Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Asymmetric Syntheses of Spiro[benzofuro-cyclopenta[1,2-b]indole-indoline] Scaffolds *via* Consecutive Cyclization

Heng Zhang, Xu-Kai Guan, Dong-Yang Sun, Guo-Feng Liu, Ji-Gang Gao, Guang-Liang Zhang, Suo-Qin Zhang*

College of Chemistry, Jilin University, 2699 Qianjin Street, Changchun 130012, China.

Fax: (+86)-431-8515-5252;
phone: (+86)-431-8515-5252;
e-mail: suoqin@jlu.edu.cn

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General Information

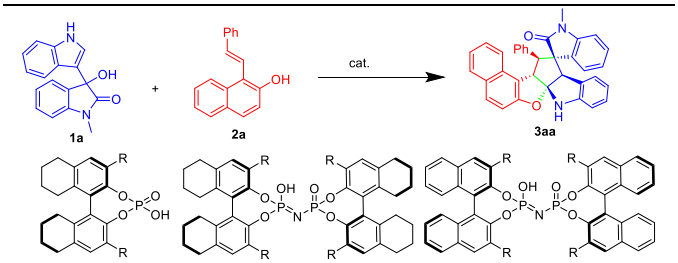
All reagents were used without purification. All solvents were purified and dried according to standard methods. The reaction products were purified by flash column chromatography on 200-300 mesh silica gel. The melting point was recorded on a melting point apparatus (MPA100, Stanford Research Systems, Inc.). Optical rotations were measured with a Jasco-P-2000 digital polarimeter at 20 or 25 ℃ and concentrations (c) are given in g ×(100 mL)$^{-1}$. ^{1}H and ^{13}C NMR spectra were recorded with Bruker 400 MHz spectrometers (400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR); chemical shifts (δ) are given in ppm. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. Analytical HPLC was recorded on a HPLC machine equipped with Elite P1201 series or Ichrom 5100 series quaternary pump with a UV diode array detector. Enantiomeric excess values were measured by analytical HPLC with Daicel ChiralPak AD-H column.

General Procedure for Enantioselective Cyclization

In a 10 mL tube, a mixture of **1** (0.12 mmol), BINOL-type imidodip-hosphoric acid **6b** (0.005 mmol), 4Å molecular sieves (50 mg) and chloroform (2 mL) was stirred at 20 ^{o}C for 10 min. Then (*E*)-1-styrylnaphthols **2** (0.1 mmol) was added. After the reaction completed, the mixture was purified by silicagel chromatography (petroleumether/ethyl acetate = 10:1) directly to afford the product **3**. (R_f=0.4 in petroleumether/ ethyl acetate=10:1).

Table S1. Optimization of the reaction conditions for the consecutive cyclization

Table S1. Screening of catalysts and optimization of the reaction conditions for the consecutive cyclization.[a]



Entry	Solvent	Catalyst[e] [mol %]	Additive	Yield[b] [%]	ee[c] [%]
1	Toluene	**4a**(5)	None	80	75
2	Toluene	**4b**(5)	None	81	79
3	Toluene	**4c**(5)	None	82	15
4	Toluene	**4d**(5)	None	81	63
5	Toluene	**5a**(5)	None	66	87
6	Toluene	**5b**(5)	None	68	80
7	Toluene	**5c**(5)	None	72	67
8	Toluene	**5d**(5)	None	67	47
9	Toluene	**6a**(5)	None	80	87
10	Toluene	**6b**(5)	None	82	91
11	Toluene	**6c**(5)	None	79	79
12	DCE	**6b**(5)	None	81	93
13	CH_2Cl_2	**6b**(5)	None	86	93
14	$CHCl_3$	**6b**(5)	None	88	97
15	THF	**6b**(5)	None	N.R.	-
16	$CHCl_3$	**6b**(5)	3Å MS	75	98
17	$CHCl_3$	**6b**(5)	4Å MS	92	99
18	$CHCl_3$	**6b**(5)	5Å MS	78	98
19[d]	$CHCl_3$	**6b**(2)	4Å MS	90	98

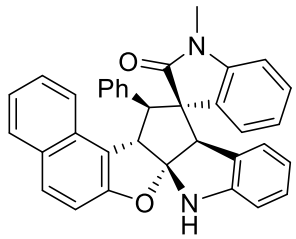
[a]Reaction condition: **1a** (0.12 mmol), **2a** (0.1 mmol), catalyst (**4**, **5** or **6**) in solvent (2 mL), 20 °C, the amount of additive was 50 mg, reaction time was 24 h. [b]Isolated yields. [c]ee value was determined by HPLC analysis on a Chiralcel AD-H column, and the d.r. was determined by ^{1}H NMR of isolated product, d.r. > 19:1. [d]the reaction time was extended to 48 h. [e]BINOL is behalf of 1,1'-Bi-2-naphthol skeleton.

After product **3aa** structure was confirmed, various phosphoric acids were used to attempt to catalyze this reaction (Table 1). When H_8-BINOL-type CPAs were used to catalyze the reaction, moderate yield (81% yield) and ee values (79% ee) were obtained (Entry 2, Table 1). Subsequently H_8-BINOL-type imidodiphosphoric acids were screened, 1-naphthyl substituted H_8-BINOL imidodiphosphoric acid catalyst (**5a**) gave the 87% ee value and 66% yield (Entry 5, Table 1). The ee value increased obviously

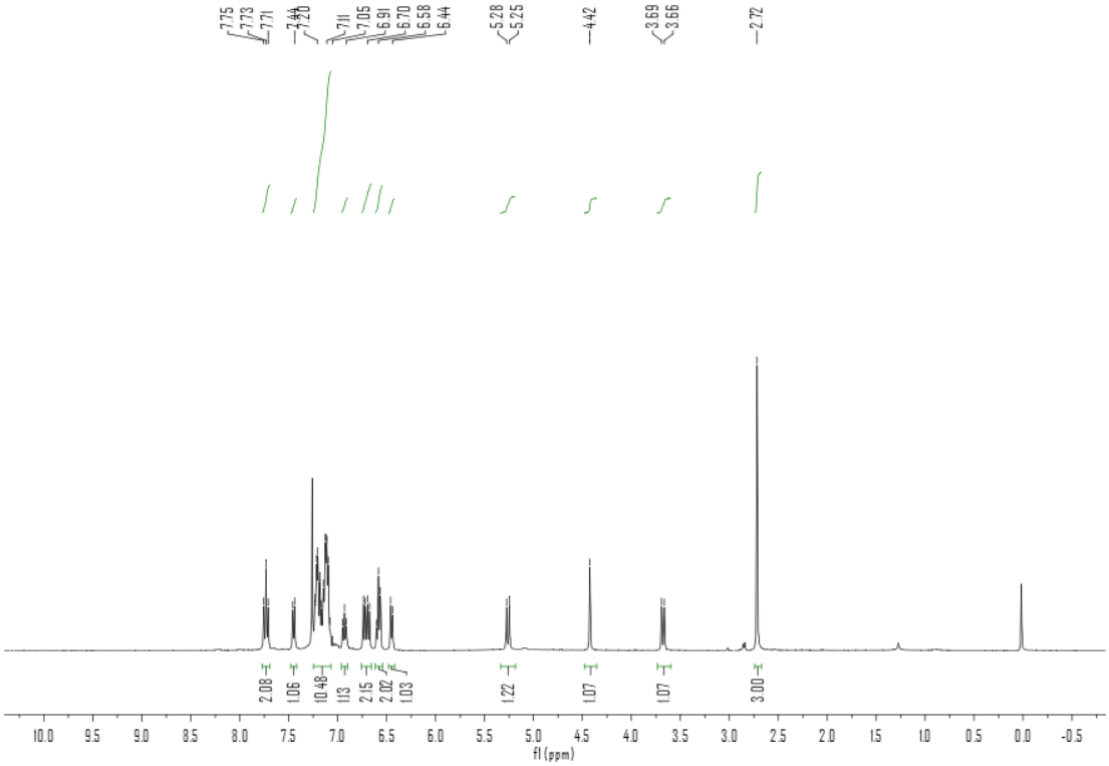
owing to stronger chiral control ability and the yield decreased because of weaker acidity compared with CPAs. Thus, BINOL-type imidodi-phosphoric acids possessing outstanding chiral control ability and stronger acidity meanwhile led to excellent results as expected. On this occasion, 2-naphthyl group substituted BINOL imidodiphosphoric acid catalyst (**6b**) afforded **3aa** with excellent enantioselectivity (91% ee), diastereoselectivity (d.r. > 19:1) and yield (82%) at 20 °C (Entry 10, Table 1). When the solvents were screened, alkyl halide solvent provided with better outcome than toluene in term of ee values (Entry 12-14, Table 1) and the reaction couldn't occur in THF (Entry 15, Table 1). The solvent $CHCl_3$ gave the best result (97% ee, 88% yield, Entry 14, Table 1). When 50 mg 4Å molecular sieves were added into the reaction, the yield and ee value (99% ee, 92% yield, Entry 17, Table 1) have increased slightly at the same time. When attempted to reduce the catalyst loading to 2 mol%, the reaction could still go on smoothly and there were no significant changes in yield and ee value despite prolonged reaction time (48 h, 98% ee, 90% yield, Entry 19, Table 1). Thus, the optimal reaction condition has been established as catalyst **6b** (5 mol %), **1a** (0.12 mmol), **2a** (0.10 mmol), 4Å molecular sieves (50 mg) in $CHCl_3$ (2 mL) at 20 °C.

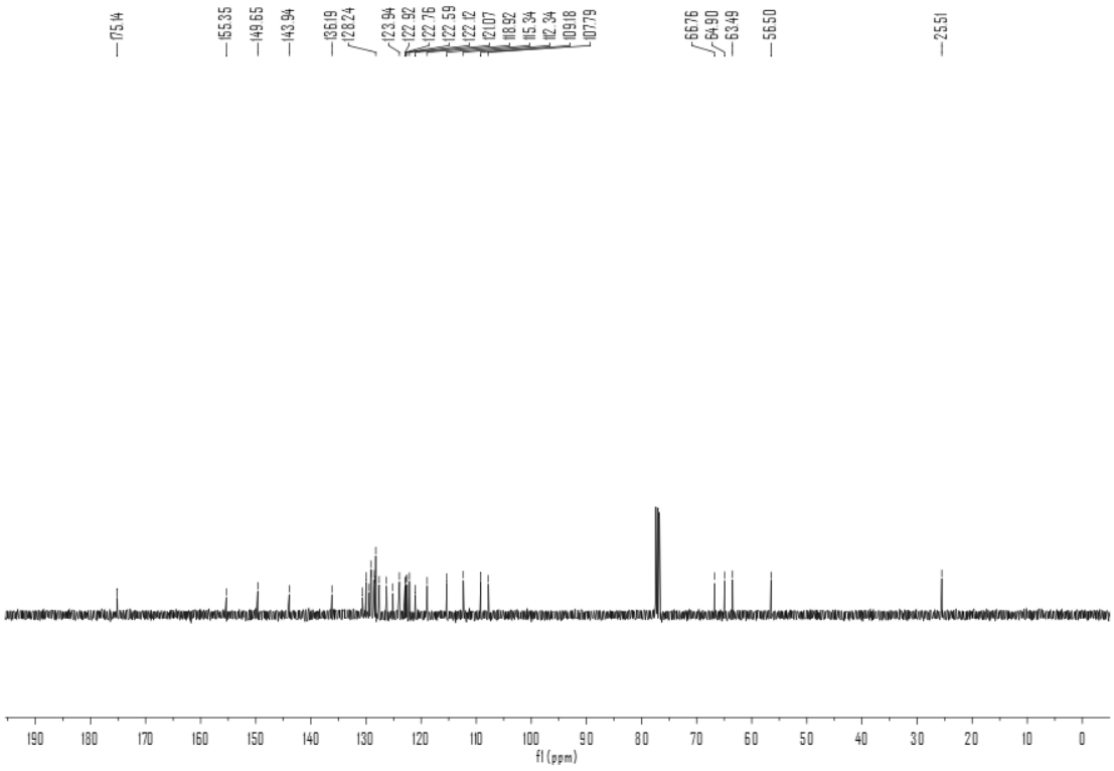
Characterization data for compounds 3aa-3am.

3aa:



(*3R,6c'S,7'S,8a'R,13a'R*)-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 198 - 200 ℃, 46.6 mg, 92% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +298.7 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.9 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.05 (m, 10H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.71 (dd, *J* = 16.7, 8.2 Hz, 2H), 6.62 – 6.54 (m, 2H), 6.45 (d, *J* = 7.3 Hz, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 4.42 (s, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 155.3, 149.6, 143.9, 136.1, 130.6, 129.9, 129.4, 129.1, 129.0, 128.4, 128.4, 128.2, 127.6, 126.2, 125.1, 123.9, 122.9, 122.7, 122.5, 122.1, 121.0, 118.9, 115.3, 112.3, 109.1, 107.7, 66.7, 64.9, 63.4, 56.5, 25.5. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 20.251 min, t_{minor} = 9.036 min. HRMS (ESI): calcd for $C_{35}H_{26}N_2O_2$ $[M + H]^+$, 507.2067; found, 507.2065.

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143.94
136.19
128.24
123.94
122.92
122.76
122.59
122.12
121.07
118.92
115.34
112.34
109.18
107.79
66.76
64.90
63.49
56.50
25.51
190
180
170
160
150
140
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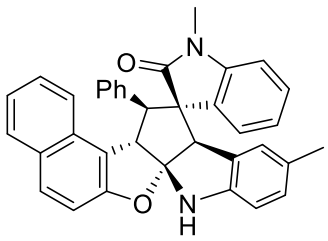
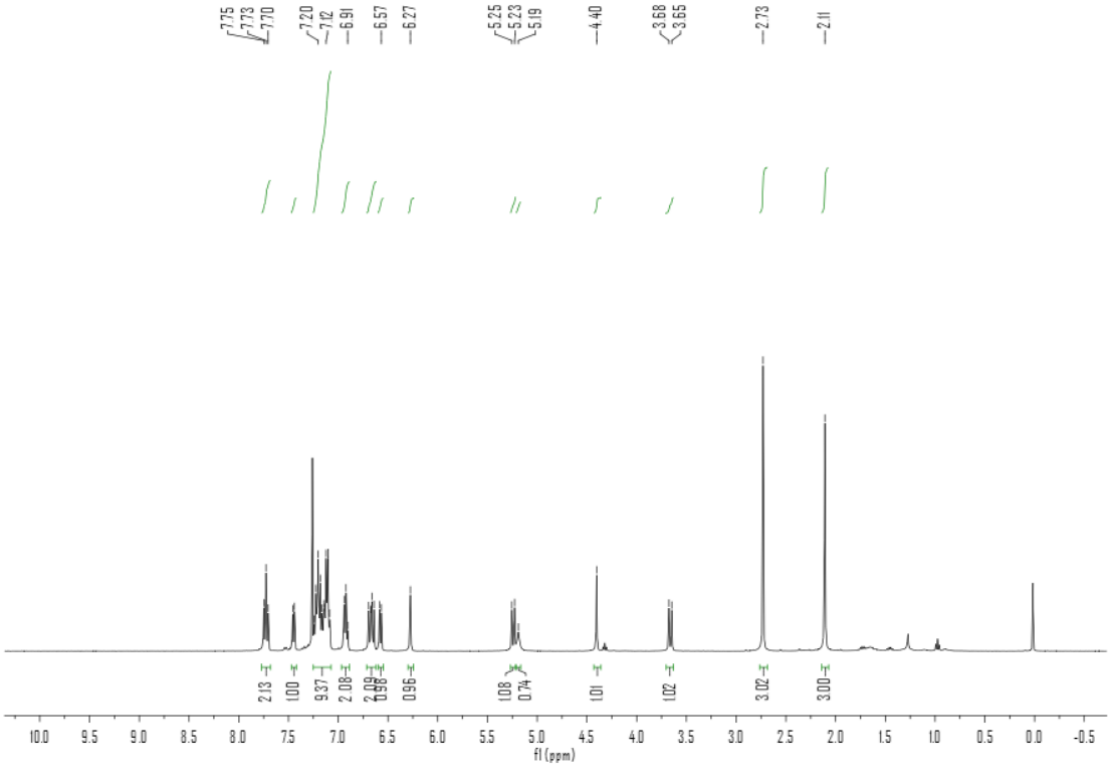
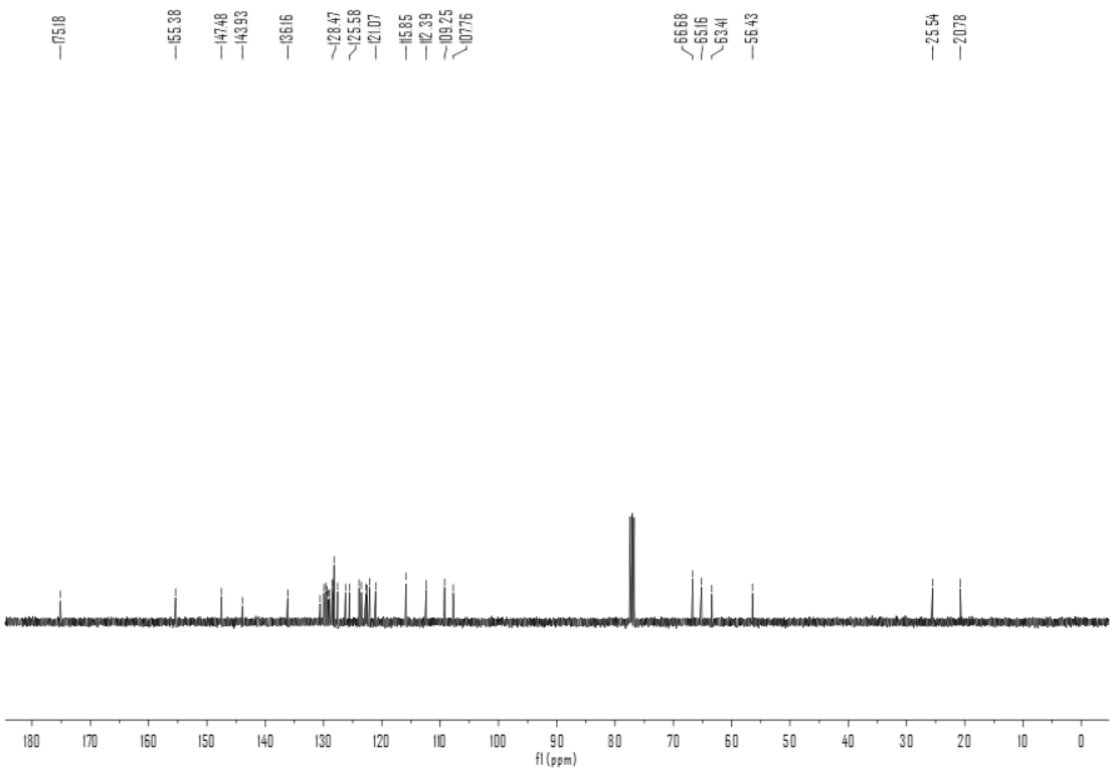
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ba:



(*3R,6c'S,7'S,8a'R,13a'R*)-1,10'-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 186 - 188 ℃, 47.0 mg, 90% yield, 95% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +276.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.07 (m, 9H), 6.92 (t, *J* = 7.1 Hz, 2H), 6.71 – 6.63 (m, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.27 (s, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 5.19 (s, 1H), 4.40 (s, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.73 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 155.3, 147.4, 143.9, 136.1, 130.6, 129.9, 129.5, 129.4, 129.1, 128.9, 128.4, 128.4, 128.3, 128.2, 127.6, 126.2, 125.5, 123.9, 123.5, 122.7, 122.5, 122.0, 121.0, 115.8, 112.3, 109.2, 107.7, 66.6, 65.1, 63.4, 56.4, 25.5, 20.7. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 18.243 min, t_{minor} = 8.745 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2230.

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143.93
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128.47
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121.07
115.85
112.39
109.25
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65.16
63.41
56.43
25.54
21.78
180
170
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80
70
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50
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30
20
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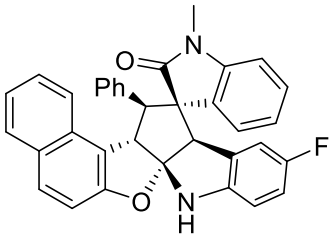
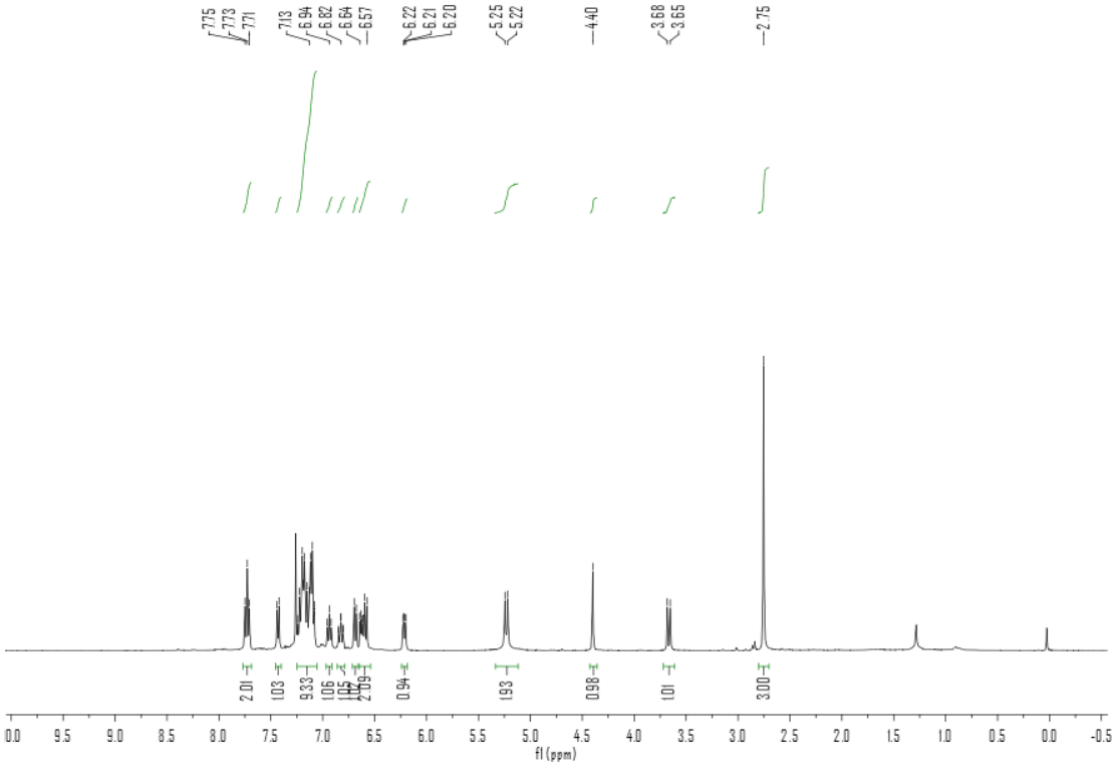
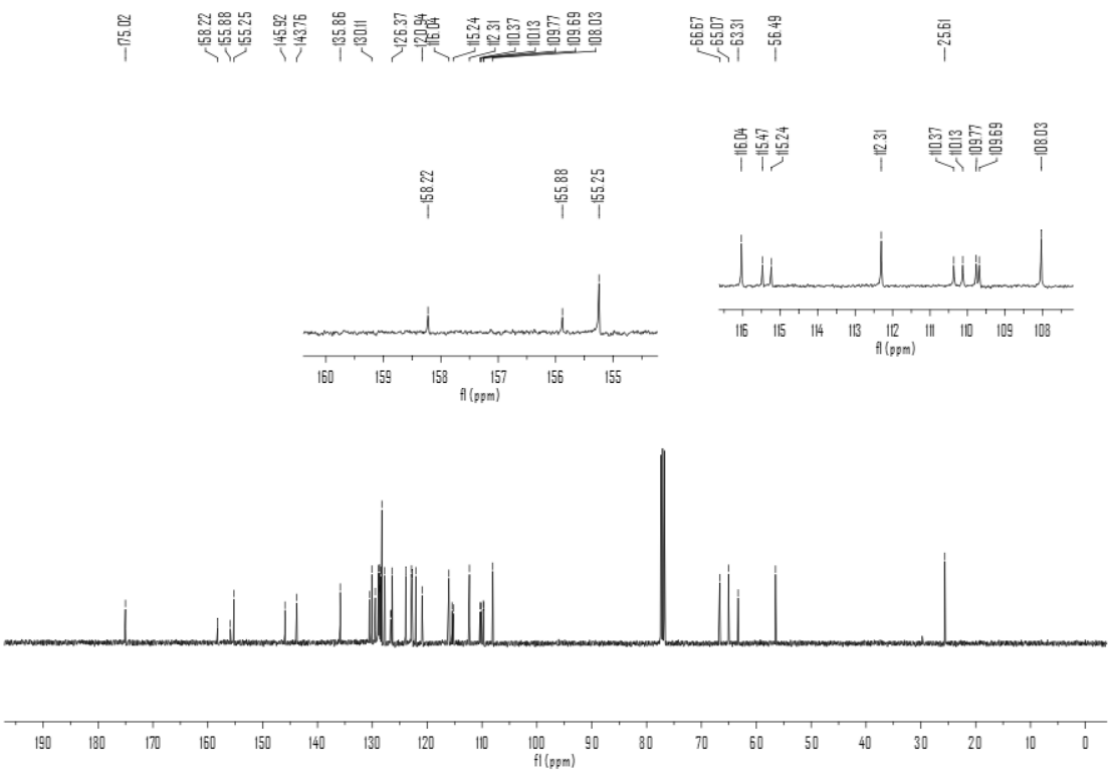
f1 (ppm)

3ca:



(*3R,6c'S,7'S,8a'R,13a'R*)-10'-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 169 - 170 ℃, 45.2 mg, 86% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +302.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.06 (m, 9H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.86 – 6.78 (m, 1H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.65 – 6.54 (m, 2H), 6.21 (dd, *J* = 8.0, 1.9 Hz, 1H), 5.23 (d, *J* = 11.1 Hz, 2H), 4.40 (s, 1H), 3.67 (d, *J* = 11.2 Hz, 1H), 2.75 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 157.0 (d, *J* = 235 Hz), 155.2, 145.9, 143.7, 135.8, 130.5, 130.1, 129.4, 128.9, 128.7, 128.6, 128.4, 128.2, 127.7, 126.6 (d, *J* = 8 Hz), 126.3, 123.8, 122.8 (d, *J* = 10 Hz), 122.0, 120.9, 116.0, 115.3 (d, *J* = 23 Hz), 112.3, 110.3 (d, *J* = 24 Hz), 109.7 (d, *J* = 7 Hz), 108.0, 66.6, 65.0, 63.3, 56.5, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 31.778 min, t_{minor} = 10.131 min. HRMS (ESI): calcd for $C_{35}H_{25}FN_2O_2$ $[M + H]^+$, 525.1973; found, 525.1971.

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63.31
56.49
25.61
f1 (ppm)

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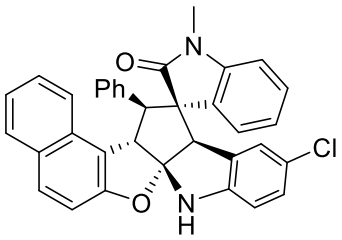
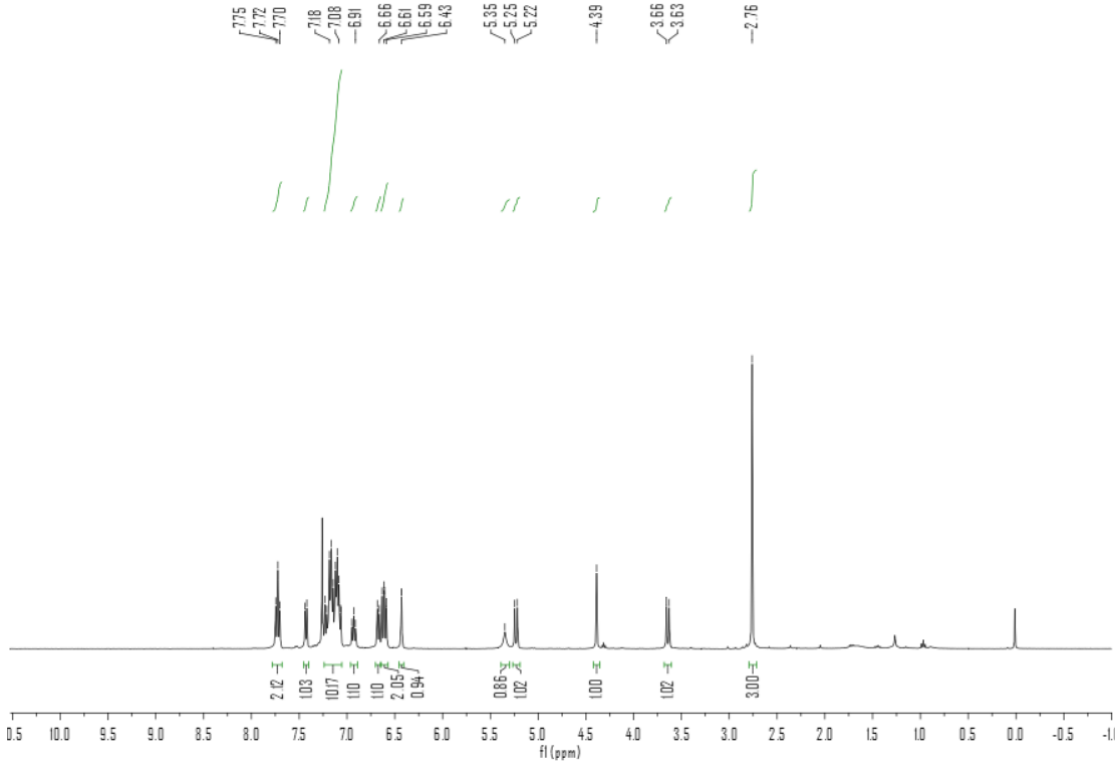
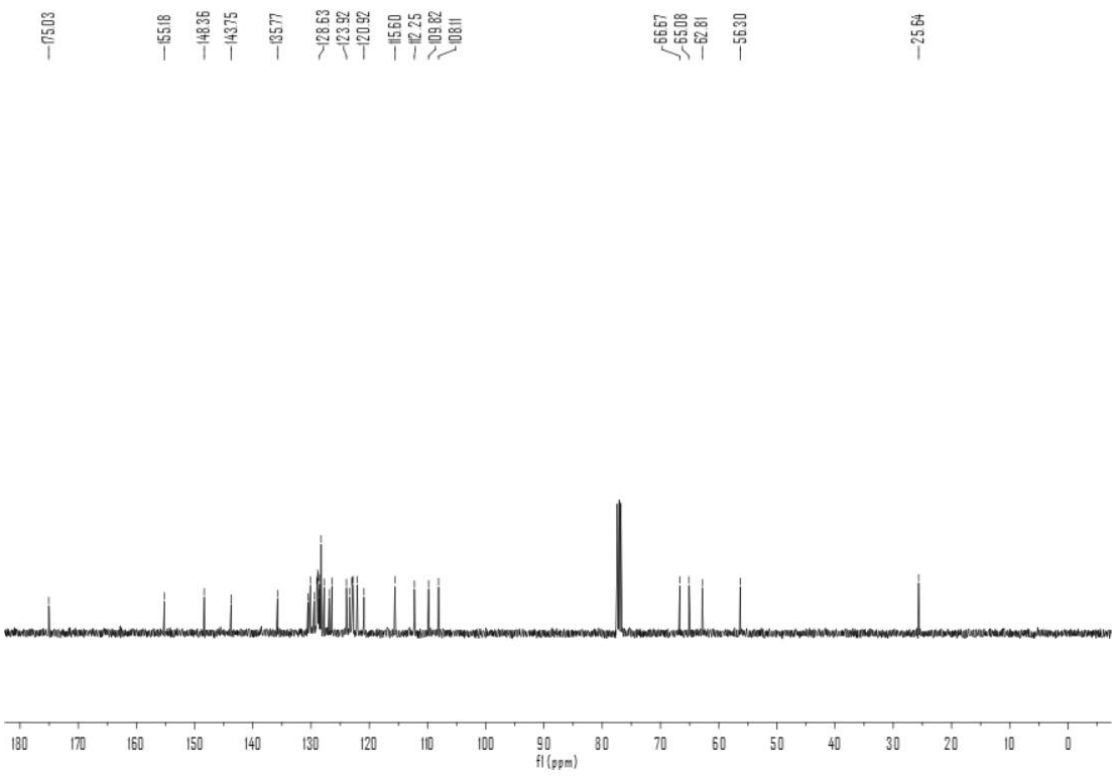


((*3R,6c'S,7'S,8a'R,13a'R)*-10'-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 188 - 190℃, 46.0 mg, 85% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +274.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 8.7 Hz, 2H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.05 (m, 10H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 6.61 (dd, *J* = 9.9, 8.4 Hz, 2H), 6.43 (d, *J* = 1.4 Hz, 1H), 5.35 (s, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.39 (s, 1H), 3.64 (d, *J* = 11.2 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 155.1, 148.3, 143.7, 135.7, 130.5, 130.1, 129.4, 129.0, 128.8, 128.8, 128.6, 128.4, 128.2, 127.7, 126.9, 126.4, 123.9, 123.3, 123.0, 122.9, 122.8, 122.0, 120.9, 115.6, 112.2, 109.8, 108.1, 66.6, 65.0, 62.8, 56.3, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 39.671 min, t_{minor} = 8.362 min. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1680.

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155.18
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143.75
135.77
128.63
123.92
120.92
115.60
112.25
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65.08
62.81
56.30
25.64
180
170
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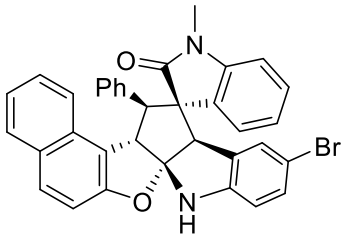
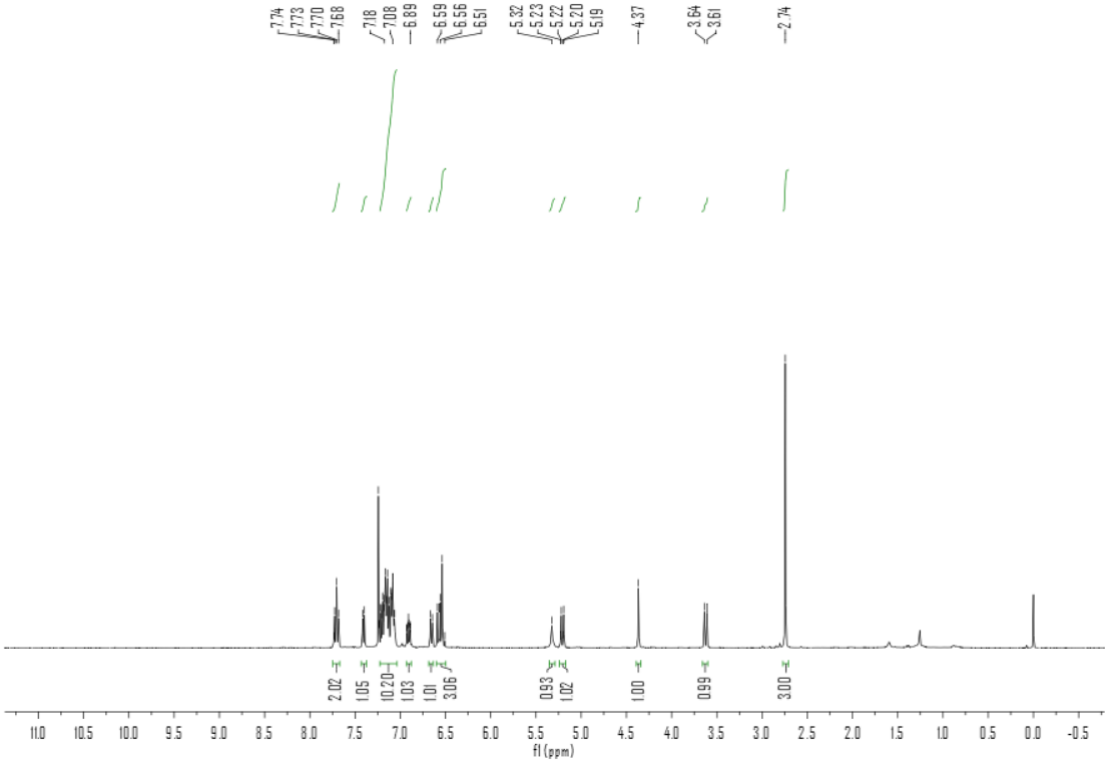
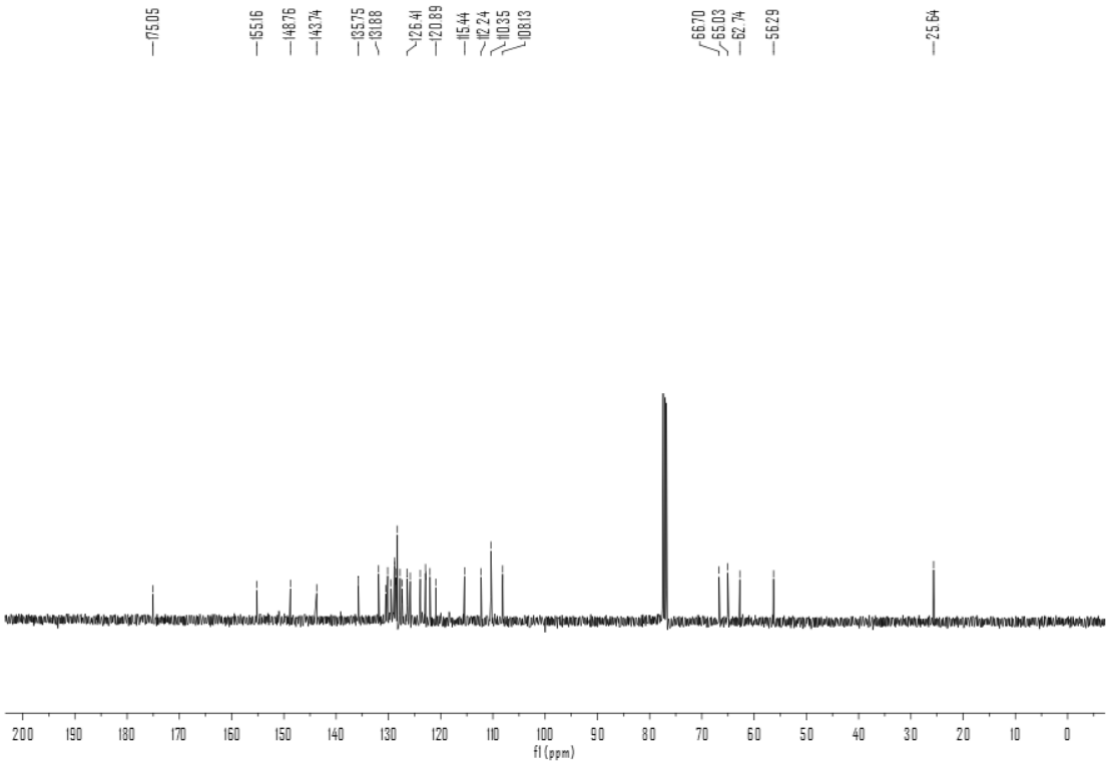
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ea:



(*3R,6c'S,7'S,8a'R,13a'R*)-10'-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 156 - 158 ℃, 49.2 mg, 84% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +263.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.41 (d, *J* = 6.9 Hz, 1H), 7.23 – 7.04 (m, 10H), 6.91 (t, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.4 Hz, 1H), 6.61 – 6.49 (m, 3H), 5.32 (s, 1H), 5.21 (d, *J* = 11.2 Hz, 1H), 4.37 (s, 1H), 3.62 (d, *J* = 11.3 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 155.1, 148.7, 143.7, 135.7, 131.8, 130.5, 130.1, 129.4, 128.8, 128.8, 128.6, 128.4, 128.2, 127.7, 127.3, 126.4, 125.8, 123.9, 122.9, 122.8, 122.0, 120.8, 115.4, 112.2, 110.3, 108.1, 66.7, 65.0, 62.7, 56.29, 25.64. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 42.040 min, t_{minor} = 8.626 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1171.

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143.74
135.75
131.88
126.41
120.89
115.44
112.24
110.35
108.13
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65.03
62.74
56.29
25.64
200
190
180
170
160
150
140
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110
100
90
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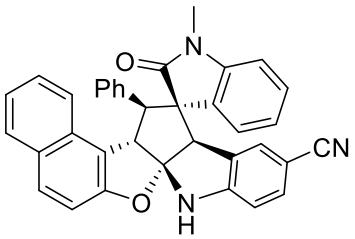
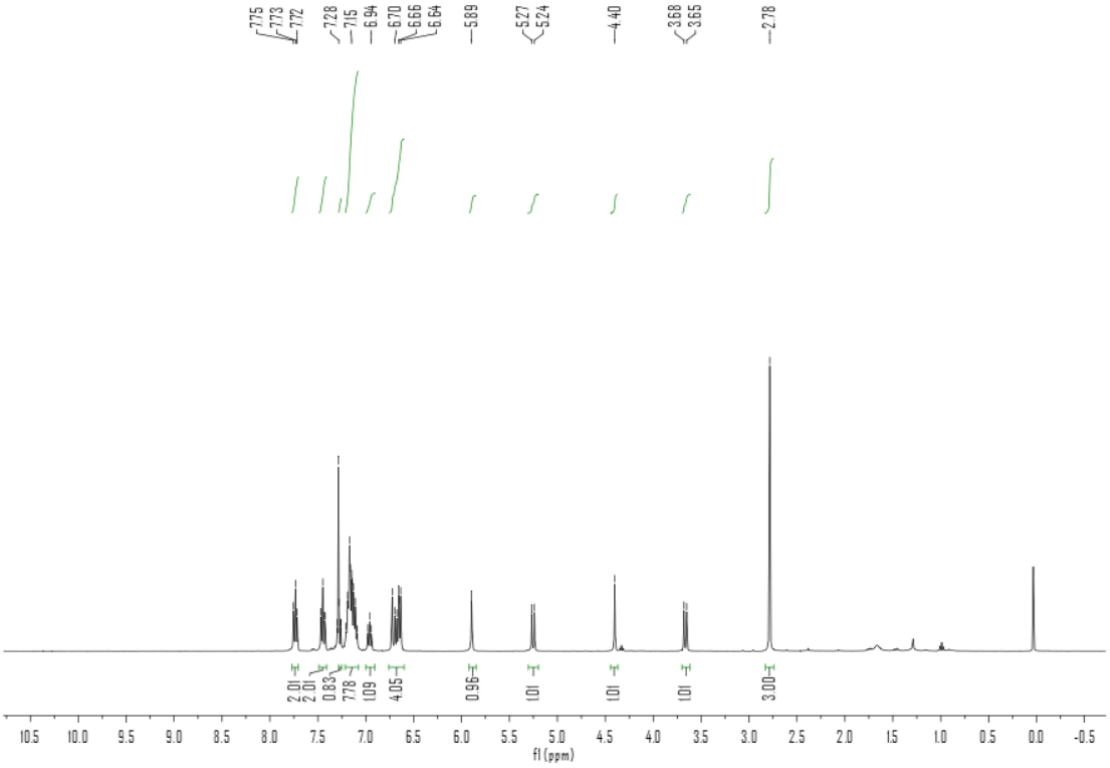
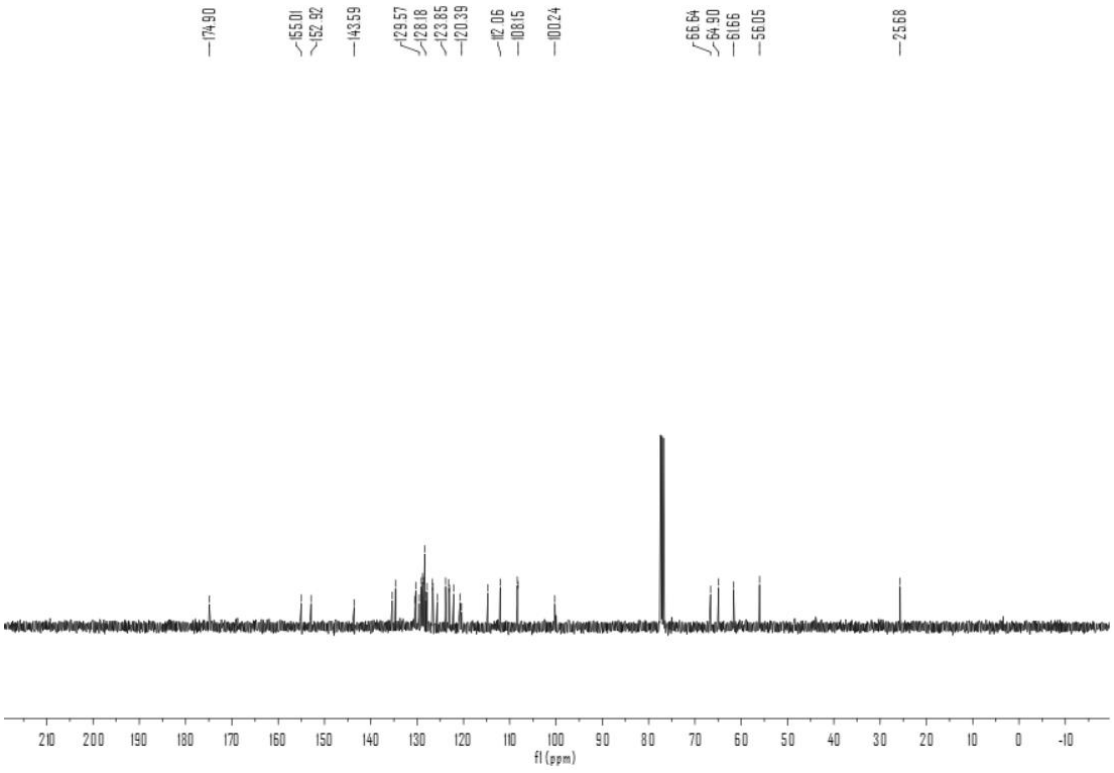
70
60
50
40
30
20
10
0
f1 (ppm)

3fa:

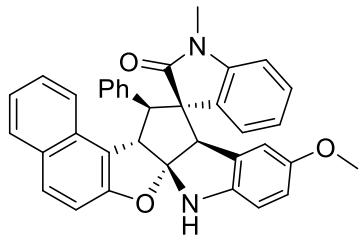


(1S,2R,3R)-3-(2-hydroxynaphthalen-1-yl)-1'-methyl-2'-oxo-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indoline]-7-carbonitrile：white solid, mp 171 - 173 ℃, 45.3 mg, 85% yield, 55% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +256.6 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 8.4 Hz, 2H), 7.31 – 7.25 (m, 1H), 7.21 – 7.07 (m, 8H), 6.96 (t, *J* = 7.2 Hz, 1H), 6.75 – 6.62 (m, 4H), 5.89 (s, 1H), 5.25 (d, *J* = 11.3 Hz, 1H), 4.40 (s, 1H), 3.66 (d, *J* = 11.3 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.0, 152.9, 143.5, 135.3, 134.6, 130.4, 130.3, 129.5, 129.0, 128.7, 128.5, 128.3, 128.1, 127.9, 126.6, 126.6, 125.6, 123.8, 123.1, 123.0, 122.0, 120.6, 120.3, 114.7, 112.0, 108.3, 108.1, 100.2, 66.6, 64.9, 61.6, 56.0, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 53.480 min, t_{minor} = 6.760 min. HRMS (ESI): calcd for $C_{36}H_{25}N_3O_2$ $[M + H]^+$, 532.2020; found, 532.2022

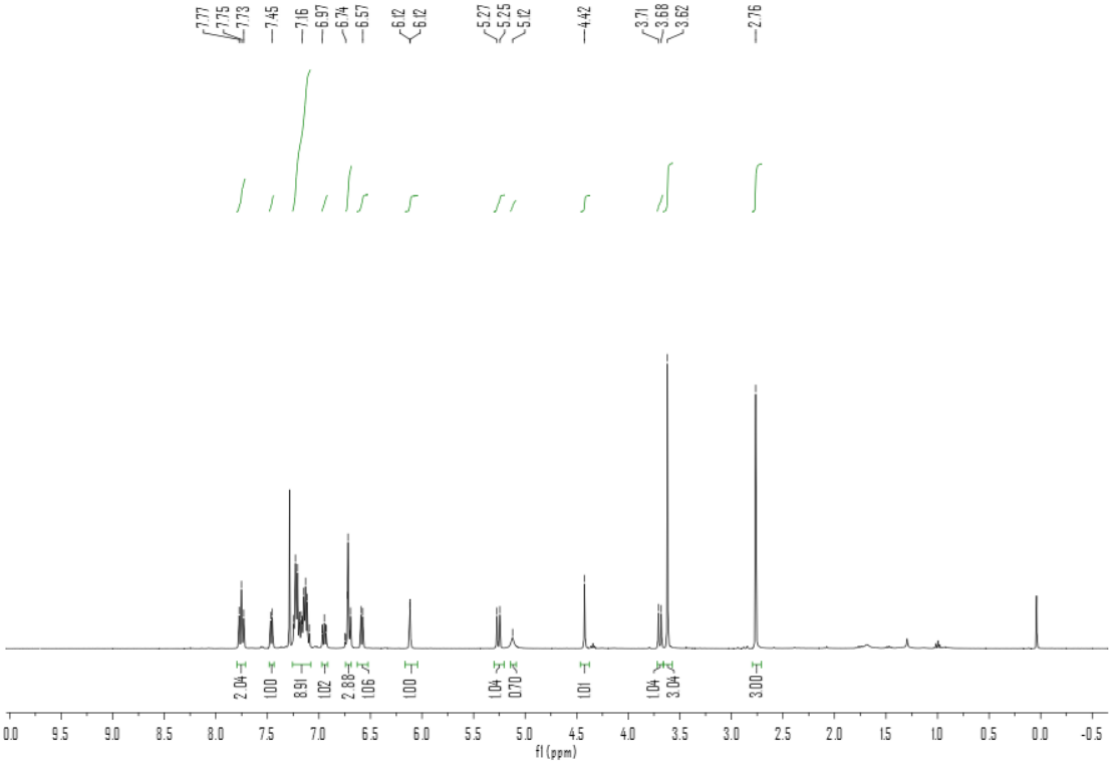


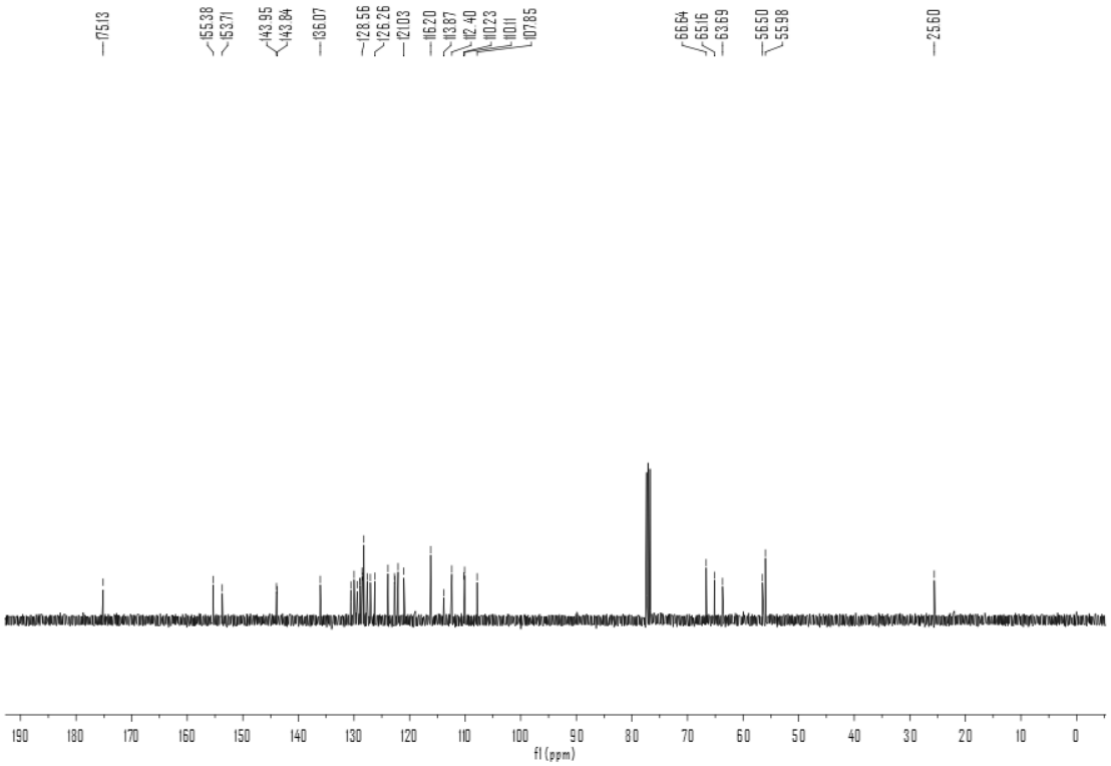

174.90
155.01
152.92
143.59
129.57
128.18
123.85
120.39
112.06
108.15
100.24
66.64
64.90
61.66
56.05
25.68
f1 (ppm)

3ga:

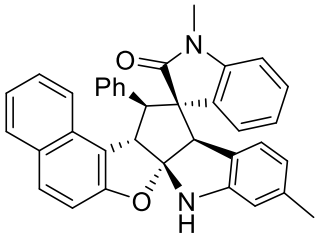


(*3R,6c'S,7'S,8a'R,13a'R*)-10'-methoxy-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 169 - 171 ℃, 48.4 mg, 90% yield, 55% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +274.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 9.0 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 1H), 7.25 – 7.07 (m, 9H), 6.95 (t, *J* = 8.4 Hz, 2H), 6.76 – 6.67 (m, 3H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.12 (s, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 5.12 (s, 1H), 4.42 (s, 1H), 3.69 (d, *J* = 11.2 Hz, 1H), 3.62 (s, 3H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 155.3, 153.7, 143.9, 143.8, 136.0, 130.5, 129.9, 129.4, 128.9, 128.9, 128.5, 128.4, 128.2, 127.6, 127.0, 126.2, 123.9, 122.7, 122.6, 122.0, 121.0, 116.2, 113.8, 112.4, 110.2, 110.1, 107.8, 66.6, 65.1, 63.6, 56.5, 55.9, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 26.356 min, t_{minor} = 12.375 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_3$ $[M + H]^+$, 537.2173; found, 537.2174.

