Supporting Information

Phosphine-catalyzed fixation of CO_2 with γ-hydroxyl alkynone under ambient temperature and pressure: kinetic resolution and further conversion

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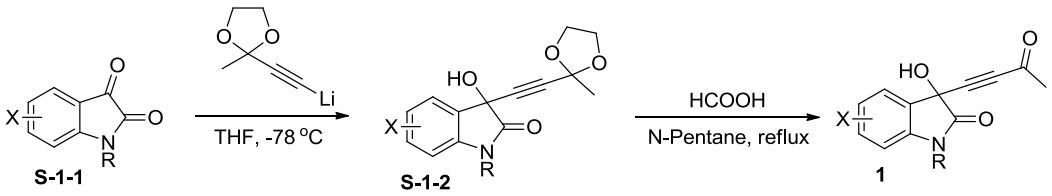
CONTENTS

1. General Remarks. ^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants (*J*) are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Mass and HRMS spectra were recorded by EI or ESI method. Organic solvents used were dried by standard methods when necessary. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-341 MC digital polarimeter; $[\alpha]_D$-values are given in unit of 10 deg^{-1} cm^2 g^{-1}. Chiral HPLC was performed on a SHIMADZU SPD-10A *vp* series with chiral columns (Chiralpak AD-H, OD-H and AS-H columns 4.6 x 250 mm, (Daicel Chemical Ind., Ltd.)). Commercially obtained reagents were used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

2. General Procedure for Synthesis of γ-Hydroxyl Alkynone 1 and Spectroscopic Data of Substrates 1

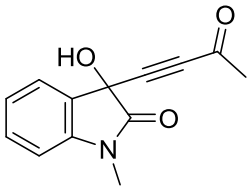


Substrates **1a-1v** and **1ac** was synthesized through the **method 1** as below.

Method 1

Step 1: To a solution of 2-methyl-1,3-dioxolan-2-yl)ethynyl (5.0 mmol, 1.0 equiv) in dry THF (20 mL) was added n-butyllithium solution (6.0 mmol, 1.2 equiv) under -78 °C to prepare ((2-methyl-1,3-dioxolan-2-yl)ethynyl)lithium solution.[1] After stirring for one hour, fresh prepared ((2-methyl-1,3-dioxolan-2-yl)ethynyl)lithium (5.0 mmol, 1.0 equiv) was added to a solution of isatin derivative **S-1-1** (6.0 mmol, 1.2 equiv) in dry THF (20 mL) under -78 °C. Then, the resulting reaction mixture was stirred at -78 °C for one hour. After that, saturated ammonium chloride solution was added to quench the reaction. The reaction was extracted with ethyl acetate three times and washed by water. Then the reaction mixture was concentrated under high vacuum and purified by a column chromatography on silica gel to give the crude products **S-1-2** (DCM:EA = 50:1 ~ 2:1).

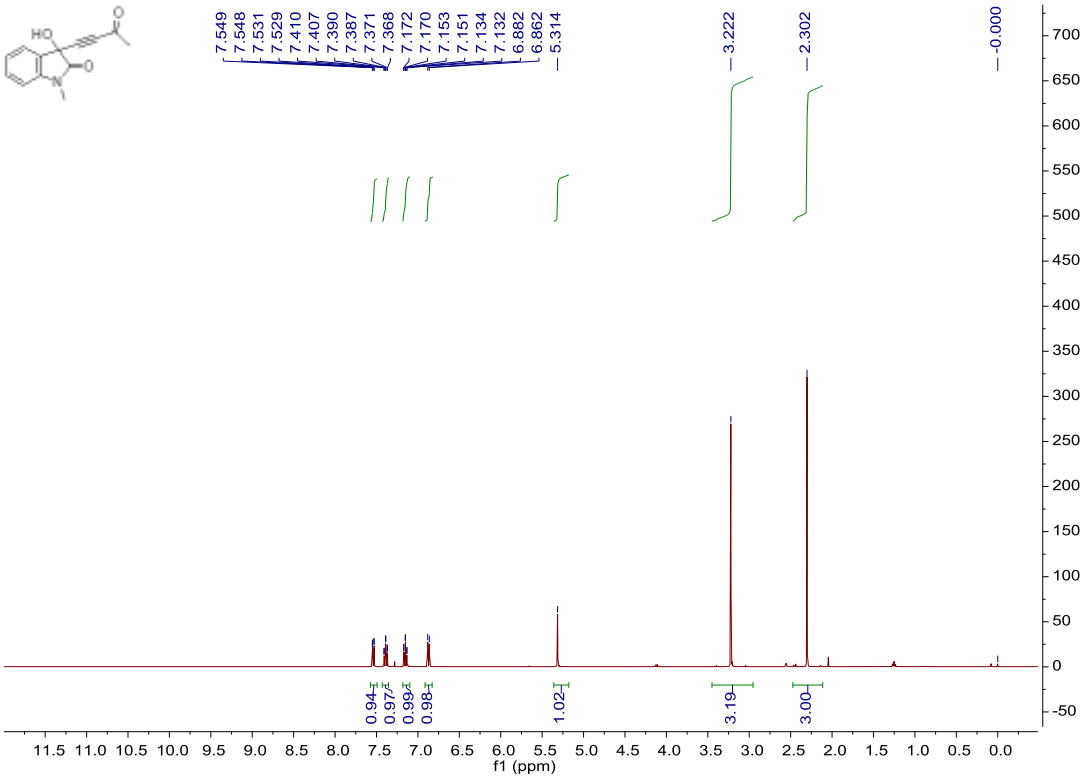
Step 2: The crude product **S-1-2** was dispersed in 50 mL n-pentane, and 1.5 mL HCOOH was added.[2] The reaction mixture was heated to reflux and stirred for 8 hours. After the reaction was completed, the reaction mixture was concentrated under high vacuum and purified by a column chromatography on silica gel to give the desired products **1** (DCM:EA = 50:1 ~ 2:1).

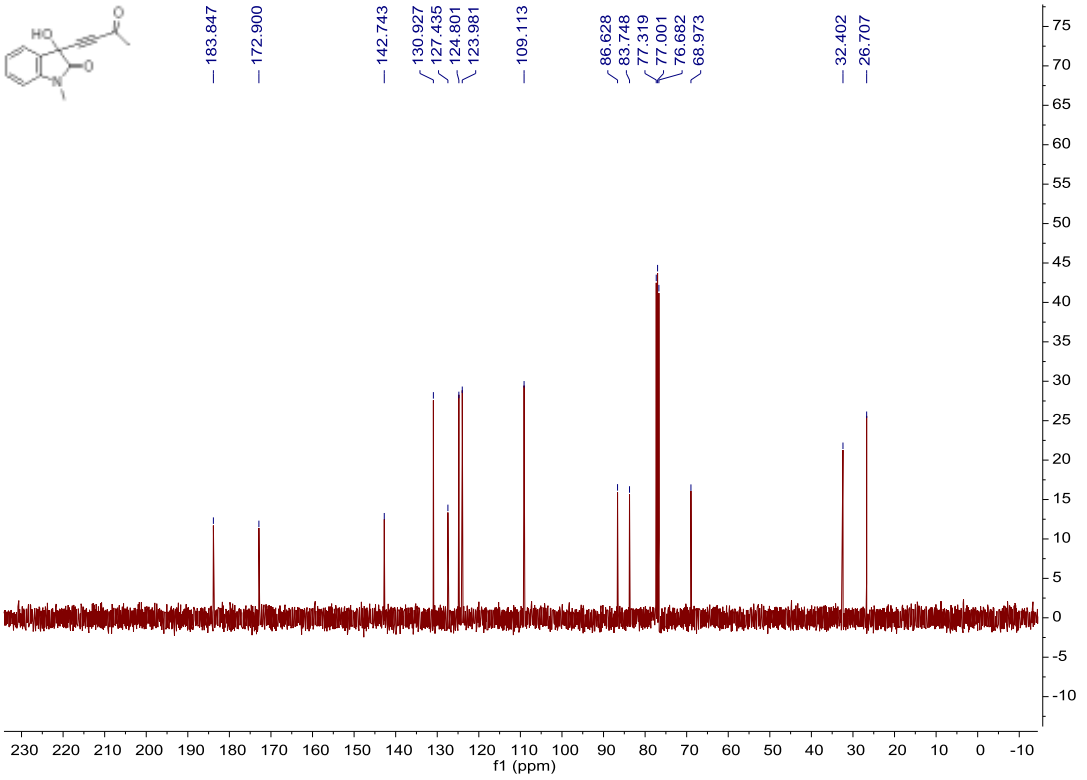


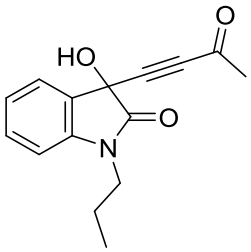
3-hydroxy-1-methyl-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1a)

A white solid, 73% yield (836 mg). M.p.: 133-135 °C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.30 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 5.31 (s, 1H, OH), 6.87 (d, *J* = 8.0 Hz, 1H, ArH), 7.15 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.39 (dt, *J* = 1.2, 8.0 Hz, 1H, ArH), 7.54 (dd, *J* = 0.4, 7.2 Hz, 1H, ArH). ^{13}C NMR

($CDCl_3$, TMS, 100 MHz) δ 26.7, 32.4, 69.0, 83,7, 86.6, 109.1, 124.0, 124.8, 127.4, 130.9, 142.7, 172.9, 183.8. IR (EtOH) ν 3279, 2966, 2922, 2218, 1711, 1678, 1493, 1376, 1196 cm^{-1}. HRMS (ESI) Calcd. For $C_{13}H_{15}N_2O_3^{+1}(M+NH_4)^+$ requires 247.1077, Found: 247.1075.

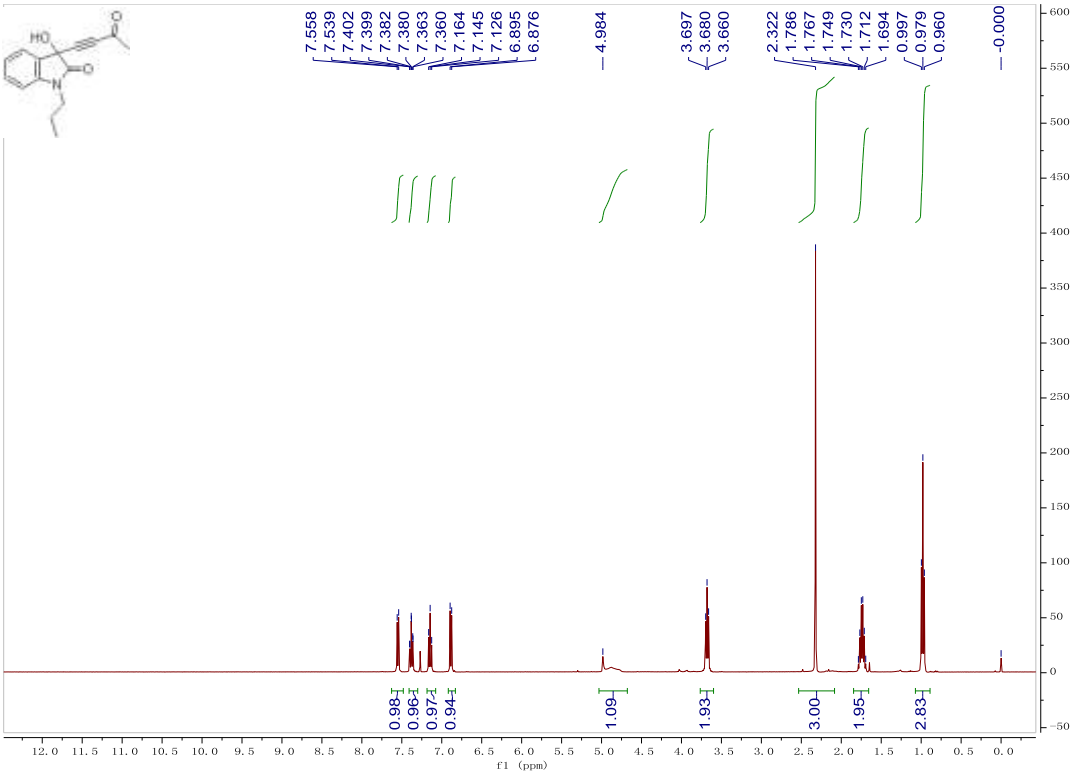


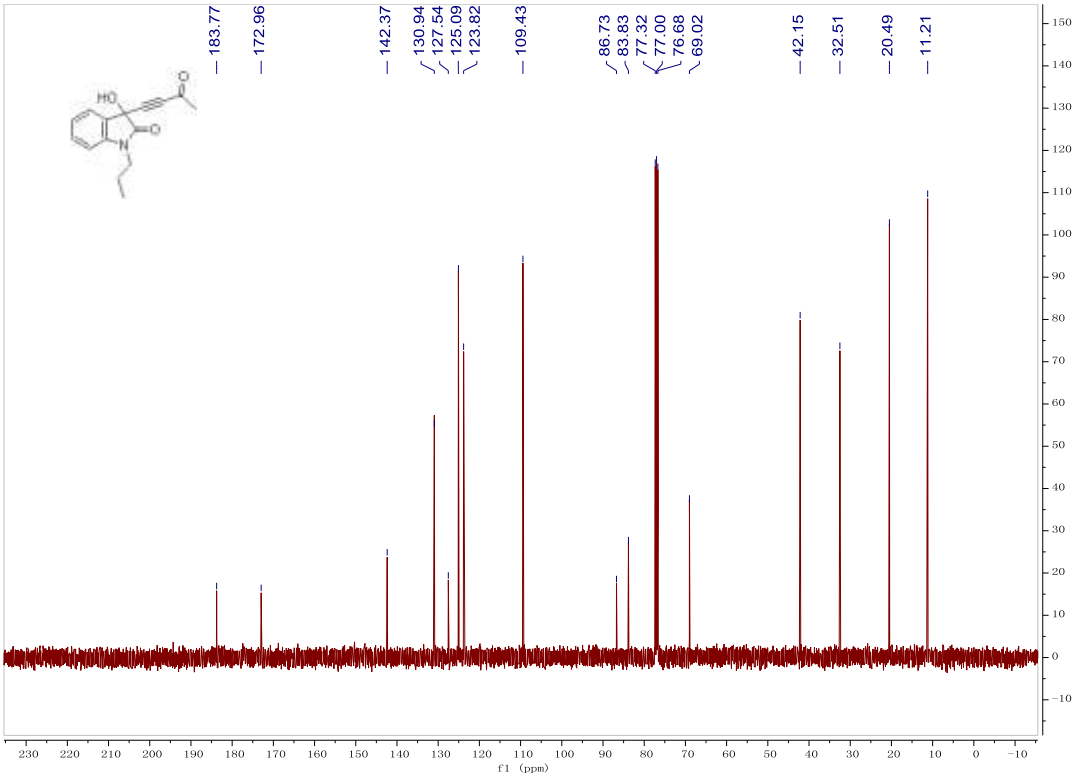




3-hydroxy-3-(3-oxobut-1-yn-1-yl)-1-propylindolin-2-one (1b)

A white solid, 74% yield (951 mg). M.p.: 110-112 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.98 (t, *J* = 7.6 Hz, 3H, CH_3), 1.69-1.79 (m, 2H, CH_2), 2.32 (s, 3H, CH_3), 3.68 (t, *J* = 6.8 Hz, 2H, CH_2), 4.98 (br, 1H, OH), 6.89 (d, *J* = 7.6 Hz, 1H, ArH), 7.15 (t, *J* = 7.6 Hz, 1H, ArH), 7.38 (dt, *J* = 0.8, 8.0 Hz, 1H, ArH), 7.55 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 11.2, 20.5, 32.5, 42.2, 69.0, 83.8, 86.7, 109.4, 123.8, 125.1, 127.5, 130.9, 142.3, 173.0, 183.8. IR (EtOH) ν 3287, 2969, 2872, 2207, 1703, 1674, 1466, 1189, 1108, 669 cm^{-1}. HRMS (ESI) Calcd. For $C_{15}H_{19}N_2O_3^{+1}$(M+NH_4)$^+$ requires 275.1390, Found: 275.1387. [α]$^{25}_D$ = +68.00 (c 0.05, CH_2Cl_2) for 97% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 46.383 min, t_{major} = 25.977 min.





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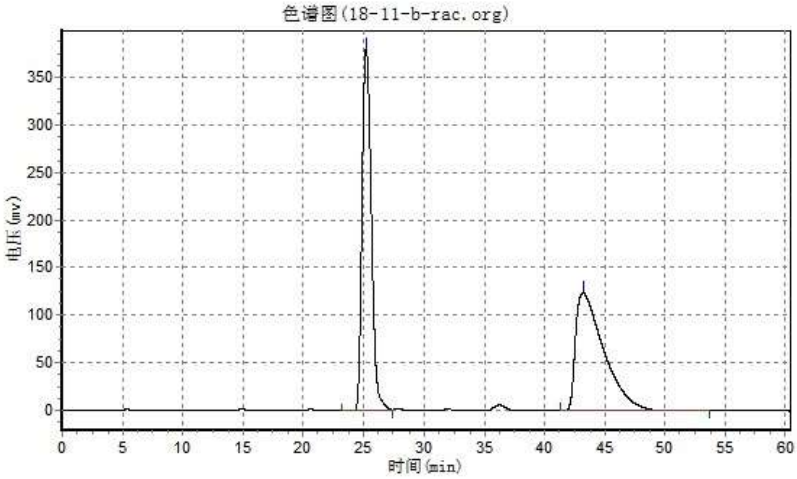

分析结果表

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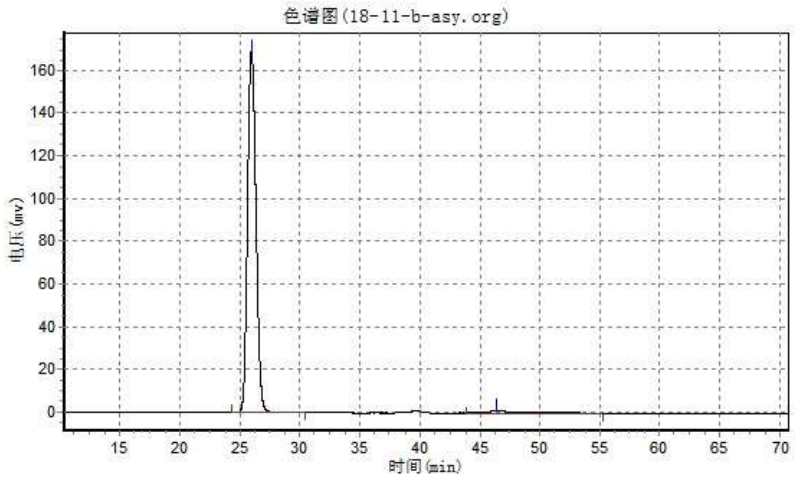

分析结果表

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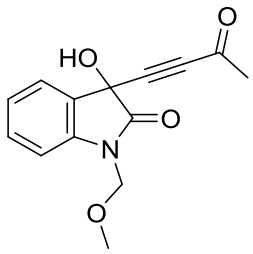
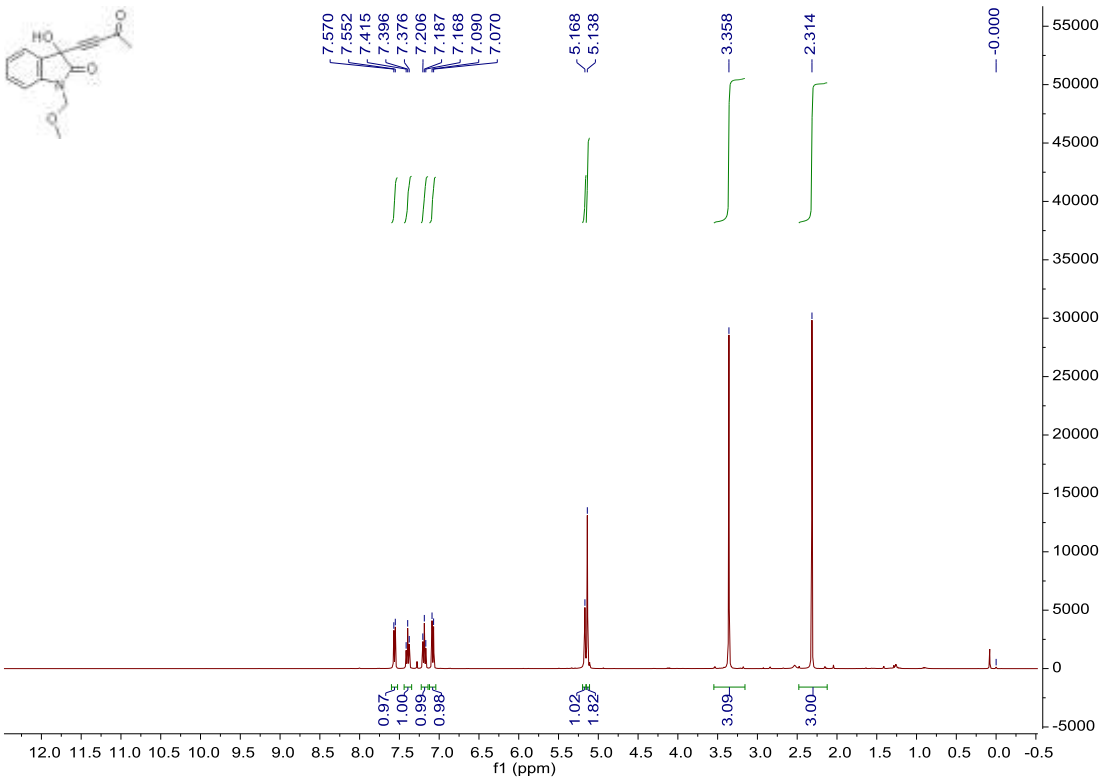


3-hydroxy-1-methyl-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1c)

A white solid, 57% yield (738 mg). M.p.: 141-143 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (s, 3H, CH_3), 3.36 (s, 3H, CH_3), 5.14 (s, 2H, CH_2), 5.17 (s, 1H, OH), 7.08 (d, *J* = 8.0 Hz, 1H, ArH), 7.19 (t, *J* = 7.6 Hz, 1H, ArH), 7.40 (t, *J* = 7.6 Hz, 1H, ArH), 7.56 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.4, 56.4, 69.2, 71.9, 84.1, 86.2, 110.6, 124.4, 125.0, 127.0, 131.1, 141.1, 173.4, 183.7. IR (EtOH) ν 3311, 3000, 2935, 2207, 1728, 1614, 1471, 1366, 1204, 1072 cm^{-1}. HRMS (ESI) Calcd. For $C_{14}H_{17}N_2O_4^{+1}(M+NH_4)^+$ requires 277.1183, Found: 277.1179. $[\alpha]^{25}_D$ = +112.50 (c 0.04, CH_2Cl_2) for 81% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 55.812 min, t_{major} = 32.023 min.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0.98
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3.00
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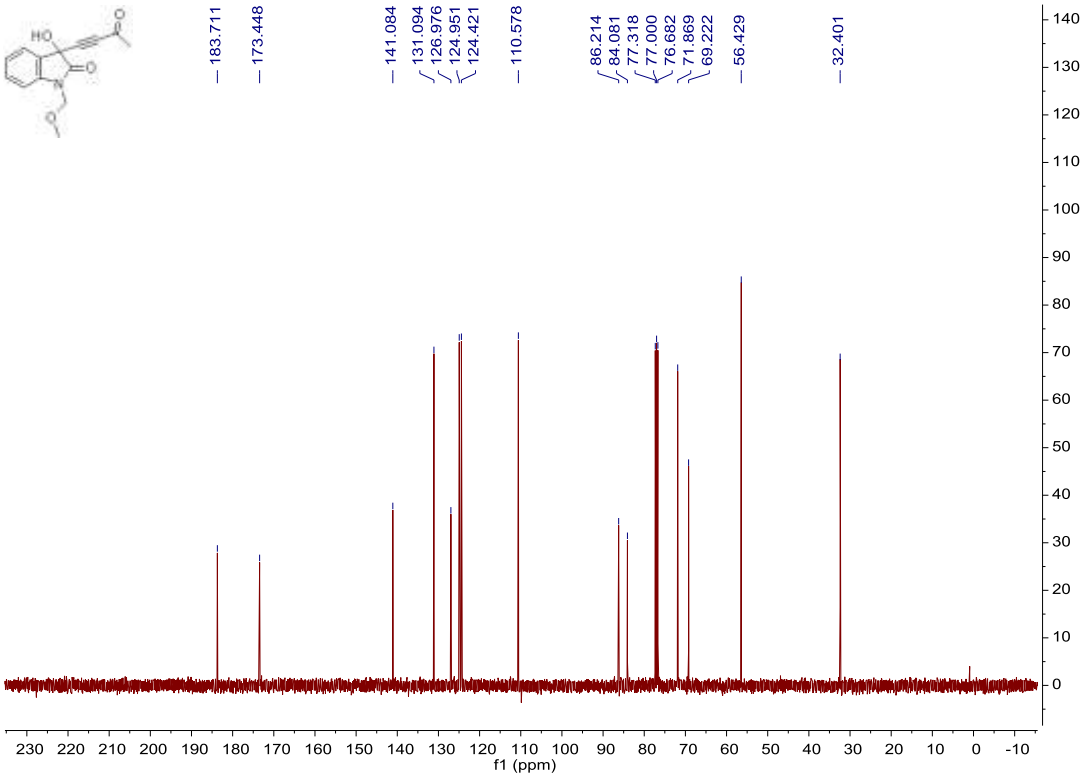
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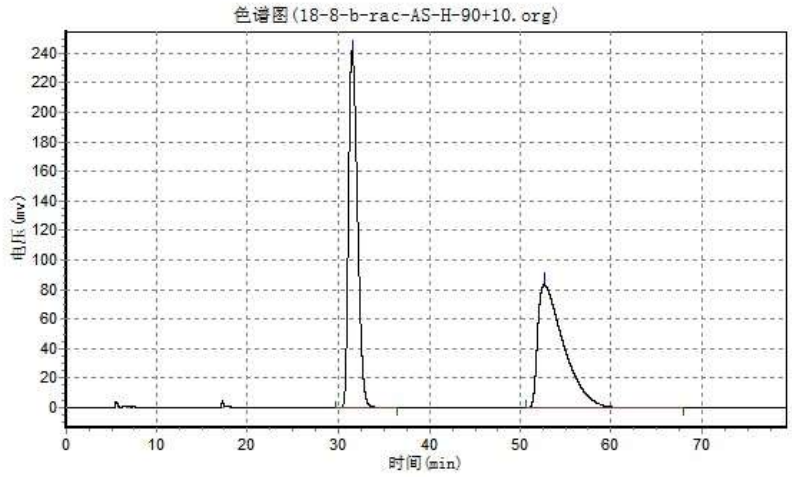

分析结果表

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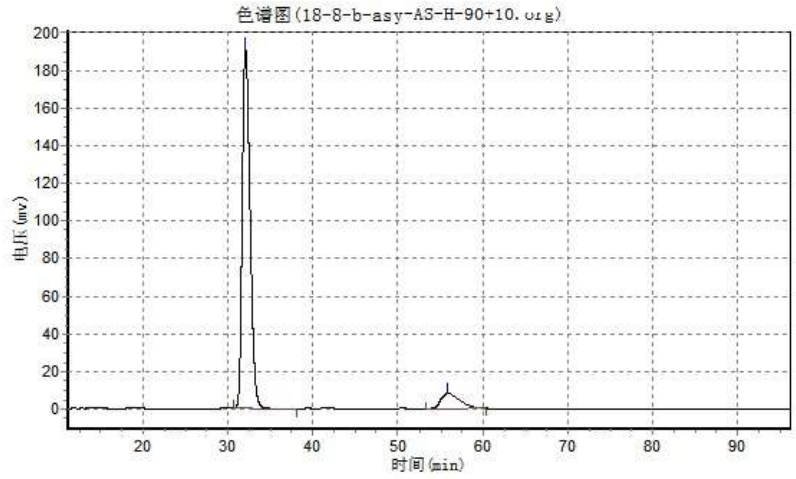

分析结果表

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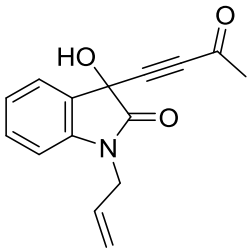
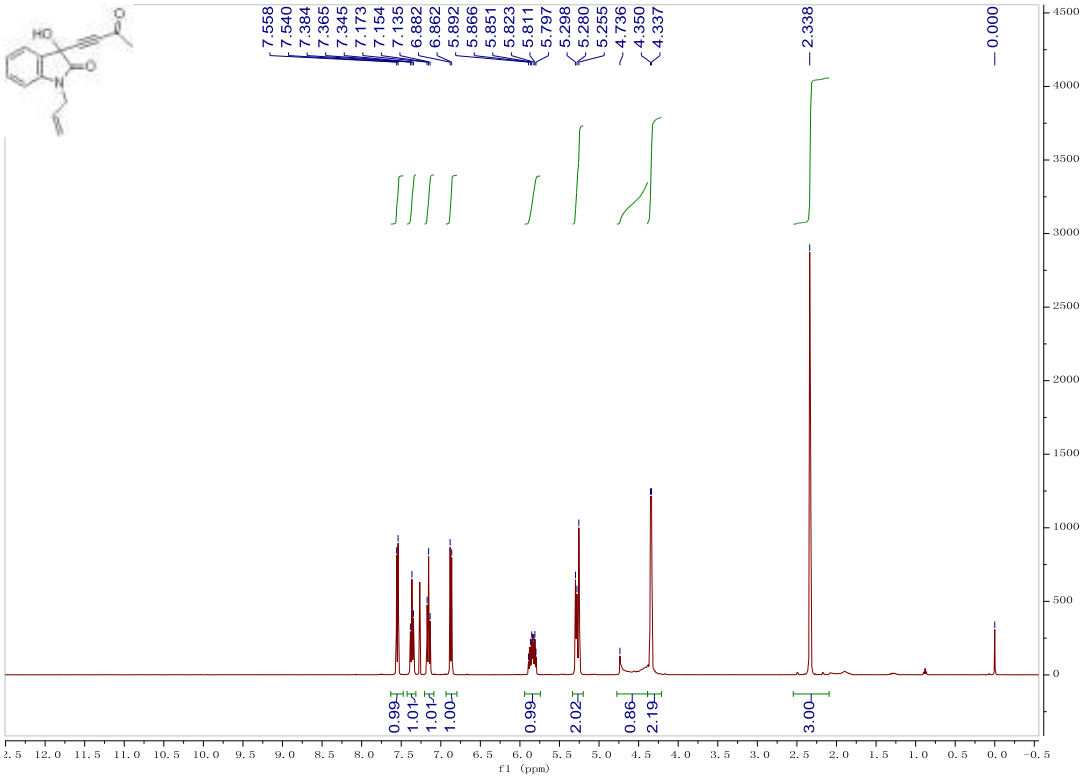
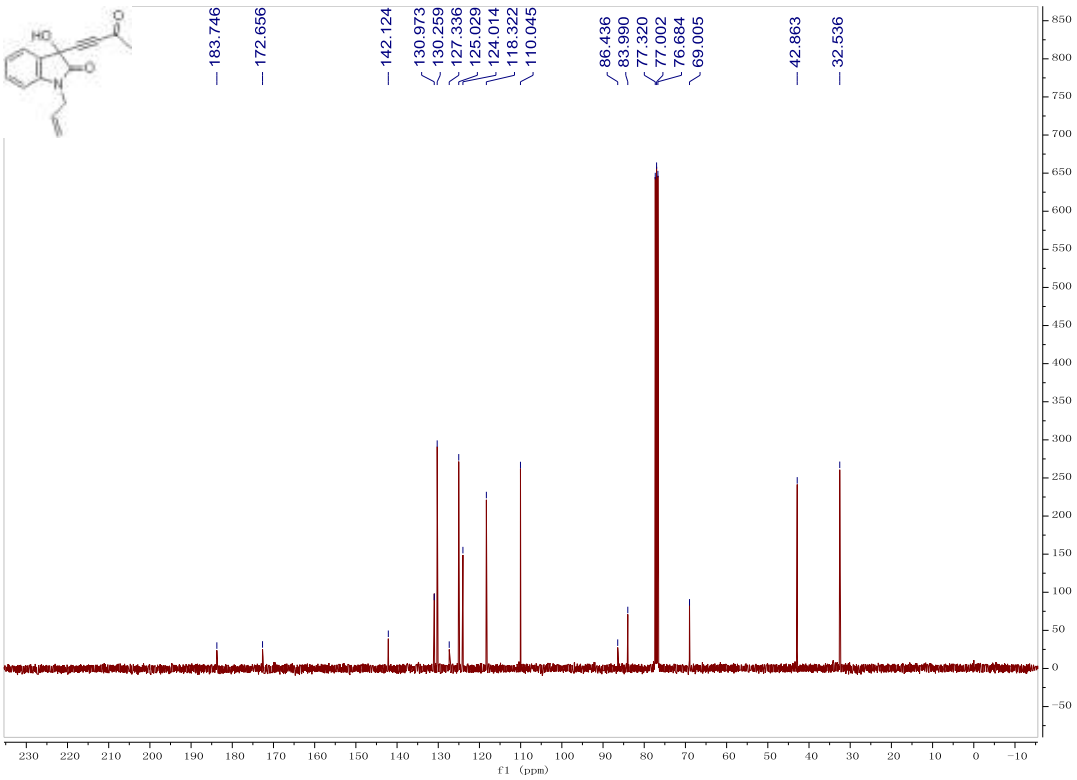


1-allyl-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1d)

A white solid, 81% yield (1033 mg). M.p.: 127-129 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 4.34 (d, *J* = 5.2 Hz, 2H, CH_2), 4.74 (br, 1H, OH), 5.25-5.30 (m, 2H, =CH_2), 5.79-5.89 (m, 1H, =CH), 6.87 (d, *J* = 8.0 Hz, 1H, ArH), 7.15 (t, *J* = 7.6 Hz, 1H, ArH), 7.37 (t, *J* = 7.6 Hz, 1H, ArH), 7.55 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 42.9, 69.0, 84.0, 86.4, 110.0, 118.3, 124.0, 125.0, 127.3, 130.3, 131.0, 142.1, 172.7, 183.7. IR (EtOH) ν 3316, 2215, 1707, 1675, 1611, 1463, 1364, 1217, 1178, 1098, 929, 760 cm^{-1}. HRMS (ESI) Calcd. For $C_{15}H_{17}N_2O_3^{+1}(M+NH_4)^+$ requires 273.1234, Found: 273.1229. $[\alpha]^{25}_D$ = +40.83 (c 0.04, CH_2Cl_2) for 97% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 28.675 min, t_{major} = 25.345 min.





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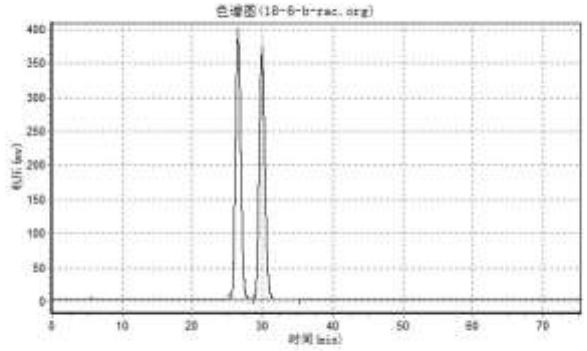

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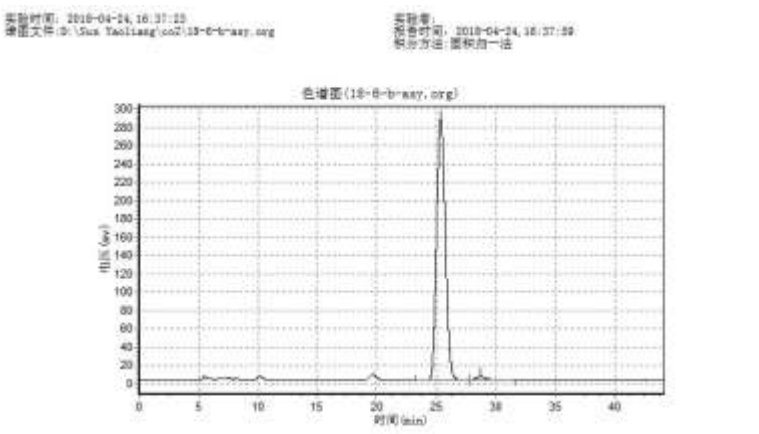

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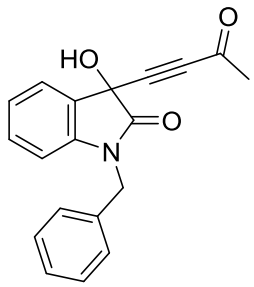
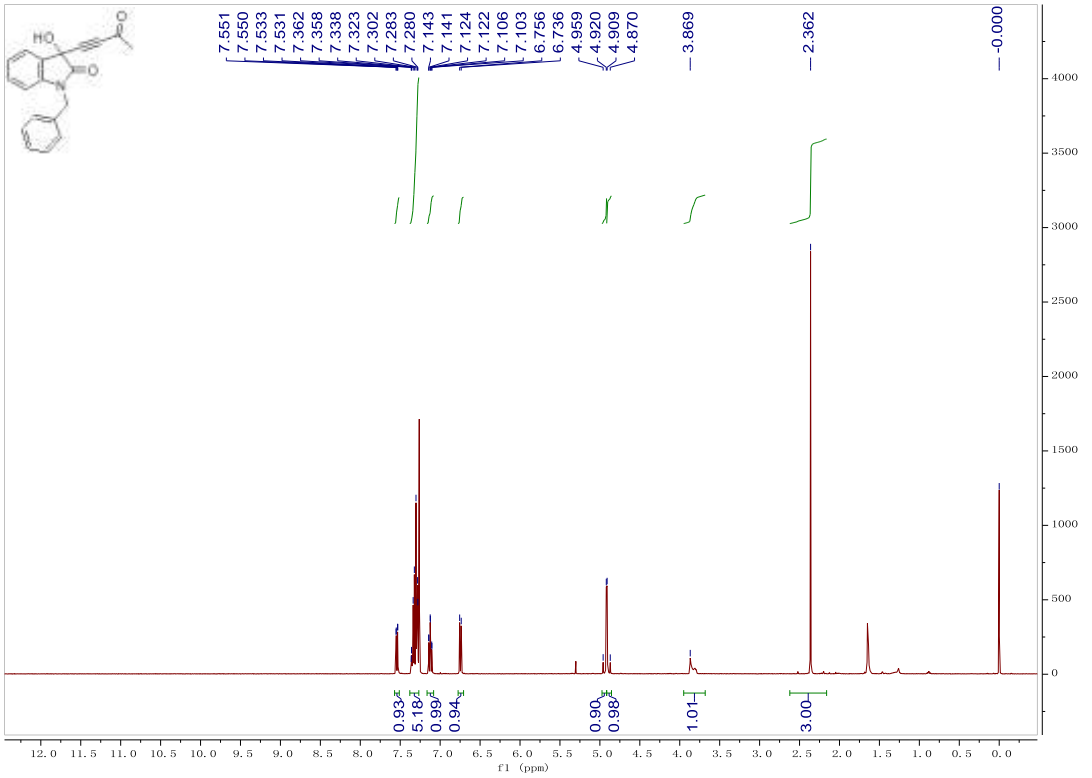


1-benzyl-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1e)

A white solid, 76% yield (1159 mg). M.p.: 151-153 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H, CH_3), 3.87 (br, 1H, OH), 4.89 (d, *J* = 15.6 Hz, 1H, CH_2), 4.94 (d, *J* = 15.6 Hz, 1H, CH_2), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 7.12 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.28-7.37 (m, 5H, ArH), 7.54 (dd, *J* = 0.4, 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 44.3, 69.1, 84.1, 86.3, 110.2, 124.1, 125.0, 127.1, 127.2, 128.0, 129.0, 131.0, 134.5, 142.1, 172.9, 183.6. IR (EtOH) ν 3305, 3055, 2922, 2207, 1705, 1676, 1376, 1175, 1071, 987, 698 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{19}N_2O_3^{+1}(M+NH_4)^+$ requires 323.1390, Found: 323.1384. $[\alpha]^{25}_D$ = +37.78 (c 0.09, CH_2Cl_2) for 91% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 46.708 min, t_{major} = 29.184 min.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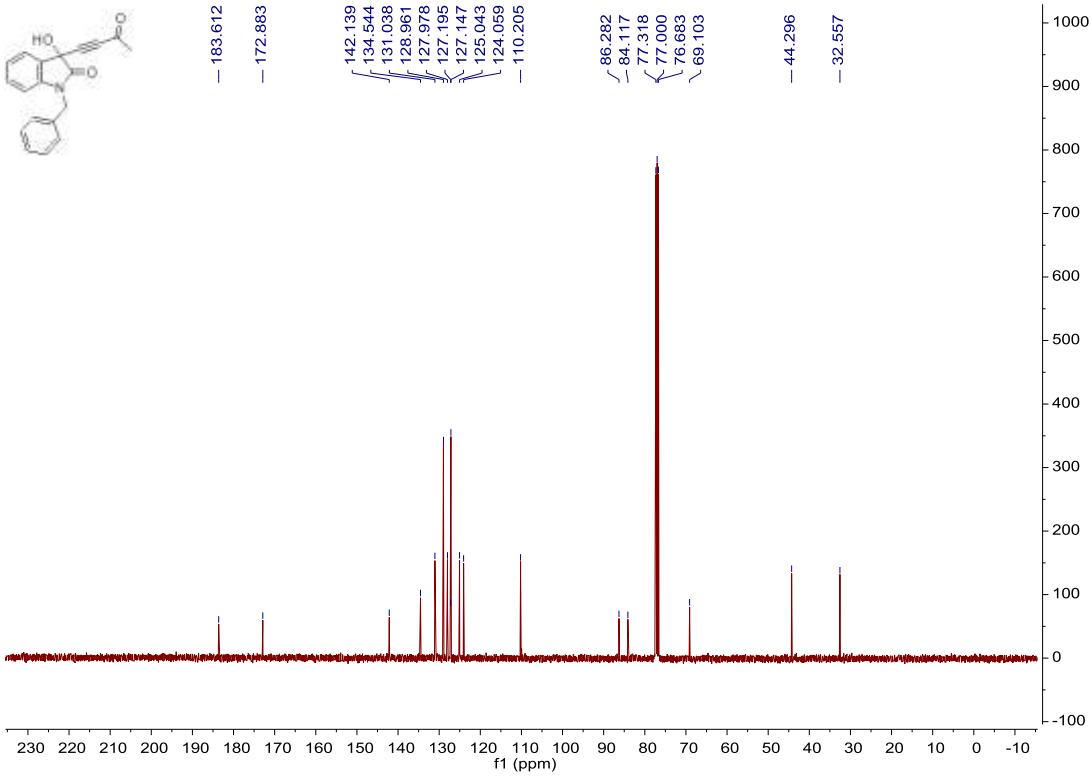
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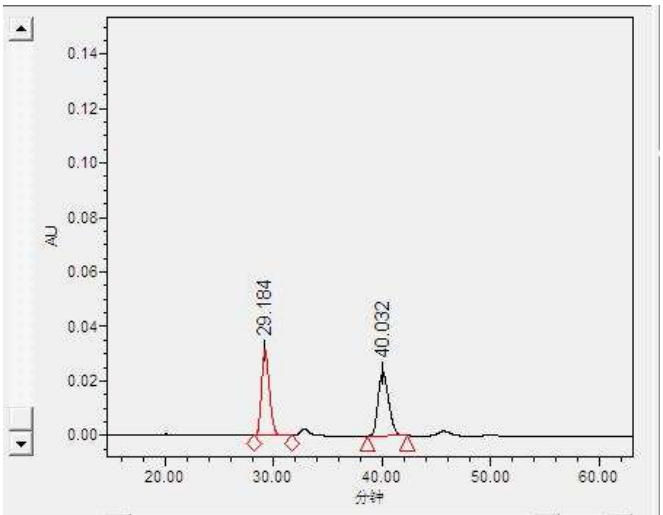

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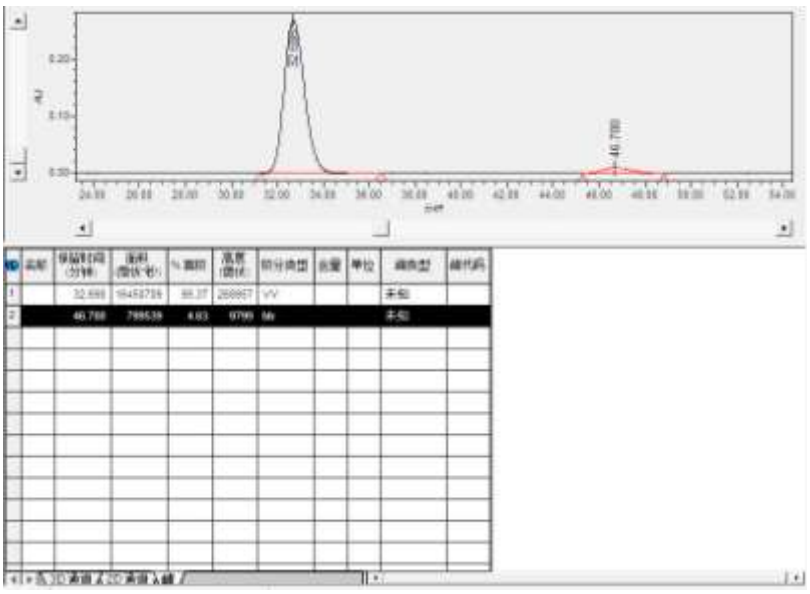
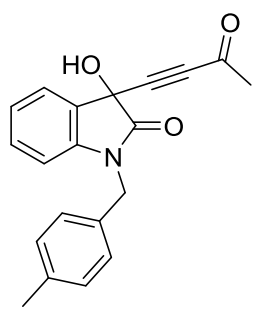
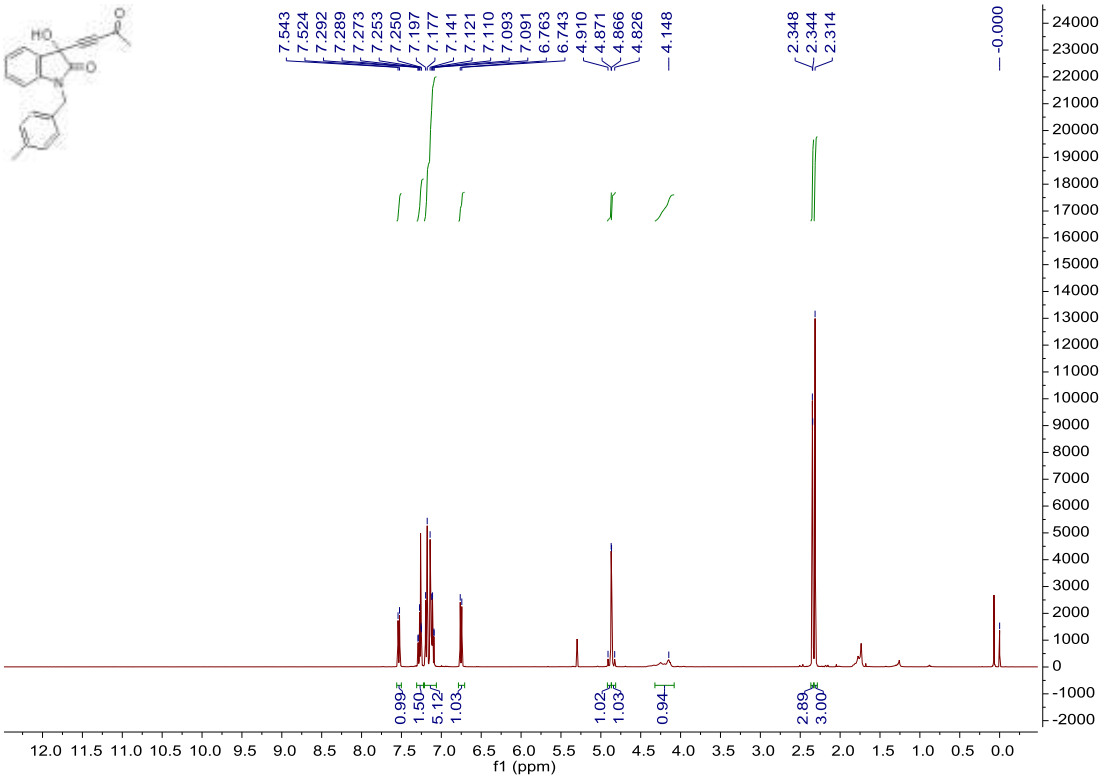
2		40.032	1572730	49.70	23198	BB			未知

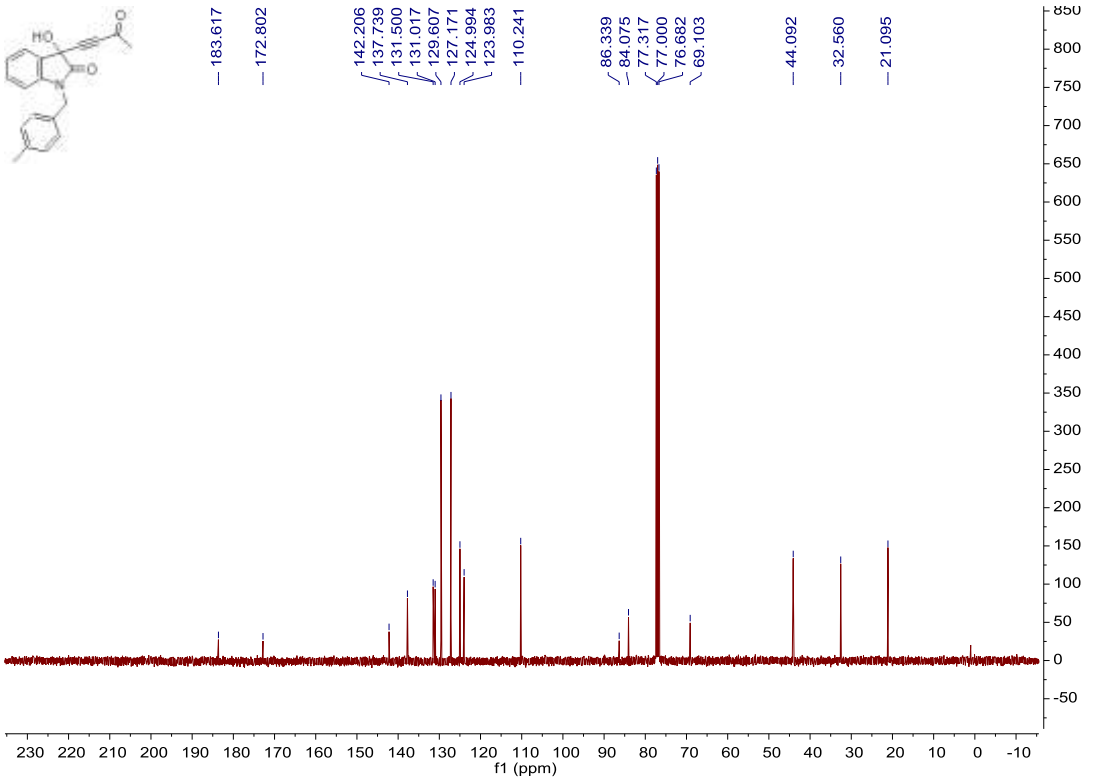


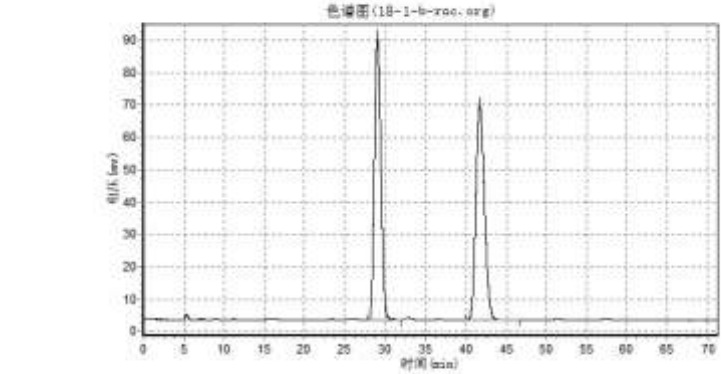


3-hydroxy-1-(4-methylbenzyl)-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1f)

A white solid, 82% yield (1324 mg). M.p.: 121-123 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (s, 3H, CH_3), 2.35 (d, *J* = 1.6 Hz, 3H, CH_3), 4.15 (br, 1H, OH), 4.85 (d, *J* = 16.0 Hz, 1H, CH_2), 4.89 (d, *J* = 16.0 Hz, 1H, CH_2), 6.75 (d, *J* = 8.0 Hz, 1H, ArH), 7.09-7.20 (m, 5H, ArH), 7.25-7.30 (m, 1H, ArH), 7.53 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 32.6, 44.1, 69.1, 84.1, 86.3, 110.2, 124.0, 125.0, 127.2, 129.6, 131.0, 131.5, 137.7, 142.2, 172.8, 183.6. IR (EtOH) ν 3243, 2919, 2867, 2220, 1716, 1363, 1208, 1170 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 337.1547, Found: 337.1540. $[\alpha]^{25}_D$ = +83.33 (c 0.04, CH_2Cl_2) for 80% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 37.917 min, t_{major} = 26.560 min.







分析结果表

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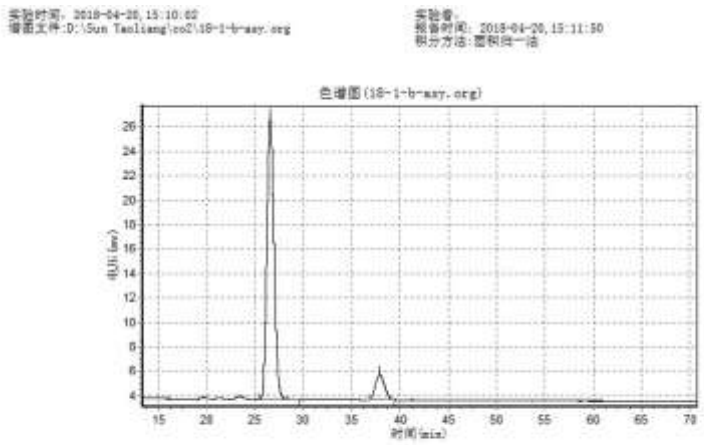
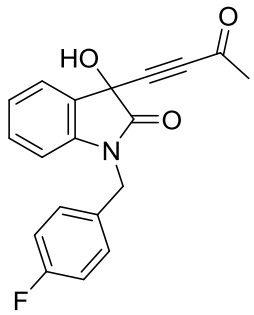
1		29.107	86808.516	4914594.500	49.8646
2		41.707	66132.703	4941276.000	50.1354
总计			152941.219	9855870.500	100.0000



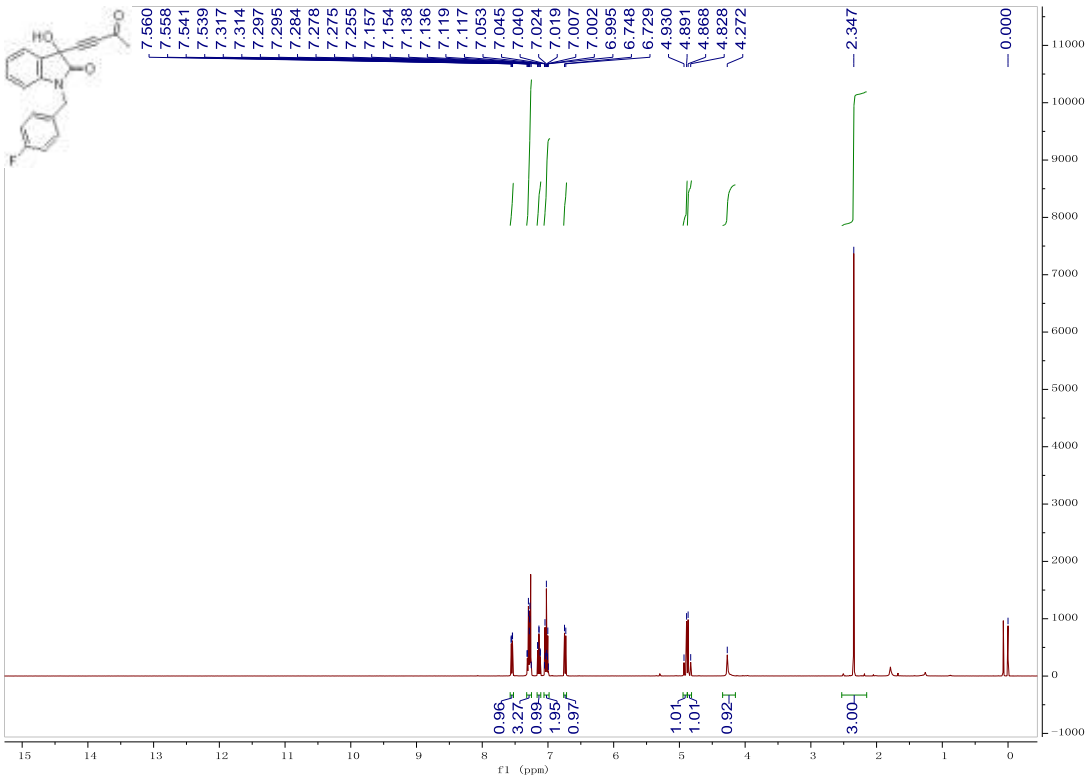
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		26.560	23081.146	1191191.750	89.7802
2		37.917	2053.476	135894.469	10.2198
总计			25134.623	1326786.219	100.0000



1-(4-fluorobenzyl)-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1g)

A white solid, 77% yield (1244 mg). M.p.: 123-125 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H, CH_3), 4.27 (br, 1H, OH), 4.85 (d, *J* = 16.0 Hz, 1H, CH_2), 4.91 (d, *J* = 16.0 Hz, 1H, CH_2), 6.74 (d, *J* = 7.6 Hz, 1H, ArH), 6.99-7.06 (m, 2H, ArH), 7.14 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.25-7.32 (m, 3H, ArH), 7.55 (dd, *J* = 0.8, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 43.6, 69.1, 84.2, 86.1, 110.0, 115.9 (d, *J* = 21.6 Hz), 124.2, 125.2, 127.2, 129.0 (d, *J* = 8.2 Hz), 130.3 (d, *J* = 3.2 Hz), 131.1, 141.9, 162.4 (d, *J* = 245.3 Hz), 172.9, 183.6. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) -114.01-(-113.93). IR (EtOH) ν 3254, 2973, 2920, 2222, 1712, 1507, 1156, 993, 817 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}FN_2O_3^{+1}$(M+NH_4)$^+$ requires 341.1296, Found: 341.1291. $[\alpha]^{25}_D$ = +86.67 (c 0.02, CH_2Cl_2) for 93% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 38.917 min, t_{major} = 28.752 min.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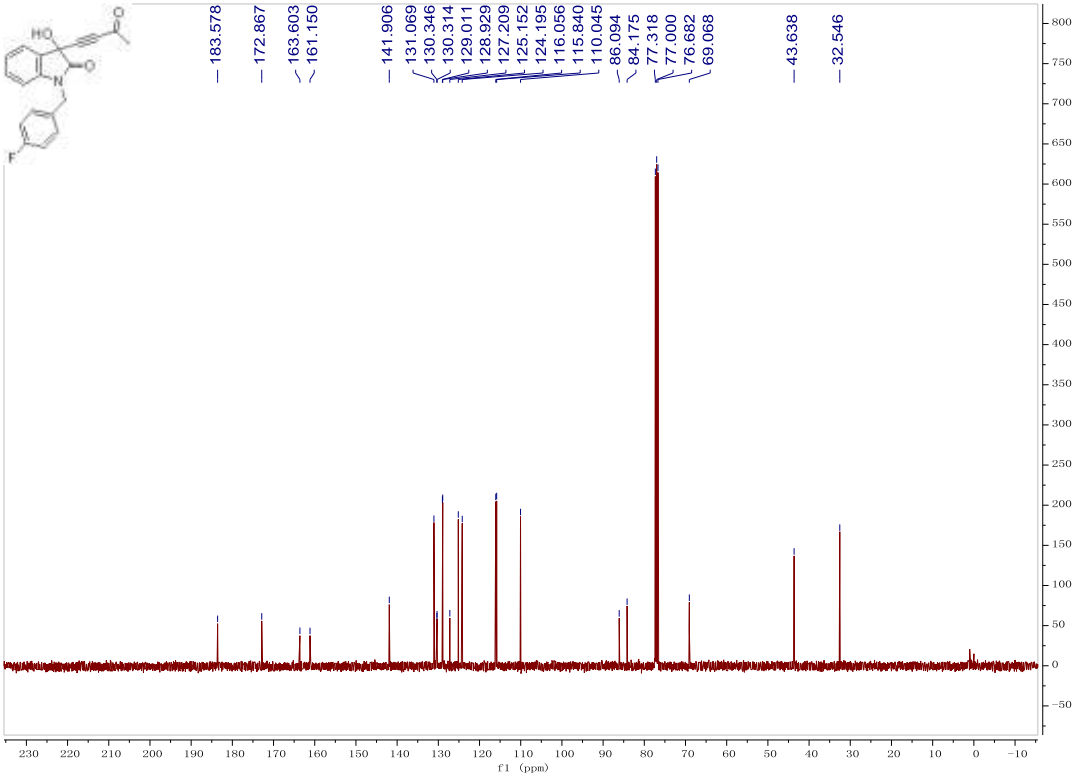
7.541
7.539
7.317
7.314
7.297
7.295
7.284
7.278
7.275
7.255
7.157
7.154
7.138
7.136
7.119
7.117
7.053
7.045
7.040
7.024
7.019
7.007
7.002
6.995
6.748
6.729
4.930
4.891
4.868
4.828
4.272
2.347
0.000
0.96
3.27
0.99
1.95
0.97
1.01
1.01
0.92
3.00
f1 (ppm)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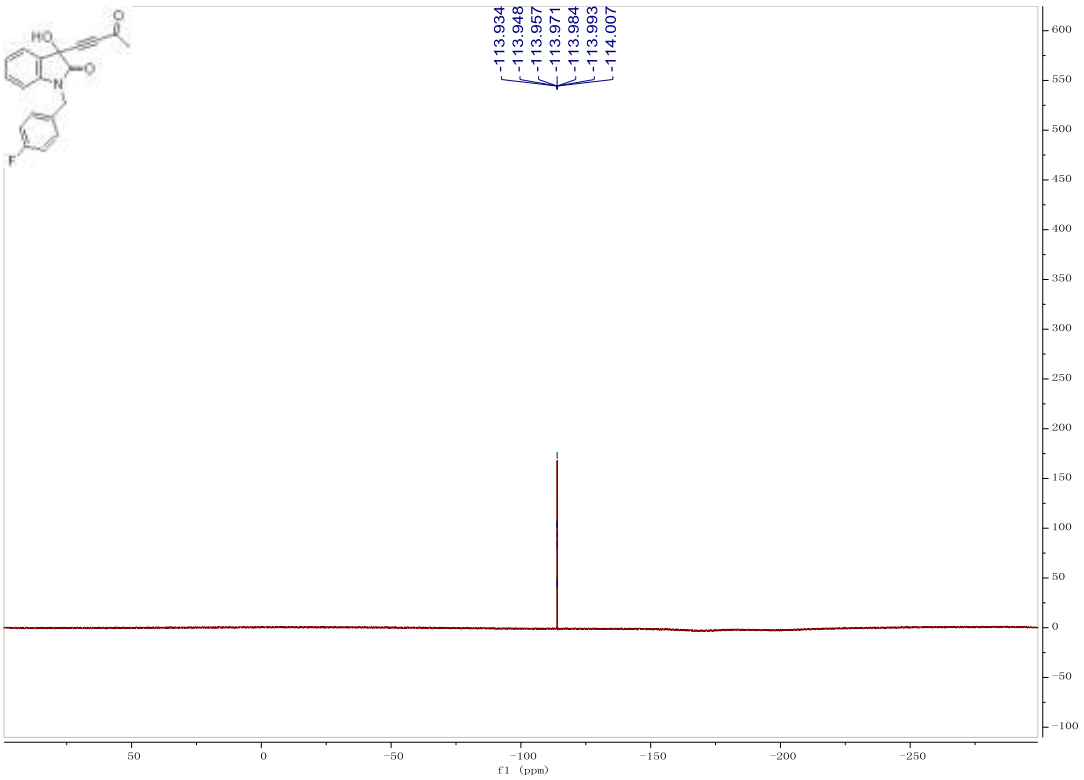
172.867
163.603
161.150
141.906
131.069
130.346
130.314
129.011
128.929
127.209
125.152
124.195
116.056
115.840
110.045
86.094
84.175
77.318
77.000
76.682
69.068
43.638
32.546
f1 (ppm)



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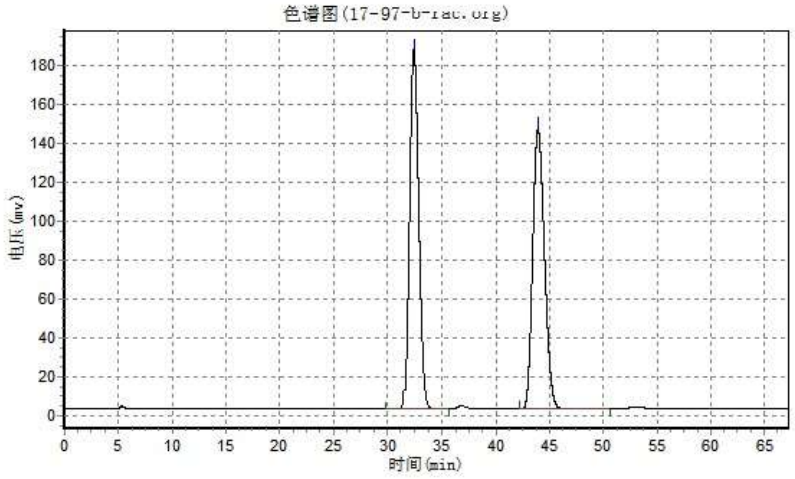

分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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2		43.932	143730.984	10992389.000	50.2556
总计			328350.281	21872957.000	100.0000

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实验者:
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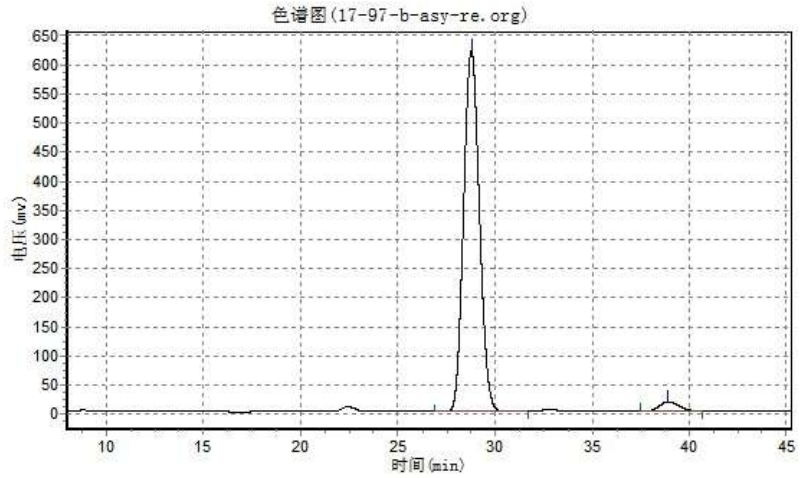
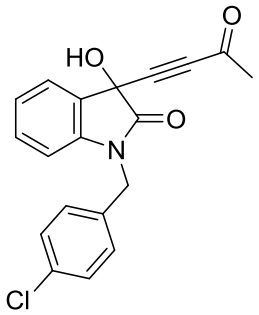


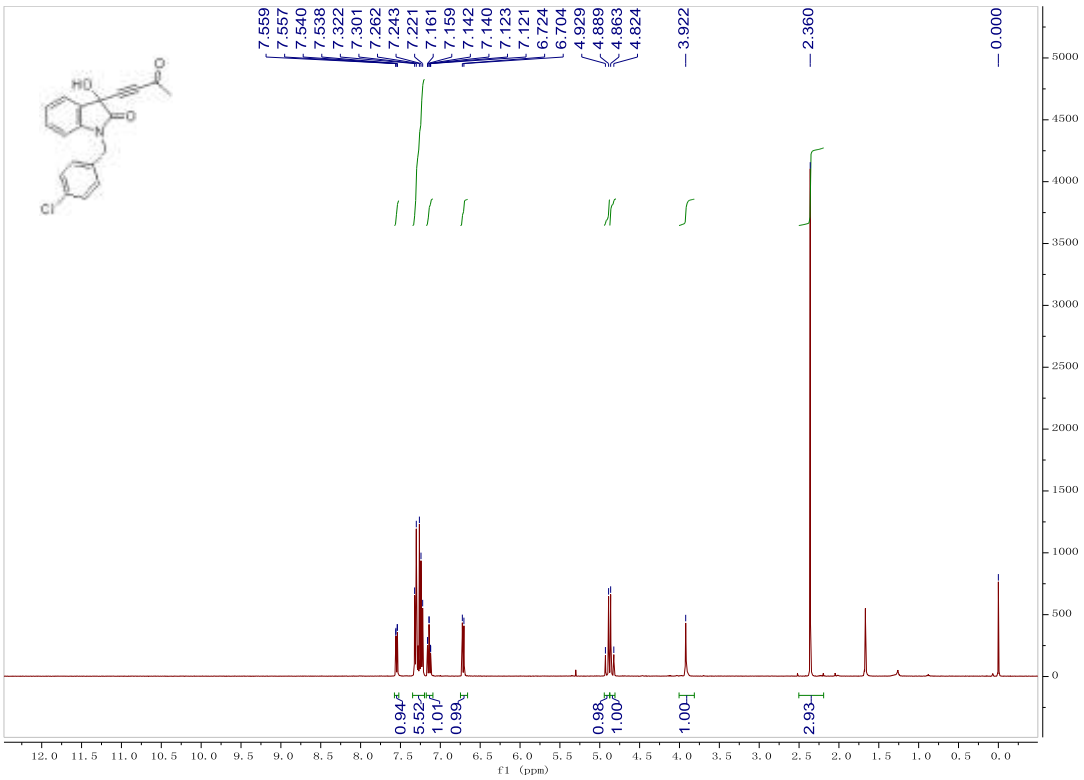
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		28.752	621475.375	35178936.000	96.6531
2		38.917	16365.487	1218182.375	3.3469
总计			637840.862	36397118.375	100.0000



1-(4-chlorobenzyl)-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1h)

A white solid, 78% yield (1322 mg). M.p.: 147-149 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H, CH_3), 3.92 (s, 1H, OH), 4.84 (d, *J* = 15.6 Hz, 1H, CH_2), 4.91 (d, *J* = 15.6 Hz, 1H, CH_2), 6.71 (d, *J* = 8.0 Hz, 1H, ArH), 7.14 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.22-7.33 (m, 5H, ArH), 7.55 (dd, *J* = 0.8, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 43.7, 69.0, 84.2, 85.9, 110.0, 124.2, 125.2, 127.1, 128.6, 129.2, 131.1, 133.1, 133.9, 141.9, 172.7, 183.5. IR (EtOH) ν 3235, 2927, 2210, 1713, 1672, 1610, 1486, 1366, 1209, 1171, 805 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}ClN_2O_3^{+1}(M+NH_4)^+$ requires 357.1000, Found: 357.0997. $[\alpha]^{25}_D$ = +27.50 (c 0.04, CH_2Cl_2) for 76% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 40.981 min, t_{major} = 28.868 min.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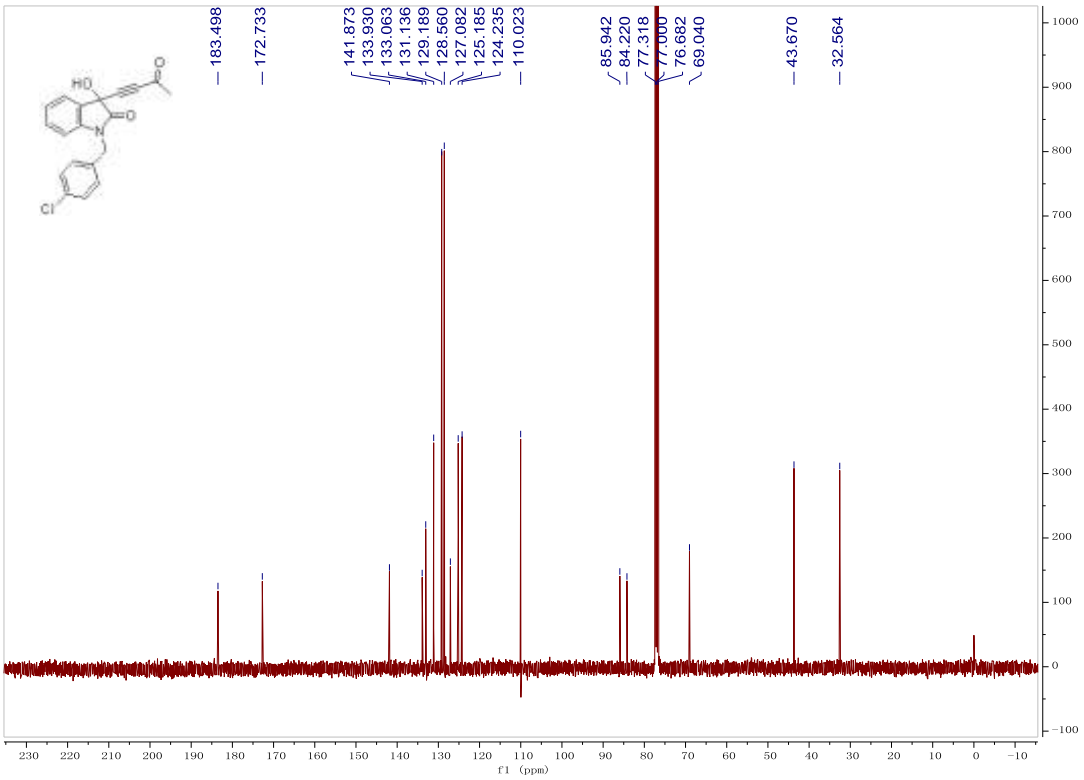
7.557
7.540
7.538
7.322
7.301
7.262
7.243
7.221
7.161
7.159
7.142
7.140
7.123
7.121
6.724
6.704
4.929
4.889
4.863
4.824
3.922
2.360
0.000
0.94
5.52
1.01
0.99
0.98
1.00
1.00
2.93
f1 (ppm)


183.498
172.733
141.873
133.930
133.063
131.136
129.189
128.560
127.082
125.185
124.235
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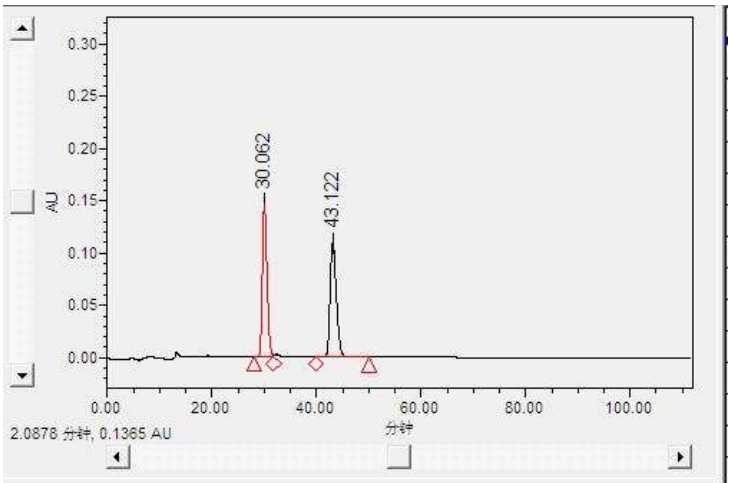
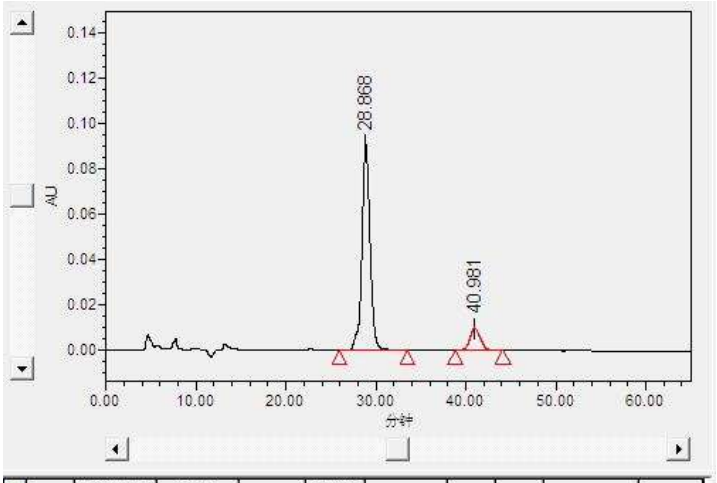
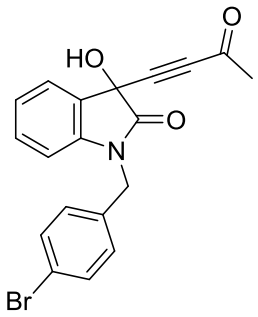
76.682
69.040
43.670
32.564
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		30.062	9093420	49.79	147386	BV			未知	
2		43.122	9169395	50.21	109423	VB			未知	

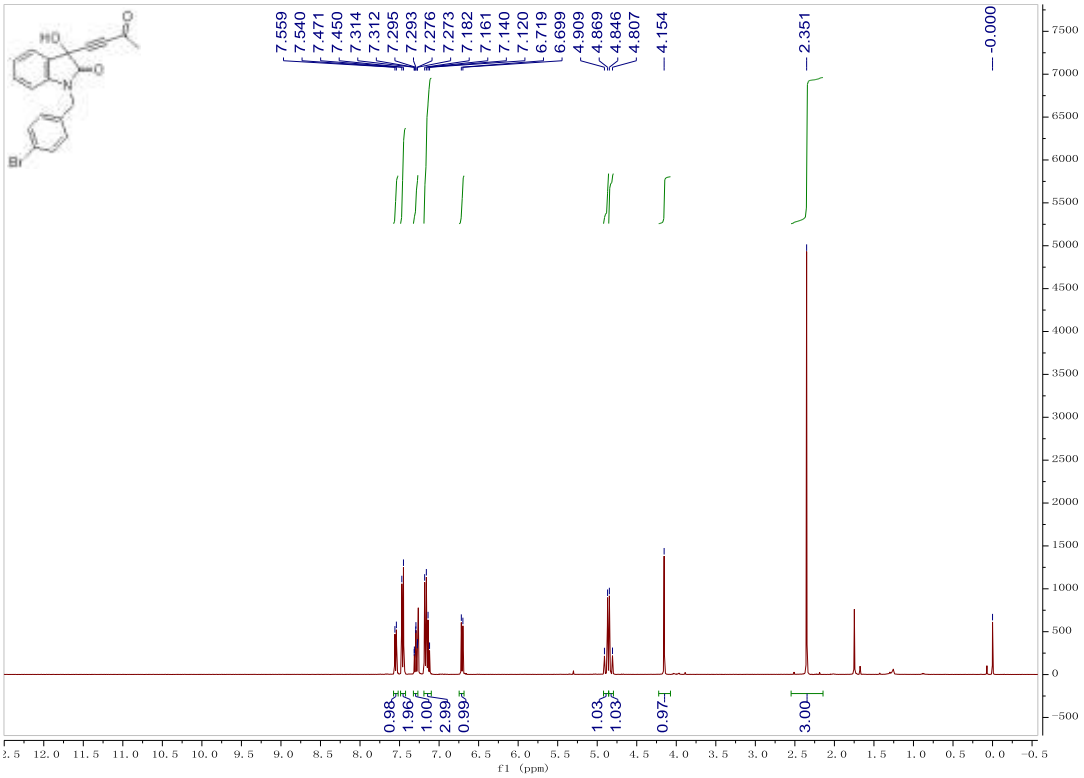


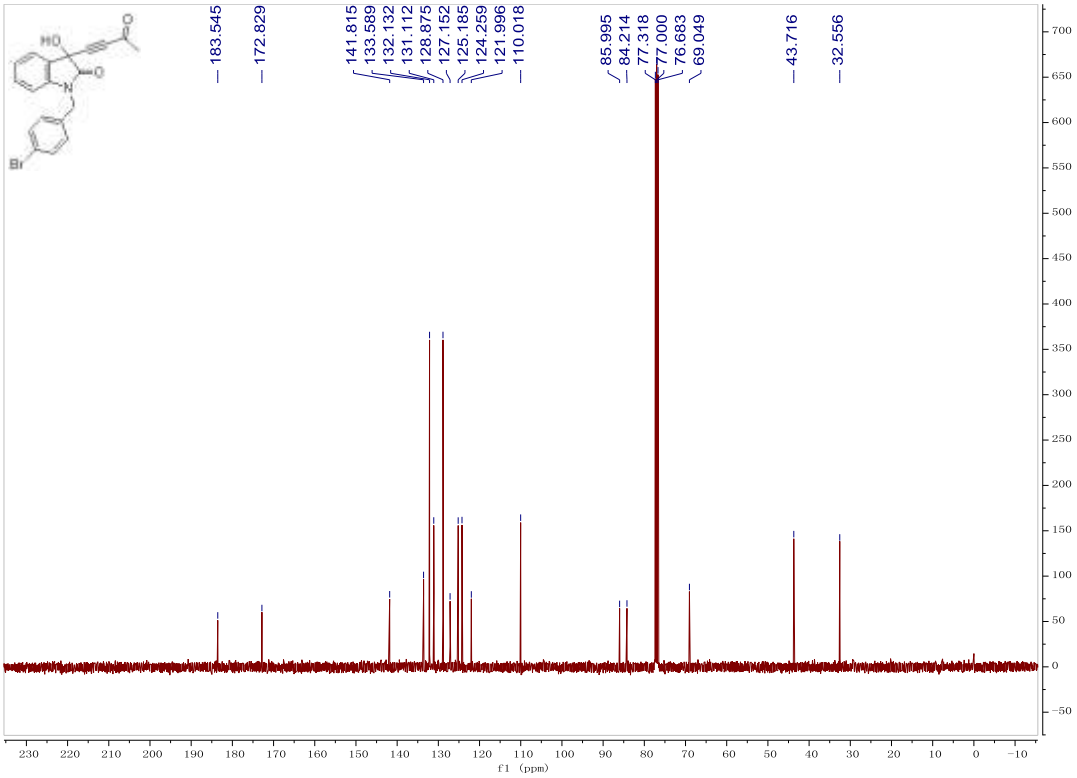
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		28.868	5734753	87.74	90501	BB			未知	
2		40.981	800974	12.26	9859	BB			未知	

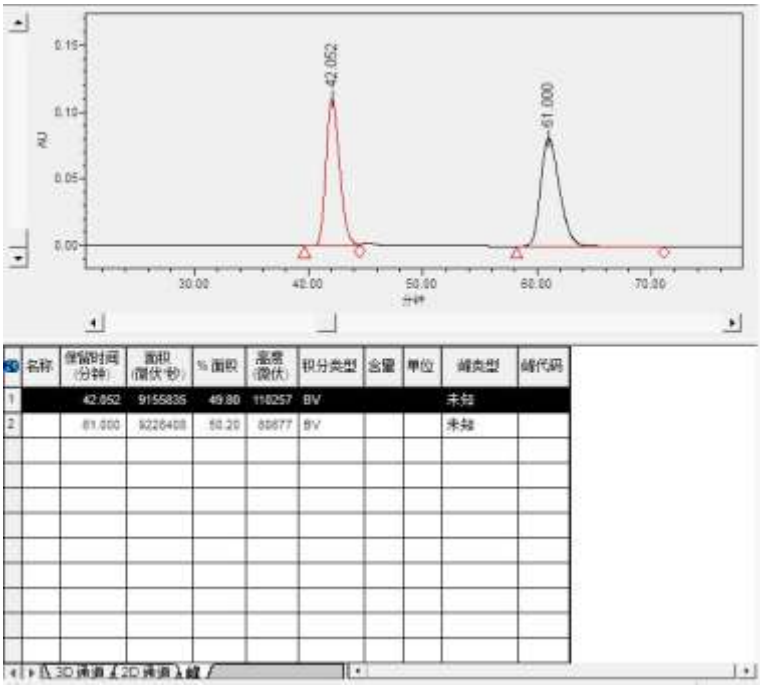


1-(4-bromobenzyl)-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1i)

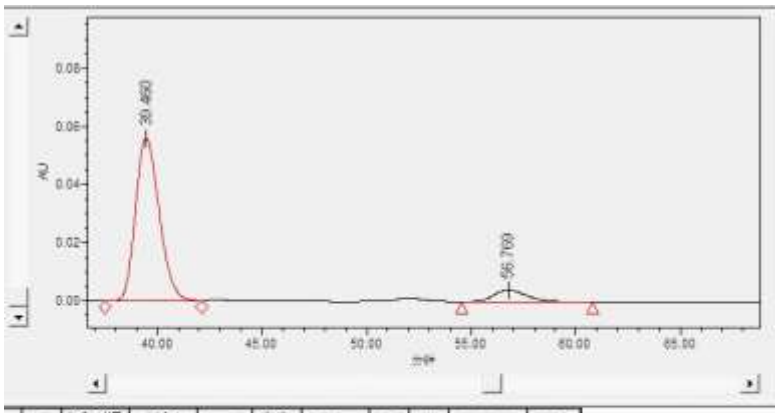
A white solid, 60% yield (1149 mg). M.p.: 152-154 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H, CH_3), 4.15 (s, 1H, OH), 4.83 (d, *J* = 15.6 Hz, 1H, CH_2), 4.89 (d, *J* = 15.6 Hz, 1H, CH_2), 6.71 (d, *J* = 8.0 Hz, 1H, ArH), 7.12-7.19 (m, 3H, ArH), 7.29 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.46 (d, *J* = 8.4 Hz, 2H, ArH), 7.55 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 43.7, 69.0, 84.2, 86.0, 110.0, 122.0, 124.3, 125.2, 127.2, 128.9, 131.1, 132.1, 133.6, 141.8, 172.8, 183.5. IR (EtOH) ν 3240, 2931, 2368, 2328, 2208, 1714, 1672, 1486, 1365, 1232m 1171, 744 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}BrN_2O_3^{+1}(M+NH_4)^+$ requires 401.0495, Found: 401.0490. $[\alpha]^{25}_D$ = +114.17 (c 0.04, CH_2Cl_2) for 83% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 56.769 min, t_{major} = 39.460 min.



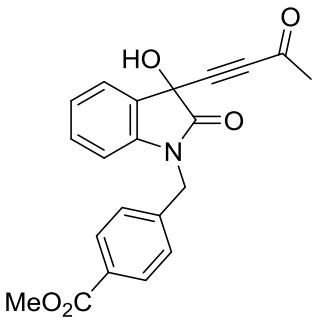




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		42.052	9155835	49.80	116257	BV			未知	
2		61.000	9226408	50.20	80677	BV			未知	

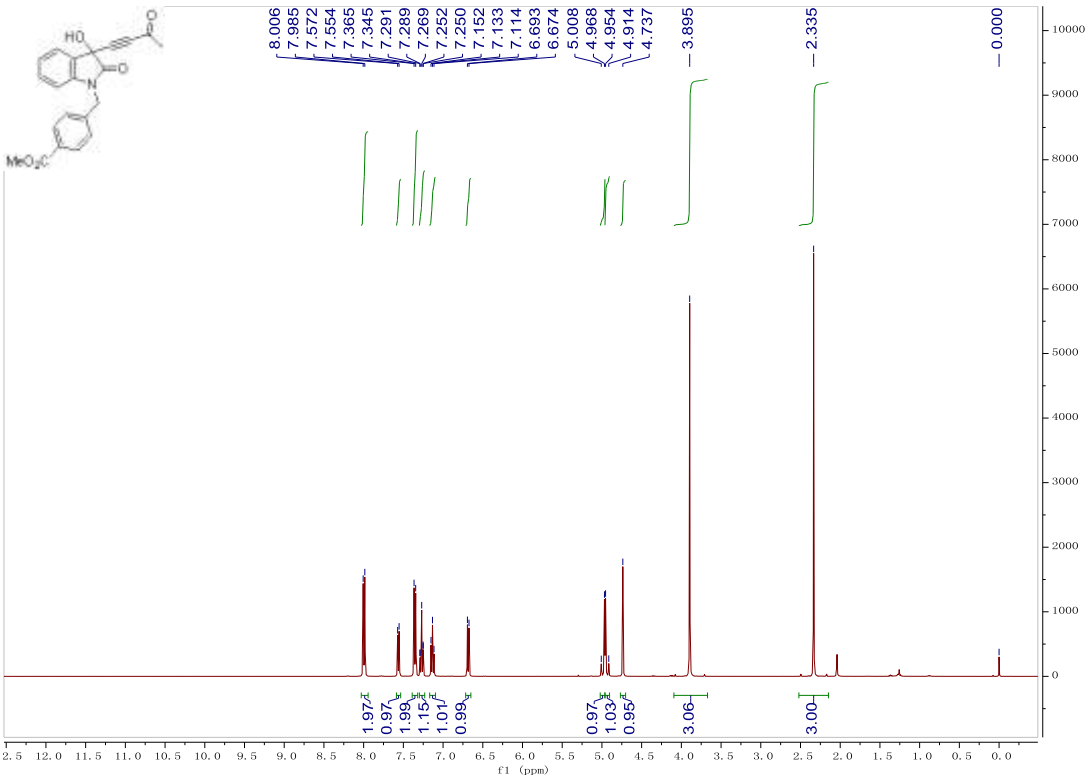


名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1	39.460	4446777	91.32	56280	VV			未知	
2	56.769	422753	8.68	3969	BB			未知	



methyl 4-((3-hydroxy-2-oxo-3-(3-oxobut-1-yn-1-yl)indolin-1-yl)methyl)benzoate (1j)

A white solid, 42% yield (387 mg). M.p.: 148-150 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 4.74 (s, 1H, OH), 4.93 (d, *J* = 16.0 Hz, 1H, CH_2), 4.99 (d, *J* = 16.0 Hz, 1H, CH_2), 6.68 (d, *J* = 7.6 Hz, 1H, ArH), 7.13 (t, *J* = 7.6 Hz, 1H, ArH), 7.25-7.30 (m, 1H, ArH), 7.36 (d, *J* = 8.0 Hz, 2H, ArH), 7.56 (d, *J* = 7.2 Hz, 1H, ArH), 8.00 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 44.0, 52.2, 69.1, 84.2, 86.1, 110.0, 124.3, 125.1, 127.0, 127.3, 129.8, 130.2, 131.0, 139.7, 141.7, 166.6, 173.0, 183.6. IR (EtOH) ν 3269, 2951, 2930, 2212, 1710, 1674, 1612, 1275, 1169 cm^{-1}. HRMS (ESI) Calcd. For $C_{21}H_{21}N_2O_5^{+1}(M+NH_4)^+$ requires 381.1445, Found: 381.1440.


8.006
7.985
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7.554
7.365
7.345
7.291
7.289
7.269
7.252
7.250
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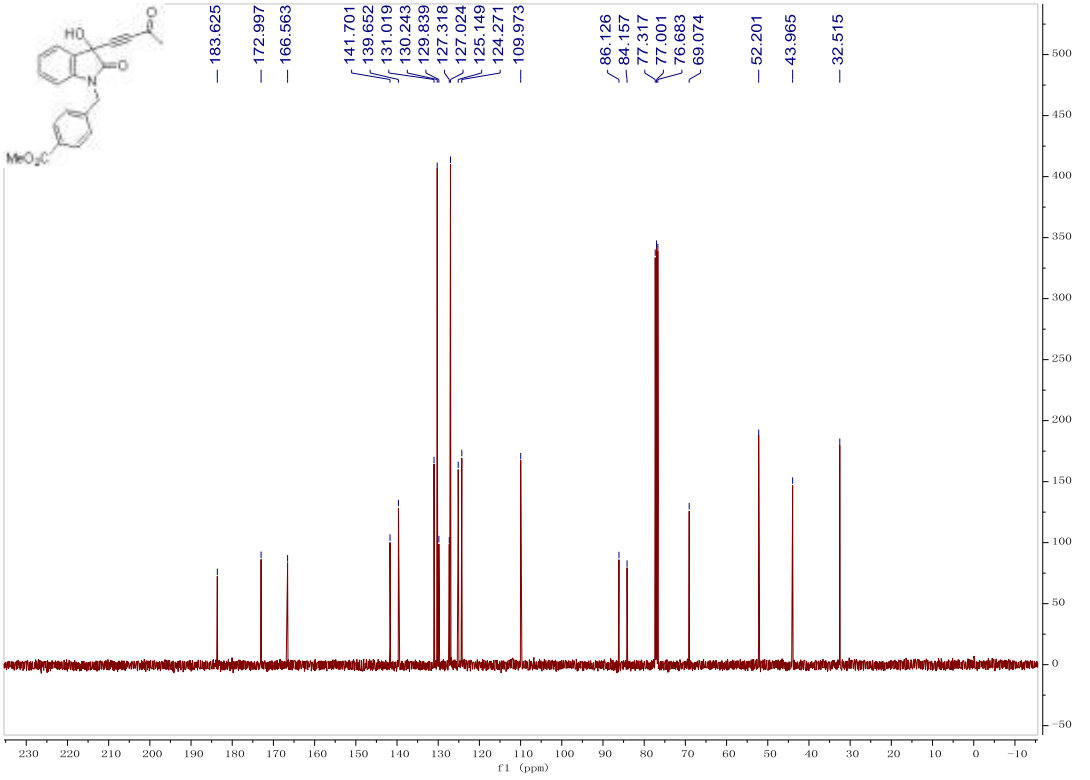
7.133
7.114
6.693
6.674
5.008
4.968
4.954
4.914
4.737
3.895
2.335
0.000
1.97
0.97
1.99
1.15
1.01
0.99
0.97
1.03
0.95
3.06
3.00
f1 (ppm)


183.625
172.997
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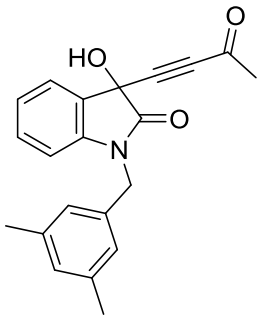
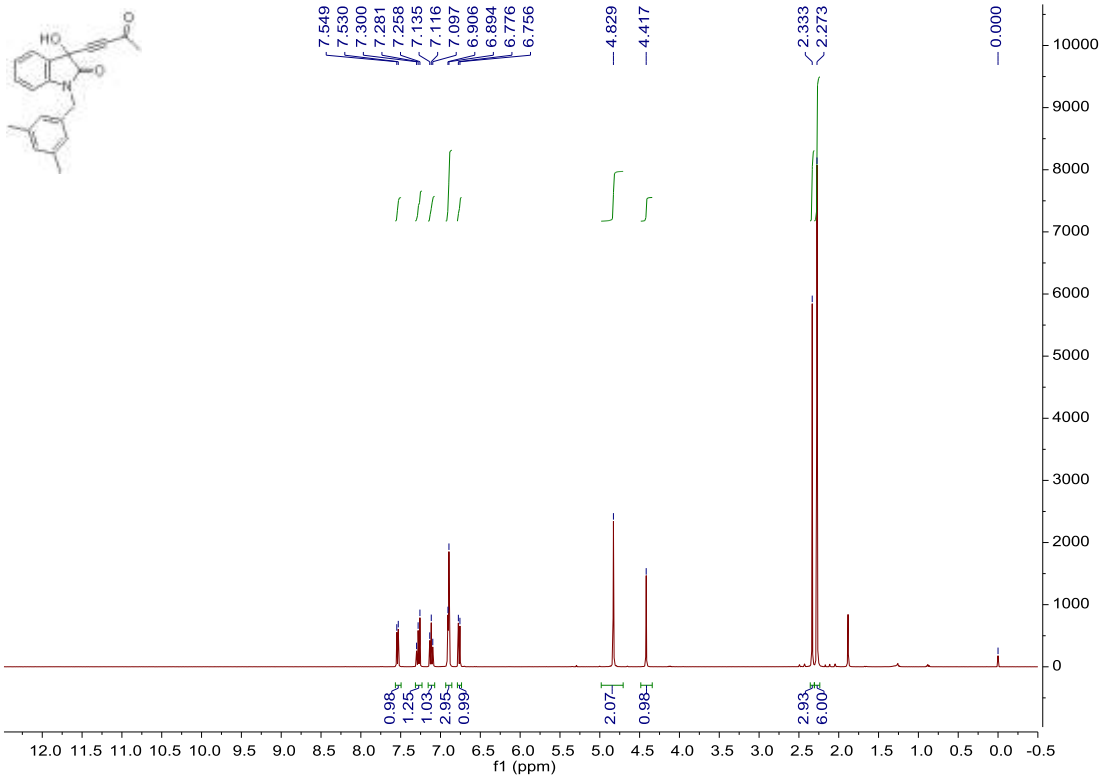
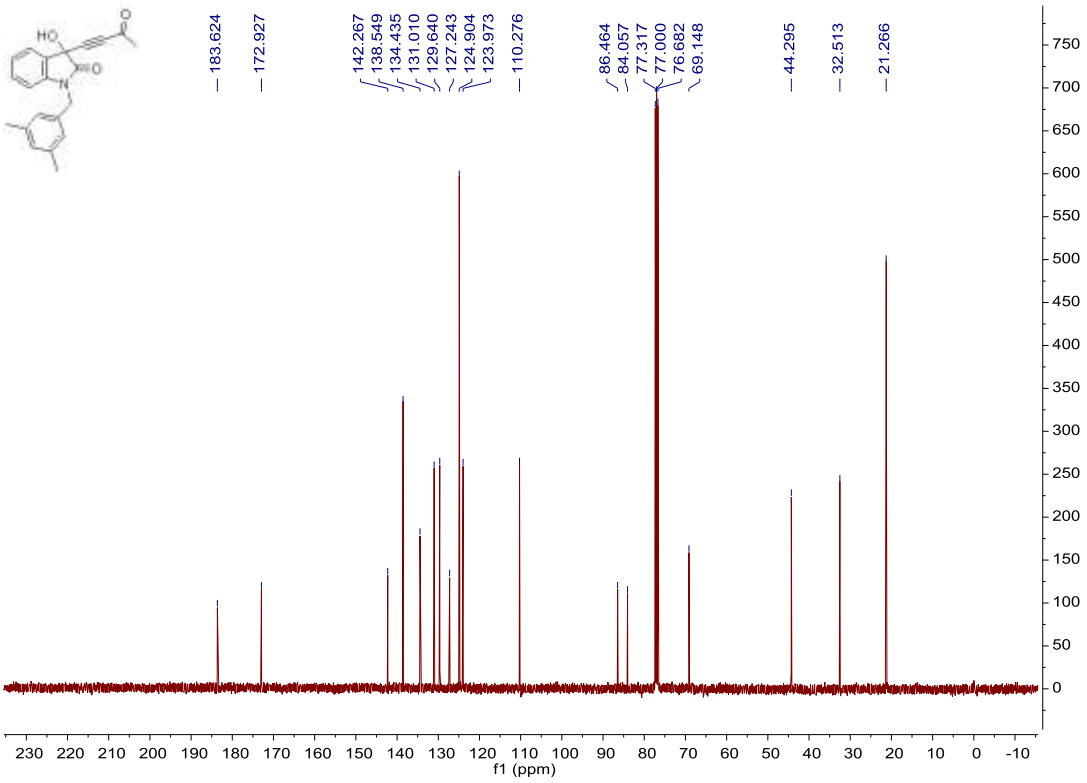
52.201
43.965
32.515
f1 (ppm)

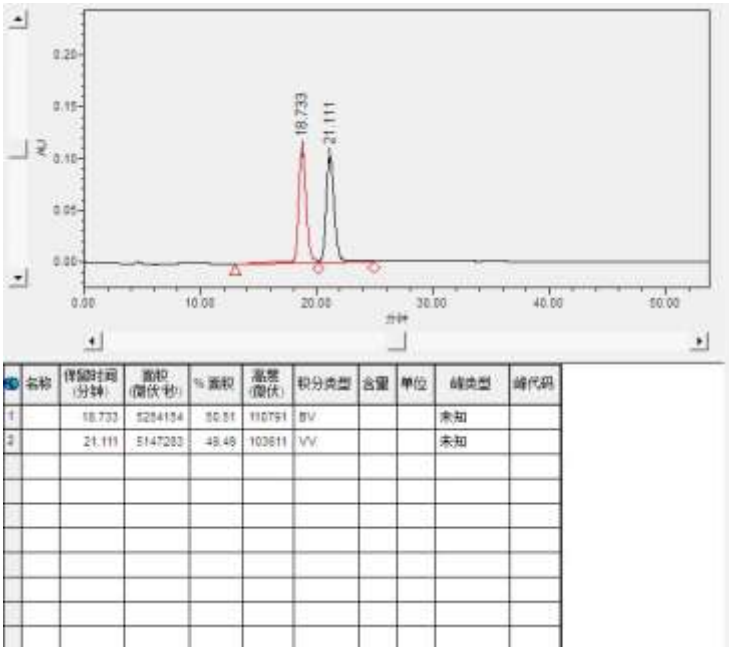


1-(3,5-dimethylbenzyl)-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1k)

A white solid, 86% yield (1431 mg). M.p.: 131-133 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.27 (s, 6H, CH_3), 2.33 (s, 3H, CH_3), 4.42 (s, 1H, OH), 4.83 (s, 2H, CH_2), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 6.89-6.91 (m, 3H, ArH), 7.12 (t, *J* = 7.6 Hz, 1H, ArH), 7.28 (t, *J* = 7.6 Hz, 1H, ArH), 7.54 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.3, 32.5, 44.3, 69.1, 84.1, 86.5, 110.3, 124.0, 124.9, 127.2, 129.6, 131.0, 134.4, 138.5, 142.3, 172.9, 183.6. IR (EtOH) ν 3290, 2917, 2854, 2215, 1716, 1611, 1362, 1211, 1171, 859 cm^{-1}. HRMS (ESI) Calcd. For $C_{21}H_{23}N_2O_3^{+1}(M+NH_4)^+$ requires 351.1703, Found: 351.1697. $[\alpha]^{25}_D$ = +24.17 (c 0.04, CH_2Cl_2) for 56% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 20.088 min, t_{major} = 18.733 min.







	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
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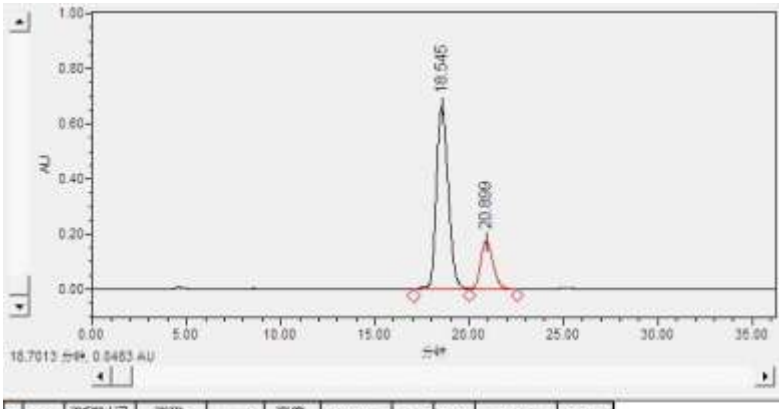
2		21.111	5147283	49.49	103611	VV			未知	



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
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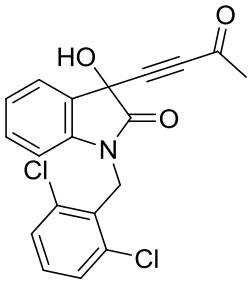
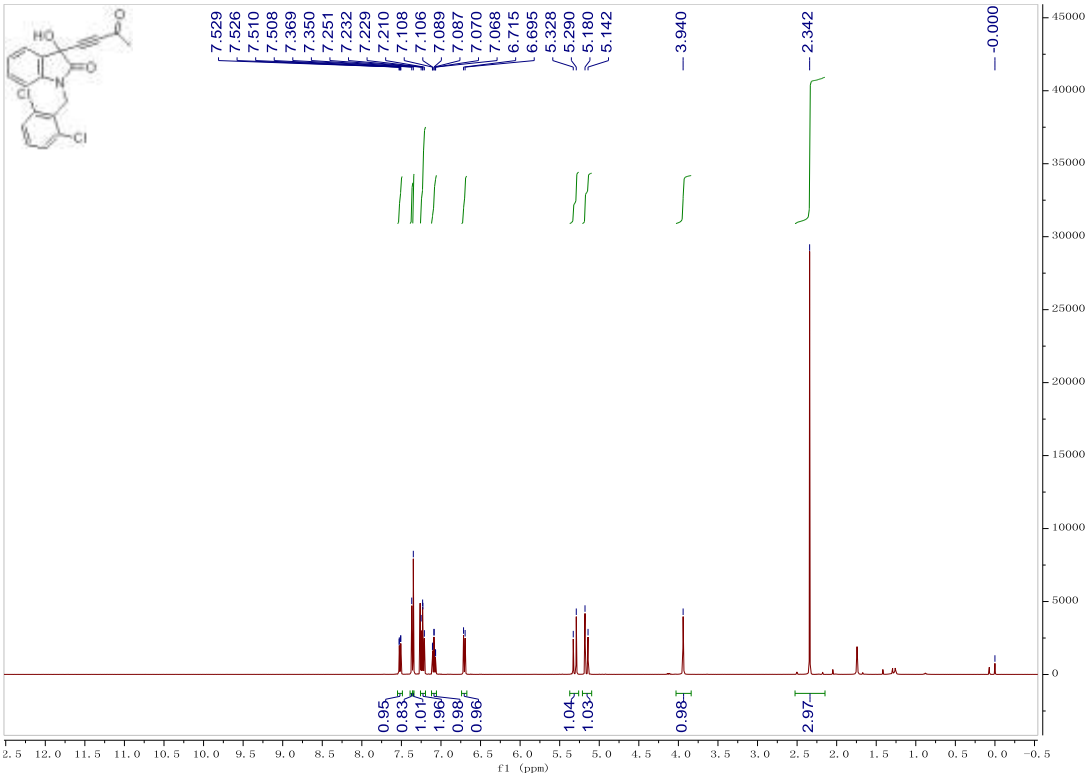
2		20.899	8226396	22.01	174824	VV			未知	



1-(2,6-dichlorobenzyl)-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1l)

A white solid, 63% yield (1174 mg). M.p.: 176-178 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 3.94 (s, 1H, OH), 5.16 (d, *J* = 15.2 Hz, 1H, CH_2), 5.31 (d, *J* = 15.2 Hz, 1H, CH_2), 6.71 (d, *J* = 8.0 Hz, 1H, ArH), 7.09 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.21-7.26 (m, 2H, ArH), 7.35 (s, 1H, ArH), 7.37 (s, 1H, ArH), 7.52 (dd, *J* = 1.2, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 40.5, 68.9, 84.0, 86.5, 110.2, 123.8, 125.0, 127.1, 129.1, 129.3, 130.1, 131.0, 136.3, 141.8, 172.1, 183.6. IR (EtOH) ν 3345, 2948, 2912, 2849, 1712, 1679, 1610, 1469, 1436, 1214, 1200, 969, 797 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{17}Cl_2N_2O_3^{+1}(M+NH_4)^+$ requires 391.0611, Found: 391.0605. $[\alpha]^{25}_D$ = -84.67 (c 0.05, CH_2Cl_2) for 28% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel OD-H column, Hexane/^{i}PrOH = 95/5, 0.7 mL/min, 254 nm, t_{minor} = 86.463 min, t_{major} = 58.402 min.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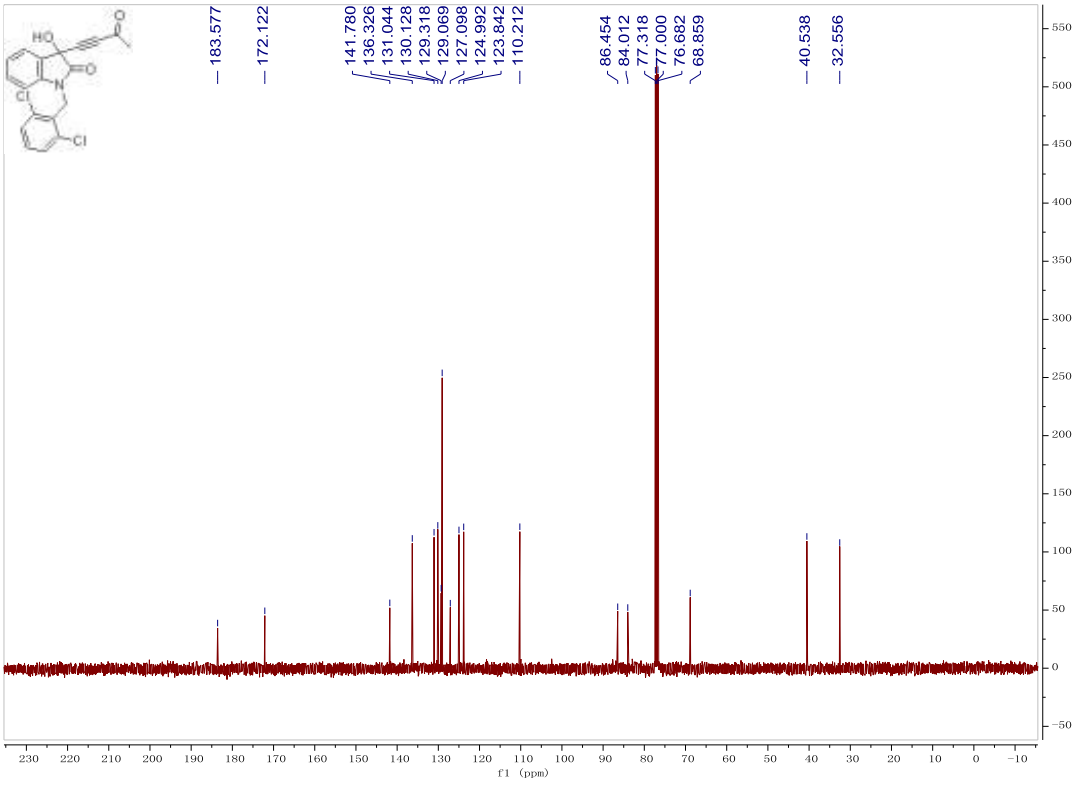
7.510
7.508
7.369
7.350
7.251
7.232
7.229
7.210
7.108
7.106
7.089
7.087
7.070
7.068
6.715
6.695
5.328
5.290
5.180
5.142
3.940
2.342
-0.000
0.95
0.83
1.01
1.96
0.98
0.96
1.04
1.03
0.98
2.97
f1 (ppm)


183.577
172.122
141.780
136.326
131.044
130.128
129.318
129.069
127.098
124.992
123.842
110.212
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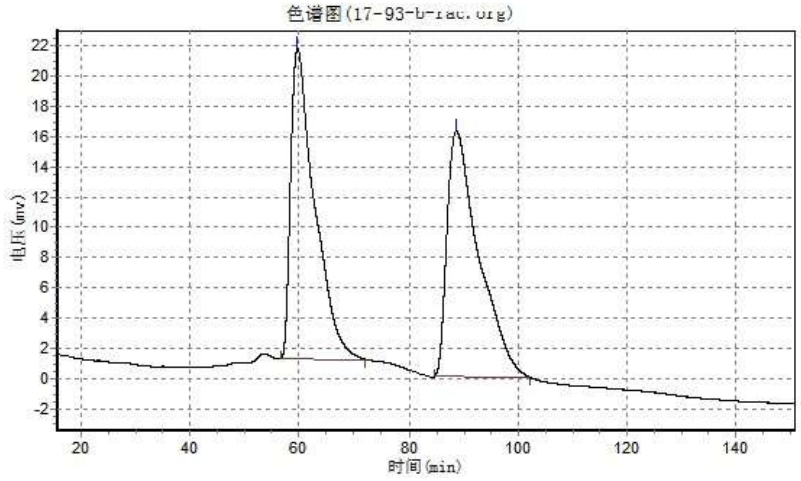
84.012
77.318
77.000
76.682
68.859
40.538
32.556
f1 (ppm)

实验时间：2019-07-16,14:22:25
谱图文件:D:\Sun Yaoliang\co2\17-93-b-rac.org

实验者:
报告时间：2019-07-16,14:24:25
积分方法:面积归一法



分析结果表

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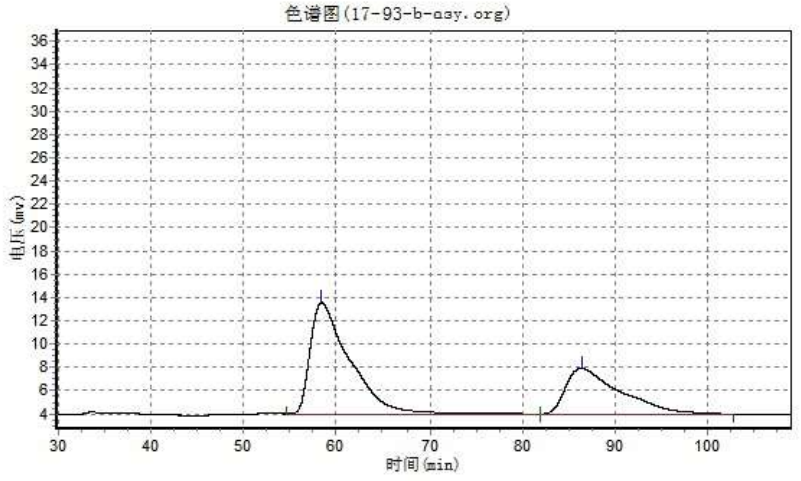
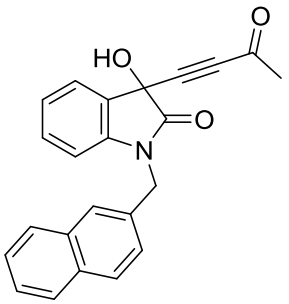
实验时间：2019-07-16,16:24:52
谱图文件:D:\Sun Yaoliang\co2\17-93-b-asy.org

实验者:
报告时间：2019-07-16,16:26:56
积分方法:面积归一法



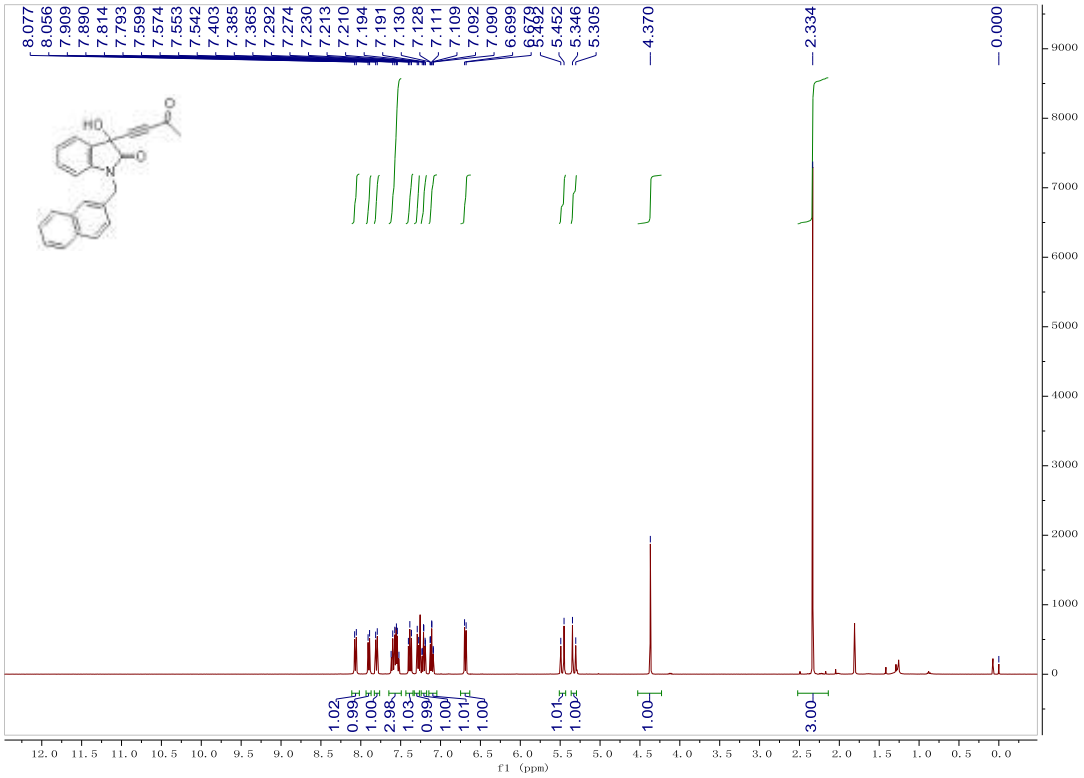
分析结果表

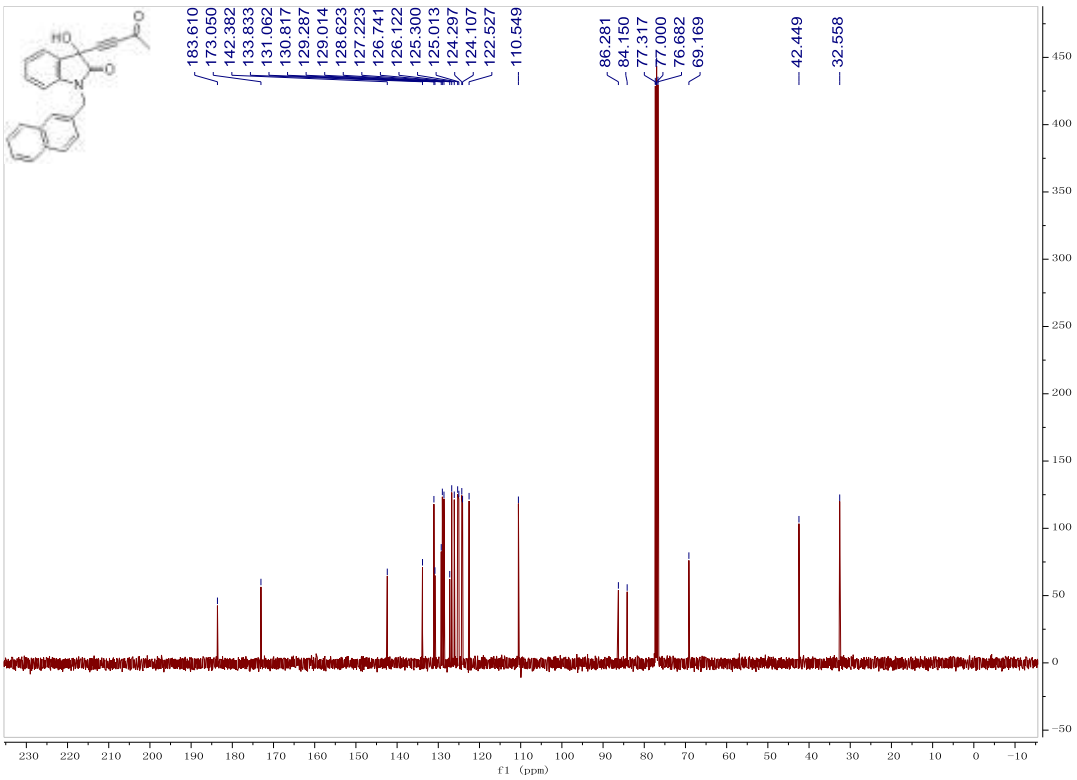
峰号	峰名	保留时间	峰高	峰面积	含量
1		58.402	9561.981	2852794.750	63.8956
2		86.463	3949.583	1611982.625	36.1044
总计			13511.564	4464777.375	100.0000

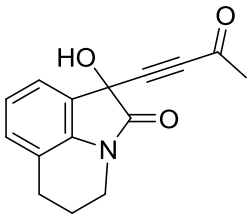


3-hydroxy-1-(naphthalen-2-ylmethyl)-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1m)

A white solid, 79% yield (1402 mg). M.p.: 135-137 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H, CH_3), 4.37 (s, 1H, OH), 5.33 (d, *J* = 16.4 Hz, 1H, CH_2), 5.47 (d, *J* = 16.4 Hz, 1H, CH_2), 6.69 (d, *J* = 8.0 Hz, 1H, ArH), 7.11 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.21 (dt, *J* = 1.2, 8.0 Hz, 1H, ArH), 7.28 (d, *J* = 7.2 Hz, 1H, ArH), 7.36-7.41 (m, 1H, ArH), 7.52-7.62 (m, 3H, ArH), 7.80 (d, *J* = 8.4 Hz, 1H, ArH), 7.90 (d, *J* = 7.6 Hz, 1H, ArH), 8.07 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 42.4, 69.2, 84.2, 86.3, 110.5, 122.5, 124.1, 124.3, 125.0, 125.3, 126.1, 126.7, 127.2, 128.6, 129.0, 129.3, 130.8, 131.1, 133.8, 142.4, 173.1, 183.6. IR (EtOH) ν 3329, 3047, 2932, 2220, 1605, 1483, 1207, 1046, 806 cm^{-1}. HRMS (ESI) Calcd. For $C_{23}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 373.1547, Found: 373.1543.

