Supporting Information

Copper-Catalyzed Diastereoselective Hydrothioetherification of Oxa(aza)benzonorbornadienes

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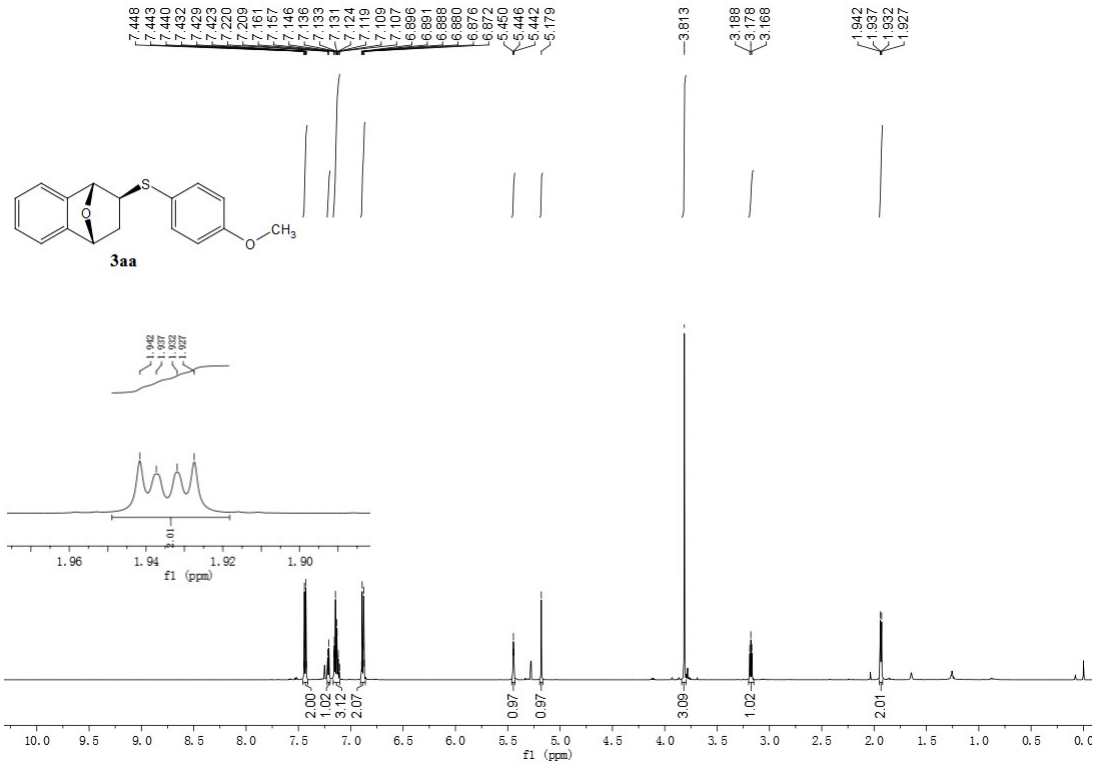
Contents

1. Deuterium-labeling experiments[a][b]

[a] **(a)** The H of the CH_2 could be seen in the ^1H NMR spectrum of adduct **3aa**. **(b)** No deuterium incorporation in the desired product was noted when using deuterated DMF as the solvent. **(c)** When using 0.2 mL D_2O and 2 mL DMF as the mixed solvent, partially labeled product with 49% deuterium was obtained. **(d)** When increasing the amount of D_2O to 0.4 mL, the deuteration ratio of the product was increased to 68%. The above results indicate that the water in the DMF or air should be the hydrogen source for this hydrothiolation reaction.

[b] **(e)** The *exo*-H and *endo*-H of the CH_2 could be seen in the ^1H NMR spectrum of adduct **3db**. **(f)** When using 0.2 mL D_2O and 2 mL DMF as the mixed solvent, partial *exo*-H of the desired product was deuterated (63% D). This result means that the hydrogen atom is introduced into the *exo* orientation of the corresponding adduct.



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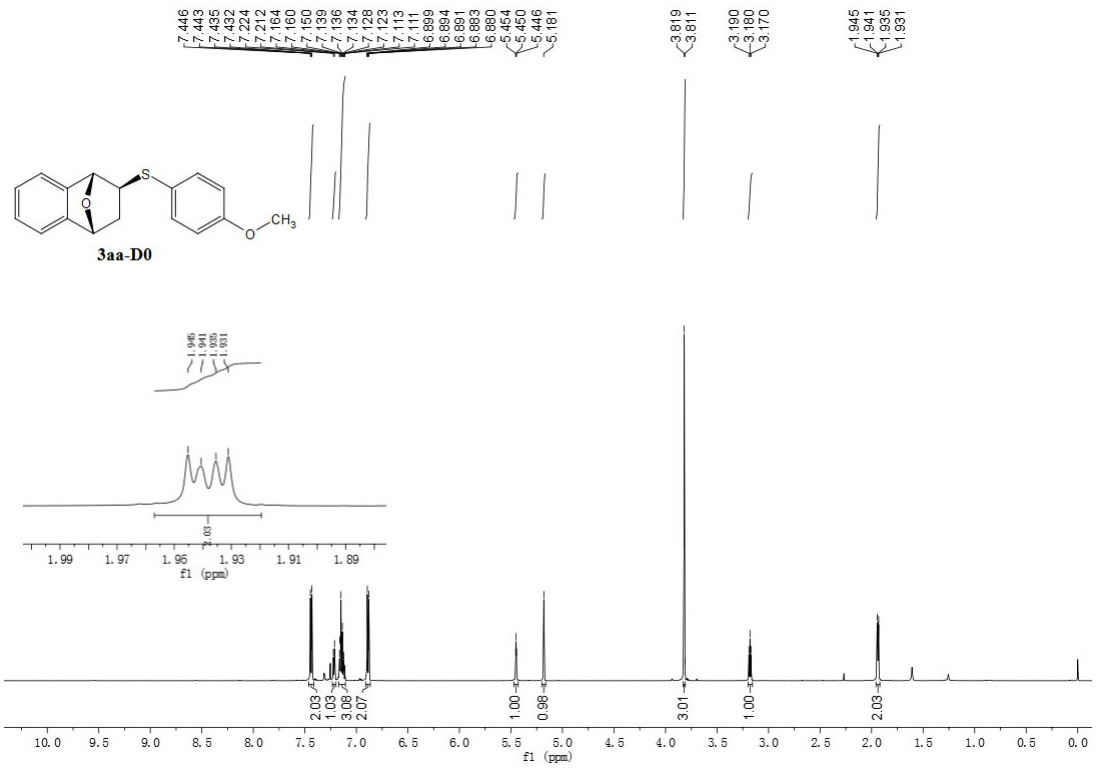
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7.128
7.123
7.113
7.111
6.899
6.894
6.891
6.883
6.880
5.454
5.450
5.446
5.181
3.819
3.811
3.190
3.180
3.170
1.945
1.941
1.935
1.931
S
O
O
CH3
3aa-D0
1.99
1.97
1.95
1.93
1.91
1.89
f1 (ppm)
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1.03
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2.07
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1.00
2.03
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9.0
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8.0
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6.5
6.0
5.5
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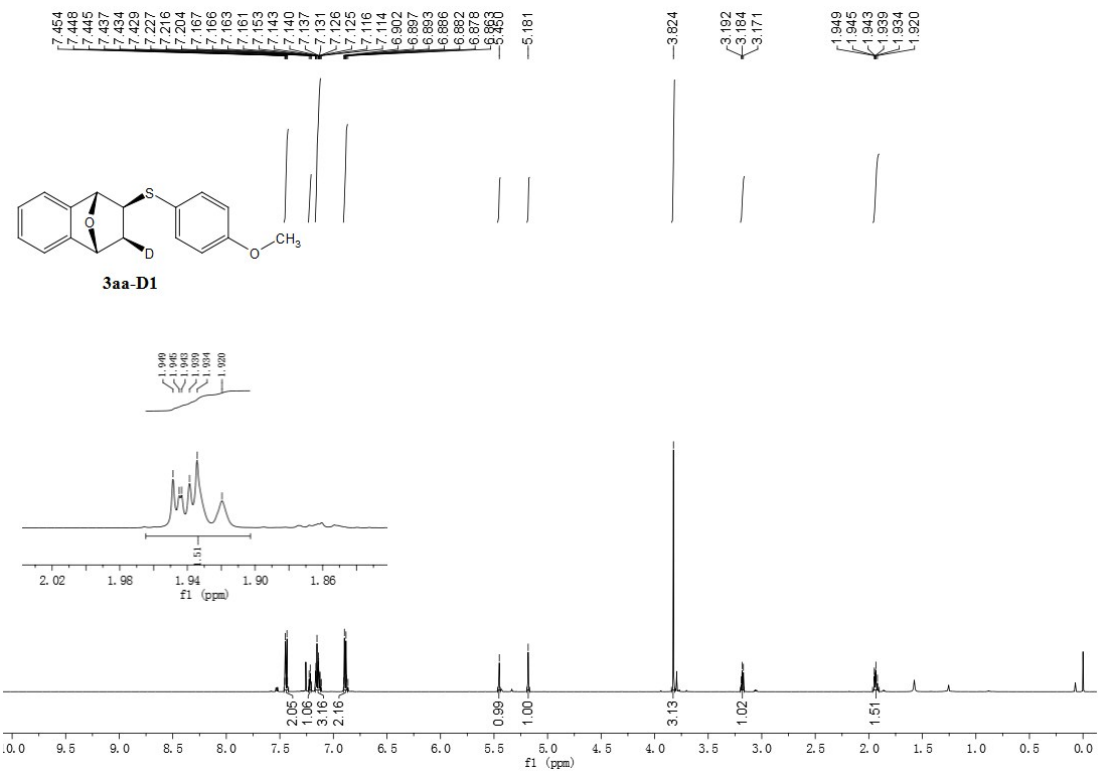
0.5
0.0
f1 (ppm)

(b)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S
O
D
O
CH3
3aa-D1
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1.90
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1.02
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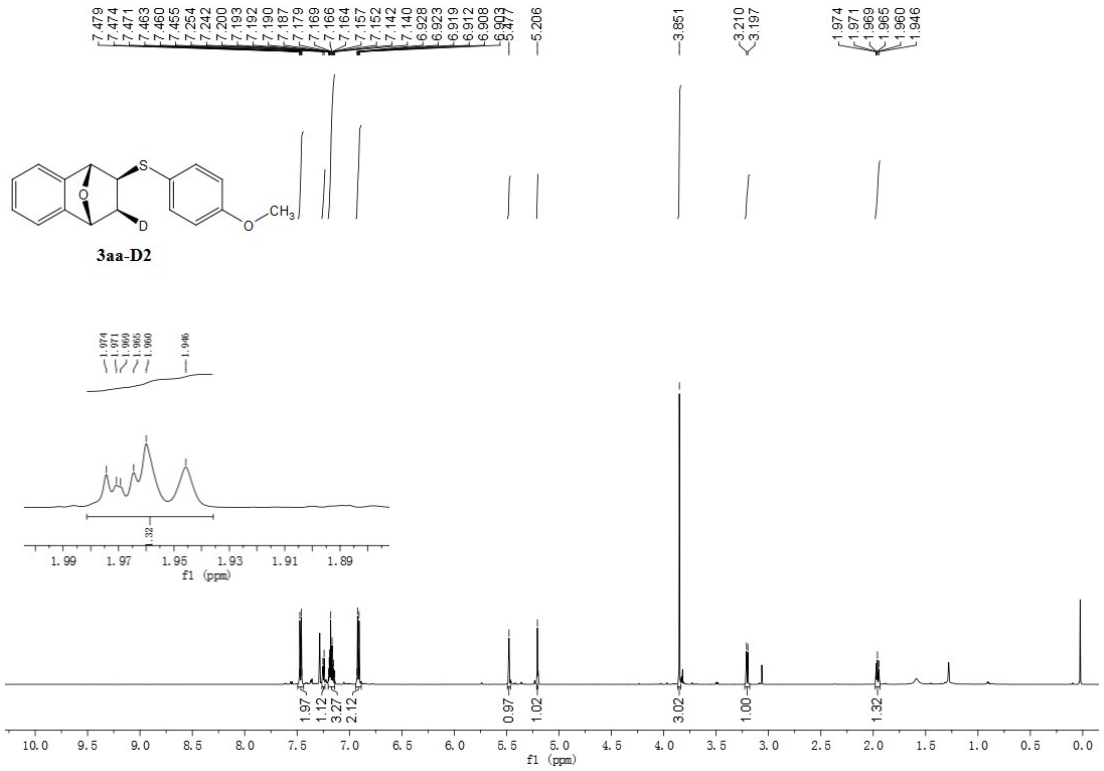
f1 (ppm)

(c)



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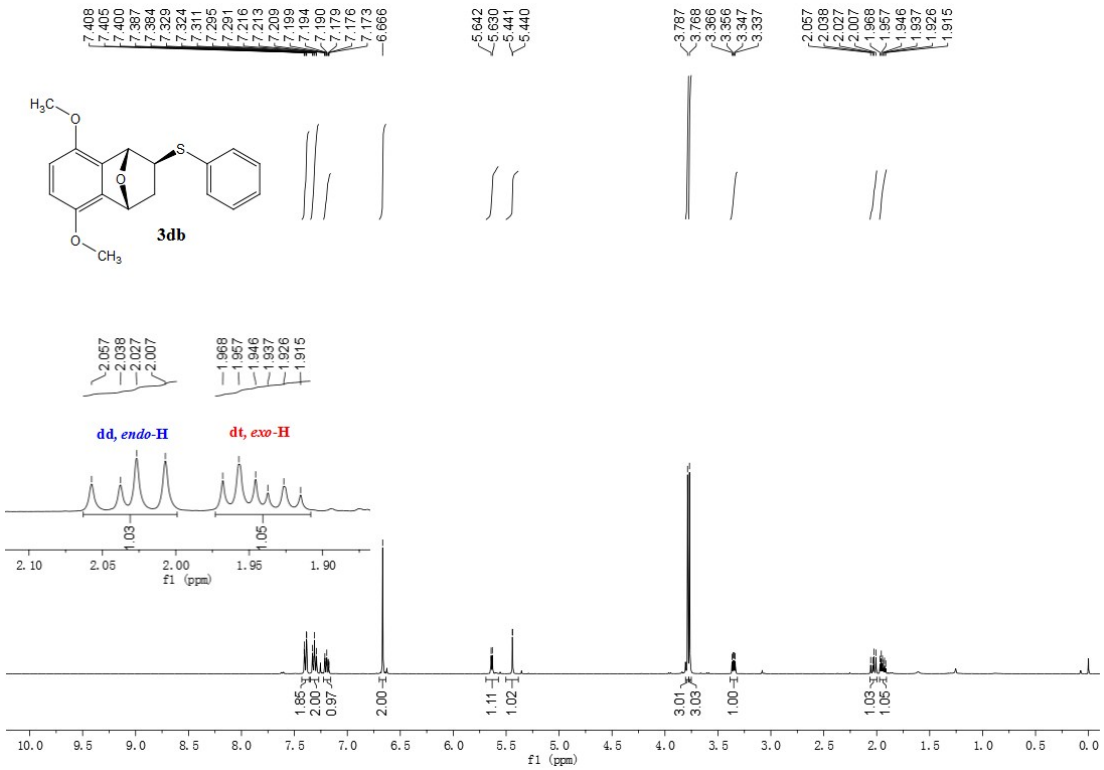

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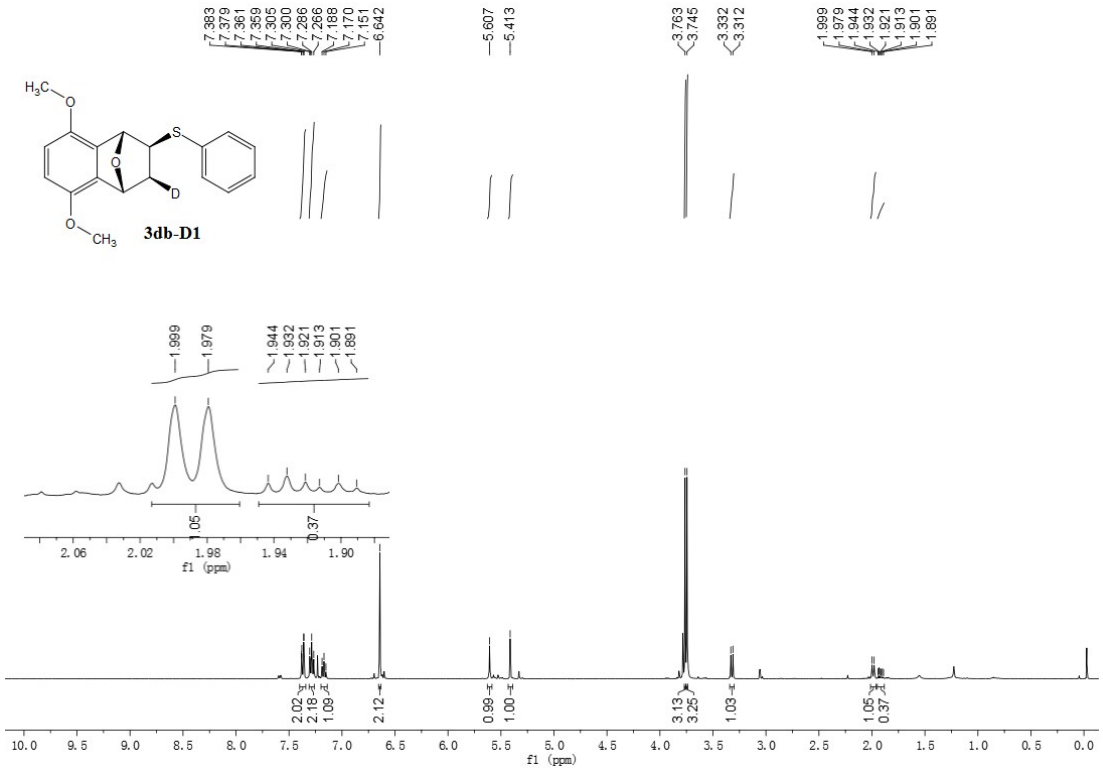
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H3C
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S
O
D
O
CH3
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7.5
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
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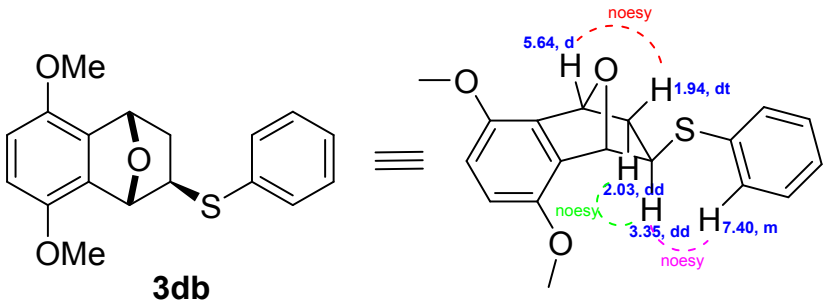
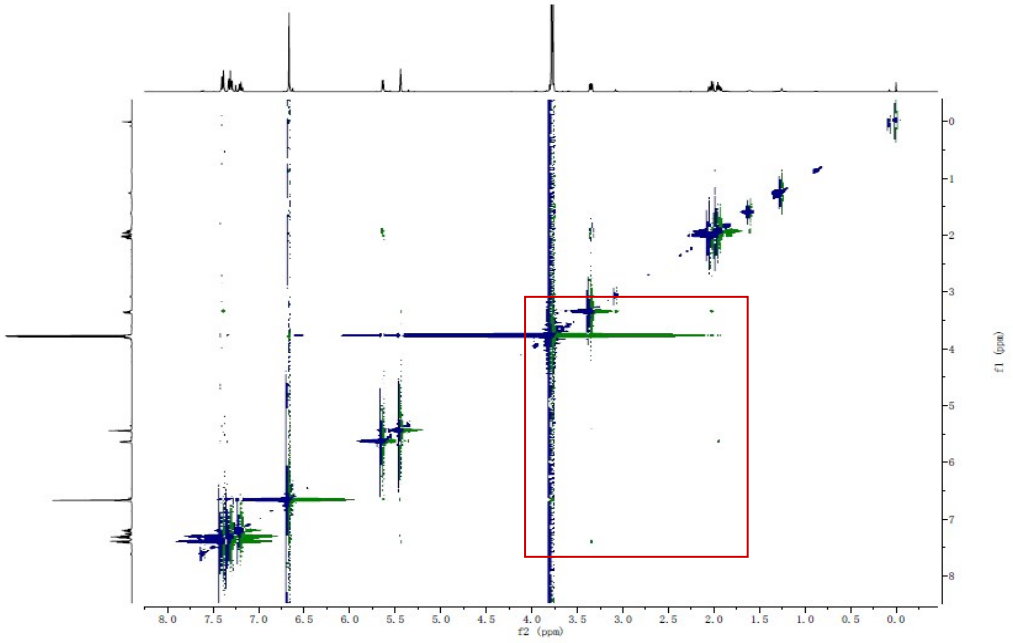
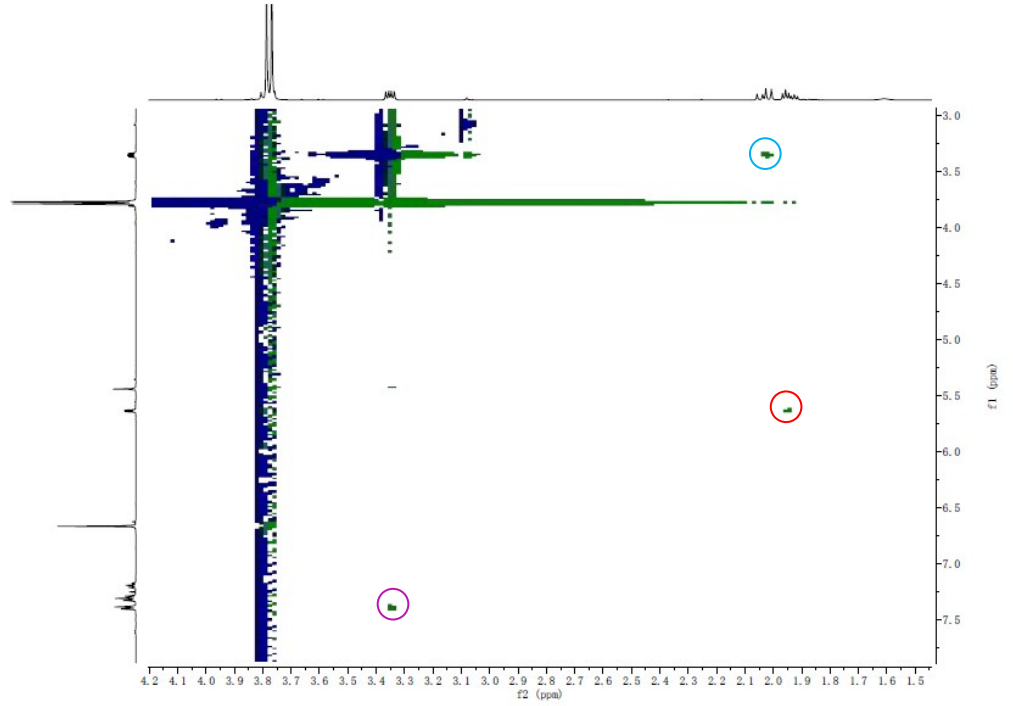
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

(f)

2. NOESY analysis of 3db.







3. Crystal data and structure refinement for 3cb (CCDC 1970314)

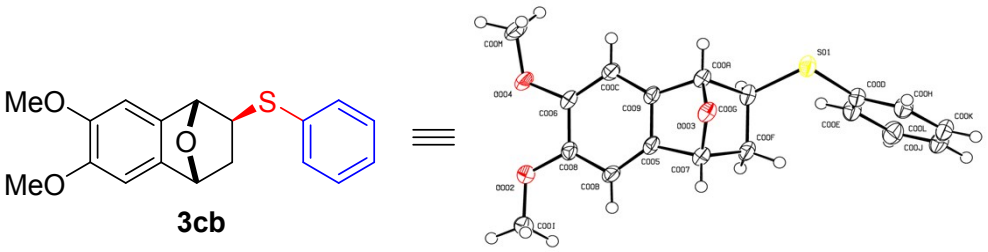


Table 1 Crystal data and structure refinement for **3cb**.

