

Supporting Information

Synthesis of 3-Aryl-3-benzazepines via Aryne [1,2] Stevens Rearrangement of 1,2,3,4-Tetrahydroisoquinolines

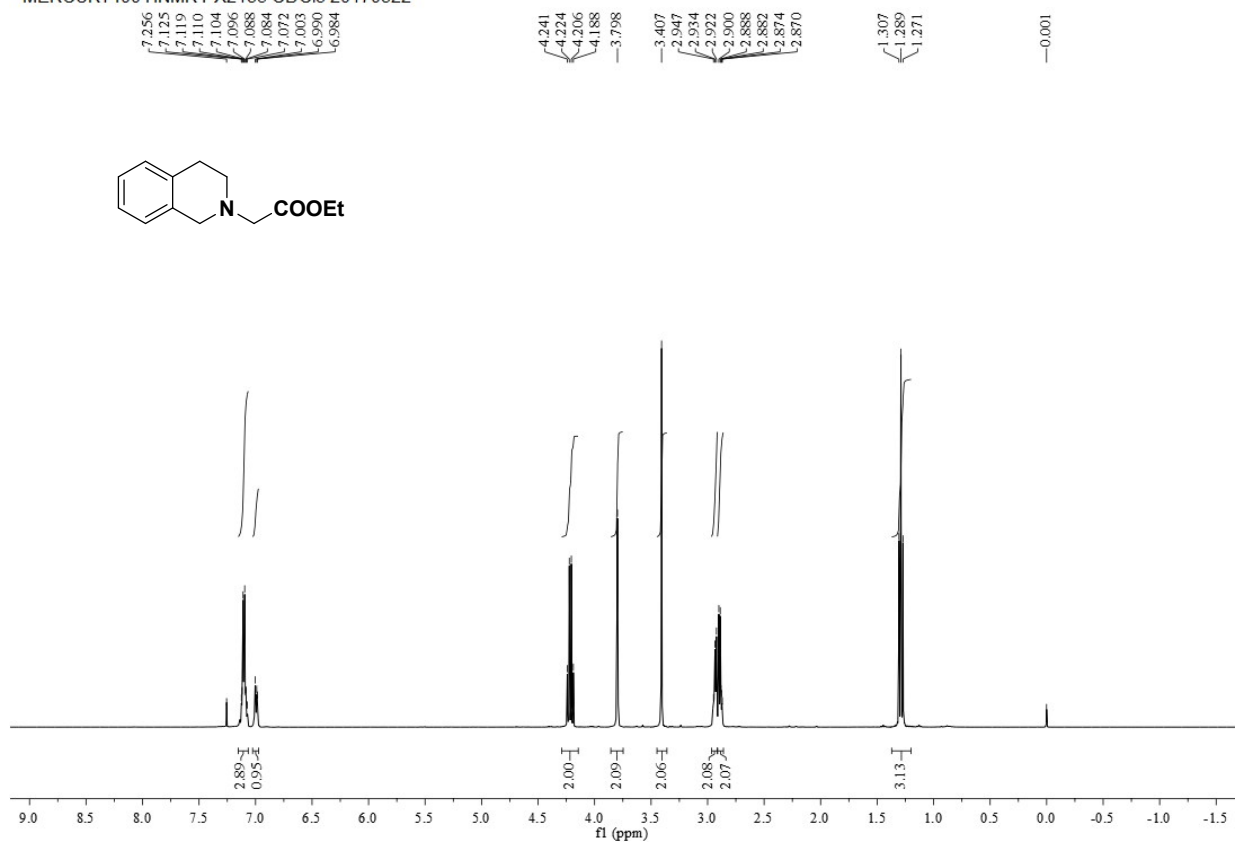
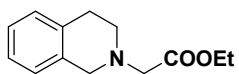
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Institute of Materia Medica, Peking Union Medical College and Chinese Academy of
Medical Sciences, Beijing 100050, P. R. China

*E-mail: liuzhazhu@imm.ac.cn

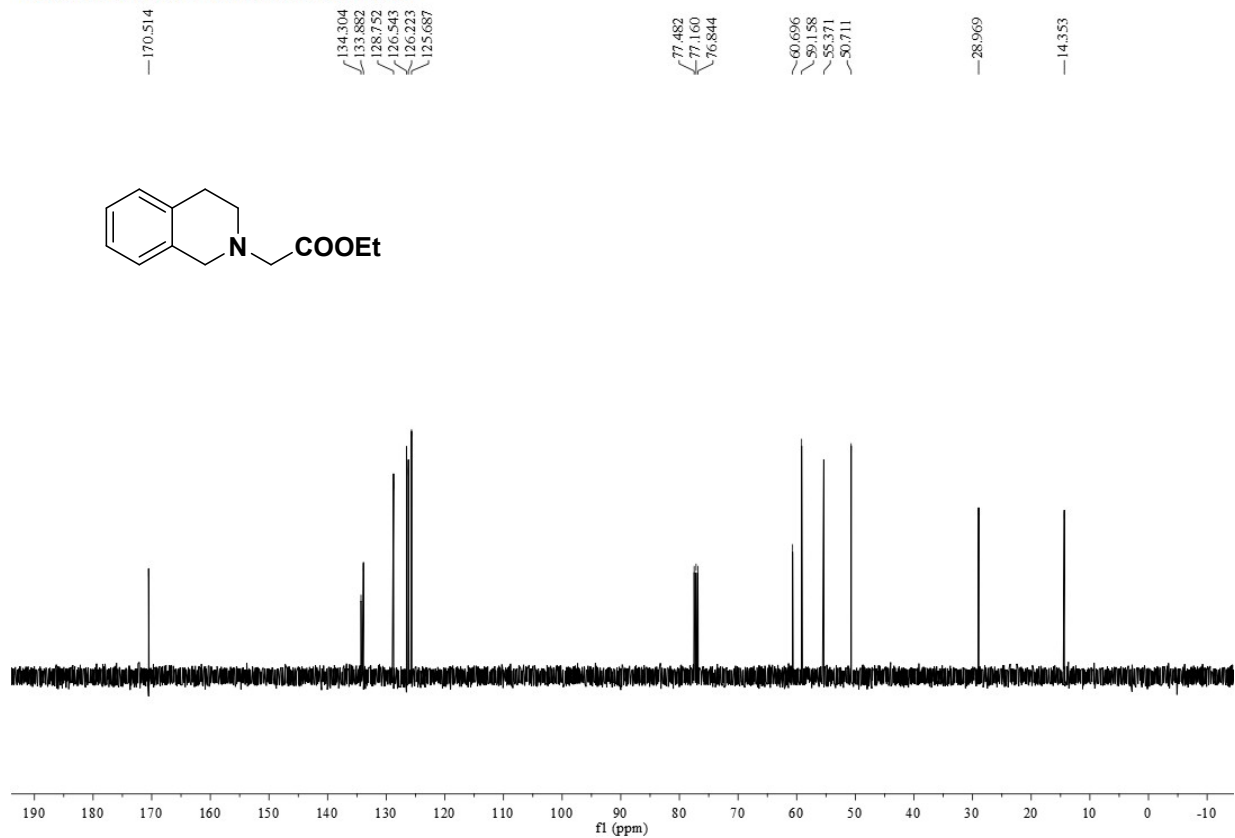
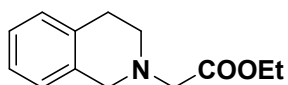
¹H NMR spectra of compound 2a

MERCURY400 HNMR PX2135 CDCl3 20170322



¹³C NMR spectra of compound 2a

MERCURY400 CNMR PX2135 CDCl3 20170322



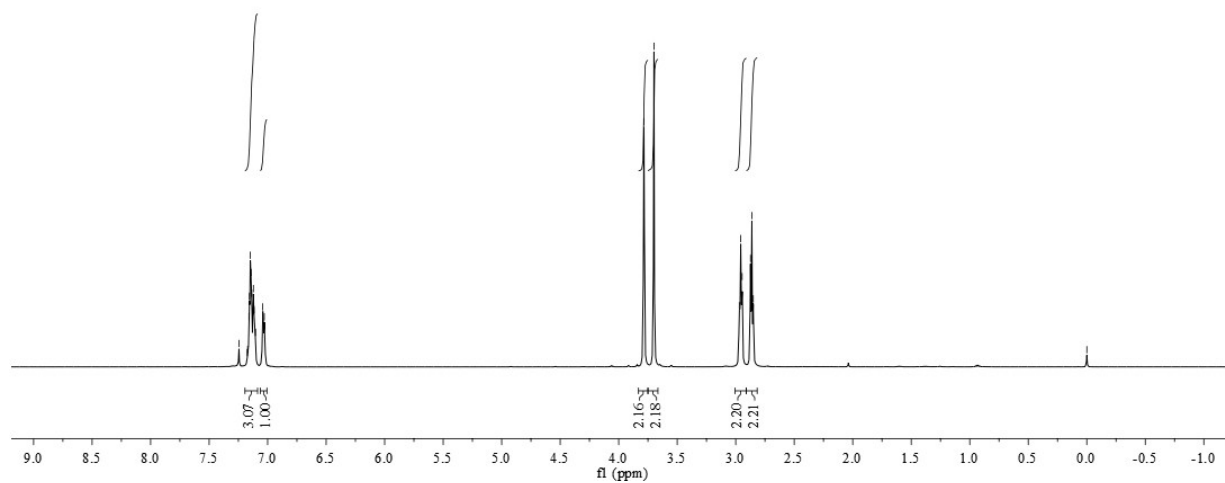
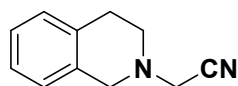
¹H NMR spectra of compound **2b**

MERCURY500 HNMR PX2148-5 CDCl₃ 20170426

7.245
7.174
7.171
7.160
7.155
7.148
7.142
7.136
7.122
7.116
7.104
7.042
7.029
7.024

3.784
3.699
2.969
2.957
2.945
2.874
2.862
2.850

— 0.000



¹³C NMR spectra of compound **2b**

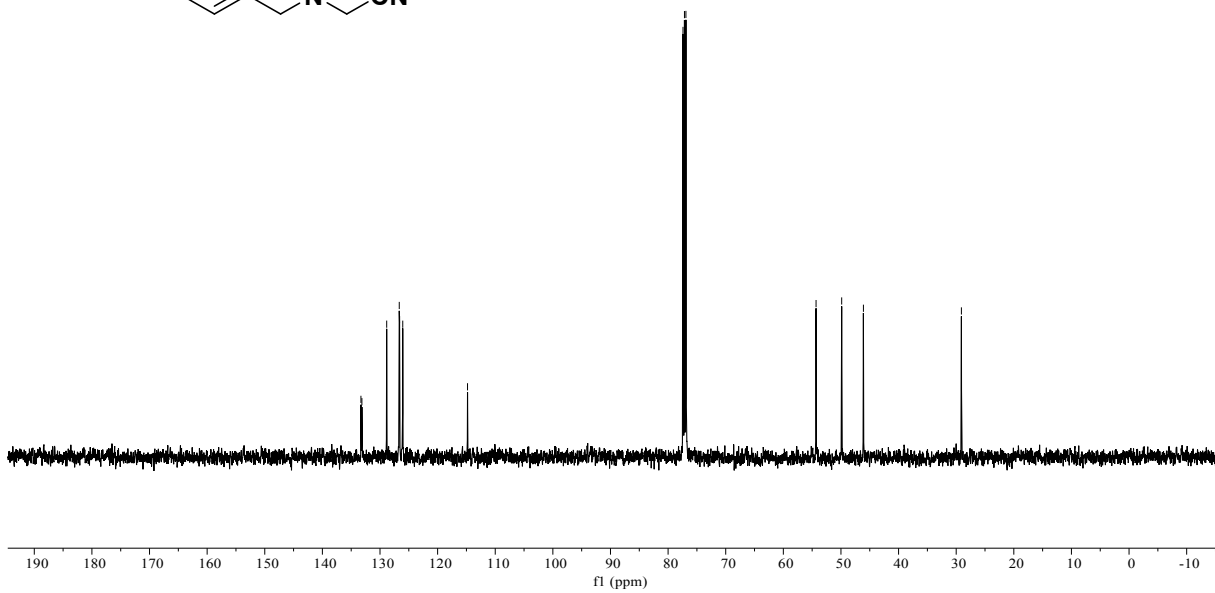
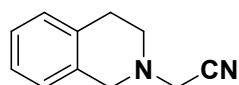
MERCURY500 CNMR PX2148-5 CDCl₃ 20170426

133.309
133.142
128.837
126.688
126.595
126.050
— 114.810

77.413
77.160
76.907

54.321
49.872
46.101

— 29.096



¹H NMR spectra of compound 2c

MERCURY500 HNMR PX2150-4 20170508

7.386
7.381
7.375
7.370
7.356
7.350
7.345
7.338
7.332
7.254
7.156
7.133
7.108
7.097
7.091
7.086
7.001
6.987

5.205

3.818

3.481

2.939

2.928

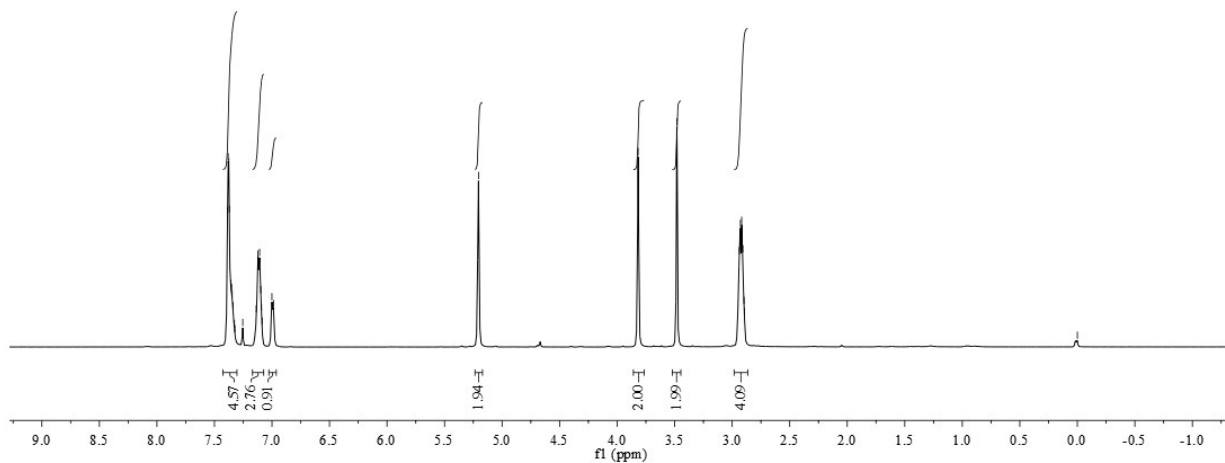
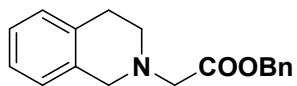
2.918

2.907

2.897

2.893

0.000



¹³C NMR spectra of compound 2c

MERCURY500 CNMR PX2150-4 CDCl3 20170508

170.383

135.834

134.281

133.893

128.792

128.695

128.474

126.583

126.293

125.748

77.415

77.160

76.906

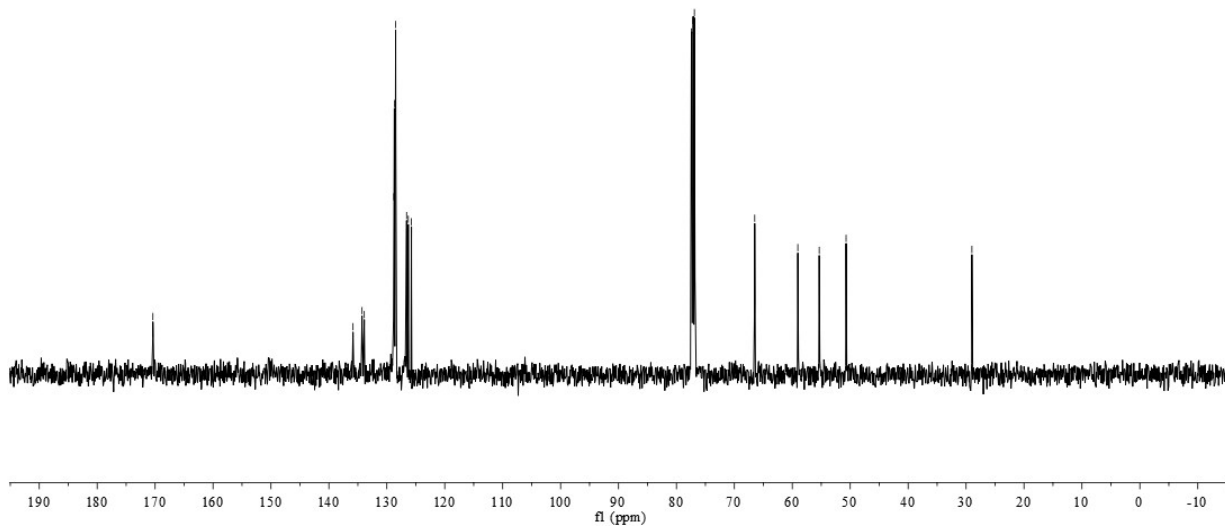
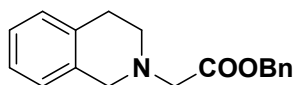
66.486

59.046

55.350

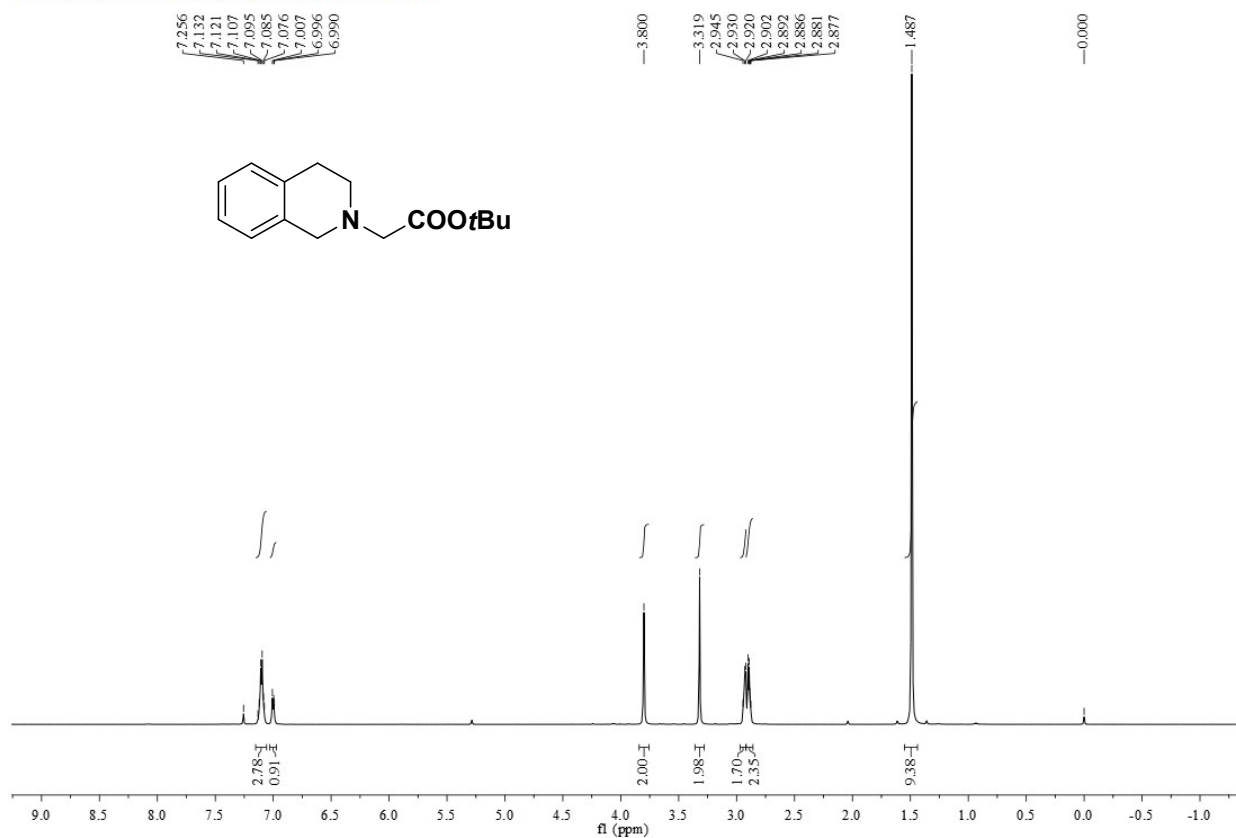
50.714

28.992



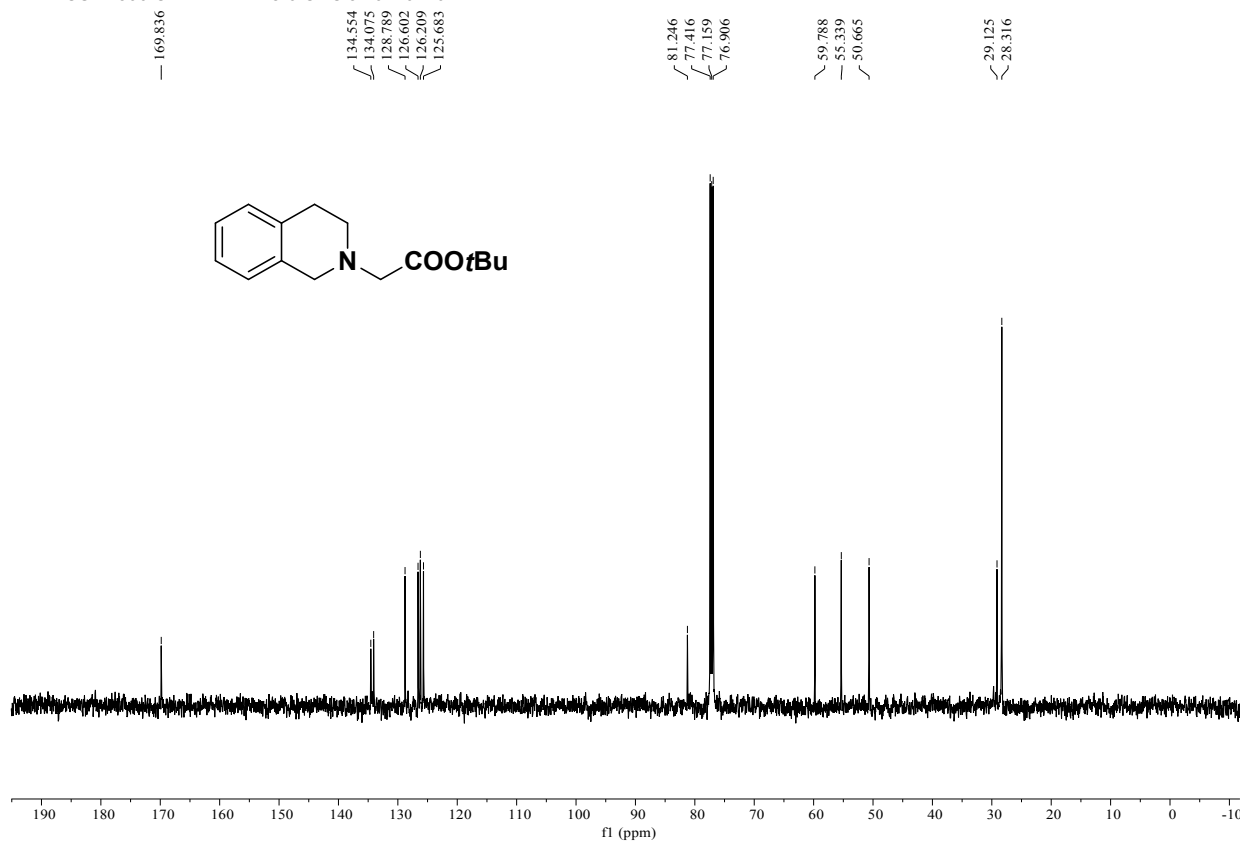
¹H NMR spectra of compound **2d**

MERCURY500 HNMR PX2148-6 CDCl₃ 20170426



¹³C NMR spectra of compound **2d**

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¹H NMR spectra of compound 2e

MERCURY500 HNMR PX2138-1 CDCl₃ 20170426

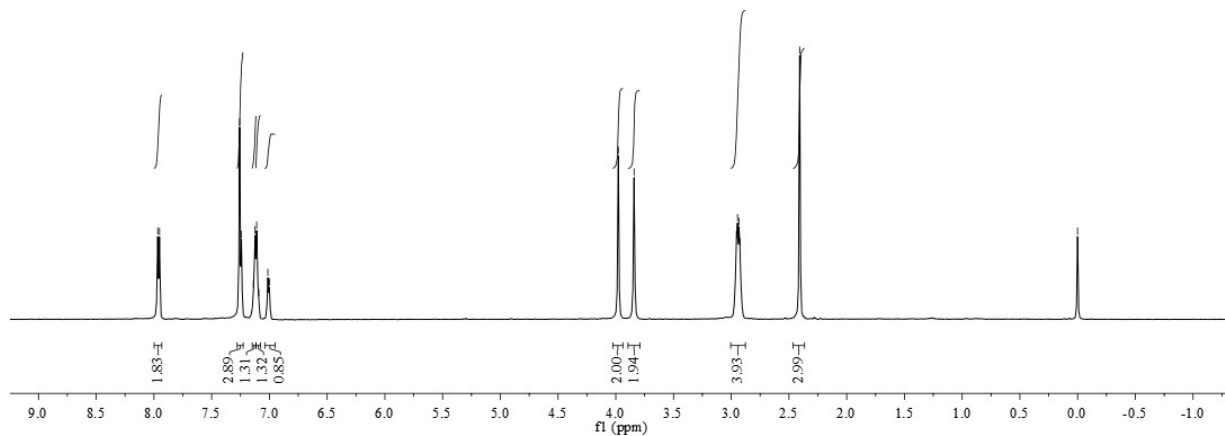
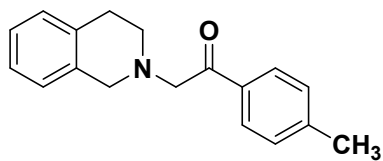
7.967
7.952
7.258
7.242
7.138
7.124
7.110
7.092
7.013
7.000

3.978
3.841

2.955
2.945
2.934
2.924

2.407

0.000



¹³C NMR spectra of compound 2e

MERCURY500 CNMR PX2148-1 CDCl₃ 20170426

196.467

144.187
134.495
134.145
133.692
129.326
128.789
128.544
126.625
126.263
125.734

77.412
77.159
76.902

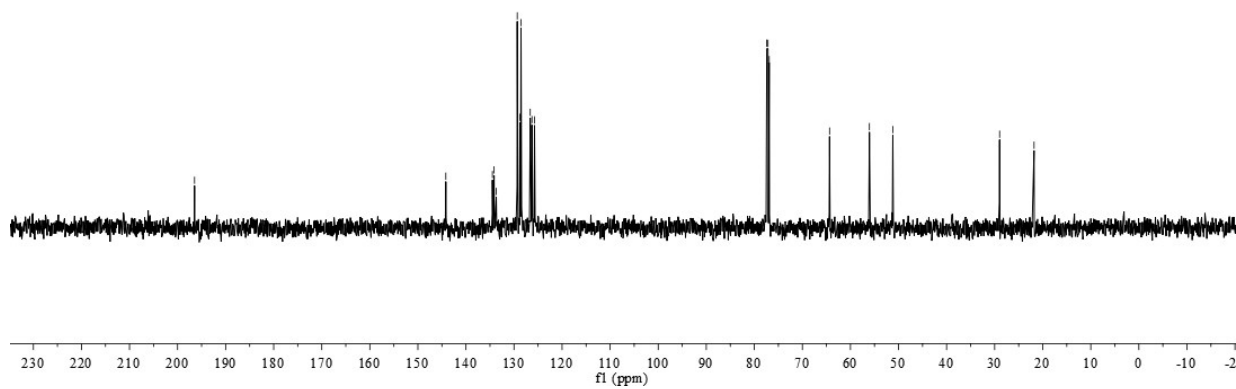
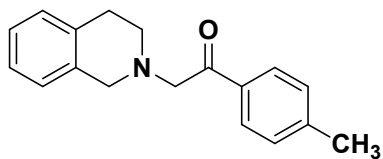
64.354

56.056

51.186

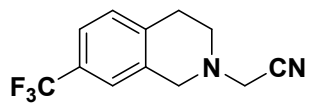
28.970

21.800



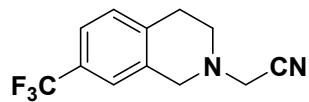
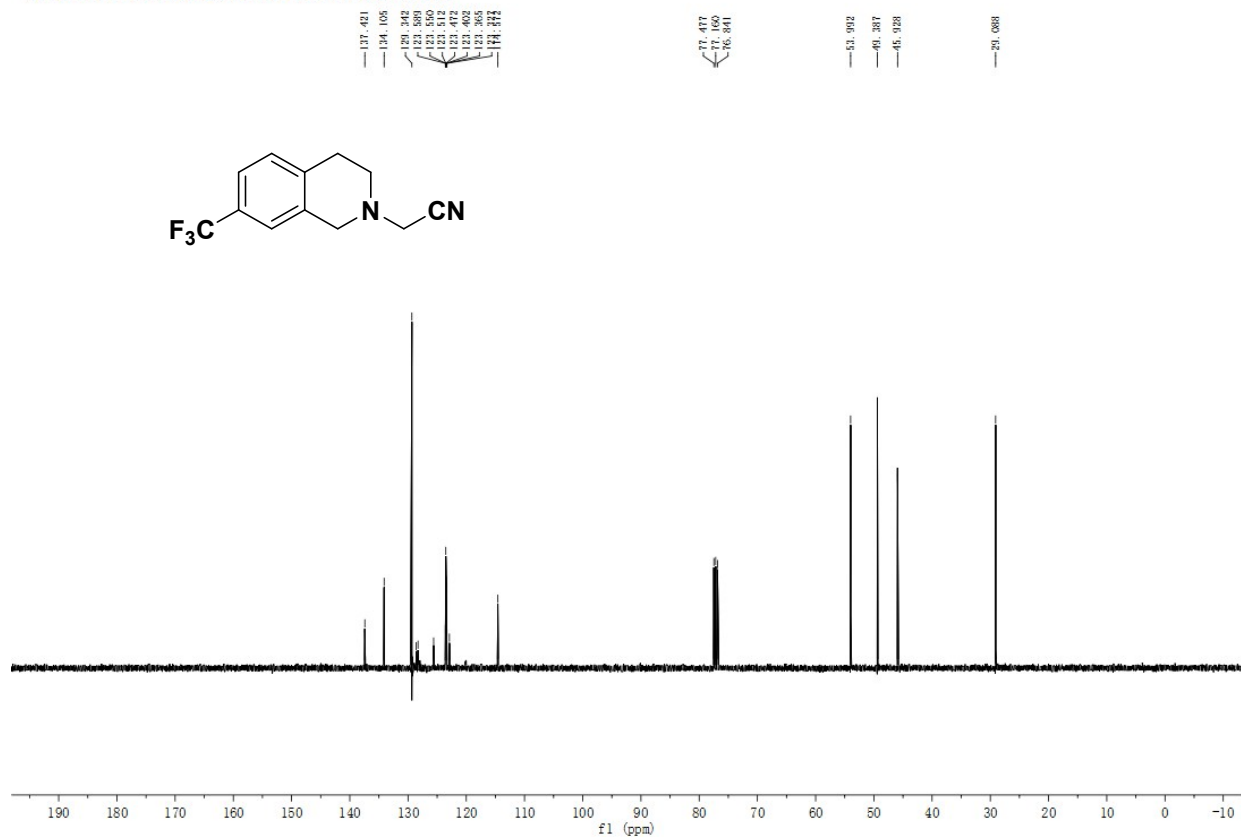
¹H NMR spectra of compound **2f**

MERCURY400 HNMR PX2227-2 CDCl₃ 20171009



¹³C NMR spectra of compound **2f**

MERCURY400 CNMR PX2227-2 CDCl₃ 20171009



¹H NMR spectra of compound **2g**

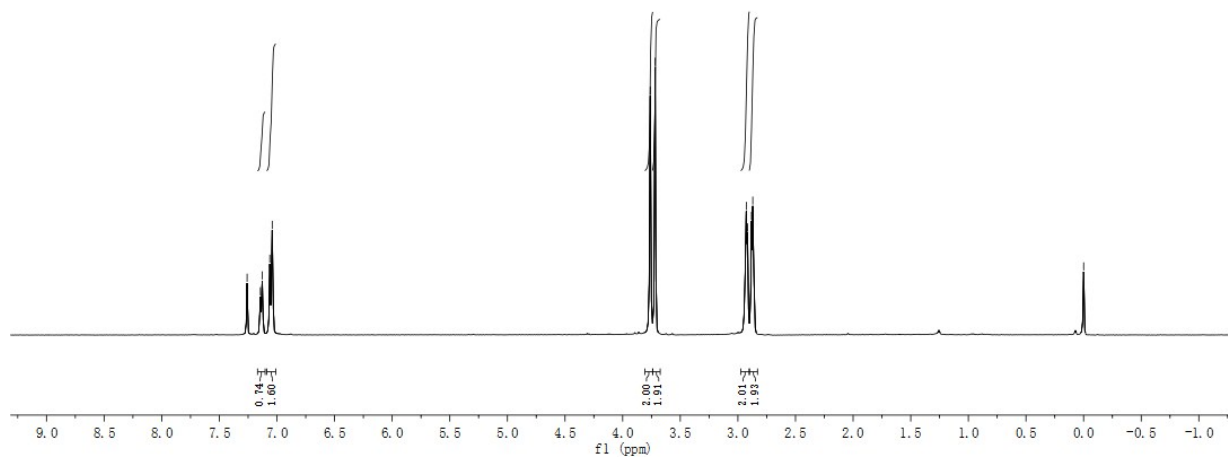
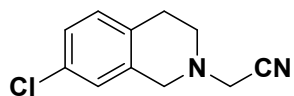
MERCURY500 HNMR PX22226-1 CDCI3 20171009

7.239
7.143
7.087
7.041

3.760
3.718

2.927
2.916
2.892
2.871

0.000



¹³C NMR spectra of compound **2g**

MERCURY500 CNMR PX22226-1 CDCI3 20171009

134.908
131.749
131.642
128.422
128.402
128.498
114.558

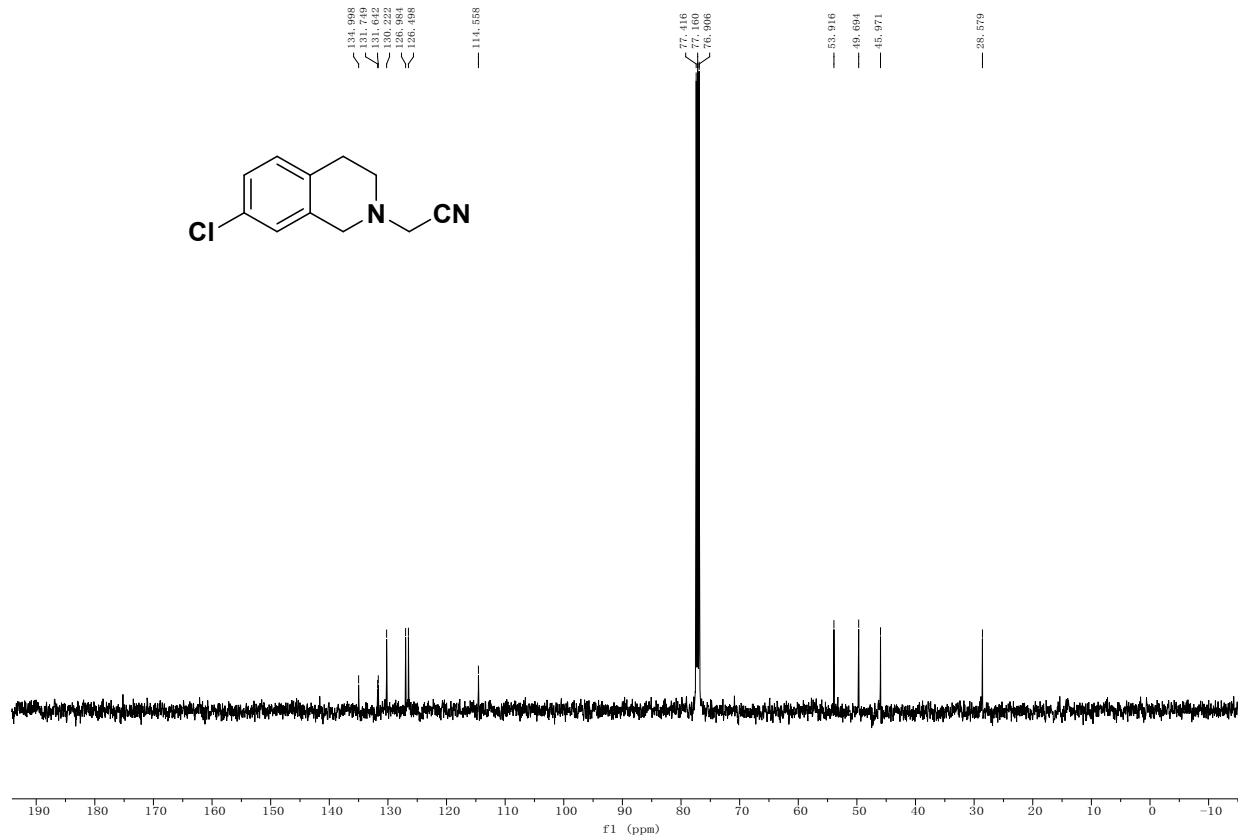
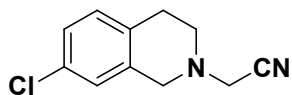
77.416
77.160
76.906

