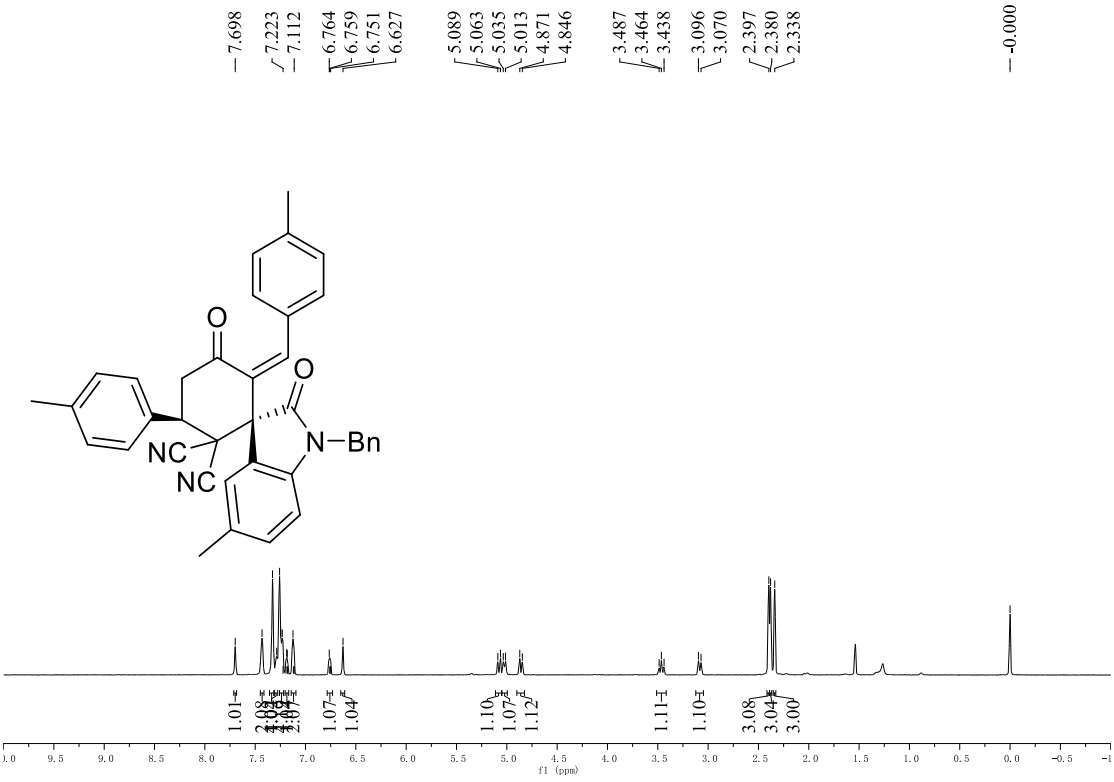
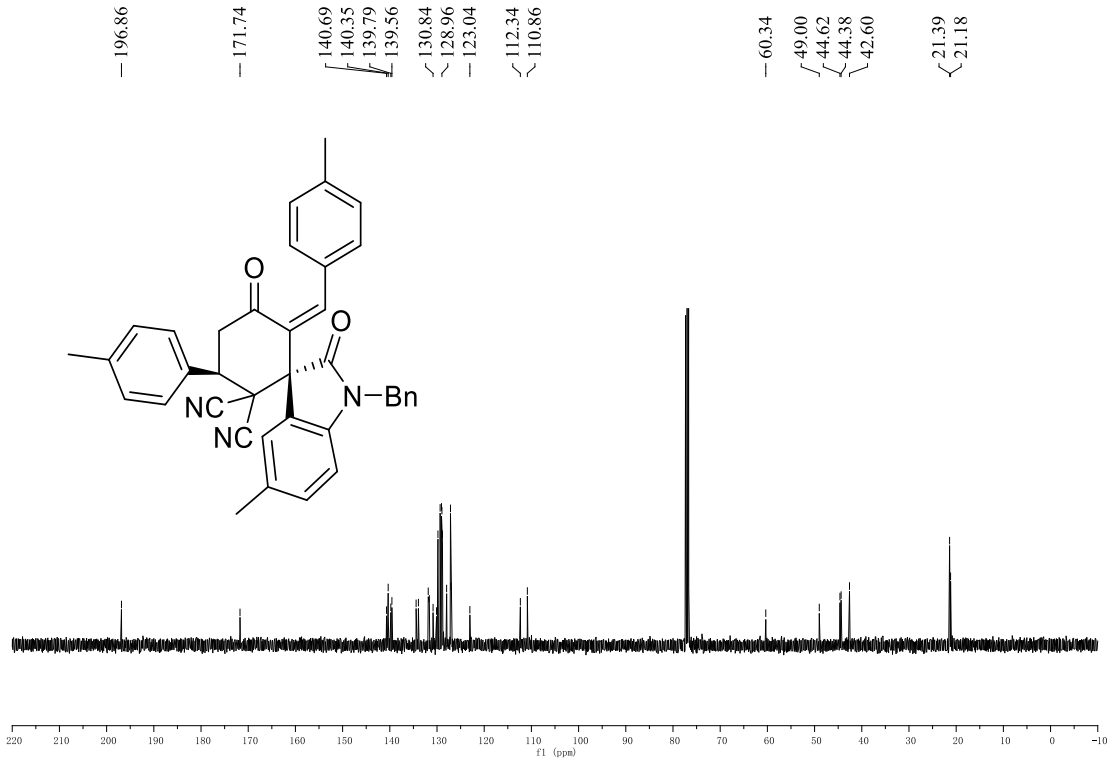
Tributylphosphine promoted domino reaction for efficient construction of spiro[cyclohexane-1,3'-indoline] and spiro[indoline-3,2'-furan-3',3''-indoline]

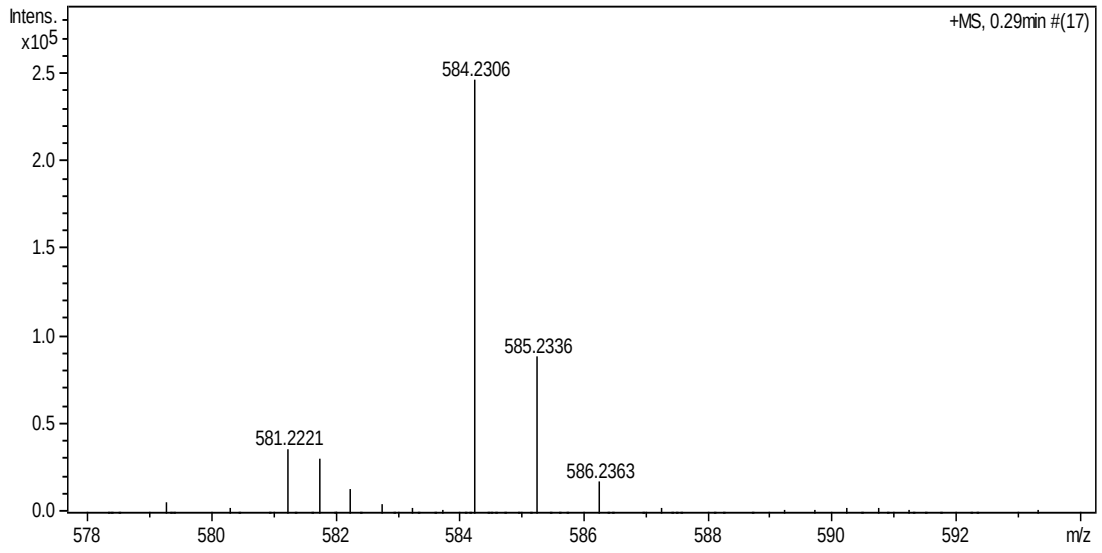
Hui Zheng, Ying Han,* Jing Sun, Chao-Guo Yan*

Supporting Information

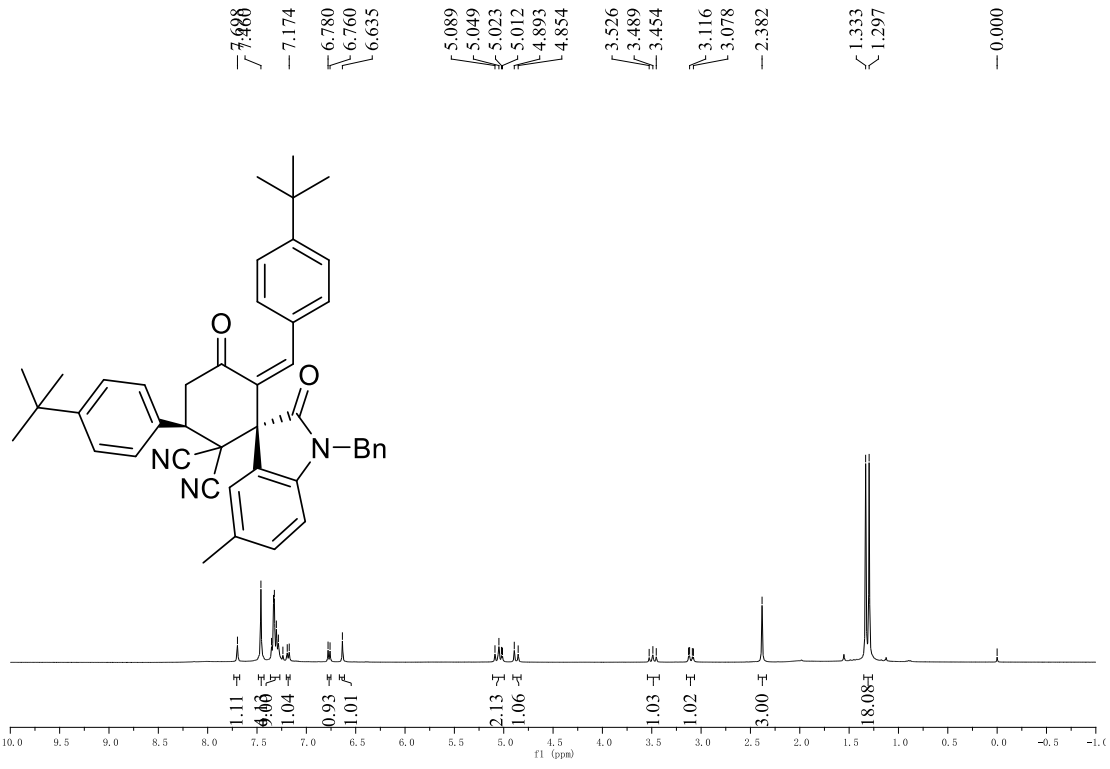
***rel*-(1*R*,3*R*)-1'-benzyl-5'-methyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3a)**: white solid, 84%, m.p. 213-215 ºC; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (s, 1H, ArH), 7.43 (s, 2H, ArH), 7.33 (s, 4H, ArH), 7.29 (s, 1H, ArH), 7.25-7.22 (m, 4H, ArH), 7.19-7.18 (m, 1H, ArH), 7.13-7.11 (m, 2H, ArH), 6.76-6.75 (m, 1H, ArH), 6.63 (s, 1H, CH), 5.07 (d, *J* = 15.6 Hz, 1H, CH_2), 5.02 (d, *J* = 13.2 Hz, 1H, CH_2), 4.86 (d, *J* = 15.0 Hz, 1H, CH_2), 3.46 (t, *J* = 13.8 Hz, 1H, CH), 3.08 (d, *J* = 15.6 Hz, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.34 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 171.7, 140.7, 140.4, 139.8, 139.6, 134.4, 134.0, 131.9, 131.6, 130.8, 130.1, 129.8, 129.3, 129.1, 129.0, 128.9, 128.0, 127.1, 127.0, 123.0, 112.3, 110.9, 60.3, 49.0, 44.6, 44.4, 42.6, 21.4, 21.2. IR (KBr) υ: 3727, 3405, 3029, 2921, 2863, 2317, 1911, 1709, 1609, 1501, 1443, 1362, 1295, 1185, 1049, 1022, 959, 920, 820, 732 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{31}NaN_3O_2$ ([M+Na]$^+$): 584.2314, found: 584.2306.

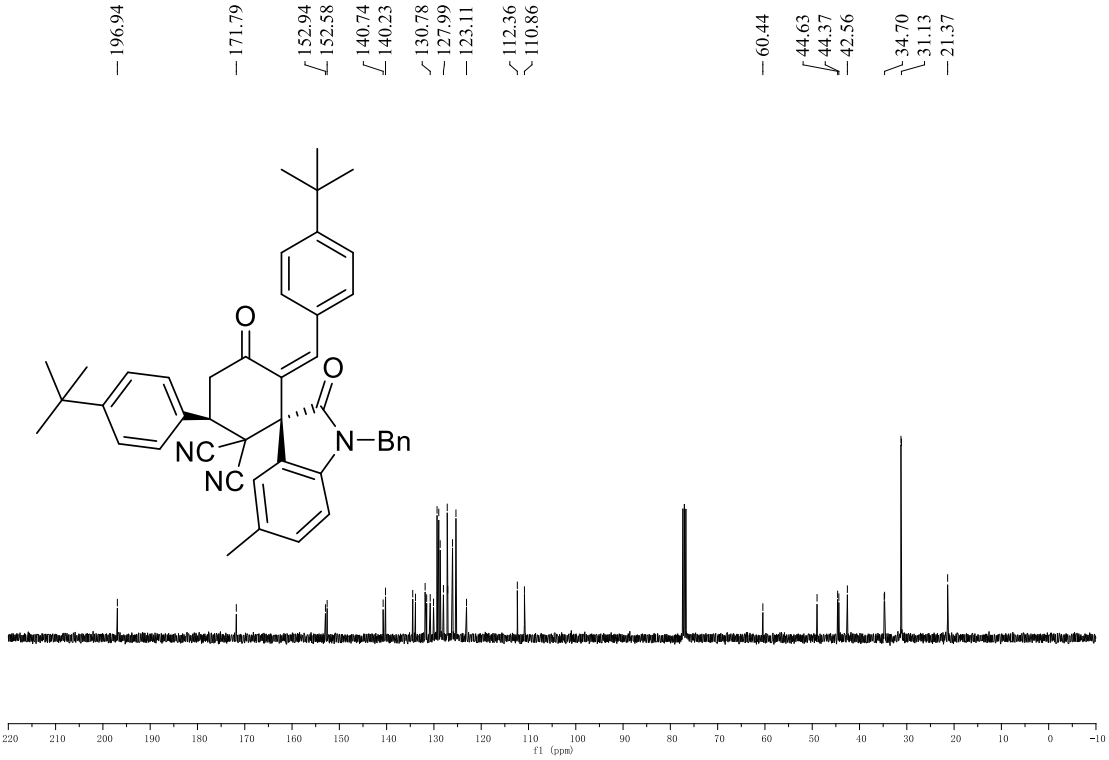


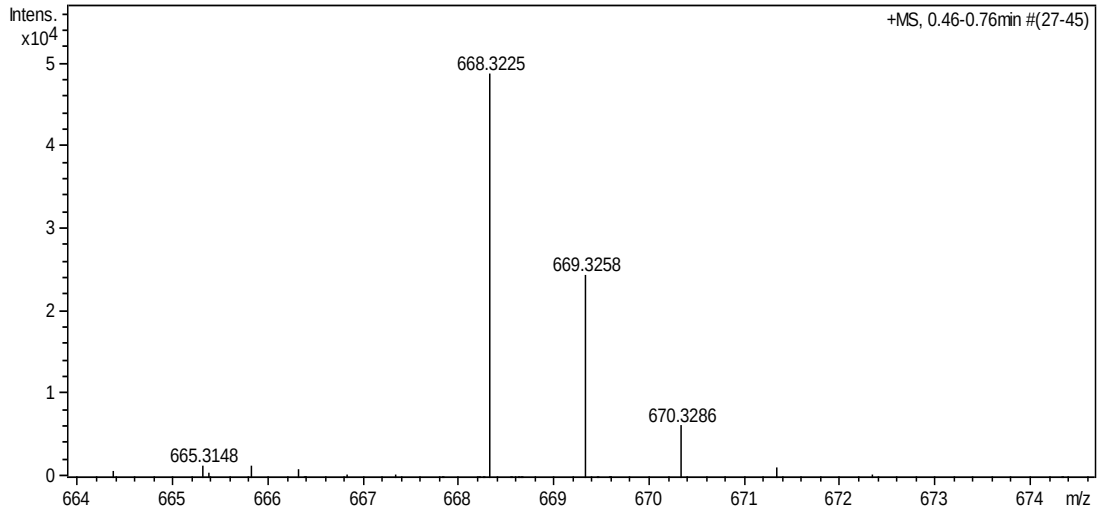

196.86
171.74
140.69
140.35
139.79
139.56
130.84
128.96
123.04
112.34
110.86
60.34
49.00
44.62
44.38
42.60
21.39
21.18
O
O
N–Bn
NC
NC
f1 (ppm)


Intens.
x10^5
+MS, 0.29min #(17)
584.2306
585.2336
581.2221
586.2363
m/z

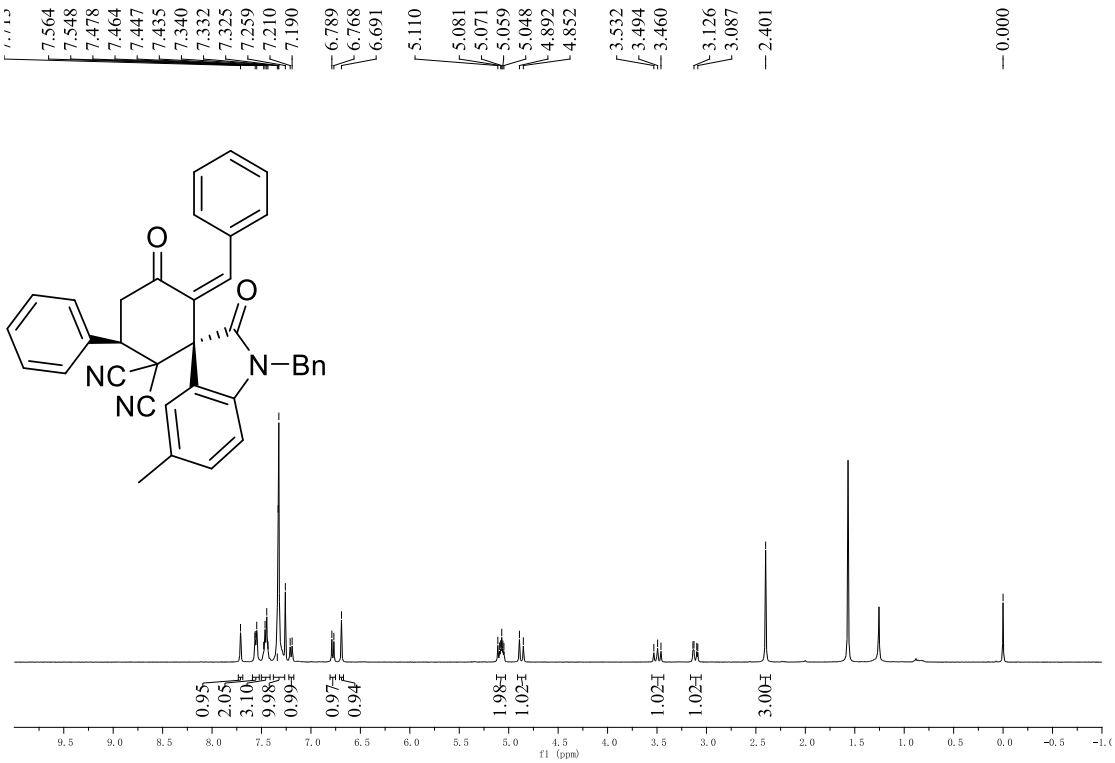
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3b)**: white solid, 80%, m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (s, 1H, ArH), 7.46 (s, 4H, ArH), 7.35-7.28 (m, 9H, ArH), 7.18 (d, *J* = 8.0 Hz, 1H, ArH), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (s, 1H, CH), 5.09-5.01 (m, 2H, CH_2), 4.87 (d, *J* = 15.6 Hz, 1H, CH_2), 3.49 (t, *J* = 14.0 Hz, 1H, CH), 3.13-3.08 (m, 1H, CH_2), 2.38 (s, 3H, CH_3), 1.33 (s, 9H, $(CH_3)_3$), 1.30 (s, 3H, $(CH_3)_3$).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 171.8, 152.9, 152.6, 140.7, 140.2, 134.5, 133.9, 131.9, 131.5, 130.8, 130.1, 129.3, 129.0, 128.7, 128.0, 127.2, 127.1, 126.1, 125.3, 123.1, 112.4, 110.9, 60.4, 49.0, 44.6, 44.4, 42.6, 34.8, 34.7, 31.2, 31.1, 21.4. IR (KBr) υ: 3288, 2963, 1728, 1614, 1499, 1358, 1306, 1266, 1207, 1112, 1058, 1021, 968, 829 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{44}H_{43}NaN_3O_2$ ([M+Na]$^+$): 668.3253, found: 668.3225.

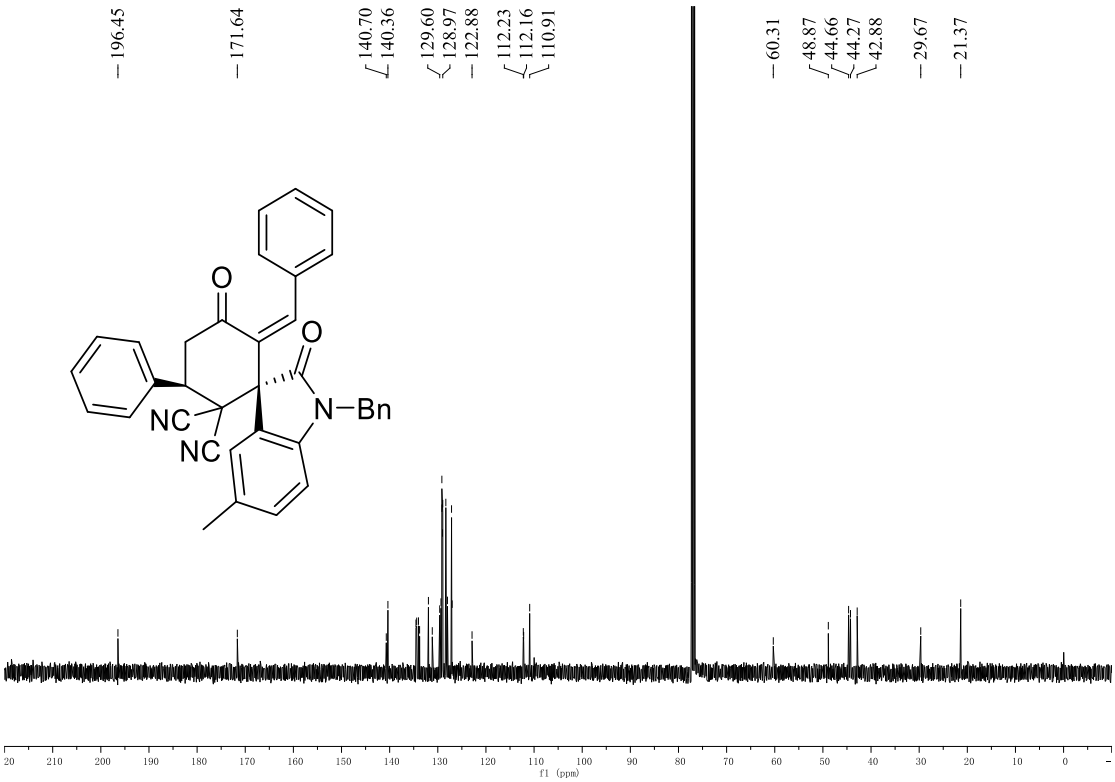


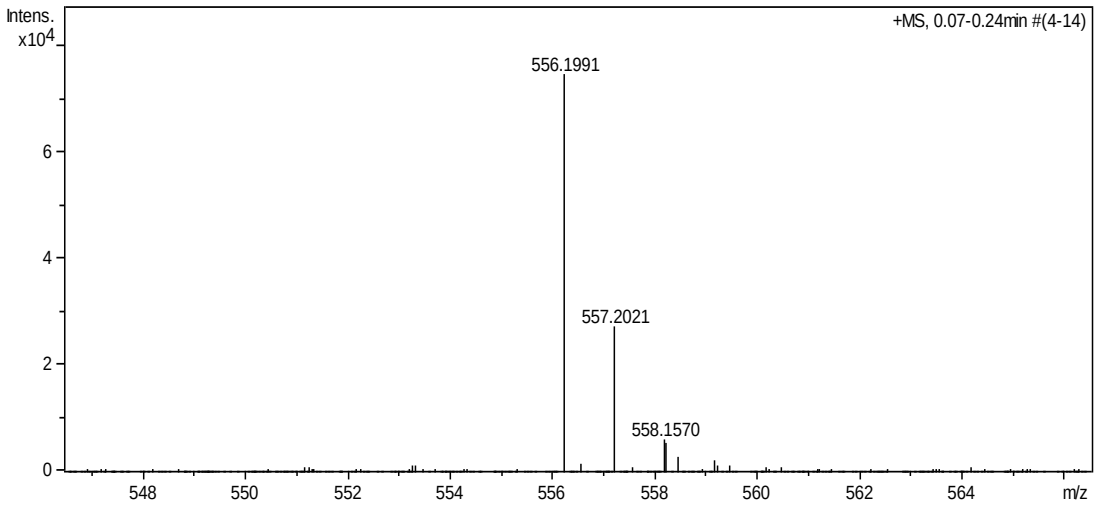

196.94
171.79
152.94
152.58
140.74
140.23
130.78
127.99
123.11
112.36
110.86
60.44
44.63
44.37
42.56
34.70
31.13
21.37
O
O
N−Bn
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.46-0.76min #(27-45)
668.3225
669.3258
670.3286
665.3148
m/z

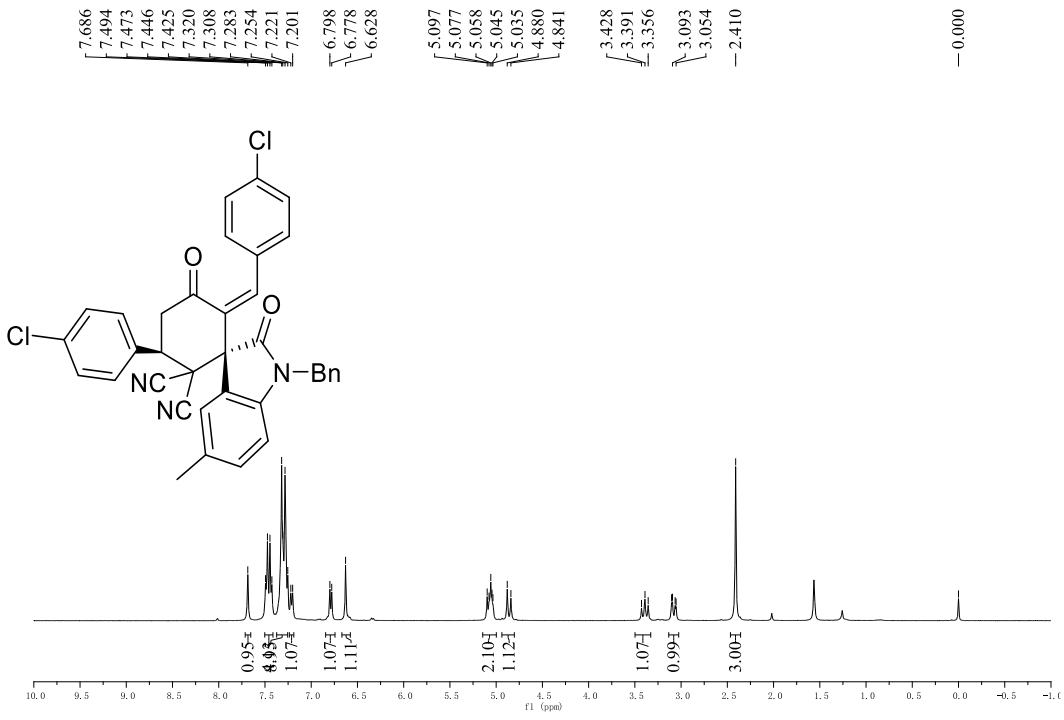
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-benzylidene)-5'-methyl-2',5-dioxo-3-phenylspiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3c)**: white solid, 80%, m.p. 162-164 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (s, 1H, ArH), 7.57-7.55 (m, 2H, ArH), 7.48-7.44 (m, 3H, ArH), 7.34-7.33 (m, 10H, ArH), 7.20 (d, *J* = 8.0 Hz, 1H, ArH), 6.78 (d, *J* = 8.4 Hz, 1H, ArH), 6.69 (s, 1H, CH), 5.11-5.05 (m, 2H, CH_2), 4.87 (d, *J* = 16.0 Hz, 1H, CH_2), 3.49 (t, *J* = 13.6 Hz, 1H, CH), 3.14-3.09 (m, 1H, CH_2), 2.40 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 171.6, 140.7, 140.4, 134.5, 134.4, 134.0, 133.8, 132.0, 131.2, 129.6, 129.3, 129.2, 129.1, 129.0, 128.9, 128.3, 128.0, 127.2, 127.0, 122.9, 112.2, 112.1, 110.9, 60.3, 48.9, 44.7, 44.3, 42.9, 29.7, 21.4. IR (KBr) υ: 3728, 3399, 3032, 2918, 2852, 2319, 1948, 1882, 1709, 1609, 1492, 1441, 1348, 1189, 1064, 1018, 926, 811, 772, 733 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{27}NaN_3O_2$ ([M+Na]$^{+}$): 556.2001, found: 556.1991.

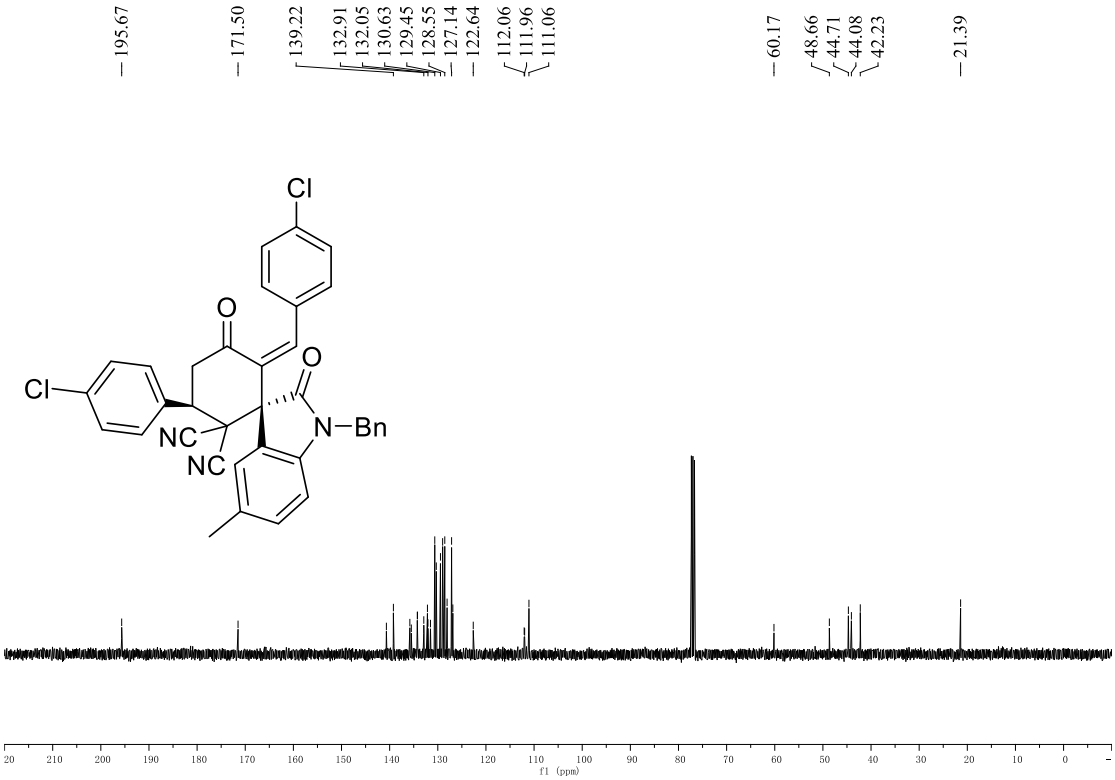


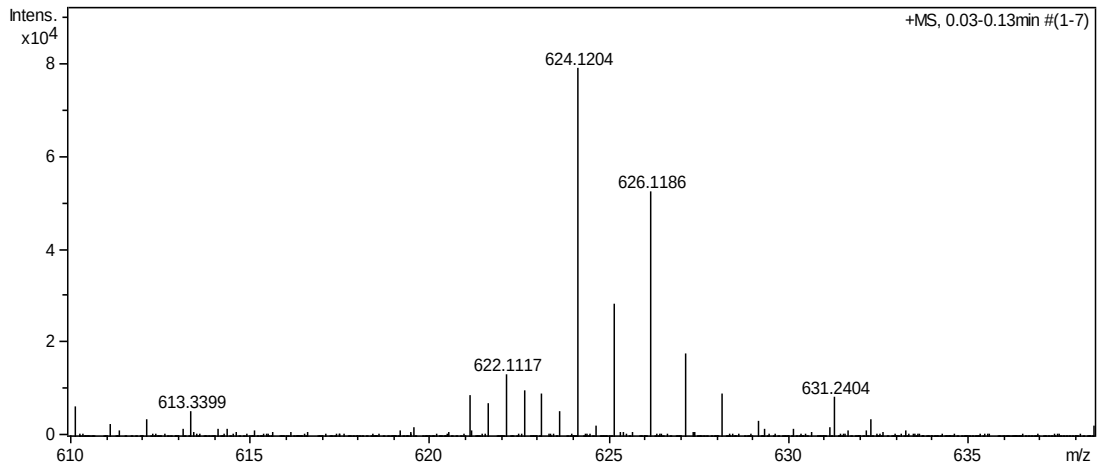

196.45
171.64
140.70
140.36
129.60
128.97
122.88
112.23
112.16
110.91
60.31
48.87
44.66
44.27
42.88
29.67
21.37
O
O
N–Bn
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.07-0.24min #(4-14)
556.1991
557.2021
558.1570
m/z

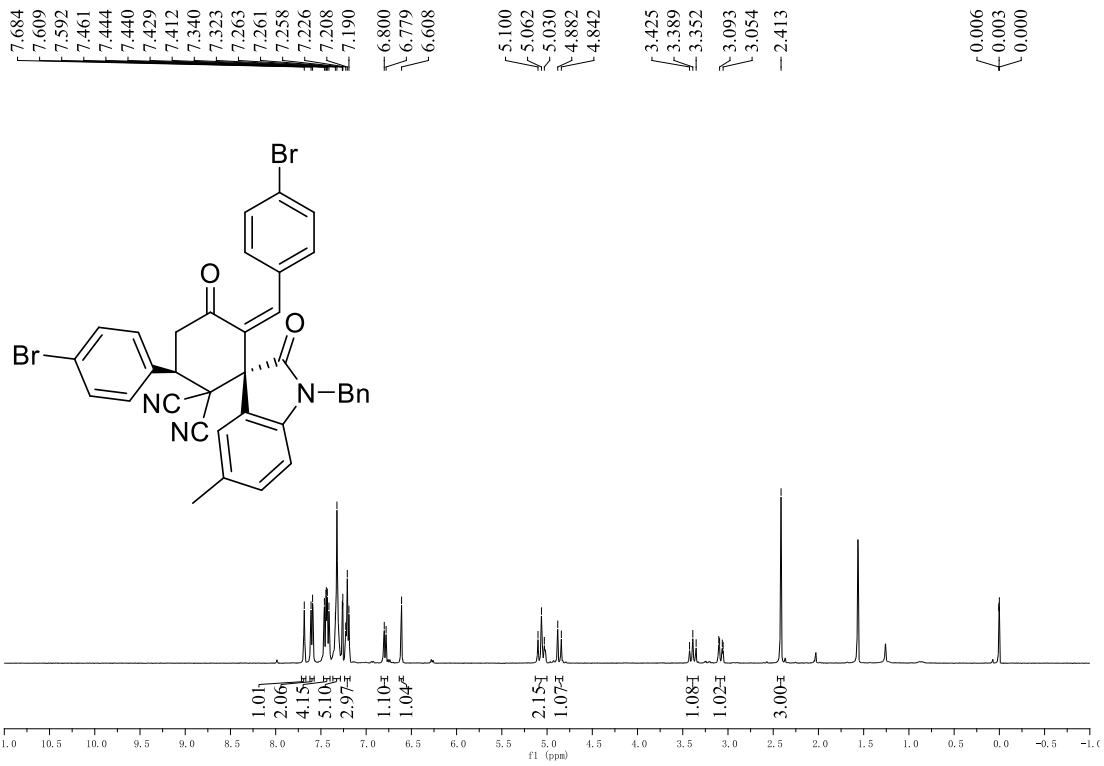
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-chlorobenzylidene)-3-(4-chlorophenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3d)**: pole pink solid, 70%, m.p. 244-246 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H, ArH), 7.49-7.43 (m, 4H, ArH), 7.32-7.28 (m, 9H, ArH), 7.21 (d, *J* = 8.0 Hz, 1H, ArH), 6.80 (d, *J* = 8.0 Hz, 1H, ArH), 6.63 (s, 1H, CH), 5.10-5.04 (m, 2H, CH_2), 4.86 (d, *J* = 15.6 Hz, 1H, CH_2), 3.39 (t, *J* = 14.0 Hz, 1H, CH), 3.10-3.05 (m, 1H, CH_2), 2.41 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 171.5, 140.7, 139.2, 135.8, 135.5, 134.3, 134.2, 132.9, 132.2, 132.1, 131.5, 130.6, 130.3, 129.5, 129.0, 128.6, 128.1, 127.1, 126.9, 122.6, 112.1, 112.0, 111.1, 60.2, 48.7, 44.7, 44.1, 42.2, 21.4. IR (KBr) υ: 3726, 3630, 3405, 3065, 2925, 2316, 1903, 1708, 1610, 1494, 1443, 1414, 1357, 1291, 1187, 1091, 1059, 1013, 917, 824, 732 cm^{-1} MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{25}NaCl_2N_3O_2$ ([M+Na]$^{+}$): 624.1222, found: 624.1204.

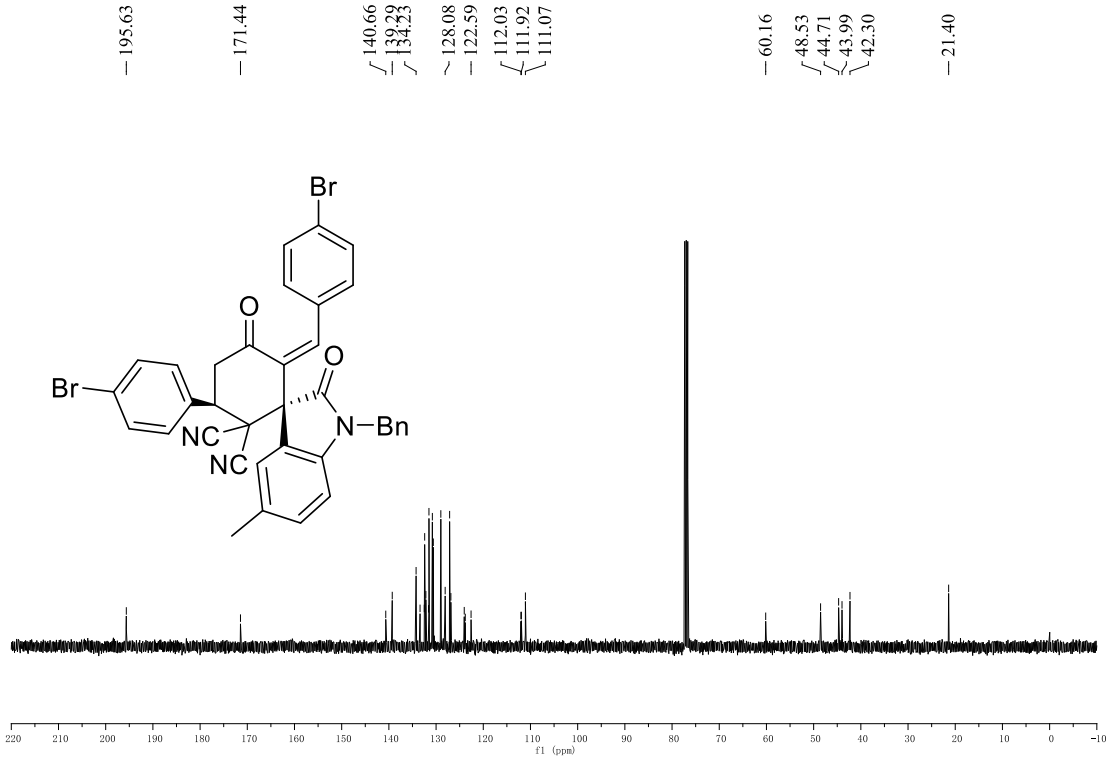


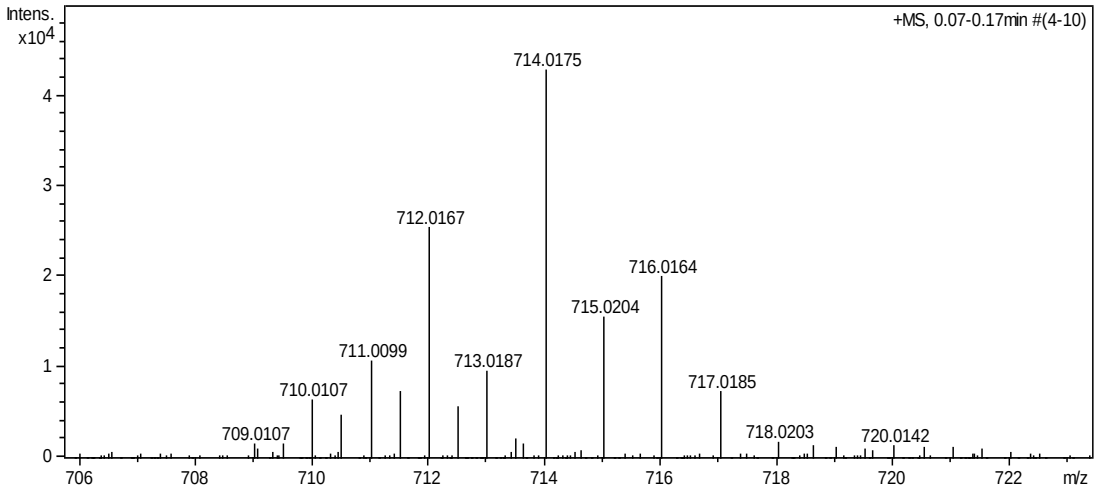

195.67
171.50
139.22
132.91
132.05
130.63
129.45
128.55
127.14
122.64
112.06
111.96
111.06
60.17
48.66
44.71
44.08
42.23
21.39
Cl
O
O
Cl
NC
NC
N–Bn
f1 (ppm)


Intens.
x10^4
+MS, 0.03-0.13min #(1-7)
624.1204
626.1186
622.1117
631.2404
613.3399
m/z

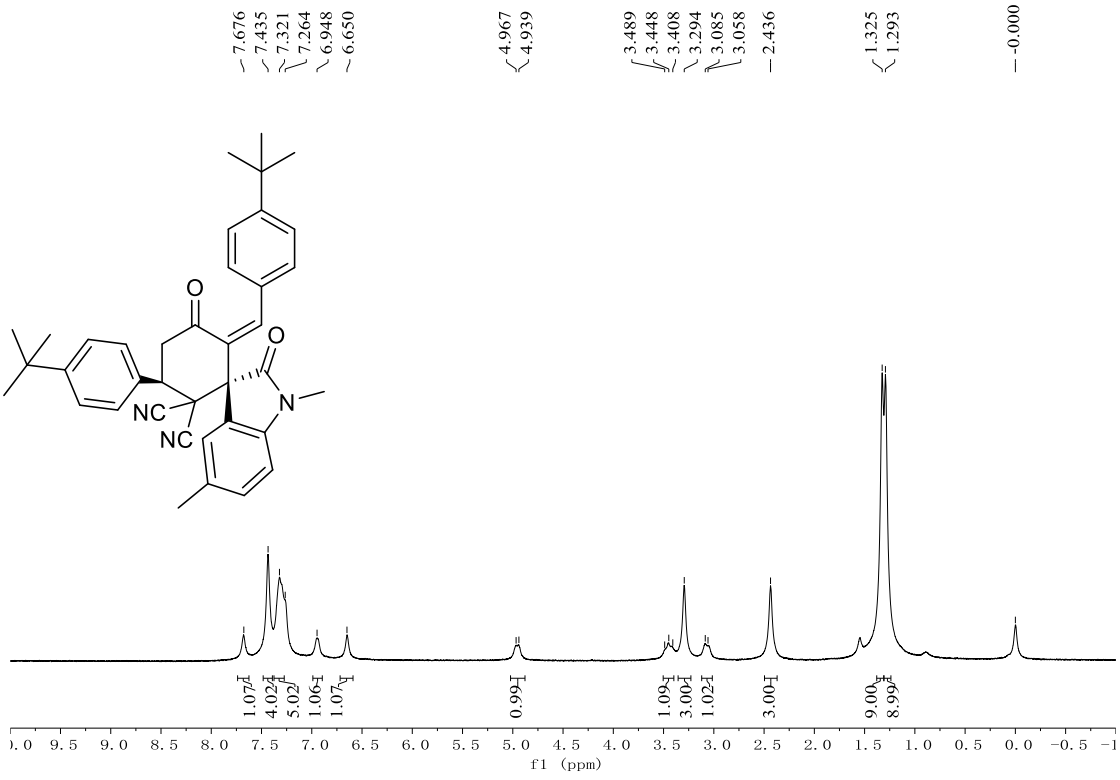
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-bromobenzylidene)-3-(4-bromophenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3e)**: white solid, 75%, m.p. 233-234 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H, ArH), 7.60 (d, *J* = 6.8 Hz, 2H, ArH), 7.46-7.41 (m, 4H, ArH), 7.36-7.30 (m, 5H, ArH), 7.23-7.19 (m, 3H, ArH), 6.79 (d, *J* = 8.4 Hz, 1H, ArH), 6.61 (s, 1H, CH), 5.10-5.02 (m, 2H, CH_2), 4.86 (d, *J* = 16.0 Hz, 1H, CH_2), 3.39 (t, *J* = 14.8 Hz, 1H, CH), 3.10-3.05 (m, 1H, CH_2), 2.41 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 171.4, 140.7, 139.3, 134.2, 133.4, 132.5, 132.4, 132.2, 131.6, 131.5, 130.8, 130.6, 129.0, 128.1, 127.1, 126.9, 124.0, 123.8, 122.6, 112.0, 111.9, 111.1, 60.2, 48.5, 44.7, 44.0, 42.3, 21.4. IR (KBr) υ: 3725, 3627, 3401, 3065, 2924, 2316, 1902, 1708, 1613, 1493, 1443, 1411, 1357, 1291, 1187, 1110, 1070, 1009, 959, 917, 821, 733 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{25}NaBr_2N_3O_2$ ([M+Na]$^{+}$): 712.0211, found: 712.0167.

