Supporting Information

For

Rh(III)-catalyzed [4+1] cyclization of aryl substituted pyrazoles with cyclopropanols via C-H activation

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Table of contents

1. General information

Materials and solvents were purchased from commercial suppliers and used without additional purification. NMR spectra were measured in $CDCl_3$ and recorded on Bruker Avance spectrometers operating for ^1H NMR at 400 MHz or 600 MHz, for ^{13}C NMR at 100 MHz or 150 MHz. Chemical shifts are expressed in ppm and *J* values are given in Hz. Mass spectroscopy data of the products were collected with an HRMS-TOF instrument GCT Premier, which is produced by WATERS company, and the collision energy is 70eV. The single crystal was formed in n-hexane/dichloromethan and the data were recorded on Bruker smart apex II.

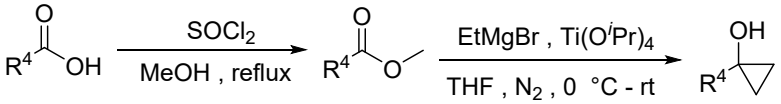
2. General procedure for the synthesis of starting materials and products

2.1 General procedure for the synthesis of aryl substituted pyrazoles:[1]

Add a solution of aryl ketone (10 mmol) in EtOAc (20 mL) to a suspension of NaH (1.6 g of dispersion in oil, 40 mmol) in EtOAc (20 mL) slowly at 0 °C, stirred the mixture at room temperature for 12 hours. Treat the mixture carefully with 10% aqueous NH_4Cl (30 mL). Adjust the reaction mixture pH 5 with hydrochloric acid, and separate the aqueous phase. Extract the reaction mixture with EtOAc, the combined organic extracts were dried with anhydrous Na_2SO_4, and the solvent was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (Petroleum ether/EtOAc = 7:1) to obtain 1-arylbutane-1,3-dione.

Hydrazine monohydrate (0.6 g, 10 mmol) in toluene (20 mL) was added dropwise to a solution of 1-arylbutane-1,3-dione (1.61 g, 10 mmol) in toluene (20 mL) kept at 0 °C. The reaction mixture was stirred at 115 °C for 3 hours in a sealed vessel. The mixture was then cooled to room temperature and solvent removed under reduced pressure. The resulting solid was filtered and washed with hexanes to obtain the aryl substituted pyrazole.

2.2 General procedure for the synthesis of cyclopropanols:[2]

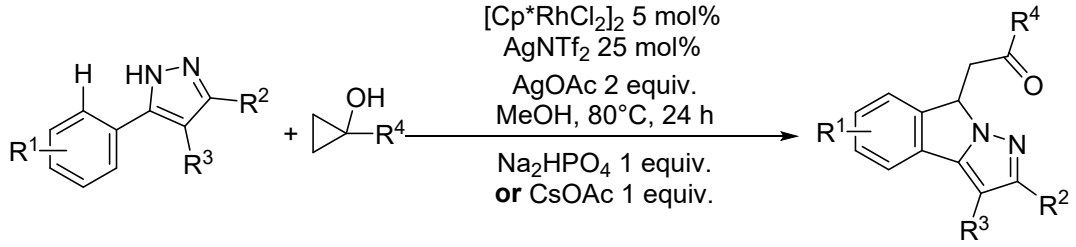


To a solution of acids (15 mmol) in MeOH (30 mL) was added $SOCl_2$ (30 mmol). This mixture was heated to reflux for 3 h before evaporation. The residue was dissolved in DCM (30 mL), washed with aqueous $NaHCO_3$, water and brine, dried over anhydrous Na_2SO_4, and concentrated

to give 100% yield of crude methyl phenylacetates which were used to next step without further purification.

Under the protection of nitrogen, EtMgBr (2.8 equiv., 1 M in THF, 28 mL) was slowly added to a solution of the ester (10.0 mmol) and $Ti(O^iPr)_4$ (14.0 mmol, 4.3 mL) in 6 mL of anhydrous THF at 0 °C over 30 min. The dark mixture was warmed to room temperature and allowed to stir overnight. Then 5 mL of water was slowly added to quench the reaction. After the precipitate was removed by filtration, the filtrate was extracted by Et_2O (20 mL × 3) and the combined organic phase was dried over anhydrous Na_2SO_4. The crude products were purified by column chromatography (PE/EA = 1/1 to 20/1) to afford the pure cyclopropanols.

2.3 General procedure for the synthesis of compound 3 and 4：

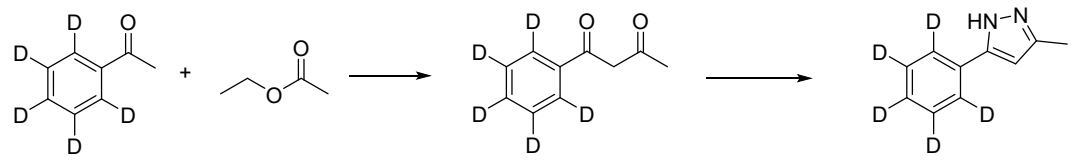


To a 25 mL sealed tube containing a magnetic stir bar, were added **1** (0.1 mmol), cyclopropanol **2** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (25 mol%), Na_2HPO_4 (0.1 mmol), AgOAc (0.2 mmol), MeOH (2.0 mL). The tube was sealed under nitrogen and heated to 80 °C with stirring for 12 h. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10, v/v) to afford the corresponding products. **3i**, **4c**-**4j**, **4m**, **4o** used CsOAc instead of Na_2HPO_4.

3. Mechanistic studies

3.1 Kinetic isotope experiment:

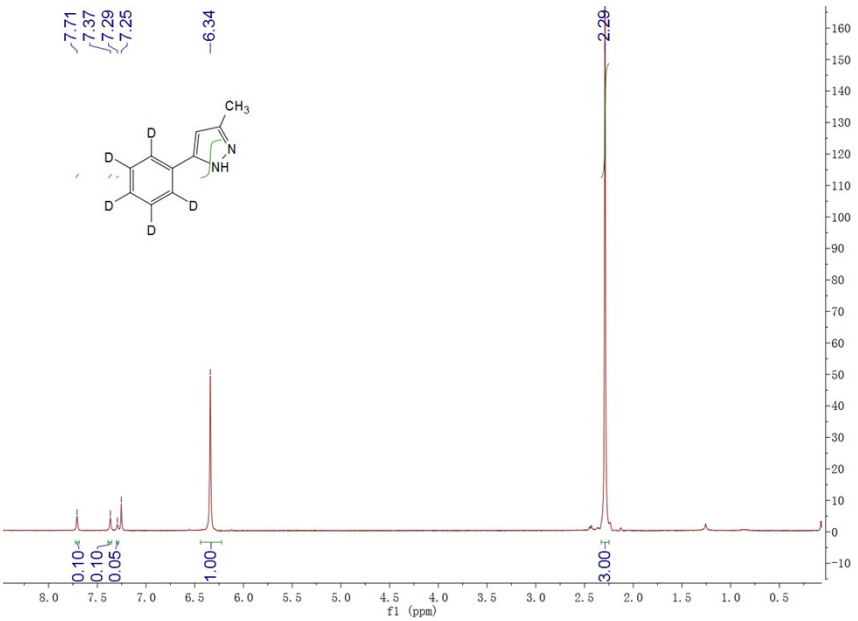
3.1.1 Procedure for synthesis of 3-methyl-5-phenyl-1*H*-pyrazole-d_5 (1b)



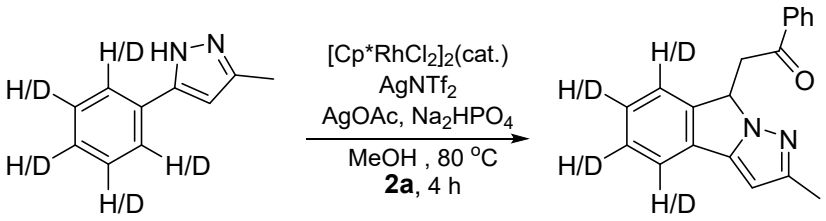
acetophenone-*d5* | 1-phenylbutane-1,3-dione-*d5* | 3-methyl-5-phenyl-*1H*-pyrazole-*d5*

1-phenylbutane-1,3-dione-d_5: Benzaldehyde-d_5 (10 mmol, 1.0 equiv.) was suspended in EtOAc (2 mL), and NaH (0.16 g of dispersion in oil, 4 mmol) was slowly added to the reaction mixture at 0 °C. The reaction mixture was heated to room temperature for 12 hours. Treat the mixture carefully with 10% aqueous NH_4Cl (3 mL). Adjust the reaction mixture pH 5 with hydrochloric acid, and separate the aqueous phase. Extract the reaction mixture with EtOAc, the combined organic extracts were dried with anhydrous Na_2SO_4, and the solvent was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel to give the product.

3-methyl-5-phenyl-1*H*-pyrazole-d_5 (1b-d_5): Hydrazine monohydrate (0.050 g, 1 mmol) in toluene (0.1 mL) was added dropwise to a solution of 1-(phenyl-d_5)butane-1,3-dione (0.167 g, 1 mmol) in toluene (1 mL) kept at 0 °C. The reaction mixture was stirred at 115 °C for 3 hours in a sealed vessel. The mixture was then cooled to room temperature and solvent removed under reduced pressure. The resulting solid was filtered and washed with hexanes to give the product.

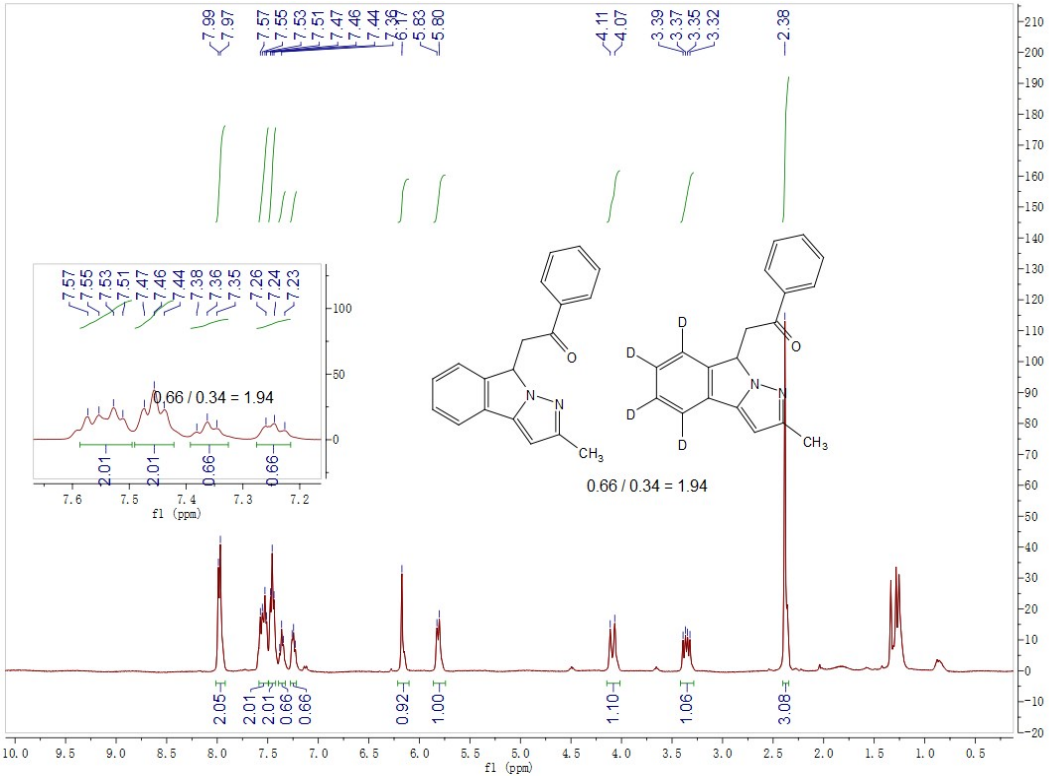


3.1.2 The investigation of 3-methyl-5-phenyl-1*H*-pyrazole (1b) and 3-methyl-5-phenyl-1*H*-pyrazole-d_5 (1b-d_5) reacting with 2a:

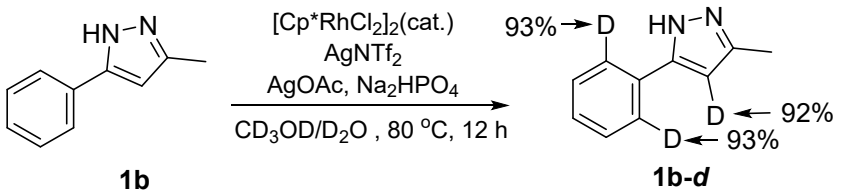


1b/1b-d_5 = 1:1 **3b: 3b-d_4,** K_H:K_D = 1.94

To a 25 mL sealed tube containing a magnetic stir bar, were added **1b** (15.8 mg, 0.05 mmol) and **1b-*d*$_5$** (16.3 mg, 0.05 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (25 mol%), Na_2HPO_4 (0.1 mmol), AgOAc (0.2 mmol), MeOH (2.0 mL). The tube was sealed under nitrogen and heated to 80 °C with stirring for 4 h. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10, v/v) to afford the corresponding products to afford the desired mixture of **3b** and **3b-*d*$_4$** products in 34.2% yield.



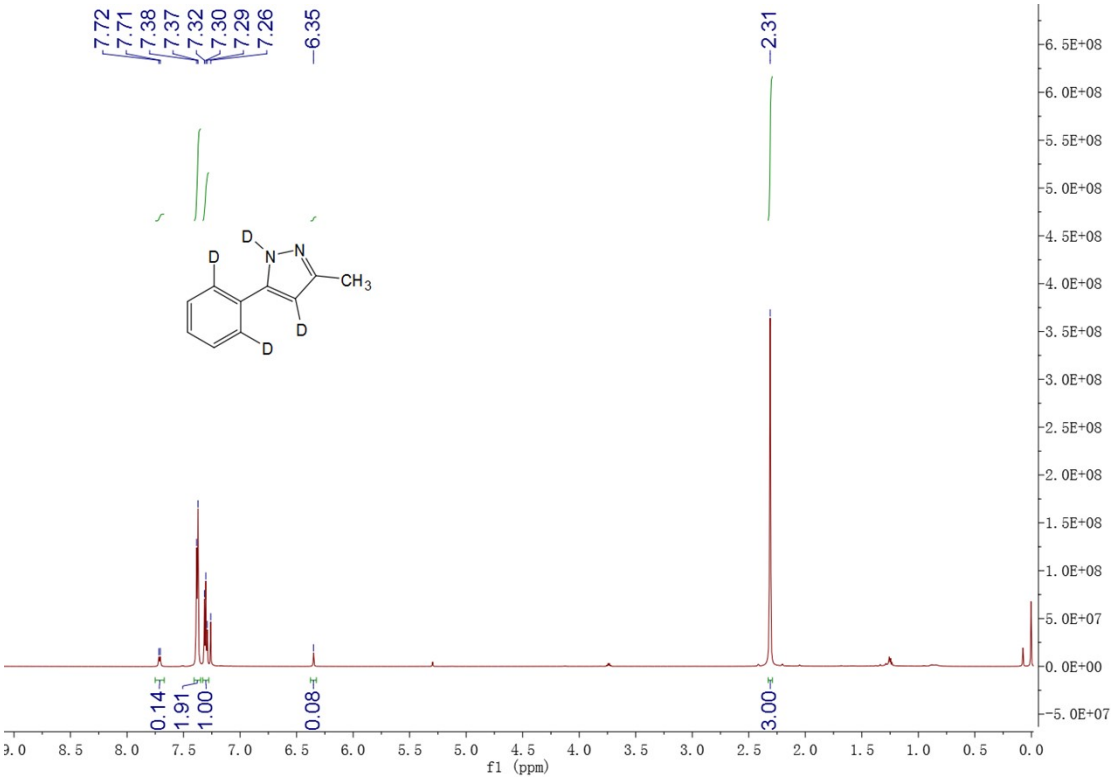
3.2 H/D Exchange experiments.



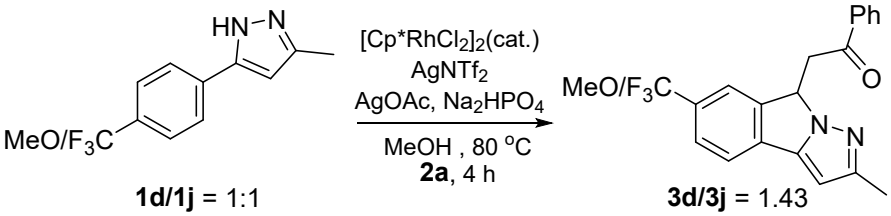
1b **1b-*d***

To a 25 mL sealed tube containing a magnetic stir bar, were added 1*H*-pyrazole **1b** (0.1 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (25 mol%), Na_2HPO_4 (0.1 mmol), AgOAc (0.2 mmol), MeOH (2.0 mL). The tube was sealed under nitrogen and heated to 110 °C with stirring for 12 h. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction

mixture was filtered through a plug of celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum ether = 1:10, v/v) to afford the corresponding products to afford a white solid product. which was characterized by ^{1}H NMR spectroscopy.



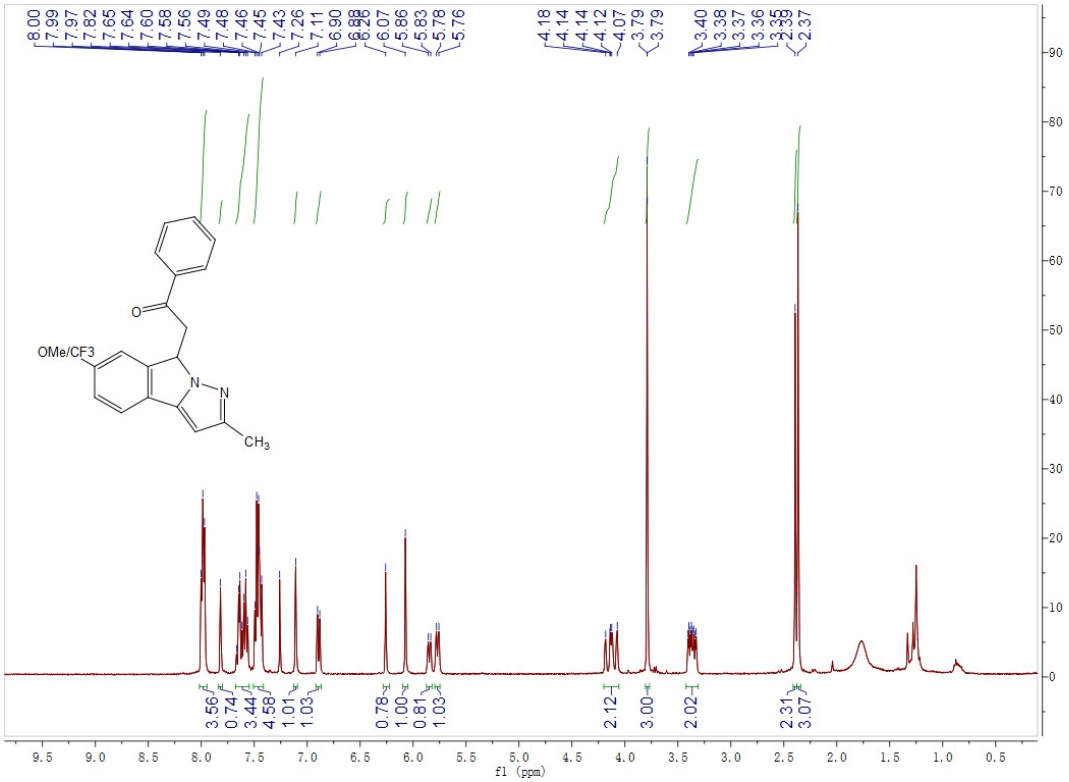
3.3 Competition reactions:



1d/1j = 1:1 **3d/3j** = 1.43

To a 25 mL sealed tube containing a magnetic stir bar, were added **1d** (0.05 mmol) and **1j** (0.05 mmol), **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (25 mol%), Na_2HPO_4 (0.1 mmol), AgOAc (33.4 mg, 0.2 mmol), MeOH (2.0 mL). The tube was sealed under nitrogen and heated to 80 °C with stirring for 4 h. Then the reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was filtered through a plug of celite and the residue was washed with ethyl acetate (2 x 5 mL). The combined organic layer was concentrated in vacuum and the residue was purified by flash column chromatography (silica gel, ethyl acetate/petroleum

ether = 1:10, v/v) to afford the corresponding products to afford the desired mixture of **3d** and **3j** products. The ratio was determined to be **3d**/**3j** = 1.43 on the basis of ^{1}H NMR analysis.

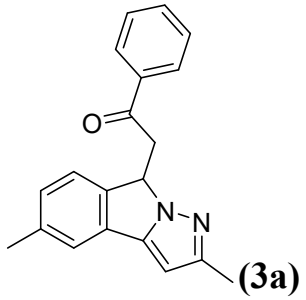


References:

(1) (a) R. Shi, F. Liao, H. Niu and A. Lei, Org. Chem. Front., 2018, 5, 1957; (b) H.-Y. Hao, Y.-J. Mao, Z.-Y. Xu, S.-J. Lou and D.-Q. Xu, Org. Lett., 2020, 22, 2396; (c) Z. Chen, Z. Ding, T. Chen, L. Meng and G. Wang, Org. Biomol. Chem., 2020, 18, 8486.

(2) S. Wang, E. Miao, H. Wang, B. Song, Wei Huang and W. Yang, Chem. Commun., 2021, 57, 5929.