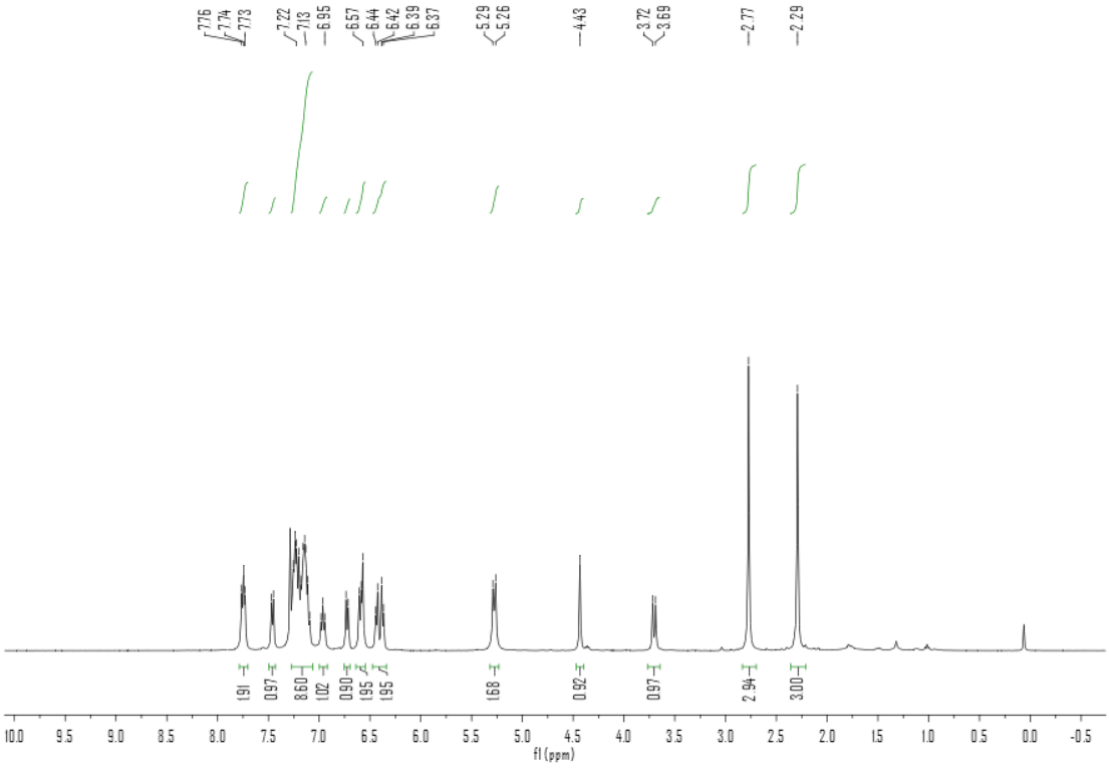


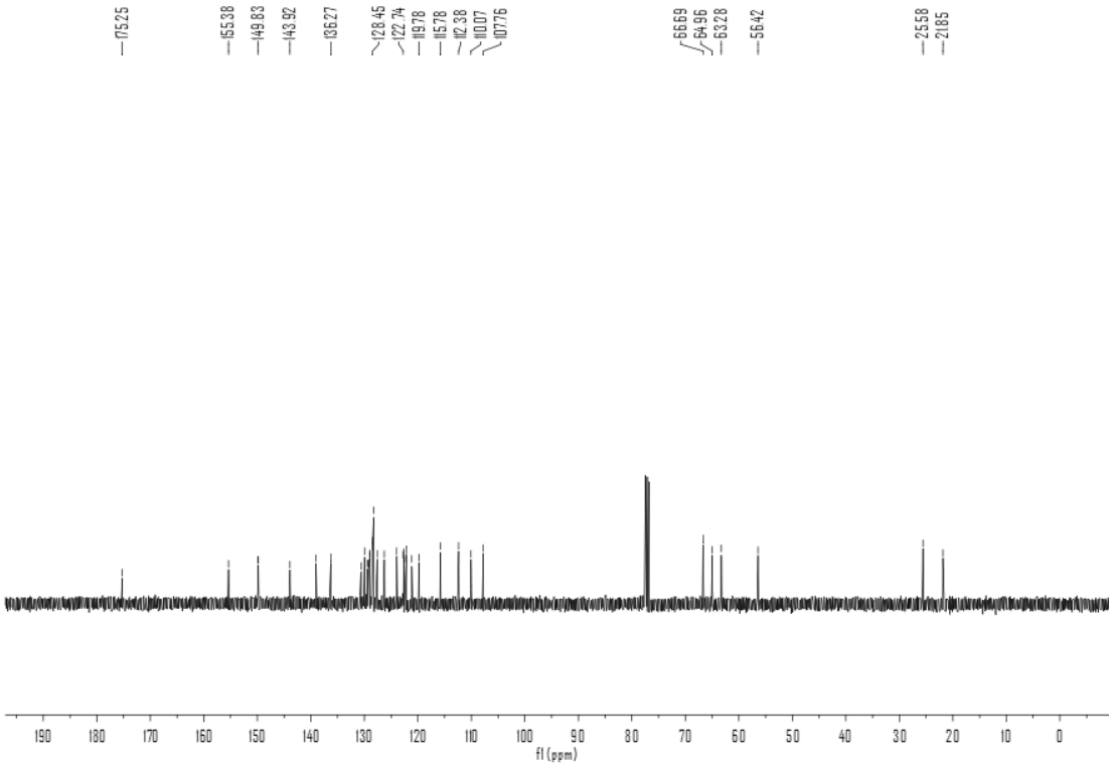

175.13
155.38
153.71
143.95
143.84
136.07
128.56
126.26
121.03
116.20
113.87
112.40
110.23
110.11
107.85
66.64
65.16
63.69
56.50
55.98
25.60
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ha：

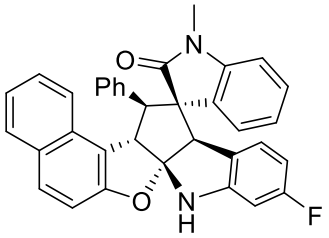


(*3R,6c'S,7'S,8a'R,13a'R*)-1,11'-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 187 - 189 ℃, 44.8 mg, 86% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +278.6 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, J = 8.0 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.27 – 7.08 (m, 9H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.63 – 6.55 (m, 2H), 6.41 (dd, *J* = 23.2, 7.3 Hz, 2H), 5.28 (d, *J* = 10.9 Hz, 1H), 4.43 (s, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 2.77 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 155.3, 149.8, 149.8, 143.9, 139.0, 136.2, 130.6, 129.9, 129.4, 129.2, 129.0, 129.0, 128.4, 128.4, 128.2, 127.5, 126.2, 123.9, 122.7, 122.6, 122.5, 122.2, 122.1, 121.1, 119.7, 115.7, 112.3, 110.0, 107.7, 66.6, 64.9, 63.2, 56.4, 25.5, 21.8. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 32.002 min, t_{minor} = 11.986 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2227.

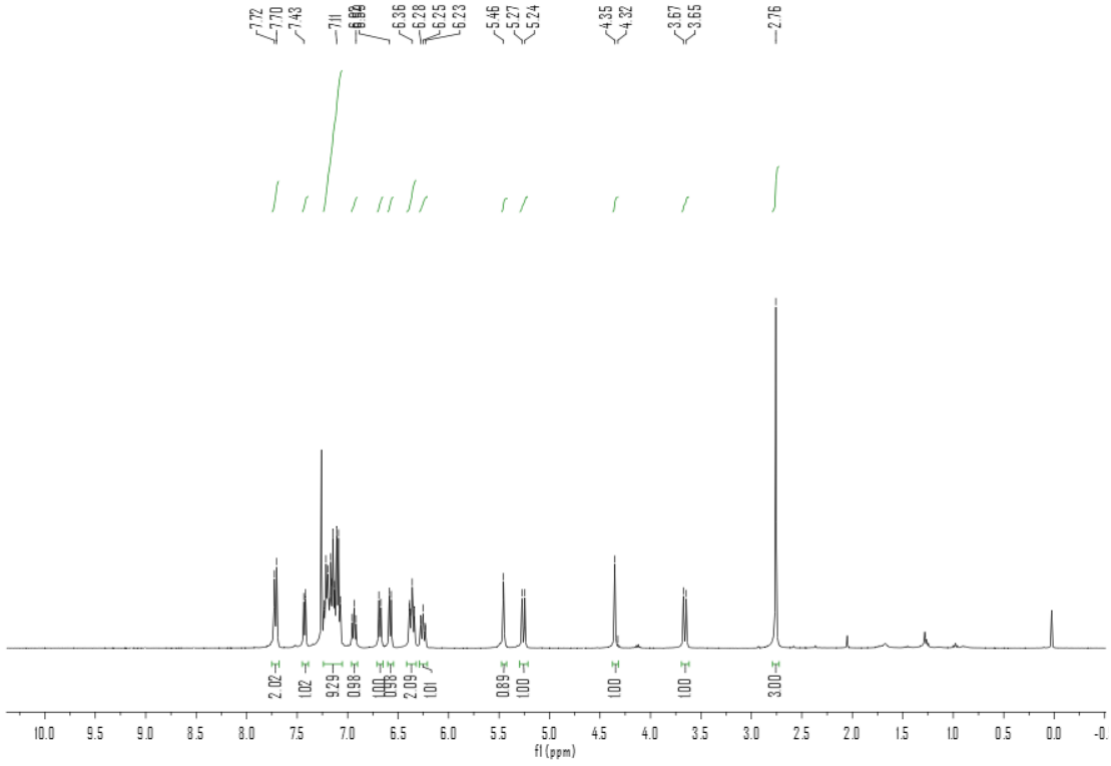


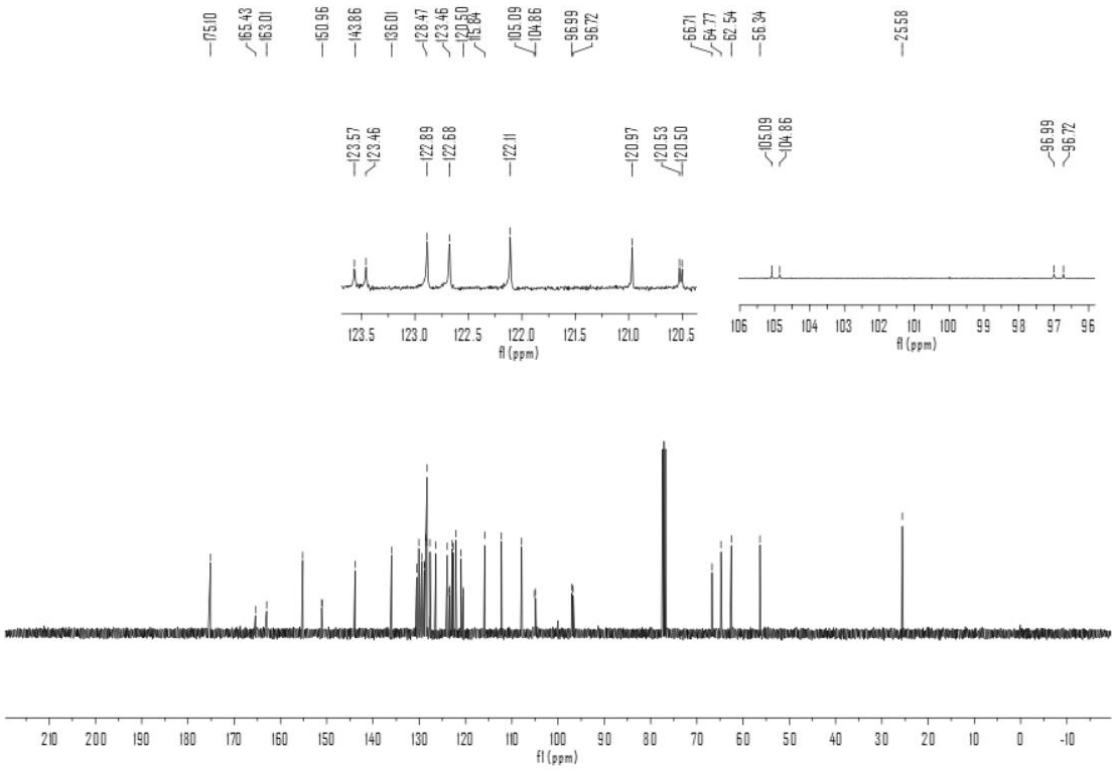

175.25
155.38
149.83
143.92
136.27
128.45
122.74
119.78
115.78
112.38
110.07
107.76
66.69
64.96
63.28
56.42
25.58
21.85
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ia：

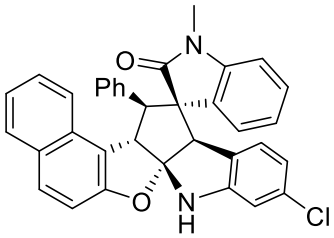


(*3R,6c'S,7'S,8a'R,13a'R*)-11'-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 183 - 185 ℃, 47.7 mg, 91% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +293.2 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.06 (m, 9H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.40 – 6.33 (m, 2H), 6.29 – 6.21 (m, 1H), 5.46 (s, 1H), 5.26 (d, *J* = 11.2 Hz, 1H), 4.34 (d, *J* = 11.9 Hz, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 164.2 (d, J = 242 Hz), 155.2, 151.0, 150.9, 143.8, 136.0, 130.5, 130.0, 129.4, 128.9, 128.8, 128.6, 128.4, 128.2, 127.6, 126.4, 123.9, 123.5 (d, *J* = 11 Hz), 122.8 (d, *J* = 21 Hz), 122.1, 120.9, 120.5 (d, *J* = 23 Hz), 115.8, 112.2, 107.8, 104.9 (d, J = 23 Hz), 96.8 (d, *J* = 27 Hz), 66.7, 64.7, 62.5, 56.3, 25.5. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 30.519 min, t_{minor} = 10.231 min. HRMS (ESI): calcd for $C_{35}H_{25}FN_2O_2$ $[M + H]^+$, 525.1973; found, 525.1980.

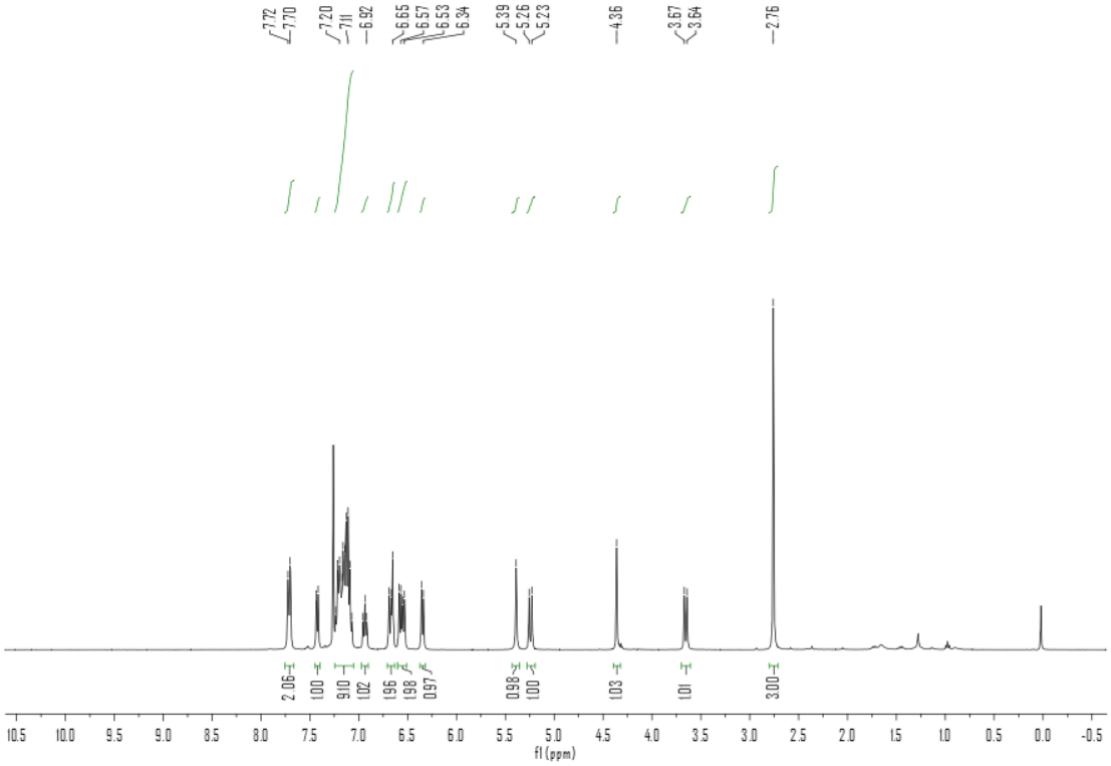


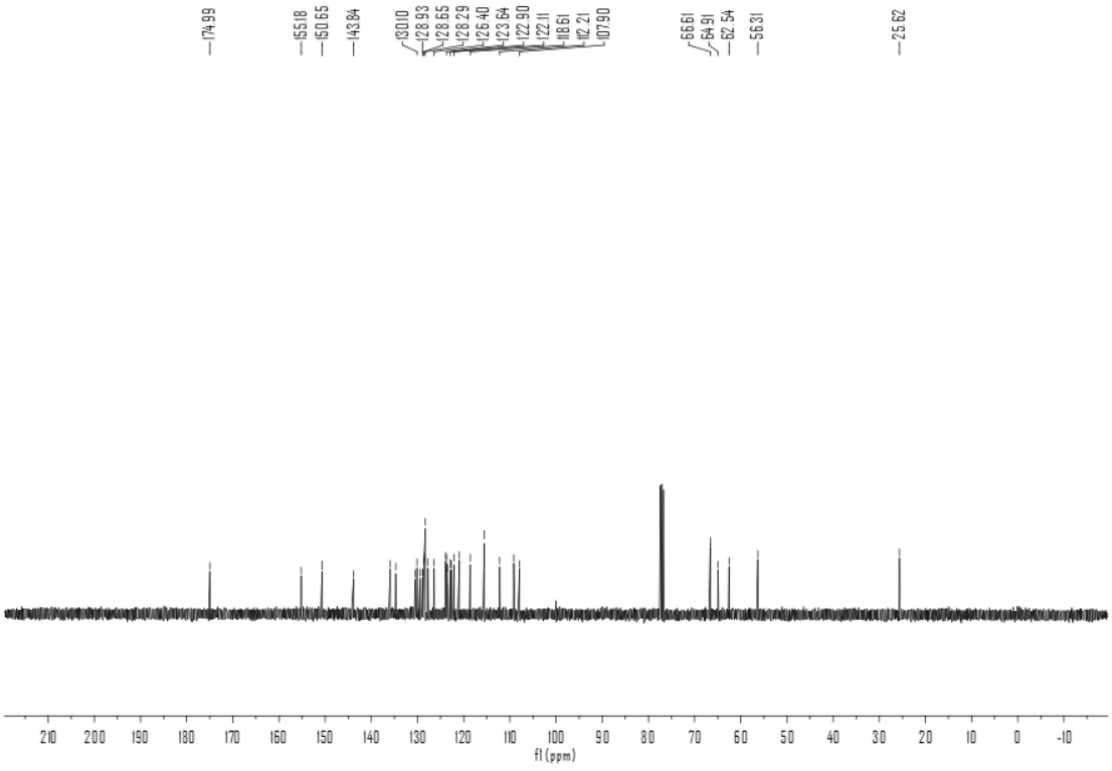

175.10
165.43
163.01
150.96
143.86
136.01
128.47
123.46
120.50
115.64
105.09
104.86
96.99
96.72
66.71
64.77
62.54
56.34
25.58
123.57
123.46
122.89
122.68
122.11
120.97
120.53
120.50
105.09
104.86
96.99
96.72
f1 (ppm)
f1 (ppm)
f1 (ppm)

3ja：

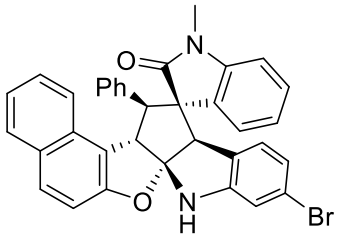


(*3R,6c'S,7'S,8a'R,13a'R*)-11'-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 175 - 177 ℃, 43.3 mg, 80% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +301.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.9 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.05 (m, 9H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.71 – 6.64 (m, 2H), 6.60 – 6.51 (m, 2H), 6.35 (d, *J* = 7.8 Hz, 1H), 5.39 (s, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 4.36 (s, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.1, 150.6, 143.8, 135.8, 134.7, 130.5, 130.1, 129.4, 128.9, 128.7, 128.6, 128.4, 128.2, 127.7, 126.4, 123.9, 123.6, 123.5, 122.9, 122.7, 122.1, 120.9, 118.6, 115.5, 112.2, 109.1, 107.9, 66.6, 64.9, 62.5, 56.3, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 29.043 min, t_{minor} = 9.878 min. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1680.

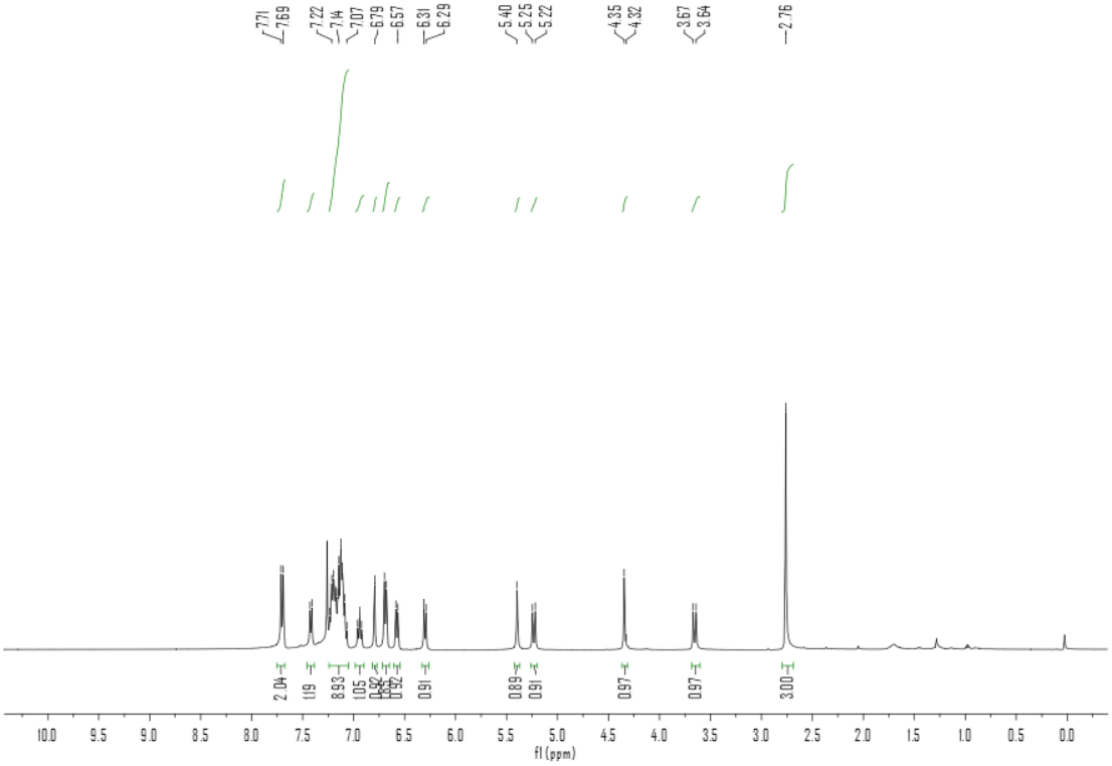


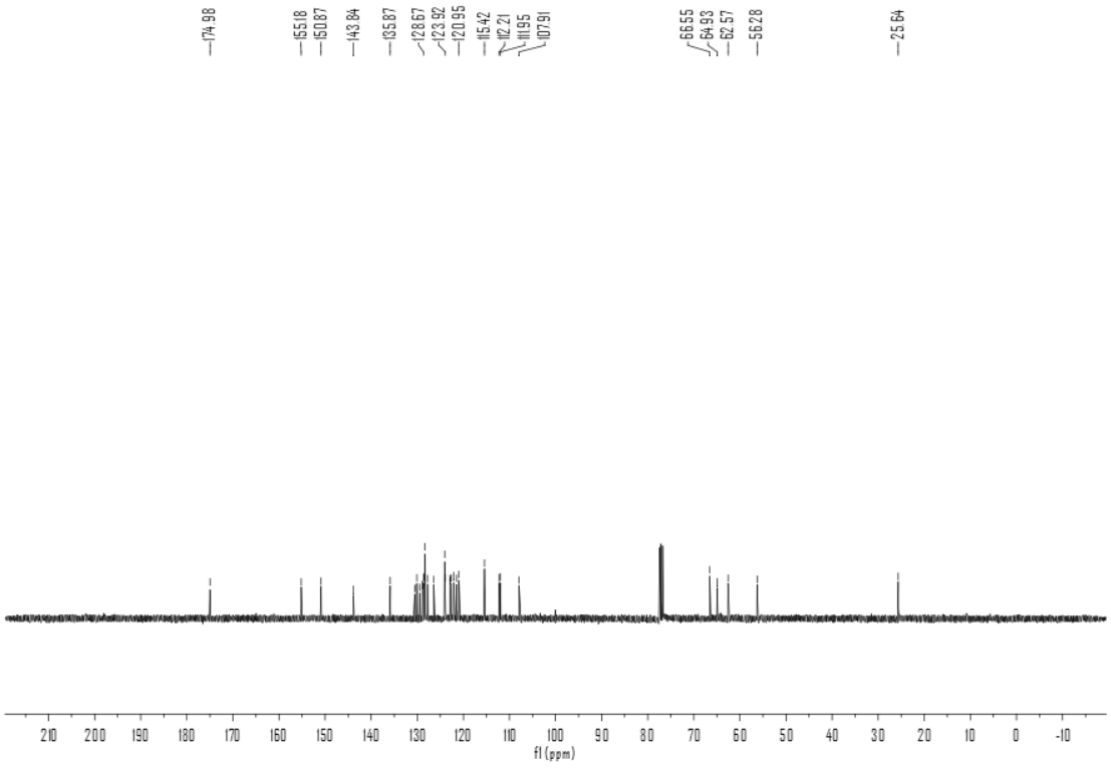

174.99
155.18
150.65
143.84
130.10
128.93
128.65
128.29
126.40
123.64
122.90
122.11
118.61
112.21
107.90
66.61
64.91
62.54
56.31
25.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ka：

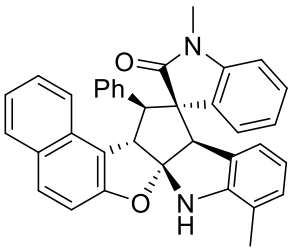


(*3R,6c'S,7'S,8a'R,13a'R*)-11'-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one： white solid, mp 173 - 175 ℃, 50.3 mg, 86% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +294.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.05 (m, 9H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.79 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 7.7 Hz, 1H), 6.30 (d, *J* = 7.8 Hz, 1H), 5.40 (s, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.35 (s, 1H), 3.66 (d, *J* = 11.2 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.1, 150.8, 143.8, 135.8, 130.5, 130.1, 129.4, 128.9, 128.7, 128.6, 128.4, 128.3, 127.7, 126.4, 124.0, 123.9, 122.9, 122.8, 122.7, 122.1, 121.4, 120.9, 115.4, 112.2, 111.9, 107.9, 66.5, 64.9, 62.5, 56.2, 25.6. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 27.169 min, t_{minor} = 9.430 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1170.

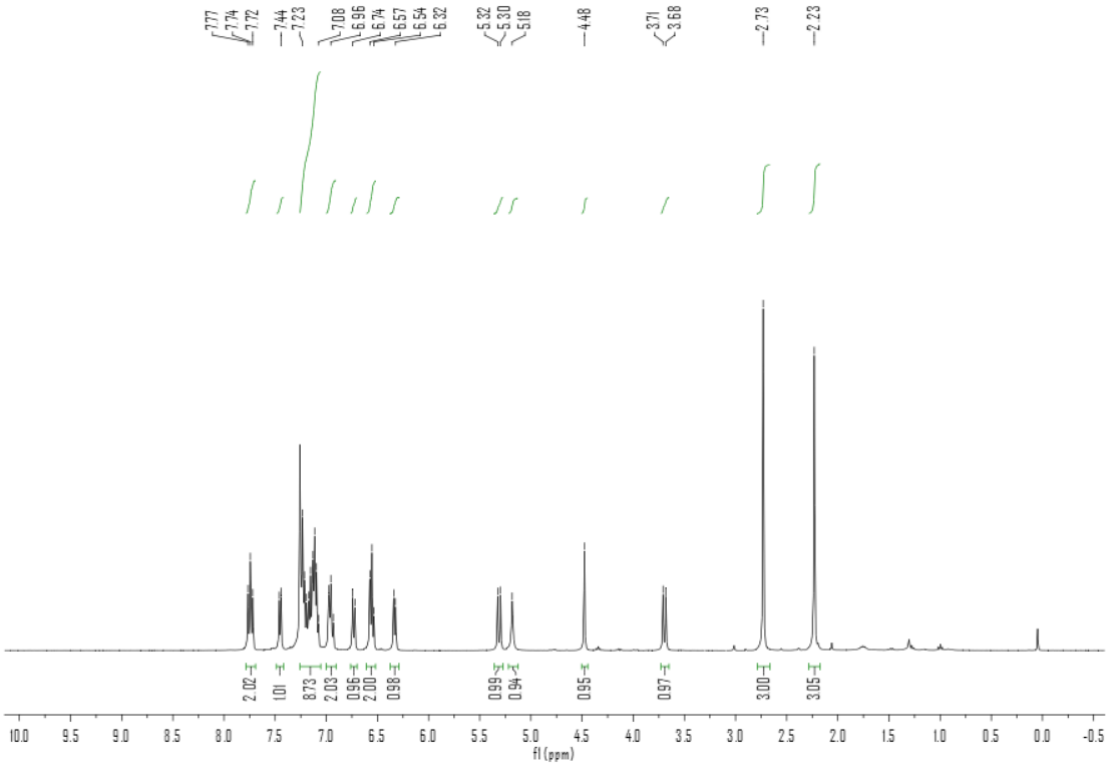


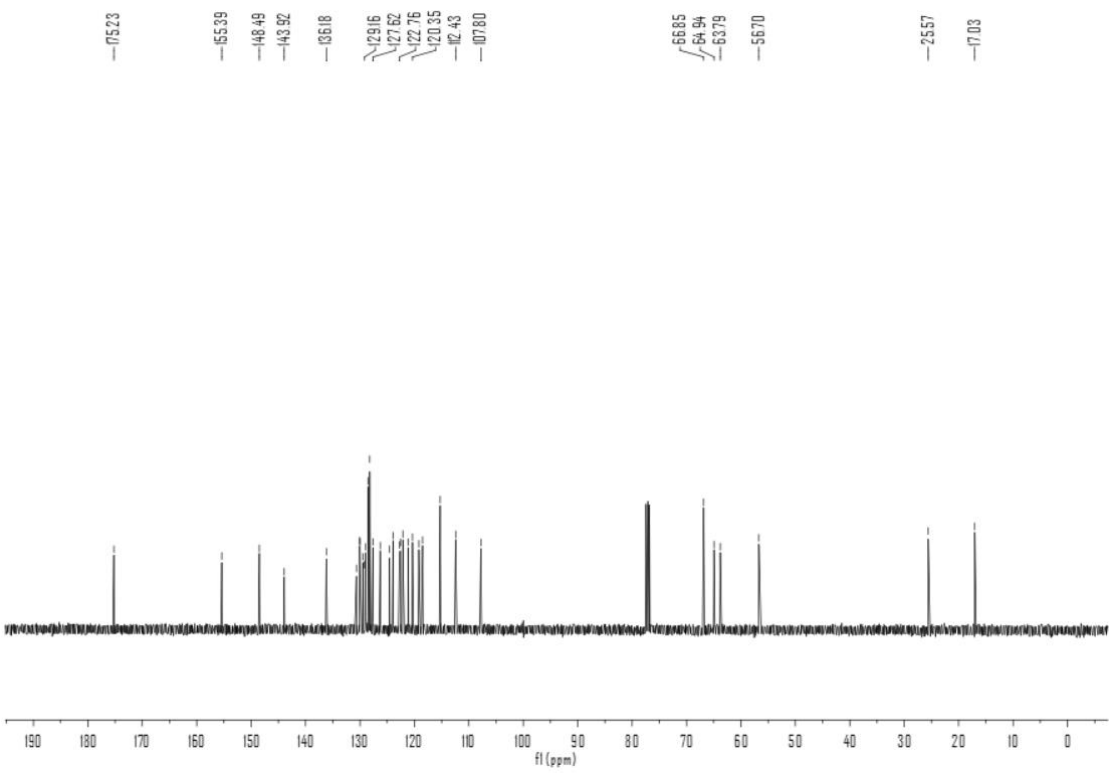

174.98
155.18
150.87
143.84
135.87
128.67
123.92
120.95
115.42
112.21
111.95
107.91
66.55
64.93
62.57
56.28
25.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3la：

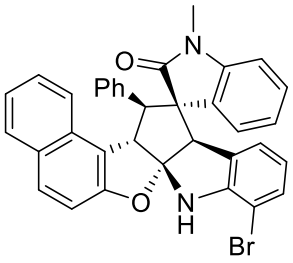


(*3R,6c'S,7'S,8a'R,13a'R*)-1,12'-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 174 - 176 ℃, 47.9 mg, 92% yield, 97% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +258.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 9.4 Hz, 2H), 7.45 (d, *J* = 7.3 Hz, 1H), 7.26 – 7.06 (m, 9H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 1H), 6.55 (t, *J* = 7.9 Hz, 2H), 6.33 (d, *J* = 7.3 Hz, 1H), 5.31 (d, *J* = 11.2 Hz, 1H), 5.18 (s, 1H), 4.48 (s, 1H), 3.69 (d, *J* = 11.2 Hz, 1H), 2.73 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 155.4, 148.5, 143.9, 136.2, 130.6, 130.0, 130.0, 129.4, 129.1, 129.0, 128.4, 128.2, 127.6, 126.3, 124.5, 123.9, 122.7, 122.6, 122.1, 121.1, 120.3, 119.2, 118.5, 115.2, 112.4, 107.8, 66.8, 64.9, 63.7, 56.7, 25.5, 17.0. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 17.915min, t_{minor} = 6.015 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2226.

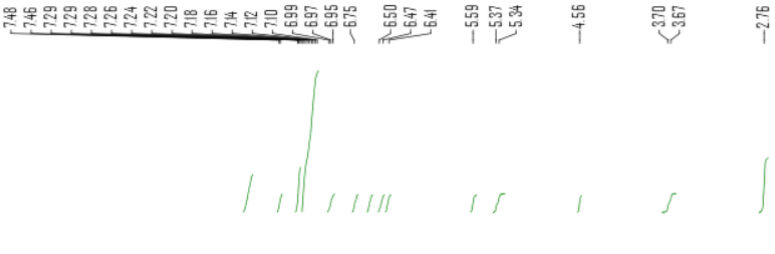


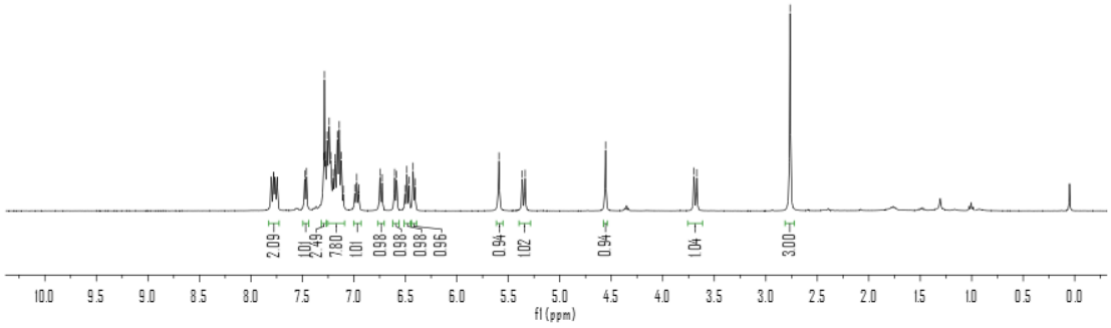

175.23
155.39
148.49
143.92
136.18
129.16
127.62
122.76
120.35
112.43
107.80
66.85
64.94
63.79
56.70
25.57
17.03
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

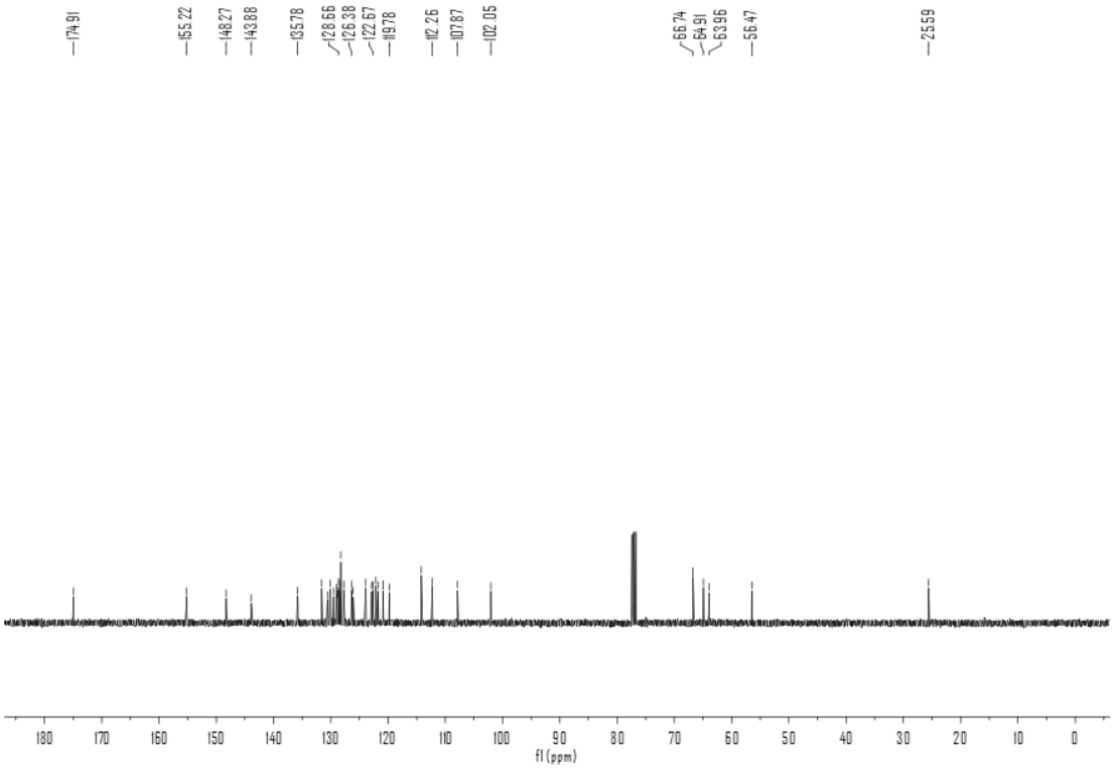
3ma：



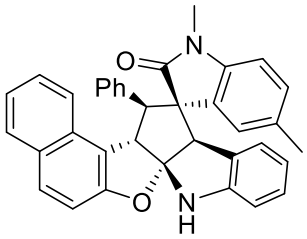
(*3R,6c'S,7'S,8a'R,13a'R*)-12'-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 152 - 154 ℃, 50.9 mg, 87% yield, 97% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +284.1 (c = 1.0, $CHCl_3$);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 7.3 Hz, 1H), 7.29 (t, *J* = 3.7 Hz, 2H), 7.17 (m, 8H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 7.7 Hz, 1H), 6.48 (t, *J* = 7.6 Hz, 1H), 6.42 (d, *J* = 7.2 Hz, 1H), 5.59 (s, 1H), 5.35 (d, *J* = 11.3 Hz, 1H), 4.56 (s, 1H), 3.68 (d, *J* = 11.3 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.2, 148.2, 143.8, 135.7, 131.5, 130.5, 130.1, 129.5, 128.9, 128.7, 128.6, 128.4, 128.2, 127.7, 126.3, 126.1, 123.9, 122.9, 122.6, 122.1, 121.7, 120.8, 119.7, 114.2, 112.2, 107.8, 102.0, 66.7, 64.9, 63.9, 56.4, 25.6. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 29.163 min, t_{minor} = 6.166 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1170.



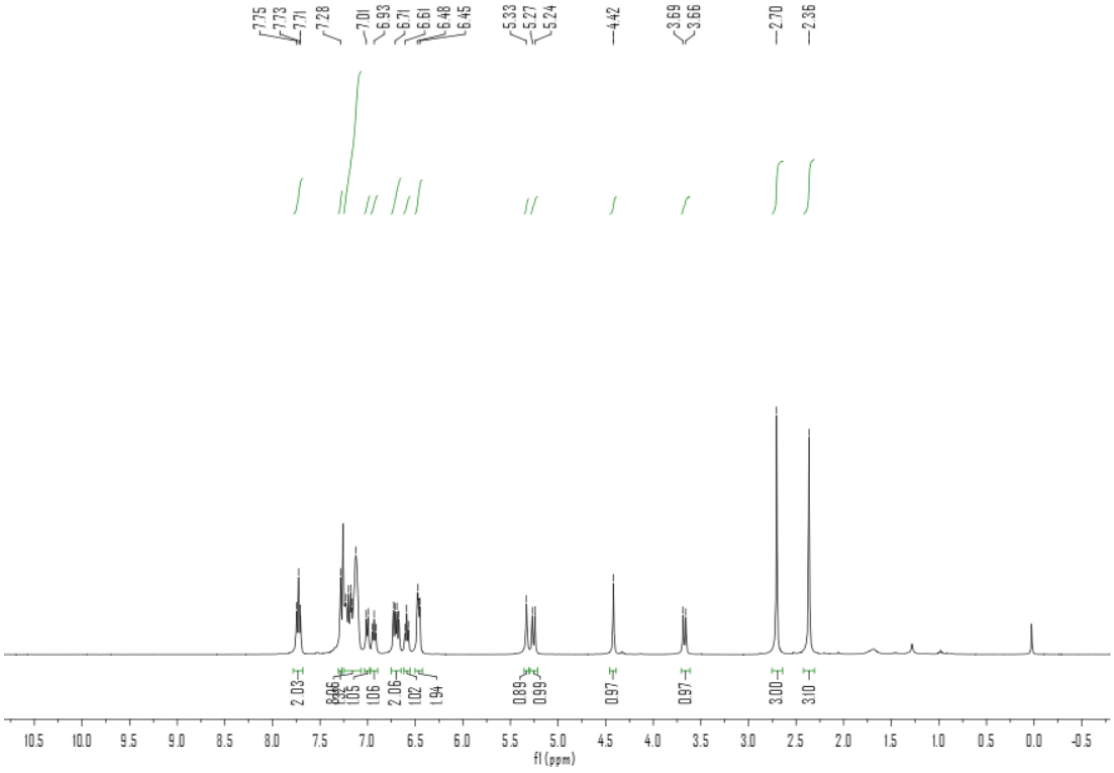


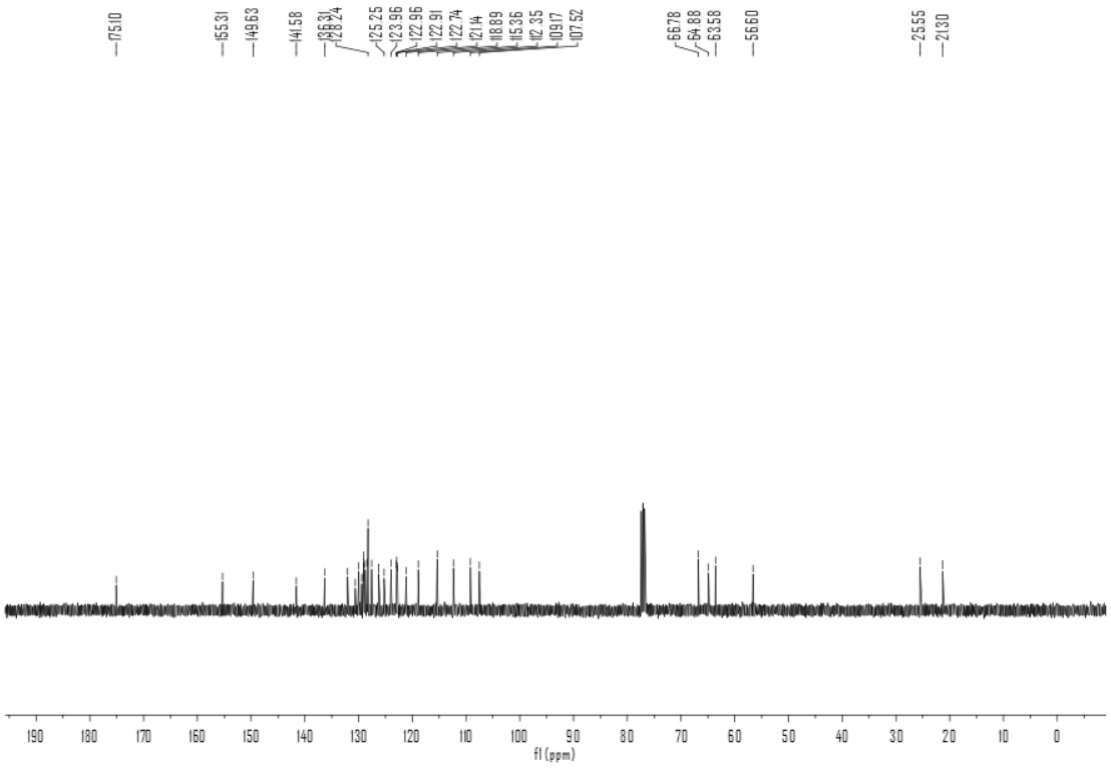

174.91
155.22
148.27
143.88
135.78
128.66
126.38
122.67
119.78
102.26
107.87
102.05
66.74
64.91
63.96
56.47
25.59
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3na：

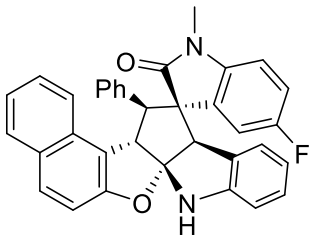


(*3R,6c'S,7'S,8a'R,13a'R*)-1,5-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 188 - 190 ℃, 46.9 mg, 90% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +282.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.2 Hz, 2H), 7.28 (s, 1H), 7.18 (m, 8H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.70 (dd, *J* = 15.4, 8.2 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.50 - 6.47 (m, 2H), 5.33 (s, 0H), 5.26 (d, *J* = 11.2 Hz, 1H), 4.42 (s, 1H), 3.67 (d, *J* = 11.2 Hz, 1H), 2.70 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 155.3, 149.6, 141.5, 136.3, 132.0, 130.6, 129.9, 129.4, 129.1, 129.0, 129.0, 128.7, 128.4, 128.2, 127.5, 126.2, 125.2, 123.9, 122.9, 122.9, 122.7, 121.1, 118.8, 115.3, 112.3, 109.1, 107.5, 66.7, 64.8, 63.5, 56.6, 25.5, 21.3. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 14.796 min, t_{minor} = 7.902 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2227.

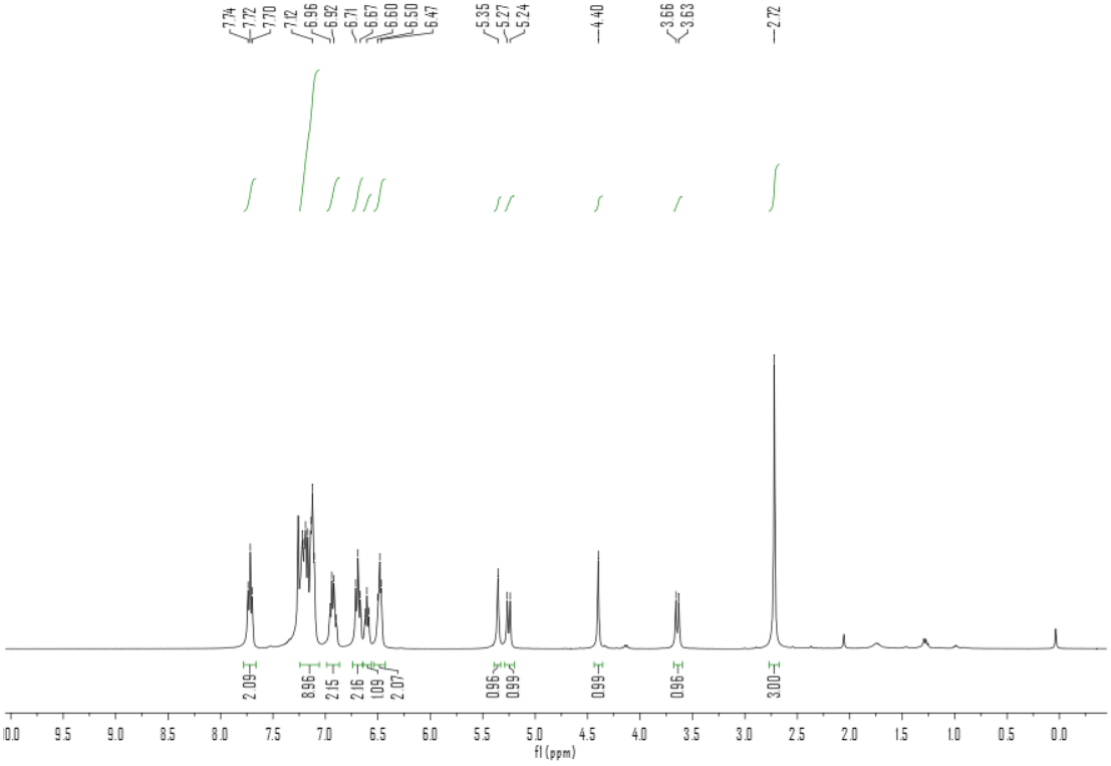


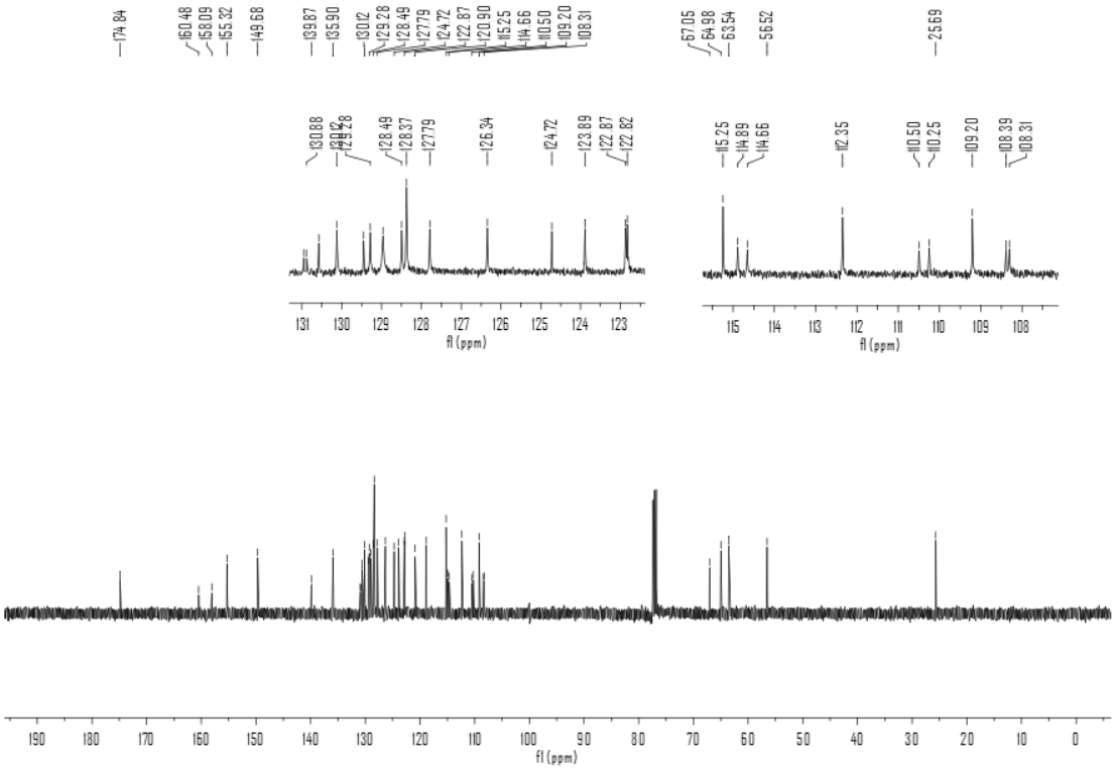

175.10
155.31
149.63
141.58
136.31
128.24
125.25
123.96
122.96
122.91
122.74
121.14
118.89
115.36
112.35
109.17
107.52
66.78
64.88
63.58
56.60
25.55
21.30
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3oa：

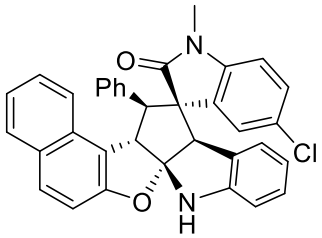


(*3R,6c'S,7'S,8a'R,13a'R*)-5-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 168 - 170 ℃, 48.3 mg, 92% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +268.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (t, *J* = 7.9 Hz, 2H), 7.25 – 7.07 (m, 9H), 6.93 (dd, *J* = 16.1, 8.3 Hz, 2H), 6.69 (t, *J* = 8.9 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.48 (t, *J* = 6.3 Hz, 2H), 5.35 (s, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 4.40 (s, 1H), 3.64 (d, *J* = 11.1 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 159.3 (d, *J* = 239 Hz), 155.3, 149.6, 139.8, 135.9, 130.9 (d, *J* = 8 Hz), 130.5, 130.1, 129.4, 129.2, 128.9, 128.4, 128.3, 127.7, 126.3, 124.7, 123.8, 122.8 (d, *J* = 5 Hz), 120.9, 118.9, 115.2, 114.8 (d, *J* = 23 Hz), 112.3, 110.3 (d, *J* = 25 Hz), 109.2, 108.3 (d, *J* = 7 Hz), 67.0, 64.9, 63.5, 56.5, 25.6. Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 14.169 min, t_{minor} = 10.485 min. HRMS (ESI): calcd for $C_{35}H_{25}FN_2O_2$ $[M + H]^+$, 525.1973; found, 525.1981.

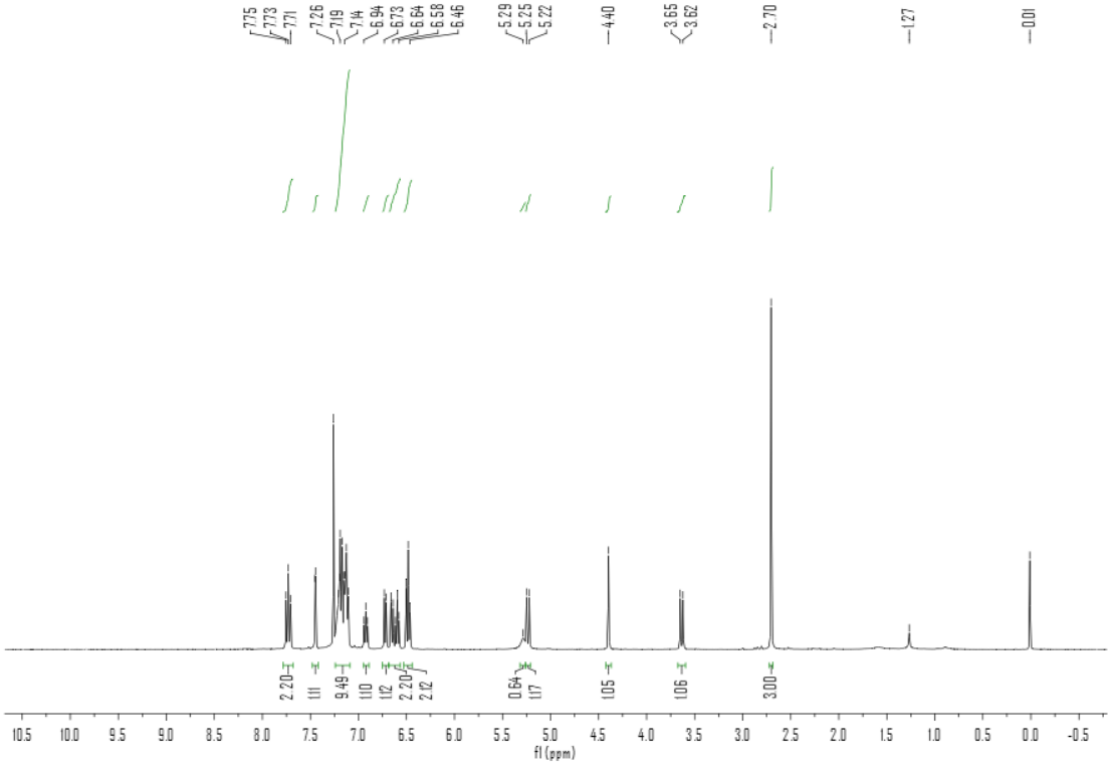


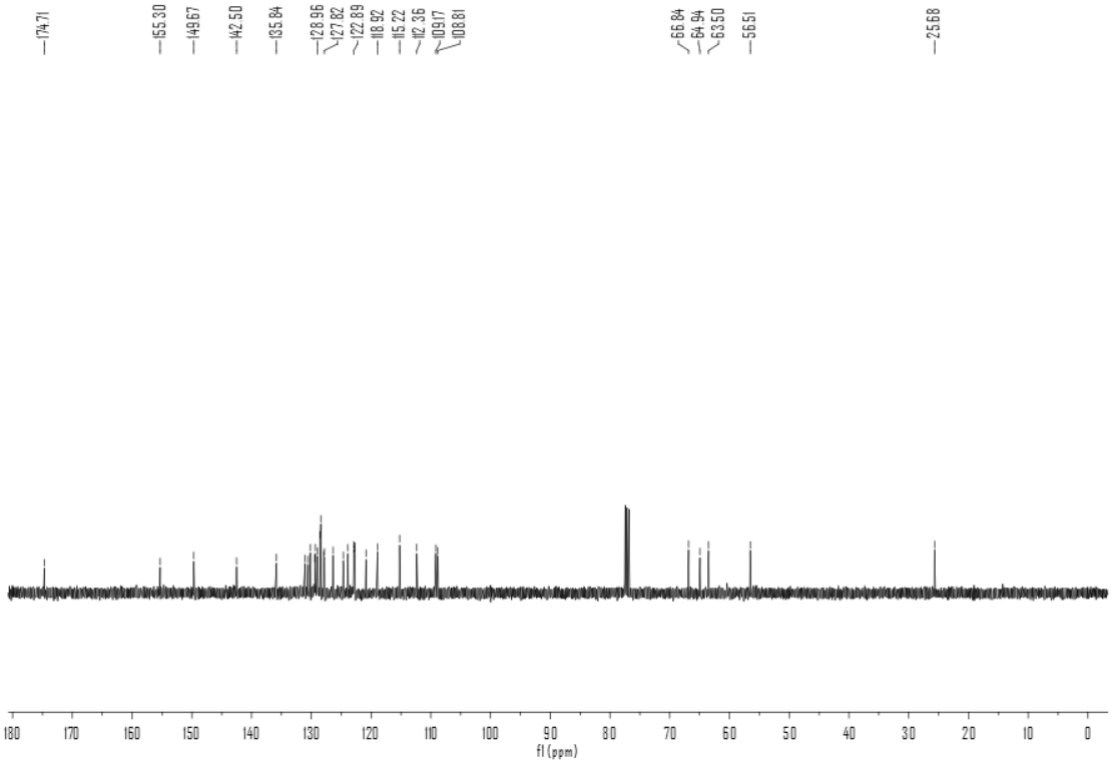

174.84
160.48
158.09
155.32
149.68
139.87
135.90
130.12
129.28
128.49
128.37
127.79
124.72
122.87
120.90
115.25
114.66
110.50
109.20
108.31
67.05
64.98
63.54
56.52
25.69
f1 (ppm)
f1 (ppm)
f1 (ppm)

3pa：

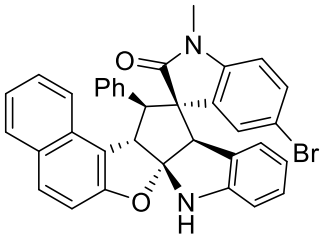


(*3R,6c'S,7'S,8a'R,13a'R*)-5-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 176 - 178 ℃, 48.2 mg, 89% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +283.2 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 9.4 Hz, 2H), 7.45 (d, *J* = 1.8 Hz, 1H), 7.24 – 7.09 (m, 9H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.68 – 6.56 (m, 2H), 6.48 (t, *J* = 8.2 Hz, 1H), 5.29 (s, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.40 (s, 1H), 3.64 (d, *J* = 11.2 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 155.3, 149.6, 142.5, 135.8, 131.0, 130.5, 130.1, 129.4, 129.3, 128.9, 128.5, 128.5, 128.4, 127.9, 127.8, 126.3, 124.6, 123.8, 122.8, 122.8, 122.6, 120.8, 118.9, 115.2, 112.3, 109.1, 108.8, 66.8, 64.9, 63.5, 56.5, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.730 min, t_{minor} = 8.310 min. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1678.

