Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Controlling the selectivity of an intramolecular Friedel-Crafts alkylation with alkenes using selenium under mild conditions

Ming-Hong Liao,† Meng Zhang,† Dai-Hui Hu, Rui-Han Zhang, Yan Zhao, Shan-Shan Liu, Yun-Xia Li, Wei-Lie Xiao,* and E Tang*

Corresponding authors:

tange@ynu.edu.cn

xiaoweilie@ynu.edu.cn

Contents

1. Optimization selenium-mediated IFAC of alkenes **1** S3

2. Crystallographic data for product **(±)-2m** S5

3. Crystallographic data for product **(±)-3l** S6

4. The intrinsic reaction coordinates paths of the key steps of the carbocyclization reactions S7

5. Computed absolute energy values and imaginary frequency of TS S14

6. References S14

7. Copies of ^{1}H NMR and ^{13}C NMR Spectra for compounds S14

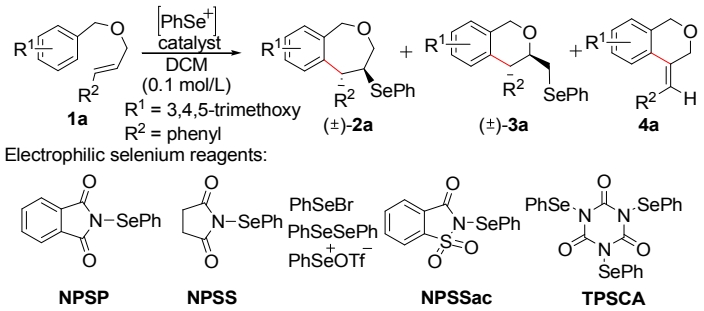
8. Copies of ^{77}Se NMR Spectra for compounds S60

9. Copies of ROESY Spectra for compounds **4a** and **(±)-13a** S63

1. Optimization selenium-mediated IFAC of alkenes 1

To a solution of the electrophilic selenium reagent in CH_2Cl_2 (10 mL) was added Lewis acid catalyst. The solution was stirred for 5 minutes. Cinnamyl-3,4,5-trimethoxybenzyl ether (**1a**, 0.5 mmol) was added and the reaction mixture was stirred until TLC showed the completion of the reaction. Saturated $NaHCO_3$ (aq., 5 mL) was added and the mixture was subjected to a conventional extractive workup (CH_2Cl_2, 3×10 mL). The combined organic solution was washed with brine and dried over $MgSO_4$. After the removal of the solvents under reduced pressure, the residue was subjected to flash chromatography on silica gel (petroleum ether (PE)/ethyl acetate (EA) = 10/1) to deliver the products.

Table S1. Optimization for the Synthesis of 2-Benzoxepin, Isochroman, and Isochromene[a]



Entry	[PhSe+]	Catalyst	Amount of the catalyst (mol%)	Temperature (°C)	Time (h)	Yield[f] of **2a** (%)	Yield[f] of **3a** (%)	Yield[f] of **4a** (%)
1	PhSeBr	$BF_3{\cdot}Et_2O$	10	rt	2		NR	
2	PhSeSePh[b]	$BF_3{\cdot}Et_2O$	10	rt	2	< 5	< 5	0
3	PhSeOTf[d]	$BF_3{\cdot}Et_2O$	10	rt	2	< 5	9	0
4	NPSSac	$BF_3{\cdot}Et_2O$	10	rt	2	< 5	15	0
5	TPSCA[e]	$BF_3{\cdot}Et_2O$	10	rt	2		NR	
6	NPSP	$BF_3{\cdot}Et_2O$	10	rt	2	93	0	0
7	NPSS	$BF_3{\cdot}Et_2O$	10	rt	2	56	0	0
8	NPSP	$FeCl_3$	10	rt	2		NR	
9	NPSP	$TiCl_4$	10	rt	2		NR	
10	NPSP	-	-	rt	2		NR	
11	NPSP	TMSOTf	10	rt	2	70	0	0
12	NPSP	$ZnCl_2$	10	rt	2	92	0	0
13	NPSP	$ZnCl_2$	20	rt	2	93	0	0
14	NPSP	$ZnCl_2$	30	rt	2	92	0	0
15	NPSP	$ZnCl_2$	5	rt	2	80	0	0
16	NPSP	$BF_3{\cdot}Et_2O$	5	rt	2	70	0	0
17	NPSP	$BF_3{\cdot}Et_2O$	10	rt	2	93	0	0
18	**NPSP**	**$BF_3{\cdot}Et_2O$**	**20**	**rt**	**2**	**95**	**0**	**0**
19	NPSP	$BF_3{\cdot}Et_2O$	30	rt	2	95	0	0

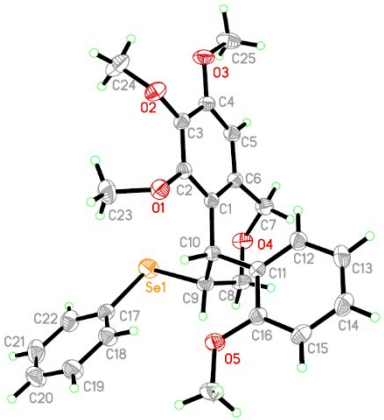
20	NPSP	$ZnCl_2$	20	rt	12	94	0	0
21	NPSP	$ZnCl_2$	20	rt	24	94	0	0
22	NPSP	$ZnCl_2$	20	rt	48	93	0	0
23	NPSP	$BF_3{\cdot}Et_2O$	20	rt	12	< 5	92	0
24	**NPSP**	**$BF_3{\cdot}Et_2O$**	**20**	**rt**	**24**	**< 5**	**94**	**0**
25	NPSP	$BF_3{\cdot}Et_2O$	20	rt	48	< 5	93	0
26	NPSP	$BF_3{\cdot}Et_2O$	20	60	2	< 5	55	45
27	PhSeOTf[d]	$BF_3{\cdot}Et_2O$	20	rt	2	< 5	65	**0**
28	PhSeOTf[d]	$BF_3{\cdot}Et_2O$	20	rt	4	< 5	72	**0**
29	PhSeOTf[d]	$BF_3{\cdot}Et_2O$	20	rt ~ 60[c]	4	< 5	70	**0**
30	NPSSac	$BF_3{\cdot}Et_2O$	20	rt	2	< 5	88	0
31	NPSSac	$BF_3{\cdot}Et_2O$	20	rt	4	< 5	90	0
32	NPSSac	$BF_3{\cdot}Et_2O$	20	rt ~ 60[c]	4	< 5	90	0
33	NPSSac	$BF_3{\cdot}Et_2O$	20	60	2	< 5	89	0
34	TPSCA[e]	$BF_3{\cdot}Et_2O$	20	rt	2		NR	
35	TPSCA[e]	$BF_3{\cdot}Et_2O$	40	rt	2	10	< 5	30
36	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	rt	2	51	< 5	45
37	TPSCA[e]	$BF_3{\cdot}Et_2O$	80	rt	2	50	< 5	45
38	TPSCA[g]	$BF_3{\cdot}Et_2O$	60	rt	2	45	< 5	35
39	TPSCA[h]	$BF_3{\cdot}Et_2O$	60	rt	2	49	< 5	42
40	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	rt	12	15	35	44
41	**TPSCA[e]**	**$BF_3{\cdot}Et_2O$**	**60**	**-78**	**2**	**92**	**0**	**0**
42	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	-20	2	80	0	13
43	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	0	2	75	0	18
44	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	40	2	17	27	50
45	**TPSCA[e]**	**$BF_3{\cdot}Et_2O$**	**60**	**60**	**2**	**< 5**	**< 5**	**95**
46	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	80	2	< 5	< 5	60
47	TPSCA[e]	$BF_3{\cdot}Et_2O$	60	60	4	< 5	< 5	95
48	-	$BF_3{\cdot}Et_2O$	60	60	2		NR	
49	TPSCA[e]	-	-	60	2		NR	

[a] The reaction was performed on a 0.5 mmol scale. [b] 0.28 Mmol of PhSeSePh was added. [c] The reaction was performed at room temperature for 2 h and then at 60 °C for 2 h. [d] PhSeOTf was produced in situ by the reaction of 0.55 mmol of PhSeBr and 0.55 mmol of AgOTf in DCM at room temperature. [e] 0.37 Equiv. of TPSCA was added. [f] Isolated yield. [g] 0.3 Equiv of TPSCA was added. [h] 0.5 Equiv. of TPSCA was added.

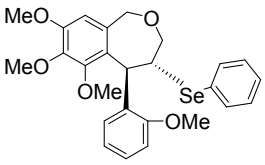
We commenced our exploration with the optimization of the IFCA of cinnamyl-3,4,5-trimethoxybenzyl ether (**1a**). An investigation using a series of Lewis acids and electrophilic selenium reagents identified TMSOTf and $ZnCl_2$ as active catalysts and NPSP, TPSCA, and NPSSac as active selenium reagents. In the presence of 20 mol% $BF_3{\cdot}Et_2O$ or 20 mol% $ZnCl_2$ and stirring for 2 h at room temperature, the NPSP-induced 7-*endo*-trig carbocyclization of **1a** was observed, providing 2-benzoxepin **2a** in 95% and 93% yield, respectively (Table S1,

entries 18 and 13). The yield of **2a** decreased when 5 mol% $BF_3{\cdot}Et_2O$ or 5 mol% $ZnCl_2$ was used (Table S1, entries 16 and 15), whereas the yield of **2a** was almost constant when 30 mol% catalyst was used (Table S1, entries 19 and 14). When the reaction time was extended to more than 12 h, the yield of **2a** was slightly increased in the presence of 20 mol% $ZnCl_2$, whereas isochroman **3a** was formed in more than 92% yield in the presence of 20 mol% $BF_3{\cdot}Et_2O$ and by a rearrangement/6-*exo*-trig oxycyclization sequence of **2a** (Table S1, entries 20 to 25). Interestingly, **3a** was also formed in 90% yield when the cyclization reaction proceeded at room temperature for 4 h and NPSSac and 20 mol% $BF_3{\cdot}Et_2O$ were used (Table S1, entry 31). When the reaction was performed at room temperature to 60 °C, the yield of product **3a** was almost constant (Table S1, entries 32 and 33). Excitingly, when using 0.37 equiv. of TPSCA and 60 mol% $BF_3{\cdot}Et_2O$, isochromene **4a** was afforded at 60 °C in 95% yield by a 6-*exo*-trig carbocyclization- /deselenenylation sequence, whereas product **2a** was formed at -78 °C in 92% yield (Table S1, entries 45 and 41). This cyclization reaction was rather sluggish in the absence of catalyst or the electrophilic selenium reagent (Table S1, entries 10, 48, and 49).

2. Crystallographic data for product 2m (CCDC 1941659)



2m



(±)-**2m**

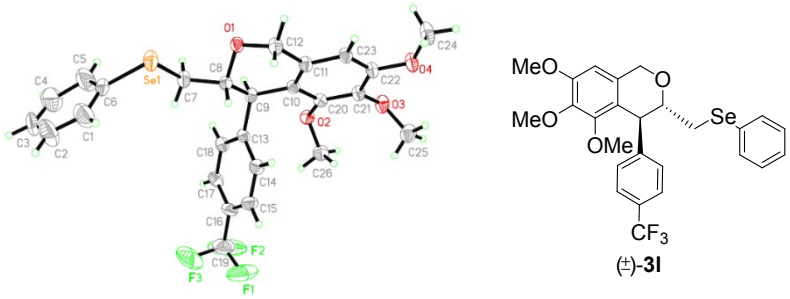
Figure S1. ORTEP structure of **2m**

Table S2. Crystal data and structure refinement for **2m**

Identification code	**2m**
Empirical formula	$C_{26}H_{28}O_5Se$
Formula weight	499.44
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Pbca
Unit cell dimensions	a = 9.3459(8) Å α = 90°. b = 19.5855(17) Å β = 90°. c = 25.163(2) Å γ = 90°.
Volume	4605.8(7) $Å^3$
Z, Calculated density	8, 1.441 Mg/m^3
Absorption coefficient	1.666 mm^{-1}
F(000)	2064

Crystal size	0.32 x 0.30 x 0.28 mm^3
θ range for data collection	1.62 to 25.15°.
Limiting indices	$-10 \le h \le 11$, $-23 \le k \le 21$, $-30 \le l \le 30$
Reflections collected / unique	24675 / 4114 [R(int) = 0.0492]
Completeness to θ = 25.15	100.0 %
Max. and min. transmission	0.6527 and 0.6178
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4114 / 0 / 293
Goodness-of-fit on F^2	1.023
Final R indices [I>2σ(I)]	$R_1 = 0.0349$, $wR_2 = 0.0857$
R indices (all data)	$R_1 = 0.0596$, $wR_2 = 0.0971$
Largest diff. peak and hole	0.323 and -0.467 e. $Å^{-3}$

3. Crystallographic data for product 3l (CCDC 1941658)



(±)-**3l**

3l

Figure S2. ORTEP structure of **3l**

Table S3. Crystal data and structure refinement for **3l**

Identification code	**3l**	
Empirical formula	$C_{26}H_{25}F_3O_4Se$	
Formula weight	537.42	
Temperature	293(2) K	
Wavelength	0.71073 A	
Crystal system, space group	Triclinic, P-1	
Unit cell dimensions	a = 6.9173(8) Å b = 13.9163(16) Å c = 14.1631(16) Å	α = 114.9980(10)°. β = 94.3680(10)°. γ = 94.2510(10)°.
Volume	1223.5(2) $Å^3$	
Z, Calculated density	2, 1.459 Mg/m^3	
Absorption coefficient	1.587 mm^{-1}	
F(000)	548	
Crystal size	0.32 x 0.30 x 0.24 mm^3	

θ range for data collection	1.60 to 25.14°.
Limiting indices	-8 ≤ h≤ 8, -16 ≤ k ≤ 16, -16 ≤ l ≤ 16
Reflections collected / unique	9448 / 4325 [R(int) = 0.0541]
Completeness to θ = 25.15	98.8 %
Max. and min. transmission	0.7019 and 0.6306
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4325 / 0 / 310
Goodness-of-fit on F^2	0.999
Final R indices [I>2σ(I)]	R_1 = 0.0814, wR_2 = 0.2602
R indices (all data)	R_1 = 0.1107, wR_2 = 0.2805
Largest diff. peak and hole	0.750 and -0.760 e. $Å^{-3}$

4. The intrinsic reaction coordinates paths of the key steps of the carbocyclization reactions

All calculations were performed with Gaussian 09[1] at B3LYP/6-31G* level. The structures of transition state (TS) were firstly optimized in gas phase and characterized by one imaginary frequency. The coordinates for the structures of TS were also provided in supporting information. The intrinsic reaction coordinates (IRC) paths were scanned to verify the TS structure and identify the structures of the reactant and product. Geometry optimizations in gas phase were applied for the reactants and products before frequency calculations. The relative Gibbs free energies at reaction temperature were given in vacuum and in CH_2Cl_2 (using SMD solvent model)

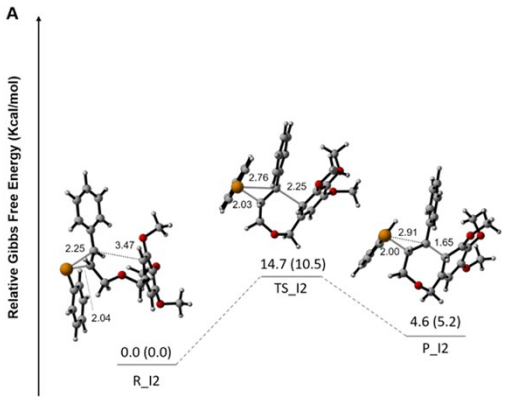


Figure S3. Geometries and relative free energies of the reactant (**R_I2**), transition state (**TS_I2**), and product (**P_I2**). All calculations were performed with B3LYP/6-31G(d). For free energy calculation, the temperature was set to reaction temperature (25 °C). The data was computed with SMD solvent model (DCM), as well as in vacuum (in parentheses). The distance between atoms were shown as Angstrom

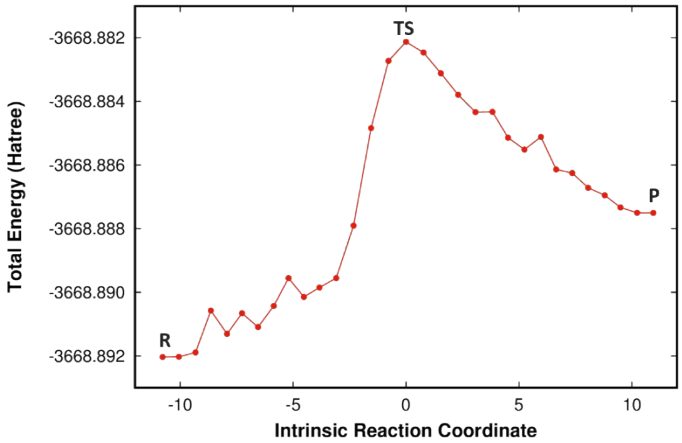


Figure S4. Intrinsic reaction coordinate (IRC) path from **R_I2** to **P_I2**

Table S4. Coordinates of **TS_I2**

1	1		
C	0	2.57218100	-2.17687000	-0.04802900
C	0	3.05415700	-0.84778500	-0.07410300
C	0	2.50748000	0.07787800	0.83539200
C	0	1.37061700	-0.28652300	1.63196900
C	0	0.96057400	-1.65175500	1.67973100
C	0	1.51025400	-2.55922800	0.80258600
C	0	-0.34972600	0.59237000	0.48473600
C	0	-1.45844100	0.61326500	1.47422000
C	0	-1.84970500	-0.65680000	2.23033800
O	0	-0.87447500	-1.05185800	3.18284200
C	0	-0.01871100	-2.08854100	2.74800600
C	0	0.18933400	1.83038800	-0.07190900
C	0	0.26969900	3.02677500	0.66930100
C	0	0.72628800	4.19718000	0.07337200
C	0	1.11385200	4.19707700	-1.27048900
C	0	1.05434000	3.01471000	-2.01598200
C	0	0.60815500	1.84069900	-1.41826900
Se	0	-3.03122400	1.21795100	0.34343800
C	0	-3.43163000	-0.34553800	-0.70253500
C	0	-4.35394500	-1.28875200	-0.23081700
C	0	-4.70423900	-2.37609400	-1.03253400
C	0	-4.14620500	-2.51615600	-2.30516200
C	0	-3.24441800	-1.56298400	-2.78488500
C	0	-2.89096000	-0.47308600	-1.98886800
H	0	1.15458900	0.35191100	2.48186200
O	0	3.06070800	-3.13987600	-0.85682400
C	0	4.47811500	-3.43620800	-0.83848900
O	0	4.09448500	-0.49952400	-0.90214900
C	0	3.75932600	-0.39570300	-2.29860000

O 0	2.90986400	1.33167000	1.04462500
C 0	4.07492900	1.93140900	0.44104100
H 0	1.20712000	-3.60157000	0.78924700
H 0	-0.37774300	-0.24581300	-0.20807000
H 0	-1.37200000	1.44623800	2.17502800
H 0	-2.06566300	-1.47408300	1.53037400
H 0	-2.76496500	-0.43512500	2.78661500
H 0	0.54012300	-2.39993100	3.63877500
H 0	-0.59676500	-2.95936400	2.40342800
H 0	-0.01481300	3.04208700	1.71680100
H 0	0.77841300	5.11293500	0.65420700
H 0	1.45875700	5.11571400	-1.73585200
H 0	1.34299300	3.01594300	-3.06298800
H 0	0.54493900	0.92561800	-2.00170700
H 0	-4.80202900	-1.16333400	0.74969500
H 0	-5.42022300	-3.10610600	-0.66656200
H 0	-4.42579300	-3.35978400	-2.92940100
H 0	-2.82686900	-1.66084200	-3.78288400
H 0	-2.21526900	0.28877500	-2.36528600
H 0	4.61020300	-4.23030800	-1.57298300
H 0	5.07821400	-2.56432200	-1.09877600
H 0	4.75789500	-3.80124800	0.15475200
H 0	4.69958200	-0.20393600	-2.81792900
H 0	3.31452900	-1.32456700	-2.66862700
H 0	3.06998200	0.43971700	-2.46613400
H 0	4.95735400	1.31083600	0.59629000
H 0	3.91487600	2.10428900	-0.62460700
H 0	4.18159100	2.88427700	0.95977900

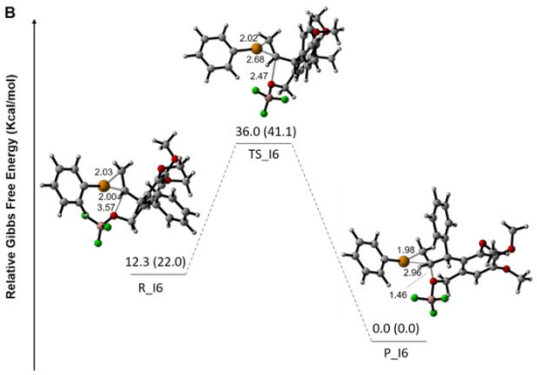


Figure S5. Geometries and relative free energies of the reactant (**R_I6**), transition state (**TS_I6**), and product (**P_I6**). All calculations were performed with B3LYP/6-31G(d). For free energy calculation, the temperature was set to reaction temperature (25 °C). The data was computed with SMD solvent model (DCM), as well as in vacuum (in parentheses). The distance between atoms were shown as Angstrom

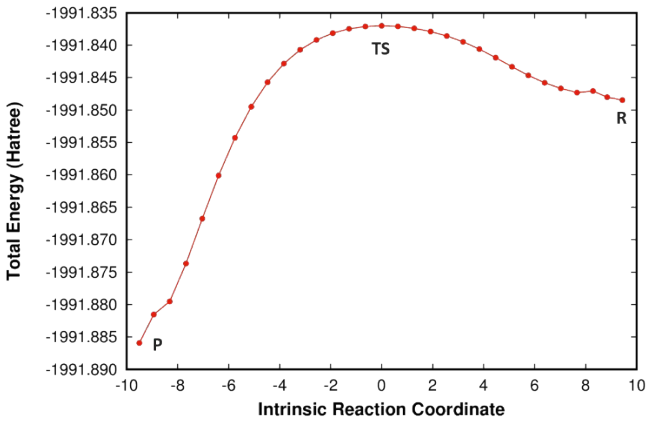


Figure S6. Intrinsic reaction coordinate (IRC) path from **R_I6** to **P_I6**

Table S5. Coordinates of **TS_I6**

0 1			
C 0	3.04271600	-2.15145800	0.87506300
C 0	3.35340500	-1.25341900	-0.15066200
C 0	2.54989400	-0.11376000	-0.34799200
C 0	1.44274400	0.14864700	0.47416300
C 0	1.12212400	-0.78628600	1.49188500
C 0	1.92620400	-1.91099200	1.67468800
C 0	0.48404700	1.34146400	0.35966900
C 0	-0.80334100	0.96400800	-0.28652200
C 0	-0.86641700	0.22304600	-1.53647000
O 0	-1.21047400	-0.09495000	1.91000000
C 0	-0.02111600	-0.57942100	2.48779300
C 0	0.76463200	2.69989300	-0.32910300
C 0	1.02447200	2.89398000	-1.69771900
C 0	1.16442300	4.18113700	-2.21610600
C 0	1.02758800	5.29690500	-1.38844600
C 0	0.73231500	5.11914000	-0.03565700
C 0	0.58231800	3.83538600	0.48456100
Se 0	-1.38705600	-1.59618300	-0.83113400
C 0	-3.29038500	-1.45554000	-1.05369400
C 0	-4.08654100	-0.93052800	-0.02957200
C 0	-5.47099600	-0.88168700	-0.20473400
C 0	-6.05324600	-1.36323900	-1.37895400
C 0	-5.25253800	-1.88886000	-2.39647900
C 0	-3.86765200	-1.93068300	-2.23884900
O 0	3.75912100	-3.30940100	1.05676300
C 0	5.10451400	-3.13557600	1.51859800
O 0	4.43580500	-1.47121600	-0.97677500
C 0	4.16545000	-2.37280200	-2.05742400
O 0	2.83390200	0.70203400	-1.41926900
C 0	4.01754000	1.50280100	-1.28762000
B 0	-1.92749300	0.96477300	2.68116800

F 0	-2.97392000	1.37511000	1.82931600
F 0	-1.04240000	2.05503600	2.90081500
H 0	1.68939800	-2.63405900	2.44987700
H 0	0.23862400	1.62712200	1.37804300
H 0	-1.71801700	1.39182900	0.11717900
H 0	0.09291400	0.07851800	-2.02926300
H 0	-1.65929500	0.52676400	-2.21758700
H 0	0.33094900	0.11397700	3.26653100
H 0	-0.21400400	-1.54162700	2.98194500
H 0	1.15564500	2.04445500	-2.35453100
H 0	1.37728500	4.31059500	-3.27395400
H 0	1.13707800	6.29742900	-1.79809800
H 0	0.60466900	5.97944700	0.61531700
H 0	0.30171700	3.69973100	1.52502200
H 0	-3.63238700	-0.53183700	0.86984800
H 0	-6.09106700	-0.46320700	0.58281000
H 0	-7.13219800	-1.32762000	-1.50404300
H 0	-5.70370000	-2.26274300	-3.31157300
H 0	-3.23450900	-2.33337700	-3.02404100
H 0	5.11572000	-2.63762100	2.49667600
H 0	5.51895000	-4.14094400	1.62062600
H 0	5.69965200	-2.55860800	0.80461000
H 0	5.09808100	-2.46567100	-2.61882600
H 0	3.86362200	-3.35543000	-1.67851400
H 0	3.38346400	-1.96897600	-2.71172500
H 0	3.94757500	2.15114900	-0.40627100
H 0	4.90678300	0.87045300	-1.22271900
H 0	4.06397000	2.12218000	-2.18584800
F 0	-2.38849400	0.47315900	3.88464300

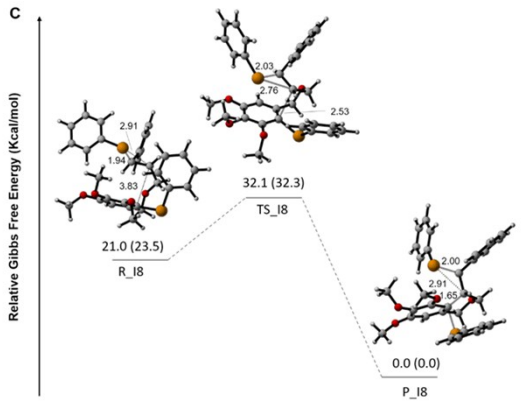


Figure S7. Geometries and relative free energies of the reactant (**R_I8**), transition state (**TS_I8**), and product (**P_I8**). All calculations were performed with B3LYP/6-31G(d). For free energy calculation, the temperature was set to reaction temperature (60 °C). The data was computed with SMD solvent model (DCM), as well as in vacuum (in parentheses). The distance between atoms were shown as Angstrom

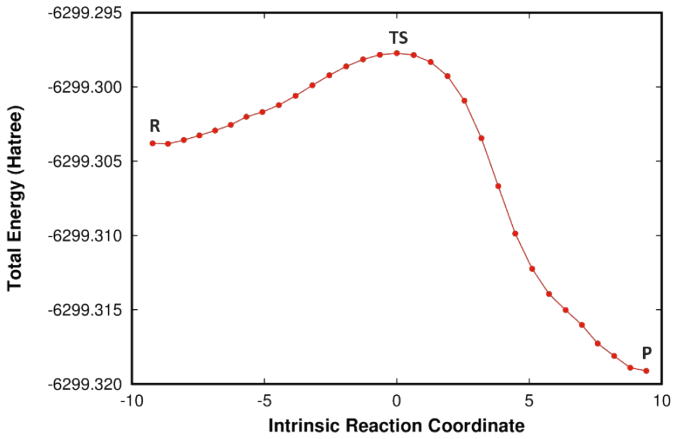


Figure S8. Intrinsic reaction coordinate (IRC) path from **R_I8** to **P_I8**

Table S6. Coordinates of **TS_I8**

1	1		
C	0	0.70516600	-2.80470300	1.04998000
C	0	-0.09046300	-2.87051200	-0.12628600
C	0	-1.21120400	-2.04678700	-0.22295900
C	0	-1.57905900	-1.13645200	0.81482000
C	0	-0.81282100	-1.15598300	2.03125200
C	0	0.31362800	-1.95668900	2.10242700
C	0	0.99710700	1.02417800	0.55849800
C	0	-0.48019200	1.12977800	0.61947700
C	0	-1.19135400	1.62285900	1.84452700
O	0	-0.68868500	1.06914200	3.03472800
C	0	-1.15852200	-0.27879700	3.21732400
Se	0	1.58126700	-0.06501900	-0.99257900
O	0	1.83288200	-3.48008500	1.28663500
C	0	2.32882900	-4.56563200	0.47496600
O	0	0.19554300	-3.77900200	-1.10330000
C	0	0.66093600	-3.27175600	-2.37234800
O	0	-1.97463600	-2.10832700	-1.35099800
C	0	-2.89709100	-3.22284600	-1.43445100
C	0	1.34030100	2.51122700	0.41617900
C	0	1.19295500	3.18377100	-0.80852200
C	0	1.47101000	4.54700400	-0.89526900
C	0	1.89139300	5.24869400	0.23607900
C	0	2.03395800	4.58426000	1.46024600
C	0	1.74669400	3.22597400	1.55613100
Se	0	-3.45986800	-0.65049400	0.88052400
C	0	-3.75017500	0.70969900	-0.46910800
C	0	-4.66918700	1.70136300	-0.10053700
C	0	-5.02204400	2.69791200	-1.01156300
C	0	-4.44173800	2.72394500	-2.28057400
C	0	-3.51937100	1.73946900	-2.63965600

C 0	-3.17859700	0.72027200	-1.74620200
C 0	3.48443700	0.06504000	-0.71173600
C 0	4.23796400	0.99239500	-1.43862300
C 0	5.62029400	1.05495500	-1.25487800
C 0	6.24511100	0.19942400	-0.34574400
C 0	5.49015100	-0.72802100	0.37628200
C 0	4.10927900	-0.80378400	0.19064100
H 0	0.93192900	-1.96043200	2.99460100
H 0	1.41771200	0.62488200	1.48070000
H 0	-1.00384400	1.27702400	-0.32468600
H 0	-2.26584900	1.44140800	1.73022800
H 0	-1.04850100	2.71022600	1.89819100
H 0	-0.65414300	-0.64109800	4.11437800
H 0	-2.23922500	-0.26772300	3.39542200
H 0	3.15636000	-4.97430100	1.05544800
H 0	1.56006200	-5.32299300	0.32247300
H 0	2.69539200	-4.19959600	-0.48612900
H 0	0.70332800	-4.13932200	-3.03182700
H 0	-0.03098900	-2.52866700	-2.77392900
H 0	1.65906400	-2.83468200	-2.26493400
H 0	-3.38546000	-3.12257600	-2.40409100
H 0	-2.35763800	-4.17153900	-1.37982400
H 0	-3.63615300	-3.13874600	-0.63418200
H 0	0.90302900	2.61965500	-1.68949900
H 0	1.36284000	5.05942200	-1.84656300
H 0	2.11077400	6.31005800	0.16717600
H 0	2.37354000	5.12650900	2.33769300
H 0	1.84240000	2.71370800	2.50960600
H 0	-5.10736500	1.69448800	0.89375700
H 0	-5.74090400	3.45838300	-0.72074600
H 0	-4.70940200	3.50440000	-2.98654900
H 0	-3.07281600	1.74869400	-3.63024500
H 0	-2.49538600	-0.06427500	-2.04741700
H 0	3.74920900	1.65852100	-2.14178500
H 0	6.20651700	1.77332700	-1.82056400
H 0	7.32068500	0.25116500	-0.20373100
H 0	5.97742900	-1.39766100	1.07939300
H 0	3.52466200	-1.53618400	0.73874900

5. Computed absolute energy values and imaginary frequency of TS

Table S7. Computed absolute energy values and imaginary frequency of TS

	E(a.u.)		G(a.u.)		Number of Imaginary Frequencies	Imaginary Frequency (Vacuum, cm^{-1})
	Vacuum	CH_2Cl_2	Vacuum	CH_2Cl_2	0	NA
I2_R	-3668.396441	-3668.479110	-3668.492320	-3668.573784	1	-205.38
I2_T	-3668.384190	-3668.463506	-3668.475621	-3668.550385	0	NA
I2_P	-3668.394511	-3668.476718	-3668.484087	-3668.566451	0	NA
I6_R	-3992.572456	-3992.615709	-3992.671516	-3992.717700	1	-148.48
I6_T	-3992.540380	-3992.582042	-3992.641135	-3992.680009	0	NA
I6_P	-3992.604855	-3992.638995	-3992.706585	-3992.737377	0	NA
I8_R	-6298.716374	-6298.799019	-6298.844795	-6298.926185	1	-125.99
I8_T	-6298.704737	-6298.785653	-6298.830796	-6298.908362	0	NA
I8_P	-6298.754964	-6298.838509	-6298.882312	-6298.959584	0	NA

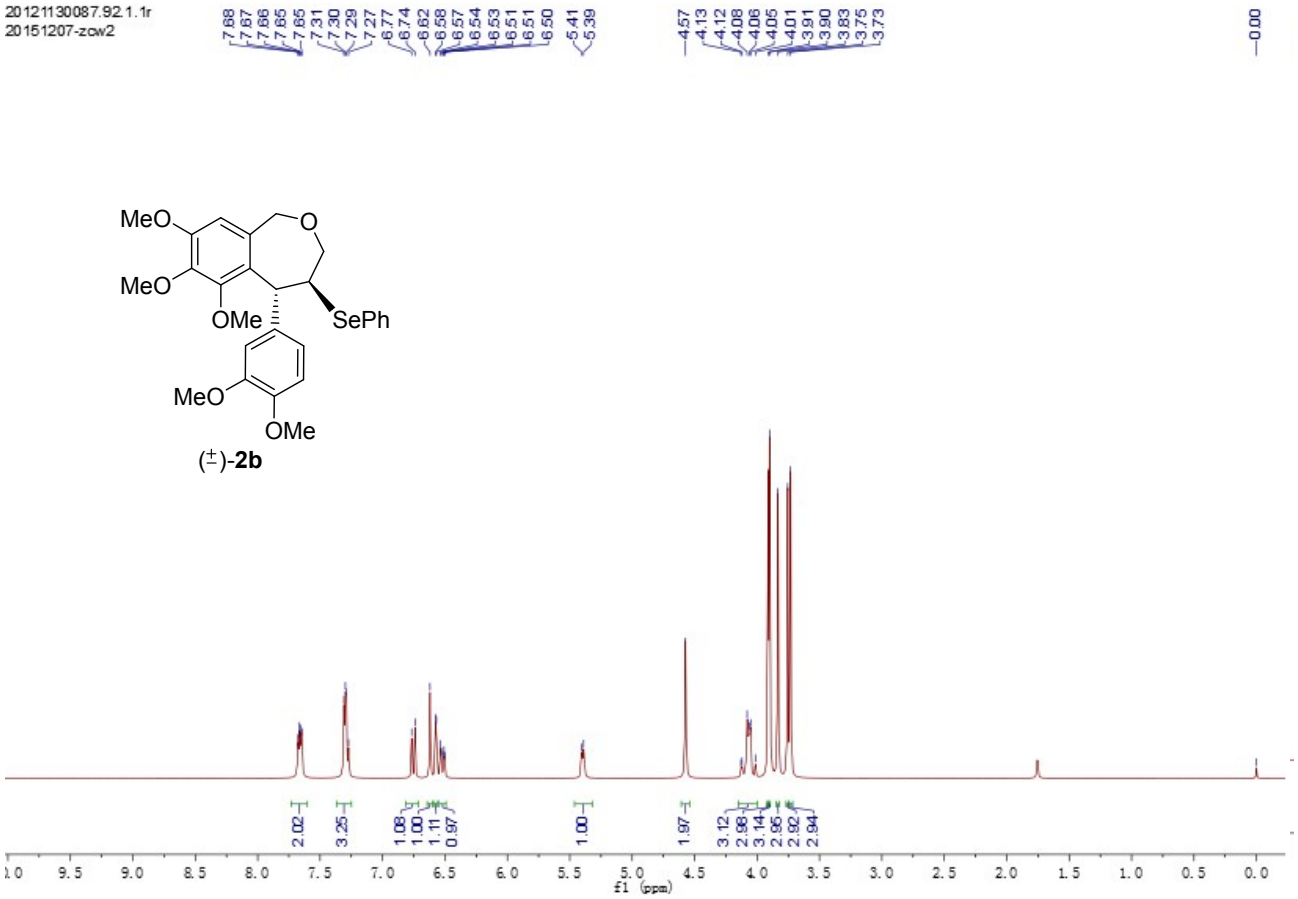
6. References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. Heyd, Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox in *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, **2009**.