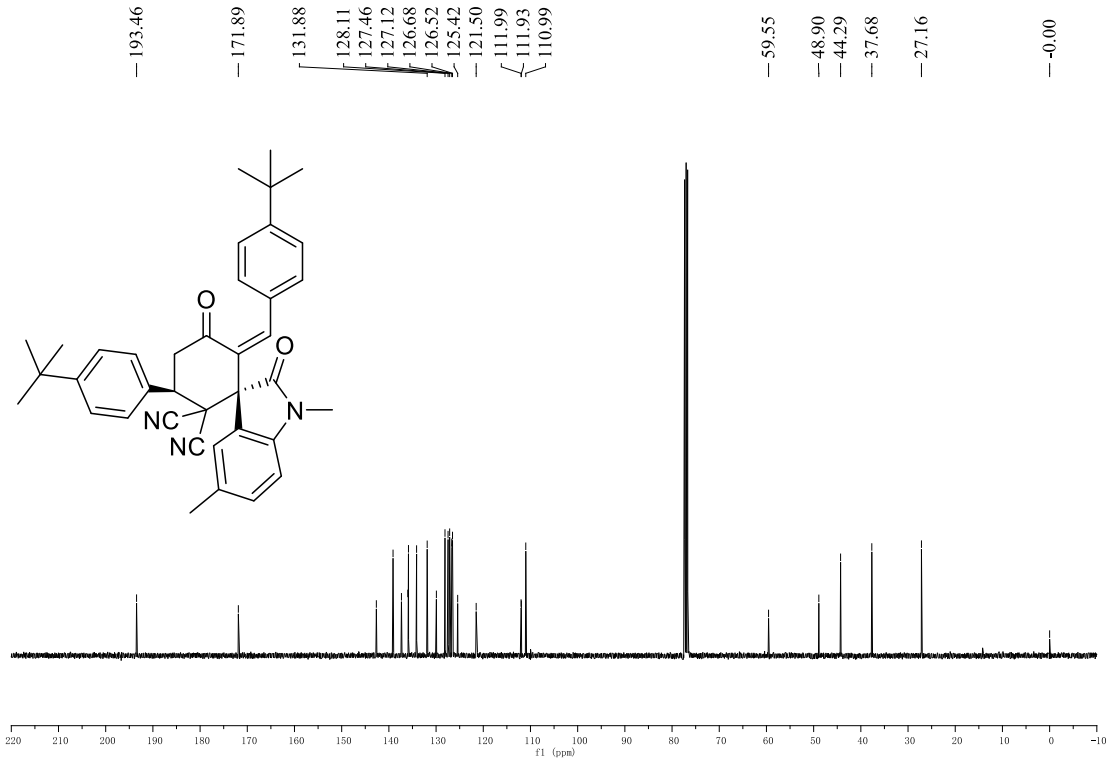



195.63
171.44
140.66
139.29
134.23
128.08
122.59
112.03
111.92
111.07
60.16
48.53
44.71
43.99
42.30
21.40
Br
O
O
Br
N–Bn
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.07-0.17min #(4-10)
714.0175
712.0167
716.0164
715.0204
711.0099
713.0187
710.0107
717.0185
709.0107
718.0203
720.0142
m/z

***rel*-(1*R*,3*R*)-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-1',5'-dimethyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3f)**: yellow solid, 42%, m.p. 212-214 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H, ArH), 7.43 (s, 4H, ArH), 7.32-7.26 (m, 5H, ArH), 6.95 (s, 1H, ArH), 6.65 (s, 1H, CH), 4.96 (d, *J* = 11.2 Hz,, 1H, CH_2), 3.45 (t, *J* = 16.0 Hz, 1H, CH), 3.29 (s, 3H, CH_3), 3.07 (d, *J* = 10.8 Hz, 1H, CH_2), 2.44 (s, 3H, CH_3), 1.32 (s, 9H, $(CH_3)_3$), 1.29 (s, 9H, $(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.5, 171.9, 142.7, 139.1, 137.3, 136.0, 135.9, 134.1, 131.9, 129.9, 128.1, 127.5, 127.1, 126.7, 126.5, 125.4, 121.5, 112.0, 111.9, 111.0, 59.6, 48.9, 44.3, 37.7, 27.2. IR (KBr) υ: 3030, 2956, 2869, 1710, 1611, 1502, 1424, 1358, 1195, 1149, 1052, 939, 817, 738 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{39}NaN_3O_2$ ($[M+Na]^+$): 592.2940, found: 592.2919.




193.46
171.89
131.88
128.11
127.46
127.12
126.68
126.52
125.42
121.50
111.99
111.93
110.99
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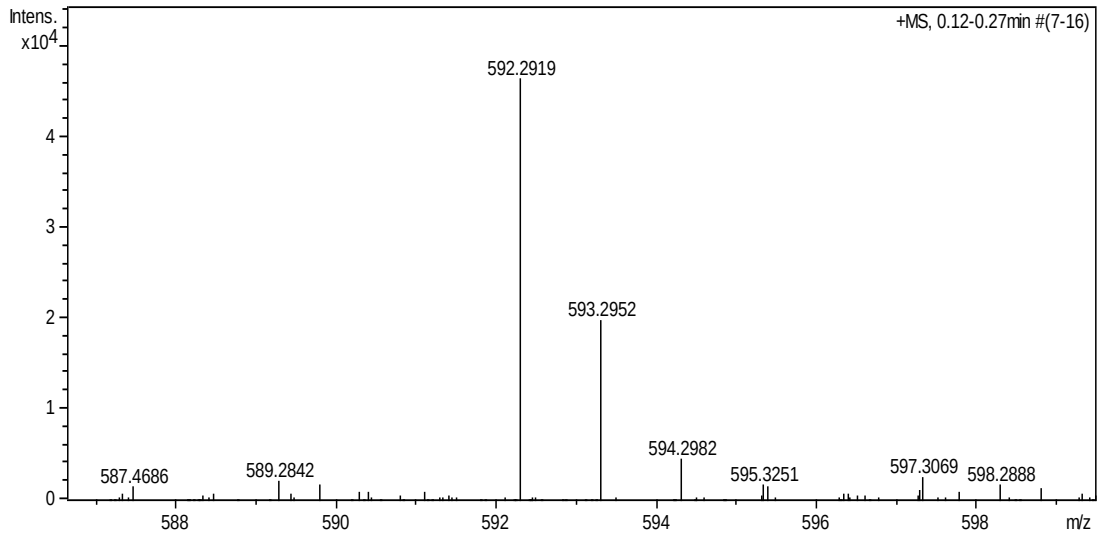
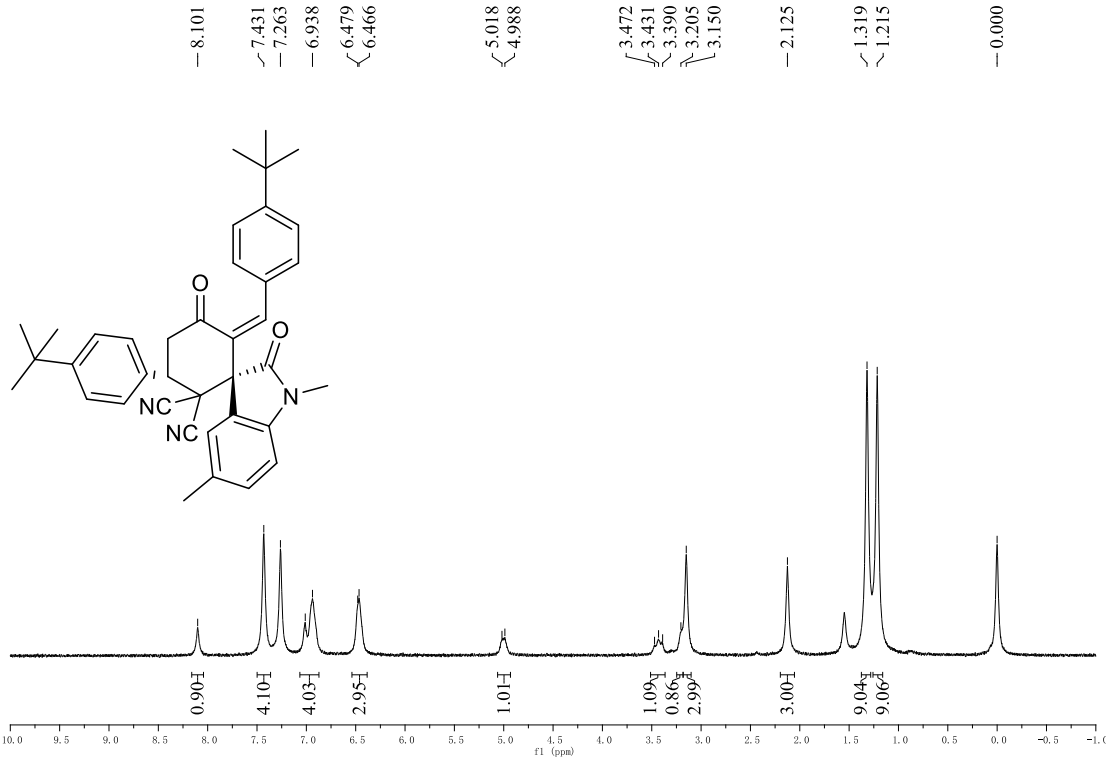
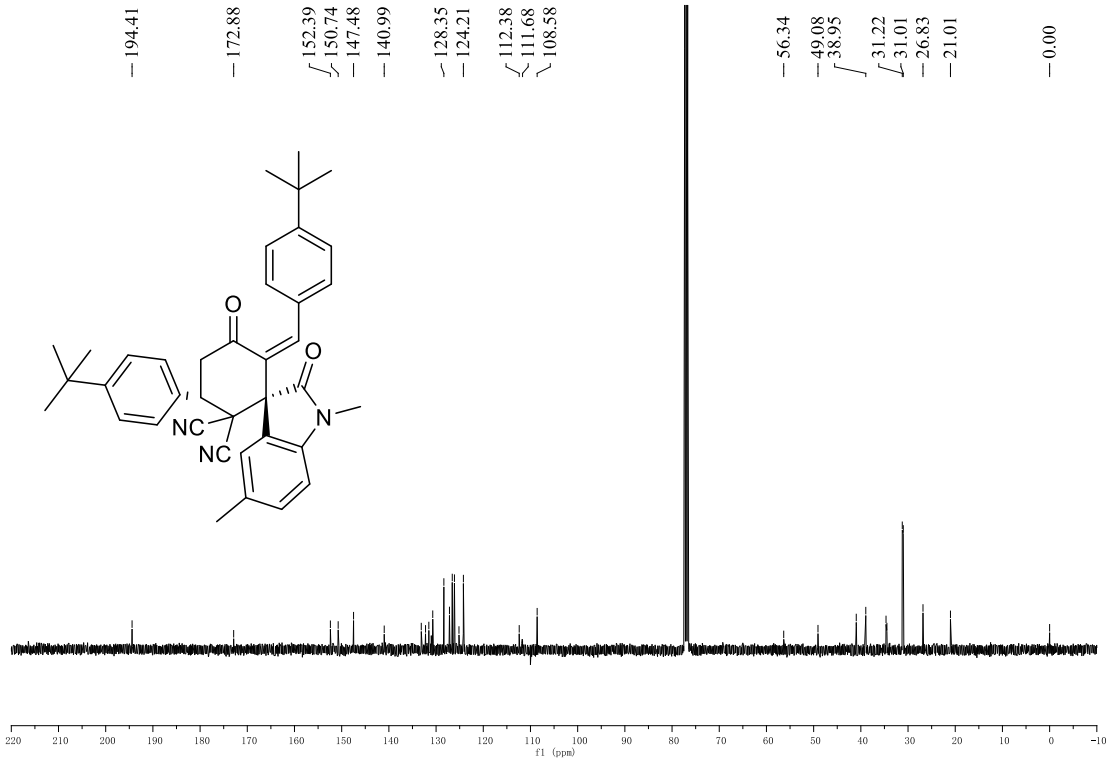
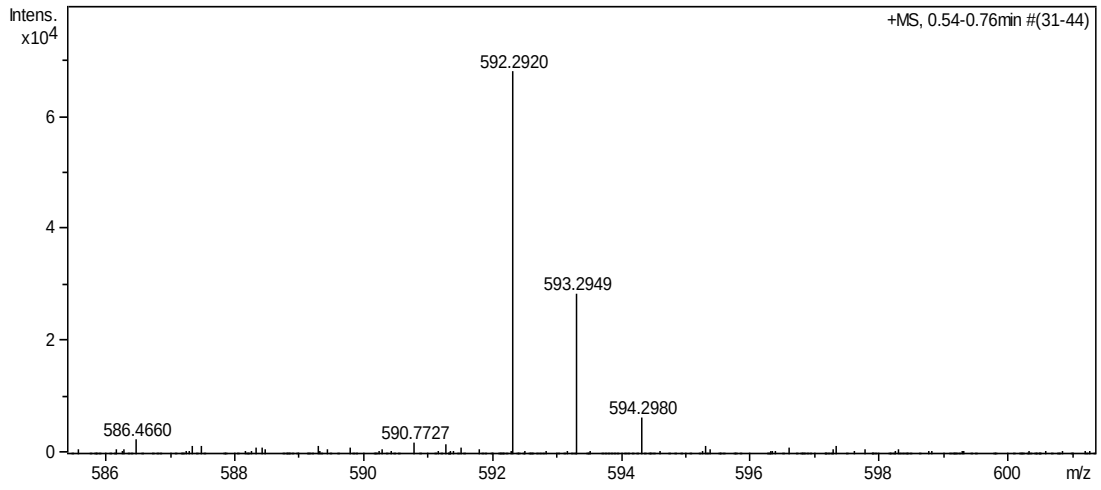
44.29
37.68
27.16
0.00
O
O
N
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.12-0.27min #(7-16)
592.2919
593.2952
594.2982
587.4686
589.2842
595.3251
597.3069
598.2888
m/z

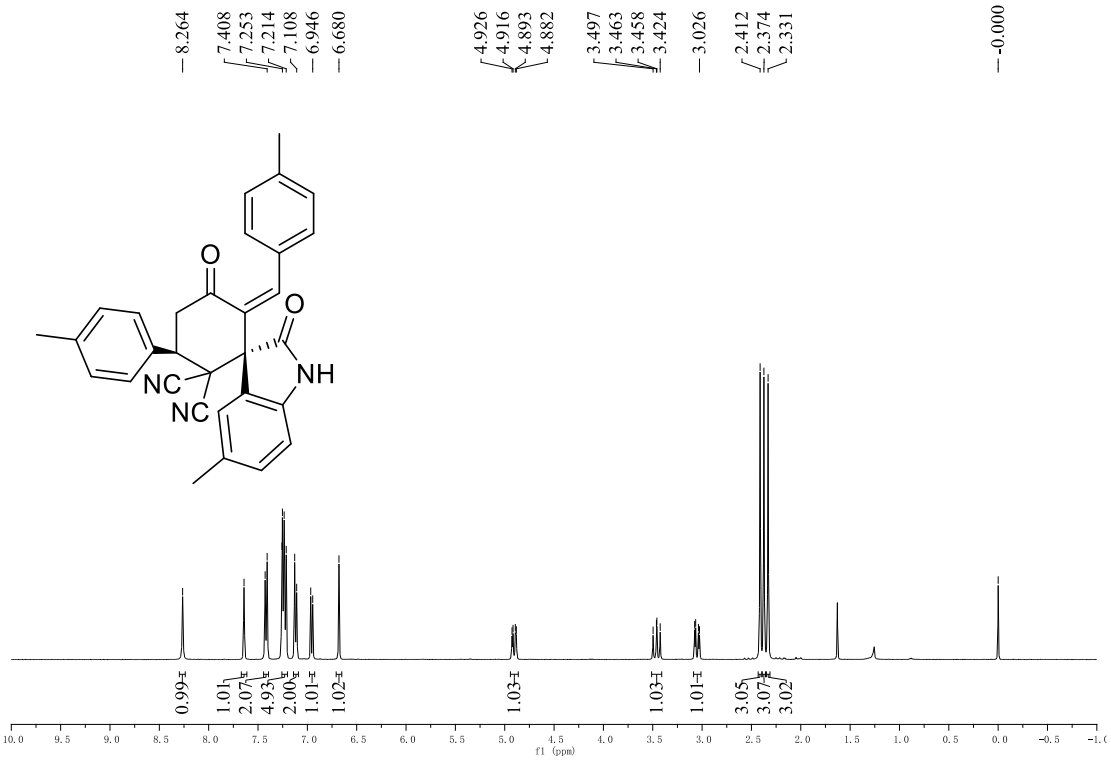
***rel*-(1*R*,3*S*)-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-1',5'-dimethyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3f')**: yellow solid, 14%, m.p. 172-174 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H, ArH), 7.43 (s, 4H, ArH), 7.01-6.94 (m, 4H, ArH), 6.48-6.47 (m, 3H, ArH), 5.02-4.99 (m, 1H, CH_2), 3.43 (m, 1H, CH), 3.21 (s, 1H, CH_2), 3.15 (s, 3H, CH_3), 2.13 (s, 3H, CH_3), 1.32 (s, 9H, $(CH_3)_3$), 1.22 (s, 9H, $(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 172.9, 152.4, 150.7, 147.5, 141.0, 133.1, 132.2, 131.5, 130.7, 128.4, 127.2, 126.6, 126.1, 125.2, 124.2, 112.4, 111.7, 108.6, 56.3, 49.1, 41.0, 39.0, 34.7, 34.5, 31.2, 31.0, 26.8, 21.0; IR (KBr) υ: 3125, 3021, 2764, 1715, 1610, 1531, 1415, 1342, 1143, 1121, 1035, 940, 815, 732 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{39}NaN_3O_2$ ([M+Na]$^{+}$): 592.2940, found: 592.2920.

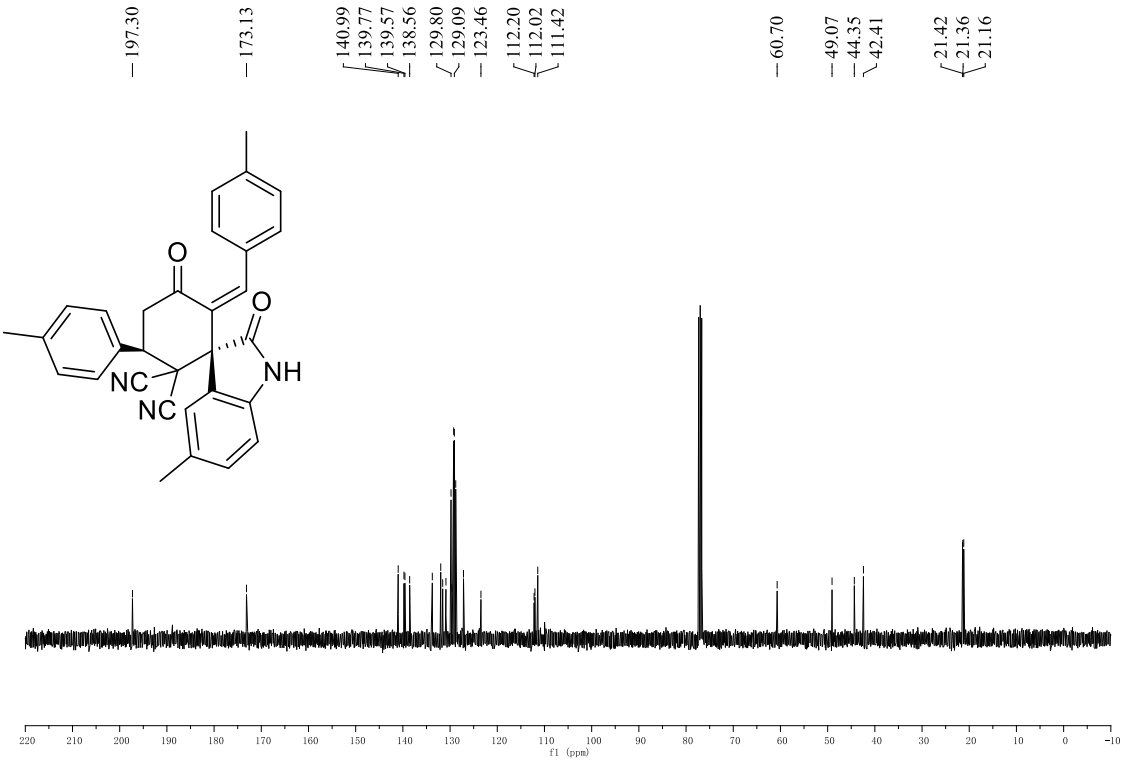


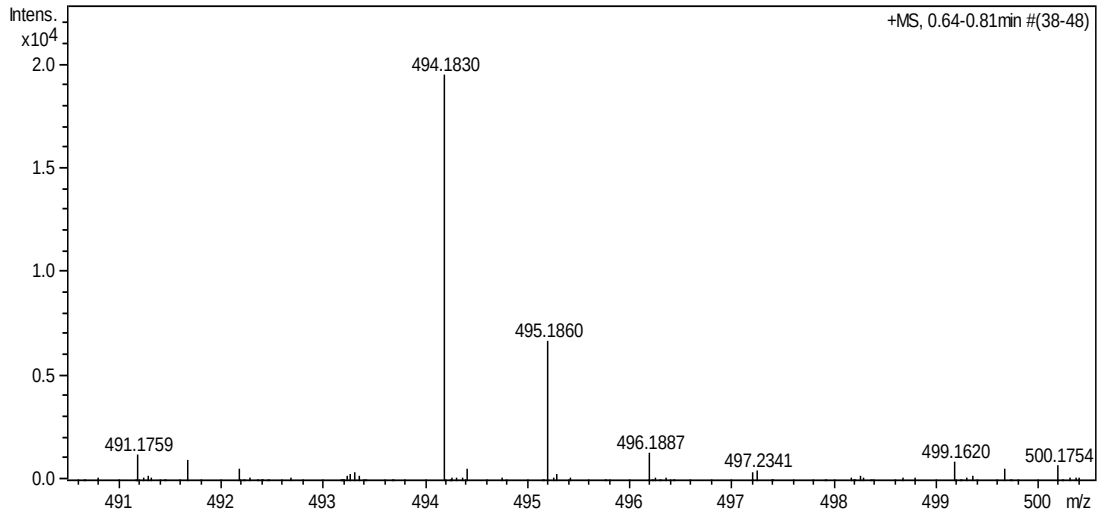

194.41
172.88
152.39
150.74
147.48
140.99
128.35
124.21
112.38
111.68
108.58
56.34
49.08
38.95
31.22
31.01
26.83
21.01
0.00
O
O
N
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.54-0.76min #(31-44)
592.2920
593.2949
594.2980
586.4660
590.7727
m/z

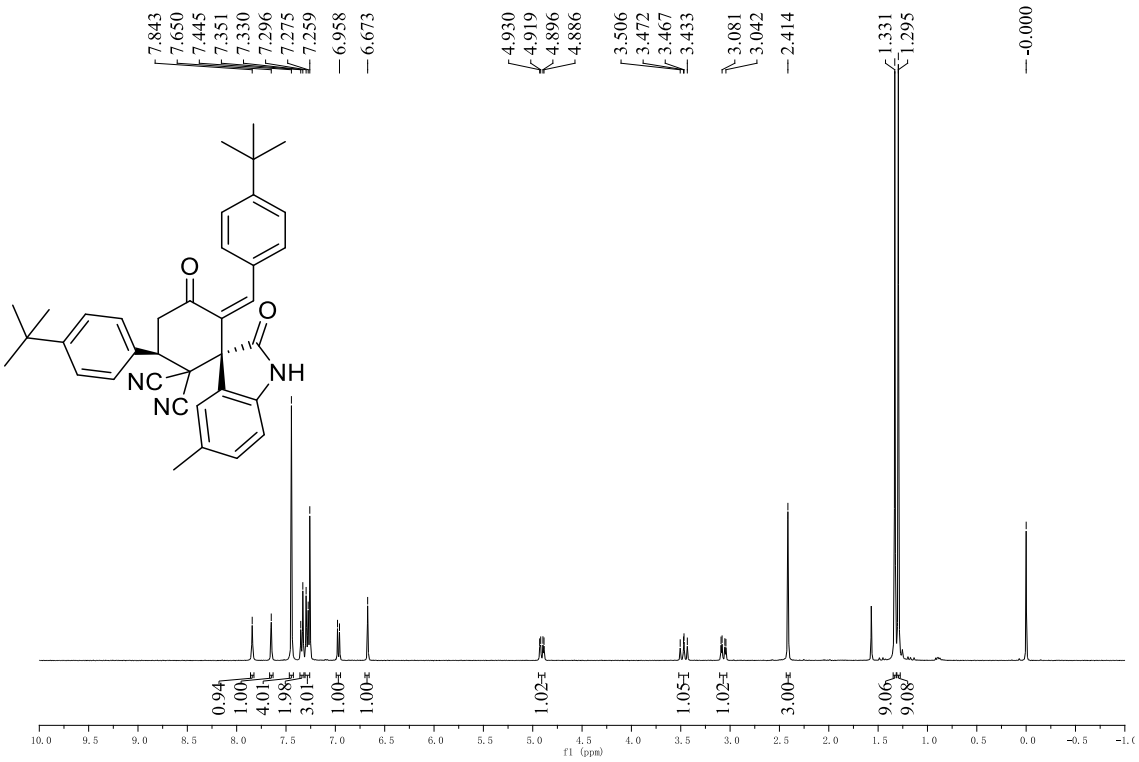
***rel*-(1*R*,3*R*)-5'-methyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3g)**: white solid, 60%, m.p. 252-254 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H, NH), 7.64 (s, 1H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.25-7.21 (m, 5H, ArH), 7.12 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 6.68 (s, 1H, CH), 4.93-4.88 (m, 1H, CH_2), 3.50-3.42 (m, 1H, CH), 3.08-3.03 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.33 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 173.1, 141.0, 139.8, 139.6, 138.6, 133.8, 132.0, 131.6, 130.9, 129.8, 129.6, 129.2, 129.1, 128.8, 127.2, 123.5, 112.2, 112.0, 111.4, 60.7, 49.1, 44.4, 42.4, 21.4, 21.4, 21.2. IR (KBr) υ: 3311, 3035, 2920, 1901, 1726, 1615, 1450, 1449, 1419, 1359, 1305, 1197, 1052, 959, 888, 818, 746 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{25}NaN_3O_2$ ([M+Na]$^{+}$): 494.1844, found: 494.1830.

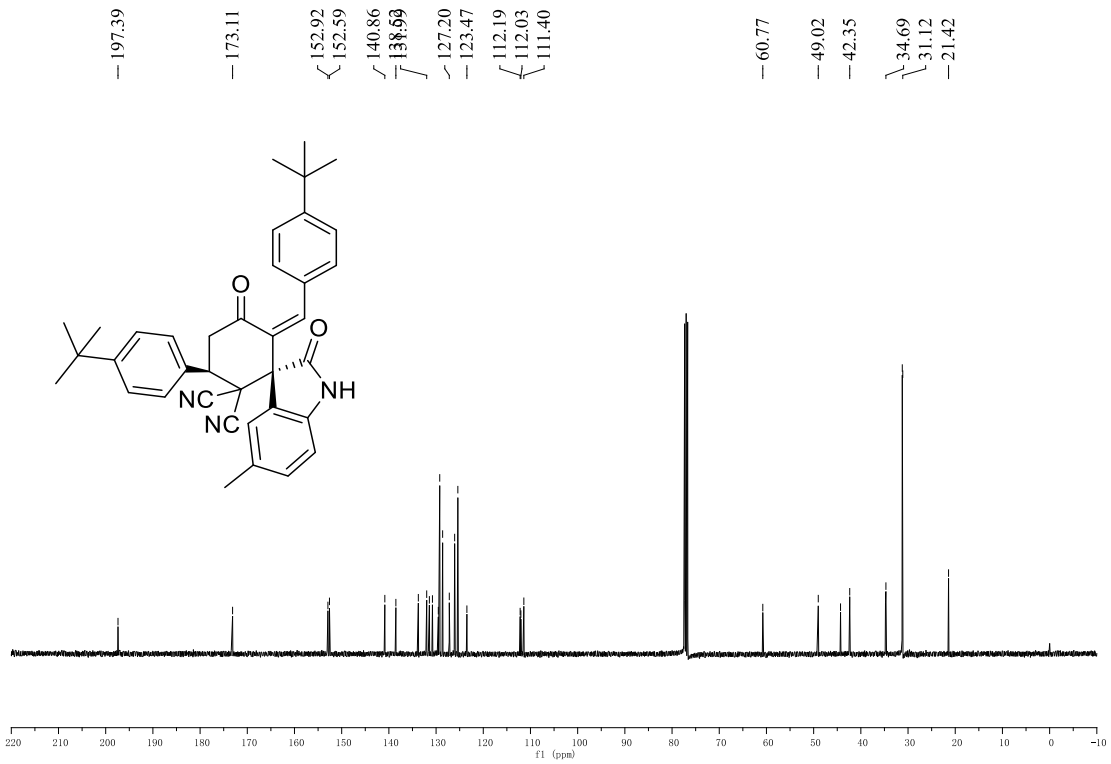


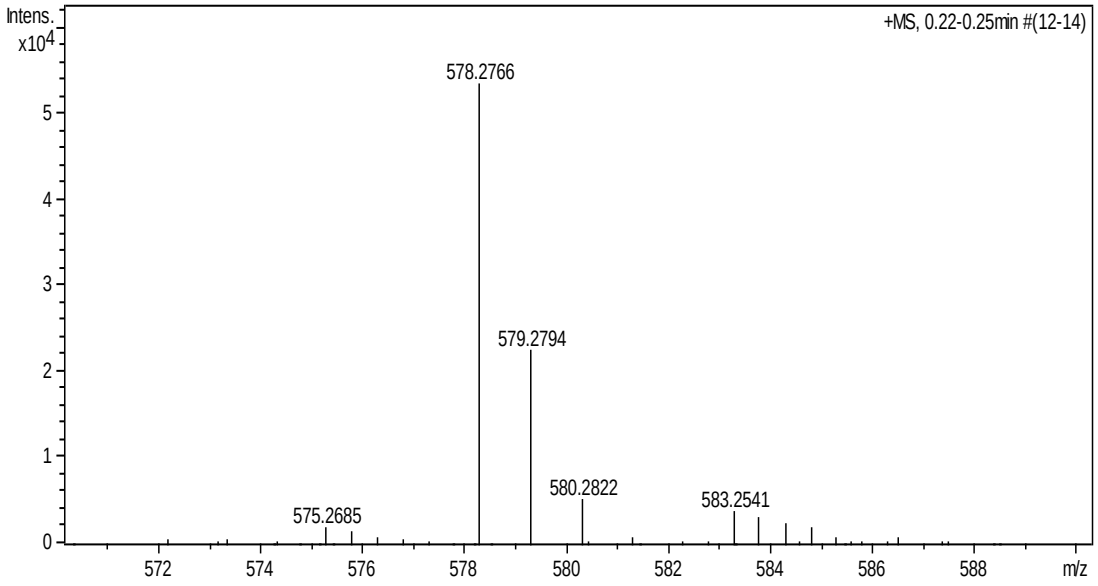

197.30
173.13
140.99
139.77
139.57
138.56
129.80
129.09
123.46
112.20
112.02
111.42
60.70
49.07
44.35
42.41
21.42
21.36
21.16
O
O
NH
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.64-0.81min #(38-48)
494.1830
495.1860
491.1759
496.1887
497.2341
499.1620
500.1754
m/z

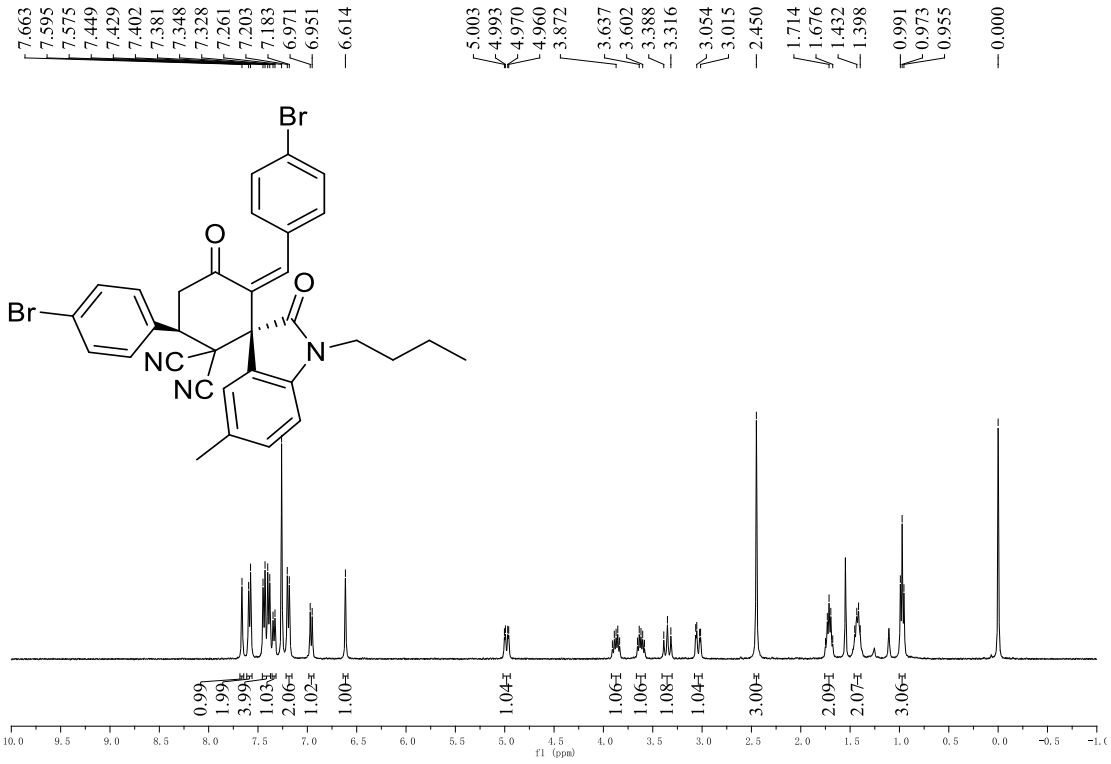
***rel*-(1*R*,3*R*)-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3h)**: pale yellow solid, 65%, m.p. 238-240 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 1H, NH), 7.65 (s, 1H, ArH), 7.45 (s, 4H, ArH), 7.34 (d, *J* = 8.4 Hz, 2H, ArH), 7.29 (d, *J* = 8.4 Hz, 3H, ArH), 6.97 (d, *J* = 8.0 Hz, 1H, ArH), 6.67 (s, 1H, CH), 4.93-4.89 (m, 1H, CH_2), 3.51-3.43 (m, 1H, CH), 3.09-3.04 (m, 1H, CH_2), 2.41 (s, 3H, CH_3), 1.33 (s, 9H, $(CH_3)_3$), 1.30 (s, 3H, $(CH_3)_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 173.1, 152.9, 152.6 140.9, 138.5, 133.8, 132.0, 131.4, 130.8, 129.5, 129.2, 128.6, 127.2, 126.1, 125.4, 123.5, 112.2, 112.0, 111.4, 60.8, 49.0, 44.3, 42.4, 34.8, 34.7, 31.2, 31.1, 21.4. IR (KBr) υ: 3684, 3288, 2964, 1728, 1614, 1500, 1358, 1307, 1266, 1207, 1112, 1058, 1021, 968, 830 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{37}NaN_3O_2$ ([M+Na]$^+$): 578.2783, found: 578.2766.

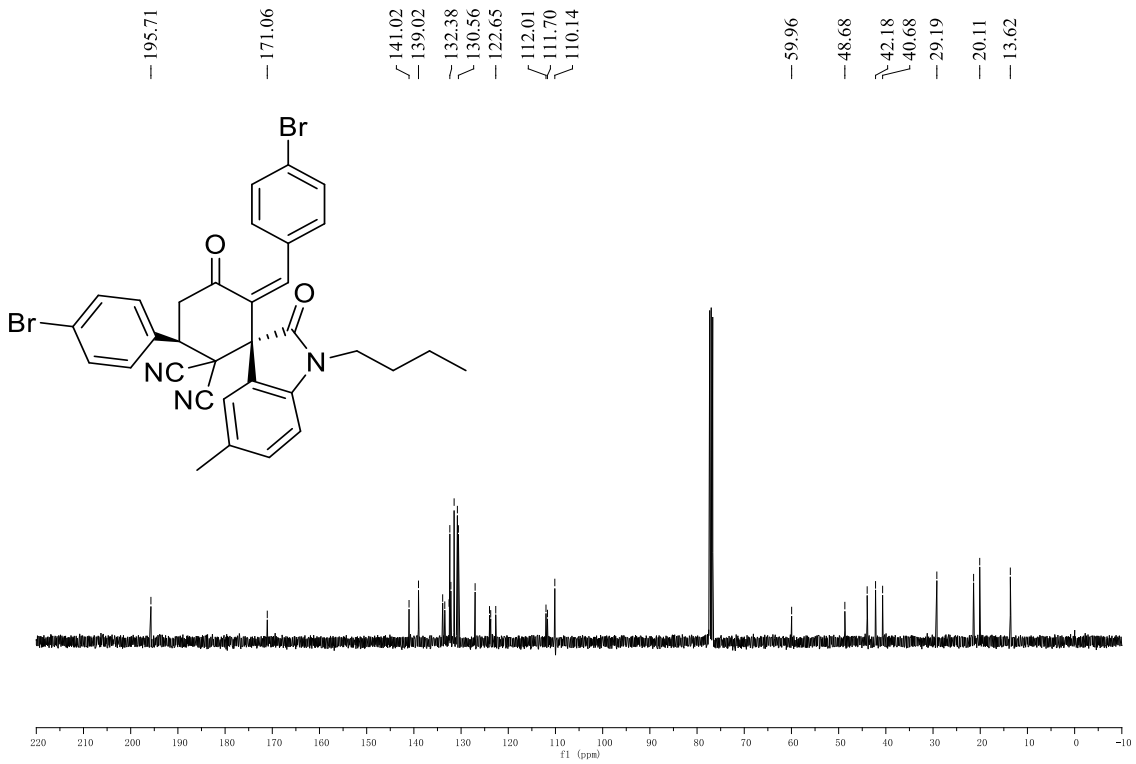


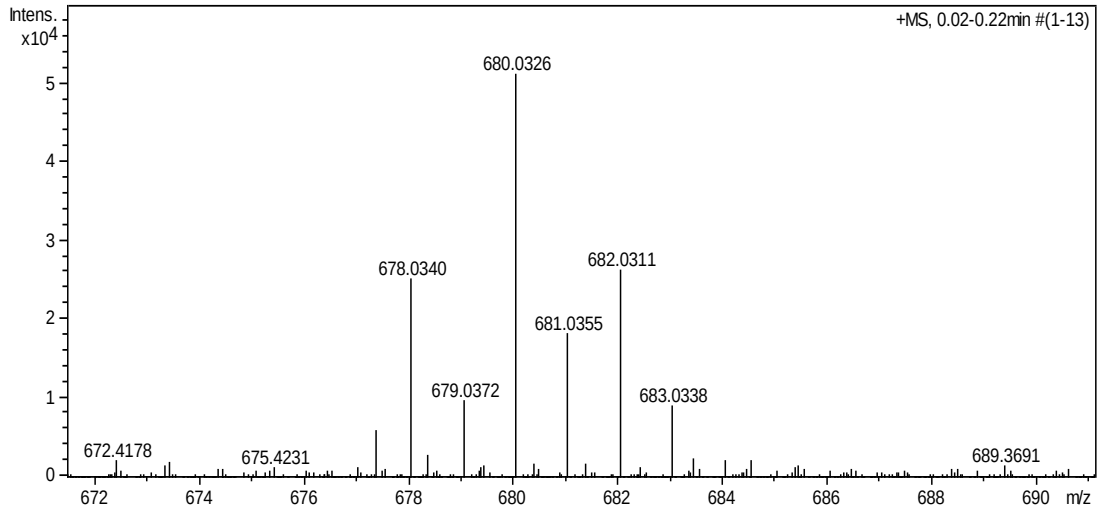

197.39
173.11
152.92
152.59
140.86
127.20
123.47
112.19
112.03
111.40
60.77
49.02
42.35
34.69
31.12
21.42
O
O
NH
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.22-0.25min #(12-14)
578.2766
579.2794
580.2822
583.2541
575.2685
m/z

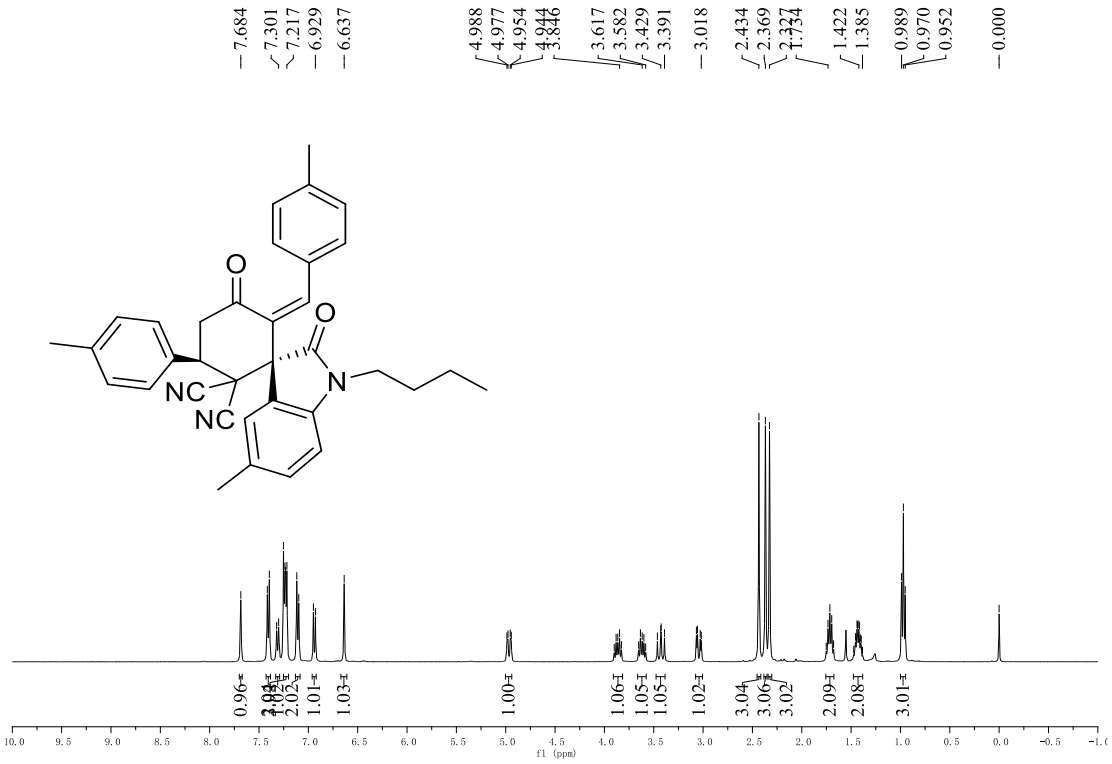
***rel*-(1*R*,3*R*)-6-((*Z*)-4-bromobenzylidene)-3-(4-bromophenyl)-1'-butyl-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3i)**: white solid, 65%, m.p. 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H, ArH), 7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.43-7.38 (m, 4H, ArH), 7.34 (d, *J* = 8.0 Hz, 1H, ArH), 7.19 (d, *J* = 8.0 Hz, 2H, ArH), 6.96 (d, *J* = 8.0 Hz, 1H, ArH), 6.61 (s, 1H, CH), 5.00-4.96 (m, 1H, CH_2), 3.91-3.84 (m, 1H, CH_2), 3.66-3.58 (m, 1H, CH_2), 3.35 (t, *J* = 14.0 Hz, 1H, CH), 3.07-3.02 (m, 1H, CH_2), 2.45 (s, 3H, CH_3), 1.75-1.68 (m, 2H, CH_2), 1.45-1.40 (m, 2H, CH_2), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 171.1, 141.0, 139.0, 133.9, 133.5, 132.6, 132.4, 132.2, 131.5, 130.8, 130.6, 127.0, 124.0, 123.7, 122.7, 112.0, 111.7, 110.1, 60.0, 48.7, 44.0, 42.2, 40.7, 29.2, 21.4, 20.1, 13.6. IR (KBr) υ: 3094, 2934, 2868, 1701, 1615, 1592, 1495, 1436, 1352, 1329, 1271, 1238, 1198, 1164, 1120, 1079, 1055, 991, 916, 857, 837, 815, 736, 713 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{33}H_{27}NaBr_2N_3O_2$ ([M+Na]$^+$): 678.0368, found: 678.0340.

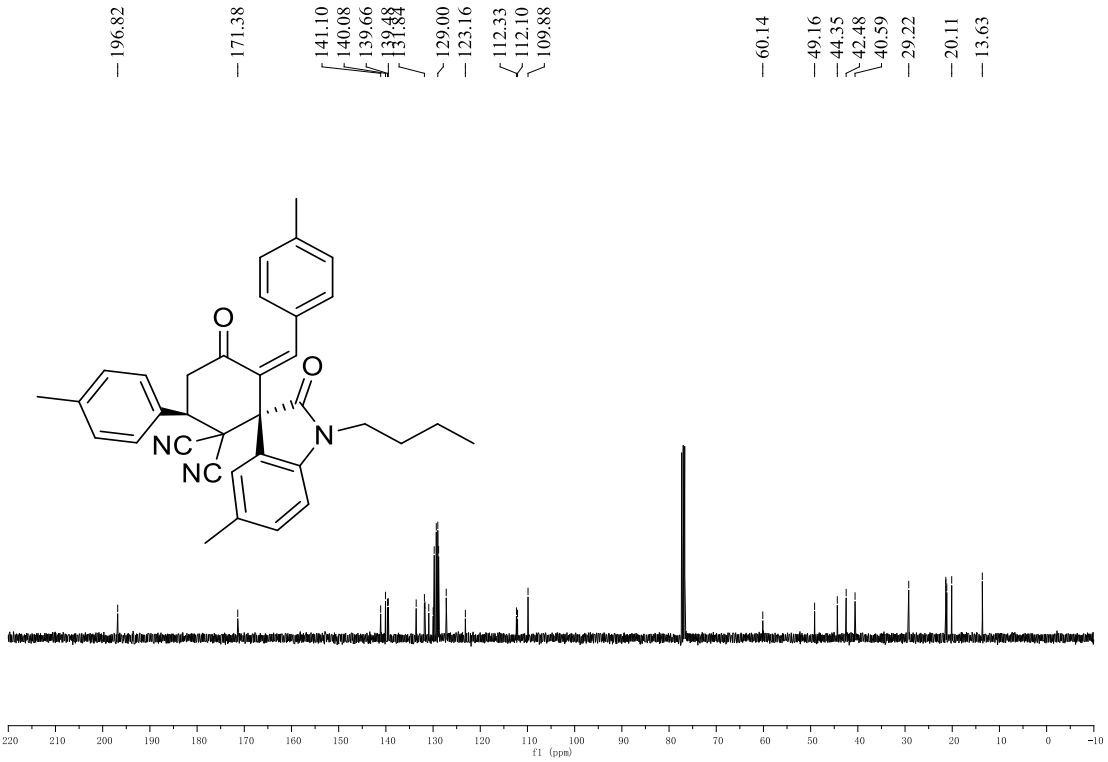


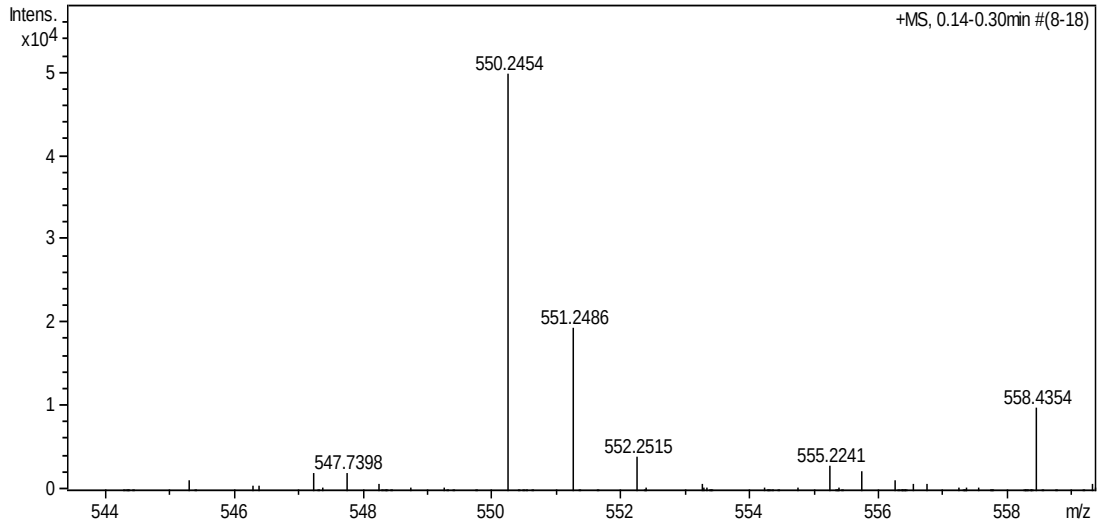

195.71
171.06
141.02
139.02
132.38
130.56
122.65
112.01
111.70
110.14
59.96
48.68
42.18
40.68
29.19
20.11
13.62
Br
O
O
Br
NC
NC
N
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.22min #(1-13)
680.0326
678.0340
682.0311
681.0355
679.0372
683.0338
672.4178
675.4231
689.3691
m/z

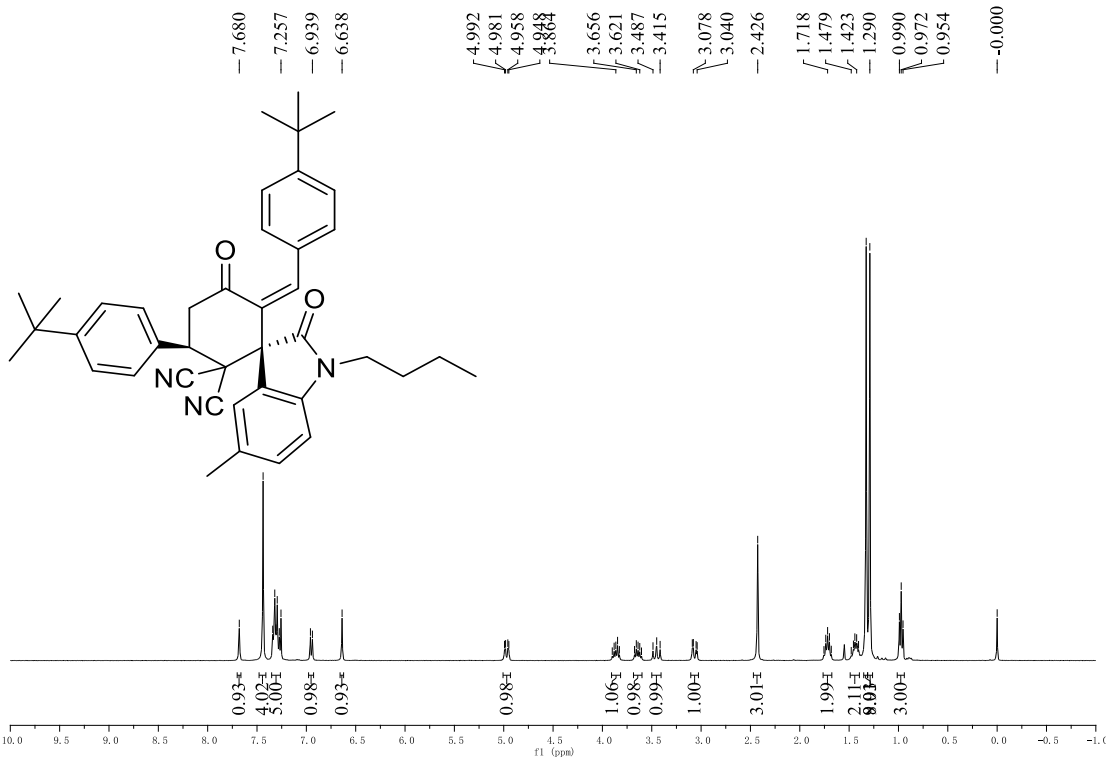
***rel*-(1*R*,3*R*)-1'-butyl-5'-methyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3j)**: white solid, 68%, m.p. 214-216 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H, ArH), 7.41 (d, *J* = 8.4 Hz, 2H, ArH), 7.31 (d, *J* = 8.0 Hz, 1H, ArH), 7.24-7.22 (m, 4H, ArH), 7.11 (d, *J* = 8.0 Hz, 2H, ArH), 6.94 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (s, 1H, CH), 4.99-4.94 (m, 1H, CH_2), 3.90-3.83 (m, 1H, CH_2), 3.65-3.58 (m, 1H, CH_2), 3.46-3.39 (m, 1H, CH), 3.07-3.02 (m, 1H, CH_2), 2.43 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 1.75-1.68 (m, 2H, CH_2), 1.46-1.39 (m, 2H, CH_2), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 171.4, 141.1, 140.1, 139.7, 139.5, 133.6, 131.8, 131.7, 130.9, 130.0, 129.8, 129.3, 129.0, 128.8, 127.2, 123.2, 112.3, 112.1, 109.9, 60.1, 49.2, 44.4, 42.5, 40.6, 29.2, 21.4, 21.3, 21.2, 20.1, 13.6. IR (KBr) υ: 3030, 2956, 2869, 1710, 1611, 1502, 1424, 1358, 1195, 1149, 1052, 939, 817, 738 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{33}NaN_3O_2$ ([M+Na]$^+$): 550.2470, found: 550.2454.

