Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Facile one-pot synthesis of spirooxindole-pyrrolidine derivatives and their antimicrobial and acethycholinesterase inhibitory activities

Ying Huang[a], Wei Min[b], Qiu-Wen Wu[c], Jing Sun[a], Da-Hua Shi[b], Chao-Guo Yan[a,*]

Supporting Information

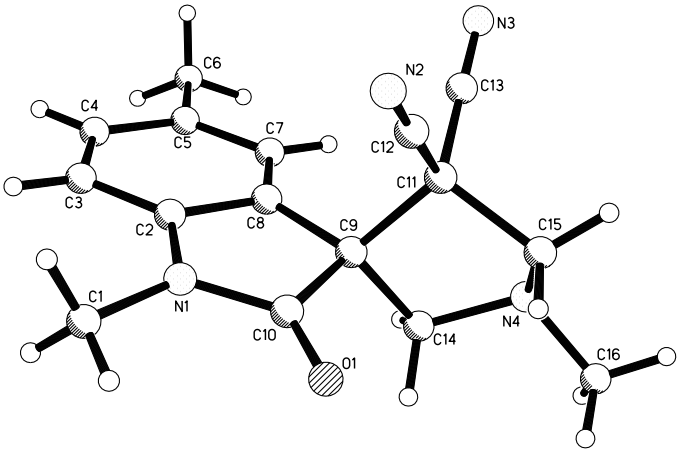


Figure s1 Single crystal structure of **4i**

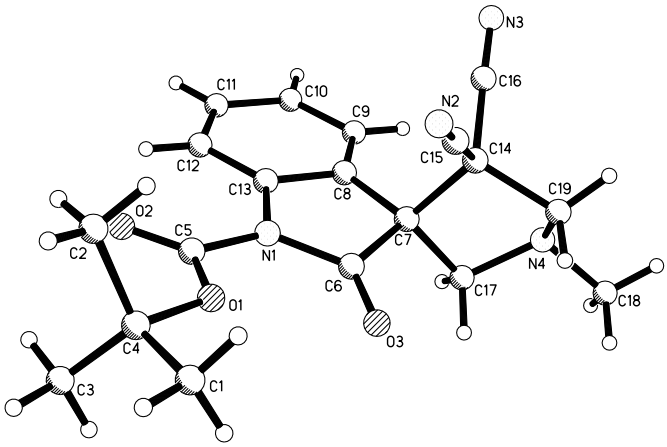


Figure s2 Single crystal structure of **4n**

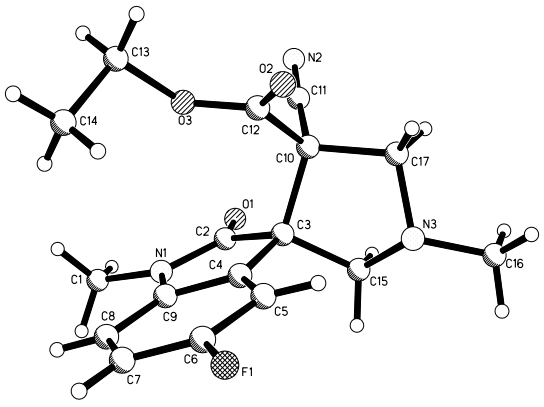


Figure s3 Single crystal structure of **6c (**major isomer)

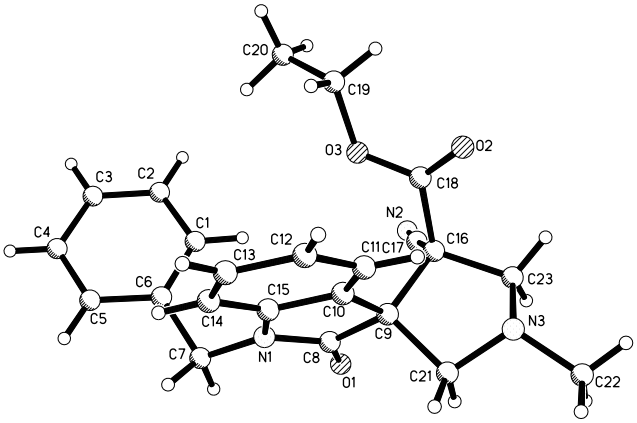


Figure s4 Single crystal structure of **6g (**major isomer)

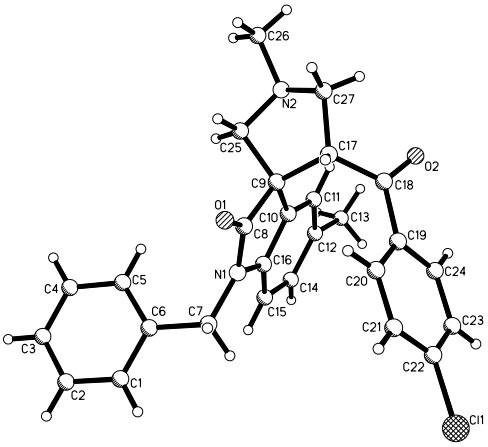


Figure s5 Single crystal structure of **8f**

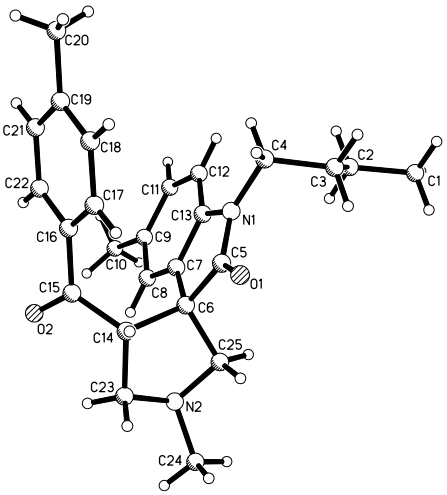
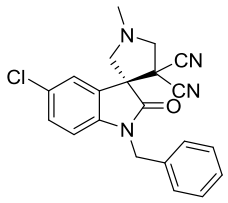
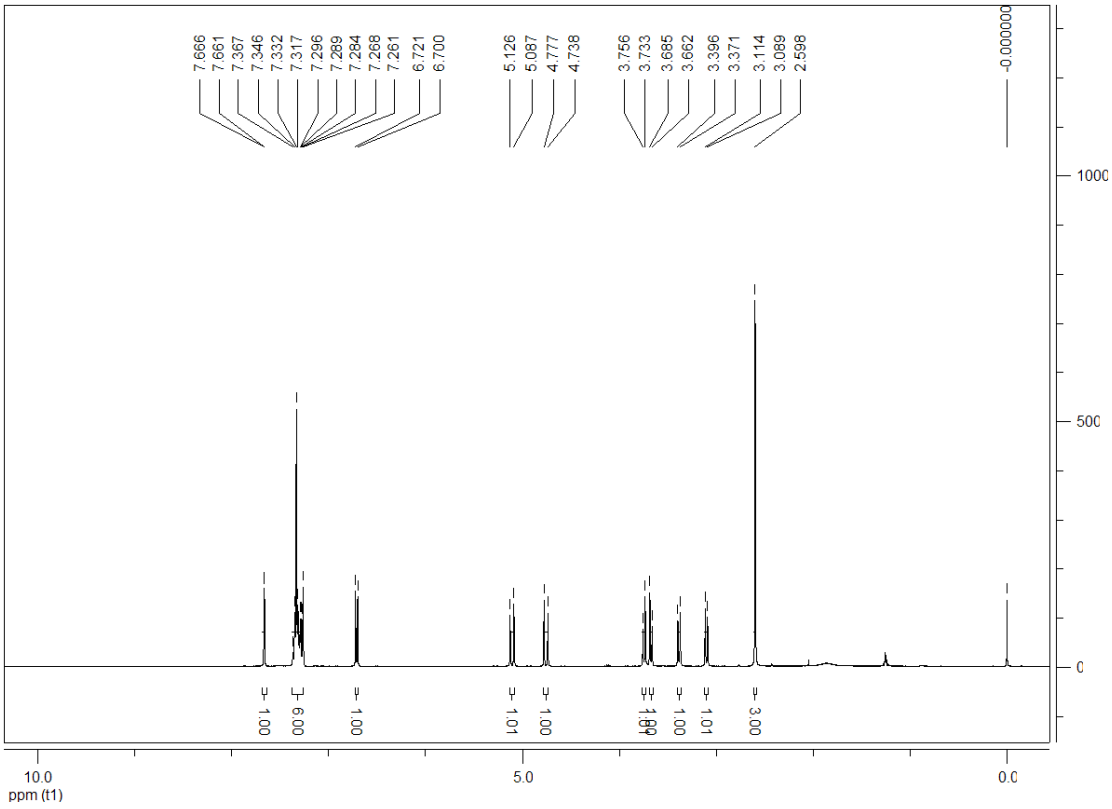


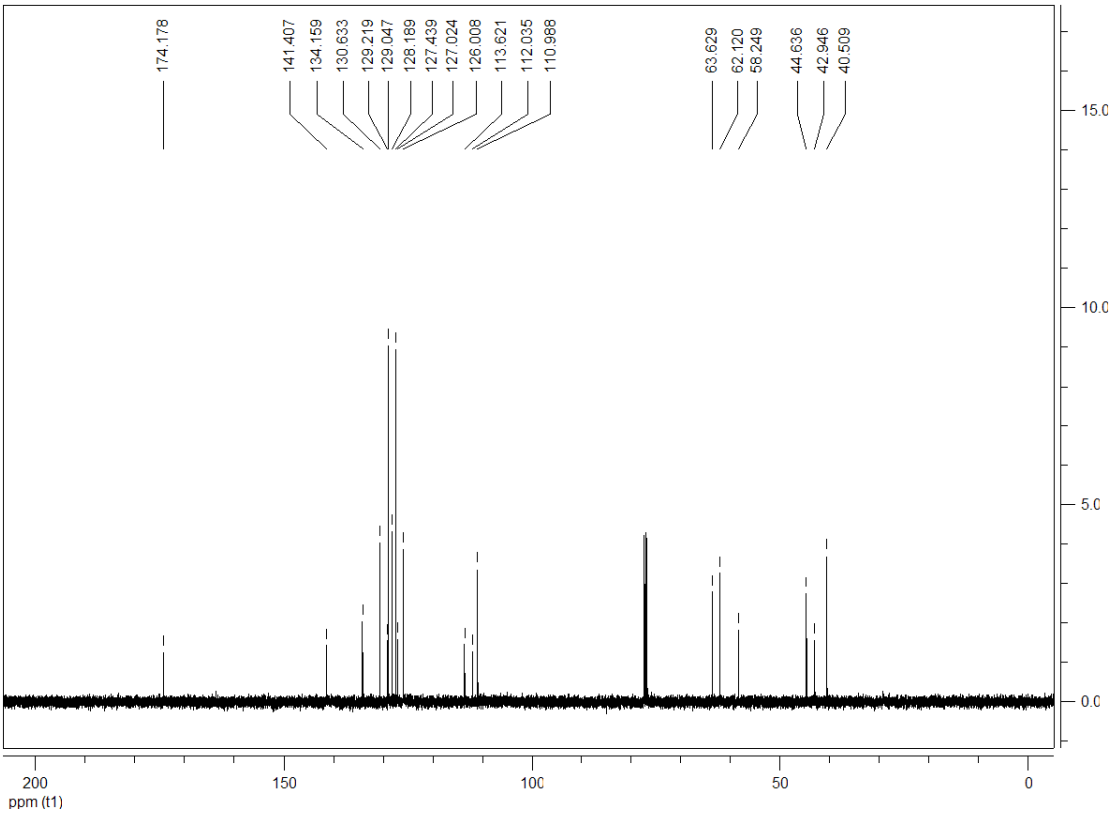
Figure s6 Single crystal structure of **8j**

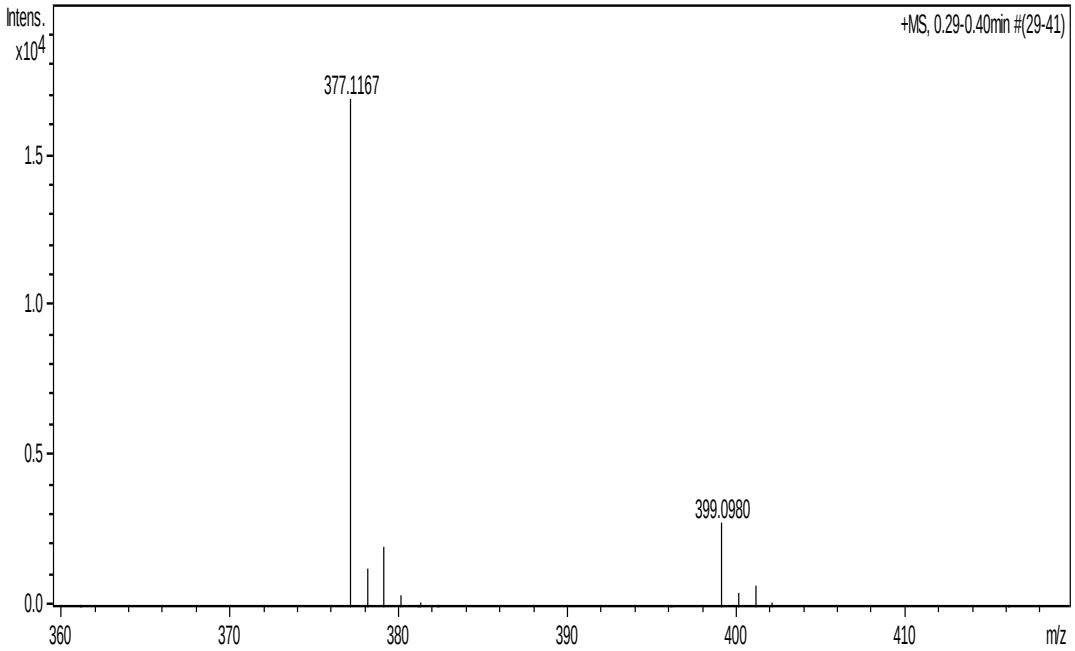
(S)-1-Benzyl-5-chloro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicar bonitrile (4a)



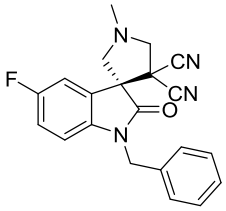
white solid, 91%, m.p. 131~133℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (d, *J* = 2.0Hz, 1H, ArH), 7.37~7.27 (m, 6H, ArH), 6.71 (d, *J* = 8.4Hz, 1H, ArH), 5.11 (d, *J* = 15.6Hz, 1H, CH), 4.76 (d, *J* = 15.6Hz, 1H, CH), 3.74 (d, *J* = 9.2Hz, 1H, CH), 3.67 (d, *J* = 9.2Hz, 1H, CH), 3.38 (d, *J* = 10.0Hz, 1H, CH), 3.10 (d, *J* = 10.0Hz, 1H, CH), 2.60 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 141.4, 134.1, 130.6, 129.2, 129.0, 128.1, 127.4, 127.0, 126.0, 113.6, 112.0, 110.9, 63.6, 62.1, 58.2, 44.6, 42.9, 40.5; IR(KBr) υ: 2963, 2852, 2806, 2248, 1957, 1875, 1713, 1606, 1486, 1433, 1367, 1342, 1272, 1248, 1200, 1172, 1127, 1079, 1026, 991, 958, 898, 874, 814, 742 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{18}ClN_4O$ ($[M+H]^+$): 377.1164, found: 377.1167.



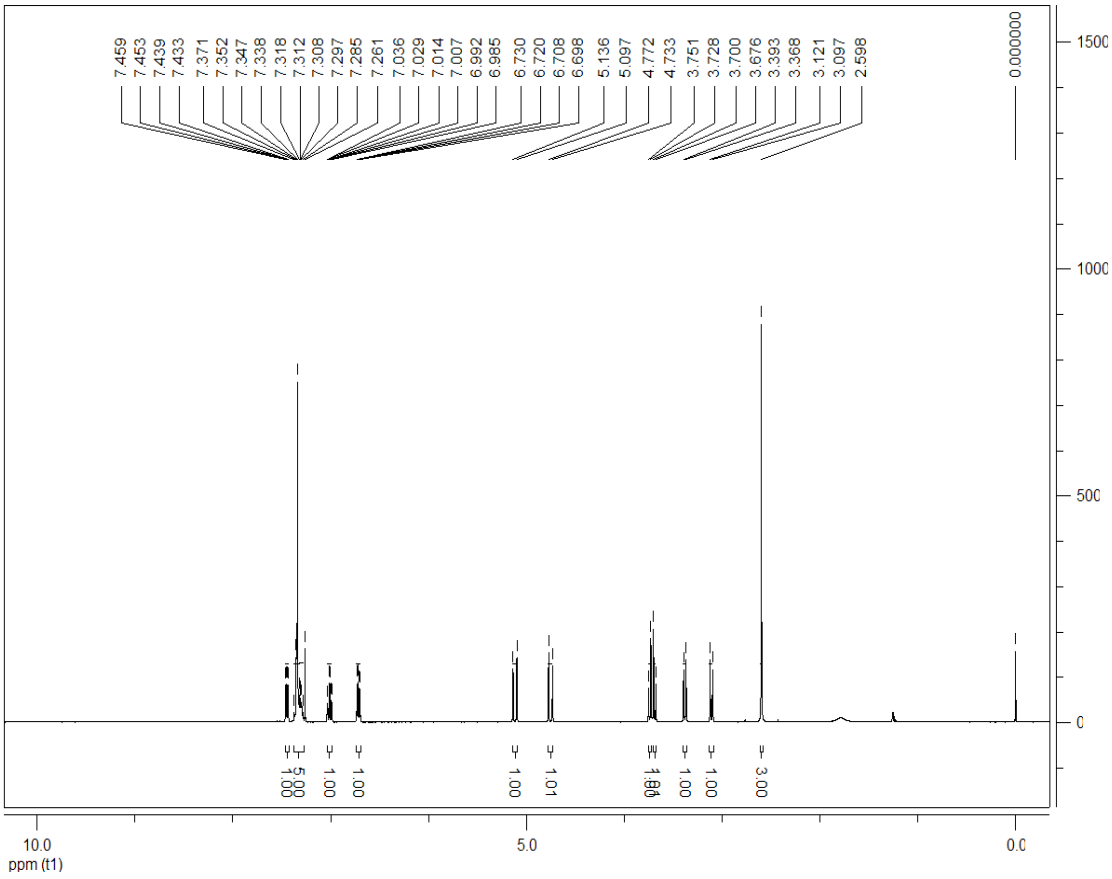

174.178
141.407
134.159
130.633
129.219
129.047
128.189
127.439
127.024
126.008
113.621
112.035
110.988
63.629
62.120
58.249
44.636
42.946
40.509
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

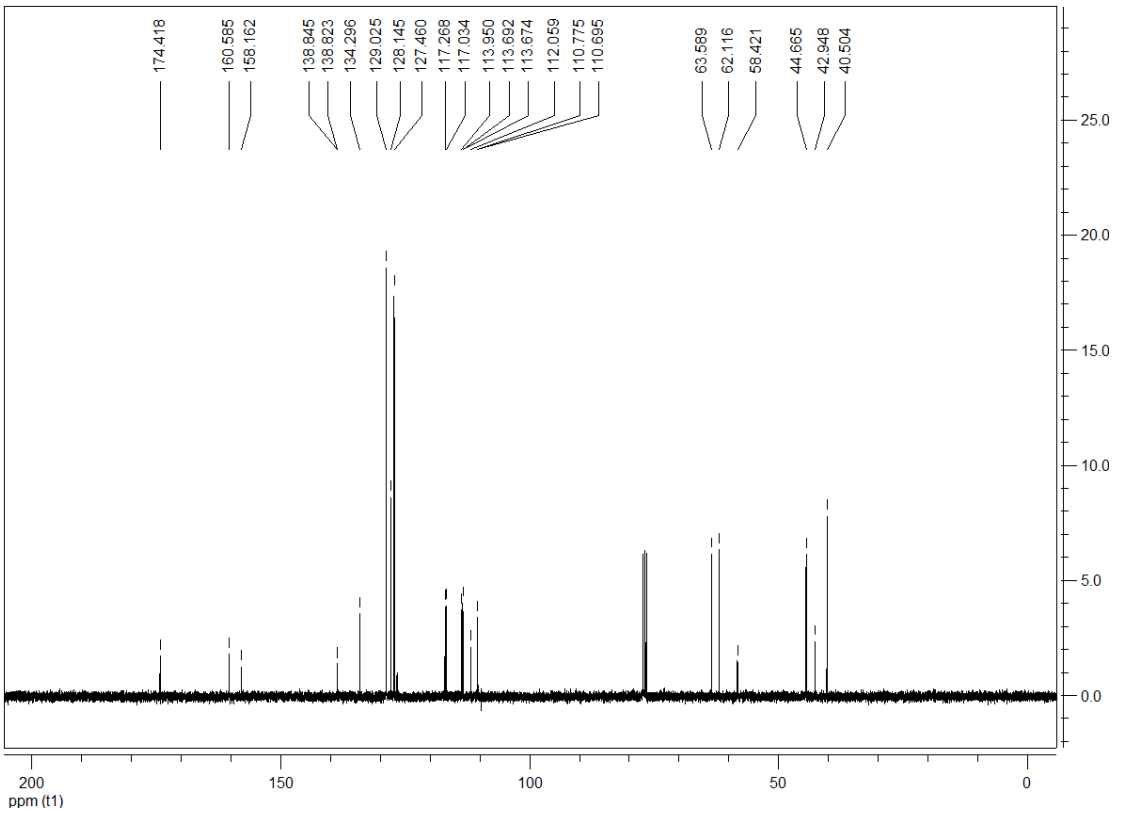

Intens.
x10^4
+MS, 0.29-0.40min #(29-41)
377.1167
399.0980
1.5
1.0
0.5
0.0
360
370
380
390
400
410
m/z

(S)-1-Benzyl-5-fluoro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicar bonitrile (4b)



white solid, 90%, m.p. 109~111℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J_1= 8.0Hz, J_2 = 2.4Hz , 1H, ArH), 7.37~7.28 (m, 5H, ArH), 7.01 (td, J_1 = 8.8Hz, J_2 = 2.8Hz , 1H, ArH), 6.71 (dd, J_1 = 8.8Hz, J_2 = 4.0Hz , 1H, ArH), 5.12 (d, J = 15.6Hz, 1H, CH), 4.75 (d, J = 15.6Hz, 1H, CH), 3.74 (d, J = 9.2Hz, 1H, CH), 3.69 (d, J = 9.6Hz, 1H, CH), 3.38 (d, J = 10.0Hz, 1H, CH), 3.11 (d, J = 9.6Hz, 1H, CH), 2.60 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 159.4 (d, J = 242.3Hz), 138.8, 138.8, 134.2, 129.0, 128.1, 127.4, 117.2 (d, J = 23.4Hz), 113.8 (d, J = 25.8Hz), 113.6, 112.0, 110.7 (d, J = 8.0Hz), 63.5, 62.1, 58.4, 44.6, 42.9, 40.5; IR(KBr) υ: 2965, 2857, 2809, 2250, 1959, 1890, 1858, 1818, 1709, 1615, 1495, 1454, 1374, 1345, 1278, 1250, 1208, 1177, 1124, 1074, 1026, 968, 919, 865, 815, 761, 732 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{18}FN_4O$ ([M+H]$^+$): 361.1459, found: 361.1476.

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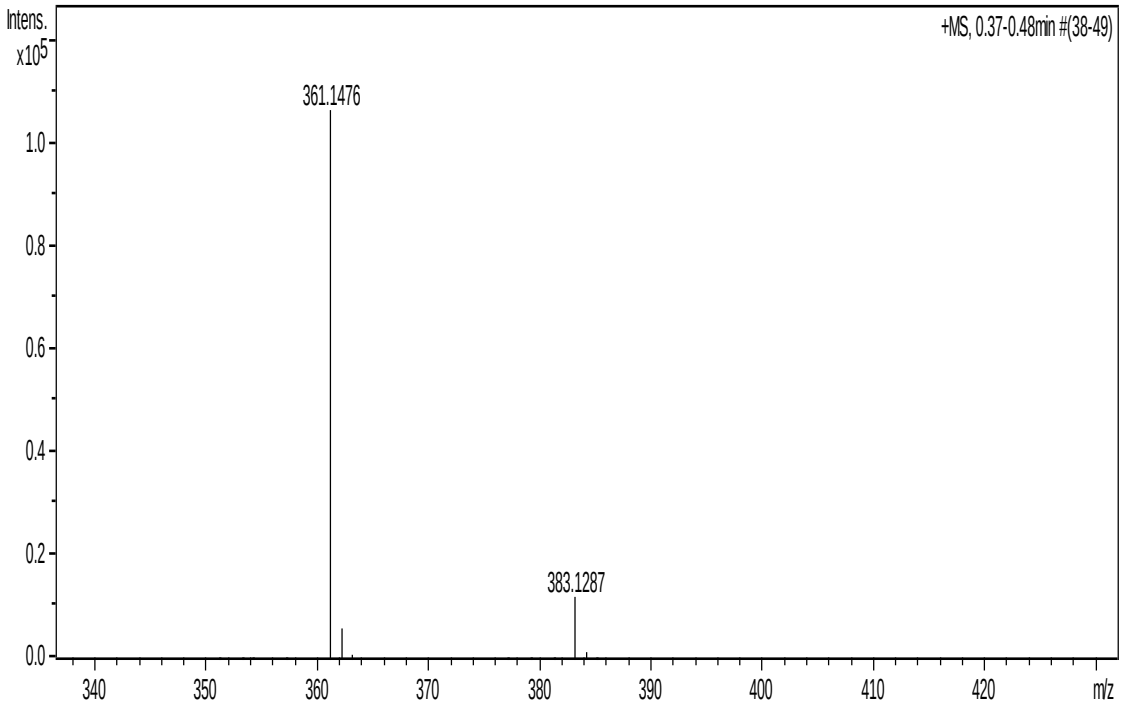
158.162
138.845
138.823
134.296
129.025
128.145
127.460
117.268
117.034
113.950
113.692
113.674
112.059
110.775
110.695
63.589
62.116
58.421
44.665
42.948
40.504
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)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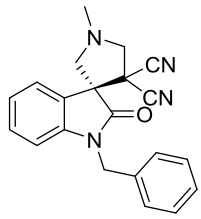
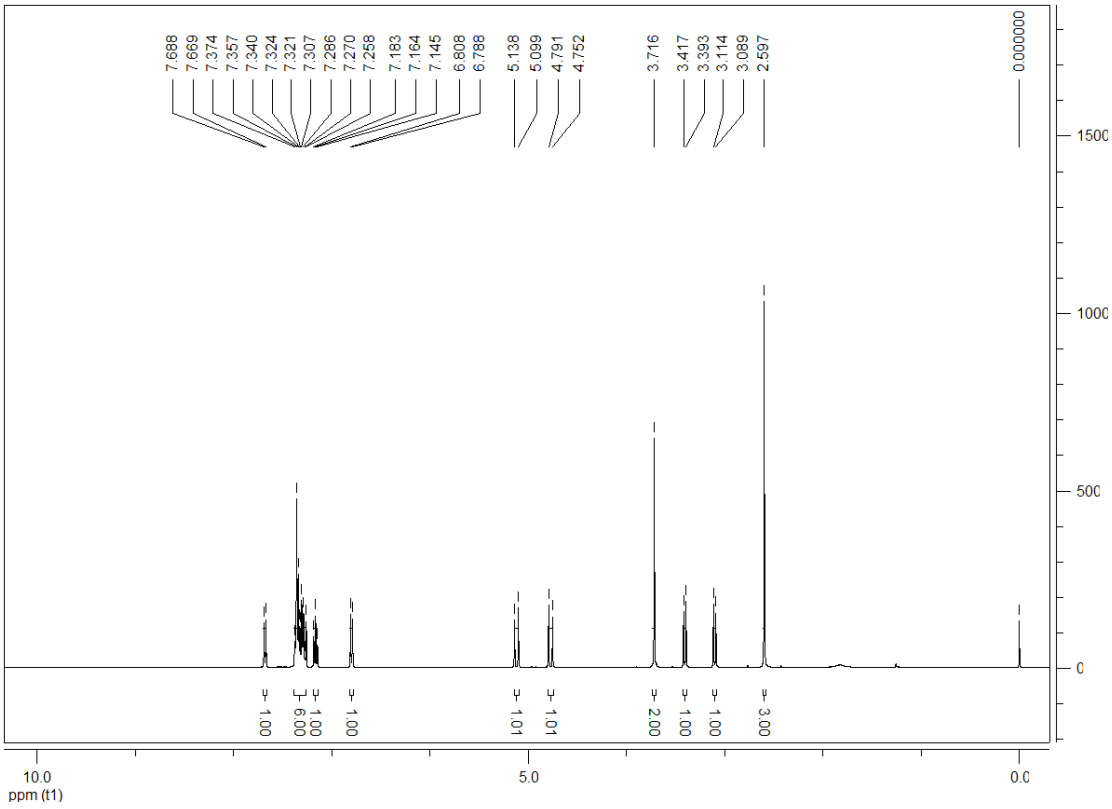
x10^5
+MS, 0.37-0.48min #(38-49)
361.1476
383.1287
1.0
0.8
0.6
0.4
0.2
0.0
340
350
360
370
380
390
400
410
420
m/z

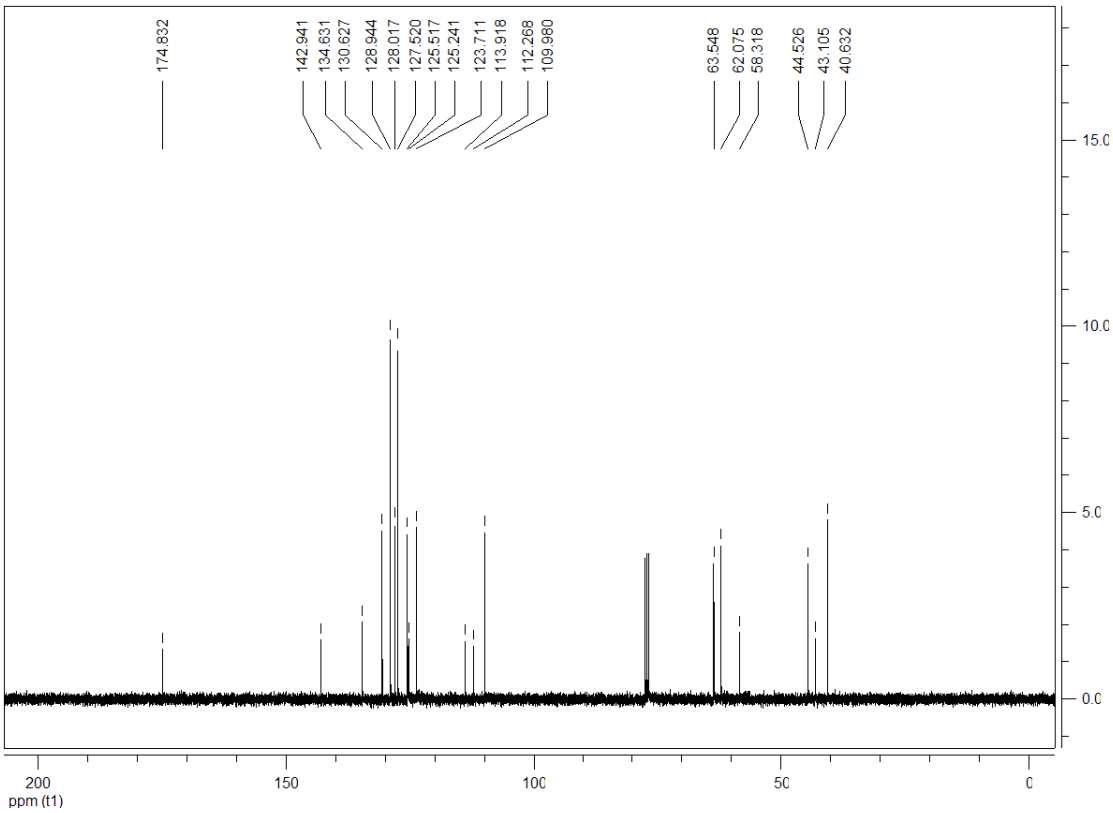
(S)-1-Benzyl-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile

(4c)



white solid, 90%, m.p. 94~96℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.68 (d, *J* = 7.4Hz, 1H, ArH), 7.37~7.27 (m, 6H, ArH), 7.16 (t, *J* = 7.6Hz, 1H, ArH), 6.80 (d, *J* = 8.0Hz, 1H, ArH), 5.12 (d, *J* = 15.6Hz, 1H, CH), 4.77 (d, *J* = 15.6Hz, 1H, CH), 3.72 (s, 2H, CH), 3.40 (d, *J* = 9.6Hz, 1H, CH), 3.10 (d, *J* = 10.0Hz, 1H, CH), 2.60 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8, 142.9, 134.6, 130.6, 128.9, 128.0, 127.5, 125.5, 125.2, 123.7, 113.9, 112.2, 109.9, 63.5, 62.0, 58.3, 44.5, 43.1, 40.6; IR(KBr) υ: 2970, 2942, 2837, 2803, 2247, 1975, 1882, 1809, 1713, 1611, 1493, 1469, 1376, 1354, 1308, 1251, 1201, 1173, 1122, 1078, 1025, 995, 950, 866, 807, 765, 730 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{19}N_4O$ ($[M+H]^+$): 343.1553, found: 343.1572.

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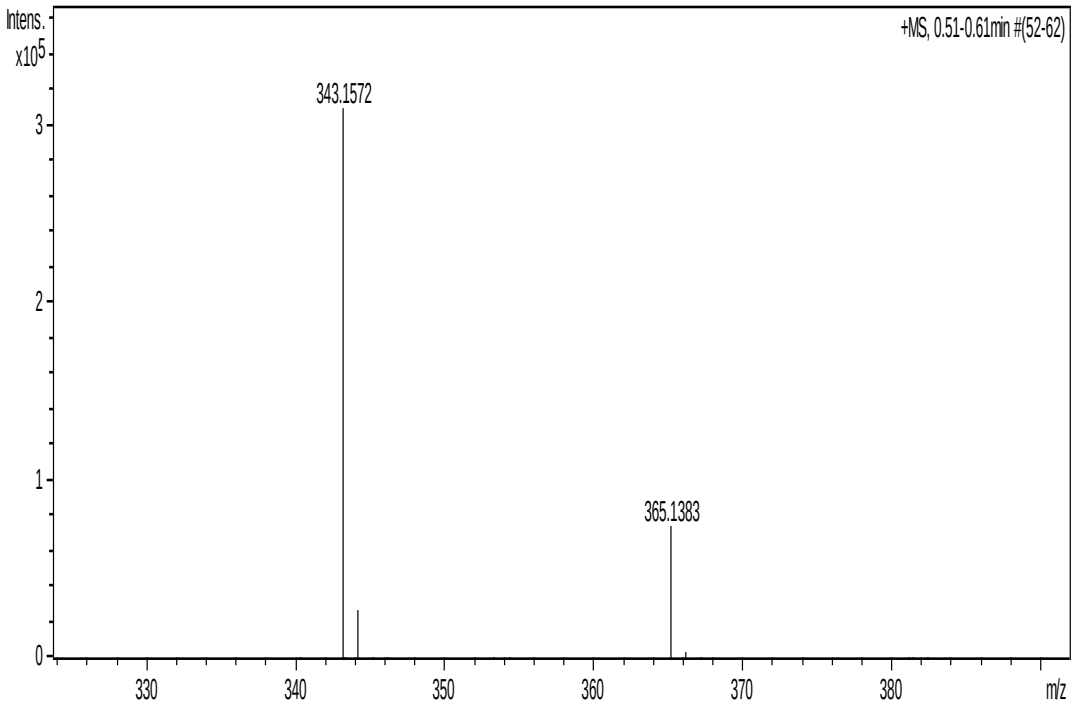
134.631
130.627
128.944
128.017
127.520
125.517
125.241
123.711
113.918
112.268
109.980
63.548
62.075
58.318
44.526
43.105
40.632
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)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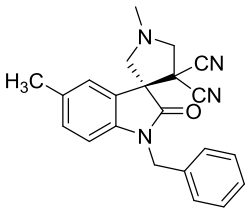
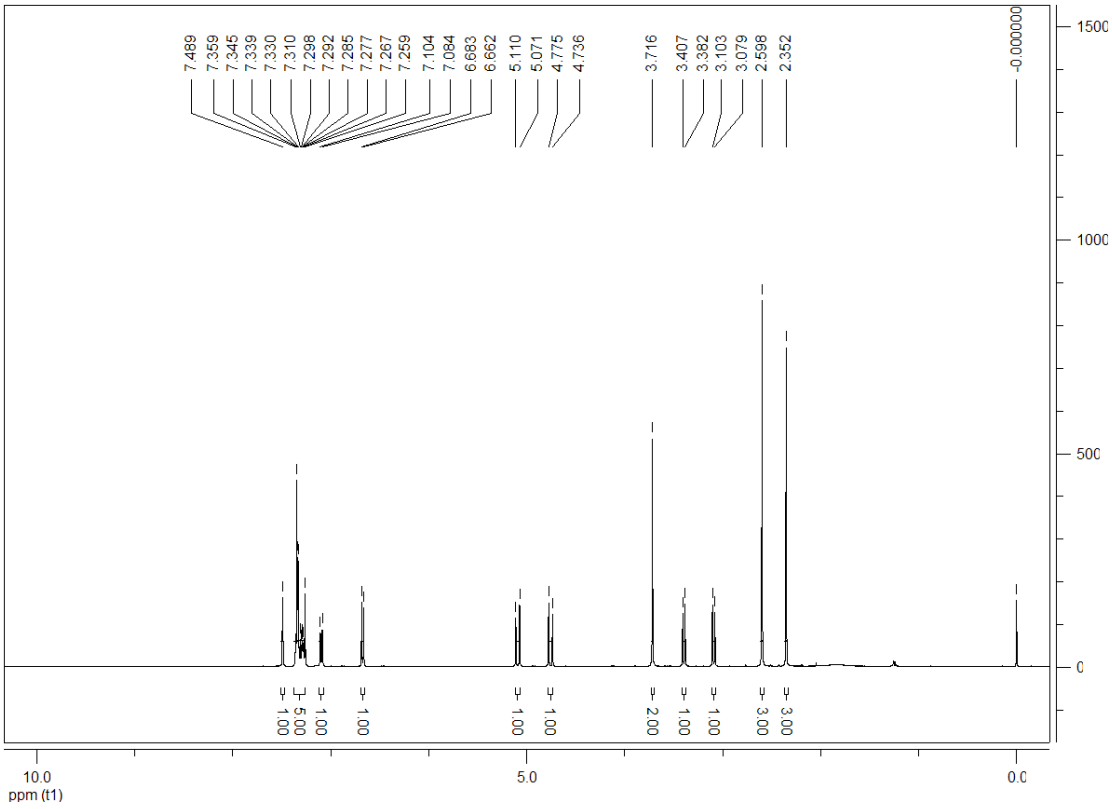
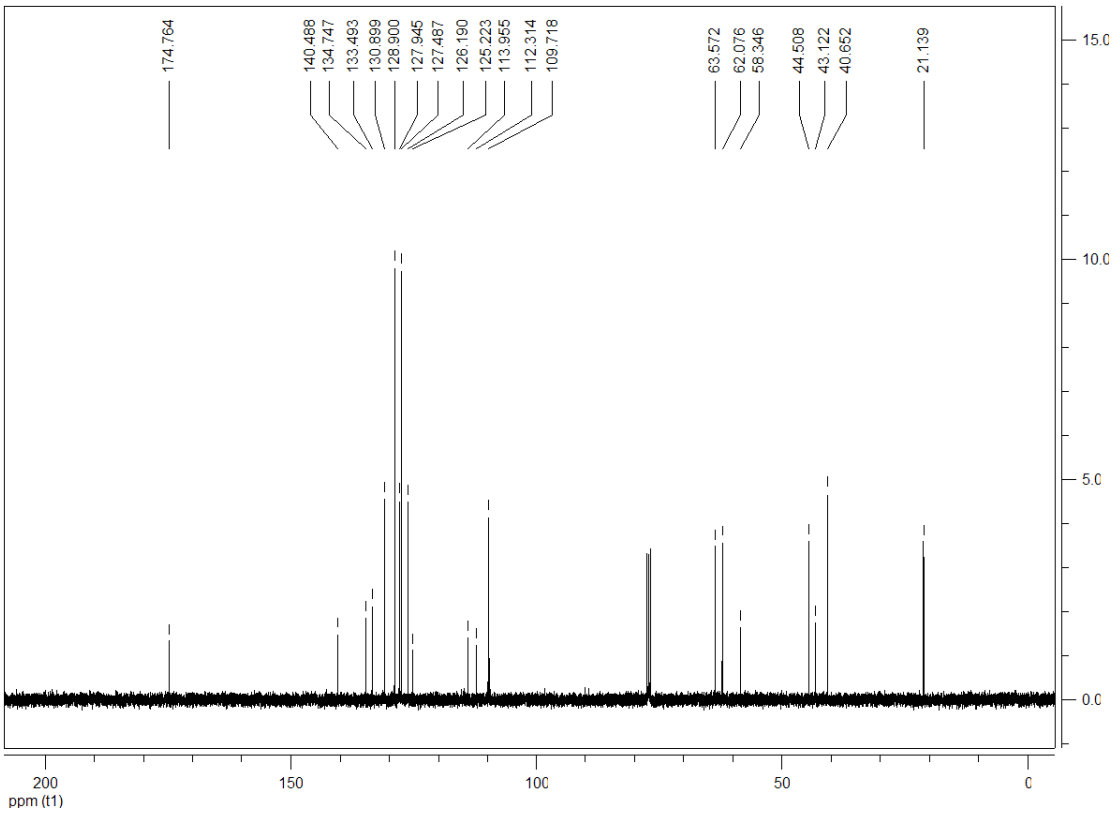
x10^5
+MS, 0.51-0.61min #(52-62)
343.1572
365.1383
3
2
1
0
330
340
350
360
370
380
m/z

(S)-1-Benzyl-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile (4d)



white solid, 94%, m.p. 127~128℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (brs, 1H, ArH), 7.36~7.27 (m, 5H, ArH), 7.09 (d, *J* = 8.0Hz, 1H, ArH), 6.67 (d, *J* = 8.4Hz, 1H, ArH), 5.09(d, *J* = 15.6Hz, 1H, CH), 4.76 (d, *J* = 15.6Hz, 1H, CH), 3.72 (s, 2H, CH), 3.39 (d, *J* = 10.0Hz, 1H, CH), 3.09 (d, *J* = 9.6Hz, 1H, CH), 2.60 (s, 3H, CH_3), 2.35(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 140.4, 134.7, 133.4, 130.8, 128.8, 127.9, 127.4, 126.1, 125.2, 113.9, 112.3, 109.7, 63.5, 62.0, 58.3, 44.5, 43.1, 40.6, 21.1; IR(KBr) υ: 2999, 2963, 2930, 2852, 2805, 2248, 1960, 1883, 1819, 1711, 1607, 1497, 1462, 1371, 1343, 1289, 1249, 1197, 1165, 1133, 1075, 1027, 991, 960, 913, 875, 810, 759, 733 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{22}H_{21}N_4O$ ($[M+H]^+$): 357.1710, found: 357.1727.

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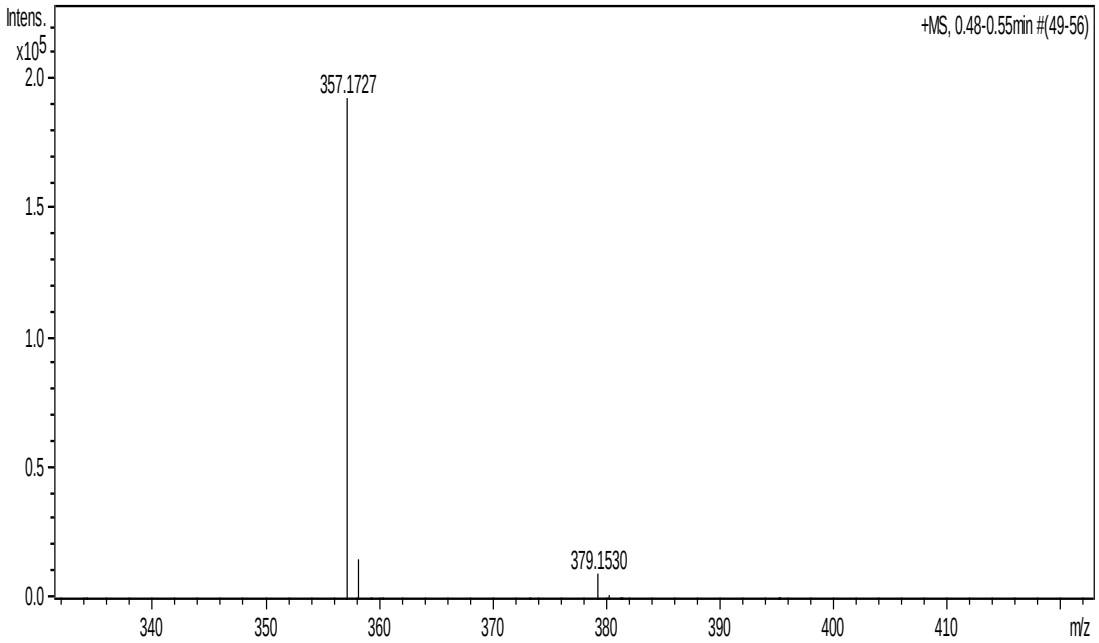
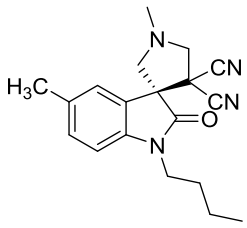
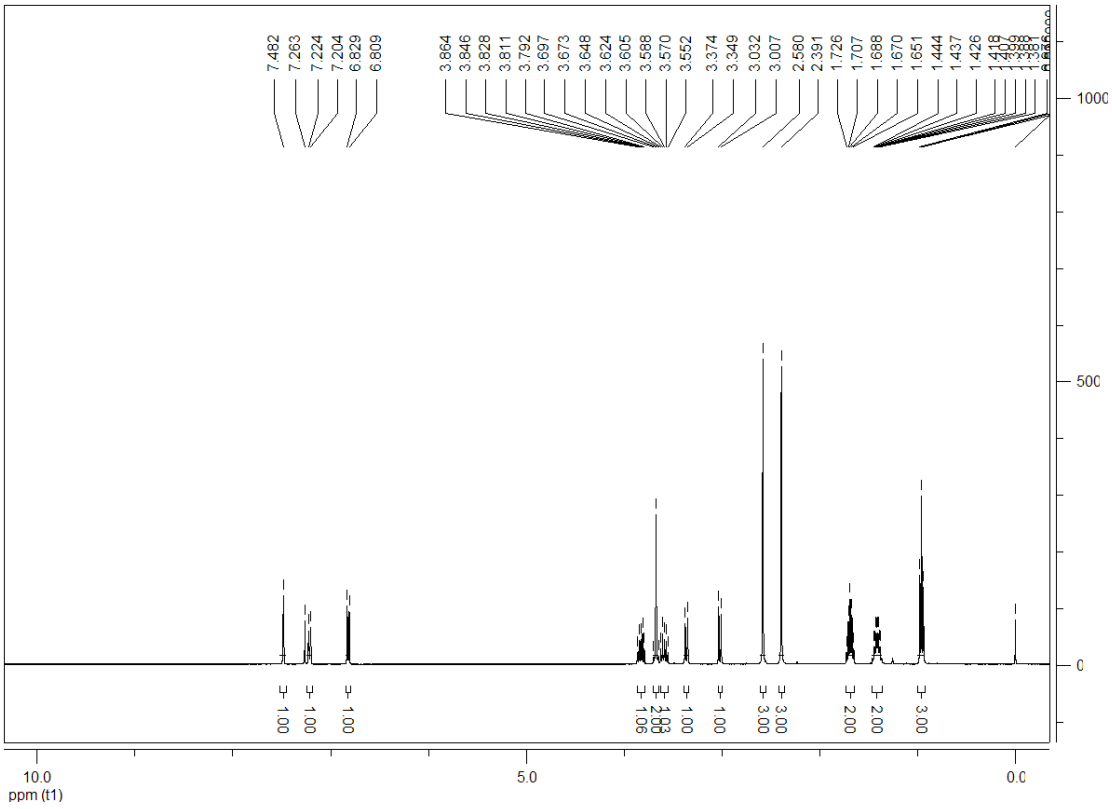
134.747
133.493
130.899
128.900
127.945
127.487
126.190
125.223
113.955
112.314
109.718
63.572
62.076
58.346
44.508
43.122
40.652
21.139
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

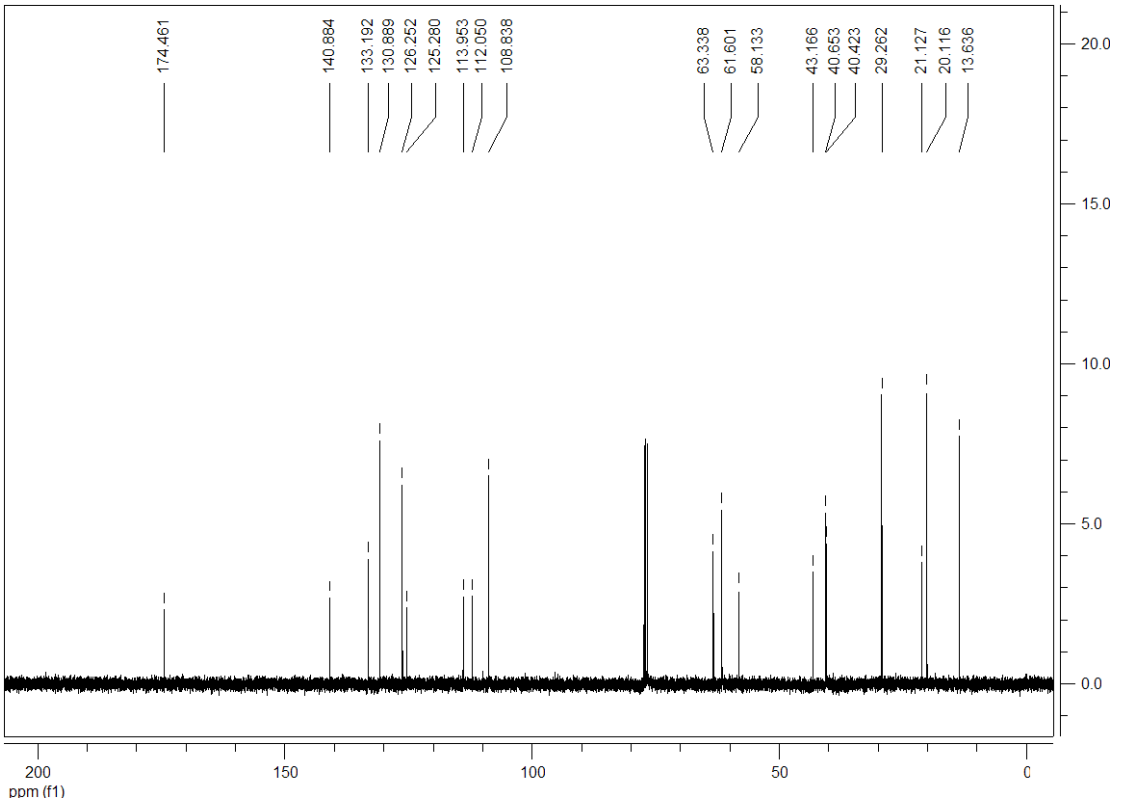

Intens.
x10^5
2.0
1.5
1.0
0.5
0.0
+MS, 0.48-0.55min #(49-56)
357.1727
379.1530
340
350
360
370
380
390
400
410
m/z

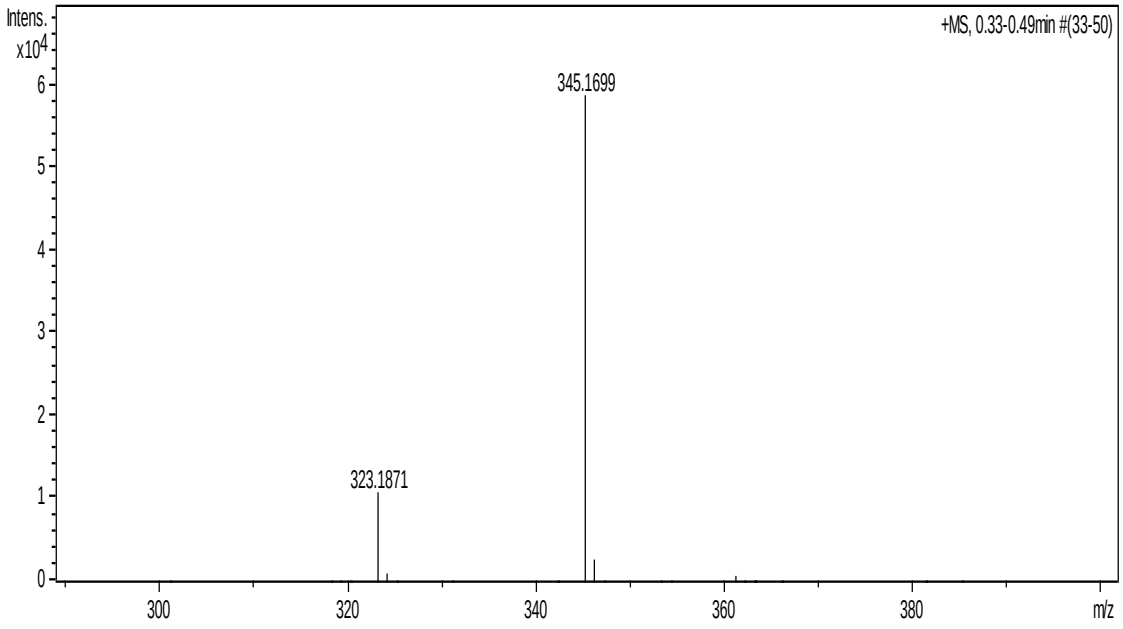
(S)-1-Butyl-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitril e (4e)



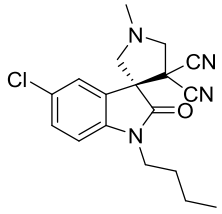
white solid, 91%, m.p. 65~67℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (brs, 1H, ArH), 7.21 (d, *J* = 8.0Hz, 1H, ArH), 6.82 (d, *J* = 8.0Hz, 1H, ArH), 3.86~3.79 (m, 1H, CH), 3.67 (t, *J* = 9.6Hz, 2H, CH), 3.62~3.55 (m, 1H, CH), 3.36 (d, *J* = 10.0Hz, 1H, CH), 3.02 (d, *J* = 10.0Hz, 1H, CH), 2.58 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 1.73~1.65 (m, 2H, CH), 1.41 (qd, J_1= 7.2Hz, J_2= 3.2Hz , 2H, CH), 0.96 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 140.8, 133.1, 130.8, 126.2, 125.2, 113.9, 112.0, 108.8, 63.3, 61.6, 58.1, 43.1, 40.6, 40.4, 29.2, 21.1, 20.1, 13.6; IR(KBr) υ: 2939, 2866, 2803, 2252, 1889, 1709, 1613, 1498, 1464, 1365, 1297, 1248, 1201, 1172, 1122, 1058, 1032, 969, 897, 872, 815, 749 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{19}H_{22}N_4NaO$ ([M+Na]$^+$): 345.1686, found: 345.1699.