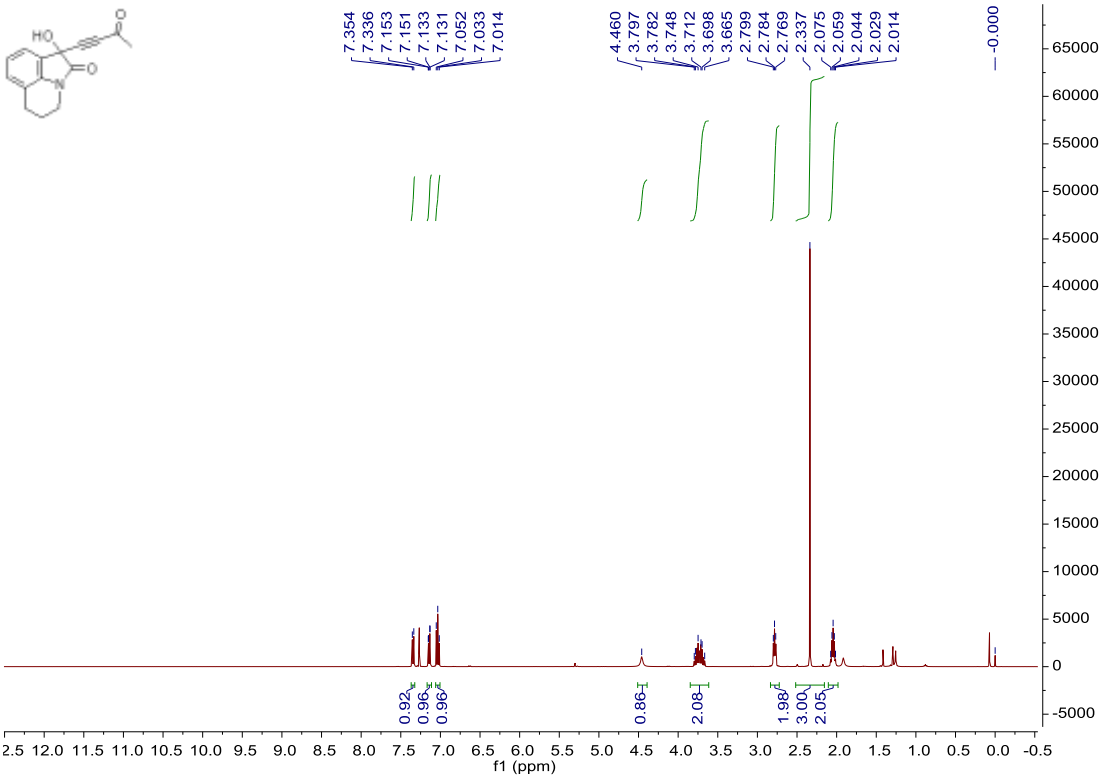






1-hydroxy-1-(3-oxobut-1-yn-1-yl)-5,6-dihydro-4H-pyrrolo[3,2,1-ij]quinolin-2(1H)-one (1n)

A white solid, 62% yield (791 mg). M.p.: 109-111 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.01-2.08 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.78 (t, *J* = 6.0 Hz, 2H, CH_2), 3.66-3.80 (m, 2H, CH_2), 4.46 (br, 1H, OH), 7.03 (t, *J* = 7.6 Hz, 1H, ArH), 7.14 (dd, *J* = 0.8, 8.0 Hz, 1H, ArH), 7.35 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 20.8, 24.2, 32.5, 39.4, 70.2, 83.9, 86.7, 121.4, 122.5, 123.4, 125.9, 129.8, 138.8, 171.6, 183.8. IR (EtOH) ν 3240, 2961, 2919, 2883, 2215, 1694, 1674, 1633, 1476, 1223, 1109, 790 cm^{-1}. HRMS (ESI) Calcd. For $C_{15}H_{17}N_2O_3^{+1}(M+NH_4)^+$ requires 273.1234, Found: 273.1230. $[\alpha]^{25}_{D}$ = +37.50 (c 0.04, CH_2Cl_2) for 96% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 36.067 min, t_{major} = 31.062 min.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O
N
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7.151
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7.033
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3.797
3.782
3.748
3.712
3.698
3.665
2.799
2.784
2.769
2.337
2.075
2.059
2.044
2.029
2.014
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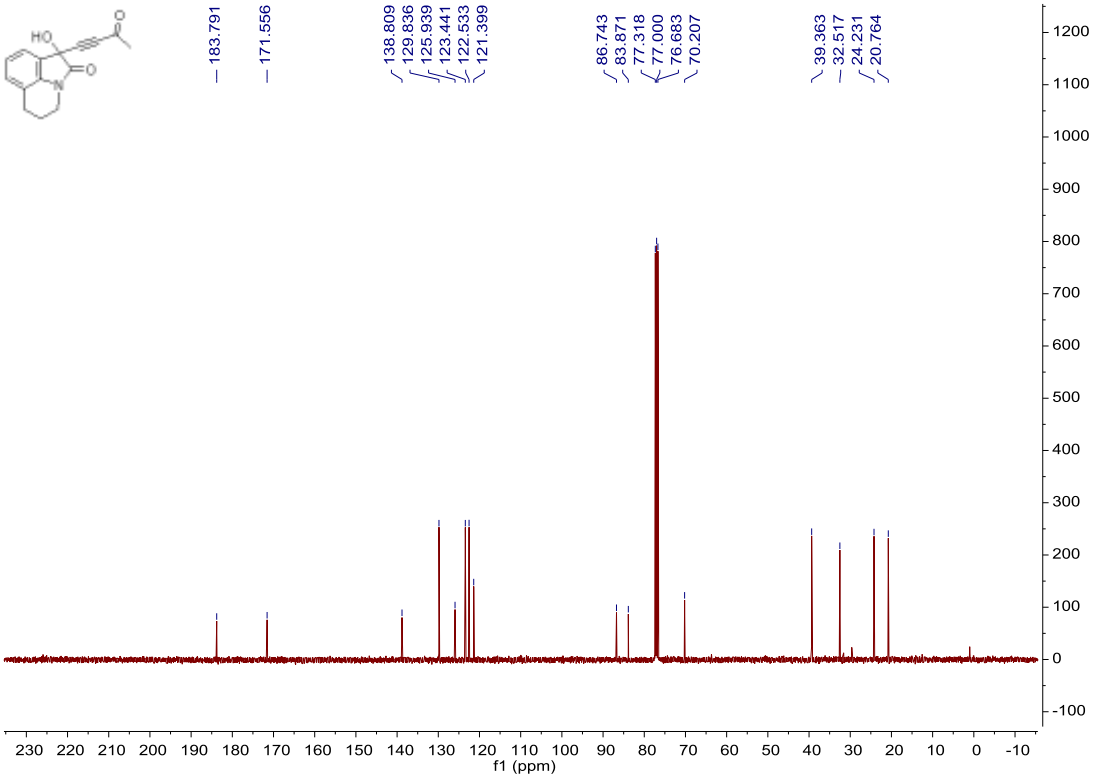
0.92
0.96
0.96
0.86
2.08
1.98
3.00
2.05
f1 (ppm)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O
N
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123.441
122.533
121.399
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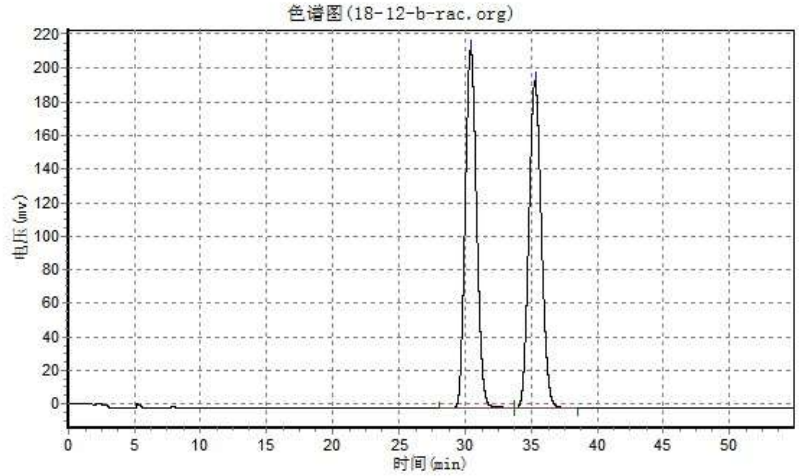
77.318
77.000
76.683
70.207
39.363
32.517
24.231
20.764
f1 (ppm)

实验时间：2018-04-28,18:39:23
谱图文件:D:\Sun Yaoliang\co2\18-12-b-rac.org

实验者:
报告时间：2018-04-28,19:34:43
积分方法:面积归一法



分析结果表

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2		35.315	194578.781	12870654.000	49.9265
总计			408336.766	25779191.000	100.0000

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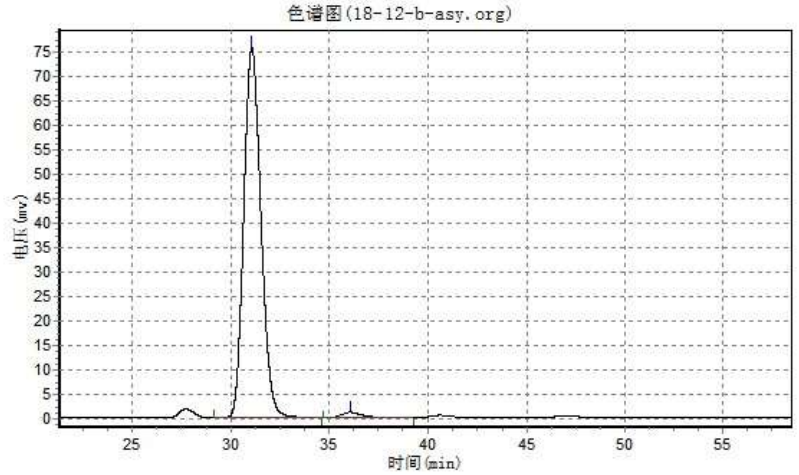
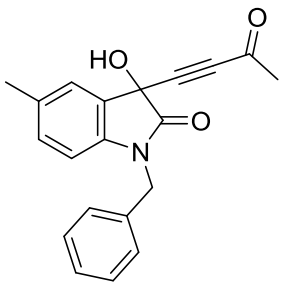
实验者:
报告时间：2018-04-28,19:53:54
积分方法:面积归一法



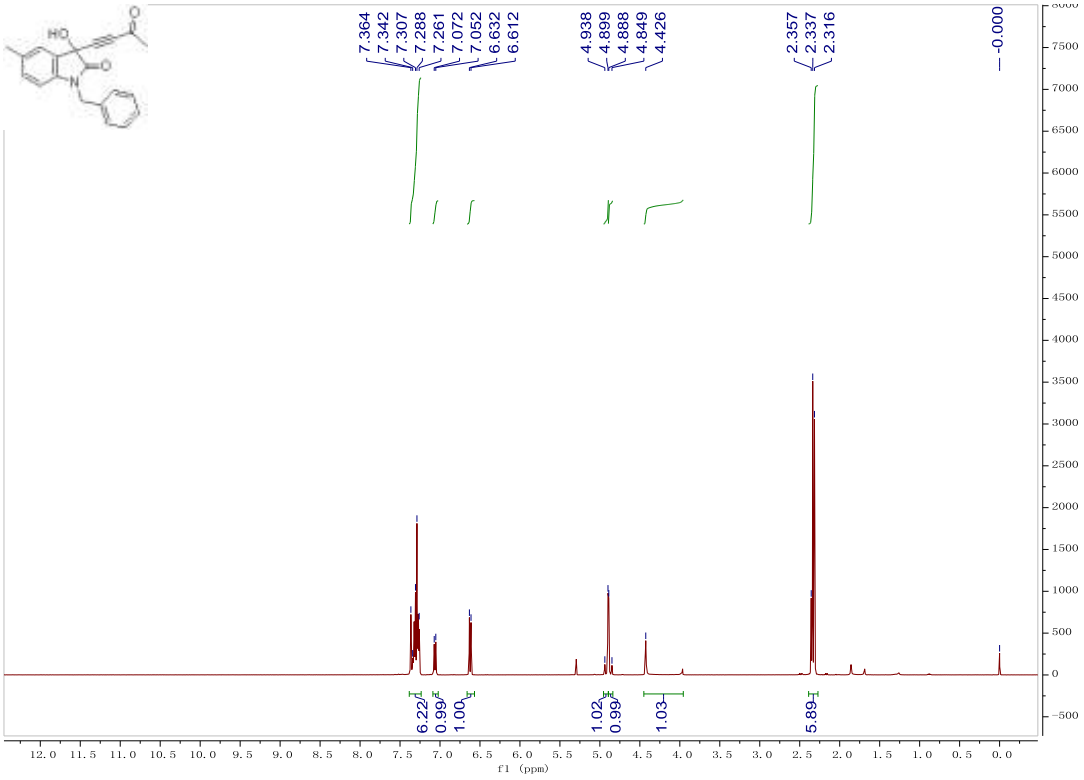
分析结果表

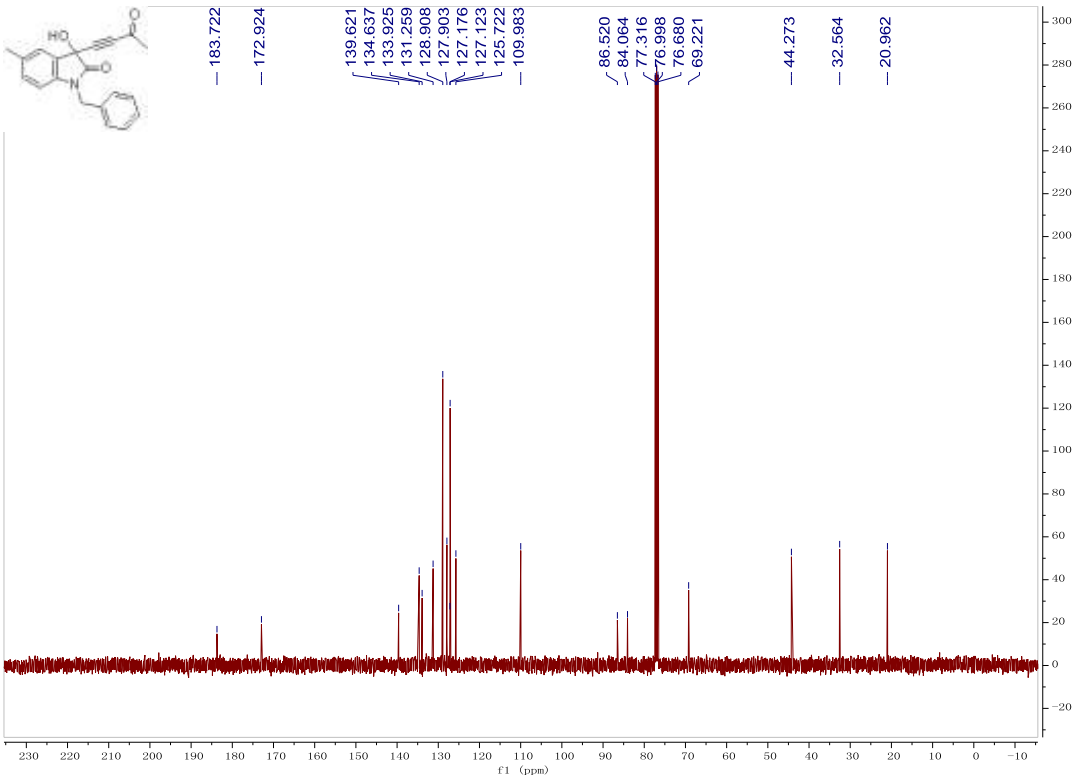
峰号	峰名	保留时间	峰高	峰面积	含量
1		31.062	75640.695	4609377.000	98.1485
2		36.067	1110.437	86954.500	1.8515
总计			76751.132	4696331.500	100.0000

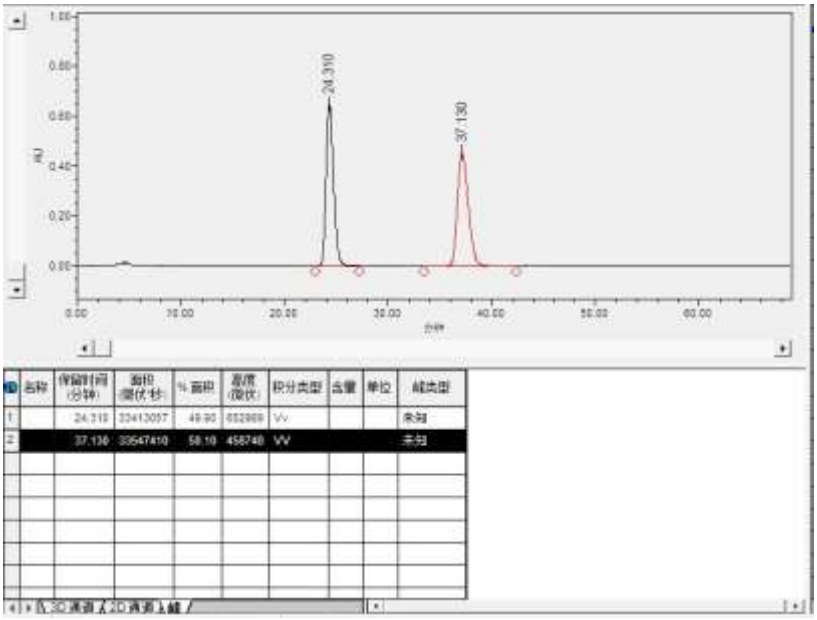


1-benzyl-3-hydroxy-5-methyl-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1o)

A white solid, 82% yield (1308 mg). M.p.: 184-186 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31-2.36 (m, 6H, CH_3), 4.43 (br, 1H, OH), 4.87 (d, *J* = 15.6 Hz, 1H, CH_2), 4.92 (d, *J* = 15.6 Hz, 1H, CH_2), 6.62 (d, *J* = 8.0 Hz, 1H, ArH), 7.06 (d, *J* = 8.0 Hz, 1H, ArH), 7.26-7.37 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.0, 32.6, 44.3, 69.2, 84.1, 86.5, 110.0, 125.7, 127.1, 127.2, 127.9, 128.9, 131.3, 133.9, 134.6, 139.6, 172.9, 183.7. IR (EtOH) ν 3272, 2912, 2220, 1701, 1674, 1497, 1348, 1250, 1229, 1107, 818 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 337.1547, Found: 337.1540. $[\alpha]^{25}_D$ = -94.17 (c 0.04, CH_2Cl_2) for 90% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 37.298 min, t_{major} = 24.329 min.







ID	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型
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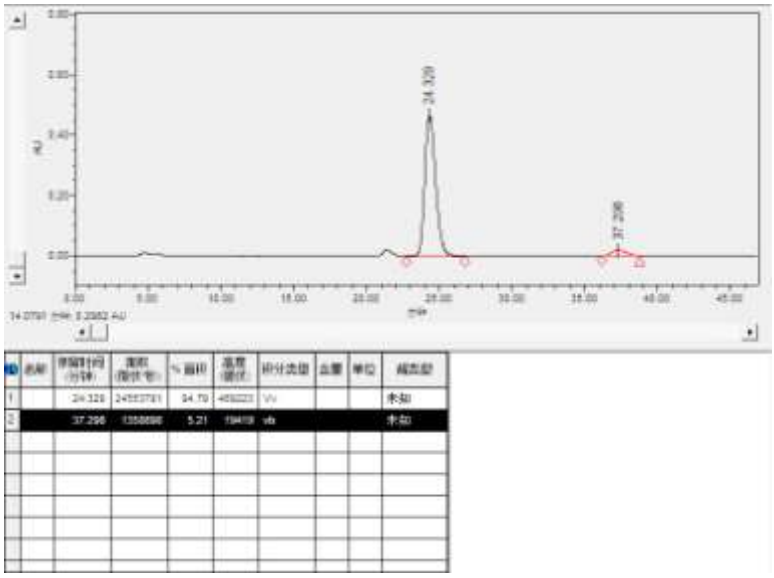
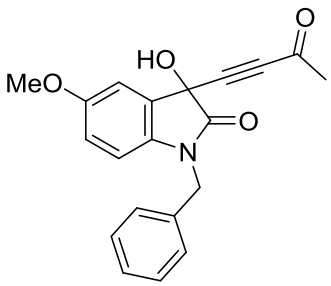
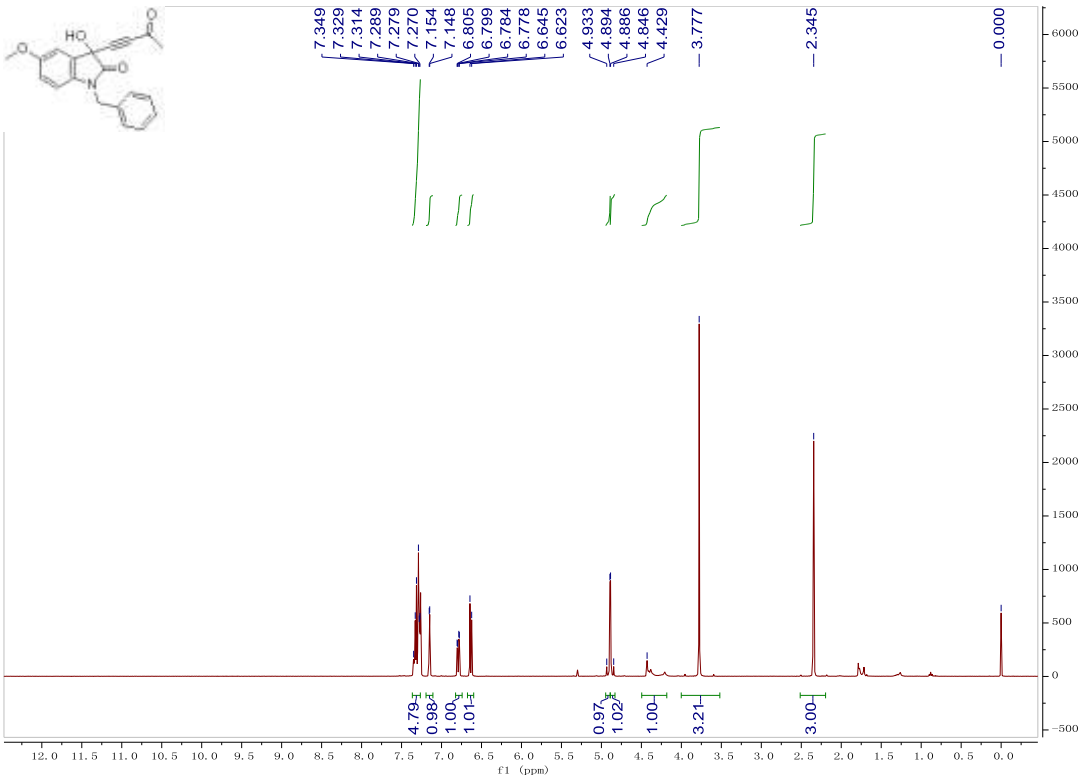




1-benzyl-3-hydroxy-5-methoxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1p)

A white solid, 71% yield (1189 mg). M.p.: 159-161 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 4.43 (br, 1H, OH), 4.87 (d, *J* = 16.0 Hz, 1H, CH_2), 4.91 (d, *J* = 16.0 Hz, 1H, CH_2), 6.63 (d, *J* = 8.8 Hz, 1H, ArH), 6.79 (dd, *J* = 2.4, 8.4 Hz, 1H, ArH), 7.15 (d, *J* = 2.4 Hz, 1H, ArH), 7.27-7.35 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 44.4, 55.8, 69.4, 84.2, 86.3, 110.9, 111.5, 116.1, 127.1, 127.9, 128.2, 128.9, 134.6, 135.2, 156.9, 172.7, 183.6. IR (EtOH) ν 3246, 2959, 2943, 2831, 2210, 1604, 1248, 1156, 772 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{21}N_2O_4^{+1}(M+NH_4)^+$ requires 353.1496, Found: 353.1489. $[\alpha]^{25}_D$ = -84.67 (c 0.05, CH_2Cl_2) for 86% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 79.002 min, t_{major} = 49.773 min.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O
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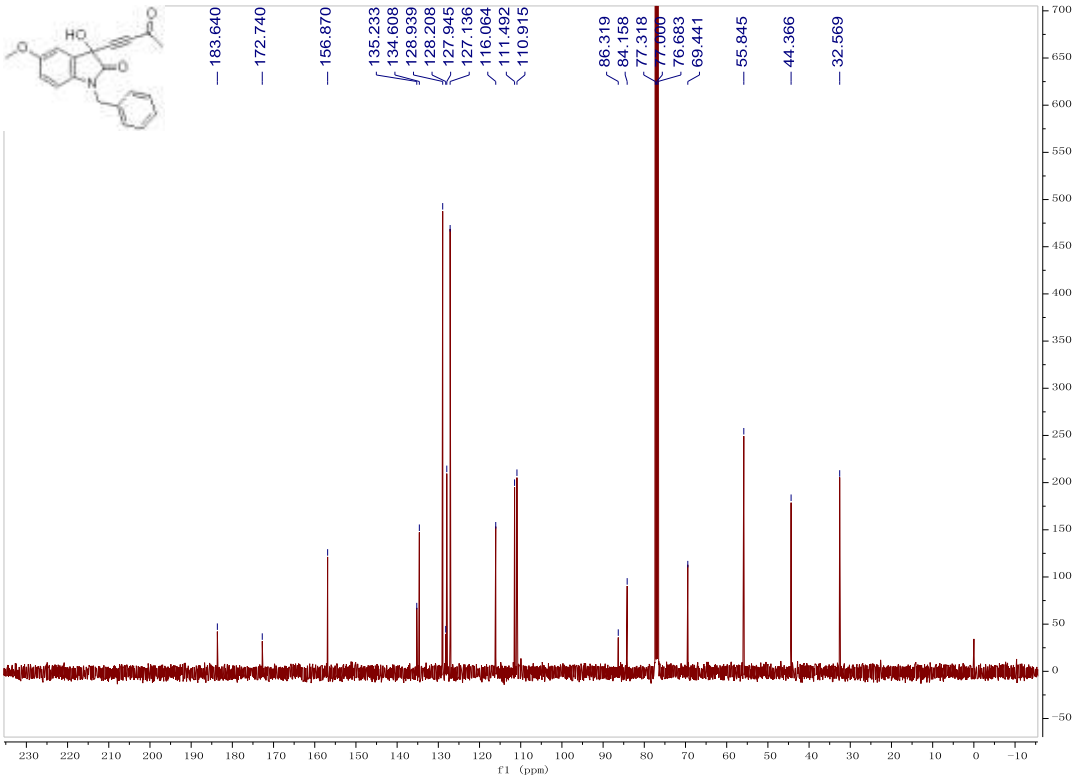
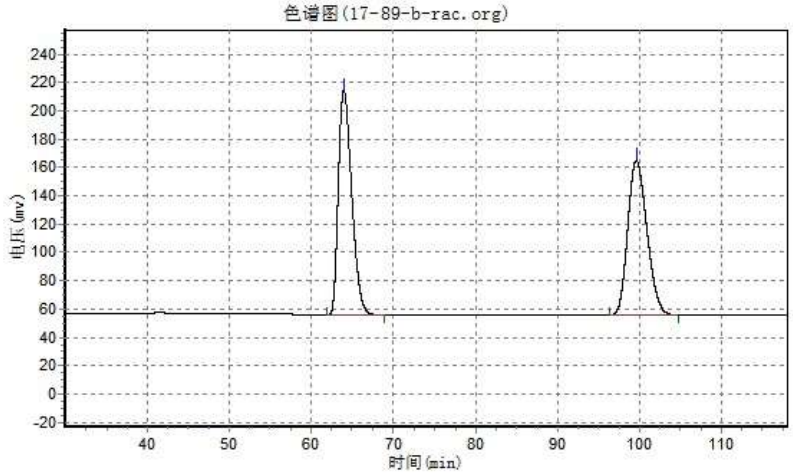
6.778
6.645
6.623
4.933
4.894
4.886
4.846
4.429
3.777
2.345
0.000
4.79
0.98
1.00
1.01
0.97
1.02
1.00
3.21
3.00
f1 (ppm)


HO
O
O
N
183.640
172.740
156.870
135.233
134.608
128.939
128.208
127.945
127.136
116.064
111.492
110.915
86.319
84.158
77.318
77.000
76.683
69.441
55.845
44.366
32.569
f1 (ppm)

实验时间：2019-07-05,12:16:39
谱图文件:D:\Sun Yaoliang\co2\17-89-b-rac.org

实验者:
报告时间：2019-07-10,11:52:37
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		64.072	158483.859	17963004.000	50.2866
2		99.637	109152.617	17758260.000	49.7134
总计			267636.477	35721264.000	100.0000

实验时间：2019-07-10,19:36:39
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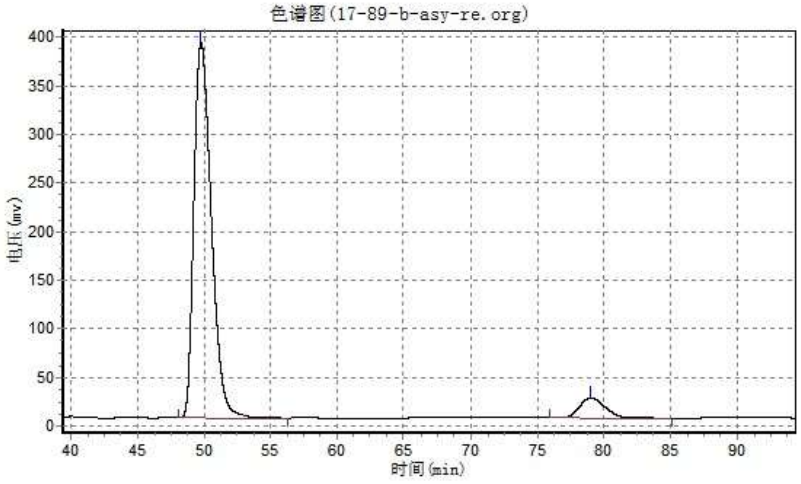
实验者:
报告时间：2019-07-10,19:37:31
积分方法:面积归一法



分析结果表

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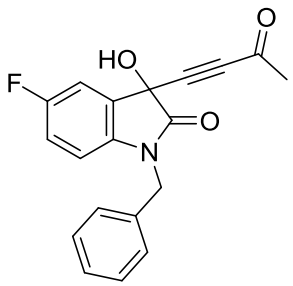
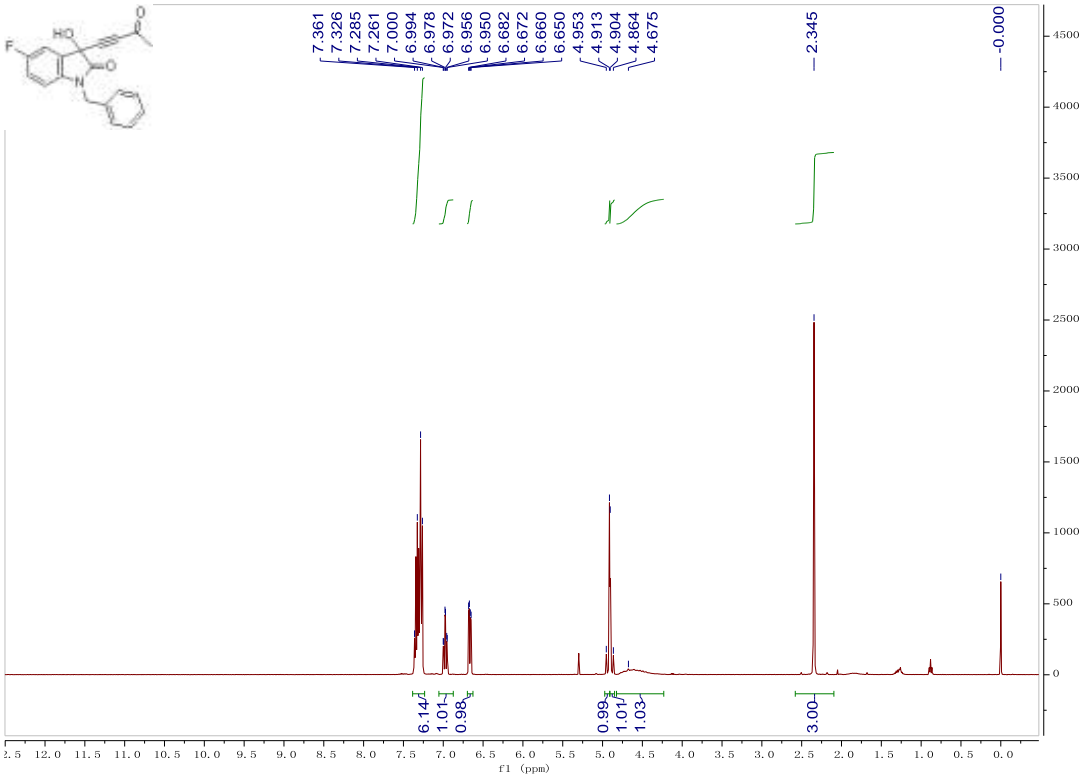
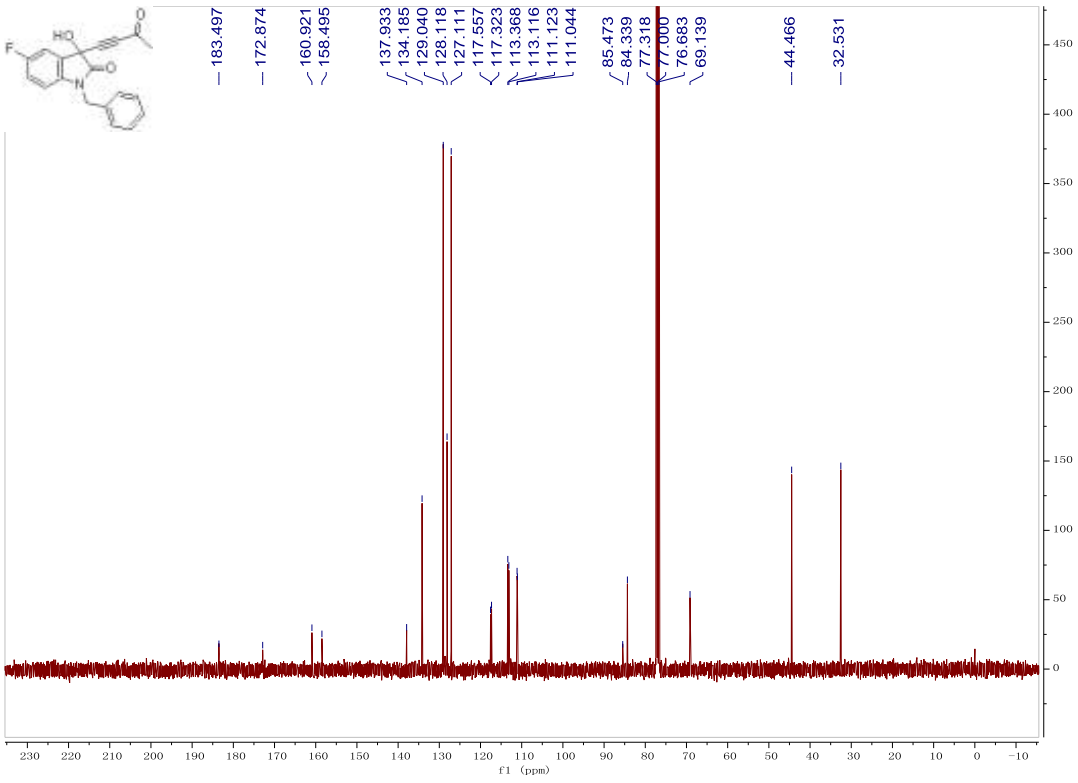
1		49.773	386891.656	35195412.000	92.8817
2		79.002	20472.156	2697318.250	7.1183
总计			407363.813	37892730.250	100.0000



1-benzyl-5-fluoro-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1q)

A white solid, 89% yield (1437 mg). M.p.: 169-171 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H, CH_3), 4.68 (br, 1H, OH), 4.88 (d, *J* = 16.0 Hz, 1H, CH_2), 4.93 (d, *J* = 16.0 Hz, 1H, CH_2), 6.67 (dd, *J* = 4.0, 8.8 Hz, 1H, ArH), 6.98 (dt, *J* = 2.4, 8.8 Hz, 1H, ArH), 7.26-7.37 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 44.5, 69.1, 84.3, 85.5, 111.1 (d, *J* = 7.9 Hz), 113.2 (d, *J* = 25.2 Hz), 117.4 (d, *J* = 23.4 Hz), 127.1, 128.1, 129.0, 134.2, 137.9, 159.7 (d, *J* = 242.6 Hz), 172.9, 183.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -117.84-(-117.78). IR (EtOH) ν 3293, 2212, 1677, 1494, 1462, 1178, 1144, 796, 698 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}FN_2O_3^{+1}(M+NH_4)^+$ requires 341.1296, Found: 341.1291. $[\alpha]^{25}_D$ = +28.33 (c 0.04, CH_2Cl_2) for 23% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254 nm, t_{minor} = 20.733 min, t_{major} = 15.098 min.

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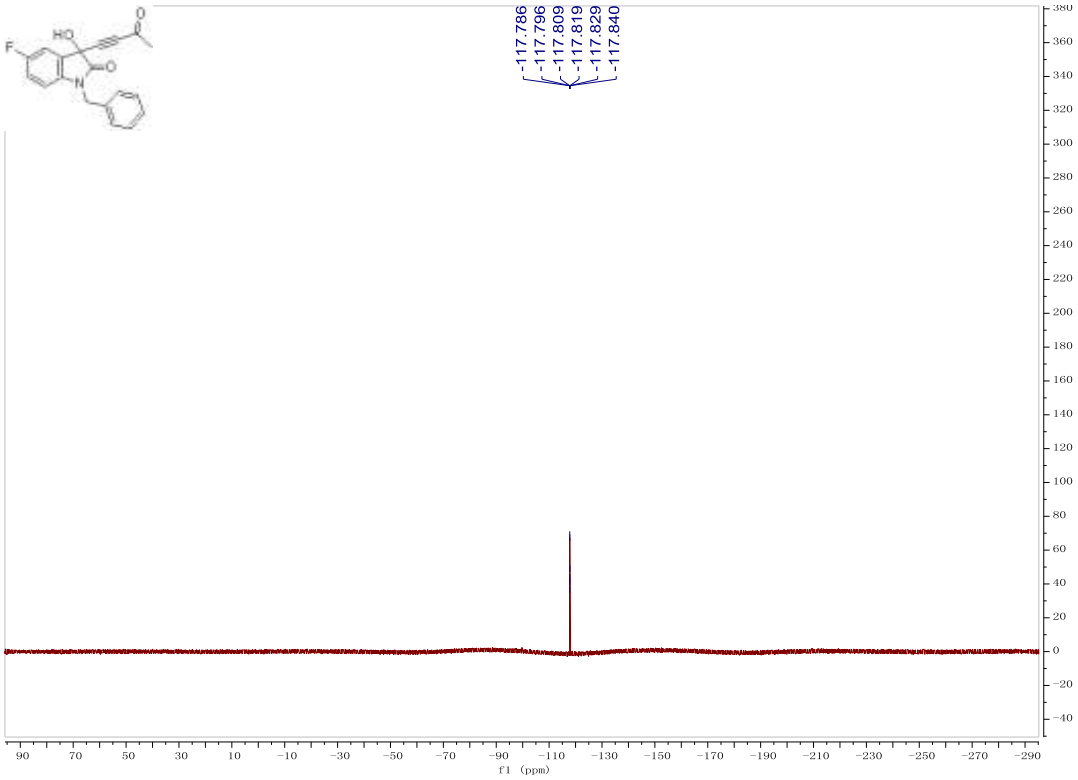
172.874
160.921
158.495
137.933
134.185
129.040
128.118
127.111
117.557
117.323
113.368
113.116
111.123
111.044
85.473
84.339
77.318
77.000
76.683
69.139
44.466
32.531
f1 (ppm)


-117.786
-117.796
-117.809
-117.819
-117.829
-117.840
f1 (ppm)

实验时间：2019-07-12,16:15:14
谱图文件:D:\Sun Yaoliang\co2\17-90-b-rac.org

实验者:
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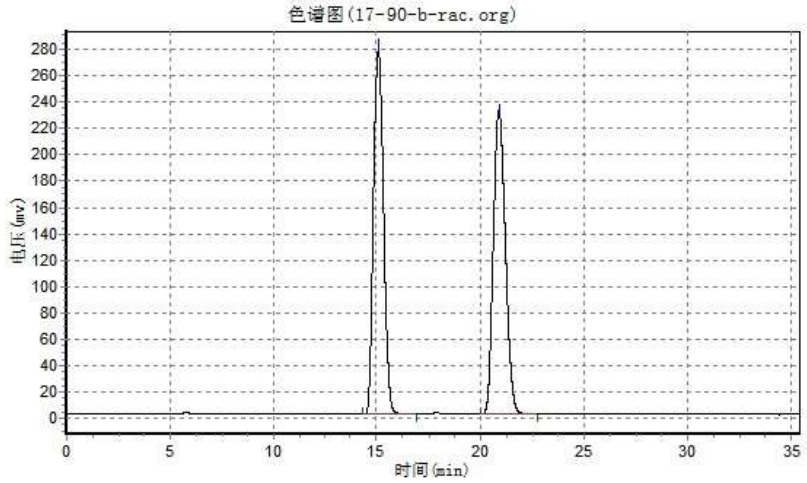
积分方法:面积归一法

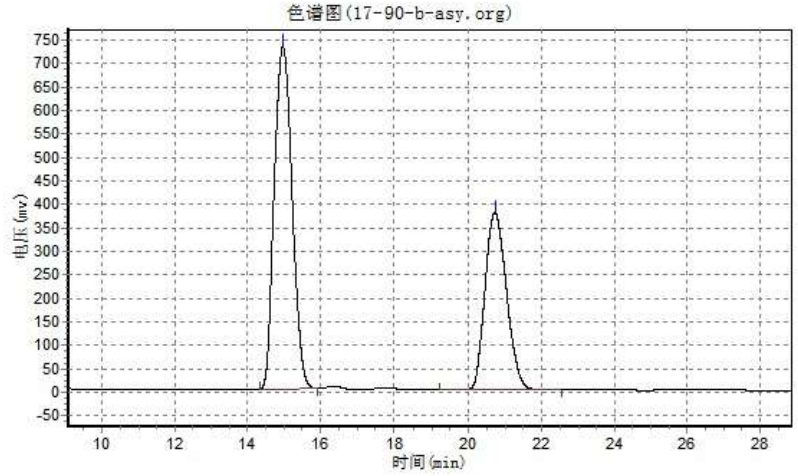


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		15.098	274719.969	9412814.000	50.1724
2		20.932	228281.344	9348120.000	49.8276
总计			503001.313	18760934.000	100.0000

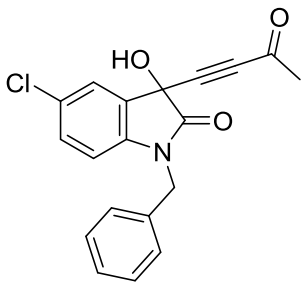
实验时间：2019-07-12,16:46:47
谱图文件:D:\Sun Yaoliang\co2\17-90-b-asy.org

实验者:
报告时间：2019-07-12,16:47:34
积分方法:面积归一法



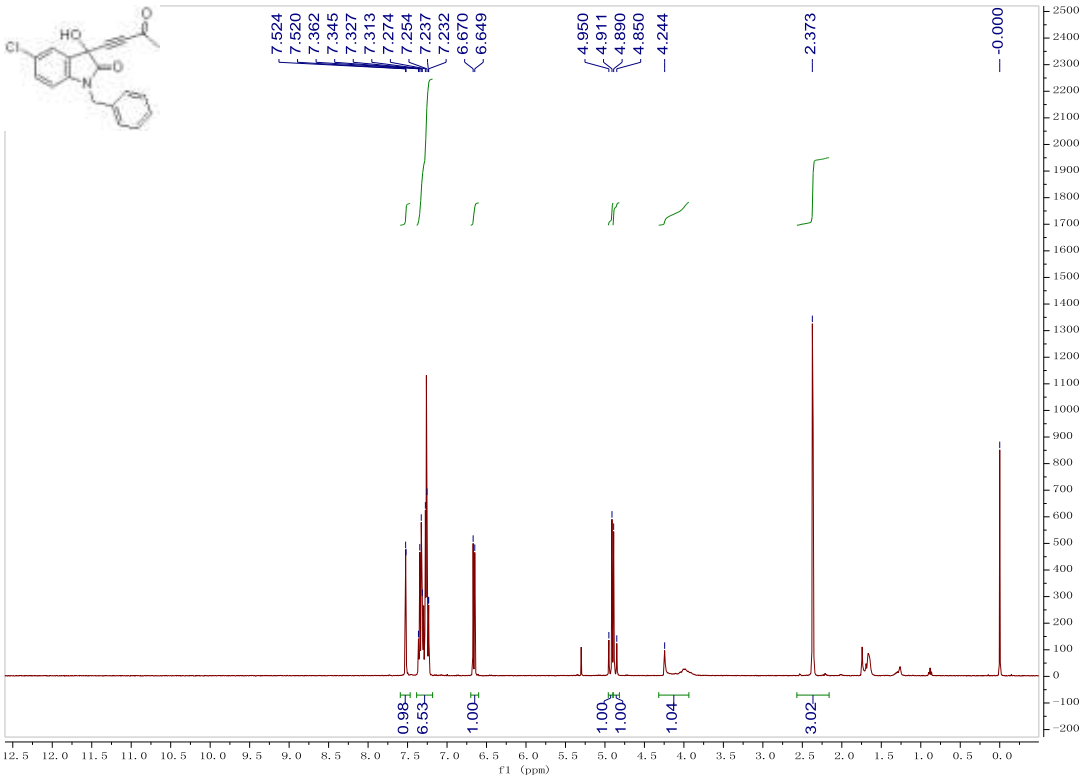
分析结果表

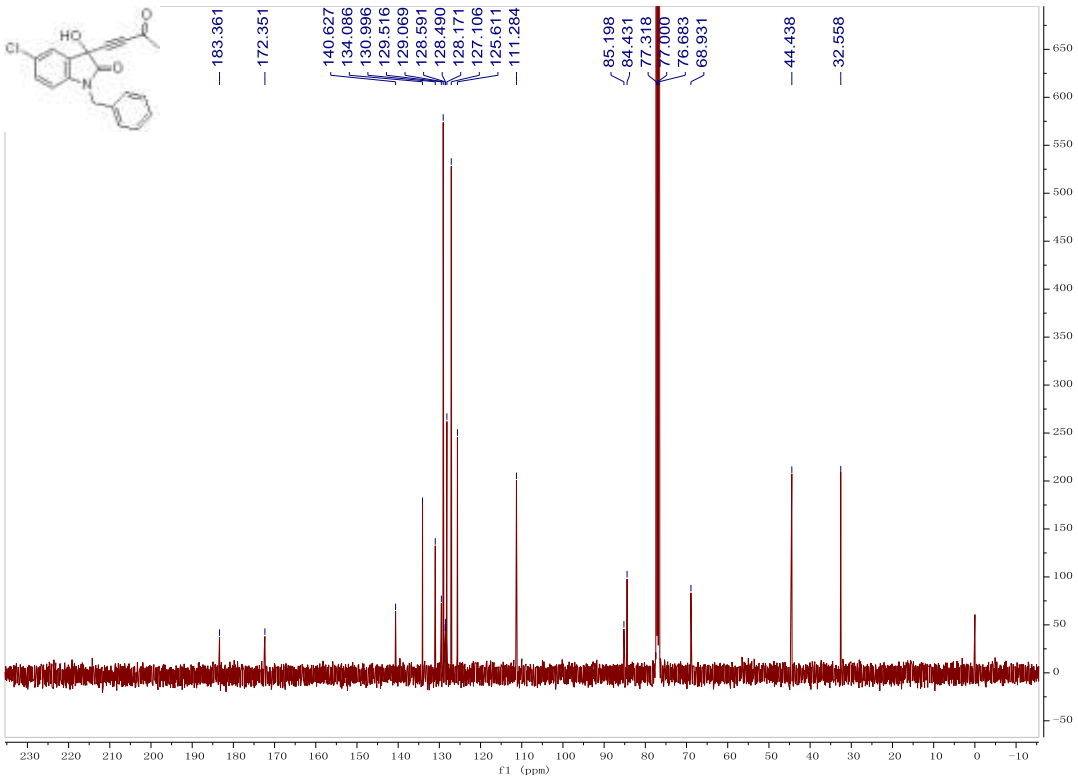
峰号	峰名	保留时间	峰高	峰面积	含量
1		14.963	730436.438	24831544.000	61.5726
2		20.733	377927.219	15497329.000	38.4274
总计			1108363.656	40328873.000	100.0000

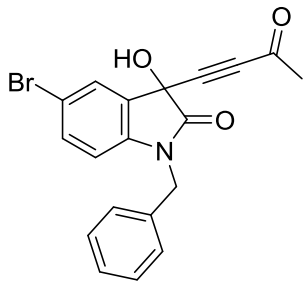


1-benzyl-5-chloro-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1r)

A white solid, 87% yield (1474 mg). M.p.: 182-184 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.37 (s, 3H, CH_3), 4.24 (br, 1H, OH), 4.87 (d, *J* = 16.0 Hz, 1H, CH_2), 4.93 (d, *J* = 16.0 Hz, 1H, CH_2), 6.66 (d, *J* = 8.4 Hz, 1H, ArH), 7.23-7.37 (m, 6H, ArH), 7.52 (d, *J* = 1.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 44.4, 68.9, 84.4, 85.2, 111.3, 125.6, 127.1, 128.2, 128.5, 128.6, 129.1, 129.5, 131.0, 134.1, 140.6, 172.4, 183.4. IR (EtOH) ν 3295, 3021, 2812, 2210, 1708, 1677, 1488, 1209, 1170, 1074, 814, 736 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}ClN_2O_3^{+1}(M+NH_4)^+$ requires 357.1000, Found: 357.0997.

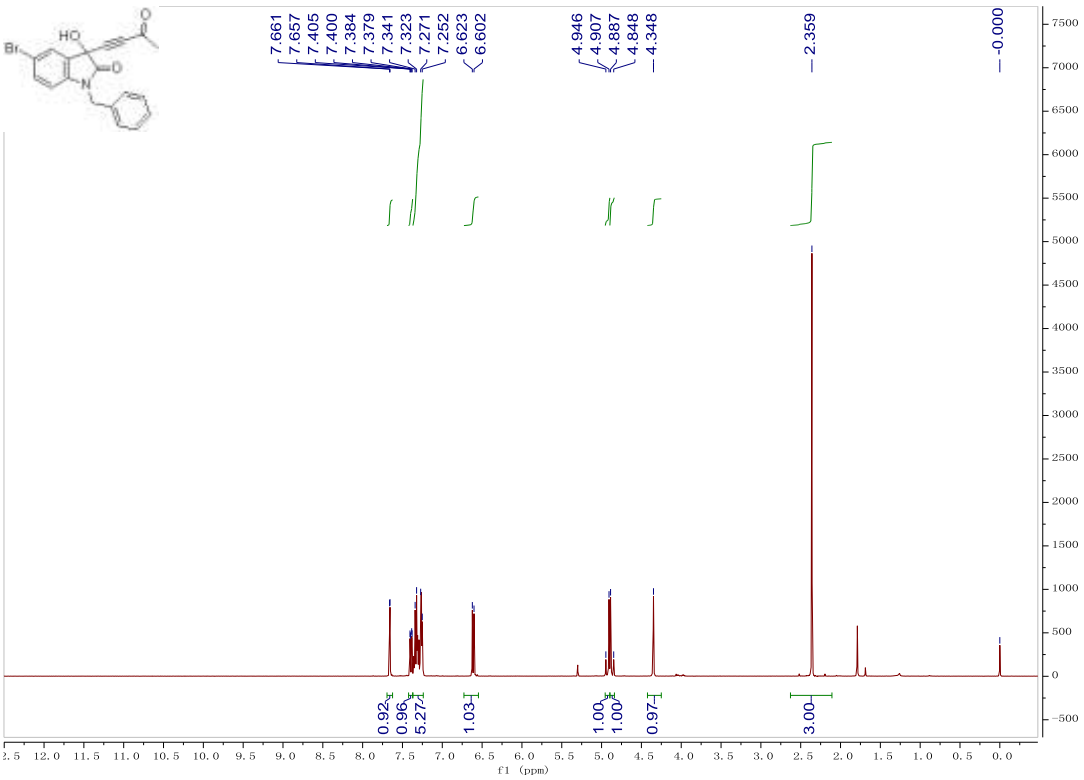






1-benzyl-5-bromo-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1s)

A white solid, 71% yield (1360 mg). M.p.: 170-172 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.36 (s, 3H, CH_3), 4.35 (br, 1H, OH), 4.87 (d, *J* = 15.6 Hz, 1H, CH_2), 4.93 (d, *J* = 15.6 Hz, 1H, CH_2), 6.61 (d, *J* = 8.4 Hz, 1H, ArH), 7.25-7.35 (m, 5H, ArH), 7.39 (dd, *J* = 2.0, 8.4 Hz, 1H, ArH), 7.66 (d, *J* = 2.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 44.4, 68.9, 84.4, 85.3, 111.7, 116.7, 127.1, 128.2, 128.3, 128.9, 129.1, 133.9, 134.0, 141.1, 172.4, 183.4. IR (EtOH) ν 3290, 2215, 1707, 1677, 1487, 1368, 1344, 1208, 1168, 1071, 812 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}BrN_2O_3^{+1}(M+NH_4)^+$ requires 401.0495, Found: 401.0491. $[\alpha]^{25}_D$ = +88.89 (c 0.018, CH_2Cl_2) for 47% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 37.569 min, t_{major} = 24.459 min.


HO
Br
O
N
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7.400
7.384
7.379
7.341
7.323
7.271
7.252
6.623
6.602
4.946
4.907
4.887
4.848
4.348
2.359
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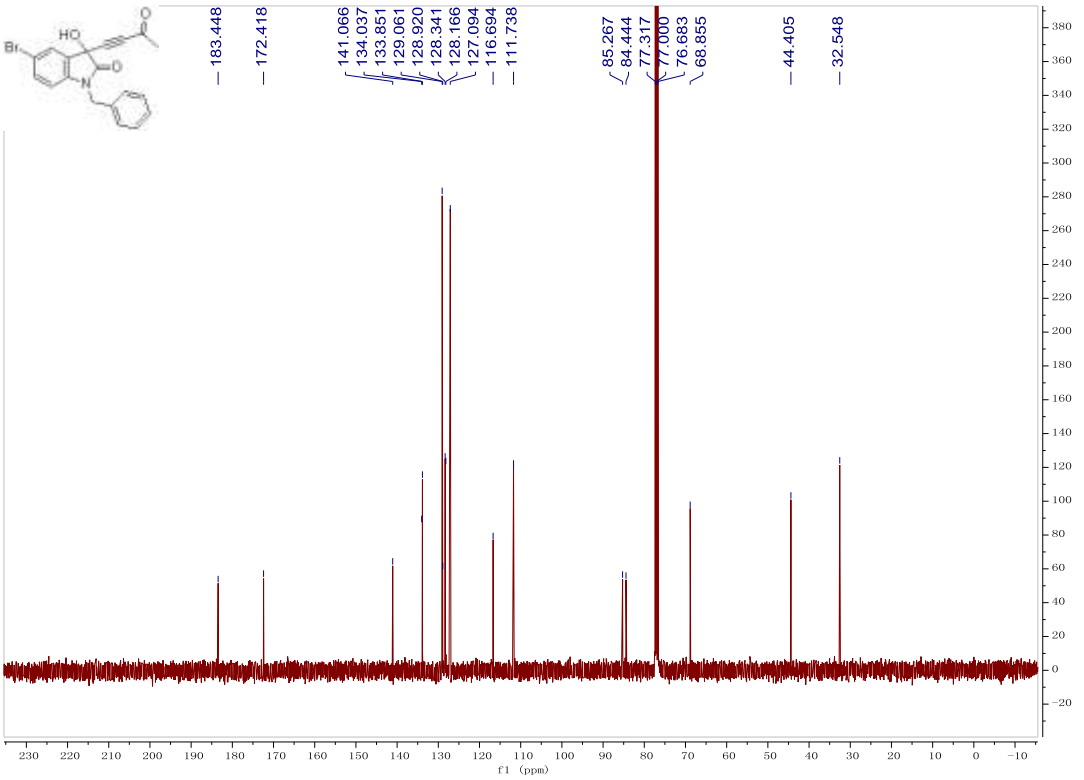
0.92
0.96
5.27
1.03
1.00
1.00
0.97
3.00
f1 (ppm)


HO
Br
O
N
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129.061
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128.341
128.166
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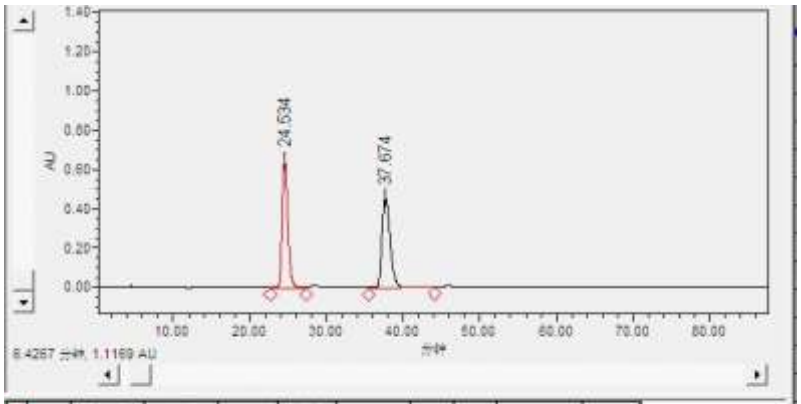
68.855
44.405
32.548
f1 (ppm)



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
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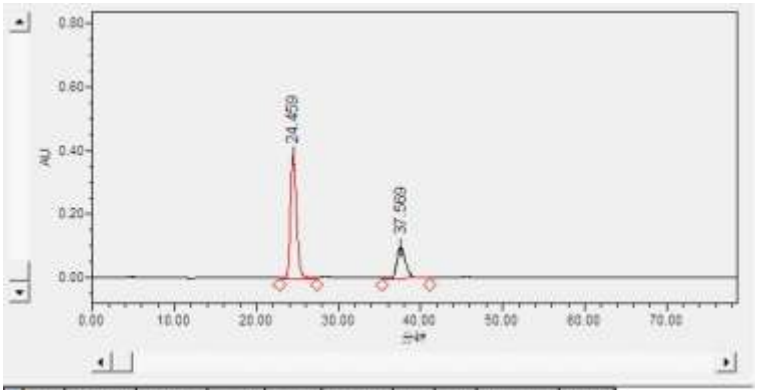
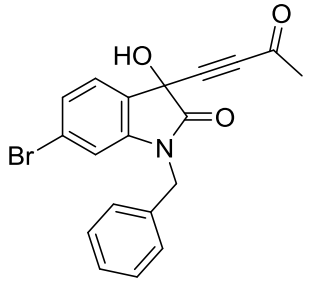
2		37.674	33948087	49.89	458228	VV			未知	

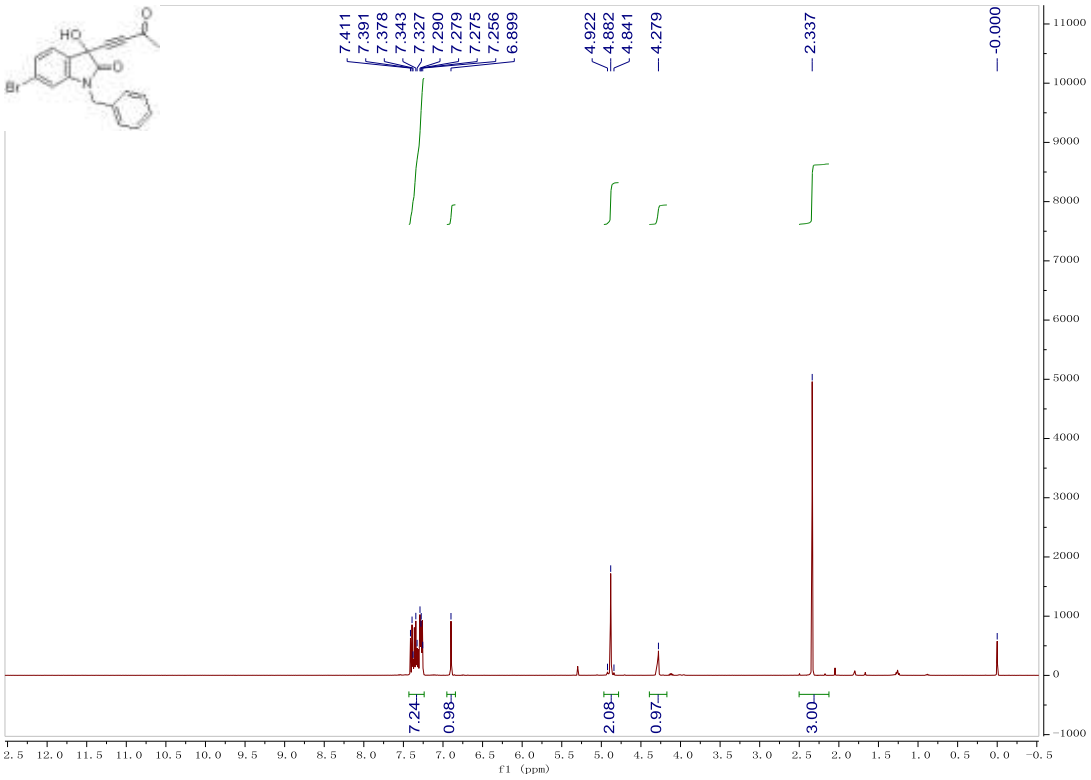


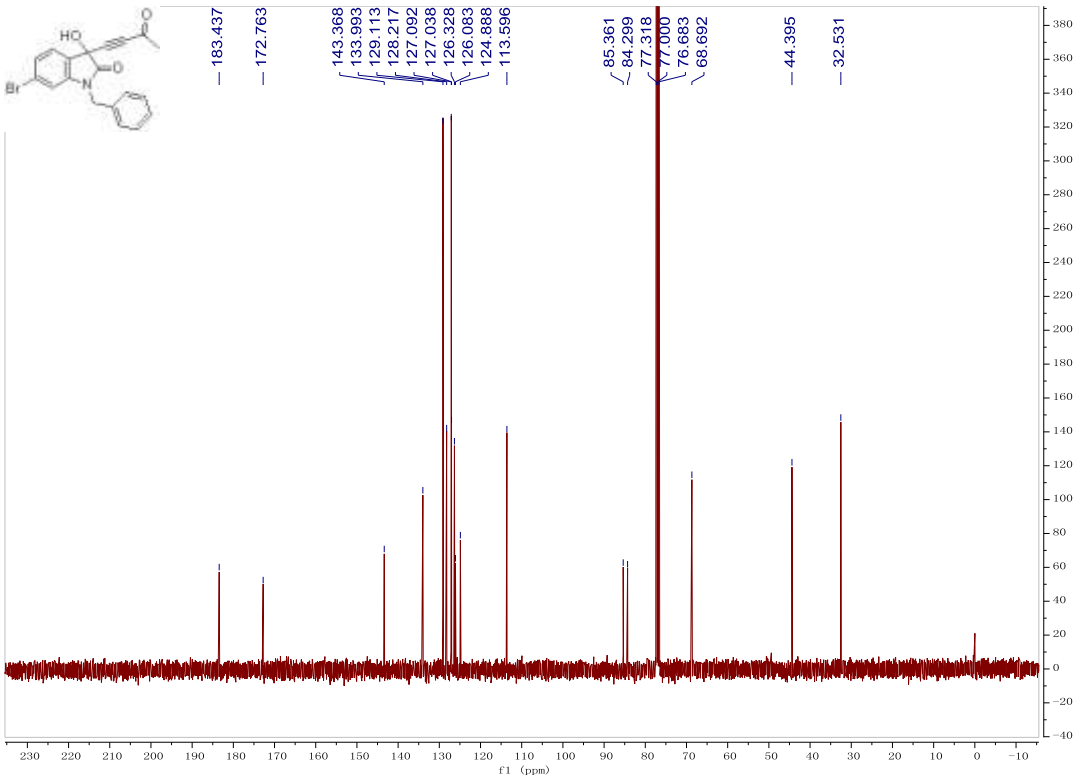
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		24.459	20159781	73.55	386658	VV			未知	
2		37.569	7250375	26.45	97125	VV			未知	

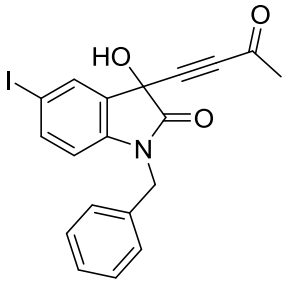


1-benzyl-6-bromo-3-hydroxy-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1t)

A white solid, 62% yield (1187 mg). M.p.: 174-176 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 4.28 (s, 1H, OH), 4.84-4.93 (m, 2H, CH_2), 6.90 (s, 1H, ArH), 7.25-7.42 (m, 7H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 44.4, 68.7, 84.3, 85.4, 113.6, 124.9, 126.1, 126.3, 127.0, 127.1, 128.2, 129.1, 134.0, 143.4, 172.8, 183.4. IR (EtOH) ν 3313, 3060, 3024, 2202, 1719, 1681, 1608, 1486, 1369, 1212, 998, 825 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}BrN_2O_3^{+1}(M+NH_4)^+$ requires 401.0495, Found: 401.0489.

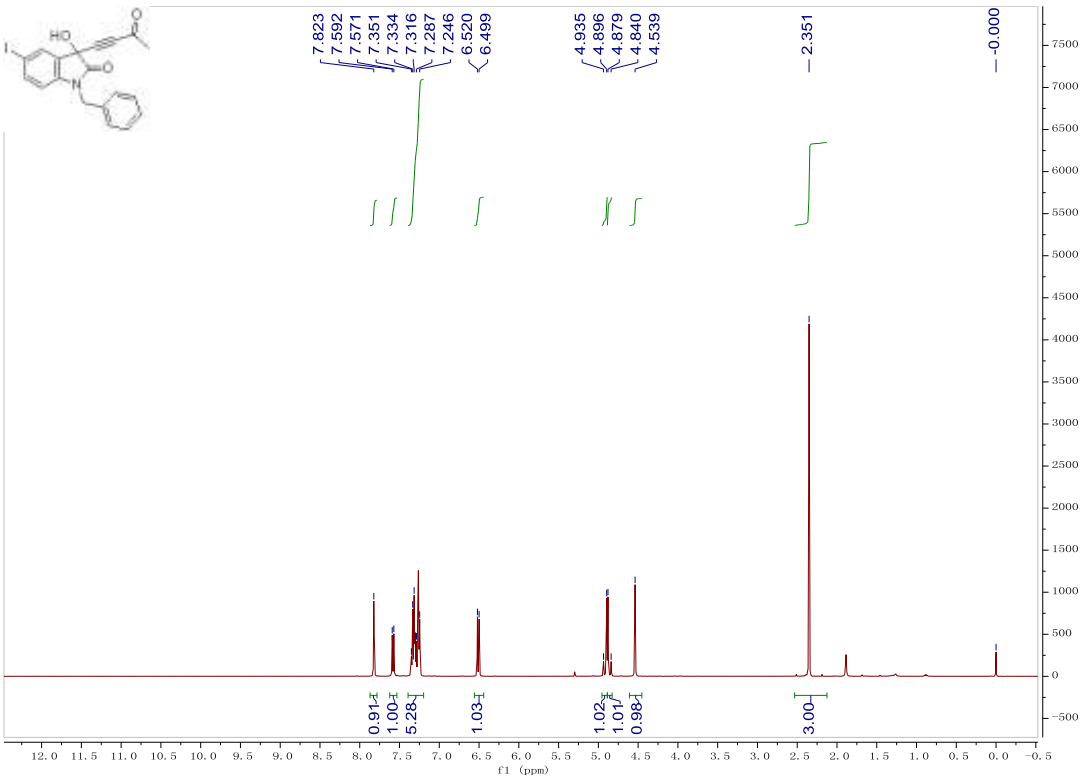






1-benzyl-3-hydroxy-5-iodo-3-(3-oxobut-1-yn-1-yl)indolin-2-one (1u)

A white solid, 55% yield (1185 mg). M.p.: 172-174 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.35 (s, 3H, CH_3), 4.54 (br, 1H, OH), 4.86 (d, *J* = 15.6 Hz, 1H, CH_2), 4.92 (d, *J* = 15.6 Hz, 1H, CH_2), 6.51 (d, *J* = 8.4 Hz, 1H, ArH), 7.24-7.36 (m, 5H, ArH), 7.58 (d, *J* = 8.4 Hz, 1H, ArH), 7.82 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 44.3, 68.7, 84.4, 85.4, 86.5, 112.2, 127.1, 128.2, 129.0, 129.2, 133.8, 134.0, 139.8, 141.7, 172.3, 183.5. IR (EtOH) ν 3290, 2228, 1726, 1681, 1354, 1338, 1074, 992, 800, 729, 699 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}IN_2O_3^{+1}(M+NH_4)^+$ requires 449.0357, Found: 449.0349.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7.334
7.316
7.287
7.246
6.520
6.499
4.935
4.896
4.879
4.840
4.539
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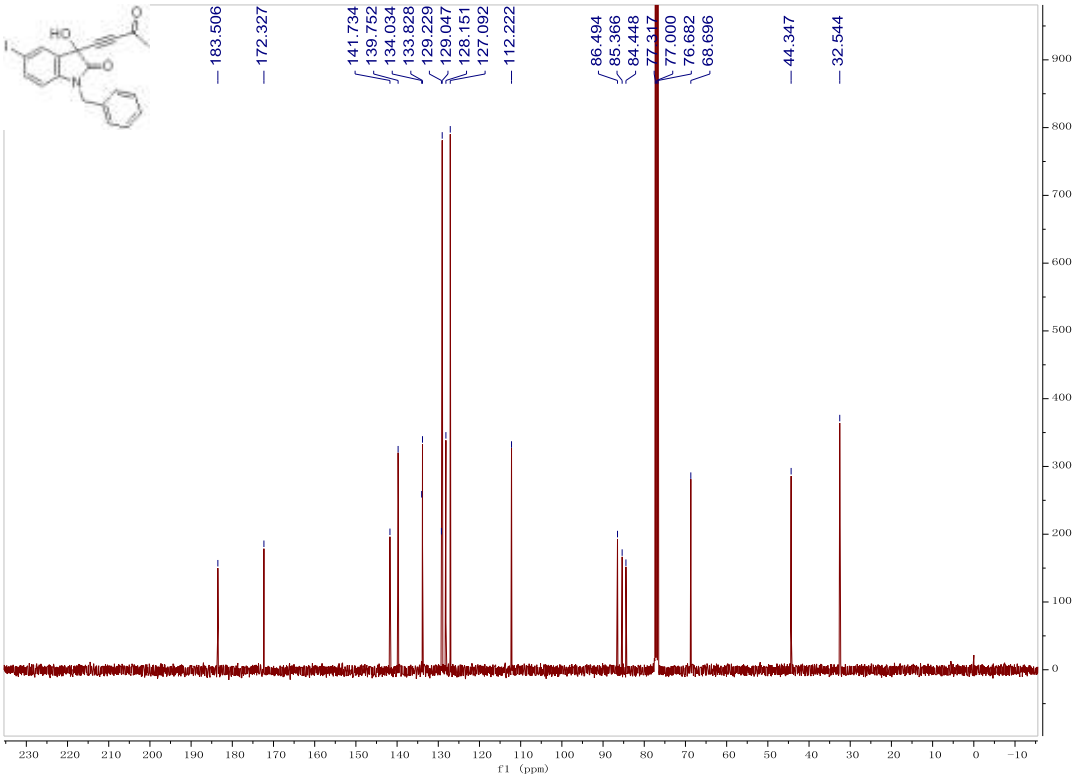
0.91
1.00
5.28
1.03
1.02
1.01
0.98
3.00
f1 (ppm)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134.034
133.828
129.229
129.047
128.151
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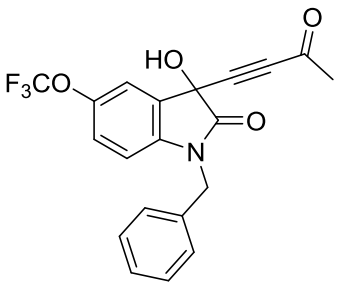
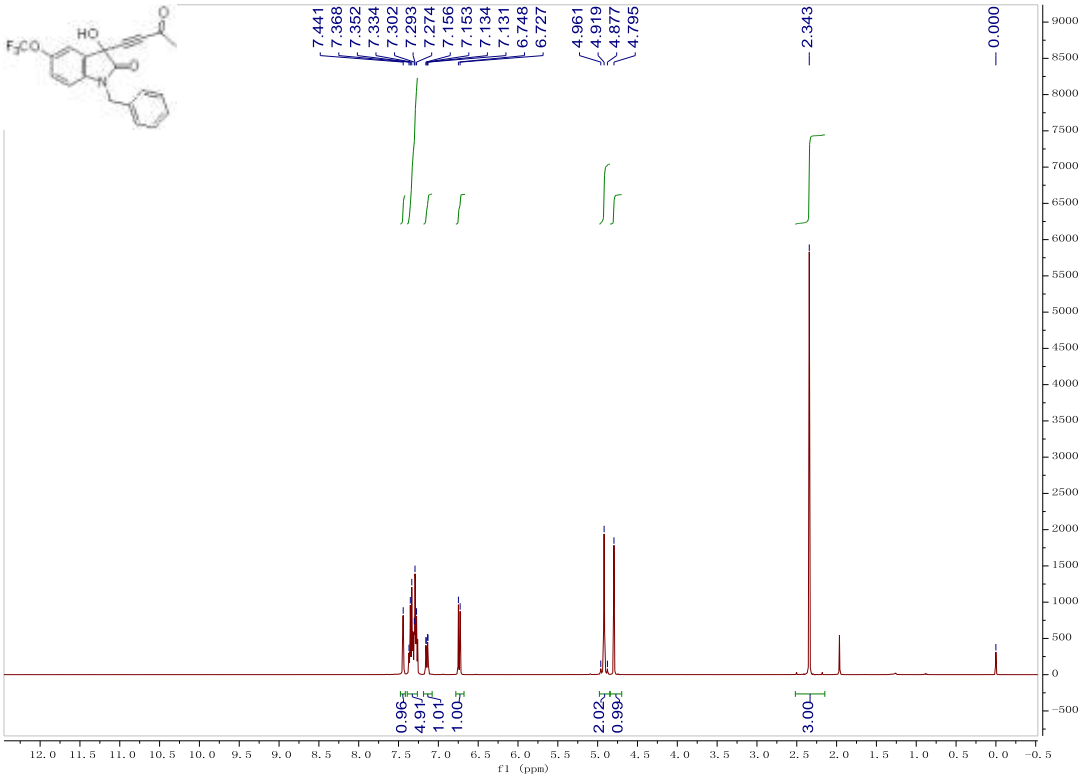
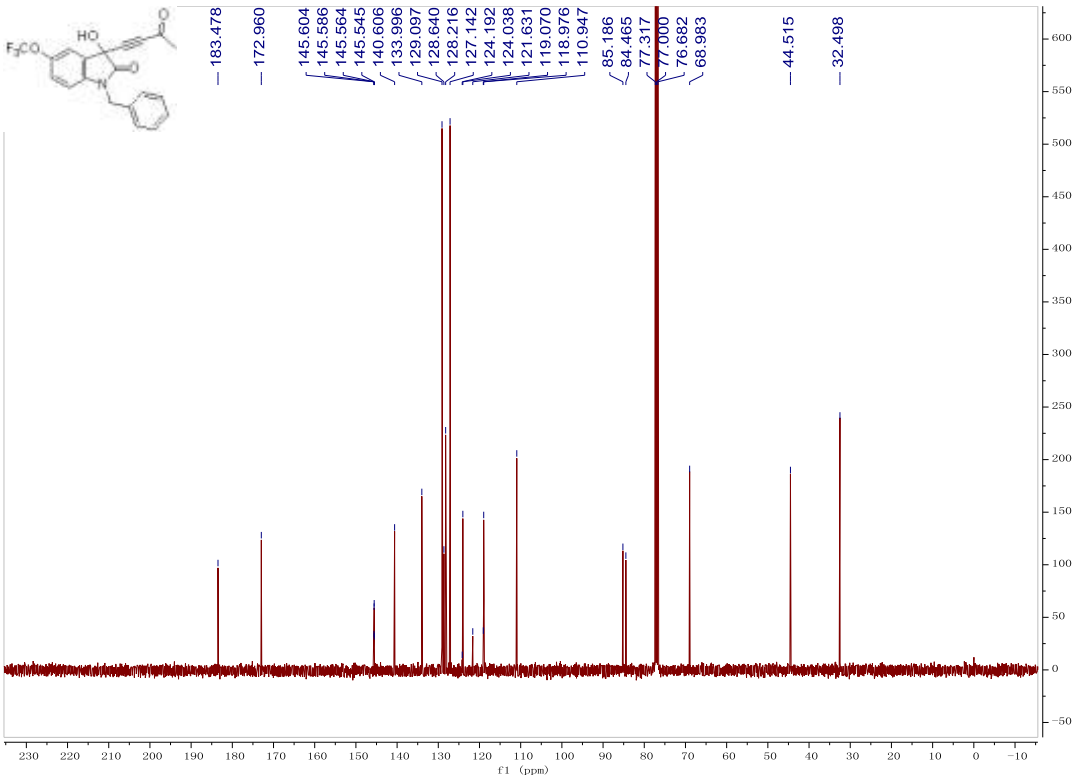
77.000
76.682
68.696
44.347
32.544
f1 (ppm)



1-benzyl-3-hydroxy-3-(3-oxobut-1-yn-1-yl)-5-(trifluoromethoxy)indolin-2-one (1v)

A white solid, 60% yield (1167 mg). M.p.: 141-143 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.34 (s, 3H, CH_3), 4.80 (s, 1H, OH), 4.87-4.97 (m, 2H, CH_2), 6.74 (d, *J* = 8.4 Hz, 1H, ArH), 7.14 (dd, *J* = 1.2, 8.8 Hz, 1H, ArH), 7.27-7.37 (m, 5H, ArH), 7.44 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.5, 44.5, 69.0, 84.5, 85.2, 110.9, 119.0, 120.4 (q, *J* = 256.1 Hz), 124.0, 127.1, 128.2, 128.6, 129.1, 134.0, 140.6, 145.6 (q, *J* = 2.2 Hz), 173.0, 183.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -58.33. IR (EtOH) ν 3287, 2922, 2223, 1728, 1682, 1496, 1265, 1212, 1144, 1121 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{18}F_3N_2O_4^{+1}$ $(M+NH_4)^+$ requires 407.1213, Found: 407.1207. $[\alpha]^{25}_D$ = -19.44 (c 0.06, CH_2Cl_2) for 65% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 22.150 min, t_{major} = 17.017 min.




183.478
172.960
145.604
145.586
145.564
145.545
140.606
133.996
129.097
128.640
128.216
127.142
124.192
124.038
121.631
119.070
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76.682
68.983
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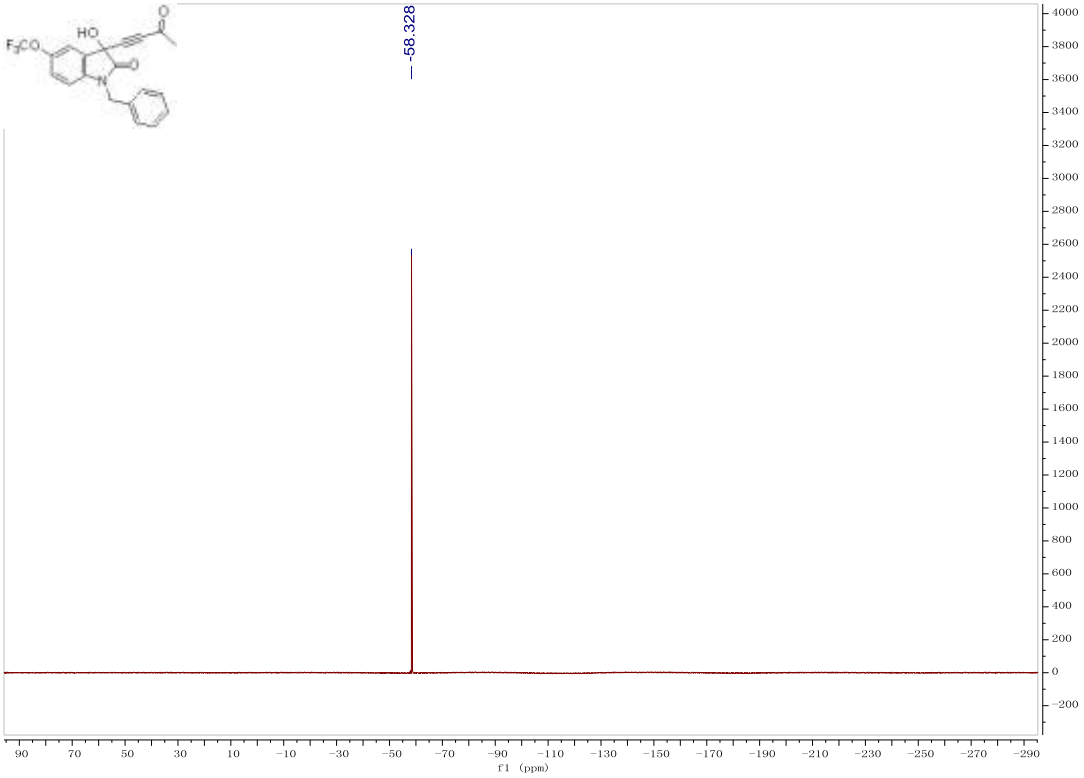
32.498
f1 (ppm)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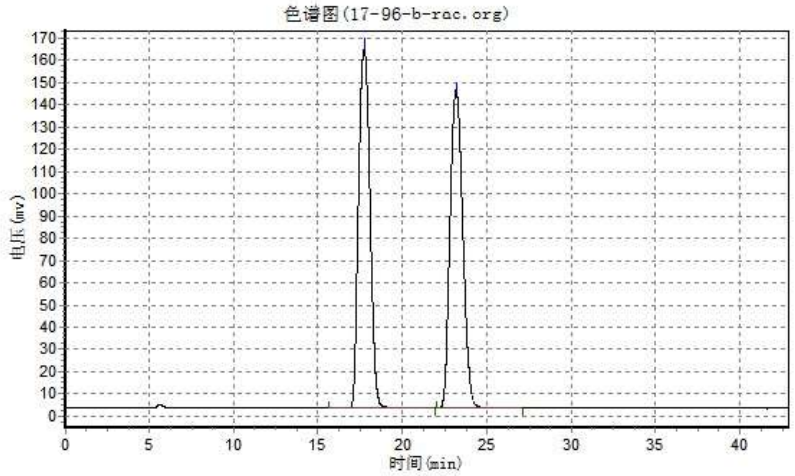
f1 (ppm)

实验时间：2019-07-18,15:43:22
谱图文件:D:\Sun Yaoliang\co2\17-96-b-rac.org

实验者:
报告时间：2019-07-18,16:34:09
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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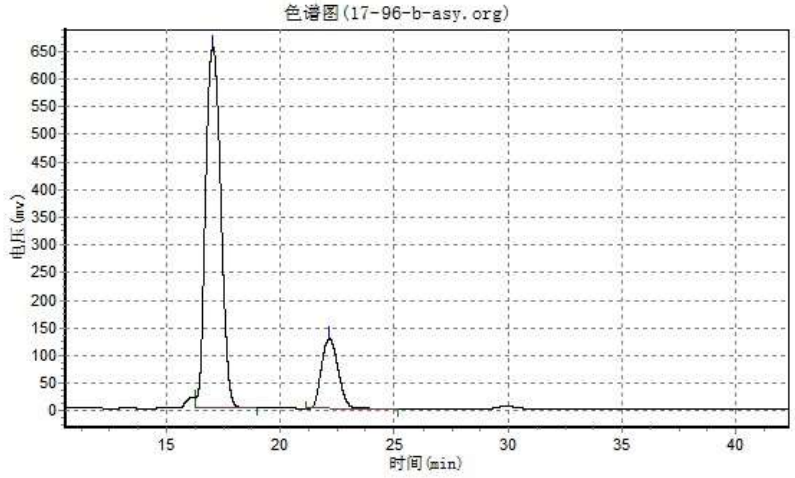
2		23.198	142526.281	7534177.500	49.6871
总计			303744.109	15163246.500	100.0000

实验时间：2019-07-18,16:47:17
谱图文件:D:\Sun Yaoliang\co2\17-96-b-asy.org

实验者:
报告时间：2019-07-18,16:48:13
积分方法:面积归一法



分析结果表

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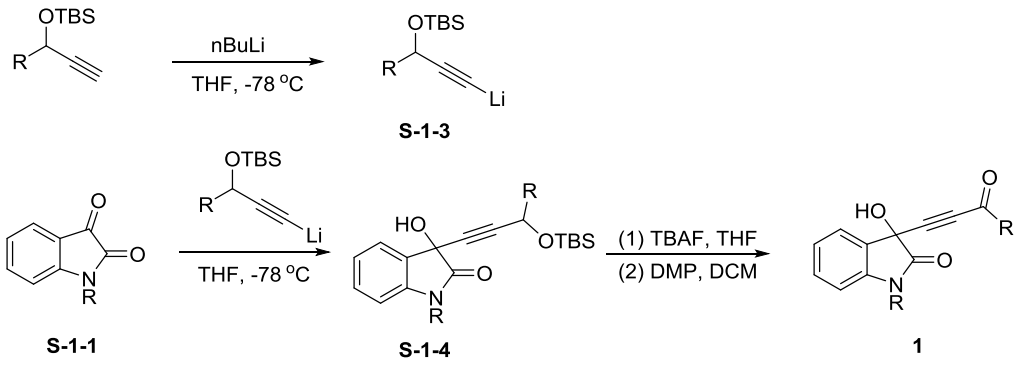
2		22.150	125830.992	6458331.000	17.5030
总计			777947.430	36898437.000	100.0000

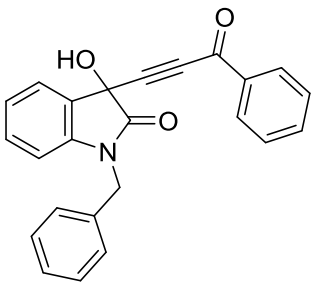


Substrates **1w-1z** was synthesized through the **method 2** as below.

Method 2

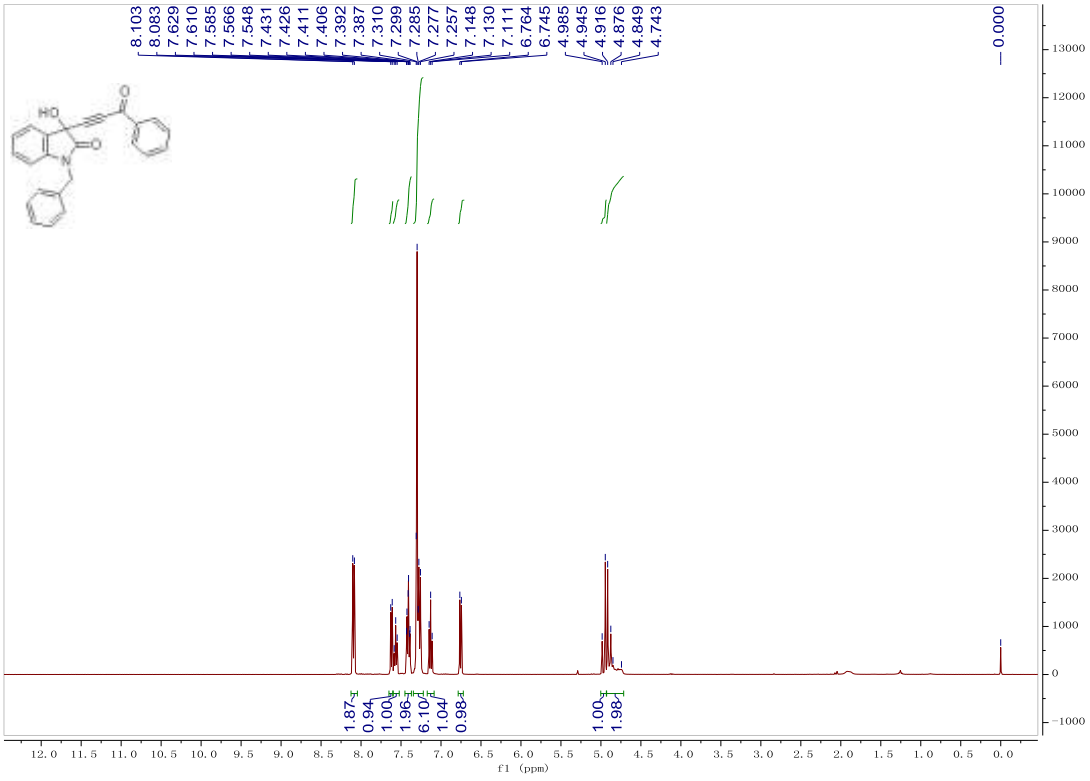
Step 1: To a solution of propargyl silicon ether **S-1-3** (5.0 mmol, 1.0 equiv) in dry THF (20 mL) was added n-butyllithium solution (6.0 mmol, 1.2 equiv) under -78 °C. After stirring for one hour, the fresh prepared alkynyl lithium reagent was added to a solution of isatin derivative **S-1-1** (6.0 mmol, 1.2 equiv) in dry THF (20 mL) under -78 °C. Then, the resulting reaction mixture was stirred at -78 °C for one hour. After warm up to room temperature, saturated ammonium chloride solution was added to quench the reaction. The reaction was extracted with ethyl acetate three times and washed by water. Then the reaction mixture was concentrated under high vacuum and purified by a column chromatography on silica gel to give the crude products **SI-1-4** (DCM:EA = 10:1 ~ 2:1).

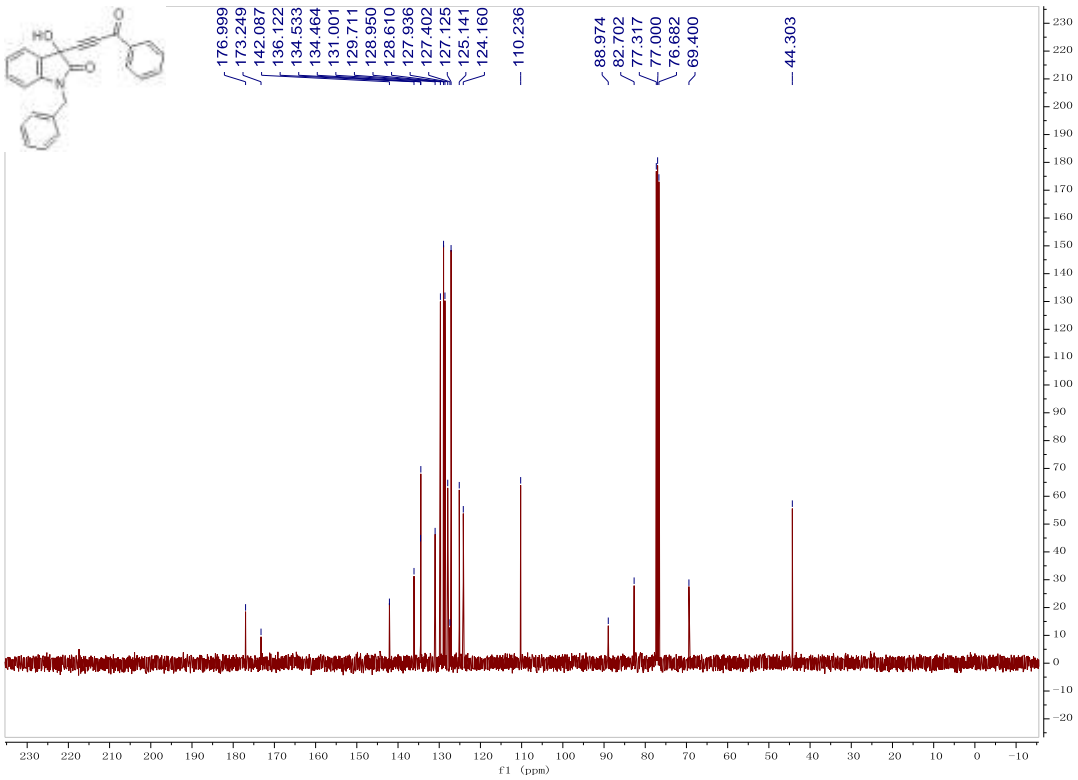
Step 2: The crude product **SI-1-4** was dispersed in 10 mL THF and TBAF solution (6.0 mL, 1.0 M, 1.2 equiv) was added. The reaction mixture was stirred for 20 mins and traced by TLC. After the reaction was completed, water was added to quench the reaction. The reaction was extracted with ethyl acetate three times and washed by water. Then the reaction mixture was concentrated under high vacuum. Then, the crude product was dispersed in 10 mL DCM and Dess-martin oxidizer (6.0 mmol, 1.2 equiv) was added. The reaction mixture was stirred for 20 mins and traced by TLC. After the reaction was completed, water was added to quench the reaction. The reaction was extracted with ethyl acetate three times and washed by water. The organic phase was concentrated under high vacuum and purified by a column chromatography on silica gel to give the desired products **1** (DCM:EA = 10:1 ~ 2:1).

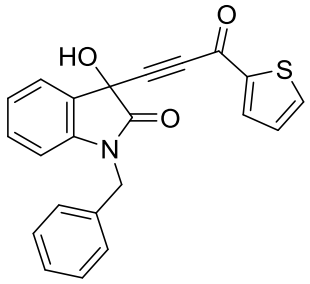


1-benzyl-3-hydroxy-3-(3-oxo-3-phenylprop-1-yn-1-yl)indolin-2-one (1w)

A white solid, 41% yield (752 mg). M.p.: 158-160 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 4.74-4.92 (m, 2H, OH, CH_2), 4.97 (d, *J* = 16.0 Hz, 1H, CH_2), 6.75 (d, *J* = 7.6 Hz, 1H, ArH), 7.13 (t, *J* = 7.2 Hz, 1H, ArH), 7.25-7.31 (m, 6H, ArH), 7.41 (dt, *J* = 2.0, 8.0 Hz, 1H, ArH), 7.57 (t, *J* = 7.6 Hz, 1H, ArH), 7.62 (d, *J* = 7.6 Hz, 1H, ArH), 8.09 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 69.4, 82.7, 89.0, 110.2, 124.2, 125.1, 127.1, 127.4, 127.9, 128.6, 129.0, 129.7, 131.0, 134.46, 134.53, 136.1, 142.1, 173.2, 177.0. IR (EtOH) ν 3371, 3055, 3024, 2218, 1718, 1642, 1487, 1173, 1128, 704 cm^{-1}. HRMS (ESI) Calcd. For $C_{24}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 385.1547, Found: 385.1543.

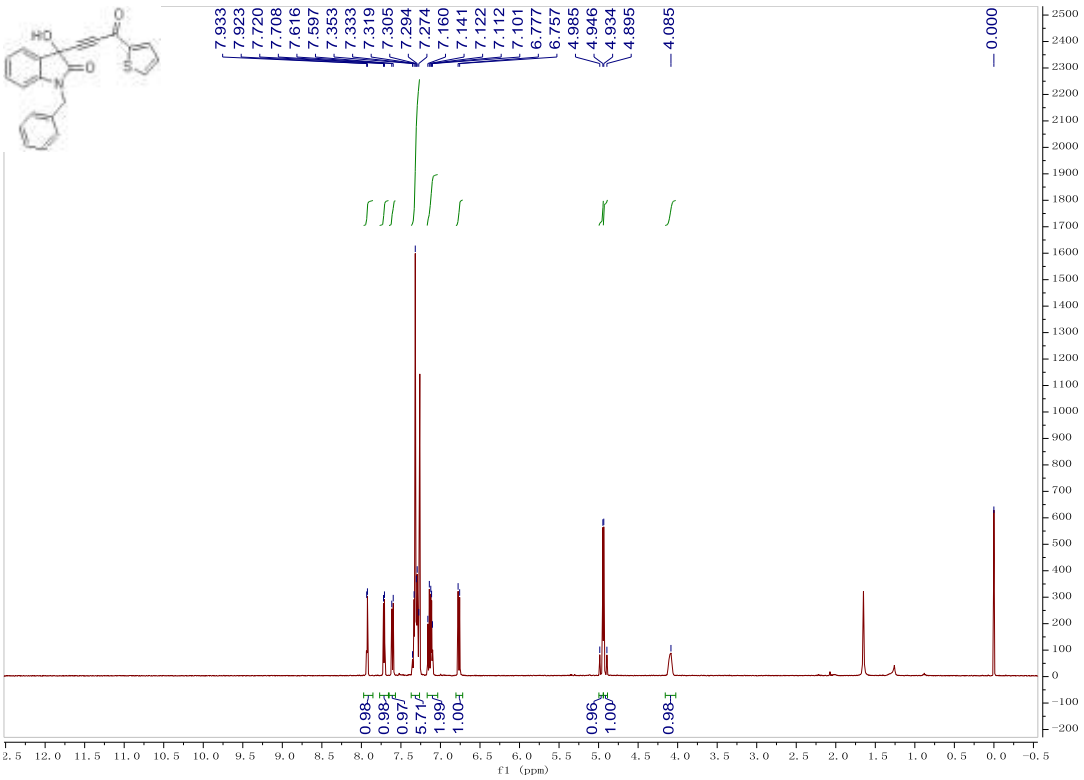


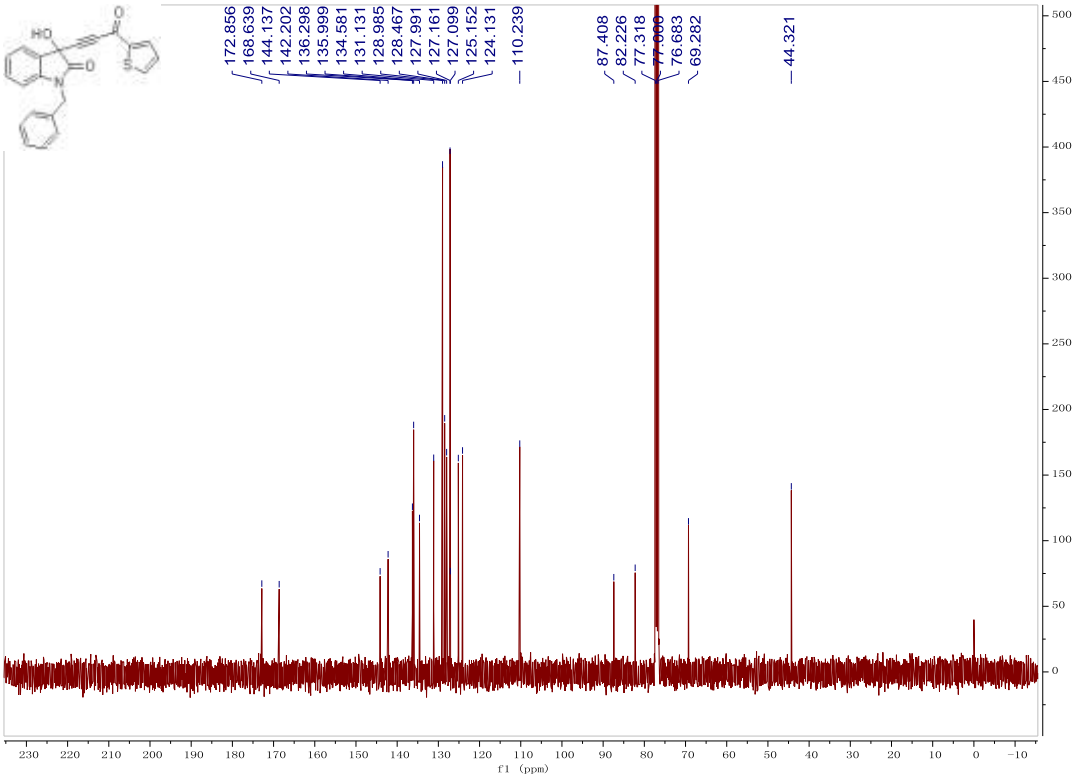




1-benzyl-3-hydroxy-3-(3-oxo-3-(thiophen-2-yl)prop-1-yn-1-yl)indolin-2-one (1x)

A white solid, 46% yield (899 mg). M.p.: 164-166 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 4.09 (s, 1H, OH), 4.91 (d, *J* = 15.6 Hz, 1H, CH_2), 4.97 (d, *J* = 15.6 Hz, 1H, CH_2), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 7.10-7.16 (m, 2H, ArH), 7.27-7.36 (m, 6H, ArH), 7.61 (d, *J* = 7.6 Hz, 1H, ArH), 7.71 (d, *J* = 4.8 Hz, 1H, ArH), 7.93 (d, *J* = 4.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 69.3, 82.2, 87.4, 110.2, 124.1, 125.2, 127.1, 127.2, 128.0, 128.5, 129.0, 131.1, 134.6, 136.0, 136.3, 142.2, 144.1, 168.6, 172.9. IR (EtOH) ν 3300, 3094, 3021, 3000, 2215, 1711, 1610, 1408, 1054, 853, 749 cm^{-1}. HRMS (ESI) Calcd. For $C_{22}H_{19}N_2O_3S^{+1}(M+NH_4)^+$ requires 391.1111, Found: 391.1107.


7.933
7.923
7.720
7.708
7.616
7.597
7.353
7.333
7.319
7.305
7.294
7.274
7.160
7.141
7.122
7.112
7.101
6.777
6.757
4.985
4.946
4.934
4.895
4.085
0.000
0.98
0.98
0.97
5.71
1.99
1.00
0.96
1.00
0.98
f1 (ppm)


172.856
168.639
144.137
142.202
136.298
135.999
134.581
131.131
128.985
128.467
127.991
127.161
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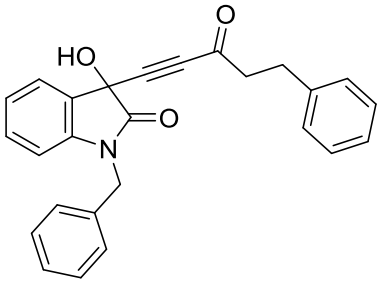
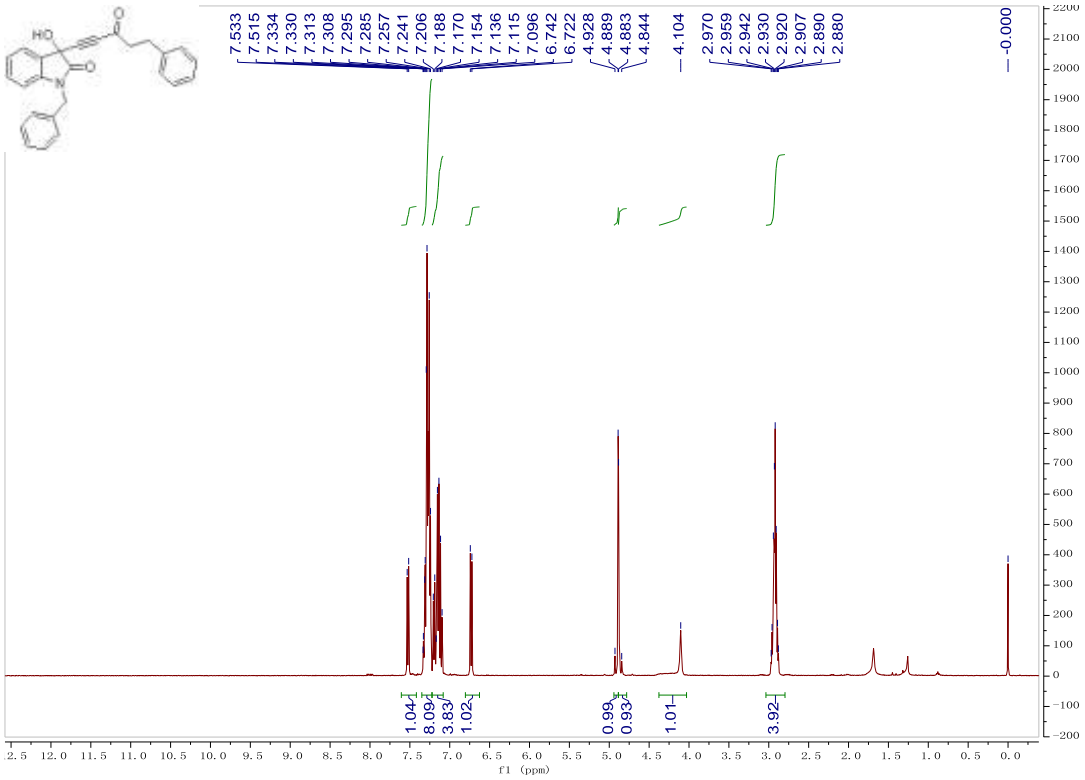
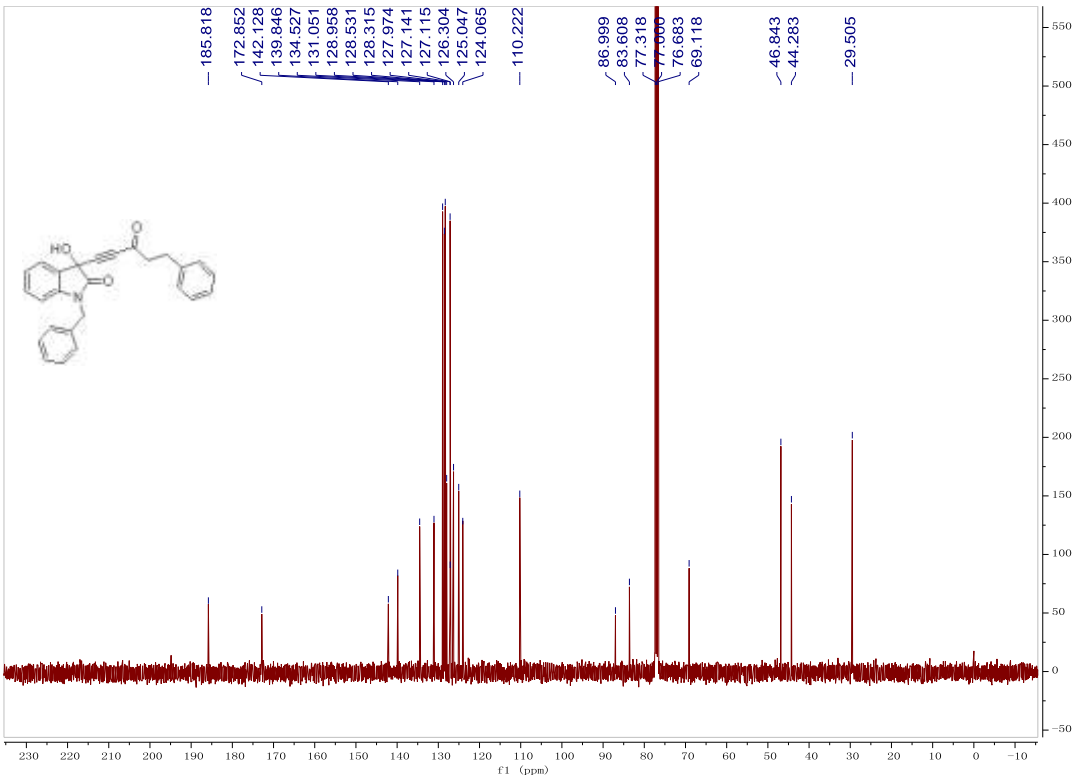
77.318
77.000
76.683
69.282
44.321
f1 (ppm)

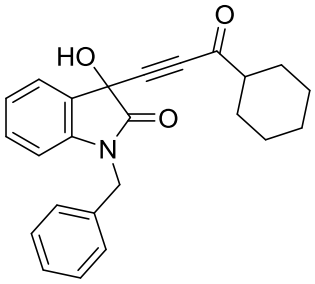


1-benzyl-3-hydroxy-3-(3-oxo-5-phenylpent-1-yn-1-yl)indolin-2-one (1y)

A white solid, 37% yield (730 mg). M.p.: 132-134 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.88-2.97 (m, 4H, CH_2), 4.10 (s, 1H, OH), 4.86 (d, *J* = 15.6 Hz, 1H, CH_2), 4.91 (d, *J* = 15.6 Hz, 1H, CH_2), 6.73 (d, *J* = 8.0 Hz, 1H, ArH), 7.09-7.21 (m, 4H, ArH), 7.24-7.34 (m, 8H, ArH), 7.52 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 29.5, 44.3, 46.8, 69.1, 83.6, 87.0, 110.2, 124.1, 125.0, 126.3, 127.12, 127.14, 128.0, 128.3, 128.5, 129.0, 134.5, 139.8, 142.1, 172.9, 185.8. IR (EtOH) ν 3319, 3026, 2932, 2212, 1701, 1677, 1175, 1158, 736, 695 cm^{-1}. HRMS (ESI) Calcd. For $C_{26}H_{25}N_2O_3^{+1}(M+NH_4)^+$ requires 413.1860, Found: 413.1854.

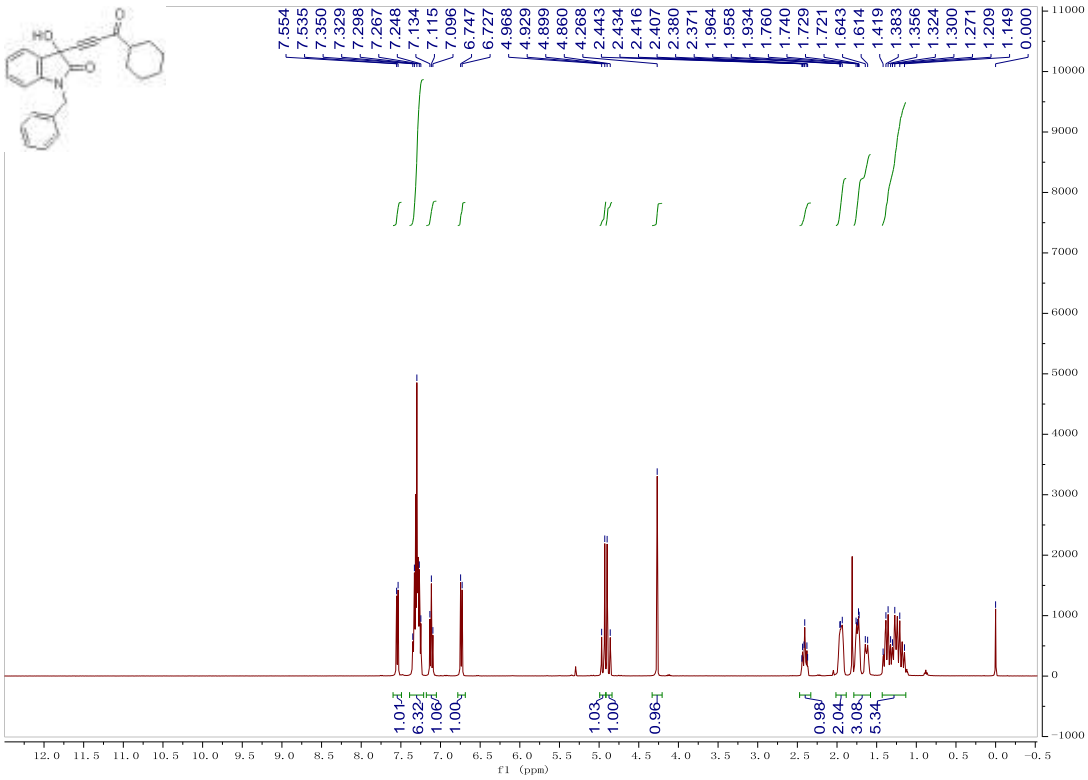






1-benzyl-3-(3-cyclohexyl-3-oxoprop-1-yn-1-yl)-3-hydroxyindolin-2-one (1z)

A white solid, 49% yield (921 mg). M.p.: 139-141 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.14-1.42 (m, 5H, CH_2), 1.61-1.76 (m, 3H, CH_2), 1.93-1.97 (m, 1H, CH_2), 2.37-2.45 (m, 1H, CH), 4.27 (s, 1H, OH), 4.88 (d, *J* = 15.6 Hz, 1H, CH_2), 4.95 (d, *J* = 15.6 Hz, 1H, CH_2), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 7.12 (t, *J* = 7.6 Hz, 1H, ArH), 7.24-7.35 (m, 6H, ArH), 7.54 (d, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 25.2, 25.3, 25.6, 27.87, 27.95, 44.2, 52.1, 69.2, 83.2, 87.3, 110.2, 124.0, 125.0, 127.1, 127.3, 127.9, 128.9, 131.0, 134.6, 142.1, 173.0, 190.4. IR (EtOH) ν 3332, 2925, 2853, 1735, 1709, 1673, 1654, 1559, 1486, 1376, 1174, 751 cm^{-1}. HRMS (ESI) Calcd. For $C_{24}H_{27}N_2O_3^{+1}(M+NH_4)^+$ requires 391.2016, Found: 391.2006.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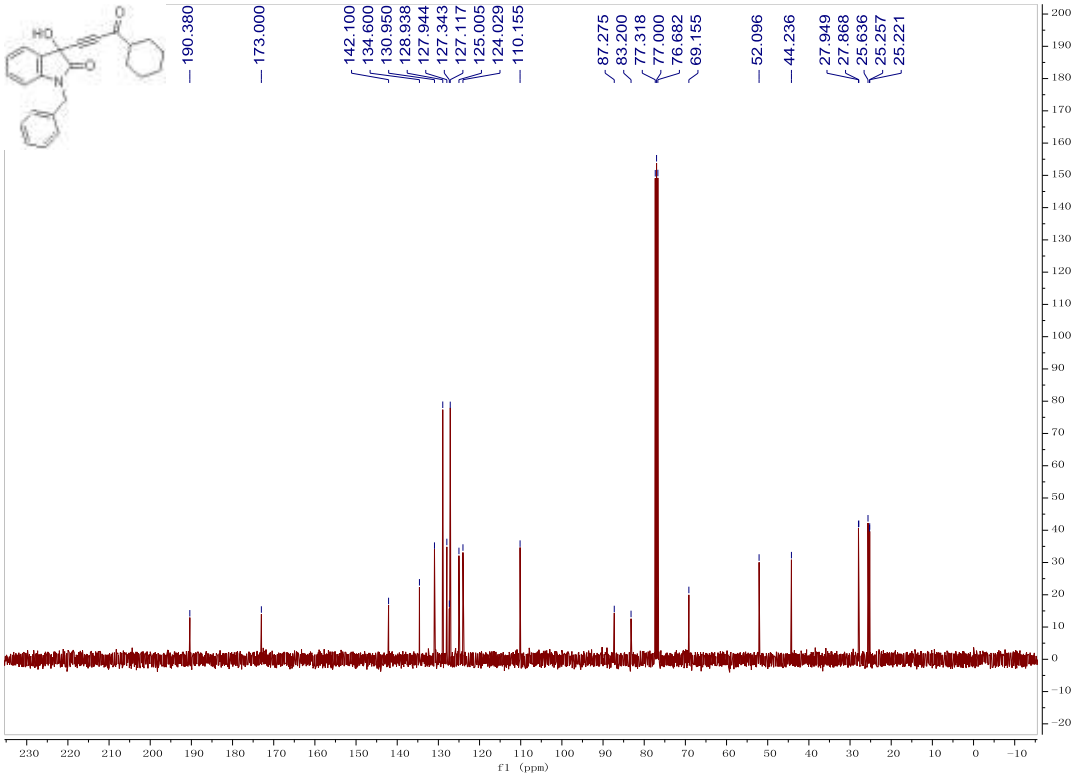
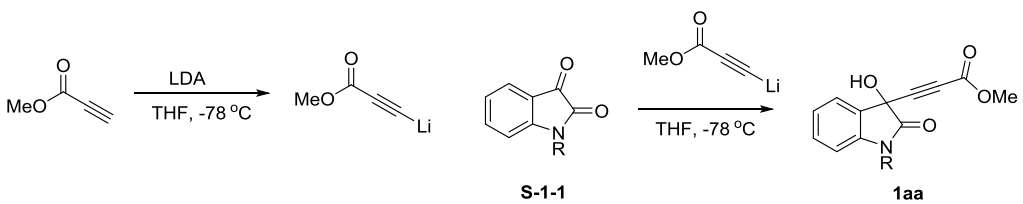
7.350
7.329
7.298
7.267
7.248
7.134
7.115
7.096
6.747
6.727
4.968
4.929
4.899
4.860
4.268
2.443
2.434
2.416
2.407
2.380
2.371
1.964
1.958
1.934
1.760
1.740
1.729
1.721
1.643
1.614
1.419
1.383
1.356
1.324
1.300
1.271
1.209
1.149
0.000
1.01
6.32
1.06
1.00
1.03
1.00
0.96
0.98
2.04
3.08
5.34
f1 (ppm)

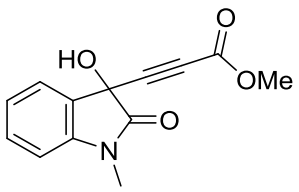

190.380
173.000
142.100
134.600
130.950
128.938
127.944
127.343
127.117
125.005
124.029
110.155
87.275
83.200
77.318
77.000
76.682
69.155
52.096
44.236
27.949
27.868
25.636
25.257
25.221
f1 (ppm)


MeO
LDA
THF, -78 °C
MeO
Li
MeO
Li
THF, -78 °C
HO
OMe
S-1-1
1aa

Substrates **1aa** was synthesized through the **method 3** as below.