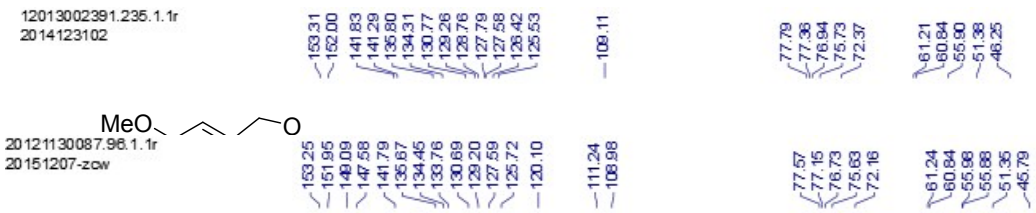
7. Copies of ^{1}H NMR and ^{13}C NMR Spectra for compounds

20121130087.92.1.1r
20151207-zcw2

(±)-**2b**

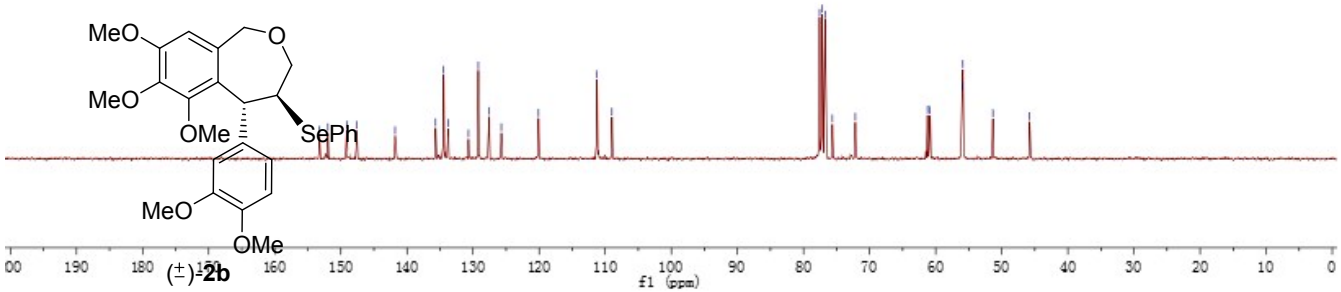


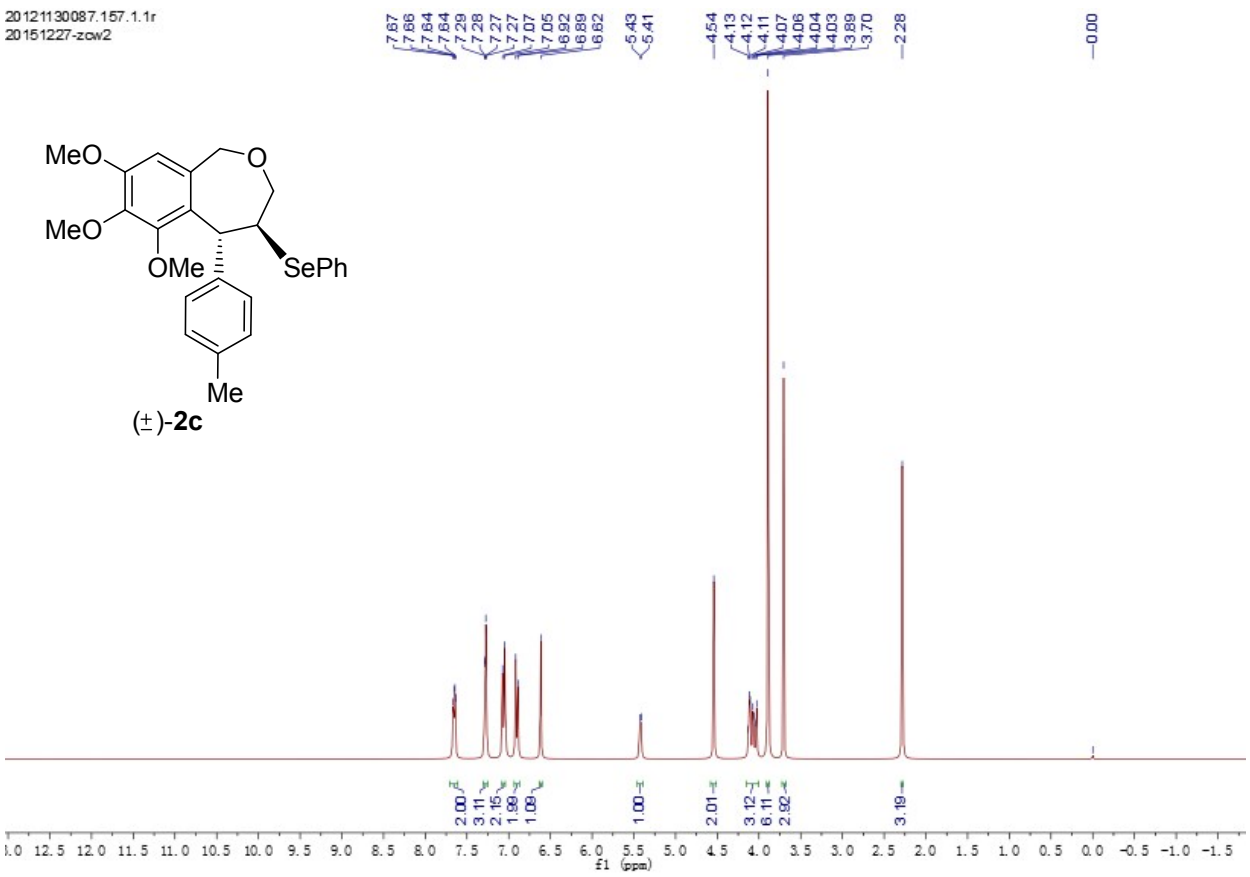
12013002391.235.1.1r
2014123102

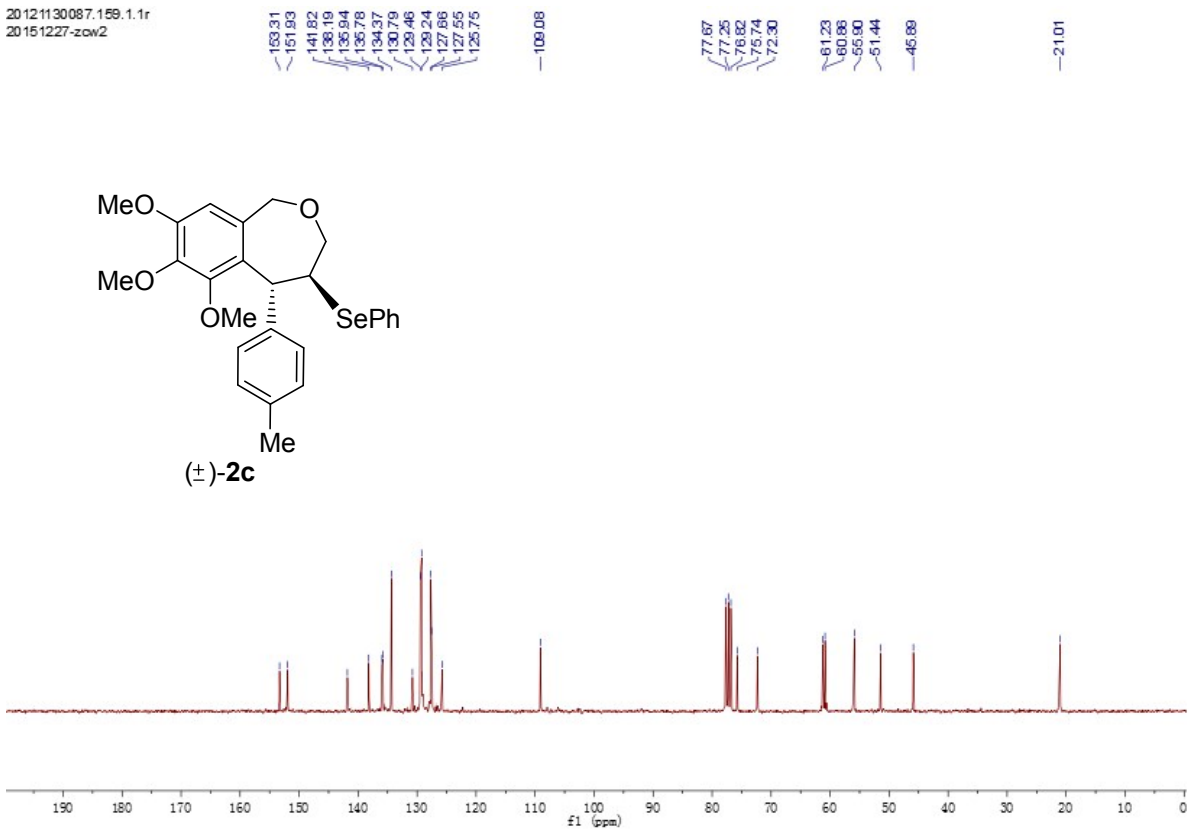


20121130087.96.1.1r
20151207-zcw

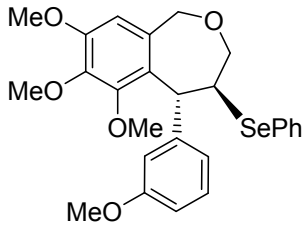
(±)-**2b**



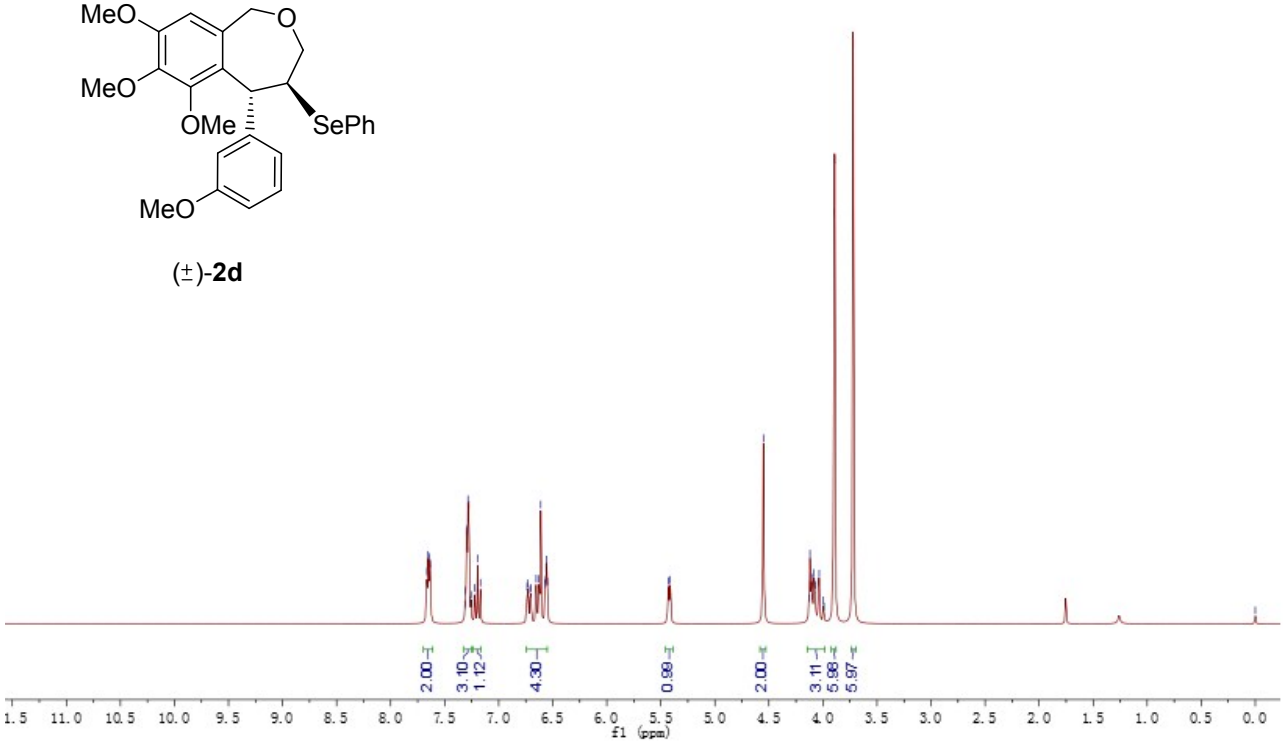

20121130087.157.1.1r
20151227-zcw2
MeO
MeO
OMe
O
SePh
Me
(±)-2c
f1 (ppm)


20121130087.159.1.1r
20151227-zcw2
MeO
MeO
OMe
O
SePh
Me
(±)-2c
f1 (ppm)

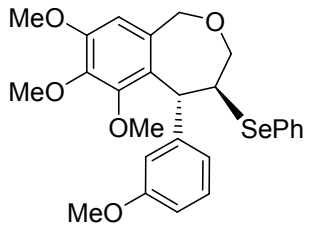
20121130087.51.1.1r
20151117-zcw2



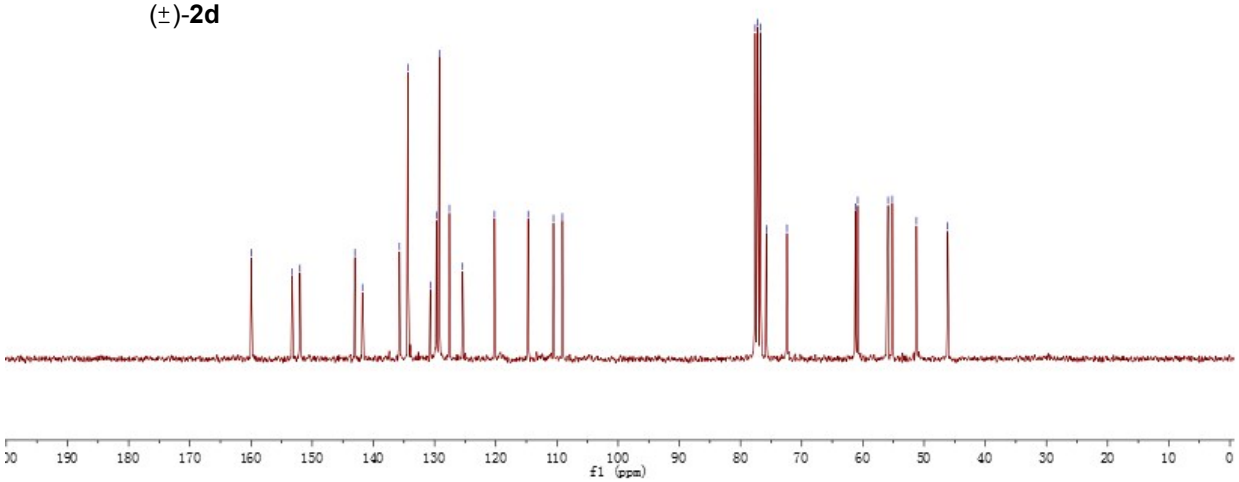
(±)-**2d**



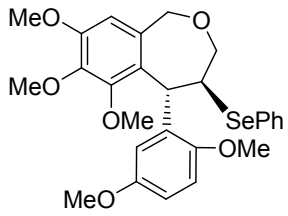
20121130087.53.1.1r
20151117-zcw2



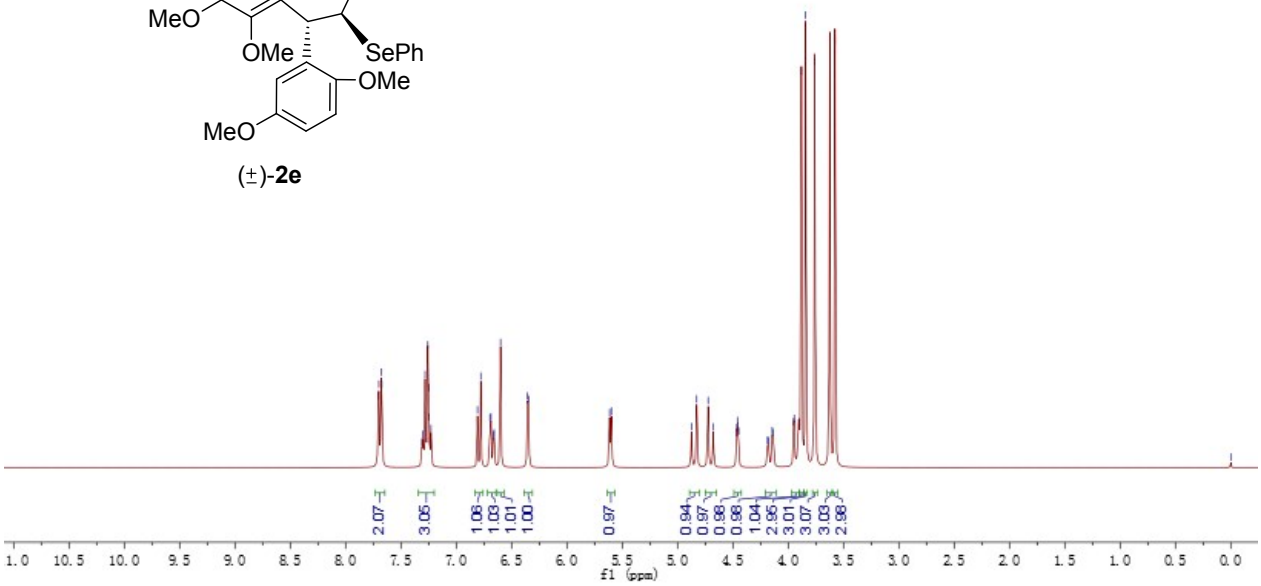
(±)-**2d**



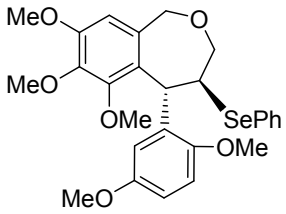
20121130087.76.1.1r
20151124-zcw1



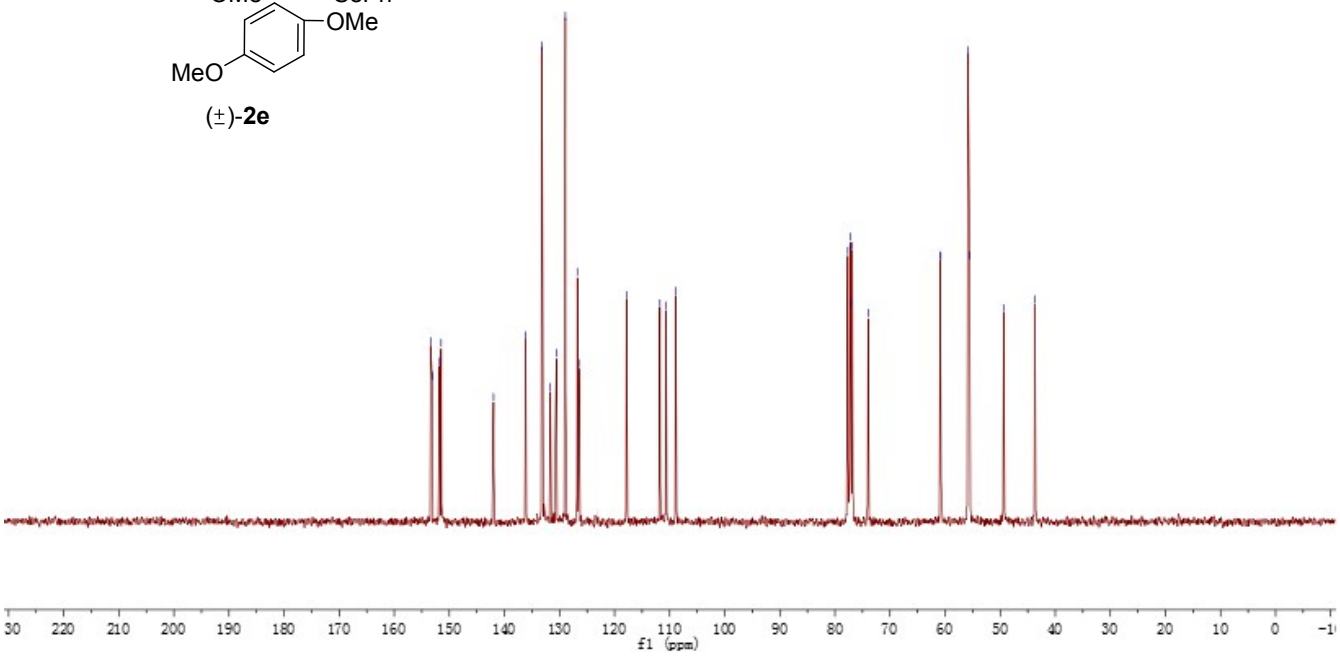
(±)-**2e**

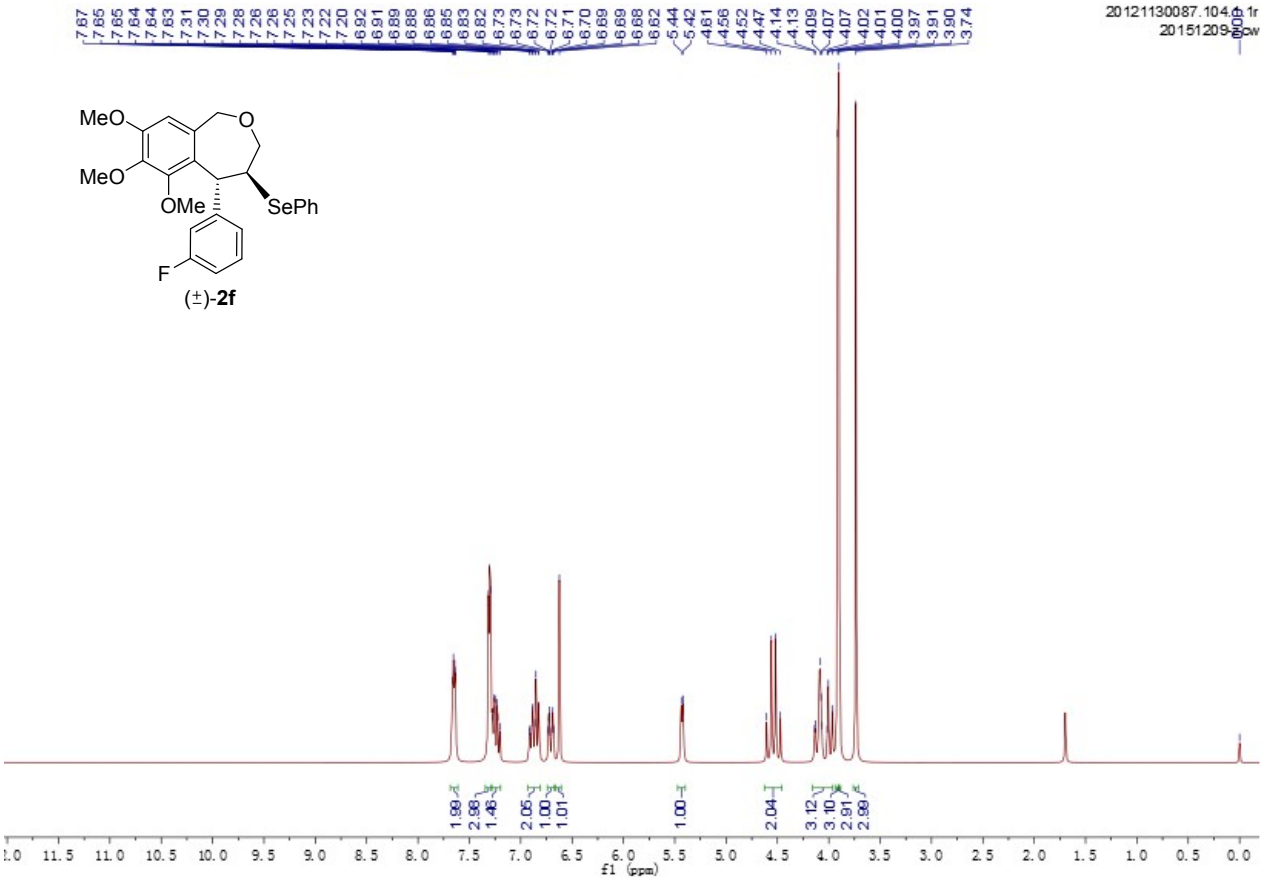


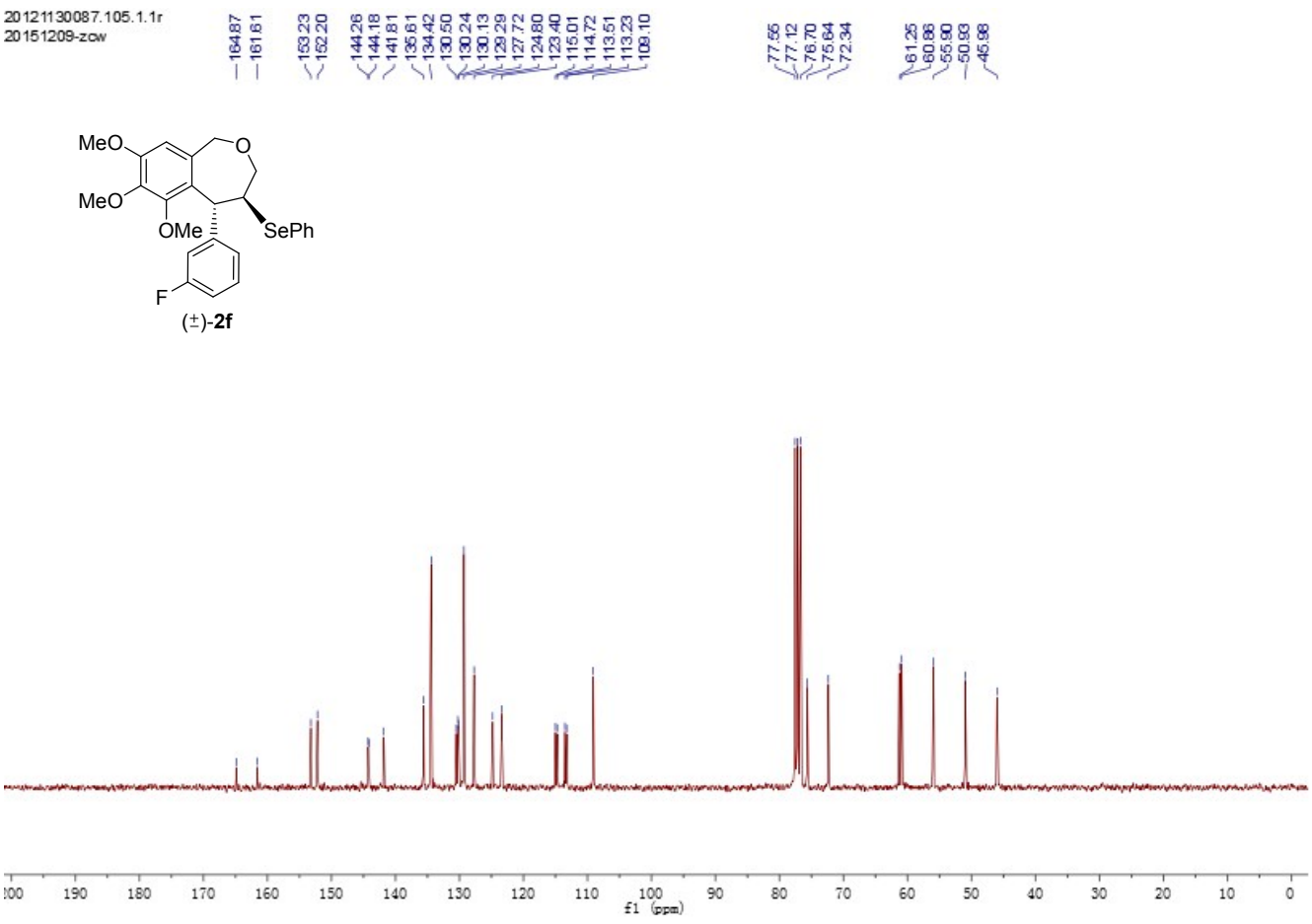
20121130087.79.1.1r
20151124-zcw1



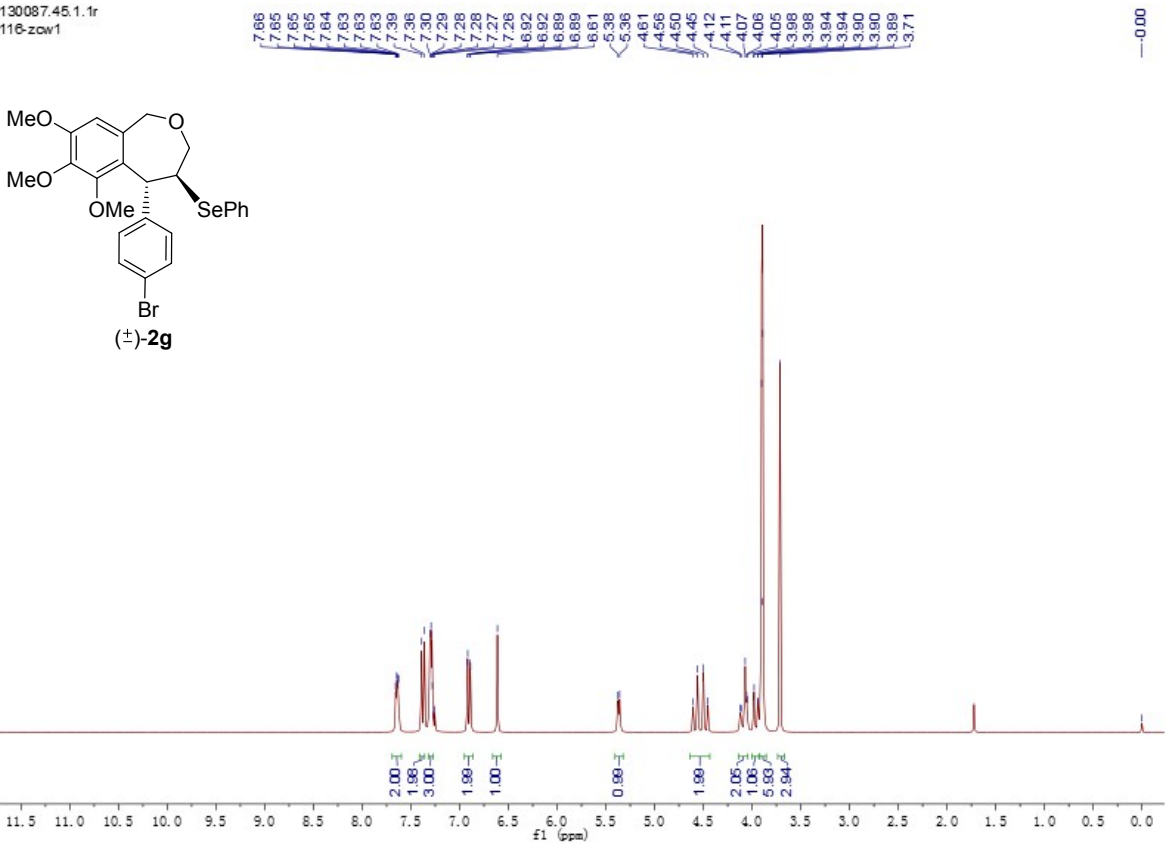
(±)-**2e**




20121130087.104.1.1r
20151209-zcw
MeO
MeO
OMe
O
SePh
F
(±)-2f
f1 (ppm)

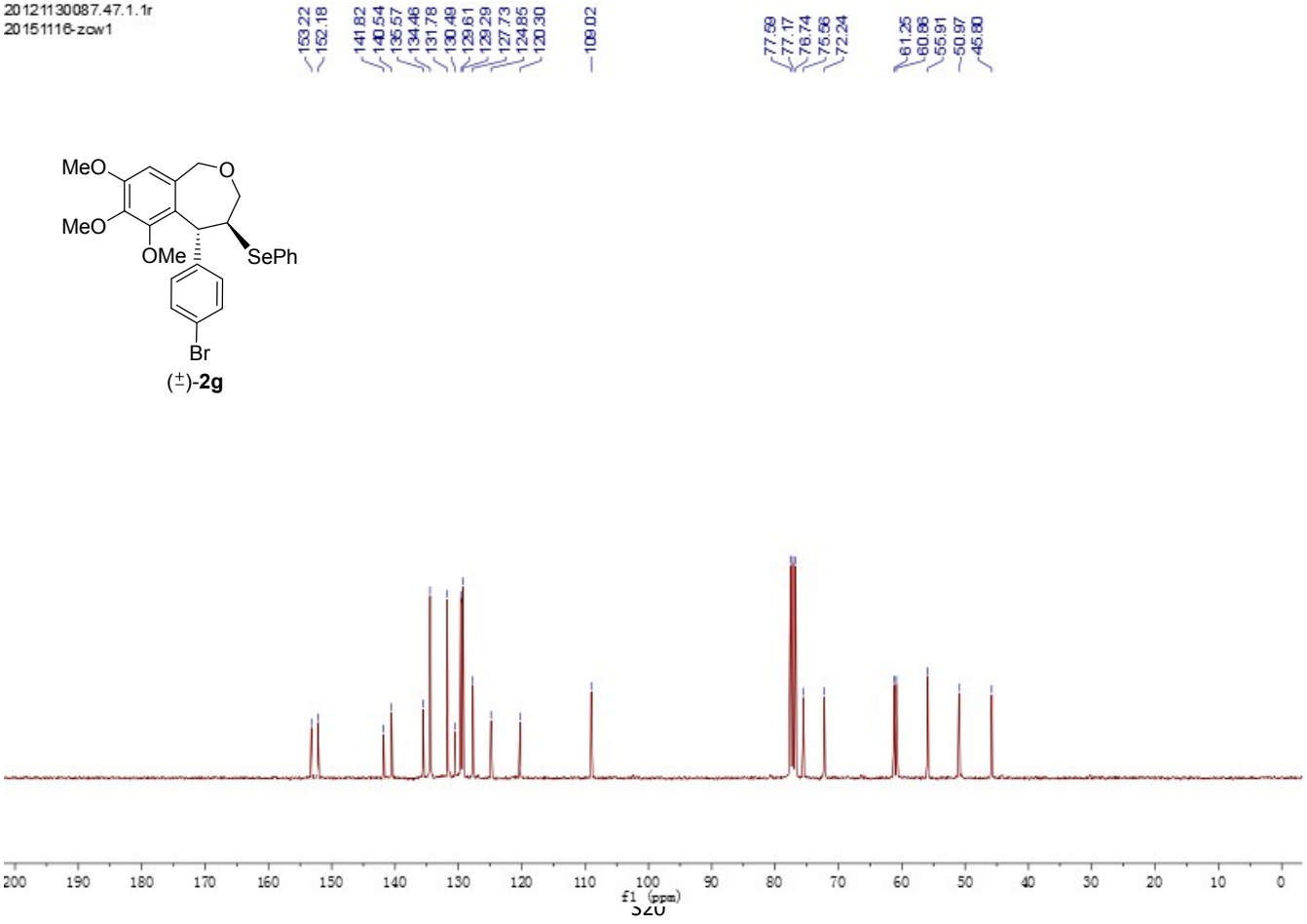

20121130087.105.1.1r
20151209-zcw
MeO
MeO
OMe
O
SePh
F
(±)-2f
f1 (ppm)