Identification code	wang_20191205
Empirical formula	$C_{18}H_{18}O_3S$
Formula weight	314.38
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	5.54660(10)
b/Å	9.9811(2)
c/Å	27.5422(5)
α/°	90
β/°	91.085(2)
γ/°	90
Volume/Å^3	1524.50(5)
Z	4
ρ_{calc}g/cm^3	1.370
μ/mm^{-1}	1.971
F(000)	664.0
Crystal size/mm^3	0.15 × 0.14 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.42 to 134.958
Index ranges	$-5 \le h \le 6$, $-11 \le k \le 11$, $-32 \le l \le 33$
Reflections collected	6733
Independent reflections	2749 [R_{int} = 0.0382, R_{sigma} = 0.0475]
Data/restraints/parameters	2749/0/201
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0404, wR_2 = 0.1143
Final R indexes [all data]	R_1 = 0.0441, wR_2 = 0.1178
Largest diff. peak/hole / e Å^{-3}	0.27/-0.40

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **3cb**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S01	11219.4(8)	1773.0(5)	5290.2(2)	28.31(17)
O002	3394(2)	3795.4(13)	2936.5(4)	29.4(3)
O003	10535(2)	4128.9(12)	4518.1(4)	25.8(3)
O004	6528(2)	2010.0(13)	2707.4(4)	30.7(3)
C005	7133(3)	3828.0(17)	4047.0(6)	23.2(4)
C006	6785(3)	2522.0(17)	3168.9(6)	23.9(4)
C007	7937(3)	4324.0(18)	4543.5(6)	25.5(4)
C008	5092(3)	3517.9(17)	3289.0(6)	23.3(4)
C009	8746(3)	2810.5(17)	3936.3(6)	22.4(4)
C00A	10447(3)	2740.9(18)	4371.0(6)	23.9(4)
C00B	5258(3)	4175.7(17)	3735.1(6)	24.5(4)
C00C	8586(3)	2134.2(18)	3497.0(6)	24.2(4)
C00D	9356(3)	1397.9(19)	5788.0(6)	27.4(4)
C00E	7269(3)	633(2)	5736.4(7)	31.5(4)
C00F	7250(3)	3248.7(18)	4920.6(6)	26.3(4)
C00G	9043(3)	2107.8(19)	4799.7(6)	25.4(4)
C00H	10077(4)	1850(2)	6248.4(7)	33.6(4)
C00I	1747(4)	4856(2)	3034.7(7)	32.9(4)
C00J	5930(4)	324(2)	6140.5(8)	38.8(5)
C00K	8722(4)	1517(2)	6652.7(7)	39.2(5)
C00L	6657(4)	760(2)	6596.3(7)	40.3(5)
C00M	8543(4)	1302(2)	2524.1(7)	39.7(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **3cb**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S01	28.6(3)	36.8(3)	19.6(3)	3.79(17)	2.25(18)	-3.09(17)
O002	29.6(7)	37.6(7)	21.2(6)	0.9(5)	1.8(5)	6.6(5)
O003	28.3(6)	28.0(6)	21.2(6)	-2.0(5)	4.6(5)	-5.5(5)
O004	33.4(7)	40.2(7)	18.7(6)	-9.3(5)	1.7(5)	6.4(6)
C005	29.1(9)	24.2(8)	16.5(8)	0.1(6)	6.6(7)	-2.5(7)
C006	28.2(9)	27.0(9)	16.6(8)	-2.6(7)	6.0(7)	-3.1(7)
C007	29.4(9)	28.0(9)	19.3(9)	-3.0(7)	4.1(7)	-0.6(7)
C008	25.9(8)	26.7(9)	17.5(8)	3.4(7)	4.0(6)	-1.4(7)
C009	26.3(9)	24.2(8)	16.9(8)	1.2(7)	5.5(7)	-1.5(7)

C00A	25.8(8)	26.8(9)	19.2(8)	-0.4(7)	4.8(7)	-2.3(7)
C00B	28.9(9)	24.5(9)	20.5(9)	0.6(7)	8.6(7)	2.6(7)
C00C	28.9(9)	23.1(8)	20.8(9)	-1.1(7)	6.0(7)	0.5(7)
C00D	32.8(9)	29.8(9)	19.5(9)	1.7(7)	2.0(7)	3.9(7)
C00E	34.9(10)	37.3(10)	22.5(9)	2.2(8)	3.0(7)	-1.8(8)
C00F	27.0(9)	35.4(10)	16.7(8)	-0.8(7)	4.8(7)	-1.6(7)
C00G	29.8(9)	29.9(9)	16.7(8)	0.9(7)	2.2(7)	-4.7(7)
C00H	42.6(11)	34.9(10)	23.3(9)	-1.3(8)	0.0(8)	3.7(8)
C00I	31.4(10)	40.1(11)	27.3(10)	7.0(8)	5.2(8)	8.7(8)
C00J	37.1(11)	48.3(12)	31.4(10)	9.3(9)	10.0(9)	-0.7(9)
C00K	57.4(13)	40.9(11)	19.4(9)	-0.2(8)	5.1(9)	12.3(10)
C00L	47.7(12)	49.0(12)	24.8(10)	9.1(9)	14.7(9)	10.1(10)
C00M	36.6(11)	56.3(13)	26.4(10)	-16.3(9)	4.2(8)	7.9(10)

Table 4 Bond Lengths for **3cb**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S01	C00D	1.7724(18)	C007	C00F	1.546(2)
S01	C00G	1.8255(18)	C008	C00B	1.394(2)
O002	C008	1.368(2)	C009	C00A	1.512(2)
O002	C00I	1.428(2)	C009	C00C	1.387(2)
O003	C007	1.457(2)	C00A	C00G	1.560(2)
O003	C00A	1.444(2)	C00D	C00E	1.392(3)
O004	C006	1.375(2)	C00D	C00H	1.397(3)
O004	C00M	1.423(2)	C00E	C00J	1.384(3)
C005	C007	1.514(2)	C00F	C00G	1.552(3)
C005	C009	1.391(2)	C00H	C00K	1.396(3)
C005	C00B	1.381(3)	C00J	C00L	1.382(3)
C006	C008	1.411(2)	C00K	C00L	1.378(3)
C006	C00C	1.389(3)			

Table 5 Bond Angles for **3cb**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C00D	S01	C00G	102.95(8)	C00C	C009	C00A	134.21(16)
C008	O002	C00I	116.75(14)	O003	C00A	C009	101.26(14)
C00A	O003	C007	96.53(12)	O003	C00A	C00G	101.01(13)

C006	O004	C00M	116.35(14)	C009	C00A	C00G	107.75(14)
C009	C005	C007	104.90(15)	C005	C00B	C008	117.78(16)
C00B	C005	C007	133.27(16)	C009	C00C	C006	117.73(16)
C00B	C005	C009	121.82(16)	C00E	C00D	S01	122.22(14)
O004	C006	C008	114.88(15)	C00E	C00D	C00H	119.54(18)
O004	C006	C00C	123.95(15)	C00H	C00D	S01	118.20(15)
C00C	C006	C008	121.15(16)	C00J	C00E	C00D	119.89(19)
O003	C007	C005	100.80(13)	C007	C00F	C00G	101.43(13)
O003	C007	C00F	101.30(14)	C00A	C00G	S01	107.55(12)
C005	C007	C00F	107.93(14)	C00F	C00G	S01	113.13(12)
O002	C008	C006	115.37(15)	C00F	C00G	C00A	101.32(14)
O002	C008	C00B	124.25(16)	C00K	C00H	C00D	119.9(2)
C00B	C008	C006	120.35(16)	C00L	C00J	C00E	120.5(2)
C005	C009	C00A	104.73(14)	C00L	C00K	C00H	120.0(2)
C00C	C009	C005	121.03(16)	C00K	C00L	C00J	120.19(18)

Table 6 Torsion Angles for **3cb**.

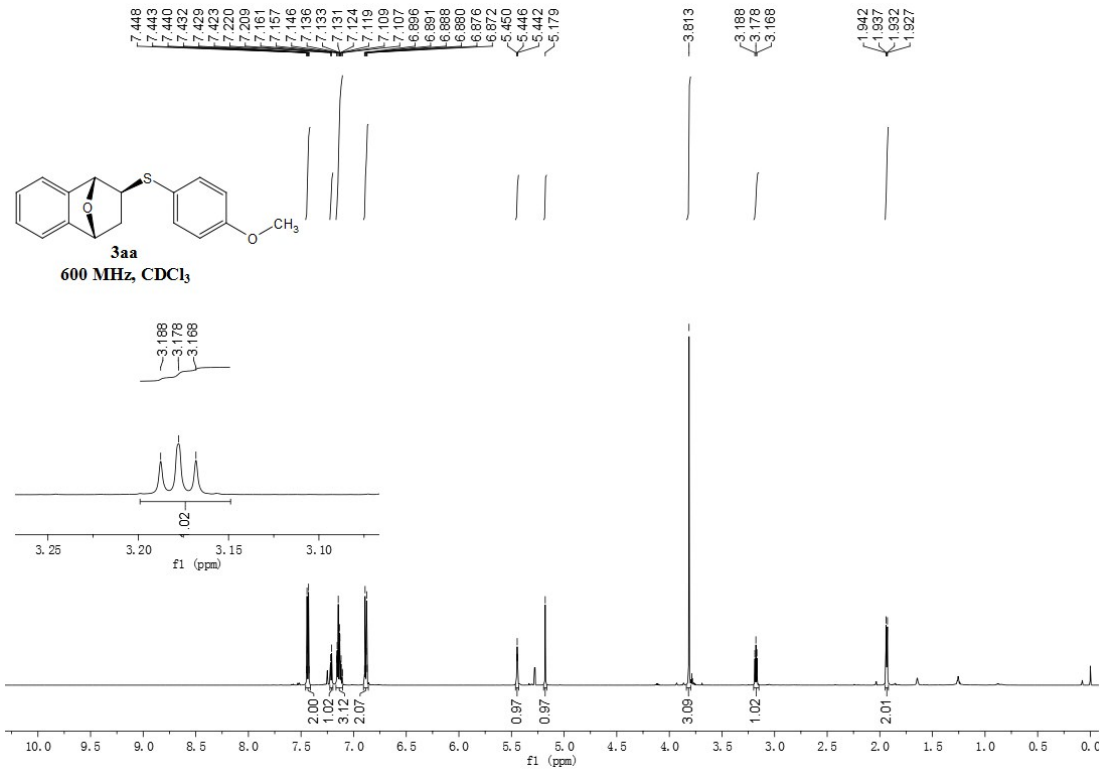
A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
S01	C00D	C00E	C00J	177.38(16)	C009	C00A	C00G	C00F	-70.20(17)
S01	C00D	C00H	C00K	-176.76(15)	C00A	O003	C007	C005	-52.34(14)
O002	C008	C00B	C005	-177.23(15)	C00A	O003	C007	C00F	58.62(14)
O003	C007	C00F	C00G	-35.20(16)	C00A	C009	C00C	C006	-177.20(17)
O003	C00A	C00G	S01	-83.39(14)	C00B	C005	C007	O003	-148.41(18)
O003	C00A	C00G	C00F	35.53(16)	C00B	C005	C007	C00F	105.8(2)
O004	C006	C008	O002	2.2(2)	C00B	C005	C009	C00A	-178.91(15)
O004	C006	C008	C00B	-175.91(15)	C00B	C005	C009	C00C	2.4(3)
O004	C006	C00C	C009	174.98(16)	C00C	C006	C008	O002	-179.20(15)
C005	C007	C00F	C00G	70.19(17)	C00C	C006	C008	C00B	2.7(3)
C005	C009	C00A	O003	-33.25(16)	C00C	C009	C00A	O003	145.13(19)
C005	C009	C00A	C00G	72.30(17)	C00C	C009	C00A	C00G	-109.3(2)
C005	C009	C00C	C006	1.0(3)	C00D	S01	C00G	C00A	168.32(12)
C006	C008	C00B	C005	0.7(2)	C00D	S01	C00G	C00F	57.28(14)
C007	O003	C00A	C009	52.51(13)	C00D	C00E	C00J	C00L	-0.5(3)
C007	O003	C00A	C00G	-58.31(14)	C00D	C00H	C00K	C00L	-1.0(3)
C007	C005	C009	C00A	-0.03(17)	C00E	C00D	C00H	C00K	0.9(3)
C007	C005	C009	C00C	-178.68(15)	C00E	C00J	C00L	C00K	0.4(3)
C007	C005	C00B	C008	178.25(17)	C00G	S01	C00D	C00E	39.98(18)
C007	C00F	C00G	S01	114.83(13)	C00G	S01	C00D	C00H	-142.39(15)
C007	C00F	C00G	C00A	0.00(17)	C00H	C00D	C00E	C00J	-0.2(3)

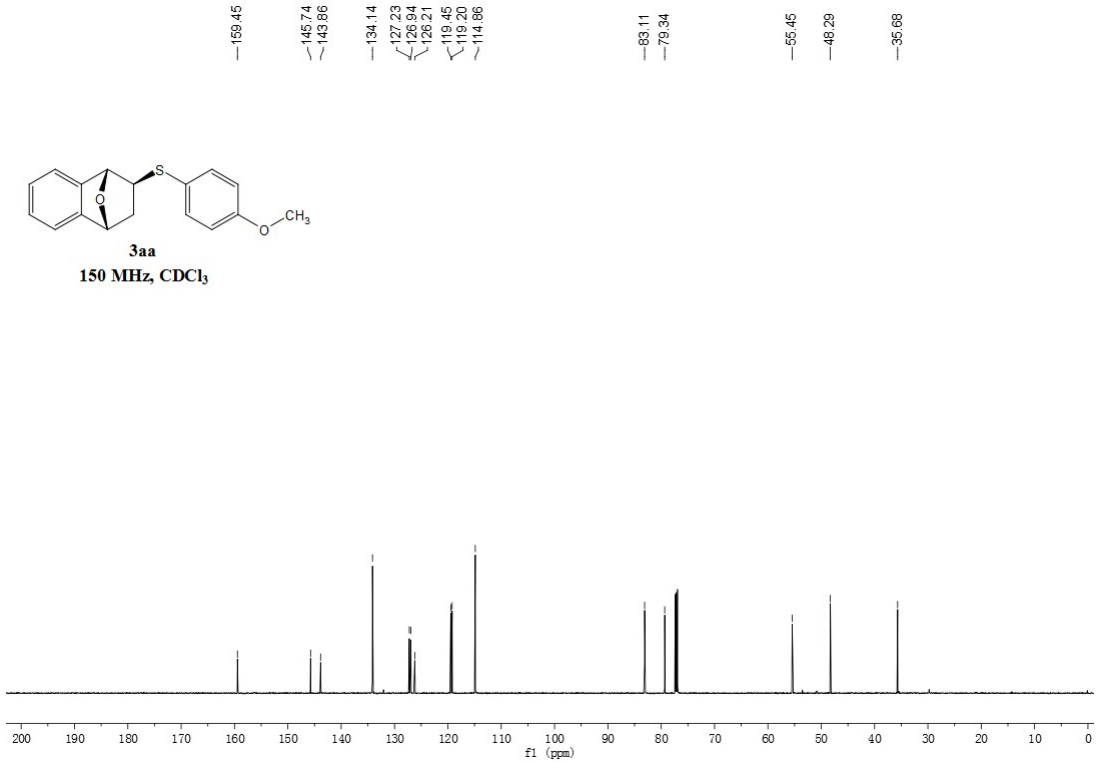
C008	C006	C00C	C009	-3.5(2)	C00H	C00K	C00L	C00J	0.3(3)
C009	C005	C007	O003	32.90(16)	C00I	O002	C008	C006	-176.24(15)
C009	C005	C007	C00F	-72.85(17)	C00I	O002	C008	C00B	1.8(2)
C009	C005	C00B	C008	-3.2(2)	C00M	O004	C006	C008	162.89(17)
C009	C00A	C00G	S01	170.88(12)	C00M	O004	C006	C00C	-15.7(2)

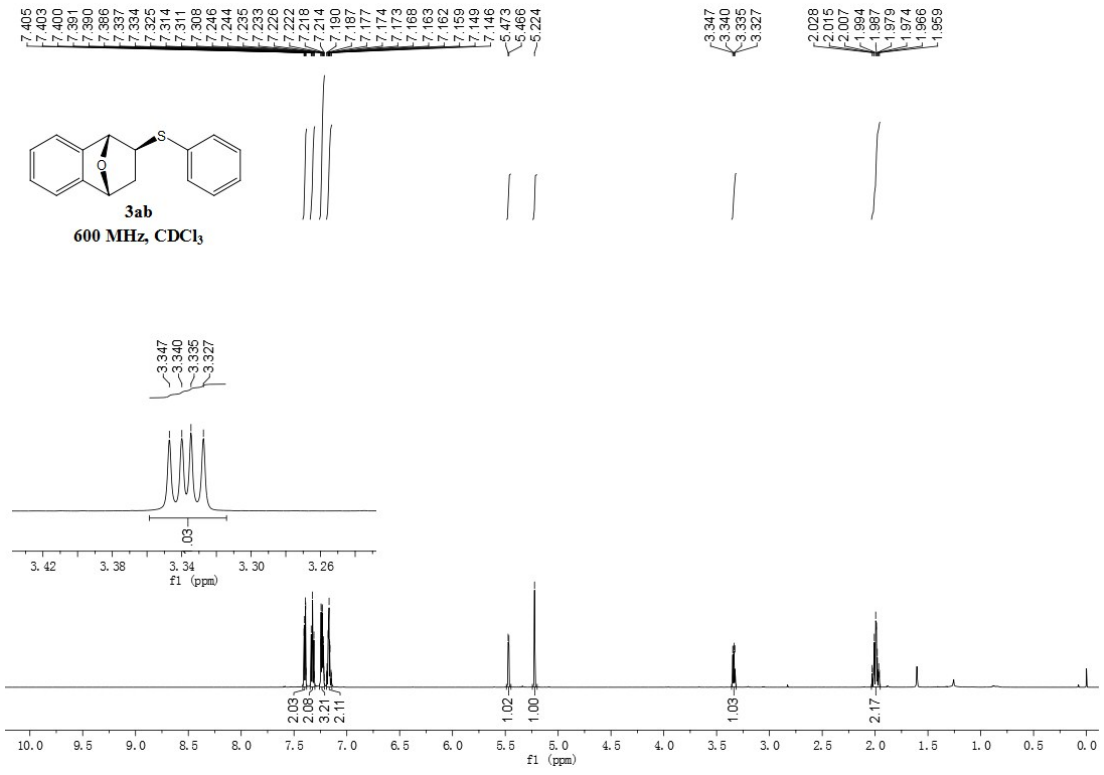
Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **3cb**.

Atom	***x***	***y***	***z***	**U(eq)**
H007	7430	5238	4622	31
H00A	12018	2333	4308	29
H00B	4142	4827	3820	29
H00C	9648	1445	3424	29
H00E	6774	331	5431	38
H00D	5590	2961	4876	32
H00F	7493	3572	5250	32
H00G	8194	1290	4698	30
H00H	11457	2373	6285	40
H00I	661	4969	2762	49
H00J	2627	5672	3090	49
H00K	845	4640	3318	49
H00L	4529	-181	6105	47
H00M	9211	1806	6960	47
H00N	5752	542	6866	48
H00O	8313	1154	2182	60
H00P	8694	455	2687	60
H00Q	9982	1818	2580	60

4. **Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra for products 3-6.**



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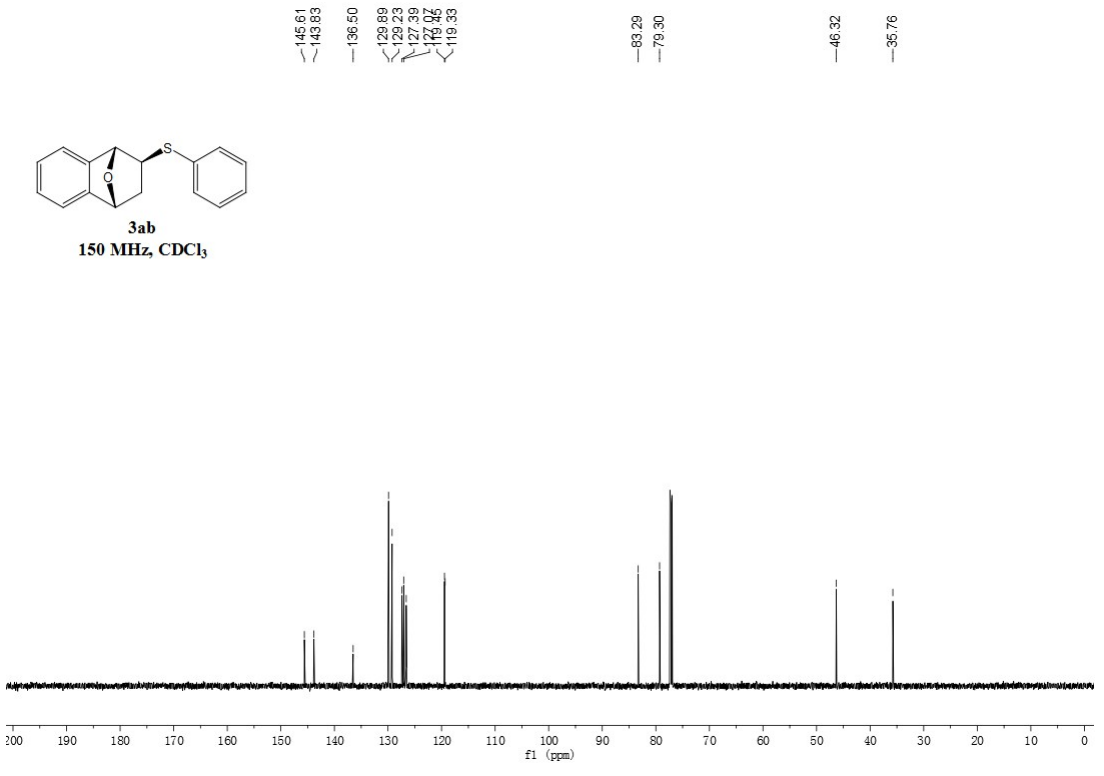
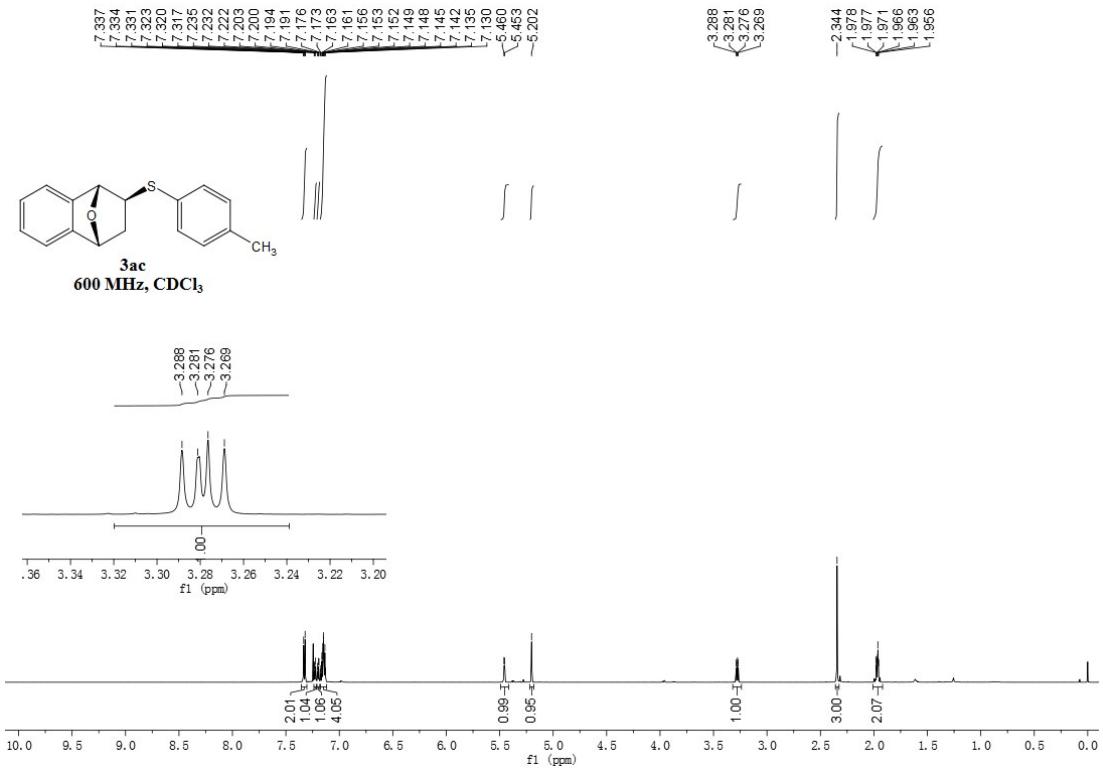
7.403
7.400
7.391
7.390
7.386
7.337
7.334
7.325
7.314
7.311
7.308
7.246
7.244
7.235
7.233
7.226
7.222
7.218
7.214
7.190
7.187
7.177
7.174
7.173
7.168
7.163
7.162
7.159
7.149
7.146
5.473
5.466
5.224
3.347
3.340
3.335
3.327
2.028
2.015
2.007
1.994
1.987
1.979
1.974
1.966
1.959
O
S
3ab
600 MHz, CDCl3
3.347
3.340
3.335
3.327
3.03
3.42
3.38
3.34
3.30
3.26
f1 (ppm)
2.03
2.08
3.21
2.11
1.02
1.00
1.03
2.17
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)


145.61
143.83
136.50
129.89
129.23
127.39
127.07
119.45
119.33
83.29
79.30
46.32
35.76
O
S
3ab
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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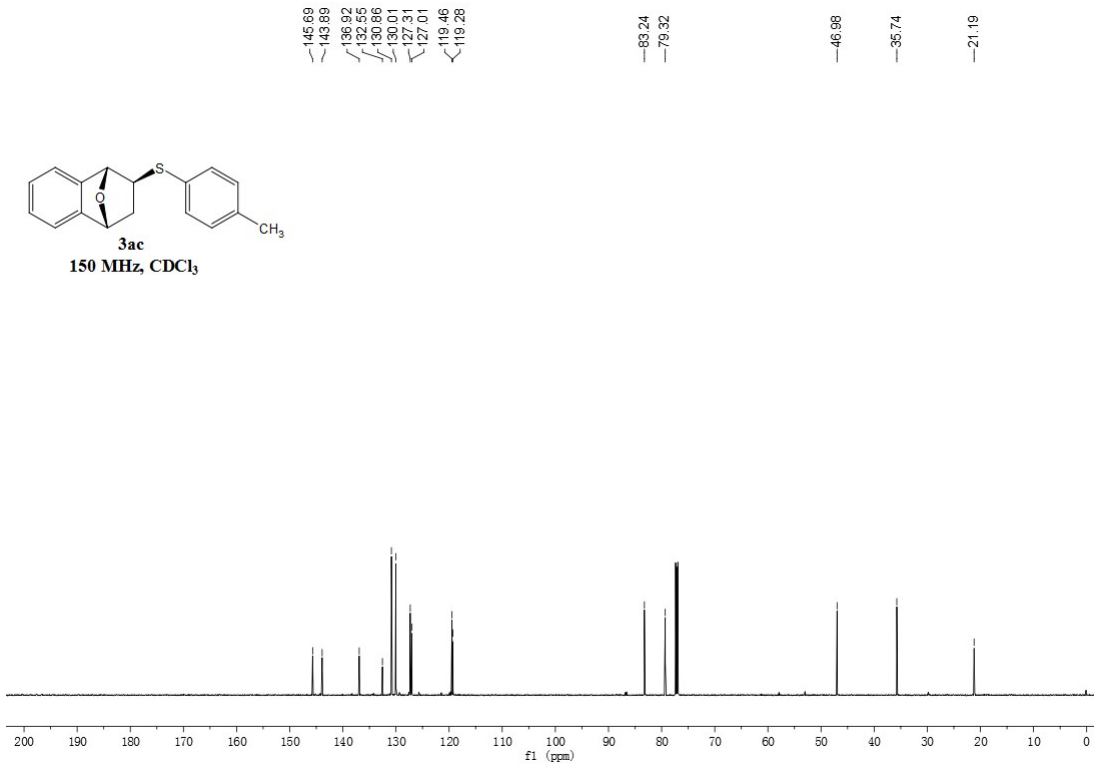
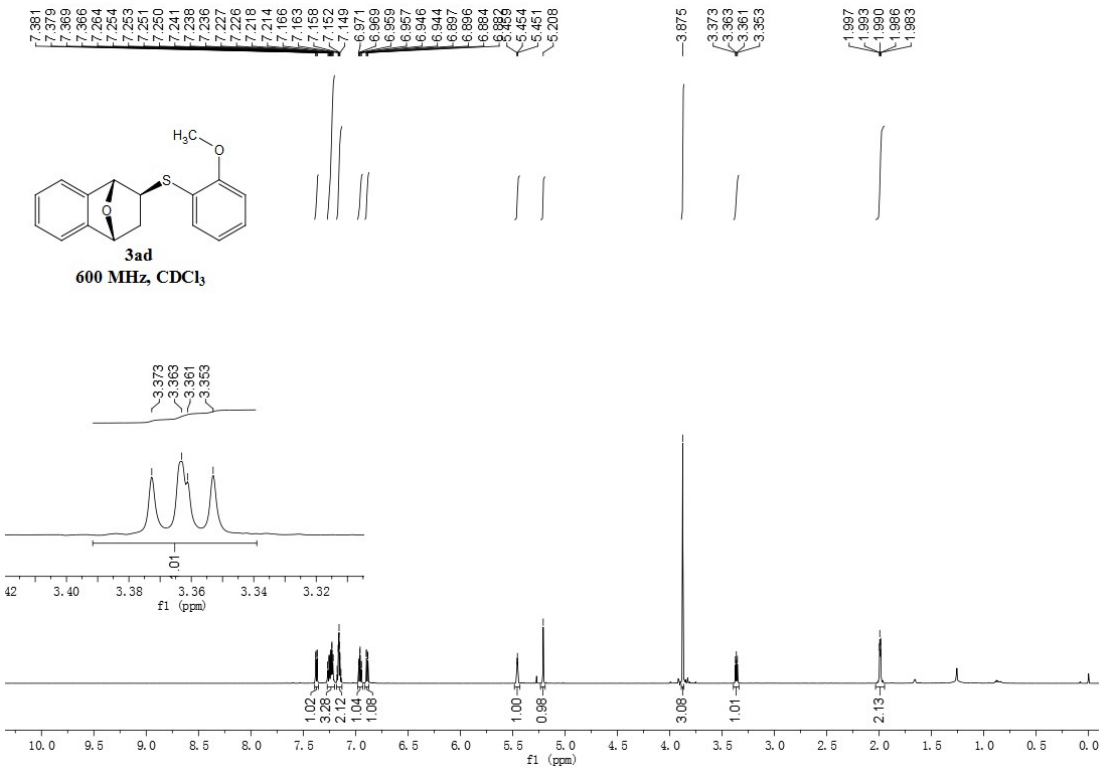
7.334
7.331
7.323
7.320
7.317
7.235
7.232
7.222
7.203
7.200
7.194
7.191
7.176
7.173
7.163
7.161
7.156
7.153
7.152
7.149
7.148
7.145
7.142
7.135
7.130
5.460
5.453
5.202
3.288
3.281
3.276
3.269
2.344
1.978
1.977
1.971
1.966
1.963
1.956
S
O
CH3
3ac
600 MHz, CDCl3
3.288
3.281
3.276
3.269
.00
.36 3.34 3.32 3.30 3.28 3.26 3.24 3.22 3.20
f1 (ppm)
2.01
1.04
1.06
4.05
0.99
0.95
1.00
3.00
2.07
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)


