Supporting Information

Silver-Catalyzed Domino Inverse Electron-Demand oxo-Diels-Alder Reaction of 3-Cyclopropylideneprop-2-en-1-ones with 2,3-Dioxopyrrolidines via Cyclobutane-fused Furan

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(A) General Information

Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra fluorous nuclear magnetic resonance (^{19}F NMR) were recorded at 400 MHz, 100 MHz and 367 MHz, respectively. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz) and integration. Mass and High-resolution mass spectra (HRMS) spectra were recorded by ESI method. The employed solvents were dry up by standard methods when necessary. Commercially obtained reagents were used without further purification. Petroleum ether refers to the fraction with boiling point in the range 60-90 ^{o}C. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

The preparation of 3-cyclopropylideneprop-2-en-1-ones **1**[1] and *N*-benzyl-4-benzylidenepyrrolidine-2,3-dione **2**[2] followed the previous literature procedure.

1. Miao, M.; Cao, J.; Zhang, J.; Huang, X.; Wu, L. *Org. Lett.* **2012**, *14*, 2718-2721.
2. Huang, Y.; Li, Y.; Sun, J.; Li, J.; Zha, Z.; Wang, Z. *J. Org. Chem.* **2018**, *83*, 8464-8472.

(B) Substrate Scopes of Substrates 1 and 2

3-cyclopropylideneprop-2-en-1-ones 1:

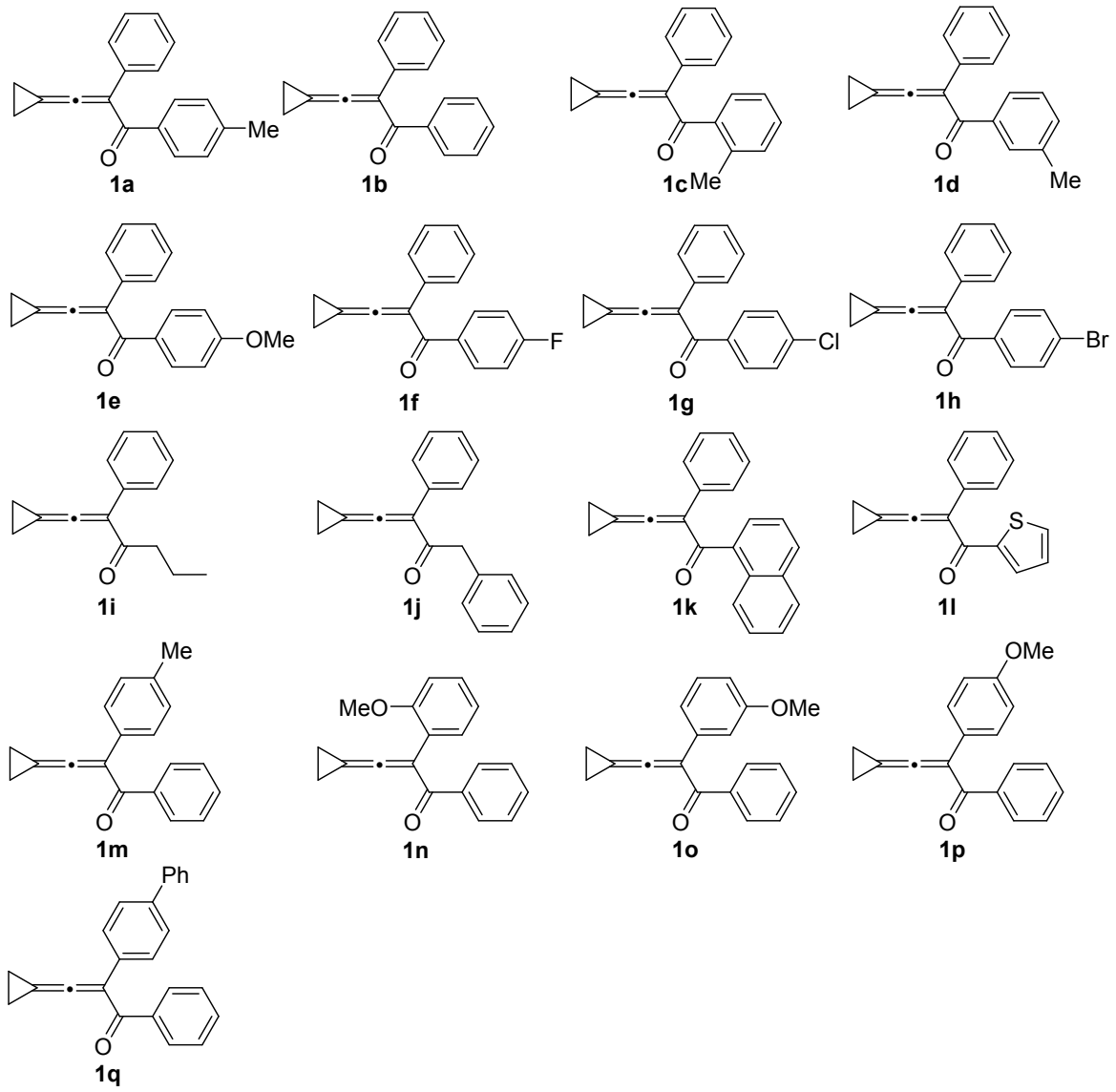
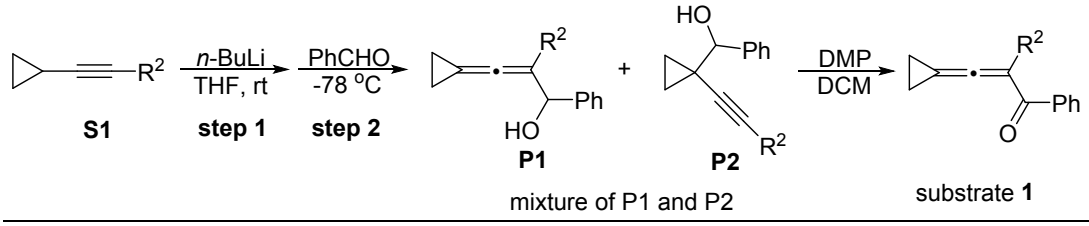


Table S1. Substrate Scope of **1**

According to the previously reported literature procedure [*Org. Lett.* **2012**, *14*, 2718-2721], the general procedure for synthesis of substrate **1** was shown in Scheme S1. Due to the instability or lability, it is impossible to prepare alkyl substituted substrate **1** (R^2 = alkyl group). We also have failed to synthesize the substrates **1**, in which R^2 were 2-pyridyl or 2-thienyl group. When R^2 was a 2-pyridyl group, product **S1** was more reactive upon treatment with *n*-BuLi and a complex mixture was obtained after **step 1** and **step 2**. Changing the reaction temperature of **step 1** and **step 2** did not give the desired substrate as well. When R^2 was a 2-thienyl group, the electron-rich aromatic ring inhibited the isomerization of alkynyl moiety, giving the undesired product **P2** in 94% yield.



R^2 = 2-pyridyl group	
1) step 1, rt; step 2, -78 °C	complex
2) step 1, 0 °C; step 2, -78 °C	complex
3) step 1, rt; step 2, -40 °C	complex

R^2 = 2-thienyl group

P1 not detected, **P2** (94%)

Scheme S1

***N*-benzyl-4-benzylidenepyrrolidine-2,3-dione 2:**

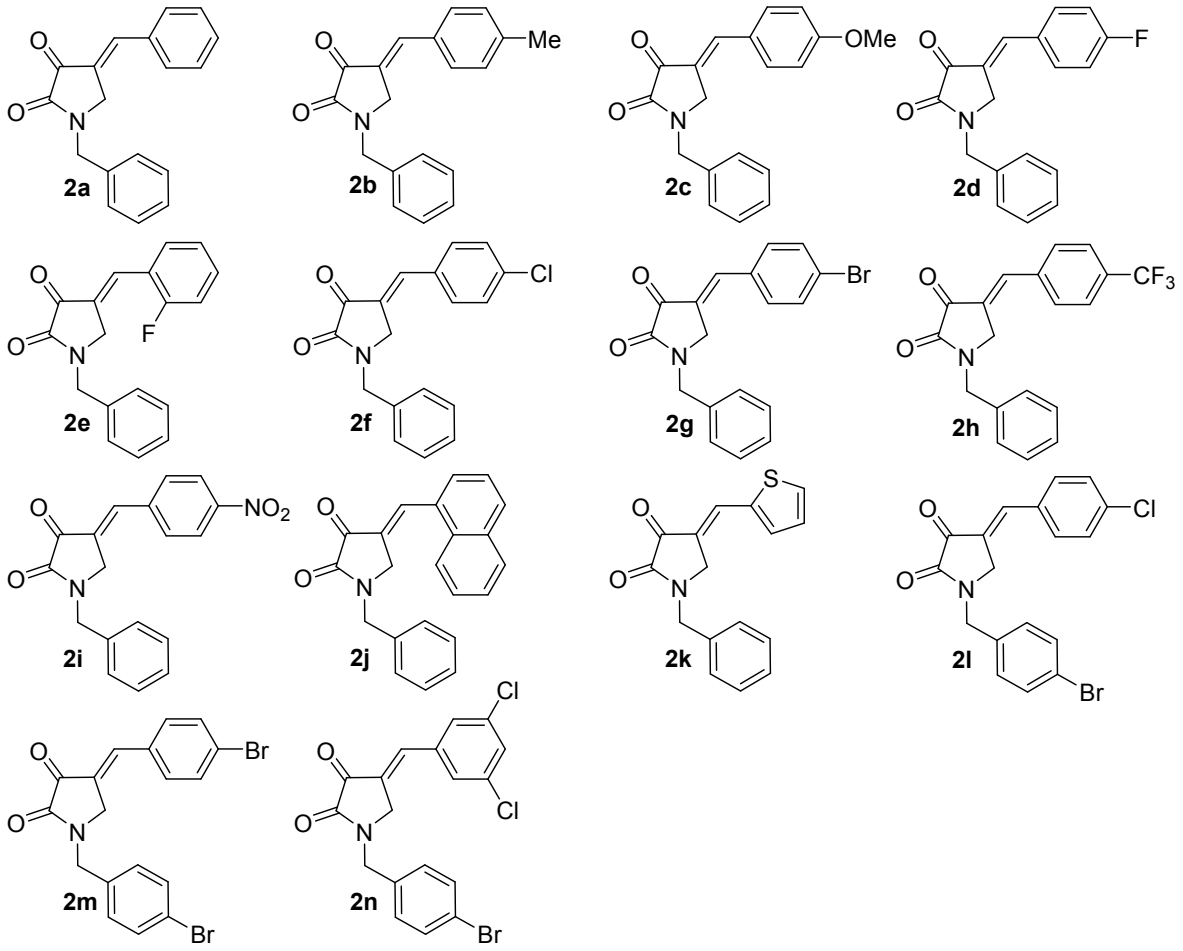
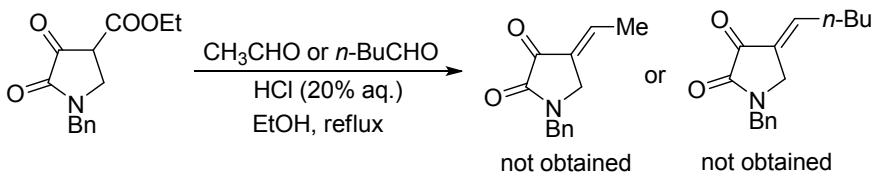


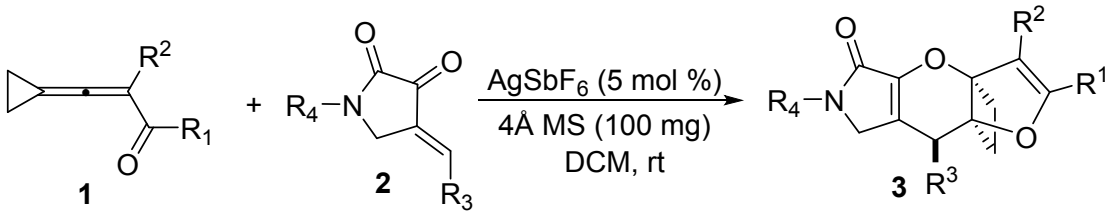
Table S2. Substrate Scope of **2**

According to the previously reported literature procedure [*J. Org. Chem.* **2018**, *83*, 8464-8472], we have attempted to synthesize substrates **2**, in which R^3 was a methyl or a *n*-butyl group, however, these desired substrates could not be obtained from these reactions (Scheme S2). The reason could be that substrates **2** with an aromatic ring were more stable than those of alkyl substituted ones due to a conjugated system of aromatic ring.

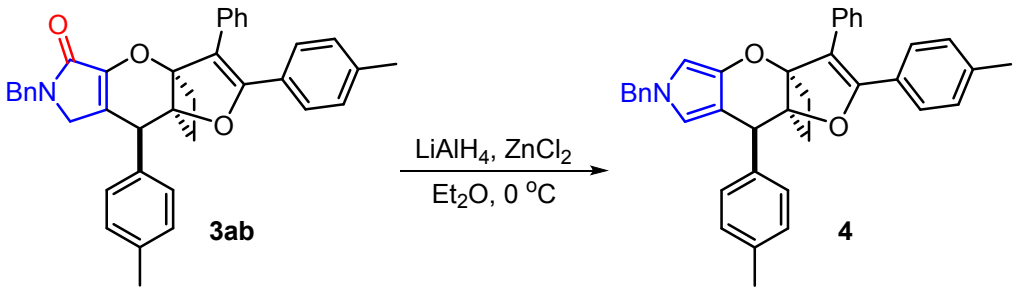


Scheme S2

(C) General Procedure for Preparation of Products 3 and 4



A dried 10 mL Schlenk tube was charged with anhydrous 4Å MS (100 mg), *N*-benezyl-4-benzylidenepyrrolidine-2,3-dione **2** (0.22 mmol, 1.1 equiv) and $AgSbF_6$ (0.01 mmol, 5 mol %), then the tube was evacuated and backfilled with argon for 3 times. Then 3-cyclopropylideneprop-2-en-1-one **1** (0.20 mmol, 1.0 equiv) and anhydrous DCM (2.0 mL) was added under argon protected atmosphere. The reaction mixture was stirred at room temperature and monitored by TLC analysis. After completion, the reaction mixture was concentrated under reduced pressure and purified by a flash silica gel chromatography (Petroleum Ether:Ethyl Acetate = 3:1, v/v) to afford product **3**.



To a solution of $LiAlH_4$ (380 mg, 10.0 mmol) in ethyl ether (70 mL) at room temperature was added $ZnCl_2$ (682 mg, 5.0 mmol) as a solid in three portions. The reaction mixture was allowed to stir for 2 hours at room temperature. Stirring was stopped and the precipitate was allowed to settle down. The clear supernatent (4.0 mL) was then added to a solution of compound **3ab** (110 mg, 0.2 mmol) in ethyl ether (1.0 mL) at 0 °C. After being stirred for 30 min, the mixture was quenched with 1.0 M HCl, extracted with ethyl acetate, dried over anhydrous $MgSO_4$, filtered, and evapotated. The residue was chromatographed through a silica gel column (Petroleum Ether:Ethyl Acetate = 10:1, v/v) to afford product **4** (53 mg, 50%).

(D) Mechanistic Investigation

The ^{1}H NMR spectroscopic tracing experiments

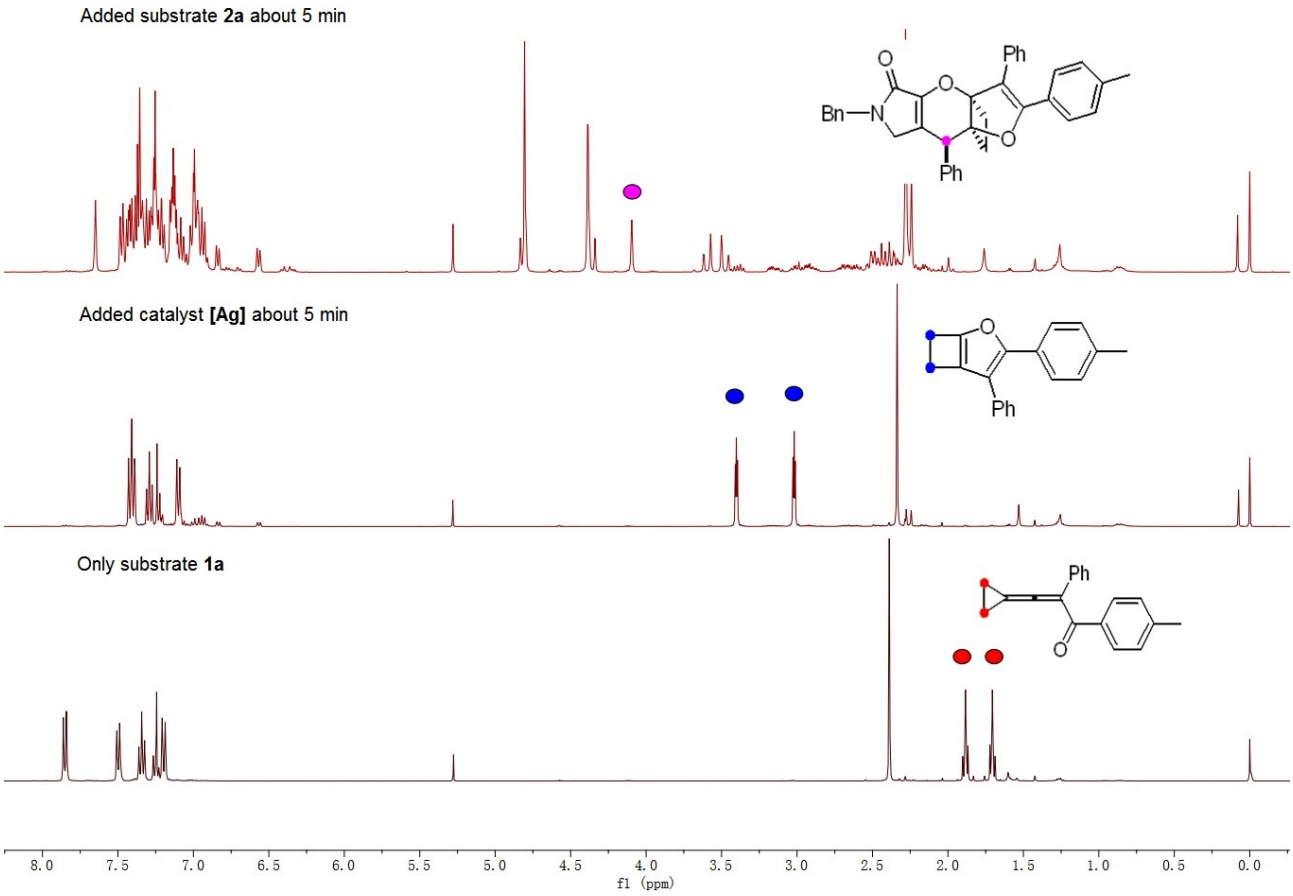
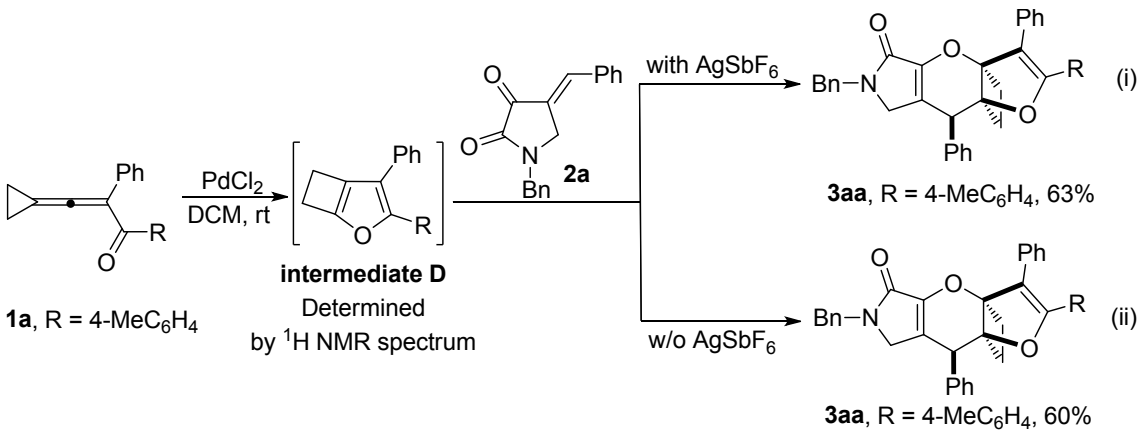


Figure S1. ^{1}H-NMR spectra of tracing experiments

Compound **1a** (30 mg, 0.11 mmol) was dissolved in $CDCl_3$ (1.0 mL) in a dried NMR tube. Then $AgSbF_6$ (2.0 mg, 5 mol %) was added; **1a** was fastly exhausted and transformed into **intermediate D**, which gave two sets of CH_2 signals in NMR spectra at δ 3.40 (t, J = 4.2 Hz, 2H) and δ 3.02 (t, J = 4.2 Hz, 2H) together with one methyl resonance signals in the high field region. Notably, the **intermediate D** was similar to the cyclobutane-fused furan, which was reported by Huang's group. This result indicates that the reaction was initiated with transformation of **1a** to **intermediate D**. When **2a** (46 mg, 0.17 mmol) was added, the **intermediate D** was rapidly consumed and converted into product **3aa** *via* an IEDDA reaction process.

The control experiments



Parallel reaction i:

Compound **1a** (52 mg, 0.20 mmol) and **$PdCl_2$** (3.5 mg, 10 mol %) was dissolved in 2 mL of dry DCM in a dried vial under argon atmosphere. After being stirred for 10 min (monitored by TLC analysis) and the subsequent filtration and removal of the solvent in vacuo, the crude product of **intermediate D** was determined by ^{1}H NMR spectrum.

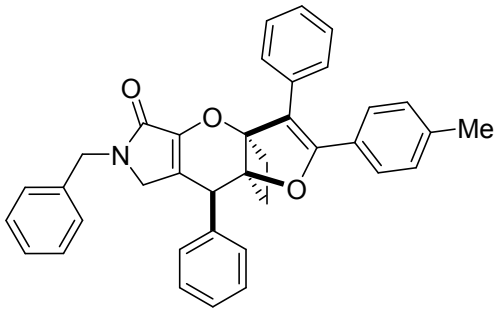
Under an atmosphere of argon, 1.5 equiv of **2a** and **$AgSbF_6$** (5 mol %) was added to a solution of **intermediate D** in 2 mL of dry DCM at room temperature to afford **3aa** in 63% yield.

Parallel reaction ii:

Compound **1a** (52 mg, 0.20 mmol) and **$PdCl_2$** (3.5 mg, 10 mol %) was dissolved in 2 mL of dry DCM in a dried vial under argon atmosphere. After being stirred for 10 min (monitored by TLC) and the subsequent filtration and removal of the solvent in vacuo, the crude product of **intermediate D** was determined by ^{1}H NMR spectrum.

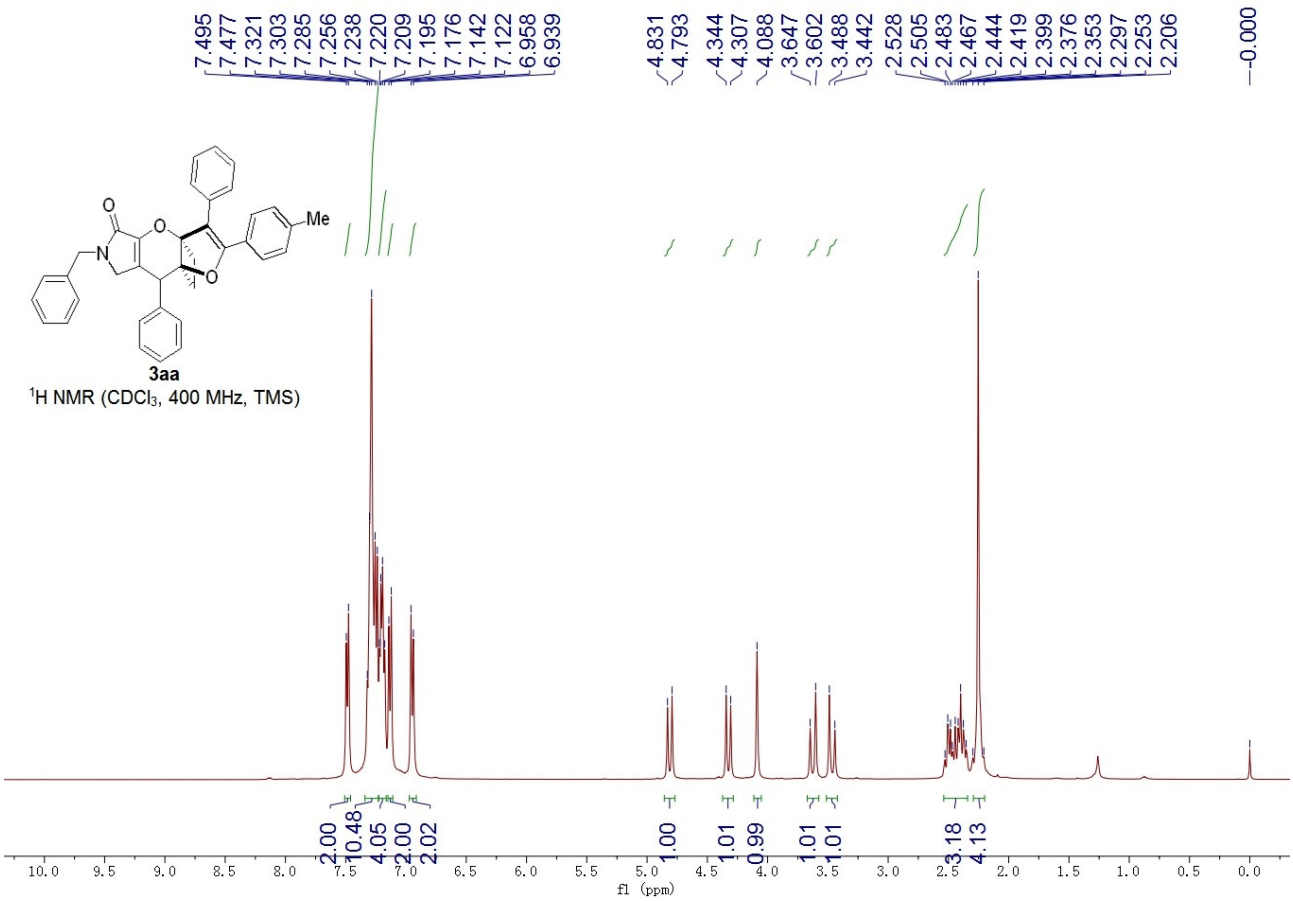
Under an atmosphere of argon, 1.5 equiv of **2a** was added to a solution of **intermediate D** in 2 mL of dry DCM at room temperature to afford **3aa** in 60% yield without **$AgSbF_6$**.

(E) Spectroscopic Data of Products 3 and 4



3aa

(3aS,8aS)-6-benzyl-3,8-diphenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3aa), the title compound was achieved as yellow solid, MP = 111-113 ^{o}C, 96.8 mg, 90% yield. R*f* = 0.35 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.32-7.24 (m, 9H), 7.22-7.20 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 2H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.33 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.62 (d, *J* = 18.4 Hz, 1H), 3.46 (d, *J* = 18.4 Hz, 1H), 2.53-2.35 (m, 3H), 2.30-2.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 153.9, 145.3, 139.4, 137.2, 135.8, 133.0, 130.2, 129.6, 128.8, 128.6, 128.3, 128.2, 128.0, 127.8, 127.7, 127.6, 127.1, 121.0, 114.1, 89.9, 86.7, 47.7, 46.6, 44.9, 29.5, 28.7, 21.4. IR (neat) ν 2922, 1698, 1490, 1452, 1354, 1230, 1179, 1098, 1030, 1004, 825, 759, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_3$: 538.2377, found: 538.2378.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7.303
7.285
7.256
7.238
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7.209
7.195
7.176
7.142
7.122
6.958
6.939
4.831
4.793
4.344
4.307
4.088
3.647
3.602
3.488
3.442
2.528
2.505
2.483
2.467
2.444
2.419
2.399
2.376
2.353
2.297
2.253
2.206
0.000
Me
3aa
1H NMR (CDCl3, 400 MHz, TMS)
2.00
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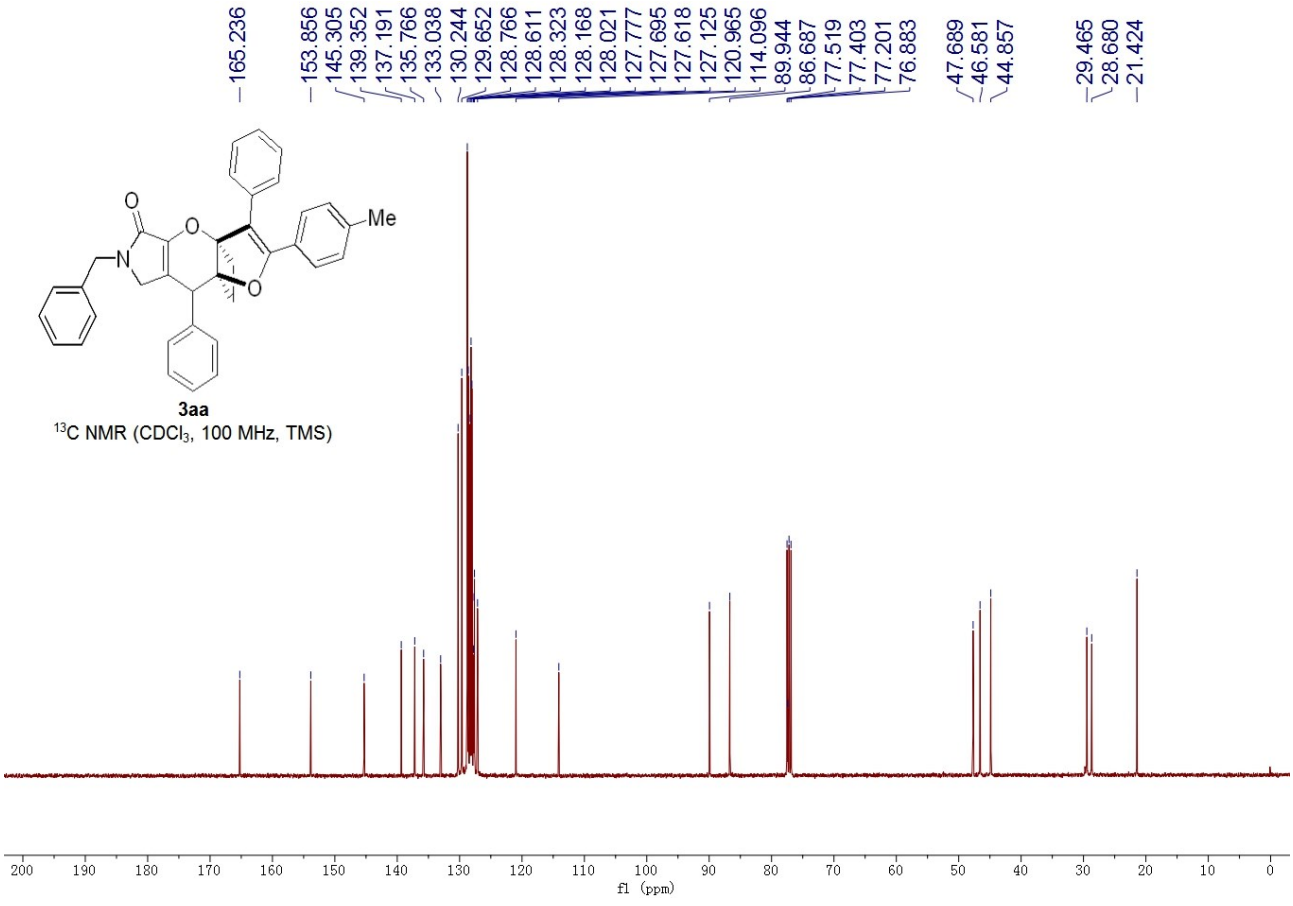
4.05
2.00
2.02
1.00
1.01
0.99
1.01
1.01
3.18
4.13
f1 (ppm)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145.305
139.352
137.191
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133.038
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128.766
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128.323
128.168
128.021
127.777
127.695
127.618
127.125
120.965
114.096
89.944
86.687
77.519
77.403
77.201
76.883
47.689
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29.465
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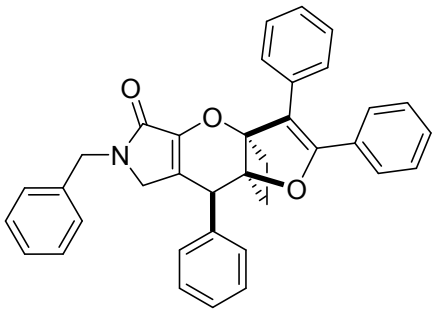
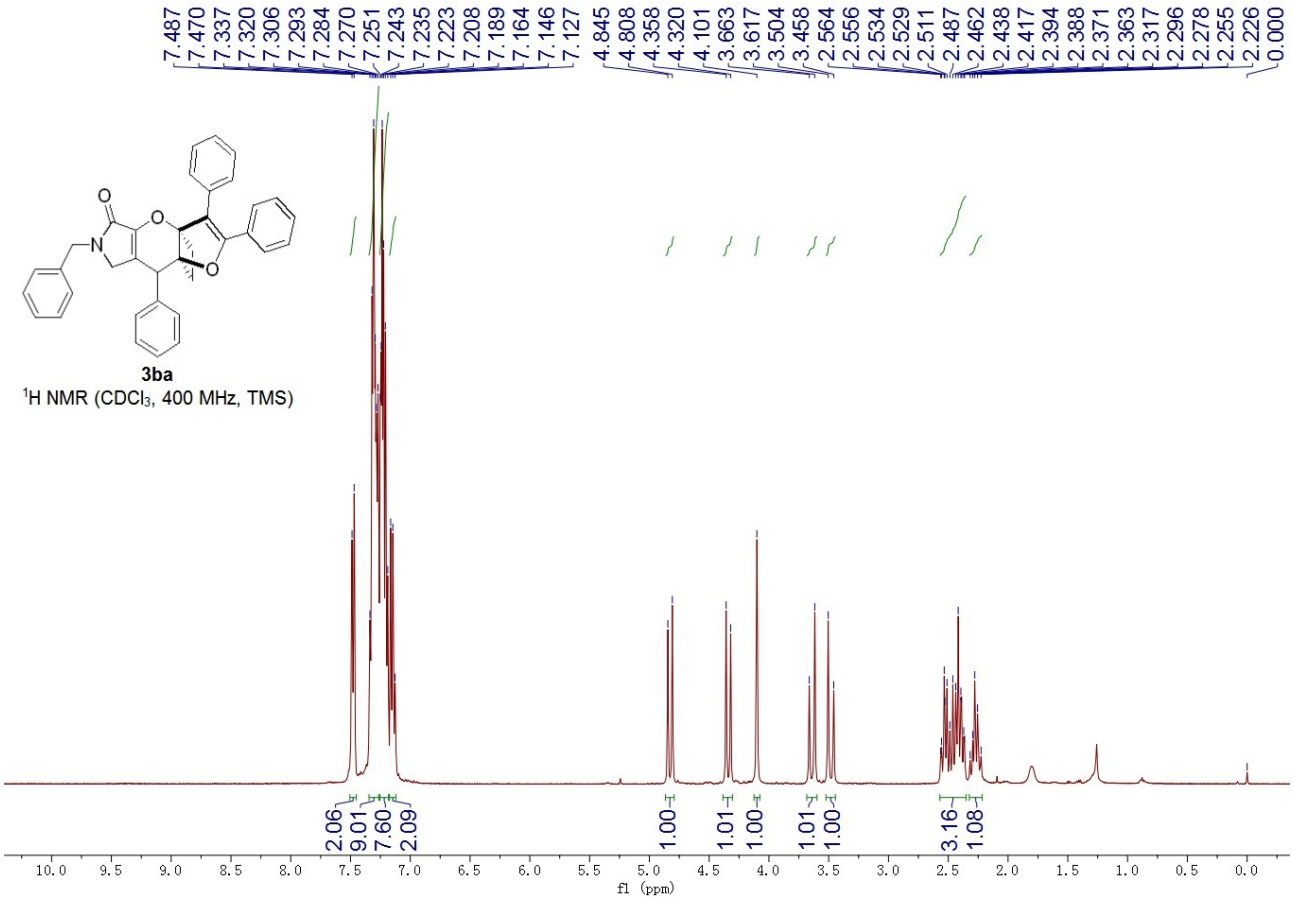
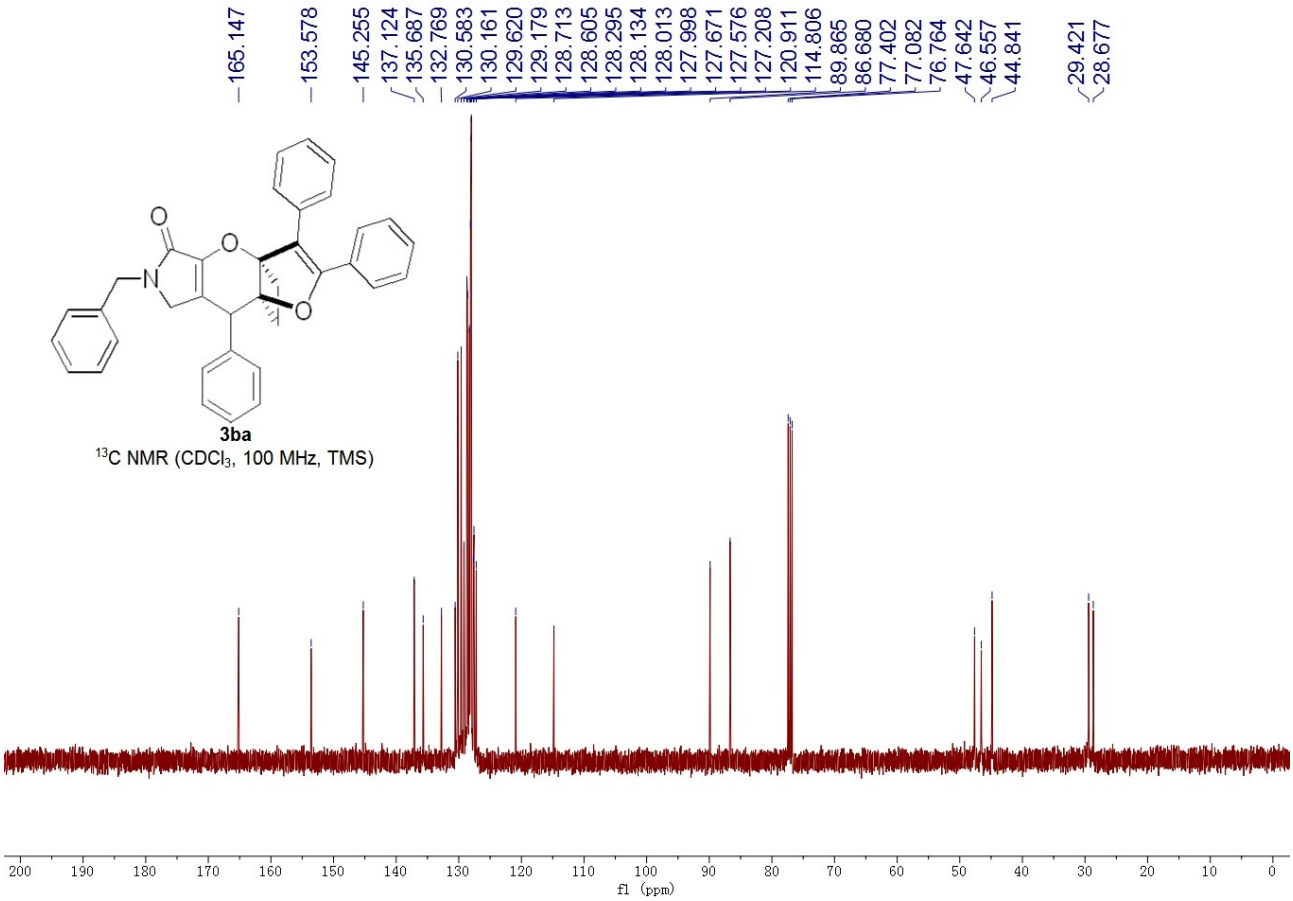
Me
3aa
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)

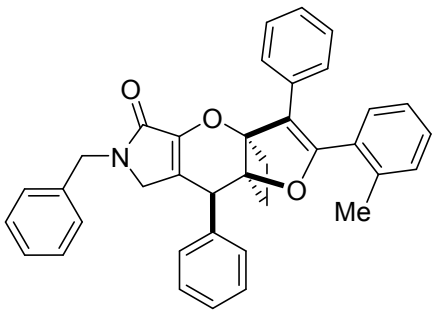


3ba

(3aS,8aS)-6-benzyl-2,3,8-triphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ba), the title compound was achieved as orange solid, MP = 90-91 °C, 96.3 mg, 92% yield. R*f* = 0.35 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 6.8 Hz, 2H), 7.34-7.27 (m, 9H), 7.25-7.19 (m, 7H), 7.16-7.13 (m, 2H), 4.83 (d, *J* = 14.8 Hz, 1H), 4.34 (d, *J* = 14.8 Hz, 1H), 4.10 (s, 1H), 3.64 (d, *J* = 18.4 Hz, 1H), 3.48 (d, *J* = 18.4 Hz, 1H), 2.56-2.36 (m, 3H), 2.32-2.23 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 153.6, 145.3, 137.1, 135.7, 132.8, 130.6, 130.2, 129.6, 129.2, 128.7, 128.6, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 127.2, 120.9, 114.8, 89.9, 86.7, 47.8, 46.6, 44.8, 29.4, 28.7. IR (neat) ν 1694, 1496, 1452, 1353, 1249, 1176, 1121, 1004, 909, 731, 696, 656 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{30}NO_3$: 524.2220, found: 524.2221.