20121130087.45.1.1r
20151116-zcw1



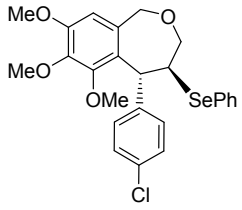
(±)-**2g**

20121130087.47.1.1r
20151116-zcw1

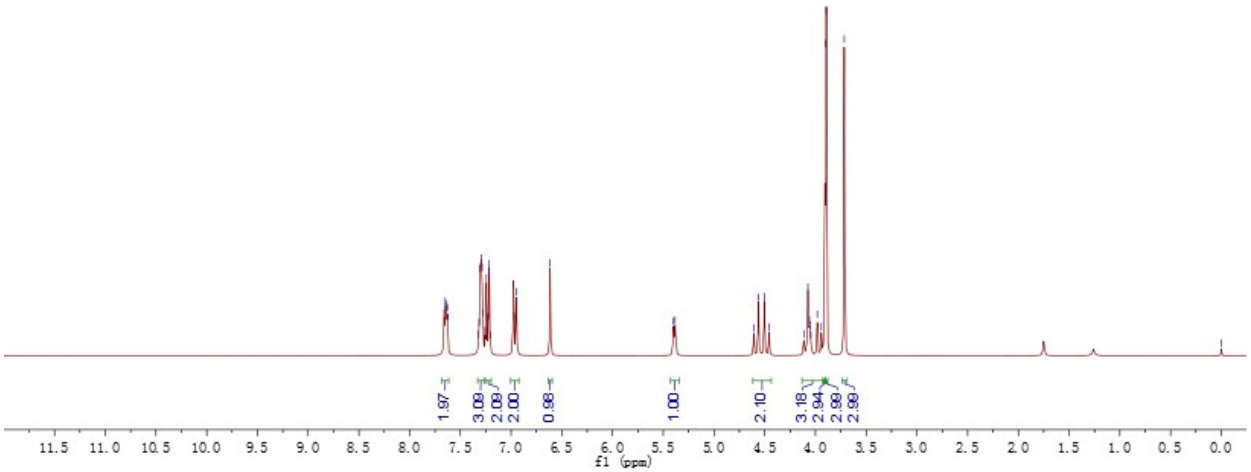


(±)-**2g**

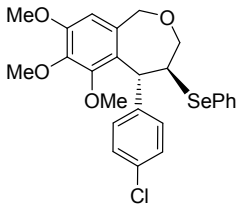
20121130087.27.1.1r
20151111-zcw1



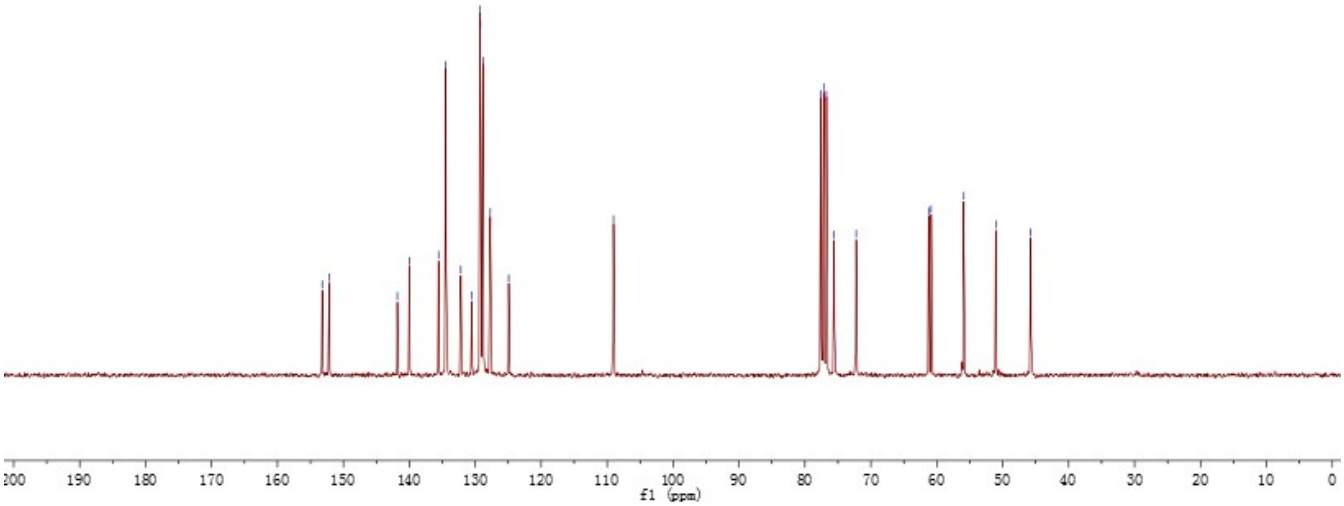
(±)-**2h**



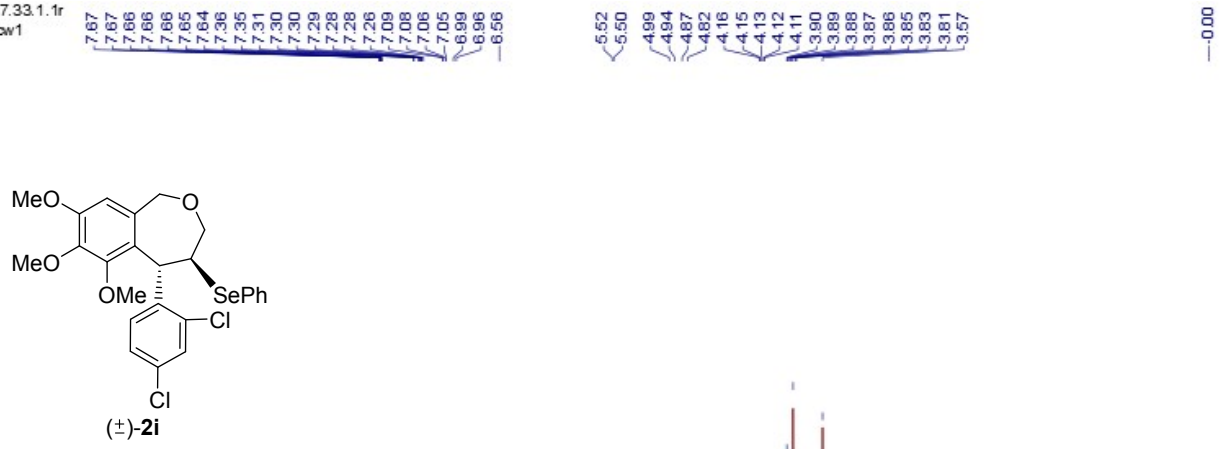
20121130087.30.1.1r
20151111-zcw1



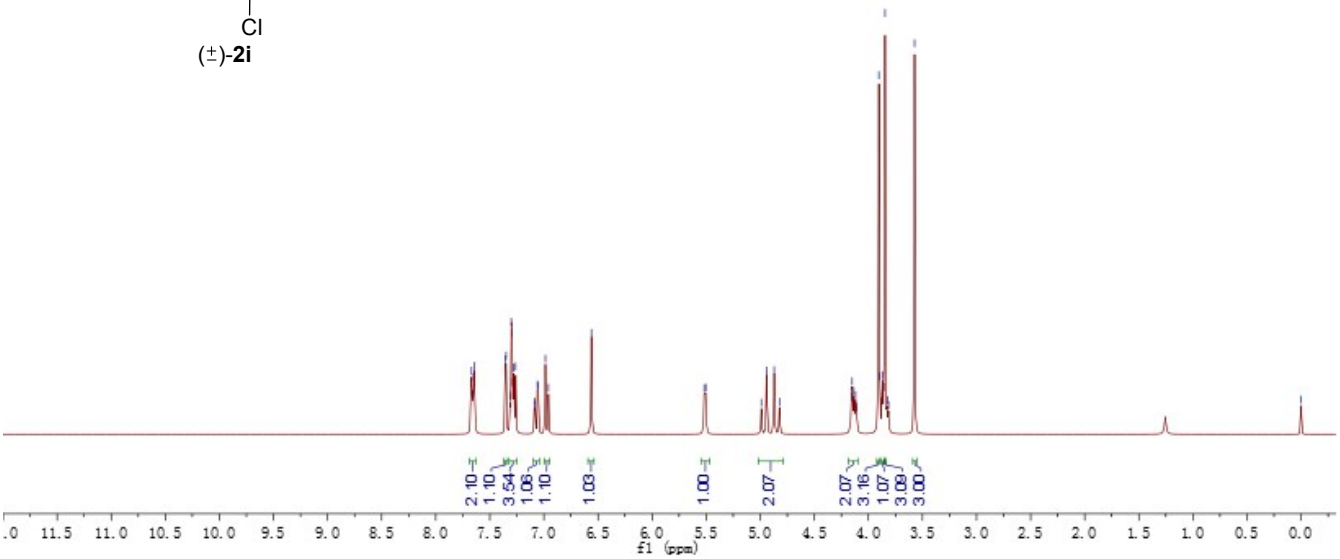
(±)-**2h**



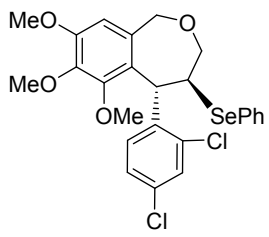
20121130087.33.1.1r
20151112-zcw1



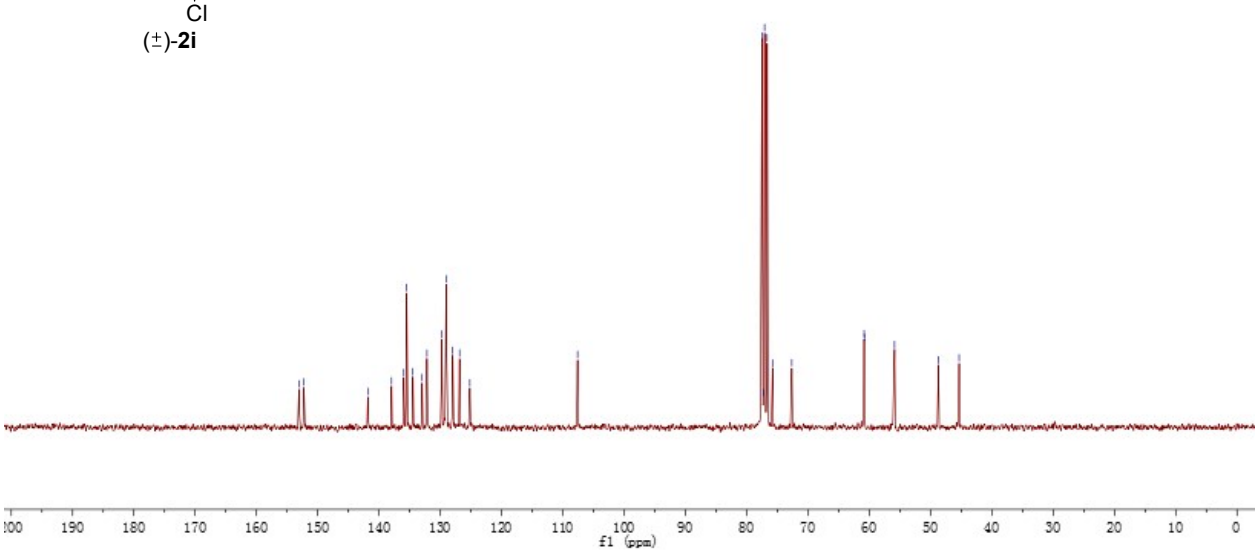
(±)-**2i**



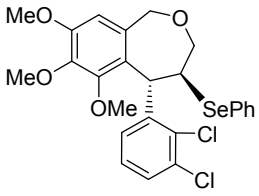
20121130087.37.1.1r
20151112-zcw1



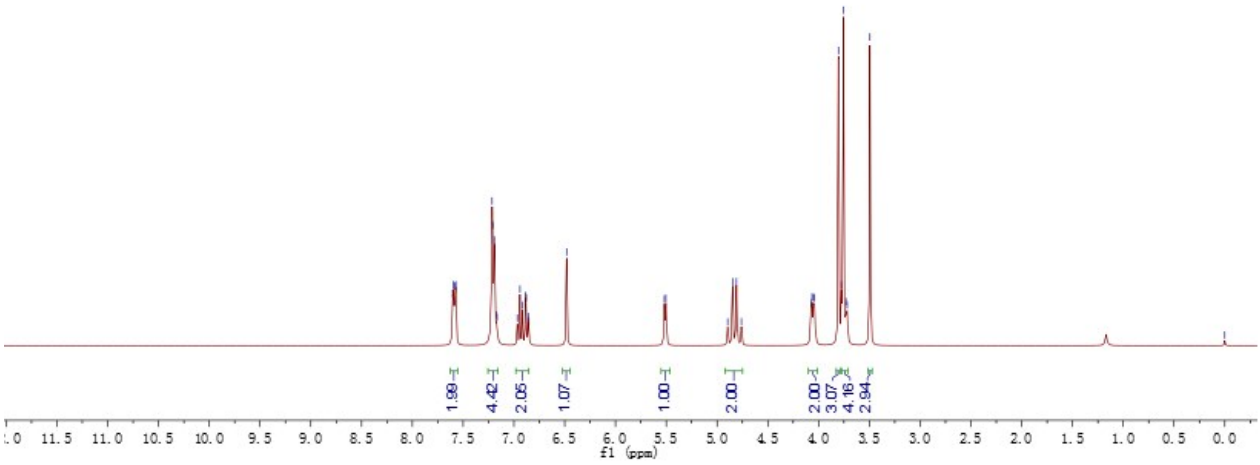
(±)-**2i**



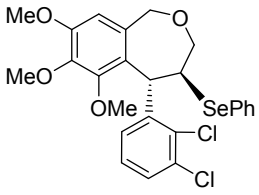
20121130087.122.1.1r
20151218-zcw



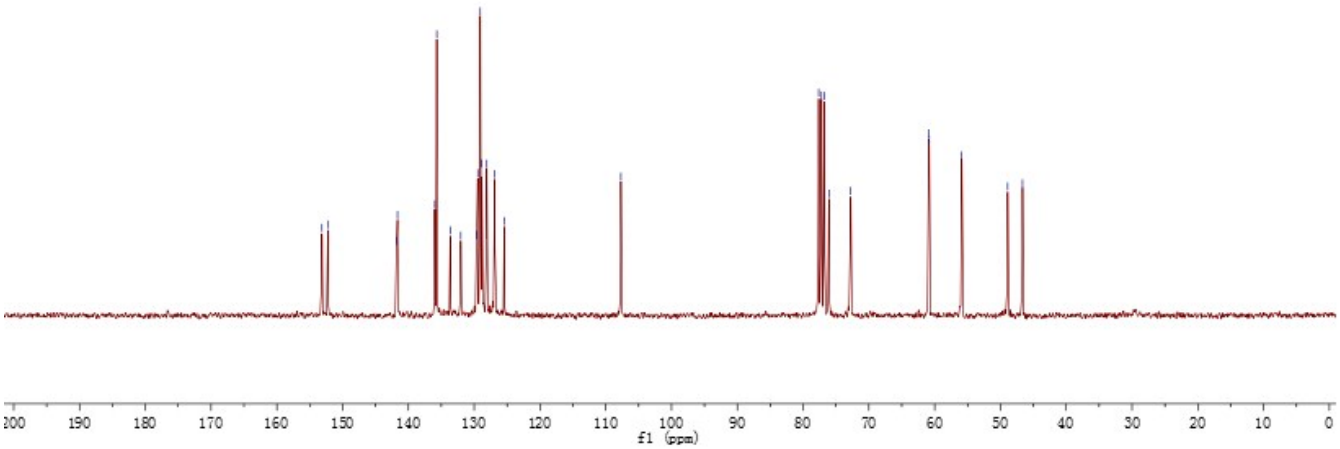
(±)-**2j**



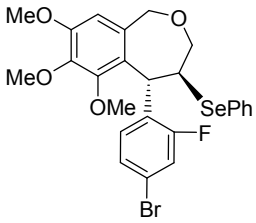
20121130087.123.1.1r
20151218-zcw



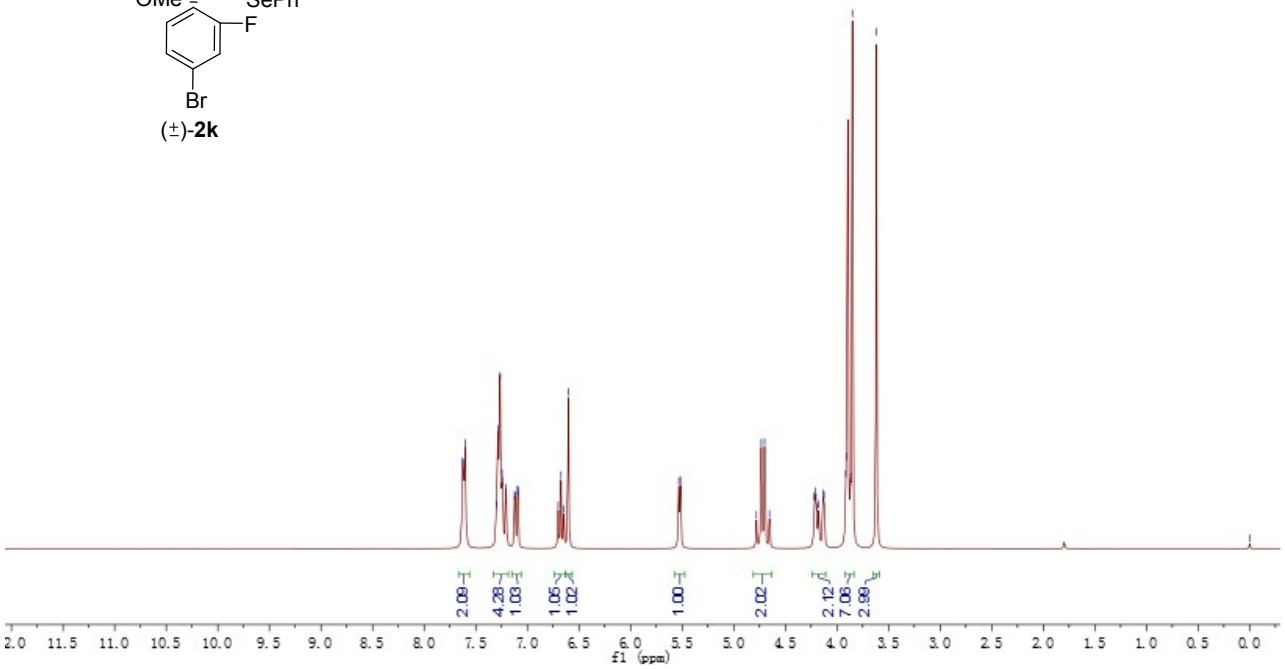
(±)-**2j**



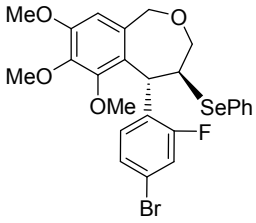
20121130087.99.1.1r
20151208-zcw



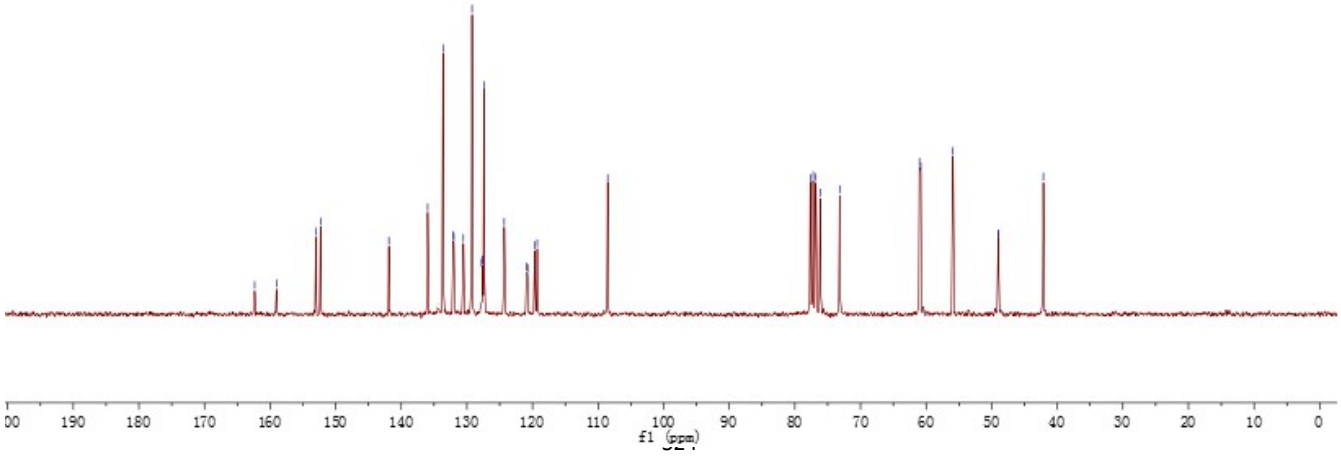
(±)-**2k**

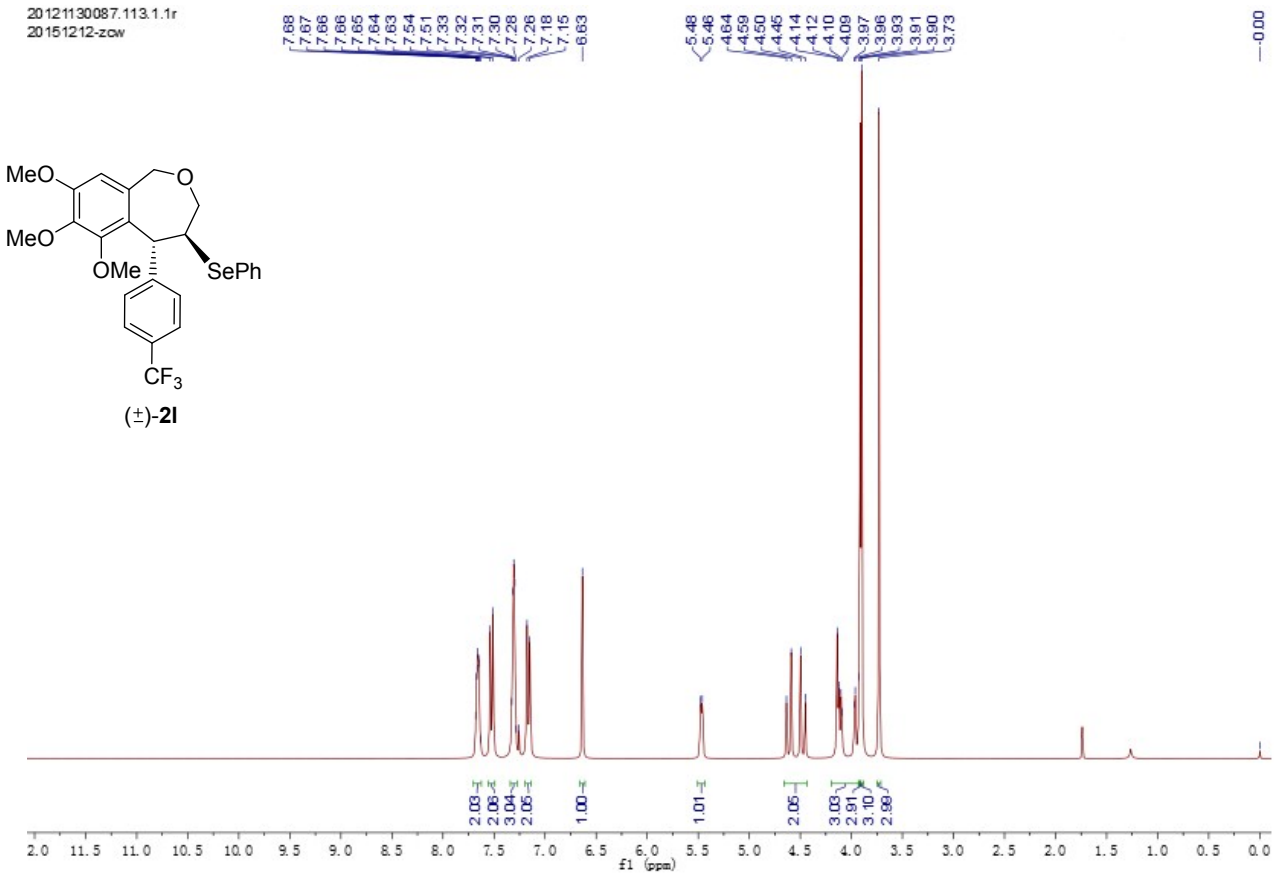


20121130087.100.1.1r
20151208-zcw

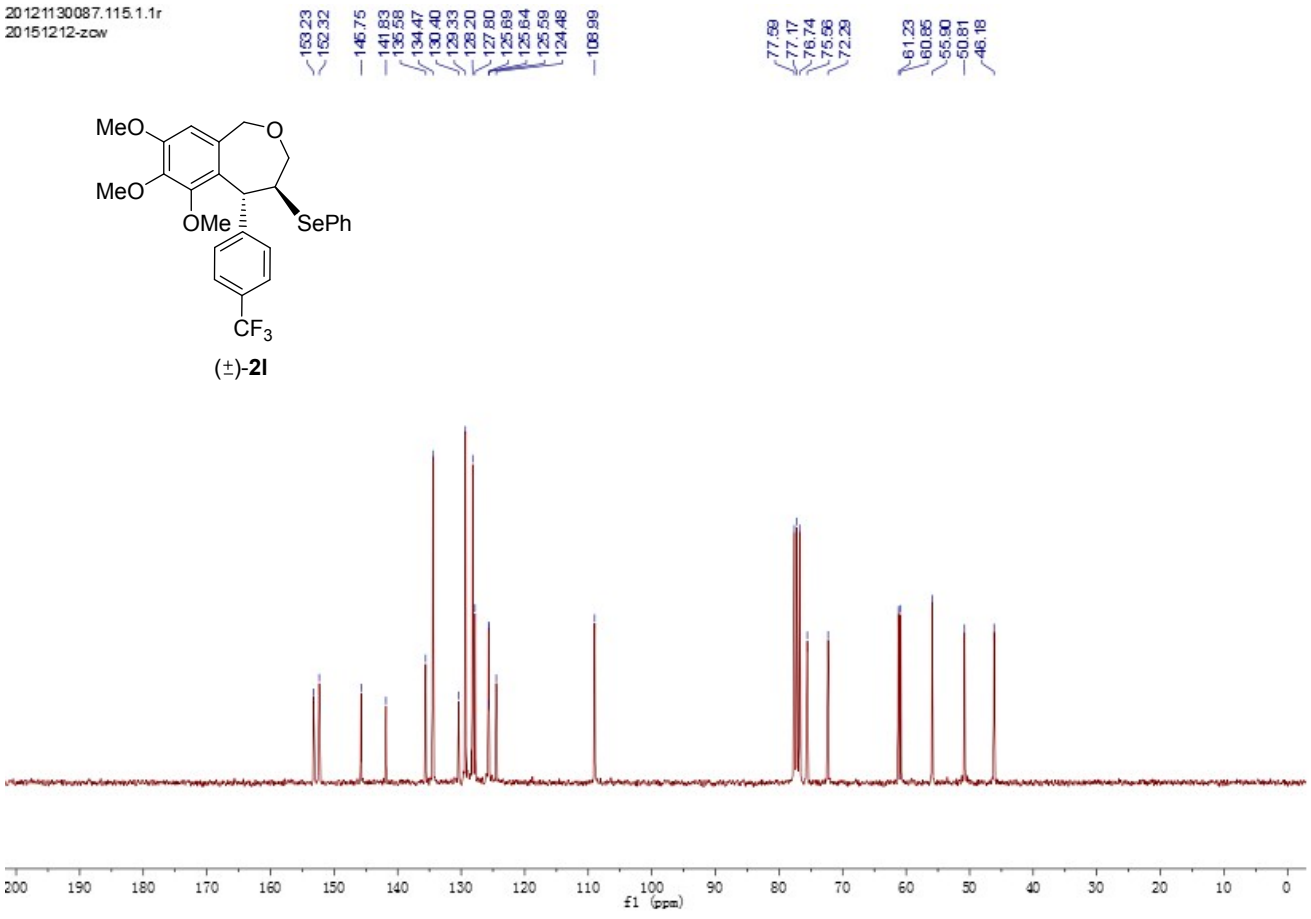


(±)-**2k**



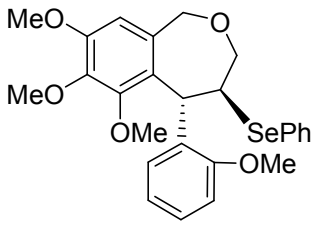

20121130087.113.1.1r
20151212-zcw
MeO
MeO
OMe
O
SePh
CF3
f1 (ppm)

(±)-**2l**

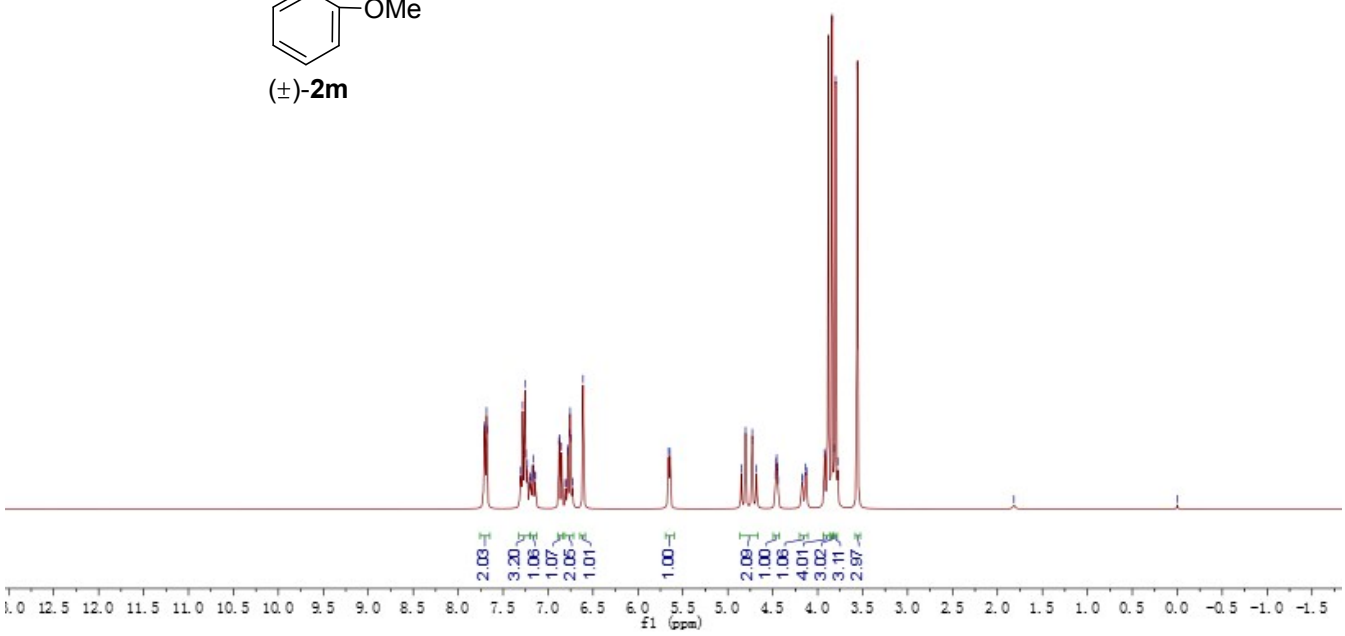

20121130087.115.1.1r
20151212-zcw
MeO
MeO
OMe
O
SePh
CF3
f1 (ppm)

(±)-**2l**

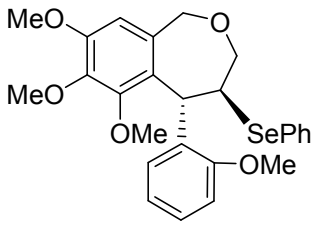

20121130087.90.1.1r
20151206-zcw2


MeO
MeO
O
OMe
SePh
OMe

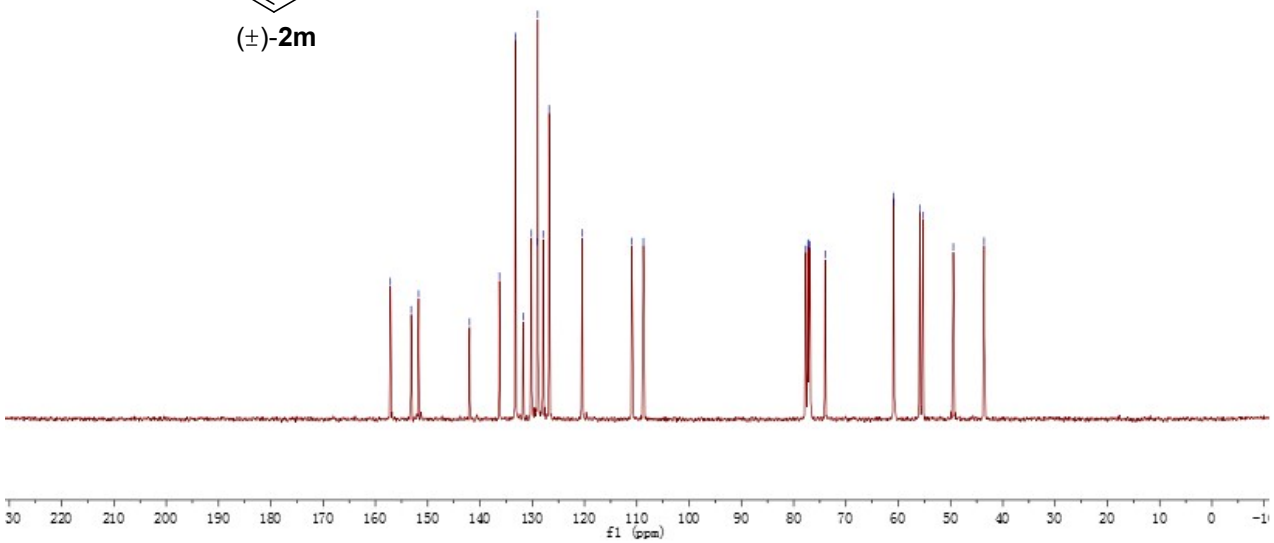
(±)-**2m**

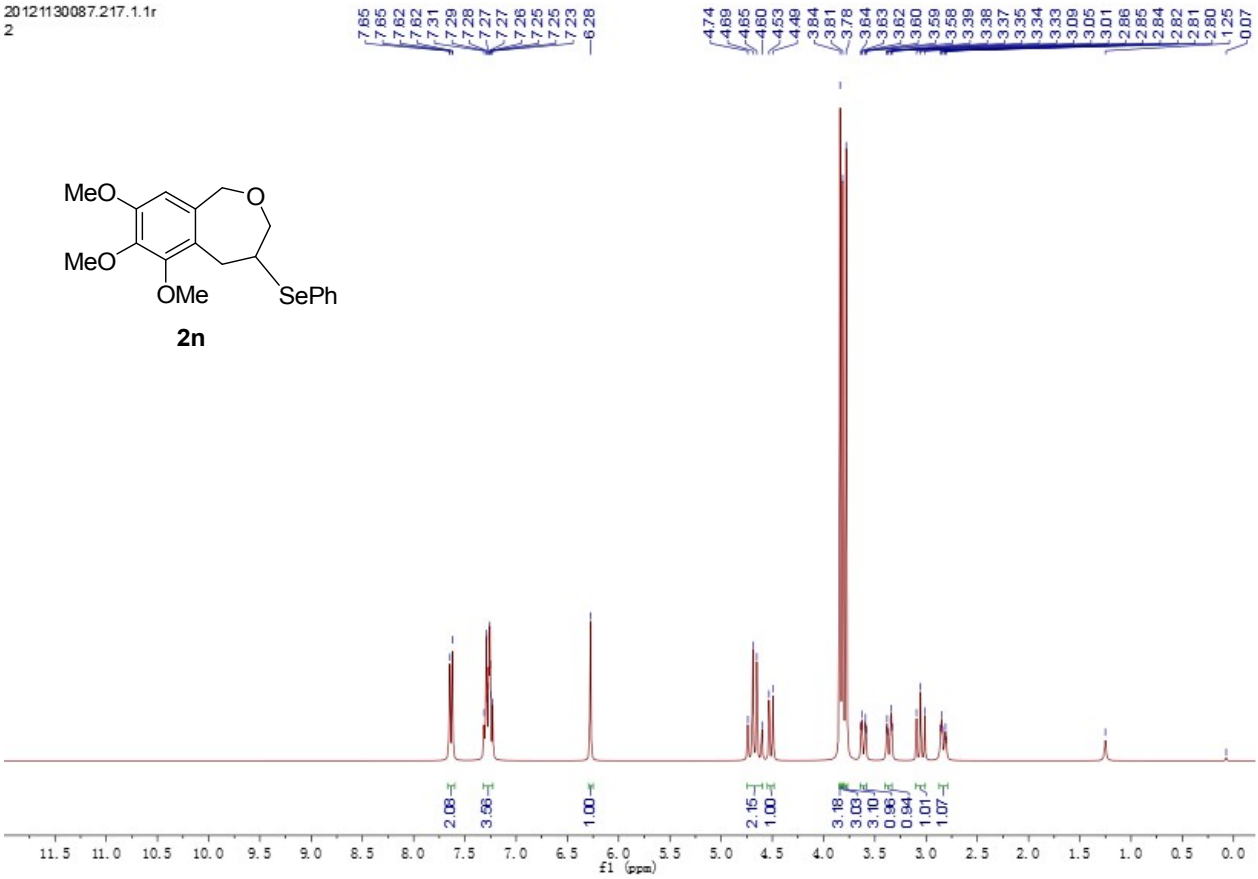

f1 (ppm)


20121130087.93.1.1r
20151206-zcw

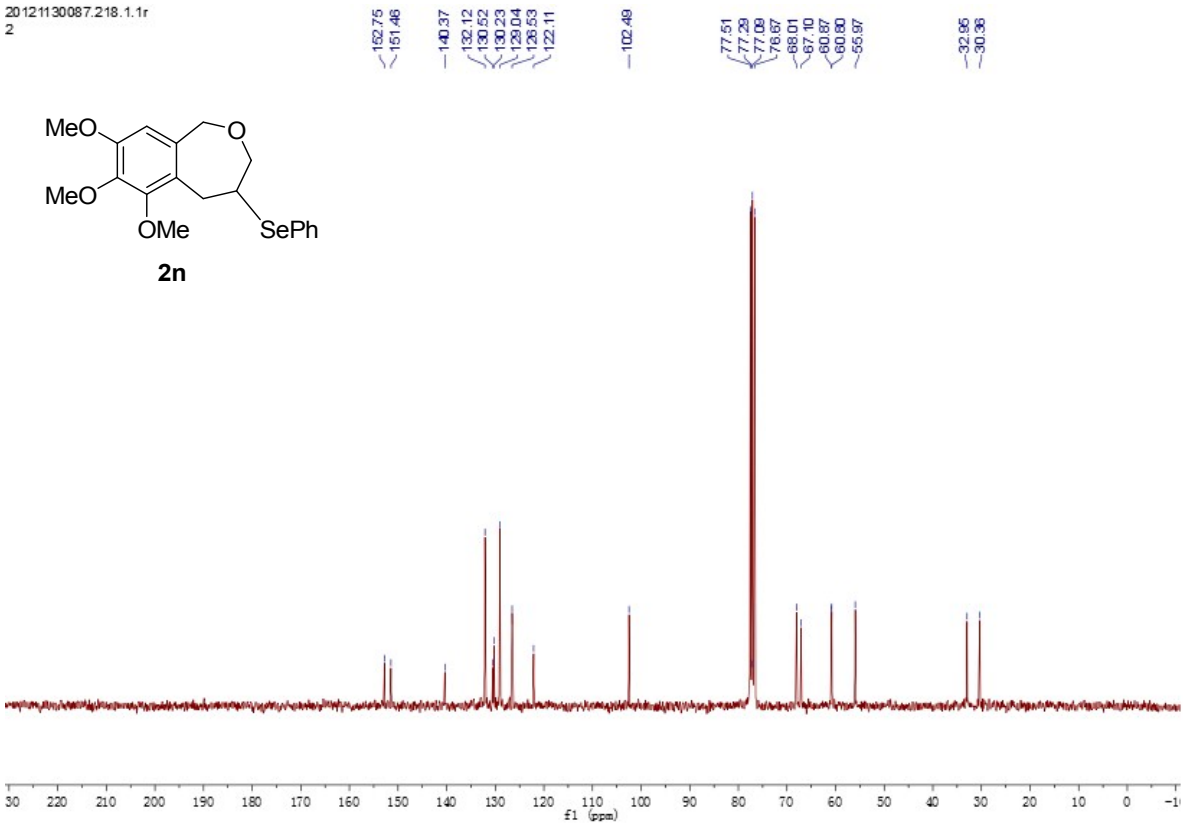

MeO
MeO
O
OMe
SePh
OMe

(±)-**2m**


f1 (ppm)

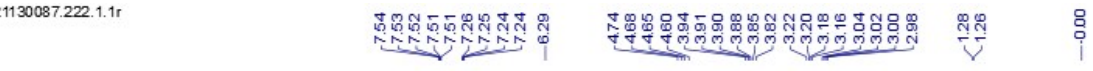

20121130087.217.1.1r
2
MeO
MeO
OMe
O
SePh
f1 (ppm)