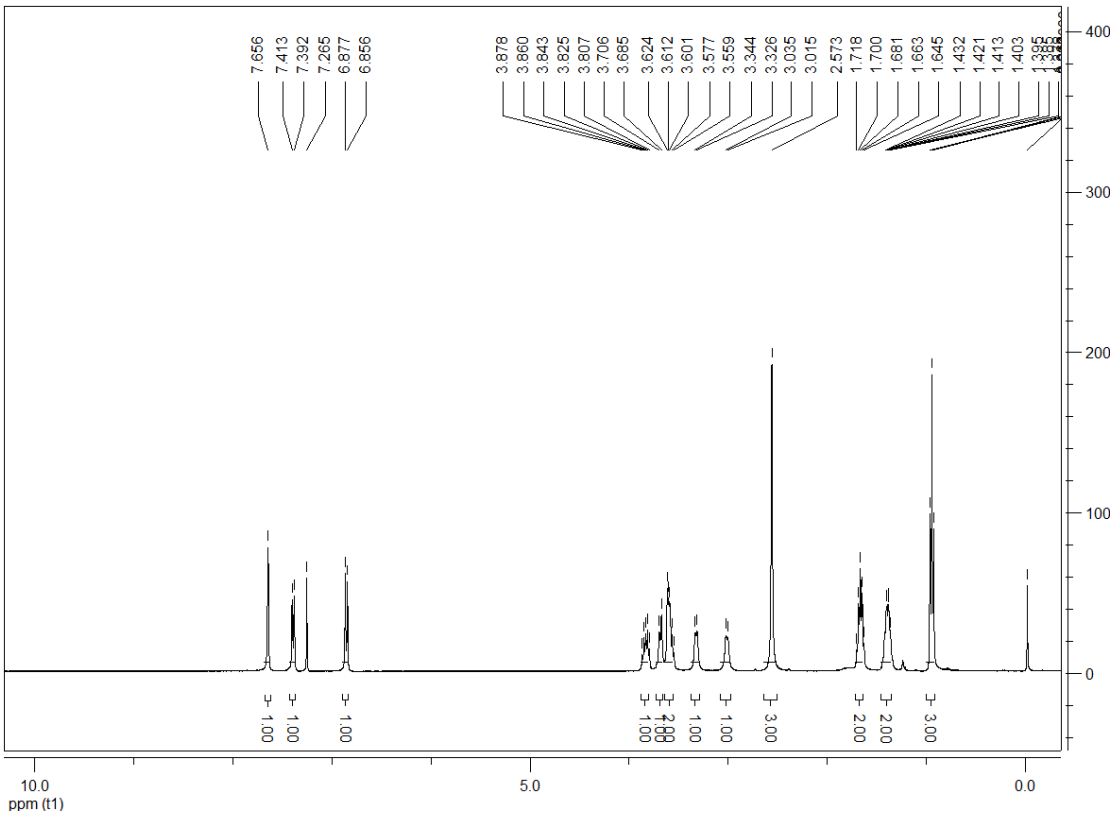

174.461
140.884
133.192
130.889
126.252
125.280
113.953
112.050
108.838
63.338
61.601
58.133
43.166
40.653
40.423
29.262
21.127
20.116
13.636
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

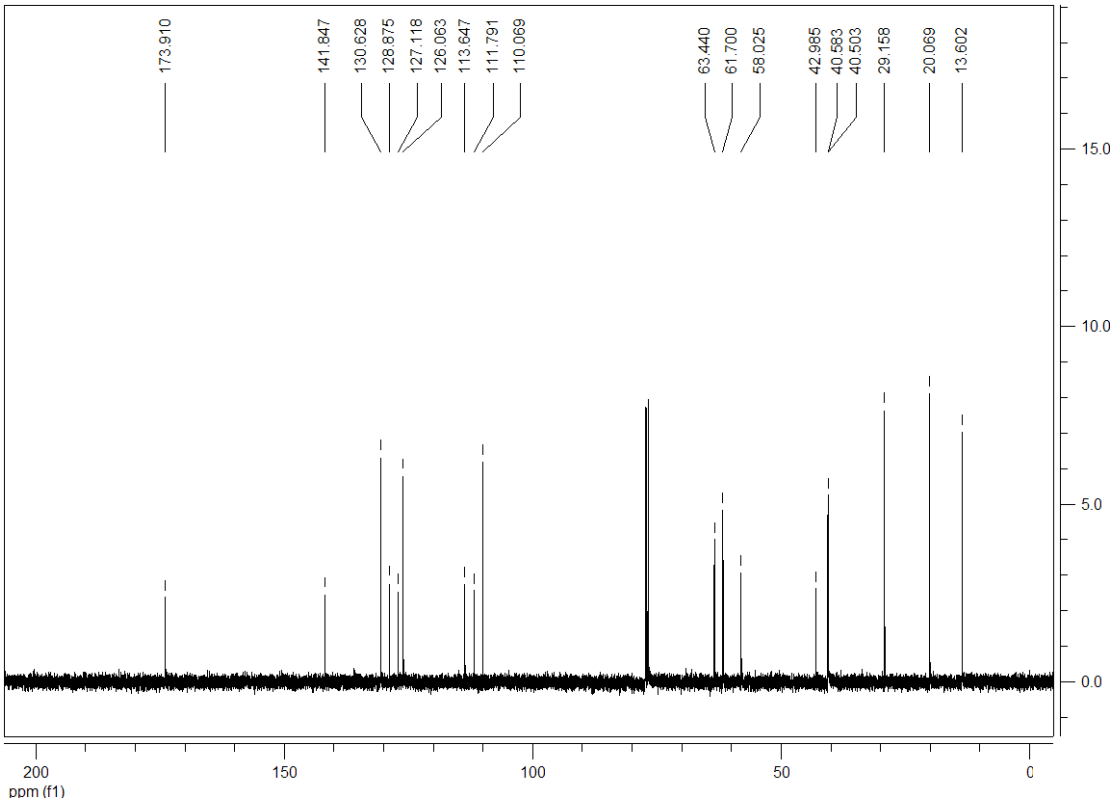

Intens.
x10^4
+MS, 0.33-0.49min #(33-50)
345.1699
323.1871
6
5
4
3
2
1
0
300
320
340
360
380
m/z

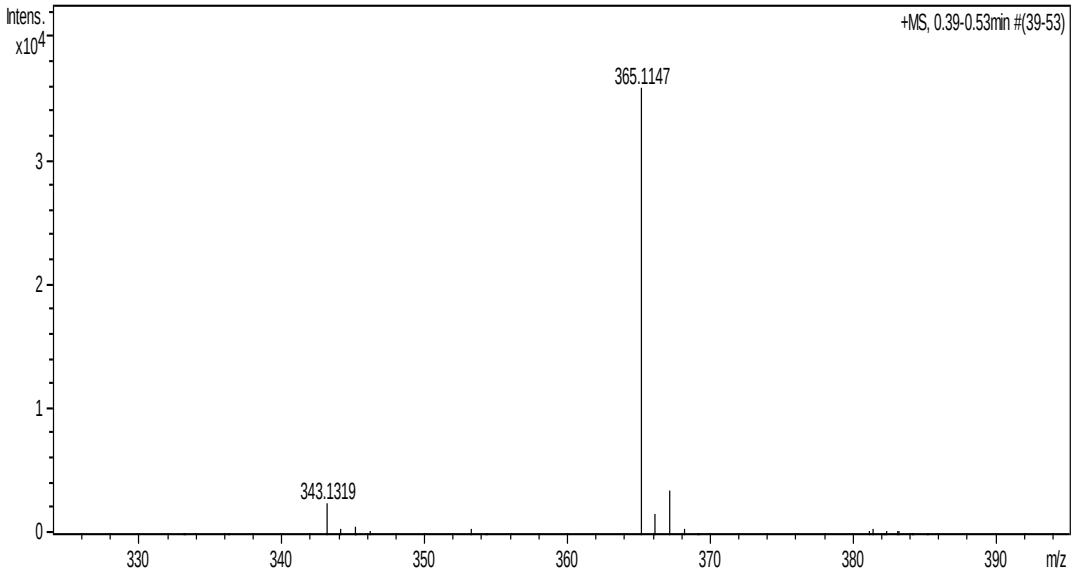
(S)-1-Butyl-5-chloro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarb onitrile (4f)



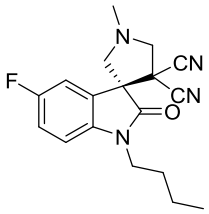
white solid, 93%, m.p. 93~95℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66 (brs, 1H, ArH), 7.40 (d, *J* = 8.4Hz, 1H, ArH), 6.87 (d, *J* = 8.4Hz, 1H, ArH), 3.88~3.81 (m, 1H, CH), 3.71~3.68 (m, 1H, CH), 3.62~3.56 (m, 2H, CH), 3.34 (d, *J* = 7.2Hz, 1H, CH), 3.02 (d, *J* = 8.0Hz, 1H, CH), 2.57 (s, 3H, CH_3), 1.72~1.64 (m, 2H, CH), 1.43~1.38 (m, 2H, CH), 0.96 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.9, 141.8, 130.6, 128.8, 127.1, 126.0, 113.6, 111.7, 110.0, 63.4, 61.7, 58.0, 42.9, 40.5, 40.5, 29.1, 20.0, 13.6; IR (KBr) υ: 2958, 2869, 2812, 2251, 1867, 1718, 1609, 1483, 1433, 1347, 1310, 1266, 1191, 1135, 1113, 1082, 1033, 986, 943, 882, 814, 735 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{18}H_{19}ClN_4NaO$ ($[M+Na]^+$): 365.1140, found: 365.1147.



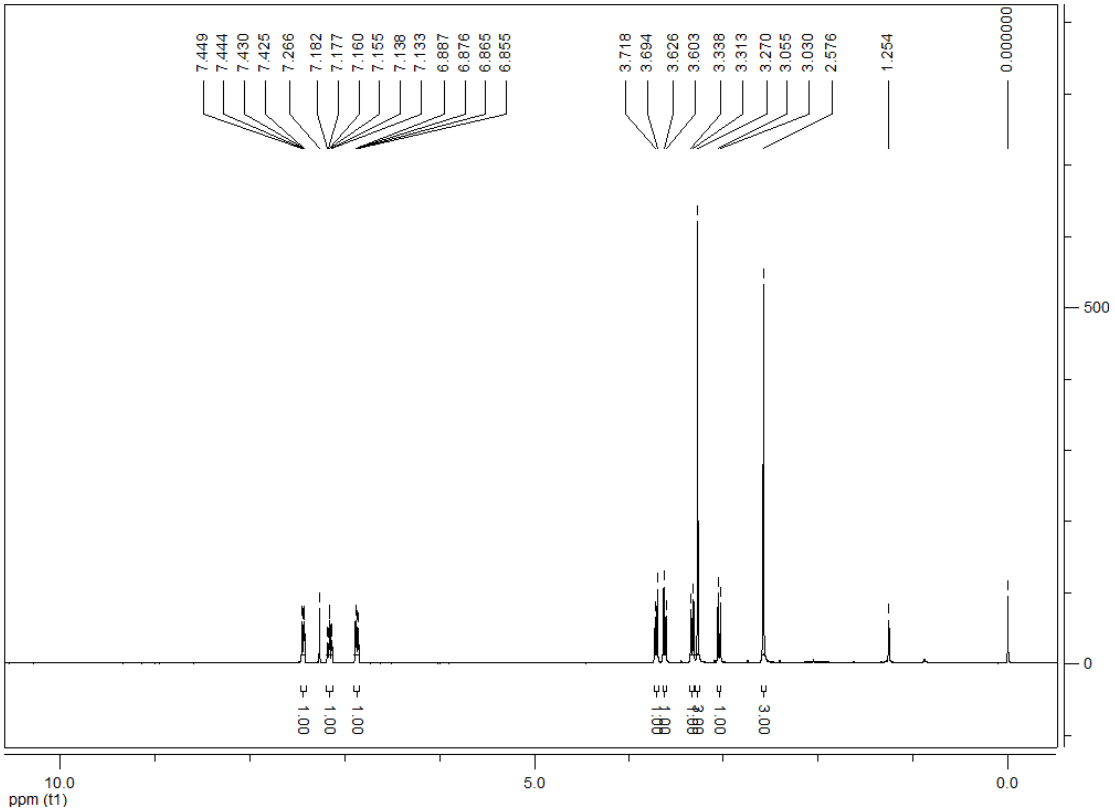

173.910
141.847
130.628
128.875
127.118
126.063
113.647
111.791
110.069
63.440
61.700
58.025
42.985
40.583
40.503
29.158
20.069
13.602
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

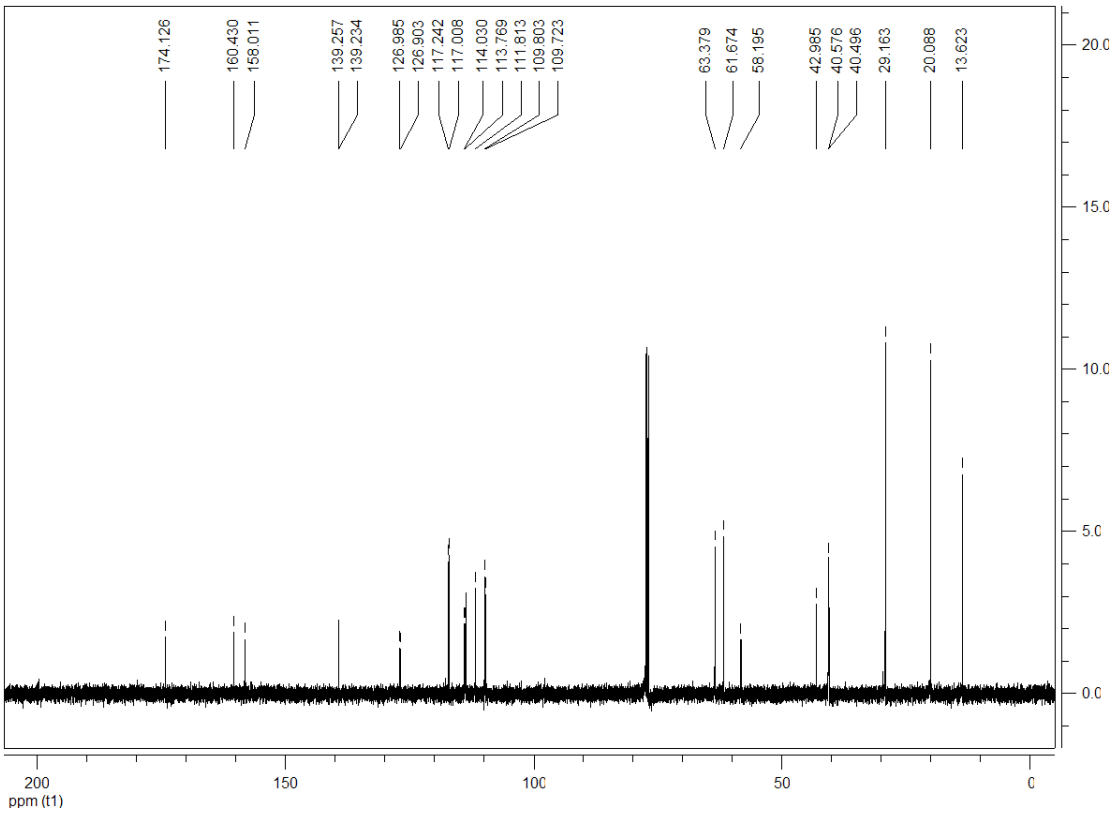

Intens.
x10^4
+MS, 0.39-0.53min #(39-53)
365.1147
343.1319
3
2
1
0
330
340
350
360
370
380
390
m/z

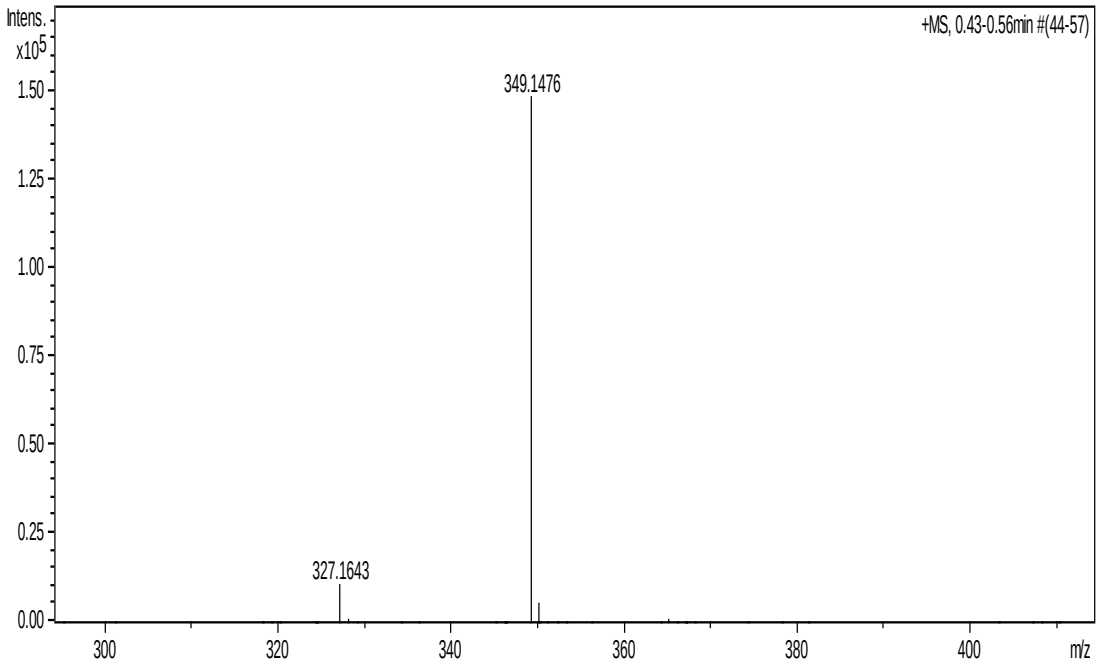
(S)-1-Butyl-5-fluoro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbo nitrile (4g)



white solid, 89%, m.p. 96~97℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J_1= 8.0Hz, J_2 = 2.4Hz , 1H, ArH), 7.14 (td, J_1 = 8.4Hz, J_2 = 2.4Hz, 1H, ArH), 6.87 (dd, J_1 = 8.4Hz, J_2 = 4.0Hz , 1H, ArH), 3.88~3.81 (m, 1H, CH), 3.69 (d, J = 9.2Hz, 1H, CH), 3.64~3.56 (m, 2H, CH), 3.33 (d, J = 9.6Hz, 1H, CH), 3.03 (d, J = 10.0Hz, 1H, CH), 2.57 (s, 3H, CH_3), 1.72~1.65 (m, 2H, CH), 1.46~1.36 (m, 2H, CH), 0.96 (t, J = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.1, 159.2 (d, J = 241.9Hz), 139.2 (d, J = 2.3Hz), 126.9 (d, J = 8.2Hz), 117.1 (d, J = 23.4Hz), 113.9 (d, J = 26.1Hz), 111.8, 109.8 (d, J = 8.0Hz), 63.5, 61.7, 58.2, 42.9, 40.5 (d, J = 8.0Hz), 29.2, 20.1, 13.6; IR(KBr) υ: 2968, 2936, 2864, 2801, 2251, 1853, 1718, 1616, 1494, 1455, 1356, 1276, 1250, 1211, 1183, 1131, 1034, 971, 915, 890, 818, 748 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{18}H_{19}FN_4ONa$ ([M+Na]$^+$): 349.1435, found: 349.1476.

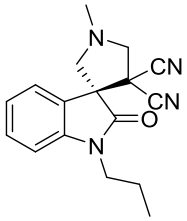



174.126
160.430
158.011
139.257
139.234
126.985
126.903
117.242
117.008
114.030
113.769
111.813
109.803
109.723
63.379
61.674
58.195
42.985
40.576
40.496
29.163
20.088
13.623
200
150
100
50
0
ppm (t1)

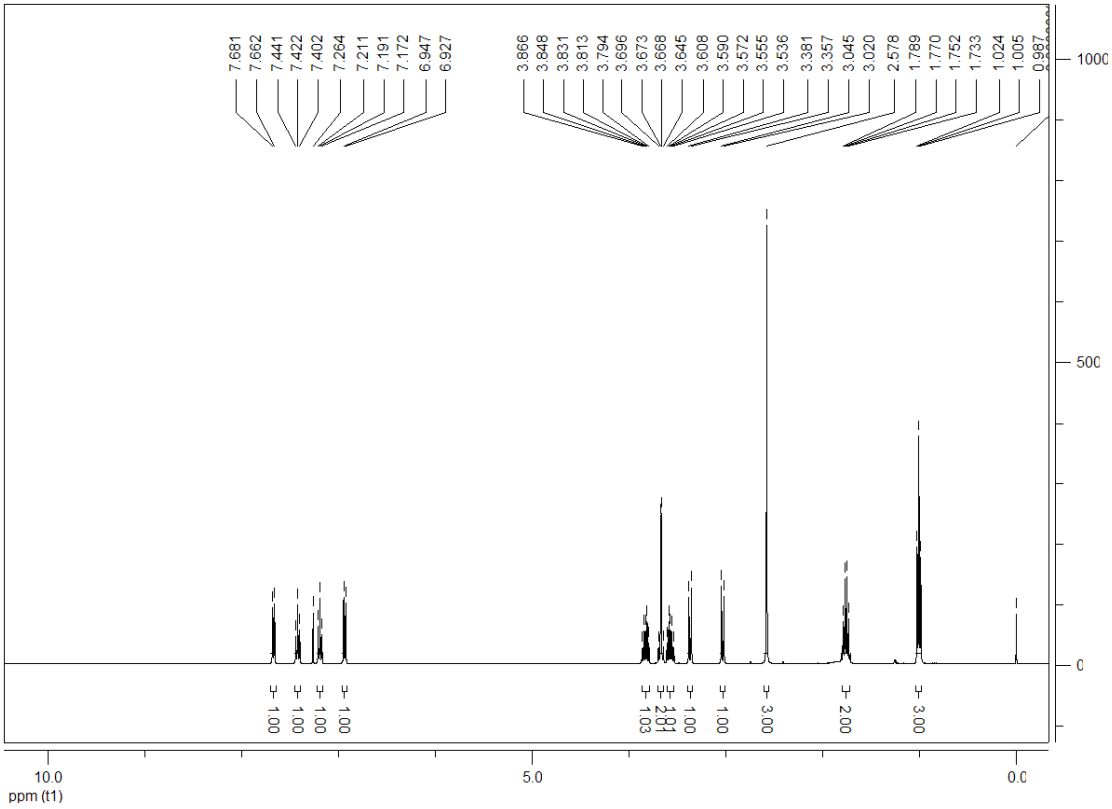

Intens.
x10^5
+MS, 0.43-0.56min #(44-57)
349.1476
327.1643
300
320
340
360
380
400
m/z

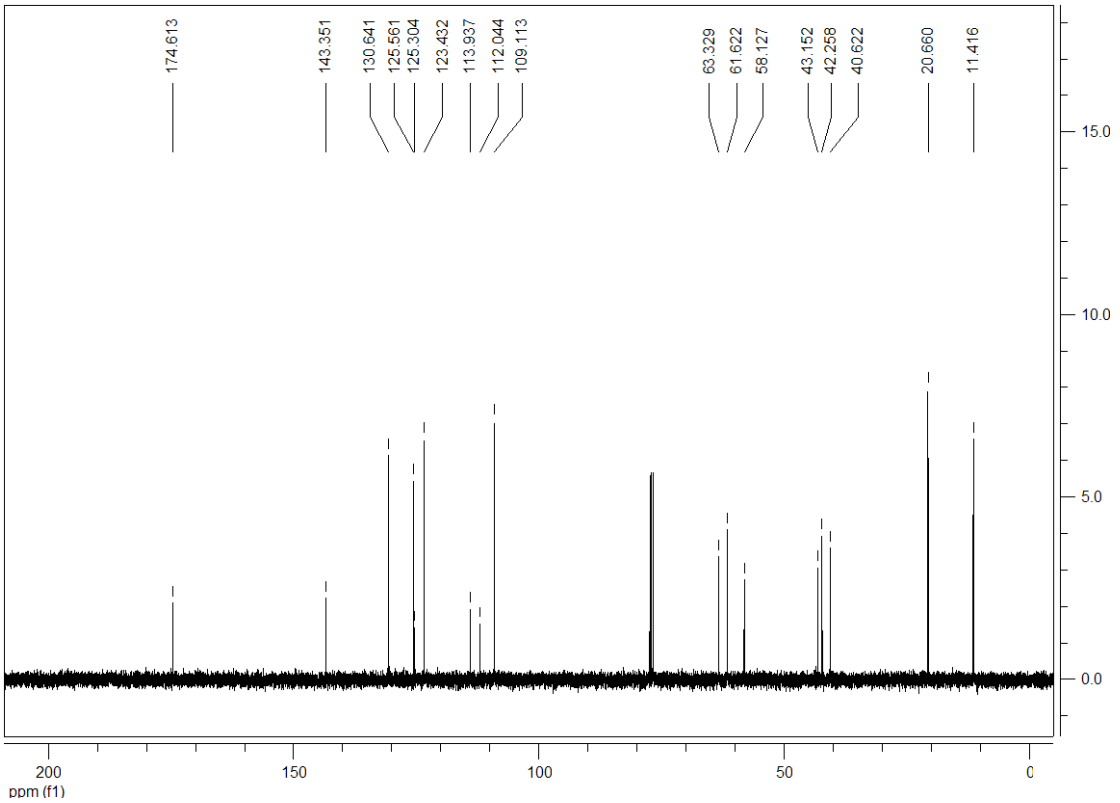
(S)-1'-Methyl-2-oxo-1-propylspiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile

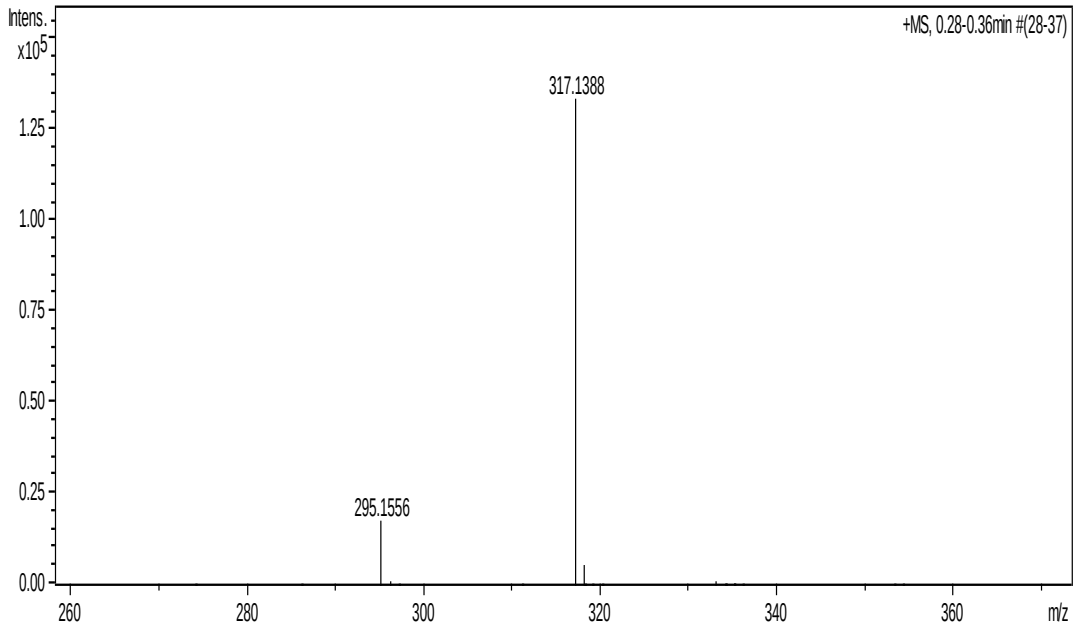
(4h)



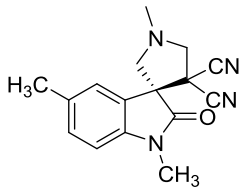
white solid, 93%, m.p. 125~127℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 7.6Hz, 1H, ArH), 7.42 (t, *J* = 7.6Hz, 1H, ArH), 7.19 (t, *J* = 7.6Hz, 1H, ArH), 6.94 (d, *J* = 8.0Hz, 1H, ArH), 3.87~3.79 (m, 1H, CH), 3.70~3.64 (m, 2H, CH), 3.61~3.57(m, 1H, CH), 3.37 (d, *J* = 9.6Hz, 1H, CH), 3.03 (d, *J* = 10.0Hz, 1H, CH), 2.58 (s, 3H, CH_3), 1.79~1.73 (m, 2H, CH), 0.96 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 143.3, 130.6, 125.5, 125.3, 123.4, 113.9, 112.0, 109.1, 63.3, 61.6, 58.1, 43.1, 42.2, 40.6, 20.6, 11.4; IR(KBr) υ: 2971, 2944, 2849, 2791, 2249, 1959, 1912, 1713, 1611, 1490, 1465, 1360, 1301, 1254, 1210, 1170, 1129, 1104, 1060, 1032, 961, 925, 886, 756 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{17}H_{18}N_4NaO$ ($[M+Na]^+$): 317.1373, found: 317.1388.



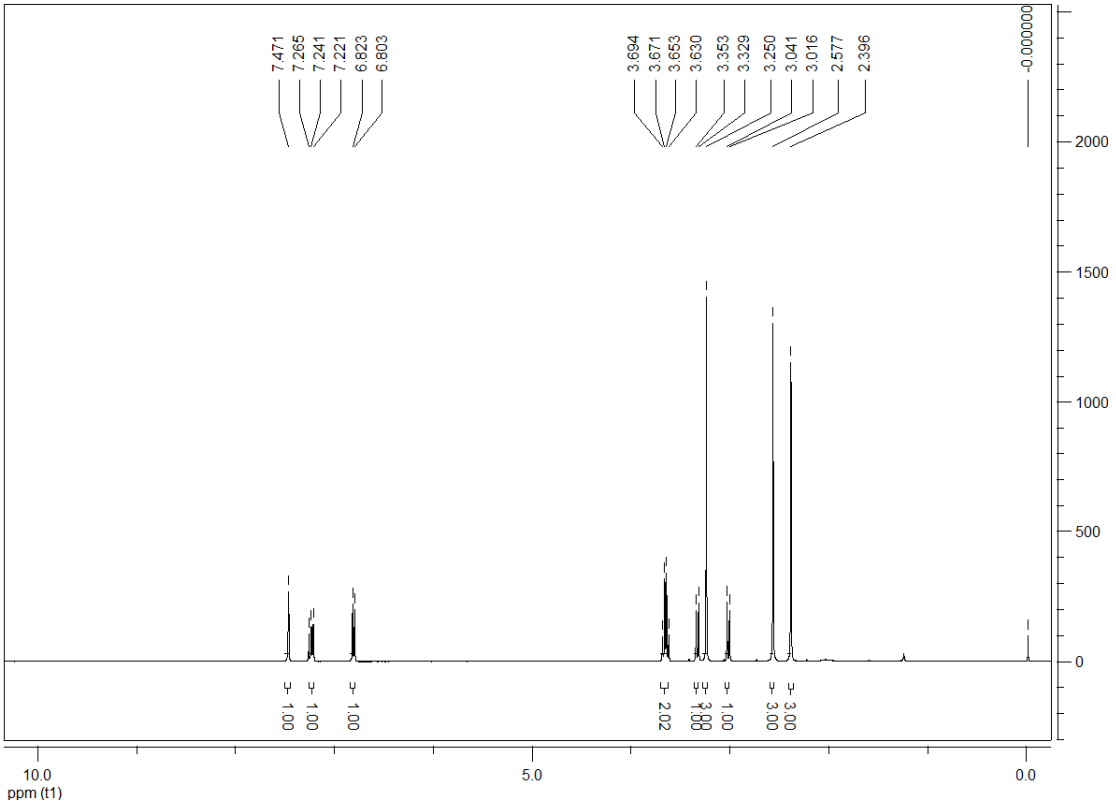

174.613
143.351
130.641
125.561
125.304
123.432
113.937
112.044
109.113
63.329
61.622
58.127
43.152
42.258
40.622
20.660
11.416
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

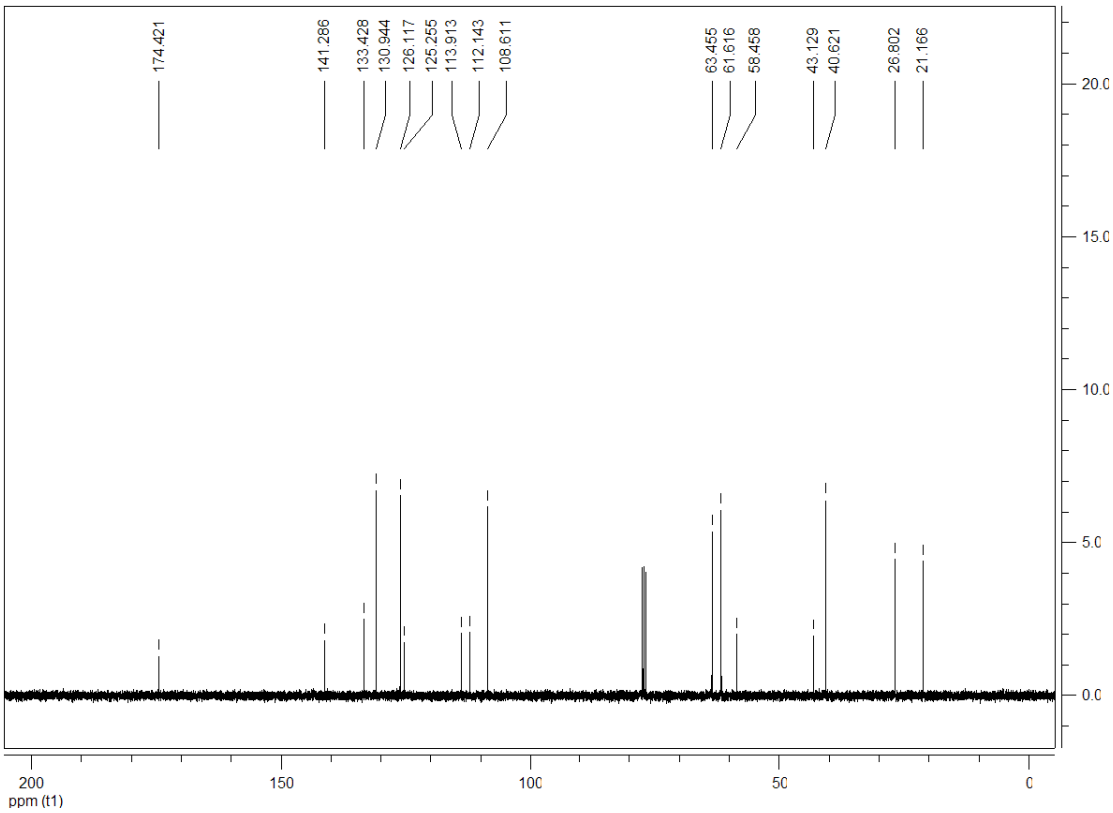

Intens.
x10^5
+MS, 0.28-0.36min #(28-37)
317.1388
295.1556
1.25
1.00
0.75
0.50
0.25
0.00
260
280
300
320
340
360
m/z

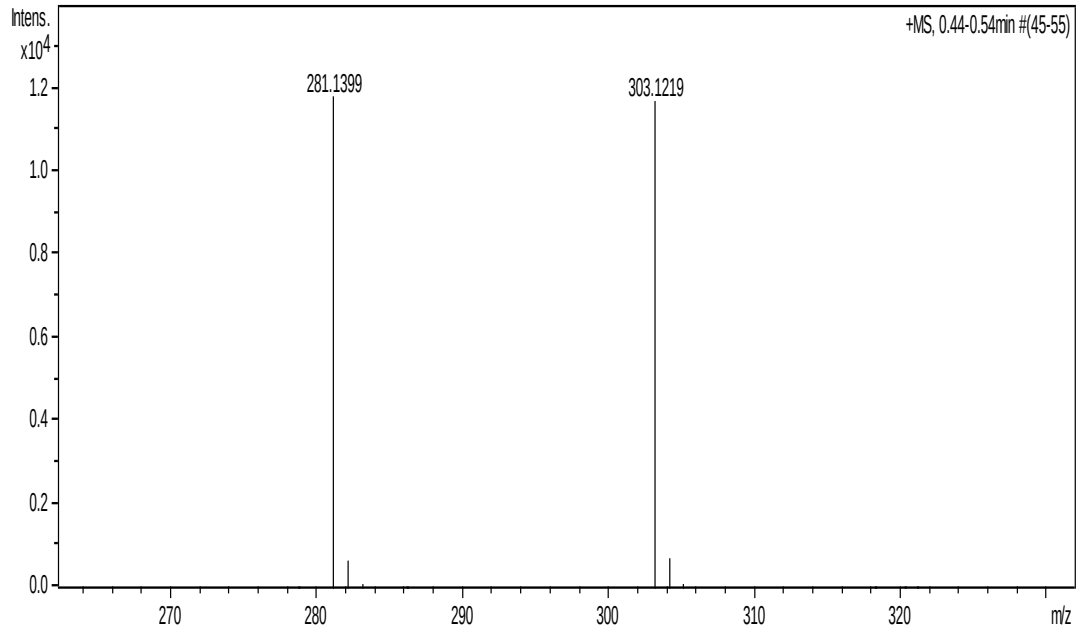
(S)-1,1',5-Trimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile (4i)



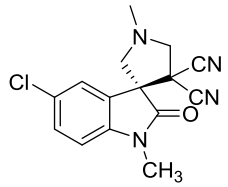
white solid, 88%, m.p. 132~134℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (s, 1H, ArH), 7.23 (d, *J* = 8.0Hz, 1H, ArH), 6.81 (d, *J* = 8.0Hz, 1H, ArH), 3.66(q, *J* = 9.2Hz, 2H, CH), 3.34 (d, *J* = 9.6Hz, 1H, CH), 3.25 (s, 3H, CH_3), 3.03 (d, *J* = 10.0Hz, 1H, CH), 2.58 (s, 3H, CH_3), 2.40(s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 141.2, 133.4, 130.9, 126.1, 125.2, 113.9, 112.1, 108.6, 63.4, 61.6, 58.4, 43.1, 40.6, 26.8, 21.1; IR(KBr) υ: 2962, 2922, 2854, 2806, 2703,2249, 1873, 1832, 1714, 1613, 1498, 1467, 1354, 1245, 1210, 1172, 1141, 1104, 1049, 1008, 962, 906, 876, 810, 744 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{16}H_{17}N_4O$ ($[M+H]^+$): 281.1397, found: 281.1399.



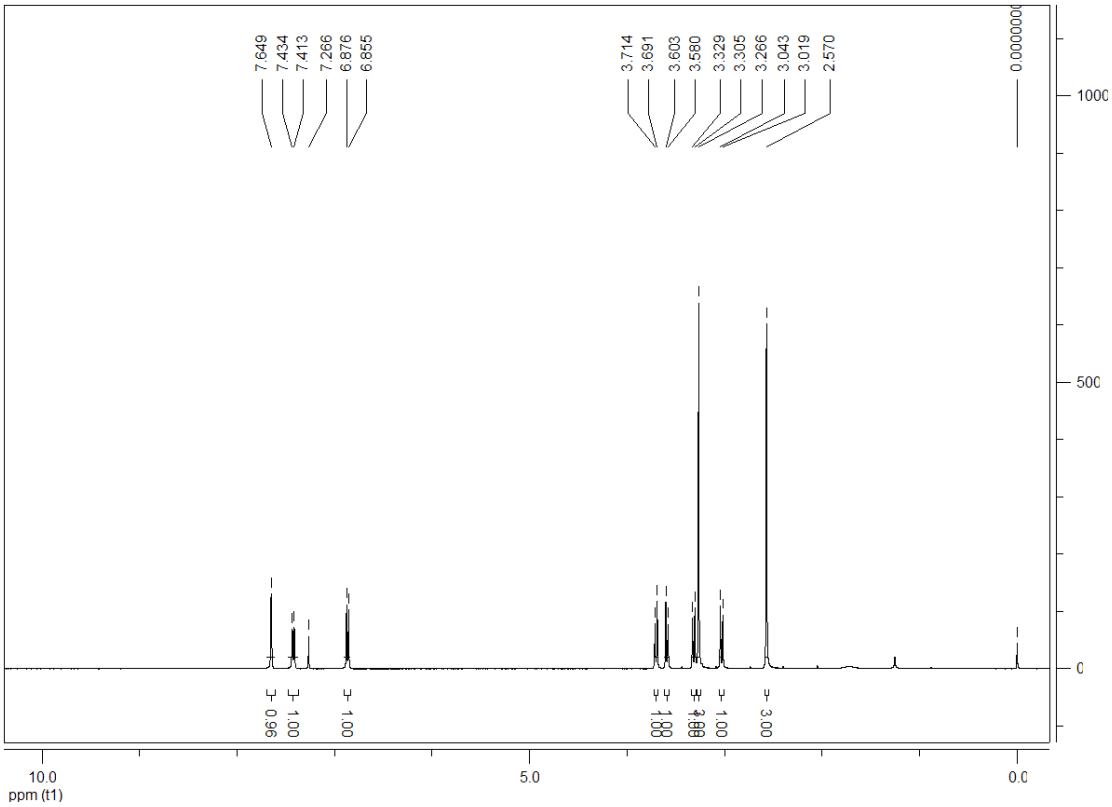

174.421
141.286
133.428
130.944
126.117
125.255
113.913
112.143
108.611
63.455
61.616
58.458
43.129
40.621
26.802
21.166
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

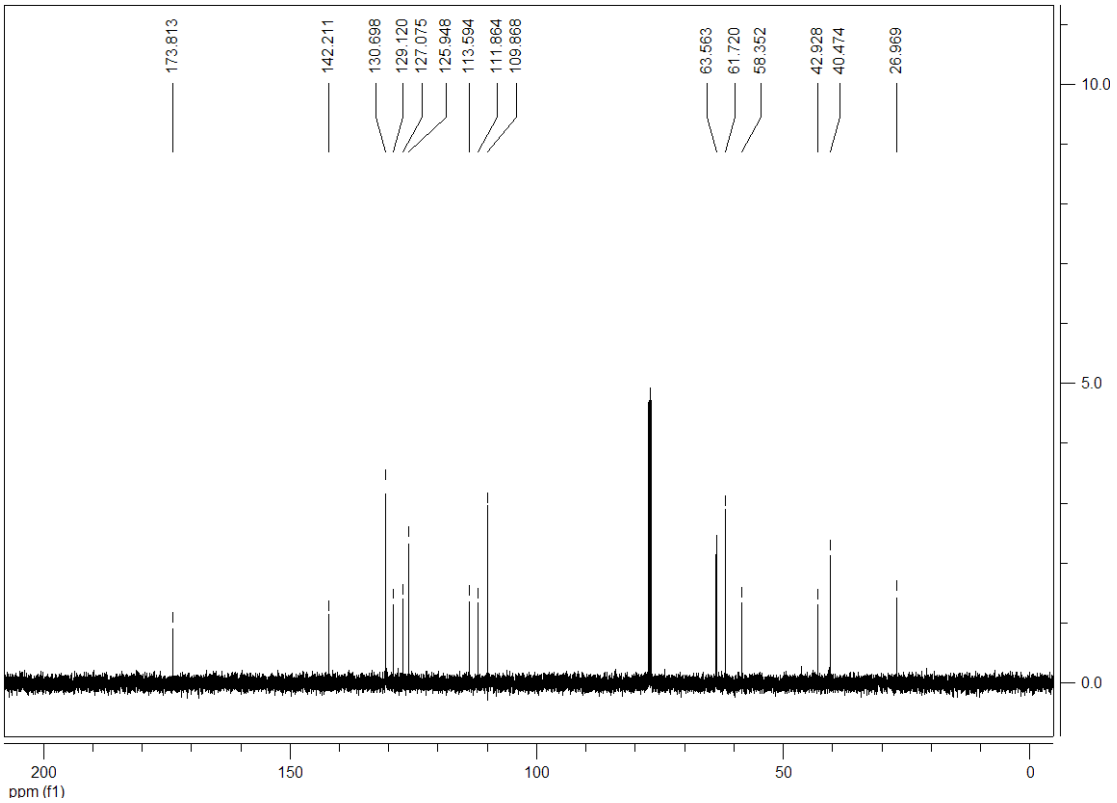

Intens.
x10^4
+MS, 0.44-0.54min #(45-55)
281.1399
303.1219
1.2
1.0
0.8
0.6
0.4
0.2
0.0
270
280
290
300
310
320
m/z

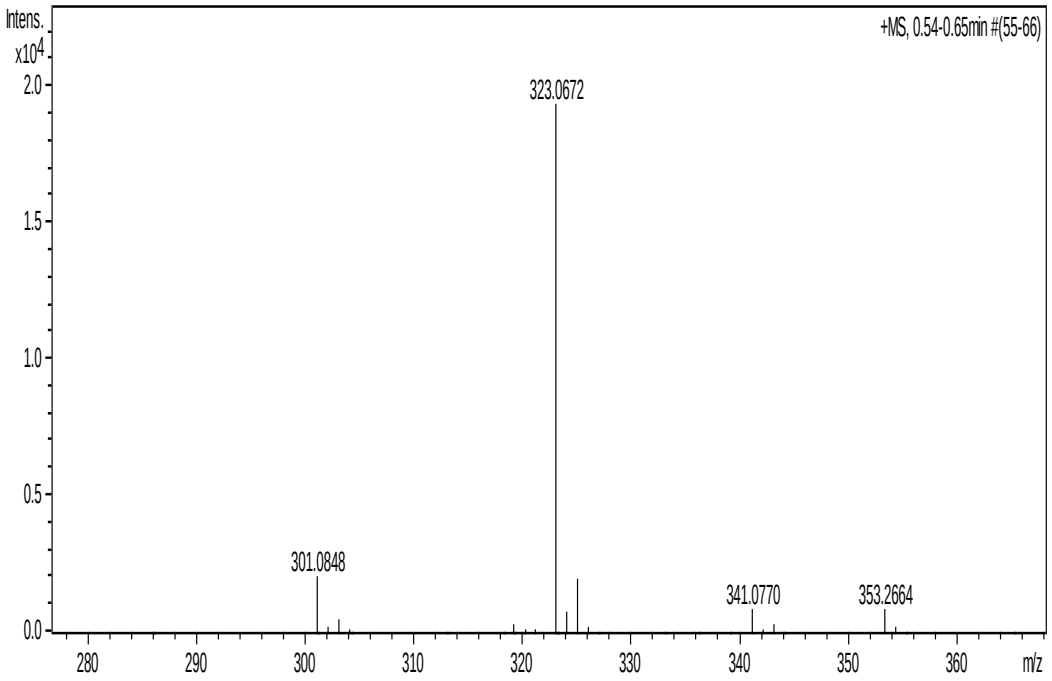
(S)-5-Chloro-1,1'-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile (4j)



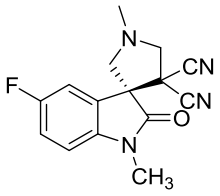
white solid, 84%, m.p. 164~166℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (brs, 1H, ArH), 7.42 (d, *J* = 8.4Hz, 1H, ArH), 6.87 (d, *J* = 8.4Hz, 1H, ArH), 3.70 (d, *J* = 9.2Hz, 1H, CH), 3.59 (d, *J* = 9.2Hz, 1H, CH), 3.32 (d, *J* = 9.4Hz, 1H, CH), 3.27 (s, 3H, CH_3), 3.03 (d, *J* = 9.6Hz, 1H, CH), 2.57 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.8, 142.2, 130.6, 129.1, 127.0, 125.9, 113.5, 111.8, 109.8, 63.5, 61.7, 58.3, 42.9, 40.4, 26.9; IR(KBr) υ: 2954, 2868, 2812, 2247 1865, 1721, 1609, 1491, 1465, 1425, 1347, 1271, 1239, 1165, 1144, 1104, 1049, 960, 907, 882, 813, 742 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{15}H_{13}ClN_4NaO$ ($[M+Na]^+$): 323.0670, found: 323.0672.