4. The ^{1}H and ^{13}C NMR spectra of compounds



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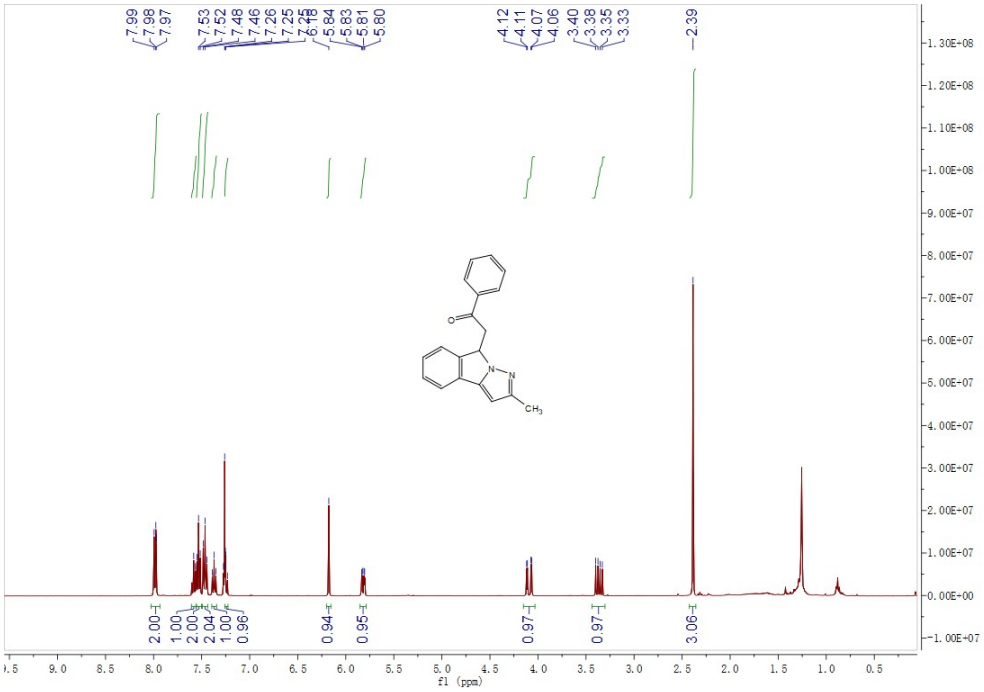
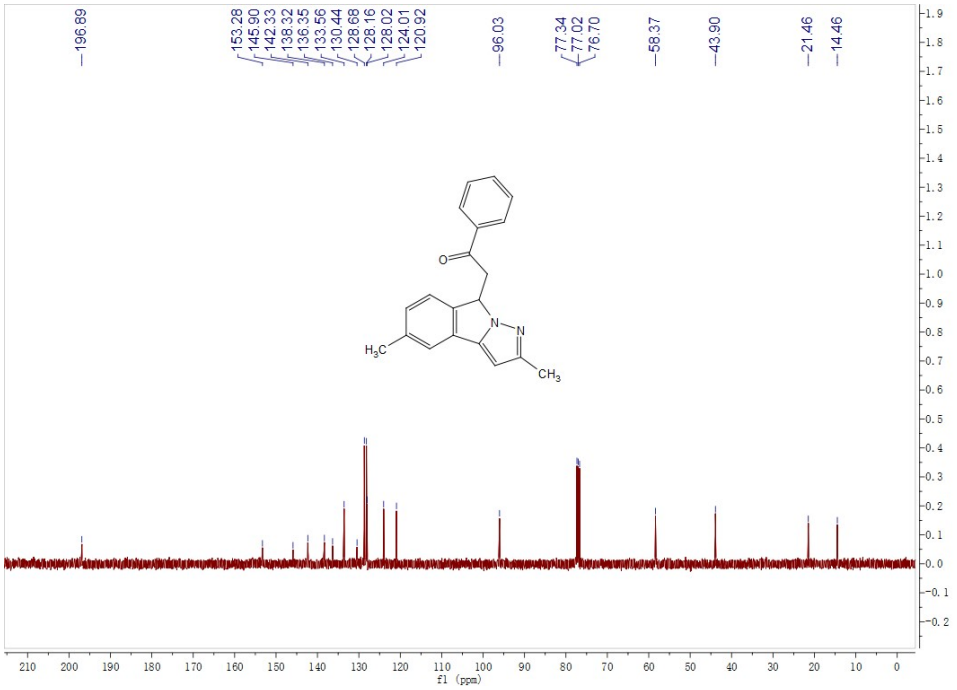
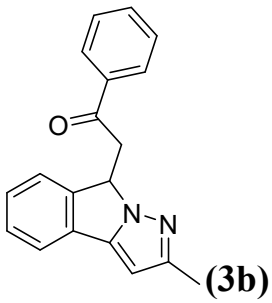
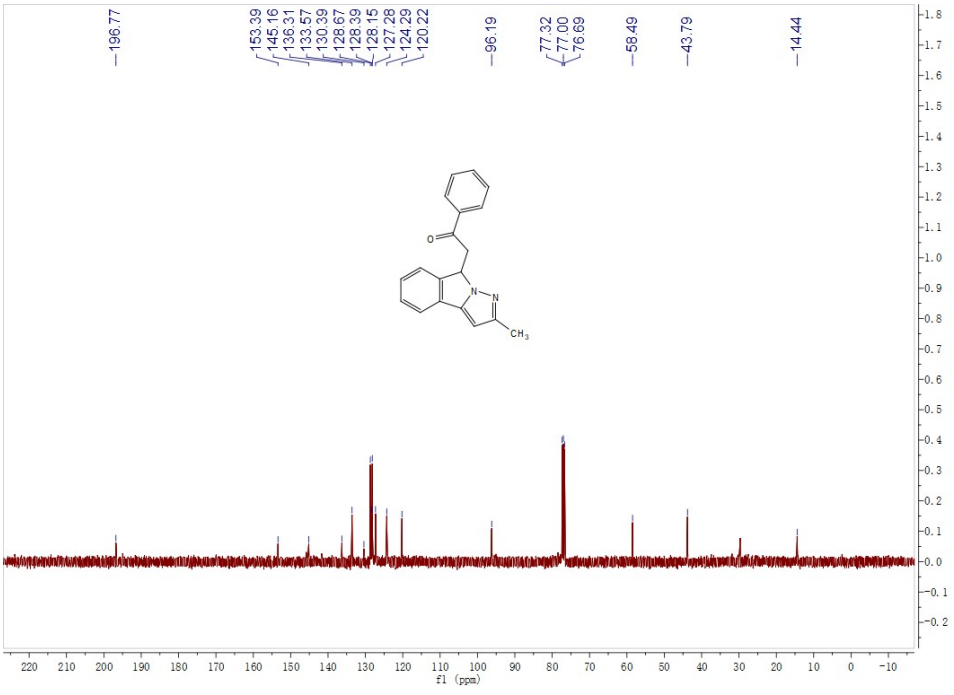





O
N
N

(3b)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136.31
133.57
130.39
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128.39
128.15
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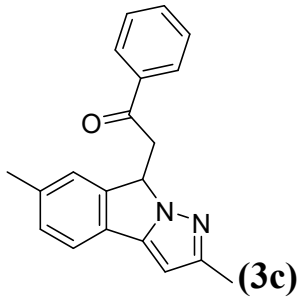
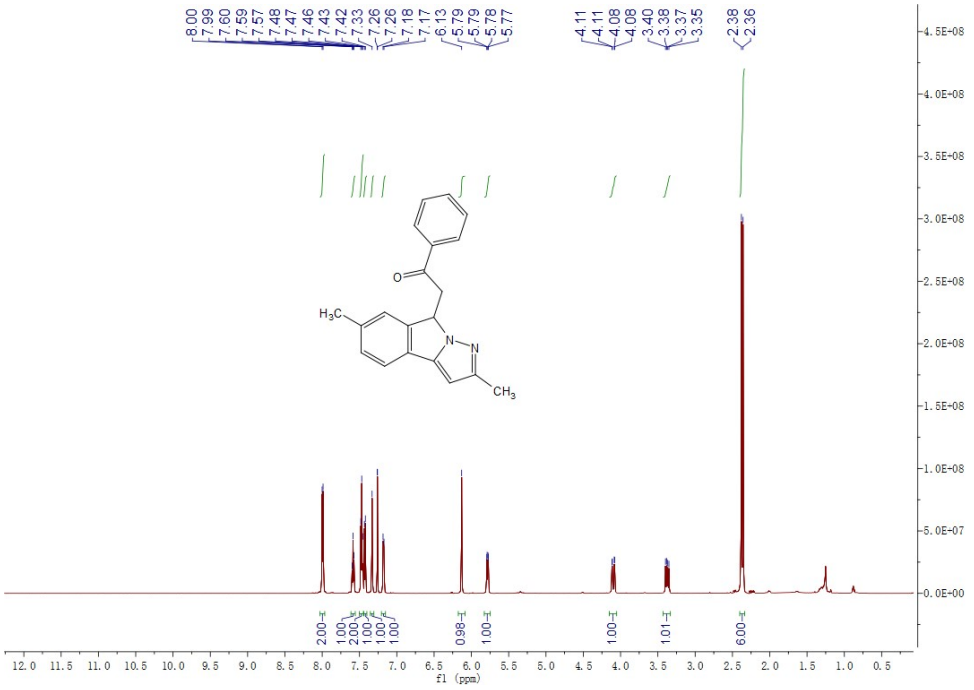
96.19
77.32
77.00
76.69
58.49
43.79
14.44
f1 (ppm)



(3c)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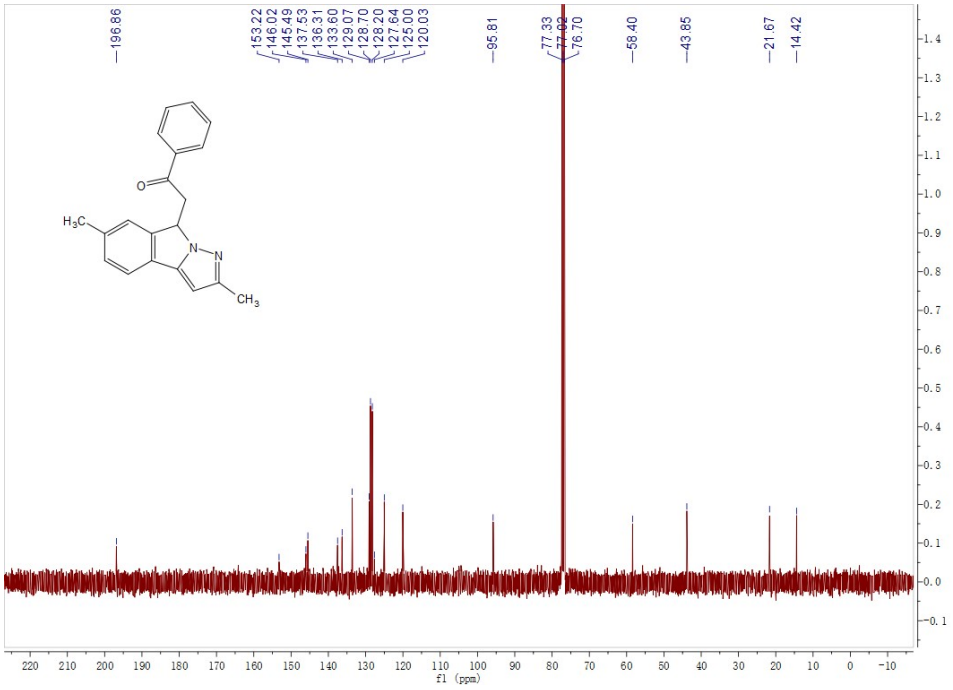
7.26
7.18
7.17
6.13
5.79
5.79
5.78
5.77
4.11
4.11
4.08
4.08
3.40
3.38
3.37
3.35
2.38
2.36
f1 (ppm)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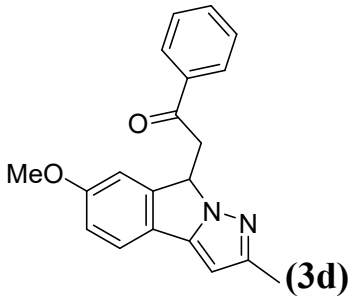
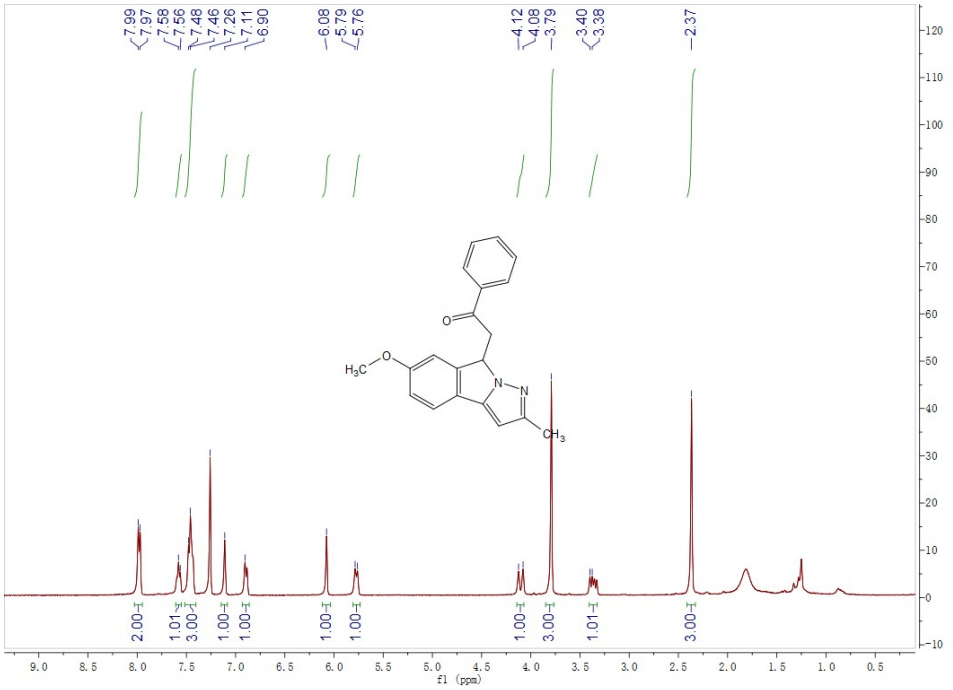
f1 (ppm)


O
MeO
N
N

(3d)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3.00
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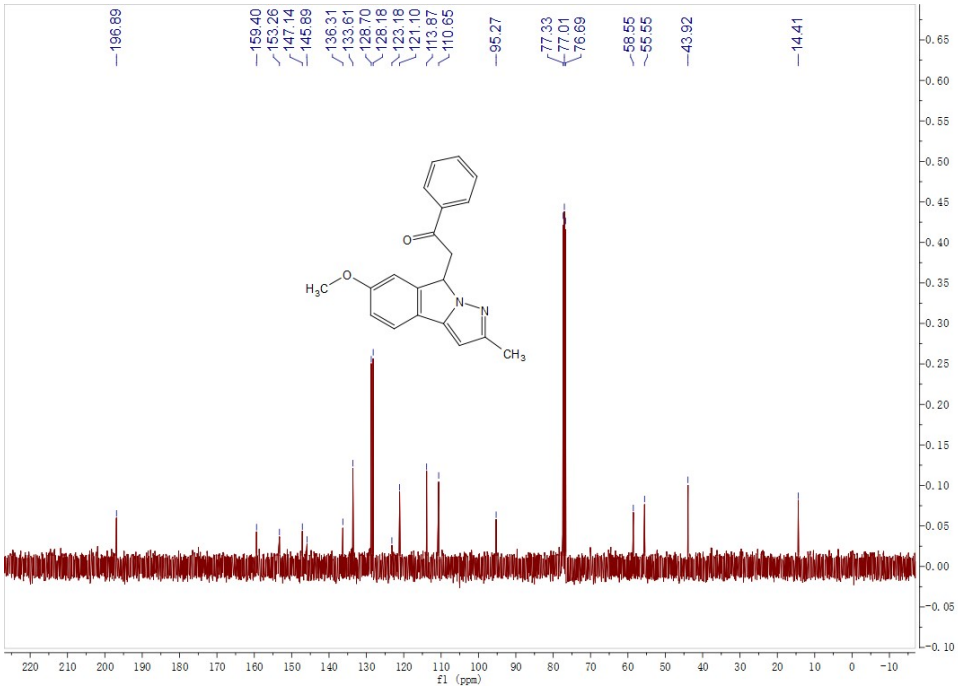
3.00
f1 (ppm)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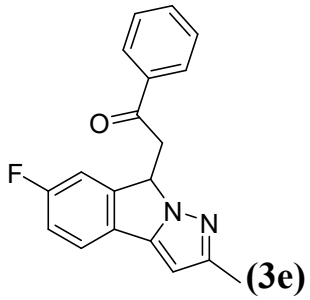
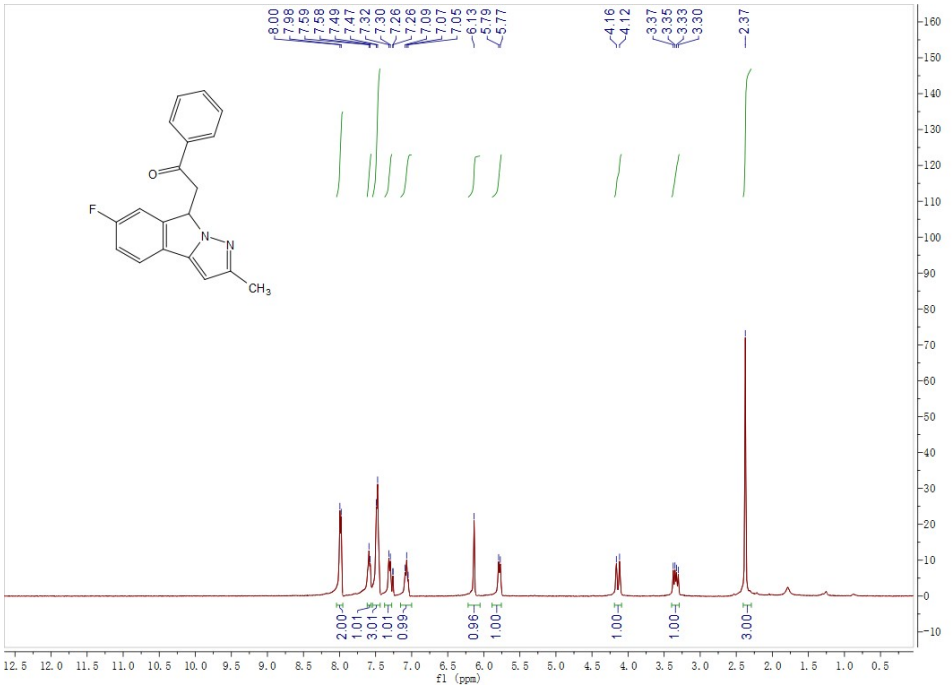
14.41
f1 (ppm)


O
F
N
N

(3e)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5.77
4.16
4.12
3.37
3.35
3.33
3.30
2.37
2.00
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3.01
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0.99
0.96
1.00
1.00
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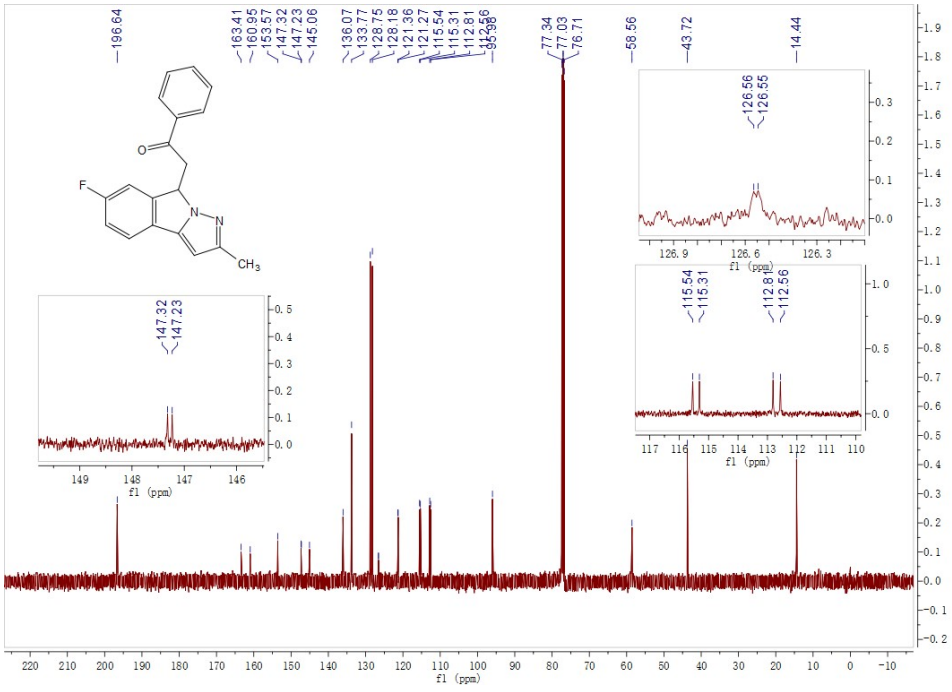
3.00
f1 (ppm)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121.27
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115.31
112.81
112.56
95.98
77.34
77.03
76.71
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115.54
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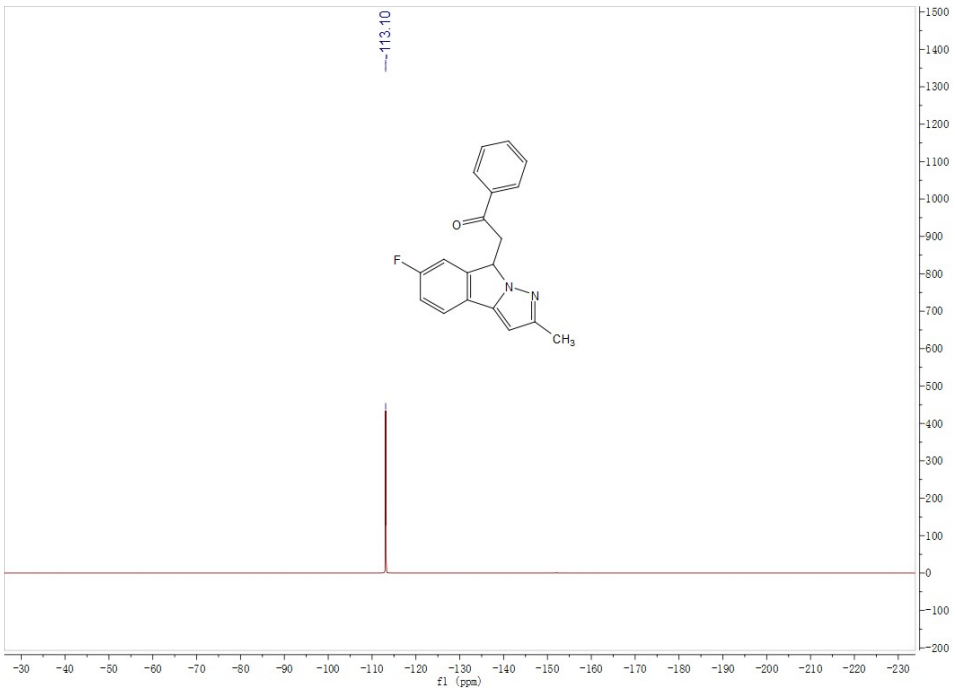
112.56
147.32
147.23
f1 (ppm)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F
N
N
CH3
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1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
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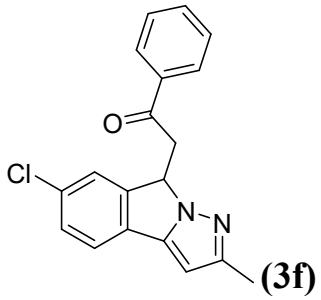
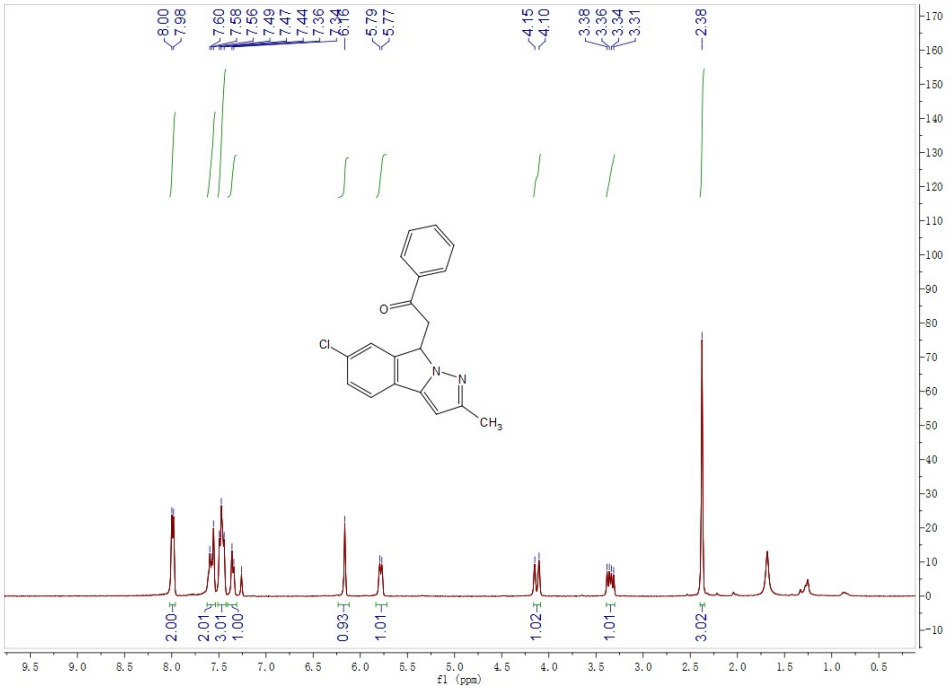
-190
-200
-210
-220
-230
f1 (ppm)