2n

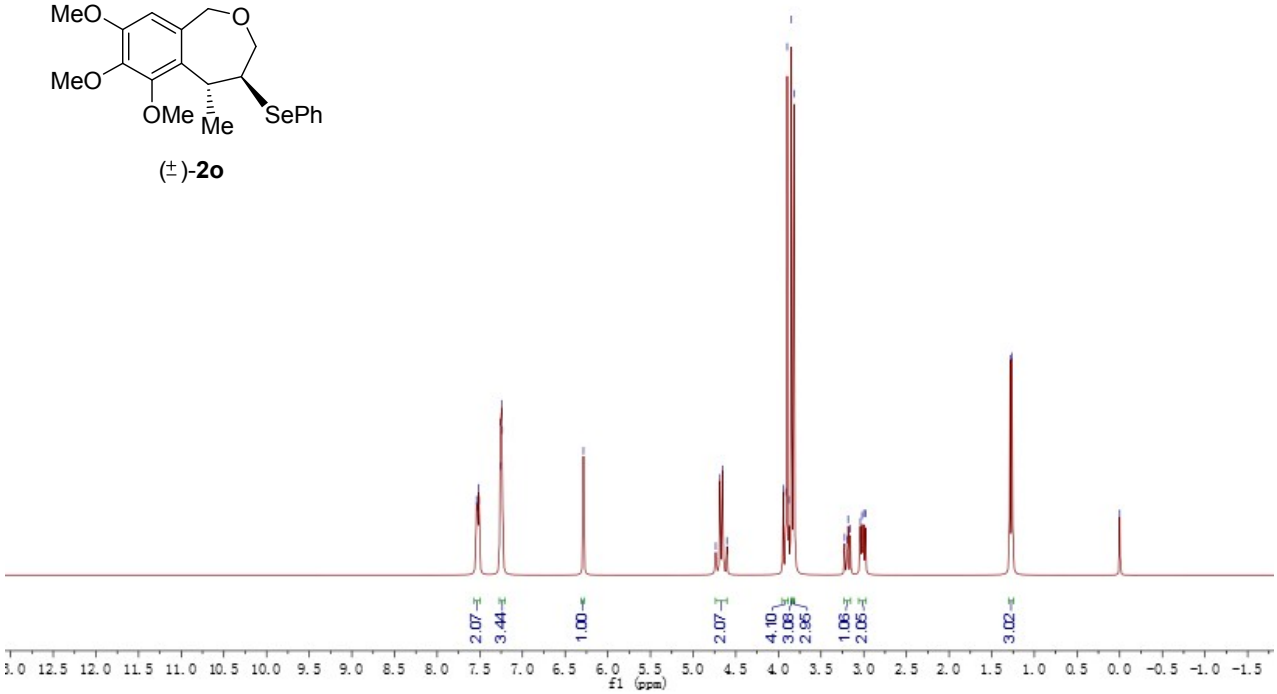

20121130087.218.1.1r
2
MeO
MeO
OMe
O
SePh
f1 (ppm)

2n

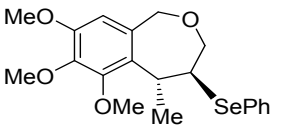
20121130087.222.1.1r
1



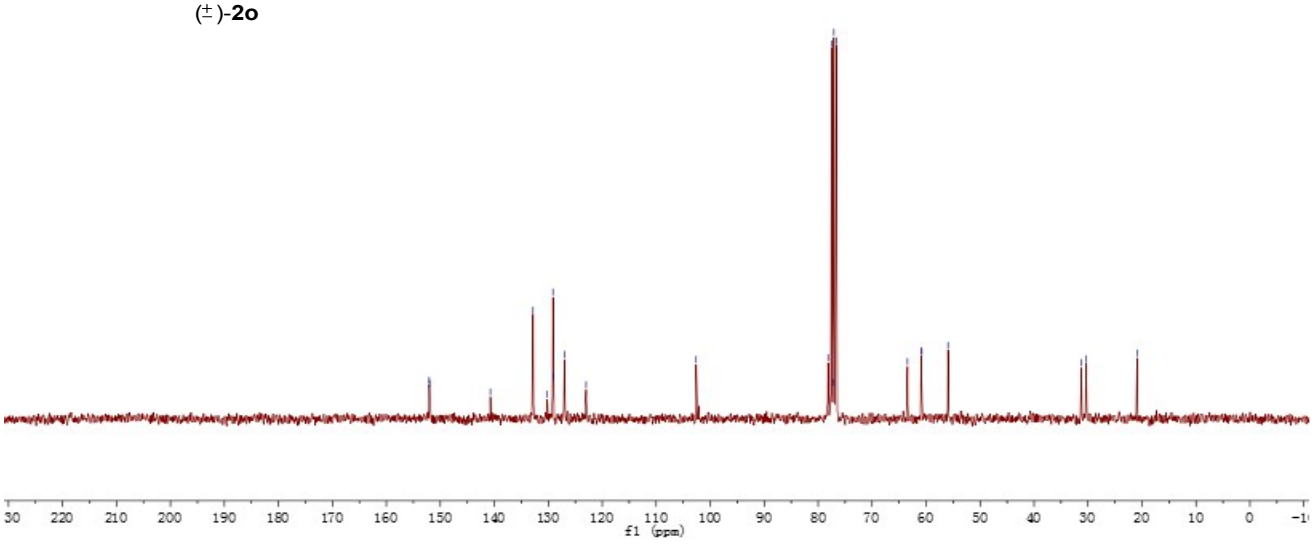
(±)-**2o**



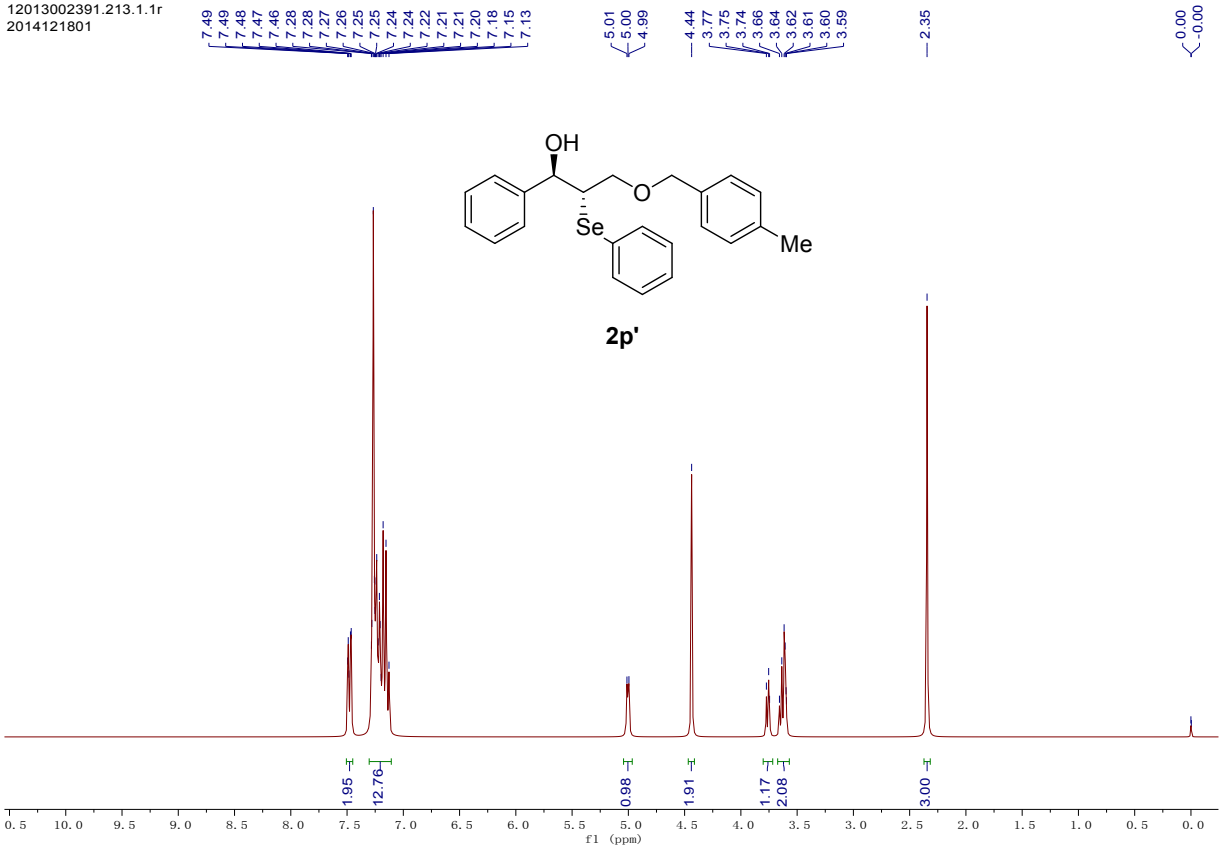
20121130087.223.1.1r
1



(±)-**2o**

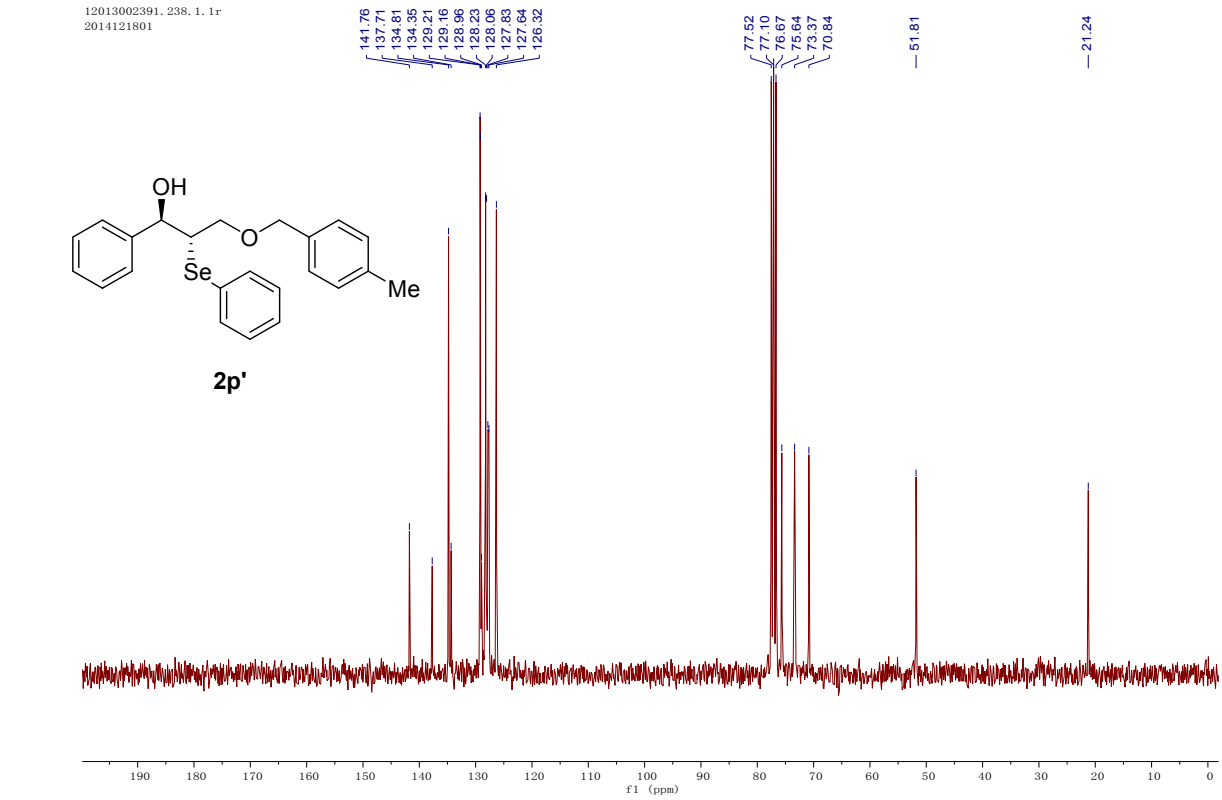


12013002391.213.1.1r
2014121801



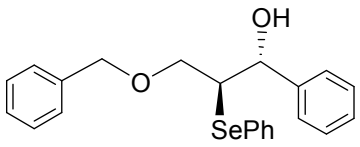
2p'

12013002391.238.1.1r
2014121801

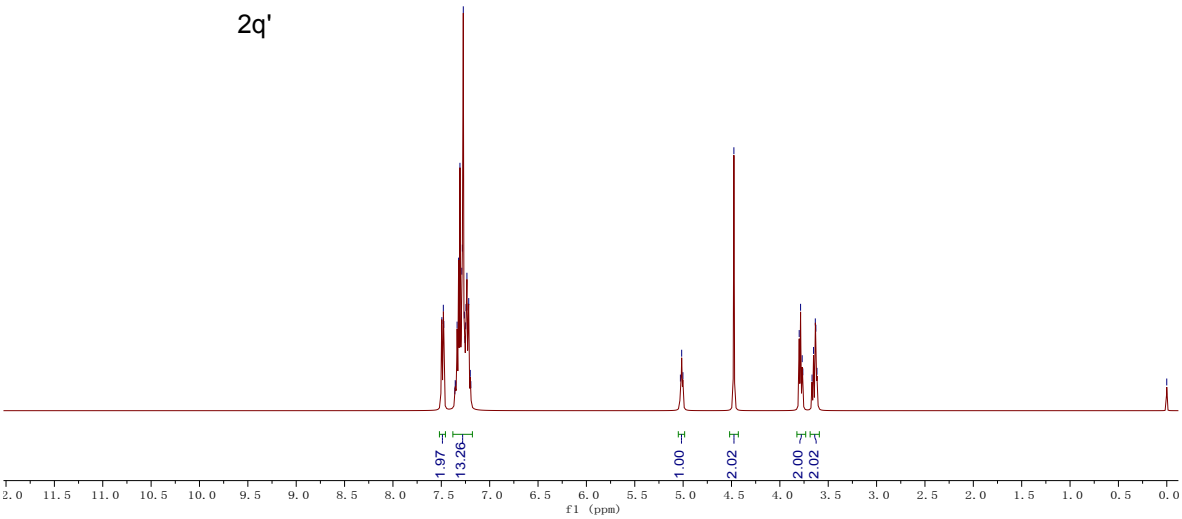


2p'

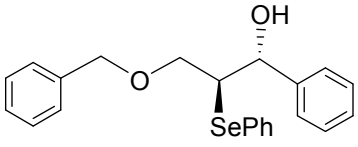
12018002142.136.1.1r
S-1112-Br



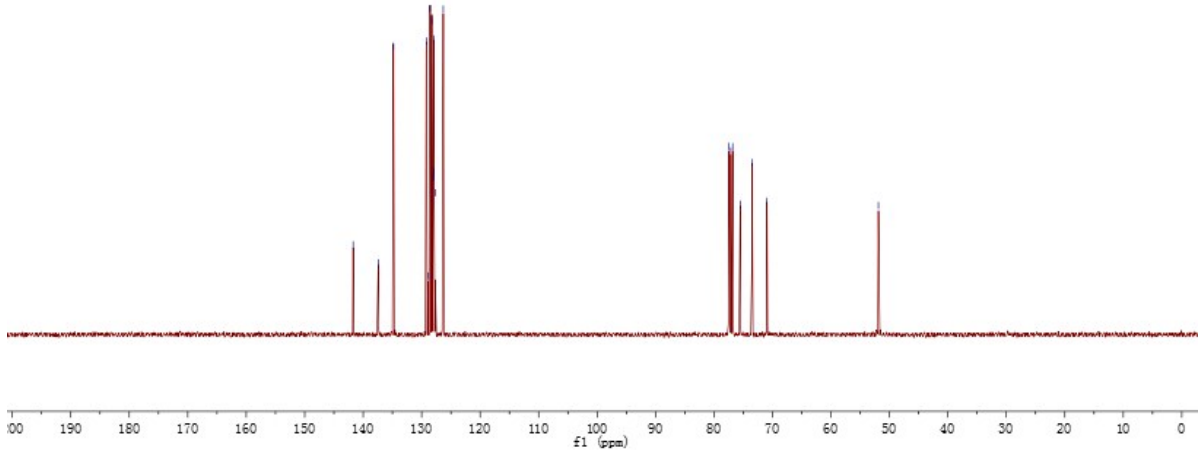
2q'



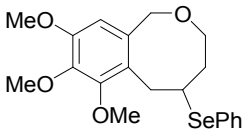
12018002142.137.1.1r
S-1112-Br



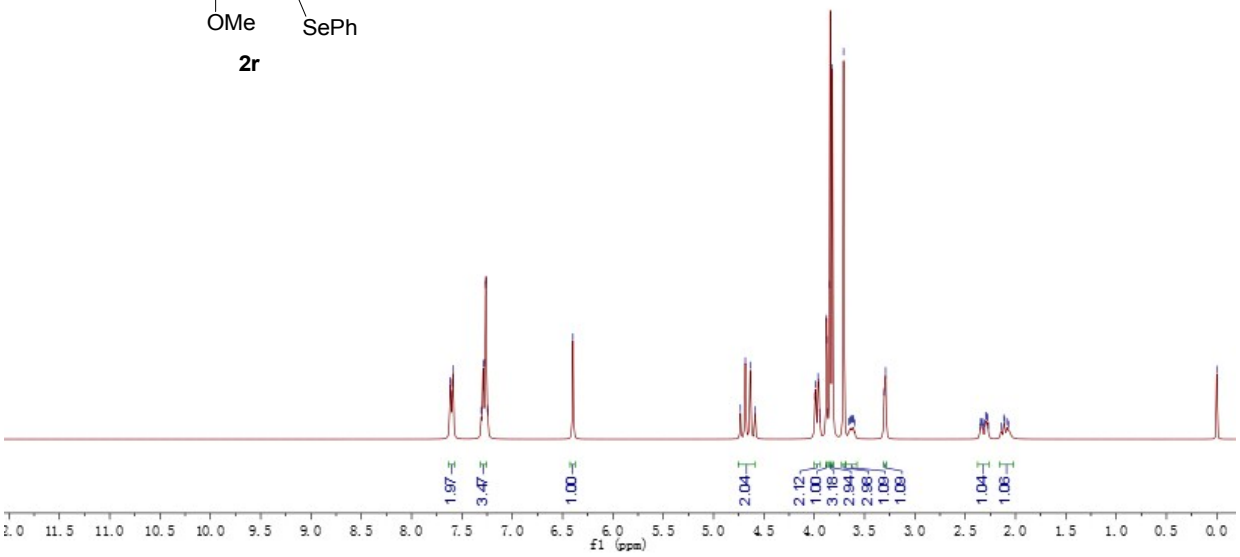
2q'



20121130087.243.1.1r
20160114-2

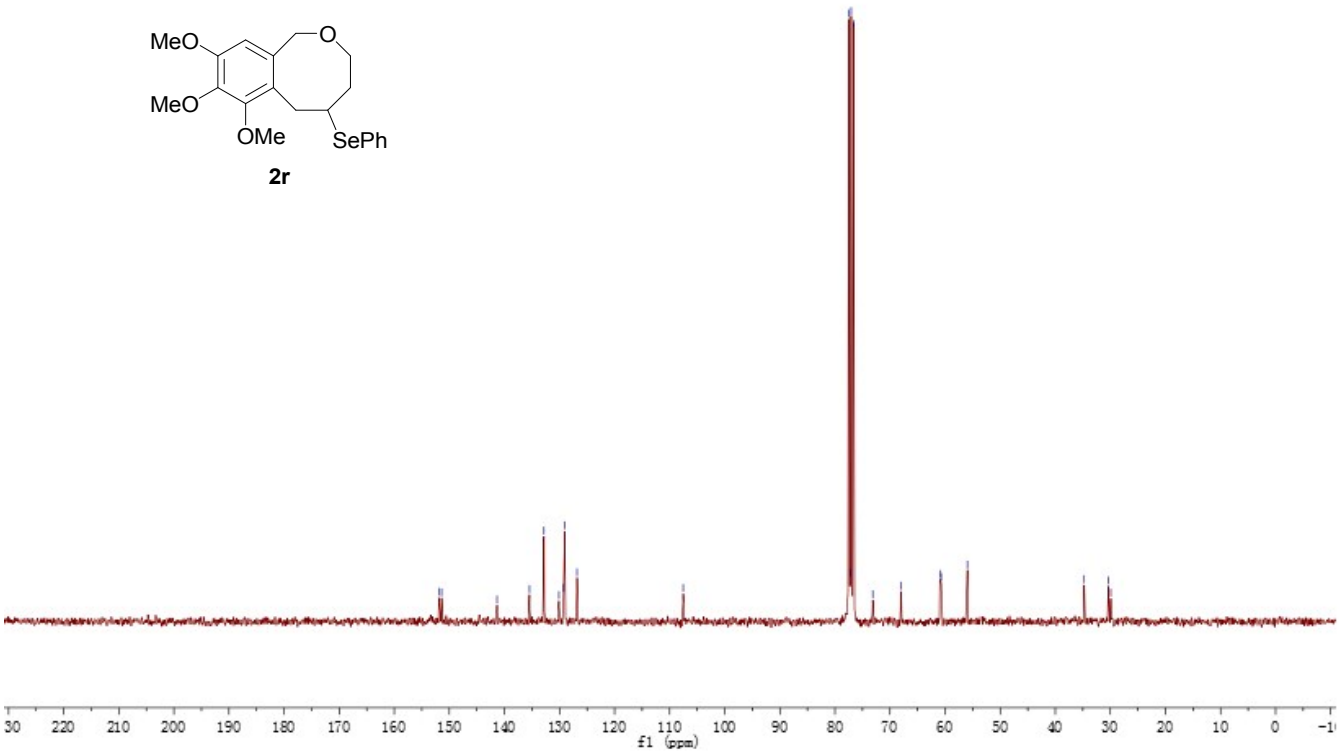


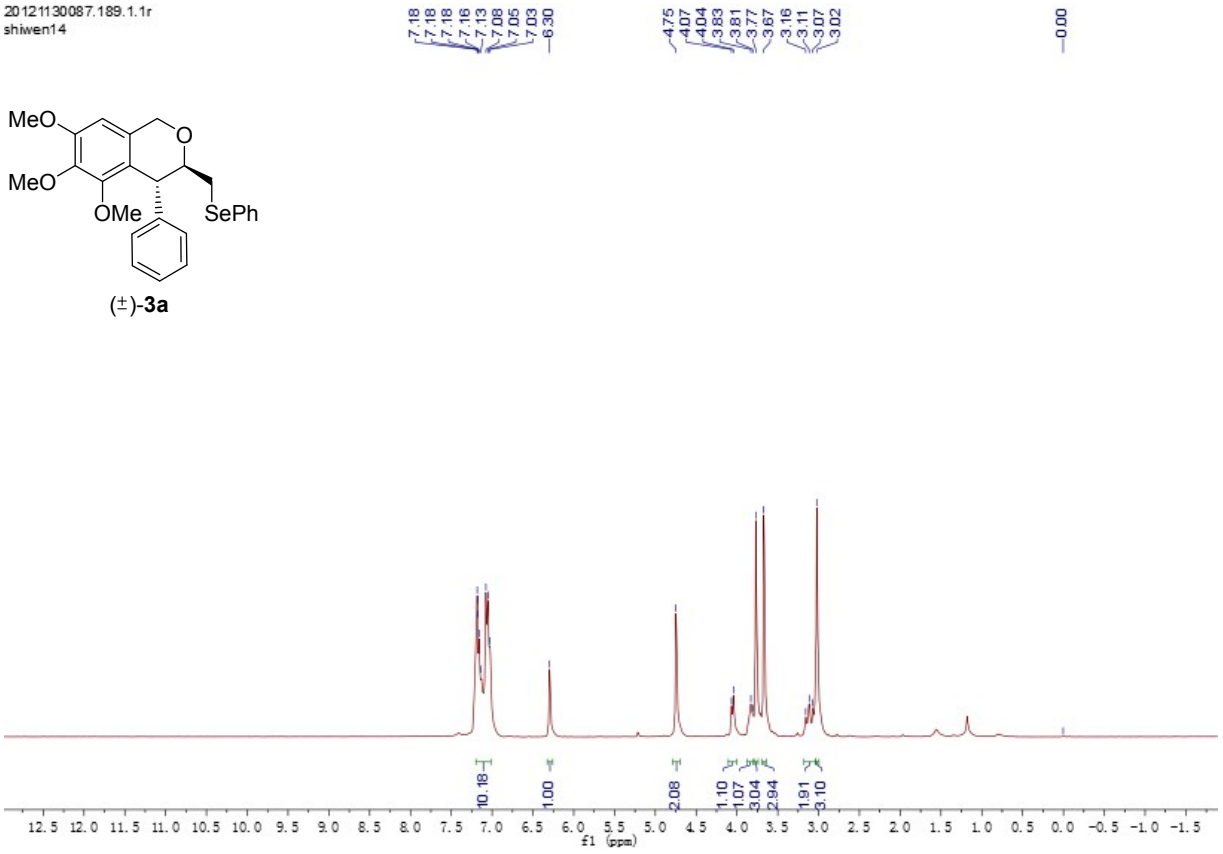
2r



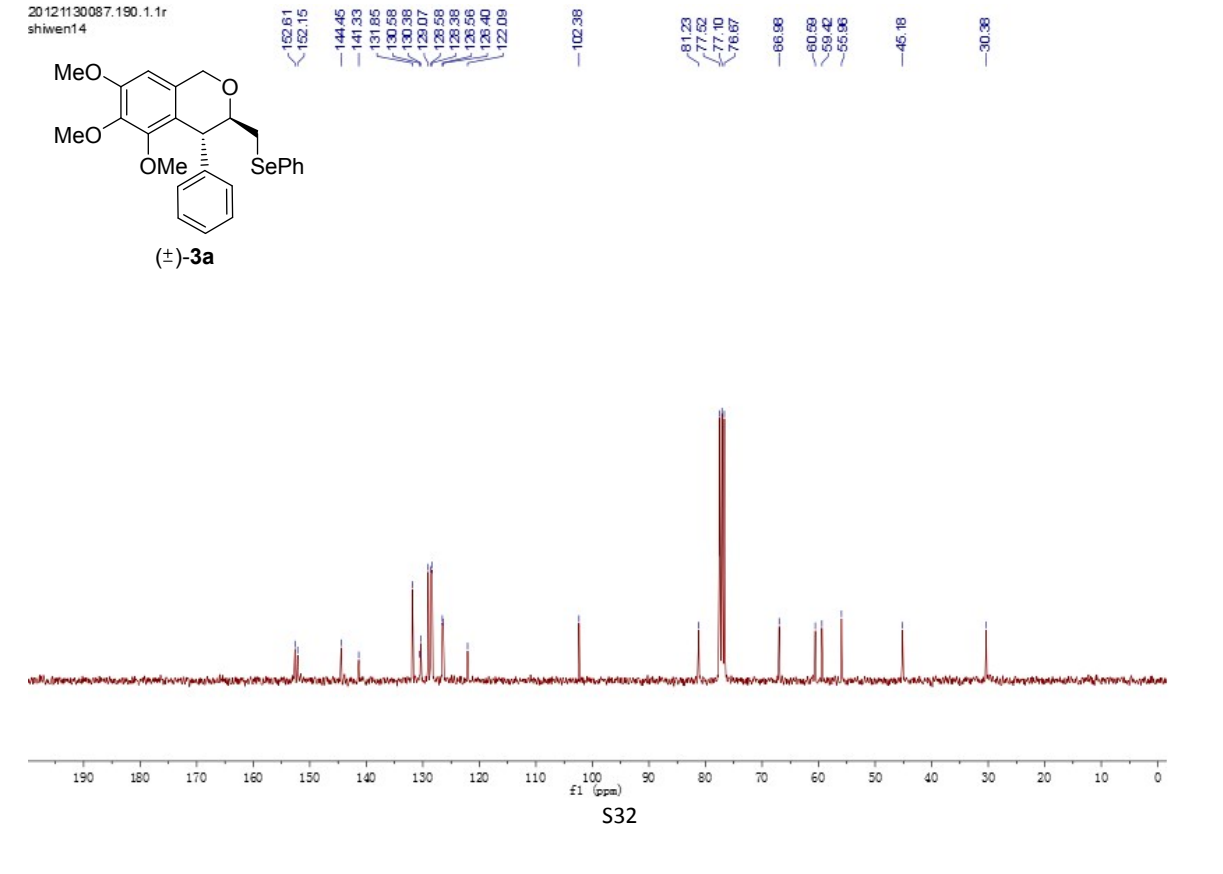
20121130087.247.1.1r
20160114-2

2r



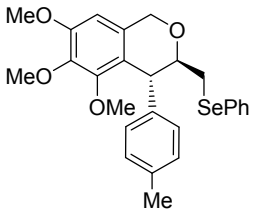

20121130087.189.1.1r
shiwen14
7.18
7.18
7.18
7.16
7.13
7.08
7.05
7.03
6.30
4.75
4.07
4.04
3.83
3.81
3.77
3.67
3.16
3.11
3.07
3.02
0.00
MeO
MeO
OMe
O
SePh
10.18
1.00
2.08
1.10
1.07
3.04
2.94
1.91
3.10
f1 (ppm)

(±)-**3a**

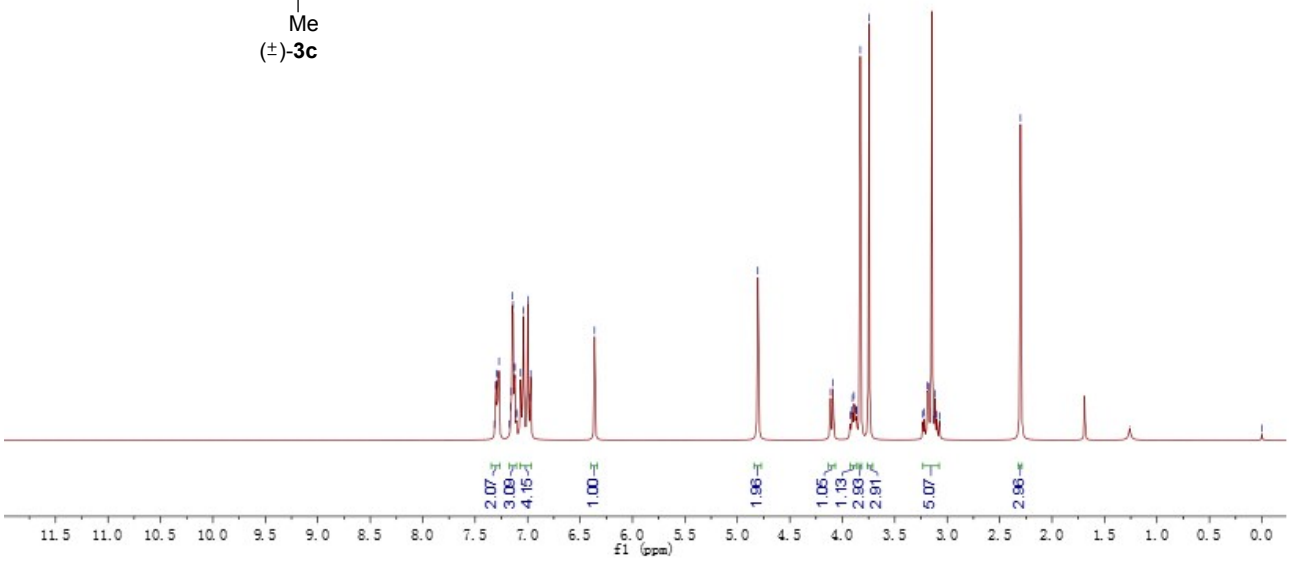

20121130087.190.1.1r
shiwen14
162.61
152.15
144.45
141.33
131.85
130.58
130.38
129.07
128.58
128.38
126.56
126.40
122.09
102.38
81.23
77.52
77.10
76.67
66.98
60.69
59.42
55.96
45.18
30.38
MeO
MeO
OMe
O
SePh
f1 (ppm)

(±)-**3a**

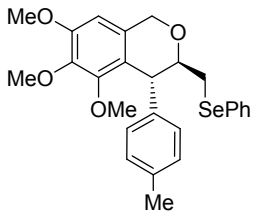
12013002391.521.1.1r
2015092902



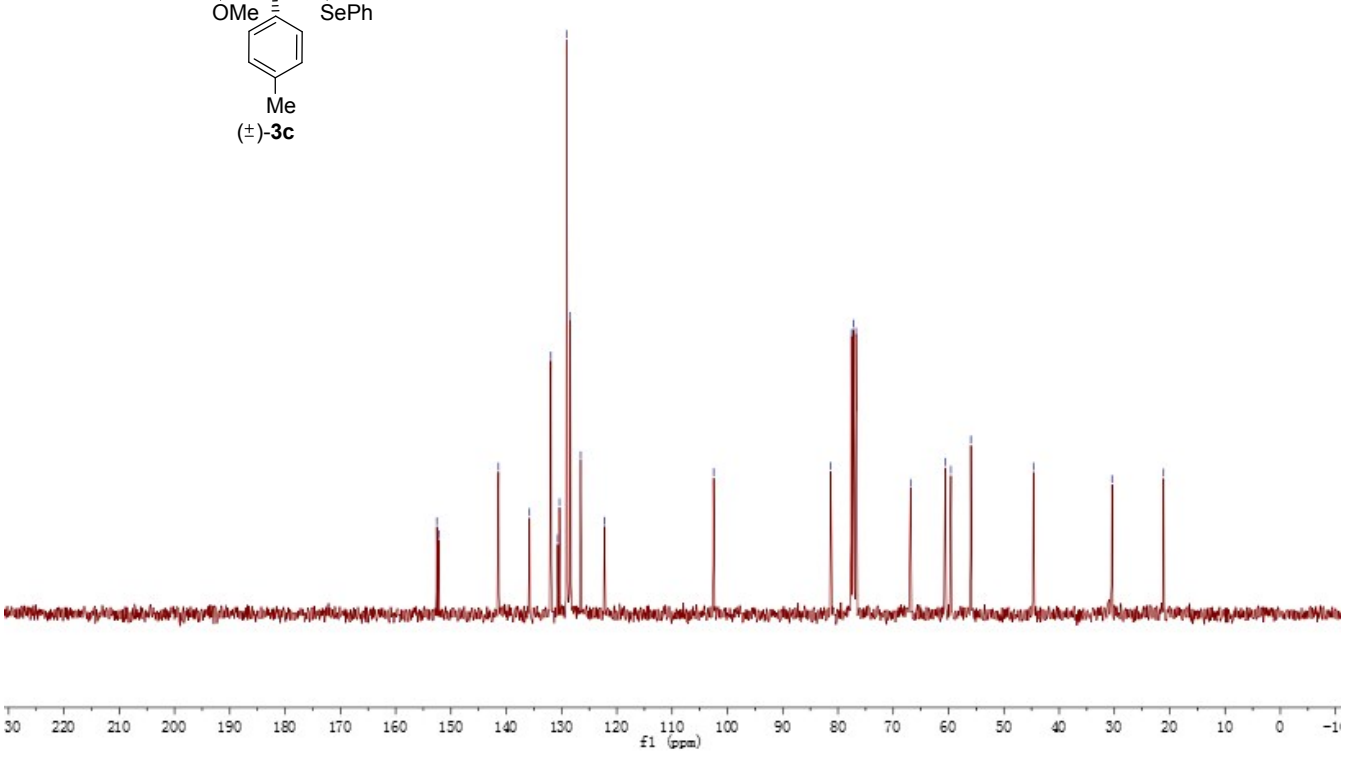
(±)-**3c**



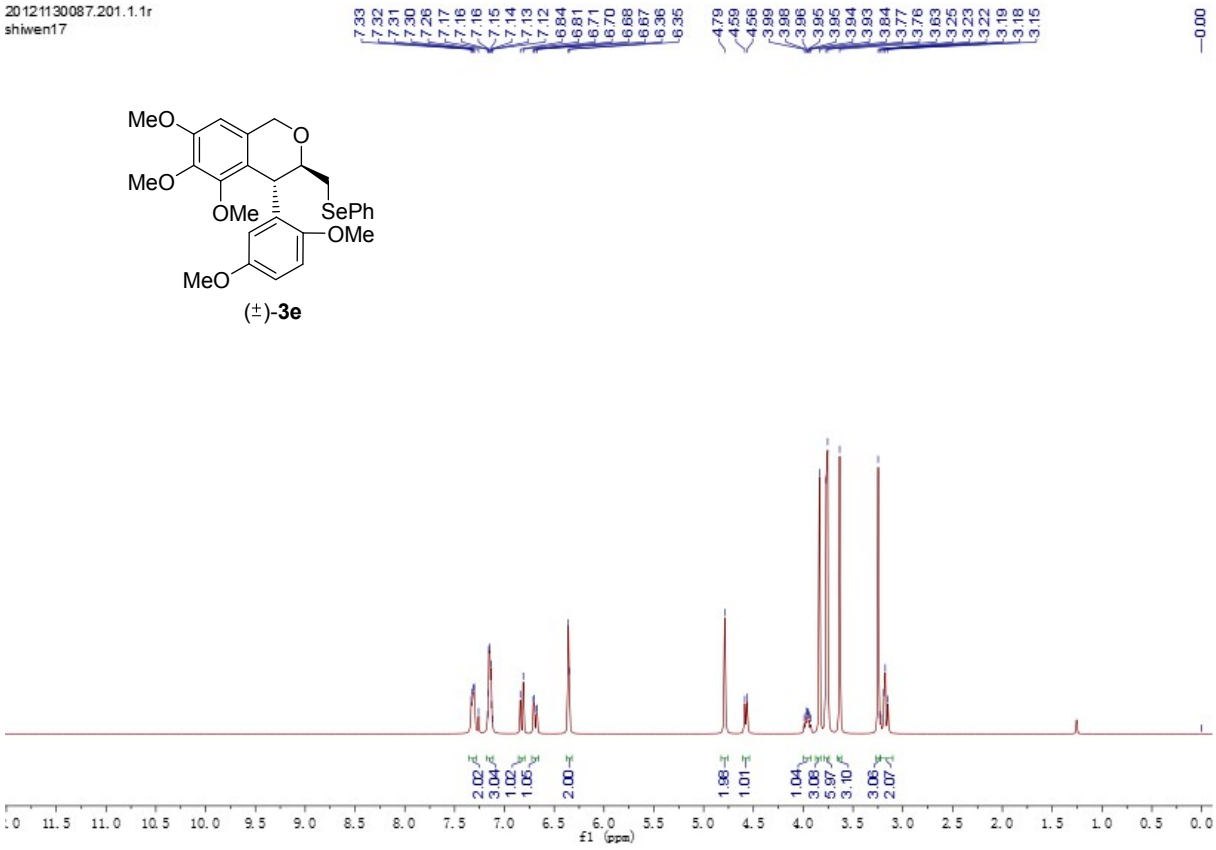
12013002391.522.1.1r
2015092902



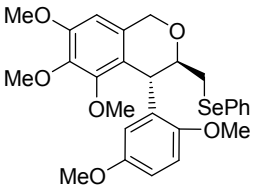
(±)-**3c**



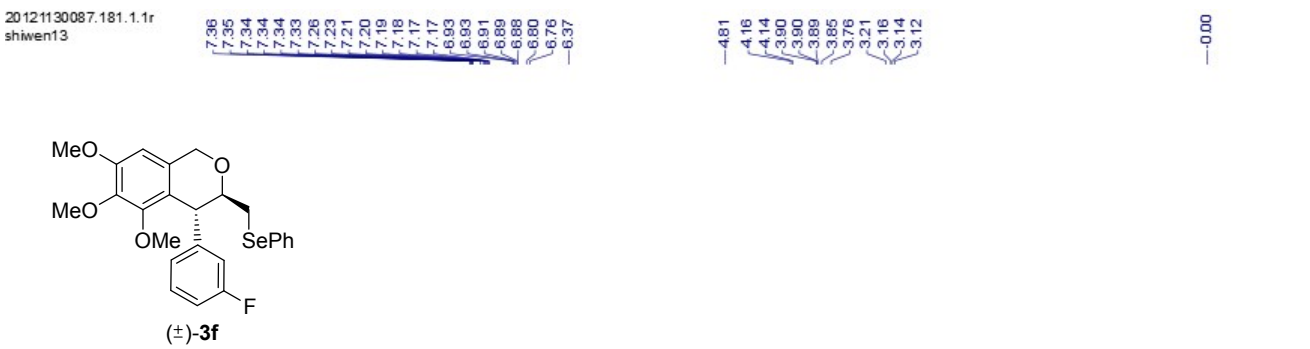
20121130087.201.1.1r
shiwen17



(±)-**3e**

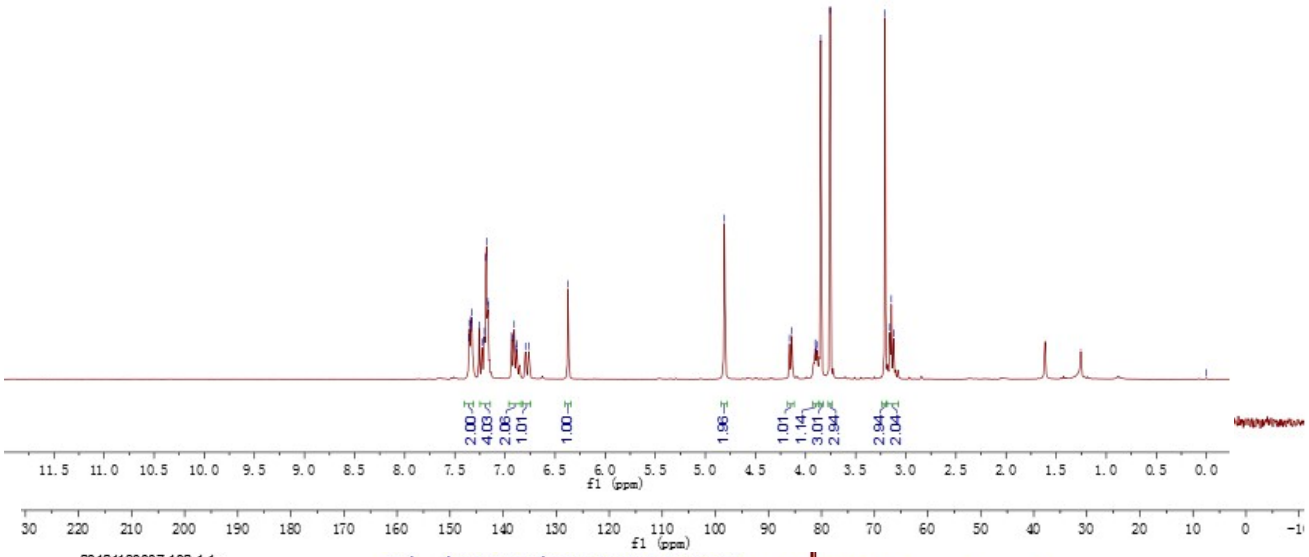


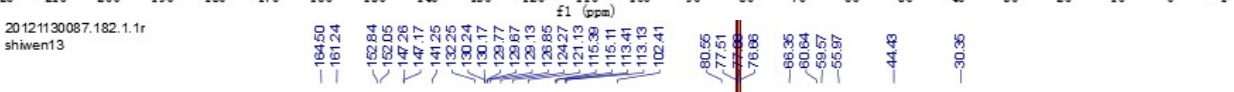
(±)-**3e**


20121130087.181.1.1r
shiwen13
7.36
7.35
7.34
7.34
7.34
7.33
7.26
7.23
7.21
7.20
7.19
7.18
7.17
7.17
6.93
6.91
6.89
6.88
6.80
6.76
6.37
4.81
4.16
4.14
3.90
3.90
3.89
3.85
3.76
3.21
3.16
3.14
3.12
0.00