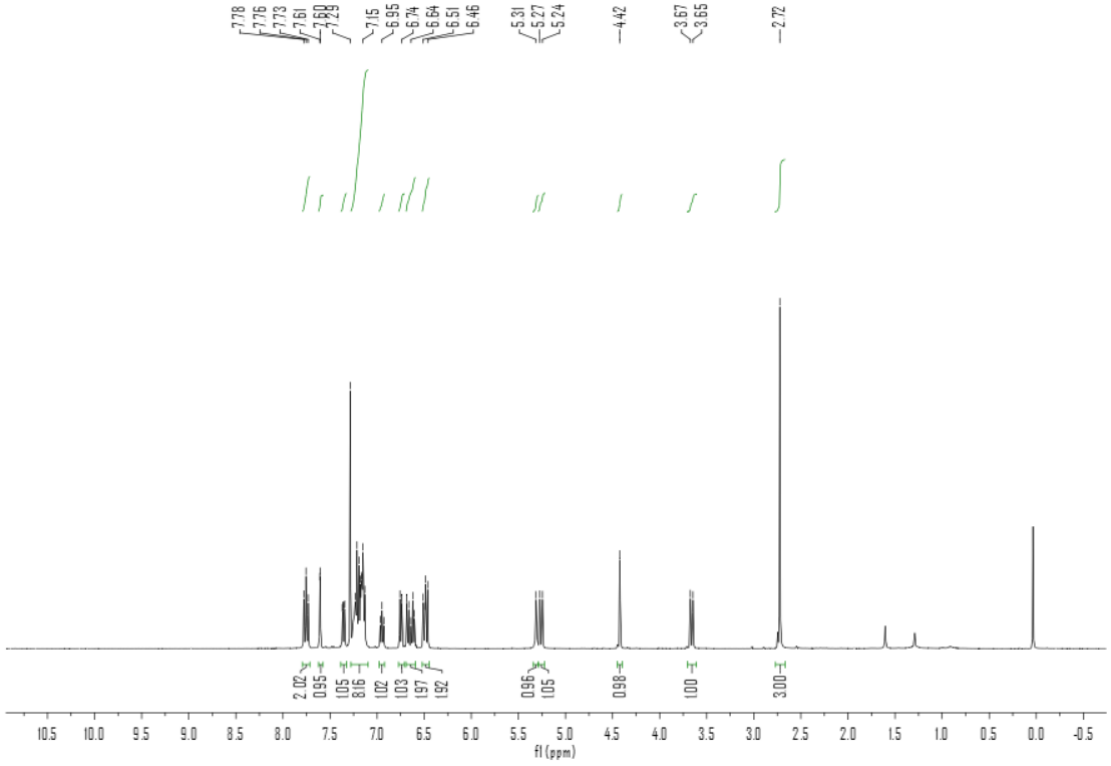


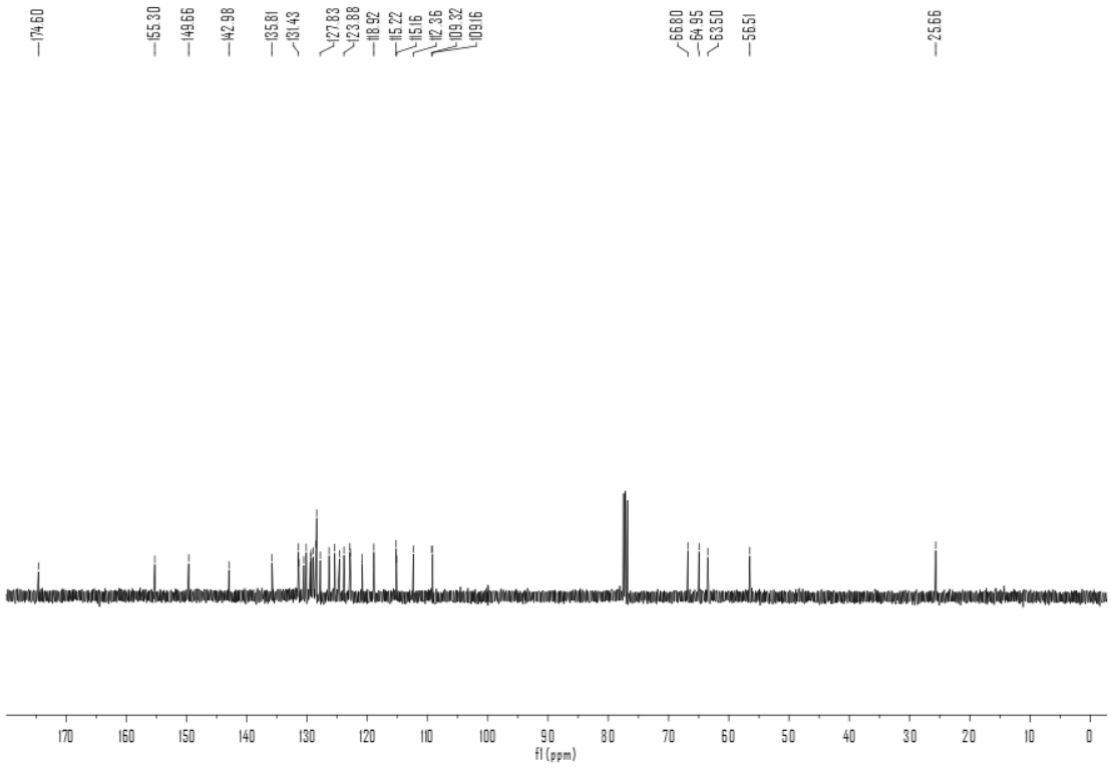

174.71
155.30
149.67
142.50
135.84
128.96
127.82
122.89
118.92
115.22
112.36
109.17
108.81
66.84
64.94
63.50
56.51
25.68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3qa：

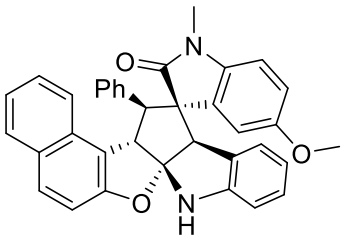


(*3R,6c'S,7'S,8a'R,13a'R*)-5-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 195 - 197 ℃, 50.9 mg, 87% yield, 92% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +283.2 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 9.4 Hz, 2H), 7.58 (d, *J* = 1.7 Hz, 1H), 7.33 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.25 – 7.08 (m, 8H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.65 (d, *J* = 8.5 Hz, 1H), 6.60 (t, *J* = 7.4 Hz, 1H), 6.50 – 6.42 (m, 2H), 5.29 (s, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.40 (s, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 155.3, 149.6, 142.9, 135.8, 131.4, 131.3, 130.5, 130.1, 129.4, 129.3, 128.9, 128.5, 128.4, 127.8, 126.3, 125.4, 124.6, 123.8, 122.9, 122.8, 120.8, 118.9, 115.2, 115.1, 112.3, 109.3, 109.1, 66.8, 64.9, 63.5, 56.5, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 15.097 min, t_{minor} = 8.741 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1174.

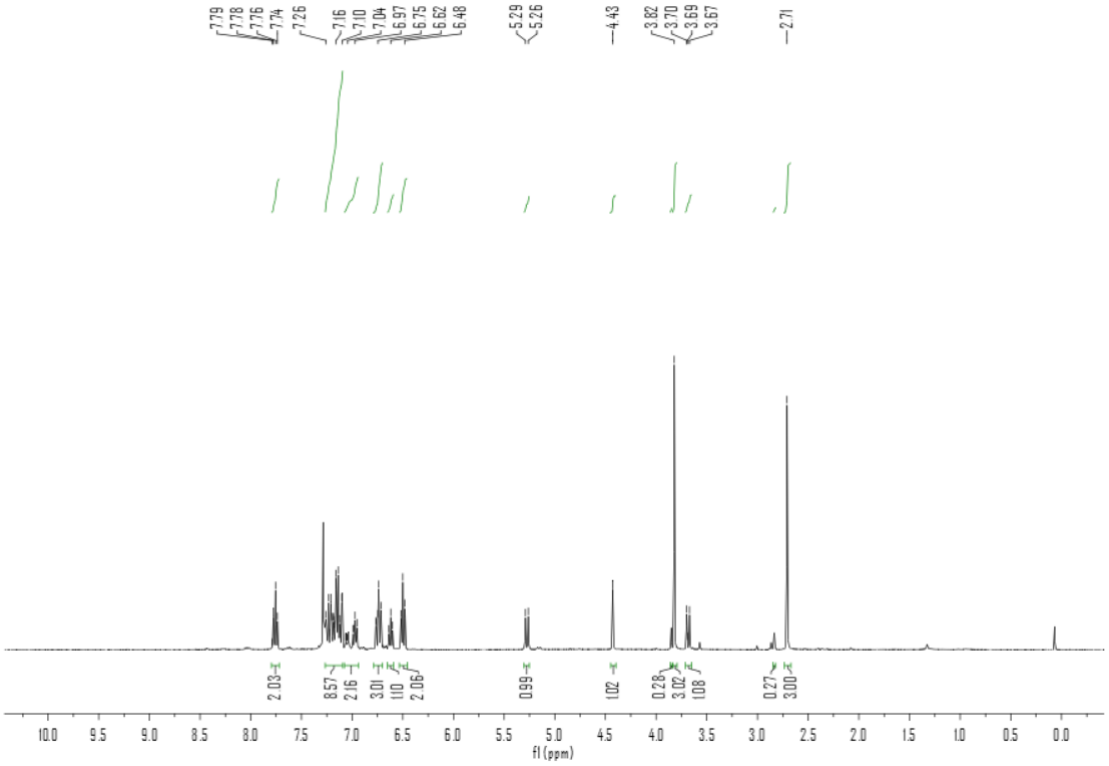


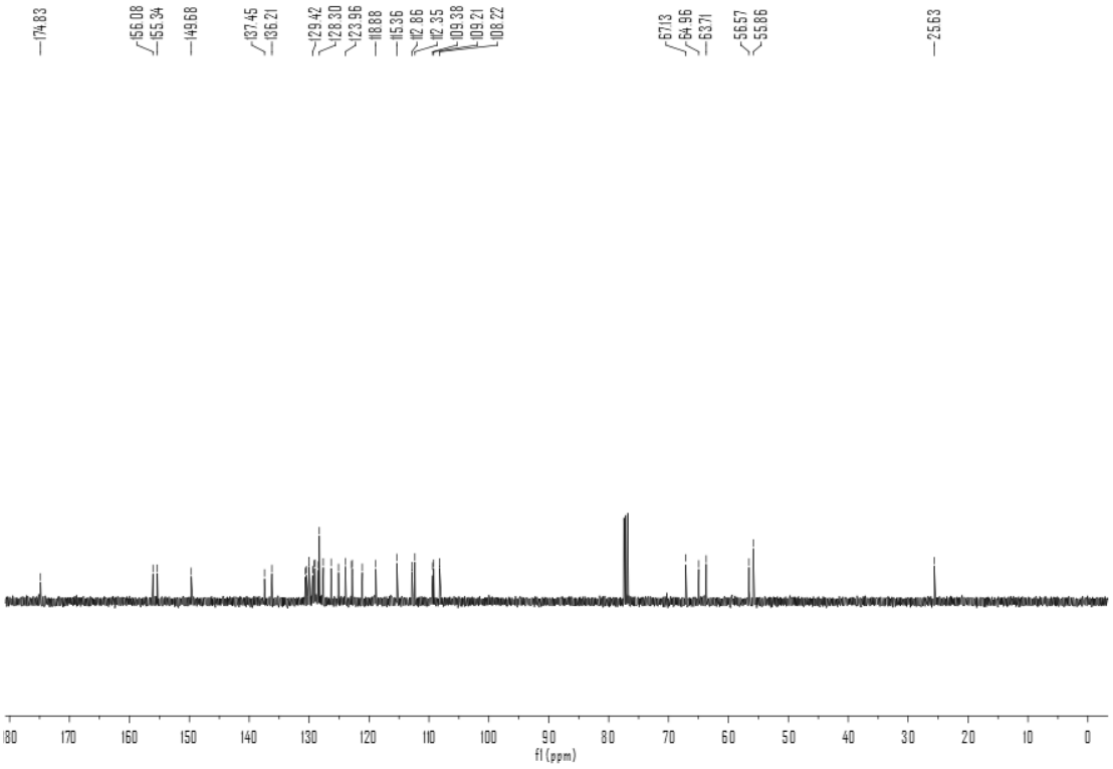

174.60
155.30
149.66
142.98
135.81
131.43
127.83
123.88
118.92
115.22
115.16
112.36
109.32
109.16
66.80
64.95
63.50
56.51
25.66
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ra：

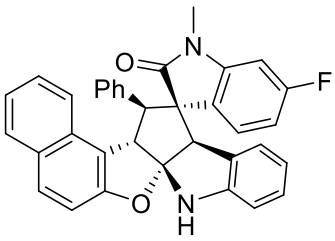


(*3R,6c'S,7'S,8a'R,13a'R*)-5-methoxy-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 182 - 184 ℃, 48.3 mg, 90% yield, 79% ee, 11:1 d.r. $[\alpha]_D^{20}$ = +274.5 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 8.2 Hz, 2H), 7.27 – 7.09 (m, 8H), 7.07 – 6.93 (m, 2H), 6.77 – 6.70 (m, 3H), 6.62 (t, *J* = 7.4 Hz, 1H), 6.50 (t, *J* = 7.6 Hz, 2H), 5.28 (d, *J* = 11.2 Hz, 1H), 4.43 (s, 1H), 3.82 (s, 3H), 3.68 (d, *J* = 11.2 Hz,1H), 2.83 (s, 0H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 156.0, 155.3, 149.6, 137.4, 136.2, 130.6, 130.4, 130.0, 129.4, 129.1, 129.0, 128.4, 128.3, 127.6, 126.3, 125.0, 123.9, 122.9, 122.8, 121.1, 118.8, 115.3, 112.8, 112.3, 109.3, 109.2, 108.2, 67.1, 64.9, 63.7, 56.5, 55.8, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 63.727 min, t_{minor} = 13.385 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_3$ $[M + H]^+$, 537.2173; found, 537.2175.

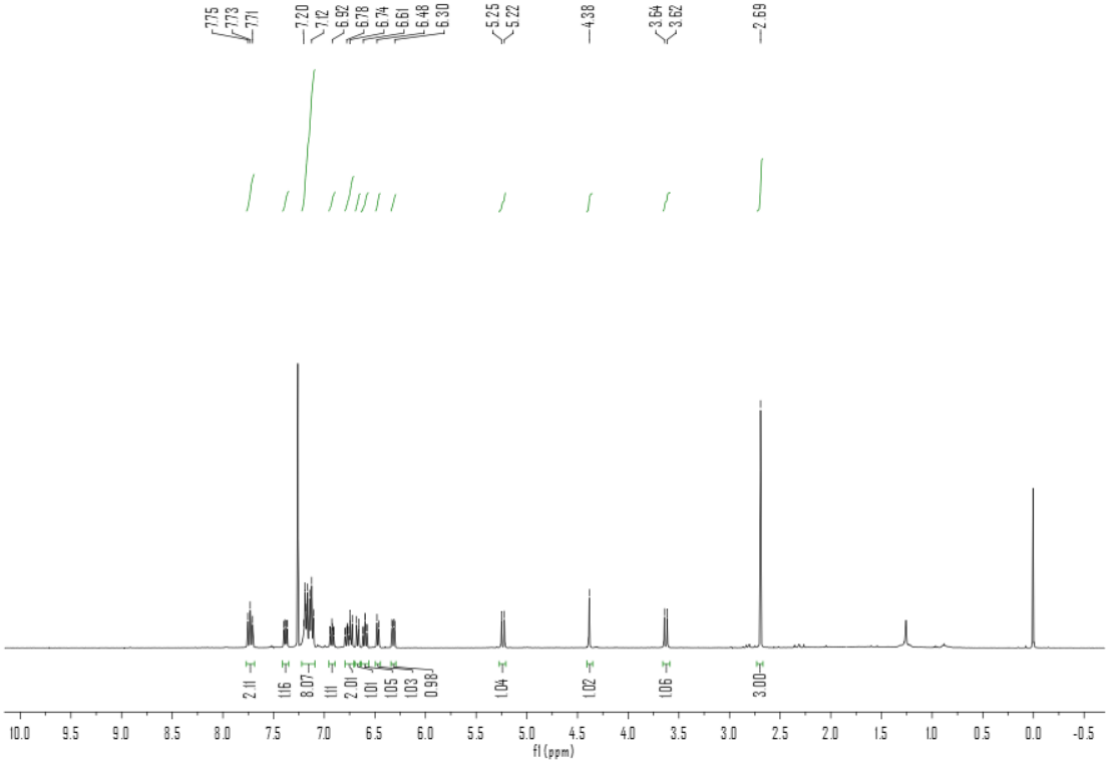


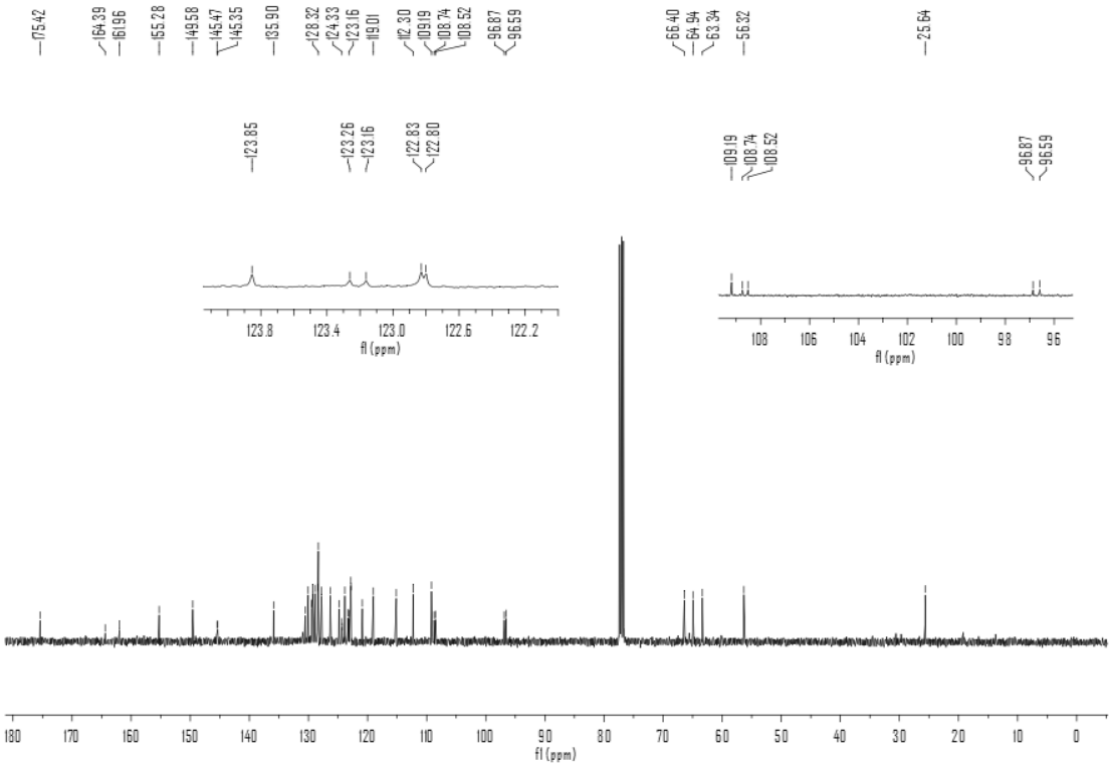

174.83
156.08
155.94
149.68
137.45
136.21
129.42
128.30
123.96
118.88
115.36
112.86
112.35
109.38
109.21
108.22
67.13
64.96
63.71
56.57
55.86
25.63
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3sa：

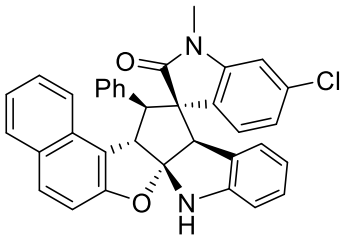


(*3R,6c'S,7'S,8a'R,13a'R*)-6-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 136 - 138 ℃, 45.1 mg, 86% yield, 99% ee, 10:1 d.r. $[\alpha]_D^{20}$ = +276.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 7.8 Hz, 2H), 7.37 – 6.31 (m, 1H), 7.21 – 7.06 (m, 8H), 6.95 – 6.86 (m, 1H), 6.79 – 6.62 (m, 3H), 6.58 (t, *J* = 7.5, 1H), 6.46 (d, *J* = 7.3 Hz, 1H), 6.30 (dd, *J* = 8.8, 2.3 Hz, 1H), 5.27 (s, 1H), 5.21 (d, *J* = 4.0, 1H), 4.37 (s, 1H), 3.62 (d, *J* = 11.2 Hz, 1H), 2.67 (s, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 163.1 (d, *J* = 243 Hz), 155.2, 149.5, 145.4 (d, *J* = 12 Hz), 135.9, 130.5, 130.0, 129.4, 129.2, 128.9, 128.4, 128.3, 127.7, 126.3, 124.8, 124.3, 124.3, 123.8, 123.2 (d, *J* = 10 Hz), 122.8 (d, J = 3 Hz), 120.8, 119.0, 115.1, 112.3, 109.1, 108.6 (d, J = 22 Hz), 96.7 (d, J = 28 Hz), 66.4, 64.9, 63.3, 56.3, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 20.451 min, t_{minor} = 9.309 min. HRMS (ESI): calcd for $C_{35}H_{25}FN_2O_2$ $[M + H]^+$, 525.1973; found, 525.1970.

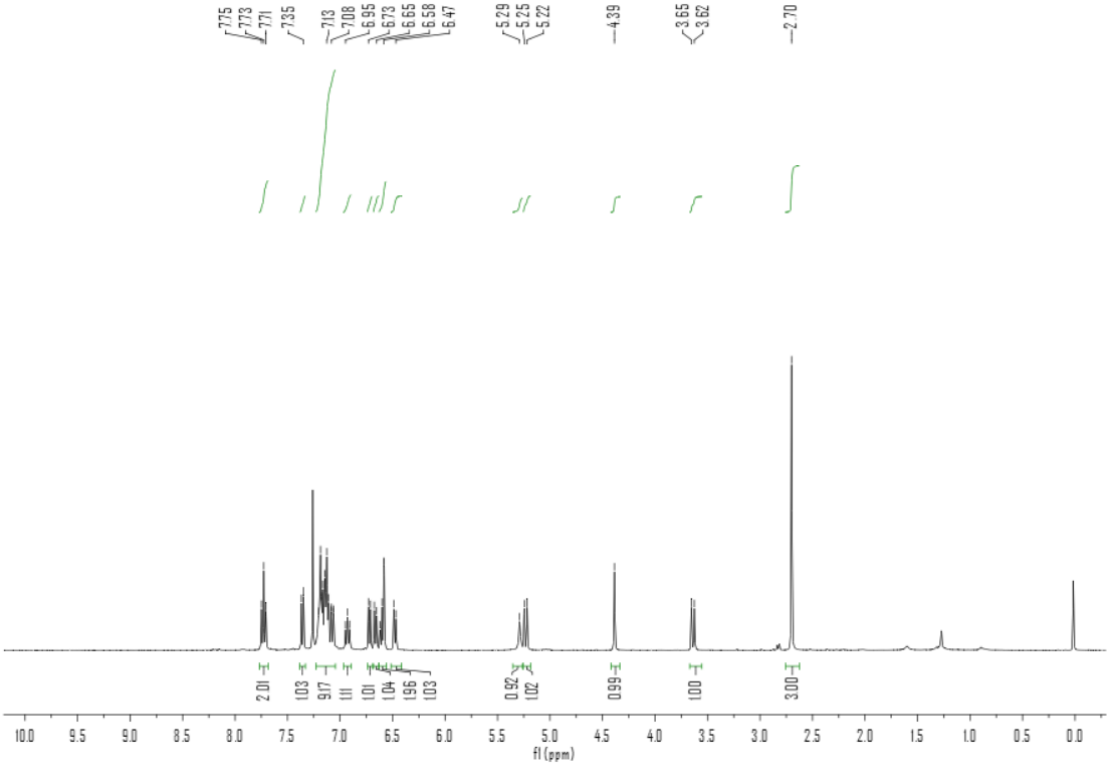


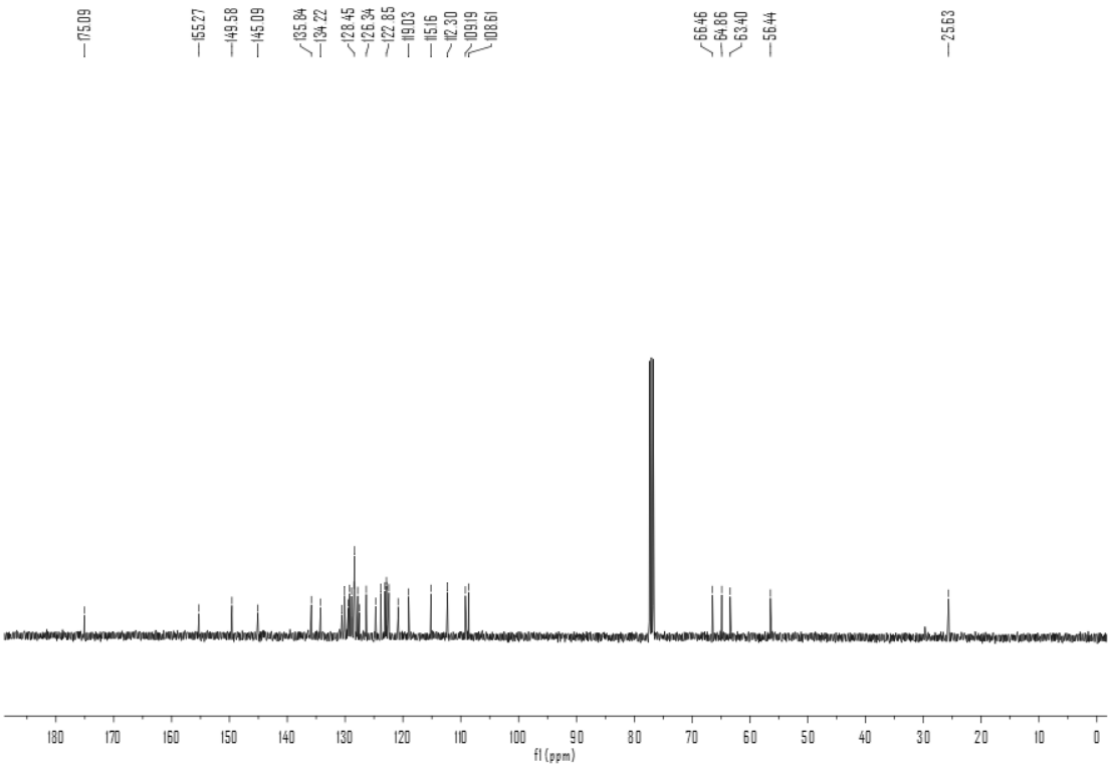

175.42
164.39
161.96
155.28
149.58
145.47
145.35
135.90
128.32
124.33
123.16
119.01
112.30
109.19
108.74
108.52
96.87
96.59
66.40
64.94
63.34
56.32
25.64
123.85
123.26
123.16
122.83
122.80
109.19
108.74
108.52
96.87
96.59
123.8
123.4
123.0
122.6
122.2
f1 (ppm)
108
106
104
102
100
98
96
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ta：

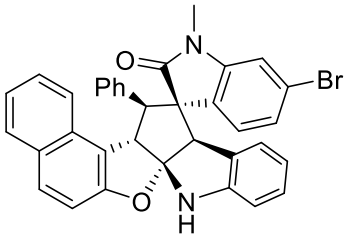


(*3R,6c'S,7'S,8a'R,13a'R*)-6-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 129 - 131 ℃, 47.6 mg, 88% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +284.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 9.2 Hz, 2H), 7.36 (t, *J* = 7.1 Hz, 1H), 7.22 – 7.05 (m, 9H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.68 – 6.56 (m, 3H), 6.47 (d, *J* = 7.3 Hz, 1H), 5.30 (s, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 4.38 (s, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 155.2, 149.5, 145.0, 135.8, 134.2, 130.5, 130.0, 129.4, 129.2, 128.9, 128.4, 128.3, 127.8, 127.5, 126.3, 124.7, 123.8, 123.1, 122.8, 122.8, 122.4, 120.8, 119.0, 115.1, 112.3, 109.1, 108.61 66.4, 64.8, 63.4, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 17.028 min, t_{minor} = 9.111 min. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1679.

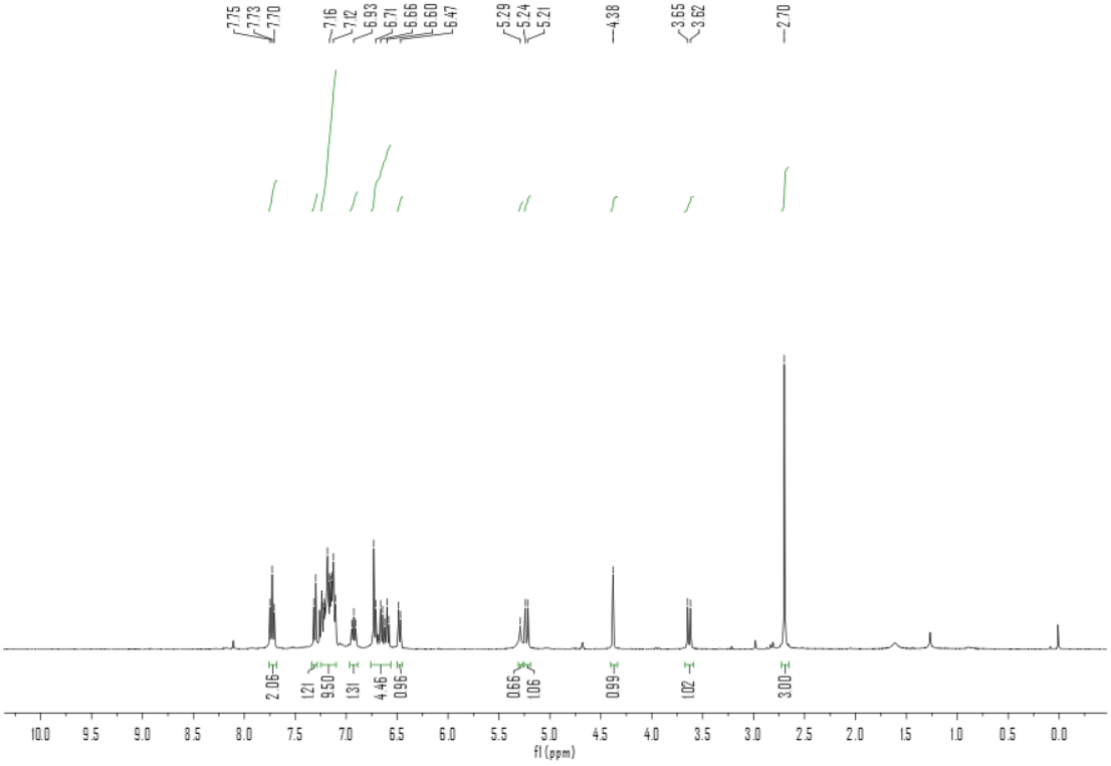


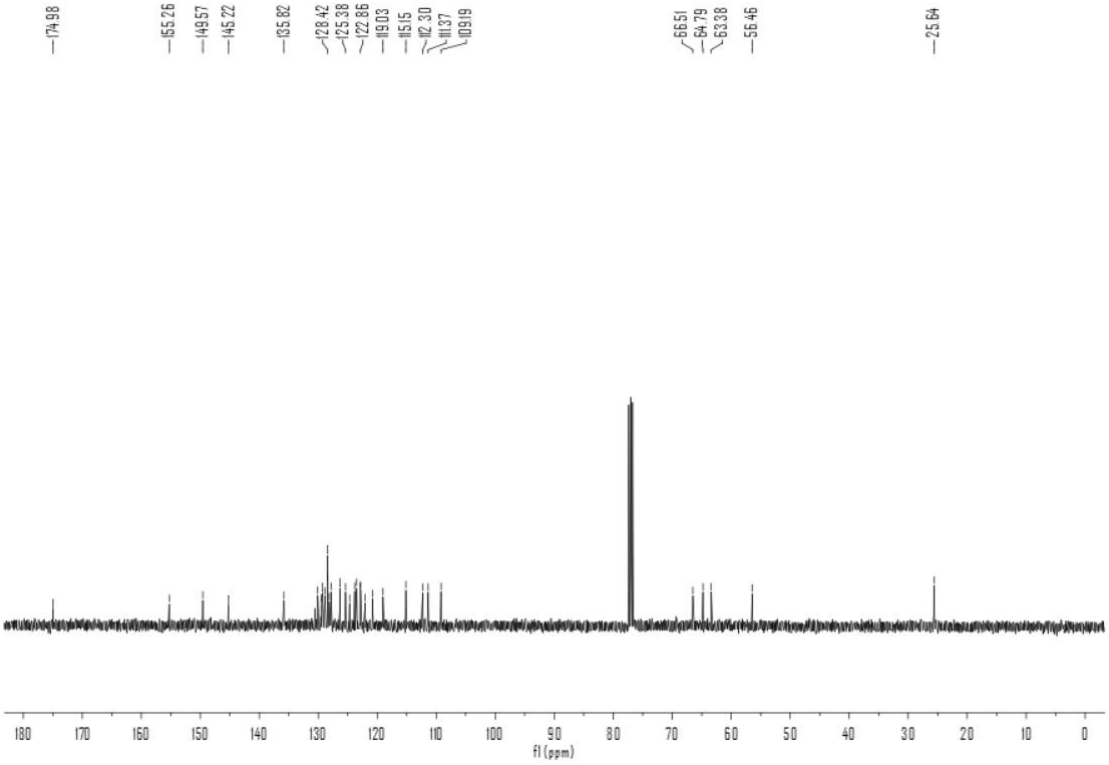

175.09
155.27
149.58
145.09
135.84
134.22
128.45
126.34
122.85
119.03
115.16
112.30
109.19
108.61
66.46
64.86
63.40
56.44
25.63
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ua：

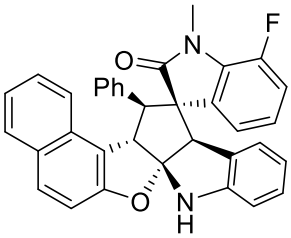


(*3R,6c'S,7'S,8a'R,13a'R*)-6-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 136 - 138 ℃, 49.7 mg, 85% yield, 94% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +264.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.26 – 7.09 (m, 9H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.74 – 6.57 (m, 4H), 6.48 (d, *J* = 7.3 Hz, 1H), 5.29 (s, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.38 (s, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 2.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.2, 149.5, 145.2, 135.8, 130.1, 129.4, 129.3, 128.9, 128.4, 128.4, 128.1, 127.8, 126.3, 125.3, 124.6, 123.8, 123.4, 122.8, 122.8, 122.0, 120.8, 119.0, 115.1, 112.3, 111.3, 109.1, 66.5, 64.7, 63.3, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 16.470 min, t_{minor} =9.430 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1170.

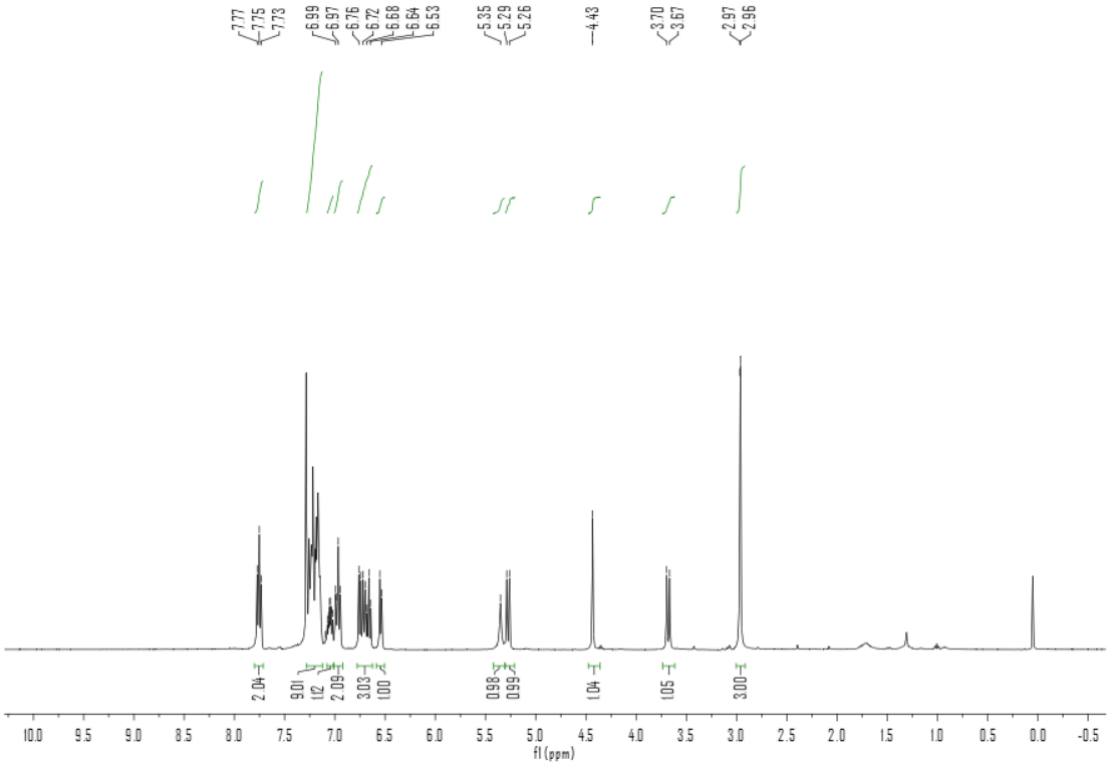


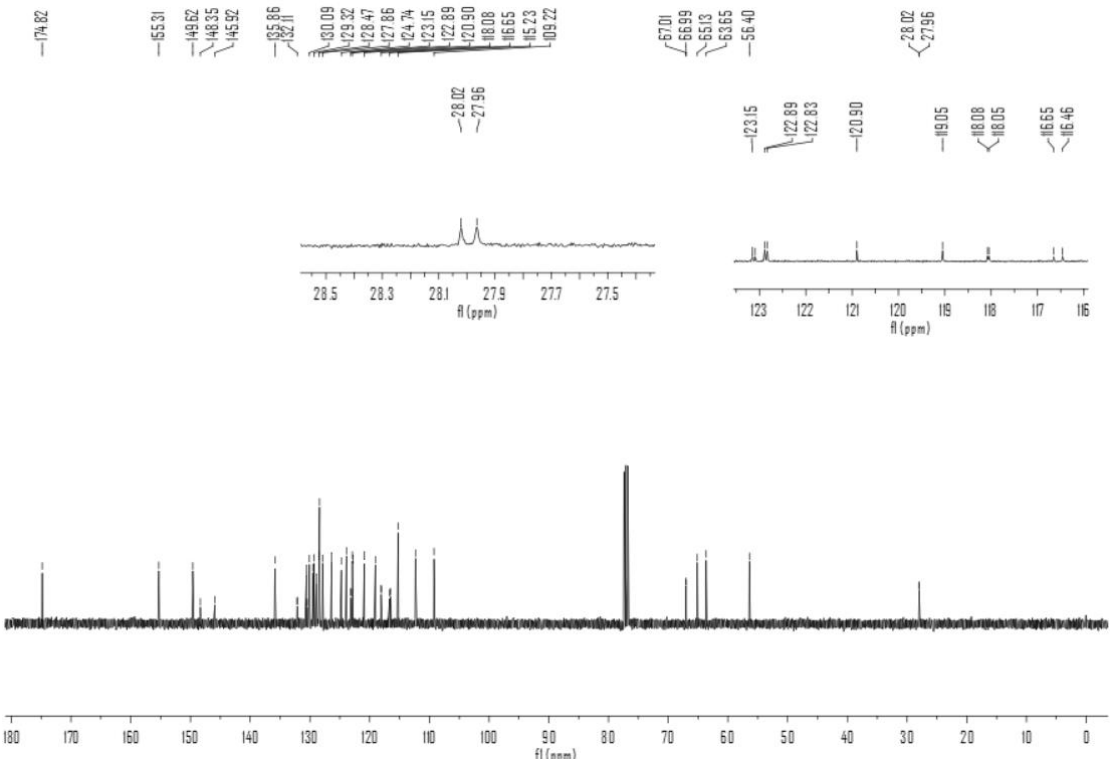

174.98
155.26
149.57
145.22
135.82
128.42
125.38
122.86
119.03
115.15
112.30
111.37
109.19
66.51
64.79
63.38
56.46
25.64
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3va：



(*3R,6c'S,7'S,8a'R,13a'R*)-7-fluoro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 185 - 187 ℃, 45.6 mg, 87% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +264.8 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.13 (m, 9H), 7.09 – 7.01 (m, 1H), 7.00 – 6.93 (m, 2H), 6.78 – 6.63 (m, 3H), 6.54 (d, *J* = 7.3 Hz, 1H), 5.35 (s, 1H), 5.27 (d, *J* = 11.2 Hz, 1H), 4.43 (s, 1H), 3.68 (d, *J* = 11.2 Hz, 1H), 2.97 (d, *J* = 4.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 155.3, 149.6, 147.1 (d, *J* = 243 Hz), 135.8, 132.1(d, *J* = 4 Hz), 130.5, 130.5, 130.4, 130.0, 129.4, 129.3, 128.9, 128.4, 128.3, 127.8, 126.3, 124.7, 123.8, 123.1 (d, *J* = 6 Hz), 122.8 (d, *J* = 6 Hz), 120.9, 119.0, 118.0 (d, *J* = 3 Hz), 116.5 (d, *J* = 19 Hz), 115.3, 112.3, 109.2, 67.0 (d, *J* = 2 Hz), 65.1, 63.6, 56.4, 28.0 (d, *J* = 6 Hz). HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 26.095 min, t_{minor} = 9.002 min. HRMS (ESI): calcd for $C_{35}H_{25}FN_2O_2$ $[M + H]^+$, 525.1973; found, 525.1977.




174.82
155.31
149.62
148.35
145.92
135.86
132.11
130.09
129.32
128.47
127.86
124.74
123.15
122.89
120.90
118.08
116.65
115.23
109.22
67.01
66.99
65.13
63.65
56.40
28.02
27.96
123.15
122.89
122.83
120.90
119.05
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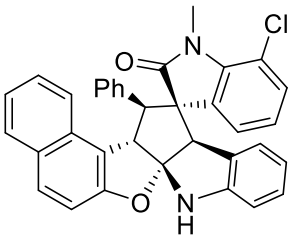
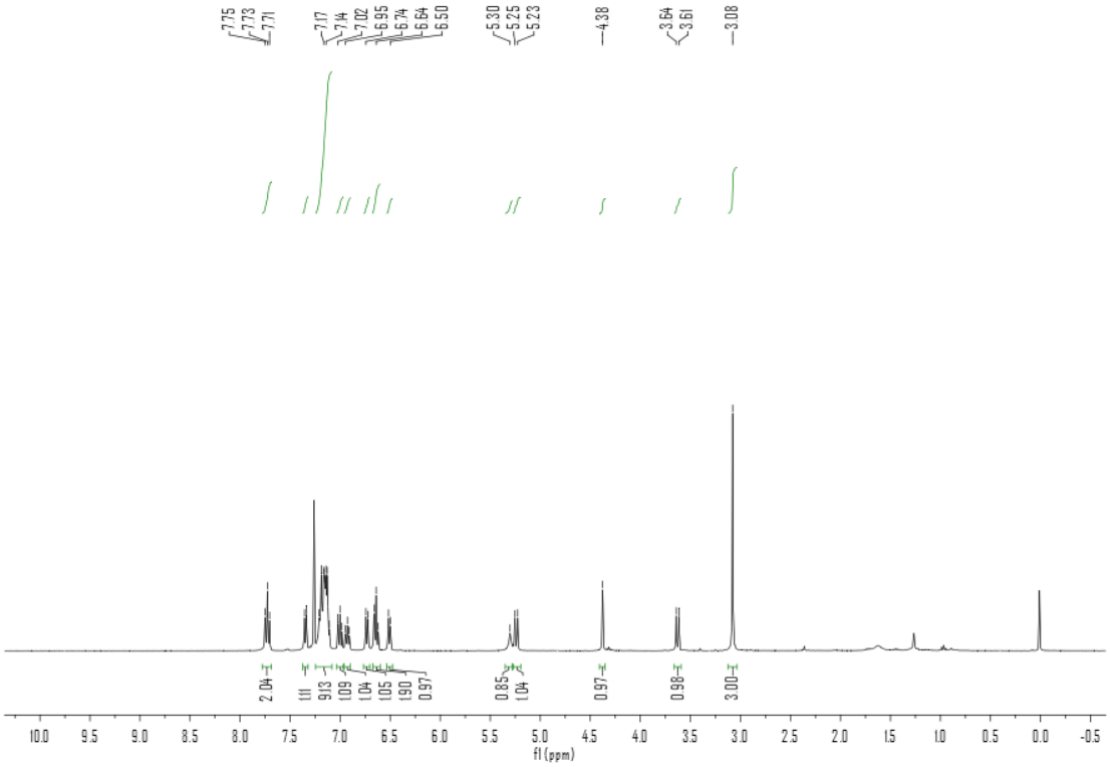
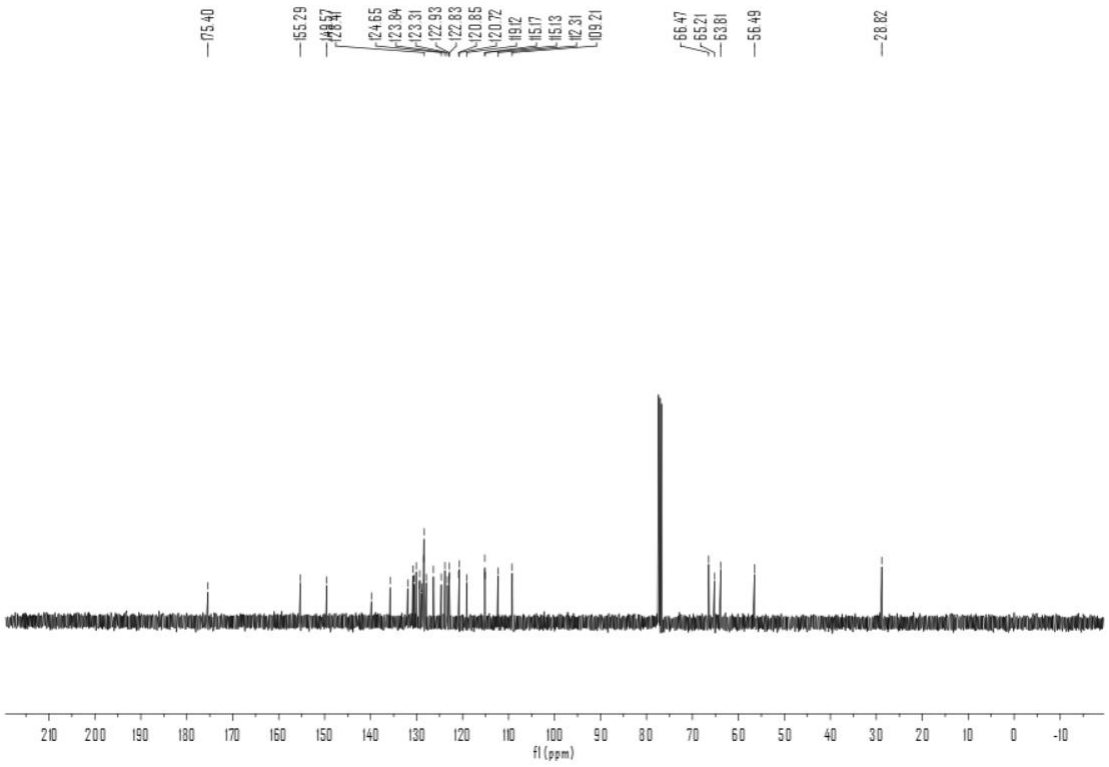
116.65
116.46
f1 (ppm)
f1 (ppm)

3wa：

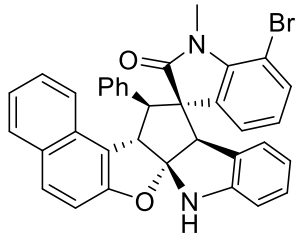


(*3R,6c'S,7'S,8a'R,13a'R*)-7-chloro-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 170 - 172 ℃, 46.5 mg, 86% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +272.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.9 Hz, 2H), 7.35 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.09 (m, 9H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 6.64 (t, *J* = 8.3 Hz, 2H), 6.51 (d, *J* = 7.3 Hz, 1H), 5.30 (s, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 4.38 (s, 1H), 3.63 (d, *J* = 11.2 Hz, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 155.2, 149.5, 139.8, 135.7, 131.9, 130.8, 130.5, 130.0, 129.4, 129.3, 128.9, 128.4, 128., 127.9, 126.3, 124.6, 123.8, 123.3, 122.9, 122.8, 120.8, 120.7, 119.1, 115.1, 115.1, 112.3, 109.2, 66.4, 65.2, 63.8, 56.4, 28.8. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 29.920 min, t_{minor} = 9.835 min. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1682.

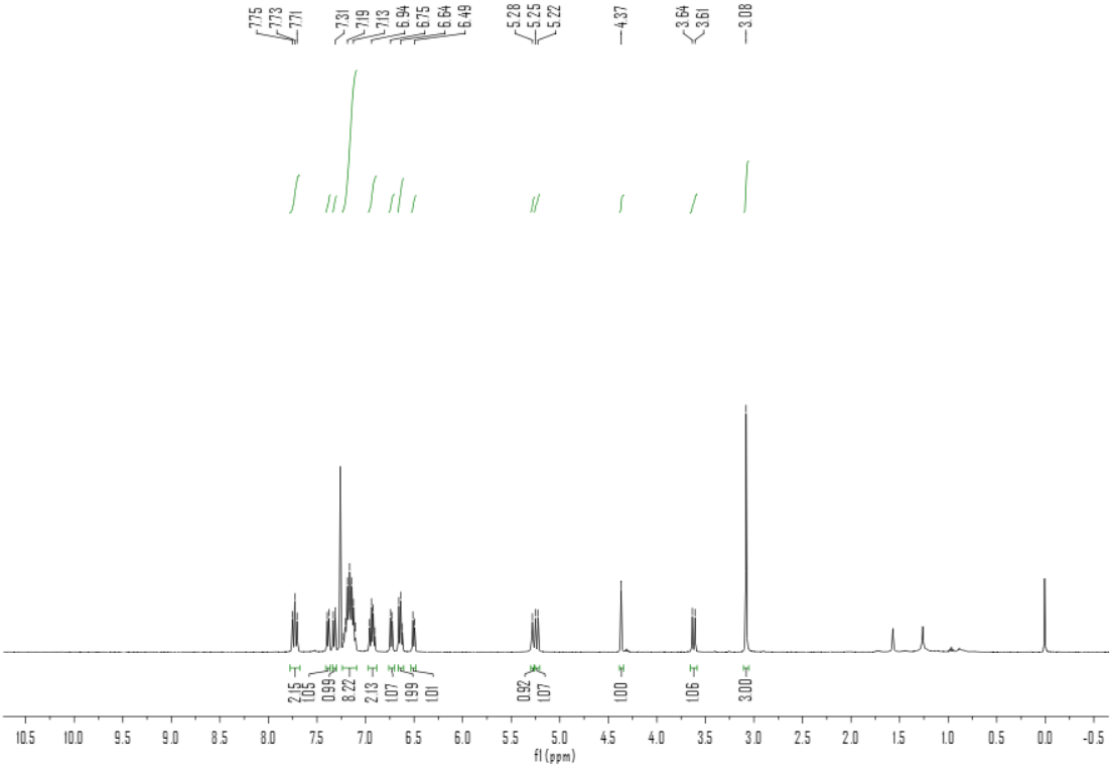


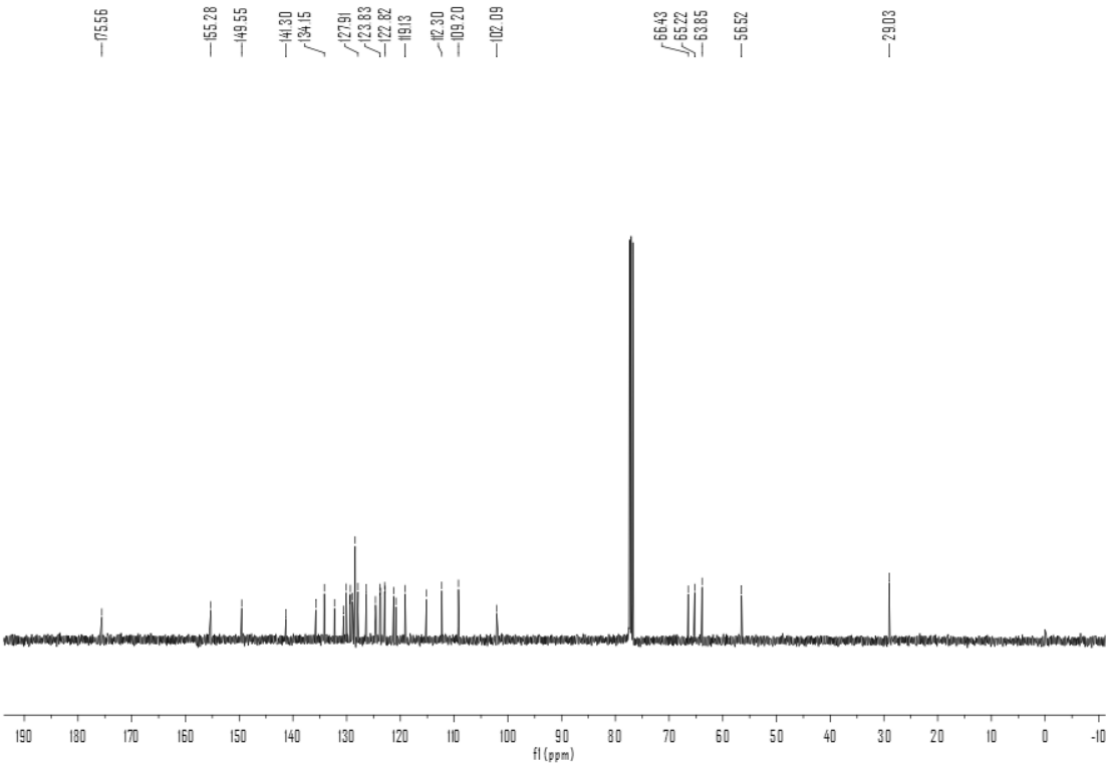

175.40
155.29
149.57
128.41
124.65
123.84
123.31
122.93
122.63
120.65
120.72
119.12
115.17
115.13
112.31
109.21
66.47
65.21
63.81
56.49
28.82
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3xa：

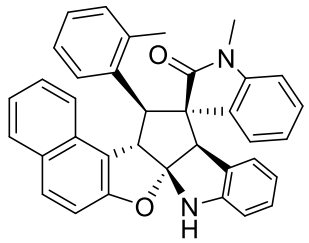


(*3R,6c'S,7'S,8a'R,13a'R*)-7-bromo-1-methyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 158 - 160 ℃, 50.3 mg, 86% yield, 97% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +281.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 9.4 Hz, 2H), 7.39 (d, *J* = 7.3 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.23 – 7.10 (m, 8H), 6.97 – 6.89 (m, 2H), 6.74 (d, *J* = 7.9 Hz, 1H), 6.66 – 6.61 (m, 2H), 6.50 (d, *J* = 7.3 Hz, 1H), 5.28 (s, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 4.37 (s, 1H), 3.62 (d, *J* = 11.2 Hz, 1H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 155.2, 149.5, 141.2, 135.7, 134.1, 132.2, 130.5, 130.0, 129.4, 129.3, 128.8, 128.4, 127.9, 126.3, 124.6, 123.8, 123.7, 122.9, 122.8, 121.2, 120.8, 119.1, 115.1, 112.3, 109.2, 102.1, 66.4, 65.2, 63.8, 56.5, 29.0. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 32.498 min, t_{minor} = 10.311 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1180.