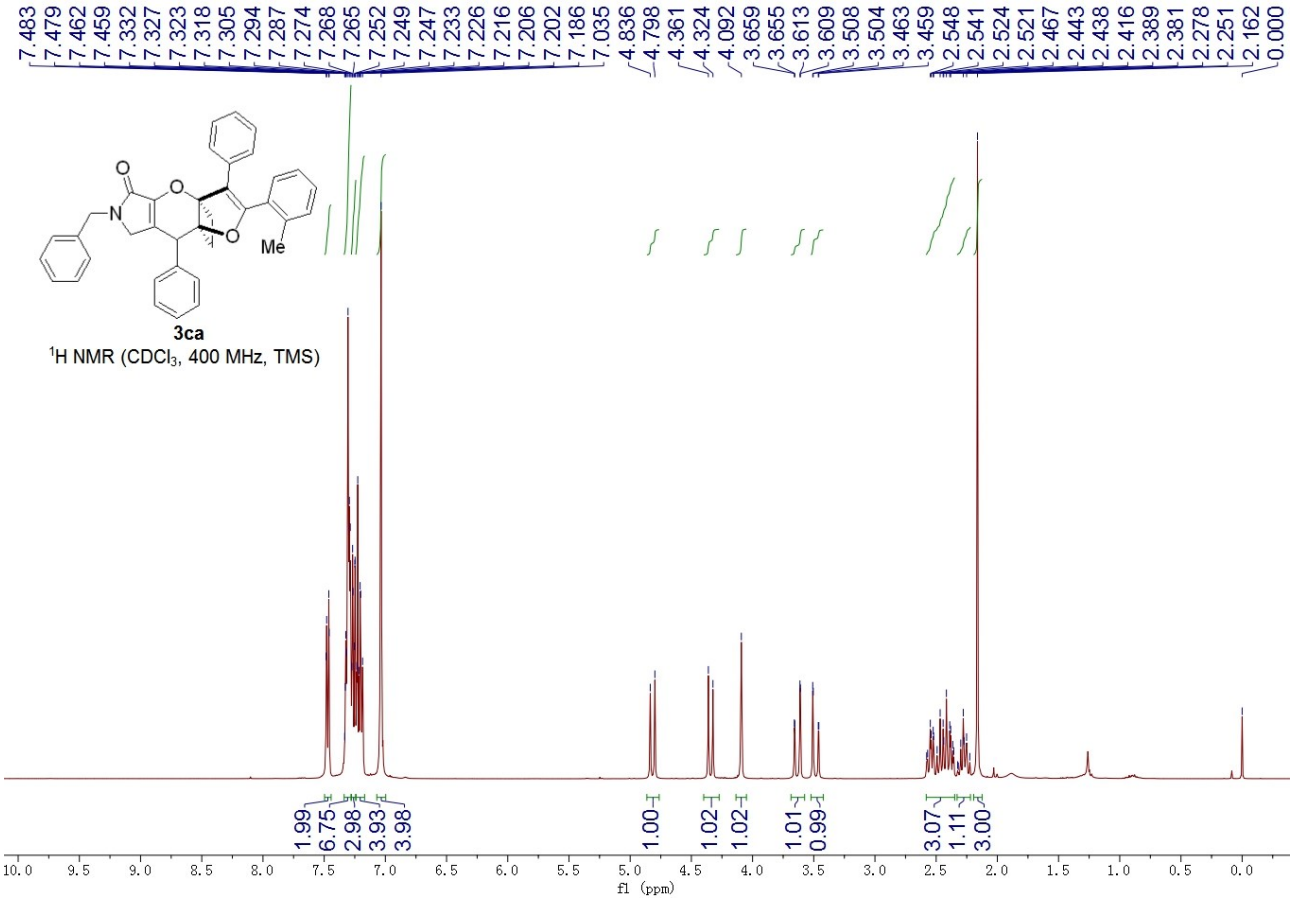


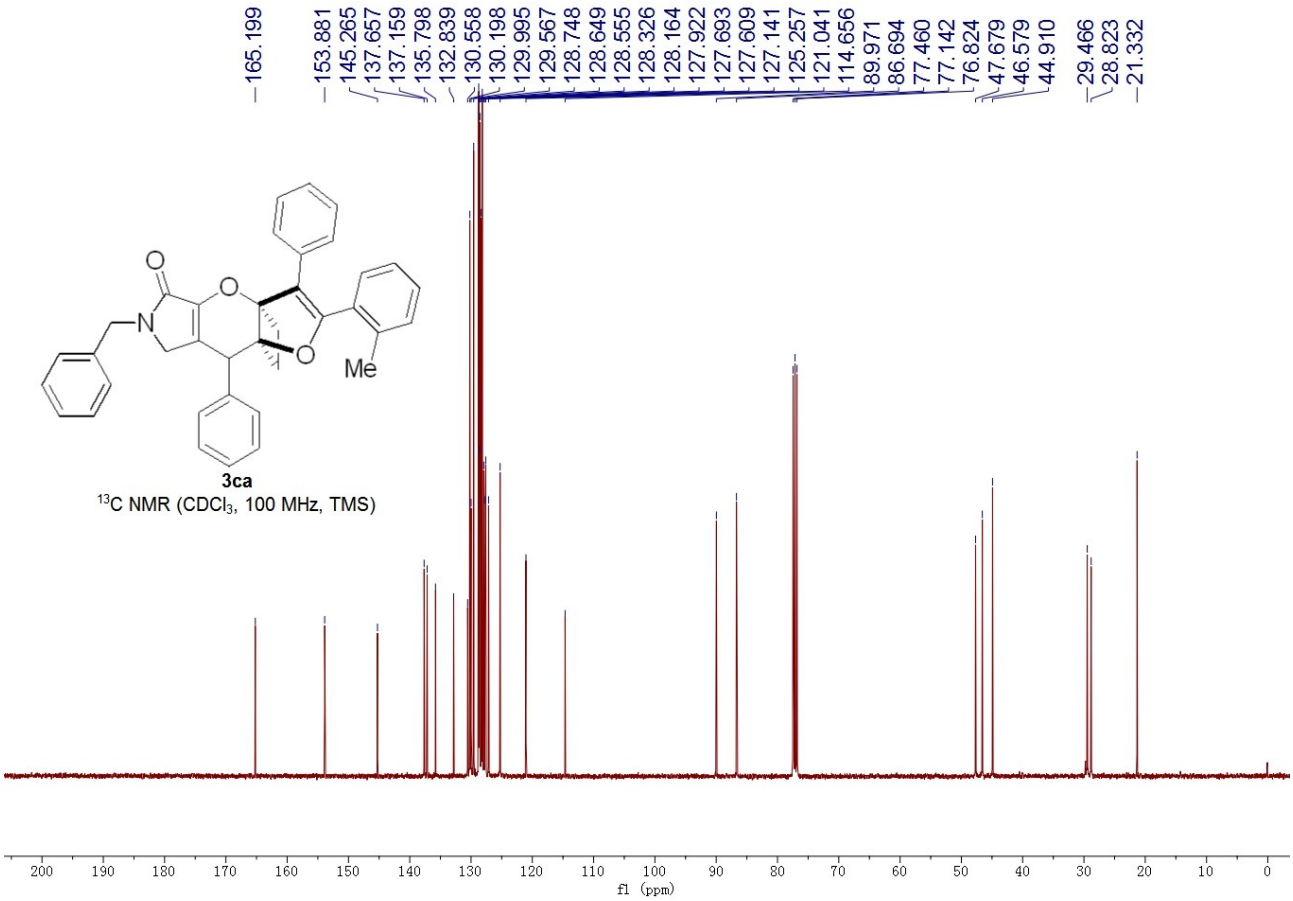


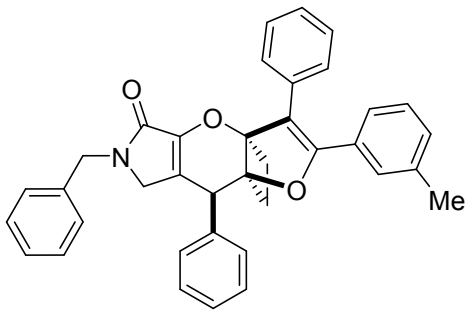
3ca

(3aS,8aS)-6-benzyl-3,8-diphenyl-2-(o-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ca), the title compound was achieved as yellow solid, MP = 106-108 °C, 98.6 mg, 83% yield. Elution: R*f* = 0.38 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.33-7.29 (m, 6H), 7.27-7.25 (m, 3H), 7.23-7.19 (m, 4H), 7.04 (s, 4H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.34 (d, *J* = 15.2 Hz, 1H), 4.10 (s, 1H), 3.63 (d, *J* = 18.4 Hz, 1H), 3.48 (d, *J* = 18.4 Hz, 1H), 2.58-2.36 (m, 3H), 2.32-2.23 (m, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 153.9, 145.3, 137.7, 137.2, 135.8, 132.8, 130.6, 130.2, 130.0, 129.6, 128.8, 128.6, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.1, 125.3, 121.0, 114.7, 90.0, 86.7, 47.7, 46.6,

44.9, 29.5, 28.8, 21.3. IR (neat) ν 2922, 1694, 1495, 1453, 1354, 1242, 1175, 1099, 1070, 1004, 756, 732, 699 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_3$: 538.2377, found: 538.2383.



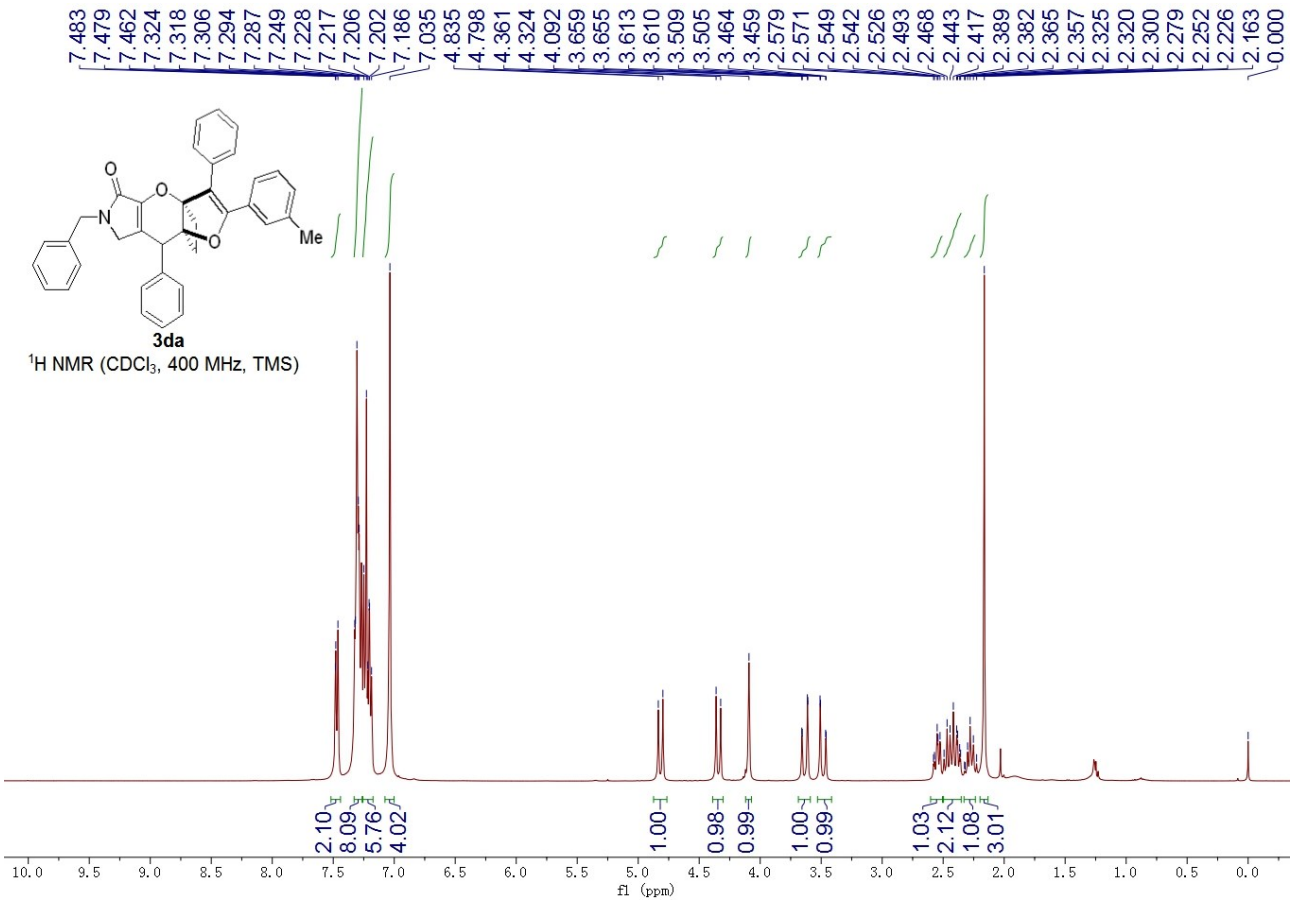


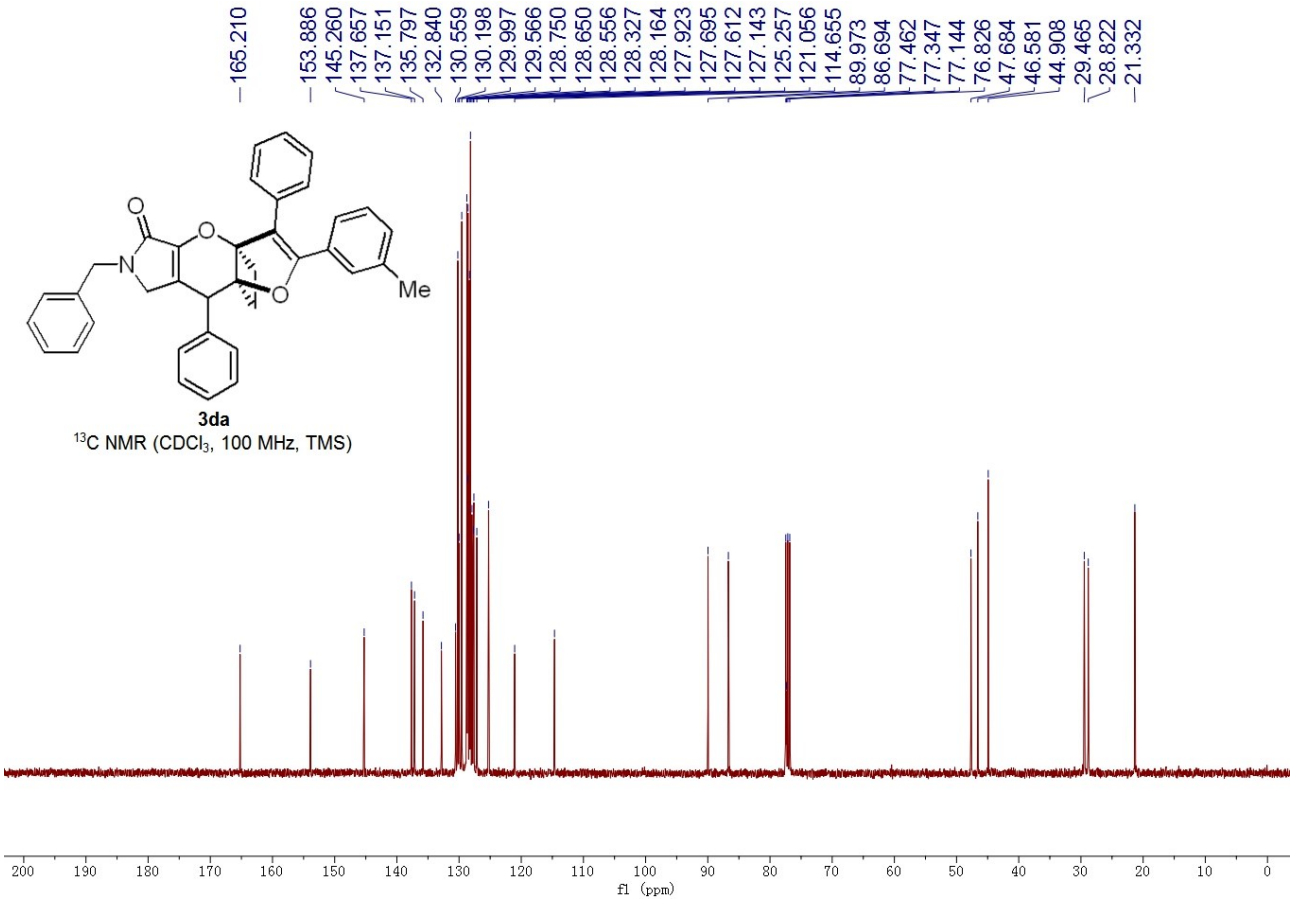


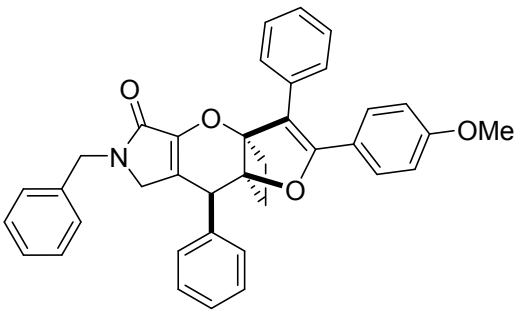
3da

(3aS,8aS)-6-benzyl-3,8-diphenyl-2-(m-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3da), the title compound was achieved as yellow solid, MP = 111-113 ^{o}C, 88.2 mg, 72% yield. R*f* = 0.35 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.47 (m, 2H), 7.32-7.27 (m, 8H), 7.25-7.19 (m, 5H), 7.04 (s, 4H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.34 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.63 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.48 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.58-2.53 (m, 1H), 2.49-2.36 (m, 2H), 2.33 – 2.23 (m, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 153.9, 145.3, 137.7, 137.2, 135.8, 132.8, 130.6, 130.2, 130.0, 129.6, 128.8, 128.7, 128.6, 128.3, 128.2, 127.9, 127.7, 127.6, 127.1, 125.3, 121.1,

114.7, 90.0, 86.7, 47.7, 46.6, 44.9, 29.5, 28.8, 21.3. IR (neat) ν 2922, 1694, 1510, 1453, 1286, 1245, 1173, 1098, 1030, 993, 834, 731, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_3$: 538.2377, found: 538.2361.



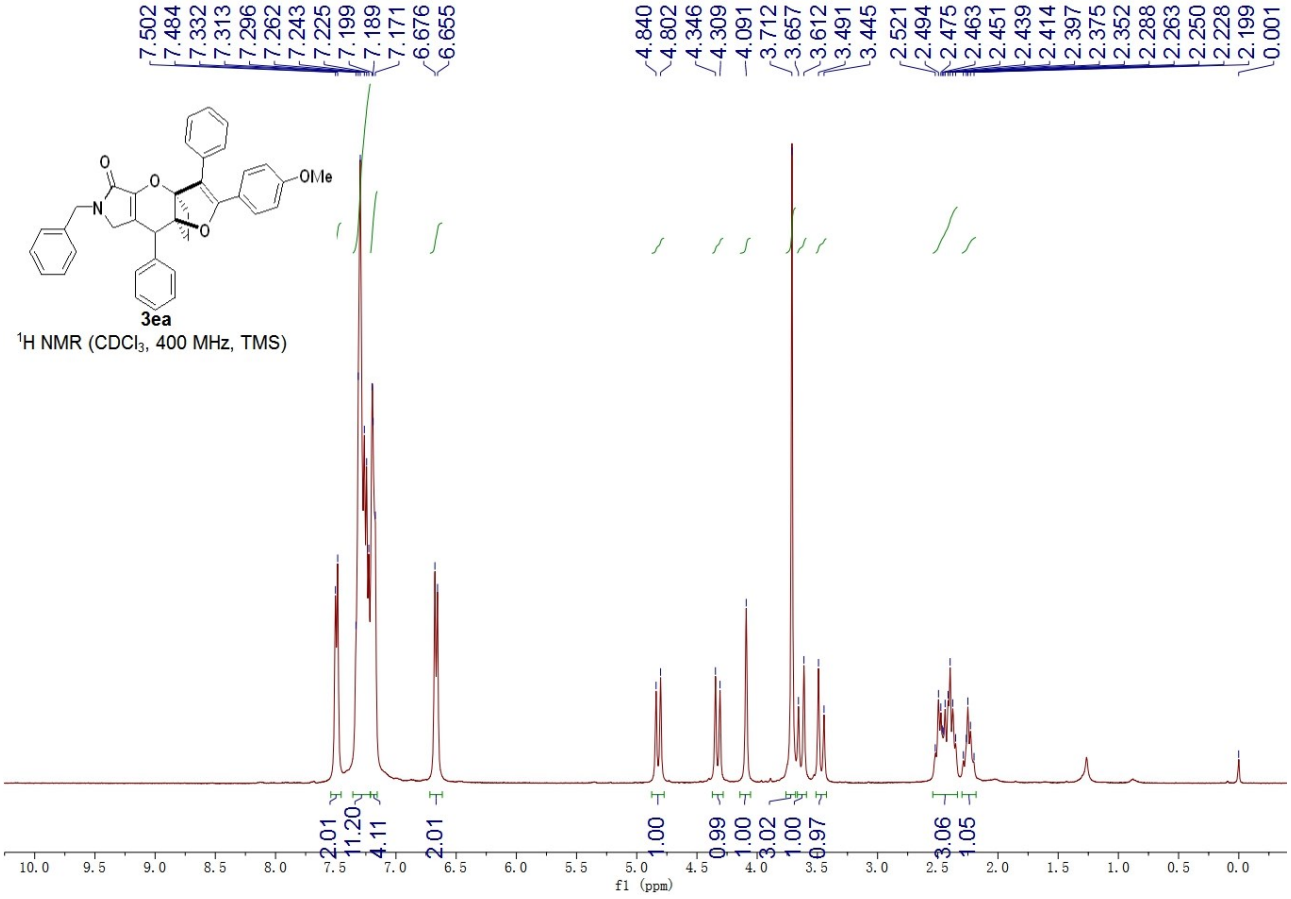


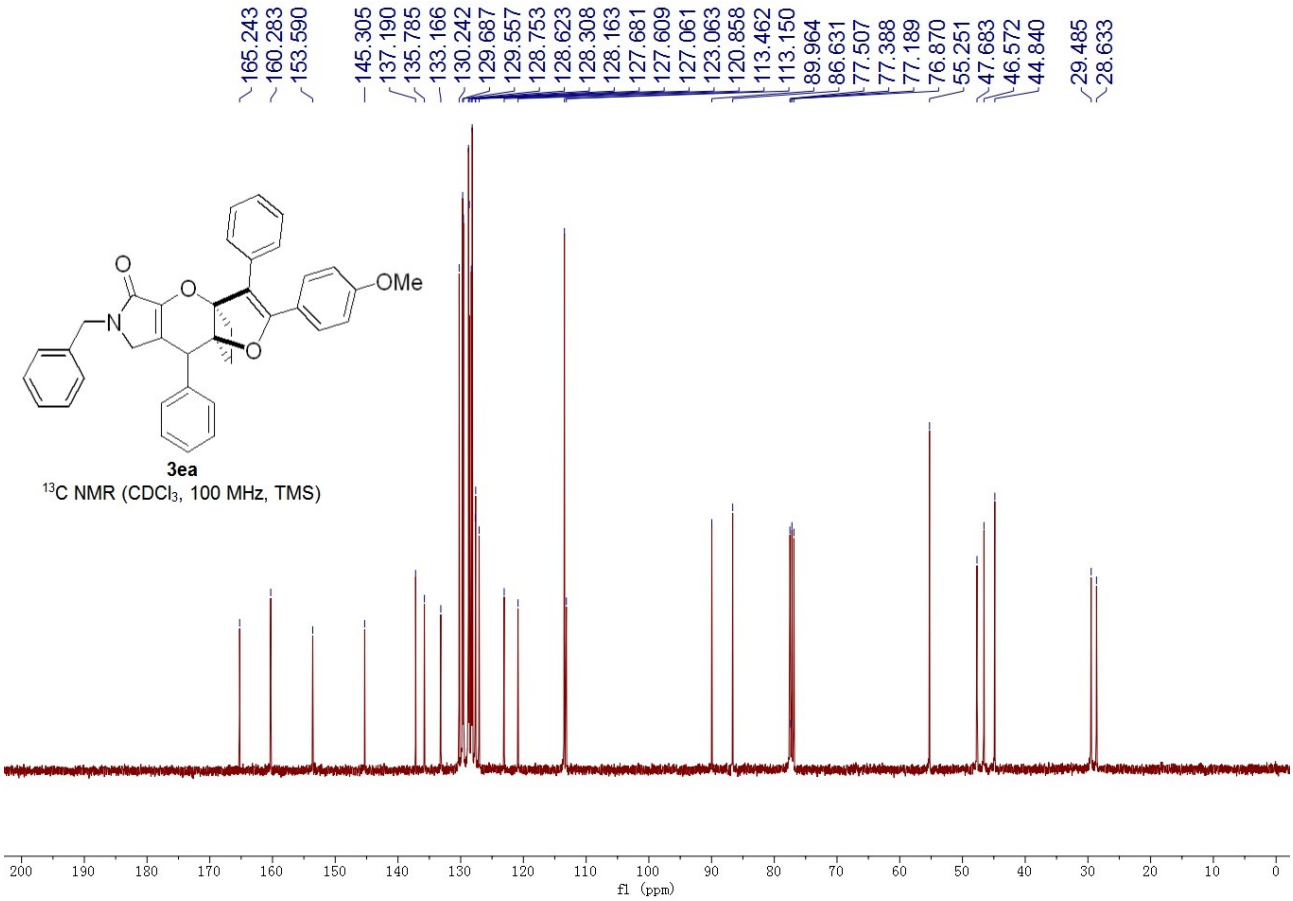


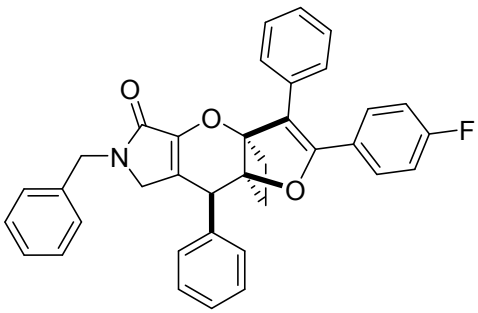
3ea

(3aS,8aS)-6-benzyl-2-(4-methoxyphenyl)-3,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ea), the title compound was achieved as yellow solid, MP = 78-79 °C, 113.5 mg, 98% yield. R*f* = 0.45 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.33-7.23 (m, 11H), 7.20-7.17 (m, 4H), 6.67 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.33 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.71 (s, 3H), 3.63 (d, *J* = 18.4 Hz, 1H), 3.47 (d, *J* = 18.4 Hz, 1H), 2.52-2.35 (m, 3H), 2.29-2.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 160.3, 153.6, 145.3, 137.2, 135.8, 133.2, 130.2, 129.7, 129.6, 128.8, 128.6, 128.3, 128.2, 127.7, 127.6, 127.1, 123.1, 120.9, 113.5, 113.2, 90.0, 86.6, 55.3,

47.7, 46.6, 44.8, 29.5, 28.6. IR (neat) ν 2920, 1694, 1495, 1453, 1375, 1243, 1174, 1099, 1070, 1004, 908, 766, 732, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_4$: 554.2326, found: 554.2310.



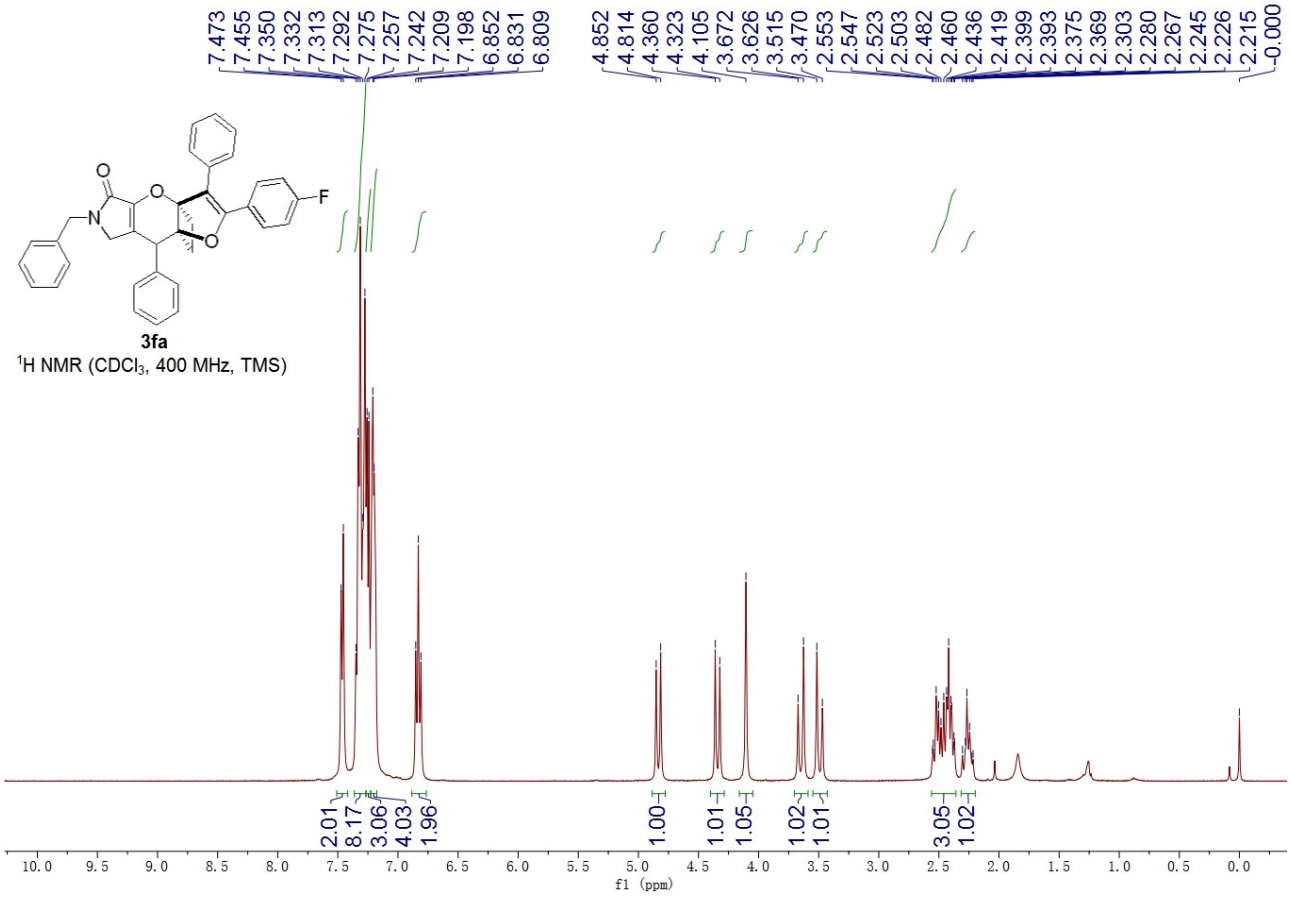


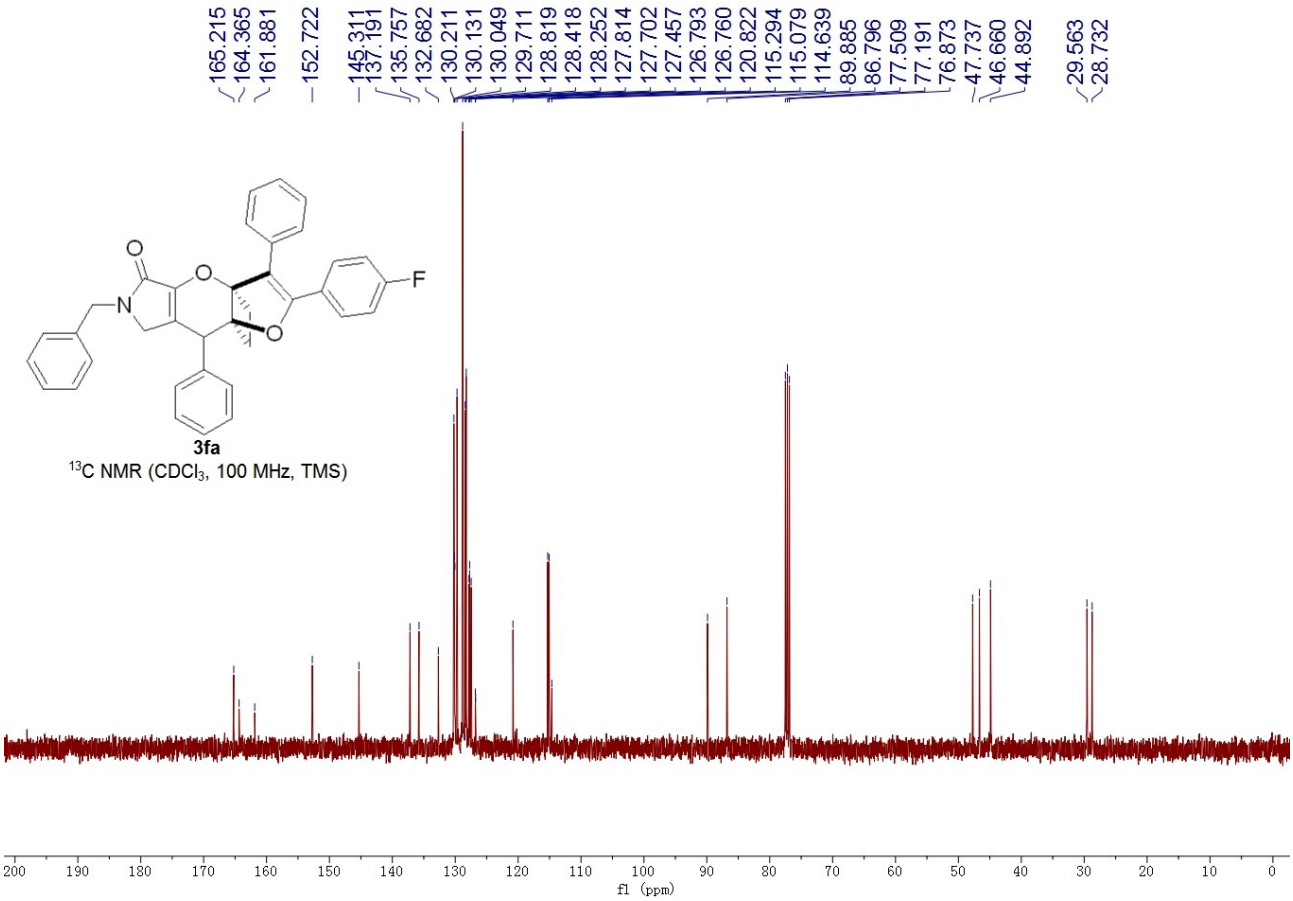


3fa

(3aS,8aS)-6-benzyl-2-(4-fluorophenyl)-3,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3fa), the title compound was achieved as brown solid, MP = 135-137 °C, 81.8 mg, 73% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.2 Hz, 2H), 7.35-7.28 (m, 8H), 7.26-7.24 (m, 3H), 7.21-7.20 (m, 4H), 6.83 (t, *J* = 8.4 Hz, 2H), 4.83 (d, *J* = 15.2 Hz, 1H), 4.34 (d, *J* = 15.2 Hz, 1H), 4.10 (s, 1H), 3.65 (d, *J* = 18.4 Hz, 1H), 3.49 (d, *J* = 18.4 Hz, 1H), 2.55-2.37 (m, 3H), 2.30-2.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 163.1 (d, J_{C-F} = 248.4 Hz), 152.7, 145.3, 137.2, 135.8, 132.7, 130.2, 130.1 (d, J_{C-F} = 8.2 Hz), 129.7, 128.8, 128.4, 128.3, 127.8, 127.7, 127.5, 126.7 (d, J_{C-F}

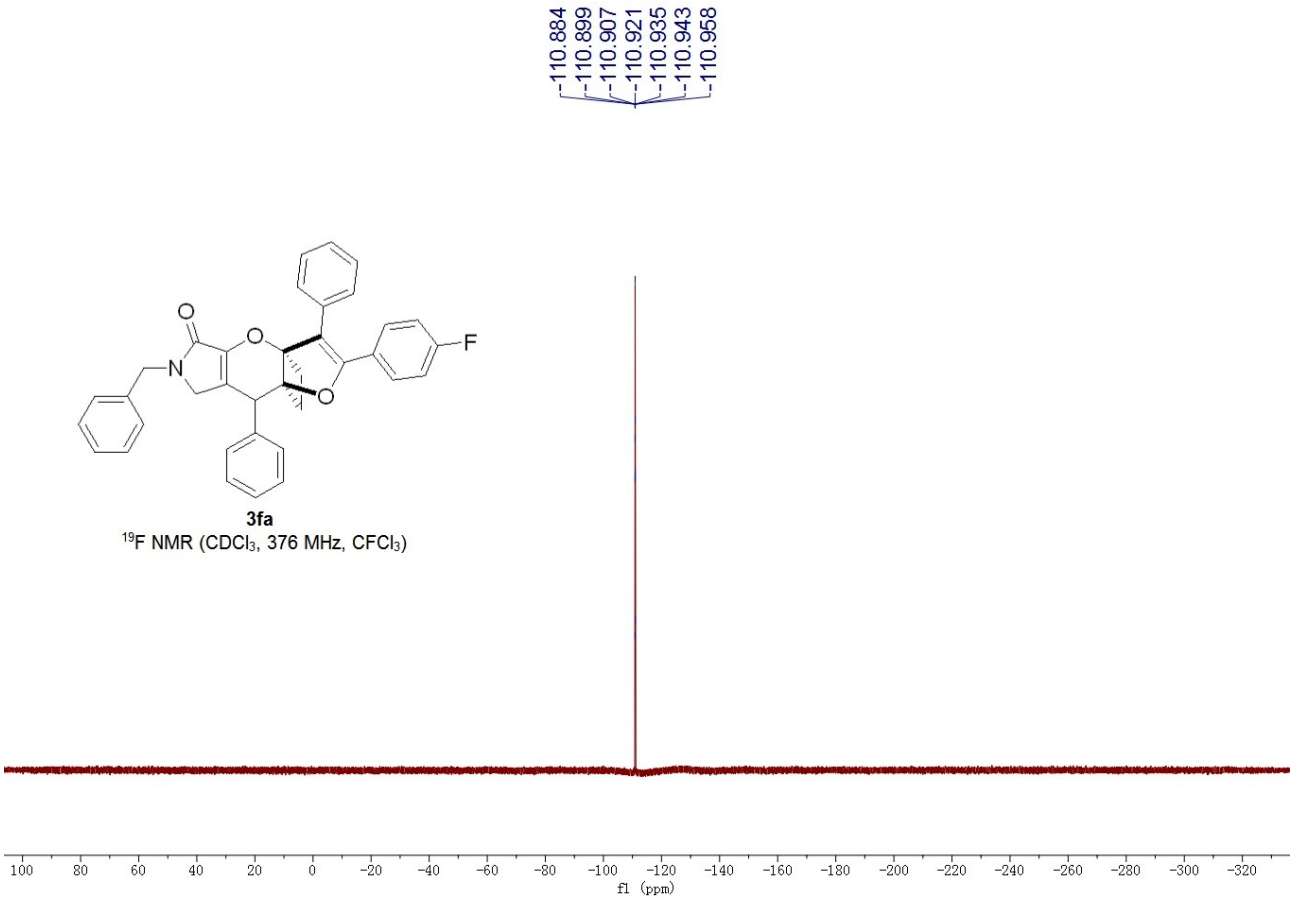
= 3.3 Hz), 120.8, 115.2 (d, $J_{C\text{-}F}$ = 21.5 Hz), 114.6, 89.9, 86.8, 47.7, 46.7, 44.9, 29.6, 28.7. ^{19}F NMR (376 MHz, $CFCl_3$): δ 110.9 (m, 1F). IR (MeOH) ν 2972, 1691, 1495, 1453, 1354, 1248, 1173, 1091, 1046, 1005, 880, 839, 766, 733, 700 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{29}NO_3F$: 542.2126, found: 542.2118.





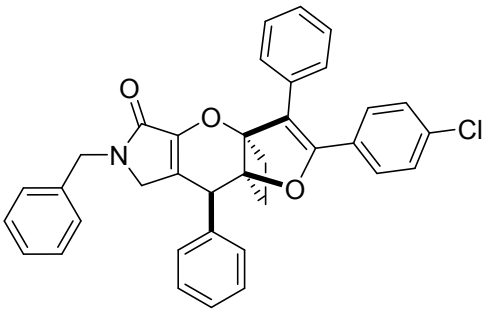
3fa

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



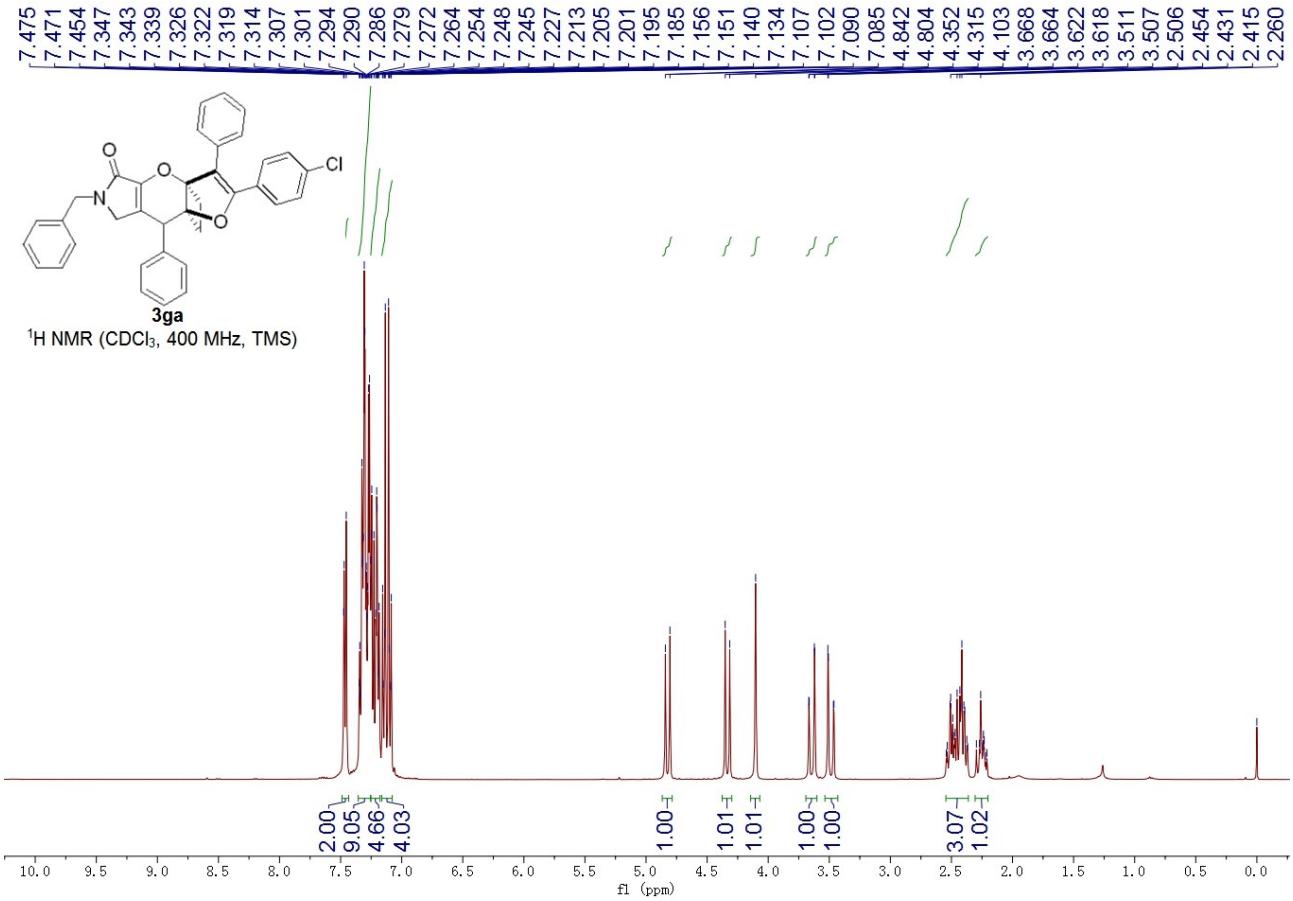
3fa

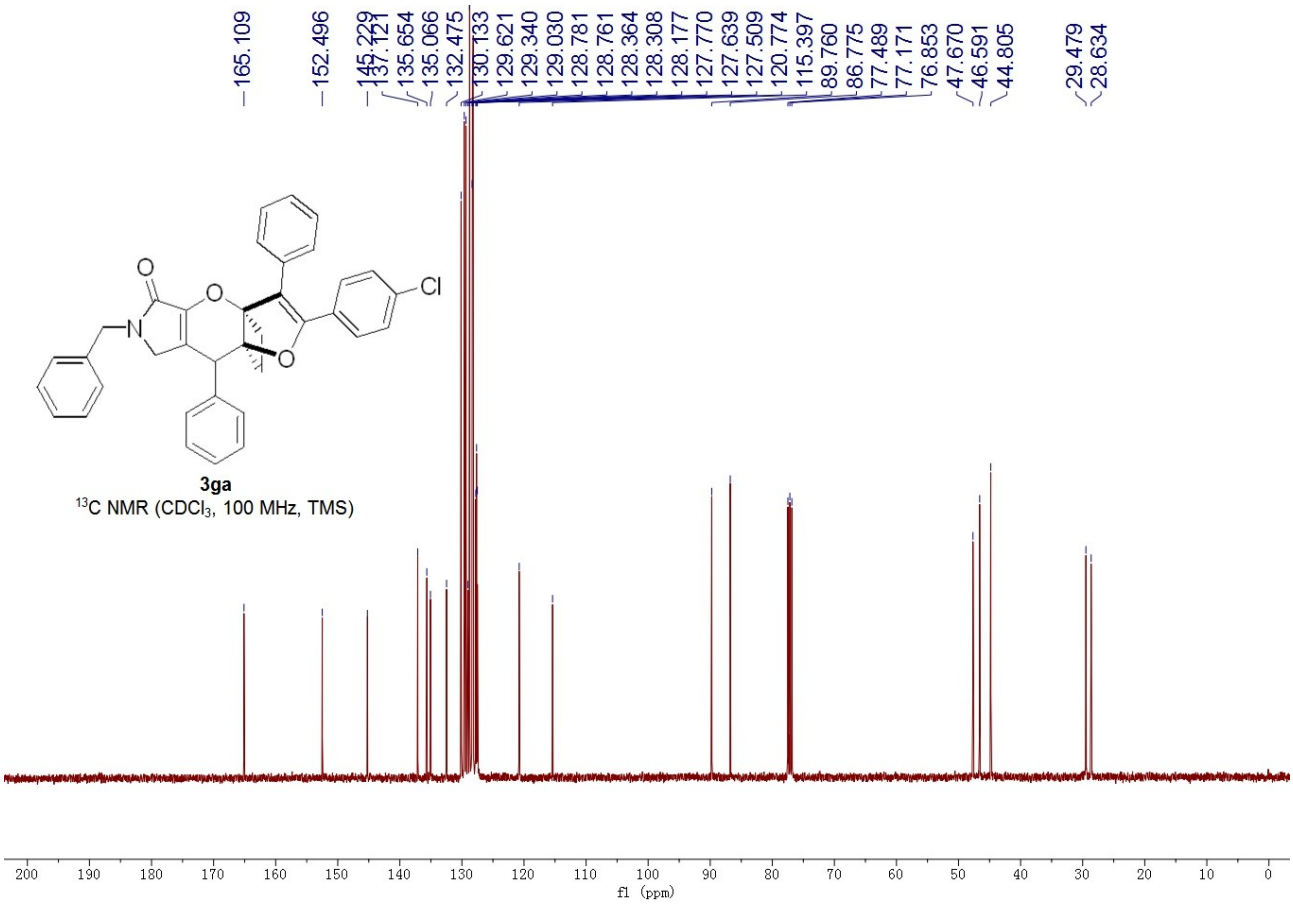
^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

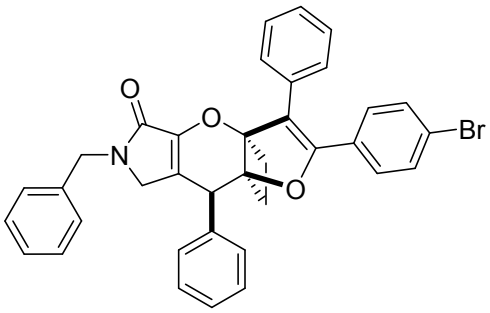


3ga

(3aS,8aS)-6-benzyl-2-(4-chlorophenyl)-3,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ga), the title compound was achieved as white solid, MP = 127-129 ^{o}C, 100.9 mg, 83% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.45 (m, 2H), 7.35-7.25 (m, 9H), 7.25-7.19 (m, 4H), 7.16-7.09 (m, 4H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.33 (d, *J* = 15.2 Hz, 1H), 4.10 (s, 1H), 3.64 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.49 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.54-2.37 (m, 3H), 2.30-2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 152.5, 145.2, 137.1, 135.7, 135.1, 132.5, 130.1, 129.6, 129.3, 129.0, 128.8, 128.7, 128.4, 128.3, 128.2, 127.8, 127.7, 127.5, 120.8, 115.4, 89.8, 86.8, 47.7, 46.6, 44.8, 29.5, 28.6. IR (MeOH) ν 2926, 1697, 1490, 1472, 1375, 1227, 1127, 1085, 1055, 1004, 898, 812, 766, 724, 699 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{29}NO_3Cl$: 558.1831, found: 558.1839.