145.69
143.89
136.92
132.55
130.86
130.01
127.31
127.01
119.46
119.28
83.24
79.32
46.98
35.74
21.19
S
O
CH3
3ac
150 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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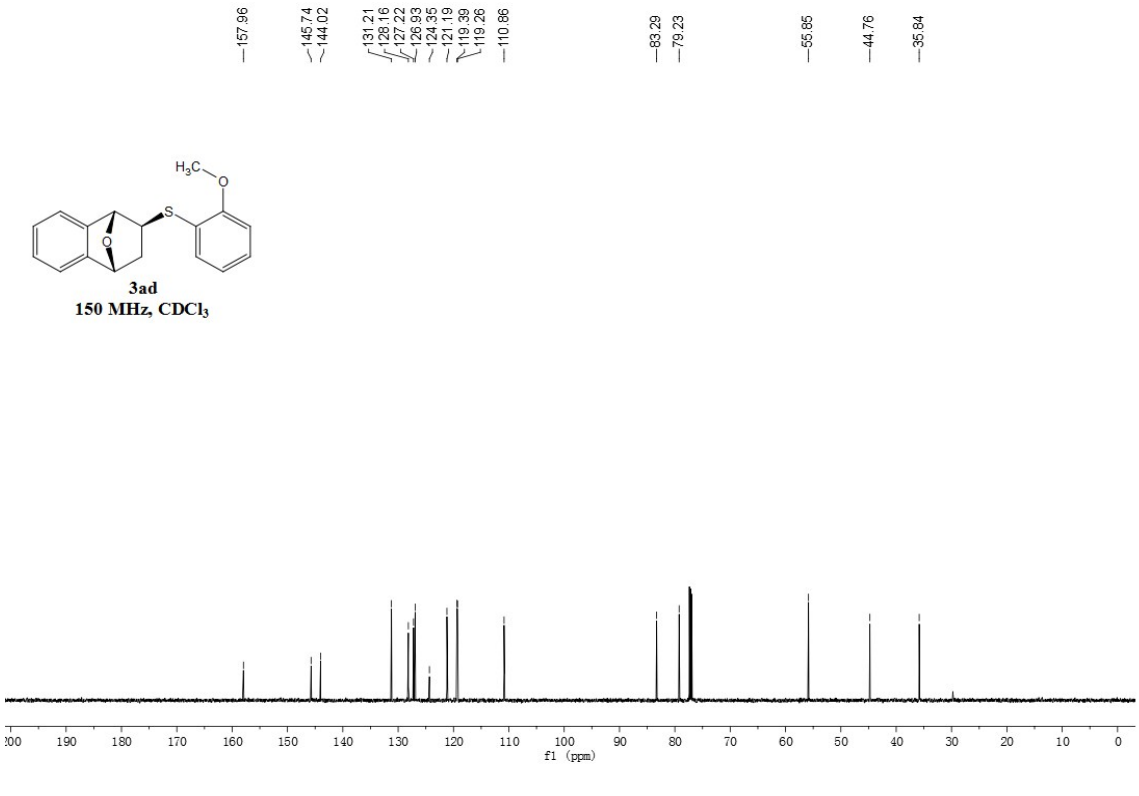
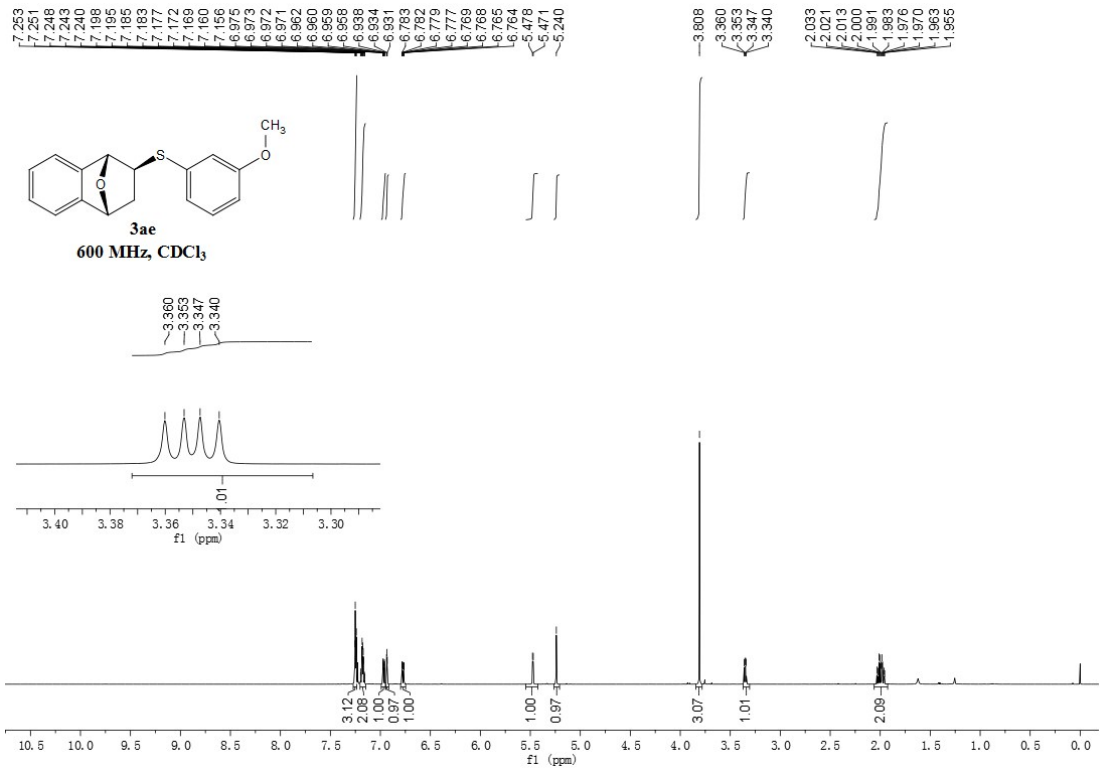
7.379
7.369
7.366
7.264
7.254
7.253
7.251
7.250
7.241
7.238
7.236
7.227
7.226
7.218
7.214
7.166
7.163
7.158
7.152
7.149
6.971
6.969
6.959
6.957
6.946
6.944
6.897
6.896
6.884
6.882
5.459
5.454
5.451
5.208
3.875
3.373
3.363
3.361
3.353
1.997
1.993
1.990
1.986
1.983
H3C
O
S
O
3ad
600 MHz, CDCl3
1.01
f1 (ppm)
1.02
3.28
2.12
1.04
1.08
1.00
0.98
3.08
1.01
2.13
f1 (ppm)


157.96
145.74
144.02
131.21
128.16
127.22
126.93
124.35
121.19
119.39
119.26
110.86
83.29
79.23
55.85
44.76
35.84
H3C
O
S
O
3ad
150 MHz, CDCl3
f1 (ppm)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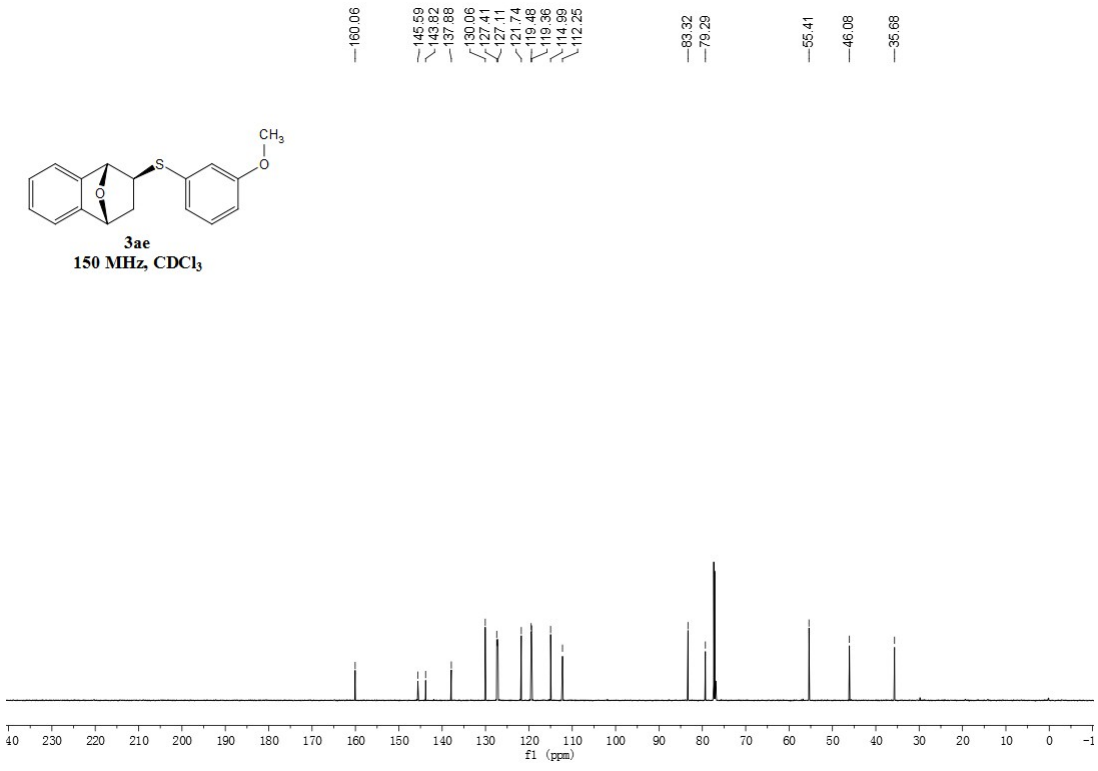
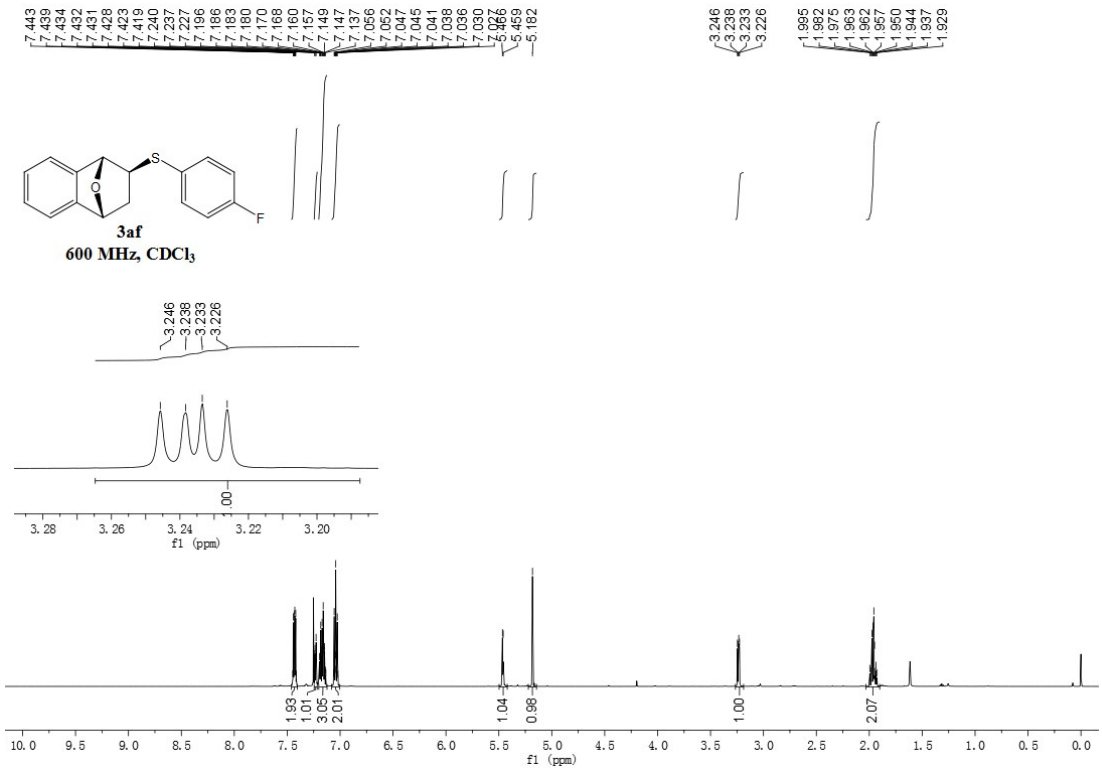
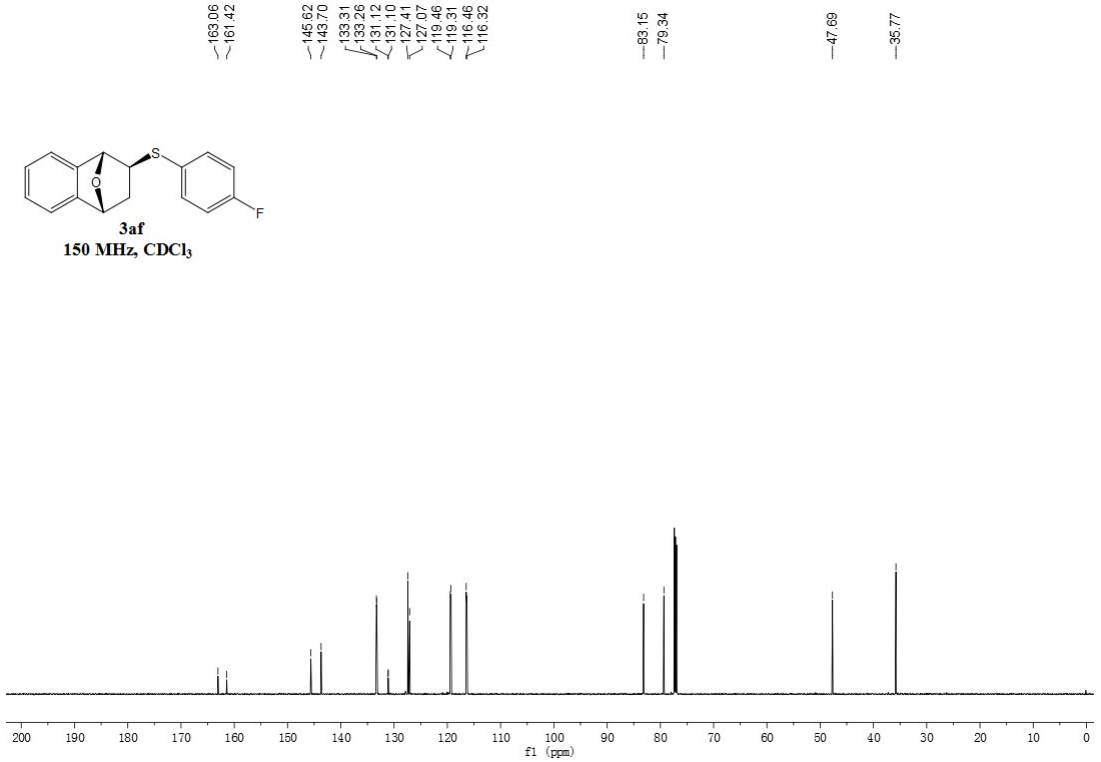
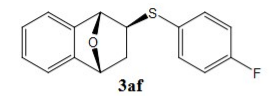
7.251
7.248
7.243
7.240
7.198
7.195
7.185
7.183
7.177
7.172
7.169
7.160
7.156
6.975
6.973
6.972
6.971
6.962
6.960
6.959
6.958
6.938
6.934
6.931
6.783
6.782
6.779
6.777
6.769
6.768
6.765
6.764
5.478
5.471
5.240
3.808
3.360
3.353
3.347
3.340
2.033
2.021
2.013
2.000
1.991
1.983
1.976
1.970
1.963
1.955
CH3
O
S
O
3ae
600 MHz, CDCl3
3.360
3.353
3.347
3.340
1.01
3.40
3.38
3.36
3.34
3.32
3.30
f1 (ppm)
3.12
2.08
1.00
0.97
1.00
1.00
0.97
3.07
1.01
2.09
10.5
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)


160.06
145.59
143.82
137.88
130.06
127.41
127.11
121.74
119.48
119.36
114.99
112.25
83.32
79.29
55.41
46.08
35.68
CH3
O
S
O
3ae
150 MHz, CDCl3
240
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

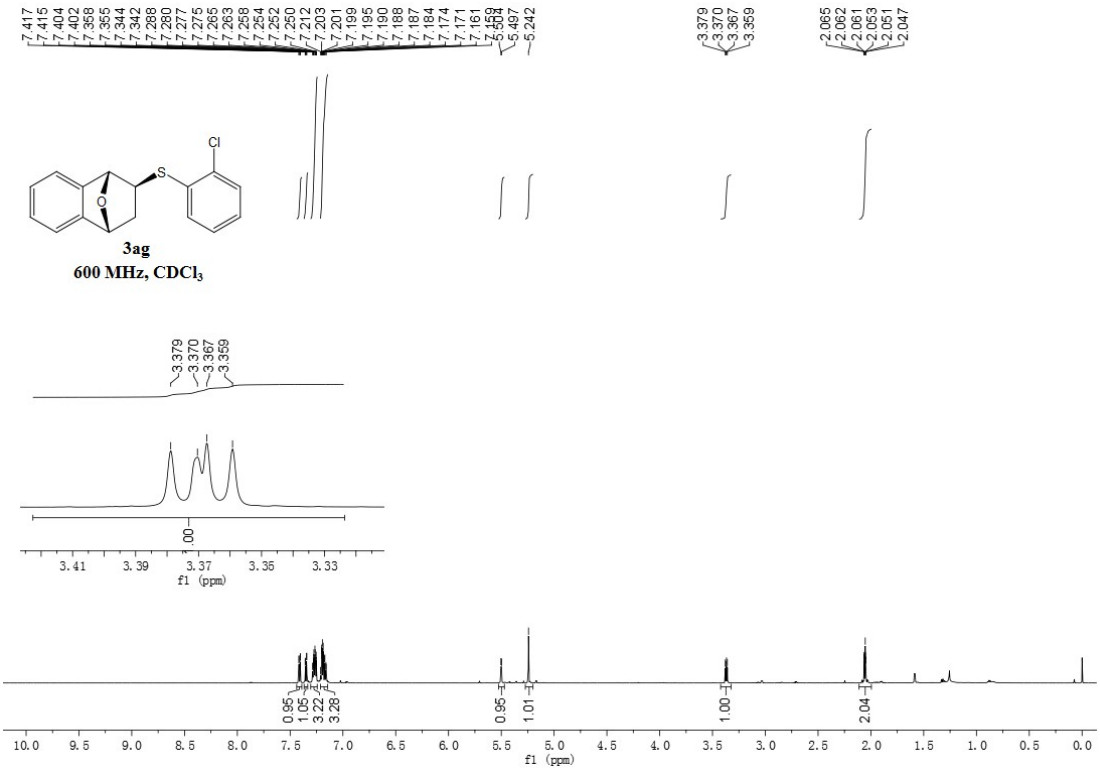

7.443
7.439
7.434
7.432
7.431
7.428
7.423
7.419
7.240
7.237
7.227
7.196
7.186
7.183
7.180
7.170
7.168
7.160
7.157
7.149
7.147
7.137
7.056
7.052
7.047
7.045
7.041
7.038
7.030
5.459
5.182
3.246
3.238
3.233
3.226
1.995
1.982
1.975
1.963
1.962
1.957
1.950
1.944
1.937
1.929
S
O
F
3af
600 MHz, CDCl3
3.246
3.238
3.233
3.226
1.00
3.28
3.26
3.24
3.22
3.20
f1 (ppm)
1.93
1.01
3.05
2.01
1.04
0.98
1.00
2.07
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)


163.06
161.42
145.62
143.70
133.31
133.26
131.12
131.10
127.41
127.07
119.46
119.31
116.46
116.32
83.15
79.34
47.69
35.77
S
O
F
3af
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