53.916

49.694

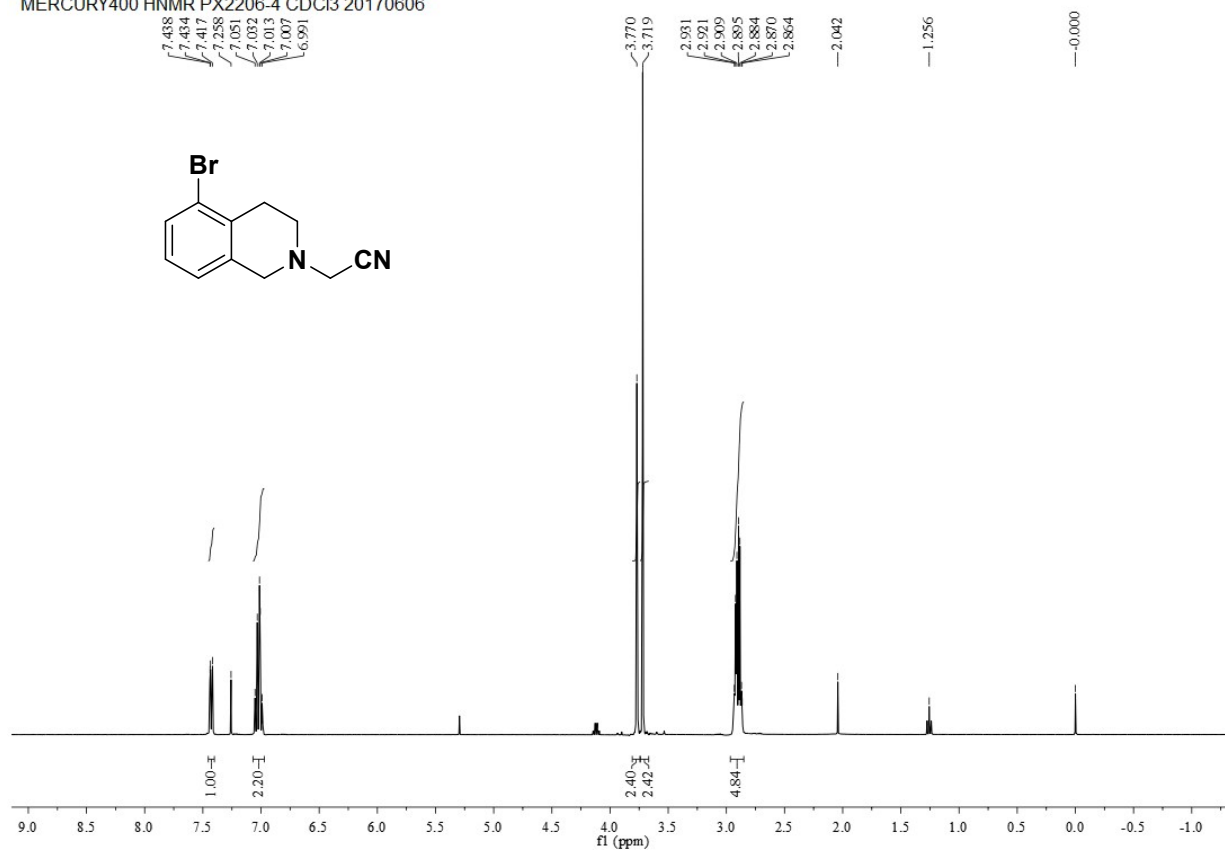
45.971

28.579



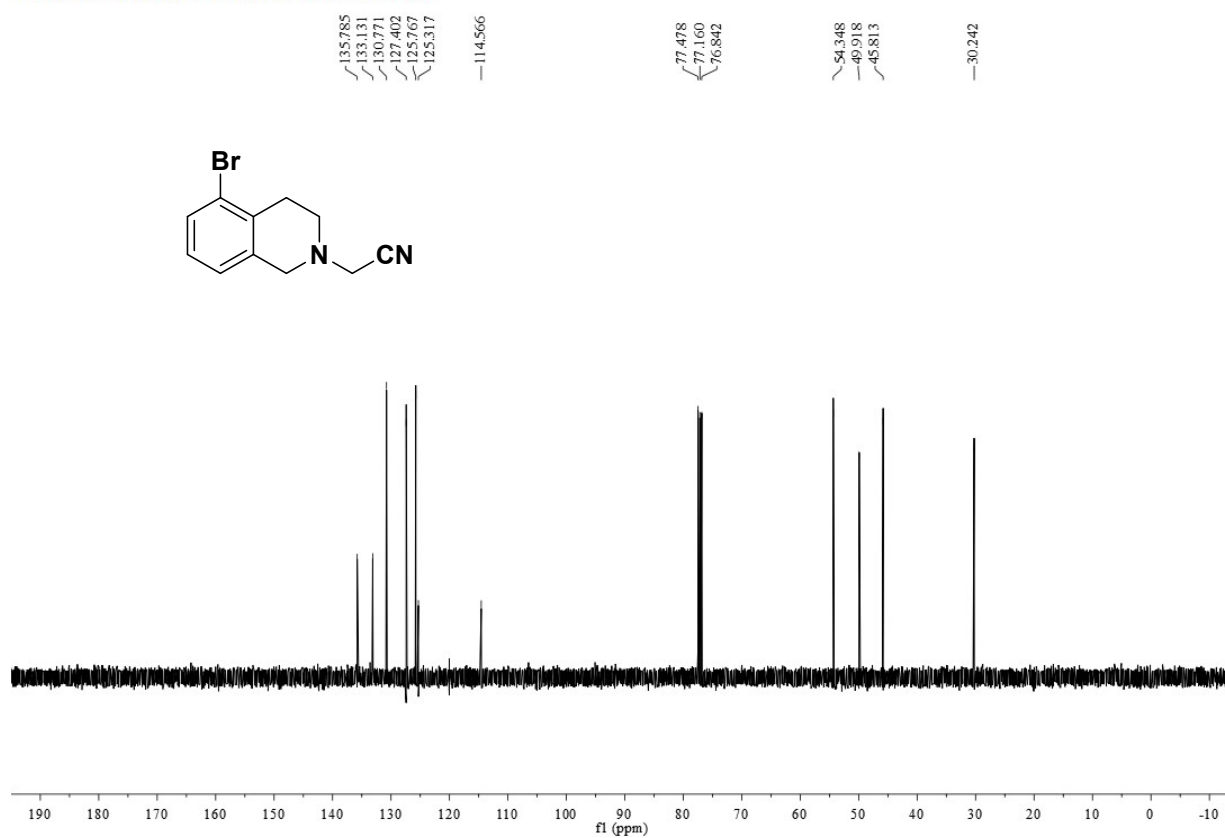
¹H NMR spectra of compound 2h

MERCURY400 HNMR PX2206-4 CDCl3 20170606



¹³C NMR spectra of compound 2h

MERCURY400 CNMR PX2206-4 CDCl3 20170606



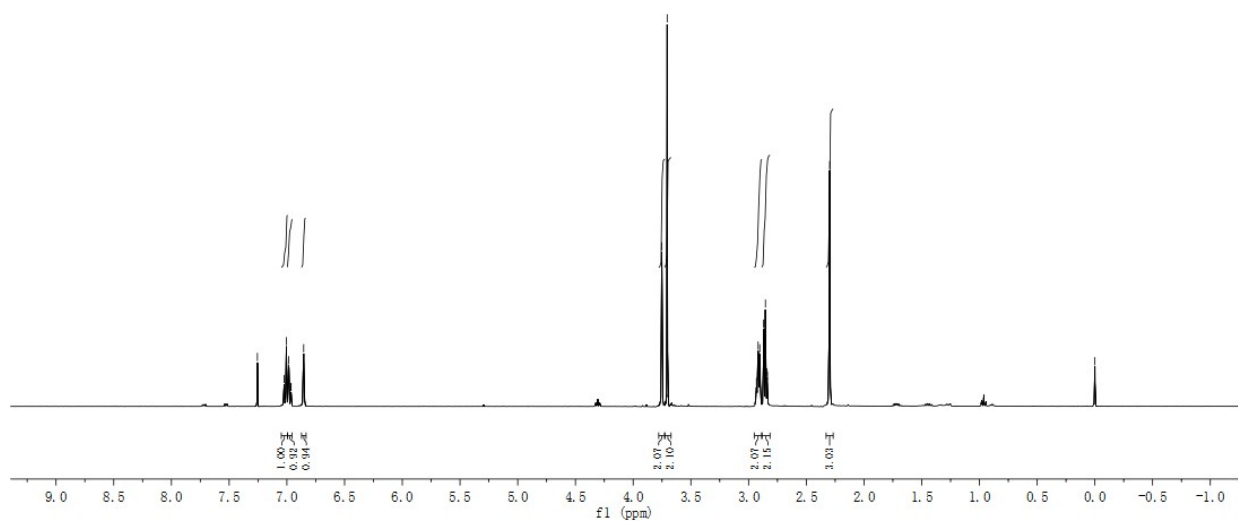
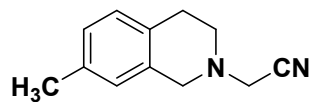
¹H NMR spectra of compound **2i**

MERCURY400 HNMR PX2233-1 CDCI3 20171018

7.355
7.024
7.004
6.985
6.965
6.854

3.755
3.706
2.932
2.917
2.898
2.887
2.874
2.840
2.837
2.827

0.000



¹³C NMR spectra of compound **2i**

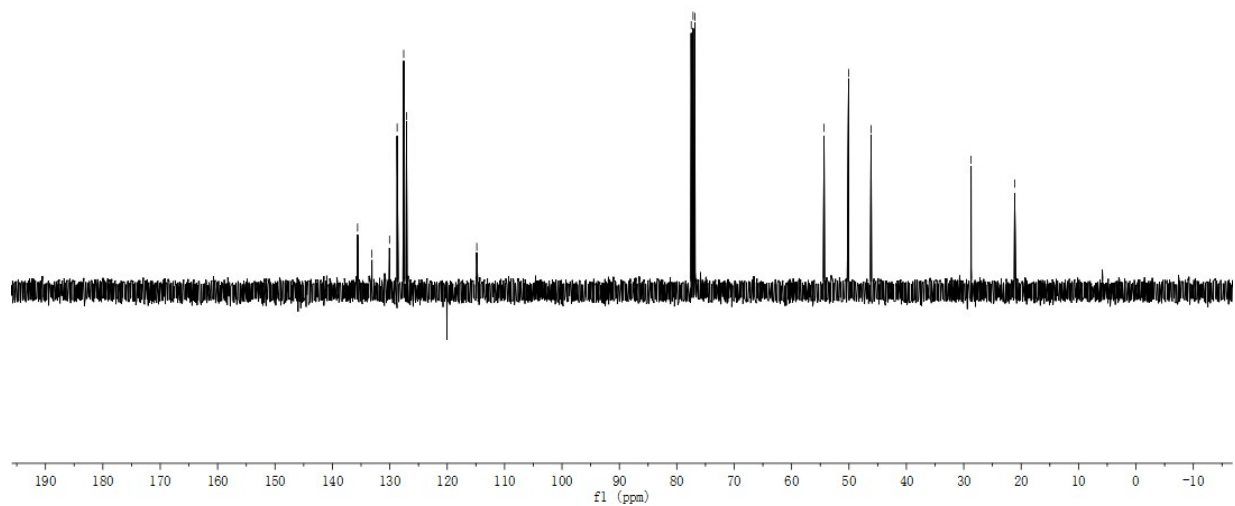
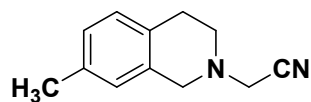
MERCURY400 CNMR PX2233-1 CDCI3 20171018

135.615
133.118
130.052
128.720
127.966
127.092

77.478
77.000
76.542

54.342
50.088
46.147

28.721
21.127



¹H NMR spectra of compound 2j

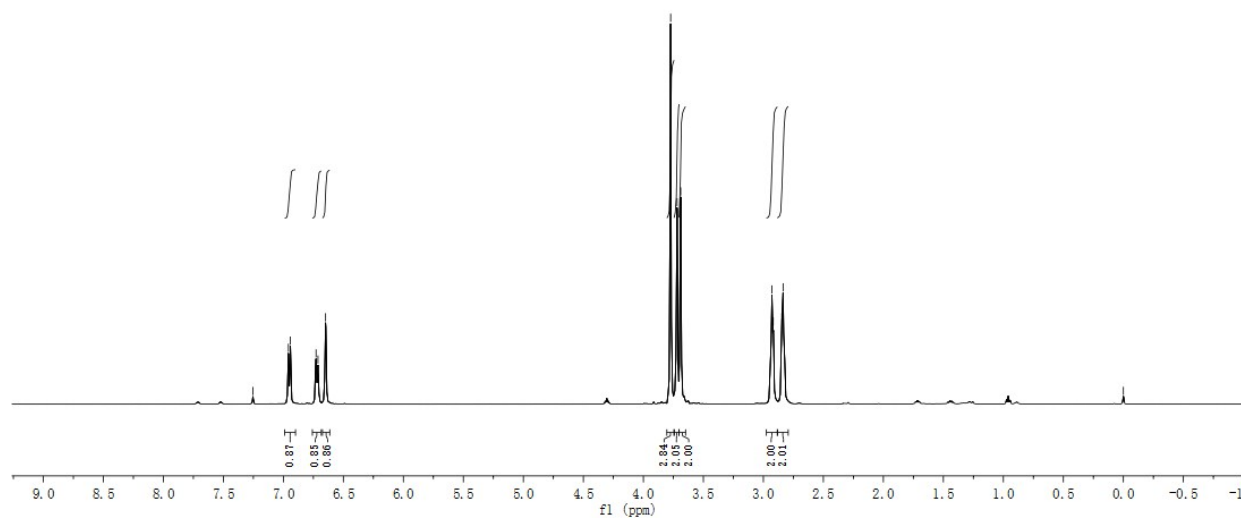
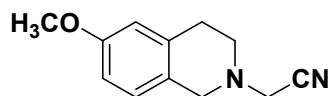
MERCURY500 HNMR PX2233-2 CDCl3 20171018

7.283
6.988
6.943
6.711
6.648

3.778
3.710
3.689

2.918
2.918
2.846
2.825

-0.000



¹³C NMR spectra of compound 2j

MERCURY500 CNMR PX2233-2 CDCl3 20171018

158.283

134.305

127.546

125.490

114.859

112.880

77.402

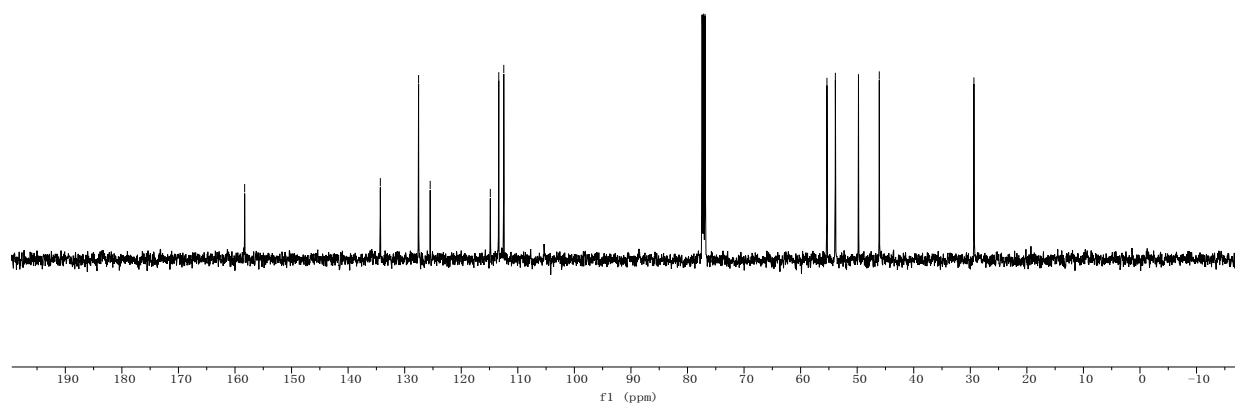
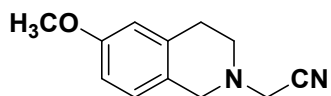
76.893

55.245

49.772

46.091

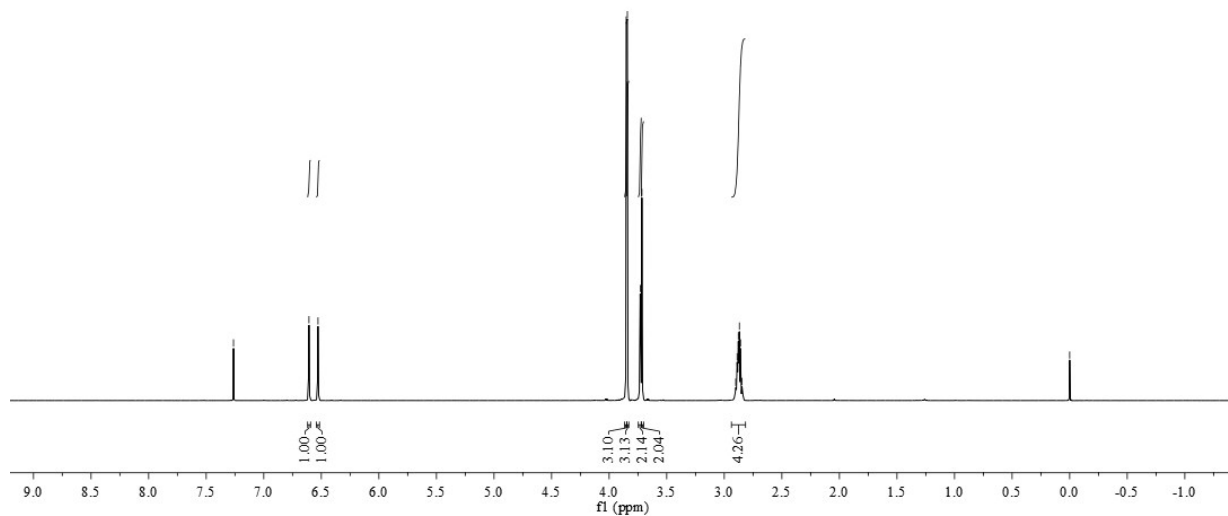
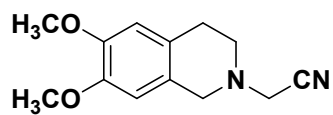
29.359



¹H NMR spectra of compound **2k**

MERCURY400 HNMR PX2206-2 CDCl₃ 20170606

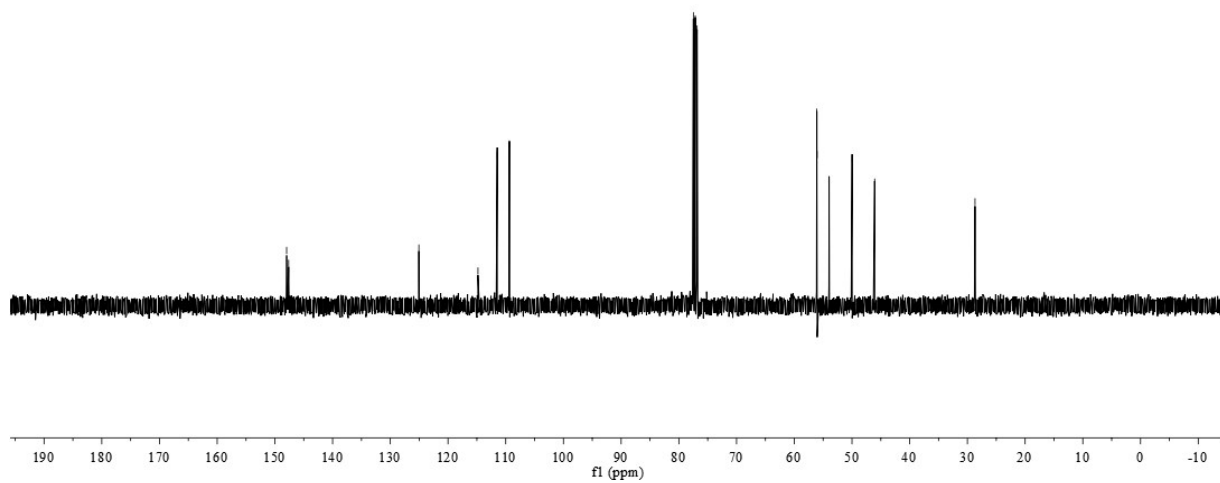
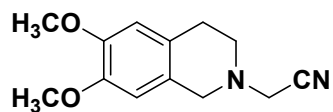
7.263
6.607
6.529
3.852
3.842
3.770
3.715
2.900
2.888
2.878
2.869
2.859
2.846
-0.000



¹³C NMR spectra of compound **2k**

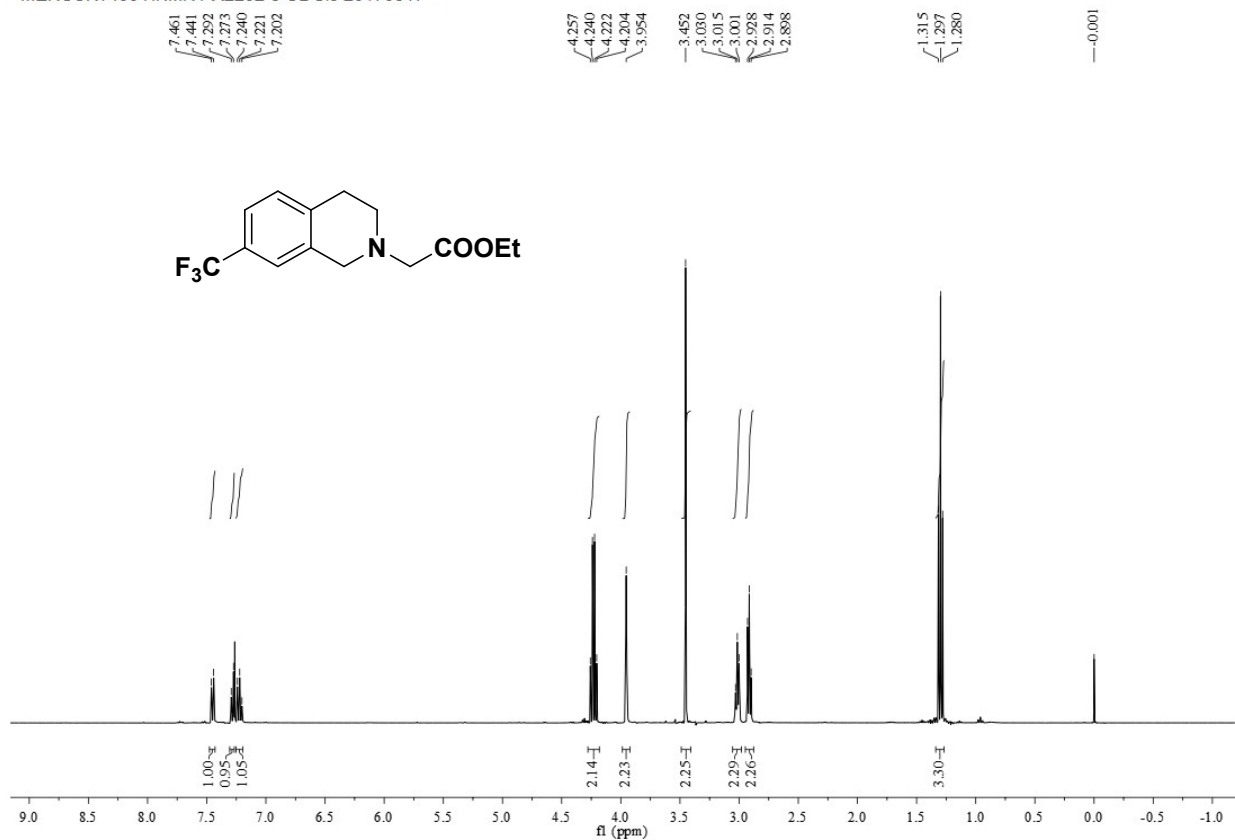
MERCURY400 CNMR PX2206-2 CDCl₃ 20170606

147.965
147.617
125.051
125.009
114.810
111.471
109.365
77.479
77.160
76.843
56.091
56.044
53.970
49.973
46.068
28.679



¹H NMR spectra of compound **21**

MERCURY400 HNMR PX2202-3 CDCl₃ 20170517



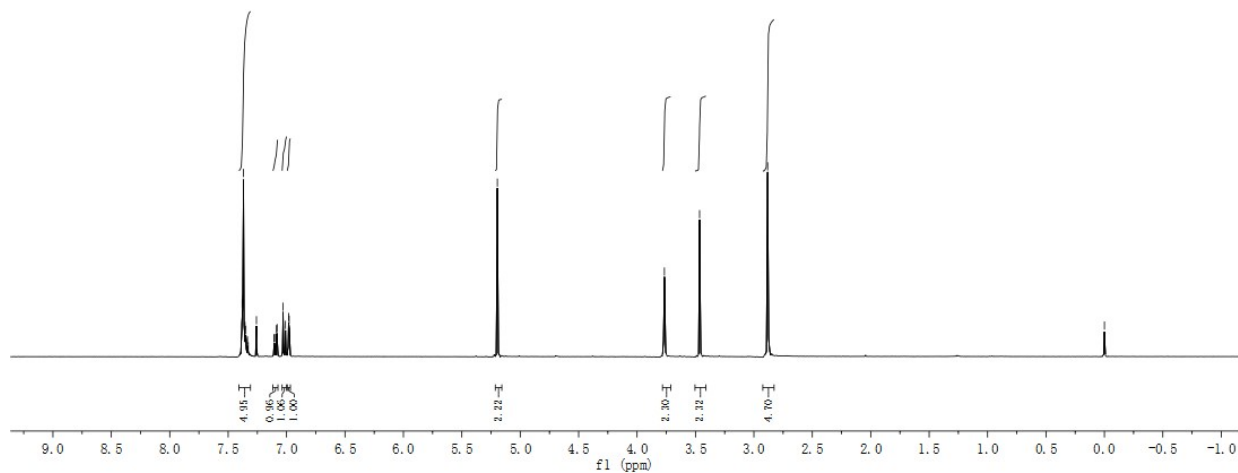
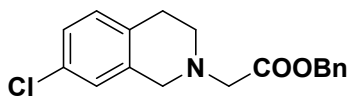
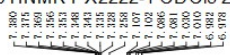
¹³C NMR spectra of compound **21**

MERCURY500 CNMR PX2202-3 CDCl₃ 20170523



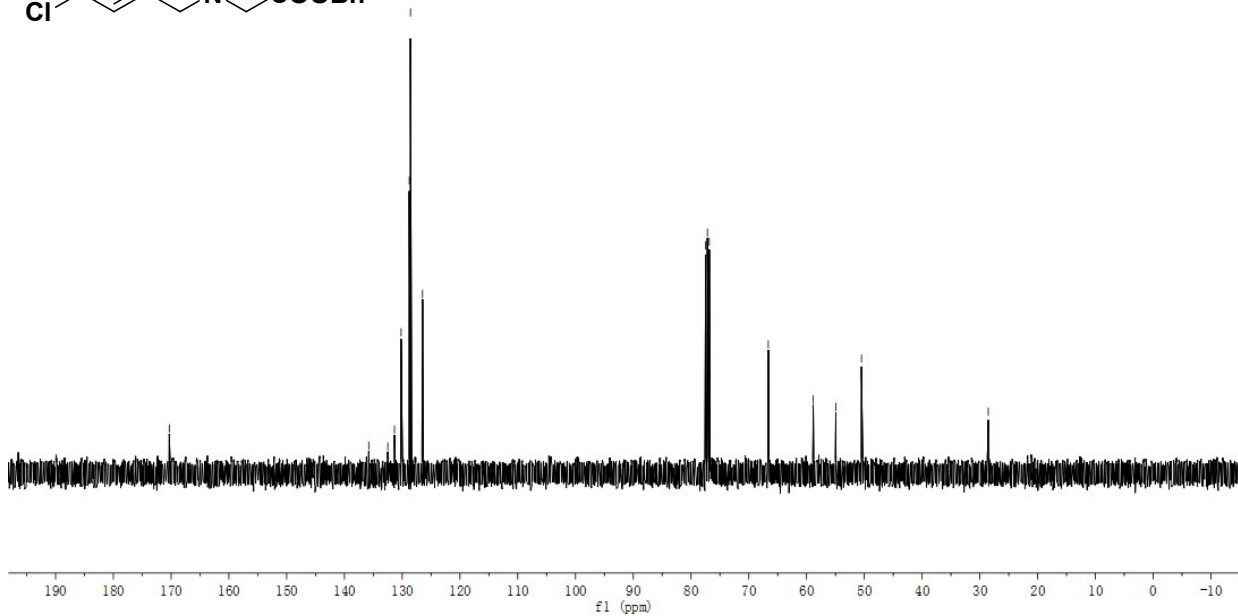
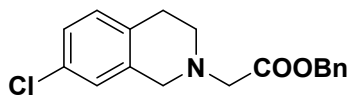
¹H NMR spectra of compound **2m**

MERCURY400 HNMR PX2222-1 CDCl₃ 20170920



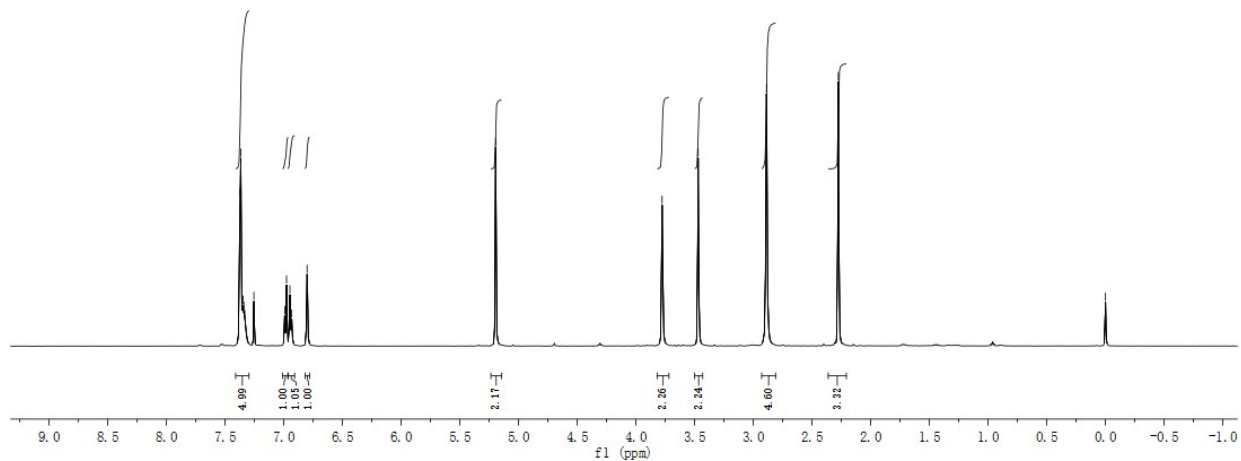
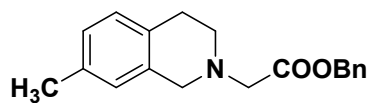
¹³C NMR spectra of compound **2m**

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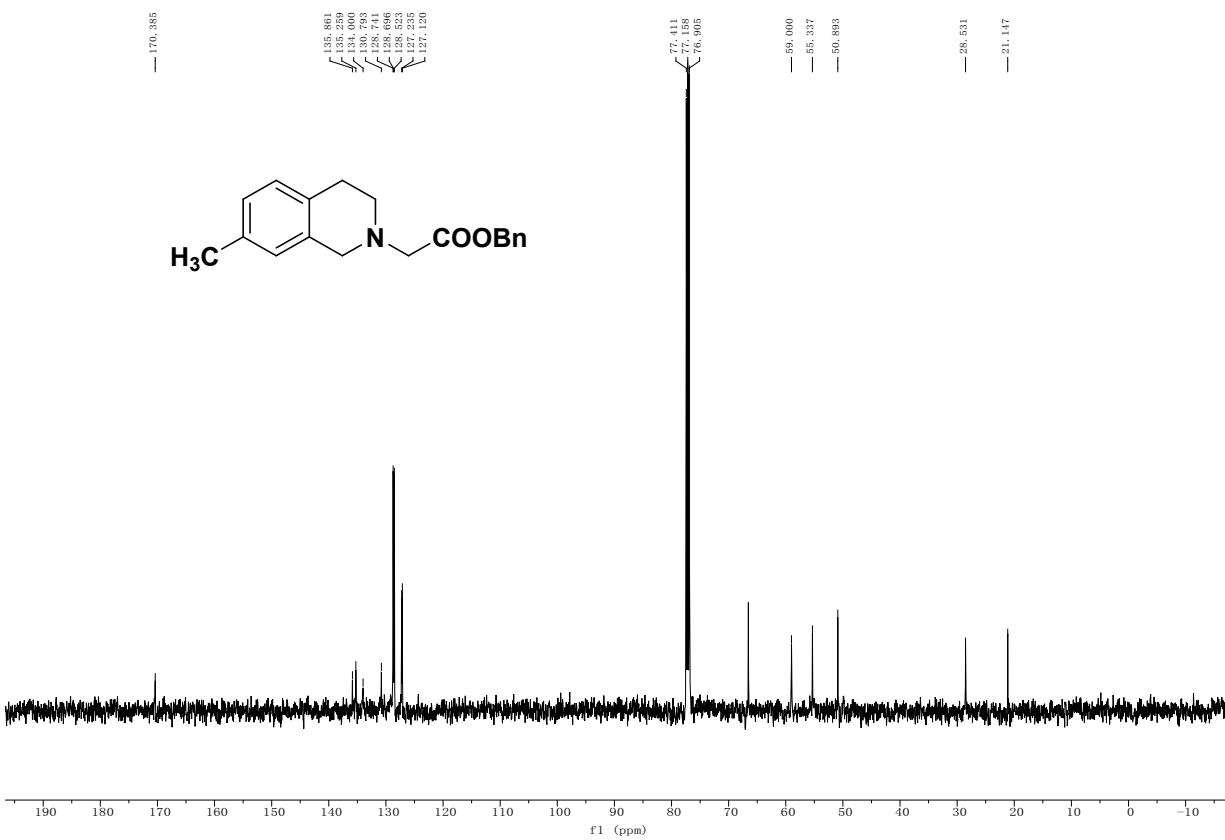
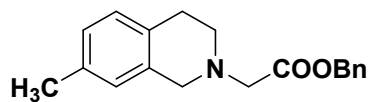
¹H NMR spectra of compound **2n**