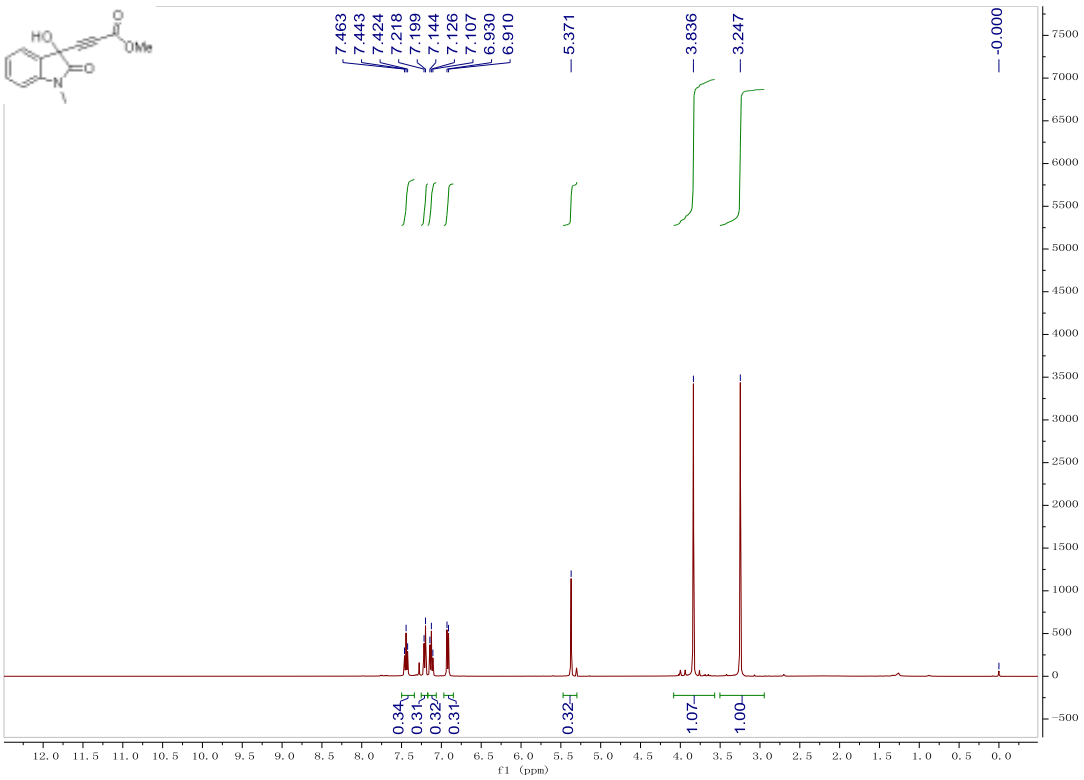
Method 3

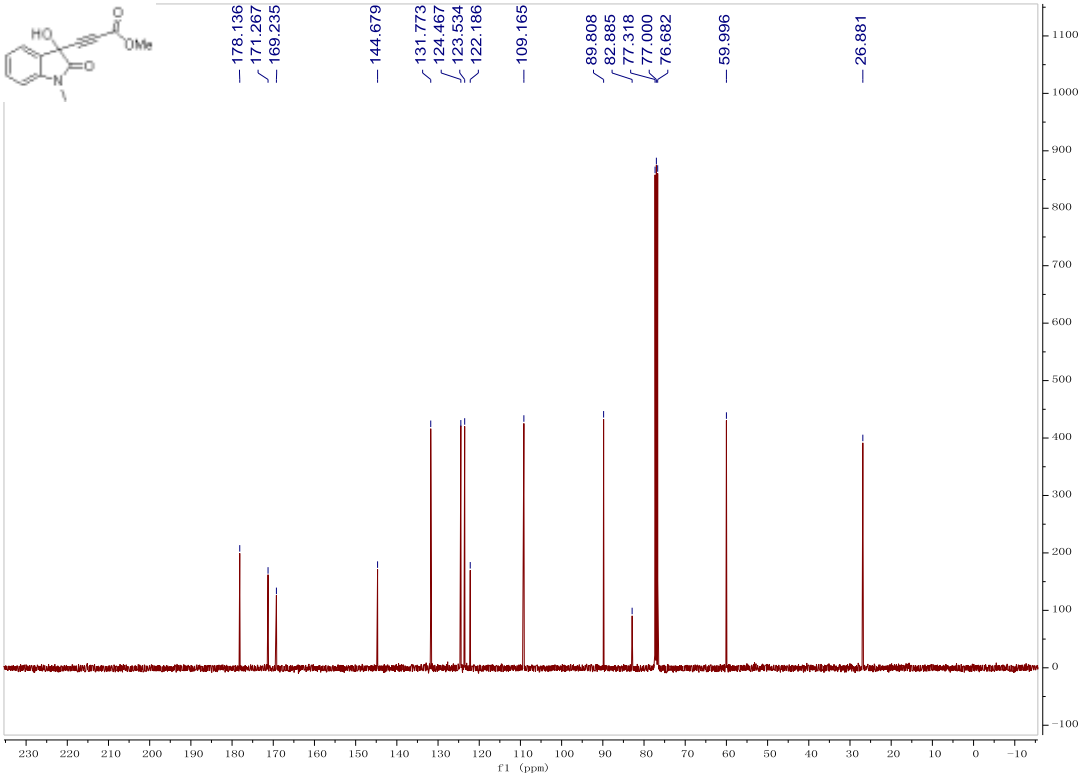
Step 1: To a solution of methyl propiolate (5.0 mmol, 1.0 equiv) in dry THF (10 mL) was added LDA (Lithium diisopropylamide) solution (5.0 mmol, 1.0 equiv) under -78 ^{o}C. After stirring for one hour, the fresh alkynyl lithium reagent was added to a solution of isatin derivative **S-1-1** (6.0 mmol, 1.2 equiv) in dry THF (10 mL) under -78 ^{o}C. Then, the resulting reaction mixture was stirred at -78 ^{o}C for one hour. After warm up to room temperature, the reaction mixture was continued to stirred for another 2 hours. Then, 20 mL water was added to quench the reaction. The mixture was extracted with ethyl acetate three times and washed by water. Then the organic phase was concentrated under high vacuum and purified by a column chromatography on silica gel to give the products **1aa** (DCM:EA = 10:1 ~ 4:1).

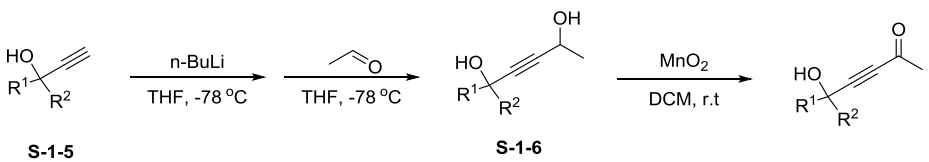


methyl 3-(3-hydroxy-1-methyl-2-oxoindolin-3-yl)propiolate (1aa)

A white solid, 53% yield (649 mg). M.p.: 142-144 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 3.25 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 5.37 (s, 1H, OH), 6.92 (d, *J* = 8.0 Hz, 1H, ArH), 7.13 (t, *J* = 7.2 Hz, 1H, ArH), 7.21 (d, *J* = 7.6 Hz, 1H, ArH), 7.44 (t, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.9, 60.0, 82.9, 89.8, 109.2, 122.2, 123.5, 124.5, 131.8, 144.7, 169.2, 171.3, 178.1. IR (EtOH) ν 3536, 3115, 2948, 1773, 1732, 1635, 1493, 1344, 1190, 1007, 783, 753 cm^{-1}. HRMS (ESI) Calcd. For $C_{13}H_{15}N_2O_4^{+1}$(M+NH_4)$^+$ requires 263.1026, Found: 263.1022.







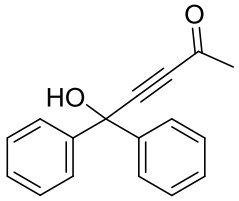
S-1-5 **S-1-6**

Substrates **1ab**, **1ad-1af** was synthesized through the **method 4** as below.

Method 4

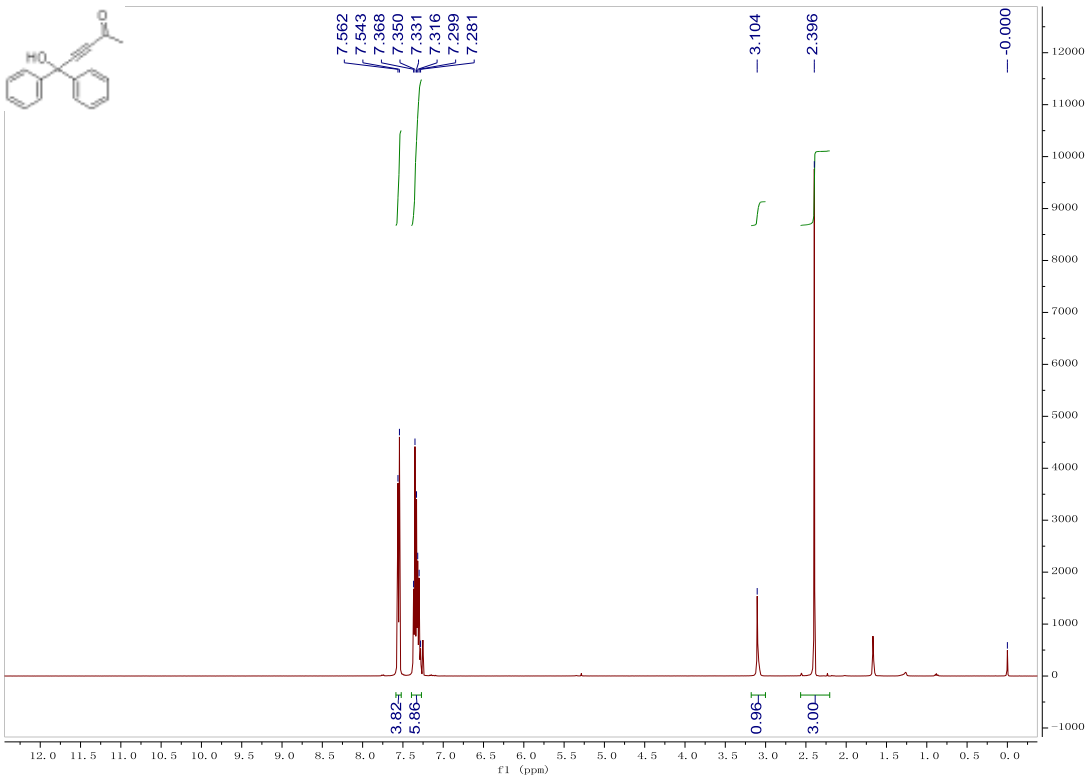
Step 1: To a solution of propargyl alcohol **S-1-5** (5.0 mmol, 1.0 equiv) in dry THF (10 mL) was added n-butyllithium solution (11.0 mmol, 2.2 equiv) under -78 ^{o}C. After stirring for one hour, pure acetaldehyde (6.0 mmol, 1.2 equiv) was added to the solution under -78 ^{o}C. Then, the resulting reaction mixture was stirred at -78 ^{o}C for one hour. After warm up to room temperature, the reaction mixture was continued to stirred for another 2 hours. Then, 20 mL water was added to quench the reaction. The mixture was extracted with ethyl acetate three times and washed by water. Then the organic phase was concentrated under high vacuum and purified by a short column chromatography on silica gel to give the crude products **S-1-6** (DCM:EA = 20:1 ~ 4:1).

Step 2: The crude product **S-1-6** was dispersed in 10 mL DCM, and activated manganese dioxide powder was added in small batch until the **S-1-6** was totally consumed. Then the reaction mixture filtered through celite to remove solid impurities and concentrated under high vacuum. After that, crude product was purified by a column chromatography on silica gel to give the desired products **1** (DCM:EA = 20:1 ~ 4:1).



5-hydroxy-5,5-diphenylpent-3-yn-2-one (1ab)

A white solid, 31% yield (386 mg). M.p.: 87-89 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.40 (s, 3H, CH_3), 3.10 (s, 1H, OH), 7.28-7.37 (m, 6H, ArH), 7.55 (d, *J* = 7.6 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.7, 74.4, 85.7, 92.5, 125.9, 128.3, 128.5, 143.1, 184.3. IR (EtOH) ν 3396, 2921, 2851, 1674, 1449, 1358, 1227, 1095, 1032, 1010, 891 cm^{-1}. HRMS (ESI) Calcd. For $C_{17}H_{18}NO_2^{+1}(M+NH_4)^+$ requires 268.1332, Found: 268.1327.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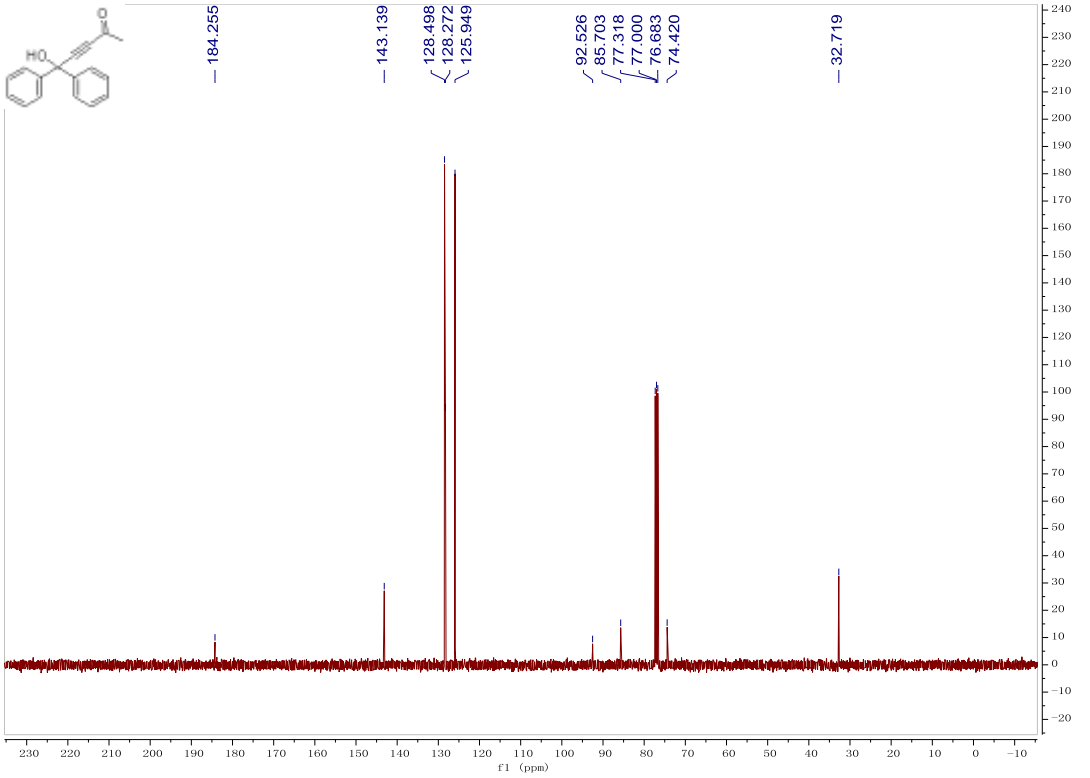
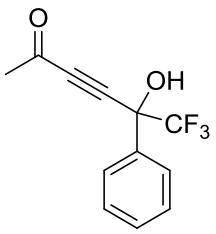
7.543
7.368
7.350
7.331
7.316
7.299
7.281
3.104
2.396
-0.000
3.82
5.86
0.96
3.00
f1 (ppm)

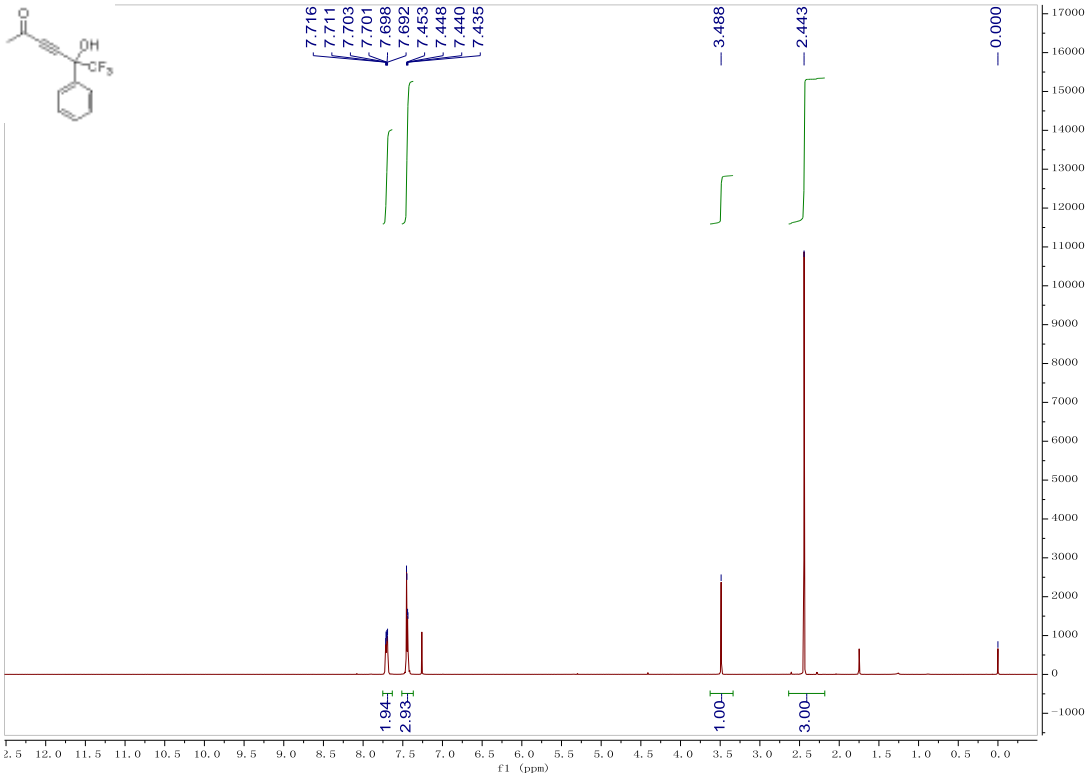

184.255
143.139
128.498
128.272
125.949
92.526
85.703
77.318
77.000
76.683
74.420
32.719
f1 (ppm)

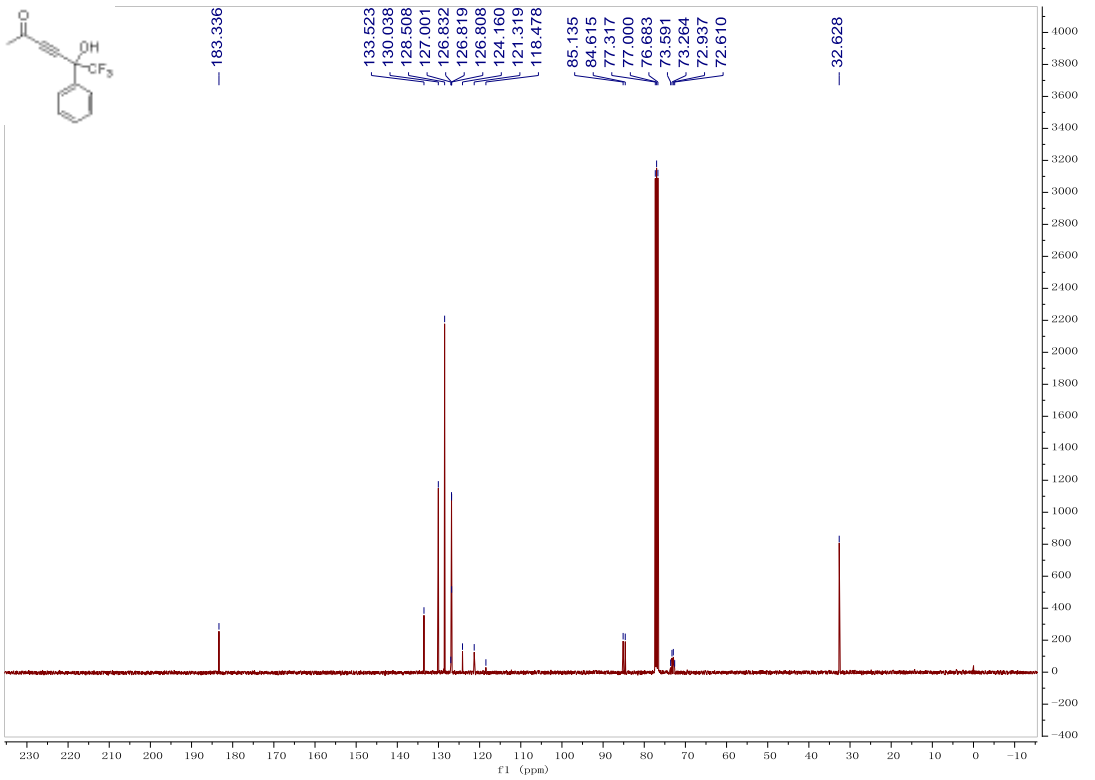

O
OH
CF3

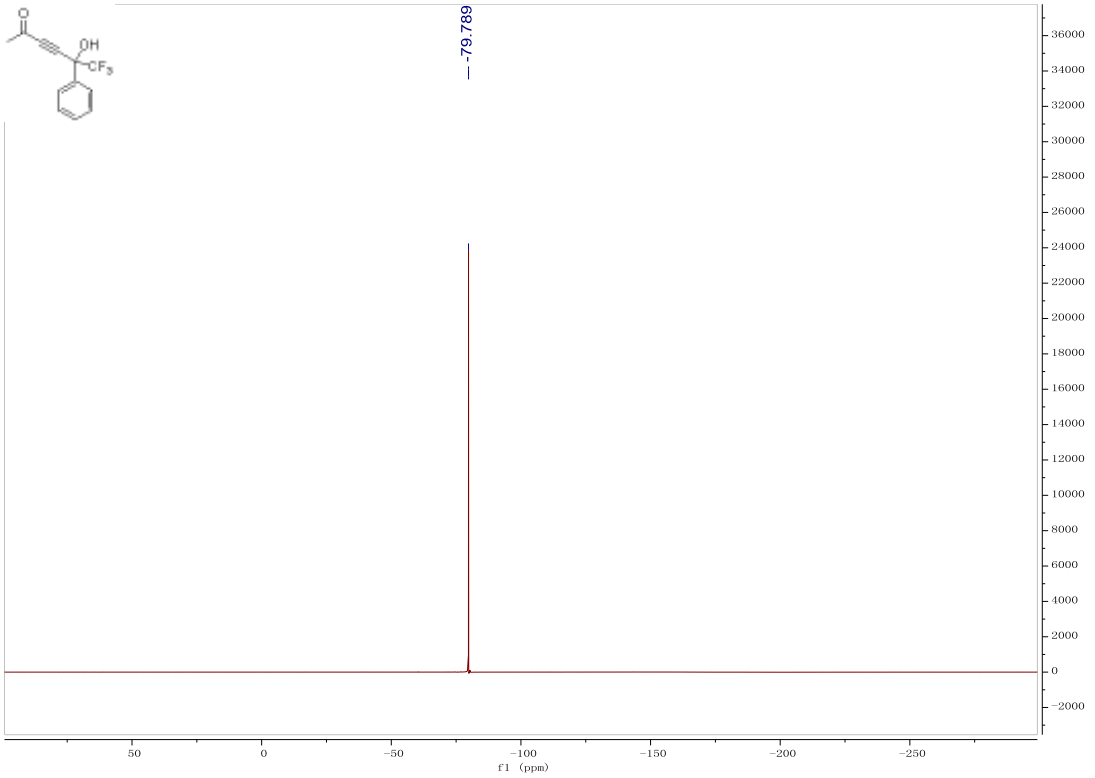
Substrates **1ac** was synthesized through the **method 1**.

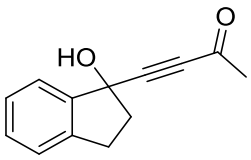
6,6,6-trifluoro-5-hydroxy-5-phenylhex-3-yn-2-one (1ac)

A white solid, 65% yield (787 mg). M.p.: 46-48 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 3.49 (s, 1H, OH), 7.43-7.46 (m, 3H, ArH), 7.69-7.72 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.6, 73.1 (q, *J* = 32.7 Hz), 84.6, 85.1, 122.7 (q, *J* = 284.1 Hz), 126.8 (q, *J* = 1.3 Hz), 128.5, 130.0, 133.5, 183.3. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -79.79. IR (EtOH) ν 3330, 3057, 2913, 1712, 1678, 1611, 1356, 1234, 1198, 753 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{12}H_{10}O_2F_3^{+1}(M+H)^+$ requires 243.0627, Found: 243.0627.



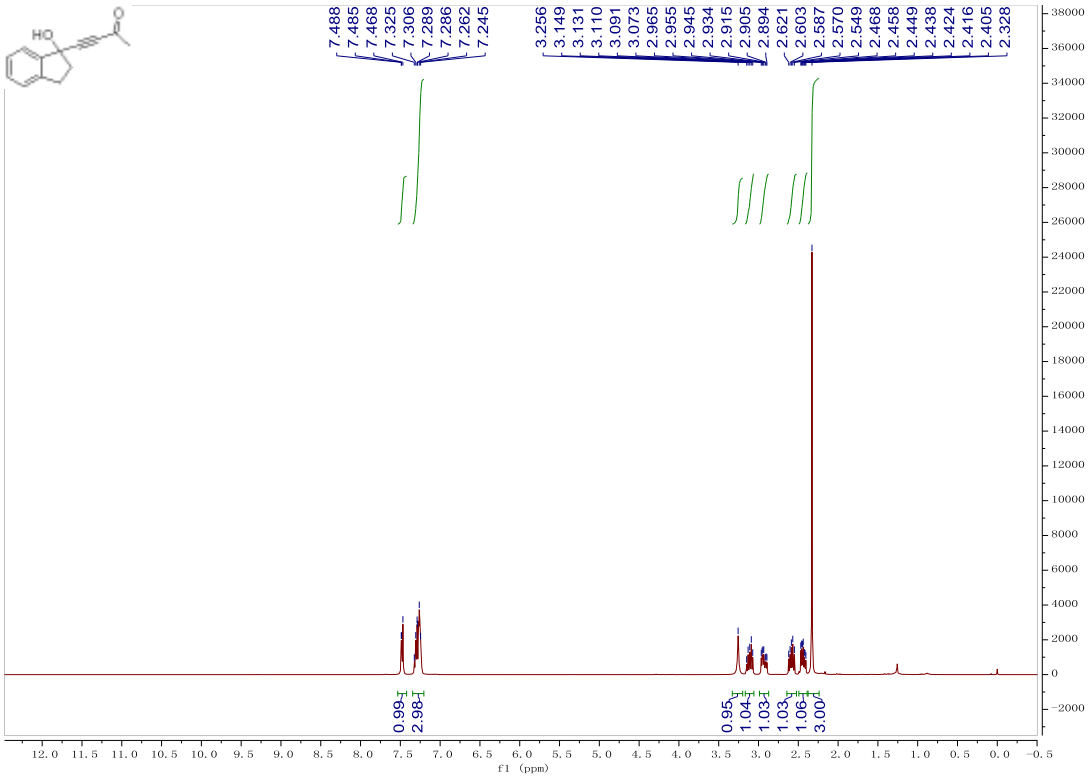


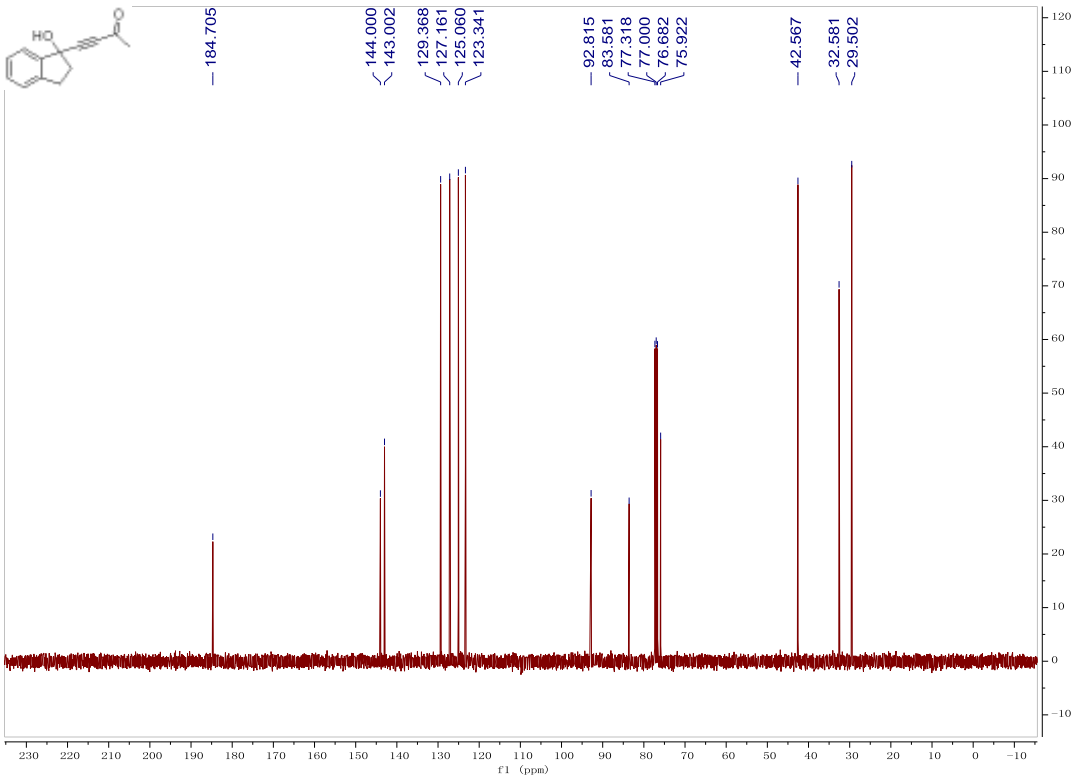


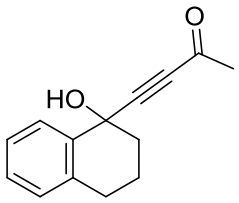


4-(1-hydroxy-2,3-dihydro-1H-inden-1-yl)but-3-yn-2-one (1ad)

A viscous liquid, 27% yield (270 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.33 (s, 3H, CH_3), 2.40-2.47 (m, 1H, CH_2), 2.54-2.62 (m, 1H, CH_2), 2.89-2.97 (m, 1H, CH_2), 3.07-3.15 (m, 1H, CH_2), 3.26 (s, 1H, OH), 7.24-7.33 (m, 3H, ArH), 7.46-7.49 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 29.5, 32.6, 42.6, 75.9, 83.6, 92.8, 123.3, 125.1, 127.2, 129.4, 143.0, 144.0, 184.7. IR (EtOH) ν 3400, 2942, 2853, 1674, 1459, 1358, 1219, 965 cm^{-1}. HRMS (ESI) Calcd. For $C_{13}H_{16}NO_2^{+1}(M+NH_4)^+$ requires 218.1176, Found: 218.1176.

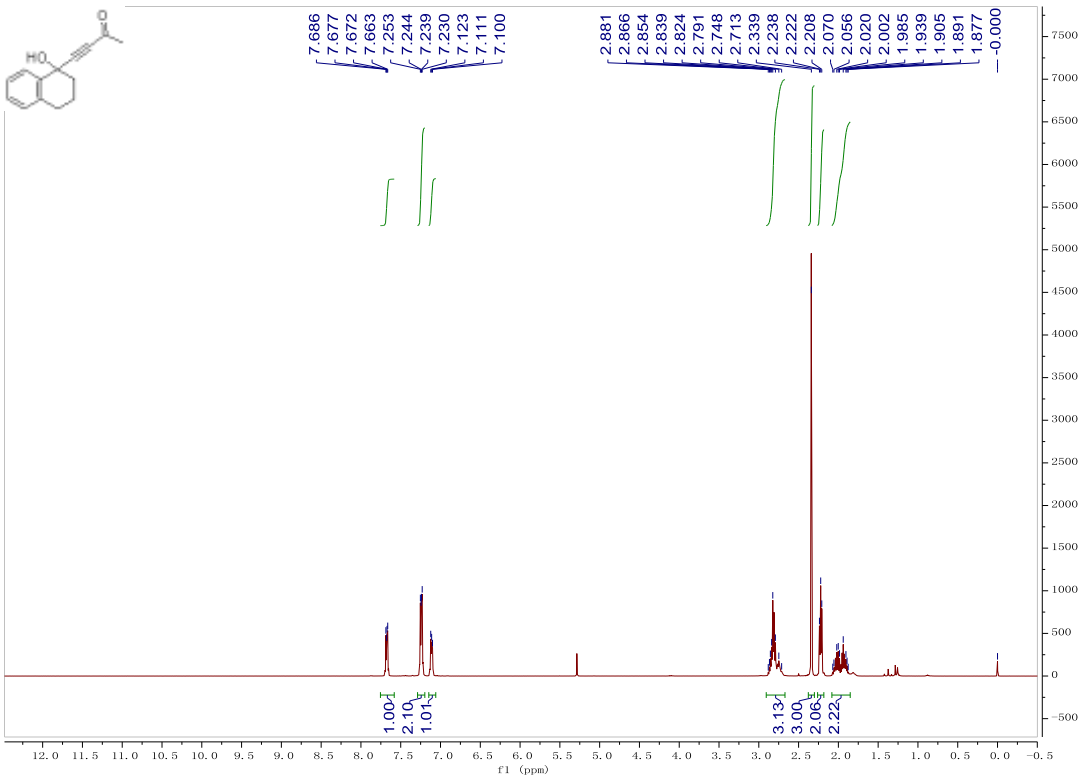


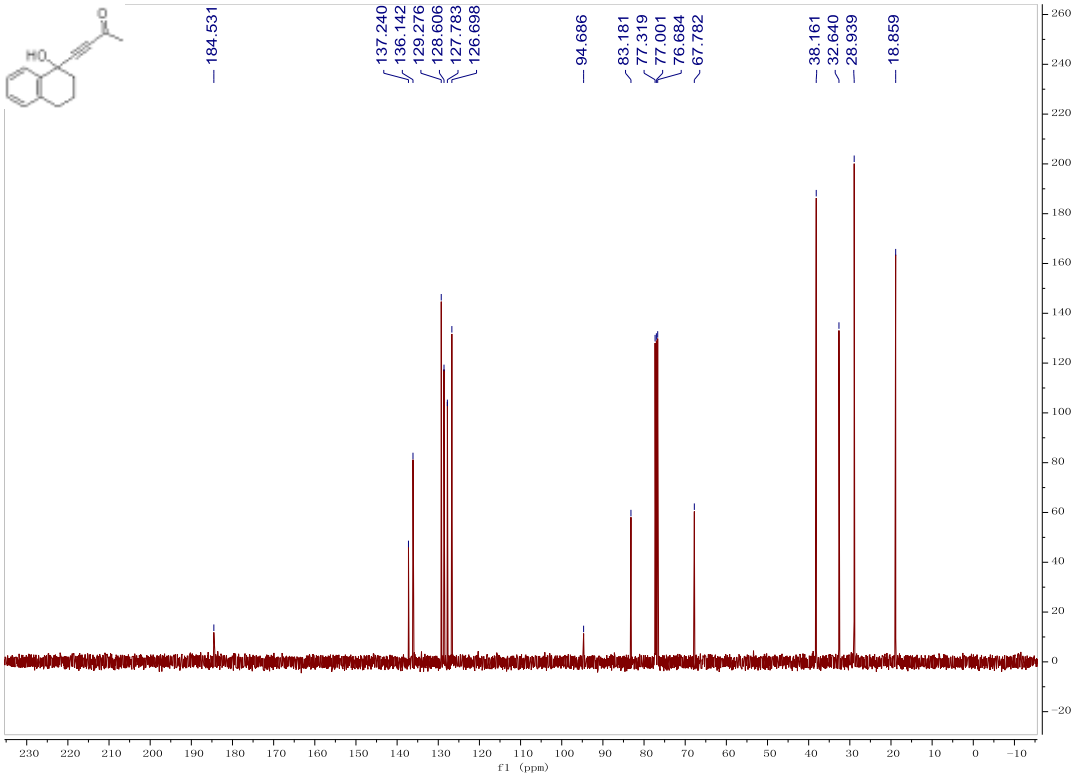


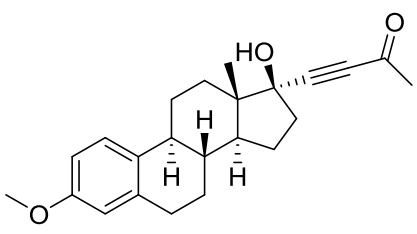


4-(1-hydroxy-1,2,3,4-tetrahydronaphthalen-1-yl)but-3-yn-2-one (1ae)

A viscous liquid, 35% yield (375 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.87-2.07 (m, 2H, CH_2), 2.20-2.24 (m, 2H, CH_2), 2.34 (s, 3H, CH_3), 2.71-2.89 (m, 3H, CH_2, OH), 7.11 (t, *J* = 4.8 Hz, 1H, ArH), 7.23-7.26 (m, 2H, ArH), 7.66-7.69 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 18.9, 28.9, 32.6, 38.2, 67.8, 83.2, 94.7, 126.7, 127.8, 128.6, 129.3, 136.1, 137.2, 184.5. IR (EtOH) ν 3423, 2944, 1675, 1450, 1227, 1017, 772 cm^{-1}. HRMS (ESI) Calcd. For $C_{14}H_{18}NO_2^{+1}(M+NH_4)^+$ requires 232.1332, Found: 232.1330.

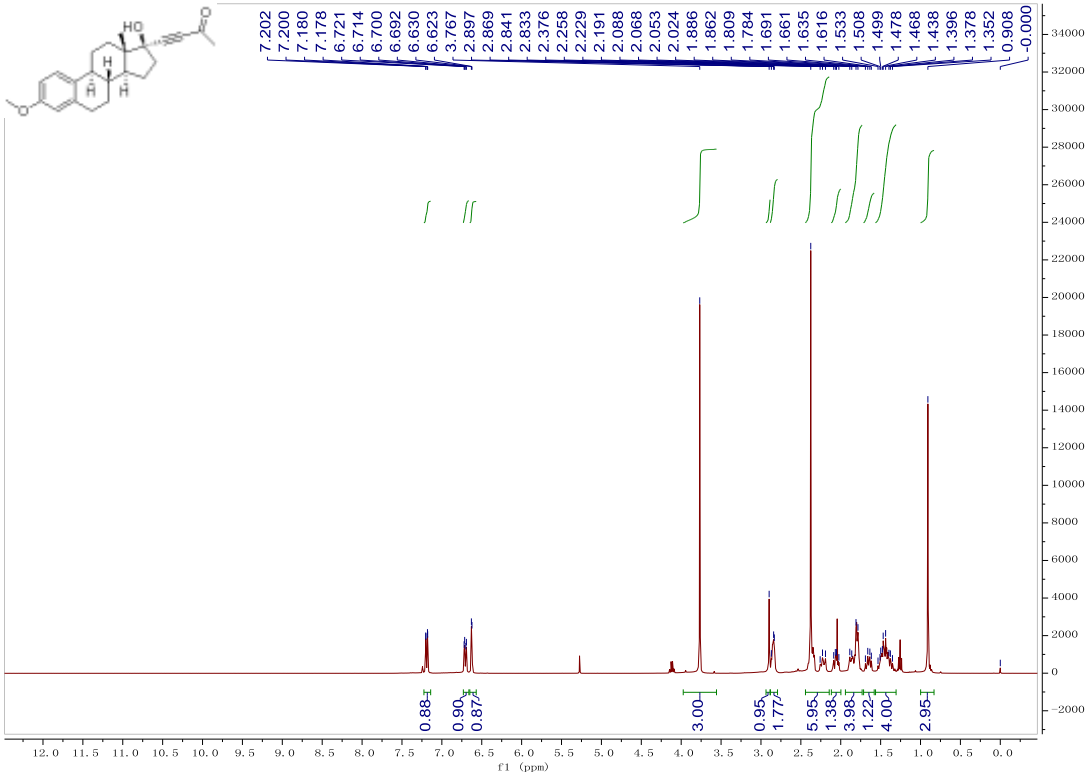

HO
O
7.686
7.677
7.672
7.663
7.253
7.244
7.239
7.230
7.123
7.111
7.100
2.881
2.866
2.854
2.839
2.824
2.791
2.748
2.713
2.339
2.238
2.222
2.208
2.070
2.056
2.020
2.002
1.985
1.939
1.905
1.891
1.877
-0.000
1.00
2.10
1.01
3.13
3.00
2.06
2.22
f1 (ppm)

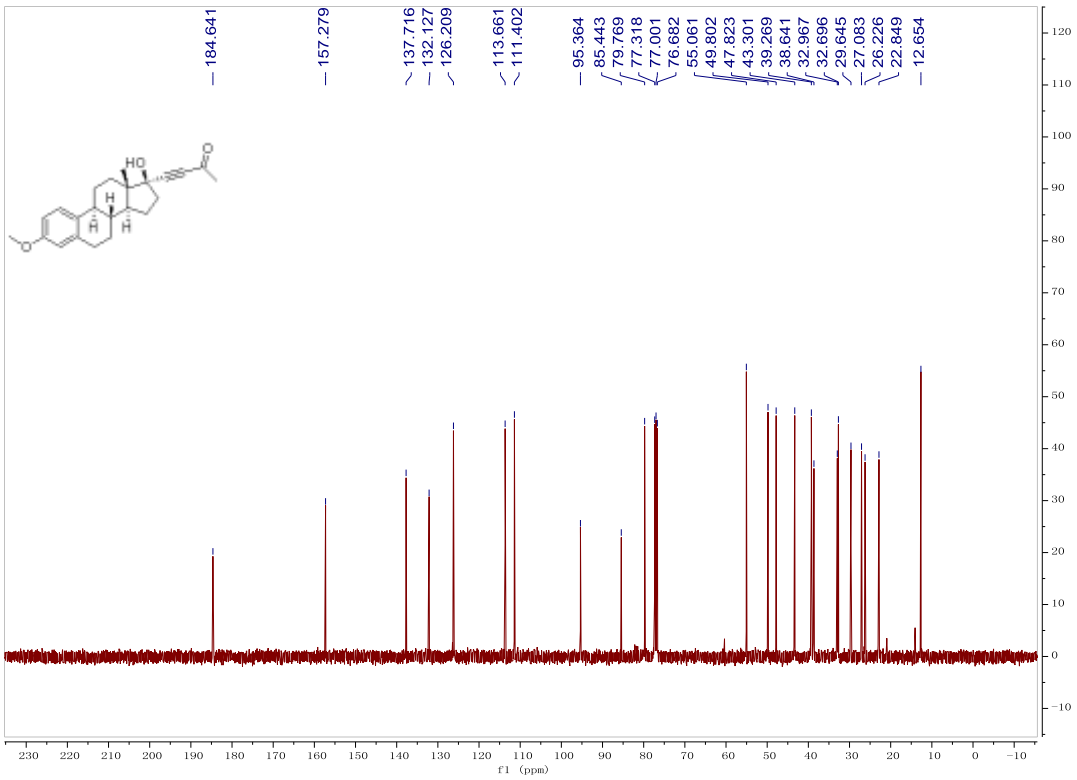

HO
O
184.531
137.240
136.142
129.276
128.606
127.783
126.698
94.686
83.181
77.319
77.001
76.684
67.782
38.161
32.640
28.939
18.859
f1 (ppm)

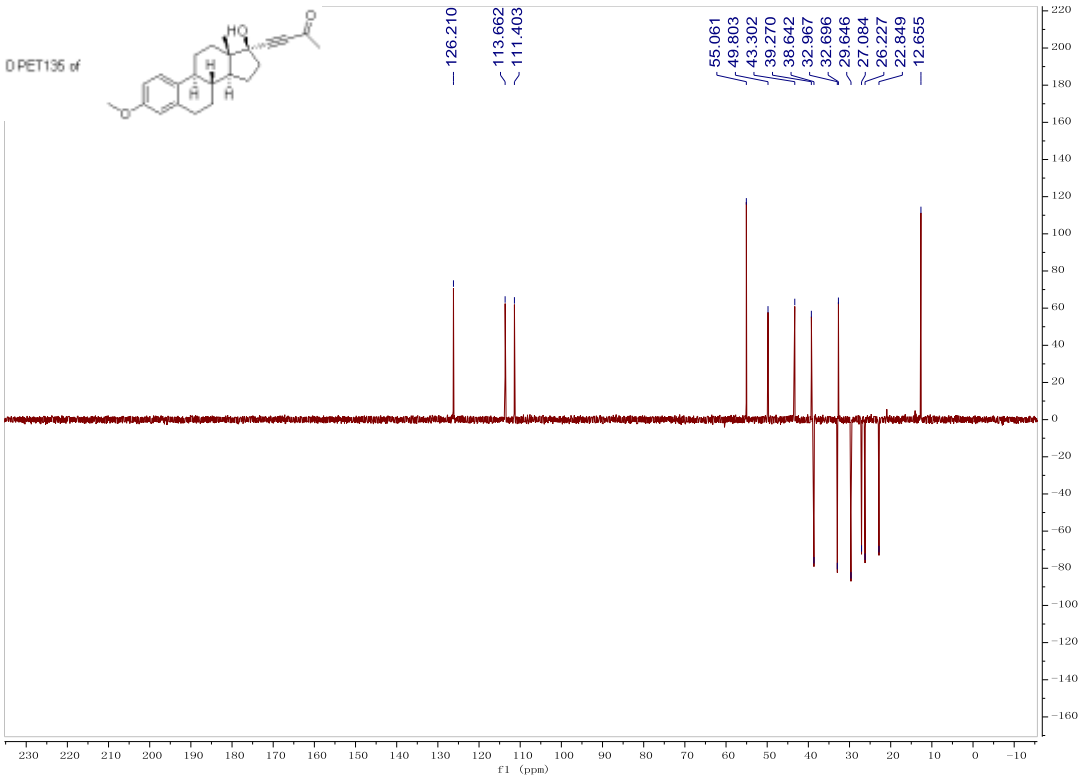

HO
O
H
H
H
O

4-((8R,9S,13S,14S,17S)-17-hydroxy-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)but-3-yn-2-one (1af)

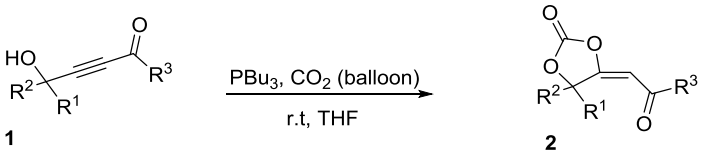
A viscous liquid, 73% yield (1285 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.91 (s, 3H, CH_3), 1.35-1.54 (m, 4H), 1.61-1.70 (m, 1H), 1.78-1.89 (m, 4H), 2.02-2.09 (m, 1H), 2.19-2.38 (m, 6H), 2.83-2.87 (m, 2H), 2.90 (s, 1H, OH), 3.77 (s, 3H, CH_3), 6.63 (d, *J* = 2.8 Hz, 1H, ArH), 6.71 (dd, *J* = 2.8, 8.4 Hz, 1H, ArH), 7.19 (dd, *J* = 0.8, 8.8 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 12.7, 22.8, 26.2, 27.1, 29.6, 32.7, 33.0, 38.6, 39.3, 43.3, 47.8, 49.8, 55.1, 79.8, 85.4, 95.4, 111.4, 113.7, 126.2, 132.1, 137.7, 157.3, 184.6. IR (EtOH) ν 3397, 2930, 2858, 1671, 1609, 1499, 1254, 1237, 1216, 1035 cm^{-1}. HRMS (ESI) Calcd. For $C_{23}H_{32}NO_3^{+1}(M+NH_4)^+$ requires 370.2377, Found: 370.2367.



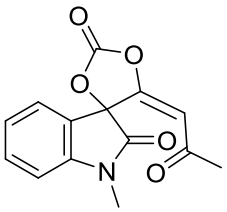

184.641
157.279
137.716
132.127
126.209
113.661
111.402
95.364
85.443
79.769
77.318
77.001
76.682
55.061
49.802
47.823
43.301
39.269
38.641
32.967
32.696
29.645
27.083
26.226
22.849
12.654
HO
H
H
H
O
O
f1 (ppm)


0 PET135 of
126.210
113.662
111.403
55.061
49.803
43.302
39.270
38.642
32.967
32.696
29.646
27.084
26.227
22.849
12.655
HO
H
H
H
O
O
f1 (ppm)

3. General Procedure for Carbon Dioxide Fixation of γ-Hydroxyl Alkynone 1 and Spectroscopic Data of Carbonate 2

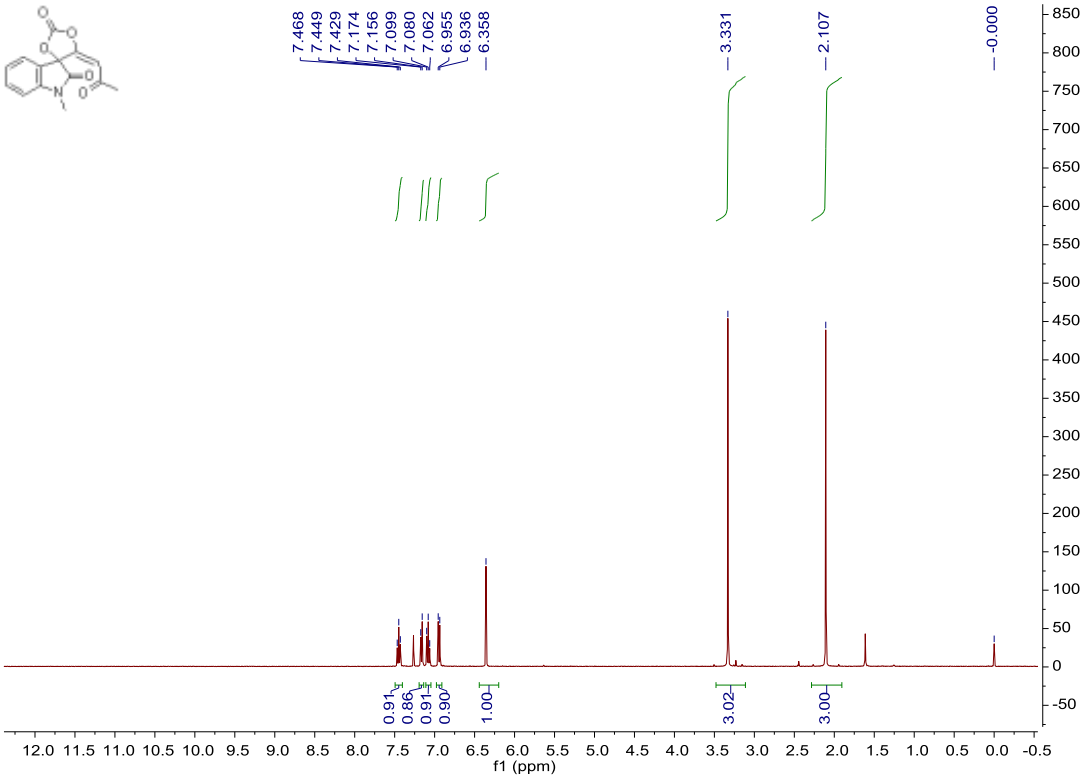


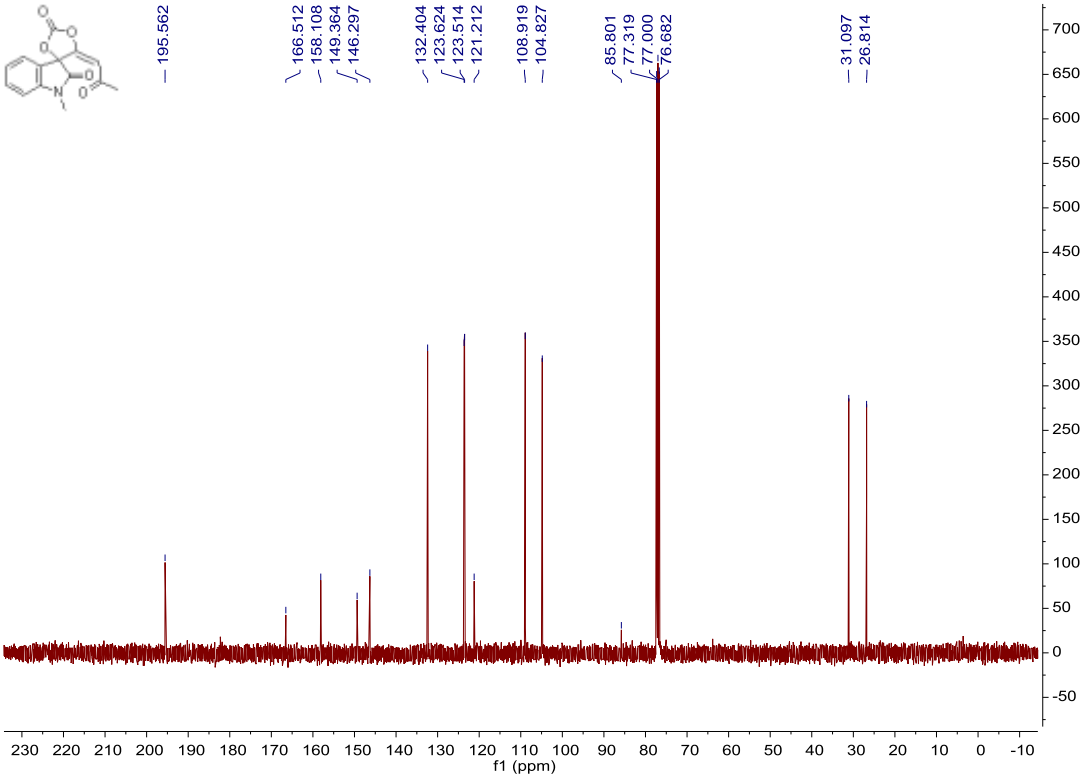
A Schlenk tube was heated under vacuum to remove ambient moisture and water, then filled with argon. After the Schlenk tube was returned to room temperature, γ-hydroxyl alkynone **1** (0.3 mmol) was added. Then the system was vacuumed and filled with CO_2. After repeating three times, THF (1.5 mL) was added and the reaction mixture was stirred for 10 minutes at room temperature. Then, PBu_3 (13 mg, 0.06 mmol) was added to the reaction mixture at room temperature. After that, the resulting mixture was stirred at room temperature until the reaction completed upon monitoring by TLC. Then the solvent was removed under reduced pressure and the residue was directly subjected to a flash column chromatography on silica gel to afford the desired products **2a-2af**. Cyclic carbonate **2** was unstable under heating; thus, the post-treatment steps should be done below 25 ^{o}C. Even so, there were still some products that were partially decomposed.



(*E*)-1-methyl-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2a)

A white solid, 81% yield (66 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.11 (s, 3H, CH_3), 3.33 (s, 3H, CH_3), 6.36 (s, 1H, =CH), 6.95 (d, *J* = 7.6 Hz, 1H, ArH), 7.08 (t, *J* = 7.6 Hz, 1H, ArH), 7.17 (d, *J* = 7.2 Hz, 1H, ArH), 7.45 (t, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 26.8, 31.1, 85.8, 104.8, 108.9, 121.2, 123.5, 123.6, 132.4, 146.3, 149.4, 158.1, 166.5, 195.6. IR (EtOH) ν 3055, 2919, 2846, 1727, 1601, 1493, 1467, 1455, 1178, 1095, 935 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{11}NO_5$ requires 273.0637, Found: 273.0630.


7.468
7.449
7.429
7.174
7.156
7.099
7.080
7.062
6.955
6.936
6.358
3.331
2.107
-0.000
0.91
0.86
0.91
0.90
1.00
3.02
3.00
f1 (ppm)


195.562
166.512
158.108
149.364
146.297
132.404
123.624
123.514
121.212
108.919
104.827
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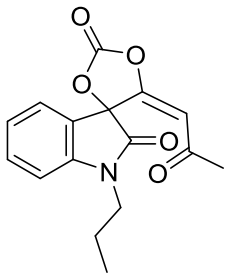
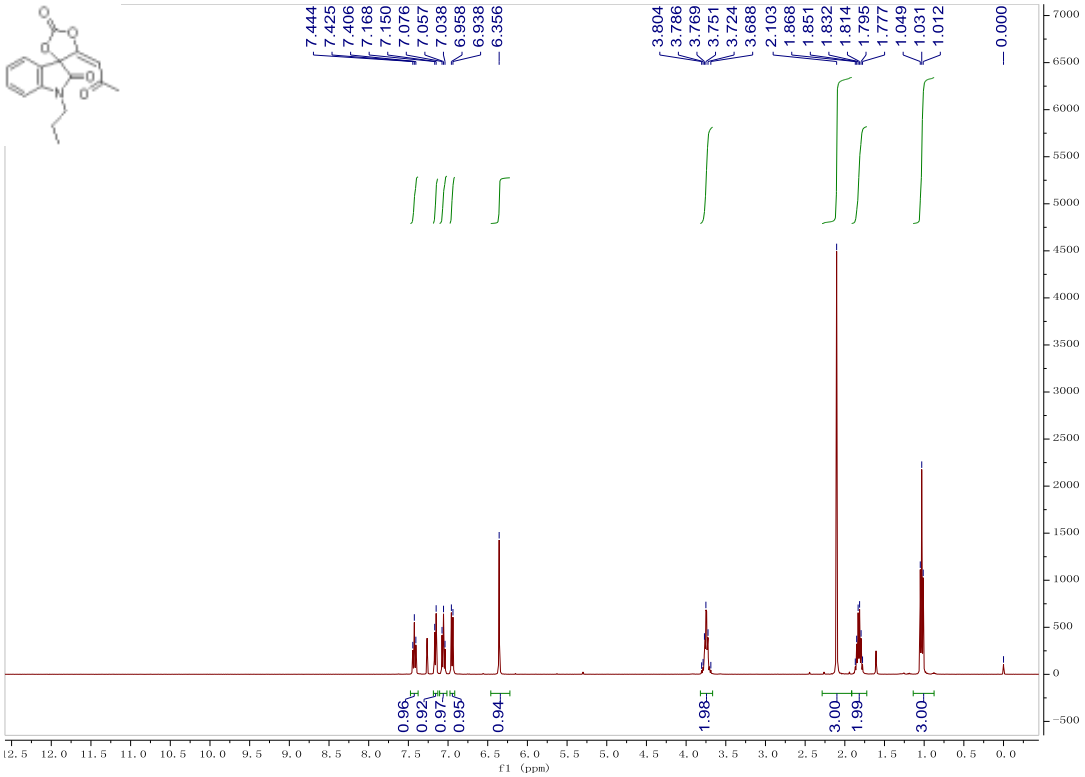
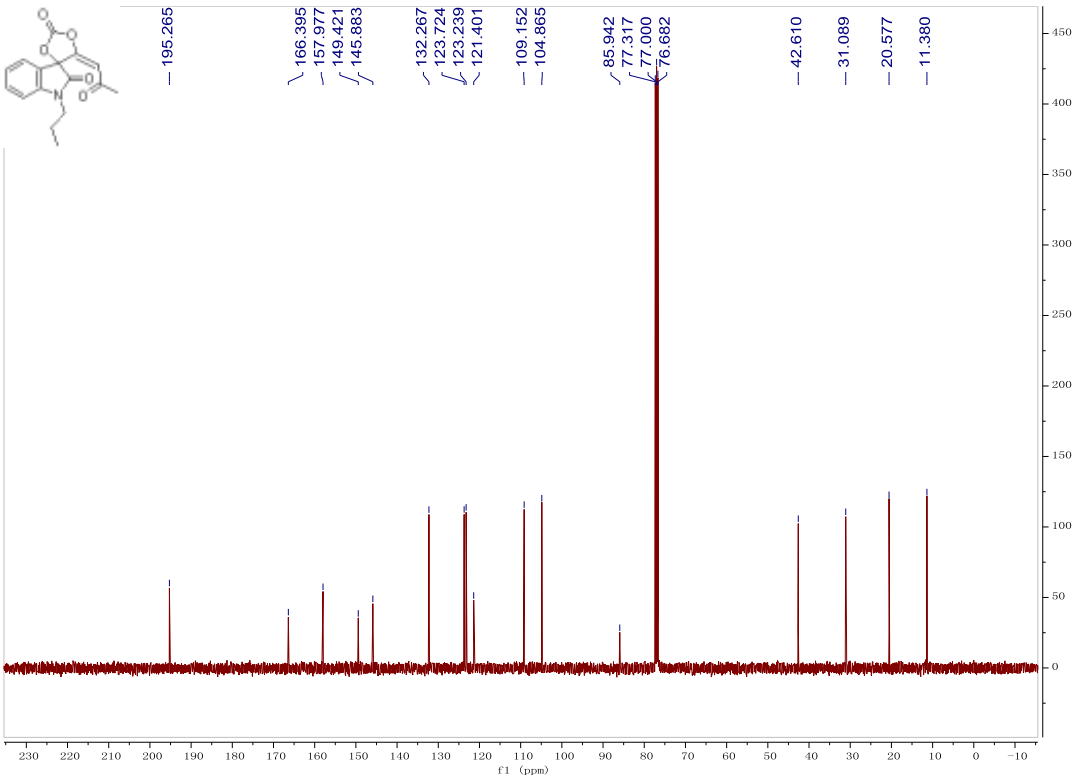
77.319
77.000
76.682
31.097
26.814
f1 (ppm)



(*E*)-5'-(2-oxopropylidene)-1-propylspiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2b)

A white solid, 83% yield (75 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.03 (t, *J* = 7.2 Hz, 3H, CH_3), 1.77-1.87 (m, 2H, CH_2), 2.10 (s, 3H, CH_3), 3.68-3.81 (m, 2H, CH_2), 6.36 (s, 1H, =CH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 7.06 (t, *J* = 7.6 Hz, 1H, ArH), 7.16 (d, *J* = 7.2 Hz, 1H, ArH), 7.43 (t, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 11.4, 20.6, 31.1, 42.6, 85.9, 104.9, 109.2, 121.4, 123.2, 123.7, 132.3, 145.9, 149.4, 158.0, 166.4, 195.3. IR (EtOH) ν 2956, 2922, 2849, 1731, 1701, 1612, 1371, 1017, 952 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{16}H_{19}O_5N_2^{+1}(M+NH_4)^+$ requires 319.1288, Found: 319.1290. $[\alpha]^{25}_D$ = +25.56 (c 0.09, CH_2Cl_2) for 82% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 28.637 min, t_{major} = 32.635 min.





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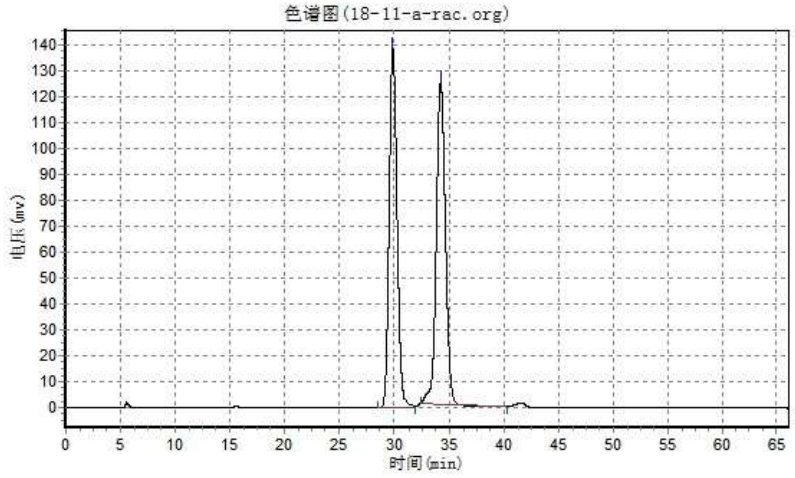
报告时间：2018-04-27,13:30:37
积分方法:面积归一法



分析结果表

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1		29.965	138873.453	6969775.500	49.1315
2		34.215	124730.258	7216182.000	50.8685
总计			263603.711	14185957.500	100.0000

实验时间：2018-04-27,13:29:03
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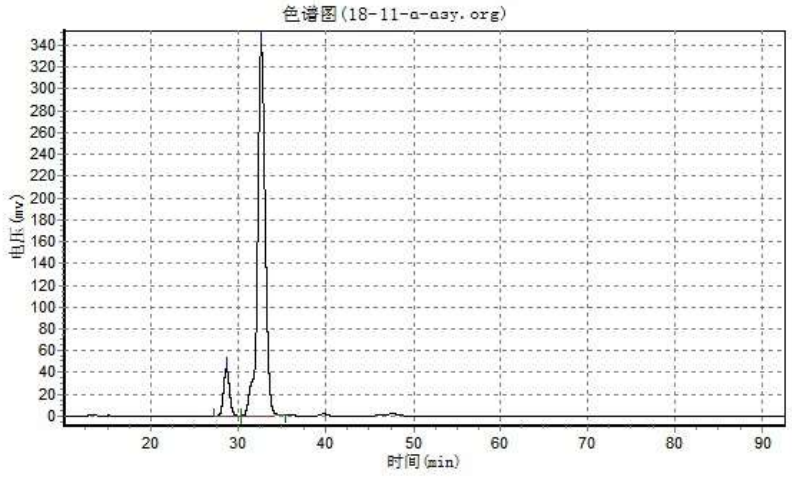
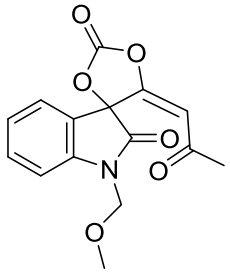
实验者：
报告时间：2018-04-27,13:31:56
积分方法:面积归一法



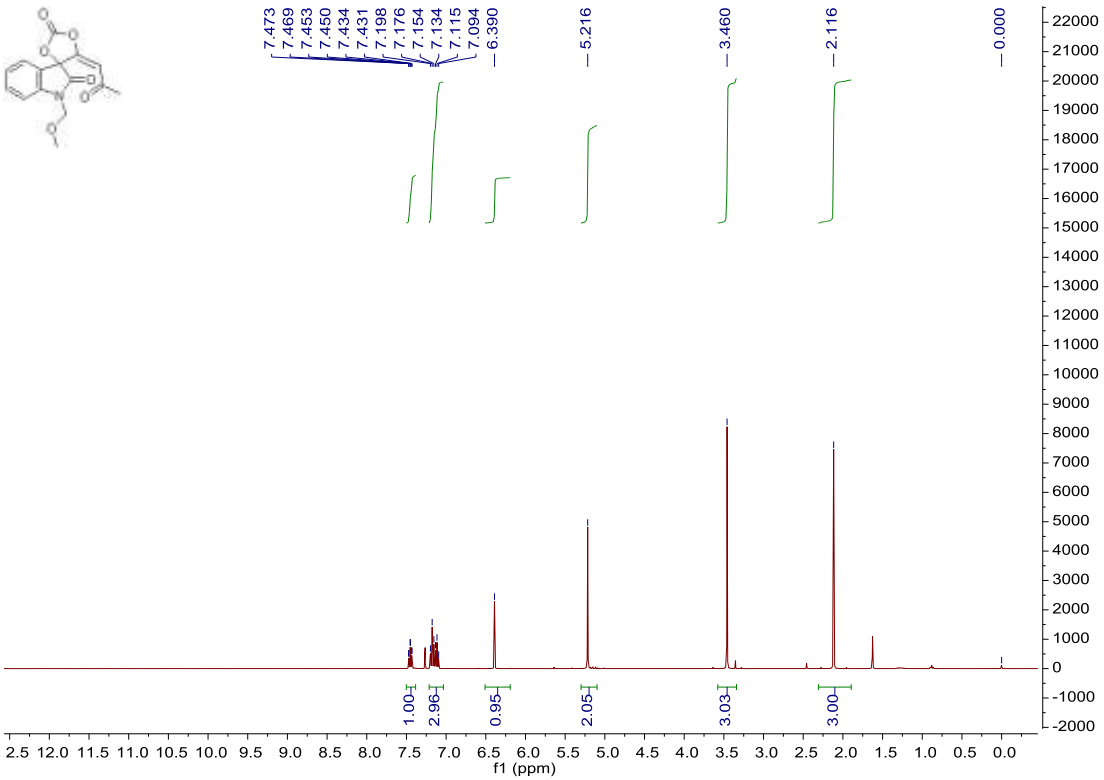
分析结果表

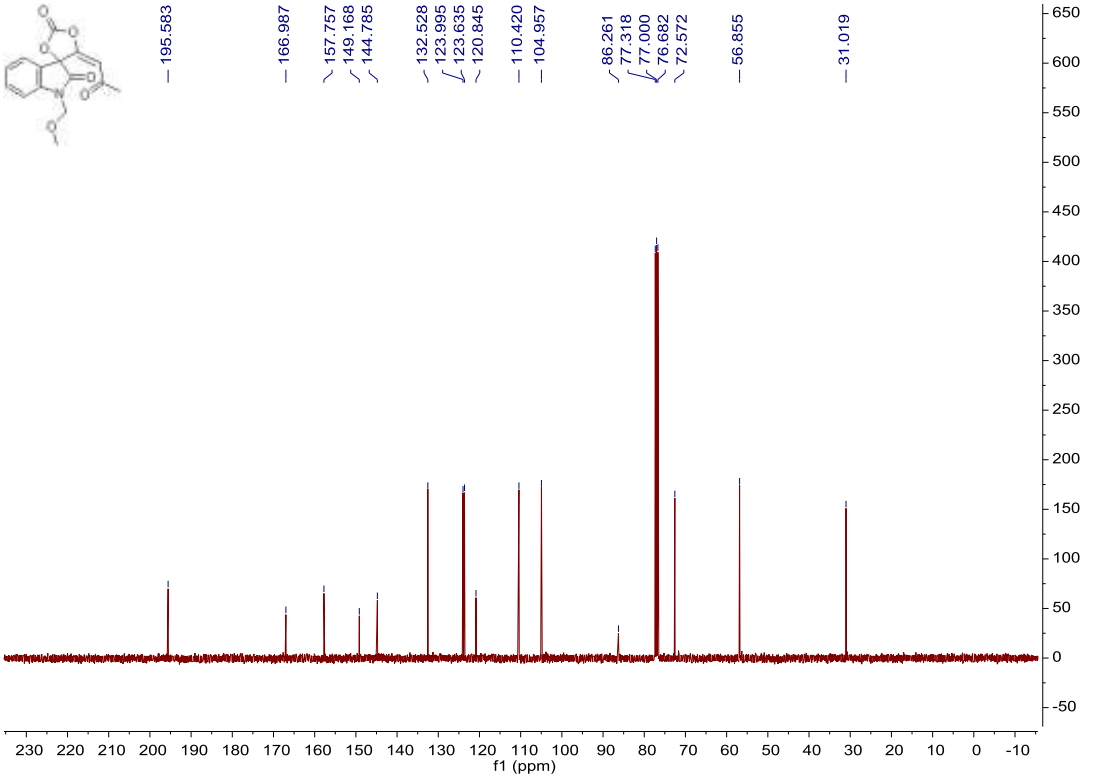
峰号	峰名	保留时间	峰高	峰面积	含量
1		28.637	43624.273	2098988.000	9.1491
2		32.635	340081.344	20843054.000	90.8509
总计			383705.617	22942042.000	100.0000



(*E*)-1-(methoxymethyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2c)

A white solid, 81% yield (74 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.12 (s, 3H, CH_3), 3.46 (s, 3H, CH_3), 5.22 (s, 2H, CH_2), 6.39 (s, 1H, =CH), 7.09-7.20 (m, 3H, ArH), 7.45 (dt, *J* = 1.2, 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.0, 56.9, 72.6, 86.3, 105.0, 110.4, 120.8, 123.6, 124.0, 132.5, 144.8, 149.2, 157.8, 167.0, 195.6. IR (EtOH) ν 3118, 2938, 2818, 1737, 1602, 1363, 1323, 1094, 1076, 936 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{15}H_{17}O_6N_2^{+1}(M+NH_4)^+$ requires 321.1081, Found: 321.1081. $[\alpha]^{25}_D$ = -27.50 (c 0.04, CH_2Cl_2) for 87% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 30.688 min, t_{major} = 27.038 min.


7.473
7.469
7.453
7.450
7.434
7.431
7.198
7.176
7.154
7.134
7.115
7.094
6.390
5.216
3.460
2.116
0.000
1.00
2.96
0.95
2.05
3.03
3.00
f1 (ppm)


195.583
166.987
157.757
149.168
144.785
132.528
123.995
123.635
120.845
110.420
104.957
86.261
77.318
77.000
76.682
72.572
56.855
31.019
f1 (ppm)

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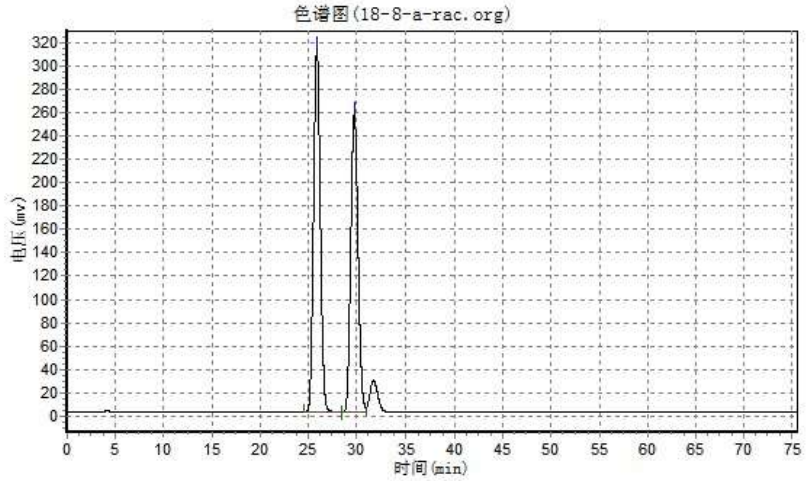
积分方法:面积归一法



分析结果表

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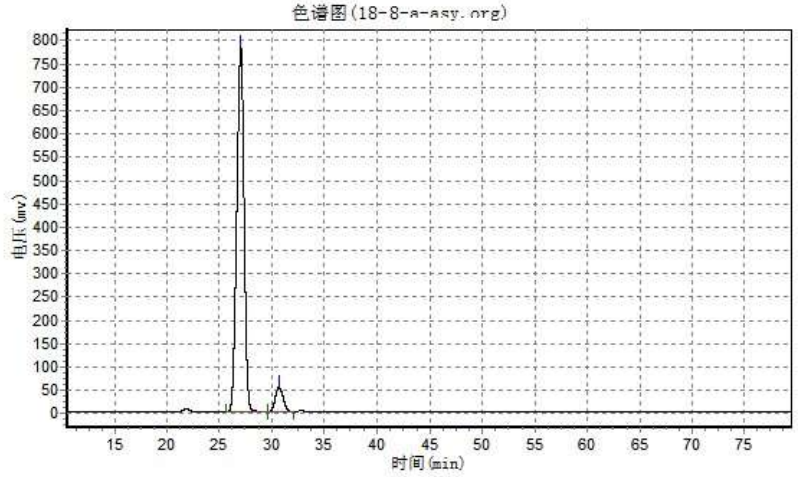
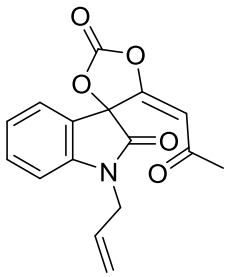
积分方法:面积归一法



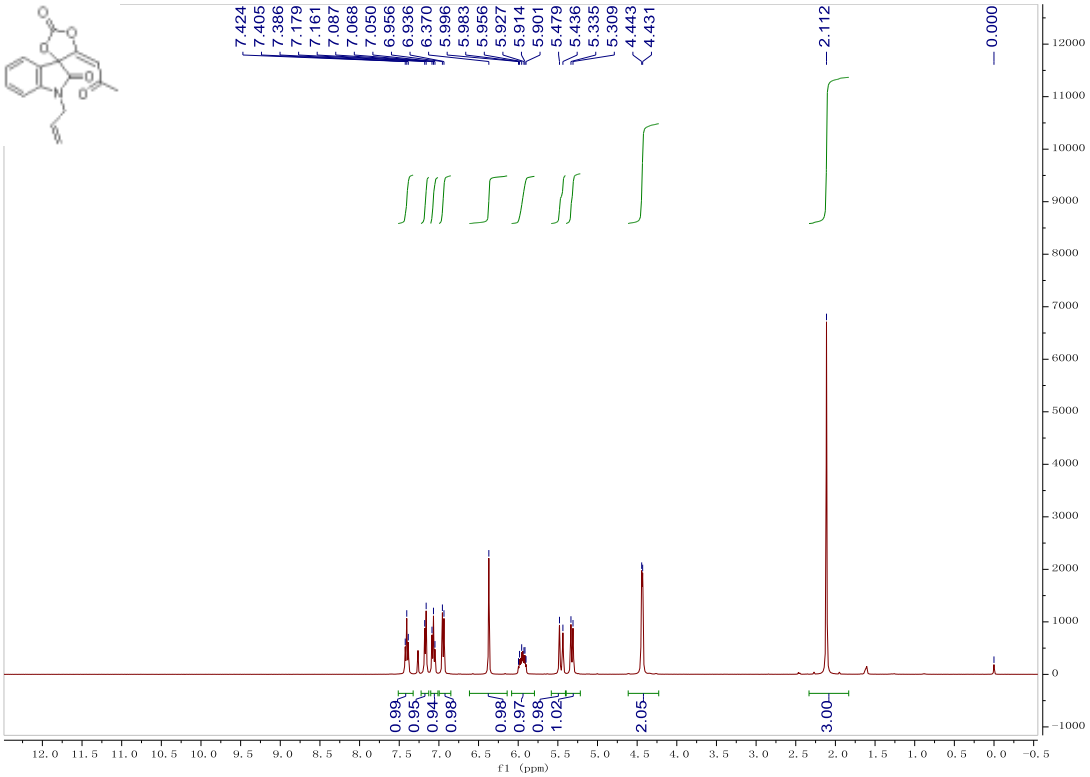
分析结果表

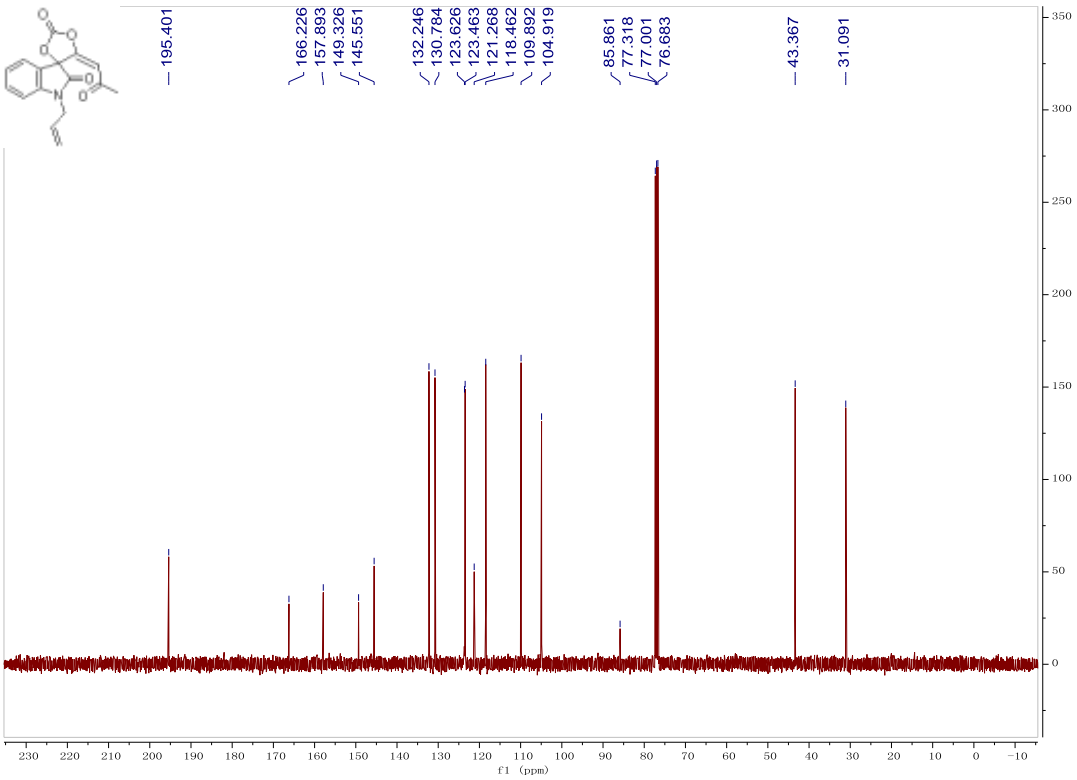
峰号	峰名	保留时间	峰高	峰面积	含量
1		27.038	782688.250	37789640.000	93.3193
2		30.688	51378.430	2705337.250	6.6807
总计			834066.680	40494977.250	100.0000

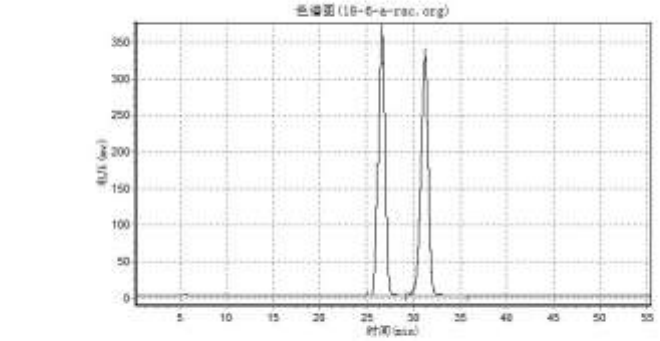


(*E*)-1-allyl-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2d)

A white solid, 85% yield (76 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.11 (s, 3H, CH_3), 4.44 (d, *J* = 4.8 Hz, 2H, CH_2), 5.32 (d, *J* = 10.4 Hz, 1H, =CH_2), 5.46 (d, *J* = 17.2 Hz, 1H, =CH_2), 5.90-6.00 (m, 1H, =CH), 6.37 (s, 1H, =CH), 6.95 (d, *J* = 8.0 Hz, 1H, ArH), 7.07 (t, *J* = 7.6 Hz, 1H, ArH), 7.37 (d, *J* = 7.2 Hz, 1H, ArH), 7.41 (t, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 43.4, 85.9 104.9, 109.9, 118.5, 121.3, 123.5, 123.6, 130.8, 132.2, 145.6, 149.3, 157.9, 166.2, 195.4. IR (EtOH) ν 3097, 3024, 2831, 1850, 1728, 1603, 1430, 1330, 1200, 963, 741 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{16}H_{17}O_5N_2^{+1}$(M+NH_4)$^+$ requires 317.1132, Found: 317.1133. $[\alpha]^{25}_D$ = +149.17 (c 0.04, CH_2Cl_2) for 79% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 29.802 min, t_{major} = 26.885 min.

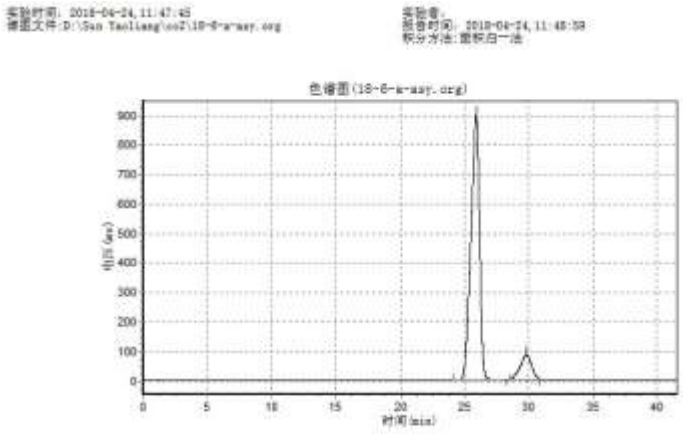






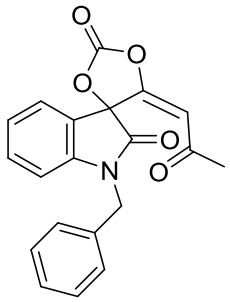
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		26.590	358362.531	17383018.000	49.0238
2		31.223	327154.063	18073870.000	50.9762
总计			685516.594	35456888.000	100.0000



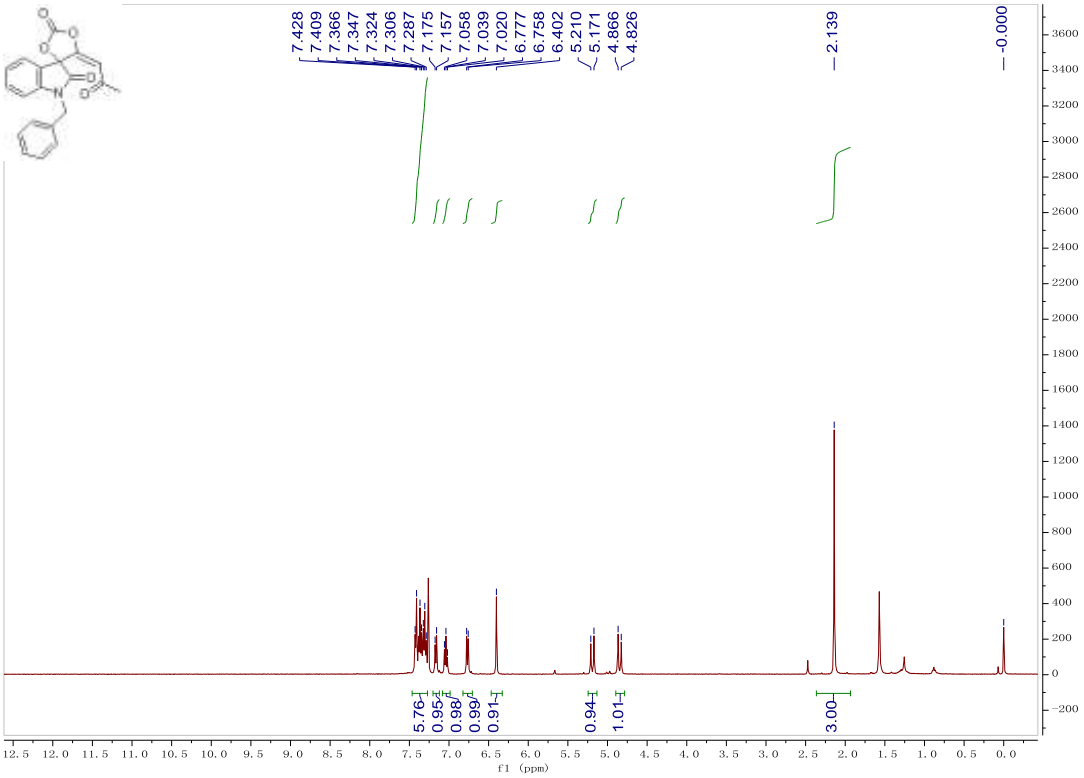
分析结果表

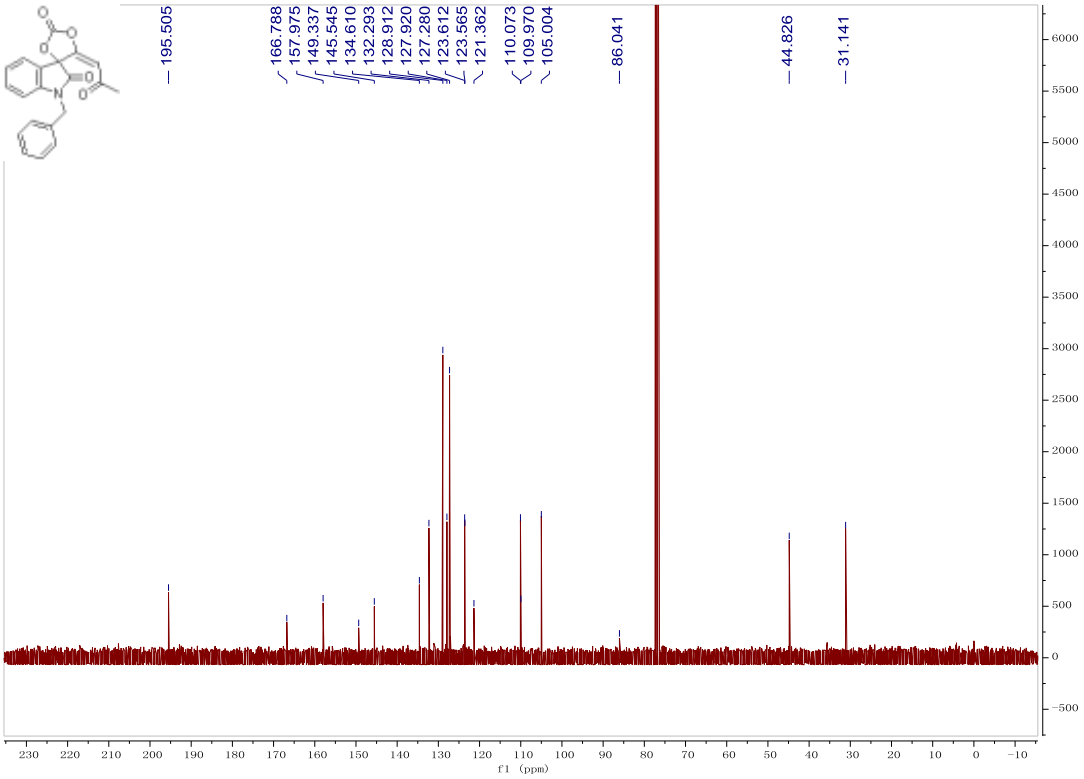
峰号	峰名	保留时间	峰高	峰面积	含量
1		25.886	899472.863	42021936.000	89.3566
2		29.902	81741.734	5005308.500	10.6434
总计			981214.297	47027244.500	100.0000



(*E*)-1-benzyl-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2e)

A white solid, 79% yield (83 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.14 (s, 3H, CH_3), 4.85 (d, *J* = 16.0 Hz, 1H, CH_2), 5.19 (d, *J* = 16.0 Hz, 1H, CH_2), 6.40 (s, 1H, =CH), 6.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.04 (t, *J* = 7.6 Hz, 1H, ArH), 7.17 (d, *J* = 7.2 Hz, 1H, ArH), 7.28-7.43 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 44.8, 86.0, 105.0, 110.0, 110.1, 121.4, 123.6, 127.3, 127.9, 128.9, 132.3, 134.6, 145.5, 149.3, 158.0, 166.8, 195.5. IR (EtOH) ν 3060, 2924, 2853, 1732, 1704, 1605, 1489, 1361, 1323, 1255, 1164, 750 cm^{-1}. HRMS (EI) calcd. for $C_{20}H_{15}NO_5$ requires 349.0950, Found: 349.0946. $[\alpha]^{25}_{D}$ = +57.50 (c 0.04, CH_2Cl_2) for 81% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 43.161 min, t_{major} = 30.346 min.


7.428
7.409
7.366
7.347
7.324
7.306
7.287
7.175
7.157
7.058
7.039
7.020
6.777
6.758
6.402
5.210
5.171
4.866
4.826
2.139
-0.000
5.76
0.95
0.98
0.99
0.91
0.94
1.01
3.00
f1 (ppm)


195.505
166.788
157.975
149.337
145.545
134.610
132.293
128.912
127.920
127.280
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110.073
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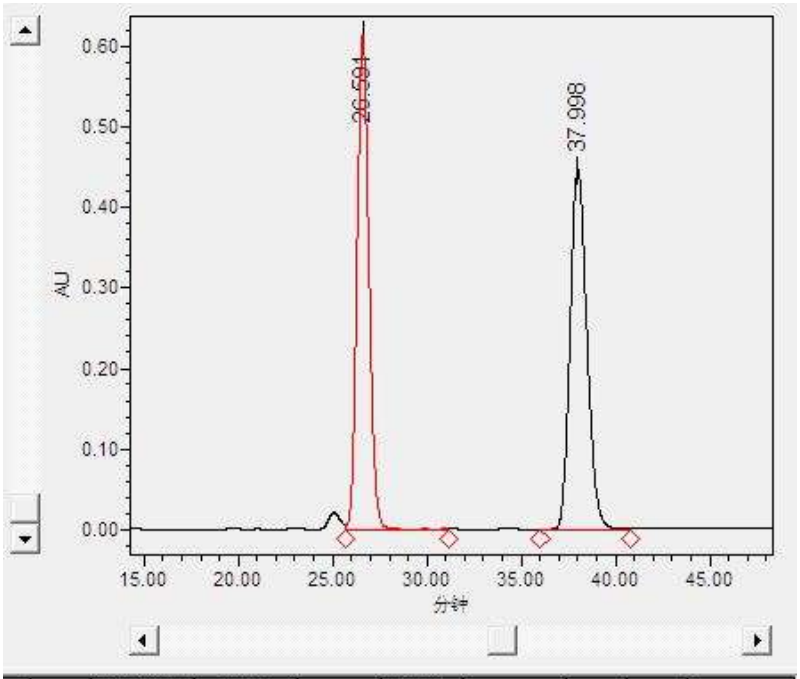
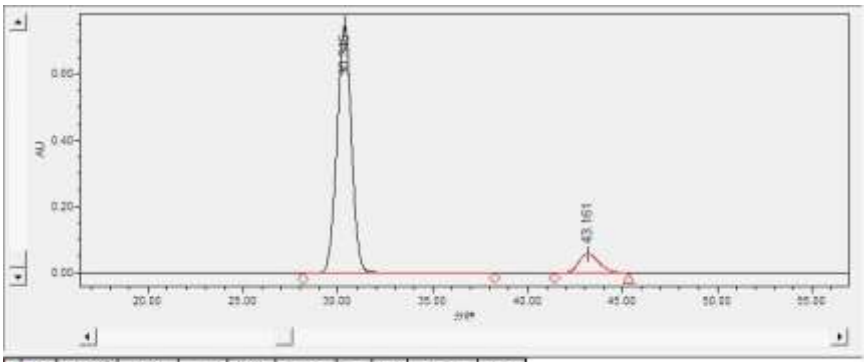
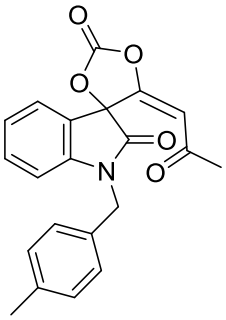
105.004
86.041
44.826
31.141
f1 (ppm)



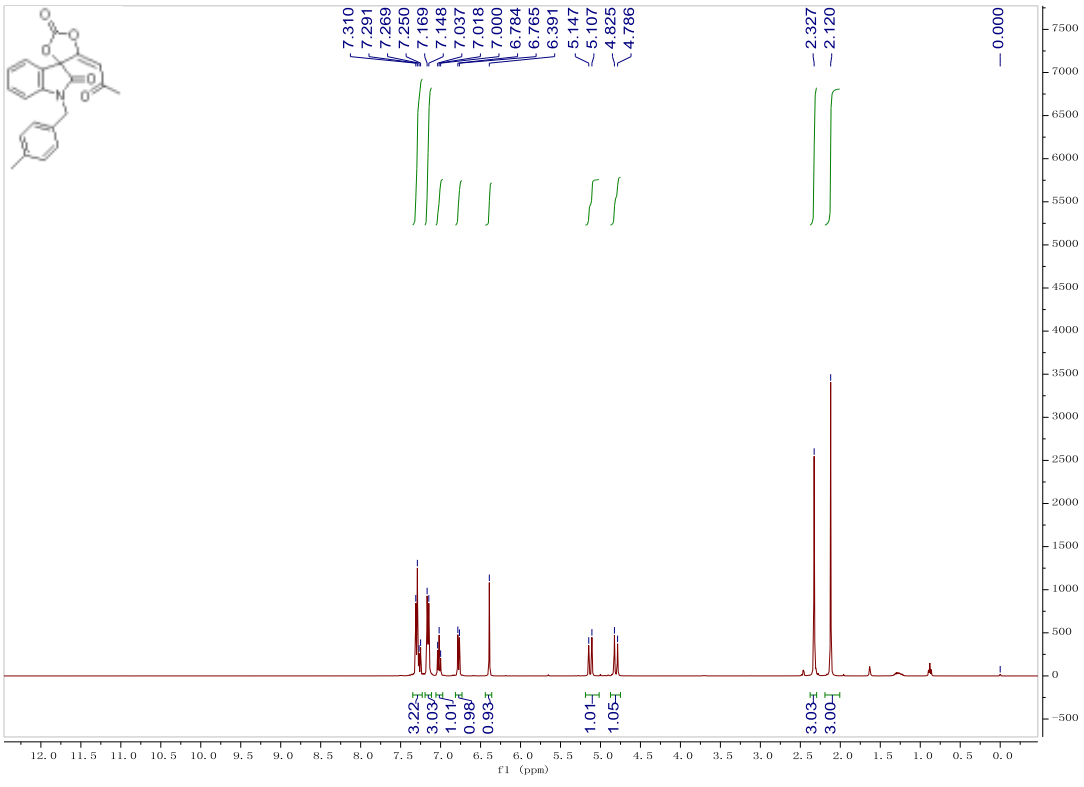
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型
1		26.591	26924124	49.15	613128	Vv			未知
2		37.998	27854077	50.85	446829	VV			未知

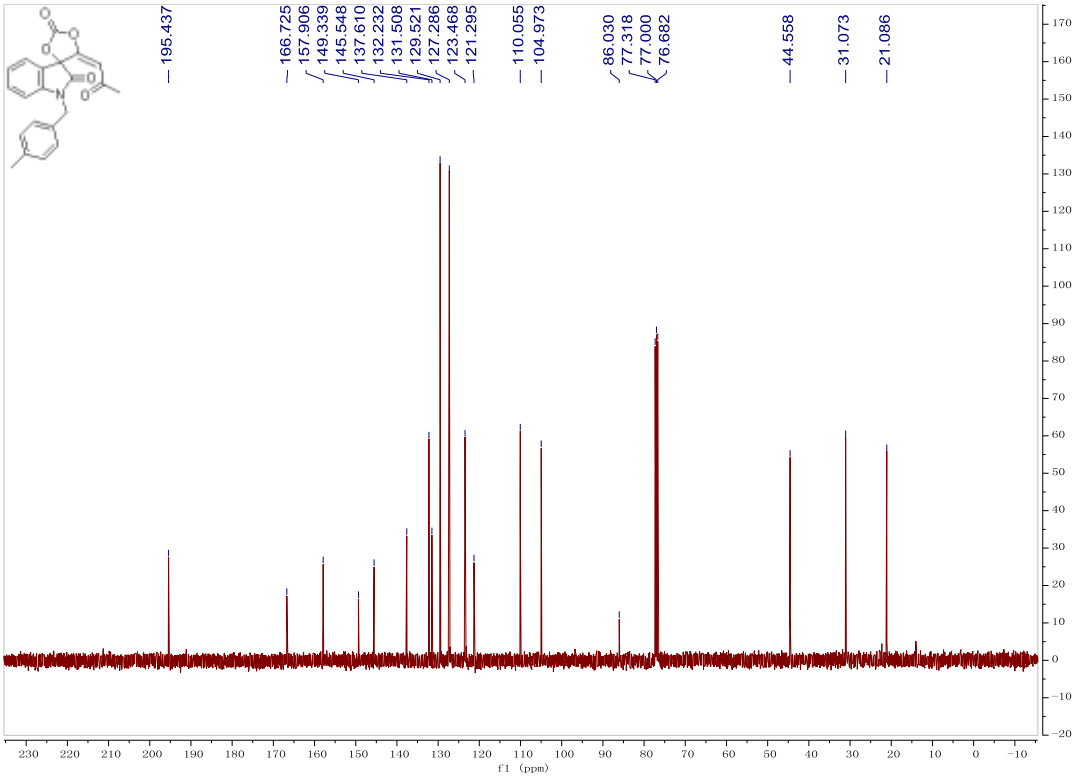


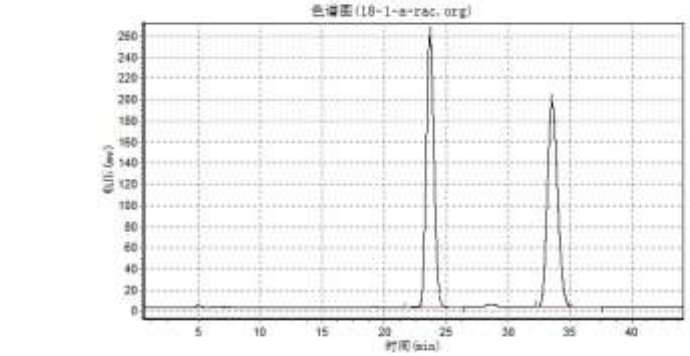


(*E*)-1-(4-methylbenzyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2f)

A white solid, 84% yield (91 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.12 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 4.81 (d, *J* = 15.6 Hz, 1H, CH_2), 5.13 (d, *J* = 15.6 Hz, 1H, CH_2), 6.39 (s, 1H, =CH), 6.77 (d, *J* = 7.6 Hz, 1H, ArH), 7.02 (t, *J* = 7.6 Hz, 1H, ArH), 7.14-7.17 (m, 3H, ArH), 7.25-7.31 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.1, 31.1, 44.6, 86.0, 105.0, 110.1, 121.3, 123.5, 127.3, 129.5, 131.5, 132.2, 137.6, 145.5, 149.3, 157.9, 166.7, 195.4. IR (EtOH) ν 3060, 2922, 2854, 1731, 1704, 1607, 1466, 1360, 1261, 1032, 990 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{21}H_{21}O_5N_2^{+1}(M+NH_4)^+$ requires 381.1445, Found: 381.1445. $[\alpha]^{25}_D$ = +59.17 (c 0.04, CH_2Cl_2) for 85% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 38.282 min, t_{major} = 26.820 min.

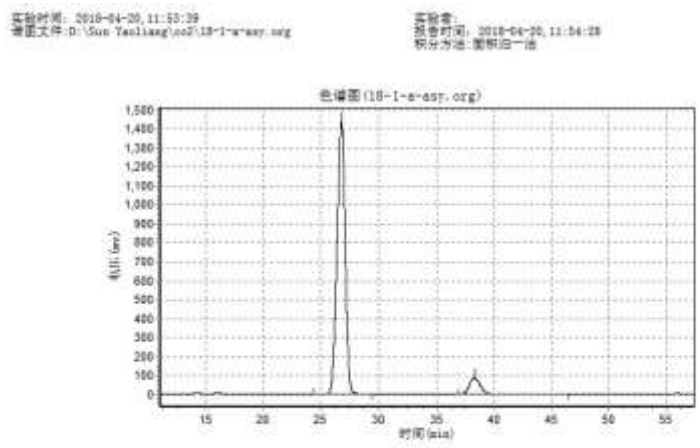






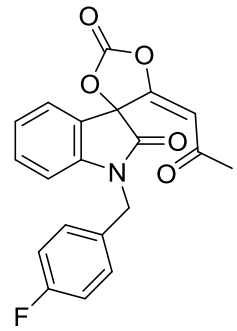
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		23.653	256415.628	11274702.000	50.1300
2		33.545	193028.578	11216246.000	49.8700
总计			449444.406	22490948.000	100.0000



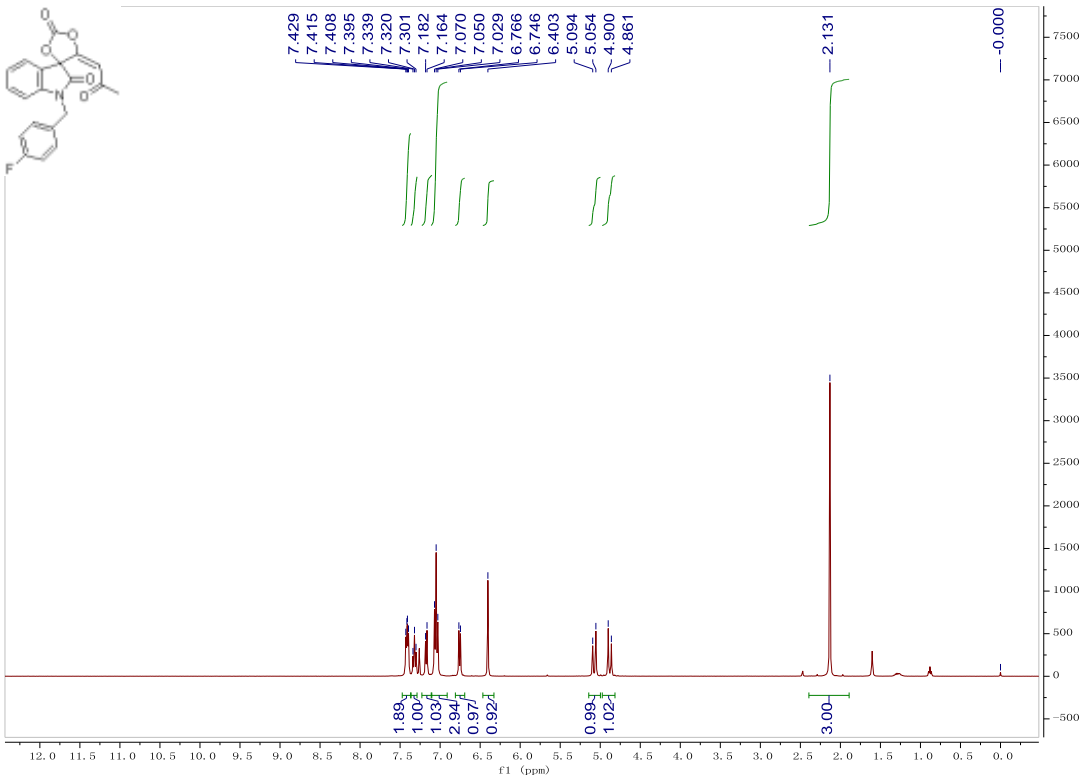
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		26.820	1436636.875	70669264.000	92.5523
2		38.282	84304.828	5686942.000	7.4477
总计			1520940.703	76348206.000	100.0000



(*E*)-1-(4-fluorobenzyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2g)

A white solid, 91% yield (100 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.13 (s, 3H, CH_3), 4.88 (d, *J* = 15.6 Hz, 1H, CH_2), 5.07 (d, *J* = 15.6 Hz, 1H, CH_2), 6.40 (s, 1H, =CH), 6.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.05 (t, *J* = 8.0 Hz, 3H, ArH), 7.17 (d, *J* = 7.2 Hz, 1H, ArH), 7.32 (t, *J* = 7.6 Hz, 1H, ArH), 7.39-7.43 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 44.2, 86.0, 105.0, 109.9, 115.8 (d, *J* = 21.4 Hz), 121.3, 123.68, 123.70, 129.1 (d, *J* = 8.1 Hz), 130.3 (d, *J* = 3.2 Hz), 132.3, 145.3, 149.3, 157.8, 162.4 (d, *J* = 244.9 Hz), 166.8, 195.6. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -114.28-(-114.20). IR (EtOH) ν 2979, 2917, 2844, 1731, 1706, 1510, 1488, 1370, 1223, 1006, 750 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{20}H_{18}O_5N_2F^{+1}(M+NH_4)^+$ requires 385.1194, Found: 385.1194. $[\alpha]^{25}_D$ = +34.00 (c 0.05, CH_2Cl_2) for 80% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 44.315 min, t_{major} = 34.033 min.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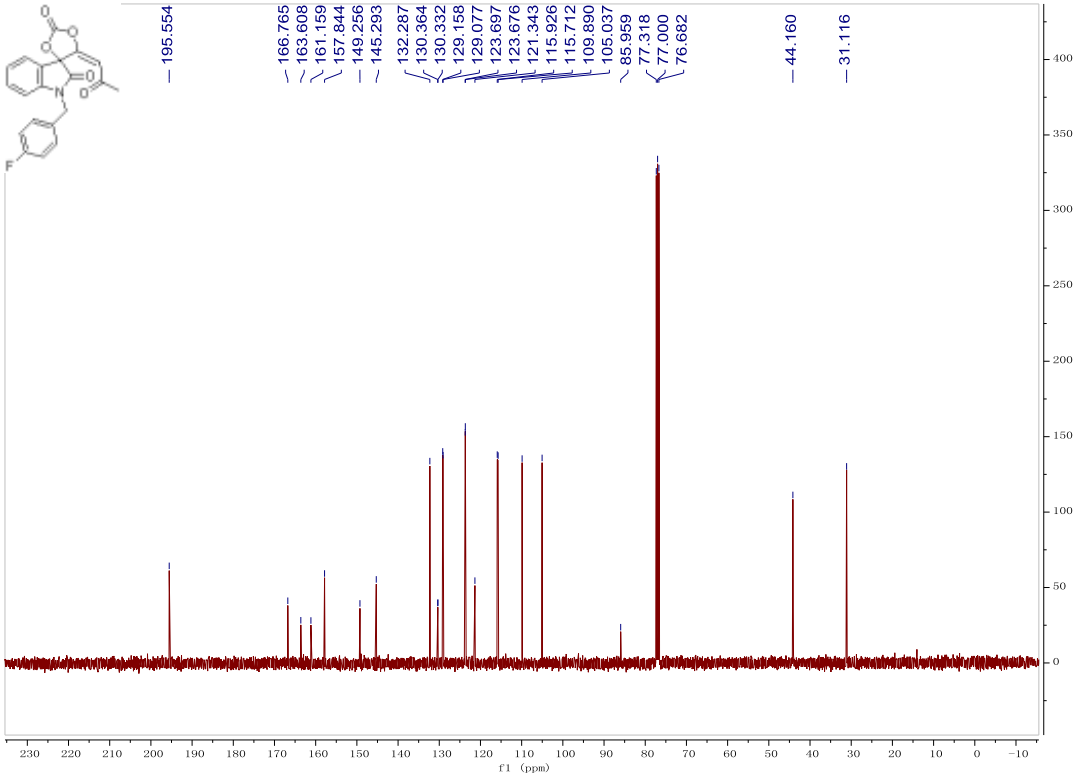
7.339
7.320
7.301
7.182
7.164
7.070
7.050
7.029
6.766
6.746
6.403
5.094
5.054
4.900
4.861
2.131
-0.000
1.89
1.00
1.03
2.94
0.97
0.92
0.99
1.02
3.00
f1 (ppm)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161.159
157.844
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145.293
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129.158
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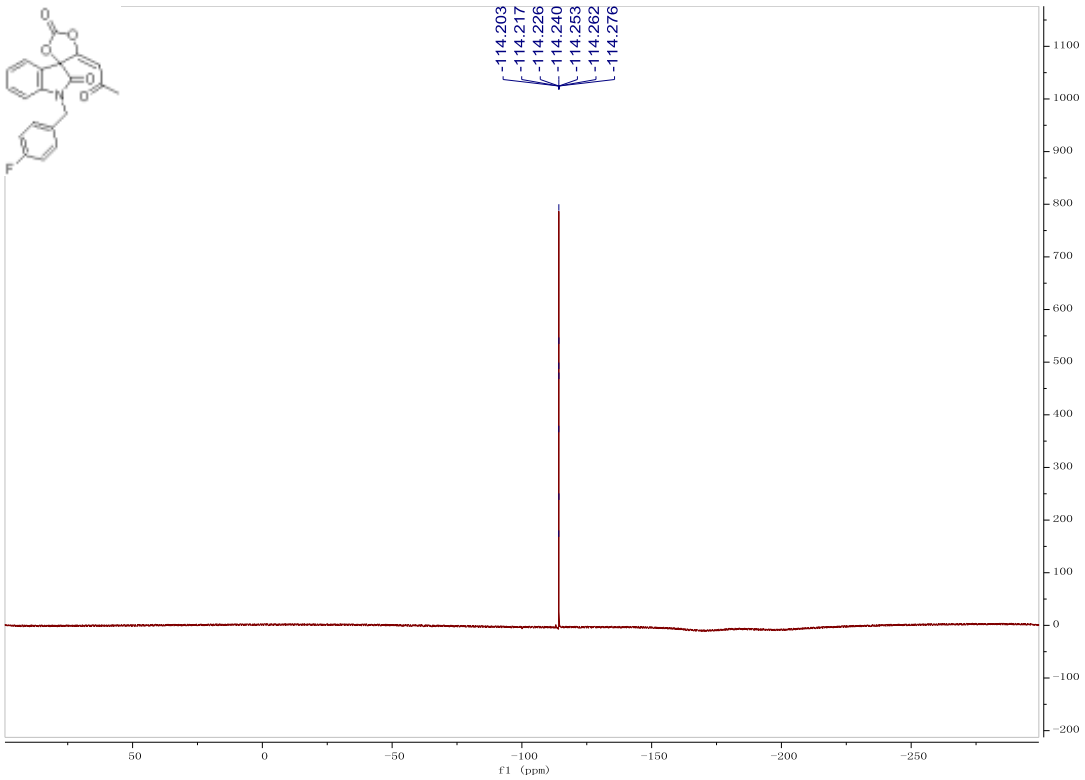
77.000
76.682
44.160
31.116
f1 (ppm)



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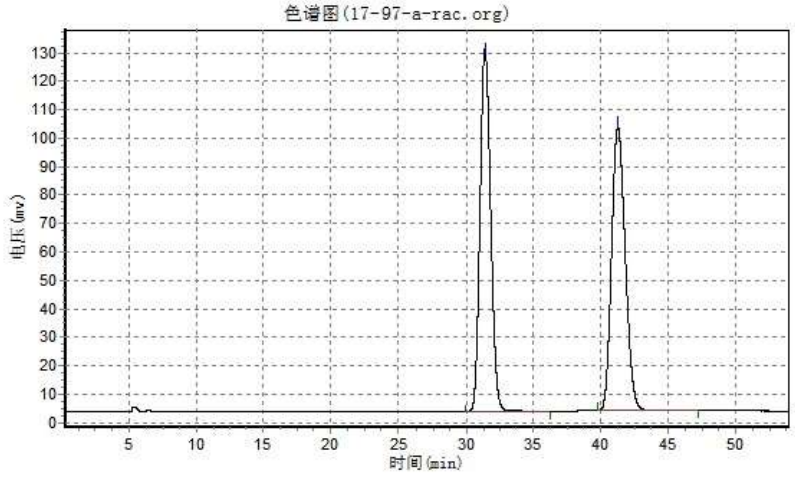
实验者:
报告时间：2019-07-19,20:20:50
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		31.457	126717.602	7011456.000	49.7774
2		41.323	99600.438	7074177.500	50.2226
总计			226318.039	14085633.500	100.0000

实验时间: 2019-07-19,14:43:51
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实验者:
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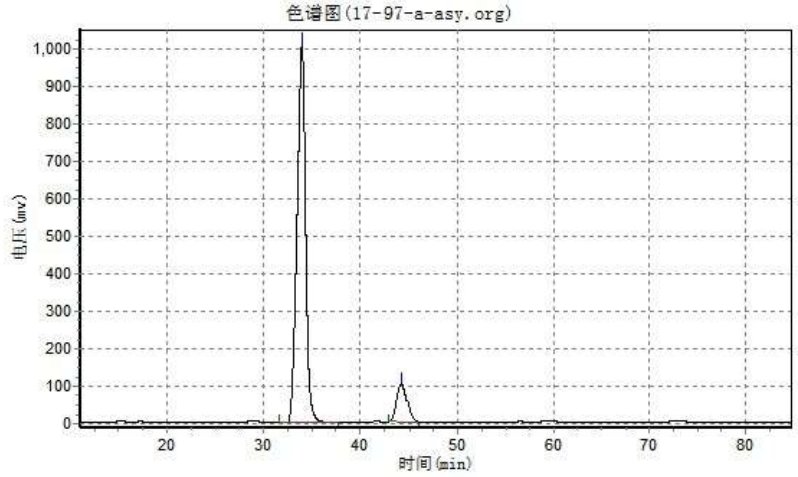
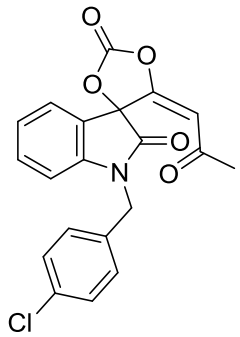
积分方法:面积归一法



分析结果表

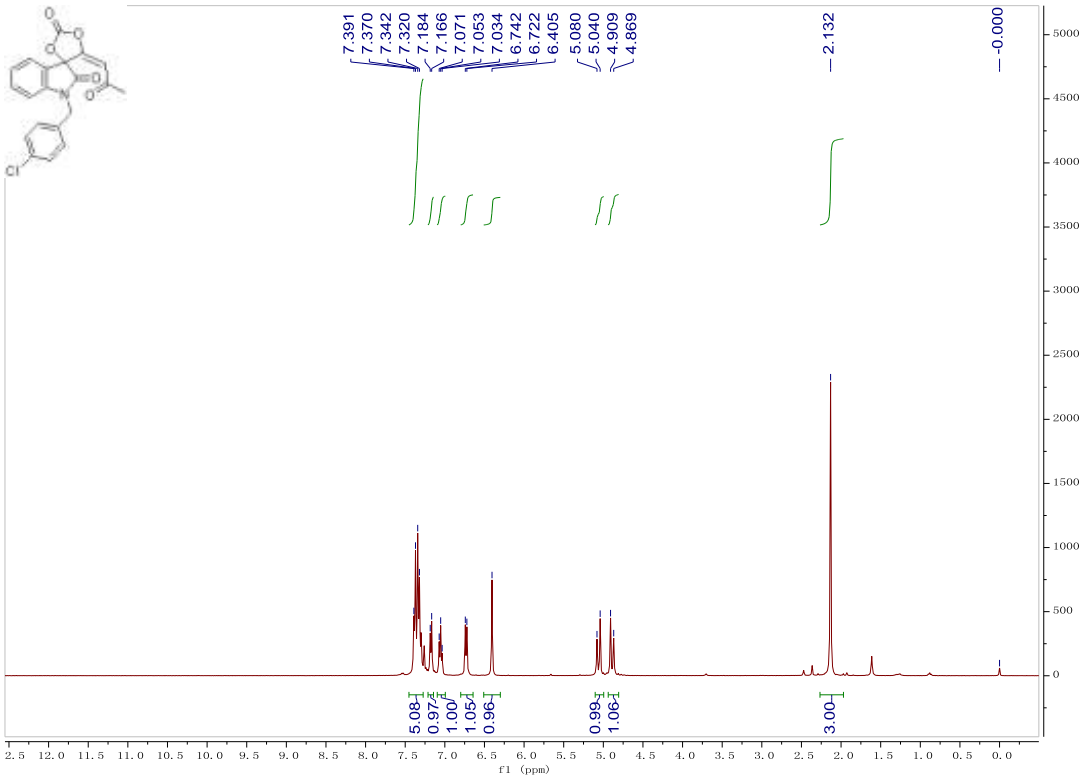
峰号	峰名	保留时间	峰高	峰面积	含量
1		34.033	1007321.813	62061524.000	89.4077
2		44.315	102006.945	7352558.000	10.5923
总计			1109328.758	69414082.000	100.0000

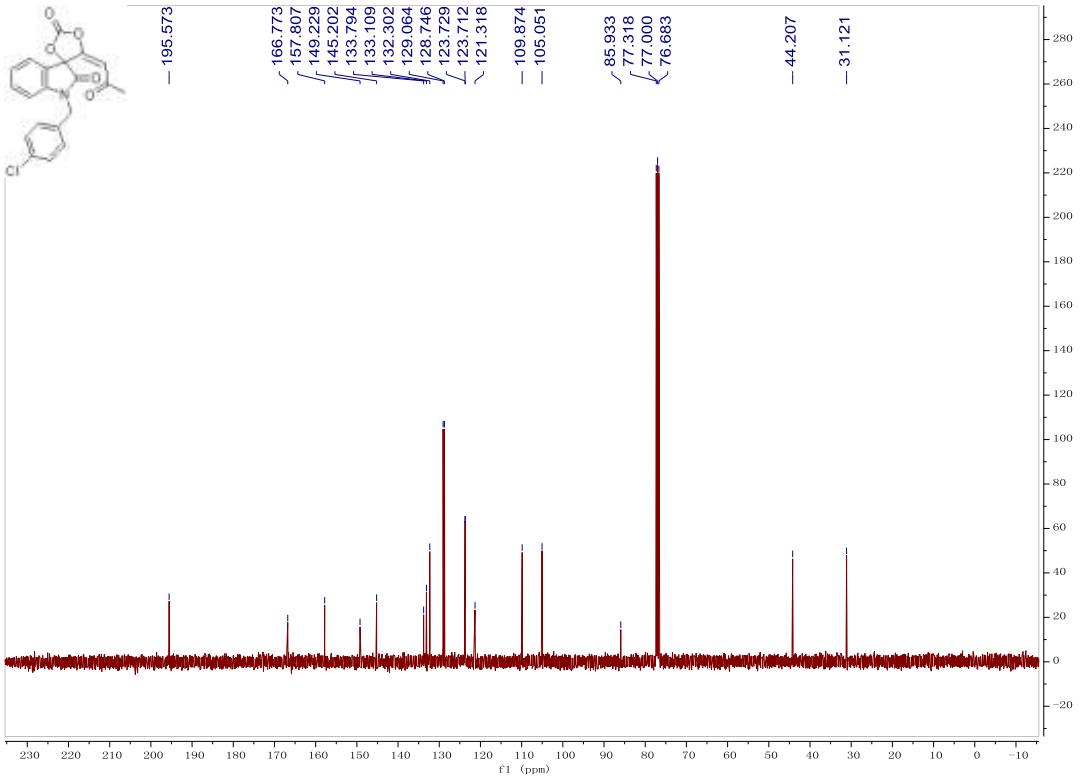


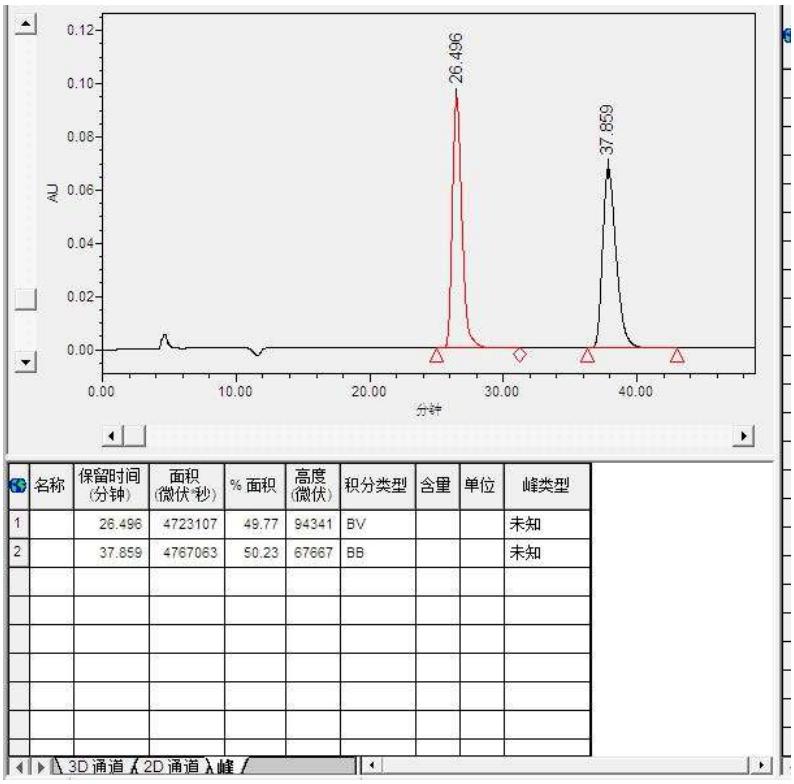
(*E*)-1-(4-chlorobenzyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2h)

A white solid, 87% yield (100 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.13 (s, 3H, CH_3), 4.89 (d, *J* = 16.0 Hz, 1H, CH_2), 5.06 (d, *J* = 16.0 Hz, 1H, CH_2), 6.41 (s, 1H, =CH), 6.73 (d, *J* = 8.0 Hz, 1H, ArH), 7.05 (t, *J* = 7.2 Hz, 1H, ArH), 7.18 (d, *J* = 7.2 Hz, 1H, ArH), 7.32-7.40 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 44.2, 85.9, 105.1, 109.9, 121.3, 123.71, 123.72, 128.7, 129.1, 132.3, 133.1, 133.8, 145.2, 149.2, 157.8, 166.8, 195.6. IR (EtOH) ν 2977, 2909, 2844, 1732, 1703, 1607, 1489, 1360, 1262, 1092, 1044, 797, 751 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{20}H_{18}O_5N_2Cl^{+1}(M+NH_4)^+$ requires 401.0899, Found: 401.0897. $[\alpha]^{25}_D$ = +81.67 (c 0.04, CH_2Cl_2) for 84% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 38.423

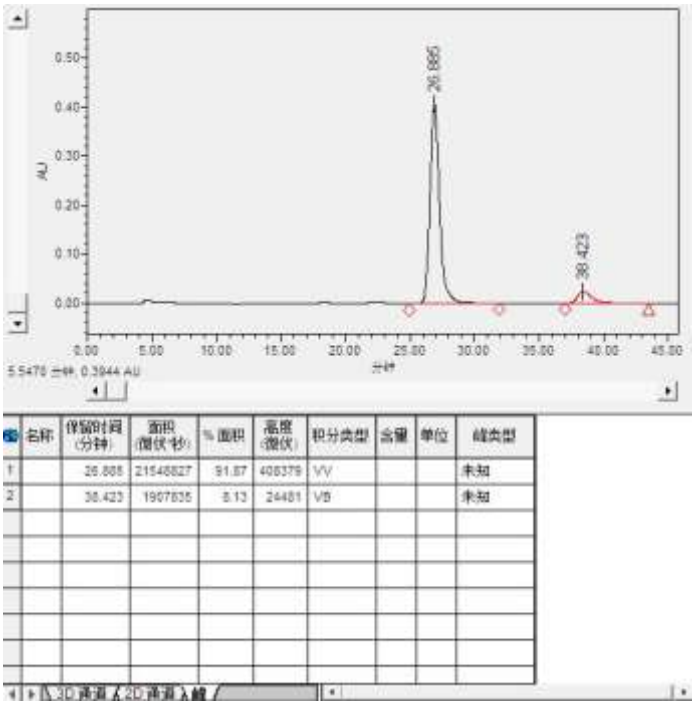
min, t_{major} = 26.885 min.