O
Cl
N
N

(3f)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7.34
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5.79
5.77
4.15
4.10
3.38
3.36
3.34
3.31
2.38
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2.01
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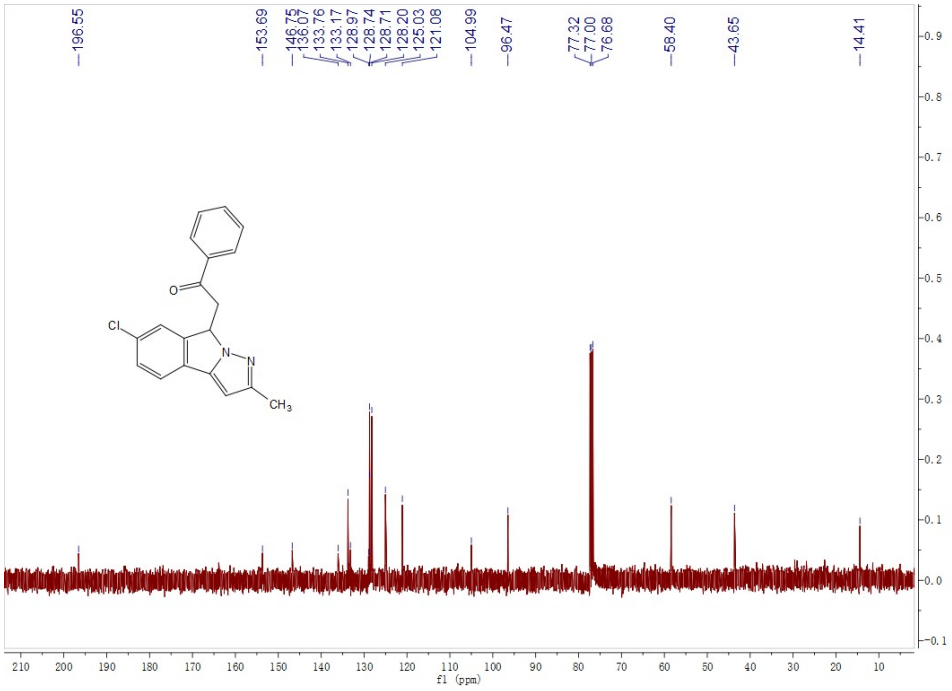
1.00
0.93
1.01
1.02
1.01
3.02
f1 (ppm)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76.68
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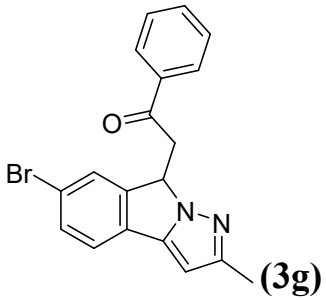
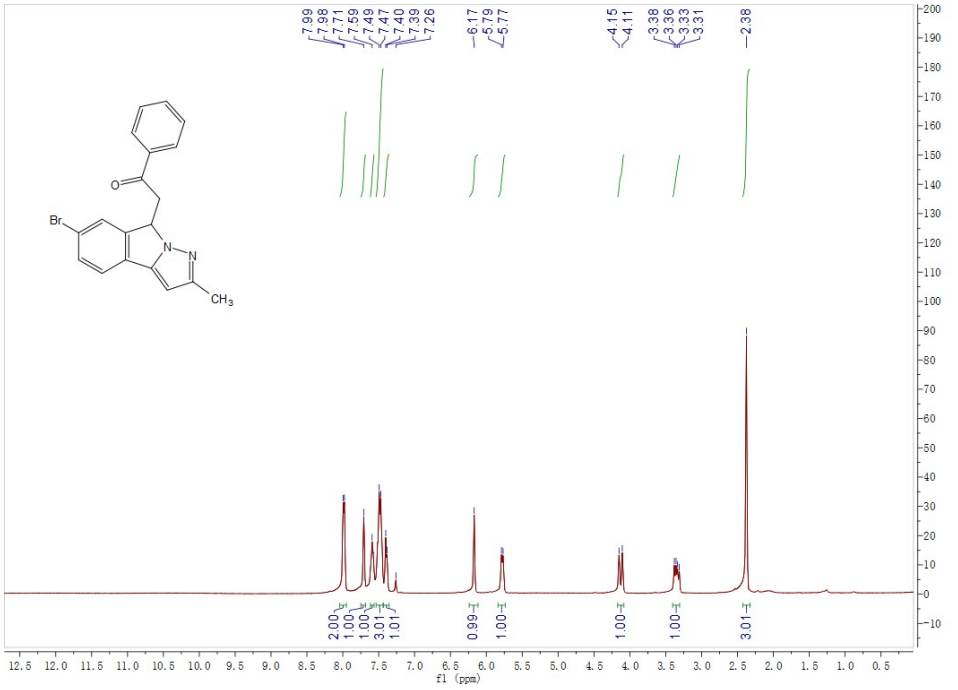
14.41
f1 (ppm)


O
Br
N
N

(3g)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7.98
7.71
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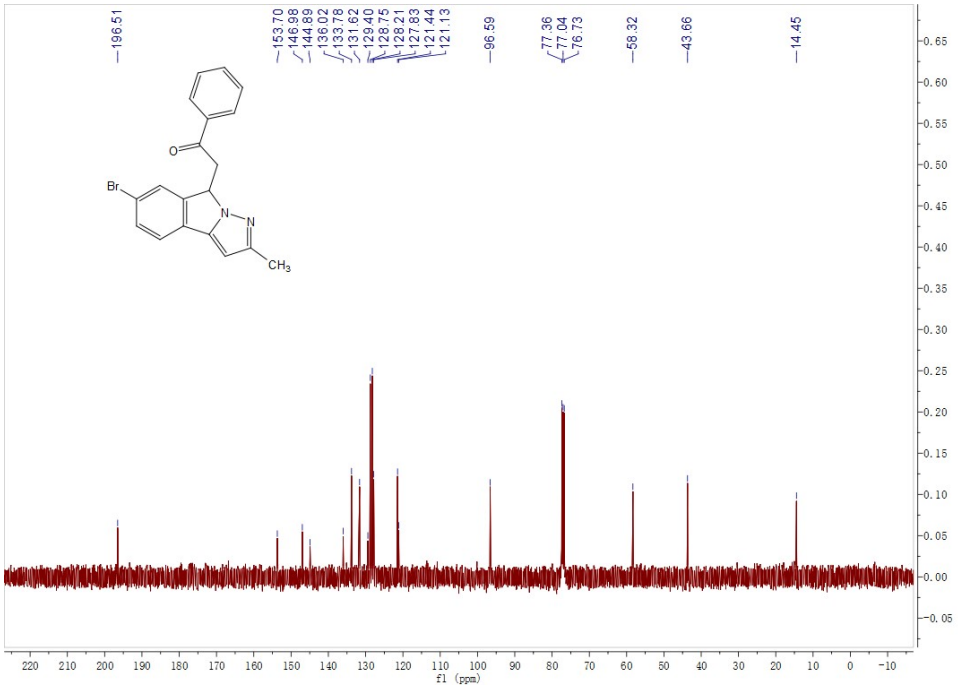
7.49
7.47
7.40
7.39
7.26
6.17
5.79
5.77
4.15
4.11
3.38
3.36
3.33
3.31
2.38
2.00
1.00
1.00
3.01
1.01
0.99
1.00
1.00
1.00
3.01
f1 (ppm)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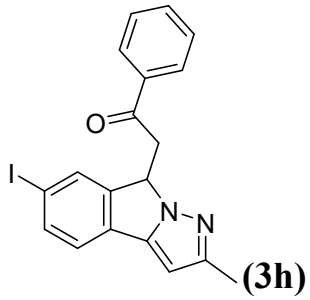
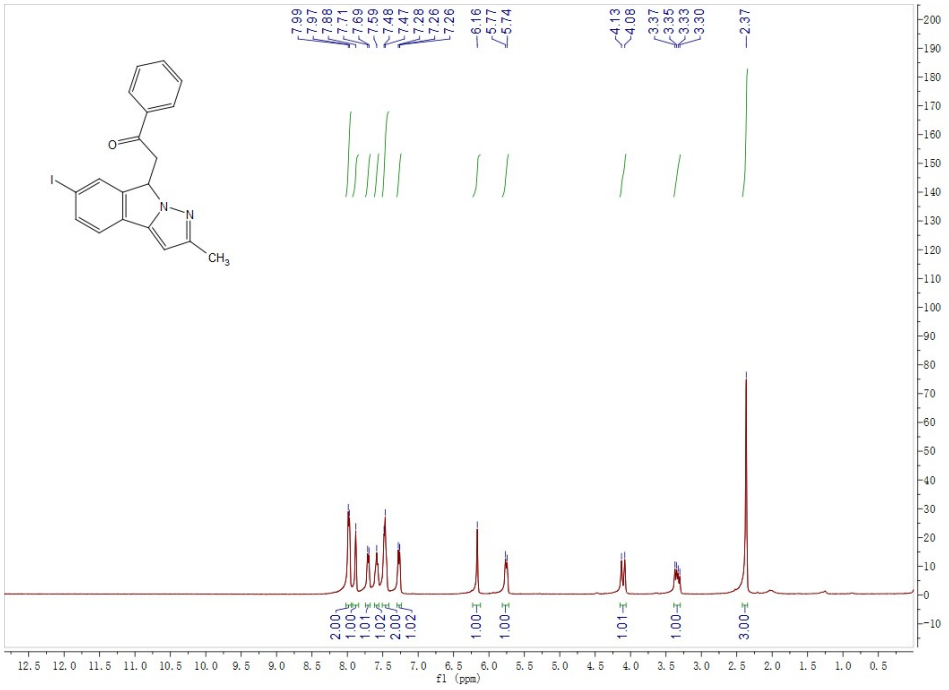
146.98
144.89
136.02
133.78
131.62
129.40
128.75
128.21
127.83
121.44
121.13
96.59
77.36
77.04
76.73
58.32
43.66
14.45
f1 (ppm)


O
I
N
N

(3h)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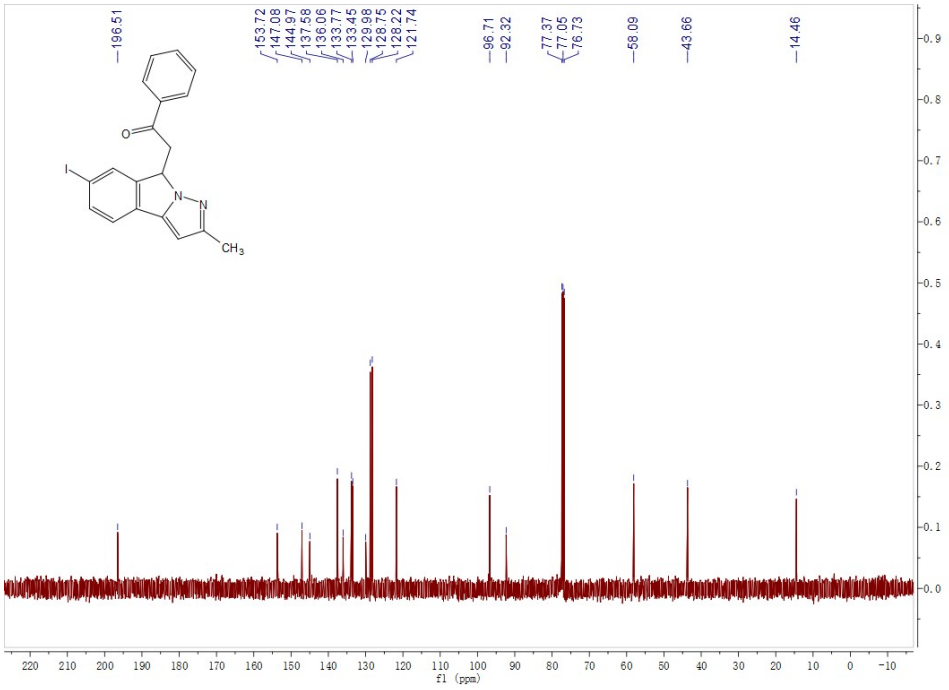
7.69
7.59
7.48
7.47
7.28
7.26
7.26
6.16
5.77
5.74
4.13
4.08
3.37
3.35
3.33
3.30
2.37
O
I
N
N
CH3
2.00
1.00
1.01
1.02
2.00
1.02
1.00
1.00
1.01
1.00
3.00
f1 (ppm)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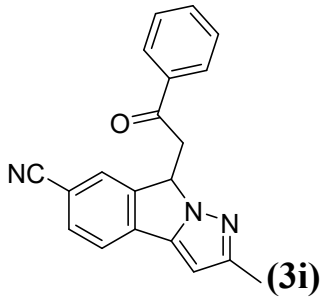
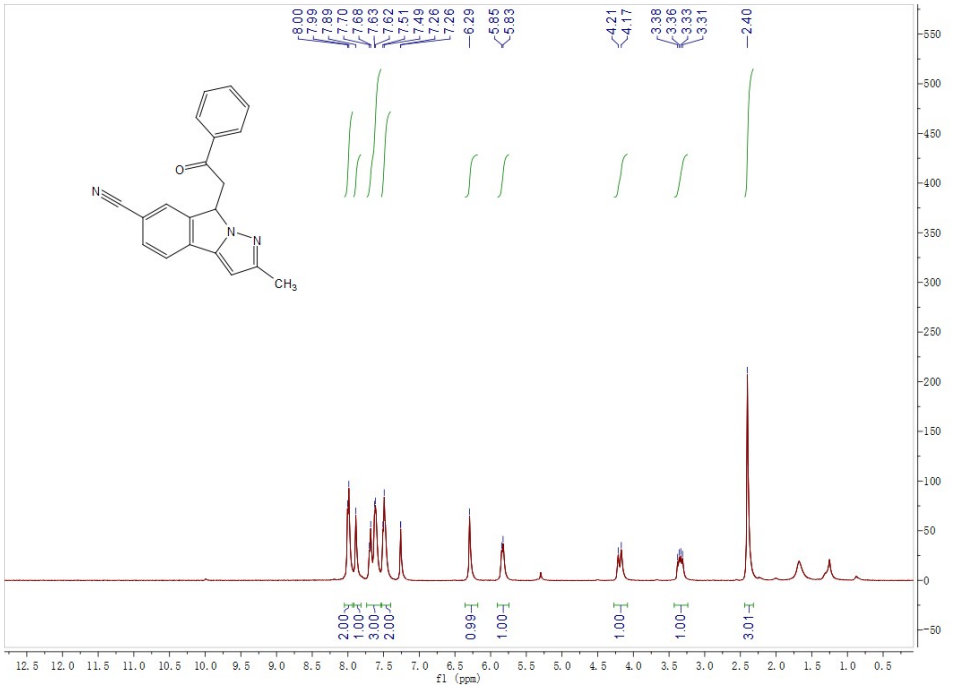
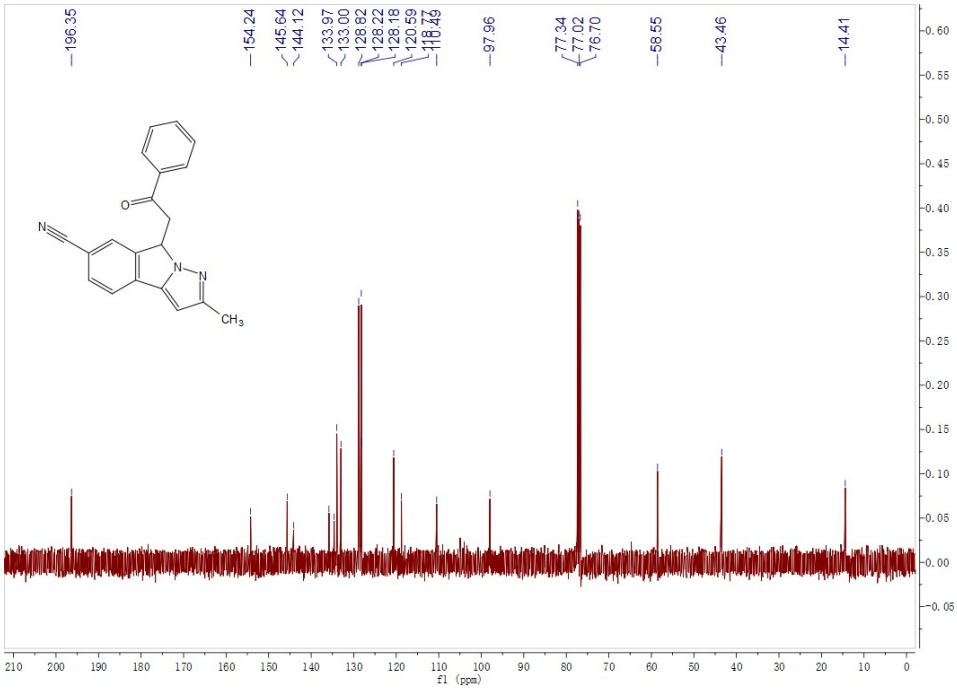
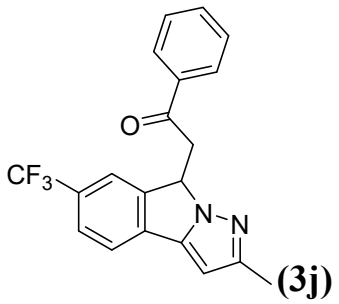
144.97
137.58
136.06
133.77
133.45
129.98
128.75
128.22
121.74
96.71
92.32
77.37
77.05
76.73
58.09
43.66
14.46
O
I
N
N
CH3
f1 (ppm)


O
NC
N
N

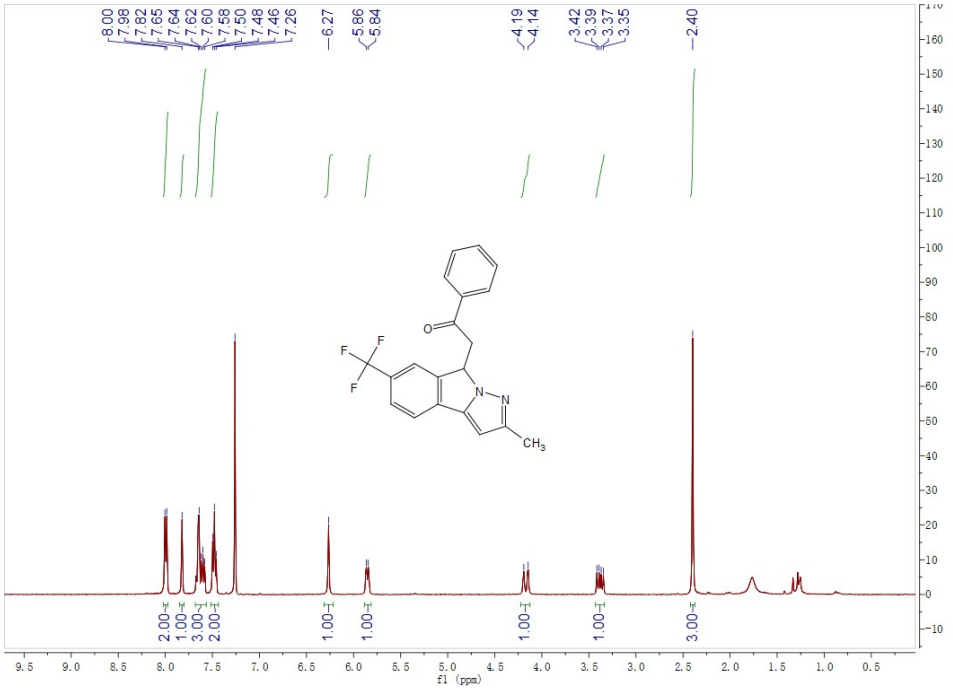
(3i)


8.00
7.99
7.89
7.70
7.68
7.63
7.62
7.51
7.49
7.26
7.26
6.29
5.85
5.83
4.21
4.17
3.38
3.36
3.33
3.31
2.40
2.00
1.00
3.00
2.00
0.99
1.00
1.00
1.00
3.01
f1 (ppm)


196.35
154.24
145.64
144.12
133.97
133.00
128.82
128.22
128.18
120.59
118.47
118.42
97.96
77.34
77.02
76.70
58.55
43.46
14.41
f1 (ppm)


O
CF3
N
N

(3j)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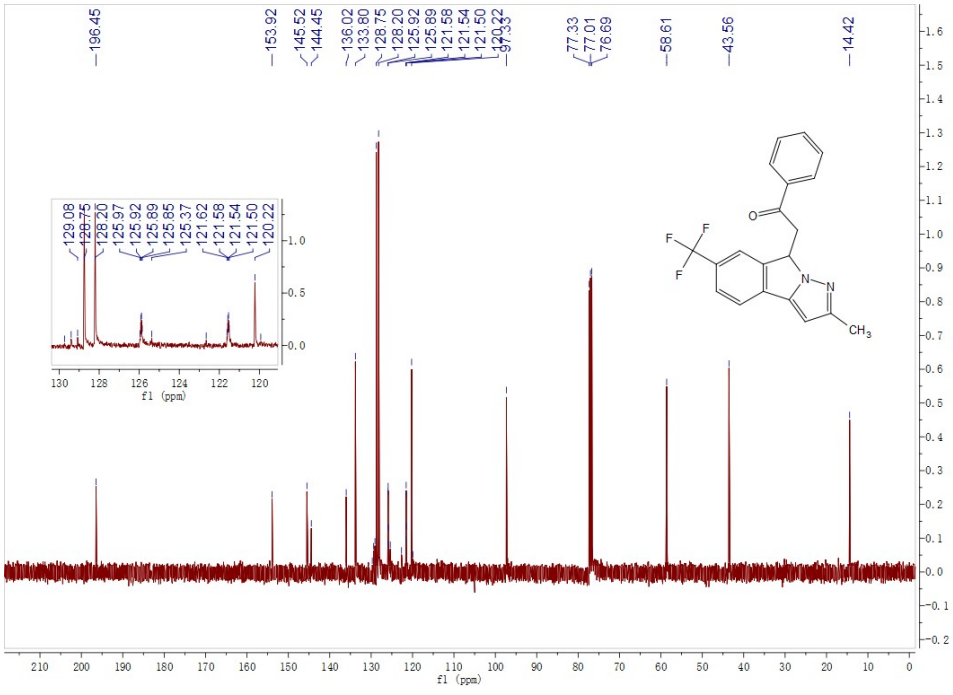
7.98
7.82
7.65
7.64
7.62
7.60
7.58
7.50
7.48
7.46
7.26
6.27
5.86
5.84
4.19
4.14
3.42
3.39
3.37
3.35
2.40
2.00
1.00
3.00
2.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)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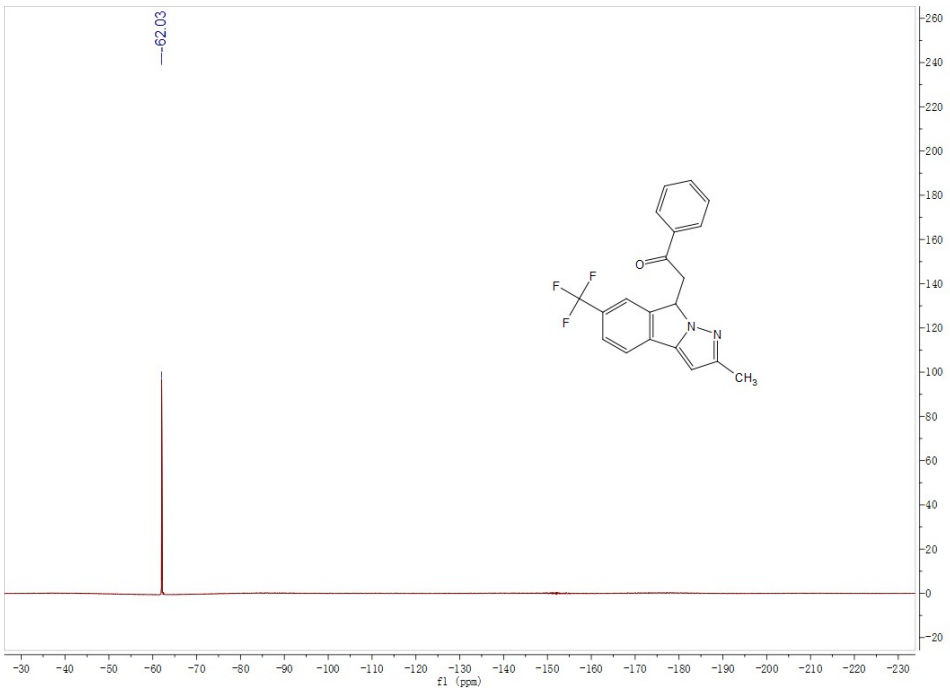
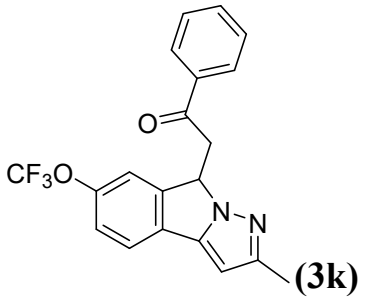
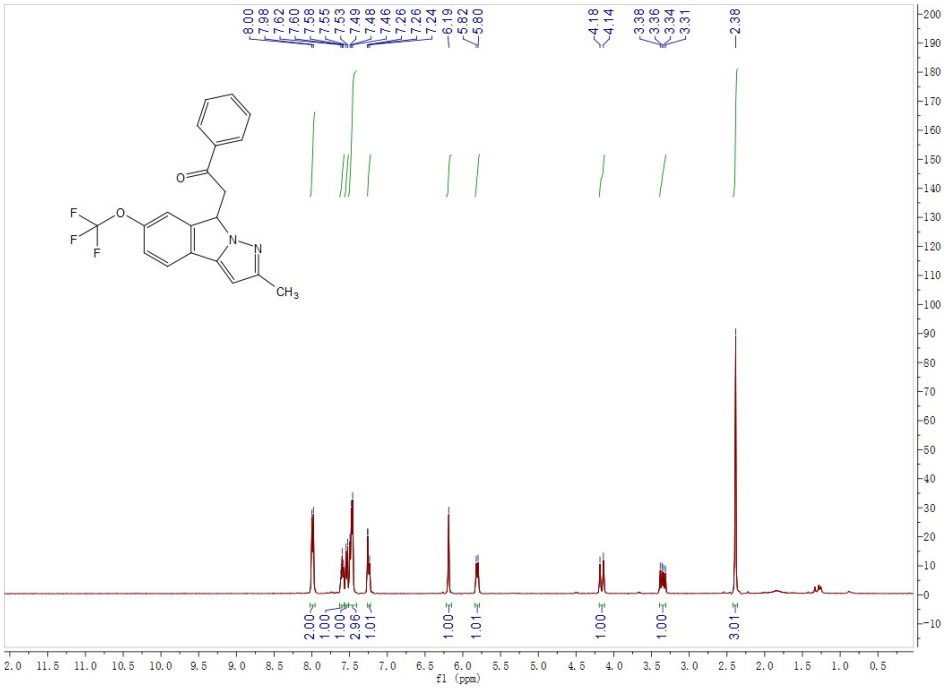
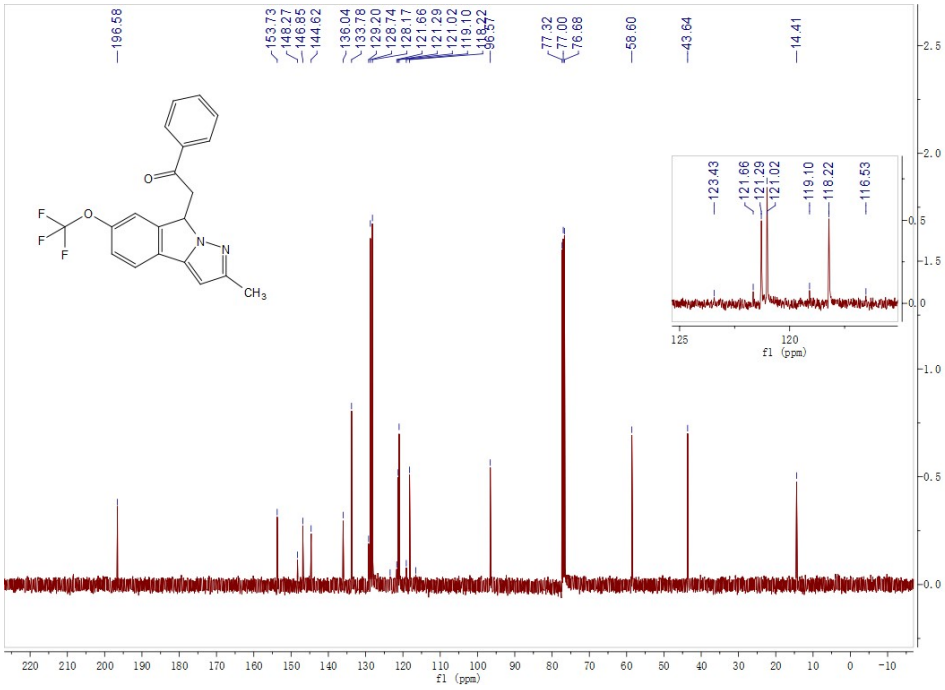
153.92
145.52
144.45
136.02
133.80
128.75
128.20
125.92
125.89
121.58
121.54
121.50
120.22
97.33
77.33
77.01
76.69
58.61
43.56
14.42
129.08
128.75
128.20
125.97
125.92
125.89
125.85
125.37
121.62
121.58
121.54
121.50
120.22
f1 (ppm)
f1 (ppm)