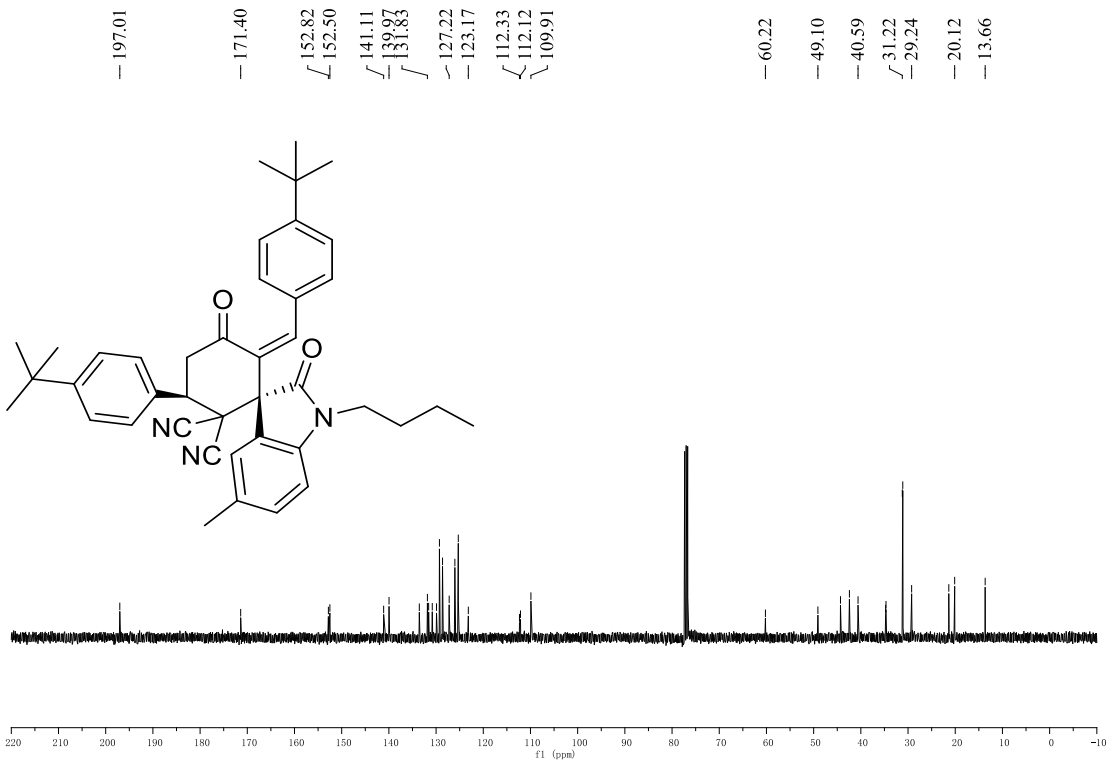


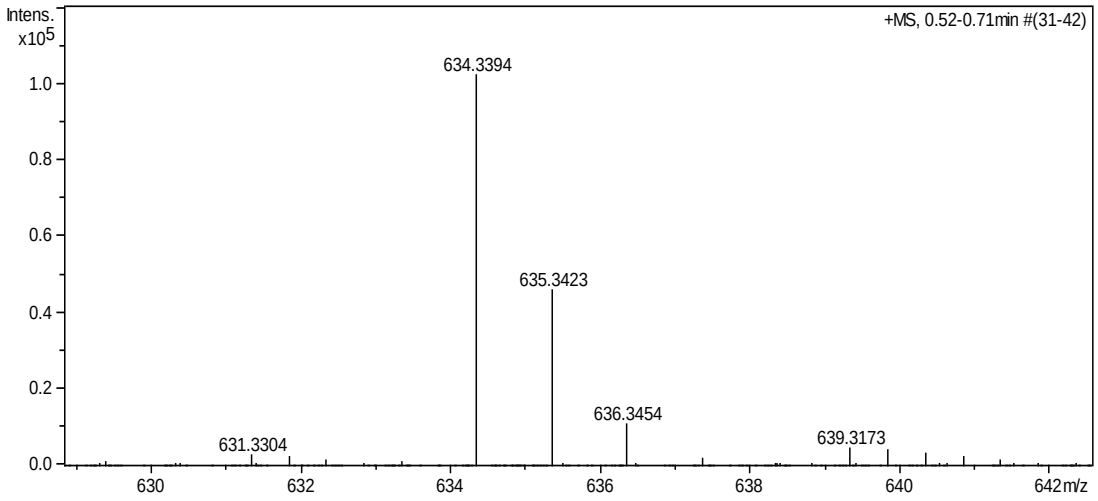

196.82
171.38
141.10
140.08
139.66
139.48
131.84
129.00
123.16
112.33
112.10
109.88
60.14
49.16
44.35
42.48
40.59
29.22
20.11
13.63
O
O
N
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.14-0.30min #(8-18)
550.2454
551.2486
552.2515
558.4354
547.7398
555.2241
m/z

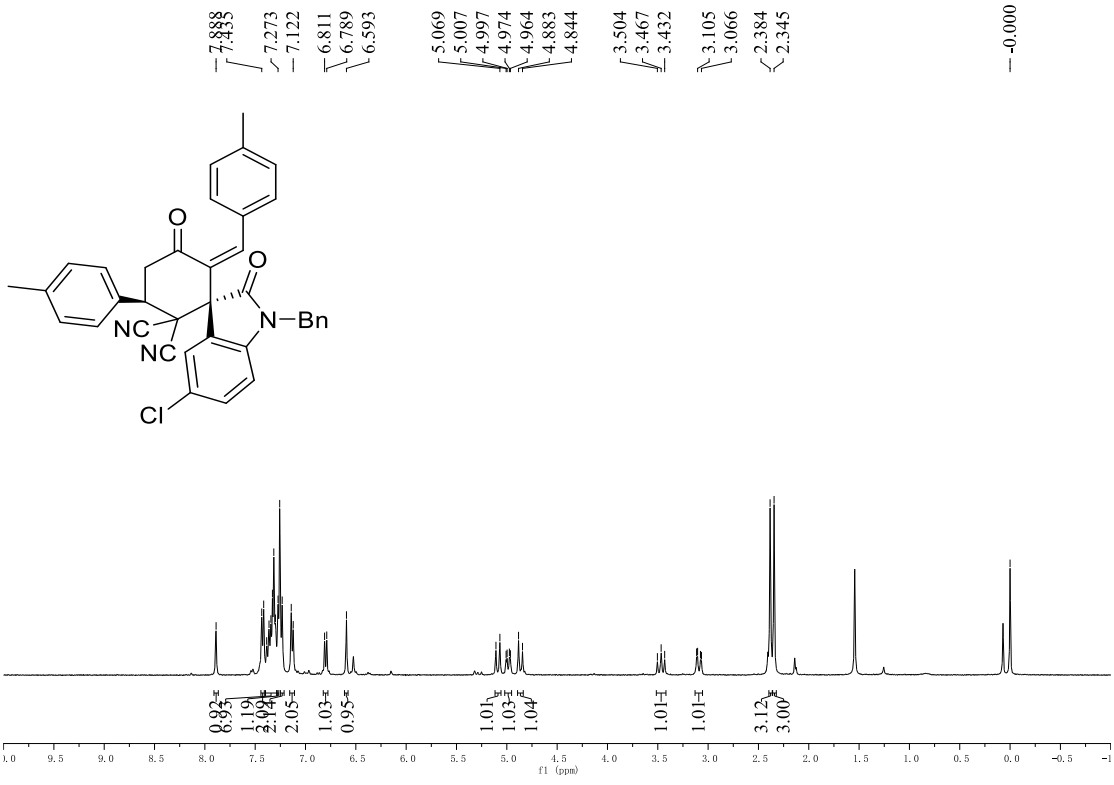
***rel*-(1*R*,3*R*)-1'-butyl-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-methyl-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3k)**: white solid, 70%, m.p. 143-145 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (s, 1H, ArH), 7.44 (s, 4H, ArH), 7.34-7.27 (m, 5H, ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.64 (s, 1H, CH), 4.99-4.95 (m, 1H, CH_2), 3.90-3.83 (m, 1H, CH_2), 3.67-3.60 (m, 1H, CH_2), 3.49-3.42 (m, 1H, CH), 3.09-3.04 (m, 1H, CH_2), 2.43 (s, 3H, CH_3), 1.76-1.68 (m, 2H, CH_2), 1.48-1.40 (m, 2H, CH_2), 1.33 (s, 9H, $(CH_3)_3$), 1.29 (s, 9H, $(CH_3)_3$), 0.97 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 171.4, 152.8, 152.5, 141.1, 140.0, 133.6, 131.8, 131.6, 130.8, 130.0, 129.3, 128.6, 127.2, 126.0, 125.3, 123.2, 112.3, 112.1, 109.9, 60.2, 49.1, 44.3, 42.4, 40.6, 34.8, 34.7, 31.2, 31.1, 29.2, 21.4, 20.1, 13.7. IR (KBr) υ: 2963, 2872, 1711, 1608, 1500, 1462, 1423, 1360, 1264, 1197, 1151, 1114, 1058, 932, 831 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{45}NaN_3O_2$ ([M+Na]$^{+}$): 634.3409, found: 634.3394.

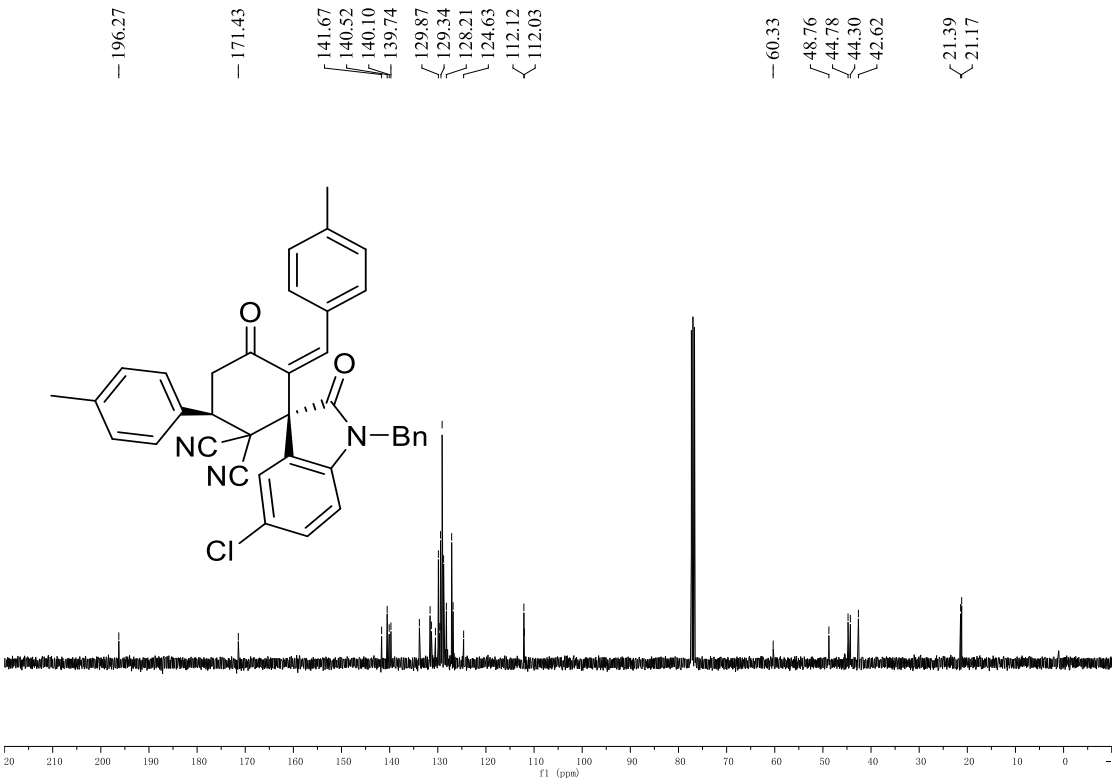


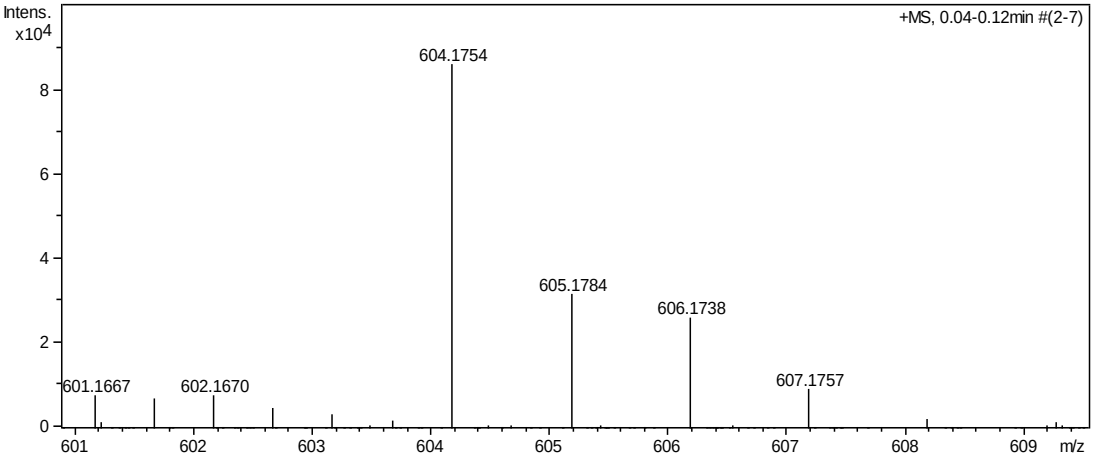

197.01
171.40
152.82
152.50
141.11
139.97
131.83
127.22
123.17
112.33
112.12
109.91
60.22
49.10
40.59
31.22
29.24
20.12
13.66
O
O
N
NC
NC
f1 (ppm)


Intens.
x10^5
+MS, 0.52-0.71min #(31-42)
634.3394
635.3423
636.3454
631.3304
639.3173
m/z

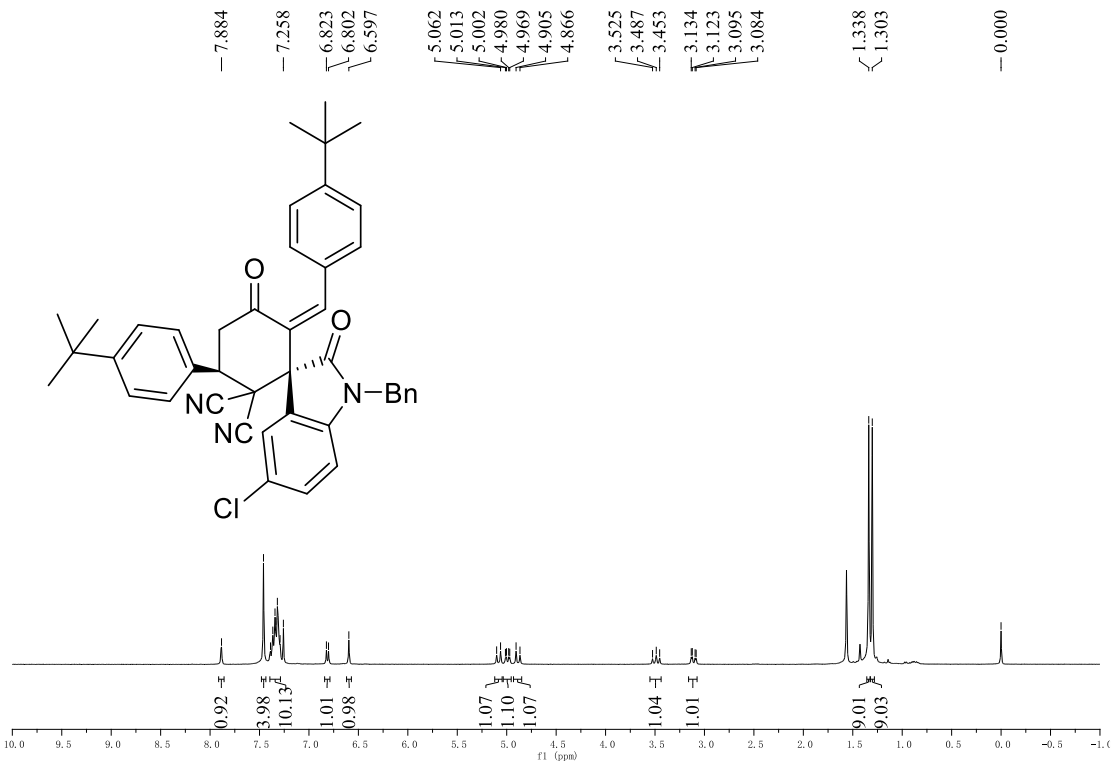
***rel*-(1*R*,3*R*)-1'-benzyl-5'-chloro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3l)**: white solid, 65%, m.p. 235-237 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H, ArH), 7.42 (d, *J* = 8.0 Hz, 2H, ArH), 7.39-7.30 (m, 7H, ArH), 7.27 (s, 1H, ArH), 7.23 (s, 2H, ArH), 7.13 (d, *J* = 8.0 Hz, 2H, ArH), 6.80 (d, *J* = 8.8 Hz, 1H, ArH), 6.60 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH_2), 5.01-4.96 (m, 1H, CH_2), 4.86 (d, *J* = 15.6 Hz, 1H, CH_2), 3.47 (t, *J* = 14.0 Hz, 1H, CH), 3.12-3.07 (m, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.35 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 171.4, 141.7, 140.5, 140.1, 139.7, 133.8, 131.6, 131.3, 130.5, 129.9, 129.7, 129.4, 129.3, 129.1, 128.8, 128.2, 127.1, 126.83, 124.6, 112.1, 112.0, 60.3, 48.8, 44.8, 44.3, 42.6, 21.4, 21.2. IR (KBr) υ: 3728, 3407, 3033, 2919, 2318, 1899, 1776, 1717, 1611, 1485, 1425, 1349, 1259, 1188, 1083, 1020, 957, 883, 816, 724 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{28}NaClN_3O_2$ ([M+Na]$^+$): 604.1768, found: 604.1754.

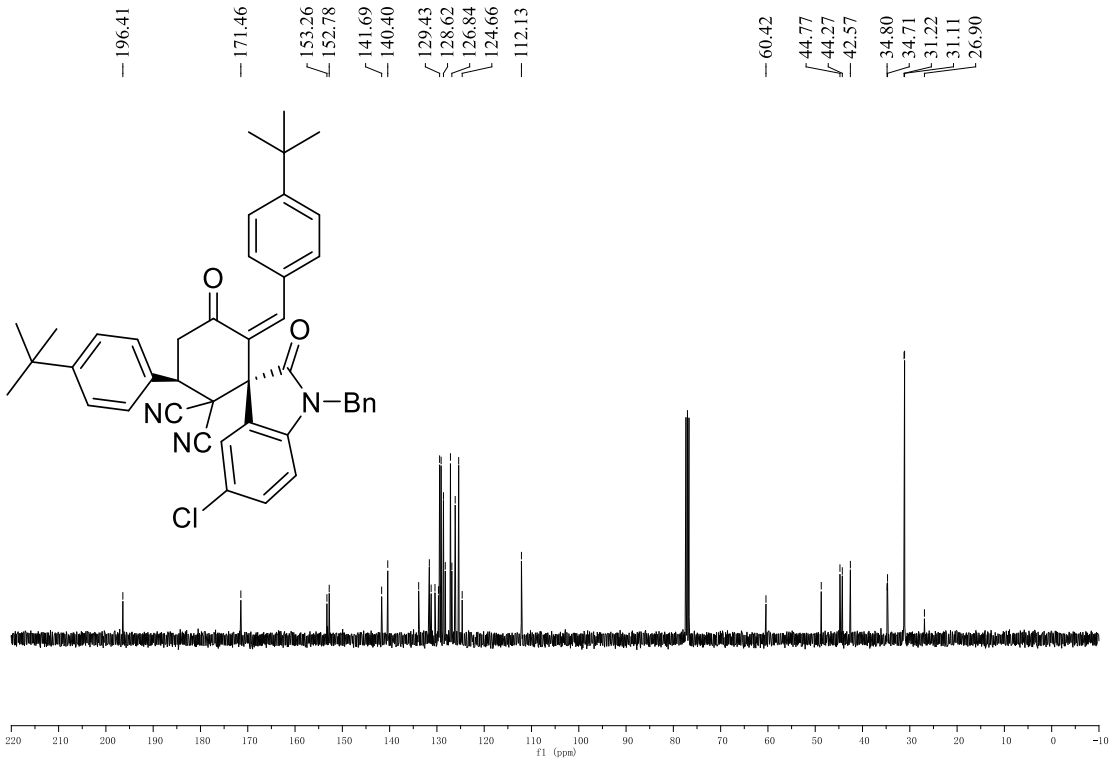


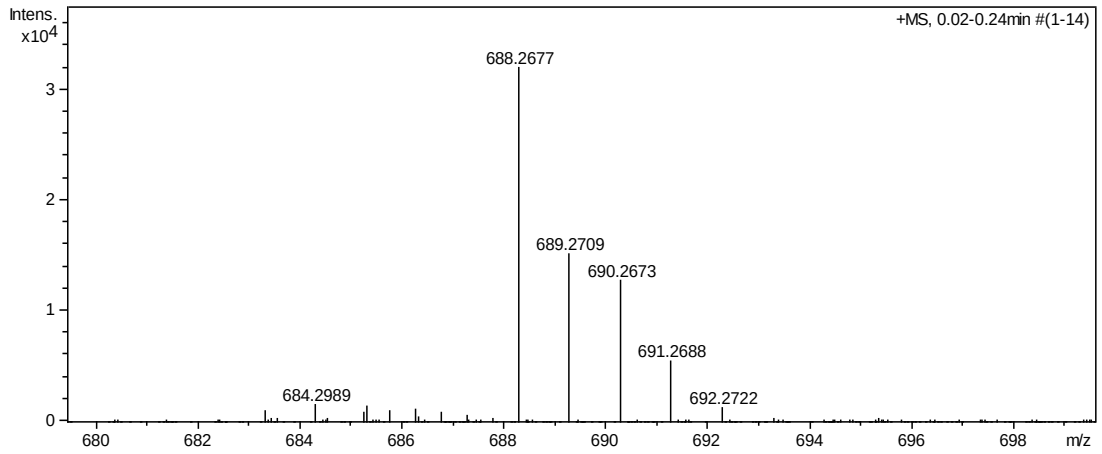

196.27
171.43
141.67
140.52
140.10
139.74
129.87
129.34
128.21
124.63
112.12
112.03
60.33
48.76
44.78
44.30
42.62
21.39
21.17
O
O
N—Bn
NC
NC
Cl
f1 (ppm)


Intens.
x10^4
+MS, 0.04-0.12min #(2-7)
604.1754
605.1784
606.1738
607.1757
601.1667
602.1670
m/z

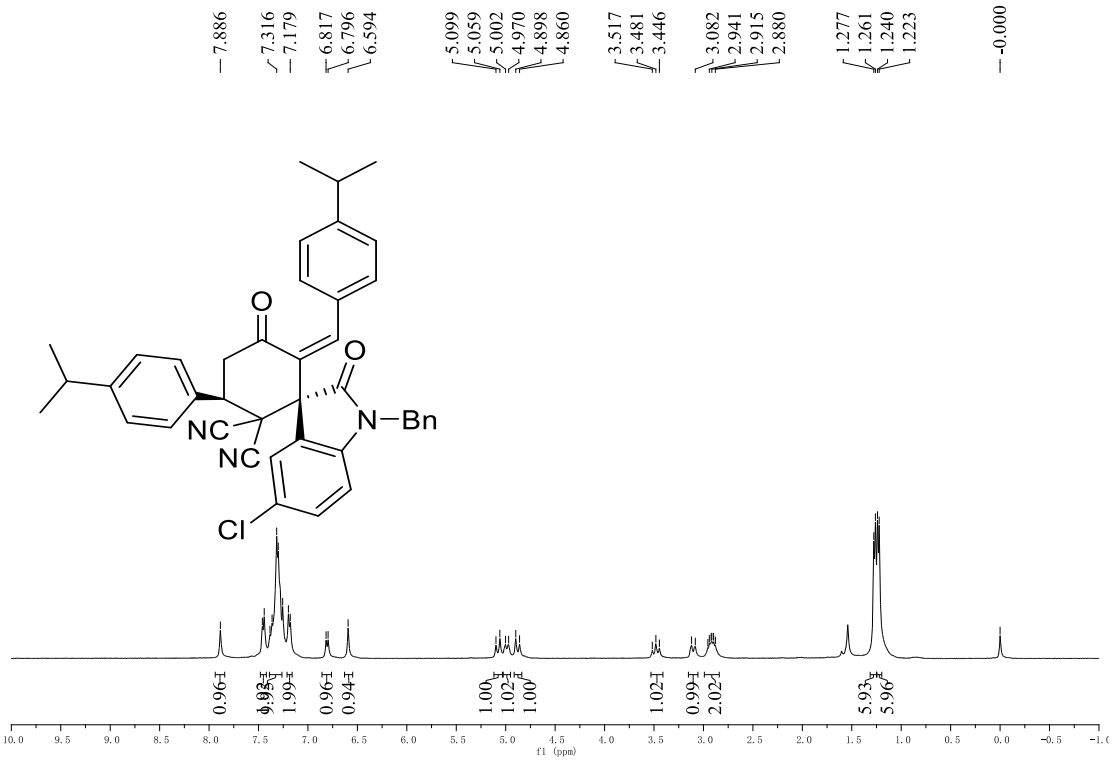
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-(*tert*-butyl)benzylidene)-3-(4-(*tert*-butyl)phenyl)-5'-chloro-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3m)**: white solid, 72%, m.p. 184-186 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H, ArH), 7.46 (s, 4H, ArH), 7.39-7.29 (m, 10H, ArH), 6.81 (d, *J* = 8.4 Hz, 1H, ArH), 6.60 (s, 1H, CH), 5.08 (d, *J* = 16.0 Hz, 1H, CH_2), 5.01-4.97 (m, 1H, CH_2), 4.99 (d, *J* = 15.6 Hz, 1H, CH_2), 3.49 (t, *J* = 13.6 Hz, 1H, CH), 3.13-3.08 (m, 1H, CH_2), 1.34 (s, 9H, $(CH_3)_3$), 1.30 (s, 9H, $(CH_3)_3$).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 171.5, 153.3, 152.8, 141.7, 140.4, 133.9, 131.6, 131.2, 130.4, 129.7, 129.4, 129.3, 129.1, 128.6, 128.2, 127.1, 126.8, 126.1, 125.4, 124.7, 112.1, 60.4, 48.7, 44.8, 44.3, 42.6, 34.8, 34.7, 31.2, 31.1, 26.9. IR (KBr) υ: 3685, 3062, 2962, 1718, 1607, 1486, 1424, 1354, 1265, 1189, 1114, 1019, 958, 832 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{43}H_{40}NaClN_3O_2$ ([M+Na]$^{+}$): 688.2707, found: 688.2677.

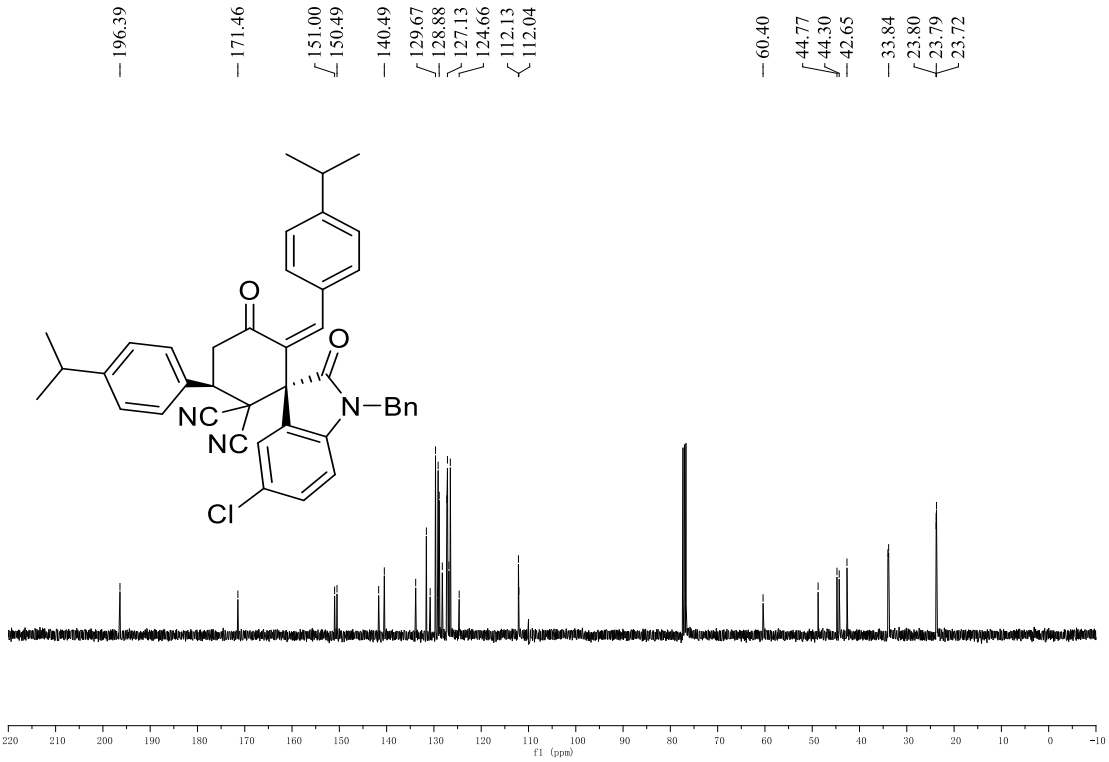


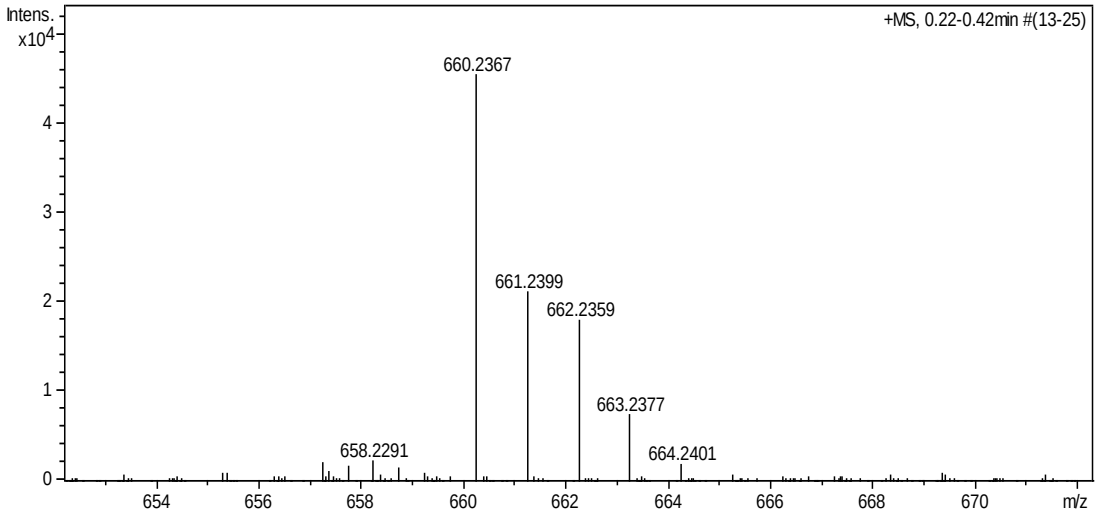

196.41
171.46
153.26
152.78
141.69
140.40
129.43
128.62
126.84
124.66
112.13
60.42
44.77
44.27
42.57
34.80
34.71
31.22
31.11
26.90
O
O
N–Bn
NC
NC
Cl
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.02-0.24min #(1-14)
688.2677
689.2709
690.2673
691.2688
684.2989
692.2722
0
1
2
3
680 682 684 686 688 690 692 694 696 698 m/z

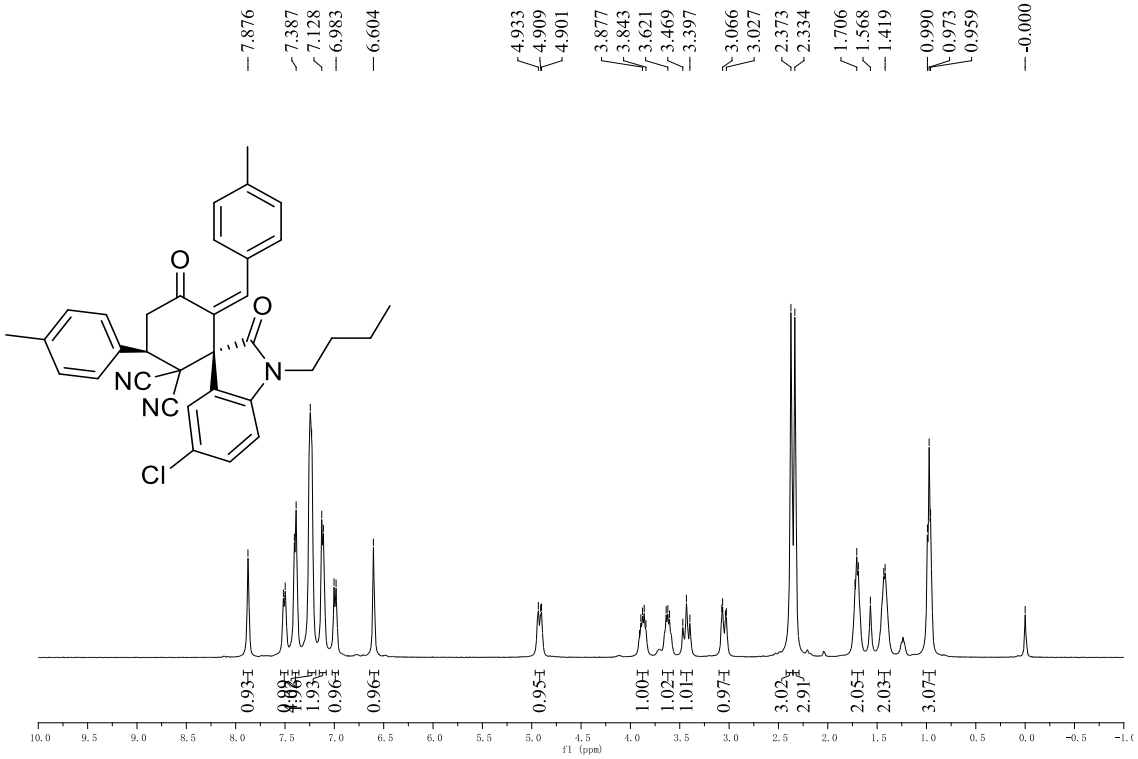
***rel*-(1*R*,3*R*)-1'-benzyl-5'-chloro-6-((*Z*)-4-isopropylbenzylidene)-3-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3n)**: white solid, 70%, m.p. 242-244 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H, ArH), 7.45 (d, *J* = 7.6 Hz, 2H, ArH), 7.38-7.30 (m, 10H, ArH), 7.19 (d, *J* = 7.6 Hz, 2H, ArH), 6.81 (d, *J* = 8.4 Hz, 1H, ArH), 6.59 (s, 1H, CH), 5.08 (d, *J* = 16.0 Hz, 1H, CH_2), 4.99 (d, *J* = 12.8 Hz, 1H, CH_2), 4.88 (d, *J* = 15.2 Hz, 1H, CH_2), 3.48 (t, *J* = 14.4 Hz, 1H, CH), 3.10 (d, *J* = 15.2 Hz, 1H, CH_2), 2.96-2.88 (m, 2H, CH), 1.27 (d, *J* = 6.4 Hz, 6H, $(CH_3)_2$), 1.23 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2$).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 171.5, 151.0, 150.5, 141.7, 140.5, 133.9, 131.6, 130.8, 129.7, 129.2, 129.1, 128.9, 128.2, 127.3, 127.1, 126.8, 126.5, 124.7, 112.1, 112.0, 60.4, 48.8, 44.8, 44.3, 42.7, 34.0, 33.8, 23.8, 23.8, 23.7. IR (KBr) υ: 3035, 2965, 1718, 1610, 1483, 1423, 1351, 1188, 1056, 1016, 958, 921, 887, 831, 721 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{36}NaClN_3O_2$ ([M+Na]$^{+}$): 660.2394, found: 660.2367.

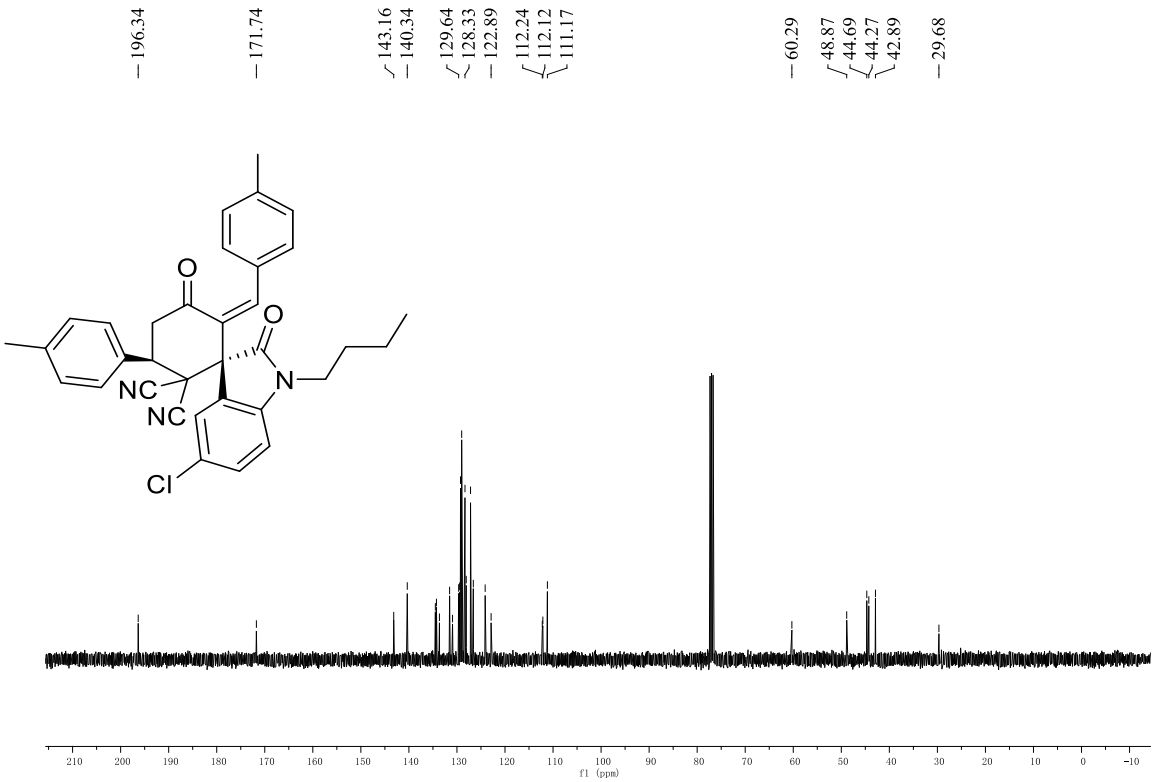


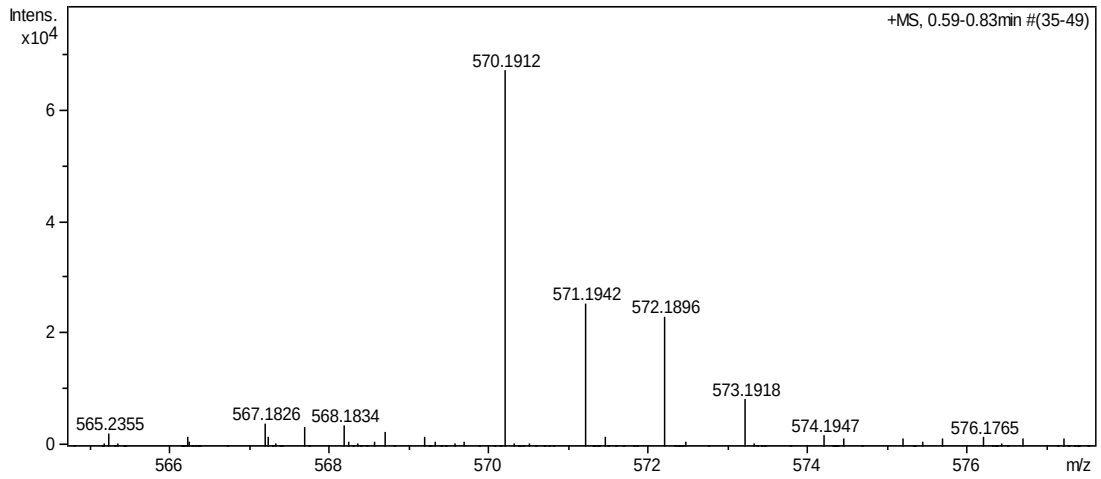

196.39
171.46
151.00
150.49
140.49
129.67
128.88
127.13
124.66
112.13
112.04
60.40
44.77
44.30
42.65
33.84
23.80
23.79
23.72
O
O
N–Bn
NC
NC
Cl
f1 (ppm)


Intens.
x10^4
+MS, 0.22-0.42min #(13-25)
660.2367
661.2399
662.2359
663.2377
664.2401
658.2291
m/z

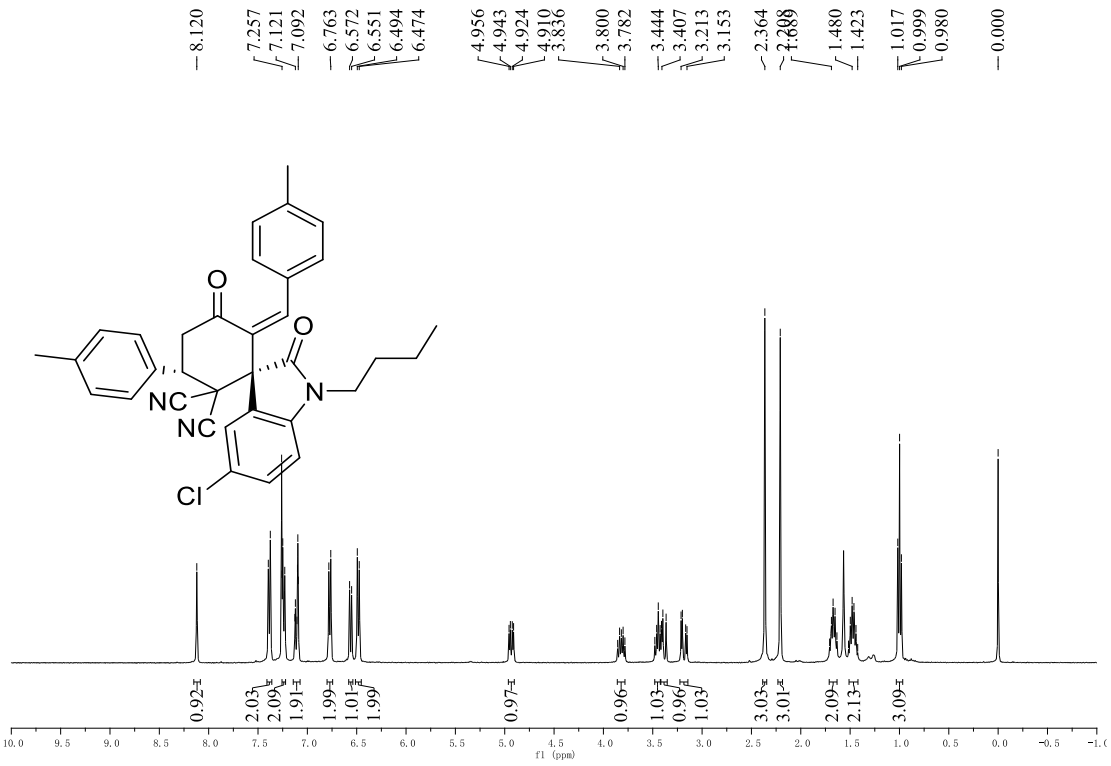
***rel*-(1*R*,3*R*)-1'-butyl-5'-chloro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3o)**: white solid, 42%, m.p. 225-227 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H, ArH), 7.51 (d, *J* = 7.2 Hz, 1H, ArH), 7.40 (d, *J* = 7.2 Hz, 2H, ArH), 7.24-7.23 (m, 4H, ArH), 7.12 (d, *J* = 6.8 Hz, 2H, ArH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH), 6.60 (s, 1H, CH), 4.93-4.90 (m, 1H, CH_2), 3.91-3.84 (m, 1H, CH_2), 3.64-3.60 (m, 1H, CH_2), 3.47-3.40 (m, 1H, CH), 3.07-3.03 (m, 1H, CH_2), 2.37-2.33 (s, 3H, CH_3), 1.72-1.69 (m, 2H, CH_2), 1.43-1.42 (m, 2H, CH_2), 0.97 (d, *J* = 5.6 Hz, 1H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 171.1, 142.1, 140.3, 140.0, 139.7, 131.6, 131.4, 130.5, 129.9, 129.4, 129.3, 129.2, 129.1, 128.8, 127.0, 124.7, 112.2, 111.9, 111.1, 60.1, 48.9, 44.3, 42.5, 40.8, 29.1, 21.4, 21.2, 20.1, 13.6. IR (KBr) υ: 3689, 2962, 2317, 1713, 1595, 1501, 1468, 1388, 1354, 1324, 1271, 1244, 1212, 1161, 1135, 1047, 882, 831 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{34}H_{30}ClNaN_3O_2$ ([M+Na]$^+$): 570.1924, found: 570.1912.