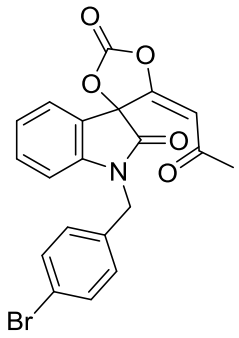




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型
1		26.496	4723107	49.77	94341	BV			未知
2		37.859	4767063	50.23	67667	BB			未知

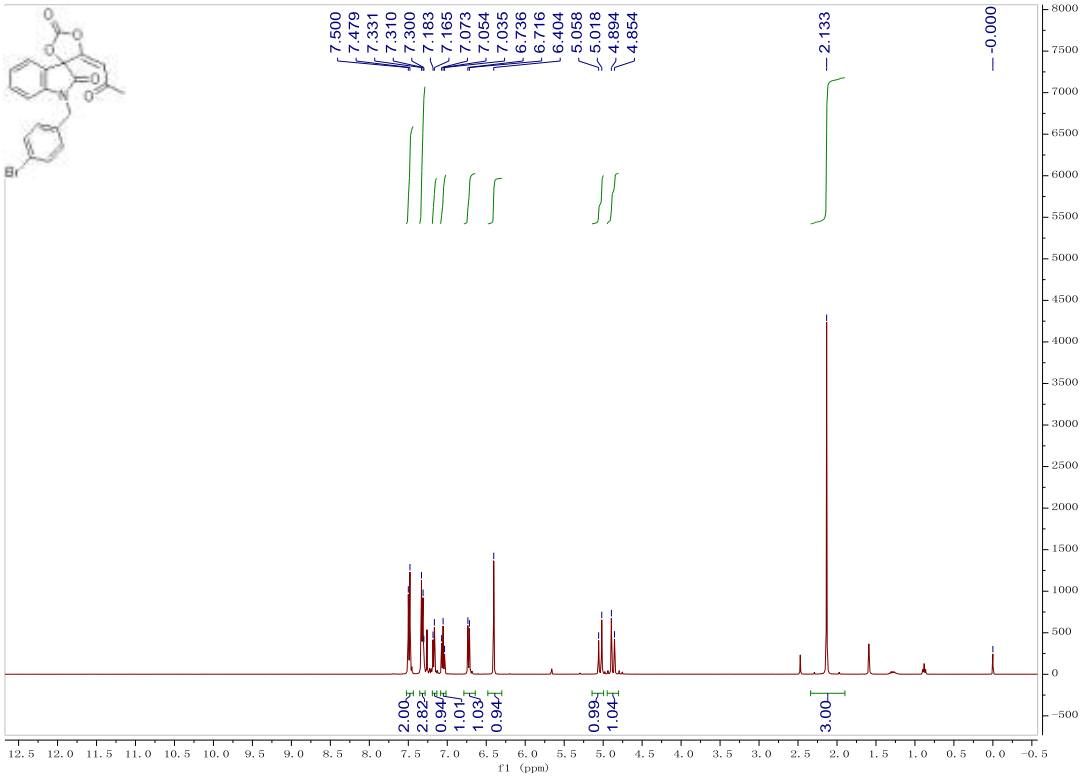


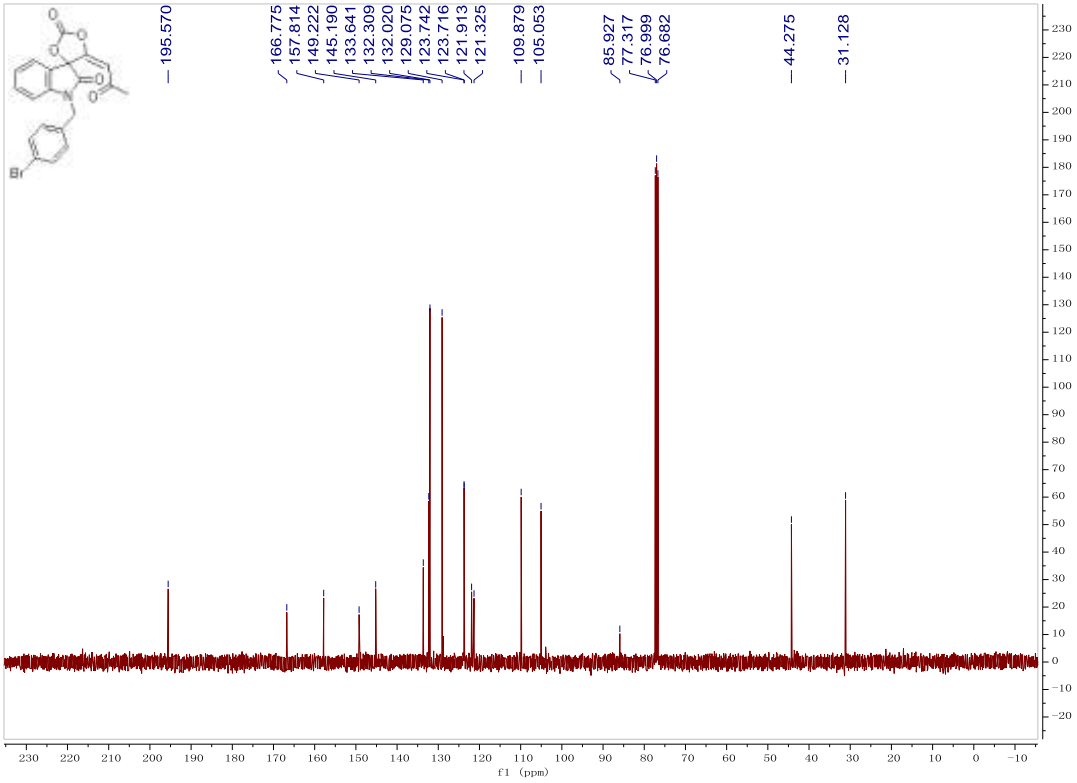
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型
1		26.885	21546827	91.87	406379	VV			未知
2		38.423	1907835	8.13	24481	VB			未知

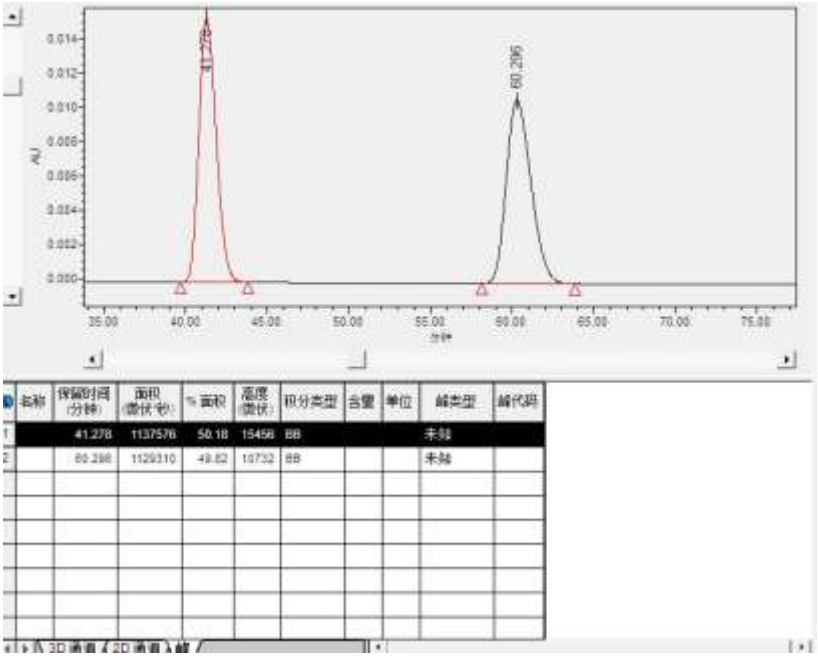


(*E*)-1-(4-bromobenzyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2i)

A white solid, 81% yield (104 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.13 (s, 3H, CH_3), 4.87 (d, *J* = 16.0 Hz, 1H, CH_2), 5.04 (d, *J* = 16.0 Hz, 1H, CH_2), 6.40 (s, 1H, =CH), 6.73 (d, *J* = 8.0 Hz, 1H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 7.17 (d, *J* = 7.2 Hz, 1H, ArH), 7.30-7.34 (m, 3H, ArH), 7.49 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 44.3, 85.9, 105.1, 109.9, 121.3, 121.9, 123.71, 123.74, 129.1, 132.0, 132.3, 133.6, 145.2, 149.2, 157.8, 166.8, 195.6. IR (EtOH) ν 2985, 2925, 2852, 1733, 1704, 1607, 1488, 1467, 1261, 1166, 1011 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{19}H_{15}O_3NBr^{+1}(M+H-CO_2)^+$ requires 384.0229, Found: 384.0230. $[\alpha]^{25}_D$ = +34.17 (c 0.04, CH_2Cl_2) for 85% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 63.191 min, t_{major} = 41.278 min.







名称	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
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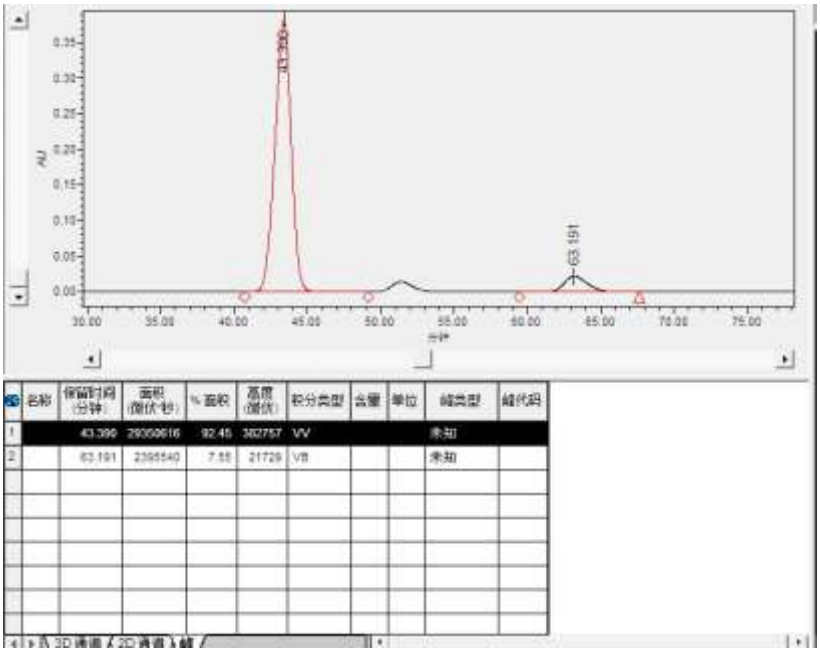
	60.286	1129310	49.82	10732	BB			未知	



	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
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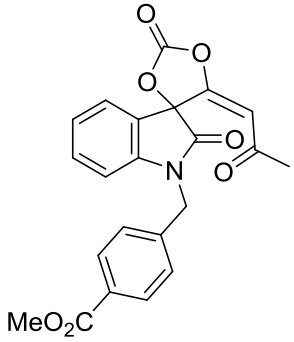
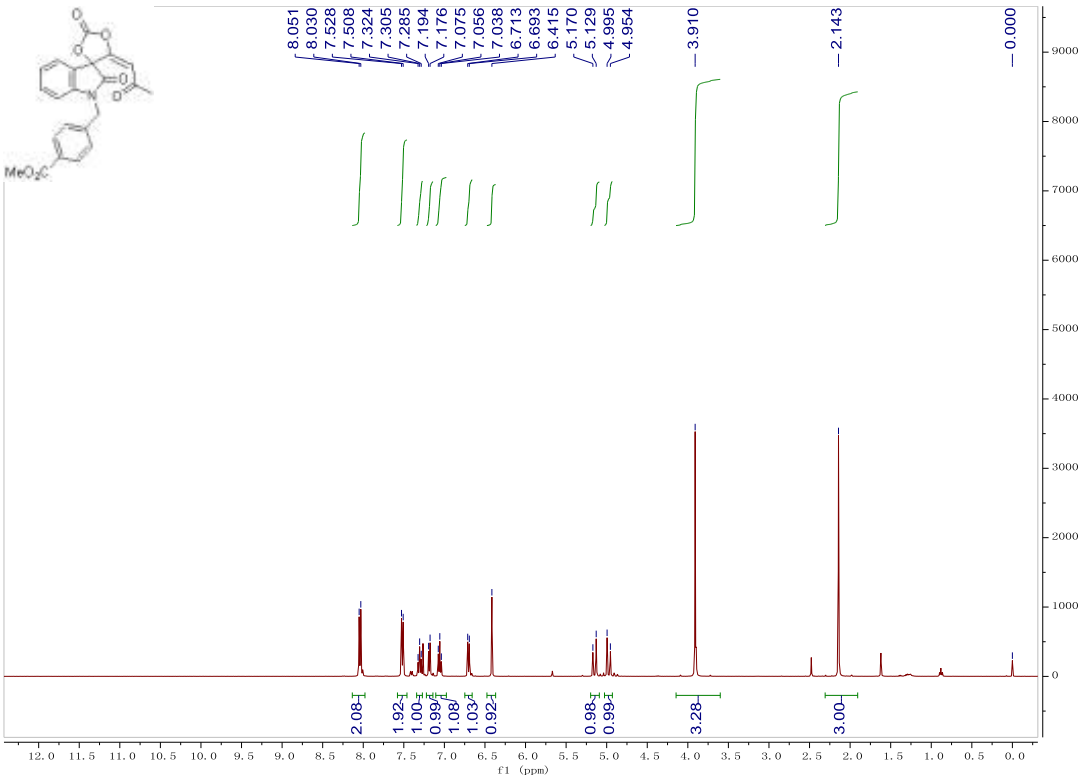


methyl

(*E*)-4-((2,2'-dioxo-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolan]-1-yl)methyl)benzoat e (2j)

A white solid, 57% yield (70 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.14 (s, 3H, CH_3), 3.91 (s, 3H, CH_3), 4.97 (d, *J* = 16.4 Hz, 1H, CH_2), 5.15 (d, *J* = 16.4 Hz, 1H, CH_2), 6.42 (s, 1H, =CH), 6.70 (d, *J* = 8.0 Hz, 1H, ArH), 7.06 (t, *J* = 7.6 Hz, 1H, ArH), 7.19 (d, *J* = 7.2 Hz, 1H, ArH), 7.31 (t, *J* = 7.6 Hz, 1H, ArH), 7.52 (d, *J* = 8.0 Hz, 2H, ArH), 8.04 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 44.6, 52.2, 85.9, 105.1, 109.9, 121.3, 123.7, 123.8, 127.2, 129.8, 130.2, 132.3, 139.7, 145.2, 149.2, 157.8, 166.6, 166.8, 195.6. IR (EtOH) ν 3115, 2959, 2925, 2846, 1722, 1704, 1607, 1488, 1434, 1360, 1165, 1019 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{21}H_{18}O_5N^{+1}(M+H-CO_2)^+$ requires 364.1179, Found: 364.1179.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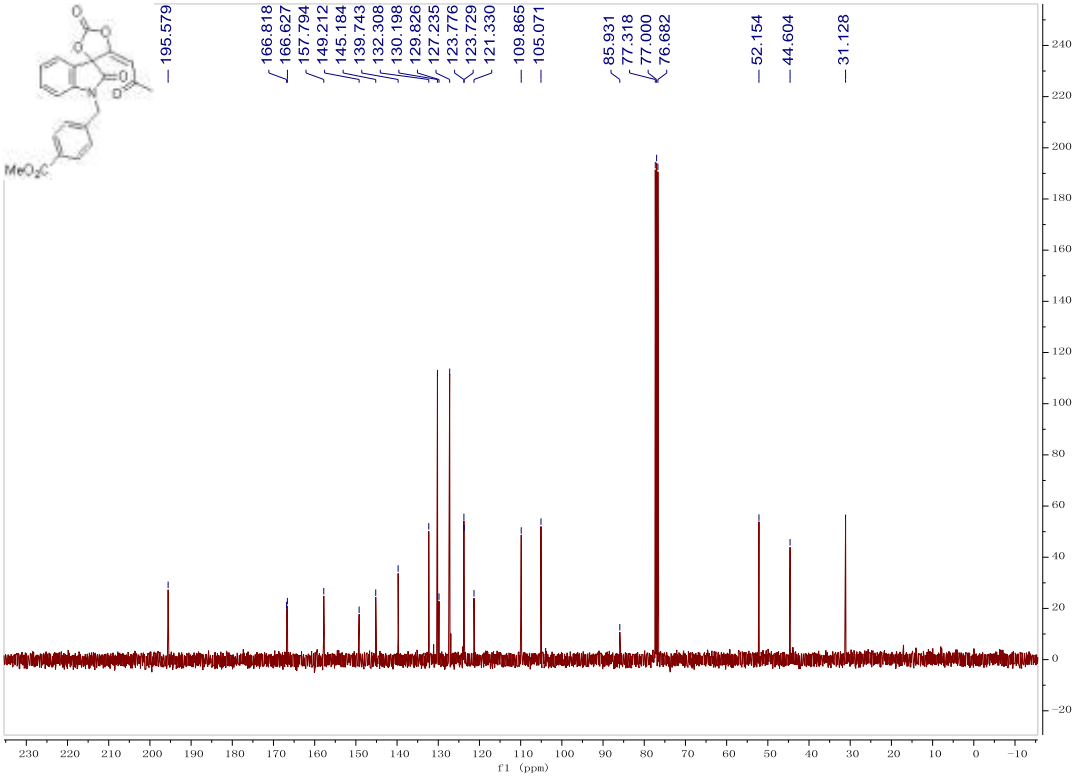
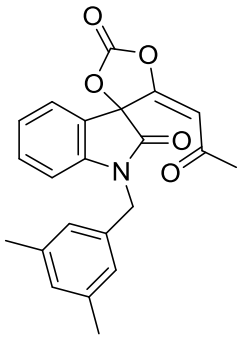
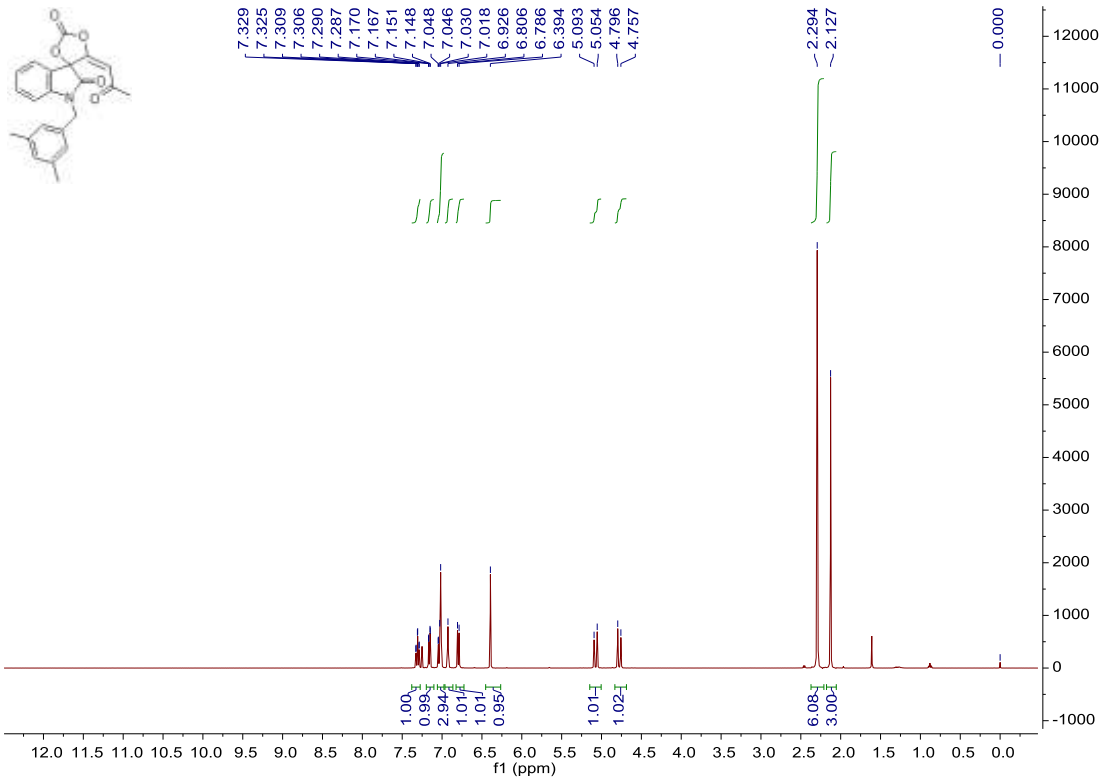
8.030
7.528
7.508
7.324
7.305
7.285
7.194
7.176
7.075
7.056
7.038
6.713
6.693
6.415
5.170
5.129
4.995
4.954
3.910
2.143
0.000
2.08
1.92
1.00
0.99
1.08
1.03
0.92
0.98
0.99
3.28
3.00
f1 (ppm)


195.579
166.818
166.627
157.794
149.212
145.184
139.743
132.308
130.198
129.826
127.235
123.776
123.729
121.330
109.865
105.071
85.931
77.318
77.000
76.682
52.154
44.604
31.128
f1 (ppm)



(*E*)-1-(3,5-dimethylbenzyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2k)

A white solid, 79% yield (89 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.13 (s, 3H, CH_3), 2.29 (s, 6H, CH_3), 4.78 (d, *J* = 15.6 Hz, 1H, CH_2), 5.07 (d, *J* = 15.6 Hz, 1H, CH_2), 6.39 (s, 1H, =CH), 6.80 (d, *J* = 8.0 Hz, 1H, ArH), 6.93 (s, 1H, ArH), 7.01-7.05 (m, 3H, ArH), 7.16 (dd, *J* = 1.2, 7.6 Hz, 1H, ArH), 7.31 (dt, *J* = 1.2, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 21.2, 31.1, 44.8, 86.1, 105.0, 110.1, 121.3, 123.46, 123.53, 125.1, 129.5, 132.3, 134.4, 138.4, 145.7, 149.4, 158.0, 166.8, 195.3. IR (EtOH) ν 2987, 2925, 2854, 1759, 1732, 1705, 1487, 1467, 1369, 1261, 1165, 1032, 752 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{22}H_{20}O_5N^{+1}(M+H)^+$ requires 378.1336, Found: 378.1335. $[\alpha]^{25}_{D}$ = +65.83 (c 0.04, CH_2Cl_2) for 82% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 24.080 min, t_{major} = 17.583 min.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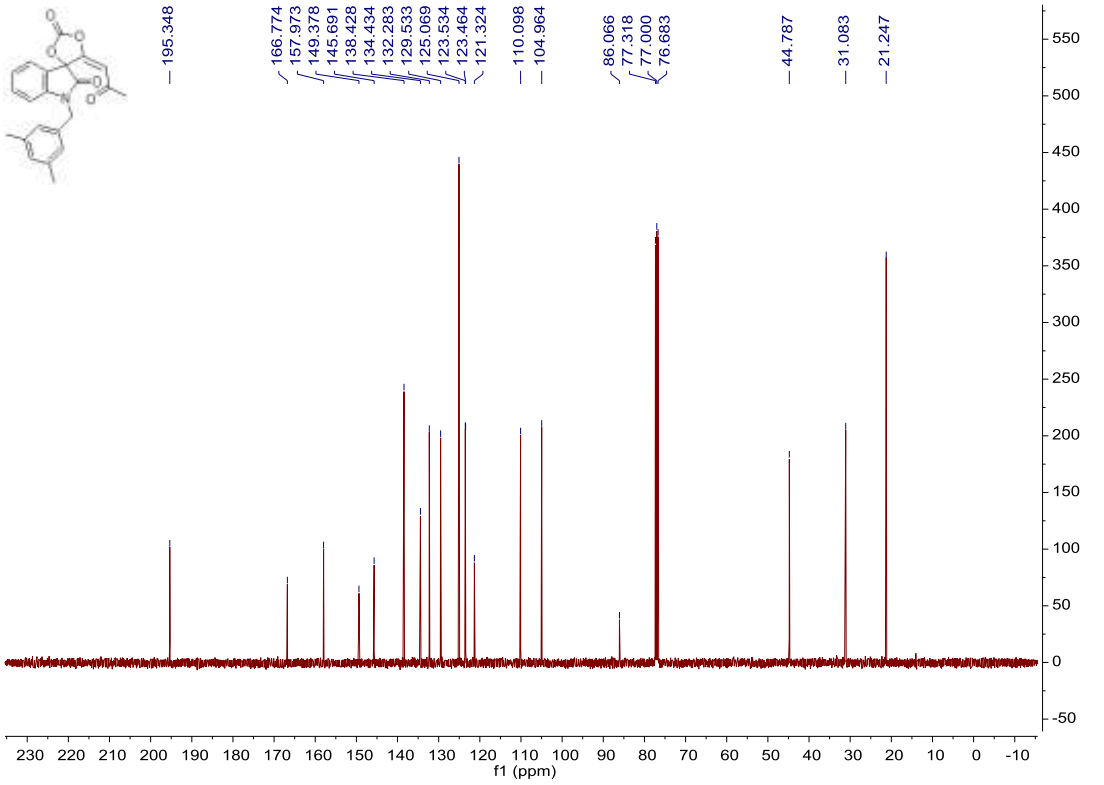
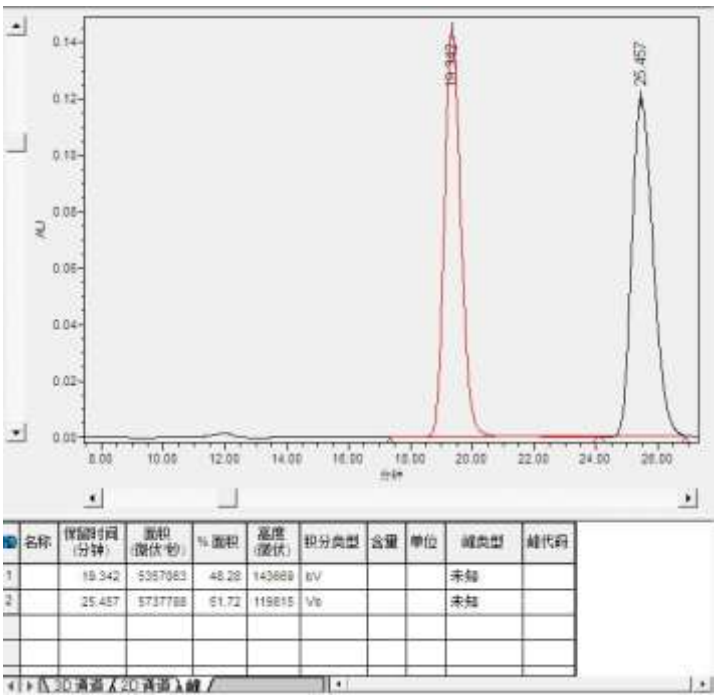
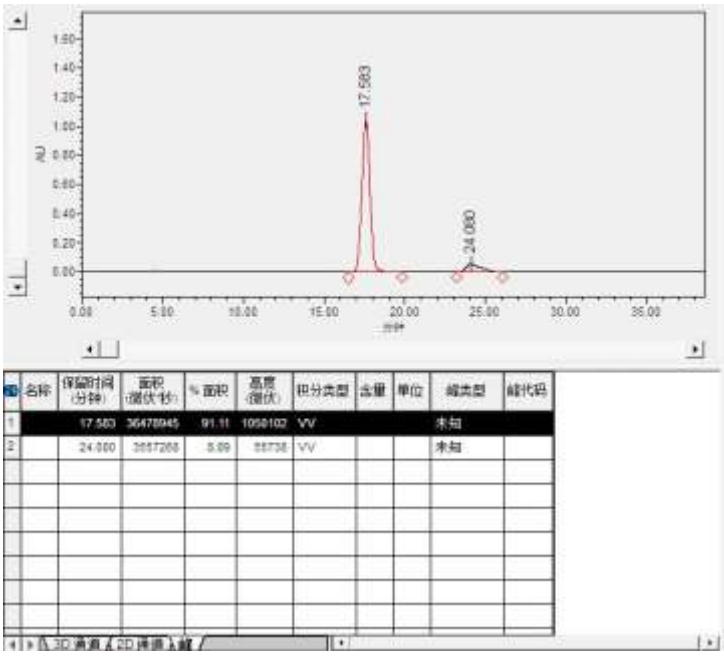
7.325
7.309
7.306
7.290
7.287
7.170
7.167
7.151
7.148
7.048
7.046
7.030
7.018
6.926
6.806
6.786
6.394
5.093
5.054
4.796
4.757
2.294
2.127
0.000
1.00
0.99
2.94
1.01
1.01
0.95
1.01
1.02
6.08
3.00
f1 (ppm)

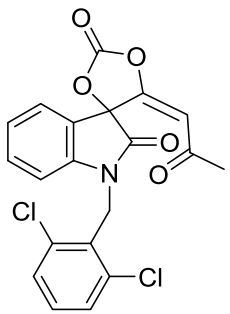

195.348
166.774
157.973
149.378
145.691
138.428
134.434
132.283
129.533
125.069
123.534
123.464
121.324
110.098
104.964
86.066
77.318
77.000
76.683
44.787
31.083
21.247
f1 (ppm)



	名称	保留时间（分钟）	面积（微伏*秒）	% 面积	高度（微伏）	积分类型	含量	单位	峰类型	峰代码
1		19.342	5387083	48.28	143669	bV			未知	
2		25.457	5737788	51.72	119815	Vb			未知	

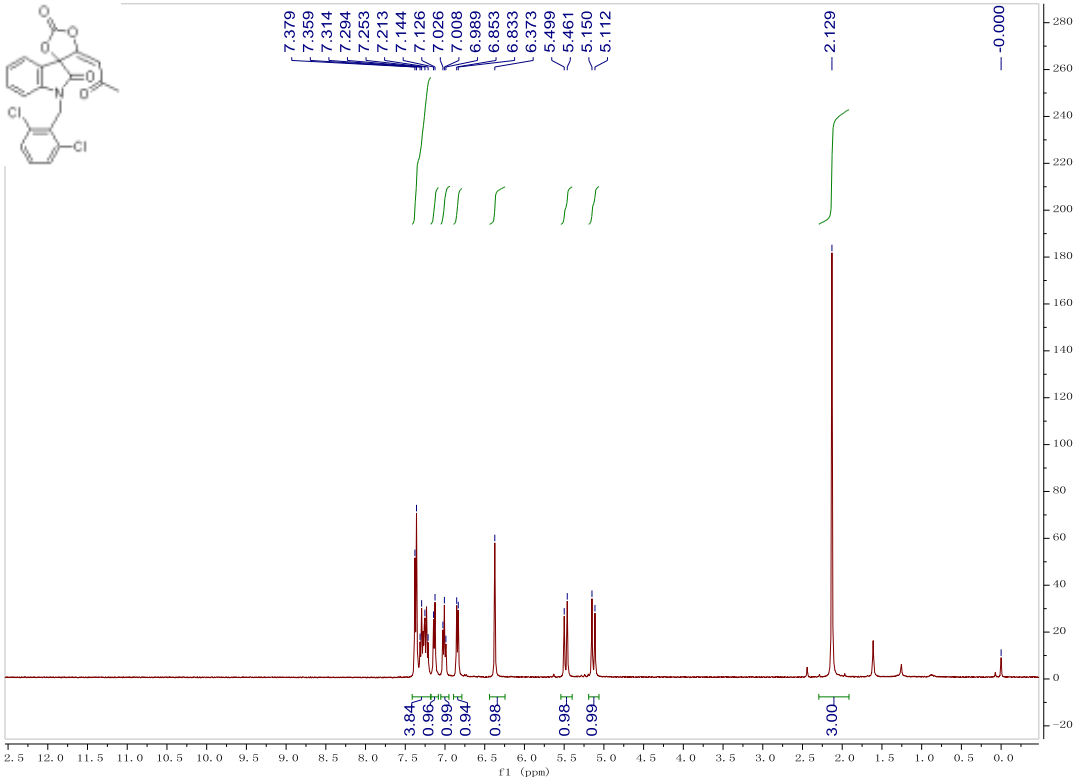


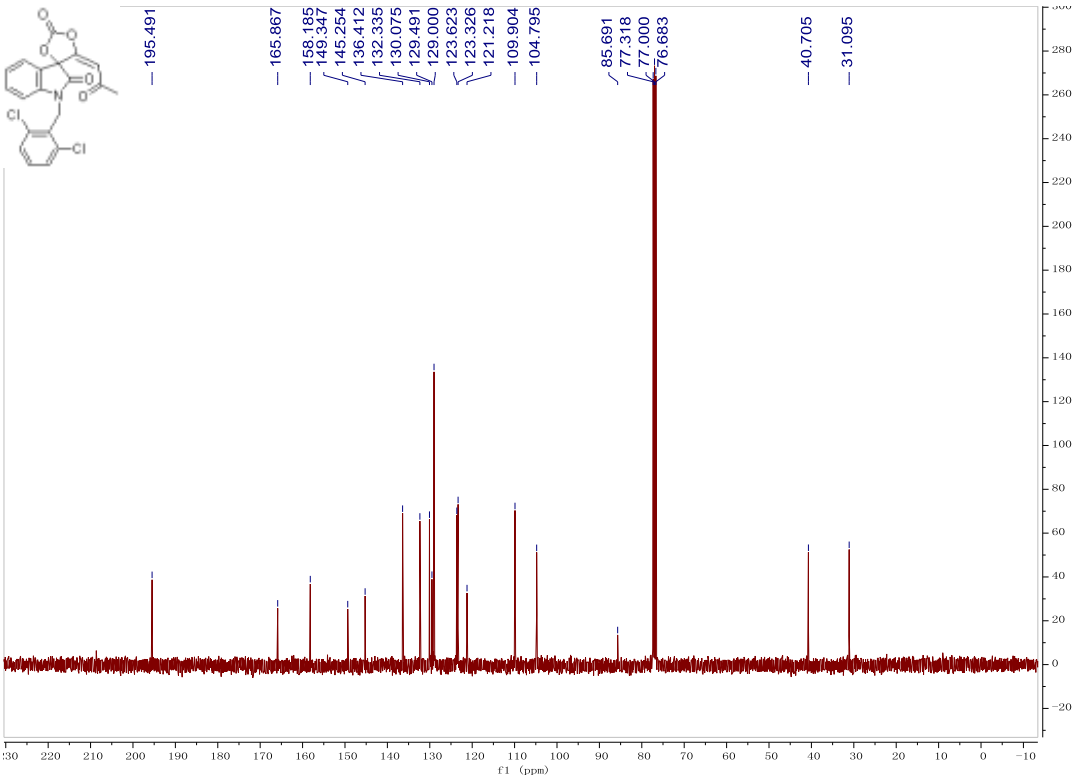
	名称	保留时间（分钟）	面积（微伏*秒）	% 面积	高度（微伏）	积分类型	含量	单位	峰类型	峰代码
1		17.583	36478945	91.11	1050102	VV			未知	
2		24.080	3557268	8.89	88738	VV			未知	



(*E*)-1-(2,6-dichlorobenzyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2l)

A white solid, 89% yield (111 mg). M.p.: 153-155 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.13 (s, 3H, CH_3), 5.13 (d, *J* = 15.2 Hz, 1H, CH_2), 5.48 (d, *J* = 15.2 Hz, 1H, CH_2), 6.37 (s, 1H, =CH), 6.84 (d, *J* = 8.0 Hz, 1H, ArH), 7.01 (t, *J* = 7.2 Hz, 1H, ArH), 7.14 (d, *J* = 7.2 Hz, 1H, ArH), 7.21-7.38 (m, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 40.7, 85.7, 104.8, 109.9, 121.2, 123.3, 123.6, 129.0, 129.5, 130.1, 132.3, 136.4, 145.3, 149.3, 158.2, 165.9, 195.5. IR (EtOH) ν 2953, 2922, 2852, 1850, 1737, 1706, 1608, 1467, 1165, 1005, 781 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{20}H_{17}O_5N_2Cl_2^{+1}(M+NH_4)^+$ requires 435.0509, Found: 435.0510. $[\alpha]^{25}_D$ = +26.00 (c 0.05, CH_2Cl_2) for 94% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 32.792 min, t_{major} = 41.460 min.





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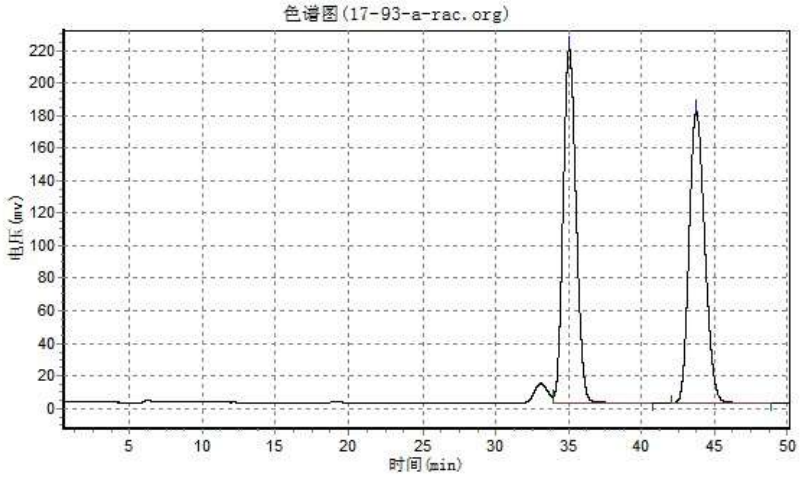
实验者:
报告时间：2019-07-15,14:40:07
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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2		43.747	179030.703	13283606.000	49.7546
总计			397358.625	26698268.000	100.0000

实验时间：2019-07-15,15:45:54
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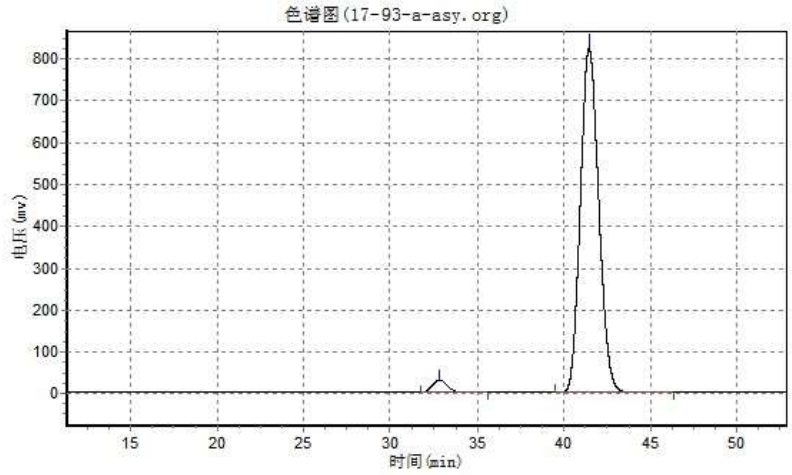
实验者:
报告时间：2019-07-15,15:46:39
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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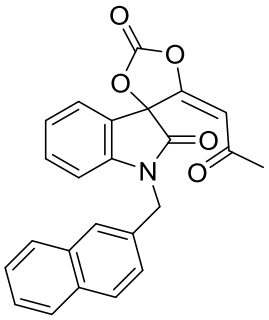
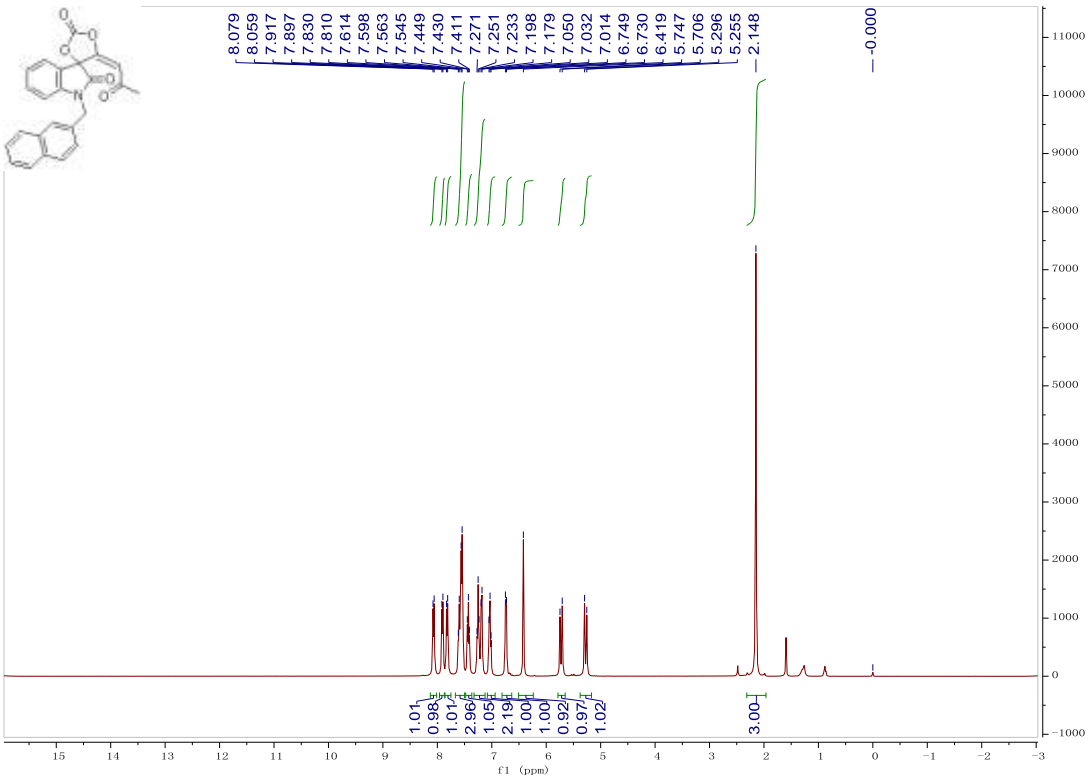
2		41.460	821401.438	60528092.000	97.1986
总计			850750.625	62272597.000	100.0000



(*E*)-1-(naphthalen-2-ylmethyl)-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2m)

A white solid, 78% yield (93 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.15 (s, 3H, CH_3), 5.28 (d, *J* = 16.4 Hz, 1H, CH_2), 5.73 (d, *J* = 16.4 Hz, 1H, CH_2), 6.42 (s, 1H, =CH), 6.74 (d, *J* = 7.6 Hz, 1H, ArH), 7.03 (t, *J* = 7.2 Hz, 1H, ArH), 7.17-7.27 (m, 2H, ArH), 7.43 (t, *J* = 7.6 Hz, 1H, ArH), 7.54-7.62 (m, 3H, ArH), 7.82 (d, *J* = 8.0 Hz, 1H, ArH), 7.91 (d, *J* = 8.0 Hz, 1H, ArH), 8.07 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 43.0, 86.1, 105.0, 110.4, 121.4, 122.6, 123.59, 123.61, 124.5, 125.4, 126.0, 126.7, 128.5, 129.0, 129.4, 130.8, 132.3, 133.8, 145.8, 149.3, 158.0, 166.9, 195.6. IR (EtOH) ν 3060, 2919, 1732, 1701, 1603, 1467, 1322, 1165, 935, 736 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{24}H_{21}O_5N_2^{+1}(M+NH_4)^+$ requires 417.1445, Found: 417.1444.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7.271
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7.233
7.198
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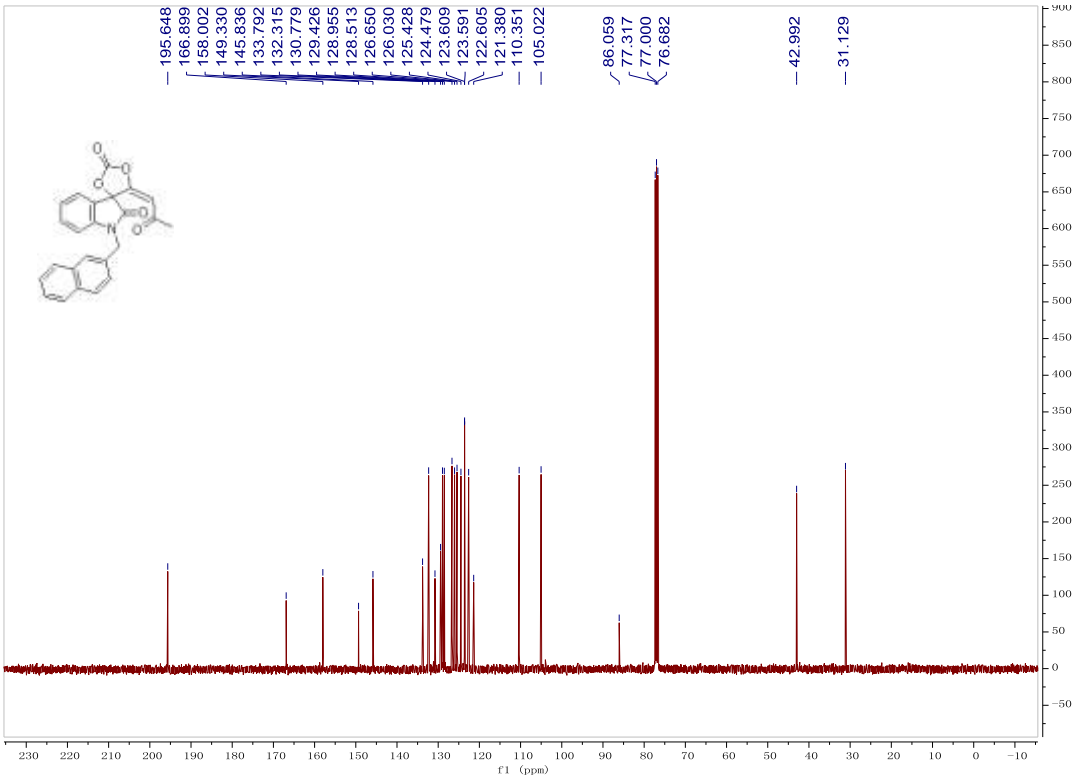
7.032
7.014
6.749
6.730
6.419
5.747
5.706
5.296
5.255
2.148
-0.000
1.01
0.98
1.01
2.96
1.05
2.19
1.00
1.00
0.92
0.97
1.02
3.00
f1 (ppm)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126.030
125.428
124.479
123.609
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122.605
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105.022
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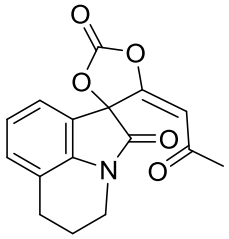
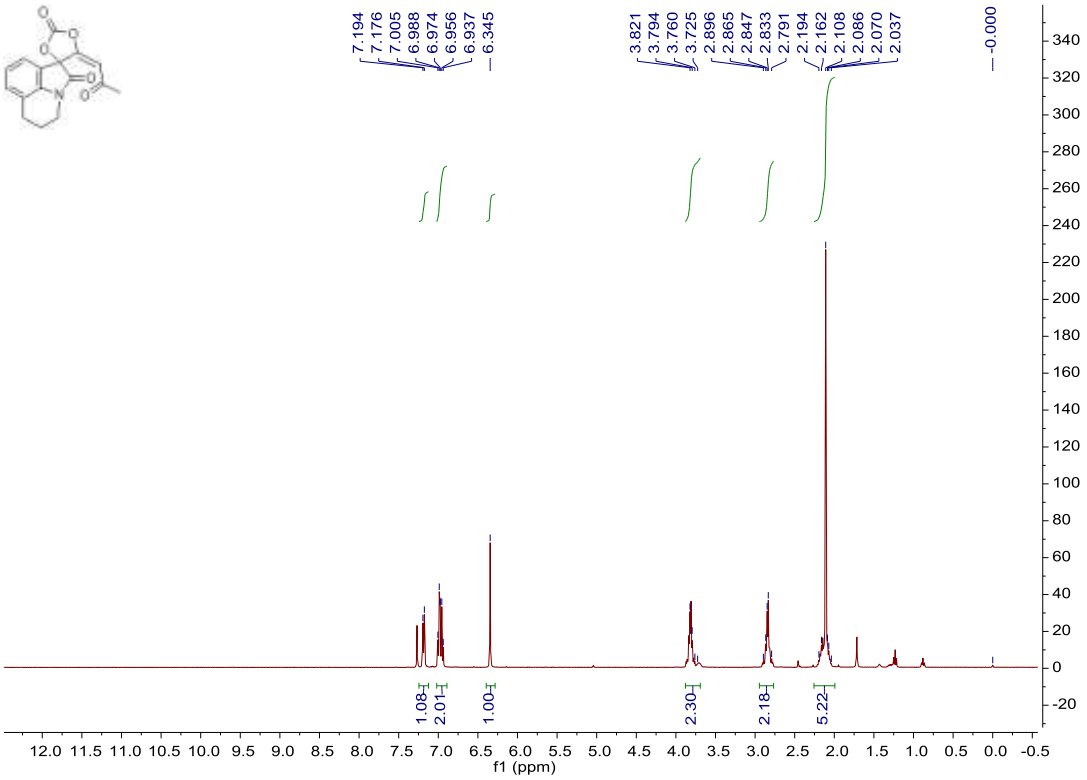
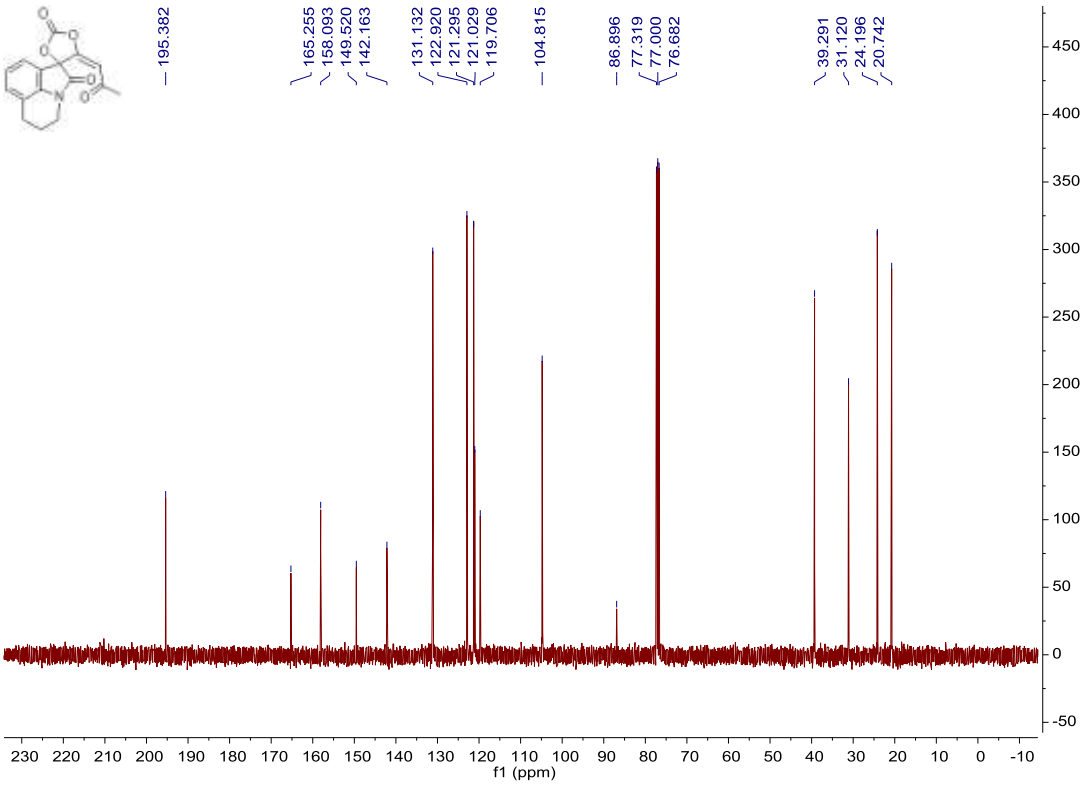
42.992
31.129
f1 (ppm)



(*E*)-5'-(2-oxopropylidene)-5,6-dihydro-2H,4H-spiro[pyrrolo[3,2,1-ij]quinoline-1,4'-[1,3]dioxolane]-2,2'-dione (2n)

A white solid, 87% yield (78 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.03-2.20 (m, 5H, CH_2, CH_3), 2.79-2.90 (m, 2H, CH_2), 3.72-3.83 (m, 2H, CH_2), 6.35 (s, 1H, =CH), 6.93-7.01 (m, 2H, ArH), 7.19 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 20.7, 24.2, 31.1, 39.3, 86.9, 104.8, 119.7, 121.0, 121.3, 122.9, 131.1, 142.2, 149.5, 158.1, 165.3, 195.4. IR (EtOH) ν 2955, 2922, 2851, 1730, 1698, 1628, 1456, 1364, 1156 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{15}H_{14}O_3N^{+1}(M+H-CO_2)^+$ requires 256.0968, Found: 256.0967. $[\alpha]^{25}_D$ = +93.33 (c 0.02, CH_2Cl_2) for 92% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 72.097 min, t_{major} = 56.102 min.





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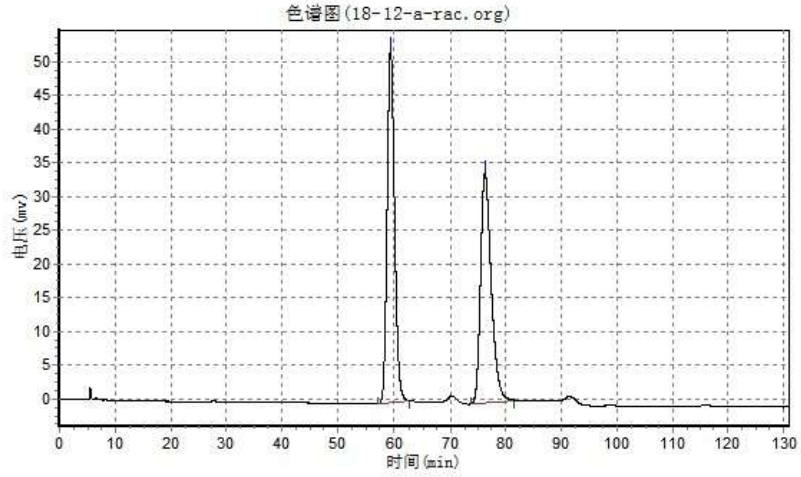
谱图文件:D:\Sun Yaoliang\co2\18-12-a-rac.org

实验者:
报告时间：2018-04-28,14:28:49
积分方法:面积归一法

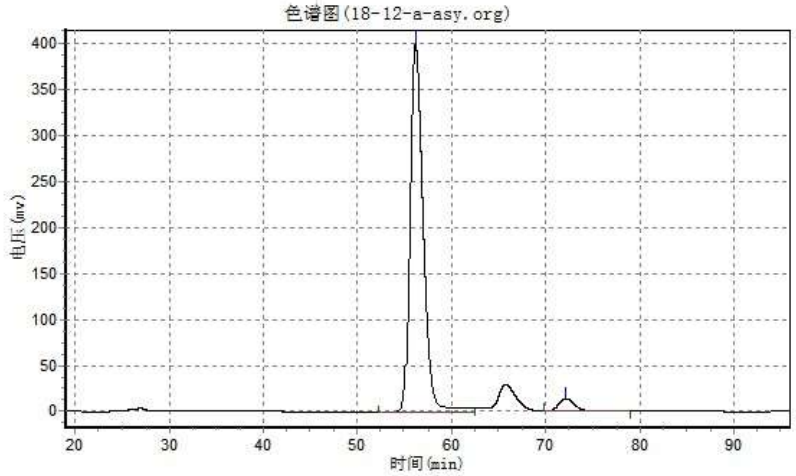


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		59.515	52374.402	4816437.000	51.5167
2		76.242	34036.715	4532835.500	48.4833
总计			86411.117	9349272.500	100.0000

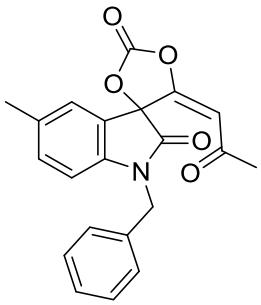
实验时间：2018-04-28,15:51:18
谱图文件:D:\Sun Yaoliang\co2\18-12-a-asy.org

实验者:
报告时间：2018-04-28,15:52:04
积分方法:面积归一法



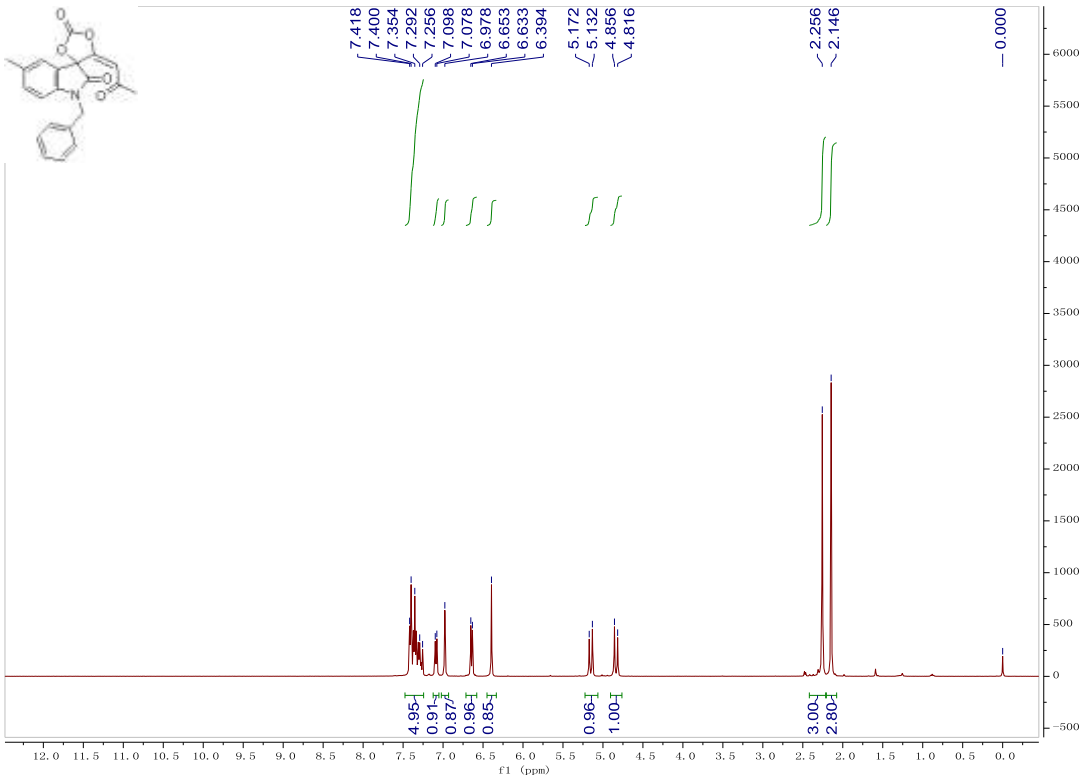
分析结果表

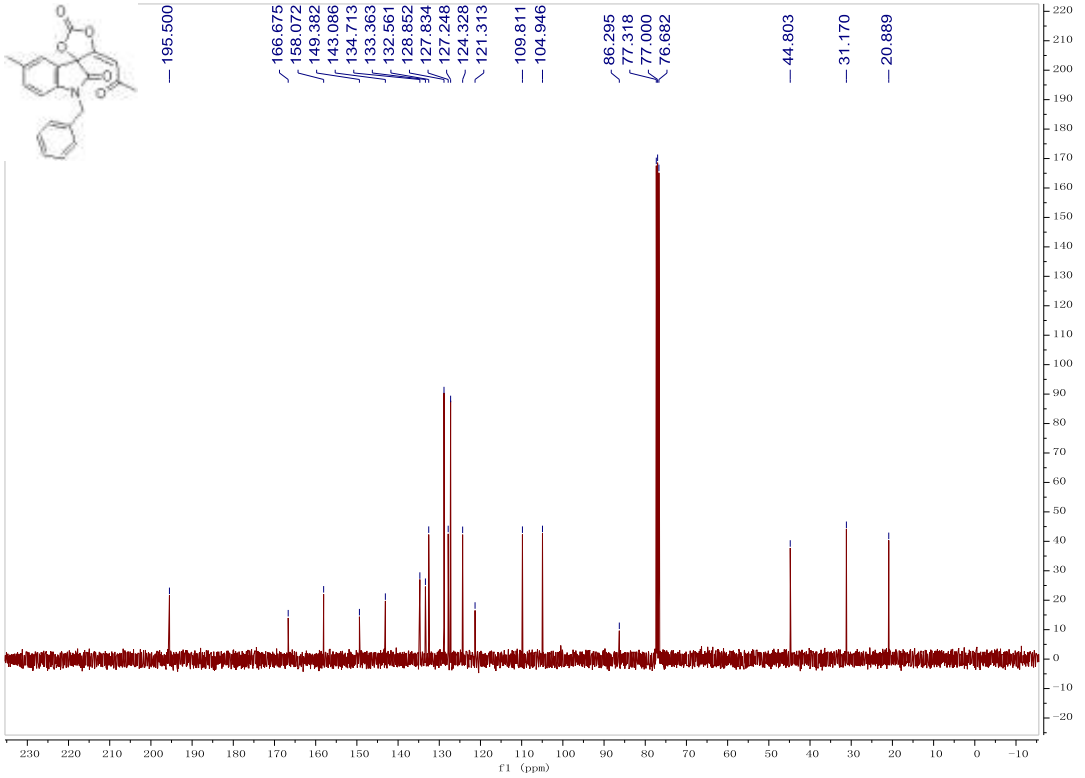
峰号	峰名	保留时间	峰高	峰面积	含量
1		56.102	399785.313	37962588.000	95.8305
2		72.097	13940.969	1651700.750	4.1695
总计			413726.281	39614288.750	100.0000

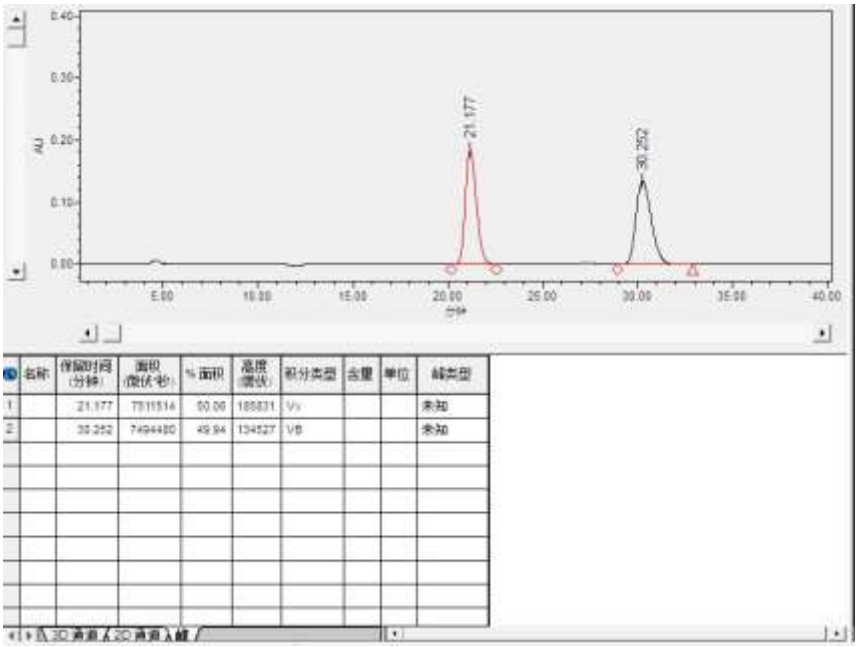


(*E*)-1-benzyl-5-methyl-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2o)

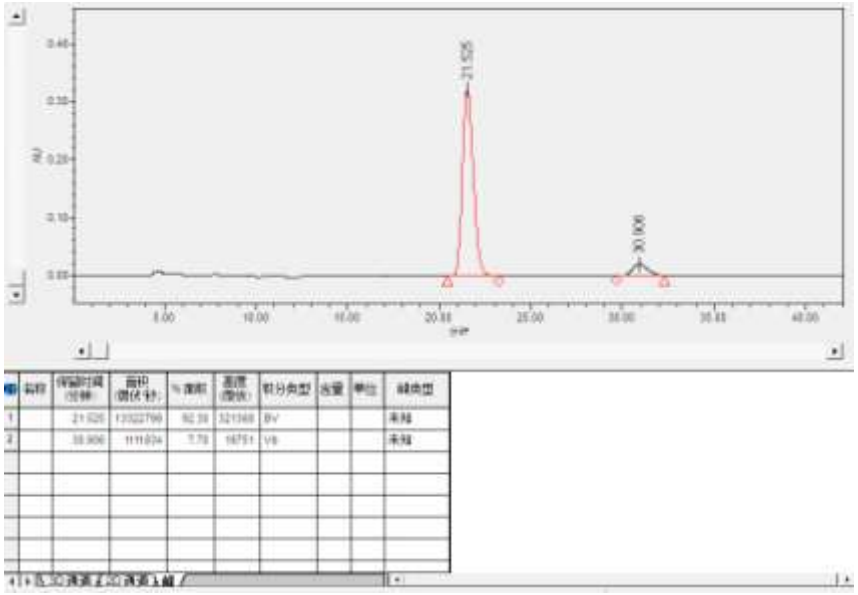
A white solid, 87% yield (95 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.15 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 4.84 (d, J = 16.0 Hz, 1H, CH_2), 5.15 (d, J = 16.0 Hz, 1H, CH_2), 6.39 (s, 1H, =CH), 6.64 (d, J = 8.0 Hz, 1H, ArH), 6.98 (s, 1H, ArH), 7.09 (d, J = 8.0 Hz, 1H, ArH), 7.25-7.42 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 20.9, 31.2, 44.8, 86.3, 104.9, 109.8, 121.3, 124.3, 127.2, 127.8, 128.9, 132.6, 133.4, 134.7, 143.1, 149.4, 158.1, 166.7, 195.5. IR (EtOH) ν 3032, 2914, 2839, 1846, 1731, 1704, 1603, 1496, 1370, 1120, 813, 734 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{21}H_{21}O_5N_2^{+1}(M+NH_4)^+$ requires 381.1445, Found: 381.1445. $[\alpha]^{25}_D$ = +125.83 (c 0.04, CH_2Cl_2) for 85% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 30.906 min, t_{major} = 21.525 min.


7.418
7.400
7.354
7.292
7.256
7.098
7.078
6.978
6.653
6.633
6.394
5.172
5.132
4.856
4.816
2.256
2.146
0.000
4.95
0.91
0.87
0.96
0.85
0.96
1.00
3.00
2.80
f1 (ppm)

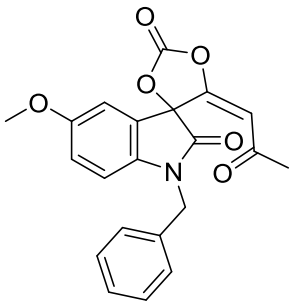

195.500
166.675
158.072
149.382
143.086
134.713
133.363
132.561
128.852
127.834
127.248
124.328
121.313
109.811
104.946
86.295
77.318
77.000
76.682
44.803
31.170
20.889
f1 (ppm)



名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	浓度	单位	峰类型
1	21.177	7511514	50.06	185831	Vv			未知
2	30.252	7494480	49.94	134527	VB			未知



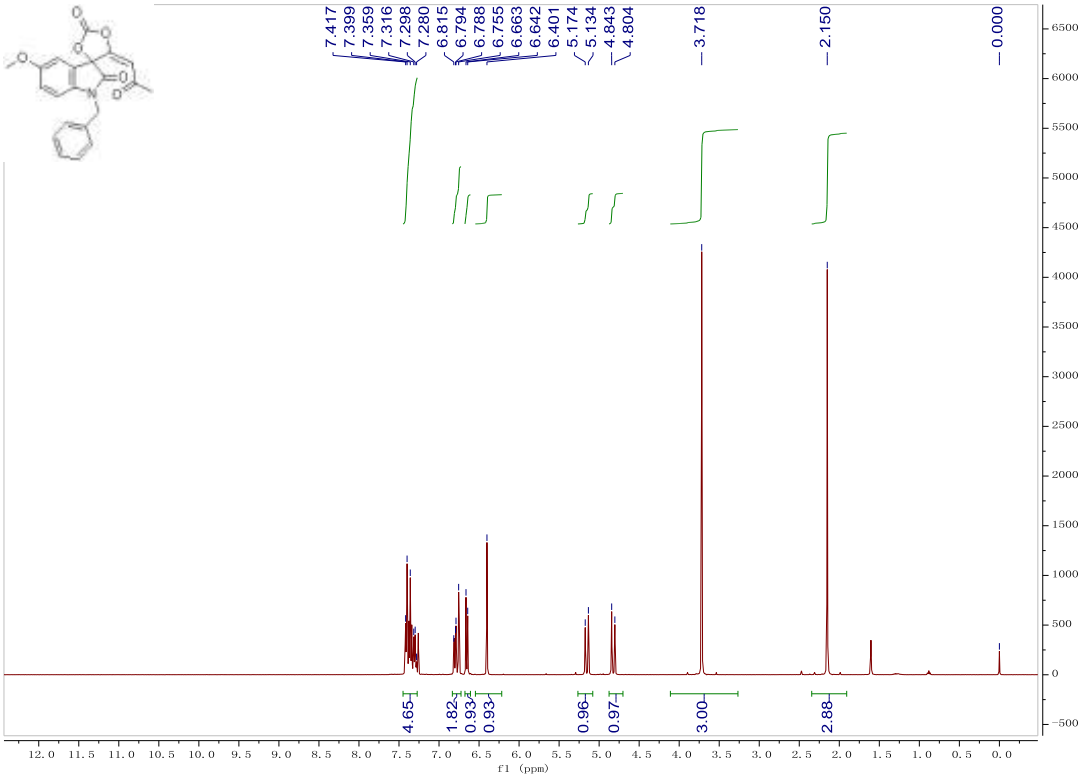
名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	浓度	单位	峰类型
1	21.525	13322799	92.30	321368	BV			未知
2	30.006	1111834	7.70	16751	VB			未知

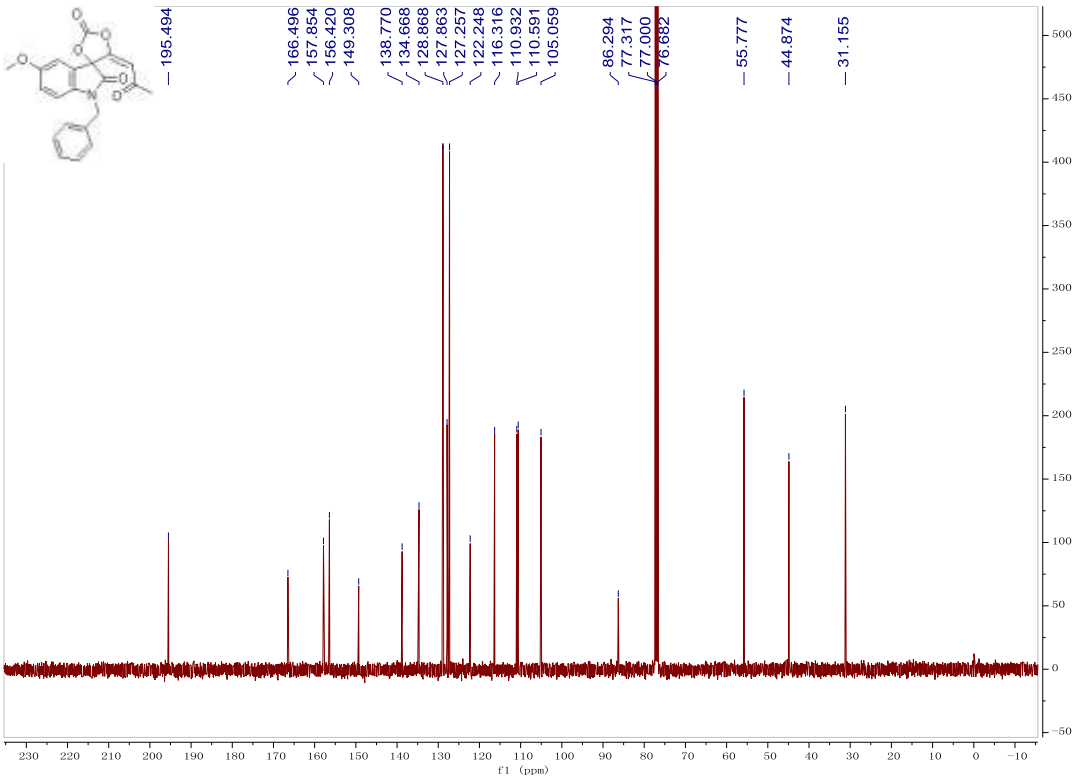


(*E*)-1-benzyl-5-methoxy-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2p)

A white solid, 90% yield (102 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400

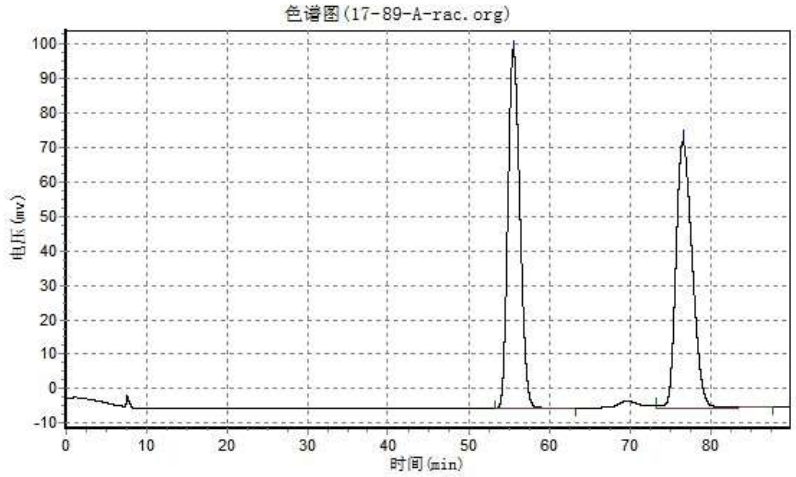
MHz) δ 2.15 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 4.82 (d, *J* = 15.6 Hz, 1H, CH_2), 5.15 (d, *J* = 15.6 Hz, 1H, CH_2), 6.40 (s, 1H, =CH), 6.65 (d, *J* = 8.4 Hz, 1H, ArH), 6.75-6.82 (m, 2H, ArH), 7.28-7.42 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.2, 44.9, 55.8, 86.3, 105.1, 110.6, 110.9, 116.3, 122.2, 127.3, 127.9, 128.9, 134.7, 138.8, 149.3, 156.4, 157.9, 166.5, 195.5. IR (EtOH) ν 3115, 3063, 2925, 2831, 1847, 1727, 1494, 1435, 1017, 697 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{20}H_{18}O_4N^{+1}(M+H-CO_2)^+$ requires 336.1230, Found: 336.1232. $[\alpha]^{25}_D$ = +35.33 (c 0.05, CH_2Cl_2) for 90% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 78.960 min, t_{major} = 56.927 min.





实验时间: 2018-07-16,19:57:23
谱图文件:D:\Sun Yaoliang\co2\17-89-A-rac.org

实验者:
报告时间: 2018-07-16,19:58:20
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		55.548	104049.469	10812250.000	49.9523
2		76.615	77233.125	10832918.000	50.0477
总计			181282.594	21645168.000	100.0000

实验时间：2019-07-10,14:17:01
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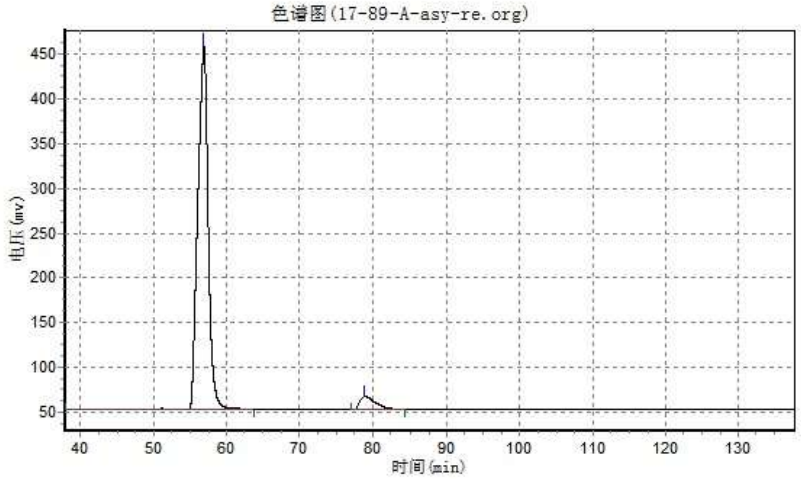
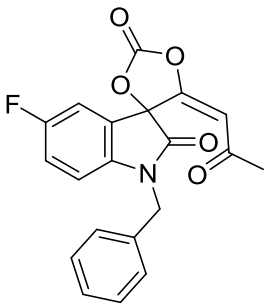
实验者:
报告时间：2019-07-10,20:41:34
积分方法:面积归一法



分析结果表

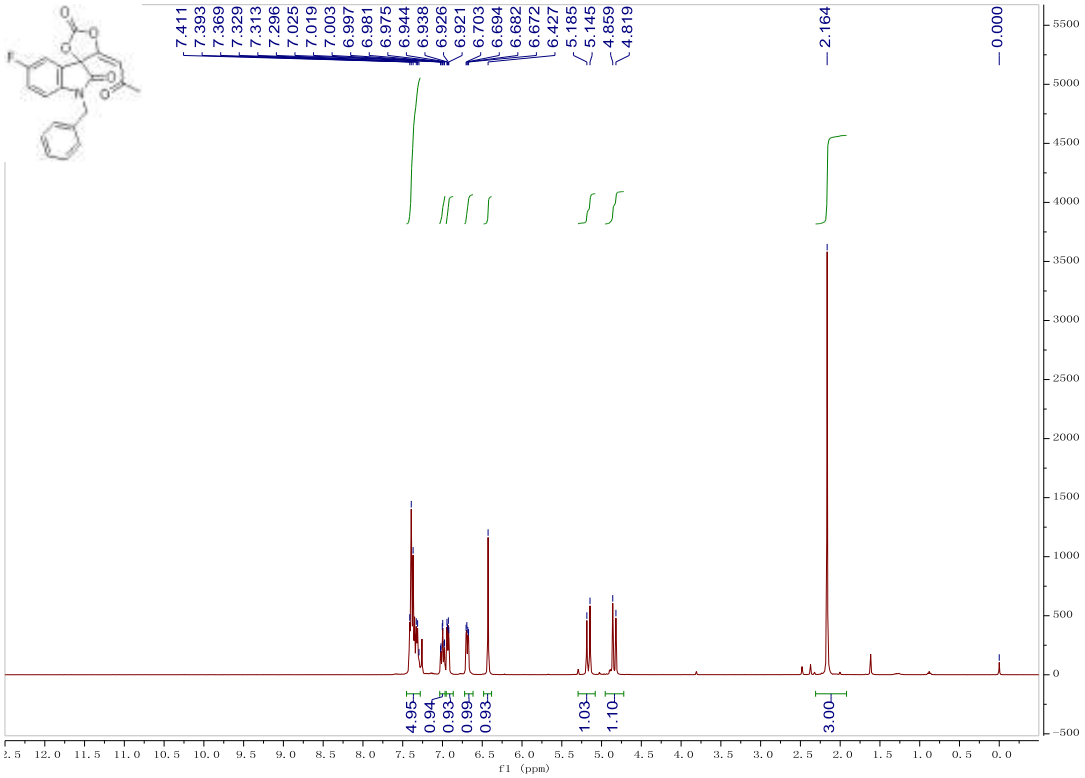
峰号	峰名	保留时间	峰高	峰面积	含量
1		56.927	404687.000	39617500.000	95.2071
2		78.960	14049.000	1994415.875	4.7929
总计			418736.000	41611915.875	100.0000

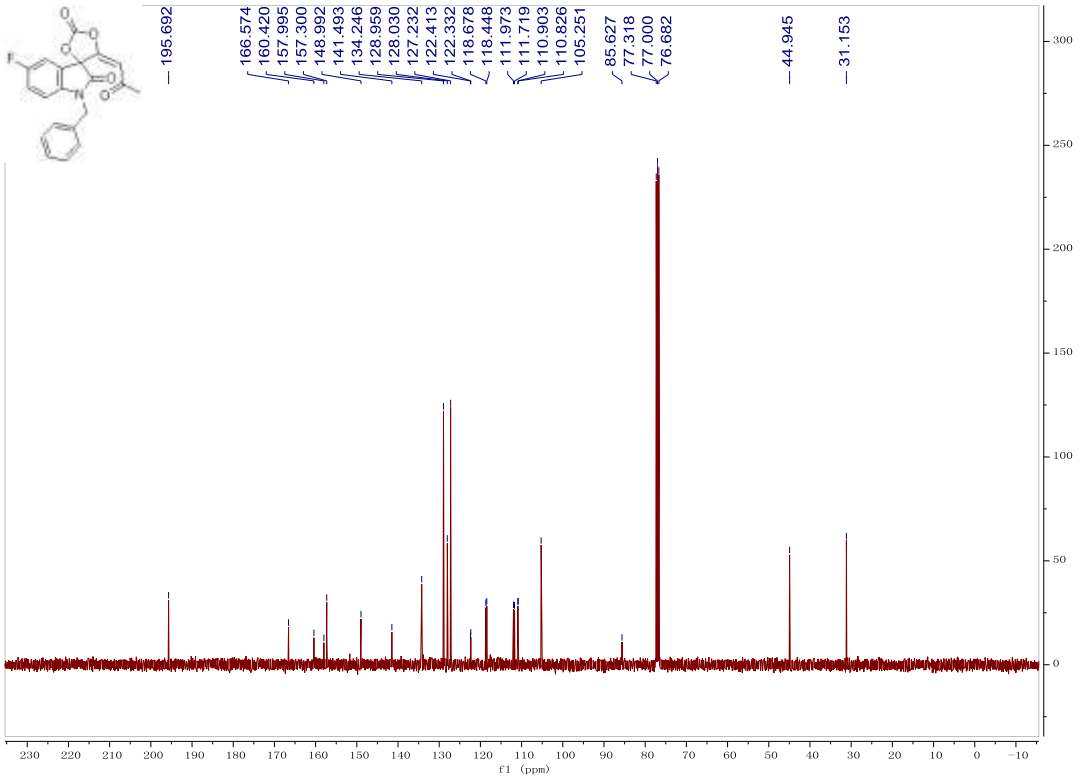


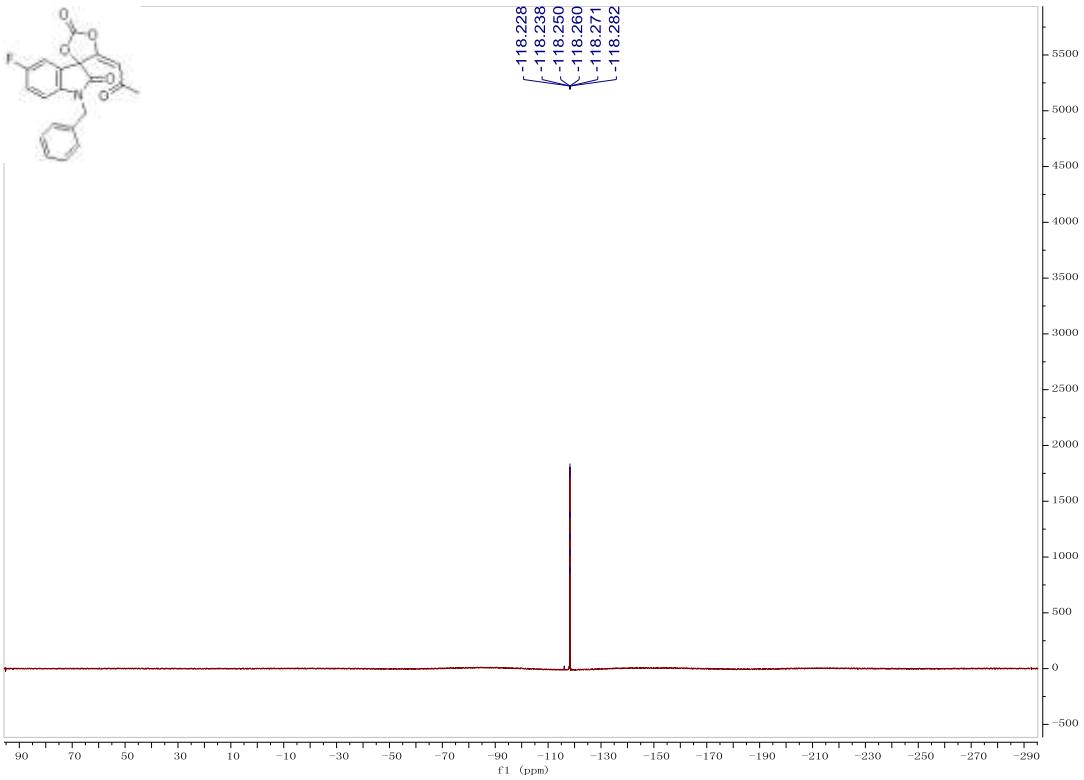
(*E*)-1-benzyl-5-fluoro-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2q)

A white solid, 83% yield (91 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.16 (s, 3H, CH_3), 4.84 (d, *J* = 16.0 Hz, 1H, CH_2), 5.17 (d, *J* = 16.0 Hz, 1H, CH_2), 6.43 (s, 1H, =CH), 6.69 (dd, *J* = 4.8, 8.4 Hz, 1H, ArH), 6.93 (dd, *J* = 2.4, 7.2 Hz, 1H, ArH), 7.00 (dt, *J* = 2.4, 8.8 Hz, 1H, ArH), 7.29-7.41 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.2, 44.9, 85.6, 105.3, 110.9 (d, *J* = 7.7 Hz), 111.8 (d, *J* = 25.4 Hz), 118.6 (d, *J* = 23.0 Hz), 122.4 (d, *J* = 8.1 Hz), 127.2, 128.0, 129.0, 134.2, 141.5, 149.0, 157.3, 159.2 (d, *J* = 242.5 Hz), 166.6, 195.7. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -118.29-(-118.22). IR (EtOH) ν 3066, 2922, 2846, 1847, 1734, 1632, 1491, 1455, 1346, 1175, 1015, 735 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{19}H_{15}O_3NF^{+1}(M+H-CO_2)^+$ requires 324.1030, Found: 324.1029. $[\alpha]^{25}_D$ = -11.11 (c 0.06, CH_2Cl_2) for 85% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column,

Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 72.100 min, t_{major} = 45.505 min.







实验时间: 2018-07-22,18:18:55
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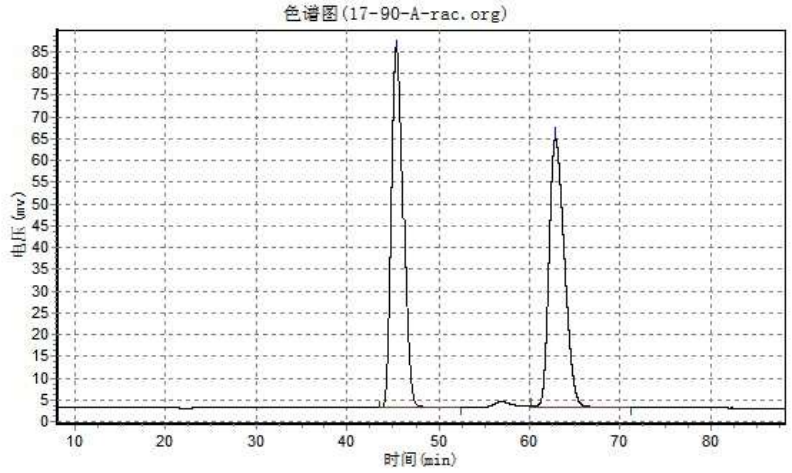
实验者:
报告时间: 2018-07-16,20:00:01
积分方法:面积归一法

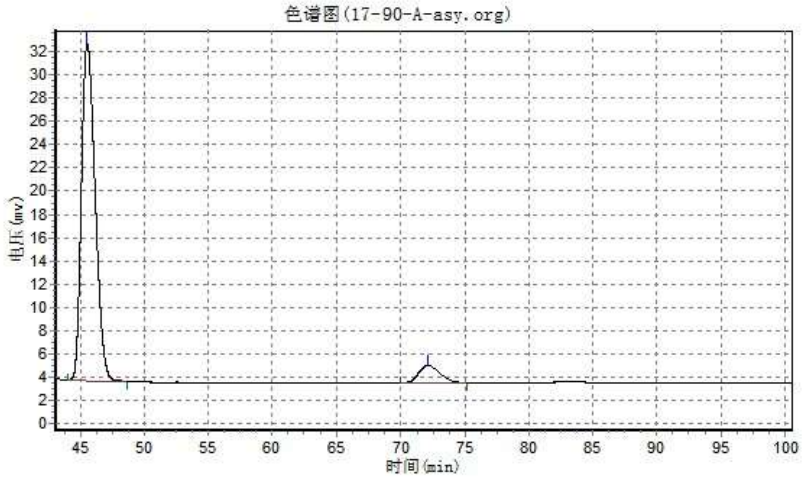


分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		45.565	82488.695	7205221.000	49.8119
2		62.898	61714.391	7259637.500	50.1881
总计			144203.086	14464858.500	100.0000

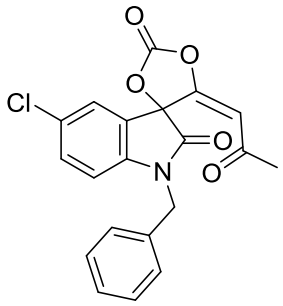
实验时间：2019-07-11,19:01:06
谱图文件:D:\Sun Yaoliang\co2\17-90-A-asy.org

实验者：
报告时间：2019-07-11,21:39:40
积分方法:面积归一法



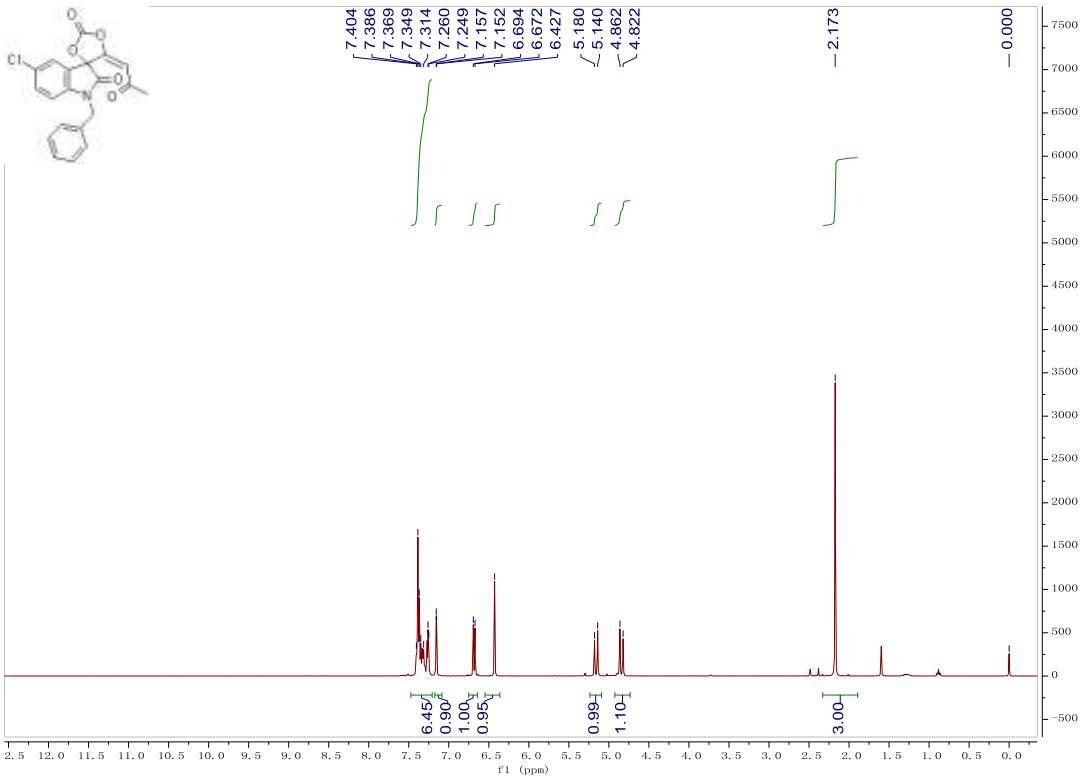
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		45.505	28902.244	2151563.250	92.6133
2		72.100	1505.467	171604.688	7.3867
总计			30407.711	2323167.938	100.0000



(*E*)-1-benzyl-5-chloro-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2r)

A white solid, 73% yield (84 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.17 (s, 3H, CH_3), 4.84 (d, *J* = 16.0 Hz, 1H, CH_2), 5.16 (d, *J* = 16.0 Hz, 1H, CH_2), 6.43 (s, 1H, =CH), 6.68 (d, *J* = 8.8 Hz, 1H, ArH), 7.15 (d, *J* = 2.0 Hz, 1H, ArH), 7.24-7.41 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.2, 44.9, 85.4, 105.2, 111.1, 122.7, 124.1, 127.2, 128.1, 128.9, 129.0, 132.1, 134.1, 144.0, 148.9, 157.2, 166.4, 195.8. IR (EtOH) ν 3120, 3063, 2927, 2852, 1853, 1737, 1705, 1633, 1455, 1324, 1165, 1015, 816 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{19}H_{15}O_3NCl^{+1}(M+H-CO_2)^+$ requires 340.0740, Found: 340.0741.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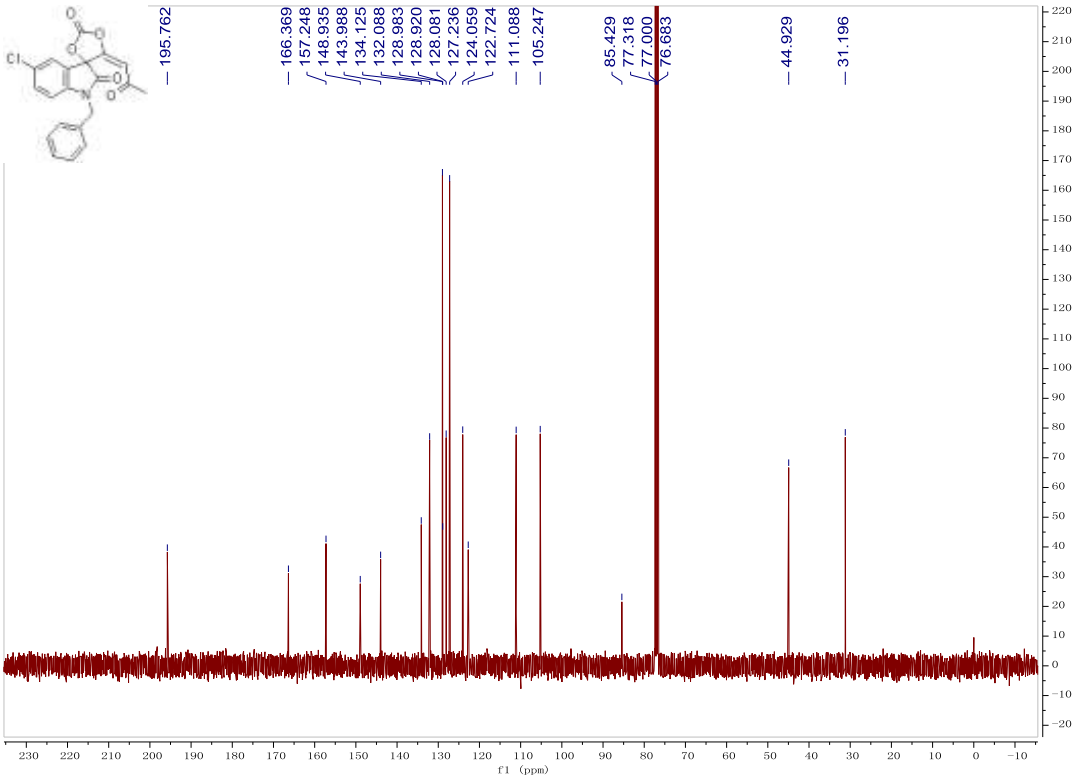
7.349
7.314
7.260
7.249
7.157
7.152
6.694
6.672
6.427
5.180
5.140
4.862
4.822
2.173
0.000
6.45
0.90
1.00
0.95
0.99
1.10
3.00
f1 (ppm)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143.988
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128.081
127.236
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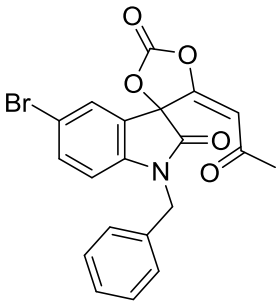
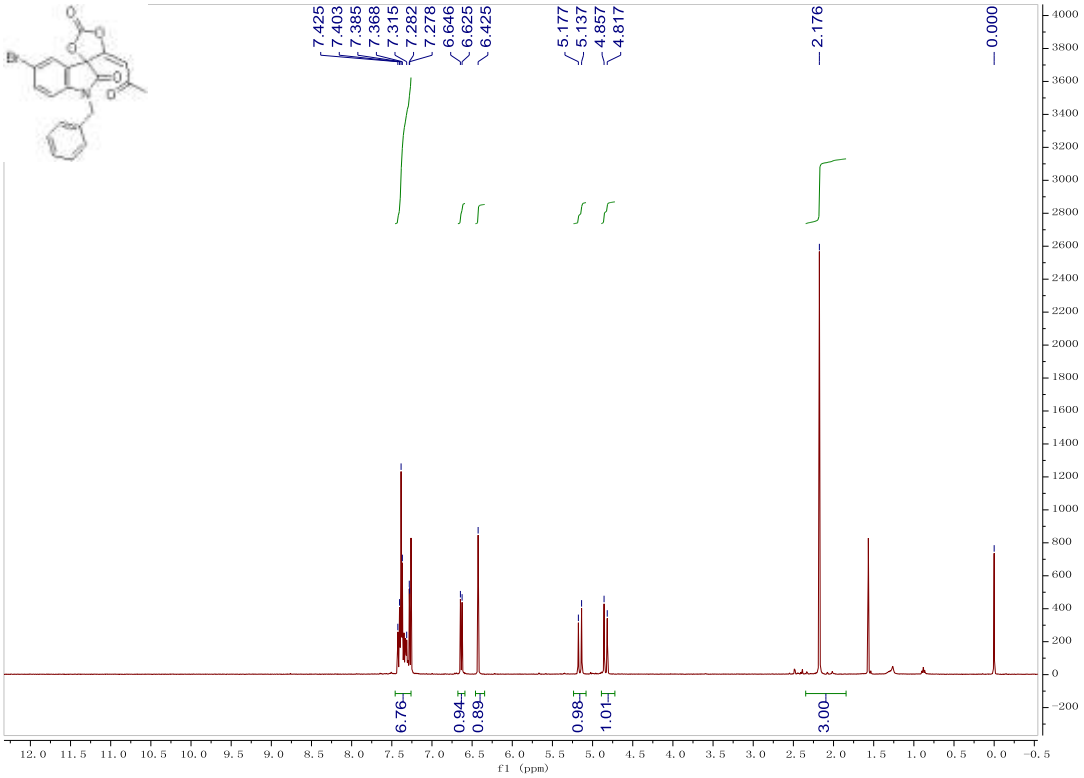
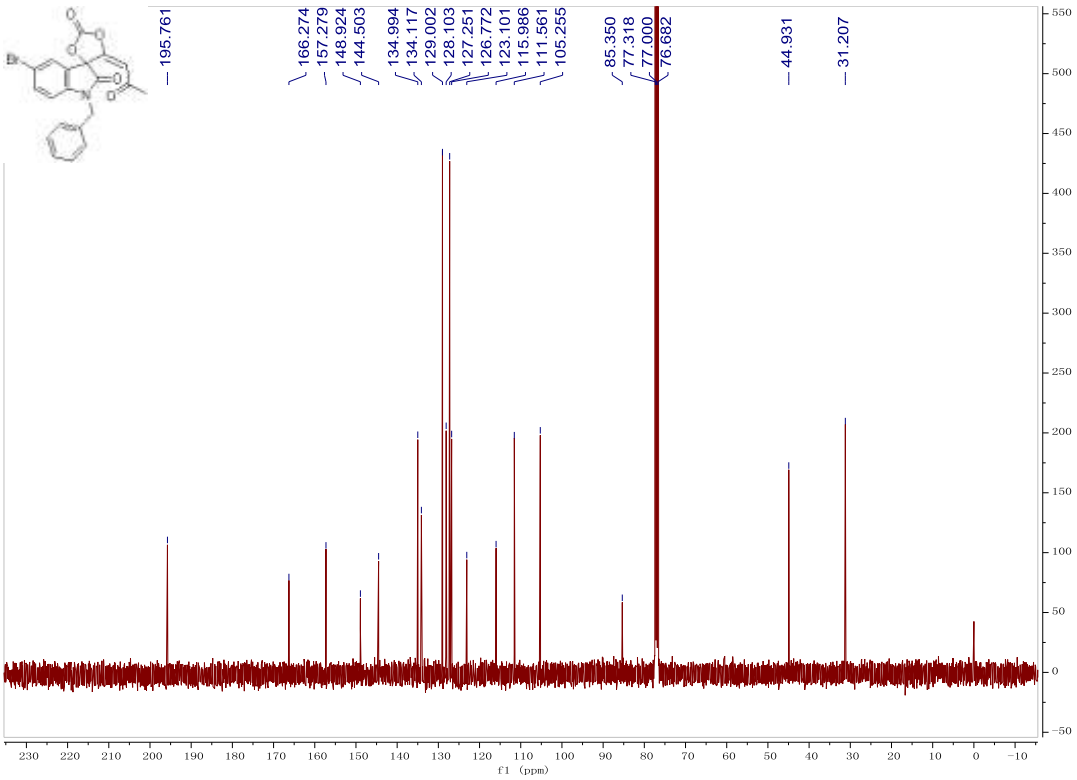
77.000
76.683
44.929
31.196
f1 (ppm)

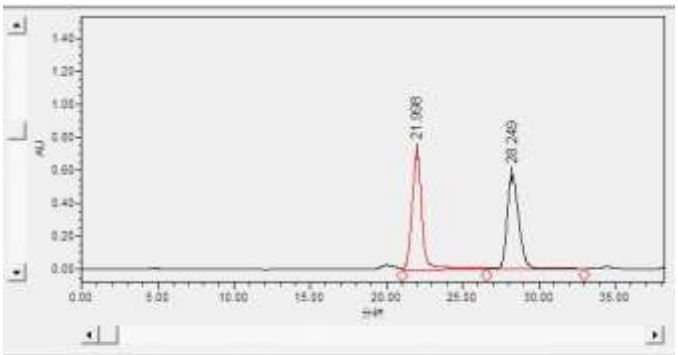


(*E*)-1-benzyl-5-bromo-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2s)

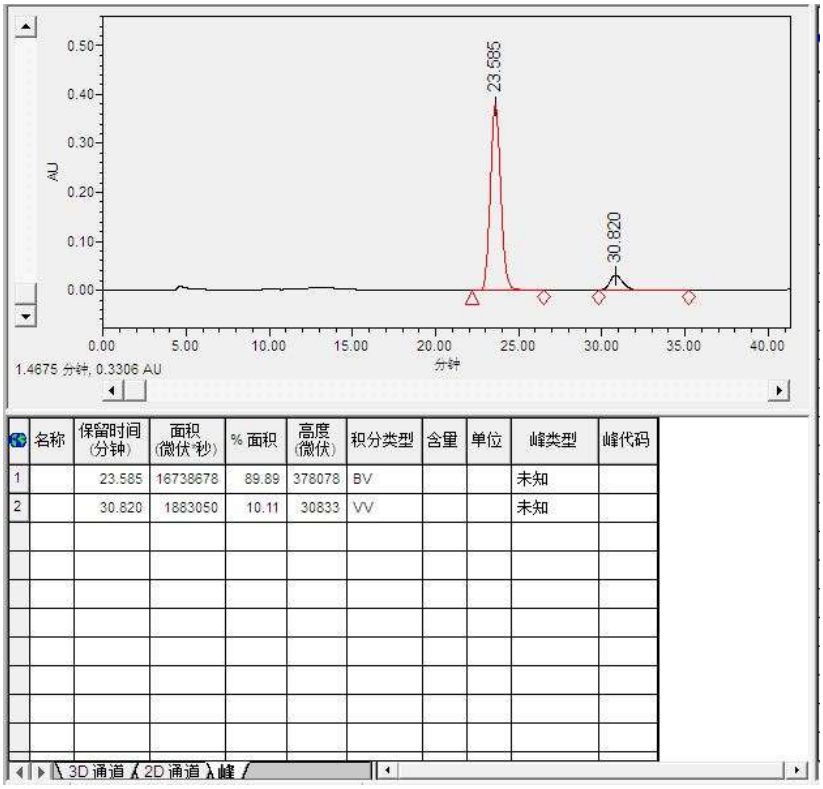
A white solid, 41% yield (53 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.18 (s, 3H, CH_3), 4.84 (d, *J* = 16.0 Hz, 1H, CH_2), 5.16 (d, *J* = 16.0 Hz, 1H, CH_2), 6.43 (s, 1H, =CH), 6.64 (d, *J* = 8.4 Hz, 1H, ArH), 7.27-7.43 (m, 7H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.2, 44.9, 85.4, 105.3, 111.6, 116.0, 123.1, 126.8, 127.3, 128.1, 129.0, 134.1, 135.0, 144.5, 148.9, 157.3, 166.3, 195.8. IR (EtOH) ν 3110, 3066, 2919, 2844, 1852, 1704, 1632, 1603, 1482, 1131, 933, 813 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{19}H_{15}O_3NBr^{+1}(M+H-CO_2)^+$ requires 384.0230, Found: 384.0228. $[\delta]^{25}_{D}$ = +40.00 (c 0.04, CH_2Cl_2) for 80% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 30.820 min, t_{major} = 23.585 min.



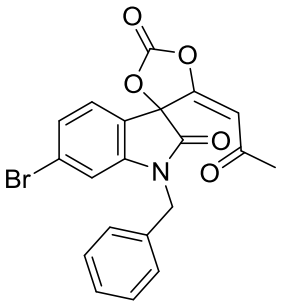




	名称	保留时间（分钟）	面积（微伏*秒）	% 面积	高度（微伏）	积分类型	含量	单位	峰类型	峰代码
1		21.998	33123836	50.62	721031	VV			未知	
2		28.249	32313022	49.38	576064	VV			未知	

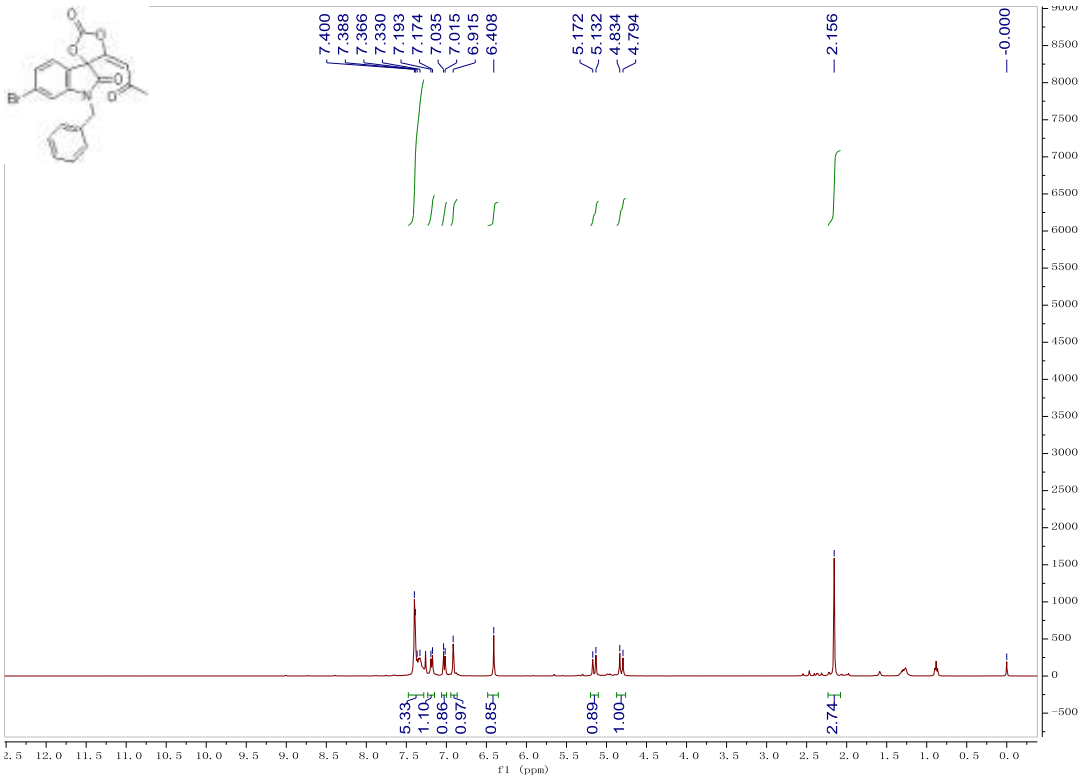


	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		23.585	16738678	89.89	378078	BV			未知	
2		30.820	1883050	10.11	30833	VV			未知	



(*E*)-1-benzyl-6-bromo-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2t)

A white solid, 67% yield (86 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.16 (s, 3H, CH_3), 4.81 (d, *J* = 16.0 Hz, 1H, CH_2), 5.15 (d, *J* = 16.0 Hz, 1H, CH_2), 6.41 (s, 1H, =CH), 6.92 (s, 1H, ArH), 7.03 (d, *J* = 8.0 Hz, 1H, ArH), 7.18 (d, *J* = 7.6 Hz, 1H, ArH), 7.33-7.40 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.2, 44.9, 85.4, 105.1, 113.5, 120.2, 124.7, 126.3, 126.5, 127.2, 128.2, 129.0, 134.0, 146.7, 149.0, 157.4, 166.7, 195.7. IR (EtOH) ν 3112, 3071, 3026, 2922, 2846, 1844, 1734, 1734, 1486, 1323, 1121, 987 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{19}H_{15}O_3NBr^{+1}(M+H-CO_2)^+$ requires 384.0230, Found: 384.0230.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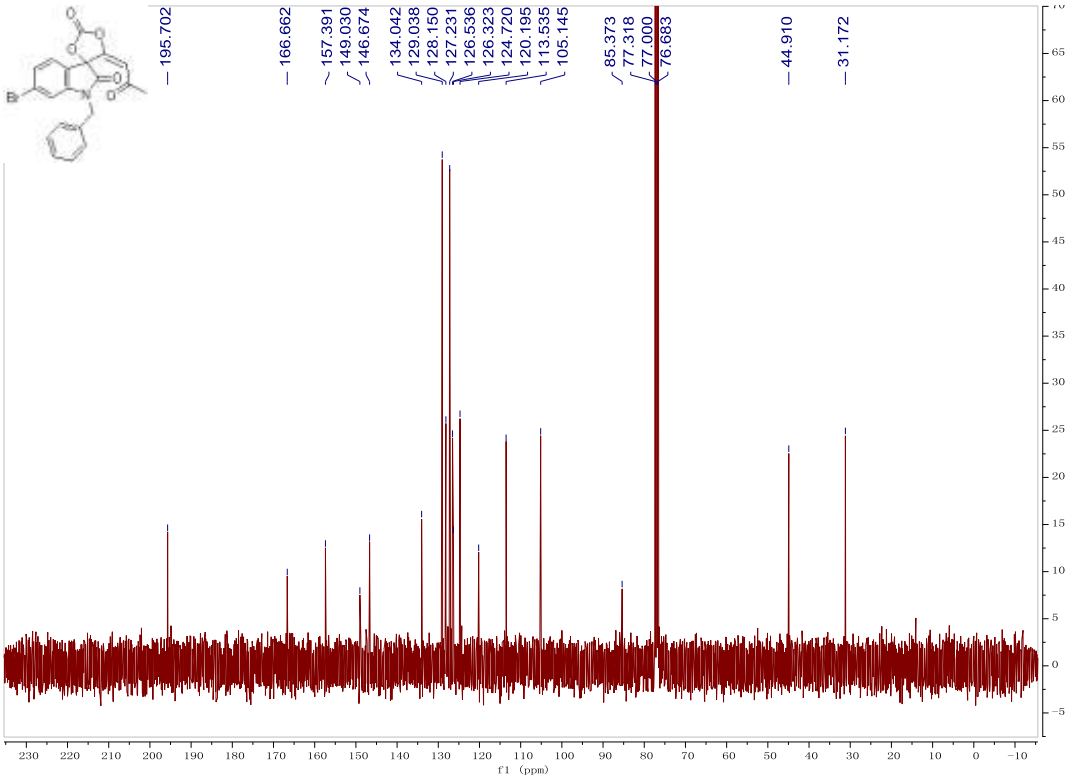
7.388
7.366
7.330
7.193
7.174
7.035
7.015
6.915
6.408
5.172
5.132
4.834
4.794
2.156
-0.000
5.33
1.10
0.86
0.97
0.85
0.89
1.00
2.74
f1 (ppm)


195.702
166.662
157.391
149.030
146.674
134.042
129.038
128.150
127.231
126.536
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124.720
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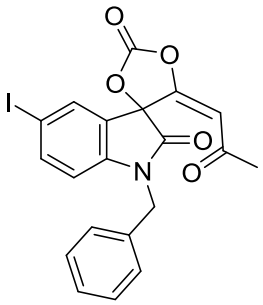
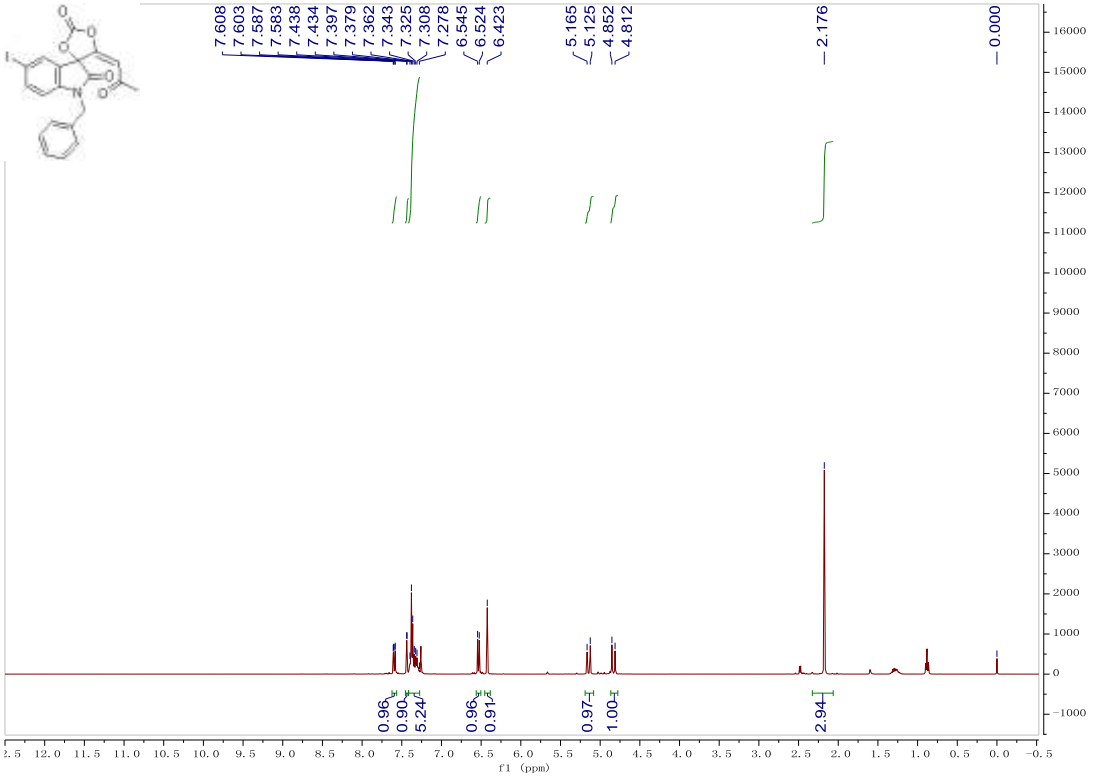
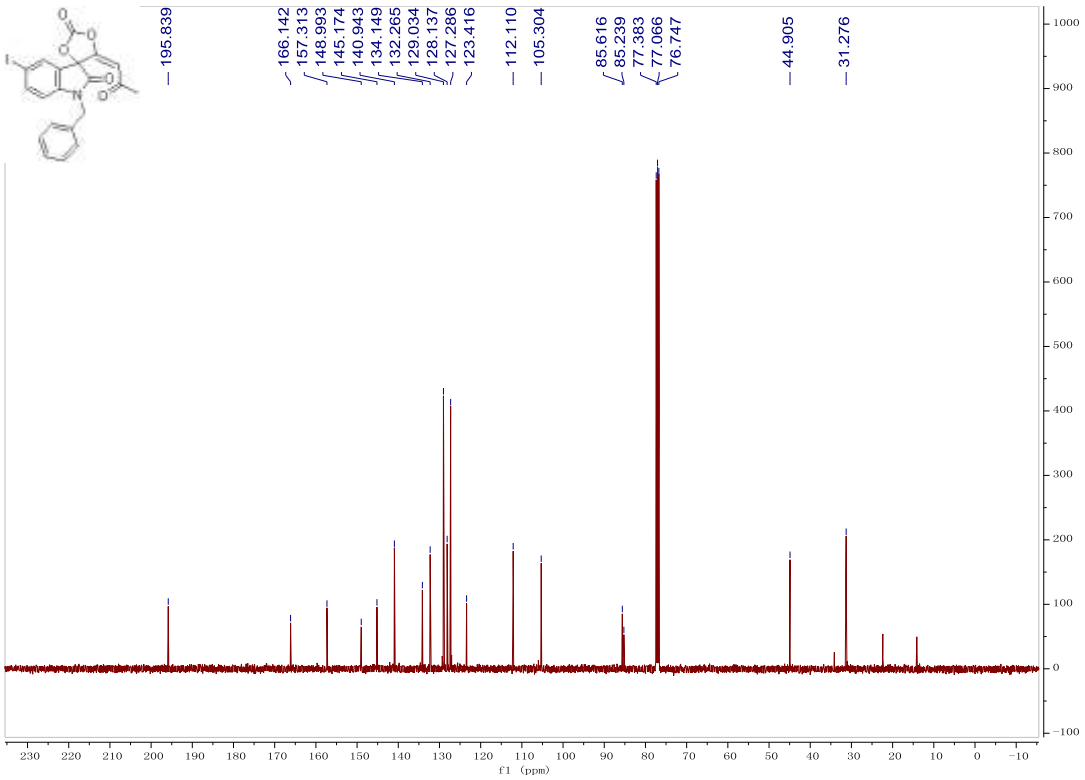
77.000
76.683
44.910
31.172
f1 (ppm)

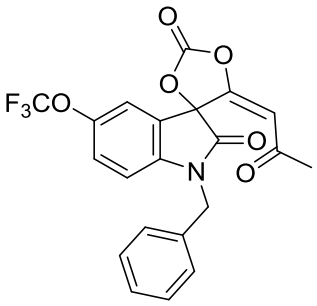


(*E*)-1-benzyl-5-iodo-5'-(2-oxopropylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2u)

A white solid, 72% yield (103 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.18 (s, 3H, CH_3), 4.83 (d, *J* = 16.0 Hz, 1H, CH_2), 5.15 (d, *J* = 16.0 Hz, 1H, CH_2), 6.42 (s, 1H, =CH), 6.53 (d, *J* = 8.4 Hz, 1H, ArH), 7.27-7.40 (m, 5H, ArH), 7.43 (d, *J* = 1.6 Hz, 1H, ArH), 7.60 (dd, *J* = 2.0, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.3, 44.9, 85.2, 85.6, 105.3, 112.1, 123.4, 127.3, 128.1, 129.0, 132.3, 134.1, 140.9, 145.2, 149.0, 157.3, 166.1, 195.8. IR (EtOH) ν 3110, 3058, 3029, 2919, 2844, 1855, 1734, 1601, 1454, 1323, 1131, 1015, 811, 735, 696 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{19}H_{15}O_3NI^{+1}(M+H-CO_2)^+$ requires 432.0091, Found: 432.0106.



