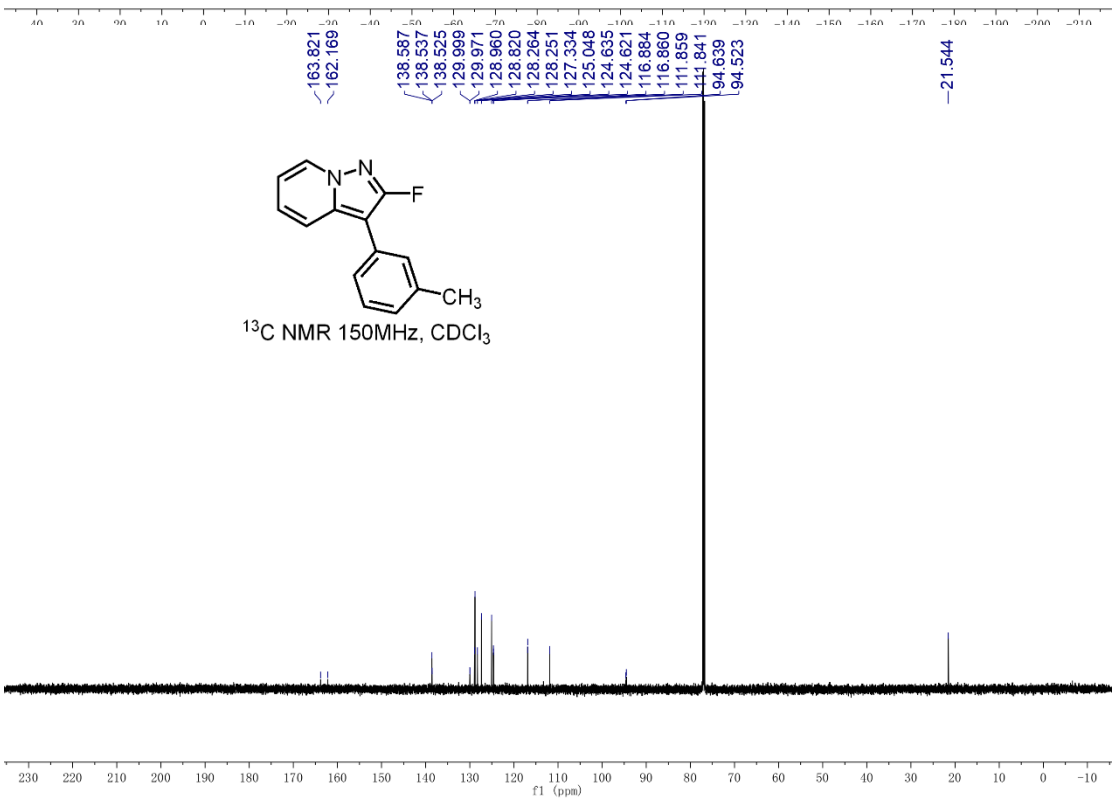


^{1}H NMR 400MHz, $CDCl_3$

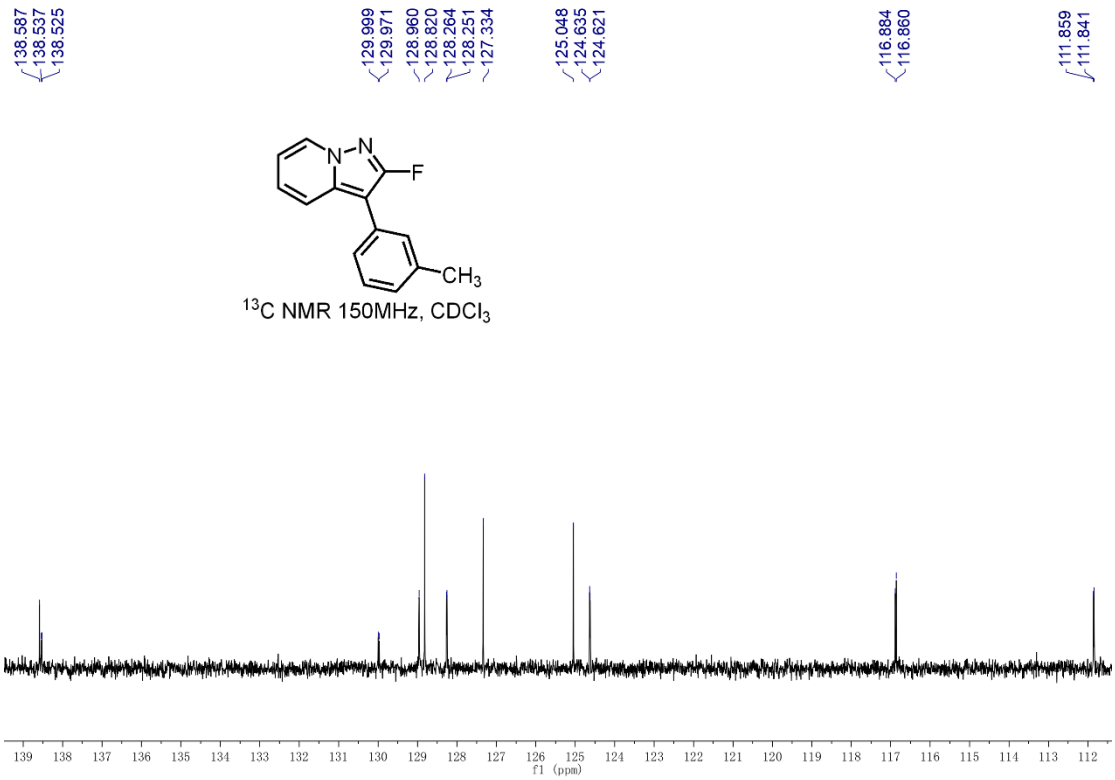




^{19}F NMR 376MHz, $CDCl_3$



^{13}C NMR 150MHz, $CDCl_3$


138.587
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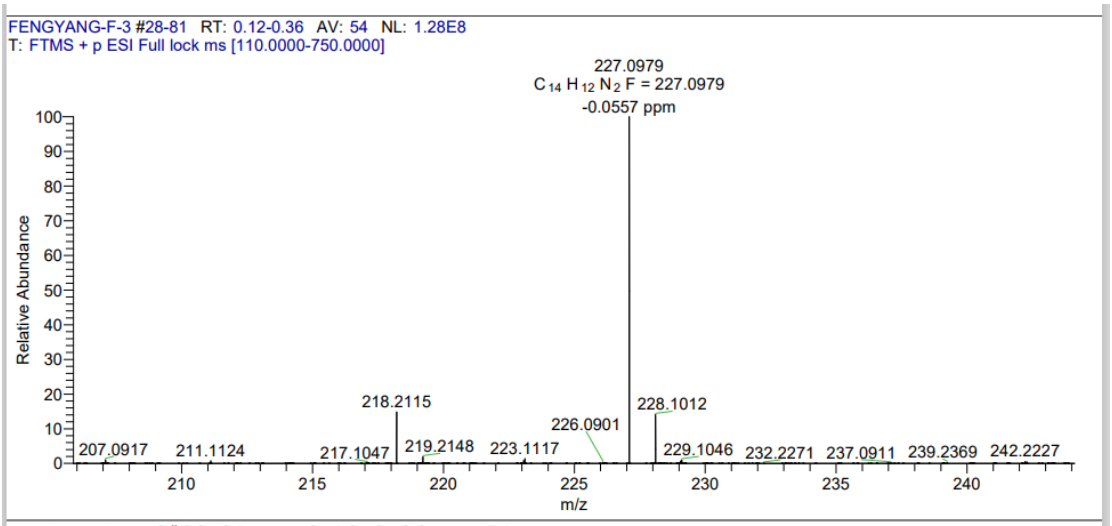
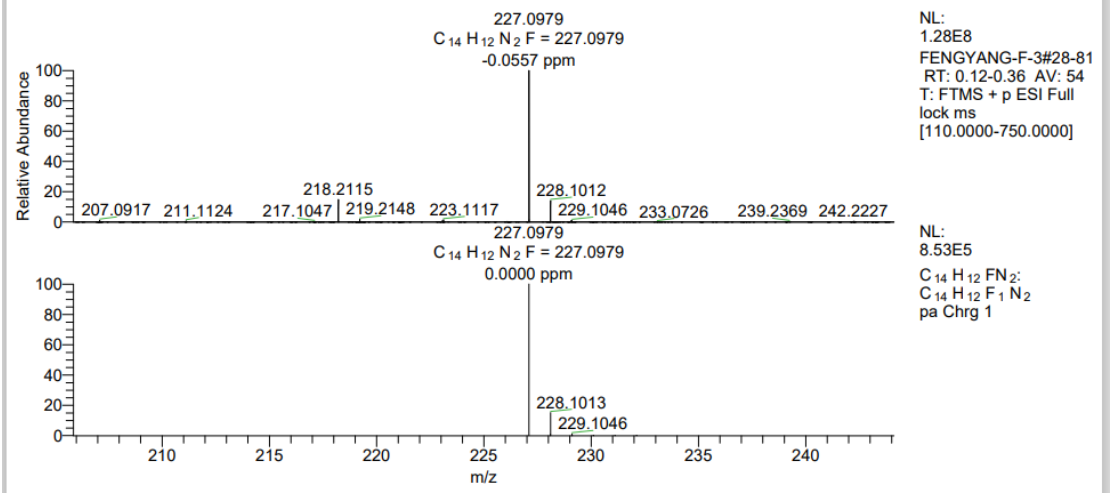
129.999
129.971
128.960
128.820
128.264
128.251
127.334
125.048
124.635
124.621
116.884
116.860
111.859
111.841
N
N
F
CH3
13C NMR 150MHz, CDCl3
139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112
f1 (ppm)

HRMS (ESI) copy of compound **4d**:

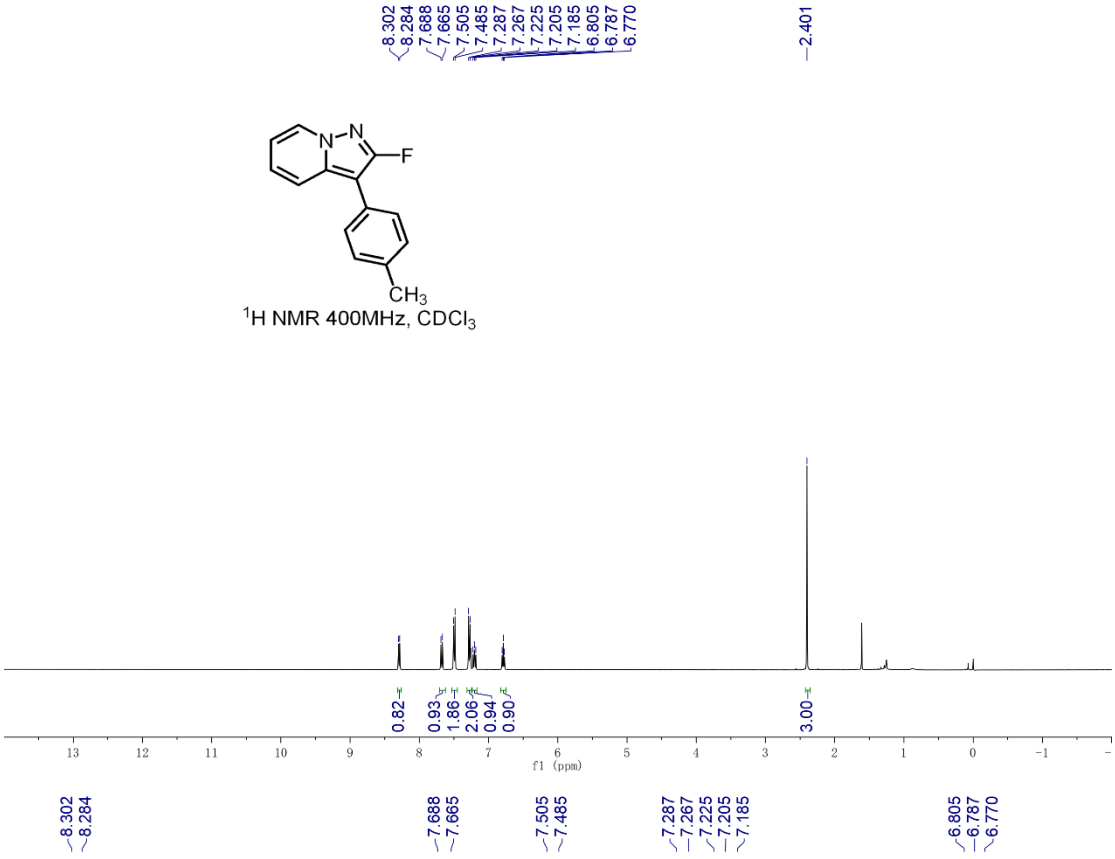


FENGYANG-F-3#28-81 RT: 0.12-0.36 AV: 54
T: FTMS + p ESI Full lock ms [110.0000-750.0000]
m/z= 205.8616-244.1026

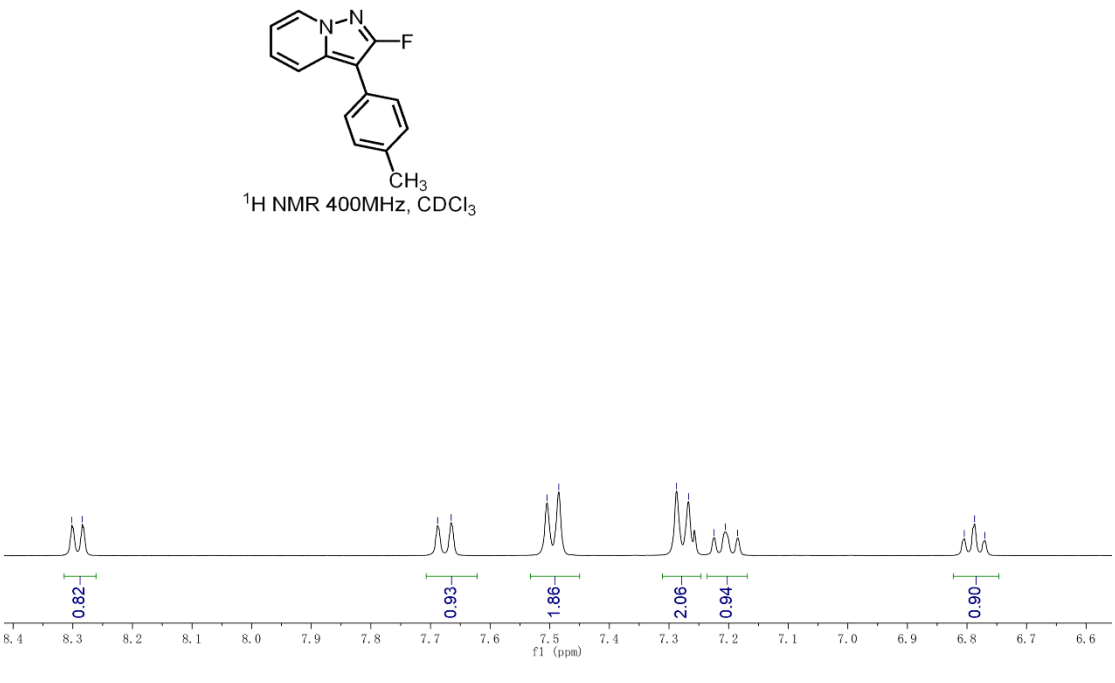
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
218.2115	19313520.0	15.11			
219.2148	2376029.8	1.86			
227.0979	127850728.0	100.00	227.0979	-0.01	C 14 H 12 N 2 F
228.1012	18390356.0	14.38			



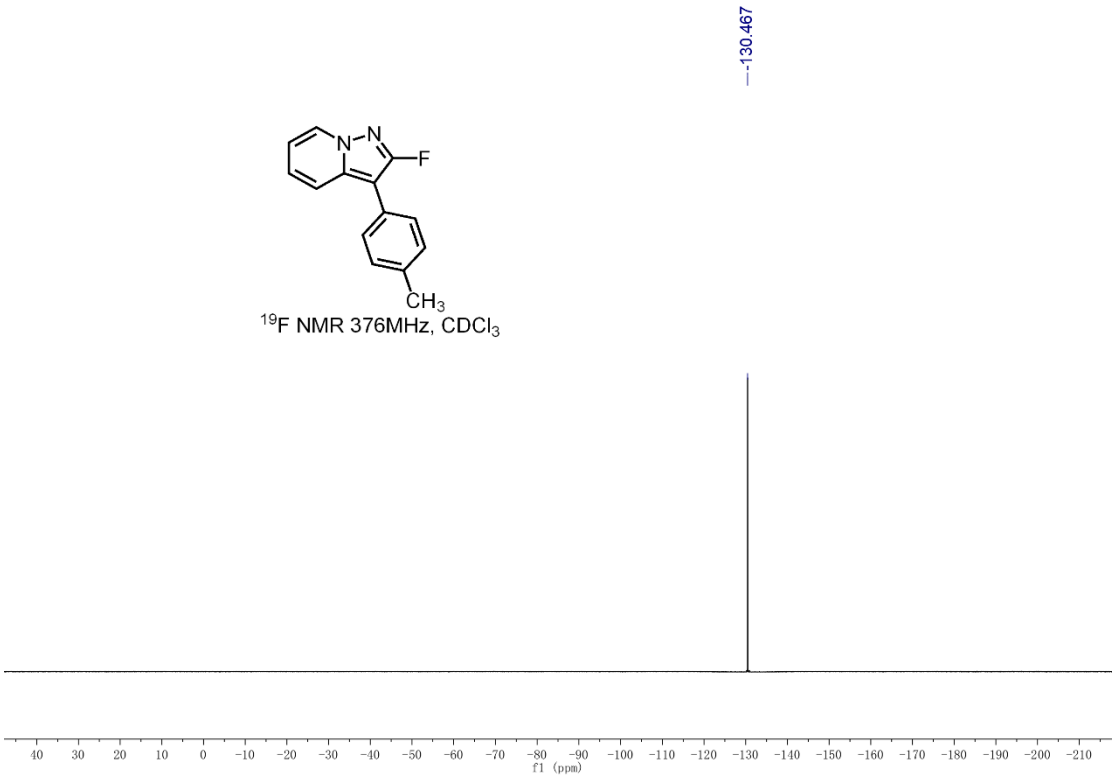
NMR copies of compound **4e:**

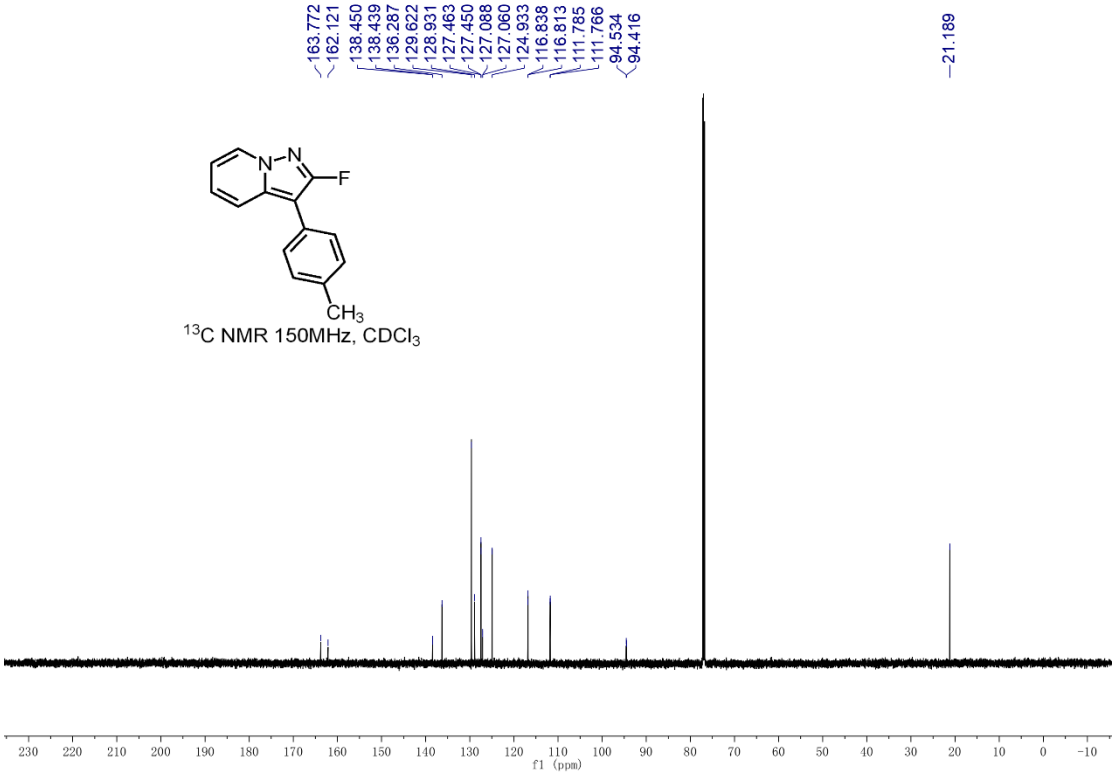


^{1}H NMR 400MHz, $CDCl_3$



^{1}H NMR 400MHz, $CDCl_3$


-130.467
F
CH3
19F NMR 376MHz, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


163.772
162.121
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136.287
129.622
128.931
127.463
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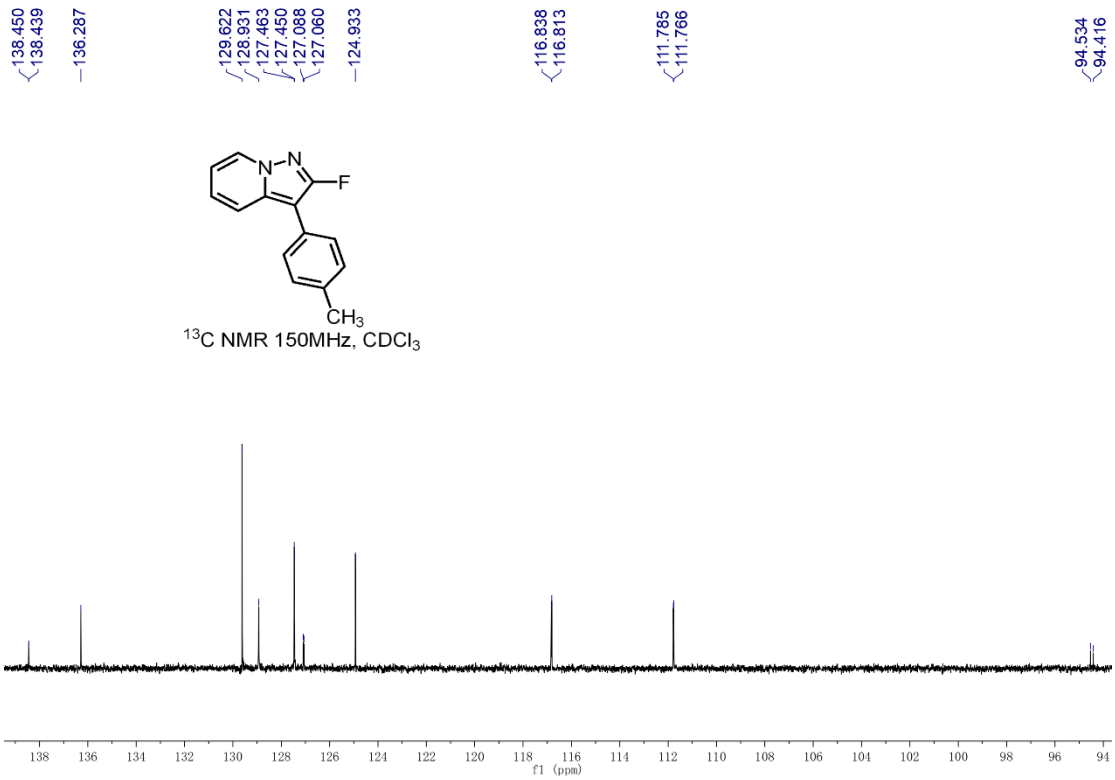
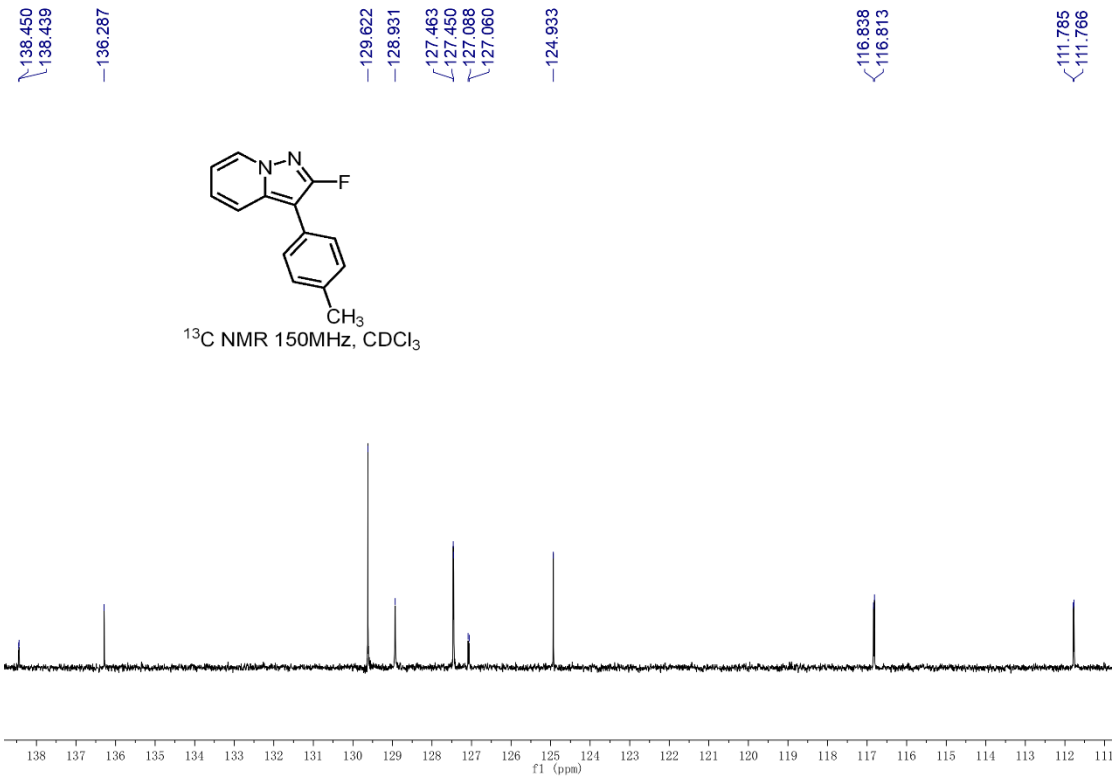
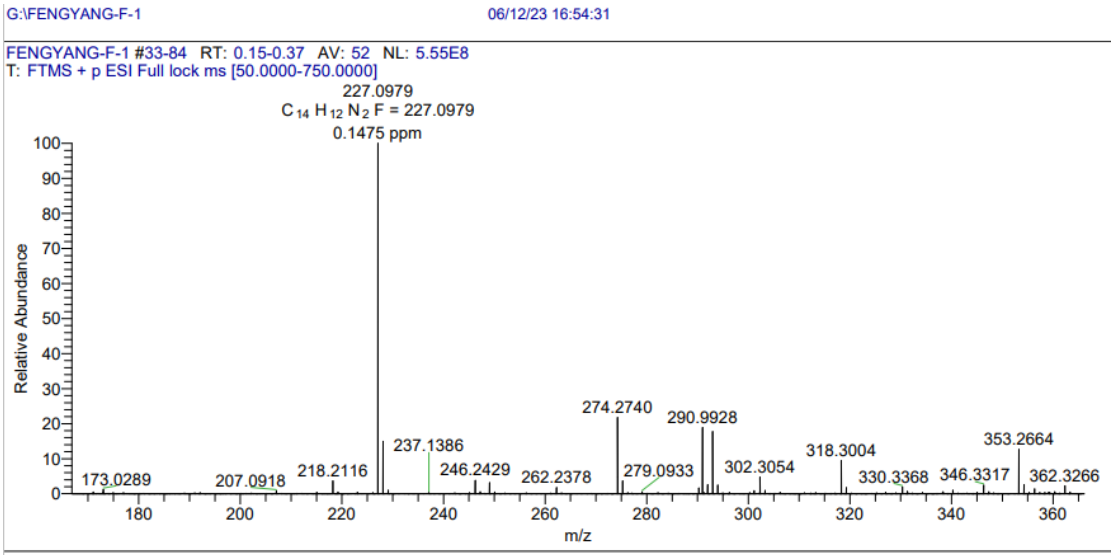
127.088
127.060
124.933
116.838
116.813
111.785
111.766
94.534
94.416
-21.189
F
CH3
13C NMR 150MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