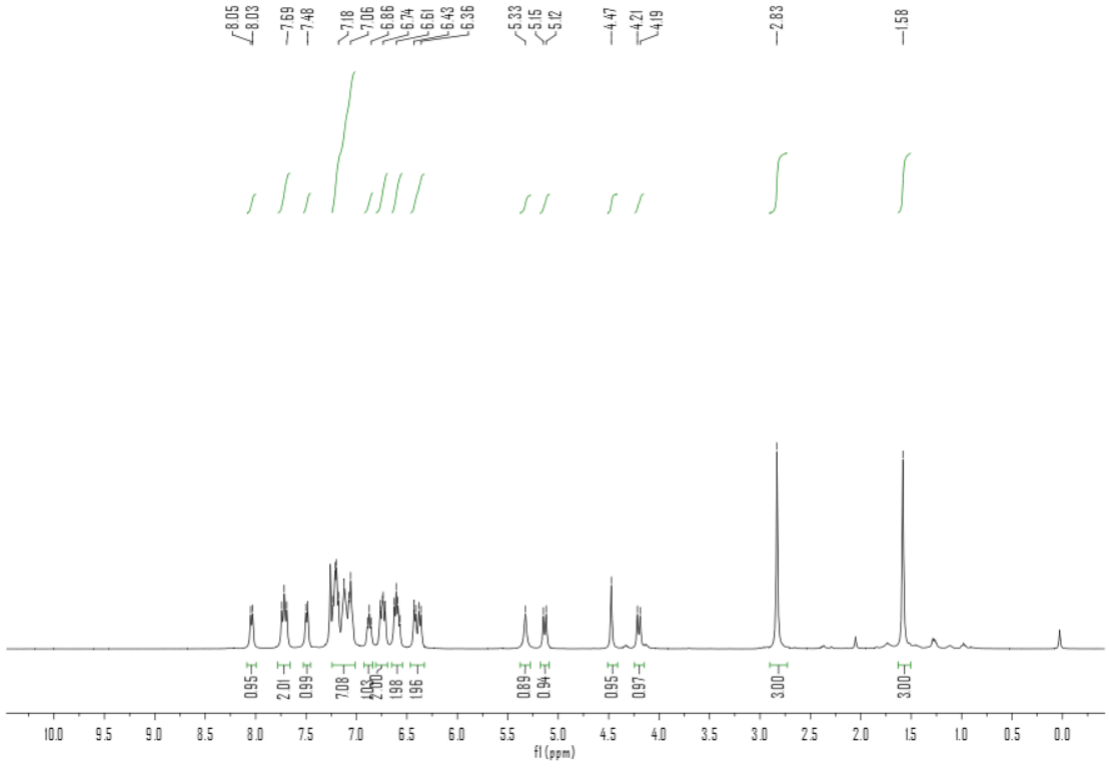


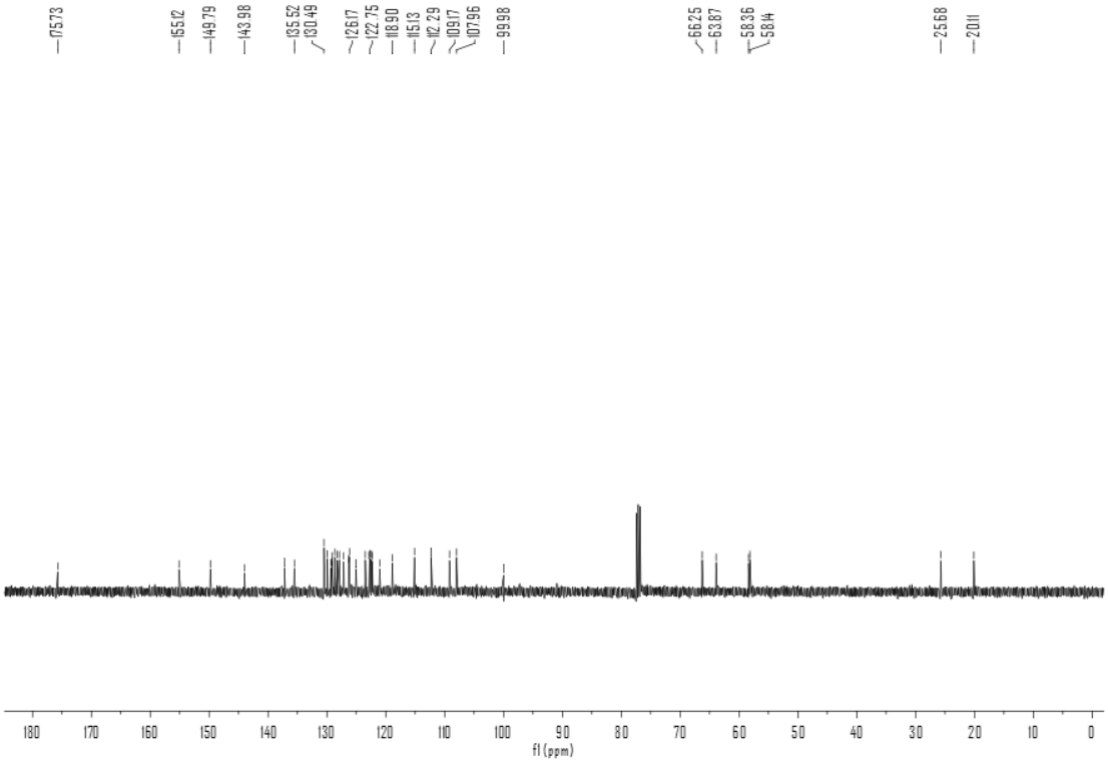

175.56
155.28
149.55
141.30
134.15
127.91
123.83
122.82
119.13
112.30
109.20
102.09
66.43
65.22
63.85
56.52
29.03
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3ab：



(*3R,6c'S,7'S,8a'R,13a'R*)-7-bromo-1-methyl-7'-(o-tolyl)-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 197- 199 ℃, 45.8 mg, 88% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +276.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.5 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.0 Hz, 1H), 7.24 – 7.01 (m, 7H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.81 – 6.69 (m, 2H), 6.65 – 6.55 (m, 2H), 6.40 (dd, *J* = 19.7, 7.6 Hz, 2H), 5.33 (s, 1H), 5.13 (d, *J* = 11.1 Hz, 1H), 4.47 (s, 1H), 4.20 (d, *J* = 11.1 Hz, 1H), 2.83 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 155.1, 149.7, 143.9, 137.2, 135.5, 130.4, 129.9, 129.3, 129.1, 129.0, 128.6, 128.2, 127.8, 127.1, 126.3, 126.1, 125.0, 123.4, 122.8, 122.7, 122.4, 122.2, 121.0, 118.9, 115.1, 112.2, 109.1, 107.9, 99.9, 66.2, 63.8, 58.3, 58.1, 25.6, 20.1. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 19.540 min, t_{minor} = 7.400 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2225.




175.73
155.12
149.79
143.98
135.52
130.49
126.17
122.75
118.90
115.13
112.29
109.17
107.96
99.98
66.25
63.87
58.36
58.14
25.68
20.11
180
170
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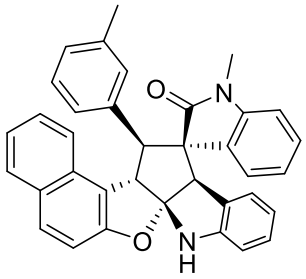
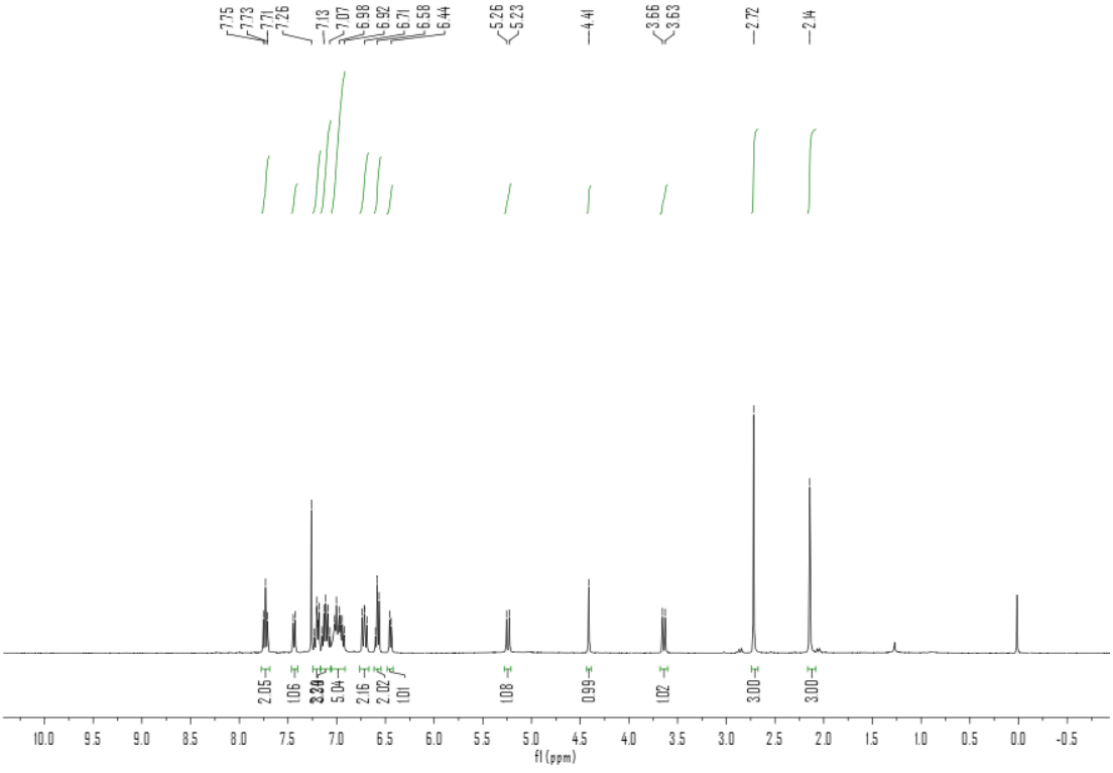
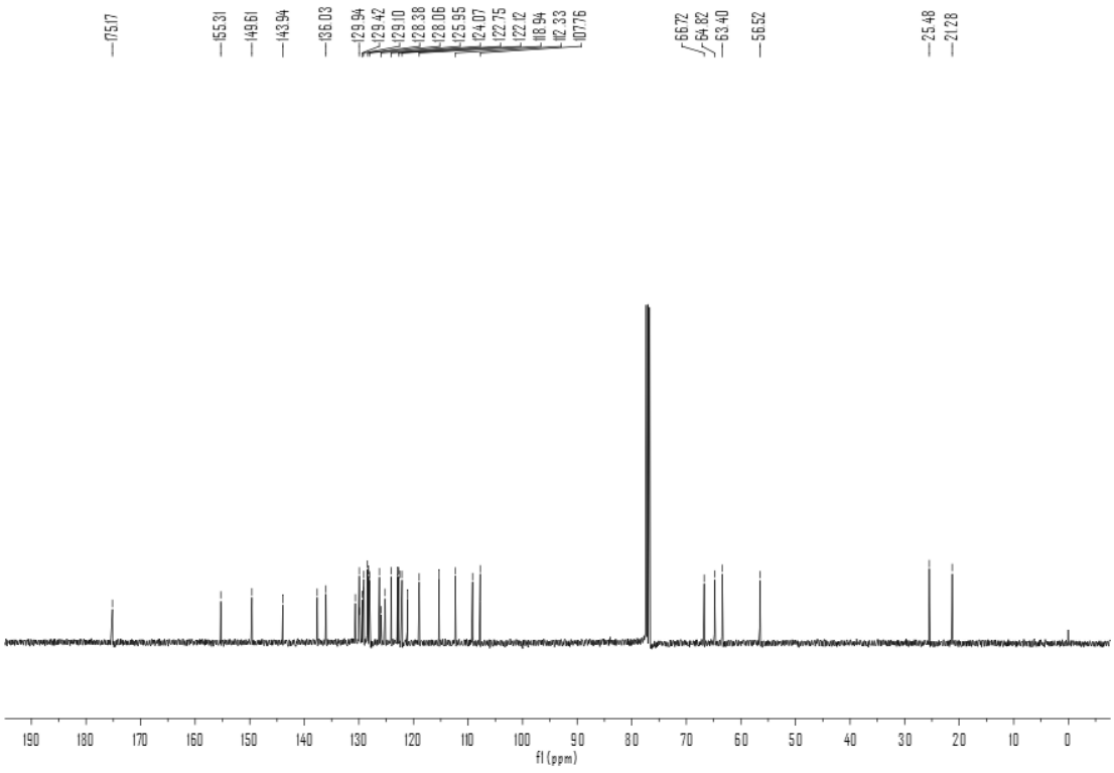
f1 (ppm)

3ac：



(*3R,6c'S,7'S,8a'R,13a'R*)-1-methyl-7'-(m-tolyl)-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 157 - 159 ℃, 45.4 mg, 87% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +269.6 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.7 Hz, 2H), 7.44 (d, *J* = 7.0 Hz, 1H), 7.24 – 6.90 (m, 10H), 6.72 (t, *J* = 7.9 Hz, 2H), 6.58 (t, *J* = 7.4 Hz, 2H), 6.45 (d, *J* = 6.9 Hz, 1H), 5.32 (s, 1H), 5.25 (d, *J* = 11.1 Hz, 1H), 4.42 (s, 1H), 3.65 (d, *J* = 11.1 Hz, 1H), 2.73 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 155.3, 149.6, 143.9, 137.6, 136.0, 130.6, 129.9, 129.8, 129.4, 129.1, 129.1, 128.4, 128.3, 128.2, 128.0, 126.2, 125.9, 125.1, 124.0, 122.9, 122.7, 122.5, 122.1, 121.1, 118.9, 115.3, 112.3, 109.1, 107.7, 66.7, 64.8, 63.4, 56.5, 25.4, 21.2. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 13.736 min, t_{minor} = 6.495 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2221. ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.17 – 7.06 (m, 3H), 7.05 – 6.92 (m, 5H), 6.72 (dd, *J* = 10.4, 8.5 Hz, 2H), 6.58 (t, *J* = 7.4 Hz, 2H), 6.45 (d, *J* = 7.3 Hz, 1H), 5.24 (d, *J* = 11.2 Hz, 1H), 4.41 (s, 1H), 3.64 (d, *J* = 11.2 Hz, 1H), 2.72 (s, 3H), 2.14 (s, 3H).




175.17
155.31
149.61
143.94
136.03
129.94
129.42
129.10
128.38
128.06
125.95
124.07
122.75
122.12
118.94
112.33
107.76
66.72
64.82
63.40
56.52
25.48
21.28
190
180
170
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110
100
90
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70
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30
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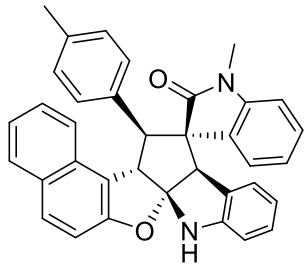
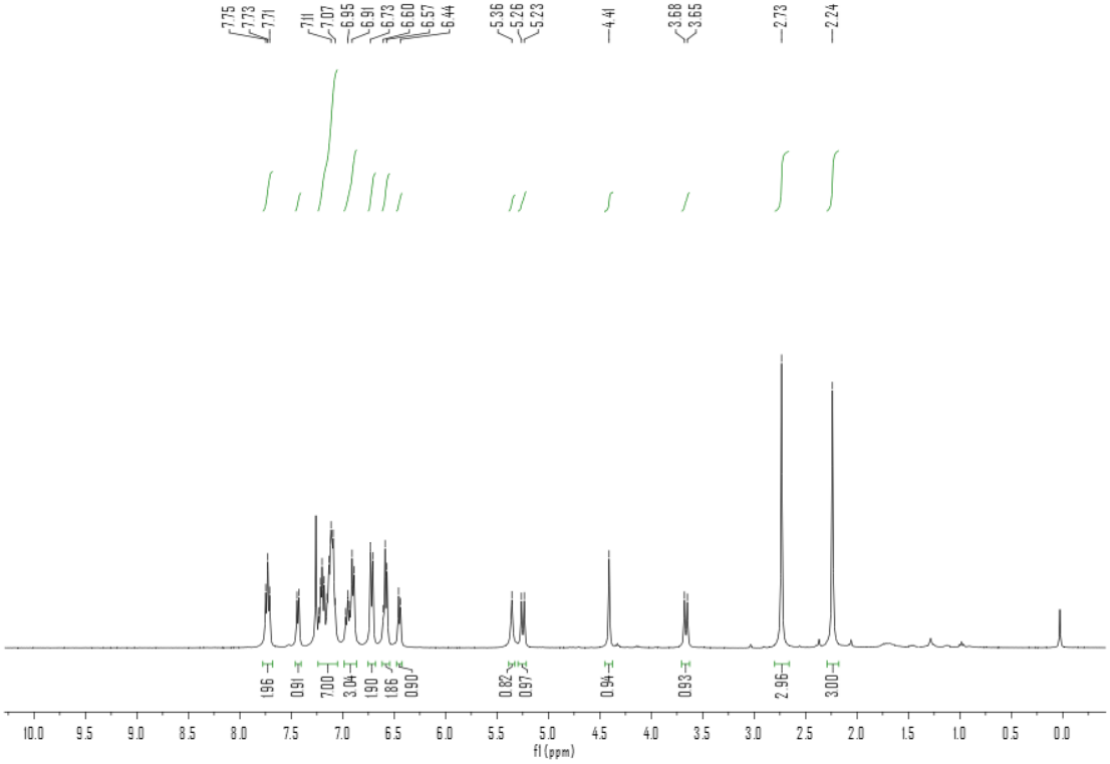
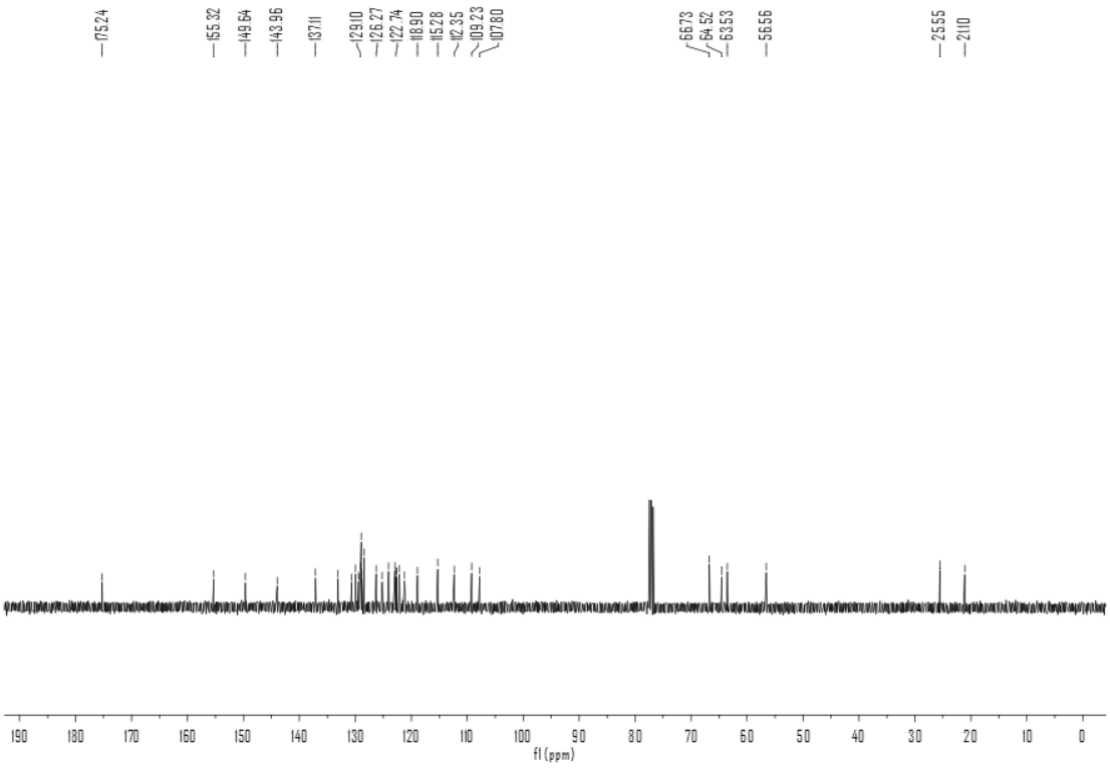
0
f1 (ppm)

3ad：



(3R,6c'S,7'S,8a'R,13a'R)-1-methyl-7'-(p-tolyl)-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 147 - 149 ℃, 45.8 mg, 88% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +295.1 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.24 – 7.05 (m, 7H), 6.98 – 6.86 (m, 3H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.59 (t, *J* = 7.1 Hz, 2H), 6.45 (d, *J* = 7.3 Hz, 1H), 5.36 (s, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 4.41 (s, 1H), 3.66 (d, *J* = 11.1 Hz, 1H), 2.73 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 155.3, 149.6, 143.9, 137.1, 133.0, 130.6, 129.9, 129.4, 129.2, 129.1, 128.9, 128.8, 128.4, 126.2, 125.1, 124.0, 122.9, 122.7, 122.5, 122.1, 121.2, 118.9, 115.2, 112.3, 109.2, 107.8, 66.7, 64.5, 63.5, 56.5, 25.5, 21.1. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 11.801 min, t_{minor} = 7.610 min. HRMS (ESI): calcd for $C_{36}H_{28}N_2O_2$ $[M + H]^+$, 521.2224; found, 521.2222.




175.24
155.32
149.64
143.96
137.11
129.10
126.27
122.74
118.90
115.28
112.35
109.23
107.80
66.73
64.52
63.53
56.56
25.55
21.10
190
180
170
160
150
140
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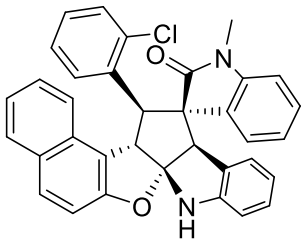
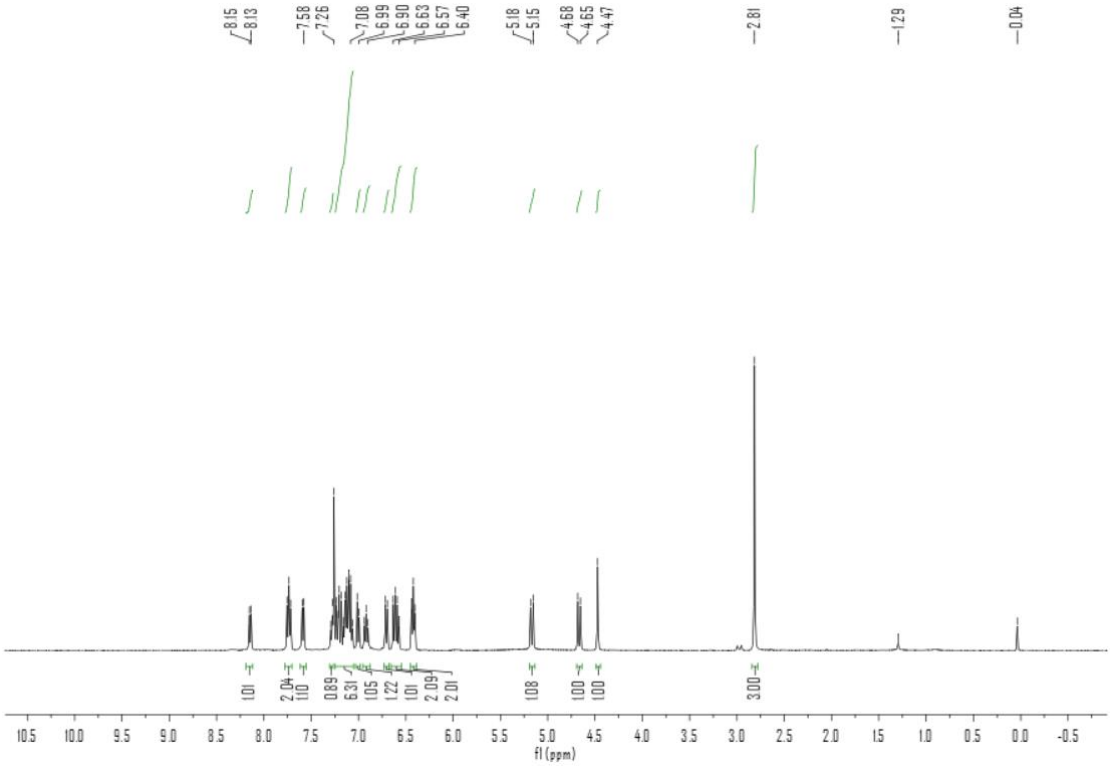
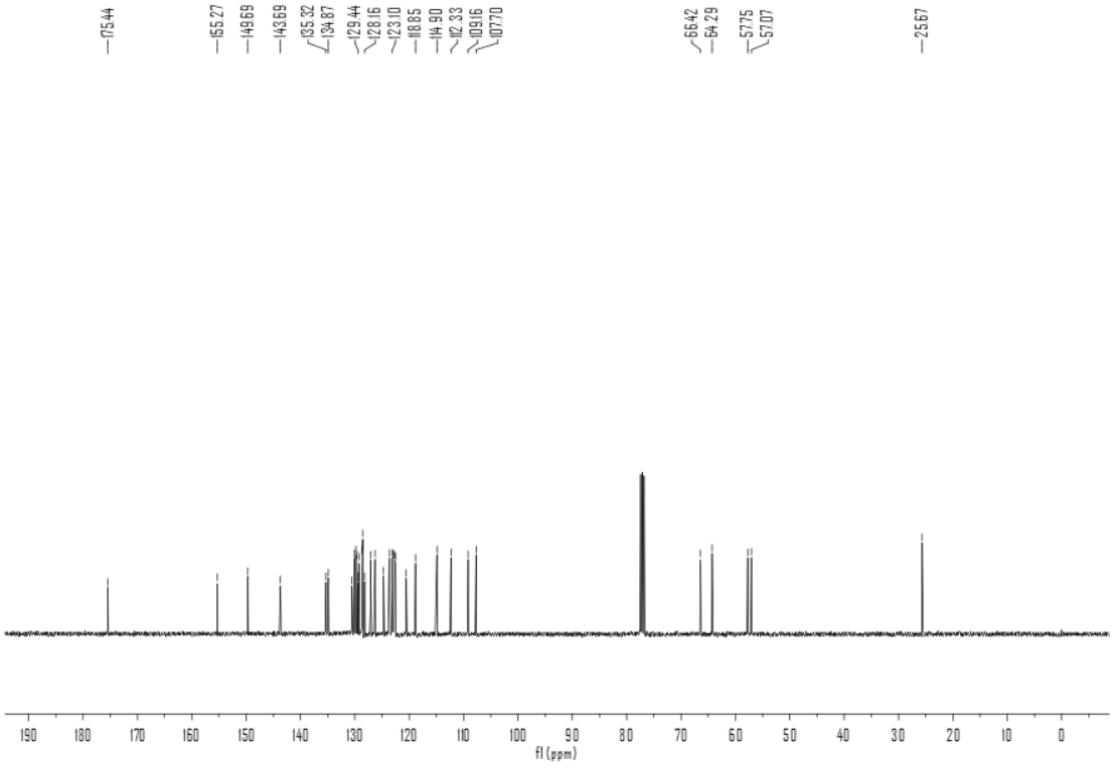
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ae:



(*3R,6c'S,7'R,8a'R,13a'R*)-7'-(2-chlorophenyl)-1-methyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 185 - 187 ℃, 46.5 mg, 86% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +286.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 2H), 7.78 – 7.70 (m, 2H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.31 – 7.27 (m, 1H), 7.24 – 7.05 (m, 6H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.9 Hz, 1H), 6.66 – 6.55 (m, 2H), 6.42 (t, *J* = 6.8 Hz, 2H), 5.17 (d, *J* = 11.3 Hz, 1H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.47 (s, 1H), 2.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 155.2, 149.7, 143.7, 135.3, 134.8, 130.5, 130.1, 129.7, 129.7, 129.4, 129.2, 128.6, 128.5, 128.5, 128.1, 127.1, 126.2, 124.7, 123.6, 123.1, 122.9, 122.7, 122.5, 120.5, 118.8, 114.9, 112.3, 109.1, 107.7, 66.4, 64.3, 57.7, 57.0, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 28.685 min, t_{minor} = 9.700. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1672.




175.44
155.27
149.69
143.69
135.32
134.87
129.44
128.16
123.10
118.85
114.90
112.33
109.16
107.70
66.42
64.29
57.75
57.07
25.67
190
180
170
160
150
140
130
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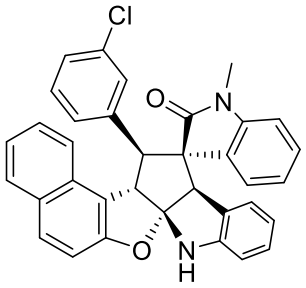
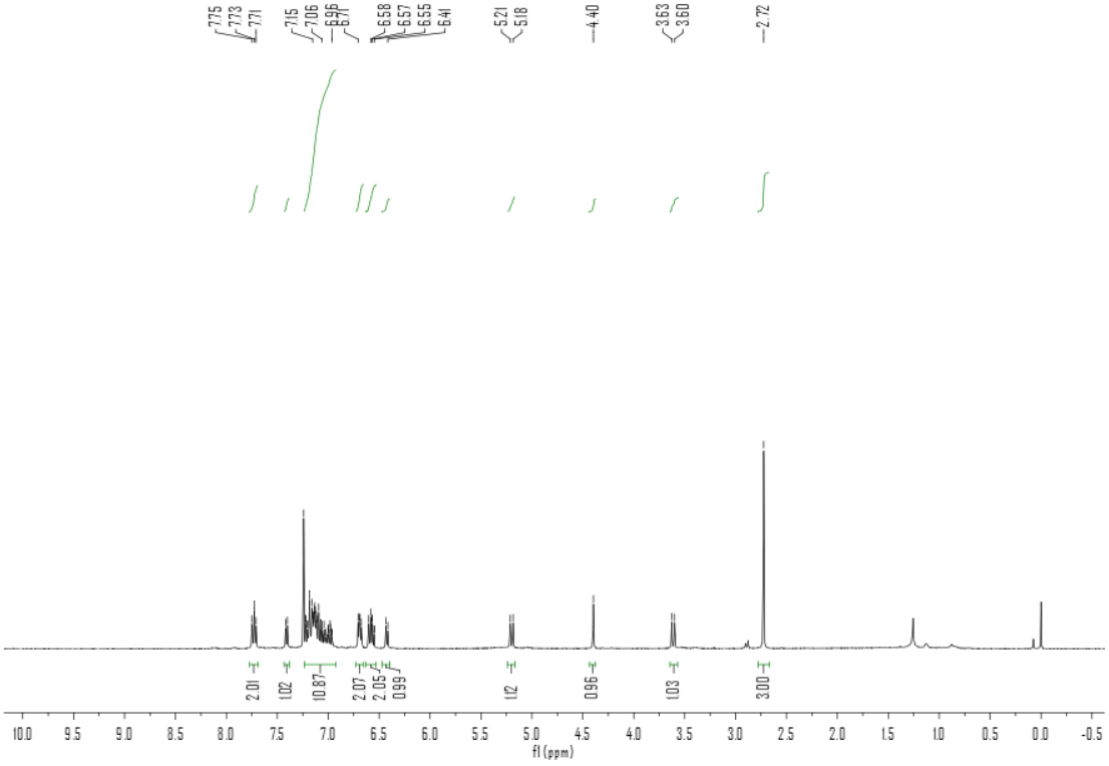
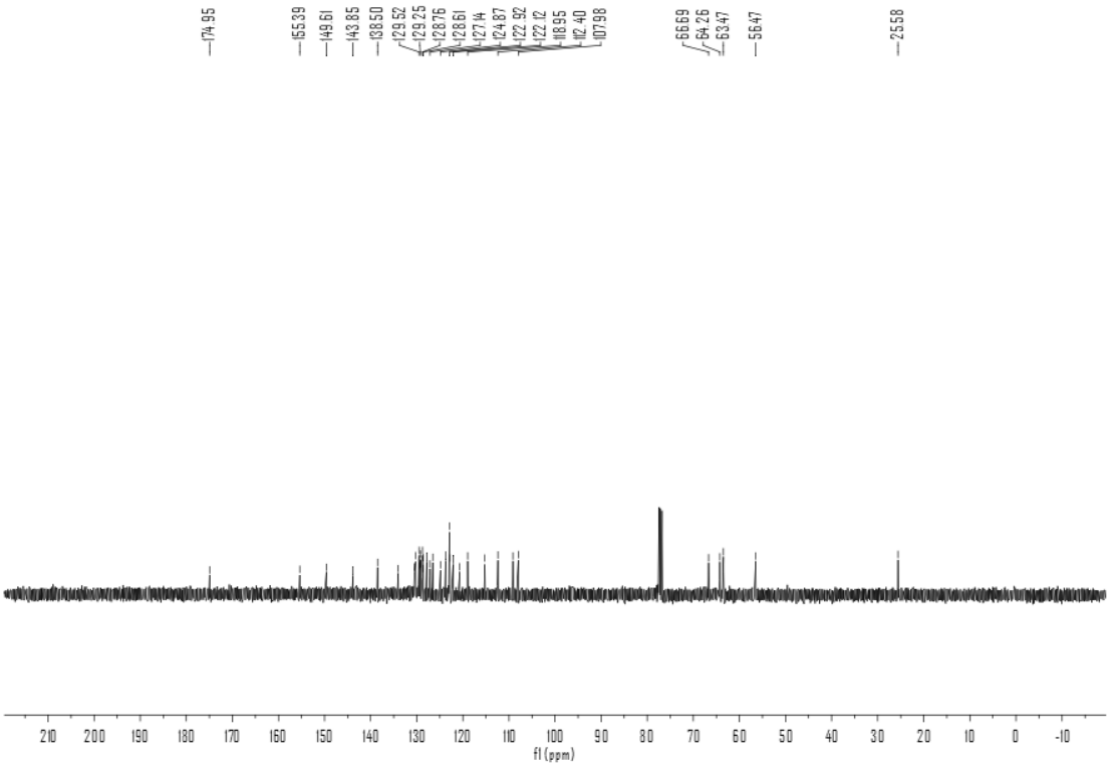
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3af:

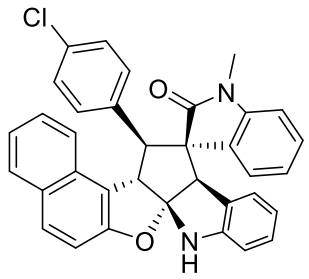


((*3R,6c'S,7'S,8a'R,13a'R*)-7'-(3-chlorophenyl)-1-methyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 161 - 163 ℃, 48.2 mg, 89% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +276.5 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (t, *J* = 7.8 Hz, 2H), 7.41 (d, *J* = 7.0 Hz, 0H), 7.23 – 6.94 (m, 11H), 6.73 – 6.64 (m, 2H), 6.62 – 6.53 (m, 2H), 6.42 (d, *J* = 7.3 Hz, 1H), 5.20 (d, *J* = 11.1 Hz, 1H), 4.40 (s, 1H), 3.61 (d, *J* = 11.2 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.3, 149.6, 143.8, 138.5, 134.0, 130.5, 130.2, 129.5, 129.4, 129.2, 129.1, 128.7, 128.6, 128.6, 127.8, 127.1, 126.5, 124.8, 123.7, 122.9, 122.8, 122.1, 120.6, 118.9, 115.2, 112.4, 109.1, 107.9, 66.6, 64.2, 63.4, 56.4, 25.5. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 15.241 min, t_{minor} = 7.690. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1671.

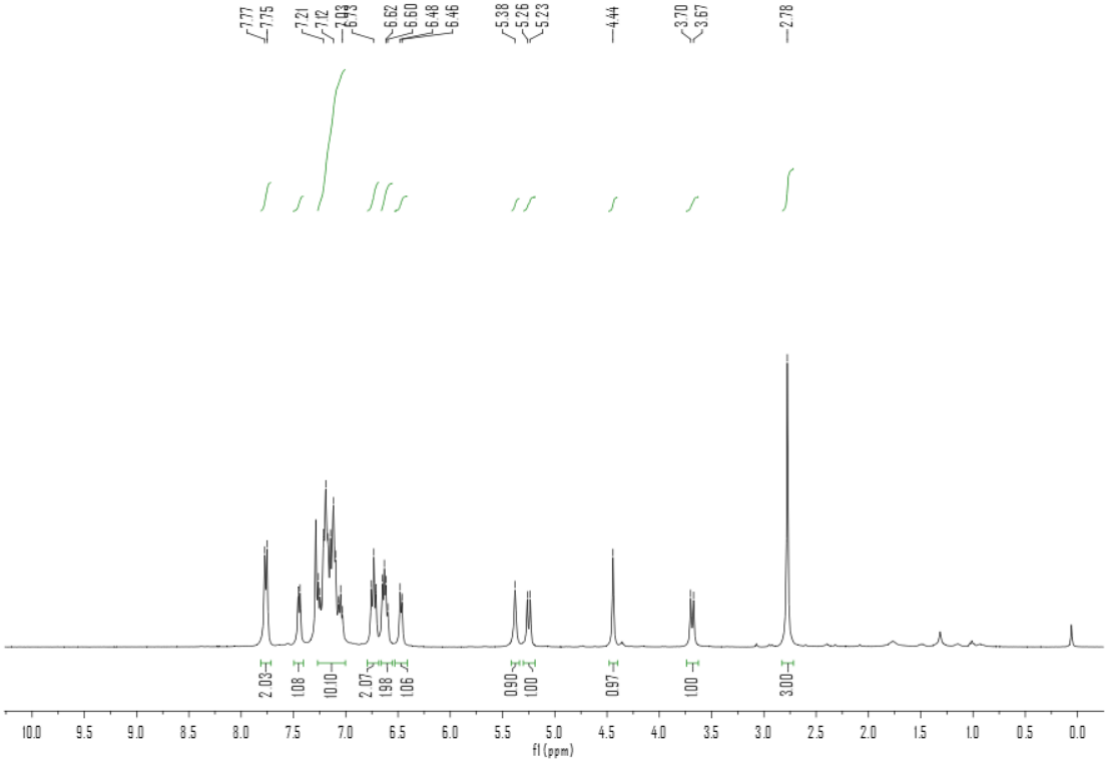


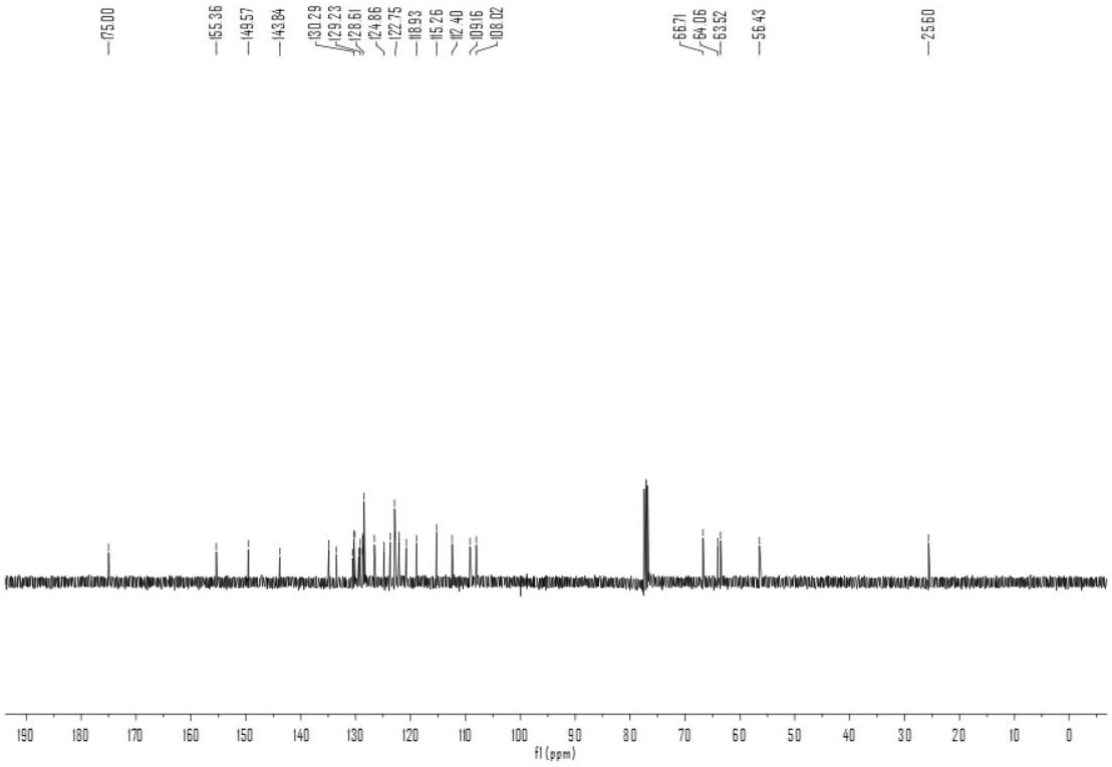

174.95
155.39
149.61
143.85
138.50
129.52
129.25
128.76
128.61
127.14
124.87
122.92
122.12
118.95
112.40
107.98
66.69
64.26
63.47
56.47
25.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

3ag:

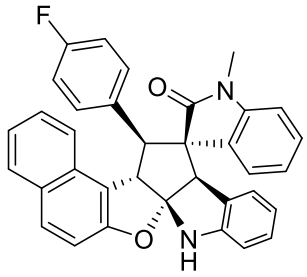


(*3R,6c'S,7'S,8a'R,13a'R*)-7'-(4-chlorophenyl)-1-methyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one: white solid, mp 194 - 196 ℃, 47.0 mg, 87% yield, 99% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +267.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.27 – 7.00 (m, 10H), 6.73 (t, *J* = 8.8 Hz, 2H), 6.66 – 6.55 (m, 2H), 6.47 (d, *J* = 7.1 Hz, 1H), 5.38 (s, 1H), 5.25 (d, *J* = 11.1 Hz, 1H), 4.44 (s, 1H), 3.69 (d, *J* = 11.1 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 155.3, 149.5, 143.8, 134.9, 133.4, 130.5, 130.2, 130.1, 129.4, 129.2, 128.7, 128.7, 128.6, 128.4, 126.5, 124.8, 123.7, 122.9, 122.7, 122.0, 120.7, 118.9, 115.2, 112.4, 109.1, 108.0, 66.7, 64.0, 63.5, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 40.441 min, t_{minor} = 37.019. HRMS (ESI): calcd for $C_{35}H_{25}ClN_2O_2$ $[M + H]^+$, 541.1677; found, 541.1674.

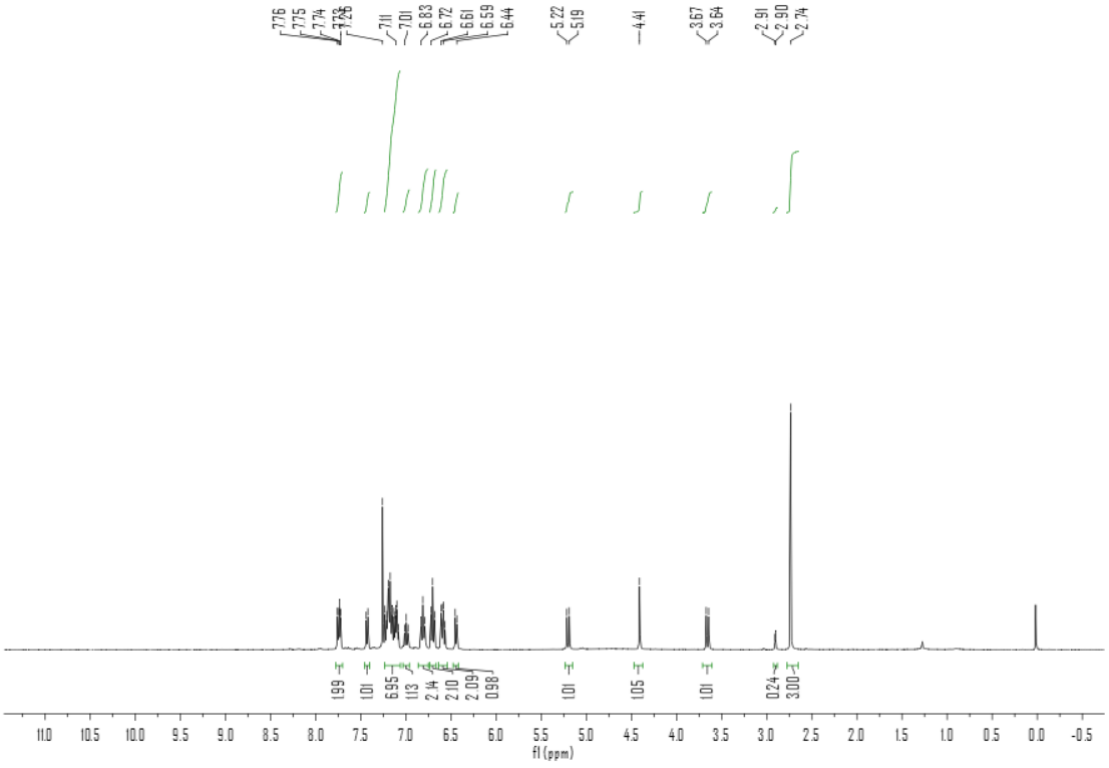


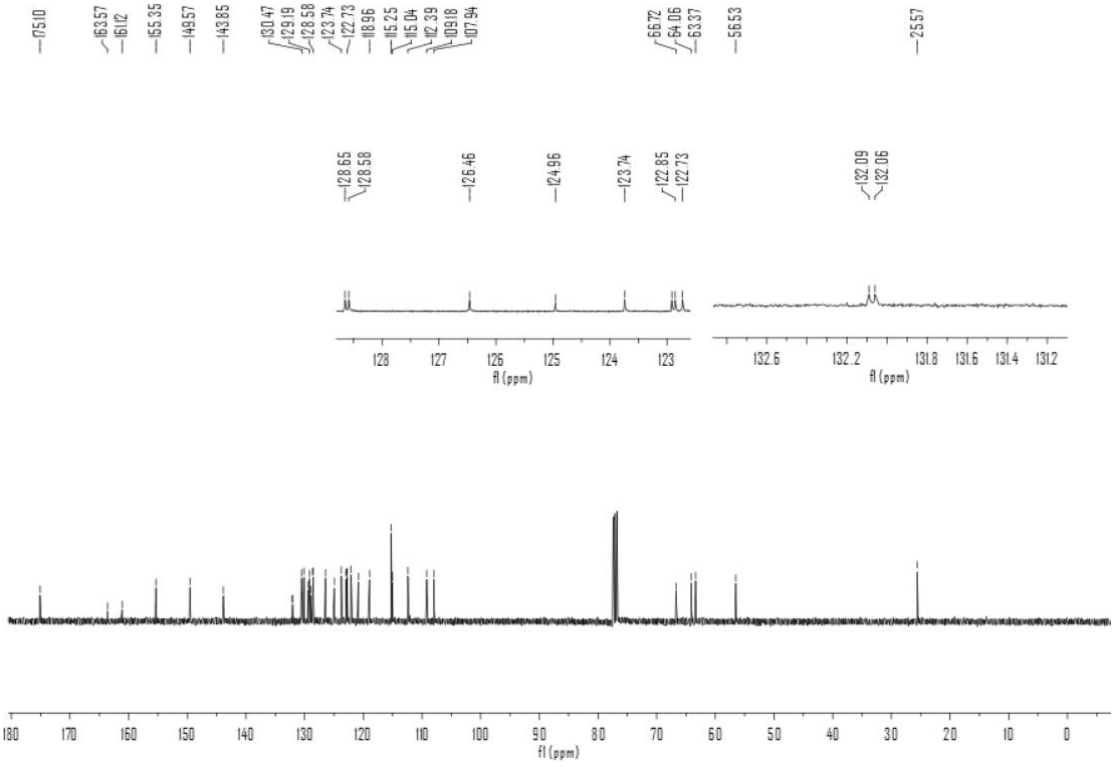

175.00
155.36
149.57
143.84
130.29
129.23
128.61
124.86
122.75
118.93
115.26
112.40
109.16
108.02
66.71
64.06
63.52
56.43
25.60
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ah:



(*3R,6c'S,7'S,8a'R,13a'R*)-7'-(4-fluorophenyl)-1-methyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 185- 187 ℃, 45.2 mg, 86% yield, 98% ee, 12:1 d.r. $[\alpha]_D^{20}$ = +344.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 6.0 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 1H), 7.24 – 7.06 (m, 7H), 7.04 – 6.96 (m, 1H), 6.81 (t, *J* = 7.5 Hz, 2H), 6.70 (t, *J* = 8.0 Hz, 2H), 6.64 – 6.54 (m, 2H), 6.45 (d, *J* = 6.6 Hz, 1H), 5.35 (s, 1H), 5.20 (d, *J* = 11.2 Hz, 1H), 4.42 (s, 1H), 3.66 (d, *J* = 10.9 Hz, 1H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 162.3 (d, *J* = 245 Hz), 155.3, 149.5, 143.8, 132.0 (d, *J* = 3 Hz), 130.5, 130.4, 130.1, 129.5, 129.1, 128.9, 128.6 (d, *J* = 7 Hz), 126.4, 124.9, 123.7, 122.8 (d, *J* = 6 Hz), 122.7, 122.0, 120.8, 118.9, 115.2, 115.0, 112.3, 109.1, 107.9, 66.7, 64.0, 63.3, 56.5, 25.57. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 19.433 min, t_{minor} = 24.662 min. HRMS (ESI): calcd for $C_{35}H_{25}FN_2O_2$ $[M + H]^+$, 525.1973; found, 525.1970.




175.10
163.57
161.12
155.35
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143.85
130.47
129.19
128.58
123.74
122.73
118.96
115.25
115.04
102.39
109.18
107.94
66.72
64.06
63.37
56.53
25.57
128.65
128.58
126.46
124.96
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122.73
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127
126
125
124
123
f1 (ppm)
132.6
132.2
131.8
131.6
131.4
131.2
f1 (ppm)
180
170
160
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110
100
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80
70
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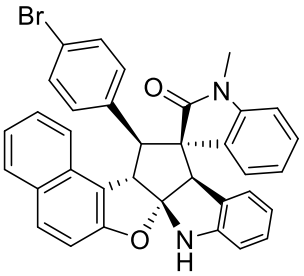
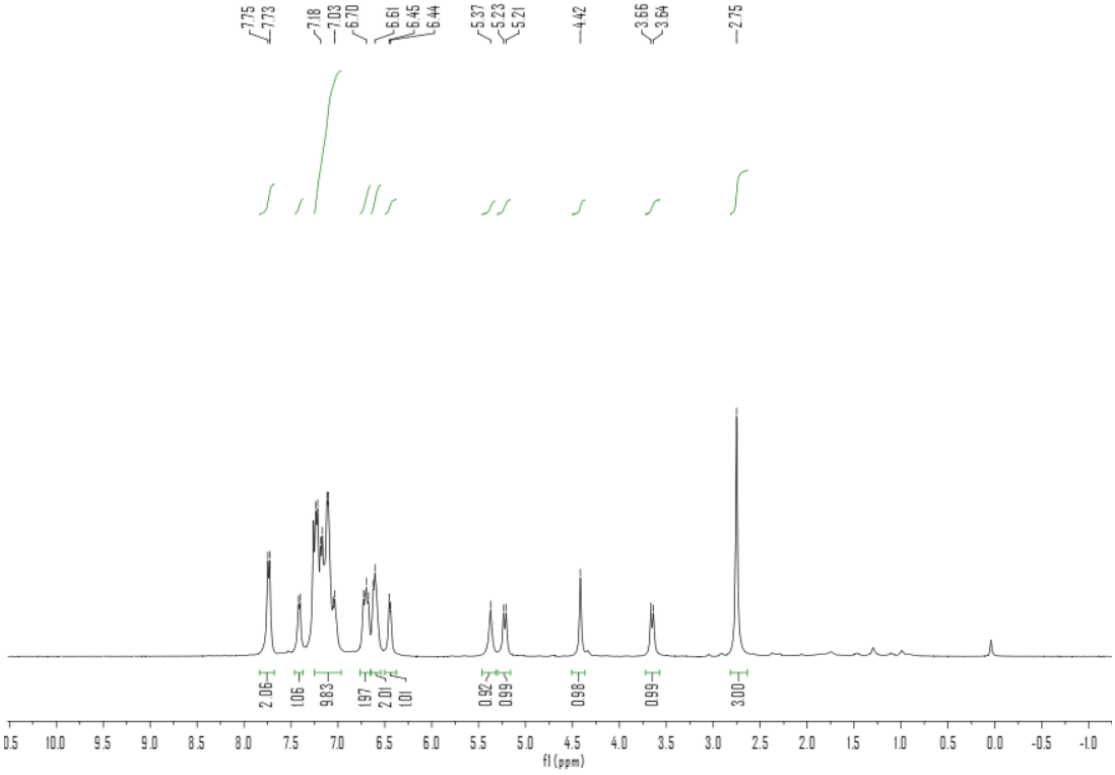
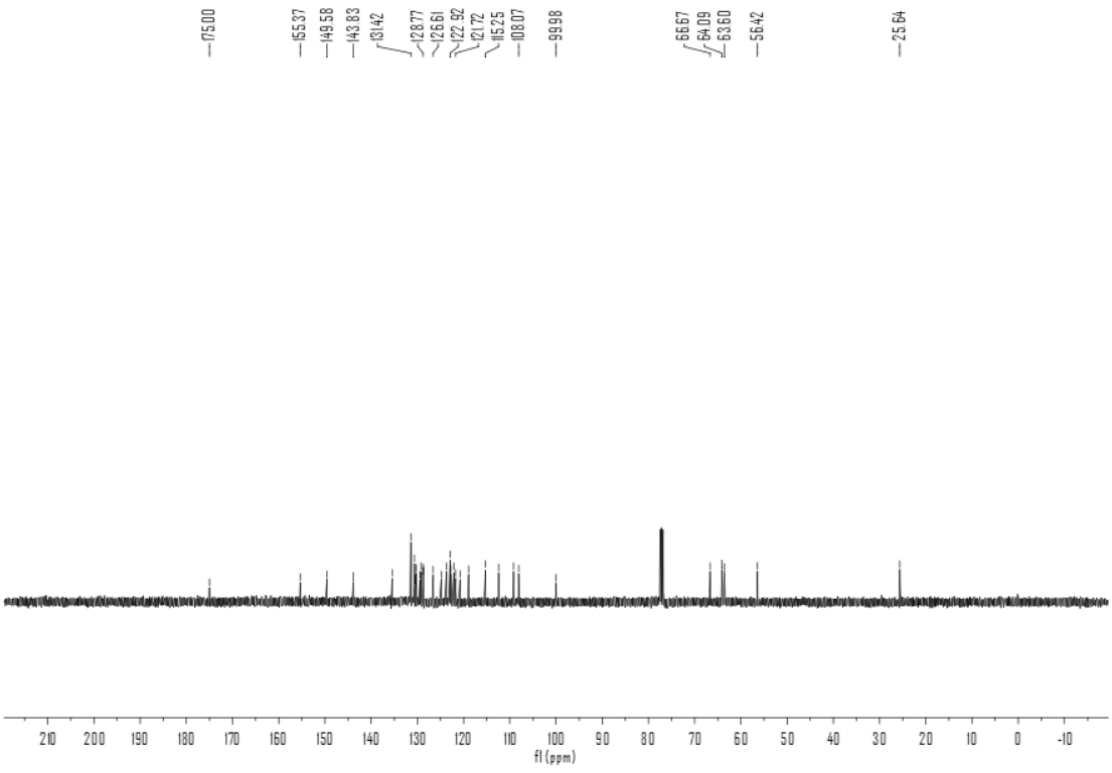
50
40
30
20
10
0
f1 (ppm)

3ai:

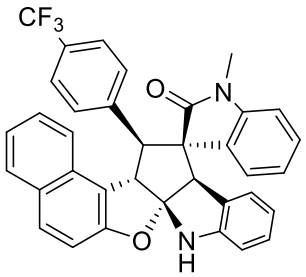


(*3R,6c'S,7'S,8a'R,13a'R*)-7'-(4-bromophenyl)-1-methyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 163 - 165 ℃, 49.7 mg, 85% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +269.8 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.9 Hz, 2H), 7.41 (d, *J* = 6.4 Hz, 1H), 7.25 – 6.97 (m, *J* = 33.2, 23.8, 7.4 Hz, 10H), 6.76 – 6.66 (m, 2H), 6.64 – 6.54 (m, 2H), 6.45 (d, *J* = 6.1 Hz, 1H), 5.37 (s, 1H), 5.22 (d, *J* = 10.7 Hz, 1H), 4.42 (s, 1H), 3.65 (d, *J* = 10.8 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 155.3, 149.5, 143.8, 135.4, 131.4, 130.6, 130.5, 130.2, 129.4, 129.2, 128.7, 128.7, 128.6, 126.6, 124.8, 123.7, 122.9, 122.7, 122.0, 121.7, 120.7, 118.9, 115.2, 112.4, 109.1, 108.0, 99.9, 66.6, 64.0, 63.6, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 21.043 min, t_{minor} = 17.755 min. HRMS (ESI): calcd for $C_{35}H_{25}BrN_2O_2$ $[M + H]^+$, 585.1172; found, 585.1174.