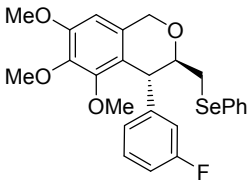
MeO
MeO
OMe
O
SePh
F

(±)-**3f**

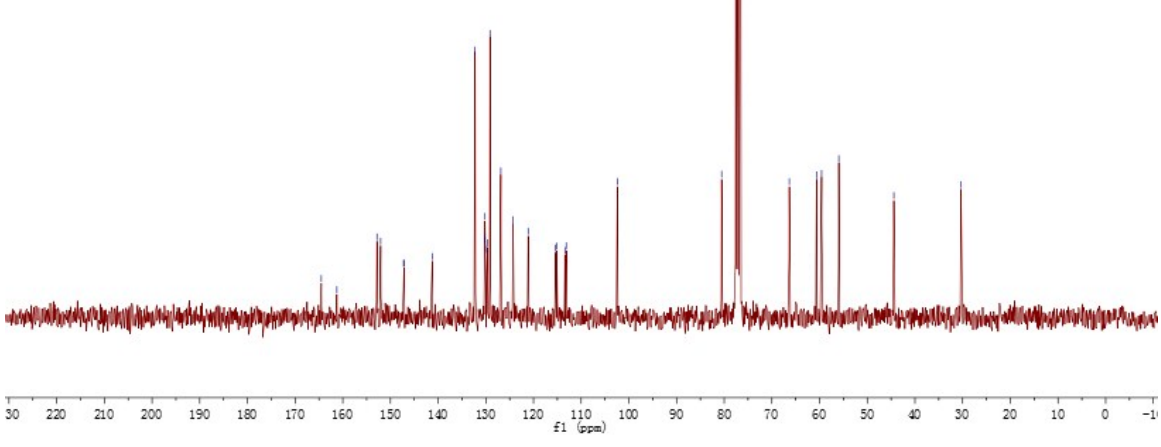

2.00
4.03
2.06
1.01
1.00
1.96
1.01
1.14
3.01
2.94
2.94
2.04
f1 (ppm)


f1 (ppm)

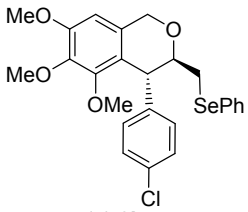
20121130087.182.1.1r
shiwen13
164.50
161.24
152.84
152.05
147.26
147.17
141.25
132.25
130.24
130.17
129.77
129.67
129.13
126.85
124.27
121.13
115.39
115.11
113.41
113.13
102.41
80.55
77.51
77.08
76.66
66.36
60.64
59.57
55.97
44.43
30.35


MeO
MeO
OMe
O
SePh
F

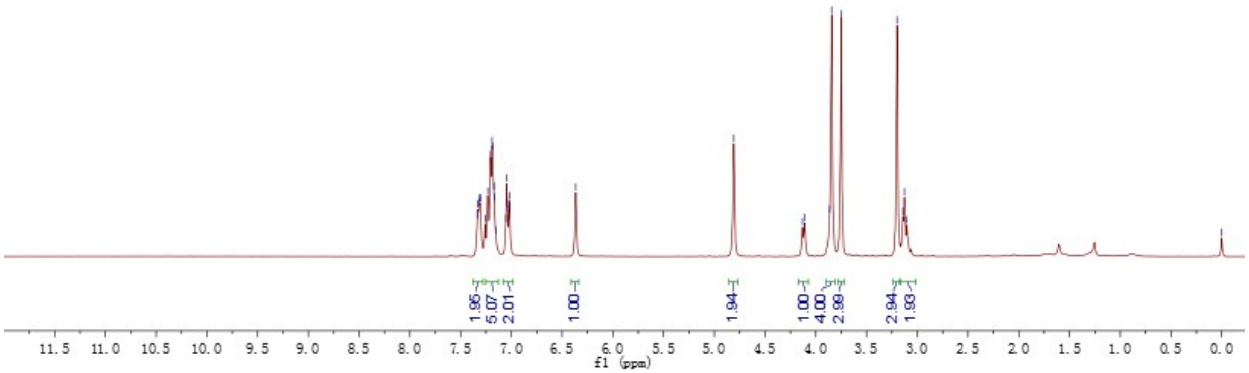
(±)-**3f**


f1 (ppm)

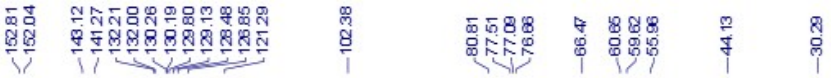
20121130087.232.1.1r
shiwen18

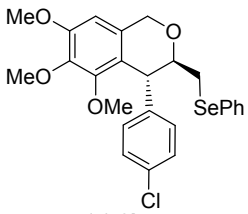


(±)-**3h**

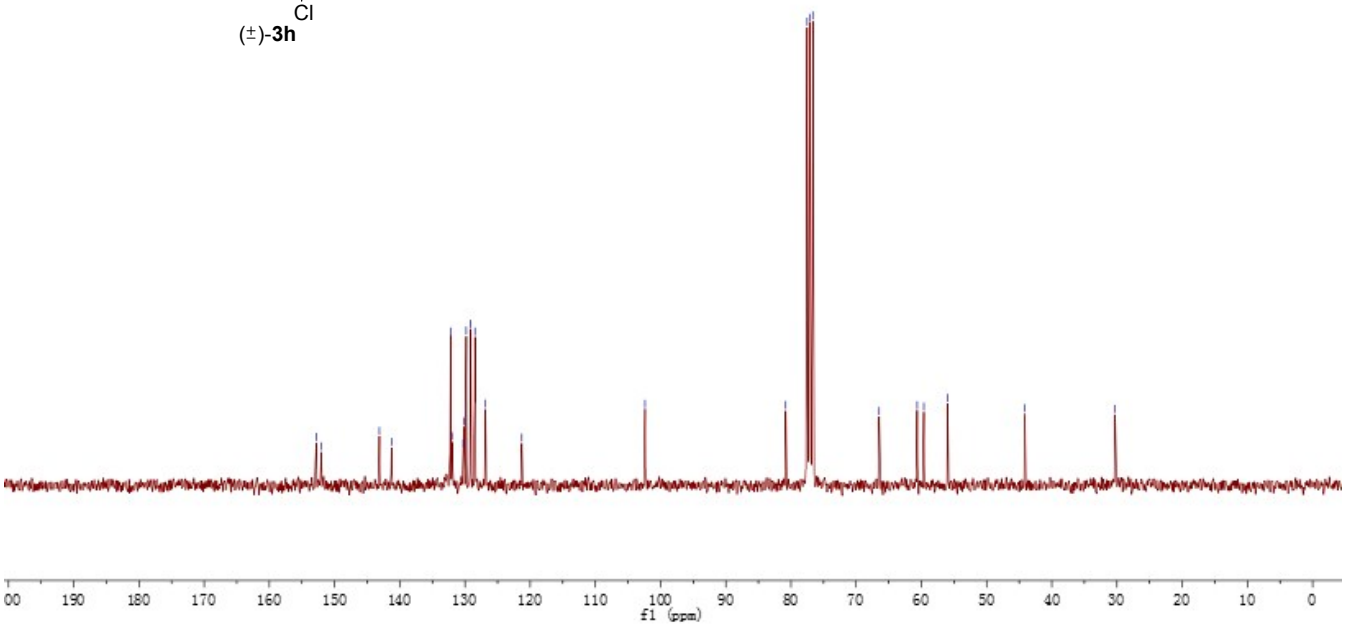


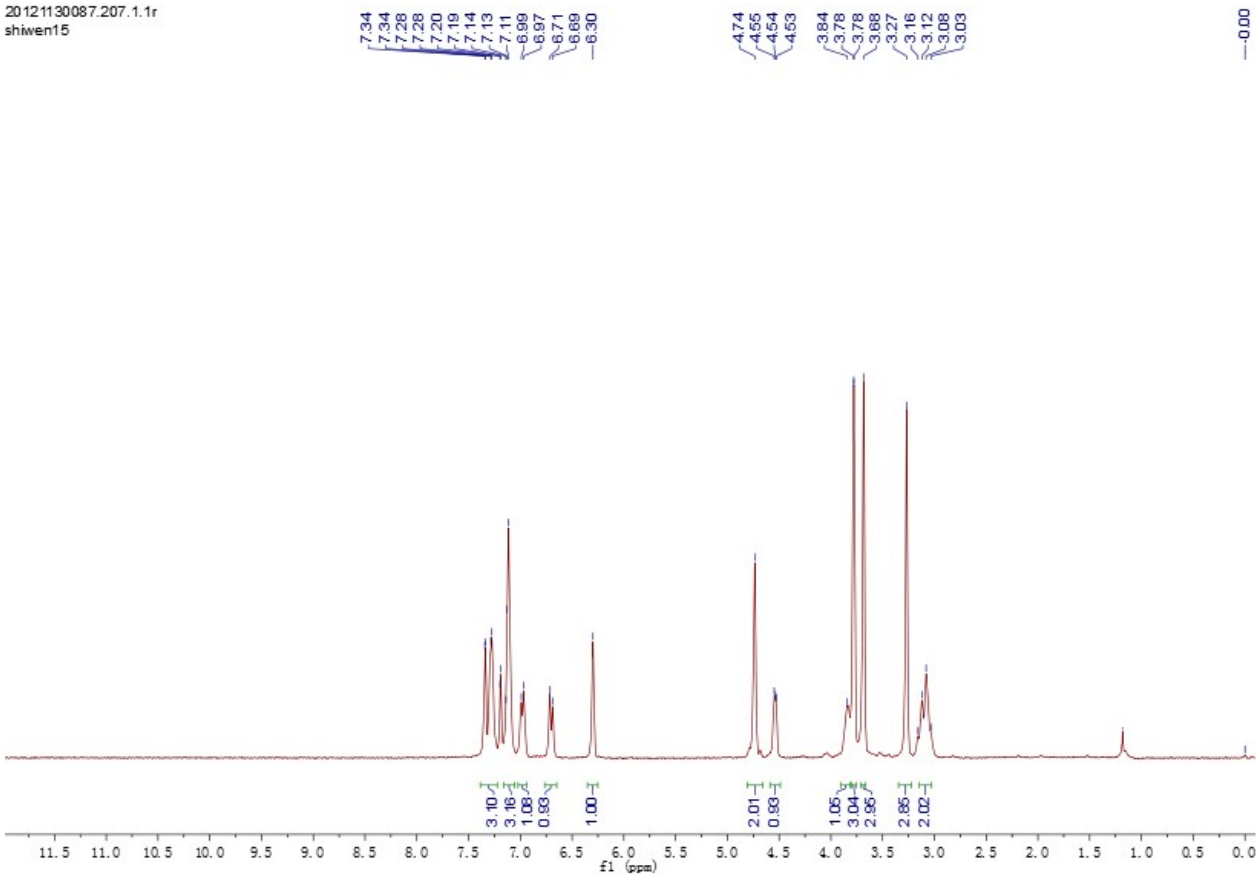
20121130087.233.1.1r
shiwen18

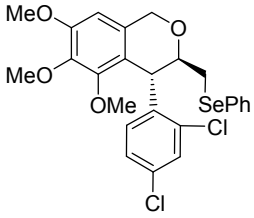




(±)-**3h**

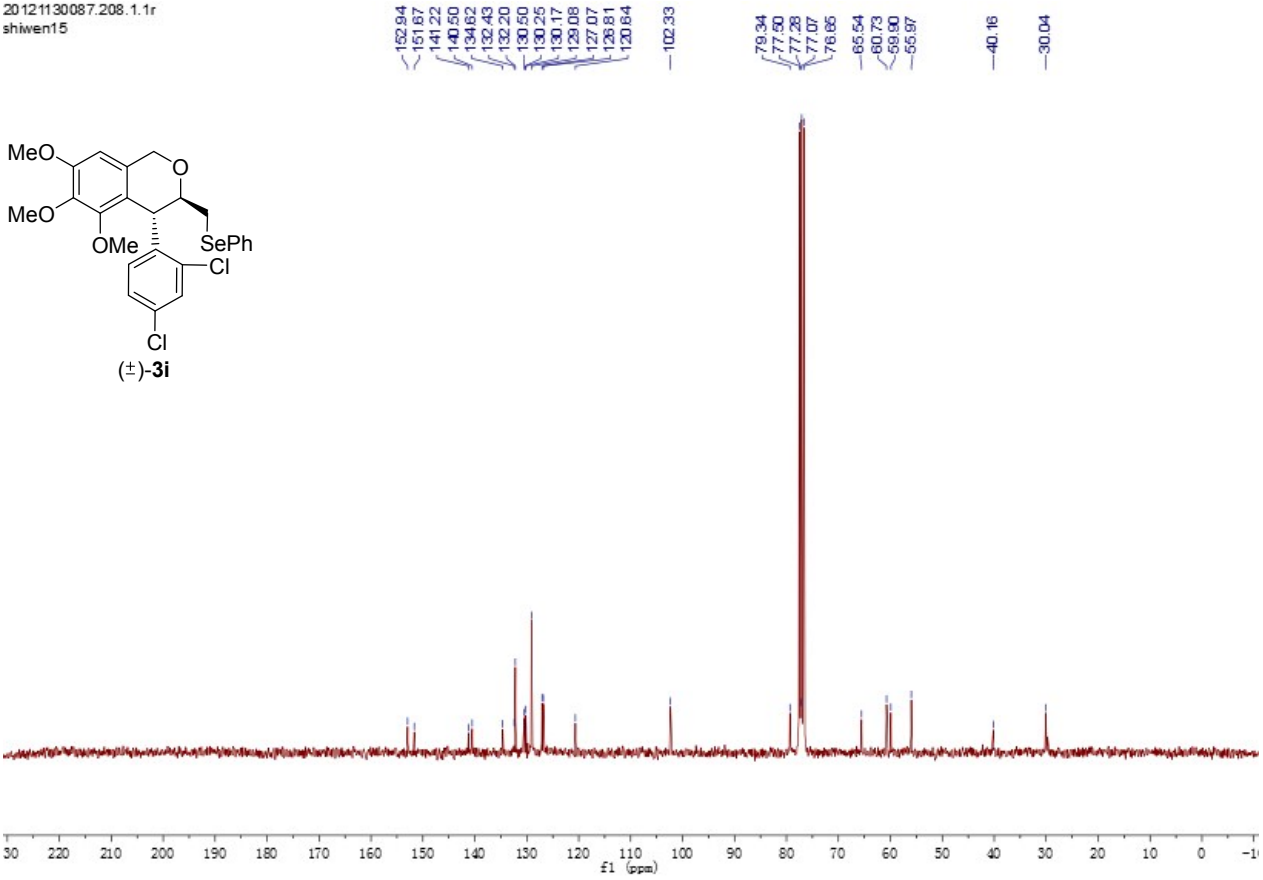



20121130087.207.1.1r
shiwen15
7.34
7.34
7.28
7.28
7.20
7.19
7.14
7.13
7.11
6.99
6.97
6.71
6.69
6.30
4.74
4.55
4.54
4.53
3.84
3.78
3.78
3.68
3.27
3.16
3.12
3.08
3.03
0.00
3.10
3.16
1.08
0.93
1.00
2.01
0.93
1.05
3.04
2.95
2.85
2.02
f1 (ppm)

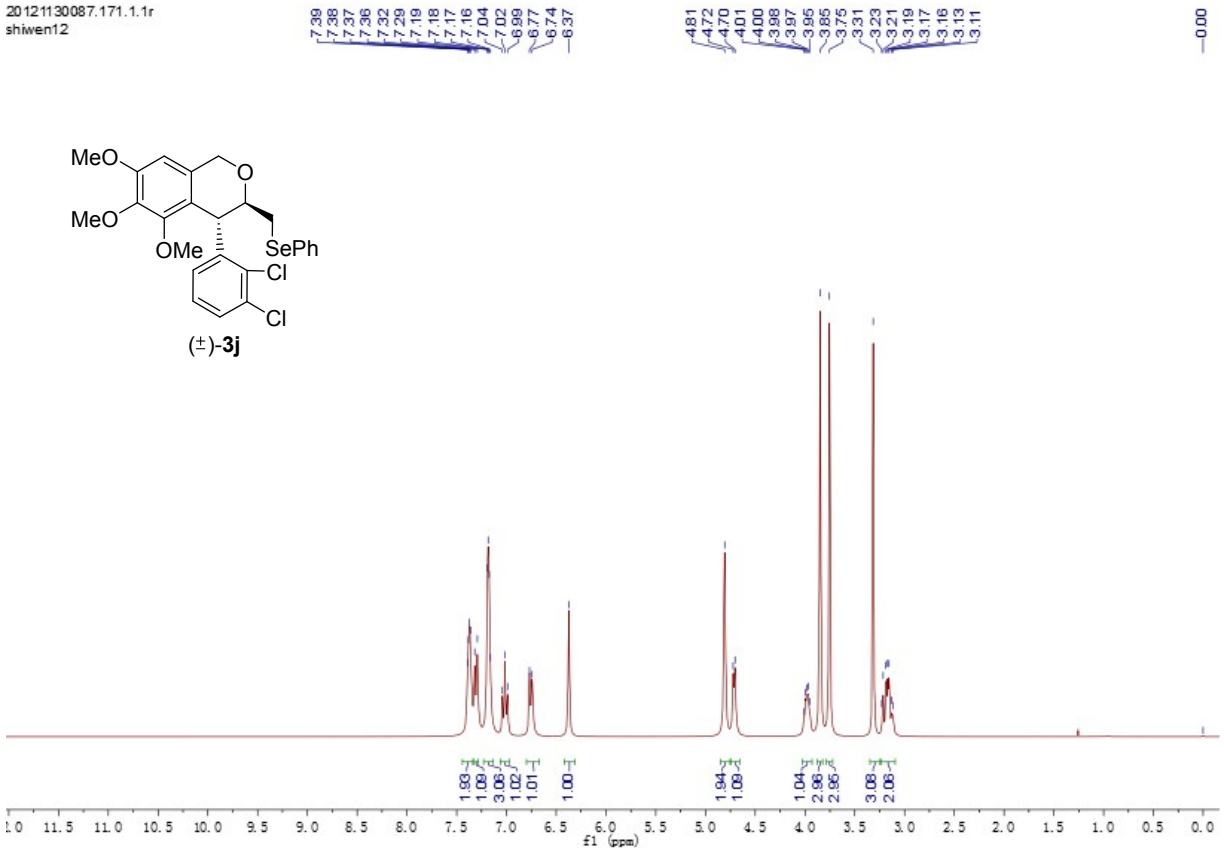


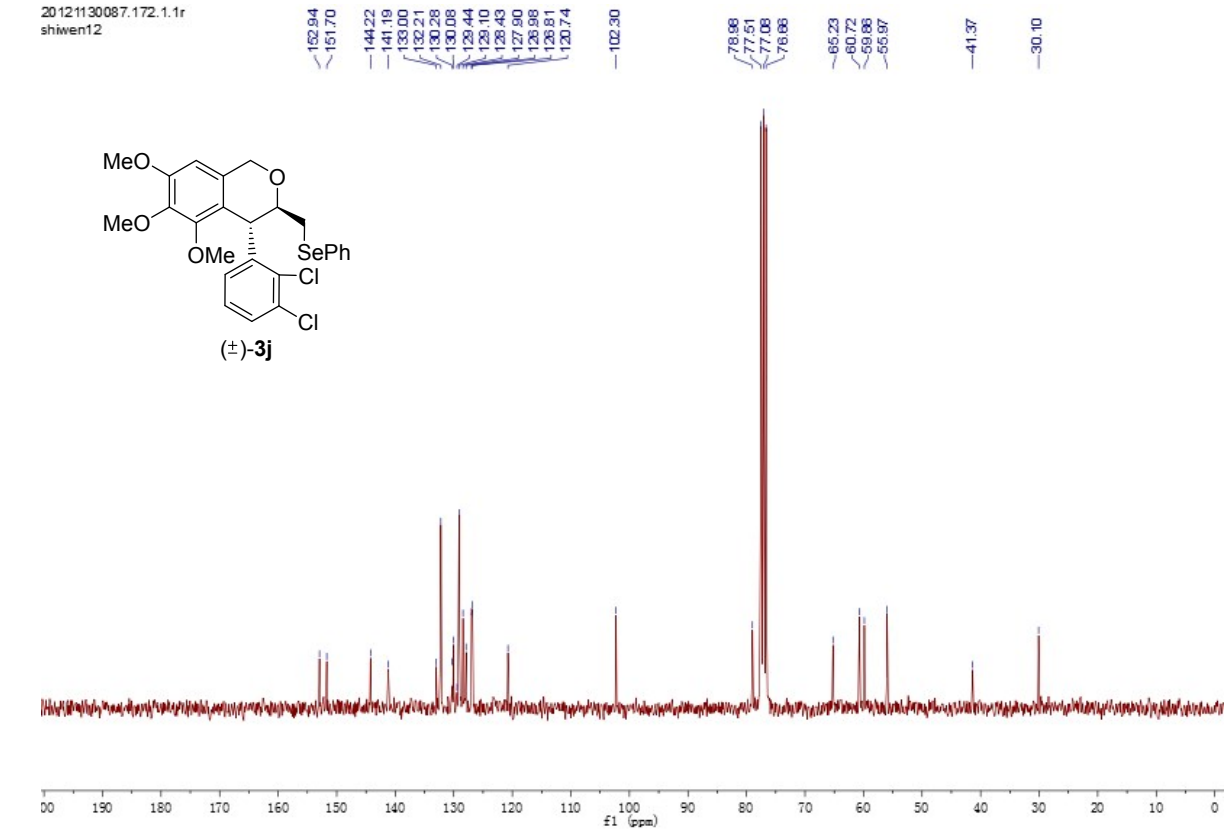
(±)-**3i**

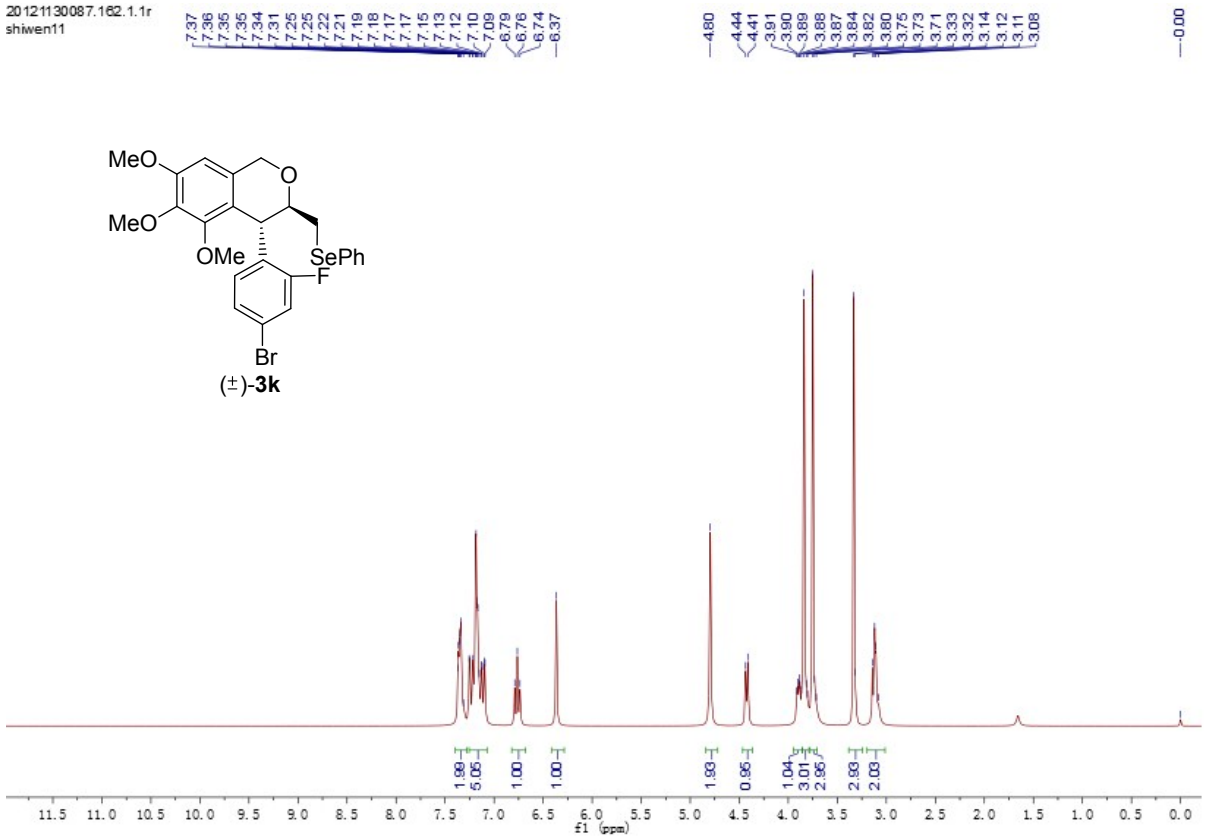
20121130087.208.1.1r
shiwen15

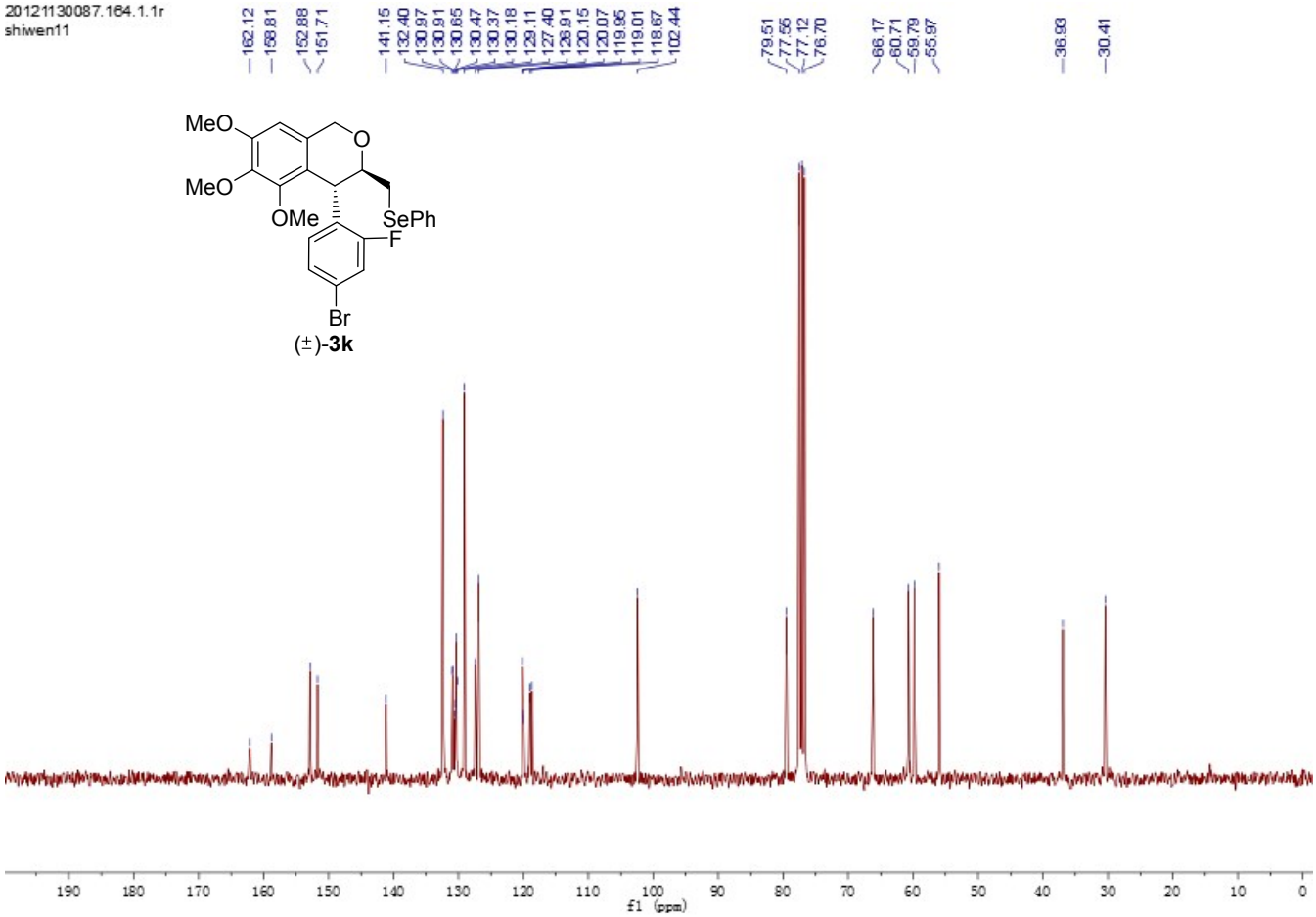


(±)-**3i**


20121130087.171.1.1r
shiwen12
MeO
MeO
OMe
O
SePh
Cl
Cl
(±)-3j
f1 (ppm)

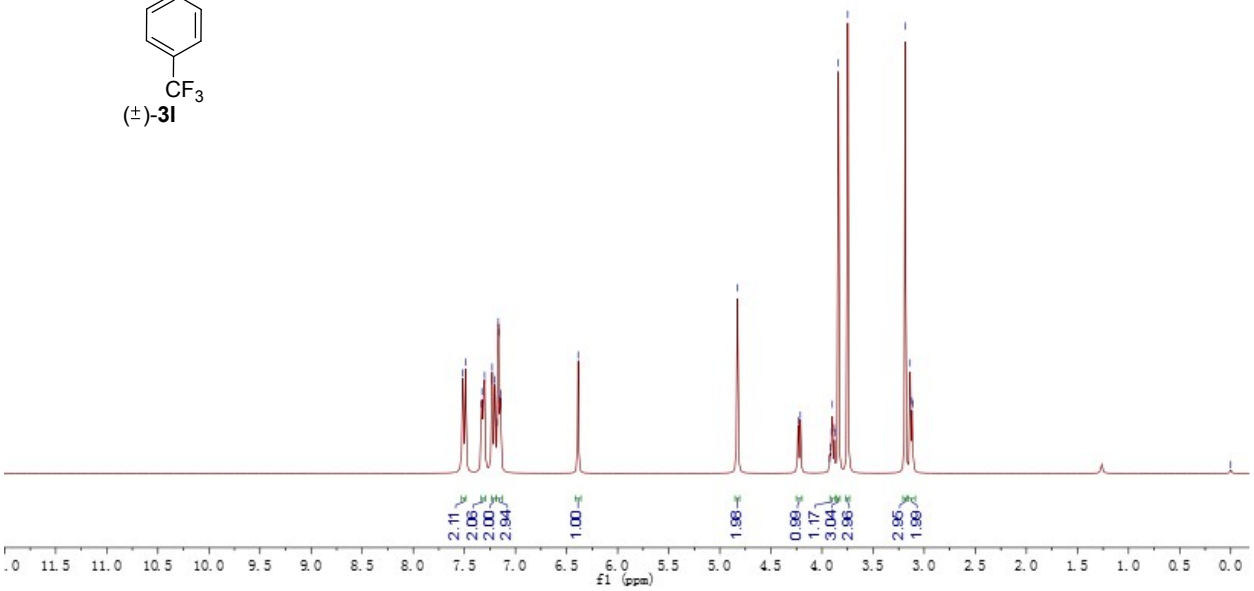

20121130087.172.1.1r
shiwen12
MeO
MeO
OMe
O
SePh
Cl
Cl
(±)-3j
f1 (ppm)


20121130087.162.1.1r
shiwen11
MeO
MeO
OMe
O
SePh
F
Br
(±)-3k
f1 (ppm)

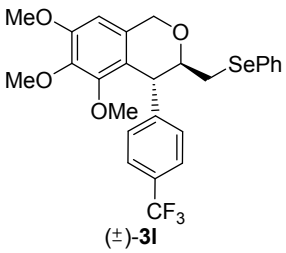

20121130087.164.1.1r
shiwen11
MeO
MeO
OMe
O
SePh
F
Br
(±)-3k
f1 (ppm)