MERCURY500 HNMR PX2233-3 CDCl₃ 20171018



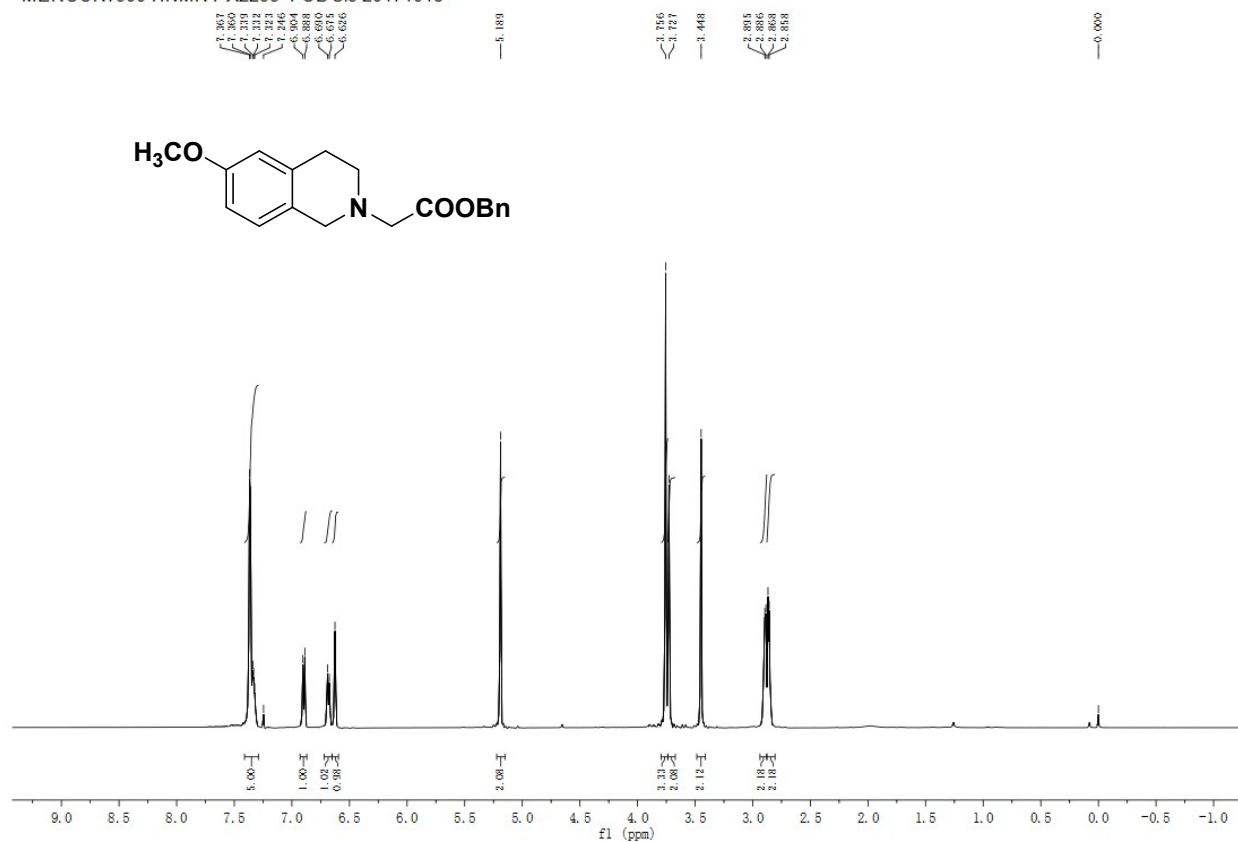
¹³C NMR spectra of compound **2n**

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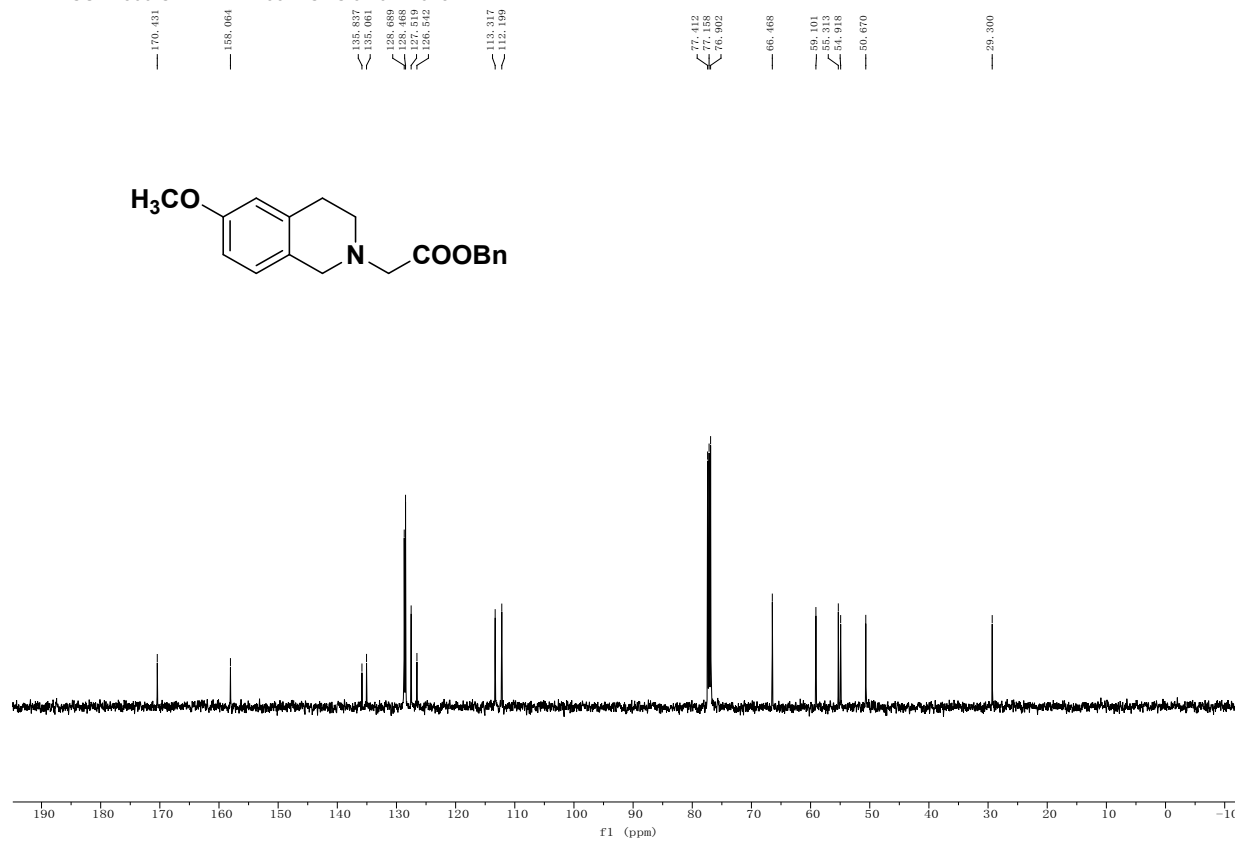
¹H NMR spectra of compound **2o**

MERCURY500 HNMR PX2233-4 CDCl₃ 20171018



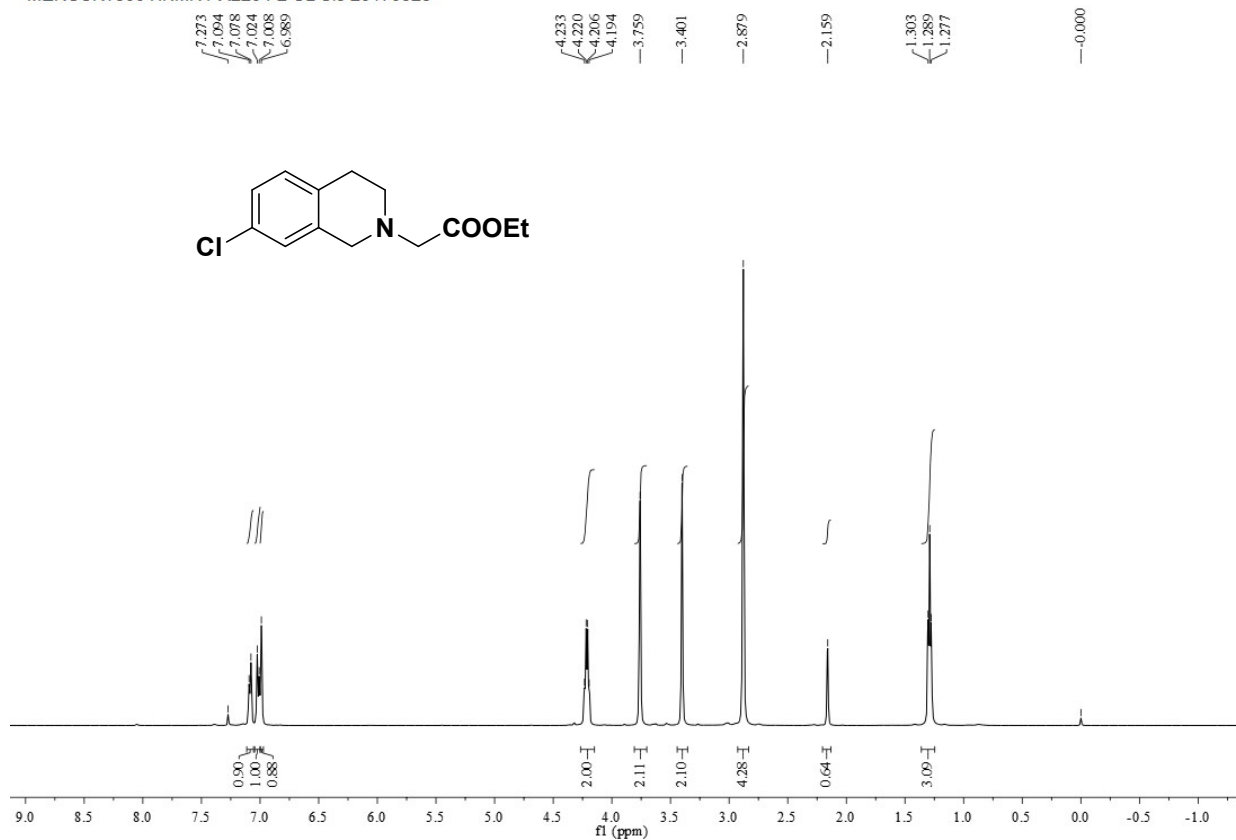
¹³C NMR spectra of compound **2o**

MERCURY500 CNMR PX2233-4 CDCl₃ 20171018



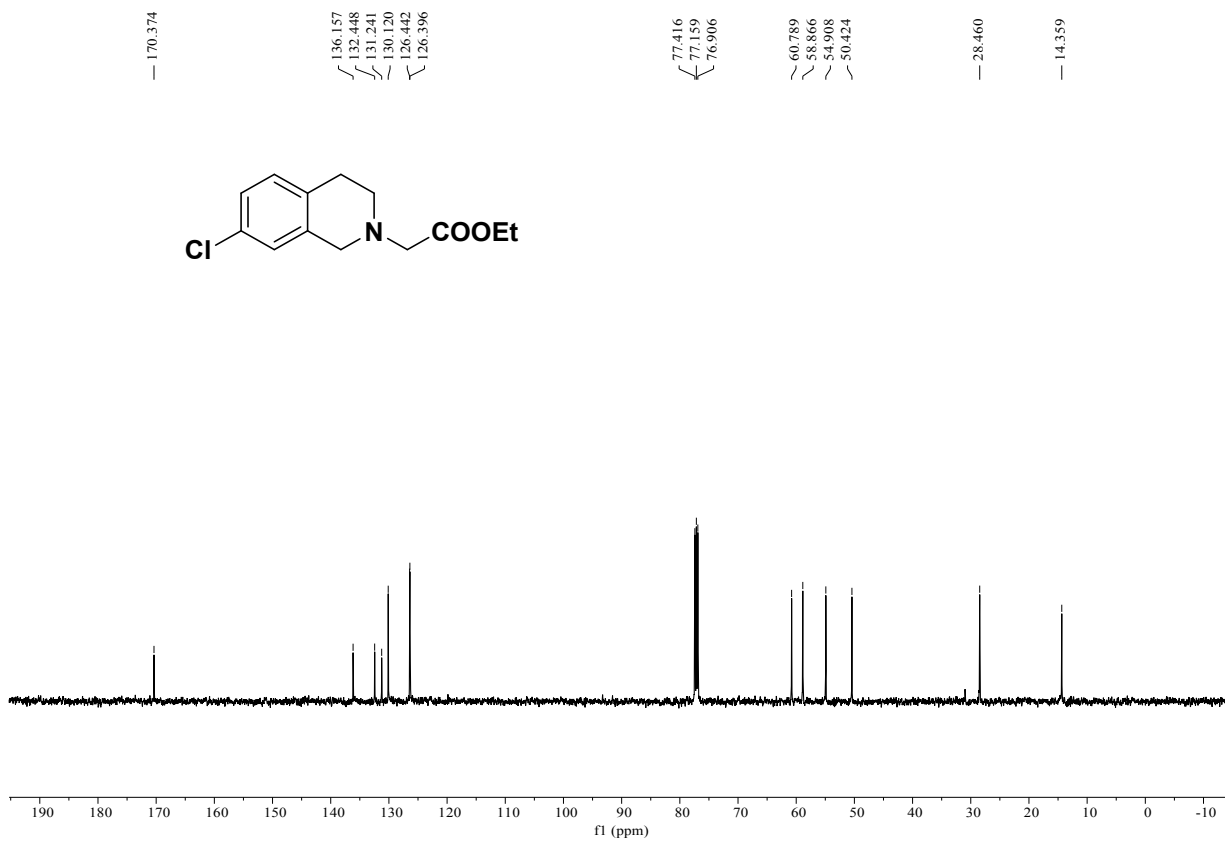
¹H NMR spectra of compound 2p

MERCURY500 HNMR PX2204-2 CDCl₃ 20170525



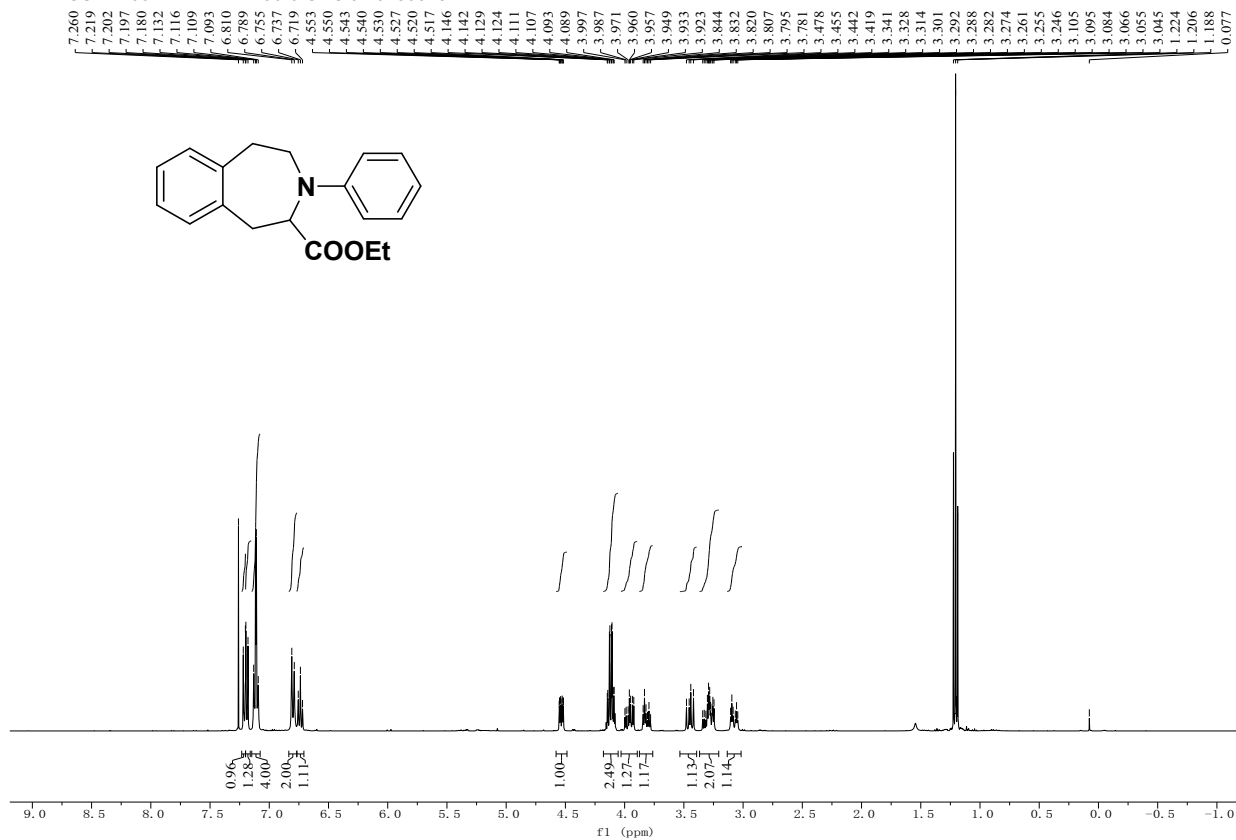
¹³C NMR spectra of compound 2p

MERCURY500 CNMR PX2204-2 CDCl₃ 20170525



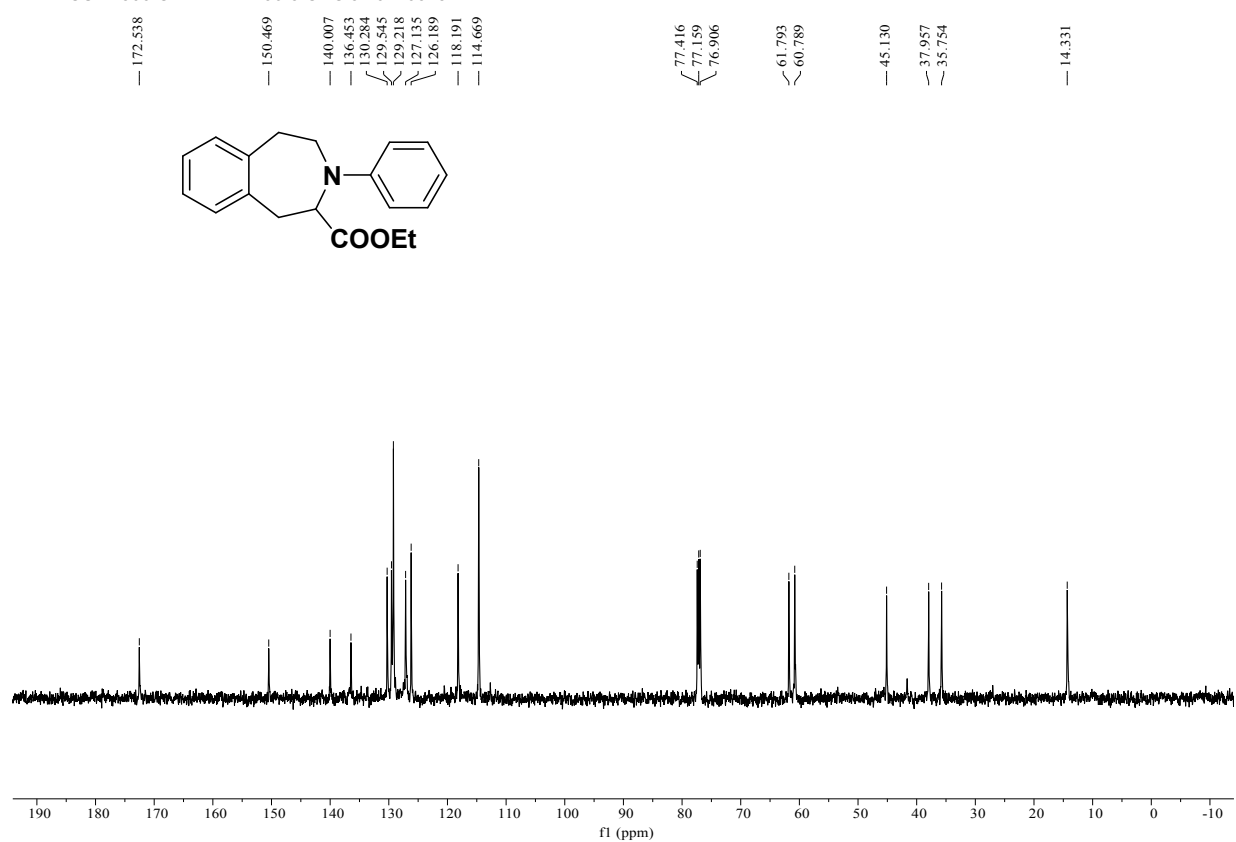
¹H NMR spectra of compound 4a

MERCURY400 HNMR PX2136-3 CDCl₃ 20180328



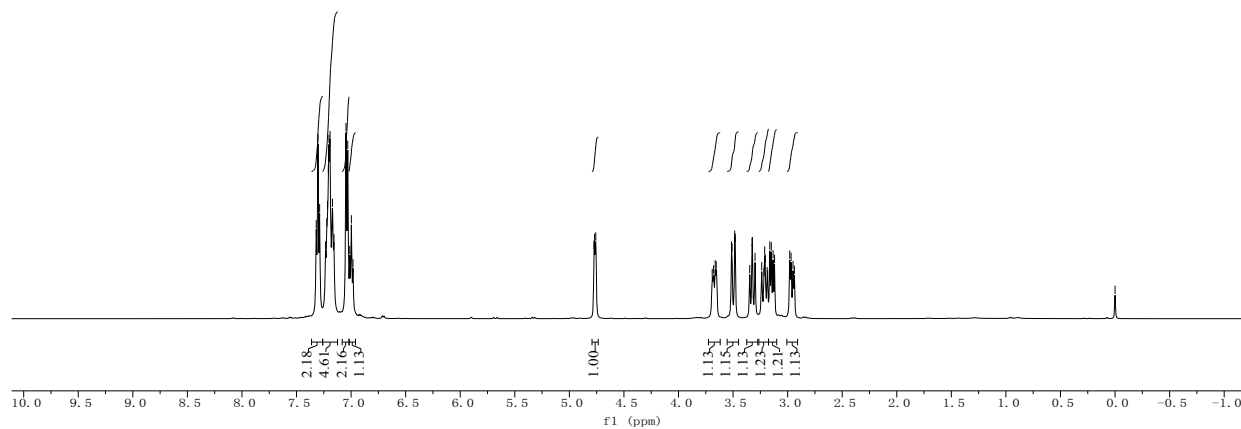
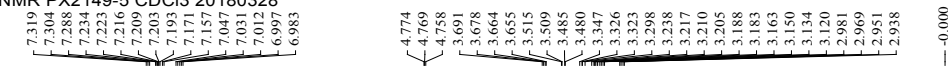
¹³C NMR spectra of compound 4a

MERCURY500 CNMR PX2136-3 CDCl₃ 20170328



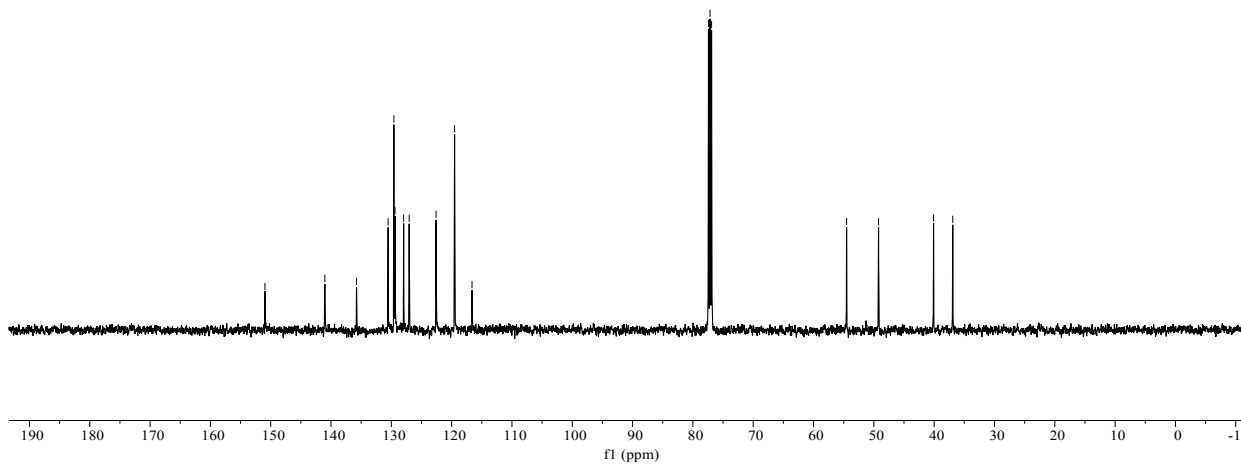
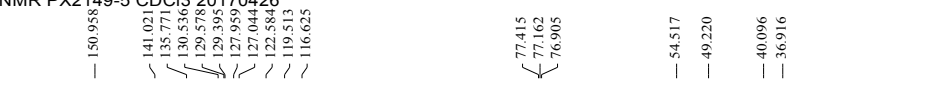
¹H NMR spectra of compound **4b**

MERCURY500 HNMR PX2149-5 CDCl₃ 20180328



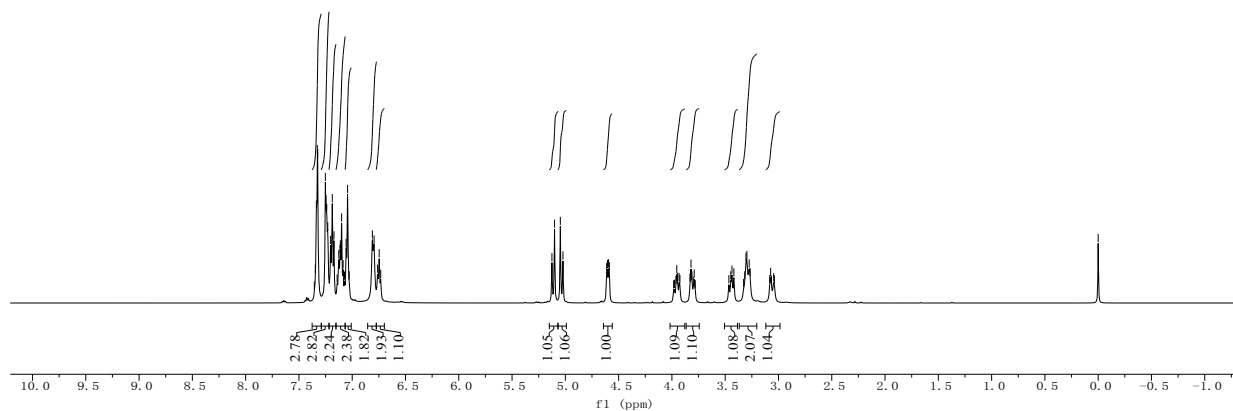
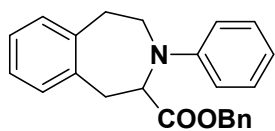
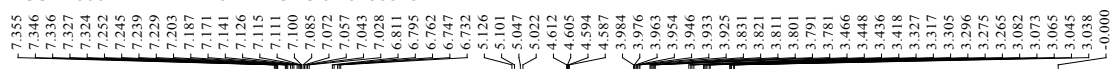
¹³C NMR spectra of compound **4b**

MERCURY500 CNMR PX2149-5 CDCl₃ 20170426



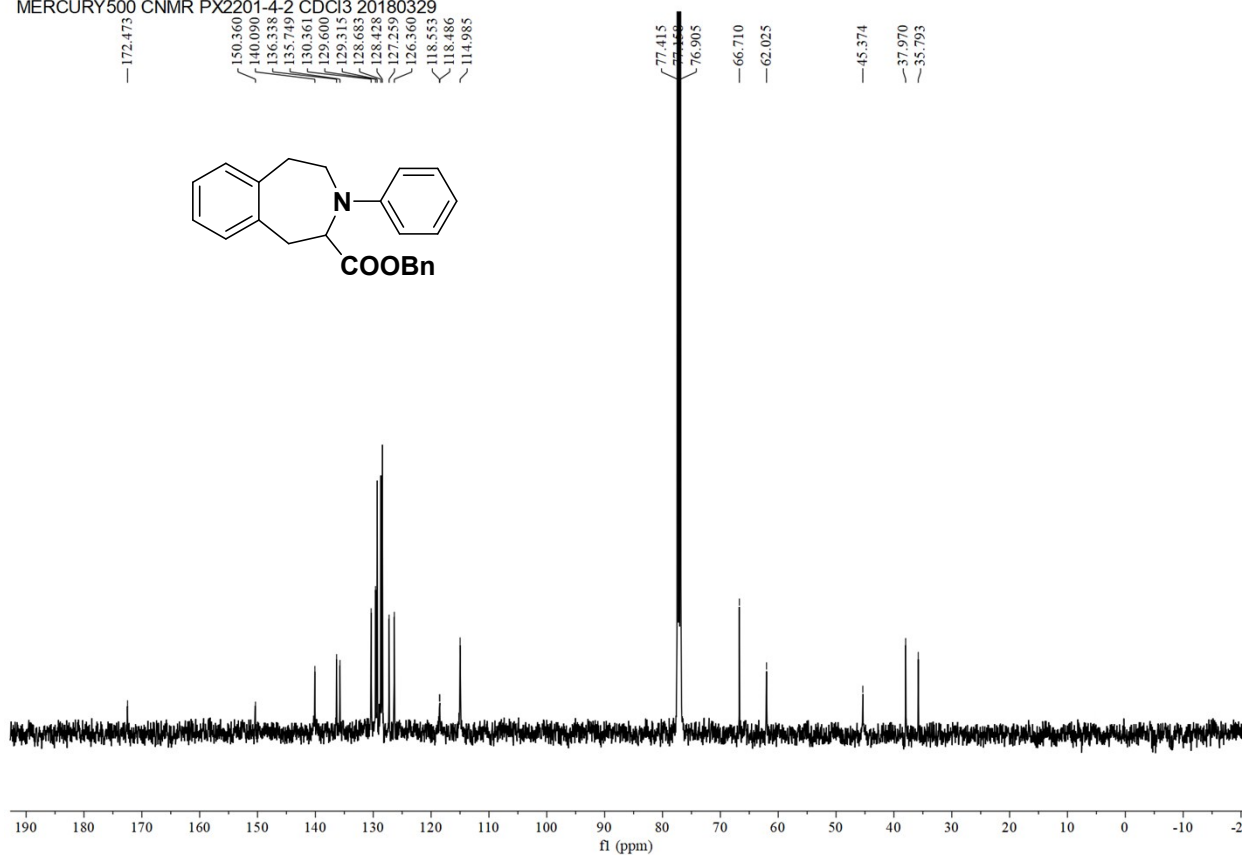
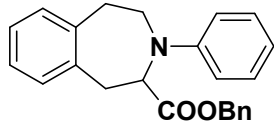
¹H NMR spectra of compound 4c

MERCURY500 HNMR PX2201-4-2 CDCl₃ 20180328



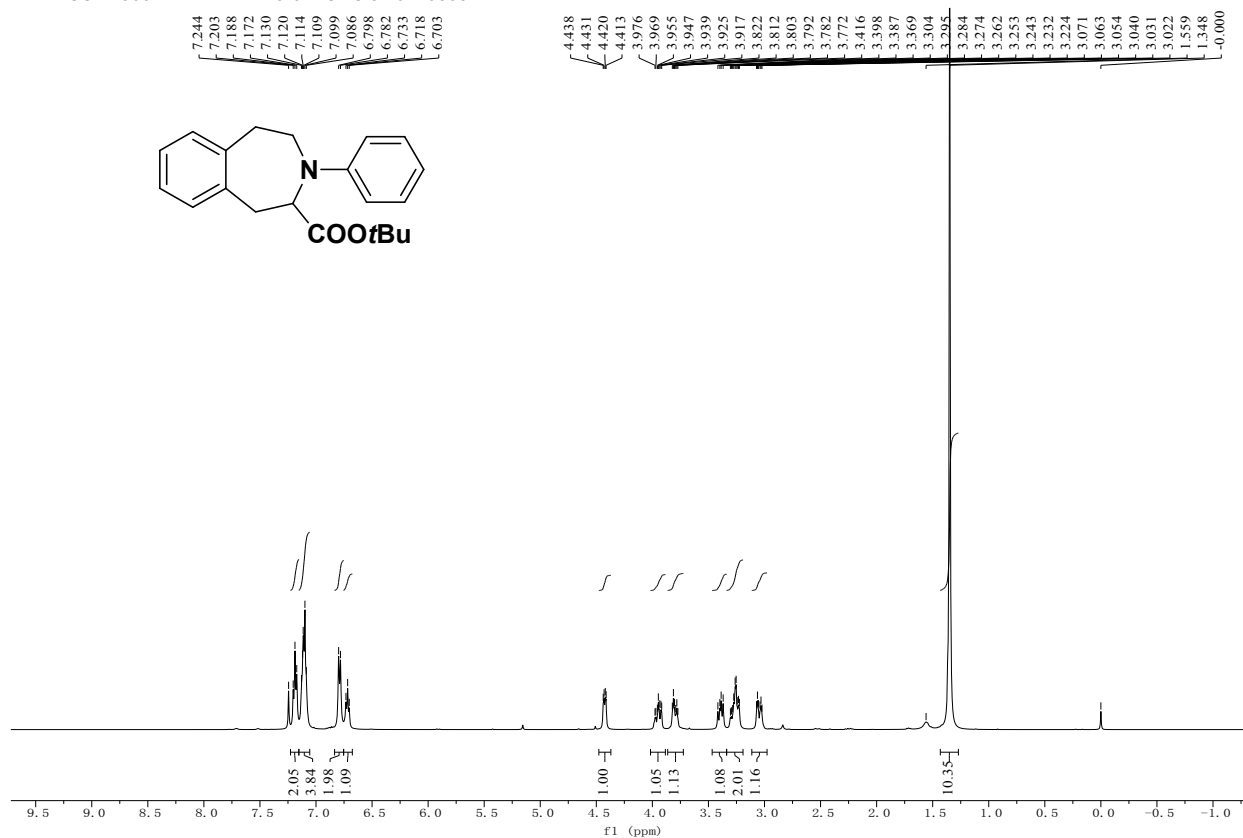
¹³C NMR spectra of compound 4c

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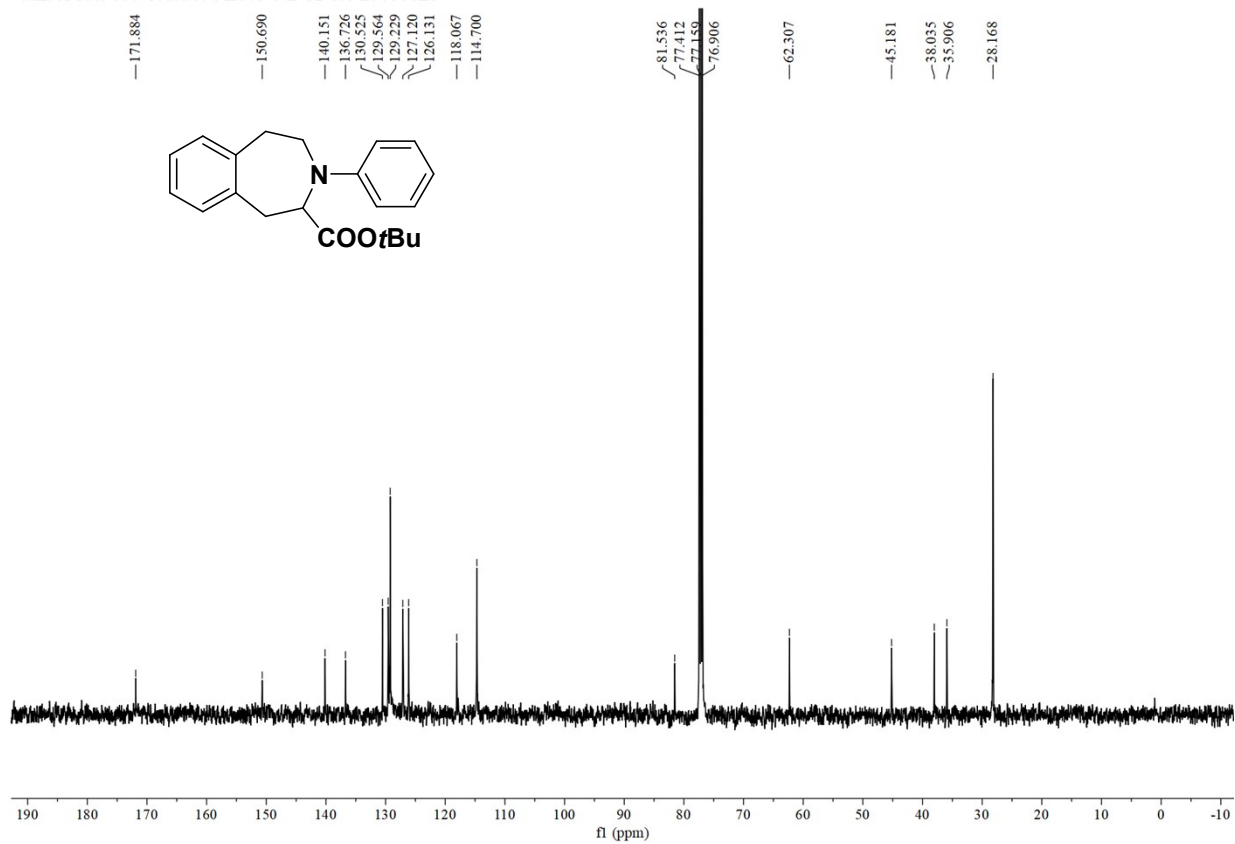
¹H NMR spectra of compound 4d