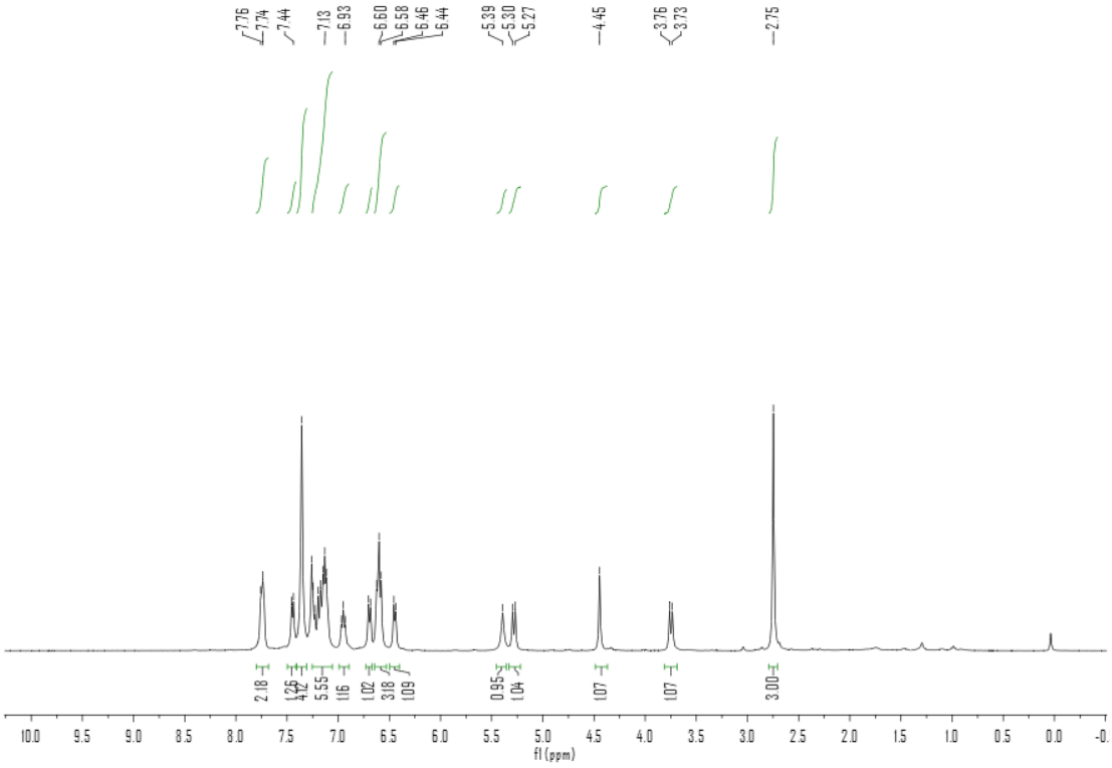


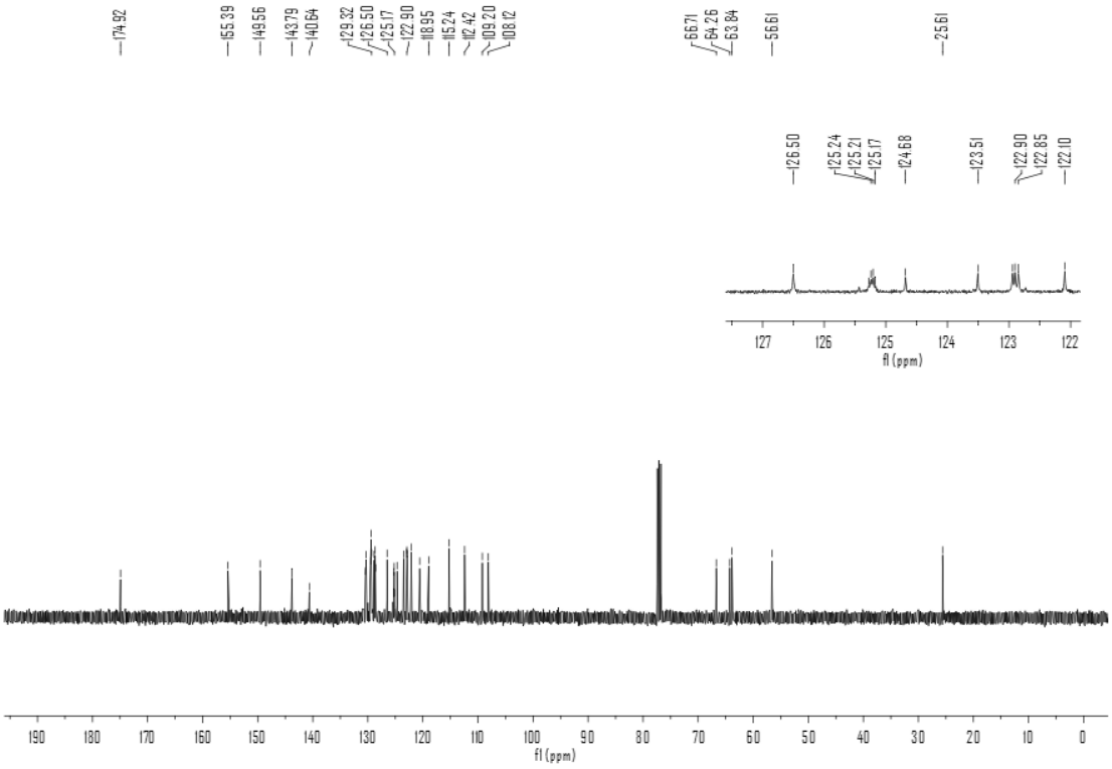

175.00
155.37
149.58
143.83
131.42
128.77
126.61
122.92
121.72
115.25
108.07
99.98
66.67
64.09
63.60
56.42
25.64
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3aj:

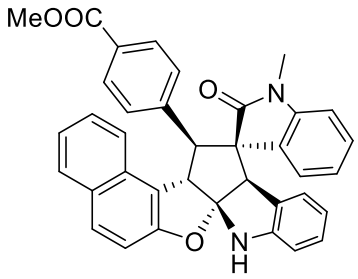


(*3R,6c'S,7'S,8a'R,13a'R*)-1-methyl-7'-(4-(trifluoromethyl)phenyl)-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 133 - 135 ℃, 49.5 mg, 86% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +351.7 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 2H), 7.45 (d, *J* = 7.0 Hz, 1H), 7.36 (s, 4H), 7.19 (m, 5H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.69 (d, *J* = 7.7 Hz, 1H), 6.60 (t, *J* = 8.8 Hz, 3H), 6.45 (d, *J* = 7.0 Hz, 1H), 5.39 (s, 1H), 5.28 (d, *J* = 11.0 Hz, 1H), 4.45 (s, 1H), 3.75 (d, *J* = 11.0 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 155.3, 149.5, 143.7, 140.6, 130.4, 130.2, 129.4, 129.4, 129.3, 128.8, 128.6, 128.5, 126.5, 125.2 (q, *J* = 4.0 Hz), 124.6, 123.5, 122.9, 122.9, 122.8, 122.1, 120.5, 118.9, 115.2, 112.4, 109.2, 108.1, 66.7, 64.2, 63.8, 56.6, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 11.440 min, t_{minor} = 14.316 min. HRMS (ESI): calcd for $C_{36}H_{25}F_3N_2O_2$ $[M + H]^+$, 575.1941; found, 575.1947.

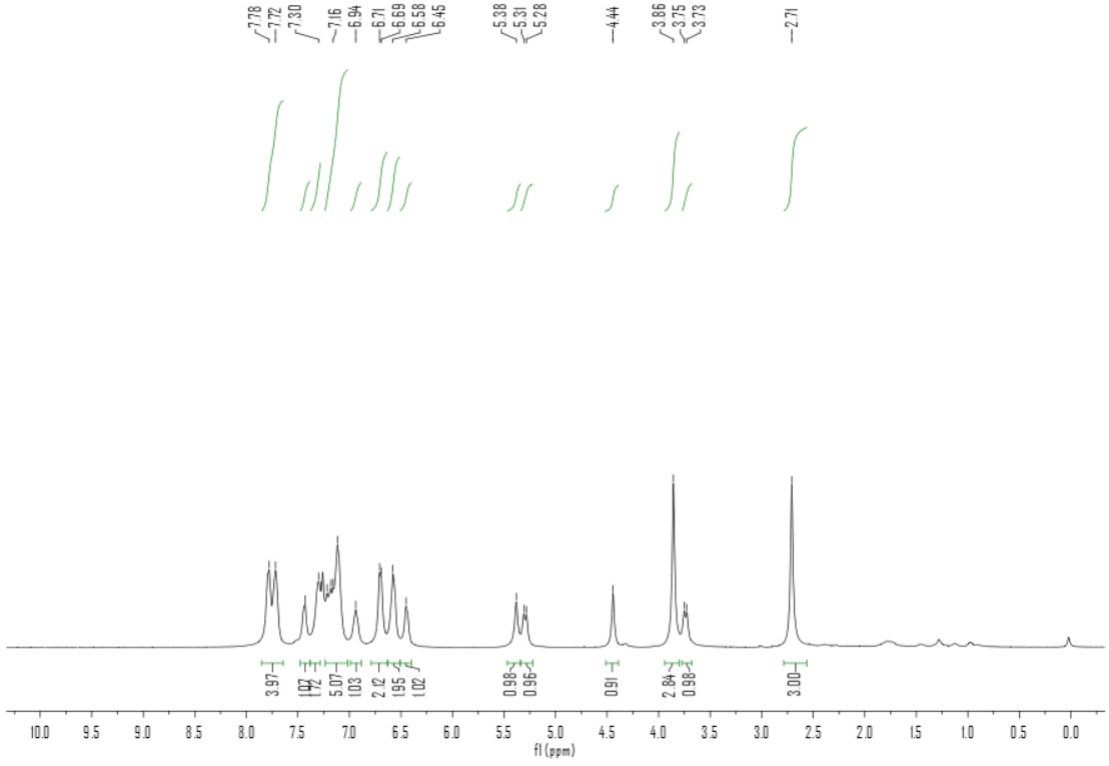


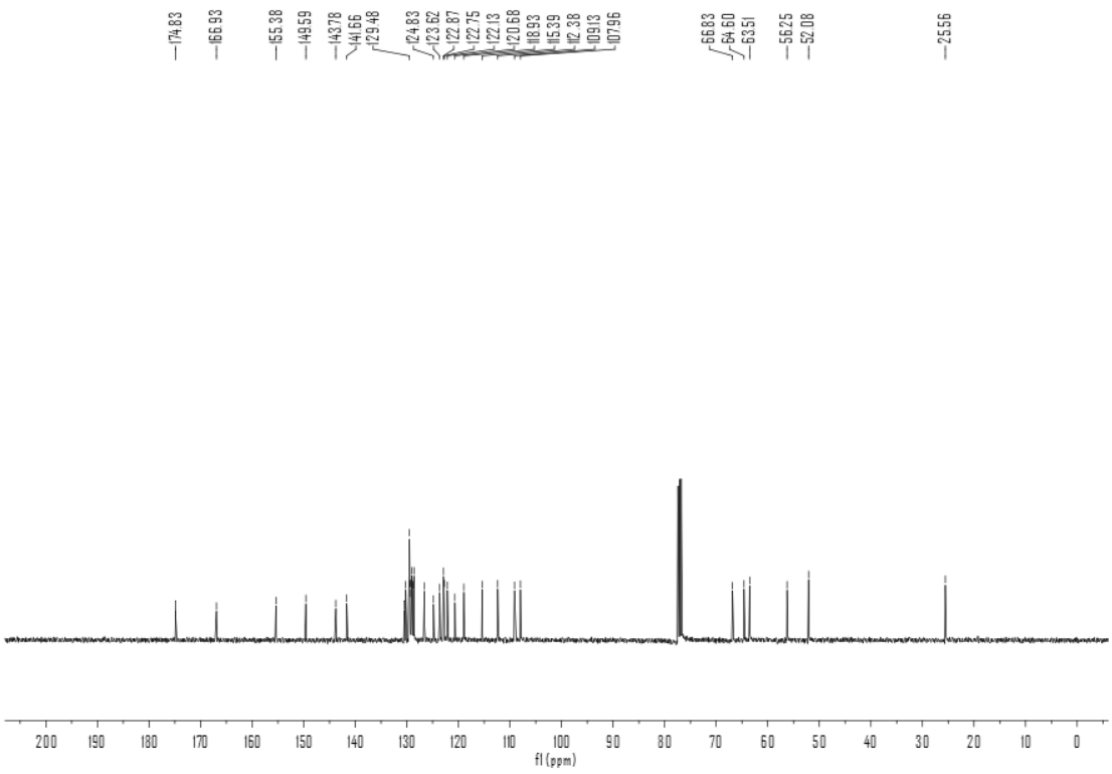

174.92
155.39
149.56
143.79
140.64
129.32
126.50
125.17
122.90
118.95
115.24
112.42
109.20
108.12
66.71
64.26
63.84
56.61
25.61
126.50
125.24
125.21
125.17
124.68
123.51
122.90
122.85
122.10
127
126
125
124
123
122
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3ak:

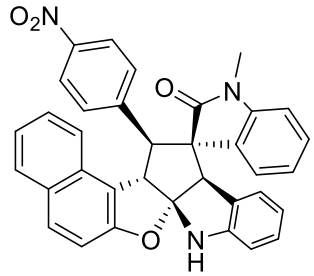


methyl-4-((*3R,6c'S,7'S,8a'R,13a'R*)-1-methyl-2-oxo-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-7'-yl)benzoate：white solid, mp 200 - 202 ℃, 46.6 mg, 87% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +287.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 24.7 Hz, 4H), 7.43 (s, 1H), 7.29 (s, 2H), 7.24 – 7.03 (m, 5H), 6.94 (s, 1H), 6.70 (d, *J* = 6.1 Hz, 2H), 6.58 (s, 1H), 6.45 (s, 1H), 5.38 (s, 1H), 5.29 (d, *J* = 10.0 Hz, 1H), 4.44 (s, 1H), 3.86 (s, 3H), 3.74 (d, *J* = 10.0 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 166.9, 155.3, 149.6, 143.7, 141.6, 130.4, 130.4, 130.2, 129.5, 129.3, 129.0, 129.0, 128.7, 126.5, 124.8, 123.6, 122.9, 122.9, 122.8, 122.7, 122.7, 122.1, 120.6, 118.9, 115.4, 112.3, 109.1, 107.9, 66.8, 64.6, 63.5, 56.2, 52.0, 25.5. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 39.309 min, t_{minor} = 31.456 min. HRMS (ESI): calcd for $C_{37}H_{28}BrN_2O_4$ $[M + H]^+$, 565.2122; found, 565.2124.

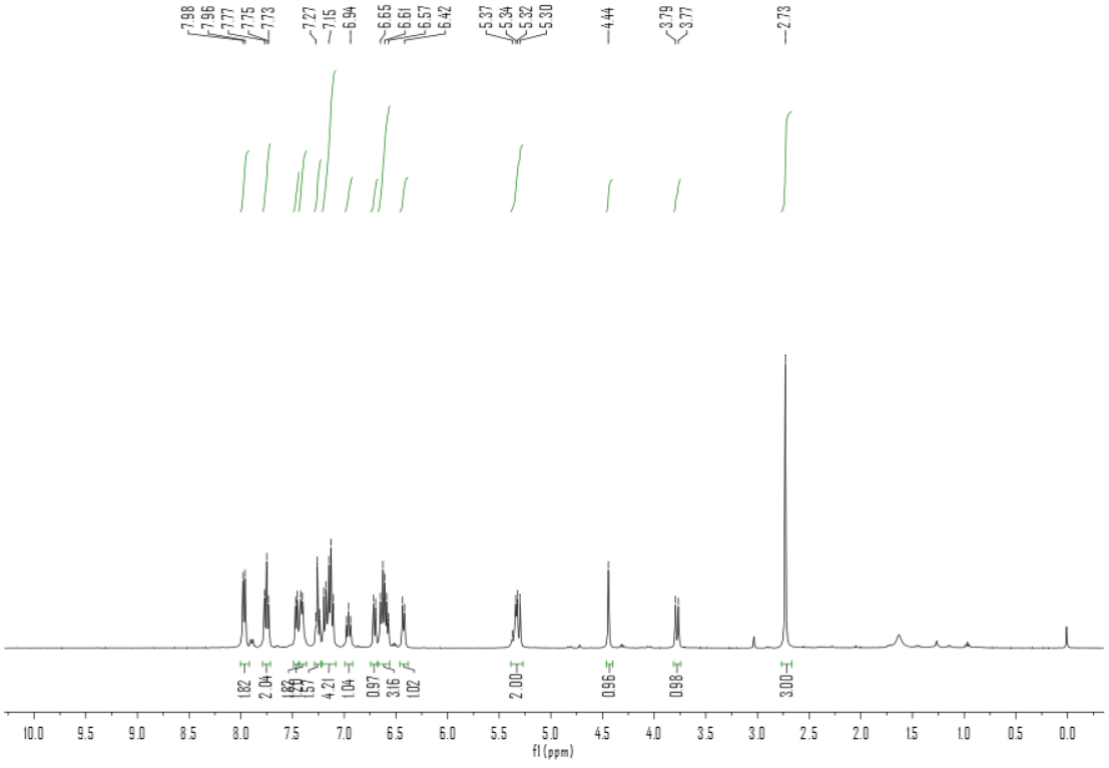


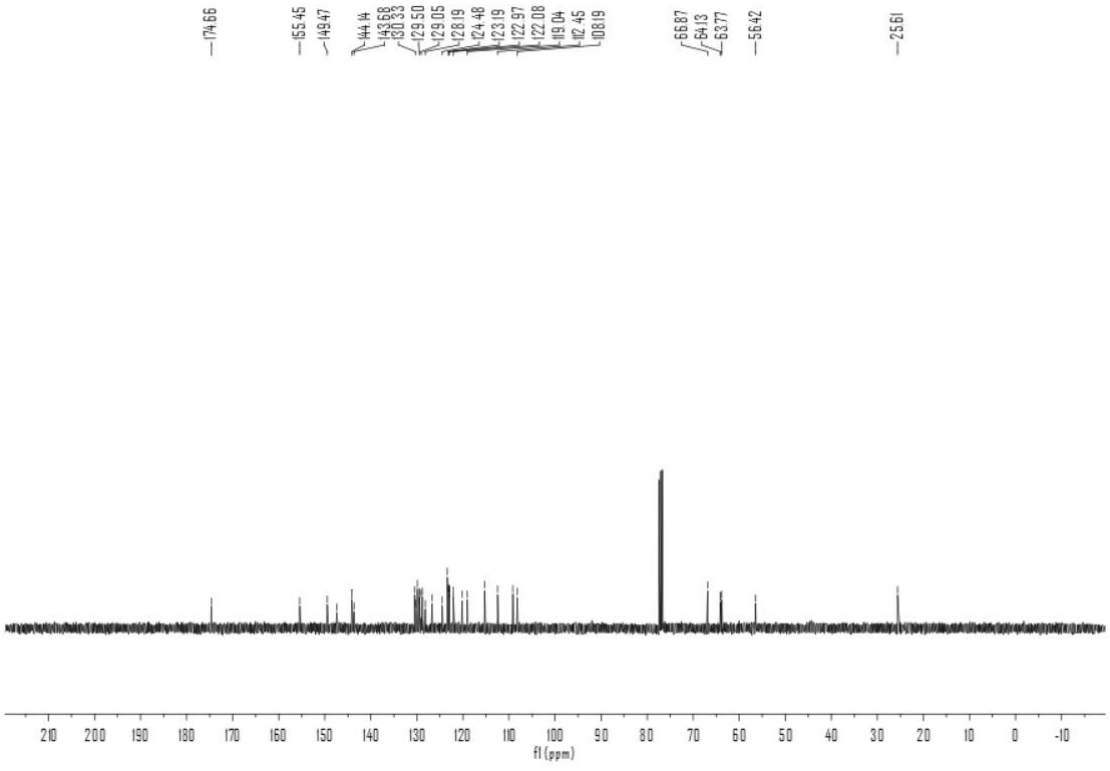

174.83
166.93
155.38
149.59
143.78
141.66
129.48
124.83
123.62
122.87
122.75
122.13
120.68
118.93
115.39
112.38
109.13
107.96
66.83
64.60
63.51
56.25
52.08
25.56
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3al:

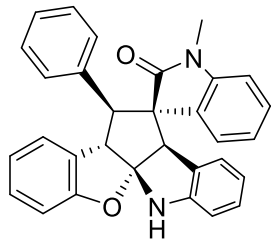


(3R,6c'S,7'S,8a'R,13a'R)-1-methyl-7'-(4-nitrophenyl)-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1'',2'':4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 181 - 183 ℃, 45.3 mg, 82% yield, 98% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +275.3 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.75 (t, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.3 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.22 – 7.09 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.67 – 6.55 (m, 3H), 6.43 (d, *J* = 7.3 Hz, 1H), 5.39 – 5.27 (m, 1H), 4.44 (s, 2H), 3.78 (d, *J* = 11.1 Hz, 1H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 155.4, 149.4, 147.4, 144.1, 143.6, 130.4, 130.3, 129.8, 129.5, 129.3, 129.0, 128.8, 128.1, 126.7, 124.4, 123.3, 123.1, 122.9, 122.9, 122.8, 122.0, 120.2, 119.0, 115.2, 112.4, 109.1, 108.1 , 66.8, 64.1, 63.7, 56.4, 25.6. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 39.309 min, t_{minor} = 31.456 min. HRMS (ESI): calcd for $C_{35}H_{25}N_3O_4$ $[M + H]^+$, 552.1918; found, 552.1920.

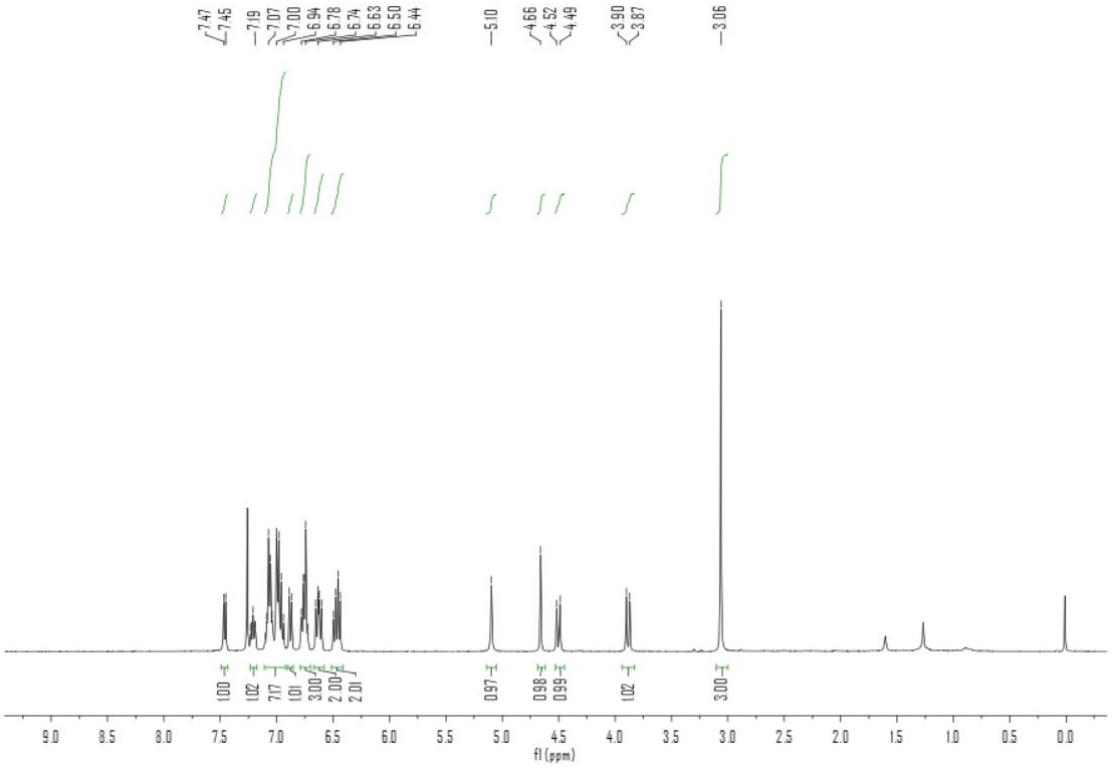


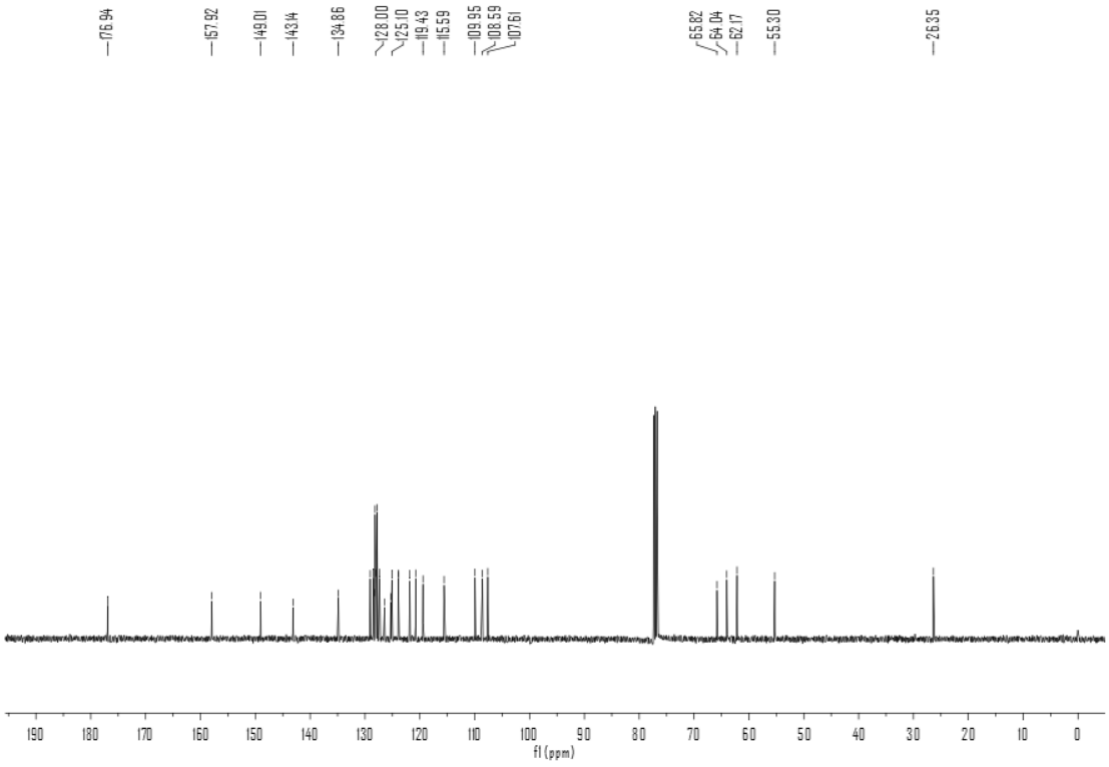

174.66
155.45
149.47
144.14
143.68
130.33
129.50
129.05
128.19
124.48
123.19
122.97
122.08
119.04
112.45
108.19
66.87
64.13
63.77
56.42
25.61
f1 (ppm)

3am:



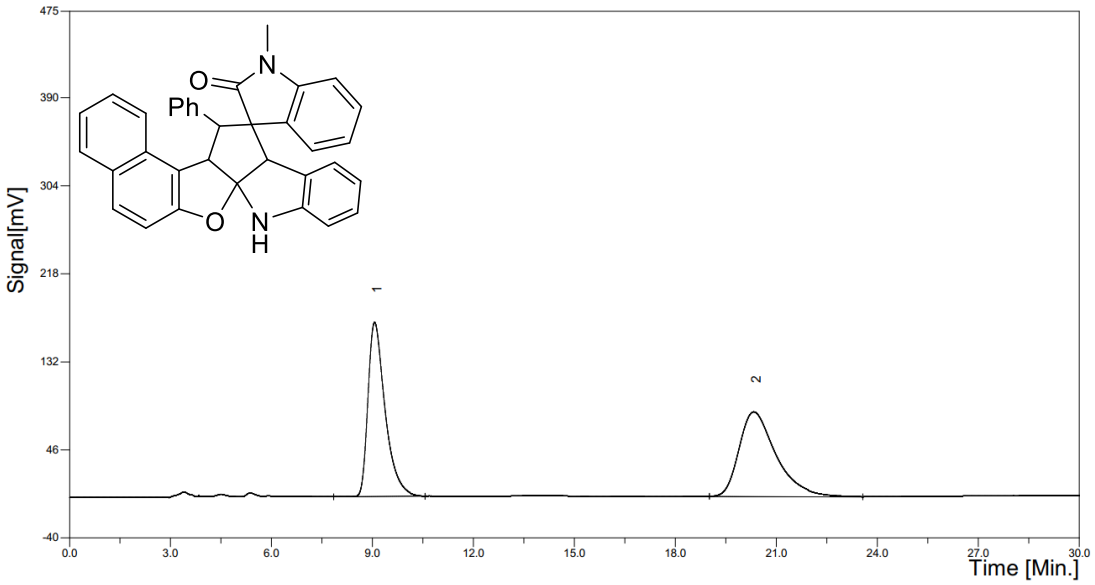
(4b*R*,5*R*,6*S*,6a*S*,11a*R*)-1'-methyl-6-phenyl-4b,6,6a,12-tetrahydrospiro[benzofuro[2',3':1,5]cyclopenta[1,2-b]indole-5,3'-indolin]-2'-one：white solid, mp 132 - 134 ℃, 45.3 mg, 62% yield, 81% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +212.3 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.5 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.12 – 6.92 (m, 7H), 6.88 (d, *J*=8.1 Hz) 6.80 – 6.71 (m, 3H), 6.67 - 6.58 (m, 2H), 6.51- 6.41 (m, 2H), 5.10 (s, 1H), 4.66 (s, 1H), 4.50 (d, *J* = 11.9 Hz, 1H), 3.88 (d, *J* = 11.9 Hz, 1H), 3.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.9, 157.9, 149.0, 143.1, 134.8, 129.0, 128.5, 128.2, 128.1, 128.0, 127.8, 127.3, 126.4, 125.3, 125.1, 123.9, 123.8, 121.8, 120.7, 119.4, 115.5, 109.9, 108.5, 107.6, 65.8, 64.0, 62.1, 55.3, 26.3. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 16.285 min, t_{minor} = 14.066 min. HRMS (ESI): calcd for $C_{31}H_{24}N_2O_2$ $[M + H]^+$, 457.1911; found, 457.1918.



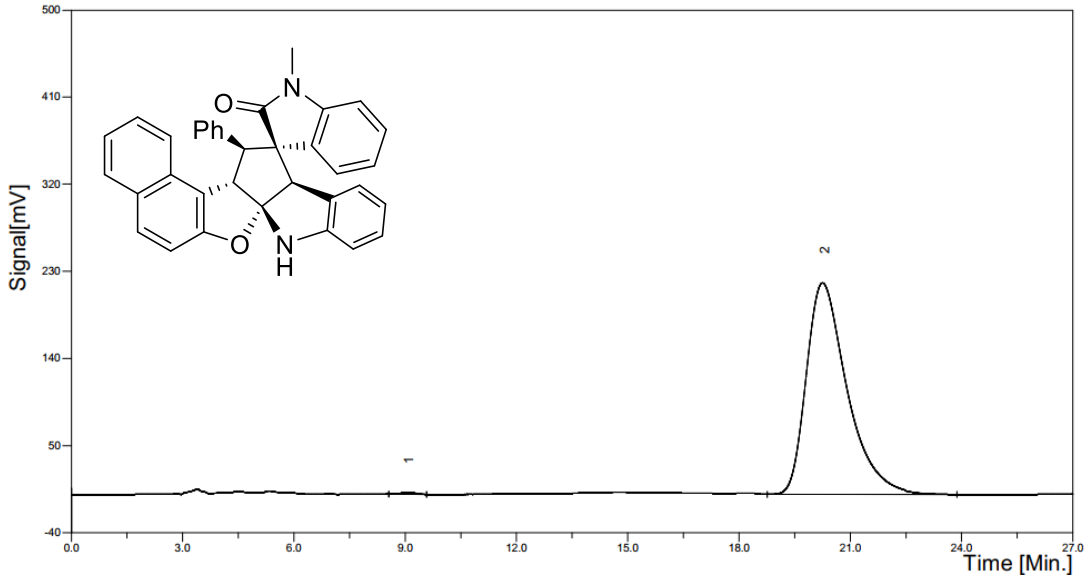

176.94
157.92
149.01
143.14
134.86
128.00
125.10
119.43
115.59
109.95
108.59
107.61
65.82
64.04
62.17
55.30
26.35
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

HPLC spectra of racemic and enantioenriched products.

3aa

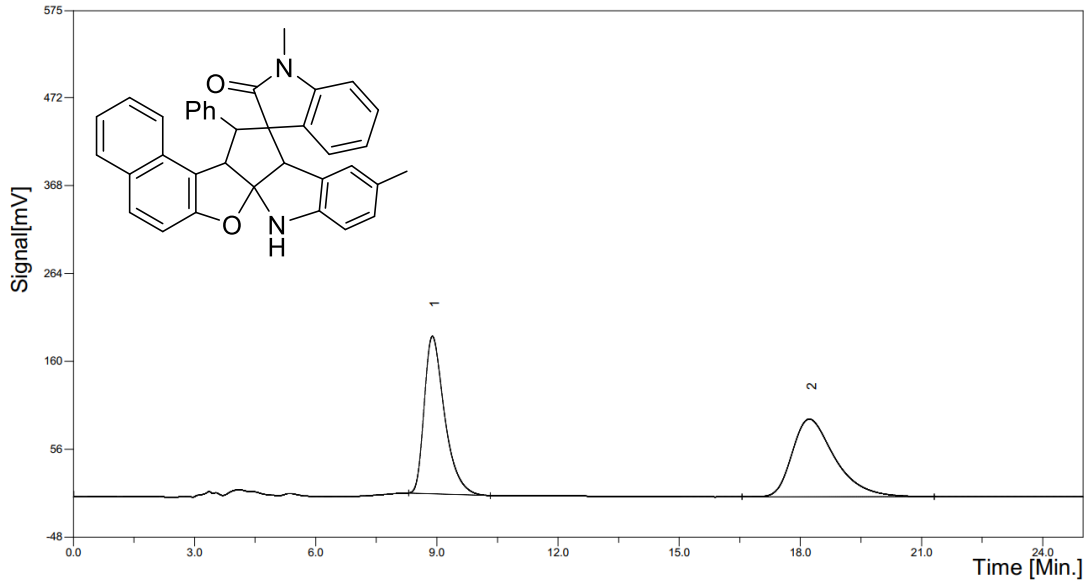


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.063	170.20	6024.45	48.8876
2	20.328	82.65	6298.61	51.1124

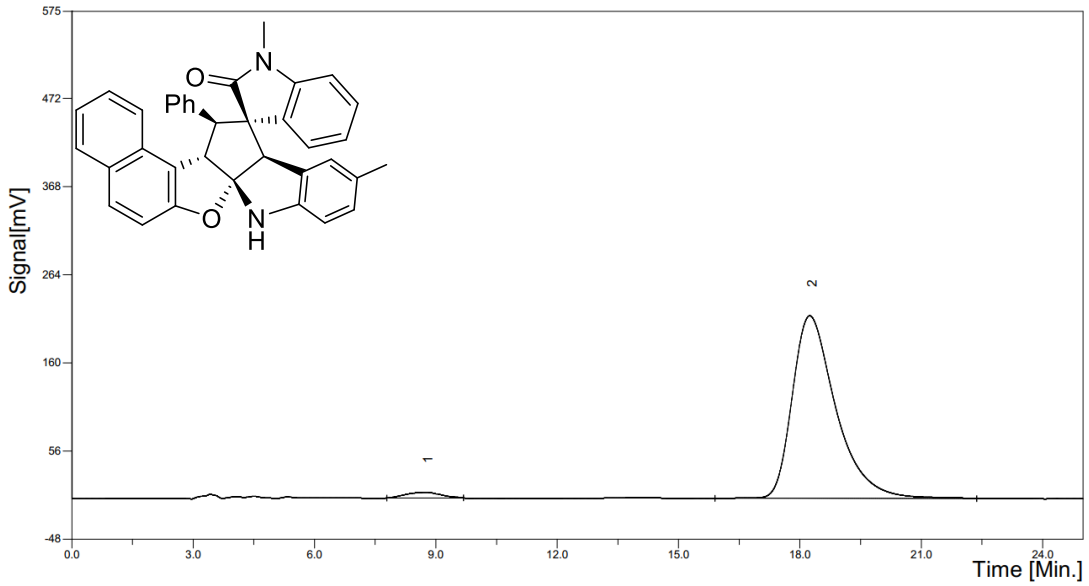


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.036	1.90	55.75	0.3334
2	20.251	218.35	16666.92	99.6666

3ba

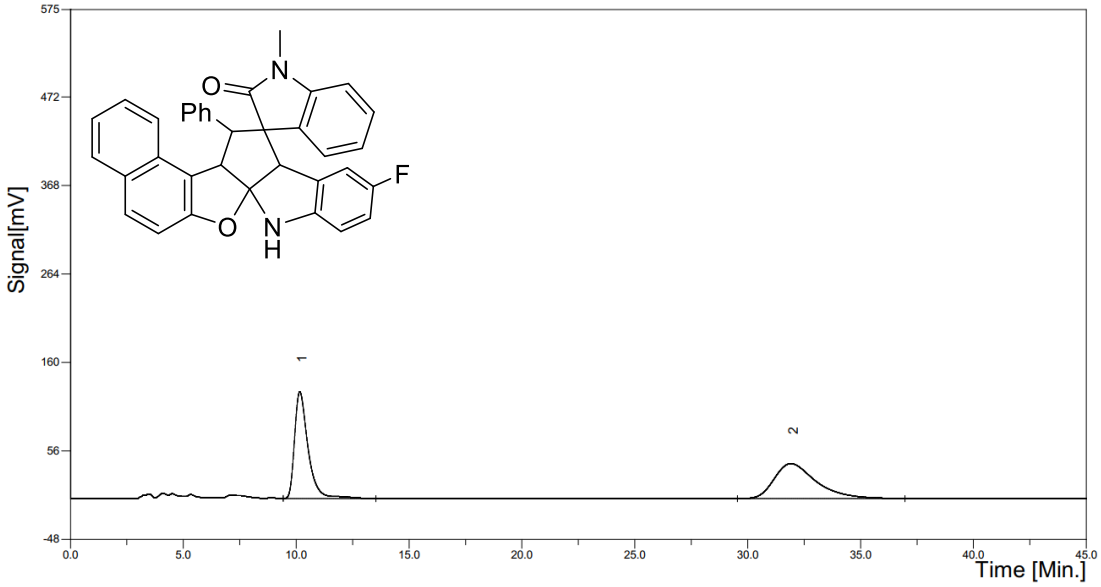


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.889	186.34	6513.02	49.1454
2	18.221	91.91	6739.54	50.8546

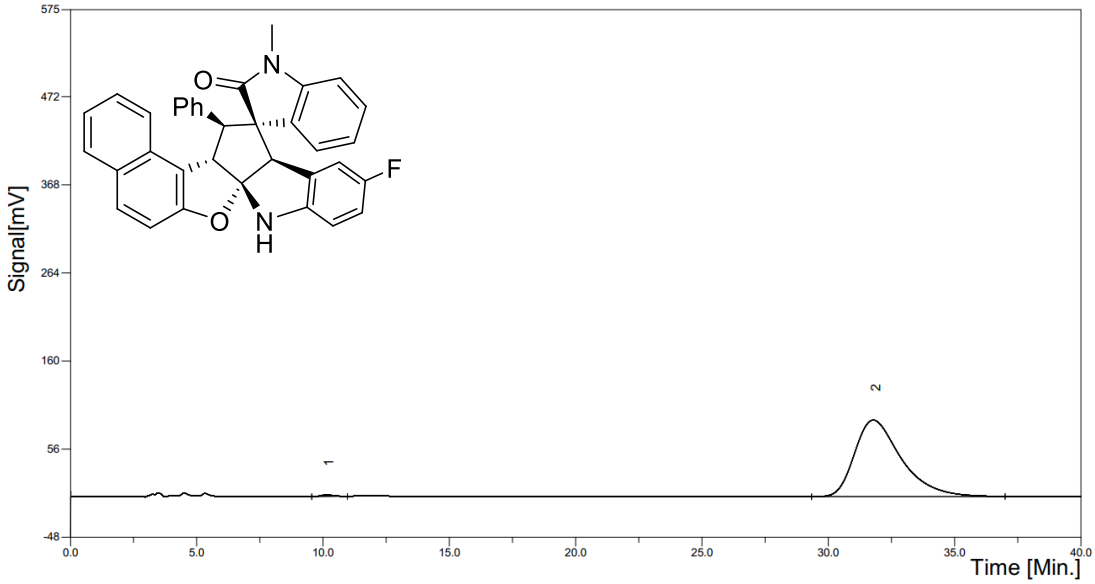


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.745	6.69	398.38	2.4036
2	18.243	215.44	16175.80	97.5964

3ca

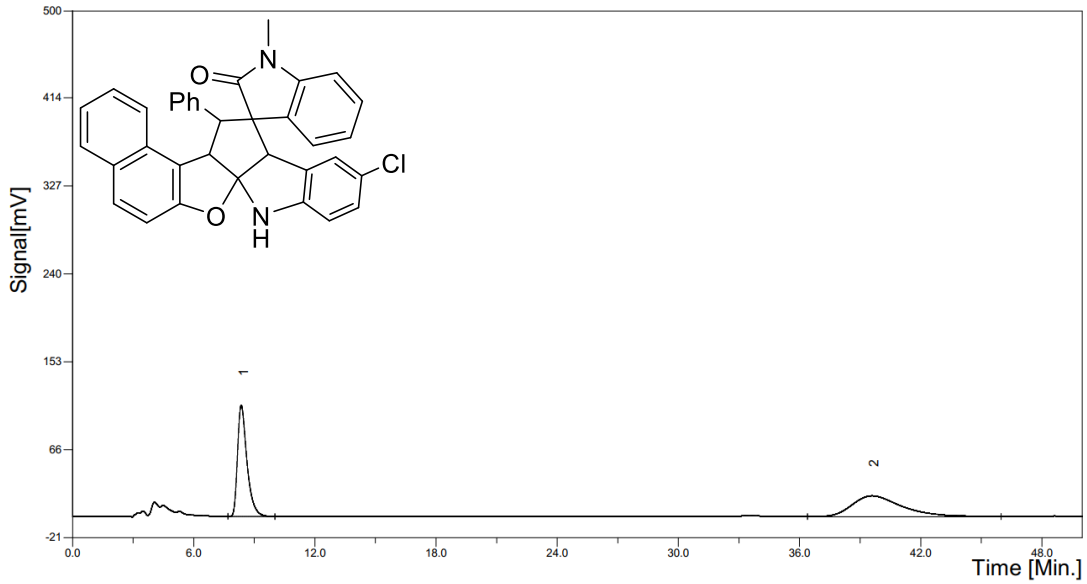


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.159	125.48	5220.73	49.6572
2	31.914	41.10	5292.80	50.3428

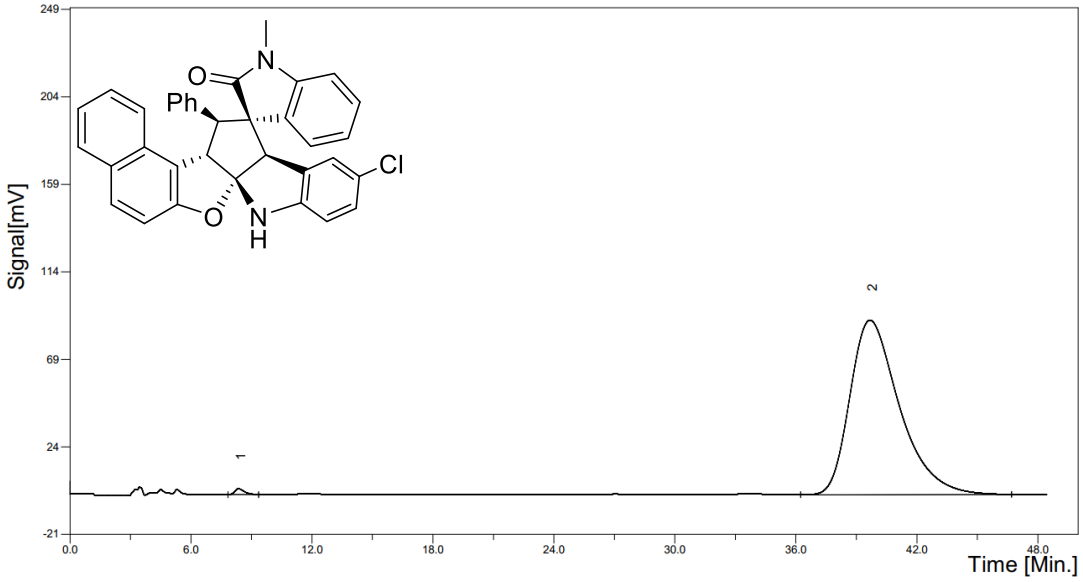


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.131	1.86	63.94	0.5487
2	31.778	90.31	11587.19	99.4513

3da

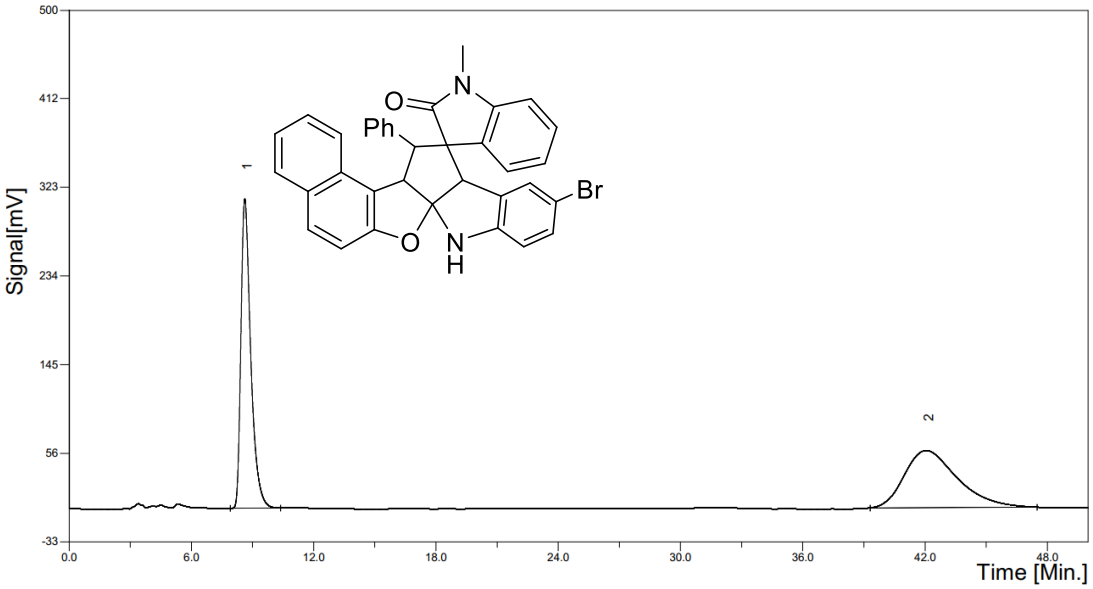


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.353	110.13 3	571.96	50.3733
2	39.573	20.51	3519.01	49.6267

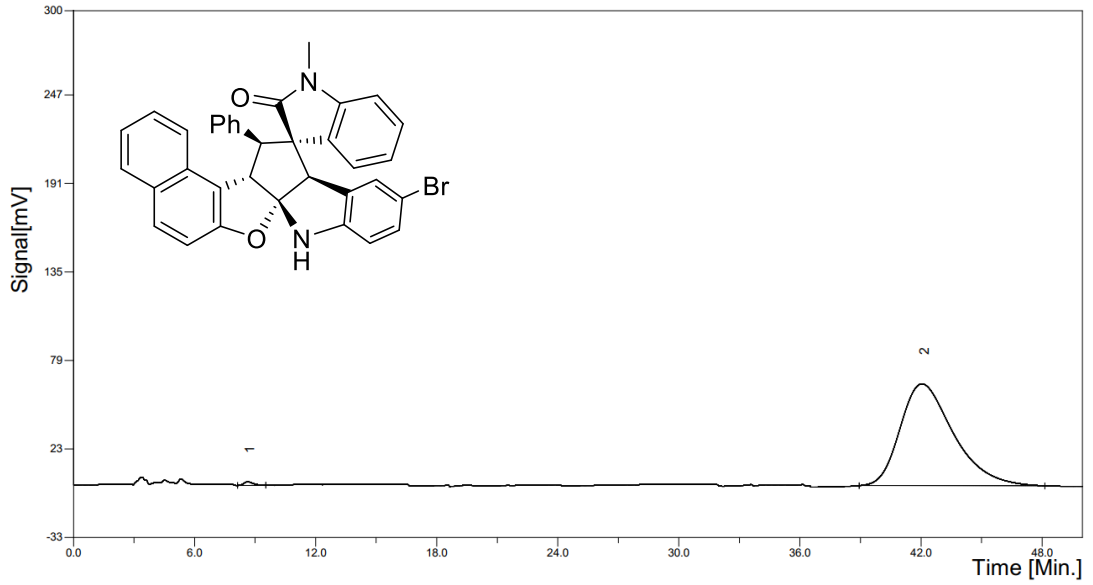


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.362	2.97	96.21	0.6247
2	39.671	89.66	15304.80	99.3753

3ea

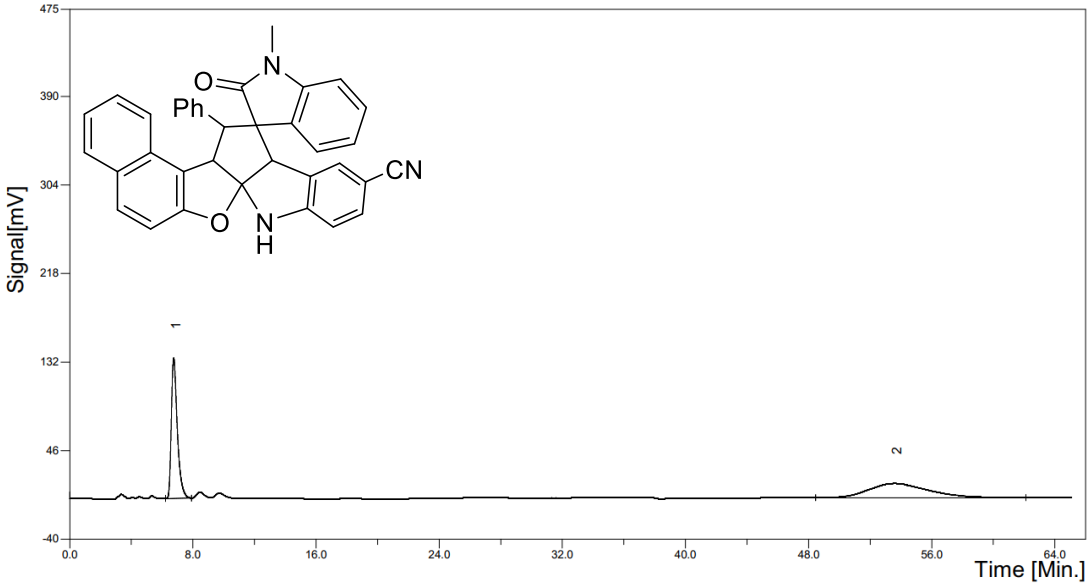


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.621	310.21	10405.89	50.1242
2	42.065	57.29	10354.34	49.8758

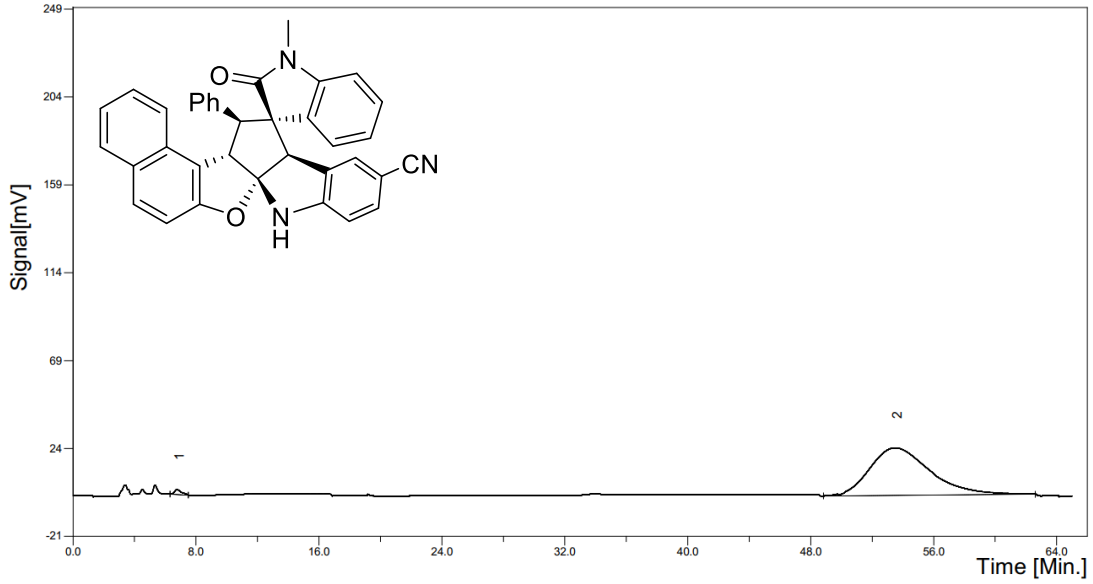


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.626	2.23	72.20	0.6069
2	42.040	64.40	1824.47	99.3931