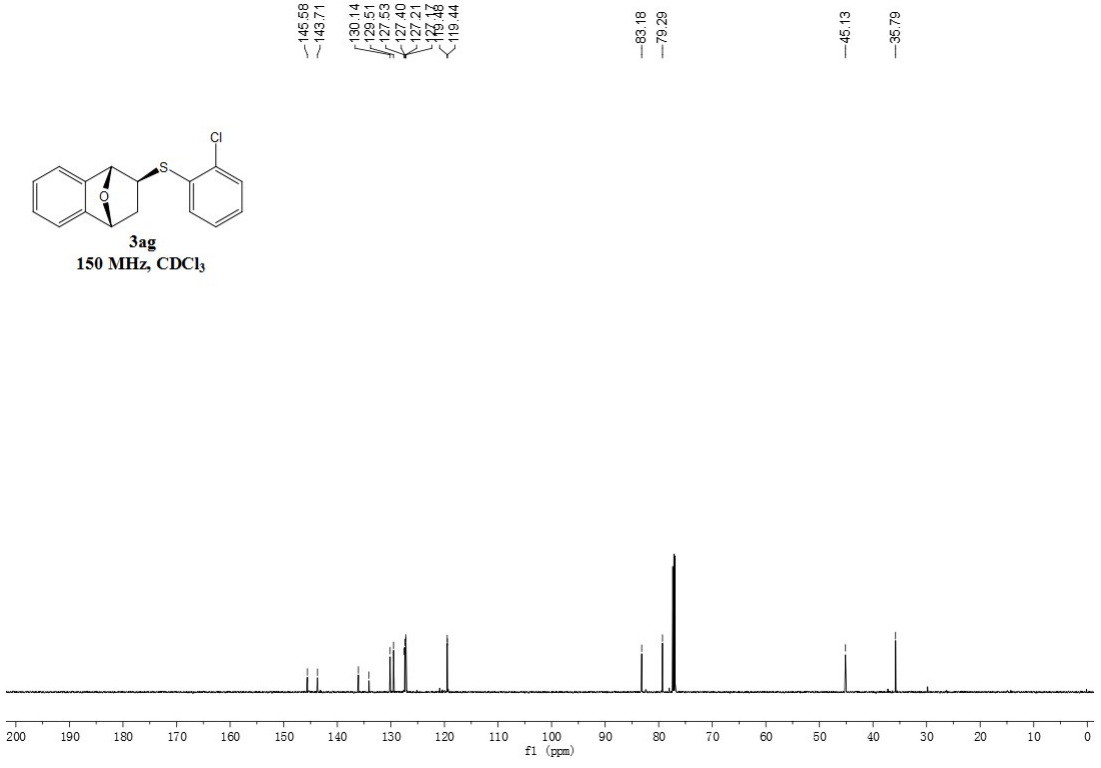
3af

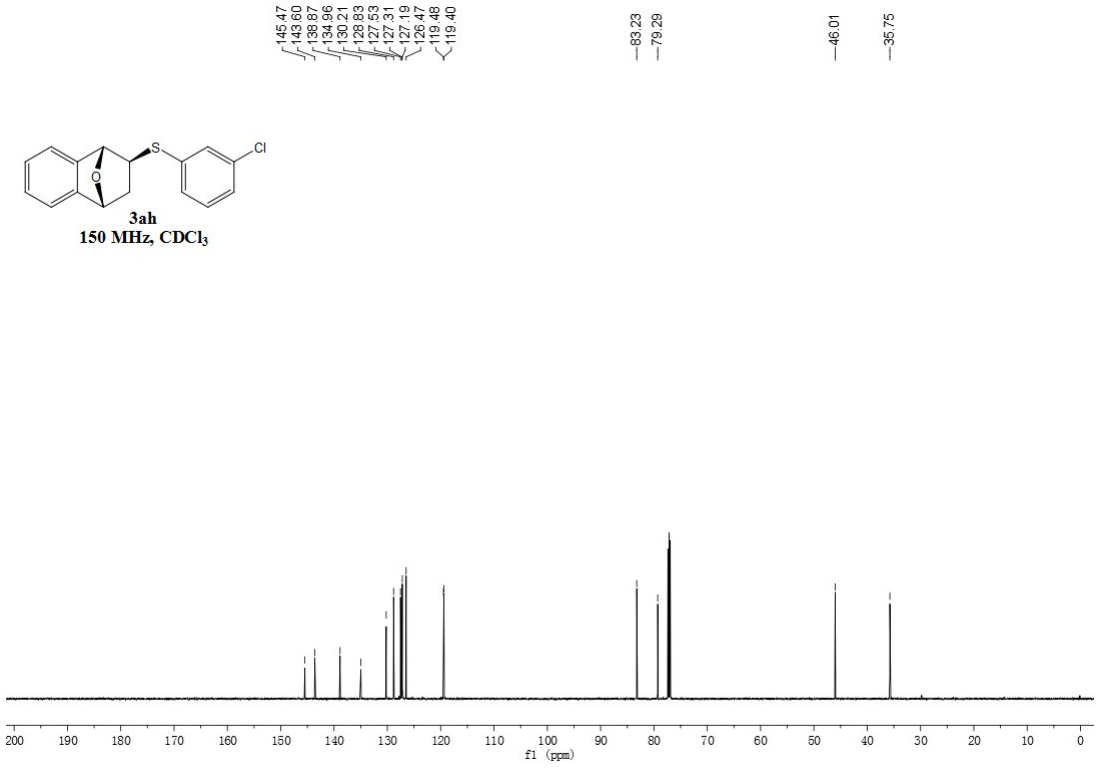
564 MHz, $CDCl_3$

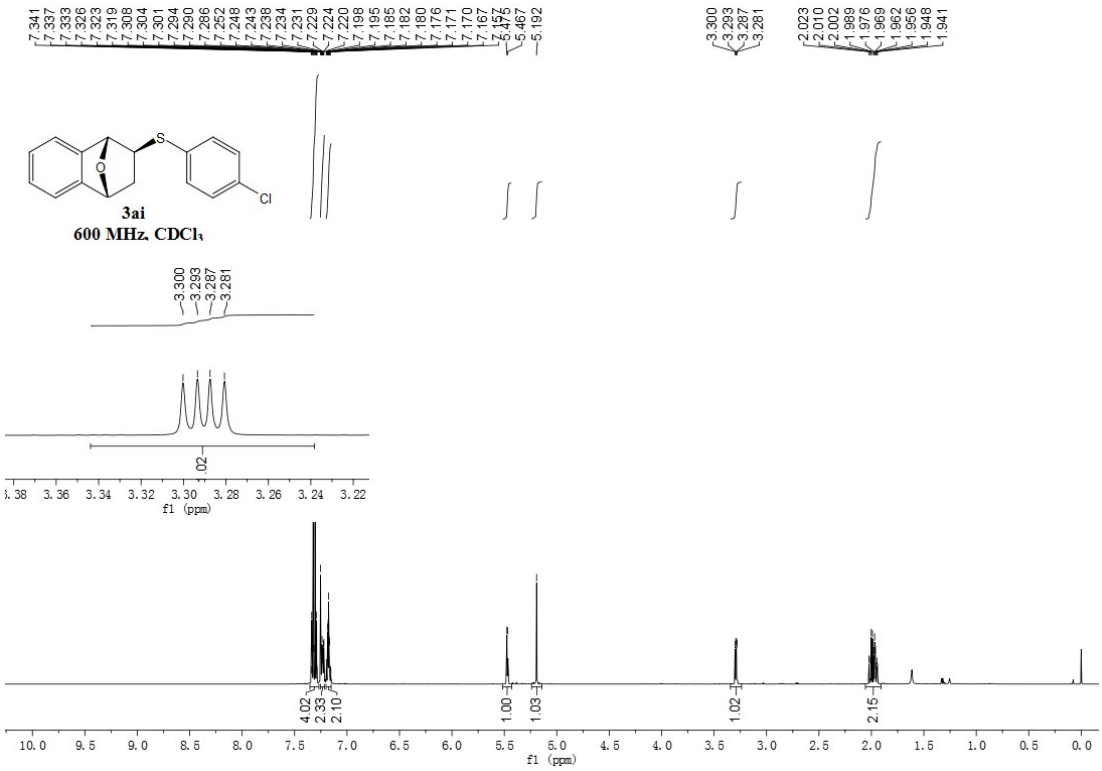


3ag

600 MHz, $CDCl_3$


145.58
143.71
130.14
129.51
127.53
127.40
127.21
127.17
119.48
119.44
83.18
79.29
45.13
35.79
Cl
S
O
3ag
150 MHz, CDCl3
f1 (ppm)
7.341
7.339
7.337
7.336
7.275
7.271
7.267
7.266
7.260
7.252
7.248
7.245
7.245
7.241
7.237
7.235
7.231
7.228
7.205
7.202
7.196
7.193
7.190
7.189
7.186
7.182
7.179
5.482
5.474
5.221
3.342
3.335
3.329
3.322
2.046
2.033
2.025
2.013
1.991
1.984
1.976
1.970
1.963
1.963
1.956
Cl
S
O
3ah
600 MHz, CDCl3
3.342
3.335
3.329
3.322
1.00
f1 (ppm)
0.95
4.33
3.03
1.00
0.99
1.00
2.09
f1 (ppm)


145.47
143.60
138.87
134.96
130.21
128.83
127.53
127.31
127.19
126.47
119.48
119.40
83.23
79.29
46.01
35.75
S
O
Cl
3ah
150 MHz, CDCl3
f1 (ppm)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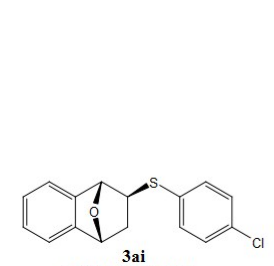
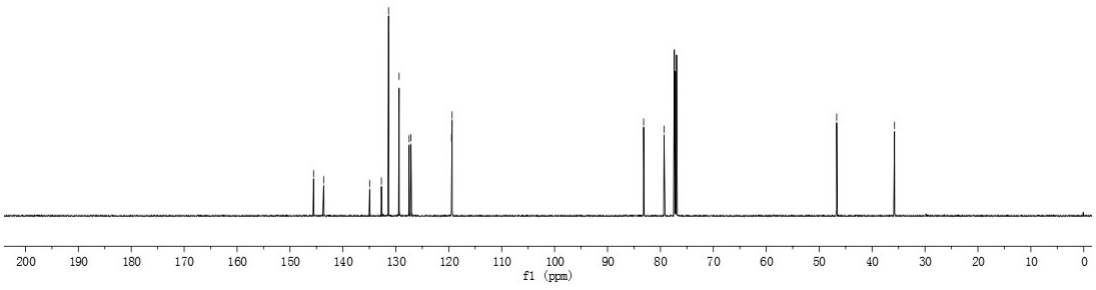
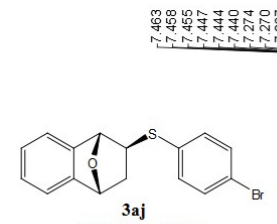
7.337
7.333
7.326
7.323
7.319
7.308
7.304
7.301
7.294
7.290
7.286
7.252
7.248
7.243
7.238
7.234
7.231
7.229
7.224
7.220
7.198
7.195
7.185
7.182
7.180
7.176
7.171
7.170
7.167
5.475
5.467
5.192
3.300
3.293
3.287
3.281
2.023
2.010
2.002
1.989
1.976
1.969
1.962
1.956
1.948
1.941
S
O
Cl
3ai
600 MHz, CDCl3
1.02
f1 (ppm)
4.02
2.33
2.10
1.00
1.03
1.02
2.15
f1 (ppm)

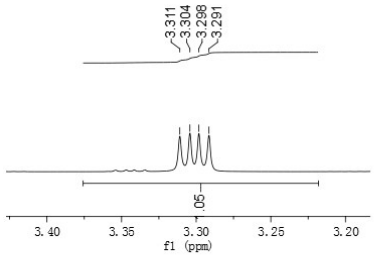


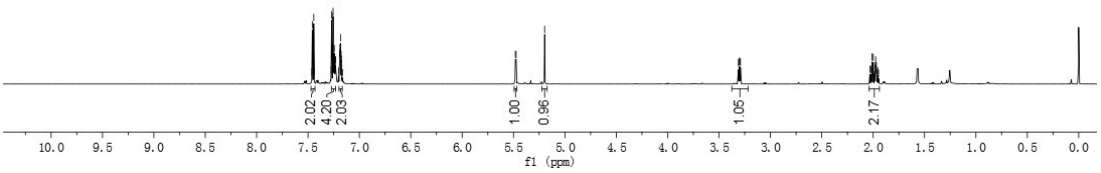
3ai
150 MHz, $CDCl_3$

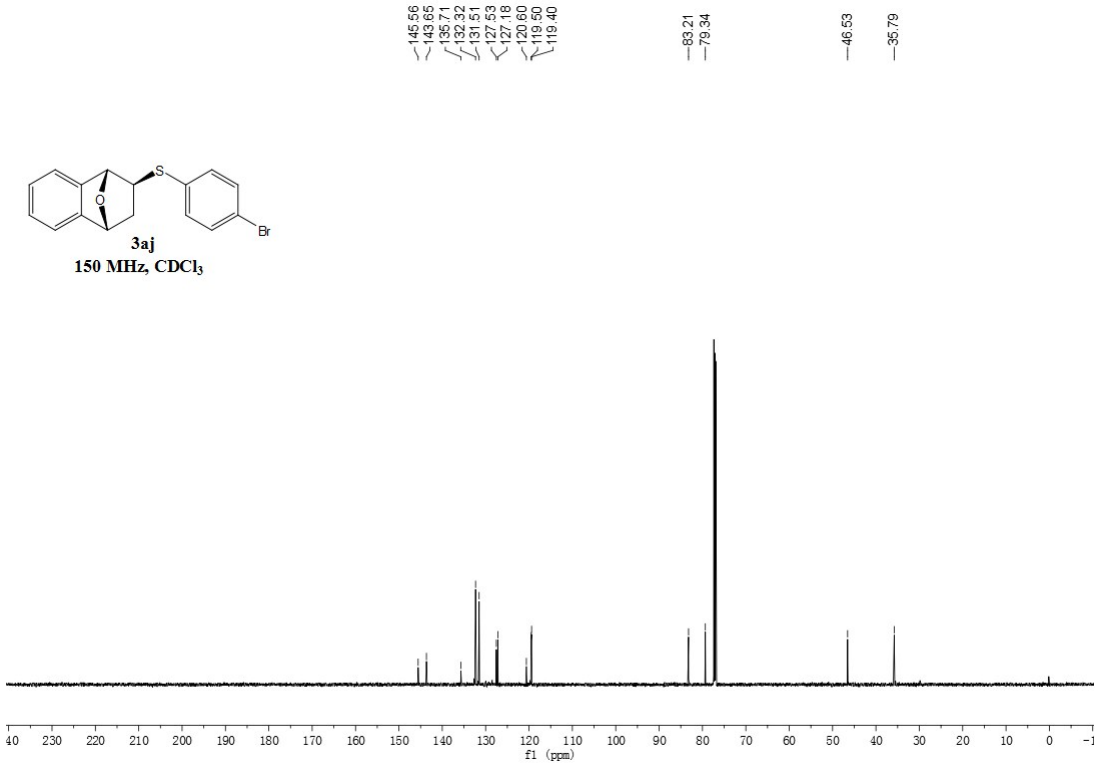


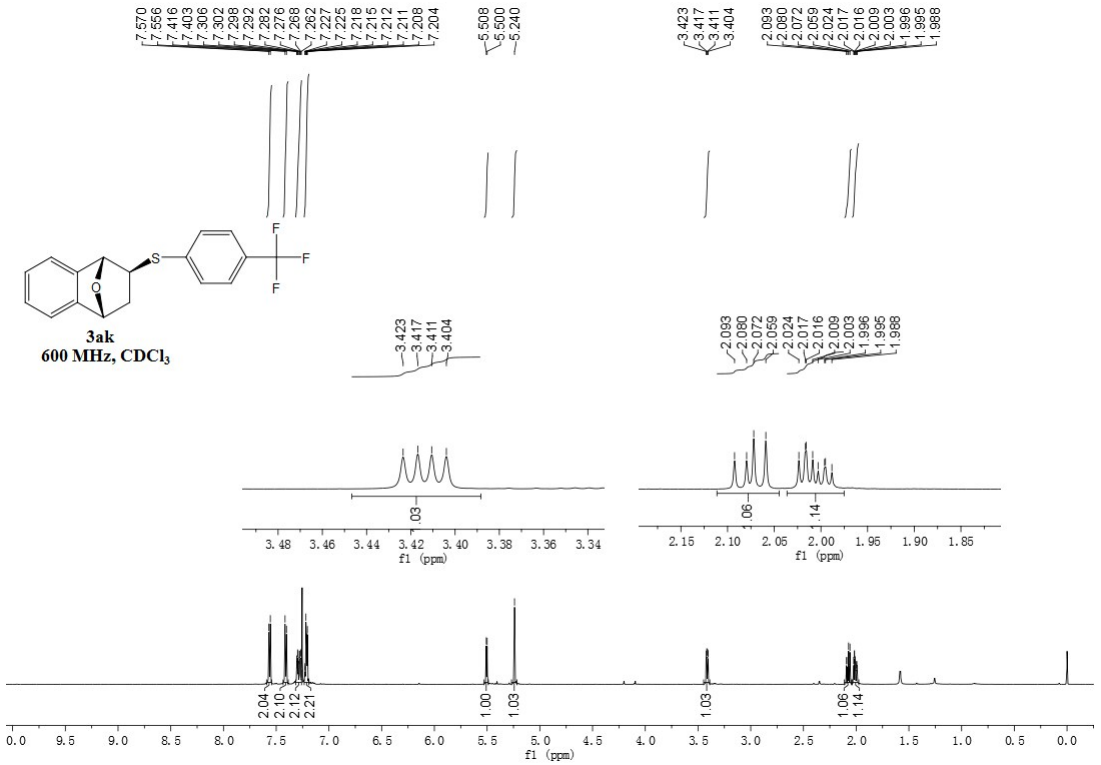


3aj
600 MHz, $CDCl_3$






145.56
143.65
135.71
132.32
131.51
127.53
127.18
120.60
119.50
119.40
83.21
79.34
46.53
35.79
S
O
Br
3aj
150 MHz, CDCl3
f1 (ppm)


7.570
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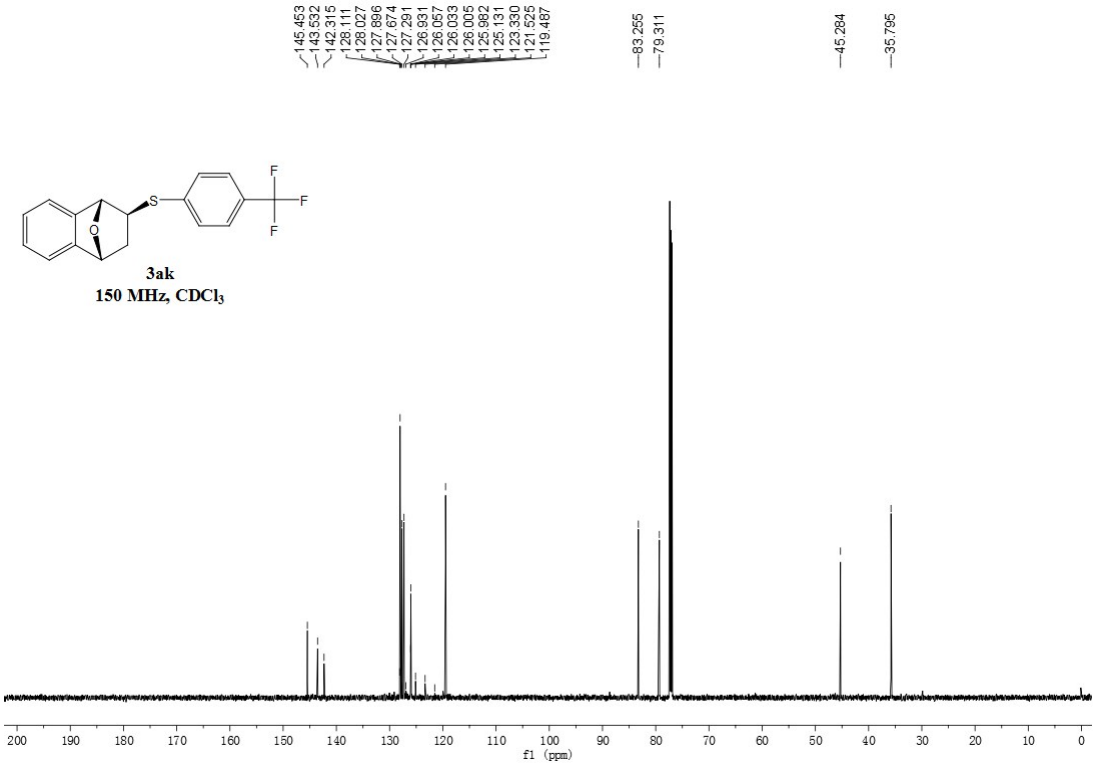
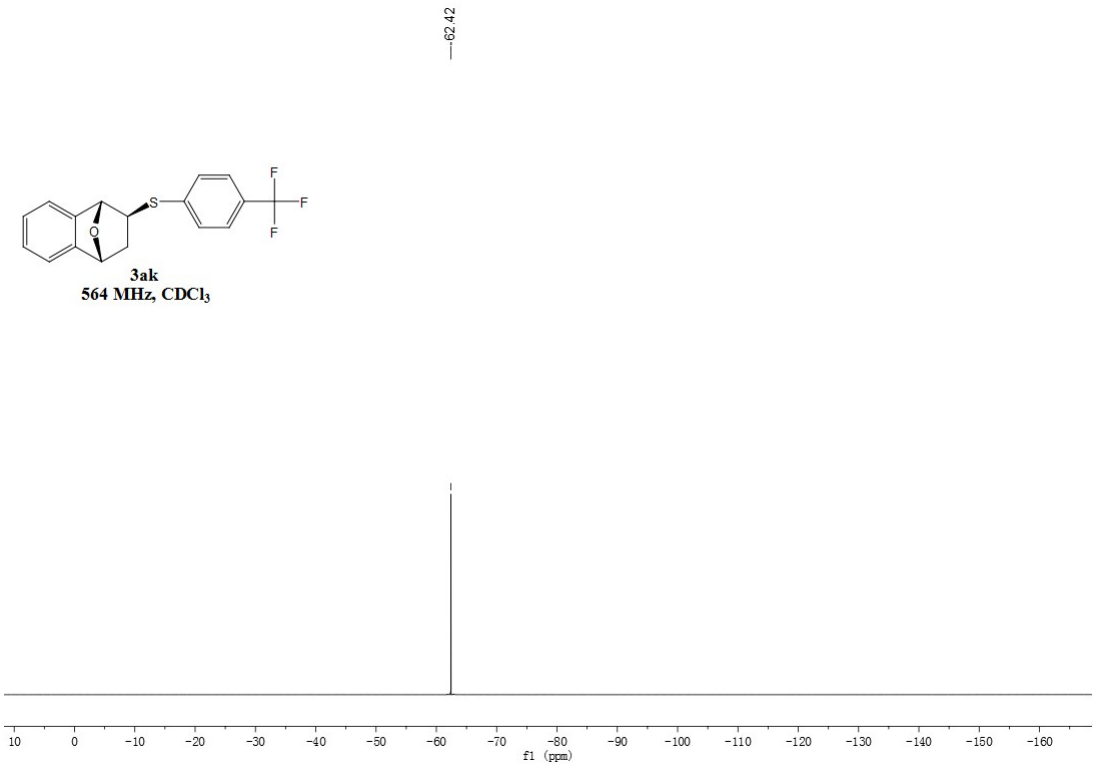
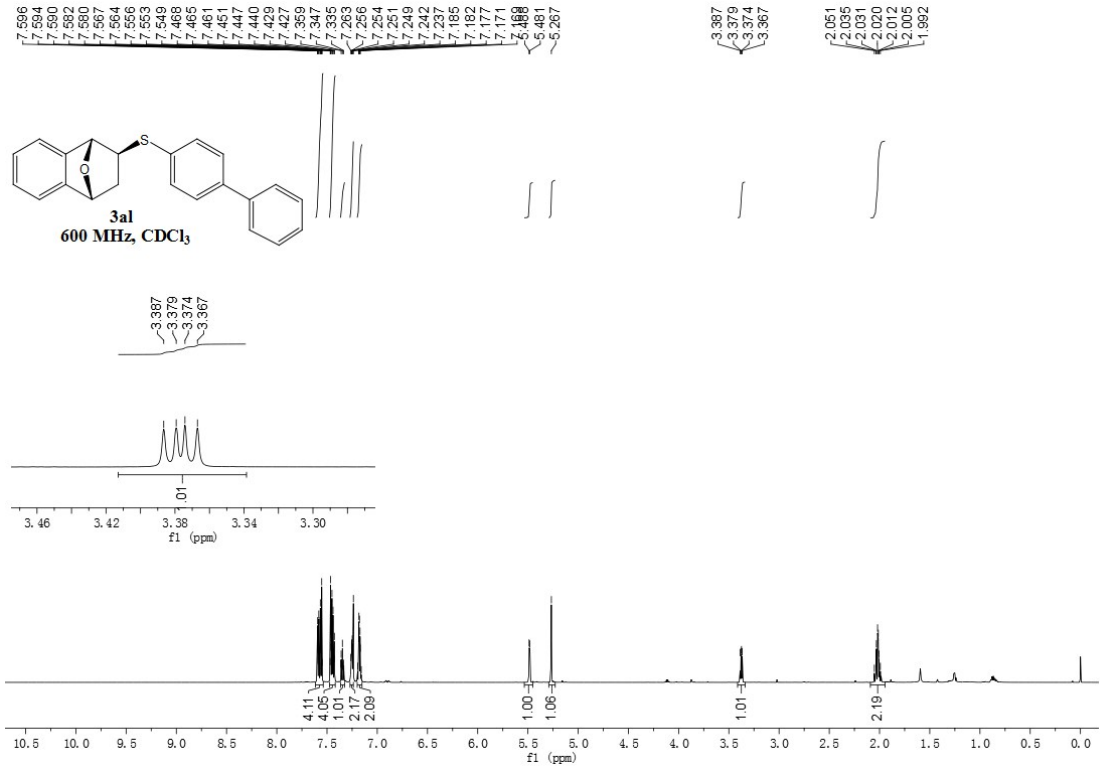
7.306
7.302
7.298
7.292
7.282
7.276
7.268
7.262
7.227
7.225
7.218
7.215
7.212
7.211
7.208
7.204
5.508
5.500
5.240
3.423
3.417
3.411
3.404
2.093
2.080
2.072
2.059
2.024
2.017
2.016
2.009
2.003
1.996
1.995
1.988
S
O
F
F
F
3ak
600 MHz, CDCl3
03
06
14
2.04
2.10
2.12
2.21
1.00
1.03
1.03
1.06
1.14
f1 (ppm)