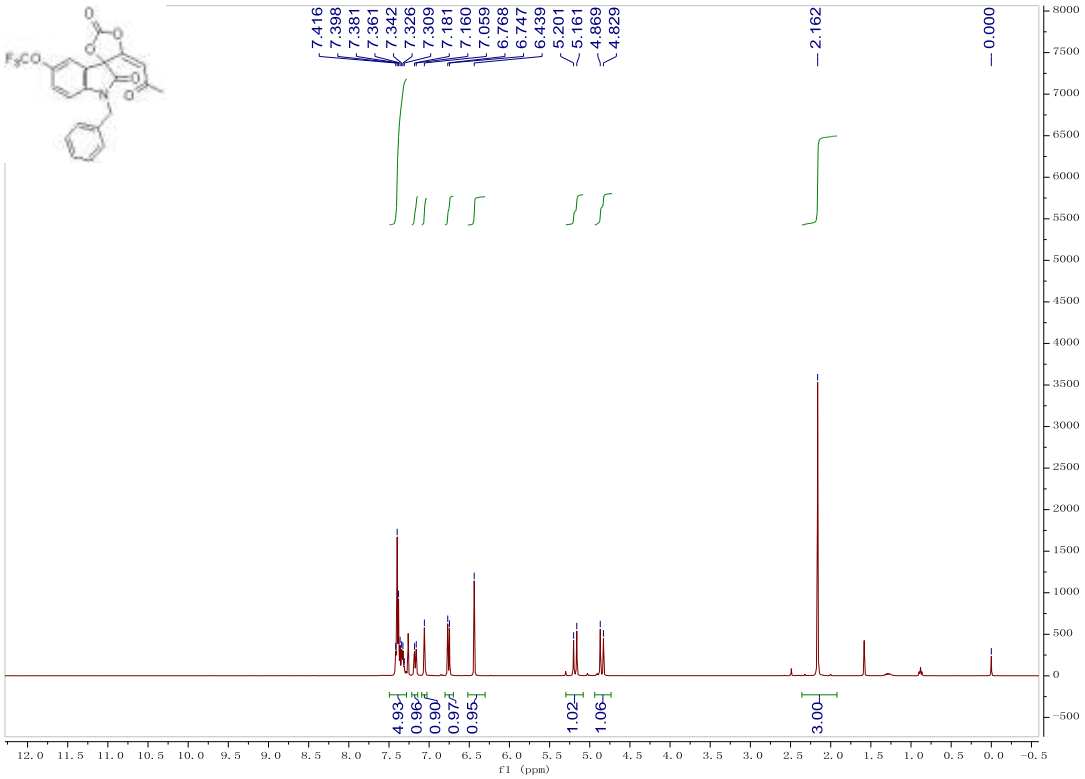


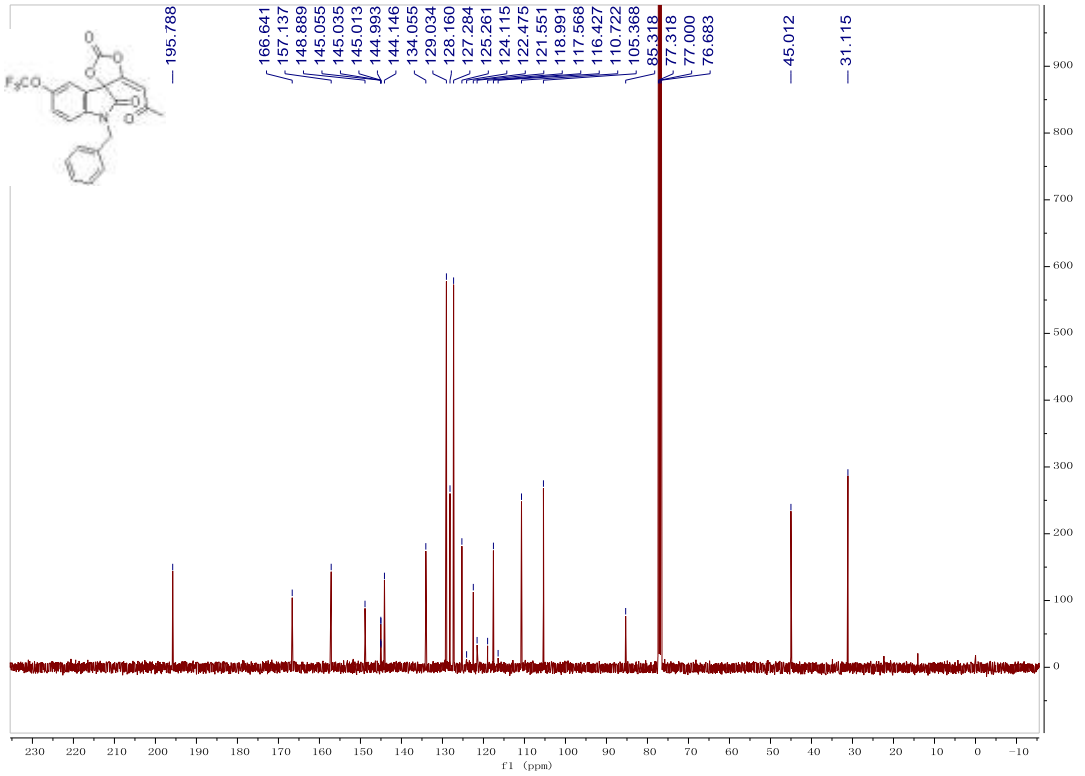


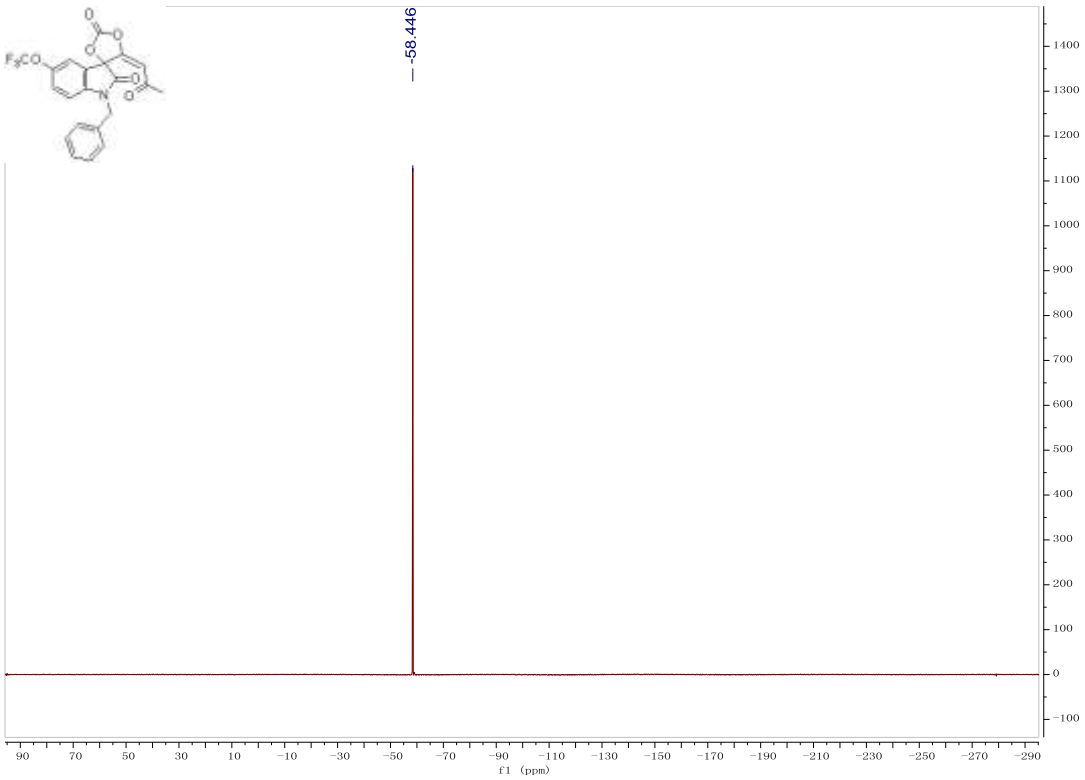
(*E*)-1-benzyl-5'-(2-oxopropylidene)-5-(trifluoromethoxy)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2v)

A white solid, 79% yield (103 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.16 (s, 3H, CH_3), 4.85 (d, *J* = 16.0 Hz, 1H, CH_2), 5.18 (d, *J* = 16.0 Hz, 1H, CH_2), 6.44 (s, 1H, =CH), 6.76 (d, *J* = 8.4 Hz, 1H, ArH), 7.06 (s, 1H, ArH), 7.17 (d, *J* = 8.4 Hz, 1H, ArH), 7.30-7.42 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 31.1, 45.0, 85.3, 105.4, 110.7, 117.6, 120.3 (q, *J* = 256.0 Hz), 122.5, 125.3, 127.3, 128.2, 129.0, 134.1, 144.1, 145.0 (q, *J* = 2.2 Hz), 148.9, 157.1, 166.6, 195.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -58.45. IR (EtOH) ν 2922, 2844, 1852, 1742, 1708, 1608, 1492, 1455, 1323, 1256, 1162 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{20}H_{15}O_4NF_3^{+1}(M+H-CO_2)^+$ requires 390.0948, Found: 390.0946. $[\alpha]^{25}_D$ = -17.78 (c 0.06, CH_2Cl_2) for 86% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H

column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 21.102 min, t_{major} = 16.747 min.







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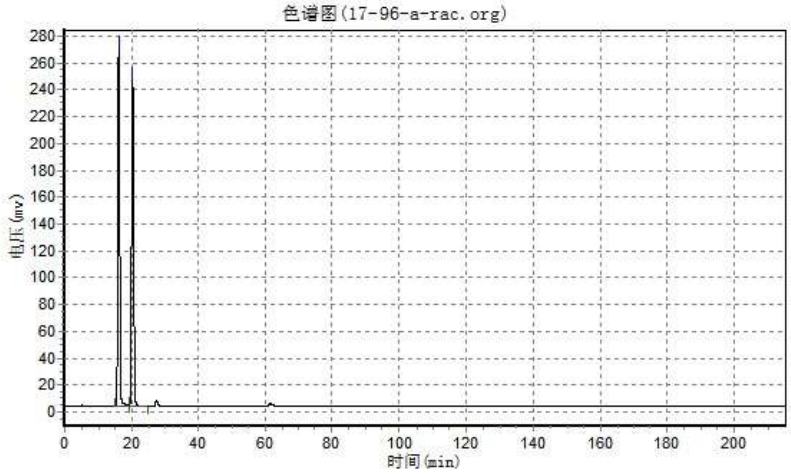
实验者:
报告时间：2019-07-18,20:29:42
积分方法:面积归一法



分析结果表

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2		20.348	244204.922	10903556.000	49.7052
总计			511223.078	21936448.000	100.0000

实验时间：2019-07-18,14:11:10
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实验者：
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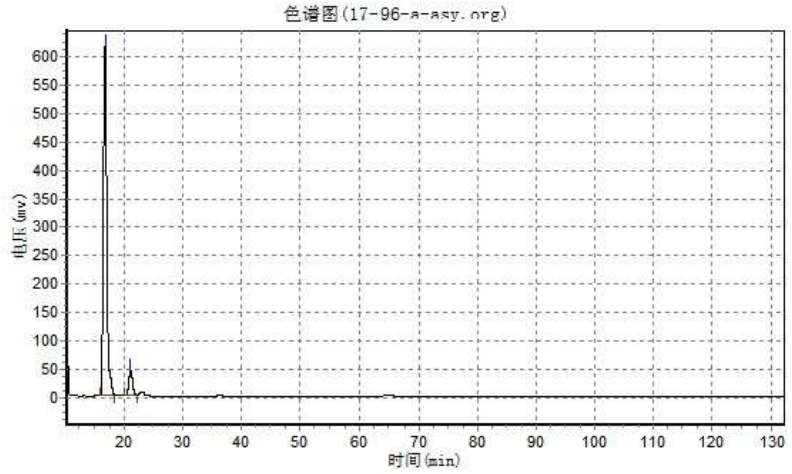
积分方法:面积归一法



分析结果表

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2		21.102	43680.922	1984732.625	7.2079
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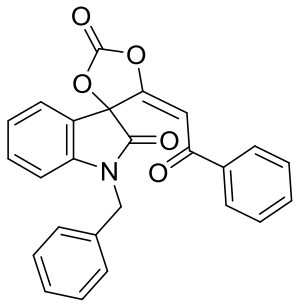
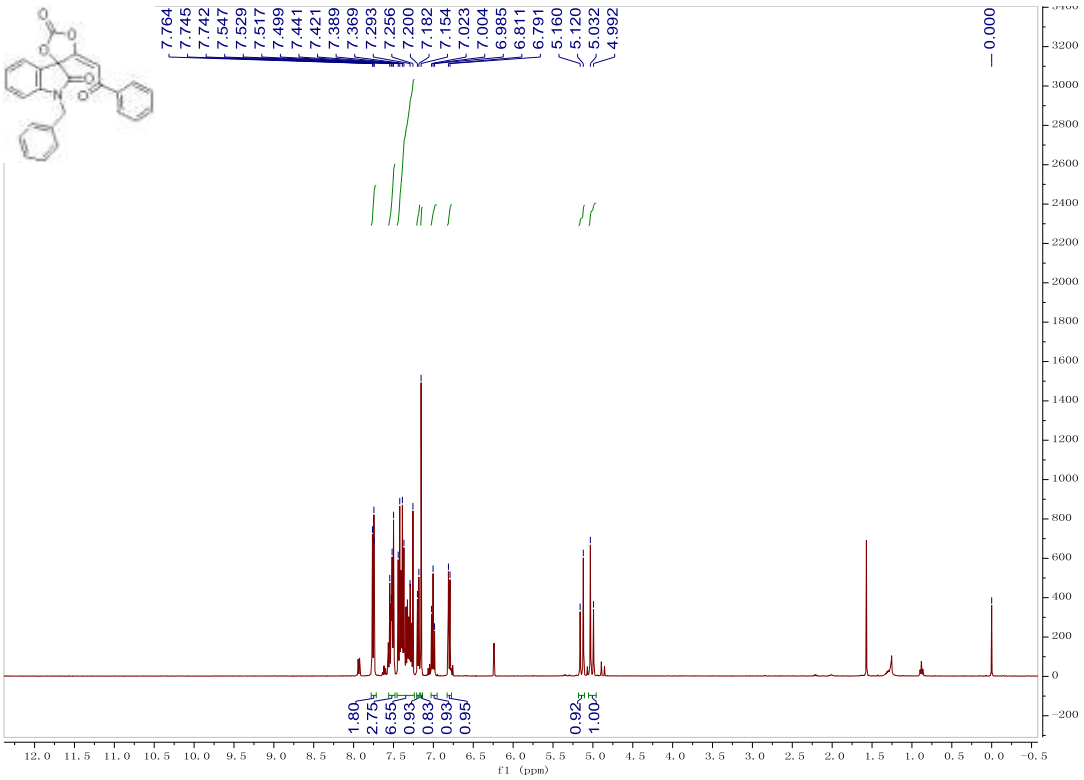


(*E*)-1-benzyl-5'-(2-oxo-2-phenylethylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2w)

A white solid, 44% yield (54 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 5.01 (d, *J* = 16.0 Hz, 1H, CH_2), 5.14 (d, *J* = 16.0 Hz, 1H, CH_2), 6.80 (d, *J* = 8.0 Hz, 1H, ArH), 7.00 (t, *J* = 7.6 Hz, 1H, ArH), 7.15 (s, 1H, =CH), 7.19 (d, *J* = 7.2 Hz, 1H, ArH), 7.25-7.45 (m, 6H, ArH), 7.49-7.55 (m, 3H, ArH), 7.74-7.77 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.9, 86.3, 101.9, 110.1, 121.4, 123.5, 123.6, 127.5, 127.9, 128.1, 128.7, 128.8, 132.2, 133.6, 134.7, 136.6, 145.6, 149.4, 159.5, 167.0, 187.4. IR (EtOH) ν 3081, 3055, 2959, 1899, 1850, 1742, 1611, 1466, 1356, 1182, 1004 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{24}H_{21}O_3N_2^{+1}(M+NH_4-CO_2)^+$ requires 385.1450, Found: 385.1450.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7.529
7.517
7.499
7.441
7.421
7.389
7.369
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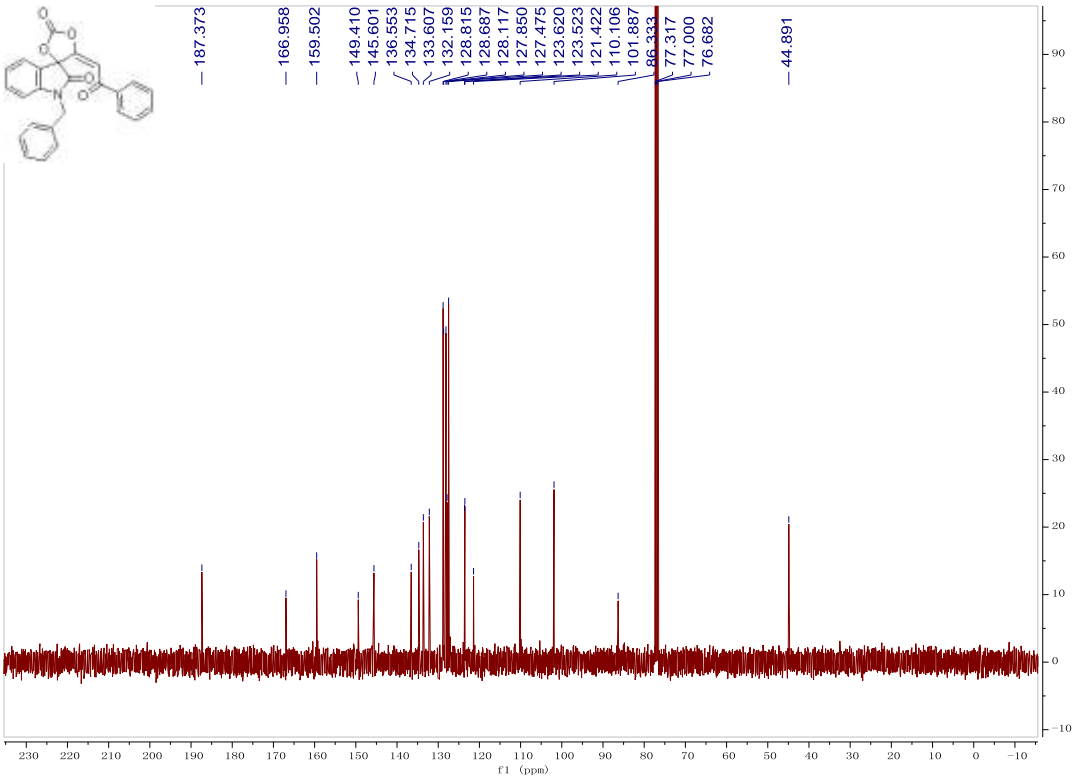
7.200
7.182
7.154
7.023
7.004
6.985
6.811
6.791
5.160
5.120
5.032
4.992
0.000
1.80
2.75
6.55
0.93
0.83
0.93
0.95
0.92
1.00
f1 (ppm)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145.601
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134.715
133.607
132.159
128.815
128.687
128.117
127.850
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121.422
110.106
101.887
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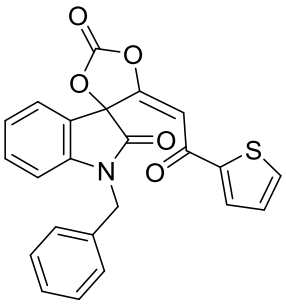
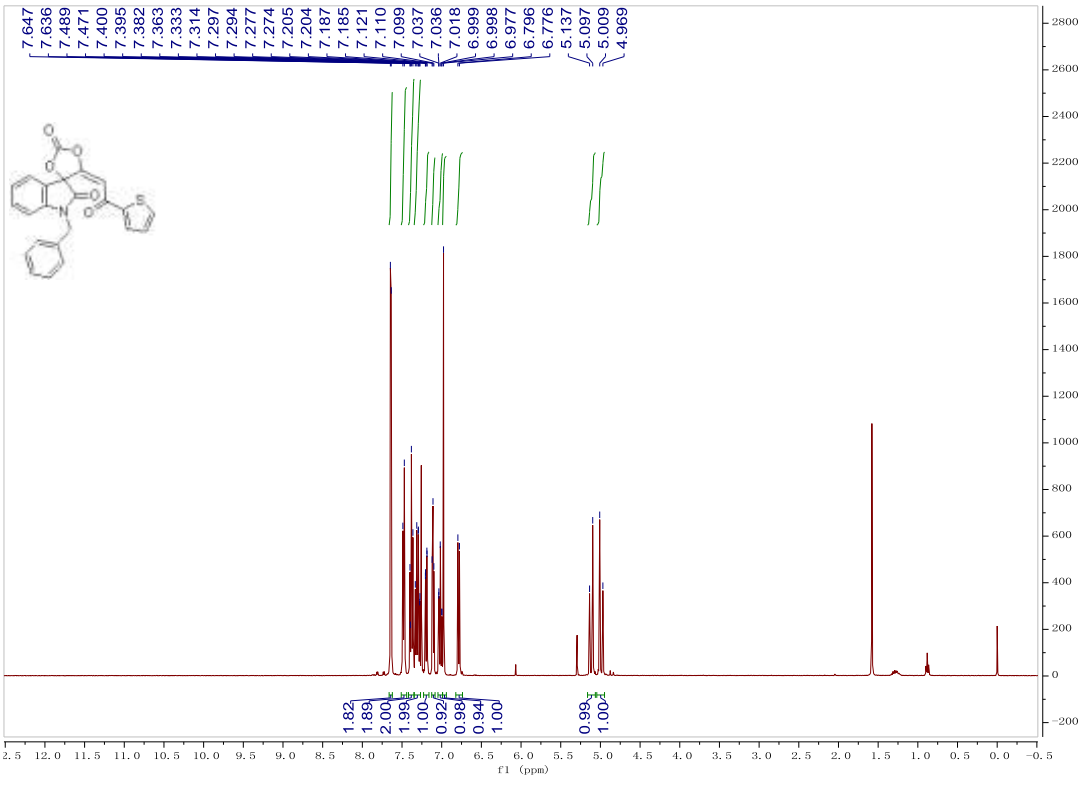
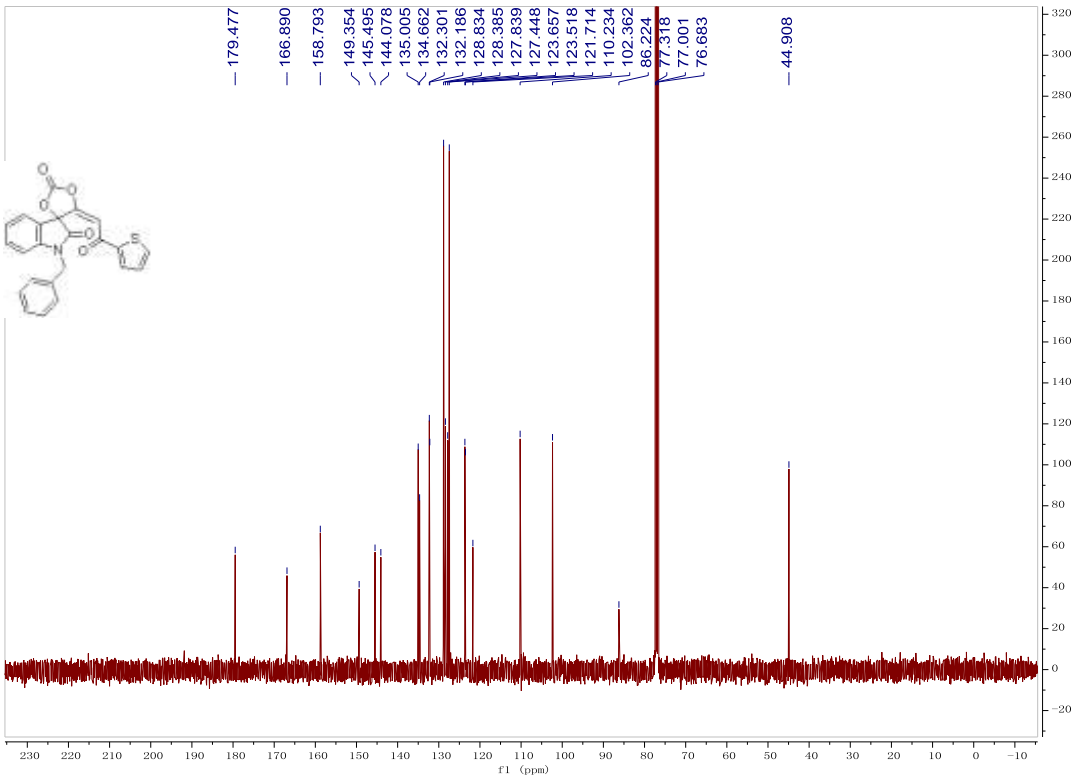
77.317
77.000
76.682
44.891
f1 (ppm)

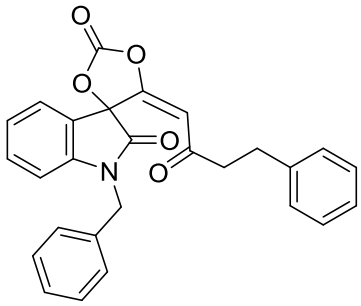


(*E*)-1-benzyl-5'-(2-oxo-2-(thiophen-2-yl)ethylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2x)

A white solid, 56% yield (70 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 4.99 (d, *J* = 16.0 Hz, 1H, CH_2), 5.12 (d, *J* = 16.0 Hz, 1H, CH_2), 6.79 (d, *J* = 8.0 Hz, 1H, ArH), 6.98 (s, 1H, =CH), 6.99-7.04 (m, 2H, ArH), 7.11 (t, *J* = 4.4 Hz, 1H, ArH), 7.20 (dd, *J* = 0.4, 7.2 Hz, 1H, ArH), 7.27-7.34 (m, 2H, ArH), 7.36-7.40 (m, 2H, ArH), 7.48 (d, *J* = 7.2 Hz, 2H, ArH), 7.64 (d, *J* = 4.4 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.9, 86.2, 102.4, 110.2, 121.7, 123.5, 123.7, 127.4, 127.8, 128.4, 128.8, 132.2, 132.3, 134.7, 135.0, 144.1, 145.5, 149.4, 158.8, 166.9, 179.5. IR (EtOH) ν 3102, 3089, 2919, 1728, 1693, 1579, 1466, 1340, 1109, 971, 835, 732 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{22}H_{16}O_3NS^{+1}$(M+H-CO_2)$^{+}$ requires 374.0845, Found: 374.0845.

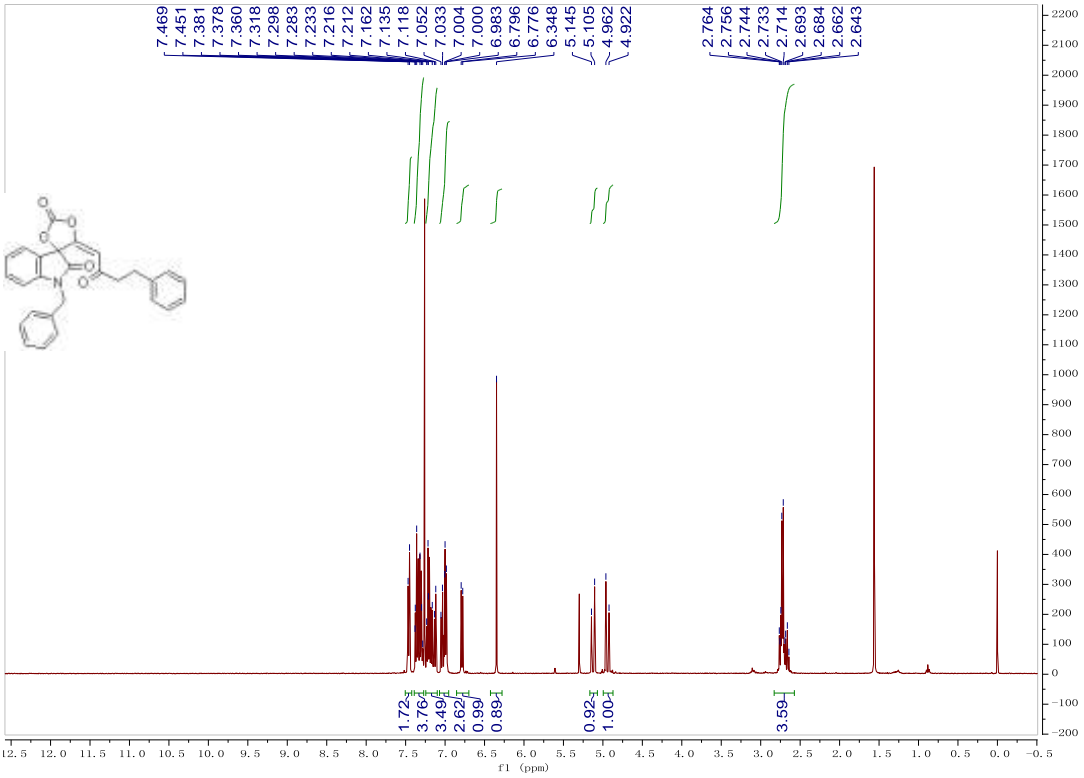






(*E*)-1-benzyl-5'-(2-oxo-4-phenylbutylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2y)

A white solid, 73% yield (96 mg). M.p.: Decomposition above 60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.64-2.77 (m, 4H, CH_2), 4.94 (d, *J* = 16.0 Hz, 1H, CH_2), 5.13 (d, *J* = 16.0 Hz, 1H, CH_2), 6.35 (s, 1H, =CH), 6.79 (d, *J* = 8.0 Hz, 1H, ArH), 6.98-7.05 (m, 3H, ArH), 7.11-7.24 (m, 4H, ArH), 7.28-7.39 (m, 4H, ArH), 7.46 (d, *J* = 7.2 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 29.6, 44.9, 45.4, 86.1, 104.6, 110.1, 121.4, 123.5, 123.6, 126.2, 127.4, 127.9, 128.2, 128.5, 128.9, 132.2, 134.6, 140.2, 145.6, 149.4, 157.9, 166.8, 196.9. IR (EtOH) ν 2924, 2853, 1844, 1731, 1702, 1583, 1467, 1455, 1415, 1022, 970, 792, 697 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{26}H_{25}O_3N_2^{+1}(M+NH_4-CO_2)^+$ requires 413.1758, Found: 413.1755.


7.469
7.451
7.381
7.378
7.360
7.318
7.298
7.283
7.233
7.216
7.212
7.162
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7.118
7.052
7.033
7.004
7.000
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6.796
6.776
6.348
5.145
5.105
4.962
4.922
2.764
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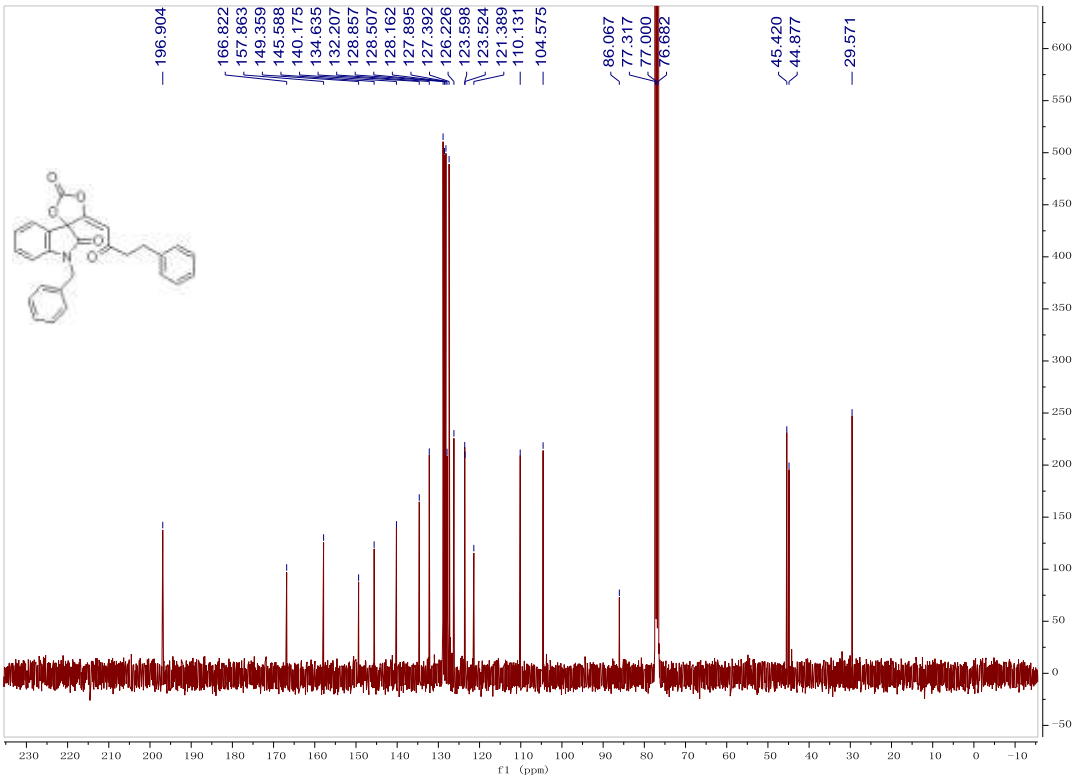
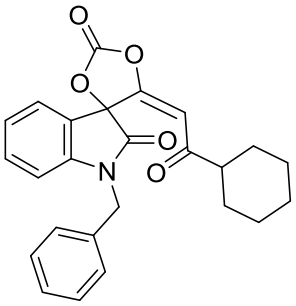
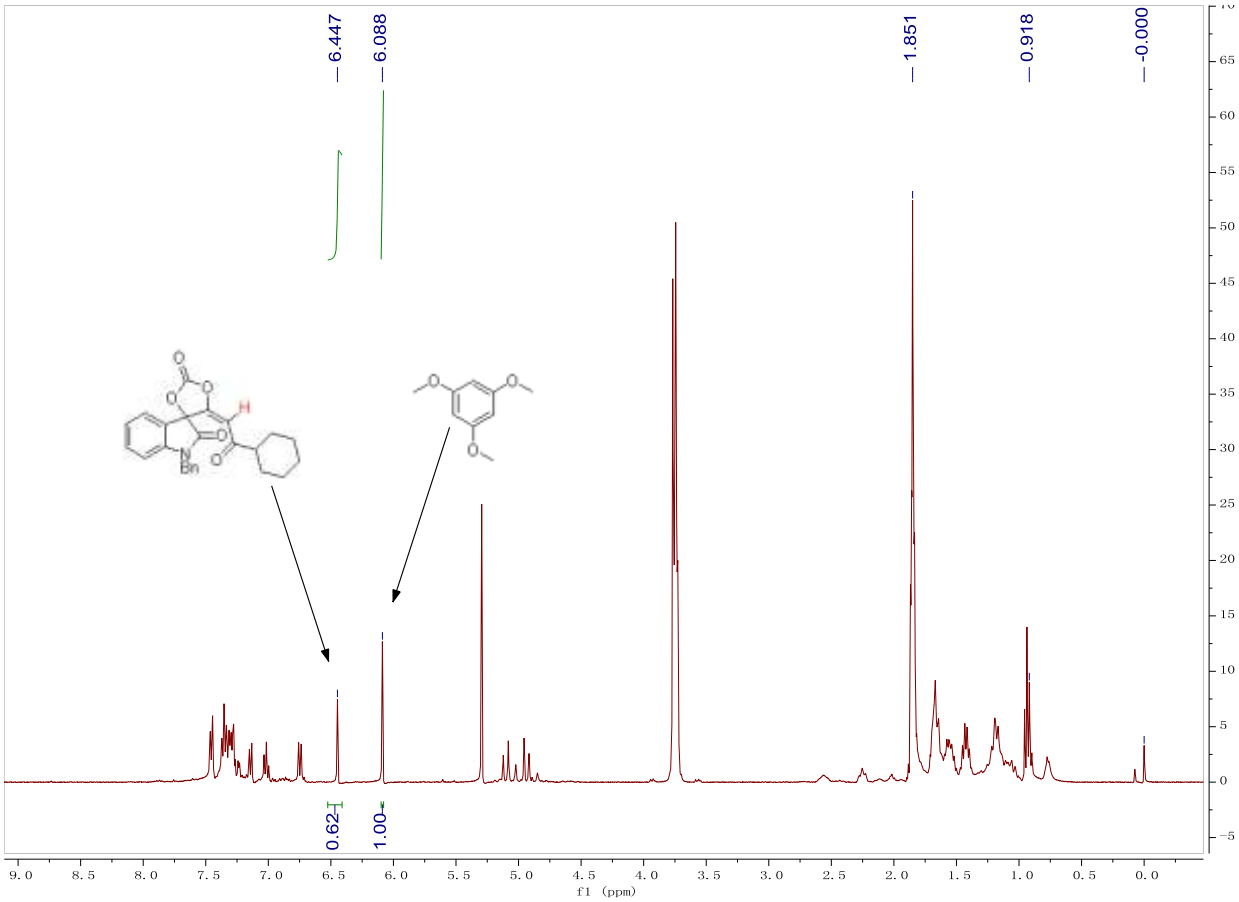
2.744
2.733
2.714
2.693
2.684
2.662
2.643
1.72
3.76
3.49
2.62
0.99
0.89
0.92
1.00
3.59
f1 (ppm)

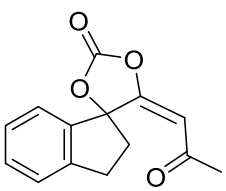

196.904
166.822
157.863
149.359
145.588
140.175
134.635
132.207
128.857
128.507
128.162
127.895
127.392
126.226
123.598
123.524
121.389
110.131
104.575
86.067
77.317
77.000
76.682
45.420
44.877
29.571
f1 (ppm)



(*E*)-1-benzyl-5'-(2-cyclohexyl-2-oxoethylidene)spiro[indoline-3,4'-[1,3]dioxolane]-2,2'-dione (2z)

Compound **2z** was very unstable in silica gel chromatography. We determined 62% yield of **2z** with ^{1}H NMR by using 1,3,5-trimethoxybenzene as an internal standard.

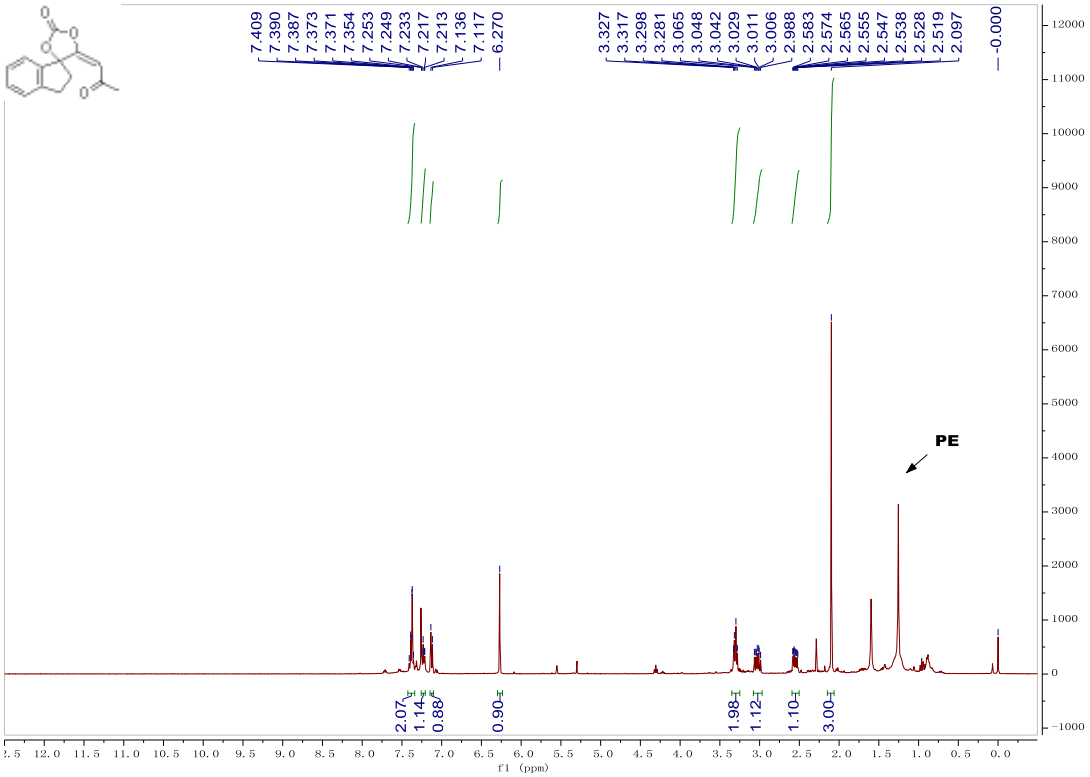


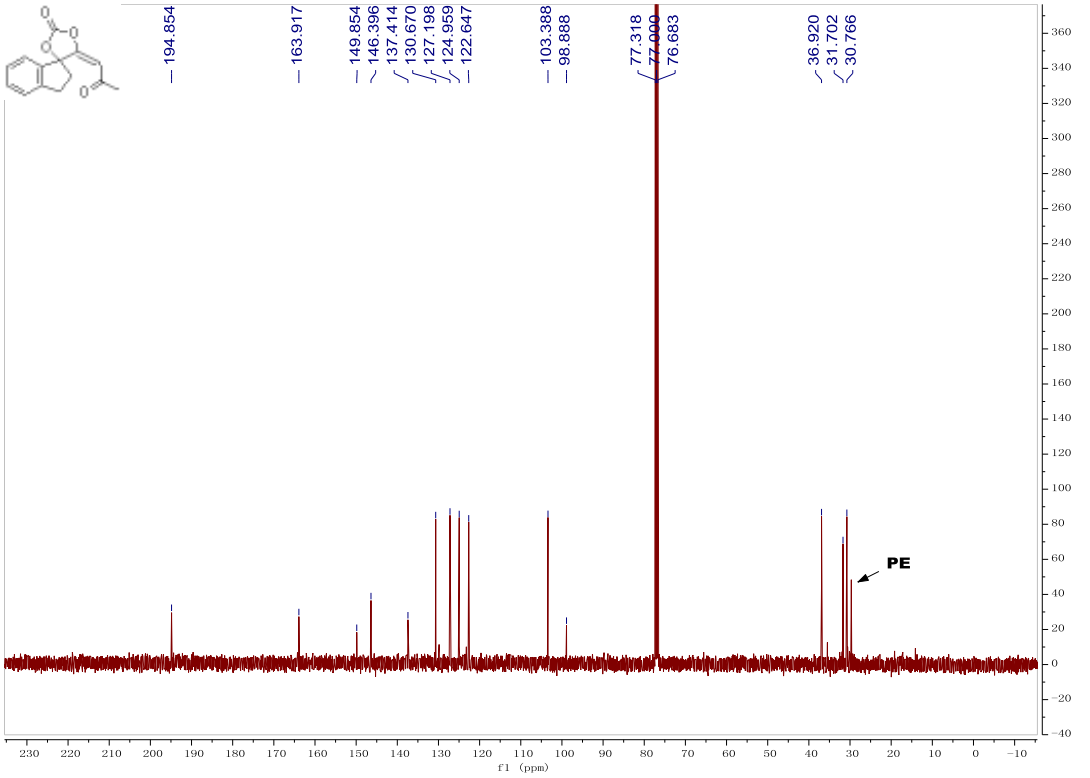


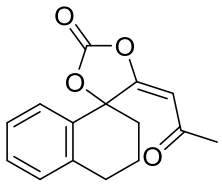
(*E*)-5'-(2-oxopropylidene)-2,3-dihydrospiro[indene-1,4'-[1,3]dioxolan]-2'-one (2ad)

A viscous liquid, 32% yield (23 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.10 (s, 3H, CH_3),

2.51-2.59 (m, 1H, CH_2), 2.98-3.07 (m, 1H, CH_2), 3.28-3.33 (m, 2H, CH_2), 6.27 (s, 1H, =CH), 7.13 (d, *J* = 7.6 Hz, 1H, ArH), 7.21-7.26 (m, 1H, ArH), 7.35-7.41 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 30.8, 31.7, 36.9, 98.9, 103.4, 122.6, 125.0, 127.2, 130.7, 137.4, 146.4, 149.9, 163.9, 194.9. IR (EtOH) ν 2937, 2861, 1835, 1695, 1595, 1491, 1384, 1340, 1119, 949, 796 cm^{-1}. HRMS (EI) calcd. for $C_{13}H_{12}O_2^{+1}(M\text{-}CO_2)^+$ requires 200.0837, Found: 200.0841.

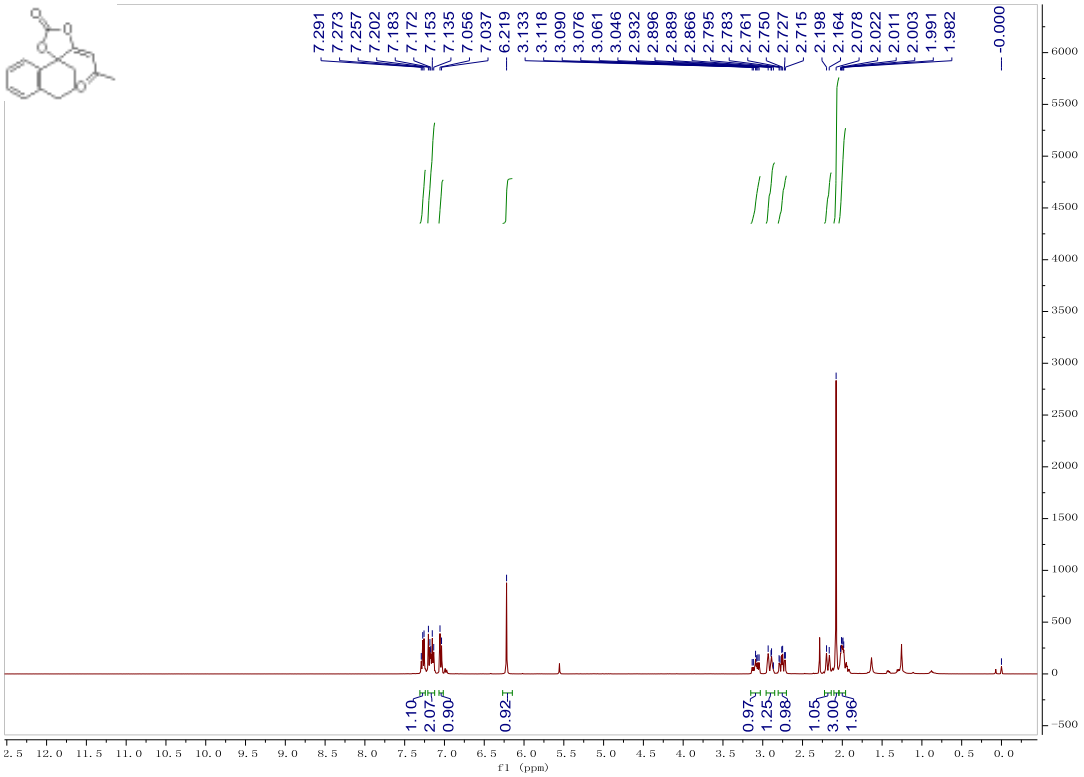


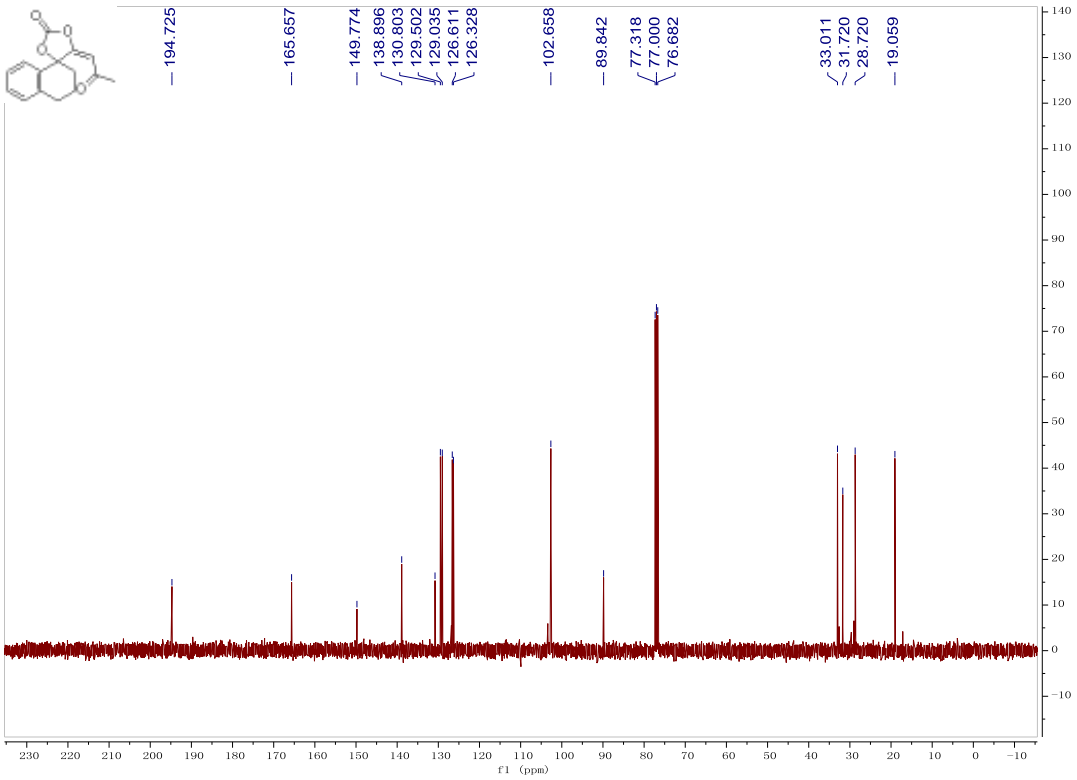


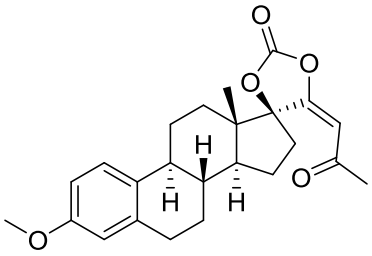


(*E*)-5'-(2-oxopropylidene)-3,4-dihydro-2H-spiro[naphthalene-1,4'-[1,3]dioxolan]-2'-one (2ae)

A viscous liquid, 39% yield (30 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.98-2.03 (m, 2H, CH_2), 2.08 (s, 3H, CH_3), 2.18 (d, *J* = 13.6 Hz, 1H, CH_2), 2.76 (dt, *J* = 4.4, 13.6 Hz, 1H, CH_2), 2.86-2.94 (m, 1H, CH_2), 3.04-3.14 (m, 1H, CH_2), 6.22 (s, 1H, =CH), 7.05 (d, *J* = 7.6 Hz, 1H, ArH), 7.13-7.21 (m, 2H, ArH), 7.25-7.30 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 19.1, 28.7, 31.7, 33.0, 89.8, 102.7, 126.3, 126.6, 129.0, 129.5, 130.8, 138.9, 149.8, 165.7, 194.7. IR (EtOH) ν 2922, 2851, 1834, 1698, 1598, 1385, 1342, 1162, 1097, 990, 914, 764 cm^{-1}. HRMS (EI) calcd. for $C_{14}H_{14}O_2^{+1}(M\text{-}CO_2)^+$ requires 214.0994, Found: 214.0990.



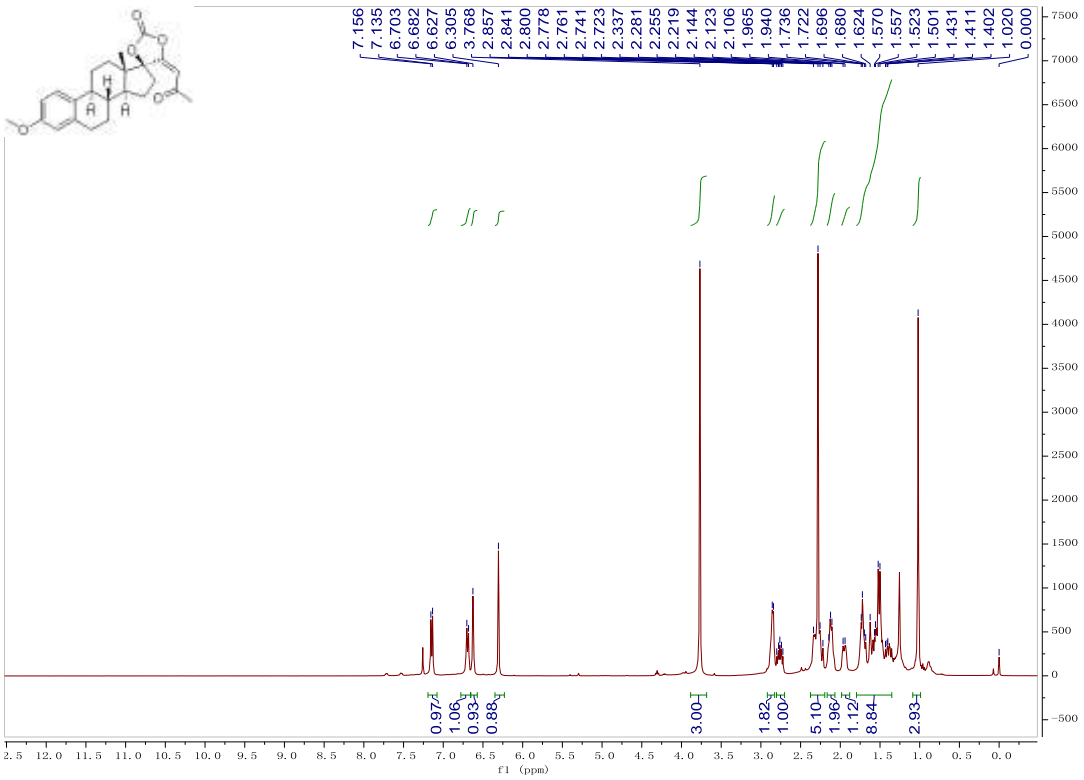


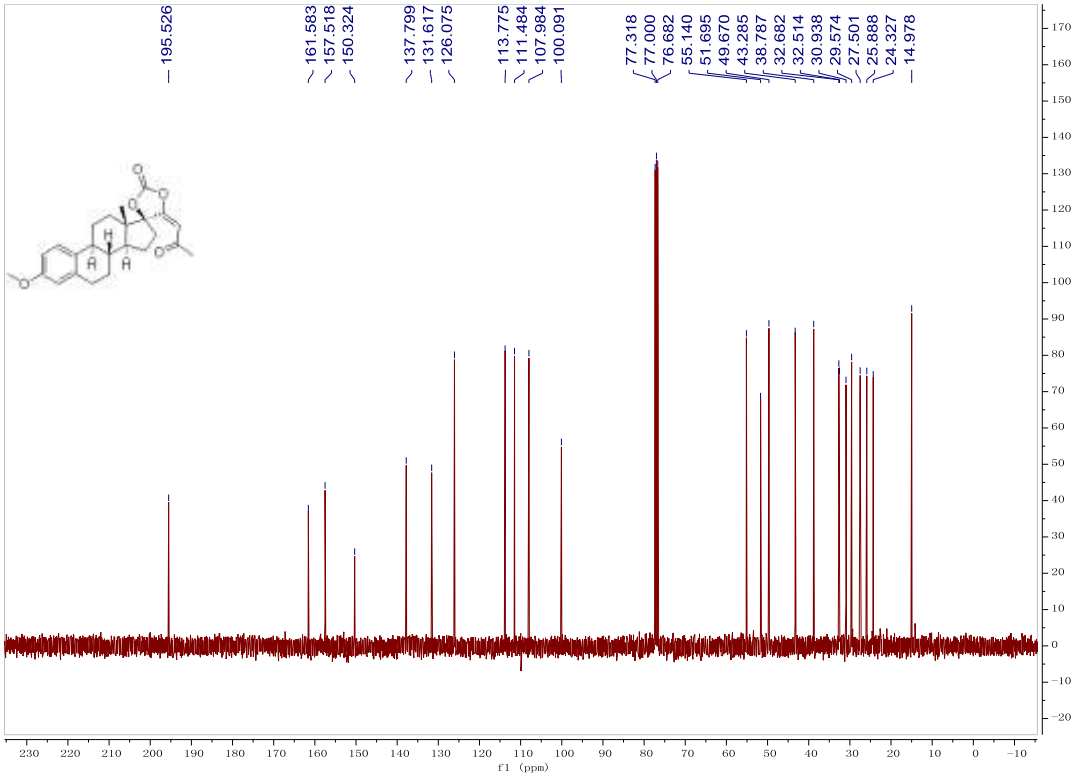


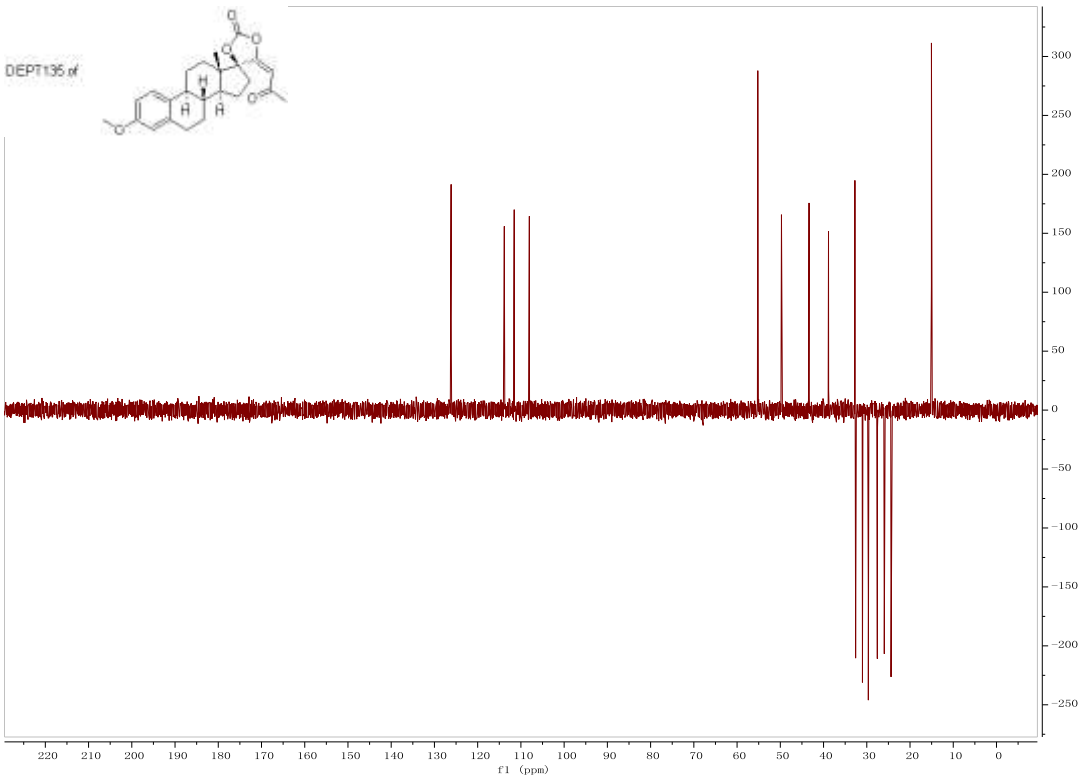
(8R,9S,13S,14S,17S,

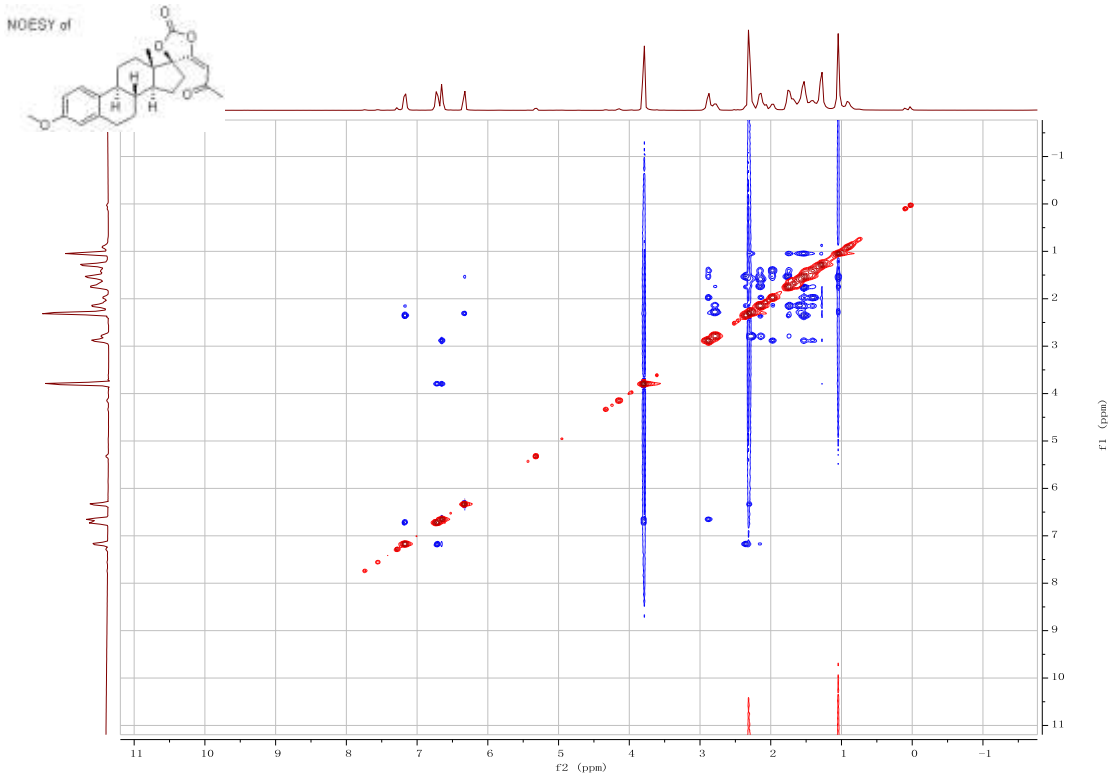
***E*)-3-methoxy-13-methyl-5'-(2-oxopropylidene)-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,4'-[1,3]dioxolan]-2'-one (2af)**

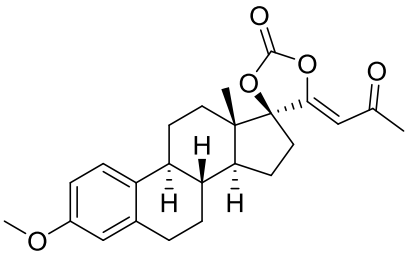
A white solid, 44.5% yield (53 mg). M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.02 (s, 3H, CH_3), 1.40-1.74 (m, 8H), 1.95 (d, *J* = 6.0 Hz, 1H), 2.10-2.15 (m, 2H), 2.21-2.34 (m, 5H), 2.72-2.80 (m, 1H), 2.84-2.91 (m, 2H), 3.77 (s, 3H, CH_3), 6.31 (s, 1H, =CH), 6.63 (s, 1H, ArH), 6.69 (d, *J* = 8.4 Hz, 1H, ArH), 7.14 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 15.0, 24.3, 25.9, 27.5, 29.6, 30.9, 32.5, 32.7, 38.8, 43.3, 49.7, 51.7, 55.1, 100.1, 108.0, 111.5, 113.8, 126.1, 131.6, 137.8, 150.3, 157.5, 161.6, 195.5. IR (EtOH) ν 2926, 2835, 1829, 175, 1633, 1499, 1267, 1069, 1027, 973 cm^{-1}. HRMS (ESI) Calcd. For $C_{24}H_{29}O_5^{+1}$(M+H)$^+$ requires 397.2010, Found: 397.2008.


7.156
7.135
6.703
6.682
6.627
6.305
3.768
2.857
2.841
2.800
2.778
2.761
2.741
2.723
2.337
2.281
2.255
2.219
2.144
2.123
2.106
1.965
1.940
1.736
1.722
1.696
1.680
1.624
1.570
1.557
1.523
1.501
1.431
1.411
1.402
1.020
0.000
0.97
1.06
0.93
0.88
3.00
1.82
1.00
5.10
1.96
1.12
8.84
2.93
f1 (ppm)


195.526
161.583
157.518
150.324
137.799
131.617
126.075
113.775
111.484
107.984
100.091
77.318
77.000
76.682
55.140
51.695
49.670
43.285
38.787
32.682
32.514
30.938
29.574
27.501
25.888
24.327
14.978
f1 (ppm)


DEPT135 of
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

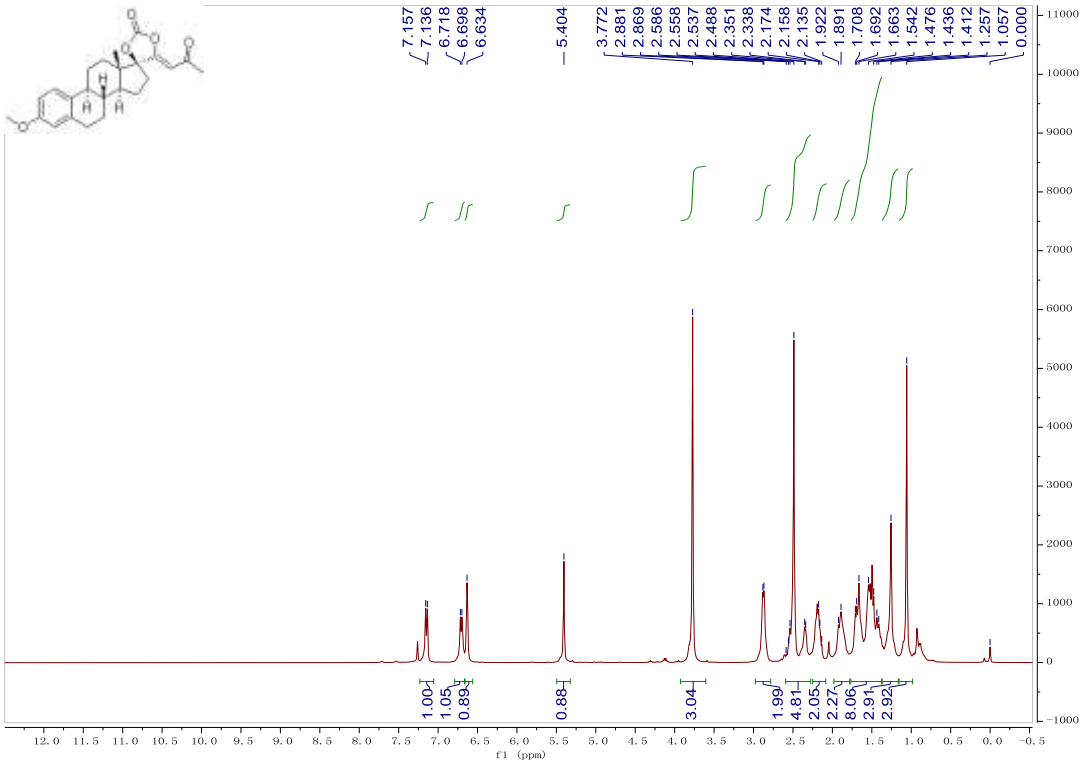

NOESY of
f1 (ppm)
11 10 9 8 7 6 5 4 3 2 1 0 -1
f2 (ppm)

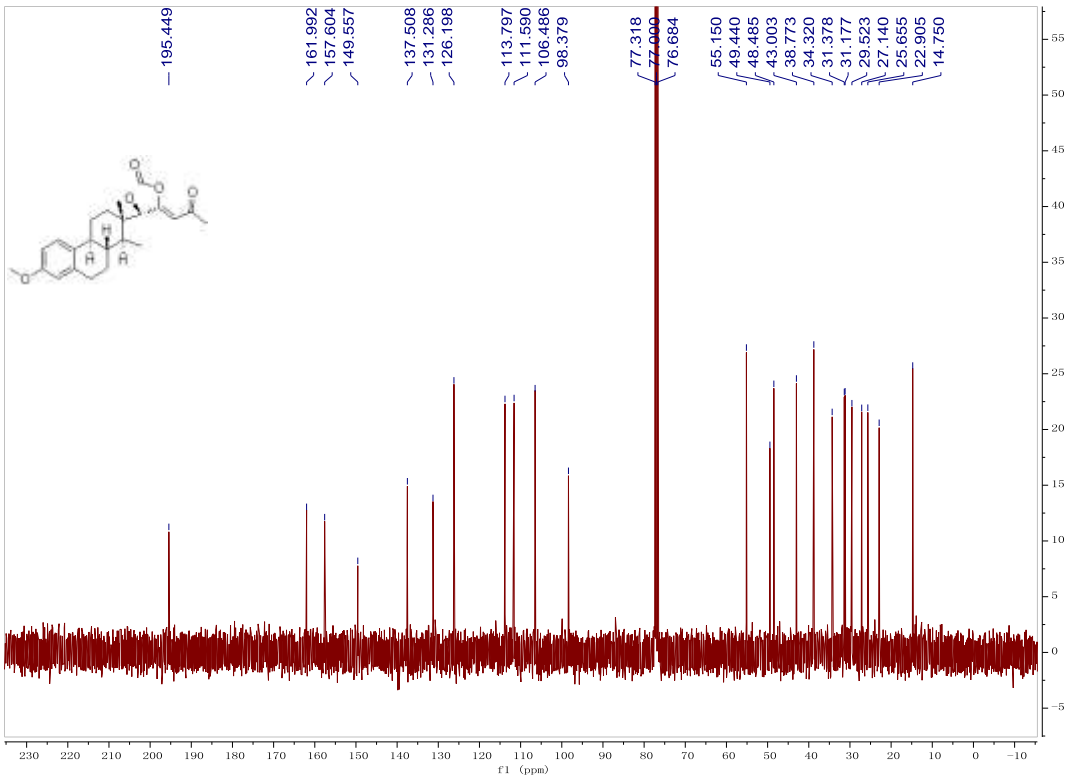


(8R,9S,13S,14S,17S,

***Z*)-3-methoxy-13-methyl-5'-(2-oxopropylidene)-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,4'-[1,3]dioxolan]-2'-one (2af')**

A white solid, 44.5% yield (53 mg). M.p.: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.06 (s, 3H, CH_3), 1.26 (br, 3H), 1.41-1.71 (m, 8H), 1.89-1.93 (m, 2H), 2.13-2.18 (m, 2H), 2.33-2.59 (m, 5H), 2.88 (d, *J* = 4.8 Hz, 2H), 3.77 (s, 3H, CH_3), 5.40 (s, 1H, =CH), 6.63 (s, 1H, ArH), 6.71 (d, *J* = 8.0 Hz, 1H, ArH), 7.15 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 14.8, 22.9, 25.7, 27.1, 29.5, 31.2, 31.4, 34.3, 38.8, 43.0, 48.5, 49.4, 55.2, 98.4, 106.5, 111.6, 113.8, 126.2, 131.3, 137.5, 149.6, 157.6, 162.0, 195.4. IR (EtOH) ν 2919, 2850, 1834, 1706, 1671, 1635, 1609, 1363, 1303, 1254, 1149, 1027, 784 cm^{-1}. HRMS (ESI) Calcd. For $C_{24}H_{32}NO_5^{+1}(M+NH_4)^+$ requires 414.2275, Found: 414.2271.




195.449
161.992
157.604
149.557
137.508
131.286
126.198
113.797
111.590
106.486
98.379
77.318
77.000
76.684
55.150
49.440
48.485
43.003
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34.320
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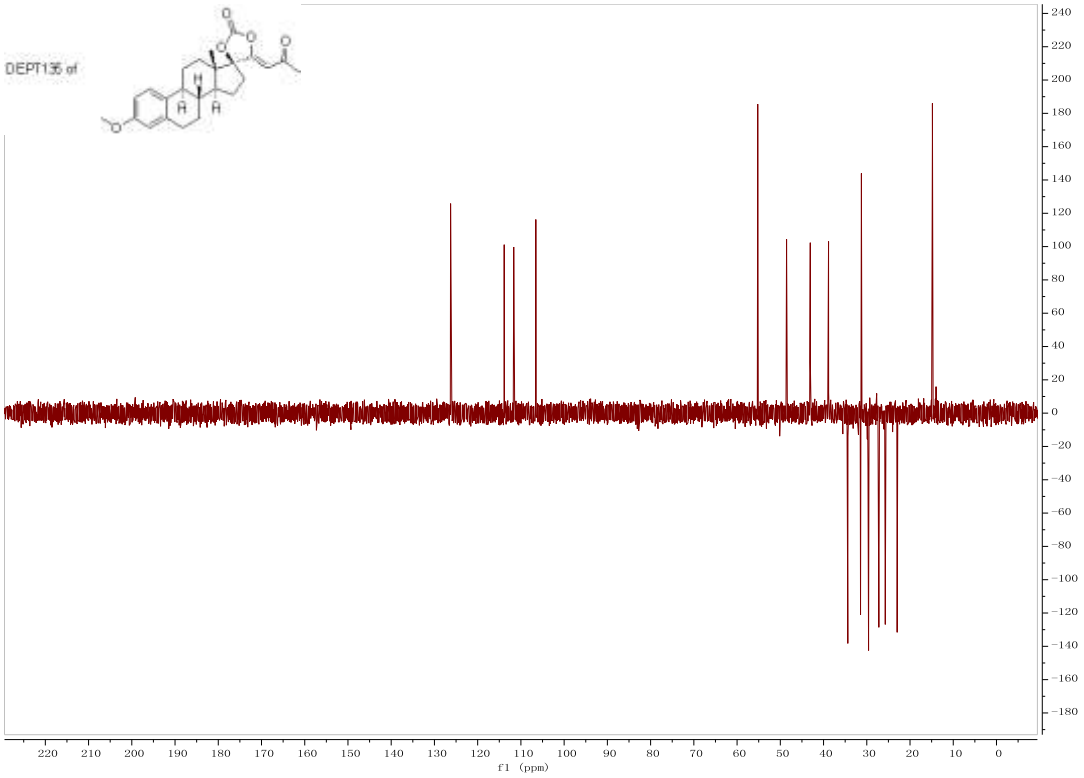
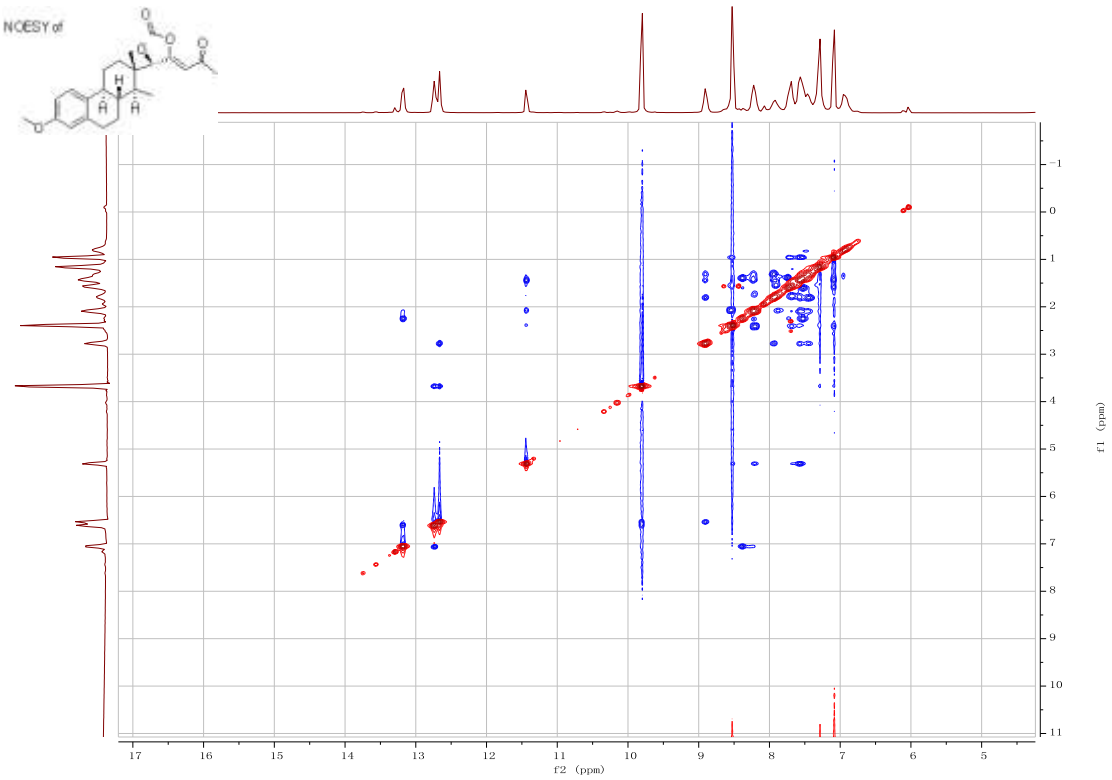
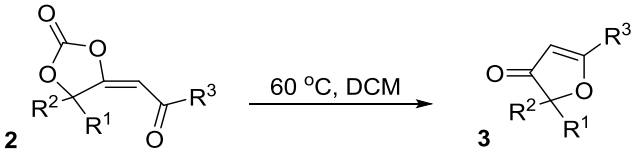
31.177
29.523
27.140
25.655
22.905
14.750
f1 (ppm)


DEPT135 of
f1 (ppm)

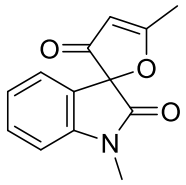

NOESY of
f2 (ppm)
f1 (ppm)

4. General Procedure for Decarboxylative Cyclization of Cyclic Carbonates 2 and Spectroscopic Data of Furanones 3



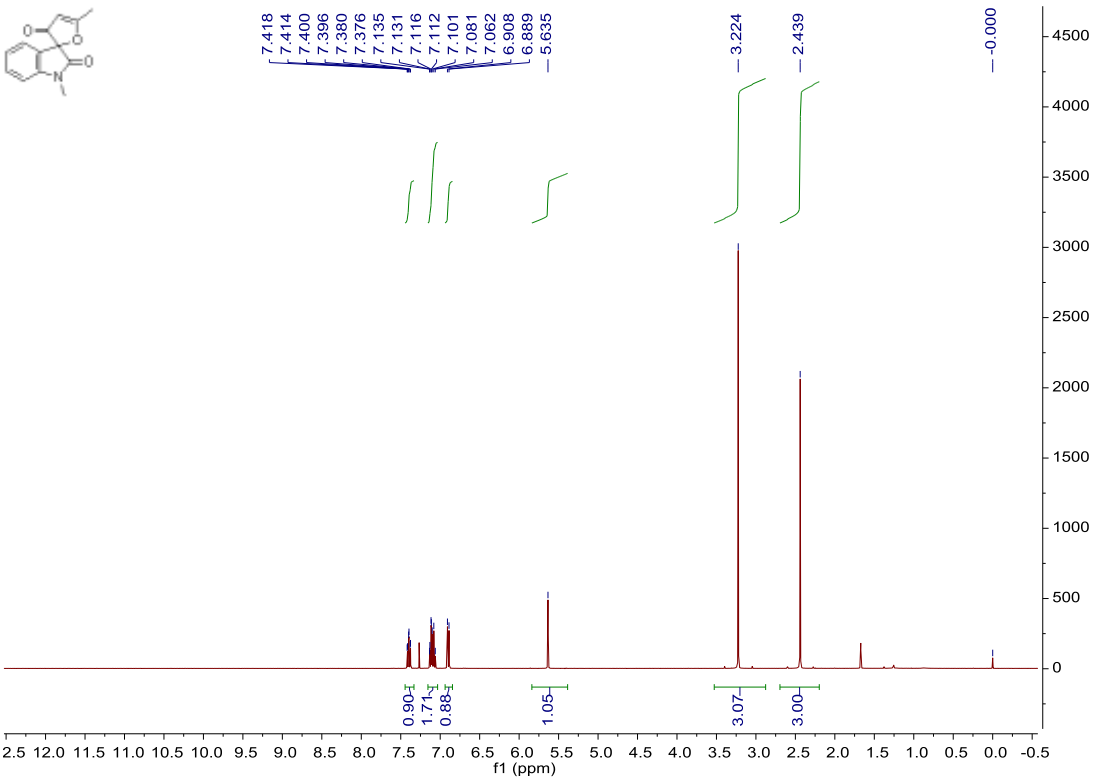
2 **3**

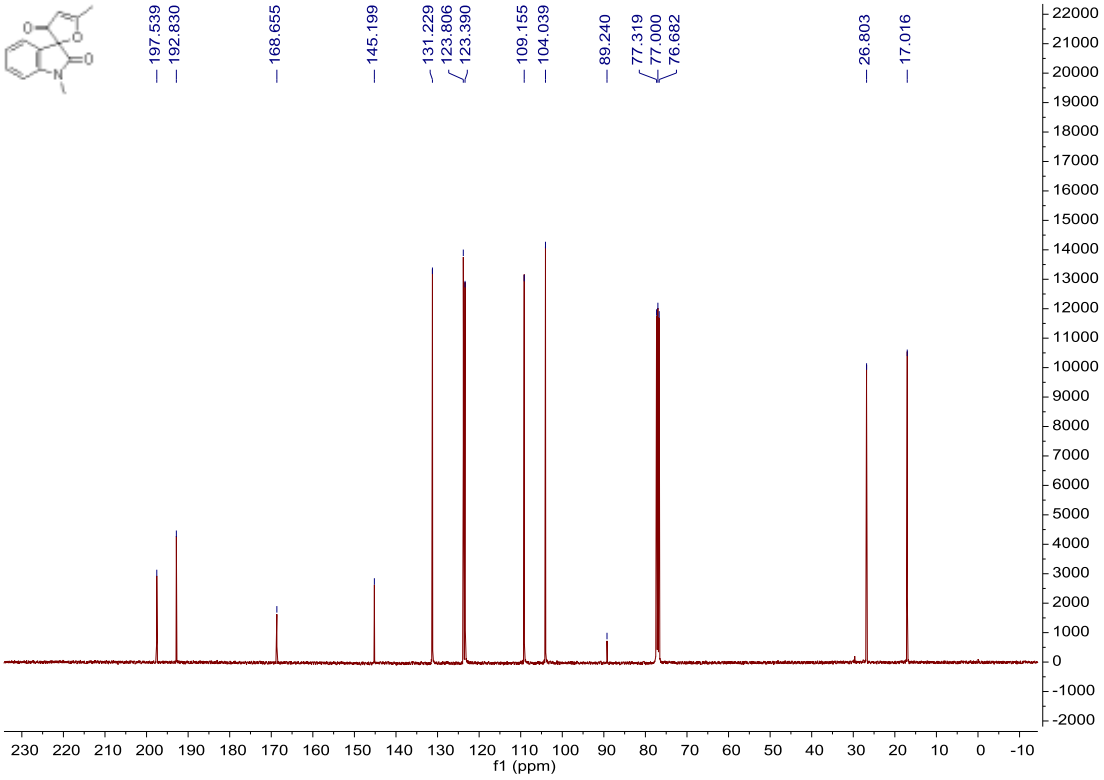
A Schlenk tube was heated under vacuum to remove ambient moisture and water, then filled with argon. After the Schlenk tube was returned to room temperature, cyclic carbonate **2** (0.2 mmol) was added and dissolved in 1.0 mL DCM. After that, the resulting mixture was heated to 60 ^{o}C and was stirred at 60 ^{o}C until the reaction completed upon monitoring by TLC. Then the solvent was removed under reduced pressure and the residue was directly subjected to a flash column chromatography on silica gel to afford the desired products **3**.

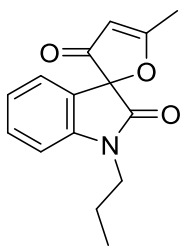


1',5-dimethyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3a)

A white solid, 86% yield (39 mg). M.p.: 117-119 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.44 (s, 3H, CH_3), 3.22 (s, 3H, CH_3), 5.64 (s, 1H, =CH), 6.90 (d, *J* = 7.6 Hz, 1H, ArH), 7.06-7.14 (m, 2H, ArH), 7.40 (dt, *J* = 1.6, 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 26.8, 89.2, 104.0, 109.2, 123.4, 123.8, 131.2, 145.2, 168.7, 192.8, 197.5. IR (EtOH) ν 3052, 2917, 2849, 1730, 1696, 1597, 1490, 1453, 1323, 1161, 978, 756 cm^{-1}. HRMS (ESI) Calcd. For $C_{13}H_{12}NO_3^{+1}(M+H)^+$ requires 230.0812, Found: 230.0809.

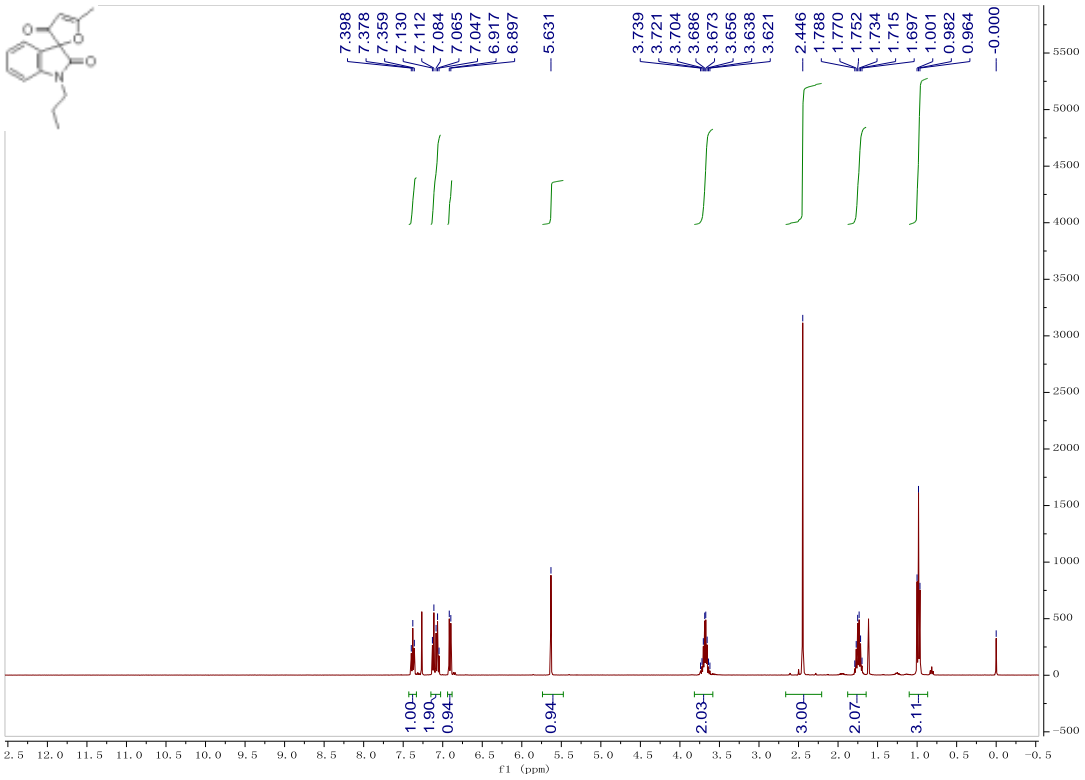

7.418
7.414
7.400
7.396
7.380
7.376
7.135
7.131
7.116
7.112
7.101
7.081
7.062
6.908
6.889
5.635
3.224
2.439
-0.000
0.90
1.71
0.88
1.05
3.07
3.00
f1 (ppm)

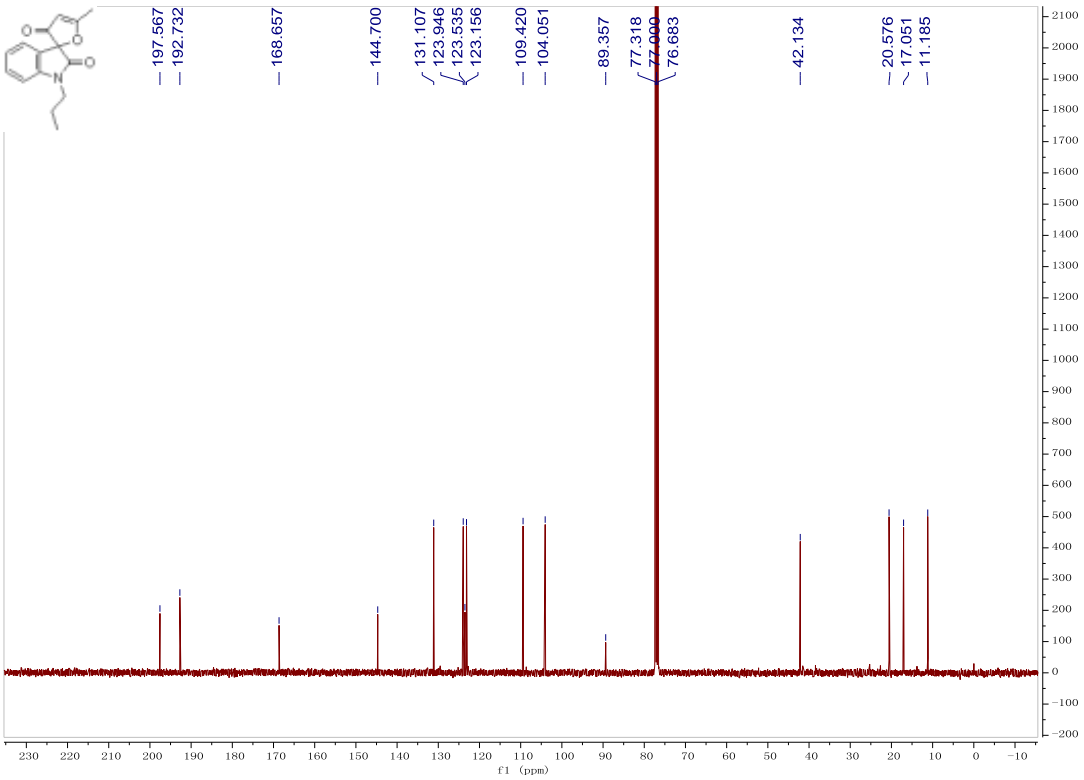

197.539
192.830
168.655
145.199
131.229
123.806
123.390
109.155
104.039
89.240
77.319
77.000
76.682
26.803
17.016
f1 (ppm)

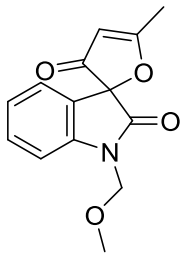

O
O
O
N

5-methyl-1'-propyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3b)

A white solid, 90% yield (46 mg). M.p.: 98-100 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.98 (t, *J* =7.6 Hz, 3H, CH_3), 1.69-1.79 (m, 2H, CH_2), 2.45 (s, 3H, CH_3), 3.62-3.74 (m, 2H, CH_2), 5.63 (s, 1H, =CH), 6.91 (d, *J* = 8.0 Hz, 1H, ArH), 7.04-7.13 (m, 2H, ArH), 7.38 (t, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 11.2, 17.1, 20.6, 42.1, 89.4, 104.1, 109.4, 123.2, 123.5, 123.9, 131.1, 144.7, 168.7, 192.7, 197.6. IR (EtOH) ν 2955, 2920, 2850, 1730, 1705, 1608, 1467, 1360, 1324, 940 cm^{-1}. HRMS (ESI) Calcd. For $C_{15}H_{16}NO_3^{+1}$(M+H)$^{+}$ requires 258.1125, Found: 258.1122.

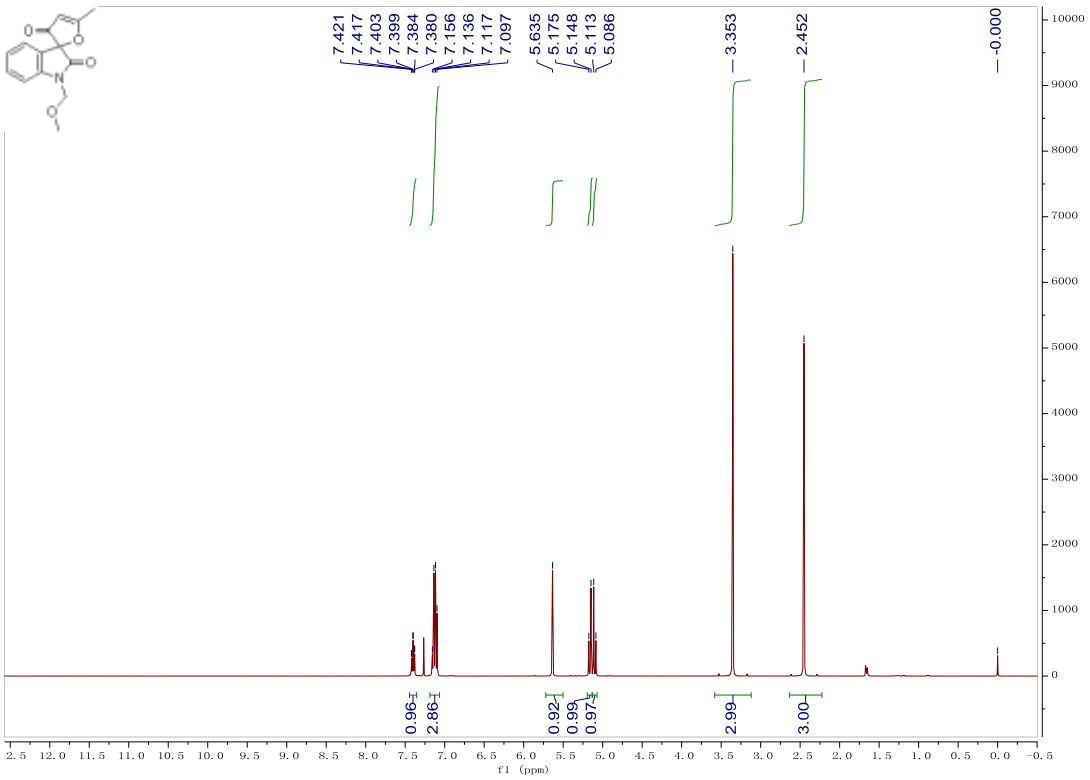


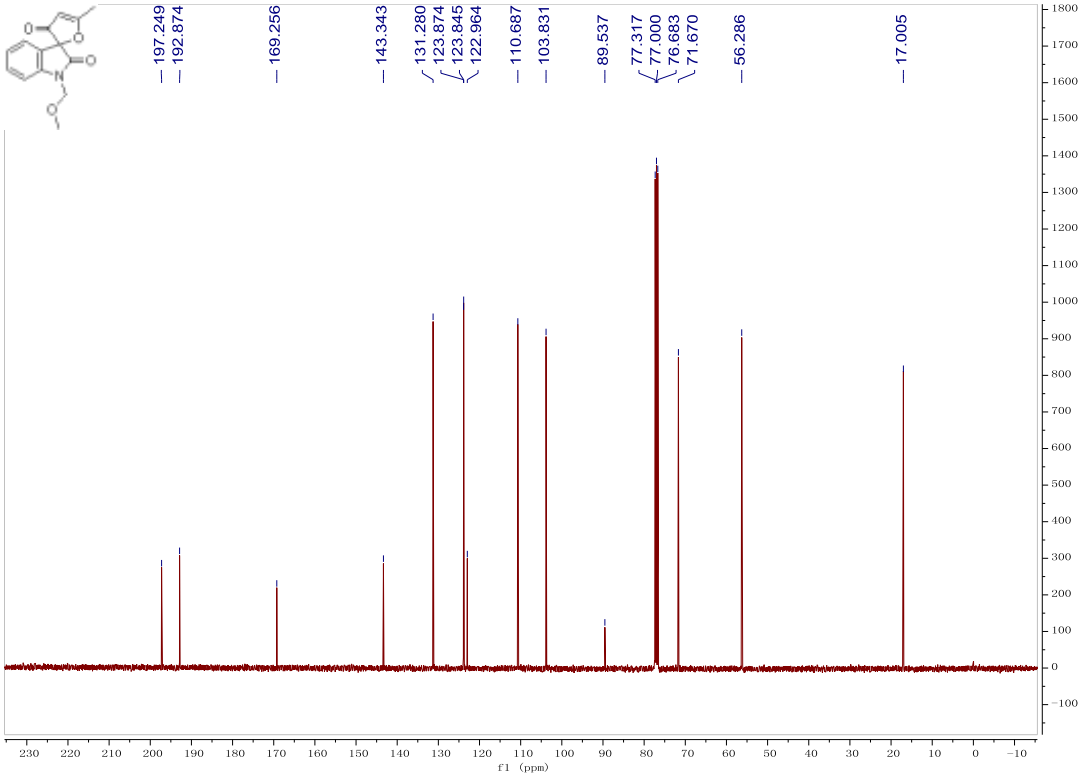




1'-(methoxymethyl)-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3c)

A white solid, 85% yield (44 mg). M.p.: 122-124 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.45 (s, 3H, CH_3), 3.35 (s, 3H, CH_3), 5.10 (d, *J* = 10.8 Hz, 1H, CH_2), 5.16 (d, *J* = 10.8 Hz, 1H, CH_2), 5.64 (s, 1H, =CH), 7.09-7.16 (m, 3H, ArH), 7.40 (dt, *J* = 1.6, 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 56.3, 71.7, 89.5, 103.8, 110.7, 123.0, 123.8, 123.9, 131.3, 143.3, 169.3, 192.9, 197.2. IR (EtOH) ν 2916, 2843, 1738, 1704, 1604, 1468, 1343, 1094, 1076, 937 cm^{-1}. HRMS (ESI) Calcd. For $C_{14}H_{17}N_2O_4^{+1}(M+NH_4)^+$ requires 277.1183, Found: 277.1177.


7.421
7.417
7.403
7.399
7.384
7.380
7.156
7.136
7.117
7.097
5.635
5.175
5.148
5.113
5.086
3.353
2.452
-0.000
0.96
2.86
0.92
0.99
0.97
2.99
3.00
f1 (ppm)


197.249
192.874
169.256
143.343
131.280
123.874
123.845
122.964
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103.831
89.537
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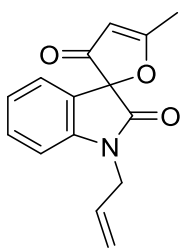
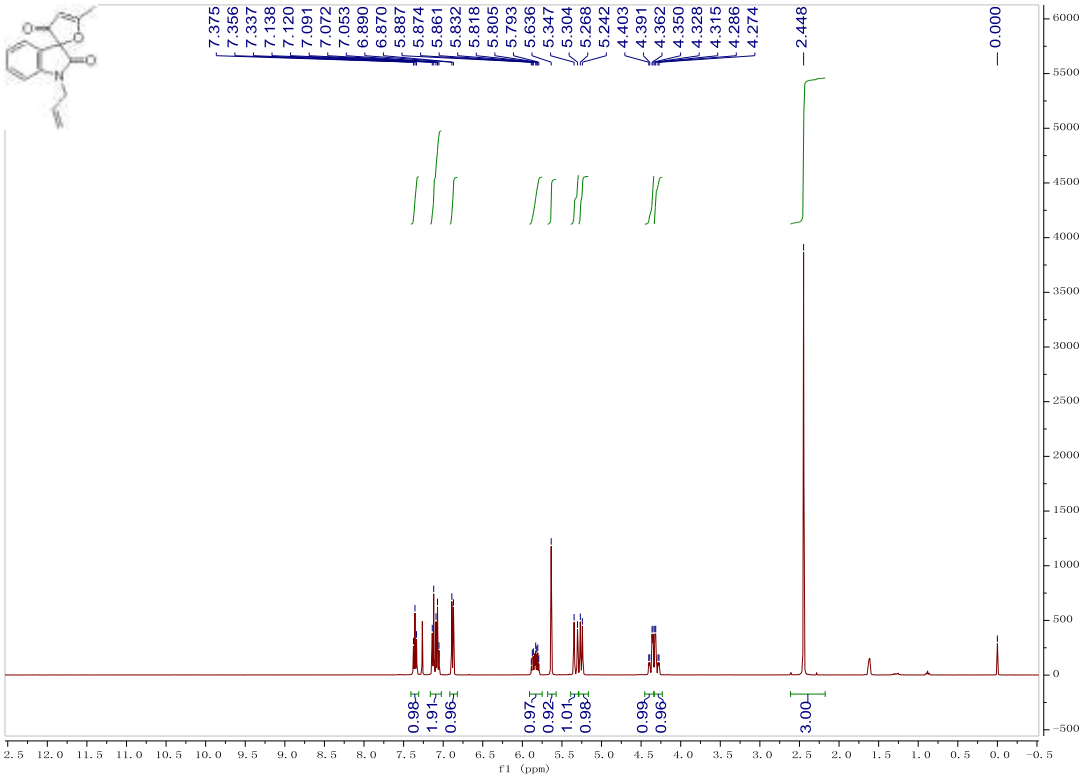
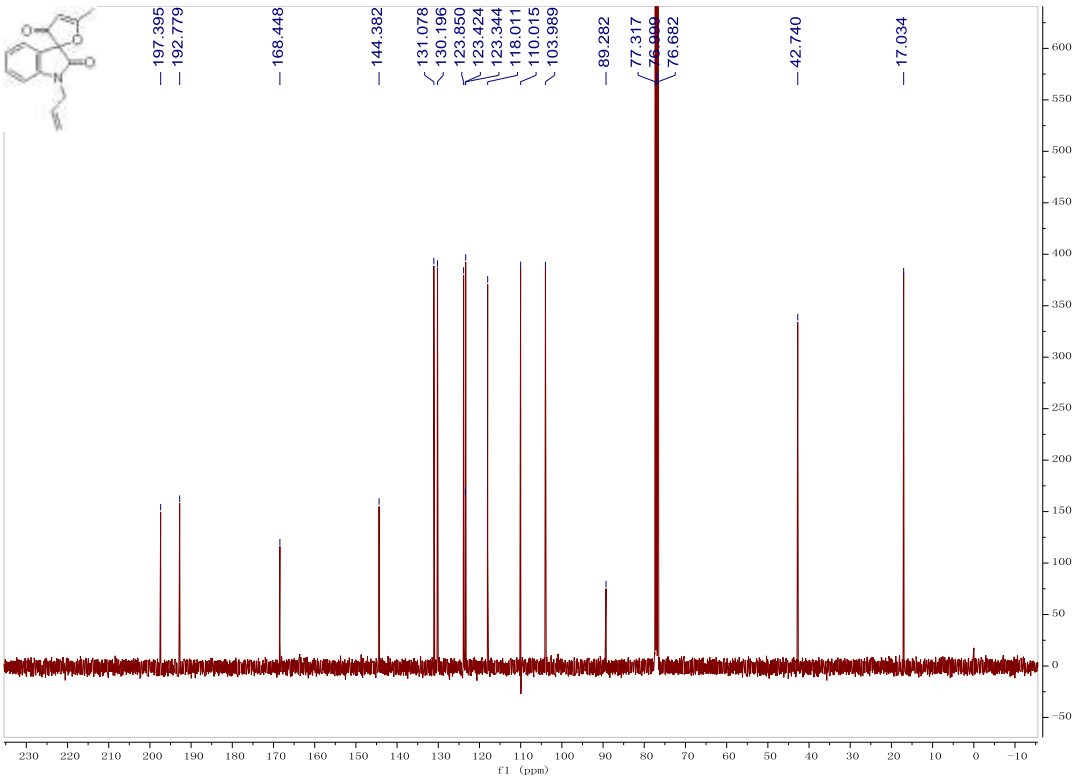
77.000
76.683
71.670
56.286
17.005
f1 (ppm)



1'-allyl-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3d)

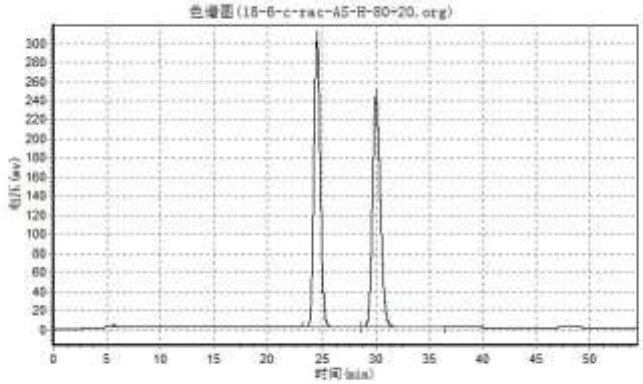
A white solid, 92% yield (47 mg). M.p.: 91-93 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.45 (s, 3H, CH_3), 4.30 (dd, *J* = 5.2, 16.8 Hz, 1H, CH_2), 4.38 (dd, *J* = 5.2, 16.8 Hz, 1H, CH_2), 5.26 (d, *J* = 10.4 Hz, 1H, =CH_2), 5.33 (d, *J* = 17.2 Hz, 1H, =CH_2), 5.64 (s, 1H, =CH), 5.79-5.89 (m, 1H, =CH), 6.88 (d, *J* = 8.0 Hz, 1H, ArH), 7.05-7.14 (m, 2H, ArH), 7.36 (t, *J* = 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 42.7, 89.3, 104.0, 110.0, 118.0, 123.3, 123.4, 123.9, 130.2, 131.1, 144.4, 168.4, 192.8, 197.4. IR (EtOH) ν 2956, 2919, 2850, 1731, 1703, 1606, 1488, 1167, 987, 937, 750 cm^{-1}. HRMS (ESI) Calcd. For $C_{15}H_{17}N_2O_3^{+1}(M+NH_4)^+$ requires 273.1234, Found: 273.1229. $[\alpha]^{25}_D$ = +100.00 (c 0.04, CH_2Cl_2) for 82% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AS-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254 nm, t_{minor} = 28.290 min, t_{major} = 23.423 min.





实验时间: 2018-04-26, 21:16:09
谱图文件:D:\Sun Yaoliang\co2\18-6-c-rac-A5-R-80-20.org

实验者:
报告时间: 2018-04-26, 21:16:57
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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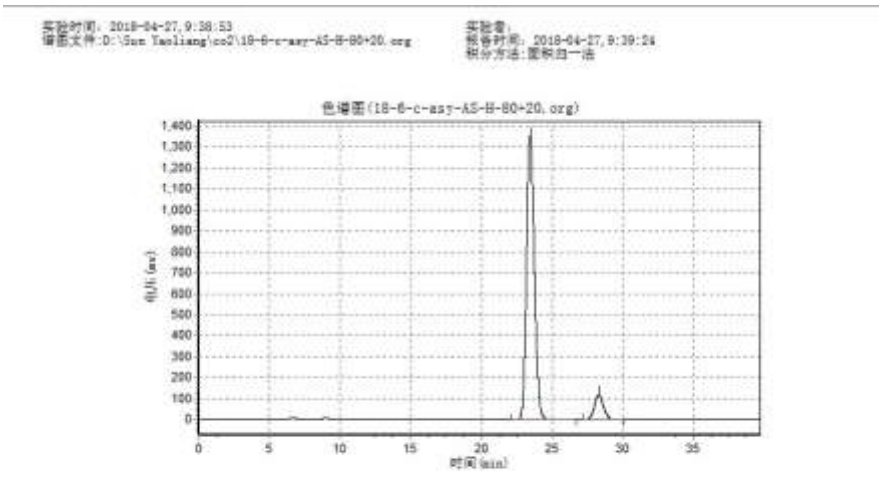
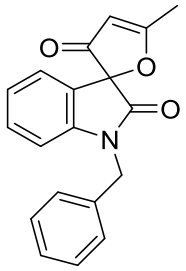
2		30.068	241303.500	12584673.000	49.9374
总计			540591.188	25200887.000	100.0000



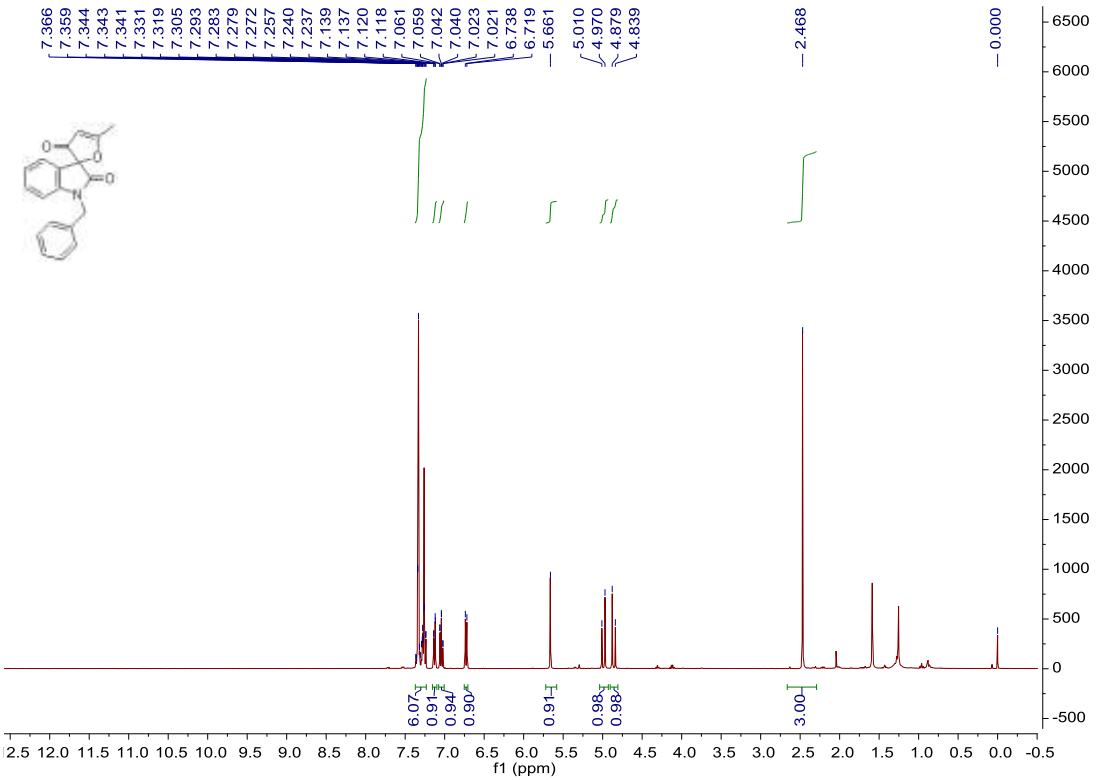
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		23.423	1351788.250	52703420.000	90.9990
2		28.290	116479.633	5213053.000	9.0010
总计			1467267.883	57916473.000	100.0000



1'-benzyl-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3e)

A white solid, 93% yield (57 mg). M.p.: 116-118 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.47 (s, 3H, CH_3), 4.60 (d, *J* = 16.0 Hz, 1H, CH_2), 4.99 (d, *J* = 16.0 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.73 (d, *J* = 7.6 Hz, 1H, ArH), 7.04 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.13 (dd, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.23-7.37 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 44.2, 89.4, 104.0, 110.2, 123.4, 123.8, 127.1, 127.8, 128.9, 131.1, 134.6, 144.3, 168.9, 192.9, 197.5. IR (EtOH) ν 3105, 3055, 2956, 2849, 1855, 1732, 1704, 1698, 1419, 1165, 824 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{19}N_2O_3^{+1}(M+NH_4)^+$ requires 323.1390, Found: 323.1385.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7.343
7.341
7.331
7.319
7.305
7.293
7.283
7.279
7.272
7.257
7.240
7.237
7.139
7.137
7.120
7.118
7.061
7.059
7.042
7.040
7.023
7.021
6.738
6.719
5.661
5.010
4.970
4.879
4.839
2.468
0.000
6.07
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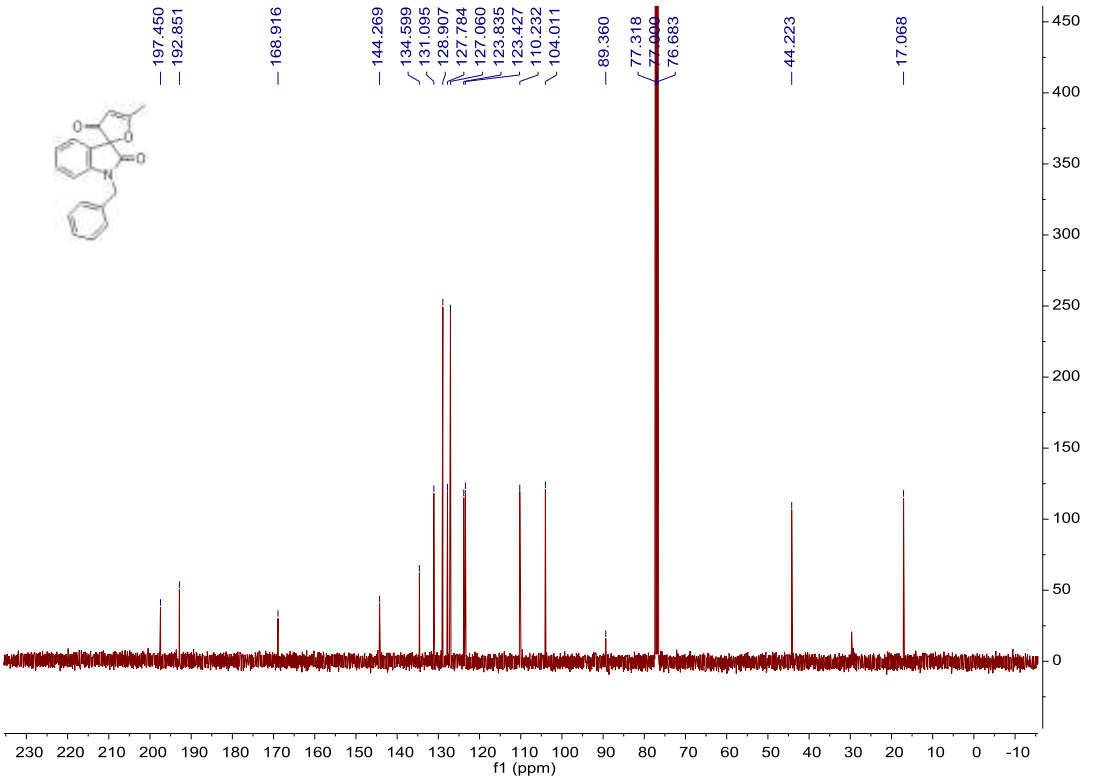
0.94
0.90
0.91
0.98
0.98
3.00
f1 (ppm)


197.450
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134.599
131.095
128.907
127.784
127.060
123.835
123.427
110.232
104.011
89.360
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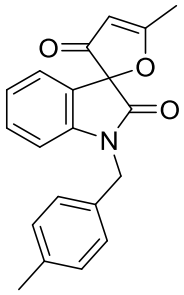
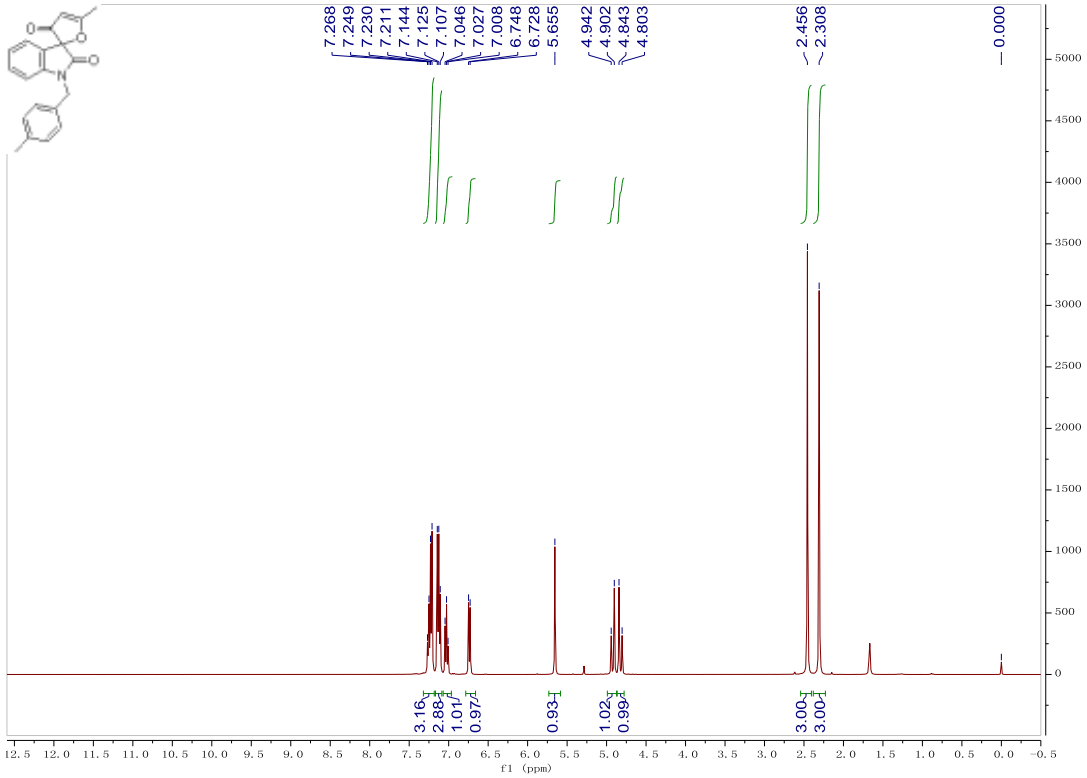
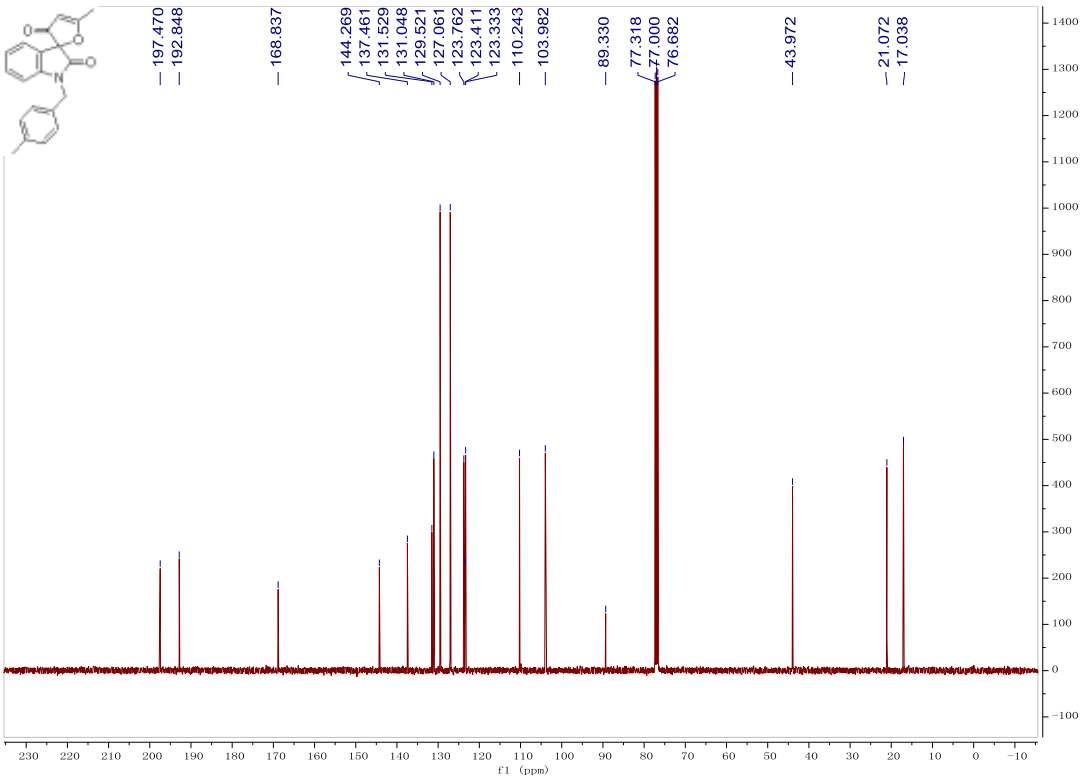
77.000
76.683
44.223
17.068
f1 (ppm)

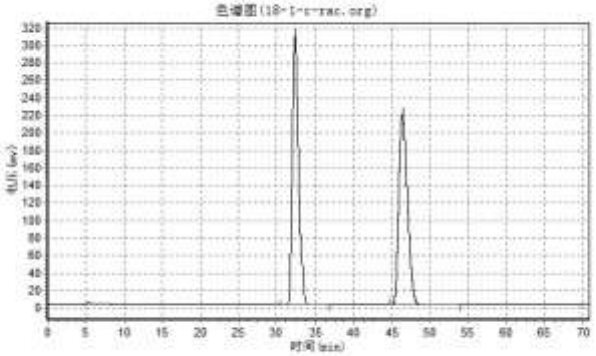


5-methyl-1'-(4-methylbenzyl)-3H-spiro[furan-2,3'-indoline]-2',3-dione (3f)

A white solid, 96% yield (61 mg). M.p.: 119-121 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.31 (s, 3H, CH_3), 2.46 (s, 3H, CH_3), 4.82 (d, *J* = 16.0 Hz, 1H, CH_2), 4.92 (d, *J* = 16.0 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.74 (d, *J* = 8.0 Hz, 1H, ArH), 7.03 (t, *J* = 7.6 Hz, 1H, ArH), 7.10-7.15 (m, 3H, ArH), 7.21-7.27 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 21.1, 44.0, 89.3, 104.0, 110.2, 123.3, 123.4, 123.8, 127.1, 129.5, 131.0, 131.5, 137.5, 144.3, 168.8, 192.8, 197.5. IR (EtOH) ν 3112, 2925, 2849, 1731, 1702, 1606, 1487, 1467, 1378, 1323, 1165, 750 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 337.1547, Found: 337.1538. $[\alpha]^{25}_D$ = +27.50 (c 0.04, CH_2Cl_2) for 85% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254 nm, t_{minor} = 31.657 min, t_{major} = 44.990 min.