-62.03
O
F
F
F
N
N
CH3
f1 (ppm)


O
CF3O
N
N

(3k)


8.00
7.98
7.62
7.60
7.58
7.55
7.53
7.49
7.48
7.46
7.26
7.24
6.19
5.82
5.80
4.18
4.14
3.38
3.36
3.34
3.31
2.38
2.00
1.00
1.00
2.96
1.01
1.00
1.01
1.00
1.00
3.01
f1 (ppm)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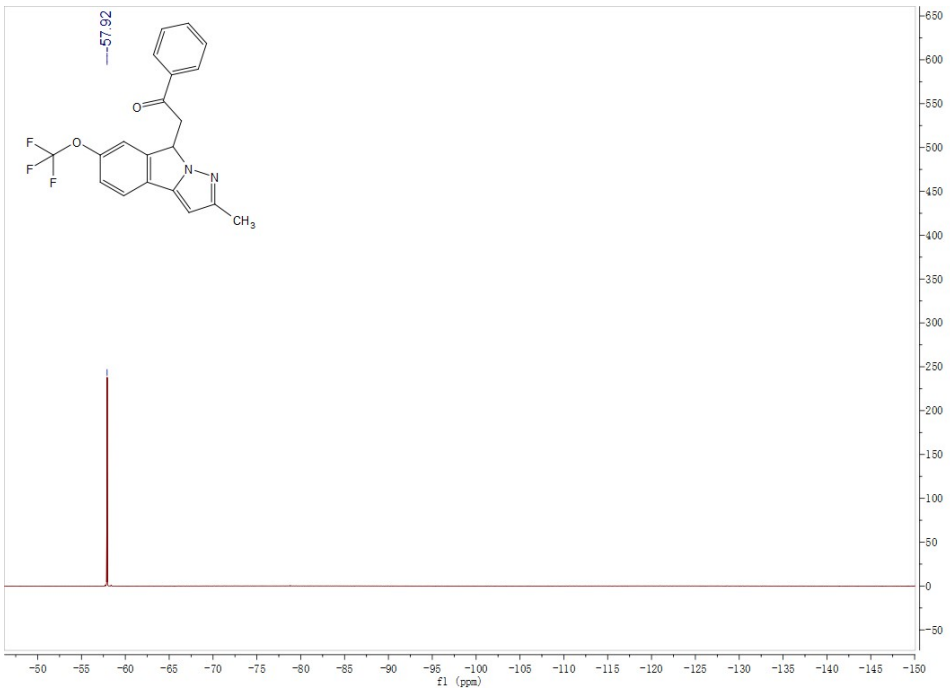
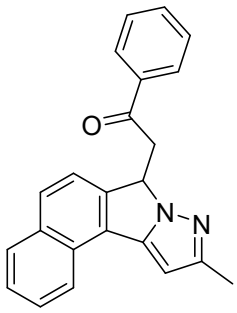
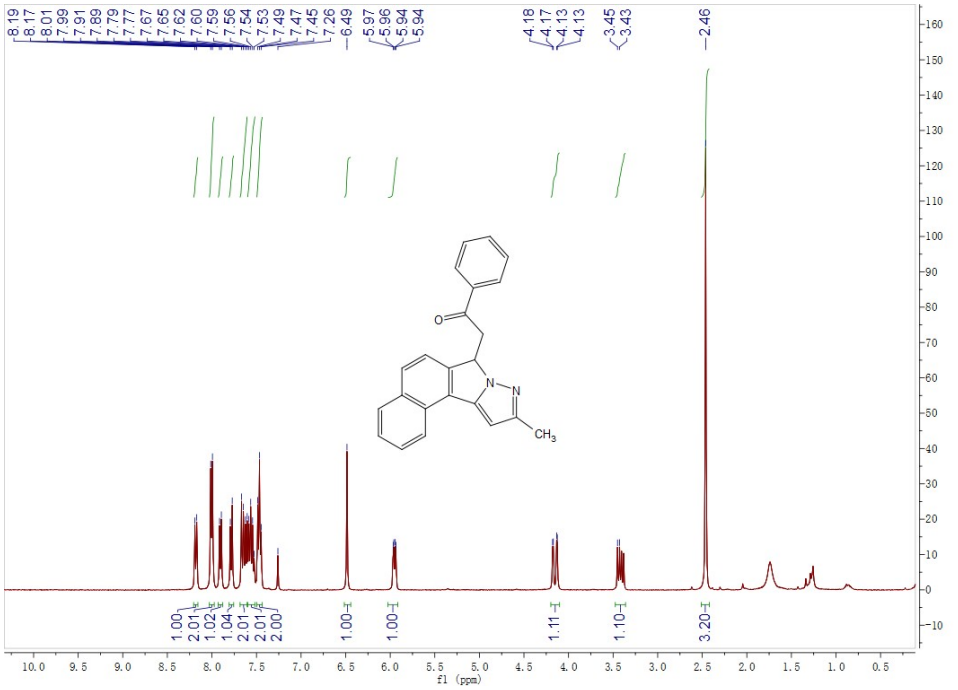
148.27
146.85
144.62
136.04
133.78
129.20
128.74
128.17
121.66
121.29
121.02
119.10
118.22
116.53
96.37
77.32
77.00
76.68
58.60
43.64
14.41
123.43
121.66
121.29
121.02
119.10
118.22
116.53
125
120
f1 (ppm)
f1 (ppm)


-57.92
O
F
F
F
O
N
N
CH3
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
f1 (ppm)



(3l)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8.17
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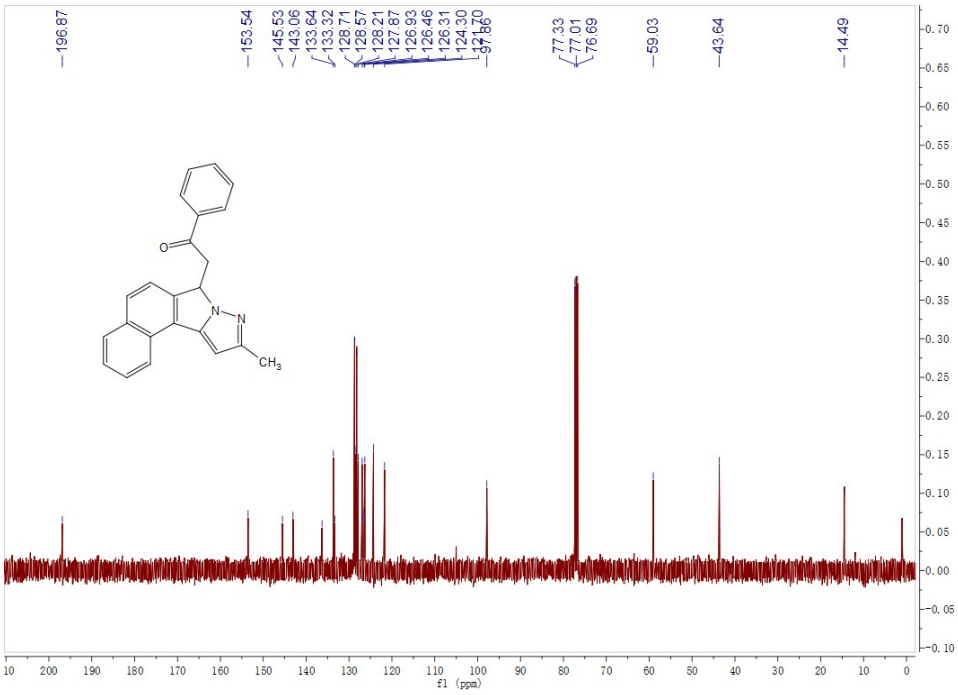
7.91
7.89
7.79
7.77
7.67
7.65
7.62
7.60
7.59
7.56
7.54
7.53
7.49
7.47
7.45
7.26
6.49
5.97
5.96
5.94
5.94
4.18
4.17
4.13
4.13
3.45
3.43
2.46
1.00
2.01
1.02
1.04
2.01
2.01
2.00
1.00
1.00
1.11
1.10
3.20
f1 (ppm)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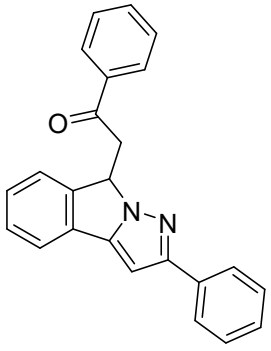
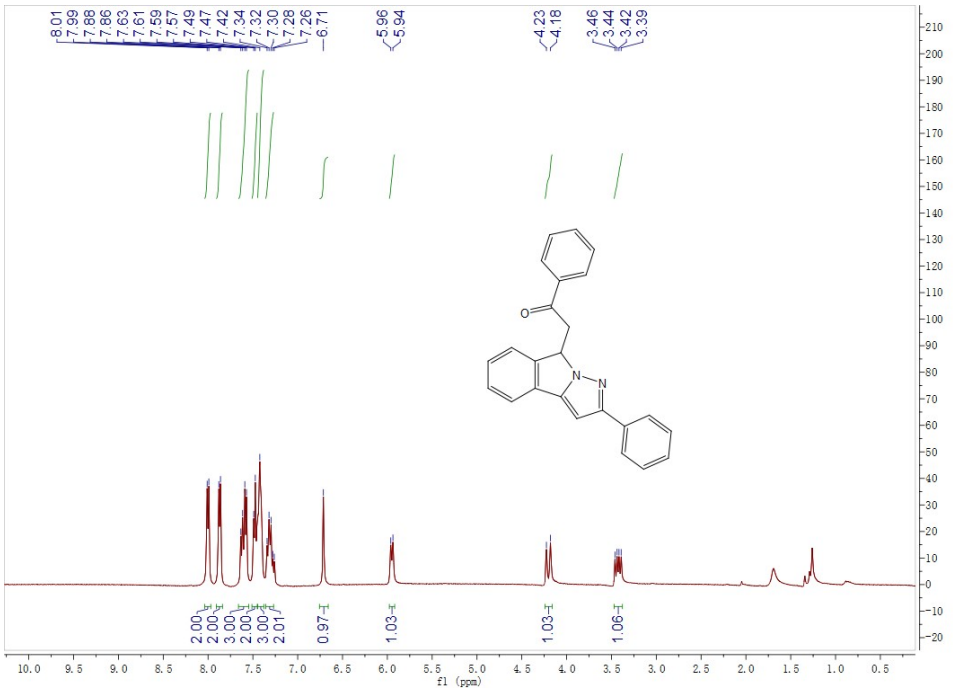
143.06
133.64
133.32
128.71
128.57
128.21
127.87
126.93
126.46
126.31
124.30
121.20
97.86
77.33
77.01
76.69
59.03
43.64
14.49
f1 (ppm)



(3m)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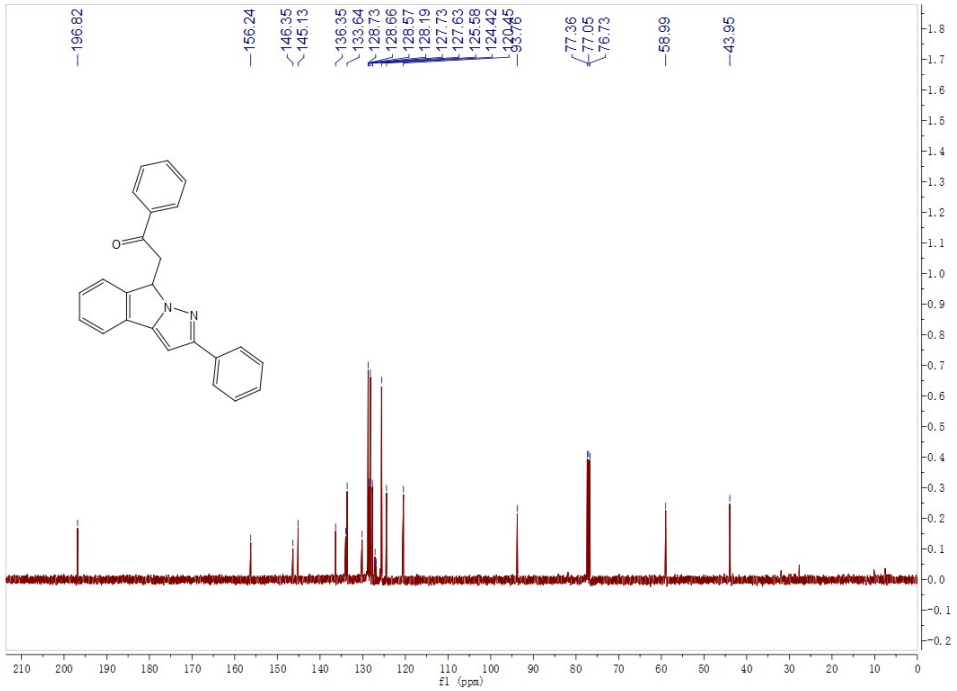
7.86
7.63
7.61
7.59
7.57
7.49
7.47
7.42
7.34
7.32
7.30
7.28
7.26
6.71
5.96
5.94
4.23
4.18
3.46
3.44
3.42
3.39
2.00
2.00
3.00
2.00
3.00
2.01
0.97
1.03
1.03
1.06
f1 (ppm)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156.24
146.35
145.13
136.35
133.64
128.73
128.66
128.57
128.19
127.73
127.63
125.58
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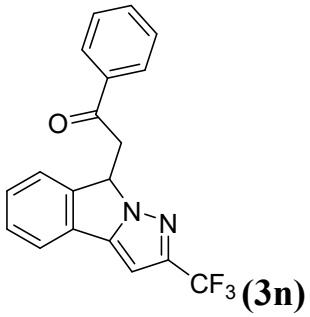
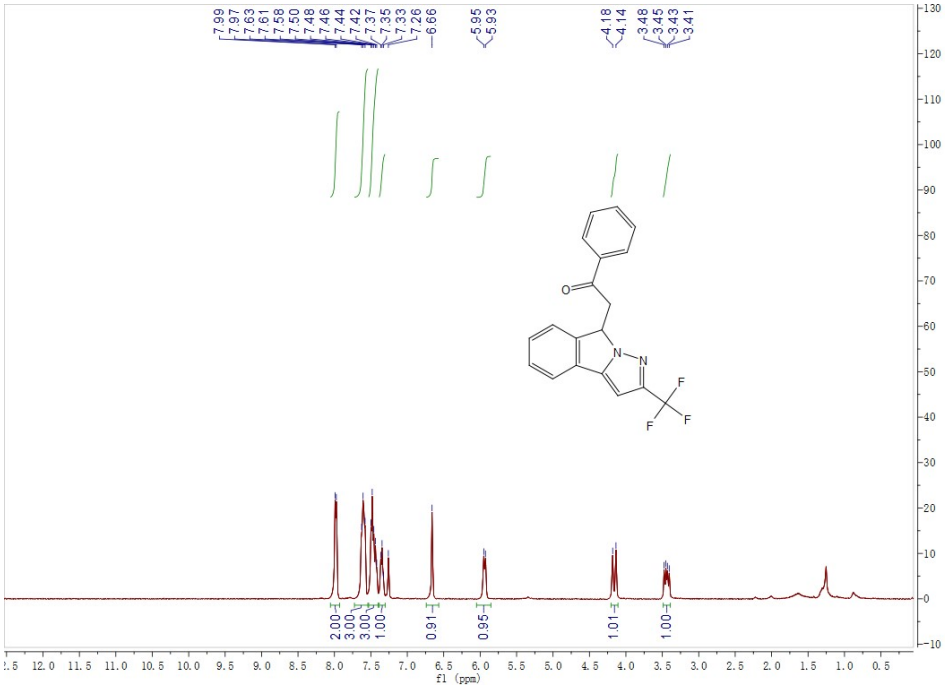
77.05
76.73
58.99
43.95
f1 (ppm)



(3n)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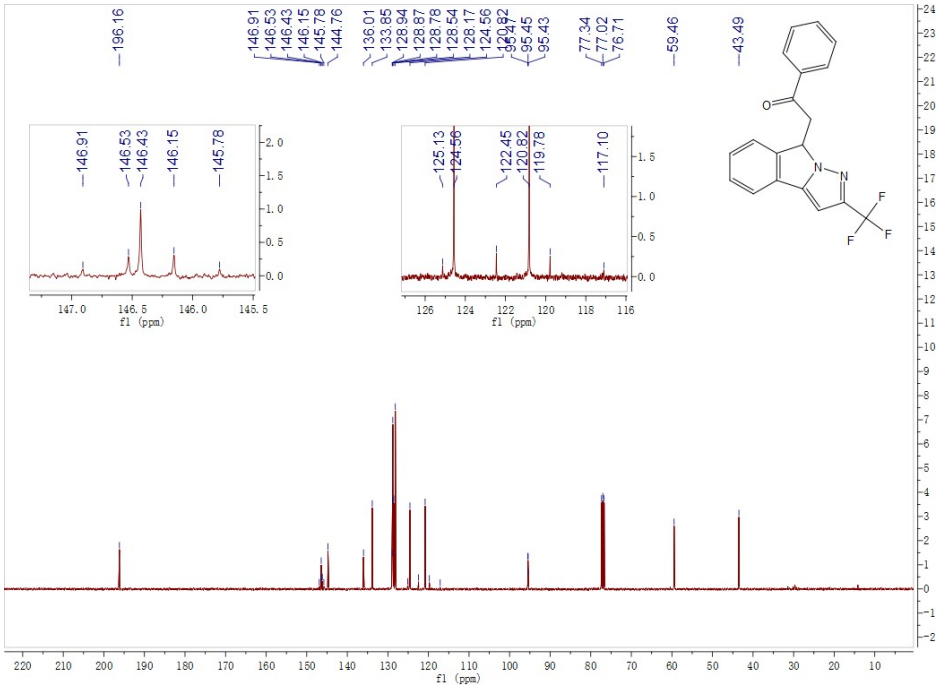
7.97
7.63
7.61
7.58
7.50
7.48
7.46
7.44
7.42
7.37
7.35
7.33
7.26
6.66
5.95
5.93
4.18
4.14
3.48
3.45
3.43
3.41
2.00
3.00
3.00
1.00
0.91
0.95
1.01
1.00
f1 (ppm)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146.53
146.43
146.15
145.78
144.76
136.01
133.85
128.94
128.87
128.78
128.54
128.17
124.56
120.82
95.47
95.45
95.43
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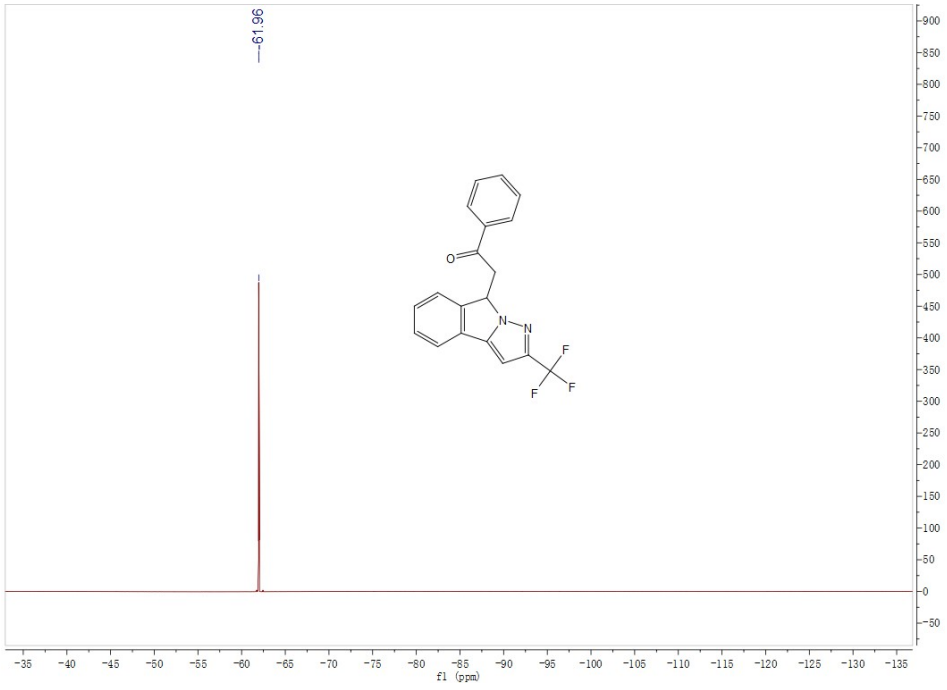
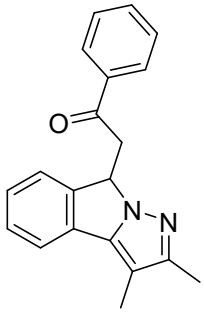
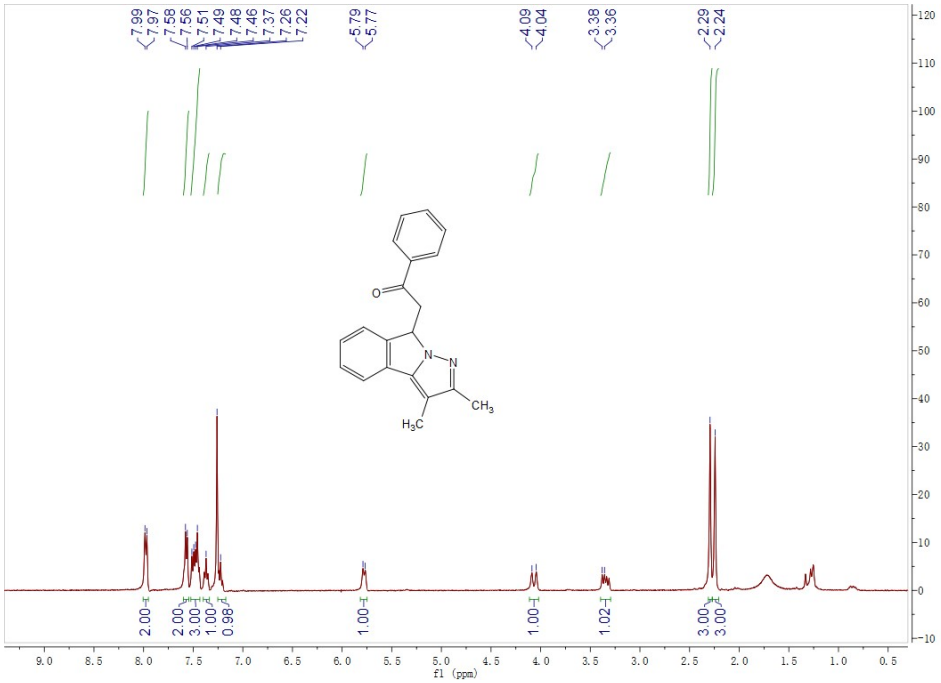
122.45
120.82
119.78
117.10
f1 (ppm)