138.450
138.439
136.287
129.622
128.931
127.463
127.450
127.088
127.060
124.933
116.838
116.813
111.785
111.766
94.534
94.416
F
CH3
13C NMR 150MHz, CDCl3
f1 (ppm)

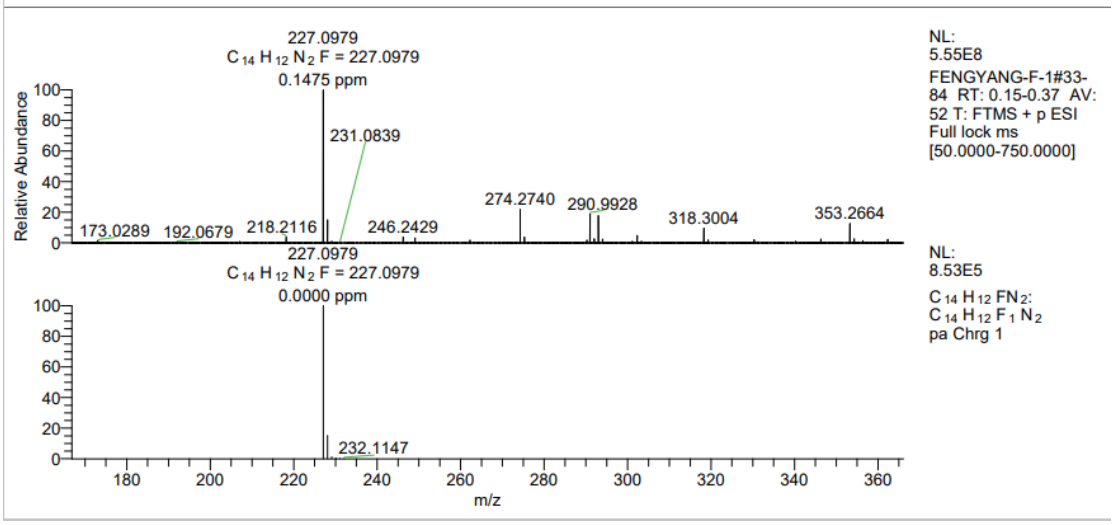

138.450
138.439
136.287
129.622
128.931
127.463
127.450
127.088
127.060
124.933
116.838
116.813
111.785
111.766
F
CH3
13C NMR 150MHz, CDCl3
f1 (ppm)

HRMS (ESI) copy of compound **4e**:

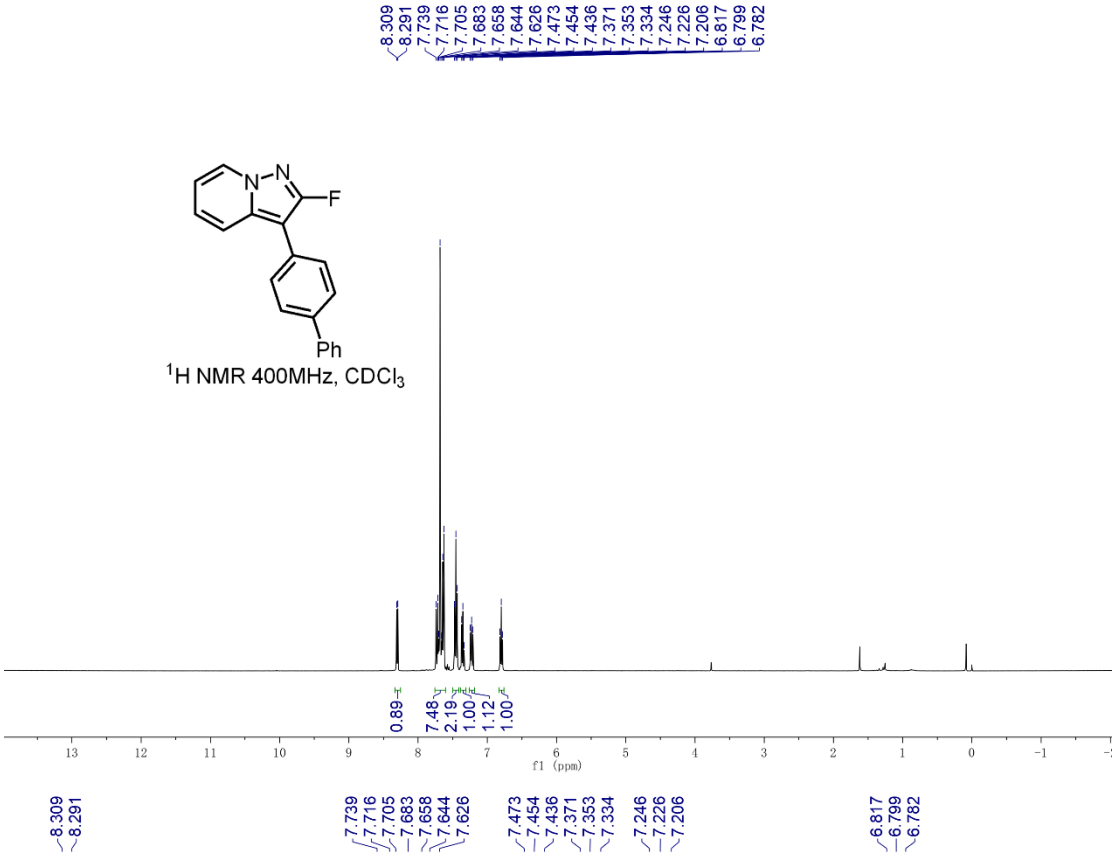


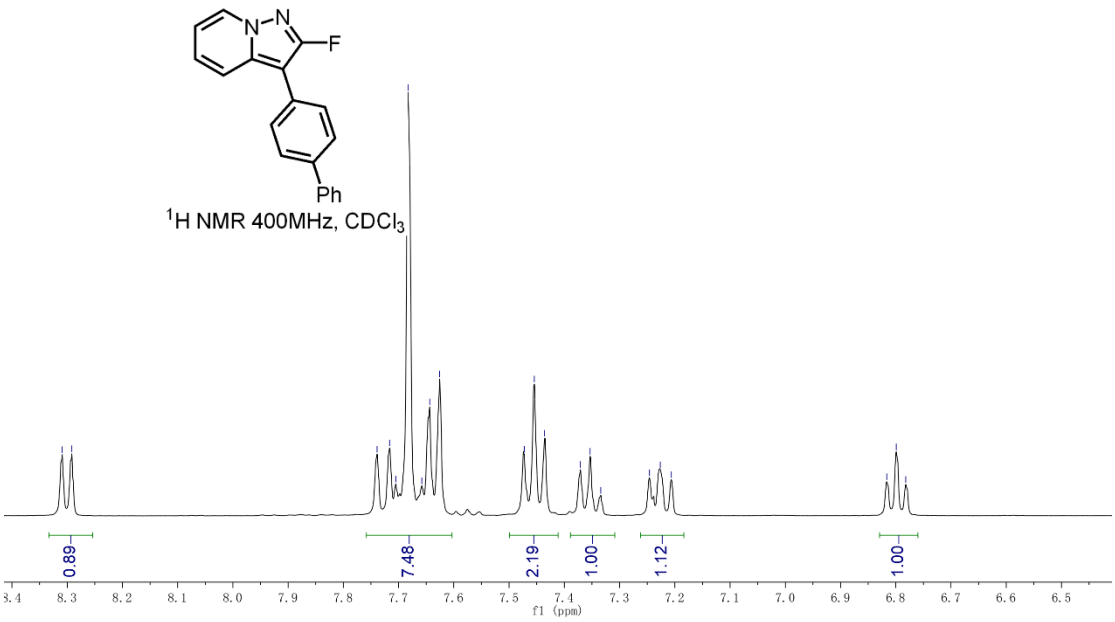
FENGYANG-F-1#33-84 RT: 0.15-0.37 AV: 52
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 166.8237-366.0834

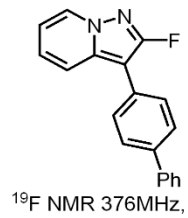
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
227.0979	556098944.0	100.00	227.0979	0.03	$C_{14}H_{12}N_2F$
274.2740	121283104.0	21.81			
290.9928	105524232.0	18.98			
292.9907	100893896.0	18.14			



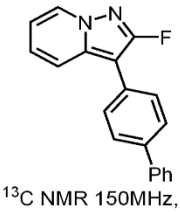
NMR copies of compound **4f:**



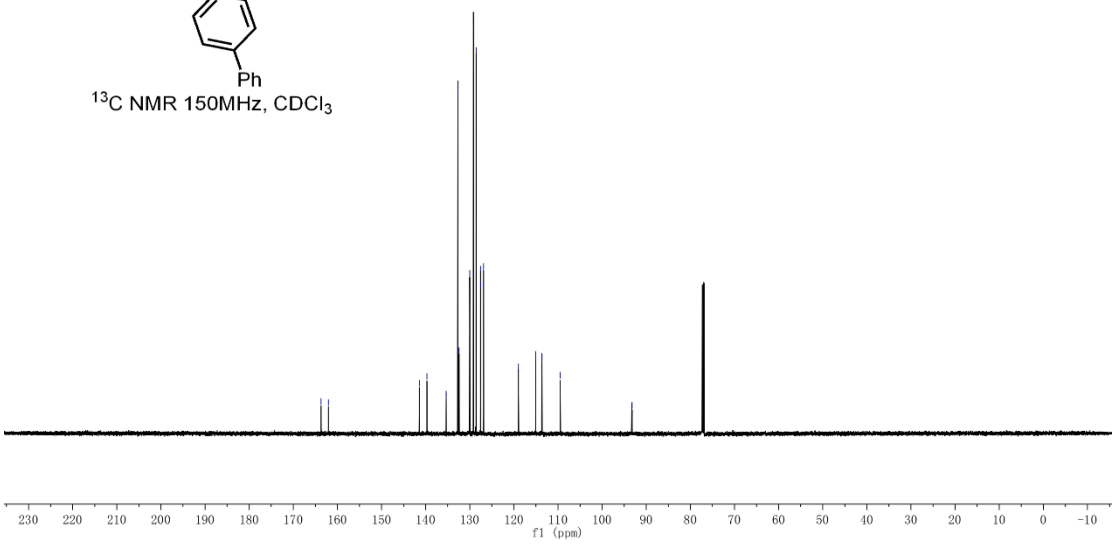


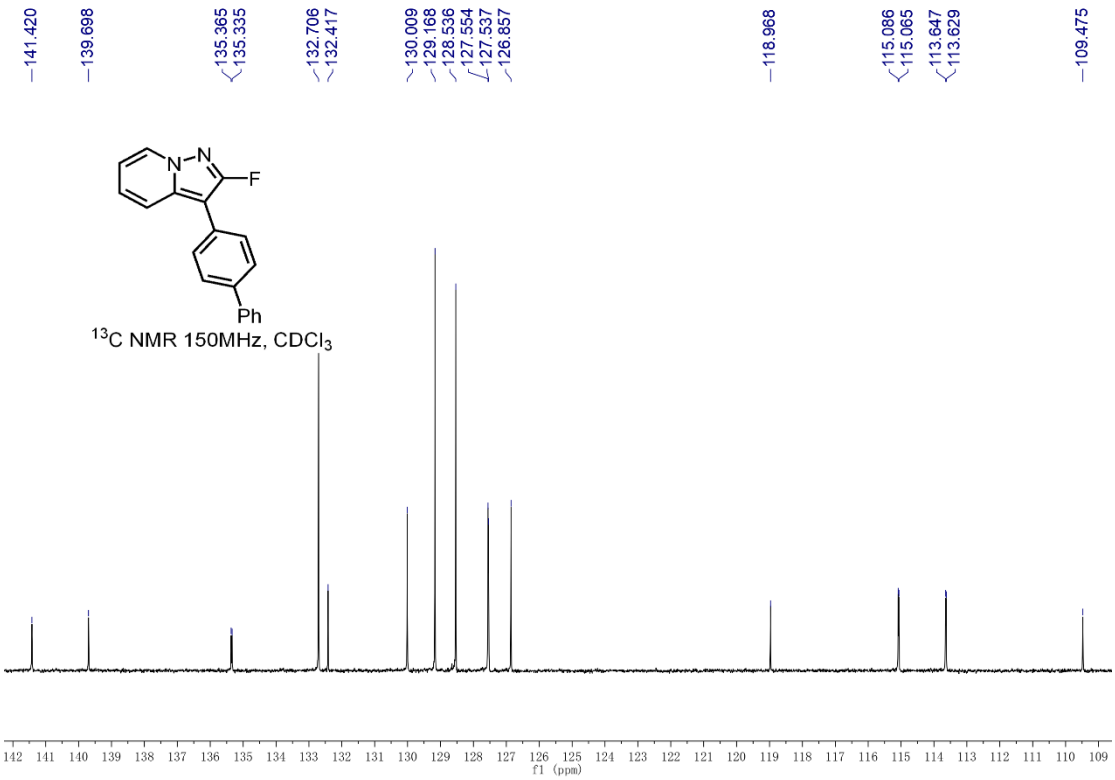


^{19}F NMR 376MHz, $CDCl_3$

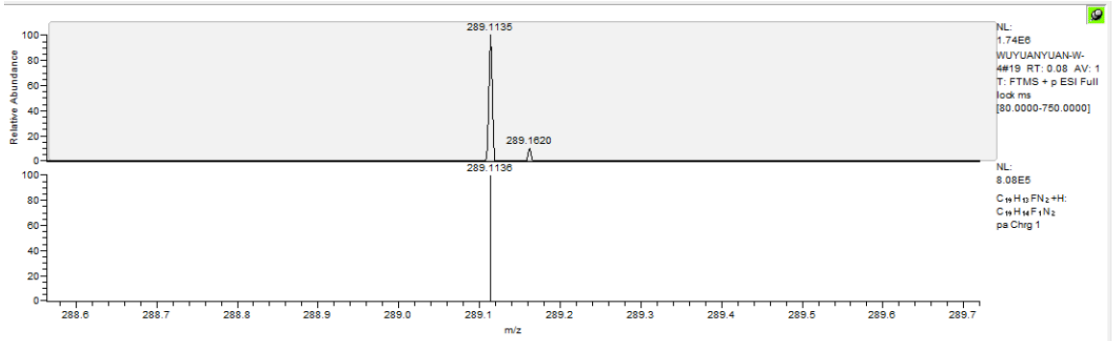


^{13}C NMR 150MHz, $CDCl_3$

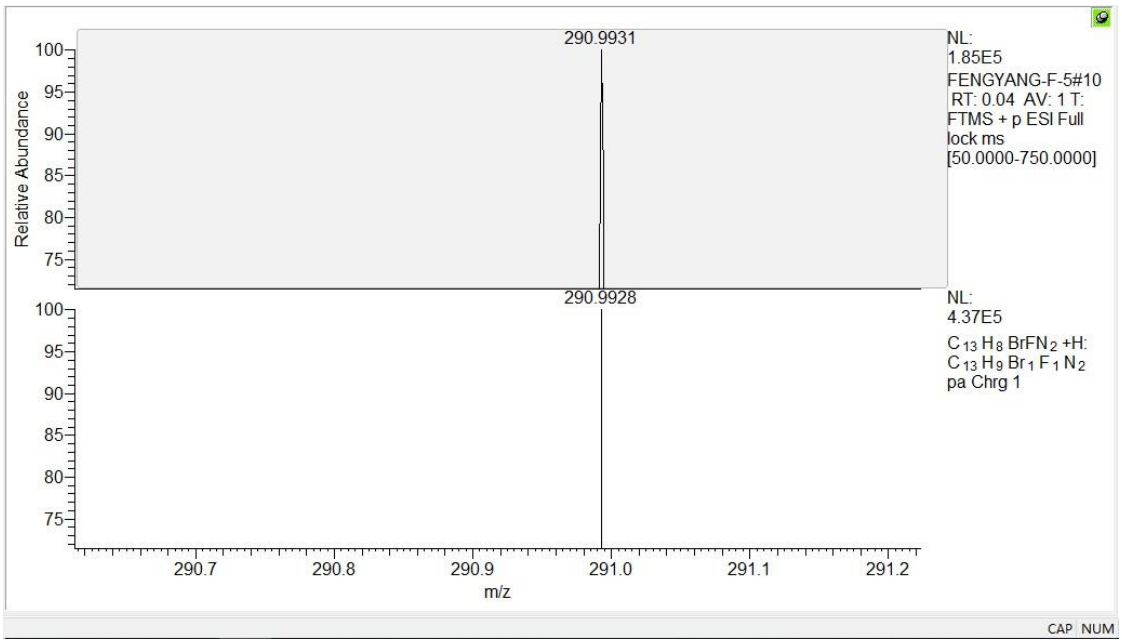




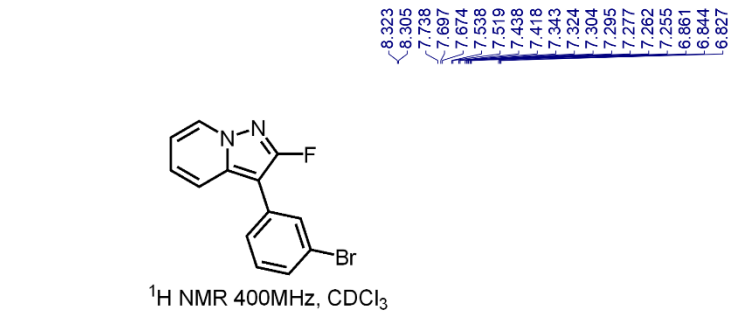
HRMS (ESI) copy of compound **4f**:



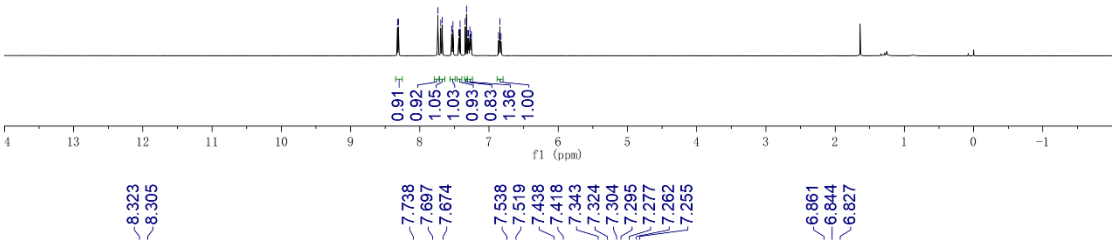
HRMS (ESI) copy of compound **4g**:

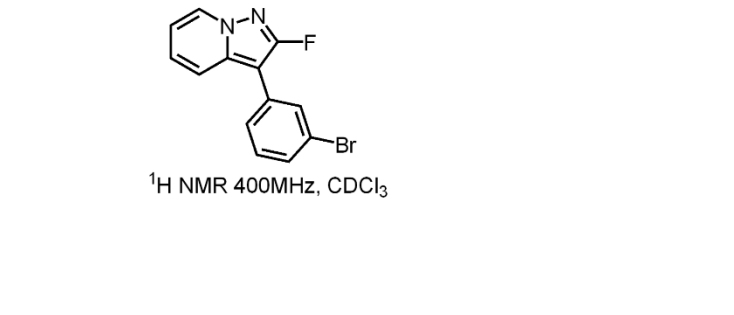


NMR copies of compound **4h:**

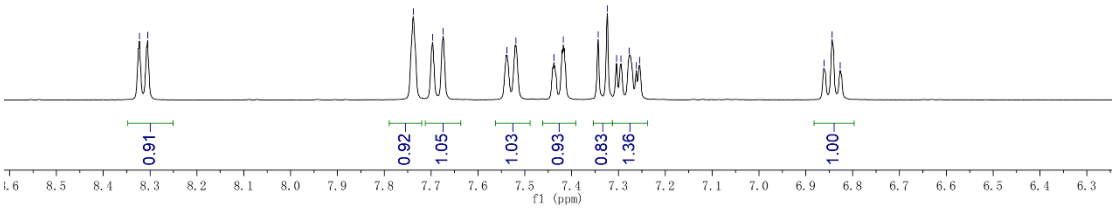


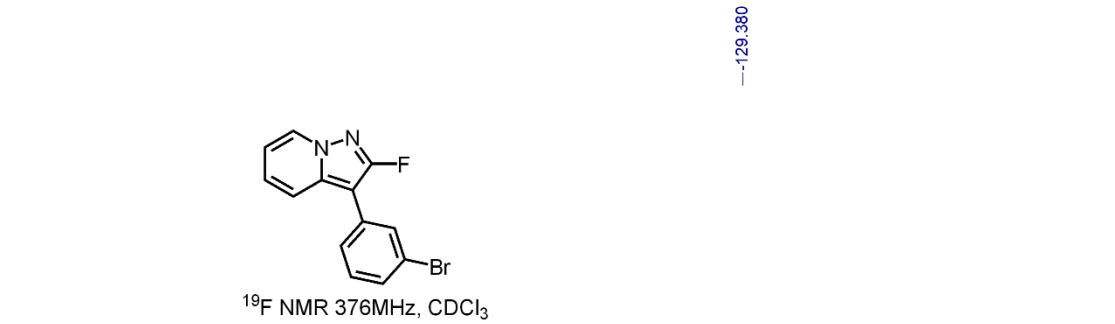
^{1}H NMR 400MHz, $CDCl_3$



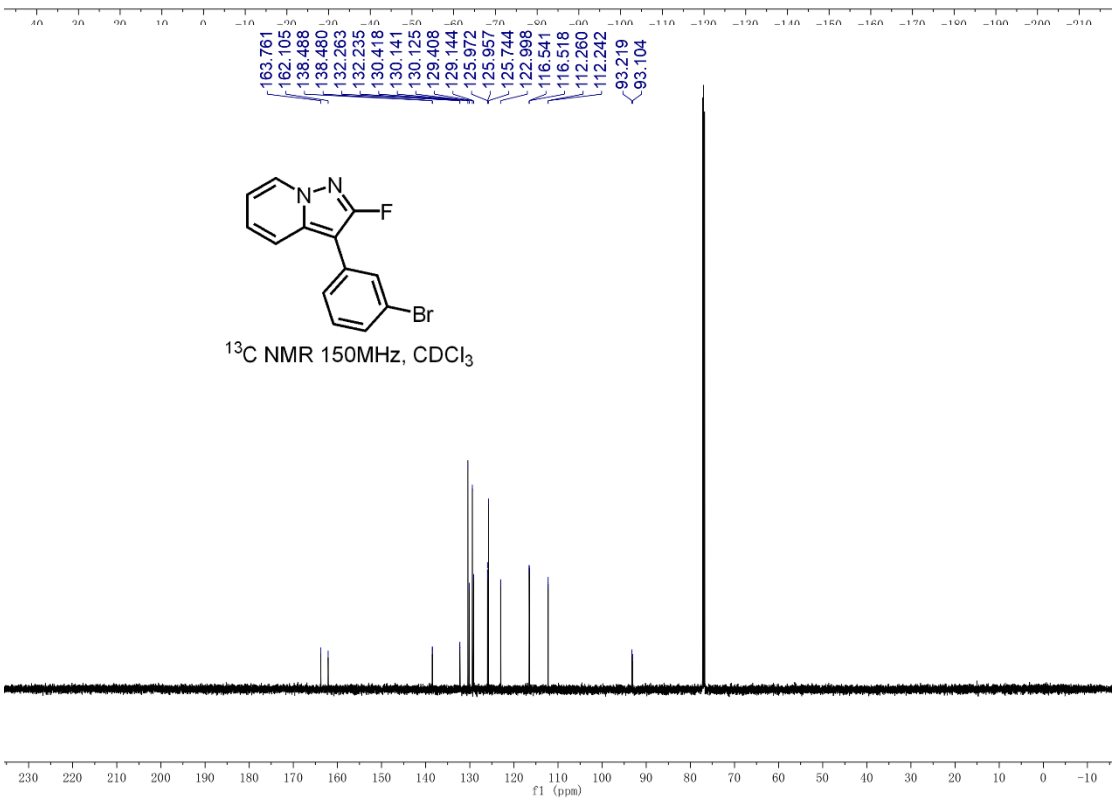


^{1}H NMR 400MHz, $CDCl_3$

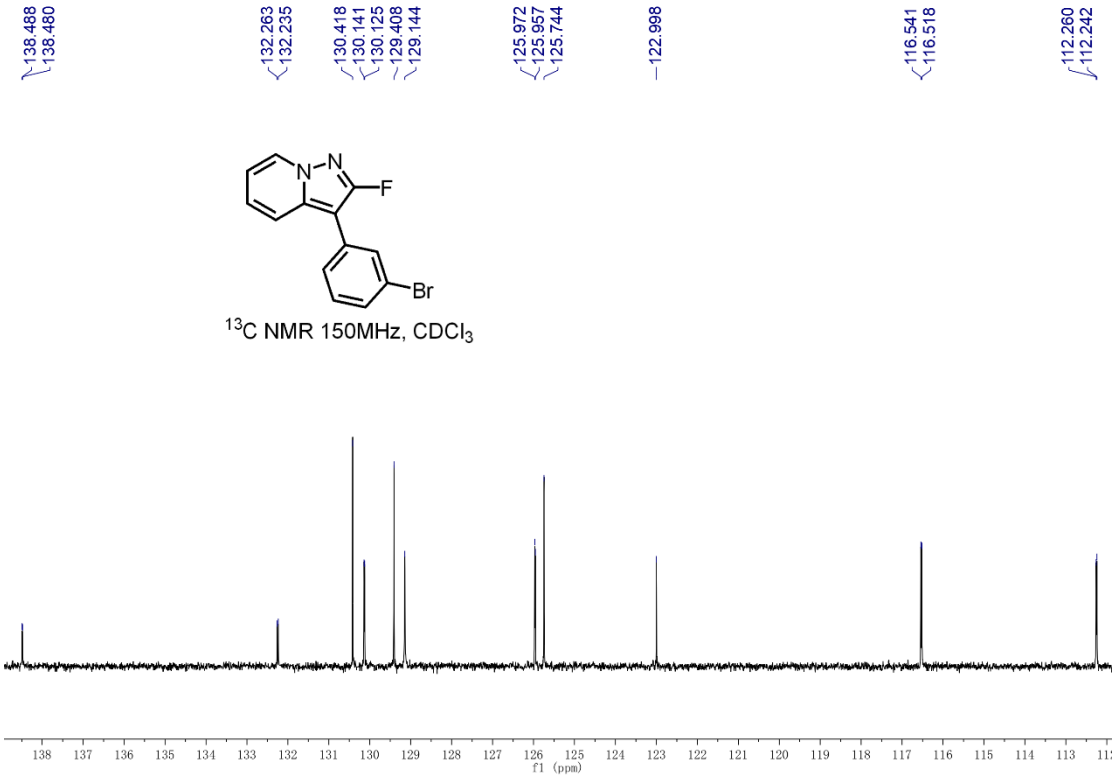


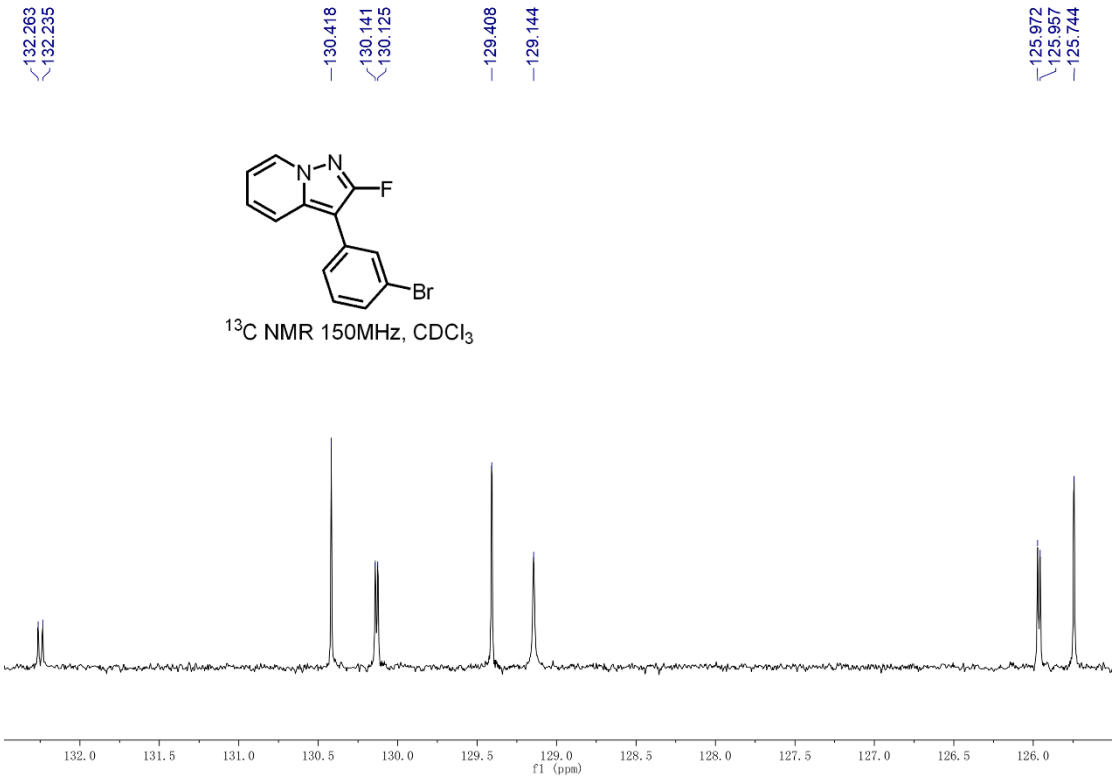


^{19}F NMR 376MHz, $CDCl_3$

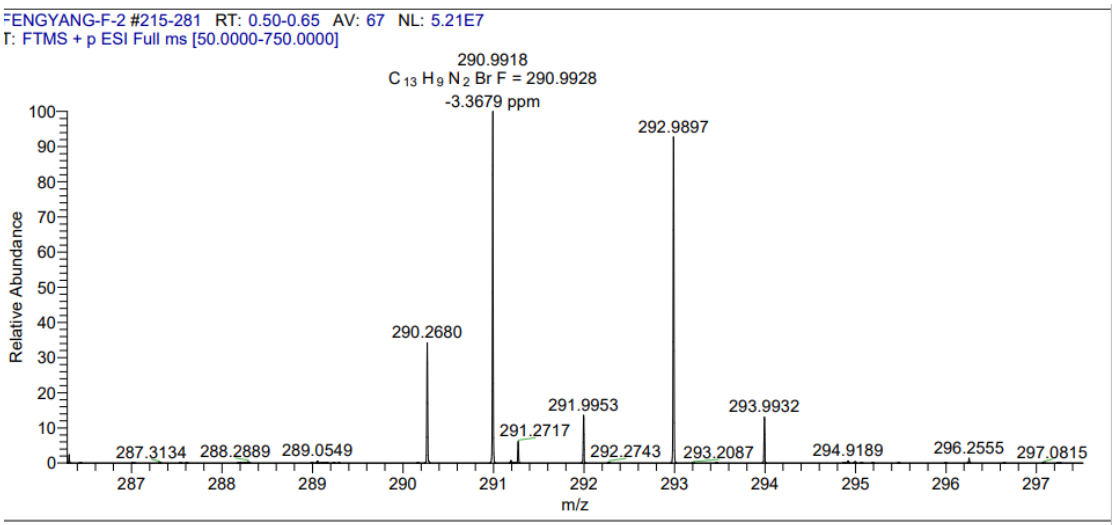


^{13}C NMR 150MHz, $CDCl_3$


138.488
138.480
132.263
132.235
130.418
130.141
130.125
129.408
129.144
125.972
125.957
125.744
122.998
116.541
116.518
112.260
112.242
N
N
F
Br
13C NMR 150MHz, CDCl3
138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113
f1 (ppm)

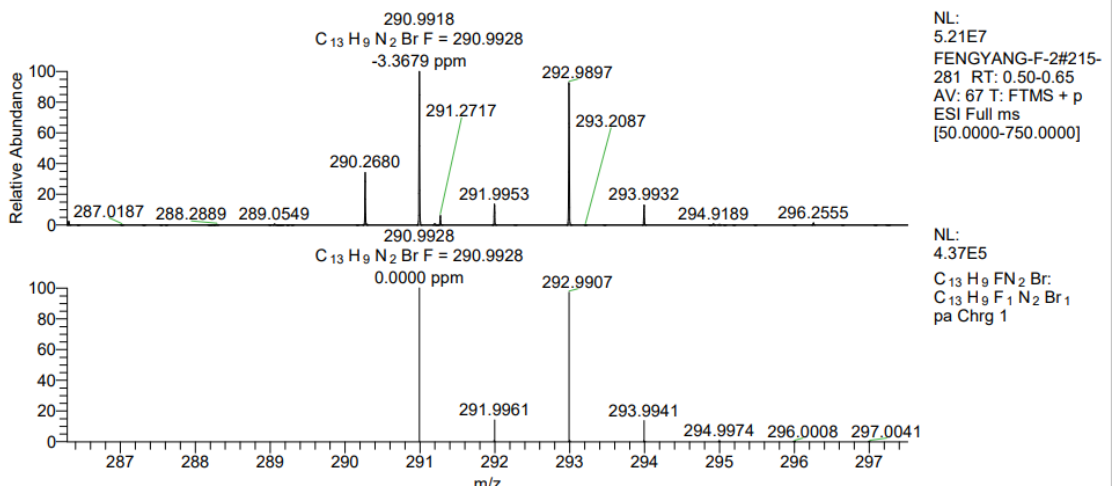

132.263
132.235
130.418
130.141
130.125
129.408
129.144
125.972
125.957
125.744
N
N
F
Br
13C NMR 150MHz, CDCl3
132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
f1 (ppm)

HRMS (ESI) copy of compound **4h**:

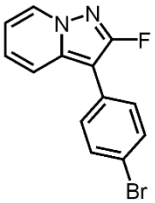


FENGYANG-F-2#215-281 RT: 0.50-0.65 AV: 67
T: FTMS + p ESI Full ms [50.0000-750.0000]
m/z= 289.3336-300.5581

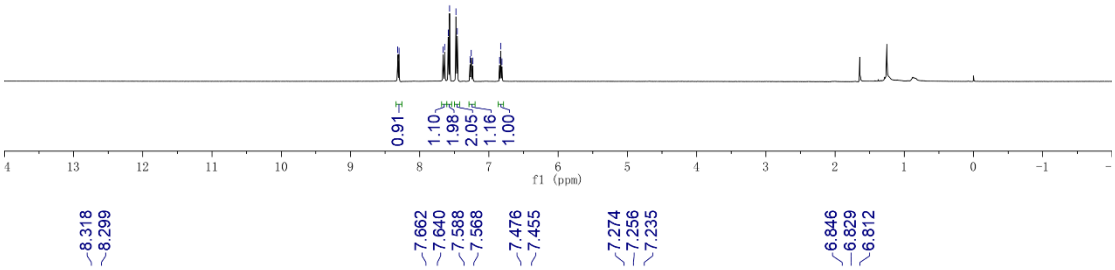
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
290.2680	17796842.0	34.18			
290.9918	52073392.0	100.00	290.9928	-0.98	$C_{13}H_9N_2BrF$
291.9953	7154697.5	13.74			
292.9897	49834656.0	95.70			

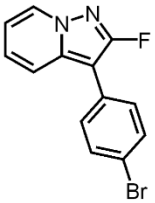


NMR copies of compound **4i:**

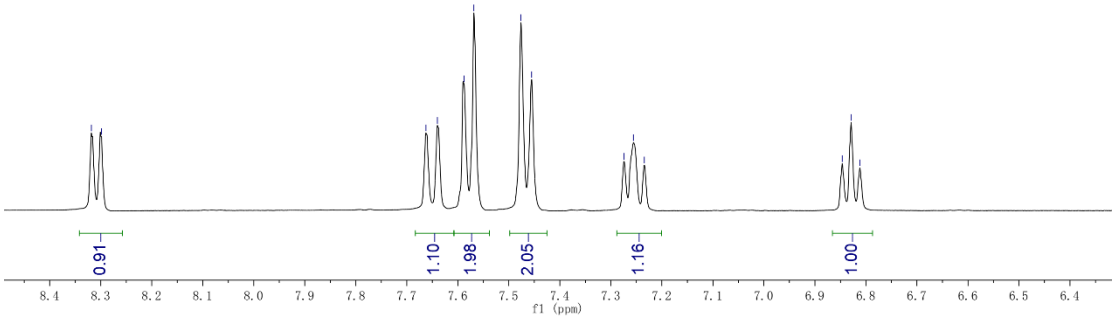


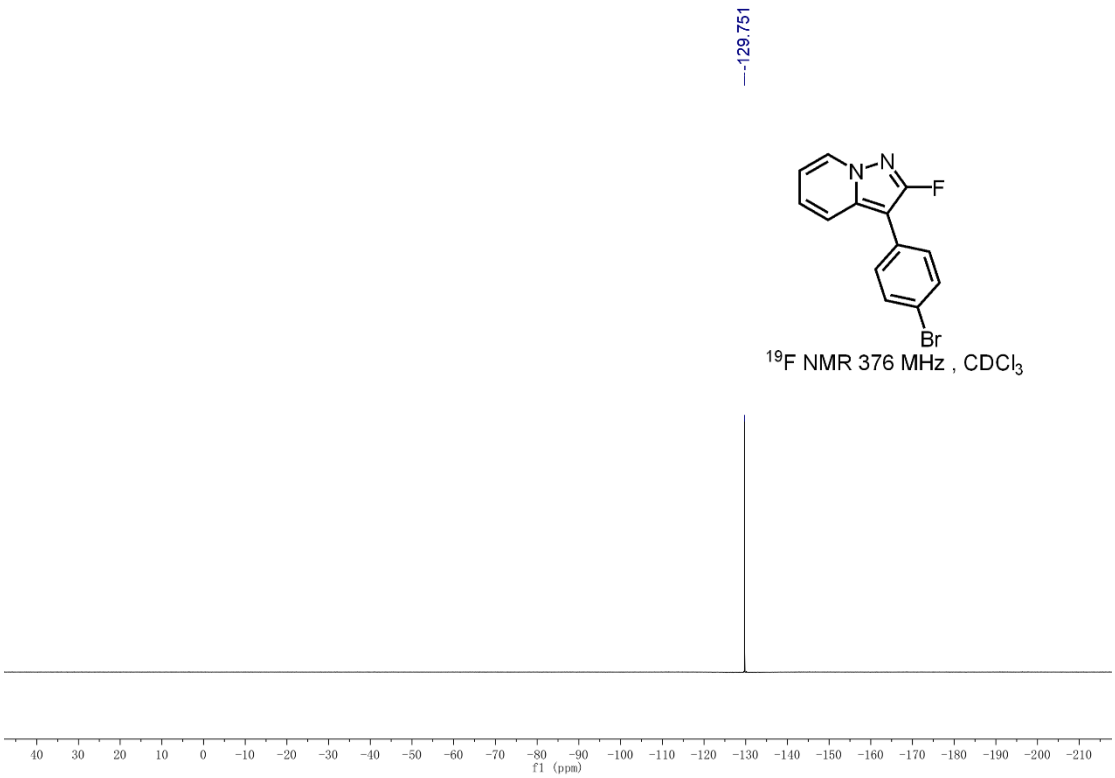
^{1}H NMR 400 MHz , $CDCl_3$



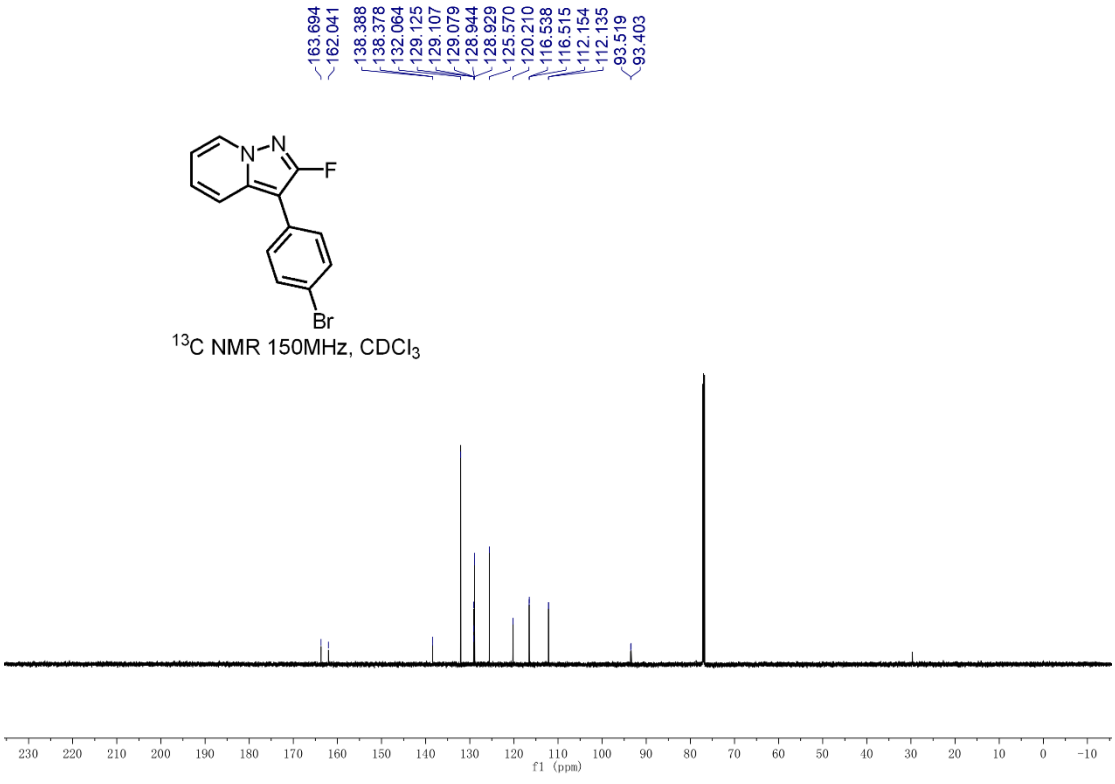


^{1}H NMR 400 MHz , $CDCl_3$

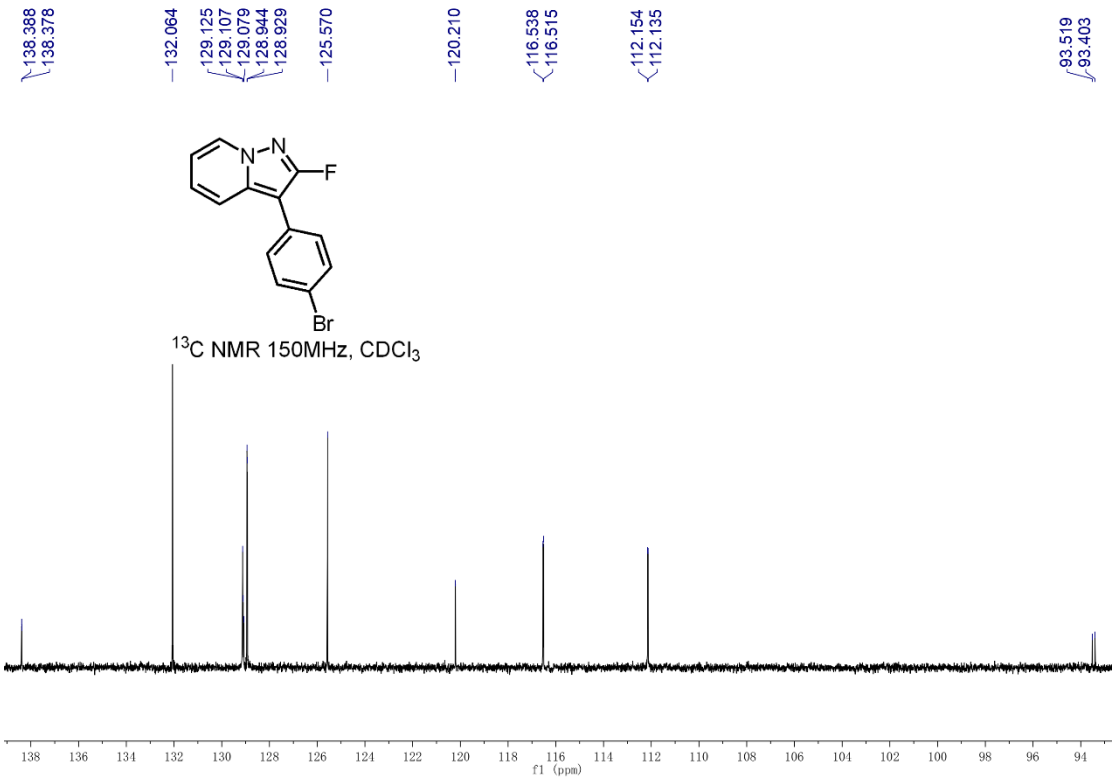


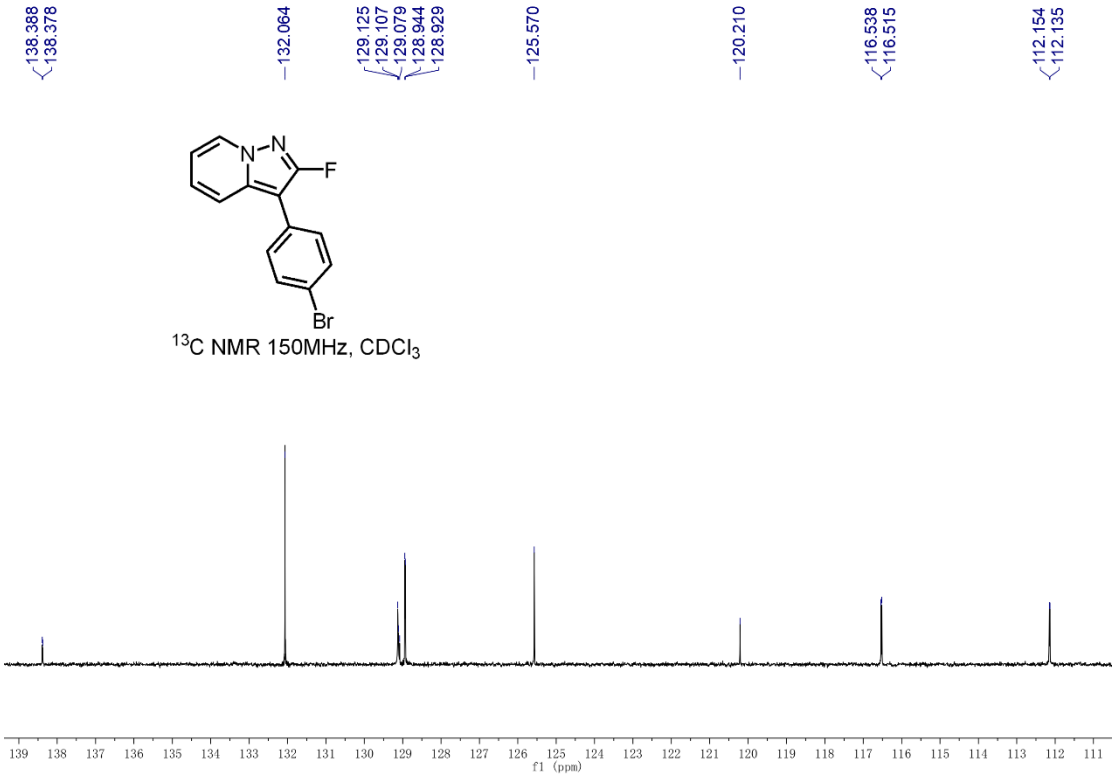


^{19}F NMR 376 MHz , $CDCl_3$

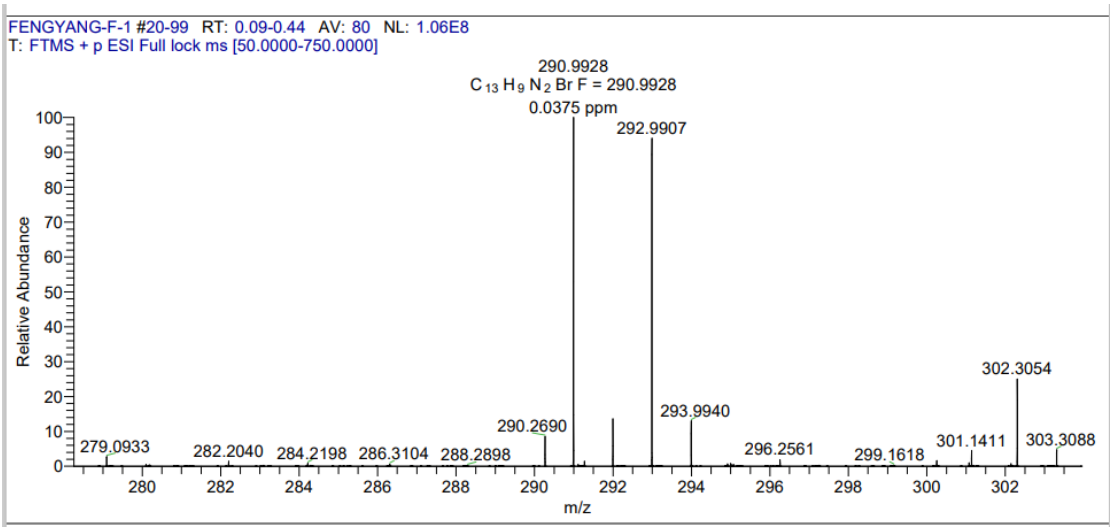


^{13}C NMR 150MHz, $CDCl_3$


138.388
138.378
132.064
129.125
129.107
129.079
128.944
128.929
125.570
120.210
116.538
116.515
112.154
112.135
93.519
93.403
N
N
F
Br
13C NMR 150MHz, CDCl3
138 136 134 132 130 128 126 124 122 120 118 116 114 112 110 108 106 104 102 100 98 96 94
f1 (ppm)