3fa

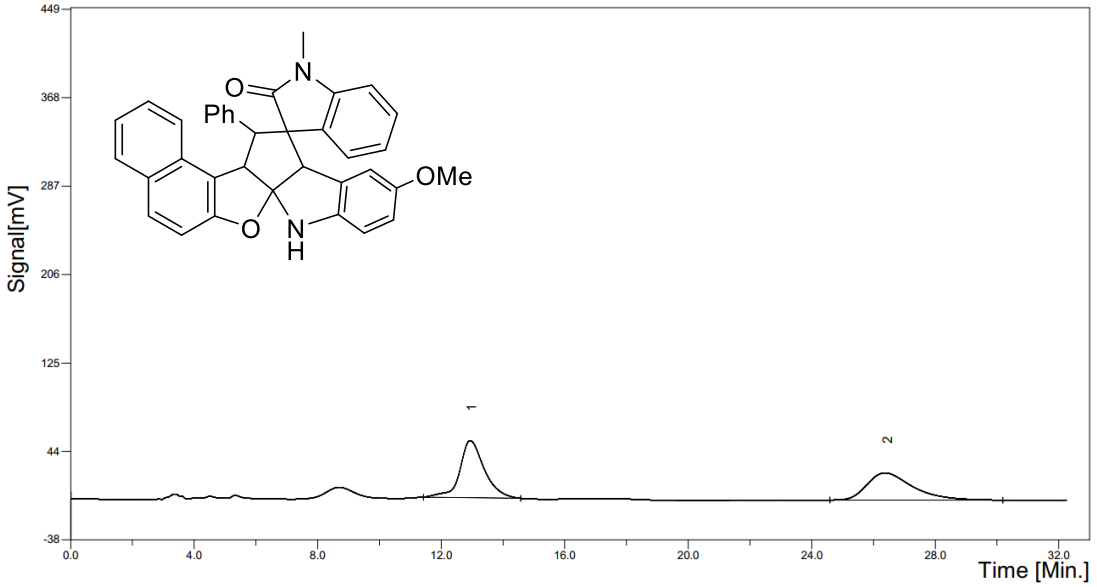


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.754	136.22	3677.95	50.0470
2	53.584	13.76	3671.05	49.9530

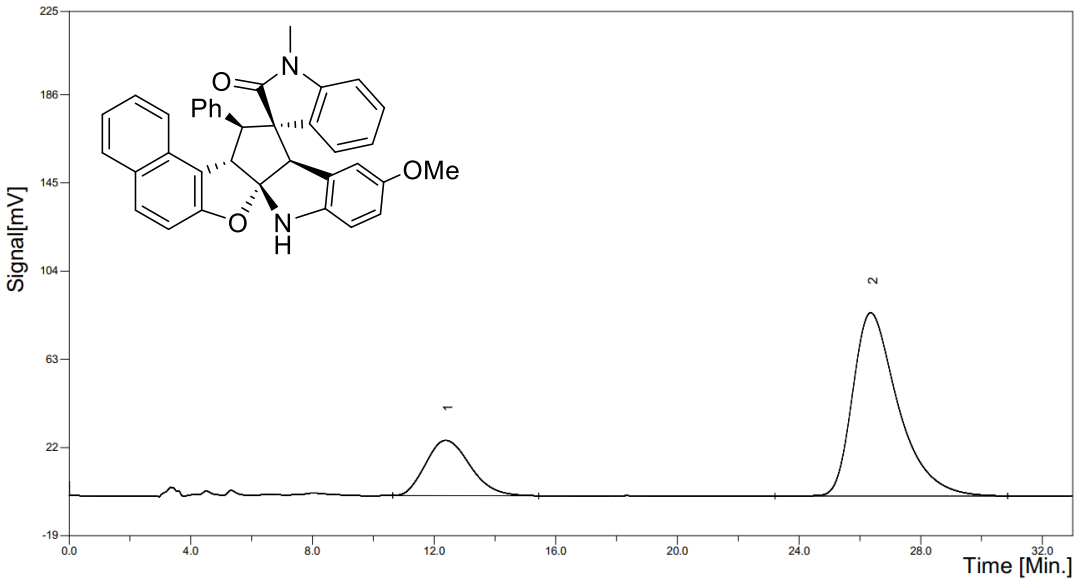


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.760	2.57	80.62	1.2047
2	53.480	24.30	6611.09	98.7953

3ga

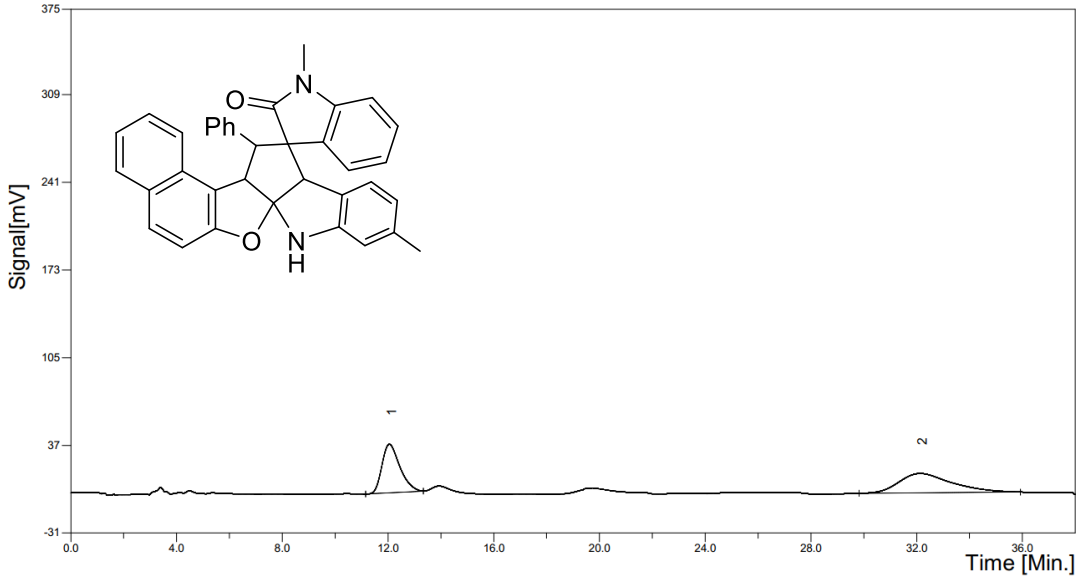


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	12.911	52.42	2893.81	53.1788
2	26.376	24.89	2547.85	46.8212

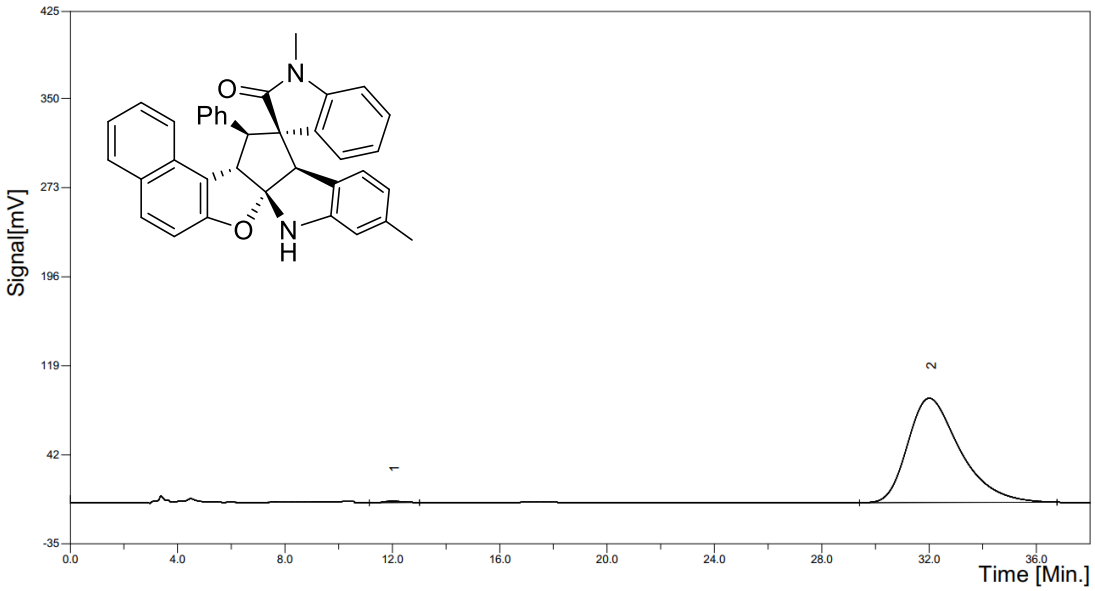


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	12.375	25.65	2548.15	22.3551
2	26.356	85.18	8850.37	77.6449

3ha

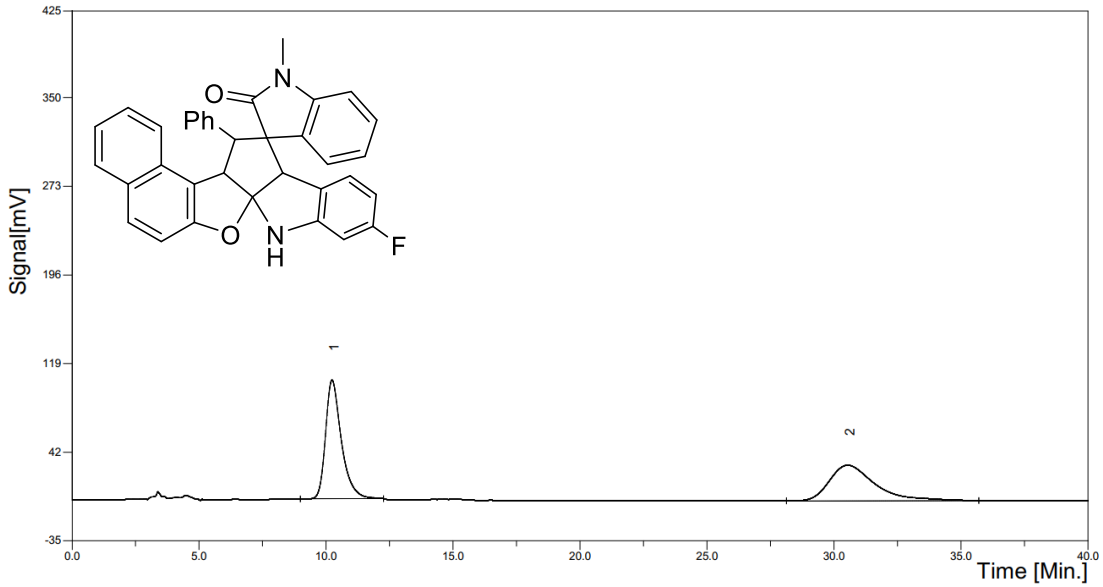


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	12.050	37.71	1777.84	46.0623
2	32.120	15.03	2081.80	53.9377

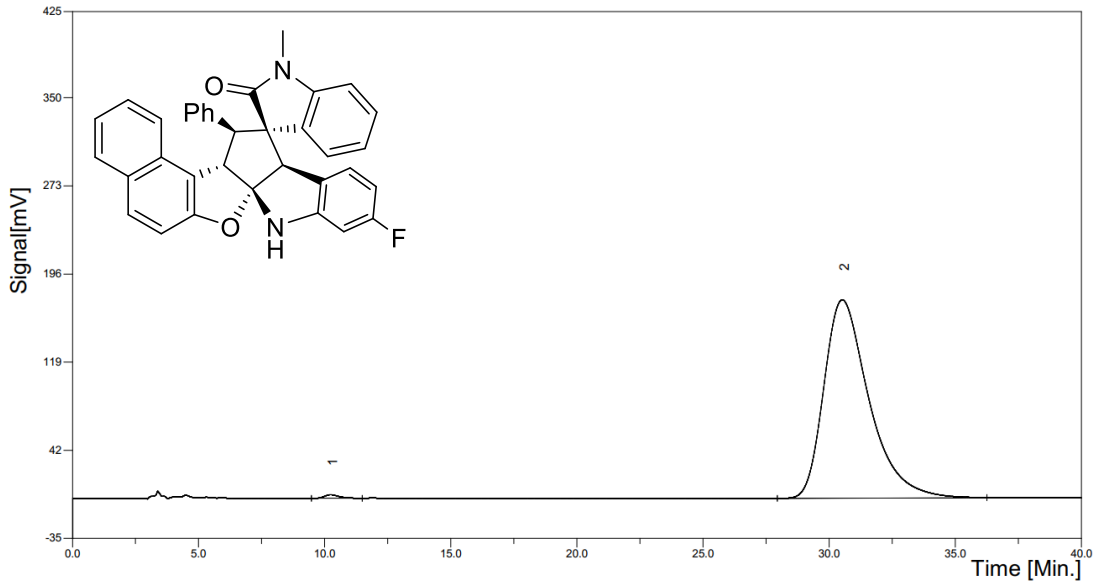


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	11.986	1.35	61.04	0.4975
2	32.002	90.21	12208.70	99.5025

3ia

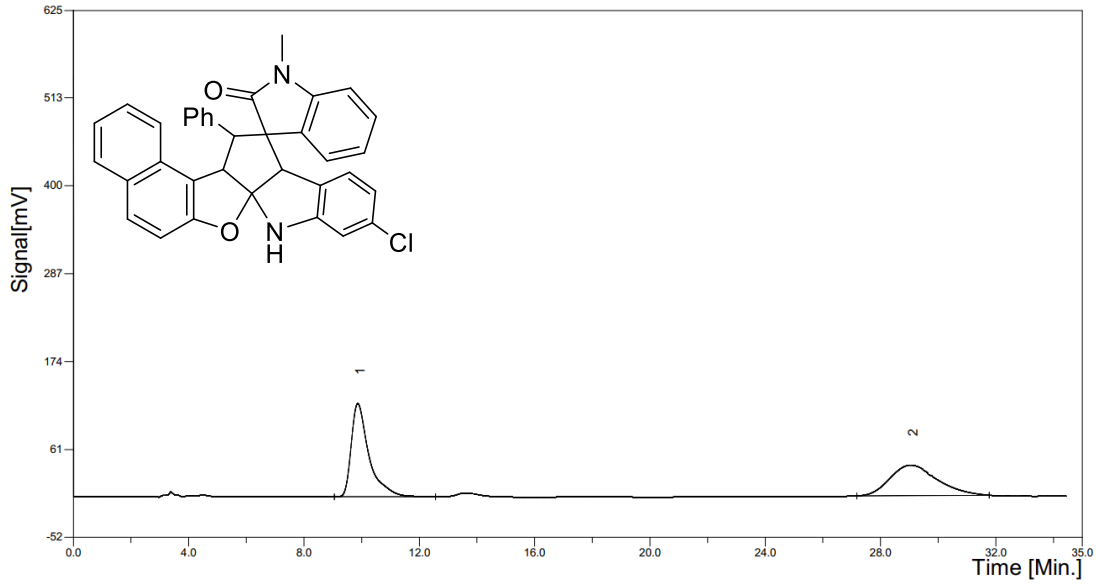


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.231	103.22	4468.30	53.8048
2	30.533	30.92	3836.35	46.1952

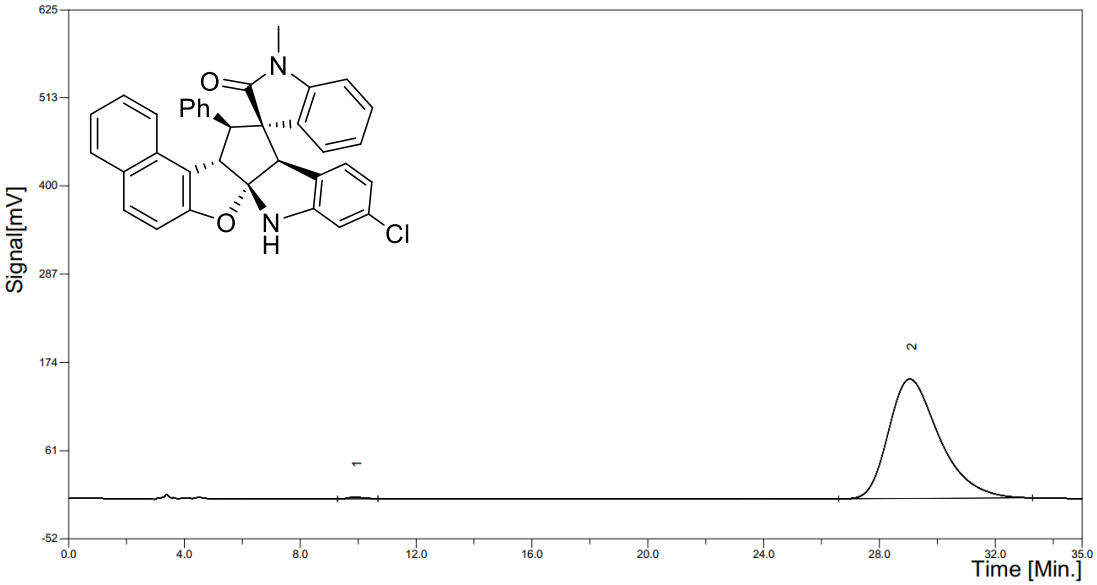


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.231	3.10	124.95	0.5776
2	30.519	173.34	21507.66	99.4224

3ja

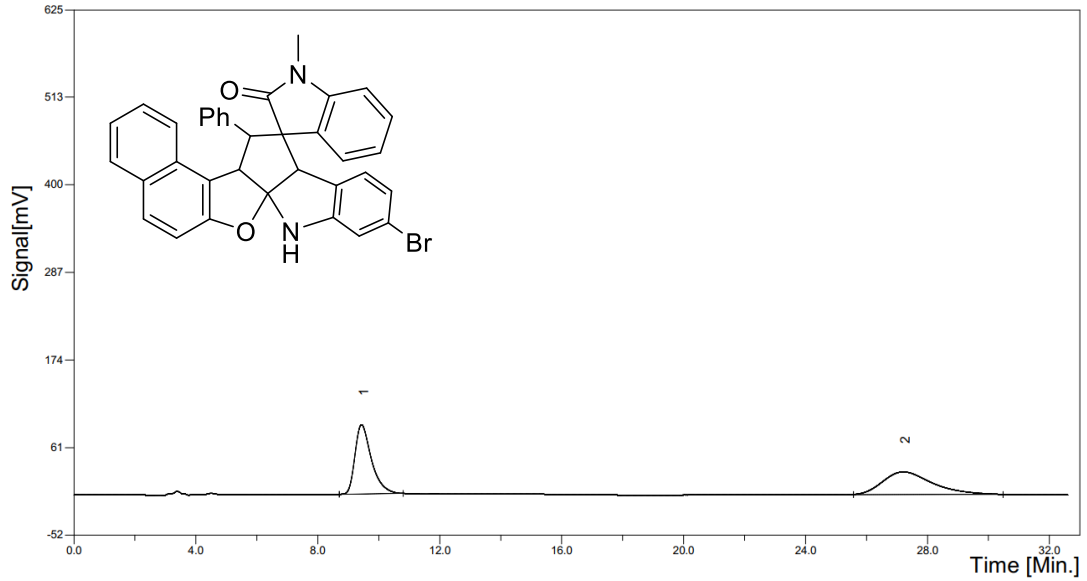


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.866	119.83	5105.99	53.4557
2	29.046	39.27	4445.82	46.5443

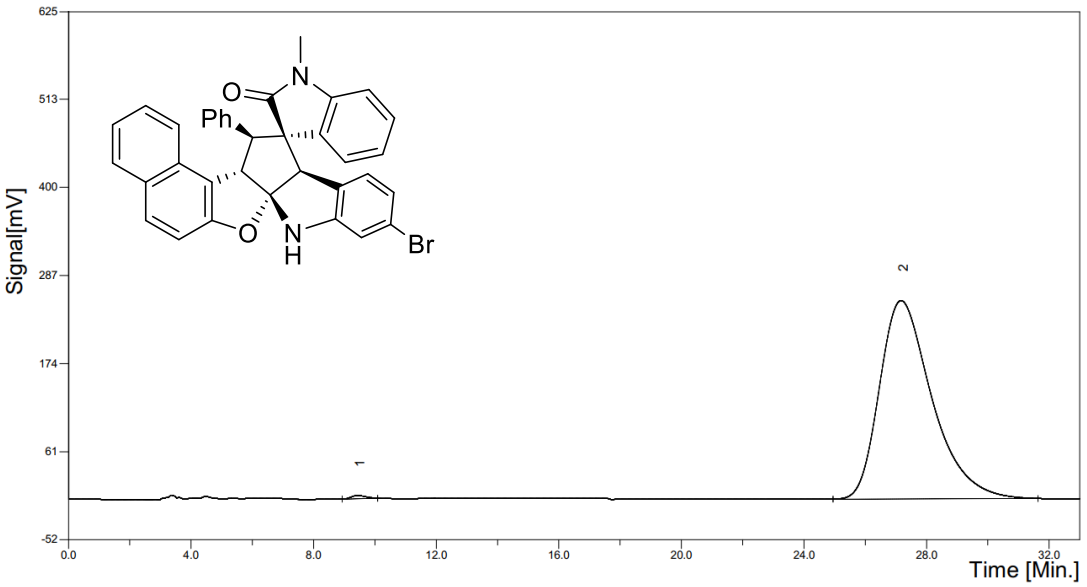


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.878	2.15	77.14	0.4118
2	29.043	152.92	18654.53	99.5882

3ka

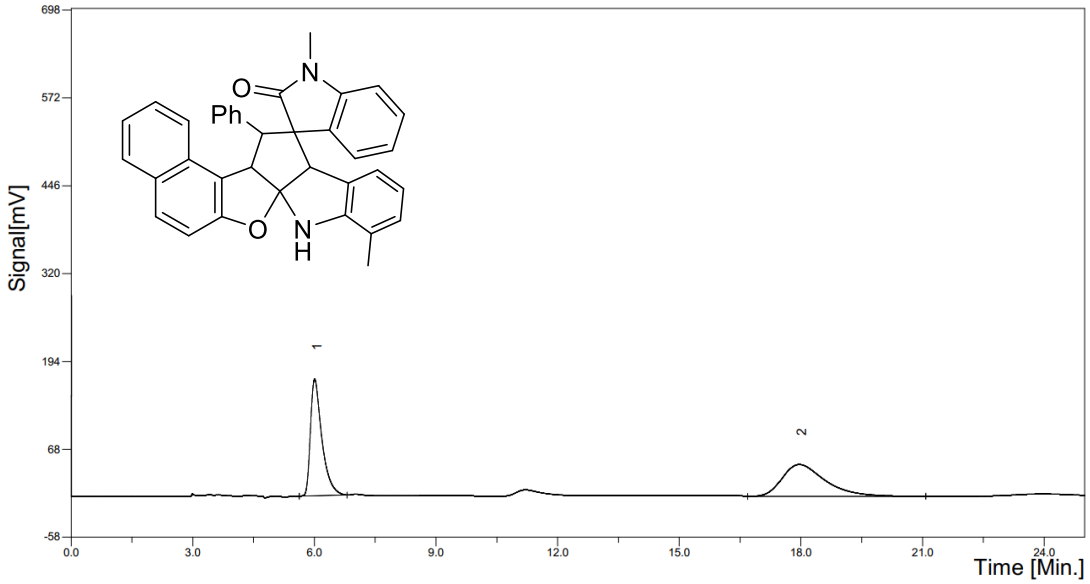


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.434	89.43	3347.49	50.4449
2	27.199	29.15	4288.45	49.5551

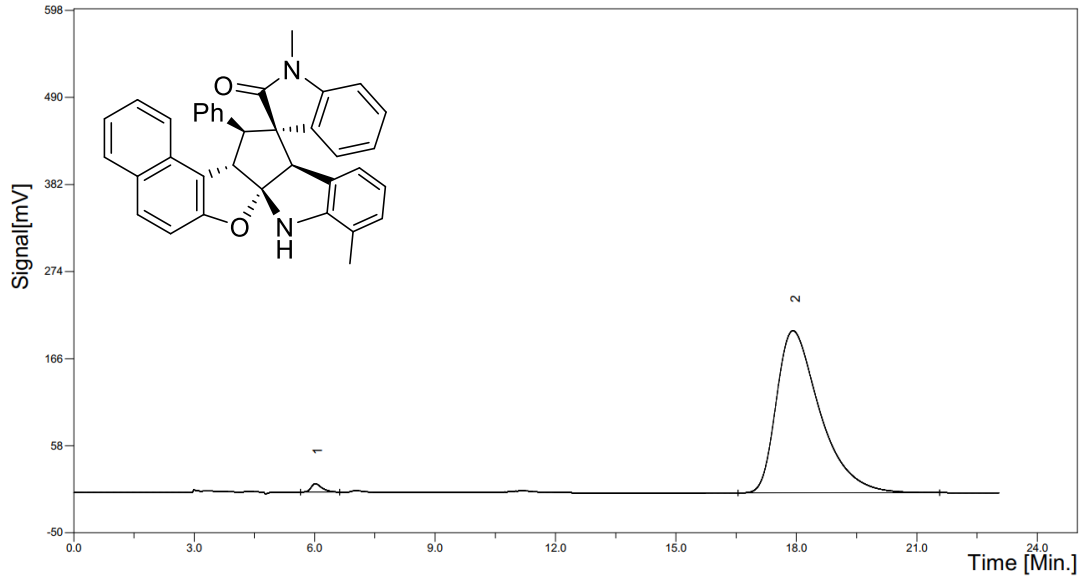


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.430	4.23	136.94	0.4513
2	27.169	254.29	30208.12	99.5487

3la

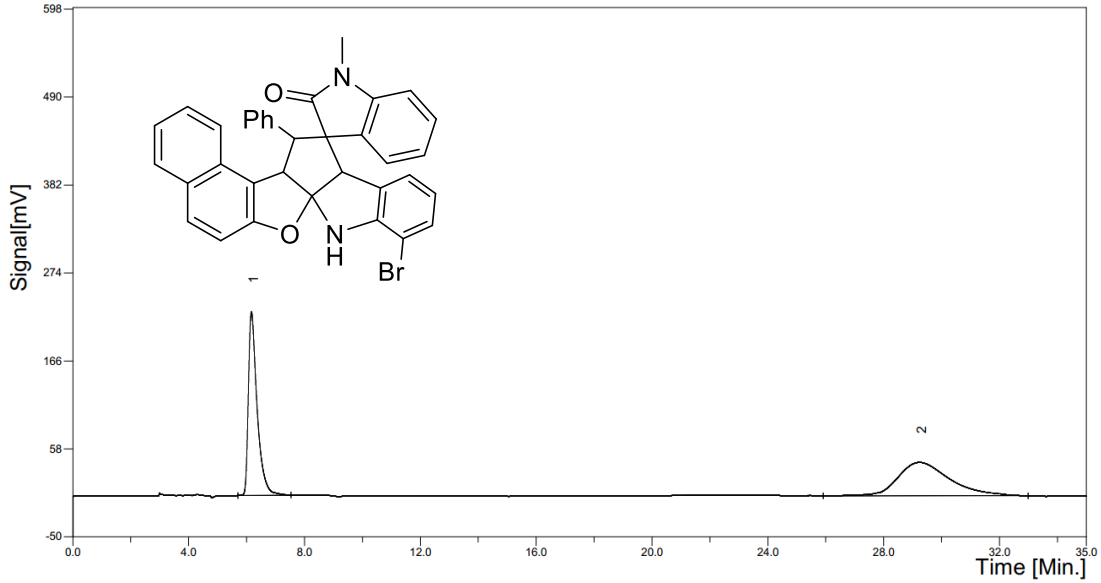


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.006	167.34	3283.07	49.1857
2	17.961	45.78	3391.78	50.8143

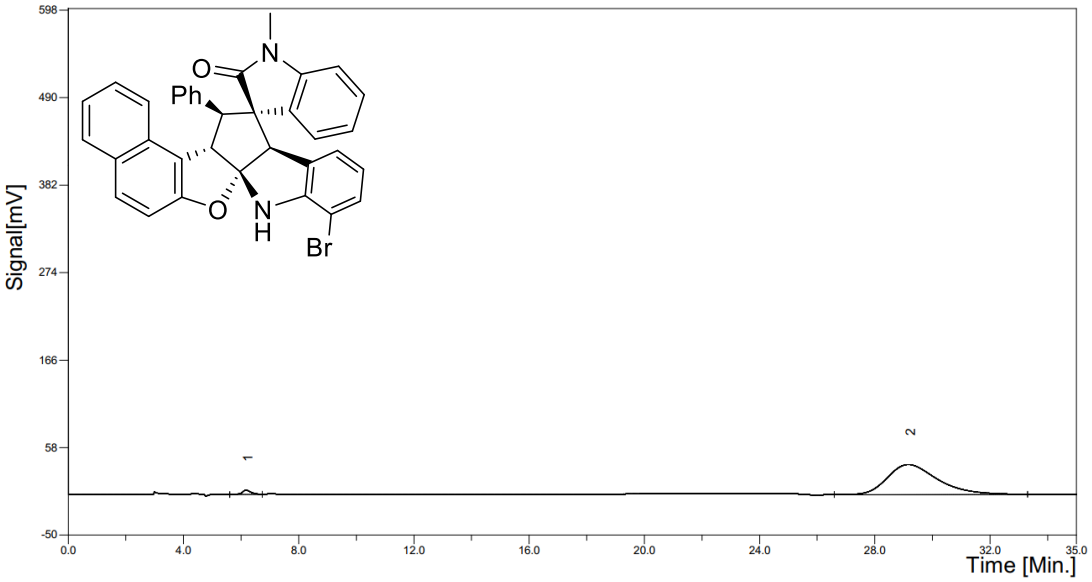


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.015	10.54	201.41	1.3112
2	17.915	201.07	15159.63	98.6888

3ma

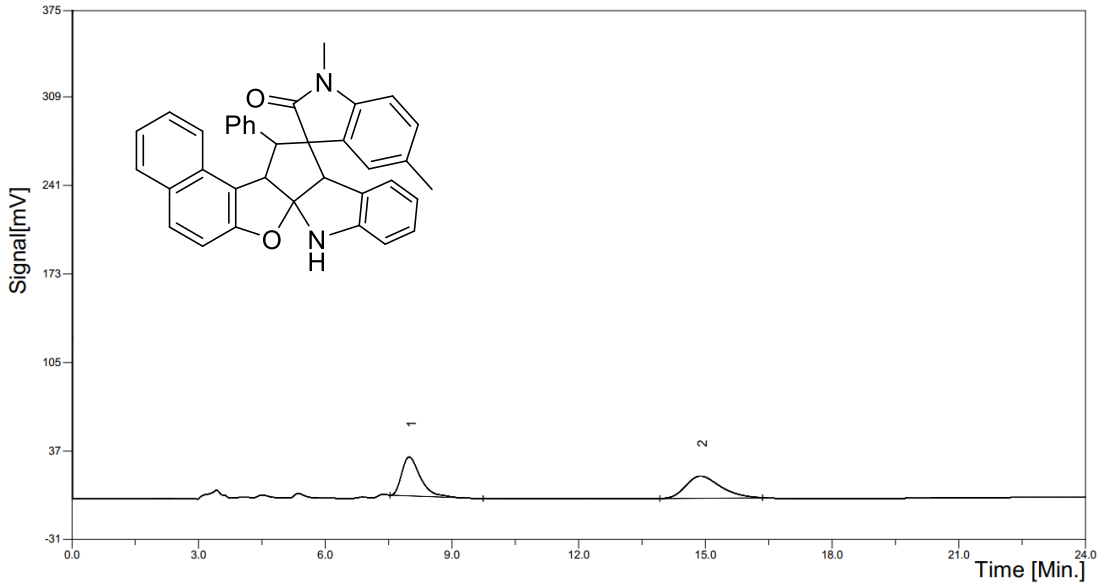


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.169	225.24	4722.60	48.2016
2	29.235	40.96	5075.00	51.7984

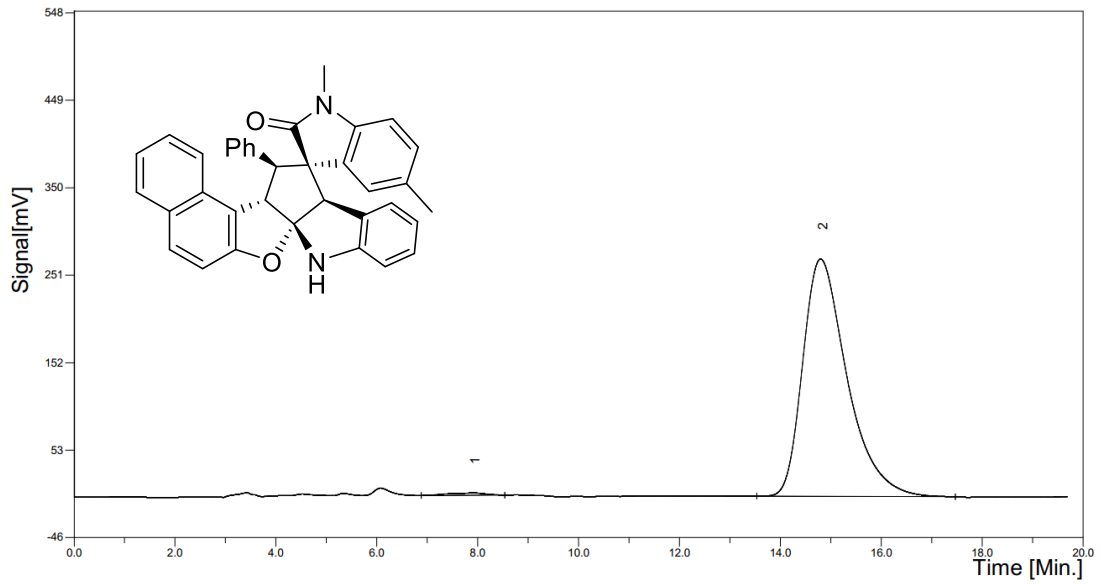


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.166	5.32	109.57	2.4008
2	29.163	36.92	4454.53	97.5992

3na

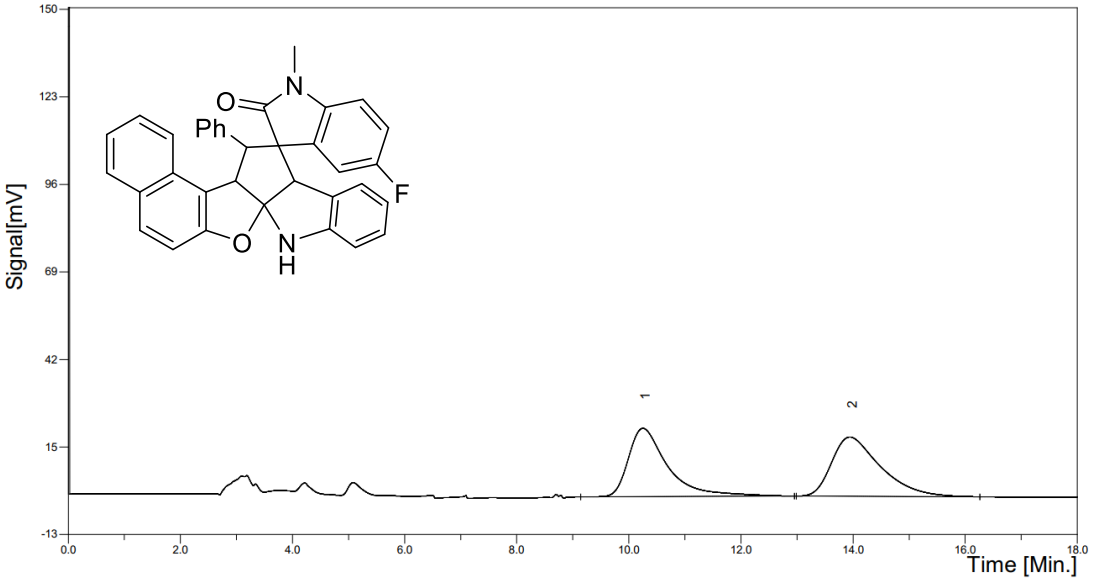


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.984	29.90	904.10	48.2259
2	14.877	16.98	970.62	51.7741

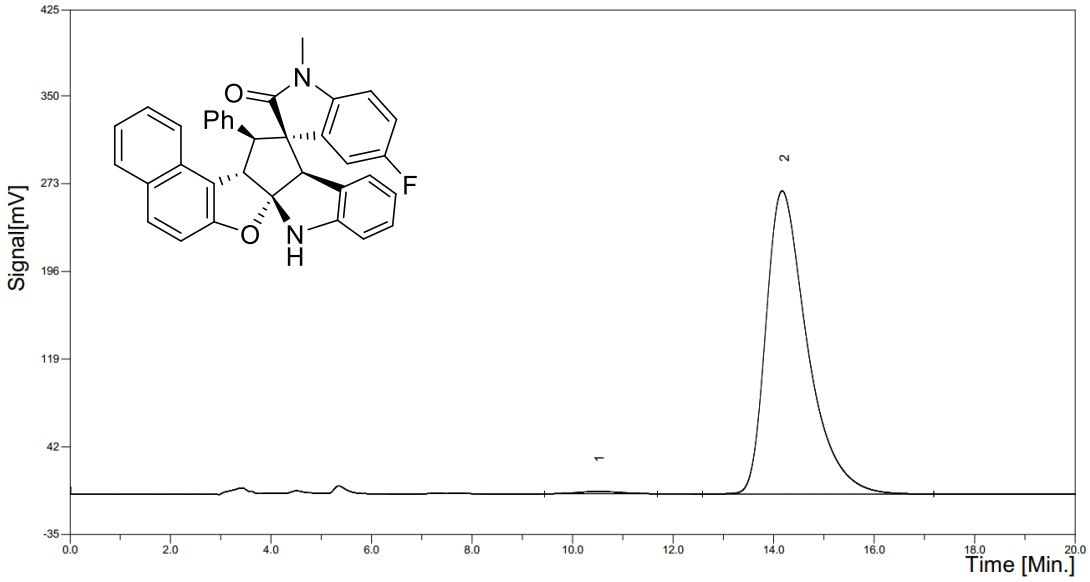


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.902	2.67	131.10	0.7961
2	14.796	268.53	16337.20	99.2039

3oa

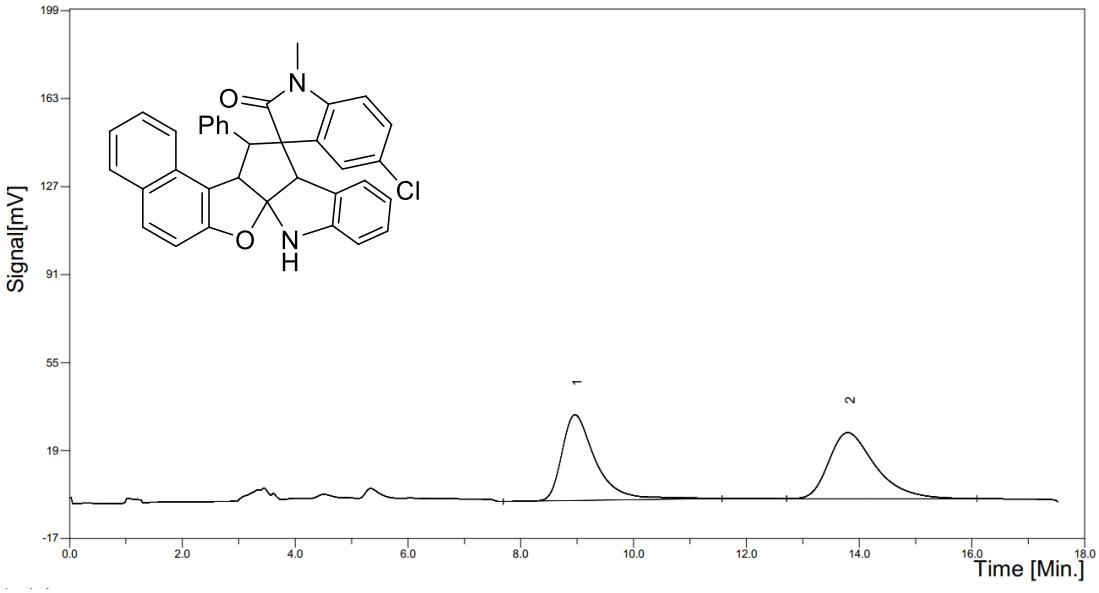


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.250	21.08	1028.18	48.1770
2	13.943	18.28	1106.00	51.8230

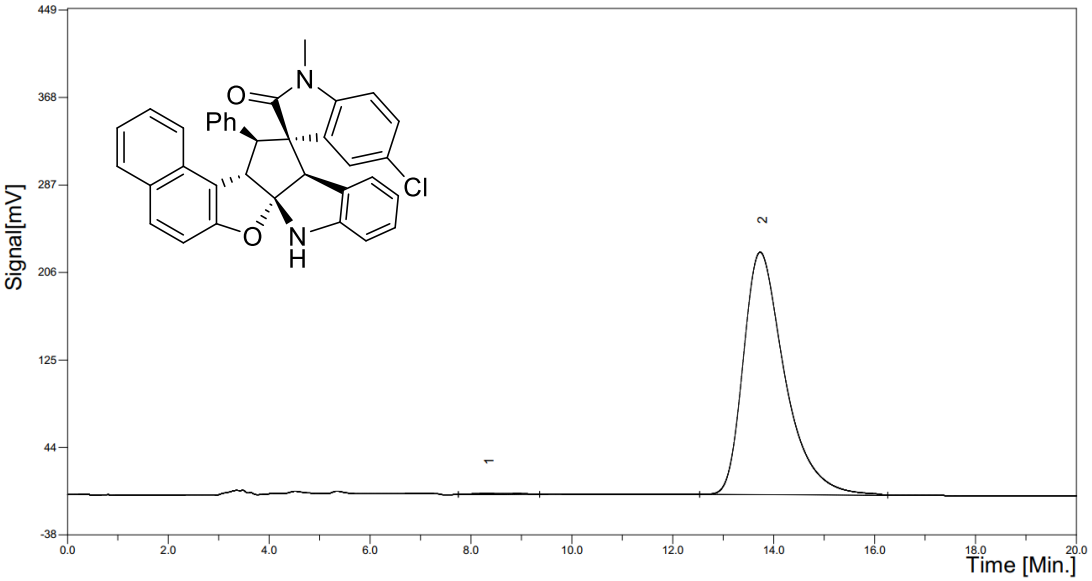


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.485	2.22	128.43	0.8412
2	14.169	266.00	15139.67	99.1588

3pa

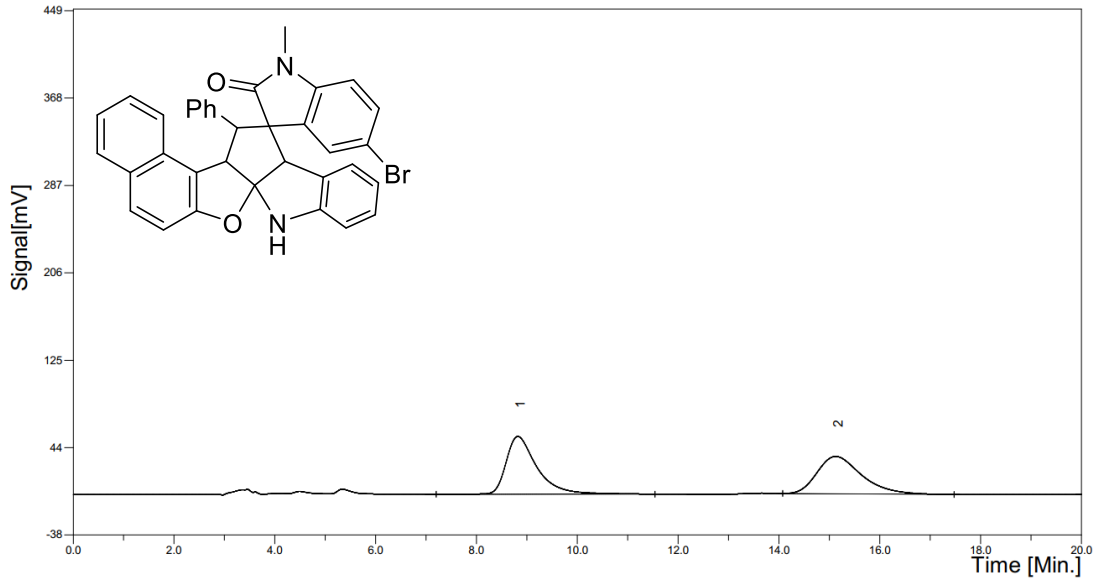


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.961	35.08	1458.75	48.5139
2	13.797	27.01	1548.12	51.4861

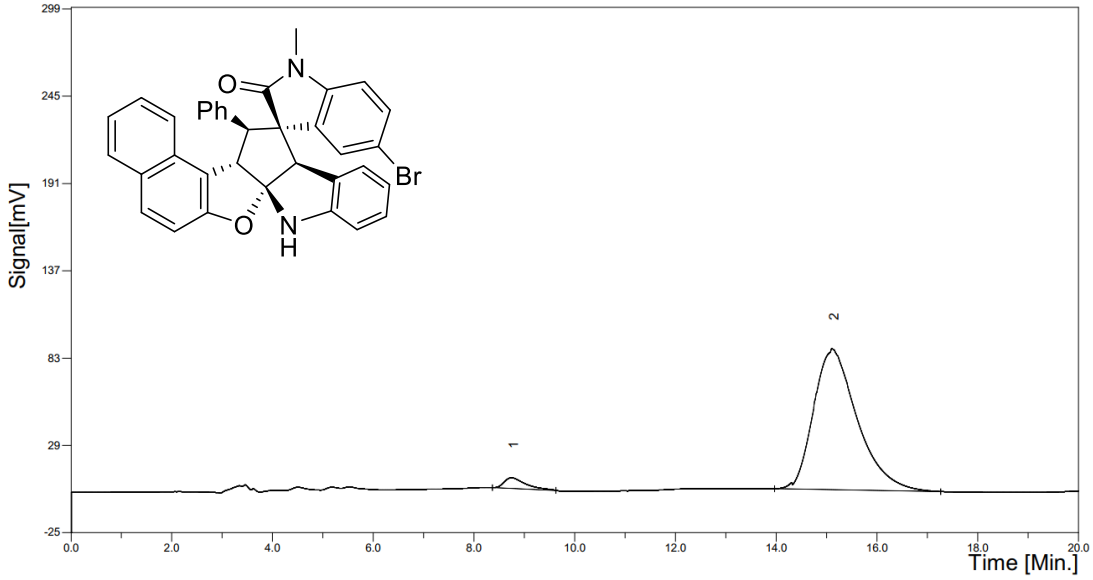


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.310	0.89	51.18	0.3985
2	13.730	224.40	12792.82	99.6015

3qa

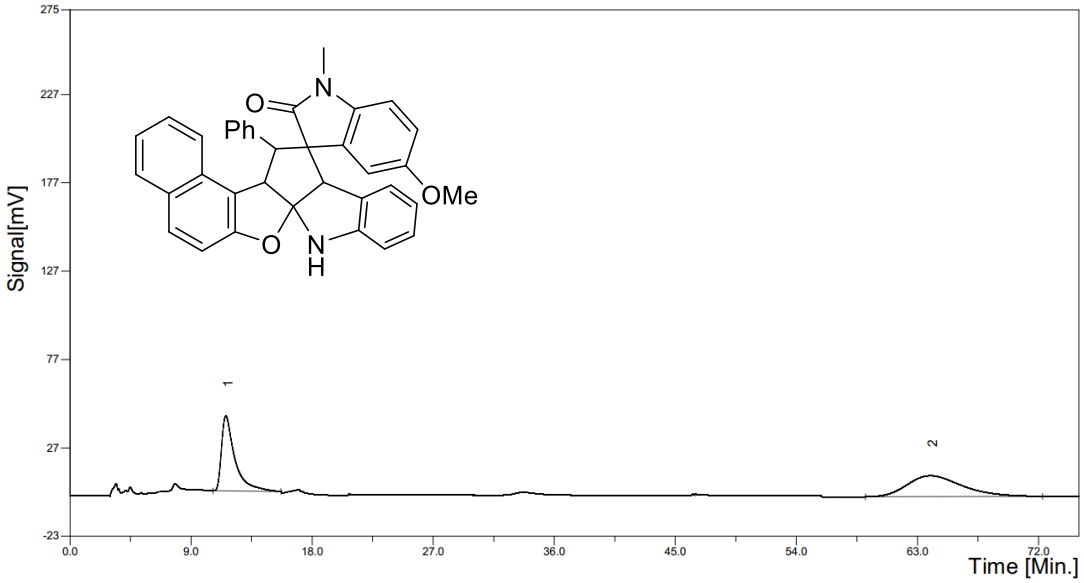


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.819	53.57	2277.63	51.7785
2	15.125	34.61	2121.17	48.2215

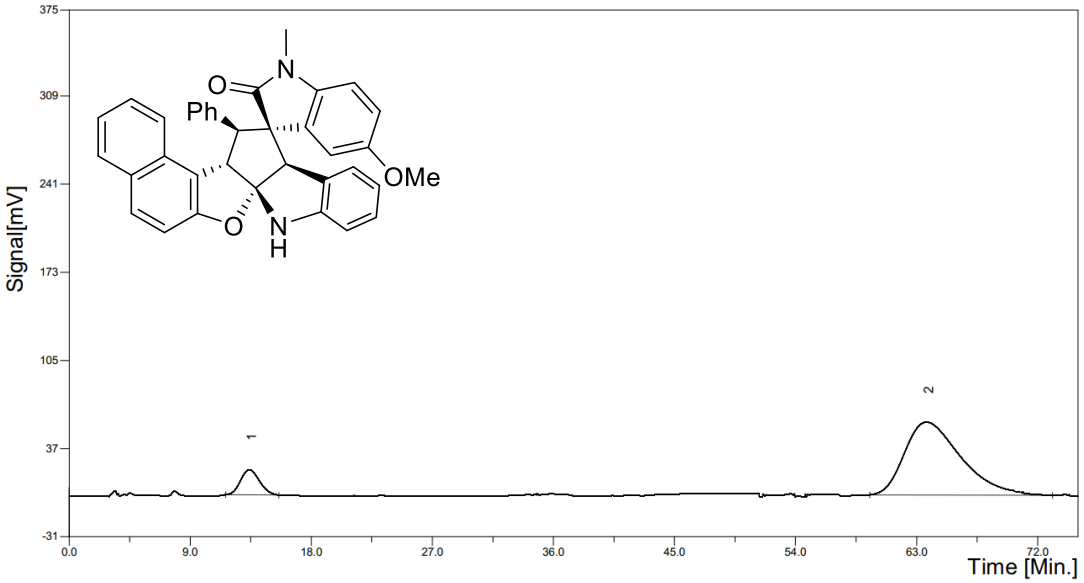


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	8.741	6.57	194.01	3.5765
2	15.097	87.23	5230.67	96.4235

3ra

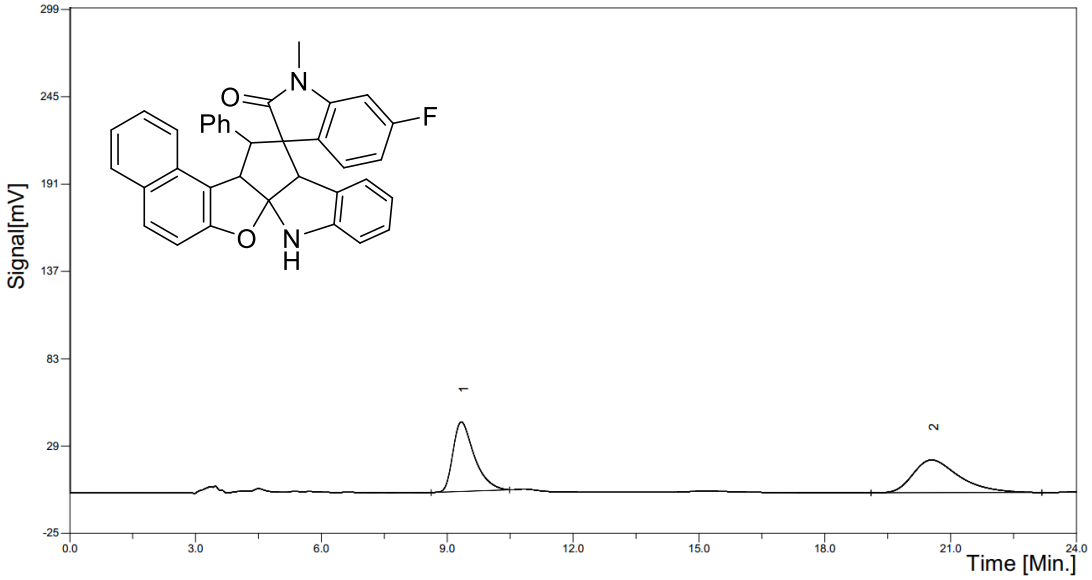


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	11.580	42.45	2925.92	47.1511
2	63.961	11.75	3279.50	52.8489

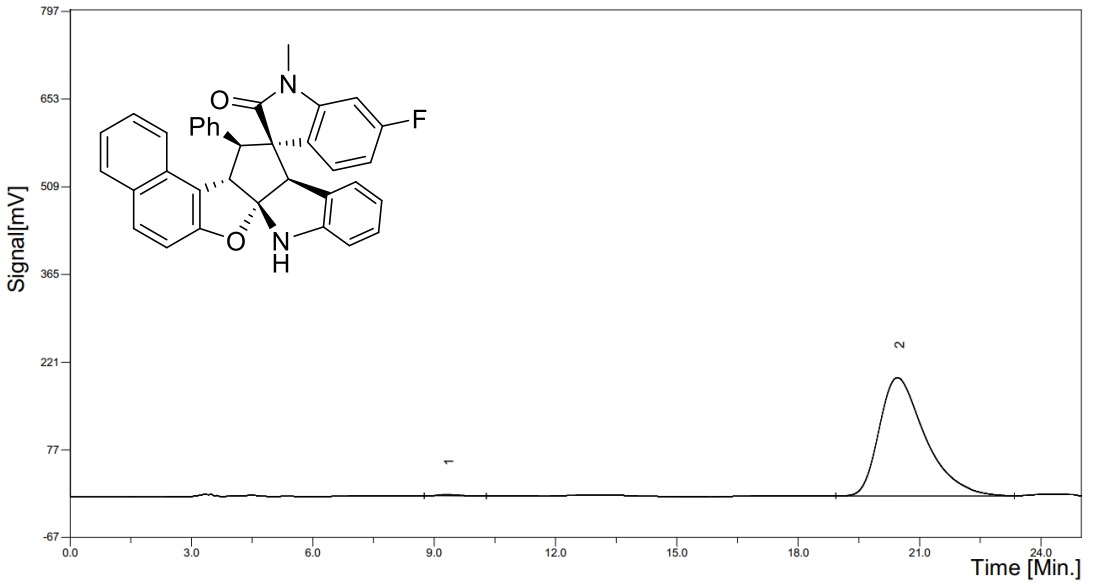


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	13.385	19.37	1885.24	10.3220
2	63.727	56.22	16379.01	89.6780

3sa

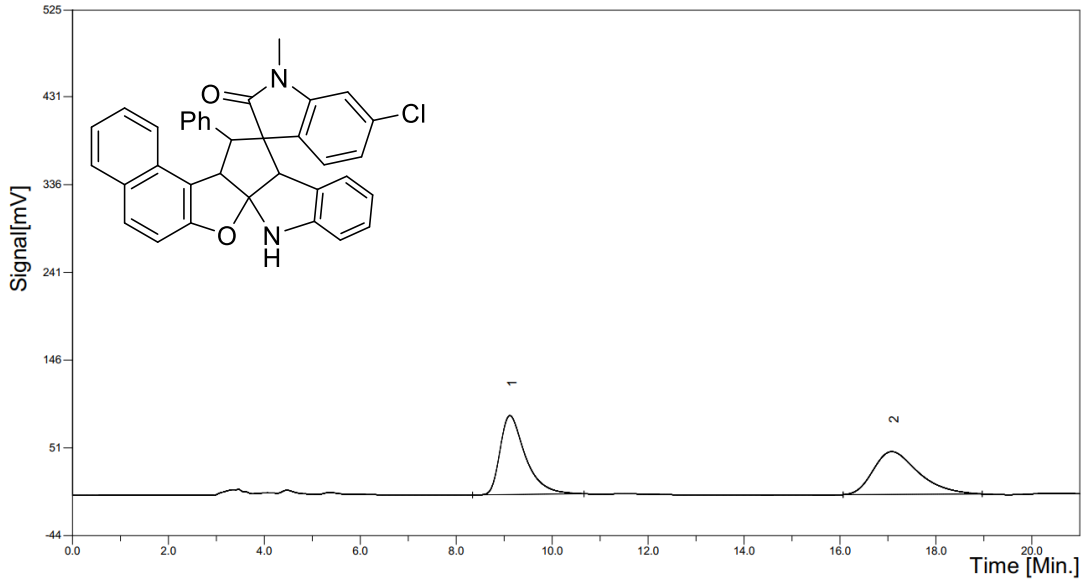


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.332	43.00	1520.44	49.4090
2	20.545	20.28	1556.81	50.5910