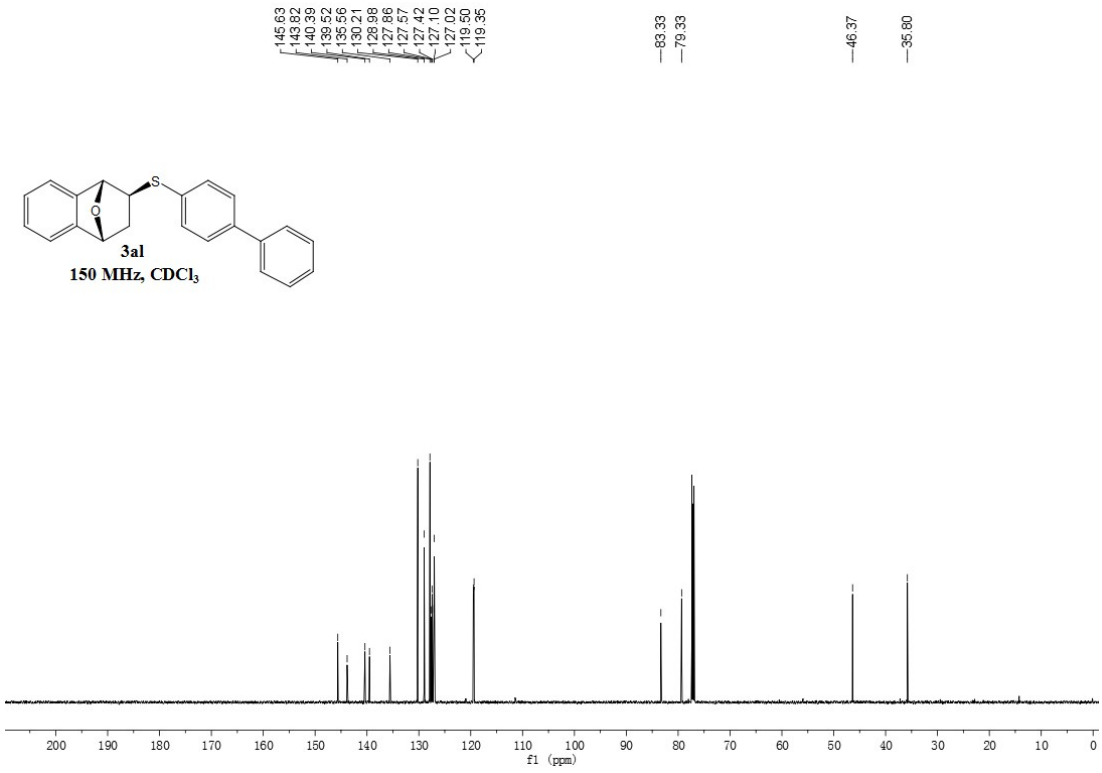


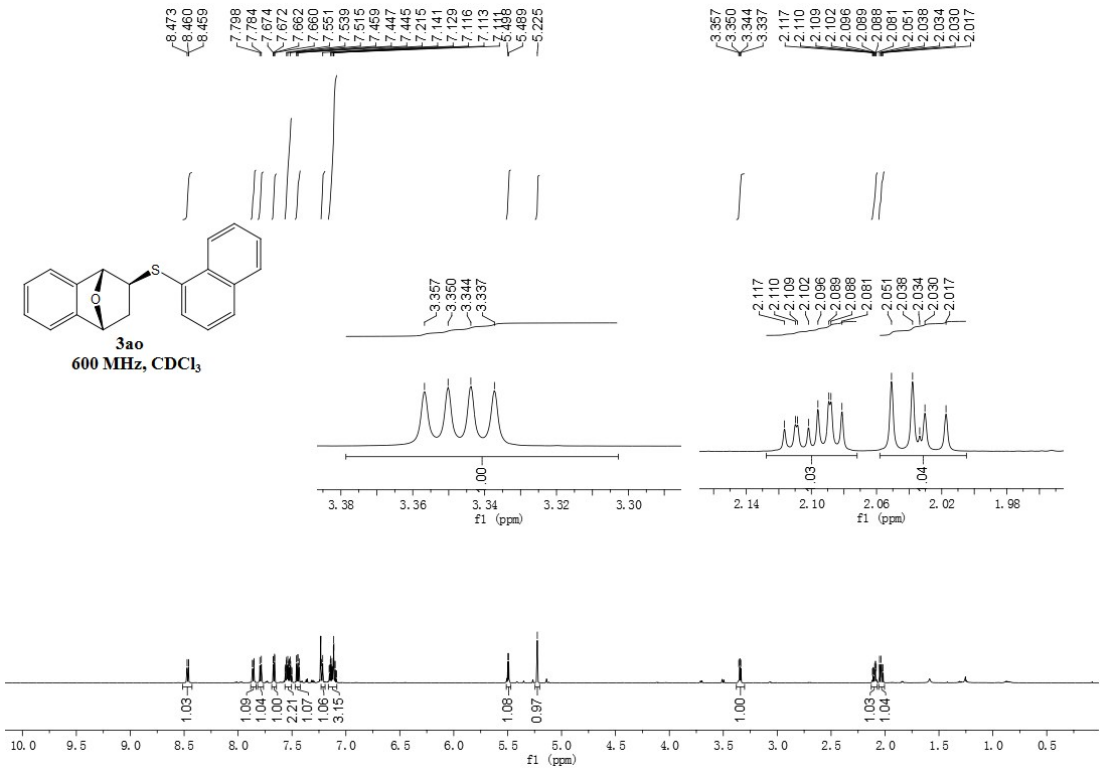
3ak
150 MHz, $CDCl_3$



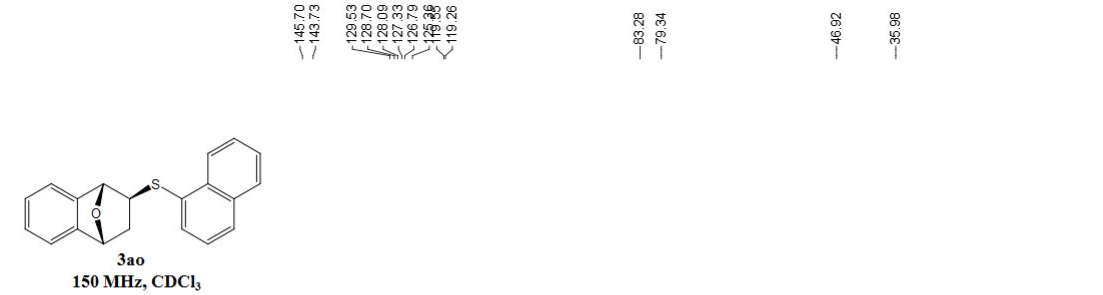
3ak
564 MHz, $CDCl_3$

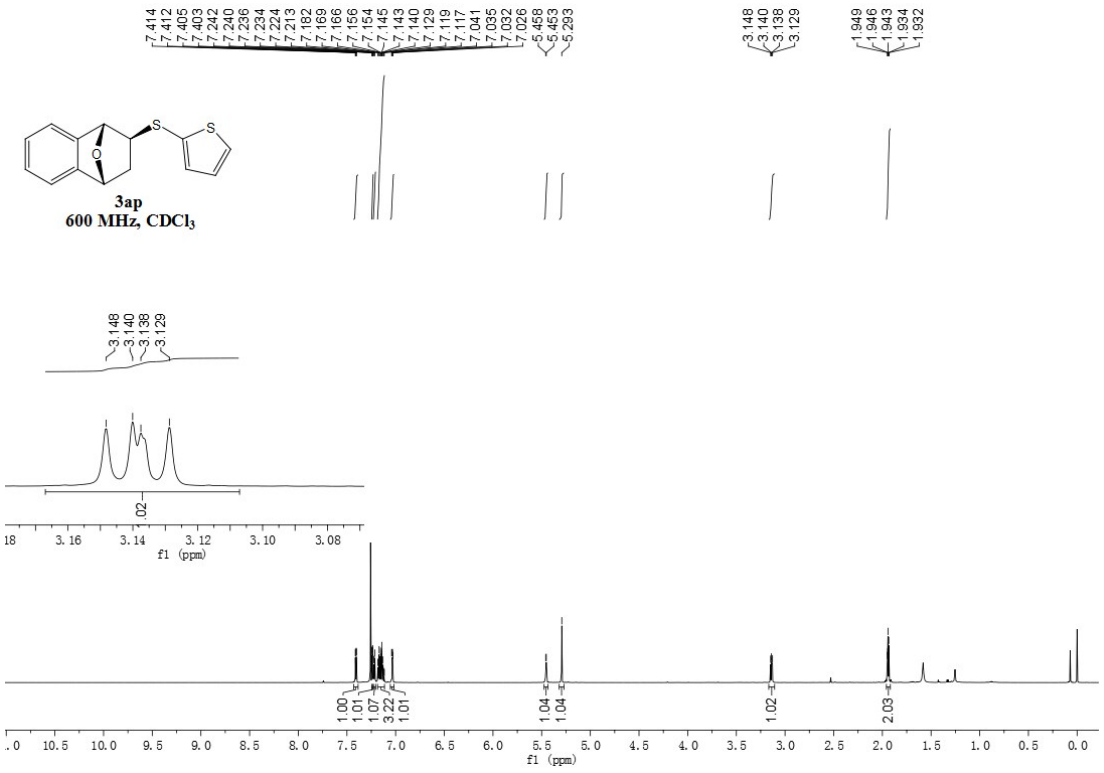

7.596
7.594
7.590
7.582
7.580
7.567
7.564
7.556
7.553
7.549
7.468
7.465
7.461
7.451
7.447
7.440
7.429
7.427
7.359
7.347
7.335
7.263
7.256
7.254
7.251
7.249
7.242
7.237
7.185
7.182
7.177
7.171
5.488
5.481
5.267
3.387
3.379
3.374
3.367
2.051
2.035
2.031
2.020
2.012
2.005
1.992
S
O
3al
600 MHz, CDCl3
3.387
3.379
3.374
3.367
1.01
3.46
3.42
3.38
3.34
3.30
f1 (ppm)
4.11
4.05
1.01
2.17
2.09
1.00
1.06
1.01
2.19
10.5
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)

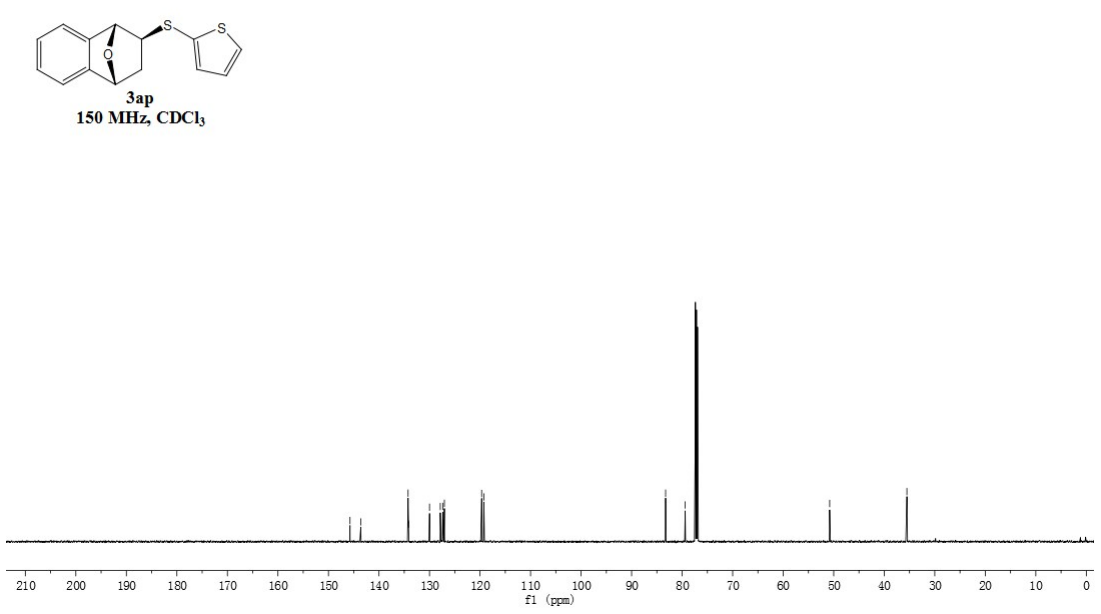

145.63
143.82
140.39
139.52
135.56
130.21
128.98
127.86
127.57
127.42
127.10
127.02
119.50
119.35
83.33
79.33
46.37
35.80
S
O
3al
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

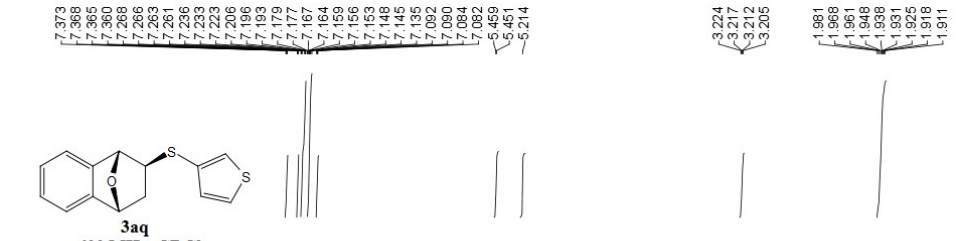

8.473
8.460
8.459
7.798
7.784
7.674
7.672
7.662
7.660
7.551
7.539
7.515
7.459
7.447
7.445
7.215
7.141
7.129
7.116
7.113
7.111
5.498
5.489
5.225
3.357
3.350
3.344
3.337
2.117
2.110
2.109
2.102
2.096
2.089
2.088
2.081
2.051
2.038
2.034
2.030
2.017
O
S
3ao
600 MHz, CDCl3
1.00
0.03
0.04
3.38
3.36
3.34
3.32
3.30
2.14
2.10
2.06
2.02
1.98
f1 (ppm)

1.03
1.09
1.04
1.00
2.21
1.07
1.06
3.15
1.08
0.97
1.00
1.03
1.04
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
f1 (ppm)

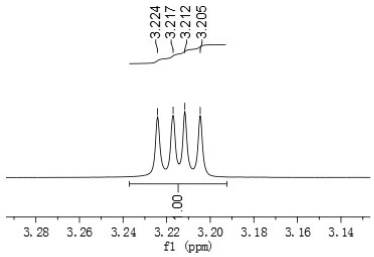

145.70
143.73
129.53
128.70
128.09
127.33
126.79
119.55
119.26
83.28
79.34
46.92
35.98
O
S
3ao
150 MHz, CDCl3
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

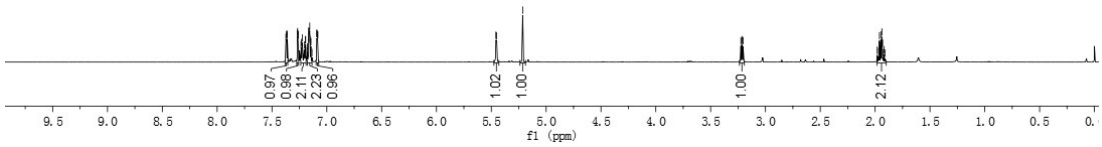

7.414
7.412
7.405
7.403
7.242
7.240
7.236
7.234
7.224
7.213
7.182
7.169
7.166
7.156
7.154
7.145
7.143
7.140
7.129
7.119
7.117
7.041
7.035
7.032
7.026
5.458
5.453
5.293
3.148
3.140
3.138
3.129
1.949
1.946
1.943
1.934
1.932
3ap
600 MHz, CDCl3
1.00
1.01
1.07
3.22
1.01
1.04
1.04
1.02
2.03
f1 (ppm)

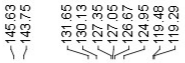

145.74
143.60
134.24
134.13
130.00
127.86
127.36
127.05
119.68
119.23
83.27
79.40
50.80
35.51
3ap
150 MHz, CDCl3
f1 (ppm)



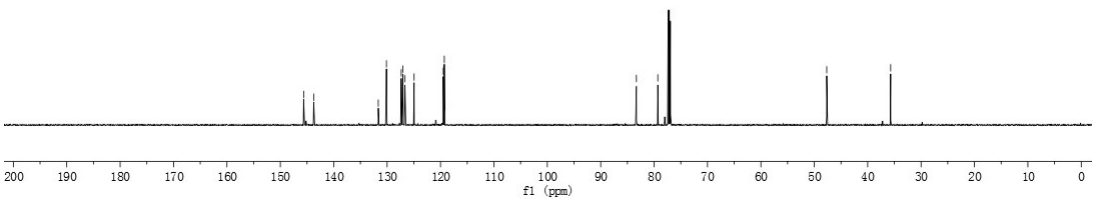
3aq
600 MHz, $CDCl_3$

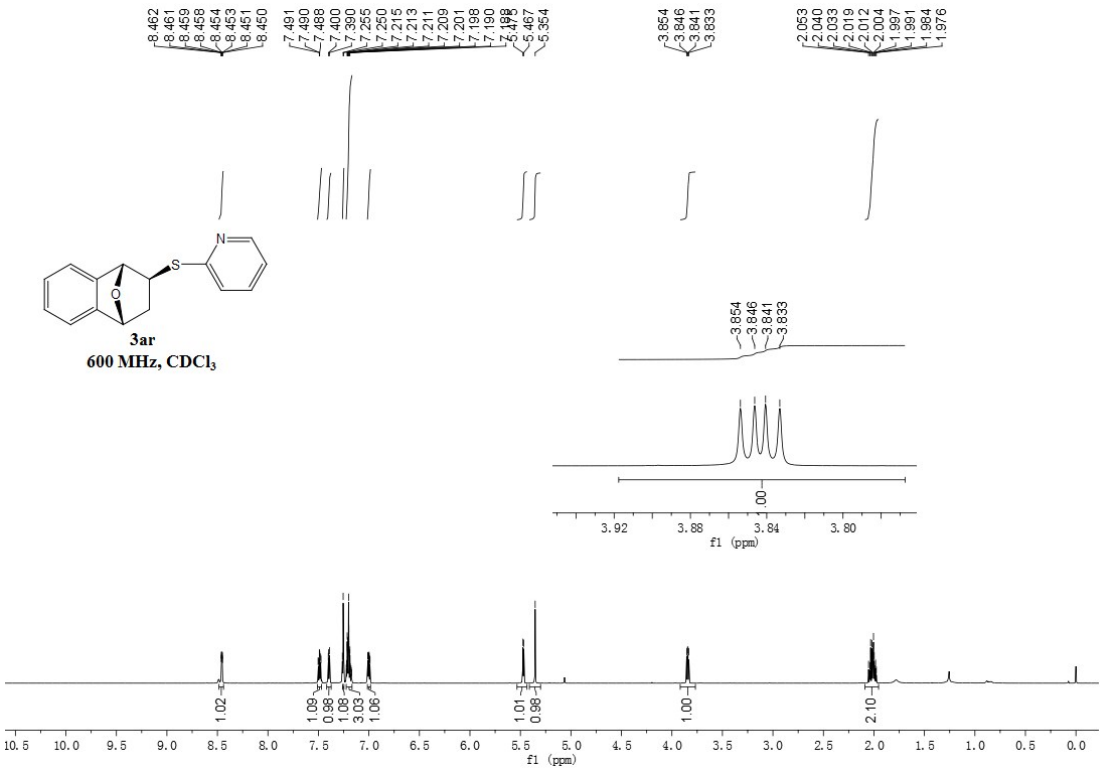


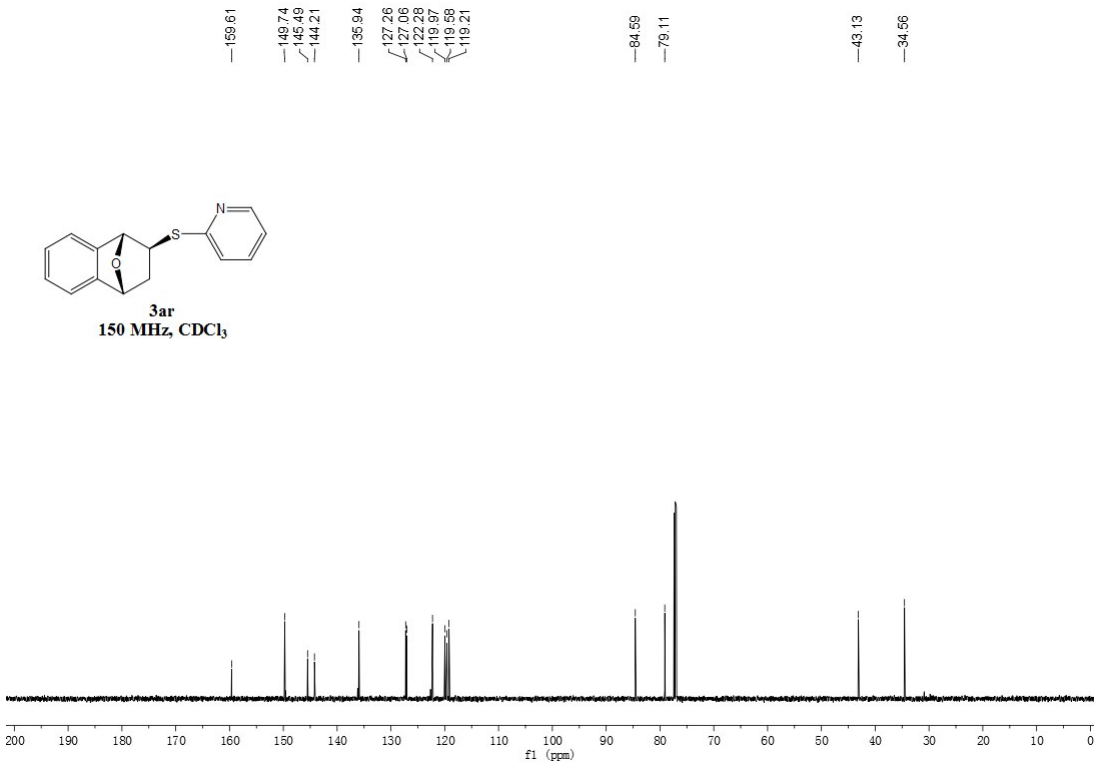


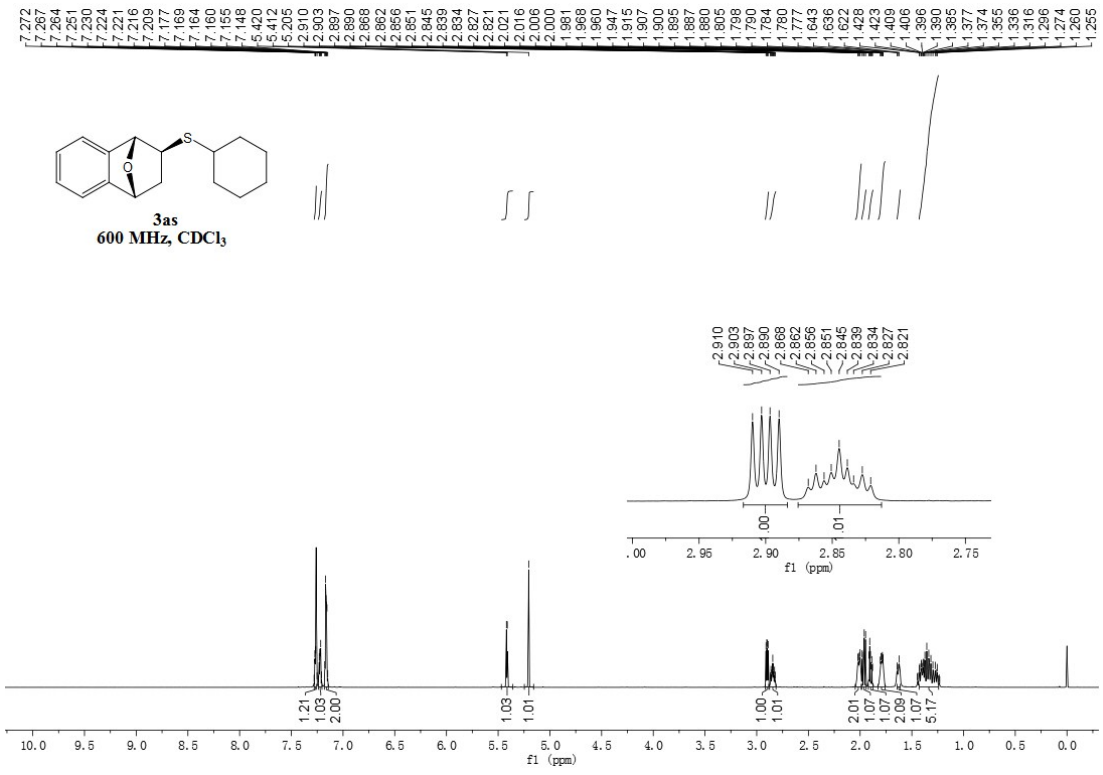


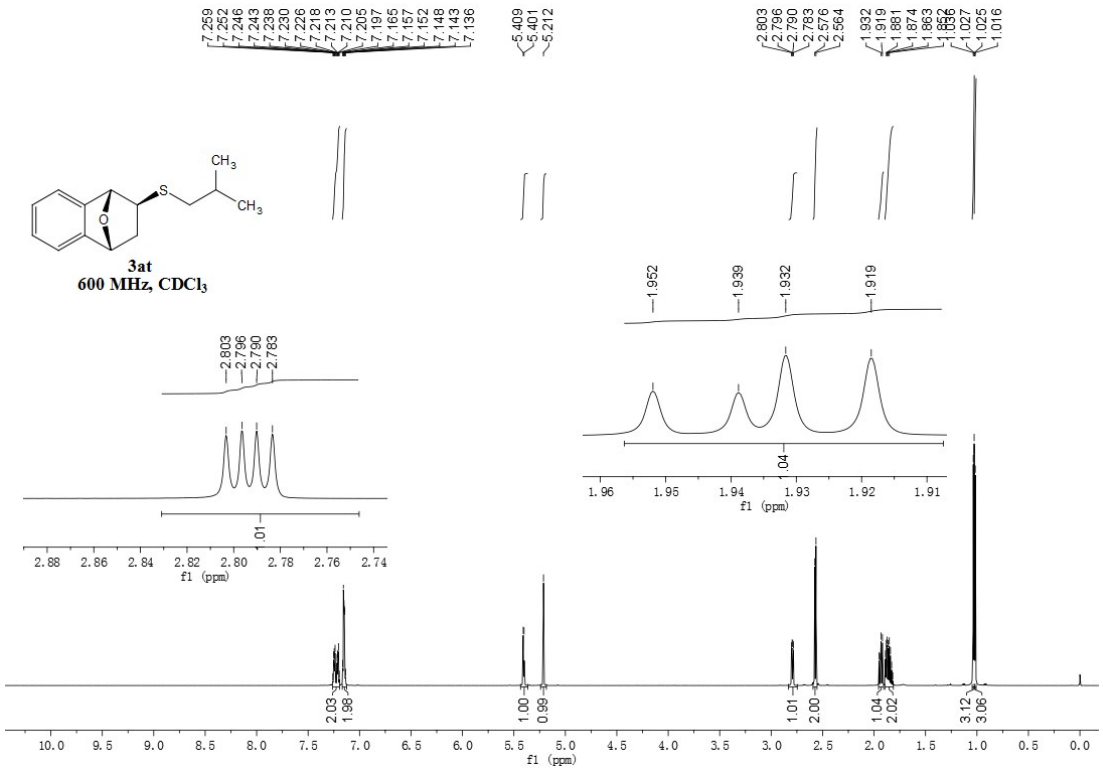
3aq
150 MHz, $CDCl_3$

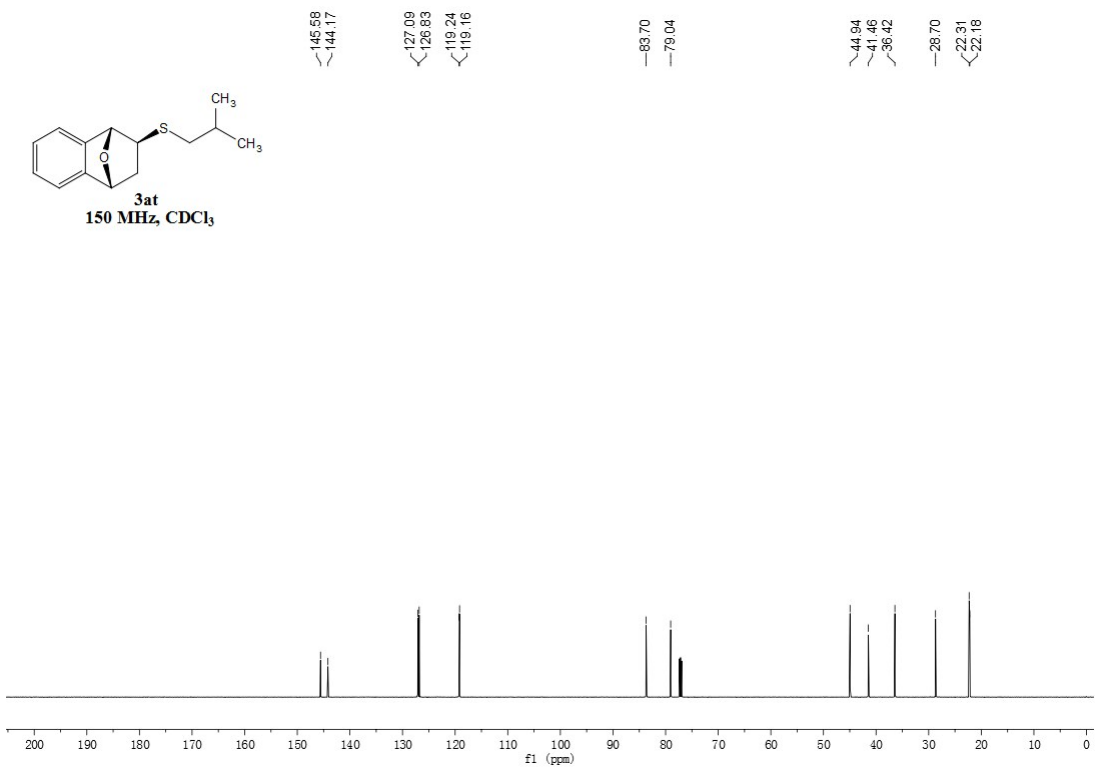


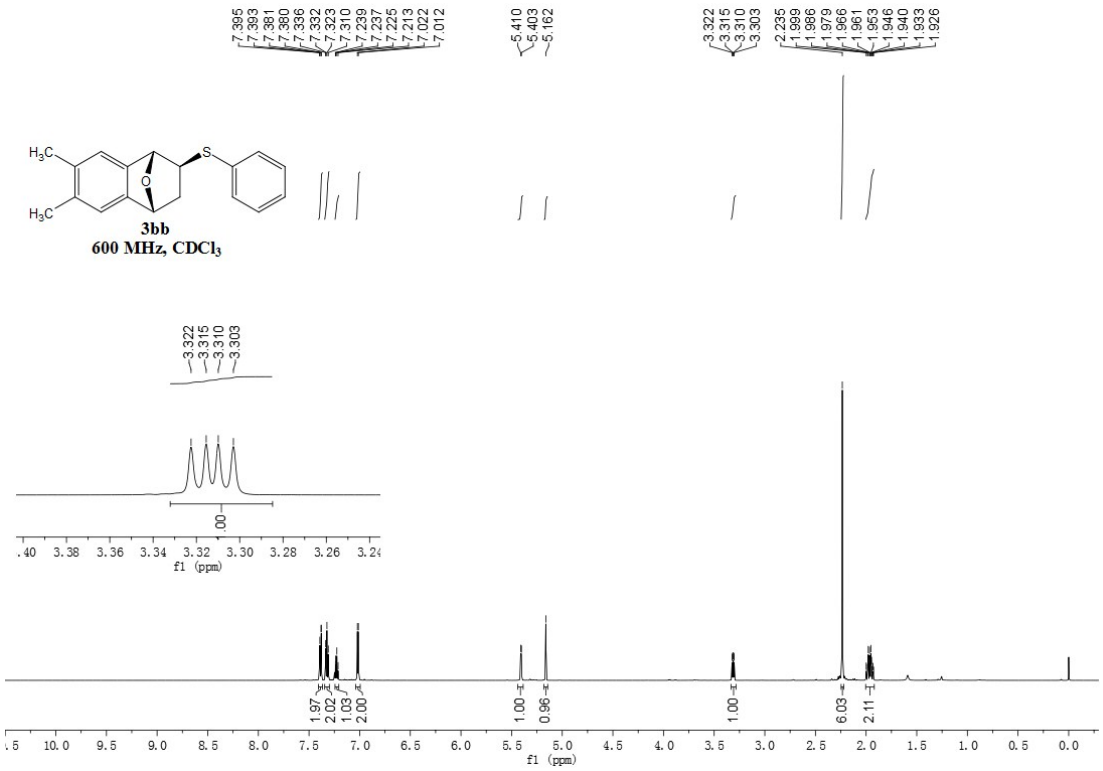

8.462
8.461
8.459
8.458
8.454
8.453
8.451
8.450
7.491
7.490
7.488
7.400
7.390
7.255
7.250
7.215
7.213
7.211
7.209
7.201
7.198
7.190
5.467
5.354
3.854
3.846
3.841
3.833
2.053
2.040
2.033
2.019
2.012
2.004
1.997
1.991
1.984
1.976
N
S
O
3ar
600 MHz, CDCl3
3.854
3.846
3.841
3.833
1.00
3.92
3.88
3.84
3.80
f1 (ppm)
1.02
1.09
0.98
1.08
3.03
1.06
1.01
0.98
1.00
2.10
10.5
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)