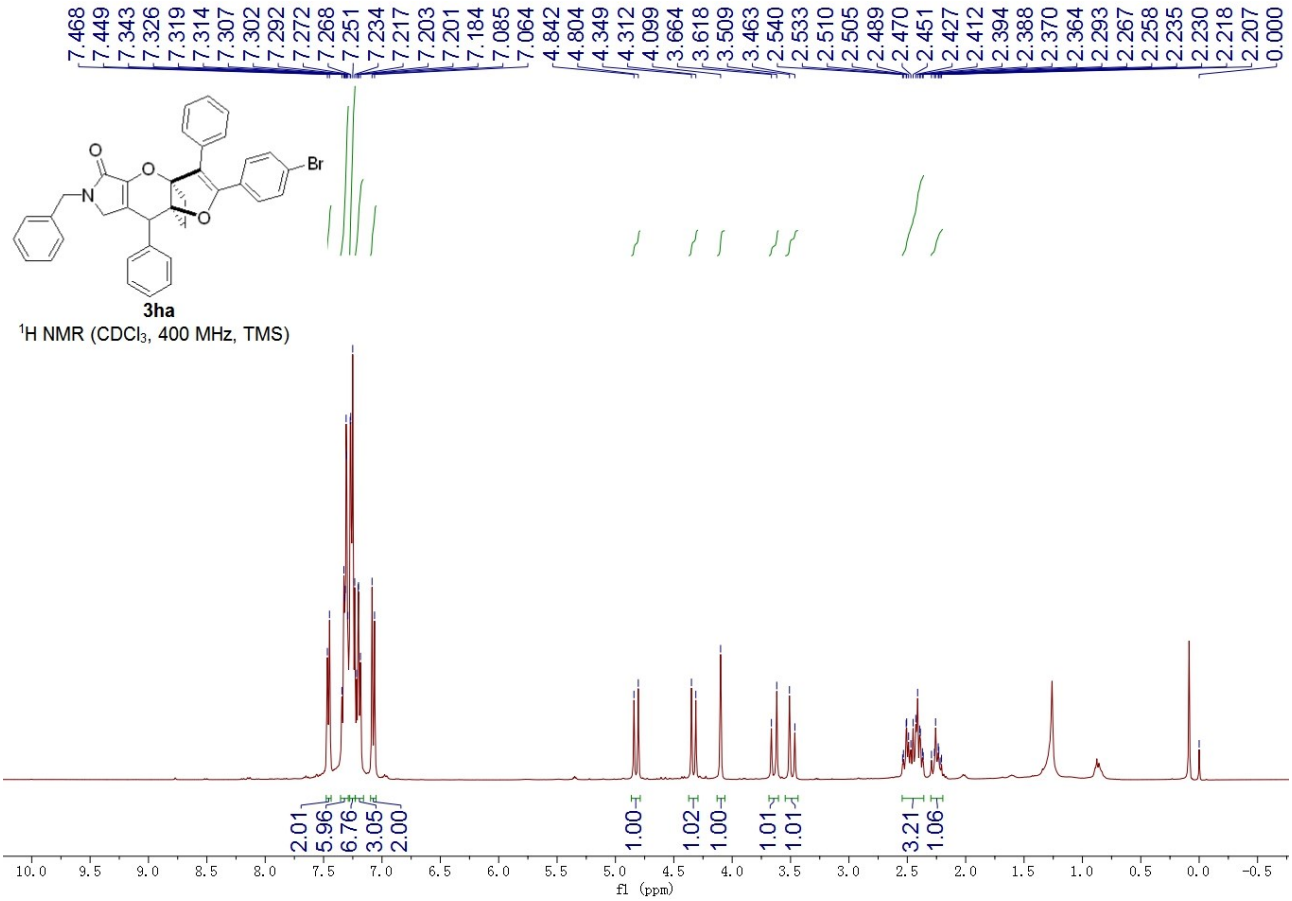

7.475
7.471
7.454
7.347
7.343
7.339
7.326
7.322
7.319
7.314
7.307
7.301
7.294
7.290
7.286
7.279
7.272
7.264
7.254
7.248
7.245
7.227
7.213
7.205
7.201
7.195
7.185
7.156
7.151
7.140
7.134
7.107
7.102
7.090
7.085
4.842
4.804
4.352
4.315
4.103
3.668
3.664
3.622
3.618
3.511
3.507
2.506
2.454
2.431
2.415
2.260
O
O
N
O
Cl
3ga
1H NMR (CDCl3, 400 MHz, TMS)
2.00
9.05
4.66
4.03
1.00
1.01
1.01
1.00
1.00
3.07
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


165.109
152.496
145.229
137.121
135.654
135.066
132.475
130.133
129.621
129.340
129.030
128.781
128.761
128.364
128.308
128.177
127.770
127.639
127.509
120.774
115.397
89.760
86.775
77.489
77.171
76.853
47.670
46.591
44.805
29.479
28.634
O
O
N
O
Cl
3ga
13C NMR (CDCl3, 100 MHz, TMS)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



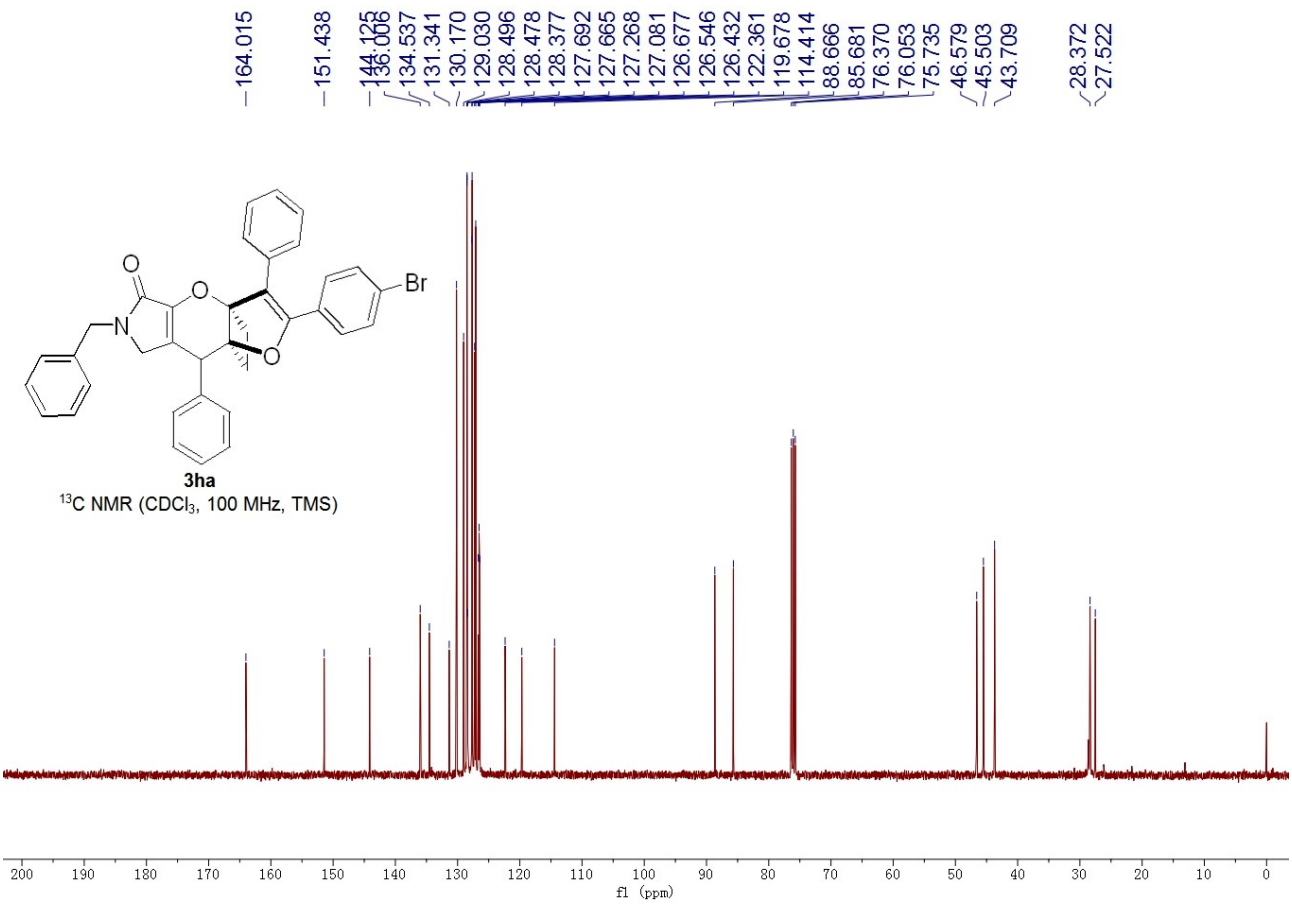
3ha

(3aS,8aS)-6-benzyl-2-(4-bromophenyl)-3,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ha), the title compound was achieved as yellow solid, MP = 103-105 ^{o}C, 102.9 mg, 83% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.34-7.29 (m, 6H), 7.27-7.23 (m, 6H), 7.22-7.18 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.33 (d, *J* = 15.8 Hz, 1H), 4.10 (s, 1H), 3.64 (d, *J* = 18.4 Hz, 1H), 3.49 (d, *J* = 18.4 Hz, 1H), 2.54-2.39 (m, 3H), 2.36-2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 152.5, 145.2, 137.0, 135.6, 132.4, 131.2, 130.6, 129.52, 129.50, 129.4, 128.7, 128.6, 128.3, 128.1, 127.7, 127.6, 127.5, 123.4, 120.7, 115.4, 89.7, 86.7, 47.6, 46.5, 44.8, 29.4, 28.6. IR (MeOH) ν 2925, 1695, 1495, 1453, 1251, 1176, 1091, 1073, 1007, 833, 801, 765, 730, 700 cm^{-1}. HRMS (ESI) calcd for $C_{36}H_{29}NO_3Br$: 602.1325, found: 602.1321.



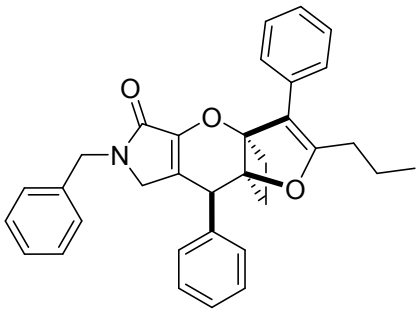
3ha

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



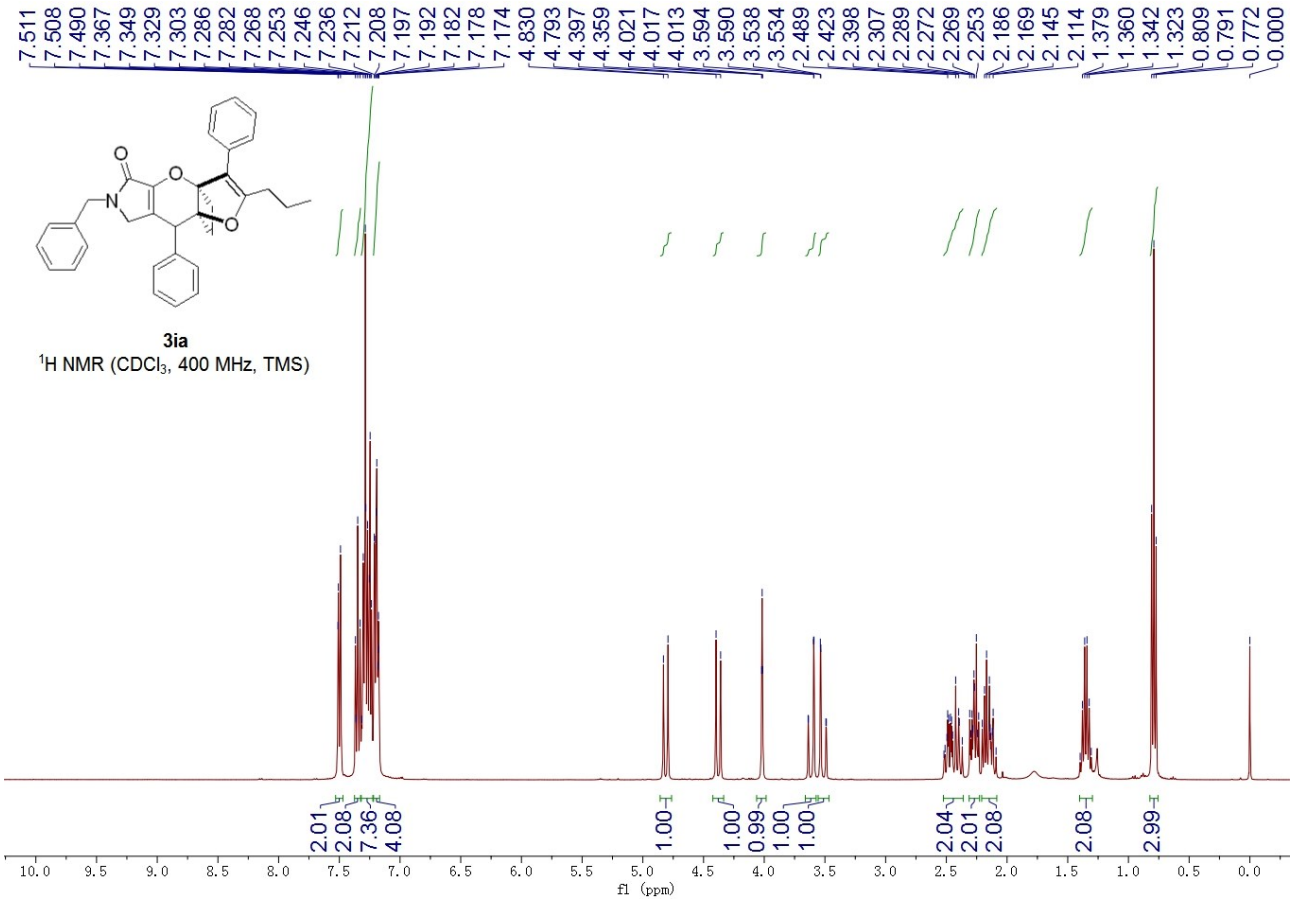
3ha

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



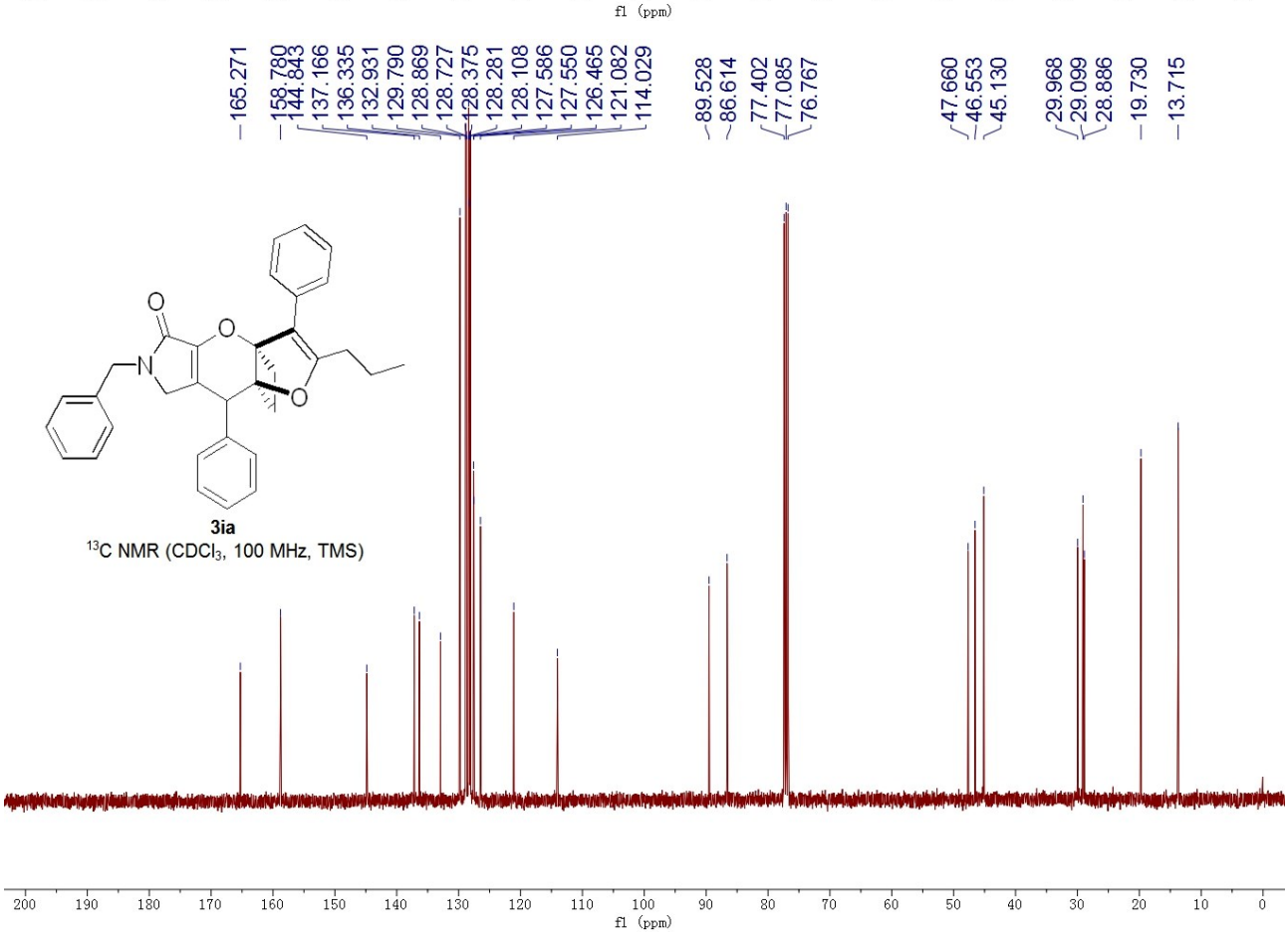
3ia

(3aS,8aS)-6-benzyl-3,8-diphenyl-2-propyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ia), the title compound was achieved as white solid, MP = 71-73 ^{o}C, 70.2 mg, 65% yield. Elution: R*f* = 0.39 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.49 (m, 2H), 7.37-7.33 (m, 2H), 7.32-7.24 (m, 7H), 7.21-7.17 (m, 4H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.38 (d, *J* = 15.2 Hz, 1H), 4.02 (s, 1H), 3.61 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.51 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.52-2.37 (m, 2H), 2.31-2.23 (m, 2H), 2.20-2.09 (m, 2H), 1.35 (m, *J* = 7.2 Hz, 2H), 0.79 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 158.8, 144.8, 137.2, 136.3, 132.9, 129.8, 128.9, 128.7, 128.4, 128.3, 128.1, 127.6, 127.5, 126.5, 121.1, 114.0, 89.5, 86.6, 47.7, 46.6, 45.1, 30.0, 29.1, 28.9, 19.7, 13.7. IR (neat) ν 2956, 2919, 1697, 1496, 1453, 1243, 1115, 1005, 956, 764, 699 cm^{-1}. HRMS (ESI) calcd for $C_{33}H_{32}NO_3$: 490.2377, found: 490.2379.



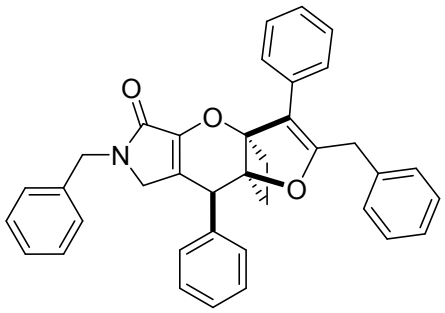
3ia

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



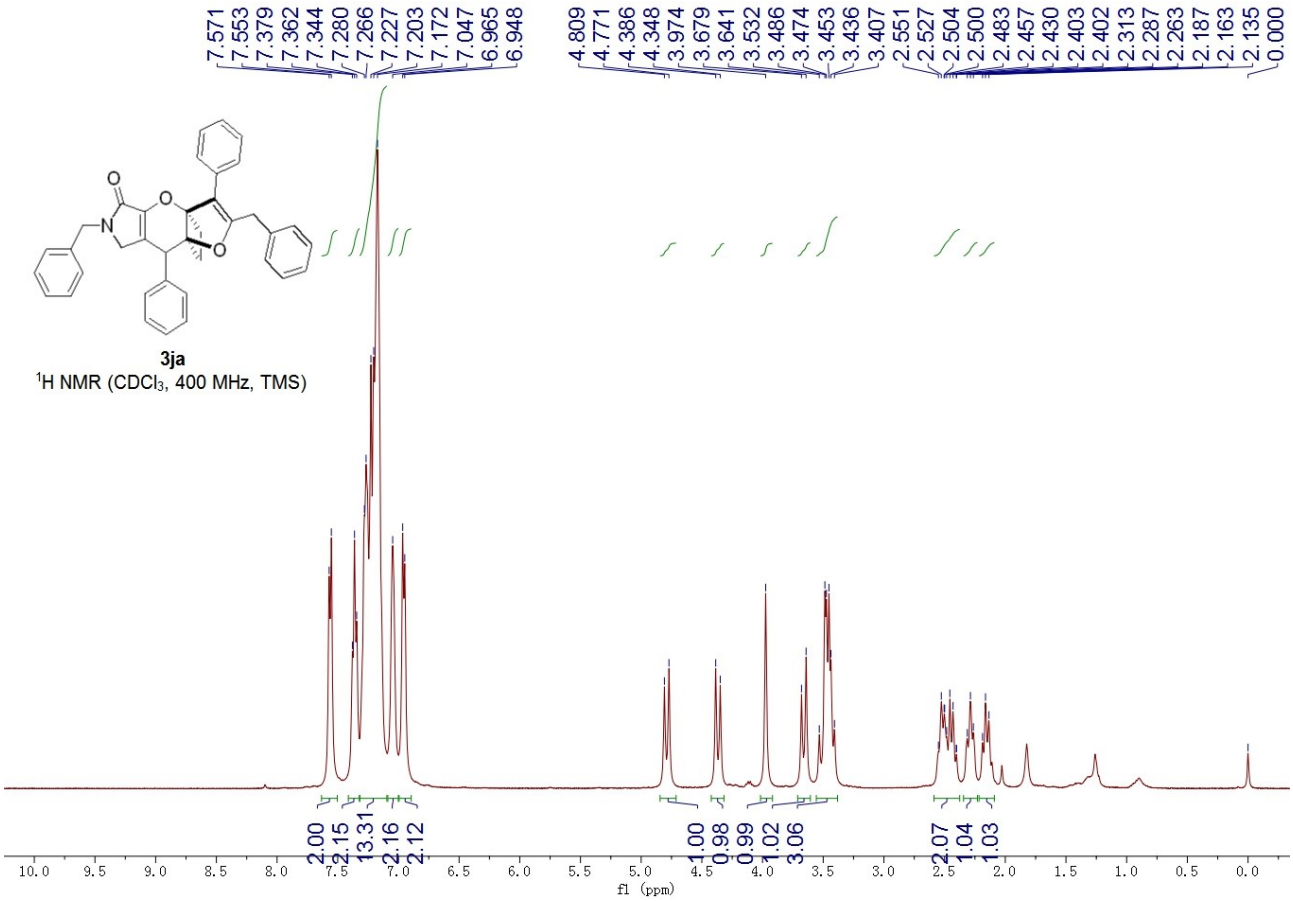
3ia

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



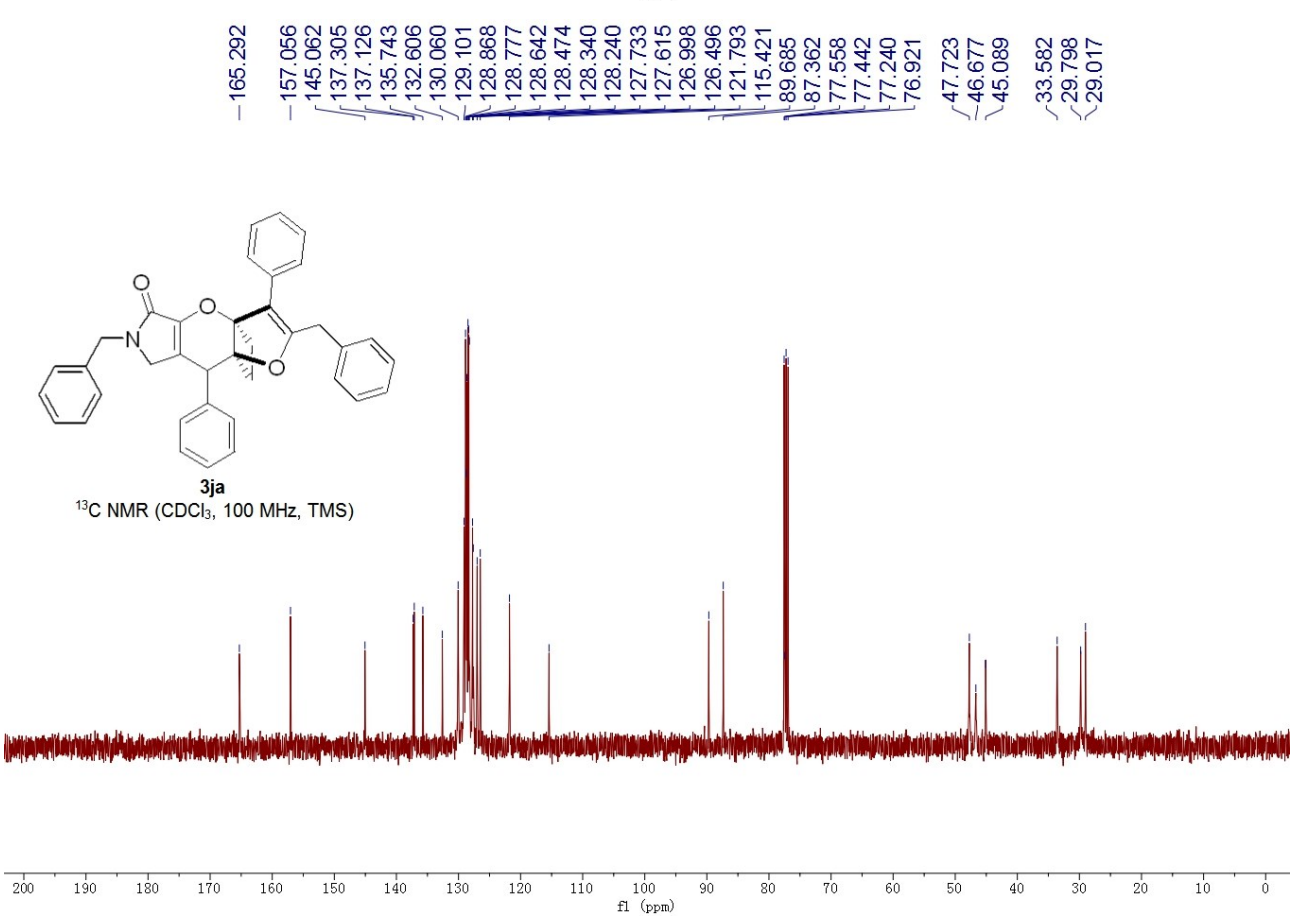
3ja

(3aS,8aS)-2,6-dibenzyl-3,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ja), the title compound was achieved as yellow oil, 95.4 mg, 76% yield. R*f* = 0.35 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.28-7.17 (m, 12H), 7.05 (s, 2H), 6.96 (d, *J* = 7.2 Hz, 2H), 4.79 (d, *J* = 15.2 Hz, 1H), 4.37 (d, *J* = 15.2 Hz, 1H), 3.97 (s, 1H), 3.66 (d, *J* = 15.2 Hz, 1H), 3.53-3.41 (m, 3H), 2.55-2.40 (m, 2H), 2.29 (t, *J* = 9.6 Hz, 1H), 2.19-2.11 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 157.1, 145.1, 137.3, 137.1, 135.7, 132.6, 130.1, 129.1, 128.9, 128.8, 128.6, 128.5, 128.3, 128.2, 127.7, 127.6, 127.0, 126.5, 121.8, 115.4, 89.7, 87.4, 47.7, 46.7, 45.1, 33.6, 29.8, 29.0. IR (neat) ν 2925, 1694, 1495, 1453, 1244, 1149, 1118, 1005, 908, 763, 729, 697 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_3$: 538.2377, found: 538.2376.



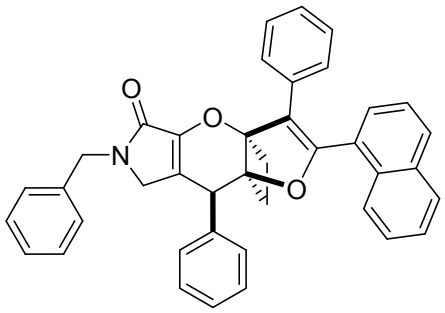
3ja

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



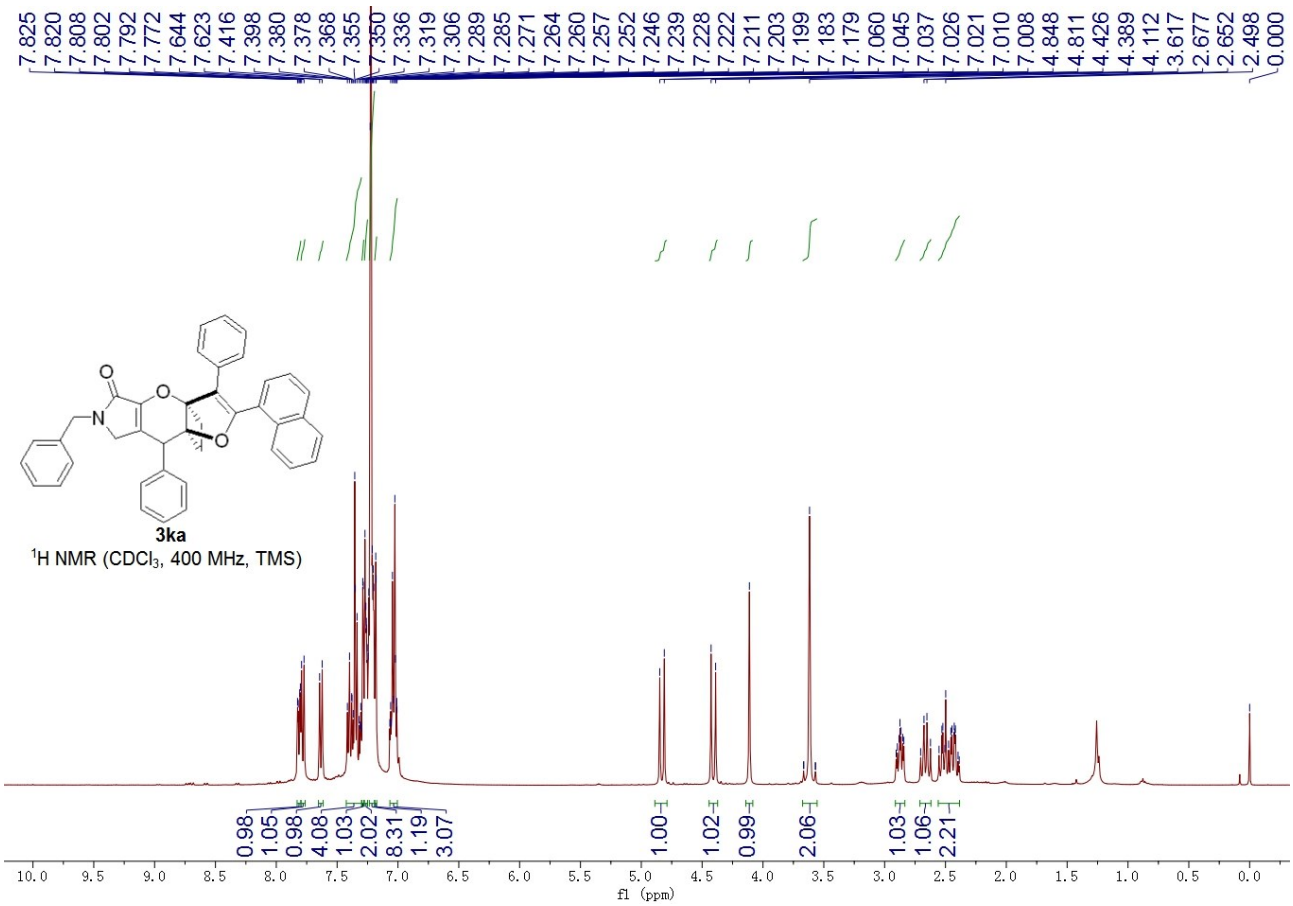
3ja

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



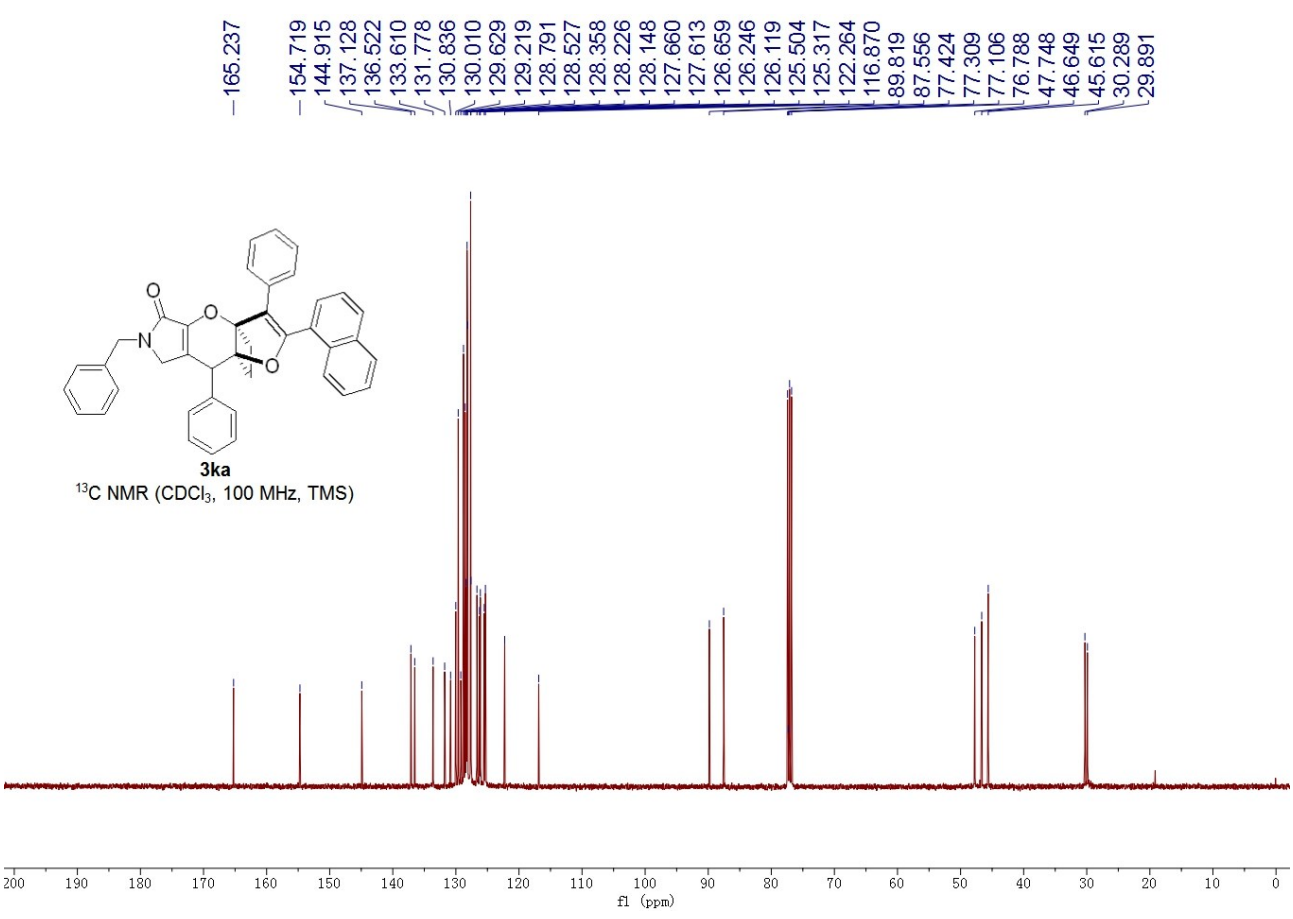
3ka

(3aS,8aS)-6-benzyl-2-(naphthalen-1-yl)-3,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ka), the title compound was achieved as brown solid, MP = 133-135 ^{o}C,126.2 mg, 87% yield. R*f* = 0.32 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.4 Hz, 1H), 7.42-7.30 (m, 4H), 7.29 (d, *J* = 1.6 Hz, 2H), 7.27-7.25 (m, 1H), 7.24-7.20 (m, 8H), 7.18 (d, *J* = 1.6 Hz, 1H), 7.07-7.01 (m, 3H), 4.83 (d, *J* = 15.2 Hz, 1H), 4.41 (d, *J* = 15.2 Hz, 1H), 4.11 (s, 1H), 3.67-3.57 (m, 2H), 2.87 (ddd, *J* = 16.0, 9.2, 3.6 Hz, 1H), 2.66 (q, *J* = 10.8 Hz, 1H), 2.55-2.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 154.7, 144.9, 137.1, 136.5, 133.6, 131.8, 130.8, 130.0, 129.6, 129.2, 128.8, 128.5, 128.4, 128.2, 128.1, 127.7, 127.6, 126.7, 126.2, 126.1, 125.5, 125.3, 122.2, 116.9, 89.8, 87.6, 47.7, 46.6, 45.6, 30.3, 29.9. IR (MeOH) ν 2972, 2926, 1688, 1453, 1383, 1245, 1172, 1088, 1047, 880, 804, 777, 701 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{32}NO_3$: 574.2377, found: 574.2373.