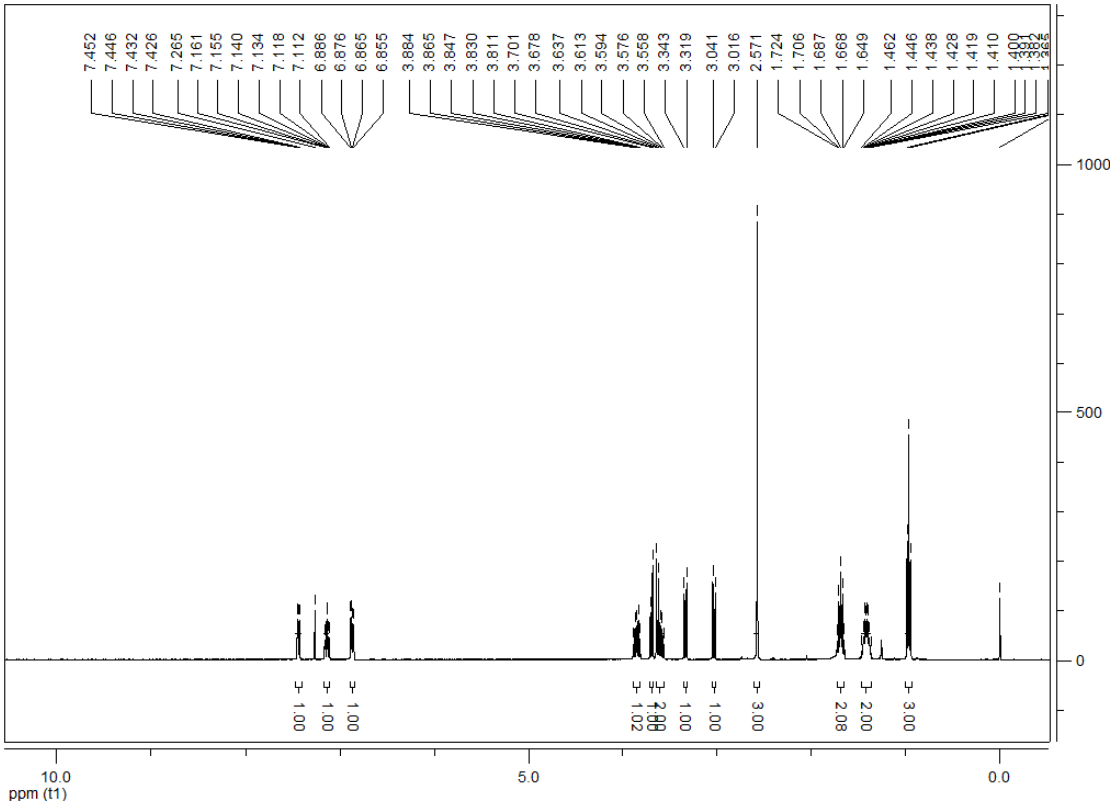

173.813
142.211
130.698
129.120
127.075
125.948
113.594
111.864
109.868
63.563
61.720
58.352
42.928
40.474
26.969
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

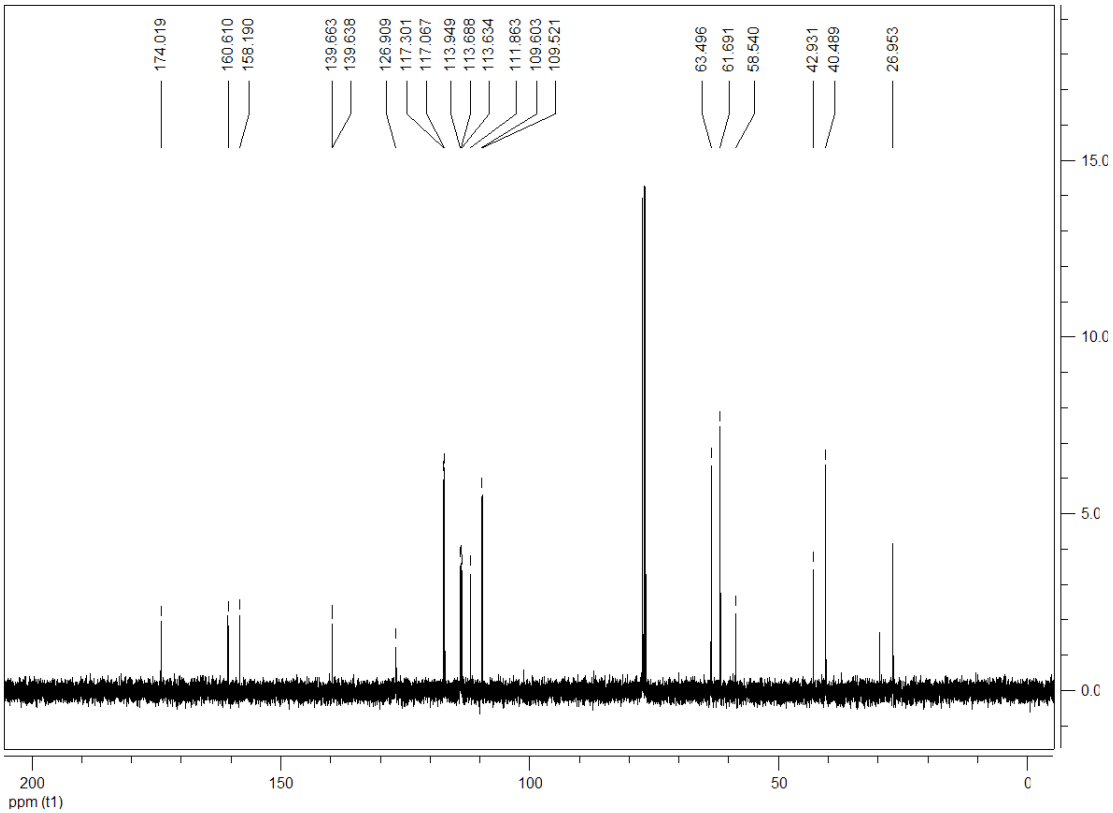

Intens.
x10^4
2.0
1.5
1.0
0.5
0.0
+MS, 0.54-0.65min #(55-66)
323.0672
301.0848
341.0770
353.2664
280
290
300
310
320
330
340
350
360
m/z

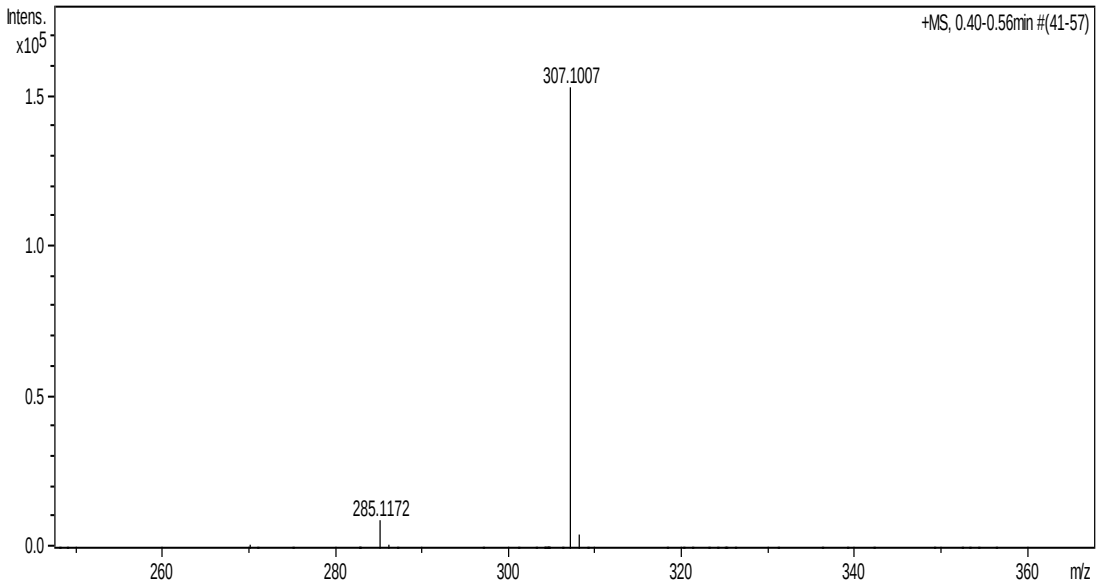
(S)-5-Fluoro-1,1'-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4',4'-dicarbonitrile (4k)



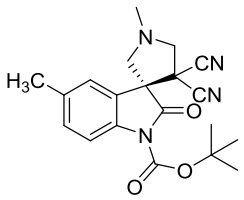
white solid, 82%, m.p. 122~123℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.44 (dd, J_1= 7.6Hz, J_2 = 2.0Hz , 1H, ArH), 7.16 (td, J_1 = 8.8Hz, J_2 = 2.0Hz , 1H, ArH), 6.87 (dd, J_1 = 8.4Hz, J_2 = 4.0Hz , 1H, ArH), 3.71 (d, J = 9.6Hz, 1H, CH), 3.61 (d, J = 9.2Hz, 1H, CH), 3.33 (d, J = 10.0Hz, 1H, CH), 3.27 (s, 3H, CH_3), 3.04 (d, J = 10.0Hz, 1H, CH), 2.58 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.0, 159.4 (d, J = 242.0Hz), 139.6 (d, J = 2.5Hz), 126.9, 117.2 (d, J = 23.4Hz), 113.8 (d, J = 26.1Hz), 113.6, 111.9, 109.6(d, J = 8.2Hz), 63.5, 61.7, 58.5, 42.9, 40.5, 26.9; IR(KBr) υ: 2971, 2920, 2870, 2812, 2702, 2249, 1850, 1727, 1617, 1496, 1465, 1355, 1275, 1237, 1212, 1167, 1107, 1046, 969, 916, 816, 754 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{158}H_{13}FN_4ONa$ ([M+Na]$^{+}$): 307.0966, found: 307.1007.



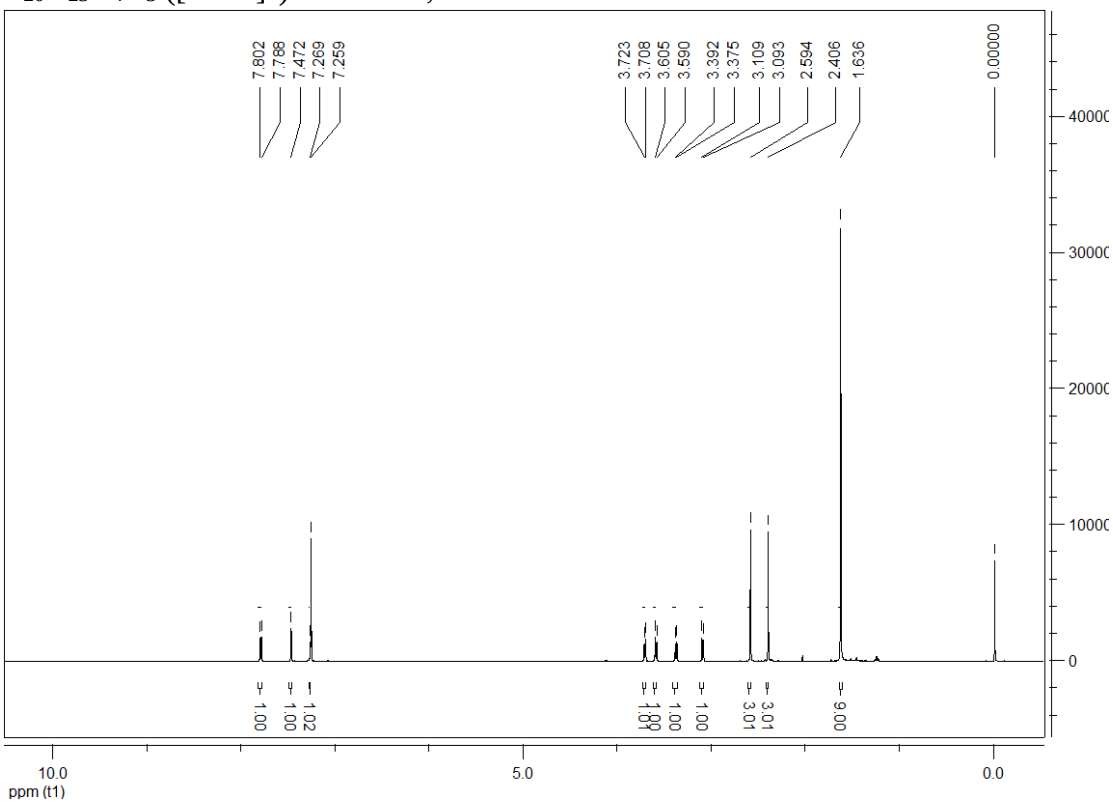

174.019
160.610
158.190
139.663
139.638
126.909
117.301
117.067
113.949
113.688
113.634
111.863
109.603
109.521
63.496
61.691
58.540
42.931
40.489
26.953
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

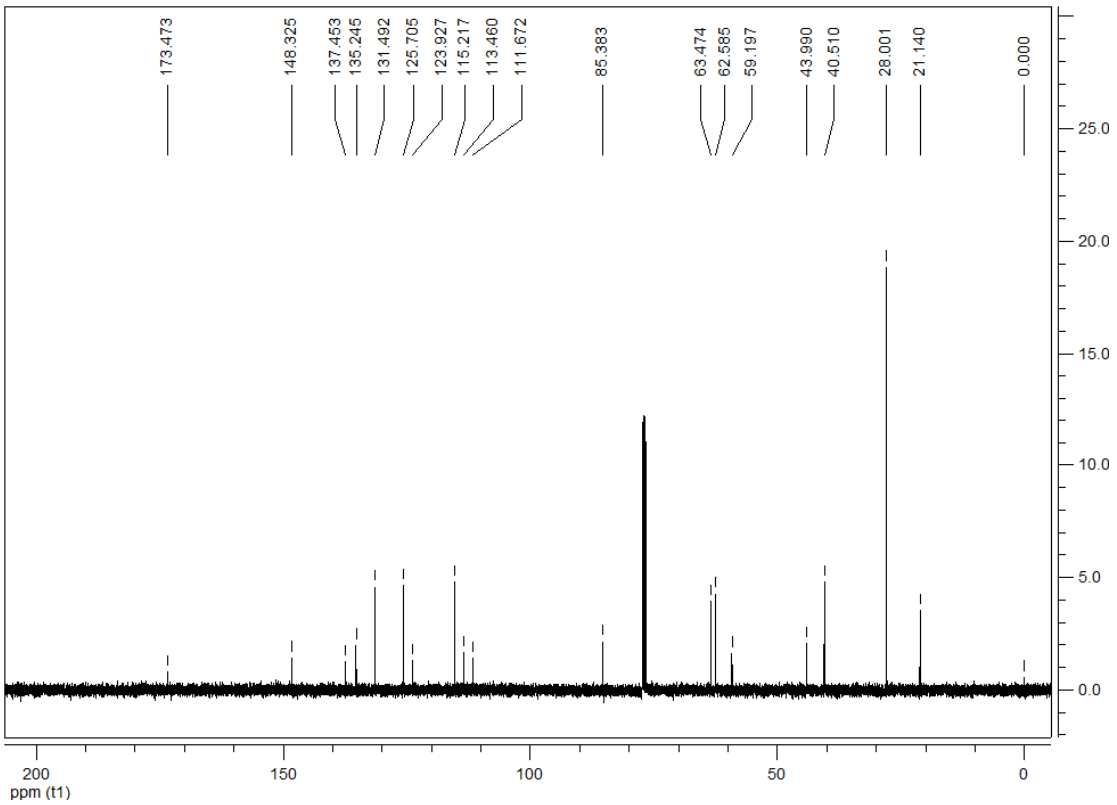

Intens.
x10^5
+MS, 0.40-0.56min #(41-57)
307.1007
285.1172
1.5
1.0
0.5
0.0
260
280
300
320
340
360
m/z

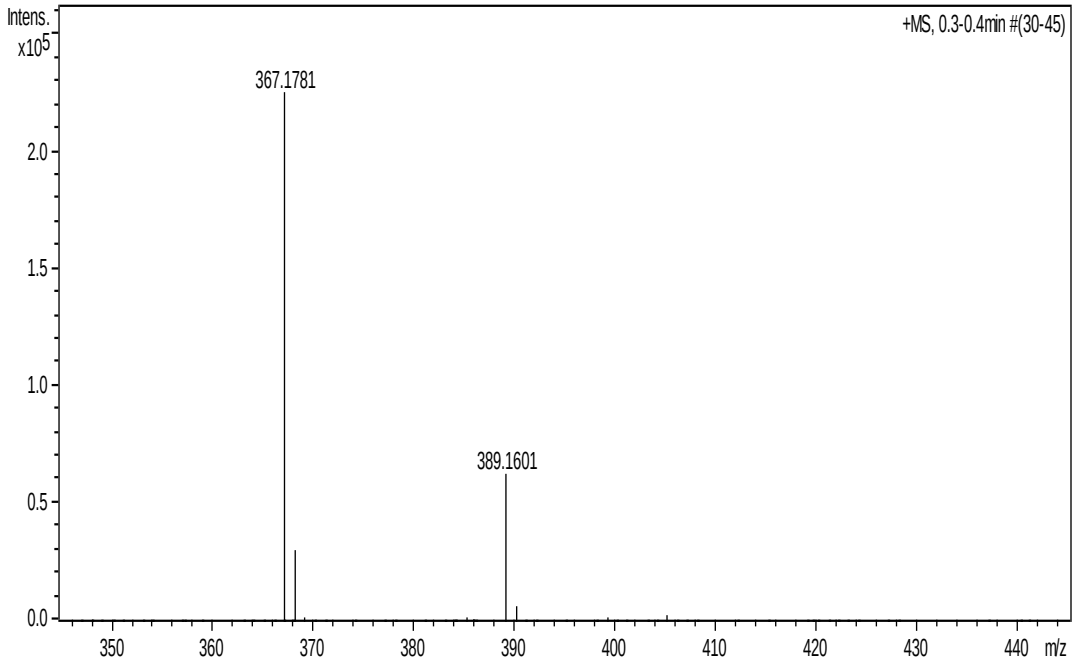
(S)-Tert-butyl-4',4'-dicyano-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1-carboxylate (4l)



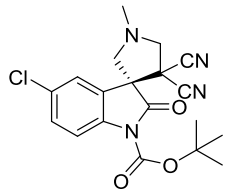
white solid, 79%, m.p. 139~141℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 8.4Hz, 1H, ArH), 7.47 (brs, 1H, ArH), 7.27 (brs, 1H, ArH), 3.72 (d, *J* = 9.6Hz, 1H, CH), 3.60 (d, *J* = 9.0Hz, 1H, CH), 3.38 (d, *J* = 10.2Hz, 1H, CH), 3.10 (d, *J* = 9.6Hz, 1H, CH), 2.59 (s, 3H, CH_3), 2.41 (s, 3H, CH_3), 1.64 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.5, 148.3, 137.4, 135.2, 131.5, 125.7, 123.9, 115.2, 113.4, 111.7, 85.4, 63.5, 62.6, 59.2, 44. 0, 40.5, 28.0, 21.1; IR(KBr) υ: 2982, 2847, 2250, 1793, 1729, 1596, 1483, 1394, 1371, 1306, 1242, 1185, 1151, 1049, 933, 905, 828, 769, 741 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{23}N_4O_3$ ($[M+H]^+$): 367.1770, found: 367.1781.



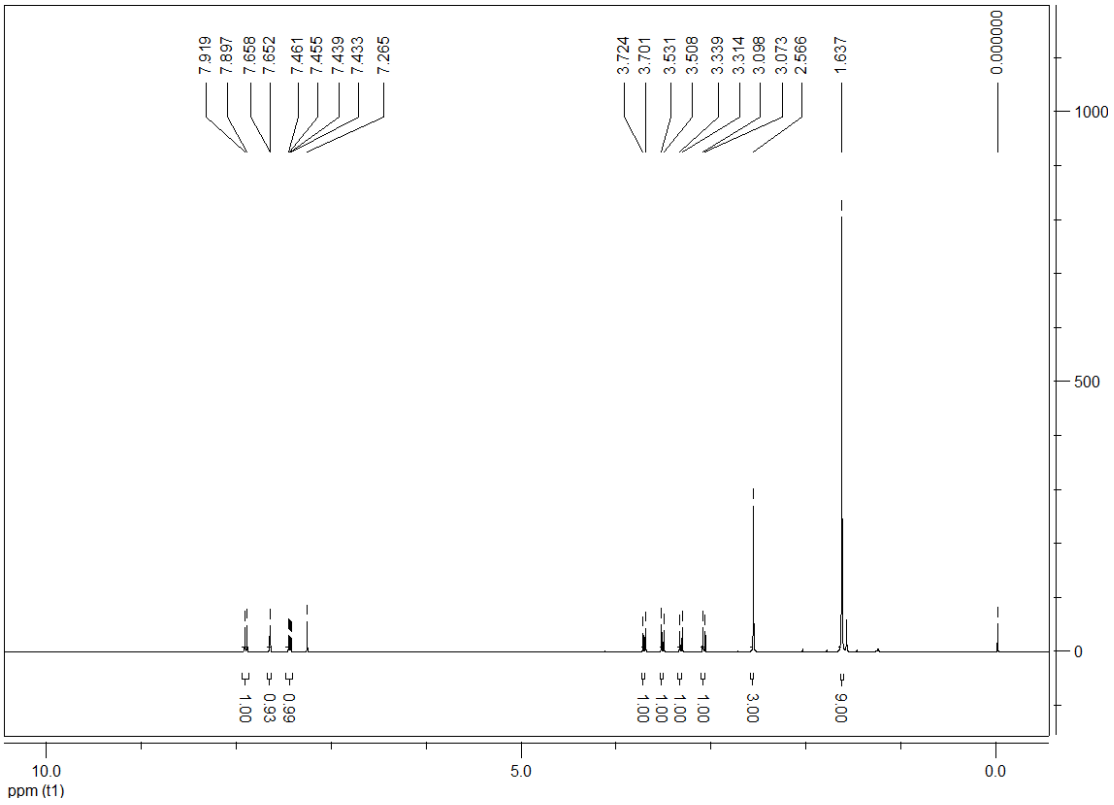

173.473
148.325
137.453
135.245
131.492
125.705
123.927
115.217
113.460
111.672
85.383
63.474
62.585
59.197
43.990
40.510
28.001
21.140
0.000
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

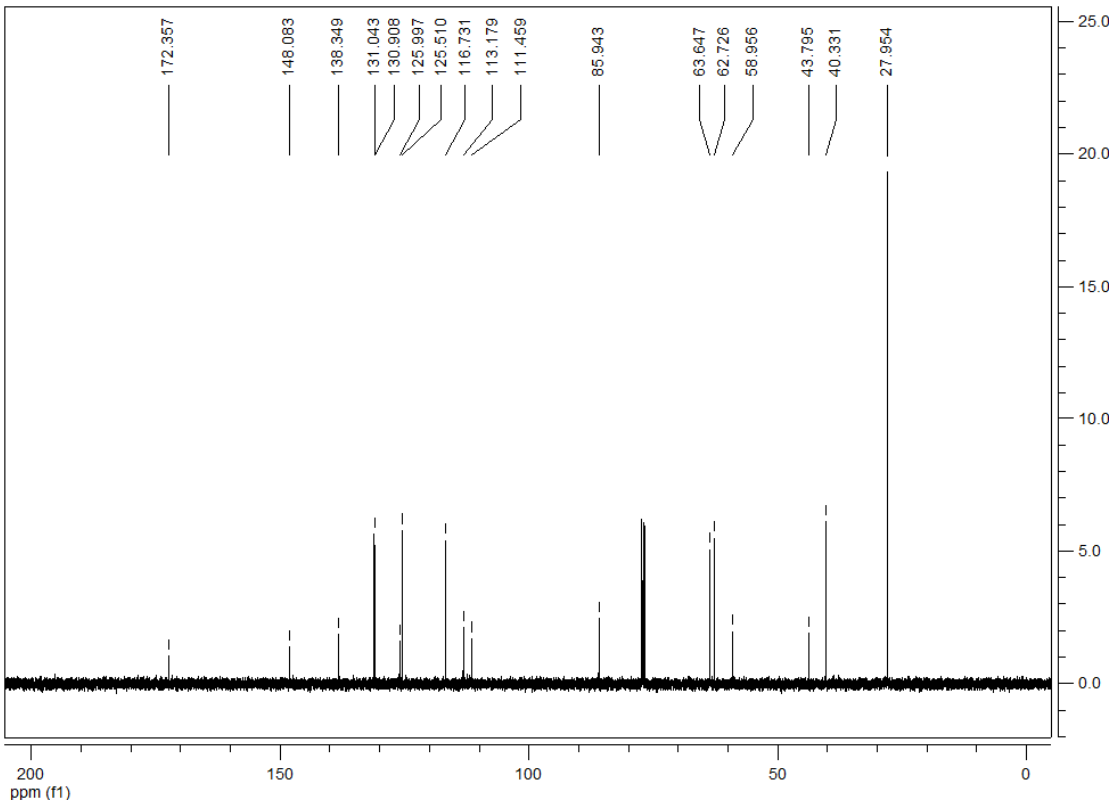

Intens.
x10^5
+MS, 0.3-0.4min #(30-45)
367.1781
389.1601
2.0
1.5
1.0
0.5
0.0
350
360
370
380
390
400
410
420
430
440
m/z

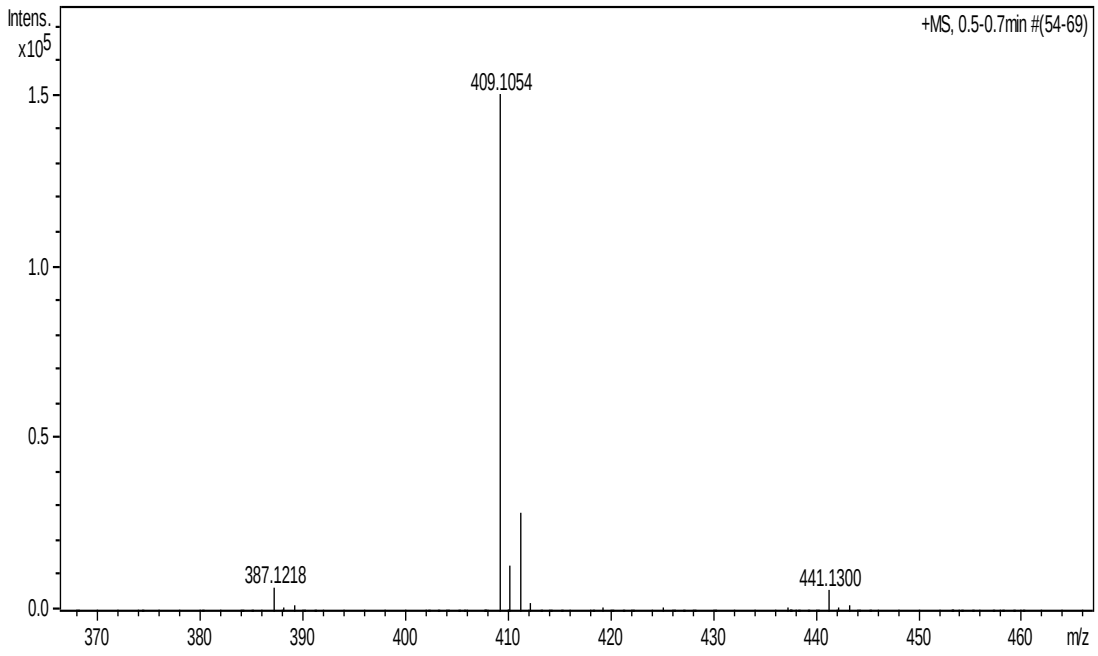
(S)-Tert-butyl-5-chloro-4',4'-dicyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1-carboxylate (4m)



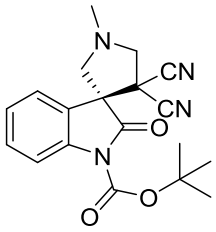
white solid, 85%, m.p. 150~152℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.91 (d, *J* = 8.8Hz, 1H, ArH), 7.65 (d, *J* = 2.4Hz, 1H, ArH), 7.45 (dd, J_1 = 8.8Hz, J_2 = 2.4Hz, 1H, ArH), 3.71 (d, *J* = 9.2Hz, 1H, CH), 3.52 (d, *J* = 9.2Hz, 1H, CH), 3.33 (d, *J* = 10.0Hz, 1H, CH), 3.08 (d, *J* = 10.0Hz, 1H, CH), 2.57 (s, 3H, CH_3), 1.64 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 148.1, 138.3, 131.0, 130.9, 126.0, 125.5, 116.7, 113.2, 111.4, 85.9, 63.6, 62.7, 58.9, 43.8, 40.3, 27.9; IR(KBr) υ: 2983, 2947, 2869, 2811, 2776, 2295, 2247, 1795, 1650, 1605, 1465, 1399, 1369, 1304, 1247, 1196, 1165, 1119, 1050, 975, 932, 896 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{19}H_{19}ClNaN_4O_3$ ($[M+Na]^+$): 409.1043, found: 409.1054.



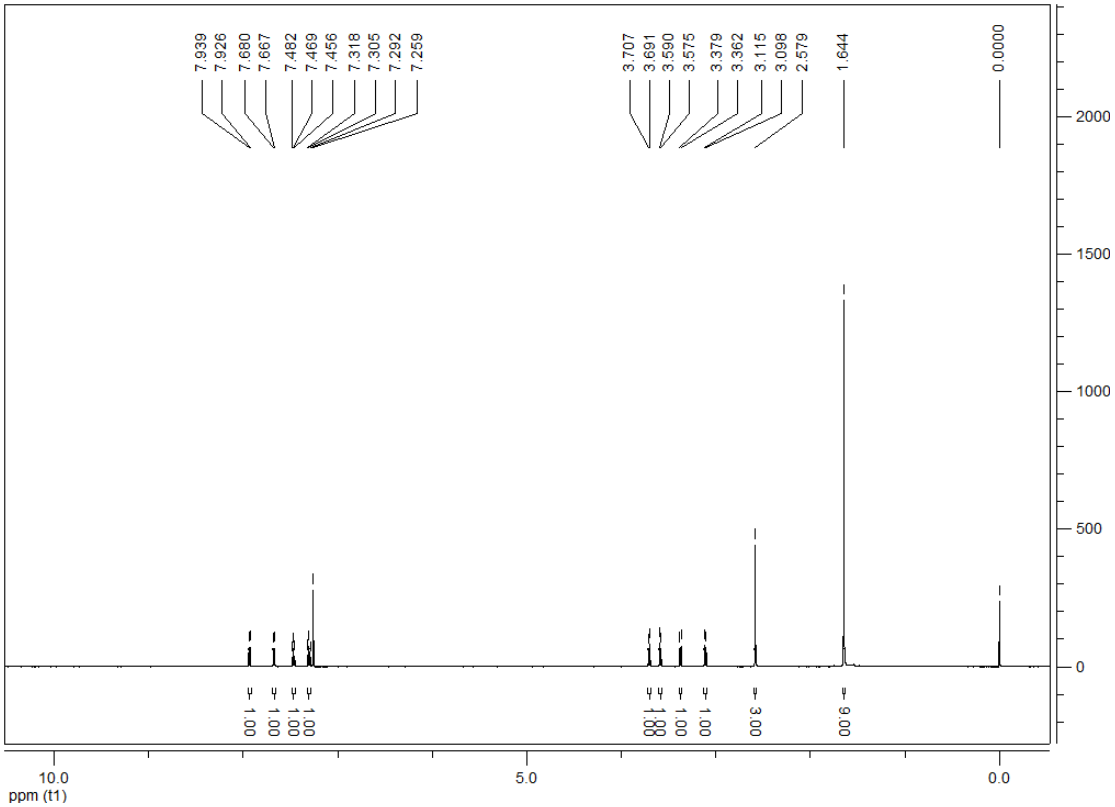

172.357
148.083
138.349
131.043
130.908
125.997
125.510
116.731
113.179
111.459
85.943
63.647
62.726
58.956
43.795
40.331
27.954
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

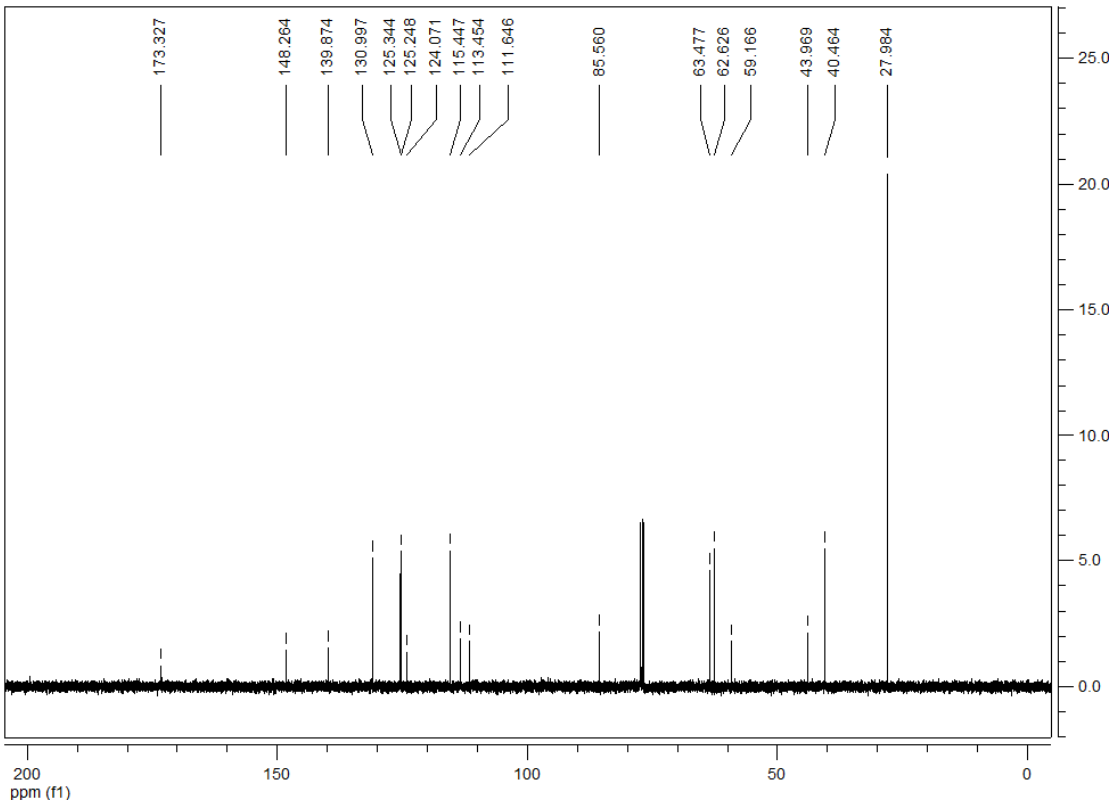

Intens.
x10^5
+MS, 0.5-0.7min #(54-69)
409.1054
387.1218
441.1300
1.5
1.0
0.5
0.0
370
380
390
400
410
420
430
440
450
460
m/z

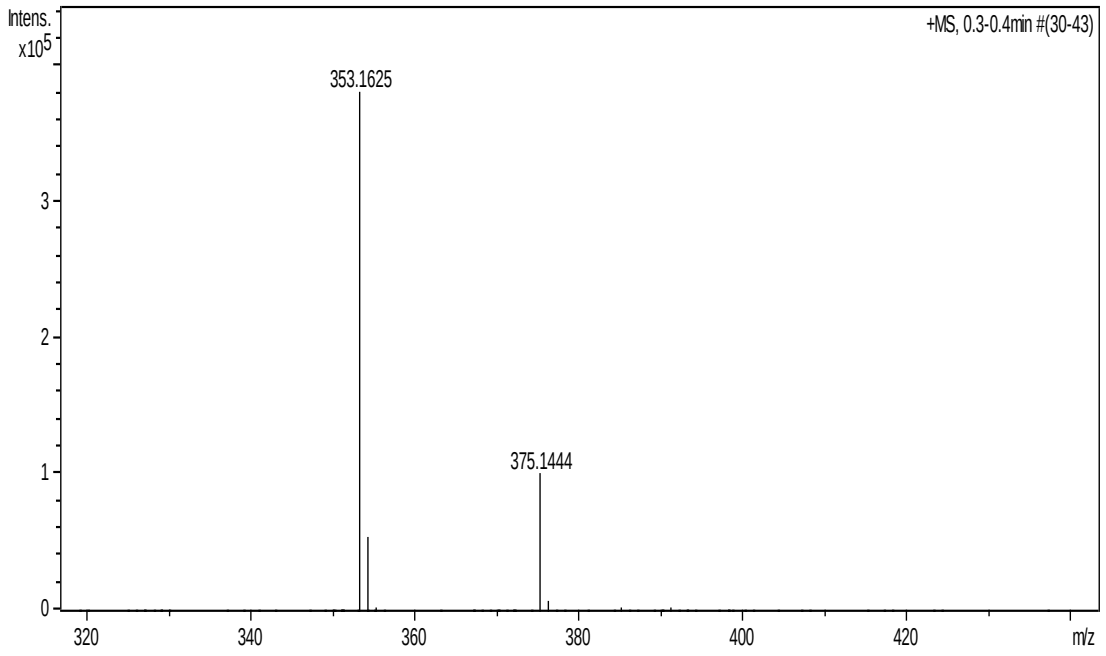
(S)-Tert-butyl-4',4'-dicyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1-carboxylate (4n)



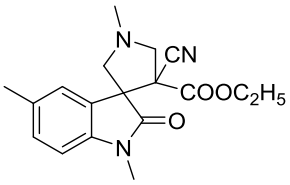
white solid, 80%, m.p. 95~97℃; ^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.93 (d, *J* = 7.8Hz, 1H, ArH), 7.67 (d, *J* = 7.8Hz, 1H, ArH), 7.47 (t, *J* = 7.8Hz, 1H, ArH), 7.30 (t, *J* = 7.8Hz, 1H, ArH), 3.70 (d, *J* = 9.6Hz, 1H, CH), 3.58 (d, *J* = 9.0Hz, 1H, CH), 3.37 (d, *J* = 10.2Hz, 1H, CH), 3.11 (d, *J* = 10.2Hz, 1H, CH), 2.58 (s, 3H, CH_3), 1.64 (s, 9H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.3, 148.3, 139.9, 131.0, 125.3, 125.2, 124.1, 115.4, 113.4, 111.6, 85.6, 63.5, 62.6, 59.2, 44.0, 40.5, 28.0; IR(KBr) υ: 2984, 2883, 2839, 2699, 2253, 1956, 1921, 1767, 1742, 1608, 1473, 1348, 1299, 1250, 1151, 1052, 1007, 942, 913, 871, 838, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{19}H_{21}N_4O_3$ ([M+H]$^+$): 353.1614, found: 353.1625.



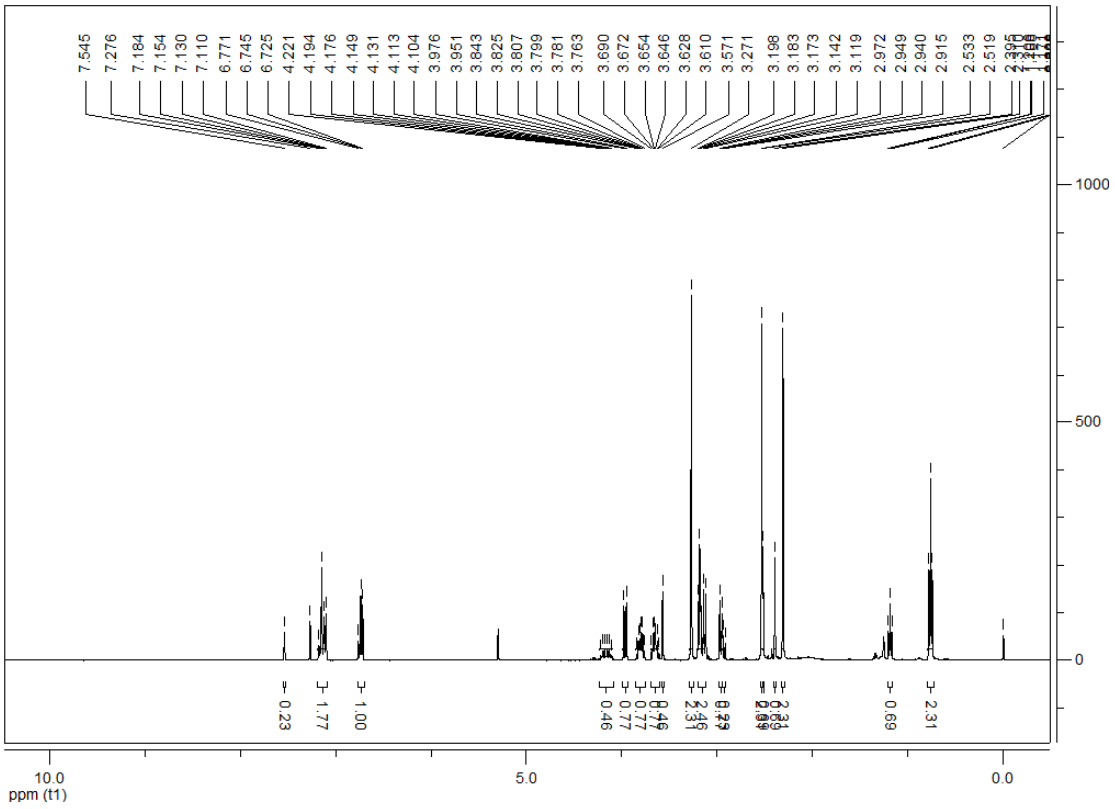

173.327
148.264
139.874
130.997
125.344
125.248
124.071
115.447
113.454
111.646
85.560
63.477
62.626
59.166
43.969
40.464
27.984
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

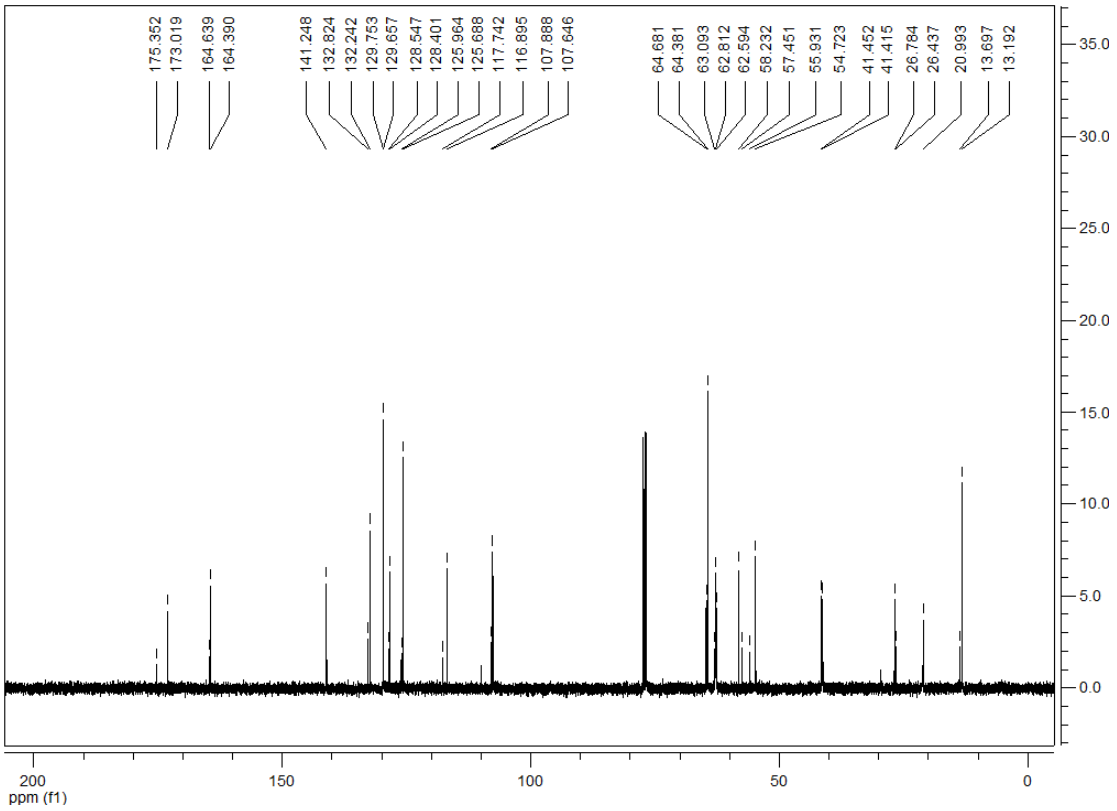

Intens.
x10^5
+MS, 0.3-0.4min #(30-43)
353.1625
375.1444
3
2
1
0
320
340
360
380
400
420
m/z

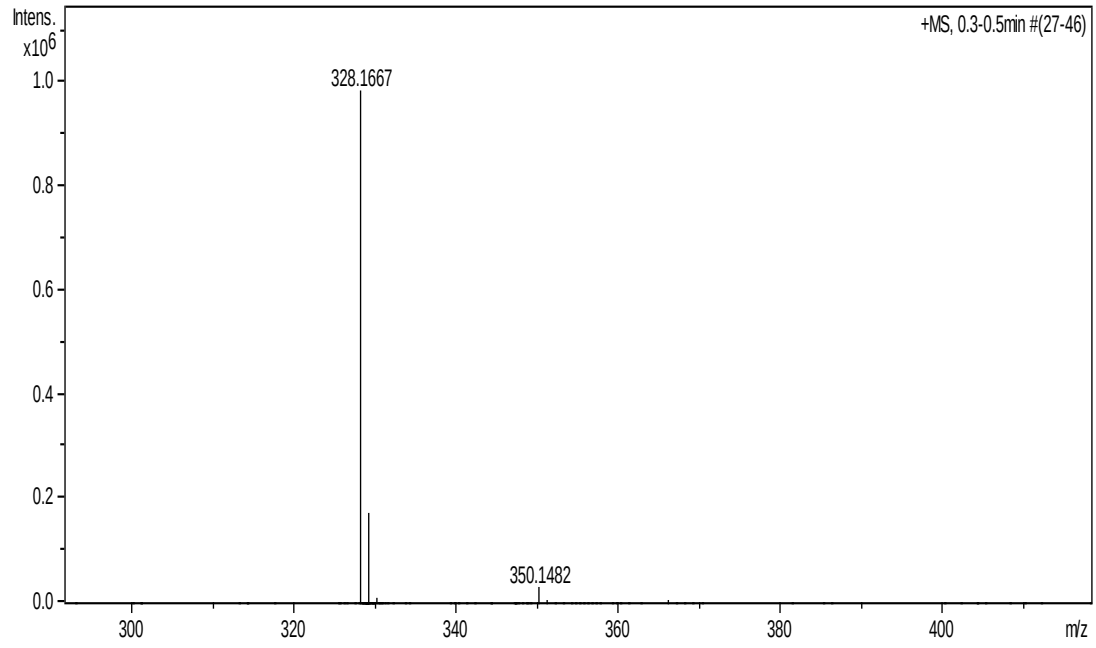
Ethyl-4'-cyano-1,1',5-trimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6a)



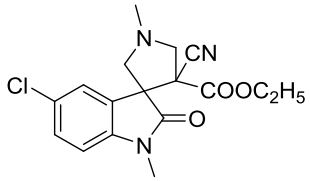
white solid, 91%, m.p. 77~79℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: **major isomer**: 7.18~7.11 (m, 2H, ArH), 6.77~6.72 (m, 1H, ArH), 3.96 (d, *J* = 10.0Hz, 1H, CH), 3.84~3.76 (m, 1H, CH), 3.69~3.61 (m, 1H, CH), 3.27 (s, 3H, CH_3), 3.20~3.12 (m, 2H, CH), 2.96 (d, *J* = 9.2Hz, 1H, CH), 2.53 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 0.76 (t, *J* = 7.2Hz, 3H, CH_3); **minor isomer:** 7.54 (brs, 1H, ArH), 7.18~7.11 (m, 1H, ArH), 6.77~6.72 (m, 1H, ArH), 4.22~4.10 (m, 2H, CH), 3.57 (brs, 2H, CH), 3.18 (s, 3H, CH_3), 3.20~3.12 (m, 1H, CH), 2.93 (d, *J* = 10.0Hz, 1H, CH), 2.52 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 1.19 (t, *J* = 7.2Hz, 3H, CH_3); **ratio of major/minor = 77:23**; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 173.0, 164.6, 164.4, 141.2, 132.8, 132.2, 129.8, 129.7, 128.5, 128.4, 126.0, 125.7, 117.7, 116.9, 107.9, 107.6, 64.7, 64.4, 63.1, 62.8, 62.6, 58.2, 57.4, 55.9, 54.7, 41.5, 41.4, 26.8, 26.4, 21.0, 13.7, 13.2; IR(KBr) υ: 2923, 2848, 2786, 2358, 2240, 1876, 1756, 1719, 1612, 1498, 1468, 1359, 1243, 1188, 1142, 1091, 1058, 1033, 1008, 958, 858, 810, 756, 720 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{18}H_{22}N_3O_3$ ($[M+H]^+$): 328.1661, found: 328.1667.



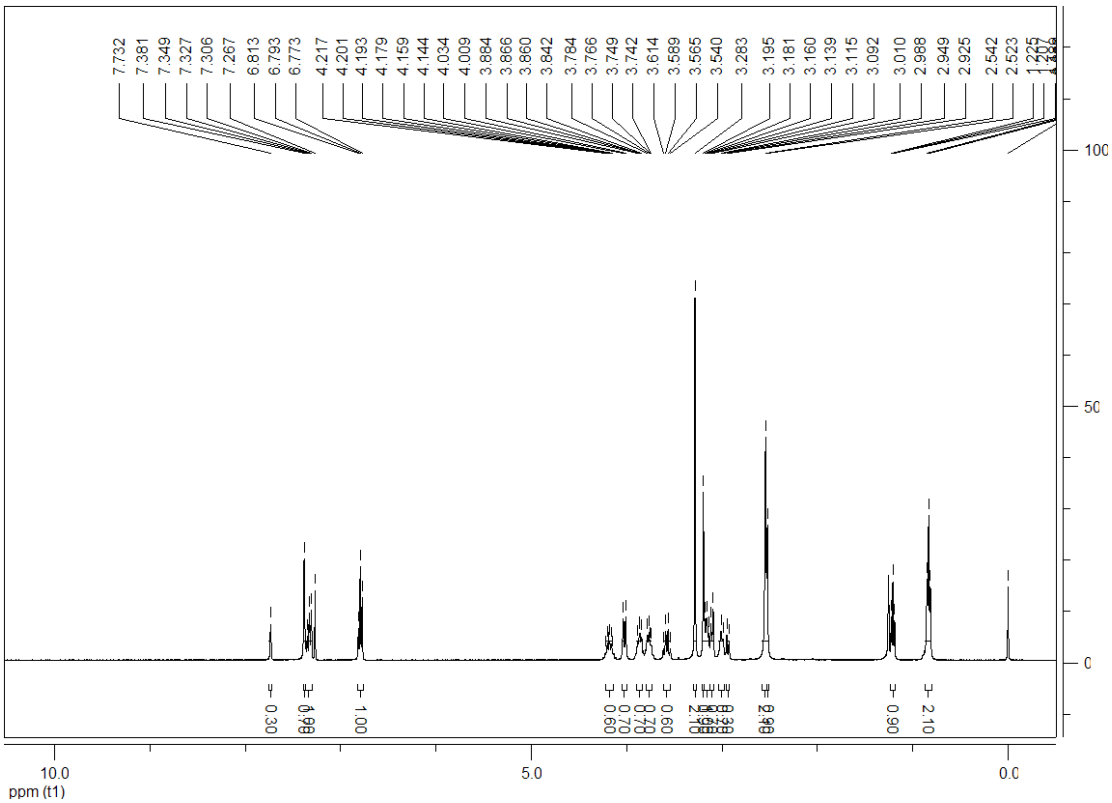

175.352
173.019
164.639
164.390
141.248
132.824
132.242
129.753
129.657
128.547
128.401
125.964
125.688
117.742
116.895
107.888
107.646
64.681
64.381
63.093
62.812
62.594
58.232
57.451
55.931
54.723
41.452
41.415
26.784
26.437
20.993
13.697
13.192
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

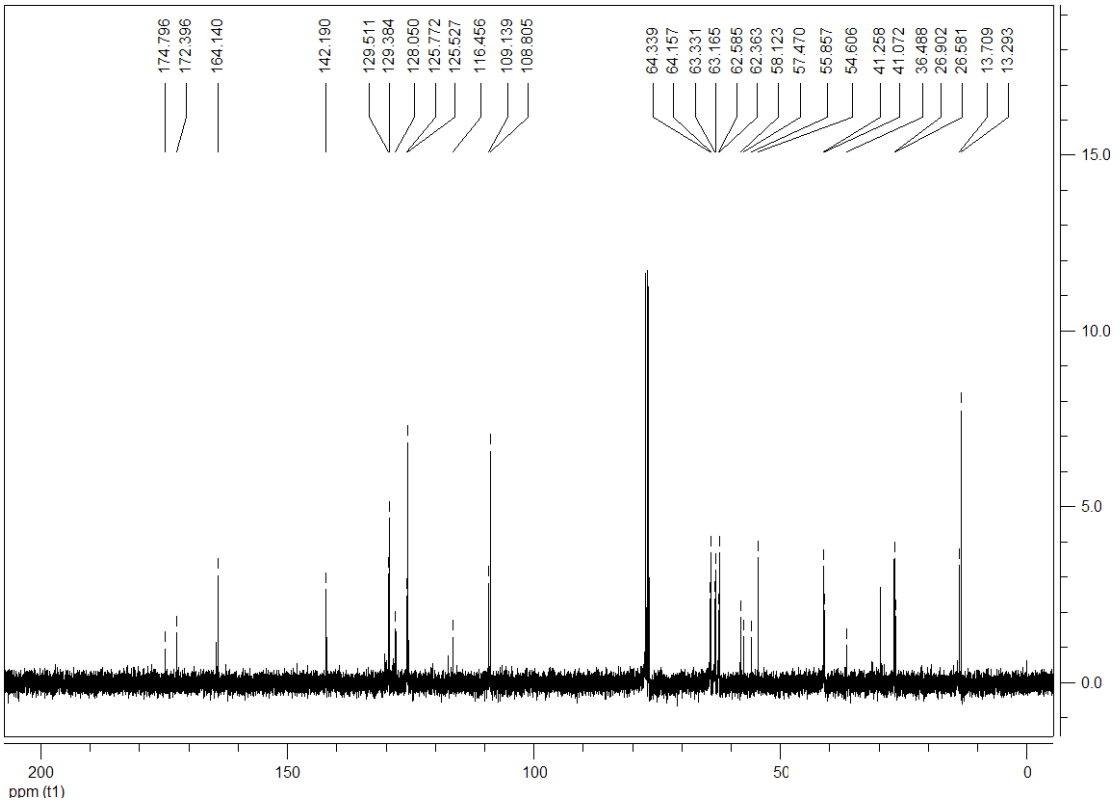

Intens.
x10^6
+MS, 0.3-0.5min #(27-46)
328.1667
350.1482
1.0
0.8
0.6
0.4
0.2
0.0
300
320
340
360
380
400
m/z

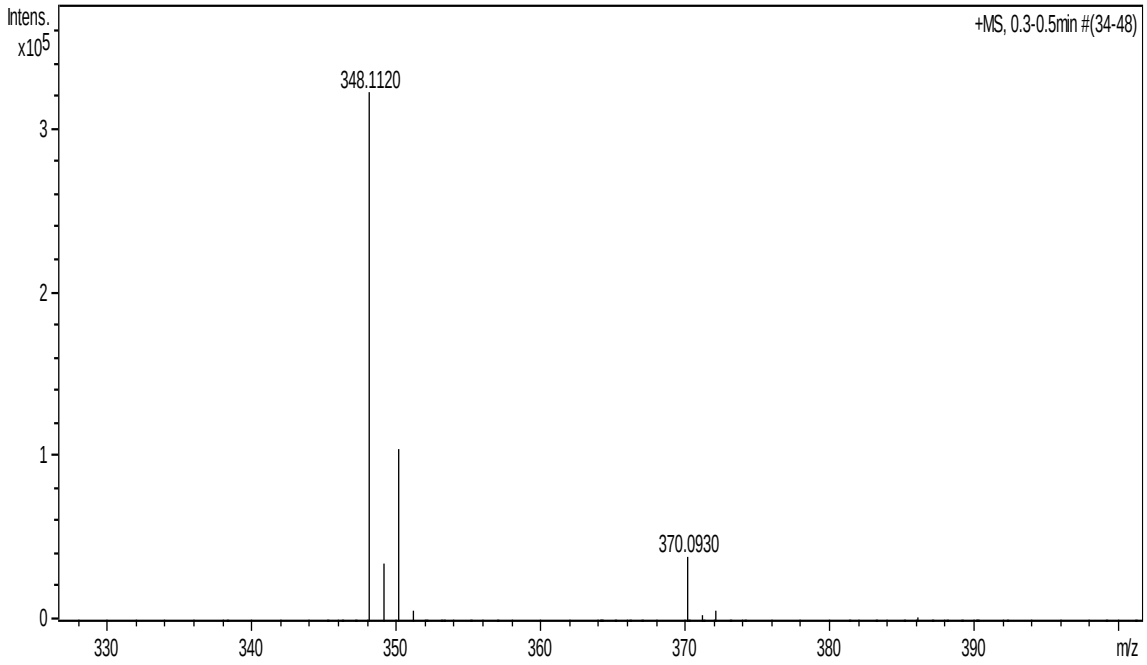
Ethyl-5-chloro-4'-cyano-1,1'-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6b)



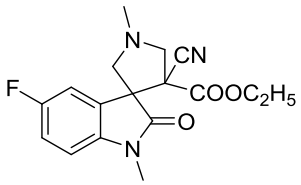
white solid, 88%, m.p. 104~105℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: **major isomer**: 7.38 (brs, 1H, ArH), 7.35~7.31 (m, 1H, ArH), 6.81~6.77 (m, 1H, ArH), 4.02 (d, *J* = 10.0Hz, 1H, CH), 3.88~3.84 (m, 1H, CH), 3.78~3.74 (m, 1H, CH), 3.28 (s, 3H, CH_3), 3.18~3.14 (m, 1H, CH), 3.10 (d, *J* = 9.2Hz, 1H, CH), 3.00 (d, *J* = 8.8Hz, 1H, CH), 2.54 (s, 3H, CH_3), 0.83 (t, *J* = 7.2Hz, 3H, CH_3); **minor isomer:** 7.73 (brs, 1H, ArH), 7.35~7.31 (m, 1H, ArH), 6.81~6.77 (m, 1H, ArH), 4.22~4.14 (m, 2H, CH), 3.61~3.54 (m, 2H, CH), 3.20 (s, 3H, CH_3), 3.18~3.14 (m, 1H, CH), 2.94 (d, *J* = 9.6Hz, 1H, CH), 2.52 (s, 3H, CH_3), 1.21 (t, *J* = 7.2Hz, 3H, CH_3); **ratio of major/minor = 70:30**; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.8, 172.4, 164.1, 142.2, 129.5, 129.4, 128.0, 125.8, 125.5, 116.5, 109.1, 108.8, 64.3, 64.2, 63.3, 63.2, 62.6, 62.4, 58.1, 57.5, 55.9, 54.6, 41.2, 41.1, 36.5, 26.9, 26.6, 13.7, 13.3; IR(KBr) υ: 2981, 2953, 2920, 2853, 2799, 2240, 1760, 1719, 1607, 1486, 1350, 1270, 1232, 1183, 1142, 1094, 1009, 955, 916, 887, 858, 813, 732 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{17}H_{19}ClN_3O_3$ ([M+H]$^+$): 348.1115, found: 348.1120.