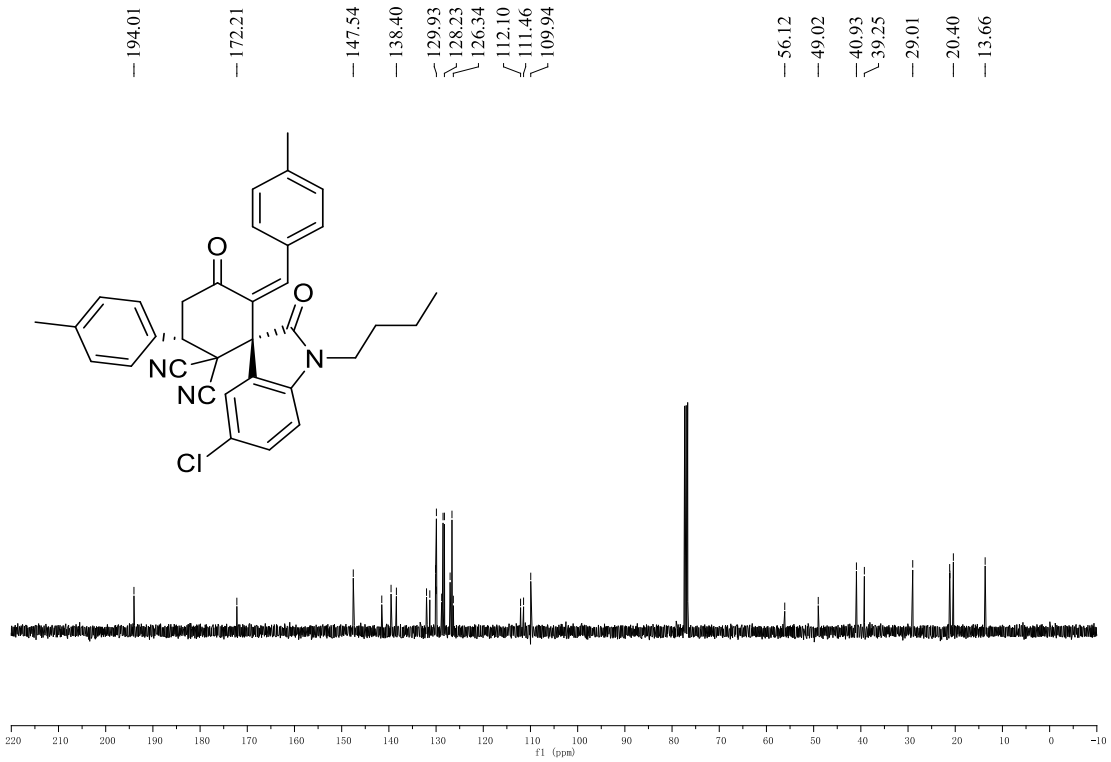


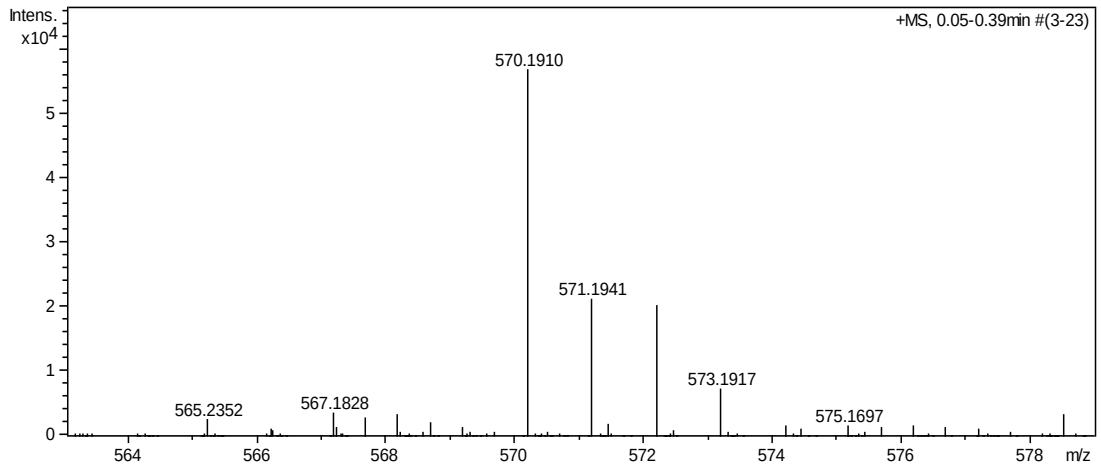

196.34
171.74
143.16
140.34
129.64
128.33
122.89
112.24
112.12
111.17
60.29
48.87
44.69
44.27
42.89
29.68
O
O
N
NC
NC
Cl
f1 (ppm)


Intens.
x10^4
+MS, 0.59-0.83min #(35-49)
570.1912
571.1942
572.1896
573.1918
565.2355
567.1826
568.1834
574.1947
576.1765
m/z

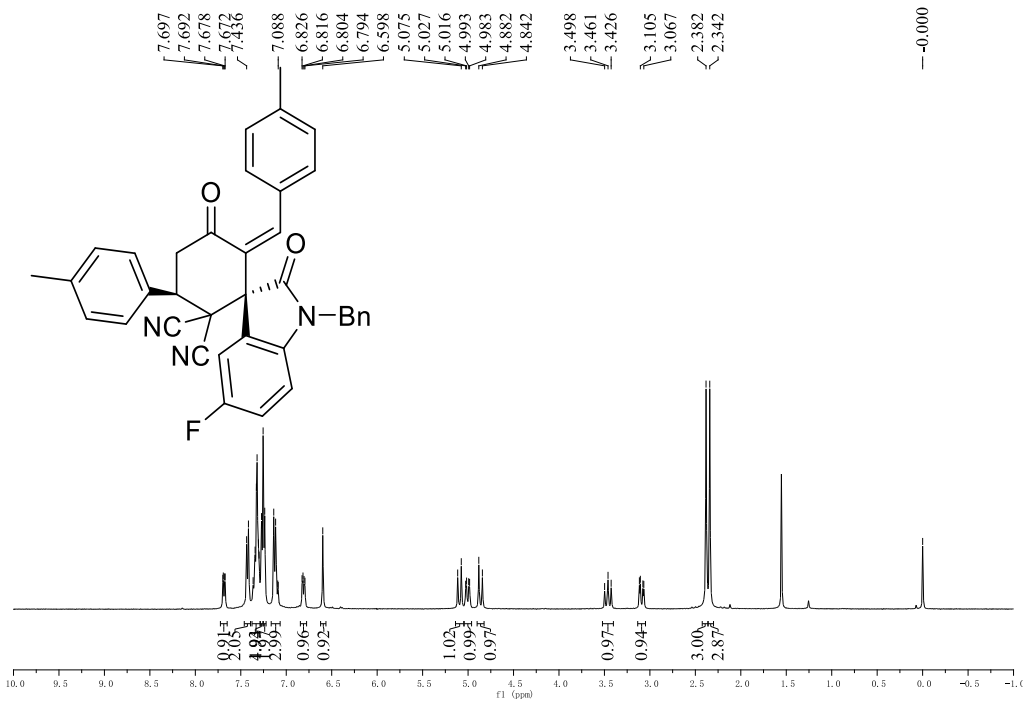
***rel*-(1*R*)-1'-butyl-5'-chloro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3o')**: lilac solid, 8%, m.p. 167-169 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, ArH), 7.39 (d, *J* = 8.4 Hz, 2H, ArH), 7.26-7.23 (m, 2H, ArH), 7.13-7.09 (m, 2H, ArH), 6.77 (d, *J* = 7.6 Hz, 2H, ArH), 6.56 (d, *J* = 8.4 Hz, 1H, CH), 6.48 (d, *J* = 8.0 Hz, 2H, ArH)), 4.96-4.91 (m, 1H, CH_2), 3.86-3.78 (m, 1H, CH_2), 3.48-3.43 (m, 1H, CH_2), 3.41-3.37 (m, 1H, CH), 3.21-3.15 (m, 1H, CH_2), 2.36 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 1.71-1.63 (m, 2H, CH_2), 1.52-1.42 (m, 2H, CH_2), 1.00 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.0, 172.2, 147.5, 141.5, 139.5, 138.4, 132.0, 131.3, 130.1, 130.0, 129.9, 128.8, 128.5, 128.2, 127.0, 126.6, 126.3, 112.1, 111.5, 109.9, 56.1, 49.0, 40.9, 39.3, 29.0, 21.2, 21.1, 20.4, 13.7; IR (KBr) υ: 3628, 3413, 3041, 2910, 2832, 1958, 1845, 1813, 1710, 1543, 1483, 1342, 1231, 1123, 1043, 1010, 945, 821, 753, 721 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{34}H_{30}ClNaN_3O_2$ ([M+Na]$^+$): 570.1924, found: 570.1910.

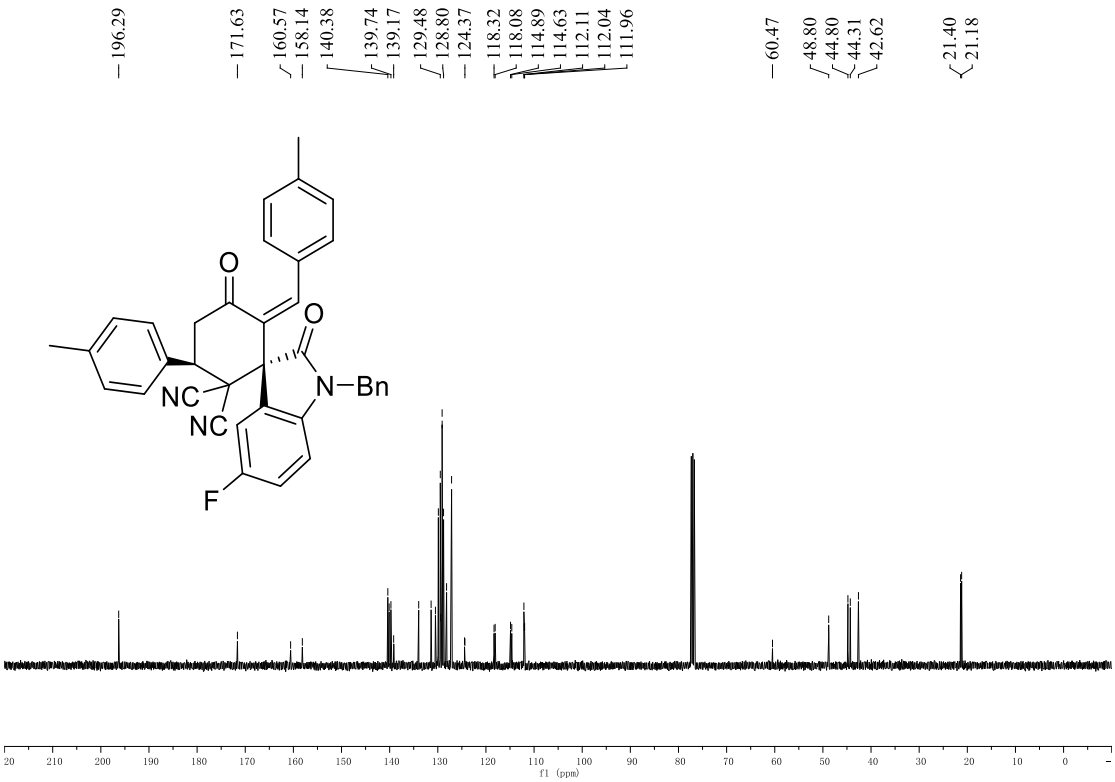


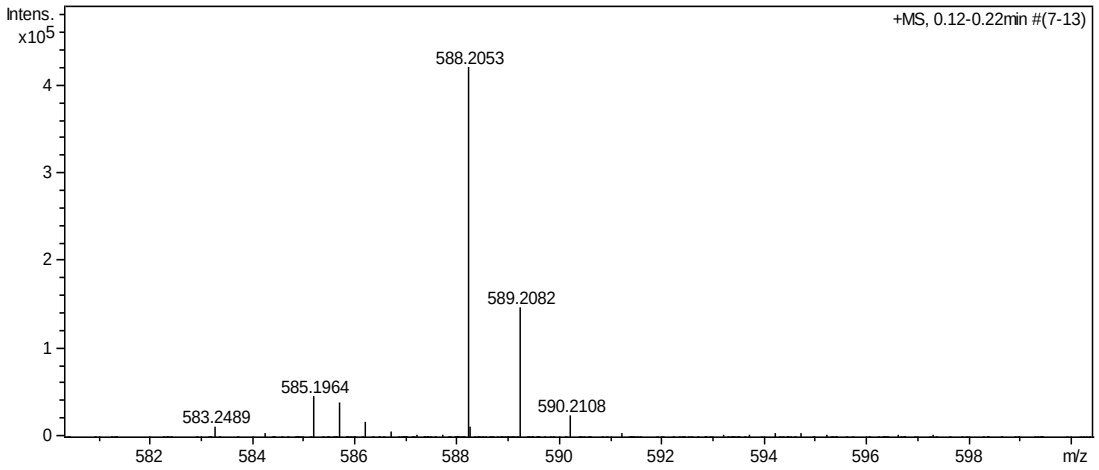

194.01
172.21
147.54
138.40
129.93
128.23
126.34
112.10
111.46
109.94
56.12
49.02
40.93
39.25
29.01
20.40
13.66
O
O
N
NC
NC
Cl
f1 (ppm)


Intens.
x10^4
+MS, 0.05-0.39min #(3-23)
570.1910
571.1941
573.1917
565.2352
567.1828
575.1697
m/z

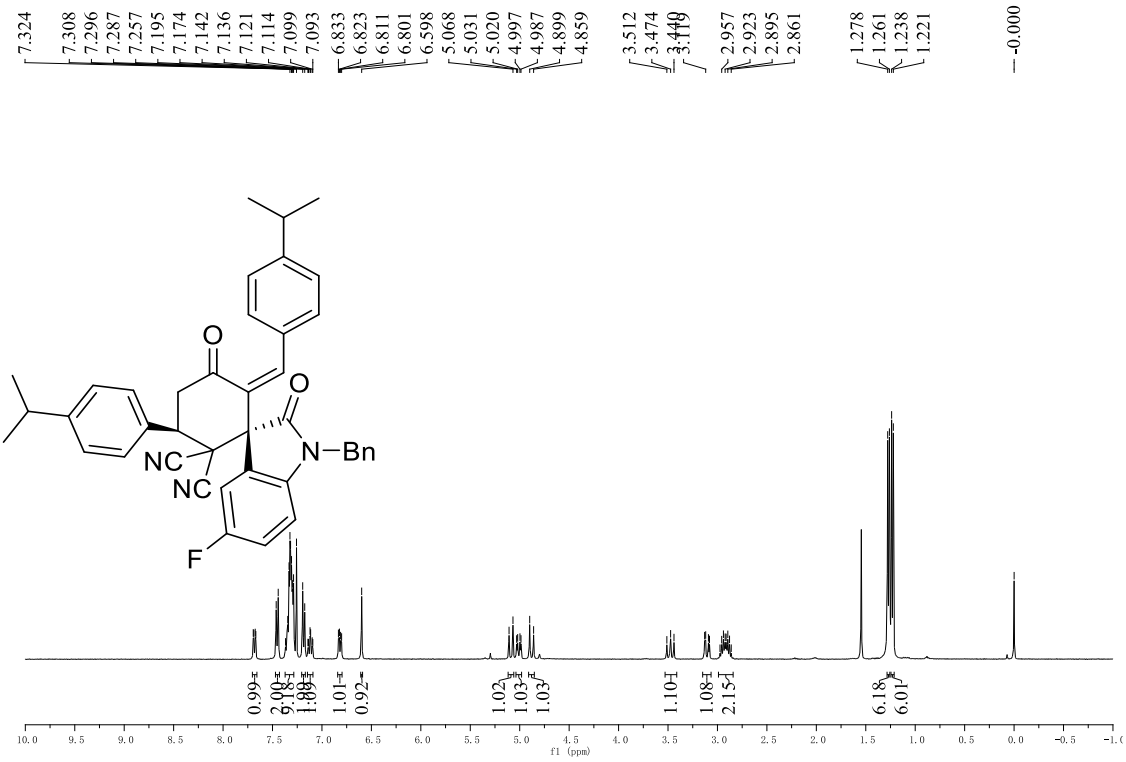
***rel*-(1*R*,3*R*)-1'-benzyl-5'-fluoro-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3p)**: white solid, 53%, m.p. 223-225 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 1H, ArH), 7.43 (d, *J* = 8.0 Hz, 2H, ArH), 7.36-7.30 (m, 5H, ArH), 7.27 (s, 2H, ArH), 7.24 (s, 2H, ArH), 7.14-7.09 (m, 3H, ArH), 6.83-6.79 (m, 1H, ArH), 6.60 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH_2), 5.03-4.98 (m, 1H, CH_2), 4.86 (d, *J* = 16.0 Hz, 1H, CH_2), 3.46 (t, *J* = 14.8 Hz, 1H, CH), 3.12-3.07 (m, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.34 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 171.6, 160.6, 158.1, 140.4, 140.1, 139.7, 139.2, 134.0, 131.4, 130.5, 129.9, 129.5, 129.4, 129.1, 129.1, 128.8, 128.2, 127.1, 124.5, 124.4, 118.3, 118.1, 114.9, 114.6, 112.1, 112.0, 112.0, 60.5, 48.8, 44.8, 44.3, 42.6, 21.4, 21.2. IR (KBr) υ: 3725, 3407, 3031, 2917, 2319, 1881, 1715, 1614, 1494, 1452, 1421, 1352, 1270, 1185, 1145, 1021, 965, 928, 875, 819, 731 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{28}NaFN_3O_2$ ([M+Na]$^{+}$): 588.2063, found: 588.2053.

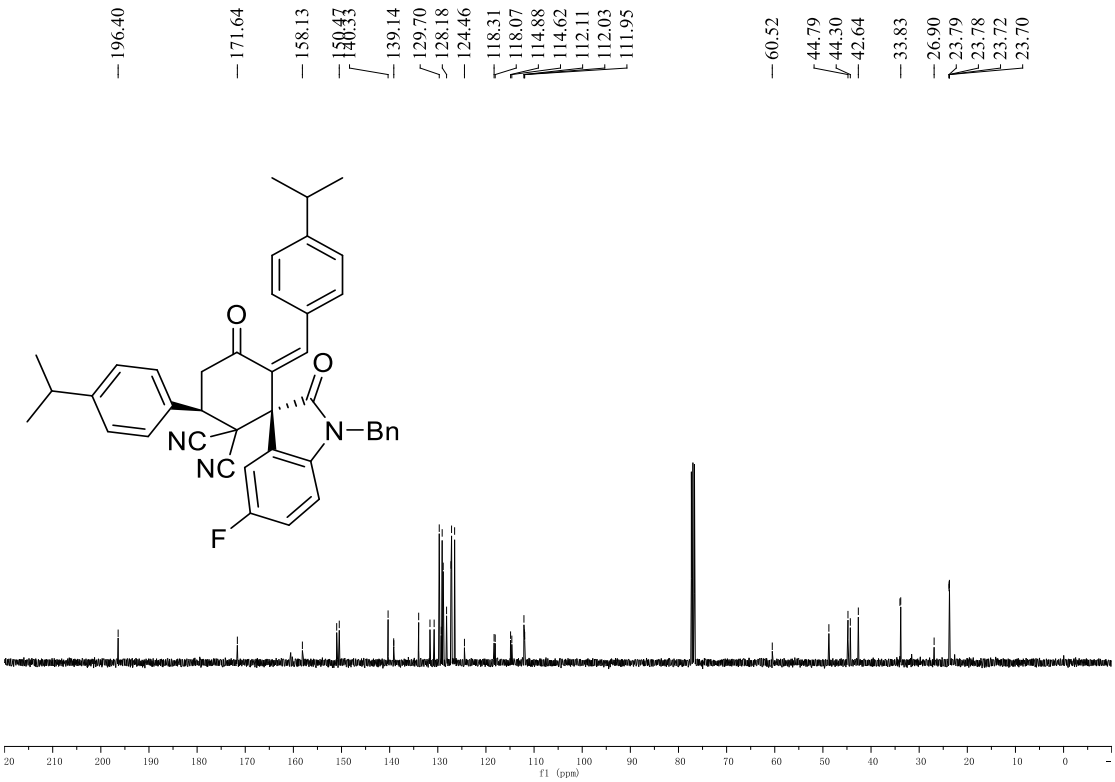



196.29
171.63
160.57
158.14
140.38
139.74
139.17
129.48
128.80
124.37
118.32
118.08
114.89
114.63
112.11
112.04
111.96
60.47
48.80
44.80
44.31
42.62
21.40
21.18
O
O
N–Bn
NC
NC
F
f1 (ppm)


Intens.
x10^5
+MS, 0.12-0.22min #(7-13)
588.2053
589.2082
585.1964
590.2108
583.2489
m/z

***rel*-(1*R*,3*R*)-1'-benzyl-5'-fluoro-6-((*Z*)-4-isopropylbenzylidene)-3-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3q)**: white solid, 72%, m.p. 195-197 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 1H, ArH), 7.45 (d, *J* = 8.4 Hz, 2H, ArH), 7.37-7.29 (m, 9H, ArH), 7.18 (d, *J* = 8.4 Hz, 2H, ArH), 7.14-7.09 (m, 1H, ArH), 6.83-6.80 (m, 1H, ArH), 6.60 (s, 1H, CH), 5.09 (d, *J* = 16.0 Hz, 1H, CH_2), 5.03-4.99 (m, 1H, CH_2), 4.88 (d, *J* = 16.0 Hz, 1H, CH_2), 3.47 (t, *J* = 15.2 Hz, 1H, CH), 3.13-3.08 (m, 1H, CH_2), 2.97-2.86 (m, 2H, CH), 1.27 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2$), 1.23 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2$).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 171.6, 158.1, 151.0, 150.5, 140.3, 139.2, 139.1, 134.0, 131.6, 130.8, 129.7, 129.3, 129.1, 128.9, 128.2, 127.3, 127.1, 126.5, 124.5, 118.3, 118.1, 114.9, 114.6, 112.1, 112.0, 111.9, 60.5, 48.8, 44.8, 44.3, 42.6, 34.0, 33.8, 26.9, 23.8, 23.8, 23.7, 23.7. IR (KBr) υ: 3059, 2961, 1715, 1612, 1492, 1454, 1420, 1353, 1270, 1185, 1058, 1018, 966, 926, 831, 727 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{36}NaFN_3O_2$ ([M+Na]$^{+}$): 644.2689, found: 644.2666.




196.40
171.64
158.13
150.47
140.33
139.14
129.70
128.18
124.46
118.31
118.07
114.88
114.62
112.11
112.03
111.95
60.52
44.79
44.30
42.64
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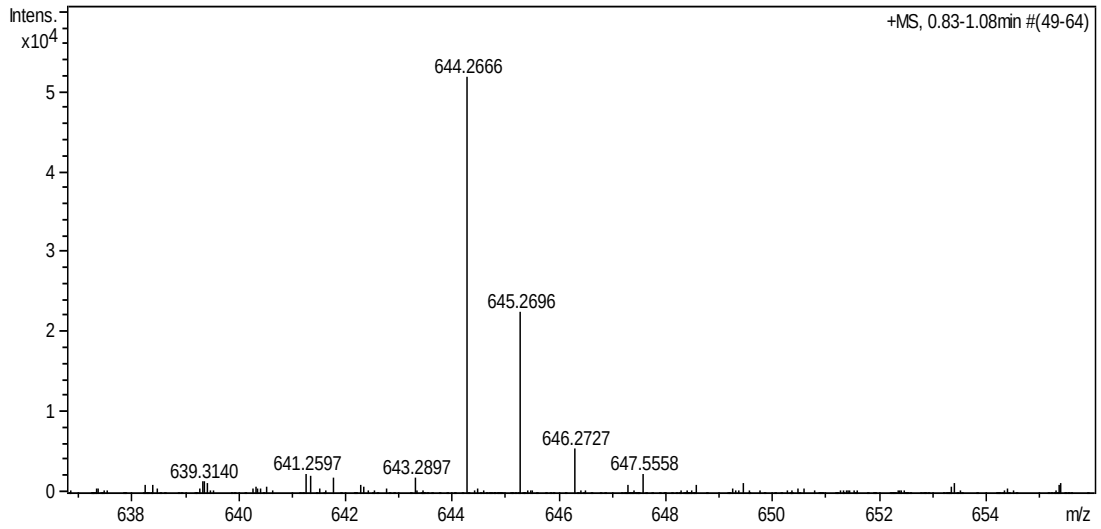
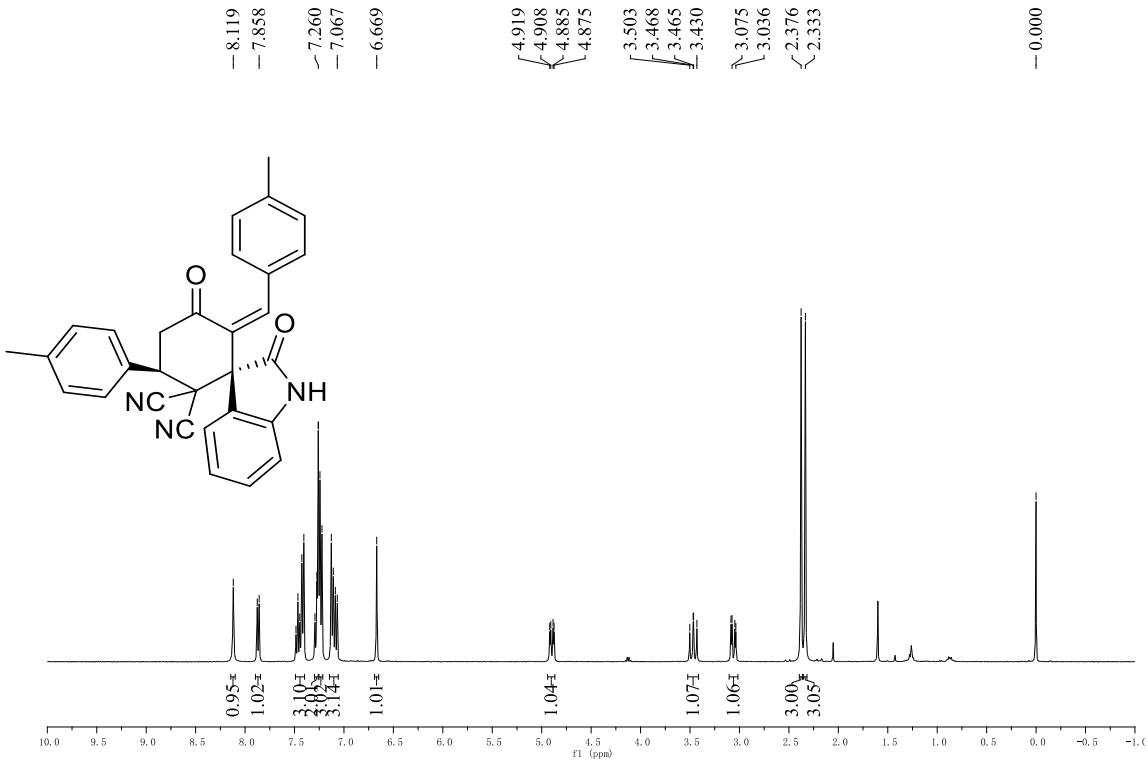
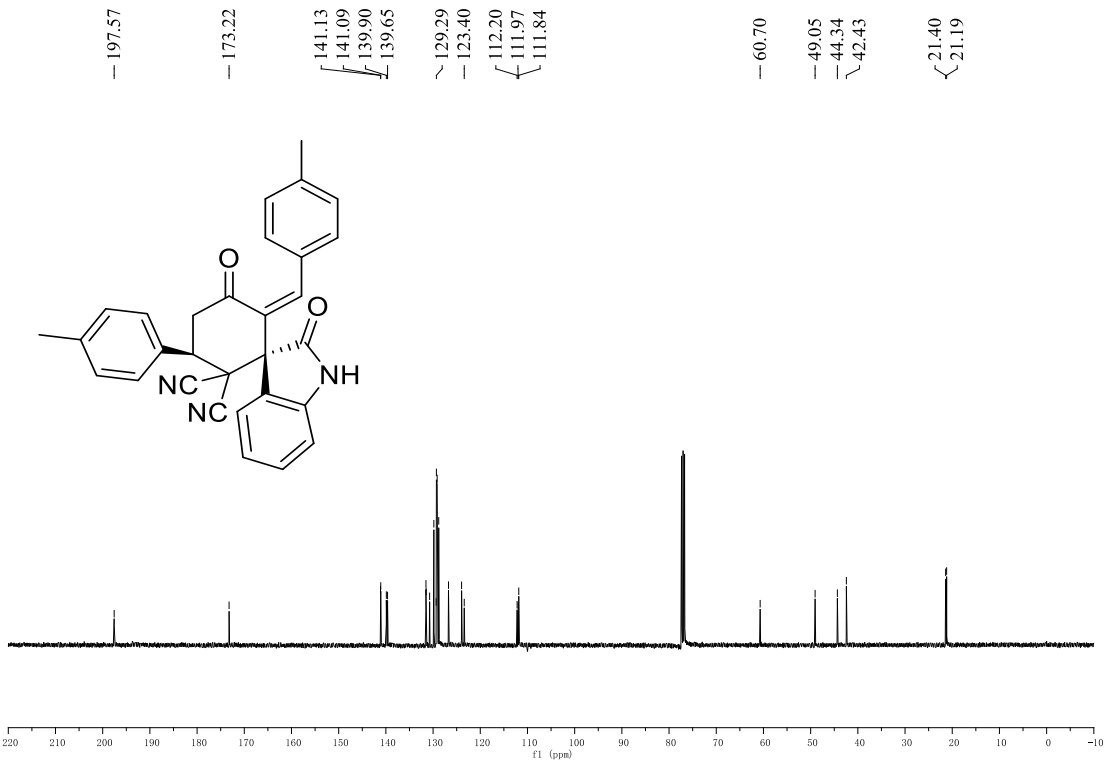
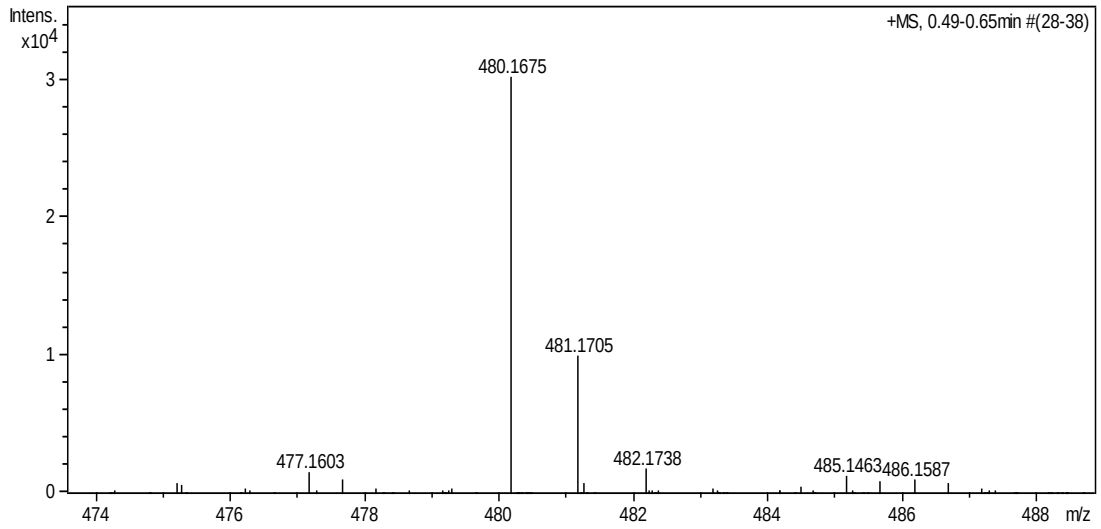
23.78
23.72
23.70
O
O
NC
NC
N−Bn
F
f1 (ppm)


Intens.
x10^4
+MS, 0.83-1.08min #(49-64)
644.2666
645.2696
646.2727
639.3140
641.2597
643.2897
647.5558
m/z

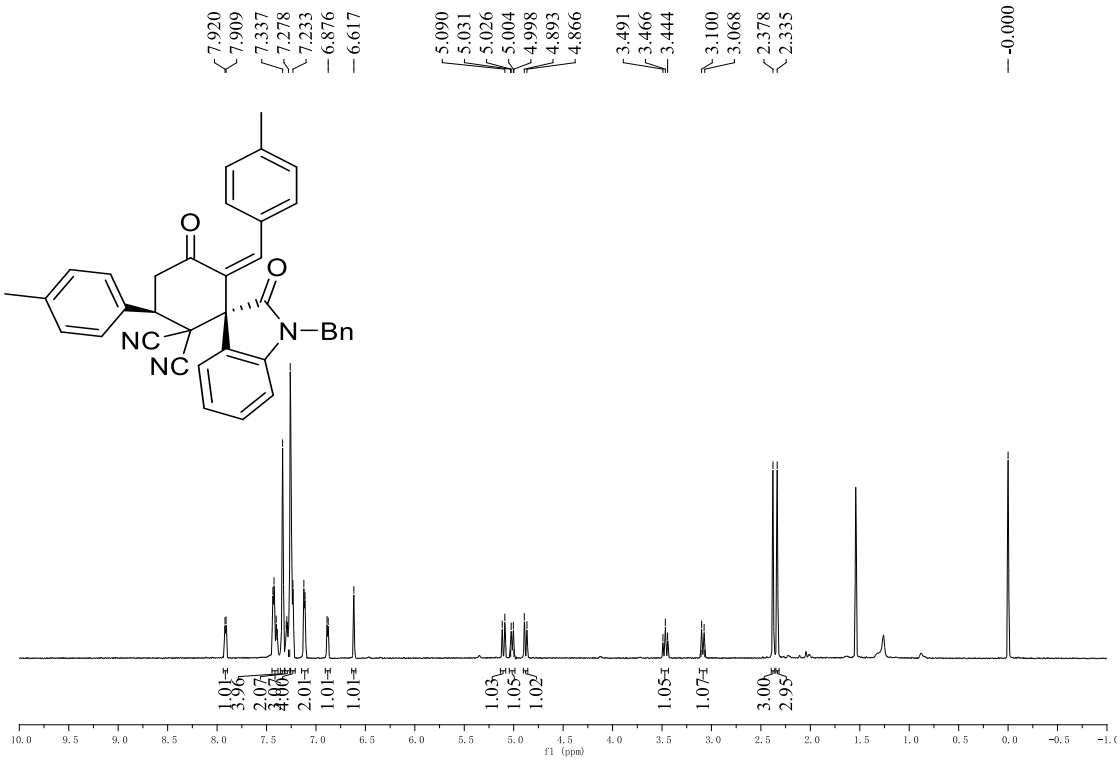
***rel*-(1*R*,3*R*)-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3r)**: pale pink solid, 56%, m.p. 252-254 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H, NH), 7.87 (d, *J* = 7.6 Hz, 1H, ArH), 7.49-7.41 (m, 3H, ArH), 7.29-7.27 (m, 2H, ArH), 7.26-7.22 (m, 3H, ArH), 6.67 (s, 1H, CH), 4.92 (m, 1H, CH_2), 3.50-3.43 (m, 1H, CH), 3.09-3.04 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 173.2, 141.1, 141.0, 139.9, 139.7, 131.5, 131.4, 130.7, 129.8, 129.2, 129.3, 129.1, 128.8, 126.7, 124.0, 123.4, 112.2, 112.0, 111.8, 60.7, 49.1, 44.3, 42.4, 21.4, 21.2. IR (KBr) υ: 3686, 3067, 1723, 1567, 1514, 1474, 1420, 1381, 1323, 1191, 1045, 821, 759 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{30}H_{23}NaN_3O_2$ ([M+Na]$^+$): 480.1688, found: 480.1675.

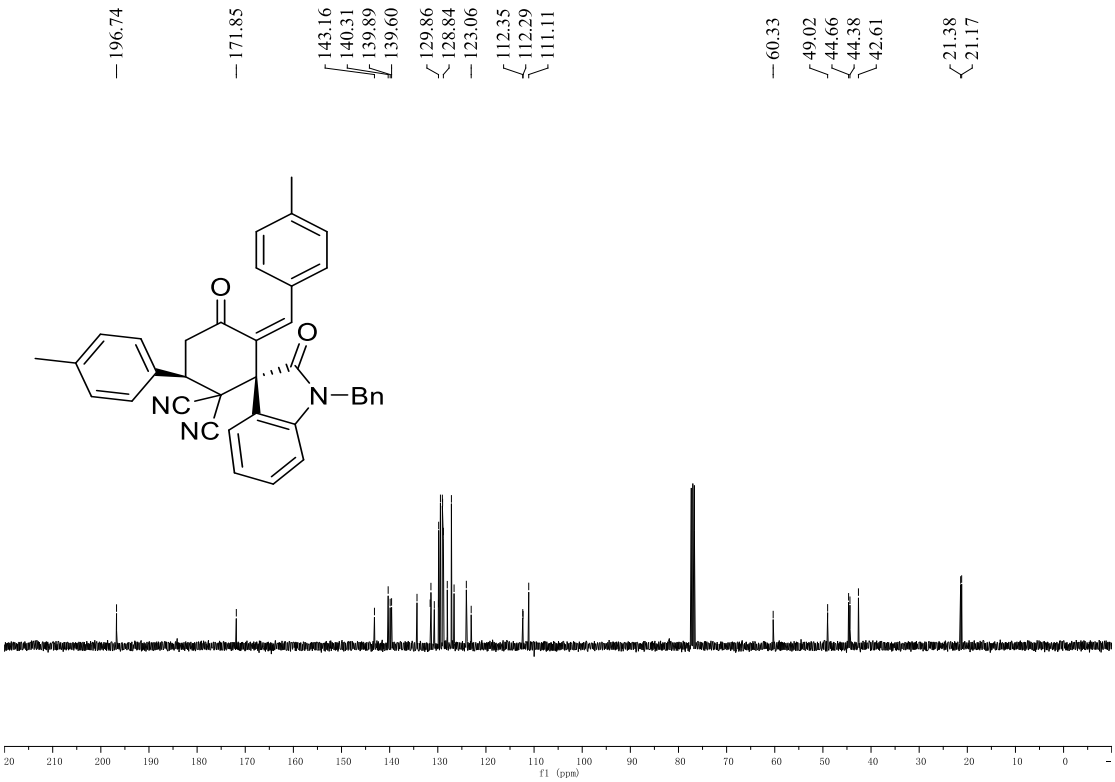


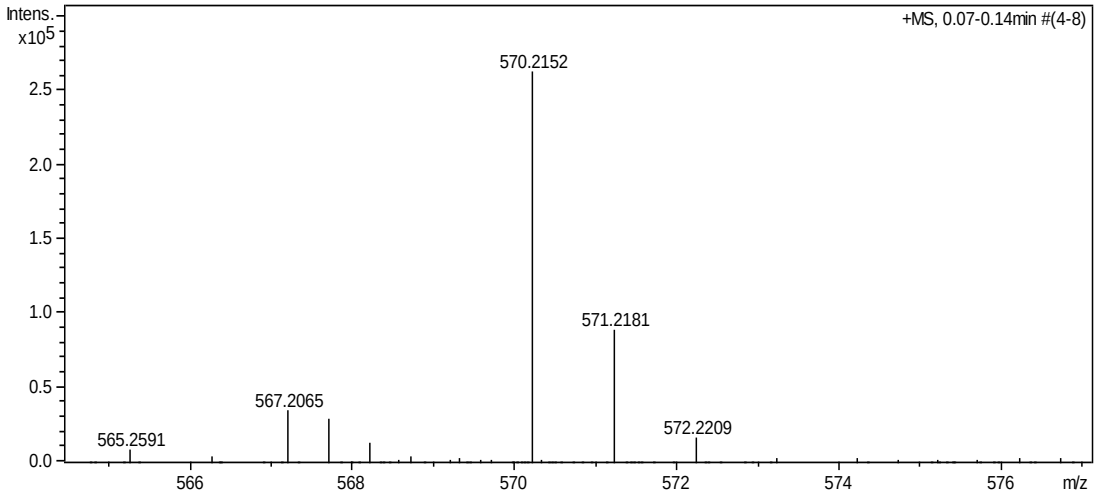

197.57
173.22
141.13
141.09
139.90
139.65
129.29
123.40
112.20
111.97
111.84
60.70
49.05
44.34
42.43
21.40
21.19
O
O
NH
NC
NC
f1 (ppm)


Intens.
x10^4
+MS, 0.49-0.65min #(28-38)
480.1675
481.1705
477.1603
482.1738
485.1463
486.1587
m/z

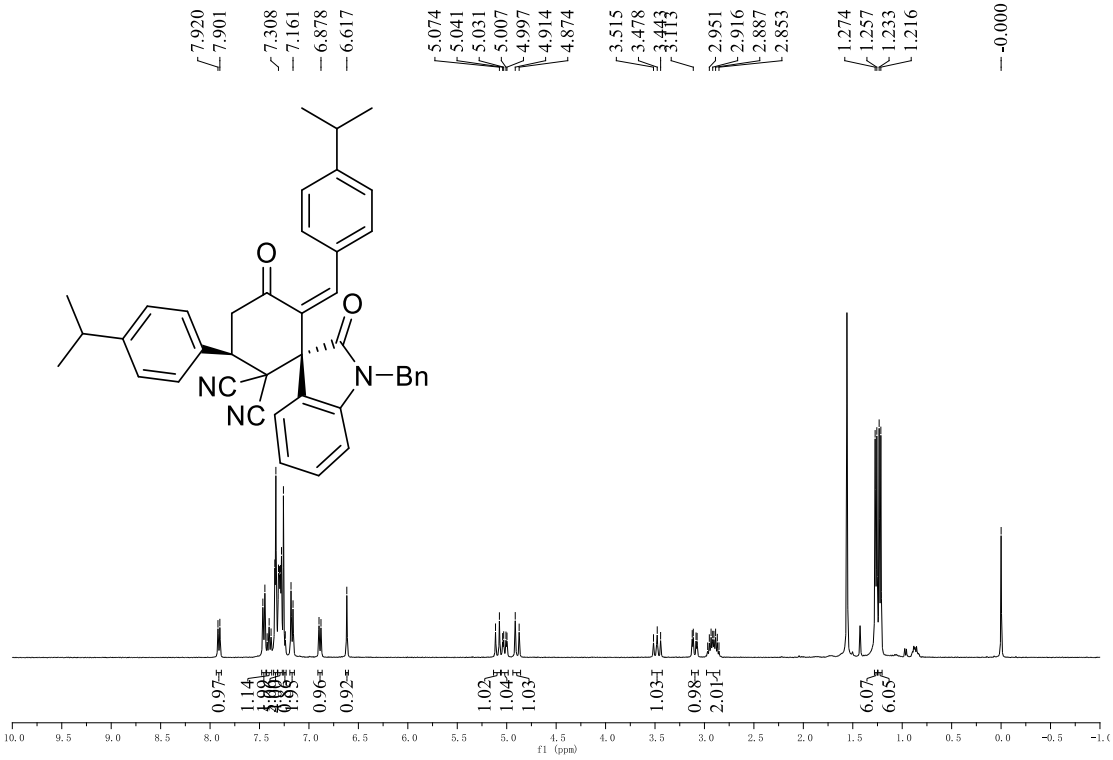
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-methylbenzylidene)-2',5-dioxo-3-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3s)**: pale yellow solid, 72%, m.p. 212-214 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 6.6 Hz, 1H, ArH), 7.44-7.39 (m, 3H, ArH), 7.34 (s, 4H, ArH), 7.30-7.27 (m, 2H, ArH), 7.25-7.23 (m, 4H, ArH), 7.11 (d, *J* = 7.2 Hz, 2H, ArH), 6.88 (d, *J* = 7.2 Hz, 1H, ArH), 6.62 (s, 1H, CH), 5.10 (d, *J* = 15.6 Hz, 1H, CH_2), 5.03-5.00 (m, 1H, CH_2), 4.88 (d, *J* = 16.2 Hz, 1H, CH_2), 3.47 (t, *J* = 13.2 Hz, 1H, CH), 3.11-3.07 (m, 1H, CH_2), 2.38 (s, 3H, CH_3), 2.34 (s, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 171.9, 143.2, 140.3, 139.9, 139.6, 134.3, 131.6, 131.4, 130.7, 129.9, 129.8, 129.5, 129.1, 129.0, 128.8, 128.0, 127.2, 126.6, 124.1, 123.1, 112.2, 112.3, 111.1, 60.3, 49.0, 44.7, 44.4, 42.6, 21.4, 21.2. IR (KBr) υ: 3729, 3407, 3029, 2965, 2922, 2859, 2319, 1980, 1903, 1805, 1710, 1607, 1482, 1362, 1298, 1183, 1153, 1120, 1045, 953, 894, 812, 763, 733 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{29}NaN_3O_2$ ([M+Na]$^+$): 570.2157, found: 570.2152.