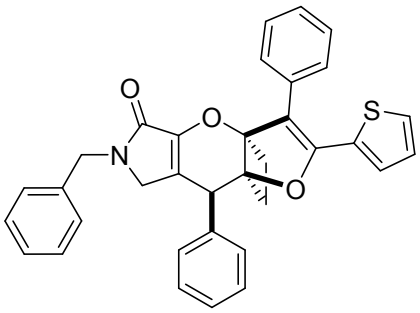
3ka

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



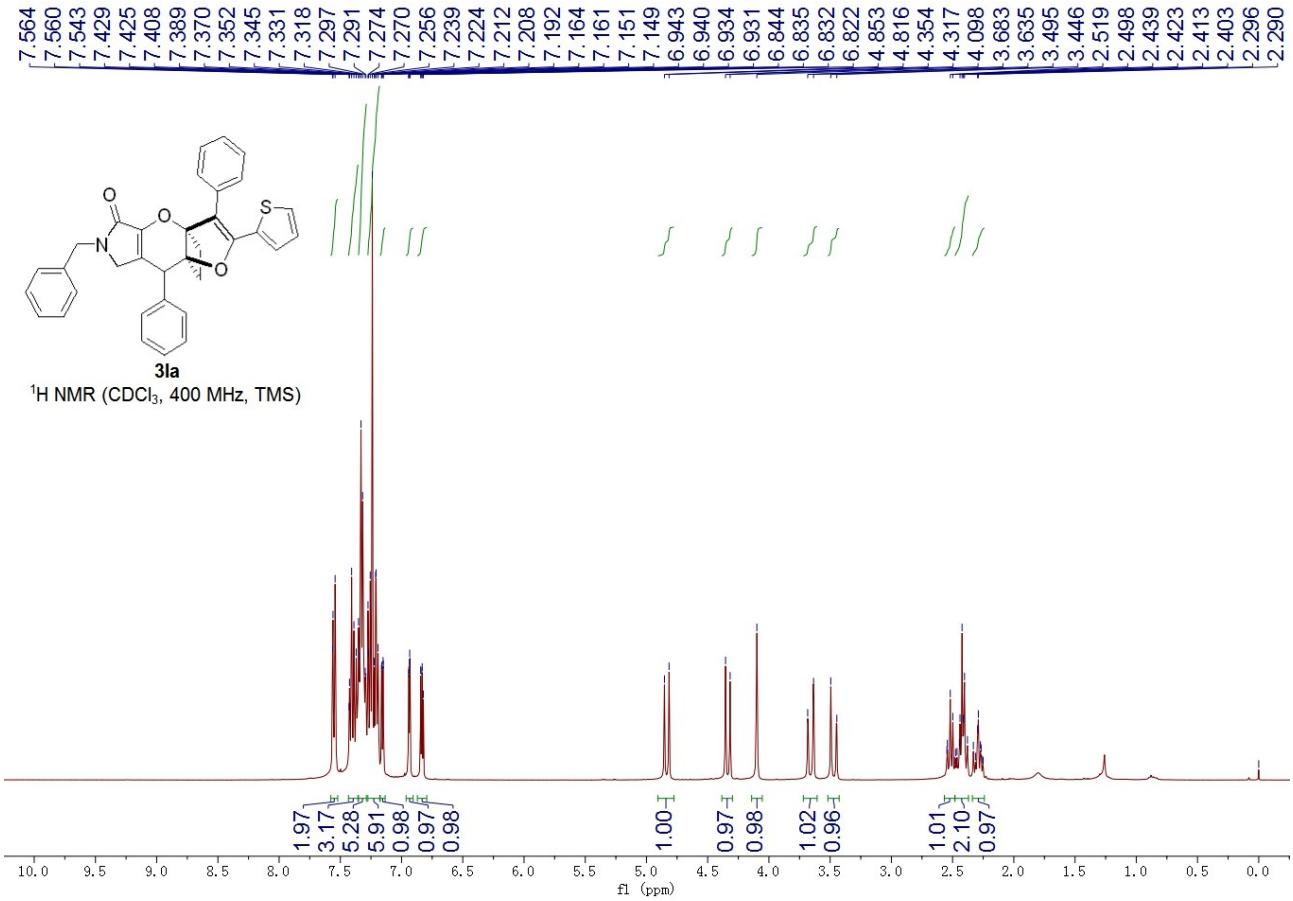
3ka

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



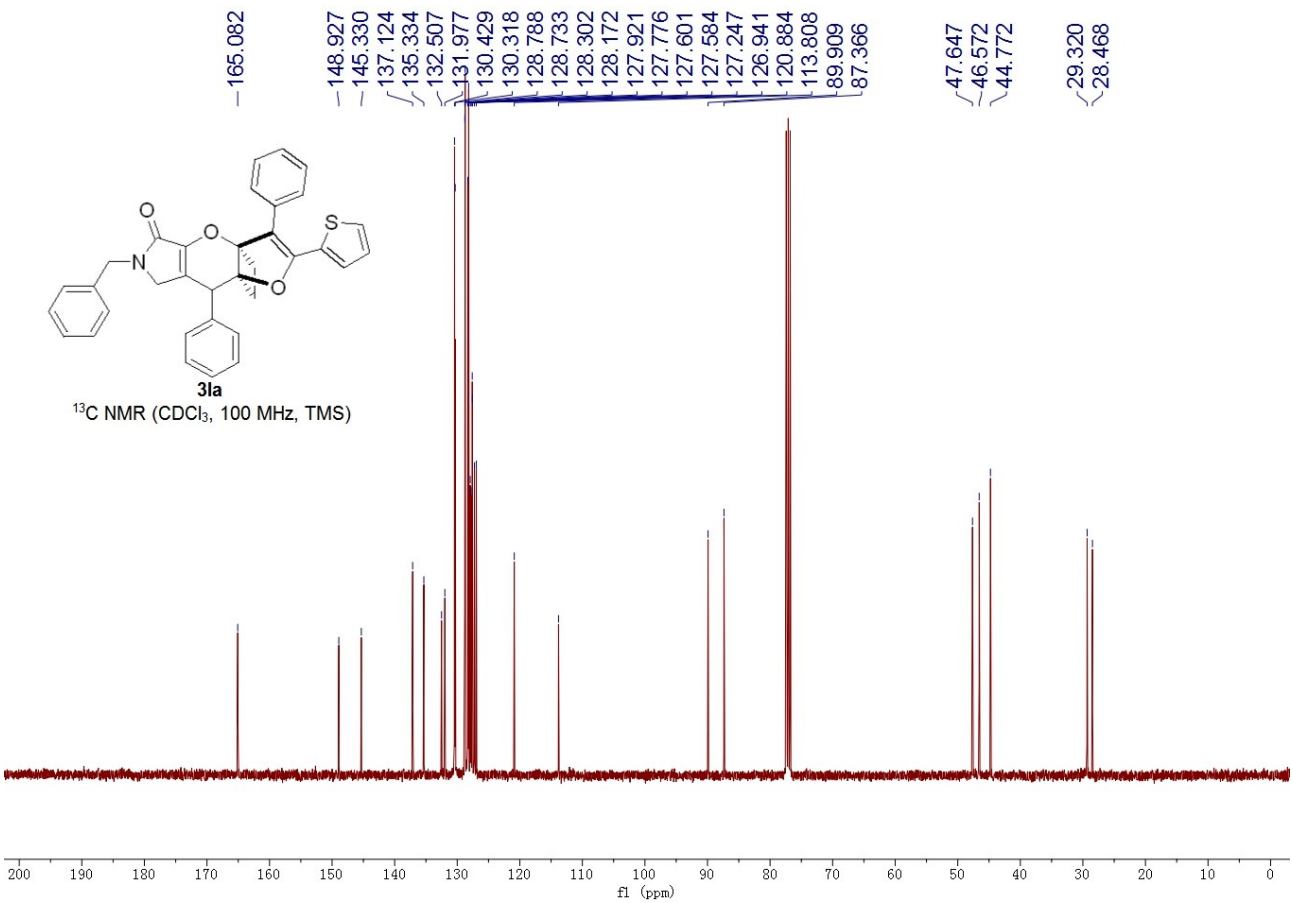
3la

(3aS,8aS)-6-benzyl-3,8-diphenyl-2-(thiophen-2-yl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3la), the title compound was achieved as brown solid, MP = 210-211 ^{o}C,46.1 mg, 50% yield. R*f* = 0.38 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.43-7.37 (m, 3H), 7.35-7.29 (m, 5H), 7.27-7.19 (m, 5H), 7.16 (dd, *J* = 4.8, 1.2 Hz, 1H), 6.94 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.83 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.83 (d, *J* = 14.8 Hz, 1H), 4.34 (d, *J* = 14.8 Hz, 1H), 4.10 (s, 1H), 3.66 (dd, *J* = 18.4, 0.8 Hz, 1H), 3.47 (dd, *J* = 18.4, 0.8 Hz, 1H), 2.55-2.49 (m, 1H), 2.48-2.38 (m, 2H), 2.33-2.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 148.9, 145.3, 137.1, 135.3, 132.5, 131.9, 130.4, 130.3, 128.8, 128.7, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.3, 126.9, 120.9, 113.8, 89.9, 87.4, 47.6, 46.6, 44.8, 29.3, 28.5. IR (neat) ν 1702, 1675, 1497, 1454, 1423, 1367, 1248, 1173, 1117, 1002, 850, 762, 709, 694 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{28}NO_3S$: 530.1784, found: 530.1786.



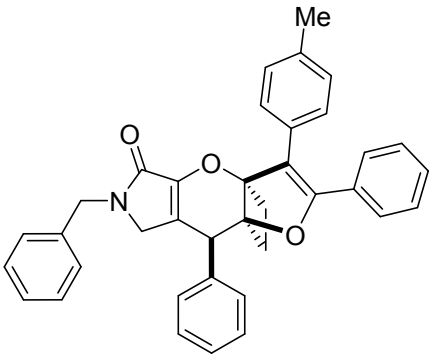
3la

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



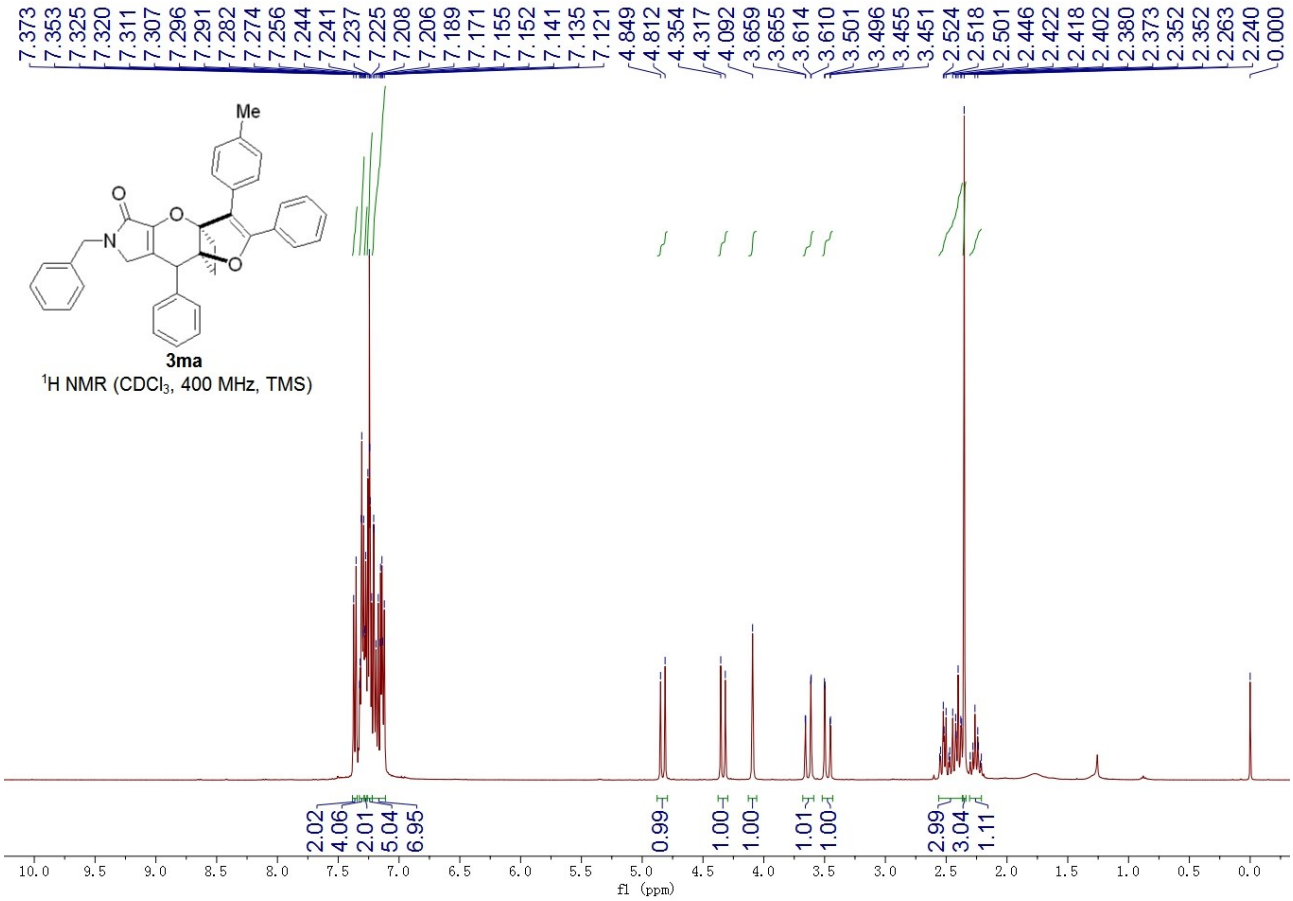
3la

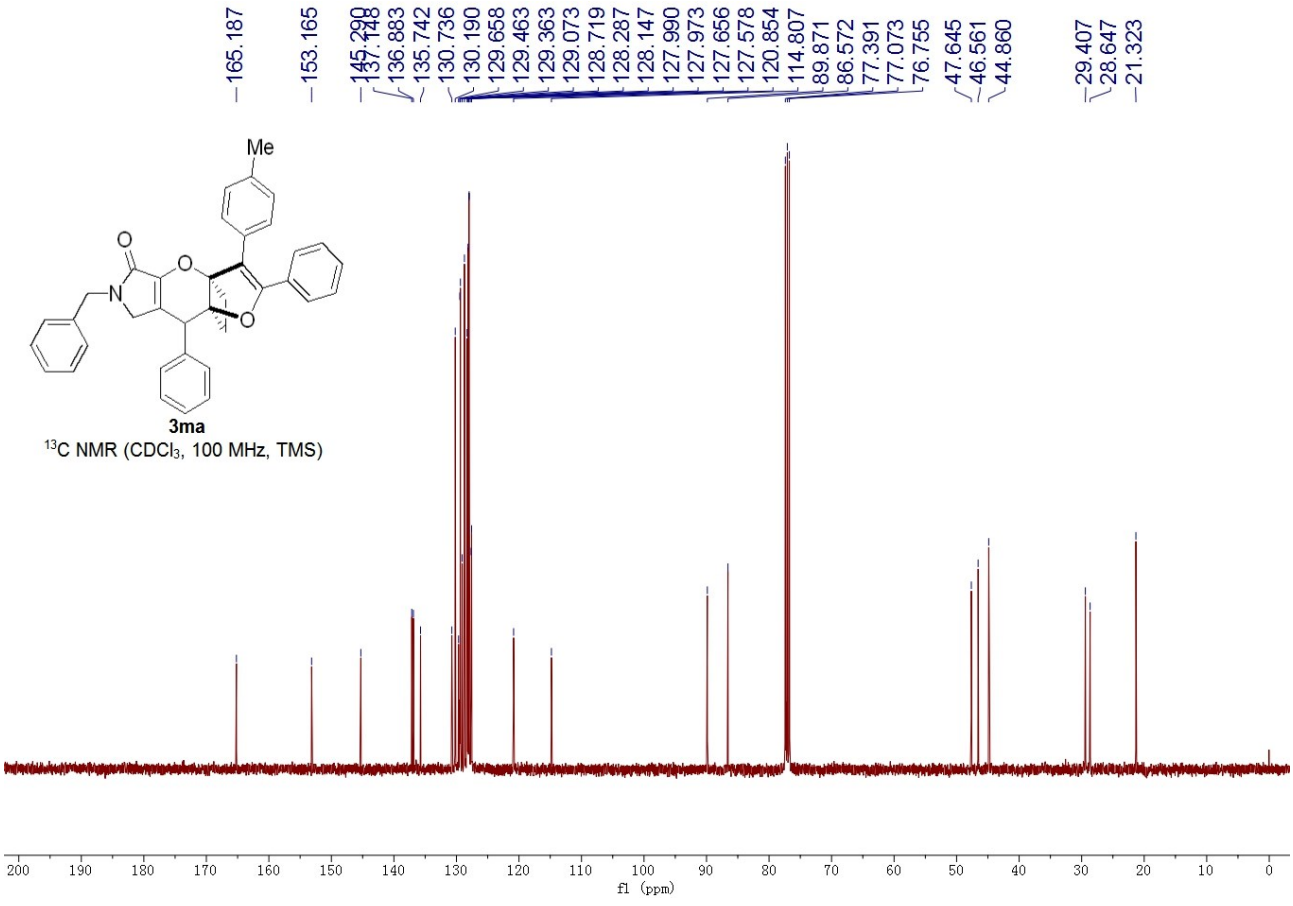
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

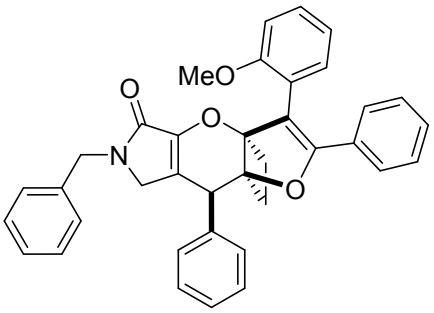


3ma

(3aS,8aS)-6-benzyl-2,8-diphenyl-3-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ma), the title compound was achieved as yellow solid, MP = 148-150 ^{o}C, 90.7 mg, 81% yield. R*f* = 0.35 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 4H), 7.28-7.27 (m, 2H), 7.26-7.23 (m, 4H), 7.21-7.12 (m, 7H), 4.83 (d, *J* = 14.8 Hz, 1H), 4.34 (d, *J* = 14.8 Hz, 1H), 4.09 (s, 1H), 3.63 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.48 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.55-2.37 (m, 3H), 2.35 (s, 3H), 2.30-2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 153.2, 145.3, 137.1, 136.9, 135.7, 130.7, 130.2, 129.7, 129.5, 129.4, 129.0, 128.7, 128.3, 128.1, 128.0, 127.9, 127.7, 127.6, 120.9, 114.8, 89.9, 86.6, 47.7, 46.6, 44.9, 29.4, 28.6, 21.3. IR (neat) ν 2942, 1693, 1477, 1452, 1354, 1230, 1129, 1078, 1007, 885, 767, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_3$: 538.2377, found: 538.2375.

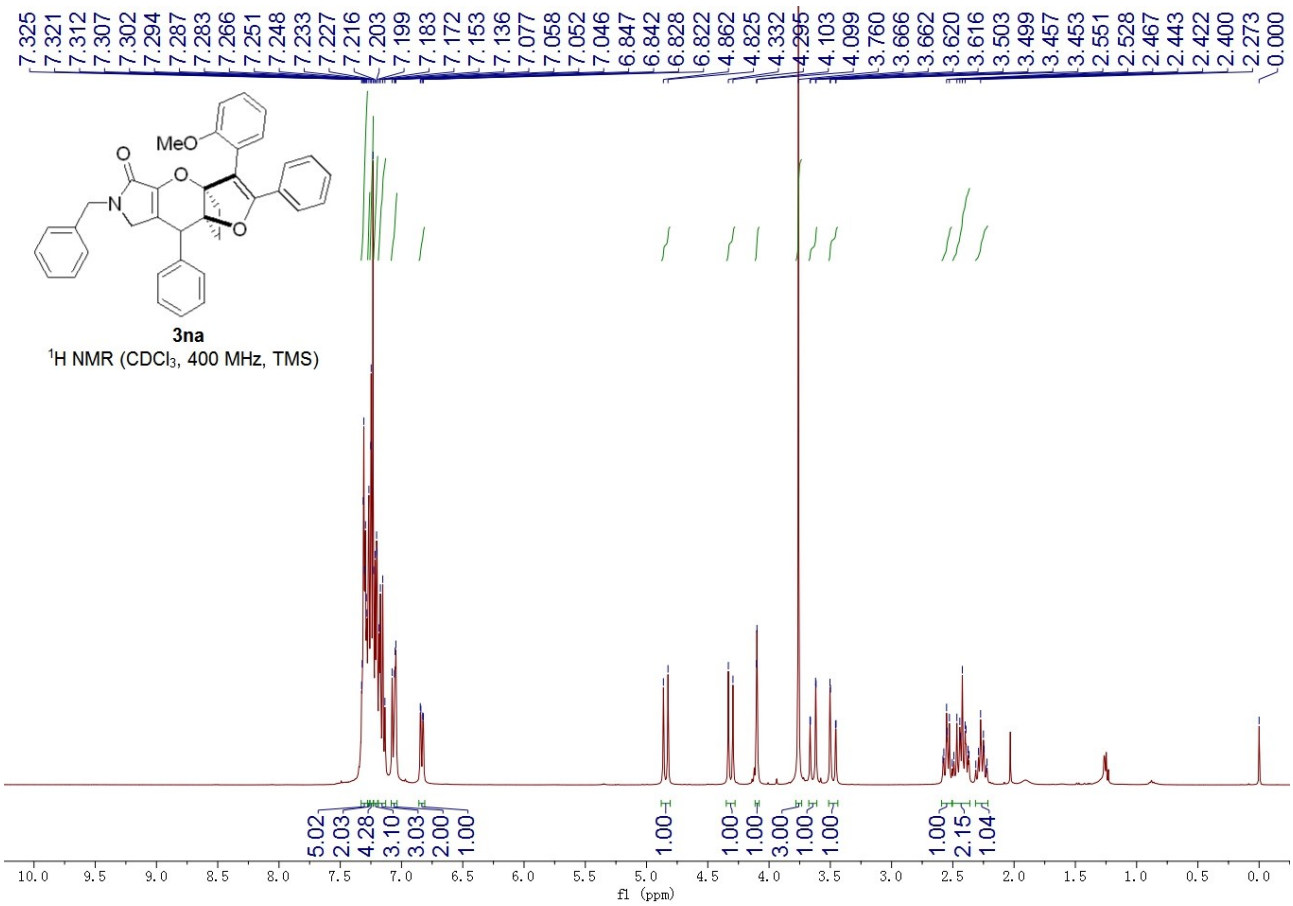

Me
O
N
O
O
3ma
^{1}H NMR ($CDCl_3$, 400 MHz, TMS)
7.373
7.353
7.325
7.320
7.311
7.307
7.296
7.291
7.282
7.274
7.256
7.244
7.241
7.237
7.225
7.208
7.206
7.189
7.171
7.155
7.152
7.141
7.135
7.121
4.849
4.812
4.354
4.317
4.092
3.659
3.655
3.614
3.610
3.501
3.496
3.455
3.451
2.524
2.518
2.501
2.446
2.422
2.418
2.402
2.380
2.373
2.352
2.352
2.263
2.240
0.000
2.02
4.06
2.01
5.04
6.95
0.99
1.00
1.00
1.01
1.00
2.99
3.04
1.11
fl (ppm)


Me
O
N
O
O
3ma
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)
165.187
153.165
145.290
137.748
136.883
135.742
130.736
130.190
129.658
129.463
129.363
129.073
128.719
128.287
128.147
127.990
127.973
127.656
127.578
120.854
114.807
89.871
86.572
77.391
77.073
76.755
47.645
46.561
44.860
29.407
28.647
21.323
fl (ppm)



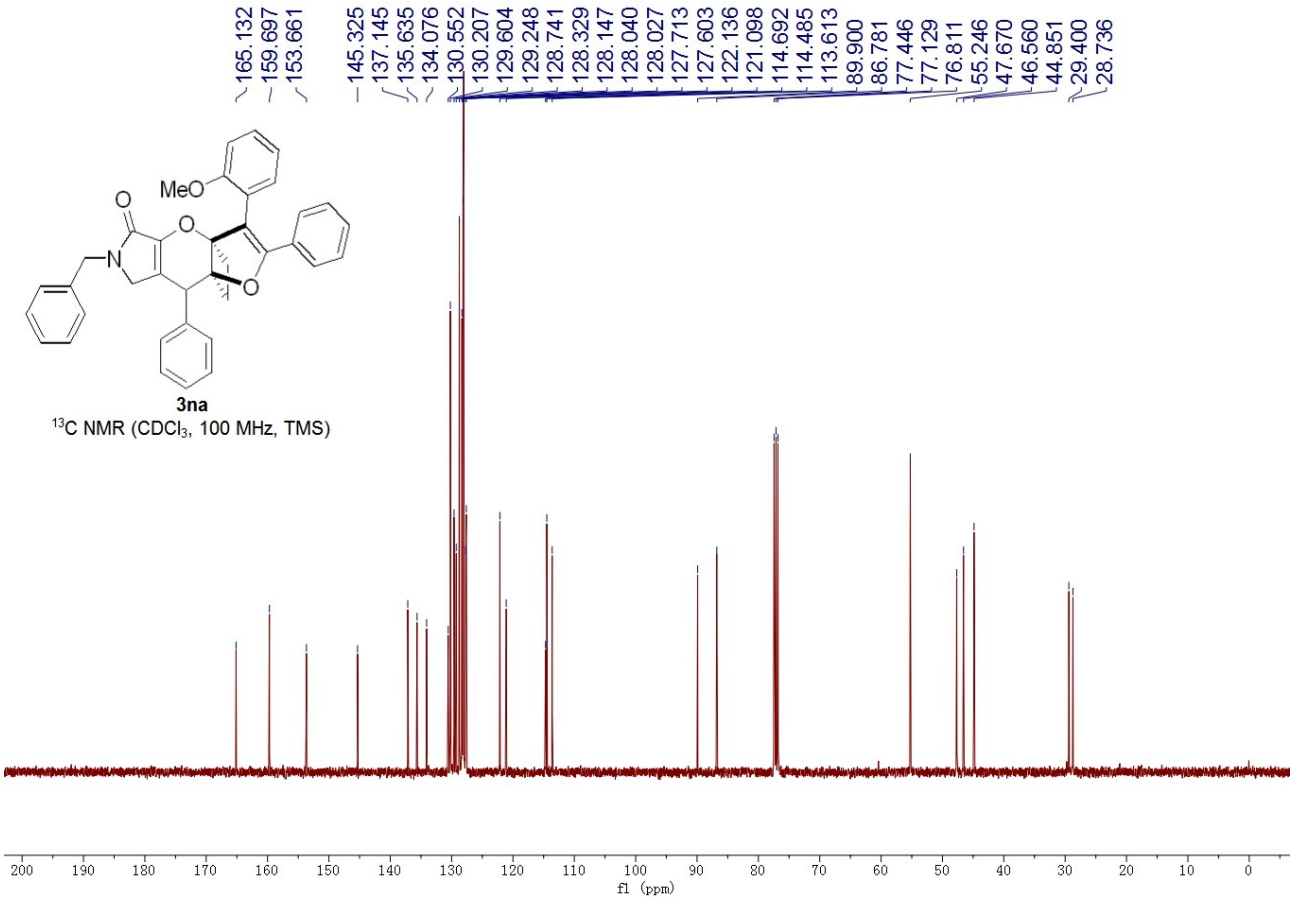
3na

(3aS,8aS)-6-benzyl-3-(2-methoxyphenyl)-2,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3na), the title compound was achieved as brown solid, MP = 134-136 ^{o}C, 64.5 mg, 53% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.28 (m, 5H), 7.27 (m, 2H), 7.25-7.24 (m, 3H), 7.23-7.20 (m, 3H), 7.18-7.14 (m, 3H), 7.08-7.05 (m, 2H), 6.83 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.83 (d, *J* = 14.8 Hz, 1H), 4.34 (d, *J* = 14.8 Hz, 1H), 4.10 (s, 1H), 3.76 (s, 3H), 3.64 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.48 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.58-2.53 (m, 1H), 2.51-2.37 (m, 2H), 2.31-2.22 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 159.7, 153.7, 145.3, 137.1, 135.6, 134.1, 130.6, 130.2, 129.6, 129.2, 128.7, 128.3, 128.1, 128.04, 128.03, 127.7, 127.6, 122.1, 121.1, 114.7, 114.5, 113.6, 89.9, 86.8, 55.2, 47.7, 46.6, 44.9, 29.4, 28.7. IR (neat) ν 2953, 2833, 1694, 1511, 1494, 1453, 1286, 1245, 1173, 1029, 993, 836, 767, 731, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_4$: 554.2326, found: 554.2320.



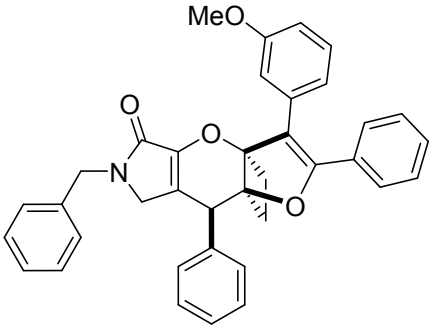
3na

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



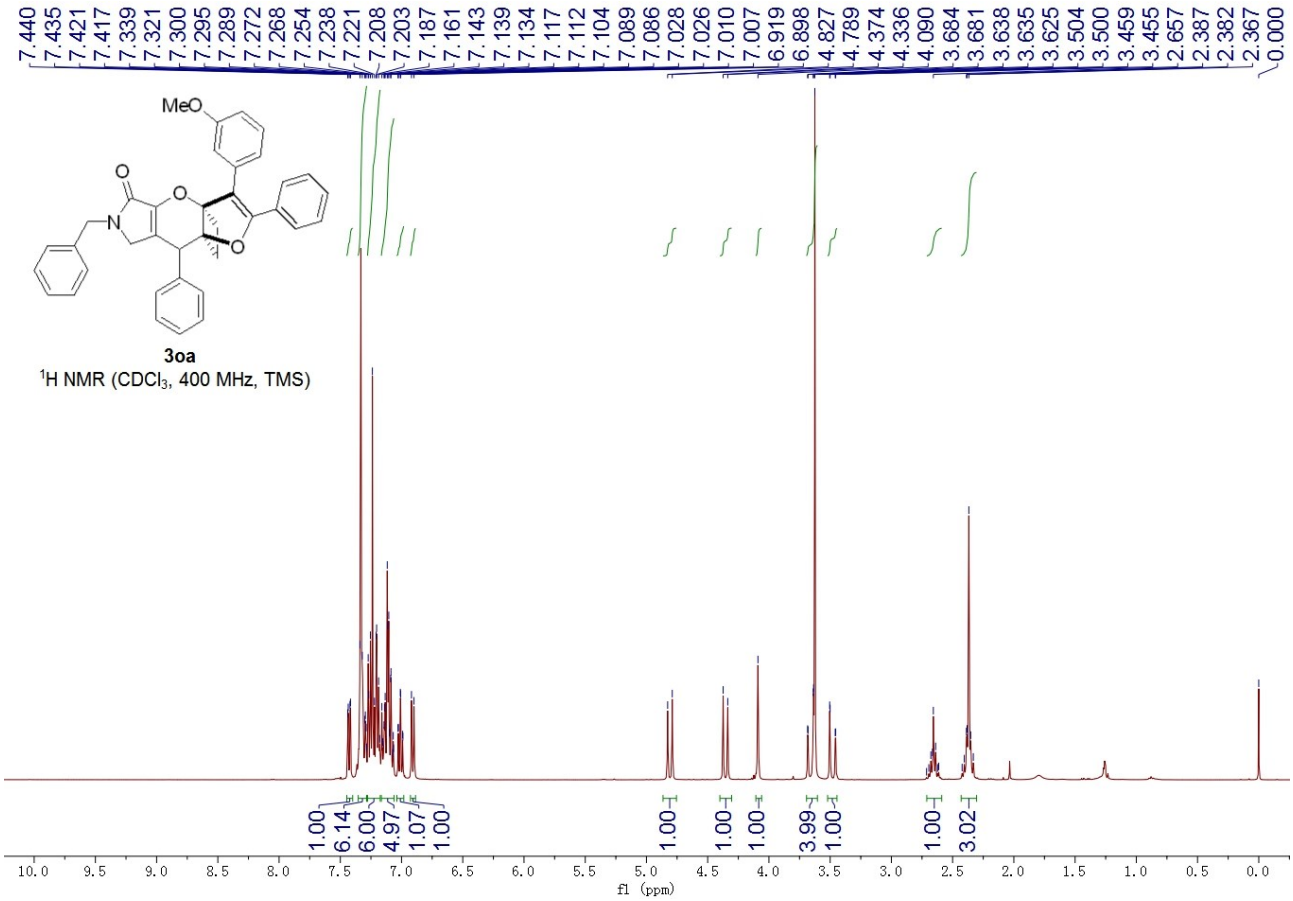
3na

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



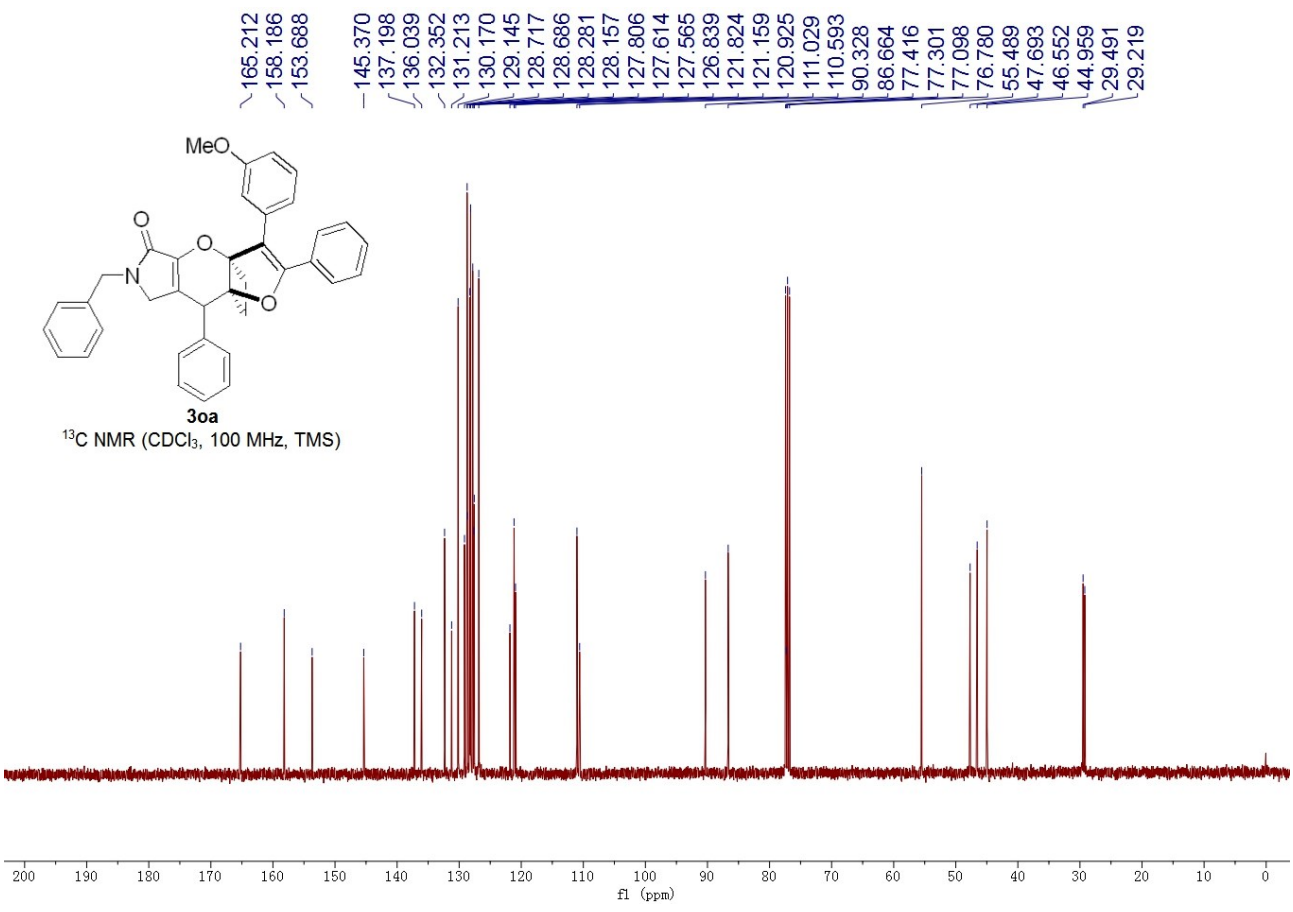
3oa

(3aS,8aS)-6-benzyl-3-(3-methoxyphenyl)-2,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3oa), the title compound was achieved as yellow solid, MP = 123-125 ^{o}C, 78.2 mg, 71% yield. R*f* = 0.31 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.34-7.29 (m, 6H), 7.27-7.18 (m, 5H), 7.16-7.07 (m, 5H), 7.01 (td, *J* = 7.2, 0.8 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.36 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.66 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.63 (s, 3H), 3.48 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.71-2.61 (m, 1H), 2.42-2.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 158.2, 153.7, 145.4, 137.2, 136.0, 132.4, 131.2, 130.2, 129.1, 128.7, 128.6, 128.3, 128.2, 127.8, 127.6, 127.5, 126.8, 121.8, 121.2, 120.9, 111.0, 110.6, 90.3, 86.7, 55.5, 47.7, 46.6, 44.9, 29.5, 29.2. IR (neat) ν 2922, 2852, 1694, 1495, 1453, 1250, 1176, 1071, 1007, 903, 833, 766, 732, 699 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_4$: 554.2326, found: 554.2319.



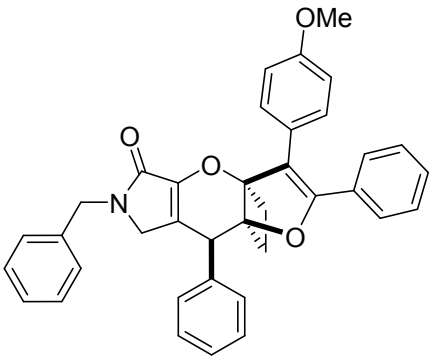
3oa

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



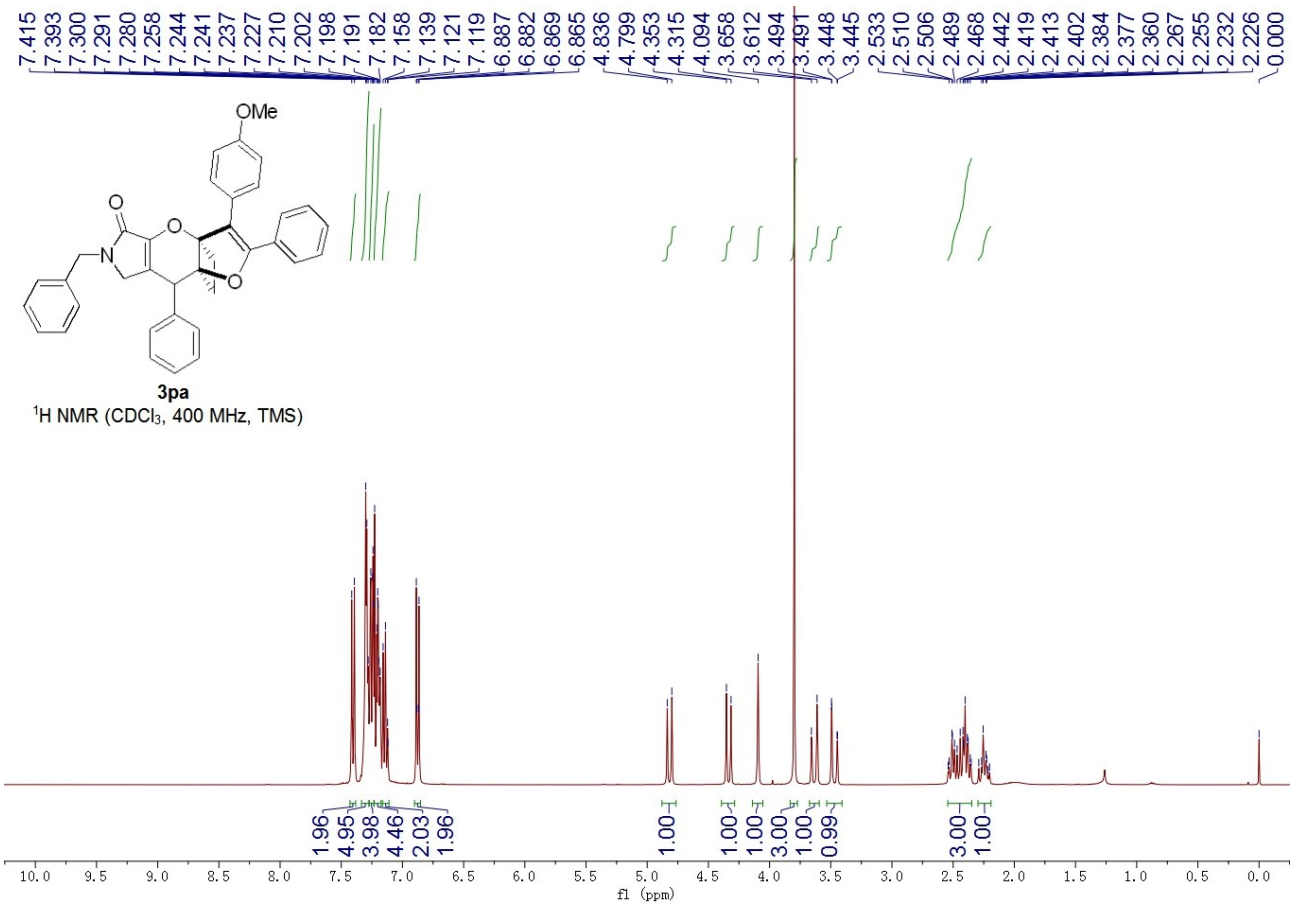
3oa

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



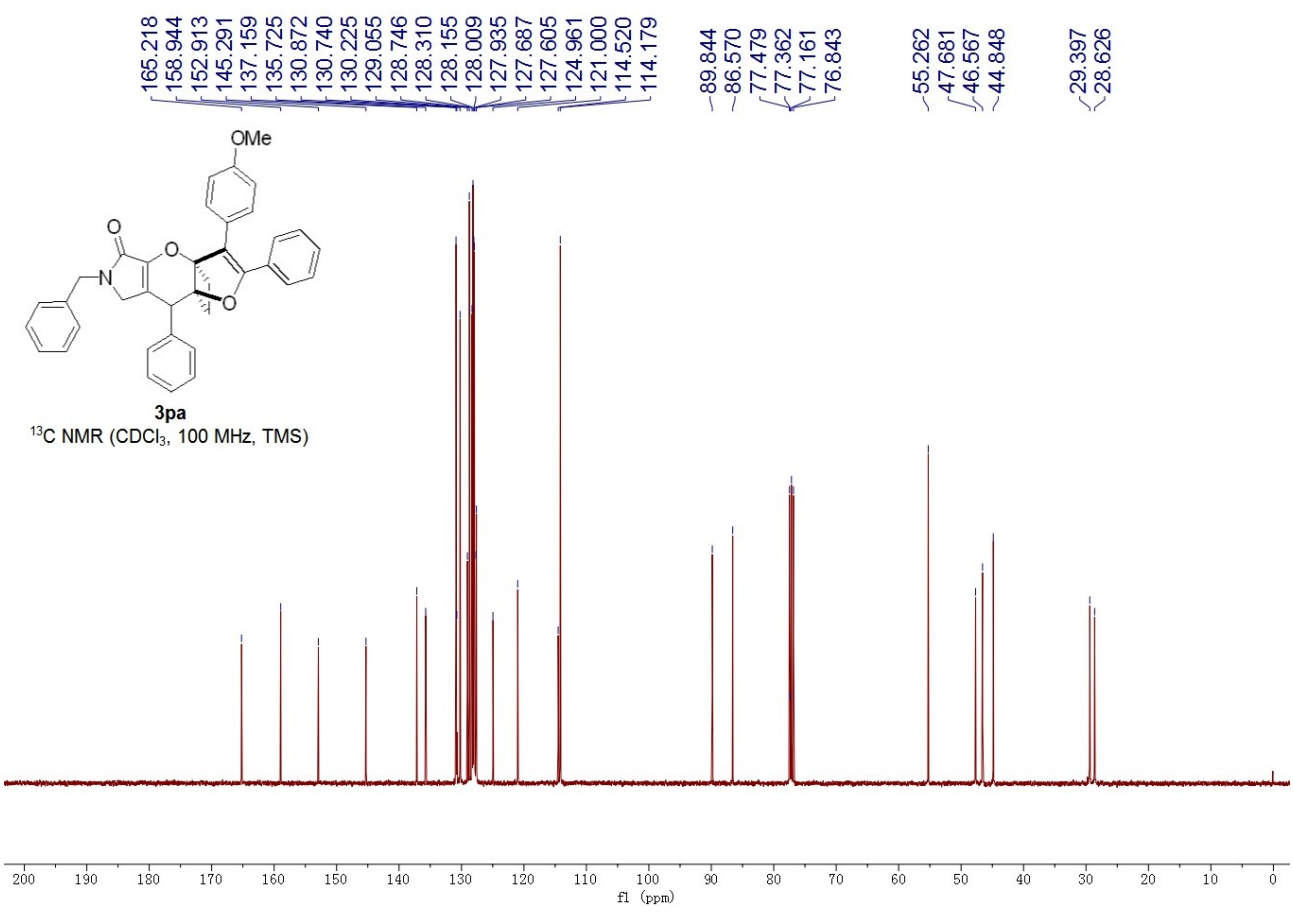
3pa

(3aS,8aS)-6-benzyl-3-(4-methoxyphenyl)-2,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3pa), the title compound was achieved as yellow solid, MP = 96-98 ^{o}C, 98.8 mg, 93% yield. R*f* = 0.34 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.33-7.28 (m, 5H), 7.26-7.24 (m, 4H), 7.23-7.18 (m, 4H), 7.16-7.14 (m, 2H), 6.89-6.86 (m, 2H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.33 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.80 (s, 3H), 3.64 (dd, *J* = 18.4, 1.2 Hz, 1H), 3.47 (dd, *J* = 18.4, 1.2 Hz, 1H), 2.54-2.35 (m, 3H), 2.29-2.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 158.9, 152.9, 145.3, 137.2, 135.7, 130.9, 130.7, 130.2, 129.1, 128.7, 128.3, 128.2, 128.0, 127.9, 127.7, 127.6, 125.0, 121.0, 114.5, 114.2, 89.8, 86.6, 55.3, 47.7, 46.6, 44.8, 29.4, 28.6. IR (MeOH) ν 3400, 2973, 1693, 1454, 1253, 1221, 1087, 1046, 1010, 879, 701 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{32}NO_4$: 554.2326, found: 554.2320.