20121130087.167.1.1r
shiwen3

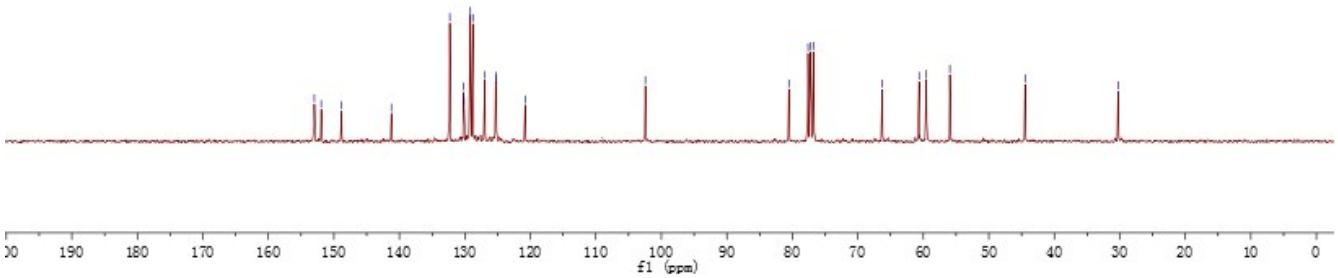
(±)-**3l**

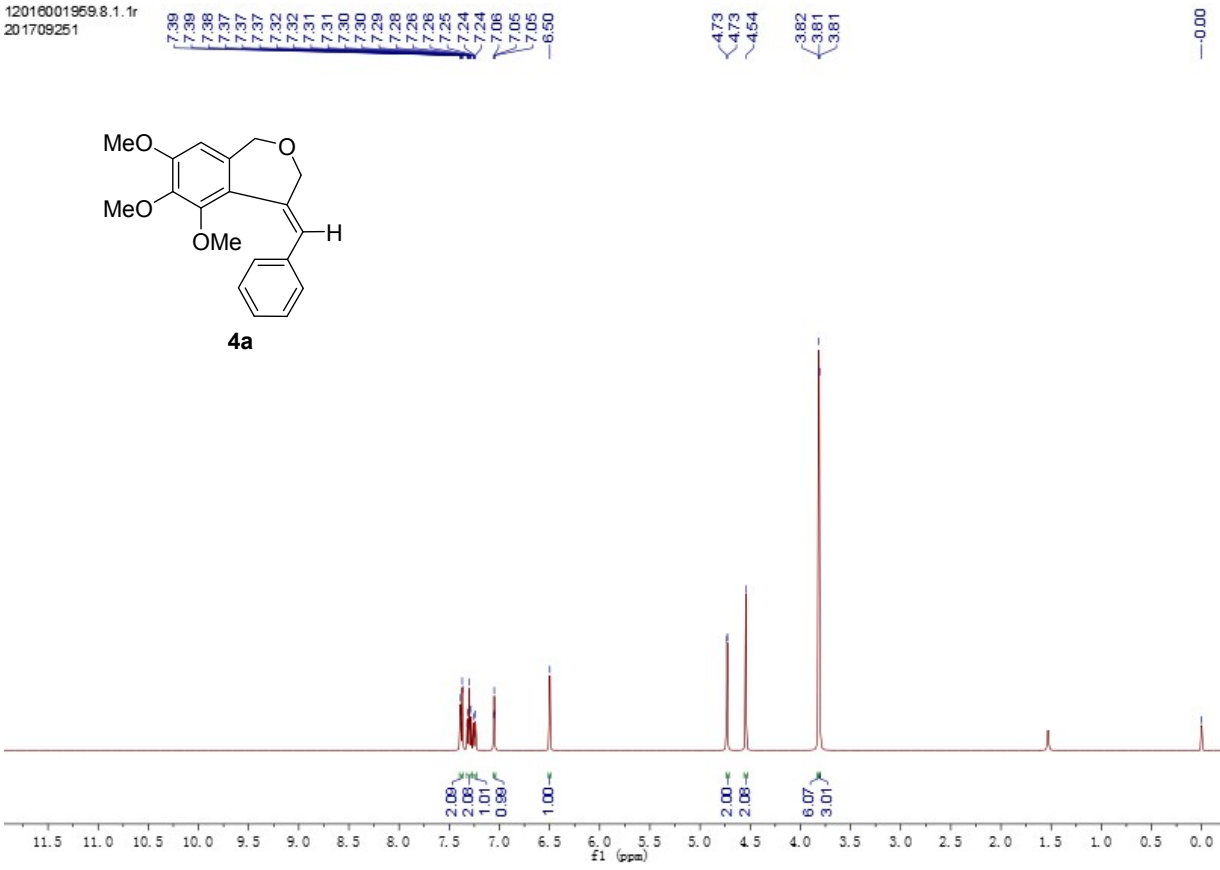


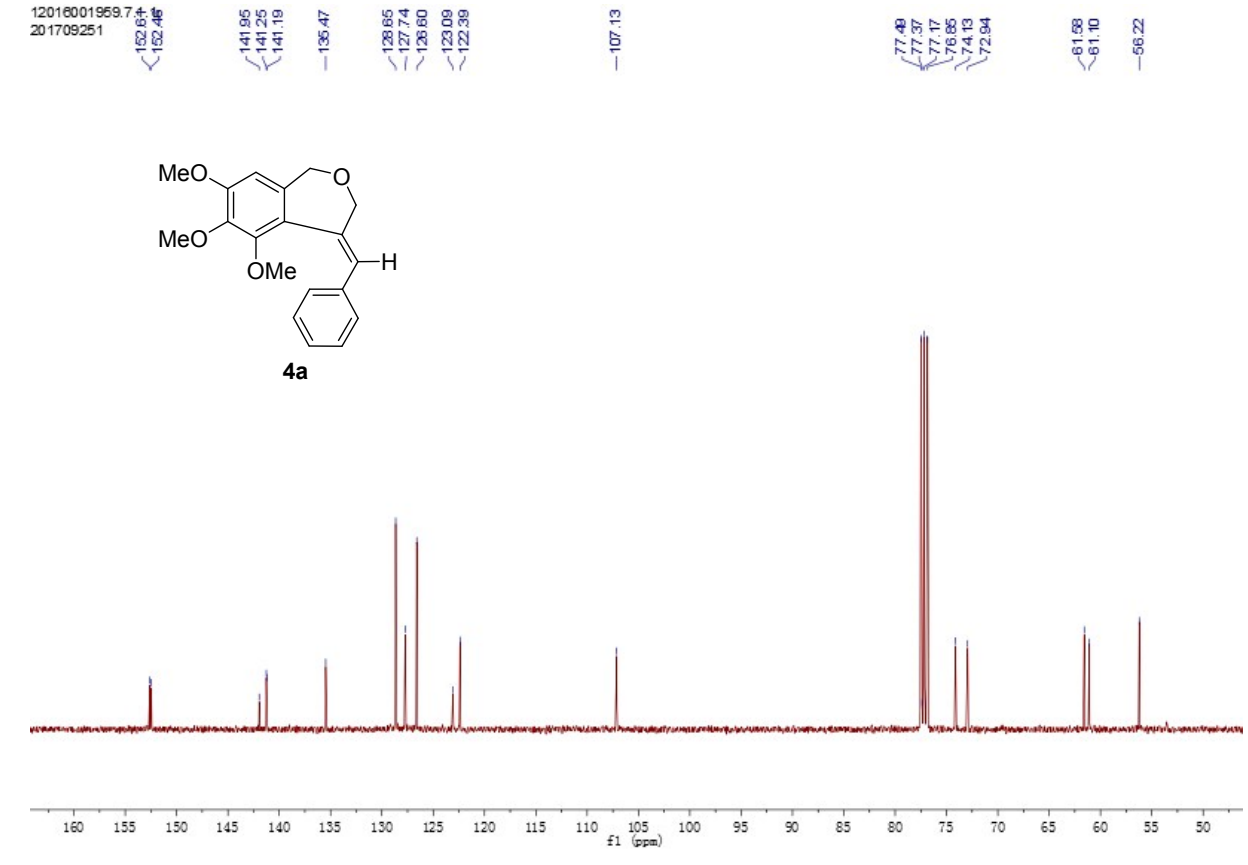
20121130087.168.1.1r
shiwen3

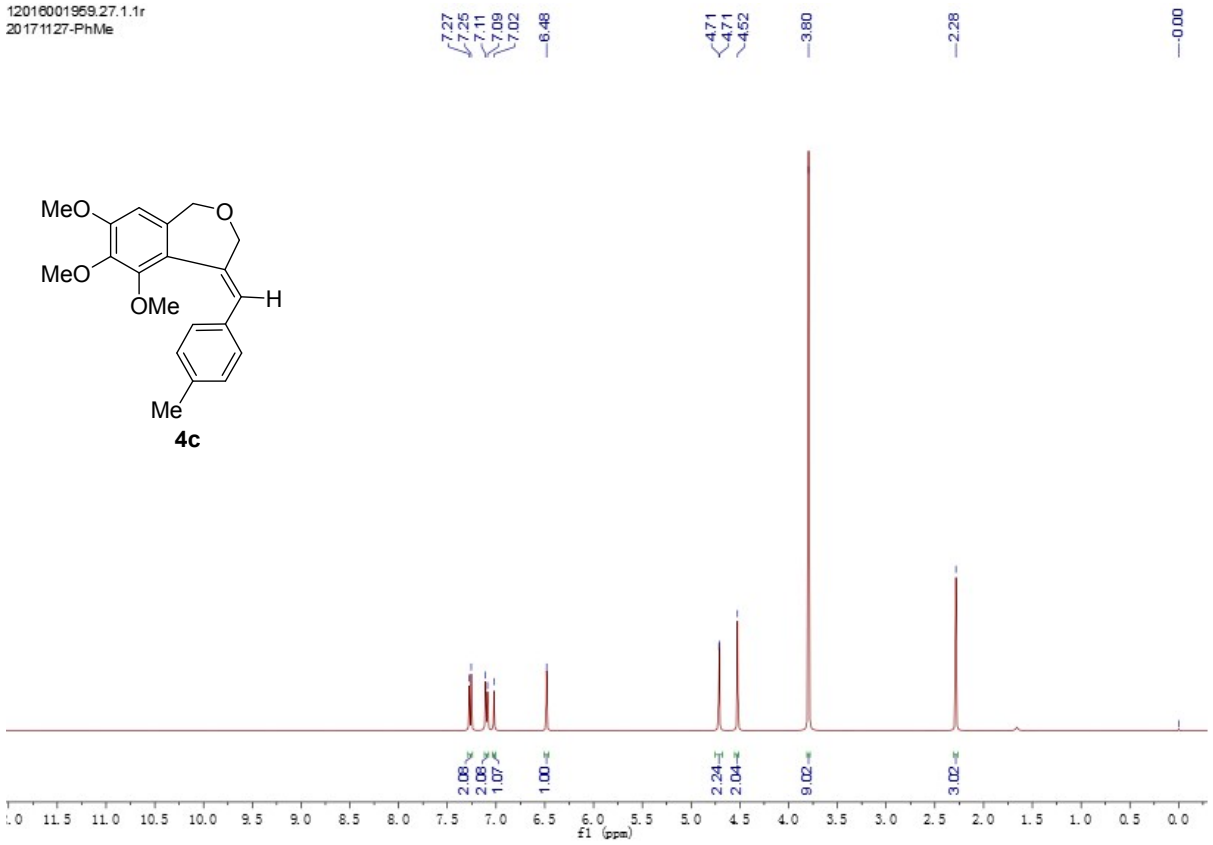


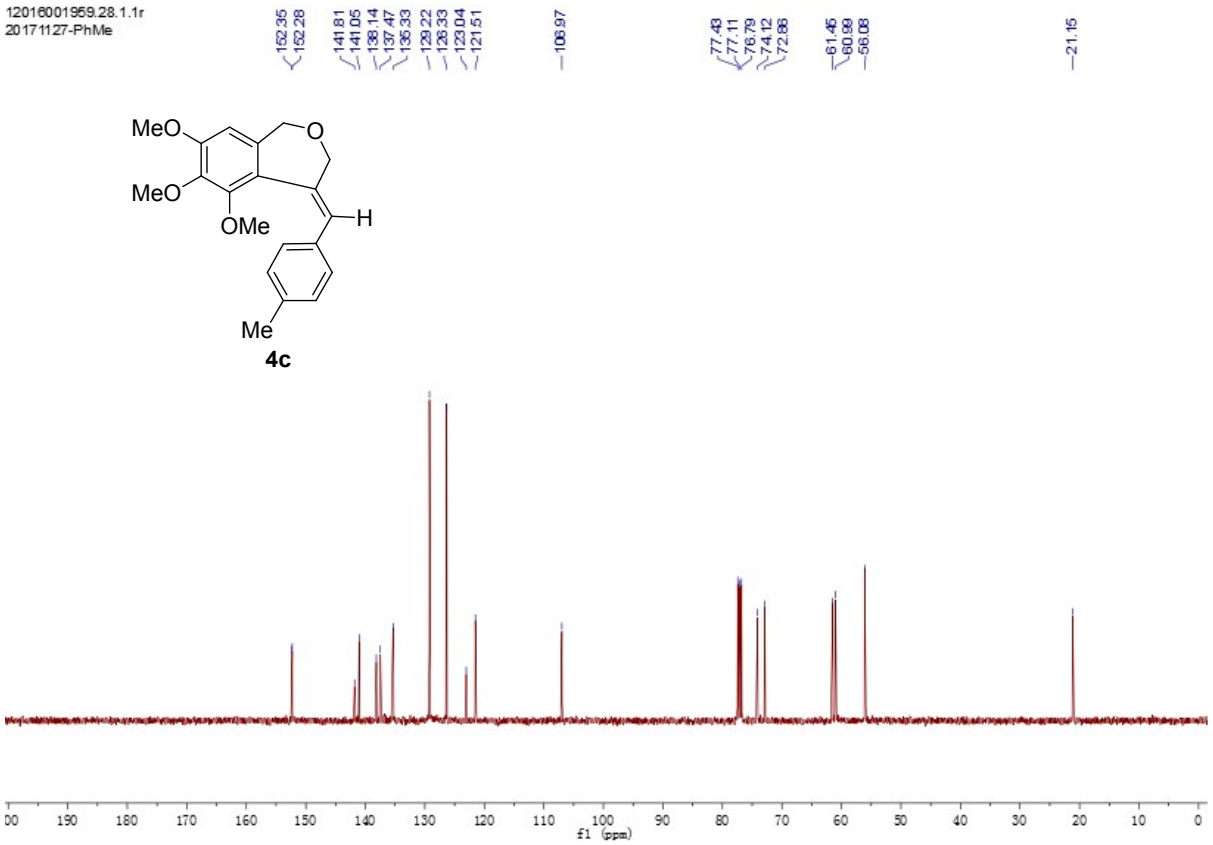
(±)-**3l**

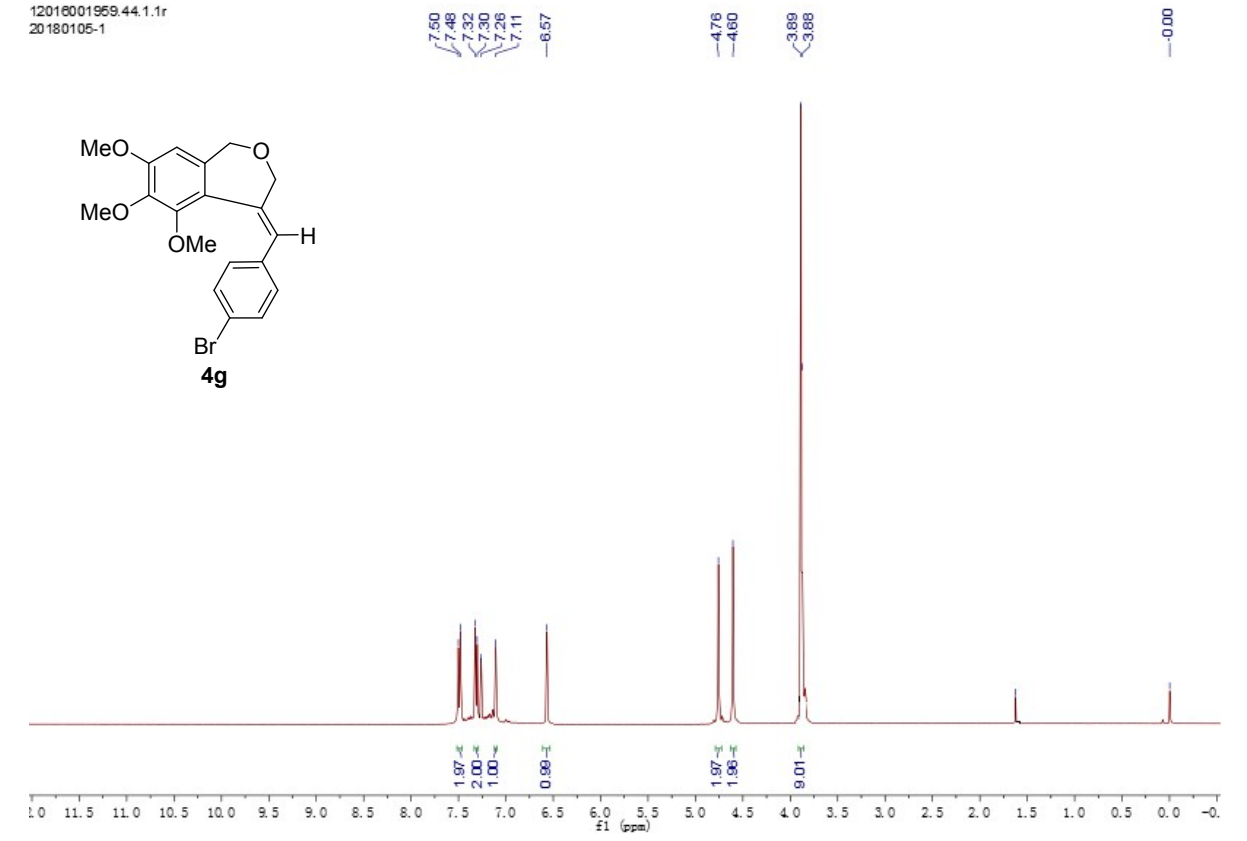


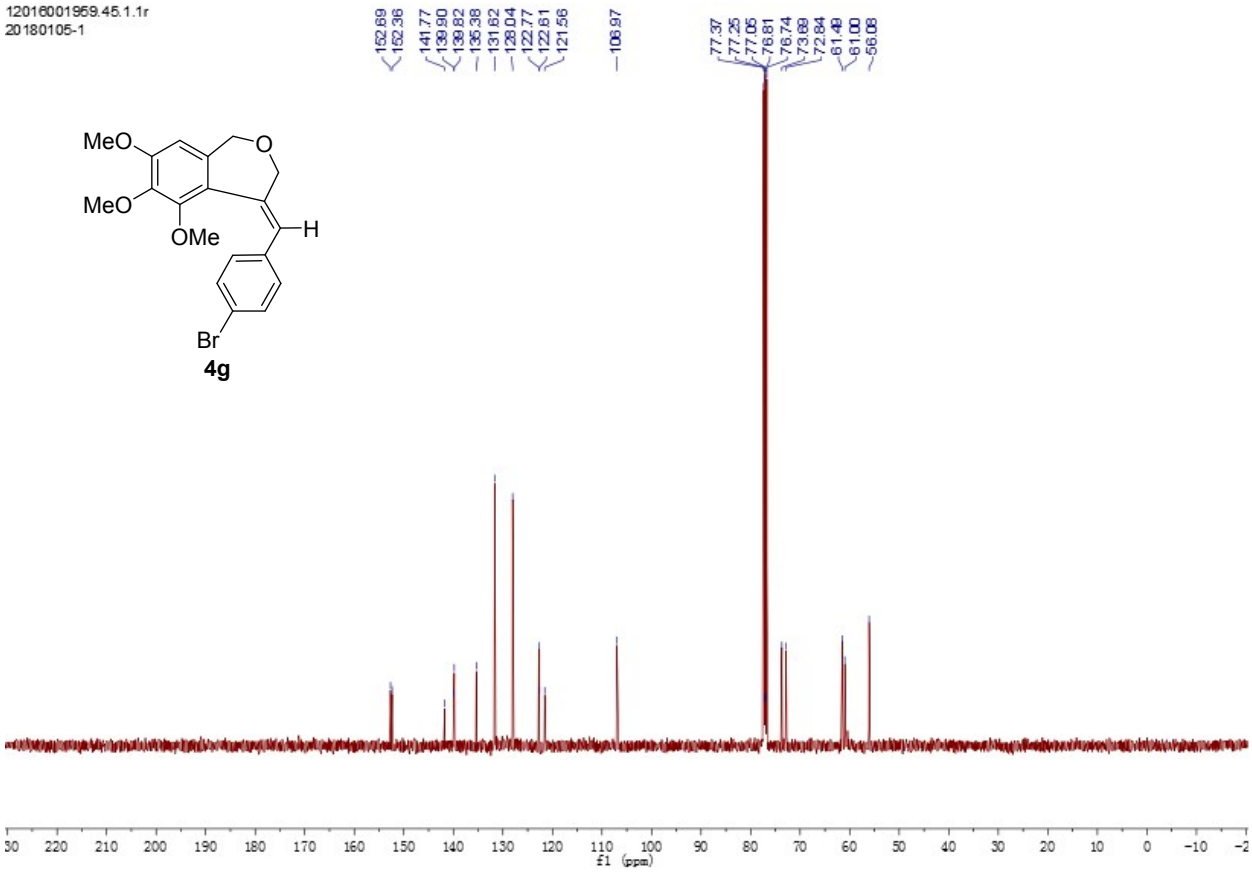

12016001959.8.1.1r
201709251
MeO
MeO
OMe
O
H
4a
f1 (ppm)


12016001959.7.1
201709251
MeO
MeO
OMe
O
H
4a
f1 (ppm)

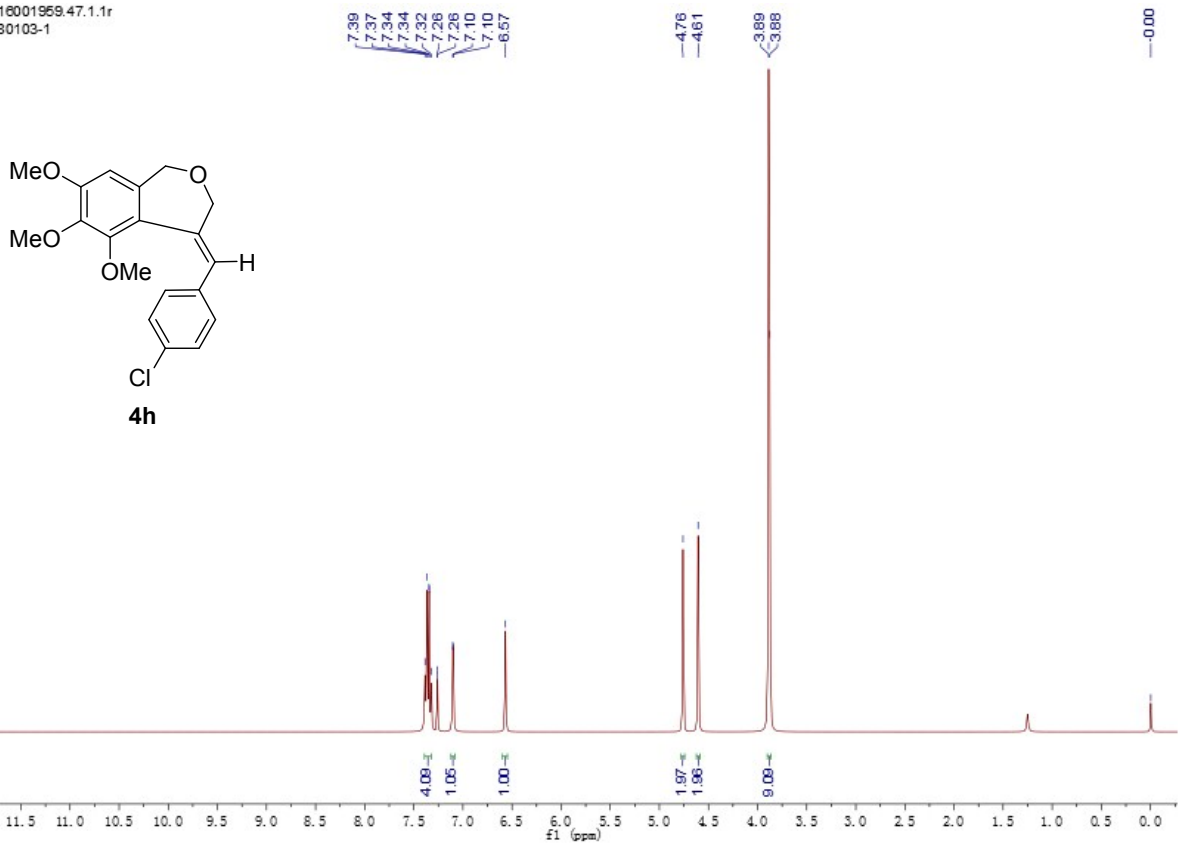

12016001959.27.1.1r
20171127-PhMe
MeO
MeO
OMe
O
H
Me
4c
f1 (ppm)


12016001959.28.1.1r
20171127-PhMe
MeO
MeO
OMe
O
H
Me
4c
f1 (ppm)


12016001959.44.1.1r
20180105-1
MeO
MeO
OMe
O
H
Br
4g
f1 (ppm)

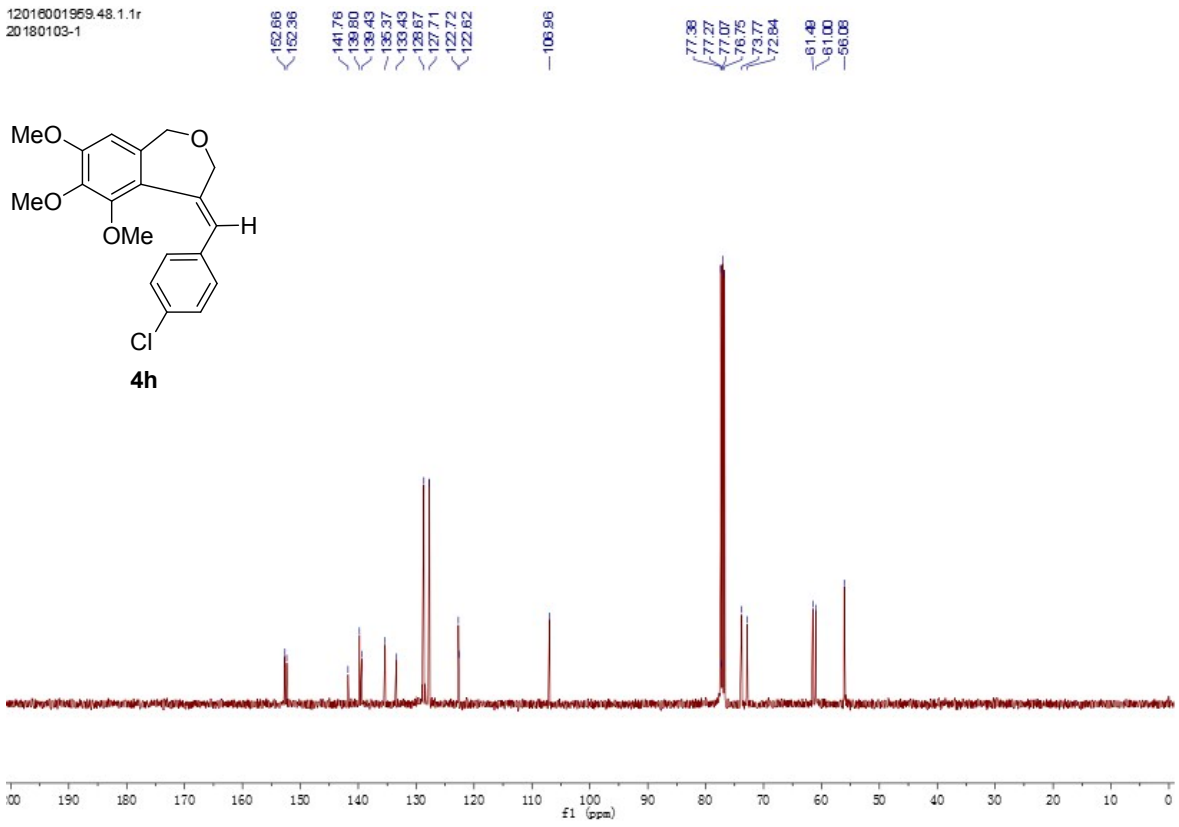

12016001959.45.1.1r
20180105-1
MeO
MeO
OMe
O
H
Br
4g
f1 (ppm)