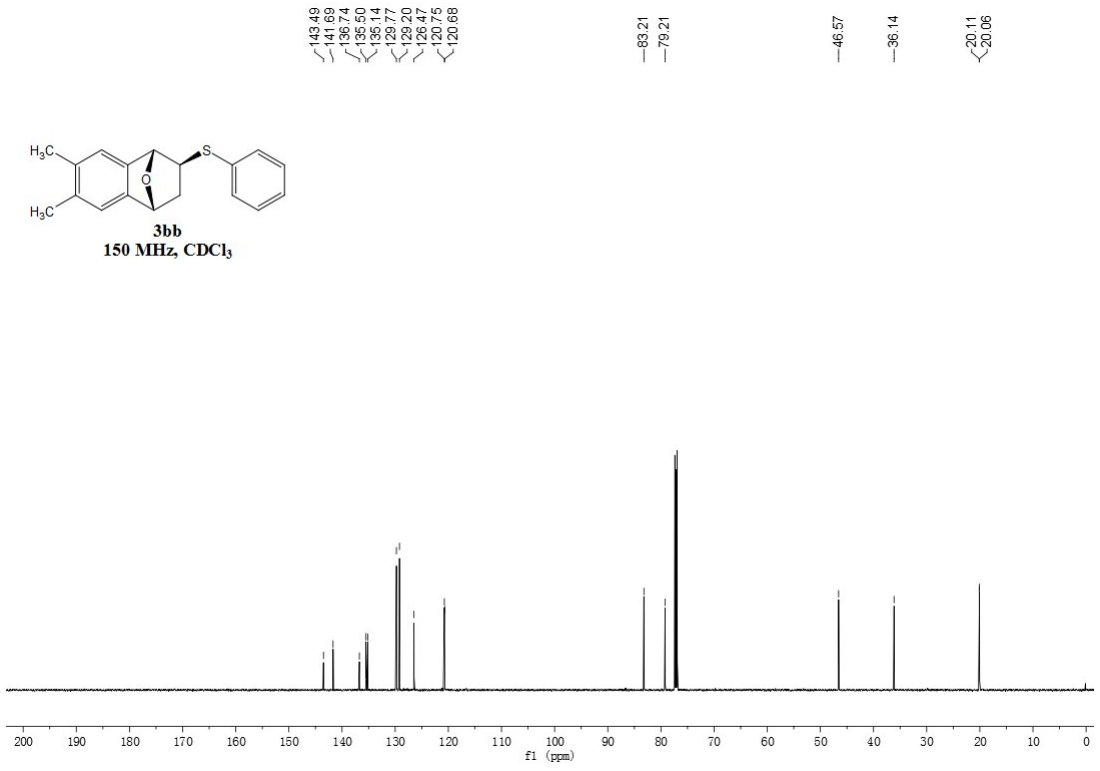

159.61
149.74
145.49
144.21
135.94
127.26
127.06
122.28
119.97
119.58
119.21
84.59
79.11
43.13
34.56
N
S
O
3ar
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

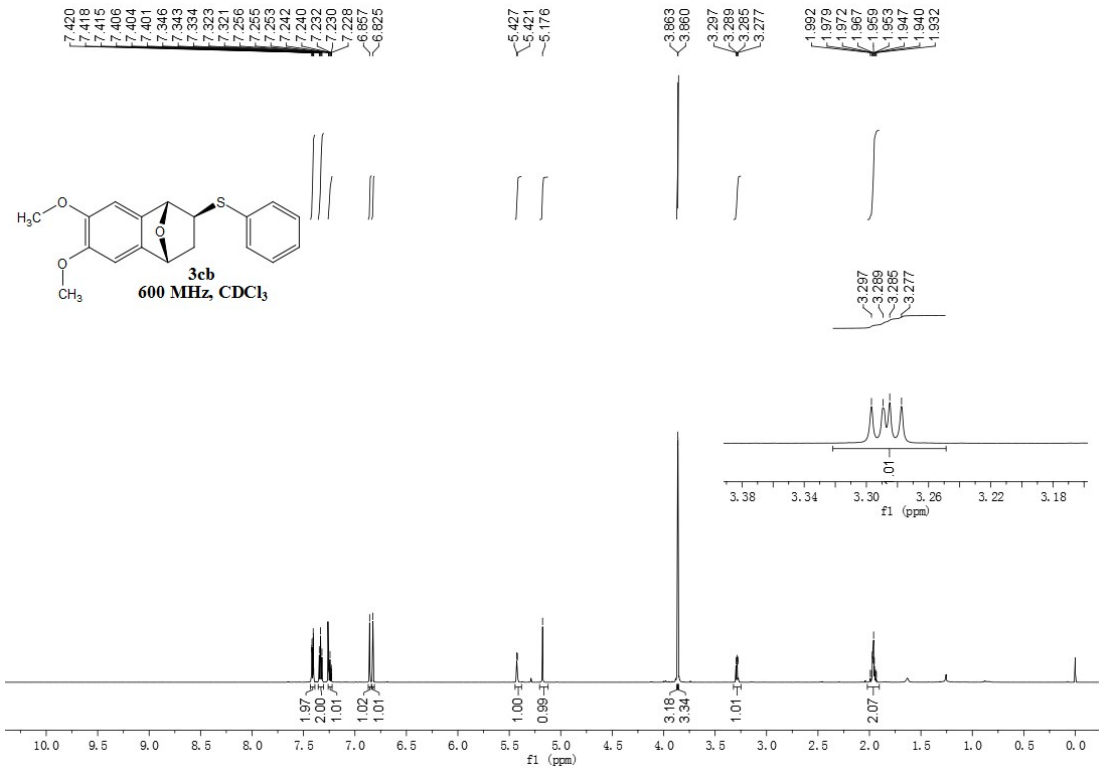

7.272
7.267
7.264
7.251
7.230
7.224
7.221
7.216
7.209
7.177
7.169
7.164
7.160
7.155
7.148
5.420
5.412
5.205
2.910
2.903
2.897
2.890
2.868
2.862
2.856
2.851
2.845
2.839
2.834
2.827
2.821
2.021
2.016
2.006
2.000
1.981
1.968
1.960
1.947
1.915
1.907
1.900
1.895
1.887
1.880
1.805
1.798
1.790
1.784
1.780
1.777
1.643
1.636
1.622
1.428
1.423
1.409
1.406
1.396
1.390
1.385
1.377
1.374
1.355
1.336
1.316
1.296
1.274
1.260
1.255
3as
600 MHz, CDCl3
2.910
2.903
2.897
2.890
2.868
2.862
2.856
2.851
2.845
2.839
2.834
2.827
2.821
1.00
1.01
.00
2.95
2.90
2.85
2.80
2.75
f1 (ppm)
1.21
1.03
2.00
1.03
1.01
1.00
1.01
2.01
1.07
1.07
2.09
1.07
5.17
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)
145.65
144.31
127.19
126.90
119.31
119.27
84.47
79.09
44.32
42.78
37.00
34.01
33.95
26.18
26.13
25.92
3as
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

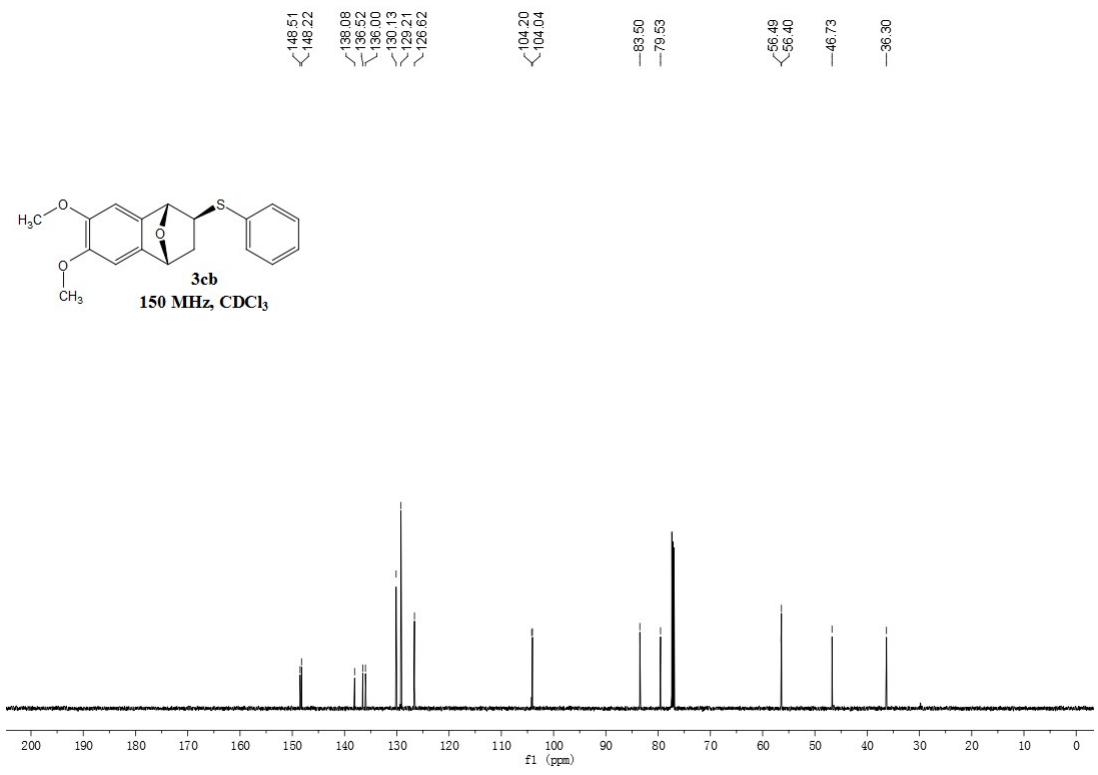

7.259
7.252
7.246
7.243
7.238
7.230
7.226
7.218
7.213
7.210
7.205
7.197
7.165
7.157
7.152
7.148
7.143
7.136
5.409
5.401
5.212
2.803
2.796
2.790
2.783
2.576
2.564
1.932
1.919
1.881
1.874
1.863
1.856
1.027
1.025
1.016
CH3
S
O
CH3
3at
600 MHz, CDCl3
1.952
1.939
1.932
1.919
2.803
2.796
2.790
2.783
1.01
1.04
2.88 2.86 2.84 2.82 2.80 2.78 2.76 2.74
1.96 1.95 1.94 1.93 1.92 1.91
f1 (ppm)
2.03
1.98
1.00
0.99
1.01
2.00
1.04
2.02
3.12
3.06
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)

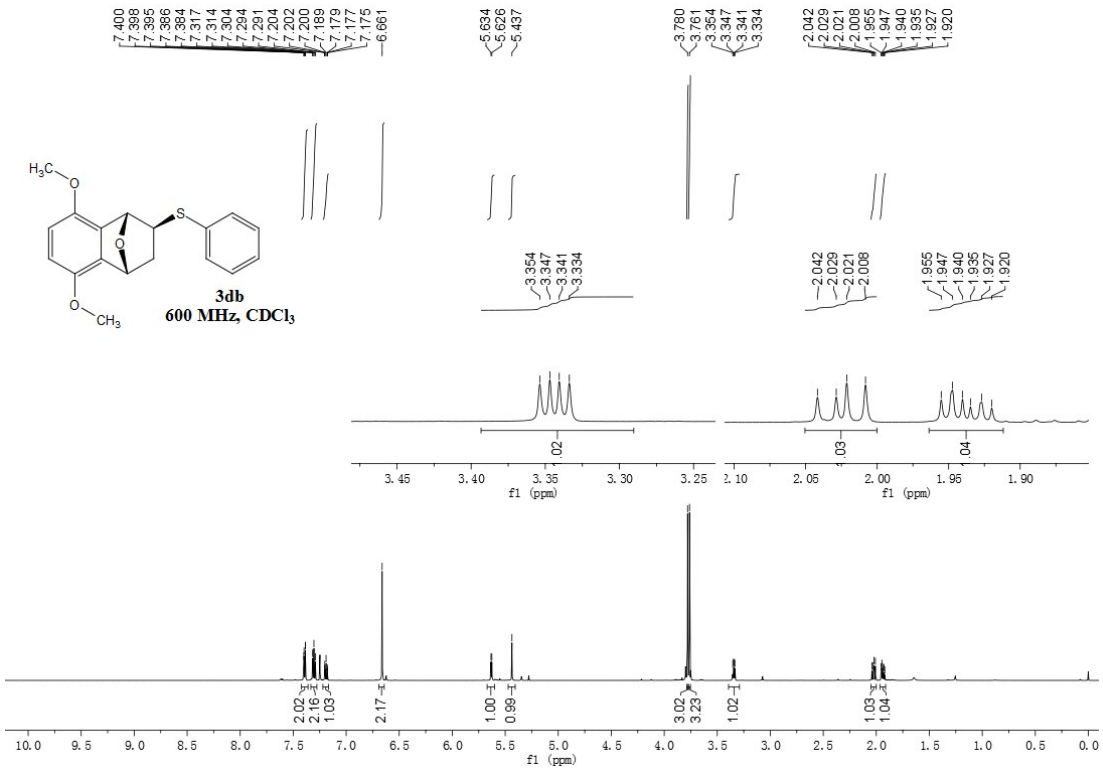

145.58
144.17
127.09
126.83
119.24
119.16
83.70
79.04
44.94
41.46
36.42
28.70
22.31
22.18
CH3
S
O
CH3
3at
150 MHz, CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

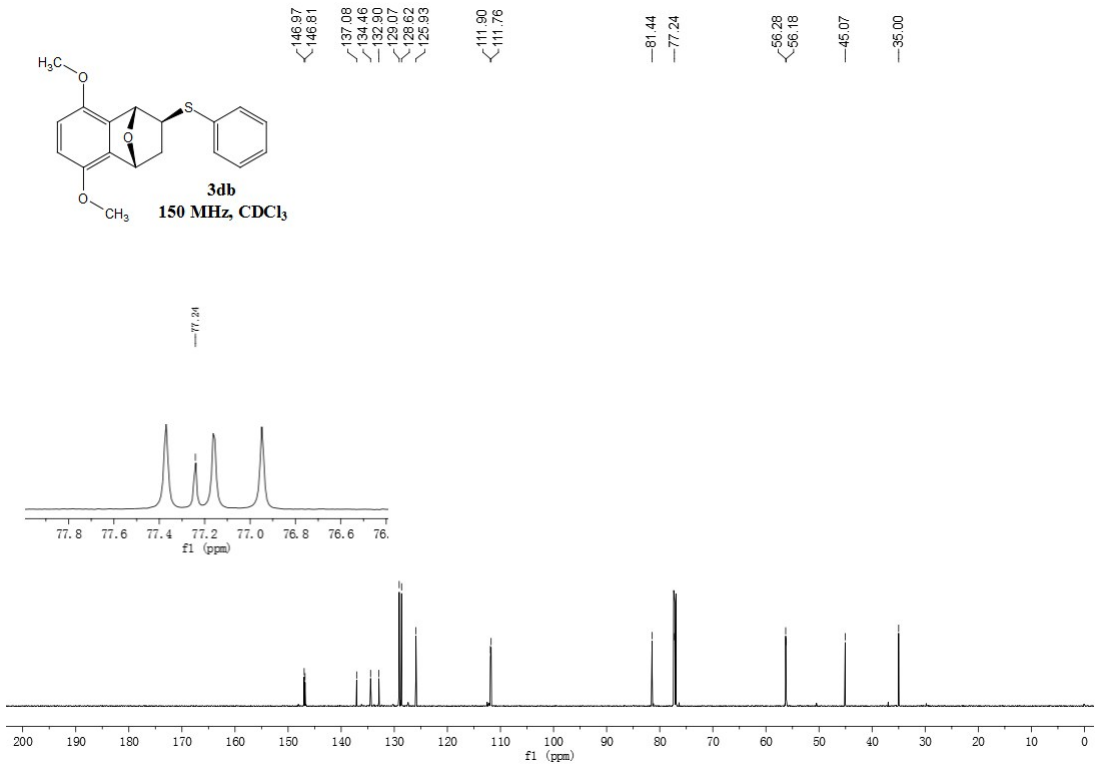

7.395
7.393
7.381
7.380
7.336
7.332
7.323
7.310
7.239
7.237
7.225
7.213
7.022
7.012
5.410
5.403
5.162
3.322
3.315
3.310
3.303
2.235
1.999
1.986
1.979
1.966
1.961
1.953
1.946
1.940
1.933
1.926
H3C
H3C
O
S
3bb
600 MHz, CDCl3
3.322
3.315
3.310
3.303
1.00
f1 (ppm)
1.97
2.02
1.03
2.00
1.00
0.96
1.00
6.03
2.11
f1 (ppm)

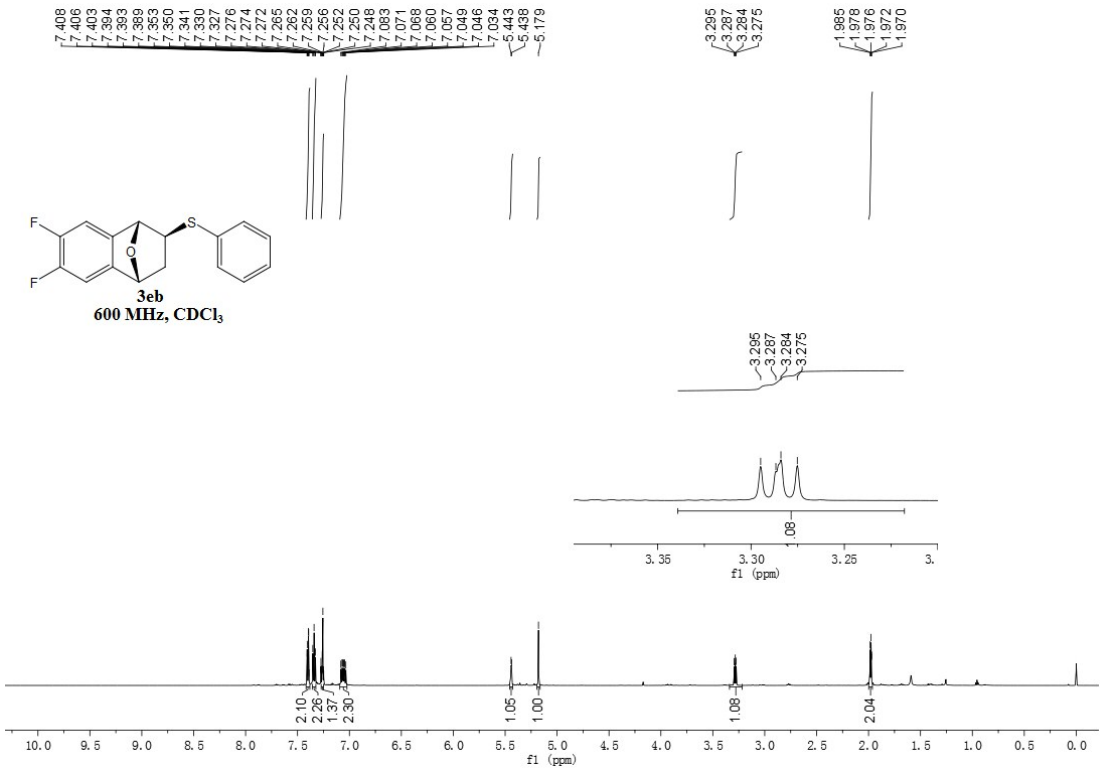

143.49
141.69
136.74
135.50
135.14
129.77
129.20
126.47
120.75
120.68
83.21
79.21
46.57
36.14
20.11
20.06
H3C
H3C
O
S
3bb
150 MHz, CDCl3
f1 (ppm)

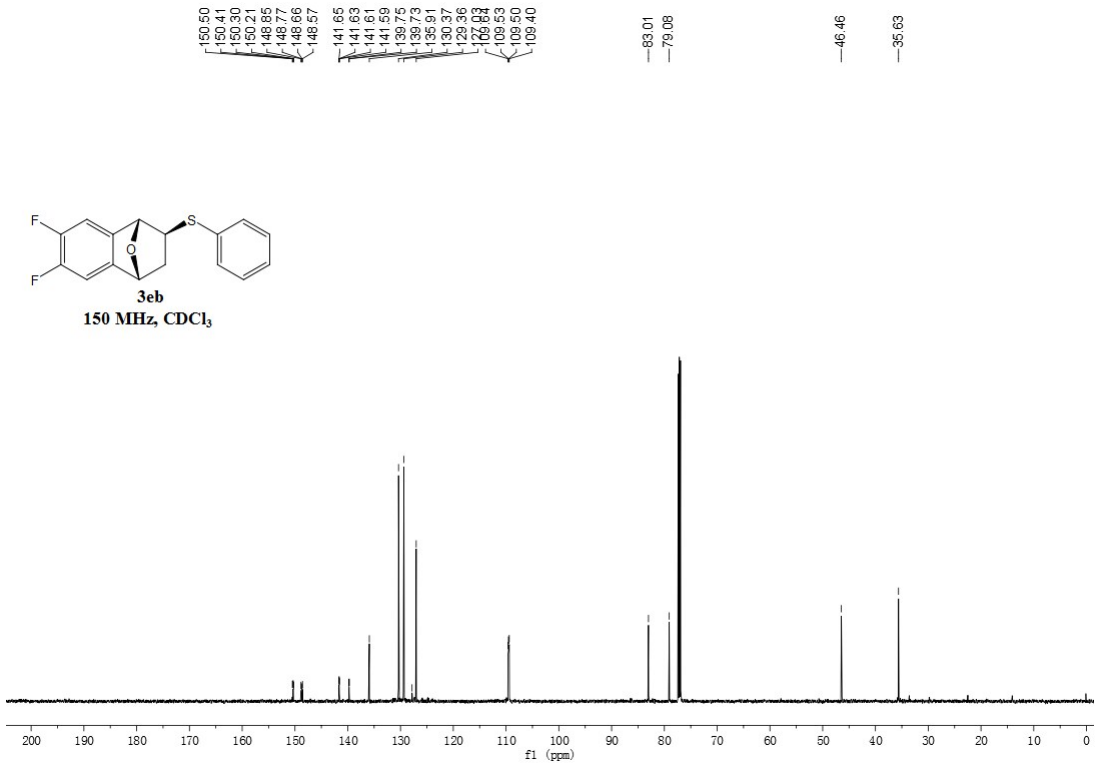

7.420
7.418
7.415
7.406
7.404
7.401
7.346
7.343
7.334
7.323
7.321
7.256
7.255
7.253
7.242
7.240
7.232
7.230
7.228
6.857
6.825
5.427
5.421
5.176
3.863
3.860
3.297
3.289
3.285
3.277
1.992
1.979
1.972
1.967
1.959
1.953
1.947
1.940
1.932
3cb
600 MHz, CDCl3
1.01
f1 (ppm)
1.97
2.00
1.01
1.02
1.01
1.00
0.99
3.18
3.34
1.01
2.07
f1 (ppm)

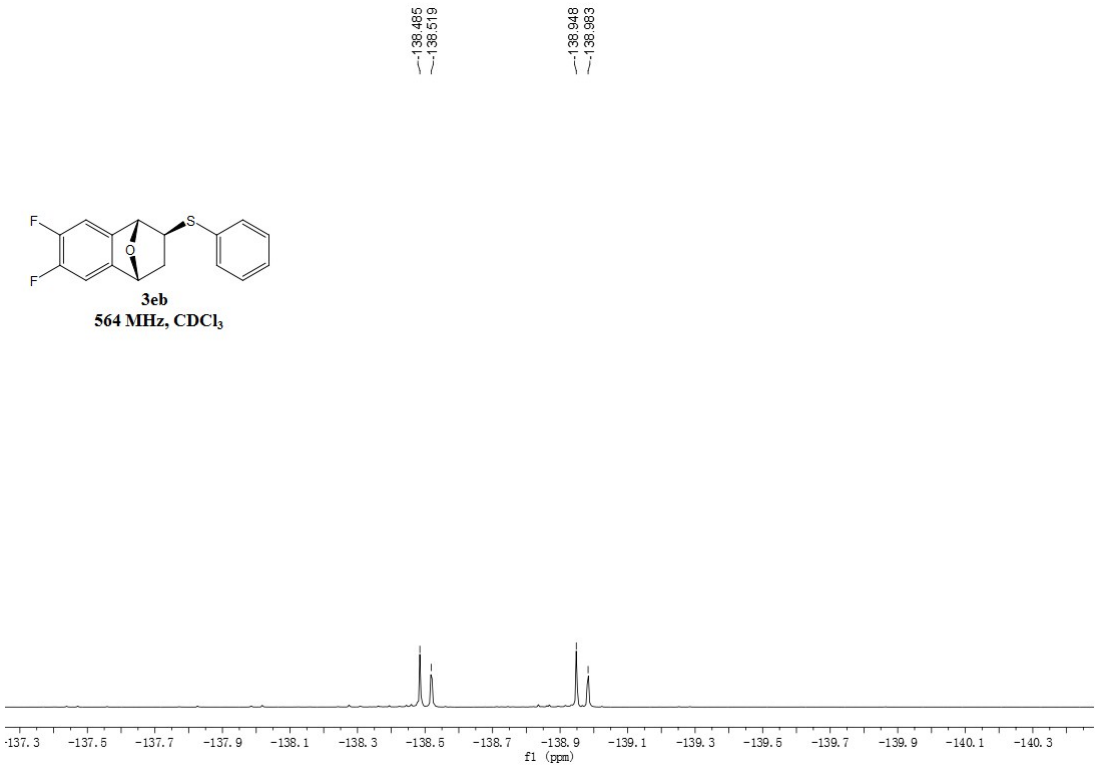

148.51
148.22
138.08
136.52
136.00
130.13
129.21
126.62
104.20
104.04
83.50
79.53
56.49
56.40
46.73
36.30
3cb
150 MHz, CDCl3
f1 (ppm)