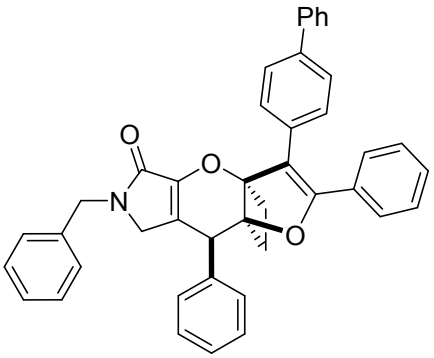
3pa

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



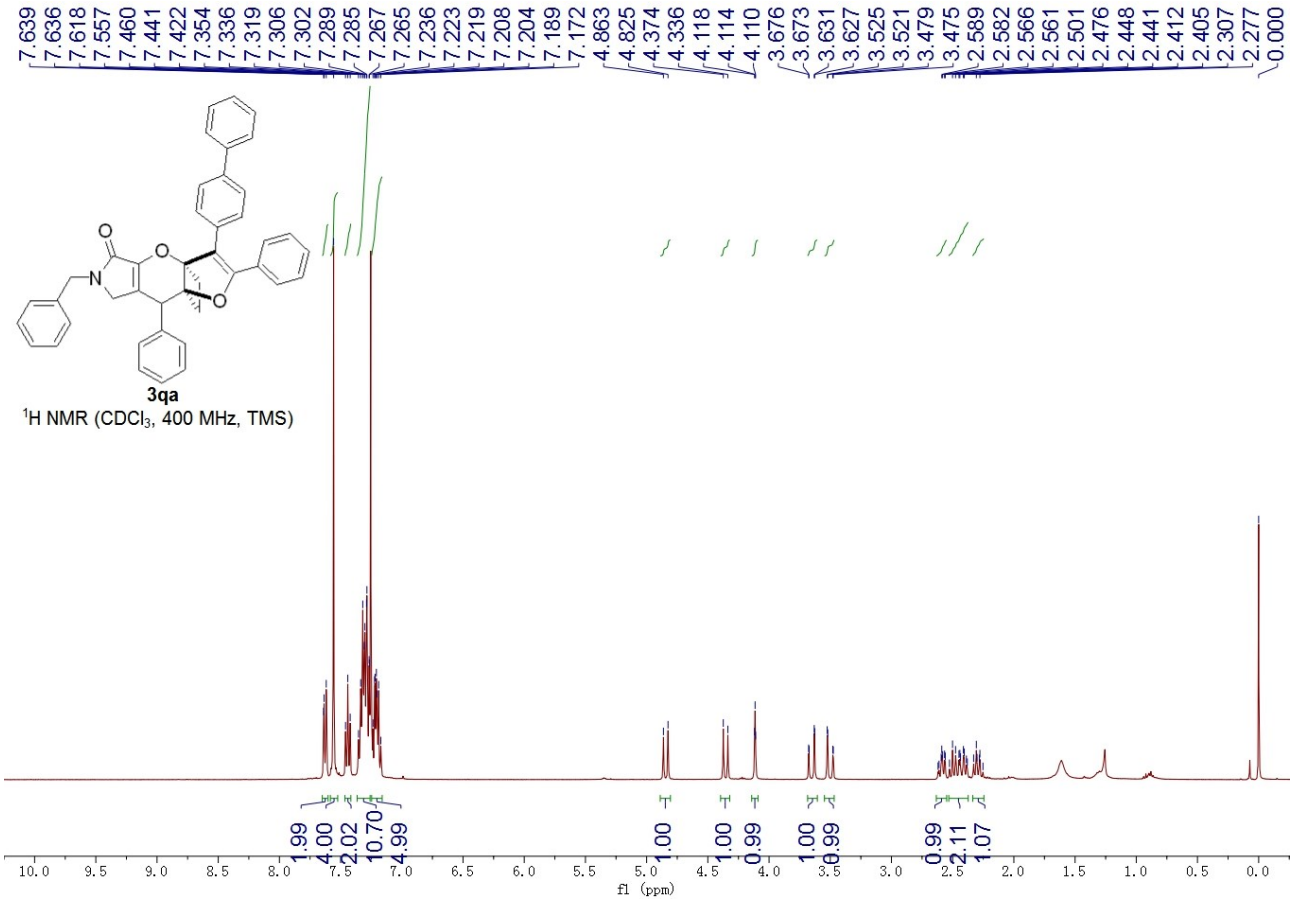
3pa

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



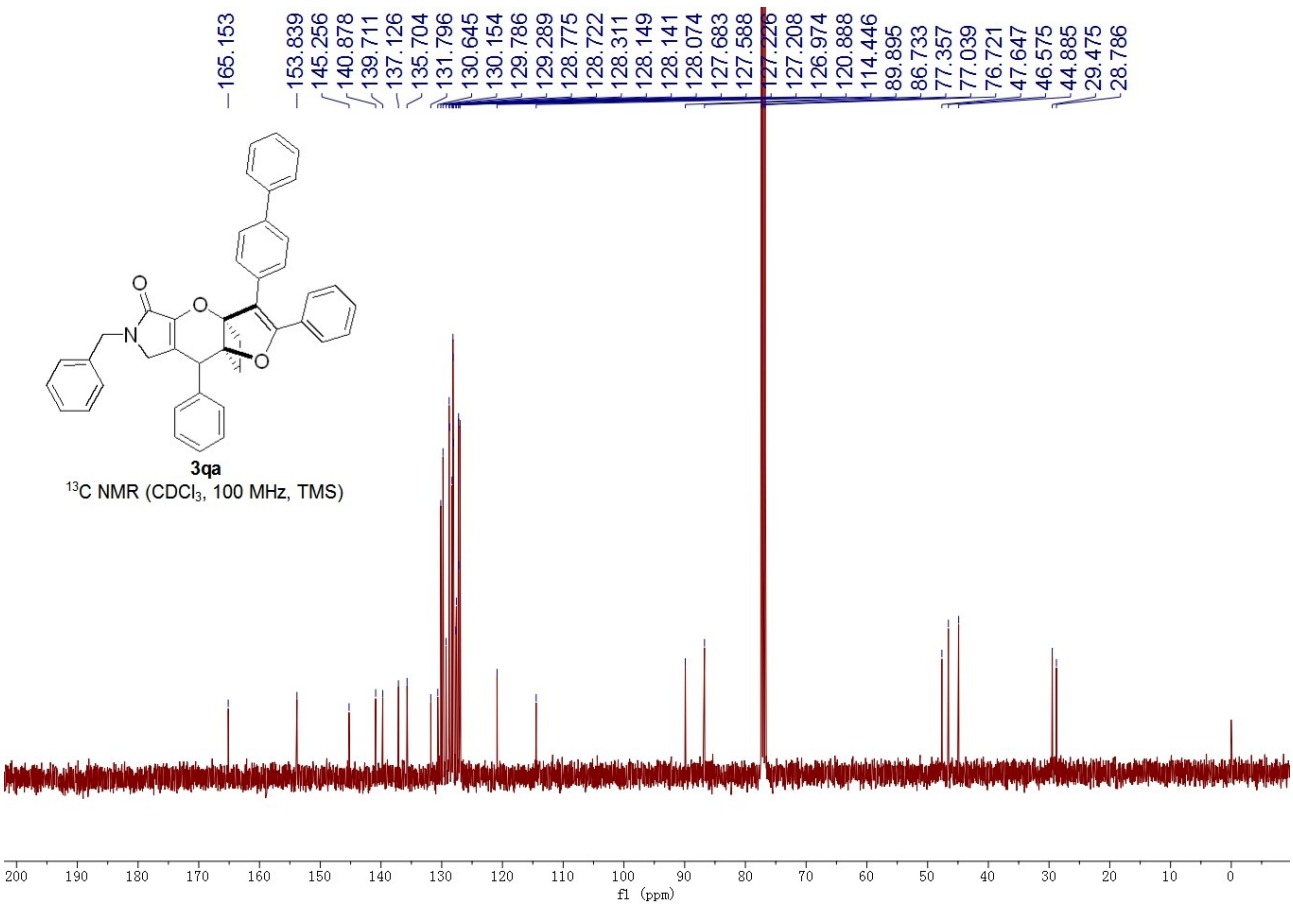
3qa

(3aS,8aS)-3-([1,1'-biphenyl]-4-yl)-6-benzyl-2,8-diphenyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3qa), the title compound was achieved as light yellow solid, MP = 200-202 ^{o}C, 50.9 mg, 45% yield. R*f* = 0.45 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64-7.62 (m, 2H), 7.56 (s, 4H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.35-7.27 (m, 11H), 7.24-7.17 (m, 5H), 4.84 (d, *J* = 15.2 Hz, 1H), 4.36 (d, *J* = 15.2 Hz, 1H), 4.11 (s, 1H), 3.65 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.50 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.62-2.56 (m, 1H), 2.53-2.38 (m, 2H), 2.33-2.25 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 153.8, 145.3, 140.9, 139.7, 137.1, 135.7, 131.8, 130.6, 130.2, 129.8, 129.3, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.7, 127.6, 127.23, 127.21, 127.0, 120.9, 114.4, 89.9, 86.7, 47.6, 46.6, 44.9, 29.5, 28.8. IR (neat) ν 2917, 1694, 1512, 1493, 1453, 1355, 1245, 1173, 1121, 1069, 1006, 898, 836, 768, 732, 700 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{34}NO_3$: 600.2533, found: 600.2533.



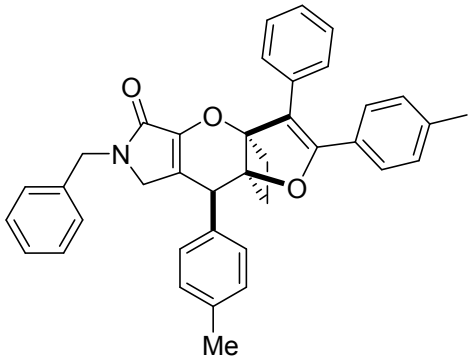
3qa

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



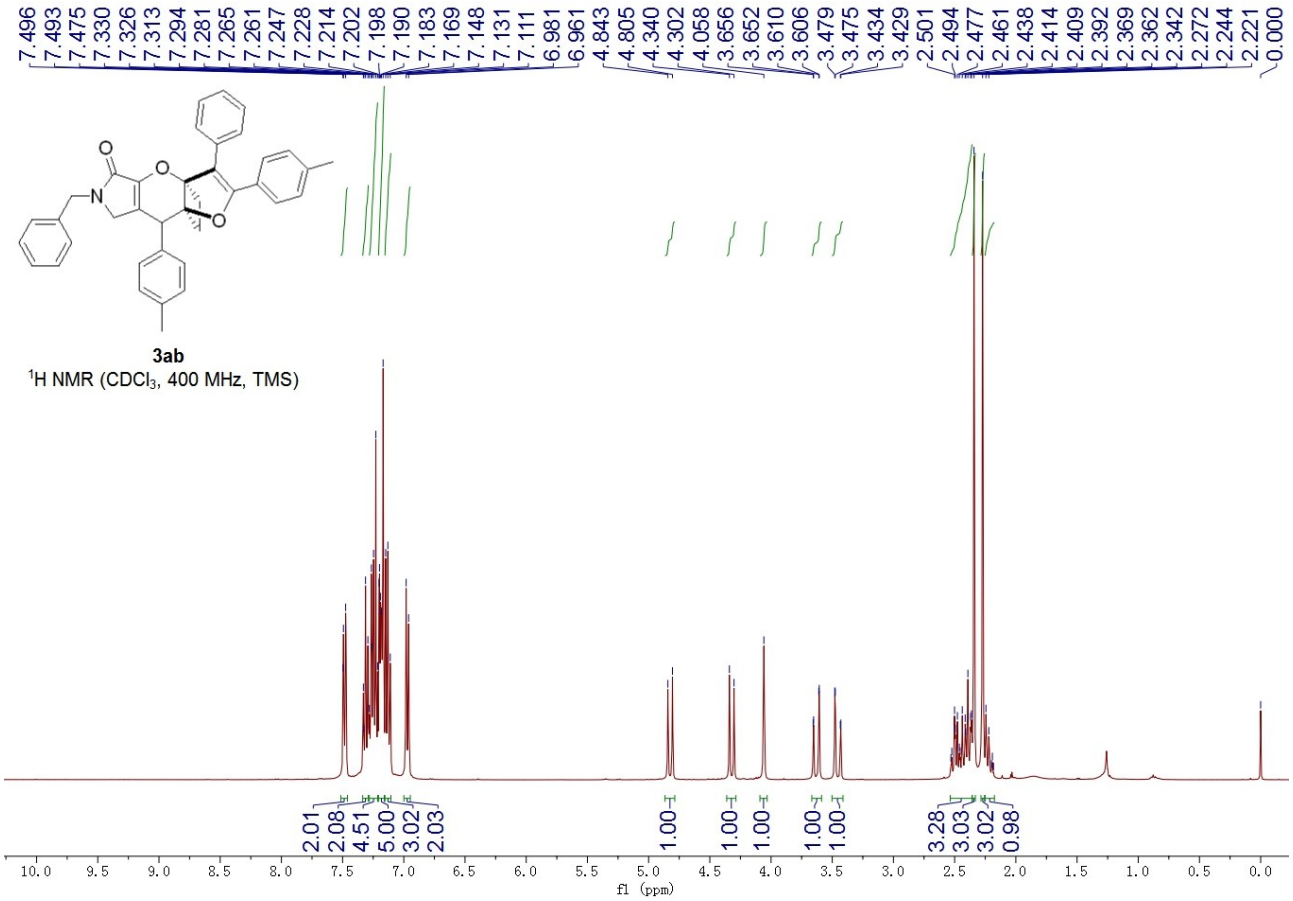
3qa

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



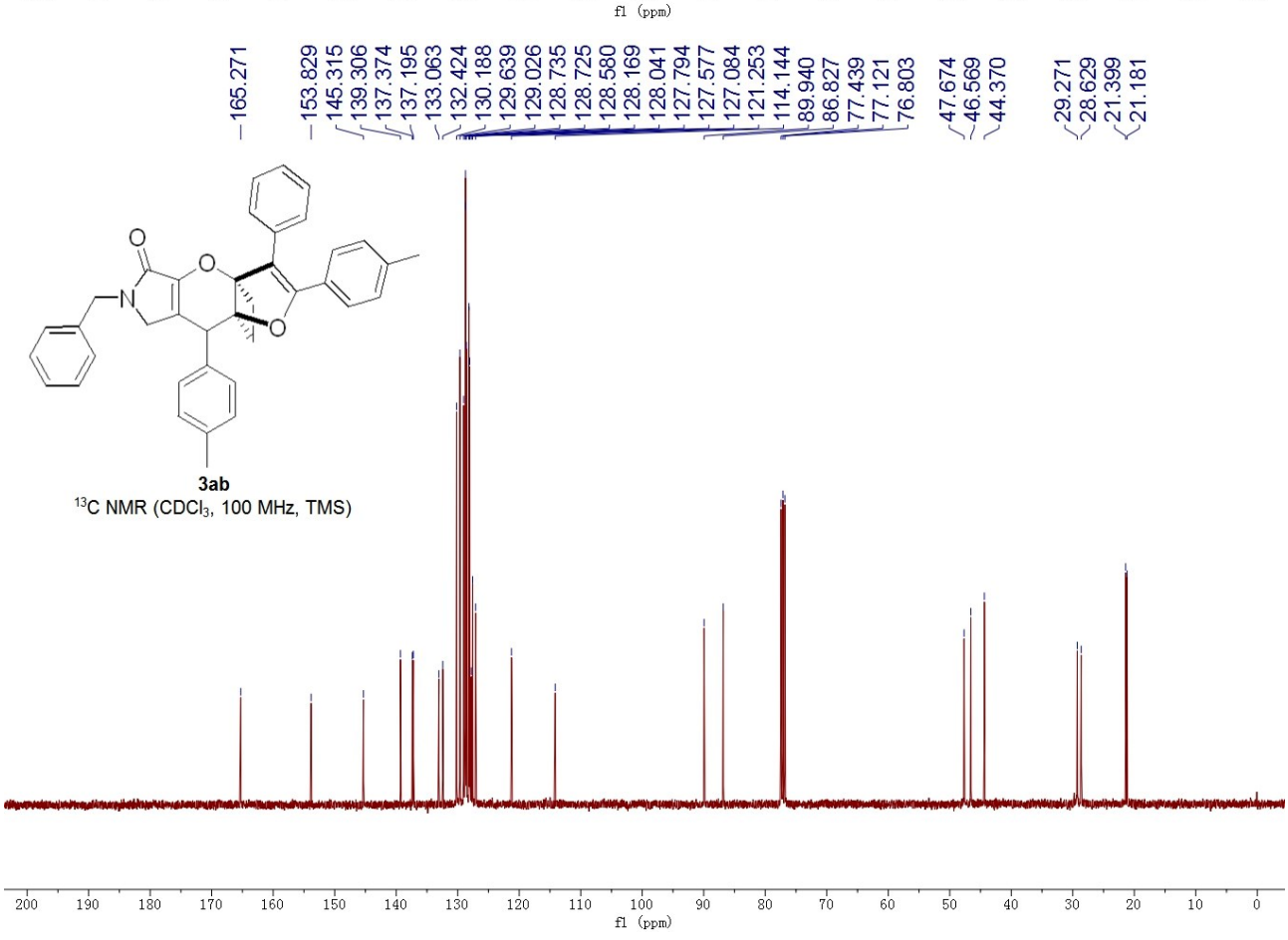
3ab

(3aS,8aS)-6-benzyl-3-phenyl-2,8-di-p-tolyl-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ab), the title compound was achieved as yellow solid, MP = 123-125 ^{o}C, 90.5 mg, 82% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.33-7.29 (m, 2H), 7.28-7.21 (m, 4H), 7.20-7.17 (m, 5H), 7.15-7.11 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.32 (d, *J* = 15.2 Hz, 1H), 4.06 (s, 1H), 3.63 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.45 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.53-2.36 (m, 3H), 2.43 (s, 3H), 2.27 (s, 3H), 2.24-2.18 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 153.8, 145.3, 139.3, 137.4, 137.2, 133.1, 132.4, 130.2, 129.6, 129.0, 128.73, 128.72, 128.6, 128.2, 128.0, 127.8, 127.6, 127.1, 121.3, 114.1, 89.9, 86.8, 47.7, 46.6, 44.4, 29.3, 28.6, 21.4, 21.2. IR (neat) ν 2925, 1694, 1513, 1452, 1353, 1249, 1175, 1118, 1002, 903, 824, 762, 725, 700 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{34}NO_3$: 552.2533, found: 552.2523.



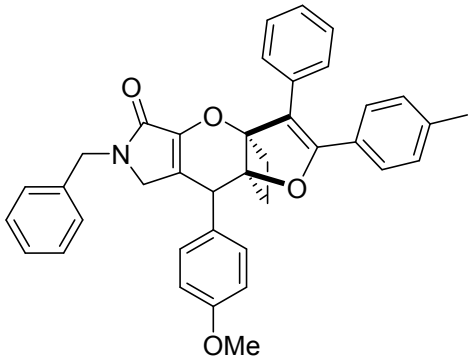
3ab

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



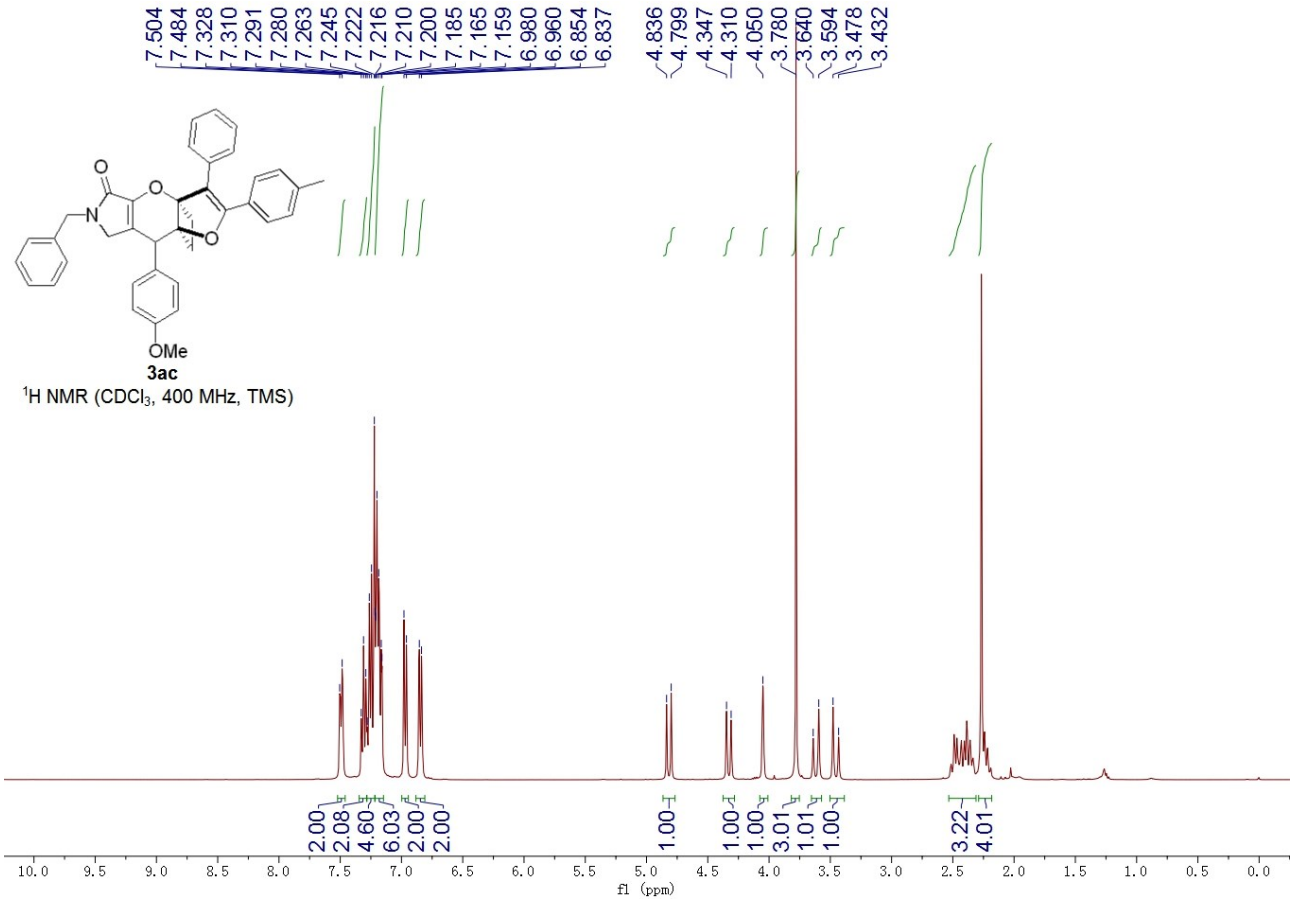
3ab

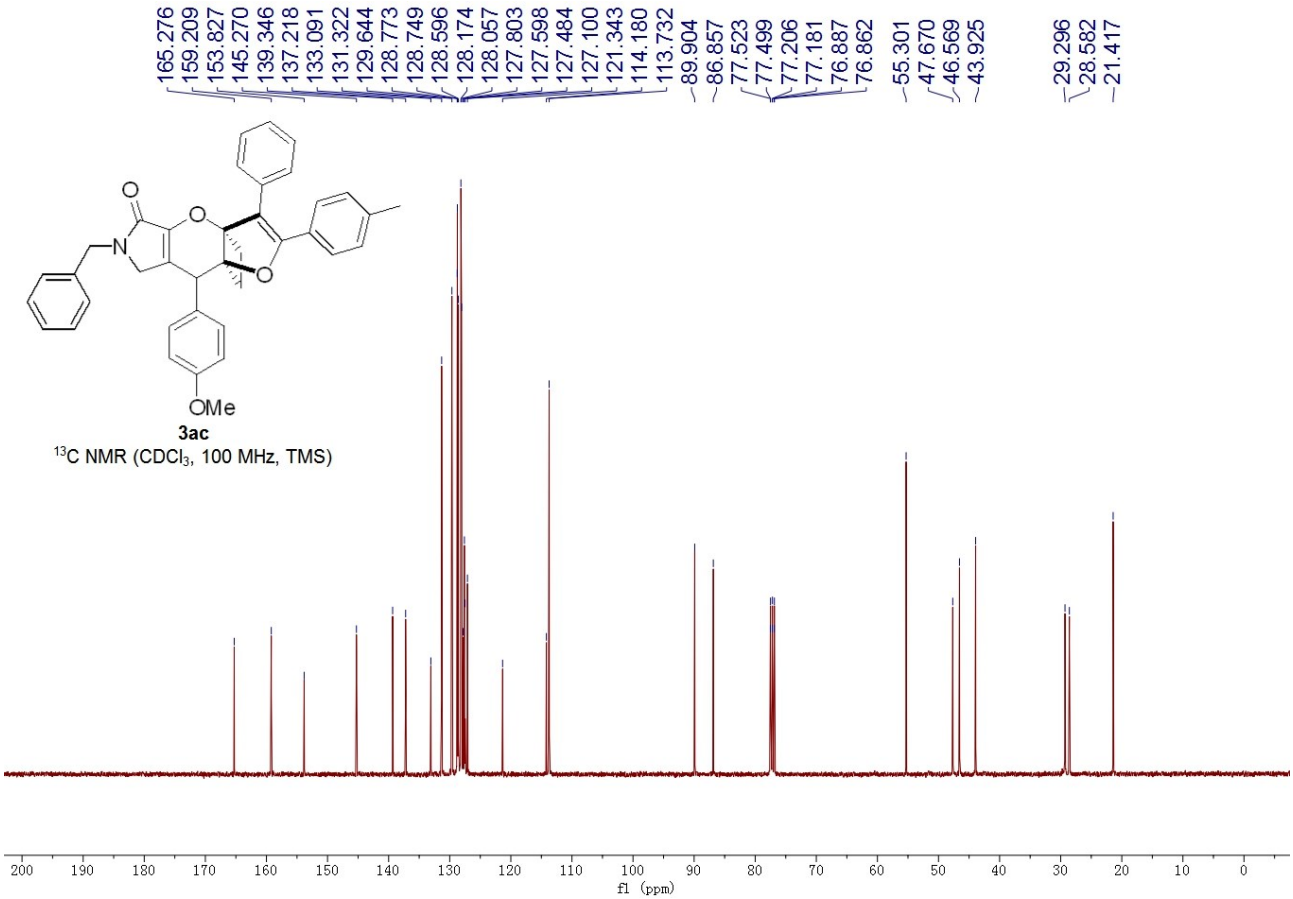
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

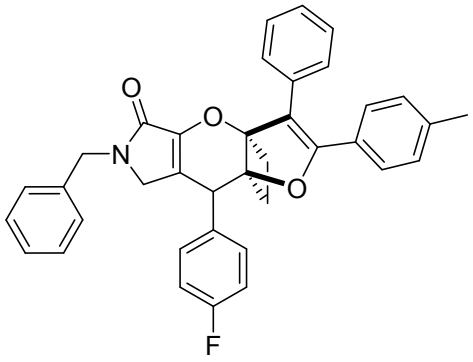


3ac

(3aS,8aS)-6-benzyl-8-(4-methoxyphenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ac), the title compound was achieved as yellow solid, MP = 117-119 ^{o}C, 102.7 mg, 89% yield. R*f* = 0.34 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.48 (m, 2H), 7.33-7.29 (m, 2H), 7.28-7.22 (m, 4H), 7.21-7.16 (m, 6H), 6.97 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 6.8 Hz, 2H), 4.82 (d, *J* = 14.8 Hz, 1H), 4.33 (d, *J* = 14.8 Hz, 1H), 4.05 (s, 1H), 3.78 (s, 3H), 3.62 (d, *J* = 18.4 Hz, 1H), 3.46 (d, *J* = 18.4 Hz, 1H), 2.51-2.34 (m, 3H), 2.27 (s, 3H), 2.24-2.19 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 159.2, 153.8, 145.3, 139.3, 137.2, 133.1, 131.3, 129.6, 128.8, 128.7, 128.6, 128.2, 128.1, 127.8, 127.6, 127.5, 127.1, 121.3, 114.2, 113.7, 89.9, 86.9, 55.3, 47.7, 46.6, 43.9, 29.3, 28.6, 21.4. IR (neat) ν 2917, 2849, 1695, 1495, 1453, 1250, 1175, 1120, 1073, 1007, 833, 765, 730, 700 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{34}NO_4$: 568.2482, found: 568.2485.

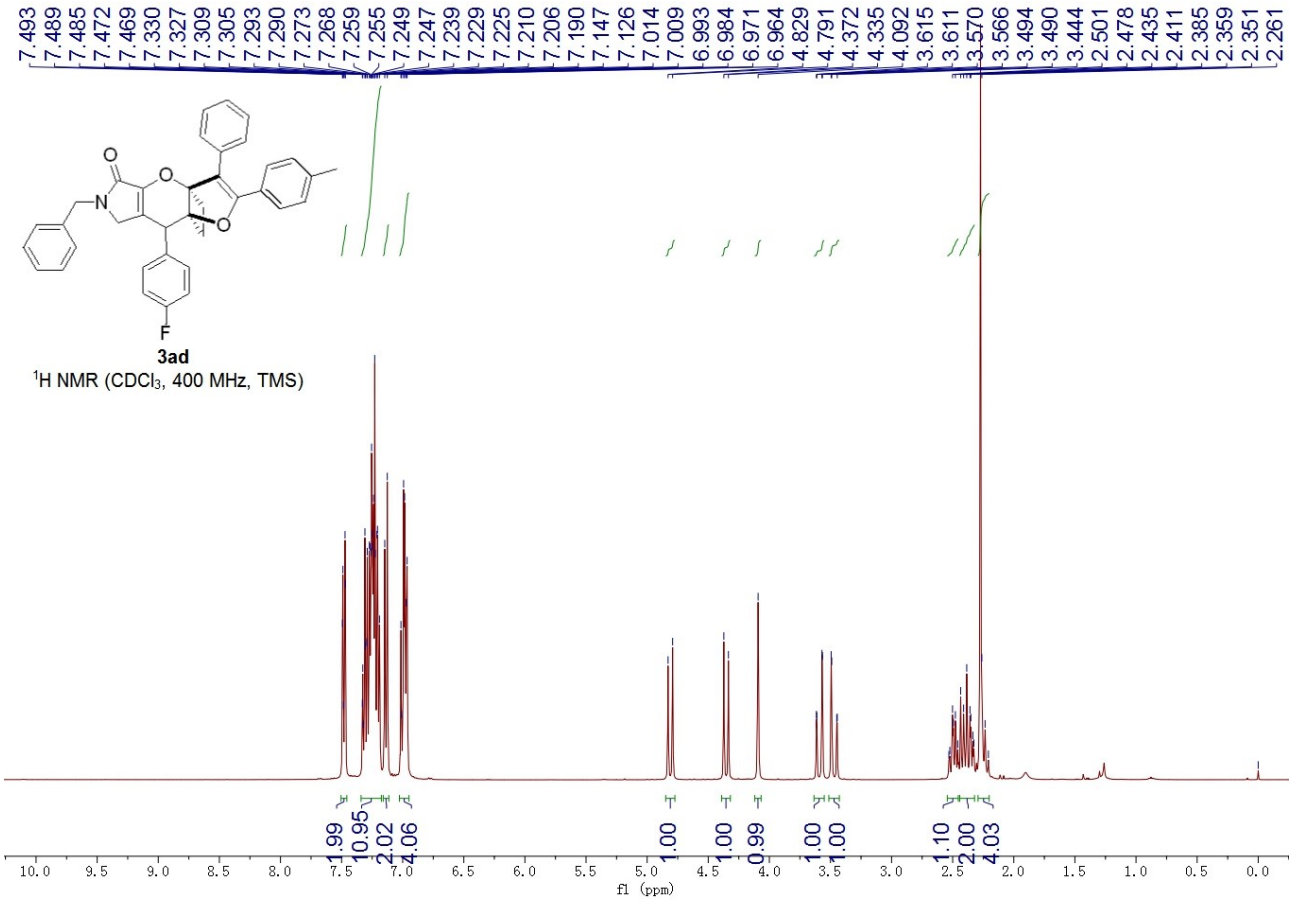

7.504
7.484
7.328
7.310
7.291
7.280
7.263
7.245
7.222
7.216
7.210
7.200
7.185
7.165
7.159
6.980
6.960
6.854
6.837
4.836
4.799
4.347
4.310
4.050
3.780
3.640
3.594
3.478
3.432
OMe
3ac
1H NMR (CDCl3, 400 MHz, TMS)
2.00
2.08
4.60
6.03
2.00
2.00
1.00
1.00
1.00
3.01
1.01
1.00
3.22
4.01
f1 (ppm)


165.276
159.209
153.827
145.270
139.346
137.218
133.091
131.322
129.644
128.773
128.749
128.596
128.174
128.057
127.803
127.598
127.484
127.100
121.343
114.180
113.732
89.904
86.857
77.523
77.499
77.206
77.181
76.887
76.862
55.301
47.670
46.569
43.925
29.296
28.582
21.417
OMe
3ac
13C NMR (CDCl3, 100 MHz, TMS)
f1 (ppm)



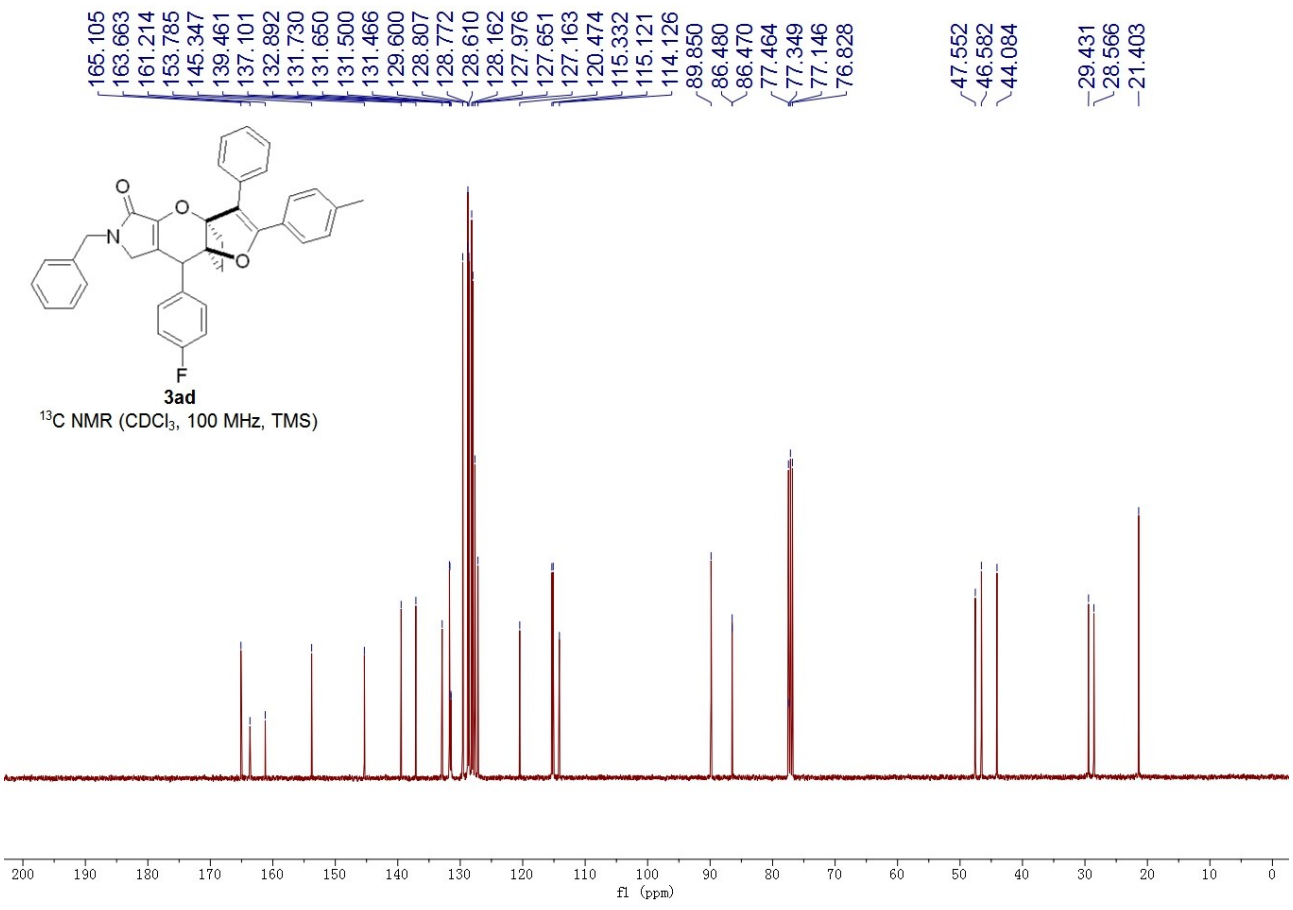
3ad

(3aS,8aS)-6-benzyl-8-(4-fluorophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ad), the title compound was achieved as yellow oil, 85.2 mg, 74% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.47 (m, 2H), 7.33-7.19 (m, 10H), 7.14 (d, *J* = 8.4 Hz, 2H), 7.01-6.96 (m, 4H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.35 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.59 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.47 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.53-2.46 (m, 1H), 2.44-2.33 (m, 2H), 2.27-2.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 162.4 (d, J_{CF} = 244.9 Hz), 153.8, 145.3, 139.5, 137.1, 132.9, 131.7 (d, J_{CF} = 8.0 Hz), 131.5 (d, J_{CF} = 3.4 Hz), 129.6, 128.8, 128.7, 128.6, 128.2, 128.0, 127.7, 127.2, 120.5, 115.2 (d, J_{CF} = 21.1 Hz), 114.1, 89.9, 86.5, 47.6, 46.6, 44.1, 29.4, 28.6, 21.4. ^{19}F NMR (376 MHz, $CFCl_3$) δ 114.7 (m, 1F). IR (neat) ν 2917, 1697, 1509, 1454, 1352, 1225, 1176, 1122, 1099, 1004, 826, 766, 702 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}NO_3F$: 556.2283, found: 556.2274.