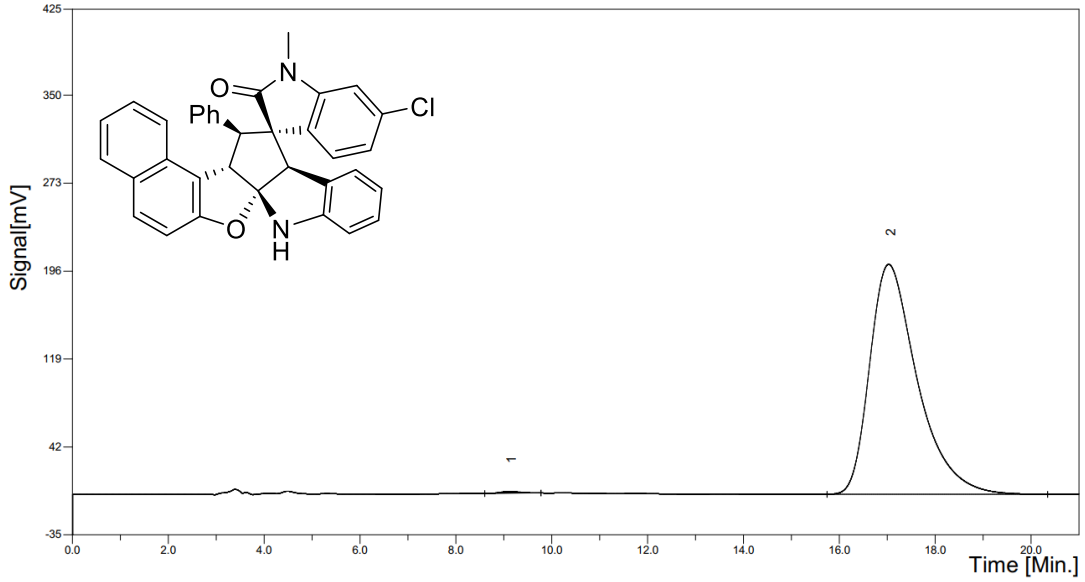


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.309	2.13	69.56	0.4526
2	20.451	194.08	15300.13	99.5474

3ta

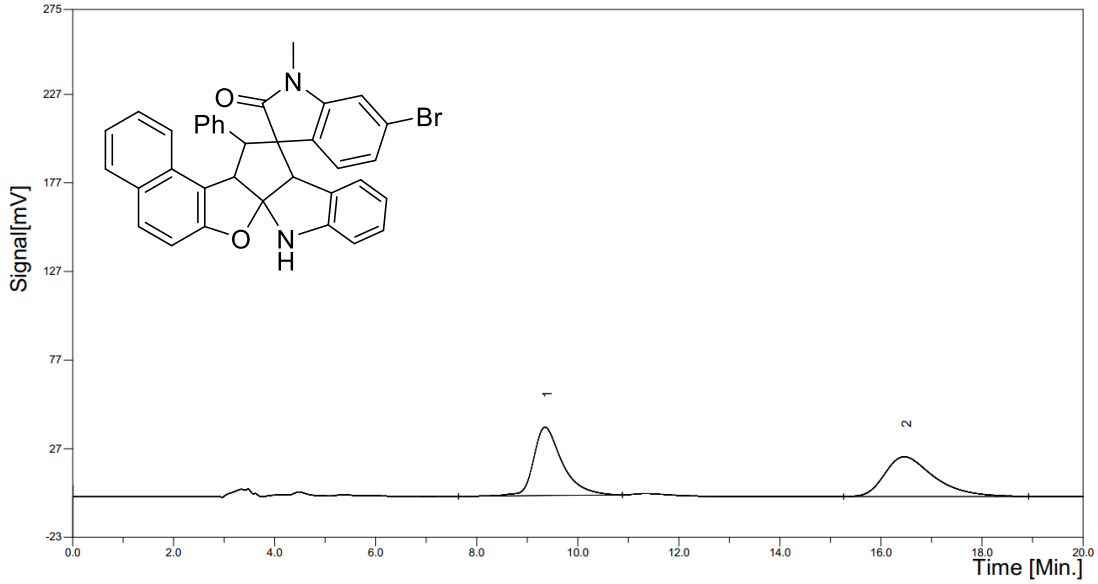


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.120	85.41	3127.73	50.8006
2	17.079	46.32	3029.15	49.1994

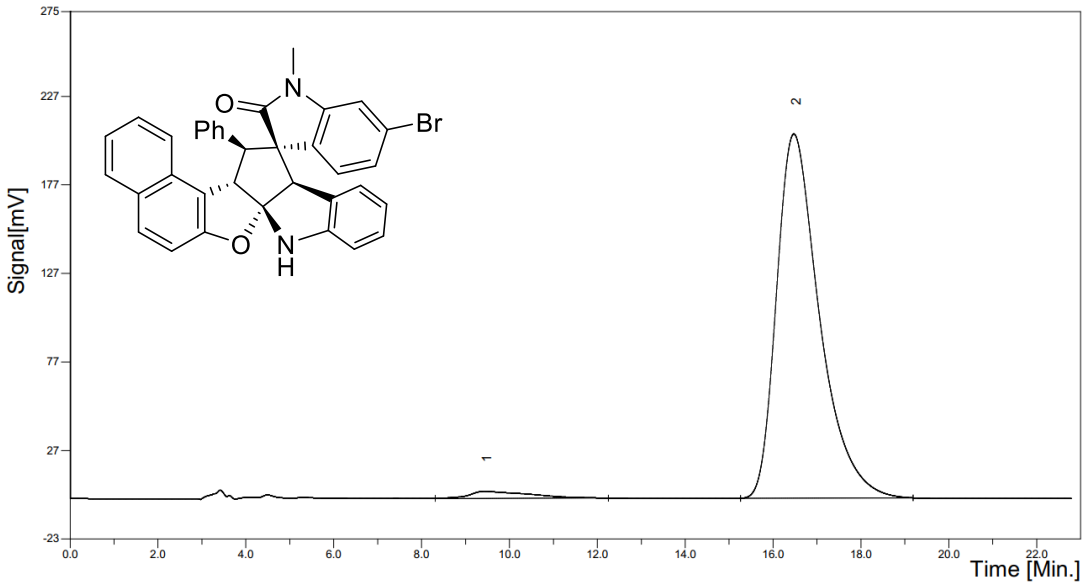


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.111	1.56	46.86	0.3365
2	17.028	201.28	13879.49	99.6635

3ua

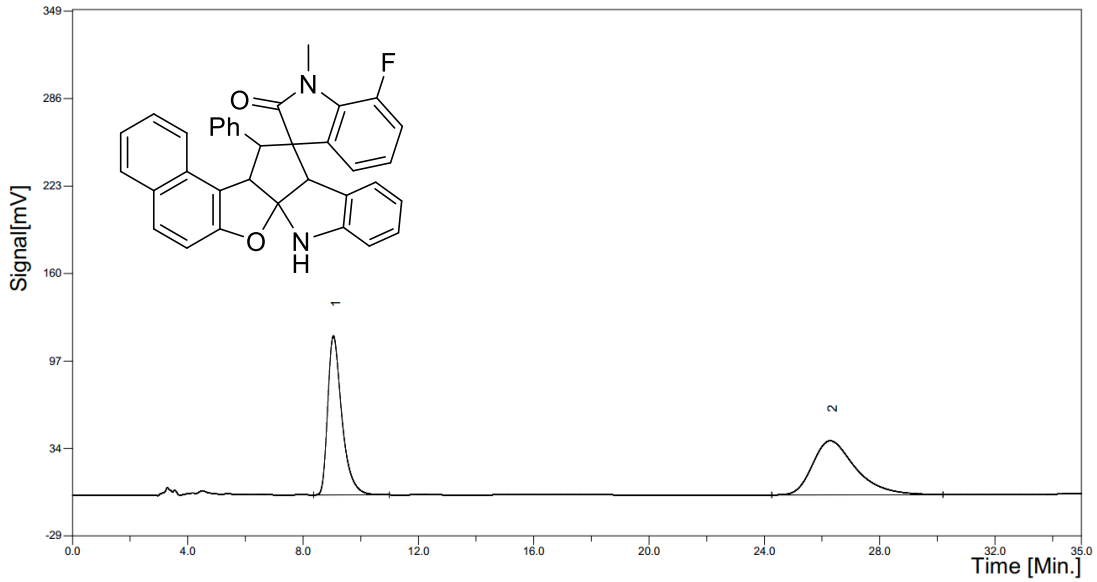


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.350	38.62	1520.47	50.0803
2	16.458	22.43	1515.59	49.9197

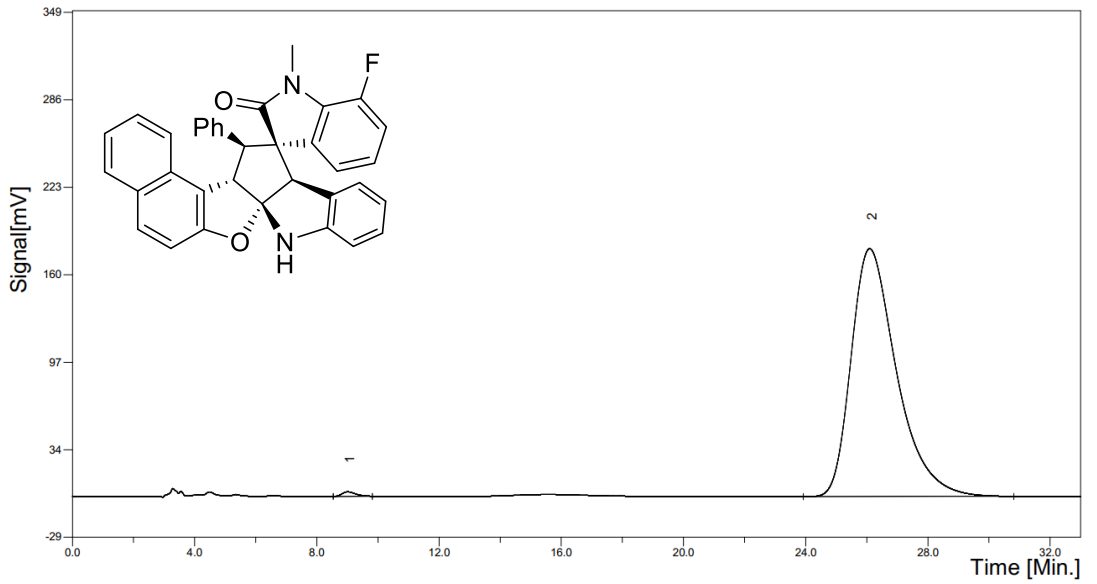


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.430	3.98	374.86	2.6164
2	16.470	205.69	13952.39	97.3836

3va

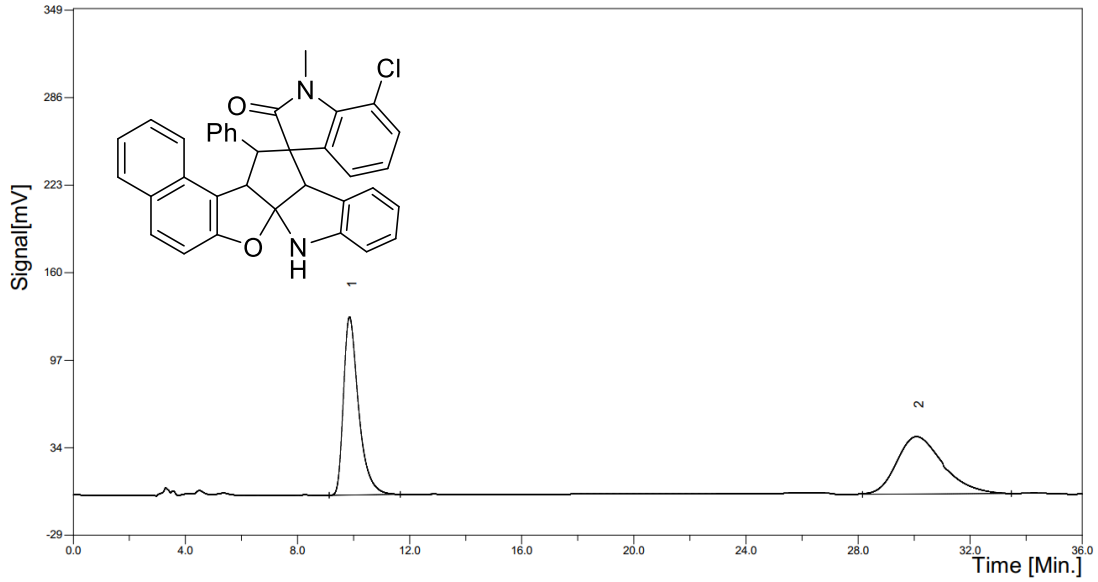


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.051	114.53	3905.48	49.1986
2	26.285	38.92	4032.72	50.8014

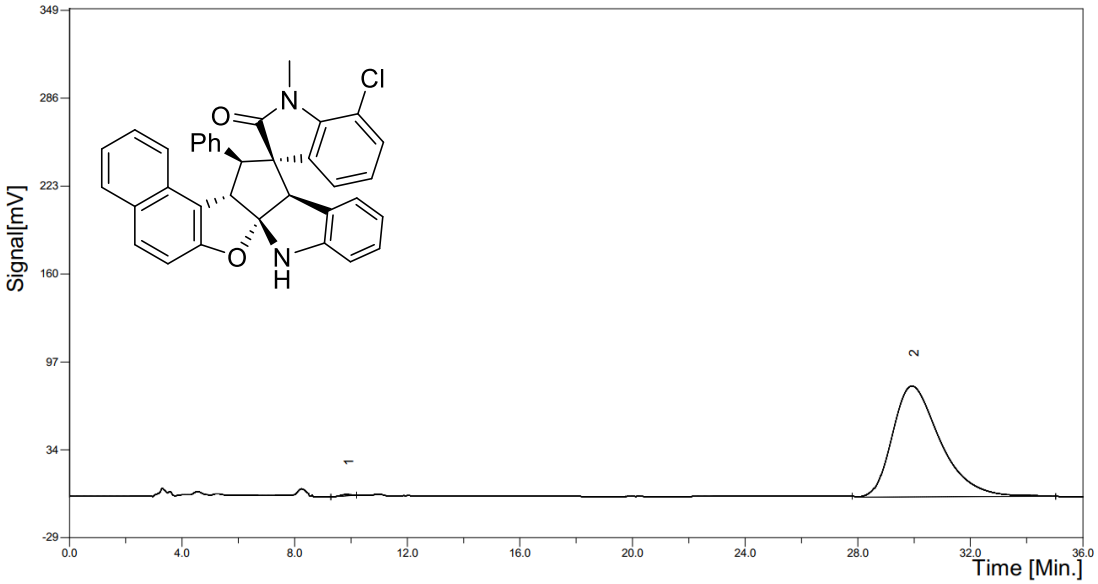


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.002	3.33	103.49	0.5584
2	26.095	178.47	18430.61	99.4416

3wa

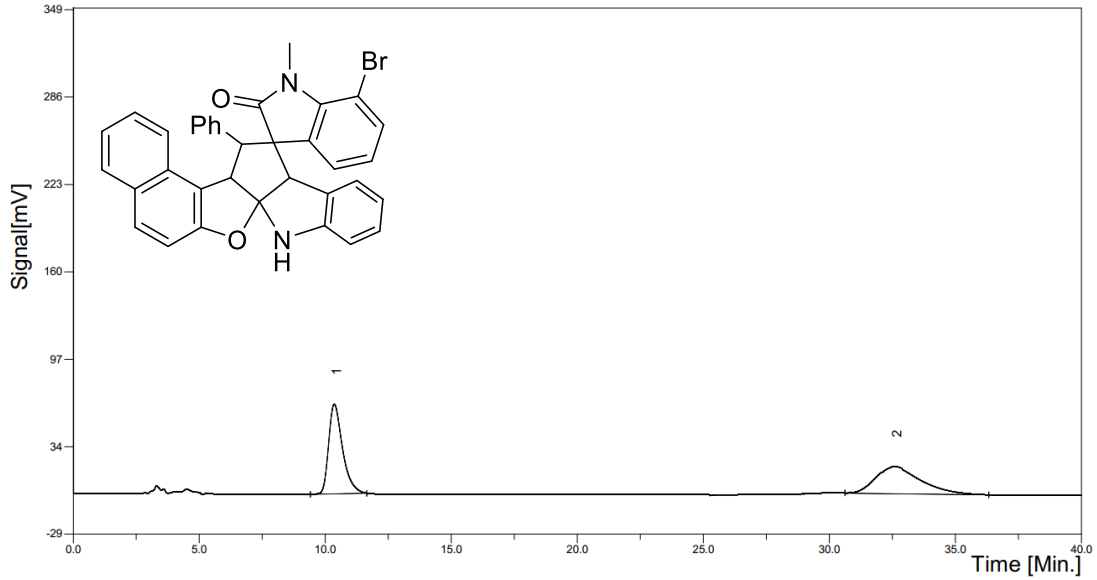


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9. 855	128. 35	4790. 67	50. 3296
2	30. 086	41. 32	4727. 93	49. 6704

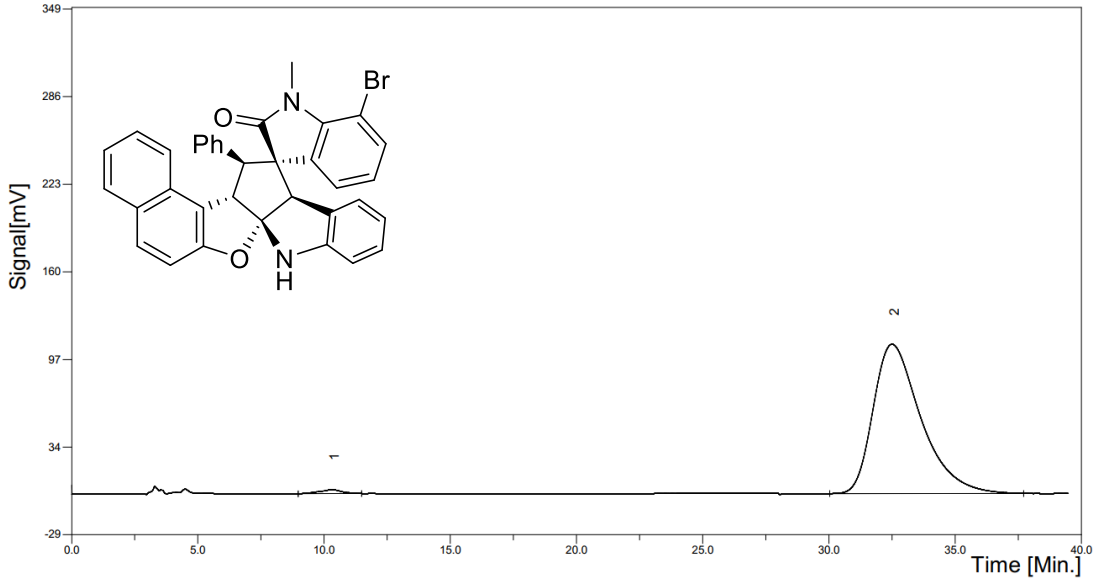


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.835	1.02	25.53	0.2765
2	29.920	78.89	9208.08	99.7235

3xa

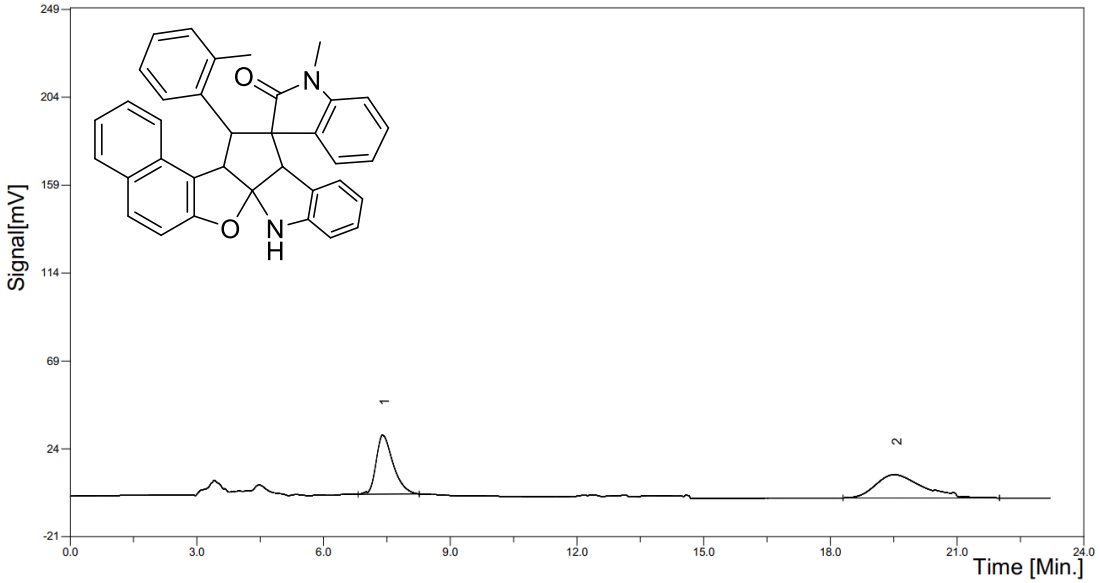


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.355	64.68	2480.24	51.3317
2	32.580	19.39	2351.55	48.6683

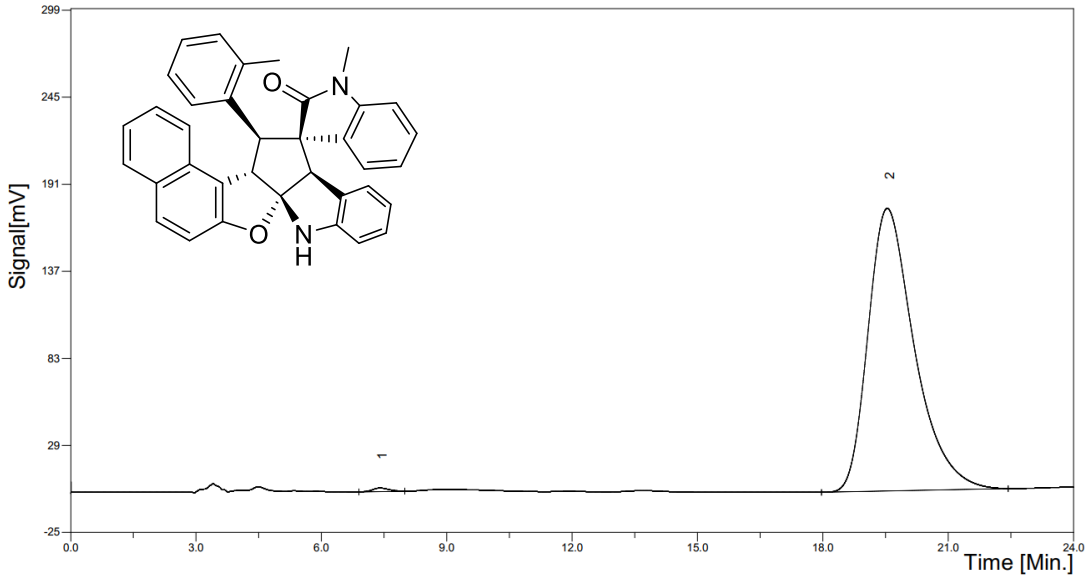


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	10.311	2.93	172.97	1.2089
2	32.498	107.36	14135.03	98.7911

3ab

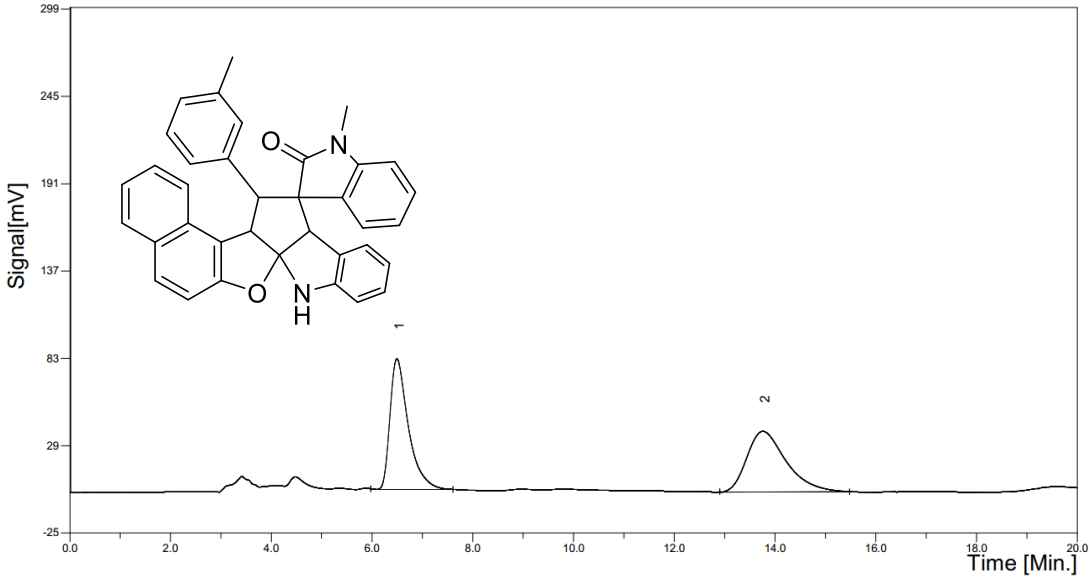


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.387	30.36	844.54	47.8134
2	19.516	11.90	921.78	52.1866

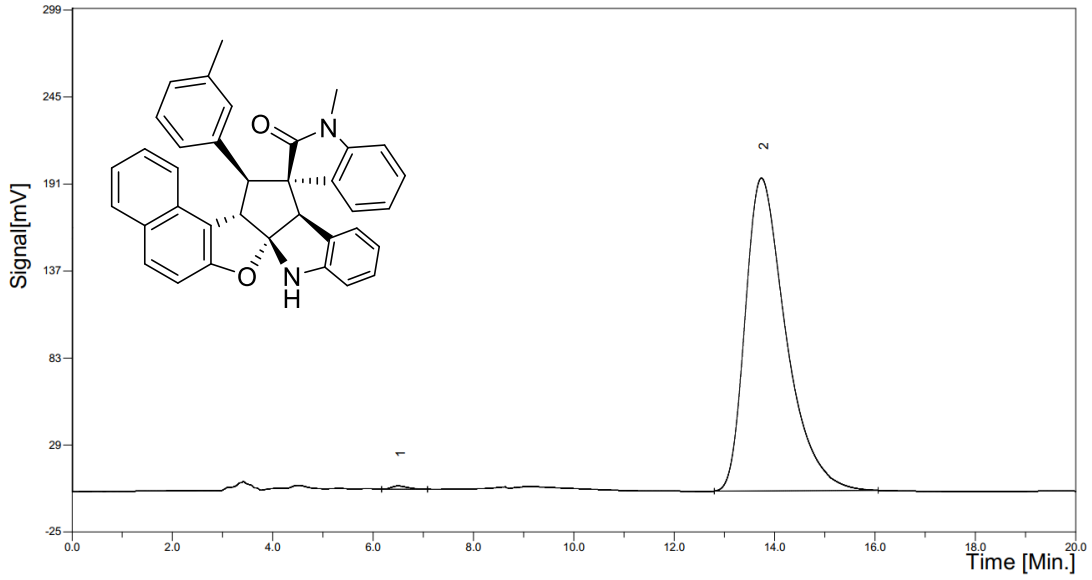


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.400	2.22	58.55	0.4313
2	19.540	175.29	13514.44	99.5687

3ac

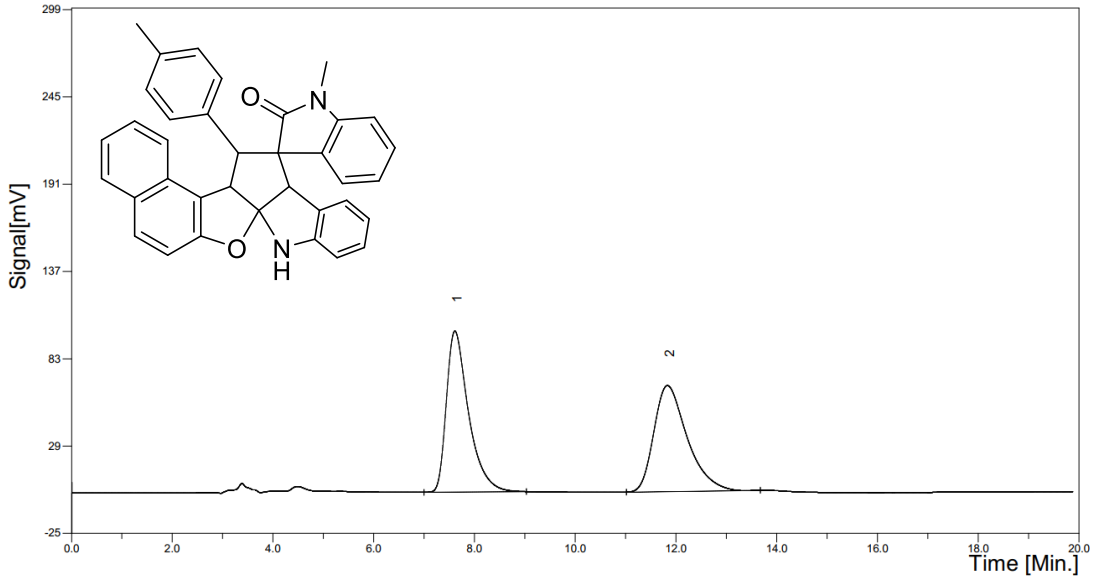


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.491	80.45	2020.74	50.2876
2	13.755	37.23	1997.63	49.7124

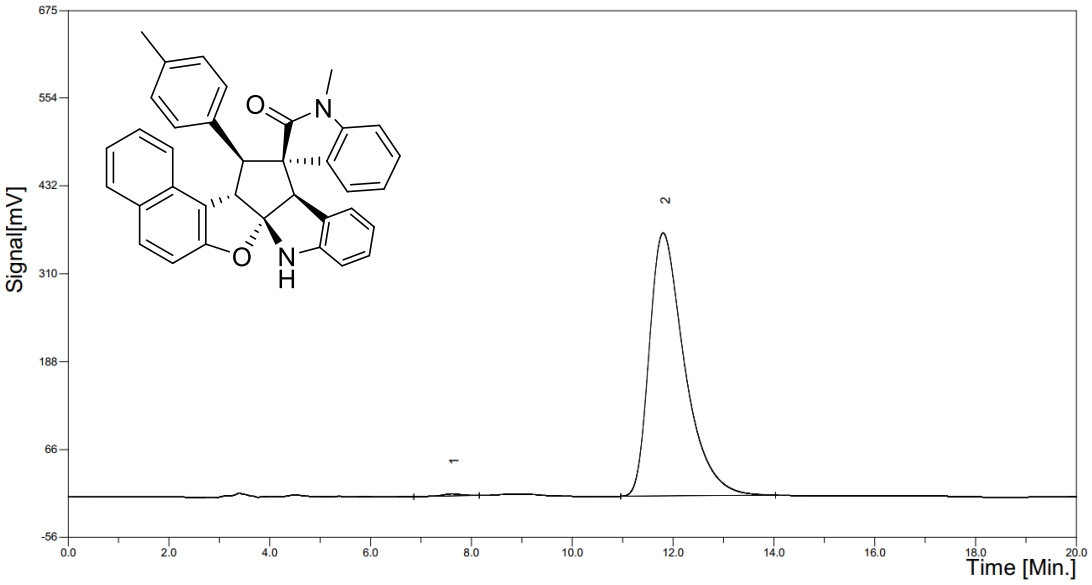


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	6.495	2.02	44.95	0.4098
2	13.736	194.11	10924.93	99.5902

3ad

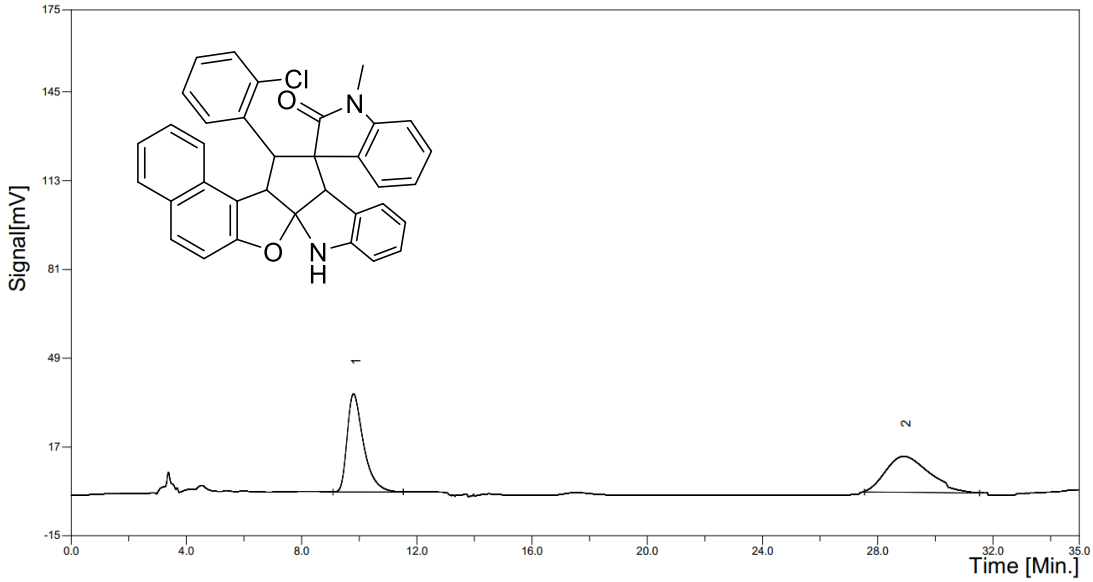


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.609	99.59	3041.09	50.3489
2	11.828	65.54	2998.94	49.6511

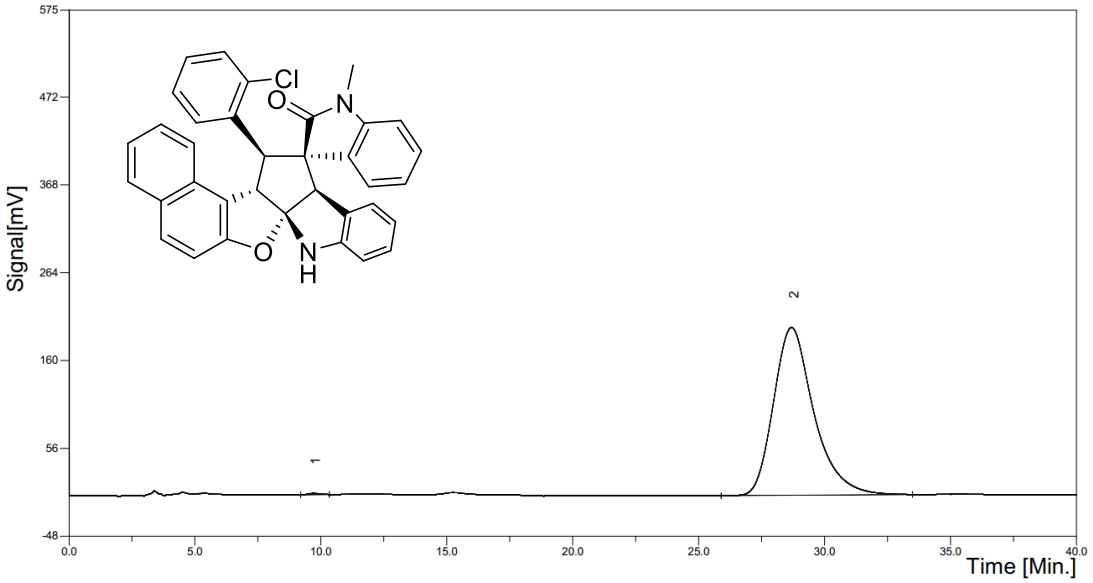


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.610	3.02	79.15	0.4442
2	11.801	365.13	17739.29	99.5558

3ae

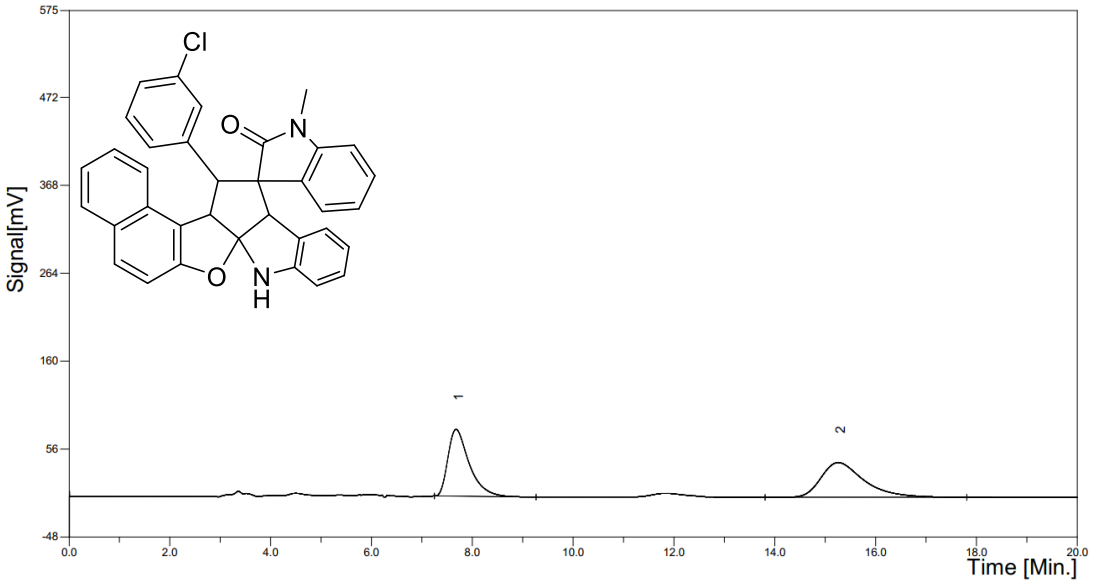


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.803	35.38	1397.55	50.5675
2	28.903	12.95	1366.18	49.4325

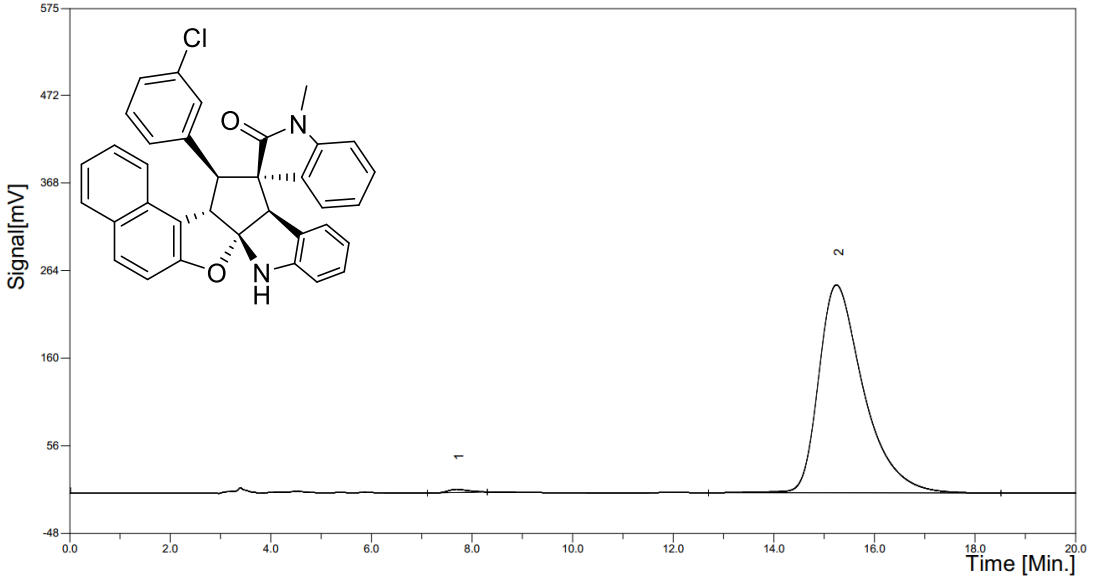


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	9.700	1.58	49.43	0.2235
2	28.685	198.61	22066.89	99.7765

3af

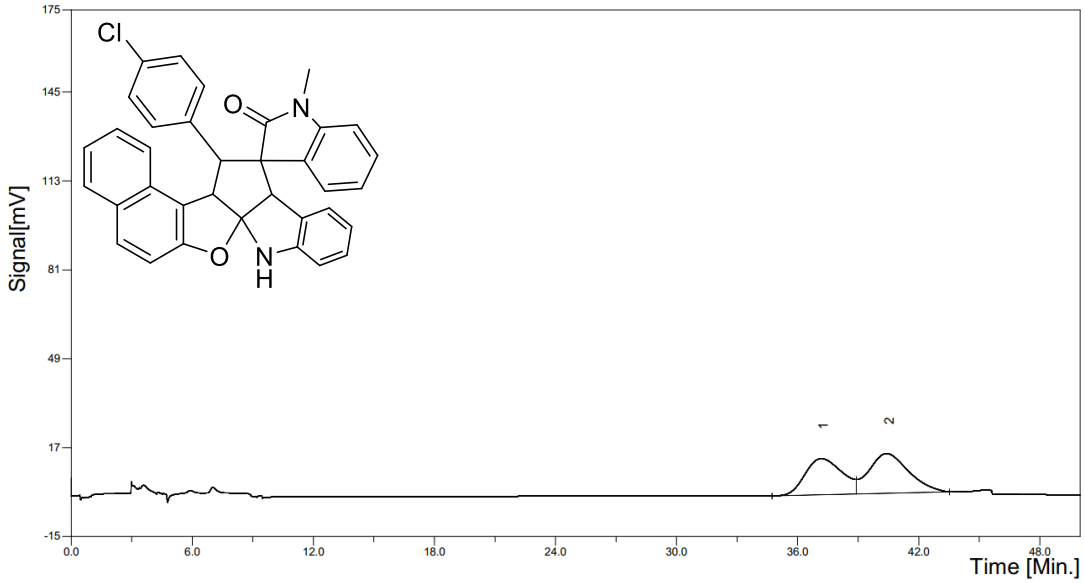


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.675	79.03	2308.95	48.7049
2	15.257	41.03	2431.75	51.2951

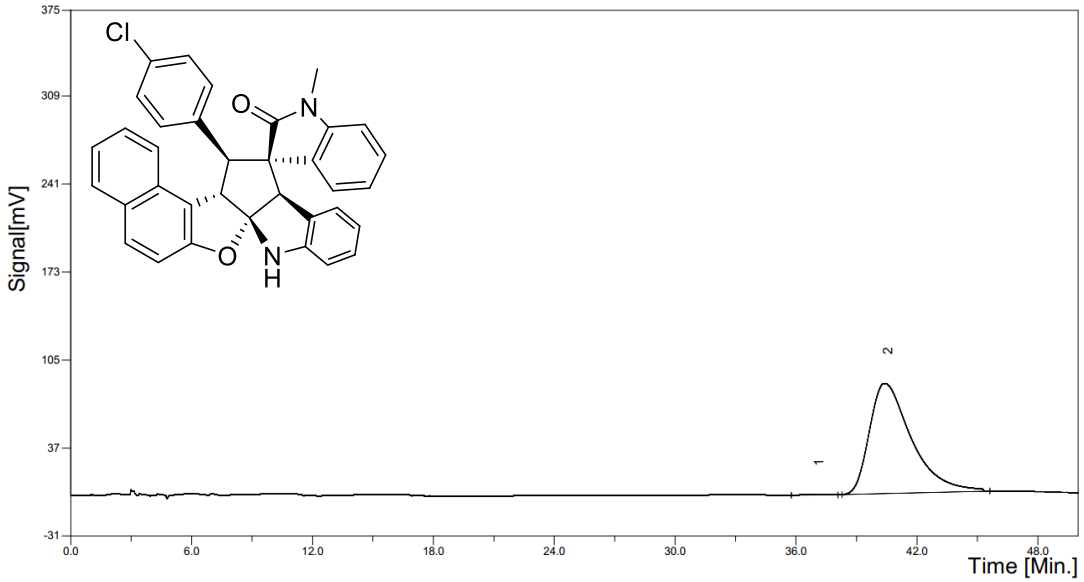


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	7.690	3.68	98.92	0.6421
2	15.241	246.67	15306.26	99.3579

3ag

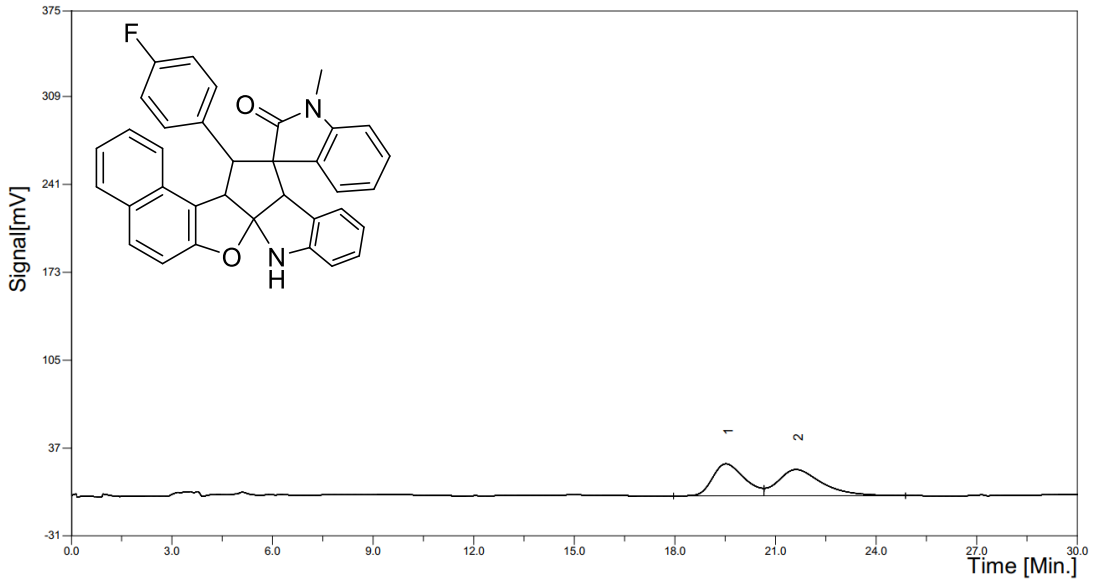


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	37.158	13.04	1667.63	47.8207
2	40.415	14.32	1819.62	52.1793

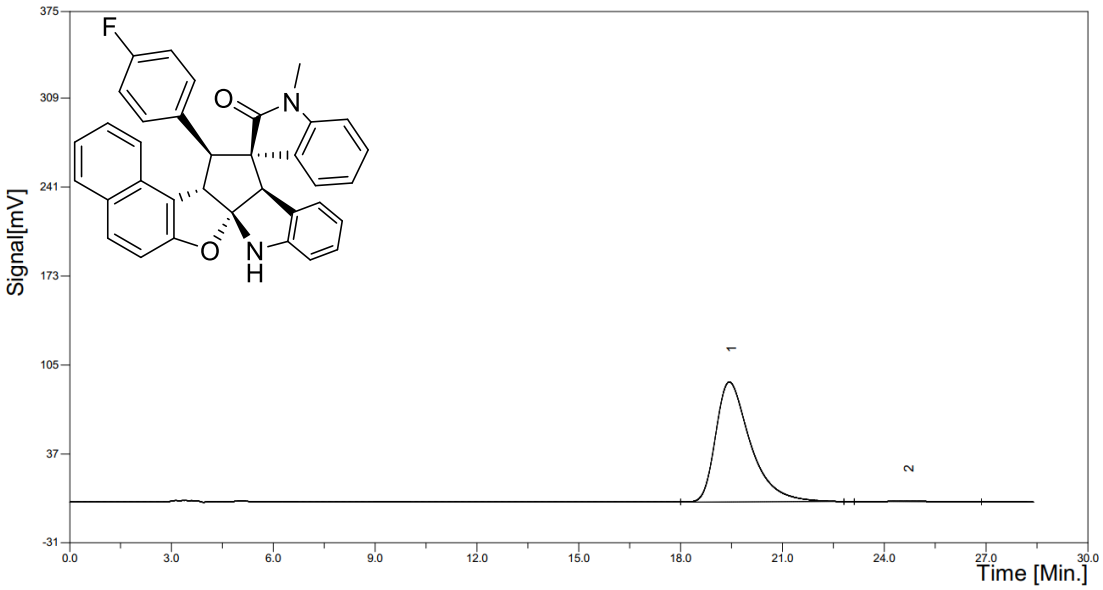


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	37.019	0.25	18.53	0.1499
2	40.441	84.96	12344.98	99.8501

3ah

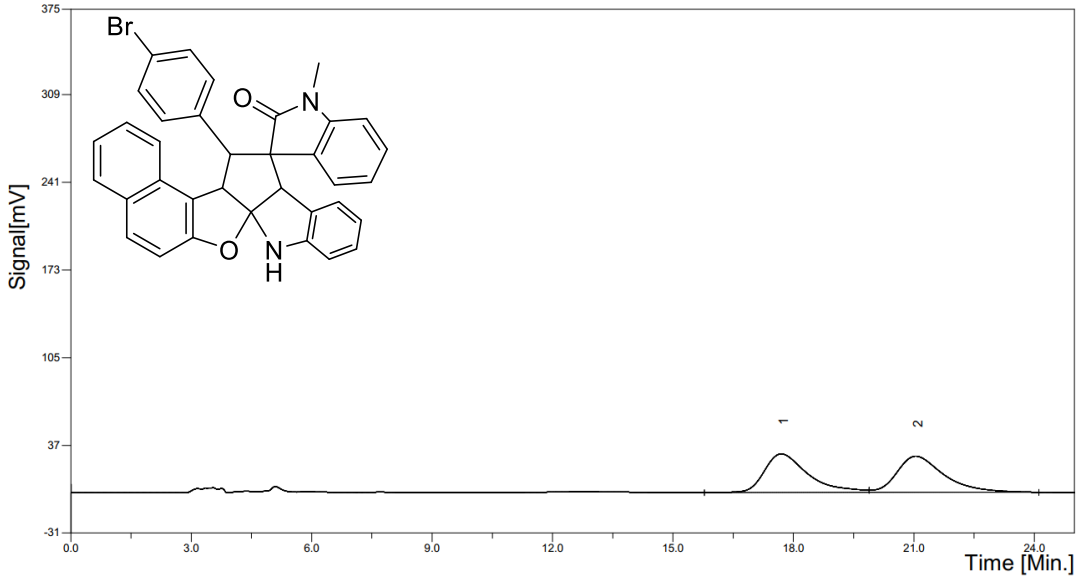


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	19.519	24.77	1640.47	47.1652
2	21.607	20.30	1837.67	52.8348

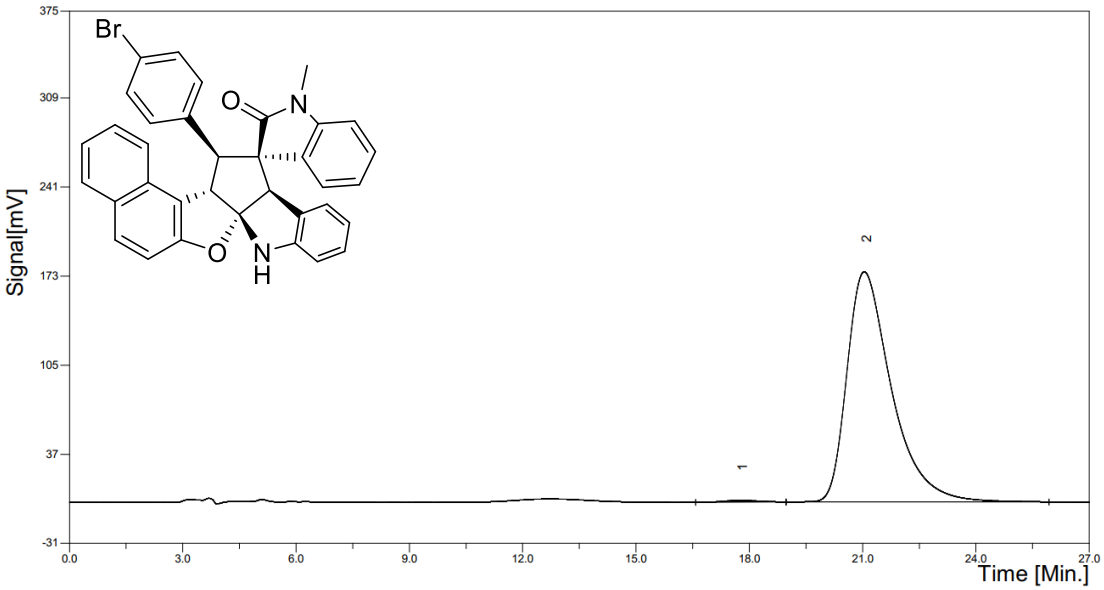


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	19.433	91.70	6509.02	99.4742
2	24.662	0.30	34.40	0.5258

3ai

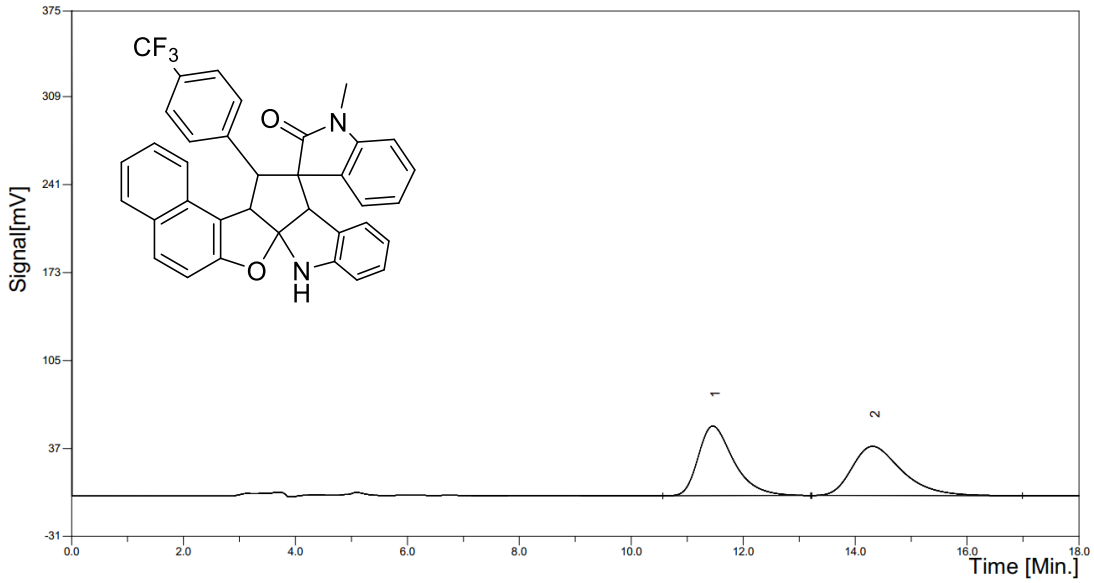


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	17.697	29.96	2275.84	49.8837
2	21.047	28.06	2286.45	50.1163

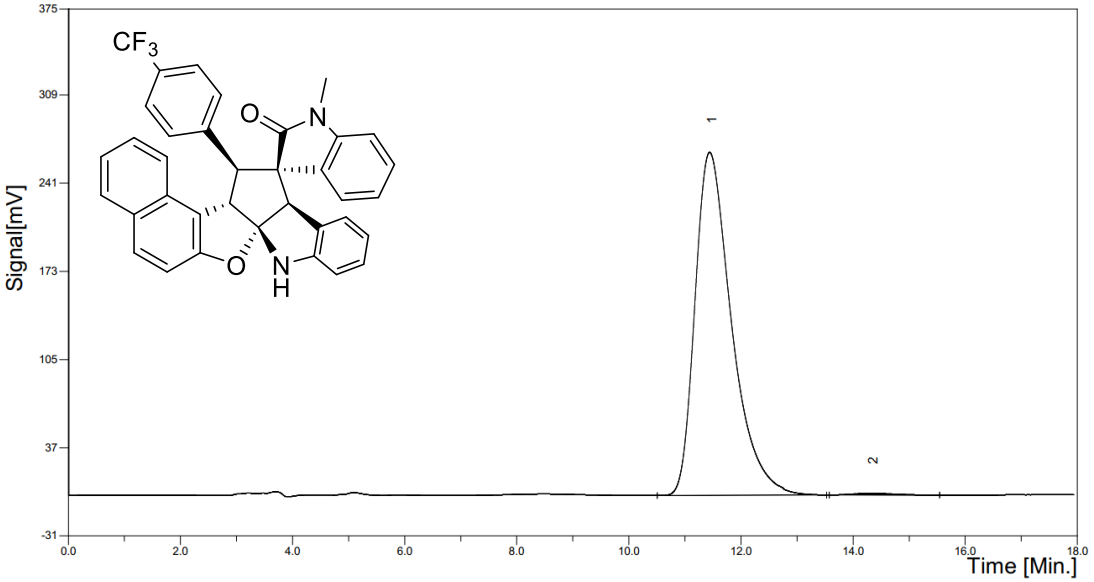


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	17.755	1.30	78.20	0.5409
2	21.043	175.70	14379.40	99.4591