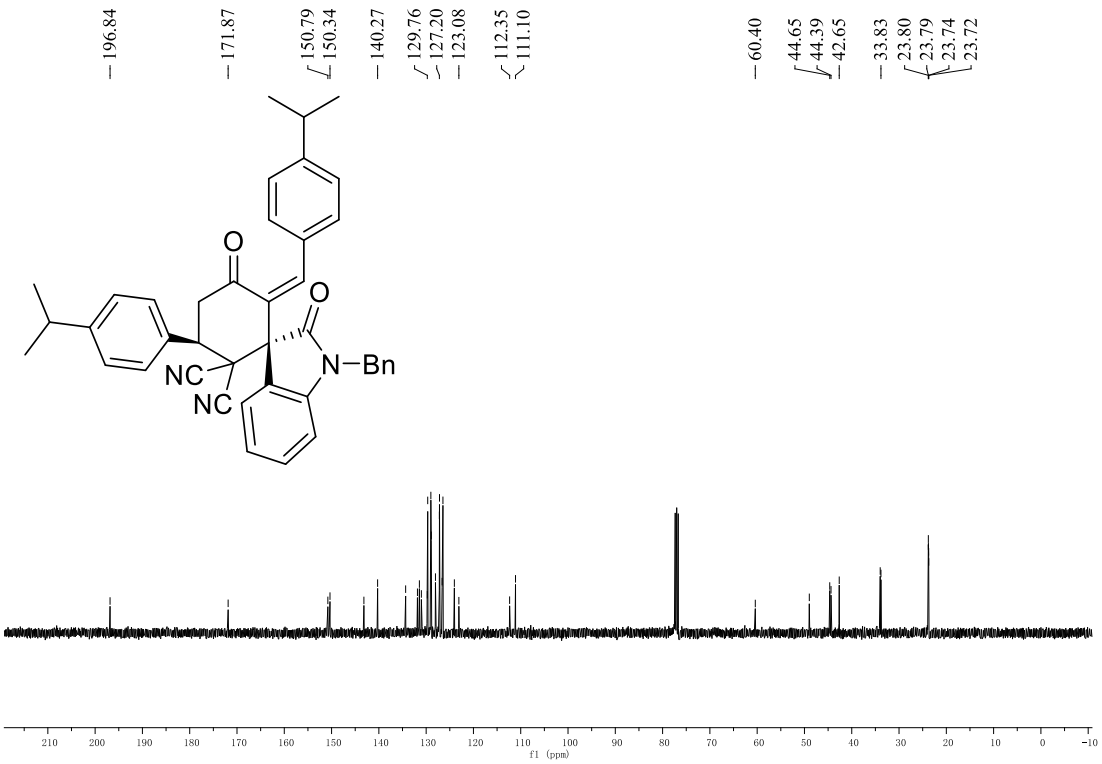


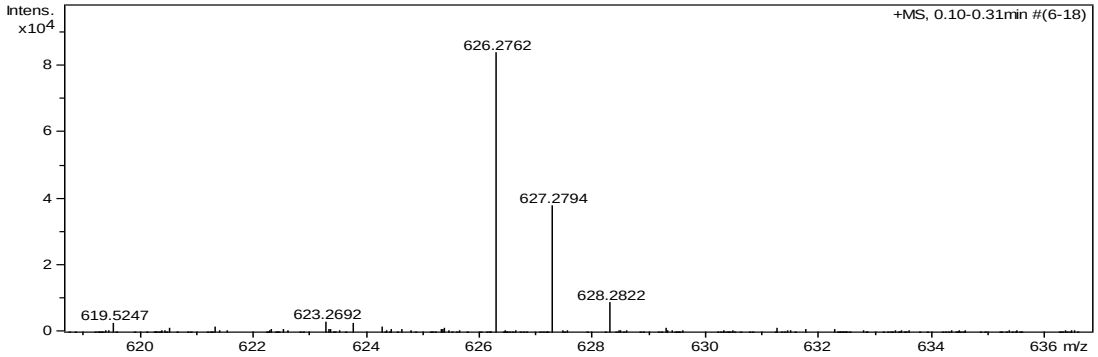

196.74
171.85
143.16
140.31
139.89
139.60
129.86
128.84
123.06
112.35
112.29
111.11
60.33
49.02
44.66
44.38
42.61
21.38
21.17
O
O
N–Bn
NC
NC
f1 (ppm)


Intens.
x10^5
+MS, 0.07-0.14min #(4-8)
570.2152
571.2181
567.2065
565.2591
572.2209
m/z

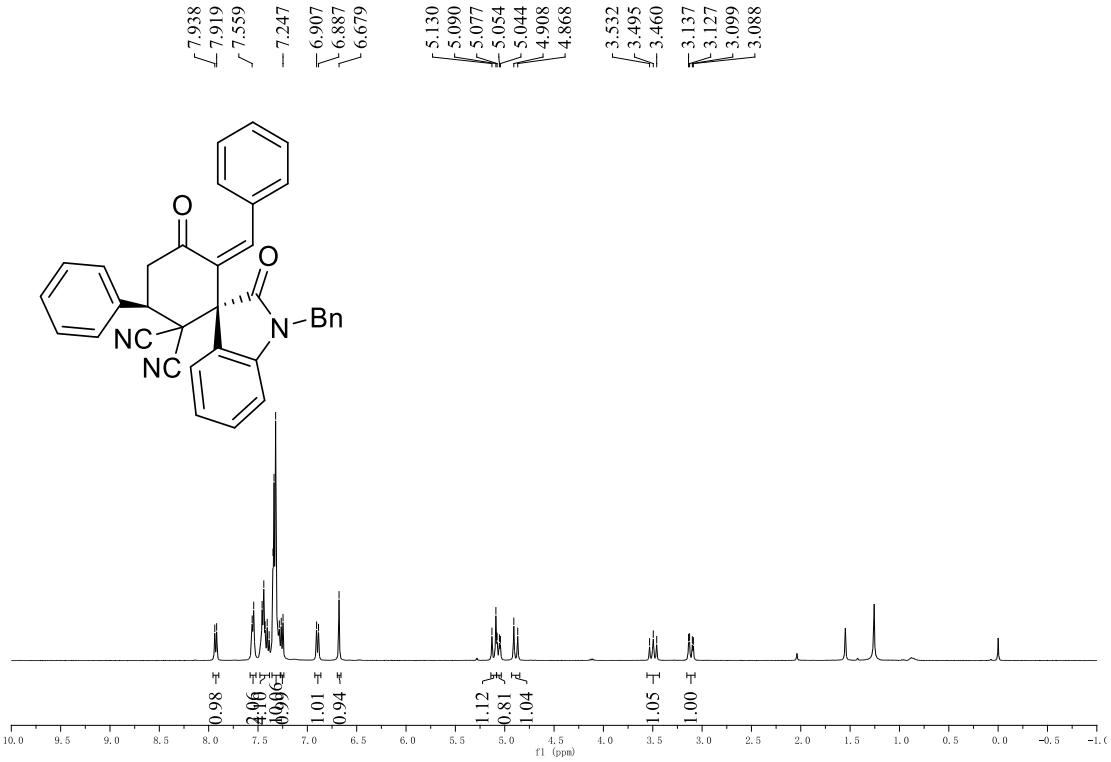
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-isopropylbenzylidene)-3-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3t)**: white solid, 68%, m.p. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.6 Hz, 1H, ArH), 7.46 (d, *J* = 8.0 Hz, 2H, ArH), 7.40 (d, *J* = 8.0 Hz, 1H, ArH), 7.35-7.33 (m, 4H, ArH), 7.35-7.33 (m, 4H, ArH), 7.31-7.28 (m, 5H, ArH), 7.24 (s, 1H, ArH), 7.17 (d, *J* = 8.0 Hz, 2H, ArH), 6.89 (d, *J* = 8.0 Hz, 1H, ArH), 6.62 (s, 1H, CH), 5.09 (d, *J* = 15.6 Hz, 1H, CH_2), 5.04-5.00 (m, 1H, CH_2), 4.89 (d, *J* = 16.0 Hz, 1H, CH_2), 3.48 (t, *J* = 14.0 Hz, 1H, CH), 3.12-3.07 (m, 1H, CH_2), 2.97-2.85 (m, 2H, CH), 1.26 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2$), 1.22 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 171.9, 150.8, 150.3, 143.2, 140.3, 134.3, 131.8, 131.4, 131.0, 129.8, 129.7, 129.0, 128.9, 128.0, 127.2, 127.1, 126.6, 126.5, 124.0, 123.1, 112.2, 111.1, 60.4, 49.0, 44.7, 44.4, 42.7, 34.0, 33.8, 23.8, 23.8, 23.7, 23.6. IR (KBr) υ: 3685, 3057, 2962, 1711, 1609, 1479, 1420, 1364, 1191, 1056, 1014, 957, 845, 754 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{37}NaN_3O_2$ ([M+Na]$^+$): 626.2783, found: 626.2762.

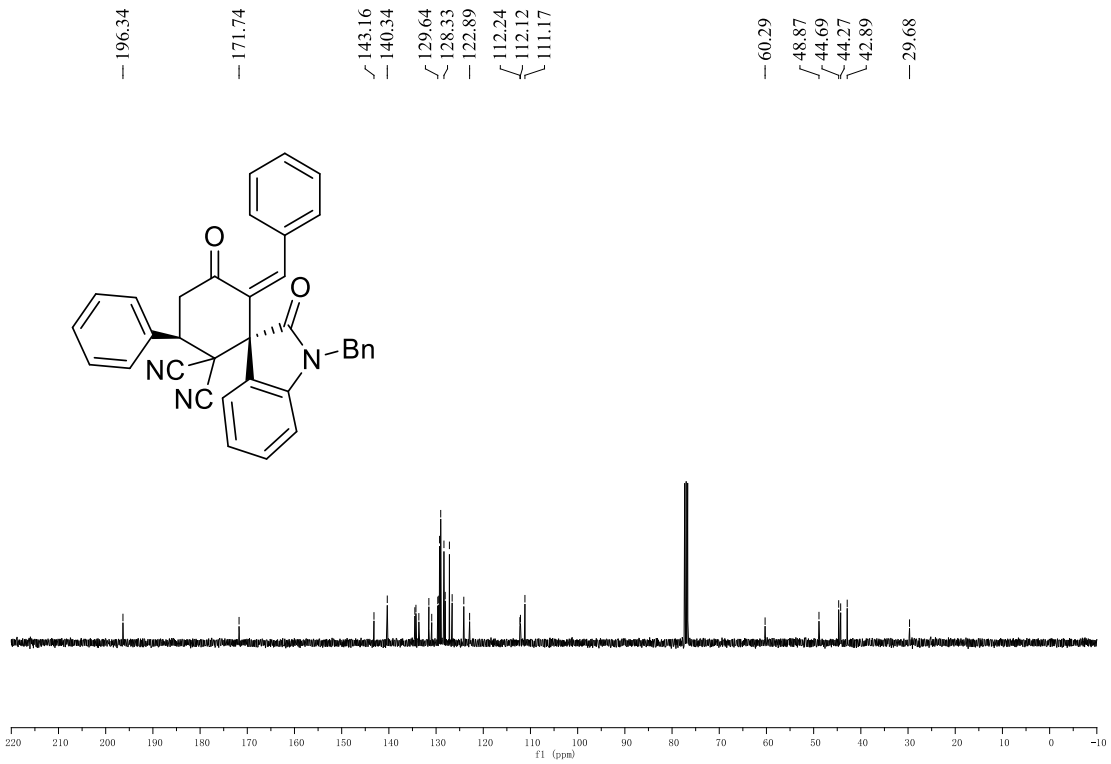


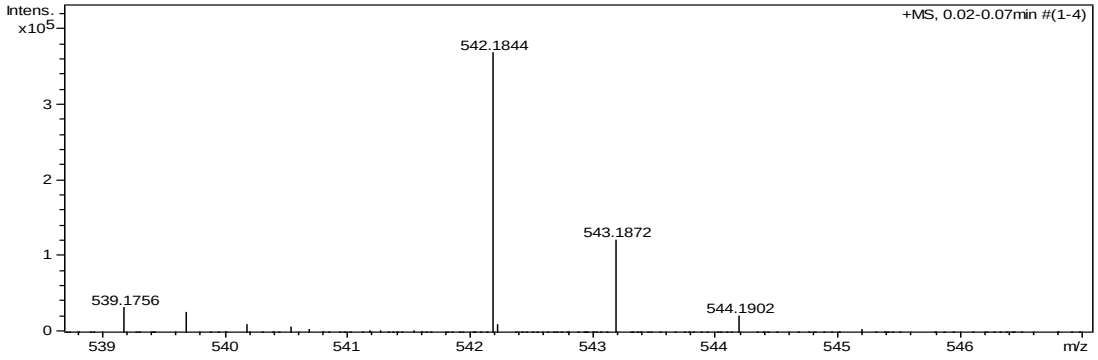

196.84
171.87
150.79
150.34
140.27
129.76
127.20
123.08
112.35
111.10
60.40
44.65
44.39
42.65
33.83
23.80
23.79
23.74
23.72
O
O
NC
NC
N–Bn
f1 (ppm)


Intens.
x10^4
+MS, 0.10-0.31min #(6-18)
626.2762
627.2794
628.2822
619.5247
623.2692
m/z

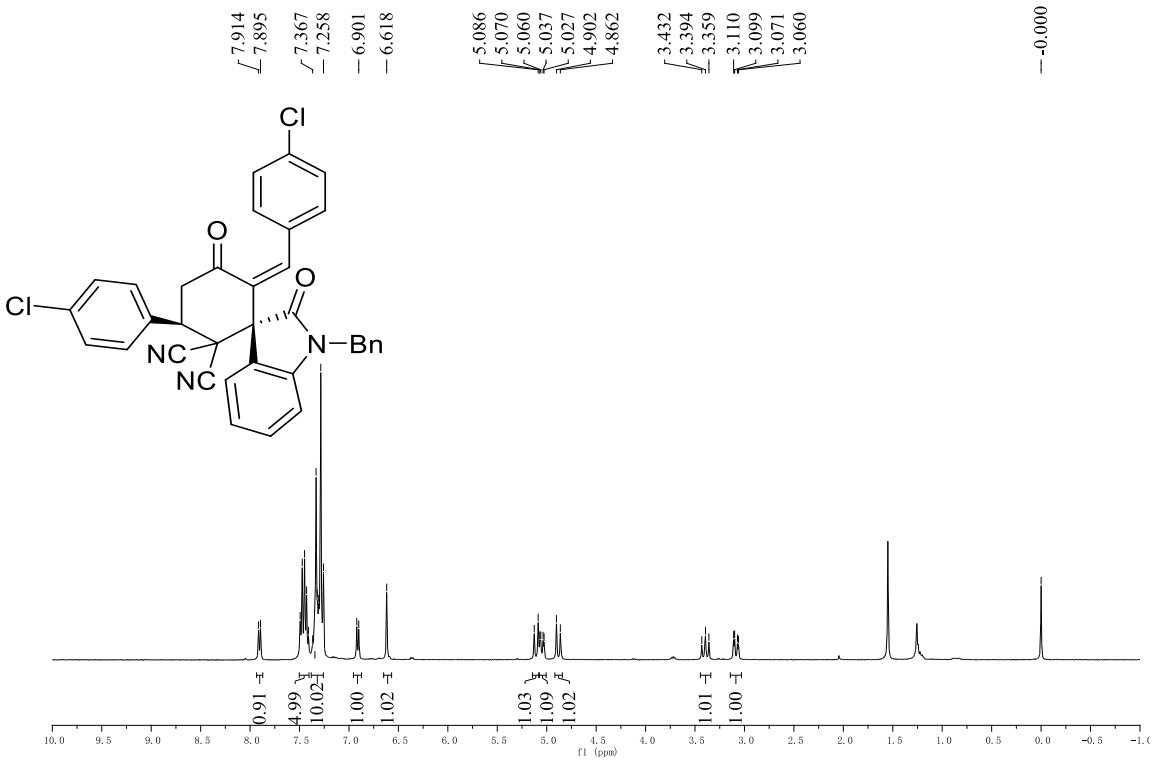
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-benzylidene)-2',5-dioxo-3-phenylspiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3u)**: pale yellow solid, 52%, m.p. 211-213 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H, ArH), 7.56-7.54 (m, 2H, ArH), 7.46-7.39 (m, 4H, ArH), 7.35-7.27 (m, 10H, ArH), 7.25 (d, *J* = 7.2 Hz, 1H, ArH), 6.90 (d, *J* = 8.0 Hz, 1H, ArH), 6.68 (s, 1H, CH), 5.11 (d, *J* = 16.0 Hz, 1H, CH_2), 5.08-5.04 (m, 1H, CH_2), 4.89 (d, *J* = 16.0 Hz, 1H, CH_2), 3.50 (t, *J* = 14.0 Hz, 1H, CH), 3.14-3.09 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 171.7, 143.2, 140.3, 134.5, 134.3, 133.7, 131.5, 130.9, 129.6, 129.4, 129.3, 129.2, 129.0, 128.3, 128.1, 127.2, 126.6, 124.1, 122.9, 112.2, 112.1, 111.2, 60.3, 48.9, 44.7, 44.3, 42.9, 29.7. IR (KBr) υ: 3728, 3413, 3040, 2919, 2852, 2317, 1958, 1888, 1813, 1711, 1607, 1483, 1457, 1356, 1231, 1187, 1069, 1009, 951, 835, 784, 746 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{25}NaN_3O_2$ ([M+Na]$^{+}$): 542.1844, found: 542.1844.

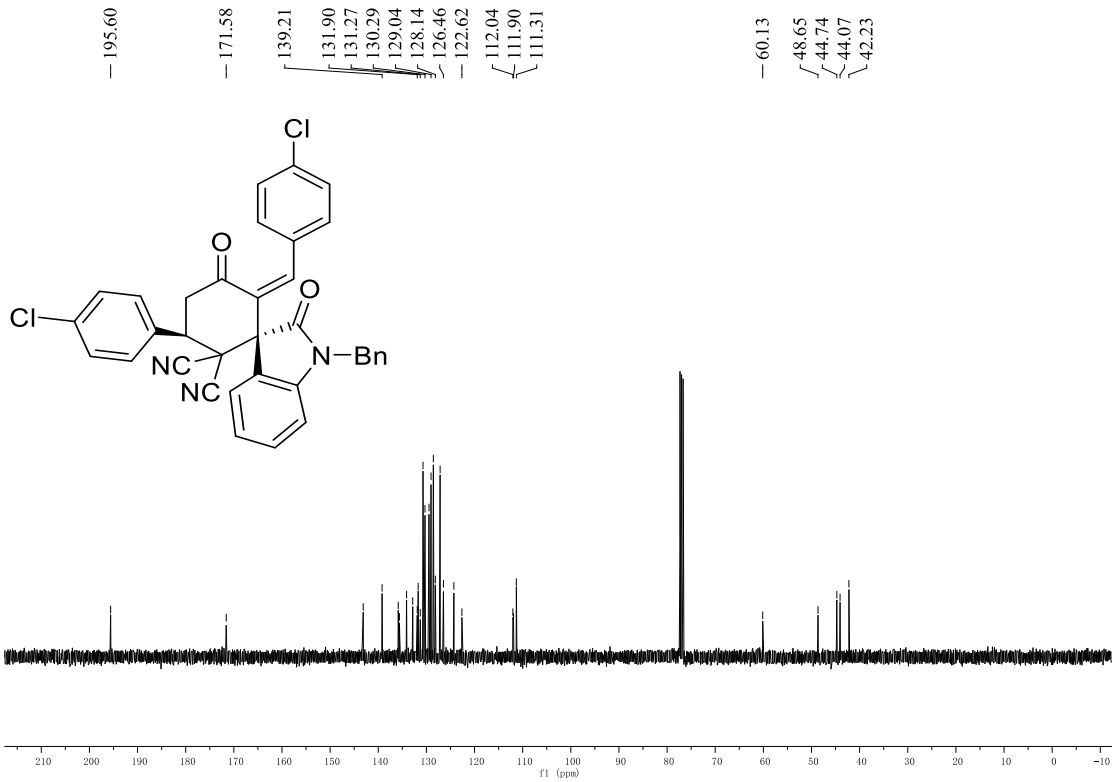


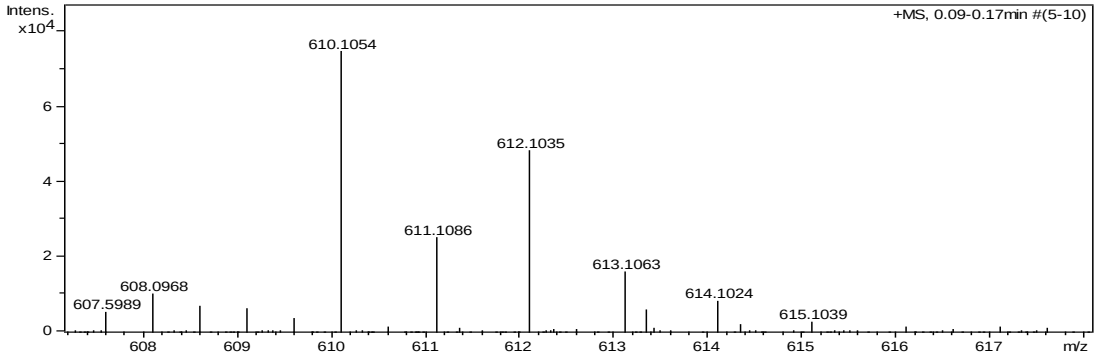

196.34
171.74
143.16
140.34
129.64
128.33
122.89
112.24
112.12
111.17
60.29
48.87
44.69
44.27
42.89
29.68
O
O
N
Bn
NC
NC
f1 (ppm)


Intens.
x10^5
+MS, 0.02-0.07min #(1-4)
542.1844
543.1872
539.1756
544.1902
m/z

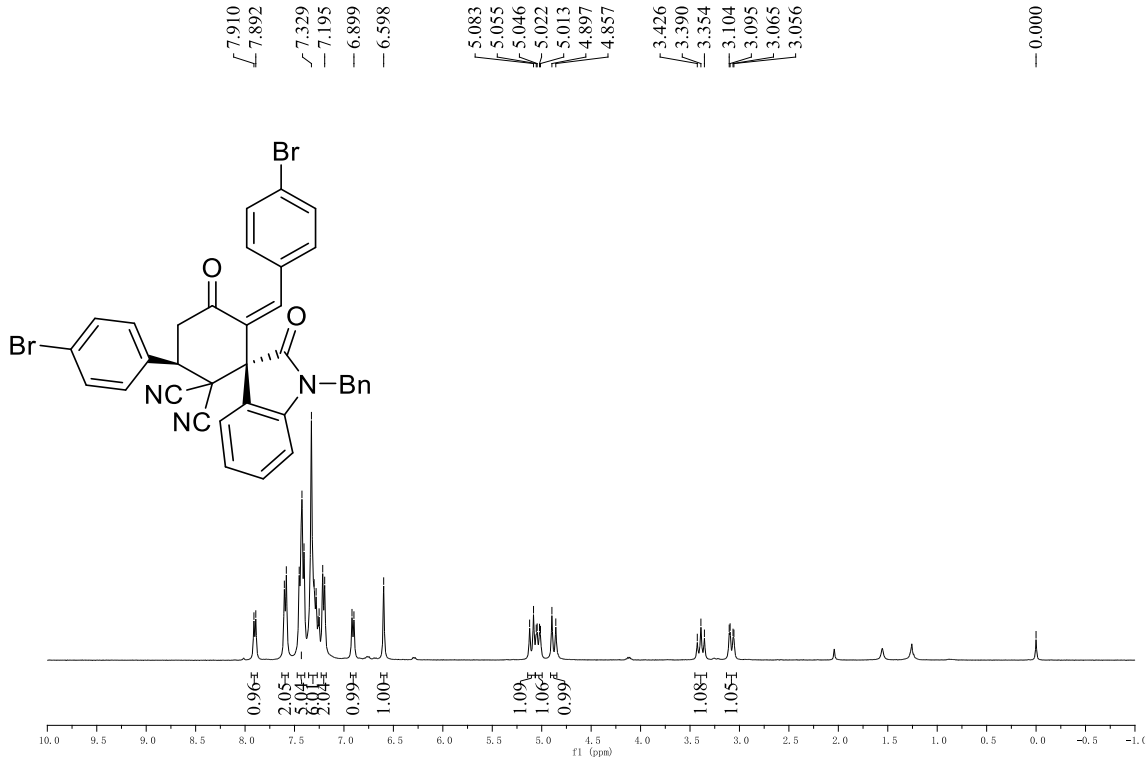
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-chlorobenzylidene)-3-(4-chlorophenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3v)**: white solid, 45%, m.p. 222-224 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.6 Hz, 1H, ArH), 7.49-7.41 (m, 5H, ArH), 7.37-7.29 (m, 10H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.62 (s, 1H, CH), 5.11 (d, *J* = 16.0 Hz, 1H, CH_2), 5.07-5.03 (m, 1H, CH_2), 4.88 (d, *J* = 16.0 Hz, 1H, CH_2), 3.39 (t, *J* = 15.2 Hz, 1H, CH), 3.11-3.06 (m, 1H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 171.6, 143.1, 139.2, 135.9, 135.6, 134.1, 132.8, 131.9, 131.7, 131.3, 130.7, 130.3, 129.5, 129.0, 128.6, 128.1, 127.2, 126.5, 124.3, 122.6, 112.0, 111.9, 111.3, 60.1, 48.65, 44.7, 44.1, 42.2. IR (KBr) υ: 3726, 3629, 3405, 3063, 2973, 2924, 2853, 2343, 1896, 1709, 1610, 1486, 1410, 1363, 1293, 1187, 1152, 1092, 1049, 1011, 953, 893, 826, 756, 734 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{23}NaClN_3O_2$ ([M+Na]$^{+}$): 610.1065, found: 610.1054.

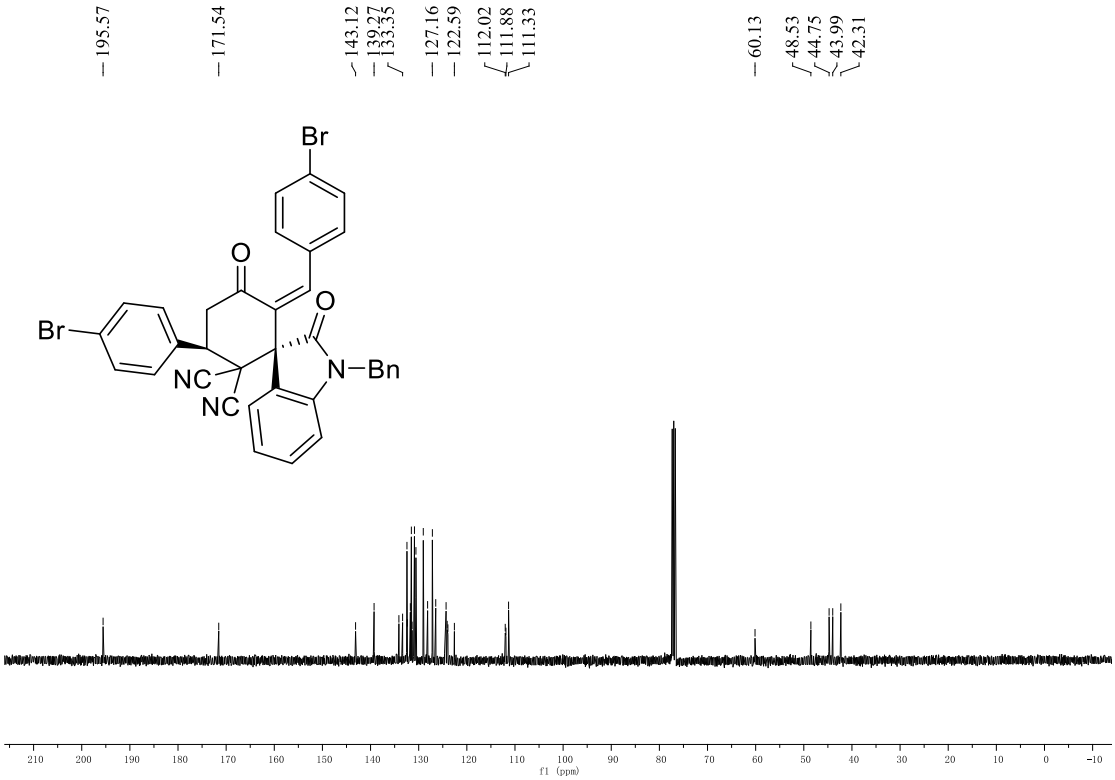


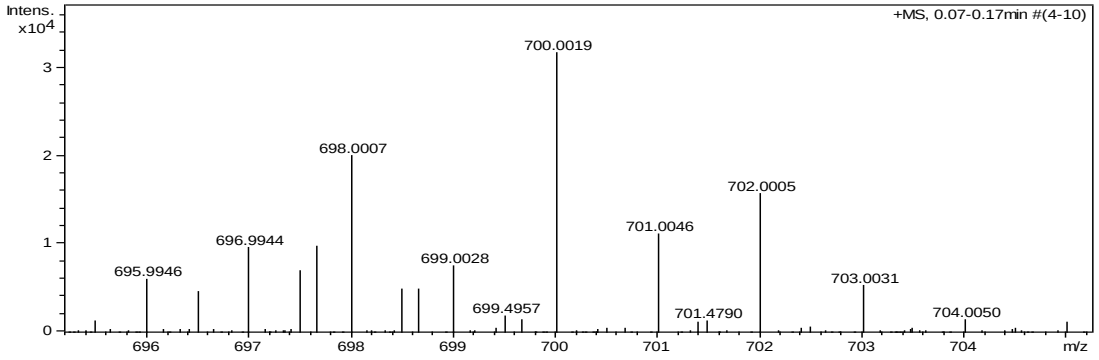

195.60
171.58
139.21
131.90
131.27
130.29
129.04
128.14
126.46
122.62
112.04
111.90
111.31
60.13
48.65
44.74
44.07
42.23
Cl
O
O
Cl
NC
NC
N–Bn
f1 (ppm)


Intens.
x10^4
+MS, 0.09-0.17min #(5-10)
610.1054
612.1035
611.1086
613.1063
608.0968
607.5989
614.1024
615.1039
m/z

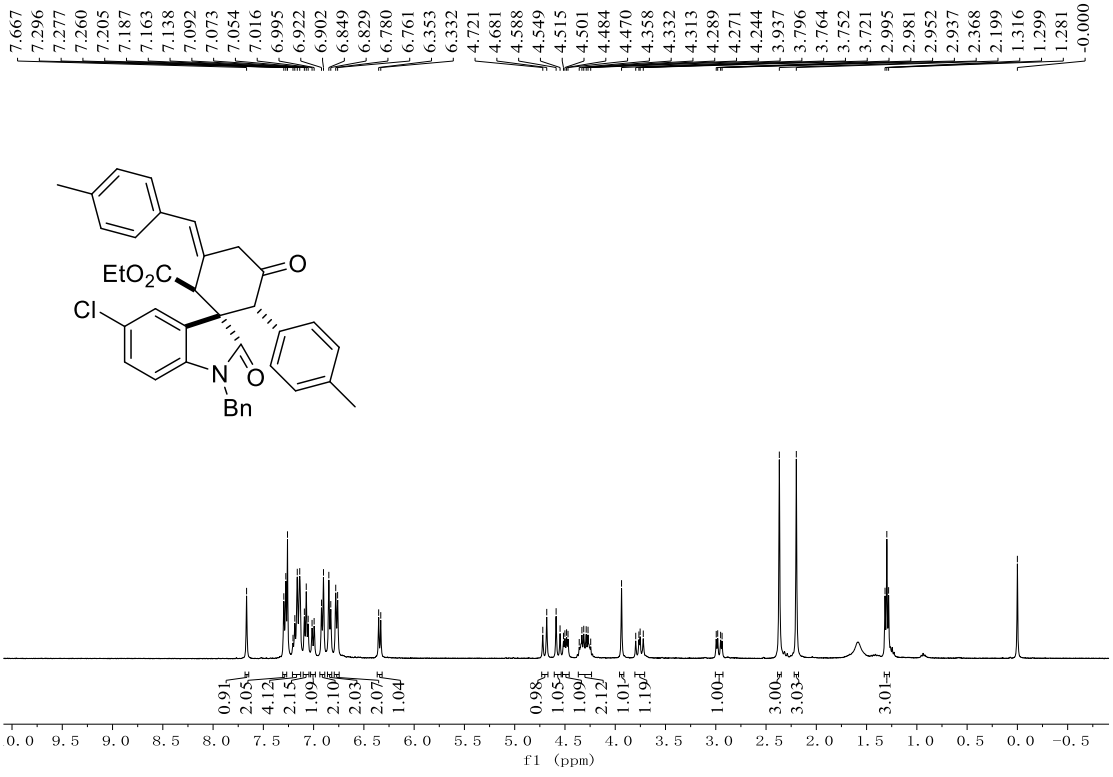
***rel*-(1*R*,3*R*)-1'-benzyl-6-((*Z*)-4-bromobenzylidene)-3-(4-bromophenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2,2-dicarbonitrile (3w)**: white solid, 50%, m.p. 221-223 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 1H, ArH), 7.59 (d, *J* = 8.0 Hz, 2H, ArH), 7.45-7.40 (m, 5H, ArH), 7.33-7.28 (m, 6H, ArH), 7.21 (d, *J* = 8.0 Hz, 2H, ArH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 6.60 (s, 1H, CH), 5.10 (d, *J* = 15.6 Hz, 1H, CH_2), 5.06-5.01 (m, 1H, CH_2), 4.88 (d, *J* = 16.0 Hz, 1H, CH_2), 3.39 (t, *J* = 14.4 Hz, 1H, CH), 3.10-3.06 (m, 1H, CH_2).^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 171.5, 143.1, 139.3, 134.1, 133.4, 132.4, 132.3, 131.7, 131.5, 131.4, 130.9, 130.6, 129.1, 128.2, 127.2, 126.5, 124.3, 124.1, 123.9, 122.6, 112.0, 111.9, 111.3, 60.1, 48.5, 44.8, 44.0, 42.3. IR (KBr) υ: 3727, 3632, 3404, 3063, 2971, 2928, 2344, 1896, 1709, 1610, 1483, 1409, 1361, 1292, 1186, 1152, 1118, 1069, 1005, 951, 893, 821, 753 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{23}NaBr_2N_3O_2$ ([M+Na]$^{+}$): 698.0055, found: 698.0007.

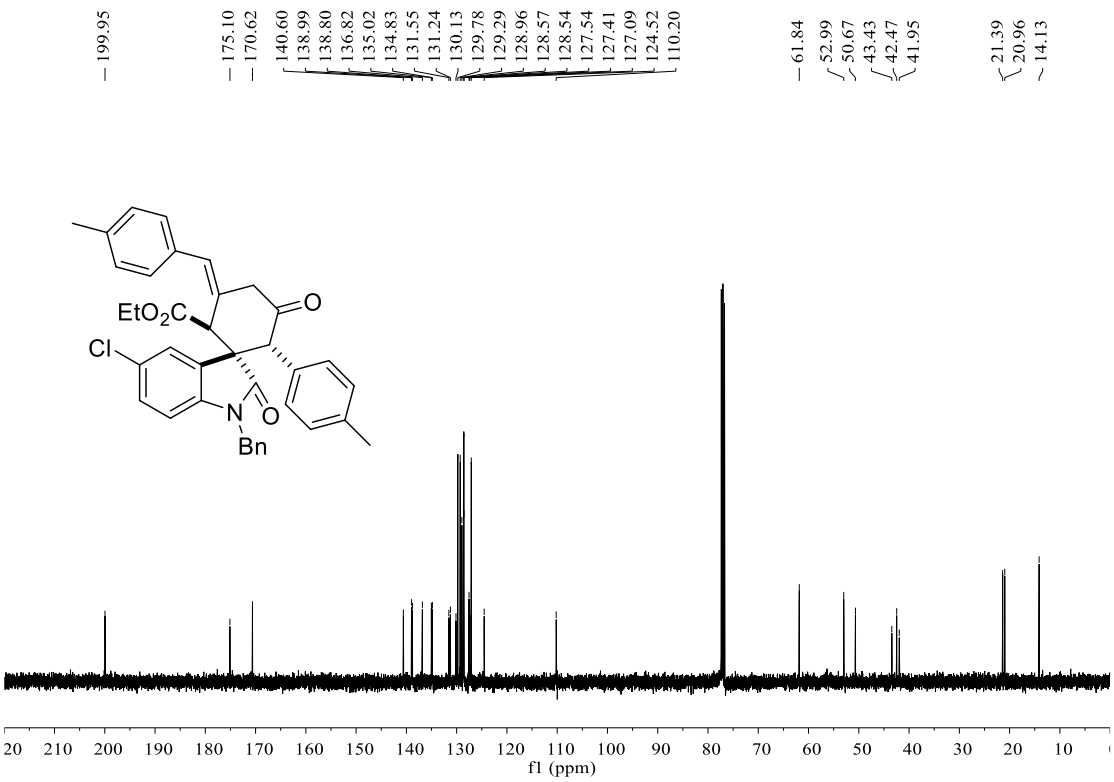


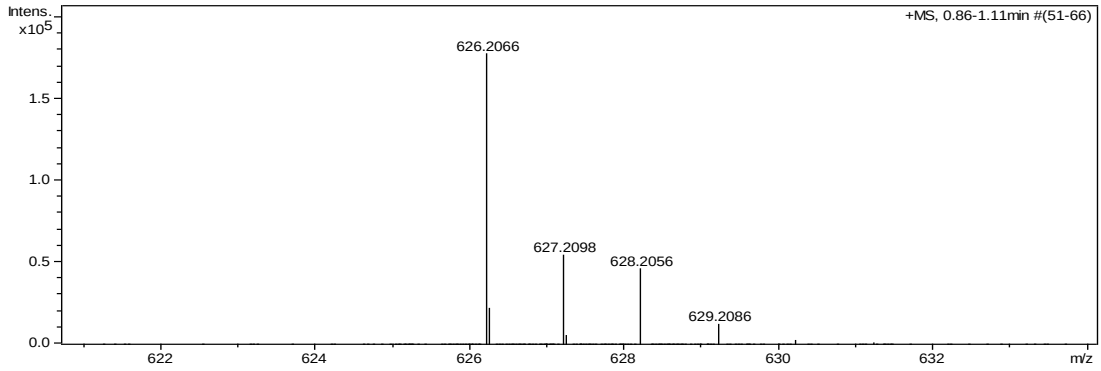

195.57
171.54
143.12
139.27
133.35
127.16
122.59
112.02
111.88
111.33
60.13
48.53
44.75
43.99
42.31
Br
O
O
Br
NC
NC
N–Bn
f1 (ppm)


Intens.
x10^4
+MS, 0.07-0.17min #(4-10)
700.0019
698.0007
702.0005
701.0046
696.9944
699.0028
695.9946
703.0031
699.4957
701.4790
704.0050
m/z

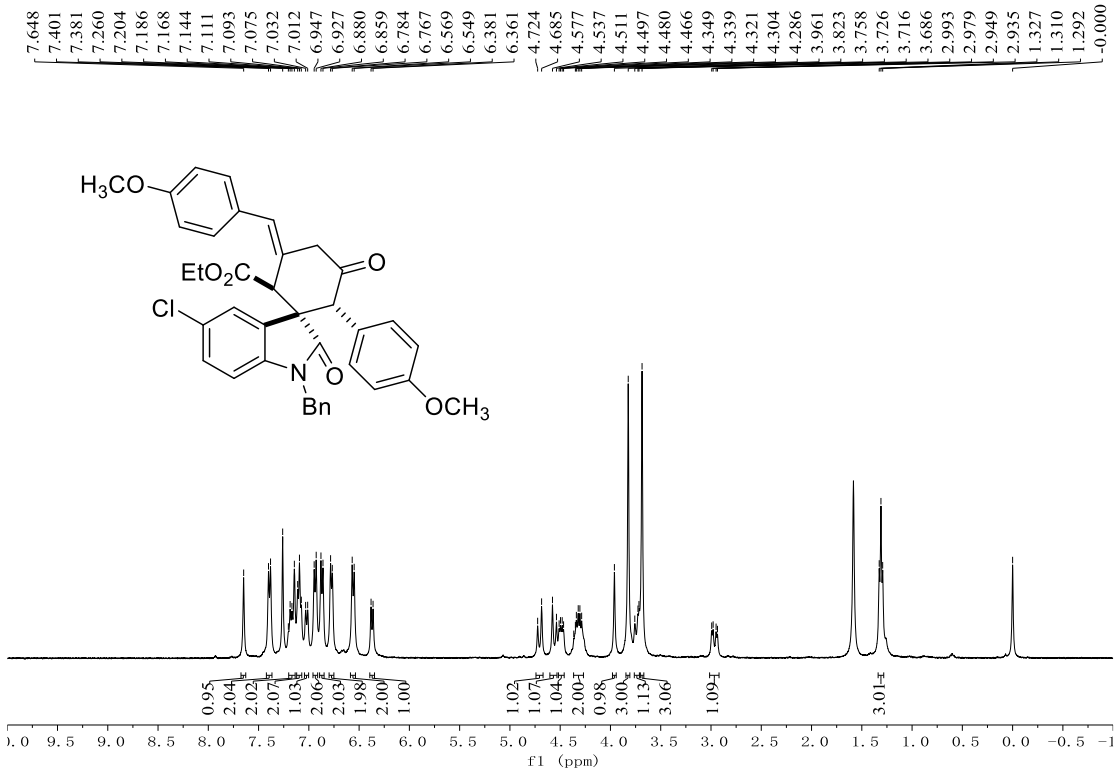
Ethyl *rel*-(1*S*,2*S*,6*R*)-1'-benzyl-5'-chloro-3-((*Z*)-4-methylbenzylidene)-2',5-dioxo-6-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2-carboxylate (5a): white solid, 60%, m.p. 221-223 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H, ArH), 7.29 (d, *J* = 7.6 Hz, 2H, ArH), 7.21-7.14 (m, 4H, ArH), 7.07 (t, *J* = 7.6 Hz, 2H, ArH), 7.01 (d, *J* = 8.4 Hz, 1H, ArH), 6.91 (d, *J* = 8.0 Hz, 2H, ArH), 6.84 (d, *J* = 8.0 Hz, 2H, ArH), 6.77 (d, *J* = 7.6 Hz, 2H, ArH), 6.34 (d, *J* = 8.4 Hz, 1H, CH), 4.70 (d, *J* = 16.0 Hz, 1H, CH_2), 4.57 (d, *J* = 15.6 Hz, 1H, CH_2), 4.52-4.47 (m, 1H, CH_2), 4.36-4.24 (m, 2H, OCH_2), 3.94 (s, 1H, CH), 3.80-3.72 (m, 1H, CH), 3.00-2.94 (m, 1H, CH_2), 2.37 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 1.30 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 175.1, 170.6, 140.6, 139.0, 138.8, 136.8, 135.0, 134.8, 131.6, 131.2, 130.1, 129.8, 129.3, 129.0, 128.6, 128.5, 127.5, 127.4, 127.1, 124.5, 110.2, 61.8, 53.0, 50.7, 43.4, 42.5, 42.0, 21.4, 21.0, 14.1. IR (KBr) υ: 3723, 3412, 2933, 2871, 2324, 1925, 1817, 1703, 1604, 1474, 1442, 1339, 1172, 1091, 1010, 904, 824, 716 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{34}ClNaNO_4$ ([M+Na]$^{+}$): 626.2069, found: 626.2066.

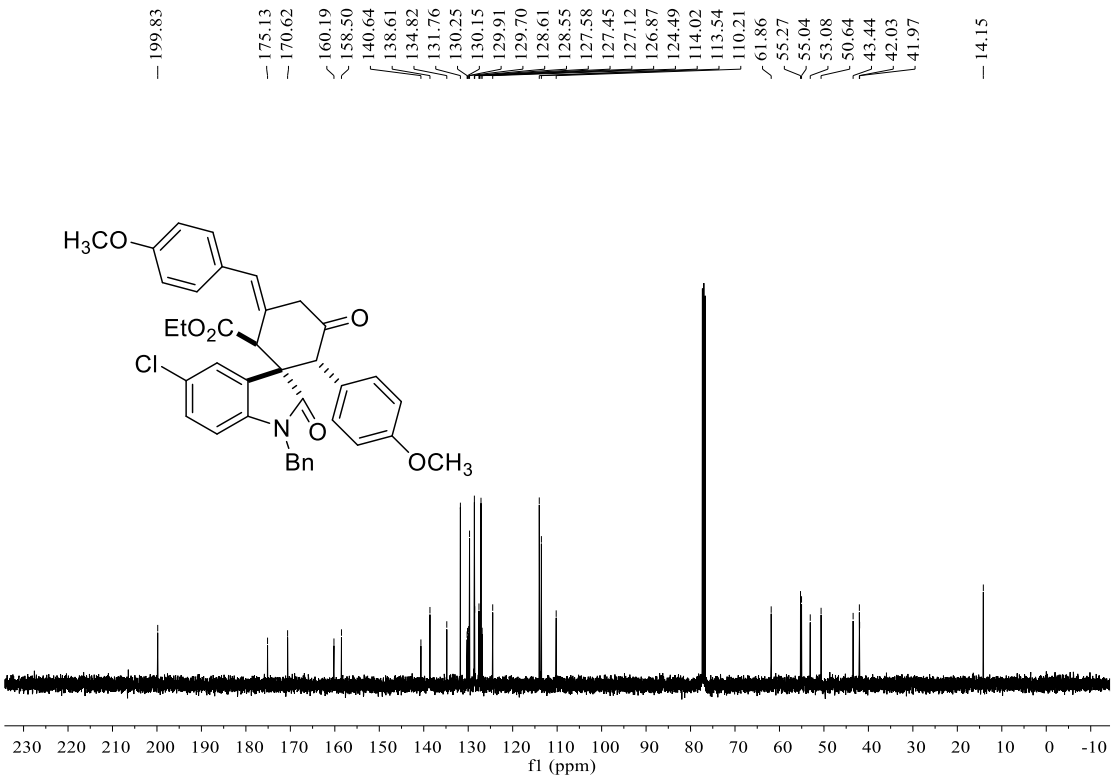


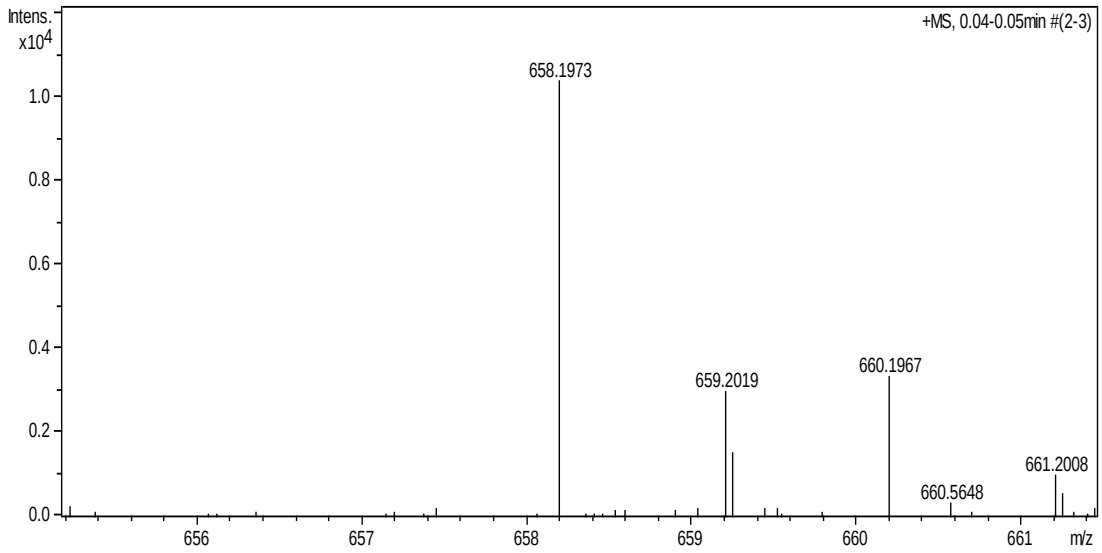

199.95
175.10
170.62
140.60
138.99
138.80
136.82
135.02
134.83
131.55
131.24
130.13
129.78
129.29
128.96
128.57
128.54
127.54
127.41
127.09
124.52
110.20
61.84
52.99
50.67
43.43
42.47
41.95
21.39
20.96
14.13
EtO2C
O
Cl
N
O
Bn
f1 (ppm)


Intens.
x10^5
+MS, 0.86-1.11min #(51-66)
626.2066
627.2098
628.2056
629.2086
m/z

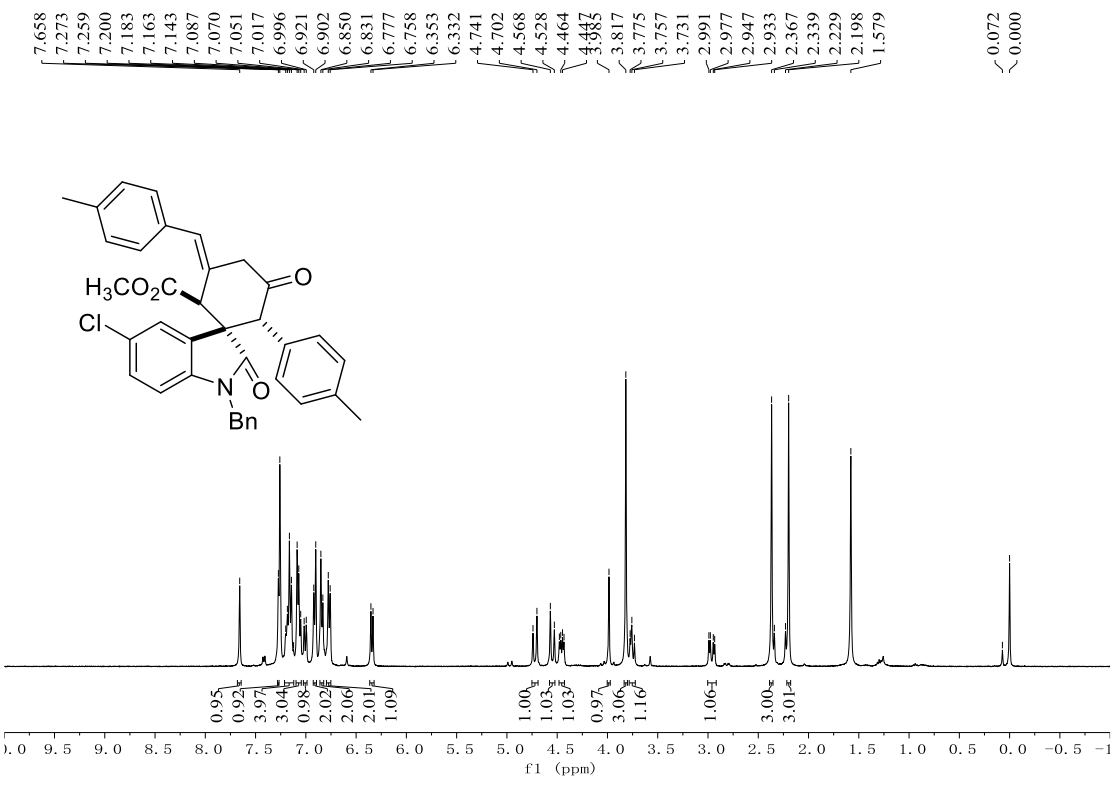
Ethyl *rel*-(1*S*,2*S*,6*R*)-1'-benzyl-5'-chloro-3-((*Z*)-4-methoxybenzylidene)-6-(4-methoxyphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2-carboxylate (5b): white solid, 57%, m.p. 231-233 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H, ArH), 7.39 (d, *J* = 8.0 Hz, 2H, ArH), 7.20-7.14 (m, 2H, ArH), 7.09 (t, *J* = 7.2 Hz, 2H, ArH), 7.02 (d, *J* = 8.0 Hz, 1H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 6.87 (d, *J* = 8.4 Hz, 2H, ArH), 6.77 (d, *J* = 6.8 Hz, 2H, ArH), 6.56 (d, *J* = 8.0 Hz, 2H, ArH), 6.37 (d, *J* = 8.0 Hz, 1H, CH), 4.70 (d, *J* = 15.6 Hz, 1H, CH_2), 4.56 (d, *J* = 16.0 Hz, 1H, CH_2), 4.51-4.47 (m, 1H, CH_2), 4.37-4.29 (m, 2H, OCH_2), 3.96 (s, 1H, CH), 3.82 (s, 3H, OCH_3), 3.76-3.72 (m, 1H, CH), 3.69 (s, 3H, OCH_3), 2.99-2.94 (m, 1H, CH_2), 1.31 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 175.1, 170.6, 160.2, 158.5, 140.6, 138.6, 134.8, 131.8, 130.3, 130.2, 129.9, 129.7, 128.6, 128.6, 127.6, 127.5, 127.1, 126.9, 124.5, 114.0, 113.5, 110.2, 61.9, 55.3, 55.0, 53.1, 50.6, 43.4, 42.0, 41.9, 14.2. IR (KBr) υ: 3734, 3410, 2940, 2843, 2421, 1930, 1843, 1715, 1623, 1443, 1340, 1065, 1003, 876, 843, 721 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{34}ClNaNO_6$ ($[M+Na]^+$): 658.1967, found: 658.1973.