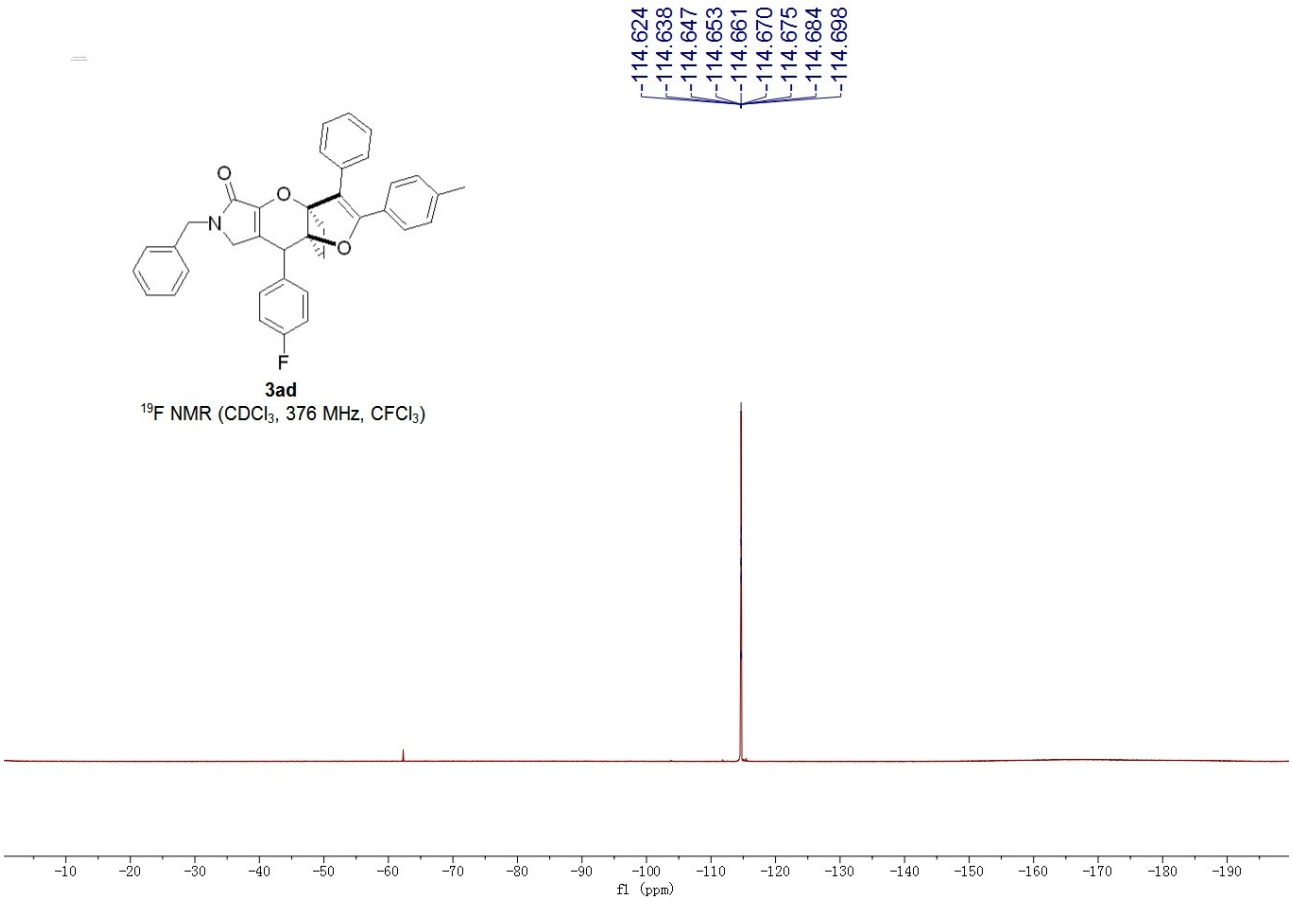
3ad

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



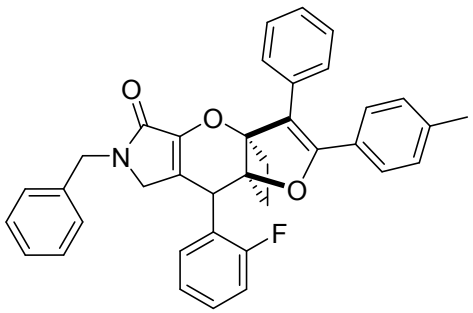
3ad

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



3ad

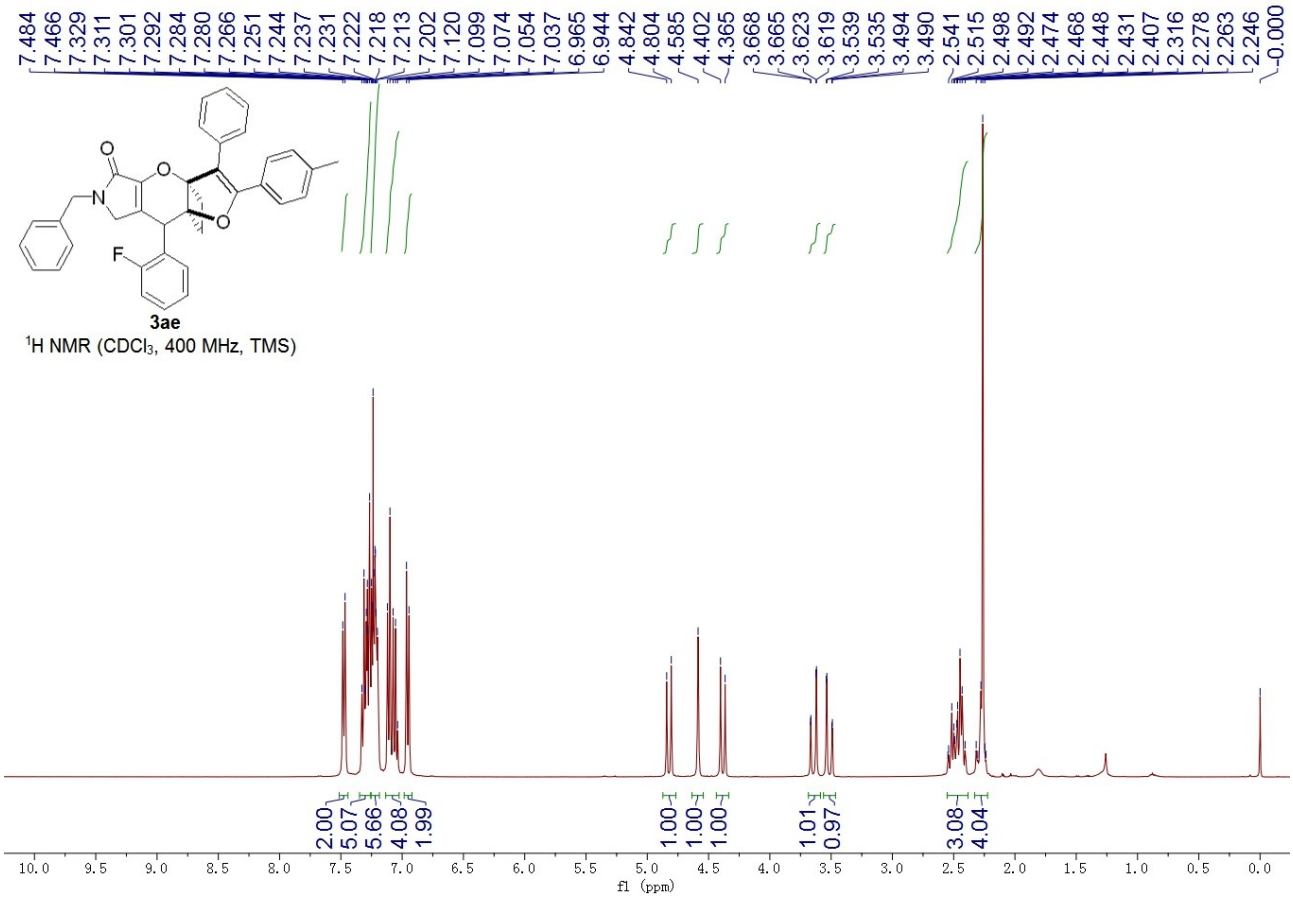
^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

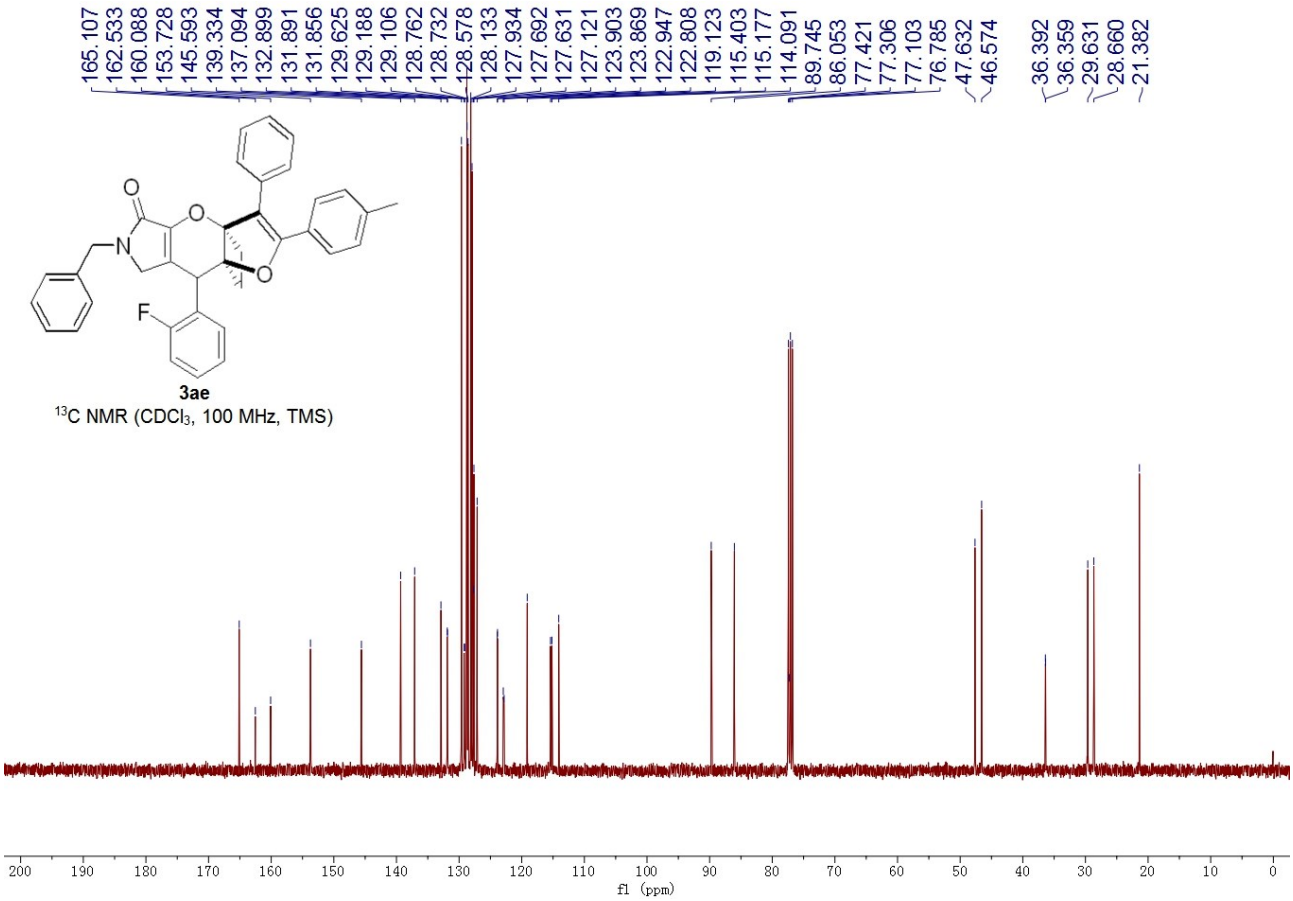


3ae

(3aS,8aS)-6-benzyl-8-(2-fluorophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ae), the title compound was achieved as brown oil, 65.5 mg, 45% yield. R*f* = 0.30 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.2 Hz, 2H), 7.33-7.27 (m, 5H), 7.25-7.20 (m, 5H), 7.12-7.04 (m, 4H), 6.95 (d, *J* = 8.4 Hz, 2H), 4.82 (d, *J* = 15.2 Hz, 1H), 4.59 (s, 1H), 4.38 (d, *J* = 15.2 Hz, 1H), 3.64 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.51 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.55-2.41 (m, 3H), 2.32-2.24 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 161.3 (d, J_{CF} = 244.5 Hz), 153.7, 145.6, 139.3, 137.1, 132.9, 131.9 (d, J_{CF} = 3.5 Hz), 129.6, 129.2 (d, J_{CF} = 8.2 Hz), 128.7 (d, J_{CF} = 4.0 Hz), 128.6, 128.1, 127.9,

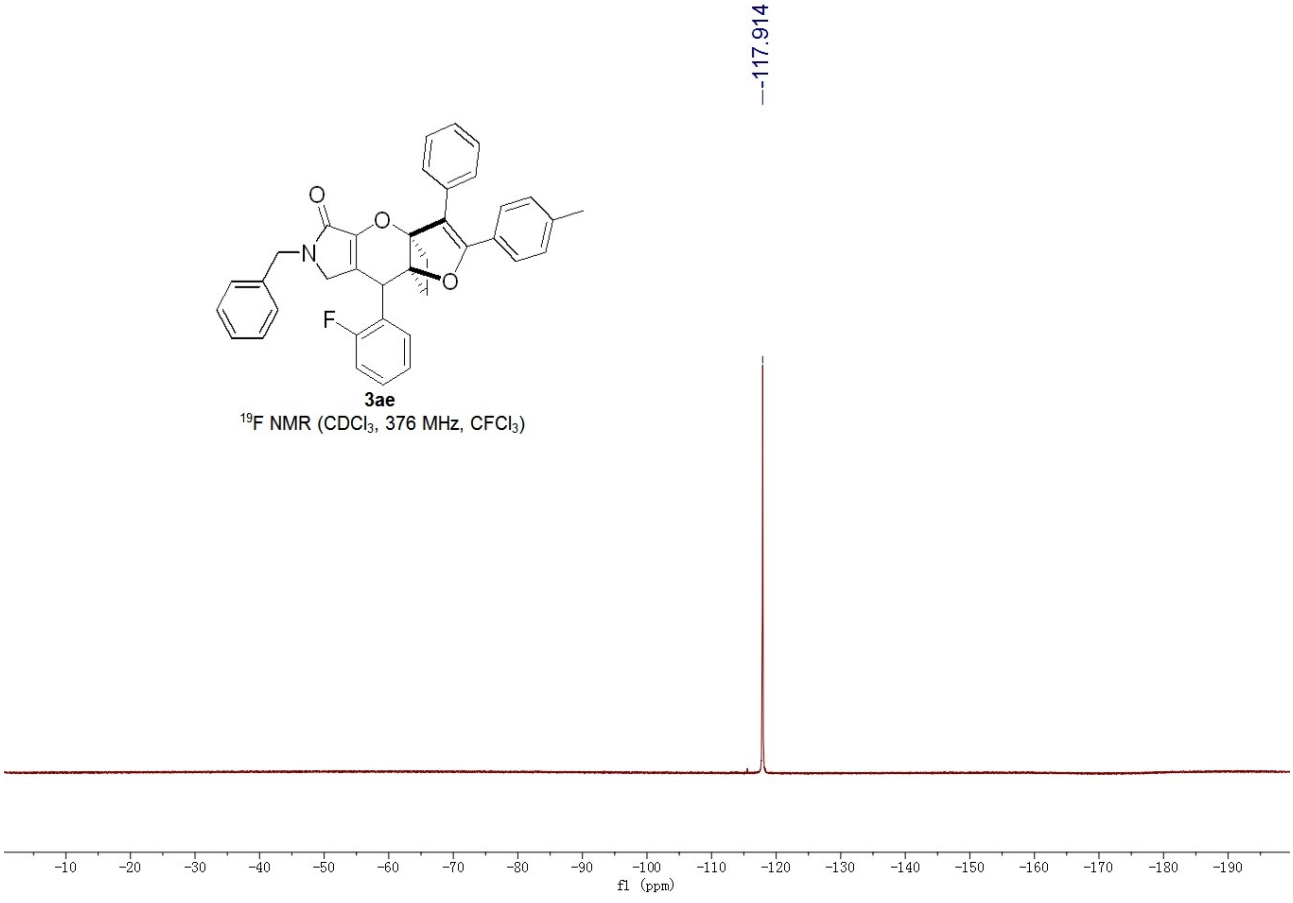
127.7, 127.6, 127.1, 123.9 (d, J_{CF} = 3.4 Hz), 122.9 (d, J_{CF} = 13.9 Hz), 119.1, 115.3 (d, J_{CF} = 22.6 Hz), 114.1, 89.7, 86.1, 47.6, 46.6, 36.4, 29.6, 28.7, 21.4. ^{19}F NMR (376 MHz, $CFCl_3$) δ 117.9 (s, 1F). IR (neat) ν 2925, 1702, 1515, 1491, 1454, 1355, 1231, 1179, 1004, 826, 761, 702 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}NO_3F$: 556.2283, found: 556.2288.





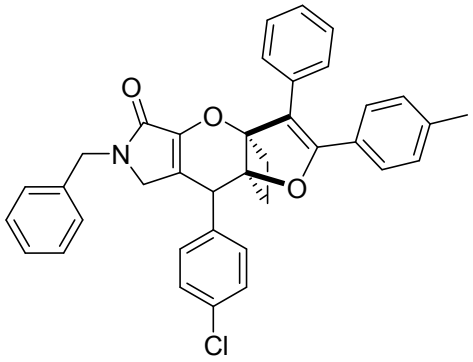
3ae

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



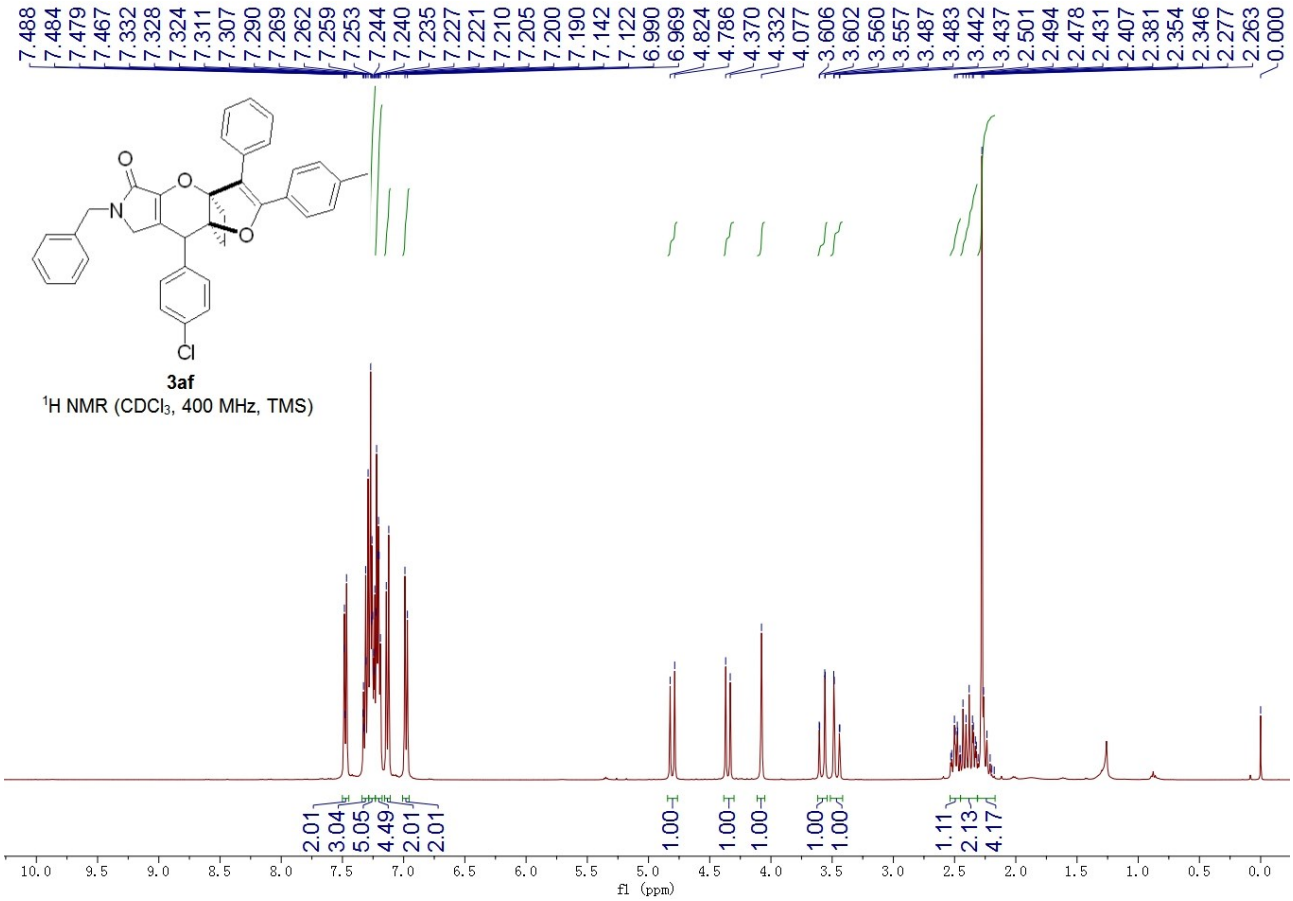
3ae

^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)



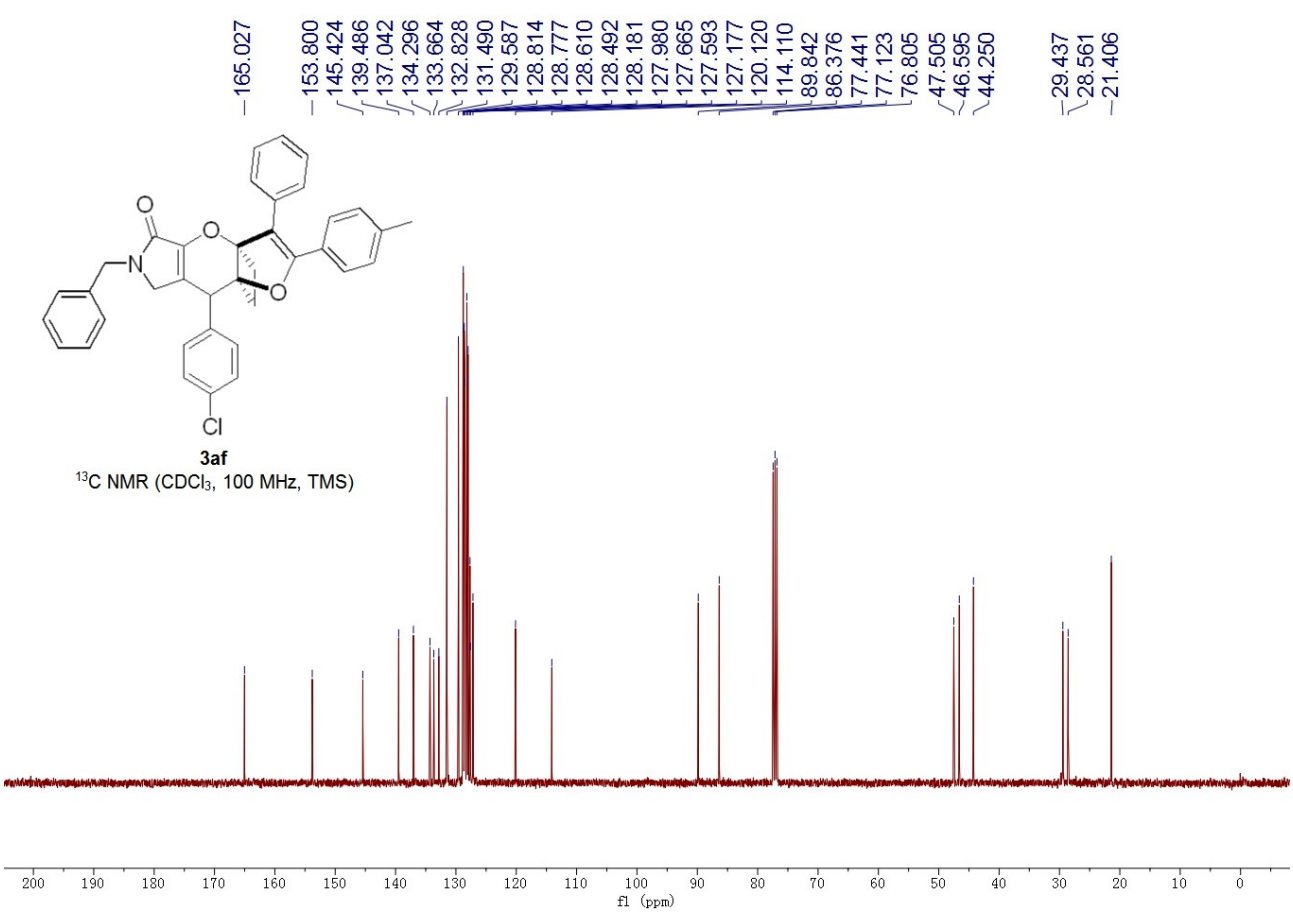
3af

(3aS,8aS)-6-benzyl-8-(4-chlorophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3af), the title compound was achieved as light yellow solid, MP = 134-136 ^{o}C, 75.3 mg, 60% yield. R*f* = 0.40 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.46 (m, 2H), 7.33-7.29 (m, 3H), 7.27-7.22 (m, 5H), 7.21-7.19 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.36 (d, *J* = 15.2 Hz, 1H), 4.08 (s, 1H), 3.51 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.46 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.54-2.46 (m, 1H), 2.41-2.31 (m, 2H), 2.28 (s, 3H), 2.27-2.21 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 153.8, 145.4, 139.5, 137.0, 134.3, 133.7, 132.8, 131.5, 129.6, 128.8, 128.6, 128.5, 128.2, 128.0, 127.7, 127.6, 127.2, 127.1, 120.1, 114.1, 89.8, 86.4, 47.5, 46.6, 44.3, 29.4, 28.5, 21.4. IR (neat) ν 2920, 1694, 1512, 1493, 1453, 1354, 1245, 1174, 1069, 1003, 897, 825, 767, 731, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}NO_3Cl$: 572.1987, found: 572.1971.



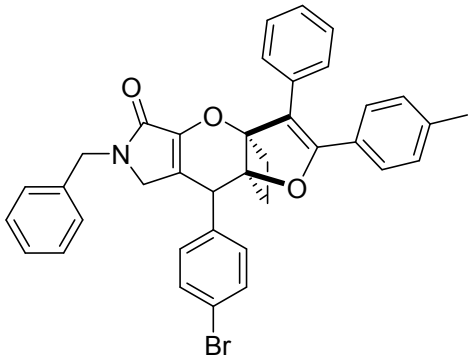
3af

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



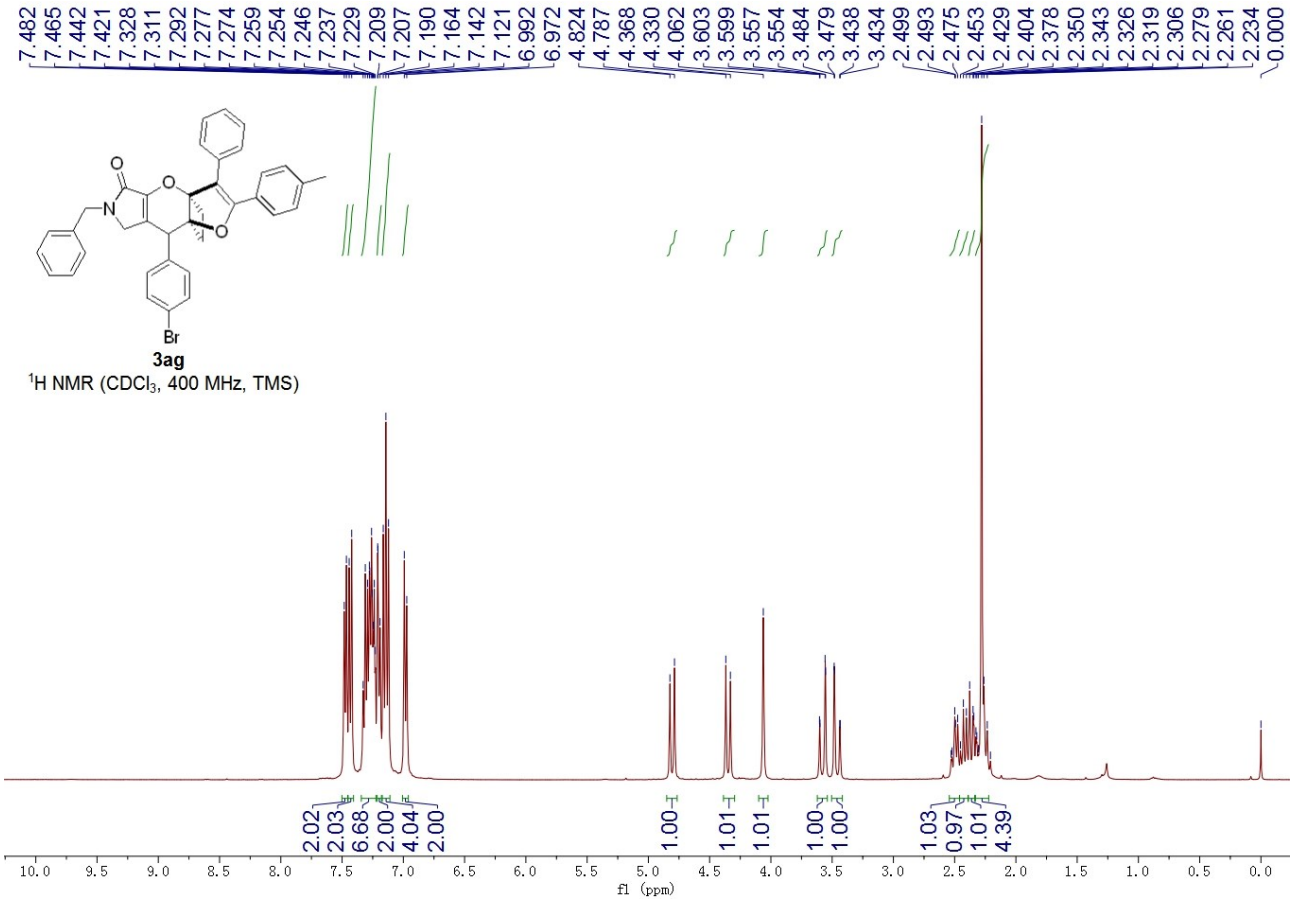
3af

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



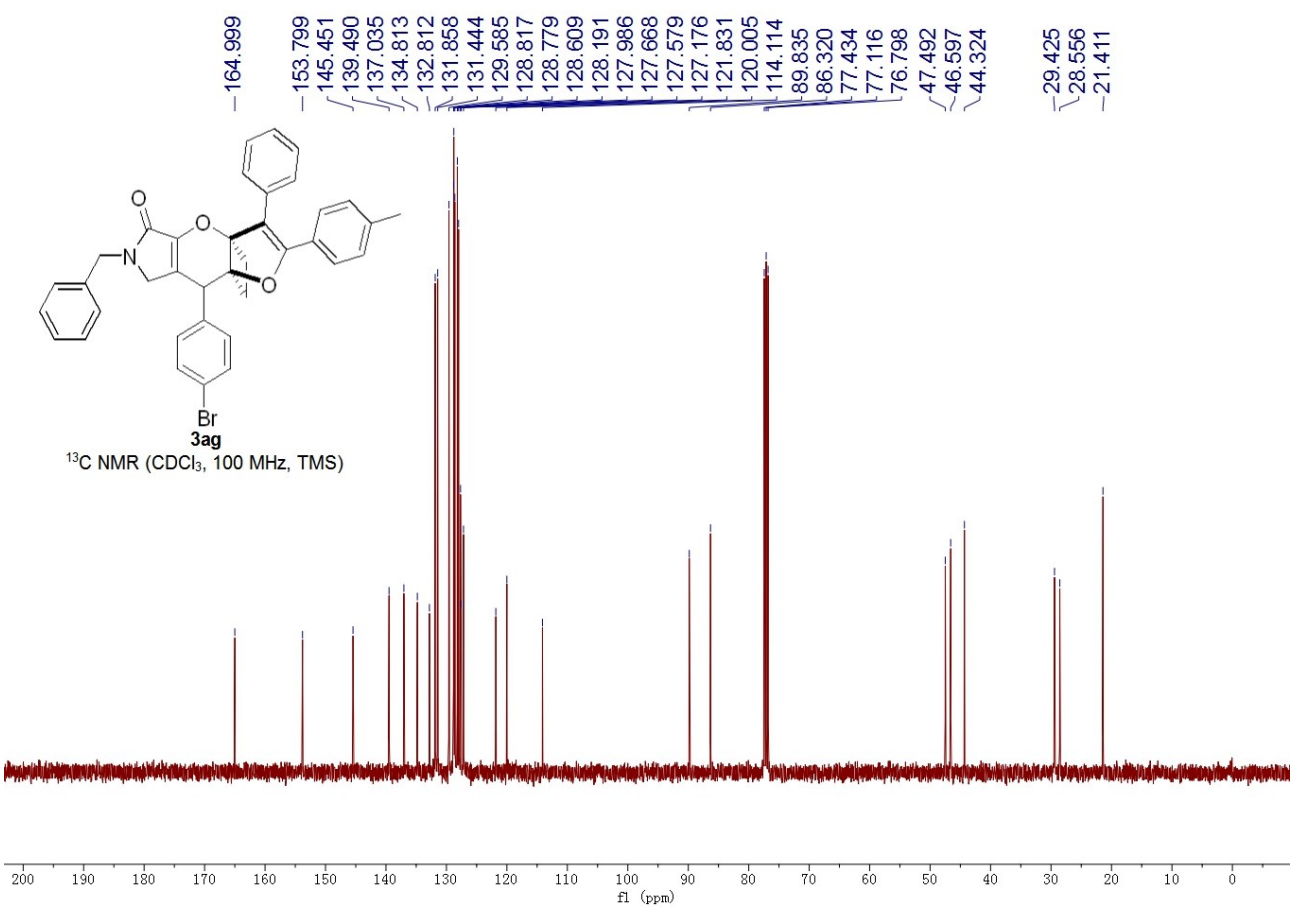
3ag

(3aS,8aS)-6-benzyl-8-(4-bromophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ag), the title compound was achieved as yellow solid, MP = 118-120 ^{o}C, 110.0 mg, 83% yield. R*f* = 0.40 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 6.8 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.33-7.23 (m, 6H), 7.21-7.19 (m, 2H), 7.14 (t, *J* = 8.8 Hz, 4H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 14.8 Hz, 1H), 4.35 (d, *J* = 15.2 Hz, 1H), 4.06 (s, 1H), 3.58 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.46 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.53-2.48 (m, 1H), 2.45-2.40 (m, 1H), 2.38-2.34 (m, 1H), 2.33-2.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 153.8, 145.5, 139.5, 137.0, 134.8, 132.8, 131.9, 131.4, 129.6, 128.8, 128.7, 128.6, 128.2, 128.0, 127.7, 127.6, 127.2, 121.8, 120.0, 114.1, 89.8, 86.3, 47.5, 46.6, 44.3, 29.4, 28.6, 21.4. IR (neat) ν 2920, 1694, 1597, 1495, 1453, 1251, 1176, 1006, 833, 766, 731, 699 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}NO_3Br$: 616.1482, found: 616.1479.



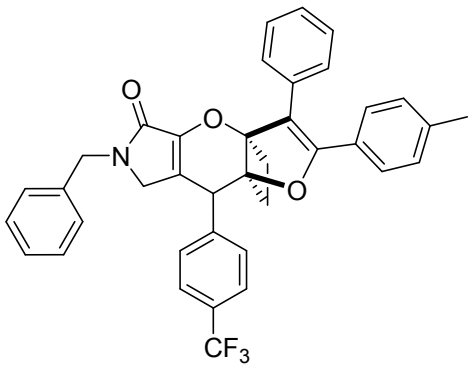
3ag

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)



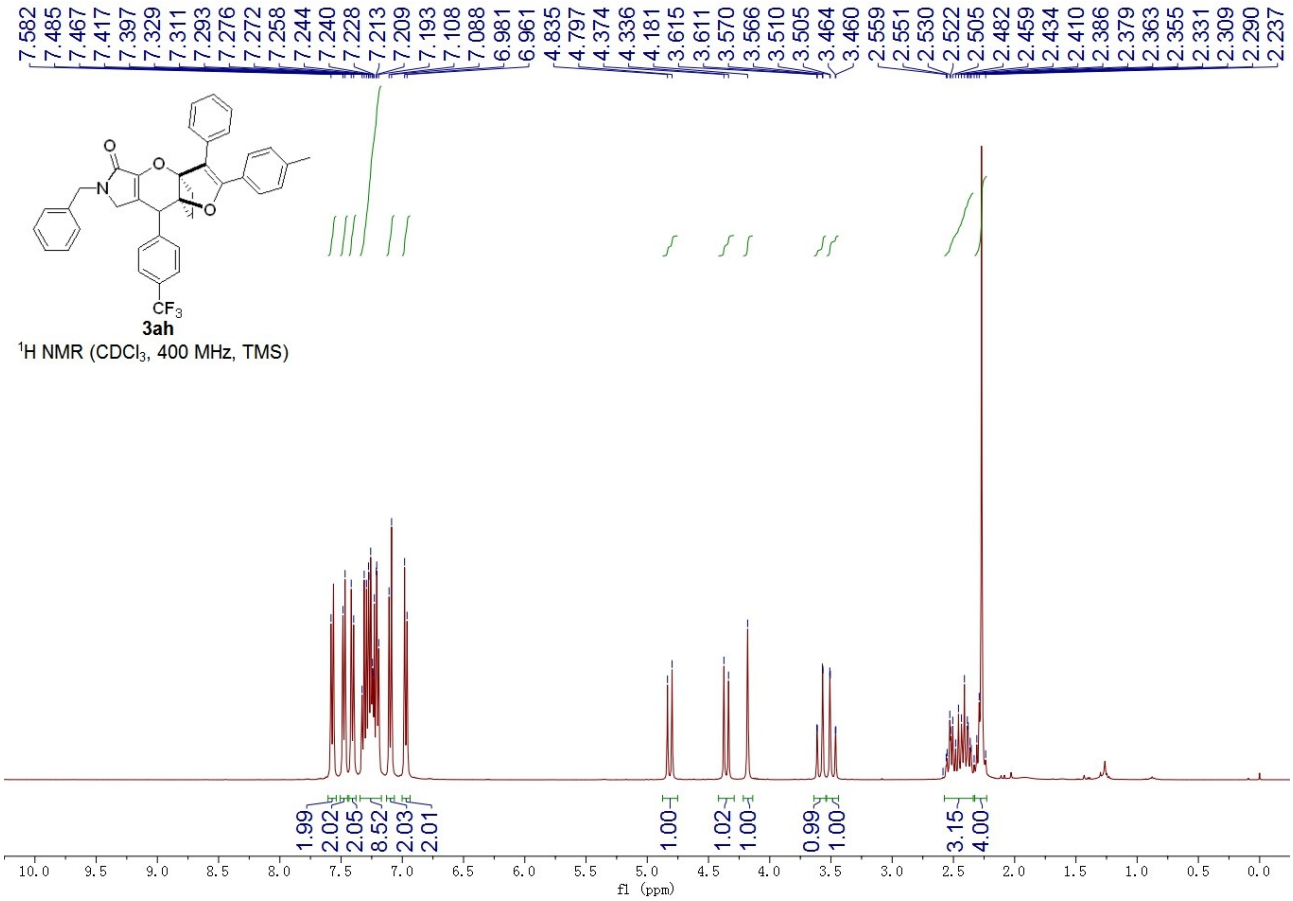
3ag

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)



3ah

(3aS,8aS)-6-benzyl-3-phenyl-2-(p-tolyl)-8-(4-(trifluoromethyl)phenyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ah), the title compound was achieved as brown soild, 111-113 ^{o}C, 100.0 mg, 81% yield. R*f* = 0.41 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.49-7.47 (m, 2H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33-7.19 (m, 8H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.87 (d, *J* = 15.2 Hz, 1H), 4.36 (d, *J* = 15.2 Hz, 1H), 4.18 (s, 1H), 3.59 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.48 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.56-2.36 (m, 3H), 2.33-2.24 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 153.9, 145.6, 140.1, 139.6, 137.0, 132.7, 130.5, 130.0 (q, J_{CF} = 32.2 Hz), 129.6, 128.9, 128.8, 128.6, 128.2, 127.9, 127.7, 127.5, 127.2, 125.3 (q, J_{CF} = 3.6 Hz), 124.2 (q, J_{CF} = 270.0 Hz), 119.7, 114.1, 89.9, 86.3, 47.5, 46.6, 44.8, 29.5, 28.7, 21.4. ^{19}F NMR (376 MHz, $CFCl_3$) δ 62.3 (s, 3F). IR (neat) ν 2910, 1699, 1587, 1497, 1453, 1278, 1153, 1007, 812, 765, 724, 701 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{31}NO_3F_3$: 606.2251, found: 606.2240.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7.272
7.258
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7.240
7.228
7.213
7.209
7.193
7.108
7.088
6.981
6.961
4.835
4.797
4.374
4.336
4.181
3.615
3.611
3.570
3.566
3.510
3.505
3.464
3.460
2.559
2.551
2.530
2.522
2.505
2.482
2.459
2.434
2.410
2.386
2.379
2.363
2.355
2.331
2.309
2.290
2.237
O
N
O
O
CF3
3ah
1H NMR (CDCl3, 400 MHz, TMS)
1.99
2.02
2.05
8.52
2.03
2.01
1.00
1.02
1.00
0.99
1.00
3.15
4.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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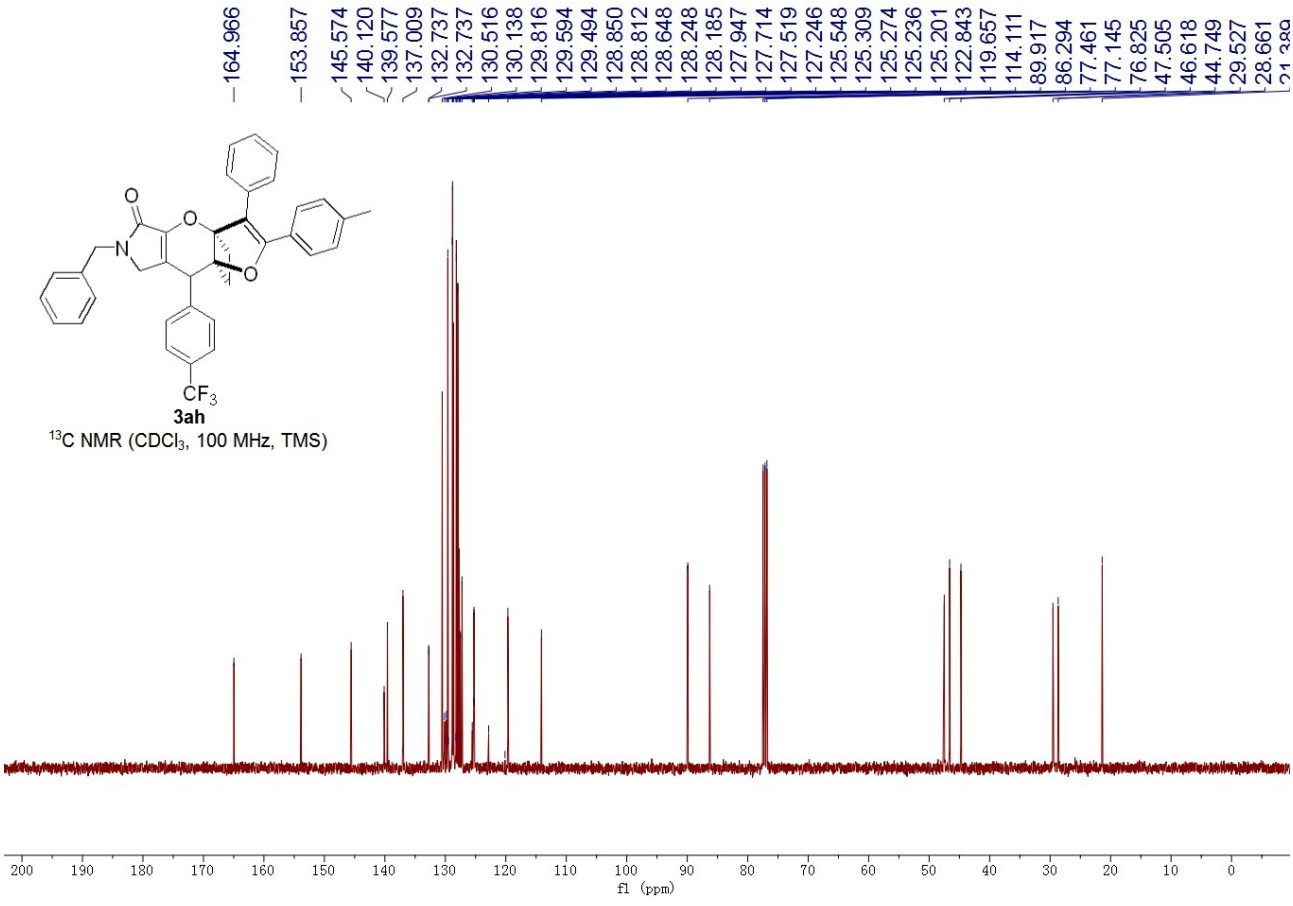
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.737
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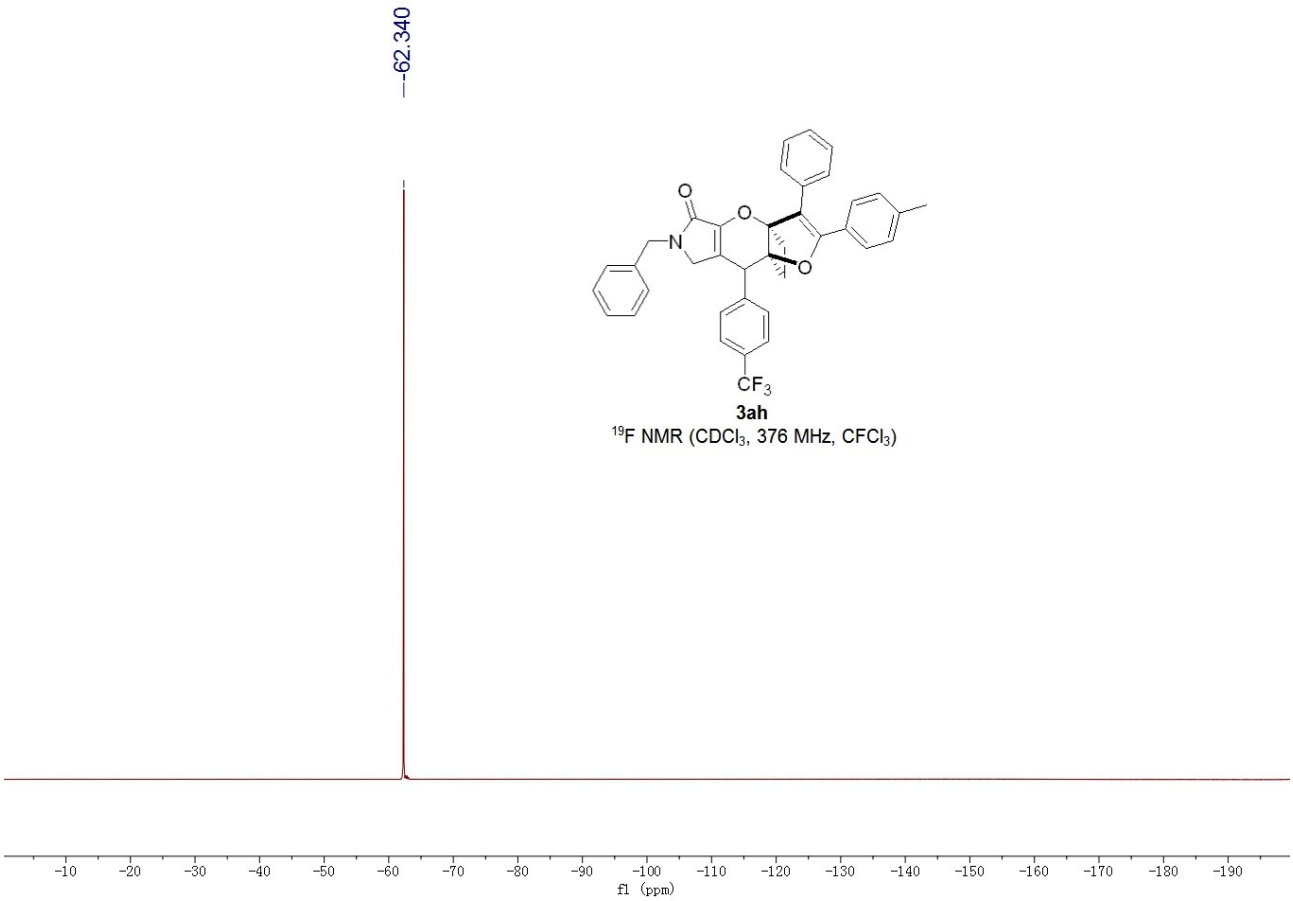
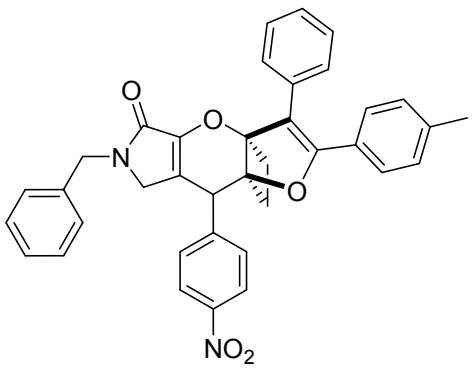
128.850
128.812
128.648
128.248
128.185
127.947
127.714
127.519
127.246
125.548
125.309
125.274
125.236
125.201
122.843
119.657
114.111
89.917
86.294
77.461
77.145
76.825
47.505
46.618
44.749
29.527
28.661
O
N
O
O
CF3
3ah
13C NMR (CDCl3, 100 MHz, TMS)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3ah