分析结果表

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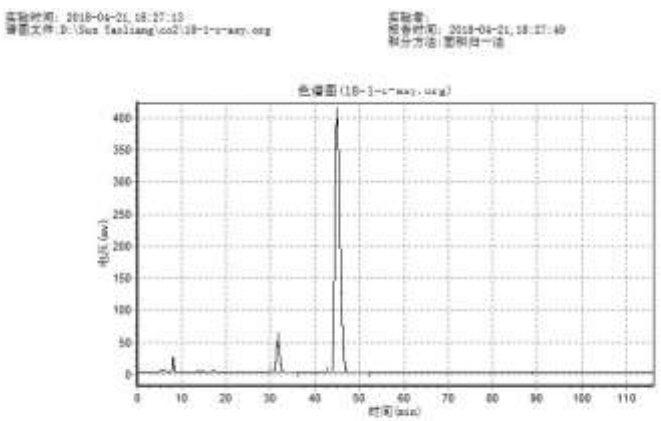
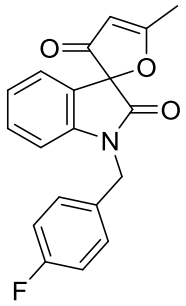
总计			523640.369	34452702.000	100.0000



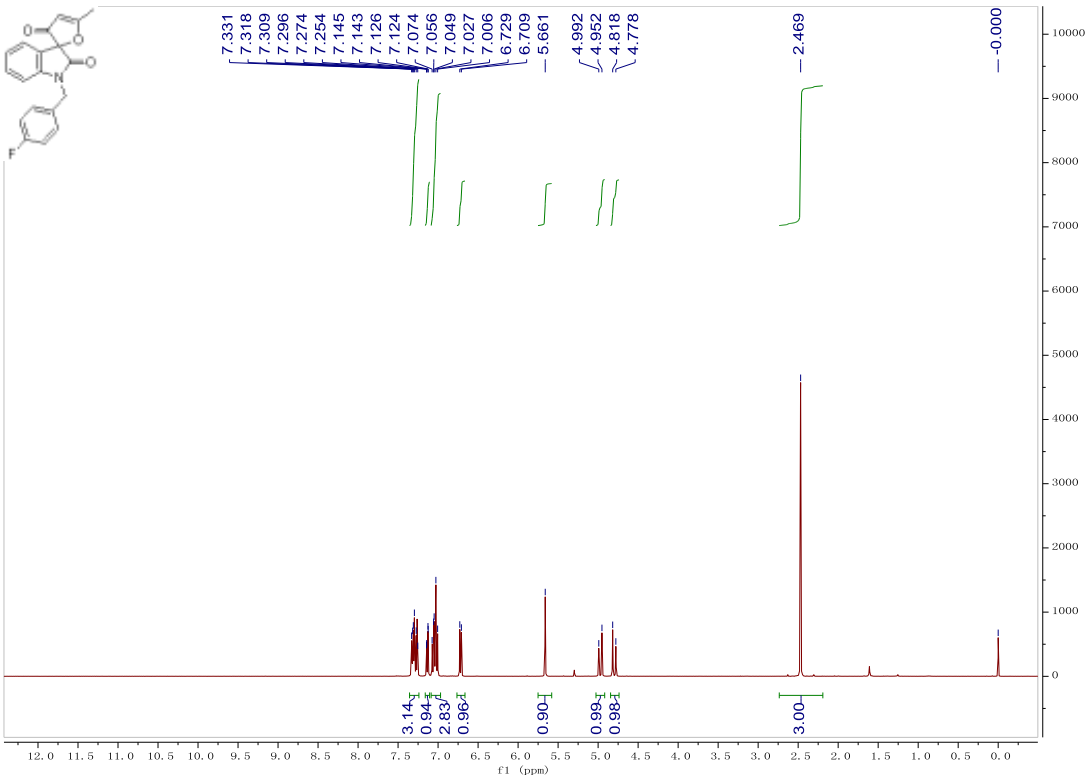
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		31.657	48715.031	2699362.769	7.7284
2		44.990	399208.125	32242136.000	92.2716
总计			447923.156	34941498.750	100.0000



1'-(4-fluorobenzyl)-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3g)

A white solid, 94% yield (61 mg). M.p.: 135-137 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.47 (s, 3H, CH_3), 4.80 (d, *J* = 16.0 Hz, 1H, CH_2), 4.97 (d, *J* = 16.0 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 7.00-7.08 (m, 3H, ArH), 7.13 (dd, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.25-7.34 (m, 3H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 43.5, 89.3, 104.0, 110.1, 115.8 (d, *J* = 21.5 Hz), 123.45, 123.53, 123.9, 128.8 (d, *J* = 8.2 Hz), 130.4 (d, *J* = 3.2 Hz), 131.1, 144.0, 162.3 (d, *J* = 244.7 Hz), 168.9, 192.9, 197.4. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -114.42-(-114.34). IR (EtOH) ν 3112, 3055, 2922, 2841, 1730, 1699, 1509, 1378, 1160, 990, 749 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}FN_2O_3^{+1}(M+NH_4)^+$ requires 341.1296, Found: 341.1290. $[\alpha]^{25}_D$ = +193.33 (c 0.02, CH_2Cl_2) for 74% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254 nm, t_{minor} = 27.065 min, t_{major} = 36.198 min.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7.124
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7.006
6.729
6.709
5.661
4.992
4.952
4.818
4.778
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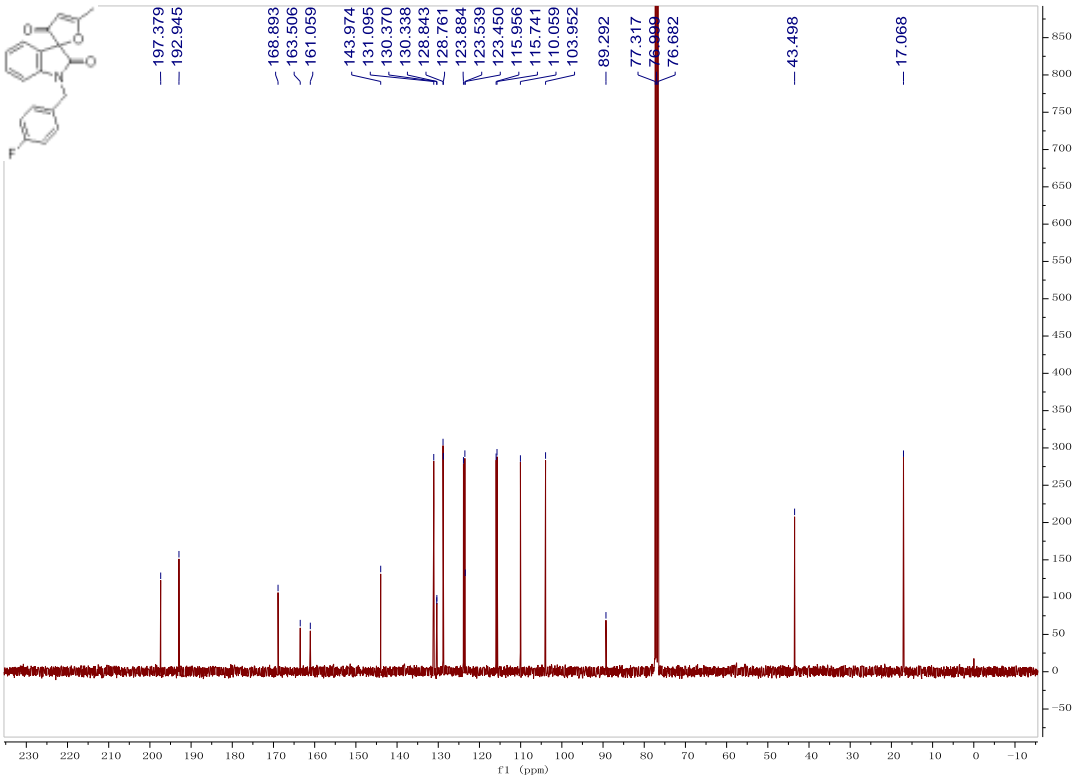
3.14
0.94
2.83
0.96
0.90
0.99
0.98
3.00
f1 (ppm)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123.539
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110.059
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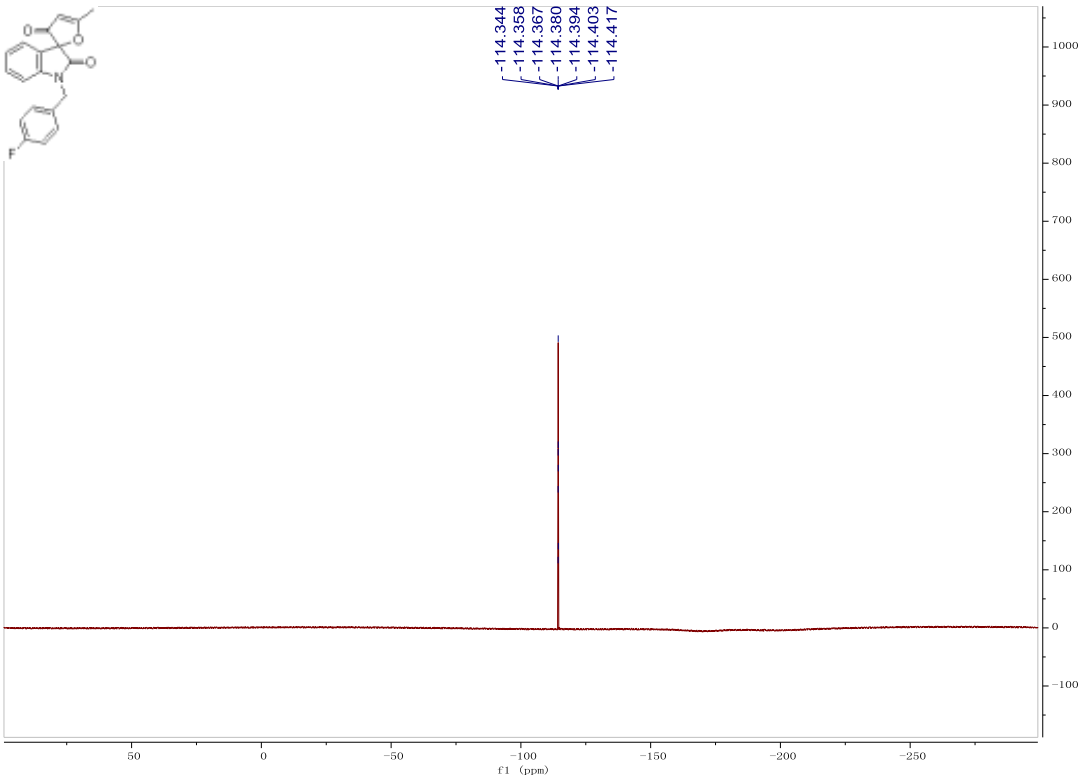
43.498
17.068
f1 (ppm)



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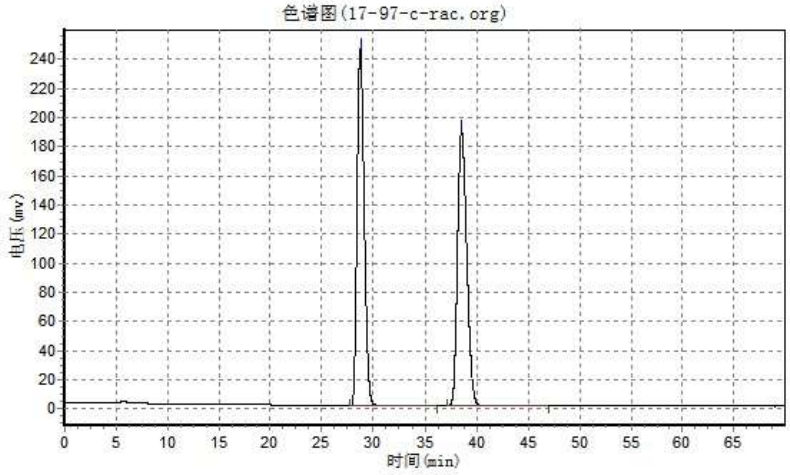
报告时间：2018-04-19,15:27:03
积分方法:面积归一法



分析结果表

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2		38.623	187981.359	11779747.000	49.8670
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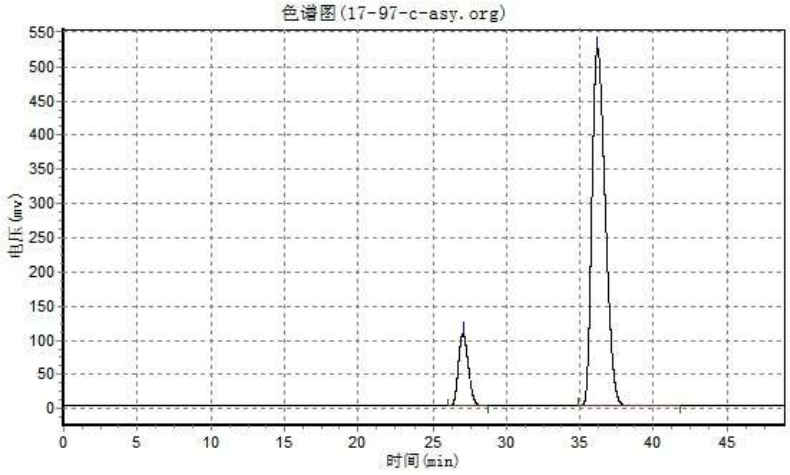
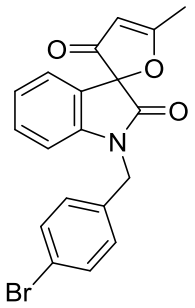
积分方法:面积归一法



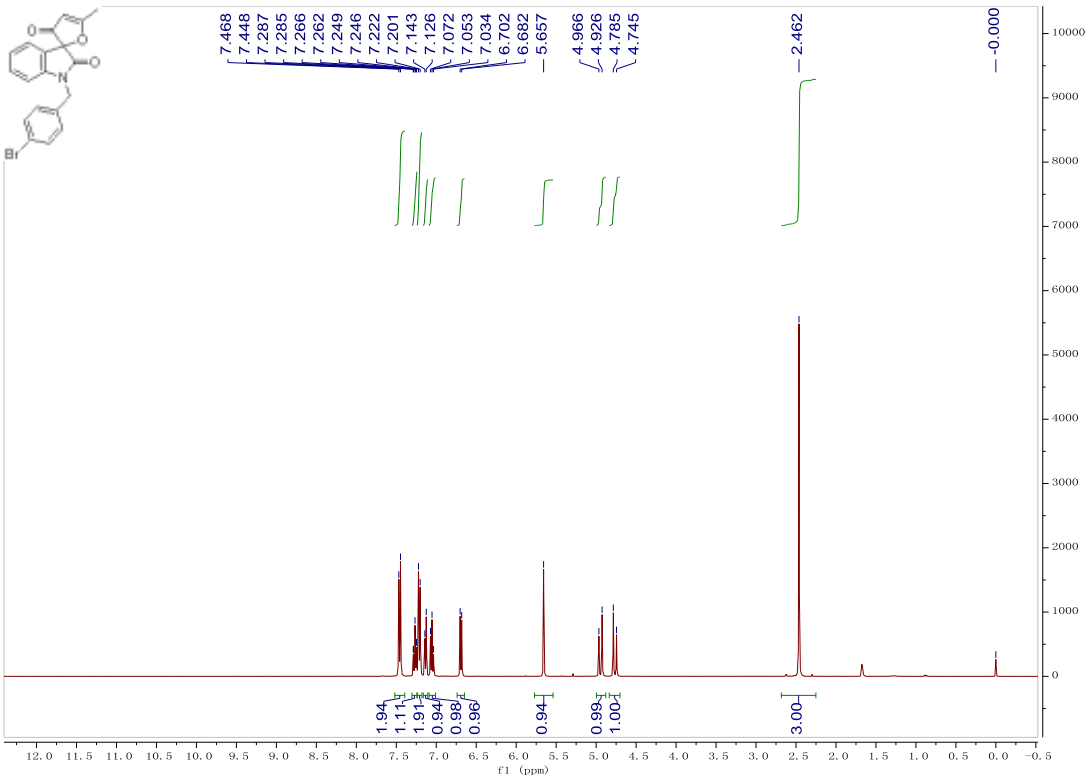
分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
1		27.065	105601.984	4989027.500	13.1351
2		36.198	522805.469	32993248.000	86.8649
总计			628407.453	37982275.500	100.0000



1'-(4-bromobenzyl)-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3i)

A white solid, 91% yield (70 mg). M.p.: 163-165 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (s, 3H, CH_3), 4.77 (d, *J* = 16.0 Hz, 1H, CH_2), 4.95 (d, *J* = 16.0 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.69 (d, *J* = 8.0 Hz, 1H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 7.13 (d, *J* = 6.8 Hz, 1H, ArH), 7.21 (d, *J* = 8.4 Hz, 2H, ArH), 7.24-7.29 (m, 1H, ArH), 7.46 (d, *J* = 8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 43.5, 89.2, 103.9, 110.0, 121.7, 123.4, 123.6, 123.9, 128.8, 131.1, 132.0, 133.6, 143.8, 168.9, 193.0, 197.3. IR (EtOH) ν 3063, 2920, 2841, 1732, 1604, 1488, 1164, 1071, 848 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}BrN_2O_3^{+1}(M+NH_4)^+$ requires 401.0495, Found: 401.0491. $[\alpha]^{25}_D$ = +172.50 (c 0.04, CH_2Cl_2) for 66% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 86.149 min, t_{major} = 103.320 min.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7.072
7.053
7.034
6.702
6.682
5.657
4.966
4.926
4.785
4.745
2.462
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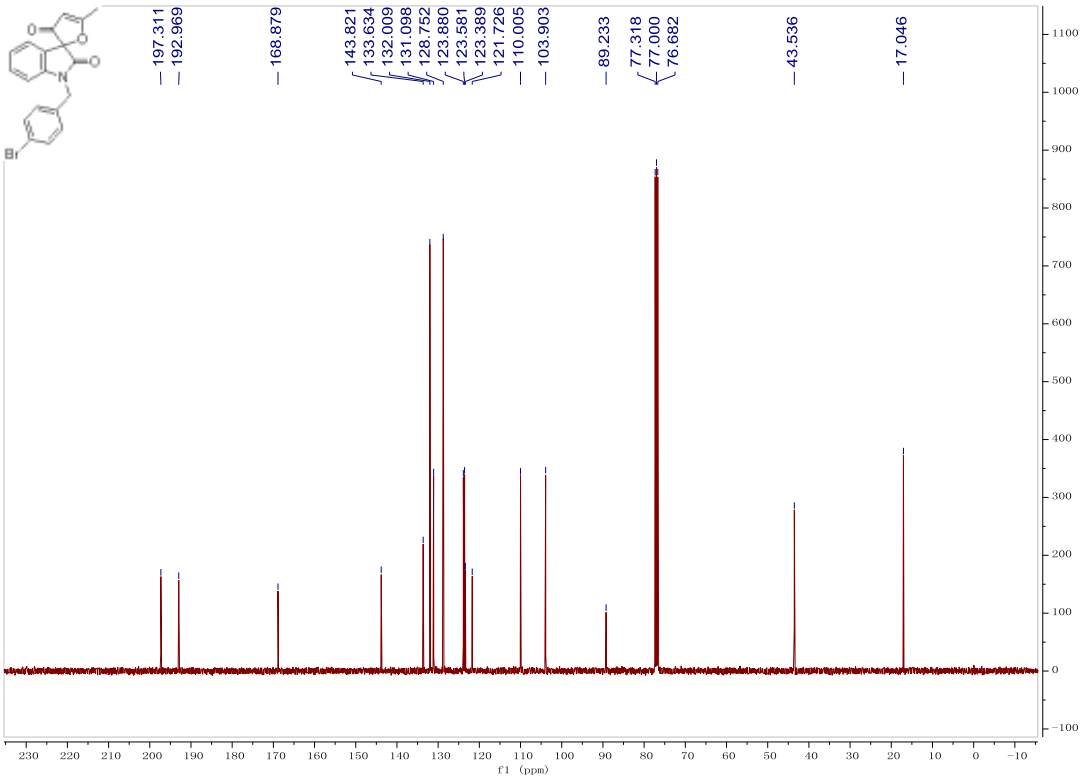
1.91
0.94
0.98
0.96
0.94
0.99
1.00
3.00
f1 (ppm)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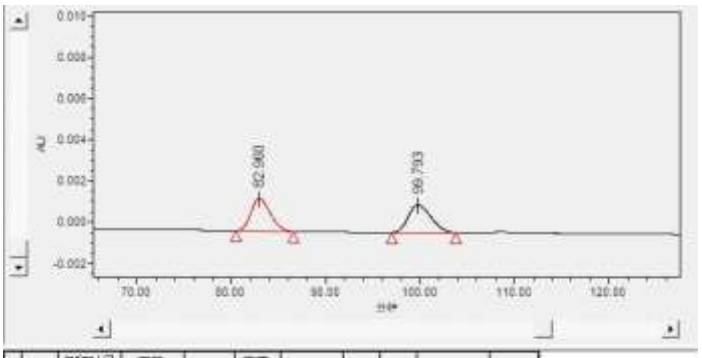
77.000
76.682
43.536
17.046
f1 (ppm)



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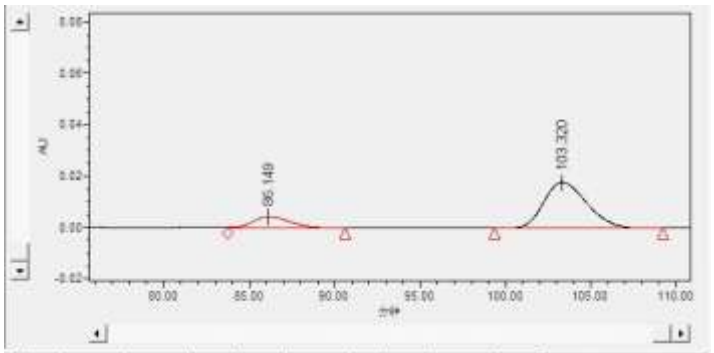
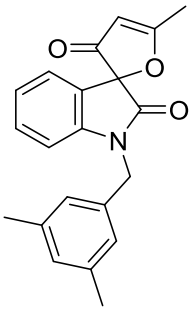
2		99.793	220800	49.93	1330	BB			未知	



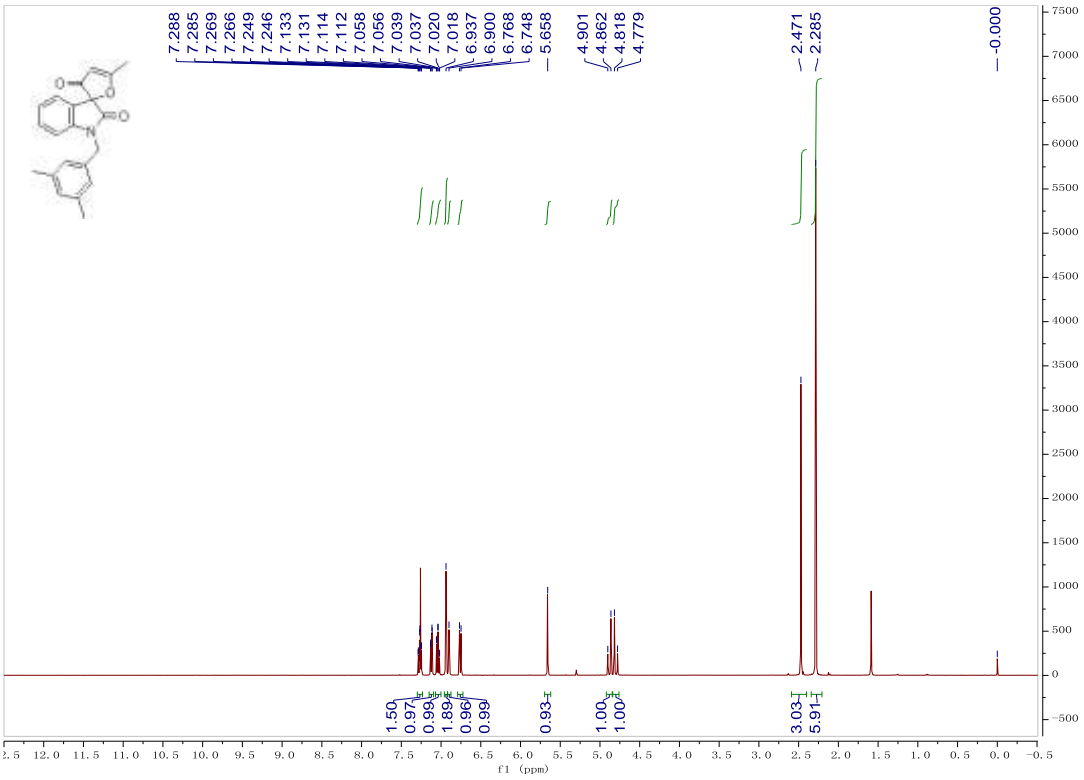
	名称	保留时间（分钟）	面积（微伏*秒）	% 面积	高度（微伏）	积分类型	含量	单位	峰类型	峰代码
1		86.149	650668	17.22	4389	VB			未知	
2		103.320	3127235	82.78	17904	BB			未知	

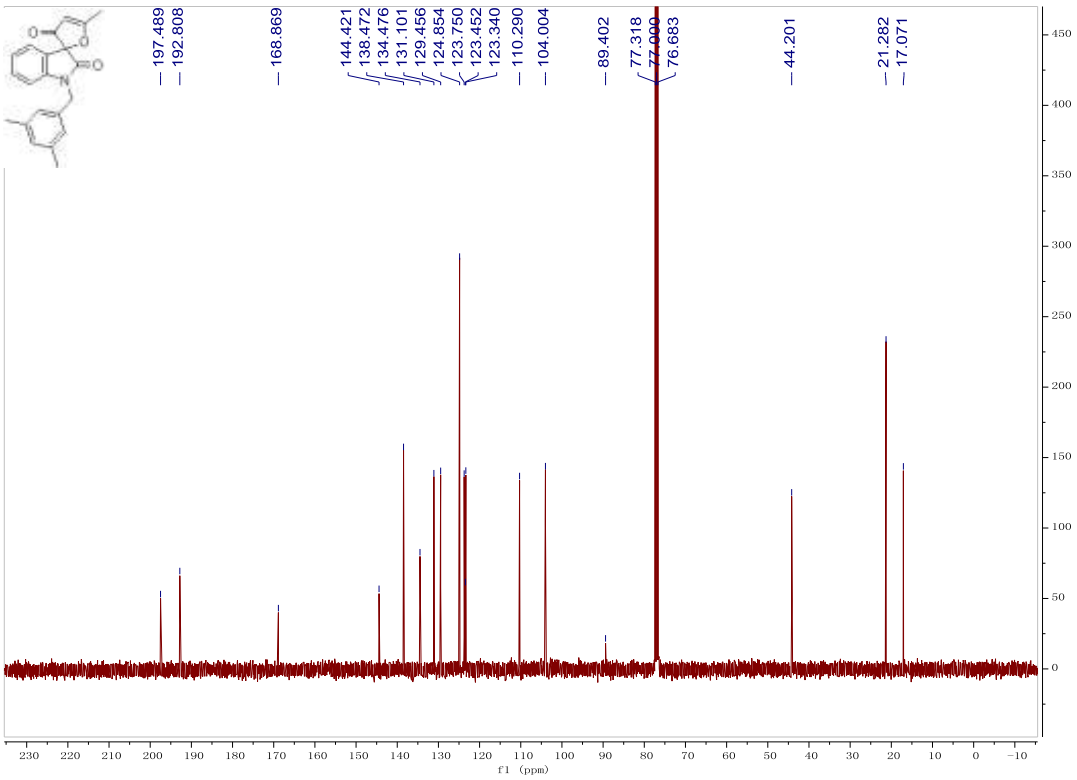


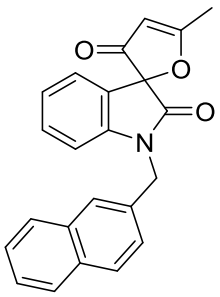
1'-(3,5-dimethylbenzyl)-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3k)

A white solid, 95% yield (63 mg). M.p.: 134-135 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29 (s,

6H, CH_3), 2.47 (s, 3H, CH_3), 4.80 (d, *J* = 15.6 Hz, 1H, CH_2), 4.88 (d, *J* = 15.6 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.76 (d, *J* = 8.0 Hz, 1H, ArH), 6.90 (s, 1H, ArH), 6.94 (s, 2H, ArH), 7.04 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.12 (dd, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.27 (dt, *J* = 1.2, 7.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 21.3, 44.2, 89.4, 104.0, 110.3, 123.3, 123.5, 123.8, 124.9, 129.5, 131.1, 134.5, 138.5, 144.4, 168.9, 192.8, 197.5. IR (EtOH) ν 2956, 2922, 2849, 1735, 1605, 1484, 1380, 1190, 1017, 936 cm^{-1}. HRMS (ESI) Calcd. For $C_{21}H_{23}N_2O_3^{+1}(M+NH_4)^+$ requires 351.1703, Found:. 351.1696

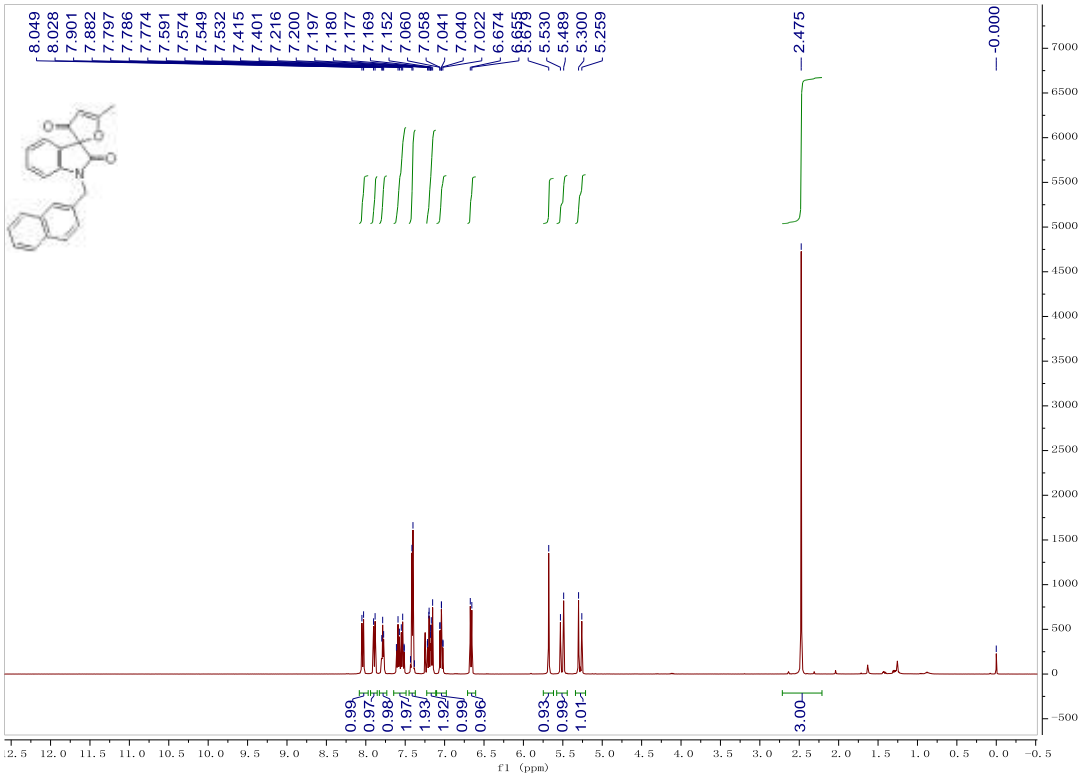






5-methyl-1'-(naphthalen-2-ylmethyl)-3H-spiro[furan-2,3'-indoline]-2',3-dione (3m)

A white solid, 91% yield (65 mg). M.p.: 154-156 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.48 (s, 3H, CH_3), 5.28 (d, *J* = 16.4 Hz, 1H, CH_2), 5.51 (d, *J* = 16.4 Hz, 1H, CH_2), 5.68 (s, 1H, =CH), 6.67 (d, *J* = 7.6 Hz, 1H, ArH), 7.04 (dt, *J* = 0.8, 7.2 Hz, 1H, ArH), 7.15-7.22 (m, 2H, ArH), 7.38-7.44 (m, 2H, ArH), 7.51-7.62 (m, 2H, ArH), 7.79 (t, *J* = 4.4 Hz, 1H, ArH), 7.89 (d, *J* = 7.6 Hz, 1H, ArH), 8.04 (d, *J* = 8.4 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 42.2, 89.4, 104.0, 110.4, 122.5, 123.45, 123.47, 123.8, 124.0, 125.5, 126.0, 126.5, 128.3, 128.9, 129.1, 130.7, 131.1, 133.7, 144.5, 169.0, 192.9, 197.4. IR (EtOH) ν 2922, 1731, 1702, 1516, 1487, 1359, 1248, 1165, 1113, 1008, 990 cm^{-1}. HRMS (ESI) Calcd. For $C_{23}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 373.1547, Found: 373.1541.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7.041
7.040
7.022
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6.655
5.879
5.530
5.489
5.300
5.259
2.475
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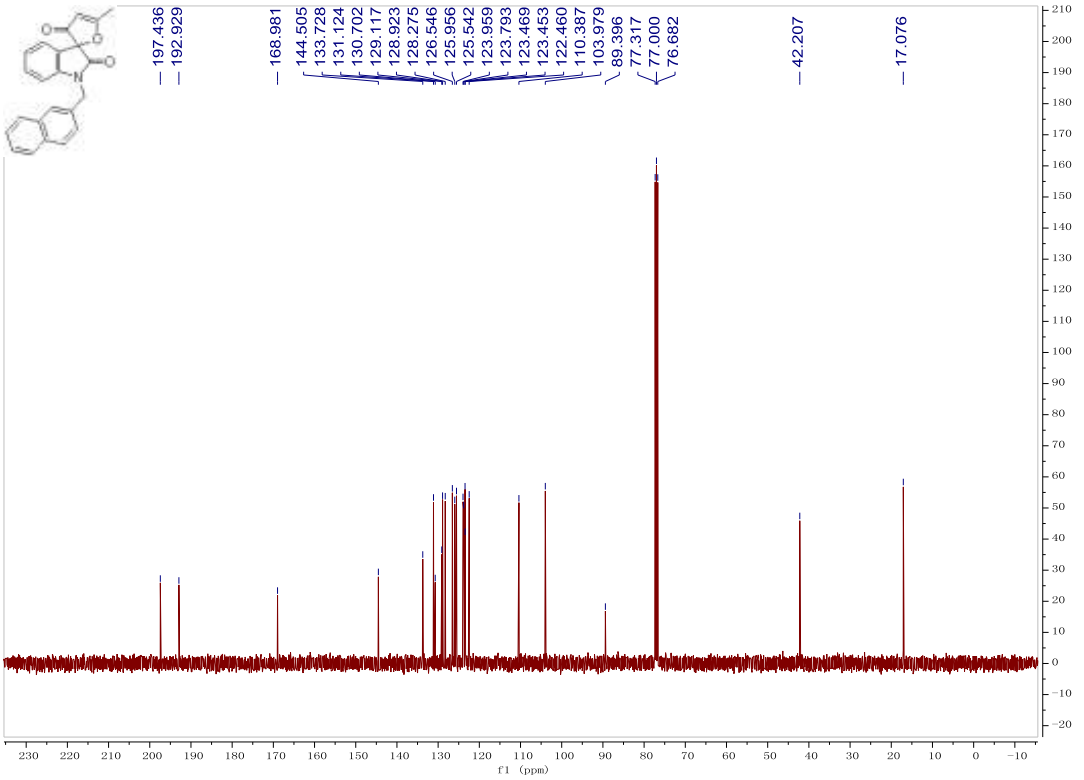
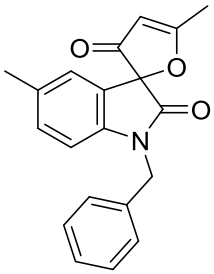
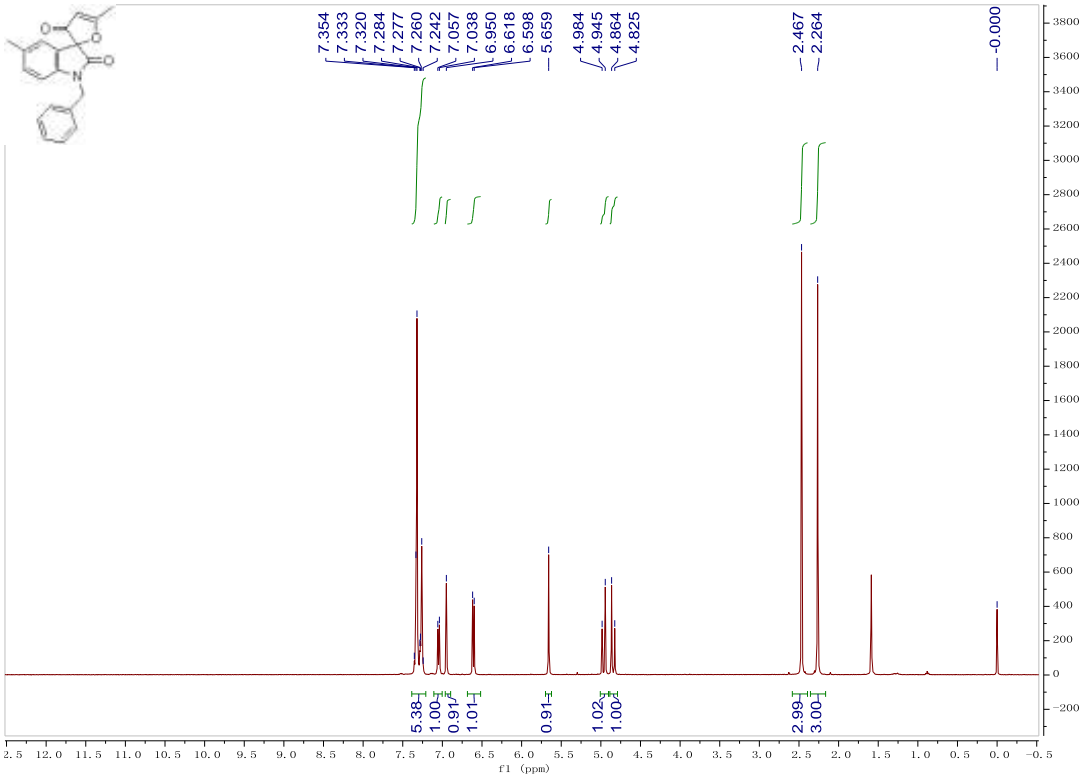
0.97
0.98
1.97
1.93
1.92
0.99
0.96
0.93
0.99
1.01
3.00
f1 (ppm)

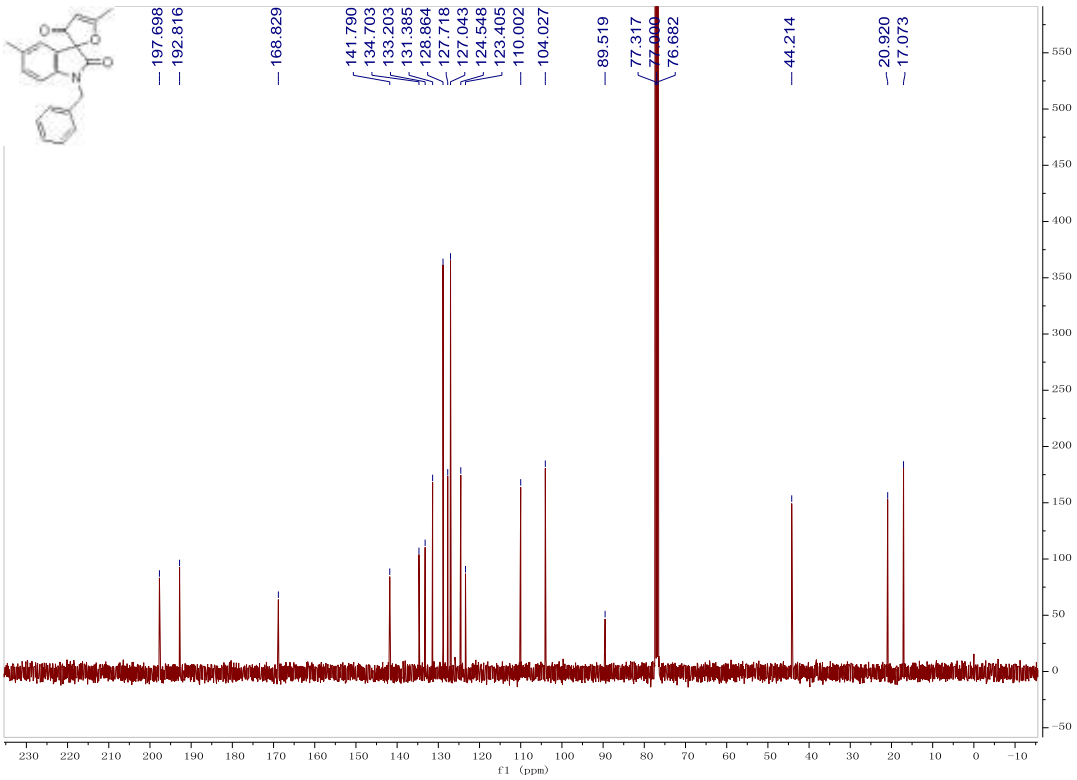

197.436
192.929
168.981
144.505
133.728
131.124
130.702
129.117
128.923
128.275
126.546
125.956
125.542
123.959
123.793
123.469
123.453
122.460
110.387
103.979
89.396
77.317
77.000
76.682
42.207
17.076
f1 (ppm)

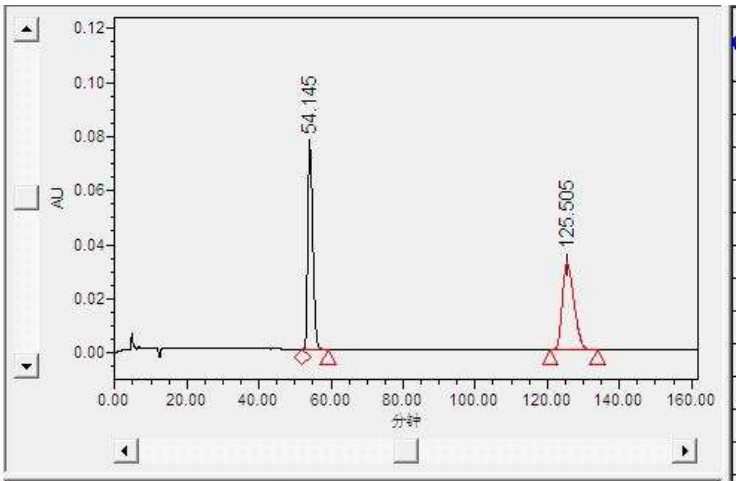


1'-benzyl-5,5'-dimethyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3o)

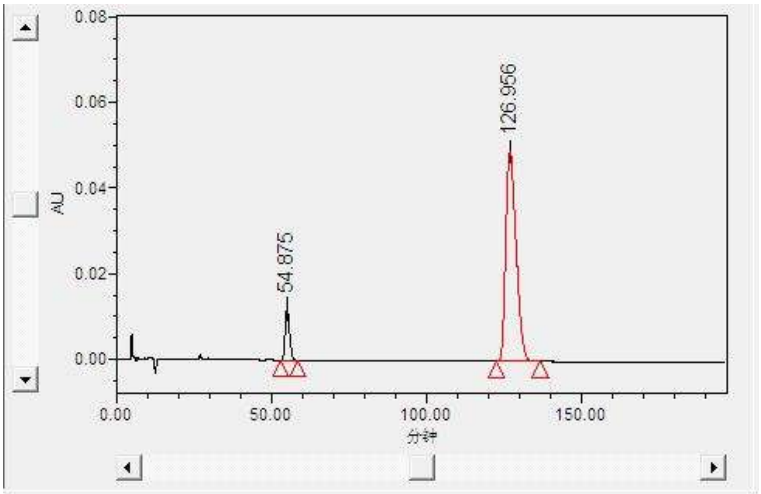
A white solid, 87% yield (56 mg). M.p.: 126-128 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.26 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 4.84 (d, *J* = 15.6 Hz, 1H, CH_2), 4.96 (d, *J* = 15.6 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.61 (d, *J* = 8.0 Hz, 1H, ArH), 6.95 (s, 1H, ArH), 7.05 (d, *J* = 7.6 Hz, 1H, ArH), 7.24-7.36 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 20.9, 44.2, 89.5, 104.0, 110.0, 123.4, 124.5, 127.0, 127.7, 128.9, 131.4, 133.2, 134.7, 141.8, 168.8, 192.8, 197.7. IR (EtOH) ν 2961, 2922, 2850, 1730, 1706, 1603, 1497, 1324, 1157, 940 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{21}N_2O_3^{+1}$(M+NH_4)$^+$ requires 337.1547, Found: 337.1540. [α]$^{25}_{D}$ = 27.50 (c 0.04, CH_2Cl_2) for 81% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 90/10, 0.7 mL/min, 254 nm, t_{minor} = 54.875 min, t_{major} = 126.965 min.



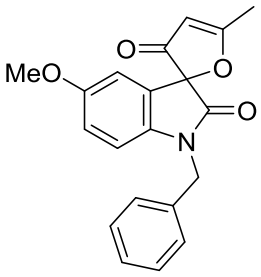




	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代
1		54.145	7220862	50.06	73867	VB			未知	
2		125.505	7202578	49.94	31866	BB			未知	

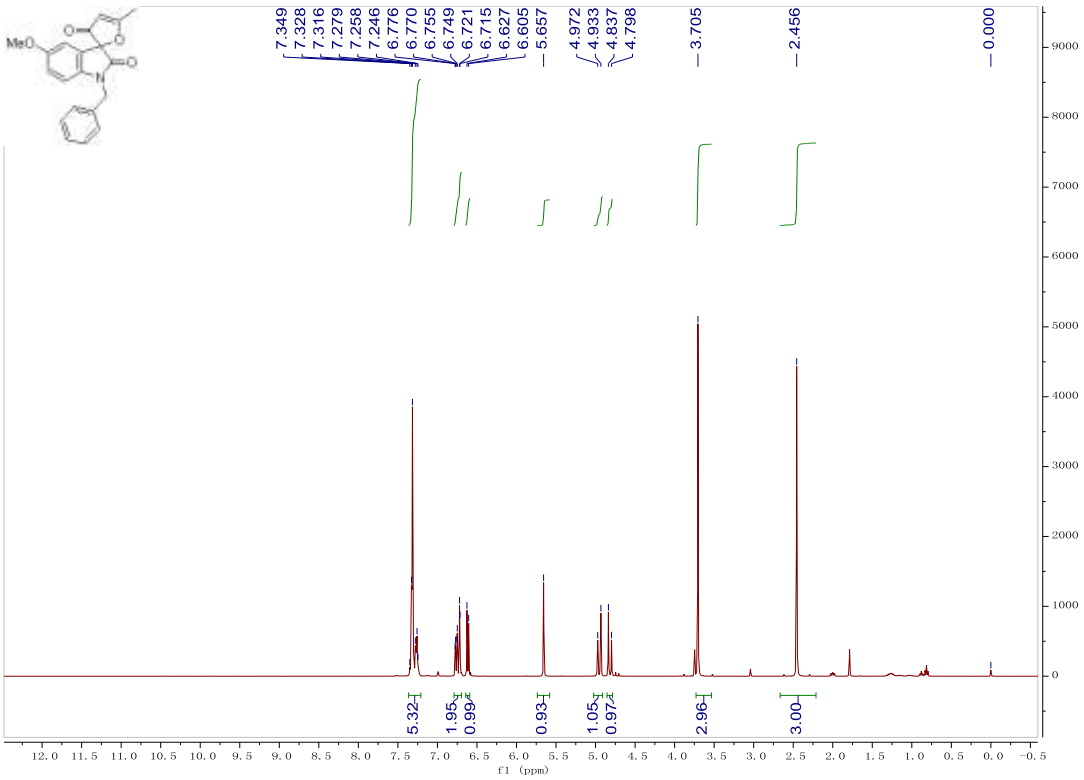


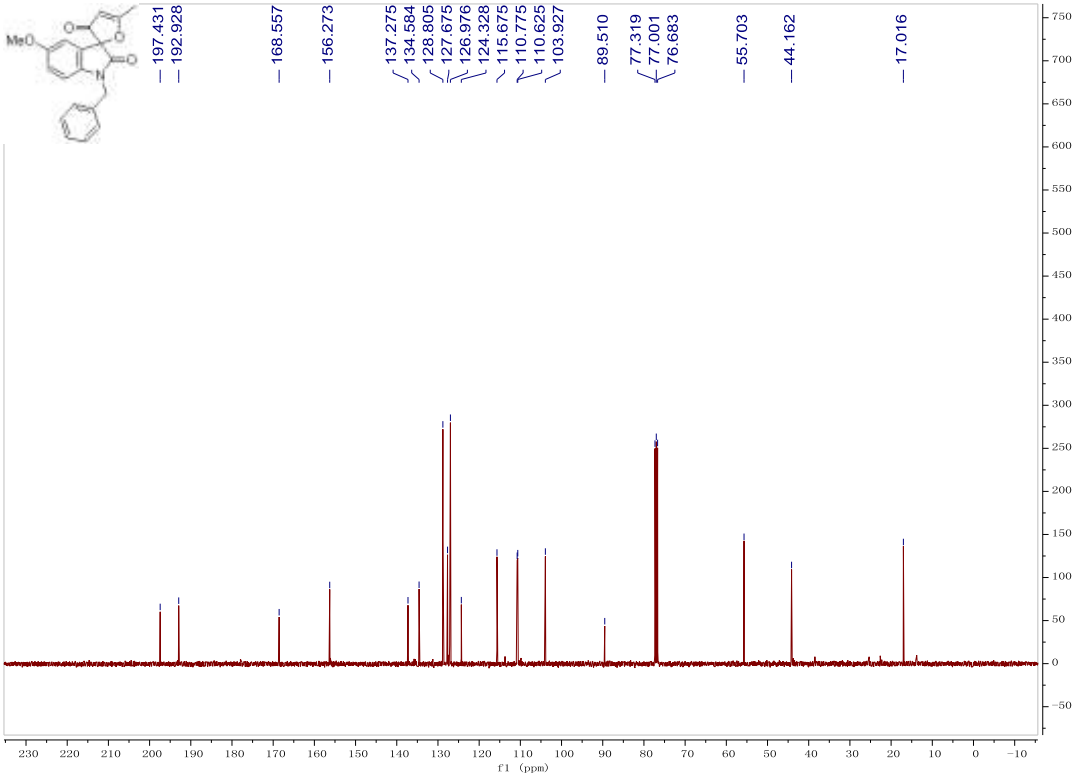
	名称	保留时间 (分钟)	面积 (微伏*秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码
1		54.875	1187284	9.39	12188	BB			未知	
2		126.956	11458233	90.61	49049	BB			未知	

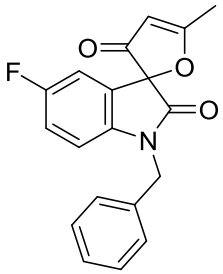


1'-benzyl-5'-methoxy-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3p)

A white solid, 96% yield (64 mg). M.p.: 144-146 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 4.82 (d, *J* = 15.6 Hz, 1H, CH_2), 4.95 (d, *J* = 15.6 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.62 (d, *J* = 8.8 Hz, 1H, ArH), 6.71-6.78 (m, 2H, ArH), 7.24-7.35 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 44.2, 55.7, 89.5, 103.9, 110.6, 110.8, 115.7, 124.3, 127.0, 127.7, 128.8, 134.6, 137.3, 156.3, 168.6, 192.9, 197.4. IR (EtOH) ν 3107, 2928, 2854, 1725, 1493, 1326, 1277, 1178, 1078, 1016, 935, 811 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{21}N_2O_4^{+1}(M+NH_4)^+$ requires 353.1496, Found: 353.1488.

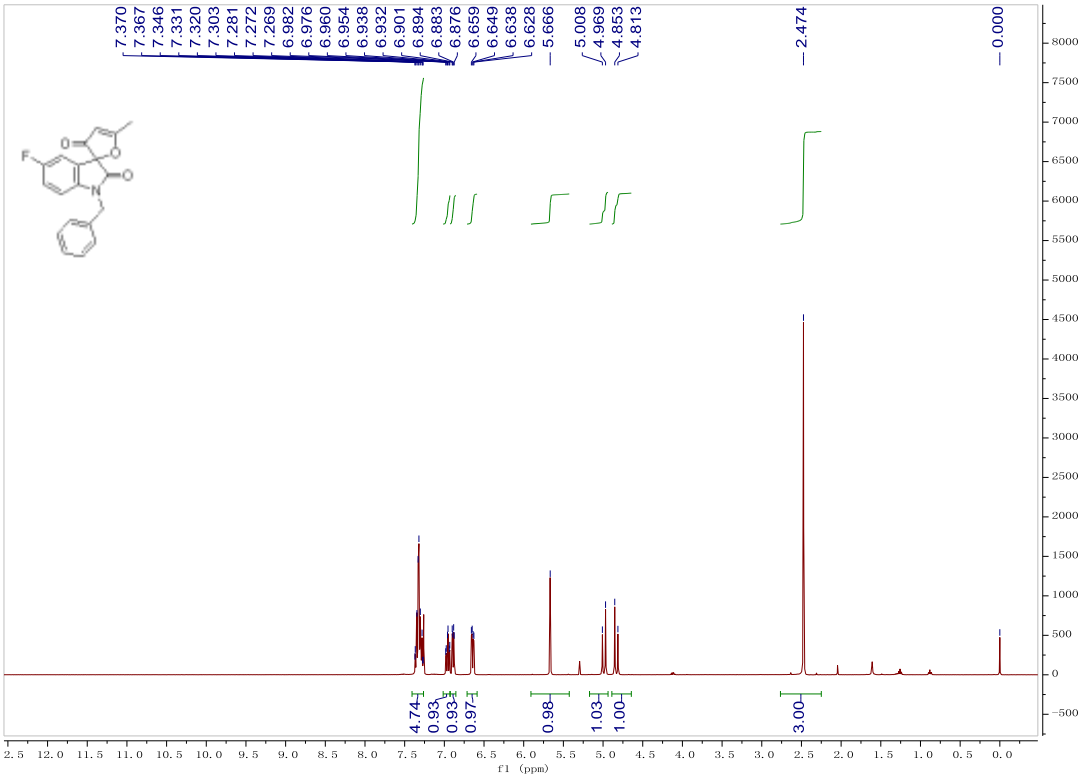

MeO
7.349
7.328
7.316
7.279
7.258
7.246
6.776
6.770
6.755
6.749
6.721
6.715
6.627
6.605
5.657
4.972
4.933
4.837
4.798
3.705
2.456
0.000
5.32
1.95
0.99
0.93
1.05
0.97
2.96
3.00
f1 (ppm)

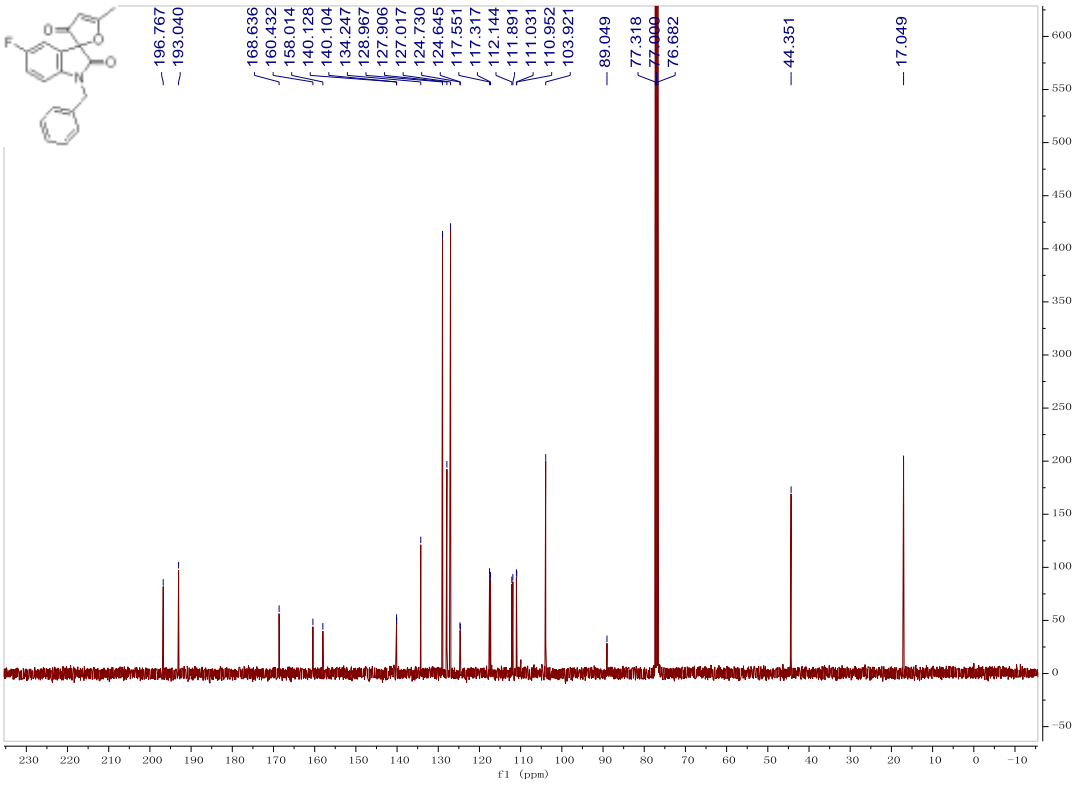

MeO
197.431
192.928
168.557
156.273
137.275
134.584
128.805
127.675
126.976
124.328
115.675
110.775
110.625
103.927
89.510
77.319
77.001
76.683
55.703
44.162
17.016
f1 (ppm)

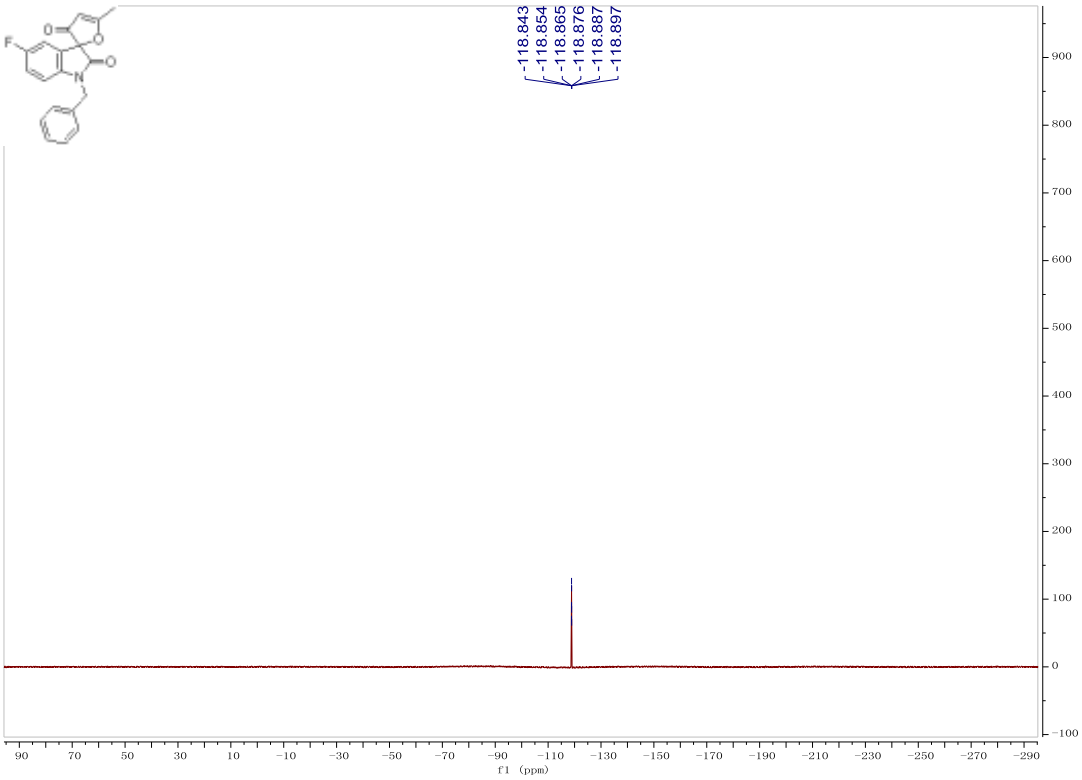


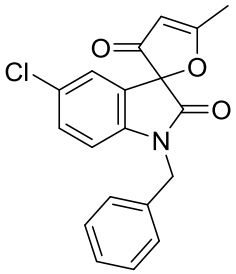
1'-benzyl-5'-fluoro-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3q)

A white solid, 97% yield (63 mg). M.p.: 122-124 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.47 (s, 3H, CH_3), 4.83 (d, *J* = 16.0 Hz, 1H, CH_2), 4.99 (d, *J* = 16.0 Hz, 1H, CH_2), 5.67 (s, 1H, =CH), 6.64 (dd, *J* = 4.0, 8.4 Hz, 1H, ArH), 6.89 (dd, *J* = 1.2, 7.2 Hz, 1H, ArH), 6.96 (dt, *J* = 2.4, 8.8 Hz, 1H, ArH), 7.26-7.37 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 44.4, 89.0, 103.9, 111.0 (d, *J* = 7.9 Hz), 112.0 (d, *J* = 25.3 Hz), 117.4 (d, *J* = 23.4 Hz), 124.7 (d, *J* = 8.5 Hz), 127.0, 127.9, 129.0, 134.2, 140.1 (d, *J* = 2.4 Hz), 159.2 (d, *J* = 241.8 Hz), 168.6, 193.0, 196.8. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -118.90-(-118.84). IR (EtOH) ν 2920, 2850, 1731, 1703, 1604, 1489, 1455, 1382, 1273, 1122, 1017, 935, 734, 668 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}FN_2O_3^{+1}(M+NH_4)^+$ requires 341.1296, Found: 341.1289.



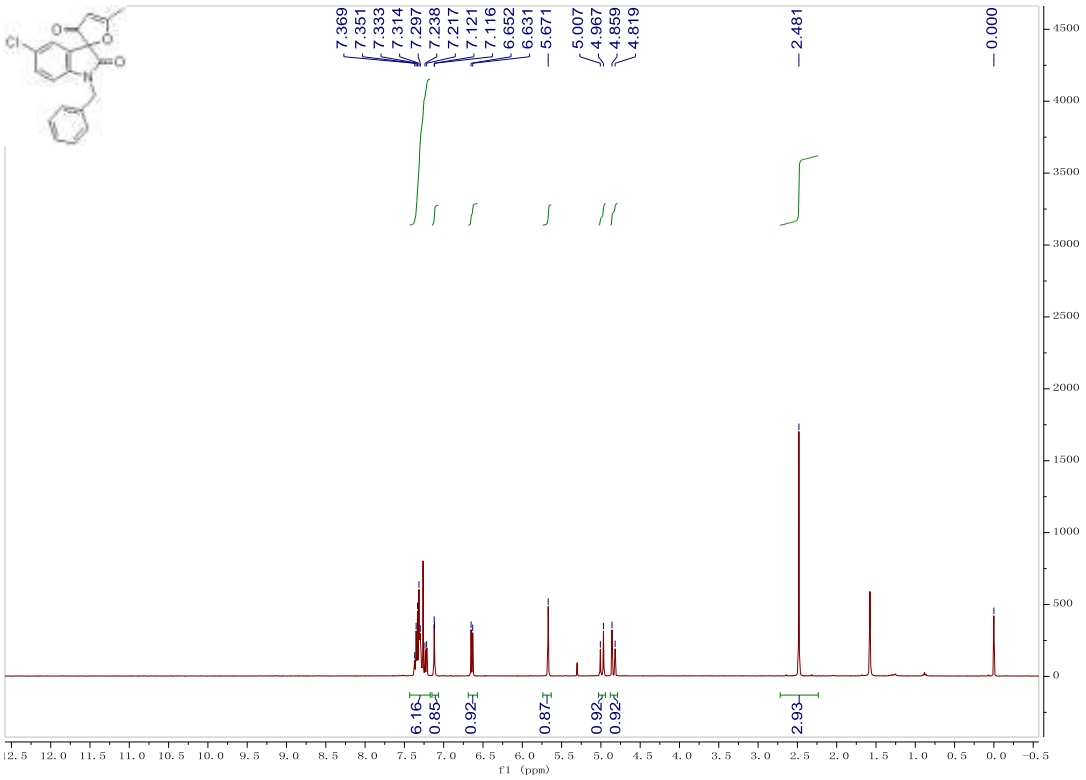

196.767
193.040
168.636
160.432
158.014
140.128
140.104
134.247
128.967
127.906
127.017
124.730
124.645
117.551
117.317
112.144
111.891
111.031
110.952
103.921
89.049
77.318
77.000
76.682
44.351
17.049
f1 (ppm)

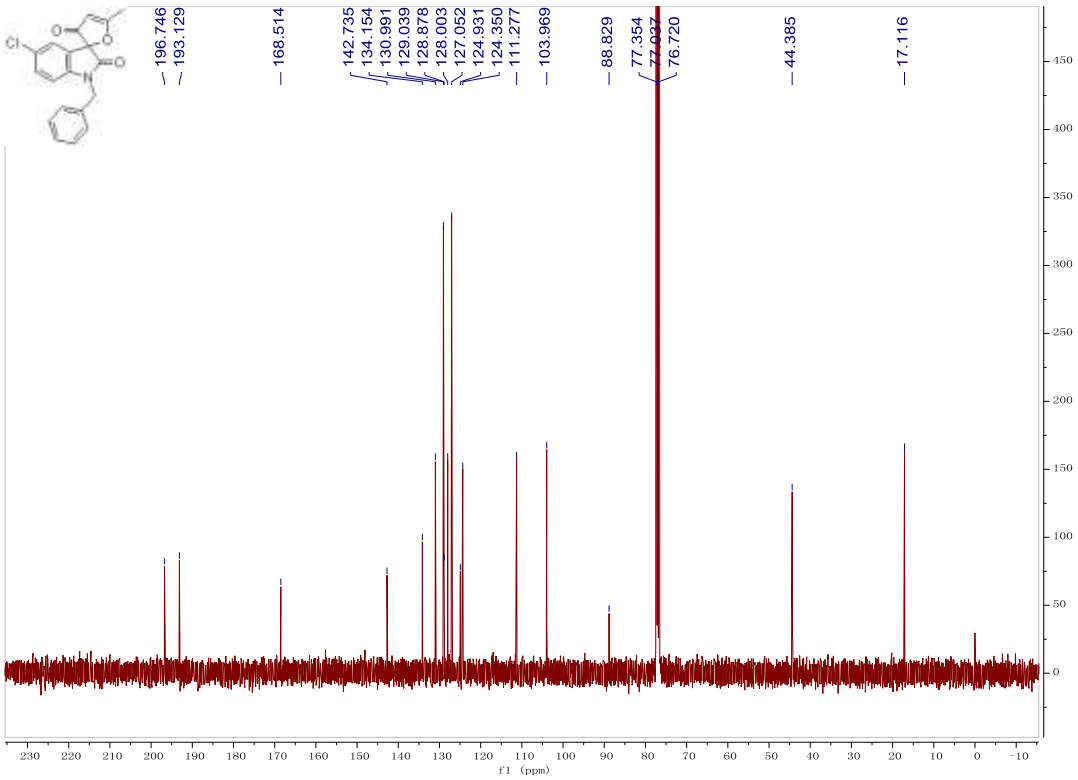

-118.843
-118.854
-118.865
-118.876
-118.887
-118.897
f1 (ppm)

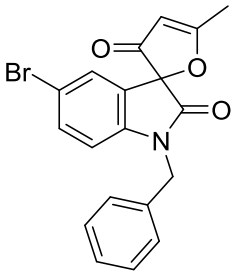


1'-benzyl-5'-chloro-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3r)

A white solid, 95% yield (64 mg). M.p.: 143-145 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.48 (s, 3H, CH_3), 4.84 (d, *J* = 16.0 Hz, 1H, CH_2), 4.99 (d, *J* = 16.0 Hz, 1H, CH_2), 5.67 (s, 1H, =CH), 6.64 (d, *J* = 8.4 Hz, 1H, ArH), 7.12 (d, *J* = 2.0 Hz, 1H, ArH), 7.21-7.37 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 44.4, 88.8, 104.0, 111.3, 124.4, 124.9, 127.1, 128.0, 128.9, 129.0, 131.0, 134.2, 142.7, 168.5, 193.1, 196.7. IR (EtOH) ν 3110, 3063, 2921, 2850, 1735, 1705, 1484, 1433, 1381, 1260, 1130, 960 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}ClN_2O_3^{+1}(M+NH_4)^+$ requires 357.1000, Found: 357.0996.

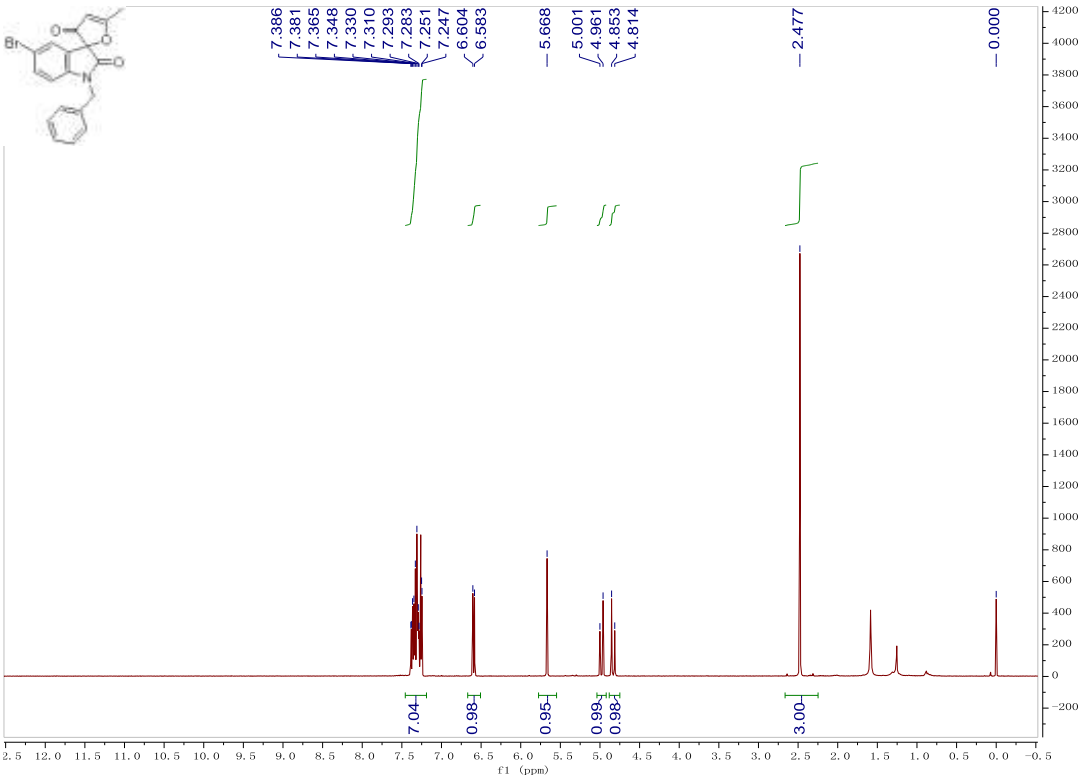


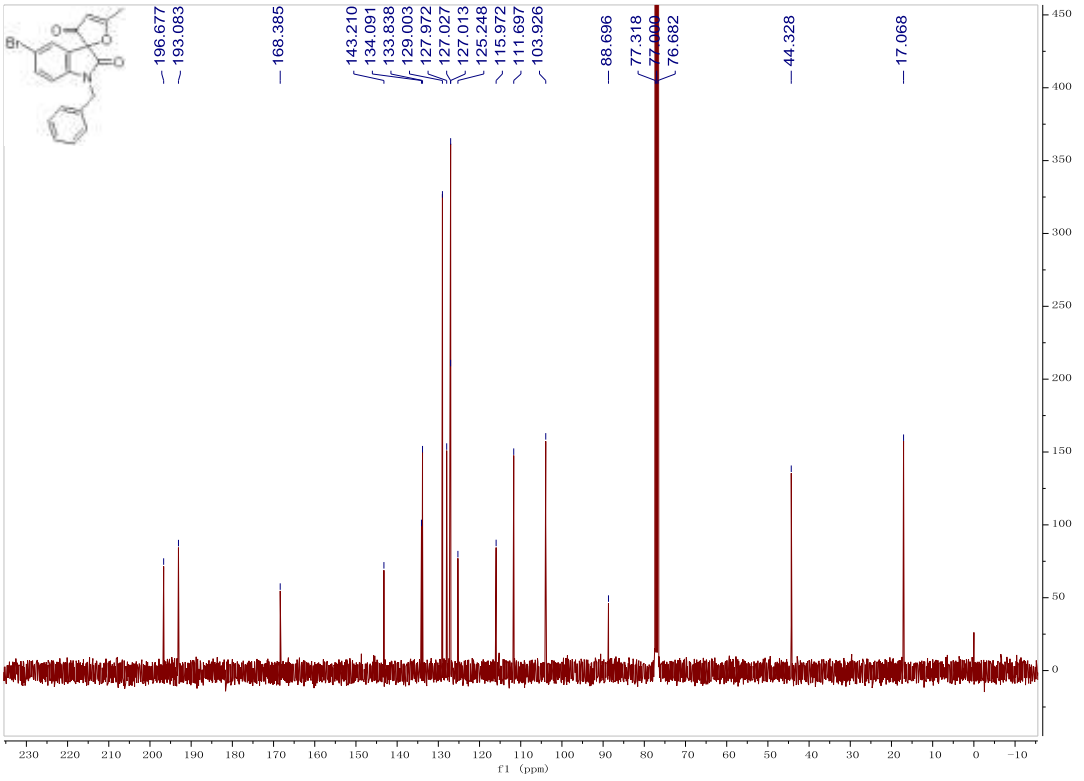




1'-benzyl-5'-bromo-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3s)

A white solid, 91% yield (70 mg). M.p.: 167-169 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.48 (s, 3H, CH_3), 4.83 (d, *J* = 15.6 Hz, 1H, CH_2), 4.98 (d, *J* = 15.6 Hz, 1H, CH_2), 5.67 (s, 1H, =CH), 6.59 (d, *J* = 8.4 Hz, 1H, ArH), 7.24-7.39 (m, 7H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 44.3, 88.7, 103.9, 111.7, 116.0, 125.2, 127.01, 127.03, 128.0, 129.0, 133.8, 134.1, 143.2, 168.4, 193.1, 196.7. IR (EtOH) ν 2920, 2850, 1736, 1704, 1603, 1455, 1427, 1381, 1121, 1079, 811 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}BrN_2O_3^{+1}(M+NH_4)^+$ requires 401.0495, Found: 401.0492.


7.386
7.381
7.365
7.348
7.330
7.310
7.293
7.283
7.251
7.247
6.604
6.583
5.668
5.001
4.961
4.853
4.814
2.477
0.000
7.04
0.98
0.95
0.99
0.98
3.00
f1 (ppm)


196.677
193.083
168.385
143.210
134.091
133.838
129.003
127.972
127.027
127.013
125.248
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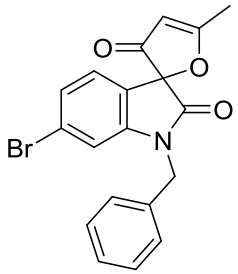
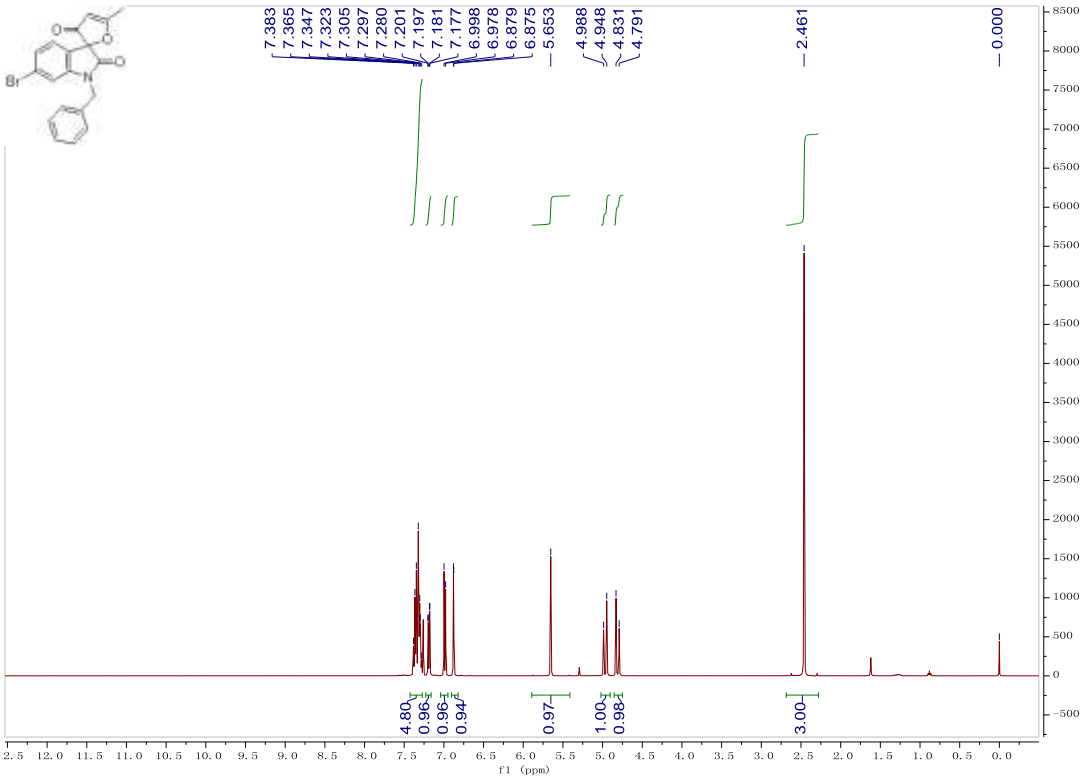
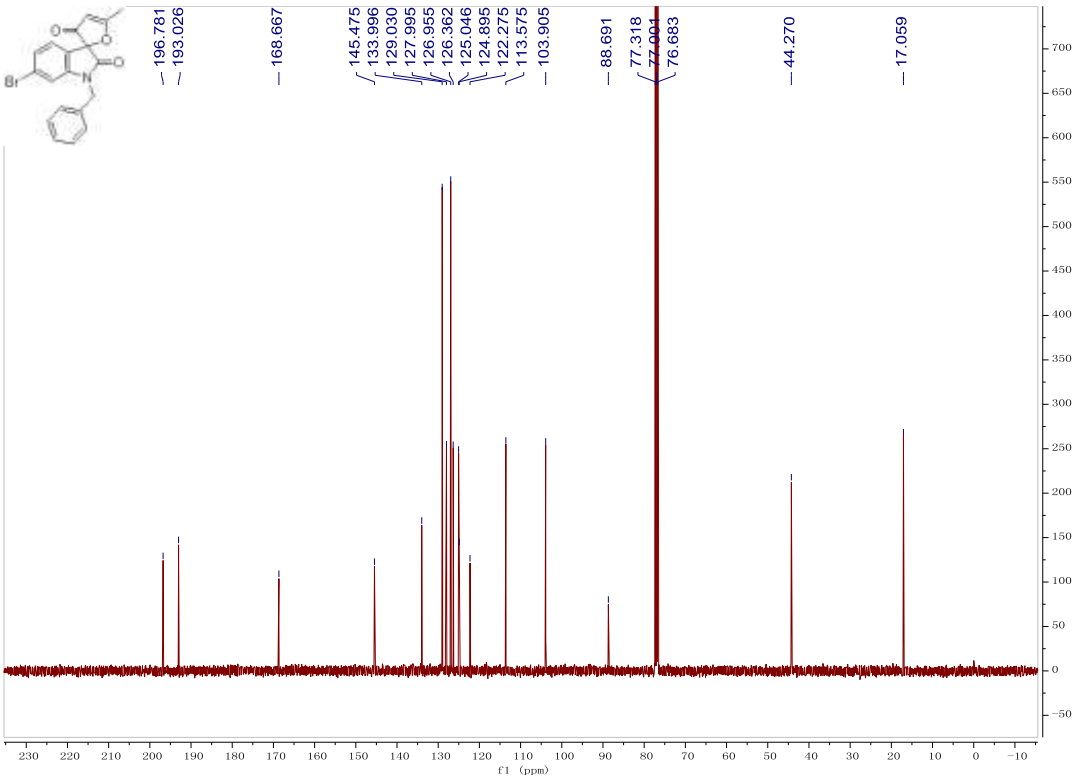
88.696
77.318
77.000
76.682
44.328
17.068
f1 (ppm)

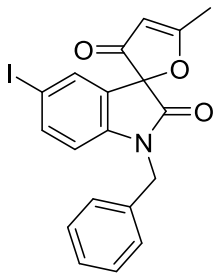


1'-benzyl-6'-bromo-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3t)

A white solid, 83% yield (64 mg). M.p.: 158-160 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (s, 3H, CH_3), 4.81 (d, *J* = 16.0 Hz, 1H, CH_2), 4.97 (d, *J* = 16.0 Hz, 1H, CH_2), 5.65 (s, 1H, =CH), 6.88 (d, *J* = 1.6 Hz, 1H, ArH), 6.99 (d, *J* = 8.0 Hz, 1H, ArH), 7.19 (dd, *J* = 1.6, 8.0 Hz, 1H, ArH), 7.28-7.39 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 44.3, 88.7, 103.9, 113.6, 122.3, 124.9, 125.0, 126.4, 127.0, 128.0, 129.0, 134.0, 145.5, 168.7, 193.0, 196.8. IR (EtOH) ν 3029, 2917, 2844, 1732, 1698, 1654, 1484, 1370, 1317, 1307, 989 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}BrN_2O_3^{+1}(M+NH_4)^+$ requires 401.0495, Found: 401.0492.

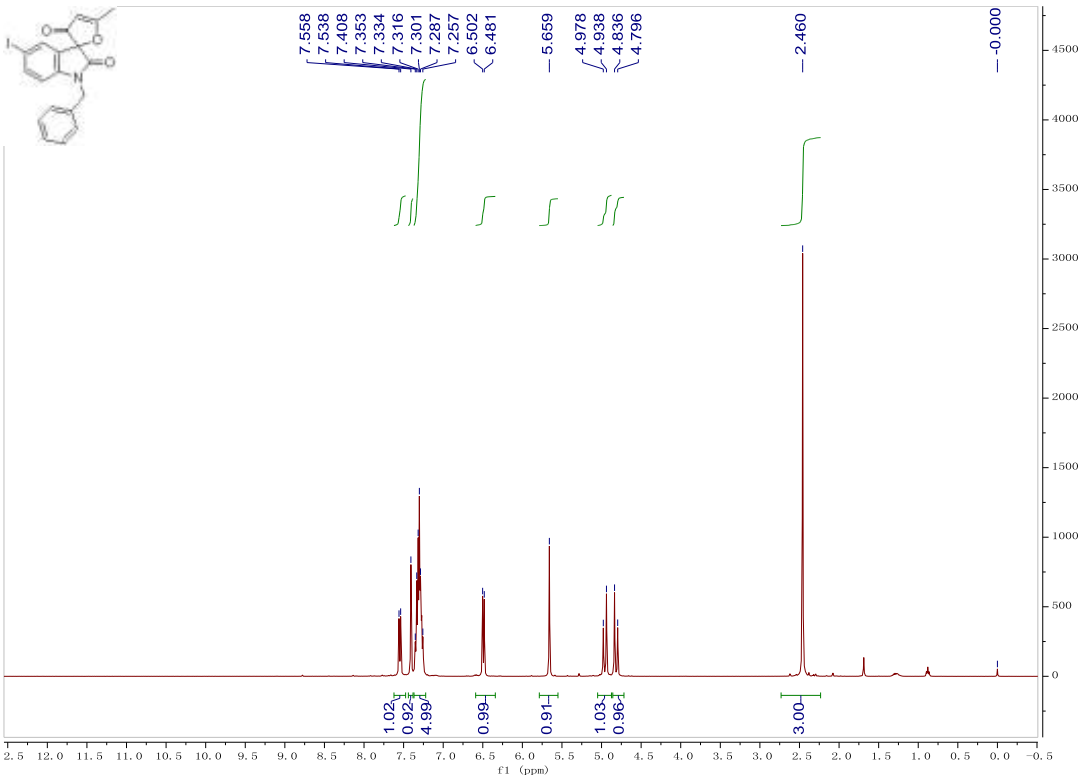


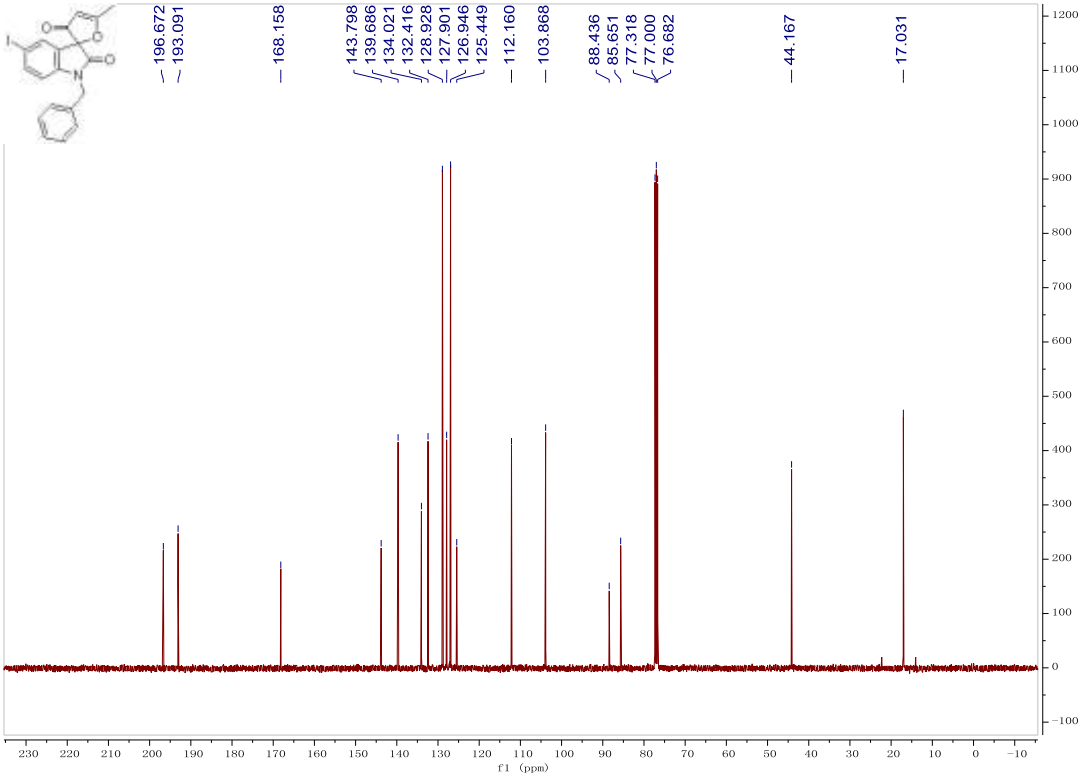




1'-benzyl-5'-iodo-5-methyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3u)

A white solid, 91% yield (78 mg). M.p.: 183-185 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.46 (s, 3H, CH_3), 4.82 (d, *J* = 16.0 Hz, 1H, CH_2), 4.96 (d, *J* = 16.0 Hz, 1H, CH_2), 5.66 (s, 1H, =CH), 6.49 (d, *J* = 8.4 Hz, 1H, ArH), 7.25-7.36 (m, 5H, ArH), 7.41 (s, 1H, ArH), 7.55 (d, *J* = 8.0 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 44.2, 85.7, 88.4, 103.9, 112.2, 125.4, 126.9, 127.9, 128.9, 132.4, 134.0, 139.7, 143.8, 168.2, 193.1, 196.7. IR (EtOH) ν 2921, 2851, 1856, 1734, 1705, 1496, 1479, 1423, 1131, 954, 697 cm^{-1}. HRMS (ESI) Calcd. For $C_{19}H_{18}IN_2O_3^{+1}(M+NH_4)^+$ requires 449.0357, Found: 449.0350.


7.558
7.538
7.408
7.353
7.334
7.316
7.301
7.287
7.257
6.502
6.481
5.659
4.978
4.938
4.836
4.796
2.460
-0.000
1.02
0.92
4.99
0.99
0.91
1.03
0.96
3.00
f1 (ppm)


196.672
193.091
168.158
143.798
139.686
134.021
132.416
128.928
127.901
126.946
125.449
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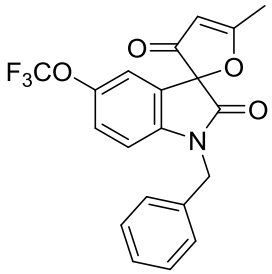
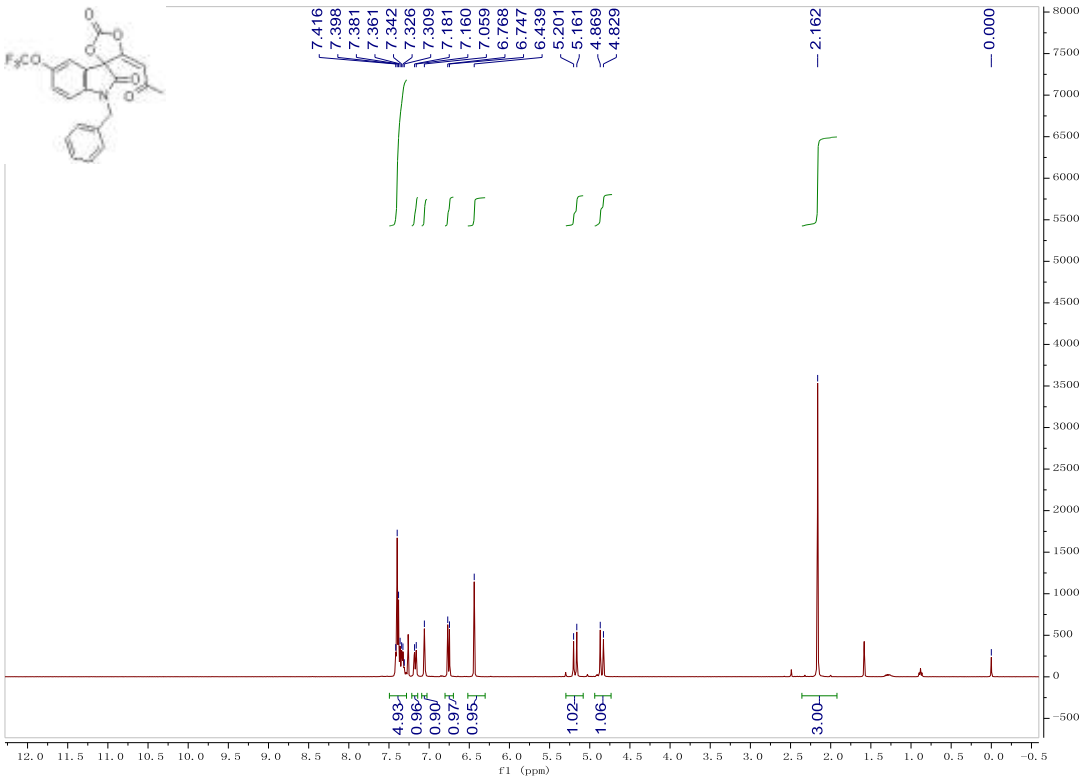
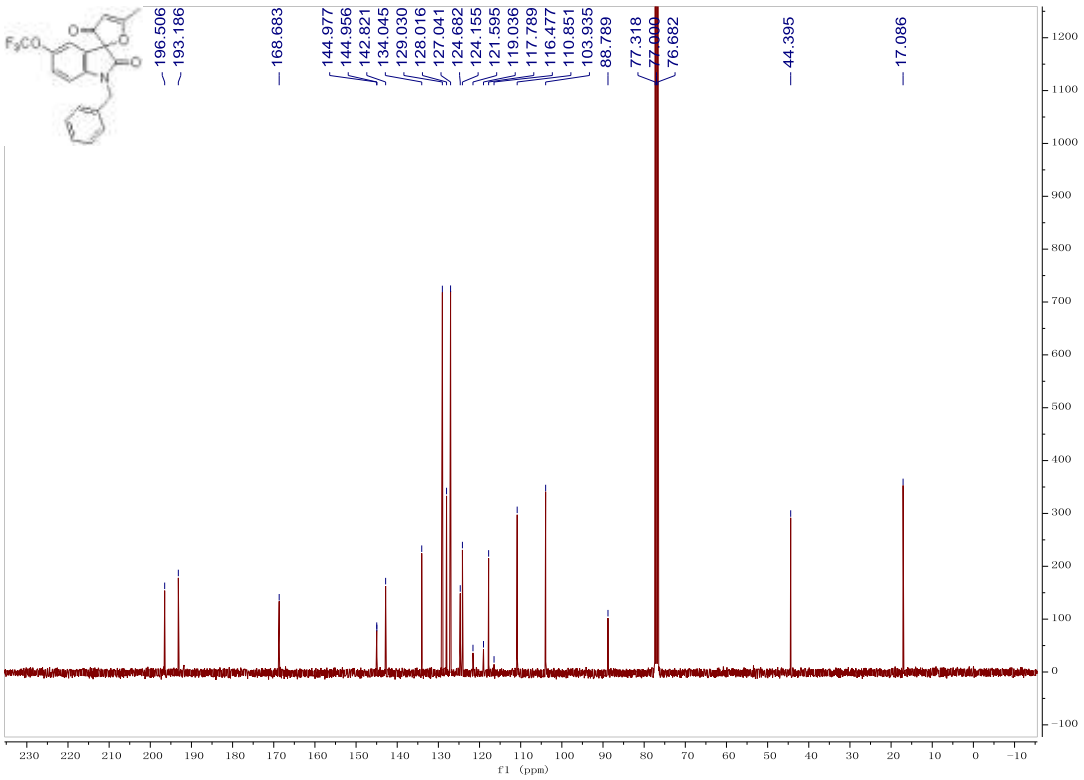
103.868
88.436
85.651
77.318
77.000
76.682
44.167
17.031
f1 (ppm)



1'-benzyl-5-methyl-5'-(trifluoromethoxy)-3H-spiro[furan-2,3'-indoline]-2',3-dione (3v)

A white solid, 94% yield (73 mg). M.p.: 134-136 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.49 (s, 3H, CH_3), 4.85 (d, *J* = 16.0 Hz, 1H, CH_2), 5.00 (d, *J* = 16.0 Hz, 1H, CH_2), 5.68 (s, 1H, =CH), 6.71 (d, *J* = 8.4 Hz, 1H, ArH), 7.02 (s, 1H, ArH), 7.13 (d, *J* = 8.8 Hz, 1H, ArH), 7.27-7.38 (m, 5H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 44.4, 88.8, 103.9, 110.9, 117.8, 120.3 (q, *J* = 255.9 Hz), 124.2, 124.7, 127.0, 128.0, 129.0, 134.0, 142.8, 145.0 (q, *J* = 2.1 Hz), 168.7, 193.2, 196.5. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -58.32. IR (EtOH) ν 2924, 2853, 1710, 1608, 1455, 1325, 1256, 1219, 1162, 1029, 820 cm^{-1}. HRMS (ESI) Calcd. For $C_{20}H_{18}F_3N_2O_4^{+1}$(M+$NH_4$)$^+$ requires 407.1213, Found: 407.1205. $[\alpha]^{25}_D$ = +11.67 (c 0.06, CH_2Cl_2) for 76% *ee*; Enantiomeric excess was determined by HPLC with a Chiralcel AD-H column, Hexane/^{i}PrOH = 80/20, 0.7 mL/min, 254 nm, t_{minor} = 15.790 min, t_{major} = 29.557 min.

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144.956
142.821
134.045
129.030
128.016
127.041
124.682
124.155
121.595
119.036
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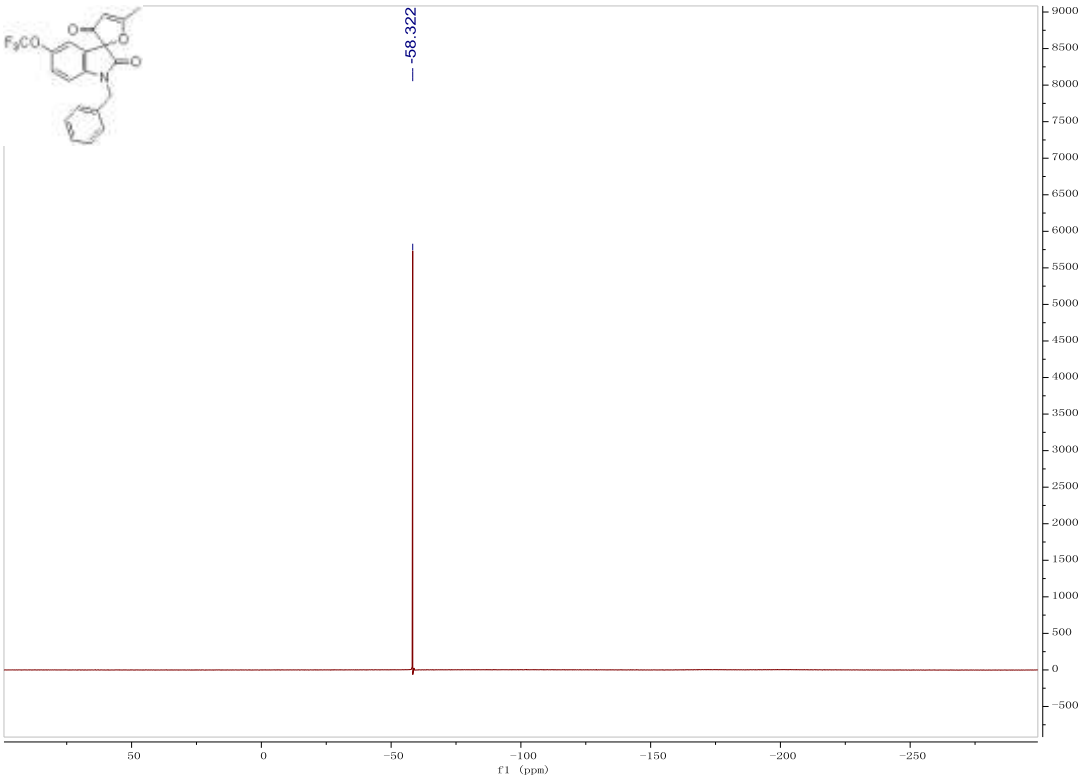
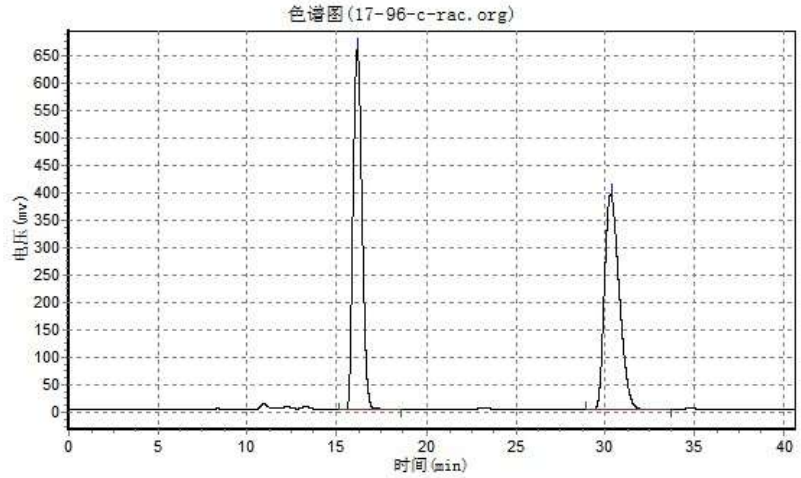
116.477
110.851
103.935
88.789
77.318
77.000
76.682
44.395
17.086
f1 (ppm)


-58.322
f1 (ppm)

实验时间：2019-07-20,11:24:19
谱图文件:D:\Sun Yaoliang\co2\17-96-c-rac.org

实验者:
报告时间：2019-07-20,12:28:34
积分方法:面积归一法



分析结果表

峰号	峰名	保留时间	峰高	峰面积	含量
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2		30.365	394007.219	22821224.000	49.6615
总计			1051861.219	45953568.000	100.0000

实验时间：2019-07-20,12:25:49
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实验者:
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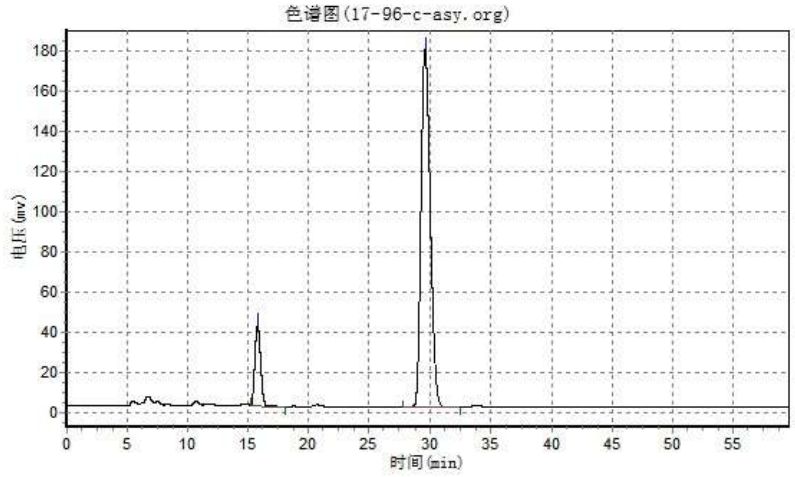
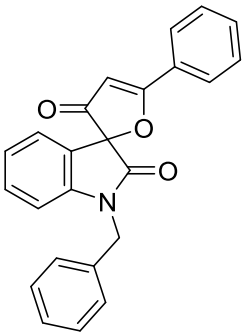
积分方法:面积归一法



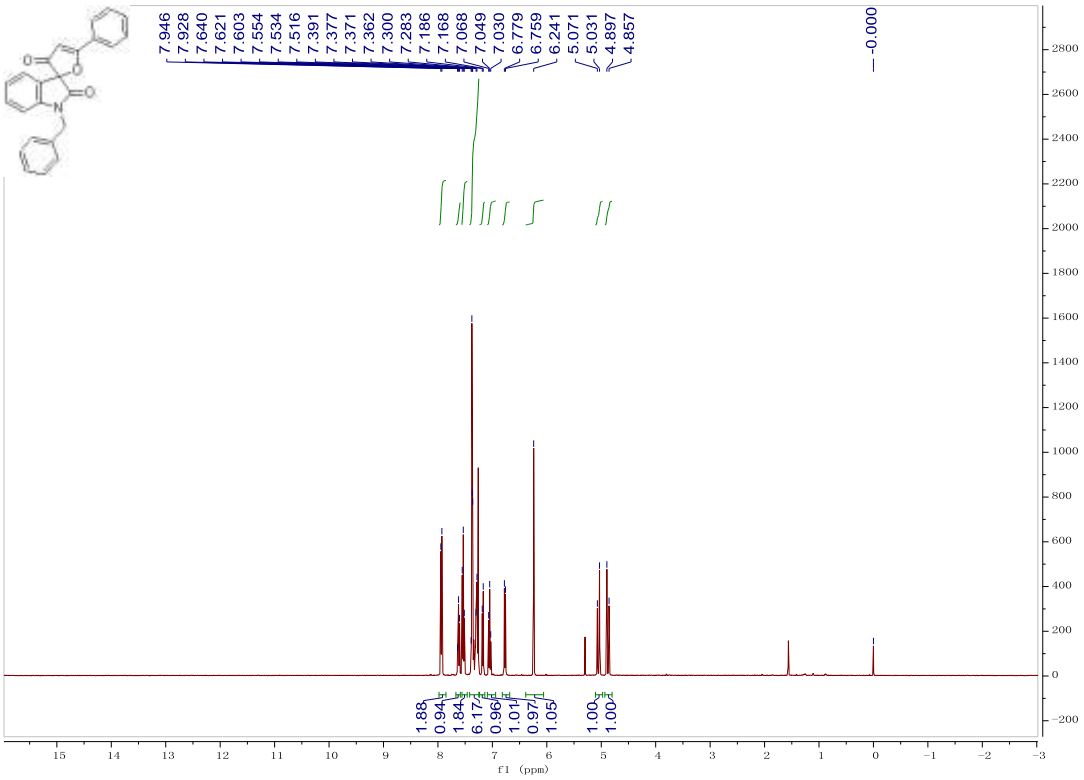
分析结果表

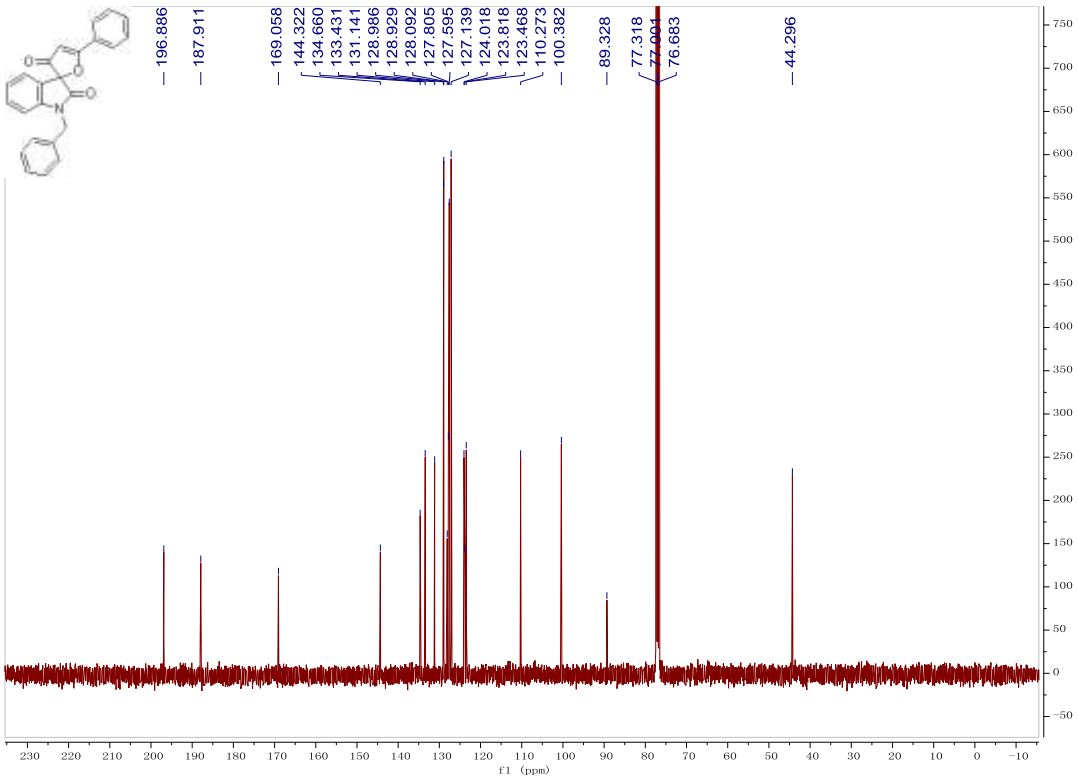
峰号	峰名	保留时间	峰高	峰面积	含量
1		15.790	40333.766	1340497.750	12.4361
2		29.557	178145.266	9438625.000	87.5639
总计			218479.031	10779122.750	100.0000

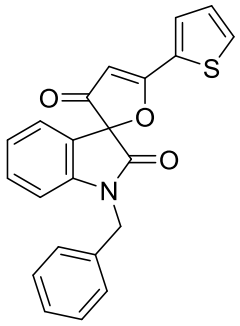


1'-benzyl-5-phenyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3w)

A white solid, 88% yield (65 mg). M.p.: 141-143 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 4.88 (d, *J* = 16.0 Hz, 1H, CH_2), 5.05 (d, *J* = 16.0 Hz, 1H, CH_2), 6.24 (s, 1H, =CH), 6.77 (d, *J* = 8.0 Hz, 1H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 7.18 (d, *J* = 7.2 Hz, 1H, ArH), 7.28-7.40 (m, 6H, ArH), 7.51-7.56 (m, 2H, ArH), 7.62 (t, *J* = 7.6 Hz, 1H, ArH), 7.94 (d, *J* = 7.2 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 89.3, 100.4, 110.3, 123.5, 123.8, 124.0, 127.1, 127.6, 127.8, 128.1, 128.9, 129.0, 131.1, 133.4, 134.7, 144.3, 169.1, 187.9, 196.9. IR (EtOH) ν 3064, 2923, 2852, 1857, 1735, 1522, 1484, 1381, 1165, 1029, 959 cm^{-1}. HRMS (ESI) Calcd. For $C_{24}H_{21}N_2O_3^{+1}(M+NH_4)^+$ requires 385.1547, Found: 385.1544.