-61.96
O
N
N
F
F
F
f1 (ppm)



(3o)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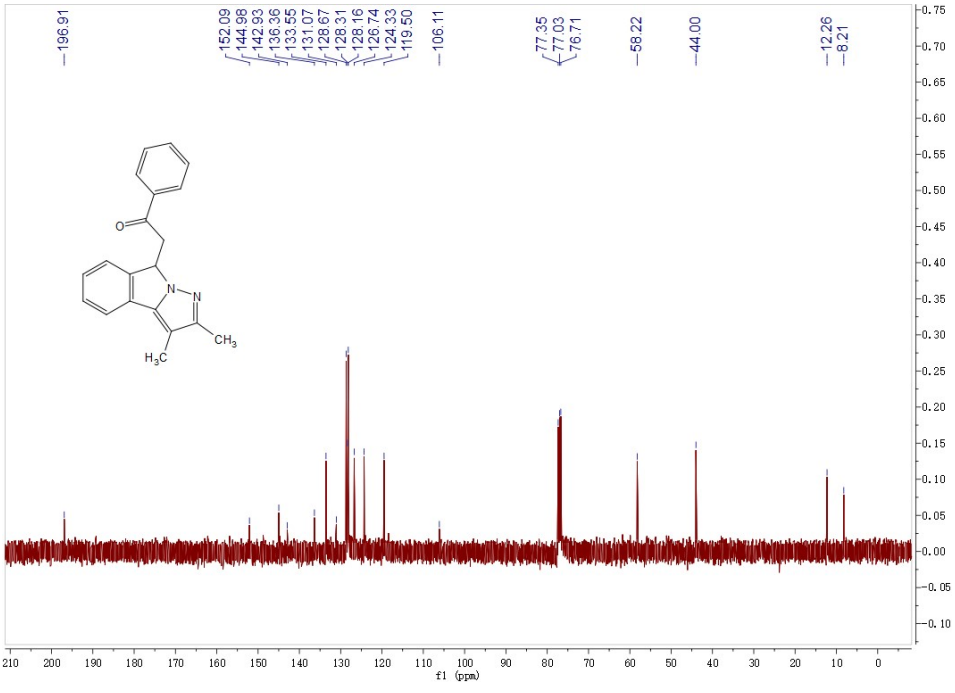
7.56
7.51
7.49
7.48
7.46
7.37
7.26
7.22
5.79
5.77
4.09
4.04
3.38
3.36
2.29
2.24
2.00
2.00
3.00
1.00
0.98
1.00
1.00
1.02
3.00
3.00
f1 (ppm)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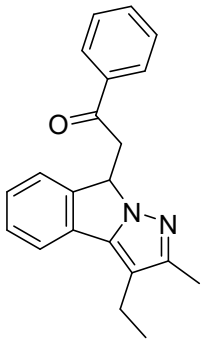
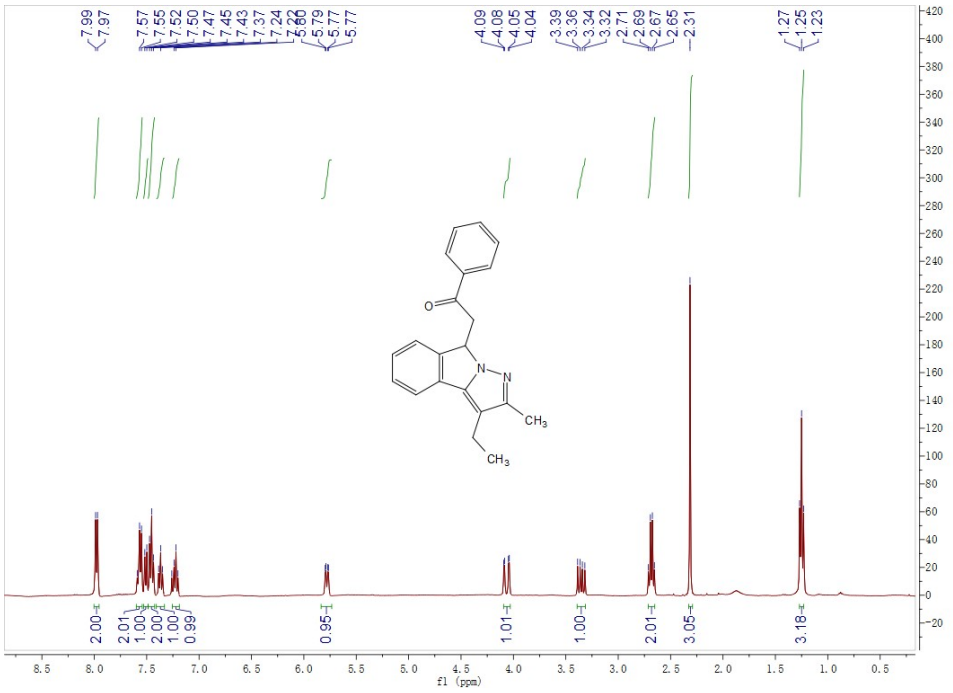
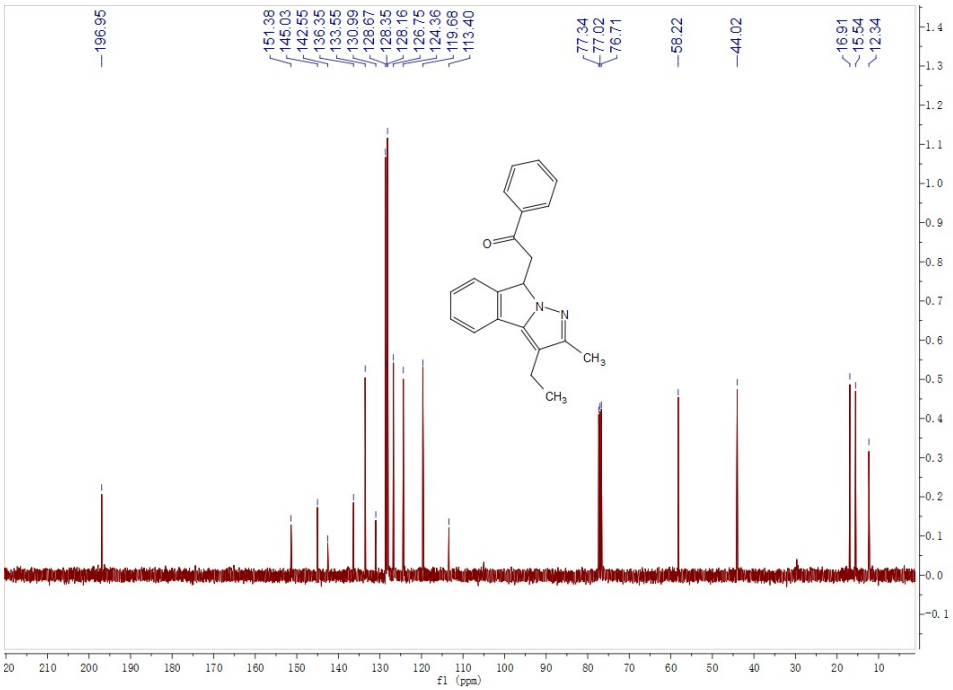
152.09
144.98
142.93
136.36
133.55
131.07
128.67
128.31
128.16
126.74
124.33
119.50
106.11
77.35
77.03
76.71
58.22
44.00
12.26
8.21
f1 (ppm)



(3p)


7.99
7.97
7.57
7.55
7.52
7.50
7.47
7.45
7.43
7.37
7.24
7.22
5.80
5.79
5.77
5.77
4.09
4.08
4.05
4.04
3.39
3.36
3.34
3.32
2.71
2.69
2.67
2.65
2.31
1.27
1.25
1.23
2.00
2.01
1.00
2.00
1.00
0.99
0.95
1.01
1.00
2.01
3.05
3.18
f1 (ppm)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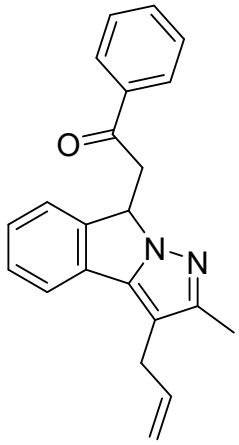
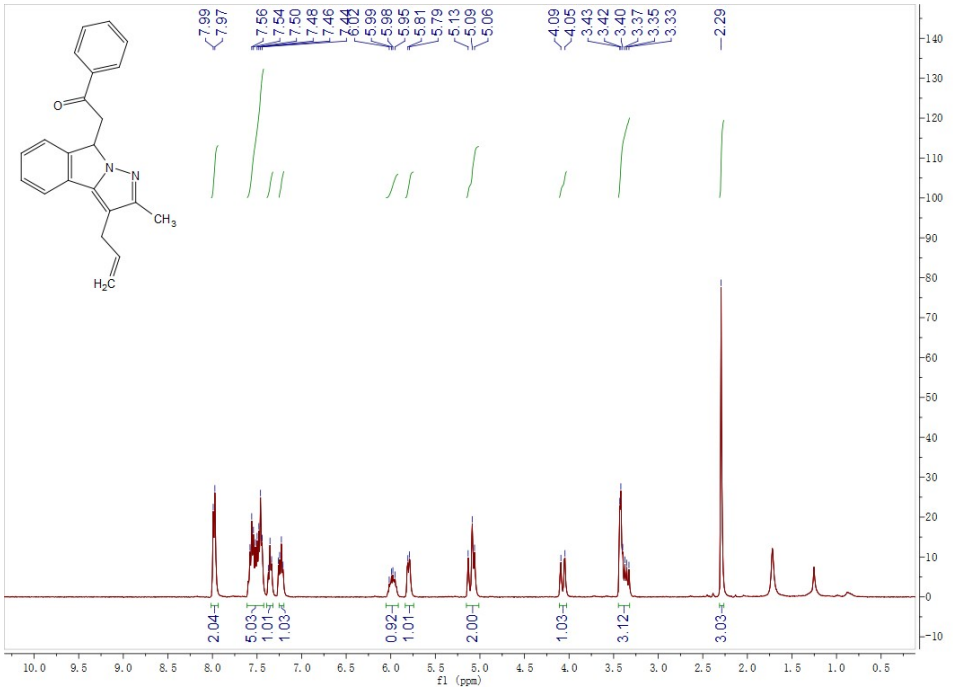
142.55
136.35
133.55
130.99
128.67
128.35
128.16
126.75
124.36
119.68
113.40
77.34
77.02
76.71
58.22
44.02
16.91
15.54
12.34
f1 (ppm)



(3q)


7.99
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7.56
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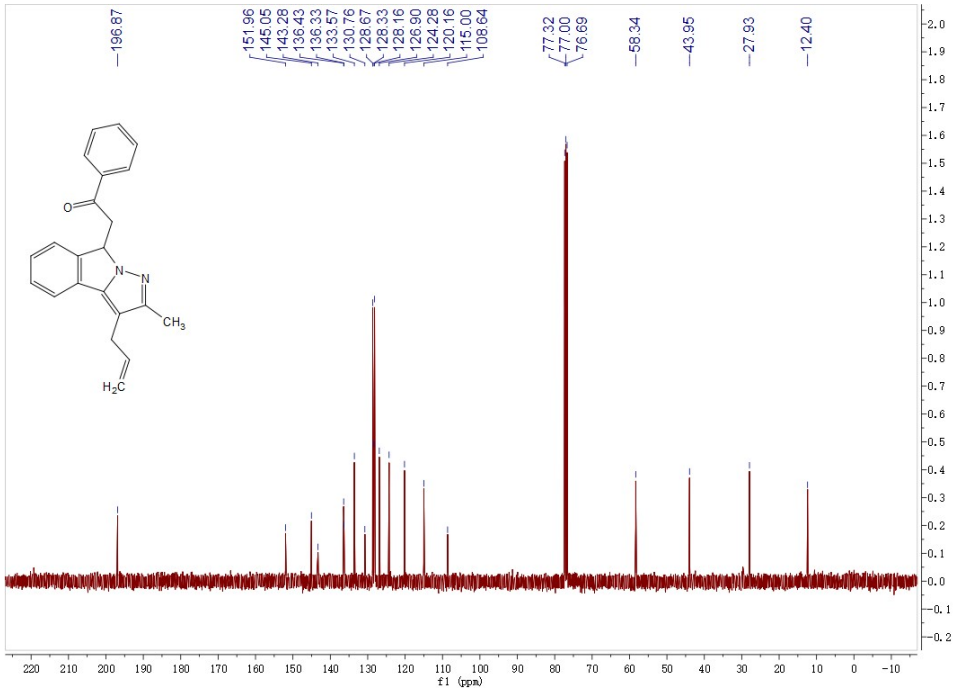
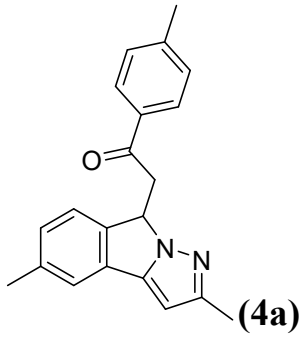
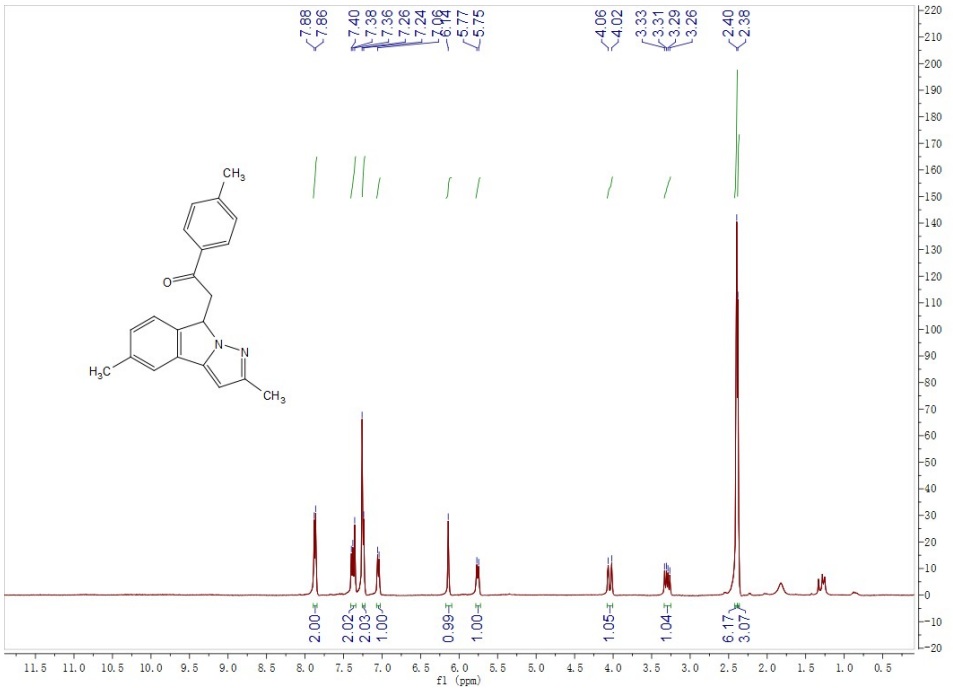
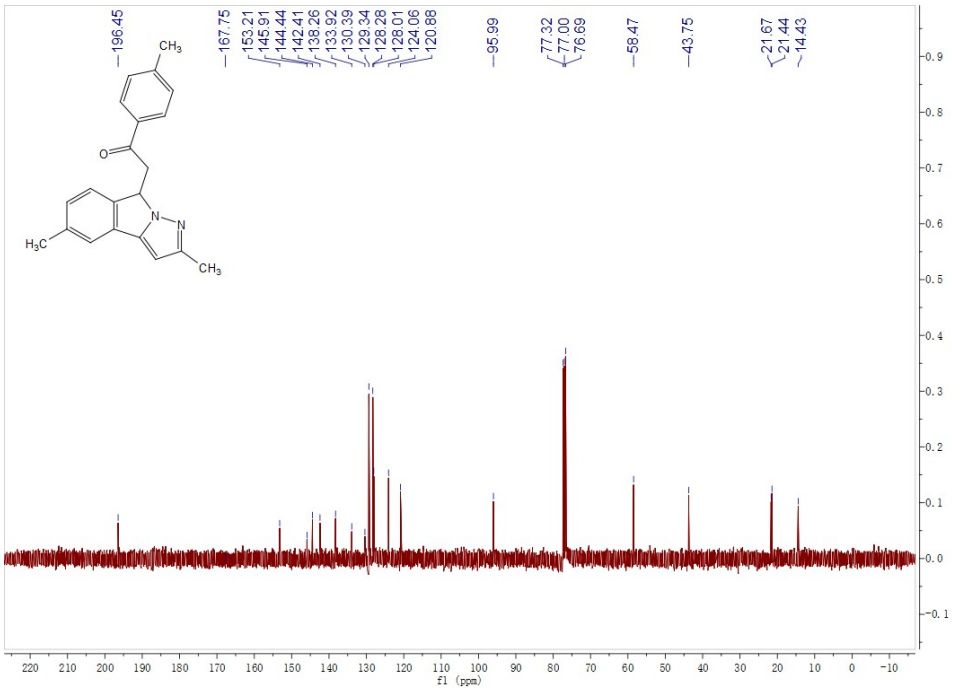
7.50
7.48
7.46
7.44
6.02
5.99
5.98
5.95
5.81
5.79
5.13
5.09
5.06
4.09
4.05
3.43
3.42
3.40
3.37
3.35
3.33
2.29
2.04
5.03
1.01
1.03
0.92
1.01
2.00
1.03
3.12
3.03
f1 (ppm)

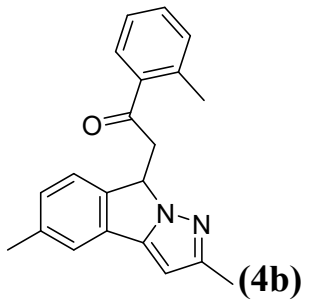

196.87
151.96
145.05
143.28
136.43
136.33
133.57
130.76
128.67
128.33
128.16
126.90
124.28
120.16
115.00
108.64
77.32
77.00
76.69
58.34
43.95
27.93
12.40
f1 (ppm)



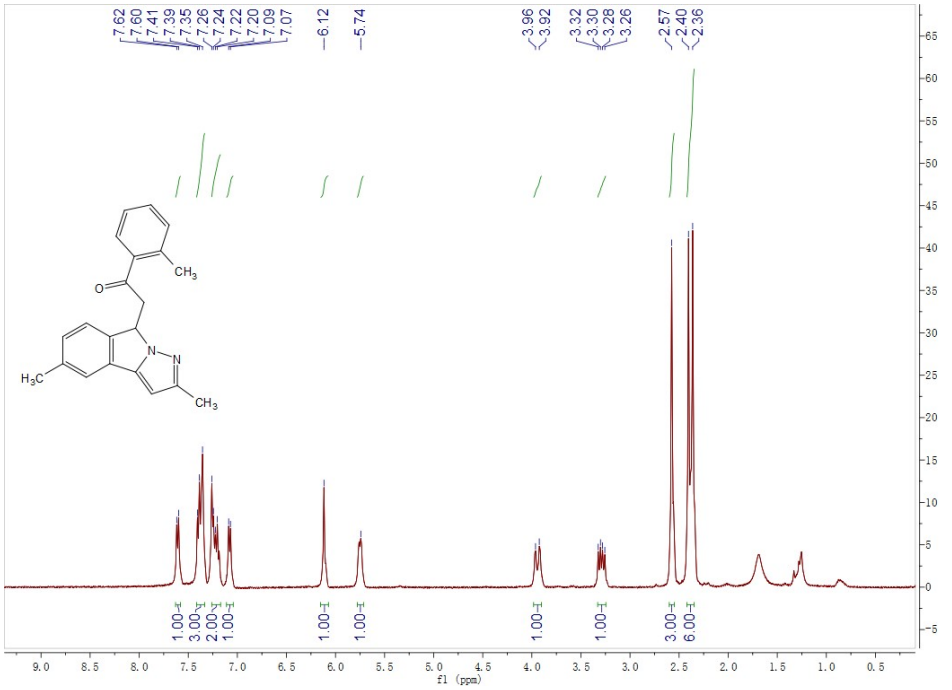
(4a)

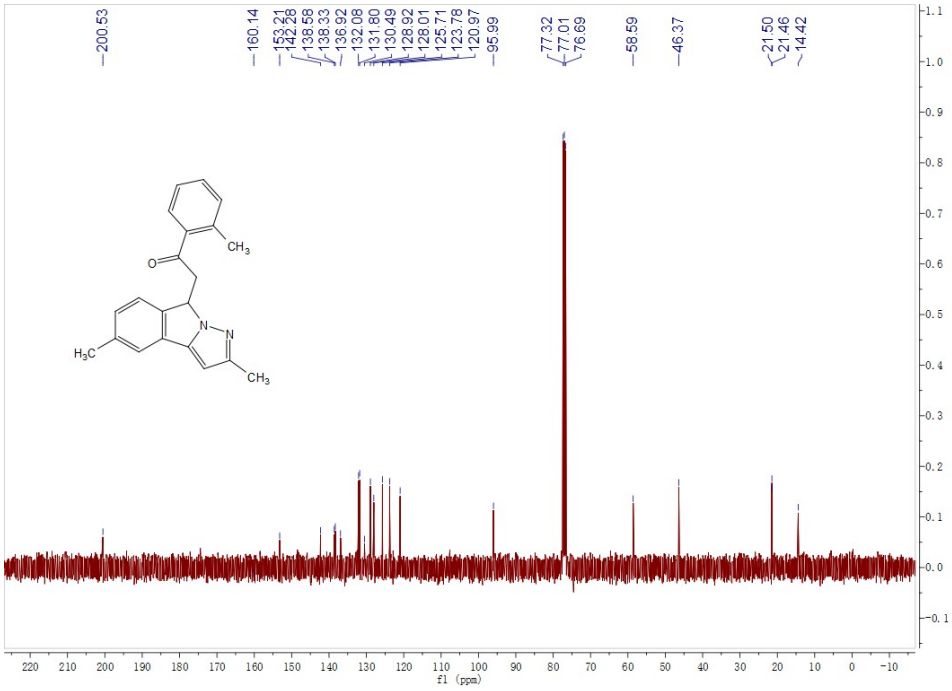

7.88
7.86
7.40
7.38
7.36
7.26
7.24
7.06
6.04
5.77
5.75
4.06
4.02
3.33
3.31
3.29
3.26
2.40
2.38
2.00
2.02
2.03
1.00
0.99
1.00
1.05
1.04
6.17
3.07
f1 (ppm)

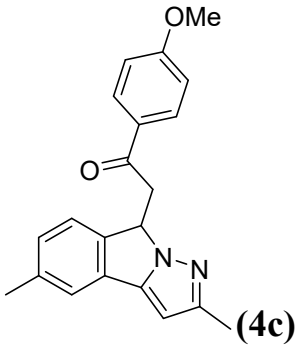

196.45
167.75
153.21
145.91
144.44
142.41
138.26
133.92
130.39
129.34
128.28
128.01
124.06
120.88
95.99
77.32
77.00
76.69
58.47
43.75
21.67
21.44
14.43
f1 (ppm)