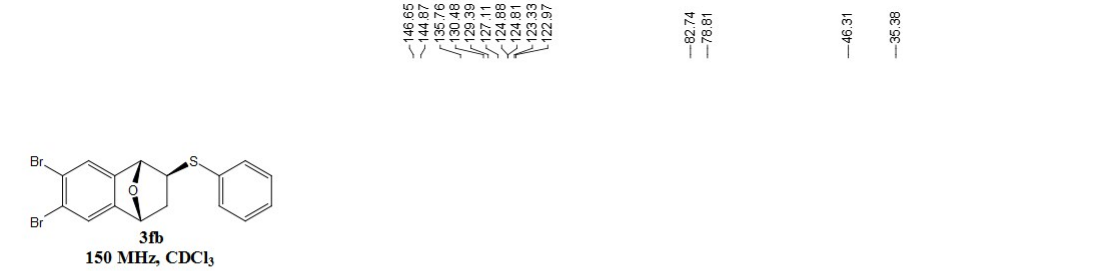

7.400
7.398
7.395
7.386
7.384
7.317
7.314
7.304
7.294
7.291
7.204
7.202
7.200
7.189
7.179
7.177
7.175
6.661
5.634
5.626
5.437
3.780
3.761
3.354
3.347
3.341
3.334
2.042
2.029
2.021
2.008
1.955
1.947
1.940
1.935
1.927
1.920
3db
600 MHz, CDCl3
f1 (ppm)
2.02
2.16
1.03
2.17
1.00
0.99
3.02
3.23
1.02
1.03
1.04


146.97
146.81
137.08
134.46
132.90
129.07
128.62
125.93
111.90
111.76
81.44
77.24
56.28
56.18
45.07
35.00
3db
150 MHz, CDCl3
f1 (ppm)

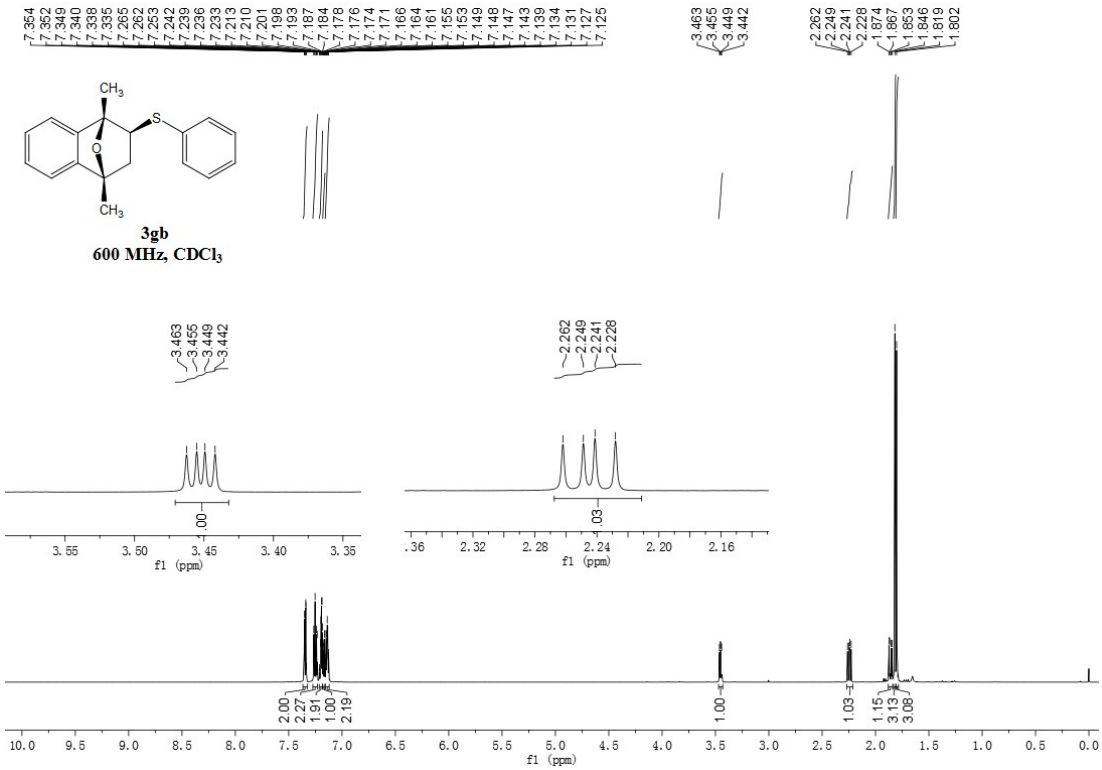

7.408
7.406
7.403
7.394
7.393
7.389
7.353
7.350
7.341
7.330
7.327
7.276
7.274
7.272
7.265
7.262
7.259
7.256
7.252
7.250
7.248
7.083
7.071
7.068
7.060
7.057
7.049
7.046
7.034
5.443
5.438
5.179
3.295
3.287
3.284
3.275
1.985
1.978
1.976
1.972
1.970
F
F
O
S
3eb
600 MHz, CDCl3
3.295
3.287
3.284
3.275
1.08
3.35
3.30
3.25
f1 (ppm)
2.10
2.26
1.37
2.30
1.05
1.00
1.08
2.04
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)


150.50
150.41
150.30
150.21
148.85
148.77
148.66
148.57
141.65
141.63
141.61
141.59
139.75
139.73
135.91
130.37
129.36
109.53
109.50
109.40
83.01
79.08
46.46
35.63
F
F
O
S
3eb
150 MHz, CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

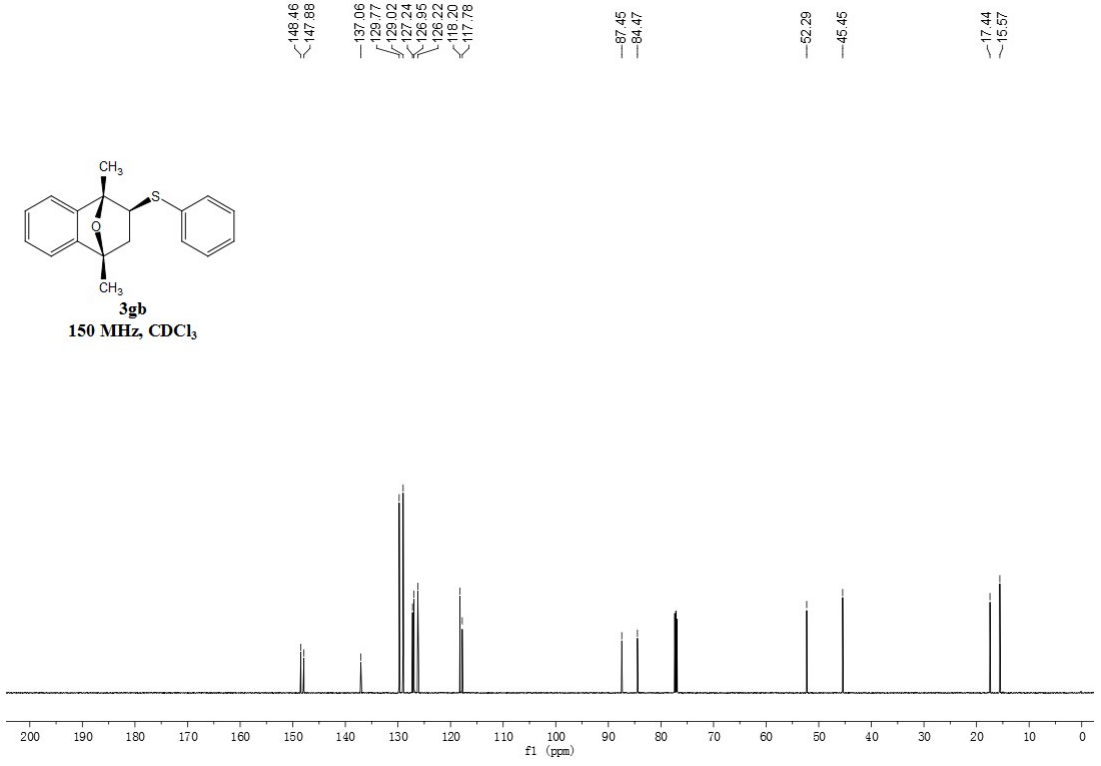

-138.485
-138.519
-138.948
-138.983
F
F
O
S
3eb
564 MHz, CDCl3
f1 (ppm)
7.501
7.468
7.405
7.393
7.357
7.344
7.331
7.278
7.266
7.257
5.423
5.416
5.158
3.311
3.303
3.298
3.291
2.022
2.009
2.001
1.989
1.982
1.975
1.969
1.961
1.954
Br
Br
O
S
3fb
600 MHz, CDCl3
1.01
0.93
2.07
2.07
1.11
1.06
1.00
1.03
2.17
f1 (ppm)

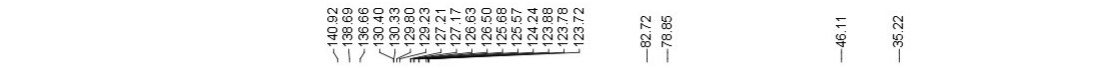


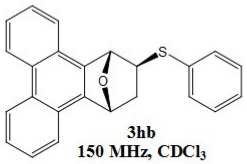
3fb
150 MHz, $CDCl_3$



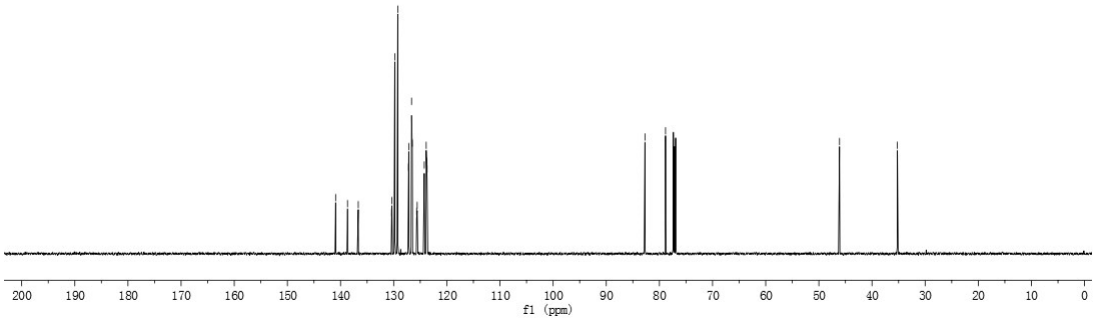
3gb
600 MHz, $CDCl_3$

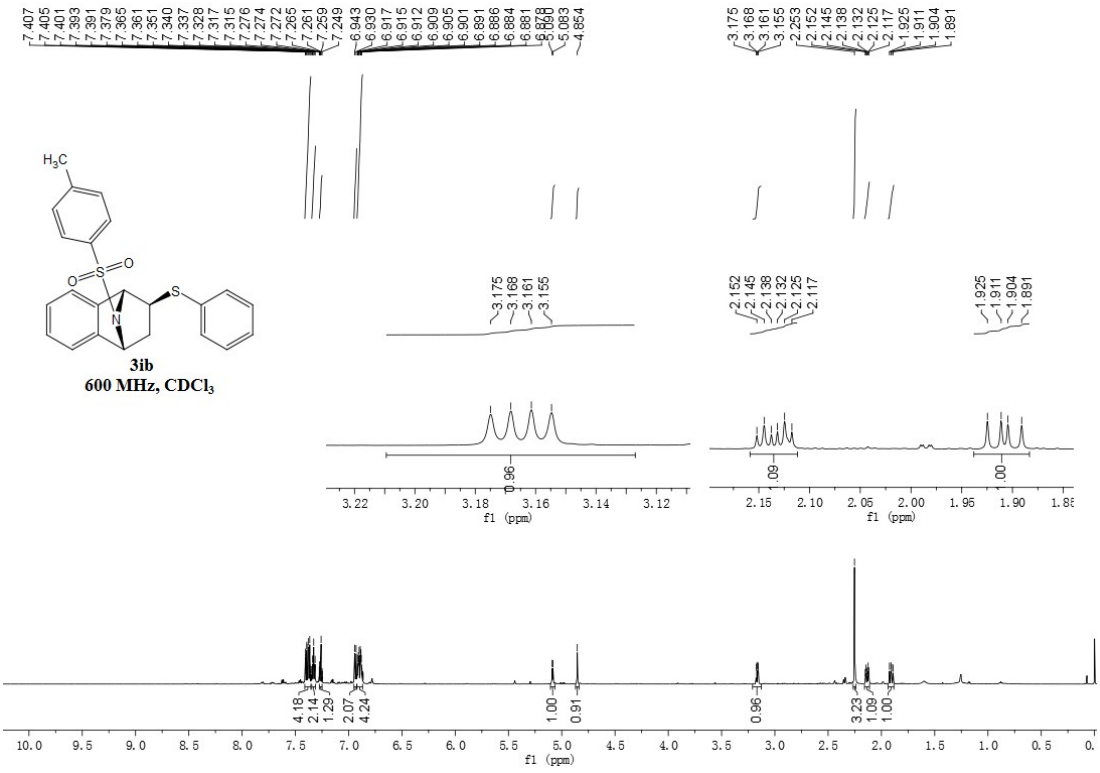

148.46
147.88
137.06
129.77
129.02
127.24
126.95
126.22
118.20
117.78
87.45
84.47
52.29
45.45
17.44
15.57
CH3
S
O
CH3
3gb
150 MHz, CDCl3
f1 (ppm)
8.663
8.657
8.651
7.617
7.612
7.610
7.607
7.601
7.595
7.592
7.438
7.436
7.424
7.423
7.353
7.340
7.327
6.035
5.741
3.277
3.270
3.264
3.258
2.089
2.081
2.075
2.069
2.061
2.055
1.953
1.940
1.933
1.920
S
O
3hb
600 MHz, CDCl3
2.07
1.05
1.11
4.07
2.02
1.99
1.05
1.01
1.01
1.00
1.04
1.02
f1 (ppm)