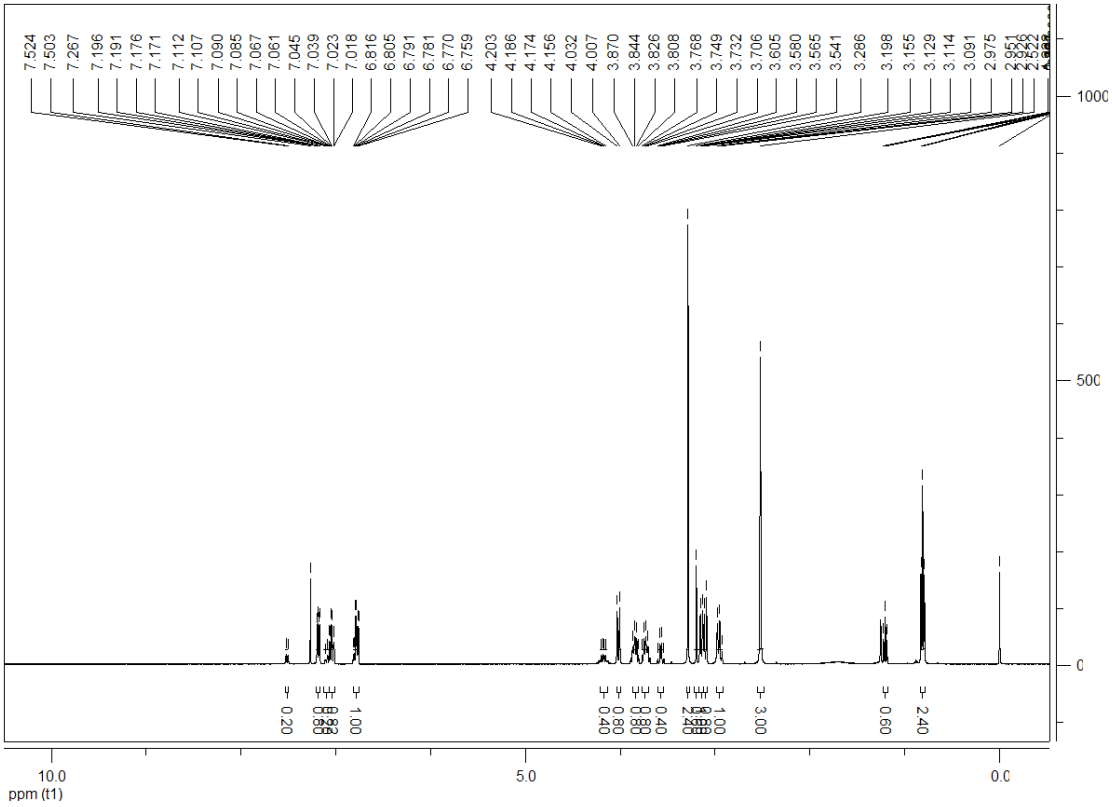

174.796
172.396
164.140
142.190
129.511
129.384
128.050
125.772
125.527
116.456
109.139
108.805
64.339
64.157
63.331
63.165
62.585
62.363
58.123
57.470
55.857
54.606
41.258
41.072
36.488
26.902
26.581
13.709
13.293
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

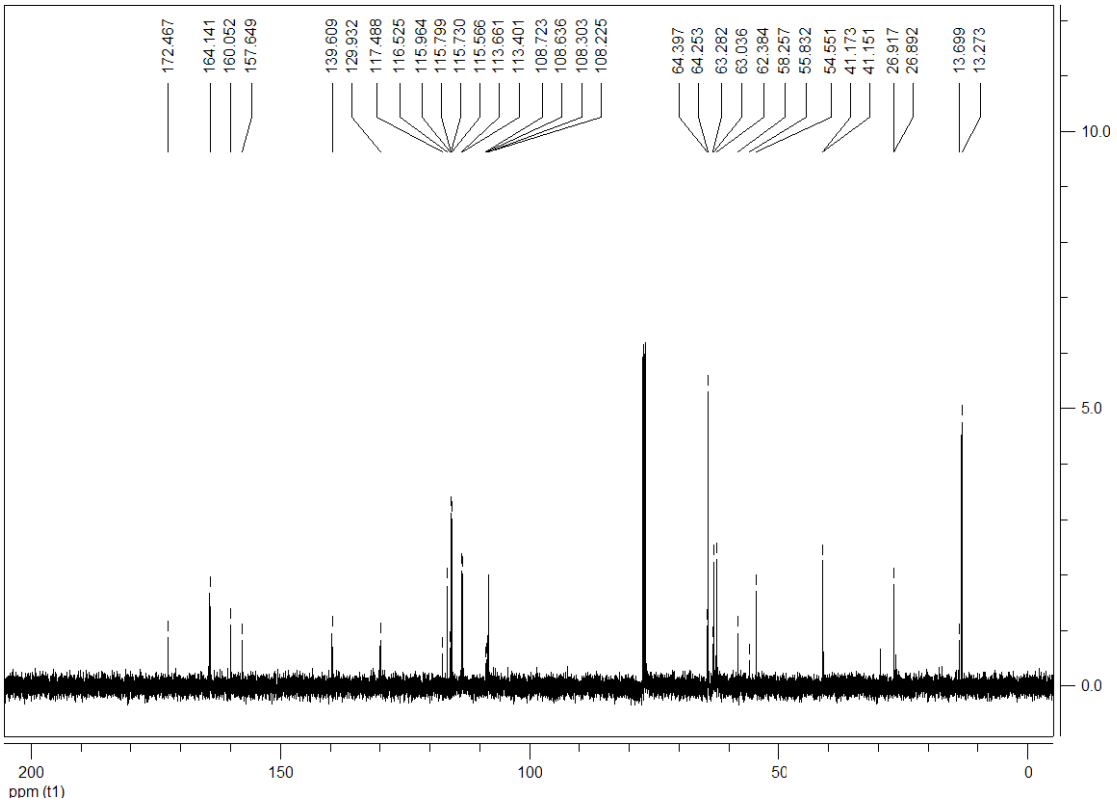

Intens.
x10^5
+MS, 0.3-0.5min #(34-48)
348.1120
370.0930
3
2
1
0
330
340
350
360
370
380
390
m/z

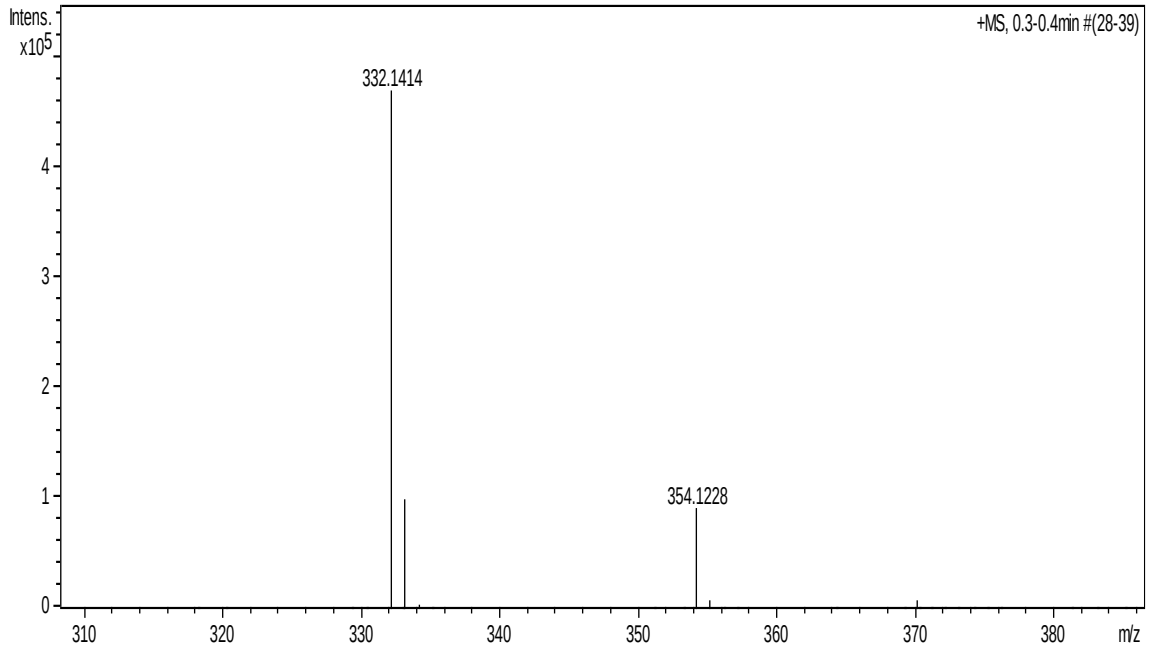
Ethyl-4'-cyano-5-fluoro-1,1'-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6c)



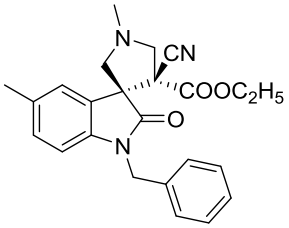
white solid, 85%, m.p. 139~140℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: **major isomer**: 7.18 (dd, J_1 = 8.0Hz, J_2 = 2.0Hz, 1H, ArH), 7.04 (td, J_1 = 8.8Hz, J_2 = 2.0Hz, 1H, ArH), 6.82~6.76 (m, 1H, ArH), 4.02 (d, J = 10.0Hz, 1H, CH), 3.87~3.81 (m, 1H, CH), 3.77~3.71 (m, 1H, CH), 3.29 (s, 3H, CH_3), 3.16~3.13 (m, 1H, CH), 3.10 (d, J = 9.2Hz, 1H, CH), 2.98~2.93 (m, 1H, CH), 2.52 (s, 3H, CH_3), 0.81 (t, J = 7.2Hz, 3H, CH_3); **minor isomer:** 7.52~7.50 (m, 1H, ArH), 7.12~7.08 (m, 1H, ArH), 6.82~6.76 (m, 1H, ArH), 4.20~4.16 (m, 2H, CH), 3.61~3.54 (m, 2H, CH), 3.20 (s, 3H, CH_3), 3.16~3.13 (m, 1H, CH), 2.98~2.93 (m, 1H, CH), 2.52 (s, 3H, CH_3), 1.20 (t, J = 7.2Hz, 3H, CH_3); **ratio of major/minor = 80:20**; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.2, 164.1, 158.5 (d, J = 24.03Hz),, 139.6, 129.9, 117.5, 116.5, 115.8 (d, J = 23.4Hz), 115.7 (d, J = 23.5Hz), 113.5 (d, J = 26.0Hz), 108.7 (d, J = 8.7Hz), 108.3 (d, J = 7.8Hz), 64.4, 64.3, 63.3, 63.0, 62.4, 58.3, 55.8, 54.6, 41.1 (d, J = 2.2Hz), 26.9 (d, J = 2.5Hz), 13.7, 13.3; IR(KBr) υ: 2986, 2958, 2854, 2798, 2240, 1754, 1714, 1621, 1497, 1473, 1353, 1276, 1240, 1191, 1128, 1088, 1007, 926, 875, 833, 769, 728 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{17}H_{19}FN_3O_3$ ($[M+H]^+$): 332.1410, found: 332.1414.



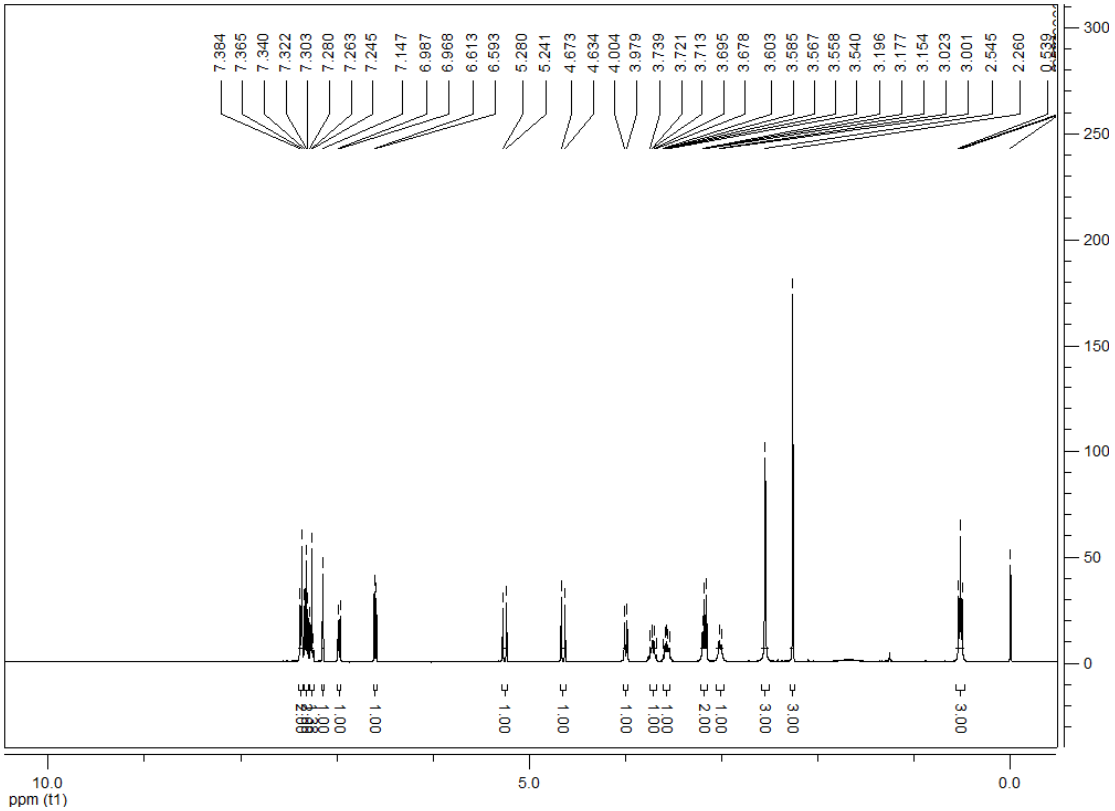

172.467
164.141
160.052
157.649
139.609
129.932
117.488
116.525
115.964
115.799
115.730
115.566
113.661
113.401
108.723
108.636
108.303
108.225
64.397
64.253
63.282
63.036
62.384
58.257
55.832
54.551
41.173
41.151
26.917
26.892
13.699
13.273
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

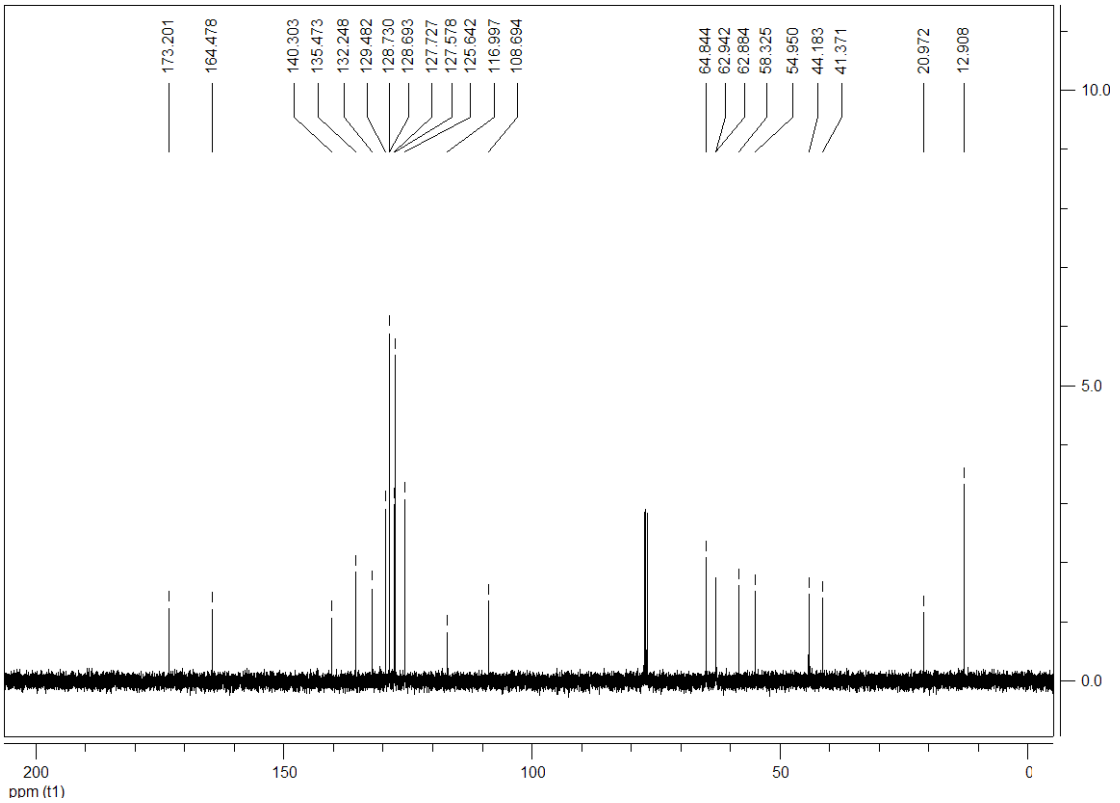

Intens.
x10^5
+MS, 0.3-0.4min #(28-39)
332.1414
354.1228
4
3
2
1
0
310
320
330
340
350
360
370
380
m/z

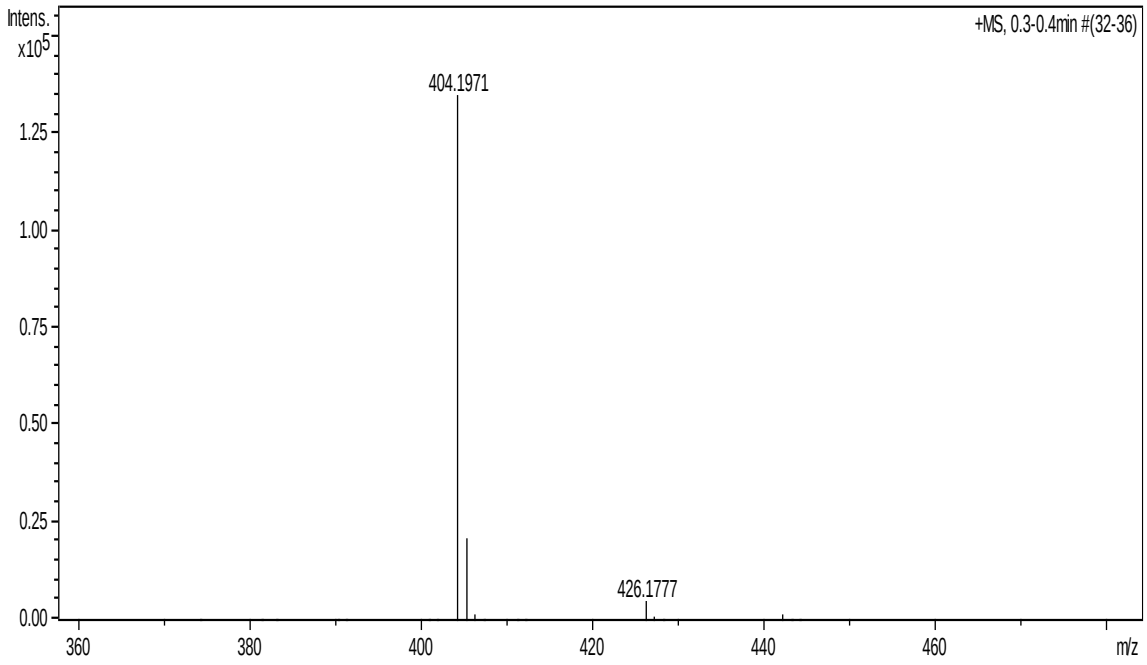
(3R,4'R)-Ethyl-1-benzyl-4'-cyano-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6d)



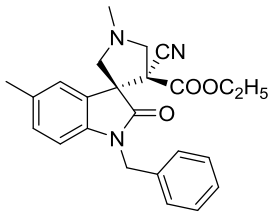
ratio of major/minor = 82:18; **major isomer (6d)**: white solid, 67%, m.p. 135~137℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (d, *J* = 7.6Hz, 2H, ArH), 7.34~7.30 (m, 2H, ArH), 7.28~7.24 (m, 1H, ArH), 7.15 (brs, 1H, ArH), 6.98 (d, *J* = 7.6Hz, 1H, ArH), 6.60 (d, *J* = 8.0Hz, 1H, ArH), 5.26 (d, *J* = 15.6Hz, 1H, CH), 4.65 (d, *J* = 15.6Hz, 1H, CH), 3.99 (d, *J* = 10.0Hz, 1H, CH), 3.74~3.68 (m, 1H, CH), 3.60~3.54 (m, 1H, CH), 3.20~3.15 (m, 2H, CH), 3.01 (d, *J* = 8.8Hz, 1H, CH), 2.54 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 0.52 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 164.5, 140.3, 135.5, 132.2, 129.5, 128.7, 128.7, 127.7, 127.6, 125.6, 117.0, 108.7, 64.8, 62.9, 62.9, 58.3, 54.9, 44.2, 41.4, 21.0, 12.9; IR(KBr) υ: 2979, 2950, 2851, 2811, 2239, 1752, 1727, 1613, 1496, 1452, 1432, 1355, 1269, 1238, 1193, 1167, 1122, 1096, 1029, 1004, 944, 898, 854, 820, 762, 727 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{26}N_3O_3$ ($[M+H]^+$): 404.1974, found: 404.1971.



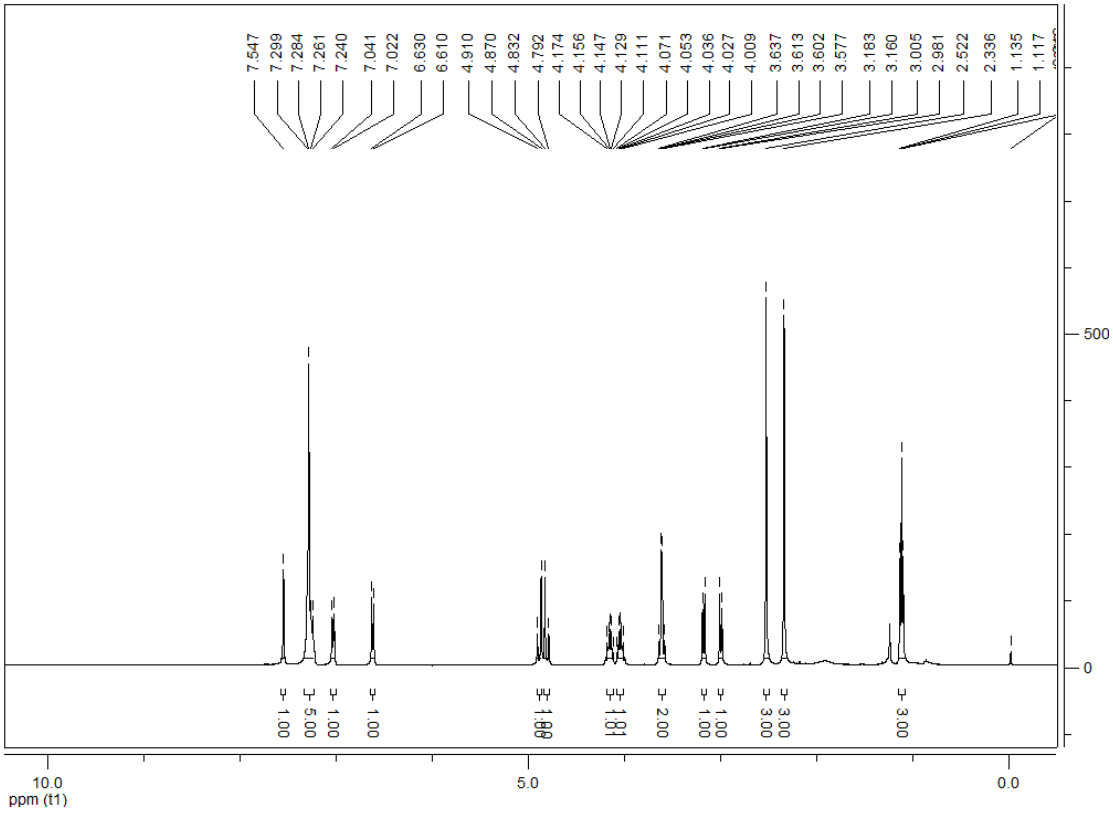

173.201
164.478
140.303
135.473
132.248
129.462
128.730
128.693
127.727
127.578
125.642
116.997
108.694
64.844
62.942
62.884
58.325
54.950
44.183
41.371
20.972
12.908
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

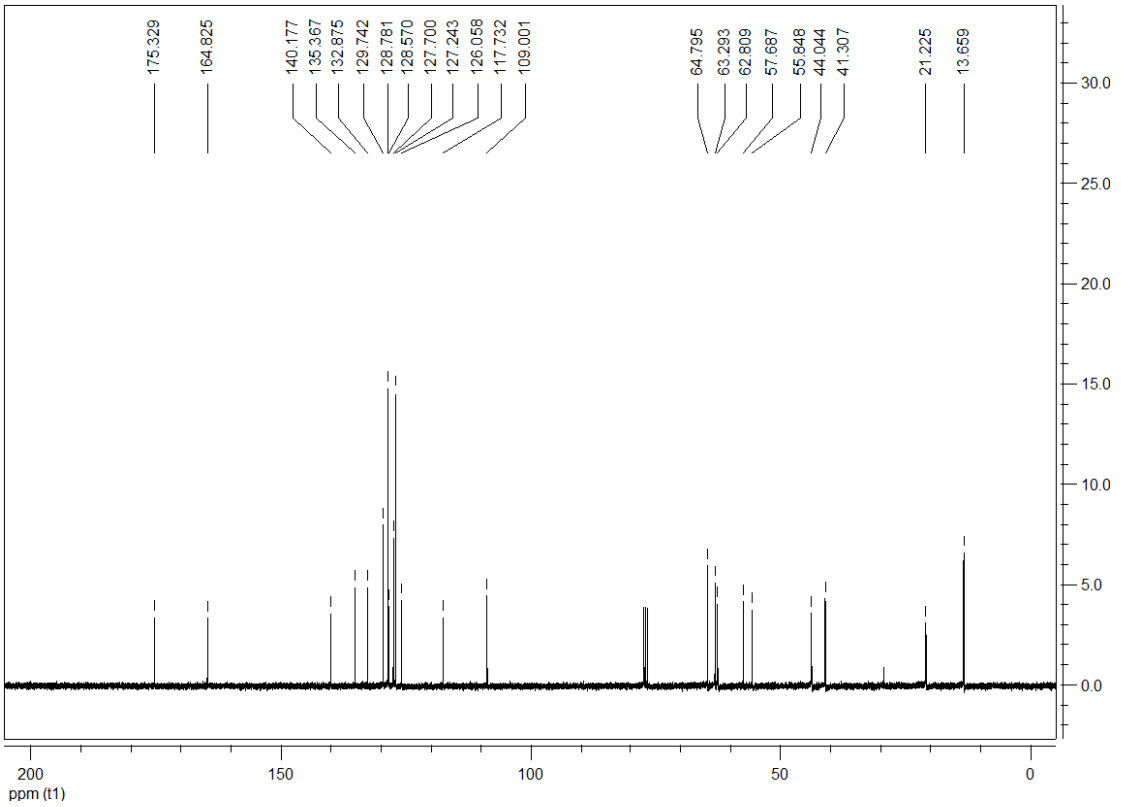

Intens.
x10^5
+MS, 0.3-0.4min #(32-36)
404.1971
426.1777
1.25
1.00
0.75
0.50
0.25
0.00
360
380
400
420
440
460
m/z

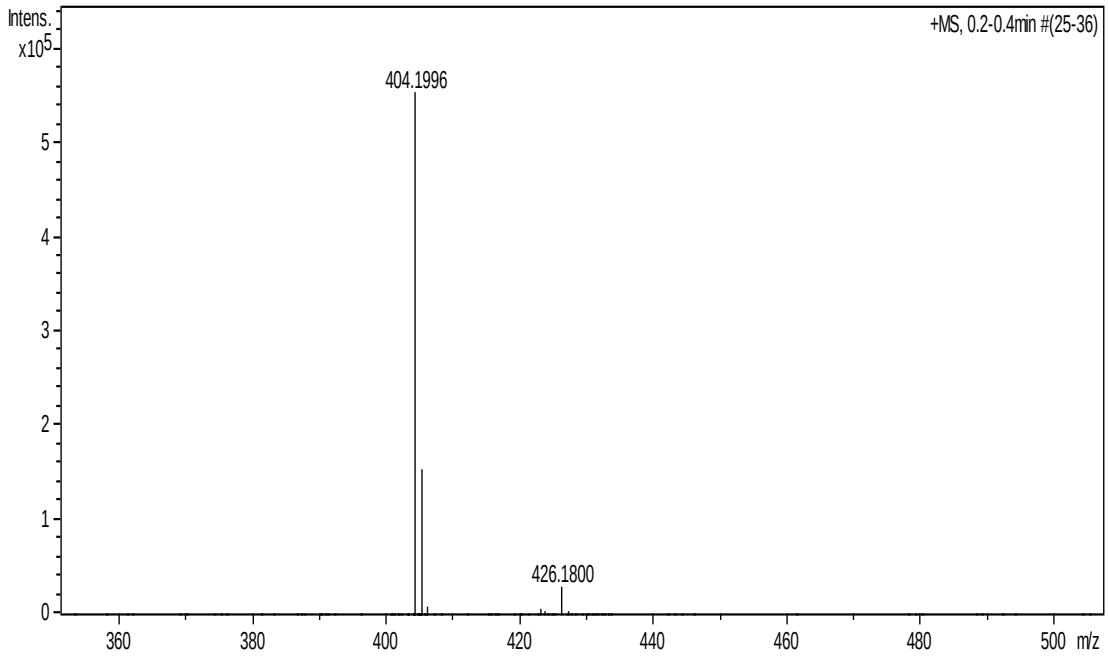
(3R,4'S)-Ethyl-1-benzyl-4'-cyano-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6d')



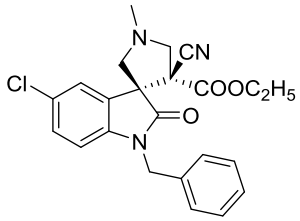
minor isomer (6d'): viscous oil, 15%; 7.56 (brs, 1H, ArH), 7.34~7.28 (m, 5H, ArH), 7.05 (d, *J* = 7.6Hz, 1H, ArH), 6.64 (d, *J* = 8.0Hz, 1H, ArH), 4.91 (d, *J* = 16.0Hz, 1H, CH), 4.83 (d, *J* = 16.0Hz, 1H, CH), 4.19~4.13 (m, 1H, CH), 4.09~4.03 (m, 1H, CH), 3.66~3.60 (m, 2H, CH), 3.19 (d, *J* = 9.2Hz, 1H, CH), 3.01 (d, *J* = 9.6Hz, 1H, CH), 2.54 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 1.14 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.3, 164.8, 140.2, 135.4, 132.9, 129.7, 128.8, 128.6, 127.7, 127.2, 126.1, 117.7, 109.0, 64.8, 63.3, 62.8, 57.7, 55.8, 44.0, 41.3, 21.2, 13.7; IR(KBr) υ: 2980, 2945, 2853, 2795, 2243, 1751, 1713, 1611, 1496, 1448, 1370, 1266, 1233, 1175, 1104, 1026, 895, 856, 812, 736, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{26}N_3O_3$ ($[M+H]^+$): 404.1974, found: 404.1996.



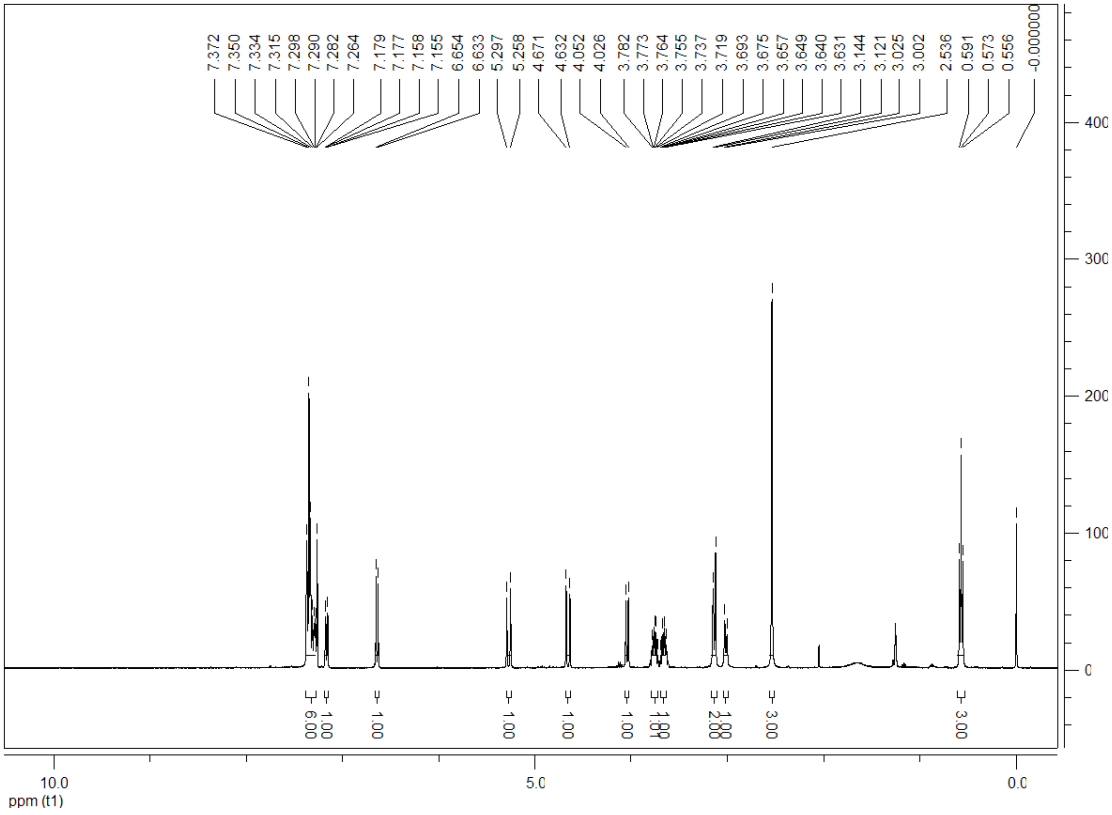

175.329
164.825
140.177
135.367
132.875
129.742
128.781
128.570
127.700
127.243
126.058
117.732
109.001
64.795
63.293
62.809
57.687
55.848
44.044
41.307
21.225
13.659
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

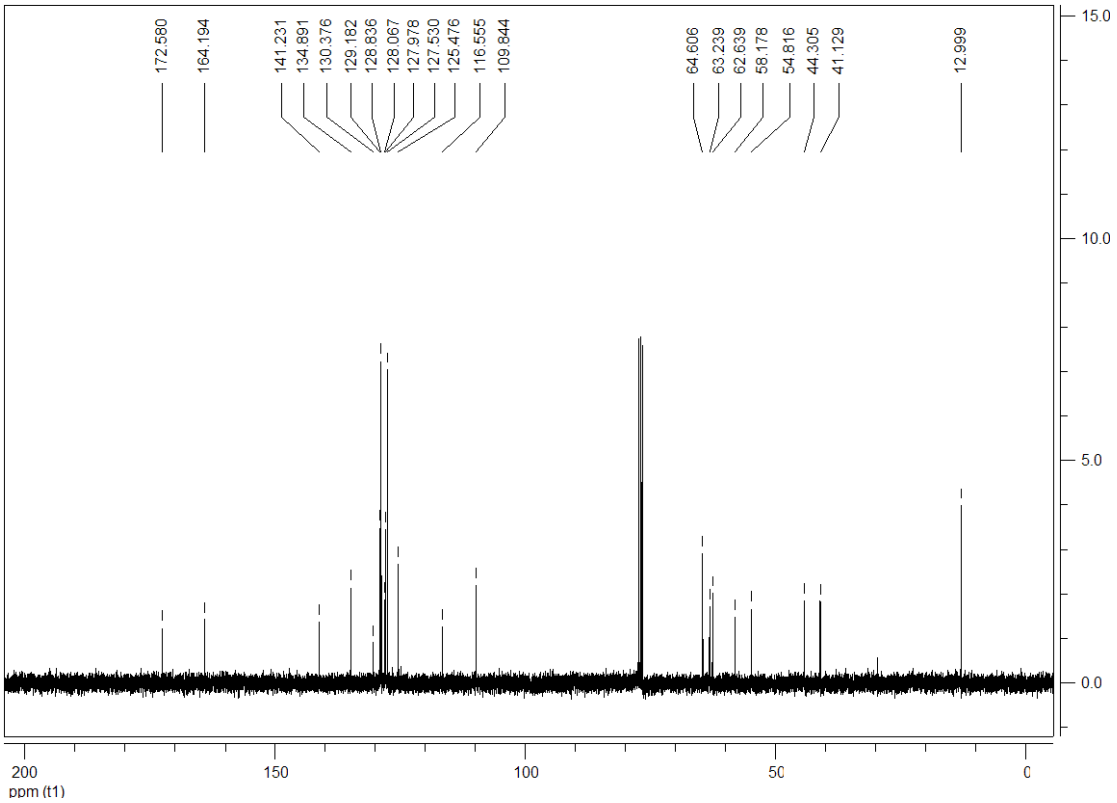

Intens.
x10^5
+MS, 0.2-0.4min #(25-36)
404.1996
426.1800
5
4
3
2
1
0
360
380
400
420
440
460
480
500 m/z

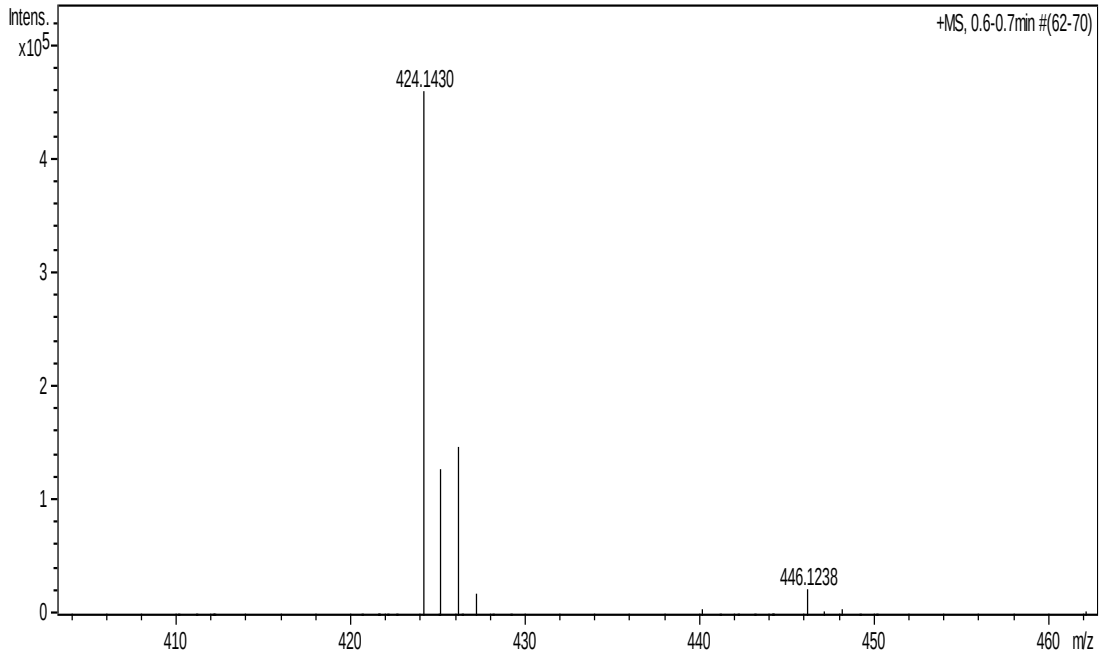
(3R,4'R)-ethyl-1-benzyl-5-chloro-4'-cyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6e)



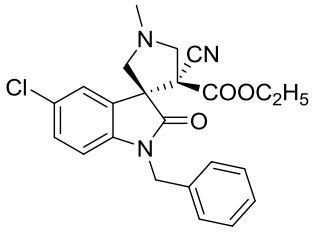
ratio of major/minor = 86:14; **major isomer (6e):** white solid, 69%, m.p. 191~192℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37~7.28 (m, 6H, ArH), 7.18~7.16 (m, 1H, ArH), 6.64 (d, *J* = 8.4Hz, 1H, ArH), 5.28 (d, *J* = 15.6Hz, 1H, CH), 4.65 (d, *J* = 15.6Hz, 1H, CH), 4.04 (d, *J* = 10.4Hz, 1H, CH), 3.78~3.72 (m, 1H, CH), 3.69~3.63 (m, 1H, CH), 3.13 (d, *J* = 9.2Hz, 2H, CH), 3.01 (d, *J* = 9.2Hz, 1H, CH), 2.54 (s, 3H, CH_3), 0.57 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.6, 164.2, 141.2, 134.9, 130.4, 129.2, 128.8, 128.1, 128.0, 127.5, 125.5, 116.6, 109.8, 64.6, 63.2, 62.6, 58.2, 54.8, 44.3, 41.1, 13.0; IR(KBr) υ: 2979, 2949, 2824, 2789, 2241, 1756, 1713, 1608, 1486, 1436, 1347, 1300, 1268, 1235, 1181, 1123, 1096, 1032, 1002, 943, 907, 850, 818, 740 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}ClN_3O_3$ ([M+H]$^+$): 424.1428, found: 424.1430.



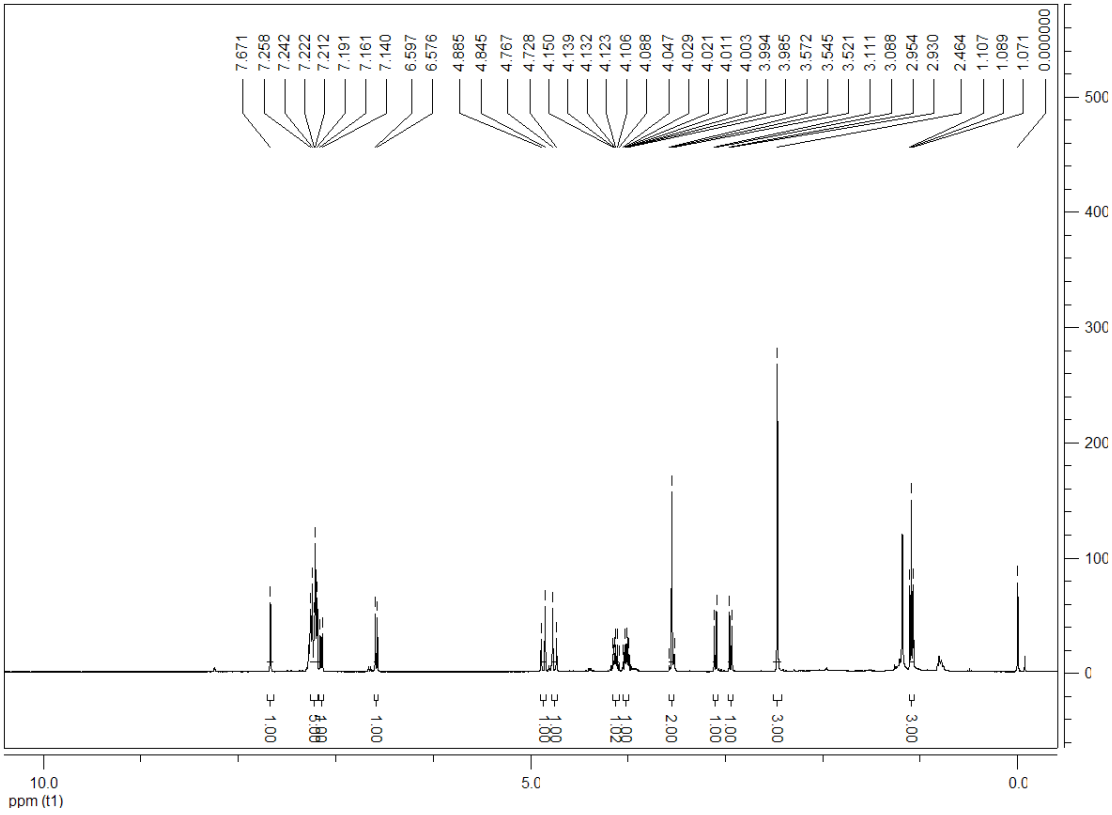

172.580
164.194
141.231
134.891
130.376
129.182
128.836
128.067
127.978
127.530
125.476
116.555
109.844
64.606
63.239
62.639
58.178
54.816
44.305
41.129
12.999
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

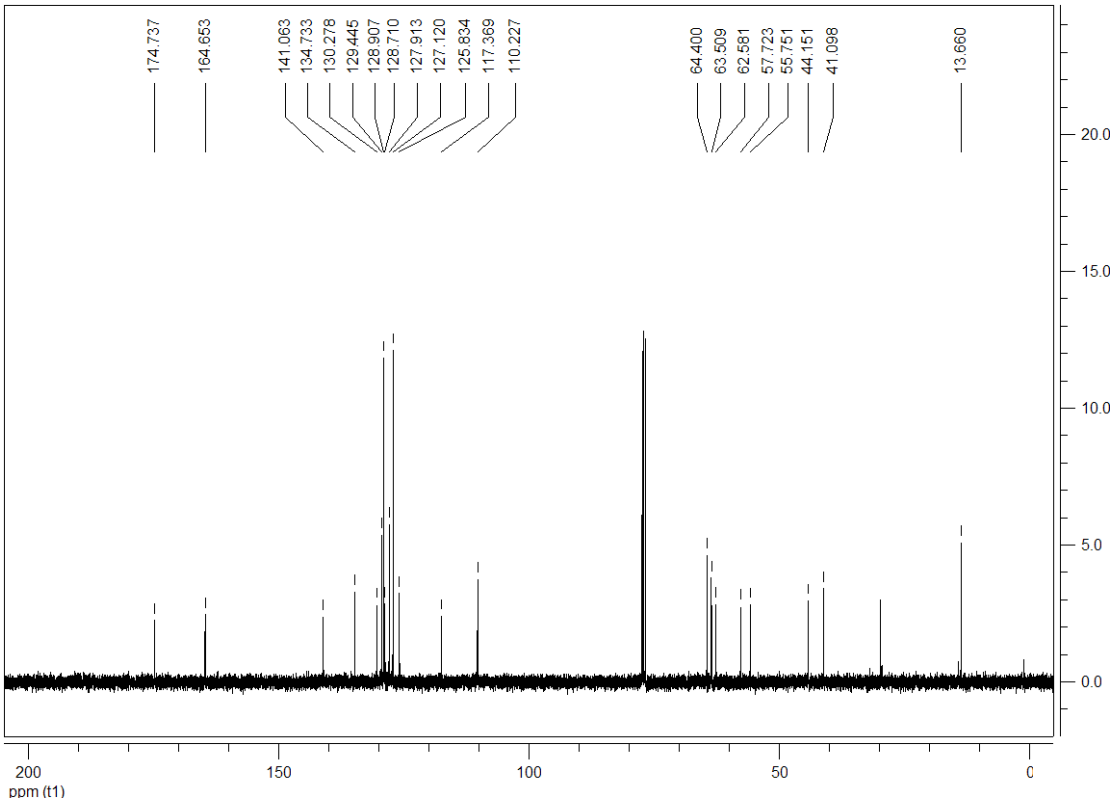

Intens.
x10^5
+MS, 0.6-0.7min #(62-70)
424.1430
446.1238
4
3
2
1
0
410
420
430
440
450
460
m/z

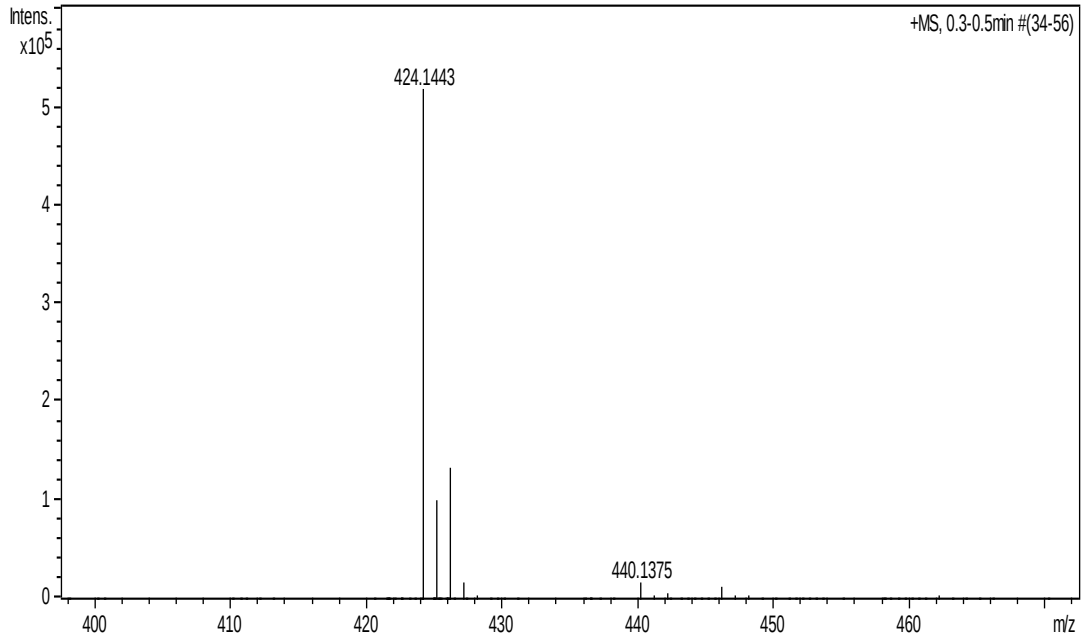
(3R,4'S)-Ethyl-1-benzyl-5-chloro-4'-cyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6e')



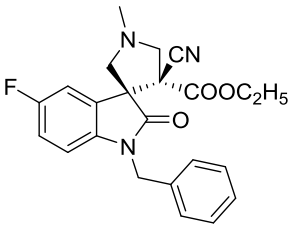
minor isomer (6e'): viscous oil, 11%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (brs, 1H, ArH), 7.24~7.19 (m, 5H, ArH), 7.16~7.14 (m, 1H, ArH), 6.59 (d, *J* = 8.4Hz, 1H, ArH), 4.86 (d, *J* = 16.0Hz, 1H, CH), 4.75 (d, *J* = 15.6Hz, 1H, CH), 4.15~4.09 (m, 1H, CH), 4.05~3.98 (m, 1H, CH), 3.57~3.52 (m, 2H, CH), 3.10 (d, *J* = 9.2Hz, 1H, CH), 2.94 (d, *J* = 9.6Hz, 1H, CH), 2.46 (s, 3H, CH_3), 1.09 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.7, 164.6, 141.1, 134.7, 130.3, 129.4, 128.9, 128.7, 127.9, 127.1, 125.8, 117.4, 110.2, 64.4, 63.5, 62.6, 57.7, 55.8, 44.2, 41.1, 13.7; IR(KBr) υ: 2976, 2894, 2538, 2360 , 2253, 1924, 1754, 1716, 1663, 1615, 1481, 1452, 1381, 1343, 1272, 1237, 1178, 1089, 1049, 882, 807, 735 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}ClN_3O_3$ ([M+H]$^{+}$): 424.1428, found: 424.1443.