O
N
N

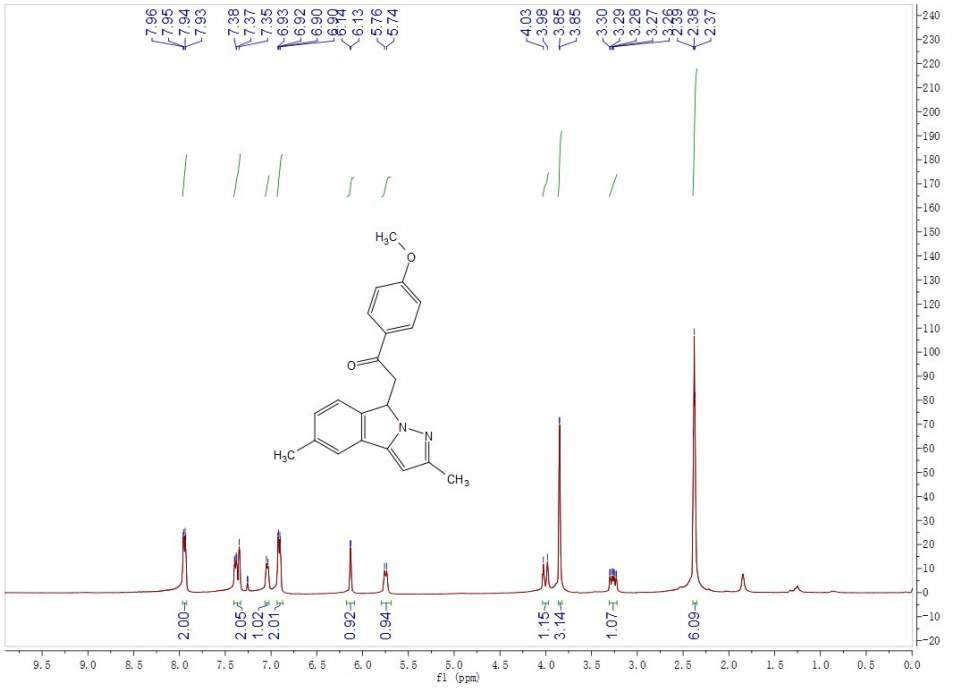
(4b)

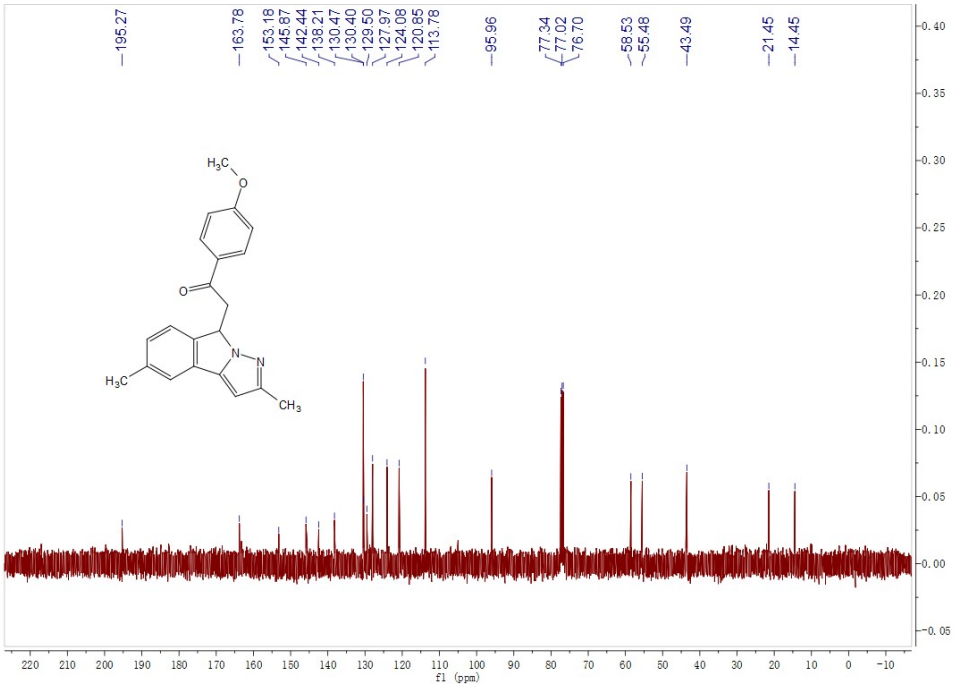

7.62
7.60
7.41
7.39
7.35
7.26
7.24
7.22
7.20
7.09
7.07
6.12
5.74
3.96
3.92
3.32
3.30
3.28
3.26
2.57
2.40
2.36
1.00
3.00
2.00
1.00
1.00
1.00
1.00
1.00
3.00
6.00
f1 (ppm)

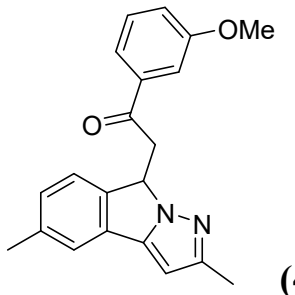

200.53
160.14
153.21
142.28
138.58
138.33
136.92
132.08
131.80
130.49
128.92
129.01
125.71
123.78
120.97
95.99
77.32
77.01
76.69
58.59
46.37
21.50
21.46
14.42
f1 (ppm)


OMe
O
N
N

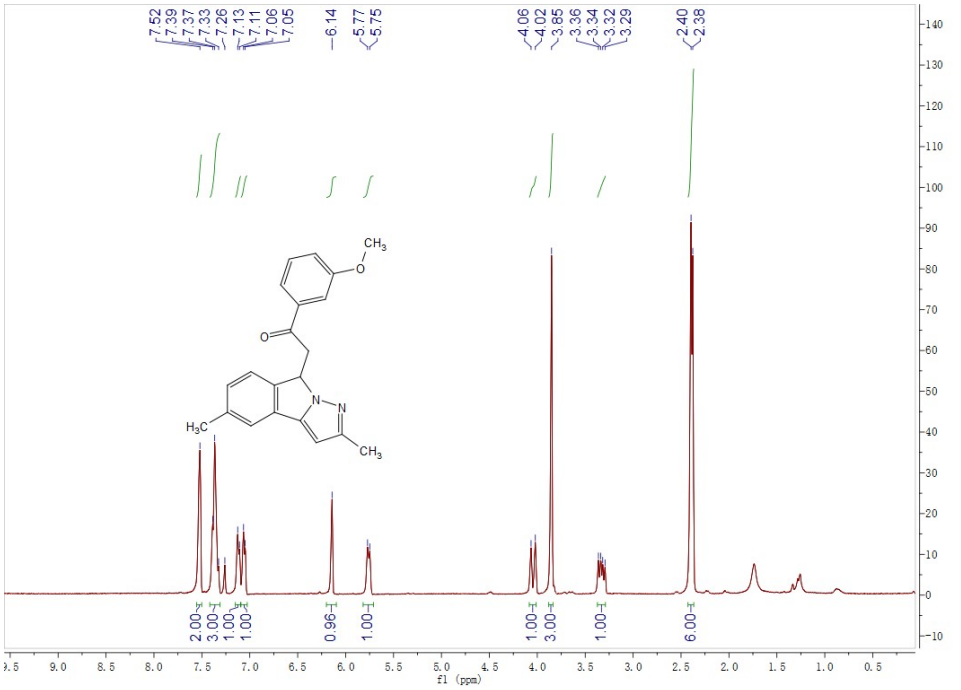
(4c)

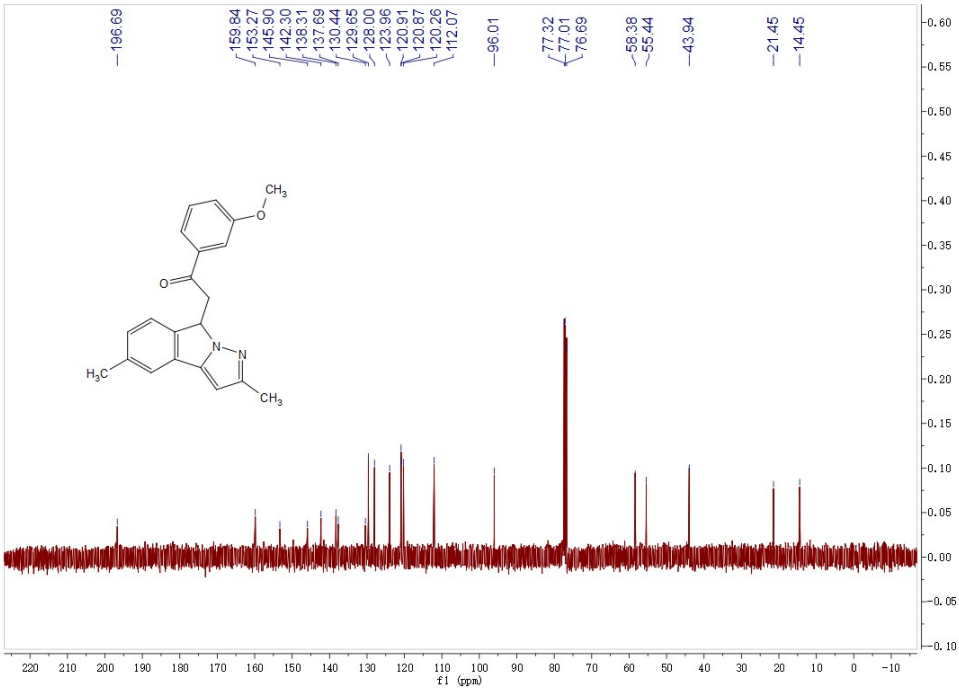

7.96
7.95
7.94
7.93
7.38
7.37
7.35
6.93
6.92
6.90
6.90
6.14
6.13
5.76
5.74
4.03
3.98
3.85
3.85
3.30
3.29
3.28
3.27
3.26
2.39
2.38
2.37
2.00
2.05
1.02
2.01
0.92
0.94
1.15
3.14
1.07
6.09
f1 (ppm)

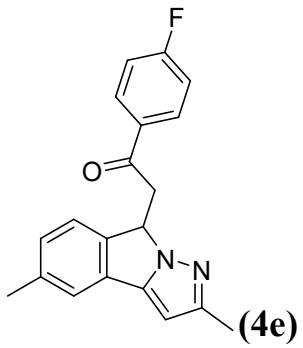

195.27
163.78
153.18
145.87
142.44
138.21
130.47
130.40
129.50
127.97
124.08
120.85
113.78
95.96
77.34
77.02
76.70
58.53
55.48
43.49
21.45
14.45
f1 (ppm)


OMe
O
N
N

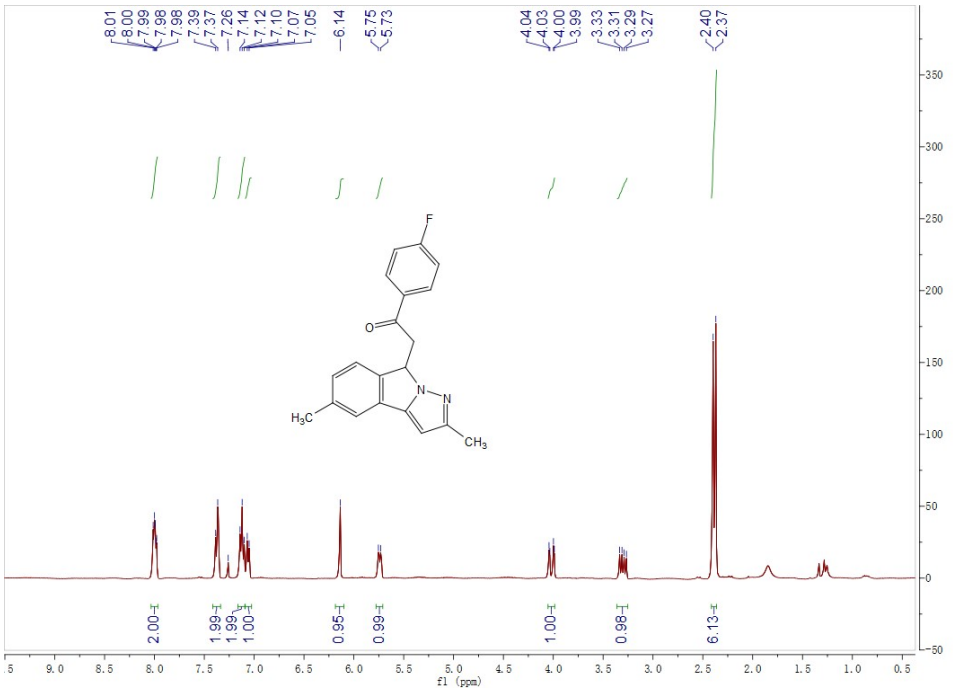
(4d)

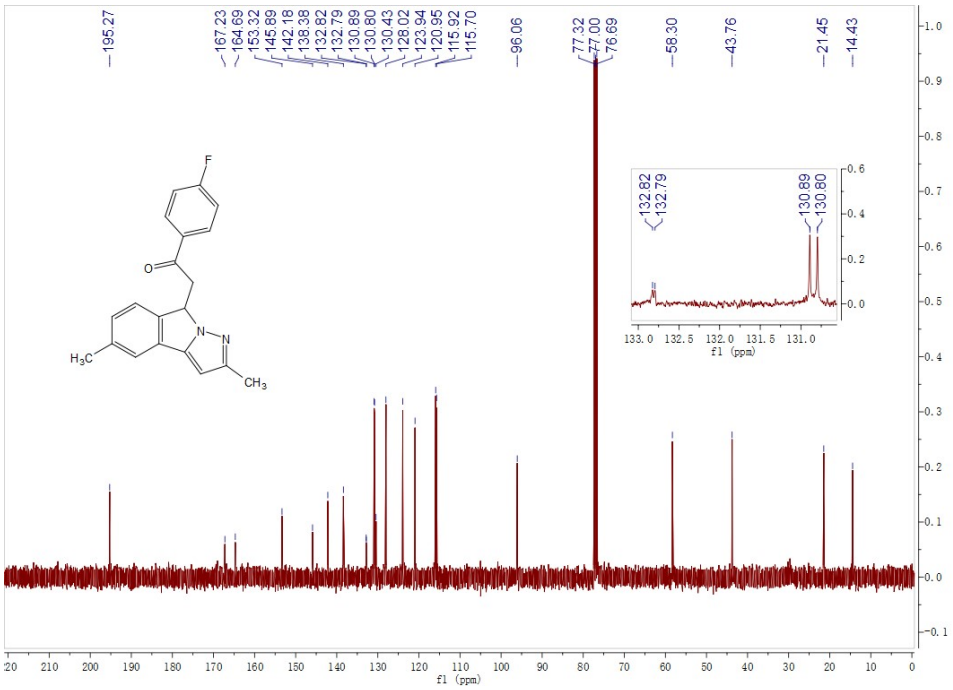

7.52
7.39
7.37
7.33
7.26
7.13
7.11
7.06
7.05
6.14
5.77
5.75
4.06
4.02
3.85
3.36
3.34
3.32
3.29
2.40
2.38
2.00
3.00
1.00
1.00
0.96
1.00
1.00
3.00
1.00
6.00
f1 (ppm)

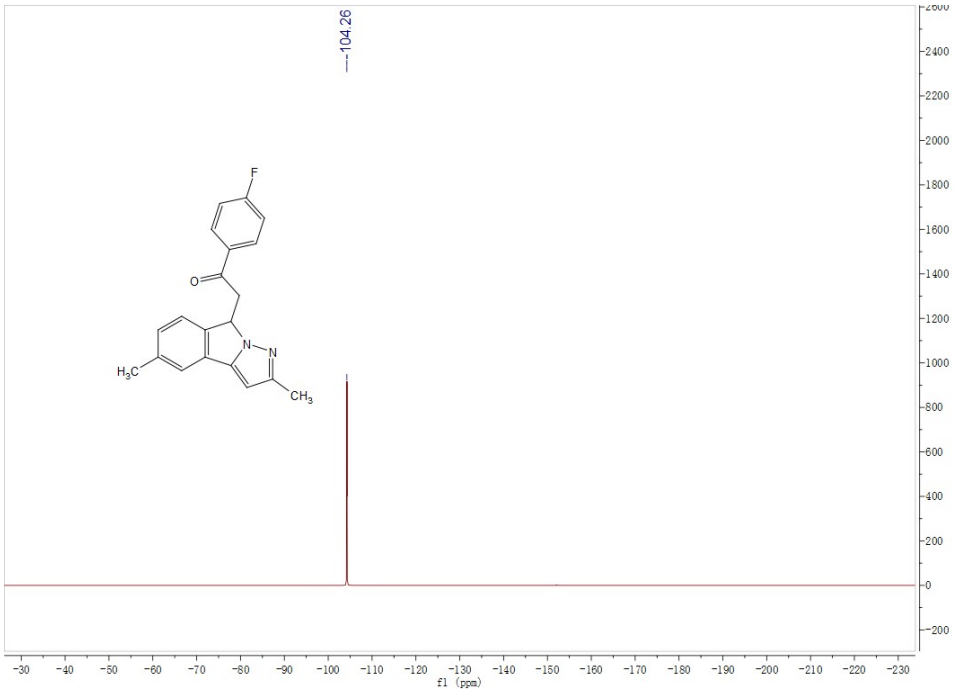

196.69
159.84
153.27
145.90
142.30
138.31
137.69
130.44
129.65
128.00
123.96
120.91
120.87
120.26
112.07
96.01
77.32
77.01
76.69
58.38
55.44
43.94
21.45
14.45
f1 (ppm)

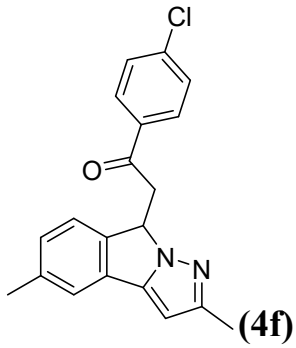

F
O
N
N

(4e)

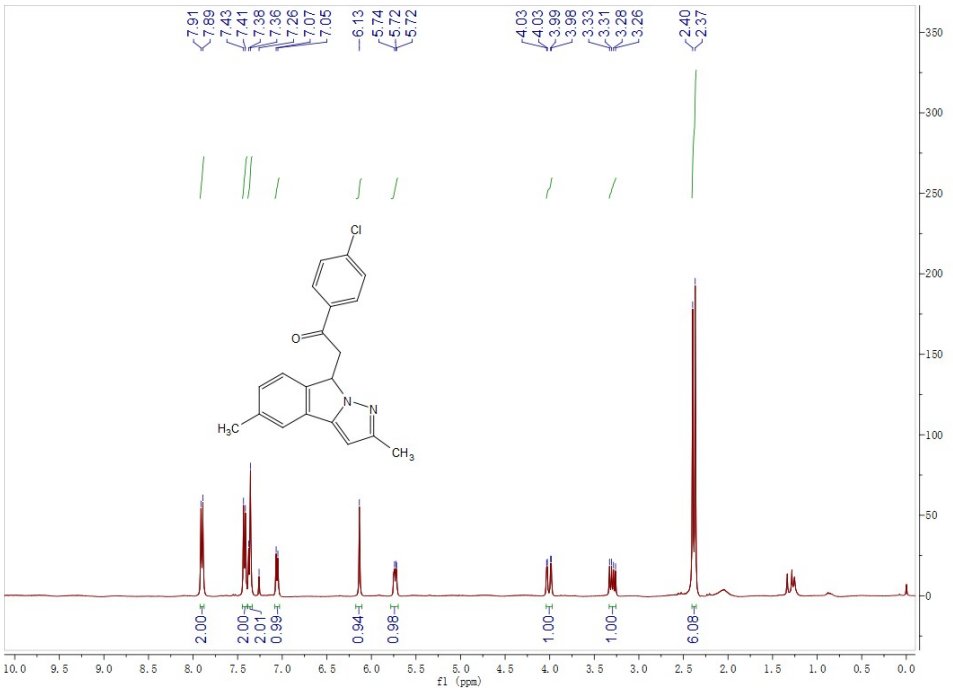

8.01
8.00
7.99
7.98
7.98
7.39
7.37
7.26
7.14
7.12
7.10
7.07
7.05
6.14
5.75
5.73
4.04
4.03
4.00
3.99
3.33
3.31
3.29
3.27
2.40
2.37
2.00
1.99
1.99
1.00
0.95
0.99
1.00
0.98
6.13
f1 (ppm)

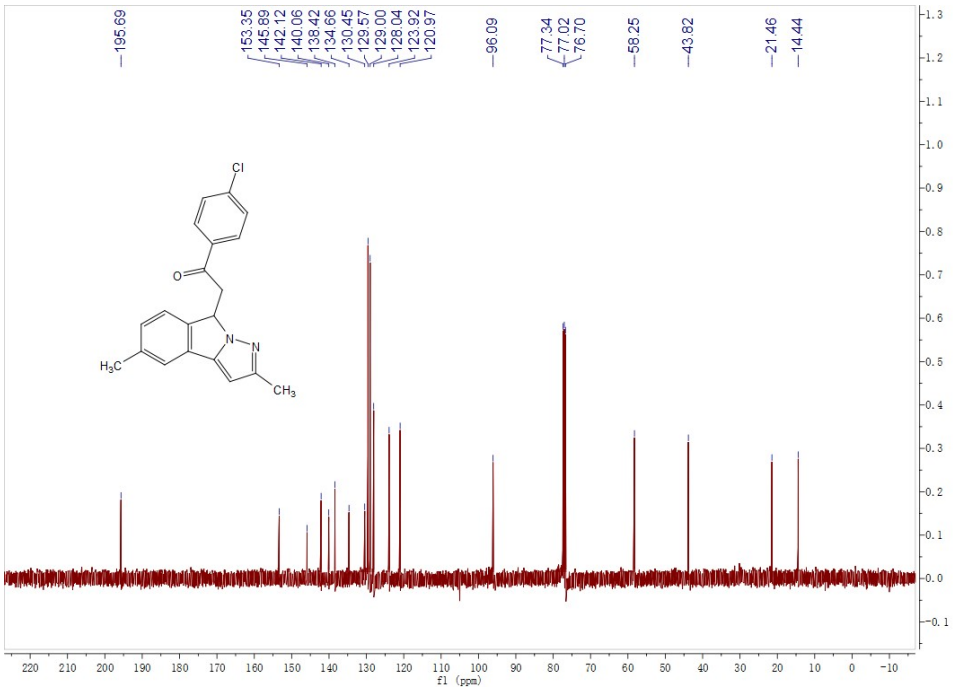

195.27
167.23
164.69
153.32
145.89
142.18
138.38
132.82
132.79
130.89
130.80
130.43
128.02
123.94
120.95
115.92
115.70
96.06
77.32
77.00
76.69
58.30
43.76
21.45
14.43
132.82
132.79
130.89
130.80
f1 (ppm)

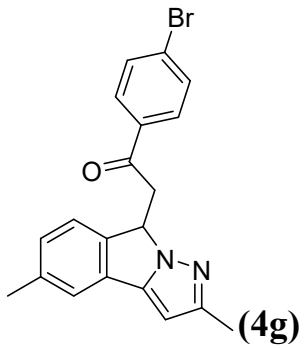

-104.26
F
O
N
N
H3C
CH3
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230
f1 (ppm)


Cl
O
N
N

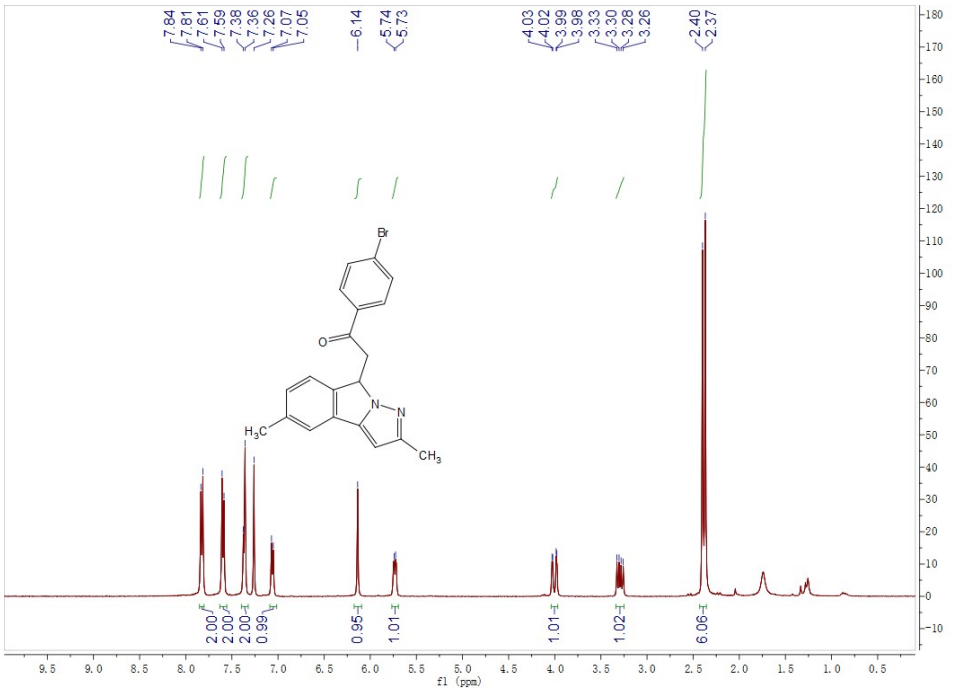
(4f)