MERCURY500 HNMR PX2149-6-2 CDCl₃ 20170508



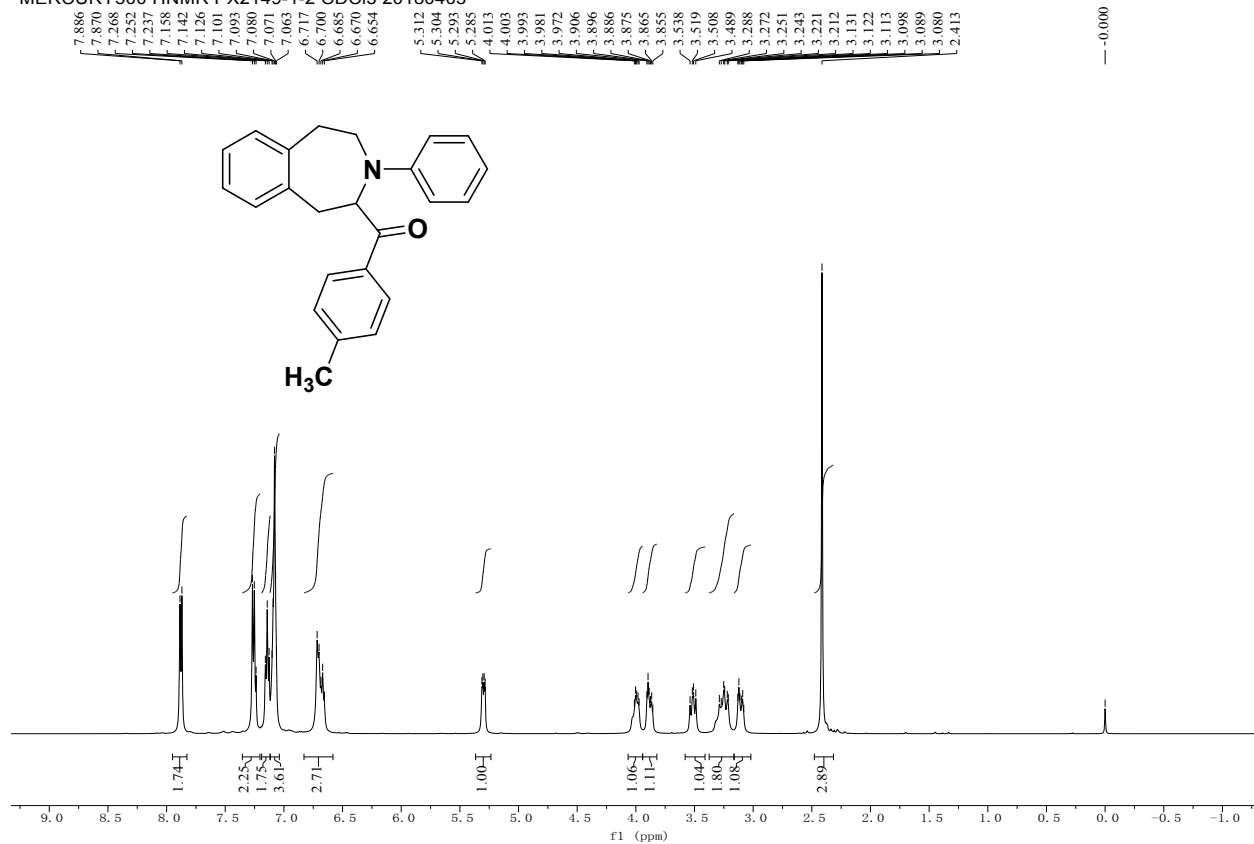
¹³C NMR spectra of compound 4d

MERCURY500 CNMR PX2149-6-2 CDCl₃ 20180329



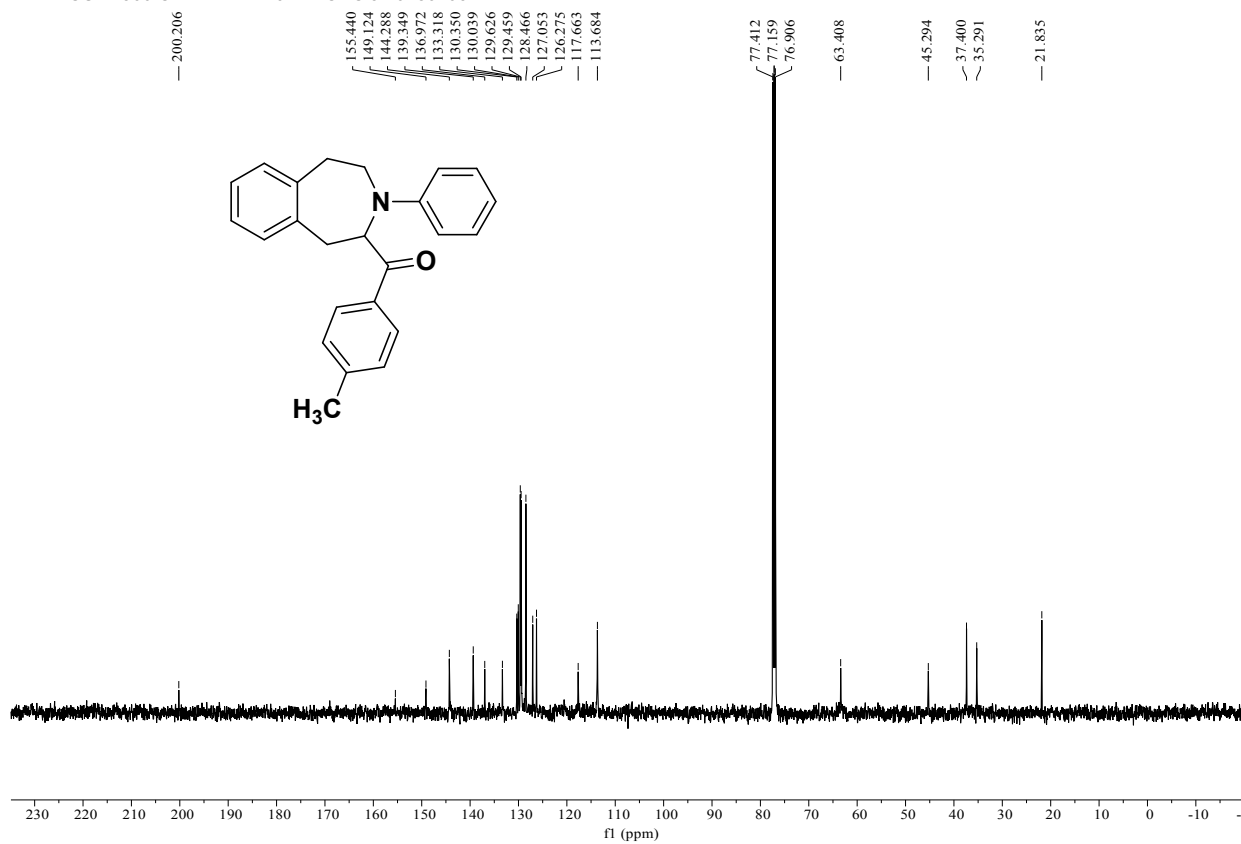
¹H NMR spectra of compound 4e

MERCURY500 HNMR PX2149-1-2 CDCl3 20180403

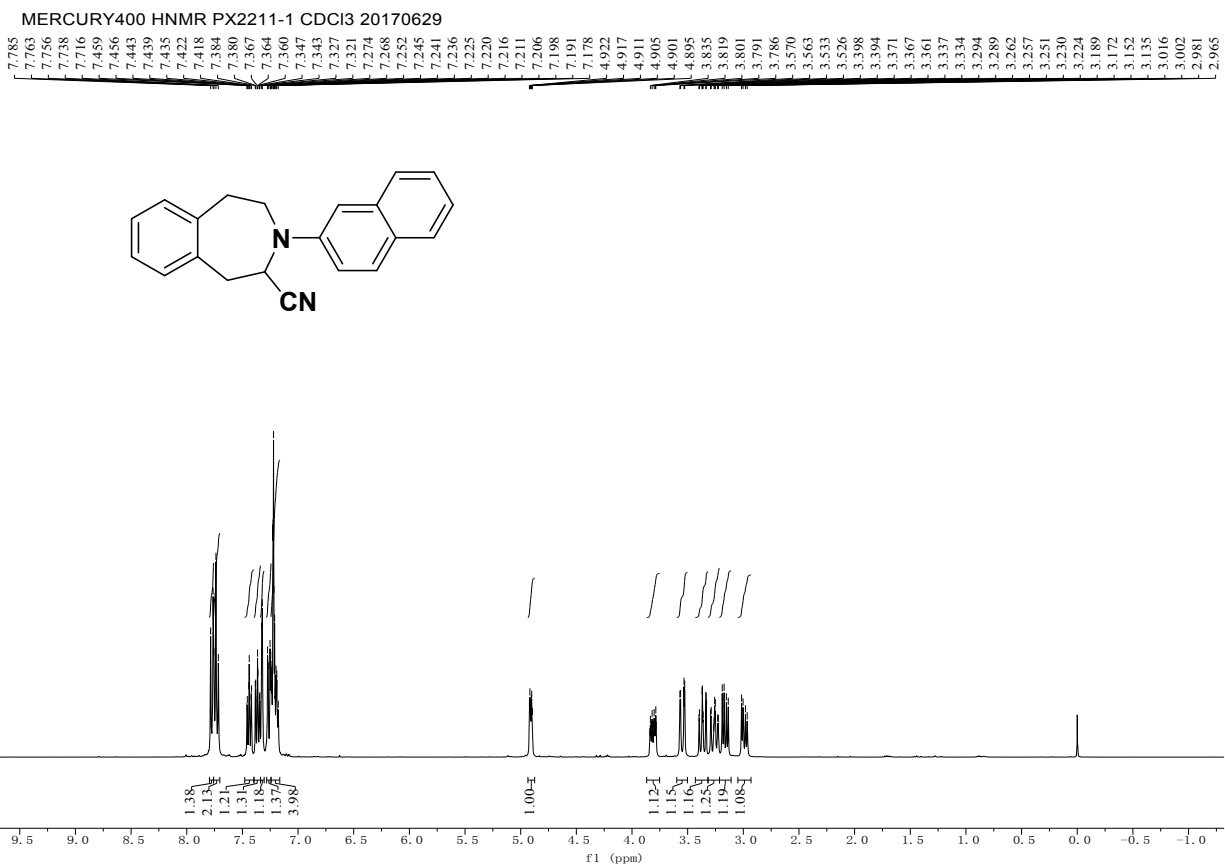


¹H NMR spectra of compound 4e

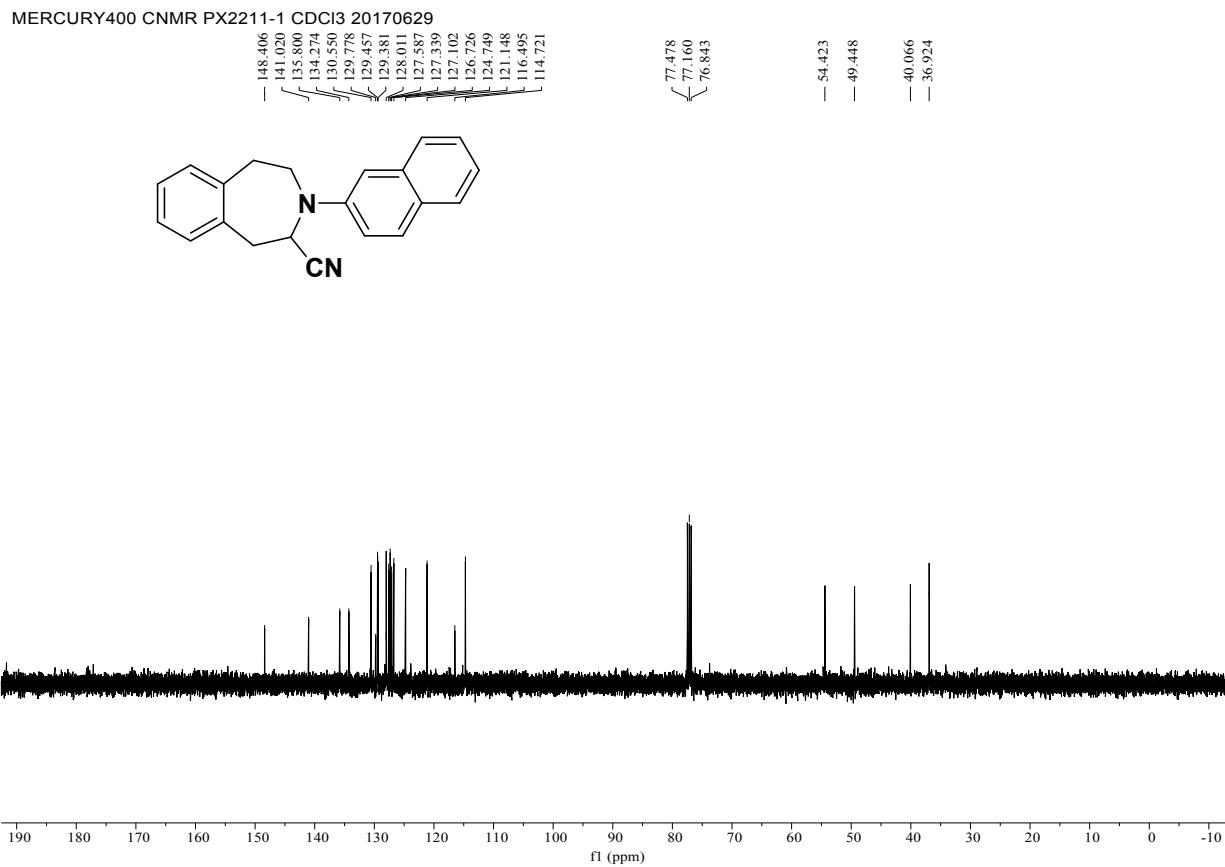
MERCURY500 CNMR PX2149-1-2 CDCl3 20180403



¹H NMR spectra of compound 4f

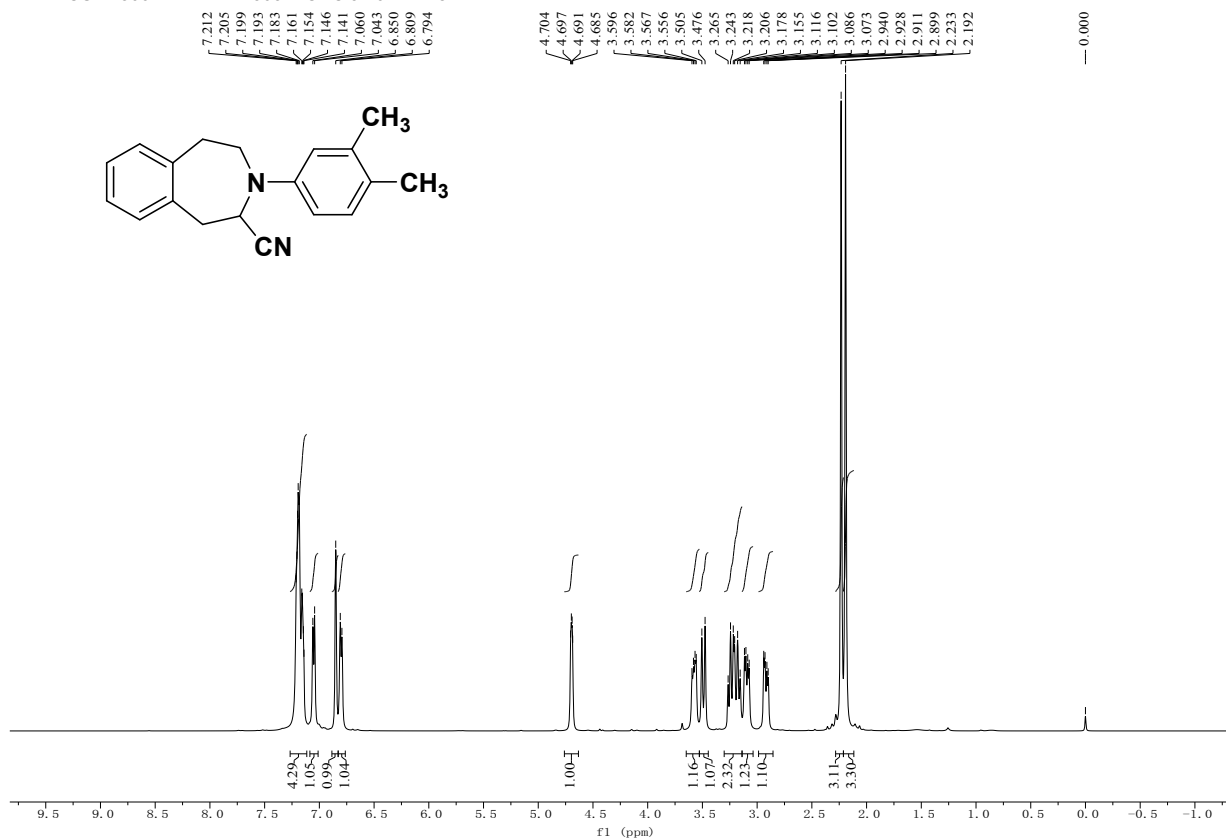


¹³C NMR spectra of compound 4f



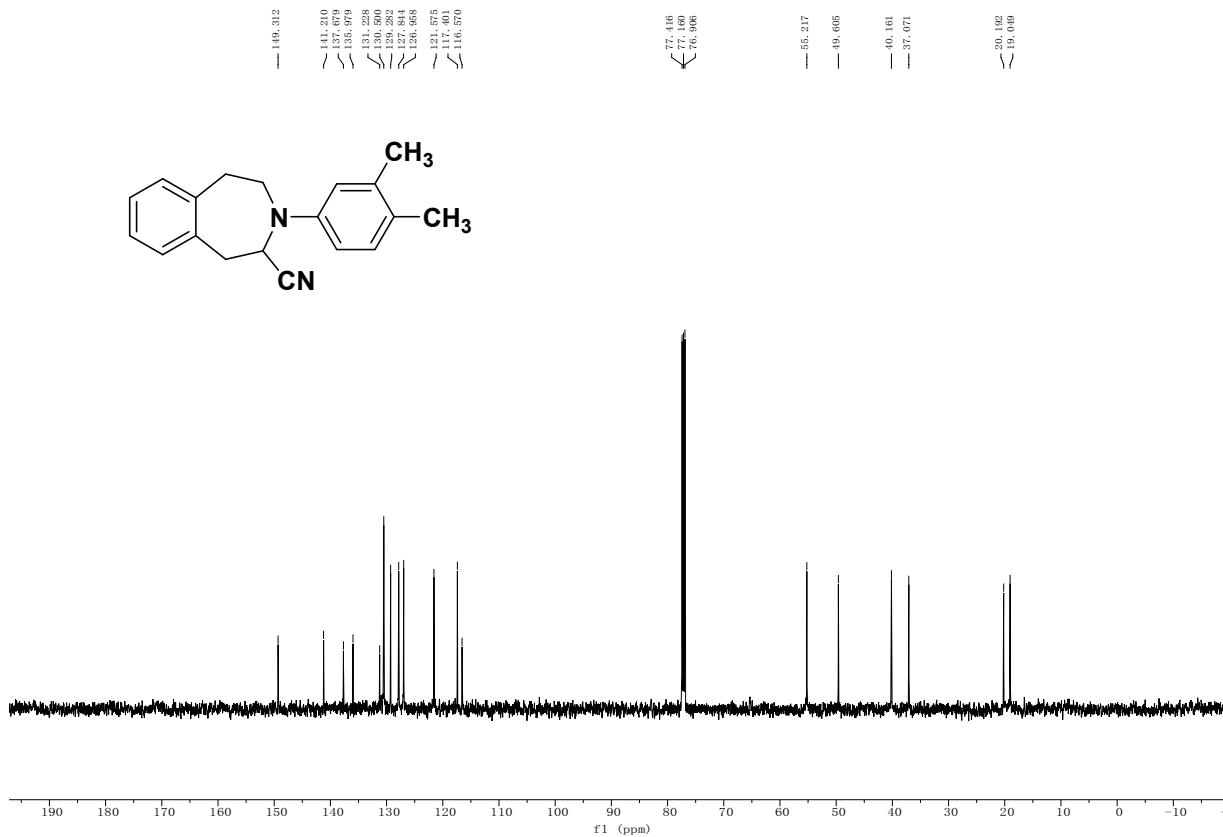
¹H NMR spectra of compound 4g

MERCURY500 HNMR PX2303-1 CDCl3 20171118



¹³C NMR spectra of compound 4g

MERCURY500 CNMR PX2303-1 CDCl3 20171118



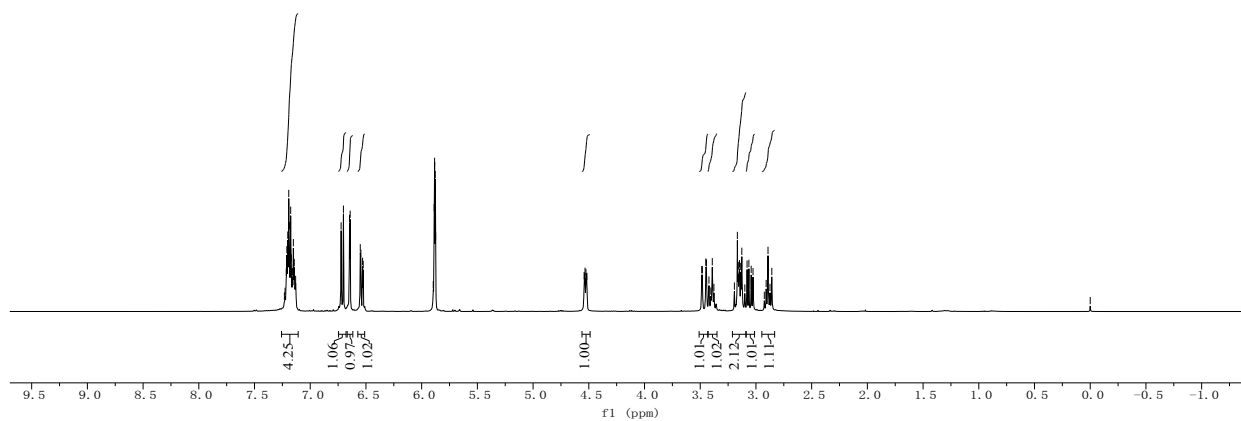
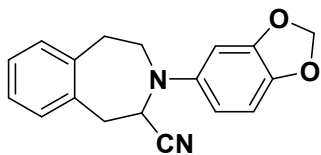
¹H NMR spectra of compound 4h

MERCURY400 HNMR PX2306-1 CDCl3 20171123

7.232
7.226
7.215
7.210
7.202
7.193
7.188
7.175
7.170
7.160
7.151
7.144
7.131
6.723
6.702
6.642
6.642
6.551
6.545
6.530
6.523
5.896
5.888
5.878
5.874

4.542
4.534
4.526
4.517
3.487
3.481
3.450
3.444
3.422
3.405
3.392
3.377
3.193
3.167
3.160
3.152
3.147
3.137
3.127
3.100
3.080
3.063
3.043
3.026
2.925
2.908
2.892
2.874
2.858

— -0.000

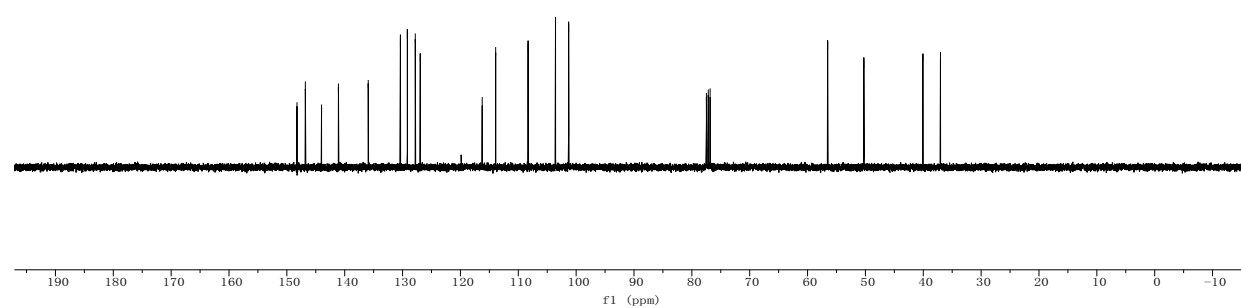
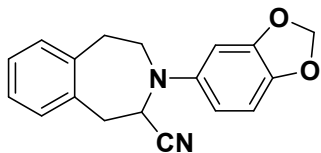


¹³C NMR spectra of compound 4h

MERCURY400 CNMR PX2306-1 CDCl3 20171123

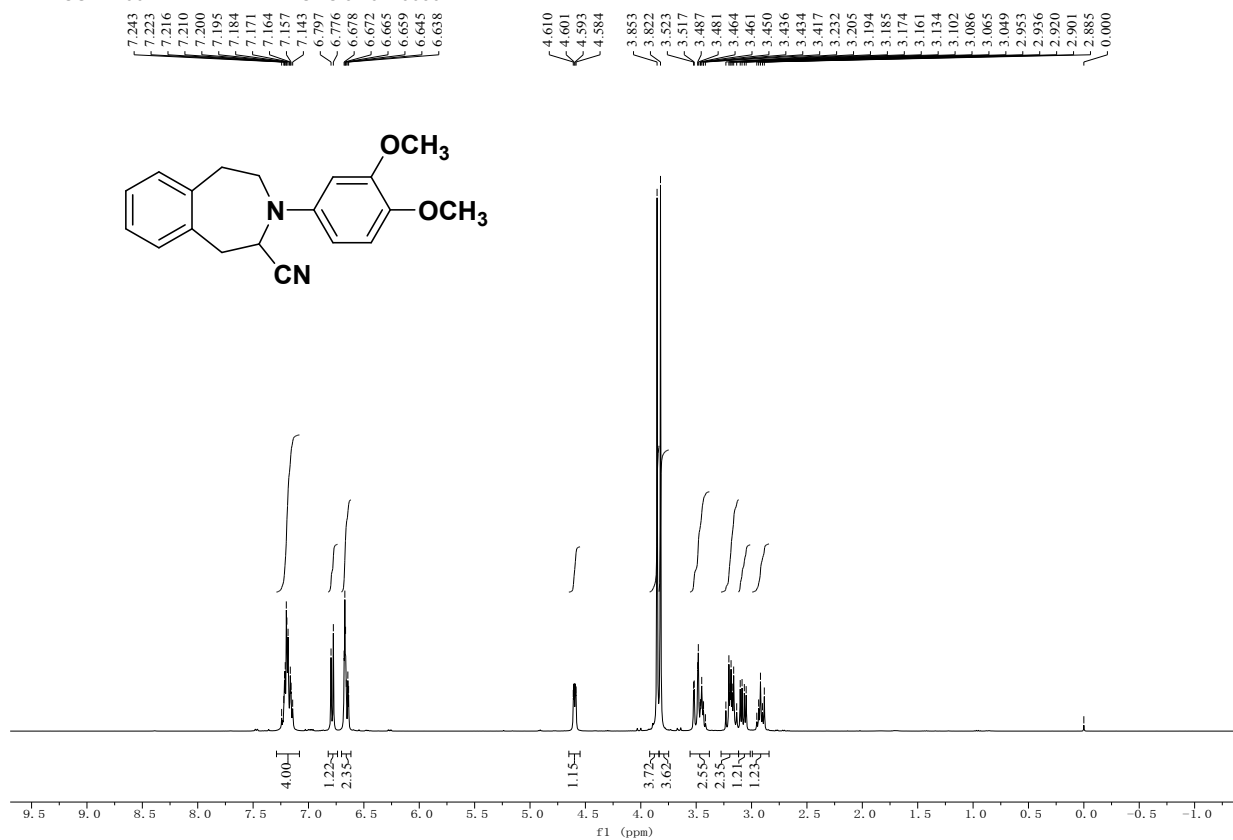
148.251
146.805
144.005
141.085
138.935
136.985
132.187
127.803
126.935
116.237
113.969
108.298
103.564
101.296

77.470
77.166
76.842
56.530
50.273
40.069
37.030



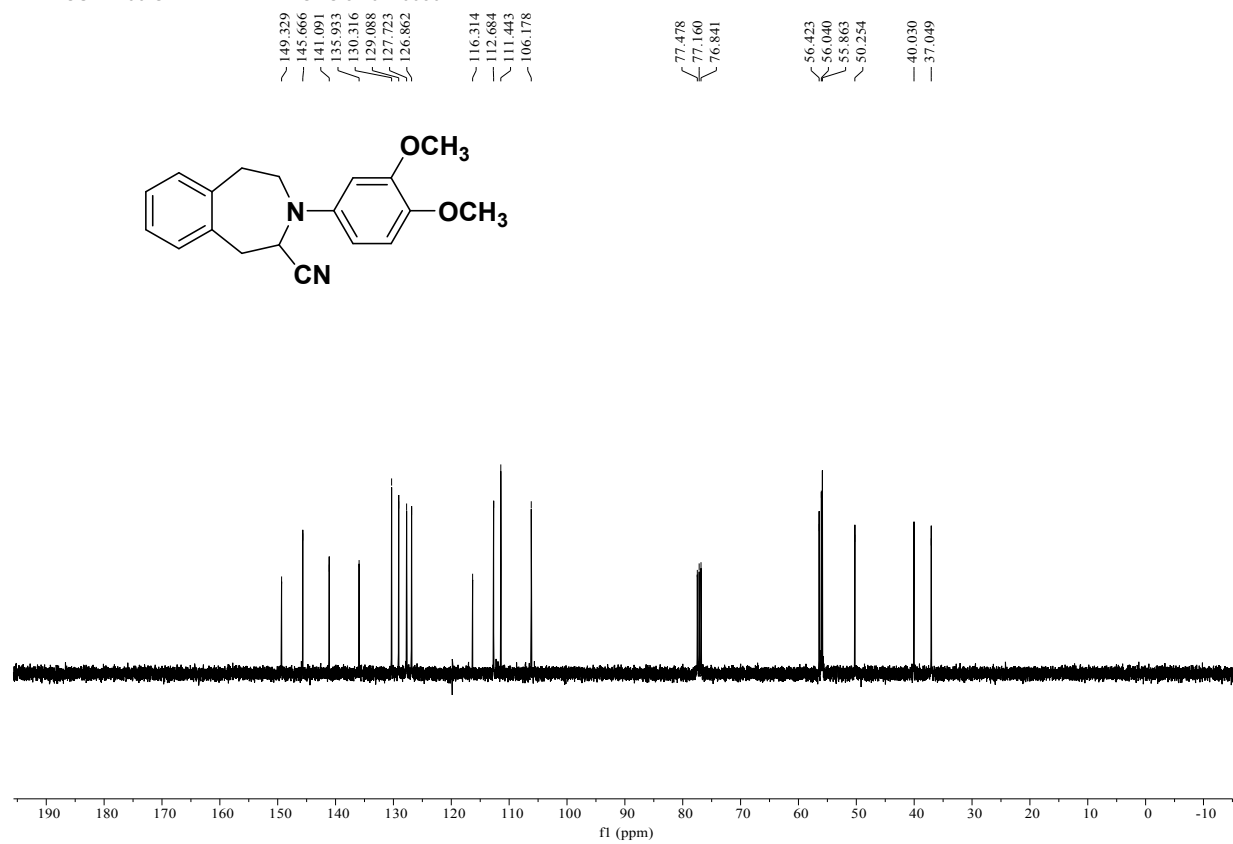
¹H NMR spectra of compound 4i

MERCURY400 HNMR PX2211-2 CDCl₃ 20170630



¹³C NMR spectra of compound 4i

MERCURY400 CNMR PX2211-2 CDCl₃ 20170630

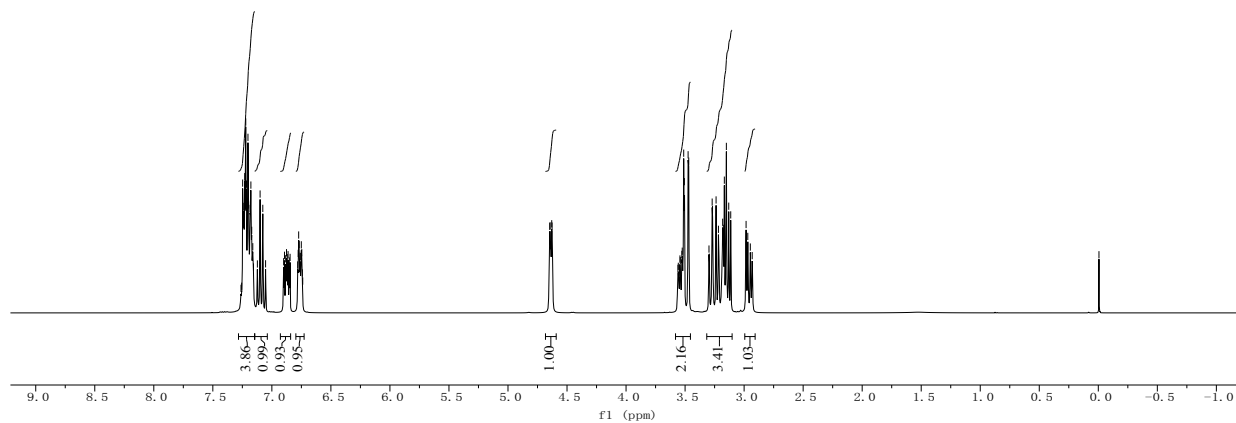
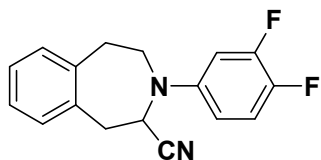


¹H NMR spectra of compound 4j

MERCURY400 HNMR PX2336-3 CDCl₃ 20180404

7.247, 7.244, 7.237, 7.233, 7.230, 7.225, 7.221, 7.215, 7.202, 7.197, 7.184, 7.178, 7.171, 7.162, 7.100, 7.077, 6.893, 6.883, 6.876, 6.869, 6.863, 6.846, 6.777, 6.773, 6.769, 6.760, 6.754, 6.751, 6.746, 6.746, 4.646, 4.643, 4.630, 4.627, 3.587, 3.557, 3.544, 3.540, 3.527, 3.527, 3.524, 3.512, 3.506, 3.474, 3.469, 3.298, 3.295, 3.271, 3.268, 3.237, 3.217, 3.182, 3.176, 3.167, 3.150, 3.130, 2.983, 2.969, 2.947, 2.932

-0.006



¹³C NMR spectra of compound 4j

MERCURY400 CNMR PX2336-3 CDCl₃ 20180404

151.915, 151.781, 149.443, 149.310, 147.971, 147.901, 147.731, 147.609, 145.300, 145.175, 140.710, 140.698, 135.528, 135.503, 130.554, 129.427, 128.151, 127.249, 117.875, 117.696, 116.114, 116.087, 115.822, 115.792, 115.769, 115.739, 109.767, 109.749, 109.577, 109.556

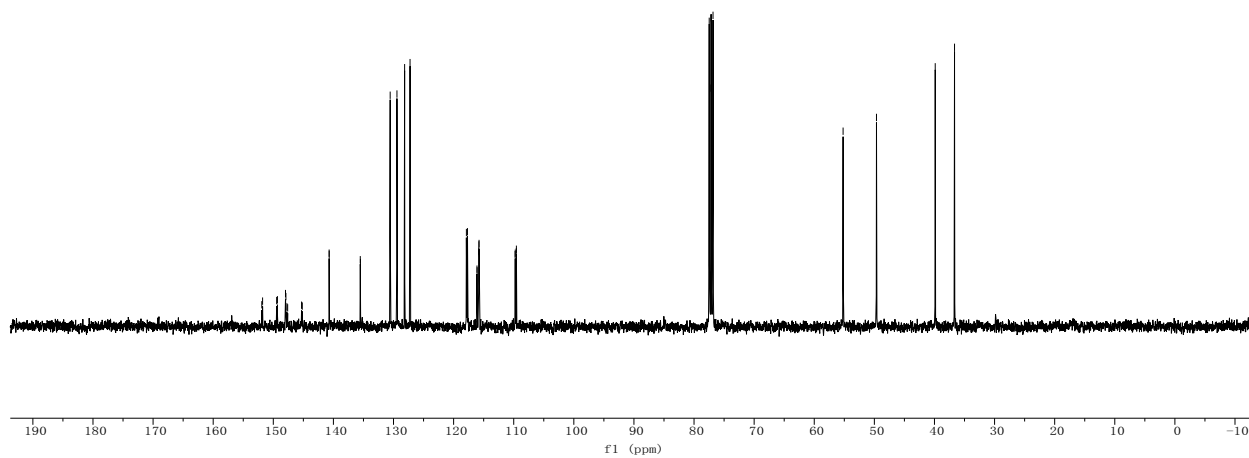
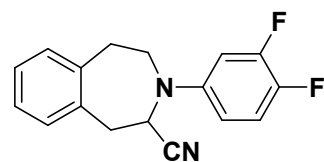
77.477, 77.189, 77.157, 76.842