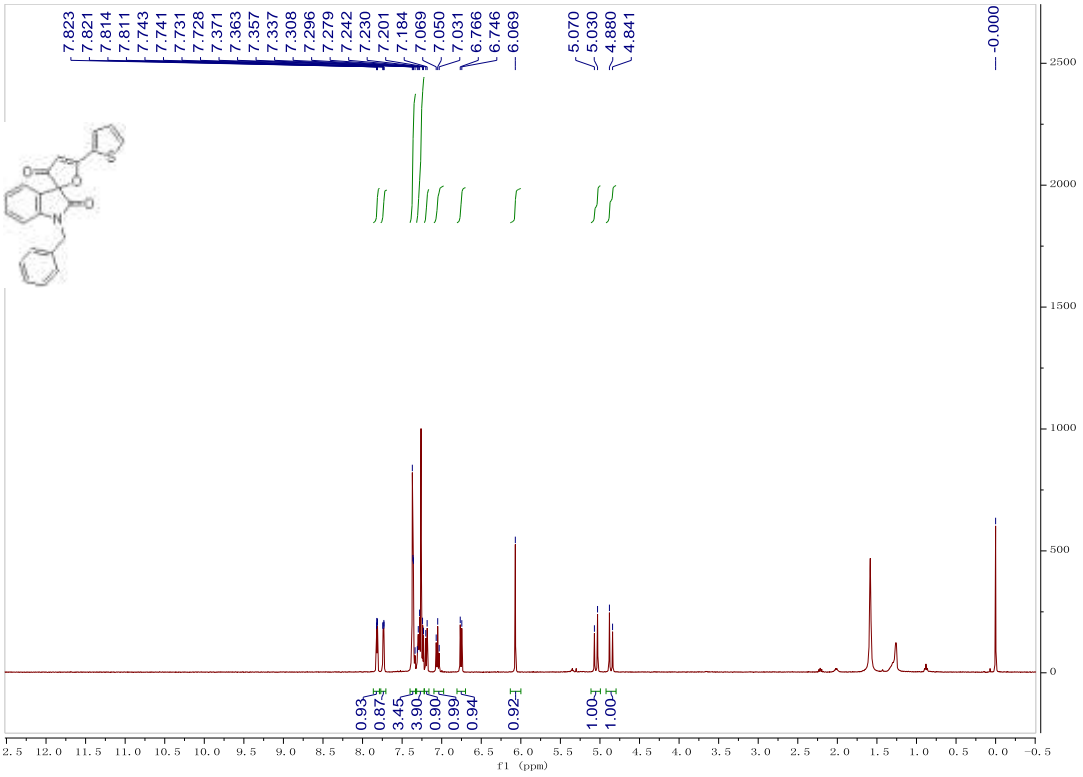






1'-benzyl-5-(thiophen-2-yl)-3H-spiro[furan-2,3'-indoline]-2',3-dione (3x)

A white solid, 73% yield (54 mg). M.p.: 162-164 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 4.86 (d, *J* = 15.6 Hz, 1H, CH_2), 5.05 (d, *J* = 15.6 Hz, 1H, CH_2), 6.07 (s, 1H, =CH), 6.76 (d, *J* = 8.0 Hz, 1H, ArH), 7.05 (t, *J* = 7.6 Hz, 1H, ArH), 7.19 (d, *J* = 6.8 Hz, 1H, ArH), 7.23-7.31 (m, 4H, ArH), 7.33-7.38 (m, 3H, ArH), 7.74 (dd, *J* = 0.8, 4.8 Hz, 1H, ArH), 7.82 (dd, *J* = 0.8, 3.6 Hz, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 44.3, 89.3, 99.2, 110.3, 123.5, 123.7, 124.1, 127.1, 127.8, 128.7, 128.9, 130.9, 131.2, 131.8, 133.1, 134.6, 144.3, 169.1, 181.9, 195.9. IR (EtOH) ν 2922, 2852, 1732, 1699, 1581, 1466, 1414, 1114, 1022, 972, 835, 750 cm^{-1}. HRMS (ESI) Calcd. For $C_{22}H_{16}NO_3S^{+1}(M+H)^+$ requires 374.0845, Found: 374.0841.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7.821
7.814
7.811
7.743
7.741
7.731
7.728
7.371
7.363
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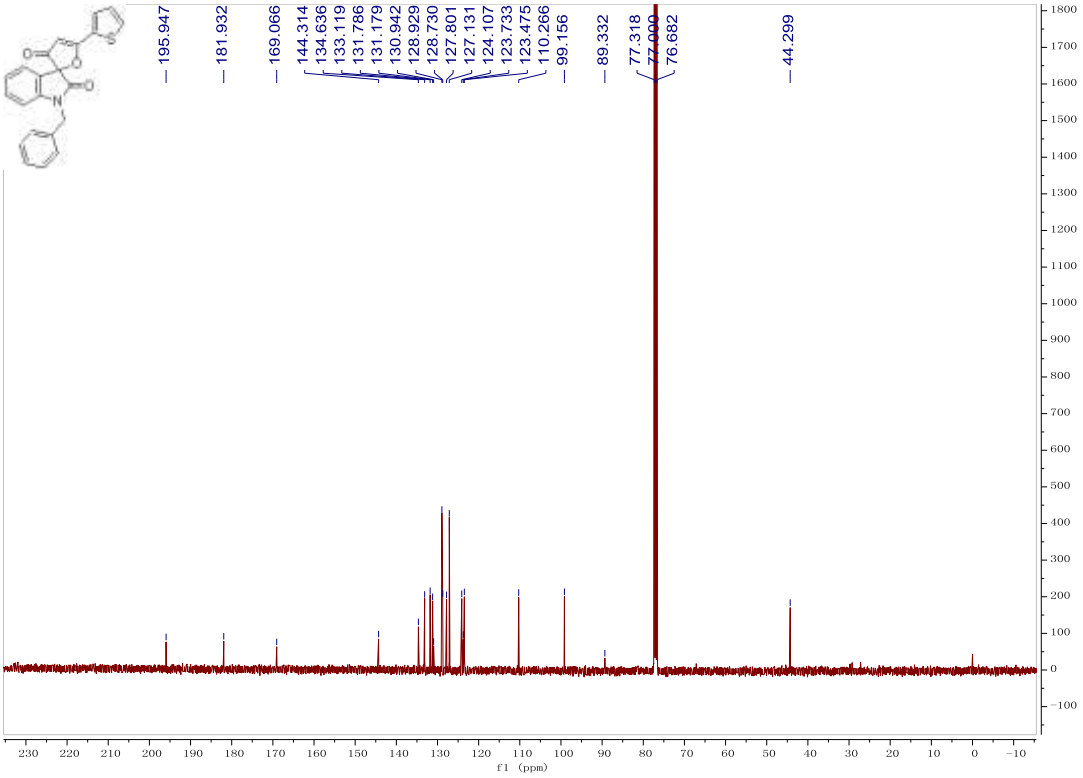
7.337
7.308
7.296
7.279
7.242
7.230
7.201
7.184
7.069
7.050
7.031
6.766
6.746
6.069
5.070
5.030
4.880
4.841
-0.000
0.93
0.87
3.45
3.90
0.90
0.99
0.94
0.92
1.00
1.00
f1 (ppm)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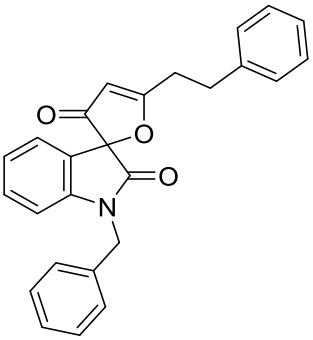
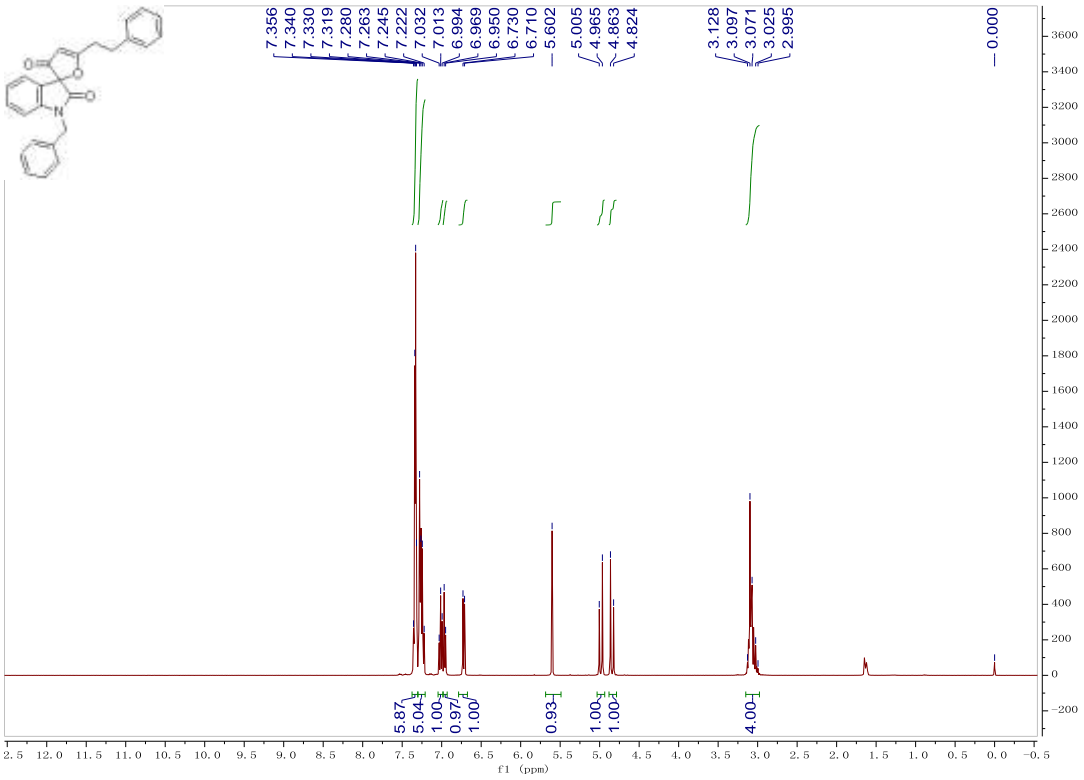
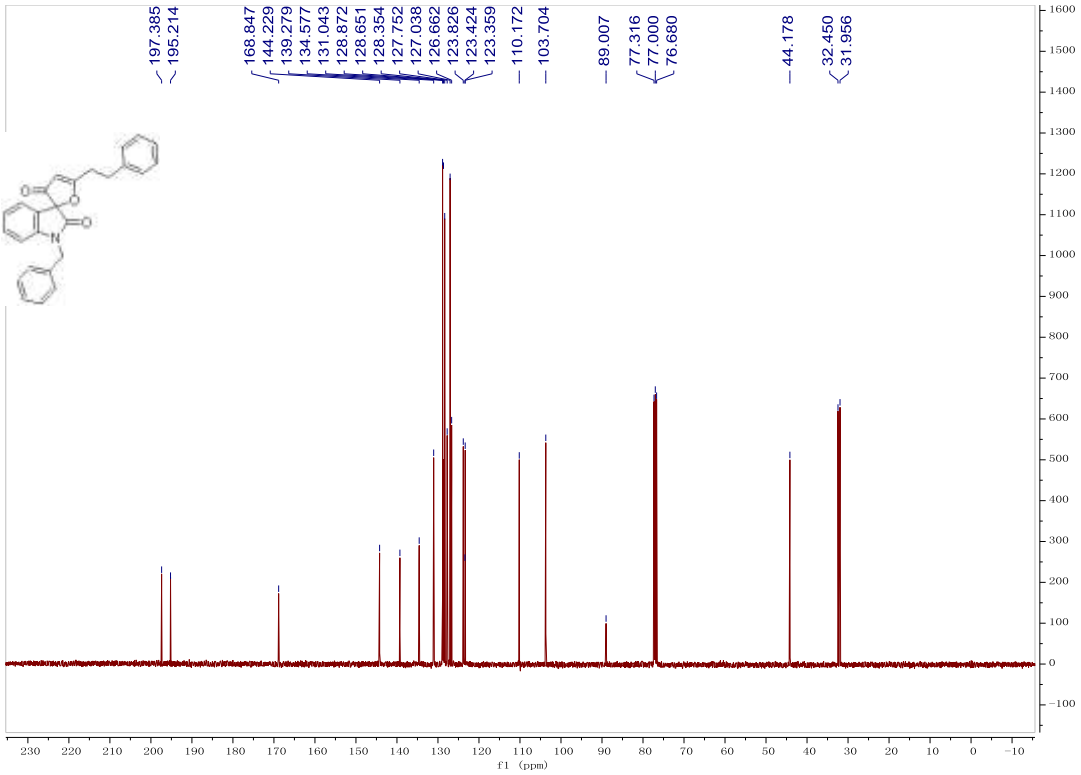
169.066
144.314
134.636
133.119
131.786
131.179
130.942
128.929
128.730
127.801
127.131
124.107
123.733
123.475
110.266
99.156
89.332
77.318
77.000
76.682
44.299
f1 (ppm)

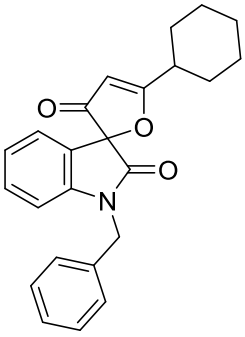


1'-benzyl-5-phenethyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3y)

A white solid, 91% yield (72 mg). M.p.: 137-139 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.99-3.13 (m, 4H, CH_2), 4.84 (d, *J* = 15.6 Hz, 1H, CH_2), 4.99 (d, *J* = 15.6 Hz, 1H, CH_2), 5.60 (s, 1H, =CH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 6.96 (d, *J* = 7.6 Hz, 1H, ArH), 7.01 (t, *J* = 7.6 Hz, 1H, ArH), 7.22-7.28 (m, 5H, ArH), 7.31-7.36 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 32.0, 32.5, 44.2, 89.0, 103.7, 110.2, 123.36, 123.42, 123.8, 126.7, 127.0, 127.8, 128.4, 128.7, 128.9, 131.0, 134.6, 139.3, 144.2, 168.8, 195.2, 197.4. IR (EtOH) ν 2958, 2916, 2845, 1733, 1599, 1487, 1466, 1360, 1170, 748 cm^{-1}. HRMS (ESI) Calcd. For $C_{26}H_{25}N_2O_3^{+1}(M+NH_4)^+$ requires 413.1860, Found: 413.1853.

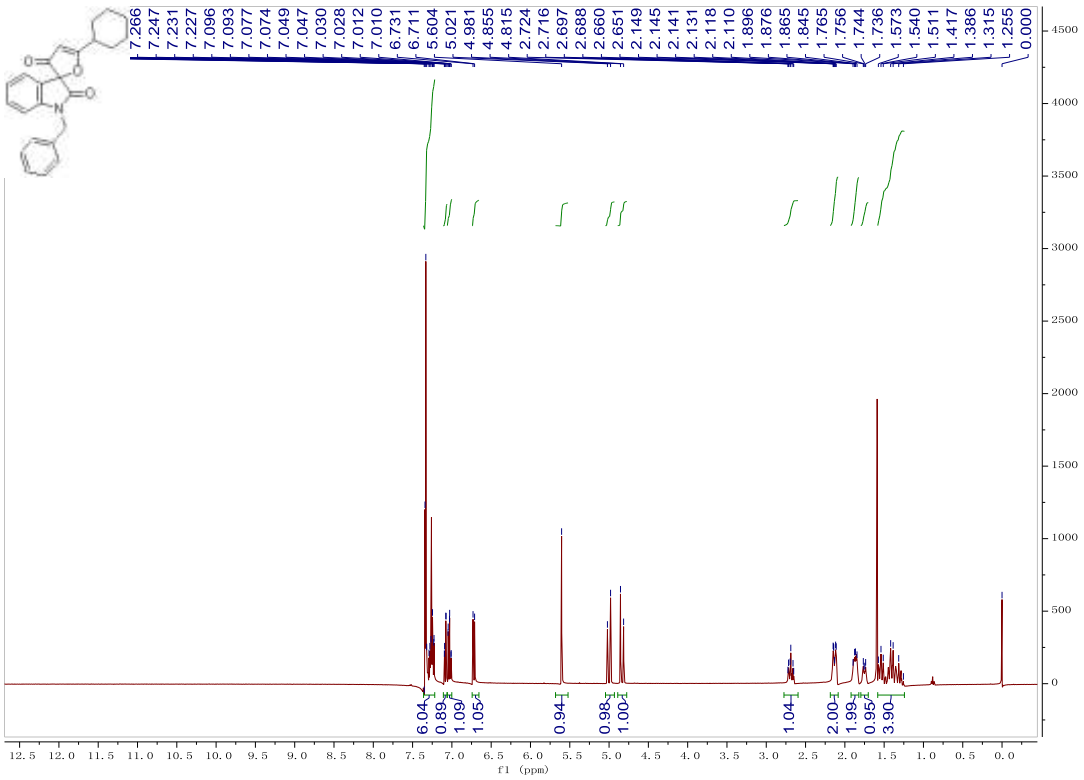






1'-benzyl-5-cyclohexyl-3H-spiro[furan-2,3'-indoline]-2',3-dione (3z)

A white solid, 59% yield (66 mg). M.p.: 152-154 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.25-1.58 (m, 4H, CH_2), 1.73-1.77 (m, 1H, CH_2), 1.84-1.90 (m, 2H, CH_2), 2.11-2.15 (m, 2H, CH_2), 2.65-2.73 (m, 1H, CH), 4.84 (d, *J* = 16.0 Hz, 1H, CH_2), 5.00 (d, *J* = 16.0 Hz, 1H, CH_2), 5.60 (s, 1H, =CH), 6.72 (d, *J* = 8.0 Hz, 1H, ArH), 7.03 (dt, *J* = 0.8, 7.6 Hz, 1H, ArH), 7.09 (dd, *J* = 1.2, 7.6 Hz, 1H, ArH), 7.22-7.36 (m, 6H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 25.4, 25.5, 25.7, 29.8, 29.9, 39.8, 44.2, 88.7, 101.4, 110.2, 123.4, 123.6, 123.7, 127.1, 127.8, 128.9, 131.0, 134.7, 144.3, 169.0, 197.6, 200.5. IR (EtOH) ν 2925, 2853, 1734, 1704, 1590, 1487, 1340, 1278, 1118, 747 cm^{-1}. HRMS (ESI) Calcd. For $C_{24}H_{27}N_2O_3^{+1}(M+NH_4)^+$ requires 391.2016, Found: 391.2006.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7.093
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7.047
7.030
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7.010
6.731
6.711
5.604
5.021
4.981
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4.815
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2.141
2.131
2.118
2.110
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1.876
1.865
1.845
1.765
1.756
1.744
1.736
1.573
1.540
1.511
1.417
1.386
1.315
1.255
0.000
6.04
0.89
1.09
1.05
0.94
0.98
1.00
1.04
2.00
1.99
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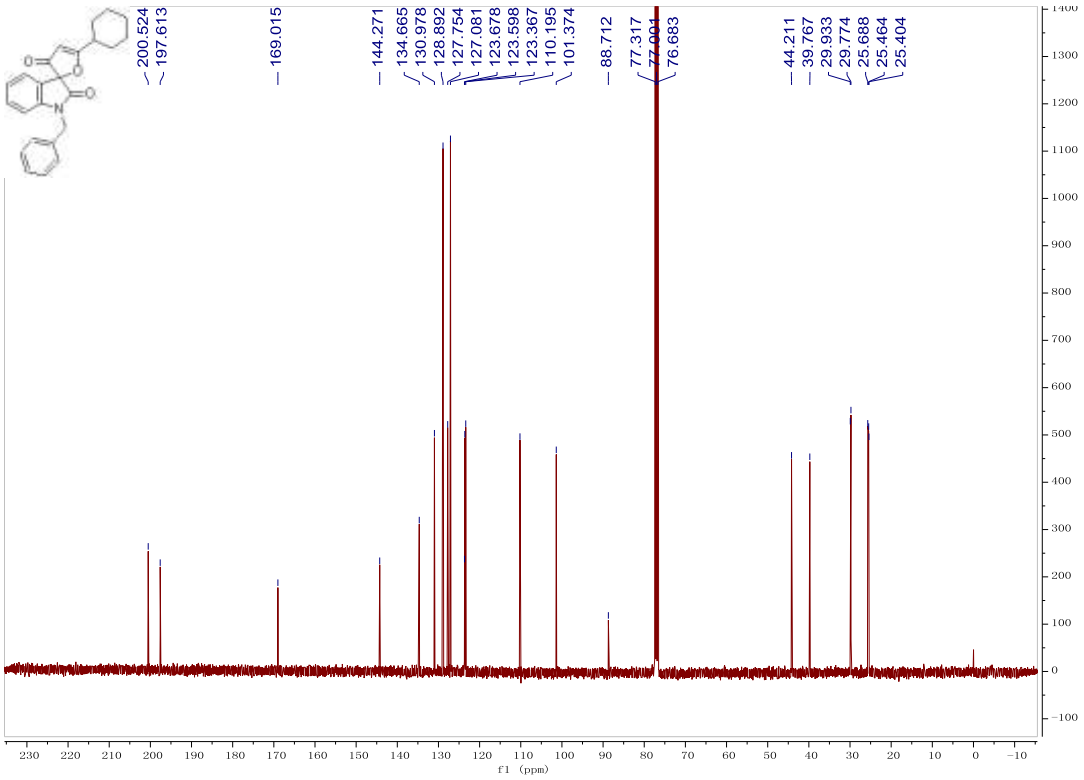
3.90
f1 (ppm)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101.374
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76.683
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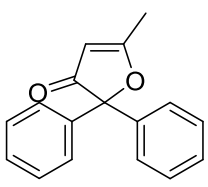
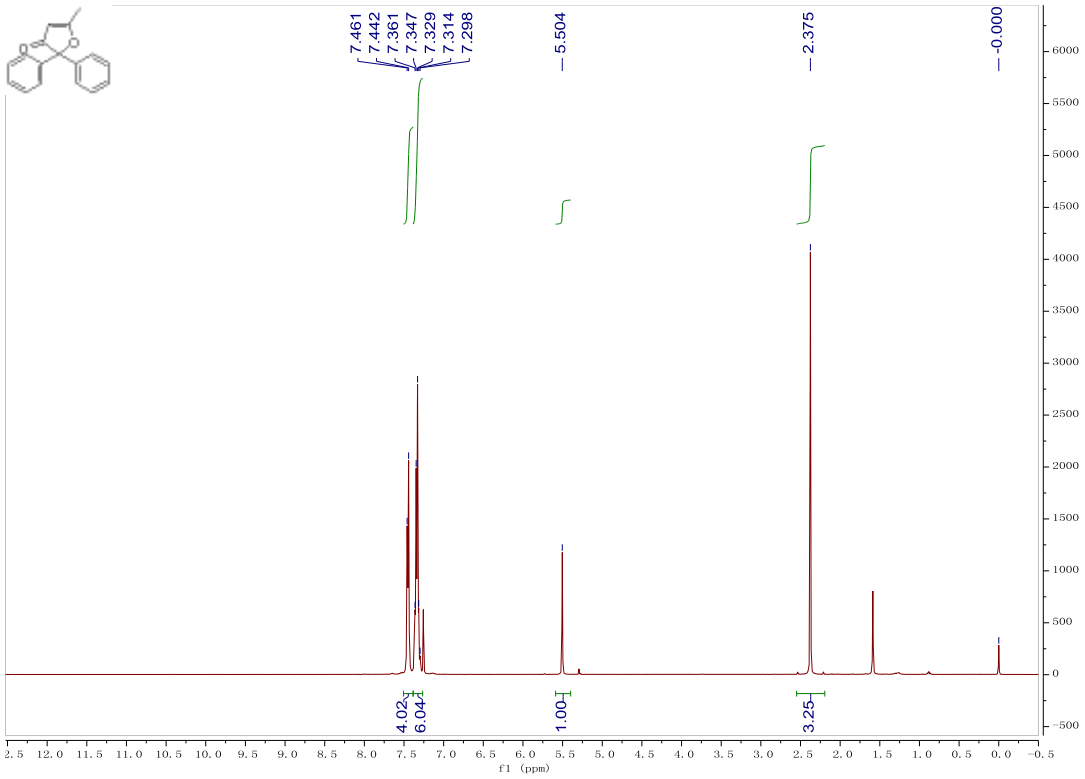
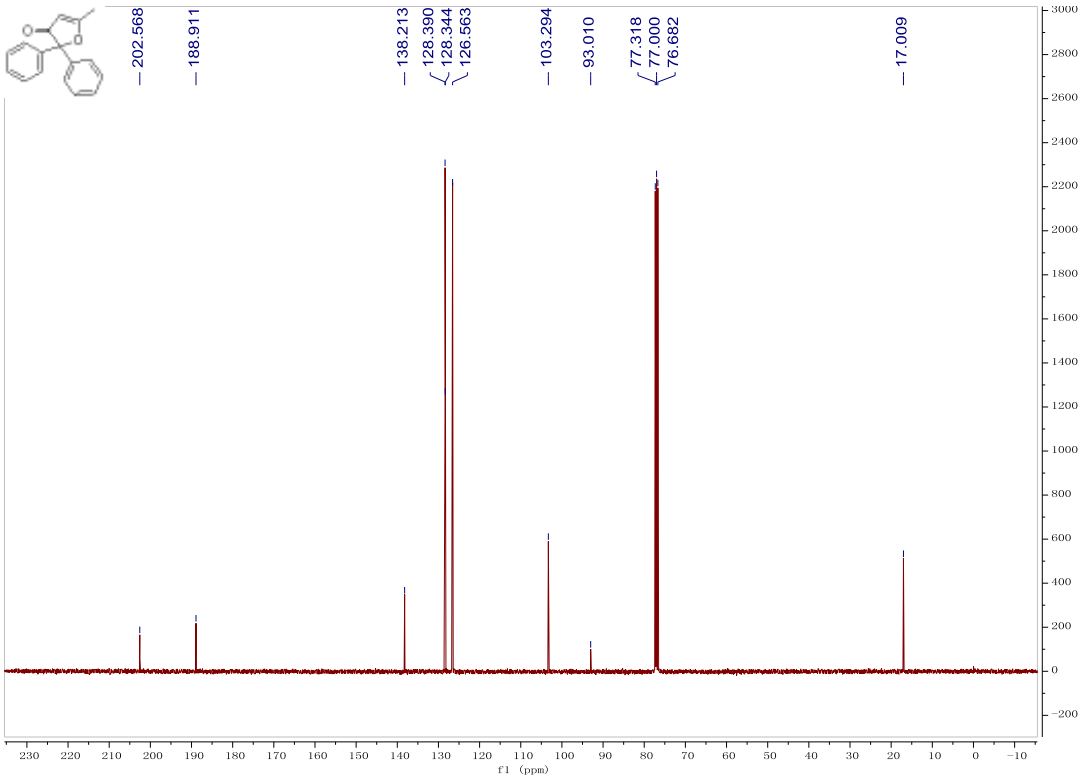
25.404
f1 (ppm)

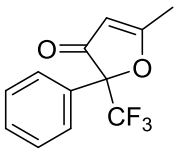


5-methyl-2,2-diphenylfuran-3(2H)-one (3ab)

A white solid, 69% yield (52 mg). M.p.: 97-99 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.38 (s, 3H, CH_3), 5.50 (s, 1H, =CH), 7.29-7.37 (m, 6H, ArH), 7.45 (d, *J* = 7.6 Hz, 4H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.0, 93.0, 103.3, 126.6, 128.3, 128.4, 138.2, 188.9, 202.6. IR (EtOH) ν 3063, 3031, 2929, 2853, 1702, 1613, 1448, 1333, 1170, 944 cm^{-1}. HRMS (ESI) Calcd. For $C_{17}H_{15}O_2^{+1}(M+H)^+$ requires 251.1067, Found: 251.1062.

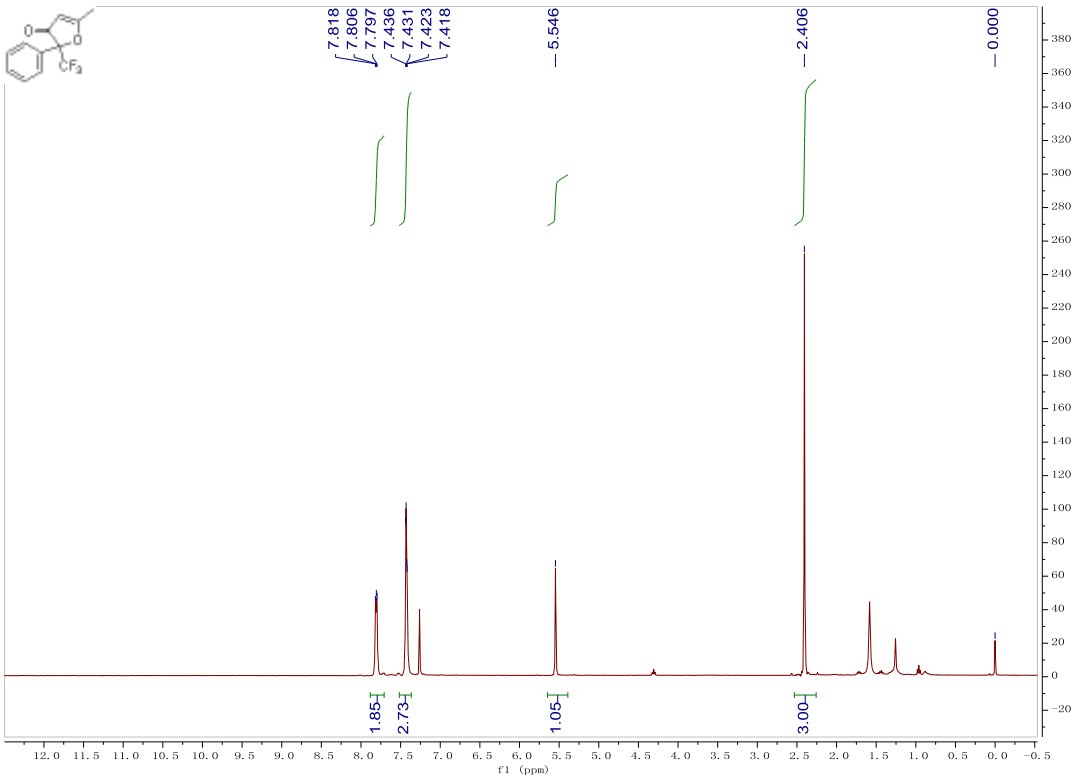






5-methyl-2-phenyl-2-(trifluoromethyl)furan-3(2H)-one (3ac)

A liquid, 46% yield (33 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.41 (s, 3H, CH_3), 5.55 (s, 1H, =CH), 7.41-7.44 (m, 3H, ArH), 7.79-7.82 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 16.8, 85.8 (q, *J* = 30.2 Hz), 104.4, 121.3 (q, *J* = 282.3 Hz), 126.2, 128.5, 129.3, 129.9, 190.2, 195.6. ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$) δ -76.93. IR (EtOH) ν 3086, 3060, 2913, 2843, 1605, 1471, 1353, 1228, 1089, 749 cm^{-1}. HRMS (DART Positive Ion Mode) Calcd. For $C_{12}H_{10}O_2F_3^{+1}(M+H)^+$ requires 243.0627, Found: 243.0627.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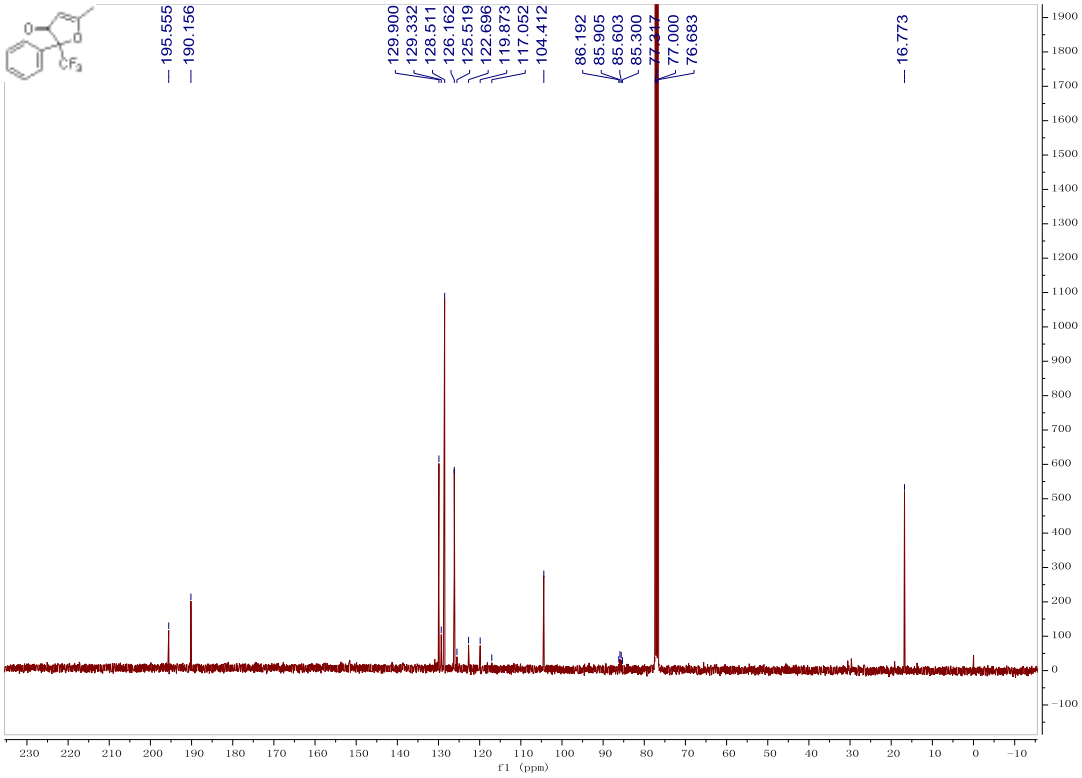
1.05
3.00
f1 (ppm)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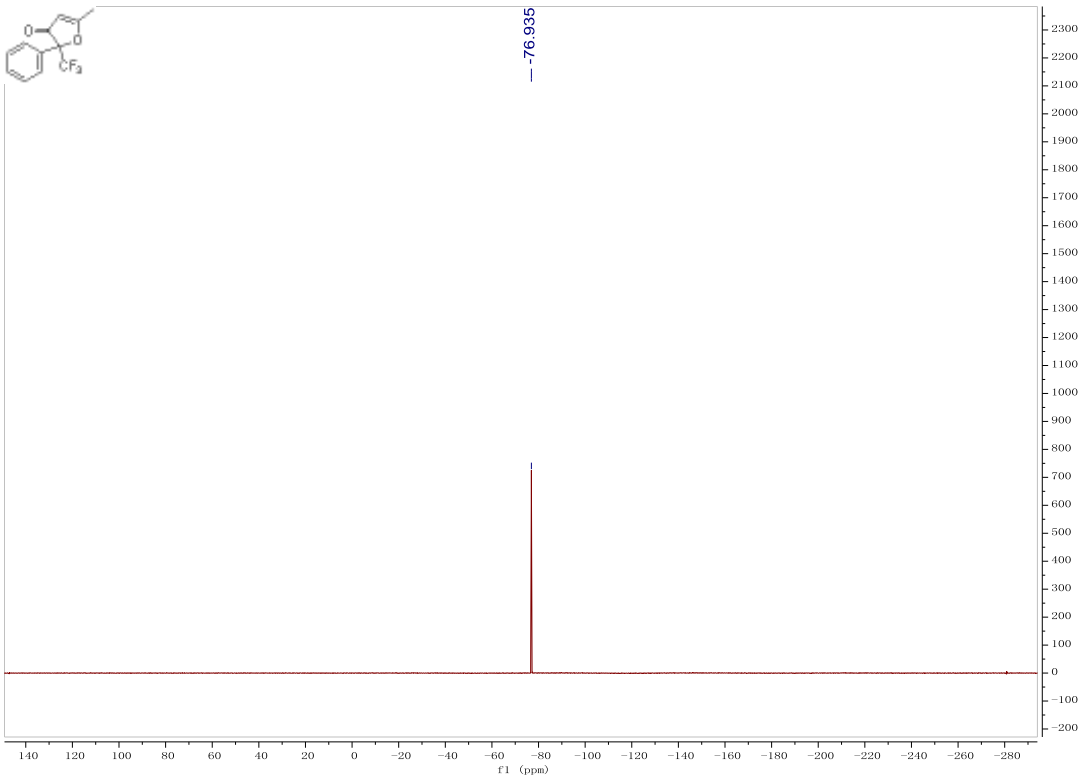
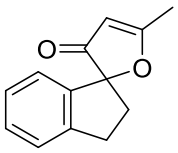
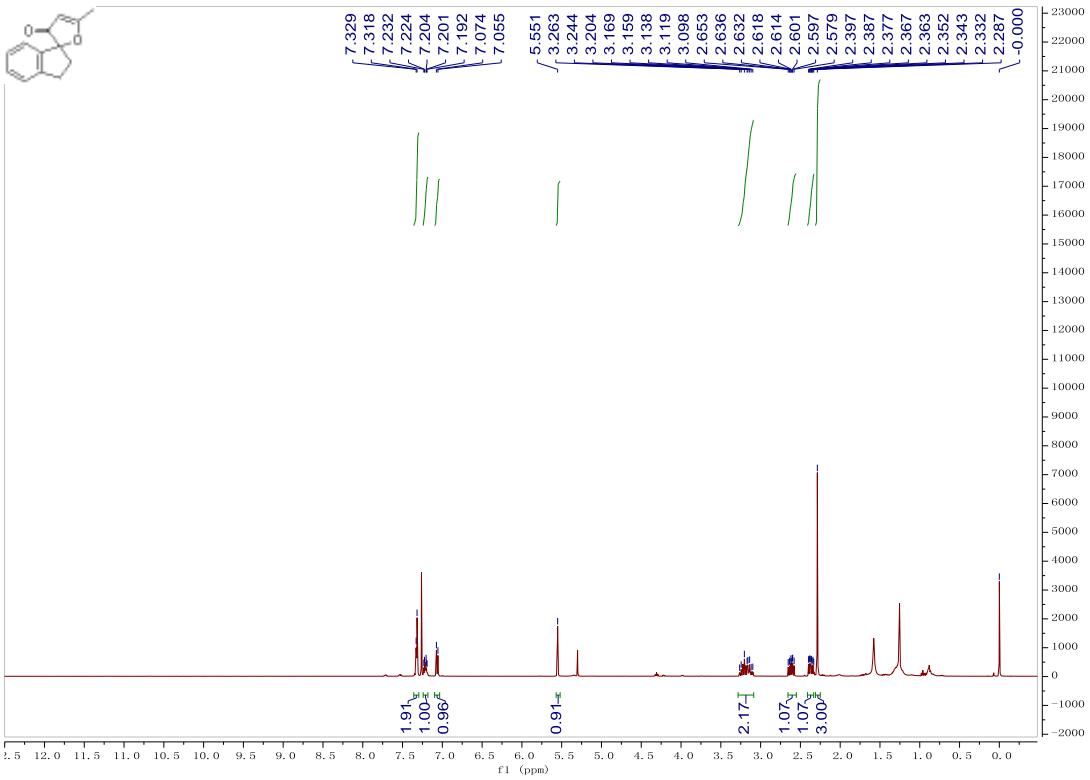
77.317
77.000
76.683
16.773
f1 (ppm)





5-methyl-2',3'-dihydro-3H-spiro[furan-2,1'-inden]-3-one (3ad)

A white solid, 79% yield (32 mg). M.p.: 84-86 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 2.29 (s, 3H, CH_3), 2.33-2.40 (m, 1H, CH_2), 2.57-2.66 (m, 1H, CH_2), 3.09-3.27 (m, 2H, CH_2), 5.55 (s, 1H, =CH), 7.06 (d, *J* = 7.6 Hz, 1H, ArH), 7.19-7.24 (m, 1H, ArH), 7.31-7.33 (m, 2H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.2, 29.7, 30.6, 35.5, 99.1, 103.3, 123.2, 125.1, 127.2, 129.9, 139.5, 145.7, 189.6, 205.1. IR (EtOH) ν 3076, 2976, 2929, 1674, 1479, 1456, 1358, 1219, 1076, 764 cm^{-1}. HRMS (ESI) Calcd. For $C_{13}H_{16}NO_2^{+1}(M+NH_4)^+$ requires 218.1176, Found: 218.1175.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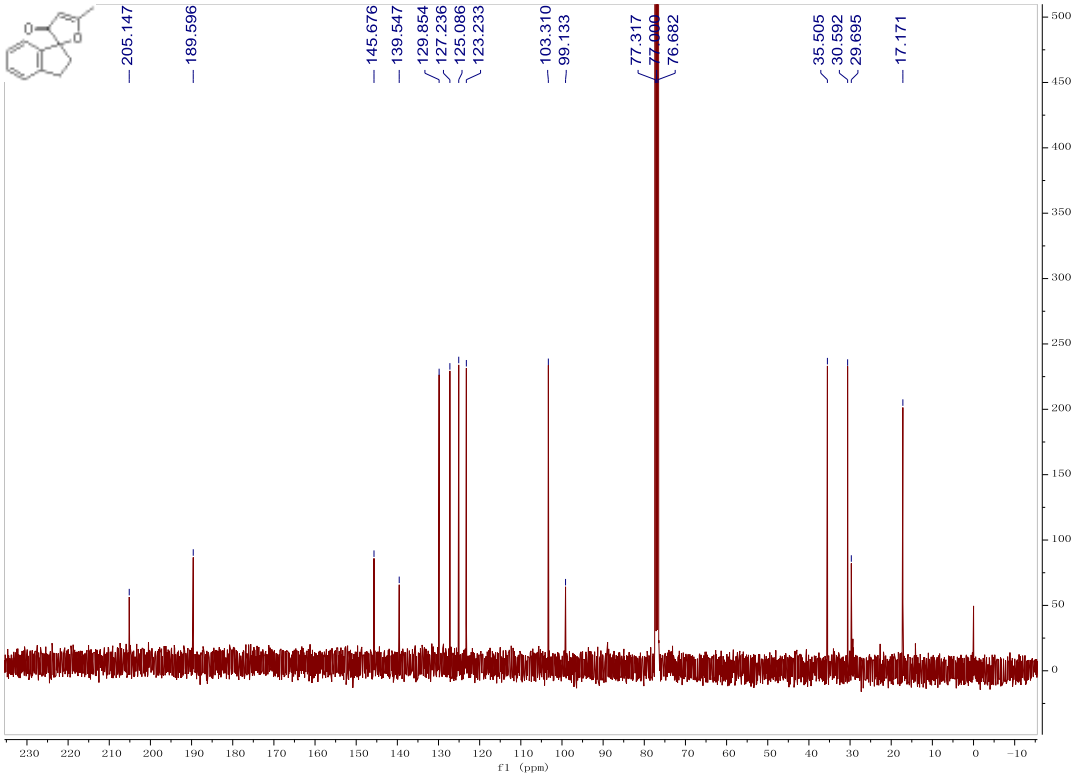
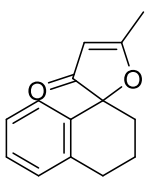
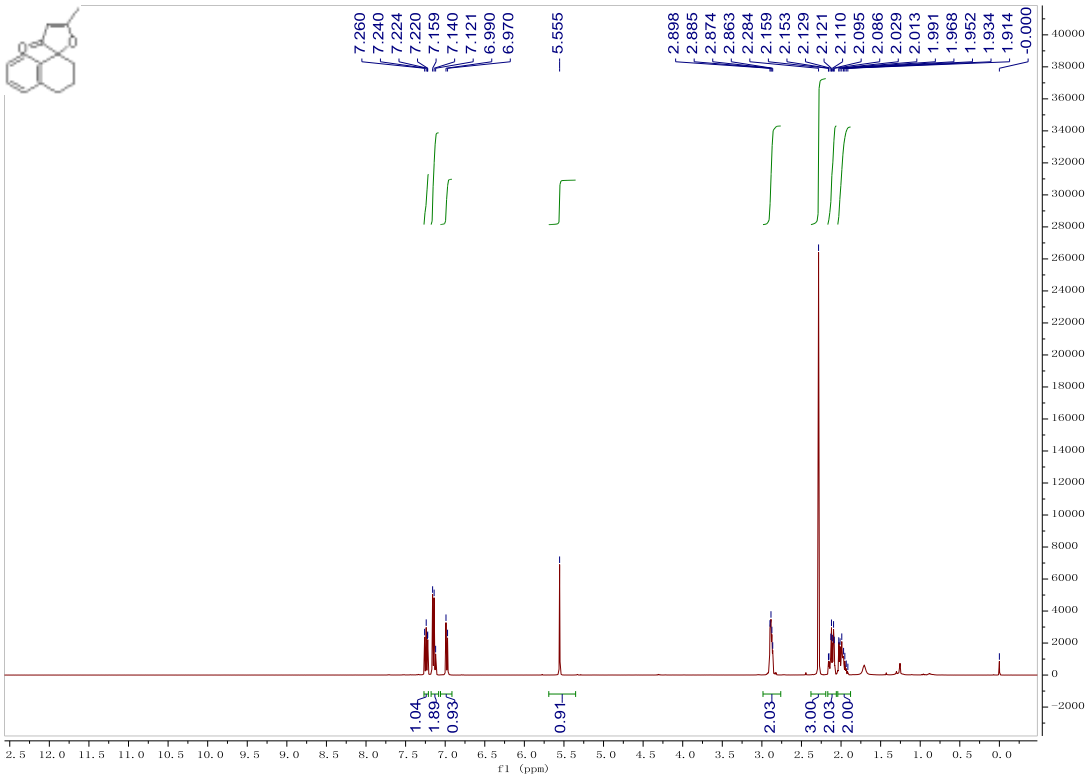
5.551
3.263
3.244
3.204
3.169
3.159
3.138
3.119
3.098
2.653
2.636
2.632
2.618
2.614
2.601
2.597
2.579
2.397
2.387
2.377
2.367
2.363
2.352
2.343
2.332
2.287
-0.000
1.91
1.00
0.96
0.91
2.17
1.07
1.07
3.00
f1 (ppm)

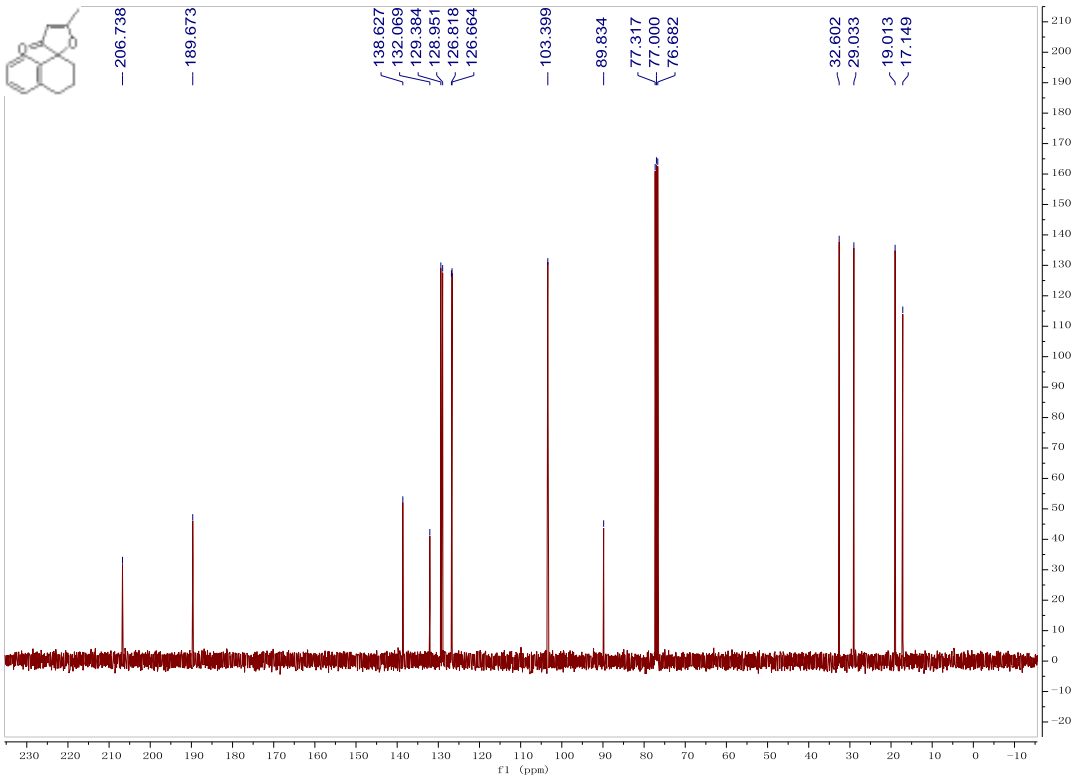

205.147
189.596
145.676
139.547
129.854
127.236
125.086
123.233
103.310
99.133
77.317
77.000
76.682
35.505
30.592
29.695
17.171
f1 (ppm)



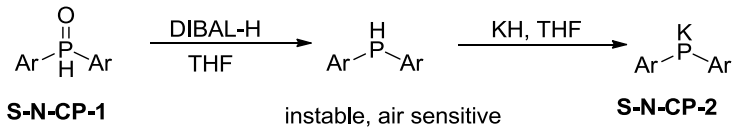
5-methyl-3',4'-dihydro-2'H,3H-spiro[furan-2,1'-naphthalen]-3-one (3ae)

A white solid, 75% yield (32 mg). M.p.: 79-81 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 1.91-2.03 (m, 2H, CH_2), 2.08-2.16 (m, 2H, CH_2), 2.28 (s, 3H, CH_3), 2.86-2.90 (m, 2H, CH_2), 5.56 (s, 1H, =CH), 6.98 (d, *J* = 8.0 Hz, 1H, ArH), 7.12-7.16 (m, 2H, ArH), 7.22-7.26 (m, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 17.1, 19.0, 29.0, 32.6, 89.8, 103.4, 126.7, 126.8, 129.0, 129.4, 132.1, 138.6, 189.7, 206.7. IR (EtOH) ν 3023, 2937, 2877, 1696, 1596, 1492, 1384, 1162, 1100, 949, 762 cm^{-1}. HRMS (ESI) Calcd. For $C_{14}H_{15}O_2^{+1}(M+H)^+$ requires 215.1067, Found: 215.1066.

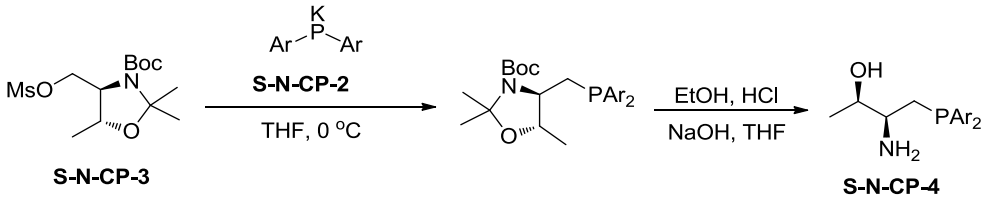



206.738
189.673
138.627
132.069
129.384
128.951
126.818
126.664
103.399
89.834
77.317
77.000
76.682
32.602
29.033
19.013
17.149
f1 (ppm)

5. General Procedure for synthesis of N-CP 1-6 and Spectroscopic Data of N-CP 1-6

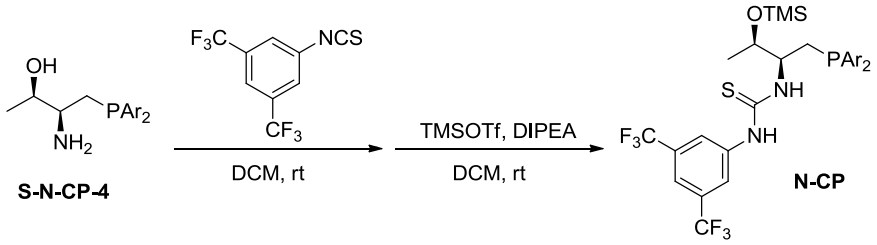


Secondary phosphines were prepared according to the literature of Busacca's group.[3 4] The crude secondary phosphines were used to prepared $KPAr_2$ **S-N-CP-2** directly, which was based on Pfaltz's report.[5]



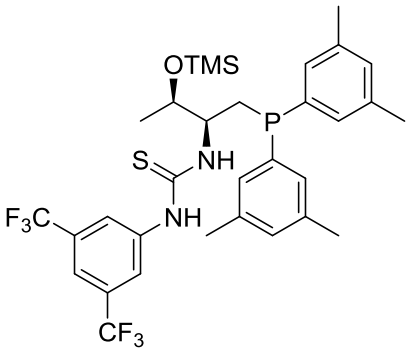
(4*S*,5*R*)-tert-Butyl2,2,5-trimethyl-4-((methylsulfonyloxy)methyl)oxazolidine-3-carboxylate **S-N-CP-3** was known compound and prepared under Lu's conditions.[6]

To a solution of **S-N-CP-3** (1.2 mmol, 1.2 equiv) in dry THF (10 mL) was added $KPAr_2$ **S-N-CP-2** solution (1.0 mmol, 1.0 equiv) under -0 °C. After stirring for 10 minutes, the resulting reaction mixture was warm up to room temperature and stirred over night. After that, ethanol (1.0 mL) was added to quench the reaction. The reaction was extracted with ethyl acetate three times and washed by water. Then the reaction mixture was concentrated under high vacuum give the crude products **S-N-CP-4**, which was very sensitive to the oxygen and unable to purify.



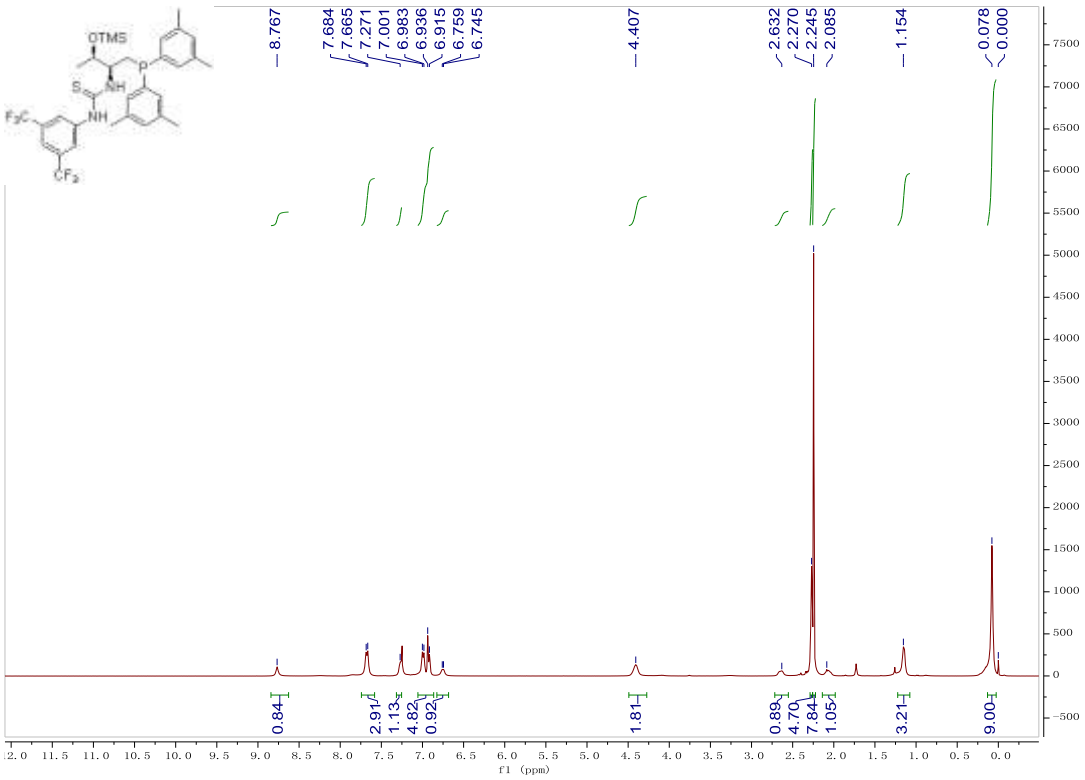
To a solution of crude **S-N-CP-4** (1.0 mol) in CH_2Cl_2 (2 mL) under argon atmosphere was added isothiocyanate (1.0 mol), and the reaction mixture was stirred at room temperature for 4 hours. Then the mixture was concentrated in vacuo and purification with fast short silica gel column

chromatography (PE/EA = 4:1) gave the corresponding crude product. To a solution of the crude product in anhydrous DCM (3 mL) at room temperature under argon atmosphere was DIPEA (0.75 mol), followed by TMSOTf (0.5 mol). The resulting mixture was stirred for 2 hours, and concentrated under vacuum after filtration. Purification with silica gel column chromatography (PE/EA = 10:1) gave the corresponding compound **N-CP**.



1-((2S,3R)-1-(bis(3,5-dimethylphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis (trifluoromethyl)phenyl)thiourea (N-CP1)

A white solid, 19% yield (128 mg). M.p.: 72-74 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.08 (s, 9H, $3CH_3$), 1.15 (s, 3H, CH_3), 2.09 (br, 1H), 2.24 (s, 8H, CH_3), 2.27 (s, 4H, CH_3), 2.63 (br, 1H), 4.41 (s, 2H), 6.75 (d, *J* = 5.6 Hz, 1H), 6.91-7.01 (m, 5H), 7.27 (br, 1H), 7.67 (d, *J* = 7.6 Hz, 3H, ArH), 8.77 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.17, 21.18, 21.22, 21.38, 31.1 (d, *J* = 14.6 Hz), 58.5 (d, *J* = 15.8 Hz), 68.3 (d, *J* = 11.1 Hz), 118.9, 122.7 (q, *J* = 269.8 Hz), 123.2, 130.2, 130.4, 130.5, 130.7, 133.1 (q, *J* = 34.7 Hz), 136.2, 137.9 (br), 138.6, 179.3. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -62.97. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 161.93 MHz): δ -25.86. IR (EtOH) ν 3279, 3026, 2927, 2857, 1523, 1284, 1277, 1134, 843, 695 cm^{-1}. HRMS (ESI) Calcd. For $C_{32}H_{40}F_6N_2OPSSi^{+1}$ $(M+H)^+$ requires 673.2267, Found: 673.2252.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P
S
NH
NH
F3C
CF3
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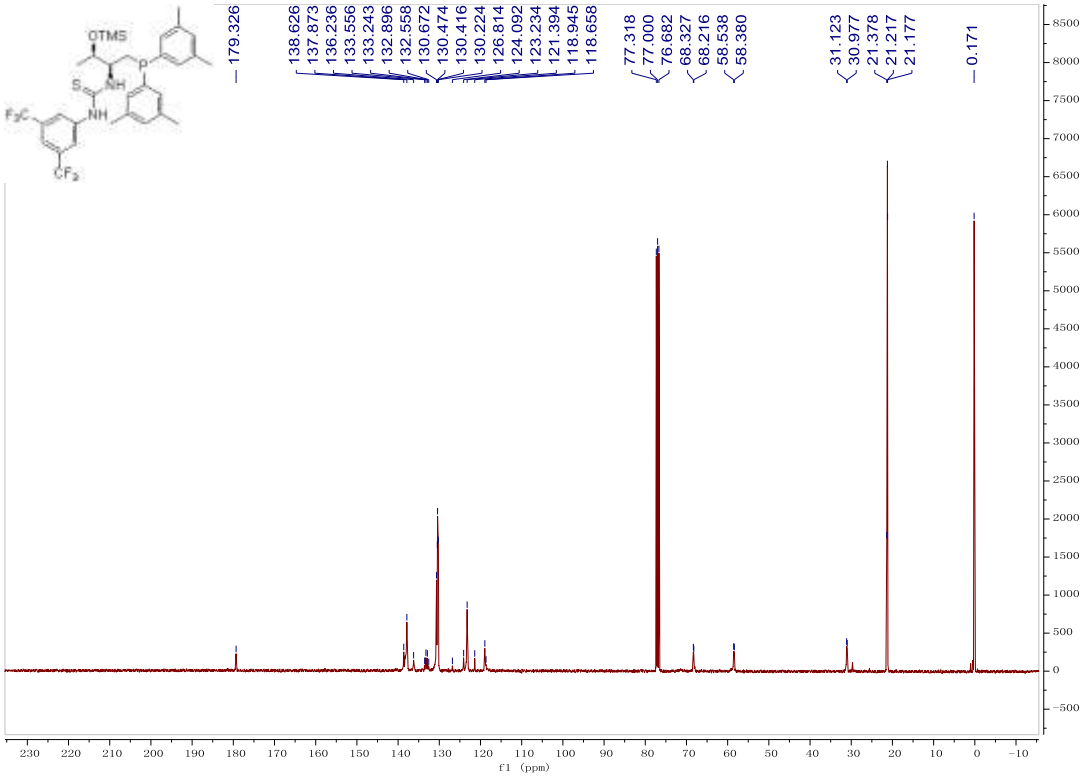
7.684
7.665
7.271
7.001
6.983
6.936
6.915
6.759
6.745
4.407
2.632
2.270
2.245
2.085
1.154
0.078
0.000
0.84
2.91
1.13
4.82
0.92
1.81
0.89
4.70
7.84
1.05
3.21
9.00
f1 (ppm)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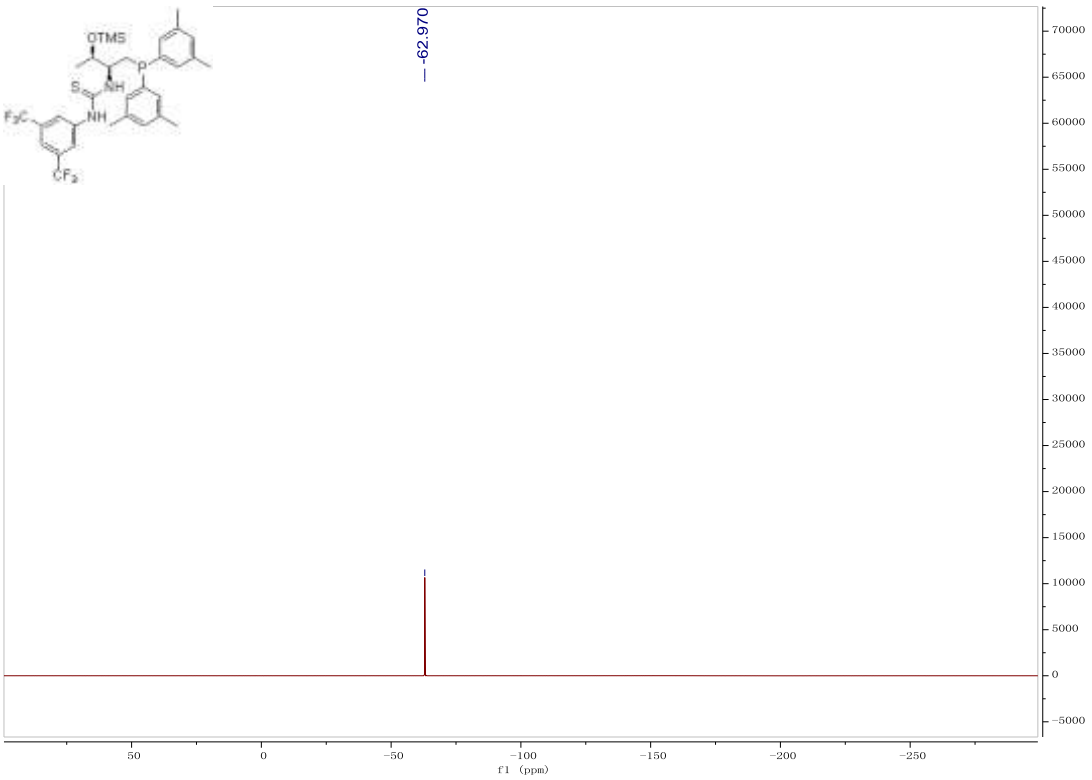
P
S
NH
NH
F3C
CF3
179.326
138.626
137.873
136.236
133.556
133.243
132.896
132.558
130.672
130.474
130.416
130.224
126.814
124.092
123.234
121.394
118.945
118.658
77.318
77.000
76.682
68.327
68.216
58.538
58.380
31.123
30.977
21.378
21.217
21.177
0.171
f1 (ppm)


OTMS
S
NH
NH
P
F3C
CF3
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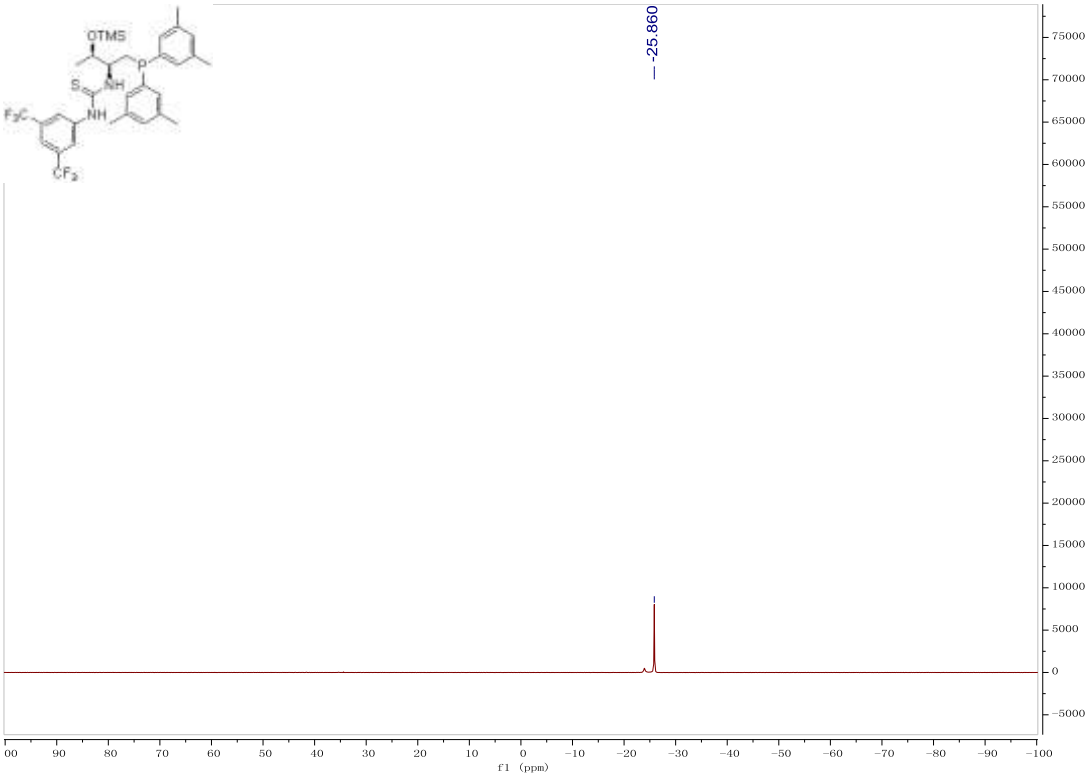
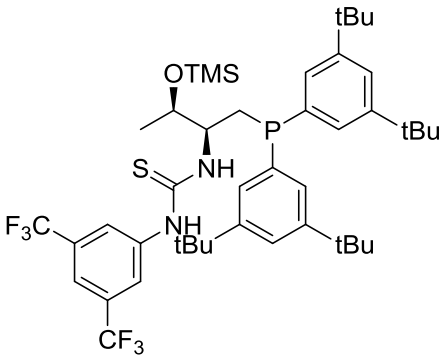
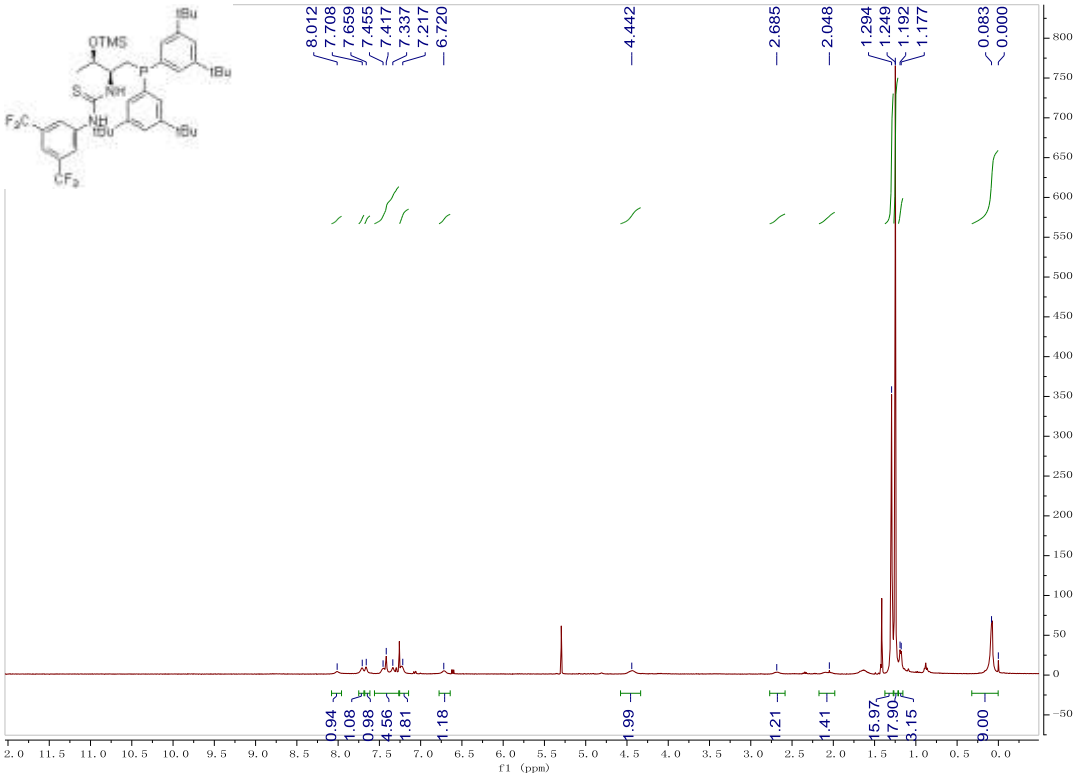
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
50
0
-50
-100
-150
-200
-250
f1 (ppm)

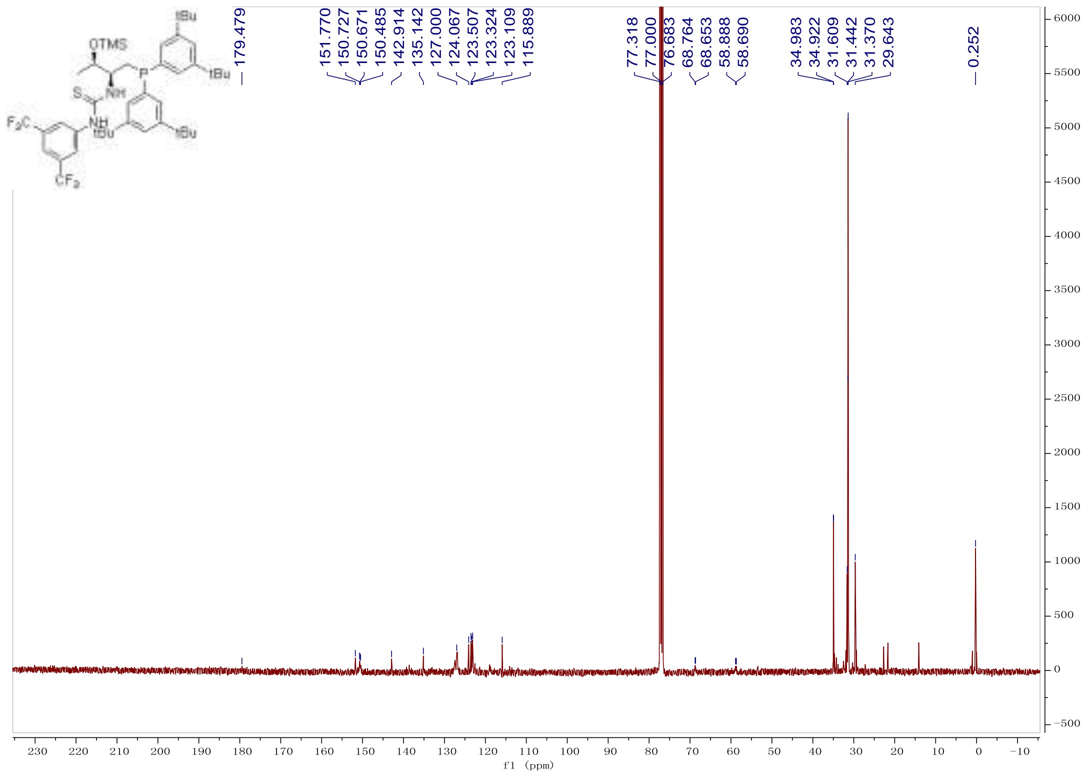

OTMS
S
NH
NH
P
F3C
CF3
-25.860
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)



1-((2S,3R)-1-(bis(3,5-di-tert-butylphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (N-CP2)

A viscous liquid, 8% yield (67 mg). ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.08 (s, 9H, $3CH_3$), 1.18 (d, *J* = 2.0 Hz, 3H, CH_3), 1.25 (s, 18H, CH_3), 1.29 (s, 18H, CH_3), 2.05 (br, 1H), 2.69 (br, 1H), 4.44 (s, 2H), 6.72 (s, 1H), 7.22 (br, 2H), 7.33-7.46 (m, 5H), 7.66 (s, 1H, ArH), 7.71 (s, 1H, ArH), 8.01 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.25, 29.6, 31.27, 31.44, 31.6, 34.9 (d, *J* = 6.1 Hz), 58.8 (d, *J* = 19.8 Hz), 68.7 (d, *J* = 11.1 Hz), 115.9, 123.1, 123.3, 123.5, 124.1, 127.0, 135.1, 142.9, 150.5, 150.67, 150.73, 151.8, 179.5. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -63.01. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 161.93 MHz): δ -21.53. IR (EtOH) ν 3334, 3277, 2963, 2919, 1523, 1474, 1385, 1363, 1178, 1137 cm^{-1}. HRMS (ESI) Calcd. For $C_{44}H_{64}F_6N_2OPSSi^{+1}$ $(M+H)^+$ requires 841.4145, Found: 841.4127.

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S
NH
P
tBu
tBu
tBu
tBu
F_3C
CF_3
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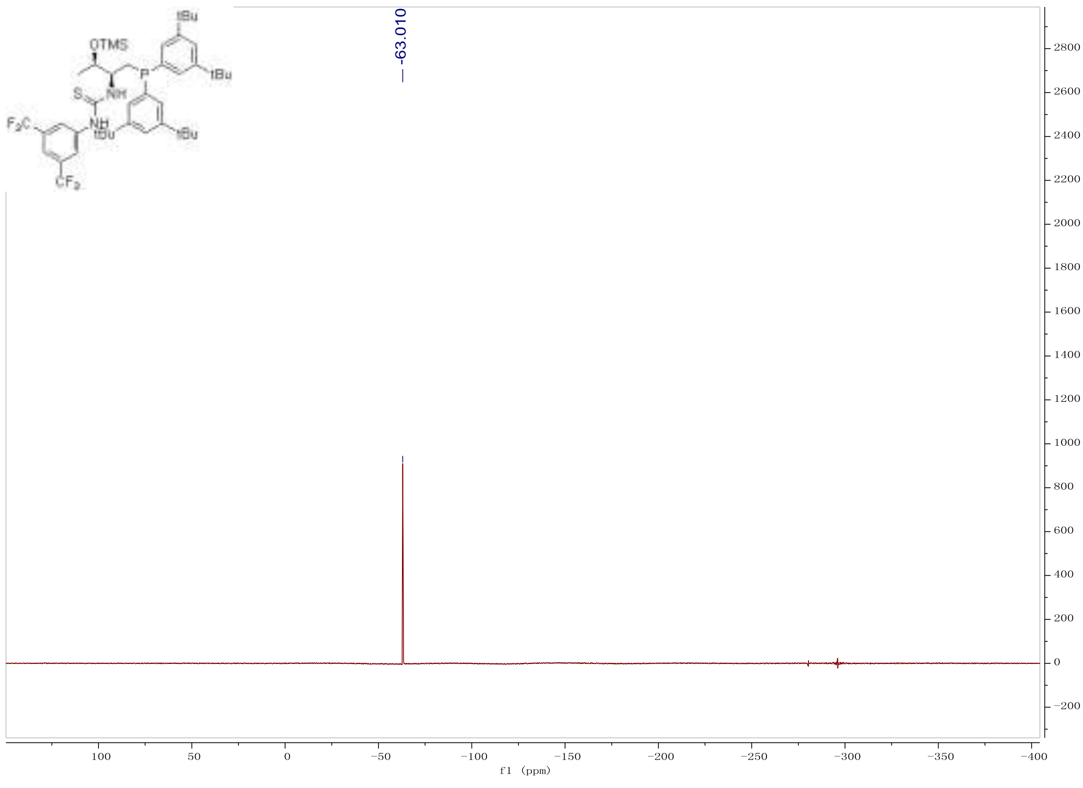
151.770
150.727
150.671
150.485
142.914
135.142
127.000
124.067
123.507
123.324
123.109
115.889
77.318
77.000
76.683
68.764
68.653
58.888
58.690
34.983
34.922
31.609
31.442
31.370
29.643
0.252
f1 (ppm)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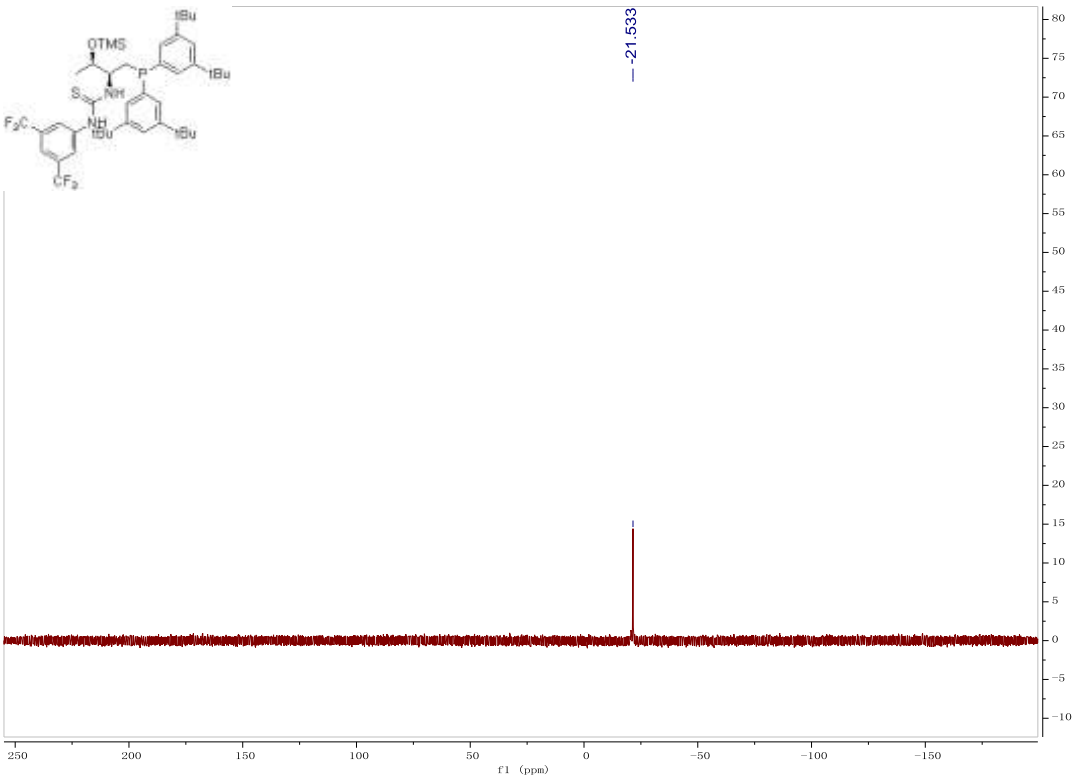
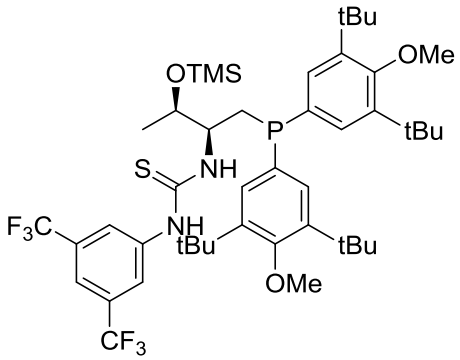
S
NH
P
tBu
tBu
tBu
tBu
F_3C
CF_3
-63.010
f1 (ppm)

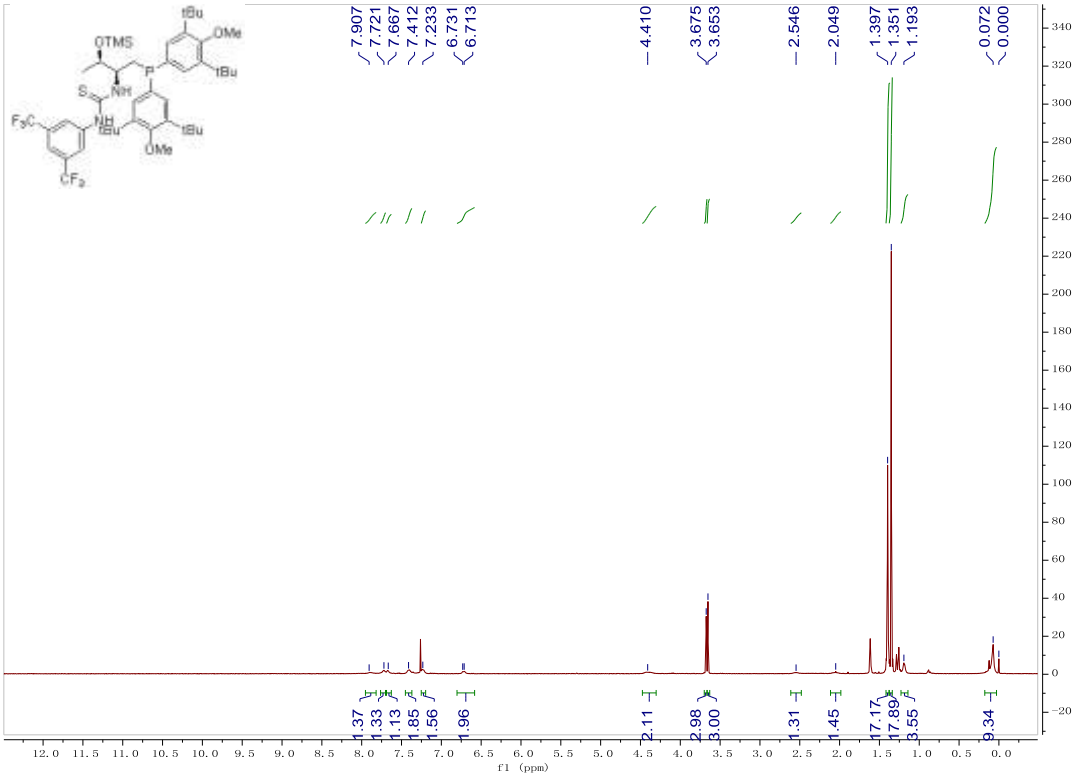


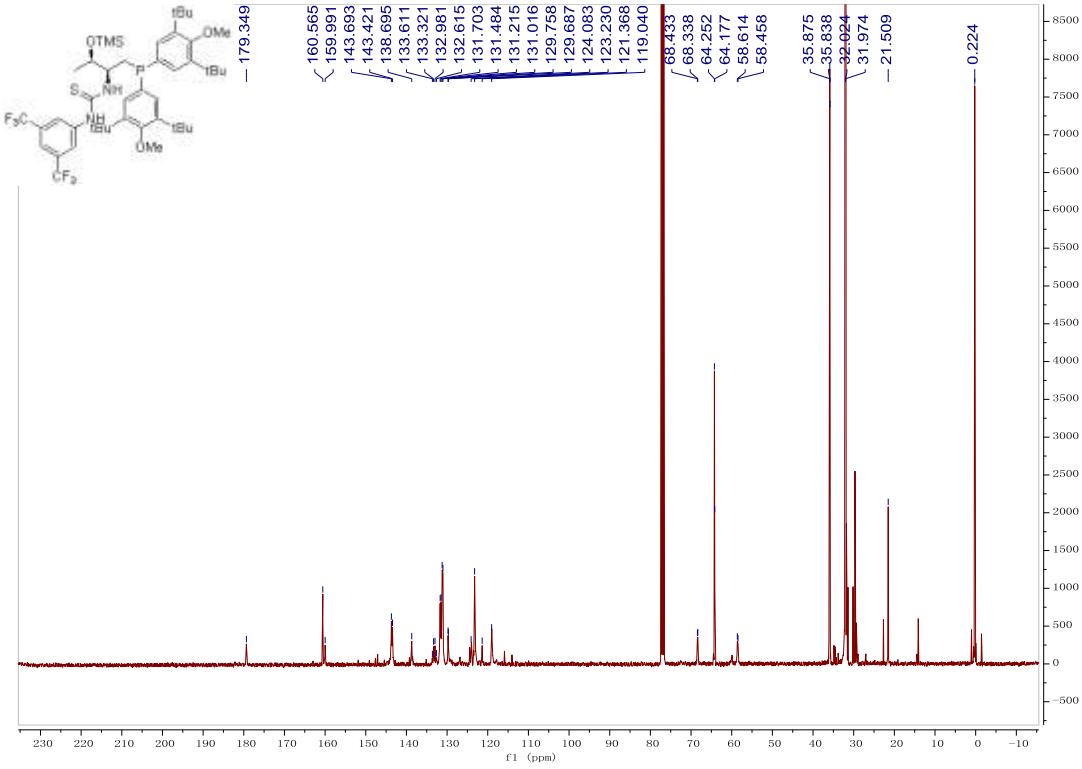


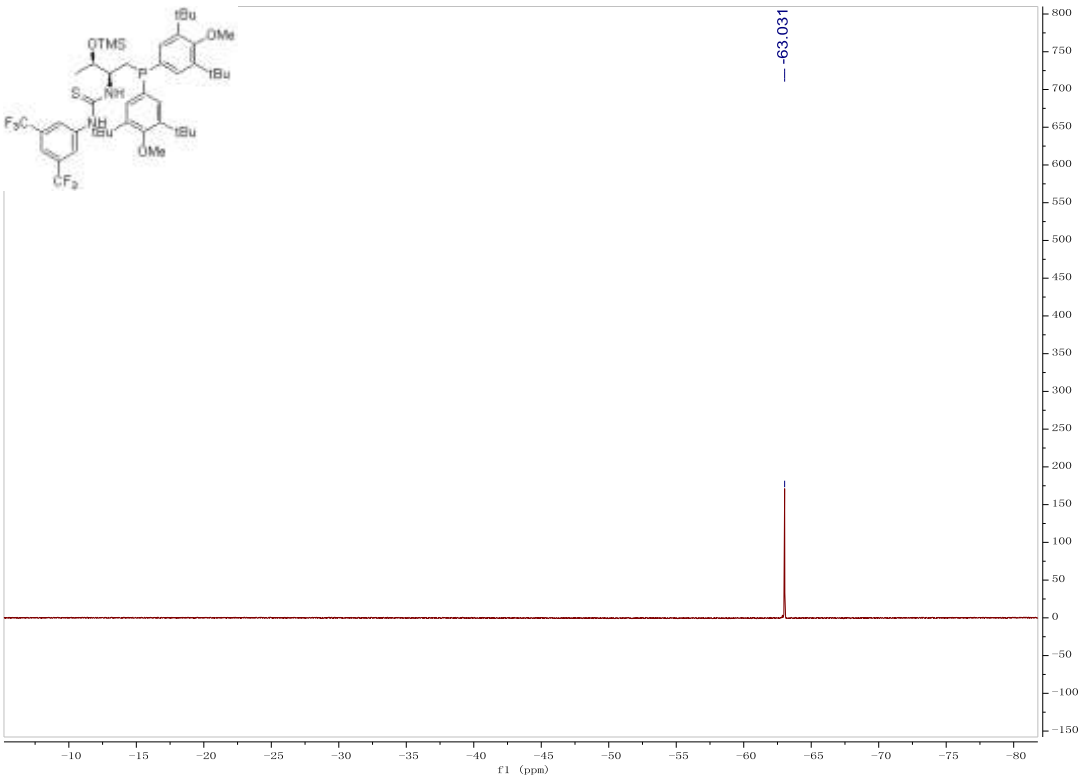
1-((2S,3R)-1-(bis(3,5-di-tert-butyl-4-methoxyphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (N-CP3)

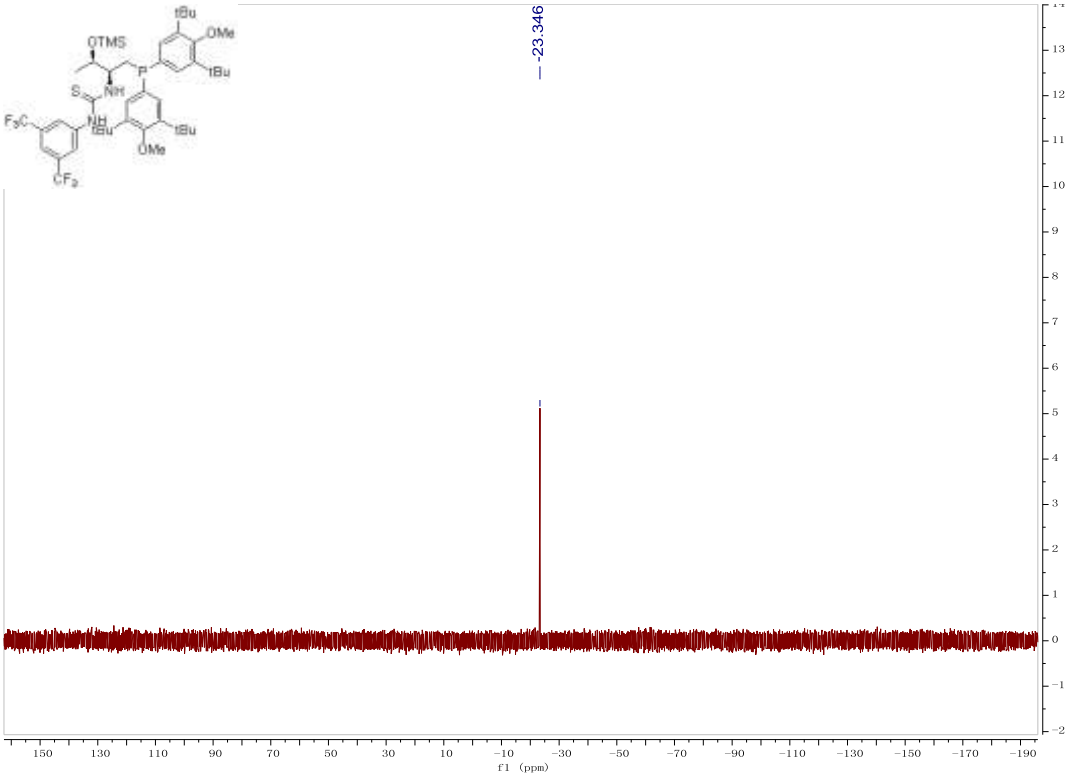
A white solid, 4% yield (36 mg). M.p.: 79-81 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.07 (s, 9H, $3CH_3$), 1.19 (br, 3H, CH_3), 1.35 (s, 18H, CH_3), 1.40 (s, 18H, CH_3), 2.05 (br, 1H), 2.55 (br, 1H), 3.65 (s, 3H, CH_3), 3.68 (s, 3H, CH_3), 4.41 (br, 2H), 6.72 (d, *J* = 7.2 Hz, 2H), 7.23 (br, 2H), 7.41 (br, 2H), 7.67 (s, 1H, ArH), 7.72 (s, 1H, ArH), 7.91 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.22, 21.5, 31.97, 32.02, 35.9 (d, *J* = 3.7 Hz), 58.5 (d, *J* = 15.6 Hz), 64.2, 64.3, 68.4 (d, *J* = 9.5 Hz), 119.0 (br), 122.7 (q, *J* = 271.5 Hz), 123.2 (br), 129.7, 129.8, 131.0, 131.2, 131.5, 131.7, 133.2 (q, *J* = 34.0 Hz), 138.7, 143.4, 143.7, 160.0, 160.6, 179.3. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -63.03. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 161.93 MHz): δ -23.35. IR (EtOH) ν 3269, 3013, 2961, 1524, 1409,

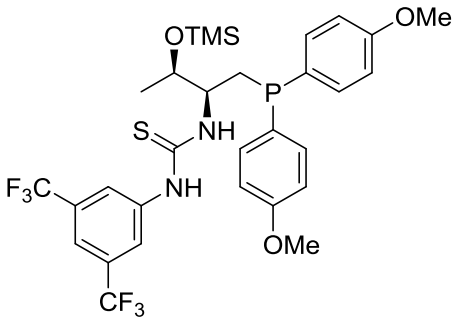
1383, 1276, 1134, 1009, 739 cm^{-1}. HRMS (ESI) Calcd. For $C_{46}H_{68}F_6N_2O_3PSSi^{+1}$ $(M+H)^+$ requires 901.4356, Found: 901.4340.





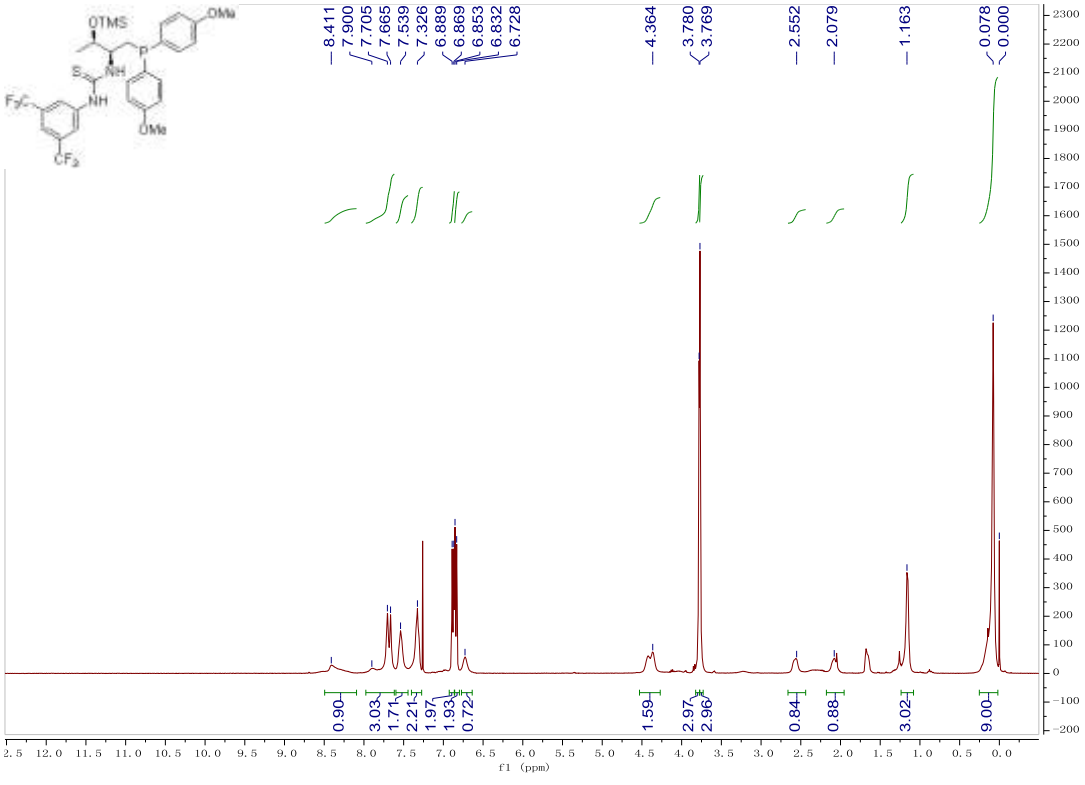

-63.031
f1 (ppm)

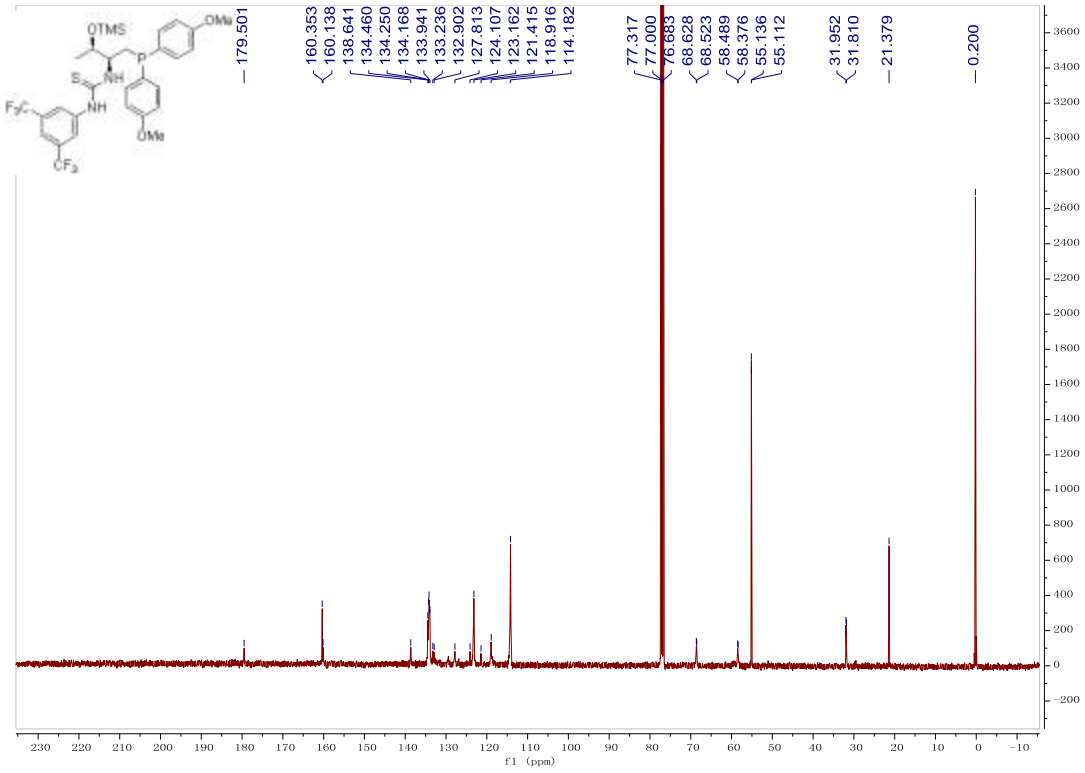

-23.346
f1 (ppm)

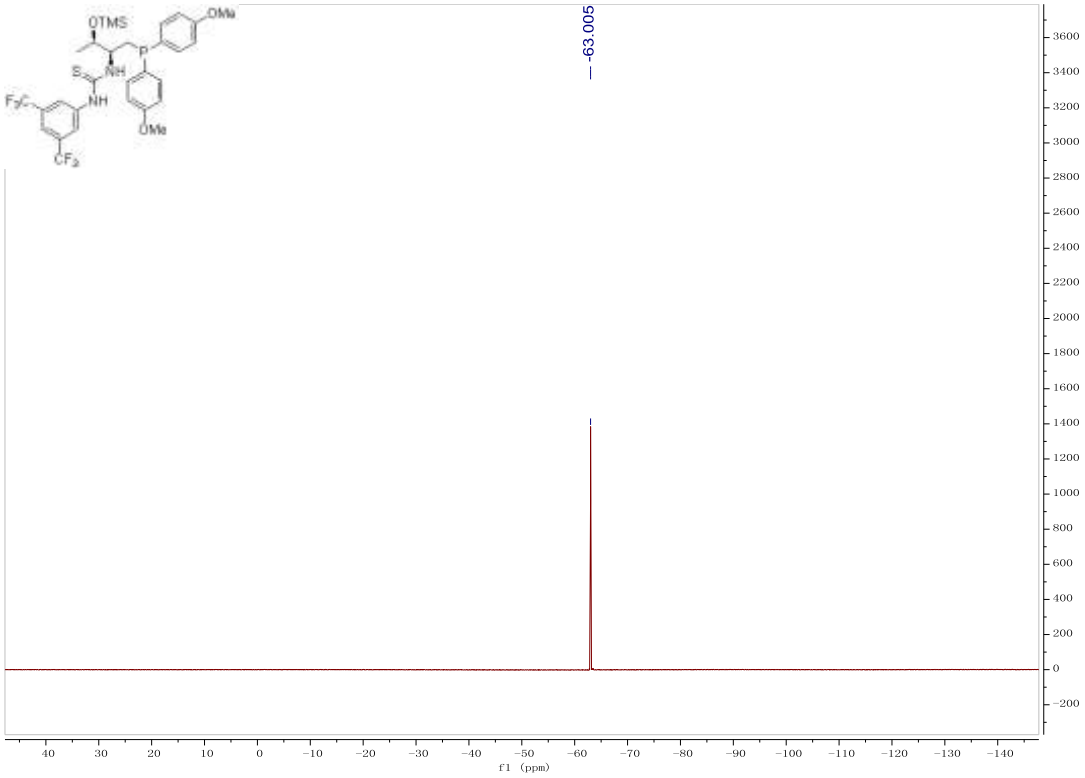


1-((2S,3R)-1-(bis(4-methoxyphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (N-CP4)

A white solid, 21% yield (142 mg). M.p.: 77-79 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.08 (s, 9H, $3CH_3$), 1.16 (s, 3H, CH_3), 2.08 (br, 1H), 2.55 (br, 1H), 3.77 (s, 3H, CH_3), 3.78 (s, 3H, CH_3), 4.36 (br, 2H), 6.73 (br, 2H), 6.84 (d, *J* = 8.4 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 7.33 (br, 2H), 7.54 (br, 2H), 7.53-7.90 (m, 3H, ArH), 8.41 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.20, 31.4, 31.9 (d, *J* = 14.2 Hz), 55.11, 55.14, 58.4 (d, *J* = 11.3 Hz), 68.6 (d, *J* = 10.5 Hz), 114.2, 118.9, 122.8 (q, *J* = 269.2 Hz), 123.2, 127.8, 133.1 (q, *J* = 33.4 Hz), 133.9, 134.2, 134.3, 134.5, 138.6, 160.1, 160.4, 179.5. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -63.01. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 161.93 MHz): δ -28.57. IR (EtOH) ν 3358, 3272, 3019, 2961, 1523, 1471, 1276, 1176, 1134, 1115 cm^{-1}. HRMS (ESI) Calcd. For $C_{30}H_{36}F_6N_2O_3PSSi^{+1}$ $(M+H)^+$ requires 677.1852, Found: 677.1836.




OTMS
OMe
P
S
NH
NH
F3C
CF3
OMe
179.501
160.353
160.138
138.641
134.460
134.250
134.168
133.941
133.236
132.902
127.813
124.107
123.162
121.415
118.916
114.182
77.317
77.000
76.683
68.628
68.523
58.489
58.376
55.136
55.112
31.952
31.810
21.379
0.200
f1 (ppm)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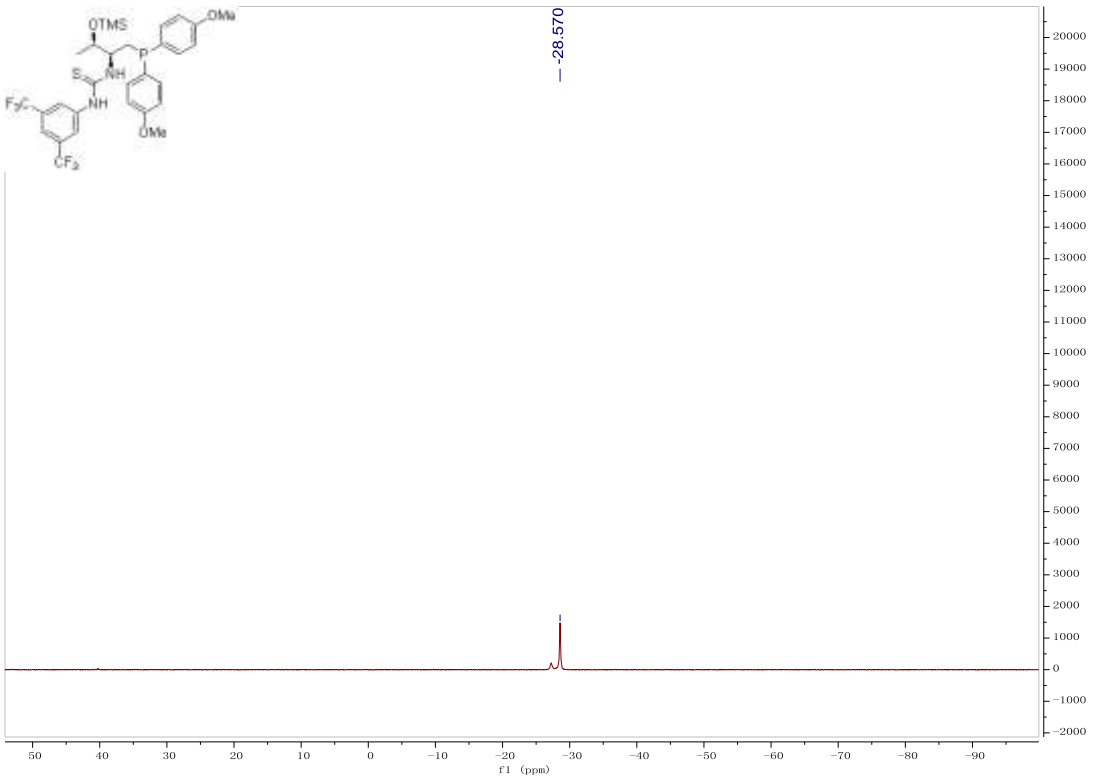
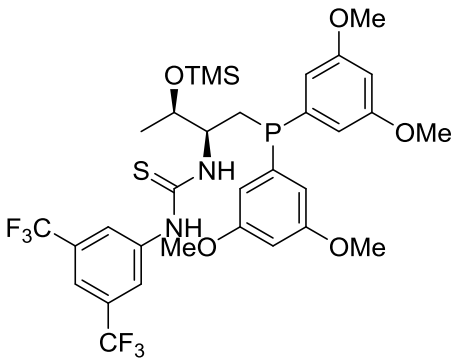
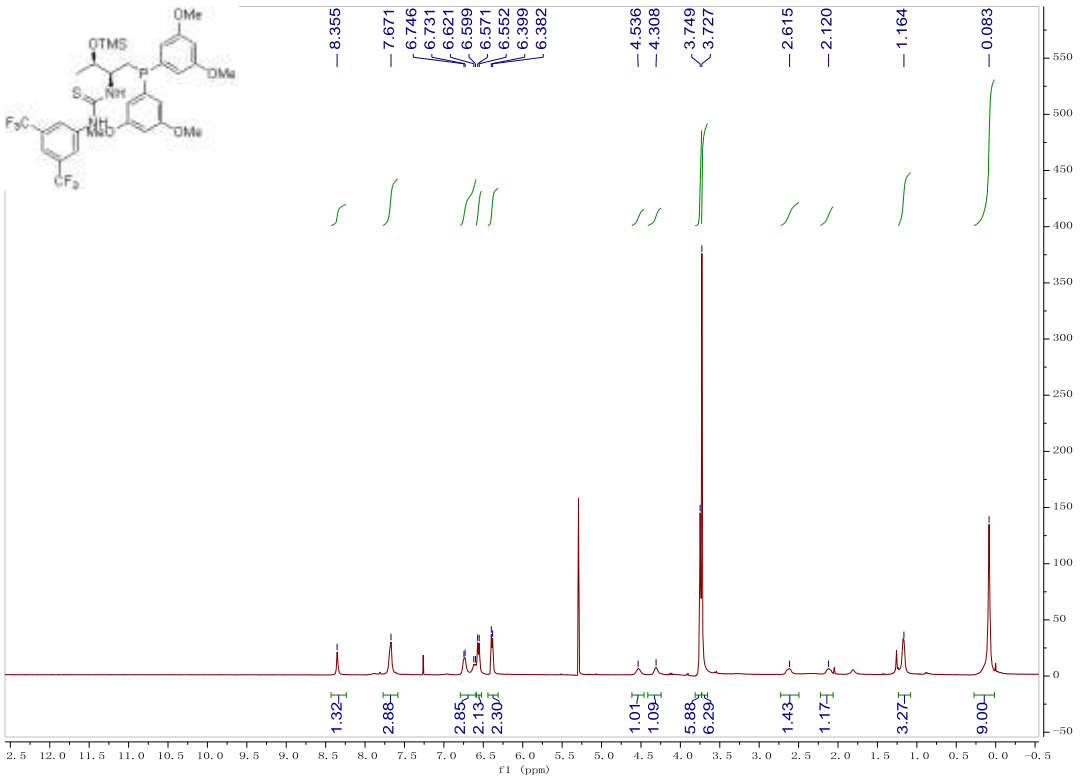
P
S
NH
NH
F3C
CF3
OMe
-63.005
f1 (ppm)





1-((2S,3R)-1-(bis(3,5-dimethoxyphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (N-CP5)

A white solid, unstable, 9% yield (66 mg). M.p.: 86-88 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.08 (s, 9H, $3CH_3$), 1.16 (s, 3H, CH_3), 2.12 (br, 1H), 2.62 (br, 1H), 3.73 (s, 6H, CH_3), 3.75 (s, 6H, CH_3), 4.31 (s, 1H), 4.54 (s, 1H), 6.39 (d, *J* = 6.8 Hz, 2H), 6.56 (d, *J* = 7.6 Hz, 2H), 6.59-6.75 (m, 3H), 7.67 (s, 3H, ArH), 8.36 (s, 1H, ArH). ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -63.01. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 161.93 MHz): δ -19.26. IR (EtOH) ν 3355, 2959, 2836, 1584, 1458, 1383, 1277, 1155, 1132, 1045, 841 cm^{-1}. HRMS (ESI) Calcd. For $C_{32}H_{40}F_6N_2O_3PSSi^{+1}$ $(M+H)^+$ requires 737.2064, Found: 737.2045.


OMe
OTMS
OMe
S
NH
P
NH
F3C
OMe
CF3
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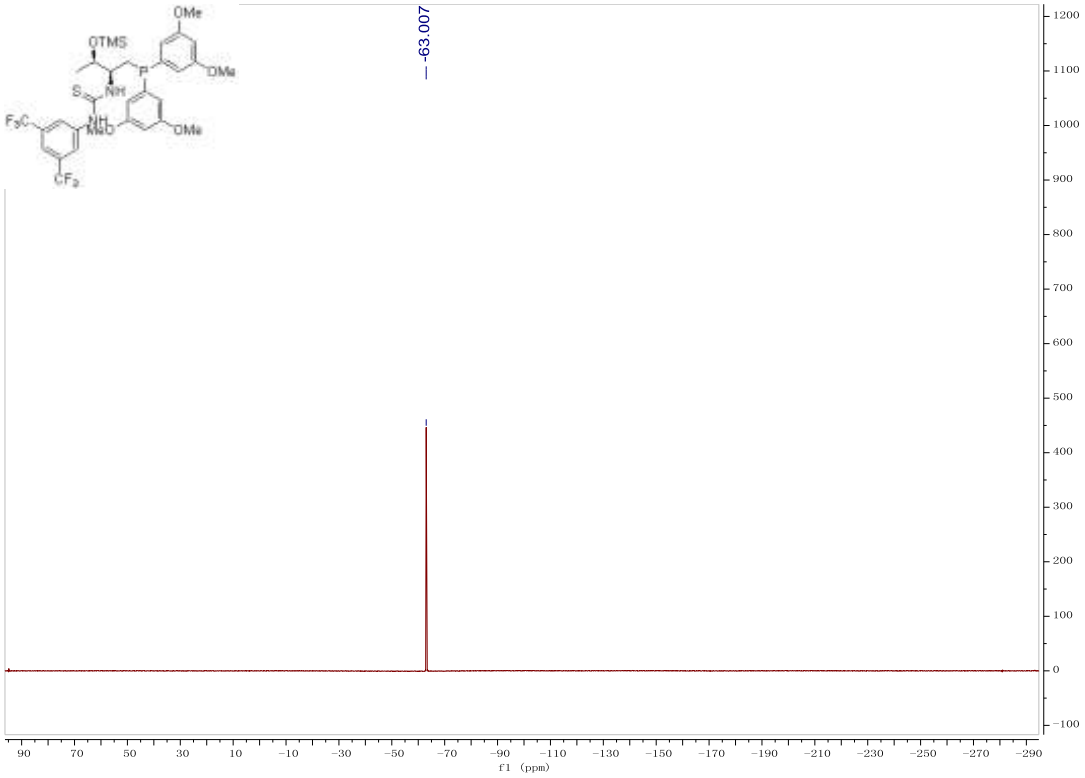
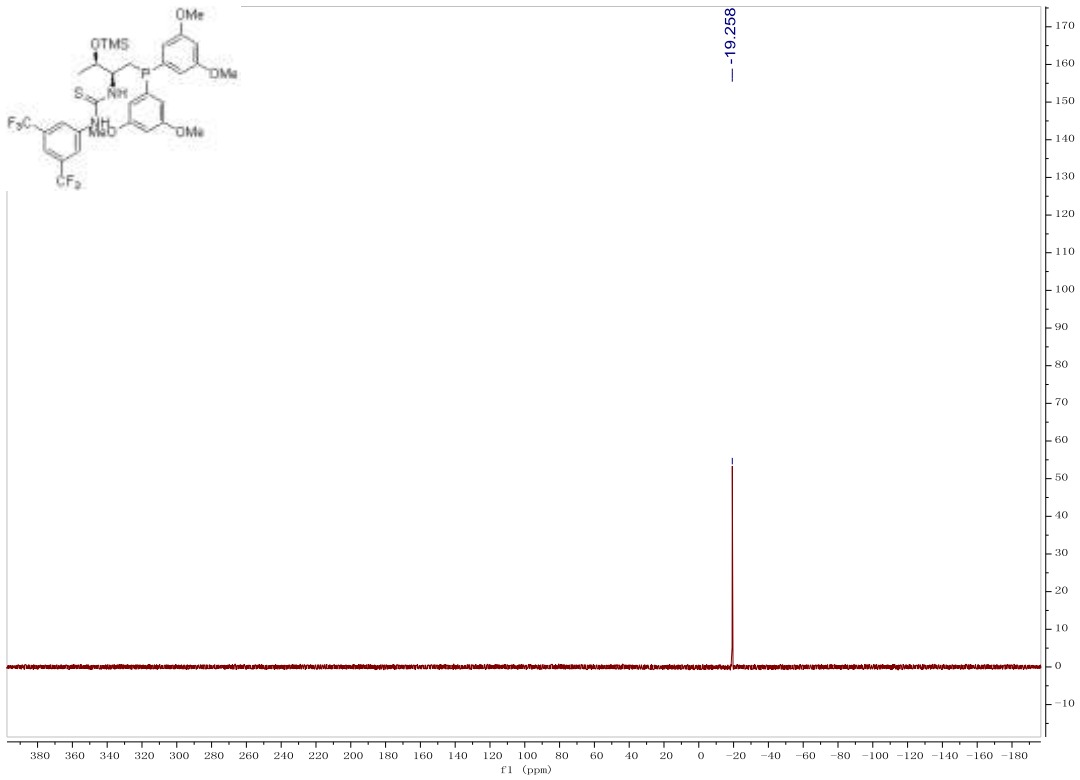
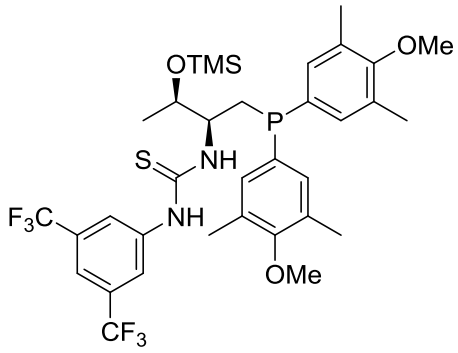
7.671
6.746
6.731
6.621
6.599
6.571
6.552
6.399
6.382
4.536
4.308
3.749
3.727
2.615
2.120
1.164
0.083
1.32
2.88
2.85
2.13
2.30
1.01
1.09
5.88
6.29
1.43
1.17
3.27
9.00
f1 (ppm)


OMe
OTMS
OMe
S
NH
P
NH
F3C
OMe
CF3
-63.007
f1 (ppm)

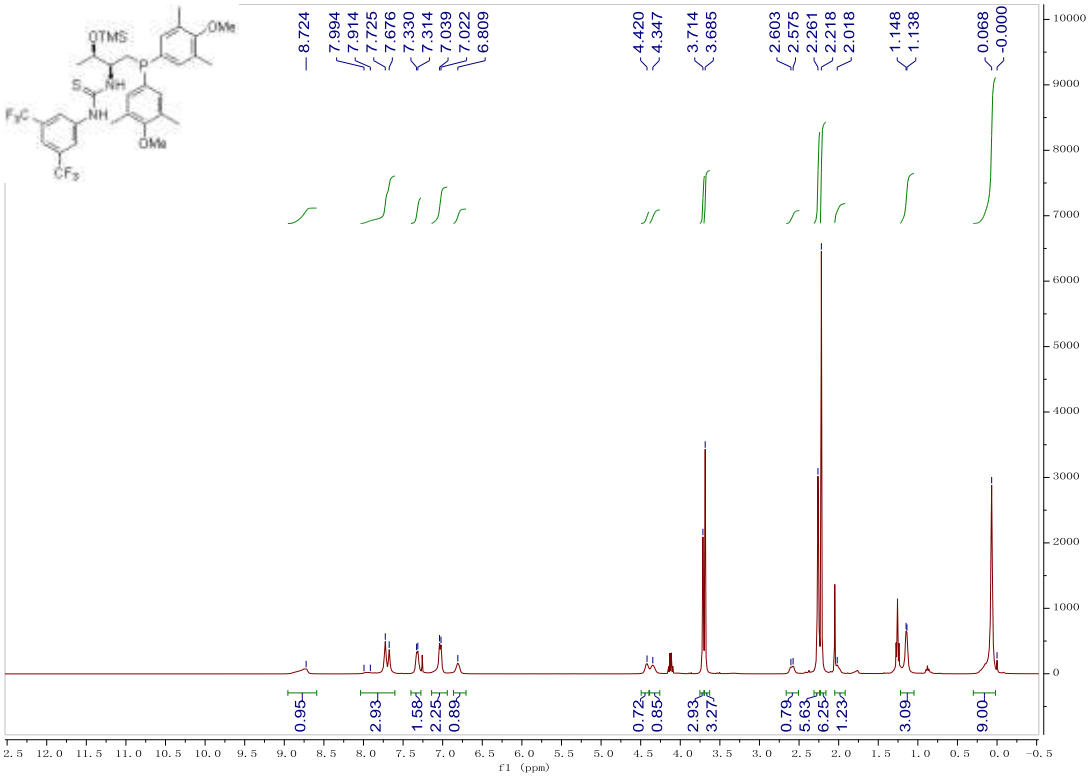


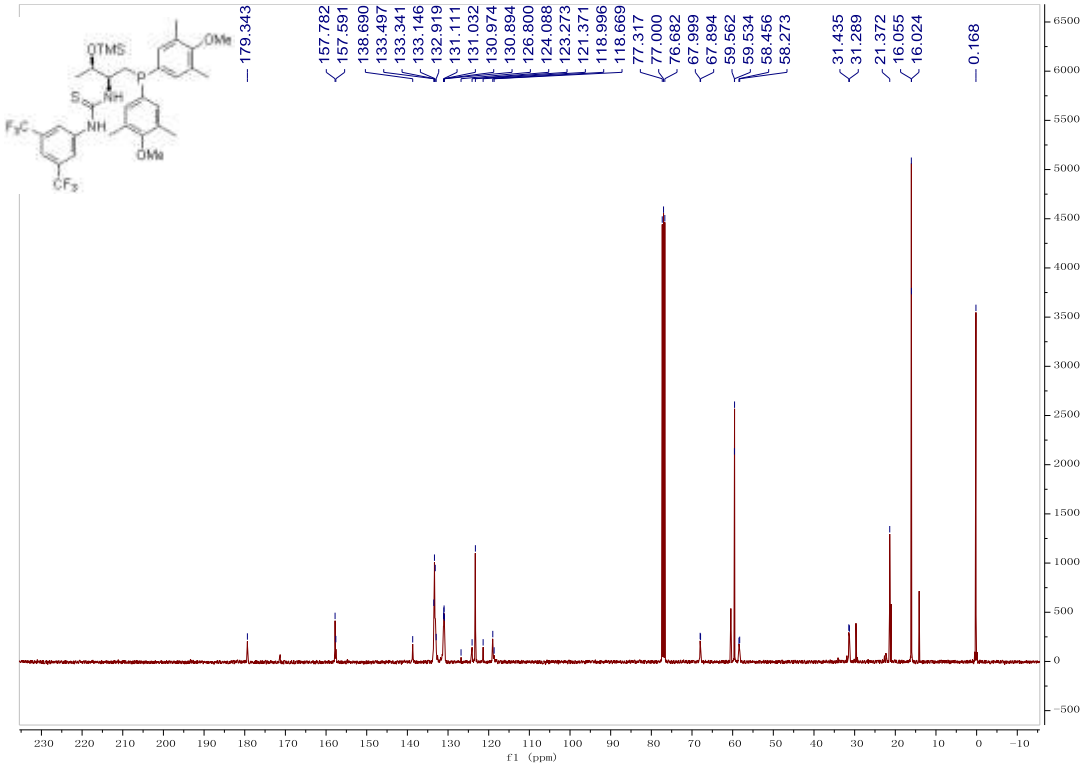


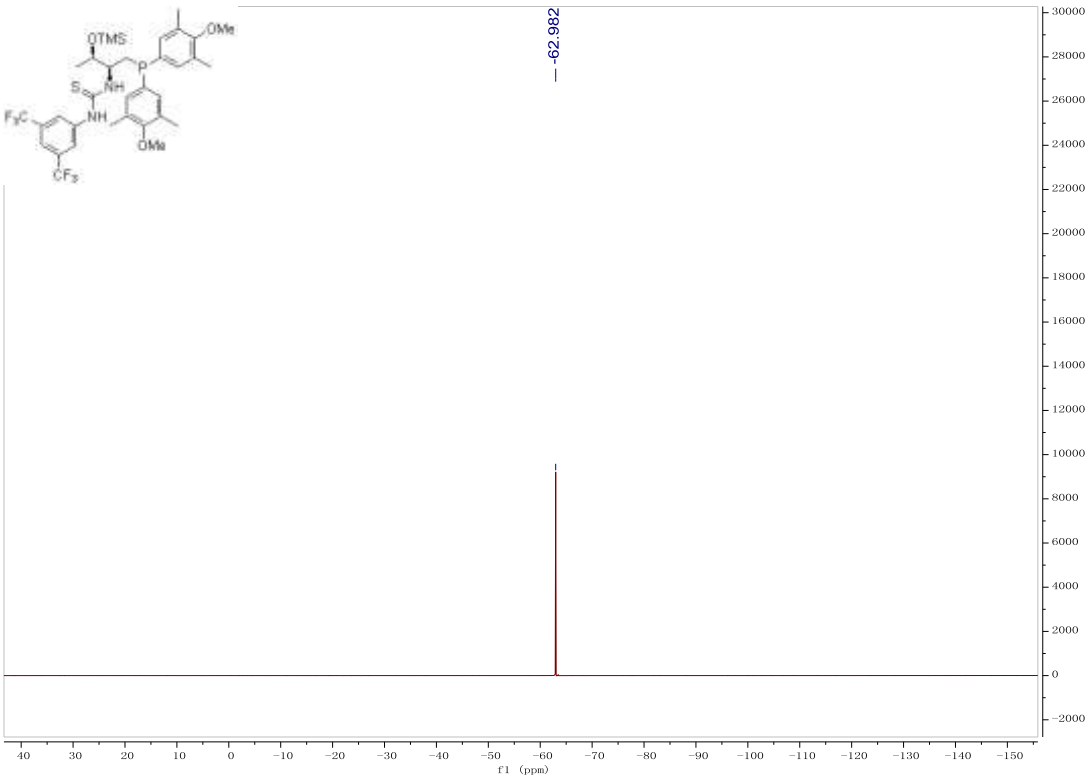
1-((2S,3R)-1-(bis(4-methoxy-3,5-dimethylphenyl)phosphanyl)-3-((trimethylsilyl)oxy)butan-2-yl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea (N-CP6)

A white solid, 13% yield (95 mg). M.p.: 68-60 ^{o}C. ^{1}H NMR ($CDCl_3$, TMS, 400 MHz) δ 0.07 (s, 9H, $3CH_3$), 1.14 (d, *J* = 4.0 Hz, CH_3), 2.02 (br, 1H), 2.22 (s, 6H, CH_3), 2.26 (s, 6H, CH_3), 2.59 (d, *J* = 11.2 Hz, CH_3), 3.69 (s, 3H, CH_3), 3.71 (s, 3H, CH_3), 4.35 (s, 2H), 4.42 (s, 2H), 6.81 (s, 1H), 7.03 (d, *J* = 6.8 Hz, 2H), 7.32 (d, *J* = 6.4 Hz, 2H), 7.67-8.00 (m, 3H, ArH), 8.72 (s, 1H, ArH). ^{13}C NMR ($CDCl_3$, TMS, 100 MHz) δ 0.17, 16.0, 16.1, 21.4, 31.4 (d, *J* = 14.6 Hz), 58.4 (d, *J* = 18.3 Hz), 59.5, 59.6, 67.9 (d, *J* = 10.5 Hz), 119.0, 122.7 (q, *J* = 271.7 Hz), 123.3, 126.8, 130.9, 130.97, 131.03, 131.1, 132.9, 133.1, 133.3, 133.5, 138.7, 157.6, 157.8, 179.3. ^{19}F NMR ($CDCl_3$, $CFCl_3$, 376 MHz) δ -62.98. ^{31}P NMR ($CDCl_3$, 85% H_3PO_4, 161.93 MHz): δ -27.95. IR (EtOH) ν 3298, 2930, 2857,

1473, 1384, 1276, 1173, 1133, 1013, 884 cm^{-1}. HRMS (ESI) Calcd. For $C_{34}H_{44}F_6N_2O_3PSSi^{+1}$ $(M+H)^+$ requires 733.2478, Found: 733.2461.