3aj

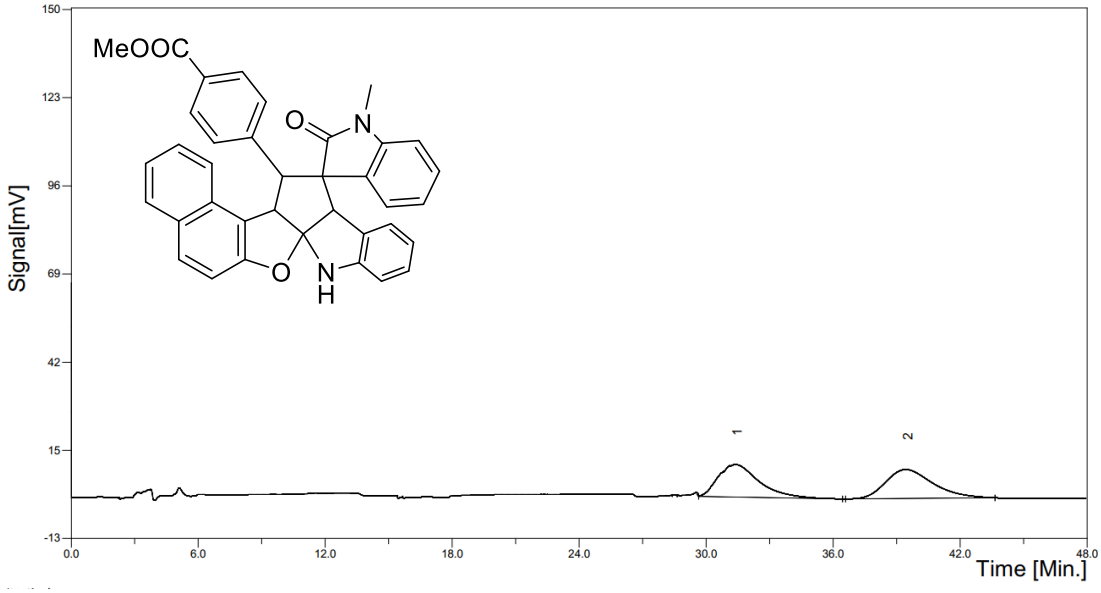


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	11.457	53.83	2362.32	50.0952
2	14.310	38.03	2353.35	49.9048

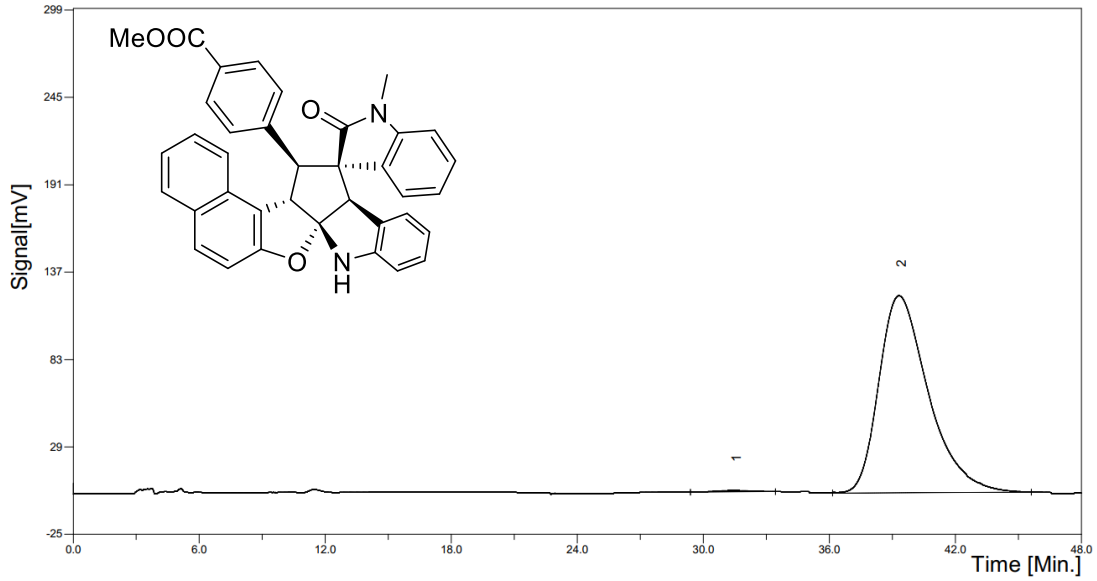


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	11.440	264.49	11978.27	99.4303
2	14.316	1.30	68.63	0.5697

3ak

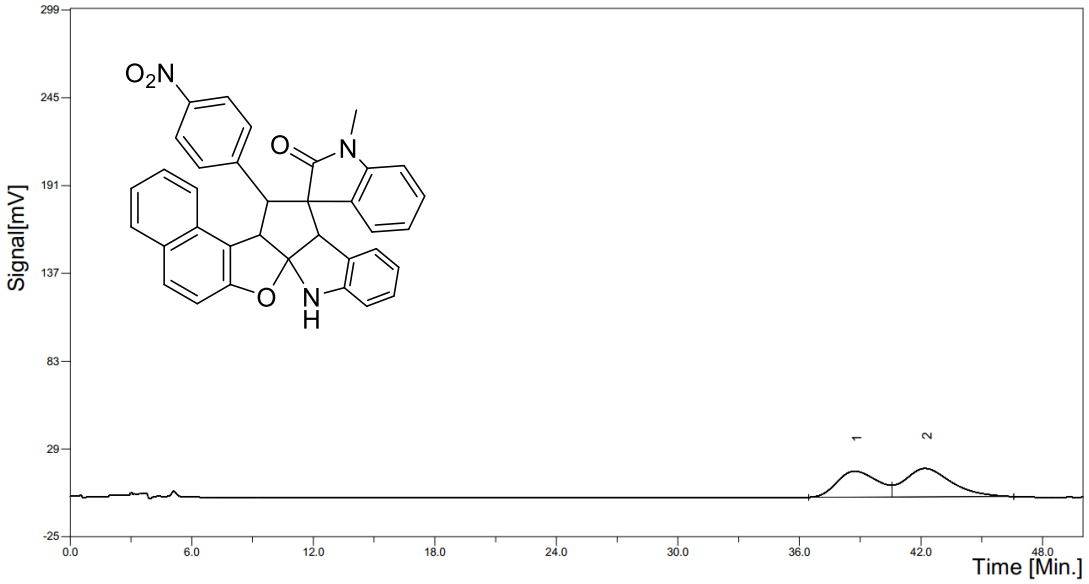


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	31.365	9.92	1322.65	49.0478
2	39.415	8.86	1374.01	50.9522

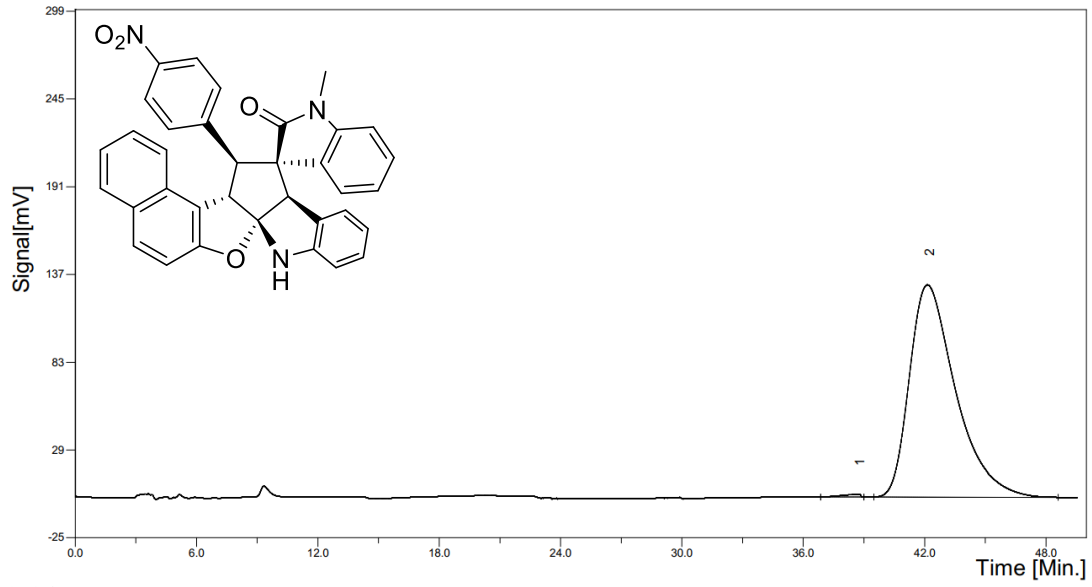


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	31.456	0.81	90.80	0.4541
2	39.309	121.69	19903.73	99.5459

3al

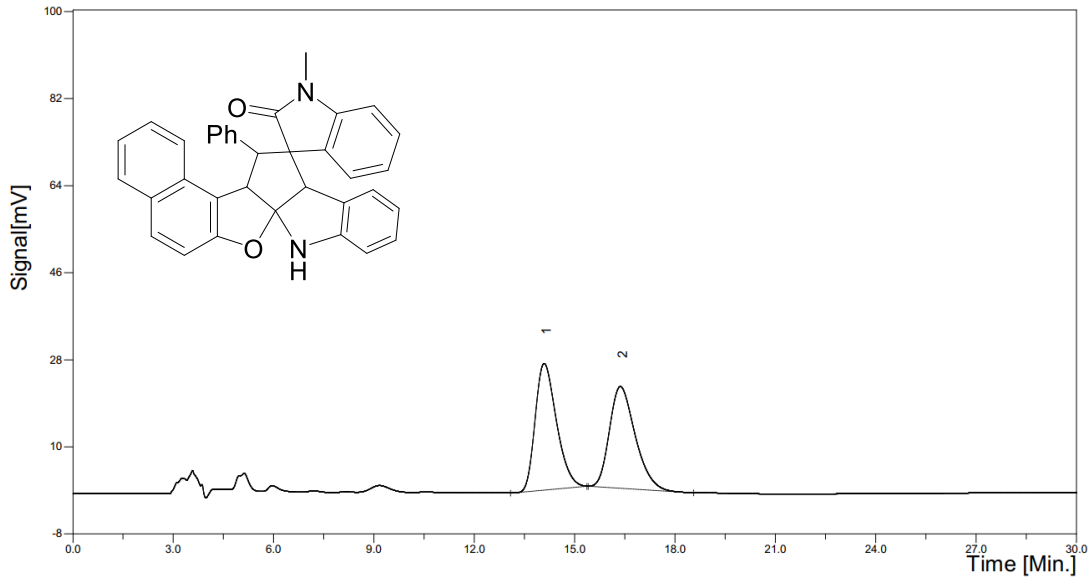


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	38.721	15.99	2238.04	46.2329
2	42.195	17.50	2602.75	53.7671

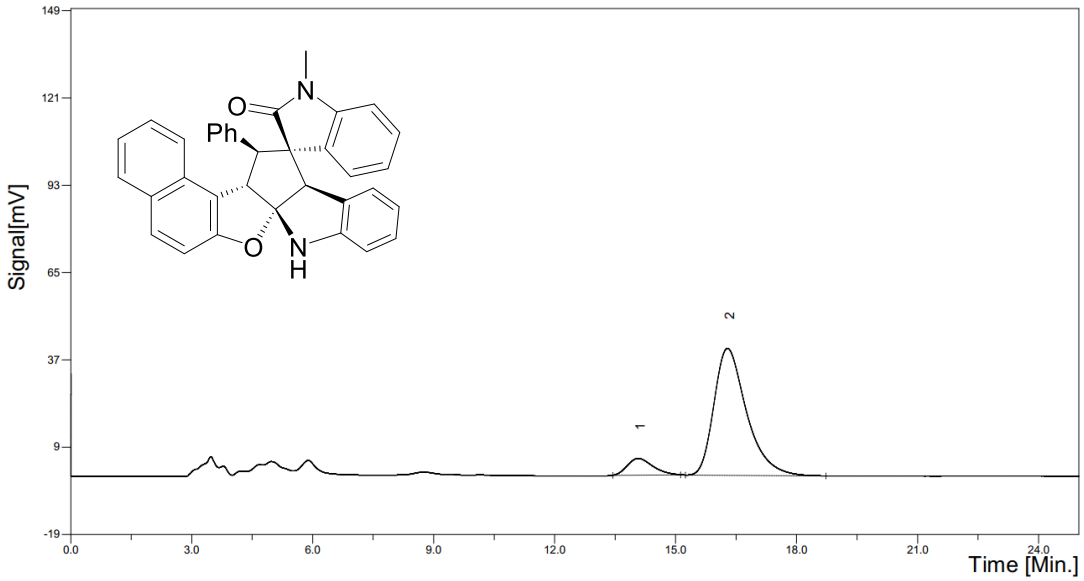


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	38.671	1.54	97.06	0.4670
2	42.136	130.58	20686.91	99.5330

3am



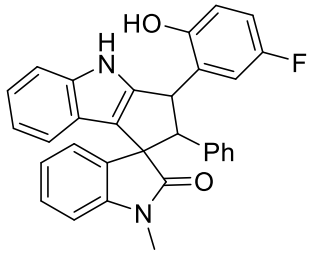
Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	14.088	26.17	1155.94	50.7392
2	16.365	21.01	1122.26	49.2608



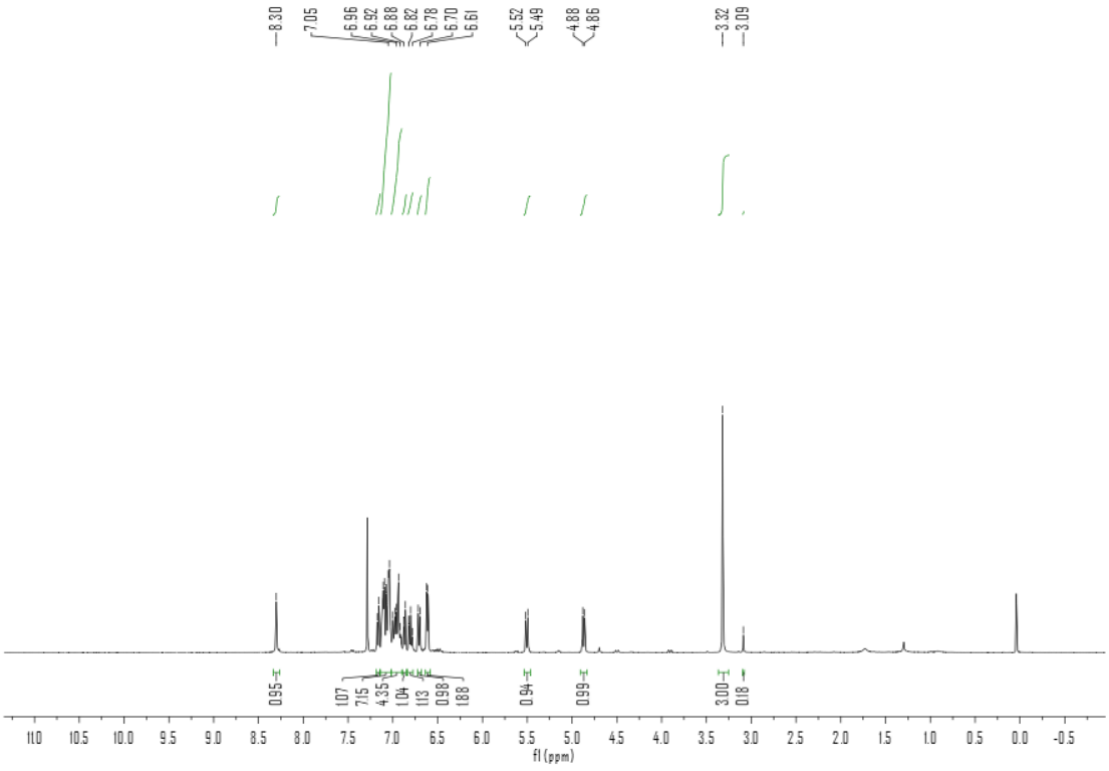
Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	14.066	5.34	233.51	9.2661
2	16.285	40.73	2286.52	90.7339

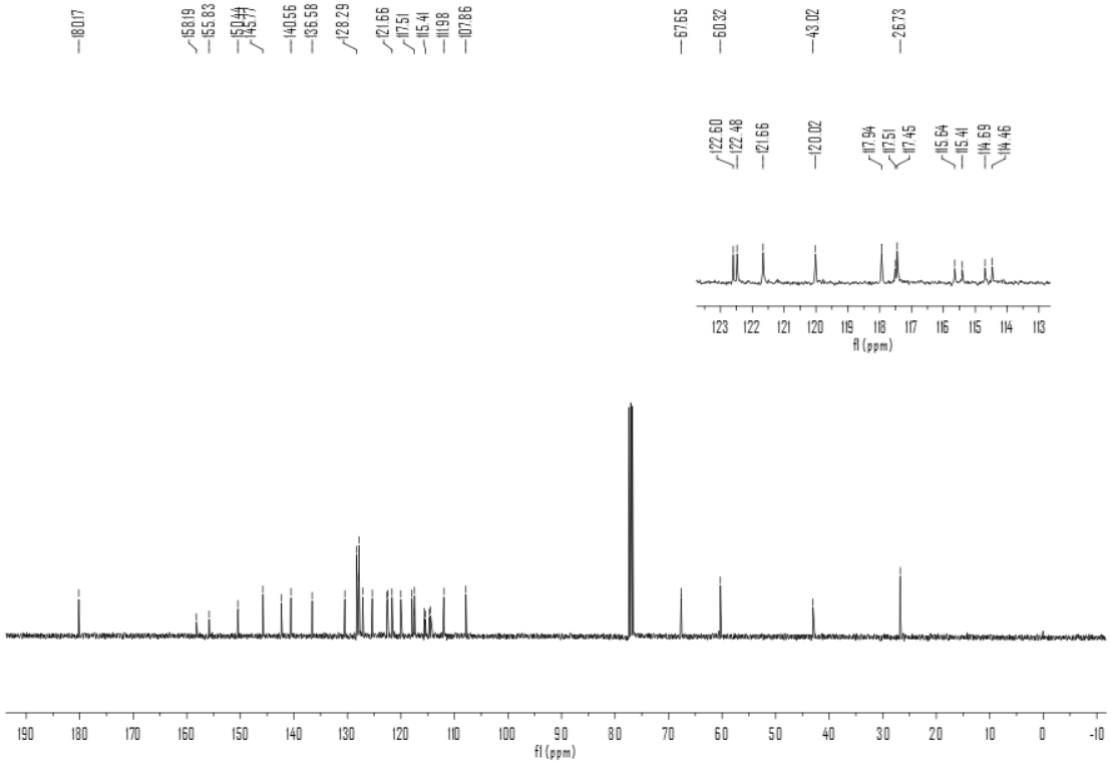
Intermediate data

7an:

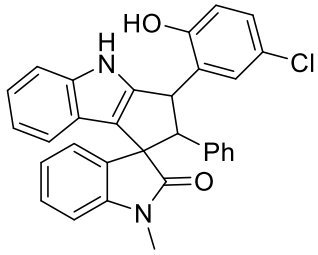


3-(5-fluoro-2-hydroxyphenyl)-1'-methyl-2-phenyl-3,4-dihydro-2H-spiro [cyclopenta[b]indole-1,3'-indolin]-2'-one: white solid, mp 113 - 115 ℃, 30mg, 63% yield. 16:1 d.r., 1H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.02 (m, 7H), 7.02 – 6.90 (m, 4H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 5.6 Hz, 2H), 5.51 (d, *J* = 9.0 Hz, 1H), 4.87 (d, *J* = 9.0 Hz, 1H), 3.32 (s, 3H) ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.1, 155.5 (d, *J*= 236 Hz), 150.4, 145.7, 142.3, 140.5, 136.5, 130.4, 128.2, 127.8, 127.8 (d, *J*=7 Hz), 125.3, 122.5 (d, *J*=12 Hz), 121.6, 120.0, 117.7 (d, *J*=49 Hz), 117.5, 115.5 (d, *J*=23 Hz), 114.5 (d, *J*=23 Hz), 111.9, 107.8, 67.6, 60.3, 43.0, 26.7. HRMS (ESI): calcd for $C_{31}H_{23}FN_2O_2$ $[M + H]^+$, 475.1816; found 475.1813.

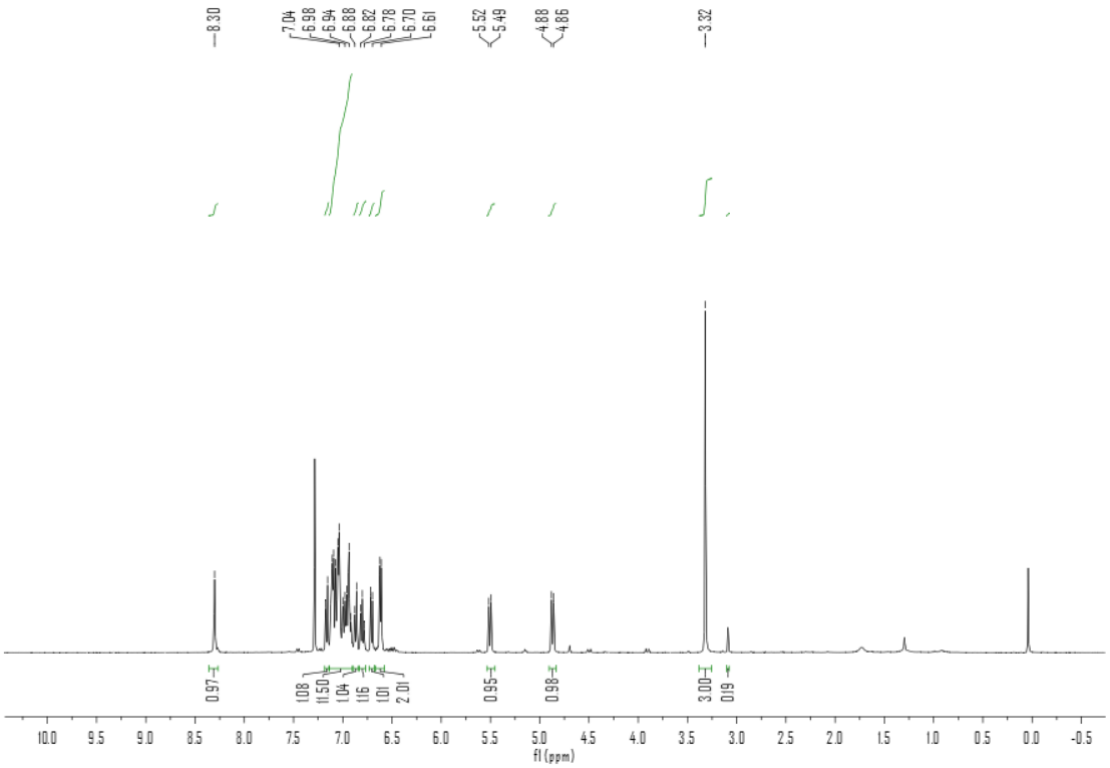


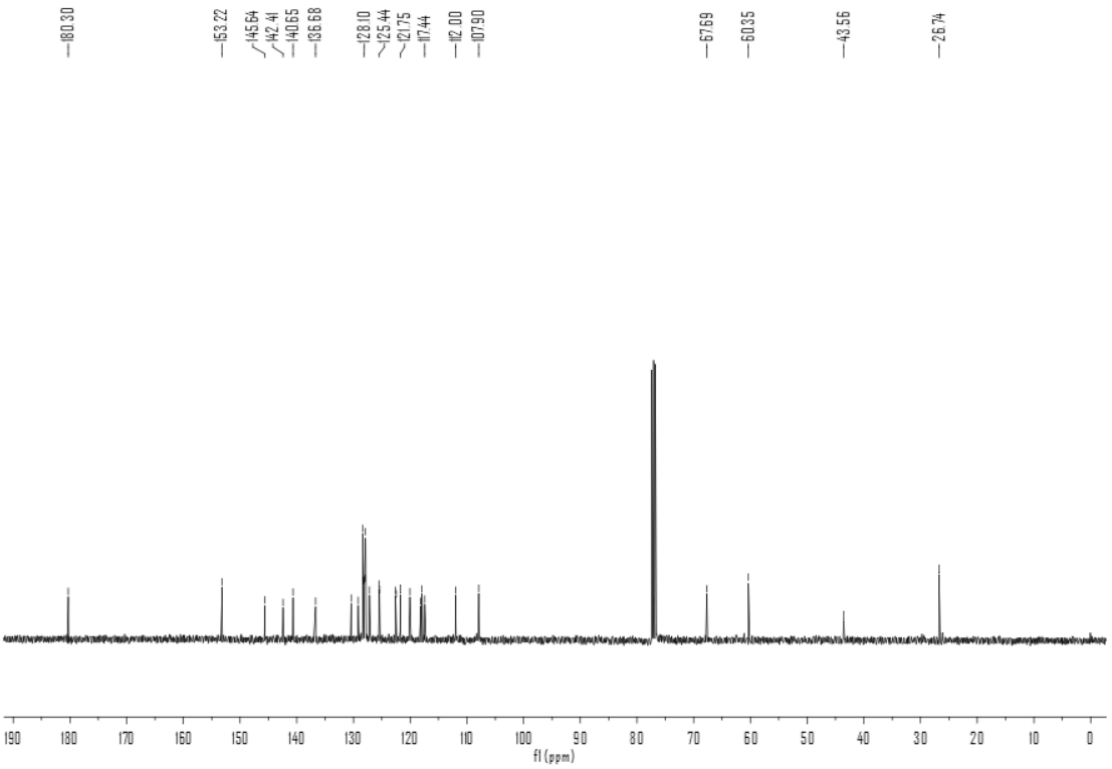

180.17
158.19
155.83
150.44
145.77
140.56
136.58
128.29
121.66
117.51
115.41
111.98
107.86
67.65
60.32
43.02
26.73
122.60
122.48
121.66
120.02
117.94
117.51
117.45
115.64
115.41
114.69
114.46
f1 (ppm)
f1 (ppm)

7ao:



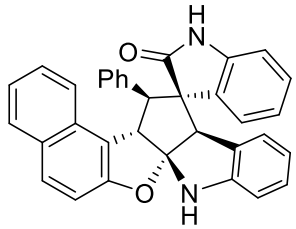
3-(5-chloro-2-hydroxyphenyl)-1'-methyl-2-phenyl-3,4-dihydro-2H-spiro[cyclopenta[b]indole-1,3'-indolin]-2'-one: white solid, mp 121 - 123 ℃, 32mg, 65% yield. 15:1 d.r., ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.16 (d, *J* = 8.1 Hz, 1H), 7.14 – 6.91 (m, 11H), 6.87 (d, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 6.62 (d, *J* = 5.6 Hz, 2H), 5.51 (d, *J* = 9.0 Hz, 1H), 4.87 (d, *J* = 9.0 Hz, 1H), 3.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 180.3, 153.2, 145.6, 142.4, 140.6, 136.6, 130.4, 129.1, 128.3, 128.2, 128.1, 127.9, 127.8, 127.1, 125.4, 125.4, 122.6, 122.4, 121.7, 120.0, 118.2, 117.9, 117.4, 112.0, 107.9, 67.6, 60.3, 43.5, 26.7. HRMS (ESI): calcd for $C_{31}H_{23}ClN_2O_2$ $[M + H]^+$, 491.1521; found 491.1526.



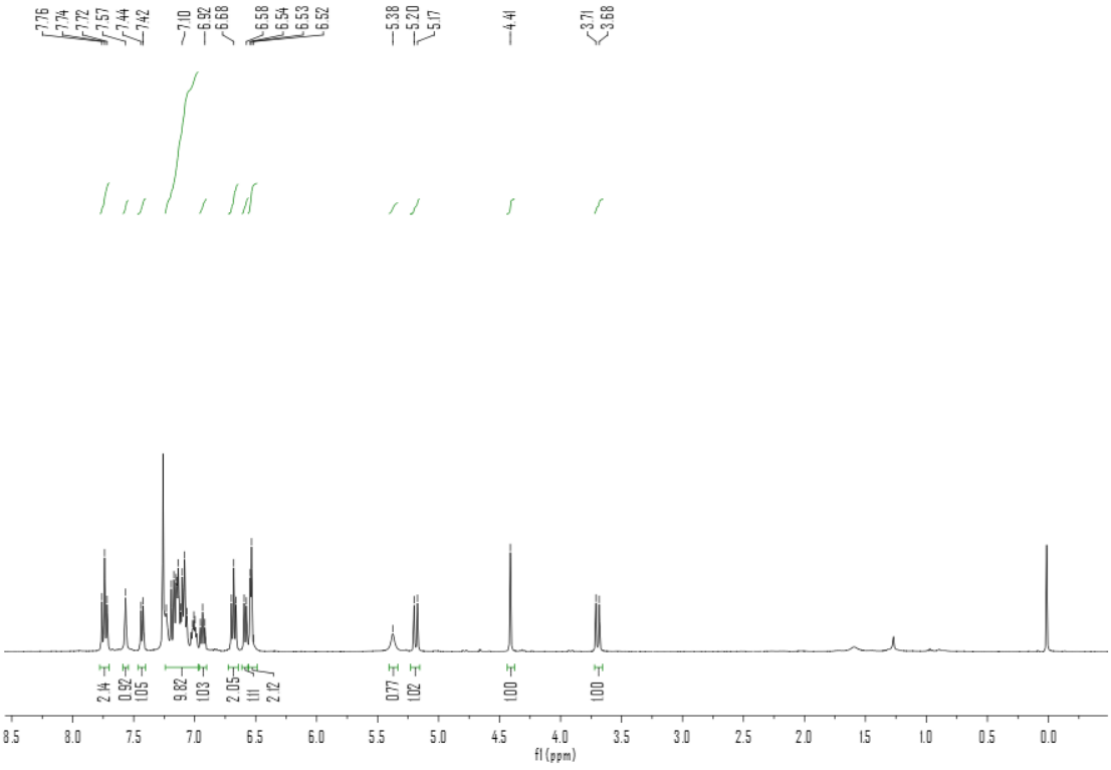

180.30
153.22
145.64
142.41
140.65
136.68
128.10
125.44
121.75
117.44
112.00
107.90
67.69
60.35
43.56
26.74
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

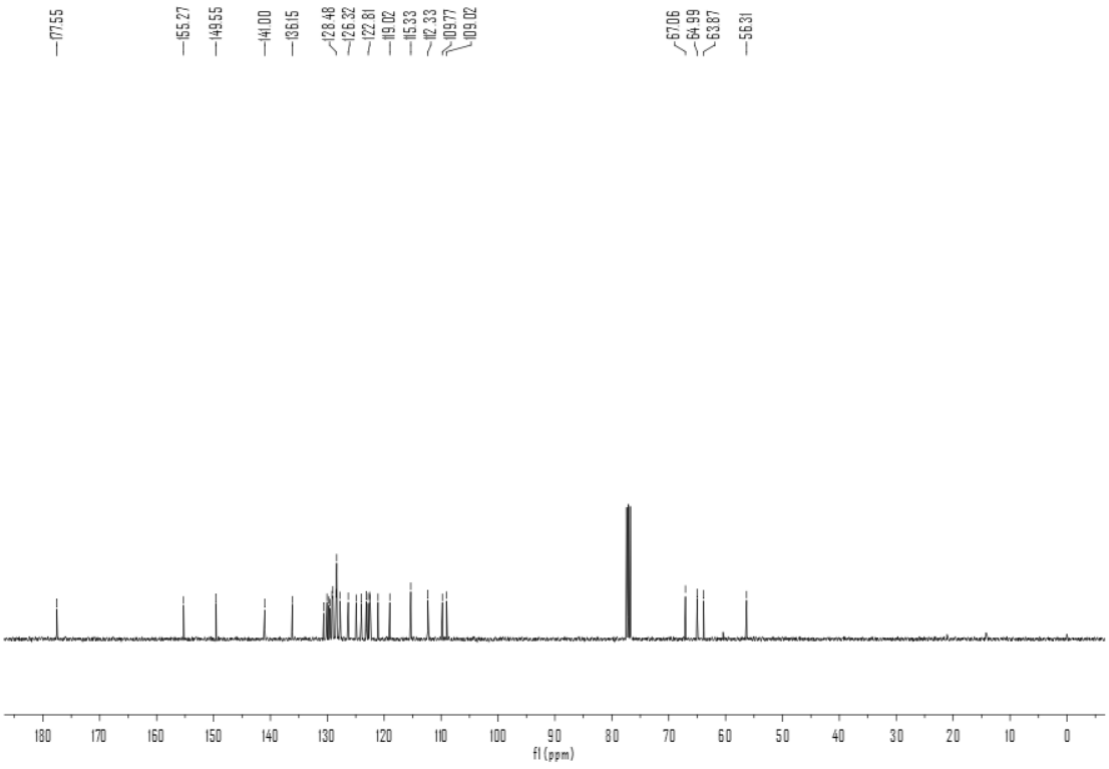
Control experiment data

3wa

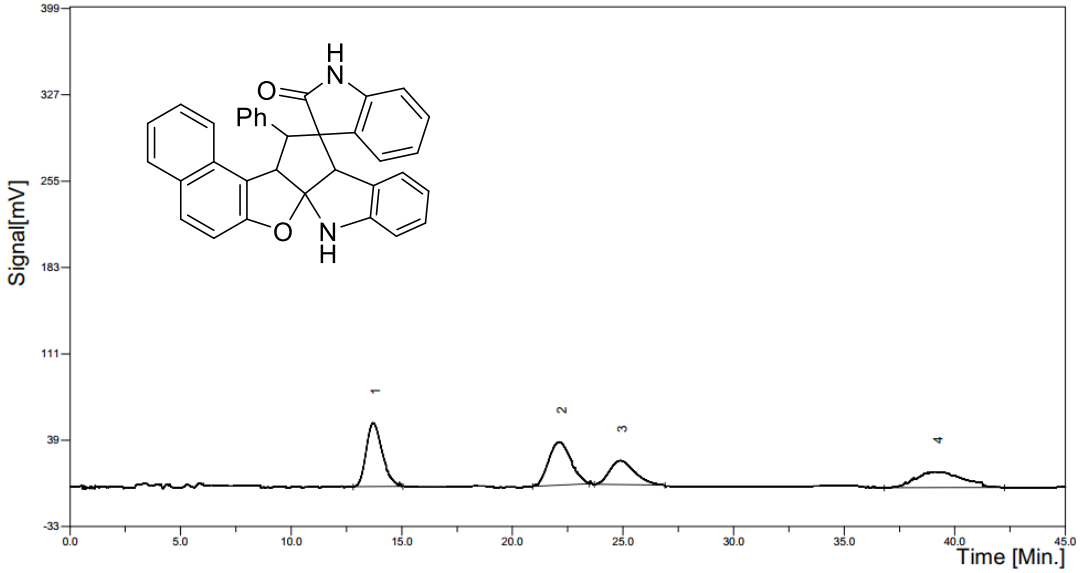


(*3R,6c'S,7'S,8a'R,13a'R*)-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 99 - 101 ℃, 35.0 mg, 71% yield, 93% ee, >19:1 d.r. $[\alpha]_D^{20}$ = +268.6 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (t, *J* = 8.4 Hz, 2H), 7.57 (s, 1H), 7.43 (d, *J* = 7.3 Hz, 1H), 7.24 – 6.97 (m, 10H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 2H), 6.59 (d, *J* = 7.6 Hz, 1H), 6.56 – 6.49 (m, 2H), 5.38 (s, 1H), 5.19 (d, *J* = 11.1 Hz, 1H), 4.41 (s, 1H), 3.70 (d, *J* = 11.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 155.2, 149.5, 141.00, 136.1, 130.6, 130.0, 129.8, 129.4, 129.1, 129.0, 128.4, 128.4, 128.3, 127.7, 126.3, 124.9, 124.0, 123.1, 122.8, 122.5, 122.4, 121.0, 119.0, 115.3, 112.3, 109.7, 109.0, 67.0, 64.9, 63.8, 56.3. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 85/15, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_{major} = 22.127 min, t_{minor} = 11.733 min. HRMS (ESI): calcd for $C_{34}H_{24}N_2O_2$. $[M + H]^+$, 493.1911; found, 493.1906.

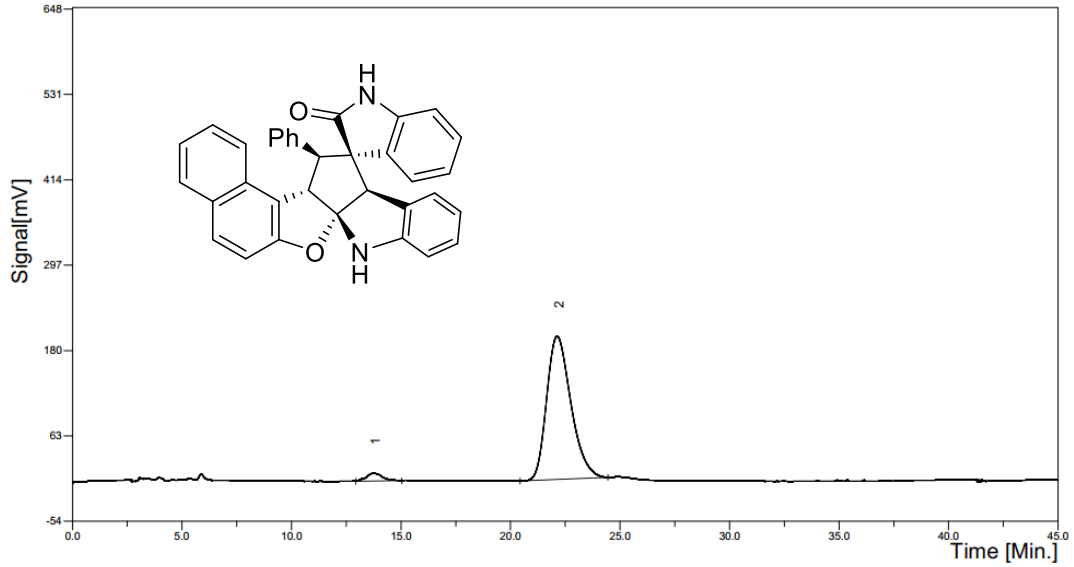



177.55
155.27
149.55
141.00
136.15
128.48
126.32
122.81
119.02
115.33
112.33
109.77
109.02
67.06
64.99
63.87
56.31
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3wa

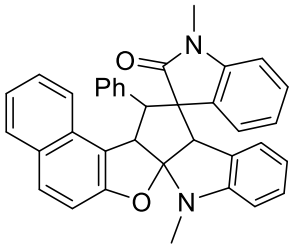


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	13.704	52.89	2672.75	30.7834
2	22.137	35.99	2514.72	28.9633
3	24.879	19.80	1547.11	17.8189
4	39.145	13.24	1947.86	22.4345

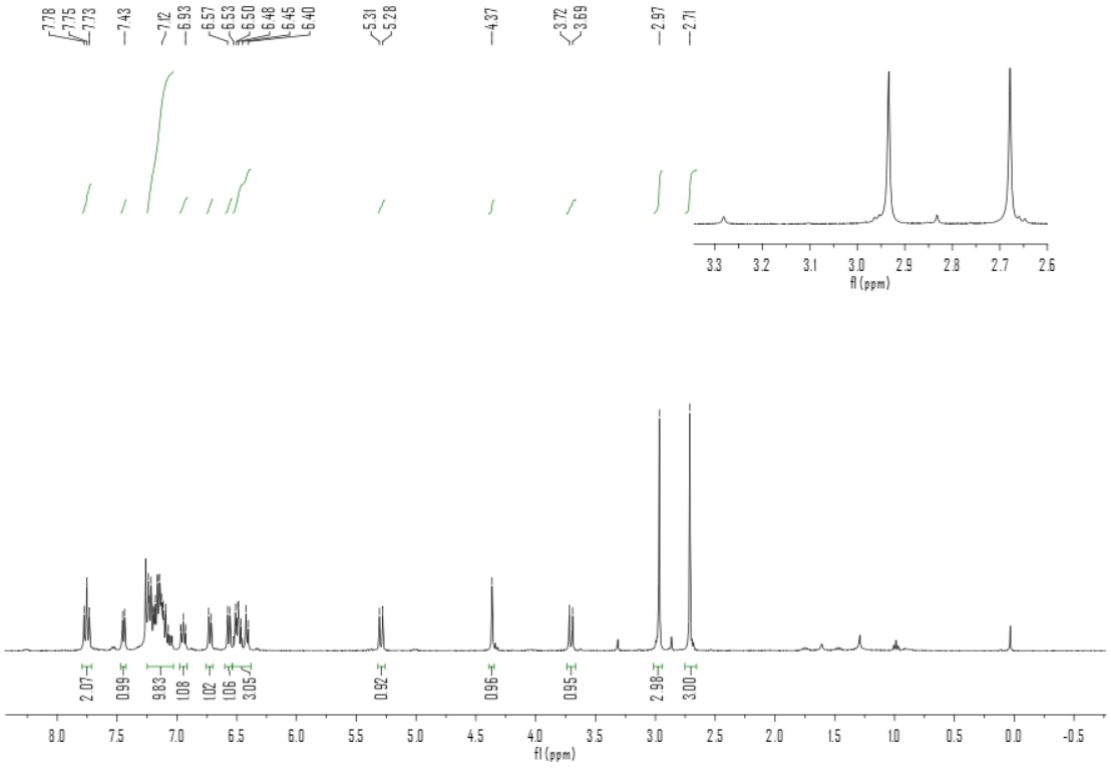


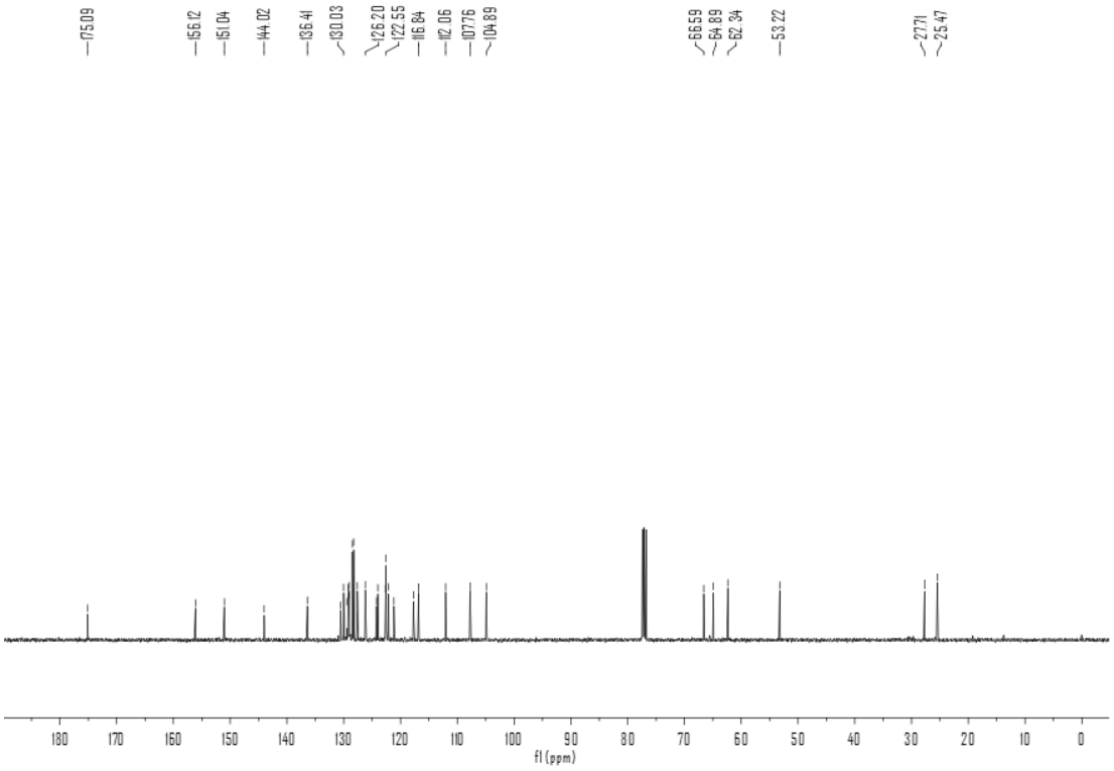
Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	13.733	11.41	538.46	3.4493
2	22.127	196.01	15072.51	96.5507

3za



(*3R,6c'S,7'S,8a'R,13a'R*)-1,13'-dimethyl-7'-phenyl-6c',7',8a',13'-tetrahydrospiro[indoline-3,8'-naphtho[1",2":4',5']furo[2',3':1,5]cyclopenta[1,2-b]indol]-2-one：white solid, mp 141 - 143 ℃, 13.0 mg, 25% yield, 21:1 d.r.; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (t, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.02 (m, 10H), 6.95 (t, *J* = 8.0, 3.9 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 4.0 Hz, 1H), 6.53 – 6.38 (m, 3H), 5.29 (d, *J* = 11.1 Hz, 1H), 4.37 (s, 1H), 3.71 (d, *J* = 11.1 Hz, 1H), 2.97 (s, 3H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 156.1, 151.0, 144.0, 136.4, 130.5, 130.0, 129.3, 129.2, 129.0, 129.0, 128.4, 128.2, 127.6, 126.2, 124.2, 124.0, 122.6, 122.5, 122.1, 121.1, 117.7, 116.8, 112.0, 107.7, 104.8, 66.5, 64.8, 62.3, 53.2, 27.7, 25.4. HPLC analysis: Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, retention time: t_1 = 5.346 min, t_2 = 9.795 min. HRMS (ESI): calcd for $C_{35}H_{26}N_2O_2$ $[M + H]^+$, 521.2224; found,521.2216.

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25.47
180
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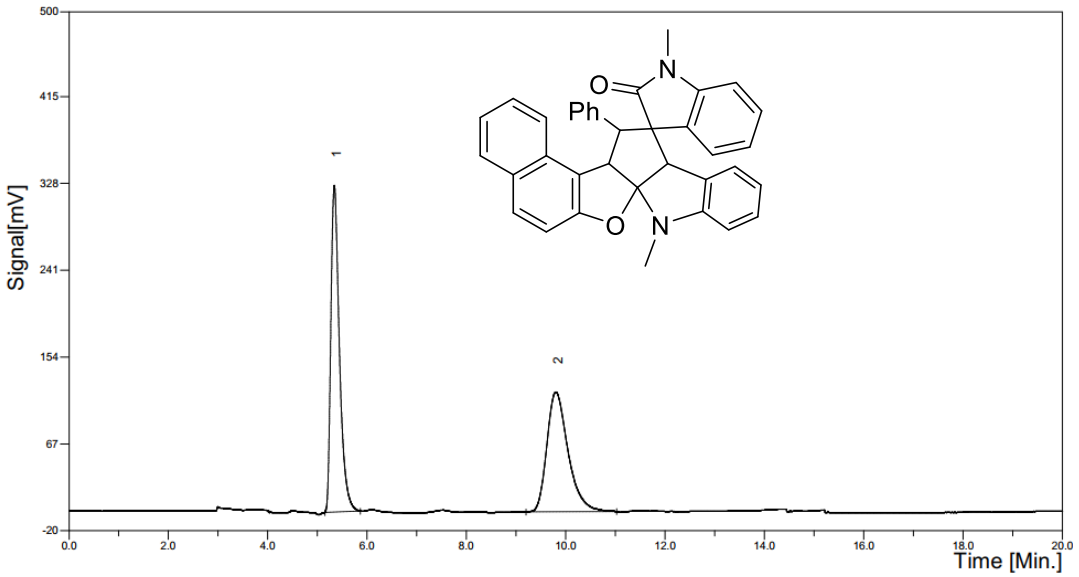
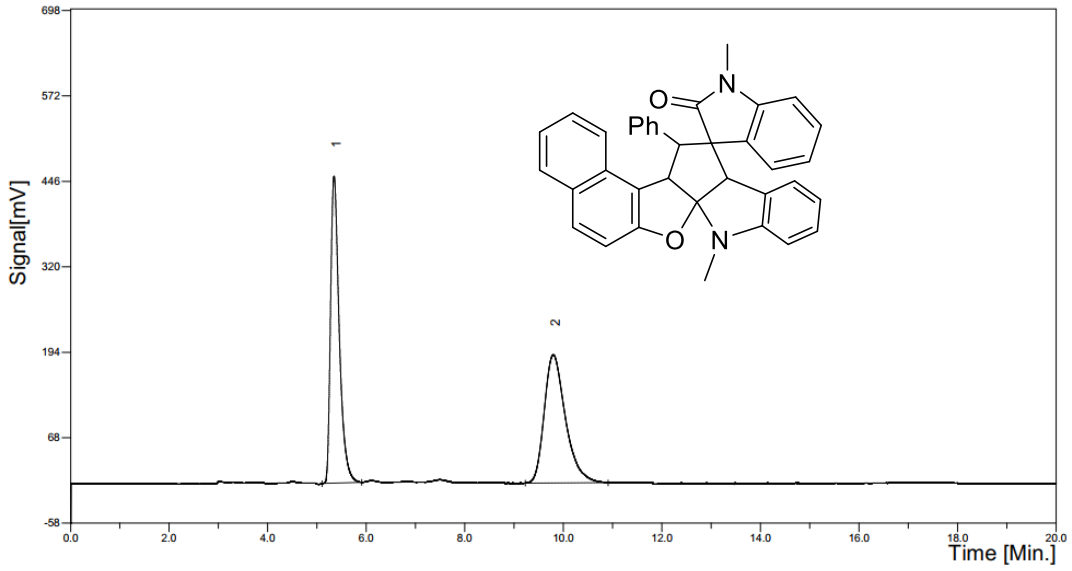
f1 (ppm)

3za



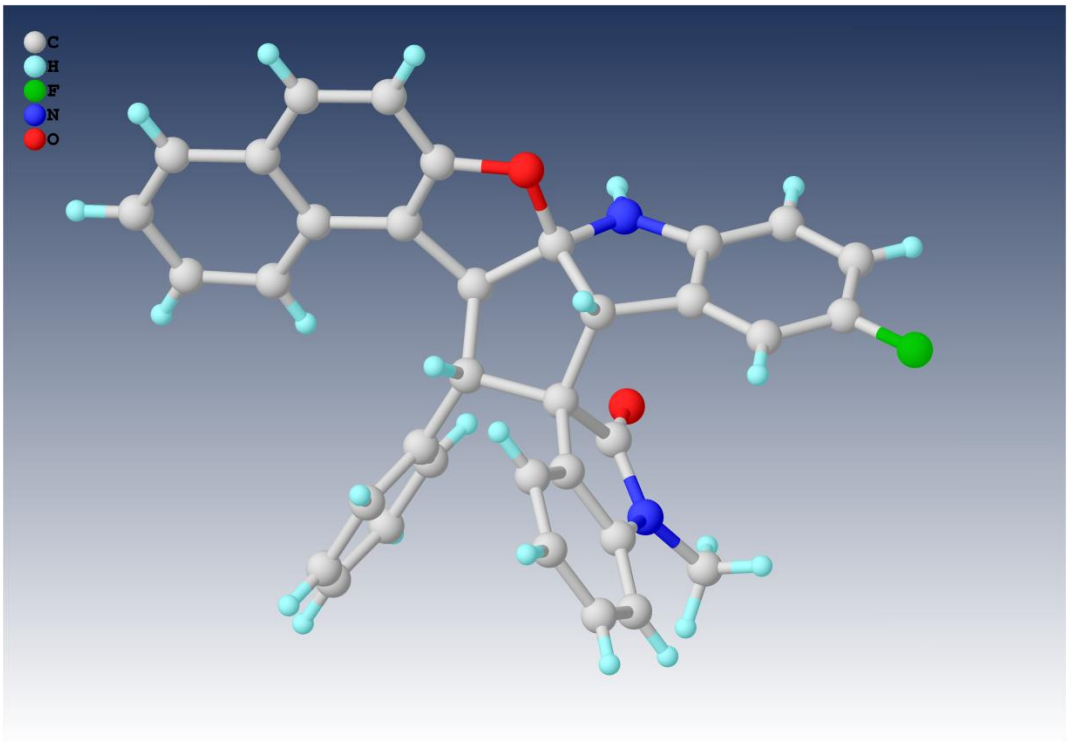
Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	5.340	327.17	3927.61	52.4777
2	9.800	120.01	3556.73	47.5223

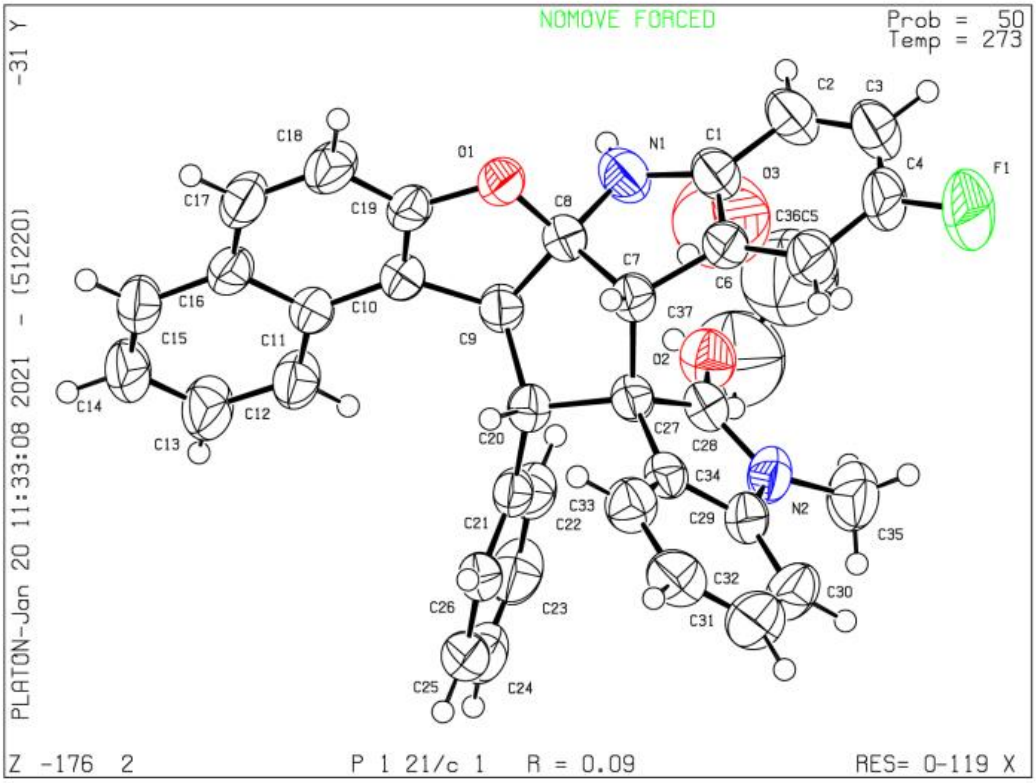


Peak	RT [min]	Heigh[mV]	Area[mV*s]	Area%
1	5.346	452.24	5534.27	49.5132
2	9.795	188.78	5643.09	50.4868

Figure 1. X-Ray Structure of 3ca:

X-ray crystallographic analysis has been established. The enantioenriched spiro[benzofuro-cyclopenta[1,2-b]indole-indoline] structure **3ca** (32 mg, 98% ee) was dissolved by 3 mL prepared solvents (ethanol:n-hexane=2:1) and transferred into a test tube. The tube was placed in dry and avoid light position for 2 days. The crystals were separated out by filtrating. The absolute configuration of **3ca** was established by X-ray crystallographic analysis. In Figure 1, the C36, C37 and O3 come from solvent ethanol. The result of X-ray crystallographic analysis shows chiral spiro[benzofuro-cyclopenta[1,2-b]indole-indoline] structure 3ca is (7*R*, 8*R*, 9*S*, 20*S*, 27*R*) configuration as shown in Figure 1. These data can be obtained free of charge from The ambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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N1
C1
C2
C3
C4
F1
C17
C19
C8
O3
C36C5
C7
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C10
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C27
C28
C34
C33
C22
C29
N2
C35
C21
C32
C30
C26
C23
C31
C25
C24