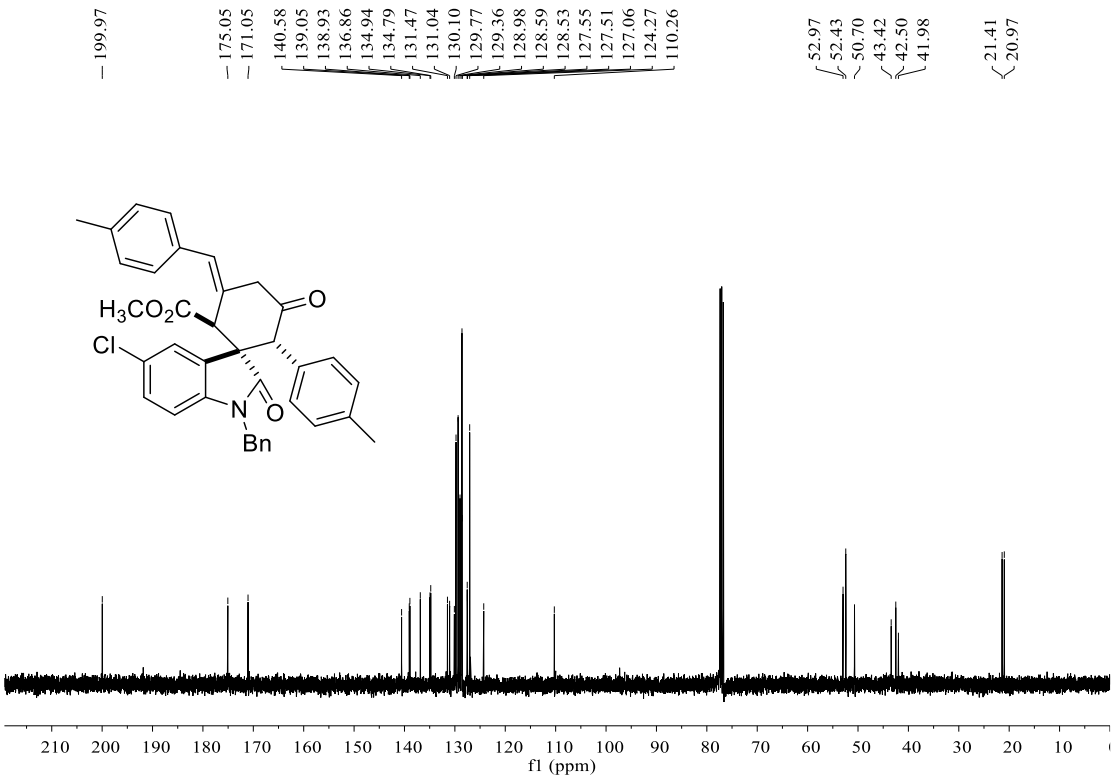


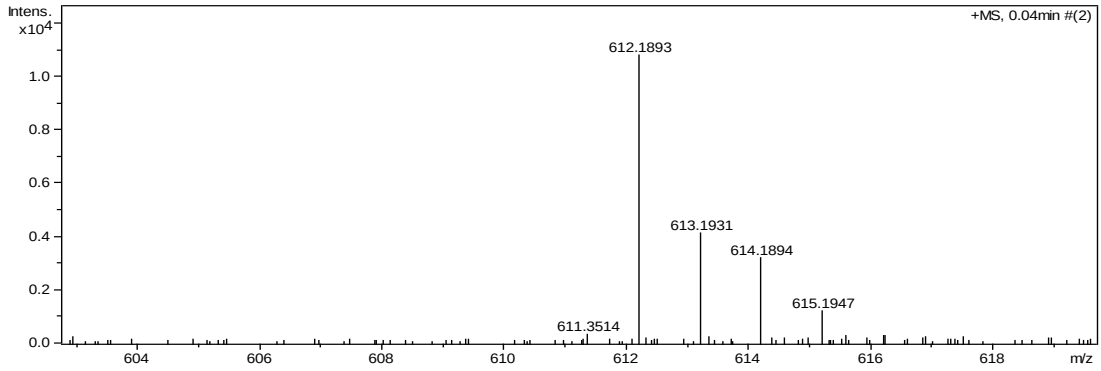

199.83
175.13
170.62
160.19
158.50
140.64
138.61
134.82
131.76
130.25
130.15
129.91
129.70
128.61
128.55
127.58
127.45
127.12
126.87
124.49
114.02
113.54
110.21
61.86
55.27
55.04
53.08
50.64
43.44
42.03
41.97
14.15
H3CO
EtO2C
O
Cl
N
O
Bn
OCH3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
x10^4
+MS, 0.04-0.05min #(2-3)
658.1973
659.2019
660.1967
661.2008
660.5648
1.0
0.8
0.6
0.4
0.2
0.0
656
657
658
659
660
661
m/z

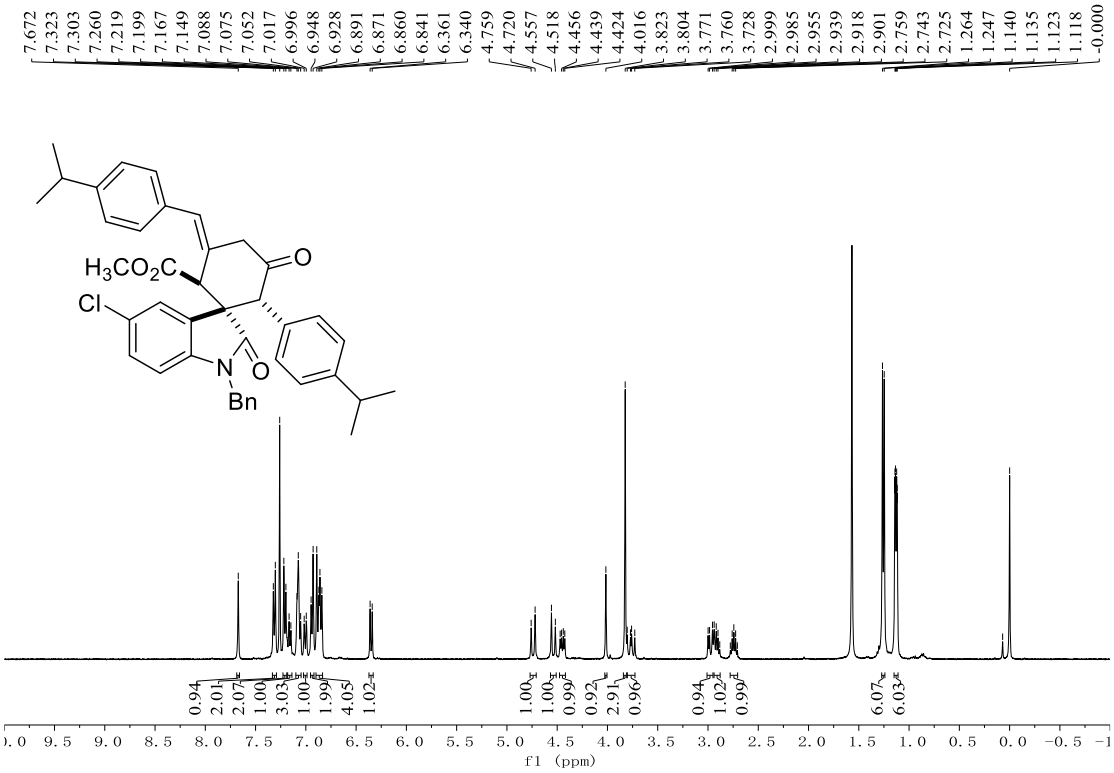
Methyl *rel*-(1*S*,2*S*,6*R*)-1'-benzyl-5'-chloro-3-((*Z*)-4-methylbenzylidene)-2',5-dioxo-6-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2-carboxylate (5c): white solid, 42%, m.p. 225-227 °C; **ratio of major/minor = 10:1**, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H, ArH), 7.27 (s, 1H, ArH), 7.20-7.12 (m, 4H, ArH), 7.09-7.05 (m, 3H, ArH), 7.01 (d, *J* = 8.4 Hz, 1H, ArH), 6.91 (d, *J* = 7.6 Hz, 2H, ArH), 6.84 (d, *J* = 7.6 Hz, 2H, ArH), 6.77 (d, *J* = 7.6 Hz, 2H, ArH), 6.32 (d, *J* = 8.4 Hz, 1H, CH), 4.72 (d, *J* = 15.6 Hz, 1H, CH_2), 4.55 (d, *J* = 16.0 Hz, 1H, CH_2), 4.48-4.43 (m, 1H, CH_2), 3.99 (s, 1H, CH), 3.82 (s, 3H, OCH_3), 3.78-3.73 (m, 1H, CH), 2.99-2.93 (m, 1H, CH_2), 2.37 (s, 3H, CH_3), 2.20 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 175.1, 171.1, 140.6, 139.1, 138.9, 136.9, 134.9, 134.8, 131.5, 131.0, 130.1, 129.8 129.4, 129.0, 128.6, 128.5, 127.6, 127.5, 127.1, 124.3, 110.3, 53.0, 52.4, 50.7, 43.4, 42.5, 42.0, 21.4, 21.0. IR (KBr) υ: 3684, 3432, 2943, 2834, 2356, 1811, 1724, 1605, 1424, 1443, 1345, 1123, 1080, 904, 859, 746 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{37}H_{32}ClNaNO_4$ ($[M+Na]^+$): 612.1912, found: 612.1893.

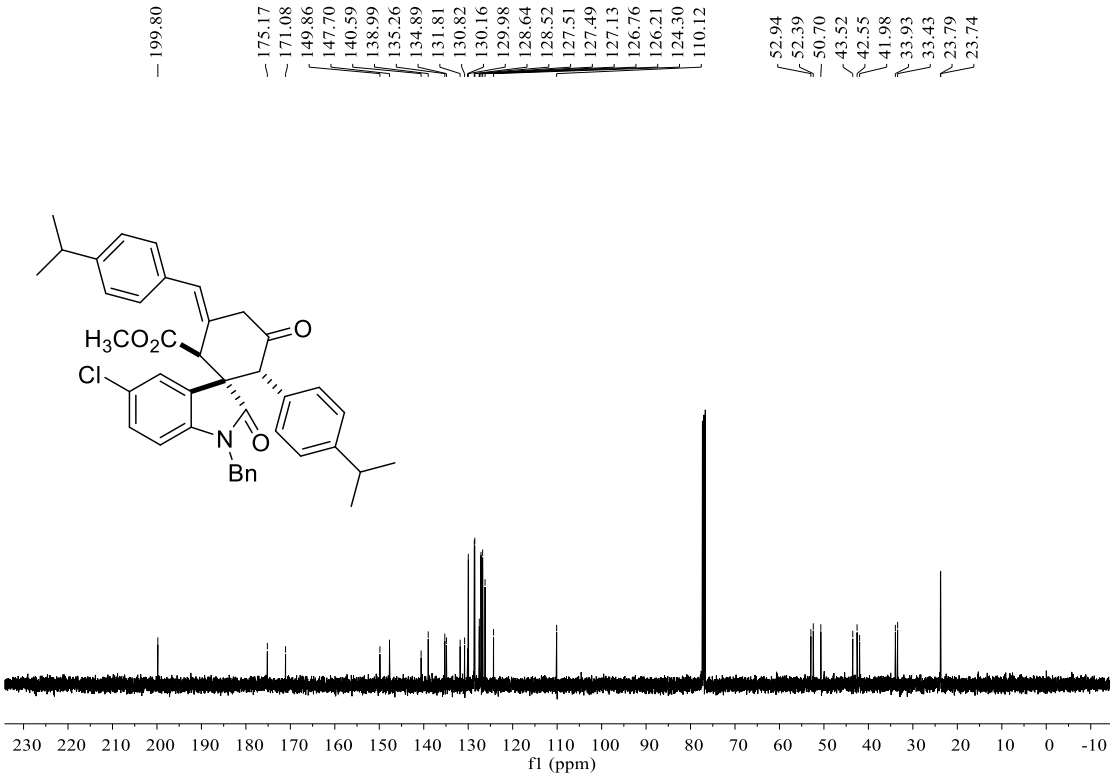


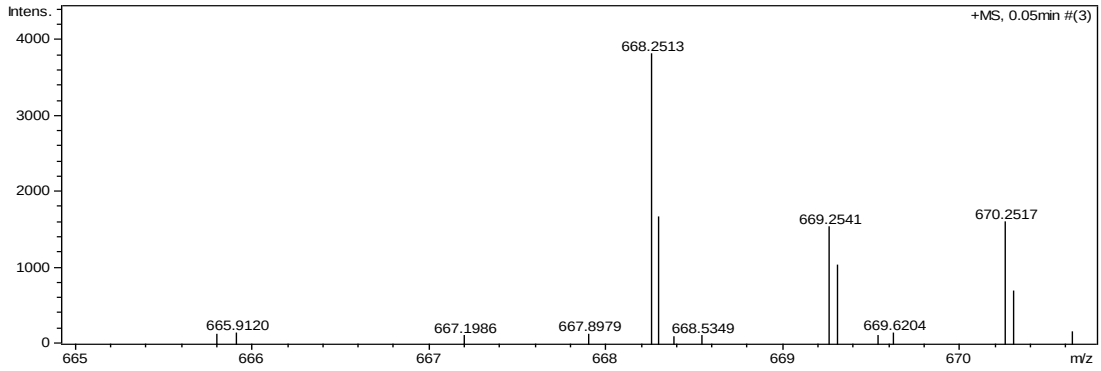

199.97
175.05
171.05
140.58
139.05
138.93
136.86
134.94
134.79
131.47
131.04
130.10
129.77
129.36
128.98
128.59
128.53
127.55
127.51
127.06
124.27
110.26
52.97
52.43
50.70
43.42
42.50
41.98
21.41
20.97
H3CO2C
Cl
O
N
O
Bn
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


Intens.
x10^4
+MS, 0.04min #(2)
612.1893
613.1931
614.1894
615.1947
611.3514
1.0
0.8
0.6
0.4
0.2
0.0
604 606 608 610 612 614 616 618
m/z

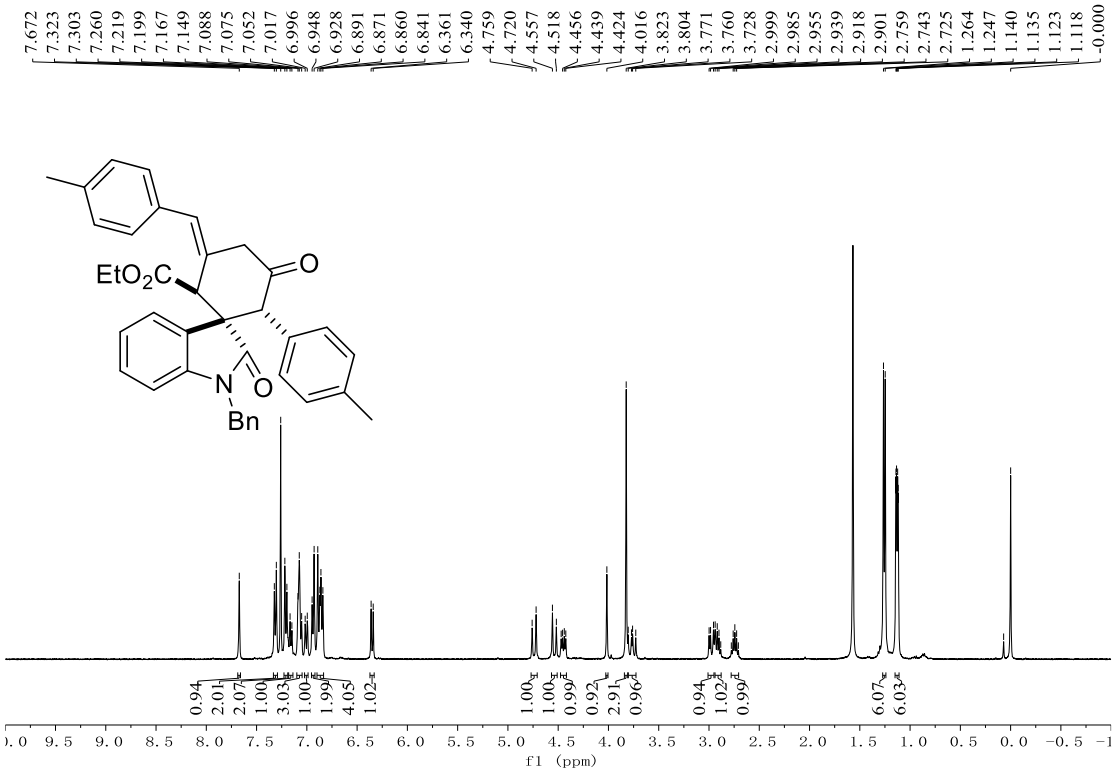
Methyl *rel*-(1*S*,2*S*,6*R*)-1'-benzyl-5'-chloro-3-((*Z*)-4-isopropylbenzylidene)-6-(4-isopropylphenyl)-2',5-dioxospiro[cyclohexane-1,3'-indoline]-2-carboxylate (5d): white solid, 58%, m.p. 226-228 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H, ArH), 7.31 (d, *J* = 8.0 Hz, 2H, ArH), 7.21 (d, *J* = 8.0 Hz, 2H, ArH), 7.16 (t, *J* = 7.2 Hz, 1H, ArH), 7.09-7.05 (m, 3H, ArH), 7.01 (d, *J* = 8.4 Hz, 1H, ArH), 6.94 (d, *J* = 8.0 Hz, 2H, ArH), 6.89-6.84 (m, 4H, ArH), 6.35 (d, *J* = 8.0 Hz, 1H, CH), 4.74 (d, *J* = 15.6 Hz, 1H, CH_2), 4.54 (d, *J* = 15.6 Hz, 1H, CH_2), 4.47-4.42 (m, 1H, CH_2), 4.02 (s, 1H, CH), 3.82 (s, 3H, OCH_3), 3.80-3.72 (m, 1H, CH), 3.00-2.96 (m, 1H, CH_2), 2.94-2.88 (m, 1H, CH), 2.78-2.71 (m, 1H, CH), 1.25 (d, *J* = 6.8 Hz, 6H, CH_3), 1.14-1.12 (m, 6H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 175.2, 171.1, 149.9, 147.7, 140.6, 139.0, 135.3, 134.9, 131.8, 130.8, 130.2, 130.0, 128.6, 128.5, 127.5, 127.5, 127.1, 126.8, 126.2, 124.3, 110.1, 52.9, 52.4, 50.7, 43.5, 42.6, 42.0, 33.9, 33.4, 23.8, 23.7. IR (KBr) υ: 3735, 3398, 2889, 2314, 1924, 1878, 1734, 1615, 1434, 1415, 1365, 1145, 1045, 904, 835, 745 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{41}H_{40}ClNaNO_4$ ($[M+Na]^+$): 668.2538, found: 668.2513.

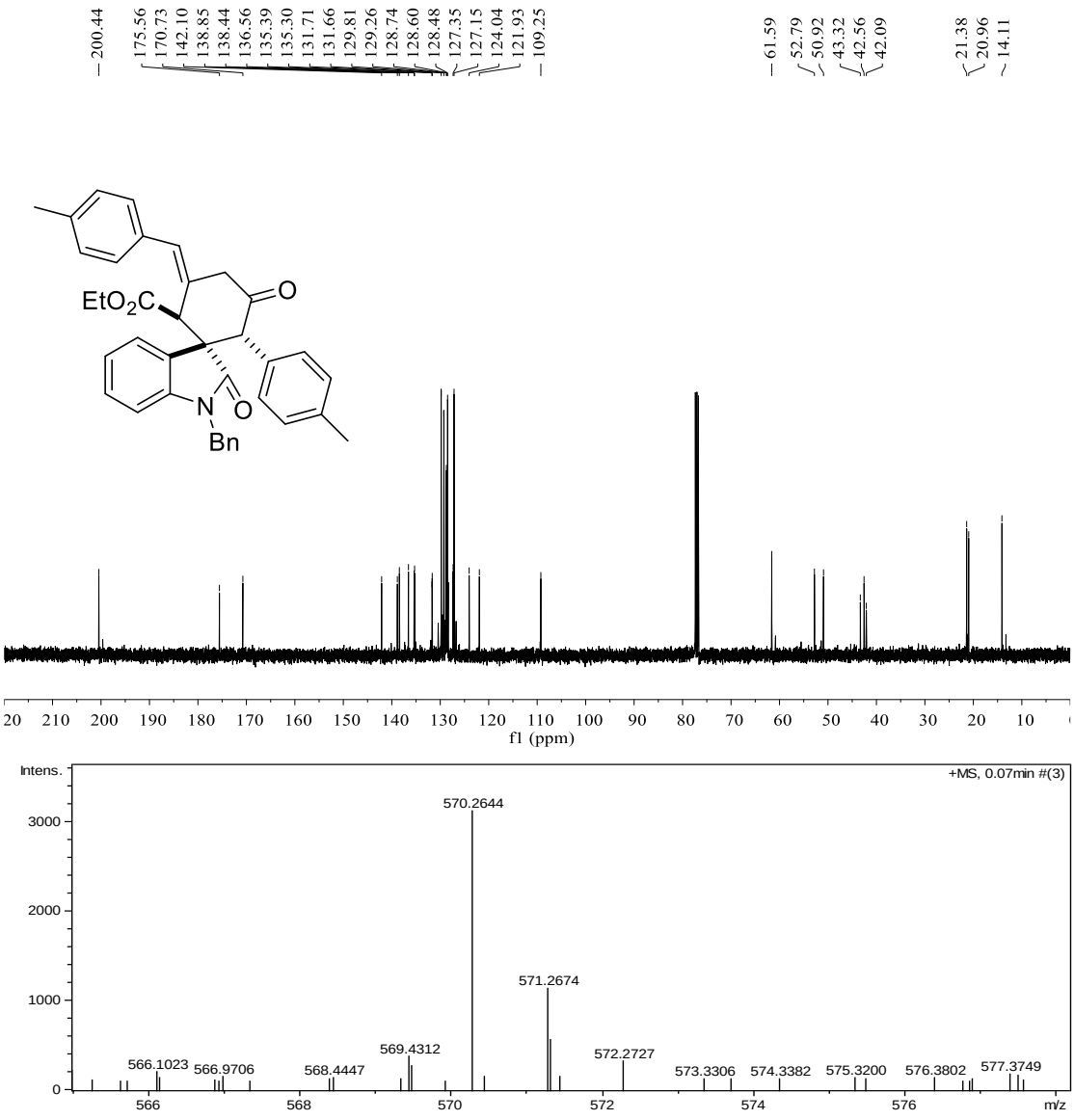



199.80
175.17
171.08
149.86
147.70
140.59
138.99
135.26
134.89
131.81
130.82
130.16
129.98
128.64
128.52
127.51
127.49
127.13
126.76
126.21
124.30
110.12
52.94
52.39
50.70
43.52
42.55
41.98
33.93
33.43
23.79
23.74
H3CO2C
O
Cl
N
O
Bn
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Intens.
+MS, 0.05min #(3)
4000
3000
2000
1000
0
668.2513
669.2541
670.2517
665.9120
667.1986
667.8979
668.5349
669.6204
665
666
667
668
669
670
m/z

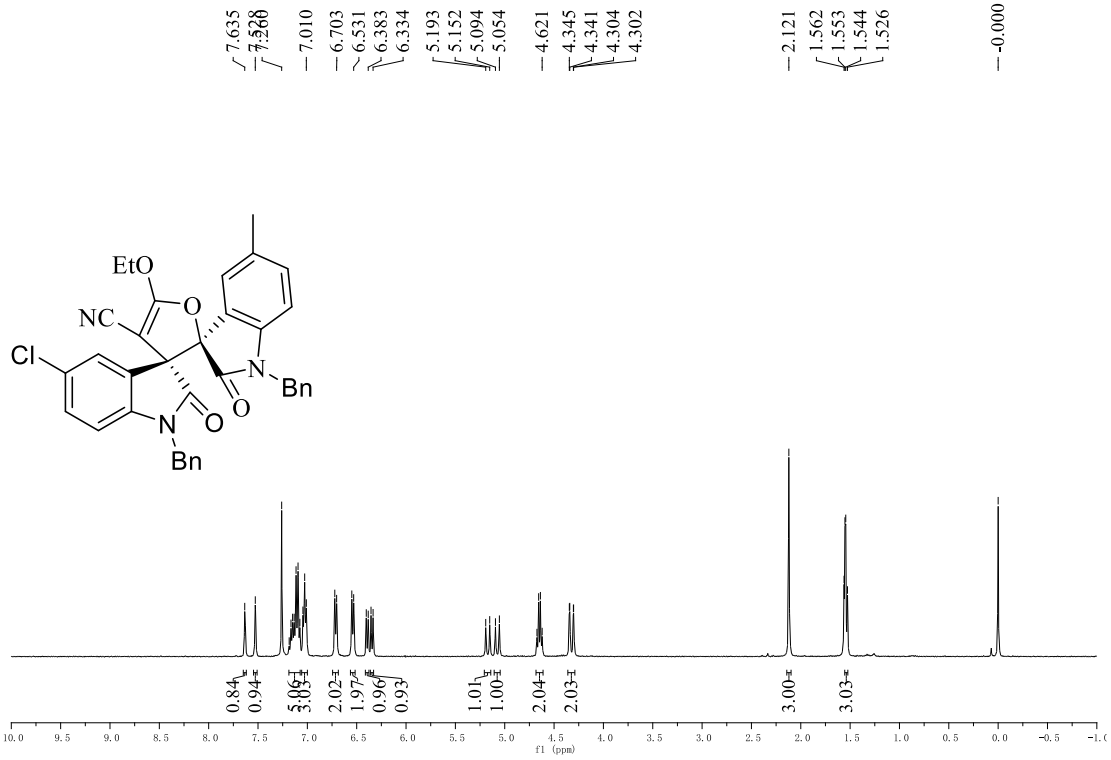
Ethyl *rel*-(1*S*,2*S*,6*R*)-1'-benzyl-3-((*Z*)-4-methylbenzylidene)-2',5-dioxo-6-(*p*-tolyl)spiro[cyclohexane-1,3'-indoline]-2-carboxylate (5e): white solid, 56%, m.p. 236-238 °C; **ratio of major/minor = 9:1,** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H, ArH), 7.29 (d, *J* = 7.6 Hz, 2H, ArH), 7.19-7.13 (m, 5H, ArH), 7.08 (d, *J* = 7.2 Hz, 1H, ArH), 7.03 (d, *J* = 8.0 Hz, 1H, ArH), 6.95 (d, *J* = 7.6 Hz, 1H, ArH), 6.90 (d, *J* = 7.6 Hz, 2H, ArH), 6.81-6.78 (m, 4H, ArH), 6.44 (d, *J* = 8.0 Hz, 1H, CH), 4.72 (d, *J* = 15.6 Hz, 1H, CH_2), 4.57 (d, *J* = 15.6 Hz, 1H, CH_2), 4.55-4.52 (m, 1H, CH_2), 4.39-4.31 (m, 1H, OCH_2), 4.23-4.16 (m, 1H, OCH_2), 3.96 (s, 1H, CH), 3.83-3.75 (1, 1H, CH), 2.99-2.93 (m, 1H, CH_2), 2.36 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 1.27 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 175.6, 170.7, 142.1, 138.9, 138.4, 136.6, 135.4, 135.3, 131.7, 131.7, 129.8, 129.3, 128.7, 128.6, 128.5, 127.4, 127.2, 124.0, 121.9, 109.3, 61.6, 52.8, 50.9, 43.3, 42.6, 42.1, 21.4, 21.0, 14.1. IR (KBr) υ: 3710, 2987, 2925, 1893, 1795, 1670, 1600, 1463, 1370, 1308, 1175, 1105, 1028, 900, 816, 744 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{38}H_{36}NO_4$ ($[M+H]^+$): 570.2639, found: 570.2644.

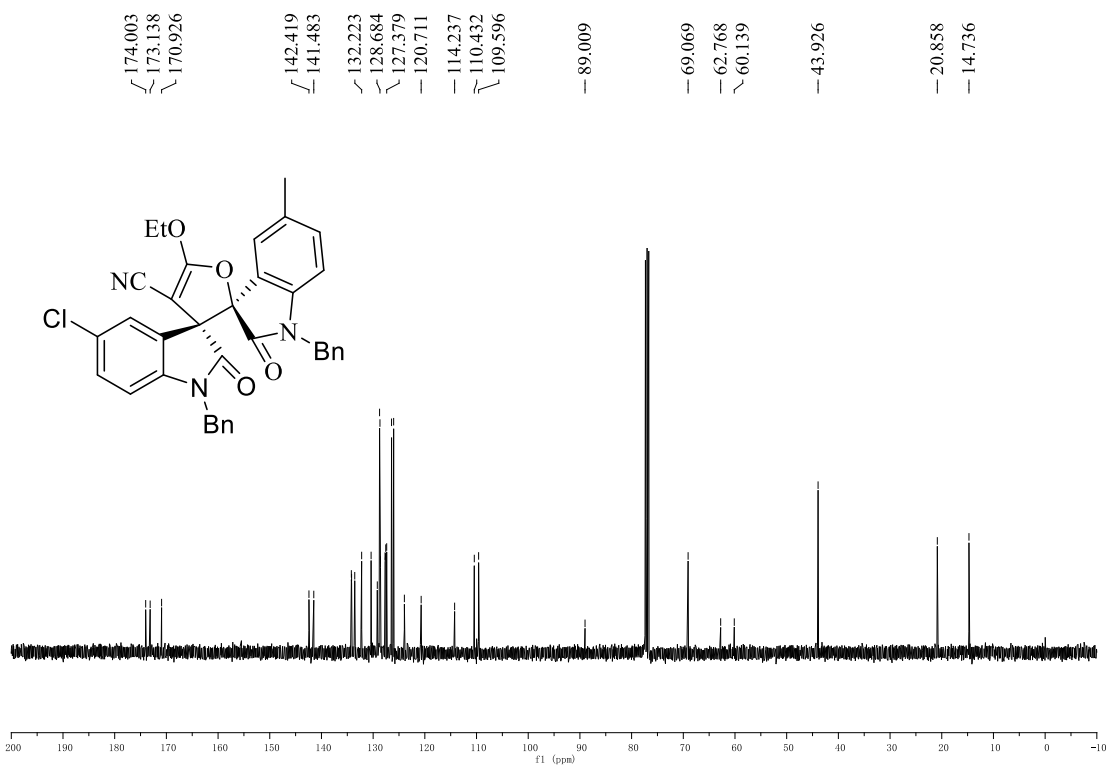


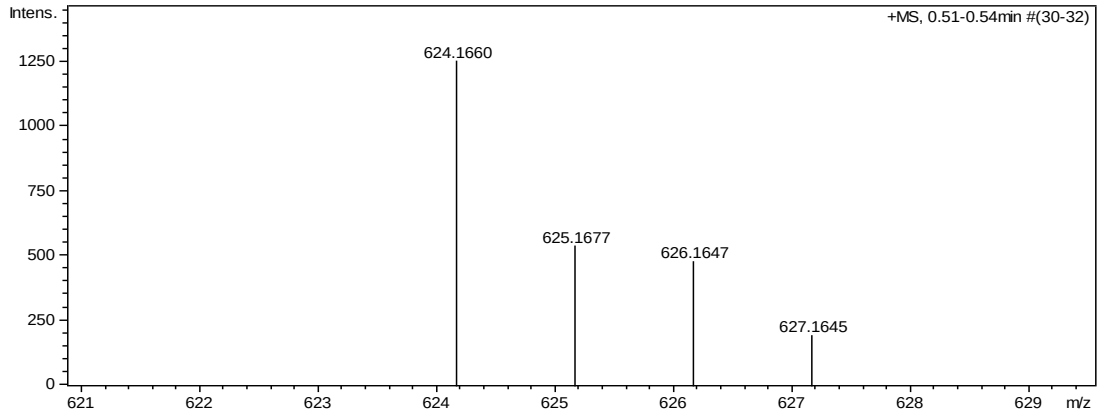

200.44
175.56
170.73
142.10
138.85
138.44
136.56
135.39
135.30
131.71
131.66
129.81
129.26
128.74
128.60
128.48
127.35
127.15
124.04
121.93
109.25
61.59
52.79
50.92
43.32
42.56
42.09
21.38
20.96
14.11
EtO2C
O
N
O
Bn
f1 (ppm)

Intens.
+MS, 0.07min #(3)
570.2644
571.2674
569.4312
572.2727
566.1023
566.9706
568.4447
573.3306
574.3382
575.3200
576.3802
577.3749
m/z

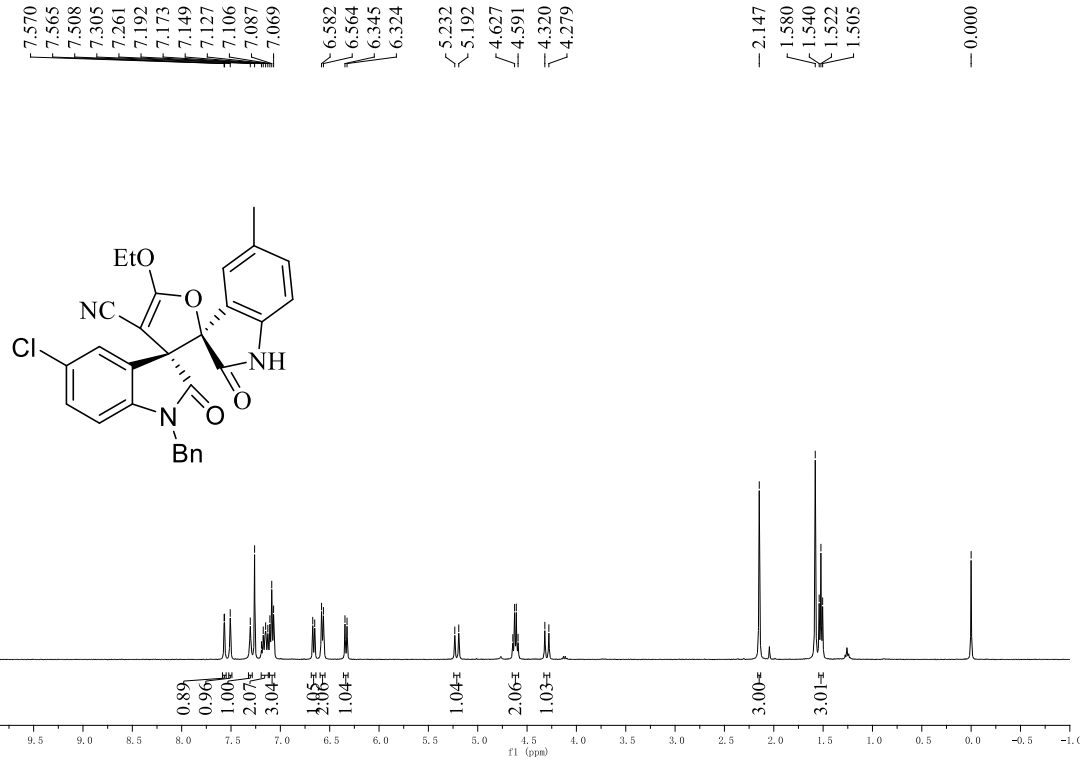
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8a)**: white solid, 71%, m.p. 175-177 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H, ArH), 7.53 (s, 1H, ArH), 7.18-7.08 (m, 5H, ArH), 7.03 (t, *J* = 6.8 Hz, 3H, ArH), 6.71 (d, *J* = 7.6 Hz, 2H, ArH), 6.54 (d, *J* = 7.2 Hz, 2H, ArH), 6.39 (d, *J* = 8.0 Hz, 1H, ArH), 6.34 (d, *J* = 8.4 Hz, 1H, ArH), 5.17 (d, *J* = 16.4 Hz, 1H, CH_2), 5.07 (d, *J* = 16.0 Hz, 1H, CH_2), 4.65 (q, *J* = 7.2 Hz, 2H, CH_2), 4.35-4.30 (m, 2H, CH_2), 2.12 (s, 3H, CH_3), 1.54 (t, *J* = 7.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.0, 173.1, 170.9, 142.4, 141.5, 134.2, 134.2, 133.6, 132.2, 130.4, 129.2, 128.8, 128.7, 128.6, 127.7, 127.6, 127.4, 126.4, 126.0, 124.0, 120.7, 114.2, 110.4, 109.6, 89.0, 69.1, 62.8, 60.1, 43.9, 20.9, 14.7. IR (KBr) υ: 3467, 3063, 3035, 2990, 2919, 2205, 1739, 1706, 1632, 1602, 1496, 1454, 1434, 1408, 1381, 1361, 1333, 1293, 1258, 1215, 1199, 1186, 1167, 1133, 1089, 1070, 1026, 997, 962, 933, 911, 895, 875, 836, 818, 776, 747 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{28}NaClN_3O_4$ ([M+Na]$^{+}$): 624.1666, found: 624.1660.

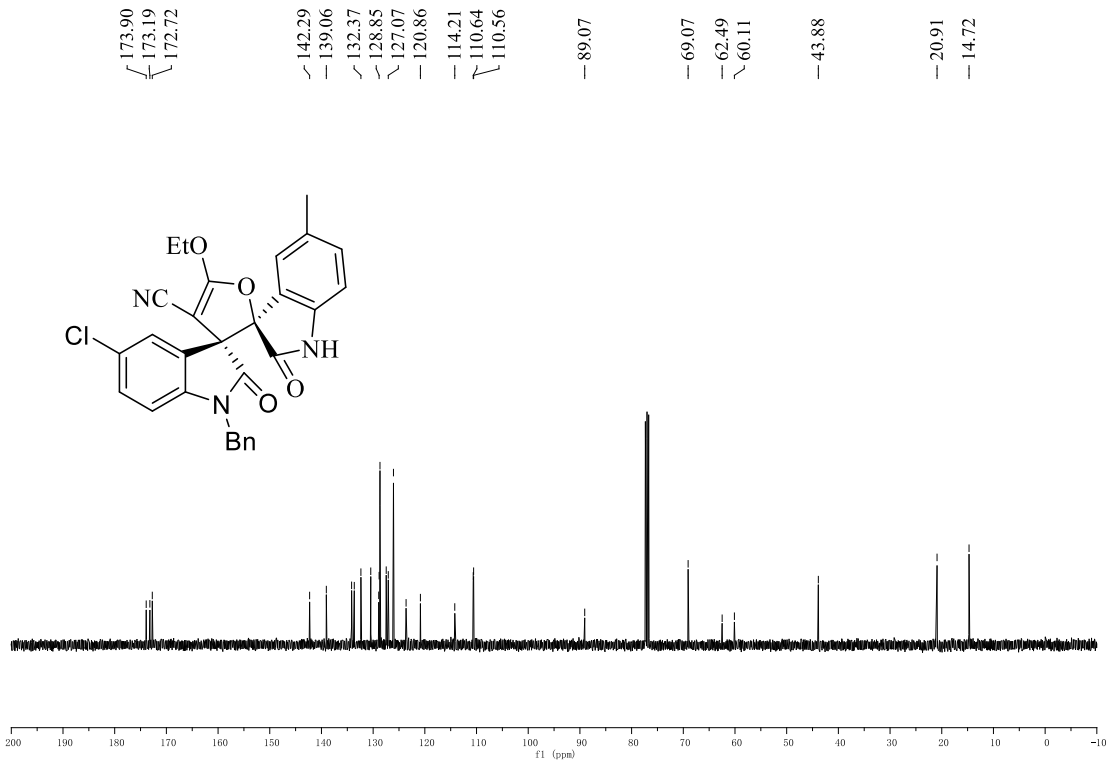


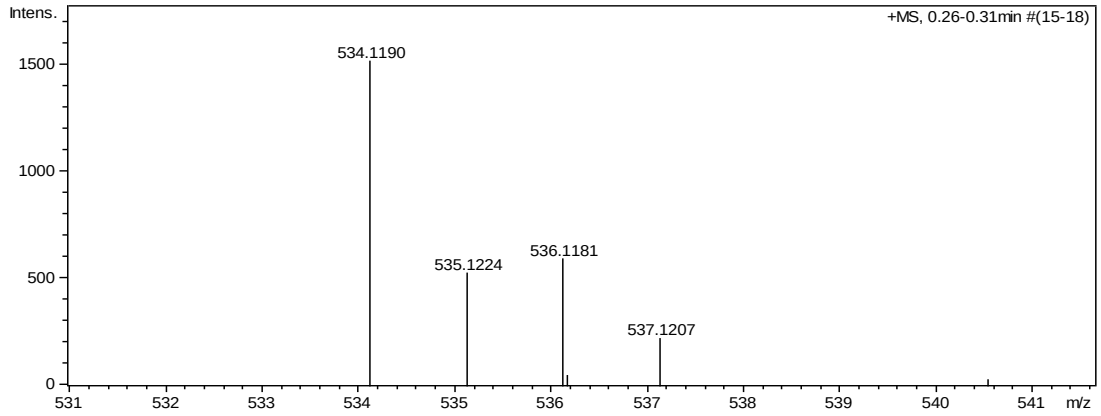

174.003
173.138
170.926
142.419
141.483
132.223
128.684
127.379
120.711
114.237
110.432
109.596
89.009
69.069
62.768
60.139
43.926
20.858
14.736
EtO
NC
O
Cl
N
Bn
O
N
O
Bn
f1 (ppm)


Intens.
+MS, 0.51-0.54min #(30-32)
624.1660
625.1677
626.1647
627.1645
m/z

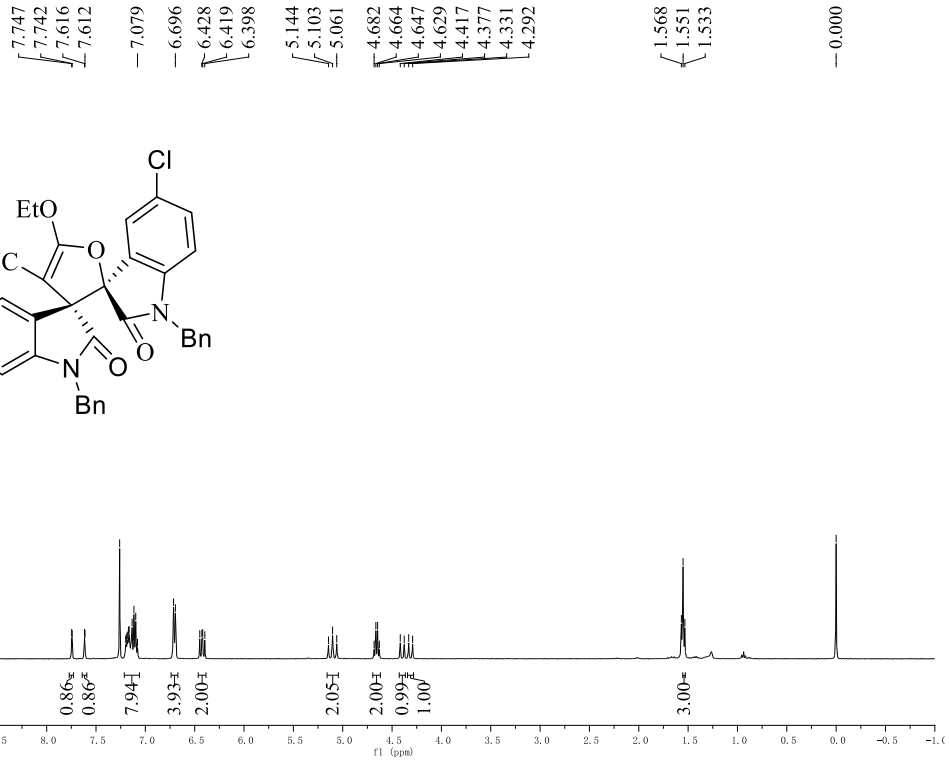
***rel*-(3*R*,3'*R*)-1''-benzyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8b)**: white solid, 70%, m.p. 140-142 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.0 Hz, 1H, ArH), 7.51 (s, 1H, NH), 7.31 (s, 1H, ArH), 7.19-7.13 (m, 2H, ArH), 7.11-7.07 (m, 3H, ArH), 6.66 (d, *J* = 8.0 Hz, 1H, ArH), 6.57 (d, *J* = 7.2 Hz, 2H, ArH), 6.34 (d, *J* = 8.4 Hz, 1H, ArH), 5.21 (d, *J* = 16.0 Hz, 1H, CH_2), 4.62 (q, *J* = 7.2 Hz, 2H, CH_2), 4.30 (d, *J* = 16.4 Hz, 1H, CH_2), 2.15 (s, 3H, CH_3), 1.52 (t, *J* = 7.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 173.2, 172.7, 142.3, 139.1, 134.2, 133.7, 132.4, 130.5, 128.9, 128.9, 128.7, 127.5, 127.1, 126.1, 123.6, 120.9, 114.2, 110.6, 110.6, 89.1, 69.1, 62.5, 60.1, 43.9, 20.9, 14.7. IR (KBr) υ: 3610, 3281, 3087, 3032, 3005, 2920, 2862, 2206, 1743, 1724, 1700, 1628, 1481, 1454, 1430, 1406, 1380, 1342, 1260, 1214, 1169, 1150, 1115, 1064, 1033, 999, 951, 928, 897, 824, 791, 765, 744, 722 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{29}H_{22}NaClN_3O_4$ ([M+Na]$^{+}$): 534.1197, found: 534.1190.