12016001959.47.1.1r
20180103-1



4h

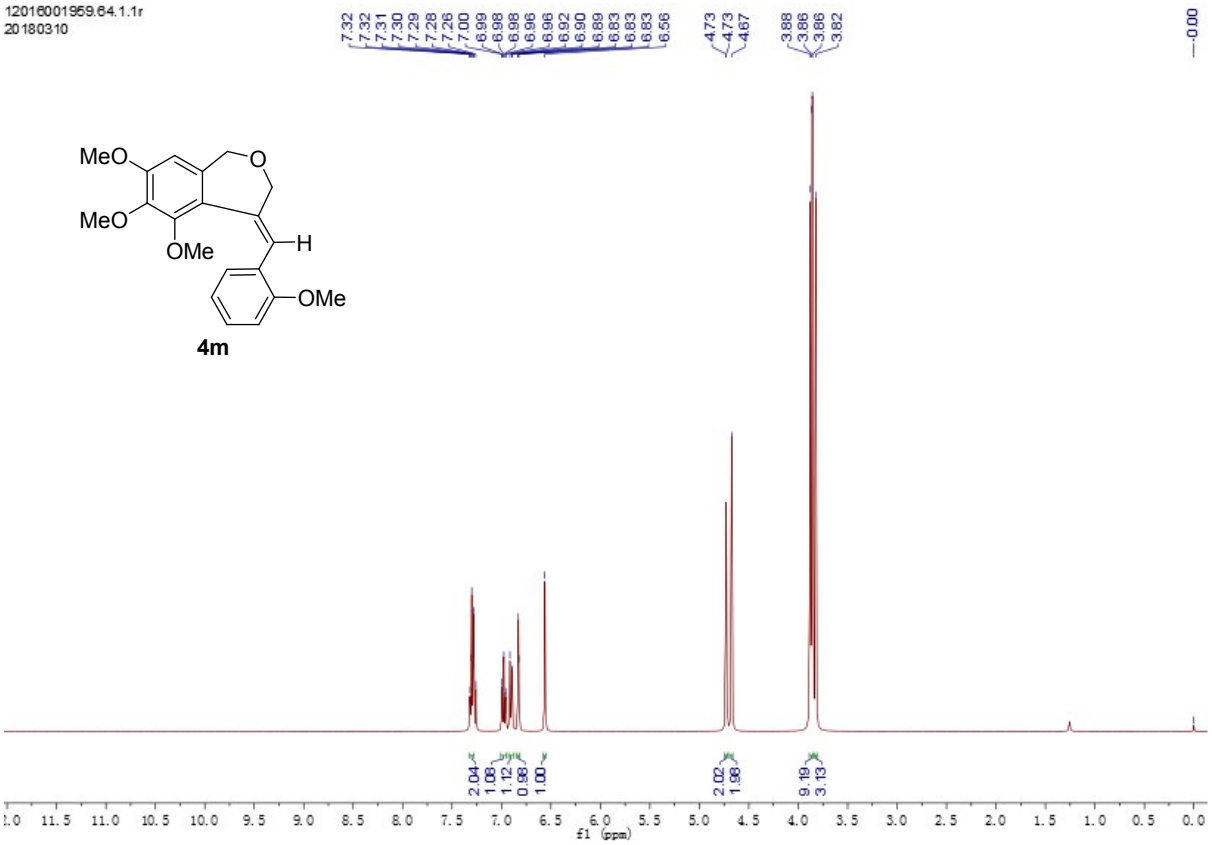
12016001959.48.1.1r
20180103-1



4h

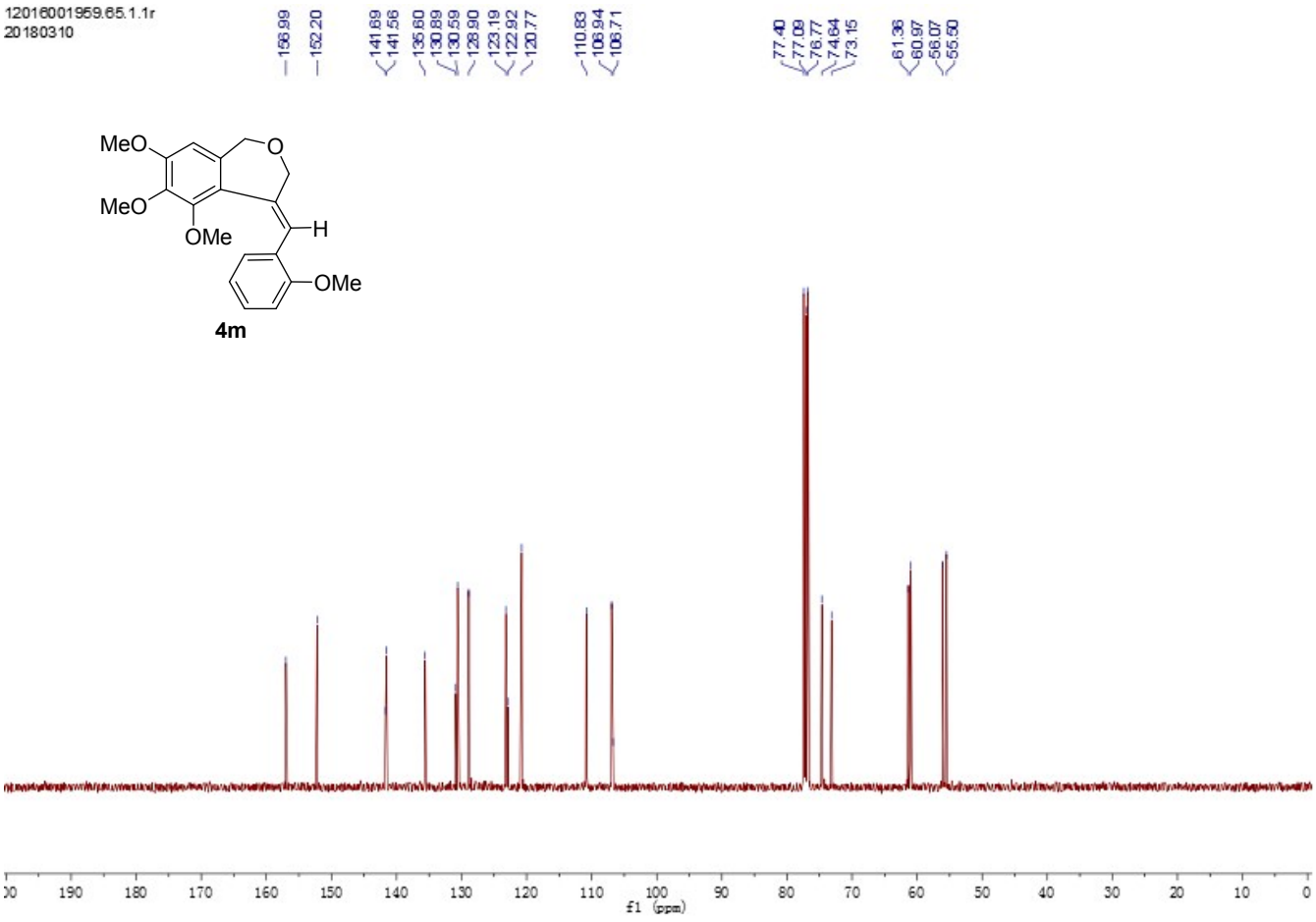
12016001959.64.1.1r
20180310

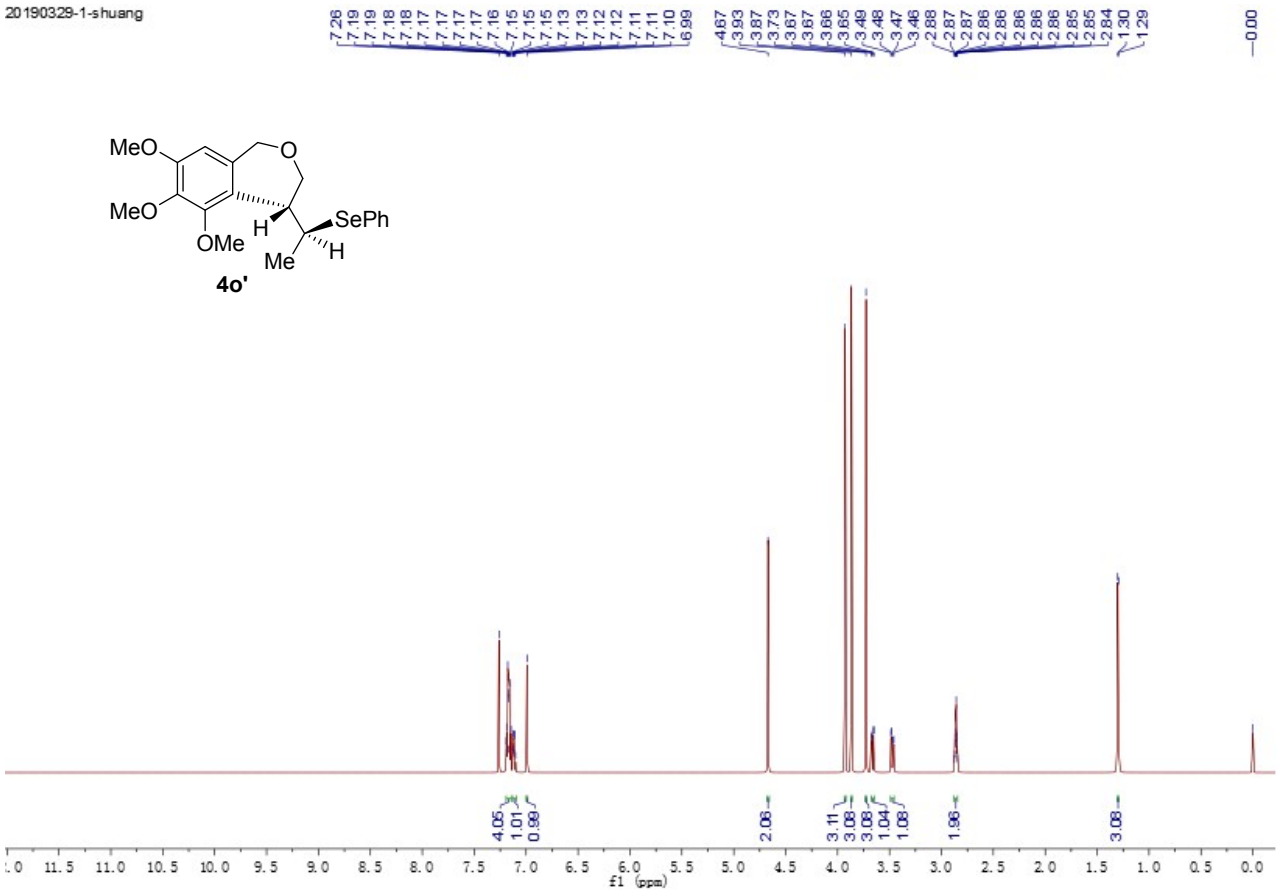
4m

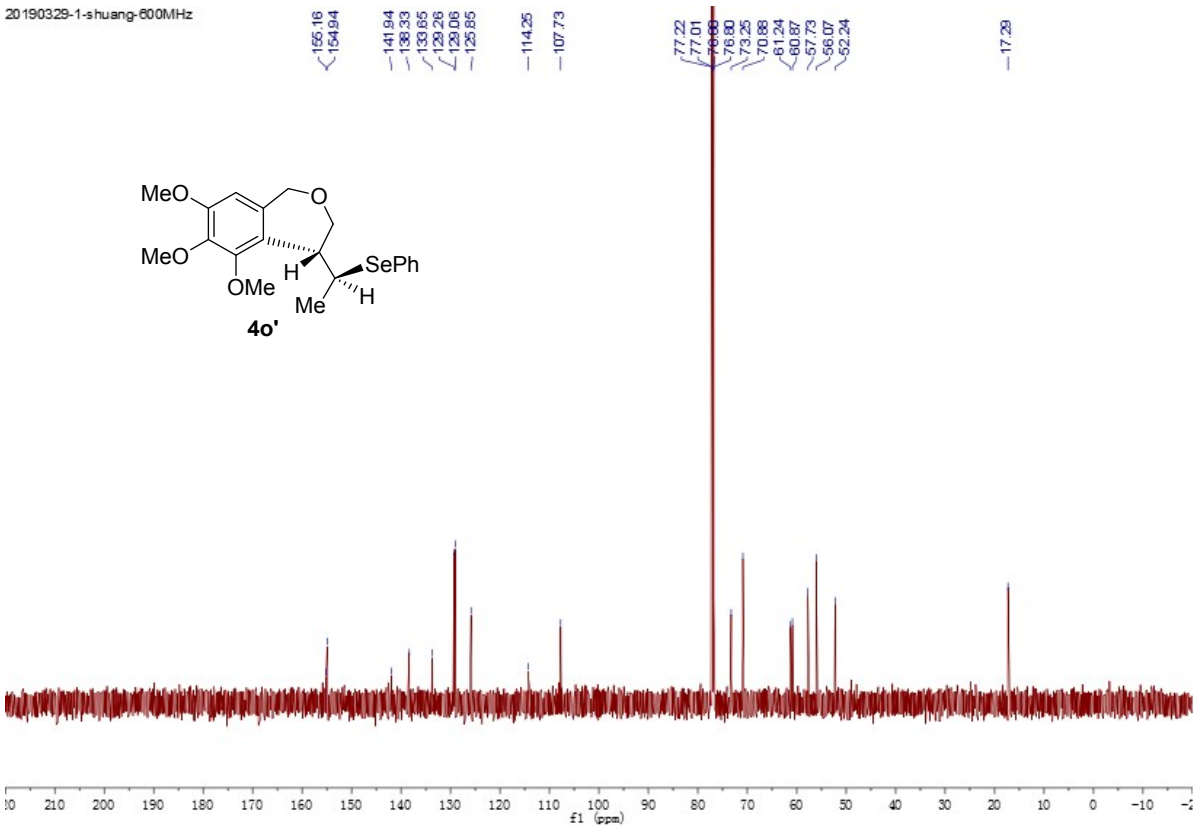


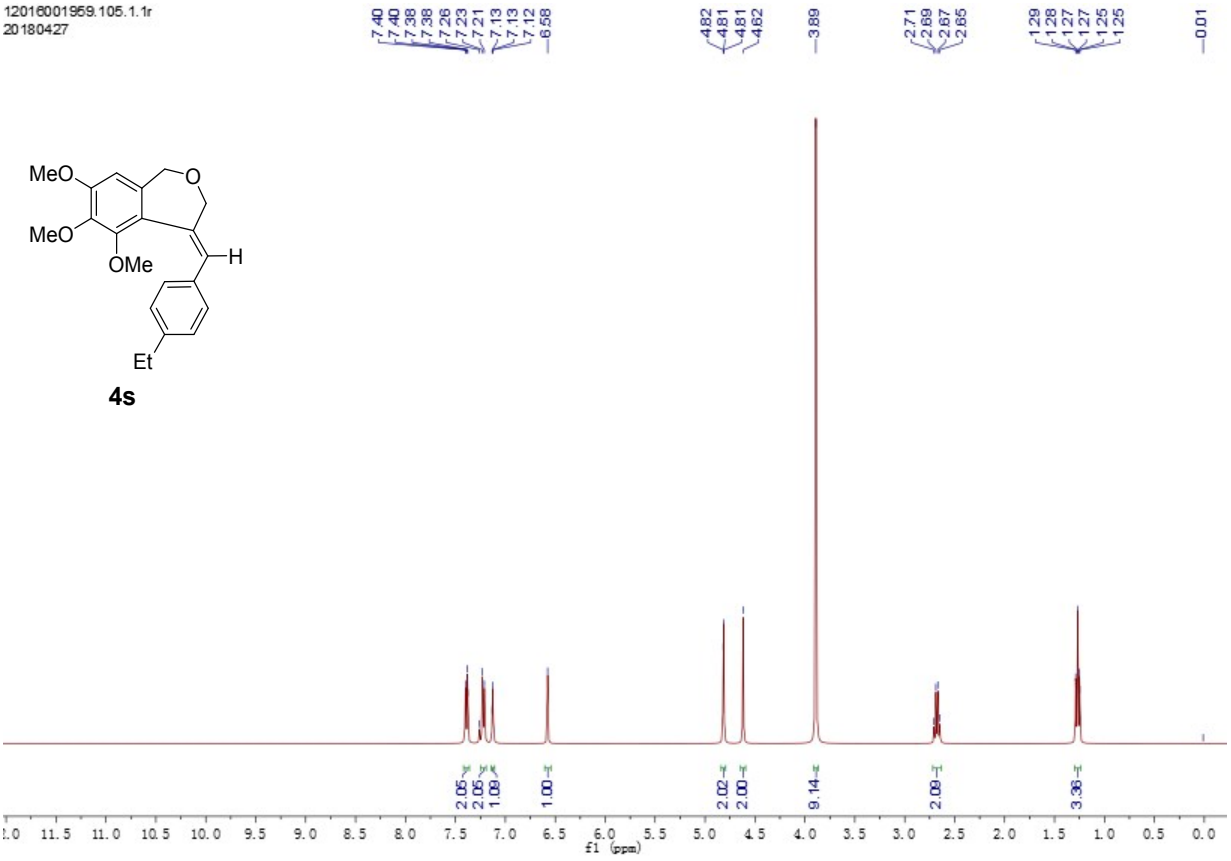
12016001959.65.1.1r
20180310

4m

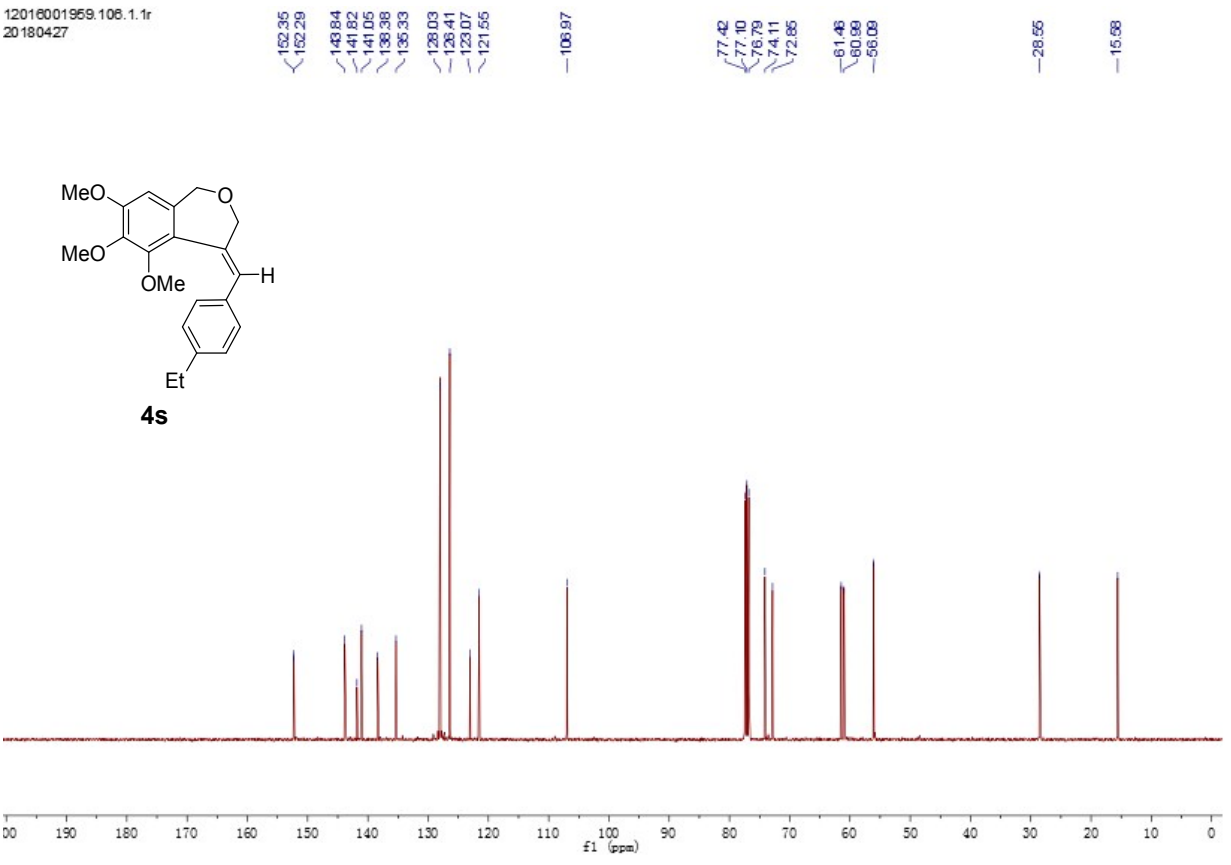



20190329-1-shuang
MeO
MeO
OMe
O
H
SePh
Me
H
4o'
f1 (ppm)

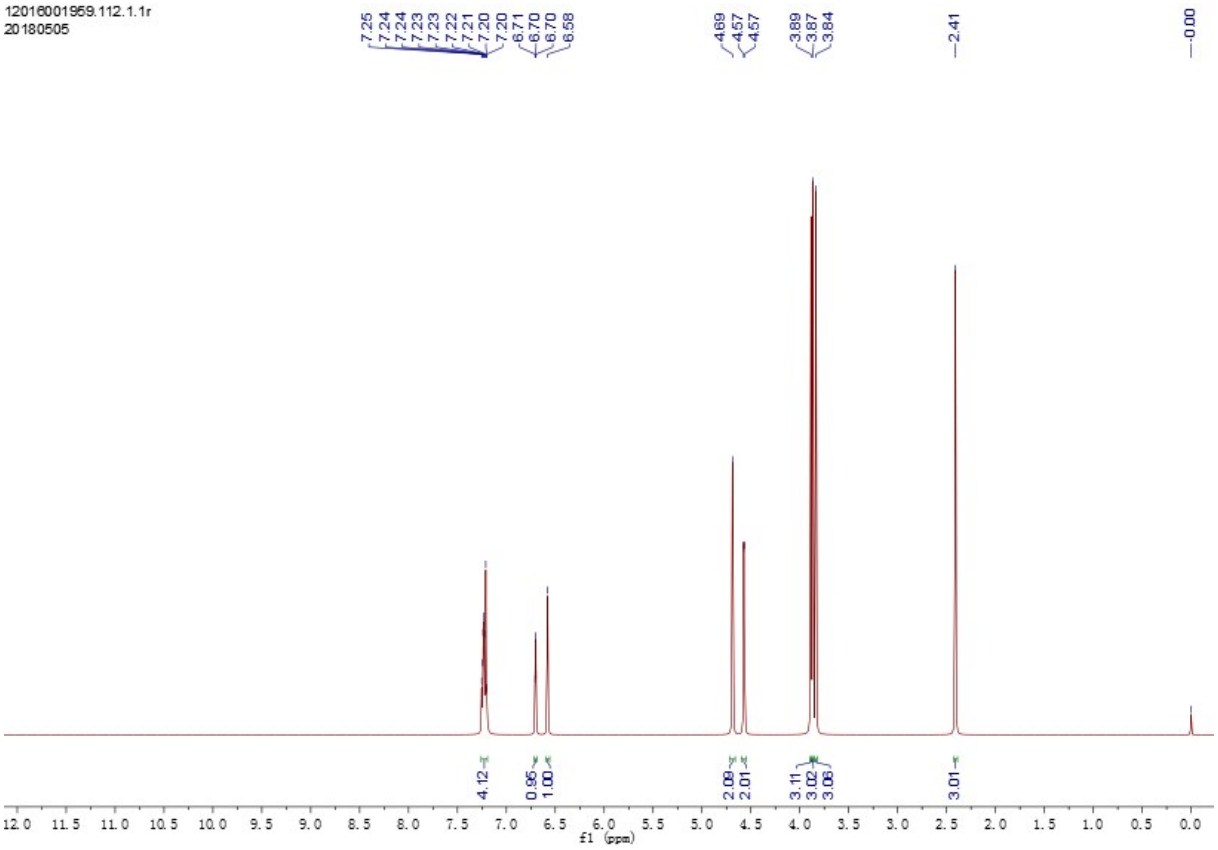

20190329-1-shuang-600MHz
MeO
MeO
OMe
O
H
SePh
Me
H
4o'
f1 (ppm)

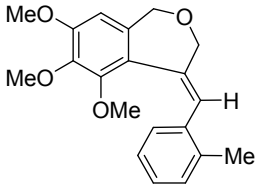

120160001959.105.1.1r
20180427
MeO
MeO
OMe
O
H
Et
f1 (ppm)

4s


120160001959.106.1.1r
20180427
MeO
MeO
OMe
O
H
Et
f1 (ppm)

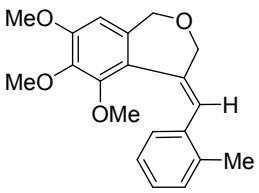
4s


12016001959.112.1.1r
20180505
7.25
7.24
7.24
7.23
7.23
7.22
7.21
7.20
7.20
6.71
6.70
6.70
6.58
4.69
4.57
4.57
3.89
3.87
3.84
2.41
0.00
4.12
0.95
1.00
2.09
2.01
3.11
3.02
3.06
3.01
12.0 11.5 11.0 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)

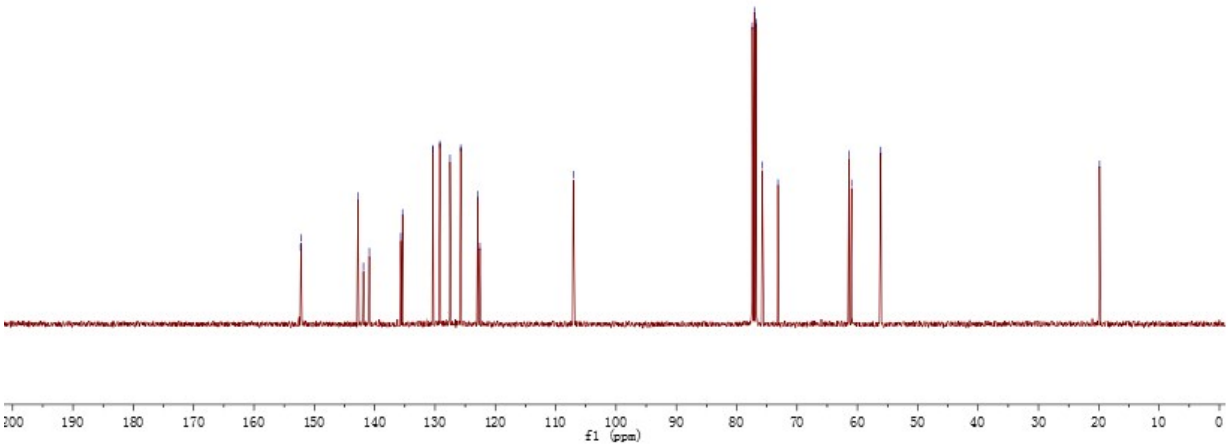

MeO
MeO
OMe
O
H
Me

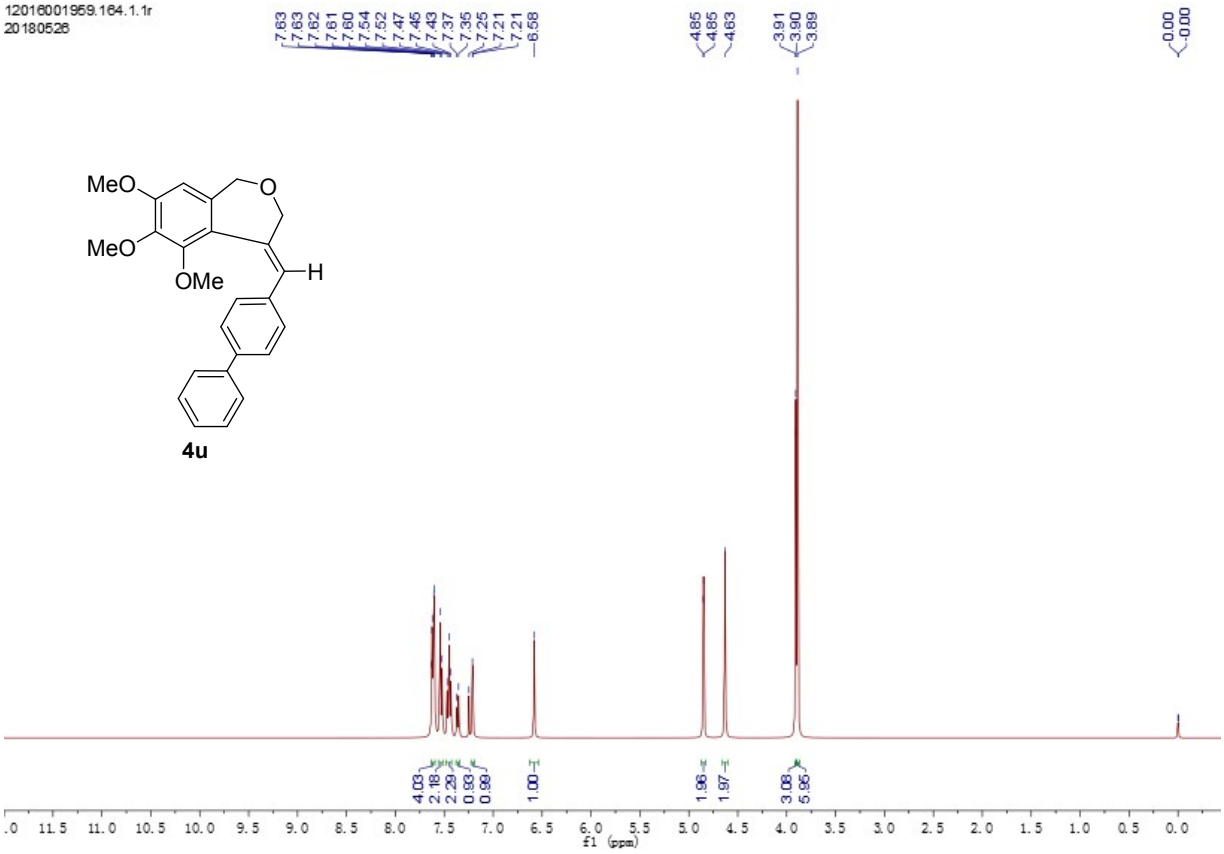
4t

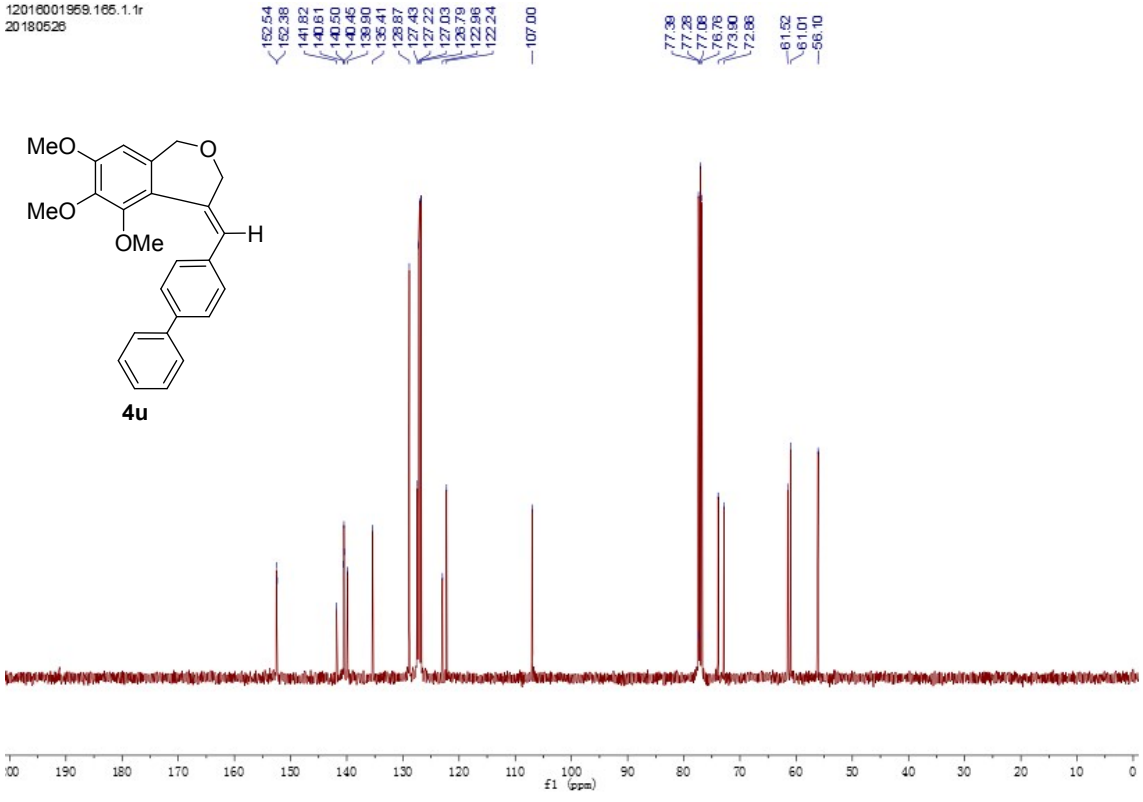

120160001959.113.1.1r
20180505
152.29
152.22
142.77
141.87
140.89
136.89
135.39
130.36
129.22
127.52
125.74
122.91
122.56
107.09
77.40
77.08
76.77
75.78
73.16
61.41
60.97
56.12
19.87

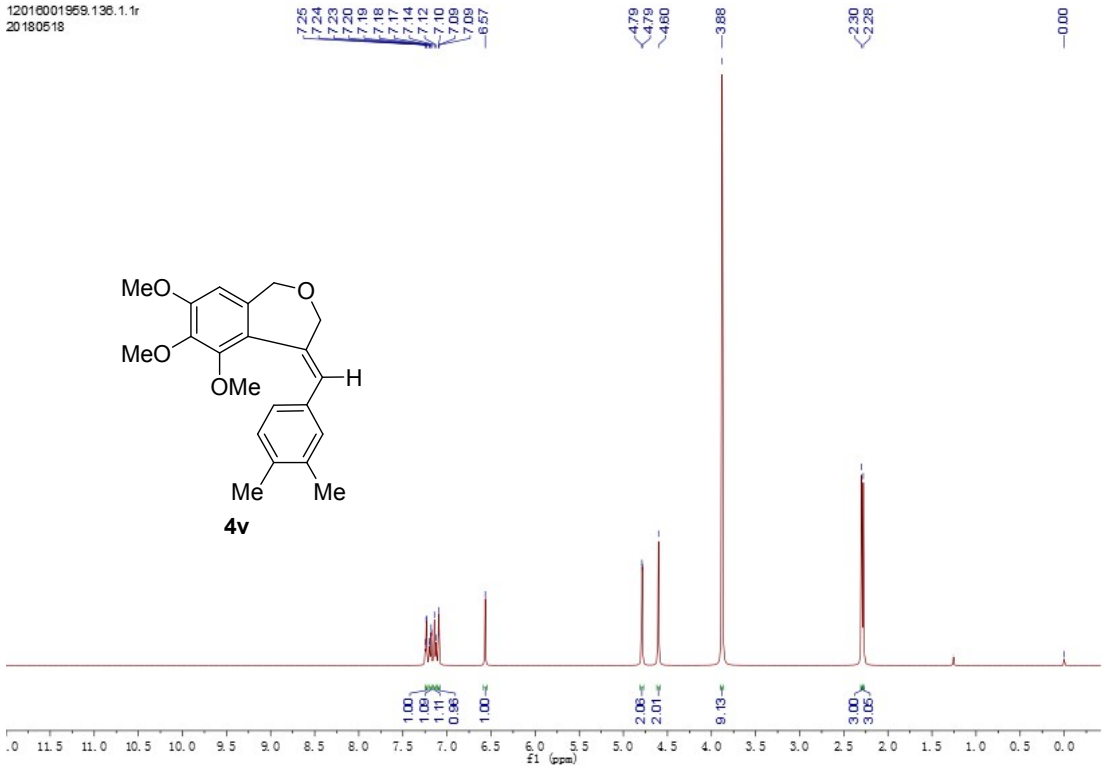

MeO
MeO
OMe
O
H
Me

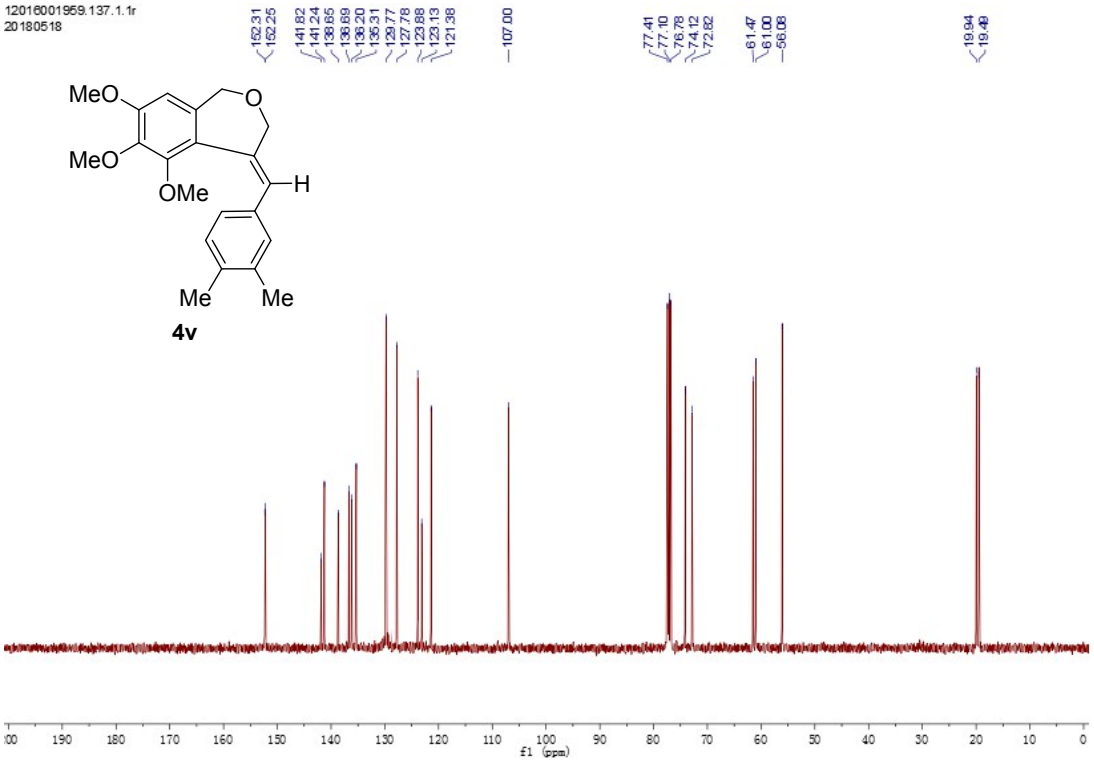
4t

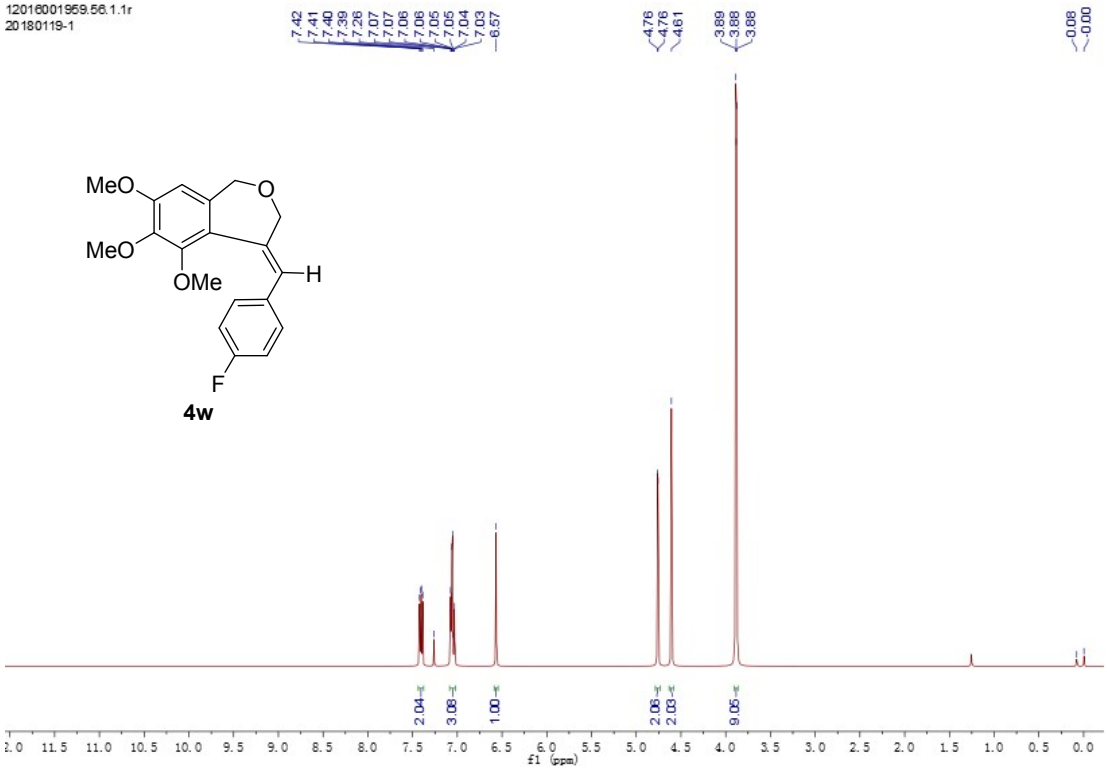

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


12016001959.164.1.1r
20180526
MeO
MeO
OMe
O
H
4u
f1 (ppm)

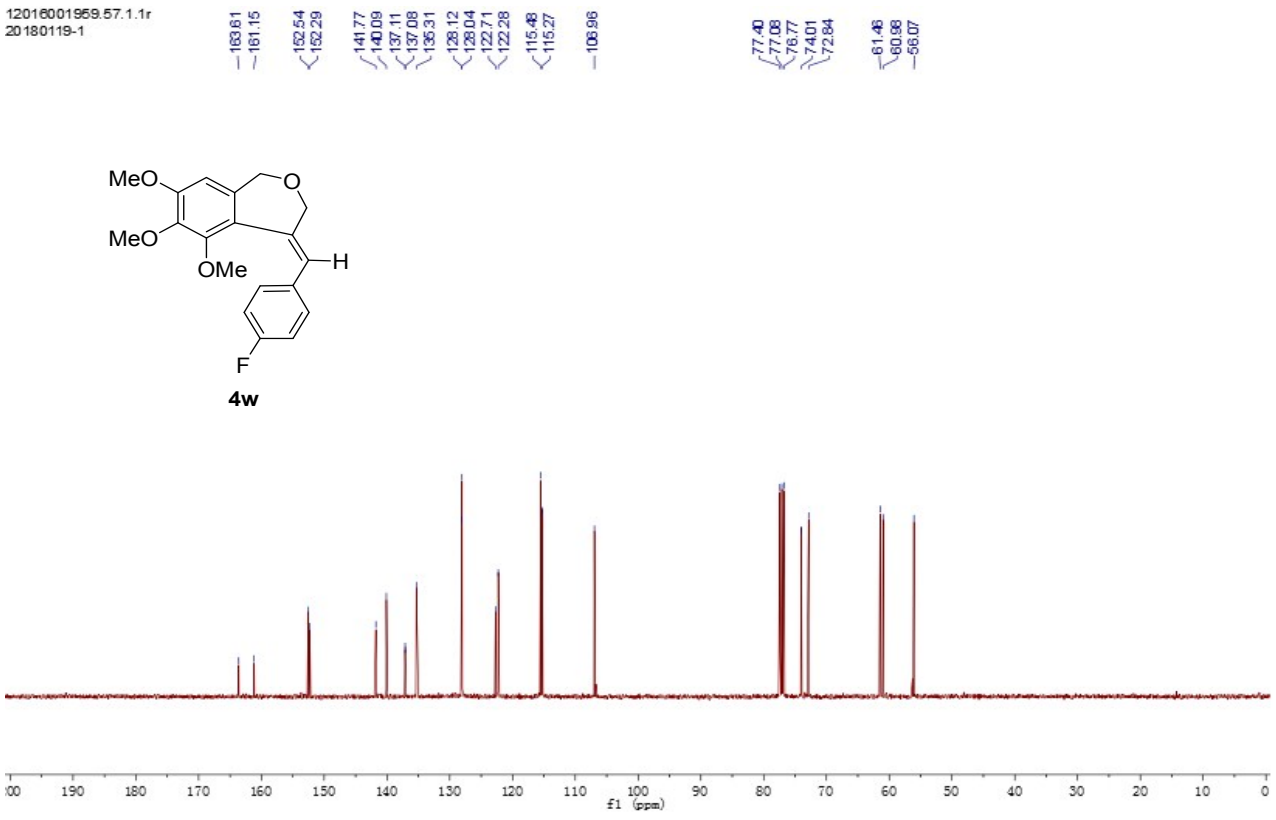

12016001959.165.1.1r
20180526
MeO
MeO
OMe
O
H
4u
f1 (ppm)


120160001959.136.1.1r
20180518
MeO
MeO
OMe
O
H
Me
Me
4v
f1 (ppm)

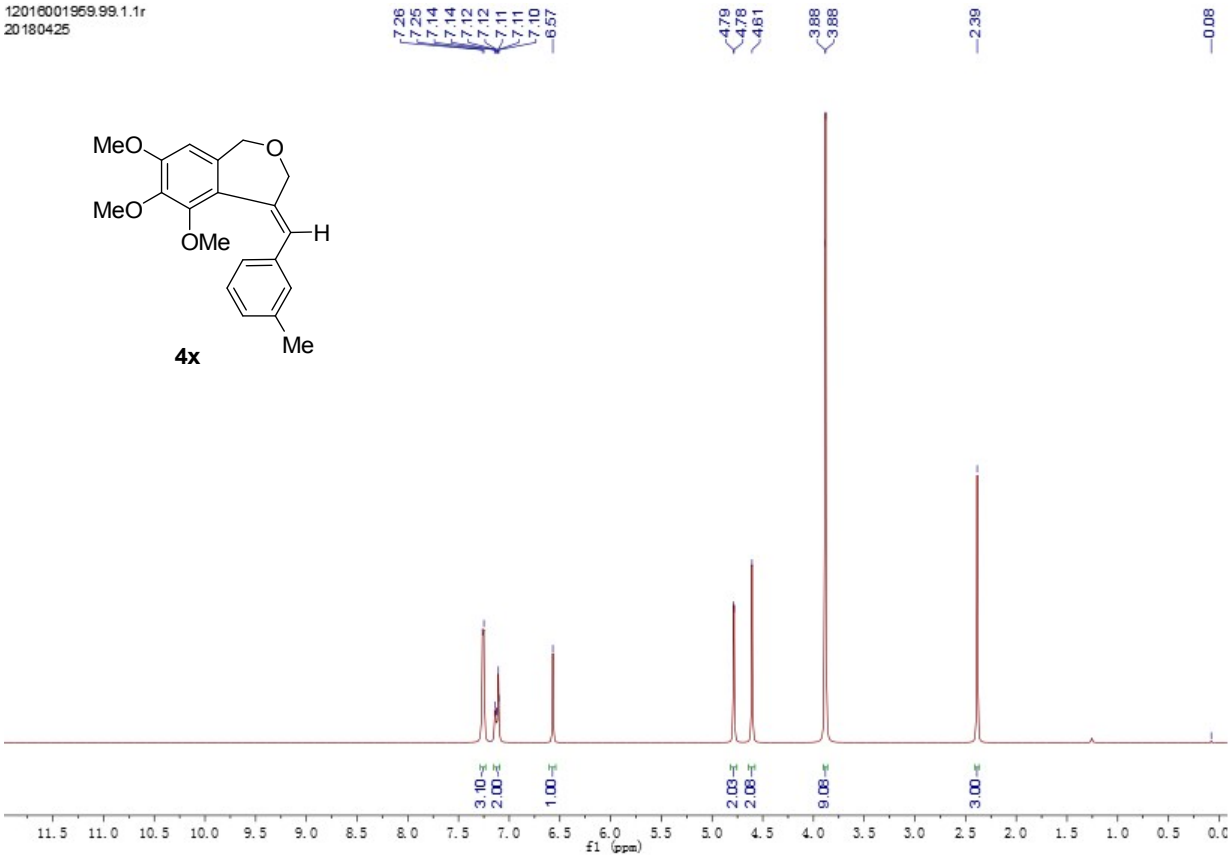

120160001959.137.1.1r
20180518
MeO
MeO
OMe
O
H
Me
Me
4v
f1 (ppm)