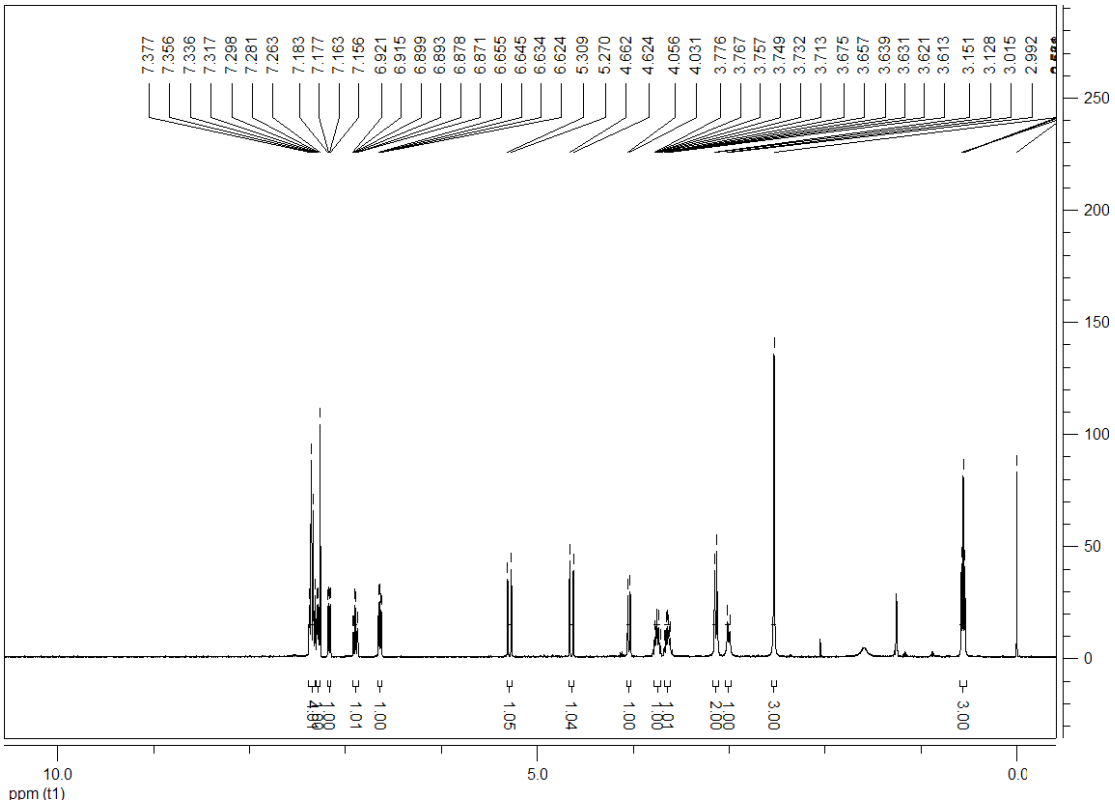

174.737
164.653
141.063
134.733
130.278
129.445
128.907
128.710
127.913
127.120
125.834
117.369
110.227
64.400
63.509
62.581
57.723
55.751
44.151
41.098
13.660
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

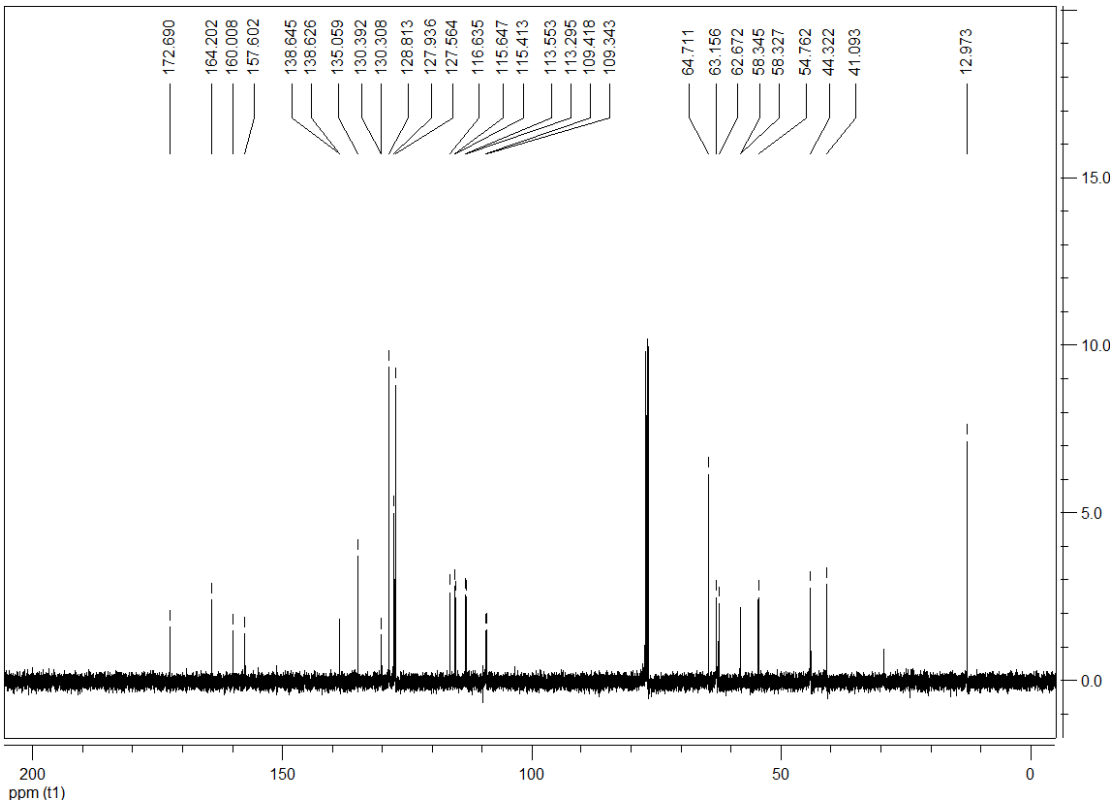

Intens.
x10^5
+MS, 0.3-0.5min #(34-56)
424.1443
440.1375
5
4
3
2
1
0
400
410
420
430
440
450
460
m/z

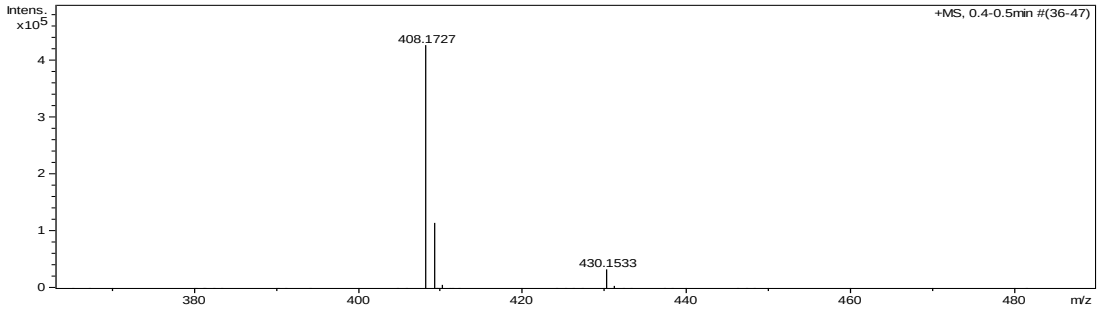
(3R,4'R)-Ethyl-1-benzyl-4'-cyano-5-fluoro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6f)



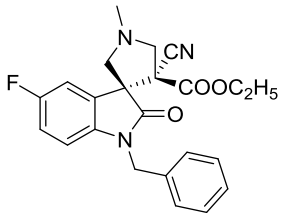
ratio of major/minor = 81:19; **major isomer (6f)**: white solid, 70%, m.p. 196~198℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38~7.32 (m, 4H, ArH), 7.30~7.28 (m, 1H, ArH), 7.17 (dd, J_1 = 8.0Hz, J_2 = 2.4Hz, 1H, ArH), 6.90 (td, J_1 = 8.8Hz, J_2 = 2.4Hz, 1H, ArH), 6.64 (td, J_1 = 8.4Hz, J_2 = 4.0Hz, 1H, ArH), 5.29 (d, J = 15.6Hz, 1H, CH), 4.64 (d, J = 15.6Hz, 1H, CH), 4.04 (d, J = 10.0Hz, 1H, CH), 3.78~3.71 (m, 1H, CH), 3.68~3.61 (m, 1H, CH), 3.14 (d, J = 9.2Hz, 2H, CH), 3.00 (d, J = 9.2Hz, 1H, CH), 2.53 (s, 3H, CH_3), 0.56 (t, J = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.7, 164.2, 158.8 (d, J = 240.6Hz), 138.6 (d, J = 1.9Hz), 135.0, 130.3 (d, J = 8.4Hz), 128.8, 127.9, 127.6, 116.6, 115.5 (d, J = 23.4Hz), 113.4 (d, J = 25.8Hz), 109.4 (d, J = 7.5Hz), 64.7, 63.2, 62.7, 58.3 (d, J = 1.8Hz), 54.8, 44.3, 41.1, 13.0; IR(KBr) υ: 2983, 2950, 2849, 2819, 2792, 2240, 1757, 1712, 1616, 1491, 1452, 1349, 1276, 1241, 1177, 1123, 1097, 1034, 1007, 937, 885, 850, 818, 768, 734 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}FN_3O_3$ ([M+H]$^+$): 408.1723, found: 408.1727.



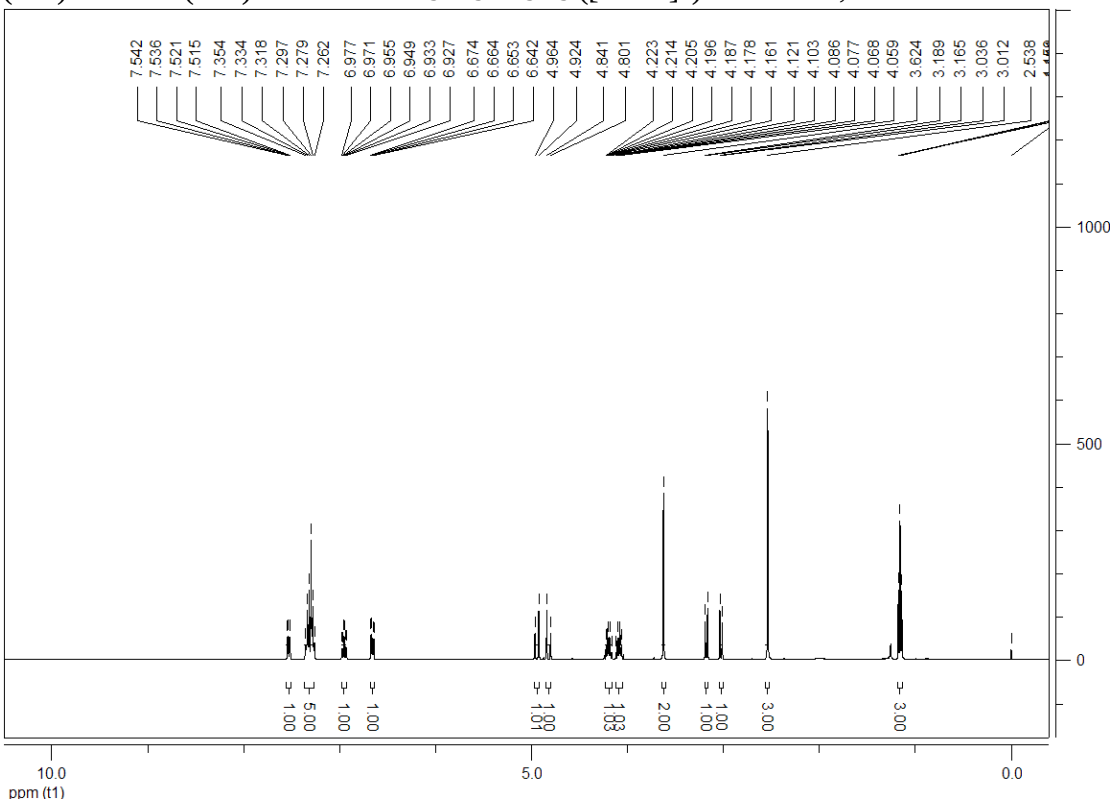

172.690
164.202
160.008
157.602
138.645
138.626
135.059
130.392
130.308
128.813
127.936
127.564
116.635
115.647
115.413
113.553
113.295
109.418
109.343
64.711
63.156
62.672
58.345
58.327
54.762
44.322
41.093
12.973
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

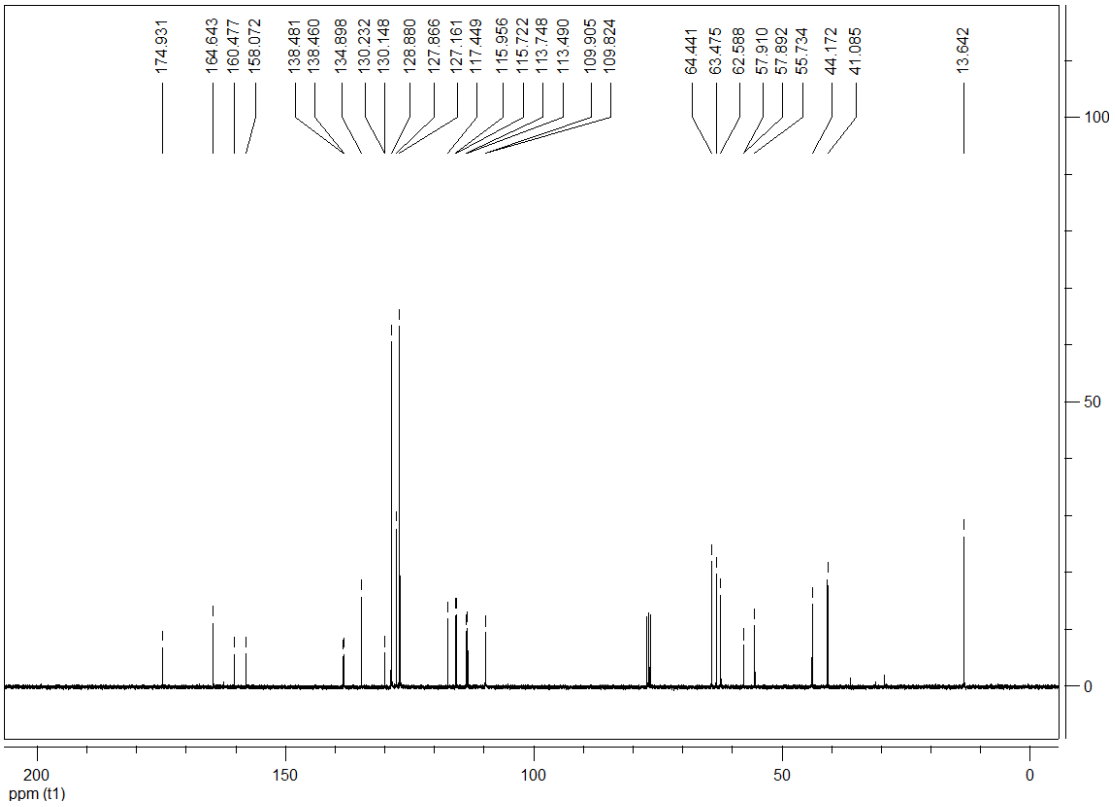

Intens.
x10^5
+MS, 0.4-0.5min #(36-47)
408.1727
430.1533
4
3
2
1
0
380
400
420
440
460
480
m/z

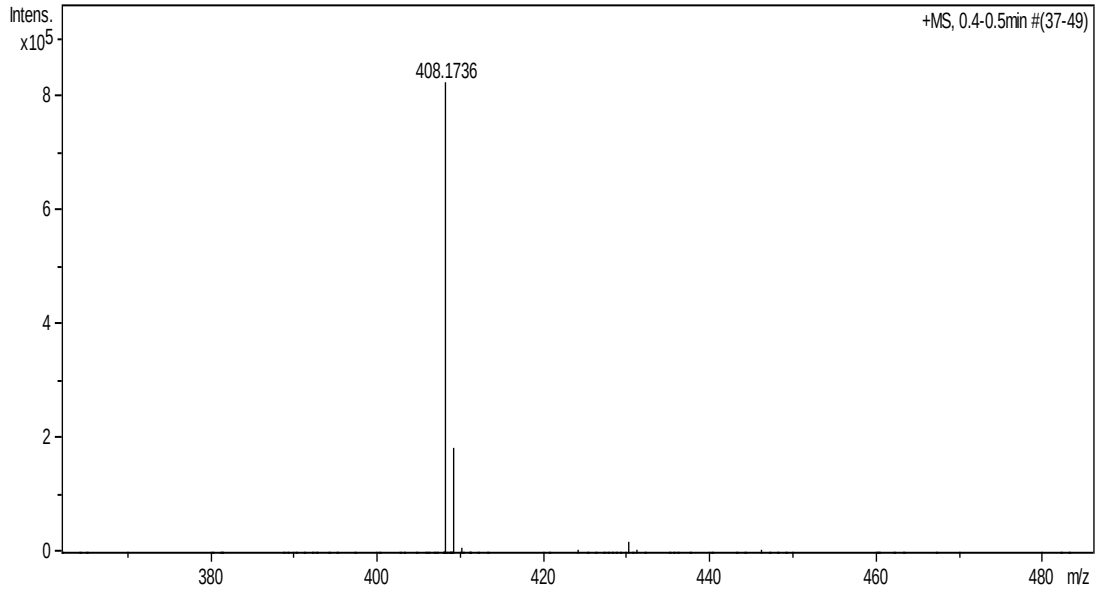
(3R,4'S)-Ethyl-1-benzyl-4'-cyano-5-fluoro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6f')



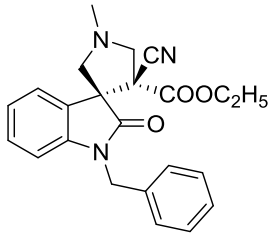
minor isomer (6f'): viscous oil, 16%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54 (dd, J_1 = 8.4Hz, J_2 = 2.4Hz, 1H, ArH), 7.35~7.28 (m, 5H, ArH), 6.95 (td, J_1 = 8.8Hz, J_2 = 2.4Hz, 1H, ArH), 6.66 (dd, J_1 = 8.6Hz, J_2 = 4.0Hz, 1H, ArH), 4.94 (d, J = 16.0Hz, 1H, CH), 4.82 (d, J = 16.0Hz, 1H, CH), 4.22~4.16 (m, 1H, CH), 4.12~4.06 (m, 1H, CH), 3.62 (s, 2H, CH), 3.18 (d, J = 9.6Hz, 1H, CH), 3.02 (d, J = 9.6Hz, 1H, CH), 2.54 (s, 3H, CH_3), 1.16 (t, J = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.9, 164.6, 159.3 (d, J = 240.5Hz), 138.5 (d, J = 2.1Hz), 134.9, 130.2 (d, J = 8.4Hz), 128.9, 127.9, 127.2, 117.4, 115.8 (d, J = 23.4Hz), 113.6 (d, J = 25.8Hz), 109.9 (d, J = 8.1Hz), 64.4, 63.5, 62.6, 57.9 (d, J = 1.8Hz), 55.7, 44.2, 41.1, 13.6; IR(KBr) υ: 2982, 2947, 2853, 2797, 2244, 1752, 1716, 1615, 1491, 1454, 1347, 1273, 1234, 1177, 1100, 1026, 931, 855, 815, 736 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}FN_3O_3$ ($[M+H]^+$): 408.1723, found: 408.1736.



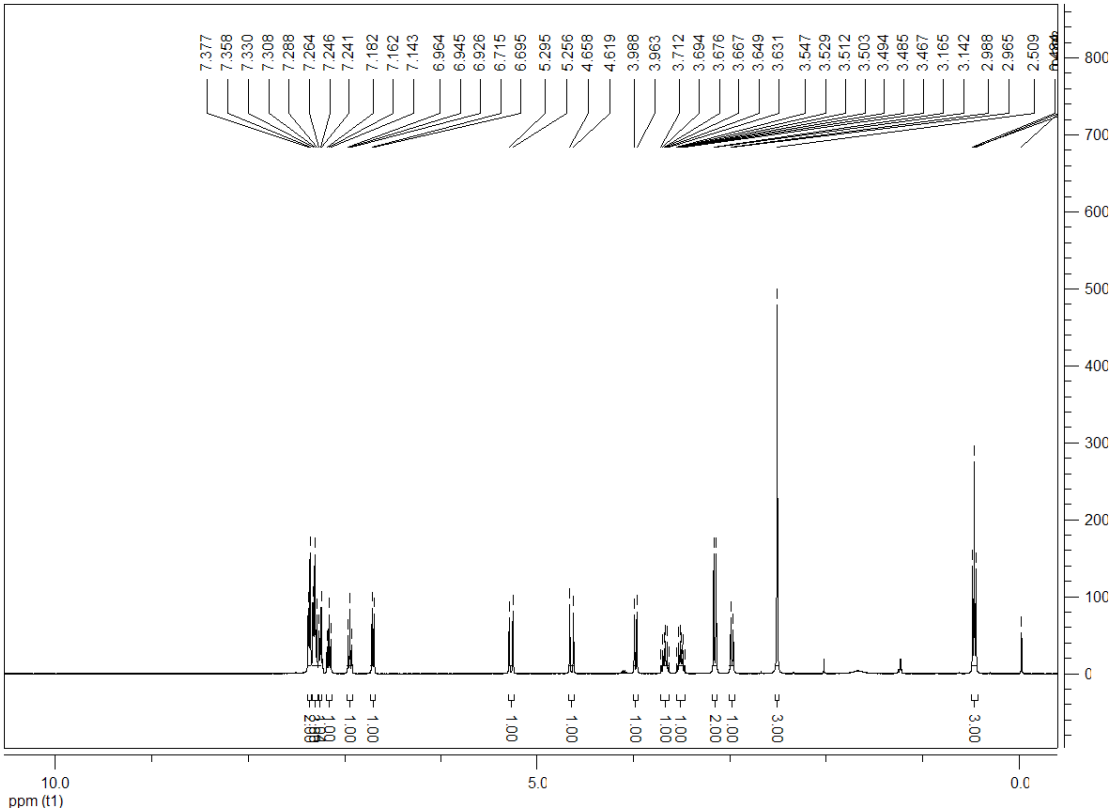

174.931
164.643
160.477
158.072
138.481
138.460
134.898
130.232
130.148
128.880
127.866
127.161
117.449
115.956
115.722
113.748
113.490
109.905
109.824
64.441
63.475
62.588
57.910
57.892
55.734
44.172
41.085
13.642
100
50
0
200
150
100
50
0
ppm (t1)

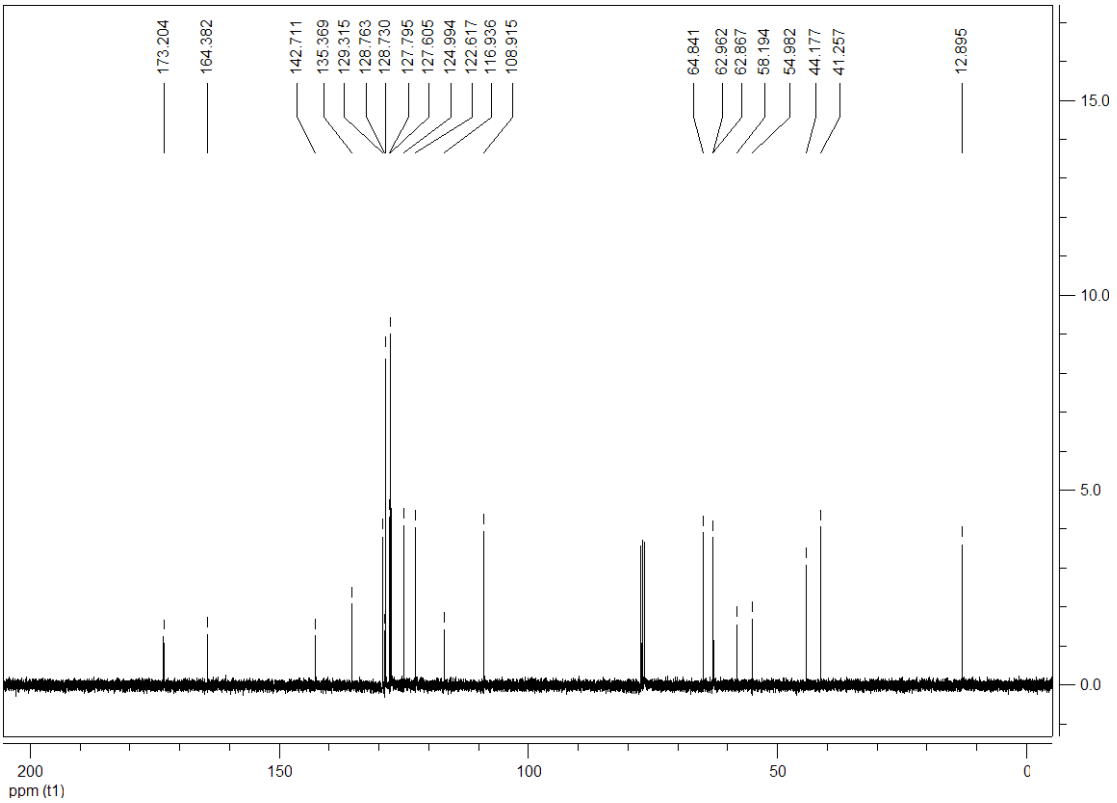

Intens.
x10^5
+MS, 0.4-0.5min #(37-49)
408.1736
8
6
4
2
0
380
400
420
440
460
480
m/z

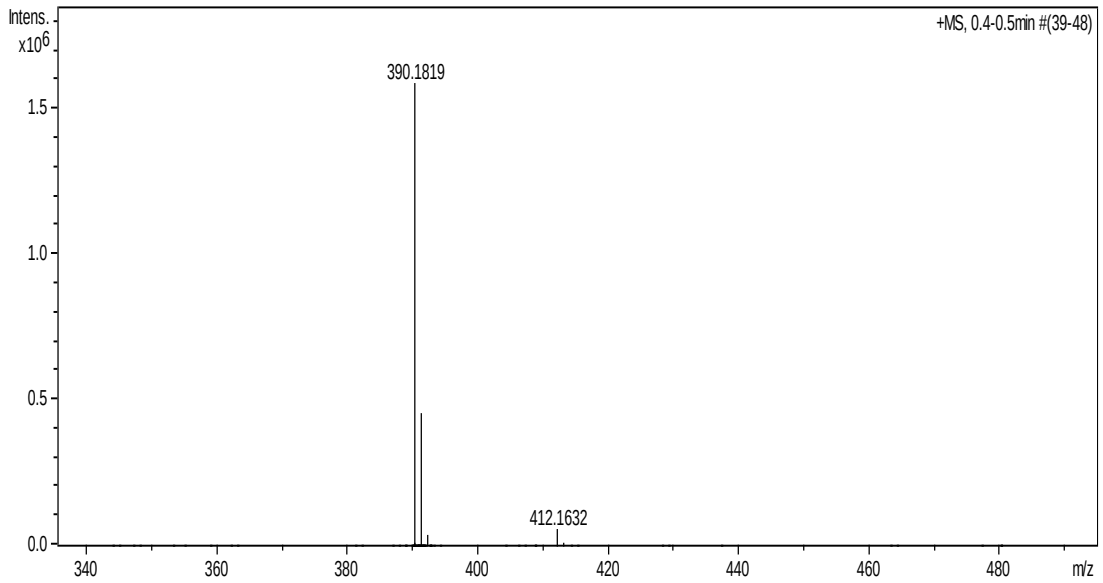
(3R,4'R)-Ethyl-1-benzyl-4'-cyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6g)



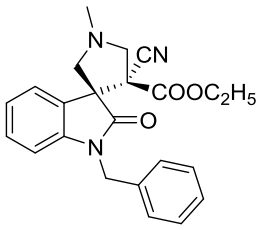
ratio of major/minor = 85:15; **major isomer (6g)**: white solid, 68%, m.p. 151~152℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38~7.36 (m, 2H, ArH), 7.33~7.29 (m, 3H, ArH), 7.26~7.24 (m, 1H, ArH), 7.18~7.14 (m, 1H, ArH), 6.94 (t, *J* = 7.6Hz, 1H, ArH), 6.70 (d, *J* = 8.0Hz, 1H, ArH), 5.28 (d, *J* = 15.6Hz, 1H, CH), 4.64 (d, *J* = 15.6Hz, 1H, CH), 3.98 (d, *J* = 10.0Hz, 1H, CH), 3.71~3.63 (m, 1H, CH), 3.55~3.47 (m, 1H, CH), 3.15 (d, *J* = 9.2Hz, 2H, CH), 2.98 (d, *J* = 9.2Hz, 1H, CH), 2.51 (s, 3H, CH_3), 0.47 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.2, 164.4, 142.7, 135.4, 129.3, 128.8, 128.7, 127.8, 127.6, 125.0, 122.6, 116.9, 108.9, 64.8, 63.0, 62.9, 58.2, 55.0, 44.2, 41.3, 12.9; IR(KBr) υ: 2978, 2941, 2903, 2836, 2791, 2240, 1963, 1879, 1752, 1713, 1608, 1491, 1465, 1355, 1271, 1235, 1169, 1132, 1096, 1034, 1008, 946, 908, 855, 793, 762, 736 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}N_3O_3$ ([M+H]$^+$): 390.1818, found: 390.1819.



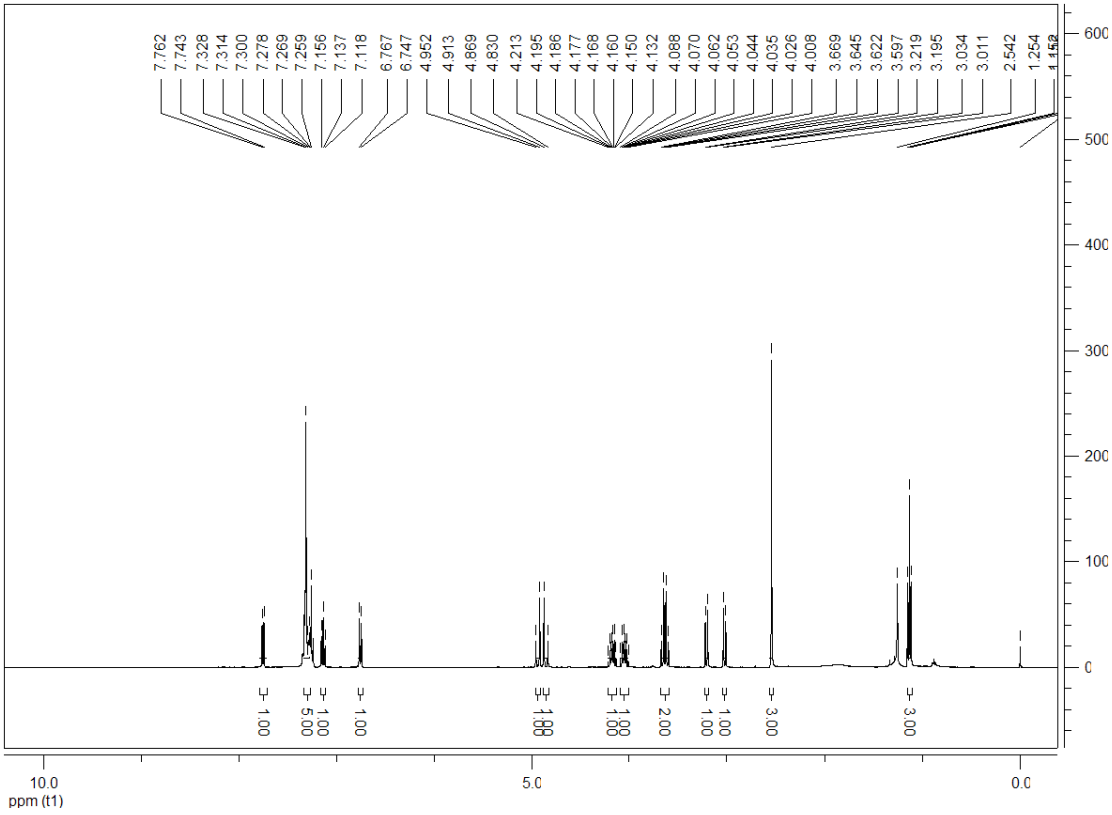

173.204
164.382
142.711
135.369
129.315
128.763
128.730
127.795
127.605
124.994
122.617
116.936
108.915
64.841
62.962
62.867
58.194
54.982
44.177
41.257
12.895
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

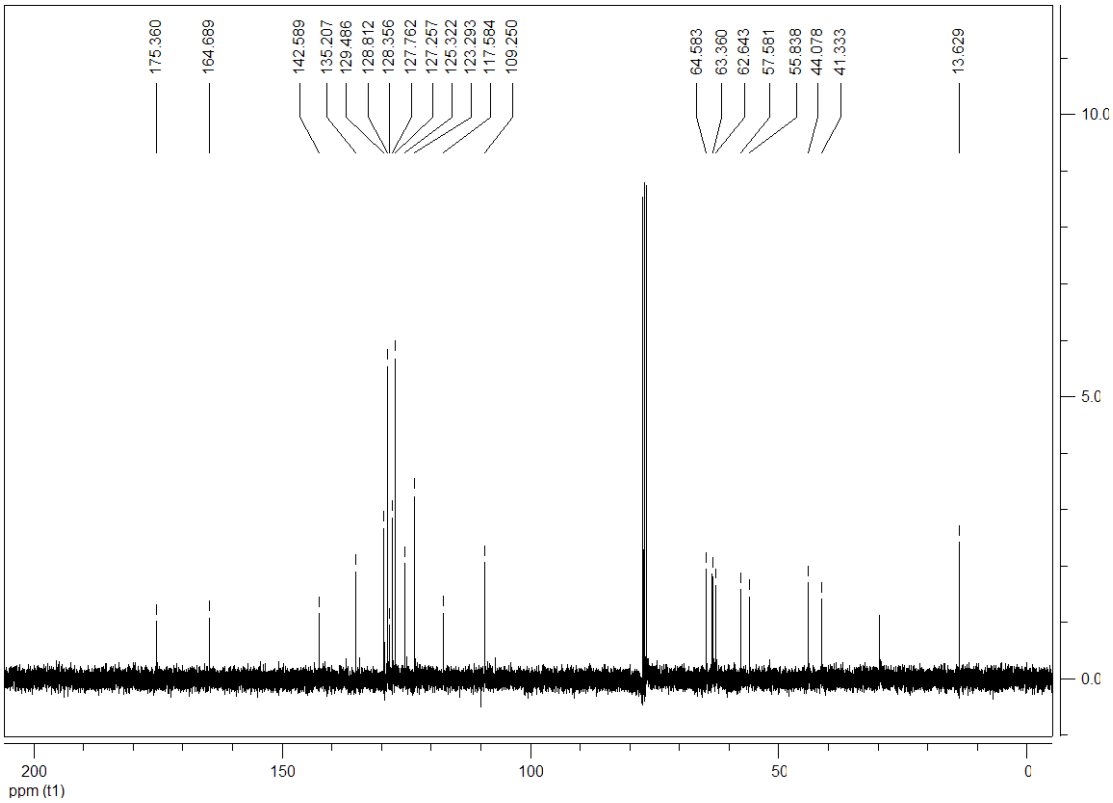

Intens.
x10^6
+MS, 0.4-0.5min #(39-48)
390.1819
412.1632
1.5
1.0
0.5
0.0
340
360
380
400
420
440
460
480
m/z

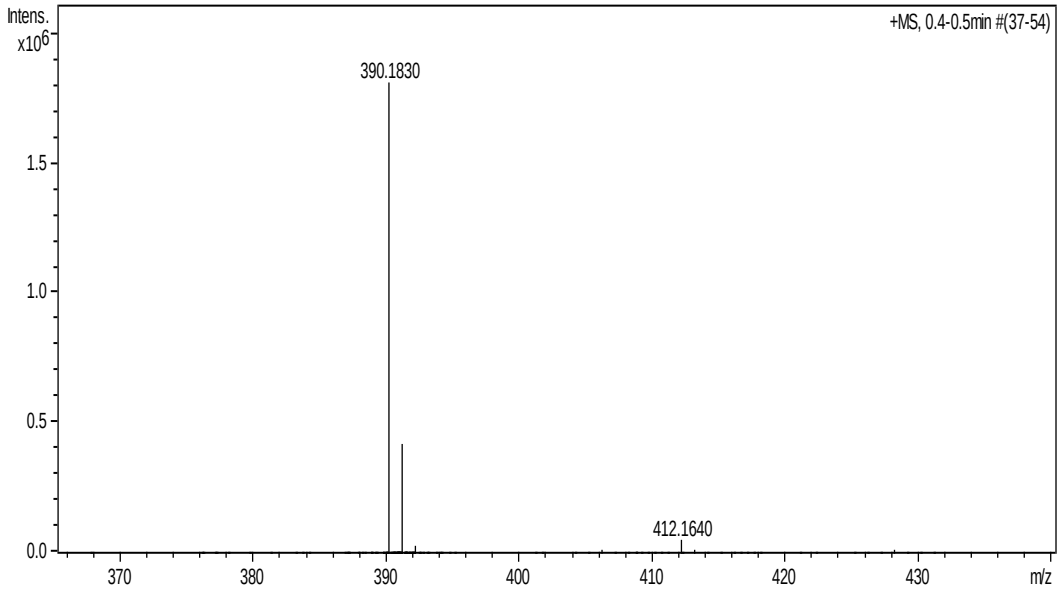
(3R,4'S)-Ethyl-1-benzyl-4'-cyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine] -4'-carboxylate (6g')



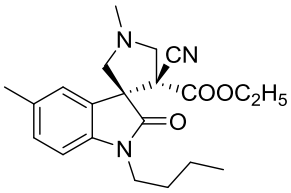
minor isomer (6g'): viscous oil, 12%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.6Hz, 1H, ArH), 7.33~7.27 (m, 5H, ArH), 7.16~7.12 (m, 1H, ArH), 6.76 (d, *J* = 8.0Hz, 1H, ArH), 4.93 (d, *J* = 15.6Hz, 1H, CH), 4.85 (d, *J* = 15.6Hz, 1H, CH), 4.21~4.13 (m, 1H, CH), 4.09~4.01 (m, 1H, CH), 3.63 (q, *J* = 9.8Hz, 2H, CH), 3.21 (d, *J* = 9.6Hz, 1H, CH), 3.02 (d, *J* = 9.2Hz, 1H, CH), 2.54 (s, 3H, CH_3), 1.13 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.4, 164.7, 142.6, 135.2, 129.5, 128.8, 128.4, 127.8, 127.3, 125.3, 123.3, 117.6, 109.2, 64.6, 63.4, 62.6, 57.6, 55.8, 44.1, 41.3, 13.6; IR(KBr) υ: 2925, 2853, 2795, 2319, 2243, 1751, 1715, 1610, 1490, 1466, 1367, 1264, 1233, 1180, 1100, 1012, 856, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{23}H_{23}N_3O_3$ ([M+H]$^{+}$): 390.1818, found: 390.1830.



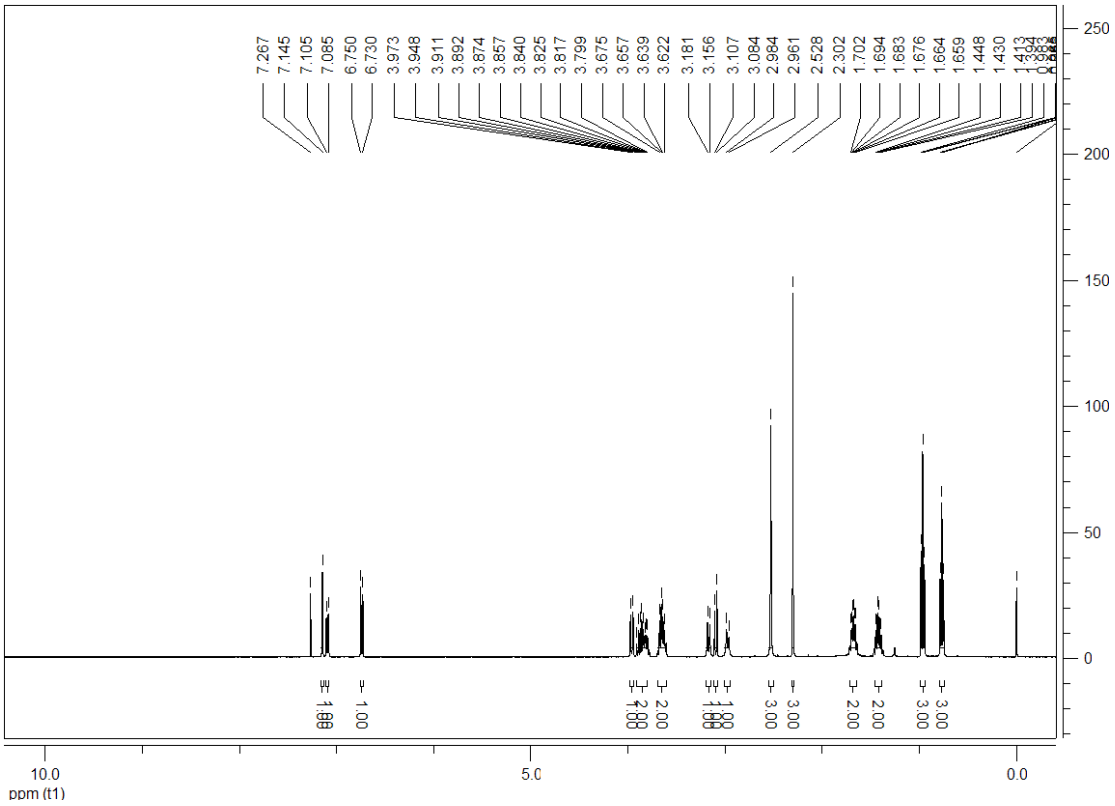

175.360
164.689
142.589
135.207
129.486
128.812
128.356
127.762
127.257
125.322
123.293
117.584
109.250
64.583
63.360
62.643
57.581
55.838
44.078
41.333
13.629
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

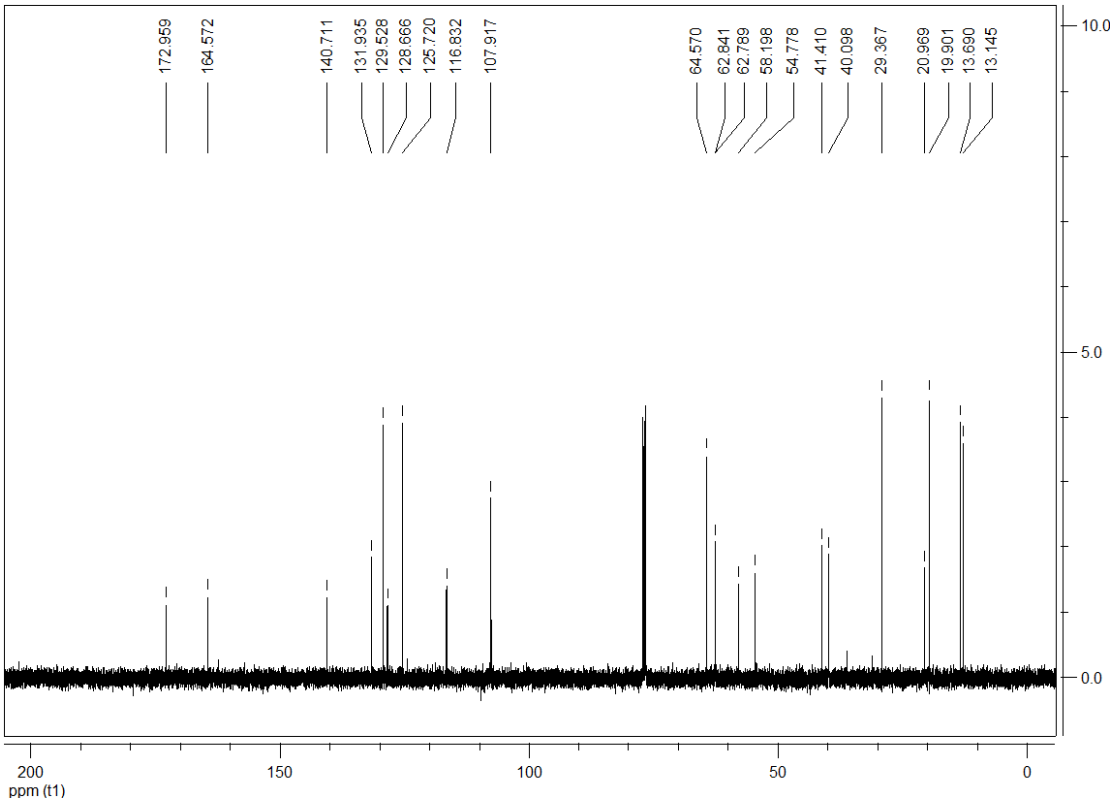

Intens.
x10^6
+MS, 0.4-0.5min #(37-54)
390.1830
412.1640
1.5
1.0
0.5
0.0
370
380
390
400
410
420
430
m/z

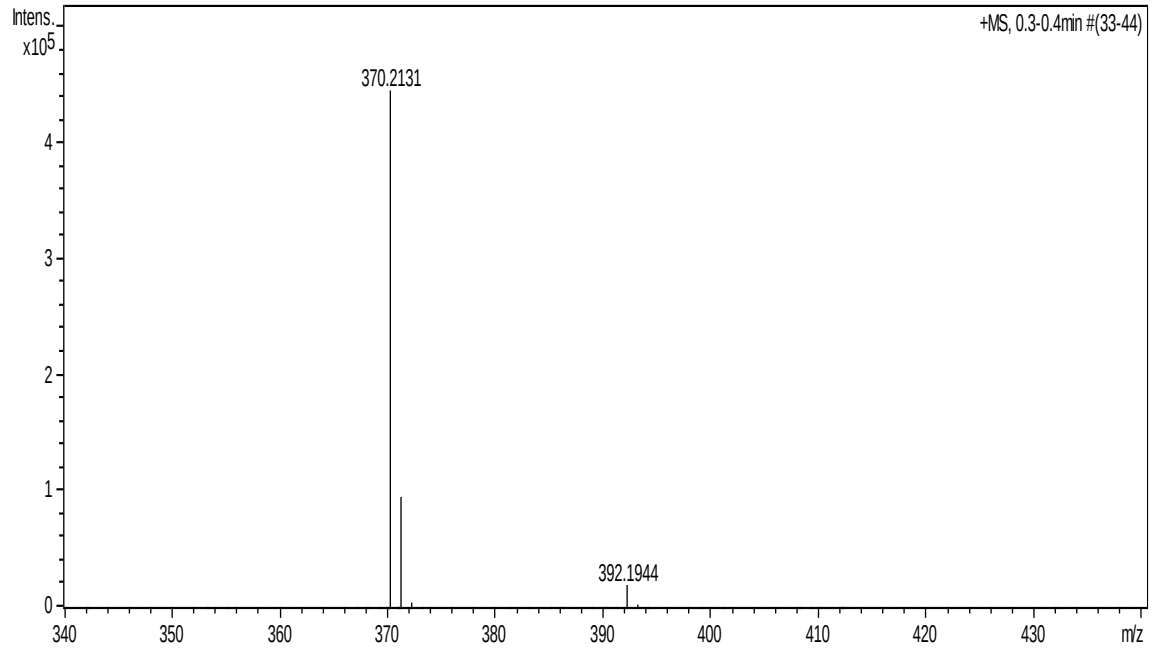
(3R,4'R)-Ethyl-1-butyl-4'-cyano-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6h)



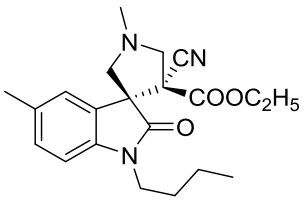
ratio of major/minor = 85:15; **major isomer (6h)**: white solid, 75%, m.p. 105~106℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14 (brs, 1H, ArH), 7.10 (d, *J* = 8.0Hz, 1H, ArH), 6.74 (d, *J* = 8.0Hz, 1H, ArH), 3.96 (d, *J* = 10.0Hz, 1H, CH), 3.91~3.80 (m, 2H, CH), 3.68~3.62 (m, 2H, CH), 3.17 (d, *J* = 10.0Hz, 1H, CH), 3.10 (d, *J* = 9.2Hz, 1H, CH), 2.97 (d, *J* = 9.2Hz, 1H, CH), 2.53 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 1.70~1.66 (m, 2H, CH), 1.45~1.39 (m, 2H, CH), 0.96 (t, *J* = 7.2Hz, 3H, CH_3), 0.77 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 173.095, 164.6, 140.7, 131.9, 129.5, 128.7, 125.7, 116.8, 107.9, 64.6, 62.8, 62.8, 58.2, 54.8, 41.4, 40.1, 29.4, 21.0, 19.9, 13.7, 13.1; IR(KBr) υ: 2957, 2931, 2867, 2784, 2240, 1904, 1744, 1708, 1612, 1498, 1460, 1368, 1297, 1259, 1200, 1121, 1093, 1032, 998, 875, 848, 822, 770, 732 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{28}N_3O_3$ ($[M+H]^+$): 370.2131, found: 370.2131.