55.202

49.646

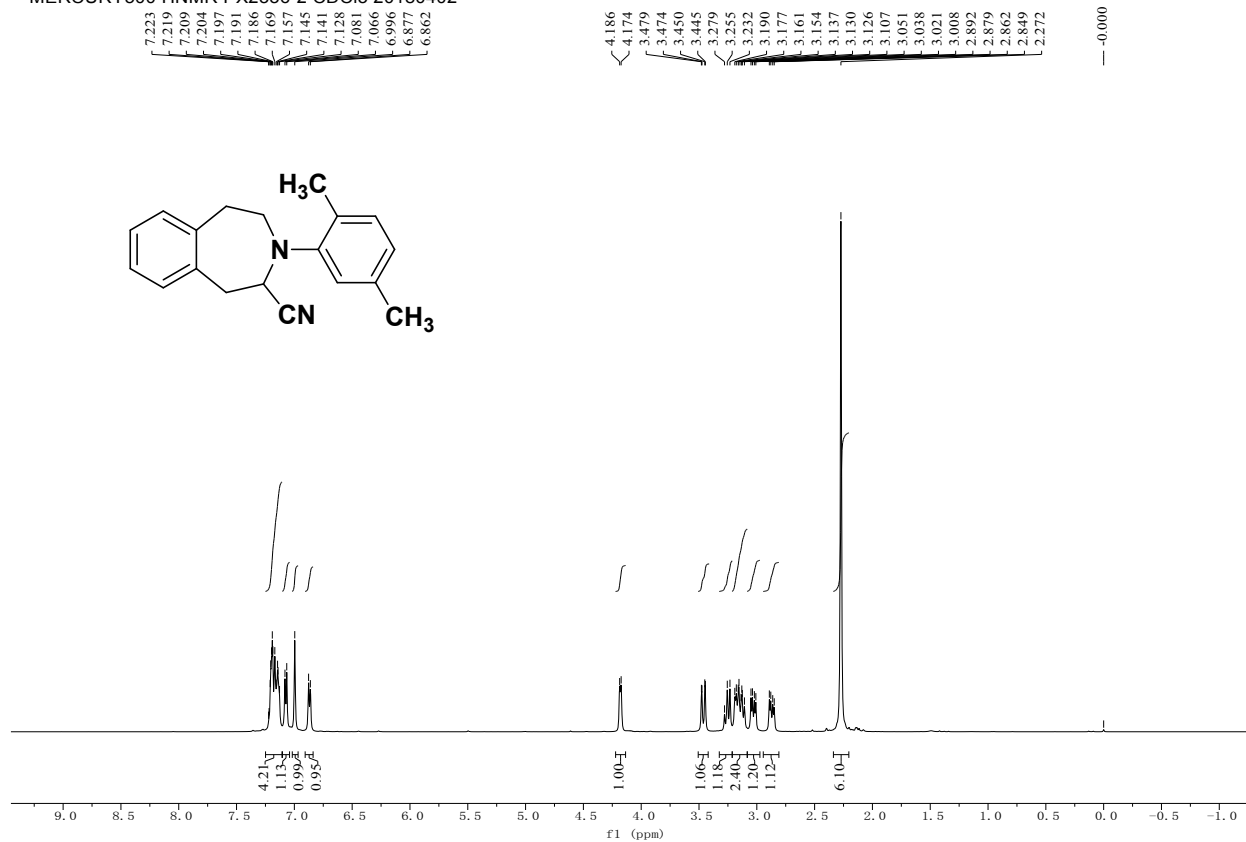
39.874

36.662



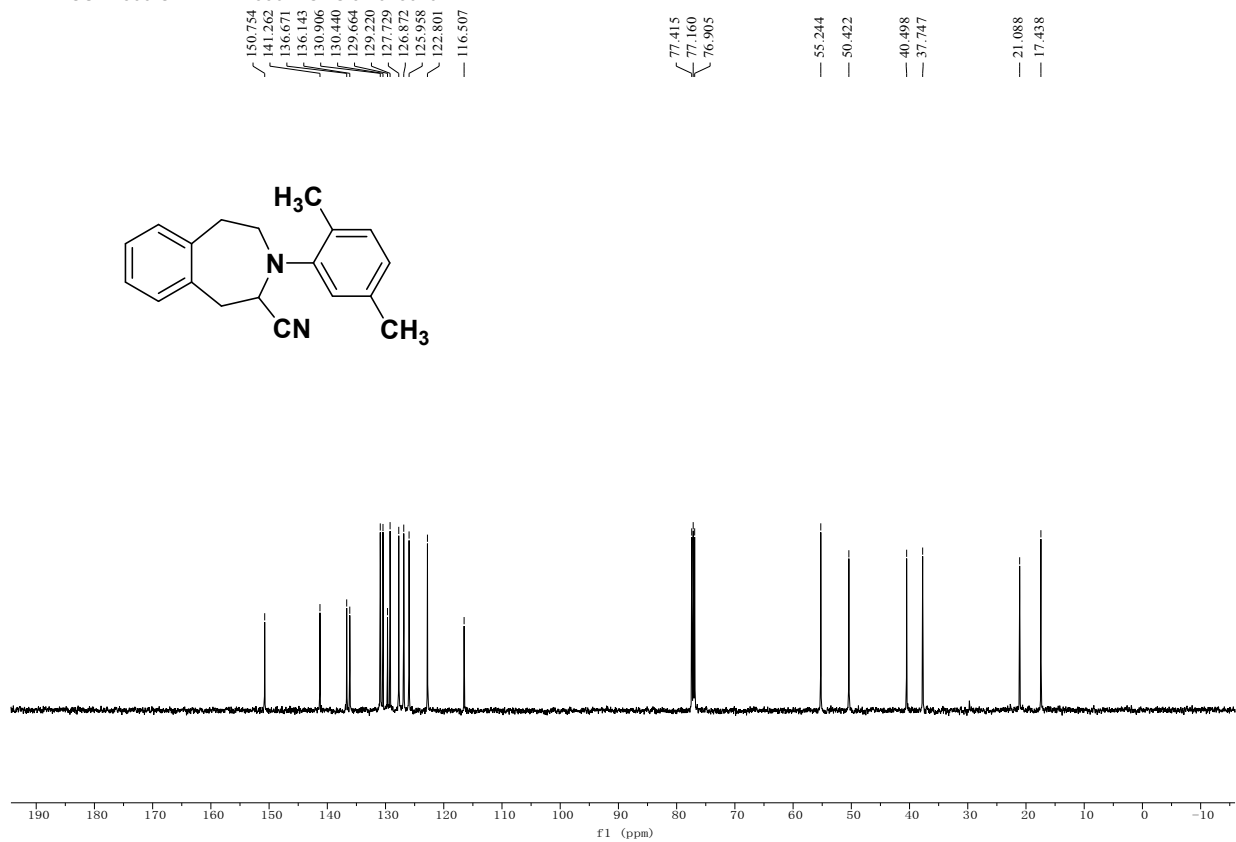
¹H NMR spectra of compound 4k

MERCURY500 HNMR PX2336-2 CDCl3 20180402



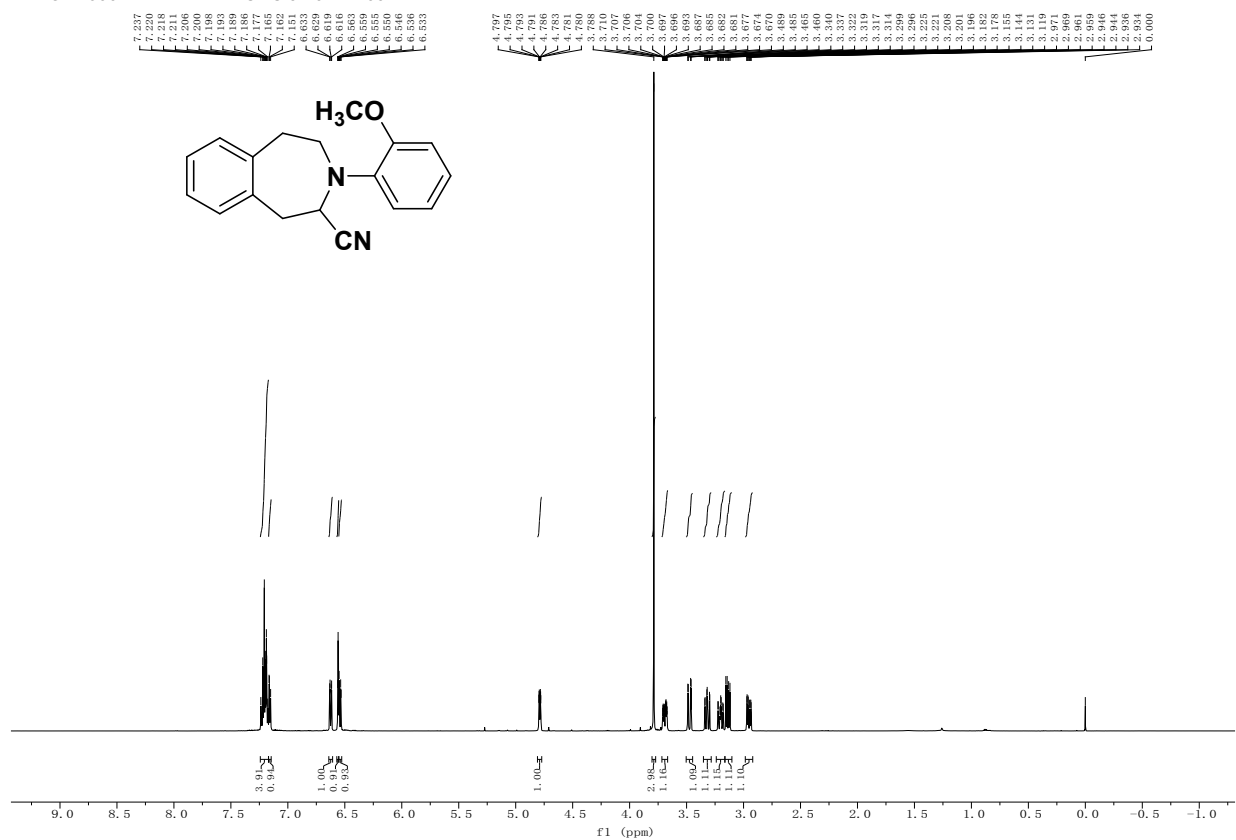
¹³C NMR spectra of compound 4k

MERCURY500 CNMR PX2336-2 CDCl3 20180402



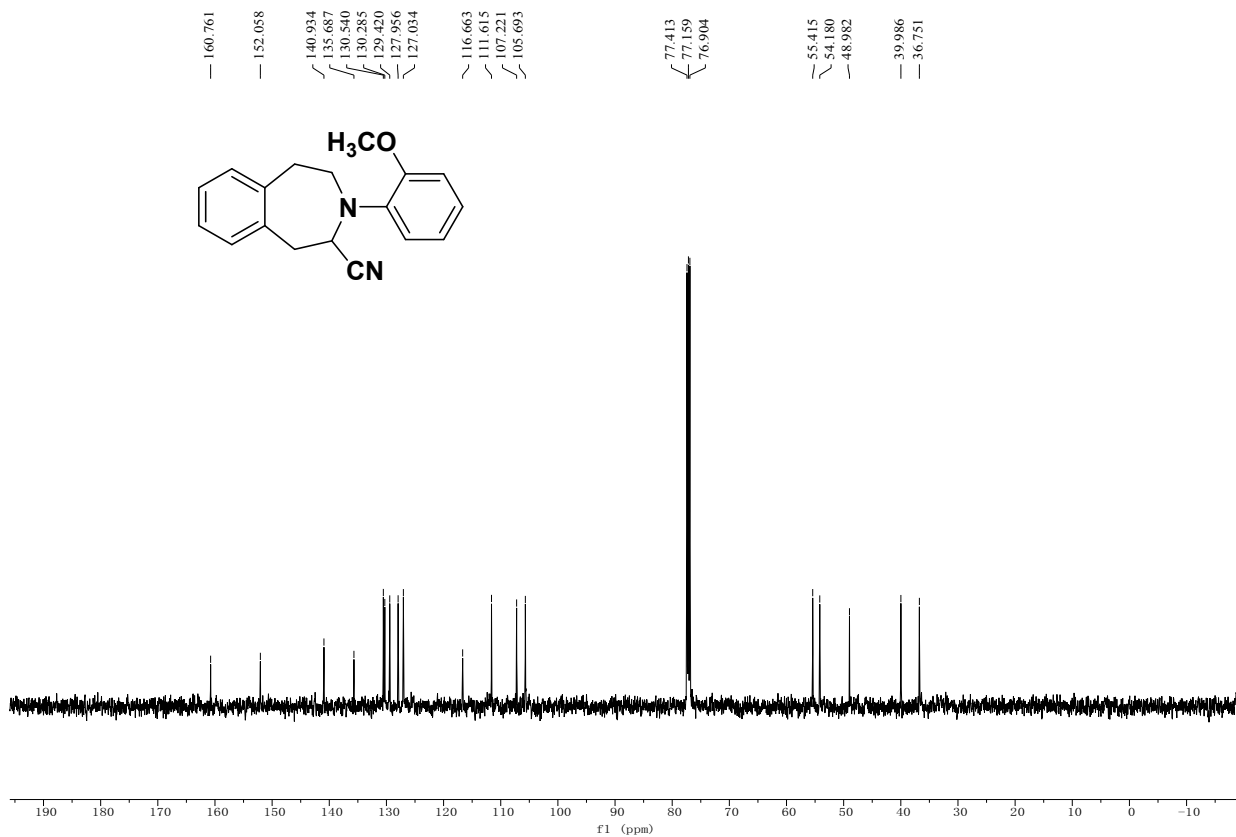
¹H NMR spectra of compound 4I

INOVA600HNMR PX2244 CDCl3 20171109



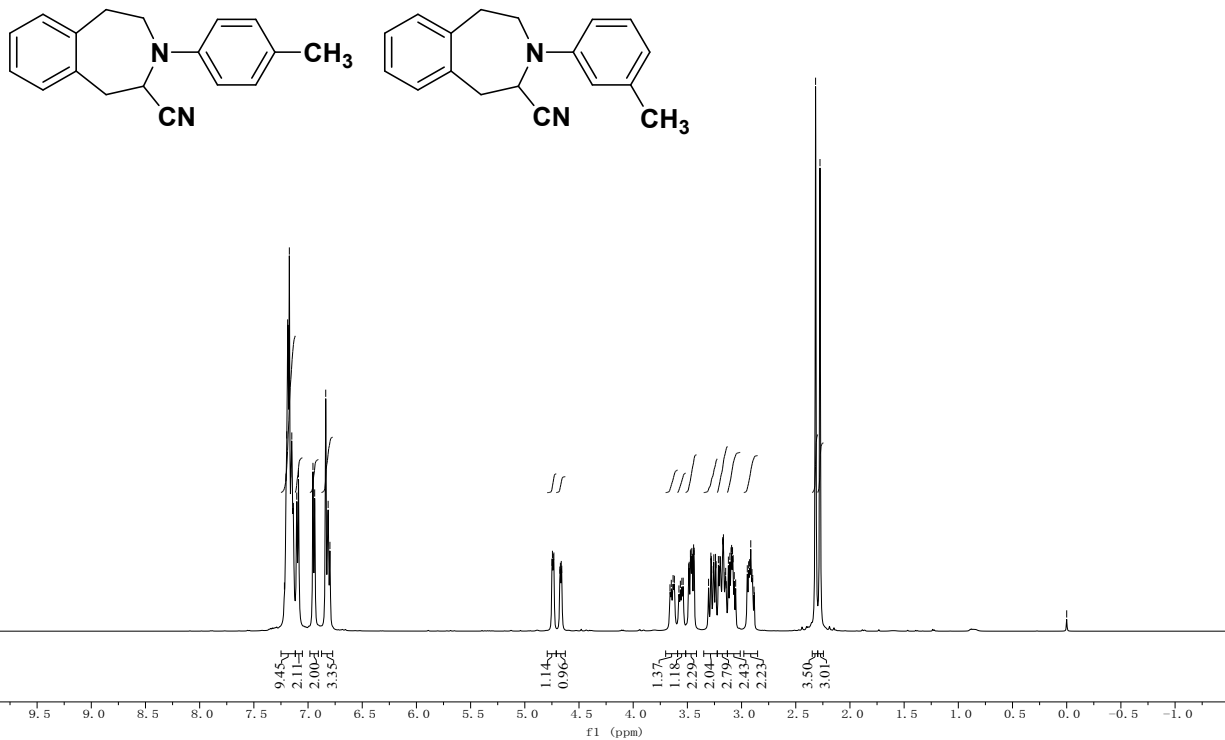
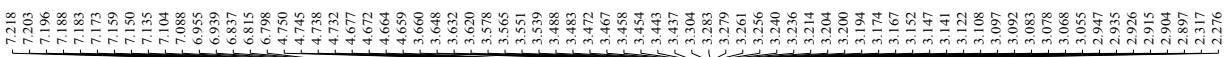
¹³C NMR spectra of compound 4I

MERCURY500 CNMR PX2244 CDCl3 20171102



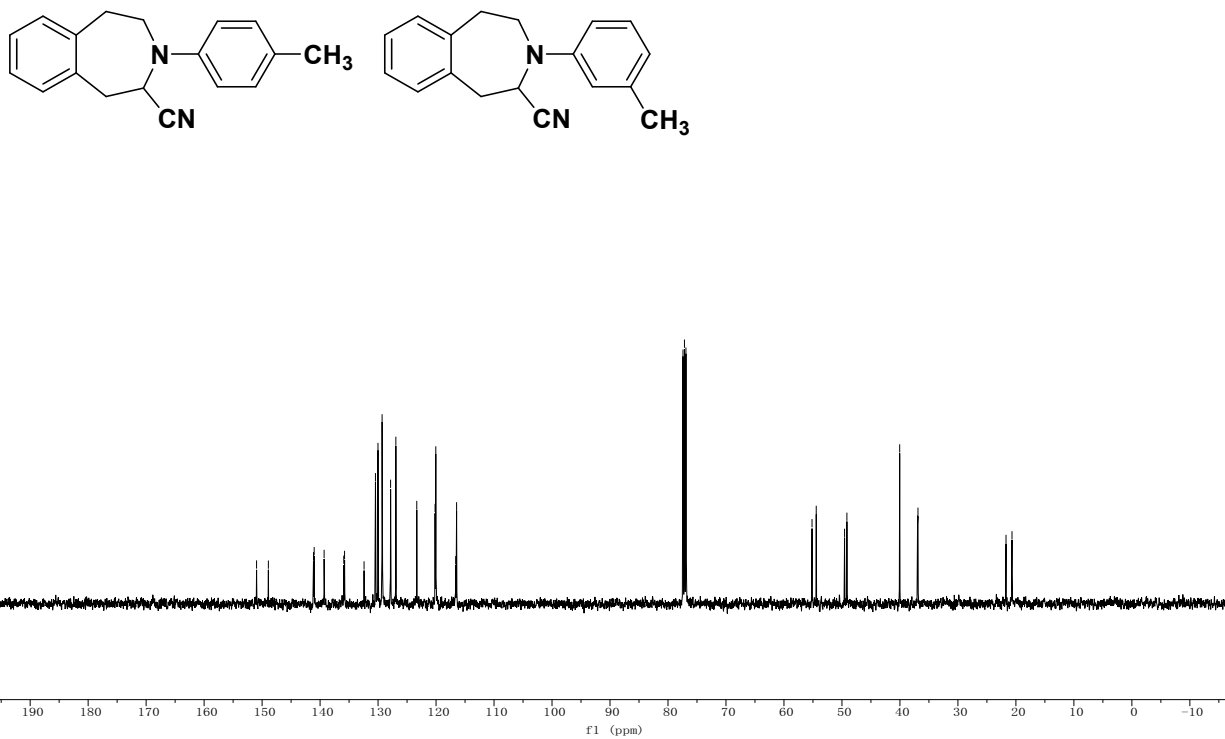
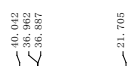
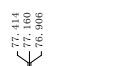
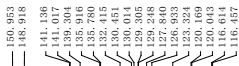
¹H NMR spectra of compounds **4ma** and **4mb**

MERCURY500 HNMR PX2239 CDCl3 20171102



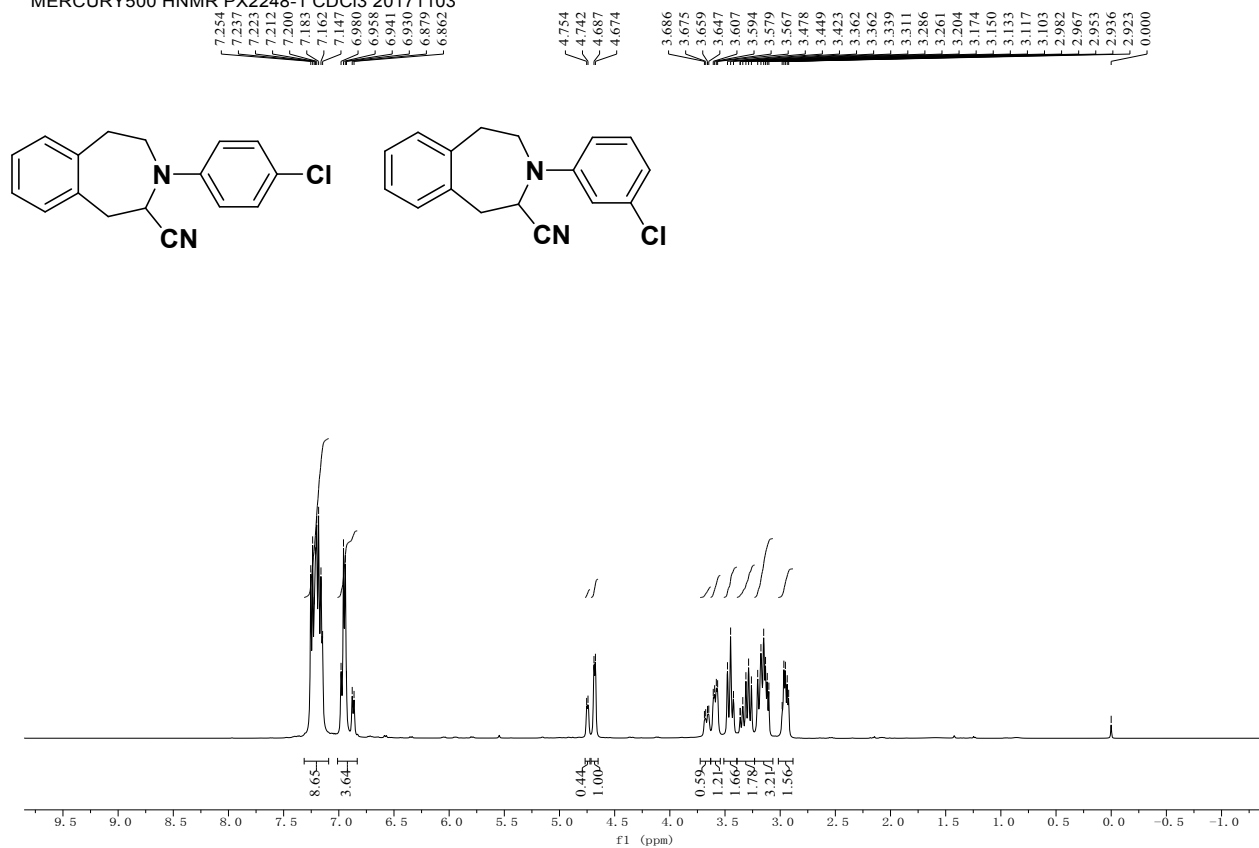
¹³C NMR spectra of compounds **4ma** and **4mb**

MERCURY500 CNMR PX2239 CDCl3 20171102



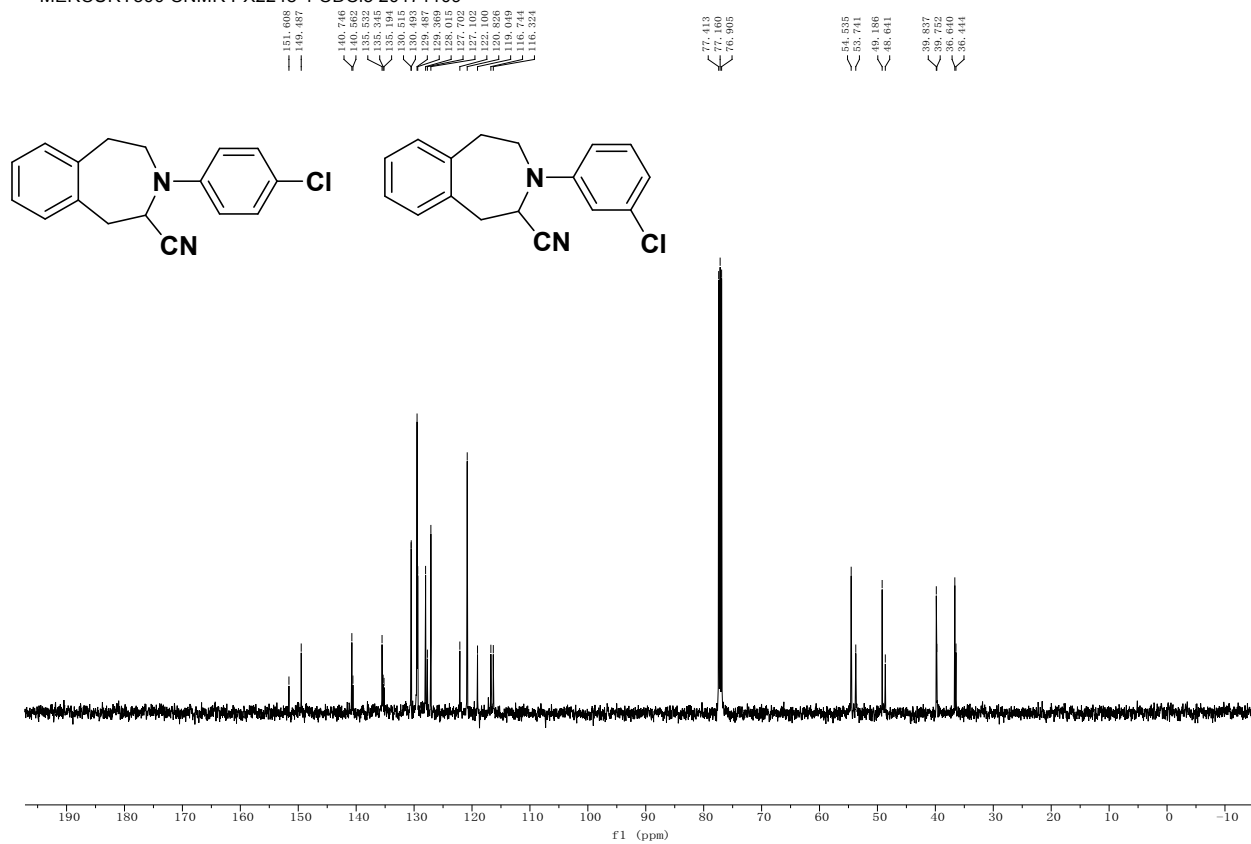
¹H NMR spectra of compounds 4na and 4nb

MERCURY500 HNMR PX2248-1 CDCl3 20171103



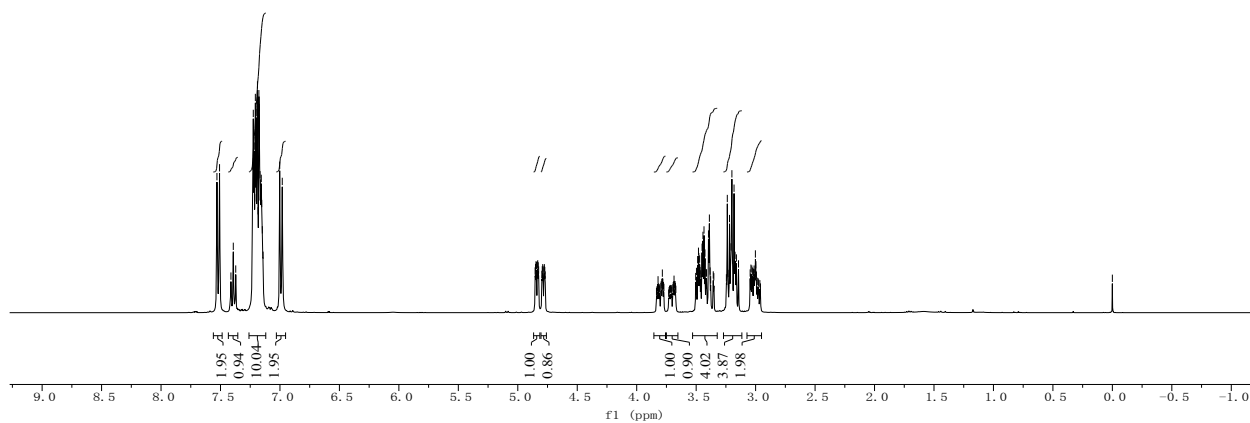
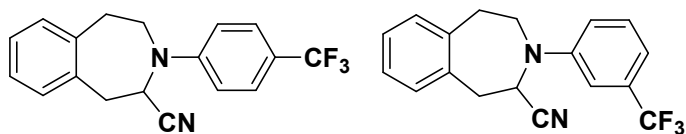
¹³C NMR spectra of compounds 4na and 4nb

MERCURY500 CNMR PX2248-1 CDCl3 20171109



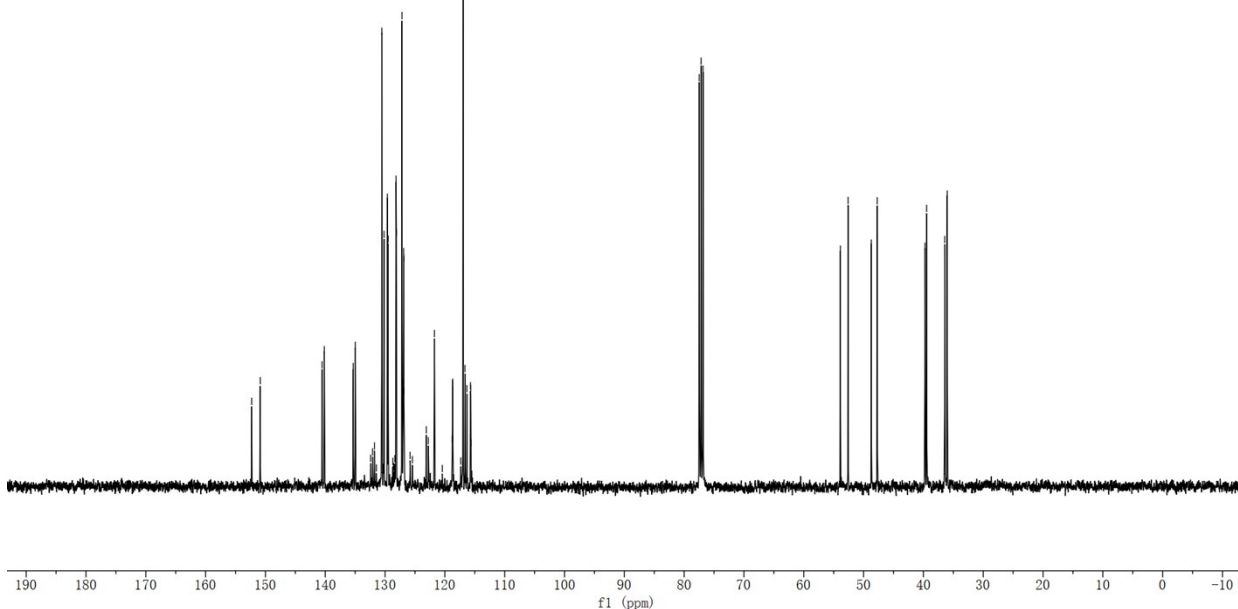
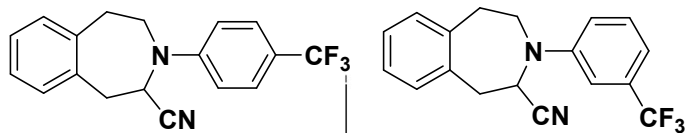
¹H NMR spectra of compounds 40a and 40b

MERCURY400 HNMR PX2338 CDCI3 20180404
7.530, 7.508, 7.392, 7.372, 7.230, 7.224, 7.216, 7.212, 7.207, 7.200, 7.193, 7.189, 7.184, 7.177, 7.173, 7.168, 7.163, 7.157, 7.153, 7.148, 7.142, 7.002, 6.981, 6.981, 4.854, 4.851, 4.847, 4.843, 4.836, 4.832, 4.828, 4.825, 4.794, 4.790, 4.787, 4.780, 4.777, 4.773, 3.497, 3.488, 3.481, 3.477, 3.471, 3.467, 3.450, 3.443, 3.434, 3.426, 3.418, 3.413, 3.397, 3.389, 3.383, 3.383, 3.238, 3.220, 3.212, 3.207, 3.199, 3.193, 3.181, 3.173, 3.167, 3.161, 3.144, 3.046, 3.039, 3.032, 3.025, 3.017, 3.013, 3.007, 2.998



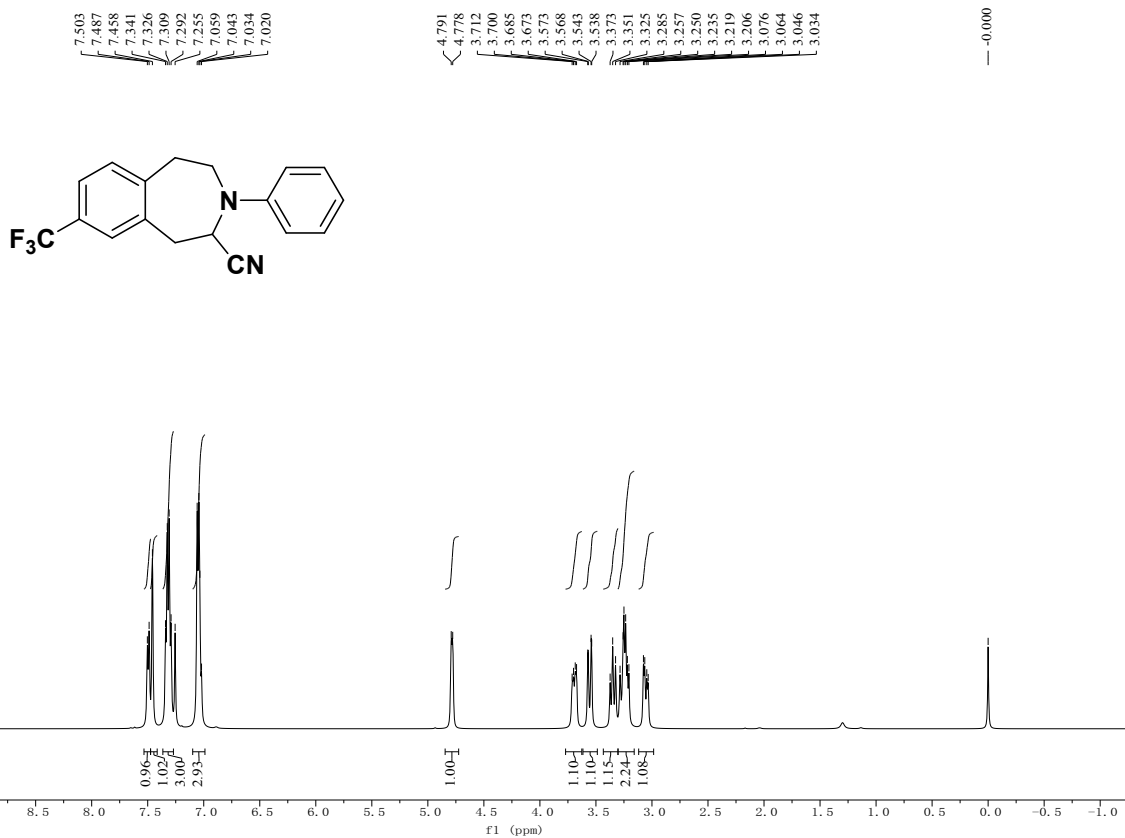
¹³C NMR spectra of compounds 40a and 40b

MERCURY400 CNMR PX2338 CDCI3 20180404
152.292, 150.862, 140.527, 140.153, 135.318, 134.974, 132.411, 132.088, 131.766, 131.449, 130.545, 130.160, 129.607, 129.477, 128.699, 128.602, 128.508, 128.378, 128.158, 128.108, 127.166, 126.936, 126.899, 126.862, 126.825, 125.814, 125.428, 123.108, 122.778, 121.742, 120.425, 118.765, 118.731, 118.692, 118.658, 117.340, 116.962, 116.648, 116.325, 115.745, 115.710, 115.670, 115.633, 77.479, 77.161, 76.842, 53.878, 52.591, 48.713, 47.725, 39.742, 39.460, 36.429, 36.021



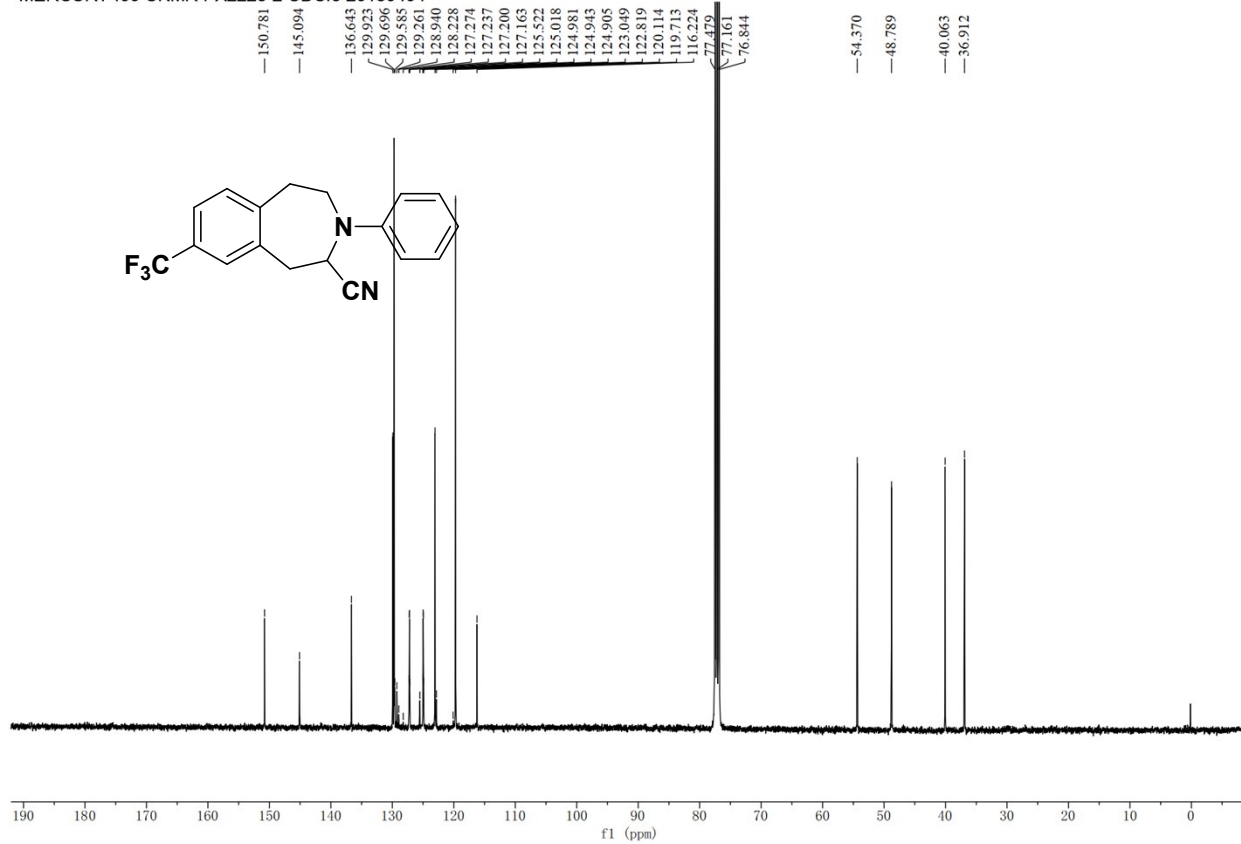
¹H NMR spectra of compound 4p

MERCURY500 HNMR PX22228-2 CDCl₃ 20180402



¹³C NMR spectra of compound 4p

MERCURY400 CNMR PX22228-2 CDCl₃ 20180404



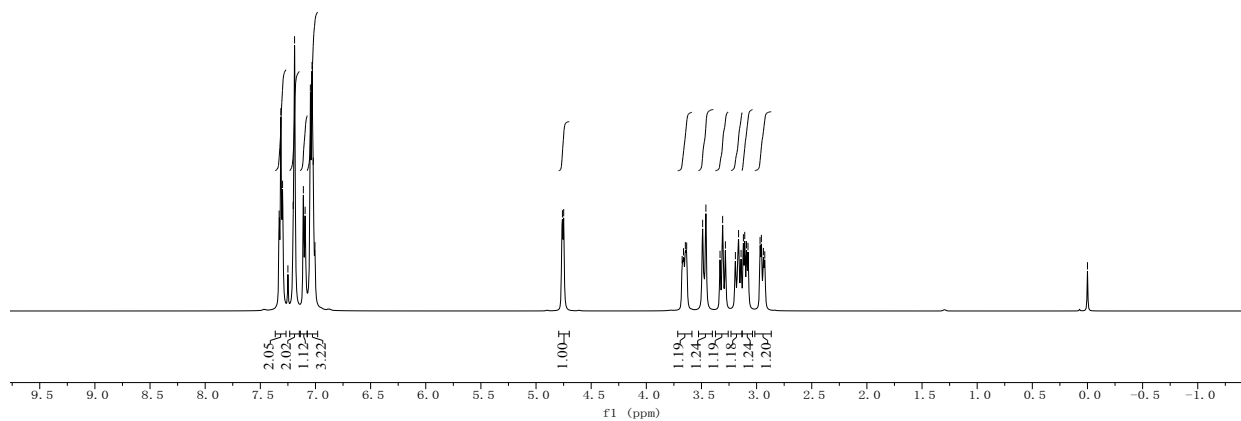
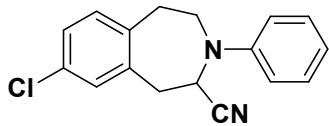
¹H NMR spectra of compound 4q