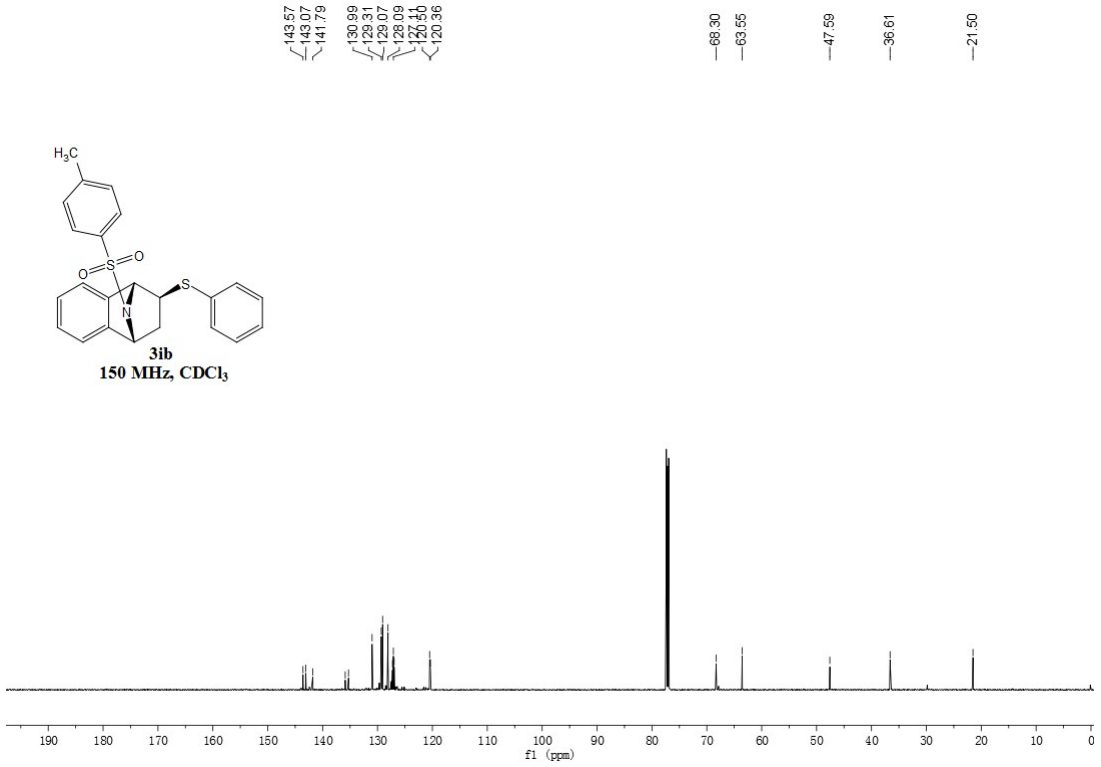


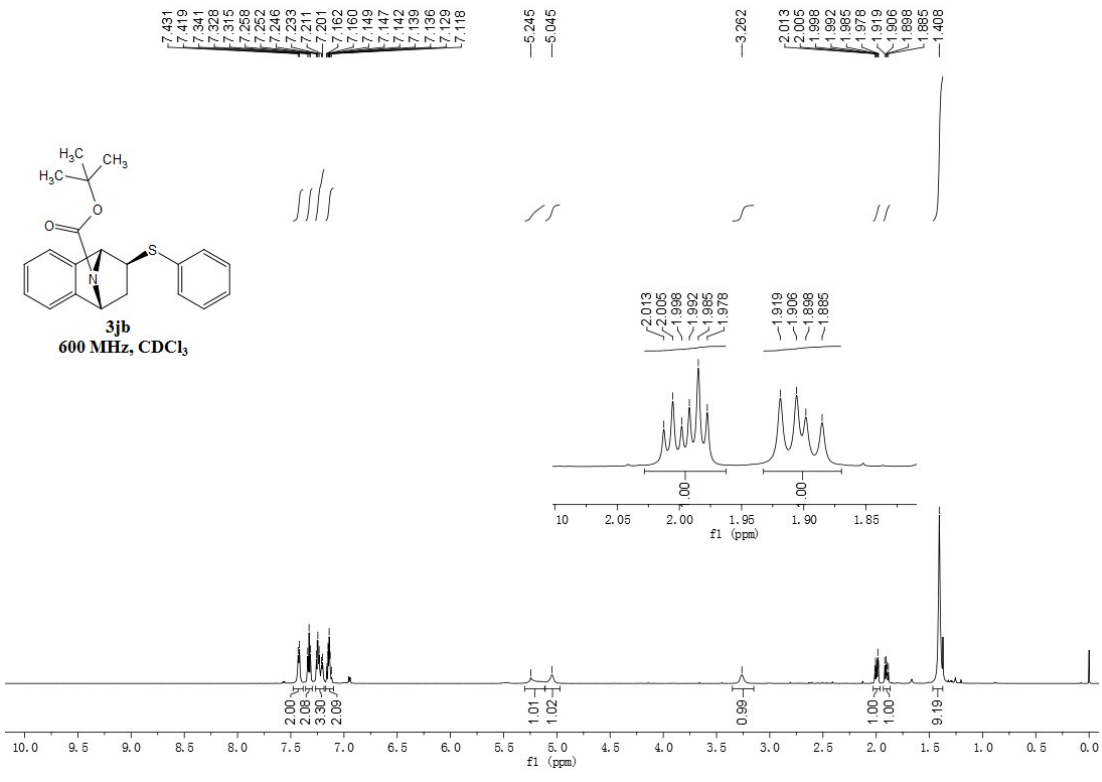
3hb
150 MHz, $CDCl_3$

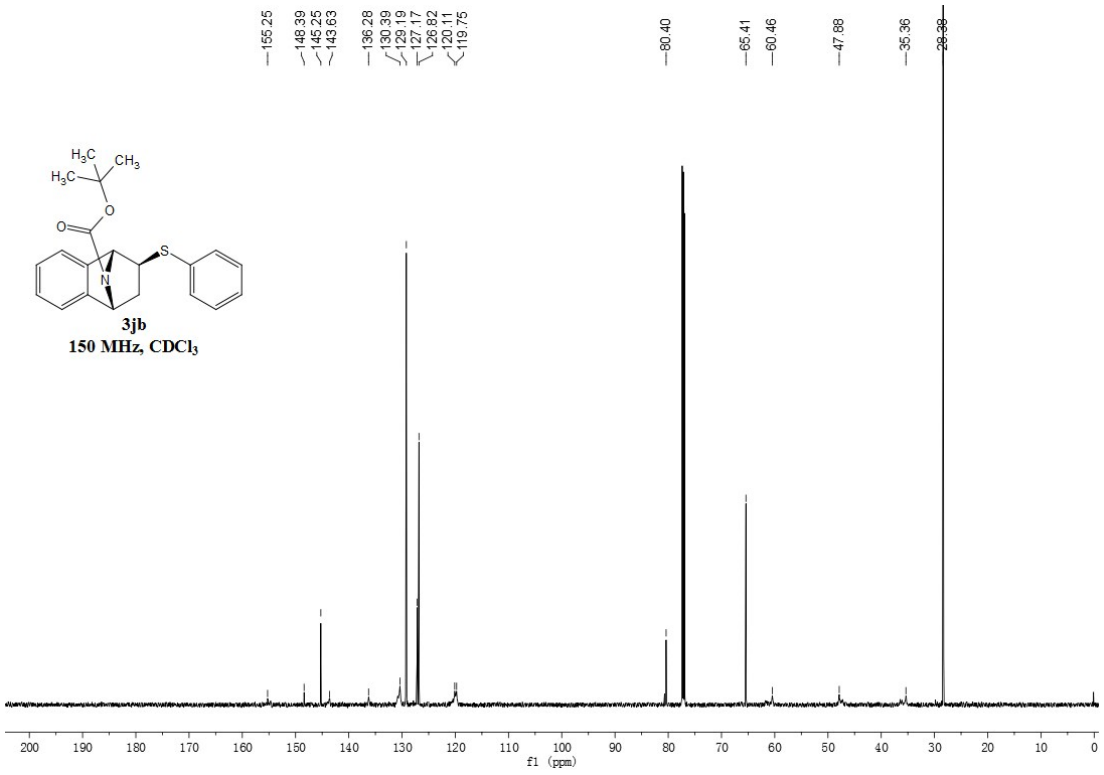


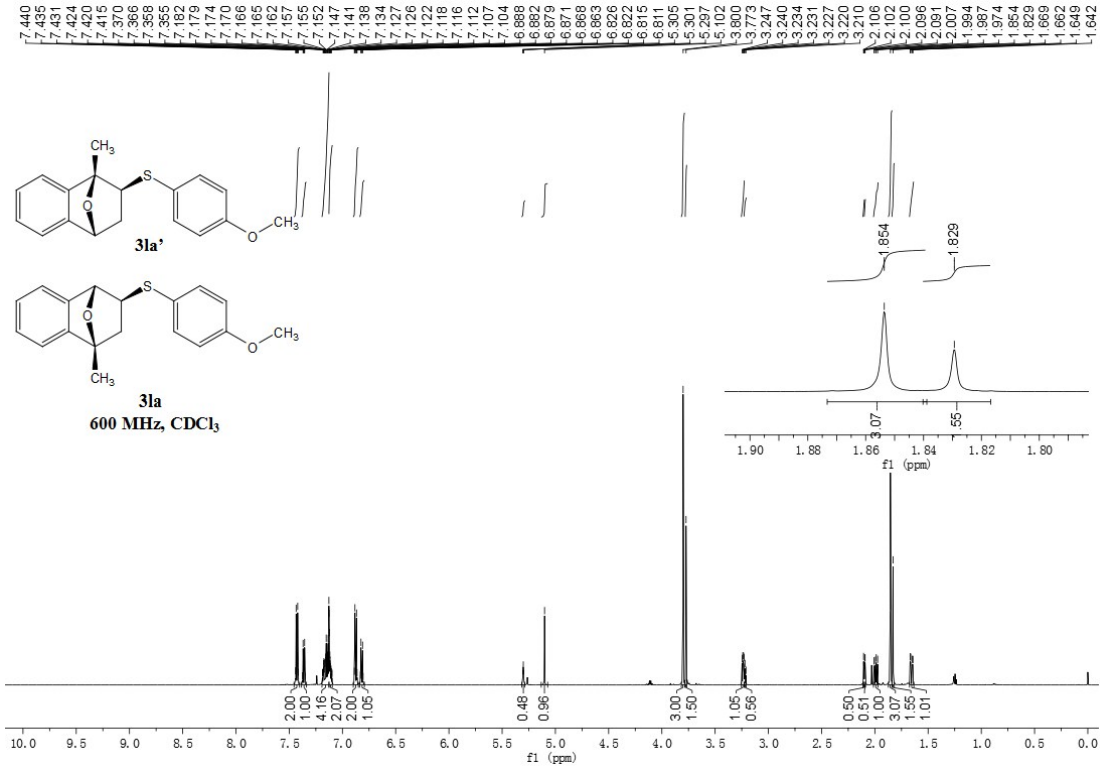


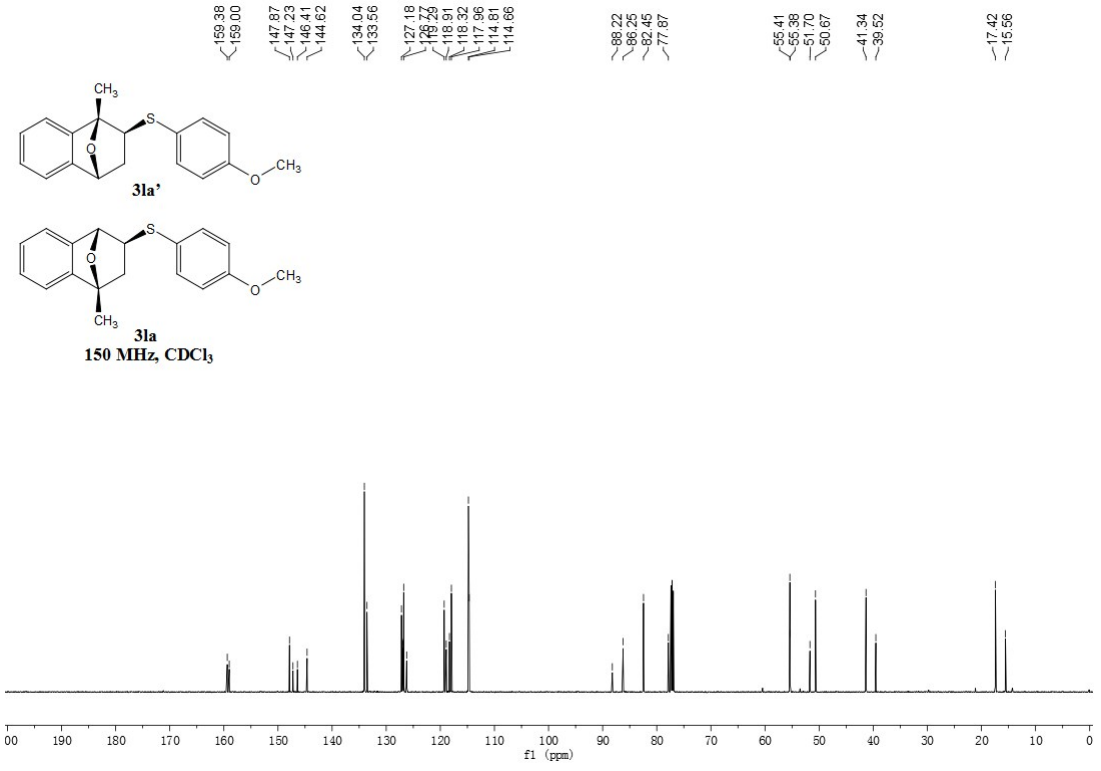
3ib
600 MHz, $CDCl_3$

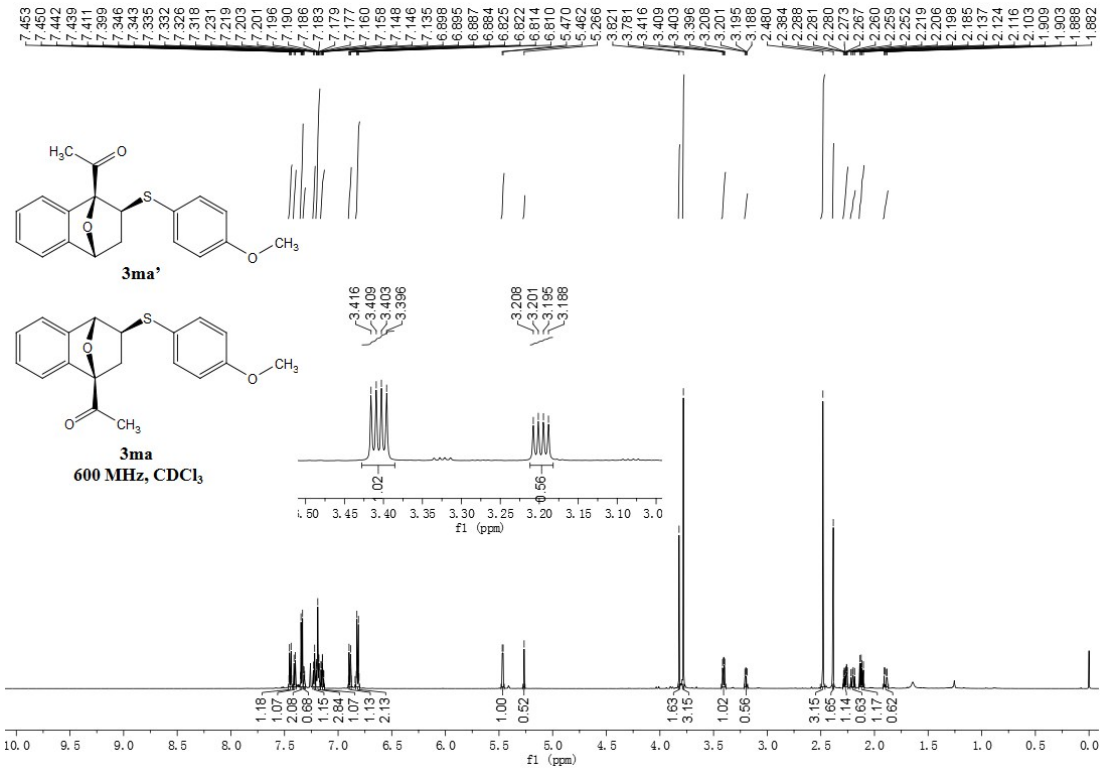

143.57
143.07
141.79
130.99
129.31
129.07
128.09
127.11
120.50
120.36
68.30
63.55
47.59
36.61
21.50
H3C
O
S
O
N
S
3ib
150 MHz, CDCl3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

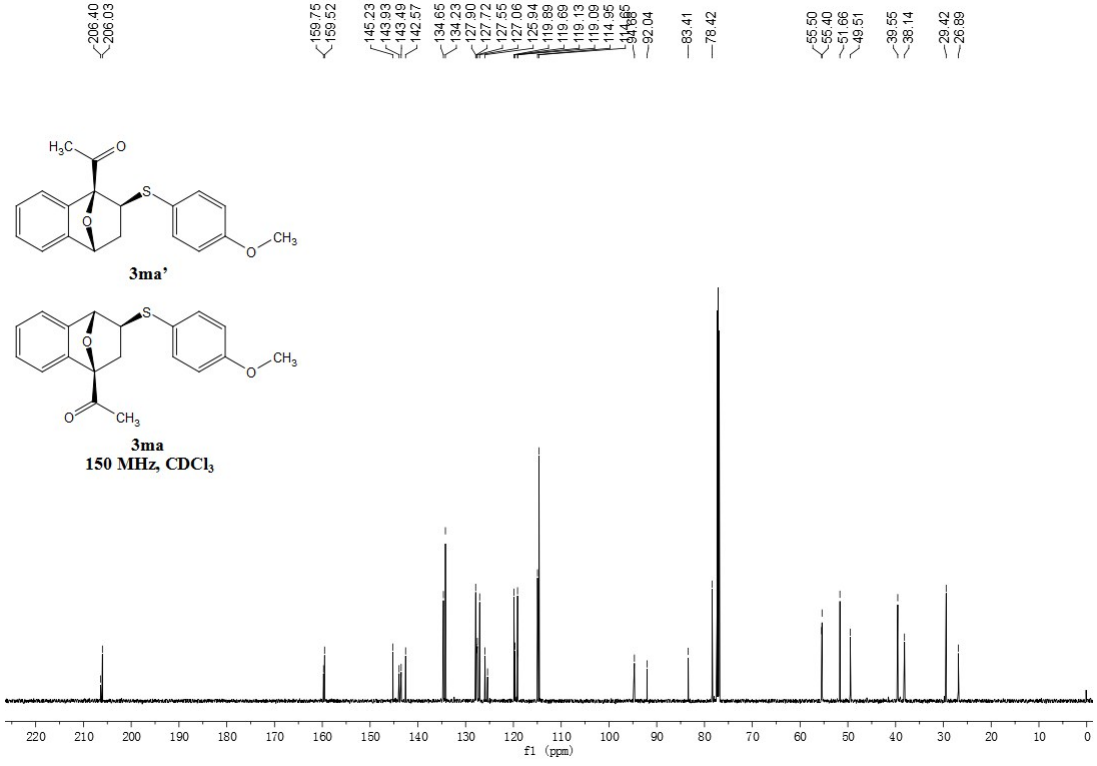

7.431
7.419
7.341
7.328
7.315
7.258
7.252
7.246
7.233
7.211
7.201
7.162
7.160
7.149
7.147
7.142
7.139
7.136
7.129
7.118
5.245
5.045
3.262
2.013
2.005
1.998
1.992
1.985
1.978
1.919
1.906
1.898
1.885
1.408
H3C
CH3
H3C
O
O
N
S
3jb
600 MHz, CDCl3
2.013
2.005
1.998
1.992
1.985
1.978
1.919
1.906
1.898
1.885
1.00
1.00
10 2.05 2.00 1.95 1.90 1.85
f1 (ppm)
2.00
2.08
3.30
2.09
1.01
1.02
0.99
1.00
1.00
9.19
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)

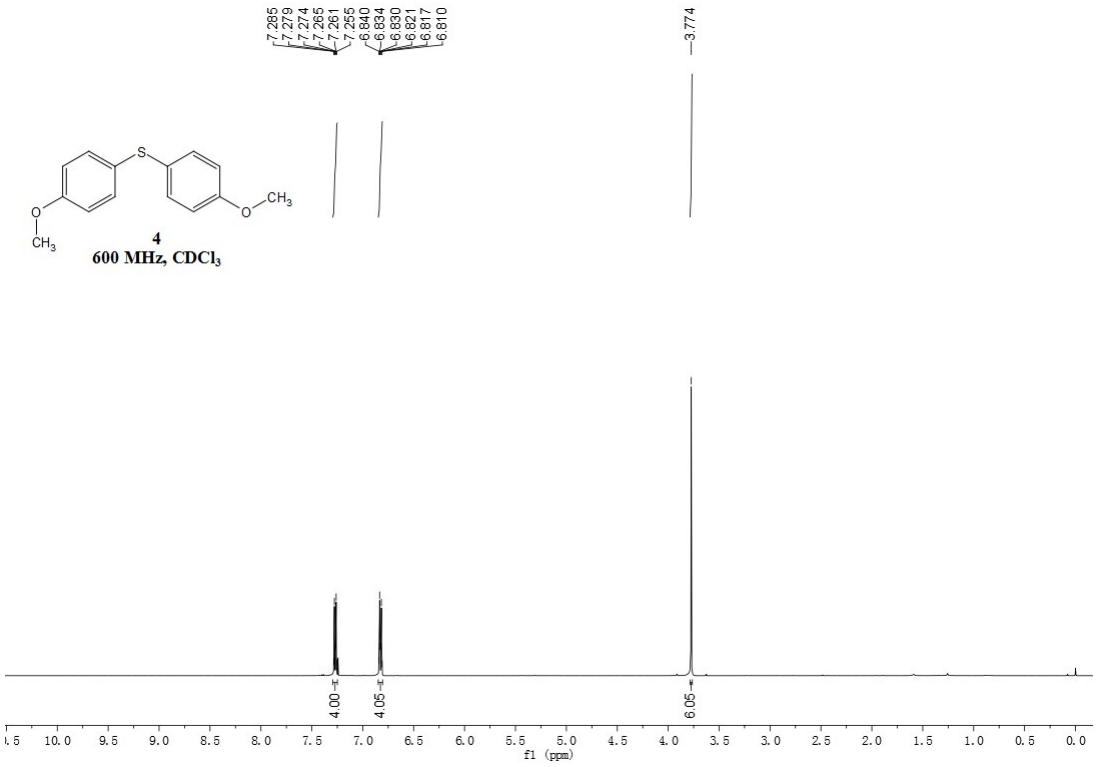

155.25
148.39
145.25
143.63
136.28
130.39
129.19
127.17
126.82
120.11
119.75
80.40
65.41
60.46
47.88
35.36
28.38
3jb
150 MHz, CDCl3
f1 (ppm)

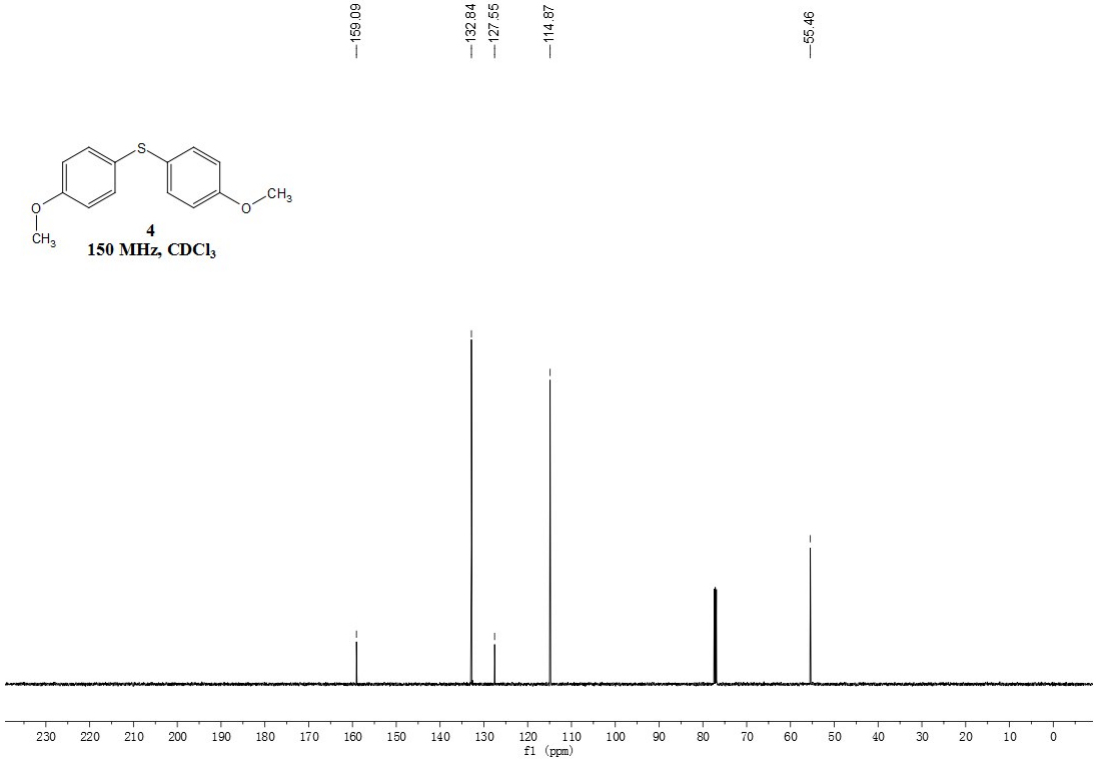

3la'
3la
600 MHz, CDCl3
1.854
1.829
3.07
1.55
f1 (ppm)

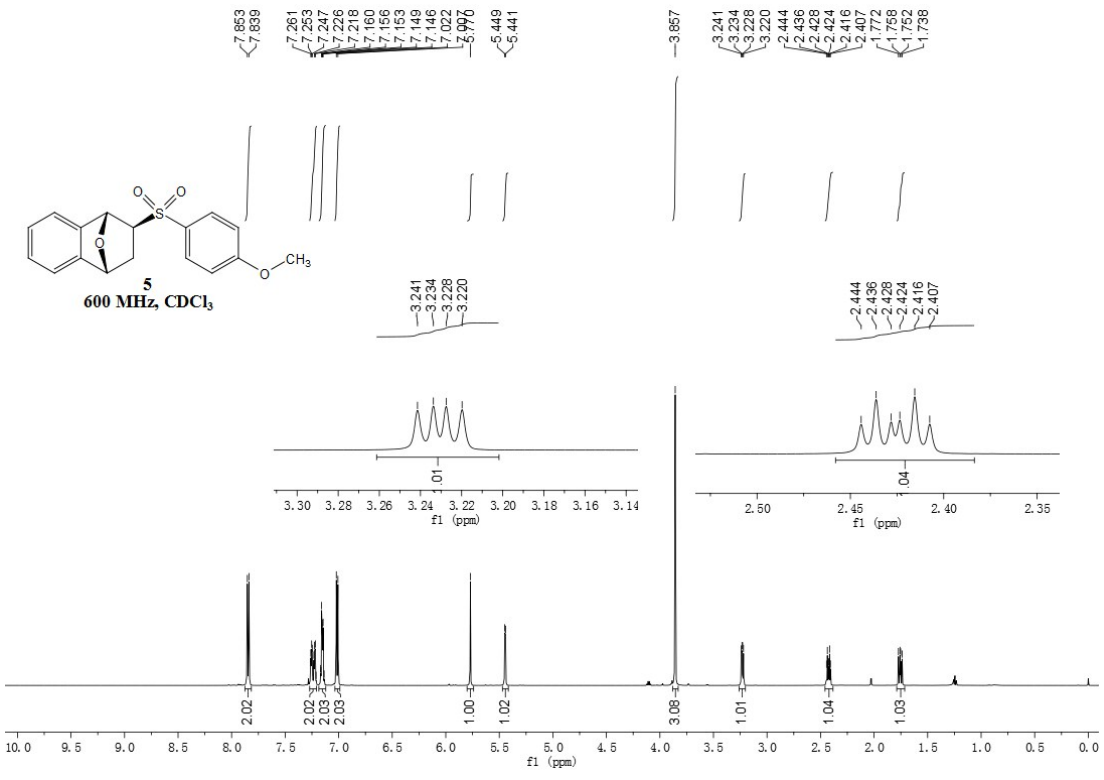

159.38
159.00
147.87
147.23
146.41
144.62
134.04
133.56
127.18
126.77
126.29
118.91
118.32
117.96
114.81
114.66
88.22
86.25
82.45
77.87
55.41
55.38
51.70
50.67
41.34
39.52
17.42
15.56
3la'
3la
150 MHz, CDCl3
f1 (ppm)

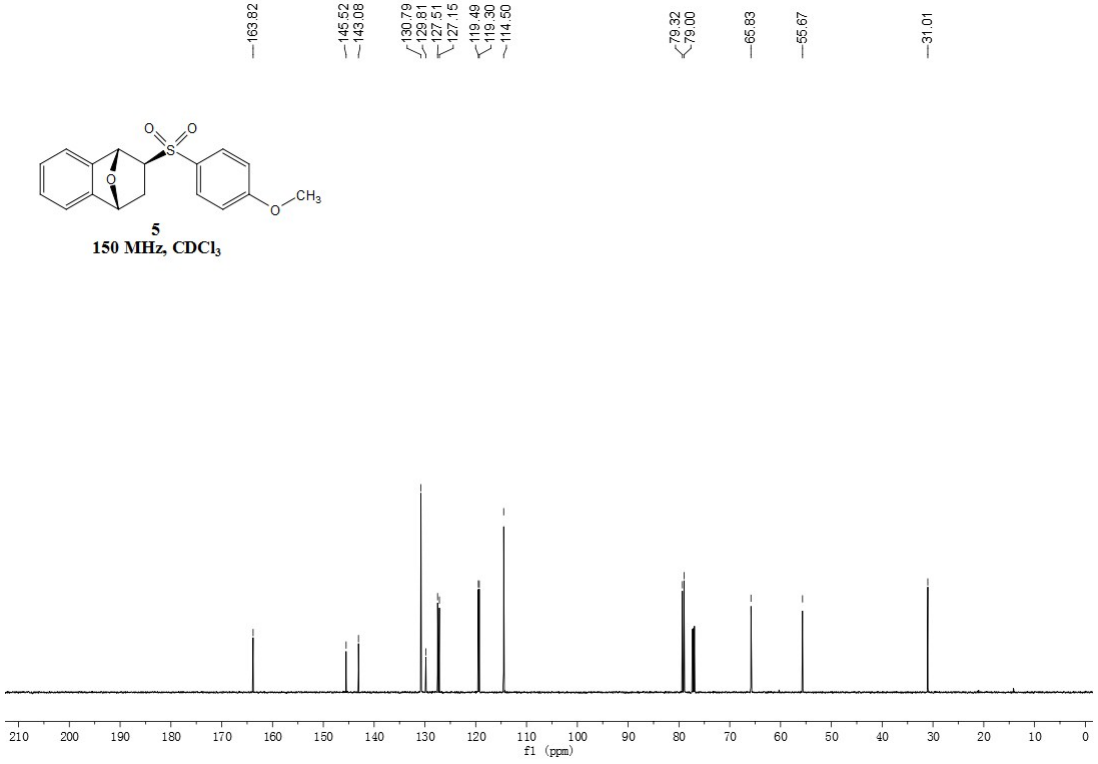

3ma'
3ma
600 MHz, CDCl3
f1 (ppm)

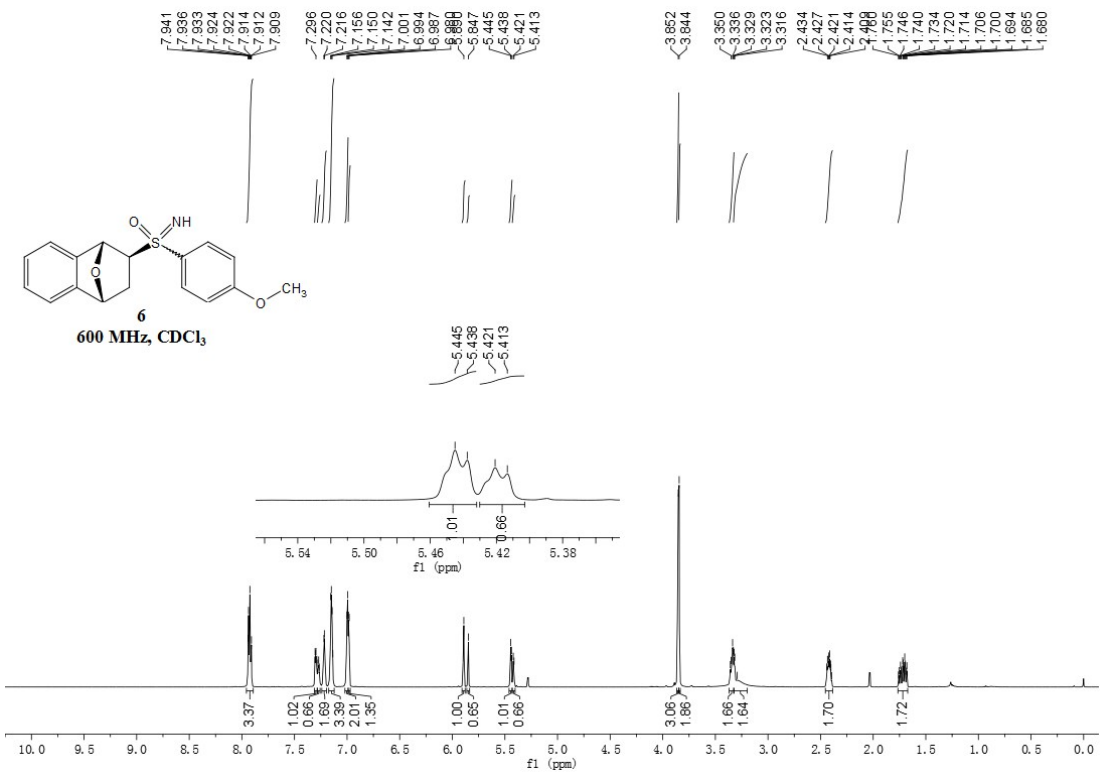

206.40
206.03
159.75
159.52
145.23
143.93
143.49
142.57
134.65
134.23
127.90
127.72
127.55
127.06
125.94
119.89
119.69
119.13
119.09
114.95
114.65
94.88
92.04
83.41
79.42
55.50
55.40
51.66
49.51
39.55
38.14
29.42
26.89
3ma'
3ma
150 MHz, CDCl3
f1 (ppm)

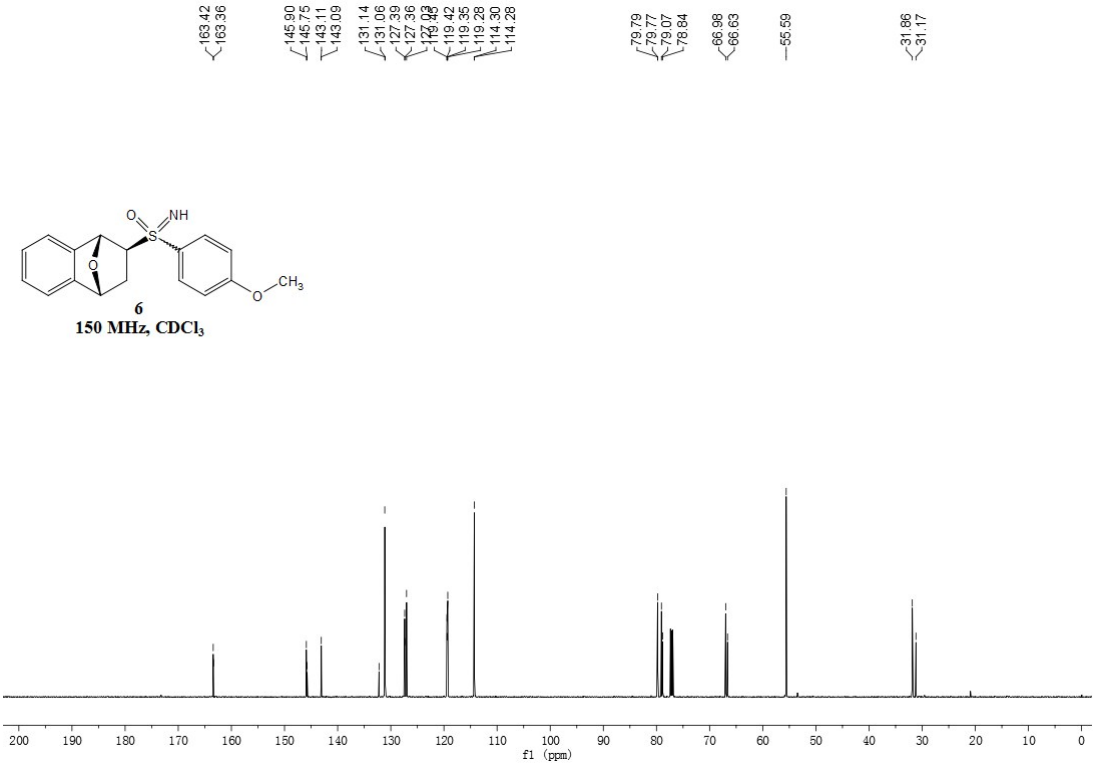

7.285
7.279
7.274
7.265
7.261
7.255
6.840
6.834
6.830
6.821
6.817
6.810
3.774
4
600 MHz, CDCl3
4.00
4.05
6.05
f1 (ppm)


159.09
132.84
127.55
114.87
55.46
4
150 MHz, CDCl3
f1 (ppm)


7.853
7.839
7.261
7.253
7.247
7.226
7.218
7.160
7.156
7.153
7.149
7.146
7.022
7.017
5.449
5.441
3.857
3.241
3.234
3.228
3.220
2.444
2.436
2.428
2.424
2.416
2.407
1.772
1.758
1.752
1.738
5
600 MHz, CDCl3
f1 (ppm)


163.82
145.52
143.08
130.79
129.81
127.51
127.15
119.49
119.30
114.50
79.32
79.00
65.83
55.67
31.01
O
O
S
O
O
CH3
5
150 MHz, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.941
7.936
7.933
7.924
7.922
7.914
7.912
7.909
7.296
7.220
7.216
7.156
7.150
7.142
7.001
6.984
6.967
5.847
5.445
5.438
5.421
5.413
3.852
3.844
3.350
3.336
3.329
3.323
3.316
2.434
2.427
2.421
2.414
1.755
1.746
1.740
1.734
1.720
1.714
1.706
1.700
1.694
1.685
1.680
O
NH
S
O
O
CH3
6
600 MHz, CDCl3
5.445
5.438
5.421
5.413
1.01
0.66
5.54 5.50 5.46 5.42 5.38
f1 (ppm)
3.37
1.02
0.66
1.69
3.39
2.01
1.35
1.00
0.65
1.01
0.66
3.06
1.86
1.66
1.64
1.70
1.72
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)



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150 MHz, $CDCl_3$