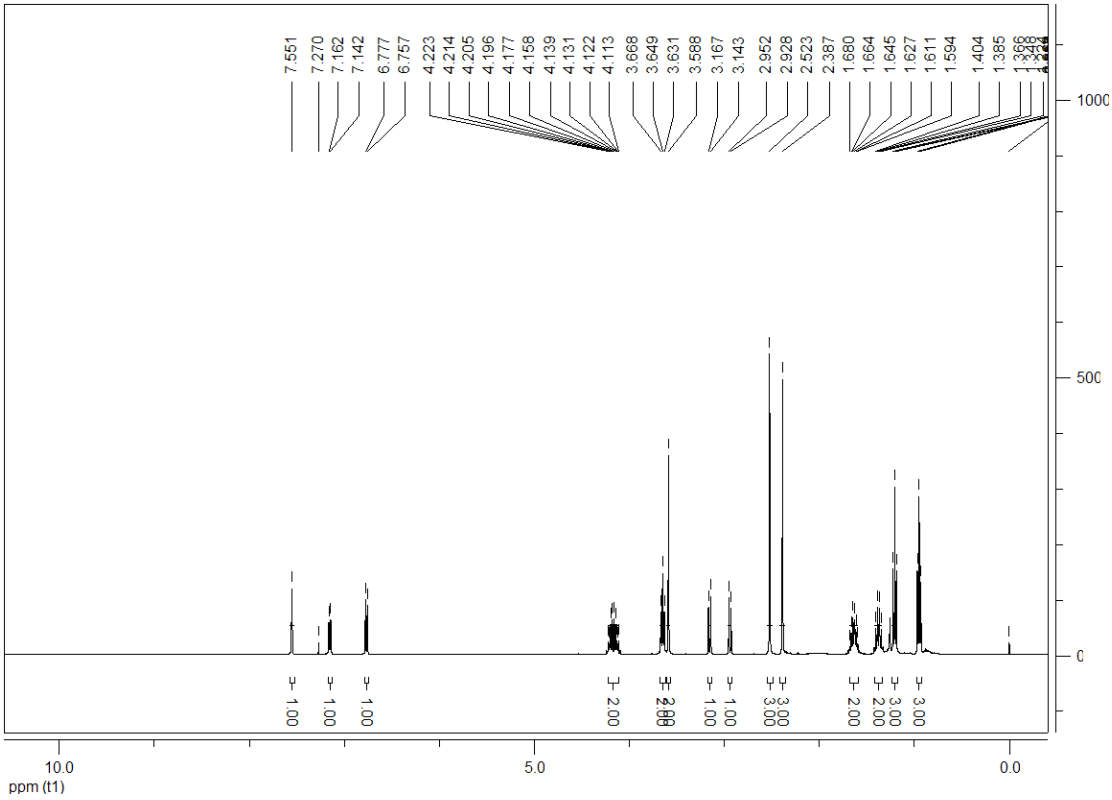

172.959
164.572
140.711
131.935
129.528
128.666
125.720
116.832
107.917
64.570
62.841
62.789
58.198
54.778
41.410
40.098
29.367
20.969
19.901
13.690
13.145
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

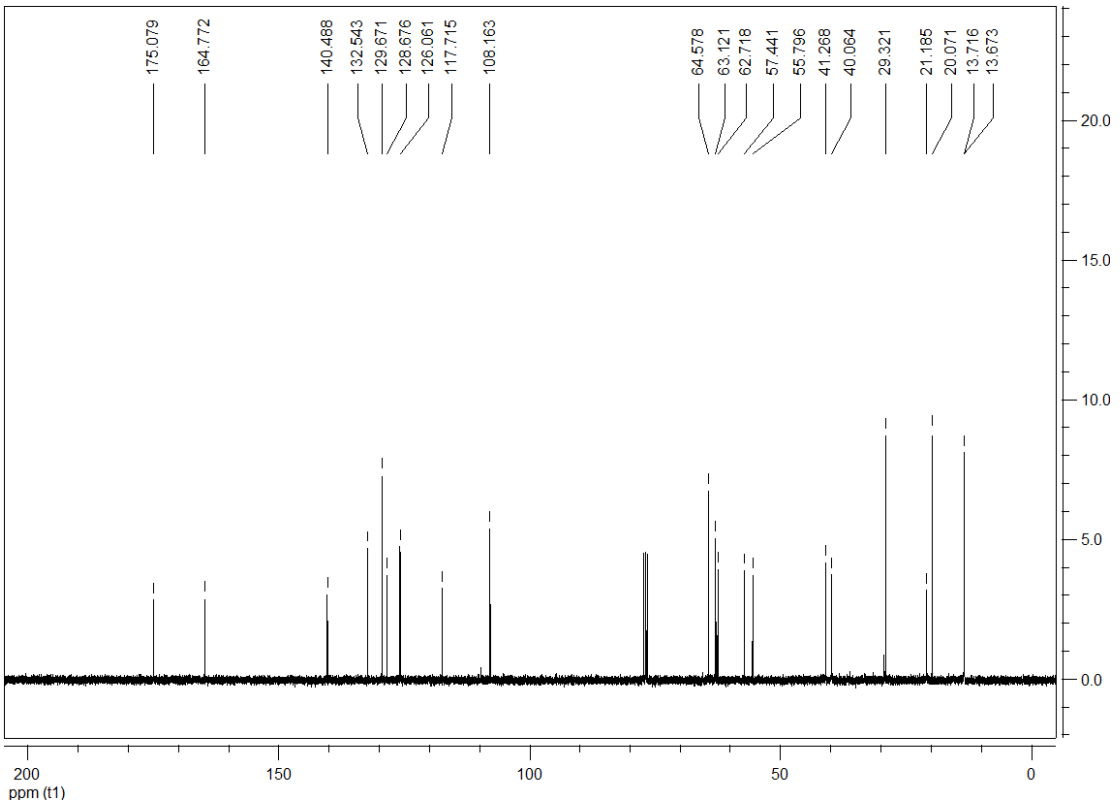

Intens.
x10^5
+MS, 0.3-0.4min #(33-44)
370.2131
392.1944
4
3
2
1
0
340
350
360
370
380
390
400
410
420
430
m/z

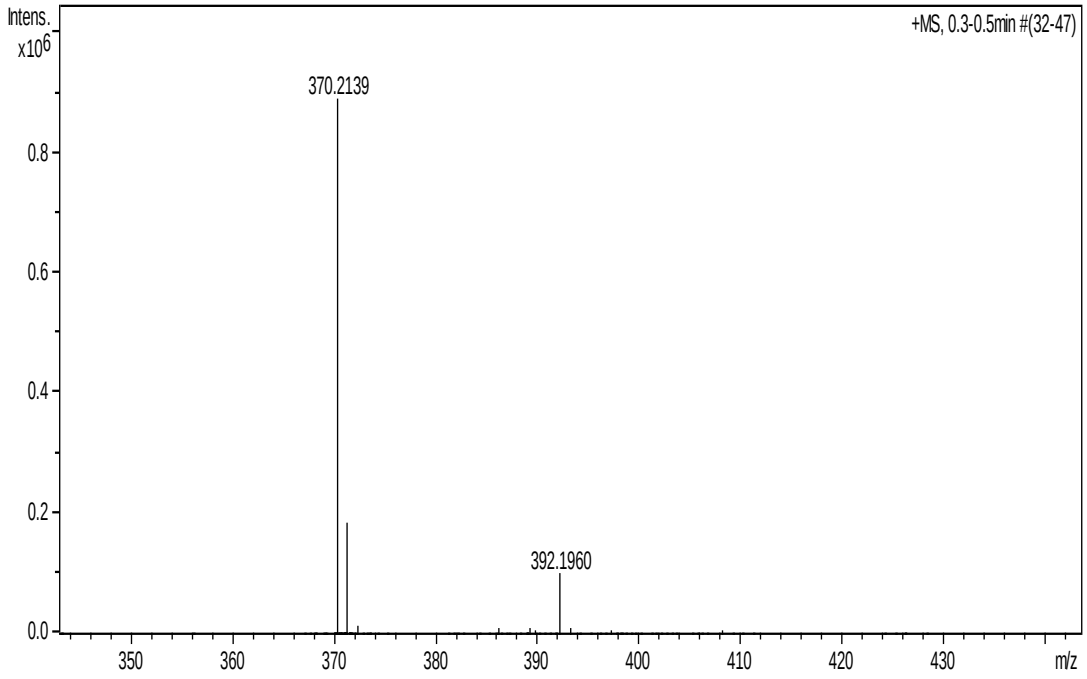
(3R,4'S)-Ethyl-1-butyl-4'-cyano-1',5-dimethyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6h')



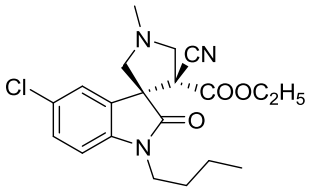
minor isomer (6h'): viscous oil, 13%; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (brs, 1H, ArH), 7.15 (d, *J* = 8.0Hz, 1H, ArH), 6.77 (d, *J* = 8.0Hz, 1H, ArH), 4.22~4.11 (m, 2H, CH), 3.65 (t, *J* = 7.2Hz, 2H, CH), 3.59 (s, 2H, CH), 3.16 (d, *J* = 9.6Hz, 1H, CH), 2.94 (d, *J* = 9.6Hz, 1H, CH), 2.52 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 1.68~1.59 (m, 2H, CH), 1.40~1.39 (m, 2H, CH), 1.21 (t, *J* = 7.2Hz, 3H, CH_3), 0.95 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.1, 164.8, 140.5, 132.5, 129.7, 128.7, 126.1, 117.7, 108.2, 64.6, 63.1, 62.7, 57.4, 55.8, 41.3, 40.1, 29.3, 21.2, 20.1, 13.7, 13.6; IR(KBr) υ: 2959, 2934, 2867, 2794, 2243, 1752, 1711, 1611, 1496, 1467, 1359, 1264, 1233, 1203, 1149, 1101, 1024, 856, 812, 736 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{21}H_{28}N_3O_3$ ($[M+H]^+$): 370.2131, found: 370.2139.



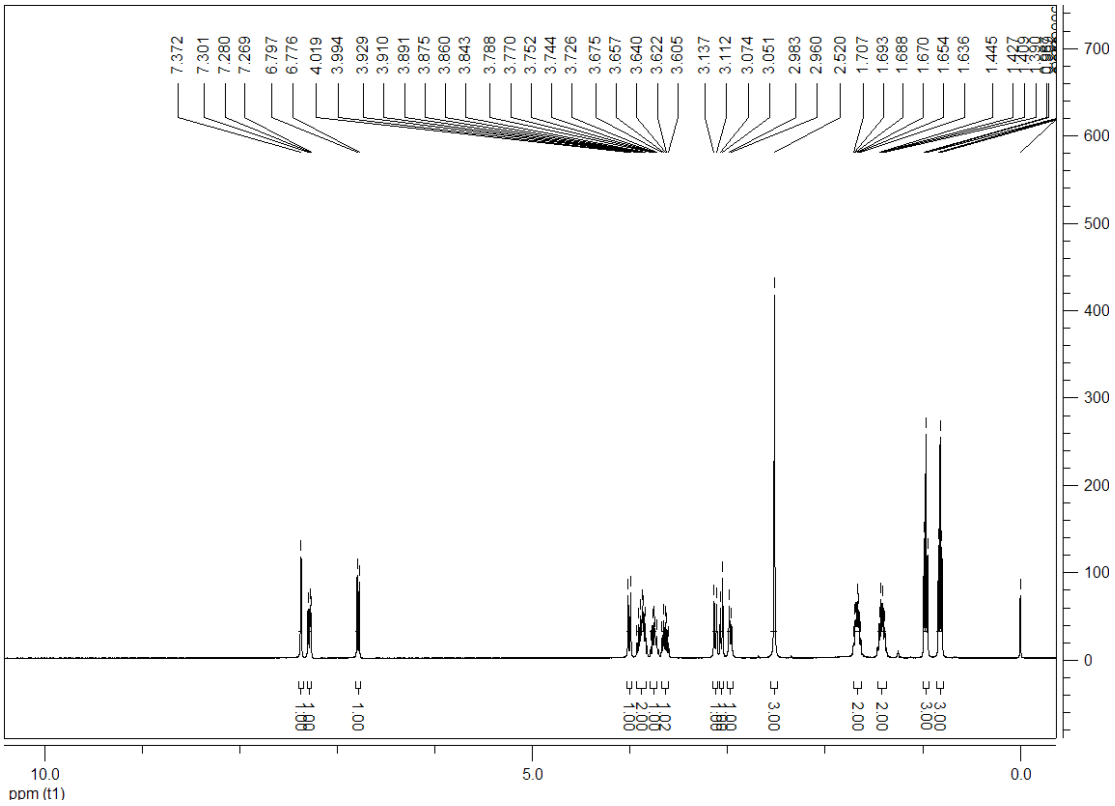

175.079
164.772
140.488
132.543
129.671
128.676
126.061
117.715
108.163
64.578
63.121
62.718
57.441
55.796
41.268
40.064
29.321
21.185
20.071
13.716
13.673
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

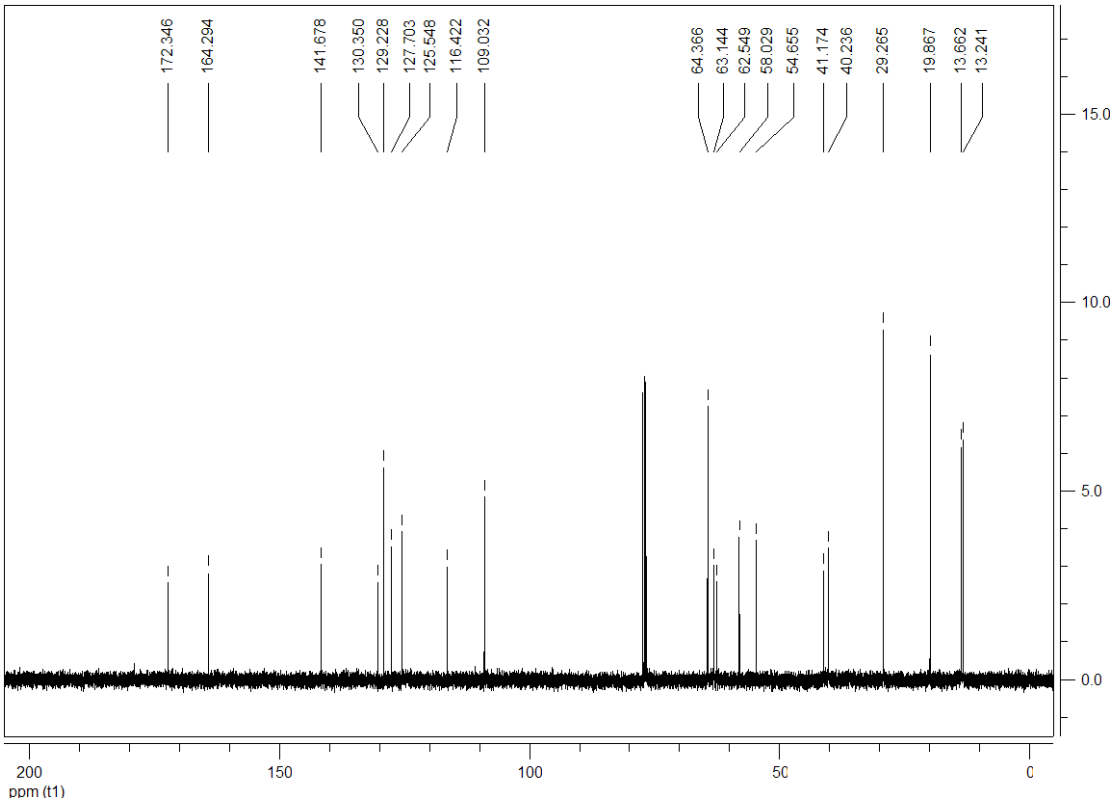

Intens.
x10^6
+MS, 0.3-0.5min #(32-47)
370.2139
392.1960
0.8
0.6
0.4
0.2
0.0
350
360
370
380
390
400
410
420
430
m/z

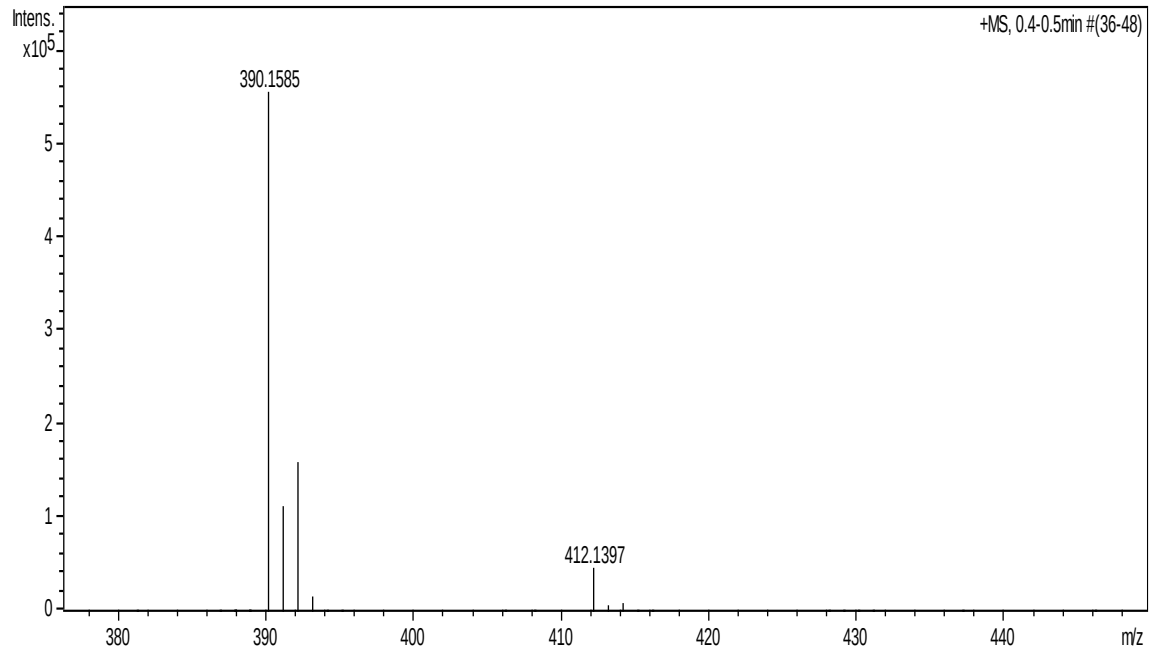
(3R,4'R)-Ethyl-1-butyl-5-chloro-4'-cyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6i)



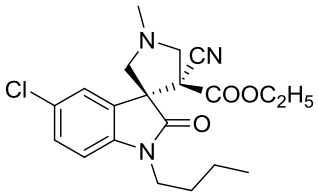
ratio of major/minor = 83:17; **major isomer (6i)**: white solid, 73%, m.p. 122~123℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (brs, 1H, ArH), 7.29 (d, *J* = 8.4Hz, 1H, ArH), 6.79 (d, *J* = 8.0Hz, 1H, ArH), 4.01 (d, *J* = 10.0Hz, 1H, CH), 3.93~3.84 (m, 2H, CH), 3.79~3.73 (m, 1H, CH), 3.68~3.60 (m, 1H, CH), 3.12 (d, *J* = 10.0Hz, 1H, CH), 3.06 (d, *J* = 9.2Hz, 1H, CH), 2.97 (d, *J* = 9.2Hz, 1H, CH), 2.52 (s, 3H, CH_3), 1.70~1.64 (m, 2H, CH), 1.44~1.39 (m, 2H, CH), 0.97 (t, *J* = 7.2Hz, 3H, CH_3), 0.82 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 164.3, 141.7, 130.4, 129.2, 127.7, 125.5, 116.4, 109.0, 64.4, 63.1, 62.5, 58.0, 54.6, 41.2, 40.2, 29.3, 19.9, 13.7, 13.2; IR(KBr) υ: 2961, 2932, 2855, 2793, 2243, 1746, 1711, 1608, 1484, 1437, 1354, 1299, 1246, 1187, 1095, 1034, 1000, 887, 846, 825, 749 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{25}ClN_3O_3$ ($[M+H]^+$): 390.1584, found: 390.1585.



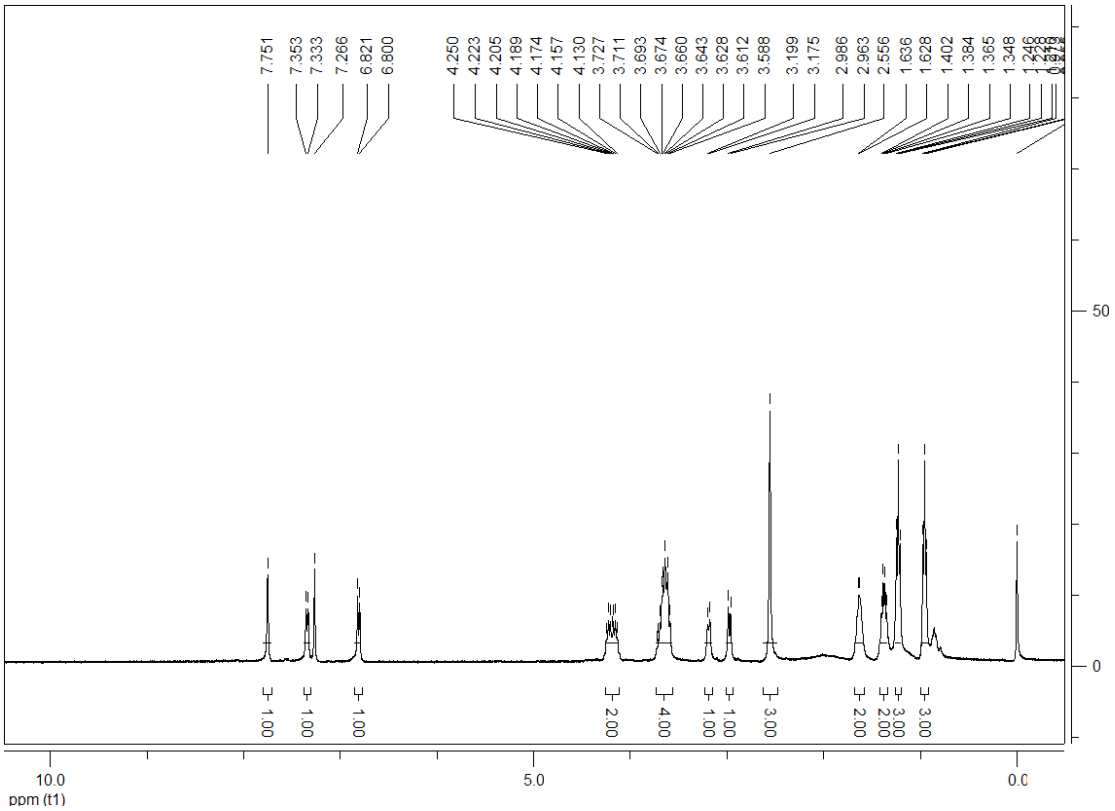

172.346
164.294
141.678
130.350
129.228
127.703
125.548
116.422
109.032
64.366
63.144
62.549
58.029
54.655
41.174
40.236
29.265
19.867
13.662
13.241
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

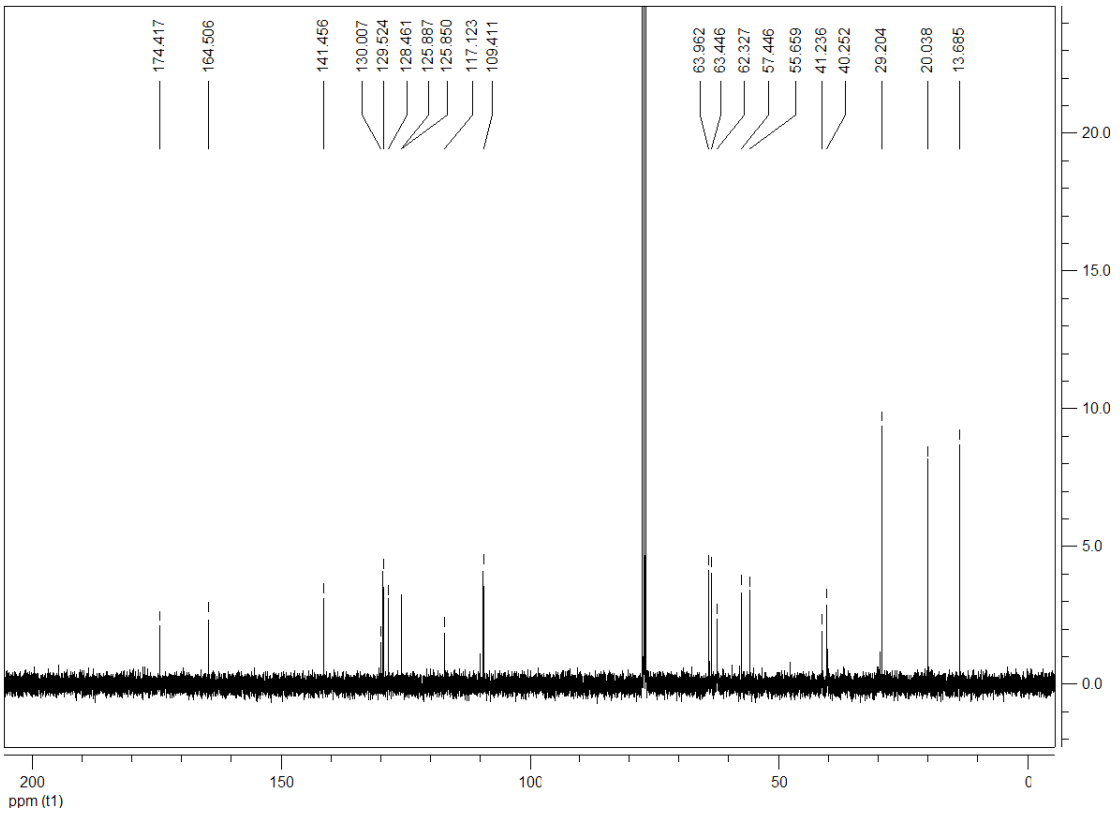

Intens.
x10^5
+MS, 0.4-0.5min #(36-48)
390.1585
412.1397
5
4
3
2
1
0
380
390
400
410
420
430
440
m/z

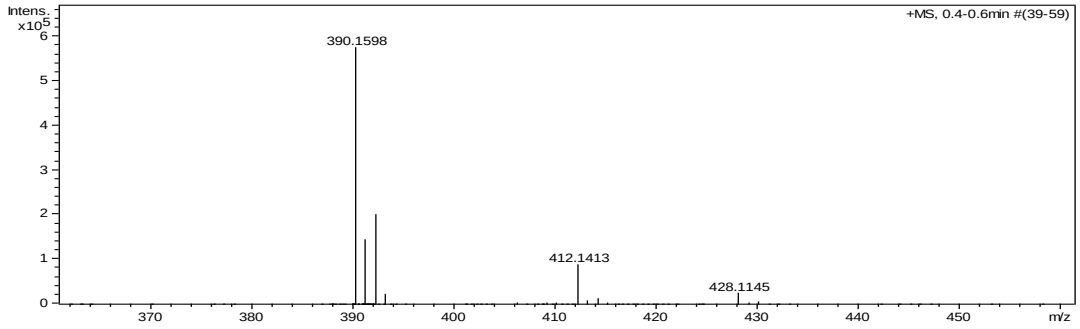
(3R,4'S)-Ethyl-1-butyl-5-chloro-4'-cyano-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6i')



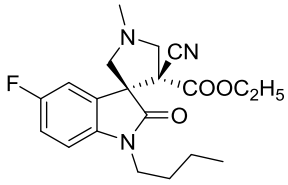
minor isomer (6i'): white solid, 15%, m.p. 60~62℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (brs, 1H, ArH), 7.34 (d, *J* = 8.0Hz, 1H, ArH), 6.81 (d, *J* = 8.4Hz, 1H, ArH), 4.25~4.13 (m, 2H, CH), 3.73~3.59 (m, 4H, CH), 3.19 (d, *J* = 10.0Hz, 1H, CH), 2.97 (d, *J* = 9.2Hz, 1H, CH), 2.56 (s, 3H, CH_3), 1.64~1.63 (m, 2H, CH), 1.40~1.35 (m, 2H, CH), 1.23 (t, *J* = 7.2Hz, 3H, CH_3), 0.96 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.4, 164.5, 141.5, 130.0, 129.5, 128.5, 125.9, 125.8, 117.1, 109.4, 64.0, 63.4, 62.3, 57.4, 55.7, 41.2, 40.2, 29.2, 20.0, 13.7; IR(KBr) υ: 2965, 2936, 2866, 2798, 2250, 1767, 1716, 1607, 1482, 1431, 1349, 1301, 1269, 1217, 1143, 1111, 1029, 1002, 945, 891, 856, 825, 741 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{25}ClN_3O_3$ ($[M+H]^+$): 390.1584, found: 390.1598.



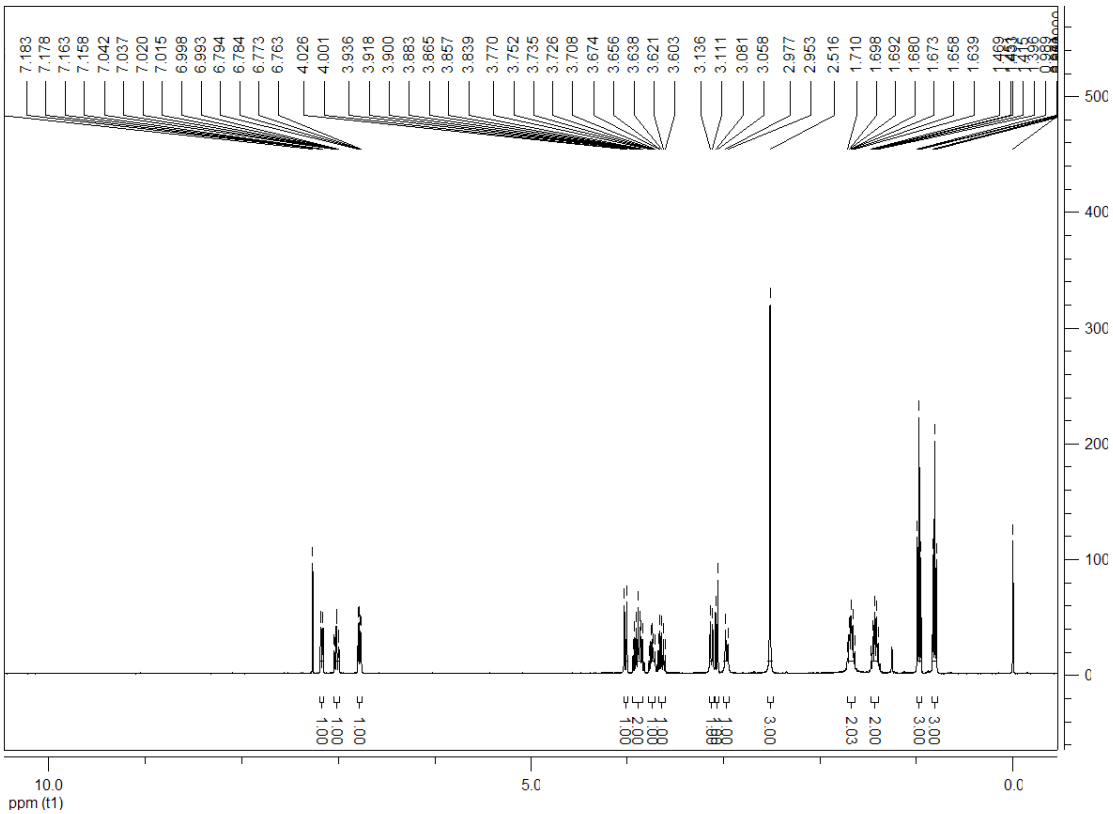

174.417
164.506
141.456
130.007
129.524
128.461
125.887
125.850
117.123
109.411
63.962
63.446
62.327
57.446
55.659
41.236
40.252
29.204
20.038
13.685
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

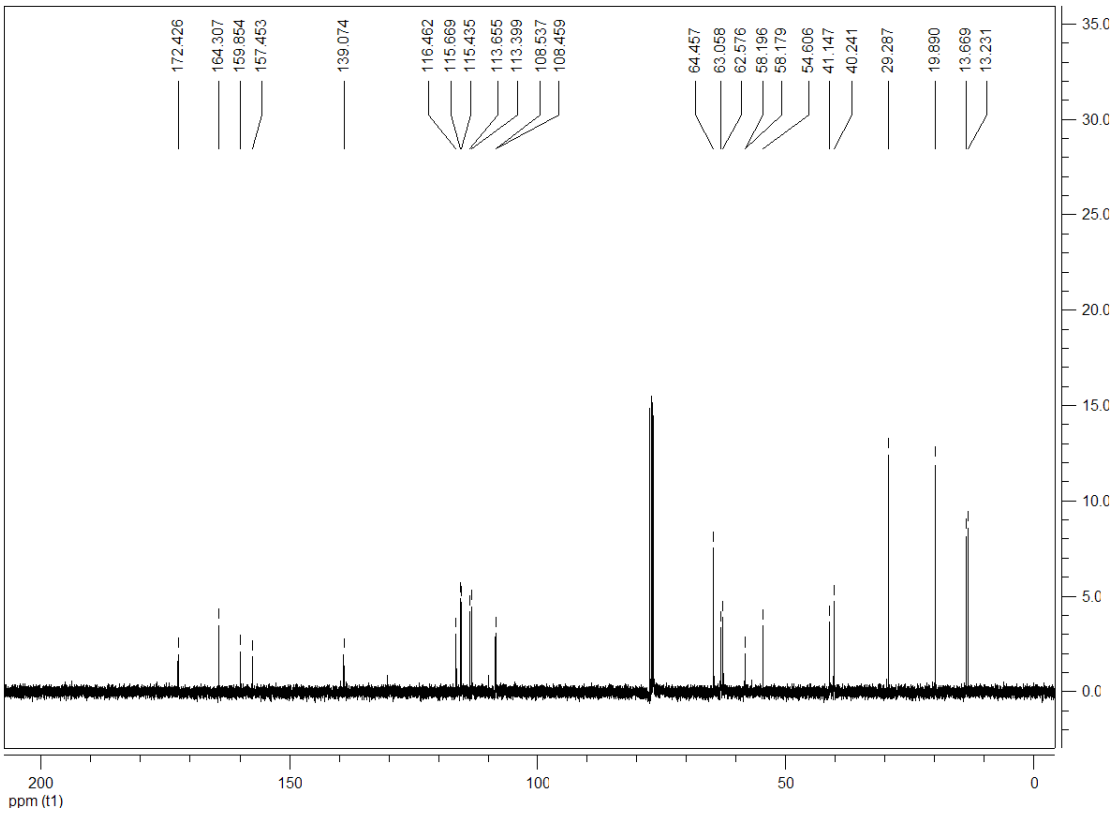

Intens.
x10^5
+MS, 0.4-0.6min #(39-59)
390.1598
412.1413
428.1145
370
380
390
400
410
420
430
440
450
m/z

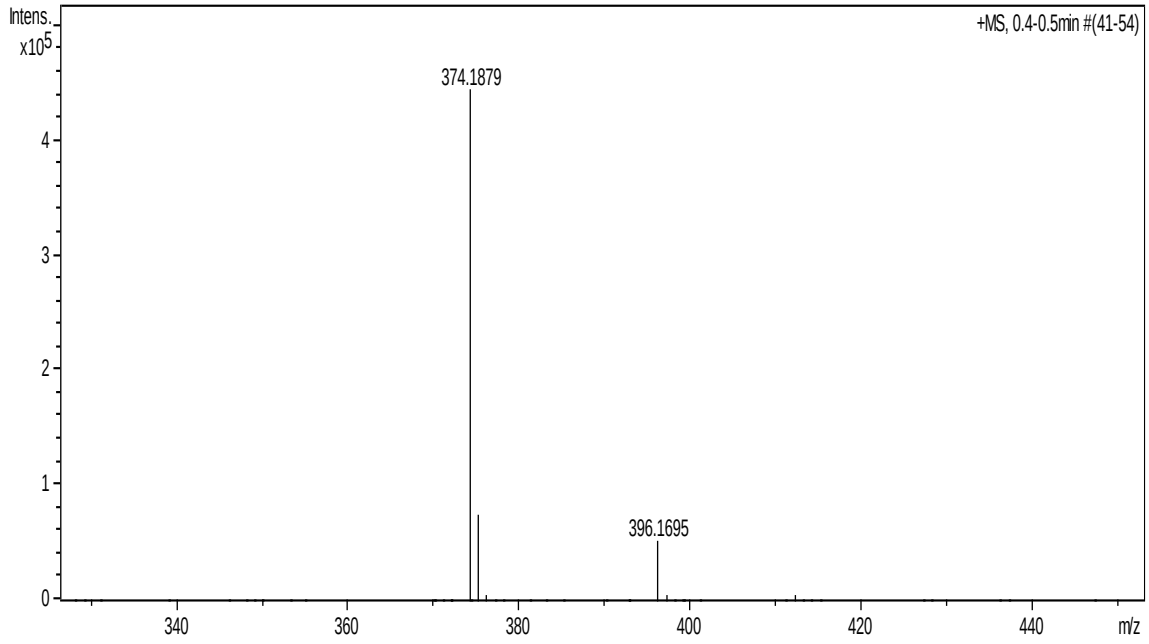
(3R,4'R)-Ethyl-1-butyl-4'-cyano-5-fluoro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6j)



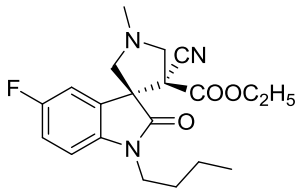
ratio of major/minor = 86:14; **major isomer (6j)**: white solid, 77%, m.p. 84~85℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17 (dd, J_1 = 8.0Hz, J_2 = 2.0Hz, 1H, ArH), 7.02 (td, J_1 = 8.8Hz, J_2 = 2.0Hz, 1H, ArH), 6.78 (dd, J_1 = 8.4Hz, J_2 = 4.0Hz, 1H, ArH), 4.01 (d, J = 10.0Hz, 1H, CH), 3.94~3.84 (m, 2H, CH), 3.77~3.71 (m, 1H, CH), 3.67~3.60 (m, 1H, CH), 3.12 (d, J = 10.0Hz, 1H, CH), 3.07 (d, J = 9.2Hz, 1H, CH), 2.96 (d, J = 9.6Hz, 1H, CH), 2.52 (s, 3H, CH_3), 1.71~1.64 (m, 2H, CH), 1.47~1.40 (m, 2H, CH), 0.97 (t, J = 7.2Hz, 3H, CH_3), 0.81 (t, J = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 164.3, 158.6 (d, J = 240.1Hz), 139.1, 116.5, 115.6 (d, J = 23.4Hz), 113.5 (d, J = 25.6Hz), 108.5 (d, J = 7.8Hz), 64.5, 63.1, 62.6, 58.2 (d, J = 1.7Hz), 54.6, 41.1, 40.2, 29.3, 19.9, 13.7, 13.2; IR(KBr) υ: 2955, 2864, 2803, 2238, 1756, 1709, 1619, 1491, 1459, 1355, 1280, 1242, 1182, 1144, 1088, 1031, 1007, 937, 914, 880, 850, 823, 762, 715 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{25}FN_3O_3$ ([M+H]$^+$): 374.1880, found: 374.1879.



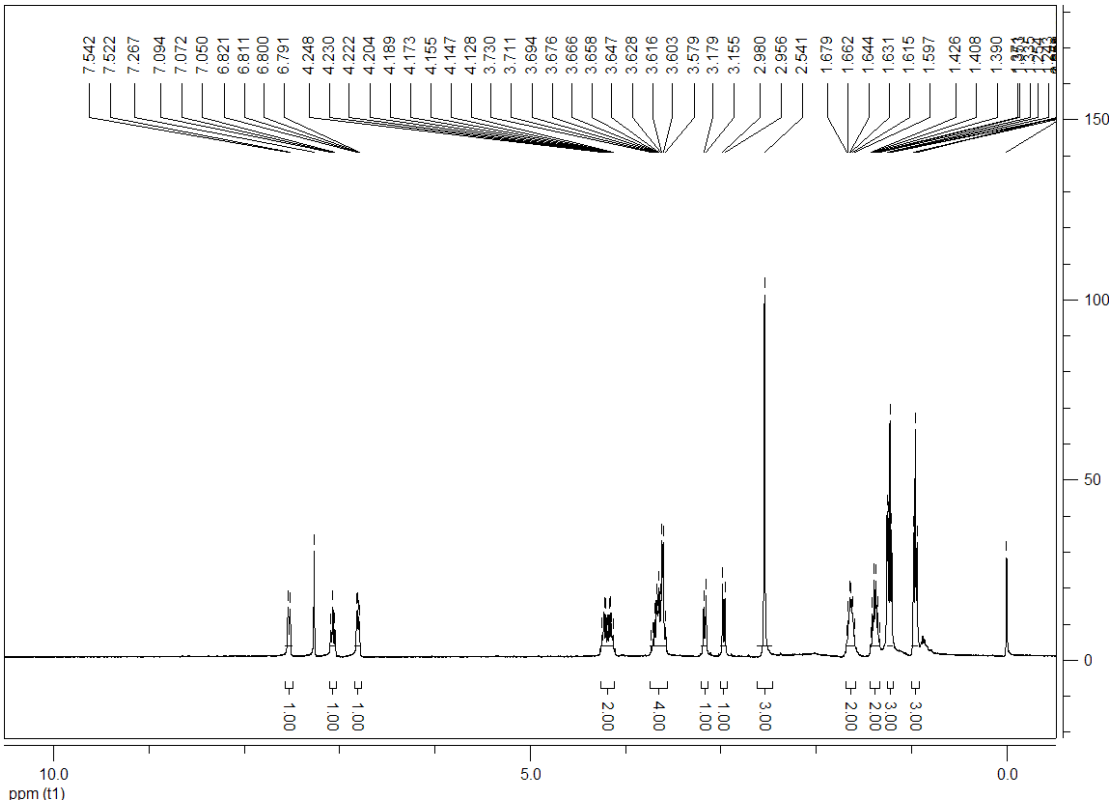

172.426
164.307
159.854
157.453
139.074
116.462
115.669
115.435
113.655
113.399
108.537
108.459
64.457
63.058
62.576
58.196
58.179
54.606
41.147
40.241
29.287
19.890
13.669
13.231
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

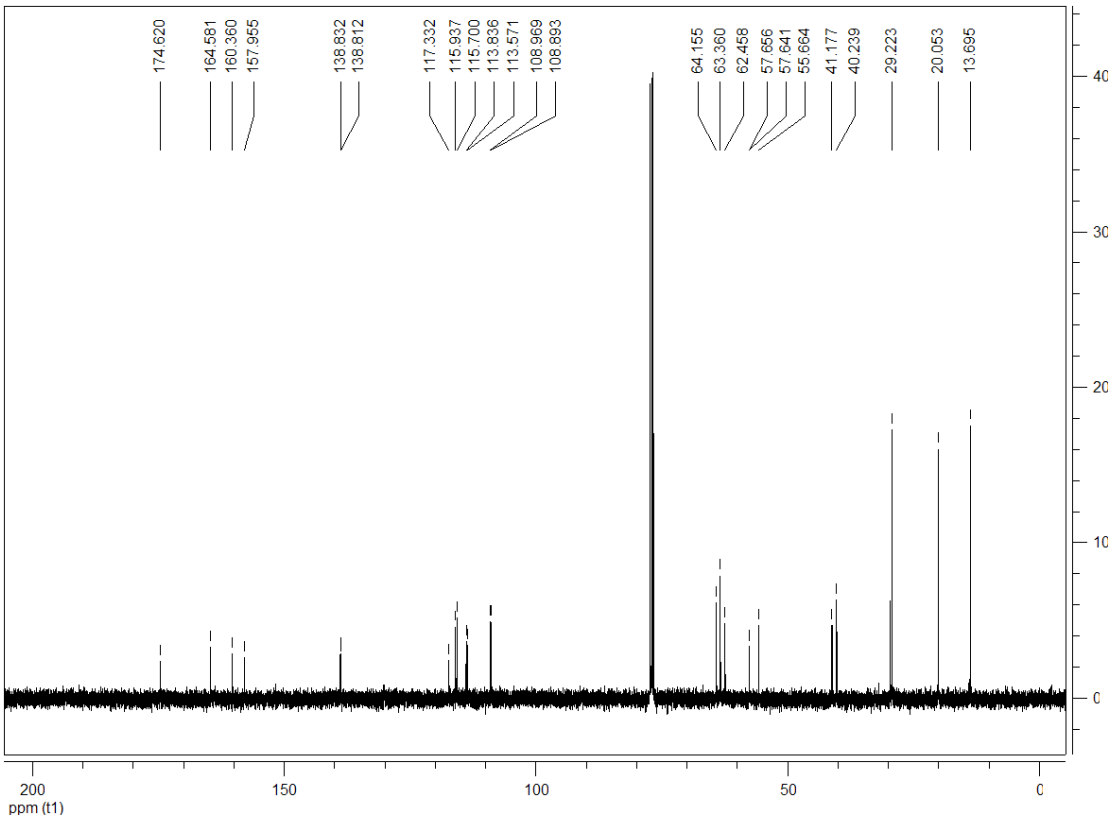

Intens.
x10^5
+MS, 0.4-0.5min #(41-54)
374.1879
396.1695
4
3
2
1
0
340
360
380
400
420
440
m/z

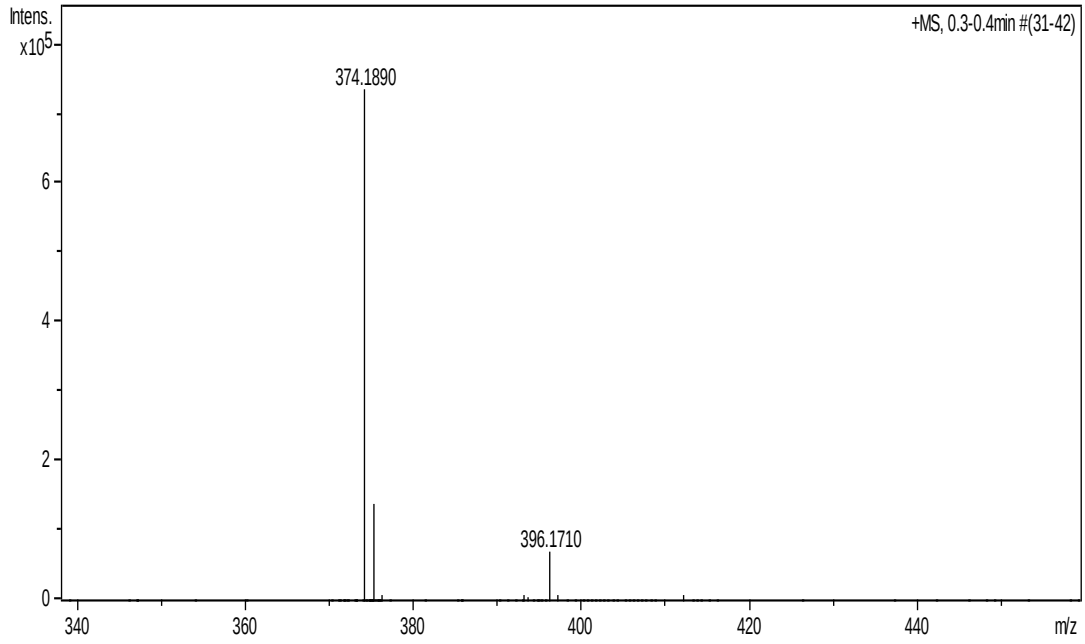
(3R,4'S)-Ethyl-1-butyl-4'-cyano-5-fluoro-1'-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-4'-carboxylate (6j')



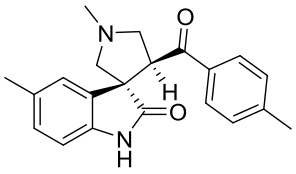
minor isomer (6j'): white solid, 12%, m.p. 67~68℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.54~7.52 (m, 1H, ArH), 7.09~7.05 (m, 1H, ArH), 6.80 (dd, J_1 = 8.0Hz, J_2 = 4.0Hz, 1H, ArH), 4.25~4.13 (m, 2H, CH), 3.73~3.58 (m, 4H, CH), 3.17 (d, J = 9.6Hz, 1H, CH), 2.97 (d, J = 9.6Hz, 1H, CH), 2.54 (s, 3H, CH_3), 1.68~1.60 (m, 2H, CH), 1.43~1.34 (m, 2H, CH), 1.22 (t, J = 7.2Hz, 3H, CH_3), 0.96 (t, J = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.6, 164.6, 159.2 (d, J = 240.5Hz), 138.8 (d, J = 2.0Hz), 117.3, 115.8 (d, J = 23.7Hz), 113.7 (d, J = 26.5Hz), 108.9 (d, J = 7.6Hz), 64.2, 63.4, 62.5, 57.6 (d, J = 1.5Hz), 55.7, 41.2, 40.2, 29.2, 20.1, 13.7; IR(KBr) υ: 2963, 2923, 2871, 2808, 2238, 1755, 1708, 1618, 1494, 1453, 1367, 1272, 1240, 1196, 1149, 1094, 1009, 954, 928, 889, 848, 813, 731 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{25}FN_3O_3$ ($[M+H]^+$): 374.1880, found: 374.1890.



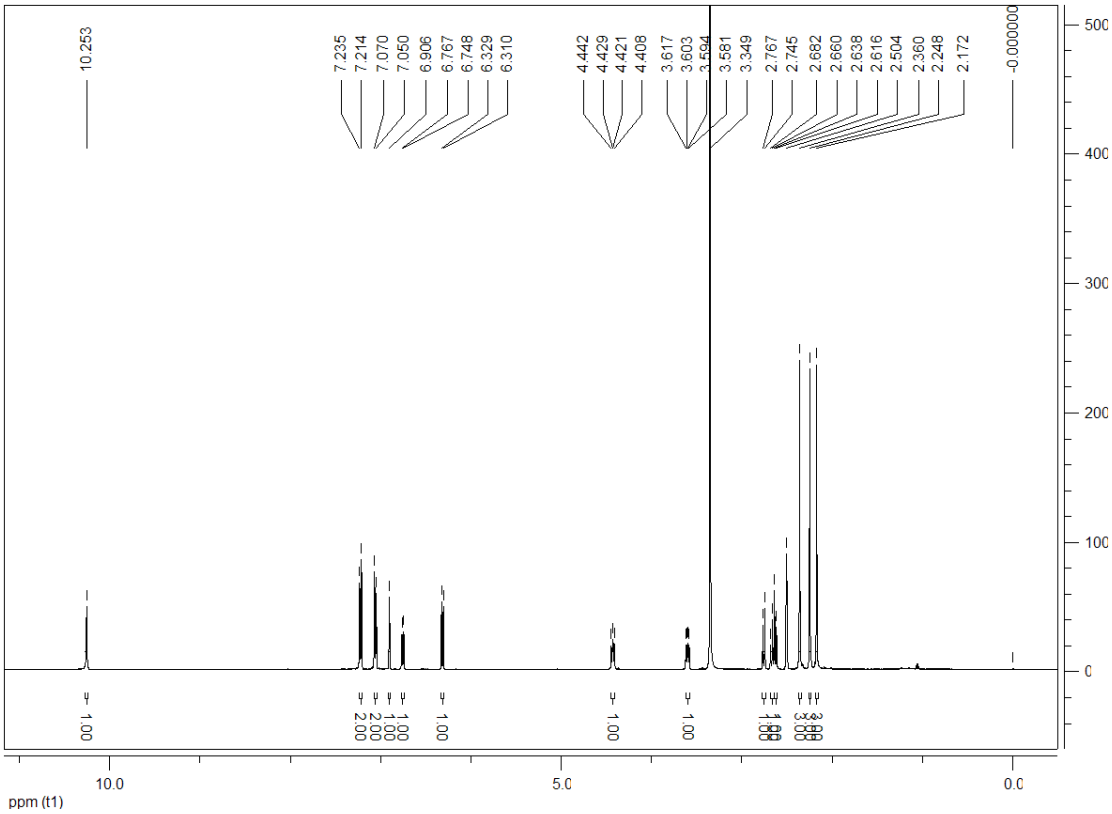

174.620
164.581
160.360
157.955
138.832
138.812
117.332
115.937
115.700
113.836
113.571
108.969
108.893
64.155
63.360
62.458
57.656
57.641
55.664
41.177
40.239
29.223
20.053
13.695
200
ppm (t1)
150
100
50
0

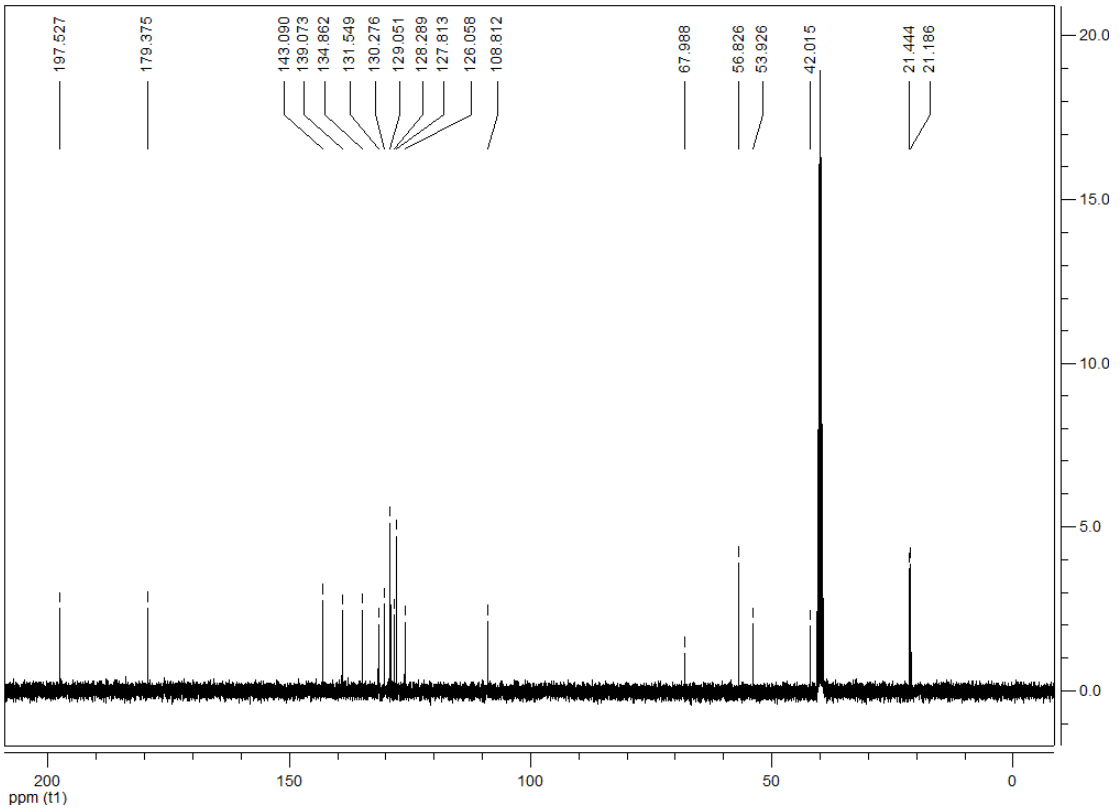

Intens.
x10^5
+MS, 0.3-0.4min #(31-42)
374.1890
396.1710
m/z

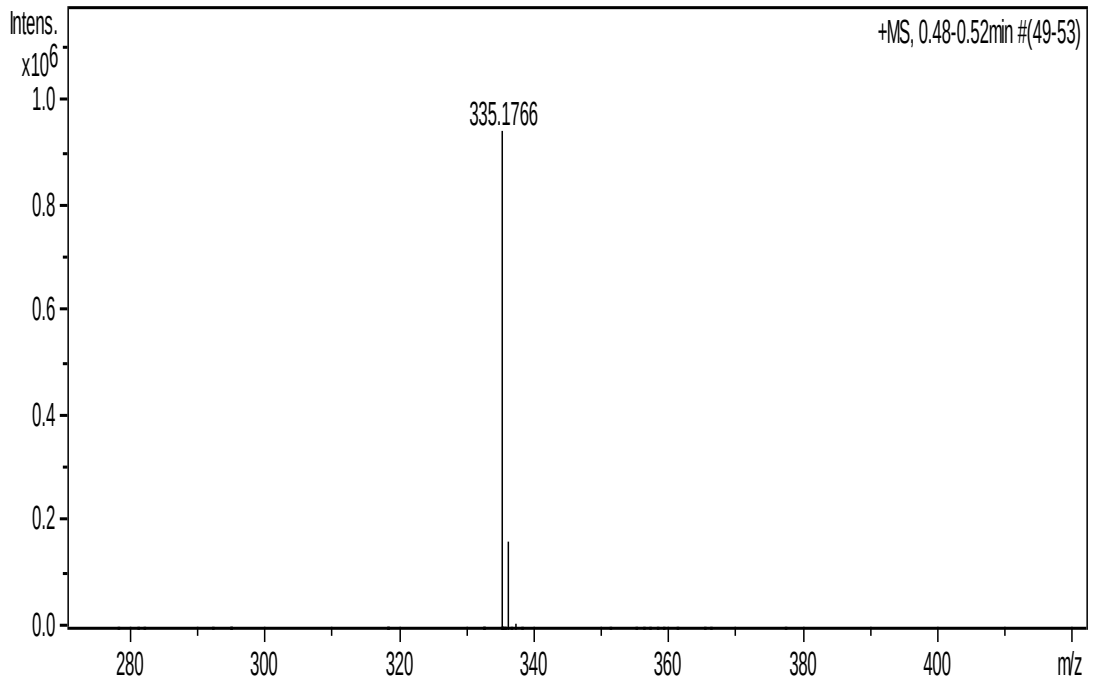
(3R,4'S)-1',5-dimethyl-4'-(4-methylbenzoyl)spiro[indoline-3,3'-pyrrolidin]-2-one (8a)



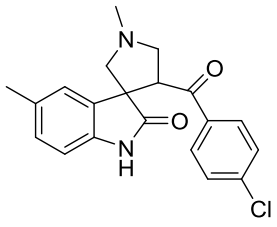
white solid, 90%, m.p.184~186℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.25 (s, 1H, NH), 7.22 (d, J = 8.4Hz, 2H, ArH), 7.06 (d, J = 8.0Hz, 2H, ArH), 6.91 (brs, 1H, ArH), 6.76 (d, J = 7.6Hz, 1H, ArH), 6.32 (d, J = 7.6Hz, 1H, ArH), 4.42 (dd, J_1 = 8.4Hz, J_2 = 5.2Hz, 1H, CH), 3.60 (dd, J_1 = 9.0Hz, J_2 = 5.2Hz, 1H, CH), 2.76 (d, J = 8.8Hz, 1H, CH), 2.66 (t, J = 8.8Hz, 1H, CH), 2.63 (d, J = 8.8Hz, 1H, CH), 2.36 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.17 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ:197.5, 179.3, 143.0, 139.0, 134.8, 131.5, 130.2, 129.0, 128.2, 127.8, 126.0, 108.8, 67.9, 56.8, 53.9, 42.0, 21.4, 21.1; IR (KBr) υ: 3408, 3150, 3076, 3026, 2949, 2921, 2847, 2816, 2791, 2686, 1915, 1808, 1719, 1672, 1606, 1571, 1492, 1412, 1356, 1313, 1269, 1246, 1204, 1174, 1129, 1099, 1062, 1035, 1014, 968, 894, 830, 784, 737 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{21}H_{23}N_2O_2$ ([M+H]$^+$): 335.1754, found: 335.1766.