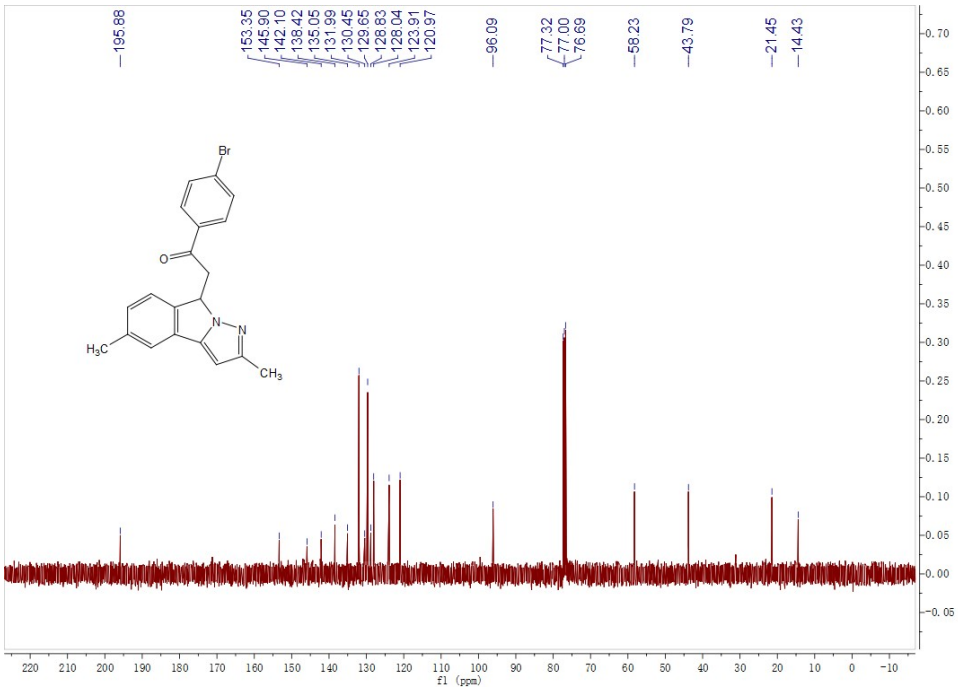

7.91
7.89
7.43
7.41
7.38
7.36
7.26
7.07
7.05
6.13
5.74
5.72
5.72
4.03
4.03
3.99
3.98
3.33
3.31
3.28
3.26
2.40
2.37
2.00
2.00
2.01
0.99
0.94
0.98
1.00
1.00
6.08
f1 (ppm)

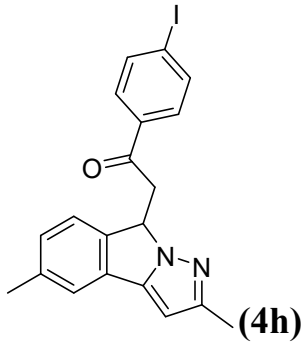

195.69
153.35
145.89
142.12
140.06
138.42
134.66
130.45
129.57
129.00
128.04
123.92
120.97
96.09
77.34
77.02
76.70
58.25
43.82
21.46
14.44
f1 (ppm)


Br
O
N
N

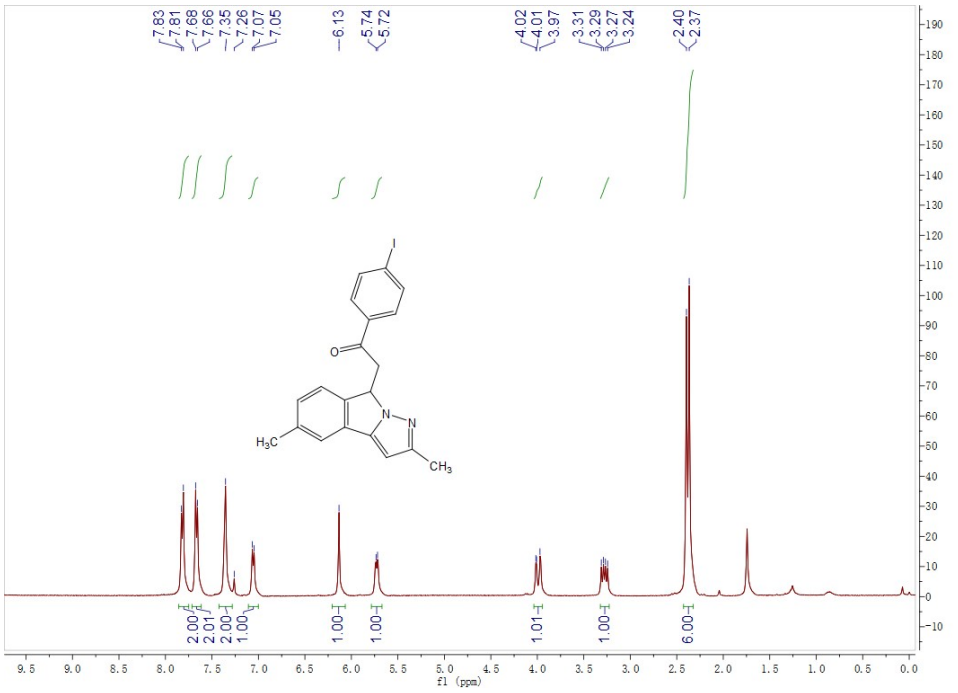
(4g)

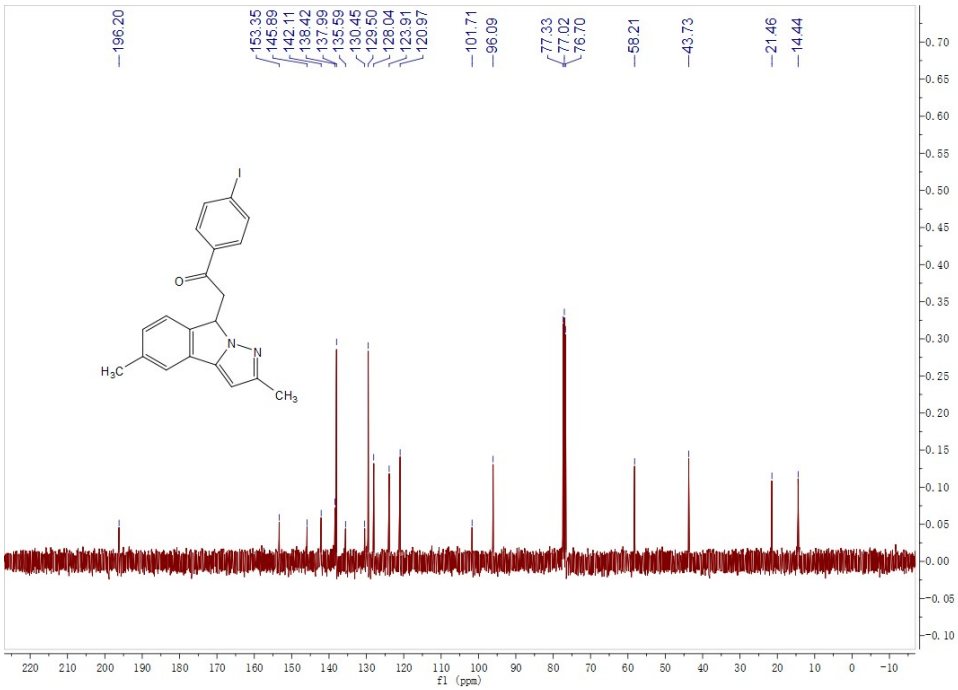

7.84
7.81
7.61
7.59
7.38
7.36
7.26
7.07
7.05
6.14
5.74
5.73
4.03
4.02
3.99
3.98
3.33
3.30
3.28
3.26
2.40
2.37
Br
O
N
N
H3C
CH3
2.00
2.00
2.00
0.99
0.95
1.01
1.01
1.02
6.06
f1 (ppm)


195.88
153.35
145.90
142.10
138.42
135.05
131.99
130.45
129.65
128.83
128.04
123.91
120.97
96.09
77.32
77.00
76.69
58.23
43.79
21.45
14.43
Br
O
N
N
H3C
CH3
f1 (ppm)



(4h)


7.83
7.81
7.68
7.66
7.35
7.26
7.07
7.05
6.13
5.74
5.72
4.02
4.01
3.97
3.31
3.29
3.27
3.24
2.40
2.37
2.00
2.01
2.00
1.00
1.00
1.00
1.01
1.00
6.00
f1 (ppm)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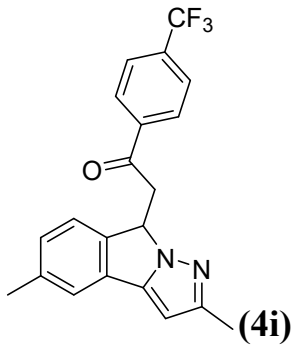
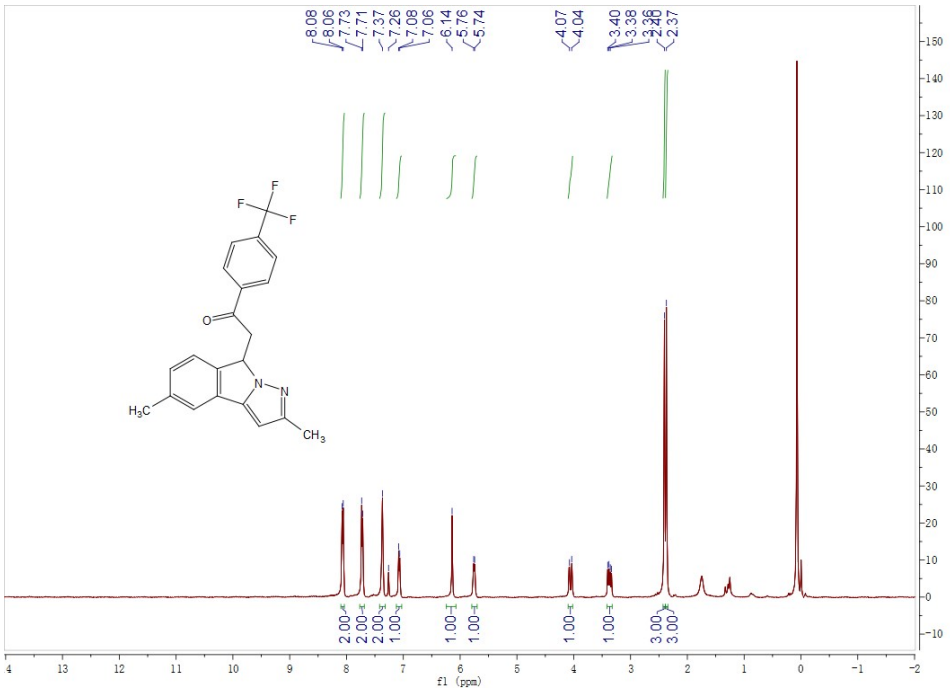
153.35
145.89
142.11
138.42
137.99
135.59
130.45
129.50
128.04
123.91
120.97
101.71
96.09
77.33
77.02
76.70
58.21
43.73
21.46
14.44
f1 (ppm)



(4i)


8.08
8.06
7.73
7.71
7.37
7.26
7.08
7.06
6.14
5.76
5.74
4.07
4.04
3.40
3.38
2.37
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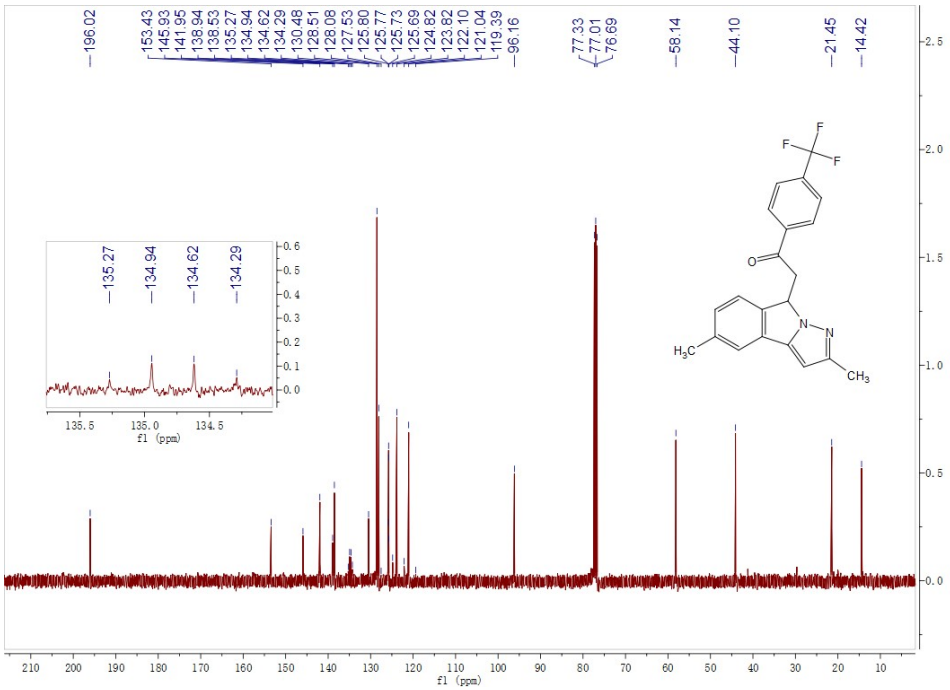
1.00
1.00
1.00
3.00
3.00
f1 (ppm)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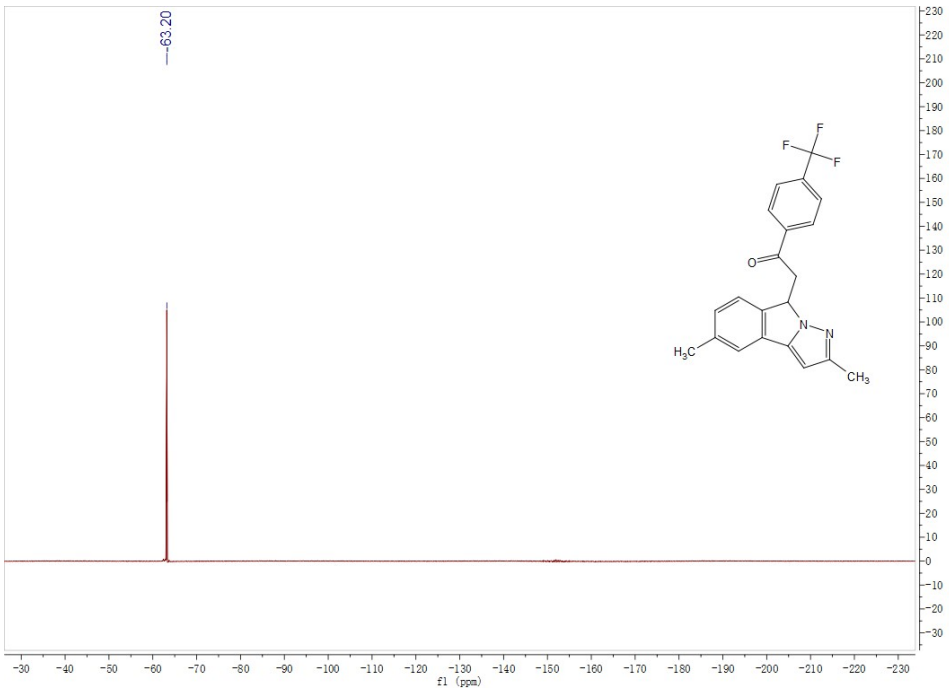
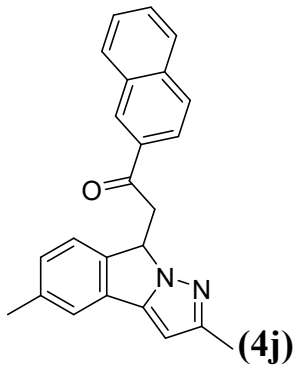
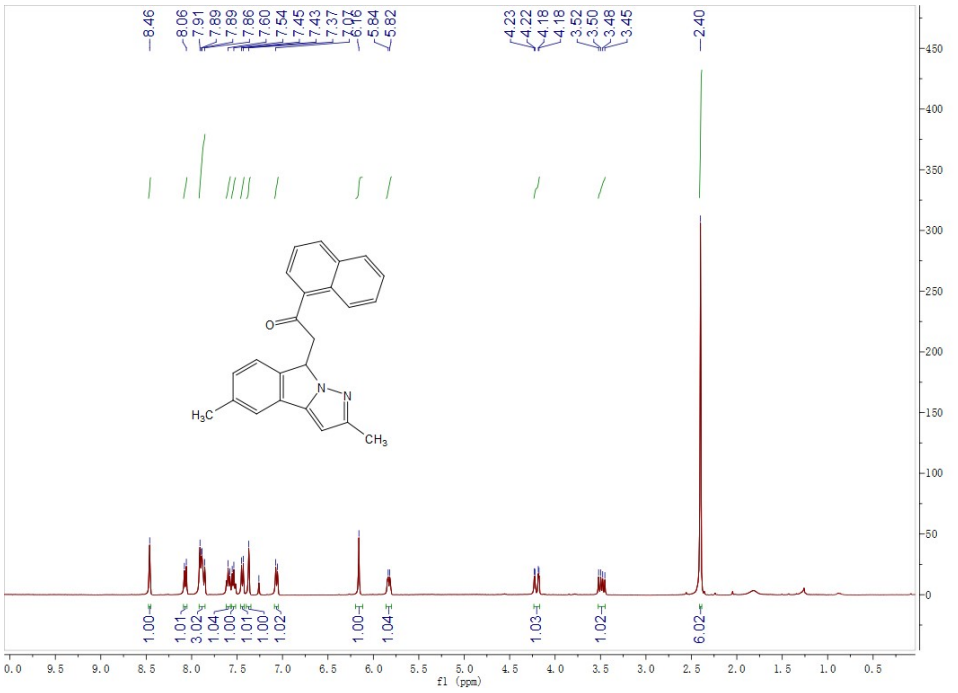
153.43
145.93
141.95
138.94
138.53
135.27
134.94
134.62
134.29
130.48
128.51
128.08
127.53
125.80
125.77
125.73
125.69
124.82
123.82
122.10
121.04
119.39
96.16
77.33
77.01
76.69
58.14
44.10
21.45
14.42
135.27
134.94
134.62
134.29
f1 (ppm)
f1 (ppm)


-63.20
F
F
F
O
N
N
H3C
CH3
f1 (ppm)



(4j)


8.46
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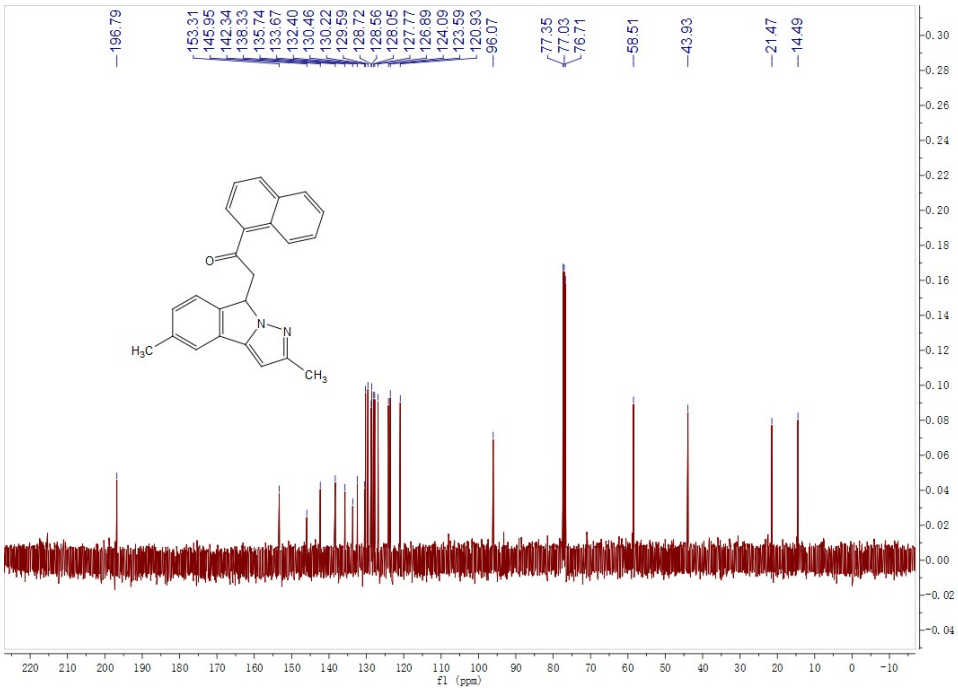
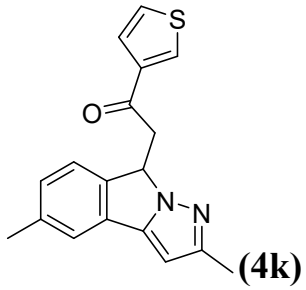
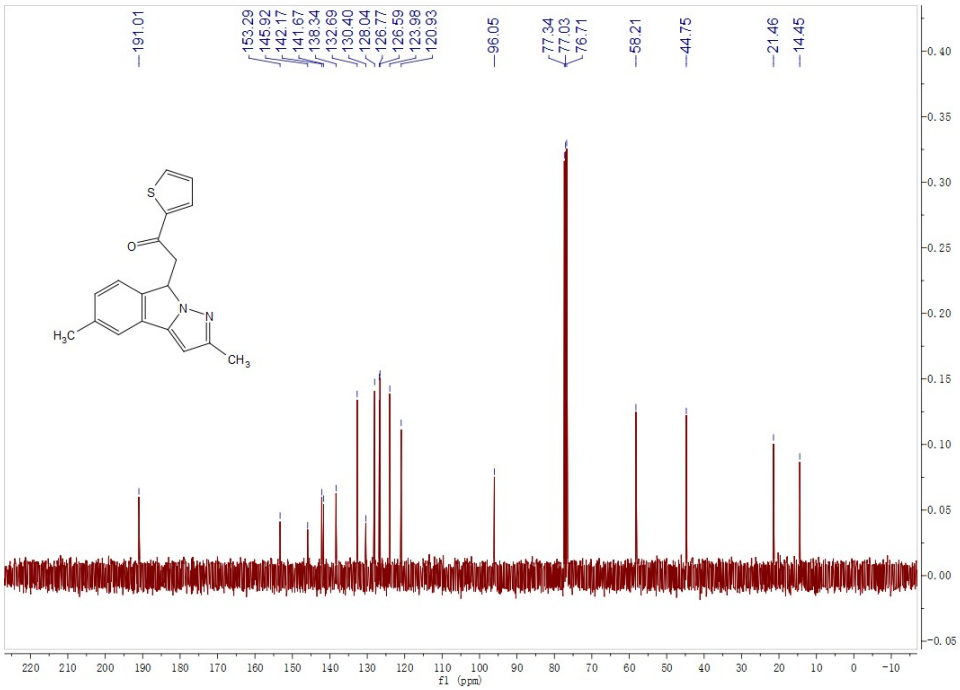
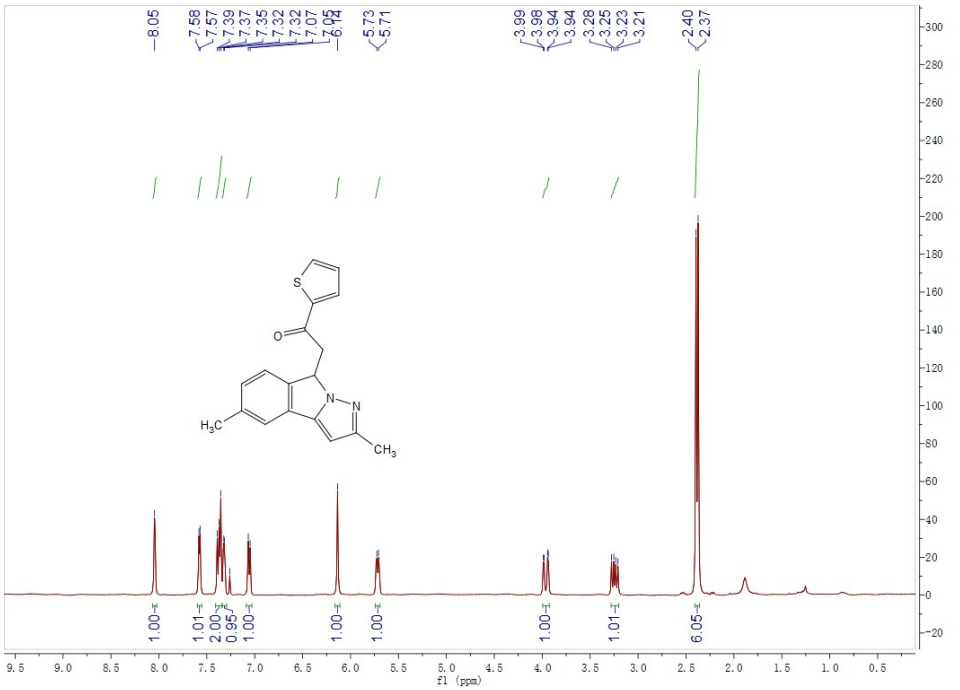
7.89
7.89
7.86
7.60
7.54
7.45
7.43
7.37
7.07
6.16
5.84
5.82
4.23
4.22
4.18
4.18
3.52
3.50
3.48
3.45
2.40
1.00
1.01
3.02
1.04
1.00
1.01
1.00
1.02
1.00
1.04
1.03
1.02
6.02
f1 (ppm)