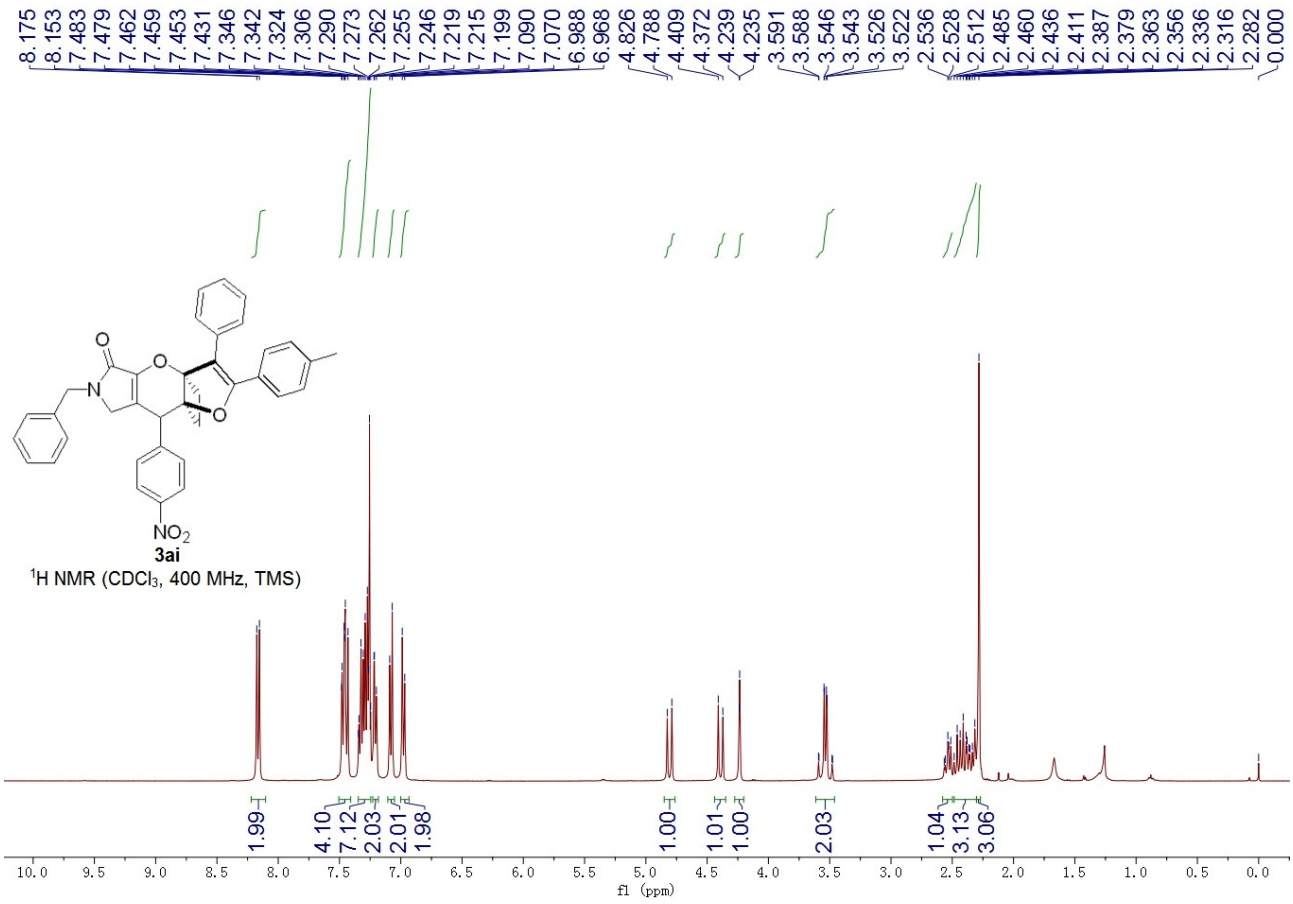
^{19}F NMR ($CDCl_3$, 376 MHz, $CFCl_3$)

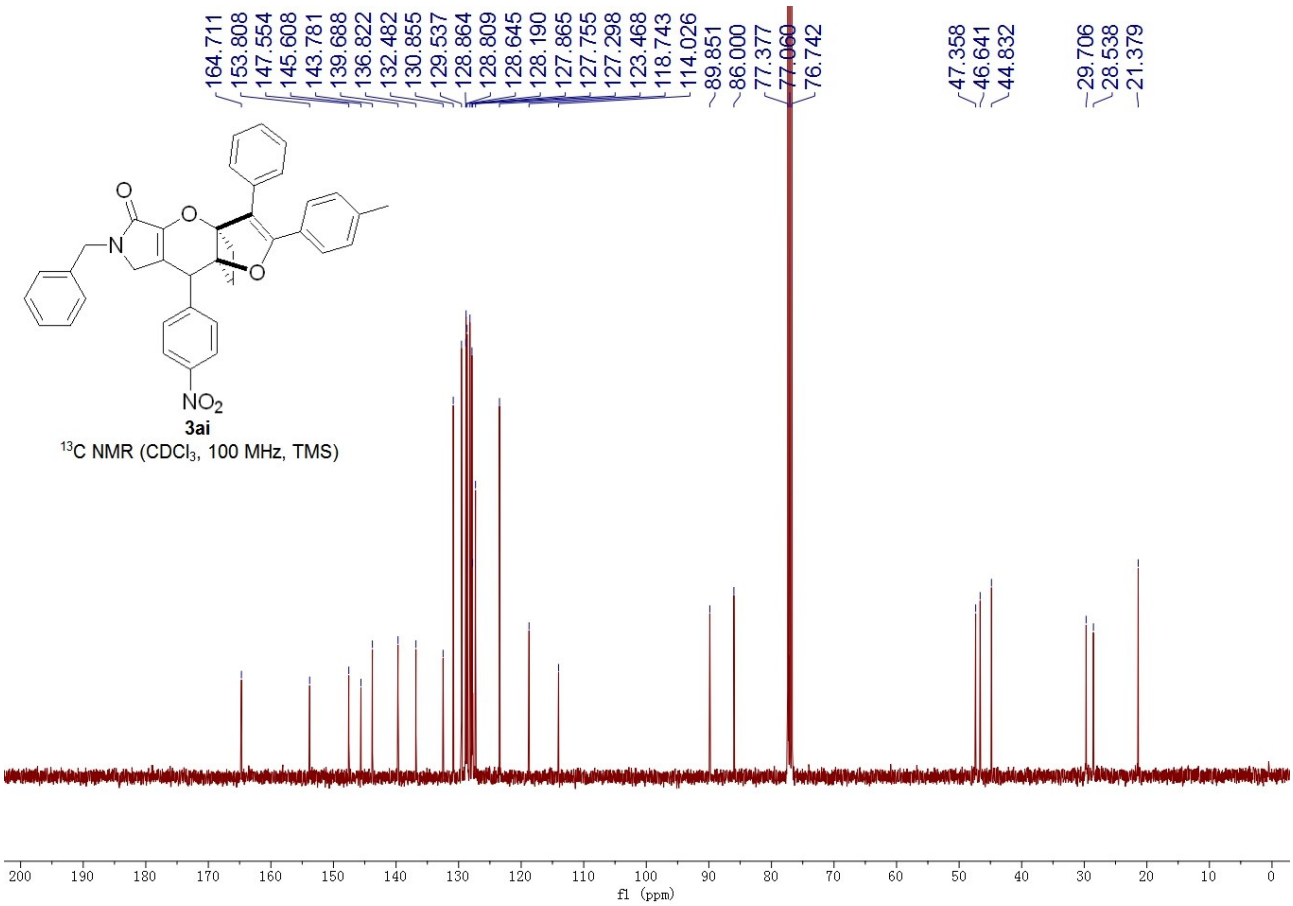


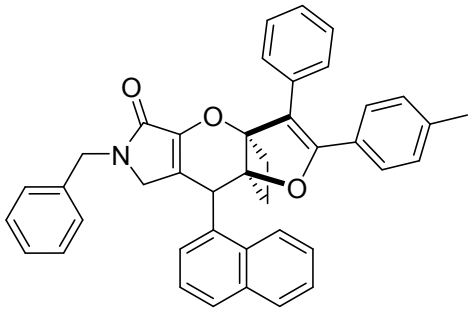
3ai

(3aS,8aS)-6-benzyl-8-(4-nitrophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ai), the title compound was achieved as brown solid, MP = 120-122 ^{o}C, 30.7 mg, 26% yield. R*f* = 0.33 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, *J* = 8.0 Hz, 2H), 7.48-7.43 (m, 4H), 7.35-7.25 (m, 6H), 7.22-7.20 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 15.2 Hz, 1H), 4.39 (d, *J* = 15.2 Hz, 1H), 4.24 (s, 1H), 3.57 (dd, *J* = 18.4, 1.2 Hz, 1H), 3.50 (d, *J* = 18.4, 1.2 Hz, 1H), 2.57-2.51 (m, 1H), 2.49-2.32 (m, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.7, 153.8, 147.6, 145.6, 143.8, 139.7, 136.8, 132.5, 130.9, 129.5, 128.9, 128.8, 128.6, 128.2, 127.9,

127.8, 127.3, 123.5, 118.7, 114.0, 89.9, 86.0, 47.4, 46.6, 44.8, 29.7, 28.5, 21.4. IR (neat) ν 2935, 1694, 1600, 1511, 1453, 1352, 1245, 1173, 1069, 994, 836, 768, 731, 700 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{31}N_2O_5$: 583.2228, found: 583.2227.



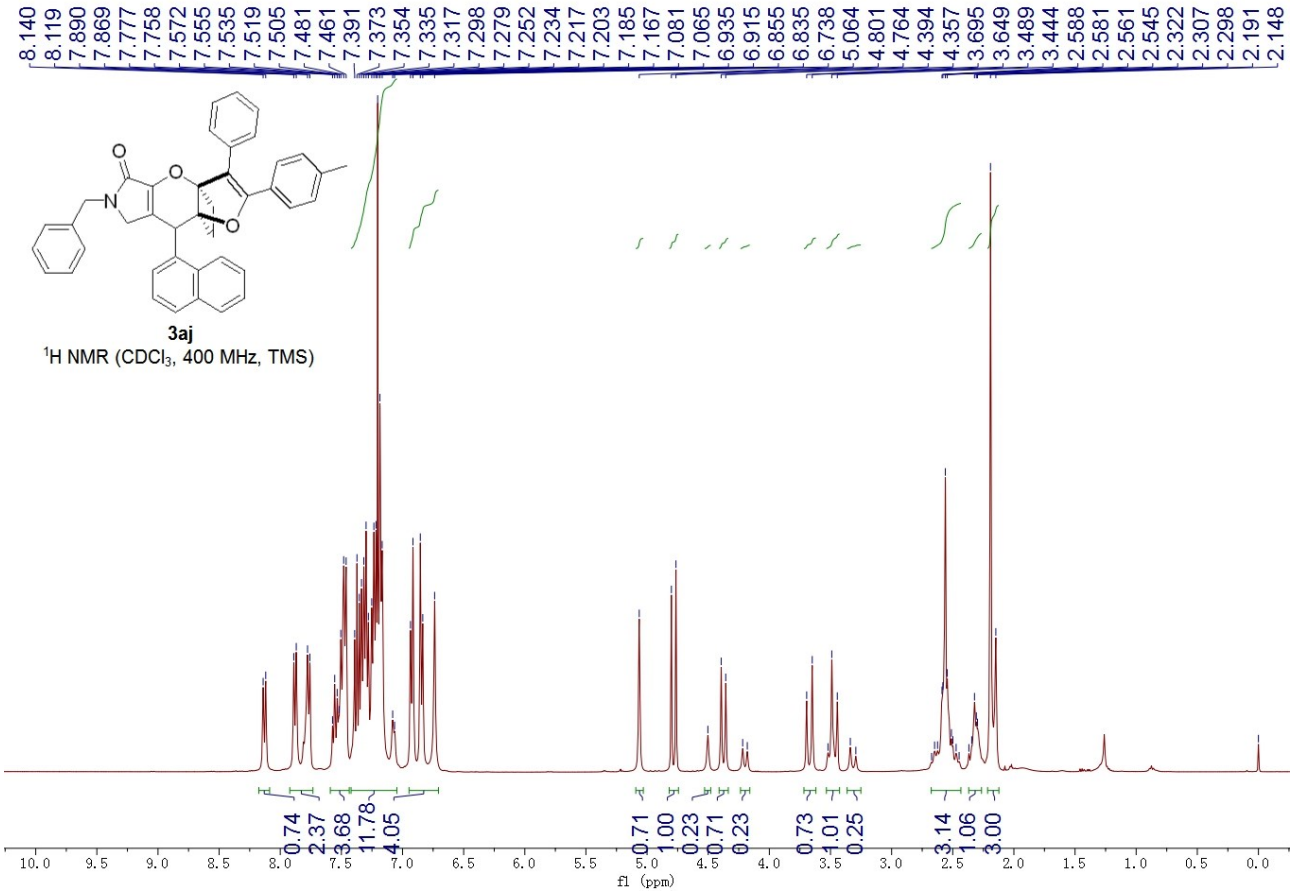


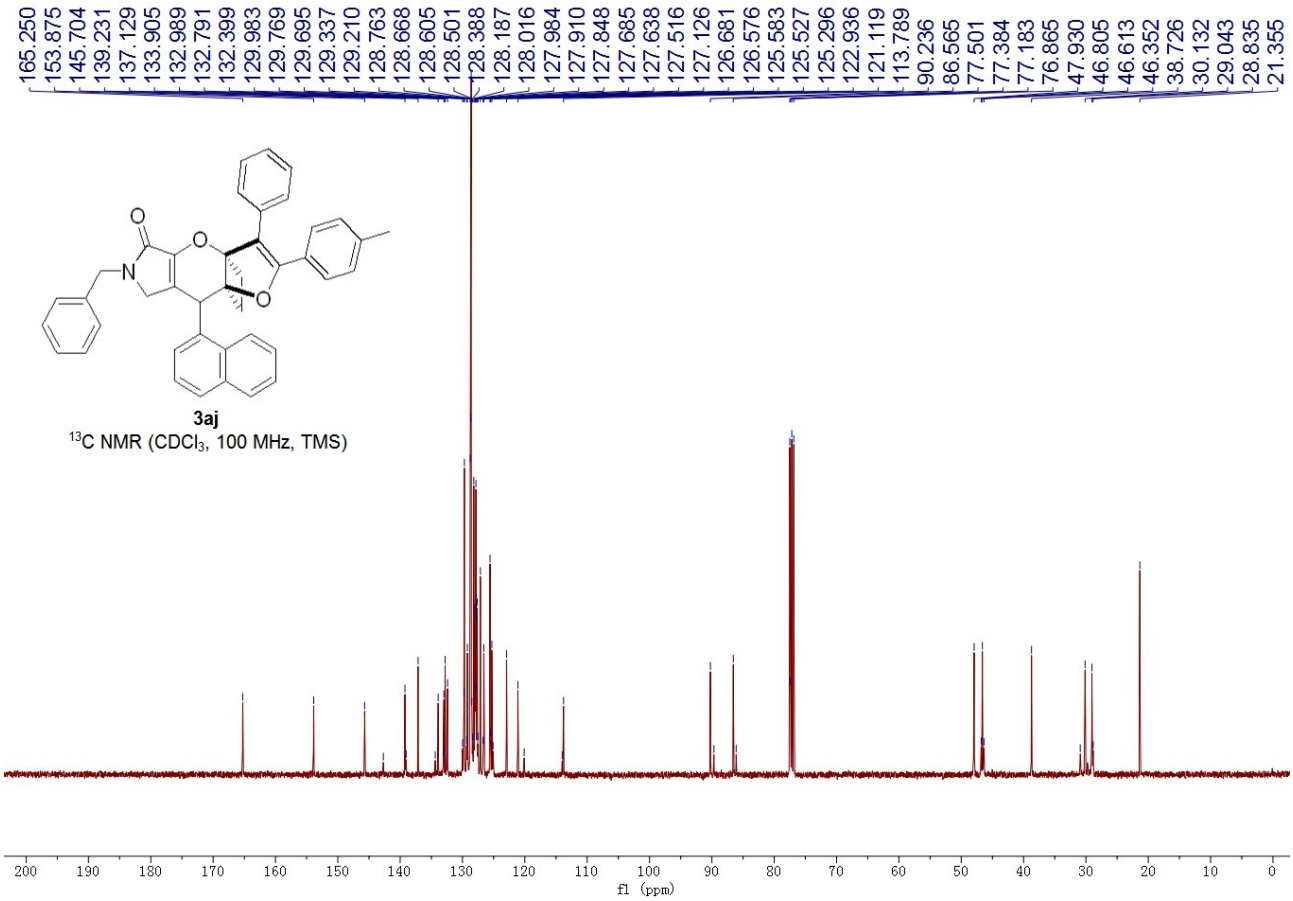


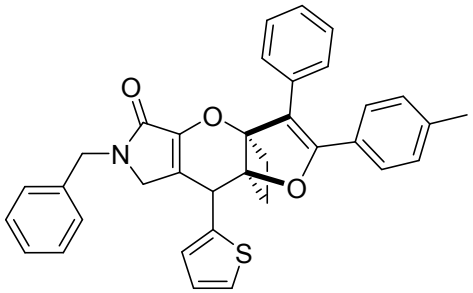
3aj

(3aS,8aS)-6-benzyl-8-(naphthalen-1-yl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3aj), the title compound was achieved as yellow solid, MP = 120-122 ^{o}C, 83.3 mg, 70% yield (**d.s. = 3:1**). R*f* = 0.35 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.4 Hz, 0.7H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.81-7.76 (m, 1.3H), 7.57-7.46 (m, 3.7H), 7.39-7.28 (m, 4H), 7.25-7.17 (m, 6H), 7.08-7.07 (m, 0.7H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.74 (s, 1H), 5.06 (s, 0.7H), 4.78 (d, *J* = 14.8 Hz, 1H), 4.50 (s, 0.3H), 4.38 (d, *J* = 14.8 Hz, 0.7H), 4.20 (d, *J* = 14.8 Hz, 0.3H), 3.67 (d, *J* = 18.4 Hz, 0.7H), 3.52-3.44 (m, 1H), 3.32 (d, *J* = 18.4 Hz, 0.3H), 2.67-2.45 (m, 3H), 2.37-2.30 (m,

1H), 2.19 (s, 2.3H), 2.15 (s, 0.7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 153.9, 145.7, 139.2, 137.1, 133.9, 133.0, 132.8, 132.4, 130.0, 129.8, 129.7, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.2, 128.0, 127.98, 127.91, 127.8, 127.7, 127.6, 127.5, 127.1, 126.7, 126.6, 125.6, 125.5, 125.3, 122.9, 121.1, 113.8, 90.2, 86.6, 47.9, 46.8, 46.6, 46.4, 38.7, 30.1, 29.0, 28.8, 21.4. IR (neat) ν 2936, 1694, 1600, 1511, 1453, 1352, 1245, 1173, 1030, 994, 836, 768, 731, 700 cm^{-1}. HRMS (ESI) calcd for $C_{41}H_{34}NO_3$: 588.2533, found: 588.2529.



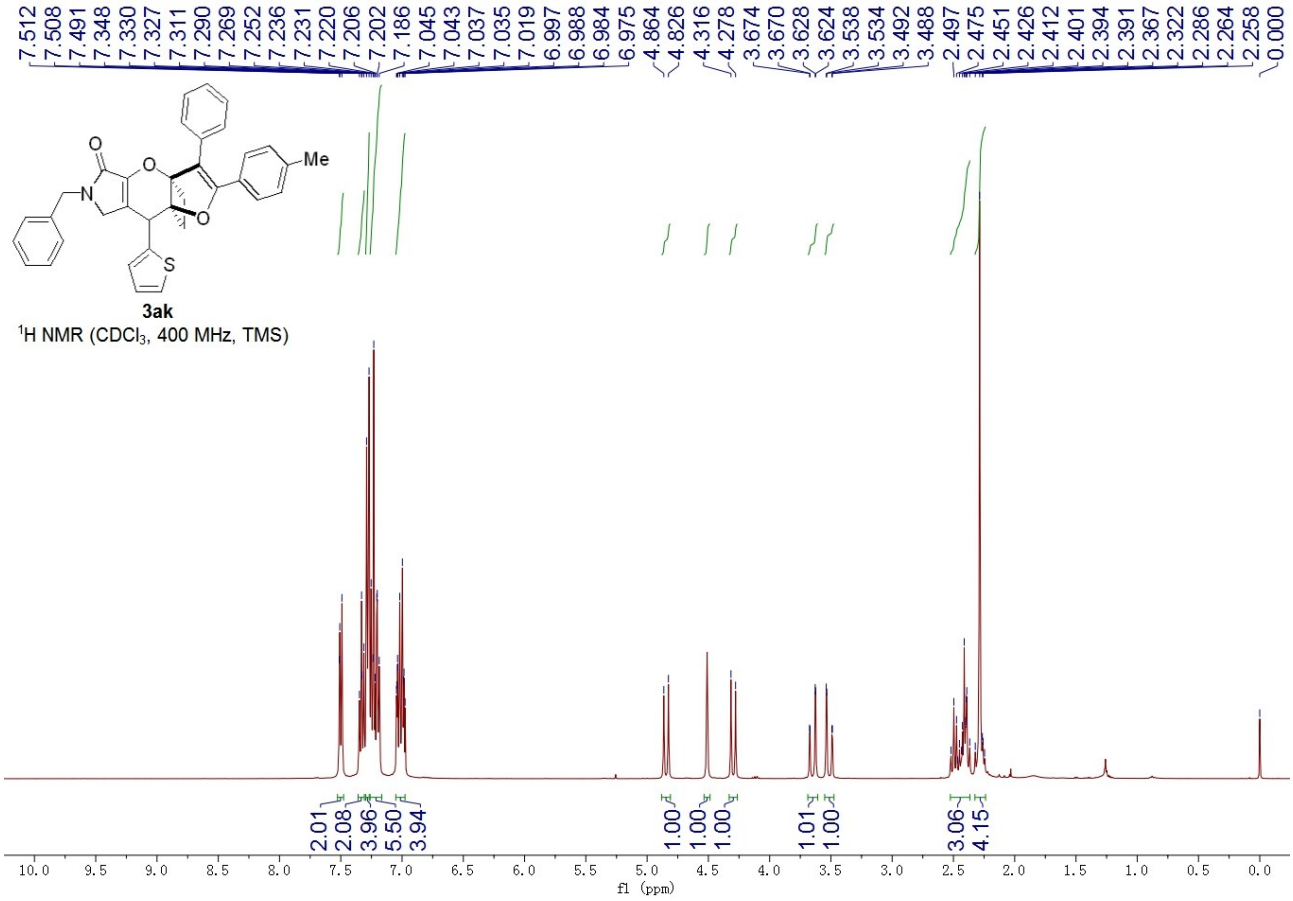


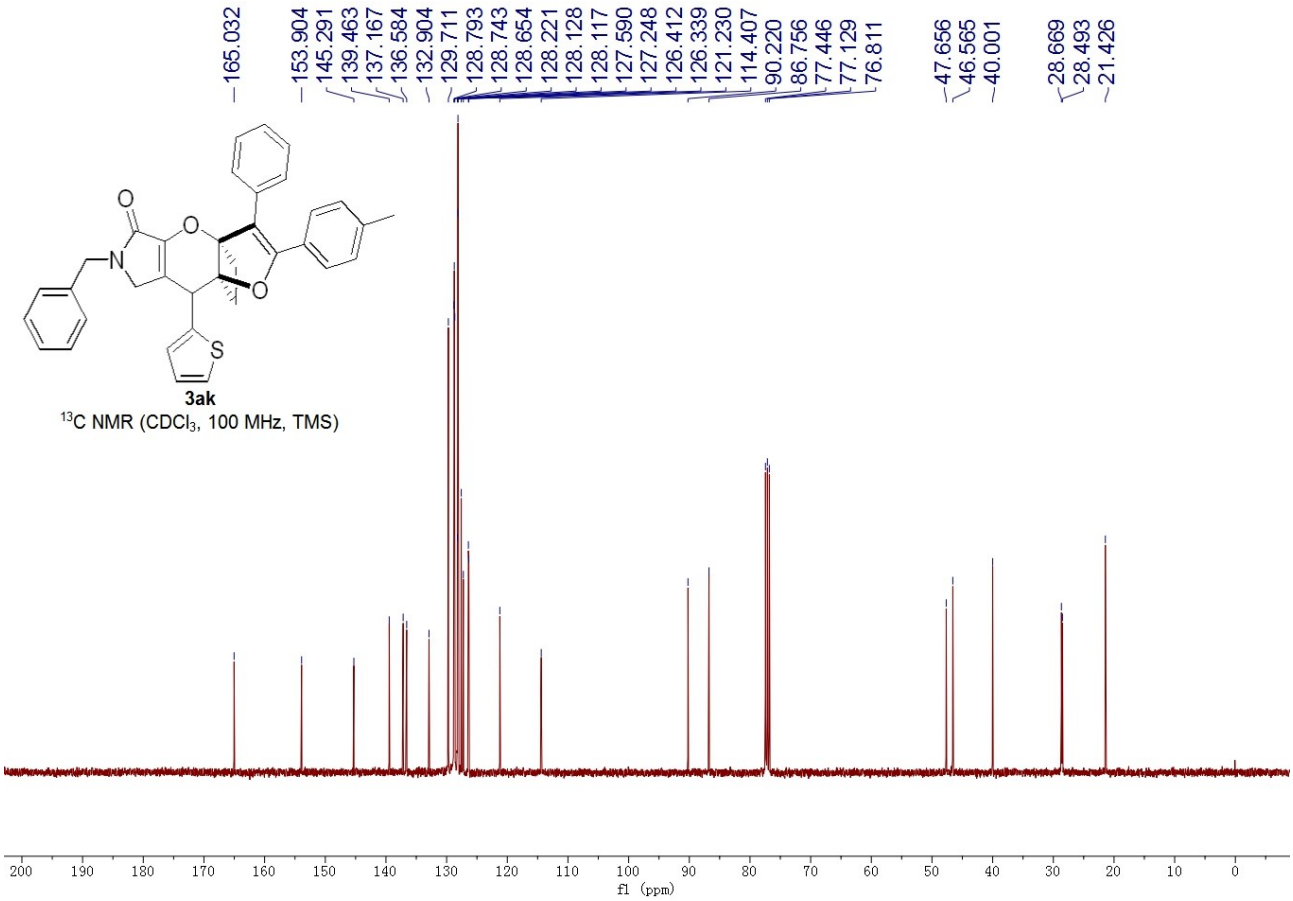


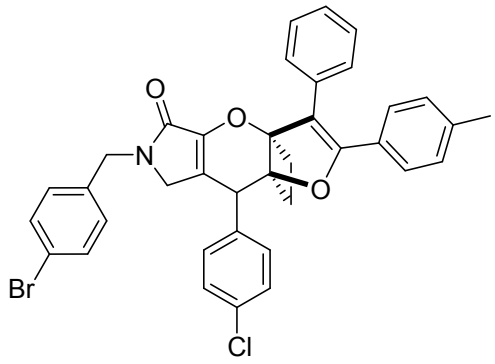
3ak

(3aS,8aS)-6-benzyl-3-phenyl-8-(thiophen-2-yl)-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3ak), the title compound was achieved as yellow solid, MP = 106-108 ^{o}C, 86.4 mg, 65% yield. R*f* = 0.38 (Petroleum Ether:Ethyl Acetate = 3:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.49 (m, 2H), 7.35-7.31 (m, 2H), 7.29-7.27 (m, 4H), 7.25-7.19 (m, 5H), 7.05-6.98 (m, 4H), 4.84 (d, *J* = 15.2 Hz, 1H), 4.51 (s, 1H), 4.30 (d, *J* = 15.2 Hz, 1H), 3.65 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.51 (dd, *J* = 18.4, 1.6 Hz, 1H), 2.52-2.37 (m, 3H), 2.32-2.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 153.9, 145.3, 139.5, 137.2, 136.6, 132.9, 129.7, 128.8, 128.7, 128.6, 128.2, 128.1, 127.6, 127.2, 126.4, 126.3, 121.2, 114.4, 90.2, 86.8, 47.7, 46.6,

40.0, 28.7, 28.5, 21.4. IR (neat) ν 2920, 1691, 1511, 1451, 1352, 1255, 1174, 1109, 1007, 827, 767, 699 cm^{-1}. HRMS (ESI) calcd for $C_{35}H_{30}NO_3S$: 544.1941, found: 544.1934.



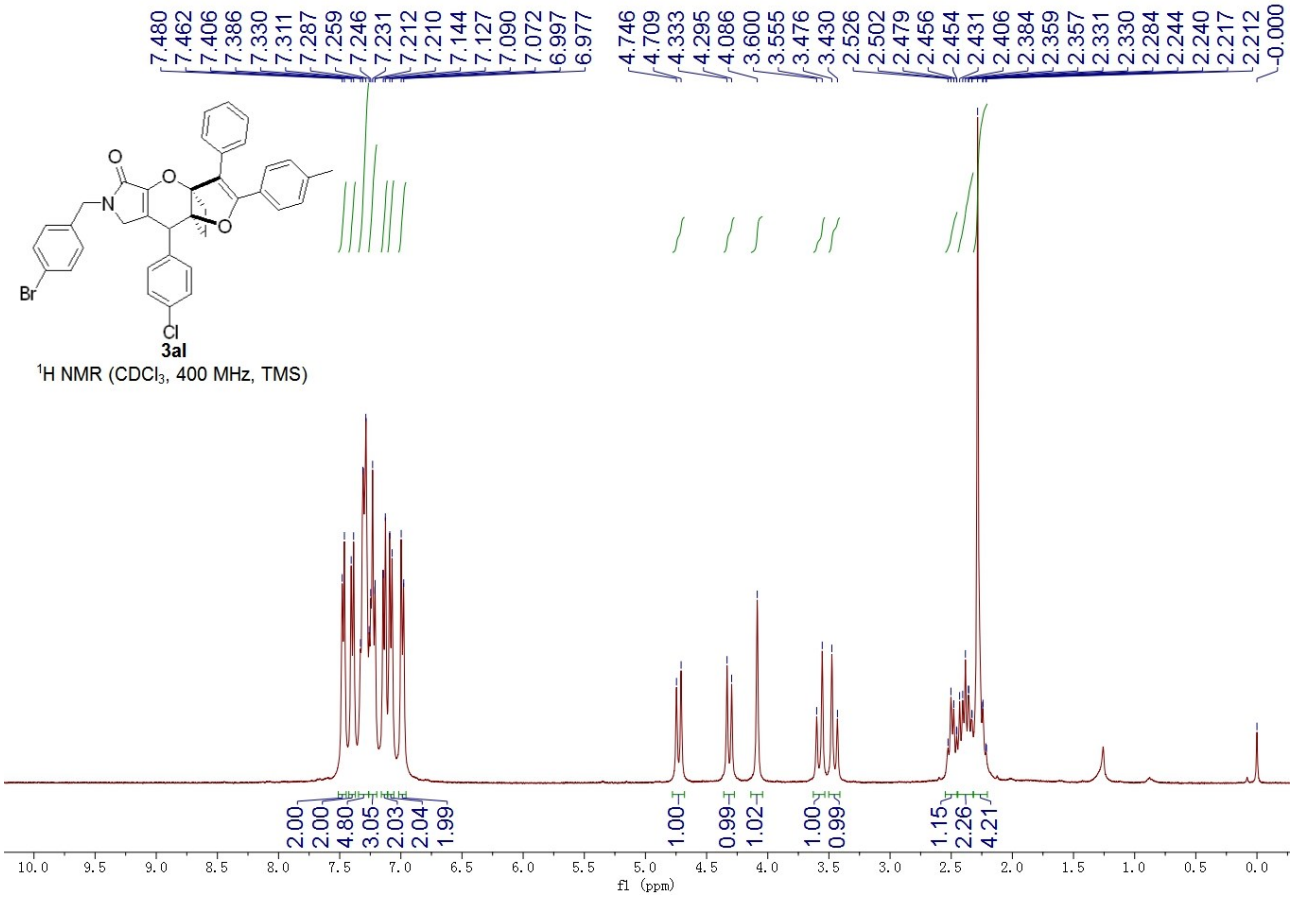


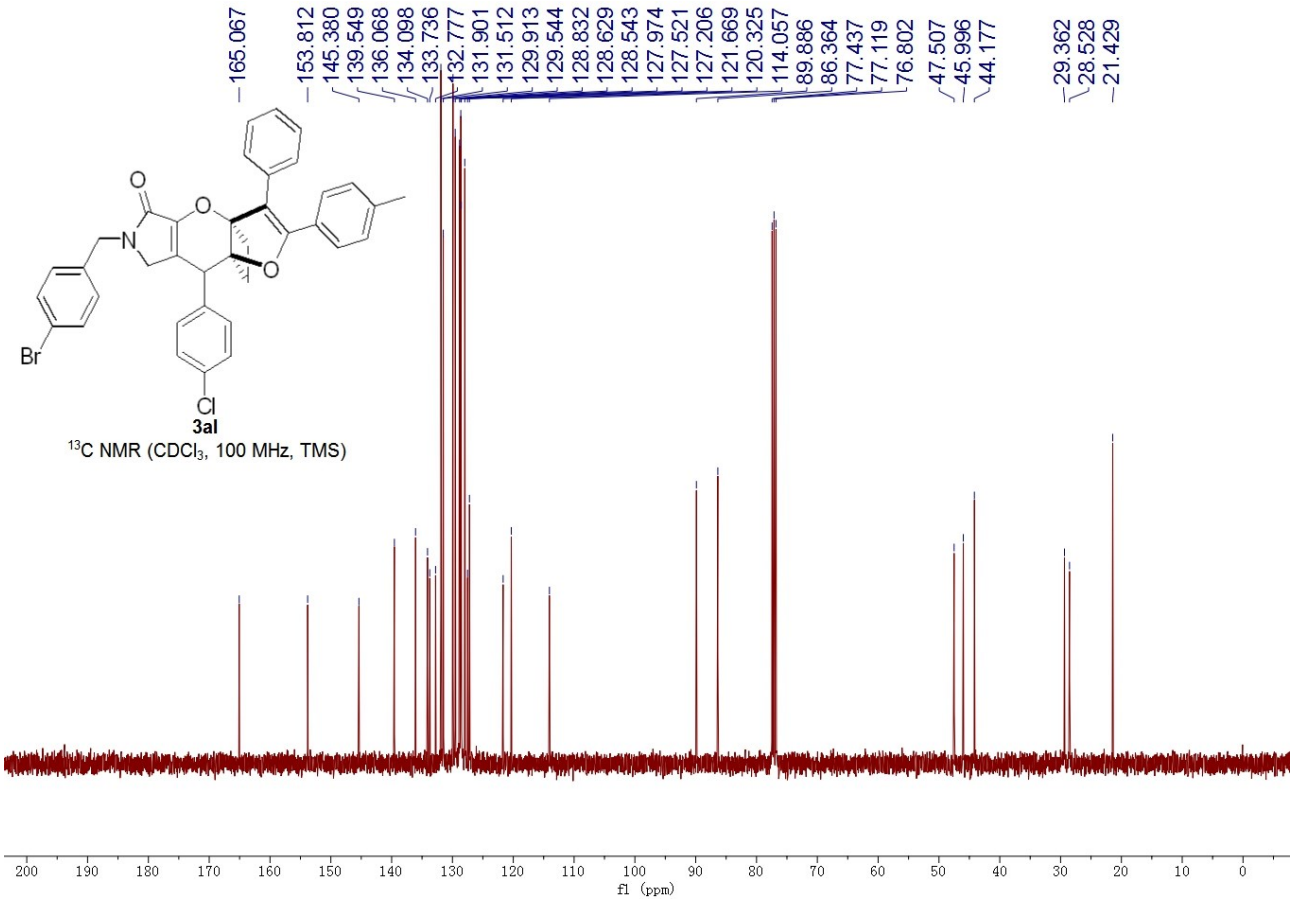


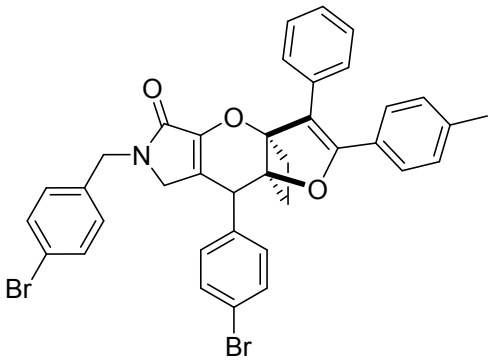
3al

(3aS,8aS)-6-(4-bromobenzyl)-8-(4-chlorophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3al), the title compound was achieved as yellow solid, MP = 121-123 °C, 102.9 mg, 78% yield. R*f* = 0.38 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 4H), 7.26-7.21 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 2H), 7.08 (d, *J* = 7.4 Hz, 2H), 6.99 (d, *J* = 7.4 Hz, 2H), 4.73 (d, *J* = 14.8 Hz, 1H), 4.31 (d, *J* = 15.2 Hz, 1H), 4.09 (s, 1H), 3.58 (d, *J* = 18.4 Hz, 1H), 3.45 (d, *J* = 18.4 Hz, 1H), 2.53-2.45 (m, 1H), 2.43-2.33 (m, 2H), 2.28-2.21 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 153.8, 145.4, 139.5, 136.1, 134.1, 133.7, 132.8, 131.9, 131.5, 129.9, 129.5, 128.8,

128.6, 128.5, 128.0, 127.5, 127.2, 121.7, 120.3, 114.1, 89.9, 86.4, 47.5, 46.0, 44.2, 29.4, 28.5, 21.4. IR (neat) ν 2917, 1698, 1489, 1406, 1353, 1251, 1176, 1087, 1013, 824, 797, 767, 700, 668 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{30}NO_3ClBr$: 650.1092, found: 650.1076.