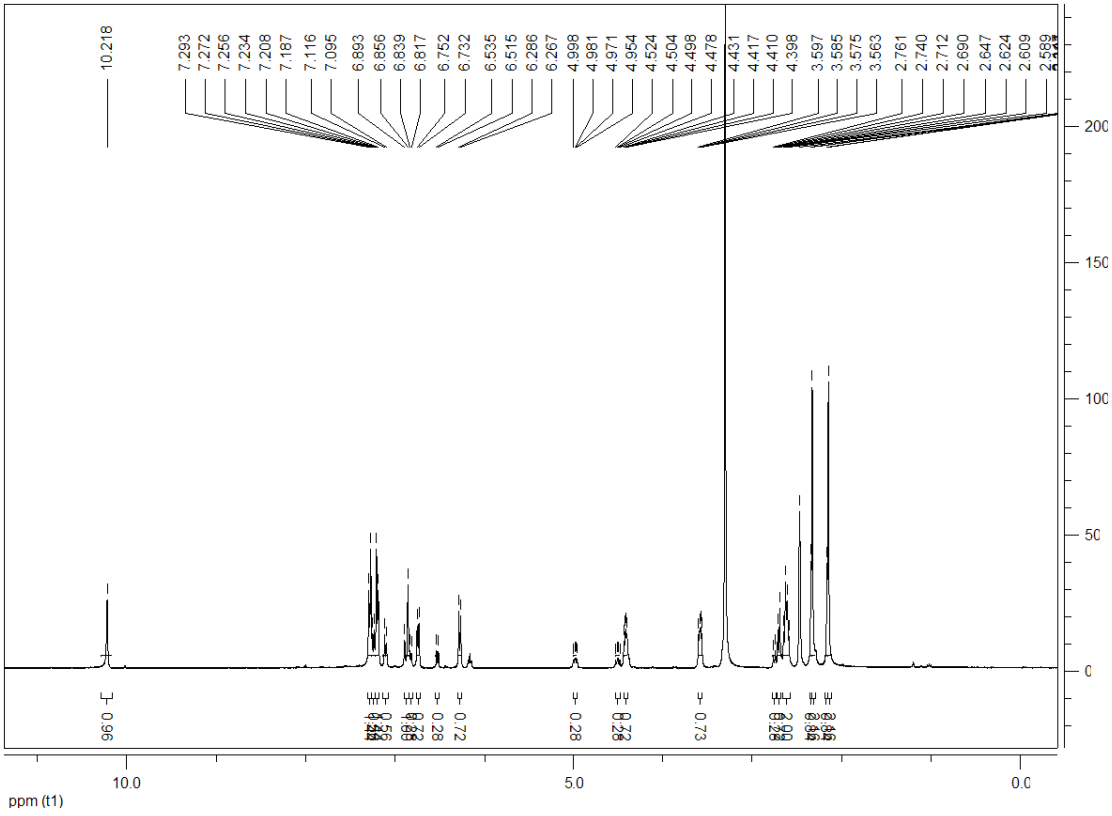

197.527
179.375
143.090
139.073
134.862
131.549
130.276
129.051
128.289
127.813
126.058
108.812
67.988
56.826
53.926
42.015
21.444
21.186
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

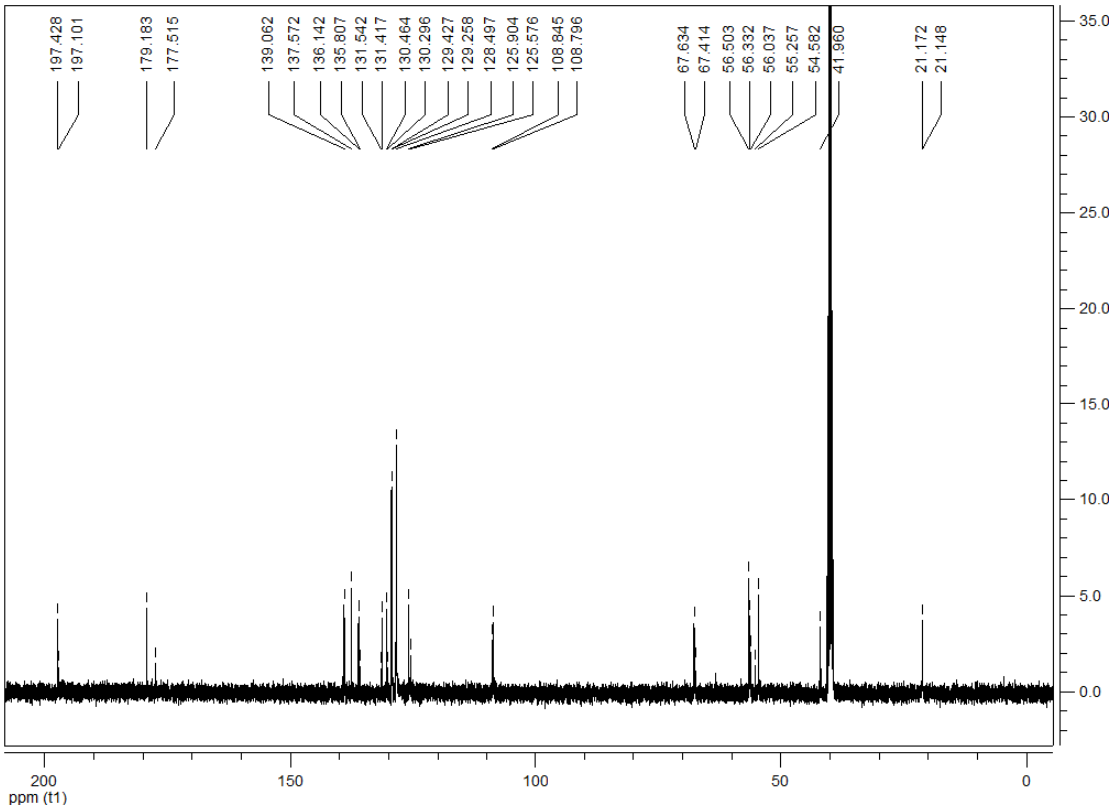

Intens.
x10^6
1.0
0.8
0.6
0.4
0.2
0.0
+MS, 0.48-0.52min #(49-53)
335.1766
280
300
320
340
360
380
400
m/z

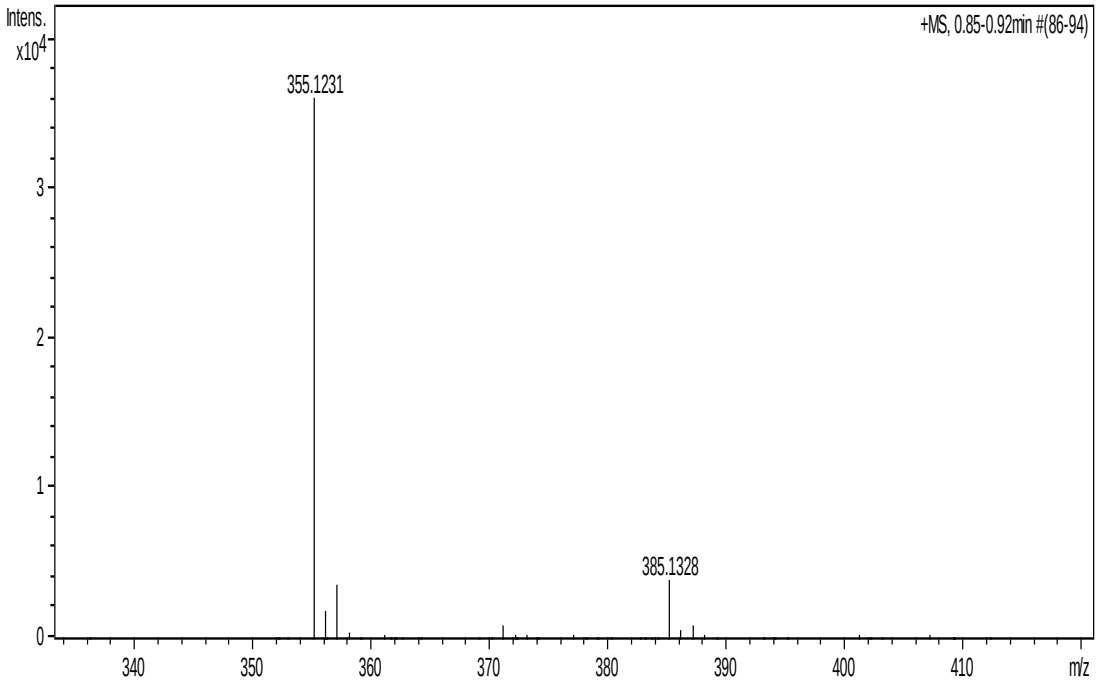
4'-(4-Chlorobenzoyl)-1',5-dimethylspiro[indoline-3,3'-pyrrolidin]-2-one (8b)



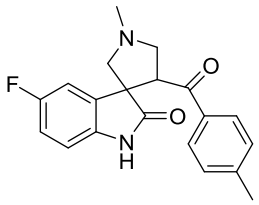
white solid, 80%, m.p.186~187℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: **major isomer**: 10.22 (s, 1H, NH), 7.28 (d, *J* = 8.4Hz, 2H, ArH), 7.20 (d, *J* = 8.4Hz, 2H, ArH), 6.89~6.86 (m, 1H, ArH), 6.74 (d, *J* = 8.0Hz, 1H, ArH), 6.28 (d, *J* = 7.6Hz, 1H, ArH), 4.43~4.40 (m, 1H, CH), 3.60~3.56 (m, 1H, CH), 2.70 (d, *J* = 8.8Hz, 1H, CH), 2.65~2.59 (m, 2H, CH), 2.33 (s, 3H, CH_3), 2.15 (s, 3H, CH_3); **minor isomer:** 10.22 (s, 1H, NH), 7.24 (d, *J* = 8.8Hz, 2H, ArH), 7.10 (d, *J* = 8.4Hz, 2H, ArH), 6.89~6.86 (m, 1H, ArH), 6.83 (d, *J* = 8.8Hz, 1H, ArH), 6.52 (d, *J* = 8.0Hz, 1H, ArH), 5.00~4.95 (m, 1H, CH), 4.52~4.48 (m, 1H, CH), 2.75 (d, *J* = 8.4Hz, 1H, CH), 2.65~2.59 (m, 2H, CH), 2.34 (s, 3H, CH_3), 2.16 (s, 3H, CH_3). **ratio of major/minor = 72:28**; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.4, 197.1, 179.2, 177.5, 139.1, 137.6, 136.1, 135.8, 131.5, 131.4, 130.5, 130.3, 129.4, 129.3, 128.5, 125.9, 125.6, 108.8, 108.8, 67.6, 67.4, 56.5, 56.3, 56.0, 55.3, 54.6, 41.9, 21.2, 21.1; IR (KBr) υ: 3406, 3307, 3140, 3074, 2952, 2921, 2844, 2819, 2790, 2688, 1910, 1714, 1677, 1623, 1591, 1493, 1456, 1399, 1360, 1313, 1264, 1204, 1167, 1133, 1091, 1060, 1036, 1010, 968, 895, 830, 738 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{20}H_{20}ClN_2O_2$ ($[M+H]^+$): 355.1208, found: 355.1231.



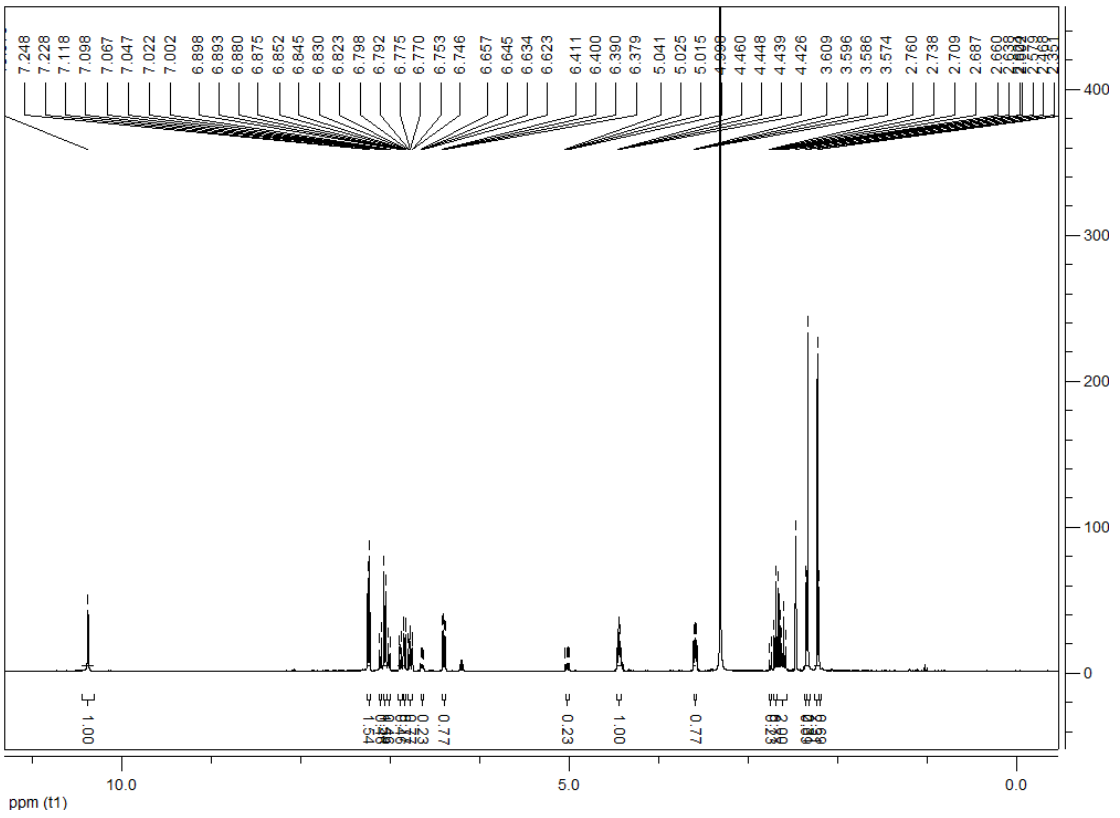

197.428
197.101
179.183
177.515
139.062
137.572
136.142
135.807
131.542
131.417
130.464
130.296
129.427
129.258
128.497
125.904
125.576
108.845
108.796
67.634
67.414
56.503
56.332
56.037
55.257
54.582
41.960
21.172
21.148
35.0
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

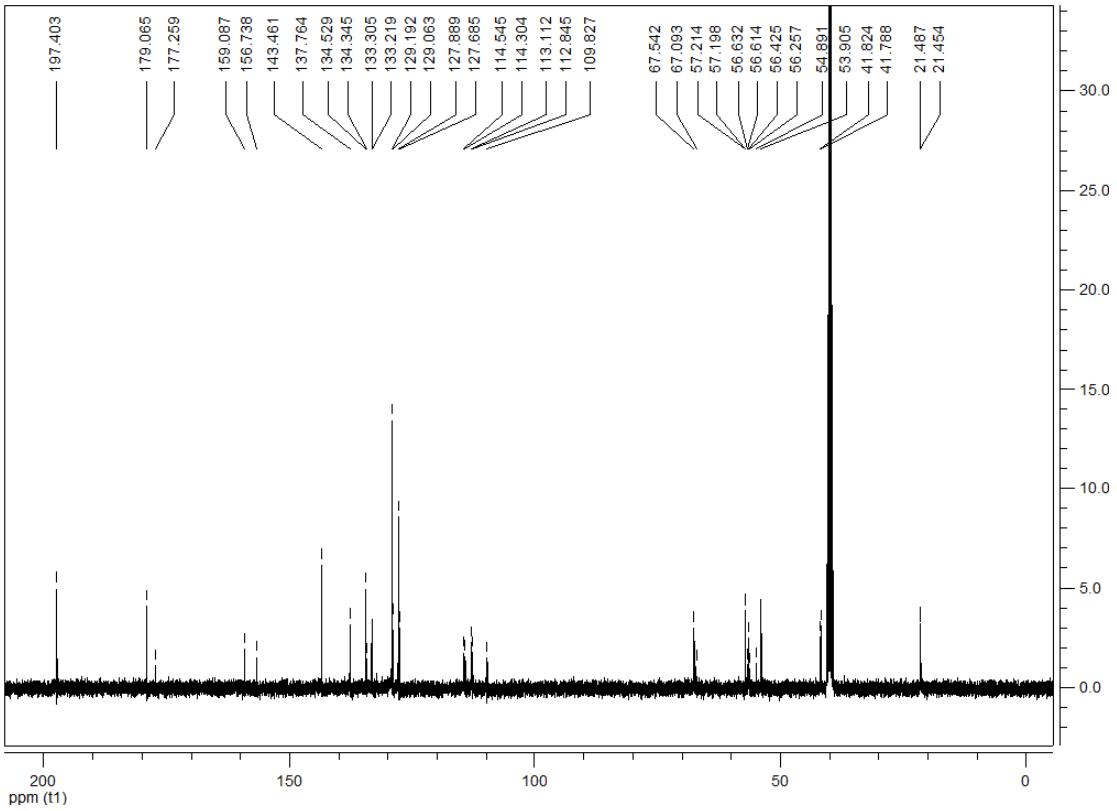

Intens.
x10^4
+MS, 0.85-0.92min #(86-94)
355.1231
385.1328
3
2
1
0
340
350
360
370
380
390
400
410
m/z

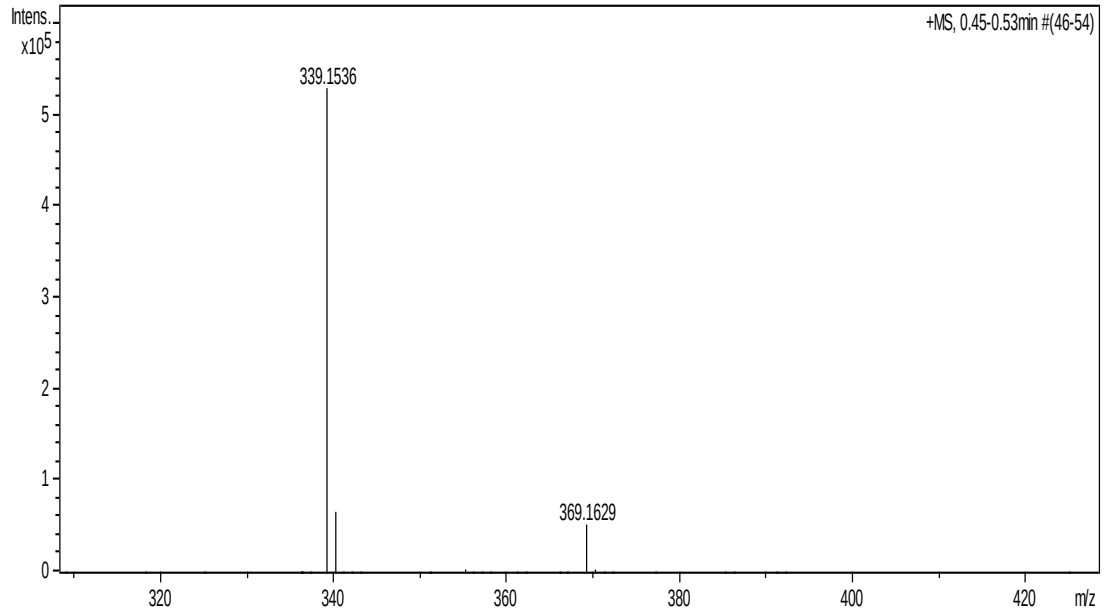
5-Fluoro-1'-methyl-4'-(4-methylbenzoyl)spiro[indoline-3,3'-pyrrolidin]-2-one (8c)



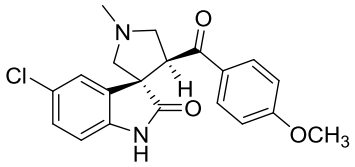
white solid, 81%, m.p.187~189 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: **major isomer**: 10.37 (s, 1H, NH), 7.24 (d, J = 8.0Hz, 2H, ArH), 7.06 (d, J = 8.0Hz, 2H, ArH), 6.84 (dd, J_1 = 8.8Hz, J_2 = 2.8Hz, 1H, ArH), 6.80~6.75 (m, 1H, ArH), 6.41~6.38 (m, 1H, ArH), 4.46~4.43 (m, 1H, CH), 3.61~3.57 (m, 1H, CH), 2.70 (d, J = 8.8Hz, 1H, CH), 2.66~2.58 (m, 2H, CH), 2.34 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); **minor isomer:** 10.37 (s, 1H, NH), 7.11 (d, J = 8.0Hz, 2H, ArH), 7.01 (d, J = 8.0Hz, 2H, ArH), 6.90~6.88 (m, 1H, ArH), 6.66~6.62 (m, 1H, ArH), 5.04~5.00 (m, 1H, CH), 4.46~4.43 (m, 1H, CH), 2.75 (d, J = 8.8Hz, 1H, CH), 2.66~2.58 (m, 2H, CH), 2.35 (s, 3H, CH_3), 2.21 (s, 3H, CH_3). **ratio of major/minor = 77:23**; ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.4, 179.1, 177.3, 157.9 (d, J = 234.9Hz), 143.5, 137.8, 134.5, 134.3, 133.2 (d, J = 8.6Hz), 129.2, 129.1, 127.9, 127.7, 114.4 (d, J = 24.1Hz), 113.0 (d, J = 26.7Hz), 109.8, 67.5, 67.1, 57.2 (d, J = 1.6Hz), 56.6 (d, J = 1.8Hz), 56.4, 56.3, 54.9, 53.9, 41.8, 41.7, 21.5, 21.4; IR (KBr) υ: 3064, 2949, 2836, 2803, 2728, 2688, 1906, 1719, 1668, 1599, 1509, 1479, 1362, 1308, 1252, 1175, 1125, 1056, 1024, 964, 883, 837, 776, 740 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{20}H_{20}FN_2O_2$ ([M+H]$^+$): 339.1503, found: 339.1536.



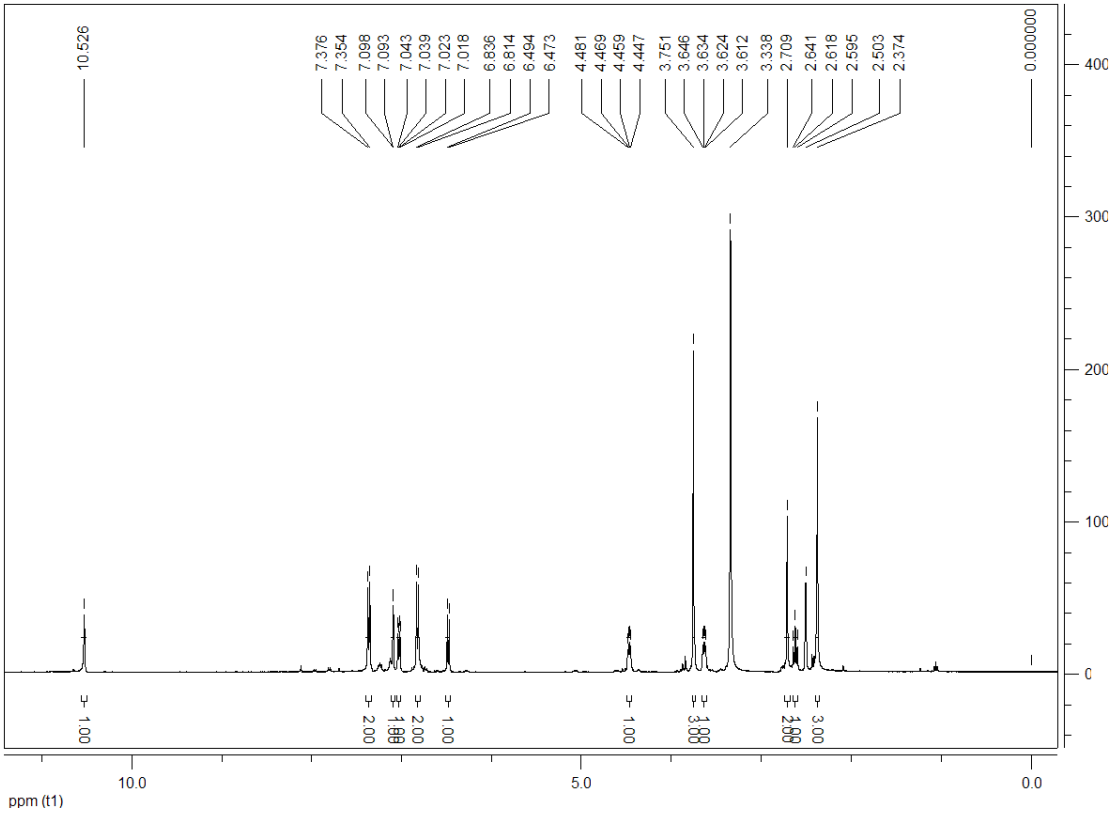

197.403
179.065
177.259
159.087
156.738
143.461
137.764
134.529
134.345
133.305
133.219
129.192
129.063
127.889
127.685
114.545
114.304
113.112
112.845
109.827
67.542
67.093
57.214
57.198
56.632
56.614
56.425
56.257
54.891
53.905
41.824
41.788
21.487
21.454
30.0
25.0
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

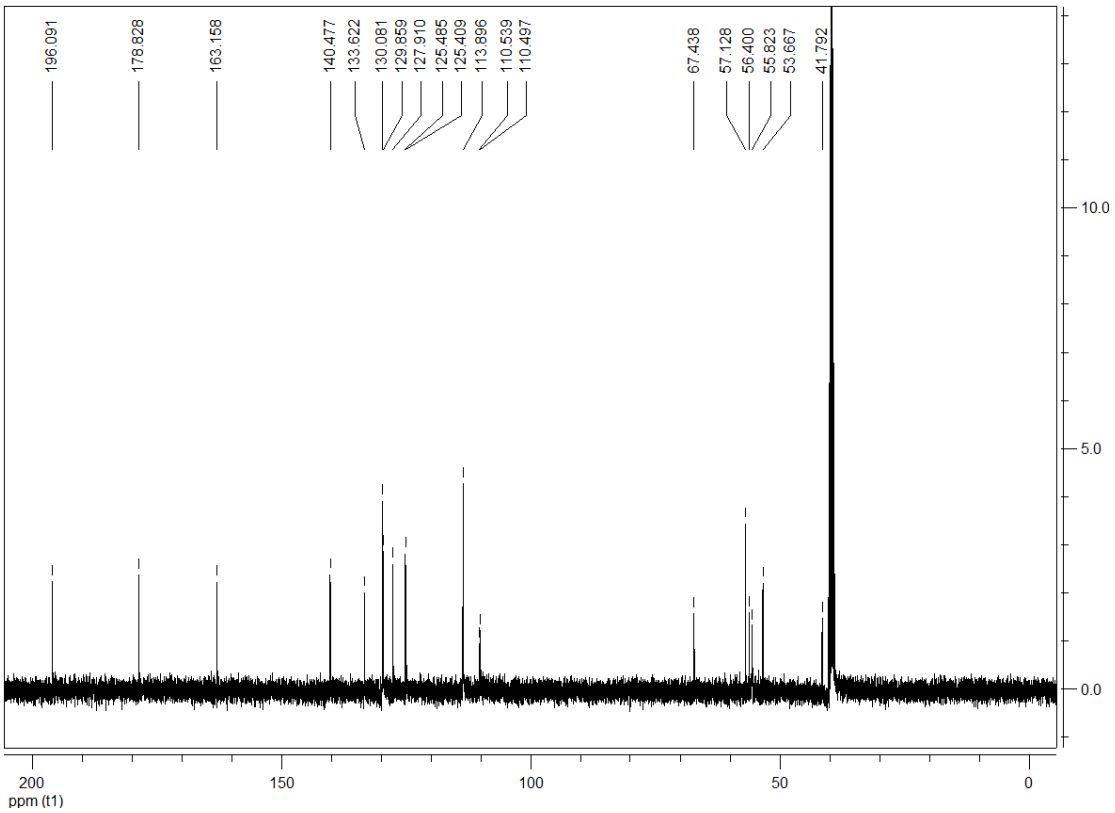

Intens.
x10^5
+MS, 0.45-0.53min #(46-54)
339.1536
369.1629
5
4
3
2
1
0
320
340
360
380
400
420
m/z

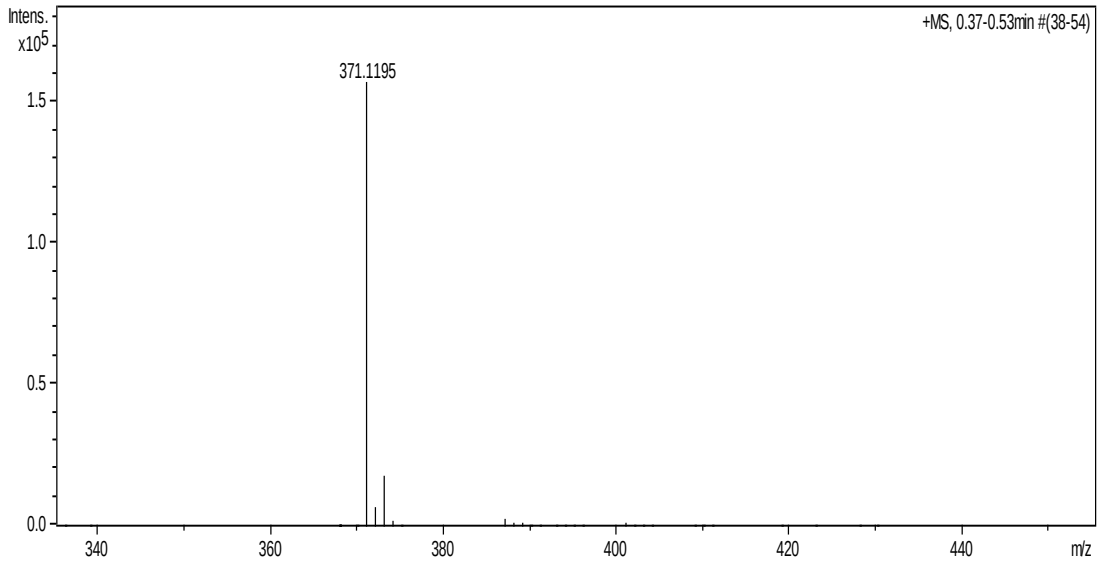
(3R,4'S)-5-Chloro-4'-(4-methoxybenzoyl)-1'-methylspiro[indoline-3,3'-pyrrolidin]-2-one (8d)



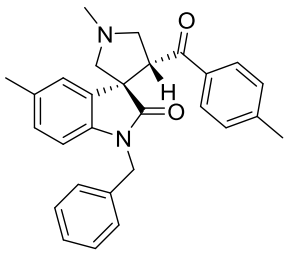
white solid, 83%, m.p.197~198℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.53 (s, 1H, NH), 7.36 (d, J = 8.8Hz, 2H, ArH), 7.09 (d, J = 2.0Hz, 1H, ArH), 7.04~7.02 (m, 1H, ArH), 6.82 (d, J = 8.8Hz, 2H, ArH), 6.48 (d, J = 8.4Hz, 1H, ArH), 4.46 (dd, J_1 = 8.8Hz, J_2 = 4.8Hz , 1H, CH), 3.75 (s, 3H, OCH_3), 3.63 (dd, J_1 = 8.8Hz, J_2 = 4.8Hz , 1H, CH), 2.71 (s, 2H, CH), 2.62 (t, J = 9.2Hz, 1H, CH), 2.37 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 196.1, 178.8, 163.2, 140.5, 133.6, 130.1, 129.9, 127.9, 125.5, 125.4, 113.9, 110.5, 110.5, 67.4, 57.1, 56.4, 55.8, 53.7, 41.8; IR (KBr) υ: 3052, 2955, 2852, 2797, 2704, 1894, 1721, 1673, 1607, 1571, 1485, 1458, 1359, 1308, 1259, 1184, 1127, 1066, 1020, 969, 896, 828, 788, 736 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{20}H_{20}ClN_2O_3$ ($[M+H]^+$): 371.1157, found: 371.1195.



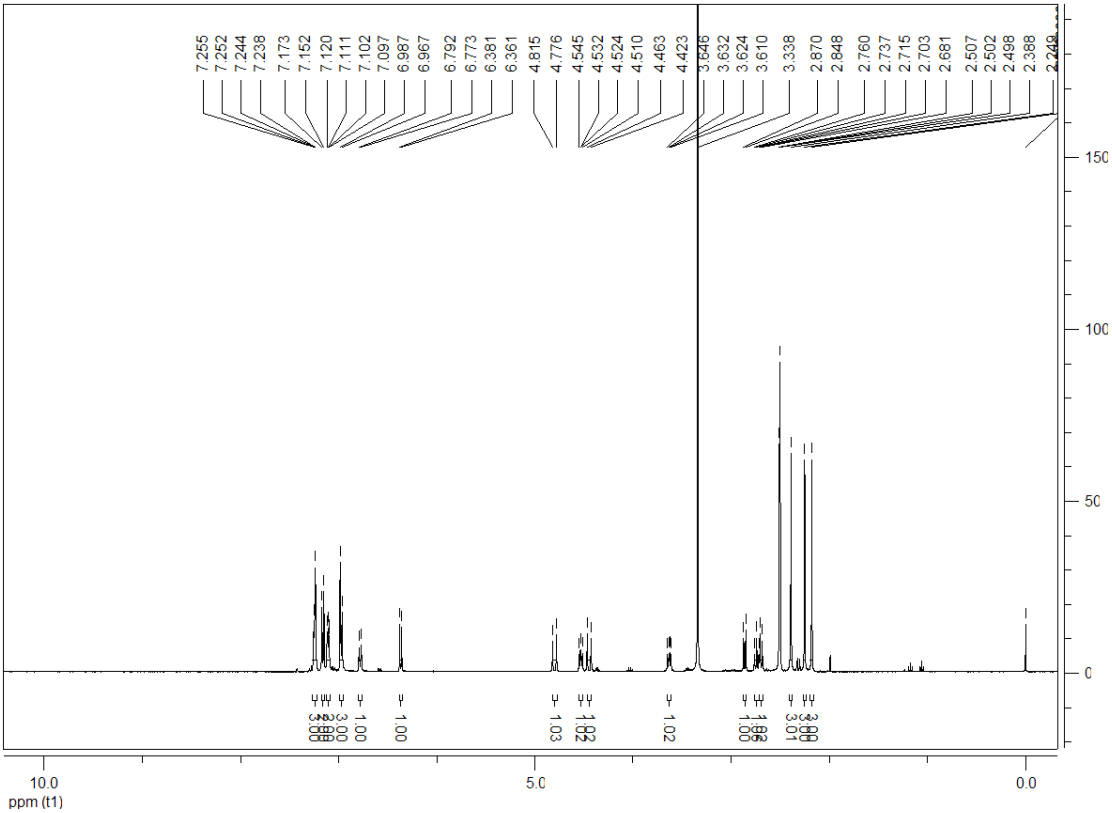

196.091
178.828
163.158
140.477
133.622
130.081
129.859
127.910
125.485
125.409
113.896
110.539
110.497
67.438
57.128
56.400
55.823
53.667
41.792
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

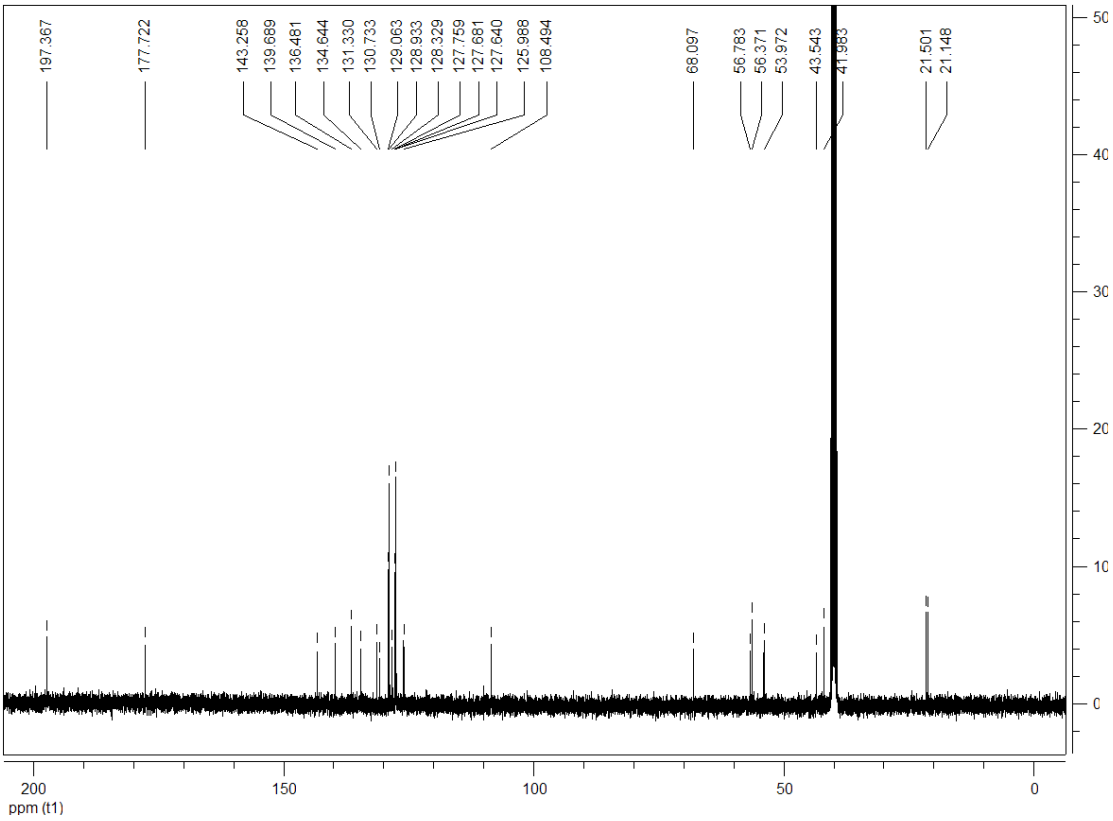

Intens.
x10^5
+MS, 0.37-0.53min #(38-54)
371.1195
1.5
1.0
0.5
0.0
340
360
380
400
420
440
m/z

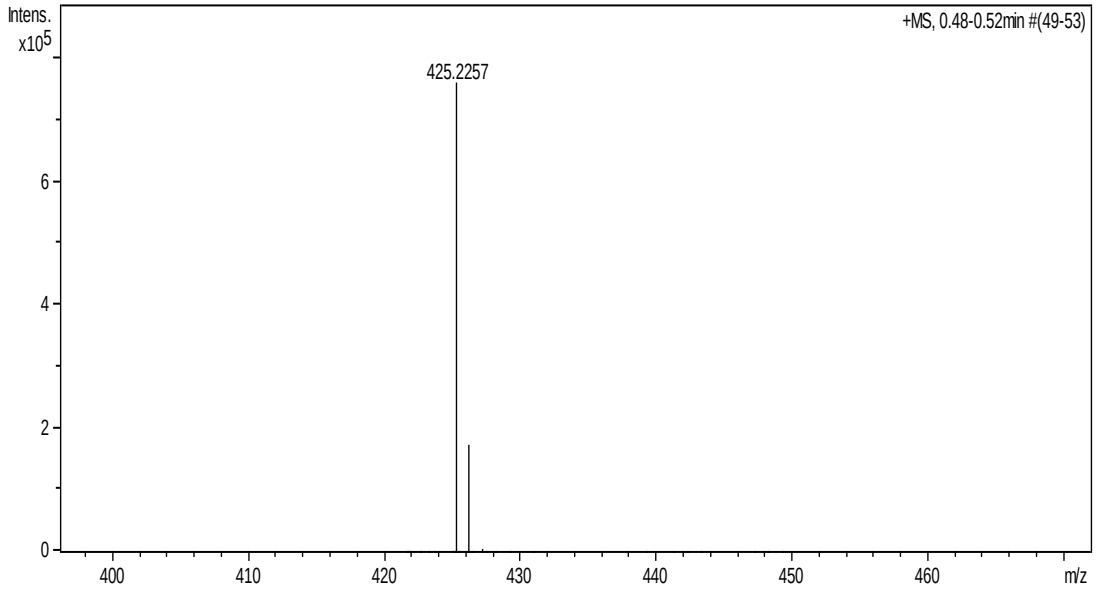
(3S,4'R)-1-Benzyl-1',5-dimethyl-4'-(4-methylbenzoyl)spiro[indoline-3,3'-pyrrolidin]-2-one (8e)



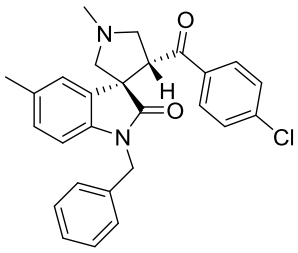
white solid, 91%, m.p.203~204℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.26~7.24 (m, 3H, ArH), 7.17~7.15 (m, 2H, ArH), 7.12~7.10 (m, 2H, ArH), 6.99~6.97 (m, 3H, ArH), 6.78 (d, J = 7.6Hz, 1H, ArH), 6.37 (d, J = 8.0Hz, 1H, ArH), 4.80 (d, J = 15.6Hz, 1H, CH), 4.53 (dd, J_1 = 8.6Hz, J_2 = 5.2Hz , 1H, CH), 4.44 (d, J = 16.0Hz, 1H, CH), 3.63 (dd, J_1 = 8.8Hz, J_2 = 5.6Hz , 1H, CH), 2.86 (d, J = 8.8Hz, 1H, CH), 2.74 (d, J = 9.2Hz, 1H, CH), 2.69 (d, J = 8.8Hz, 1H, CH), 2.39 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.18 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.3, 177.7, 143.2, 139.6, 136.4, 134.6, 131.3, 130.7, 129.0, 128.9, 128.3, 127.7, 127.6, 127.6, 125.9, 108.4, 68.0, 56.7, 56.3, 53.9, 43.5, 41.9, 21.5, 21.1; IR (KBr) υ: 3389, 3030, 2971, 2938, 2835, 2786, 1705, 1602, 1491, 1448, 1354, 1297, 1249, 1178, 1111, 1022, 949, 926, 901, 823, 765, 733 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{28}H_{29}N_2O_2$ ([M+H]$^+$): 425.2224, found: 425.2257.



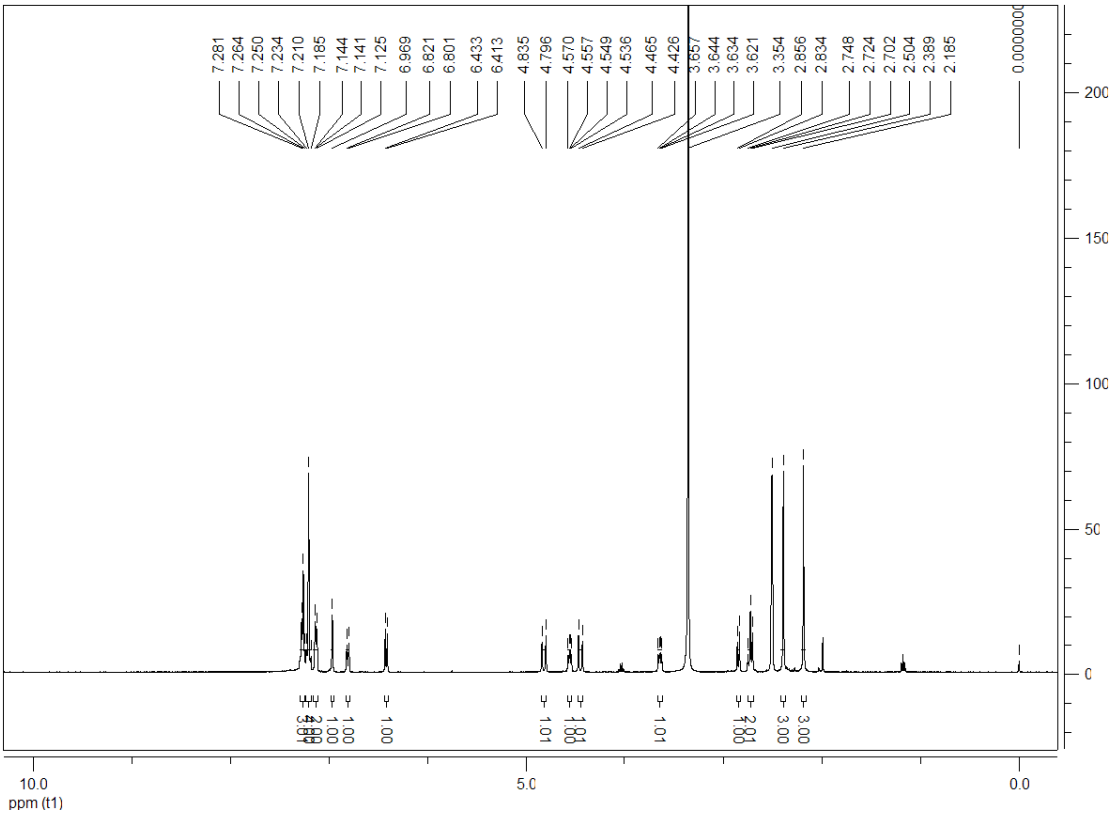

197.367
177.722
143.258
139.689
136.481
134.644
131.330
130.733
129.063
128.933
128.329
127.759
127.681
127.640
125.988
108.494
68.097
56.783
56.371
53.972
43.543
41.983
21.501
21.148
200
150
100
50
0
ppm (t1)

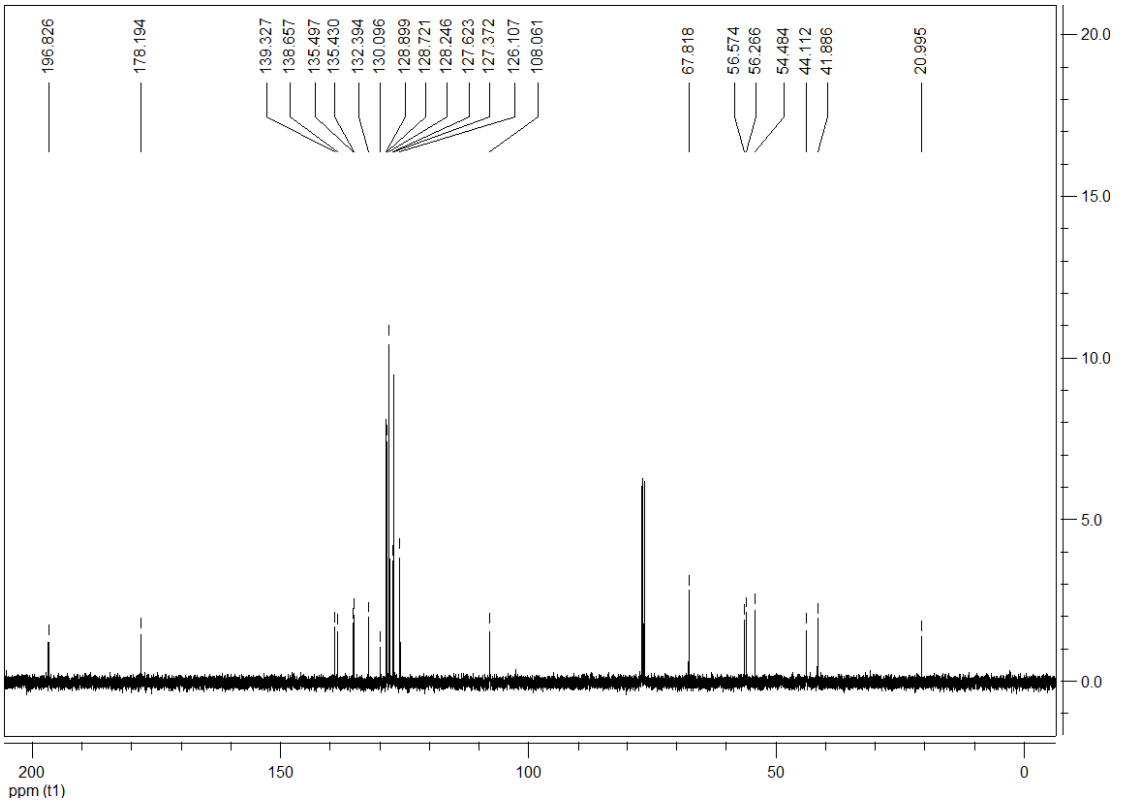

Intens.
x10^5
+MS, 0.48-0.52min #(49-53)
425.2257
6
4
2
0
400
410
420
430
440
450
460
m/z

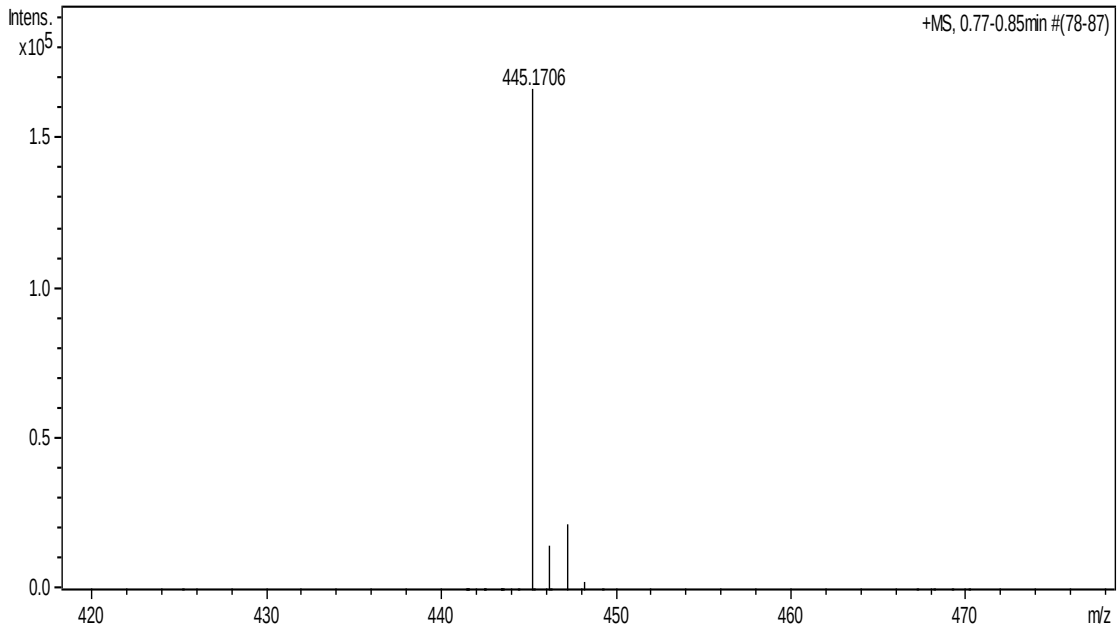
(3S,4'R)-1-Benzyl-4'-(4-chlorobenzoyl)-1',5-dimethylspiro[indoline-3,3'-pyrrolidin]-2-one (8f)



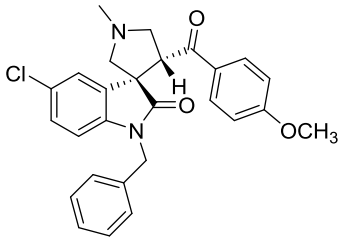
white solid, 92%, m.p.201~202℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.28~7.25 (m, 3H, ArH), 7.23~7.18 (m, 4H, ArH), 7.14~7.12 (m, 2H, ArH), 6.97 (brs, 1H, ArH), 6.81 (d, J = 8.0Hz, 1H, ArH), 6.42 (d, J = 8.0Hz, 1H, ArH), 4.82 (d, J = 15.6Hz, 1H, CH), 4.55 (dd, J_1 = 8.4Hz, J_2 = 5.2Hz , 1H, CH), 4.44 (d, J = 15.6Hz, 1H, CH), 3.64 (dd, J_1 = 9.2Hz, J_2 = 5.2Hz , 1H, CH), 2.84 (d, J = 8.8Hz, 1H, CH), 2.75~2.70 (m, 2H, CH), 2.39 (s, 3H, CH_3), 2.18 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 196.8, 178.1, 139.3, 138.6, 135.4, 135.4, 132.3, 130.0, 128.8, 128.7, 128.2, 127.6, 127.3, 126.1, 108.0, 67.8, 56.5, 56.2, 54.4, 44.1, 41.8, 20.9; IR (KBr) υ: 3391, 3058, 2970, 2938, 2834, 2782, 1705, 1592, 1491, 1449, 1356, 1244, 1214, 1174, 1138, 1089, 1050, 1014, 949, 925, 902, 843, 813, 734 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{26}ClN_2O_2$ ([M+H]$^+$): 445.1677, found: 445.1706.