196.79
153.31
145.95
142.34
138.33
135.74
133.67
132.40
130.46
130.22
129.59
128.72
128.56
128.05
127.77
126.89
124.09
123.59
120.93
96.07
77.35
77.03
76.71
58.51
43.93
21.47
14.49
f1 (ppm)



(4k)


191.01
153.29
145.92
142.17
141.67
138.34
132.69
130.40
128.04
126.77
126.59
123.98
120.93
96.05
77.34
77.03
76.71
58.21
44.75
21.46
14.45
f1 (ppm)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7.58
7.57
7.39
7.37
7.35
7.32
7.32
7.07
6.14
5.73
5.71
3.99
3.98
3.94
3.94
3.28
3.25
3.23
3.21
2.40
2.37
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1.01
2.00
0.95
1.00
1.00
1.00
1.00
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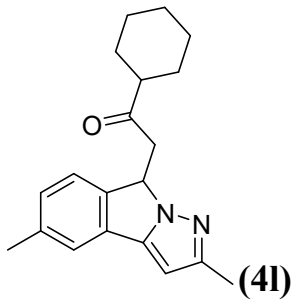
6.05
f1 (ppm)



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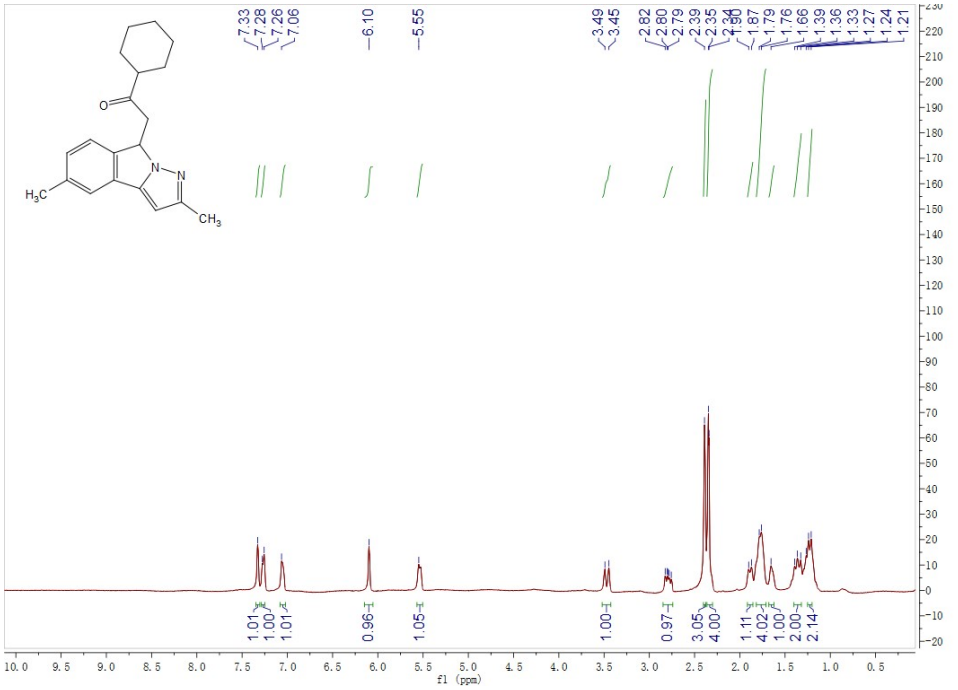
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7.26
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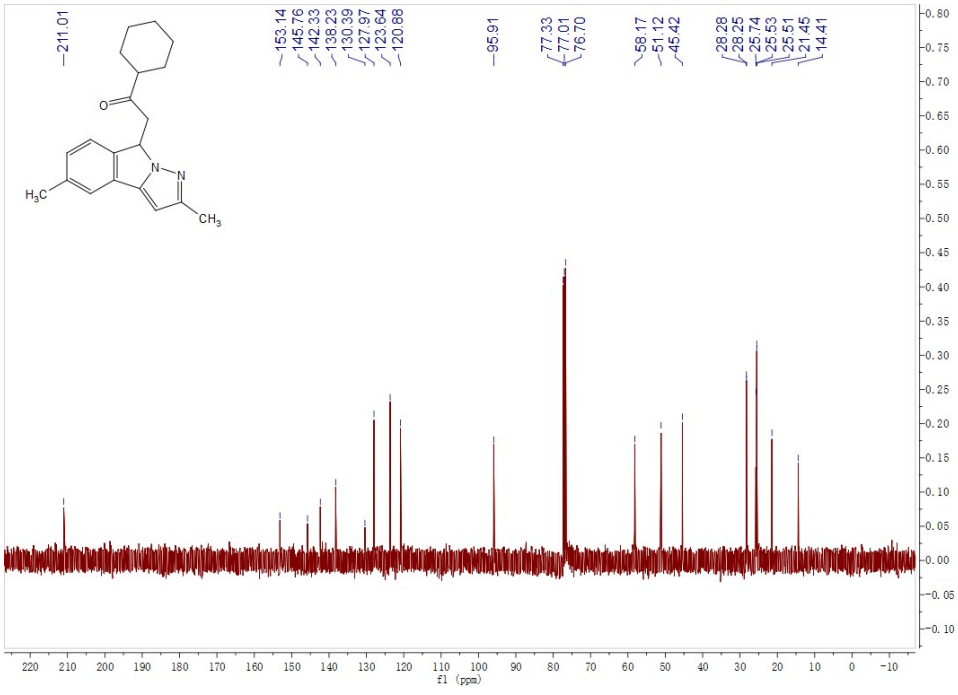
6.10
5.55
3.49
3.45
2.82
2.80
2.79
2.39
2.35
2.34
1.90
1.87
1.79
1.76
1.66
1.39
1.36
1.33
1.27
1.24
1.21
1.01
1.00
1.01
0.96
1.05
1.00
0.97
3.05
4.00
1.11
4.02
1.00
2.00
2.14
f1 (ppm)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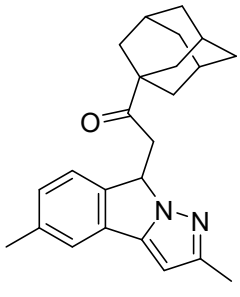
153.14
145.76
142.33
138.23
130.39
127.97
123.64
120.88
95.91
77.33
77.01
76.70
58.17
51.12
45.42
28.28
28.25
25.74
25.53
25.51
21.45
14.41
f1 (ppm)



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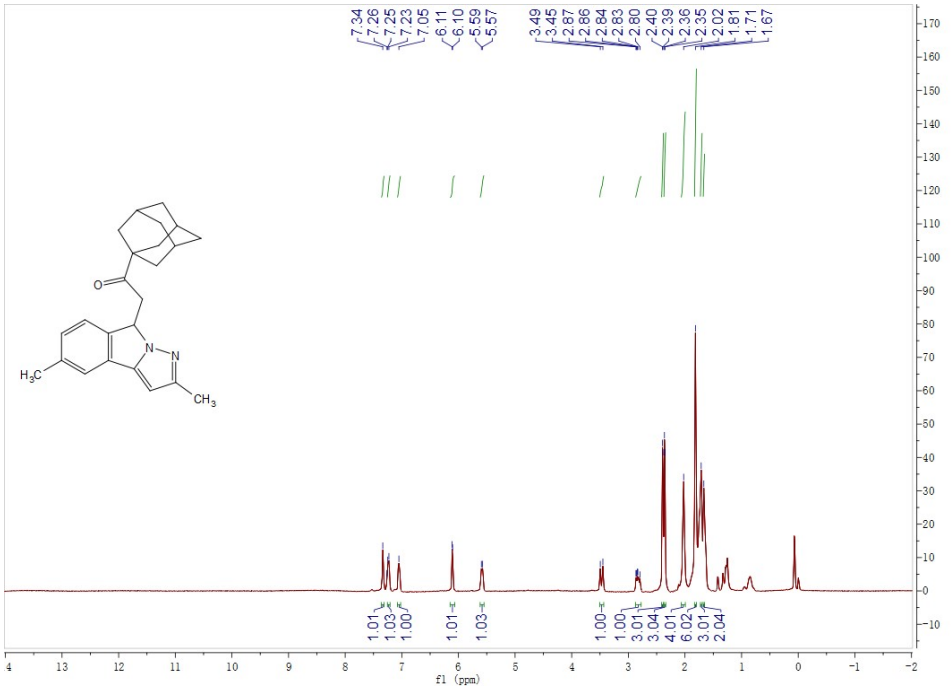
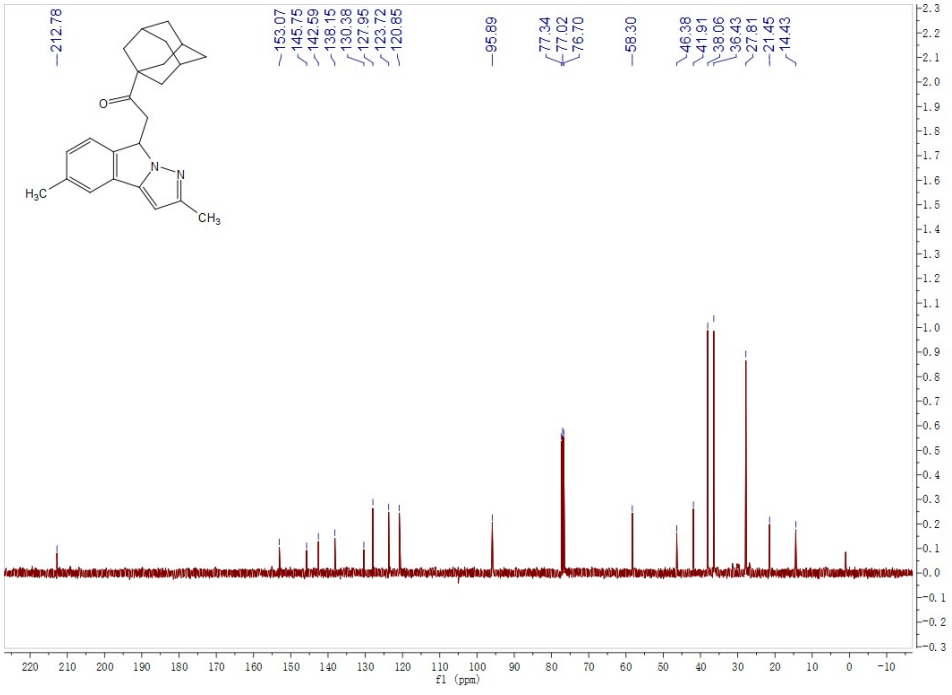

7.34
7.26
7.25
7.23
7.05
6.11
6.10
5.59
5.57
3.49
3.45
2.87
2.86
2.84
2.83
2.80
2.40
2.39
2.36
2.35
2.02
1.81
1.71
1.67
1.01
1.03
1.00
1.01
1.03
1.00
1.00
3.01
3.04
4.01
6.02
3.01
2.04
f1 (ppm)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95.89
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77.02
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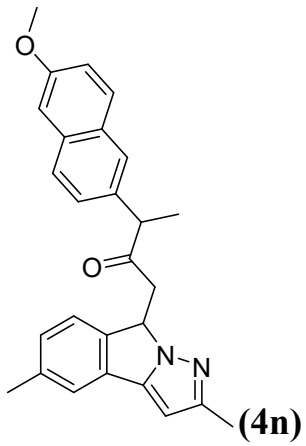
36.43
27.81
21.45
14.43
f1 (ppm)



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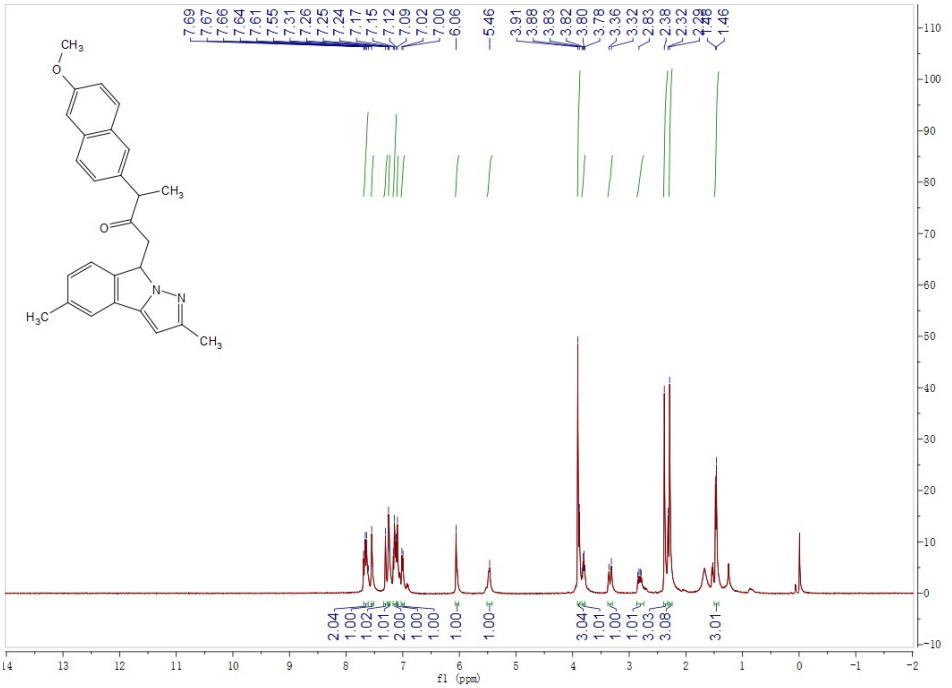
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7.55
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7.26
7.25
7.24
7.17
7.15
7.12
7.09
7.02
7.00
6.06
5.46
3.91
3.88
3.83
3.82
3.80
3.78
3.36
3.32
2.83
2.38
2.32
2.29
1.48
1.46
2.04
1.00
1.02
1.01
2.00
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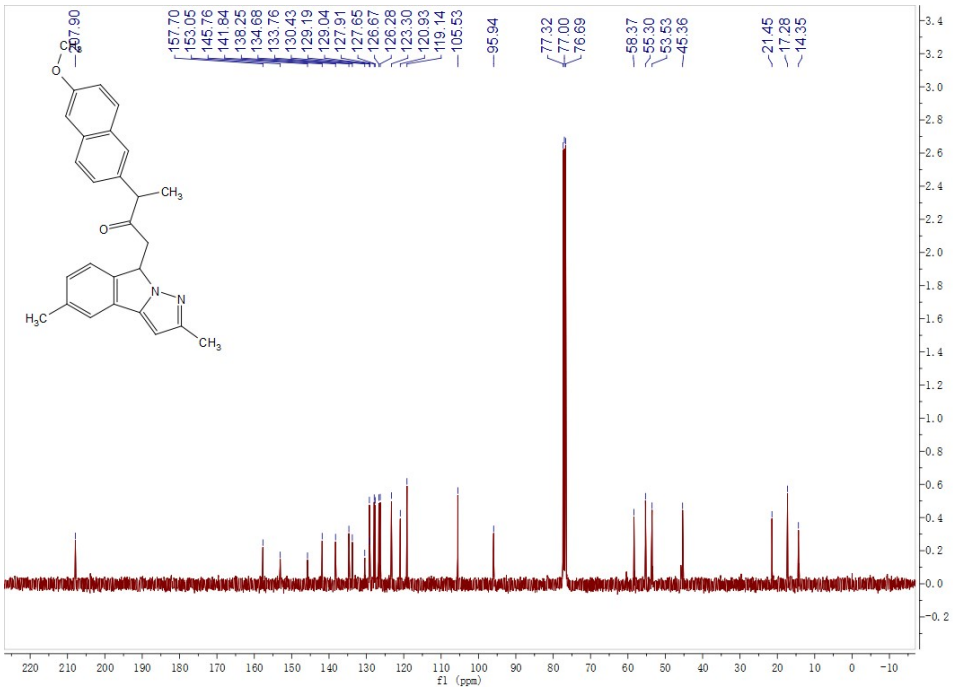
1.01
3.03
3.08
3.01
f1 (ppm)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141.84
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133.76
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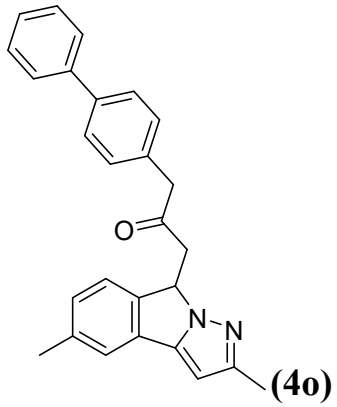
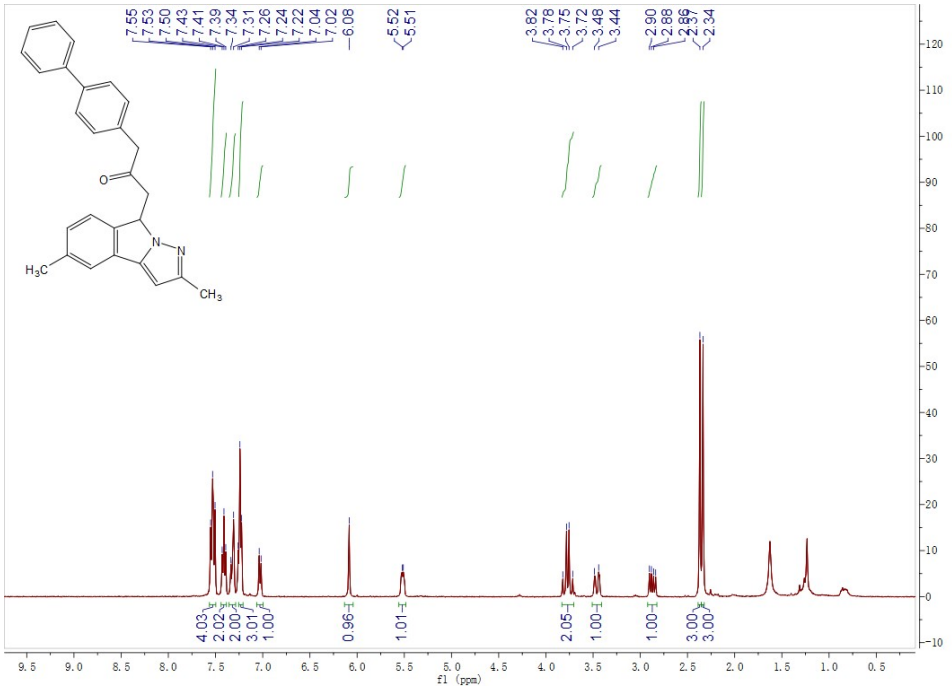
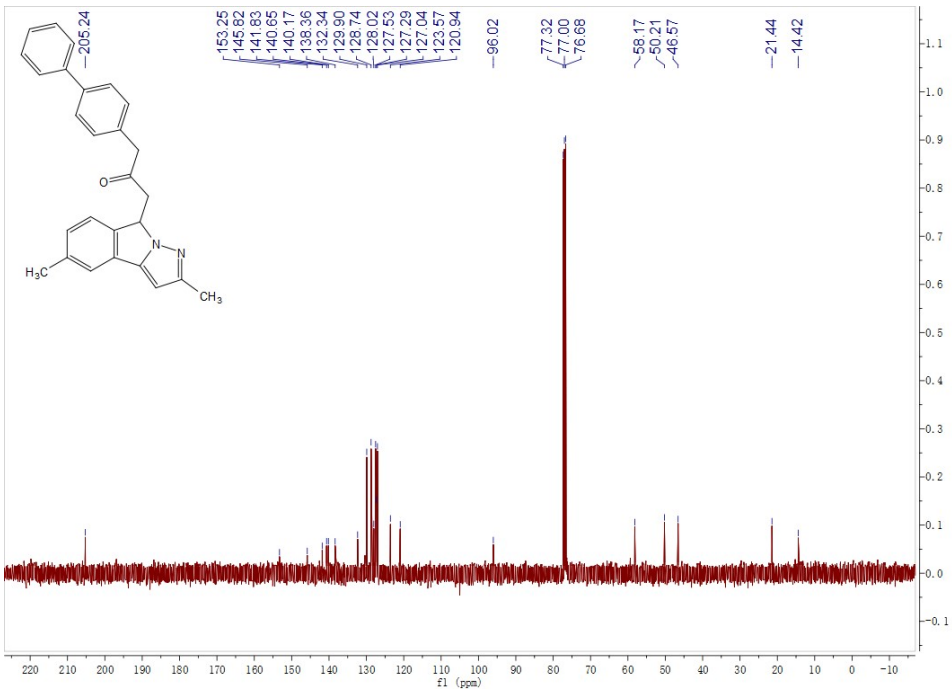
129.19
129.04
127.91
127.65
126.67
126.28
123.30
120.93
119.14
105.53
95.94
77.32
77.00
76.69
58.37
55.30
53.53
45.36
21.45
17.28
14.35
f1 (ppm)


O
N
N

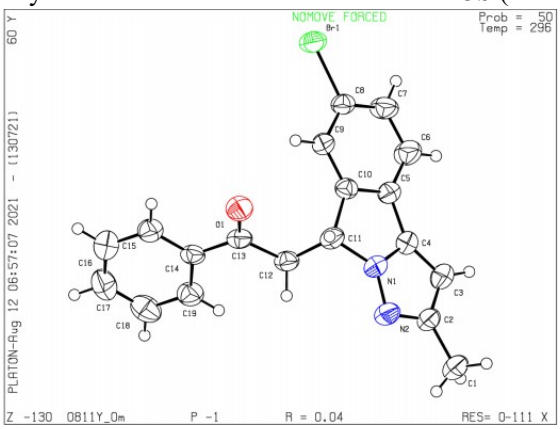
(4o)


7.55
7.53
7.50
7.43
7.41
7.39
7.34
7.31
7.26
7.24
7.22
7.04
7.02
6.08
5.52
5.51
3.82
3.78
3.75
3.72
3.48
3.44
2.90
2.88
2.86
2.37
2.34
4.03
2.02
2.00
3.01
1.00
0.96
1.01
2.05
1.00
1.00
3.00
3.00
f1 (ppm)


205.24
153.25
145.82
141.83
140.65
140.17
138.36
132.34
129.90
128.74
128.02
127.53
127.29
127.04
123.57
120.94
96.02
77.32
77.00
76.68
58.17
50.21
46.57
21.44
14.42
f1 (ppm)

5. X-ray of **3g**

Crystal data and structure refinement for **3b** (The ellipsoid contour was 50% levels)



Empirical formula	$C_{19}H_{15}BrN_2O$
Formula weight	367.24
Temperature/K	296(2)
Crystal system	triclinic
Space group	P-1
a/Å	5.537(3)
b/Å	11.122(5)
c/Å	13.317(6)
α/°	100.097(6)
β/°	96.581(6)
γ/°	96.739(6)
Volume/Å^3	794.1(7)
Z	2
ρ_{calc}g/cm^3	1.536
μ/mm^{-1}	2.594
F(000)	372.0
Crystal size/mm^3	0.180 × 0.130 × 0.060
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.41 to 54.97
Index ranges	$-7 \le h \le 7$, $-14 \le k \le 14$, $-17 \le l \le 17$
Reflections collected	7463
Independent reflections	3591 [R_{int} = 0.0305, R_{sigma} = 0.0499]
Data/restraints/parameters	3591/0/209
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0700
Final R indexes [all data]	R_1 = 0.0563, wR_2 = 0.0752
Largest diff. peak/hole / e Å^{-3}	0.26/-0.32