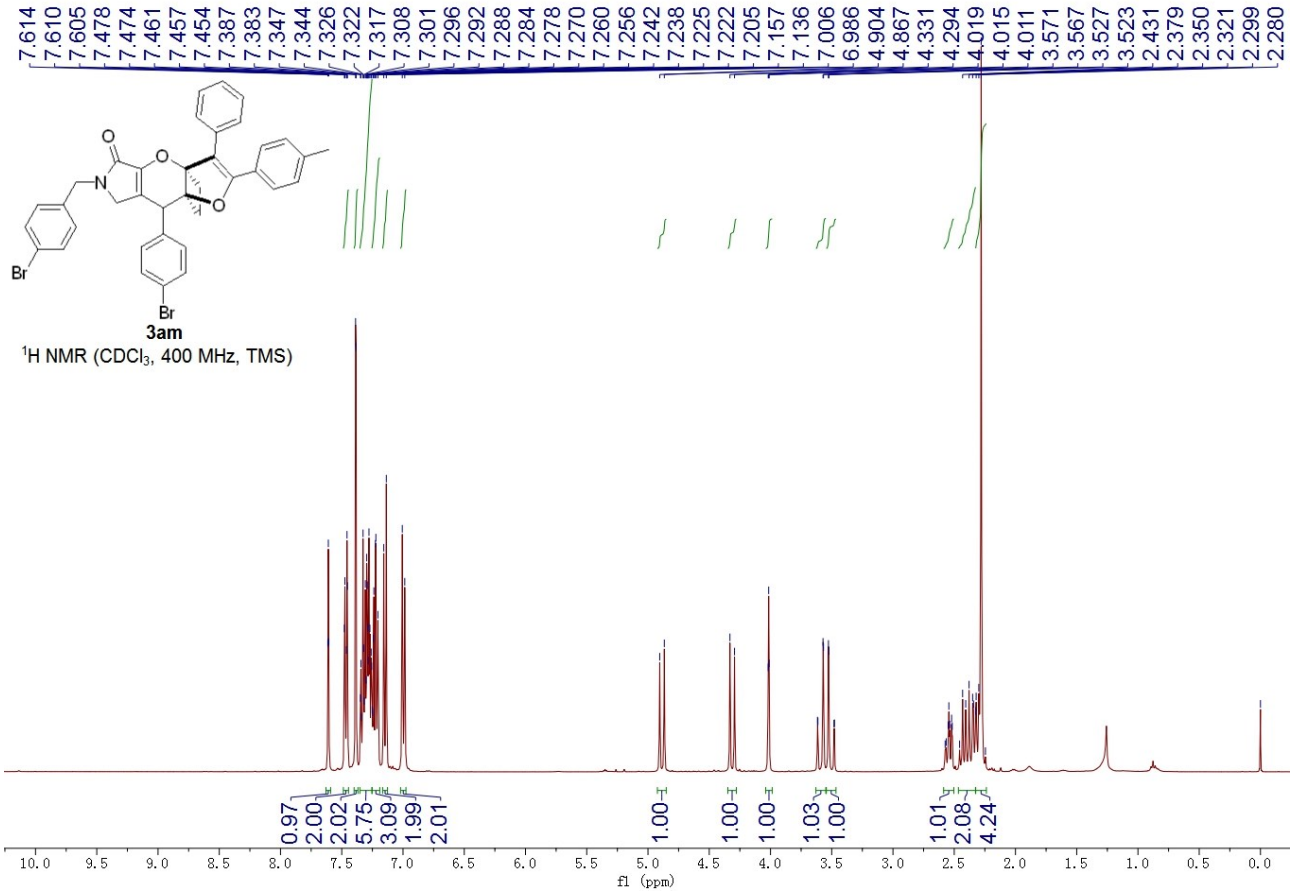


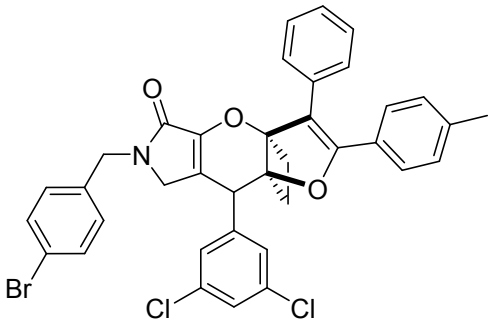


3am

(3aS,8aS)-6-(4-bromobenzyl)-8-(4-bromophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3am), the title compound was achieved as colorless solid, MP = 138-140 ^{o}C, 101.1 mg, 68% yield. R*f* = 0.38 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (t, *J* = 2.0 Hz, 1H), 7.48-7.45 (m, 2H), 7.38 (d, *J* = 1.6 Hz, 2H), 7.34-7.25 (m, 5H), 7.25-7.21 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 14.8 Hz, 1H), 4.31 (d, *J* = 14.8 Hz, 1H), 4.02 (s, 1H), 3.59 (dd, *J* = 18.4, 1.6 Hz, 1H), 3.50 (dd, *J* = 18.0, 1.6 Hz, 1H), 2.57-2.52 (m, 1H), 2.46-2.38 (m, 2H), 2.35-2.25 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 153.6, 145.6, 140.0, 139.6, 136.9, 133.4, 132.6, 131.8, 129.7, 128.9, 128.8,

128.7, 128.2, 127.8, 127.7, 127.4, 127.3, 122.8, 119.0, 114.0, 90.0, 85.9, 47.4, 46.6, 44.4, 29.6, 28.7, 21.5. IR (neat) ν 2917, 1694, 1584, 1550, 1456, 1427, 1240, 1177, 1099, 1005, 825, 767, 744, 699 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{30}NO_3Br_2$: 694.0587, found: 694.0587.

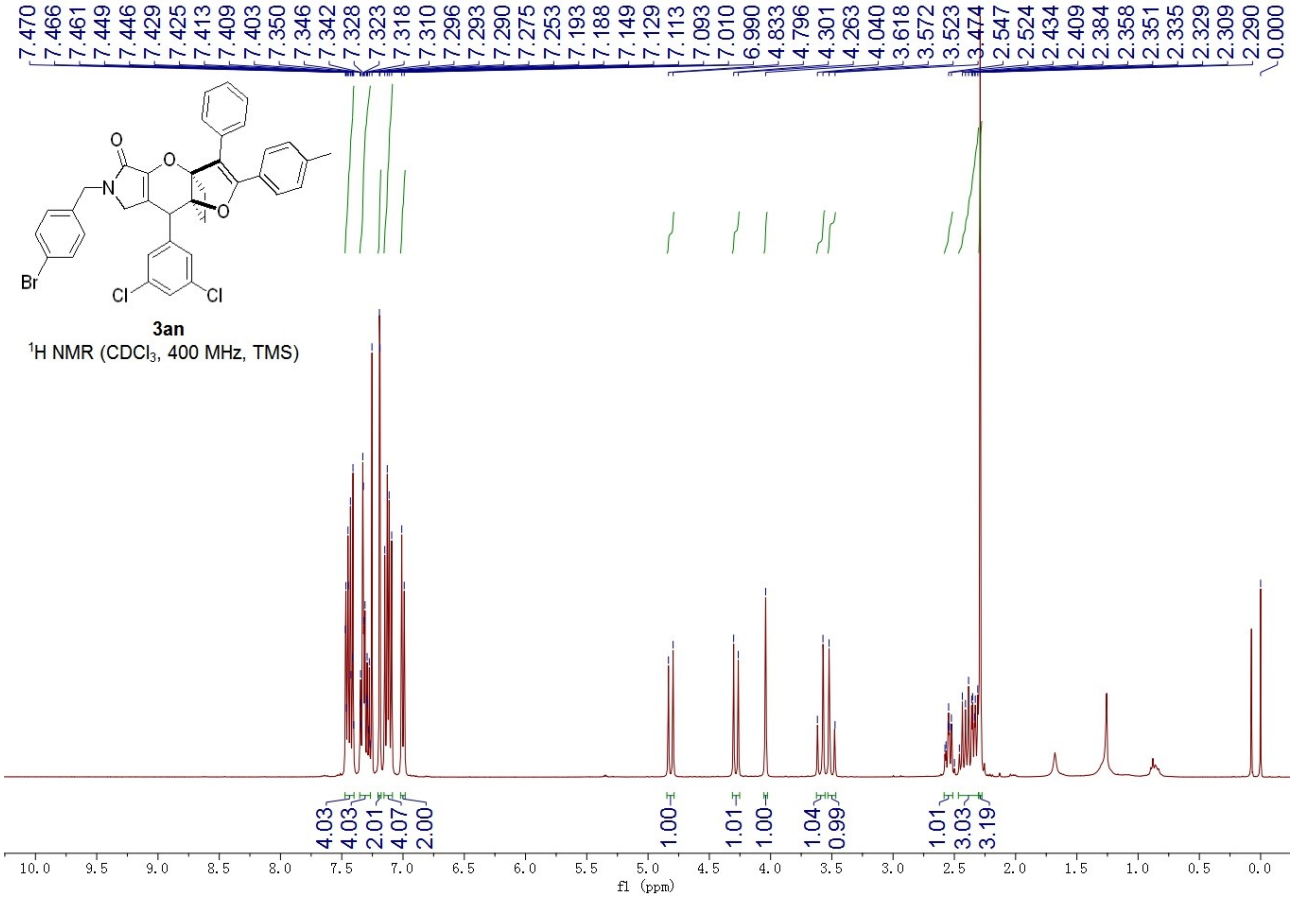


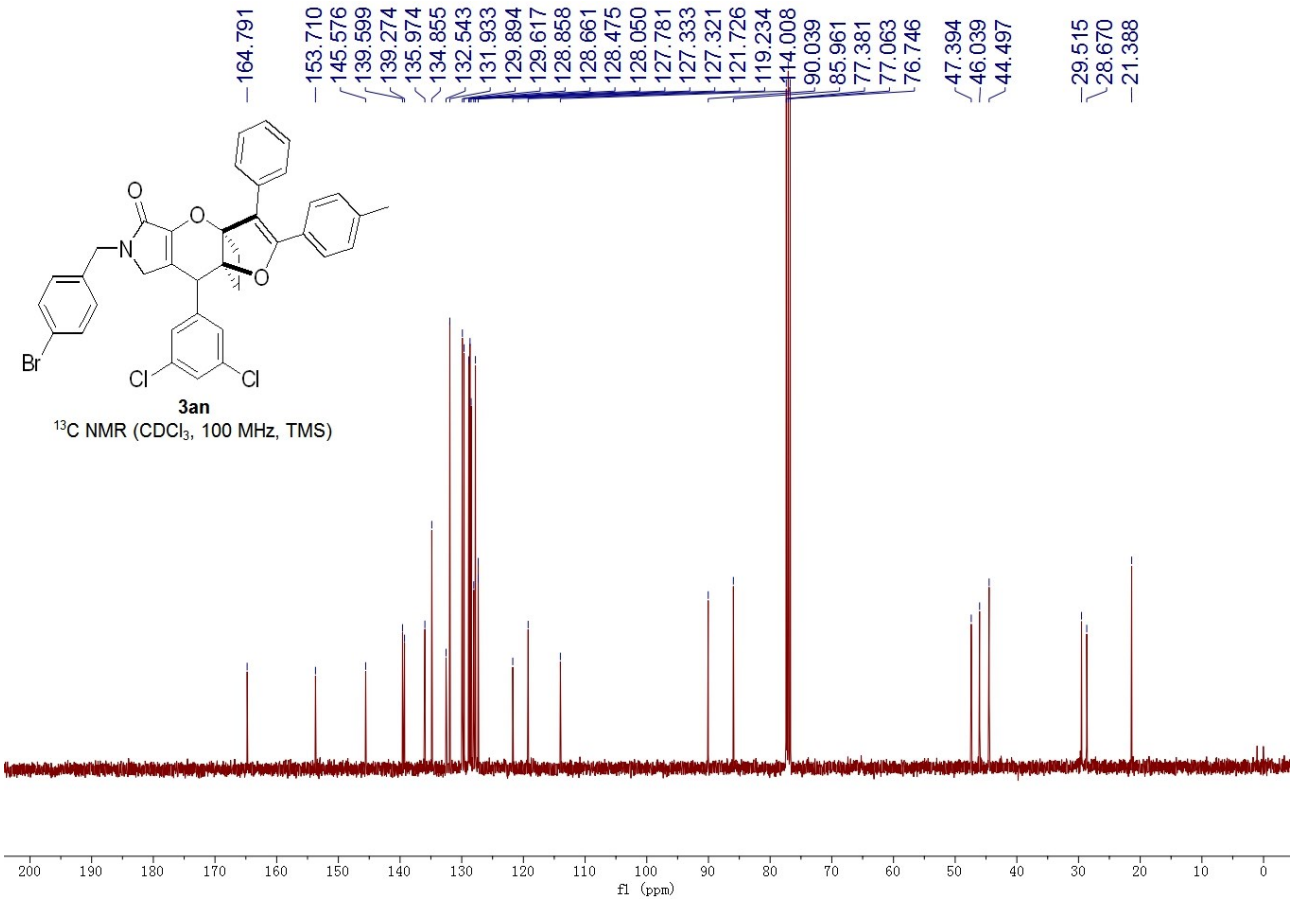


3an

(3aS,8aS)-6-(4-bromobenzyl)-8-(3,5-dichlorophenyl)-3-phenyl-2-(p-tolyl)-6,7-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrol-5(8H)-one (3an), the title compound was achieved as white solid, MP = 125-127 °C, 65.5 mg, 74% yield (0.13 mmol reaction). R*f* = 0.38 (Petroleum Ether:Ethyl Acetate = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.40 (m, 4H), 7.35-7.27 (m, 4H), 7.19 (d, *J* = 2.0 Hz, 2H), 7.15-7.09 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.81 (d, *J* = 14.8 Hz, 1H),

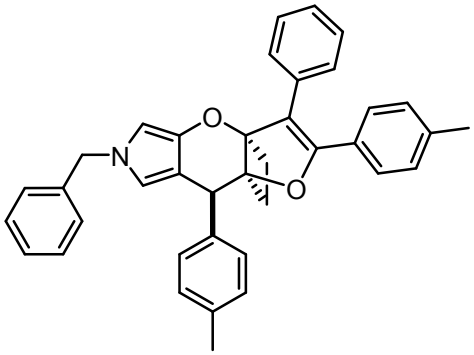
4.28 (d, *J* = 15.2 Hz, 1H), 4.04 (s, 1H), 3.59 (d, *J* = 18.4 Hz, 1H), 3.50 (d, *J* = 18.4 Hz, 1H), 2.58-2.52 (m, 1H), 2.46-2.31 (m, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.8, 153.7, 145.6, 139.6, 139.3, 136.0, 134.9, 132.5, 131.9, 129.9, 129.6, 128.9, 128.7, 128.5, 128.1, 127.8, 127.33, 127.32, 121.7, 119.2, 114.0, 90.0, 86.0, 47.4, 46.0, 44.5, 29.5, 28.7, 21.4. IR (neat) ν 2917, 1694, 1495, 1484, 1453, 1251, 1176, 1120, 1072, 1007, 909, 833, 765, 730, 699 cm^{-1}. HRMS (ESI) calcd for $C_{37}H_{29}NO_3Cl_2Br$: 684.0702, found: 684.0688.



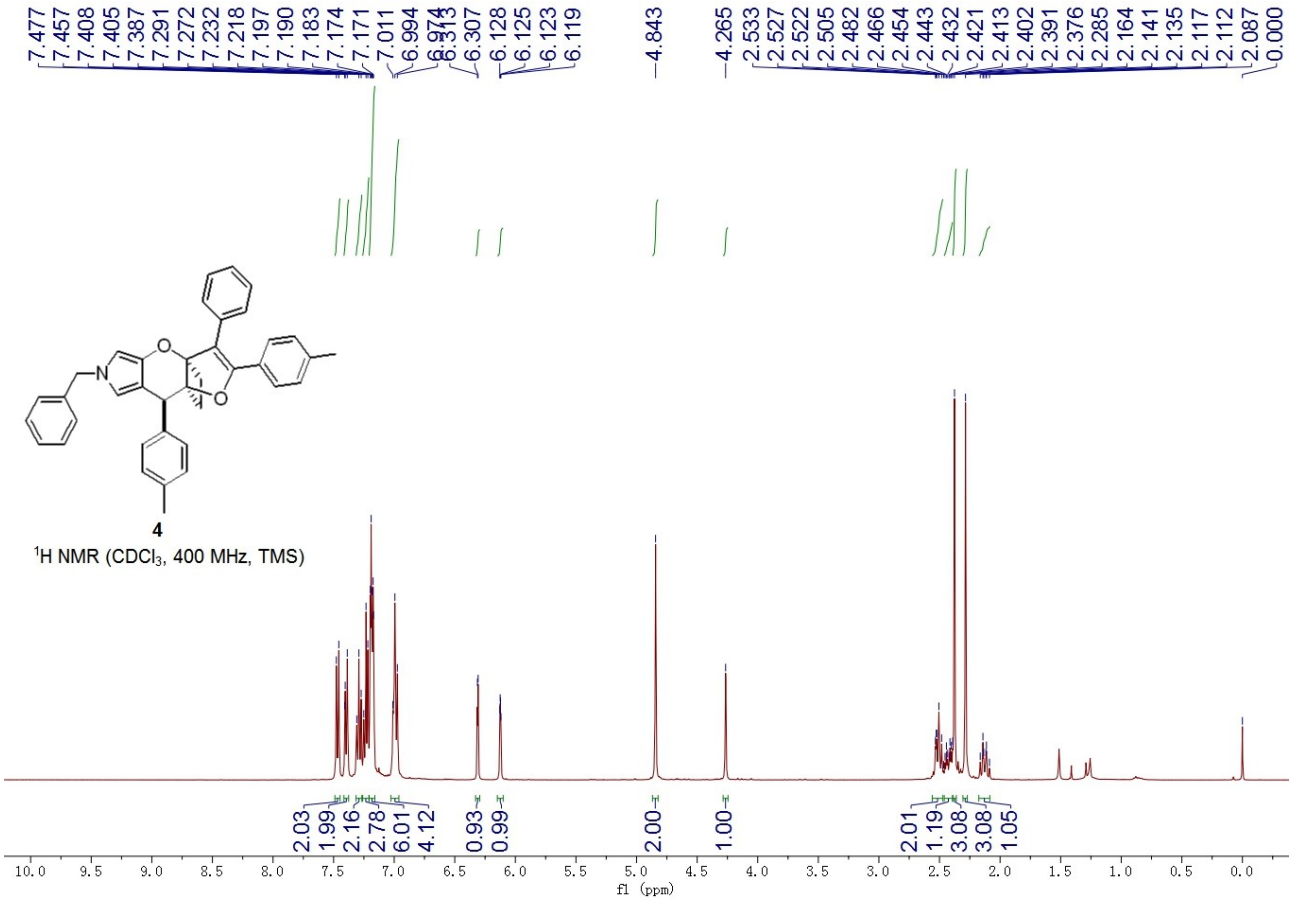


3an

^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

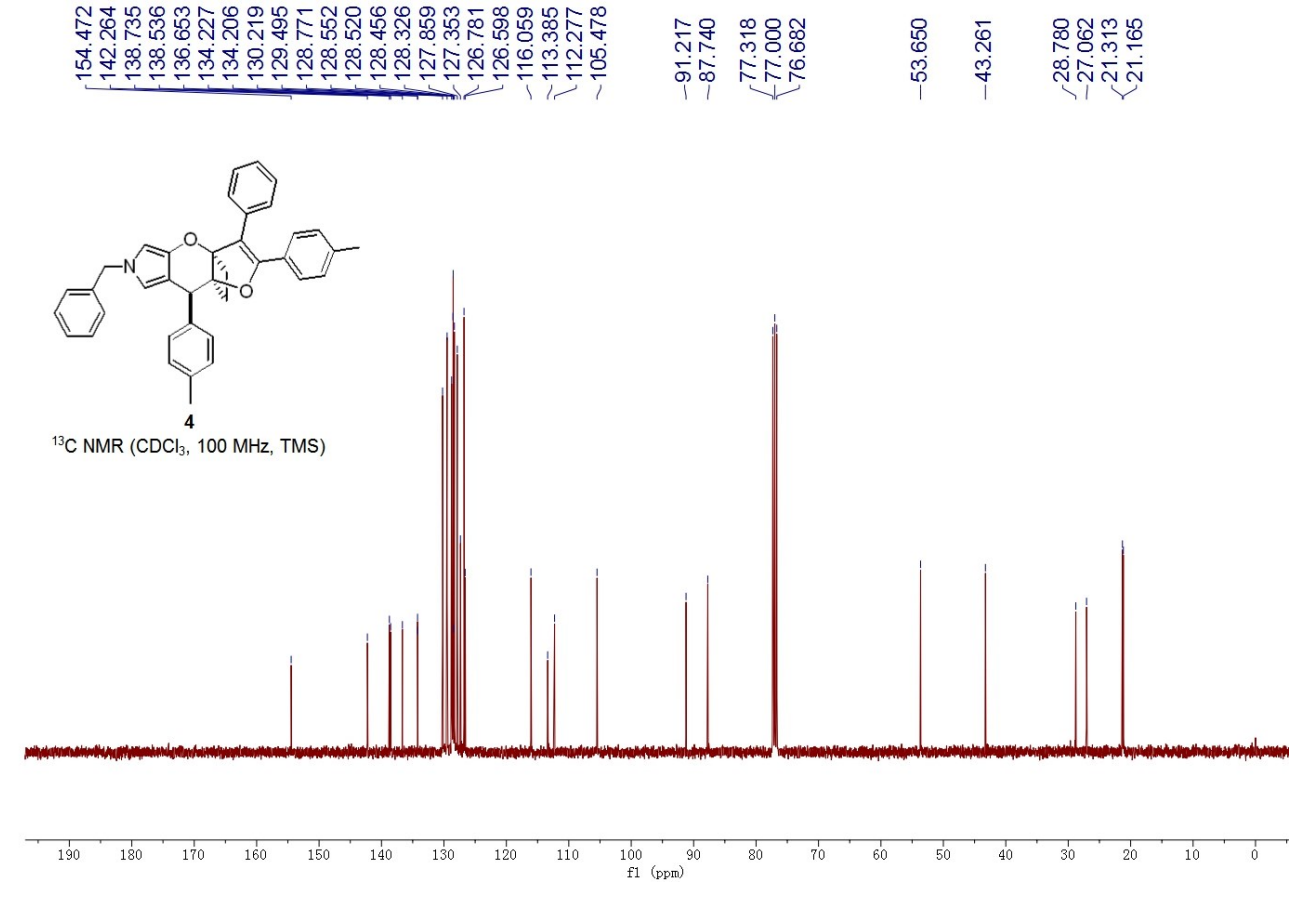


(3aS,8S,8aS)-6-benzyl-3-phenyl-2,8-di-*p*-tolyl-6,8-dihydro-3a,8a-ethanofuro[2',3':5,6]pyrano[2,3-c]pyrrole (4), the title compound was achieved as brown solid, MP = 113-115 ^{o}C, 53.5 mg, 50% yield. R*f* = 0.48 (Petroleum Ether:Ethyl Acetate = 10:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.0 Hz, 2H), 7.41-7.39 (m, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.25-7.22 (m, 2H), 7.20-7.17 (m, 6H), 7.01-6.97 (m, 4H), 6.31 (d, *J* = 2.4 Hz, 1H), 6.13-6.12 (m, 1H), 4.84 (s, 2H), 4.27 (s, 1H), 2.53-2.48 (m, 2H), 2.47-2.39 (m, 1H), 2.38 (s, 3H), 2.29 (s, 3H), 2.16-2.09 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 154.5, 142.3, 138.7, 138.5, 136.7, 134.23, 134.21, 130.2, 129.5, 128.8, 128.6, 128.5, 128.4, 128.3, 127.9, 127.4, 126.8, 126.6, 116.1, 113.4, 112.3, 105.5, 91.2, 87.7, 53.7, 43.3, 28.8, 27.1, 21.3, 21.2. IR (neat) ν 2917, 1513, 1175, 1117, 1070, 992, 908, 821, 763, 731, 699 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{34}NO_2$: 536.2584, found: 536.2578.



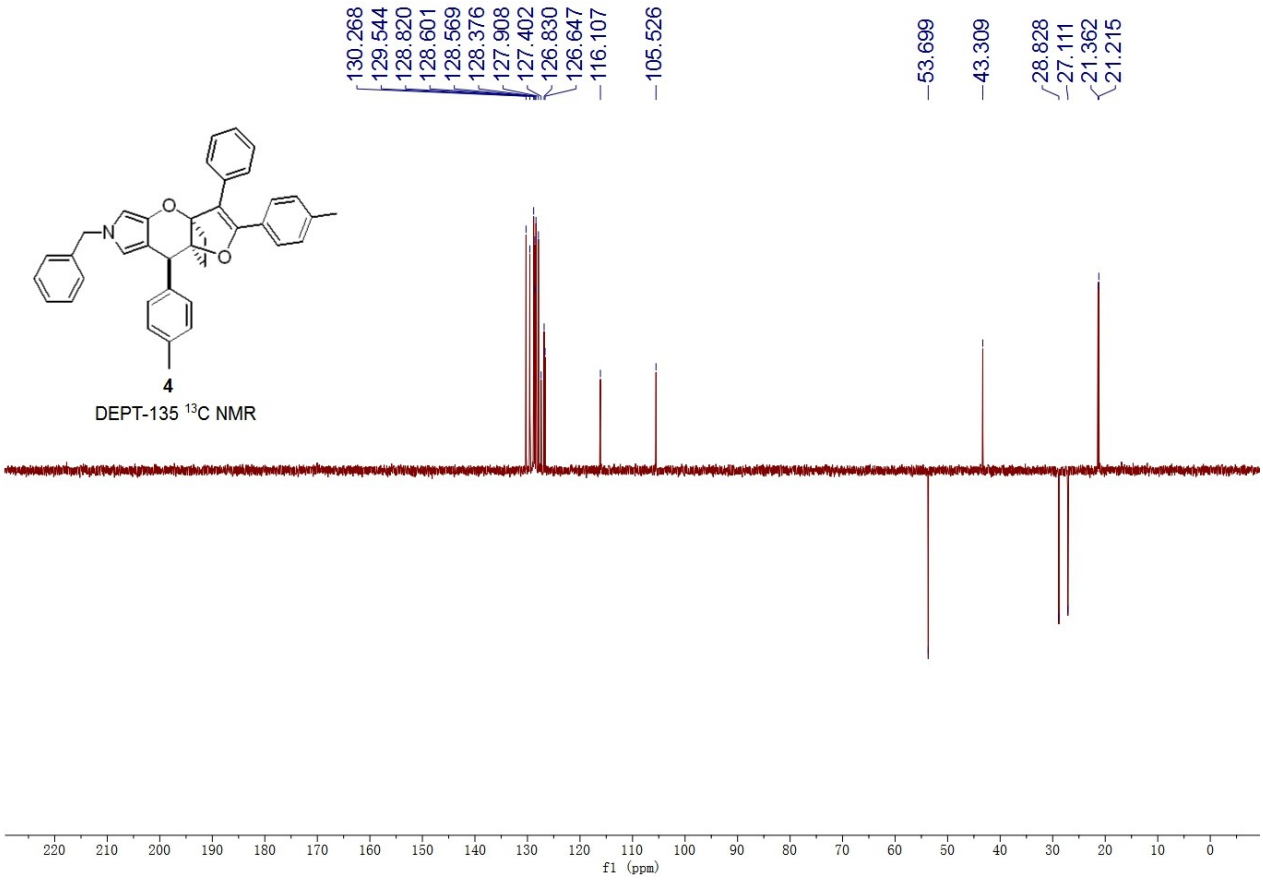
4

^{1}H NMR ($CDCl_3$, 400 MHz, TMS)

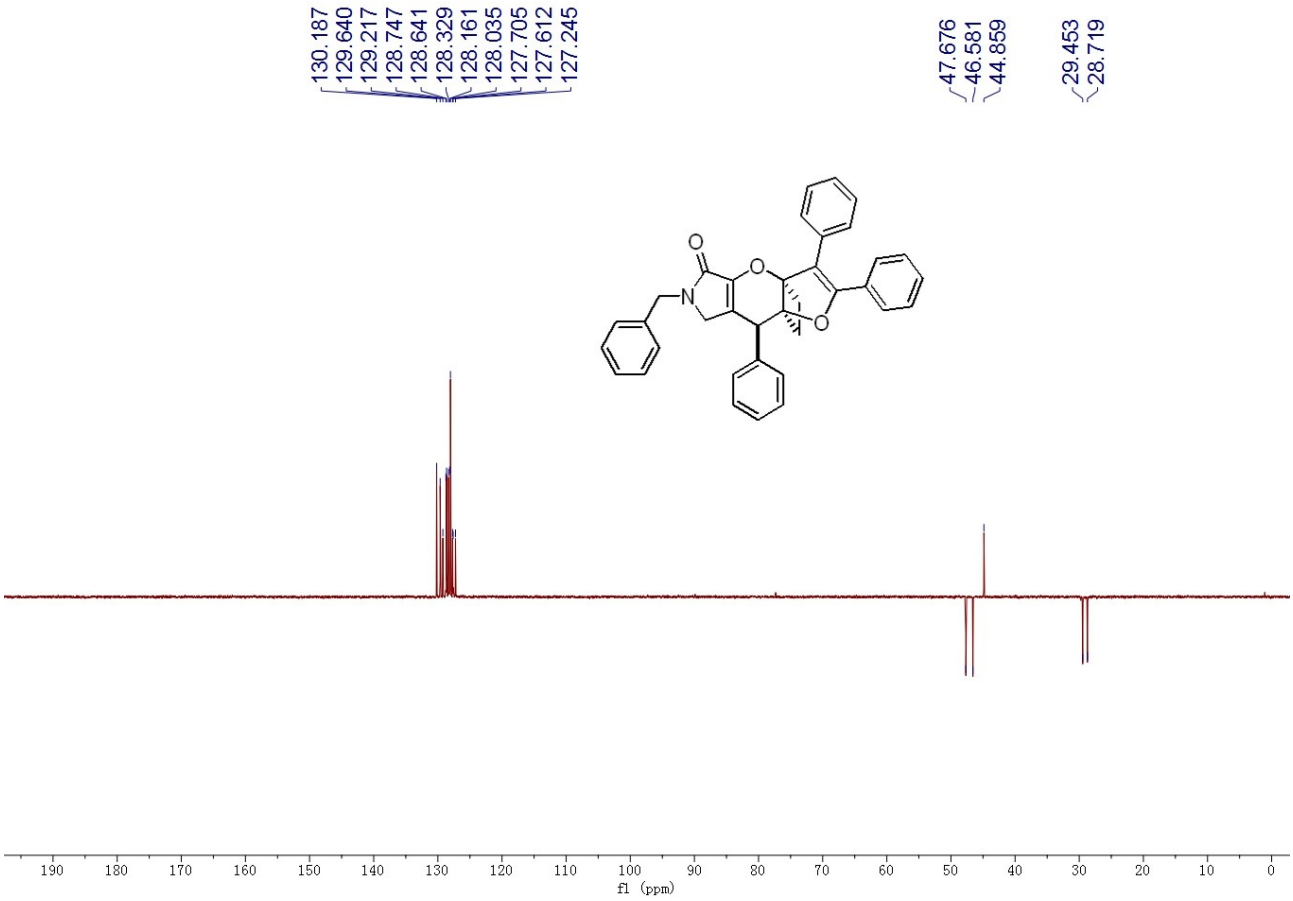


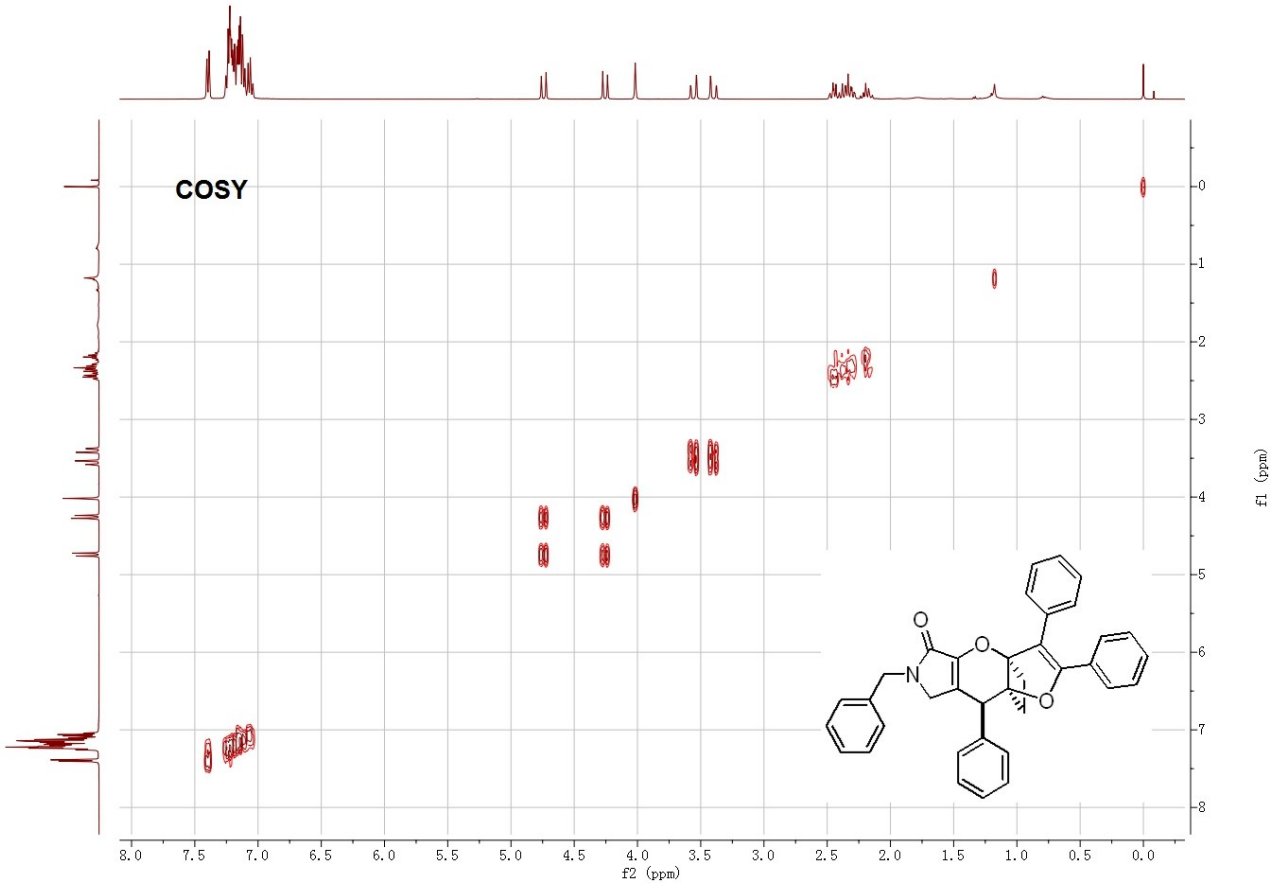
4

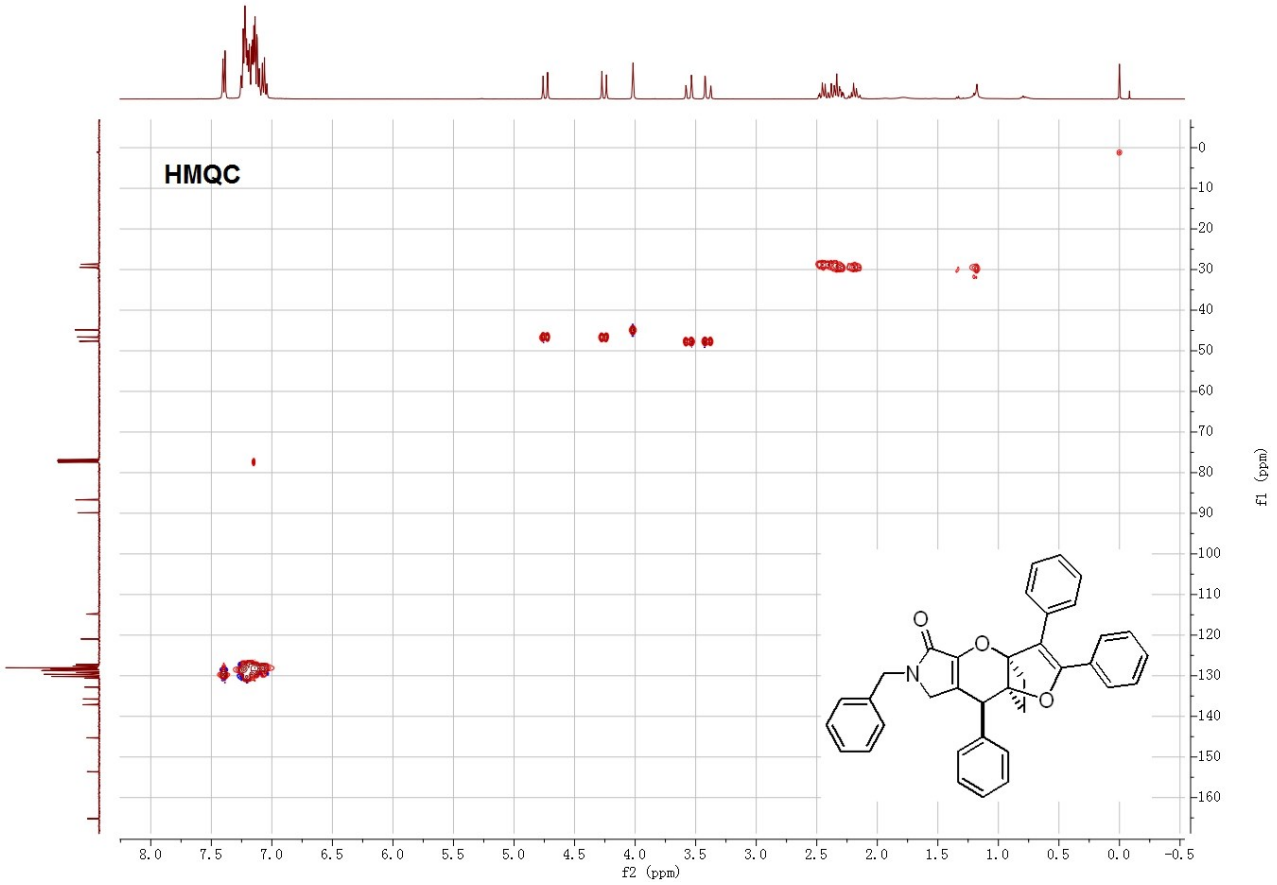
^{13}C NMR ($CDCl_3$, 100 MHz, TMS)

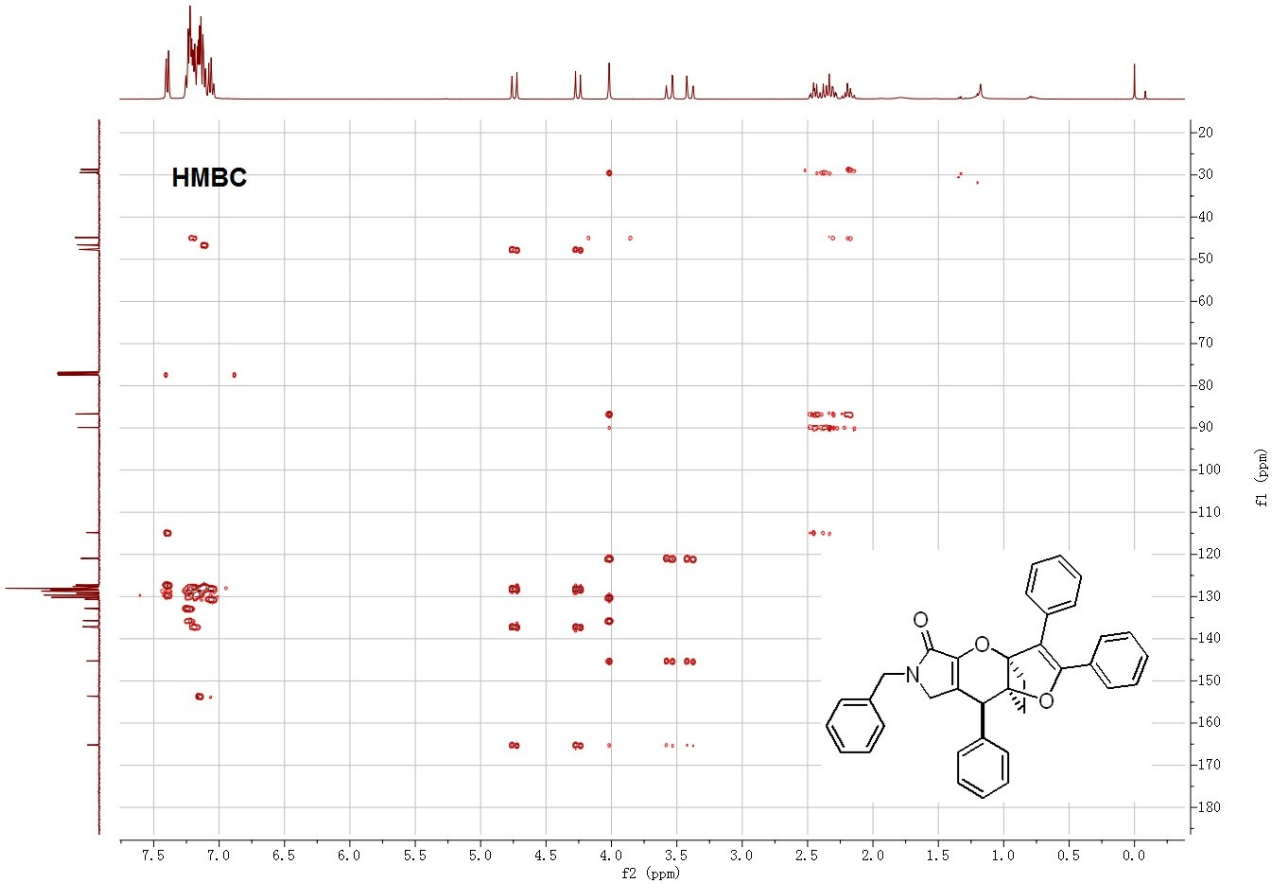

130.268
129.544
128.820
128.601
128.569
128.376
127.908
127.402
126.830
126.647
116.107
105.526
53.699
43.309
28.828
27.111
21.362
21.215
4
DEPT-135 13C NMR
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

DEPT-135 spectra and 2D NMR spectra of **3ba**

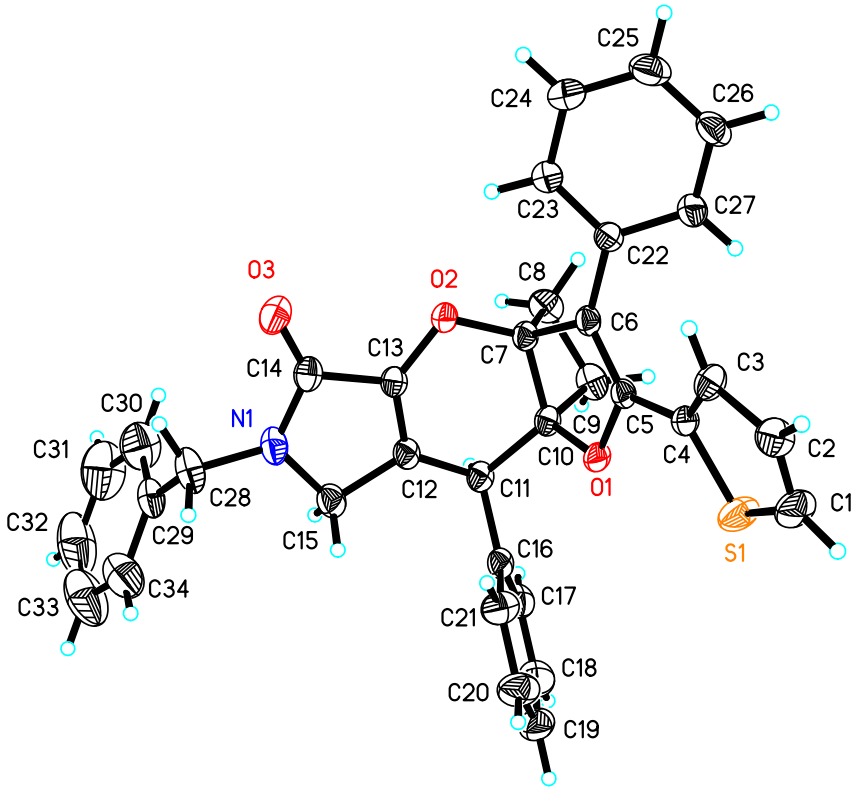



COSY
f2 (ppm)
f1 (ppm)


HMQC
f2 (ppm)
f1 (ppm)


HMBC
f2 (ppm)
f1 (ppm)
O
N
O
O

(F) X-ray of Product 3la



The crystal data of **3la** have been deposited in CCDC with number 2052391. Empirical Formula: $C_{34}H_{27}NO_3S$; Formula Weight: 529.62; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.150 x 0.100 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 10.5667(4) Å, b = 10.7003(5) Å, c = 13.9406(6) Å, α = 69.3010(10)°, β = 88.1310(10)°, γ = 67.2510(10)°, V = 1349.84(10) $Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.303 g/cm^3; F_{000} = 556; Final R indices [I>2sigma(I)] R1 = 0.0657, wR2 = 0.1745.