MERCURY500 HNMR PX22228-1 CDCl3 20171013

7.329
7.314
7.298
7.250
7.202
7.190
7.110
7.094
7.046
7.031
7.020
7.005

4.761
4.749
3.675
3.663
3.646
3.634
3.489
3.460
3.332
3.308
3.283
3.192
3.164
3.141
3.120
3.108
3.091
3.078
2.969
2.957
2.938
2.926

0.000

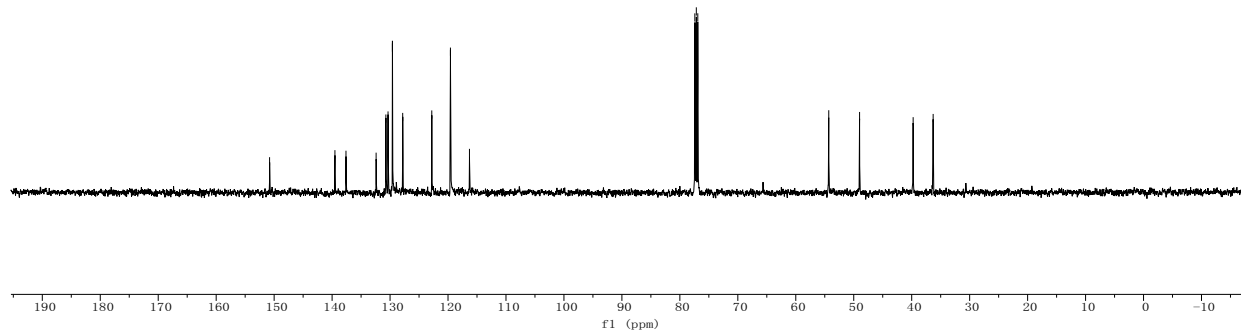
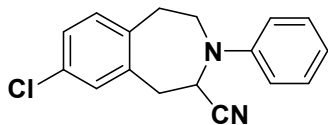


¹³C NMR spectra of compound 4q

MERCURY500 CNMR PX22228-1 CDCl3 20171102

150.787
138.512
137.606
132.405
130.753
129.728
129.595
127.820
122.802
116.582
116.300

77.415
77.000
76.606
51.310
48.992
39.750
36.290



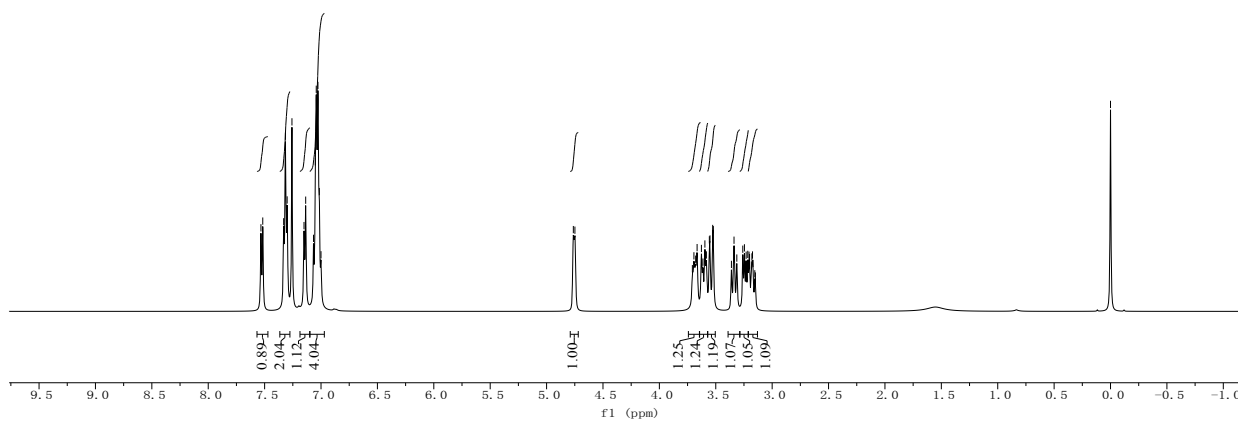
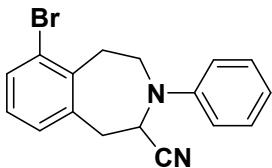
¹H NMR spectra of compound 4r

MERCURY500 HNMR PX2207-2-2 CDCl₃ 20180402

7.533
7.517
7.331
7.316
7.300
7.258
7.151
7.136
7.066
7.051
7.042
7.027
7.015
7.000

4.763
4.749
3.707
3.694
3.678
3.666
3.627
3.614
3.596
3.583
3.557
3.551
3.527
3.522
3.361
3.338
3.313
3.260
3.246
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3.205
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3.185
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0.000

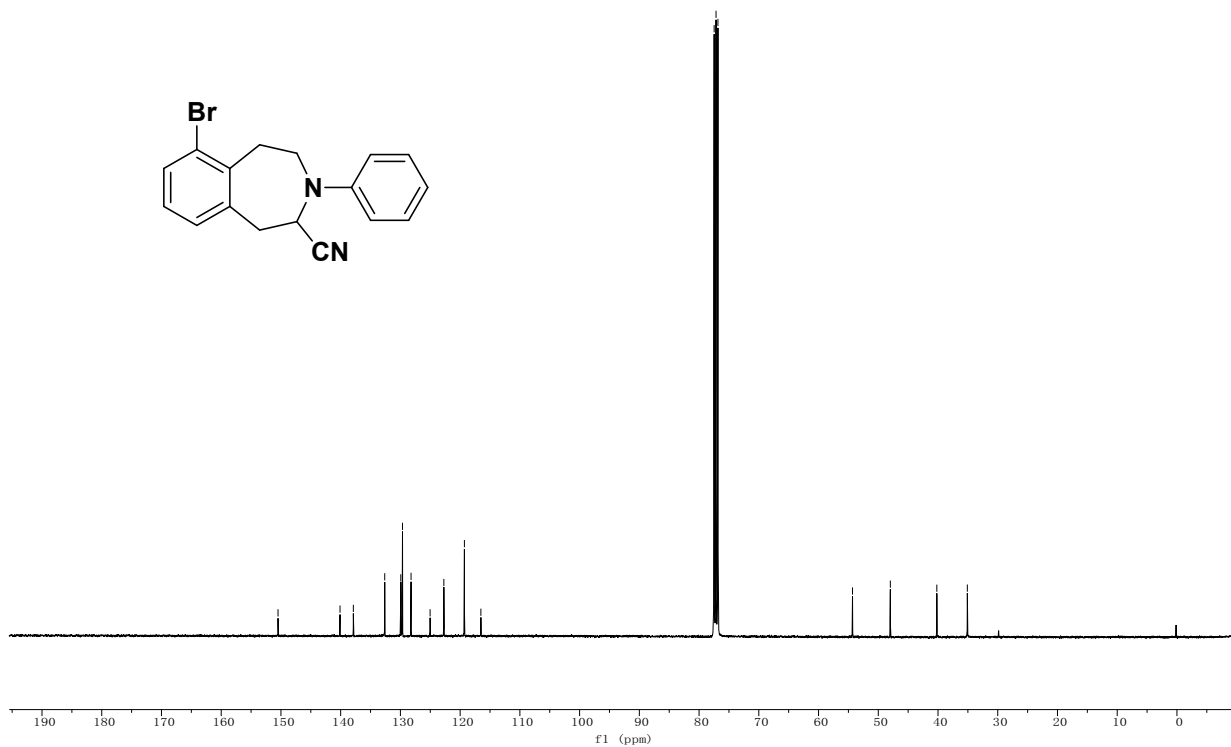
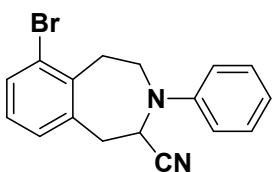


¹³C NMR spectra of compound 4r

MERCURY400 CNMR PX2207-2-2 CDCl₃ 20180403

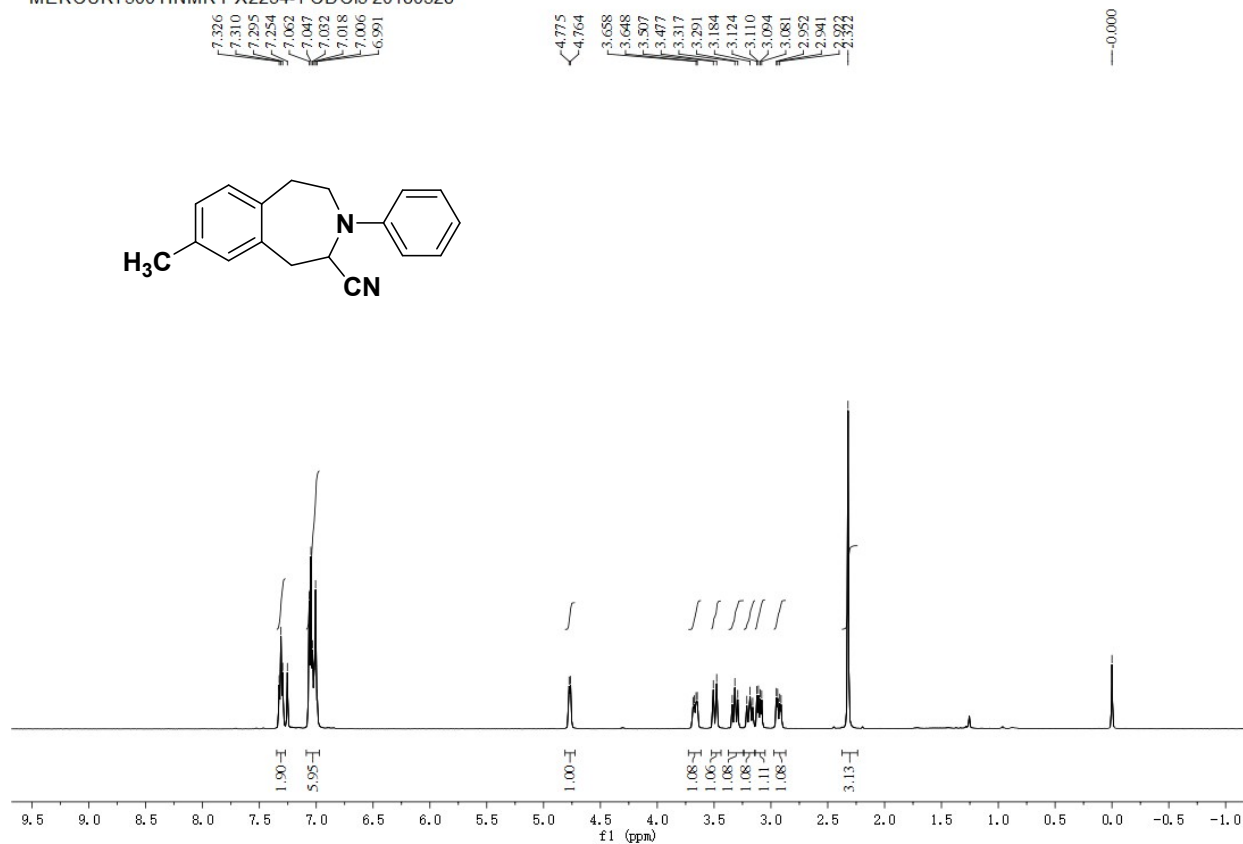
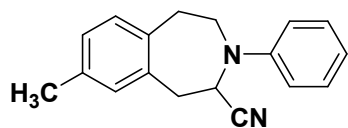
150.488
140.109
137.878
132.624
129.936
129.649
128.217
125.028
122.728
119.285
116.526

77.477
77.160
76.845
54.312
47.981
40.198
35.091



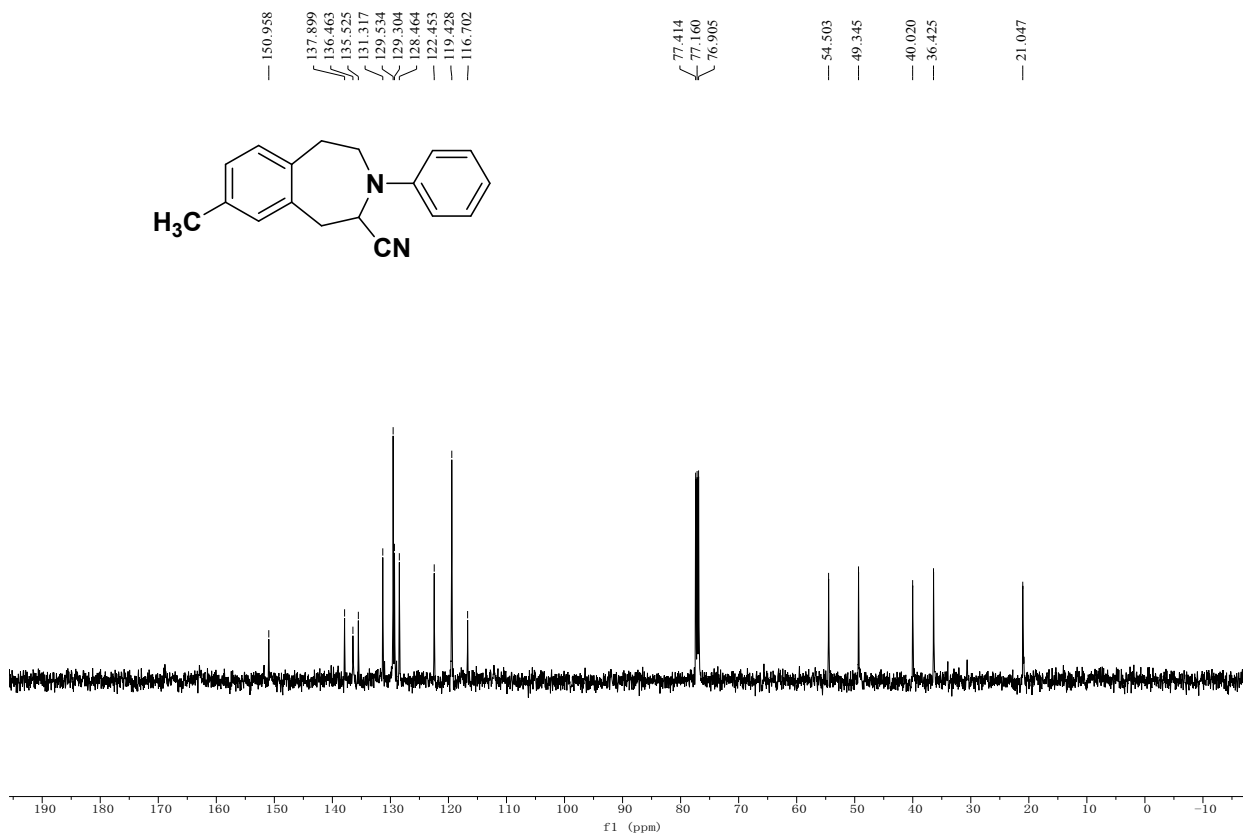
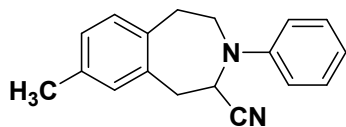
¹H NMR spectra of compound 4s

MERCURY500 HNMR PX2234-1 CDCl₃ 20180328

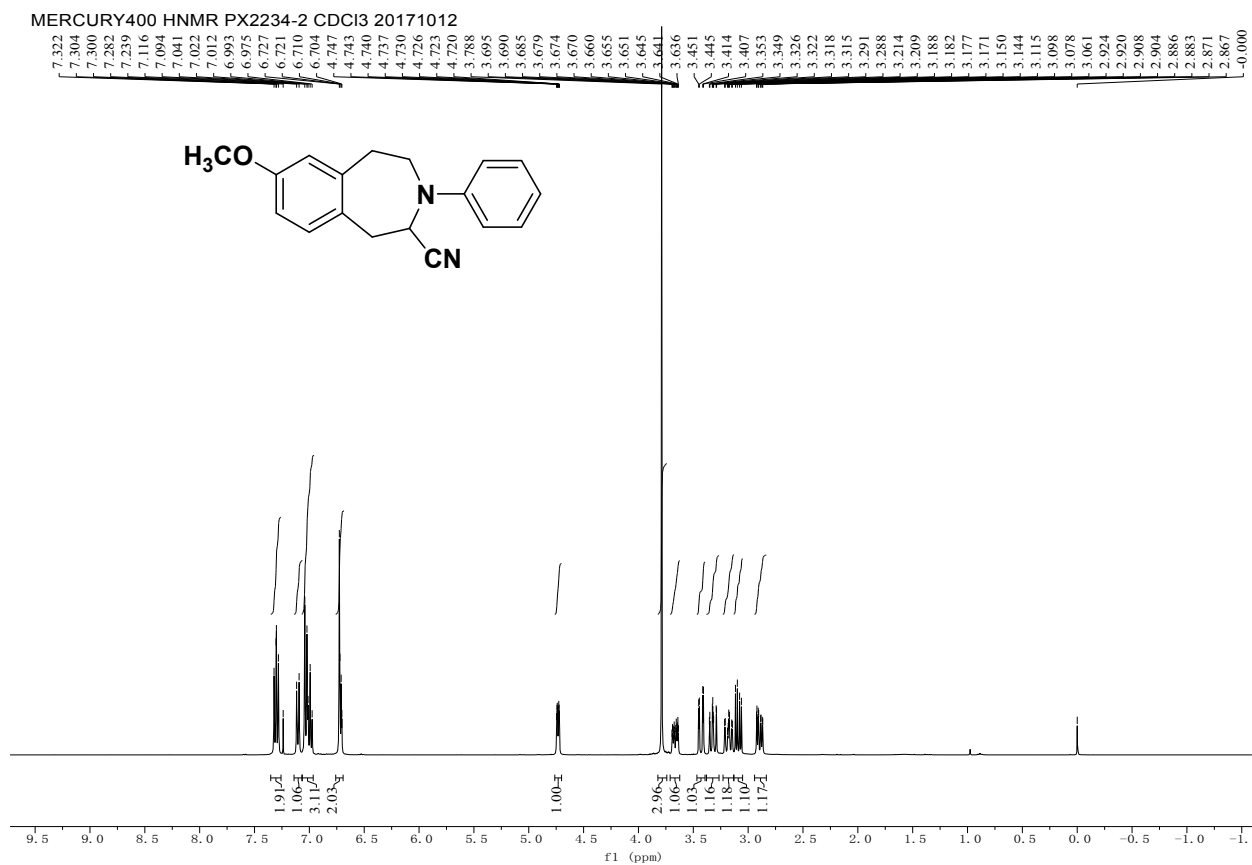


¹³C NMR spectra of compound 4s

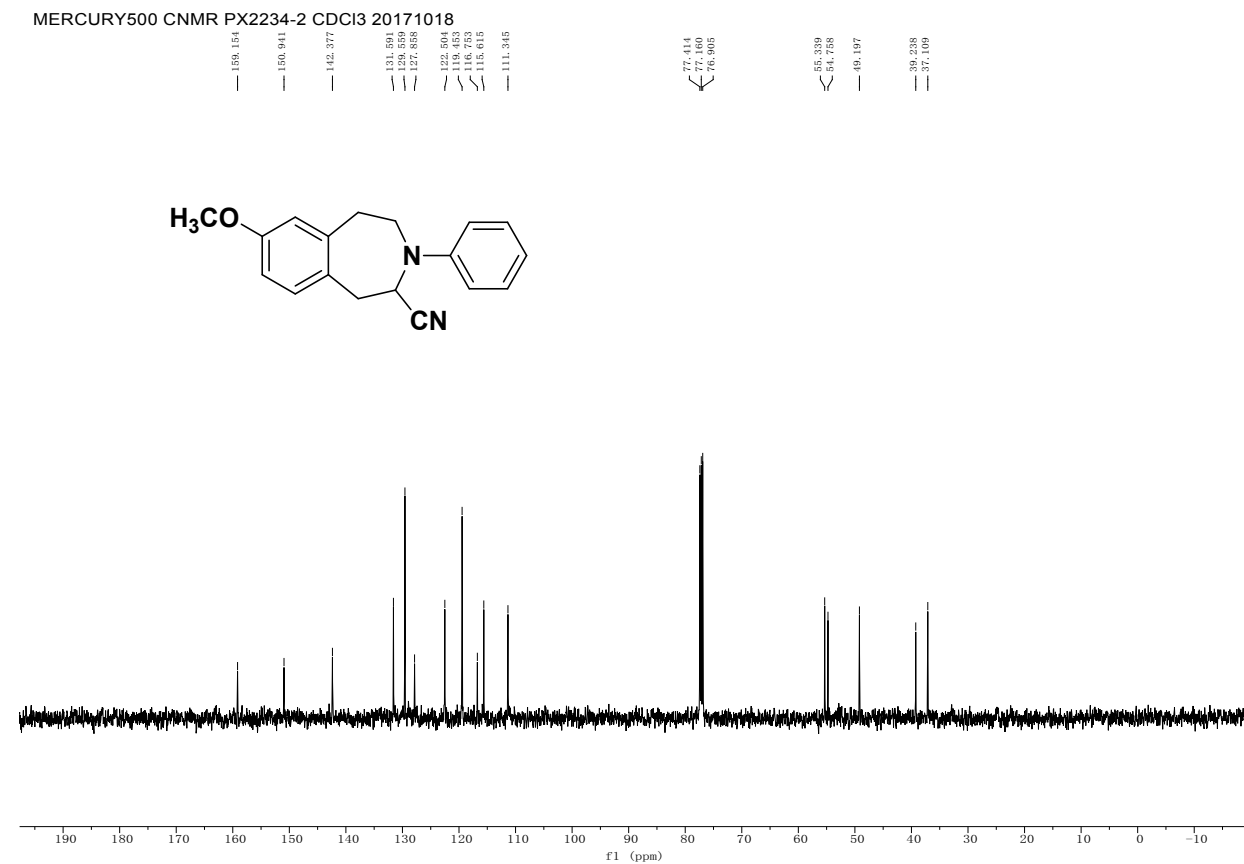
MERCURY500 CNMR PX2234-1 CDCl₃ 20170523



¹H NMR spectra of compound 4t

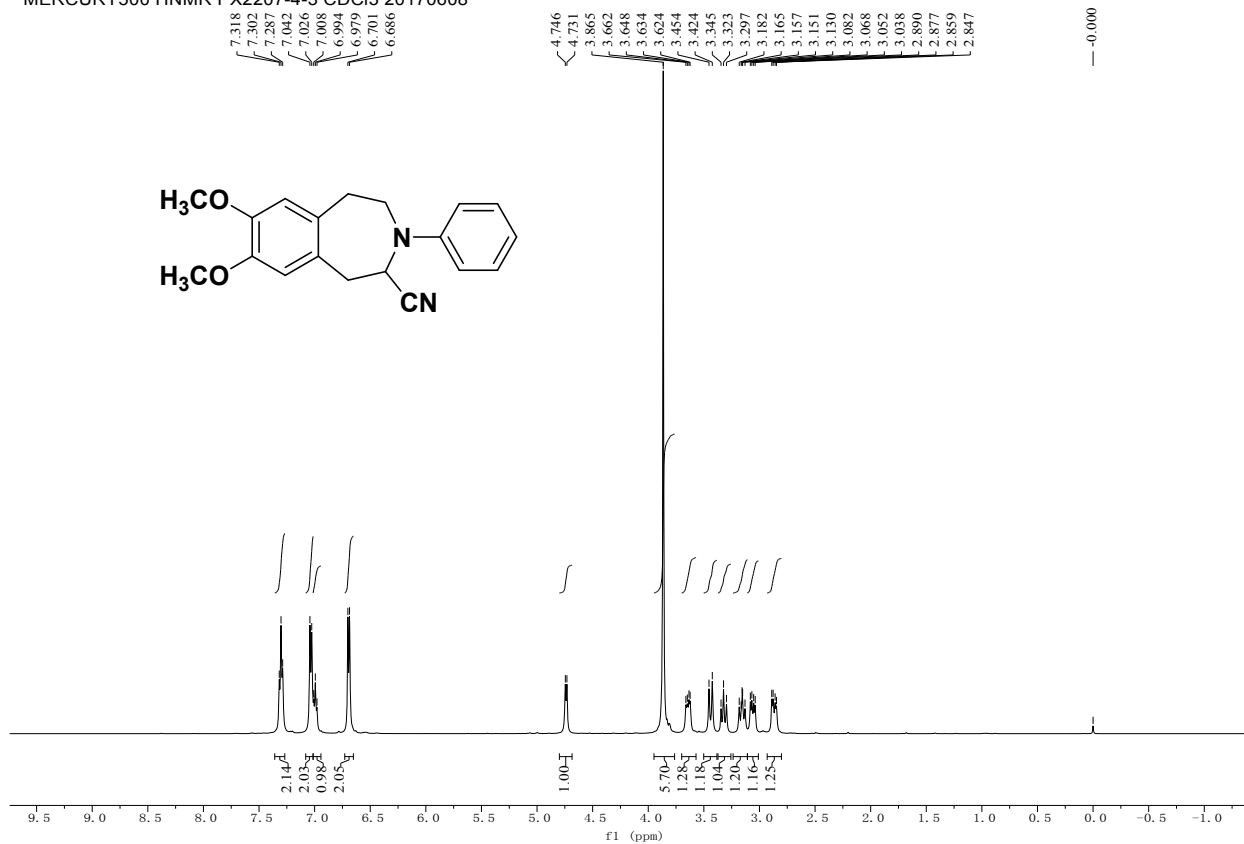


¹³C NMR spectra of compound 4t



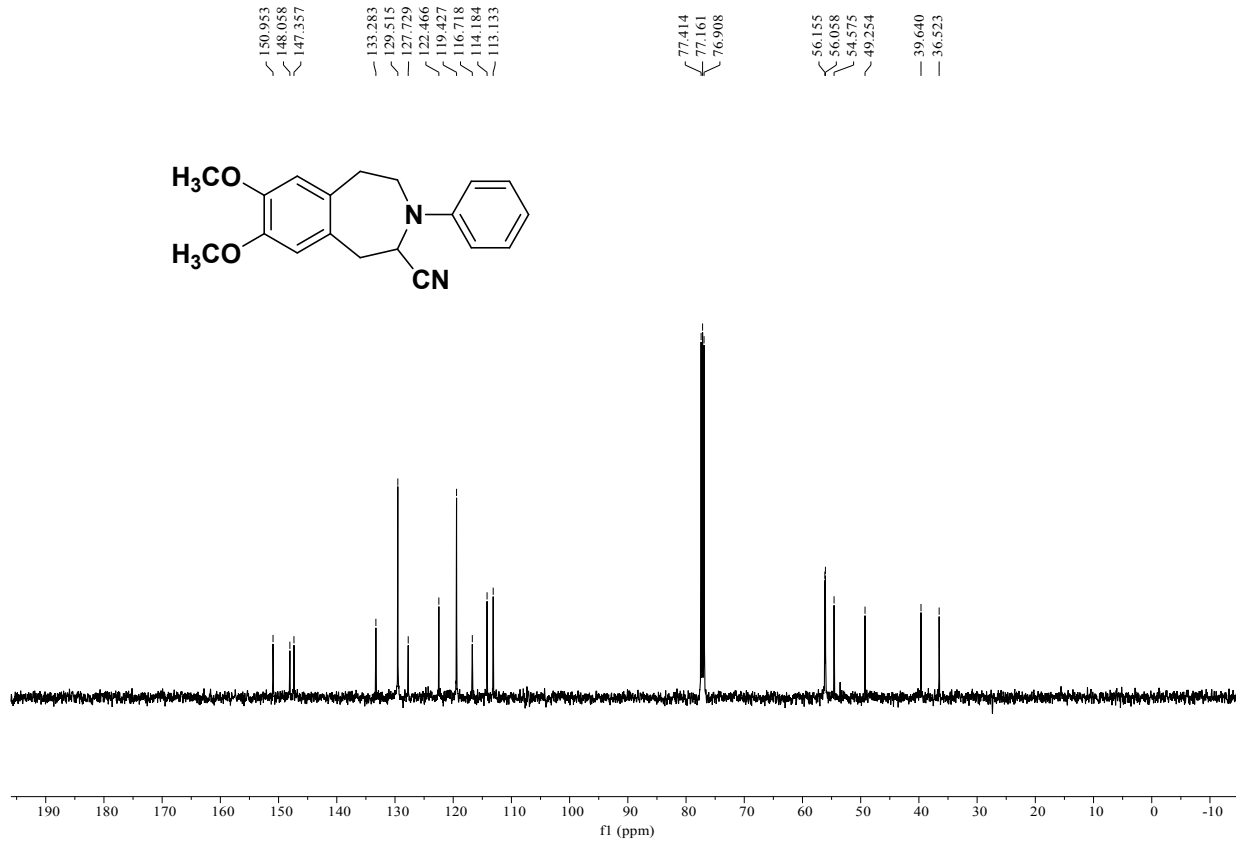
¹H NMR spectra of compound 4u

MERCURY500 HNMR PX2207-4-3 CDCl₃ 20170608



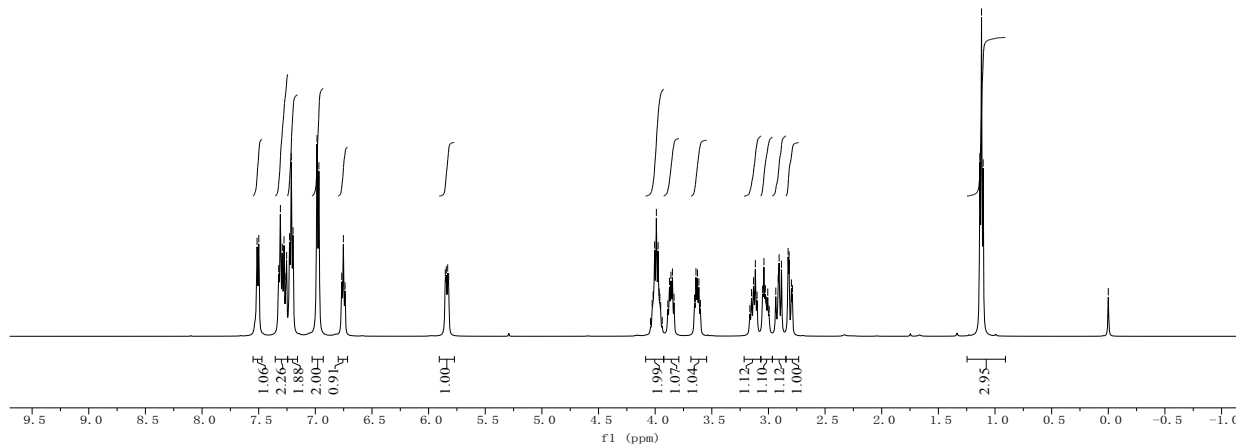
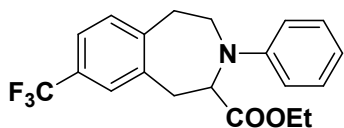
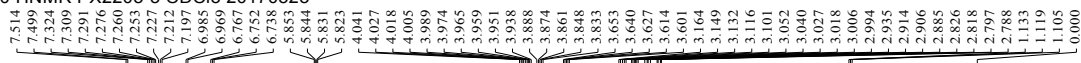
¹³C NMR spectra of compound 4u

MERCURY500 CNMR PX2207-4-3 CDCl₃ 20170608



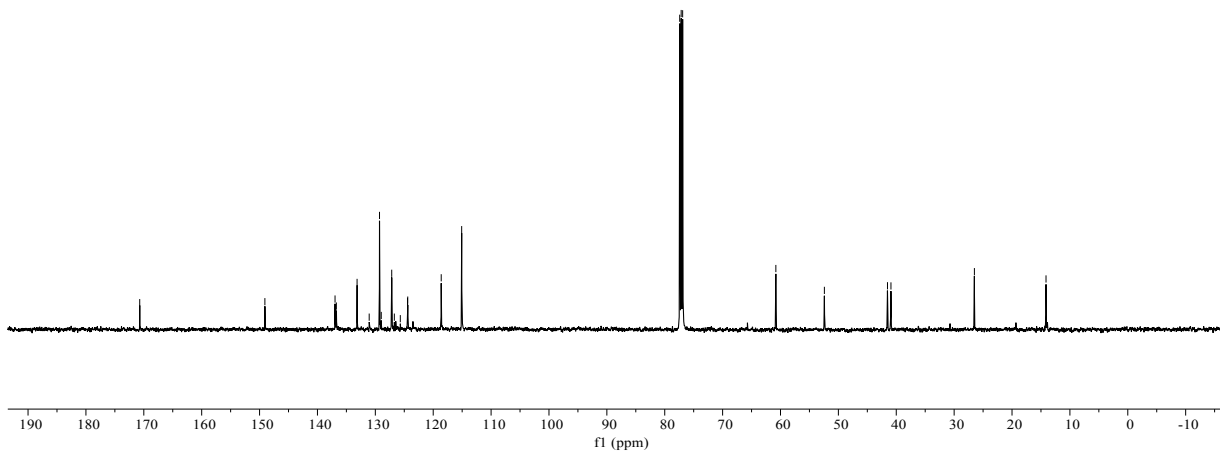
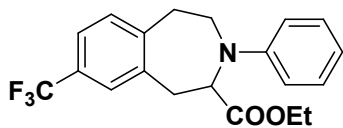
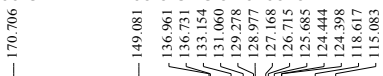
¹H NMR spectra of compound 4v

MERCURY500 HNMR PX2203-3 CDCl3 20170523



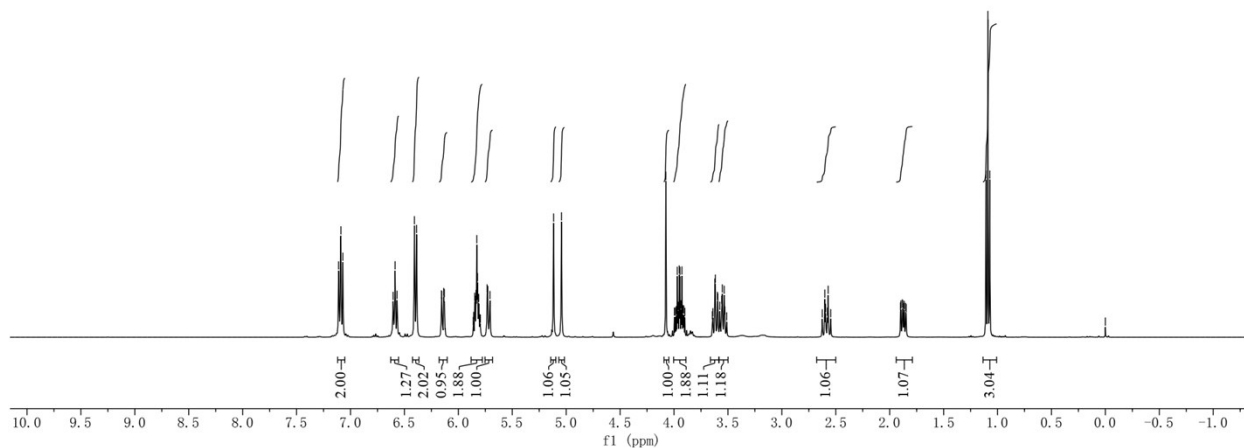
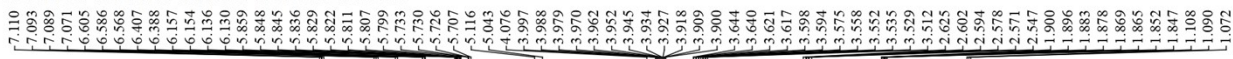
¹³C NMR spectra of compound 4v