OTMS
OMe
P
S
NH
NH
F3C
OMe
CF3
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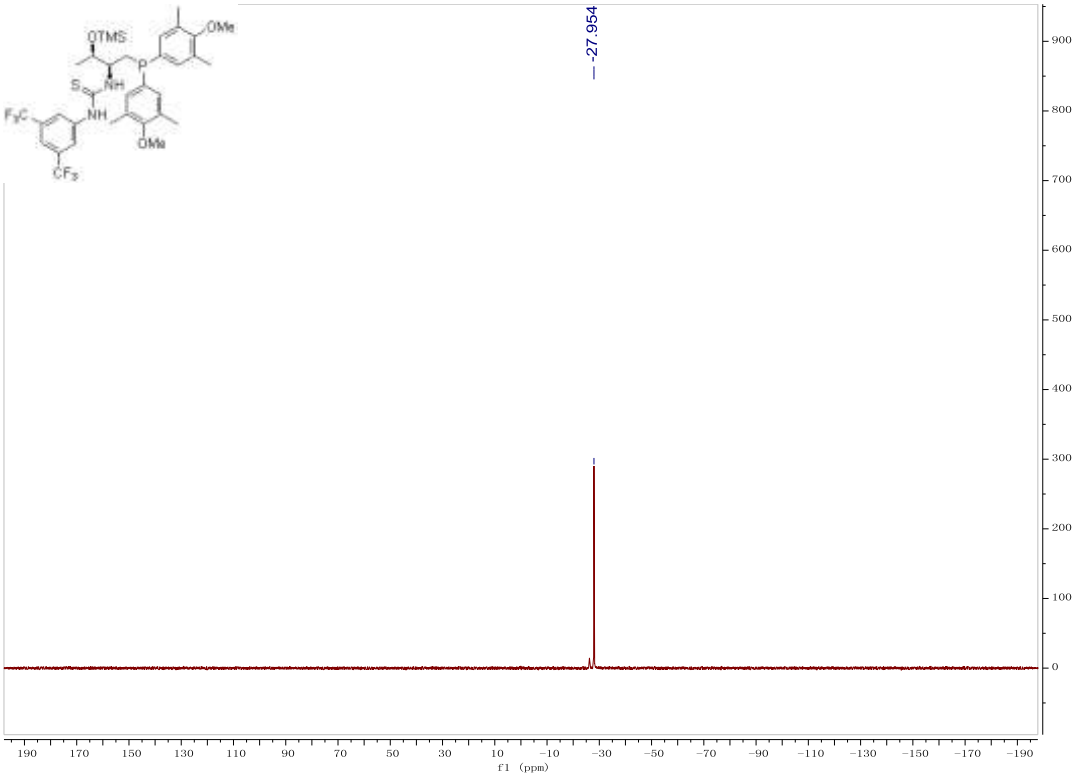
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150
f1 (ppm)


OTMS
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NH
F3C
OMe
CF3
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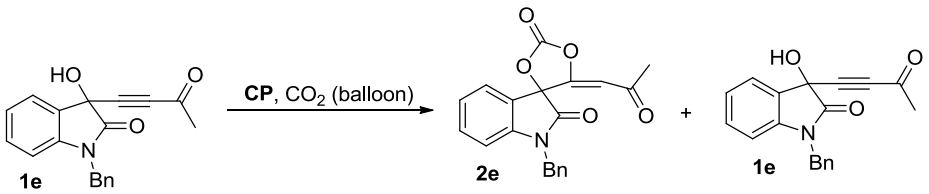
900
800
700
600
500
400
300
200
100
0
190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)

6. Kinetic Resolutions *via* Carbon Dioxide Fixation of γ-Hydroxyl Alkynone 1.

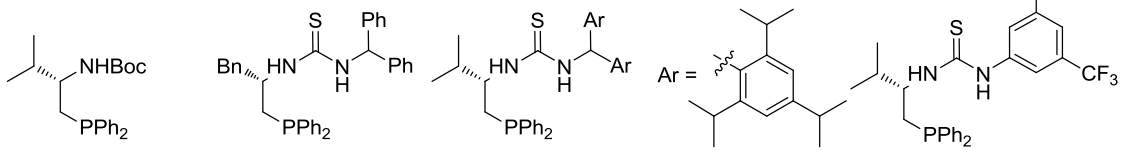
A Schlenk tube was heated under vacuum to remove ambient moisture and water, then filled with argon. After the Schlenk tube was returned to room temperature, γ-hydroxyl alkynone **1** (0.1 mmol) was added. Then the system was vacuumed and filled with CO_2. After repeating three times, THF (0.5 mL) was added and the reaction mixture was stirred for 10 minutes at indicated temperature. Then, chiral phosphine (0.01~0.04 mmol) was dissolved in 100 μL THF and slowly added to the reaction mixture at indicated temperature. After that, the resulting mixture was stirred overnight. After the reaction was finished, the solution was directly subjected to a flash column chromatography (PE:EA:DCM = 20:1:1~5:1:1) on silica gel to separate chiral γ-hydroxyl alkynone **1** and chiral cyclic carbonate **2** quickly.

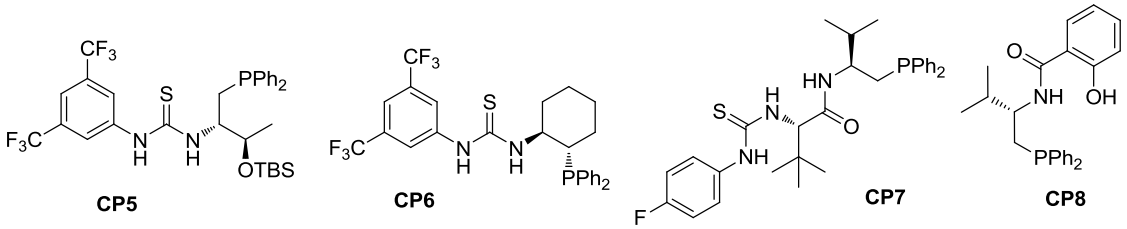
Table S1. Optimization of the reaction conditions with a variety of chiral phosphines.



entry[a]	CP	solvent	temp (°C)	time (h)	conv. (%)	yield (%)[b]		*ee* (%)[c]	
						2e	**1e**	**2e**	**1e**
1	**CP1** (20 mol%)	THF	-20	9	>50	34	-	12	-
2	**CP2** (20 mol%)	THF	-15	11	>99	-	-	-	-
3	**CP2** (20 mol%)	THF	-20	4	>99	-	-	-	-
4	**CP3**	THF	-20	2.5	51	43	49	30	11
5	**CP3** (5 mol%)	THF	-20	5	34	29	66	27	11
6	**CP3**	THF	-20	12	54	46	46	33	34
7	**CP4**	THF	-40	12	60	47	39	40	36
8	**CP5** (20 mol%)	THF	-40	12	31	29	68	68	22
9	**CP6** (20 mol%)	THF	-20	12	64	29	6	36	rac
10	**CP7**	THF	-40	12	trace	-	-	-	-
11	**CP8**	THF	-40	12	trace	-	-	-	-
12	**CP9**	THF	-20	8	nr	-	-	-	-
13	**CP9**	THF	r.t	12	trace	-	-	-	-
14	**CP10**	THF	-20	8	trace	-	-	-	-
15	**CP10**	THF	r.t	12	complex	-	-	-	-
16	**CP10**	THF	10	12	67	26	33	5	-
17	**CP11**	THF	-20	12	-	-	-	-	-
18	**CP12**	THF	-40	12	-	-	-	-	-
19	**CP12**	THF	-20	12	-	-	-	-	-
20	**CP13** (20 mol%)	THF	-20	4	complex	-	-	-	-

[a] The reaction was carried out using **1e** (0.1 mmol), cat. (0.01~0.04 mmol), in the indicated solvent (0.5 mL) in a Schlenk tube at the indicated temperature.[b] Isolated yields. [c] The *ee* value was determined by HPLC analysis using a chiral stationary phase.





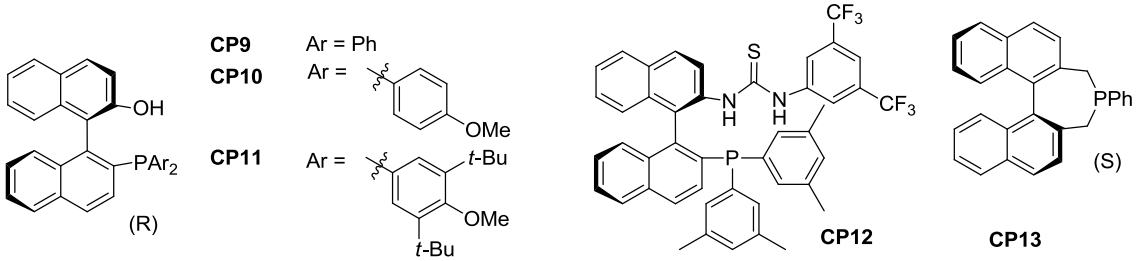
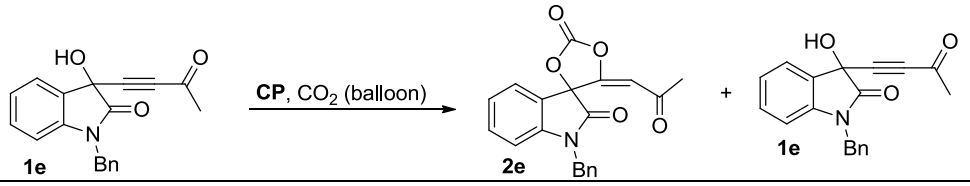
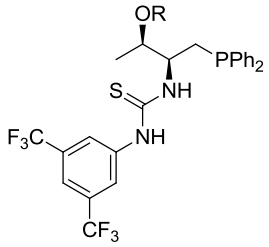


Table S2. Optimization of the reaction conditions with threonine derived chiral phosphines as catalysts

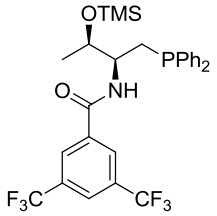


entry[a]	cat	solvent	temp (°C)	time (h)	conv. (%)	yield (%)[b]		*ee* (%)[c]	
						2e	**1e**	**2e**	**1e**
1	**CP5**	THF	-40	12	31	29	69	68	20
2	**CP14**	THF	-40	12	44	41	56	68	40
3	**CP15**	THF	-40	12	65	60	35	10	5
4	**CP16**	THF	-40	12	trace	-	-	-	-
5	**CP17**	THF	-40	12	trace	-	-	-	-
6	**CP18**	THF	-40	12	59	49	41	60	50
7	**CP19**	THF	-40	12	59	51	41	60	72
8	**CP20**	THF	-40	12	67	62	33	40	72
9	**CP21**	THF	-40	12	-	-	-	-	-

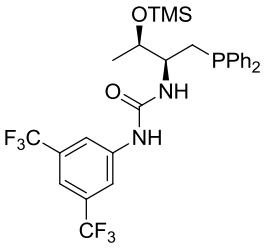
[a] The reaction was carried out using **1e** (0.1 mmol), **CP** (0.02 mmol), in the indicated solvent (0.5 mL) in a Schlenk tube at the indicated temperature.[b] Isolated yields. [c] The *ee* value was determined by HPLC analysis using a chiral stationary phase.



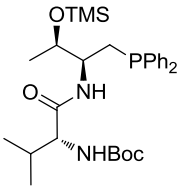
R = TBS **CP5**
R = TMS **CP14**



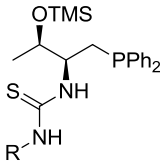
CP15

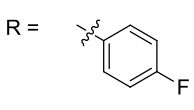


CP16

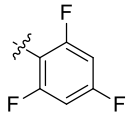


CP17



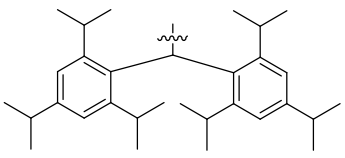


CP18



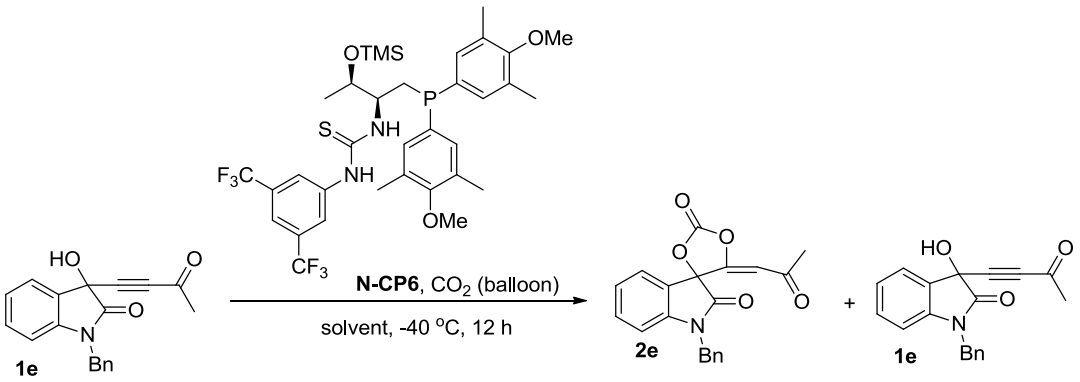
CP19

CP20



CP21

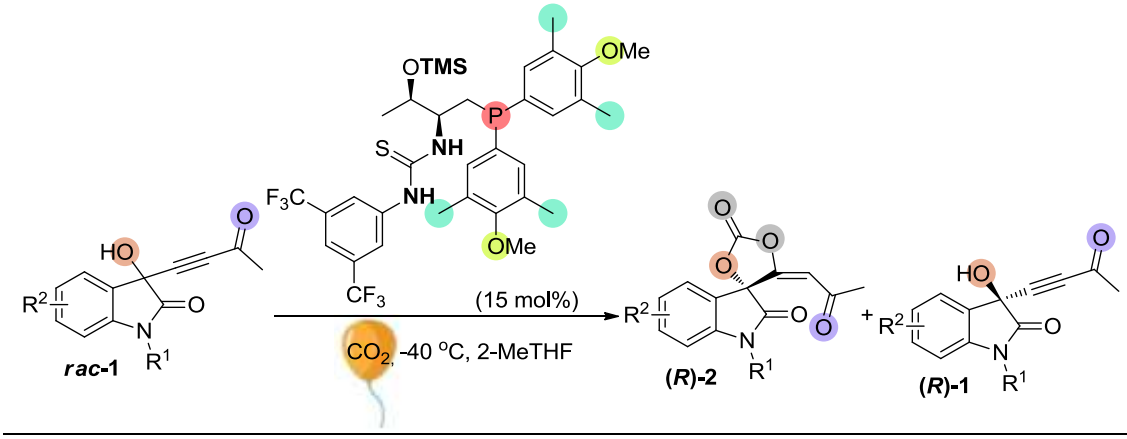
Table S3. Optimization of the reaction temperature with threonine derived chiral phosphine **N-CP6**

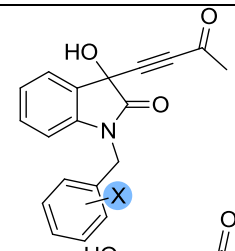
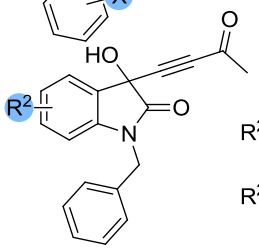


entry[a]	**N-CP6** (X mol %)	solvent	conv. (%)	yield (%)[b]		*ee* (%)[c]		*s*
				2e	**1e**	**2e**	**1e**	
1	15 mol %	(2.0 mL)	54	49	46	81	91	24.6
2	10 mol %	(2.0 mL)	53	46	47	80	88	23.2
3	15 mol %	(2.0 mL) + (0.2 mL)	62	57	38	80	93	11.7
4	15 mol %	(1.5 mL) + (0.5 mL)	64	51	36	76	96	12.2
5	15 mol %	(1.0 mL) + (1.0 mL)	58	47	42	80	87	12.0
6	15 mol %	(0.5 mL) + (1.5 mL)	59	42	41	81	82	8.9
7	10 mol %	(1.5 mL) + (0.5 mL)	49	41	51	84	70	13.0

[a] The reaction was carried out using **1e** (0.1 mmol), **N-CP6** (X mol %), in the indicated solvent (2.0 mL) in a Schlenk tube at the indicated temperature. [b] Isolated yields. [c] The *ee* value was determined by HPLC analysis using a chiral stationary phase.

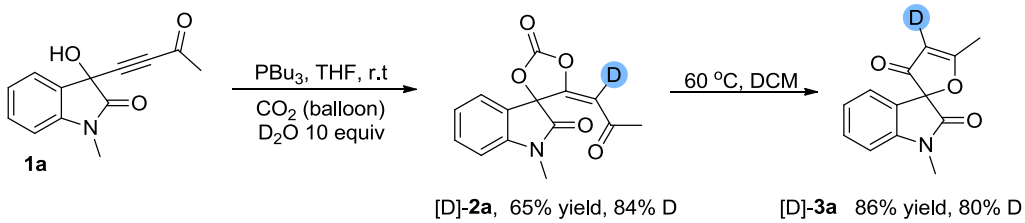
Table S4. Other substrates for the kinetic resolution [a]



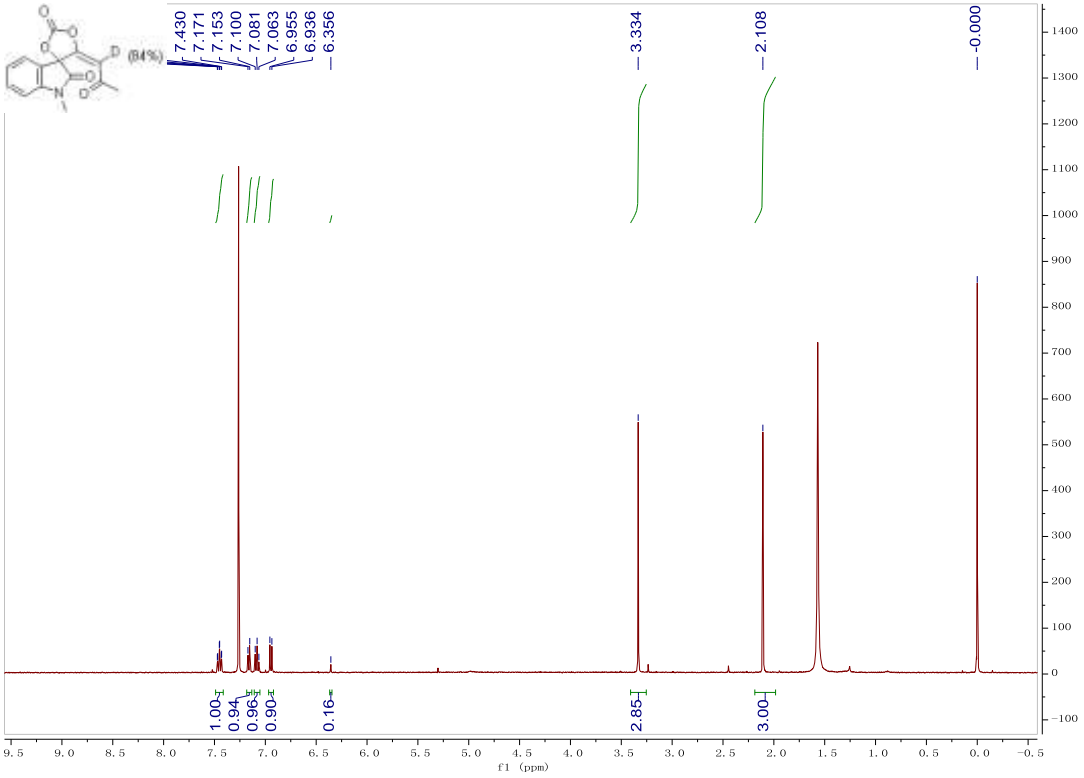
entry[a]	starting materials		time (h)	conv. (%)	yield (%)[b]		*ee* (%)[c]		*s*-factor[d]
					(*R*)-2	(*R*)-1	(*R*)-2	(*R*)-1	
1		X = 3,5-2Me, **1k**:	12	48	37	52	82	56	7
2		X = 2,6-2Cl, **1l**:	16	37	26	63	94	28	3.7
3		R^2 = 5-F, **1q**:	12	32	22	68	85	23	3.9
4		R^2 = 5-Br, **1s**:	12	41	32	59	80	47	8.2

[a] The reaction was carried out using ***rac*-1** (0.1 mmol), cat. (0.015 mmol) in the indicated solvent (2.0 mL) in a Schlenk tube at the indicated temperature. [b] Isolated yields. [c] The *ee* value was determined by HPLC analysis using a chiral stationary phase. [d] Selectivity (*s*-factor) calculated as $s = \ln[(1-C)(1-ee\text{SM})]/\ln[(1-C)(1+ee\text{SM})]$.

7. Isotope Labeling Experiments

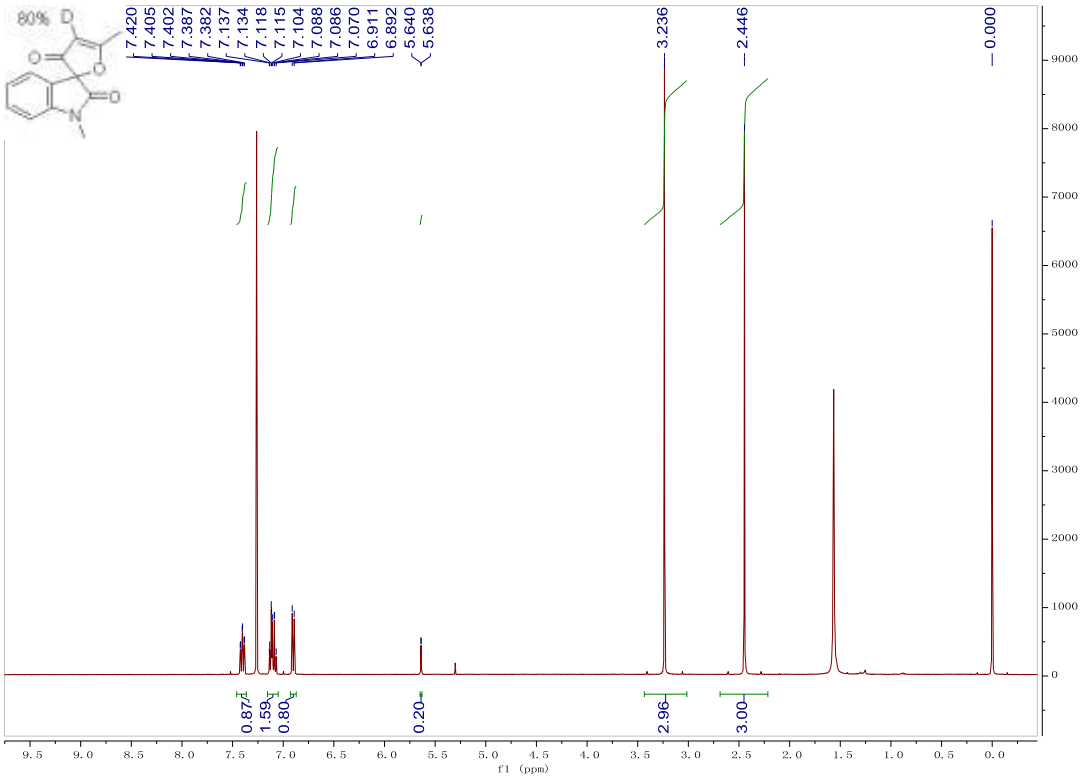


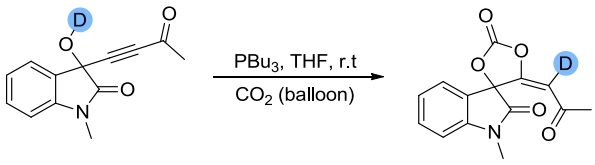
Step 1: A Schlenk tube was heated under vacuum to remove ambient moisture and water, then filled with argon. After the Schlenk tube was returned to room temperature, γ-hydroxyl alkynone **1a** (0.3 mmol) was added. Then, the system was vacuumed and filled with CO_2. After repeating three times, THF (1.5 mL) with D_2O (60 mg, 2.0 mmol) was added and the reaction mixture was stirred for 10 minutes at room temperature. Then, PBu_3 (0.06 mmol) was added to the reaction mixture at room temperature. After that, the resulting mixture was stirred at room temperature until the reaction completed upon monitoring by TLC. Then the solvent was removed under reduced pressure and the residue was directly subjected to a flash column chromatography on silica gel to afford the desired product [D]-**2a**.



Step 2: A Schlenk tube was heated under vacuum to remove ambient moisture and water, then

filled with argon. After the Schlenk tube was returned to room temperature, cyclic carbonate [D]-**2a** (0.1 mmol) was added and dissolved in 0.5 mL DCM. After that, the resulting mixture was heated to 60 ^{o}C and was stirred at 60 ^{o}C until the reaction completed upon monitoring by TLC. Then the solvent was removed under reduced pressure and the residue was directly subjected to a flash column chromatography on silica gel to afford the desired product [D]-**3**.

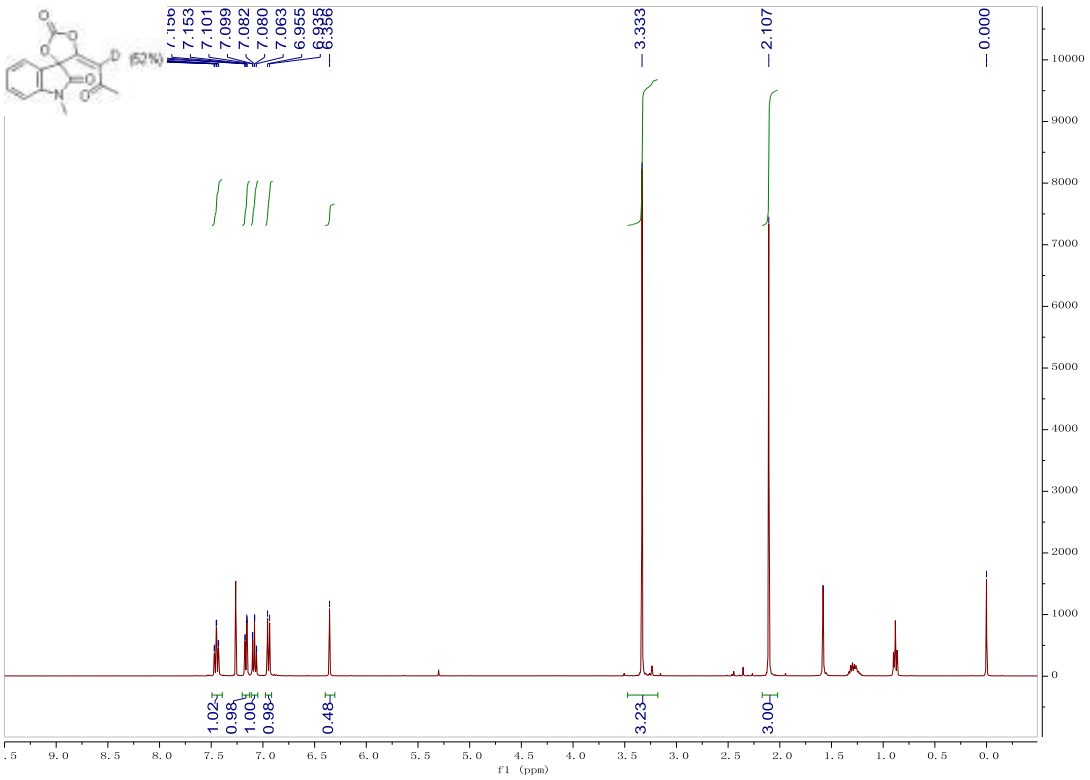




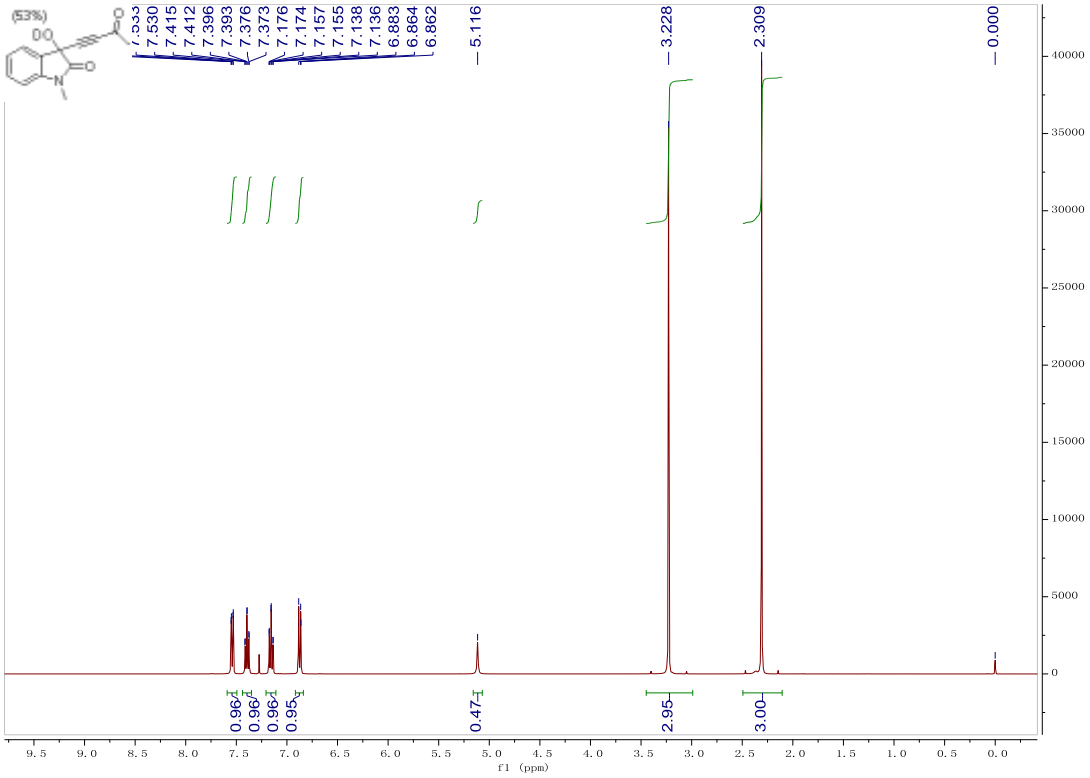
[D]-**1a**, 53% D

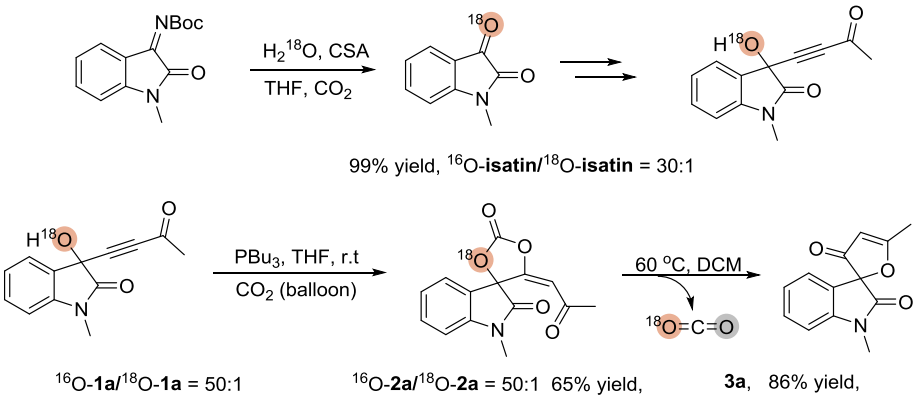
[D]-**2a'**, 81% yield, 52% D

A Schlenk tube was heated under vacuum to remove ambient moisture and water, then filled with argon. After the Schlenk tube was returned to room temperature, γ-Hydroxyl Alkynone [D]-**1a** (0.3 mmol) was added. Then vacuuming the system and filled with CO_2. After repeating three times, THF (1.5 mL) was added and the reaction mixture stirred for 10 minutes at room temperature. Then, PBu_3 (0.06 mmol) was added to the reaction mixture at room temperature. After that, the resulting mixture was stirred at room temperature until the reaction completed upon monitoring by TLC. Then the solvent was removed under reduced pressure and the residue was directly subjected to a flash column chromatography on silica gel to afford the desired product [D]-**2a'**.



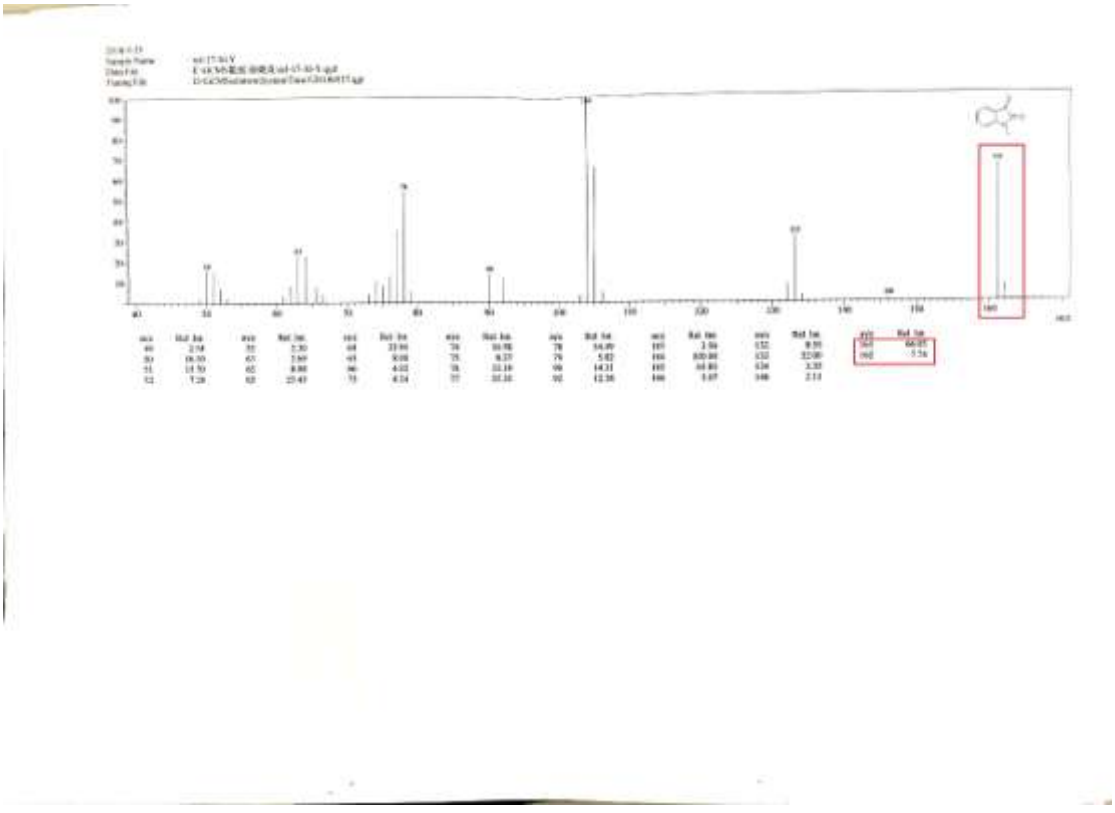
Synthesis of [D]-**1a**: Under argon atmosphere, to a solution of **1a** (300 mg) in $CDCl_3$ (10 mL) was added D_2O (5 mL) at room temperature. The resulting mixture was stirred at room temperature for two days. Then the solvent was removed under reduced pressure. The crude product was used for the next reaction without further purification.



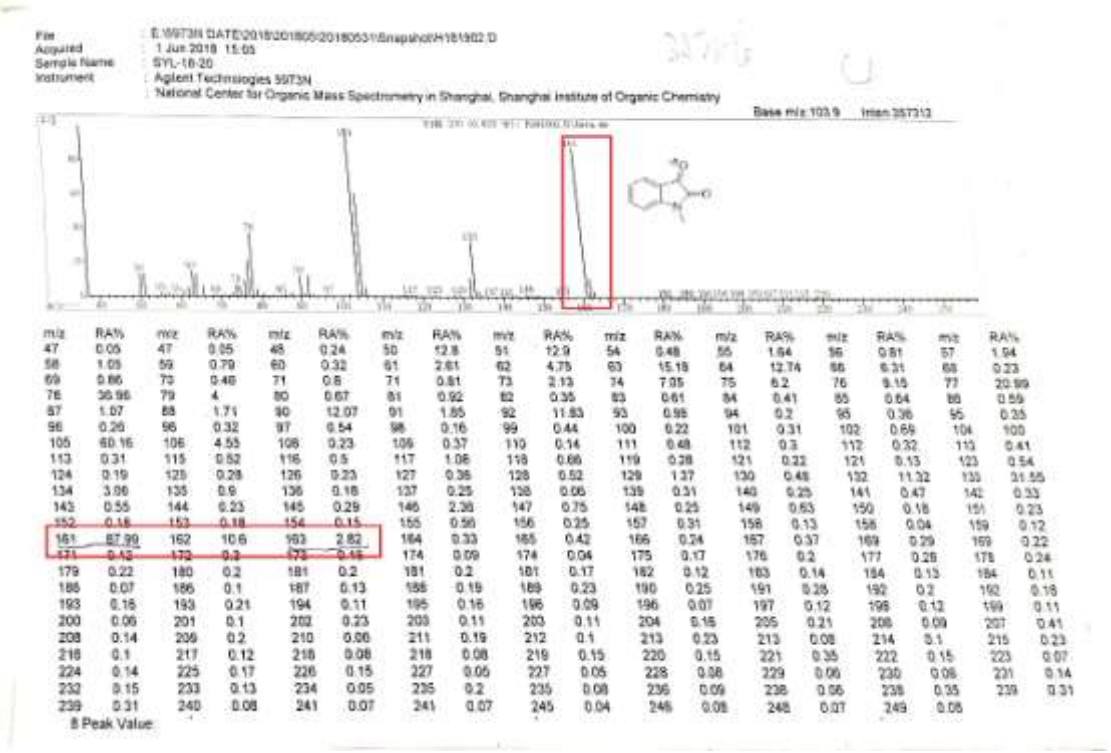


In a Schlenk tube, tert-butyl (*E*)-(1-methyl-2-oxoindolin-3-ylidene)carbamate (1.0 mmol) was dissolve in THF (10 mL), then added into the $H_2{}^{18}O$ (5.0 mmol) dropwise. The mixture was stirred under argon atmosphere at room temperature for 5 min. Then CSA (0.1 mmol) was added into the reaction mixture and heated to reflux. After 1 hour, the mixture was cooled to room temperature and the organic layer was concentrated to afforded ^{18}O-**isatin** as a red solid in 99% yield. The ^{16}O/^{18}O ratio of **isatin** is 30/1 according to the MS report shown as below:

^{16}O-**isatin**:



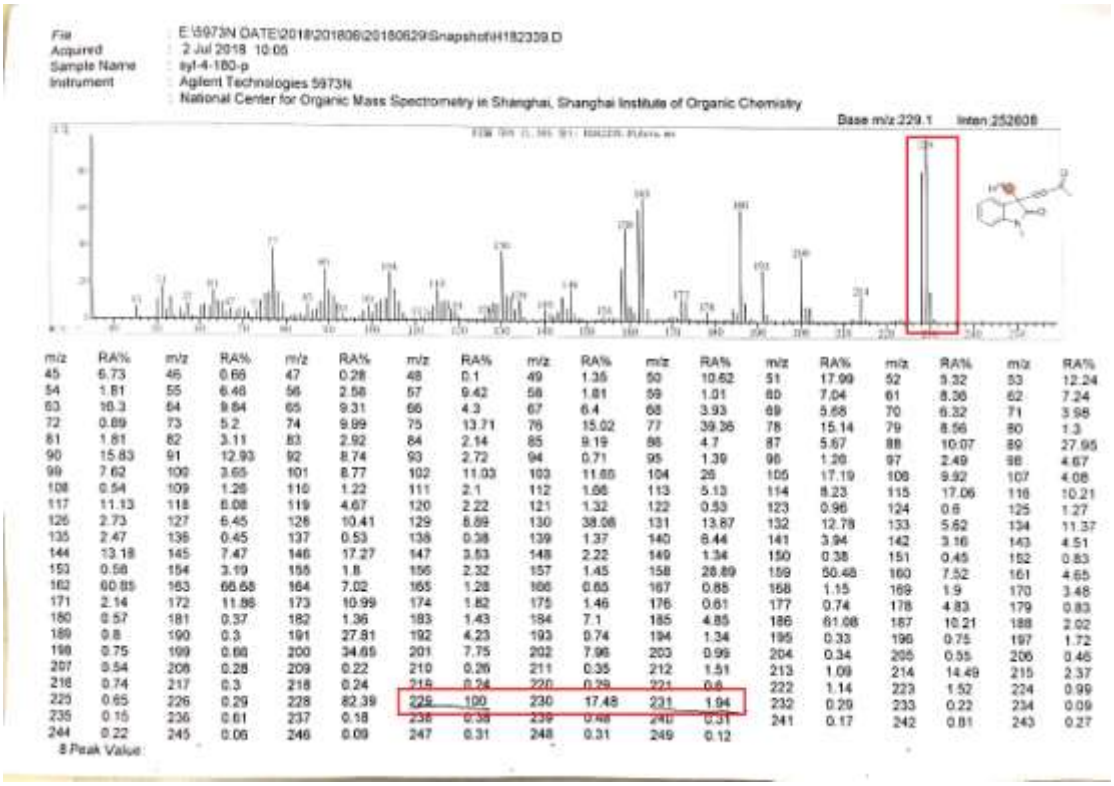
^{18}O-**isatin**:



m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
47	0.05	47	0.05	48	0.24	50	12.8	51	12.9	54	0.48	55	1.64	56	0.81	57	1.94
58	1.05	59	0.79	60	0.32	61	2.61	62	4.75	63	15.18	64	12.74	66	6.31	68	0.23
69	0.86	70	0.48	71	0.8	71	0.81	73	2.13	74	7.05	75	6.2	76	9.15	77	20.99
78	36.96	79	4	80	0.67	81	0.92	82	0.35	83	0.61	84	0.41	85	0.64	86	0.59
87	1.07	88	1.71	90	12.07	91	1.55	92	11.83	93	0.98	94	0.2	95	0.36	95	0.35
96	0.26	96	0.32	97	0.54	98	0.16	99	0.44	100	0.22	101	0.31	102	0.69	104	100
105	60.16	106	4.55	108	0.23	109	0.37	110	0.14	111	0.48	112	0.3	112	0.32	113	0.41
113	0.31	115	0.52	116	0.5	117	1.08	118	0.86	119	0.28	121	0.32	121	0.13	123	0.54
124	0.19	125	0.28	126	0.23	127	0.36	128	0.52	129	1.37	130	0.48	132	11.32	133	31.55
134	3.86	135	0.9	136	0.16	137	0.25	138	0.06	139	0.31	140	0.25	141	0.47	142	0.33
143	0.55	144	0.23	145	0.29	146	2.38	147	0.75	148	0.25	149	0.63	150	0.18	151	0.23
152	0.18	153	0.18	154	0.15	155	0.56	156	0.25	157	0.31	158	0.13	158	0.04	159	0.12
161	87.99	162	10.6	163	2.82	164	0.33	165	0.42	166	0.24	167	0.37	169	0.29	169	0.22
171	0.13	172	0.3	173	0.15	174	0.09	174	0.04	175	0.17	176	0.2	177	0.28	178	0.24
179	0.22	180	0.2	181	0.2	181	0.2	181	0.17	182	0.12	183	0.14	184	0.13	184	0.11
186	0.07	186	0.1	187	0.13	188	0.19	189	0.23	190	0.25	191	0.28	192	0.2	192	0.18
193	0.16	193	0.21	194	0.11	195	0.16	196	0.09	196	0.07	197	0.12	198	0.13	199	0.11
200	0.06	201	0.1	202	0.23	203	0.11	203	0.11	204	0.15	205	0.21	206	0.09	207	0.41
208	0.14	209	0.2	210	0.06	211	0.19	212	0.1	213	0.23	213	0.08	214	0.1	215	0.23
216	0.1	217	0.12	218	0.08	218	0.08	219	0.15	220	0.15	221	0.35	222	0.15	223	0.07
224	0.14	225	0.17	226	0.15	227	0.05	227	0.05	228	0.08	229	0.06	230	0.06	231	0.14
232	0.15	233	0.13	234	0.05	235	0.2	235	0.08	236	0.09	238	0.06	238	0.35	239	0.31
239	0.31	240	0.08	241	0.07	241	0.07	245	0.04	246	0.08	248	0.07	249	0.05		

8 Peak Value

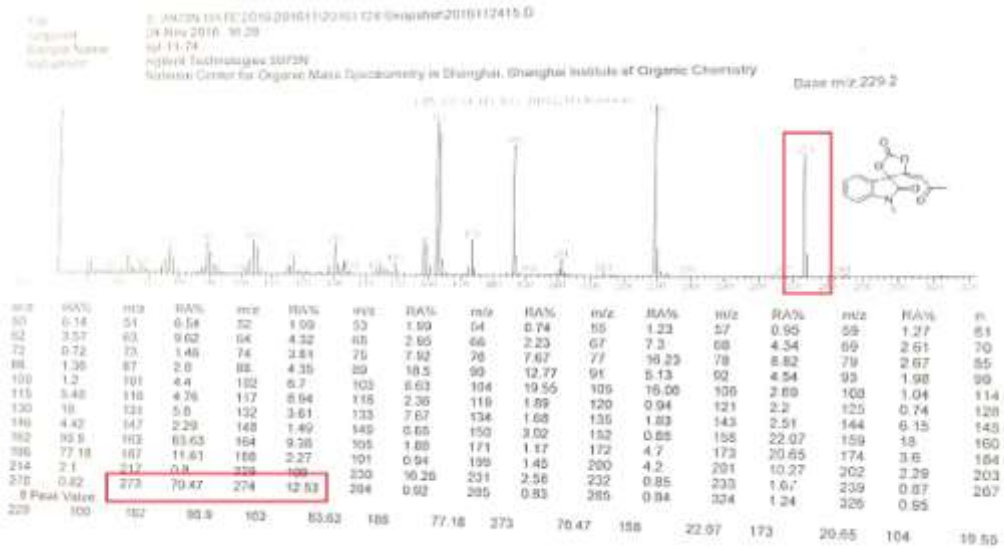
^{16}O-**1a**/^{18}O-**1a** = 50:1



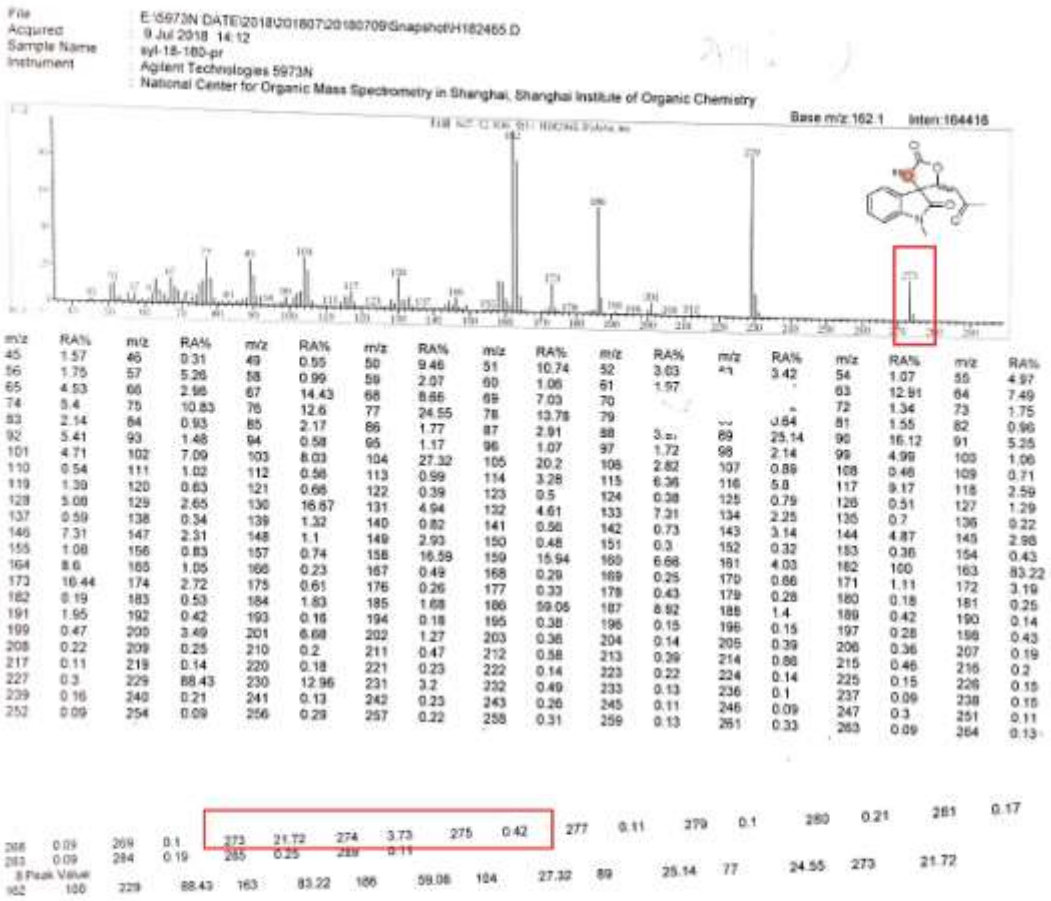
m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%	m/z	RA%
45	6.73	46	0.66	47	0.28	48	0.1	49	1.35	50	10.62	51	17.99	52	3.32	53	12.24
54	1.81	55	6.48	56	2.58	57	9.42	58	1.81	59	1.01	60	7.04	61	8.38	62	7.24
63	10.3	64	9.84	65	9.31	66	4.3	67	6.4	68	3.93	69	5.68	70	6.32	71	3.98
72	0.89	73	5.2	74	9.99	75	13.71	76	15.02	77	39.36	78	15.14	79	8.56	80	1.3
81	1.81	82	3.11	83	2.92	84	2.14	85	9.19	86	4.7	87	5.67	88	10.07	89	27.95
90	15.83	91	12.93	92	8.74	93	2.72	94	0.71	95	1.39	96	1.26	97	2.49	98	4.67
99	7.62	100	3.65	101	8.77	102	11.03	103	11.86	104	26	105	17.19	106	9.92	107	4.08
108	0.54	109	1.26	110	1.22	111	2.1	112	1.66	113	5.13	114	8.23	115	17.06	116	10.21
117	11.13	118	8.08	119	4.67	120	2.22	121	1.32	122	0.53	123	0.96	124	0.6	125	1.27
126	2.73	127	6.45	128	10.41	129	8.89	130	38.08	131	13.87	132	12.78	133	5.62	134	11.37
135	2.47	136	0.45	137	0.53	138	0.38	139	1.37	140	6.44	141	3.94	142	3.16	143	4.51
144	13.18	145	7.47	146	17.27	147	3.53	148	2.22	149	1.34	150	0.38	151	0.45	152	0.83
153	0.58	154	3.19	155	1.8	156	2.32	157	1.45	158	28.89	159	50.48	160	7.52	161	4.65
162	60.85	163	66.68	164	7.02	165	1.28	166	0.65	167	0.85	168	1.15	169	1.9	170	3.48
171	2.14	172	11.88	173	10.99	174	1.82	175	1.46	176	0.61	177	0.74	178	4.83	179	0.83
180	0.57	181	0.37	182	1.36	183	1.43	184	7.1	185	4.85	186	61.08	187	10.21	188	2.02
189	0.8	190	0.3	191	27.81	192	4.23	193	0.74	194	1.34	195	0.33	196	0.75	197	1.72
198	0.75	199	0.66	200	34.69	201	7.75	202	7.96	203	0.99	204	0.34	205	0.55	206	0.46
207	0.54	208	0.28	209	0.22	210	0.26	211	0.35	212	1.51	213	1.09	214	14.49	215	2.37
216	0.74	217	0.3	218	0.24	219	0.24	220	0.29	221	0.6	222	1.14	223	1.52	224	0.99
225	0.65	226	0.29	228	82.39	229	100	230	17.48	231	1.94	232	0.29	233	0.22	234	0.09
235	0.15	236	0.61	237	0.18	238	0.38	239	0.48	240	0.31	241	0.17	242	0.81	243	0.27
244	0.22	245	0.06	246	0.09	247	0.31	248	0.31	249	0.12						

8 Peak Value

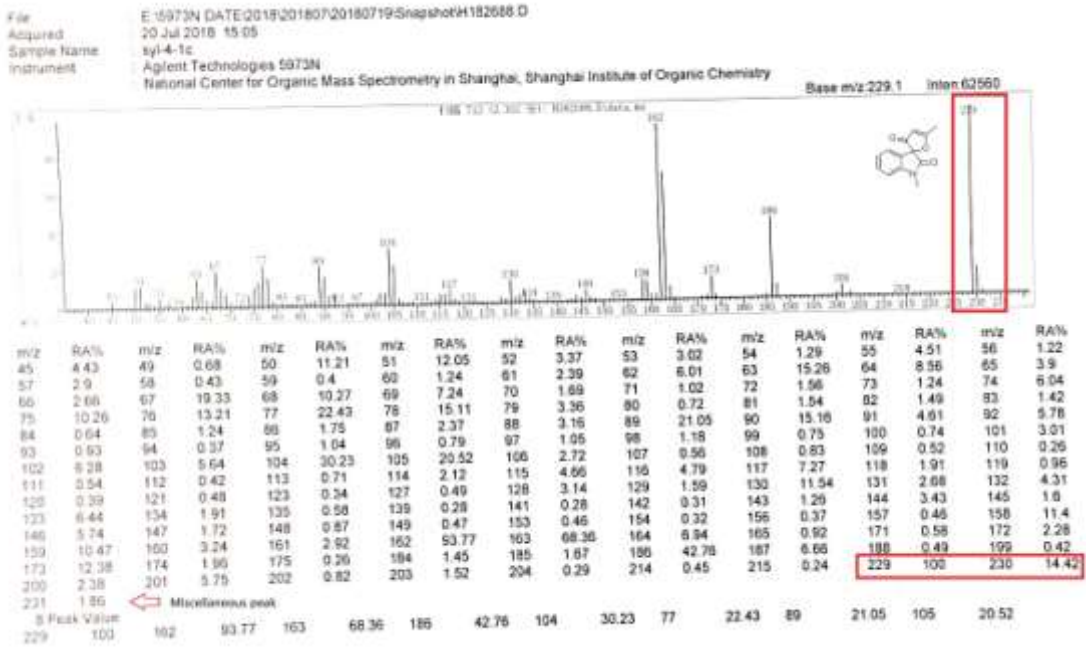
^{16}O-**2a**:



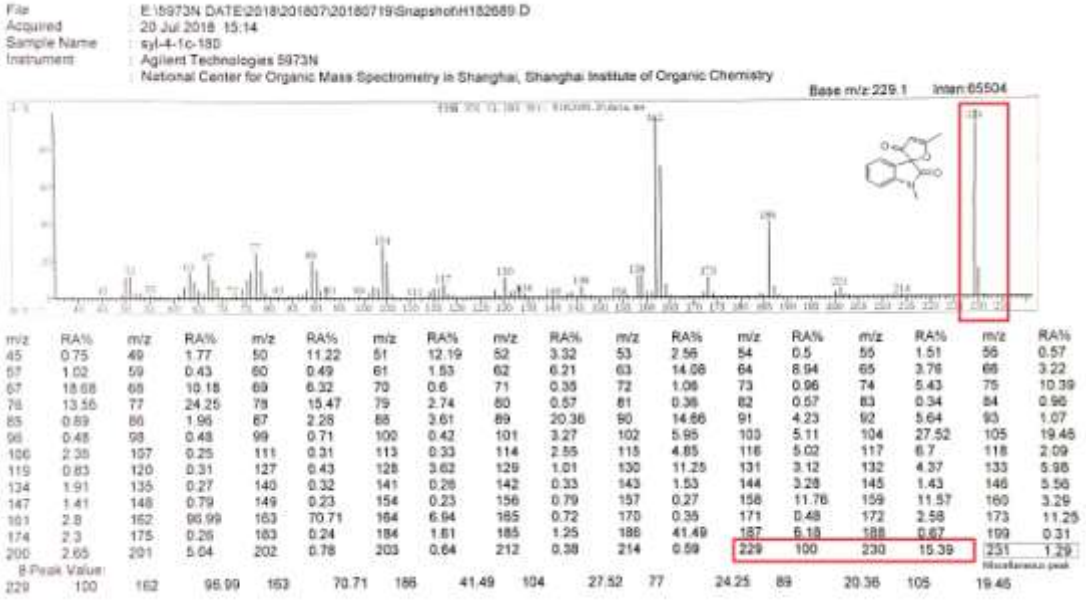
^{16}O-**2a**/^{18}O-**2a** = 50:1



3a was converted from **2a**:



3a was converted from ^{16}O-**2a**/^{18}O-**2a**:



8. Computational Details

The total energies, enthalpies and free energies of the lowest conformers of all species shown in Scheme 3a and 3c (Table S5)

Table S5.[a]

	E_{tot} (E_h)	$H_{298,THF}$	$G_{298,THF}$
1a	-782.0848623	-781.8547246	-781.9180546
PBu_3	-814.6382214	-814.2494482	-814.3182312
INT1	-1596.755835	-1596.133858	-1596.237701
TS1	-1596.741613	-1596.125061	-1596.227886
INT2	-1596.759752	-1596.137422	-1596.240483
CO_2	-188.560743	-188.5451942	-188.5694532
INT3	-1785.338296	-1784.698178	-1784.808336
TS2	-1785.323461	-1784.684355	-1784.792590
INT4	-1785.330827	-1784.689680	-1784.794910
TS3	-1785.313888	-1784.674867	-1784.778770
INT5	-1785.333482	-1784.694735	-1784.802603
2a	-970.718415	-970.470013	-970.533946
(*S*)-**TS3**	-4254.794939	-4253.766433	-4253.935851
(*R*)-**TS3**	-4254.786325	-4253.75899	-4253.933787

a. SMD/M06/6-311+G(d,p)//M06/6-31G(d) (THF as solvent)

The total energies, enthalpies and free energies of the lowest conformers of all species shown in Scheme 3b (Table S6)

Table S6.[a]

	E_{tot} (E_h)	$H_{298,DCM}$	$G_{298,DCM}$
2a	-970.6841295	-970.4357281	-970.499661
TS4	-970.6455038	-970.3999605	-970.464657
INT6	-970.717971	-970.4700303	-970.536811
3a	-782.1518763	-781.9208941	-781.977722

CO_2	-188.5587642	-188.5432528	-188.567500

b. SMD/M06/6-311+G(d,p)//M06/6-31G(d) (DCM as solvent)

Archive entries

1a

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PBu_3

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INT1

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0,2.0761219817,2.9571582662,3.7983348503\C,0,1.9083068616,5.506135657,
2.7684224751\H,0,3.6024955855,4.2719936806,2.2441109174\H,0,2.31241240
56,4.2632247027,1.0411862509\H,0,2.3135645551,6.4278229215,2.333580958
1\H,0,0.8178146486,5.5282747589,2.6361860959\H,0,2.1085666844,5.530902
3481,3.8490186284\C,0,1.8203069884,-0.1737872079,4.1382038531\C,0,3.25
52432242,-0.4150961711,4.5912071535\H,0,1.1810323407,-1.0502711333,4.3
171542456\H,0,1.3638126358,0.6571144781,4.6925029422\C,0,3.3314632206,
-0.7393081145,6.0779211802\H,0,3.7057760153,-1.2447971538,4.0206483812
\H,0,3.8788924362,0.4716859321,4.3860624253\C,0,4.7564434789,-0.980703
94,6.5451930201\H,0,2.8810576388,0.0875839785,6.6493620469\H,0,2.70914

43366,-1.6237886367,6.2852552866\H,0,4.8006419528,-1.212014377,7.61609
24701\H,0,5.2129101467,-1.8211642732,6.0044201288\H,0,5.3853694372,-0.
0971381571,6.3694185625\O,0,-0.926296705,0.988634994,3.7792211576\H,0,
-1.7227590794,0.9575262881,4.3295540654\C,0,-1.2157183992,0.3392530878
,2.5486926591\C,0,-2.5057731487,0.7816580293,1.9296682677\C,0,-1.45628
17864,-1.1767242281,2.757960068\C,0,-3.3523264597,-0.3189821353,1.7994
512761\C,0,-2.9176251298,2.0346521346,1.5262956205\C,0,-4.6247631967,-
0.2033173854,1.2672976132\C,0,-4.2010420326,2.1772143988,0.9922653419\
H,0,-2.2399301879,2.8829582044,1.6167759469\C,0,-5.0356558112,1.070931
5647,0.8656569334\H,0,-5.2817333752,-1.065184737,1.1630139712\H,0,-4.5
469129232,3.1550920581,0.6639359694\H,0,-6.0311387189,1.1954964084,0.4
427004852\N,0,-2.711740573,-1.4730966,2.2836985414\C,0,-3.2691979171,-
2.7995367528,2.2600419294\H,0,-4.1915454986,-2.8490673809,2.854293689\
H,0,-3.4938928899,-3.1104221319,1.231091156\H,0,-2.5255917354,-3.47714
45267,2.6895580702\O,0,-0.6684599539,-1.9783767516,3.2279556172\C,0,0.
8646021262,1.1242176269,-0.6783469271\O,0,1.4872391131,2.1893456394,-0
.8623639013\C,0,0.9478659207,0.0214867474,-1.7231149822\H,0,0.53413891
38,0.3877029313,-2.6712694628\H,0,2.0049622999,-0.2190659746,-1.905028
1028\H,0,0.4030924729,-0.8884409394,-1.4367119365\\Version=ES64L-G16Re
vA.03\State=1-A\HF=-1596.755835\RMSD=5.267e-09\Dipole=-0.153063,-2.138
4375,2.4294373\Quadrupole=19.4837412,-6.2275674,-13.2561738,1.7422246,
4.0911667,12.3218167\PG=C01 [X(C25H38N1O3P1)]\\@

TS1

1\1\GINC-OM112\SP\RM06\6-311+G(d,p)\C25H38N1O3P1\WEIY\27-Oct-2018\0\\#
p m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=THF)\\Title Car
d Required\\0,1\C\C,1,1.33356284\P,2,1.77367829,1,124.00779974\C,3,1.8
3037818,2,109.25839038,1,-69.95208455,0\C,4,1.52517864,3,116.68973431,
2,153.09897285,0\H,4,1.10093819,3,105.71102389,2,30.37417,0\H,4,1.1026
9946,3,106.20775652,2,-81.90928149,0\C,5,1.52289768,4,111.62786337,3,1
77.71365541,0\H,5,1.10145156,4,109.62902622,3,-61.06146161,0\H,5,1.101
98565,4,110.84740443,3,55.65938564,0\C,8,1.51885403,5,112.26634902,4,1
78.8422055,0\H,8,1.10151847,5,109.19705234,4,-58.74783405,0\H,8,1.1014
4667,5,109.0845821,4,56.57969053,0\H,11,1.09609799,8,111.69593852,5,17
9.93800833,0\H,11,1.0983181,8,111.10082835,5,-59.85829311,0\H,11,1.098
56606,8,111.13479587,5,59.72397804,0\C,3,1.81671302,2,110.19277216,1,5
0.45274252,0\C,17,1.52755133,3,112.46060252,2,57.62928806,0\H,17,1.100
41738,3,106.06244388,2,-61.70053706,0\H,17,1.10083729,3,108.93217345,2
,-178.03101948,0\C,18,1.52194945,17,111.08135055,3,-168.61146589,0\H,1
8,1.1010148,17,109.92130158,3,-47.18918902,0\H,18,1.10338962,17,110.30
440889,3,69.30208031,0\C,21,1.51872842,18,111.97835294,17,-178.0108766
2,0\H,21,1.10279833,18,109.67623366,17,-55.45744625,0\H,21,1.10064063,
18,108.29268742,17,60.22458892,0\H,24,1.09660416,21,111.70832713,18,-1
78.71851411,0\H,24,1.09773267,21,110.83822443,18,-58.42136656,0\H,24,1
.09881258,21,111.19685994,18,60.88815778,0\C,3,1.82366967,2,110.754523

98,1,170.44455038,0\C,30,1.52366399,3,116.39915611,2,179.64977737,0\H,
30,1.10167067,3,106.69346499,2,56.26351641,0\H,30,1.10212737,3,106.210
94655,2,-57.14181579,0\C,31,1.52377488,30,110.86969392,3,176.29517723,
0\H,31,1.10238735,30,110.19034949,3,-62.86911879,0\H,31,1.10289151,30,
110.89344879,3,54.72926702,0\C,34,1.51851851,31,112.47814478,30,177.44
354776,0\H,34,1.10172337,31,108.89290964,30,-60.24268677,0\H,34,1.1024
069,31,108.92590899,30,54.87520378,0\H,37,1.09609654,34,111.70446504,3
1,179.47556932,0\H,37,1.0985284,34,111.13751891,31,-60.31876757,0\H,37
,1.09852938,34,111.10489554,31,59.30580644,0\C,2,1.58412779,1,109.3518
2622,3,179.12911284,0\C,43,1.51578228,2,110.8585413,1,125.61308913,0\C
,43,1.55008856,2,109.20158545,1,-123.38622432,0\C,44,1.39778883,43,109
.37178269,2,121.40361051,0\C,44,1.37882813,43,130.51496092,2,-58.35997
77,0\C,46,1.38614609,44,121.86118766,43,-178.5754318,0\C,47,1.40030664
,44,119.11388876,43,178.9146795,0\H,47,1.09171715,44,119.49437196,43,-
1.00540029,0\C,49,1.39094001,47,120.15876338,44,0.16705878,0\H,48,1.08
932905,46,121.56297086,44,179.46447828,0\H,49,1.08867894,47,120.080938
01,44,179.93729159,0\H,51,1.08898207,49,119.64017662,47,-179.95381685,
0\N,45,1.39112567,43,107.69409777,2,-124.62308917,0\C,55,1.43569407,45
,123.34343577,43,176.18924506,0\H,56,1.09796552,55,111.39506714,45,127
.84366349,0\H,56,1.10293162,55,110.86187766,45,-111.1994487,0\H,56,1.0
9465,55,107.36958569,45,8.16530743,0\O,45,1.21384172,43,128.02102704,2
,53.69780762,0\C,1,1.4500412,2,133.62122699,43,-178.26230921,0\O,61,1.
22742563,1,124.21137377,2,-67.6049343,0\C,61,1.51132298,1,114.57517829
,2,116.85123961,0\H,63,1.09825144,61,109.05797677,1,78.37584976,0\H,63
,1.09479826,61,109.86794661,1,-162.68692353,0\H,63,1.09838471,61,111.8
7000796,1,-39.31076327,0\H,1,1.27746064,2,95.06542706,43,0.39050483,0\
O,43,1.33722618,2,106.80554594,1,-1.26554782,0\\Version=ES64L-G16RevA.
03\State=1-A\HF=-1596.741613\RMSD=5.397e-09\Dipole=3.7970498,-2.180075
3,3.5422943\Quadrupole=-8.6404154,3.8541741,4.7862413,0.3424318,-11.31
5135,11.3558758\PG=C01 [X(C25H38N1O3P1)]\\@

INT2

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C25H38N1O3P1\WEIY\25-Oct-2018\0\\#
p m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=THF)\\Title Car
d Required\\0,1\C,0,0.1203375283,-0.0186449536,0.0479997017\C,0,0.1408
724797,-0.0524206194,1.3888413123\P,0,1.5323476353,-0.1739267266,2.635
1266602\C,0,2.3041023711,-1.7784597472,2.0208941174\C,0,3.8208201528,-
1.9012731343,1.9433107226\H,0,1.8950166883,-1.9978578649,1.0285939175\
H,0,1.895956722,-2.5590158478,2.6859431753\C,0,4.2682236964,-3.3377675
356,1.707829825\H,0,4.1863036283,-1.2680783624,1.1201654763\H,0,4.3058
53223,-1.5282143193,2.8601409979\C,0,5.7754269293,-3.4627185137,1.5644
998469\H,0,3.9157554338,-3.9675245997,2.5419896165\H,0,3.76982092,-3.7
270548359,0.8055370096\H,0,6.0881198935,-4.501279046,1.4003082172\H,0,
6.1406208424,-2.8661943179,0.7172704646\H,0,6.2887273348,-3.0992666106
,2.4657597665\C,0,2.7864538497,1.1366675935,2.3516726059\C,0,2.8788254

305,2.1849061932,3.452684373\H,0,2.5122451361,1.6075873518,1.396706247
6\H,0,3.7614850992,0.6587668036,2.1849186061\C,0,3.8803861848,3.277609
3656,3.1034331557\H,0,1.8855941282,2.622773488,3.6238820949\H,0,3.1789
34561,1.7143949489,4.4046465578\C,0,3.9932371416,4.3261607752,4.196987
3107\H,0,4.8674238581,2.8263293242,2.9115597788\H,0,3.5791480348,3.753
6011546,2.1563315187\H,0,4.709739604,5.1147556736,3.9364600865\H,0,3.0
222212107,4.8042807015,4.3846694039\H,0,4.3234868638,3.8753741394,5.14
31197791\C,0,1.4651473403,-0.6130335654,4.4326444534\C,0,2.6936892178,
-1.2704811799,5.0475276348\H,0,0.5721179193,-1.2460714965,4.5455845428
\H,0,1.2296084309,0.3240800854,4.9504949861\C,0,2.5308674504,-1.420910
0831,6.5558158084\H,0,2.883047045,-2.2636073996,4.6104981308\H,0,3.599
5888451,-0.6715408655,4.8487822074\C,0,3.7324000494,-2.0861905179,7.20
48552933\H,0,2.3634569518,-0.4273485826,7.0014394731\H,0,1.6179193633,
-2.0010754686,6.7632975265\H,0,3.6083482288,-2.1850480404,8.2901137224
\H,0,3.896082095,-3.0925548955,6.7952771529\H,0,4.6491068801,-1.507146
5828,7.0260078677\O,0,0.1205563671,1.1555250119,3.1528777667\C,0,-0.83
89897543,0.6298429298,2.3118931743\C,0,-1.7913517151,1.6170131165,1.70
05710123\C,0,-1.8068576229,-0.3910440861,2.961401309\C,0,-3.1021724549
,1.2034296495,1.9449752706\C,0,-1.5456683781,2.7934579508,1.024161399\
C,0,-4.192113189,1.9357679154,1.5047751565\C,0,-2.6302230608,3.5505832
689,0.5713500248\H,0,-0.5168086743,3.1160180908,0.8596016663\C,0,-3.93
20111799,3.1200517957,0.8091312738\H,0,-5.2130233182,1.609521594,1.696
6390934\H,0,-2.4580753656,4.4821251403,0.0357499887\H,0,-4.7691407908,
3.7176039063,0.451807227\N,0,-3.0956634218,0.0081920005,2.6788839796\C
,0,-4.2687272993,-0.6930348371,3.128107846\H,0,-4.8782192465,-0.058717
353,3.7860295042\H,0,-4.8843166413,-1.0157285318,2.2776577092\H,0,-3.9
315320422,-1.5723744129,3.6848468173\O,0,-1.4988447738,-1.3912684244,3
.580147975\C,0,1.2472186308,-0.2873356657,-0.8654506056\O,0,2.41221639
62,-0.2682652567,-0.5020095623\C,0,0.8712289883,-0.5510038888,-2.30010
5889\H,0,0.3494112729,0.3190393566,-2.7218309012\H,0,1.767573435,-0.75
94959582,-2.890150406\H,0,0.1749063692,-1.3977939322,-2.3676730815\H,0
,-0.8194507706,0.2831578635,-0.4270474516\\Version=ES64L-G16RevA.03\St
ate=1-A\HF=-1596.7597516\RMSD=2.810e-09\Dipole=-0.9002205,-0.0323053,-
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996,-2.416854\PG=C01 [X(C25H38N1O3P1)]\\@

INT3

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C26H38N1O5P1\WEIY\25-Oct-2018\0\\#
p m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=THF)\\Title Car
d Required\\0,1\C,0,0.2174569051,0.6348242278,0.279613621\C,0,0.224452
6303,0.524607096,1.6204435671\P,0,1.6902440278,-0.0159210828,2.6199089
74\C,0,2.1645994177,-1.6870723196,2.0349169035\C,0,3.6633022612,-1.961
3313358,1.9651307196\H,0,1.7103383456,-1.8558529571,1.0529735921\H,0,1
.6654881566,-2.3726335864,2.7379989424\C,0,3.941966477,-3.4358472078,1
.7078965392\H,0,4.1039225536,-1.3529845282,1.1618227237\H,0,4.16487481

16,-1.6627966291,2.8995343309\C,0,5.4273264959,-3.7277374108,1.5841135
677\H,0,3.5063208852,-4.0328629543,2.5257425939\H,0,3.4174064399,-3.74
8828333,0.7912339644\H,0,5.6186059293,-4.7920464338,1.4037607434\H,0,5
.8725597805,-3.163169439,0.7537862734\H,0,5.9636283743,-3.4440001018,2
.5000002188\C,0,3.0046668417,1.2377843613,2.4203192916\C,0,2.538084615
1,2.6627911885,2.7208717325\H,0,3.4093041114,1.1581871237,1.4053382567
\H,0,3.80370895,0.9429149059,3.1188670891\C,0,3.7109353228,3.633357672
3,2.7152901853\H,0,1.7996720943,2.971201913,1.9636539215\H,0,2.0039959
955,2.716202164,3.6813820926\C,0,3.2632143544,5.0647271431,2.956729910
3\H,0,4.4353494731,3.3317046595,3.4889610394\H,0,4.2463409092,3.560083
1921,1.7545365425\H,0,4.11128537,5.7597393027,2.9668534529\H,0,2.56794
1991,5.3973556059,2.1739956391\H,0,2.740600163,5.1557961092,3.91780067
9\C,0,1.459552091,-0.2007613668,4.4227316231\C,0,2.6137488208,-0.91743
14082,5.1207918843\H,0,0.5194389006,-0.7505159577,4.5640177421\H,0,1.3
058576097,0.7955128684,4.8565750223\C,0,2.3496866891,-0.9754695085,6.6
219003352\H,0,2.7448087973,-1.9447450037,4.7412058978\H,0,3.5723562729
,-0.3978811319,4.9492825599\C,0,3.485437616,-1.6404342744,7.3795150838
\H,0,2.1805900888,0.0450138916,6.9970553075\H,0,1.4070186958,-1.515641
0961,6.7964861234\H,0,3.2817605743,-1.683425439,8.4558598974\H,0,3.647
9461723,-2.6699295595,7.0307290051\H,0,4.4287034002,-1.0935079215,7.24
21841794\O,0,-0.3361039321,1.6738230069,3.4741125541\C,0,-0.9568139404
,0.9506281873,2.4694372554\C,0,-2.059906869,1.6944346341,1.768229859\C
,0,-1.6889568246,-0.3700523968,2.884048789\C,0,-3.216019113,0.91312456
81,1.7664937943\C,0,-2.0752882999,2.9740521394,1.2533478102\C,0,-4.403
6285439,1.3788470056,1.2271575127\C,0,-3.2623536178,3.4619417844,0.699
3184966\H,0,-1.1753033789,3.588360371,1.2967574019\C,0,-4.4053544118,2
.6682953897,0.689285651\H,0,-5.3073082268,0.7720396632,1.2339872808\H,
0,-3.2975736174,4.4684326028,0.2875405789\H,0,-5.3267257961,3.06062017
2,0.2619456337\N,0,-2.959133469,-0.3234191388,2.3607644507\C,0,-3.9551
05742,-1.3257464879,2.6345144465\H,0,-4.727539003,-0.9288097949,3.3068
496856\H,0,-4.4257228934,-1.6724002791,1.705302591\H,0,-3.452618431,-2
.1656481675,3.1219821839\O,0,-1.168876267,-1.3531488051,3.3797430392\C
,0,1.3106129677,0.3330793669,-0.6650130315\O,0,2.4263060149,-0.0064605
682,-0.2993427529\C,0,0.9652627804,0.4750781284,-2.1199090316\H,0,0.64
94092277,1.5048757629,-2.3358732176\H,0,1.8279836195,0.2172798134,-2.7
391988242\H,0,0.1154191796,-0.1715627099,-2.3773116855\H,0,-0.70858927
7,1.00276408,-0.1697939823\C,0,-1.0303204801,1.6998192261,4.8312017258
\O,0,-0.2977724653,2.2341220207,5.6436860906\O,0,-2.1281931689,1.15436
37912,4.7927053383\\Version=ES64L-G16RevA.03\State=1-A\HF=-1785.338296
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0002373,-1.309184,-8.6910533,3.7581555,20.8636671,-13.1621235\PG=C01 [
X(C26H38N1O5P1)]\\@

TS2

1\1\GINC-OM111\SP\RM06\6-311+G(d,p)\C26H38N1O5P1\WEIY\25-Oct-2018\0\\#

p m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=THF)\\Title Car
d Required\\0,1\C,0,0.0558821806,-2.3990531342,0.9005343978\C,0,0.2872
985225,-1.2133491168,0.3111750252\P,0,-0.9496844196,0.1161973679,0.373
2970742\C,0,-2.3335740241,-0.2707348622,-0.7600514351\C,0,-3.722220183
1,0.1062743348,-0.2558942176\H,0,-2.2768368759,-1.3482356849,-0.964567
0676\H,0,-2.0984226787,0.2509324816,-1.7017941004\C,0,-4.7893484229,-0
.1926230833,-1.3001809891\H,0,-3.9371696006,-0.4575344928,0.6631361292
\H,0,-3.766107829,1.1764919841,0.0092766139\C,0,-6.1844360441,0.152858
1576,-0.8087739558\H,0,-4.5645051897,0.3661738683,-2.2225842681\H,0,-4
.7373820916,-1.2586036292,-1.5703976938\H,0,-6.9459258971,-0.062616688
8,-1.5672603943\H,0,-6.4388511266,-0.422210928,0.0915937296\H,0,-6.262
4423795,1.2185398299,-0.552881113\C,0,-1.4425902676,0.4962324137,2.090
7984355\C,0,-0.2396615208,0.8466076699,2.9656651544\H,0,-1.9832612306,
-0.3652831122,2.4933159369\H,0,-2.1572063561,1.3317402298,2.042813231\
C,0,-0.6535024624,1.1065116442,4.4078522598\H,0,0.5006148243,0.0321987
493,2.9329883943\H,0,0.2811137939,1.7376153776,2.5756866772\C,0,0.5396
783172,1.4497091729,5.2832514831\H,0,-1.3945750215,1.9218529607,4.4376
911376\H,0,-1.1669971333,0.2153593875,4.8017353149\H,0,0.2444388671,1.
616707927,6.3257820564\H,0,1.2821155418,0.6412199027,5.2672328552\H,0,
1.0411896903,2.3601229554,4.9277451119\C,0,-0.2412224228,1.6895904547,
-0.2336492873\C,0,-1.1286545363,2.9158069956,-0.0448267919\H,0,-0.0258
353564,1.5547896369,-1.3012267454\H,0,0.7297589529,1.8492232503,0.2573
825604\C,0,-0.4886071901,4.1359323443,-0.6972386704\H,0,-2.1247798501,
2.7479271747,-0.4883254888\H,0,-1.2957407017,3.1244271487,1.0243370063
\C,0,-1.3118187001,5.396961093,-0.5048887366\H,0,0.5223877903,4.272829
6011,-0.2797510212\H,0,-0.3423653287,3.9337248963,-1.7700255217\H,0,-0
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-0.9402528508\H,0,-1.4390799817,5.6290522897,0.5613231287\C,0,1.696093
4197,-1.0581970757,-0.3248252698\C,0,1.7500376451,-0.1643748499,-1.561
659537\C,0,2.548070636,-0.2243805189,0.6927147933\C,0,2.6528818338,0.8
78043877,-1.3188214963\C,0,1.1156449345,-0.241242557,-2.7890090198\C,0
,2.9234789918,1.8581303862,-2.258704664\C,0,1.3712734789,0.7429952629,
-3.7525104392\H,0,0.434143148,-1.0657691428,-2.9908649233\C,0,2.263214
1903,1.7761149914,-3.4881978013\H,0,3.622503456,2.6668138328,-2.049990
5609\H,0,0.8757392965,0.6902944751,-4.7202901126\H,0,2.4567612142,2.53
27050504,-4.2470974776\N,0,3.1281817833,0.8176381798,-0.0045277064\C,0
,4.0483011329,1.7540382913,0.582549642\H,0,5.0143171675,1.740388928,0.
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,1.4577192891,1.6252211283\O,0,2.7041130635,-0.4498790855,1.8732561129
\C,0,-1.2022000128,-2.8819325728,1.4848741174\O,0,-2.2489549659,-2.246
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97,2.5888503424\H,0,-0.8694532445,-4.9879880708,1.4037708229\H,0,0.902
4813552,-3.0895991005,0.8479910371\O,0,0.5103443293,-3.0490448193,-1.9
996762609\C,0,1.6030168352,-3.4575575177,-1.7226011474\O,0,2.334414069

3,-2.2306576303,-0.4685523417\O,0,2.4588361755,-4.2694332219,-1.810785
3275\\Version=ES64L-G09RevE.01\State=1-A\HF=-1785.323461\RMSD=6.563e-0
9\Dipole=-3.5430893,4.9984704,1.3339517\Quadrupole=-2.4647121,-2.41592
69,4.8806389,22.0857367,2.8741428,-15.0945151\PG=C01 [X(C26H38N1O5P1)]
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INT4

1\1\GINC-OM112\SP\RM06\6-311+G(d,p)\C26H38N1O5P1\WEIY\25-Oct-2018\0\\#
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d Required\\0,1\C,-0.0655920003,-2.5508010112,0.1553790007\C,0.2029610
009,-1.2753170056,-0.2098650009\P,-1.0106800045,0.0536280002,0.1030100
005\C,-2.6333740116,-0.3001850013,-0.6607460029\C,-3.851320017,0.03432
70002,0.1898360008\H,-2.6342690116,-1.354708006,-0.9529490042\H,-2.619
1930115,0.2652040012,-1.6040910071\C,-5.1386640226,-0.2401010011,-0.57
70160025\H,-3.8377280169,-0.5696220025,1.1074740049\H,-3.8387440169,1.
0916040048,0.5048410022\C,-6.3760890281,0.0713740003,0.2465270011\H,-5
.1441130226,0.3500890015,-1.5071270066\H,-5.1485570227,-1.2958630057,-
0.8889810039\H,-7.2970220321,-0.1378840006,-0.3103490014\H,-6.39877802
82,-0.5294590023,1.1657630051\H,-6.3997470282,1.129093005,0.5434600024
\C,-1.0850600048,0.2941950013,1.9159720084\C,0.2867340013,0.5853360026
,2.5229770111\H,-1.5213030067,-0.6080940027,2.3568370104\H,-1.78398000
79,1.1200360049,2.1160510093\C,0.1991230009,0.8863820039,4.0126230177\
H,0.9513720042,-0.2813960012,2.3656880104\H,0.7767020034,1.4348600063,
2.0161170089\C,1.5700110069,1.1035490049,4.6293070204\H,-0.4309880019,
1.7768470078,4.1657600183\H,-0.3174360014,0.0579770003,4.5219090199\H,
1.5045060066,1.365086006,5.6918530251\H,2.1846750096,0.1961170009,4.54
822102\H,2.1082560093,1.9152180084,4.1185650181\C,-0.5380760024,1.6928
600075,-0.5390720024\C,-1.5259460067,2.8073060124,-0.2061600009\H,-0.4
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570007\C,-1.0379440046,4.1326040182,-0.7805770034\H,-2.5245560111,2.58
22330114,-0.6138630027\H,-1.6517320073,2.9177180128,0.8837730039\C,-1.
9903920088,5.2771380232,-0.4827280021\H,-0.0380980002,4.3517380192,-0.
3725250016\H,-0.900775004,4.0249430177,-1.8679750082\H,-1.6237590071,6
.2259540274,-0.8915220039\H,-2.9823310131,5.0902910224,-0.916029004\H,
-2.1237250094,5.4110020238,0.5996290026\C,1.5733810069,-1.0990630048,-
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-1.6328260072,0.1085470005\C,2.9879700132,0.6132580027,-0.1203800005\C
,1.9447100086,1.1828200052,-2.2068390097\C,3.6079570159,1.8492110081,-
0.0255790001\C,2.5839900114,2.4244790107,-2.1514290095\H,1.3019490057,
0.913244004,-3.0426990134\C,3.3754090149,2.7627150122,-1.0581440047\H,
4.2797700188,2.0890570092,0.7968630035\H,2.4574760108,3.1336240138,-2.
9671460131\H,3.852236017,3.7407380165,-1.0174250045\N,3.188951014,-0.5
140850023,0.686551003\C,4.1691450184,-0.5943290026,1.7376330077\H,5.16
27690227,-0.2930940013,1.3777260061\H,3.8842530171,0.0542760002,2.5782
670114\H,4.2103990185,-1.6338960072,2.0749680091\O,2.8248670124,-2.774

4660122,0.4371970019\C,-1.2498860055,-3.0954470136,0.8272390036\O,-2.1
838420096,-2.4038920106,1.2193970054\C,-1.2445280055,-4.5846830202,1.0
208590045\H,-1.1854770052,-5.0905580224,0.0476660002\H,-0.3535500016,-
4.8926370215,1.584405007\H,-2.1477760095,-4.9007250216,1.5490250068\H,
0.6932180031,-3.2874980145,-0.1114200005\O,-0.3849590017,-0.7503600033
,-2.4555590108\C,0.3850590017,-1.6421400072,-2.9157820128\O,1.55483400
68,-1.8838710083,-2.0771480091\O,0.3426320015,-2.3291800103,-3.9084860
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TS3

1\1\GINC-OM112\SP\RM06\6-311+G(d,p)\C26H38N1O5P1\WEIY\25-Oct-2018\0\\#
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P,0,-1.057617,-0.017302,0.036222\C,0,-2.664044,-0.183896,-0.828573\C,0
,-3.887932,0.105092,0.032157\H,0,-2.70599,-1.20474,-1.219749\H,0,-2.60
8573,0.499949,-1.690211\C,0,-5.16725,0.002396,-0.787696\H,0,-3.918298,
-0.618203,0.85821\H,0,-3.832184,1.111132,0.482336\C,0,-6.406471,0.2713
23,0.048509\H,0,-5.121079,0.709235,-1.632143\H,0,-5.223718,-1.001883,-
1.234824\H,0,-7.324086,0.189688,-0.546078\H,0,-6.482332,-0.443003,0.87
927\H,0,-6.38037,1.280335,0.483283\C,0,-1.139615,0.12784,1.857215\C,0,
0.213311,0.381551,2.516095\H,0,-1.599452,-0.789184,2.23743\H,0,-1.8343
51,0.953724,2.074198\C,0,0.066666,0.580955,4.018961\H,0,0.87921,-0.476
312,2.325788\H,0,0.713184,1.266241,2.082362\C,0,1.404891,0.783404,4.70
7579\H,0,-0.589983,1.445398,4.207899\H,0,-0.449151,-0.291576,4.448362\
H,0,1.289094,0.936106,5.787012\H,0,2.056632,-0.089923,4.564091\H,0,1.9
29135,1.661684,4.303417\C,0,-0.503149,1.646509,-0.500878\C,0,-1.431352
,2.79235,-0.107359\H,0,-0.412707,1.605059,-1.594507\H,0,0.503415,1.850
406,-0.11649\C,0,-0.905675,4.116342,-0.649898\H,0,-2.451994,2.625248,-
0.488056\H,0,-1.518373,2.865428,0.98952\C,0,-1.782413,5.292354,-0.2570
58\H,0,0.124315,4.268056,-0.288484\H,0,-0.828812,4.049365,-1.746856\H,
0,-1.394689,6.238119,-0.653379\H,0,-2.805713,5.167815,-0.636638\H,0,-1
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,0.306395,-1.186395\C,0,2.599991,-1.464234,0.313649\C,0,2.913383,0.763
19,-0.133926\C,0,1.947192,1.084344,-2.314684\C,0,3.4433,2.043104,-0.11
843\C,0,2.490125,2.372524,-2.331191\H,0,1.380422,0.708799,-3.165924\C,
0,3.202706,2.849648,-1.23541\H,0,4.050224,2.398104,0.71258\H,0,2.35581
6,3.00463,-3.206387\H,0,3.610212,3.858963,-1.256697\N,0,3.106208,-0.26
4185,0.79423\C,0,4.000425,-0.187907,1.919262\H,0,5.020282,0.07023,1.60
1536\H,0,3.648018,0.565597,2.637472\H,0,4.013423,-1.171204,2.399113\O,
0,2.841122,-2.551465,0.774262\C,0,-1.256997,-3.034707,0.683837\O,0,-2.
253813,-2.292148,0.823091\C,0,-1.353851,-4.471541,1.131493\H,0,-1.8189
72,-5.066202,0.333567\H,0,-0.375564,-4.912705,1.35148\H,0,-2.003273,-4
.540276,2.011074\H,0,0.775419,-3.315226,0.033696\O,0,-0.276564,-1.2883

93,-2.169536\C,0,0.703561,-1.920932,-2.7656\O,0,1.838702,-1.95592,-1.962105\O,0,0.71735,-2.420936,-3.855102\\Version=ES64L-G16RevA.03\State=1-A\HF=-1785.3138884\RMSD=4.431e-09\Dipole=-0.2471048,4.9272113,3.0668449\Quadrupole=9.9136444,-1.8853168,-8.0283276,8.6122117,10.0371399,-12.7646342\PG=C01 [X(C26H38N1O5P1)]\\@

INT5

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C26H38N1O5P1\WEIY\30-Oct-2018\0\\#p m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=THF)\\Title Card Required\\0,1\C,0,-0.1224108895,0.0038411693,0.1003622156\C,0,-0.0253273298,0.076864503,1.4343715298\P,0,3.5861512493,-0.2170716512,-0.0360558515\C,0,3.8050444702,-1.7940181559,-1.0257181898\C,0,4.1247754944,-1.7351094624,-2.5148365368\H,0,2.8766110378,-2.3712886991,-0.886601108\H,0,4.5819838212,-2.3725696177,-0.4975595498\C,0,4.3135500794,-3.1214495614,-3.1172876207\H,0,3.3125172866,-1.2200283361,-3.0539513087\H,0,5.0301773832,-1.1353939432,-2.6991377775\C,0,4.5977595759,-3.0752682389,-4.6091103858\H,0,5.1362153902,-3.634194076,-2.5931330278\H,0,3.4129469471,-3.7264495459,-2.9238042301\H,0,4.7354173941,-4.0777939618,-5.0320042215\H,0,3.7729993897,-2.5947978234,-5.153599084\H,0,5.5082381897,-2.4973010277,-4.8197515499\C,0,3.1269969919,1.0071012653,-1.3660473654\C,0,2.9635829301,2.422523993,-0.8282507355\H,0,2.1634544317,0.6598213733,-1.7790440127\H,0,3.8386964137,0.9938011506,-2.2067345152\C,0,2.4701852273,3.4107814645,-1.8751296391\H,0,2.255908526,2.4166848217,0.0159498201\H,0,3.9229146888,2.7829674831,-0.4166852451\C,0,2.2217667939,4.7890585852,-1.2866324805\H,0,3.1983605747,3.4700391316,-2.7007309003\H,0,1.5349740231,3.0295864523,-2.3167519865\H,0,1.899095776,5.5100364771,-2.0480083373\H,0,1.440950265,4.738617704,-0.5136307716\H,0,3.1297049647,5.1869095266,-0.810195443\C,0,5.3485864144,0.2741112129,0.3407073784\C,0,6.368877286,0.4299088225,-0.777571742\H,0,5.7110680841,-0.4672216144,1.0719628469\H,0,5.2731240828,1.2191574722,0.9053755597\C,0,7.7107516169,0.9469294423,-0.2739455894\H,0,6.5258100184,-0.5385576252,-1.2807737106\H,0,5.9886770384,1.1177597765,-1.5519287271\C,0,8.7365959378,1.0864620221,-1.3857389958\H,0,7.5588125982,1.919218749,0.2221846968\H,0,8.0907705763,0.2678416144,0.5063435088\H,0,9.6970835039,1.4629756228,-1.0134293392\H,0,8.9246073607,0.1196732958,-1.8728656476\H,0,8.3850208668,1.780525619,-2.1616881702\C,0,-0.0965365006,1.2324747211,2.396779679\C,0,1.0775825906,2.1548919977,2.4979006015\C,0,-1.2826203007,2.2012109054,2.1469841379\C,0,0.6051880105,3.4654594836,2.3996488466\C,0,2.4140835964,1.8903235937,2.7187125878\C,0,1.470815541,4.5444311286,2.4648886884\C,0,3.2968035086,2.9700658852,2.8086081136\H,0,2.7714371395,0.8631486731,2.7969422096\C,0,2.8259919567,4.2722471639,2.6696240791\H,0,1.1118398911,5.567293304,2.3677004006\H,0,4.3556452082,2.7913045211,2.9846434807\H,0,3.5261464766,5.1038359798,2.7290534921\N,0,-0.7838177493,3.4777390351,2.2518501315\C,0,-1.5430433383,4.6315896373,1.8414389183\H,0,-1.4802489159,5.4282166464,2.5924242087\H,0,-1.170447

6574,5.003296513,0.8758600615\H,0,-2.5852793827,4.3202797018,1.7304437
067\O,0,-2.4234851818,1.8682178898,1.942969493\C,0,-0.3542140862,1.176
7891848,-0.7428778333\O,0,-0.2951709269,2.3187804775,-0.3048118215\C,0
,-0.7060149376,0.8987283762,-2.1791240831\H,0,-0.7654969901,1.83669559
71,-2.7382574456\H,0,0.0286653205,0.229445779,-2.647454325\H,0,-1.6774
928969,0.3875153117,-2.228426797\H,0,-0.0841949852,-0.9862458286,-0.35
2791049\O,0,0.1112981055,-1.0493390139,2.1774709878\C,0,-0.1182335501,
-0.7657460484,3.5070729051\O,0,-0.3141188638,0.5505103959,3.6471988355
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2a

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C14H11N1O5\WEIY\05-Jun-2018\0\\#p
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9,1.9261063132\C,0,2.2066627462,-0.6293960506,1.2011230374\C,0,2.27305
0877,-0.0859419042,-0.0797788763\C,0,1.1258333806,0.4422354545,-0.6801
037416\C,0,-2.2450020617,0.6352046056,0.9496544539\H,0,0.9661987611,-1
.082586686,2.9253760966\H,0,3.104552033,-1.0496892615,1.651260732\H,0,
3.2175711935,-0.0850931842,-0.6195423921\H,0,1.1580999703,0.8537858947
,-1.6892029828\N,0,-1.4073609828,0.0098856602,1.8411022326\C,0,-1.8169
328942,-0.437292807,3.1490063425\H,0,-1.685486883,-1.5233178743,3.2362
417539\H,0,-1.2358720434,0.0685297403,3.9316751638\H,0,-2.8755465861,-
0.1902948221,3.2697113801\O,0,-3.3988734171,0.9553706877,1.1229109113\
C,0,-1.438679497,0.8298269055,-0.3519959905\C,0,-0.6694762383,-3.13614
66337,0.0879691509\O,0,-1.3847490692,-3.0206917814,1.0020121795\O,0,-2
.0844597017,-1.2698568762,-1.422070292\C,0,-2.0629335238,-0.0551655452
,-1.4600686906\C,0,-2.5653709658,0.8869359287,-2.4271000941\H,0,-3.095
2364293,0.6360433408,-3.3379219458\O,0,0.0748910045,-3.2905818042,-0.7
923369194\C,0,-2.2628063977,2.1321158961,-1.9871306661\O,0,-1.57841464
49,2.1682187367,-0.8234831632\C,0,-2.5553795909,3.4569538479,-2.567970
9464\H,0,-1.6273875457,4.0266168896,-2.703785523\H,0,-3.0652619918,3.3
602437584,-3.5307241801\H,0,-3.1909771874,4.0302968329,-1.8809665166\\
Version=ES64L-G16RevA.03\State=1-A\HF=-970.717971\RMSD=7.470e-09\Dipol
e=1.3113455,1.3685453,0.025662\Quadrupole=-6.3002858,-3.2184002,9.5186
86,-3.6583348,6.8294757,-14.5269342\PG=C01 [X(C14H11N1O5)]\\@

TS4

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C14H11N1O5\WEIY\05-Jun-2018\0\\#p
m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=Dichloromethane)\
\Title Card Required\\0,1\C,0,0.0024041145,-0.0800706647,0.0237077903\
C,0,-0.0728733963,-0.0299806859,1.4252797661\C,0,1.0713165504,0.108729

2865,2.1914963012\C,0,2.2928585451,0.1957445451,1.5155708958\C,0,2.372
849346,0.1453117496,0.1238885096\C,0,1.213507112,0.0044015202,-0.63945
73093\C,0,-2.2589273777,-0.2722994827,0.7801304697\H,0,1.0286730142,0.
1446930311,3.2784649107\H,0,3.2073571564,0.3026671417,2.0967095603\H,0
,3.3418658502,0.2105640477,-0.365557605\H,0,1.2554007639,-0.0447963582
,-1.7277240522\N,0,-1.3965401906,-0.1419015625,1.8479550871\C,0,-1.829
2283498,-0.162272945,3.2236626096\H,0,-1.3799110287,-1.0098204719,3.75
68448965\H,0,-1.5571613693,0.7734305566,3.7287361618\H,0,-2.9173979224
,-0.2709977341,3.2298132214\O,0,-3.4597856018,-0.3725916603,0.80238658
69\C,0,-1.3572593291,-0.2392605947,-0.4567088883\C,0,-1.4204441212,-2.
7647908309,-1.4211619179\O,0,-1.2945620998,-2.2991883553,-0.2716689128
\O,0,-1.7606576728,-1.6165350725,-2.3949693019\C,0,-1.8283180515,-0.44
08414114,-1.8614754248\C,0,-2.2898504088,0.6667826975,-2.5191417186\H,
0,-2.6701828901,0.6329279197,-3.5346422533\O,0,-1.3575874091,-3.824603
9812,-1.9659483159\C,0,-2.2488962408,1.8265696933,-1.7058364932\O,0,-1
.7603556873,1.710614174,-0.5513568733\C,0,-2.7815943019,3.1452846649,-
2.1496125852\H,0,-2.2332053058,3.9597507111,-1.6667251805\H,0,-2.74126
06972,3.2514761629,-3.2389561596\H,0,-3.8333813475,3.2192757023,-1.841
1384938\\Version=ES64L-G16RevA.03\State=1-A\HF=-970.6455038\RMSD=2.907
e-09\Dipole=1.2644644,3.9495885,0.712512\Quadrupole=3.0098324,-16.1691
016,13.1592692,-5.9401427,6.2714871,-14.0000682\PG=C01 [X(C14H11N1O5)]
\\@

INT6

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C14H11N1O5\WEIY\05-Jun-2018\0\\#p
m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=Dichloromethane)\
\Title Card Required\\0,1\C,0,-0.056615424,0.4295725282,0.0326648149\C
,0,-0.111830464,-0.1080419841,1.3221252709\C,0,1.0104088995,-0.6522627
9,1.9261063132\C,0,2.2066627462,-0.6293960506,1.2011230374\C,0,2.27305
0877,-0.0859419042,-0.0797788763\C,0,1.1258333806,0.4422354545,-0.6801
037416\C,0,-2.2450020617,0.6352046056,0.9496544539\H,0,0.9661987611,-1
.082586686,2.9253760966\H,0,3.104552033,-1.0496892615,1.651260732\H,0,
3.2175711935,-0.0850931842,-0.6195423921\H,0,1.1580999703,0.8537858947
,-1.6892029828\N,0,-1.4073609828,0.0098856602,1.8411022326\C,0,-1.8169
328942,-0.437292807,3.1490063425\H,0,-1.685486883,-1.5233178743,3.2362
417539\H,0,-1.2358720434,0.0685297403,3.9316751638\H,0,-2.8755465861,-
0.1902948221,3.2697113801\O,0,-3.3988734171,0.9553706877,1.1229109113\
C,0,-1.438679497,0.8298269055,-0.3519959905\C,0,-0.6694762383,-3.13614
66337,0.0879691509\O,0,-1.3847490692,-3.0206917814,1.0020121795\O,0,-2
.0844597017,-1.2698568762,-1.422070292\C,0,-2.0629335238,-0.0551655452
,-1.4600686906\C,0,-2.5653709658,0.8869359287,-2.4271000941\H,0,-3.095
2364293,0.6360433408,-3.3379219458\O,0,0.0748910045,-3.2905818042,-0.7
923369194\C,0,-2.2628063977,2.1321158961,-1.9871306661\O,0,-1.57841464
49,2.1682187367,-0.8234831632\C,0,-2.5553795909,3.4569538479,-2.567970
9464\H,0,-1.6273875457,4.0266168896,-2.703785523\H,0,-3.0652619918,3.3

602437584,-3.5307241801\H,0,-3.1909771874,4.0302968329,-1.8809665166\\
Version=ES64L-G16RevA.03\State=1-A\HF=-970.717971\RMSD=7.470e-09\Dipol
e=1.3113455,1.3685453,0.025662\Quadrupole=-6.3002858,-3.2184002,9.5186
86,-3.6583348,6.8294757,-14.5269342\PG=C01 [X(C14H11N1O5)]\\@

3a

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C13H11N1O3\WEIY\05-Jun-2018\0\\#p
m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=Dichloromethane)\
\Title Card Required\\0,1\C,0,-0.166368785,-0.7601959016,0.6598647138\
C,0,-1.1862223904,0.1250239209,1.0195846773\C,0,-2.4343760392,-0.32946
91081,1.4110238677\C,0,-2.6349657966,-1.7134200343,1.44047709\C,0,-1.6
235477455,-2.6037291047,1.0886508397\C,0,-0.3733388258,-2.1245818408,0
.6837821325\C,0,0.595401513,1.4929937806,0.5683091875\H,0,-3.231290847
9,0.3587233424,1.6878217631\H,0,-3.6061748169,-2.0996126209,1.74571341
76\H,0,-1.809119424,-3.675317043,1.1222505203\H,0,0.424831258,-2.80938
23773,0.3959364413\N,0,-0.7287498378,1.4475770715,0.9358793199\C,0,-1.
5016122056,2.6114605949,1.2890369344\H,0,-2.3832640763,2.6984793105,0.
6413427092\H,0,-1.8266458674,2.5600355521,2.3370119429\H,0,-0.86478082
79,3.4902208791,1.1522745765\O,0,1.3042573944,2.4712915657,0.498104043
\C,0,1.006060128,0.0480345656,0.222805797\O,0,0.4665800063,0.162893927
5,-2.1597981867\C,0,1.2990514056,-0.0354118305,-1.300025118\C,0,2.7032
517769,-0.3618377864,-1.3708898584\H,0,3.2774571835,-0.4821395956,-2.2
814909923\C,0,3.1694162616,-0.4702413268,-0.1046861725\O,0,2.238851155
,-0.2838291661,0.8575060901\C,0,4.5250106452,-0.7585368818,0.403487437
\H,0,4.5055386507,-1.6336329885,1.065384285\H,0,5.222276472,-0.9423606
094,-0.4188947507\H,0,4.8866026358,0.0902637051,0.998030293\\Version=E
S64L-G16RevA.03\State=1-A\HF=-782.1518763\RMSD=5.982e-09\Dipole=0.1192
394,-1.1938843,1.4478248\Quadrupole=15.7568309,-2.9571305,-12.7997004,
-9.0119482,-7.6820927,2.804658\PG=C01 [X(C13H11N1O3)]\\@

CO_2

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C1O2\WEIY\06-Jun-2018\0\\#p m06/6-
311+g(d,p) scrf=(iefpcm,smd,solvent=Dichloromethane)\\Title Card Requi
red\\0,1\C,0,-0.22388059,-1.30936226,0.\O,0,0.9403027785,-1.30936226,0
.\O,0,-1.3880639585,-1.30936226,0.\\Version=ES64L-G16RevA.03\State=1-S
GG\HF=-188.5587642\RMSD=6.072e-09\Dipole=0.,0.,0.\Quadrupole=-2.609253
,1.3046265,1.3046265,0.,0.,0.\PG=D*H [O(C1),C*(O1.O1)]\\@

(*S*)-**TS3**

1\1\GINC-OM103\SP\RM06\6-311+G(d,p)\C48H54F6N3O8P1S1Si1\WEIY\26-Feb-20
19\0\\#p m06/6-311+g(d,p) geom=check scrf=(iefpcm,smd,solvent=THF)\\Ti
tle Card Required\\0,1\C,0,1.8053801171,-3.1273340928,0.4008783502\C,0
,1.6958076772,-2.0306697181,-0.4863125655\P,0,1.4109309048,-0.35767595
38,0.3562548515\C,0,1.2761913792,1.1028341548,-0.7874656479\C,0,0.5435
439871,1.2414687445,-2.1218953336\H,0,2.2993474233,1.4558896604,-0.950

8069425\H,0,0.8361179279,1.8560919956,-0.1176362555\C,0,0.8753462196,2
.6410424278,-2.7056933912\H,0,0.9908643168,0.5553552971,-2.8511764421\
C,0,-0.0643039411,3.0082550546,-3.8351503701\H,0,1.8973164867,2.529884
3356,-3.1272899724\H,0,0.2901965053,3.9080444715,-4.3550711106\H,0,-0.
1151679797,2.194814086,-4.5706281334\H,0,-1.0748837445,3.1954395552,-3
.4526637662\C,0,2.5691694874,-2.1138694771,-1.7770677011\C,0,3.9378690
762,-1.4974494669,-1.6848318571\C,0,2.9137453612,-3.6095246123,-2.0345
511103\C,0,4.870999729,-2.5368136803,-1.5677031294\C,0,4.3767633236,-0
.1891085165,-1.7204291297\C,0,6.220405488,-2.2906570453,-1.3821773188\
C,0,5.7359983856,0.0832197064,-1.5437500468\H,0,3.6804187022,0.6237649
838,-1.9127444784\C,0,6.6381853705,-0.9574793499,-1.3566536387\H,0,6.9
363136825,-3.1042281335,-1.2826906163\H,0,6.0854308557,1.1135487849,-1
.5630461833\H,0,7.6955569261,-0.7368426592,-1.2152738975\N,0,4.2473944
76,-3.7761179615,-1.7360830813\C,0,4.9387765566,-5.0322560614,-1.88166
14426\H,0,5.7069311329,-4.9660146985,-2.663879741\H,0,5.4126539697,-5.
3276979064,-0.9372591115\H,0,4.1981150989,-5.784587358,-2.1673247606\O
,0,2.1481470657,-4.4534787635,-2.4308262751\C,0,1.6348458593,-3.037219
6893,1.8022666479\O,0,1.5455718632,-1.951379431,2.4054011339\C,0,1.575
0282145,-4.316889918,2.5984022101\H,0,0.529124133,-4.5115451405,2.8728
171796\H,0,1.9495210529,-5.1861921701,2.0462802321\H,0,2.1356872433,-4
.197829094,3.5321759358\H,0,1.9070010325,-4.115968688,-0.0387077021\O,
0,0.224390777,-2.0226323347,-1.3554133711\C,0,0.4676779928,-1.79436160
59,-2.6113576888\O,0,1.8044952902,-1.6563834863,-2.8700524849\O,0,-0.3
502157954,-1.6082885255,-3.4849487928\C,0,-0.1745107543,-0.3107415568,
1.2460577005\C,0,-0.4660749416,0.8452699535,1.9647379135\C,0,-1.092938
996,-1.3629135725,1.2339487549\C,0,-1.6586126099,0.9765376923,2.673376
5501\H,0,0.2189542499,1.6942454859,1.9744156449\C,0,-2.2854571862,-1.2
728784617,1.9417129625\H,0,-0.8850304965,-2.2676820616,0.6663745454\C,
0,-2.5510803237,-0.0973526812,2.6563952579\C,0,-3.2785420676,-2.395676
79,1.9279652744\H,0,-3.195419373,-3.018457627,2.830478682\H,0,-4.30764
9221,-2.0168196175,1.8937479795\H,0,-3.1223267417,-3.0519894729,1.0632
569774\C,0,-1.9985517074,2.2543402045,3.3764179911\H,0,-3.0628656034,2
.4939223048,3.261987992\H,0,-1.7898403459,2.2023802346,4.4547889945\H,
0,-1.413151659,3.0869505315,2.9674399273\O,0,-3.762826656,0.0272063275
,3.2880223184\C,0,-3.7473875633,-0.311103723,4.6591429113\H,0,-4.76309
08099,-0.1529388332,5.031613792\H,0,-3.4617689871,-1.3637043838,4.8098
960116\H,0,-3.0500184082,0.3247172026,5.2256463673\C,0,2.8975525623,0.
198418462,1.2617666413\C,0,3.0737283254,1.5459888119,1.5823142913\C,0,
3.9407247679,-0.6958904283,1.5108630741\C,0,4.2694914379,2.0120609326,
2.1300950476\H,0,2.2880306385,2.2813237383,1.4050178225\C,0,5.15484772
07,-0.2643965863,2.0272728012\H,0,3.8167902939,-1.7502935129,1.2703769
09\C,0,5.3053578895,1.0955969972,2.3222768736\C,0,6.2790083799,-1.2214
693813,2.2787777141\H,0,7.1610555499,-0.9828908104,1.6677098767\H,0,6.
6029961702,-1.1890229829,3.3263592898\H,0,5.9781030371,-2.247608547,2.
0388659265\C,0,4.4329173568,3.4563087277,2.4966435071\H,0,5.1655735378

,3.5756017356,3.3022252943\H,0,4.7780150076,4.0597752321,1.6440695623\
H,0,3.4802221845,3.8871642721,2.8273184564\O,0,6.5017164768,1.51836907
39,2.8477261407\C,0,7.3820671373,2.0517278759,1.8818491734\H,0,6.96690
11119,2.9549978044,1.4078586596\H,0,8.3089448649,2.3141168286,2.400244
7936\H,0,7.6042031981,1.314648591,1.093209755\N,0,-0.8573305138,0.8439
594278,-2.1139164486\C,0,-1.8794349672,1.2318392324,-1.3054124045\H,0,
-1.0195663618,0.0158255475,-2.6880712819\N,0,-2.8456238837,0.249958715
1,-1.26935597\H,0,-2.5617597922,-0.6232034168,-1.7093245993\C,0,-4.071
7054938,0.1341552229,-0.6015307532\C,0,-4.834708509,-0.9907939223,-0.9
204423733\C,0,-4.532970623,1.0029556846,0.3946788898\C,0,-6.0244145663
,-1.2537594268,-0.2527495285\H,0,-4.4916154374,-1.6835571663,-1.690152
0783\C,0,-5.7224539157,0.7214913859,1.0475049574\H,0,-3.9445244287,1.8
727765816,0.6641784507\C,0,-6.4841231918,-0.4018051764,0.73911284\H,0,
-7.4086159889,-0.6097044595,1.2719789256\C,0,-6.2233669421,1.621159302
6,2.1380322399\C,0,-6.7348790911,-2.5325560228,-0.5716656363\F,0,-7.93
90789902,-2.602836722,-0.0006652562\F,0,-6.0233563929,-3.5865496788,-0
.1430484431\F,0,-6.8986468037,-2.6912872171,-1.89028351\F,0,-7.3913387
115,2.182290028,1.7933236508\F,0,-5.3751710265,2.6112390878,2.42753595
97\F,0,-6.452119331,0.9386858919,3.2682882533\O,0,0.9403759497,3.58479
78441,-1.6795837577\Si,0,0.8910563819,5.2472578851,-1.6614729069\C,0,-
0.7483035168,5.9664018622,-2.2141486025\H,0,-1.5819598284,5.466237648,
-1.7045358139\H,0,-0.7864575401,7.0349218614,-1.9596483753\H,0,-0.9128
602822,5.8790249157,-3.2951517304\C,0,2.279776963,5.9236397045,-2.7333
436644\H,0,3.2568652653,5.5447784179,-2.4061809102\H,0,2.1507094803,5.
6442180762,-3.7880502165\H,0,2.3151075466,7.020369418,-2.6900293983\C,
0,1.1776454486,5.618419079,0.151238273\H,0,2.1721567372,5.2782853017,0
.4698561969\H,0,1.094815187,6.6879124906,0.3819100023\H,0,0.4287035237
,5.0827201024,0.7517547457\S,0,-1.947269093,2.7083169537,-0.5216858342
\\Version=ES64L-G16RevA.03\State=1-A\HF=-4254.7949394\RMSD=4.006e-09\D
ipole=5.8929919,0.8679889,0.2783531\Quadrupole=18.2256915,0.3518175,-1
8.5775091,-1.5829142,-13.5003715,-11.9450353\PG=C01 [X(C48H54F6N3O8P1S
1Si1)]\\@

(*R*)-**TS3**

1\1\GINC-LOCALHOST\FTS\RM06\6-31G(d)\C48H54F6N3O8P1S1Si1\YIN\18-Feb-20
19\0\\#p opt=(calcfc,ts,noeigen) 6-31g(d) m06\\Title Card Required\\0,
1\C,0.0054677296,0.0025915745,0.0041967927\C,0.0034670532,0.0004537655
,1.4044765895\P,1.6732067945,-0.0013898709,2.2602207453\C,1.7849796978
,-0.3740185665,4.0756027751\C,1.1278136156,-1.4192141711,5.0136131051\
H,1.6317173902,0.5912802281,4.5773976476\H,2.8681423193,-0.5748612086,
4.1188770293\C,2.0714858431,-1.5903521848,6.2365298822\H,0.2546155351,
-0.9174189187,5.4360809045\C,1.6532016651,-2.7555696098,7.1097957727\H
,1.9340316405,-0.6558404784,6.8199516695\H,2.2107271119,-2.7436181378,
8.0559241179\H,0.5841639845,-2.6925584994,7.3503035446\H,1.8413772887,
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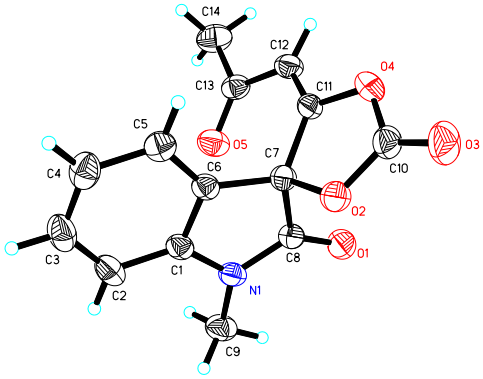
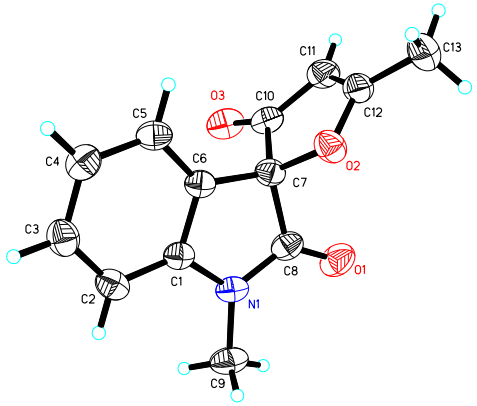
Si1)]\\@

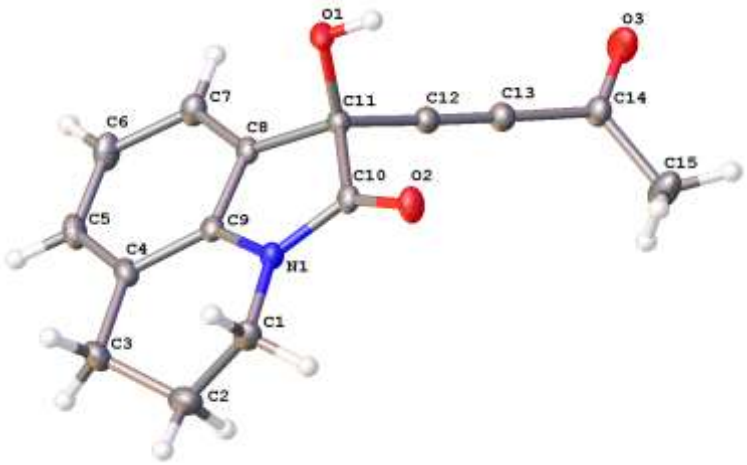
9. X-ray data of 2a, 3a and (*R*)-1n



The crystal data of **2a** have been deposited in CCDC with number 1524876. Empirical Formula: $C_{14}H_{11}NO_5$; Formula Weight: 273.24; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.0859(16) Å, alpha = 90 deg. b = 9.2256(13) Å, beta = 101.245(3) deg. c = 12.6525(18) Å, gamma = 90 deg.; V = 1269.2(3) $Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.430 g/cm^3; F_{000} = 568; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0416, 0.1097.



The crystal data of **3a** have been deposited in CCDC with number 1519502. Empirical Formula: $C_{13}H_{11}NO_3$; Formula Weight: 229.23; Crystal Color, Habit: colorless; Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 9.4606(16) Å, alpha = 90 deg. b = 8.7844(15) Å, beta = 91.450(4) deg. c = 13.698(2) Å, gamma = 90 deg.; V = 1138.0(3) $Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.338 g/cm^3; F_{000} = 480; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0434, 0.1065.



The crystal data of **(*R*)-1n** have been deposited in CCDC with number 1856499. Empirical Formula: $C_{15}H_{13}NO_3$; Formula Weight: 255.26; Crystal Color, Habit: colorless; Crystal Dimensions: 0.12 x 0.1 x 0.08 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 5.27760(10) Å, alpha = 90 deg. b = 10.8907(2) Å, beta = 90 deg. c = 22.1326(4) Å, gamma = 90 deg.; V = 1272.11(4) $Å^3$; Space group: $P2_12_12_1$; Z = 4; D_{calc} = 1.333 g/cm^3; F_{000} = 536; Diffractometer: Rigaku AFC7R; Residuals: R; R_w: 0.0327, 0.0874.

10. References:

1. Ando, K.; Houk, K. N.; Busch, J.; Menasse, A.; Sequin, U., Experimental and computational studies of nucleophilic additions of metal hydrides and organometallics to hindered cyclohexanones. *J. Org. Chem.* **1998**, *63* (6), 1761-1766.

2. Mekonnen, A.; Westerlund, A.; Havelkova, M.; Descomps, A.; Carlson, R., Synthesis of 1-Bromo-3-butyn-2-one and 1,3-Dibromo-3-buten-2-one. *Synth. Commun.* **2009**, *39* (14), 2472-2480.

3. Goto, M.; Konishi, T.; Kawaguchi, S.; Yamada, M.; Nagata, T.; Yamano, M., Process Research on the Asymmetric Hydrogenation of a Benzophenone for Developing the Manufacturing Process of the Squalene Synthase Inhibitor TAK-475. *Org. Process Res. Dev.* **2011**, *15* (5), 1178-1184.

4. Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, S.; Varsolona, R.; Wei, X.; Senanayake, C. H., A Superior Method for the Reduction of Secondary Phosphine Oxides. *Org. Lett.* **2005**, *7* (19), 4277-4280.

5. Isenegger, P. G.; Bächle, F.; Pfaltz, A., Asymmetric Morita–Baylis–Hillman Reaction: Catalyst Development and Mechanistic Insights Based on Mass Spectrometric Back-Reaction Screening. *Chem. Eur. J.* **2016**, *22* (49), 17595-17599.

6. Albert, B. J.; Sivaramakrishnan, A.; Naka, T.; Czaicki, N. L.; Koide, K., Total Syntheses, Fragmentation Studies, and Antitumor/Antiproliferative Activities of FR901464 and Its Low Picomolar Analogue. *J. Am. Chem. Soc.* **2007**, *129* (9), 2648-2659.