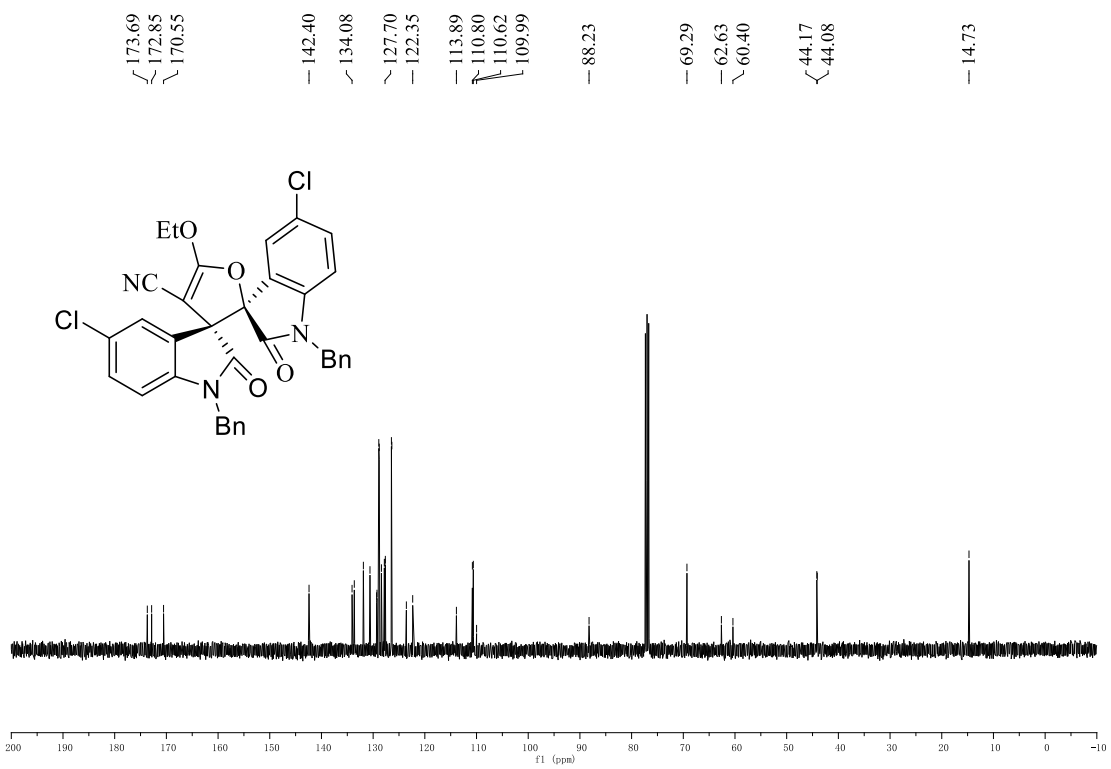


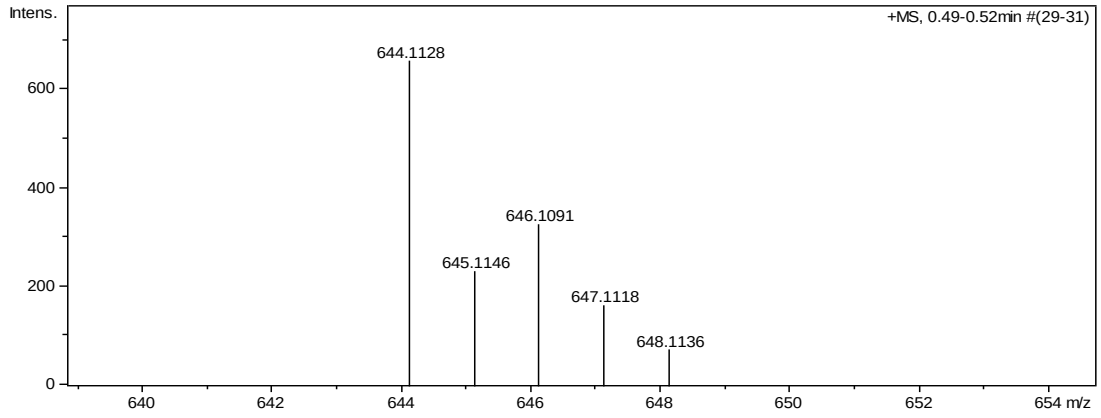

173.90
173.19
172.72
142.29
139.06
132.37
128.85
127.07
120.86
114.21
110.64
110.56
89.07
69.07
62.49
60.11
43.88
20.91
14.72
EtO
NC
O
Cl
NH
O
O
N
Bn
f1 (ppm)


Intens.
+MS, 0.26-0.31min #(15-18)
534.1190
535.1224
536.1181
537.1207
m/z

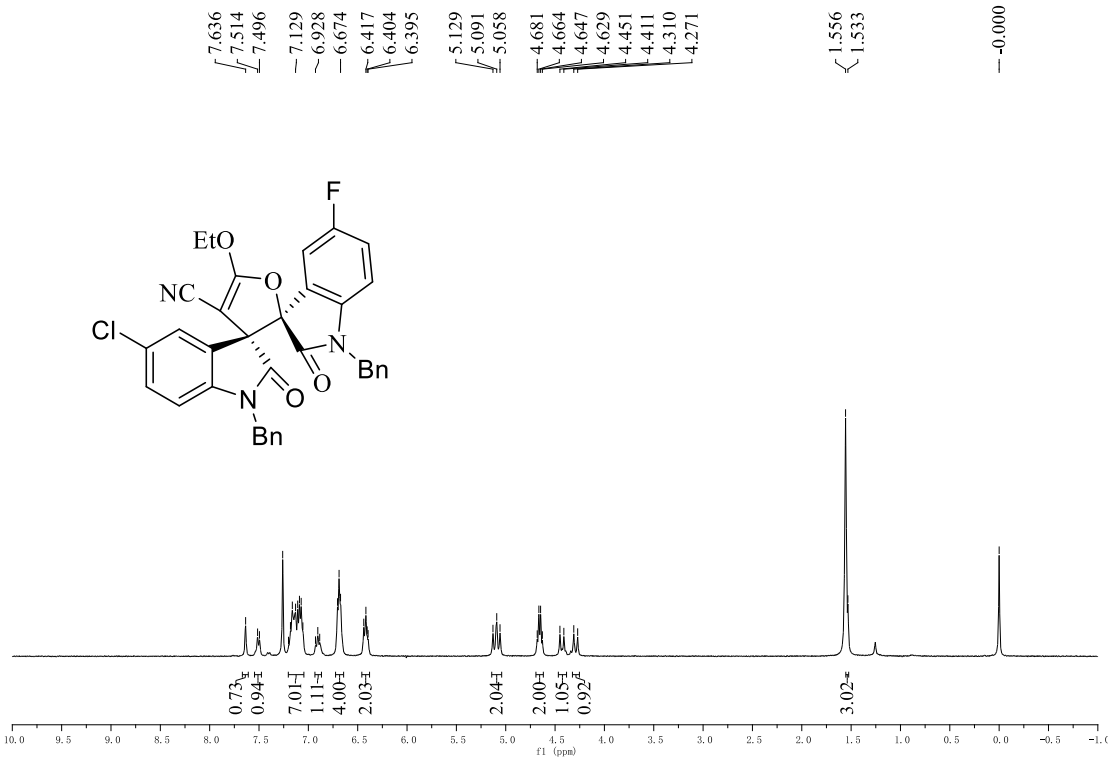
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5,5''-dichloro-5'-ethoxy-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8c)**: lilac solid, 57%, m.p. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.74 (m, 1H, ArH), 7.62-7.61 (m, 1H, ArH), 7.19-7.08 (m, 8H, ArH), 6.70 (d, *J* = 7.2 Hz, 4H, ArH), 6.45-6.40 (m, 2H, ArH), 5.10 (t, *J* = 16.4 Hz, 2H, CH_2), 4.65 (q, *J* = 6.8 Hz, 2H, CH_2), 4.40 (d, *J* = 16.0 Hz, 1H, CH_2), 4.31 (d, *J* = 15.6 Hz, 1H, CH_2), 1.55 (t, *J* = 7.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.9, 170.6, 142.4, 134.1, 133.7, 131.9, 130.6, 129.3, 129.3, 128.9, 128.8, 128.4, 127.9, 127.7, 127.6, 126.5, 126.4, 123.6, 122.4, 113.9, 110.8, 110.6, 110.0, 88.2, 69.3, 62.6, 60.4, 44.2, 44.1, 14.7. IR (KBr) υ: 3108, 3061, 3034, 2993, 2928, 2868, 2208, 1895, 1816, 1729, 1644, 1609, 1484, 1428, 1413, 1377, 1357, 1334, 1250, 1217, 1177, 1151, 1121, 1079, 995, 946, 903, 826, 752 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{25}NaCl_2N_3O_4$ ([M+Na]$^+$): 644.1120, found: 644.1128.

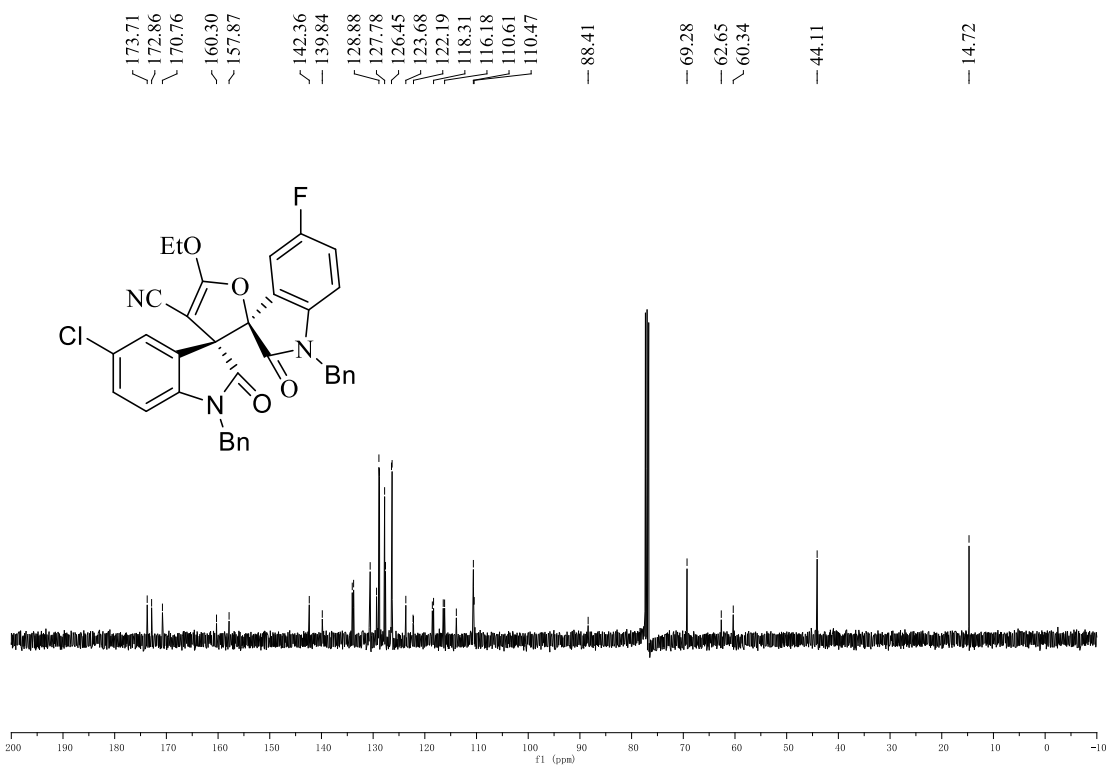


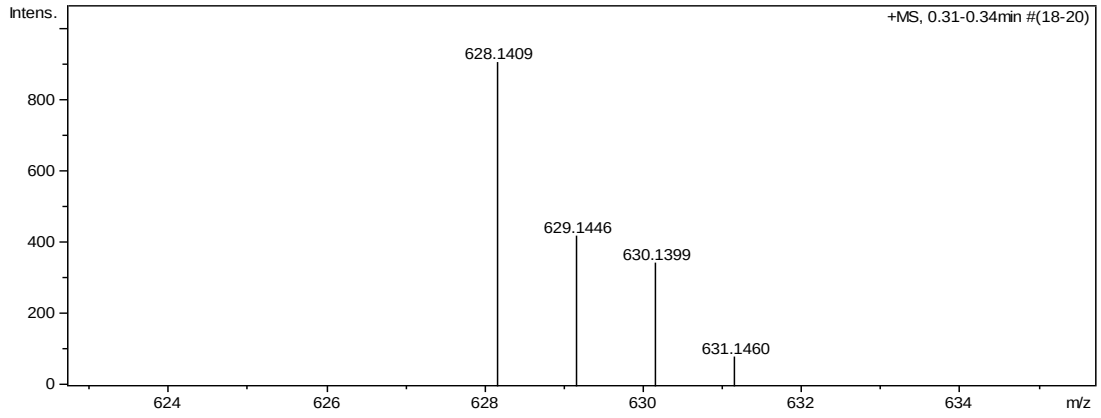

173.69
172.85
170.55
142.40
134.08
127.70
122.35
113.89
110.80
110.62
109.99
88.23
69.29
62.63
60.40
44.17
44.08
14.73
Cl
EtO
NC
O
Cl
N
Bn
O
N
O
Bn
f1 (ppm)


Intens.
+MS, 0.49-0.52min #(29-31)
644.1128
646.1091
645.1146
647.1118
648.1136
m/z

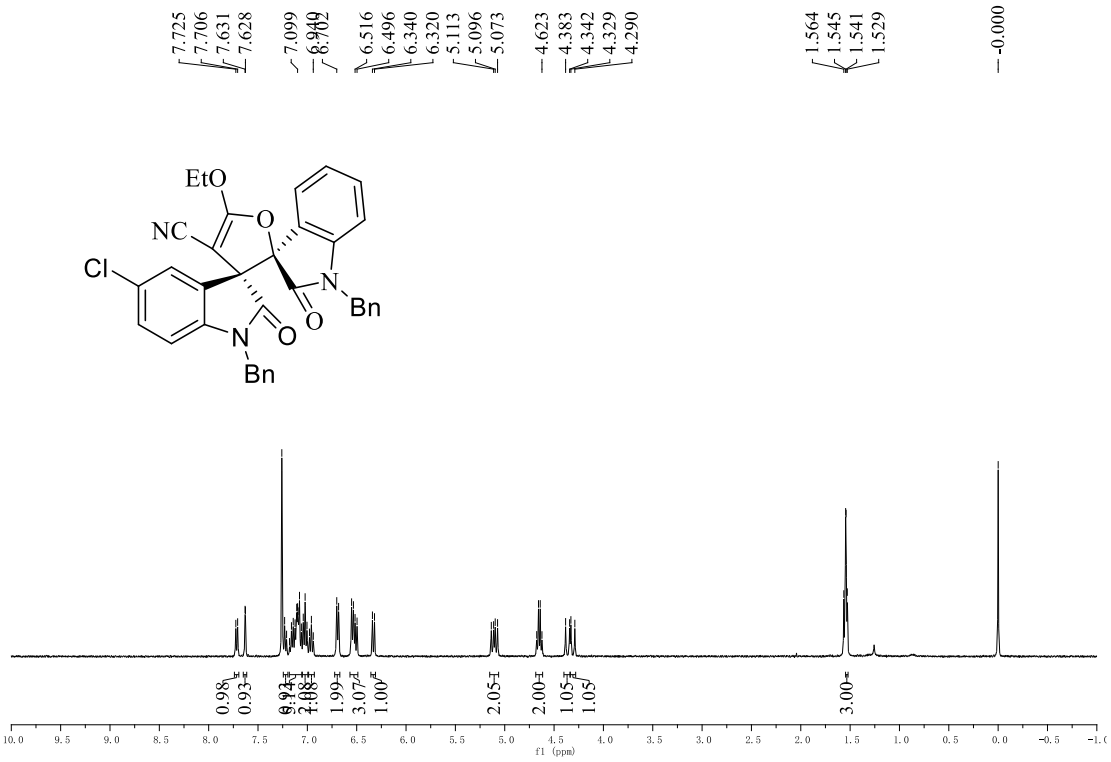
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5''-chloro-5'-ethoxy-5-fluoro-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8d)**: white solid, 56%, m.p. 137-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H, ArH), 7.50 (d, *J* = 7.2 Hz, 1H, ArH), 7.20-7.06 (m, 7H, ArH), 6.90 (t, *J* = 7.6 Hz, 1H, ArH), 6.70-6.67 (m, 4H, ArH), 6.44-6.40 (m, 2H, ArH), 5.09 (t, *J* = 15.2 Hz, 2H, CH_2), 4.65 (q, *J* = 6.8 Hz, 2H, CH_2), 4.43 (d, *J* = 16.0 Hz, 1H, CH_2), 4.29 (d, *J* = 15.6 Hz, 1H, CH_2), 1.55 (t, *J* = 9.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 172.9, 170.8, 159.1 (d, *J* = 243.0 Hz), 142.4, 139.8, 134.0, 133.8, 130.6, 129.3, 128.9, 128.8, 127.8, 127.6, 126.5, 126.3, 123.7, 122.2 (d, *J* = 9.0 Hz), 118.4 (d, *J* = 24.0 Hz), 116.3 (d, *J* = 26.0 Hz), 113.9, 110.6, 110.5 (d, *J* = 8.0 Hz), 88.4, 69.3, 62.7, 60.3, 44.1, 14.7. IR (KBr) υ: 3062, 3036, 2993, 2929, 2868, 2209, 1883, 1728, 1643, 1489, 1453, 1412, 1378, 1336, 1273, 1217, 1178, 1152, 1117, 1078, 998, 954, 925, 899, 879, 846, 828, 785, 763, 748, 700 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{25}NaClFN_3O_4$ ([M+Na]$^+$): 628.1415, found: 628.1409.

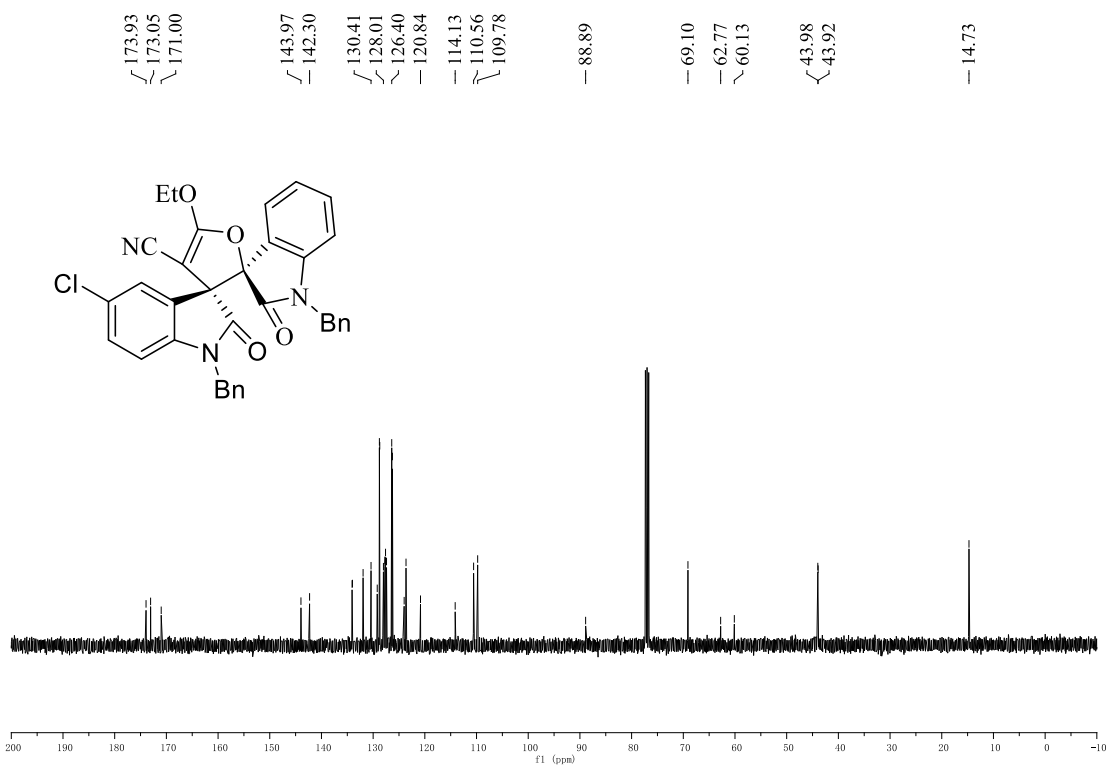


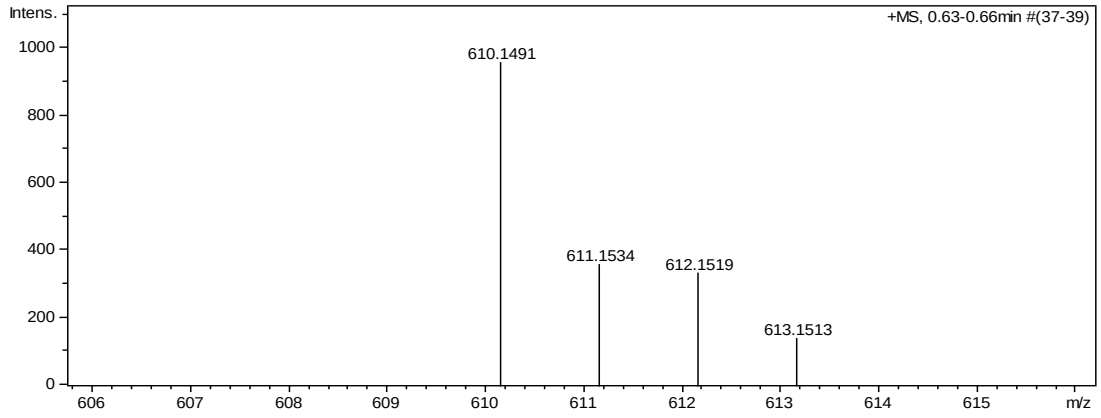

173.71
172.86
170.76
160.30
157.87
142.36
139.84
128.88
127.78
126.45
123.68
122.19
118.31
116.18
110.61
110.47
88.41
69.28
62.65
60.34
44.11
14.72
F
EtO
NC
O
Cl
N
Bn
O
N
O
Bn
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Intens.
+MS, 0.31-0.34min #(18-20)
628.1409
629.1446
630.1399
631.1460
800
600
400
200
0
624
626
628
630
632
634
m/z

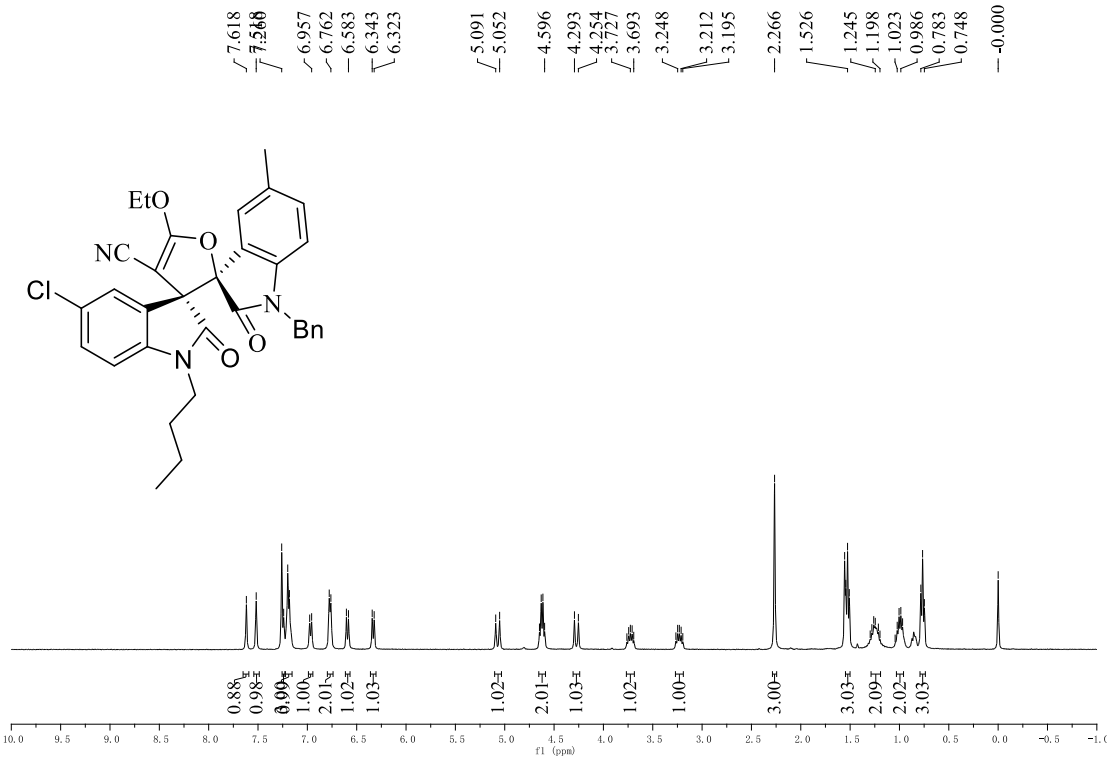
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5''-chloro-5'-ethoxy-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8e)**: white solid, 54%, m.p. 170-172 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H, ArH), 7.63 (d, *J* = 1.2 Hz, 1H, ArH), 7.22 (d, *J* = 7.2 Hz, 1H, ArH), 7.18-7.06 (m, 5H, ArH), 7.02 (t, *J* = 7.6 Hz, 2H, ArH), 6.96 (t, *J* = 7.6 Hz, 1H, ArH), 6.69 (d, *J* = 7.6 Hz,, 2H, ArH), 6.55-6.50 (m, 3H, ArH), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 5.14-5.07 (m, 2H, CH_2), 4.65 (q, *J* = 7.2 Hz, 2H, CH_2), 4.36 (d, *J* = 16.4 Hz, 1H, CH_2), 4.31 (d, *J* = 15.6 Hz, 1H, CH_2), 1.55 (t, *J* = 4.8 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 173.1, 171.0, 144.0, 142.3, 134.1, 134.0, 132.0, 130.4, 129.2, 128.8, 128.7, 128.0, 127.8, 127.6, 127.4, 126.4, 126.3, 124.0, 123.64, 120.8, 114.1, 110.6, 109.8, 88.9, 69.1, 62.8, 60.1, 44.0, 43.9, 14.7. IR (KBr) υ: 3063, 3034, 2986, 2936, 2207, 1727, 1641, 1611, 1484, 1467, 1429, 1412, 1378, 1336, 1251, 1213, 1178, 1150, 1112, 1079, 991, 942, 917, 904, 823, 769, 745 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{26}NaClN_3O_4$ ($[M+Na]^+$): 610.1510, found: 610.1491.

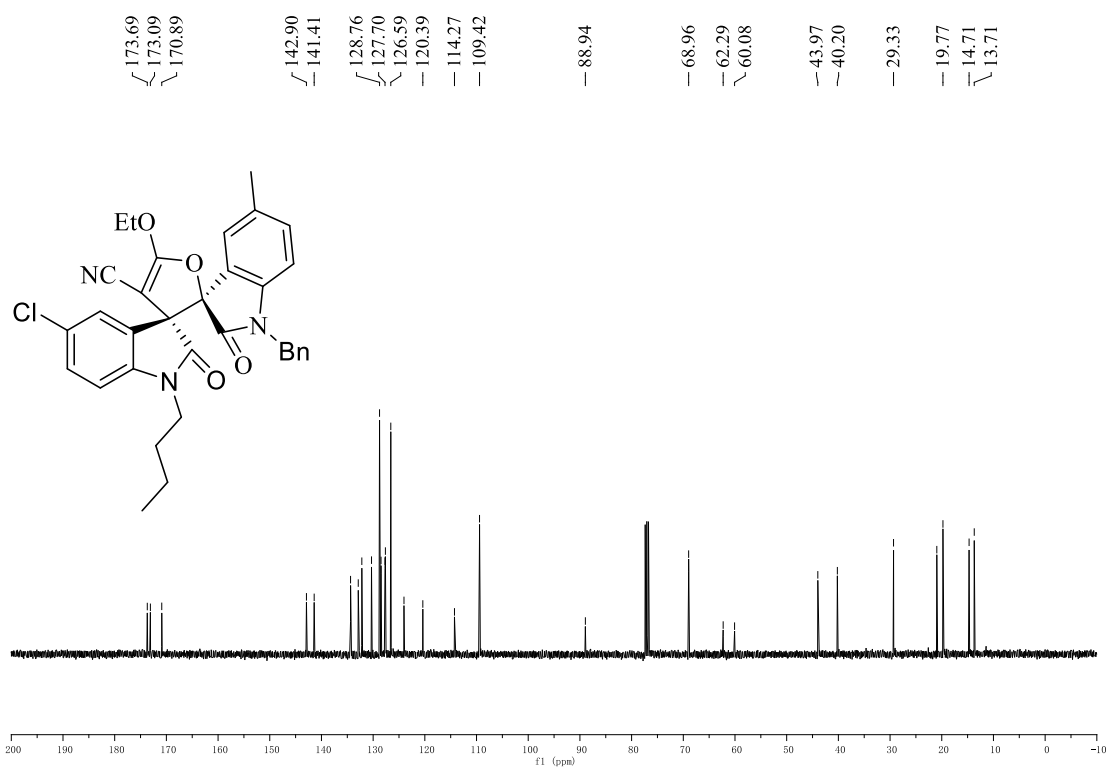


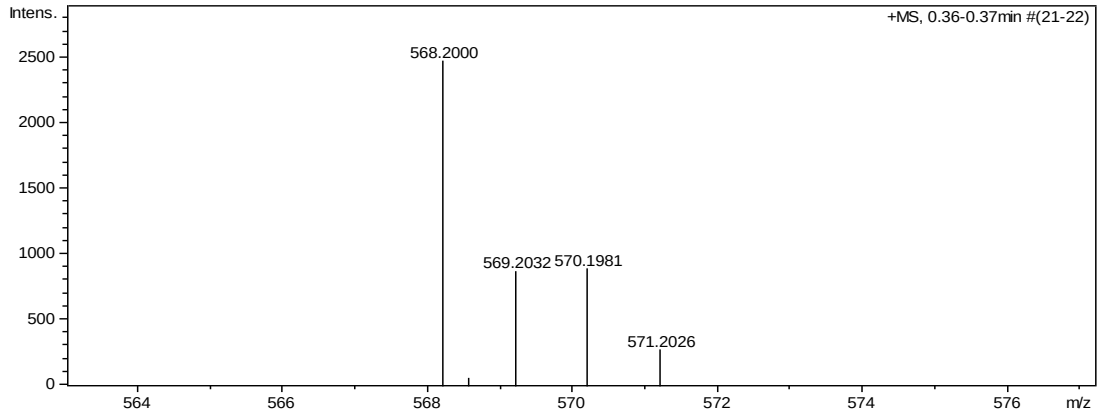

173.93
173.05
171.00
143.97
142.30
130.41
128.01
126.40
120.84
114.13
110.56
109.78
88.89
69.10
62.77
60.13
43.98
43.92
14.73
EtO
NC
O
Cl
N
Bn
O
O
N
Bn
f1 (ppm)


Intens.
+MS, 0.63-0.66min #(37-39)
1000
800
600
400
200
0
610.1491
611.1534
612.1519
613.1513
606
607
608
609
610
611
612
613
614
615
m/z

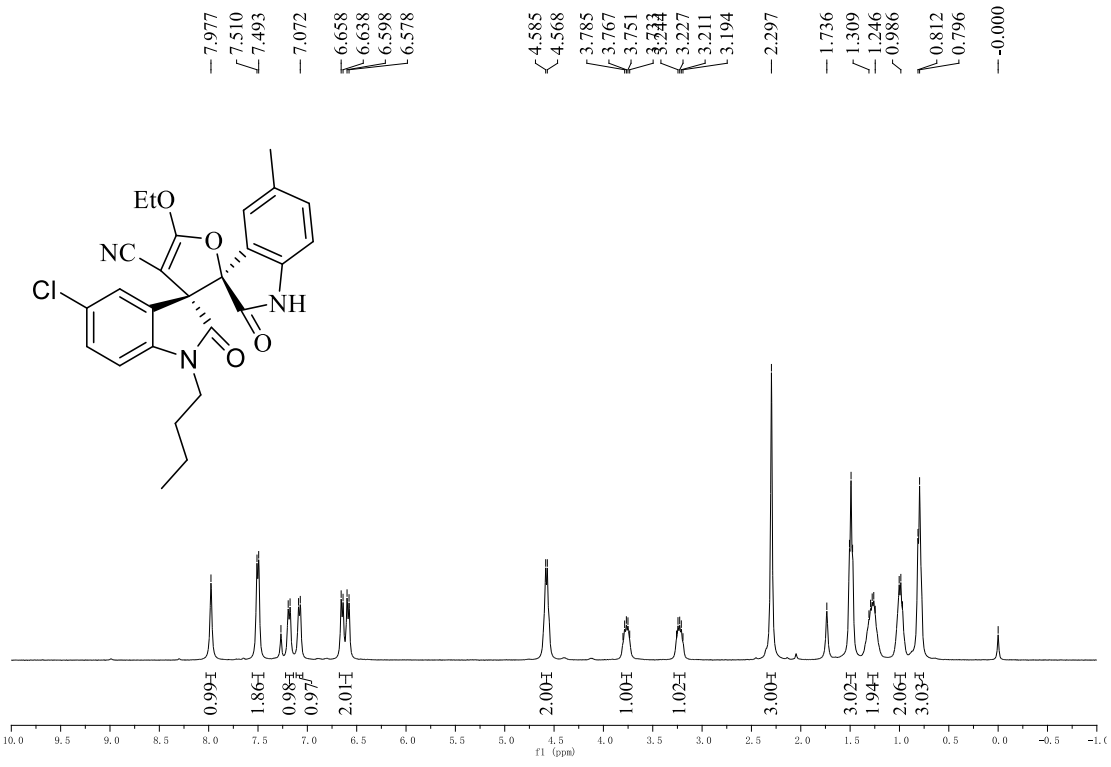
***rel*-(3*R*,3'*R*)-1-benzyl-1''-butyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8f)**: white solid, 76%, m.p. 142-144 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H, ArH), 7.52 (s, 1H, ArH), 7.24 (s, 1H, ArH), 7.20-7.18 (m, 3H, ArH), 6.97 (d, *J* = 7.6 Hz, 1H, ArH), 6.77 (d, *J* = 6.4 Hz, 2H, ArH), 6.59 (d, *J* = 8.4 Hz, 1H, ArH), 6.33 (d, *J* = 8.0 Hz, 1H, ArH), 5.07 (d, *J* = 15.6 Hz,, 1H, CH_2), 4.62 (q, *J* = 6.8 Hz, 2H, CH_2), 4.27 (d, *J* = 15.6 Hz, 1H, CH_2), 3.76-3.69 (m, 1H, CH_2), 3.27-3.20 (m, 1H, CH_2), 2.27 (s, 3H, CH_3), 1.53 (t, *J* = 6.8 Hz, 3H, CH_3), 1.30-1.20 (m, 2H, CH_2), 1.04-0.97 (m, 2H, CH_2), 0.77 (t, *J* = 7.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.7, 173.1, 170.9, 142.9, 141.4, 134.4, 132.9, 132.2, 130.3, 128.8, 128.5, 127.7, 127.6, 126.6, 124.0, 120.4, 114.3, 109.4, 88.9, 69.0, 62.3, 60.1, 44.0, 40.2, 29.3, 21.0, 19.8, 14.7, 13.7. IR (KBr) υ: 3664, 3434, 3068, 3035, 2959, 2933, 2871, 2741, 2202, 1952, 1885, 1724, 1659, 1635, 1607, 1494, 1430, 1408, 1379, 1336, 1261, 1210, 1168, 1147, 1107, 1072, 997, 951, 928, 897, 846, 819, 729 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{33}H_{31}ClN_3O_4$ ([M+H]$^{+}$): 568.2003, found: 568.2000.

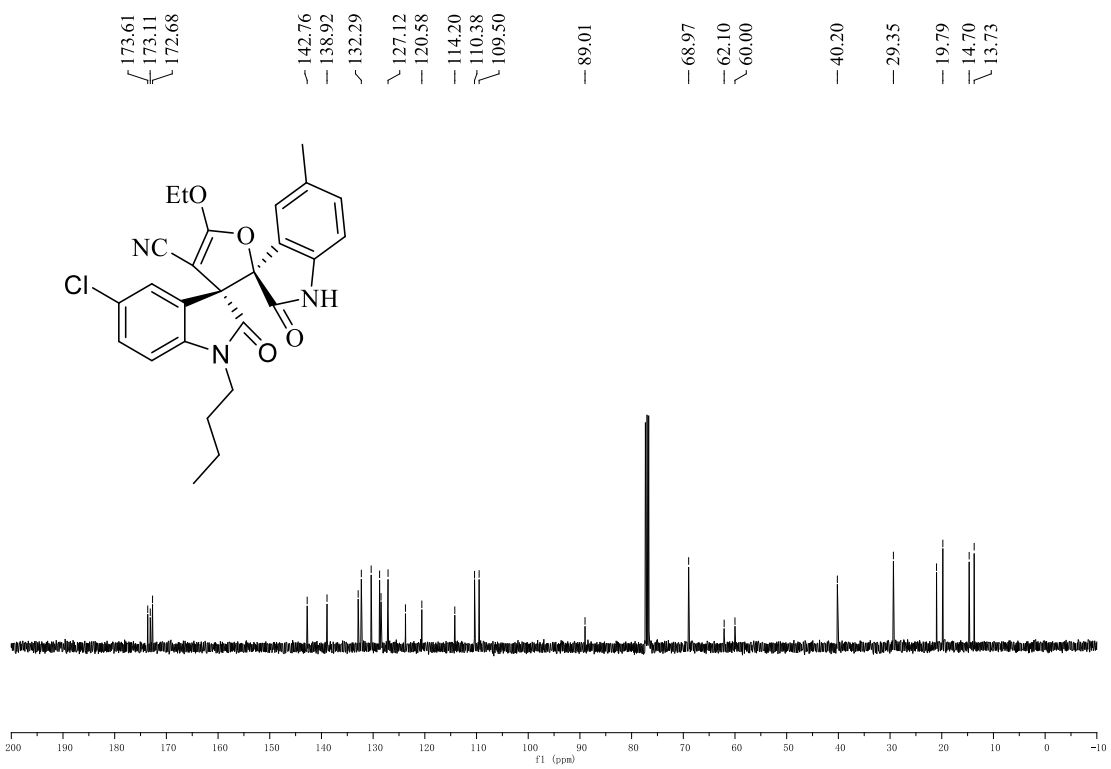


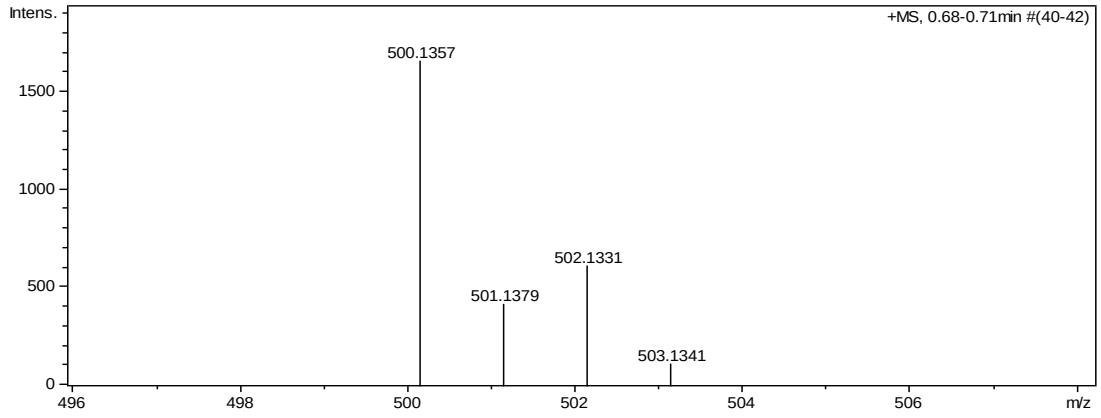

173.69
173.09
170.89
142.90
141.41
128.76
127.70
126.59
120.39
114.27
109.42
88.94
68.96
62.29
60.08
43.97
40.20
29.33
19.77
14.71
13.71
EtO
NC
O
Cl
N
Bn
O
N
O
f1 (ppm)


Intens.
+MS, 0.36-0.37min #(21-22)
568.2000
569.2032
570.1981
571.2026
m/z

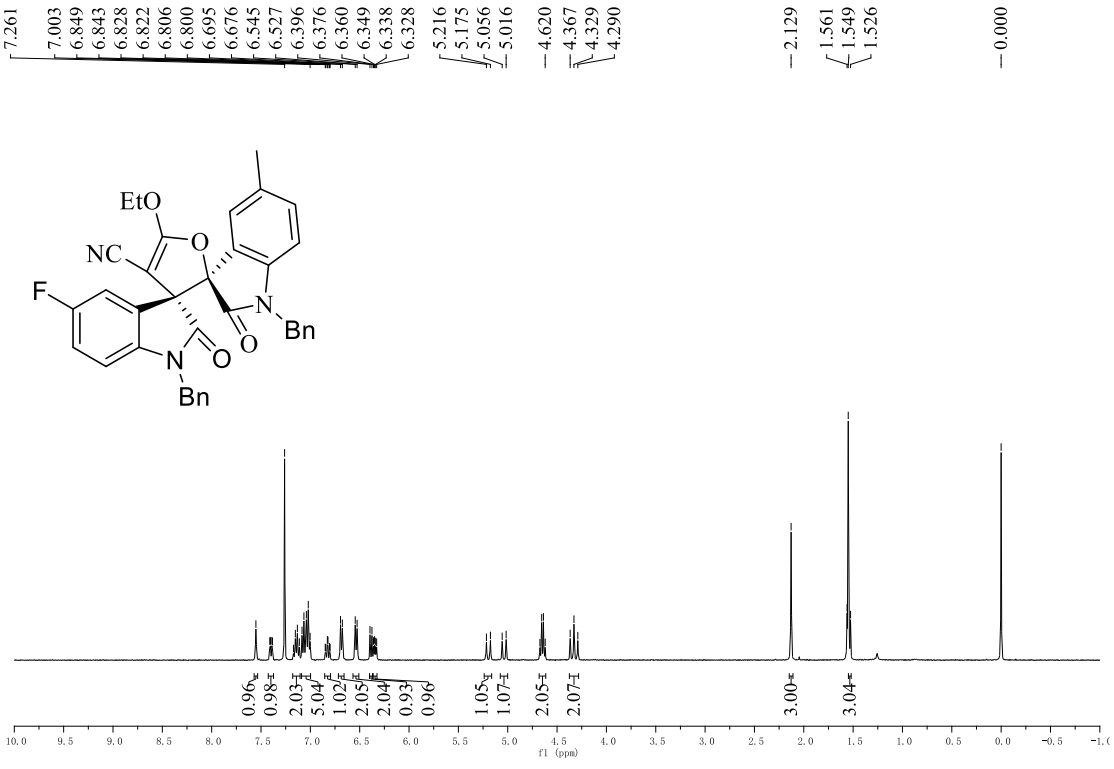
***rel*-(3*R*,3'*R*)-1''-butyl-5''-chloro-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8g)**: white solid, 73%, m.p. 189-191 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H, NH), 7.50 (d, *J* = 6.8 Hz, 2H, ArH), 7.18 (d, *J* = 7.6 Hz, 1H, ArH), 7.08 (d, *J* = 6.8 Hz, 1H, ArH), 6.66-6.58 (m, 2H, ArH), 4.59-4.57 (m, 2H, CH_2), 3.80-3.73 (m, 1H, CH_2), 3.26-3.19 (m, 1H, CH_2), 2.30 (s, 3H, CH_3), 1.49 (t, *J* = 6.4 Hz, 3H, CH_3), 1.31-1.25 (m, 2H, CH_2), 1.00-0.97 (m, 2H, CH_2), 0.80 (t, *J* = 6.4 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6, 173.1, 172.7, 142.8, 138.9, 132.9, 132.3, 130.4, 128.8, 128.5, 127.1, 123.8, 120.6, 114.2, 110.4, 109.5, 89.0, 69.0, 62.1, 60.0, 40.2, 29.4, 21.0, 19.8, 14.7, 13.7. IR (KBr) υ: 3236, 3072, 2968, 2935, 2864, 2208, 1748, 1719, 1643, 1606, 1487, 1411, 1382, 1347, 1301, 1266, 1244, 1208, 1188, 1166, 1150, 1106, 1075, 1045, 1000, 951, 923, 900, 879, 844, 814, 794, 715 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{26}H_{24}NaClN_3O_4$ ([M+Na]$^+$): 500.1353, found: 500.1357.