MERCURY500 CNMR PX2203-3 CDCl3 2070523



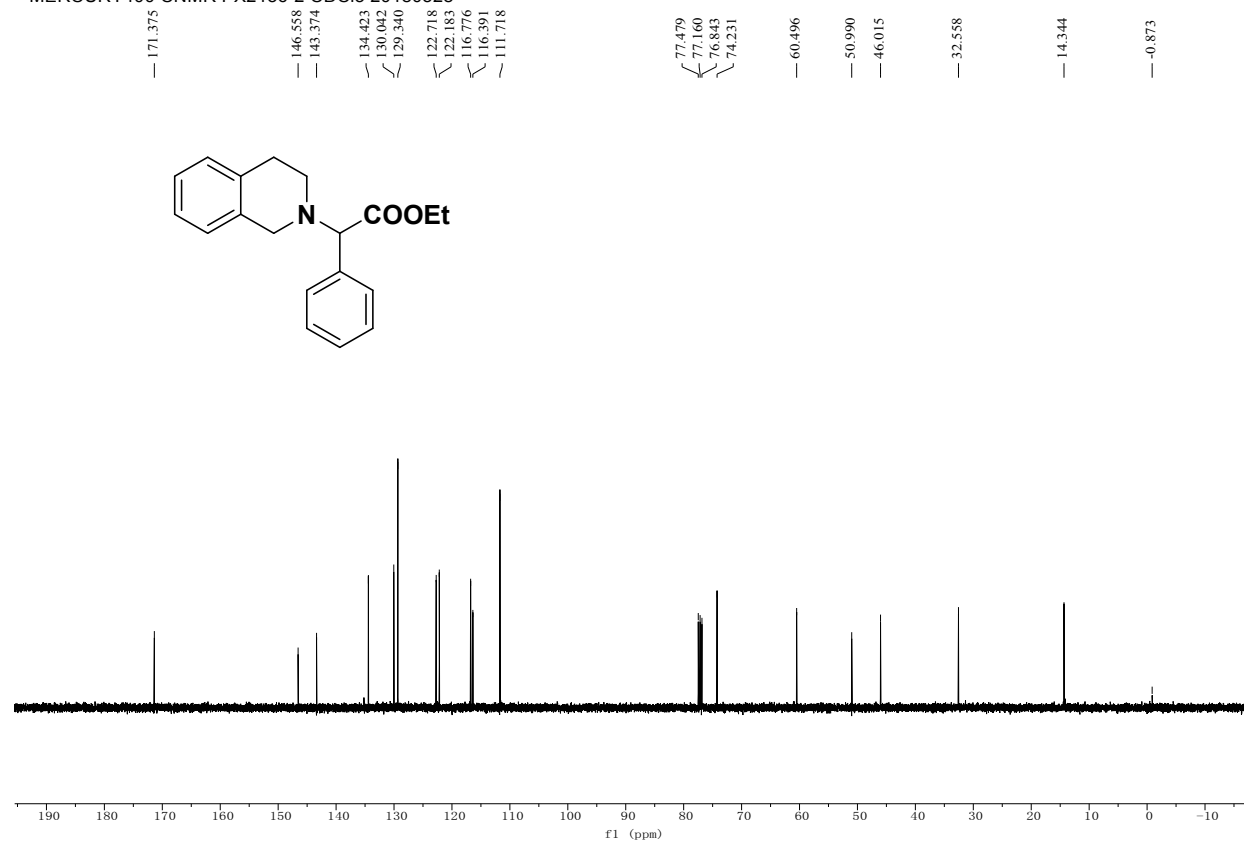
¹H NMR spectra of compound 5a

MERCURY400 HNMR PX2136-2 CDCl3 20180328

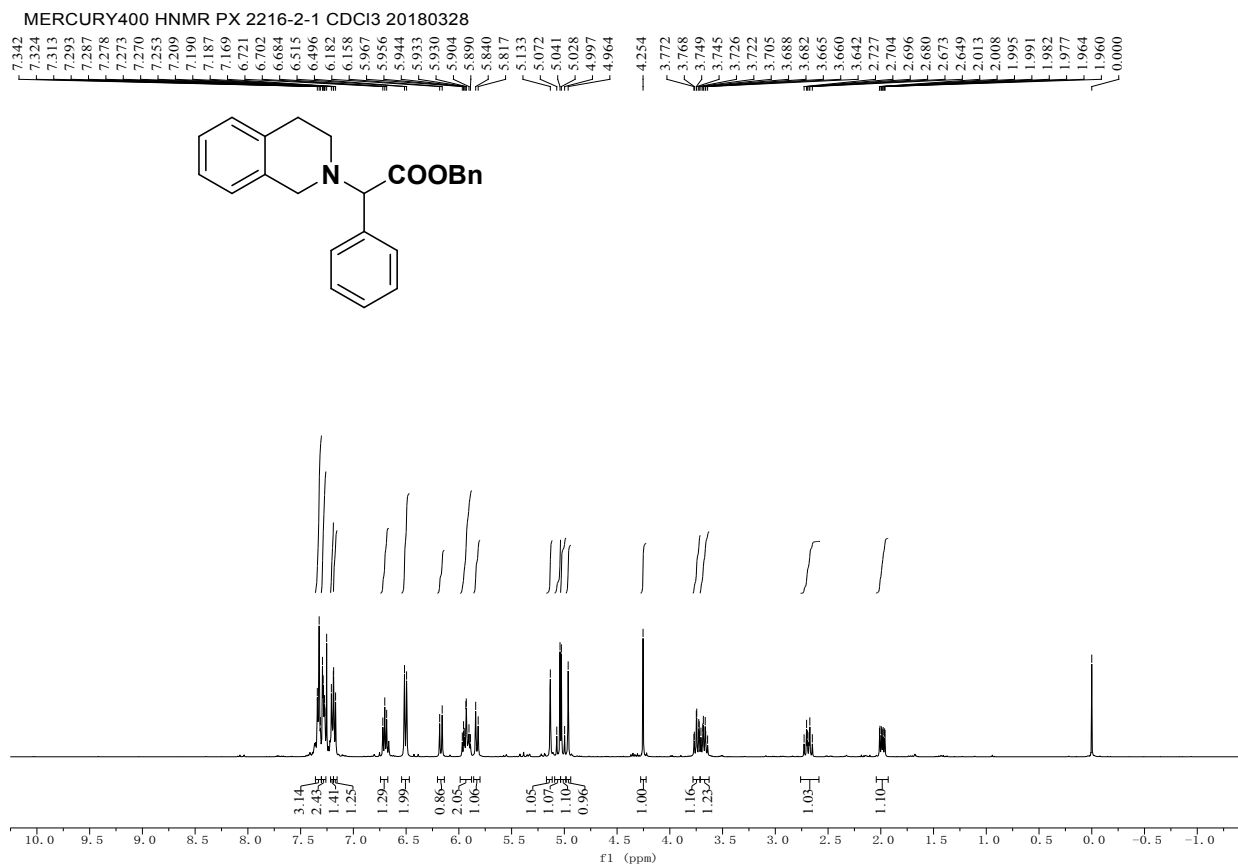


¹³C NMR spectra of compound 5a

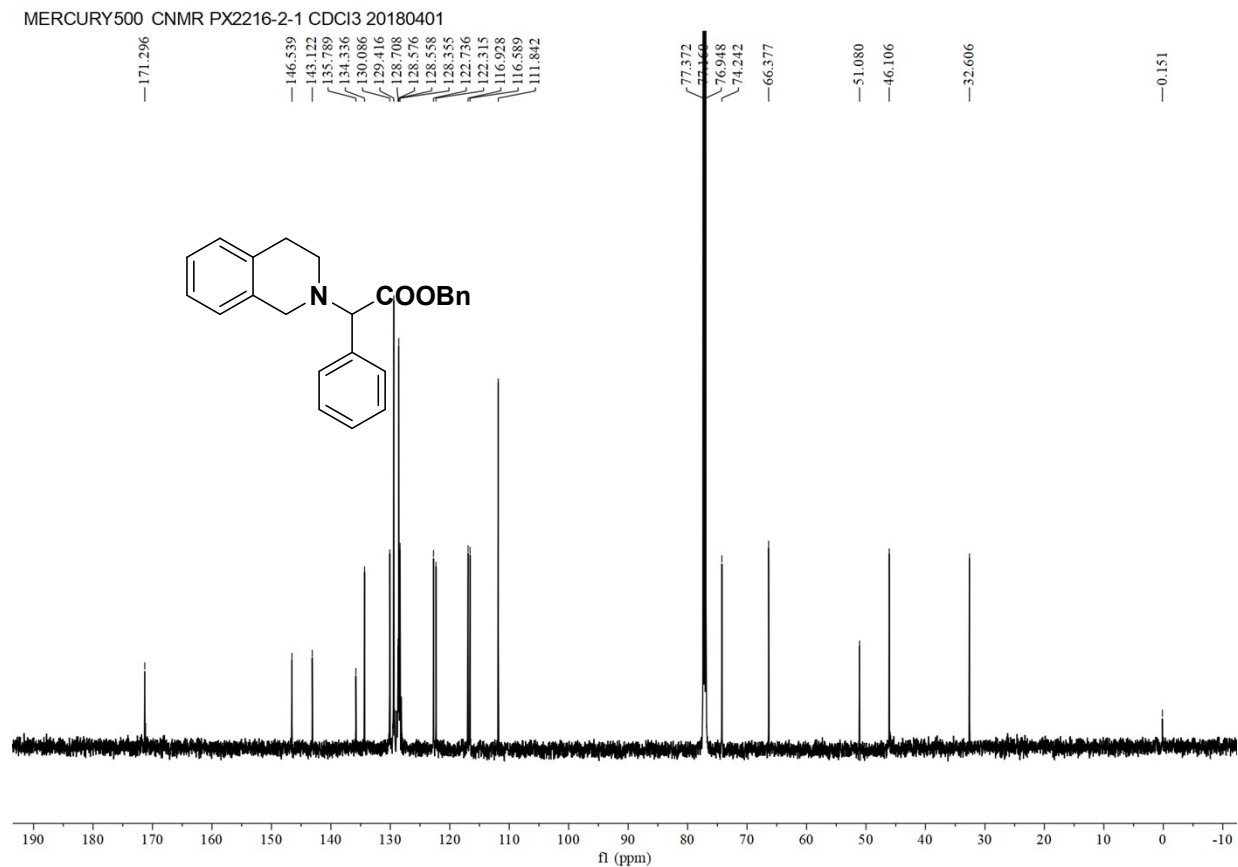
MERCURY400 CNMR PX2136-2 CDCl3 20180328



¹H NMR spectra of compound **5b**



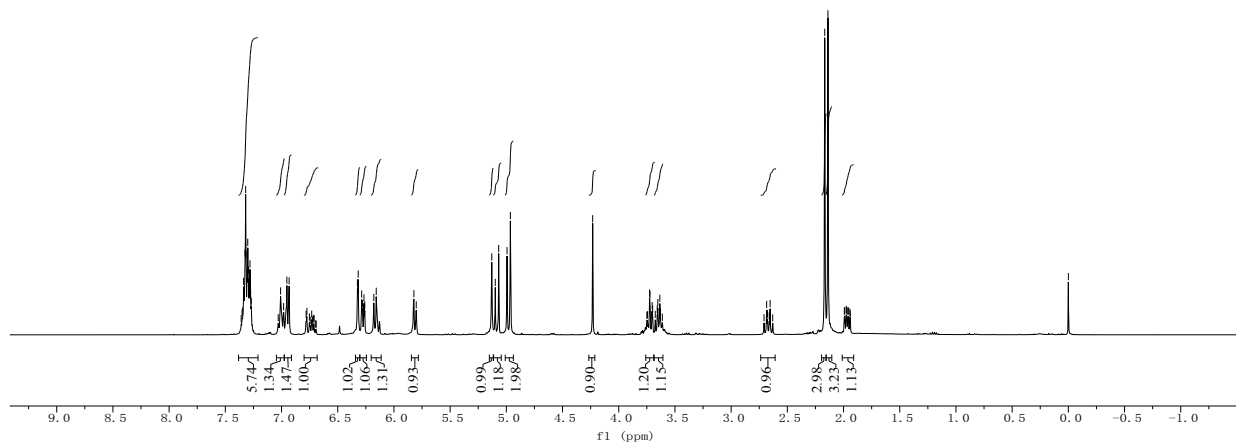
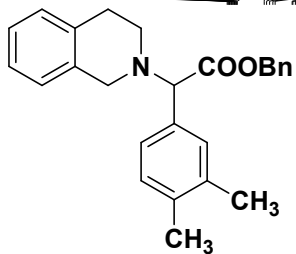
¹³C NMR spectra of compound **5b**



¹H NMR spectra of compound 5c

MERCURY400 HNMR PX2303 CDCl3 20180329

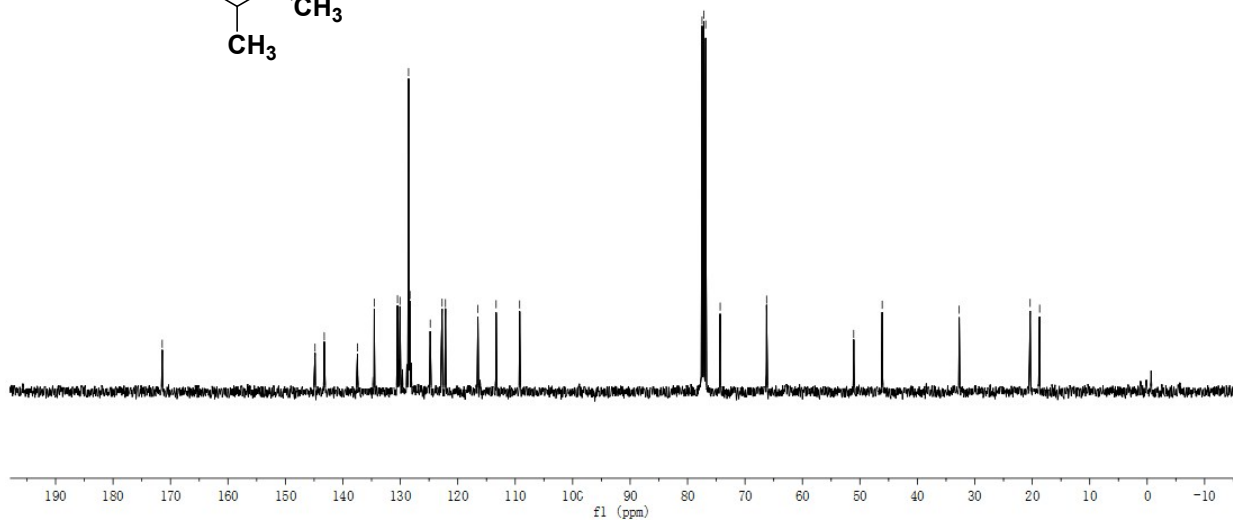
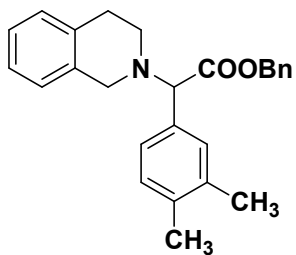
7.359 7.351 7.345 7.338 7.333 7.325 7.319 7.314 7.307 7.301 7.294 7.287 7.281 7.275 7.269 7.029 7.008 6.981 6.952 6.932 6.781 6.774 6.752 6.731 6.714 6.710 6.325 6.318 6.287 6.280 6.266 6.259 6.179 6.158 5.822 5.802 5.129 5.098 5.068 4.994 4.964 4.232 3.750 3.744 3.726 3.722 3.707 3.703 3.698 3.675 3.675 3.658 3.652 3.635 3.629 3.612 2.708 2.684 2.676 2.661 2.653 2.650 2.167 2.139 1.993 1.989 1.976 1.971 1.962 1.957 1.945 1.940 0.000



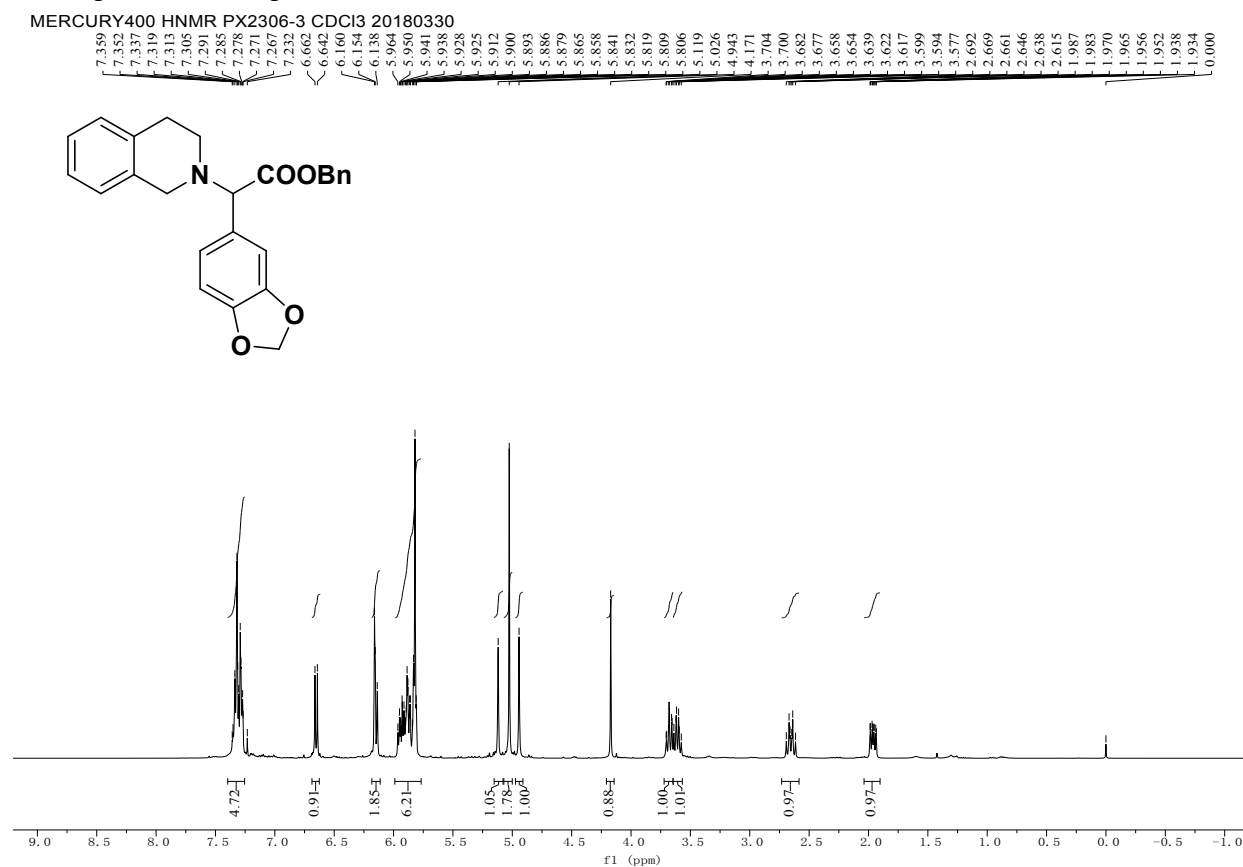
¹³C NMR spectra of compound 5c

MERCURY400 CNMR PX2303-3 CDCl3 20171023

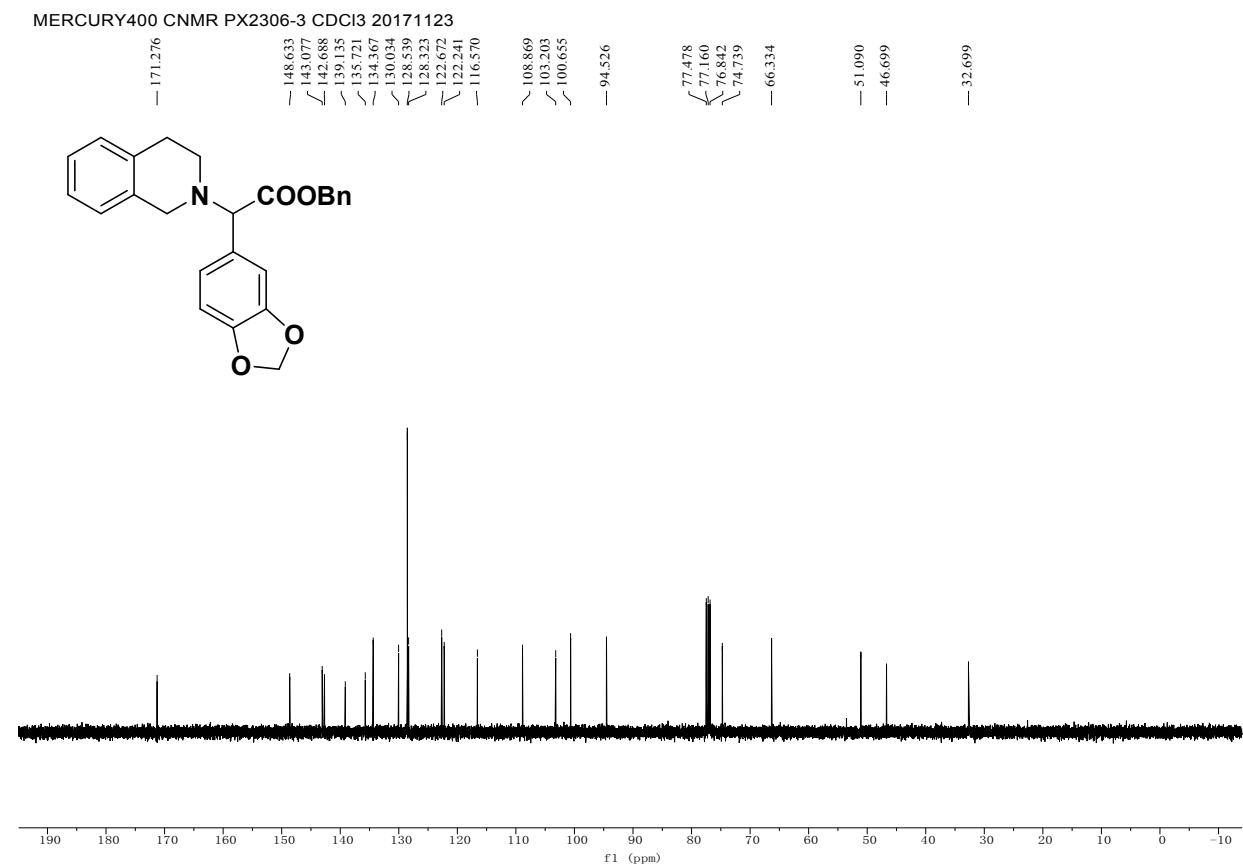
171.440 144.845 143.238 137.451 134.537 130.654 128.559 128.489 128.304 124.783 122.724 122.138 116.404 113.322 109.226 77.478 77.160 76.842 76.521 66.243 51.082 46.116 32.718 20.369 18.713



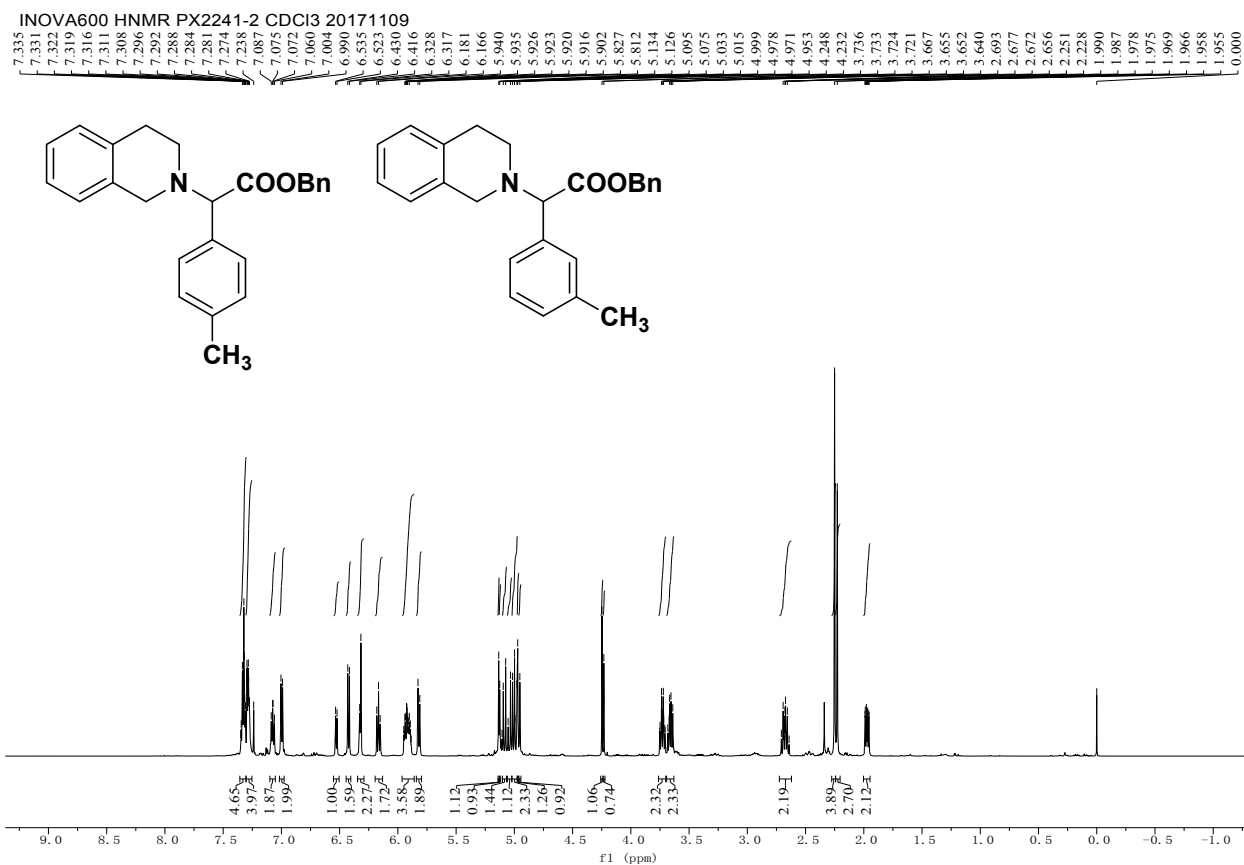
¹H NMR spectra of compound 5d



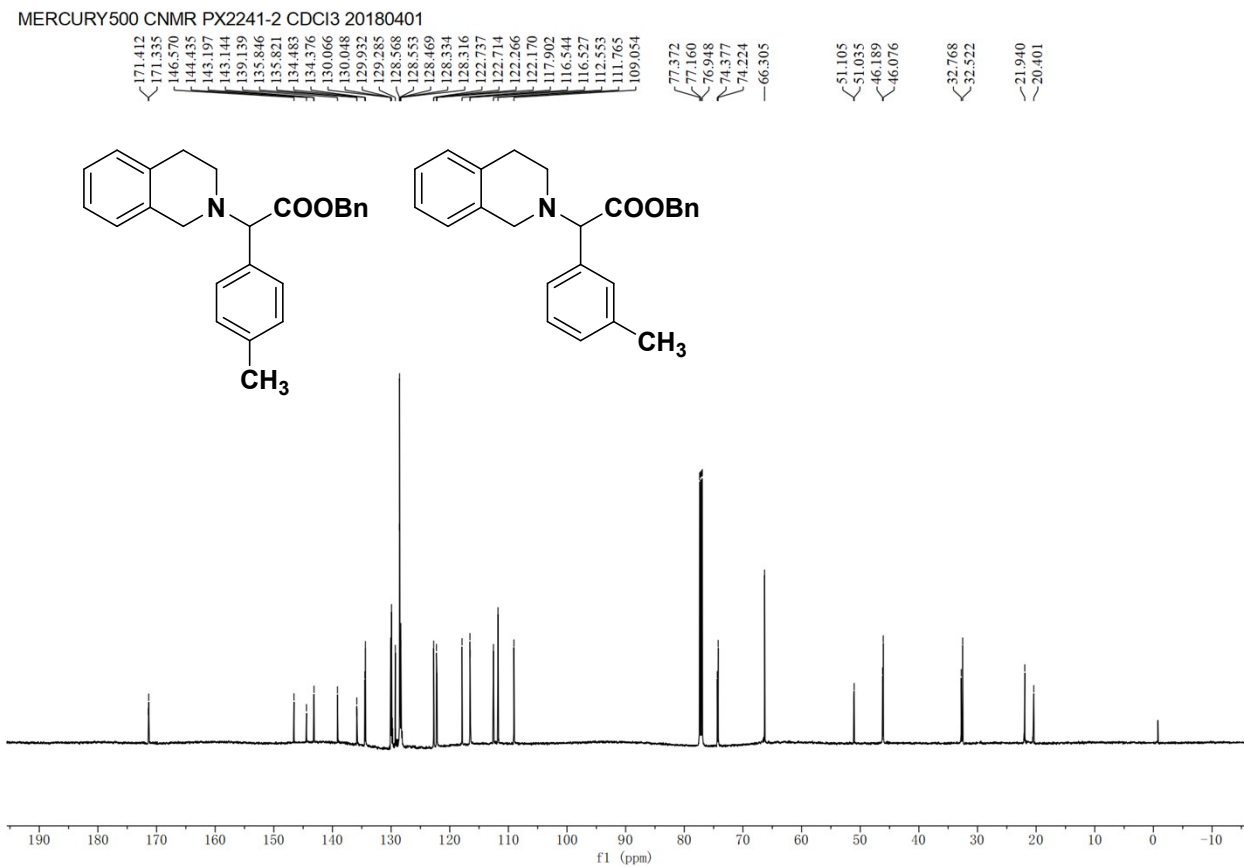
¹³C NMR spectra of compound 5d



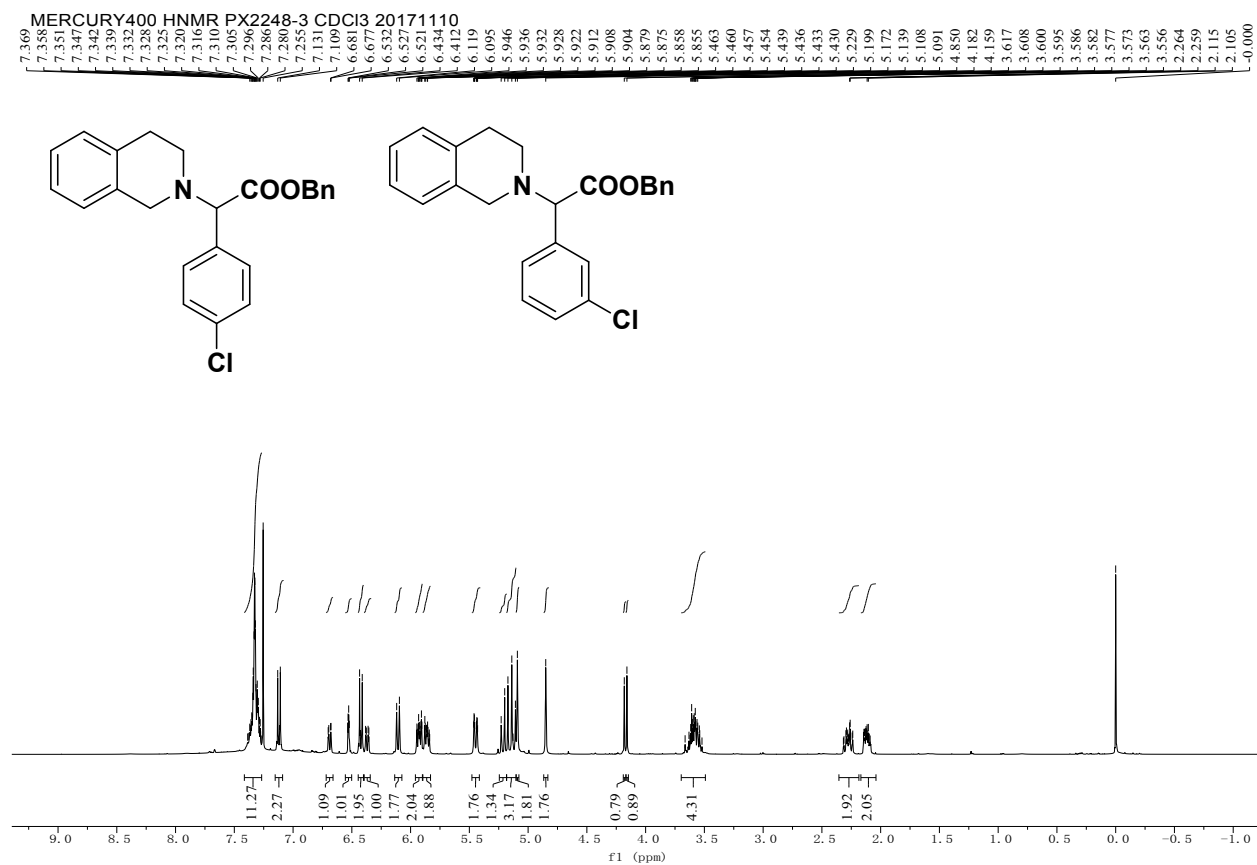
¹H NMR spectra of compounds **5ea** and **5eb**



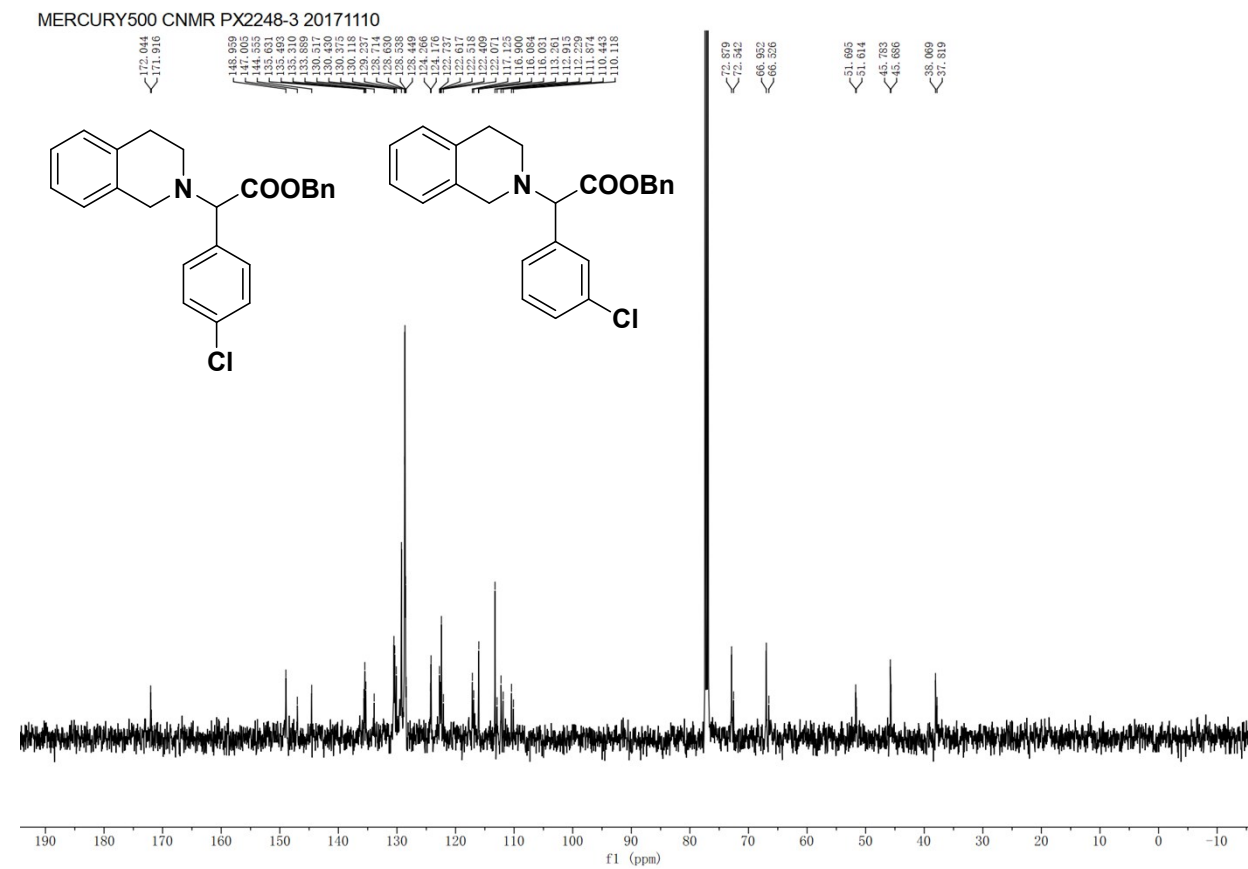
¹³C NMR spectra of compounds **5ea** and **5eb**