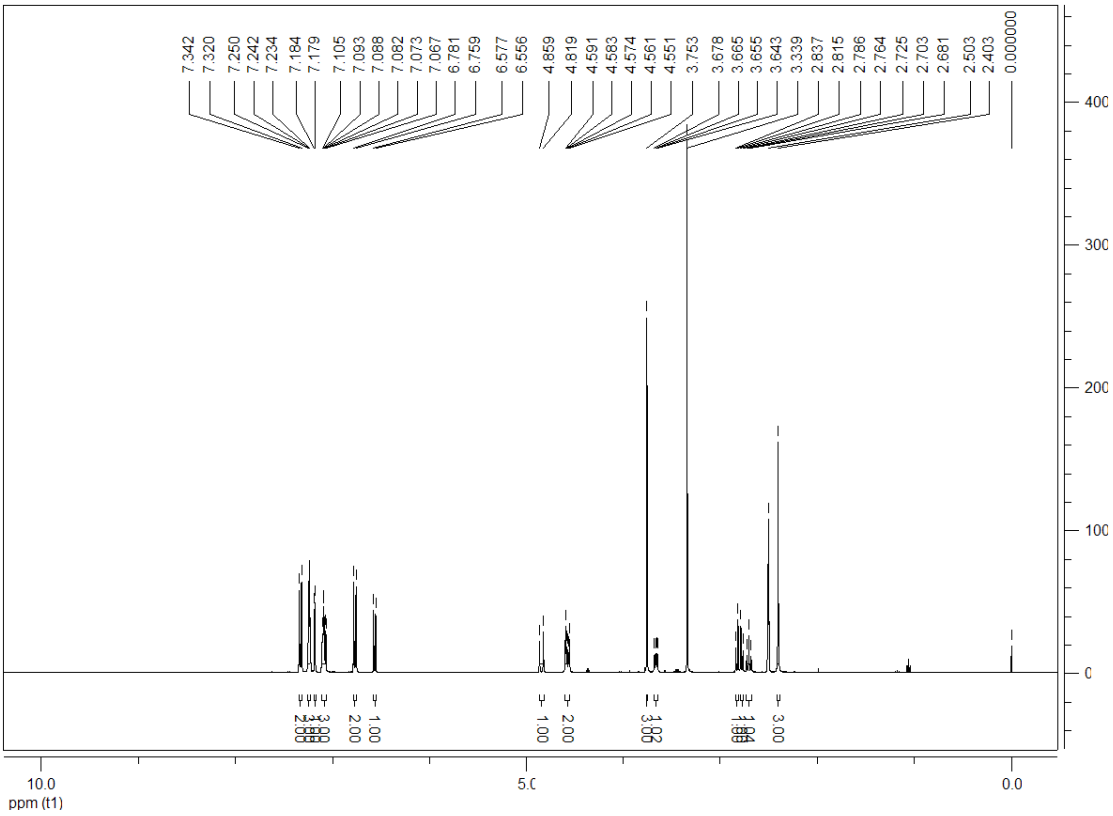

196.826
178.194
139.327
138.657
135.497
135.430
132.394
130.096
128.899
128.721
128.246
127.623
127.372
126.107
108.061
67.818
56.574
56.266
54.484
44.112
41.886
20.995
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

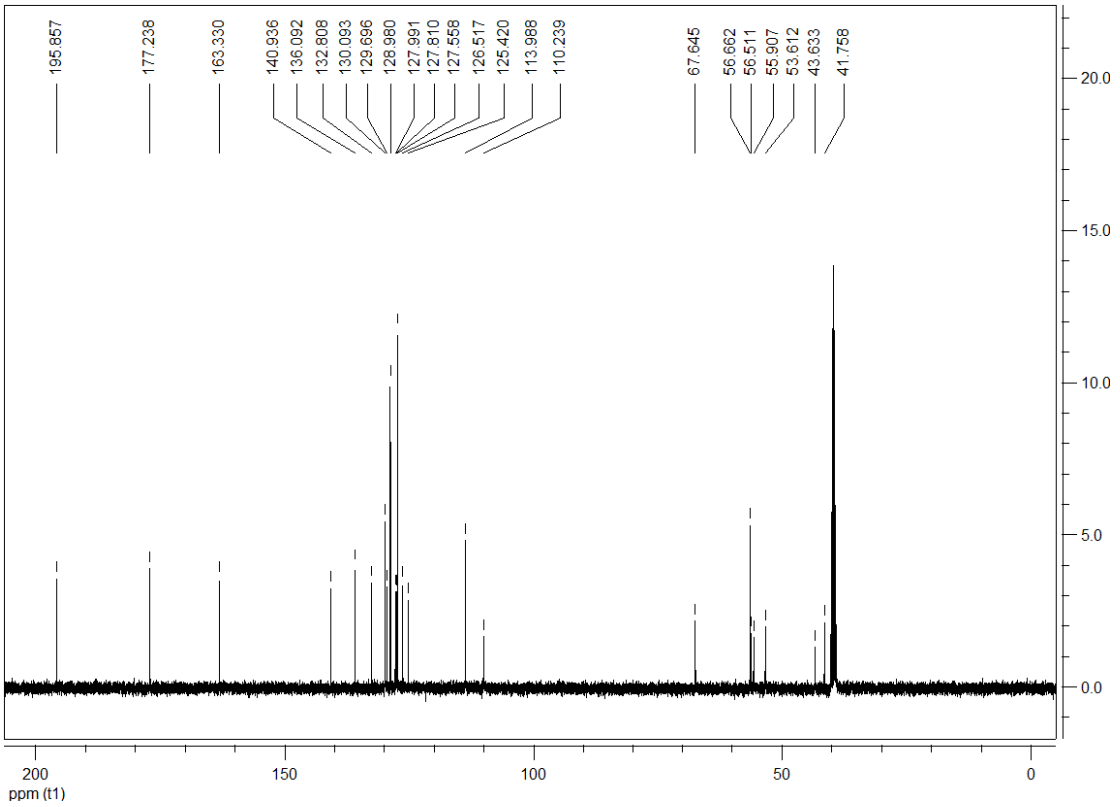

Intens.
x10^5
+MS, 0.77-0.85min #(78-87)
445.1706
1.5
1.0
0.5
0.0
420
430
440
450
460
470
m/z

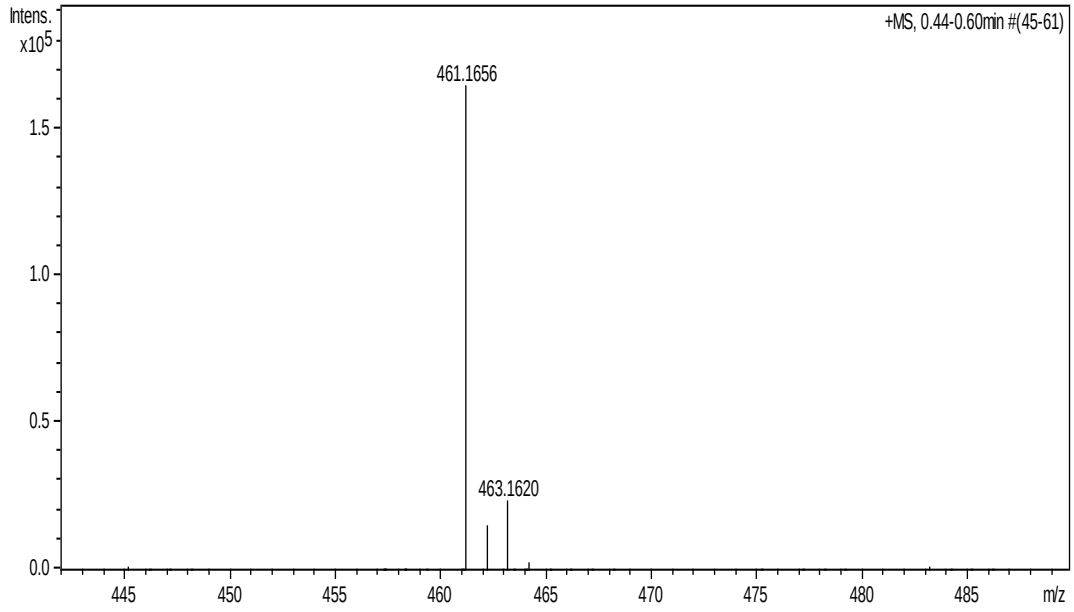
(3S,4'R)-1-Benzyl-5-chloro-4'-(4-methoxybenzoyl)-1'-methylspiro[indoline-3,3'-pyrrolidin]-2-one (8g)



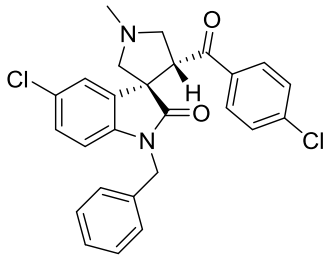
white solid, 90%, m.p.151~152℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.34~7.32 (m, 2H, ArH), 7.25~7.23 (m, 3H, ArH), 7.18 (d, J = 2.0Hz, 1H, ArH), 7.10~7.07 (m, 3H, ArH), 6.78~6.76 (m, 2H, ArH), 6.57 (d, J = 8.4Hz, 1H, ArH), 4.84 (d, J = 16.0Hz, 1H, CH), 4.59~4.55 (m, 2H, CH), 3.75 (s, 3H, OCH_3), 3.66 (dd, J_1 = 9.0Hz, J_2 = 5.2Hz , 1H, CH), 2.83 (d, J = 8.8Hz, 1H, CH), 2.78 (d, J = 8.8Hz, 1H, CH), 2.70 (d, J = 8.8Hz, 1H, CH), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 195.8, 177.2, 163.3, 140.9, 136.0, 132.8, 130.0, 129.6, 128.9, 127.9, 127.8, 127.5, 126.5, 125.4, 113.9, 110.2, 67.6, 56.6, 56.5, 55.9, 53.6, 43.6, 41.7; IR (KBr) υ: 3414, 3069, 3026, 2945, 2839, 2782, 1715, 1678, 1603, 1574, 1480, 1454, 1427, 1349, 1315, 1248, 1224, 1175, 1111, 1075, 1024, 973, 948, 901, 845, 815, 788, 738 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{27}H_{26}ClN_2O_3$ ([M+H]$^+$): 461.1626, found: 461.1656.



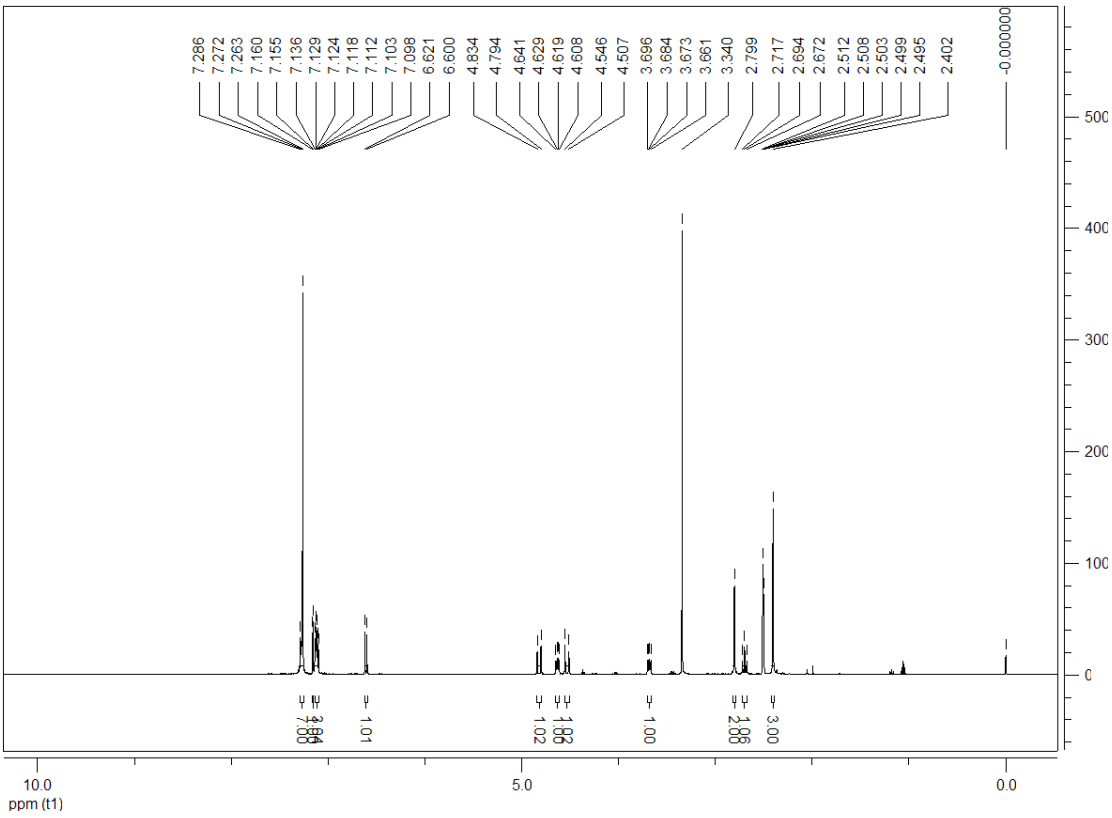

195.857
177.238
163.330
140.936
136.092
132.808
130.093
129.696
128.980
127.991
127.810
127.558
126.517
125.420
113.988
110.239
67.645
56.662
56.511
55.907
53.612
43.633
41.758
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

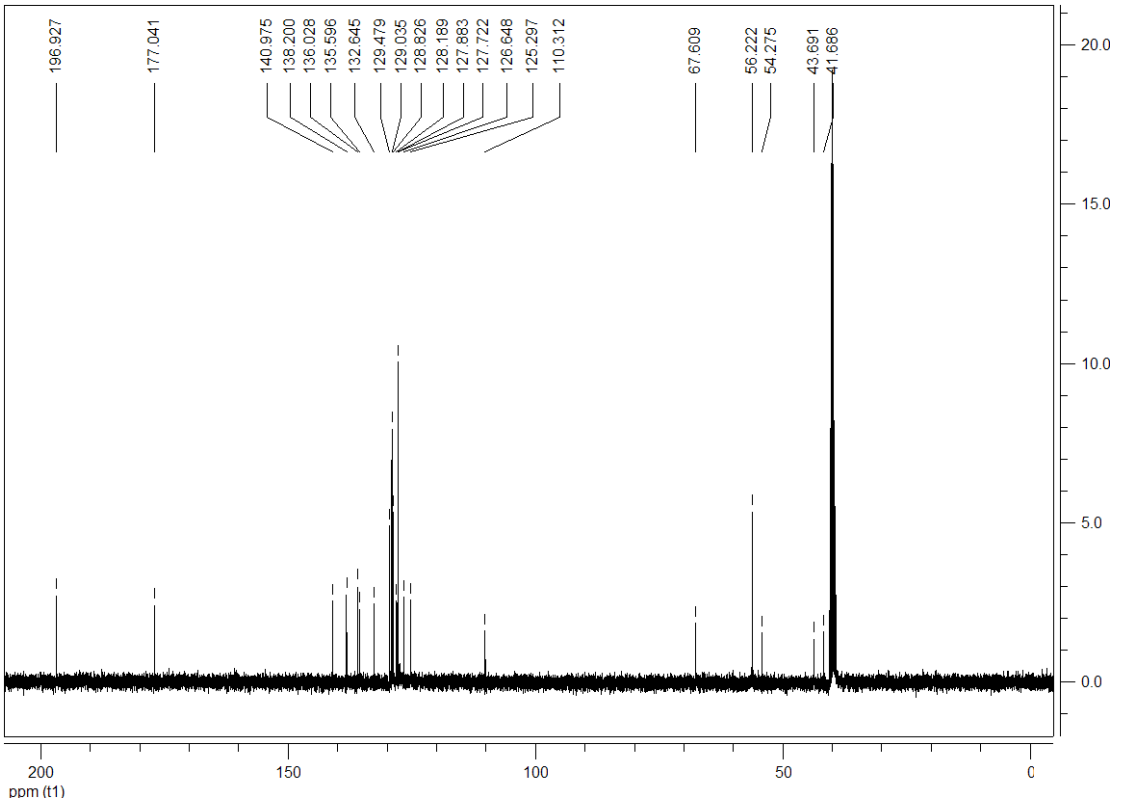

Intens.
x10^5
+MS, 0.44-0.60min #(45-61)
461.1656
463.1620
1.5
1.0
0.5
0.0
445
450
455
460
465
470
475
480
485
m/z

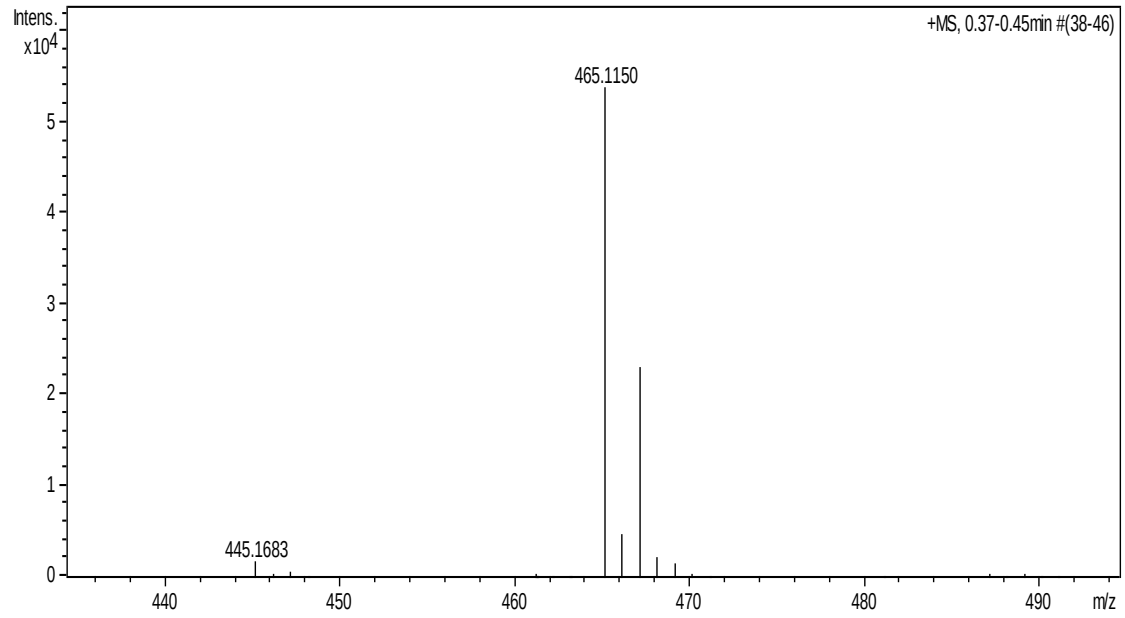
(3S,4'R)-1-Benzyl-5-chloro-4'-(4-chlorobenzoyl)-1'-methylspiro[indoline-3,3'-pyrrolidin]-2-one (8h)



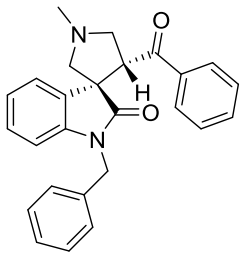
white solid, 90%, m.p.174~175℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.29~7.26 (m, 7H, ArH), 7.16 (d, J = 2.0Hz, 1H, ArH), 7.14~7.10 (m, 3H, ArH), 6.61 (d, J = 8.4Hz, 1H, ArH), 4.81 (d, J = 16.0Hz, 1H, CH), 4.62 (dd, J_1 = 8.6Hz, J_2 = 4.8Hz, 1H, CH), 4.53 (d, J = 15.6Hz, 1H, CH), 3.68 (dd, J_1 = 9.2Hz, J_2 = 4.8Hz, 1H, CH), 2.80 (s, 2H, CH), 2.69 (d, J = 8.8Hz, 1H, CH), 2.40 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 196.9, 177.0, 140.9, 138.1, 136.0, 135.5, 132.6, 129.4, 129.0, 128.8, 128.1, 127.8, 127.7, 126.6, 125.2, 110.3, 67.6, 56.2, 54.2, 43.6, 41.6; IR (KBr) υ: 3404, 3063, 2972, 2942, 2839, 2812, 2785, 1711, 1587, 1482, 1431, 1398, 1349, 1245, 1217, 1176, 1111, 1089, 1014, 949, 922, 898, 844, 818, 787, 734 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{26}H_{23}Cl_2N_2O_2$ ([M+H]$^+$): 465.1131, found: 465.1150.



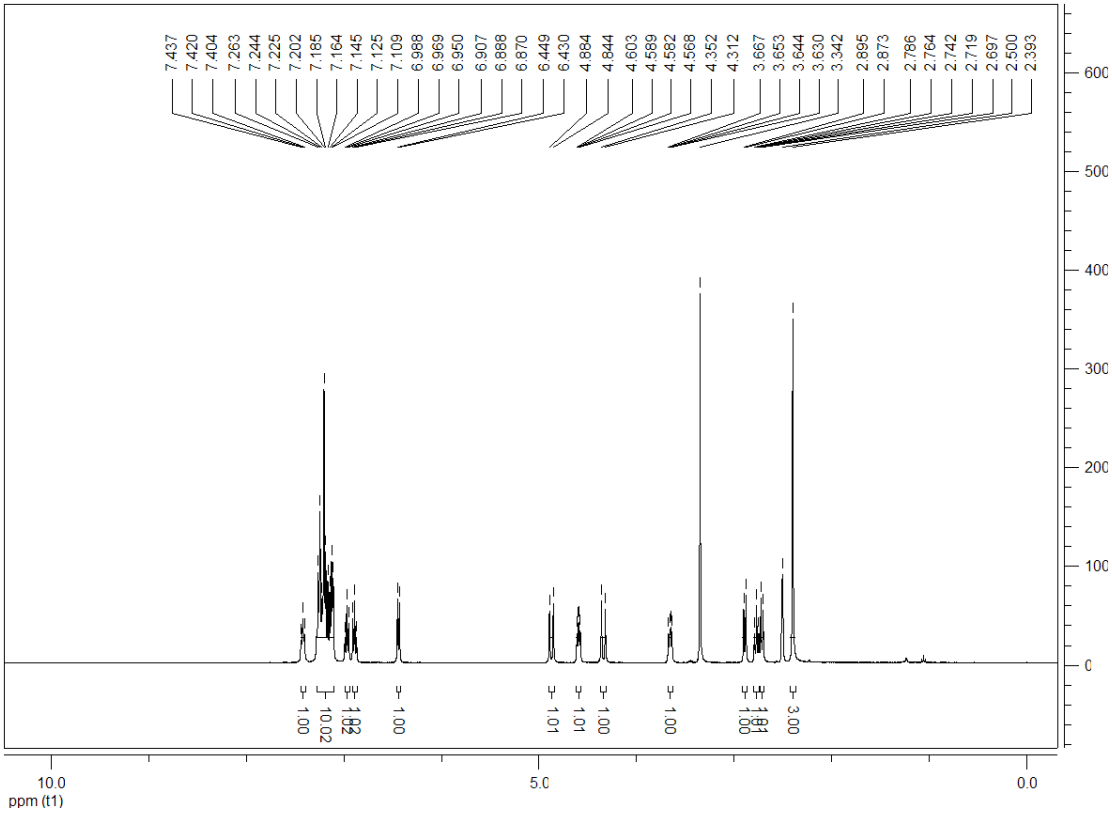

196.927
177.041
140.975
138.200
136.028
135.596
132.645
129.479
129.035
128.826
128.189
127.883
127.722
126.648
125.297
110.312
67.609
56.222
54.275
43.691
41.686
20.0
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

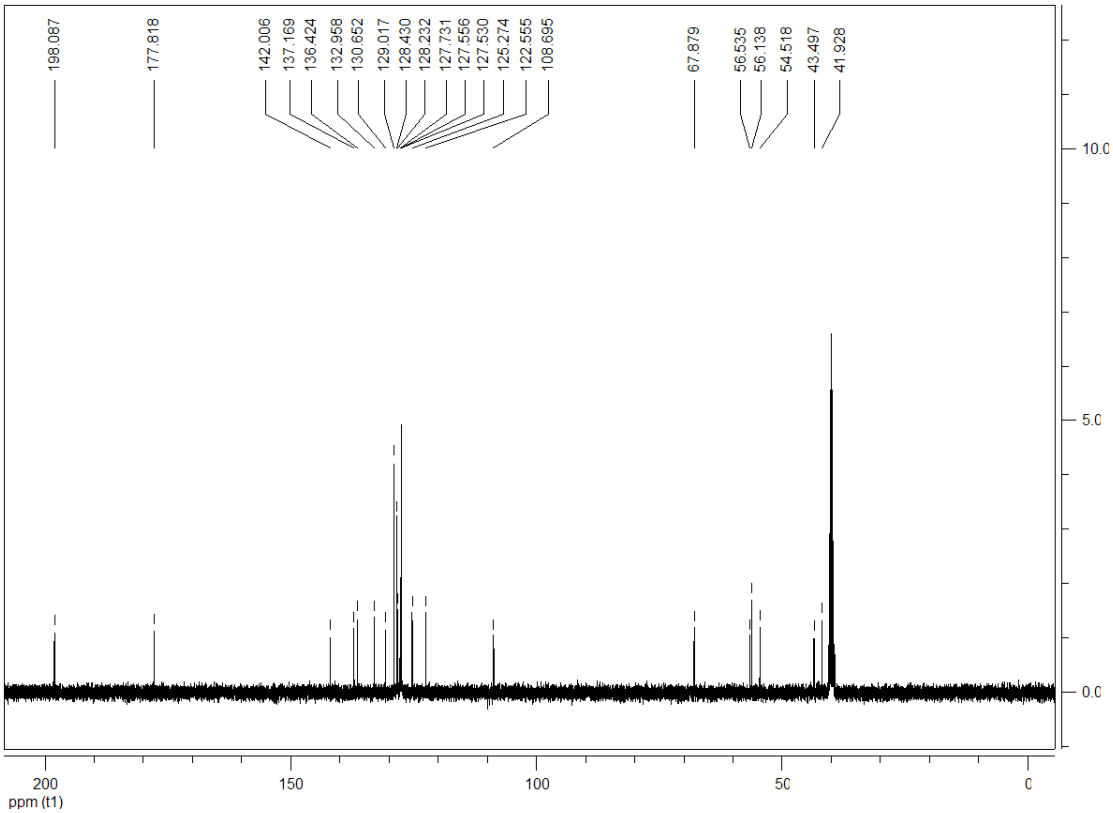

Intens.
x10^4
+MS, 0.37-0.45min #(38-46)
465.1150
445.1683
5
4
3
2
1
0
440
450
460
470
480
490
m/z

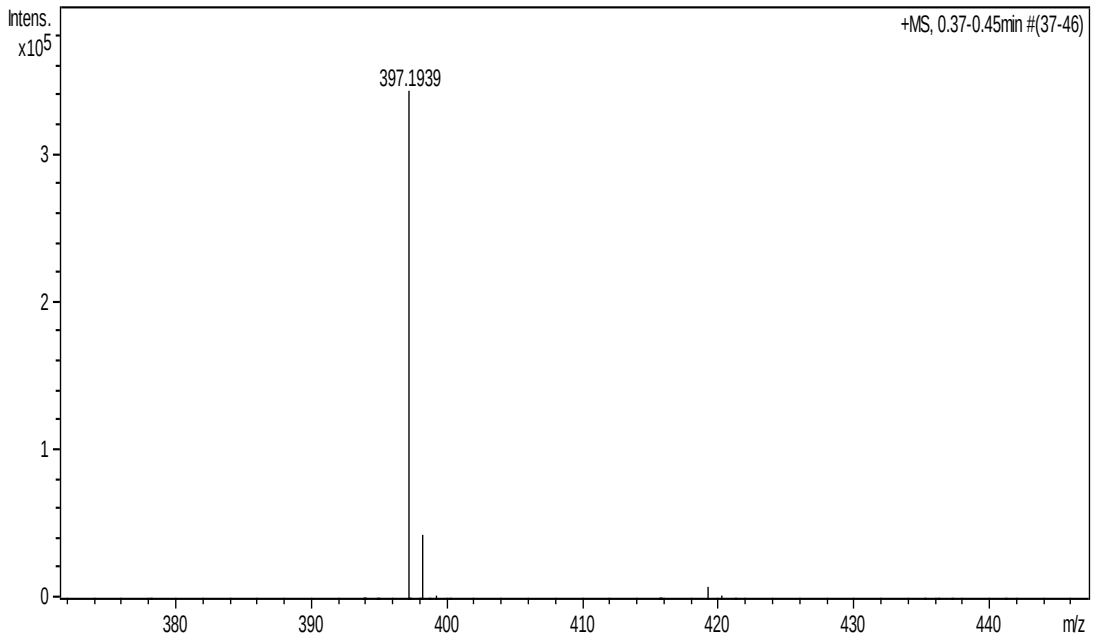
(3S,4'R)-4'-Benzoyl-1-benzyl-1'-methylspiro[indoline-3,3'-pyrrolidin]-2-one (8i)



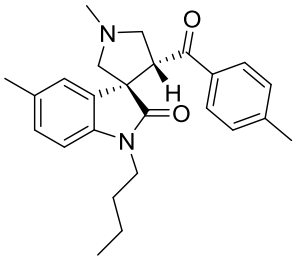
white solid, 89%, m.p.123~125 ℃ ; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.44~7.40 (m, 1H, ArH), 7.26~7.11 (m, 10H, ArH), 6.99~6.95 (m, 1H, ArH), 6.91~6.87 (m, 1H, ArH), 6.44 (d, J = 7.6Hz, 1H, ArH), 4.86 (d, J = 16.0Hz, 1H, CH), 4.58 (dd, J_1 = 8.4Hz, J_2 = 5.6Hz, 1H, CH), 4.33 (d, J = 16.0Hz, 1H, CH), 3.65 (dd, J_1 = 9.2Hz, J_2 = 5.6Hz , 1H, CH), 2.88 (d, J = 8.8Hz, 1H, CH), 2.76 (d, J = 9.2Hz, 1H, CH), 2.71 (d, J = 8.8Hz, 1H, CH), 2.39 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 198.0, 177.8, 142.0, 137.1, 136.4, 132.9, 130.6, 129.0, 128.4, 128.2, 127.7, 127.5, 127.5, 125.2, 122.5, 108.6, 67.8, 56.5, 56.1, 54.5, 43.4, 41.9; IR (KBr) υ: 3402, 3033, 2973, 2945, 2831, 2782, 1966, 1711, 1682, 1607, 1489, 1465, 1448, 1421, 1367, 1307, 1246, 1218, 1179, 1147, 1105, 1014, 952, 922, 892, 845, 796, 761, 730 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{25}N_2O_2$ ([M+H]$^+$): 397.1911, found: 397.1939.



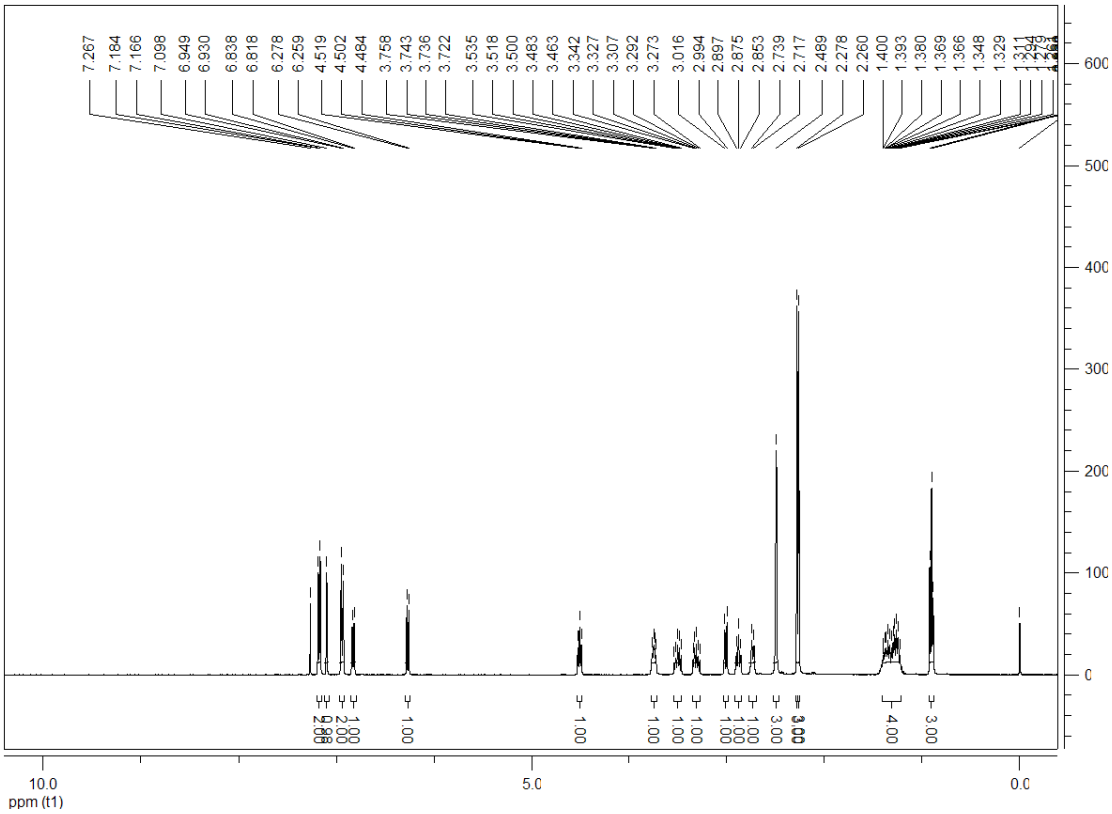

198.087
177.818
142.006
137.169
136.424
132.958
130.652
129.017
128.430
128.232
127.731
127.556
127.530
125.274
122.555
108.695
67.879
56.535
56.138
54.518
43.497
41.928
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)

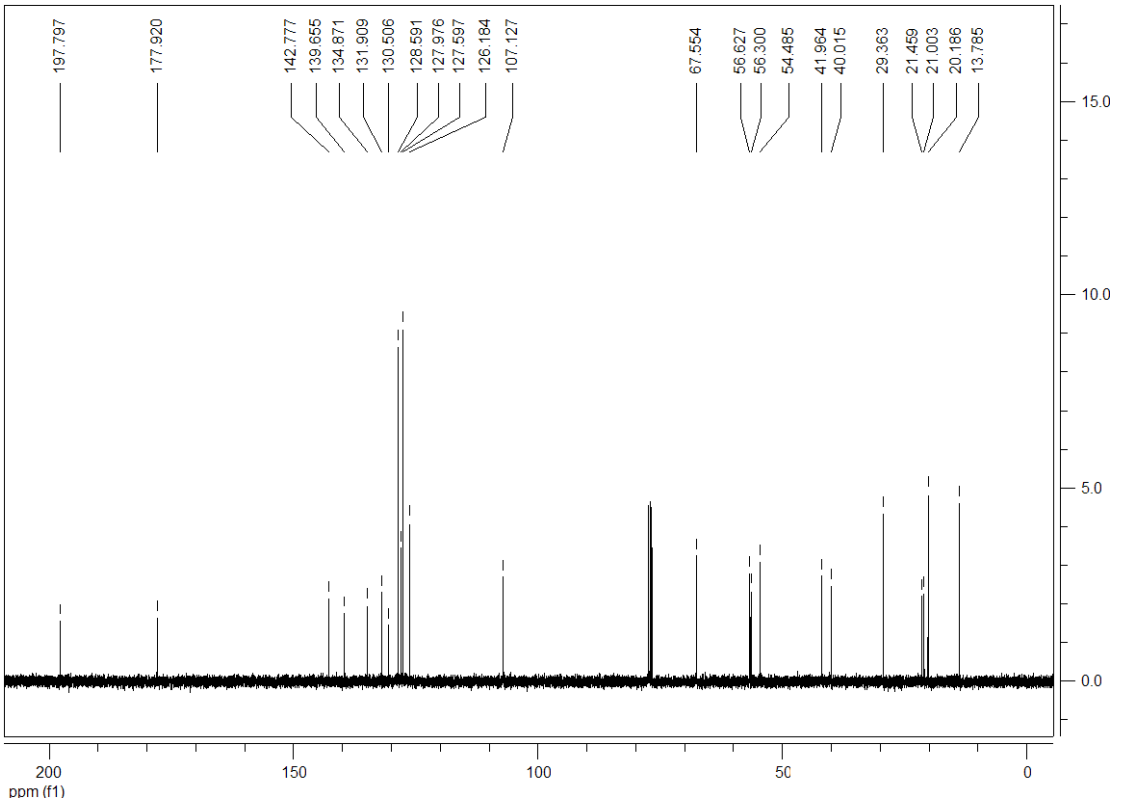

Intens.
x10^5
+MS, 0.37-0.45min #(37-46)
397.1939
3
2
1
0
380
390
400
410
420
430
440
m/z

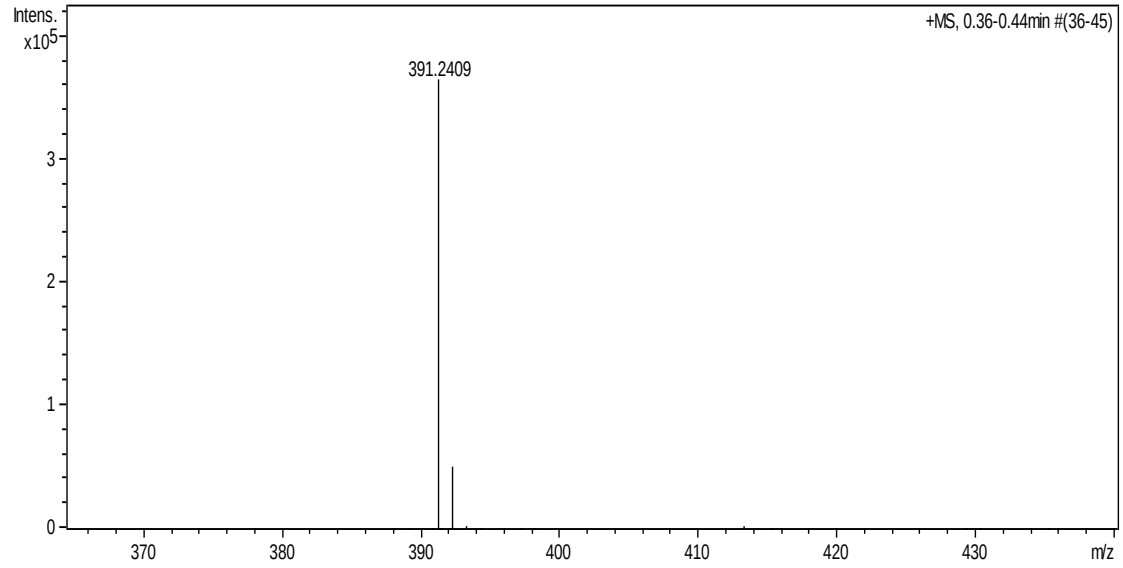
(3S,4'R)-1-Butyl-1',5-dimethyl-4'-(4-methylbenzoyl)spiro[indoline-3,3'-pyrrolidin]-2-one (8j)



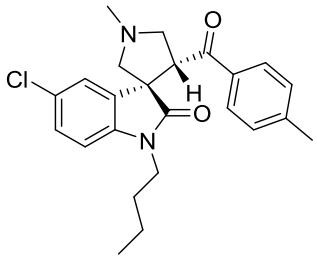
white solid, 91%, m.p.87~89℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (d, *J* = 7.2Hz, 2H, ArH), 7.10 (brs, 1H, ArH), 6.94 (d, *J* = 7.6Hz, 1H, ArH), 6.83 (d, *J* = 8.0Hz, 1H, ArH), 6.27 (d, *J* = 7.6Hz, 1H, ArH), 4.52~4.48 (m, 1H, CH), 3.76~3.72 (m, 1H, CH), 3.54~3.46 (m, 1H, CH), 3.34~3.27 (m, 1H, CH), 3.00 (d, *J* = 8.8Hz, 1H, CH), 2.88 (t, *J* = 8.8Hz, 1H, CH), 2.73 (d, *J* = 8.8Hz, 1H, CH), 2.49 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 1.40~1.22 (m, 4H, CH), 0.90 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.7, 177.9, 142.7, 139.6, 134.8, 131.9, 130.5, 128.5, 127.9, 127.5, 126.1, 107.1, 67.5, 56.6, 56.2, 54.4, 41.9, 40.0, 29.3, 21.4, 21.0, 20.1, 13.7; IR (KBr) υ: 3388, 3035, 2928, 2831, 2780, 1918, 1704, 1603, 1492, 1453, 1350, 1242, 1188, 1143, 1110, 1082, 1040, 1018, 972, 942, 893, 839, 811, 737 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{25}H_{31}N_2O_2$ ($[M+H]^+$): 391.2380, found: 391.2409.



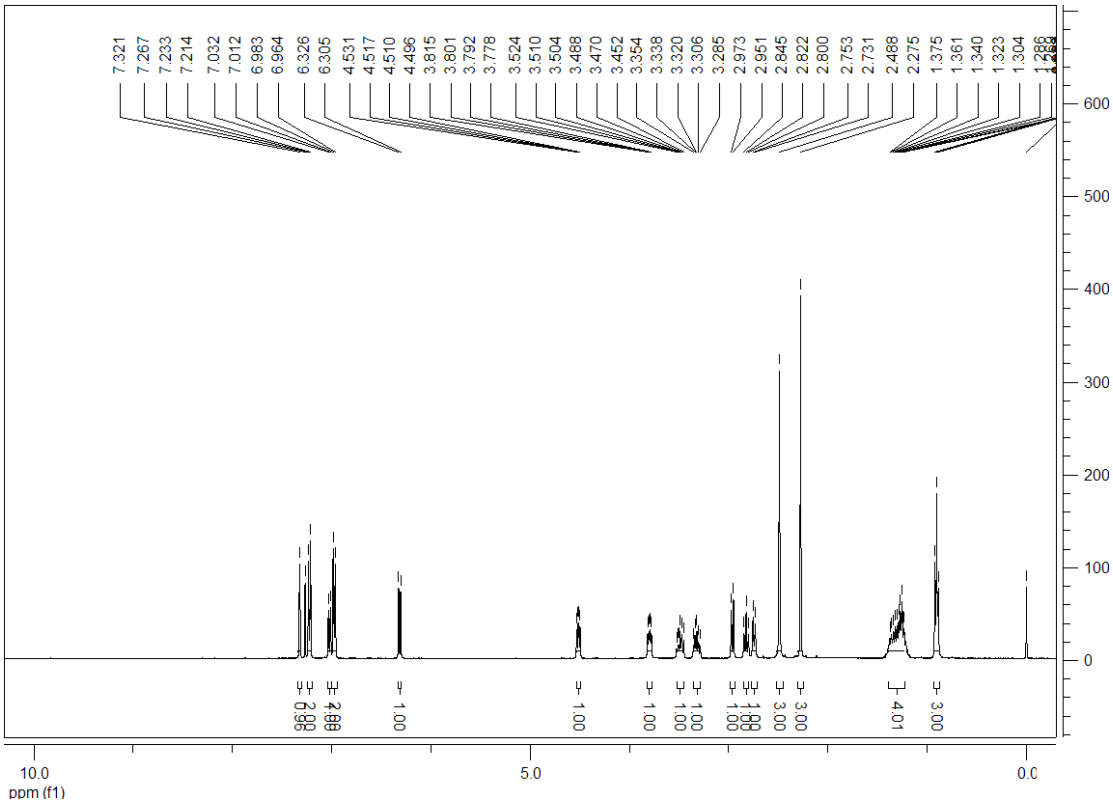

197.797
177.920
142.777
139.655
134.871
131.909
130.506
128.591
127.976
127.597
126.184
107.127
67.554
56.627
56.300
54.485
41.964
40.015
29.363
21.459
21.003
20.186
13.785
15.0
10.0
5.0
0.0
200
150
100
50
0
ppm (f1)

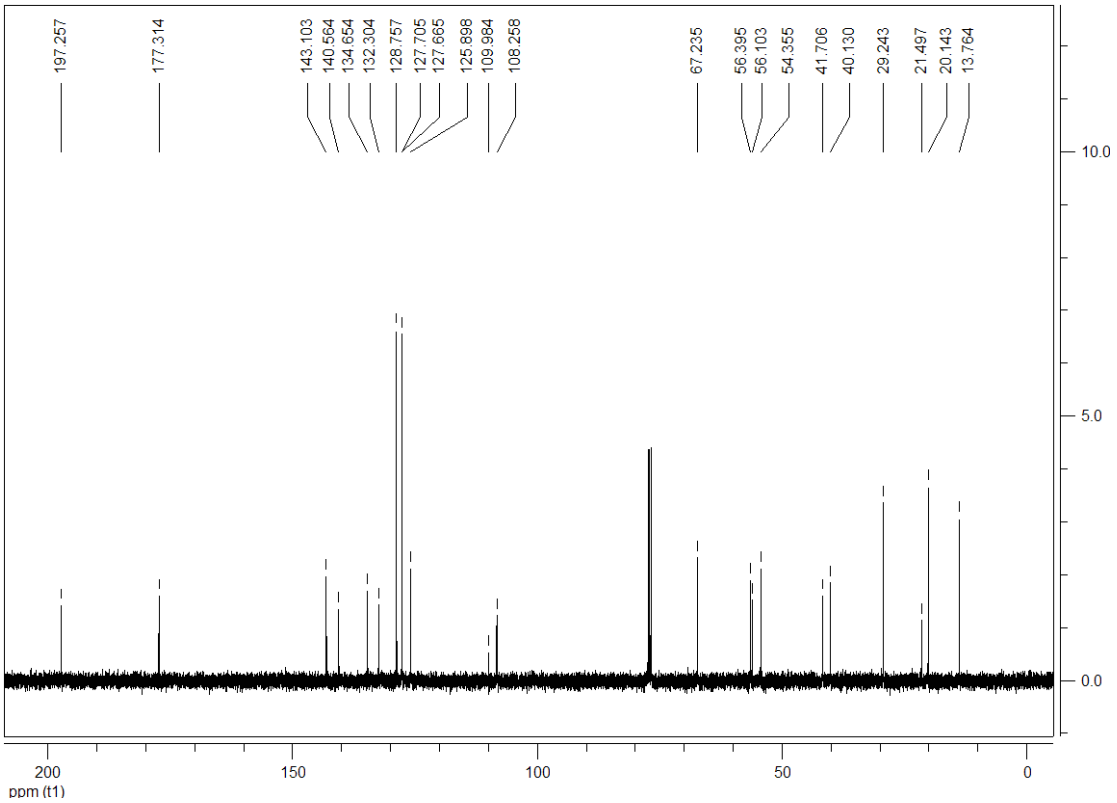

Intens.
x10^5
+MS, 0.36-0.44min #(36-45)
391.2409
3
2
1
0
370
380
390
400
410
420
430
m/z

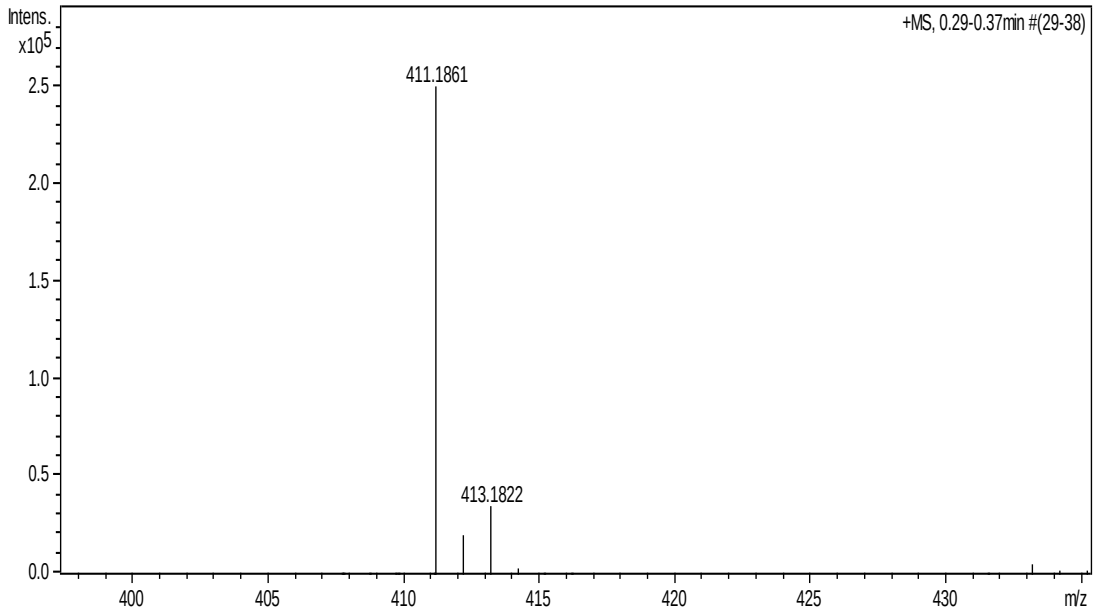
(3S,4'R)-1-Butyl-5-chloro-1'-methyl-4'-(4-methylbenzoyl)spiro[indoline-3,3'-pyrrolidin]-2-one (8k)



white solid, 90%, m.p.103~105℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32 (brs, 1H, ArH), 7.28 (d, *J* = 7.6Hz, 2H, ArH), 7.02 (d, *J* = 8.0Hz, 1H, ArH), 6.97 (d, *J* = 7.6Hz, 2H, ArH), 6.32 (d, *J* = 8.4Hz, 1H, ArH), 4.51 (dd, J_1 = 8.4Hz, J_2 = 5.6Hz, 1H, CH), 3.80 (dd, J_1 = 9.2Hz, J_2 = 5.6Hz , 1H, CH), 3.52~3.45 (m, 1H, CH), 3.35~3.28 (m, 1H, CH), 2.96 (d, *J* = 8.8Hz, 1H, CH), 2.82 (t, *J* = 8.8Hz, 1H, CH), 2.74 (d, *J* = 8.8Hz, 1H, CH), 2.49 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 1.38~1.23 (m, 4H, CH), 0.90 (t, *J* = 7.2Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 197.3, 177.3, 143.1, 140.6, 134.6, 132.3, 128.8, 127.7, 127.7, 125.9, 110.0, 108.3, 67.2, 56.4, 56.1, 54.4, 41.7, 40.1, 29.2, 21.5, 20.1, 13.8; IR (KBr) υ: 3418, 3065, 2956, 2868, 2830, 2790, 1717, 1683, 1605, 1477, 1432, 1349, 1245, 1187, 1145, 1110, 1077, 1019, 967, 936, 907, 890, 841, 801, 768, 737 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{24}H_{28}ClN_2O_2$ ($[M+H]^+$): 411.1834, found: 411.1861.




197.257
177.314
143.103
140.564
134.654
132.304
128.757
127.705
127.665
125.898
109.984
108.258
67.235
56.395
56.103
54.355
41.706
40.130
29.243
21.497
20.143
13.764
10.0
5.0
0.0
200
150
100
50
0
ppm (t1)


Intens.
x10^5
+MS, 0.29-0.37min #(29-38)
411.1861
413.1822
2.5
2.0
1.5
1.0
0.5
0.0
400
405
410
415
420
425
430
m/z