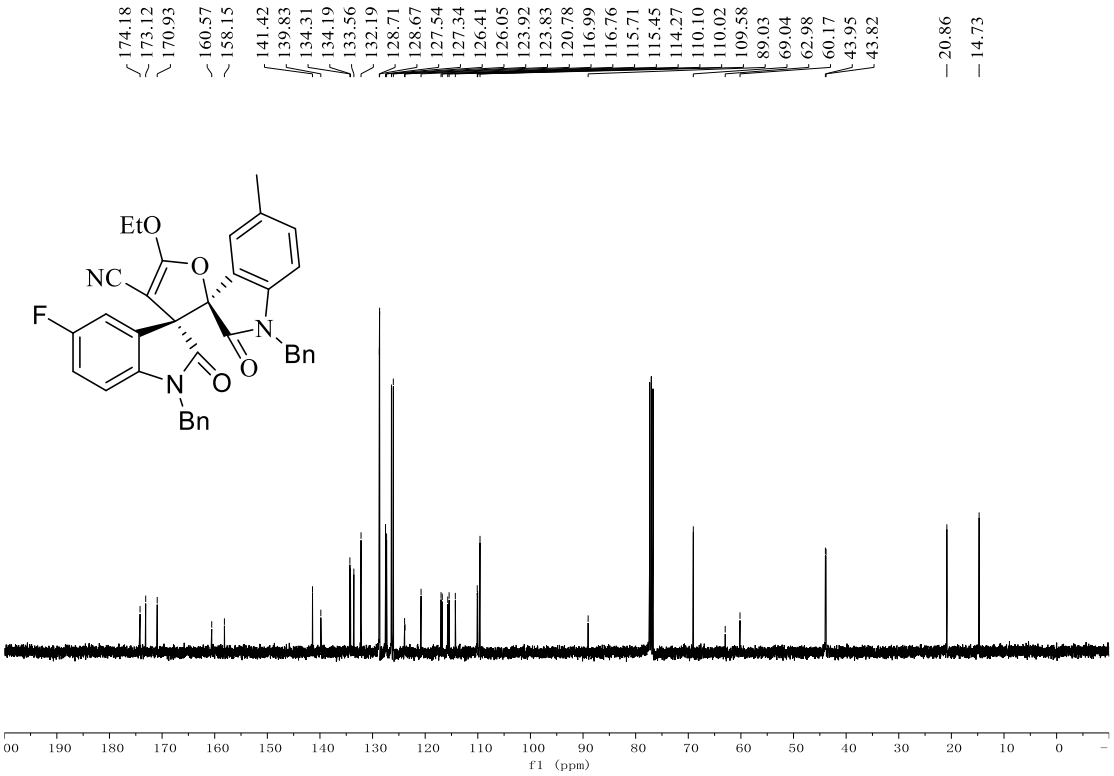


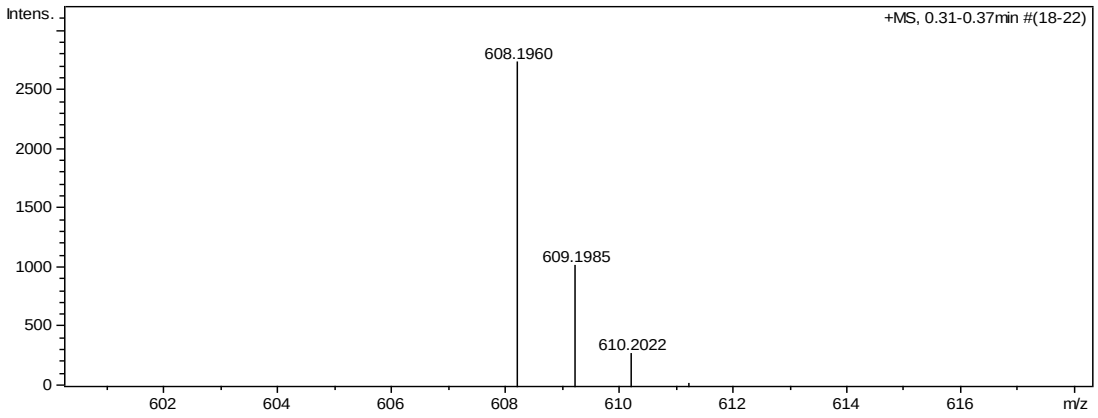

173.61
173.11
172.68
142.76
138.92
132.29
127.12
120.58
114.20
110.38
109.50
89.01
68.97
62.10
60.00
40.20
29.35
19.79
14.70
13.73
EtO
NC
O
Cl
NH
O
N
O
f1 (ppm)


Intens.
+MS, 0.68-0.71min #(40-42)
500.1357
502.1331
501.1379
503.1341
m/z

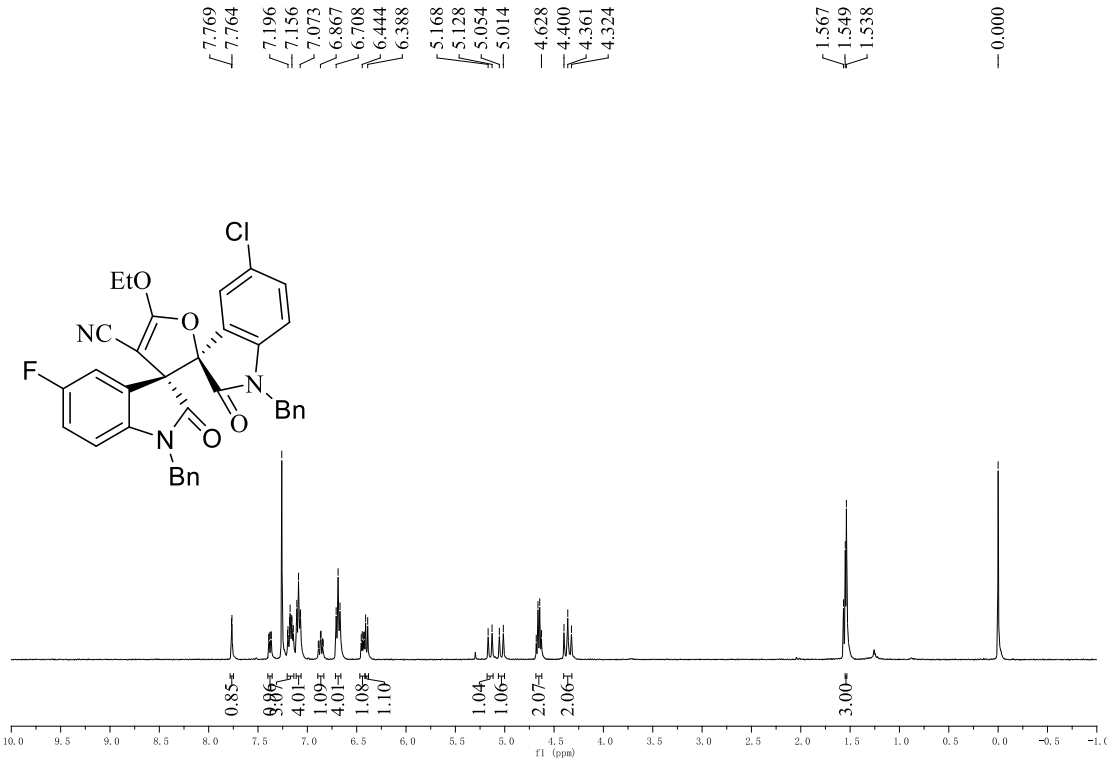
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5'-ethoxy-5''-fluoro-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8h)**: white solid, 69%, m.p. 158-160 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H, ArH), 7.40 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.17-7.11 (m, 2H, ArH), 7.08-7.00 (m, 5H, ArH), 6.85-6.80 (m, 1H, ArH), 6.69 (d, *J* = 7.6 Hz, 2H, ArH), 6.54 (d, *J* = 7.2 Hz, 2H, ArH), 6.39 (d, *J* = 8.0 Hz, 1H, ArH), 6.36-6.33 (m, 1H, ArH), 5.20 (d, *J* = 16.4 Hz, 1H, CH_2), 5.04 (d, *J* = 16.0 Hz, 1H, CH_2), 4.65 (q, *J* = 7.2 Hz, 2H, CH_2), 4.33 (t, *J* = 15.6 Hz, 2H, CH_2), 2.13 (s, 3H, CH_3), 1.55 (t, *J* = 9.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 173.1, 170.9, 159.4 (d, *J* = 242.0 Hz), 141.4, 139.8, 134.3, 134.2, 133.6, 132.2, 128.7, 128.6, 127.5, 127.3, 126.4, 126.1, 123.9 (d, *J* = 9.0 Hz), 120.8, 116.9 (d, *J* = 23.0 Hz), 115.6 (d, *J* = 26.0 Hz), 114.3, 110.1 (d, *J* = 8.0 Hz), 109.6, 89.0, 69.0, 63.0, 60.2, 44.0, 43.8, 20.9, 14.7. IR (KBr) υ: 3064, 3033, 2989, 2918, 2208, 1723, 1633, 1491, 1453, 1411, 1378, 1337, 1281, 1261, 1224, 1167, 1131, 1079, 1027, 996, 965, 928, 888, 846, 819.63, 773, 732, 702 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{28}NaFN_3O_4$ ($[M+Na]^+$): 608.1962, found: 608.1960.

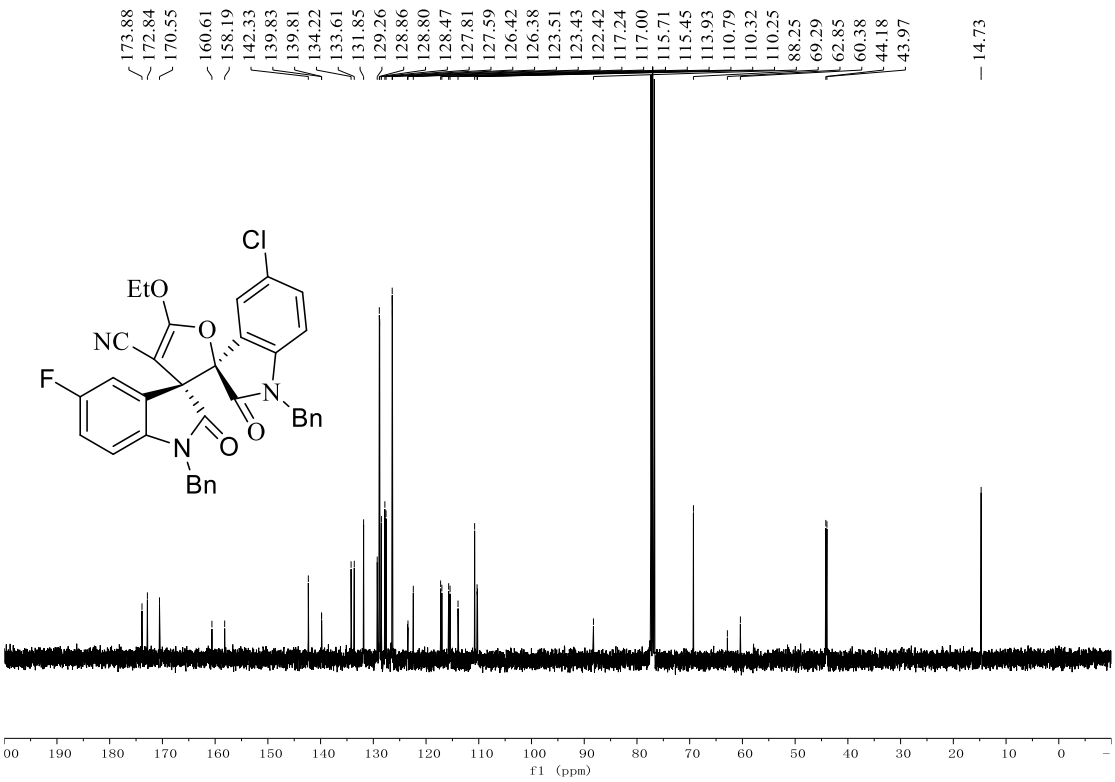


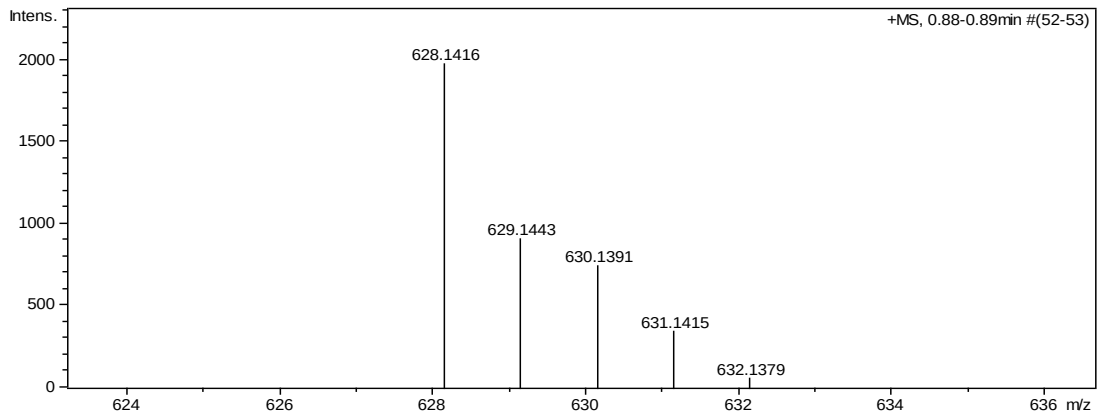

174.18
173.12
170.93
160.57
158.15
141.42
139.83
134.31
134.19
133.56
132.19
128.71
128.67
127.54
127.34
126.41
126.05
123.92
123.83
120.78
116.99
116.76
115.71
115.45
114.27
110.10
110.02
109.58
89.03
69.04
62.98
60.17
43.95
43.82
20.86
14.73
EtO
NC
O
F
N
Bn
O
O
N
Bn
f1 (ppm)


Intens.
+MS, 0.31-0.37min #(18-22)
608.1960
609.1985
610.2022
m/z

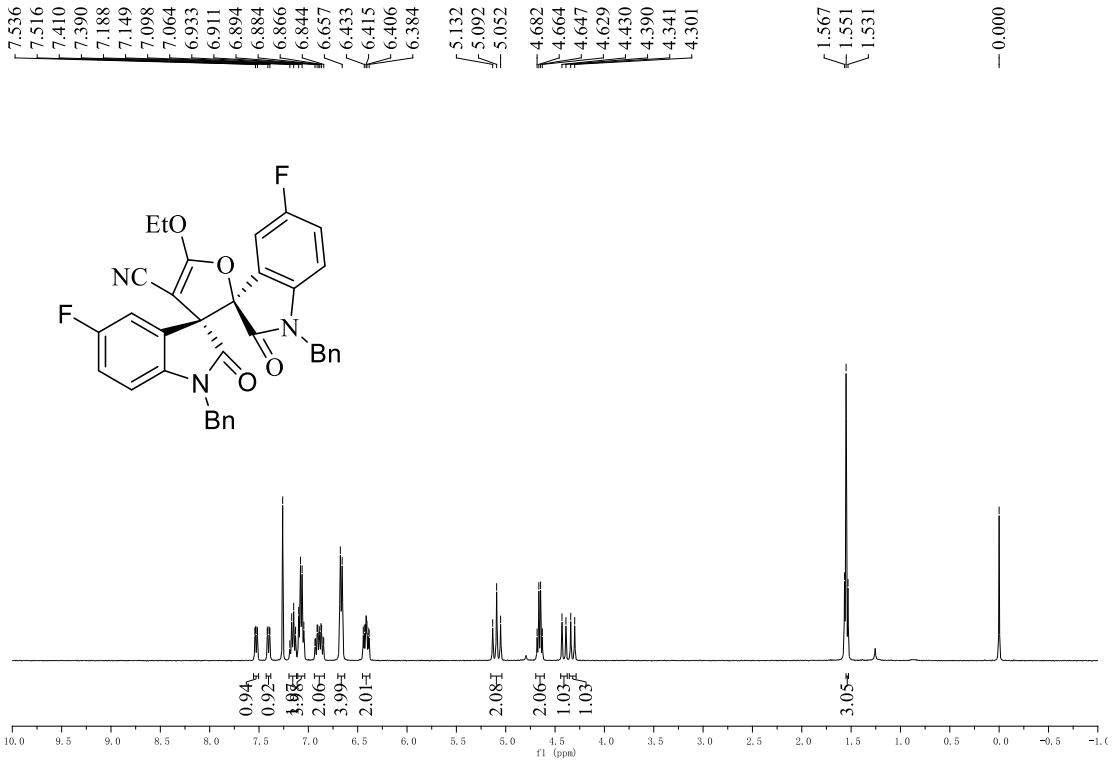
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5-chloro-5'-ethoxy-5''-fluoro-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8i)**: white solid, 47%, m.p. 150-152 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H, ArH), 7.38 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.18-7.14 (m, 3H, ArH), 7.11-7.07 (m, 4H, ArH), 6.89-6.84 (m, 1H, ArH), 6.69 (t, *J* = 7.6 Hz, 4H, ArH), 6.45-6.42 (m, 1H, ArH), 6.40 (d, *J* = 8.8 Hz, 1H, ArH), 5.15 (d, *J* = 16.0 Hz, 1H, CH_2), 5.03 (d, *J* = 16.0 Hz, 1H, CH_2), 4.65 (q, *J* = 7.2 Hz, 2H, CH_2), 4.36 (t, *J* = 15.6 Hz, 2H, CH_2), 1.54 (t, *J* = 4.4 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 172.8, 170.6, 160.6, 158.2, 141.1 (d, *J* = 250.0 Hz),139.8, 134.2, 133.6, 131.7, 129.3, 128.8, 128.5, 127.8, 127.6, 126.4, 126.3, 123.5 (d, *J* = 8.0 Hz), 122.4, 117.1 (d, *J* = 24.0 Hz), 115.6 (d, *J* = 26.0 Hz), 113.9, 110.8, 110.3 (d, *J* = 7.0 Hz), 88.3, 69.3, 62.9, 60.4, 44.2, 44.0, 14.7. IR (KBr) υ: 3082, 3032, 2980, 2936, 2361, 2206, 1885, 1724, 1637, 1612, 1487, 1452, 1437, 1408, 1379, 1334, 1263, 1222, 1178, 1130, 1078, 1029, 994, 963, 922, 902, 881, 841, 817, 746 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{25}NaClFN_3O_4$ ([M+Na]$^{+}$): 628.1415, found: 628.1416.

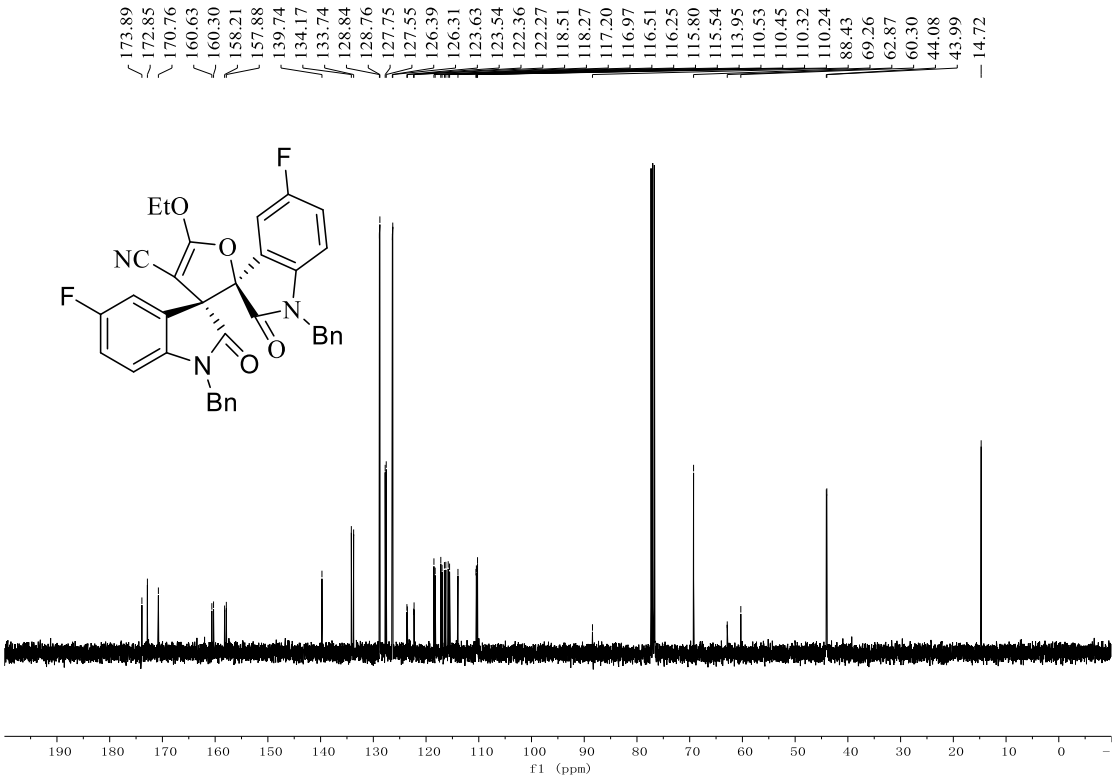


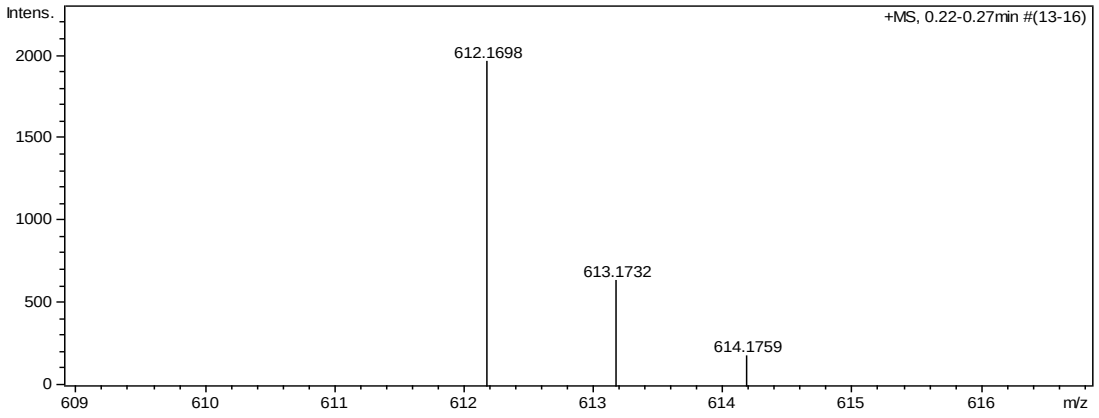

173.88
172.84
170.55
160.61
158.19
142.33
139.83
139.81
134.22
133.61
131.85
129.26
128.86
128.80
128.47
127.81
127.59
126.42
126.38
123.51
123.43
122.42
117.24
117.00
115.71
115.45
113.93
110.79
110.32
110.25
88.25
69.29
62.85
60.38
44.18
43.97
14.73
Cl
EtO
NC
O
F
N
Bn
O
O
N
Bn
f1 (ppm)


Intens.
+MS, 0.88-0.89min #(52-53)
628.1416
629.1443
630.1391
631.1415
632.1379
m/z

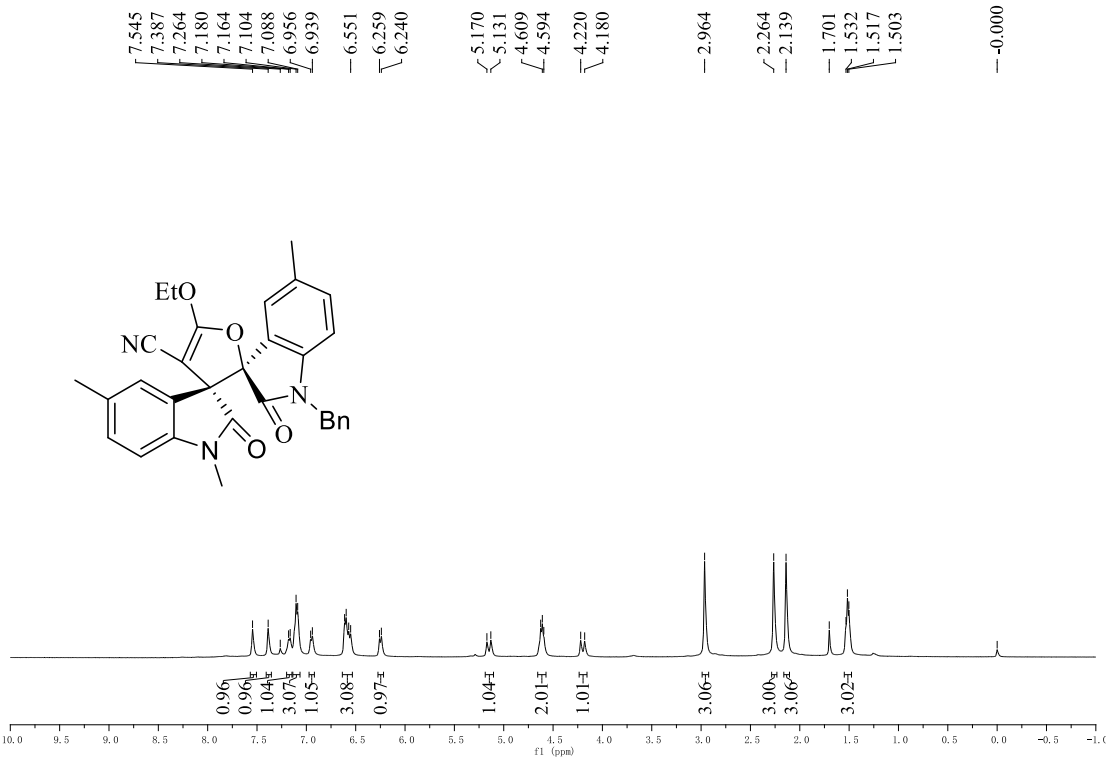
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5'-ethoxy-5,5''-difluoro-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8j)**: white solid, 35%, m.p. 168-170 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 1H, ArH), 7.40 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H, ArH), 7.19-7.13 (m, 2H, ArH), 7.10-7.05 (m, 4H, ArH), 6.93-6.84 (m, 2H, ArH), 6.67 (d, J = 7.6 Hz, 4H, ArH), 6.44-6.38 (m, 2H, ArH), 5.09 (t, J = 16.0 Hz, 2H, CH_2), 4.65 (q, J = 6.8 Hz, 2H, CH_2), 4.41 (d, J = 16.0 Hz, 1H, CH_2), 4.32 (d, J = 16.0 Hz, 1H, CH_2), 1.55 (t, J = 8.0 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 172.9, 170.8, 159.4 (d, J = 242.0 Hz), 159.1 (d, J = 242.0 Hz), 139.7, 134.2, 133.7, 128.8, 128.7, 127.8, 127.6, 126.4, 126.3, 123.6 (d, J = 9.0 Hz), 122.4 (d, J = 9.0 Hz), 118.4 (d, J = 24.0 Hz), 117.1 (d, J = 23.0 Hz), 116.4 (d, J = 26.0 Hz), 115.7 (d, J = 26.0 Hz), 114.0, 110.5 (d, J = 8.0 Hz), 110.3 (d, J = 8.0 Hz), 88.4, 69.3, 62.9, 60.3, 44.1, 44.0, 14.7. IR (KBr) υ: 3085, 3035, 2980, 2942, 2361, 2206, 1887, 1723, 1638, 1490, 1452, 1410, 1382, 1336, 1272, 1222, 1176, 1131, 1077, 1029, 997, 964, 930, 882, 846, 814, 776, 738, 701 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{35}H_{25}NaF_2N_3O_4$ ([M+Na]$^+$): 612.1711, found: 612.1698.

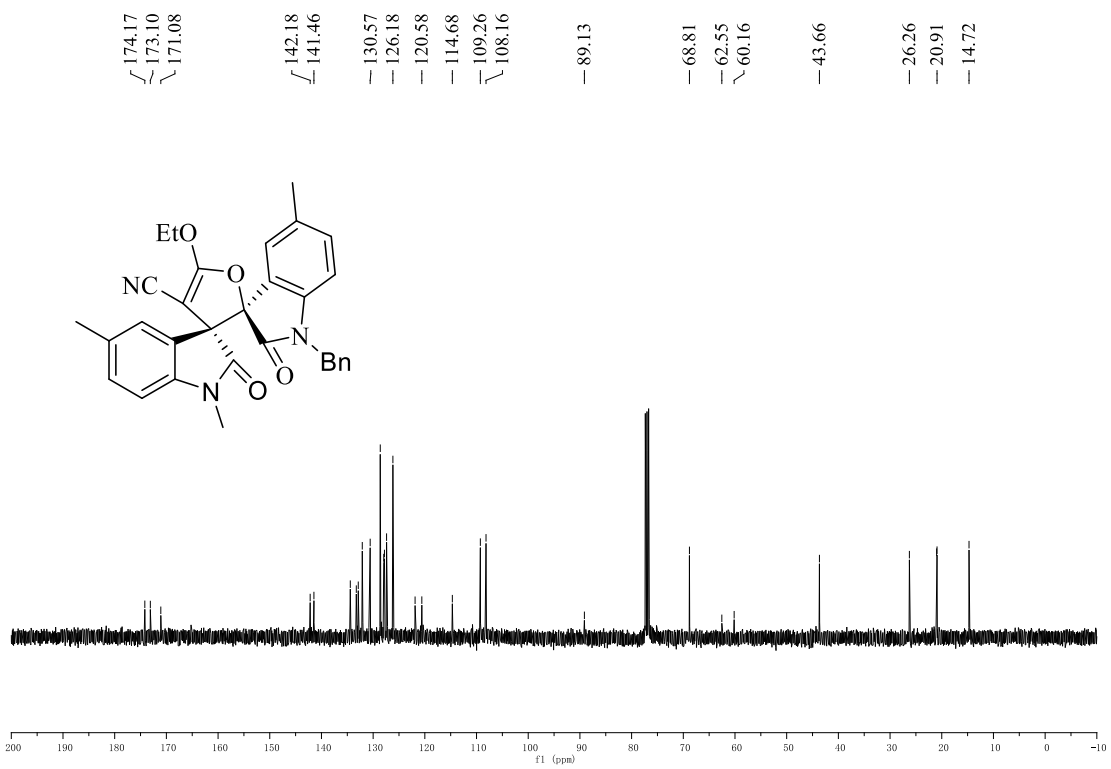


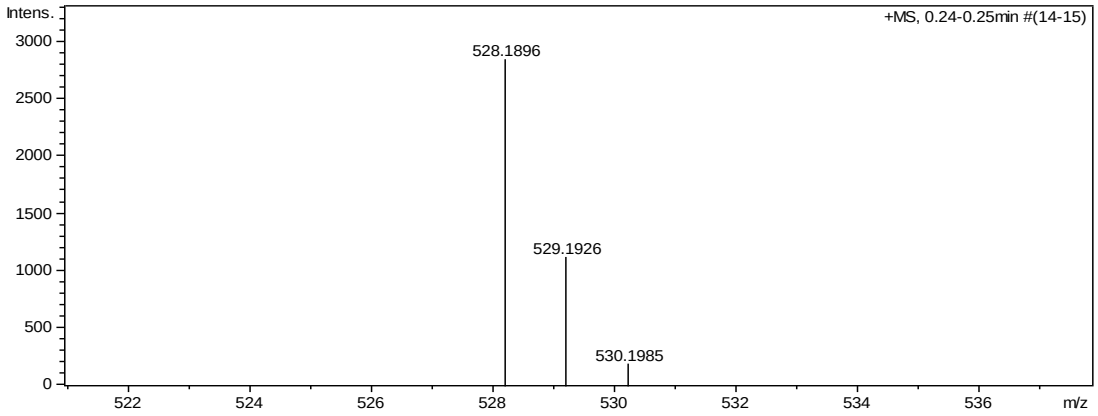

173.89
172.85
170.76
160.63
160.30
158.21
157.88
139.74
134.17
133.74
128.84
128.76
127.75
127.55
126.39
126.31
123.63
123.54
122.36
122.27
118.51
118.27
117.20
116.97
116.51
116.25
115.80
115.54
113.95
110.53
110.45
110.32
110.24
88.43
69.26
62.87
60.30
44.08
43.99
14.72
F
EtO
NC
O
F
N
Bn
O
N
O
Bn
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Intens.
+MS, 0.22-0.27min #(13-16)
2000
1500
1000
500
0
612.1698
613.1732
614.1759
609
610
611
612
613
614
615
616
m/z

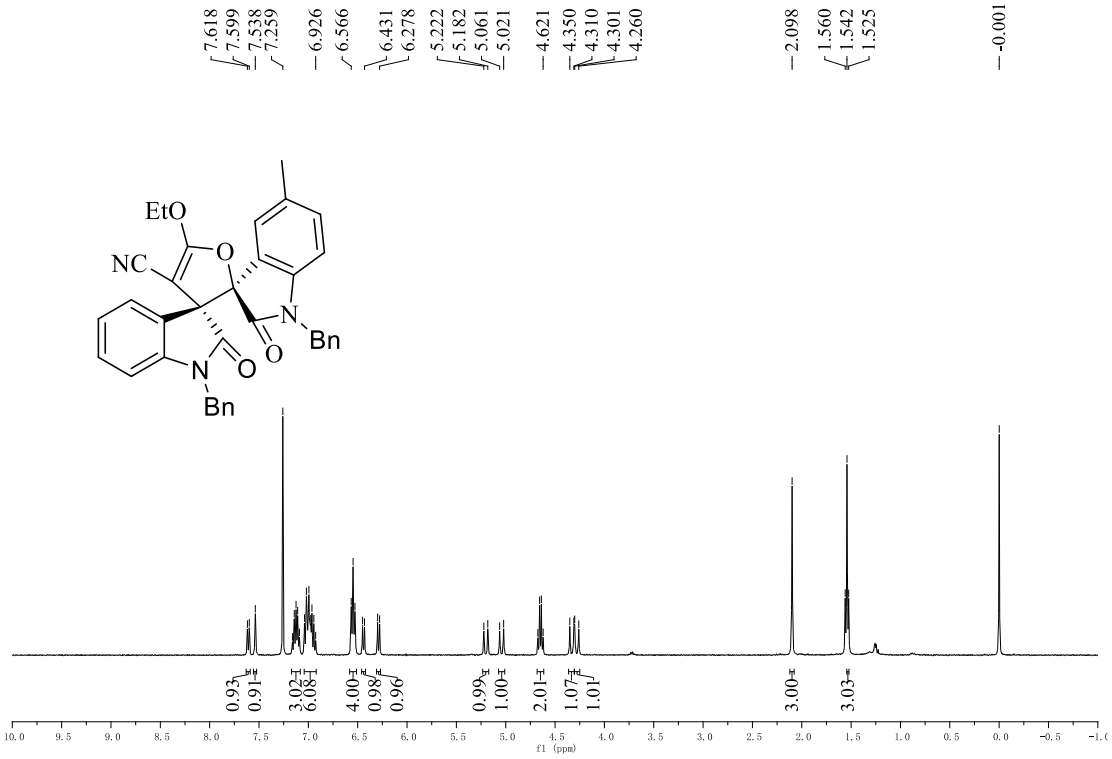
***rel*-(3*R*,3'*R*)-1-benzyl-5'-ethoxy-1'',5,5''-trimethyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8k)**: white solid, 77%, m.p. 173-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H, ArH), 7.39 (s, 1H, ArH), 7.20-7.16 (m, 1H, ArH), 7.11 (t, *J* = 7.6 Hz, 3H, ArH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 6.61 (d, *J* = 7.6 Hz, 2H, ArH), 6.56 (d, *J* = 8.0 Hz, 1H, ArH), 6.25 (d, *J* = 8.0 Hz, 1H, ArH), 5.15 (d, *J* = 16.0 Hz, 1H, CH_2), 4.63 (q, *J* = 7.2 Hz, 2H, CH_2), 4.20 (d, *J* = 16.4 Hz, 1H, CH_2), 2.97 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 1.53 (t, *J* = 7.2 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 173.1, 171.1, 142.2, 141.5, 134.4, 133.3, 132.9, 132.1, 130.6, 128.6, 128.0, 127.8, 127.4, 126.2, 121.9, 120.6, 114.7, 109.3, 108.2, 89.1, 68.8, 62.6, 60.2, 43.7, 26.3, 21.0, 20.9, 14.7. IR (KBr) υ: 3467, 3063, 3035, 2990, 2919, 2205, 1739, 1706, 1632, 1602, 1496, 1454, 1434, 1408, 1381, 1361, 1333, 1293, 1258, 1215, 1199, 1186, 1167, 1133, 1089, 1070, 1026, 997, 962, 933, 911, 895, 875, 836, 818, 776, 747 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{31}H_{27}NaN_3O_4$ ([M+Na]$^+$): 528.1899, found: 528.1896.

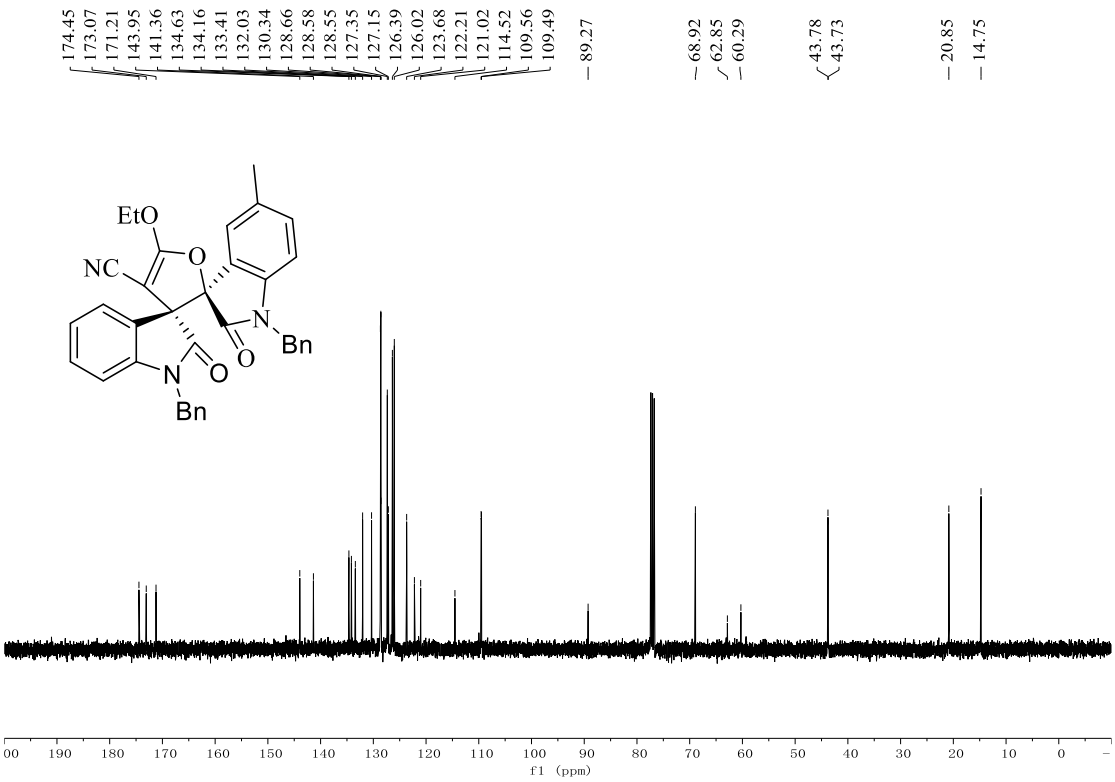


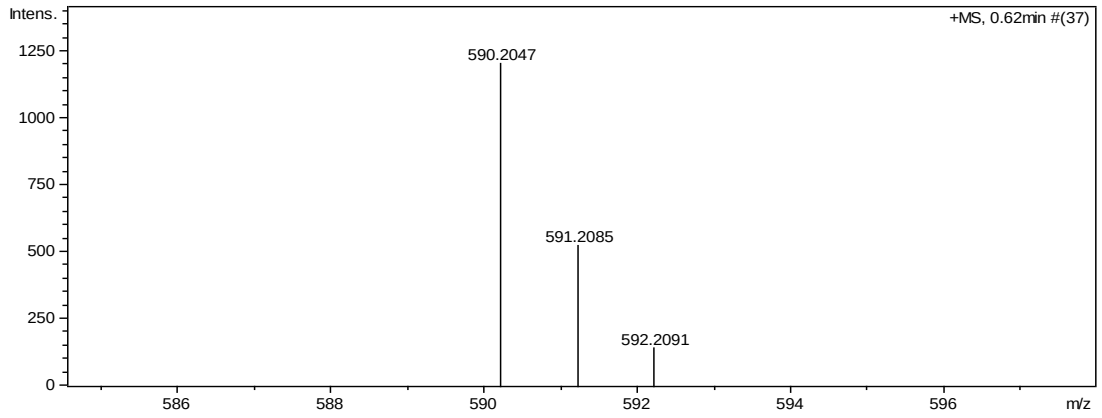

174.17
173.10
171.08
142.18
141.46
130.57
126.18
120.58
114.68
109.26
108.16
89.13
68.81
62.55
60.16
43.66
26.26
20.91
14.72
EtO
NC
O
N
Bn
O
N
O
f1 (ppm)


Intens.
+MS, 0.24-0.25min #(14-15)
528.1896
529.1926
530.1985
m/z

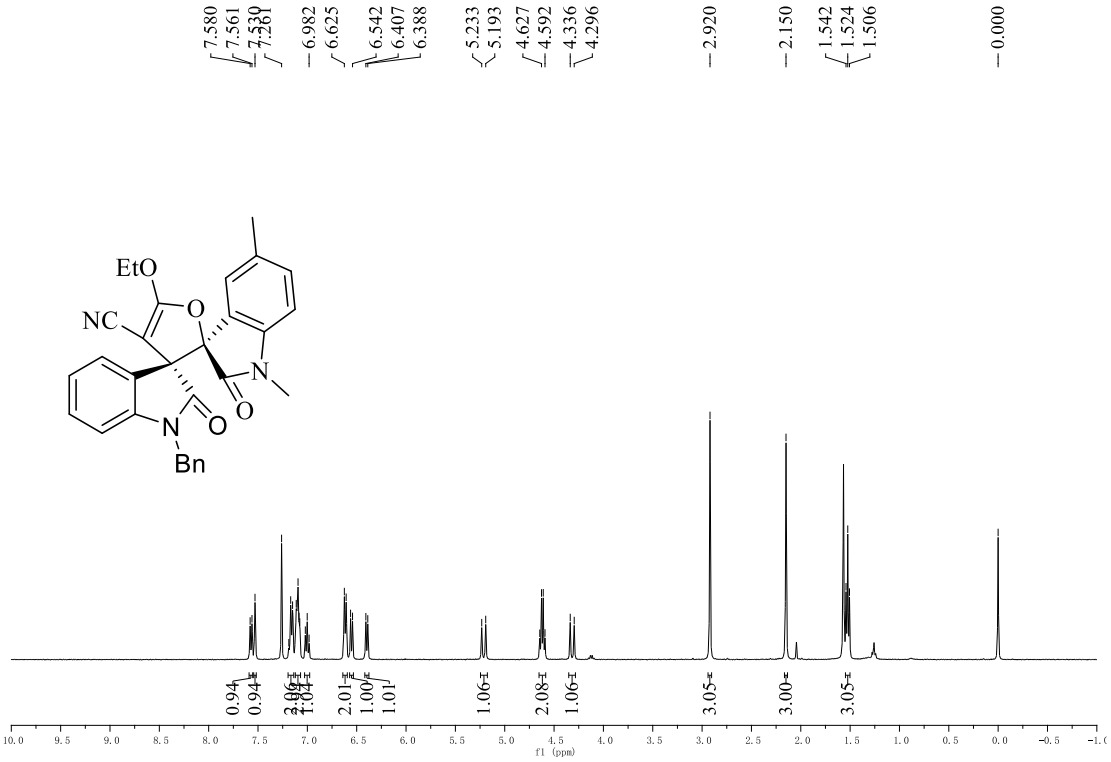
***rel*-(3*R*,3'*R*)-1,1''-dibenzyl-5'-ethoxy-5-methyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8l)**: white solid, 83%, m.p. 141-143 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.54 (s, 1H, ArH), 7.16-7.09 (m, 3H, ArH), 7.04-6.93 (m, 6H, ArH), 6.55 (d, *J* = 7.6 Hz, 4H, ArH), 6.44 (d, *J* = 8.0 Hz, 1H, ArH), 6.29 (d, *J* = 8.0 Hz, 1H, ArH), 5.20 (d, *J* = 16.0 Hz, 1H, CH_2), 5.04 (d, *J* = 16.0 Hz, 1H, CH_2), 4.65 (q, *J* = 6.8 Hz, 2H, CH_2), 4.33 (d, *J* = 16.0 Hz, 1H, CH_2), 4.28 (d, *J* = 16.4 Hz, 1H, CH_2), 2.10 (s, 3H, CH_3) 1.54 (t, *J* = 6.8 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 173.1, 171.2, 144.0, 141.4, 134.6, 134.2, 133.4, 132.0, 130.3, 128.7, 128.6, 128.5, 127.4, 127.2, 126.4, 126.0, 123.7, 122.2, 121.0, 114.5, 109.6, 109.5, 89.3, 68.9, 62.9, 60.3, 43.8, 43.7, 20.9, 14.8.IR (KBr) υ: 3675, 3032, 2984, 2920, 2859, 2361, 2206, 1724, 1637, 1496, 1467, 1438, 1408, 1376, 1335, 1214, 1166, 1094, 1077, 1053, 1029, 994, 927, 902, 874, 848, 816, 779, 760, 737, 700 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{36}H_{29}NaN_3O_4$ ($[M+Na]^+$): 590.2056, found: 590.2047.

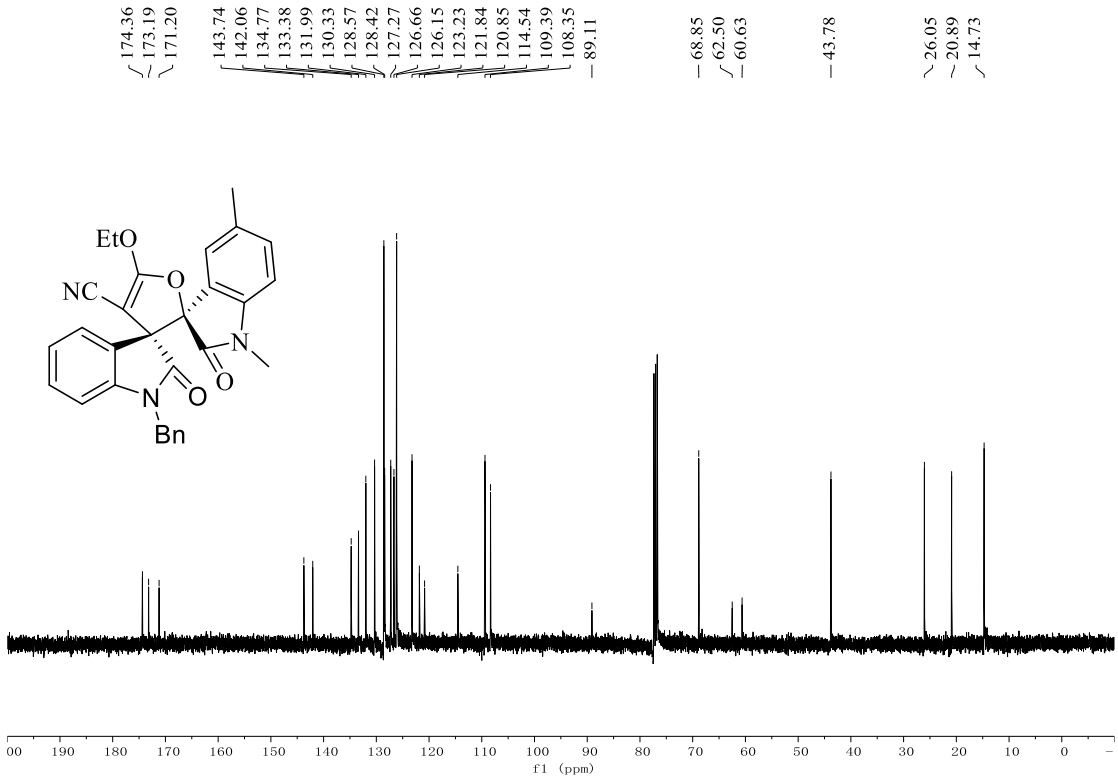


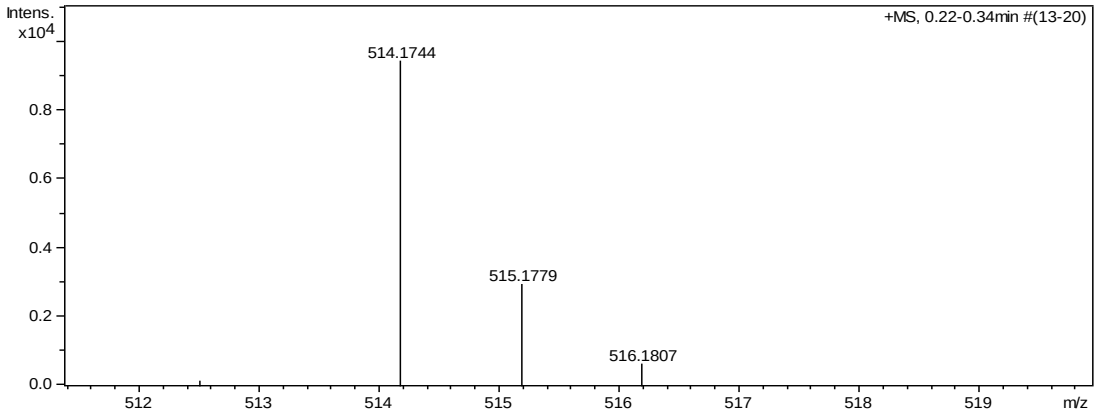

174.45
173.07
171.21
143.95
141.36
134.63
134.16
133.41
132.03
130.34
128.66
128.58
128.55
127.35
127.15
126.39
126.02
123.68
122.21
121.02
114.52
109.56
109.49
89.27
68.92
62.85
60.29
43.78
43.73
20.85
14.75
EtO
NC
O
N
Bn
O
N
O
Bn
f1 (ppm)


Intens.
+MS, 0.62min #(37)
590.2047
591.2085
592.2091
m/z

***rel*-(3*R*,3'*R*)-1''-benzyl-5'-ethoxy-1,5-dimethyl-2,2''-dioxodispiro[indoline-3,2'-furan-3',3''-indoline]-4'-carbonitrile (8m)**: white solid, 62%, m.p. 174-175 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.6 Hz, 1H, ArH), 7.53 (s, 1H, ArH), 7.19-7.15 (m, 2H, ArH), 7.11-7.08 (m, 3H, ArH), 7.00 (t, *J* = 8.0 Hz, 1H, ArH), 6.62 (d, *J* = 7.2 Hz, 2H, ArH), 6.55 (d, *J* = 8.0 Hz, 1H, ArH), 6.40 (d, *J* = 7.6 Hz, 1H, ArH), 5.21 (d, *J* = 16.0 Hz, 1H, CH_2), 4.62 (q, *J* = 6.8 Hz, 2H, CH_2), 4.32 (d *J* = 16.0 Hz, 1H, CH_2), 2.92 (s, 3H, CH_3), 2.15 (s, 3H, CH_3), 1.52 (t, *J* = 7.2 Hz, 3H, CH_3).^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 173.2, 171.2, 143.7, 142.1, 134.8, 133.4, 132.0, 130.3, 128.6, 128.4, 127.3, 126.7, 126.2, 123.2, 121.8, 120.9, 115.5, 109.4, 108.4, 89.1, 68.9, 62.5, 60.6, 43.8, 26.1, 20.9, 14.7. IR (KBr) υ: 3057, 3029, 2987, 2964, 2927, 2360, 2204, 1955, 1731, 1650, 1609, 1499, 1465, 1410, 1380, 1343, 1293, 1242, 1214, 1179, 1136, 1097, 1063, 1006, 937, 906, 858, 815, 755, 739 cm^{-1}; MS (*m*/*z*): HRMS (ESI) Calcd. for $C_{30}H_{25}NaN_3O_4$ ([M+Na]$^+$): 514.1743, found: 514.1744.




174.36
173.19
171.20
143.74
142.06
134.77
133.38
131.99
130.33
128.57
128.42
127.27
126.66
126.15
123.23
121.84
120.85
114.54
109.39
108.35
89.11
68.85
62.50
60.63
43.78
26.05
20.89
14.73
EtO
NC
O
N
O
N
O
Bn
f1 (ppm)


Intens.
x10^4
+MS, 0.22-0.34min #(13-20)
514.1744
515.1779
516.1807
m/z