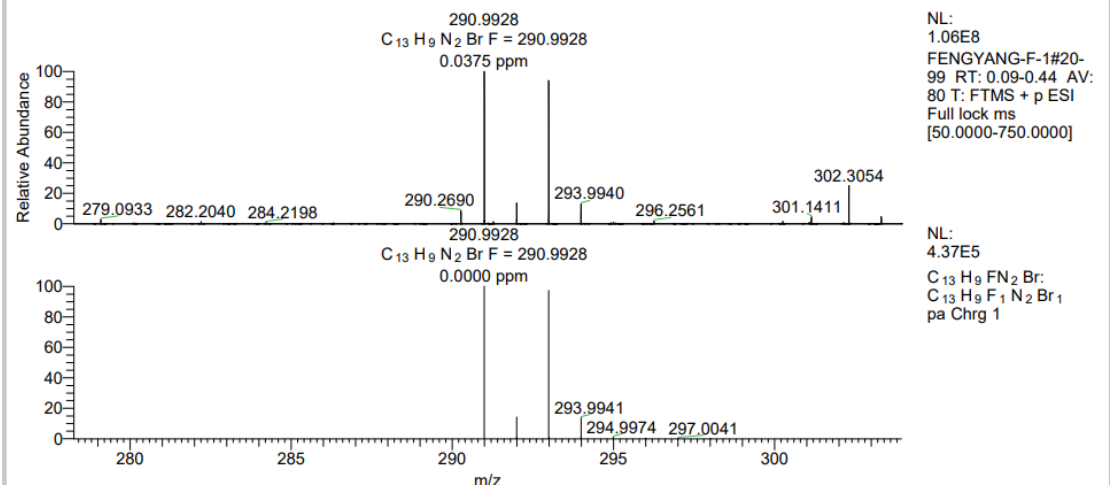

138.388
138.378
132.064
129.125
129.107
129.079
128.944
128.929
125.570
120.210
116.538
116.515
112.154
112.135
N
N
F
Br
13C NMR 150MHz, CDCl3
139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112 111
f1 (ppm)

HRMS (ESI) copy of compound **4i**:

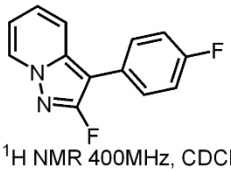


FENGYANG-F-1#20-99 RT: 0.09-0.44 AV: 80
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 278.2546-303.9316

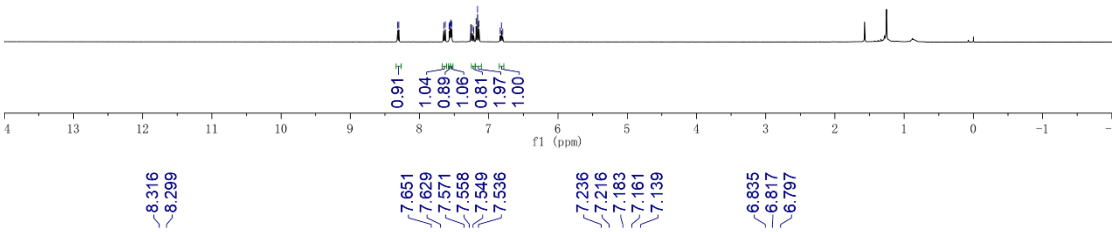
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
290.9928	106855304.0	100.00	290.9928	0.01	$C_{13}H_9N_2BrF$
291.9961	14480088.0	13.55			
292.9907	102131216.0	95.58			
302.3054	26627254.0	24.92			

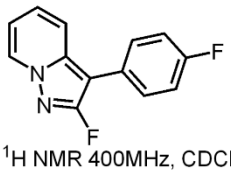


NMR copies of compound **4j:**

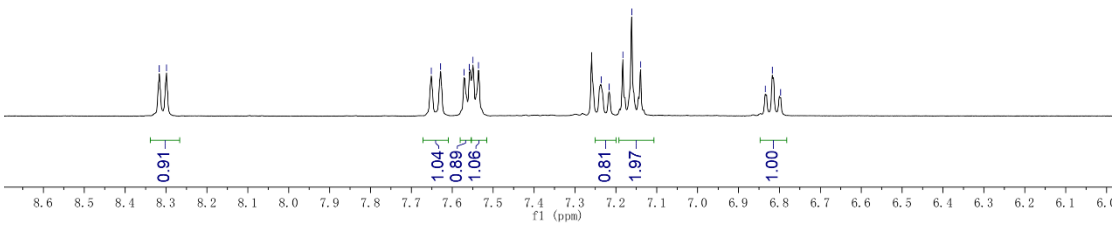


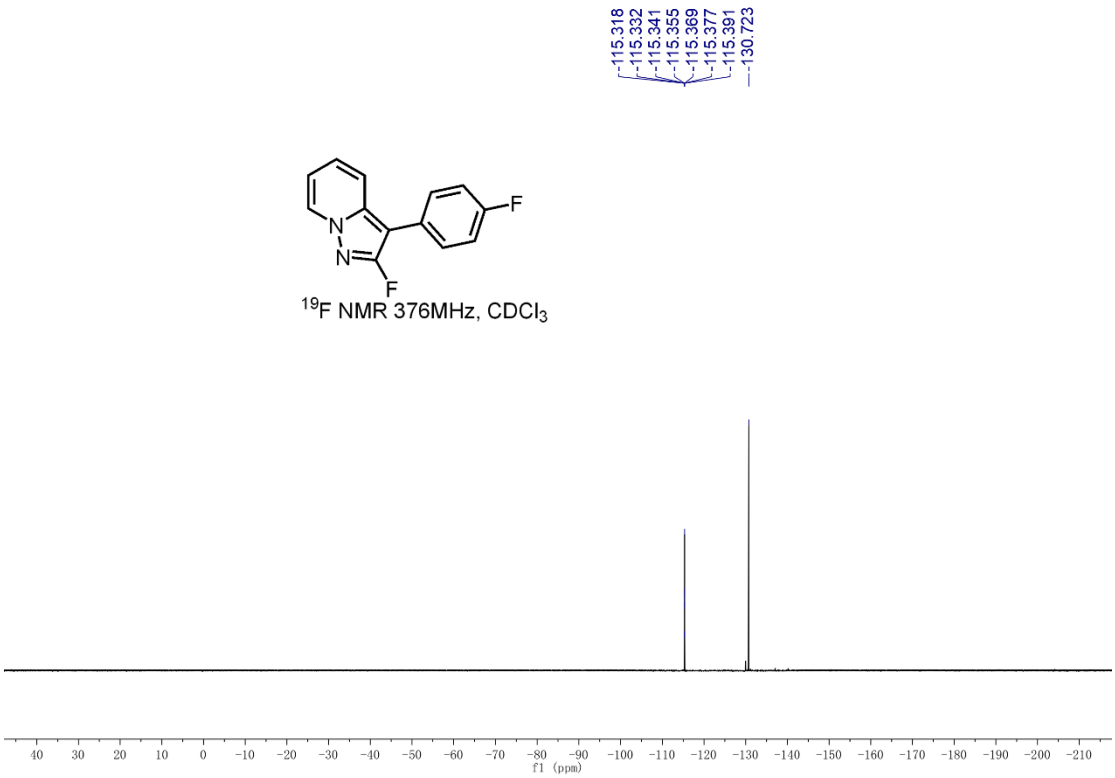
^{1}H NMR 400MHz, $CDCl_3$



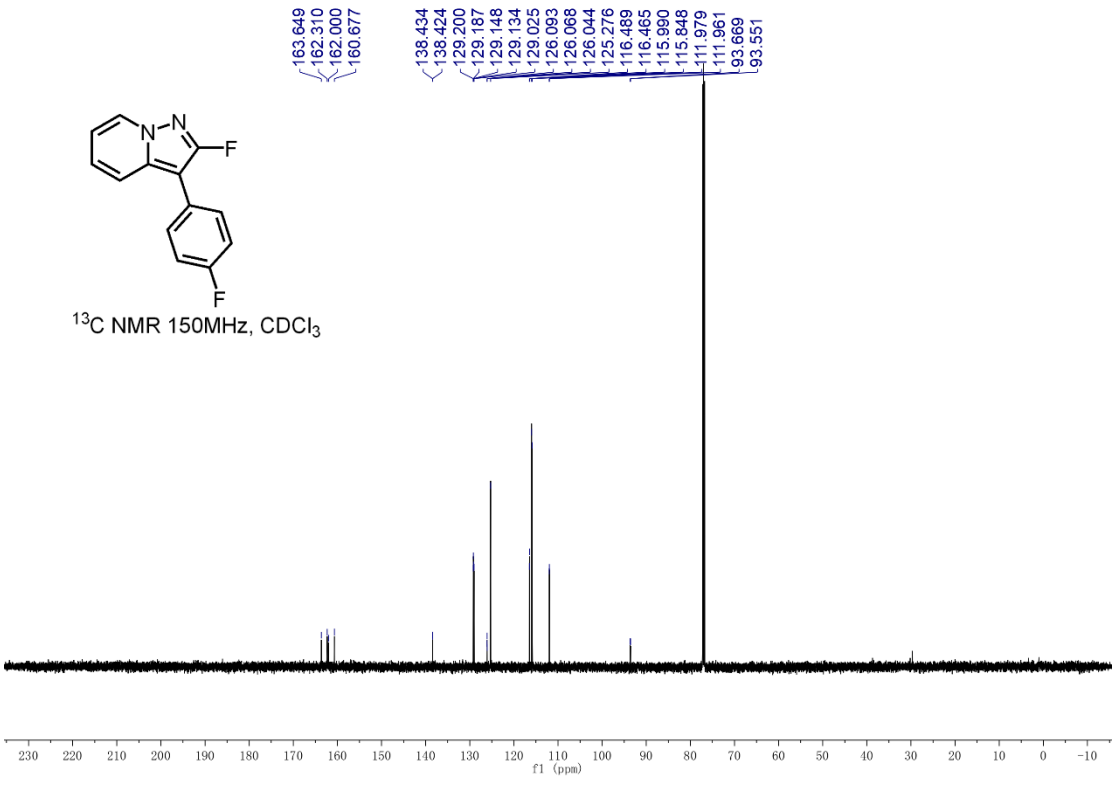


^{1}H NMR 400MHz, $CDCl_3$

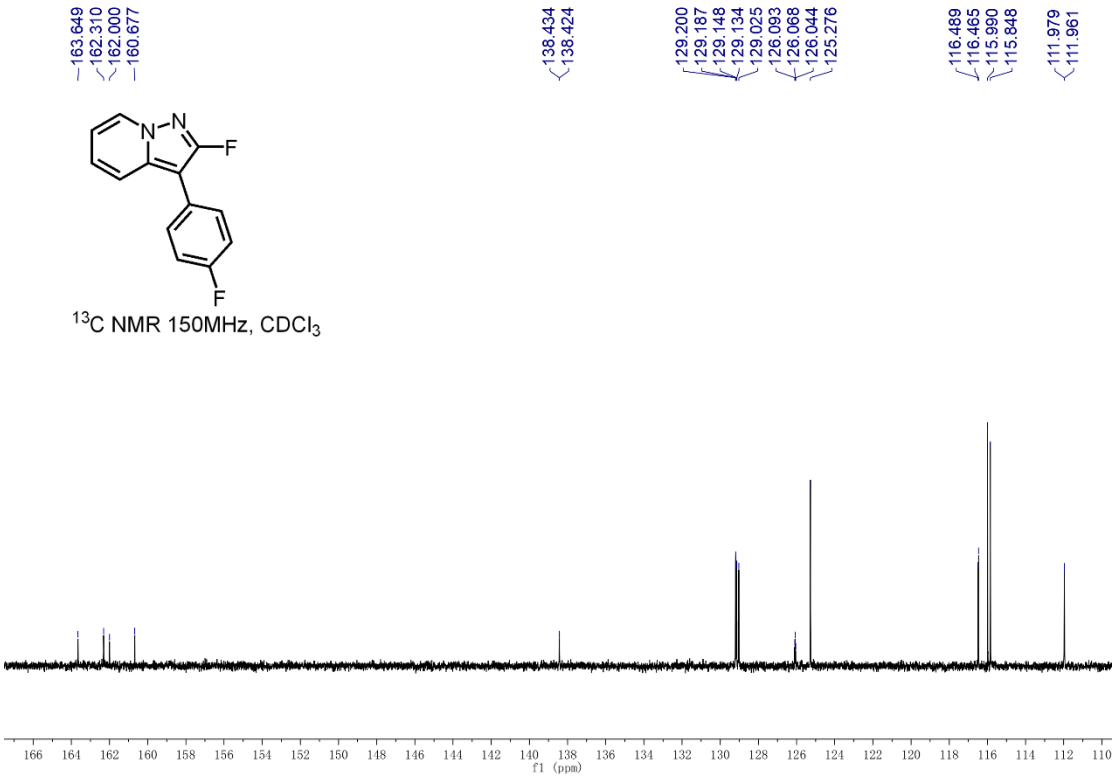




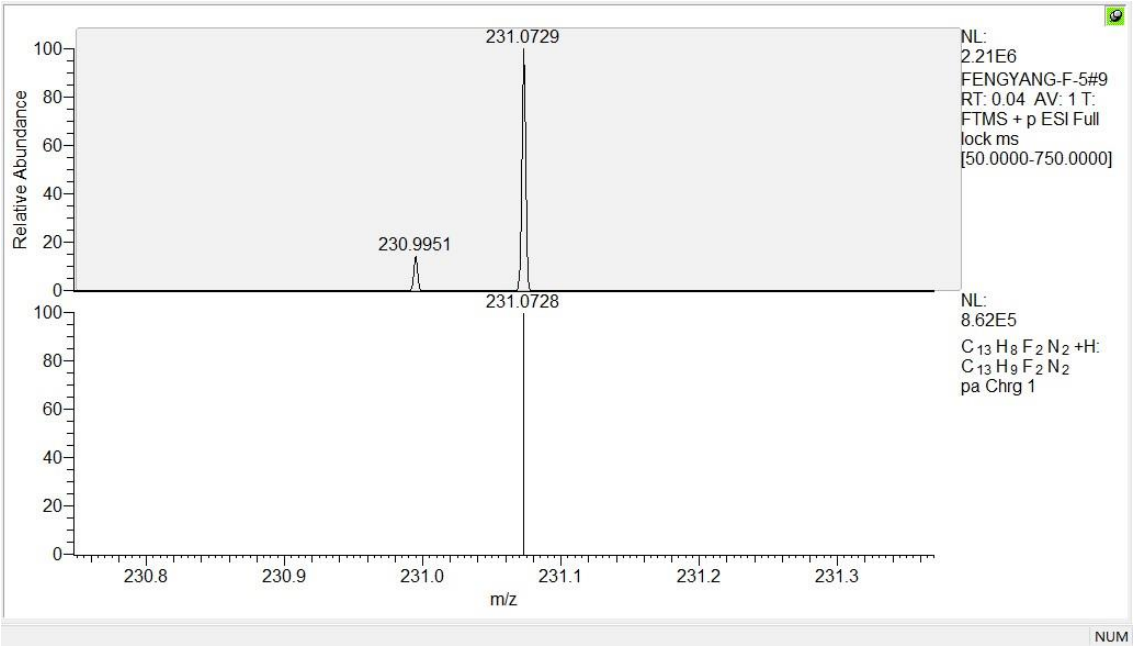
^{19}F NMR 376MHz, $CDCl_3$



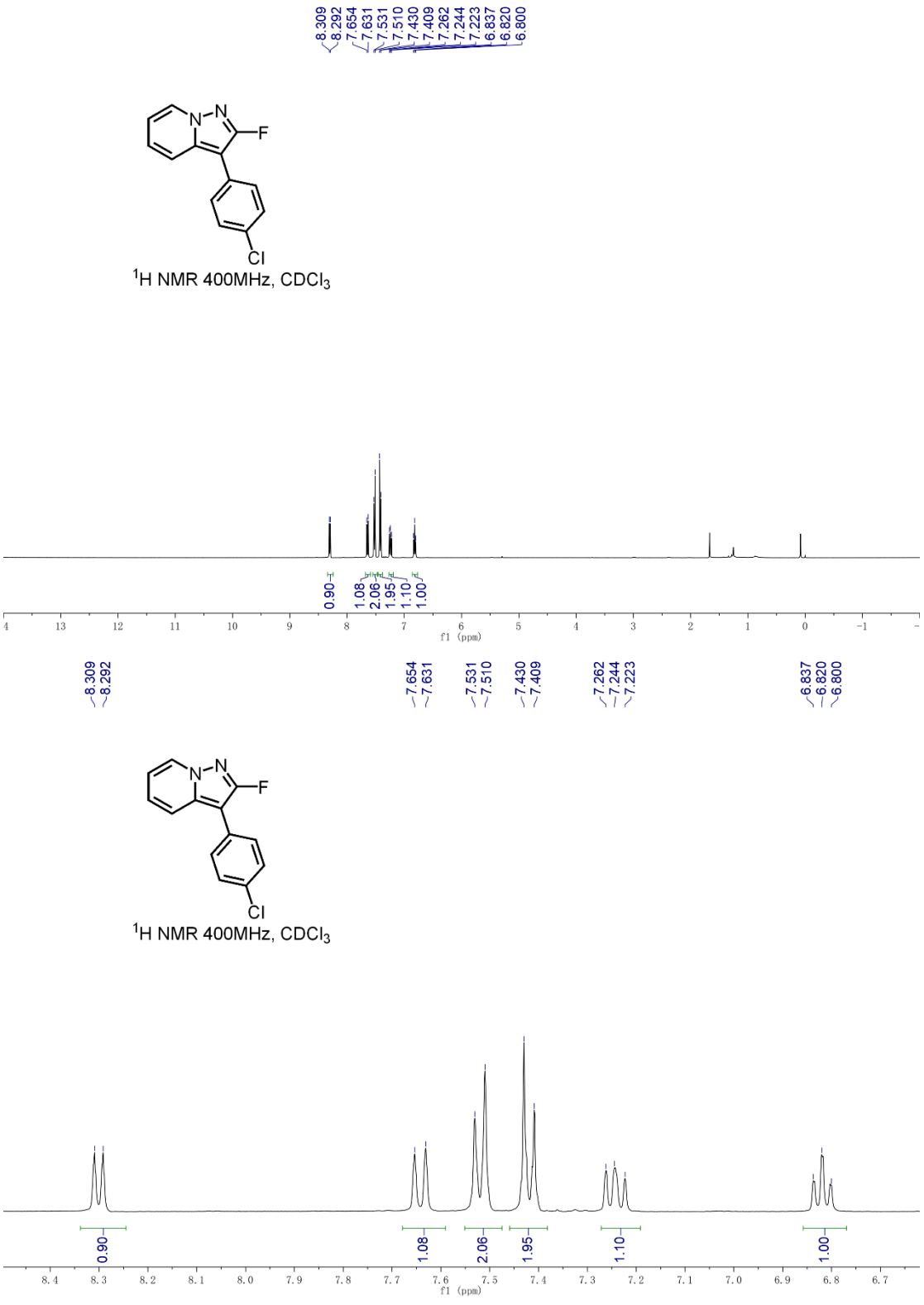
^{13}C NMR 150MHz, $CDCl_3$

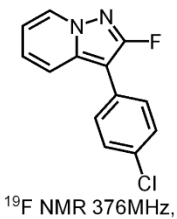


HRMS (ESI) copy of compound **4j**:

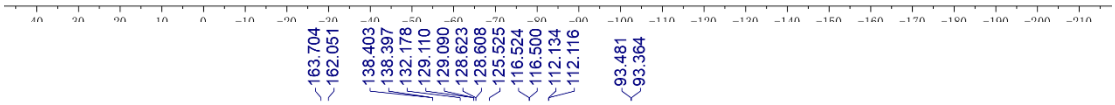


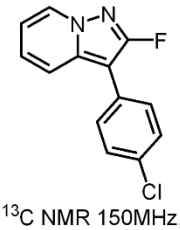
NMR copies of compound **4k:**



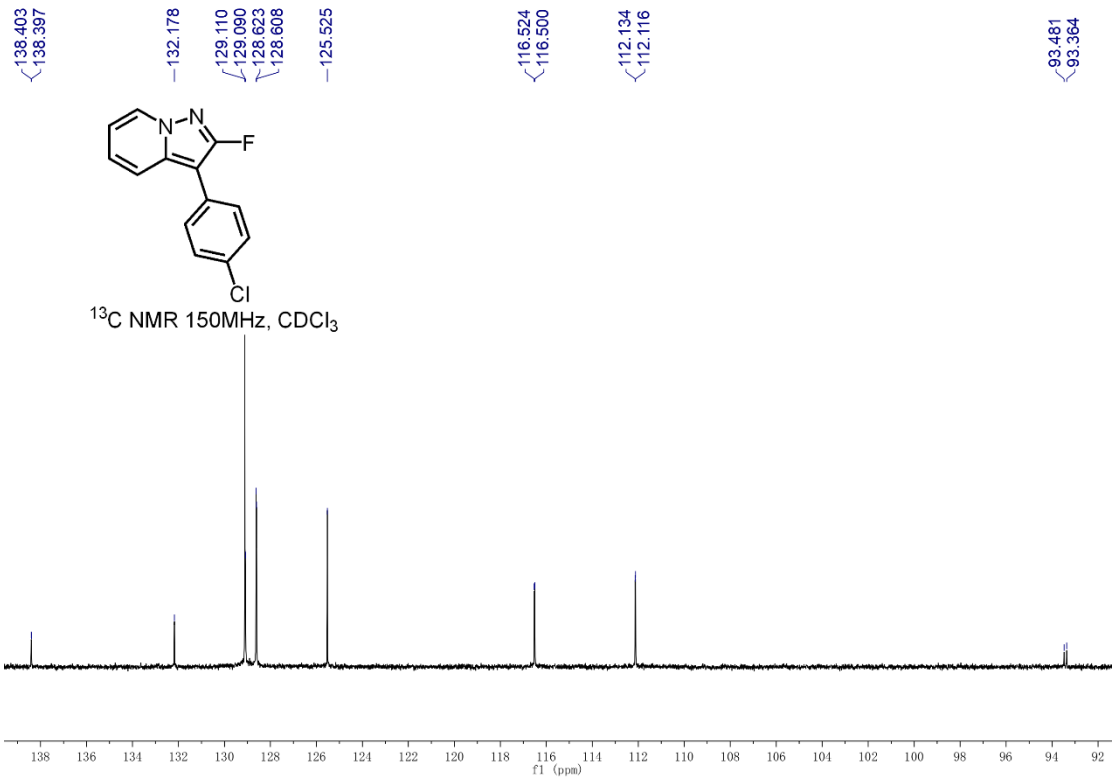


^{19}F NMR 376MHz, $CDCl_3$

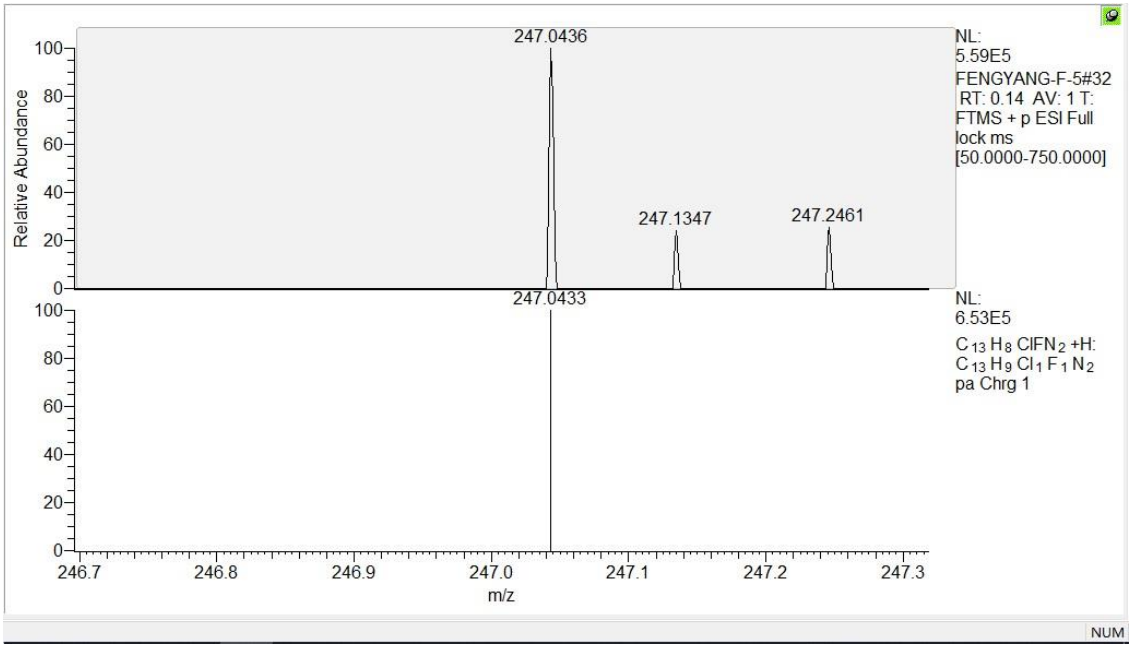




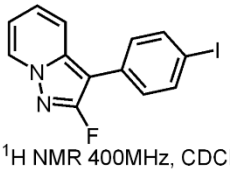
^{13}C NMR 150MHz, $CDCl_3$



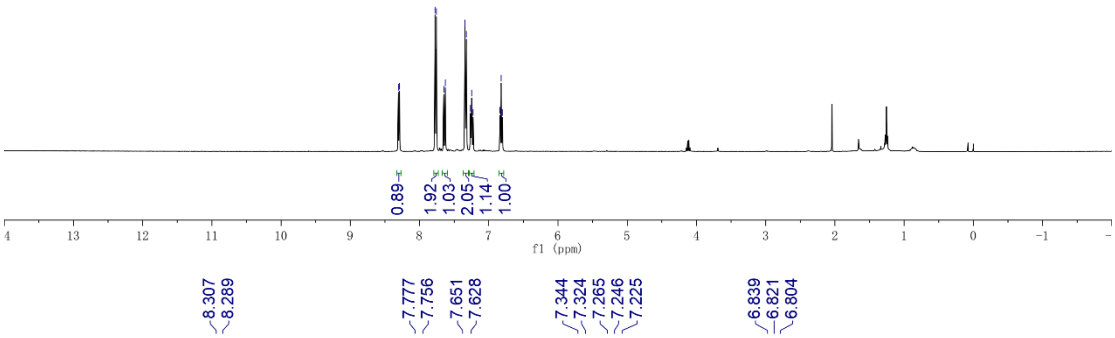
HRMS (ESI) copy of compound **4k**:

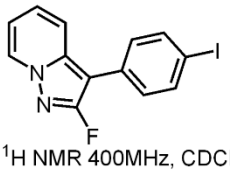


NMR copies of compound **4l:**

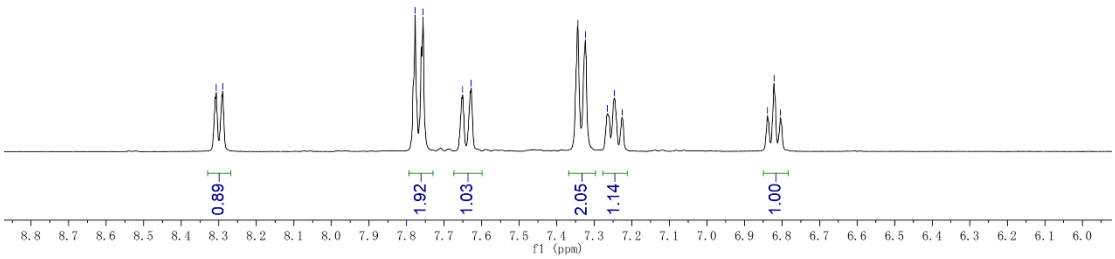


^{1}H NMR 400MHz, $CDCl_3$

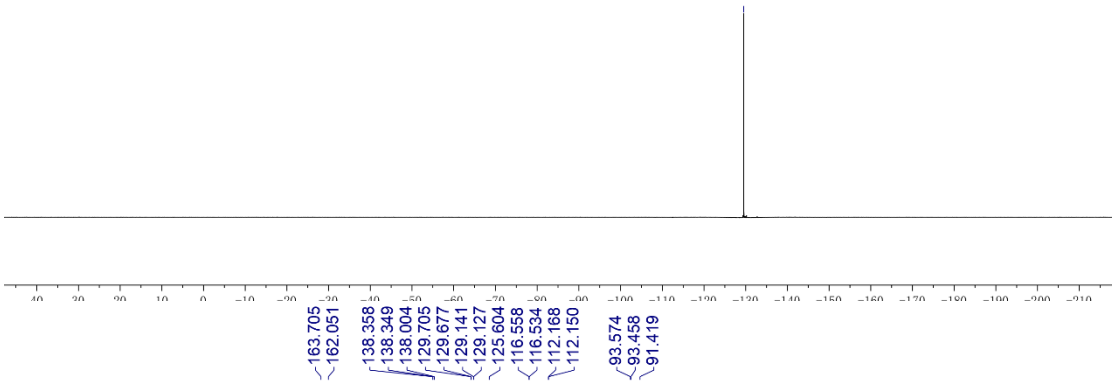


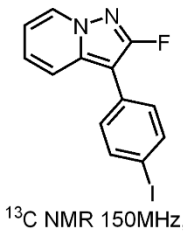


^{1}H NMR 400MHz, $CDCl_3$

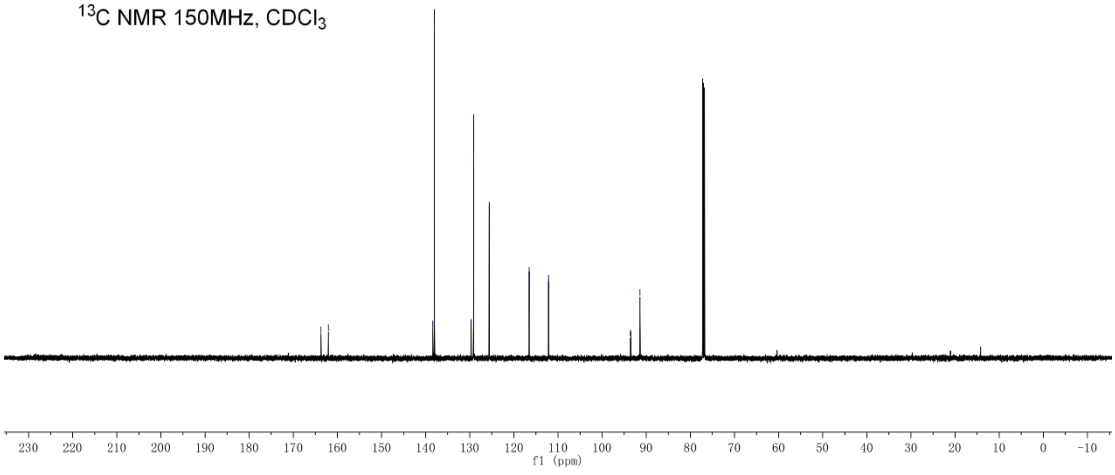


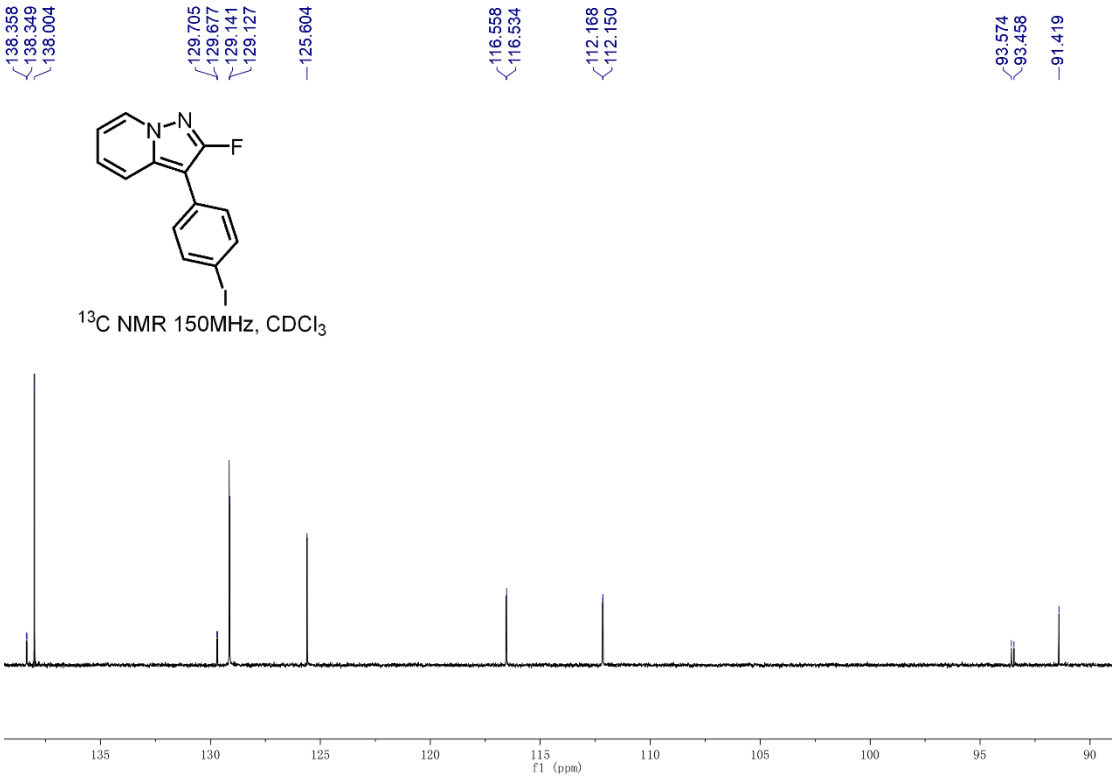
^{19}F NMR 376MHz, $CDCl_3$





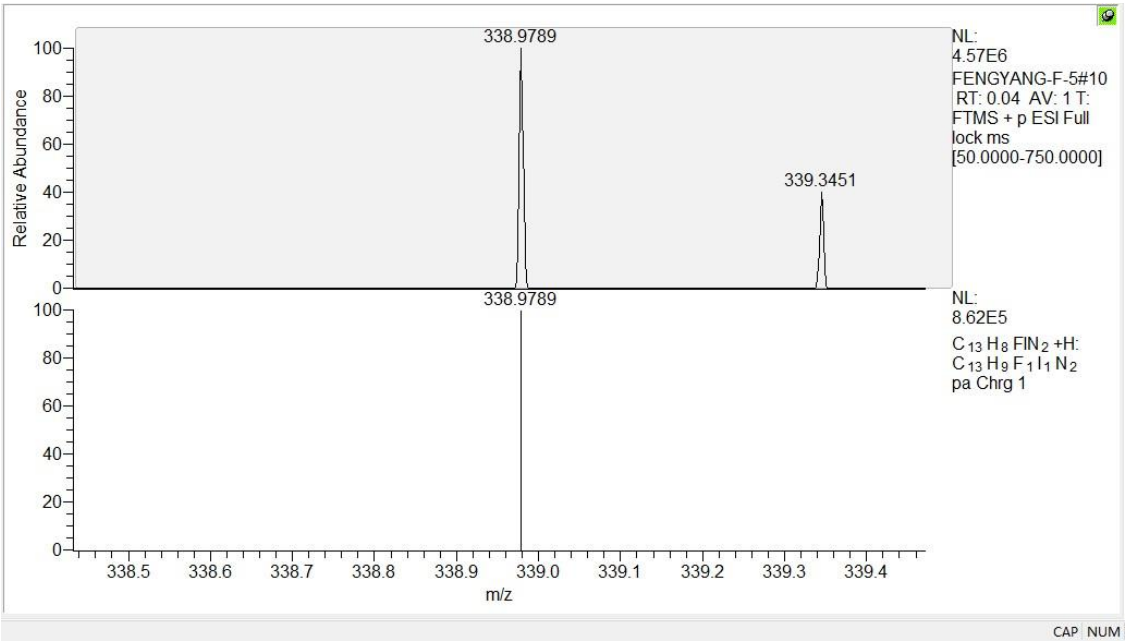
^{13}C NMR 150MHz, $CDCl_3$



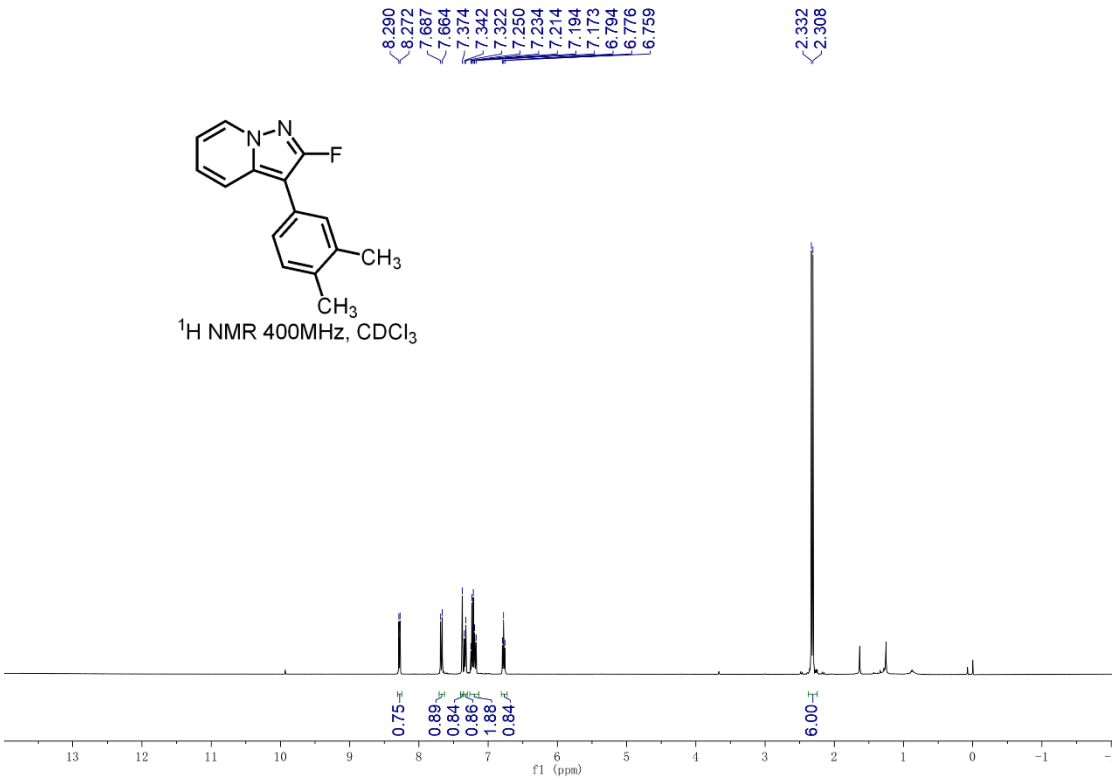


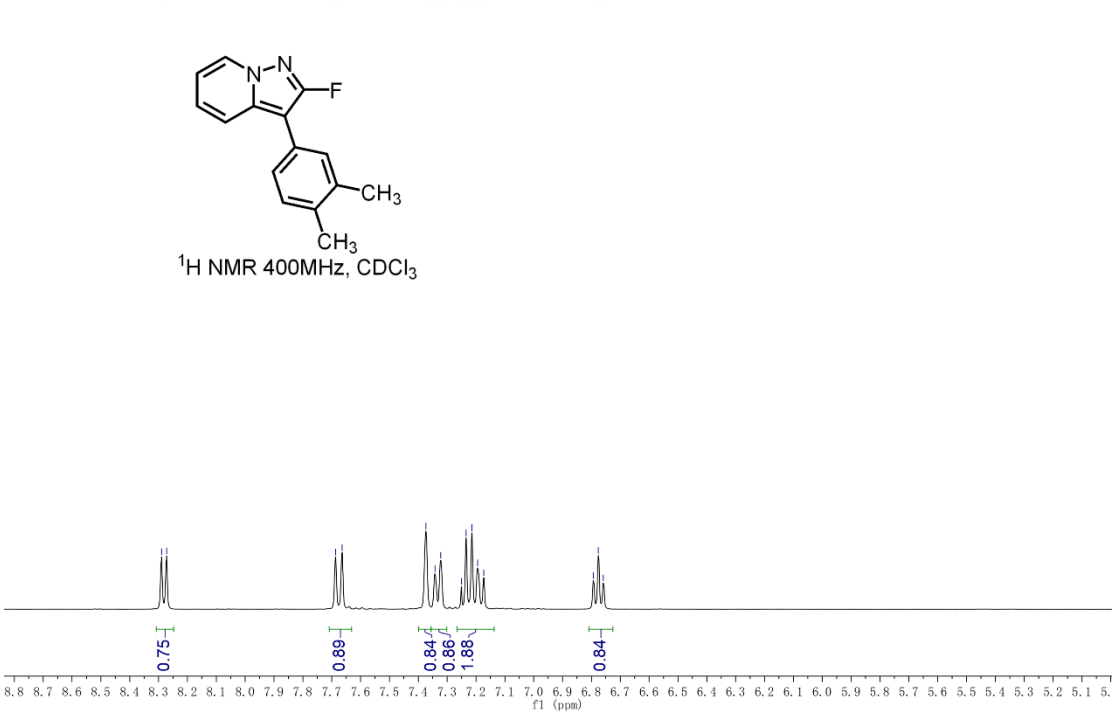
^{13}C NMR 150MHz, $CDCl_3$

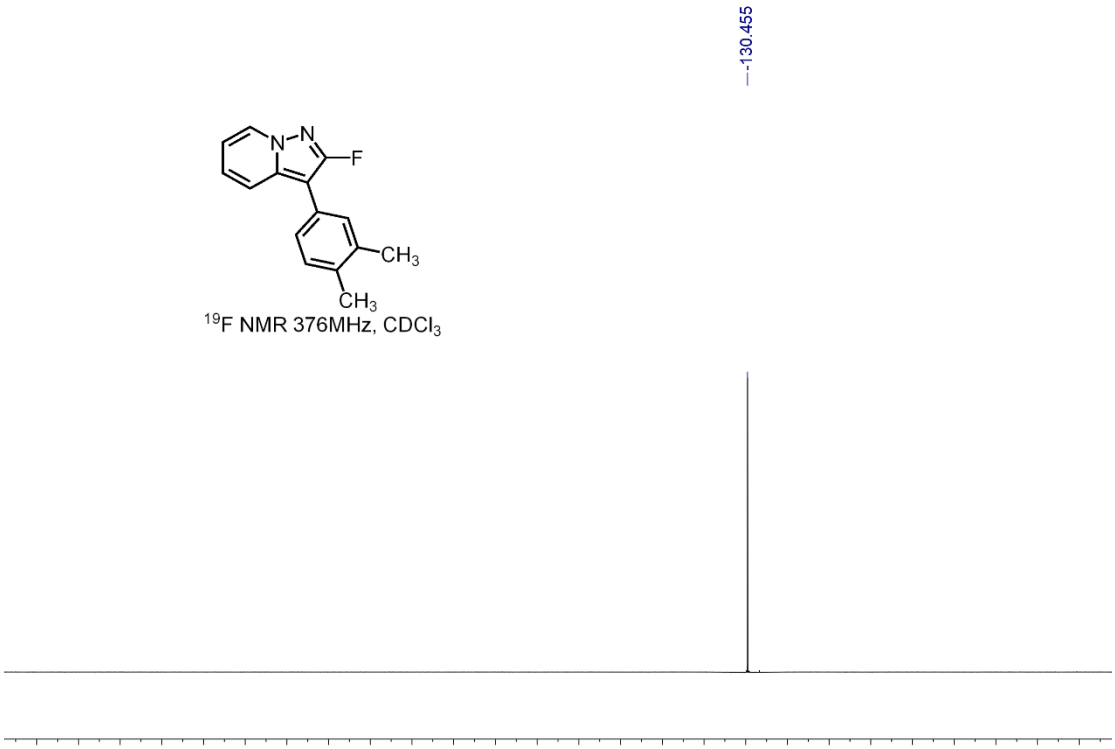
HRMS (ESI) copy of compound **4l**:



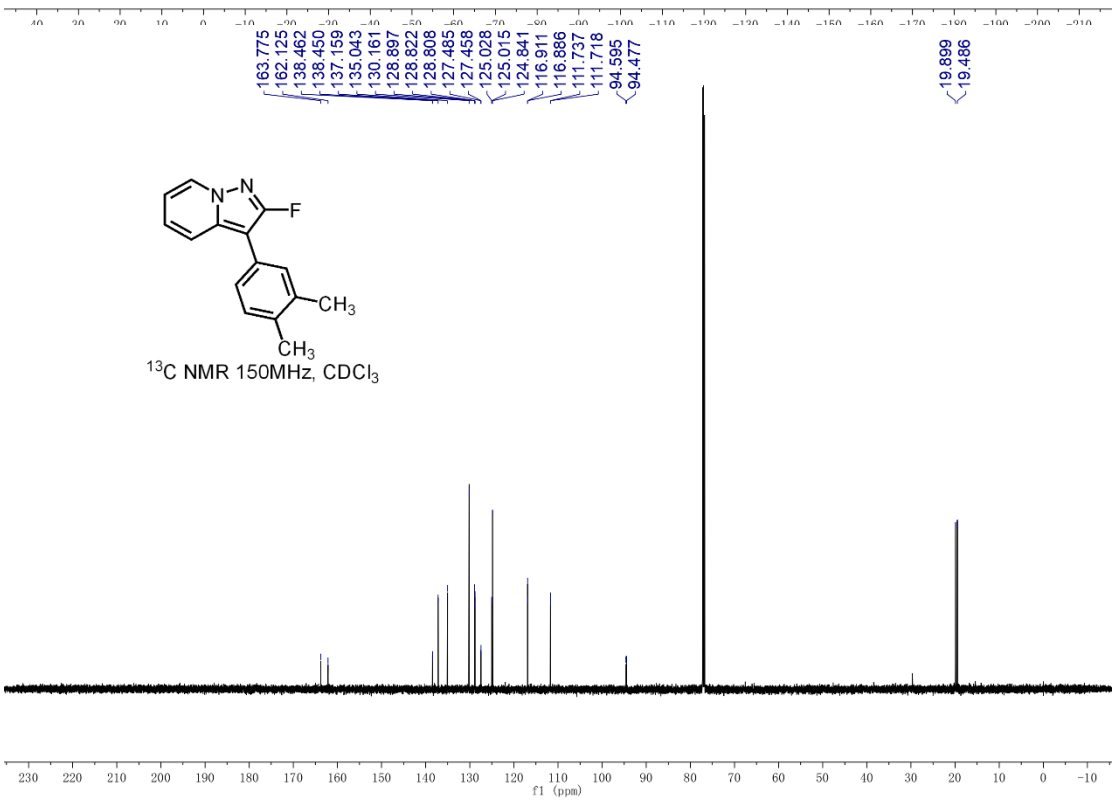
NMR copies of compound **4m:**



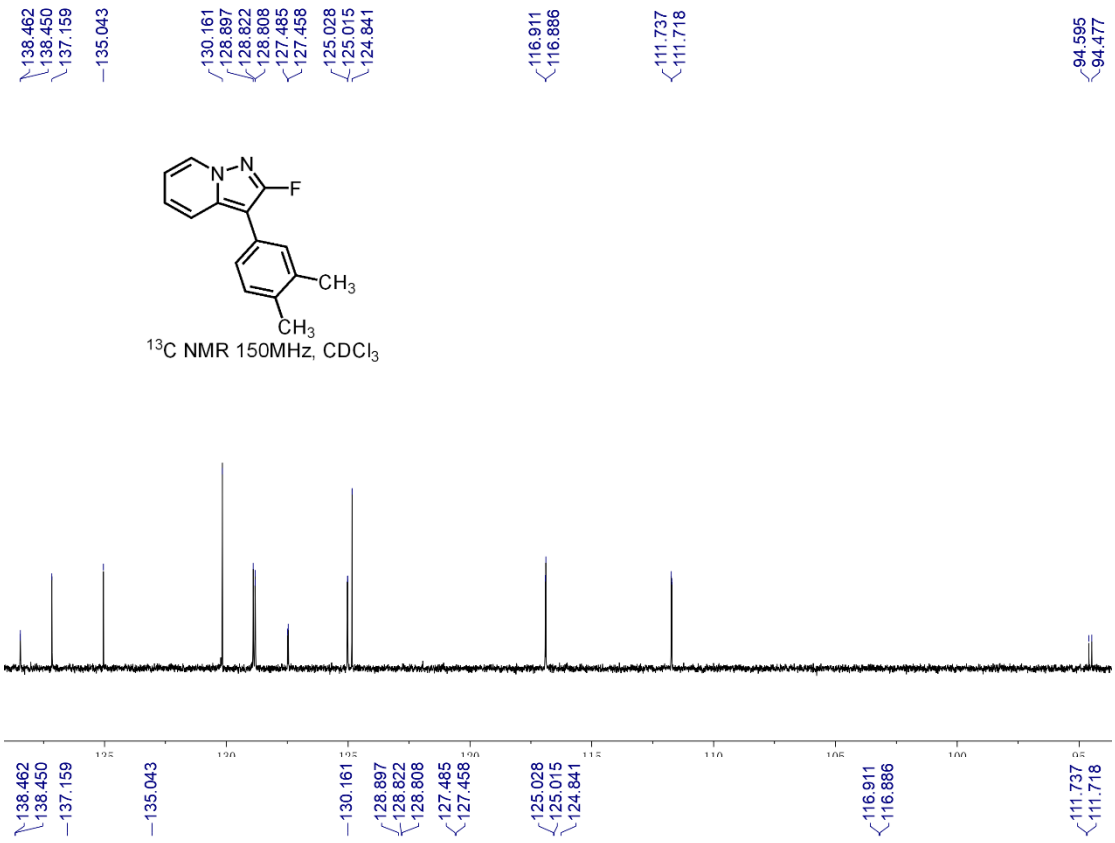


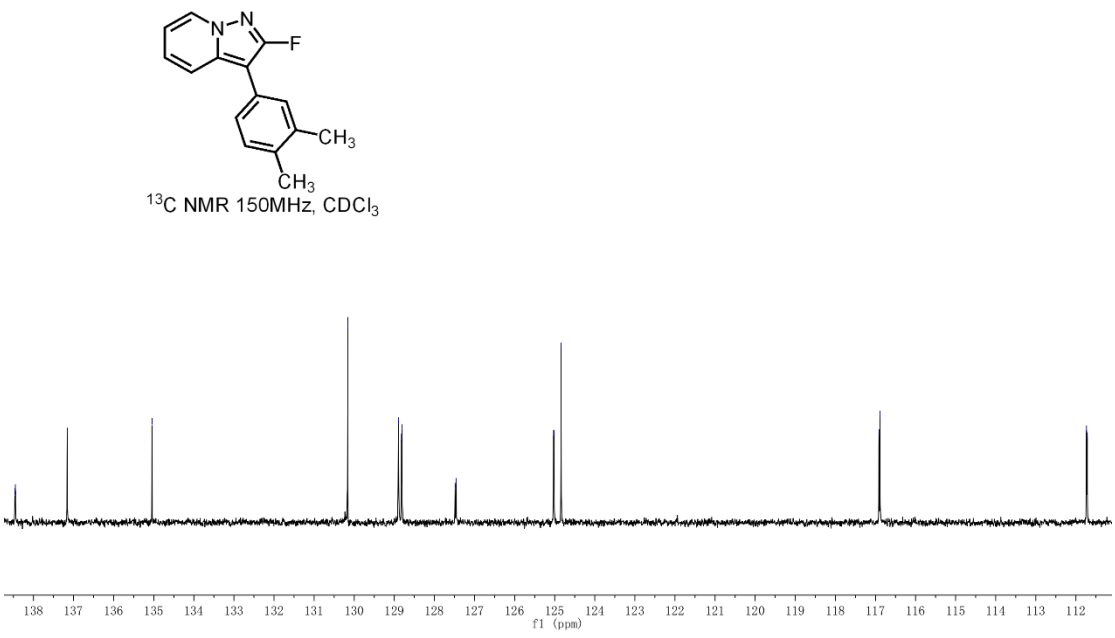


^{19}F NMR 376MHz, $CDCl_3$

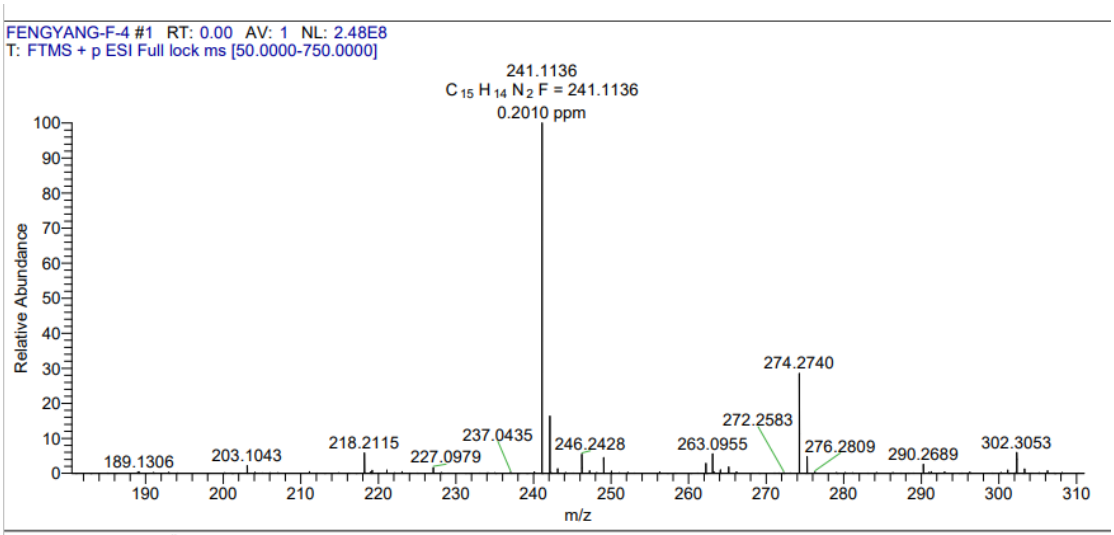


^{13}C NMR 150MHz, $CDCl_3$


138.462
138.450
137.159
135.043
130.161
128.897
128.822
128.808
127.485
127.458
125.028
125.015
124.841
116.911
116.886
111.737
111.718
94.595
94.477
F
CH3
CH3
13C NMR 150MHz, CDCl3

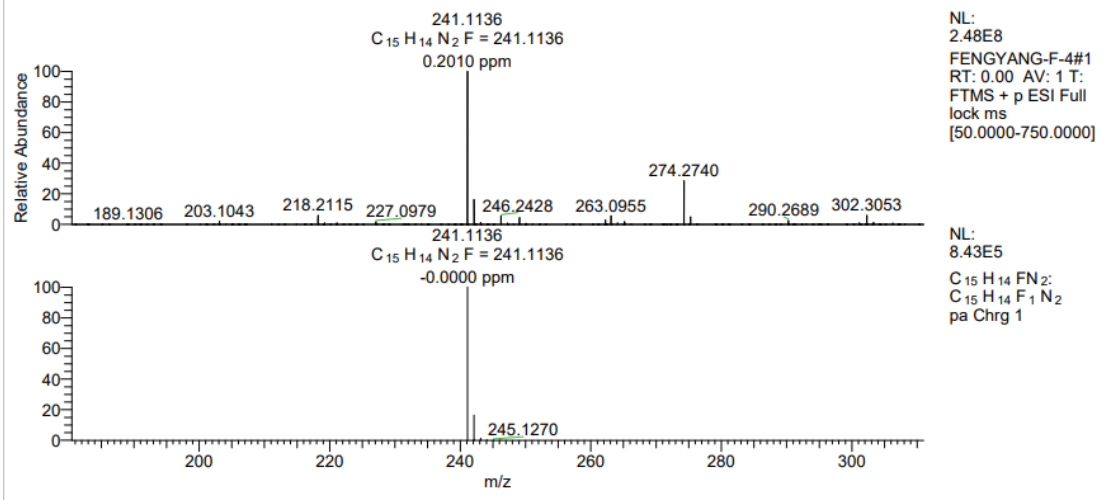

138.462
138.450
137.159
135.043
130.161
128.897
128.822
128.808
127.485
127.458
125.028
125.015
124.841
116.911
116.886
111.737
111.718
F
CH3
CH3
13C NMR 150MHz, CDCl3
f1 (ppm)

HRMS (ESI) copy of compound **4m**:

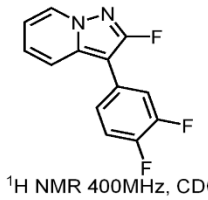


FENGYANG-F-4#1 RT: 0.00
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 180.4845-310.9690

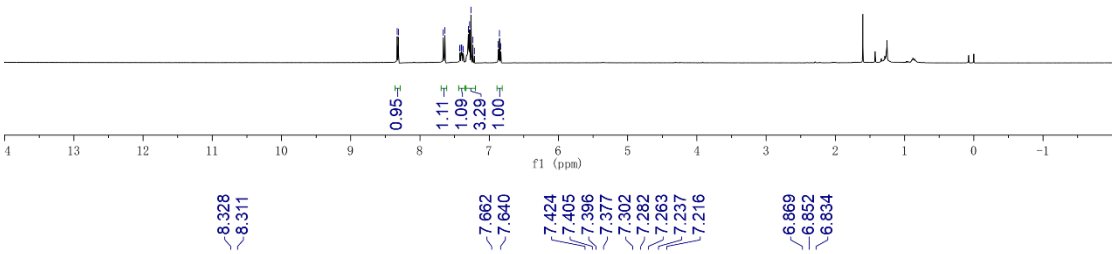
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
241.1136	249920704.0	100.00	241.1136	0.05	$C_{15}H_{14}N_2F$
242.1169	40768068.0	16.31			
274.2740	71721320.0	28.70			
302.3053	15407469.0	6.16			

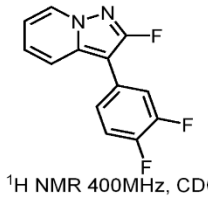


NMR copies of compound **4n:**

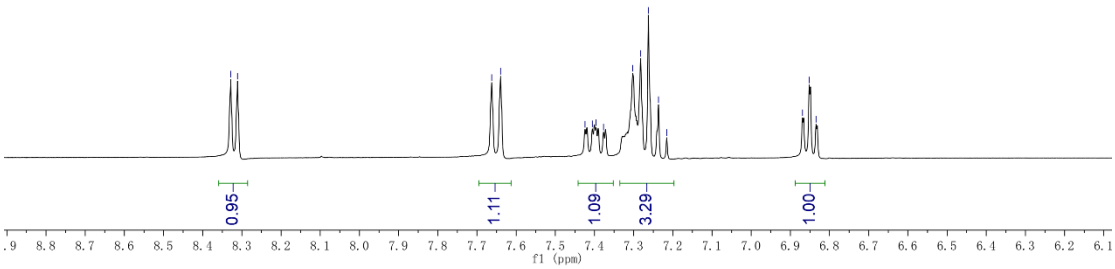


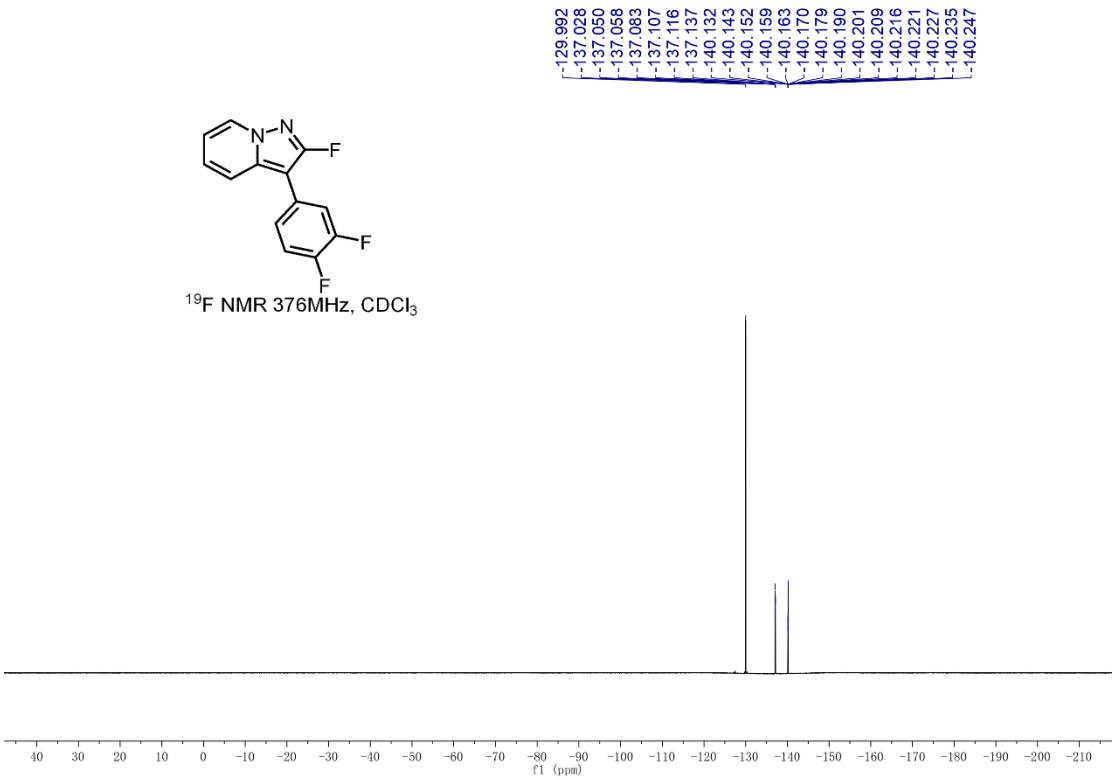
^{1}H NMR 400MHz, $CDCl_3$



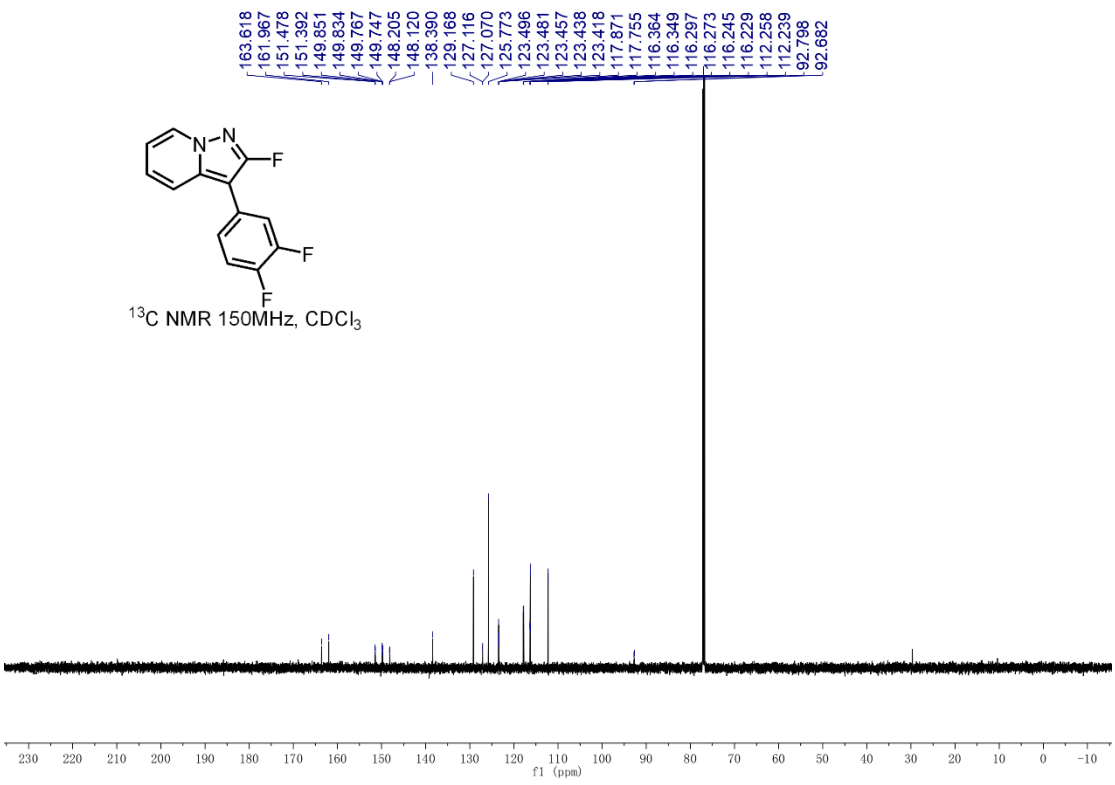


^{1}H NMR 400MHz, $CDCl_3$

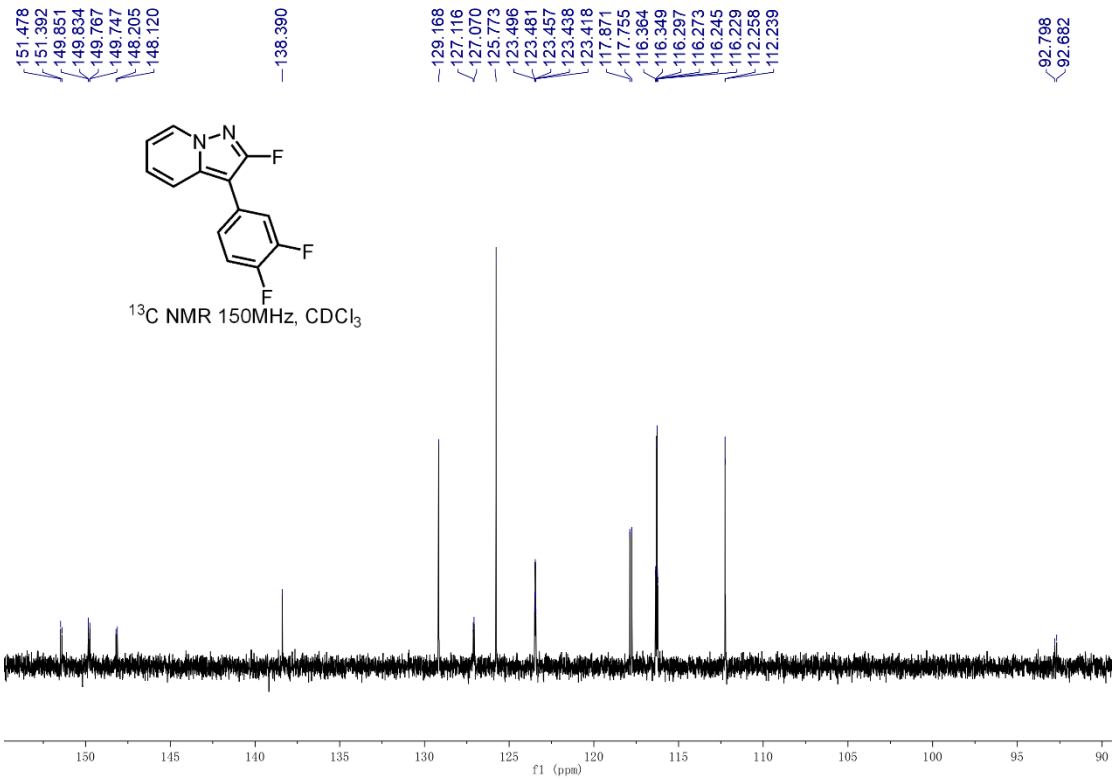


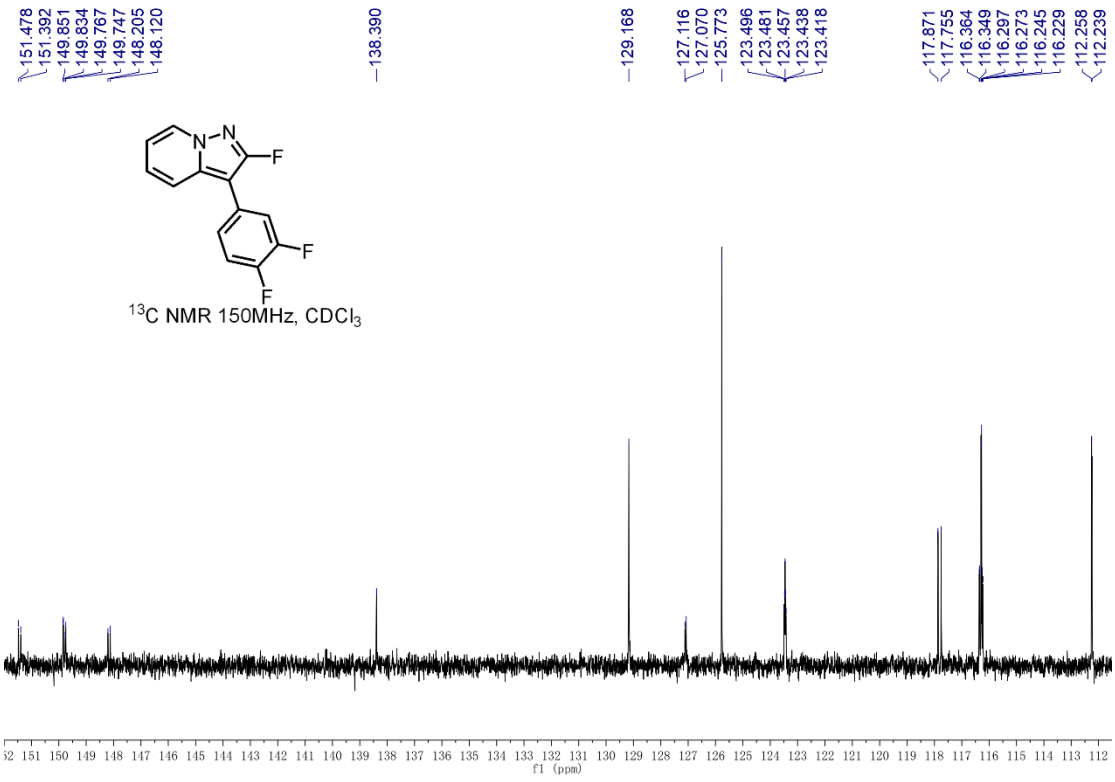


^{19}F NMR 376MHz, $CDCl_3$

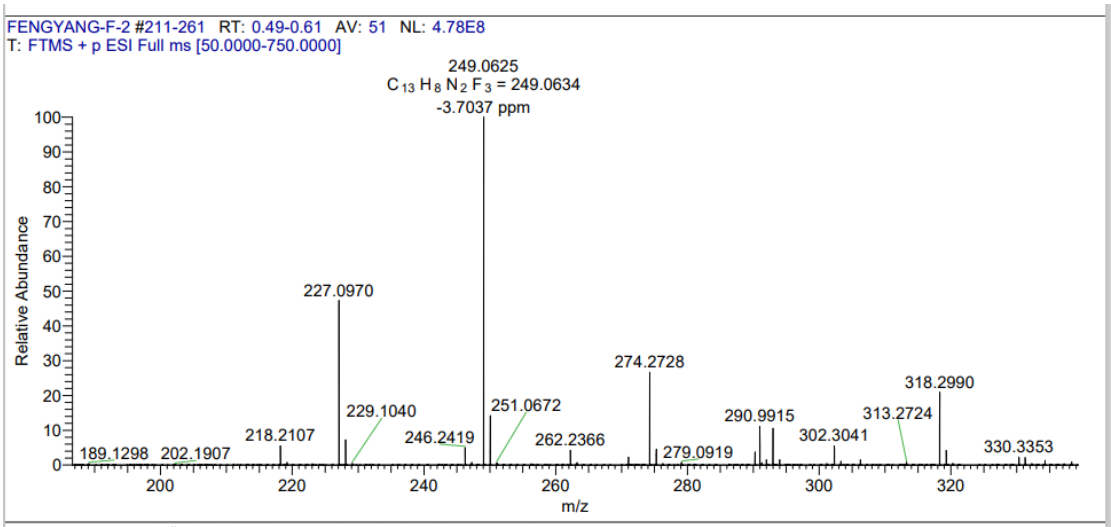


^{13}C NMR 150MHz, $CDCl_3$


151.478
151.392
149.851
149.834
149.767
149.747
148.205
148.120
138.390
129.168
127.116
127.070
125.773
123.496
123.481
123.457
123.438
123.418
117.871
117.755
116.364
116.349
116.297
116.273
116.245
116.229
112.258
112.239
92.798
92.682
F
F
F
13C NMR 150MHz, CDCl3
150
145
140
135
130
125
120
115
110
105
100
95
90
f1 (ppm)

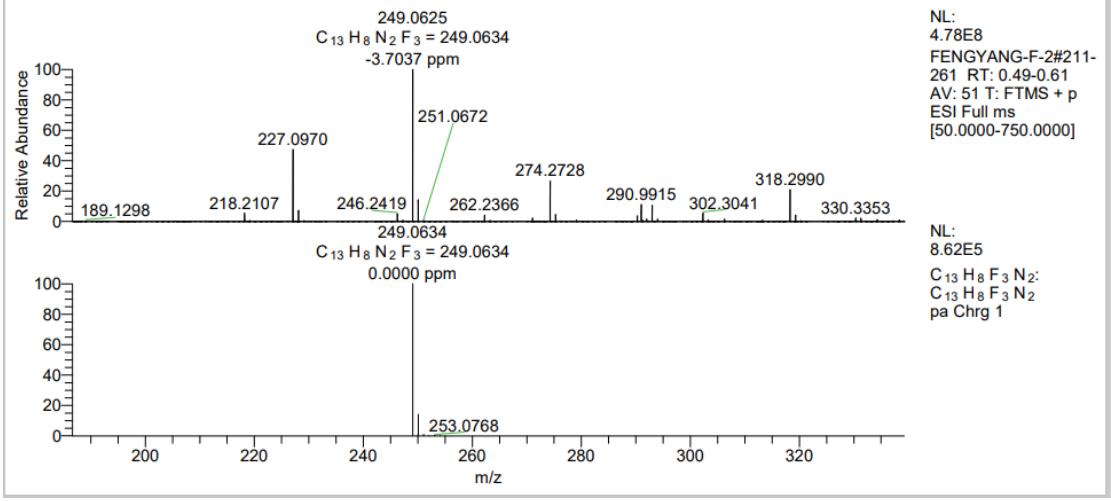

151.478
151.392
149.851
149.834
149.767
149.747
148.205
148.120
138.390
129.168
127.116
127.070
125.773
123.496
123.481
123.457
123.438
123.418
117.871
117.755
116.364
116.349
116.297
116.273
116.245
116.229
112.258
112.239
F
F
F
13C NMR 150MHz, CDCl3
f1 (ppm)

HRMS (ESI) copy of compound **4n**:

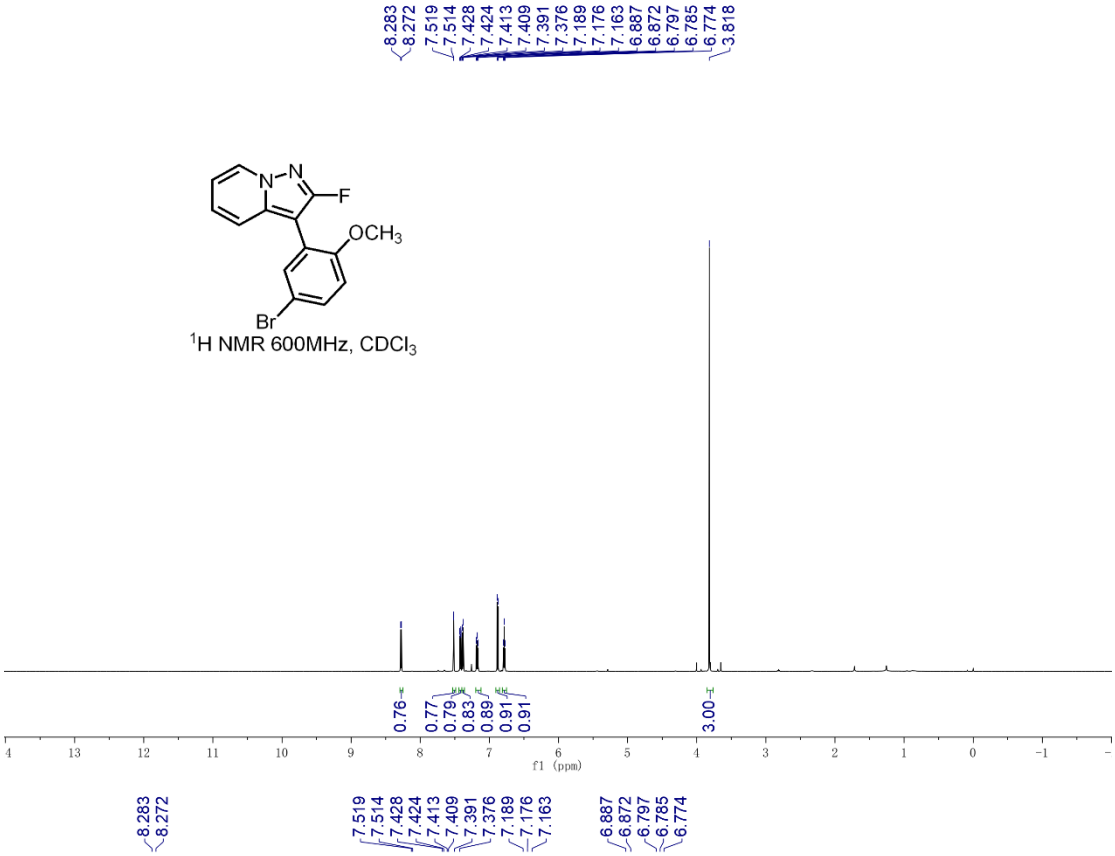


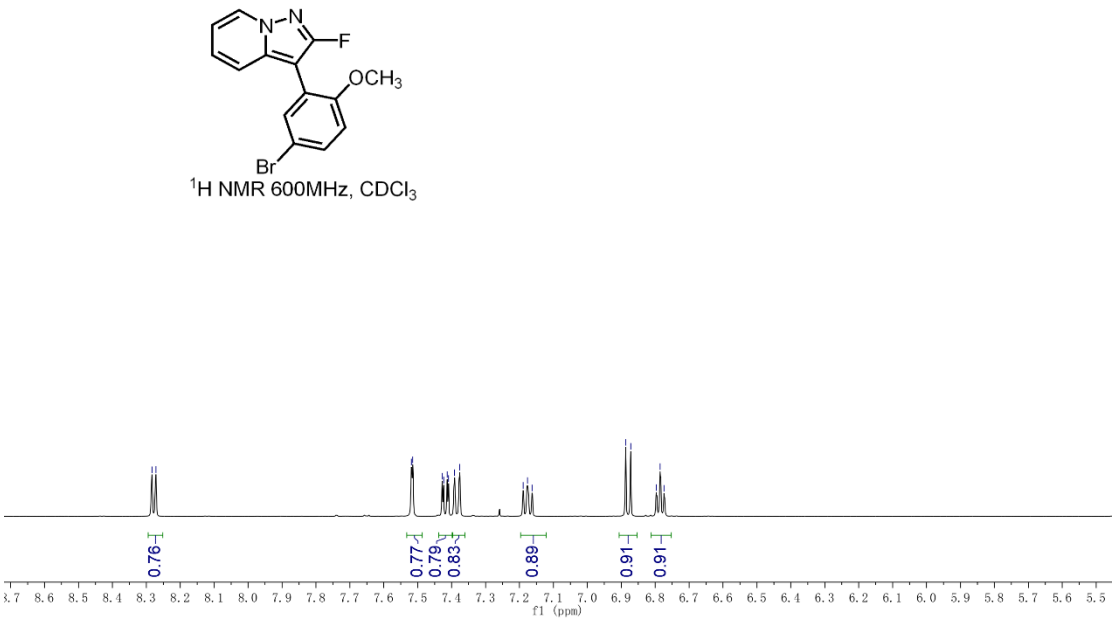
FENGYANG-F-2#211-261 RT: 0.49-0.61 AV: 51
T: FTMS + p ESI Full ms [50.0000-750.0000]
m/z= 186.6083-339.2328

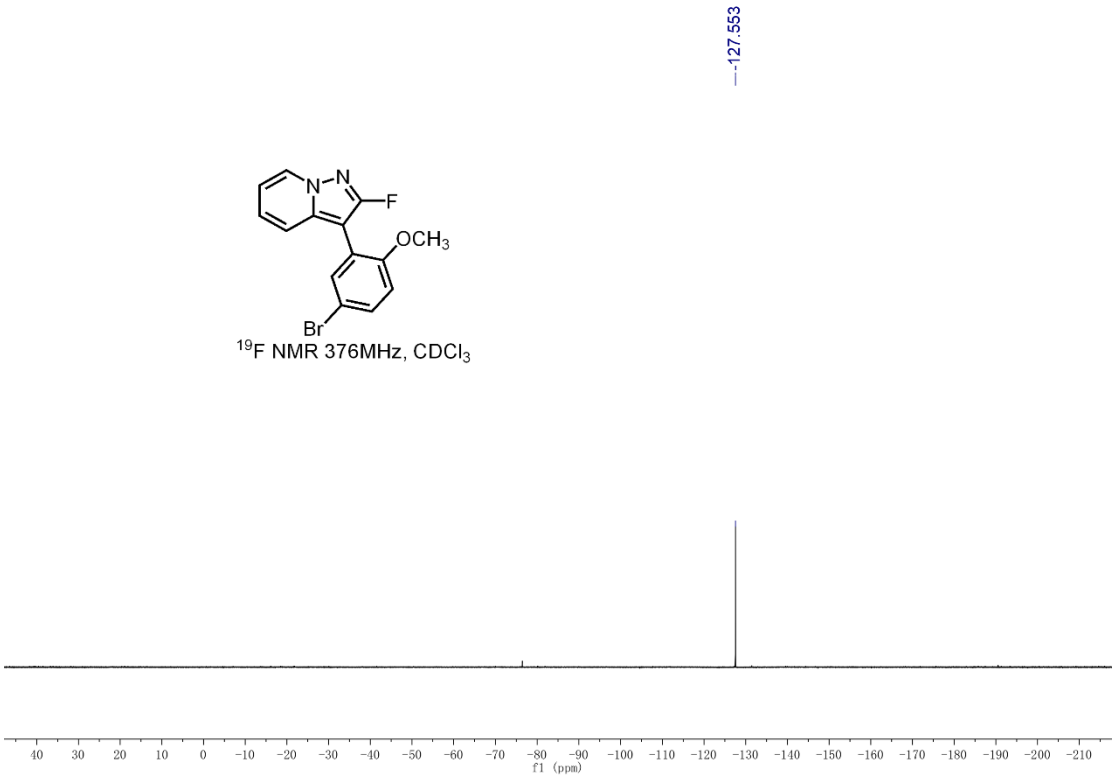
m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
227.0970	231312192.0	48.16			
249.0625	480347936.0	100.00	249.0634	-0.92	$C_{13}H_8N_2F_3$
274.2728	127533264.0	26.55			
318.2990	100580936.0	20.94			

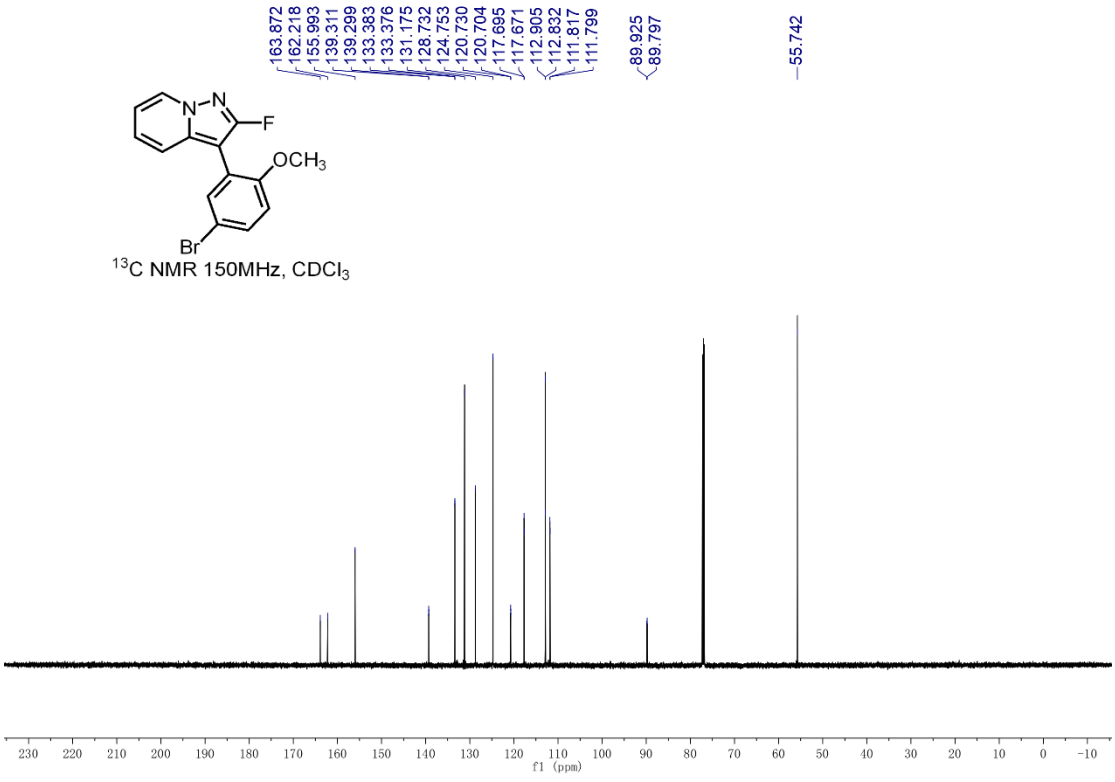


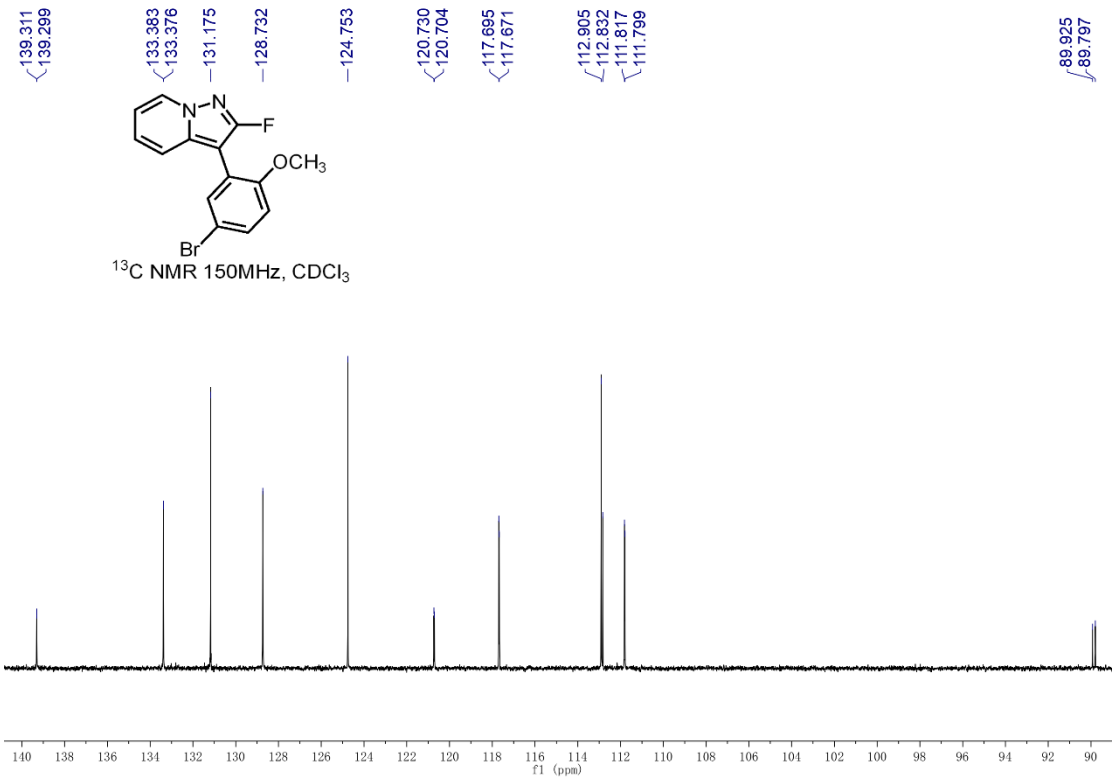
NMR copies of compound **4o:**



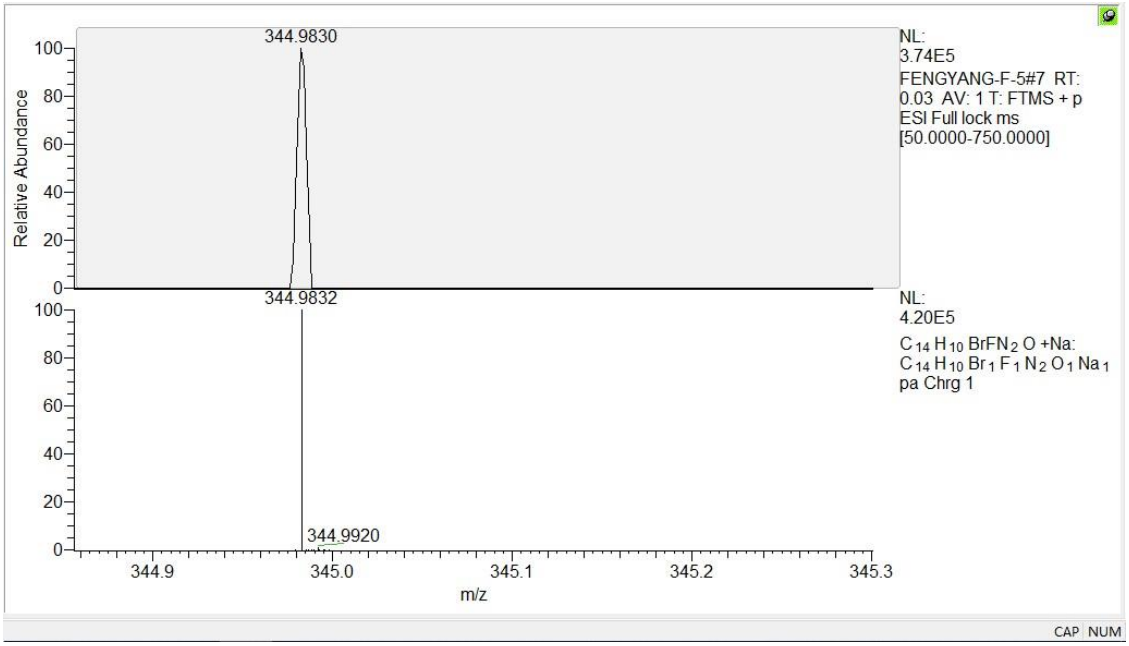



-127.553
F
OCH3
Br
19F NMR 376MHz, CDCl3
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

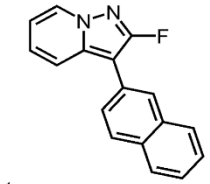

163.872
162.218
155.993
139.311
139.299
133.383
133.376
131.175
128.732
124.753
120.730
120.704
117.695
117.671
112.905
112.832
111.817
111.799
89.925
89.797
55.742
F
OCH3
Br
13C NMR 150MHz, CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



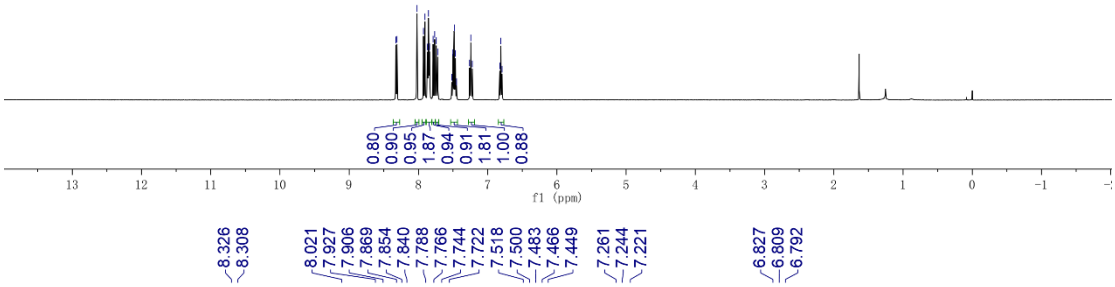
HRMS (ESI) copy of compound **4o**:

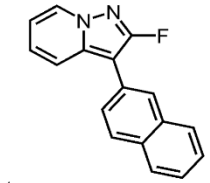


NMR copies of compound **4p:**

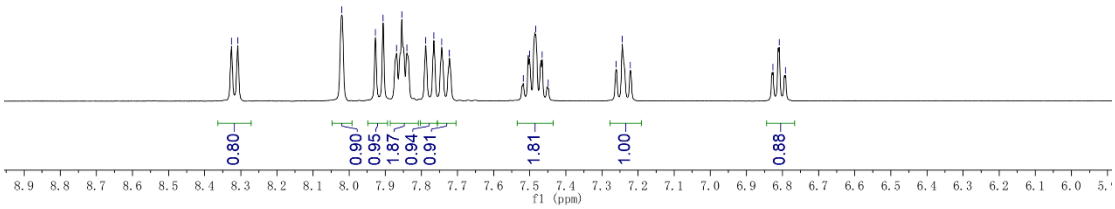


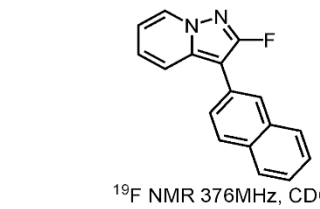
^{1}H NMR 400MHz, $CDCl_3$



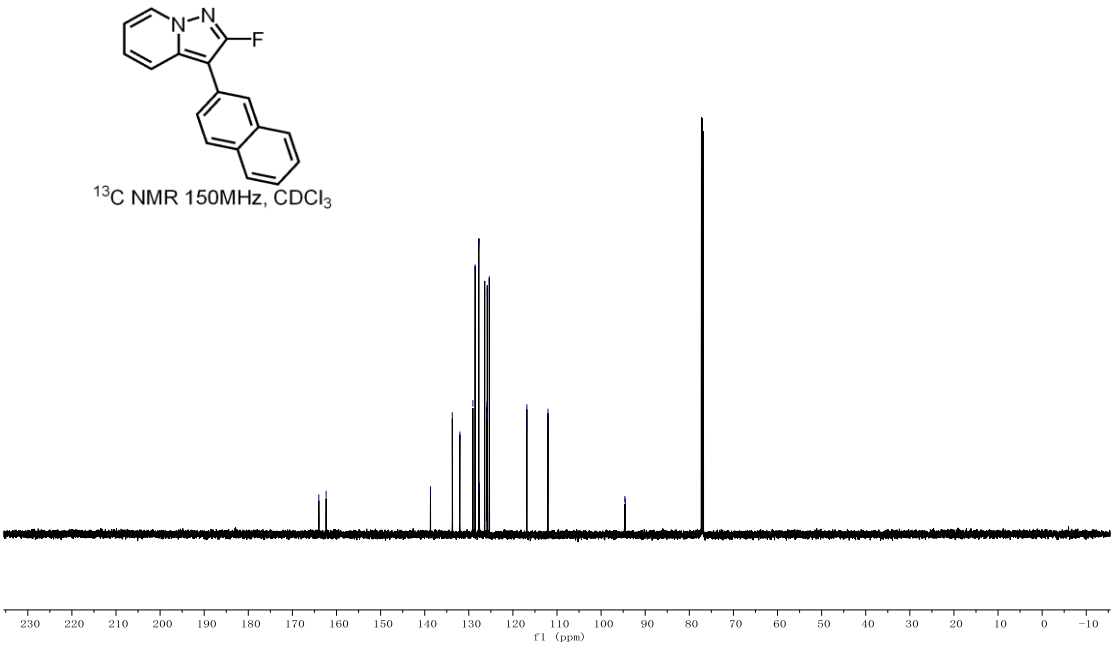


^{1}H NMR 400MHz, $CDCl_3$

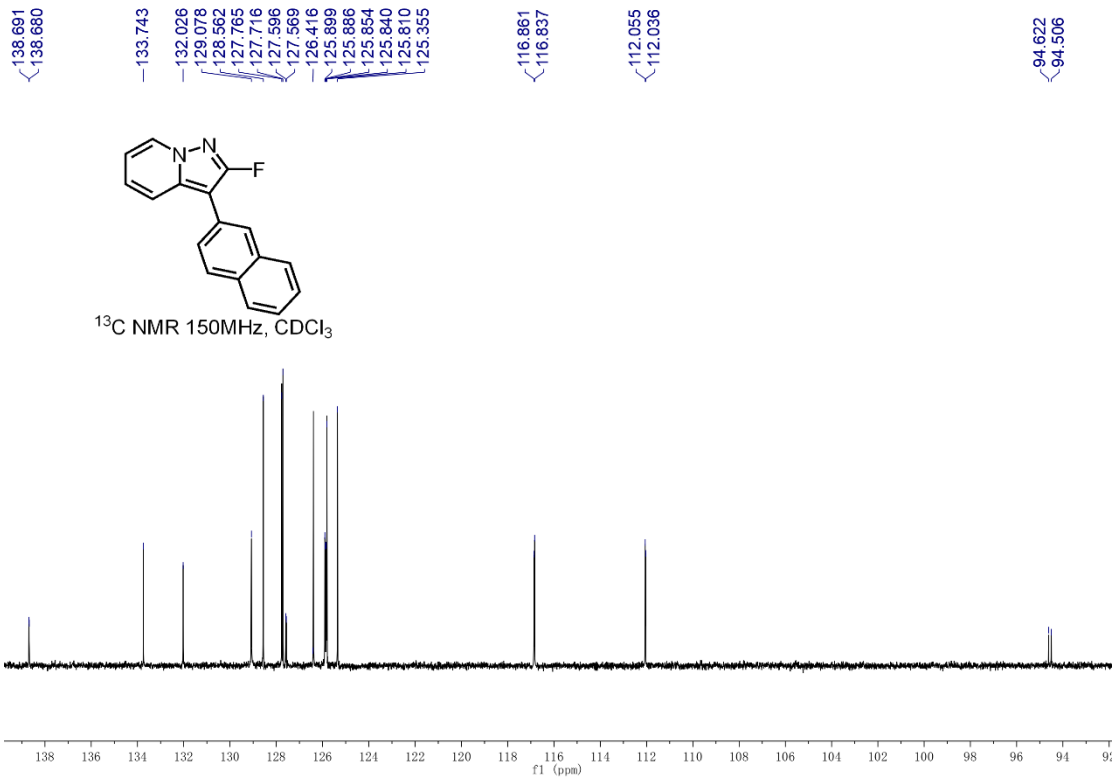




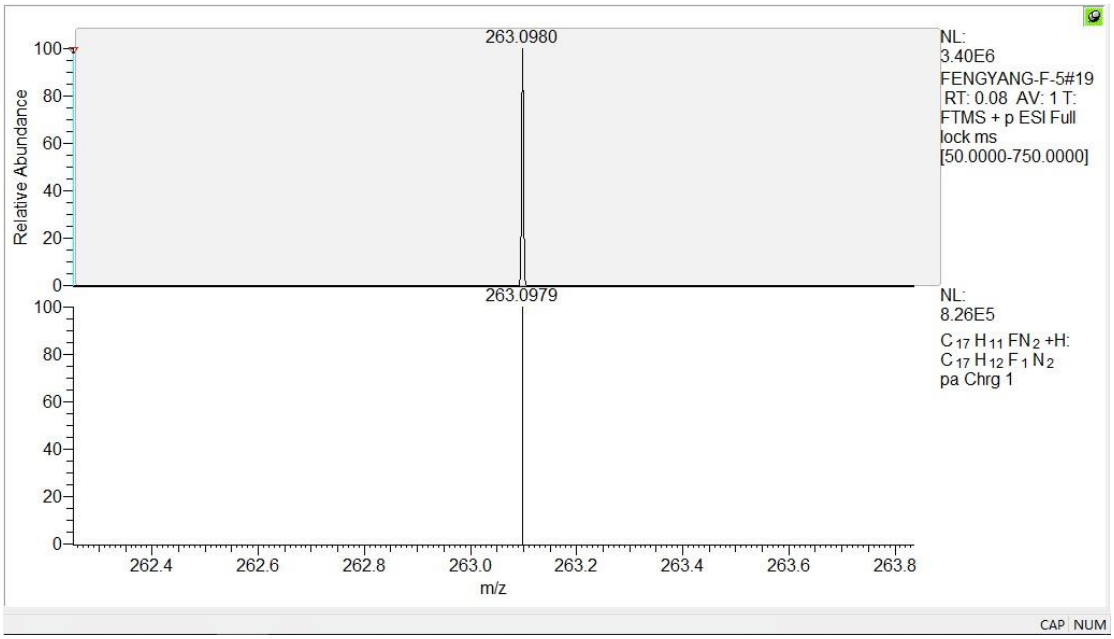
^{19}F NMR 376MHz, $CDCl_3$



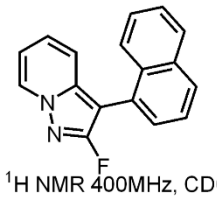
^{13}C NMR 150MHz, $CDCl_3$



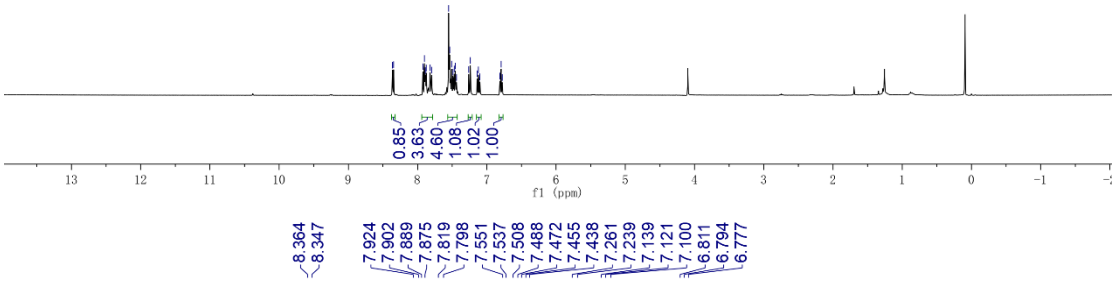
HRMS (ESI) copy of compound **4p**:

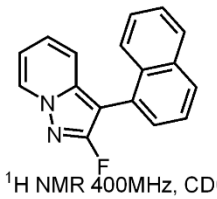


NMR copies of compound **4q:**

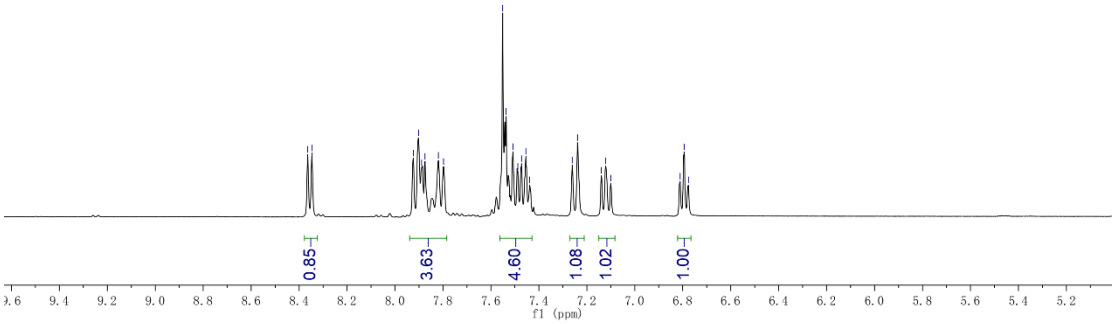


^{1}H NMR 400MHz, $CDCl_3$

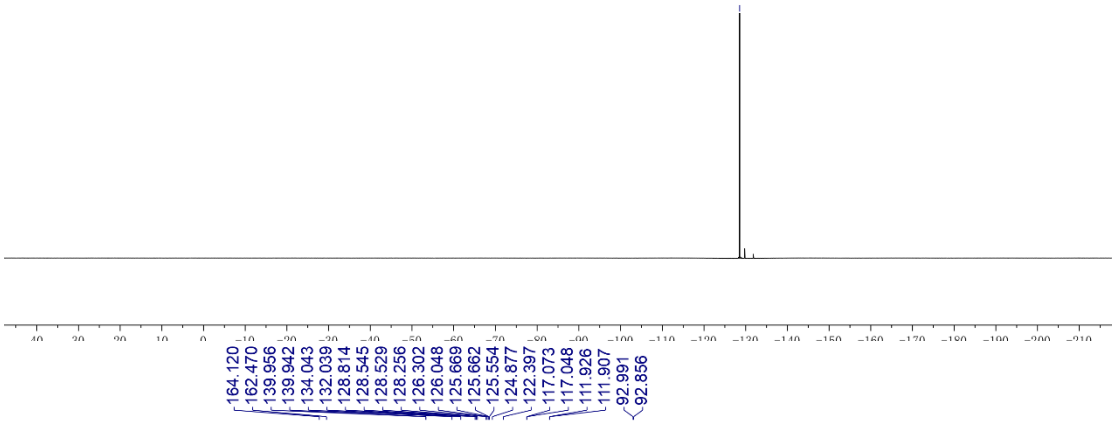


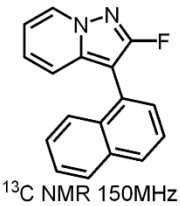


^{1}H NMR 400MHz, $CDCl_3$

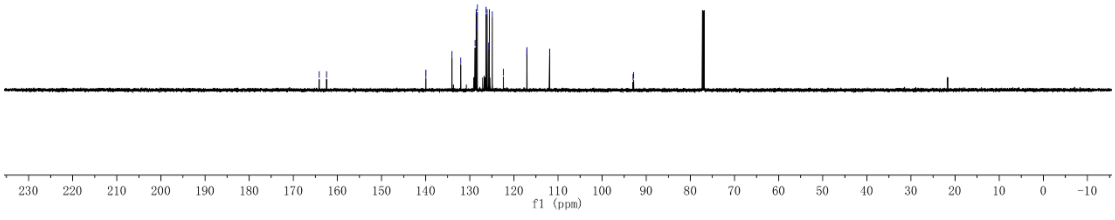


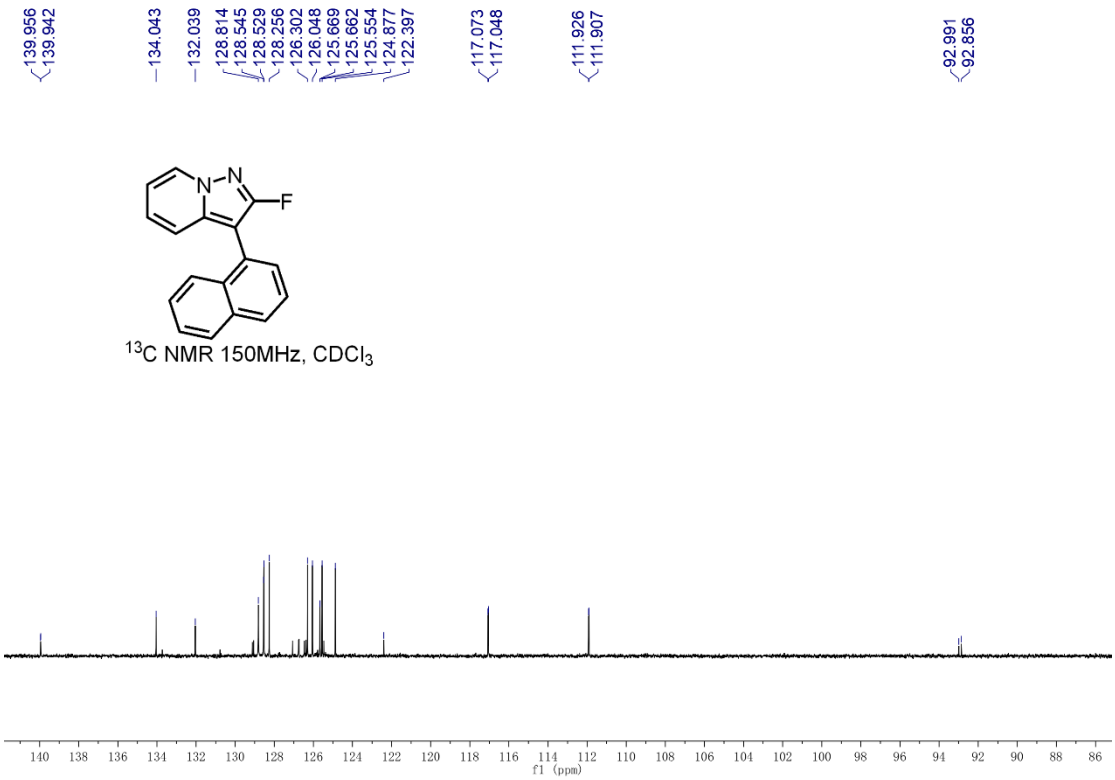
^{19}F NMR 376MHz, $CDCl_3$



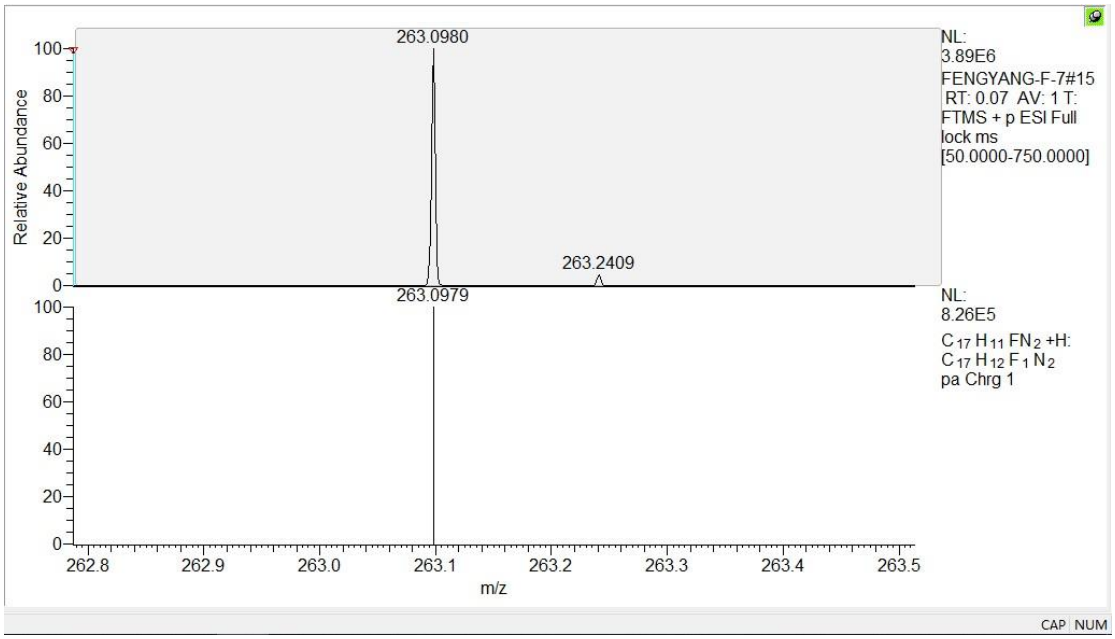


^{13}C NMR 150MHz, $CDCl_3$

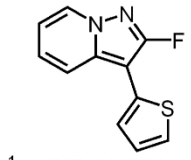




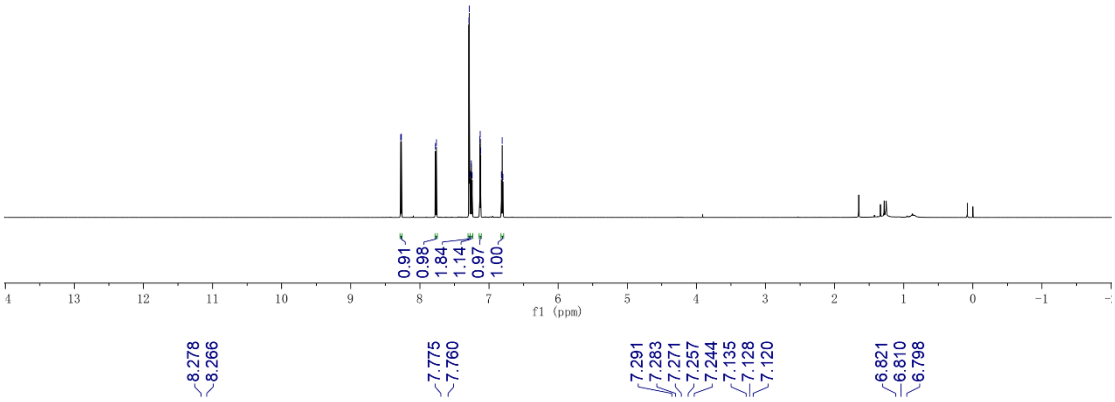
HRMS (ESI) copy of compound **4q**:

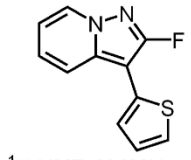


NMR copies of compound **4r:**

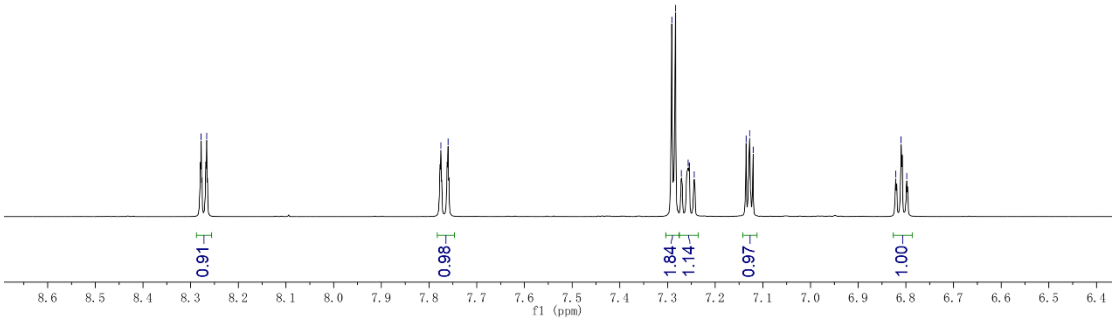


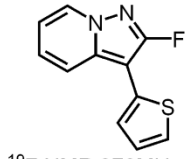
^{1}H NMR 600MHz, $CDCl_3$



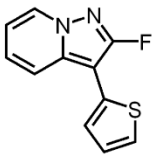


^{1}H NMR 600MHz, $CDCl_3$

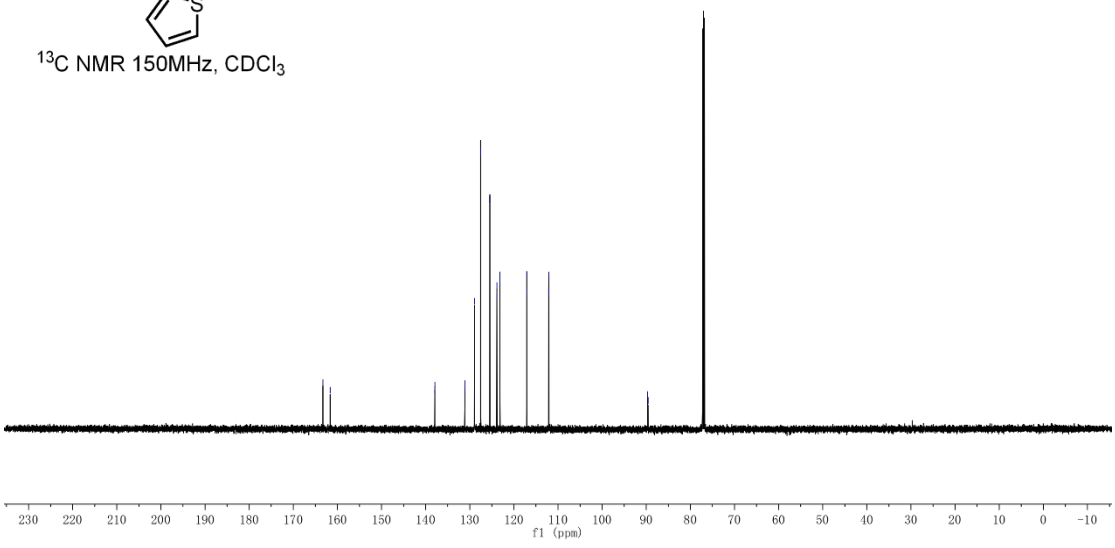


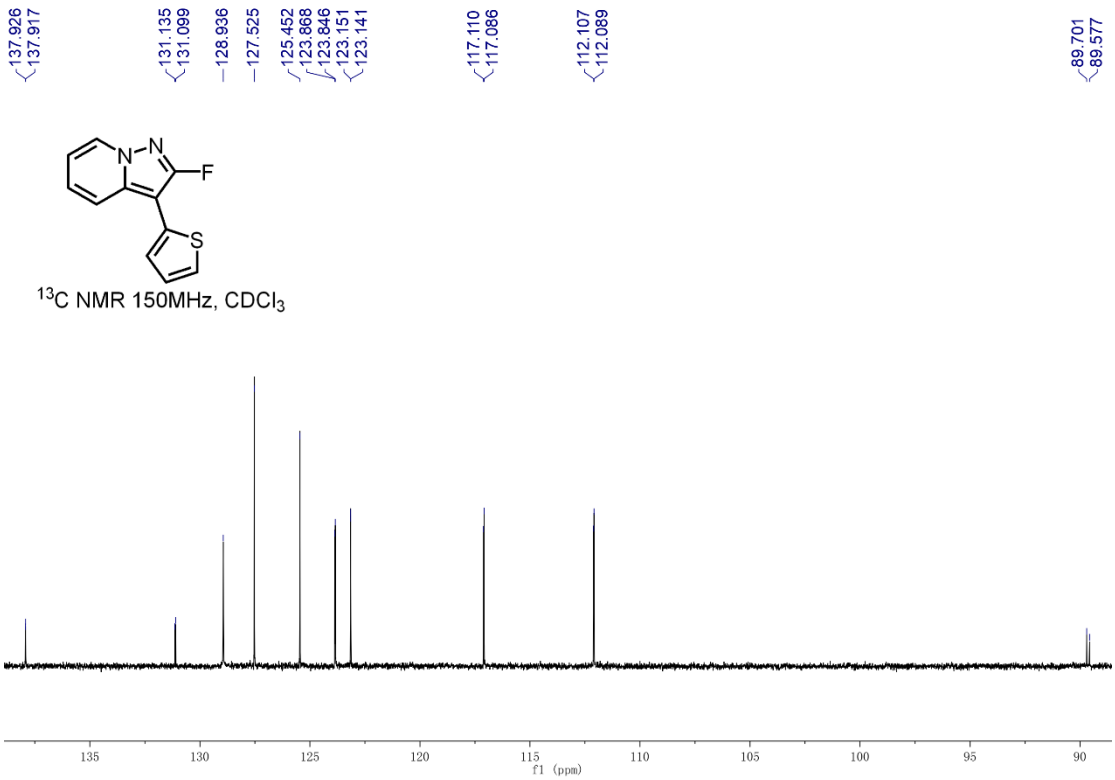


^{19}F NMR 376MHz, $CDCl_3$



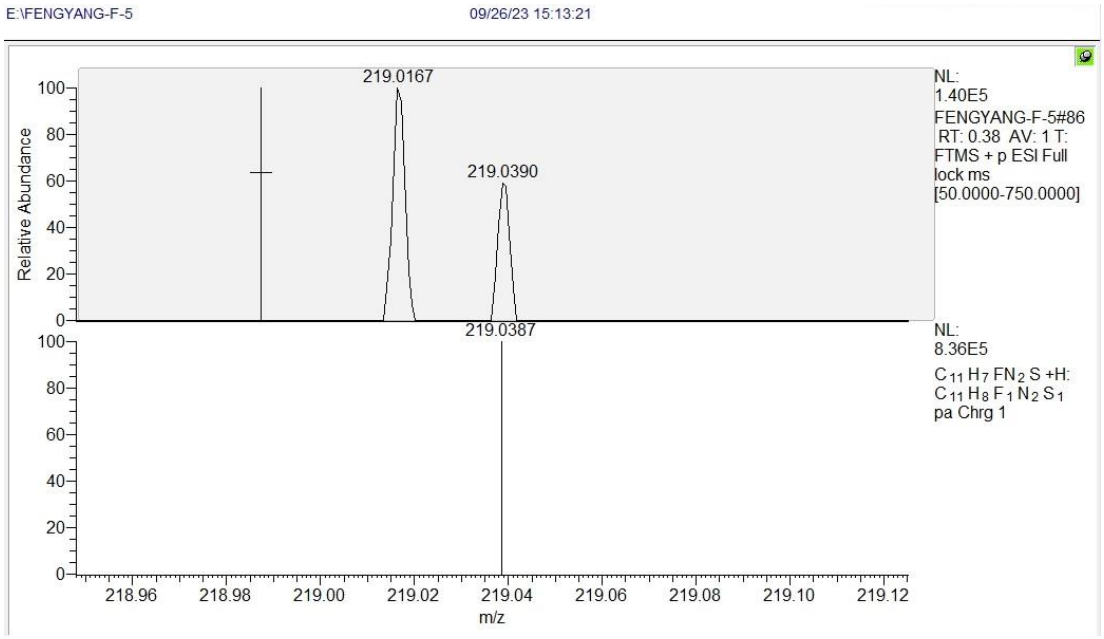
^{13}C NMR 150MHz, $CDCl_3$





^{13}C NMR 150MHz, $CDCl_3$

HRMS (ESI) copy of compound **4r**:



7. Crystallography data of compound 3c

Crystallographic data for compound **3c** (CCDC-2300843) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, by application to CCDC（Email:deposit@ccdc.cam.ac.uk).

Datablock: 1

Bond precision: C-C = 0.0022 A Wavelength=0.71073

Cell: a=27.7164(13) b=7.2580(3) c=17.6388(7)
alpha=90 beta=118.023(1) gamma=90
Temperature: 298 K

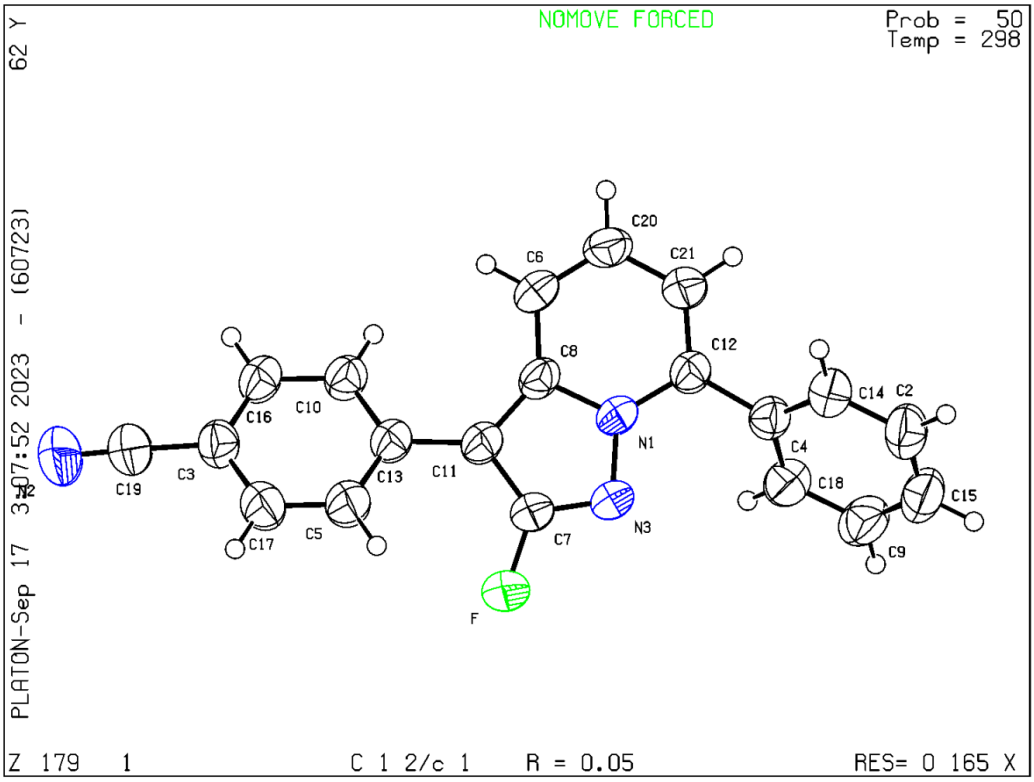
	Calculated	Reported
Volume	3132.3(2)	3132.3(2)
Space group	C 2/c	C 1 2/c 1
Hall group	-C 2yc	-C 2yc
Moiety formula	C20 H12 F N3	C20 H12 F N3
Sum formula	C20 H12 F N3	C20 H12 F N3
Mr	313.33	313.33
Dx,g cm-3	1.329	1.329
Z	8	8
Mu (mm-1)	0.089	0.089
F000	1296.0	1296.0
F000'	1296.54	
h,k,lmax	36,9,23	36,9,23
Nref	3906	3890
Tmin,Tmax	0.990,0.994	0.711,0.746
Tmin'	0.986	

Correction method= # Reported T Limits: Tmin=0.711 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 28.291

R(reflections)= 0.0459(2411) wR2(reflections)= 0.1171(3890)

S = 1.027 Npar= 217


NOMOVE FORCED
Prob = 50
Temp = 298
62 Y
PLATON-Sep 17 3 07:52 2023 - (60723)
C20
C6
C21
C8
C12
C14
C2
C16
C10
N1
C4
C3
C13
C11
C18
C15
C19
N2
C5
C7
N3
C17
C9
F
Z 179 1
C 1 2/c 1
R = 0.05
RES= 0 165 X

8. The electron cloud density of two unsaturated carbons of (2,2-difluorovinyl)benzene：