¹H NMR spectra of compounds **5fa** and **5fb**

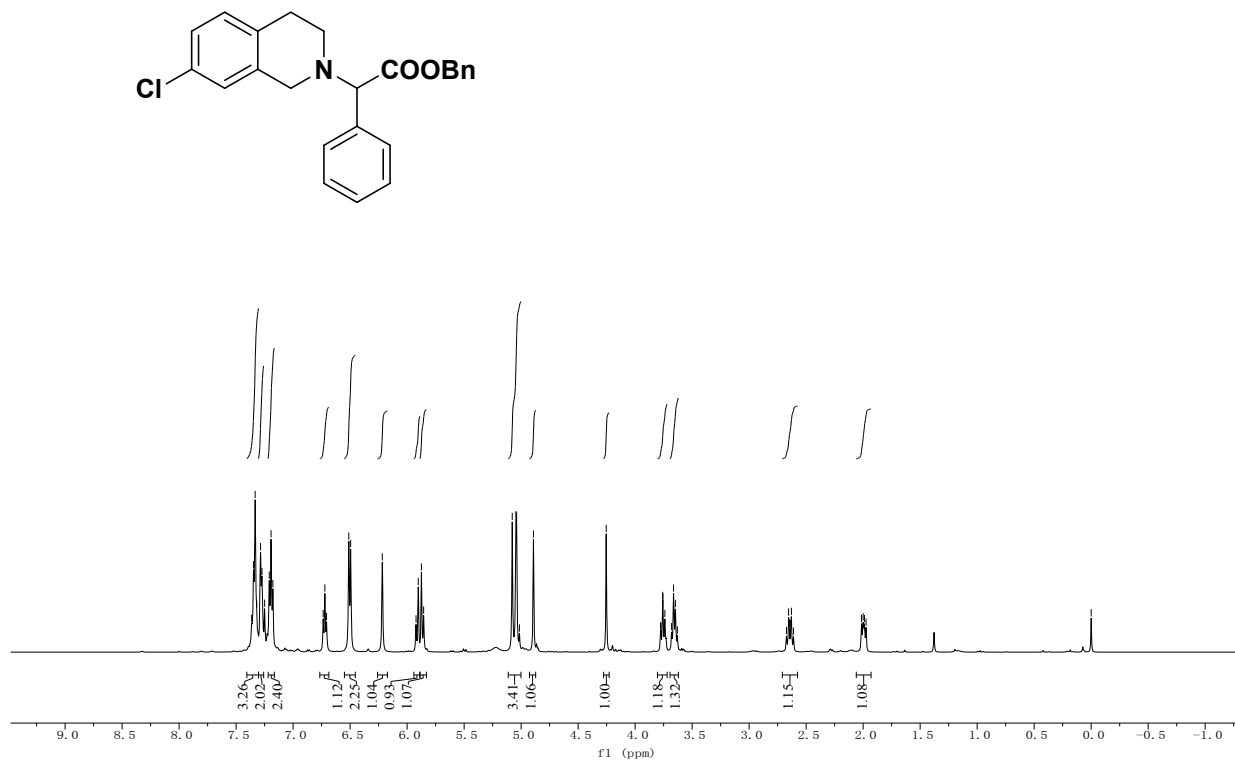
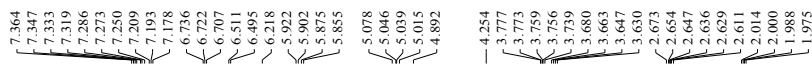


¹³C NMR spectra of compounds **5fa** and **5fb**



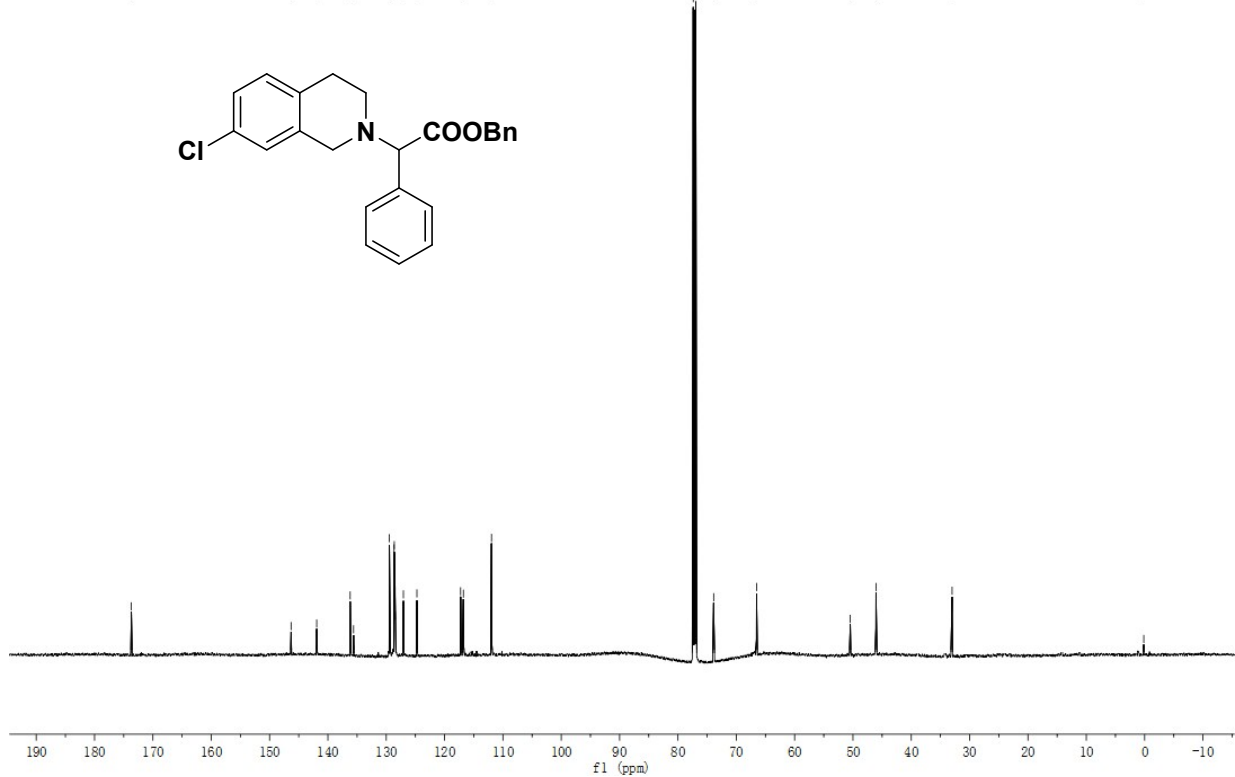
¹H NMR spectra of compound 5g

MERCURY500 HNMR PX2229-1 CDCl₃ 20171013



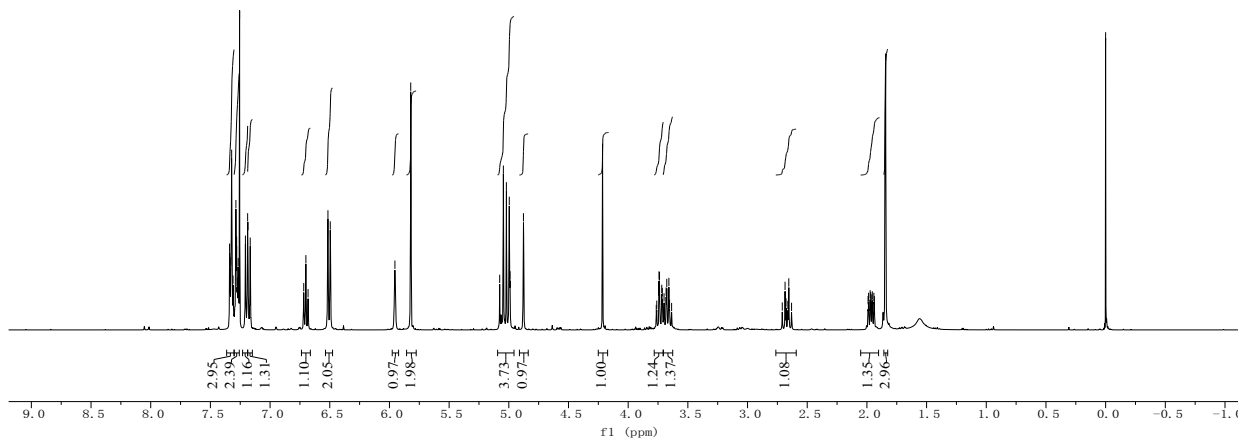
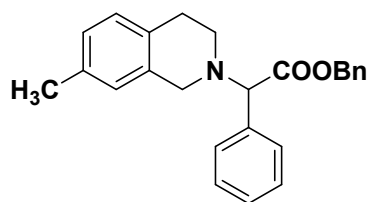
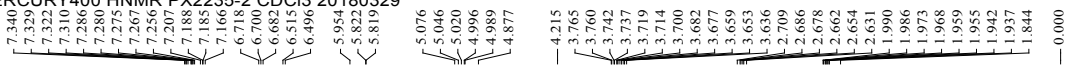
¹³C NMR spectra of compound 5g

INOVA600 CNMNR PX2229-1 CDCl₃ 20171030



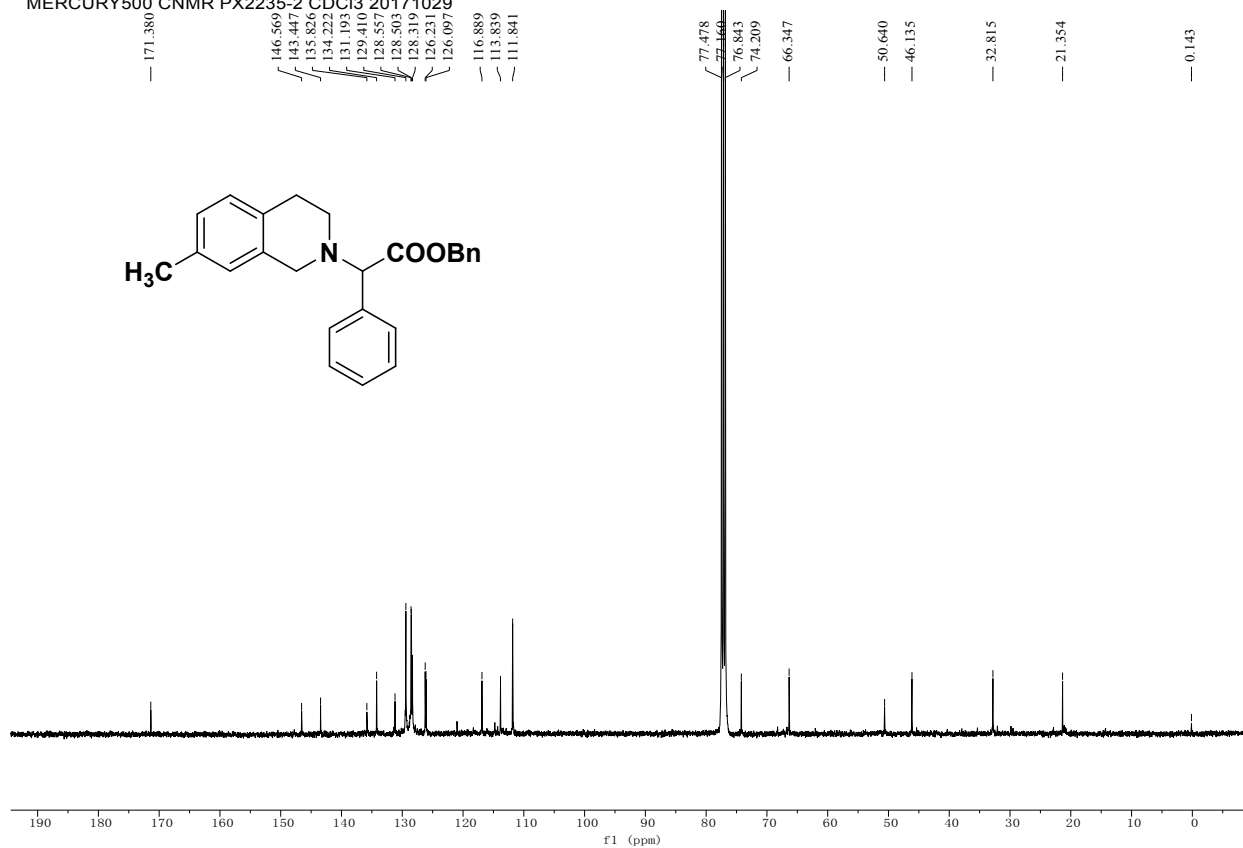
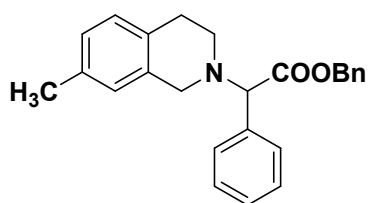
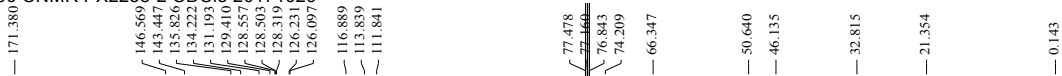
¹H NMR spectra of compound 5h

MERCURY400 HNMR PX2235-2 CDCl3 20180329



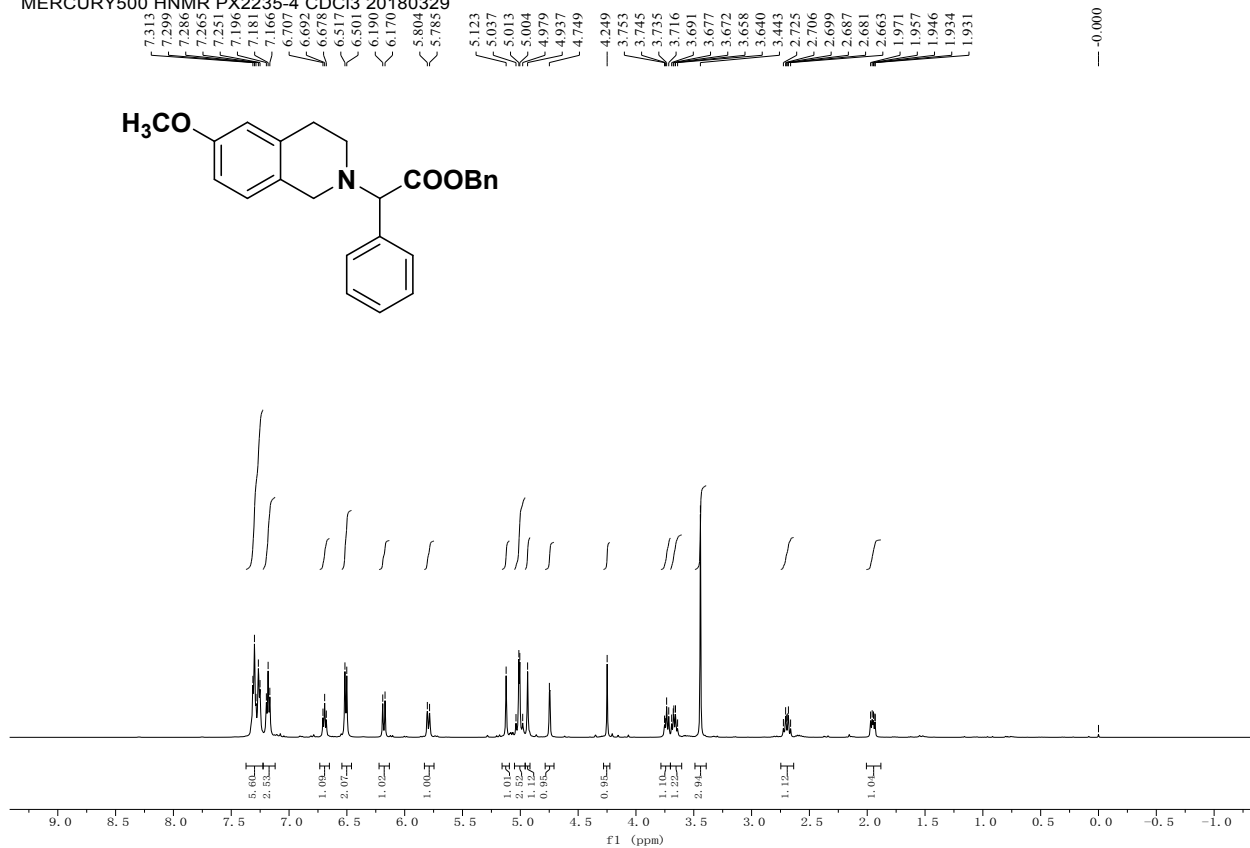
¹³C NMR spectra of compound 5h

MERCURY500 CNMR PX2235-2 CDCl3 20171029



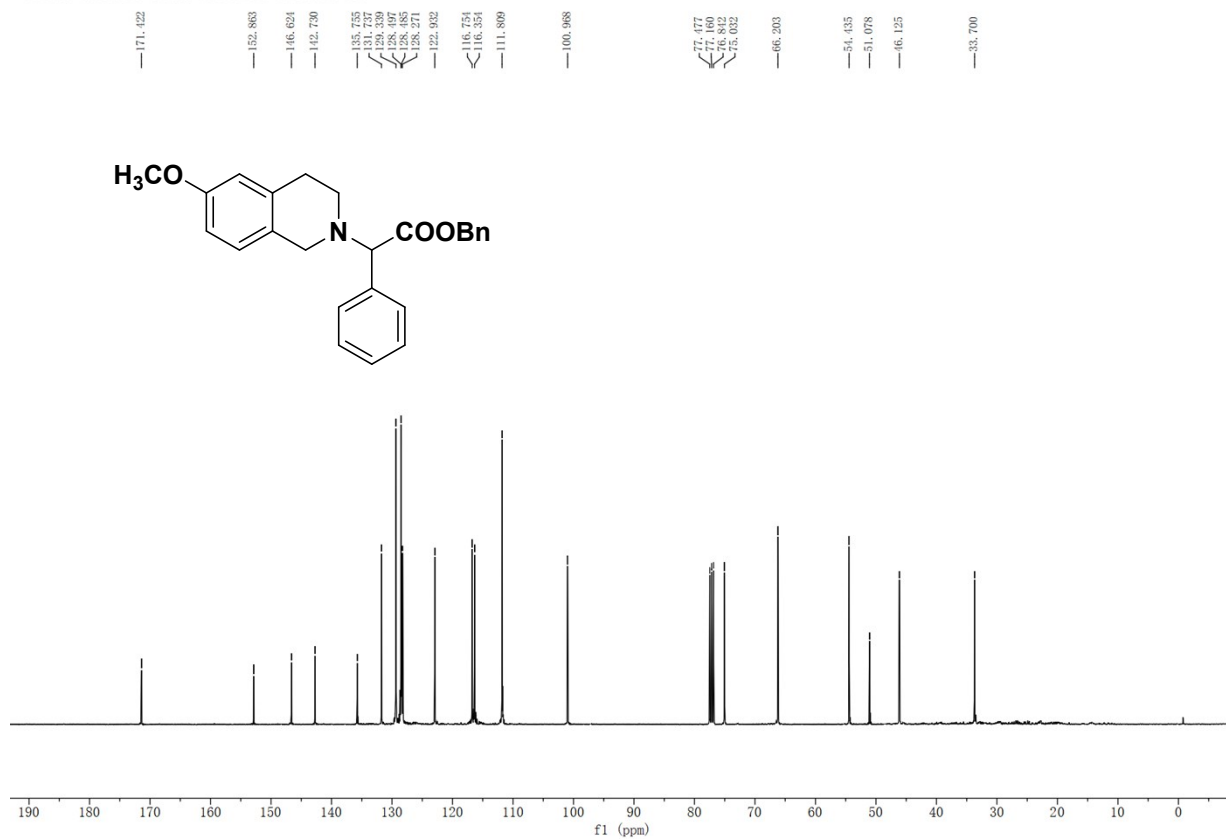
¹H NMR spectra of compound **5i**

MERCURY500 HNMR PX2235-4 CDCI3 20180329



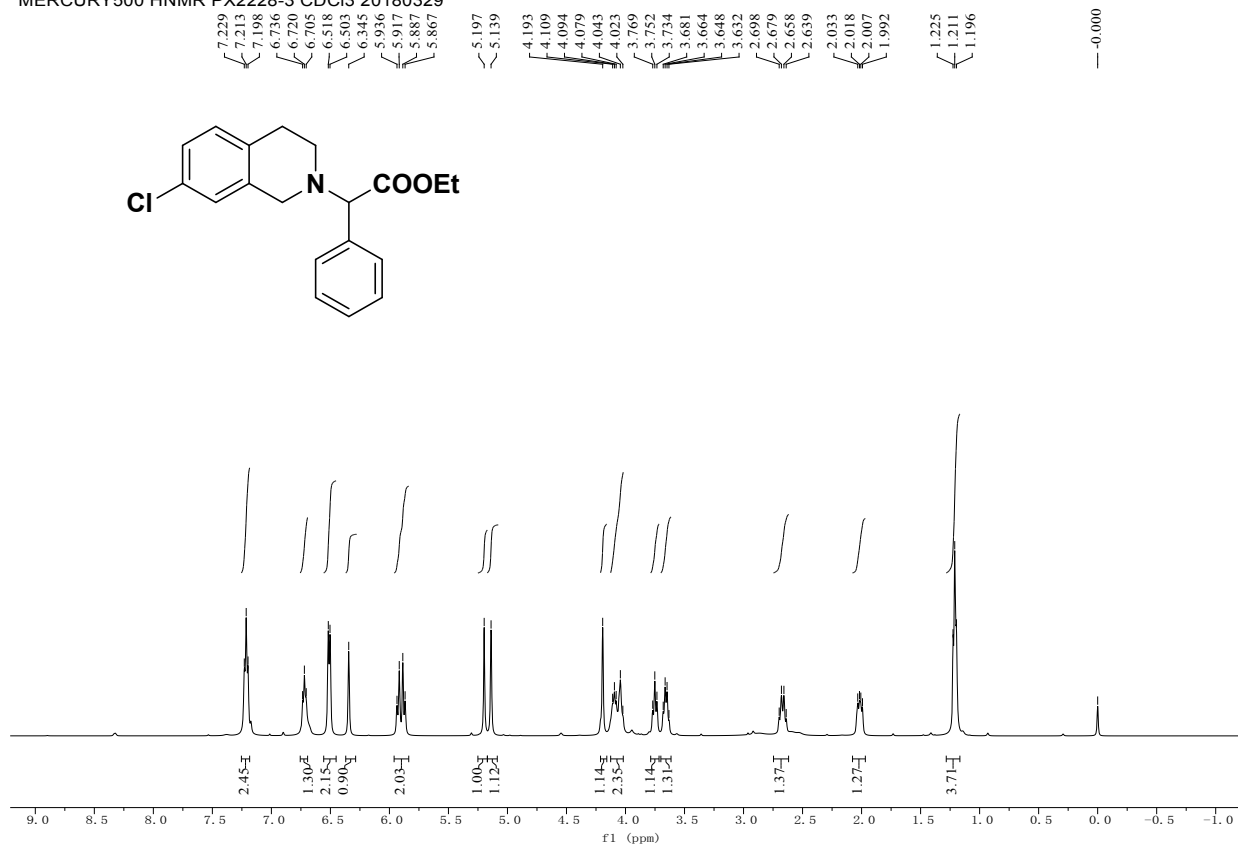
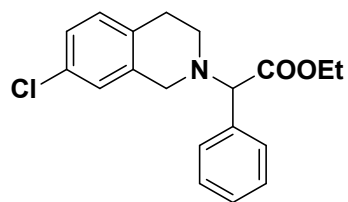
¹³C NMR spectra of compound **5i**

MERCURY500 CNMR PX2235-4 20180401



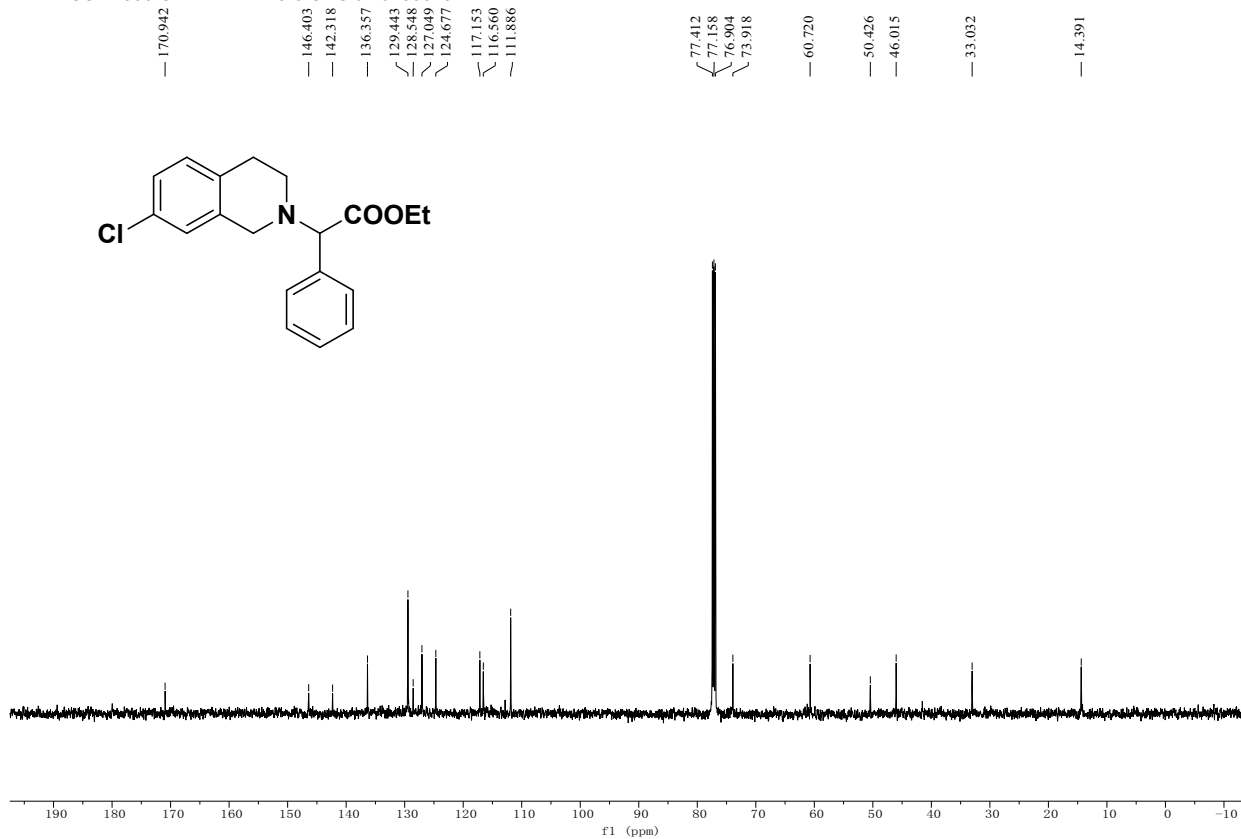
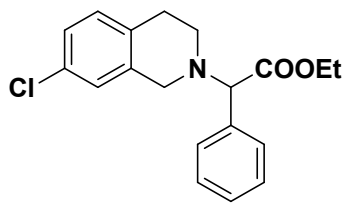
¹H NMR spectra of compound 5j

MERCURY500 HNMR PX2228-3 CDCl₃ 20180329



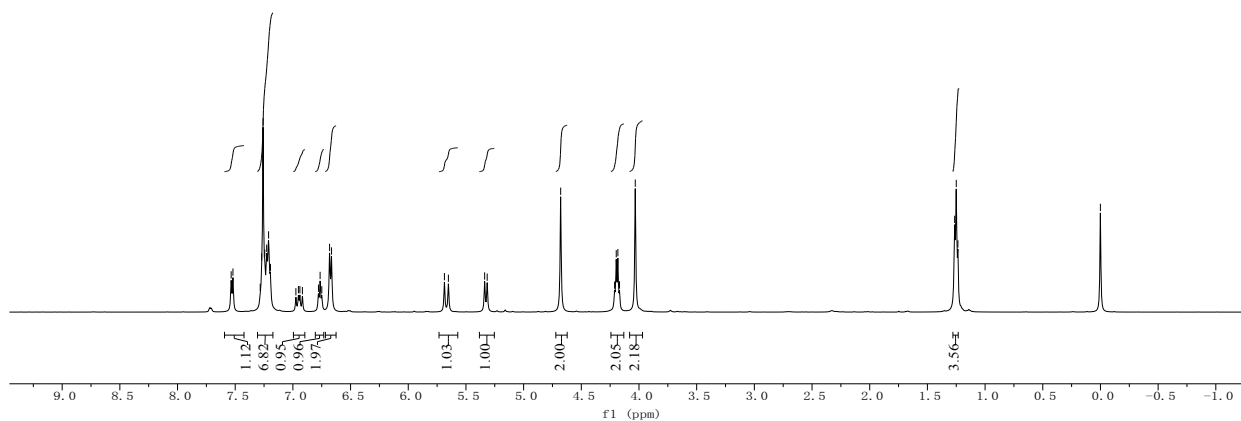
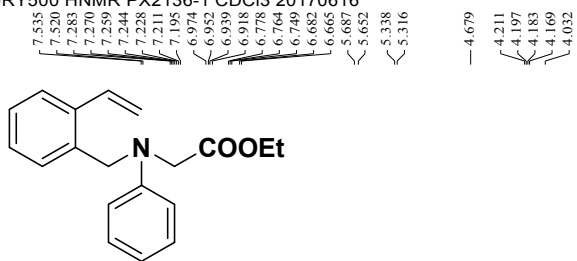
¹³C NMR spectra of compound 5j

MERCURY500 CNMR PX2228-3 CDCl₃ 20180329



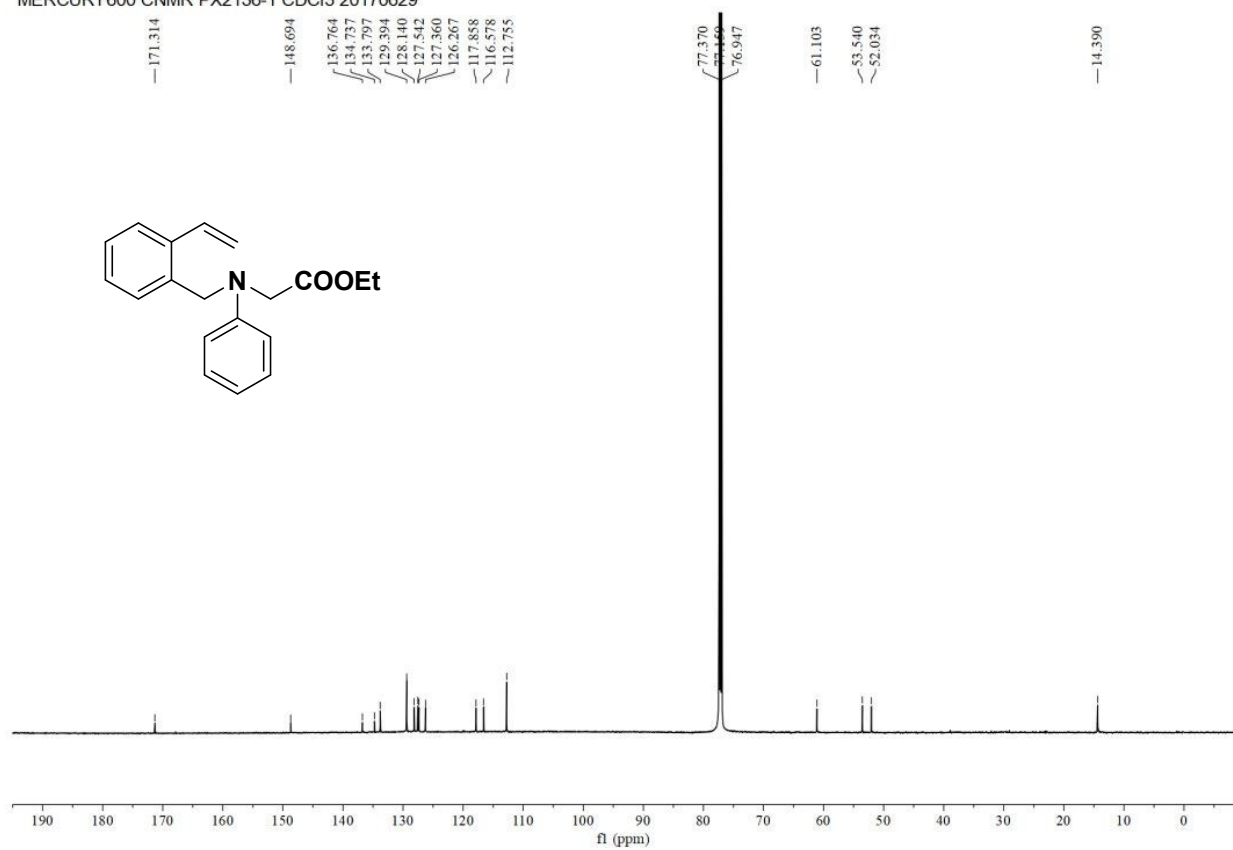
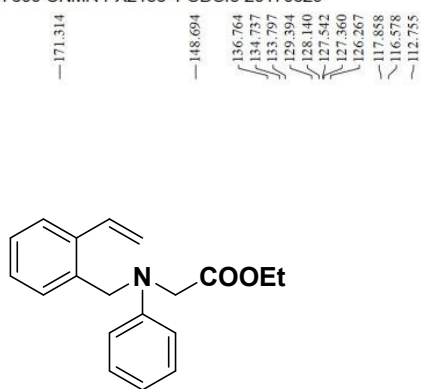
¹H NMR spectra of compound 6a

MERCURY500 HNMR PX2136-1 CDCl₃ 20170616



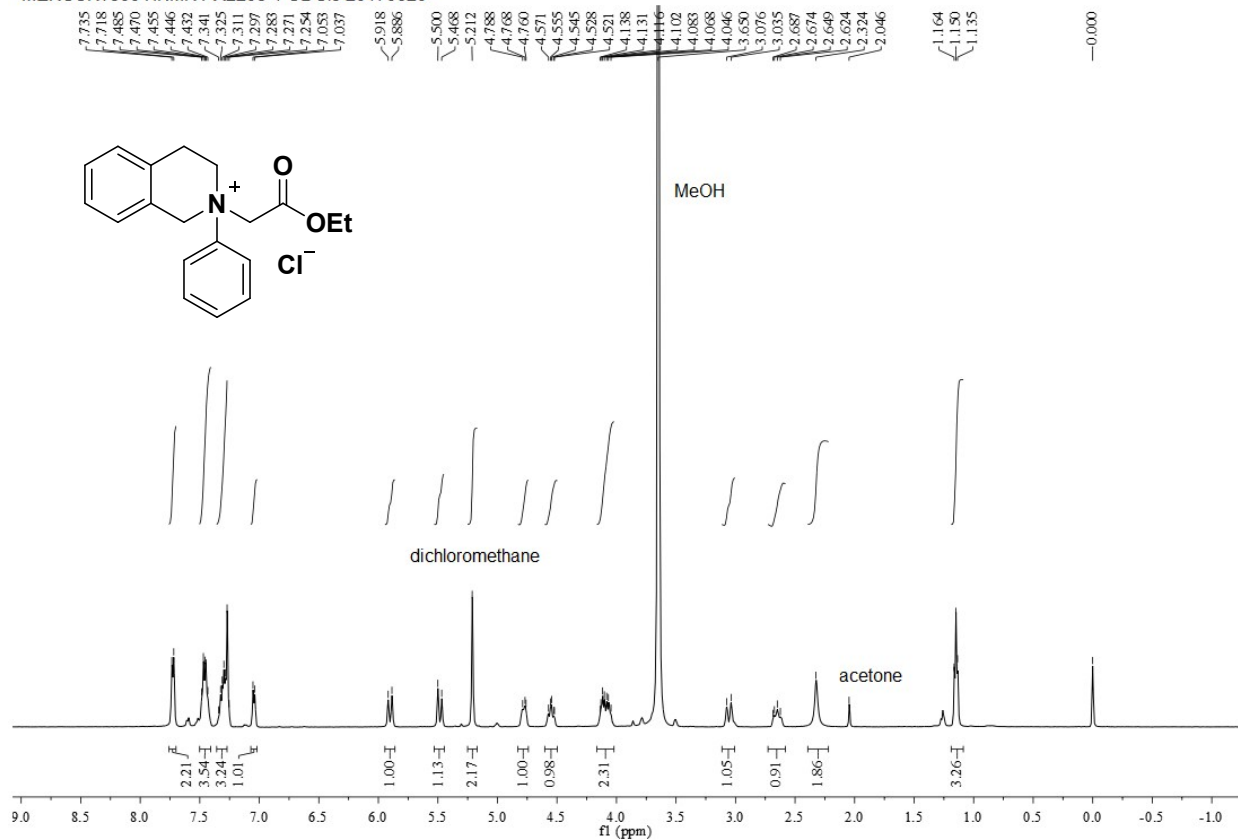
¹³C NMR spectra of compound 6a

MERCURY600 CNMR PX2136-1 CDCl₃ 20170629



¹H NMR spectra of quaternary ammonium salt

MERCURY500 HNMR PX2208-1 CDCl₃ 20170620



¹³C NMR spectra of quaternary ammonium salt

MERCURY400 CNMR PX2208-1 CDCl₃ 20170721