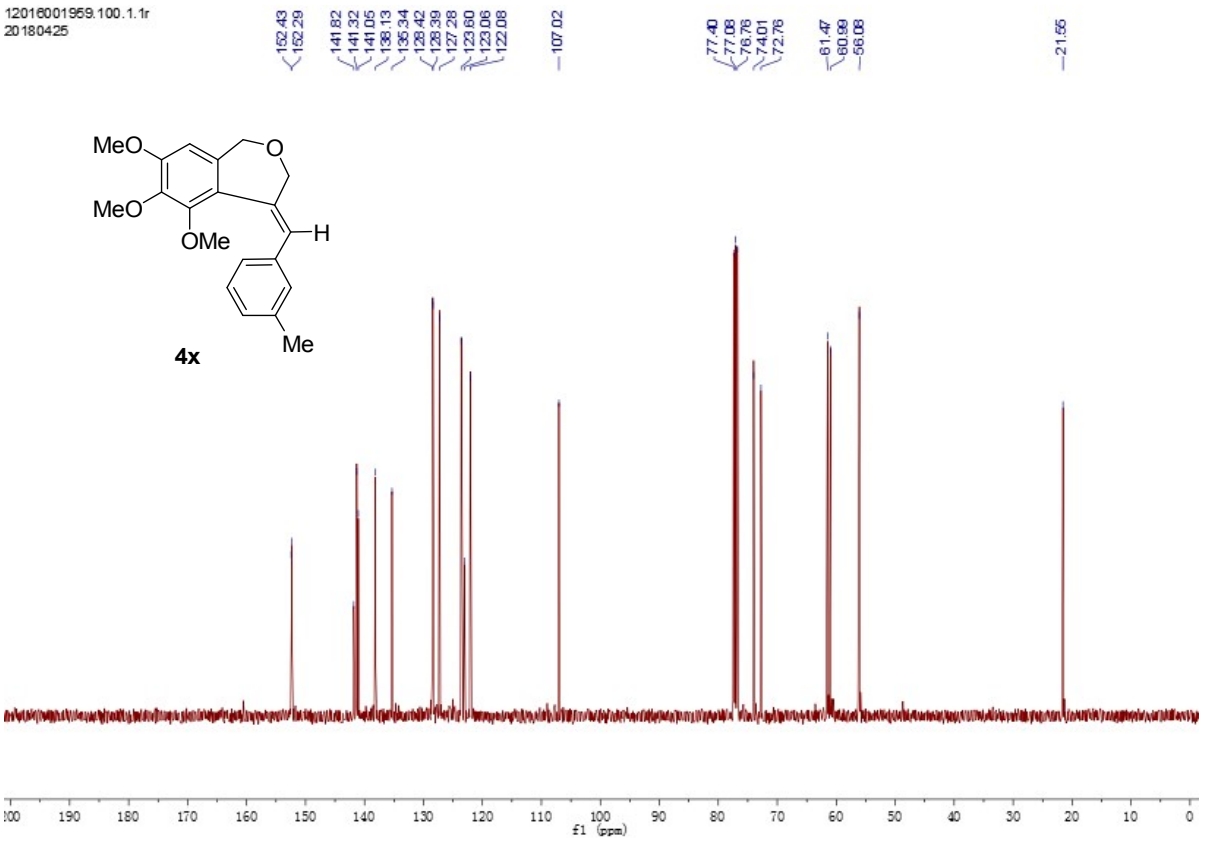

12016001959.56.1.1r
20180119-1
MeO
MeO
OMe
O
H
F

4w

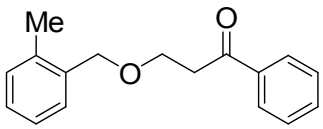

12016001959.57.1.1r
20180119-1
MeO
MeO
OMe
O
H
F

4w

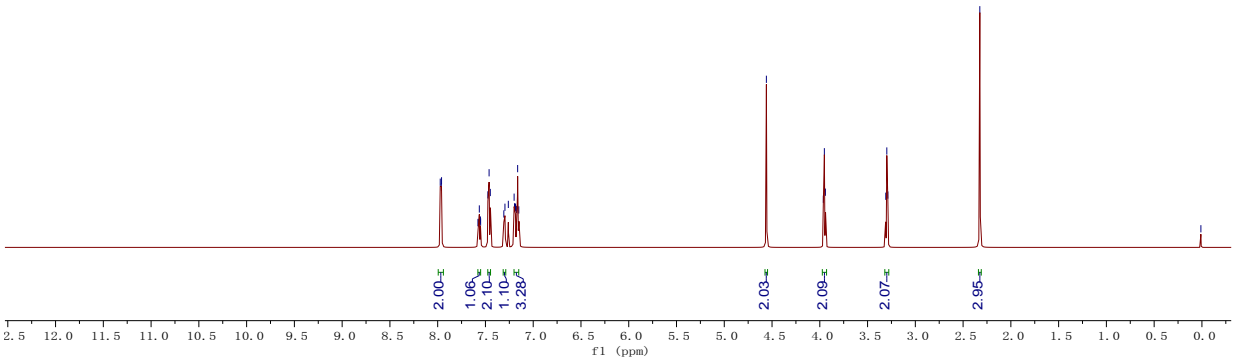

12016001959.99.1.1r
20180425
MeO
MeO
OMe
O
H
Me
4x


12016001959.100.1.1r
20180425
MeO
MeO
OMe
O
H
Me
4x

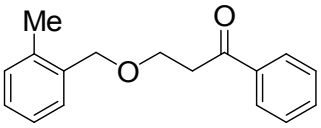
Sep04-2019-tange.30.1.1r
YUNNAN UNIVERSITY ASCEND AVIIIHD600 L-0904-3
PROTON CDCl3 {D:\tange} tange 4



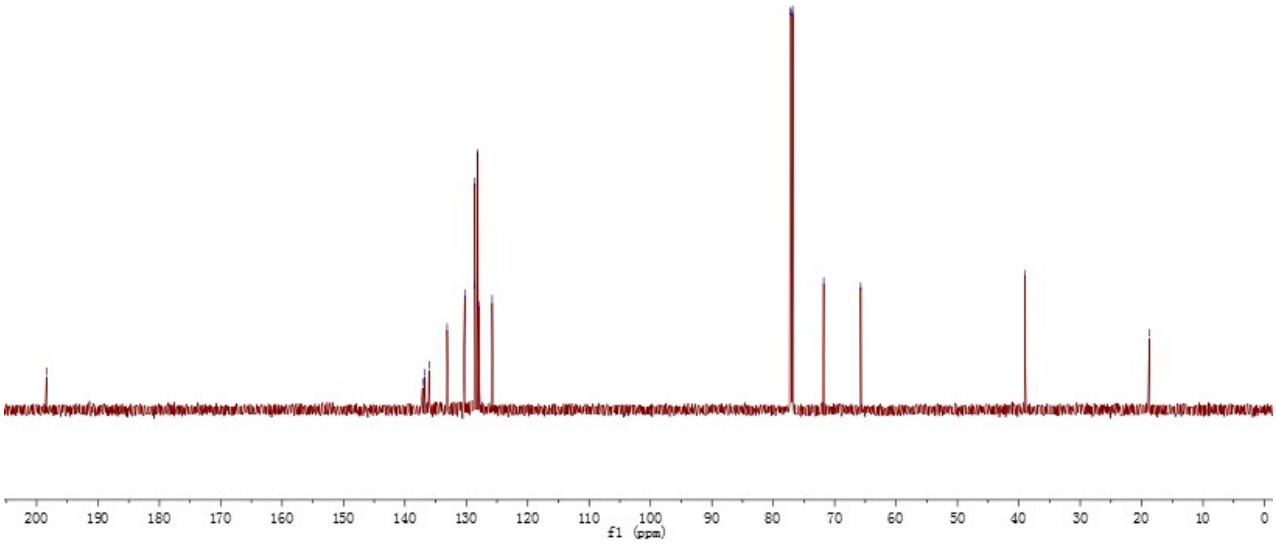
4y'

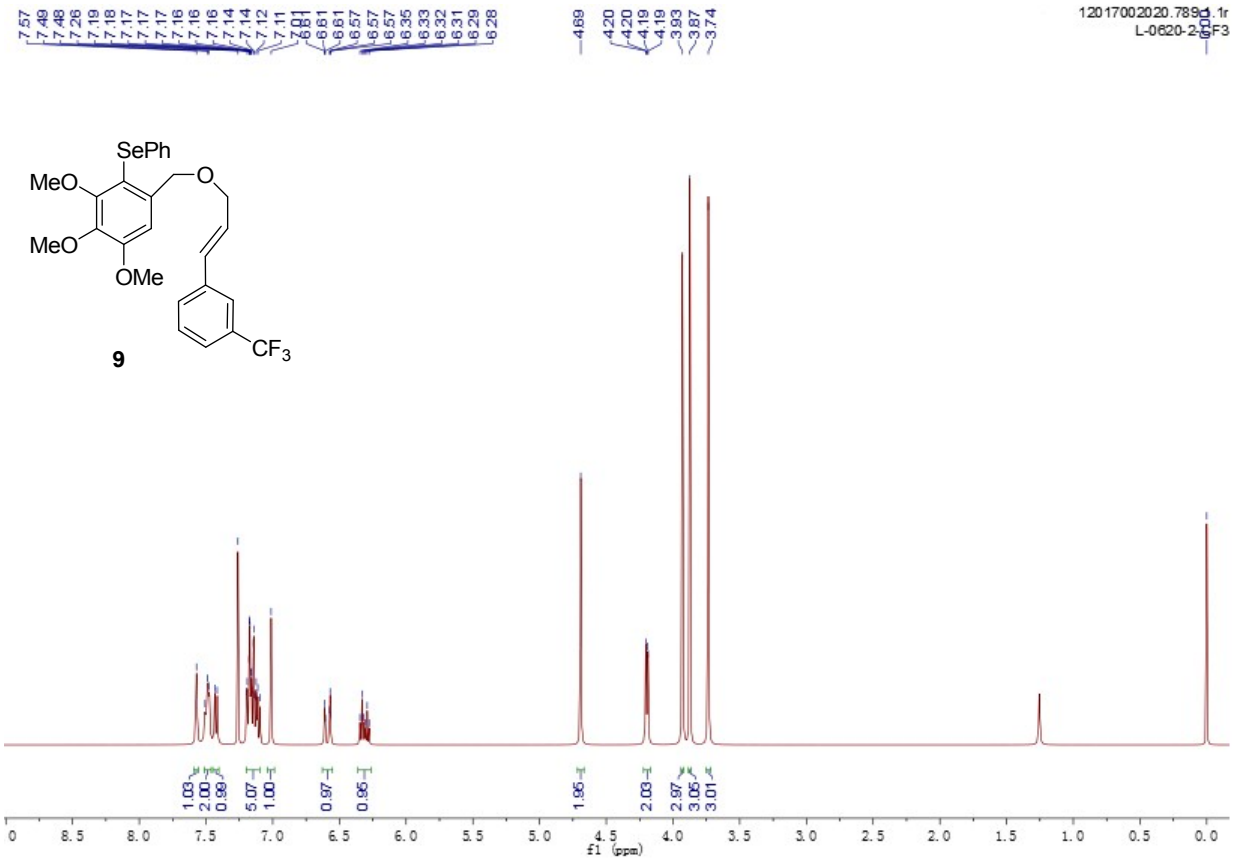


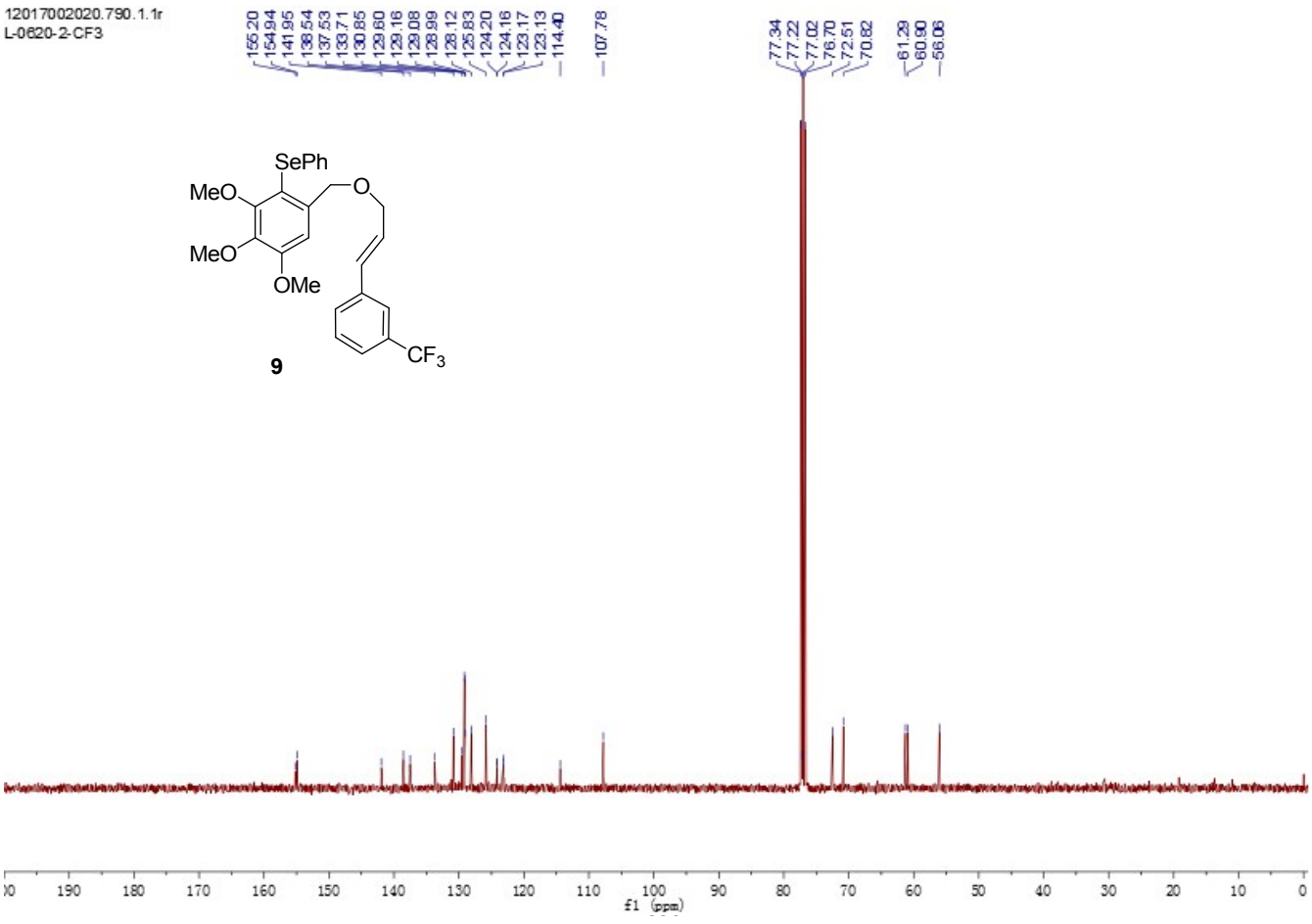
Sep05-2019-tange.30.1.1r
YUNNAN UNIVERSITY ASCEND AVIIIHD600 L-0904-3
C13CPD CDCl3 {D:\tange} tange 15



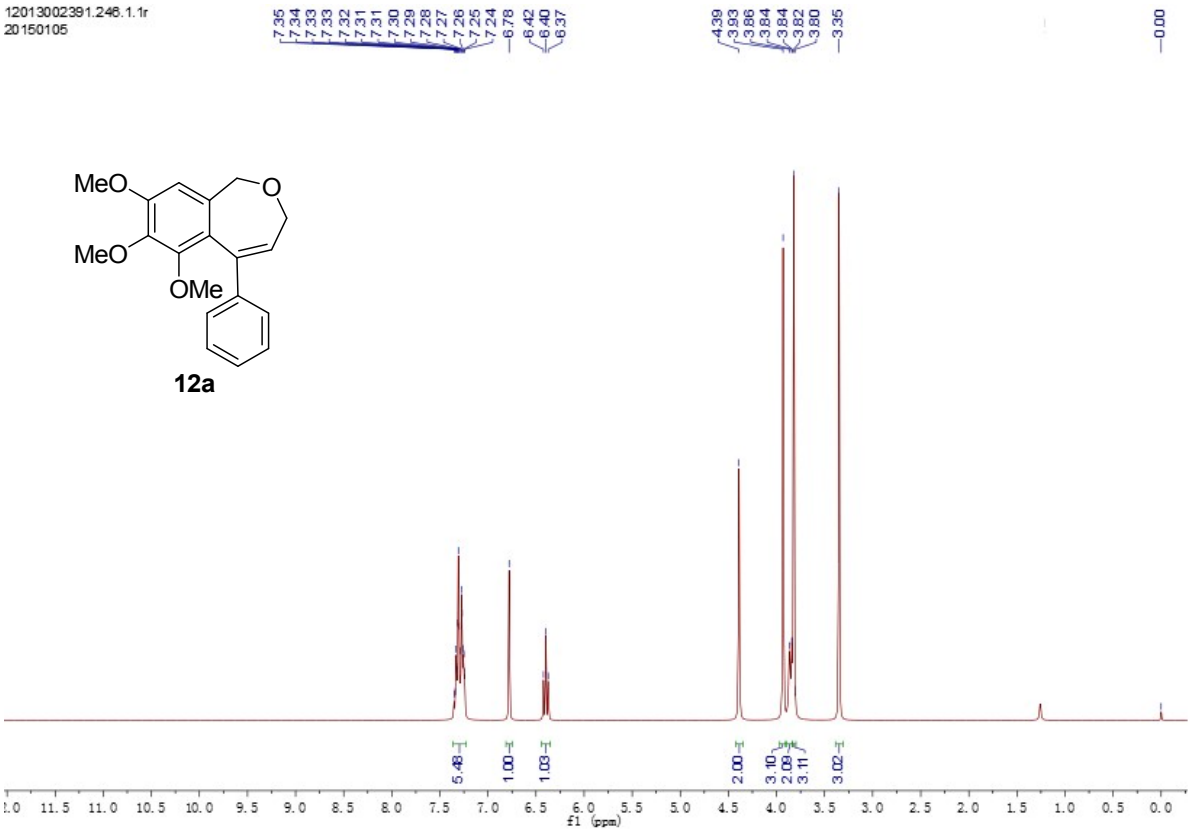
4y'




7.57
7.49
7.48
7.26
7.19
7.18
7.17
7.17
7.17
7.16
7.16
7.16
7.14
7.14
7.12
7.11
7.01
6.61
6.61
6.57
6.57
6.57
6.35
6.33
6.32
6.31
6.29
6.28
4.69
4.20
4.20
4.19
4.19
3.93
3.87
3.74
12017002020.789.1.1r
L-0620-2-CF3
SePh
MeO
MeO
OMe
O
CF3
9
1.03
2.00
0.99
5.07
1.00
0.97
0.95
1.95
2.03
2.97
3.06
3.01
f1 (ppm)

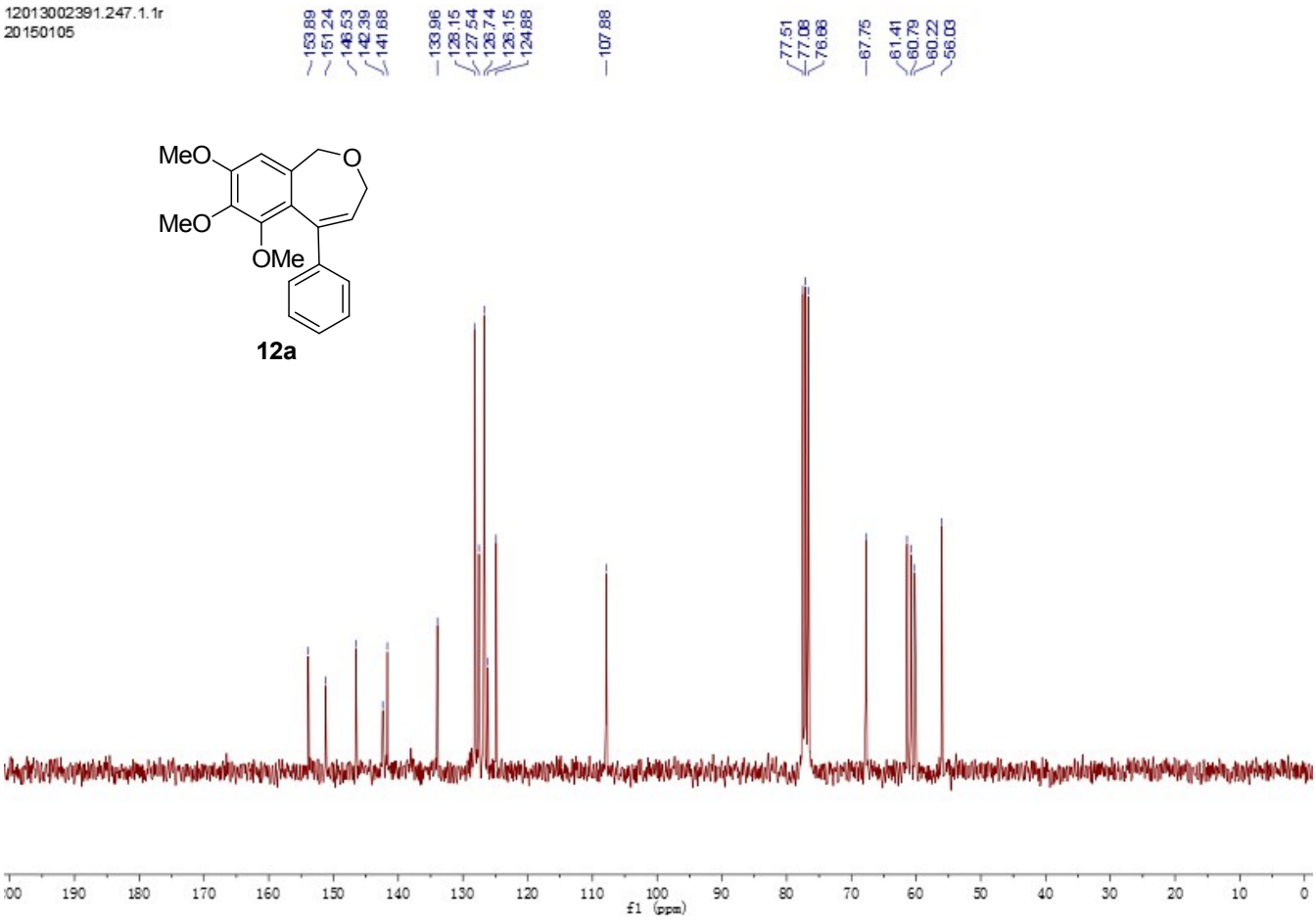

12017002020.790.1.1r
L-0620-2-CF3
155.20
154.94
141.95
138.54
137.53
133.71
130.85
129.60
129.16
129.08
128.99
128.12
125.83
124.20
124.16
123.17
123.13
114.40
107.78
77.34
77.22
77.02
76.70
72.51
70.82
61.29
60.90
56.06
SePh
MeO
MeO
OMe
O
CF3
9
f1 (ppm)

12013002391.246.1.1r
20150105



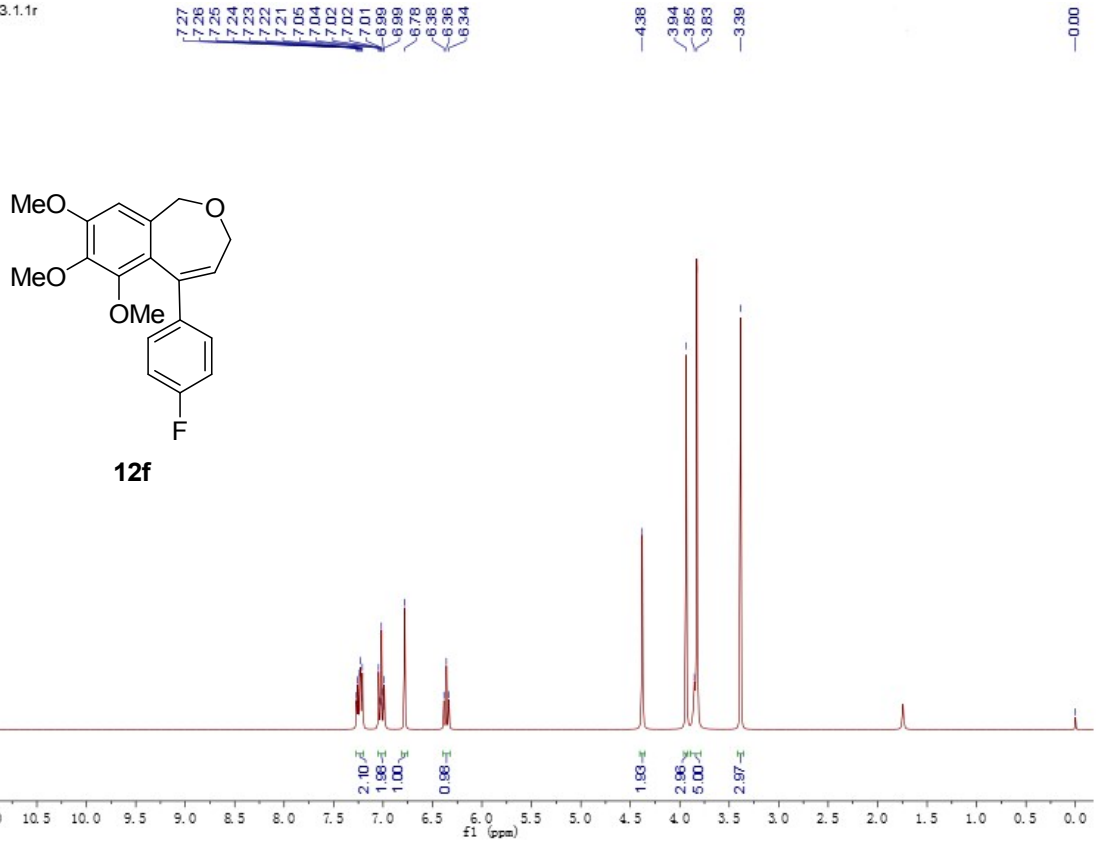
12a

12013002391.247.1.1r
20150105



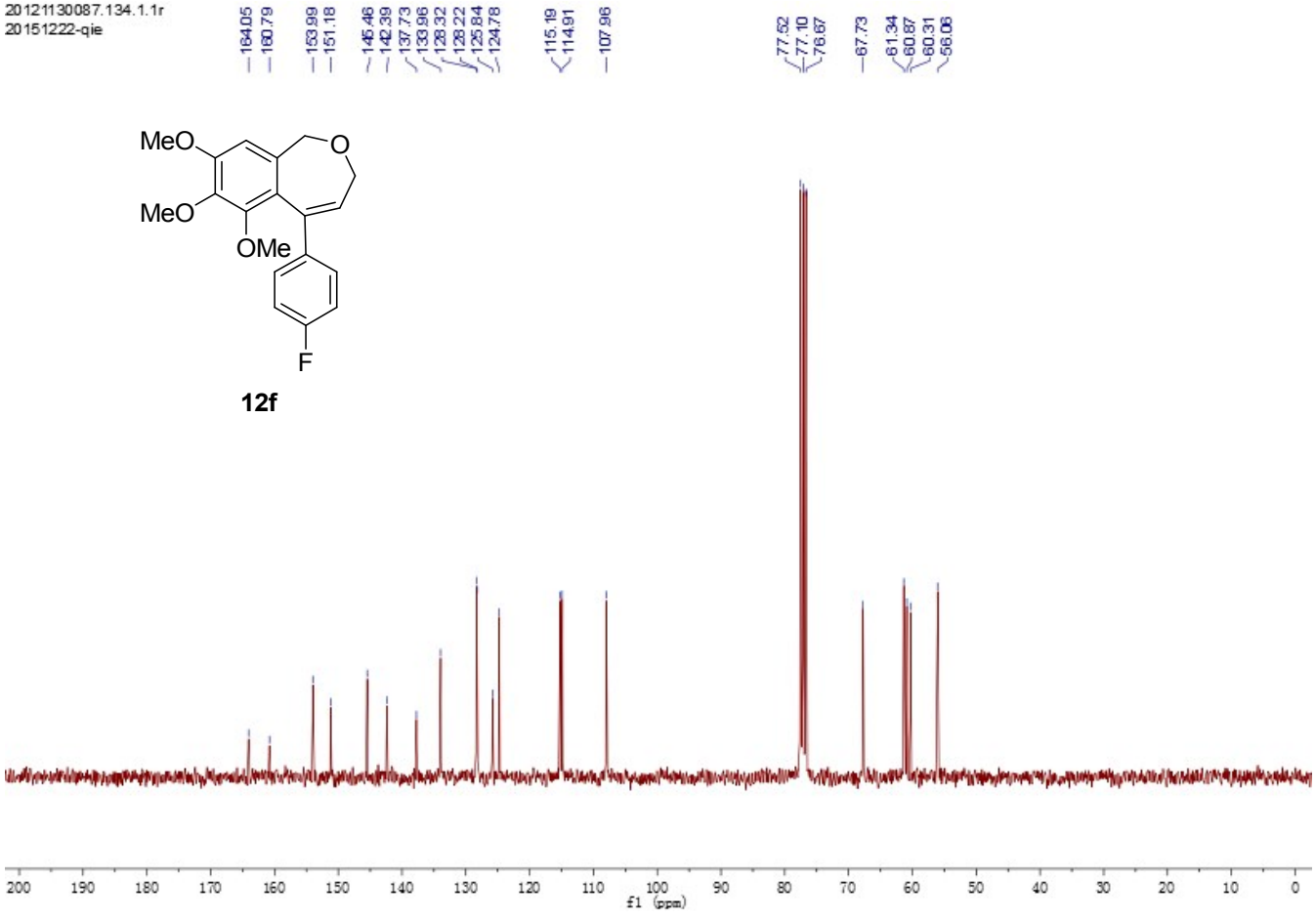
12a

20121130087.133.1.1r
20151222-qie



12f

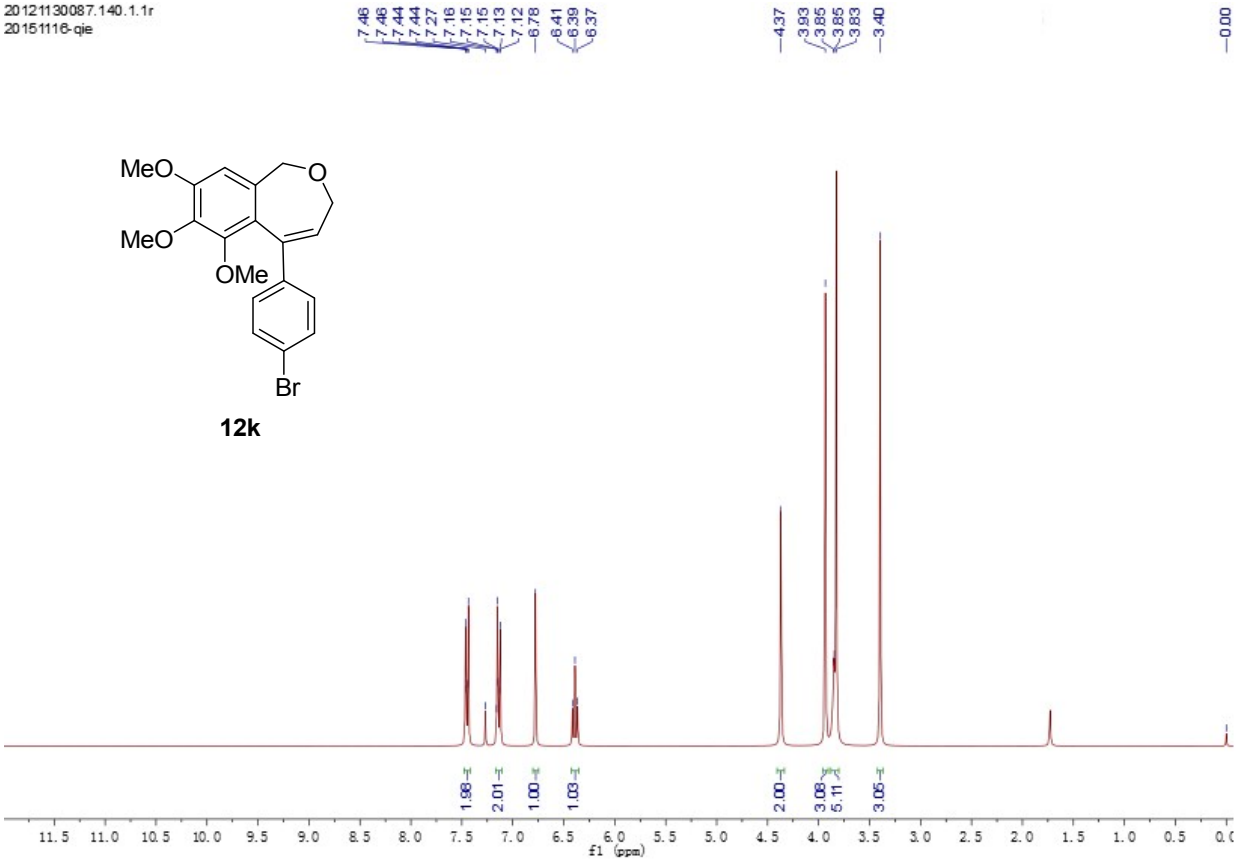
20121130087.134.1.1r
20151222-qie



12f

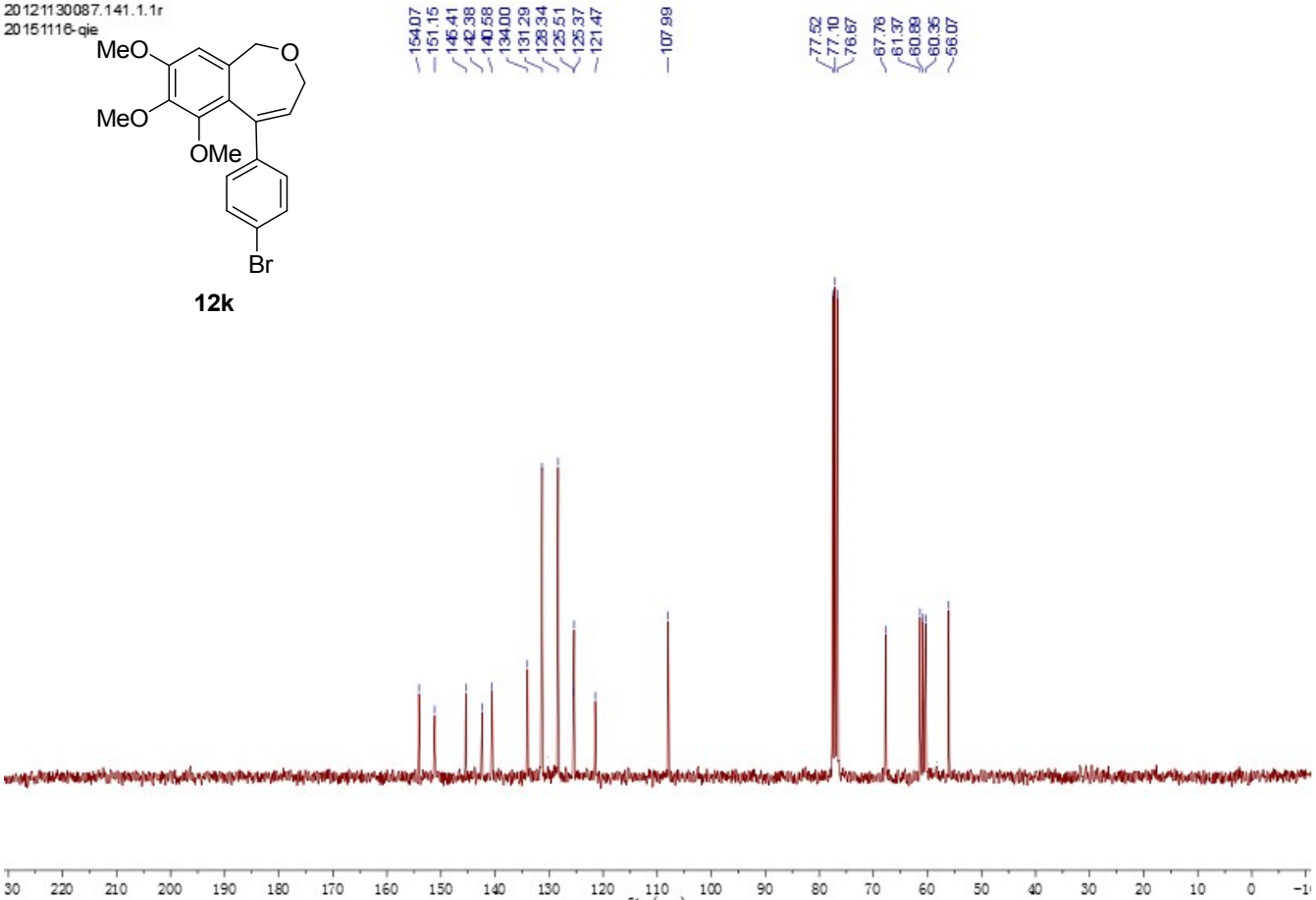
20121130087.140.1.1r
20151116-qie

12k

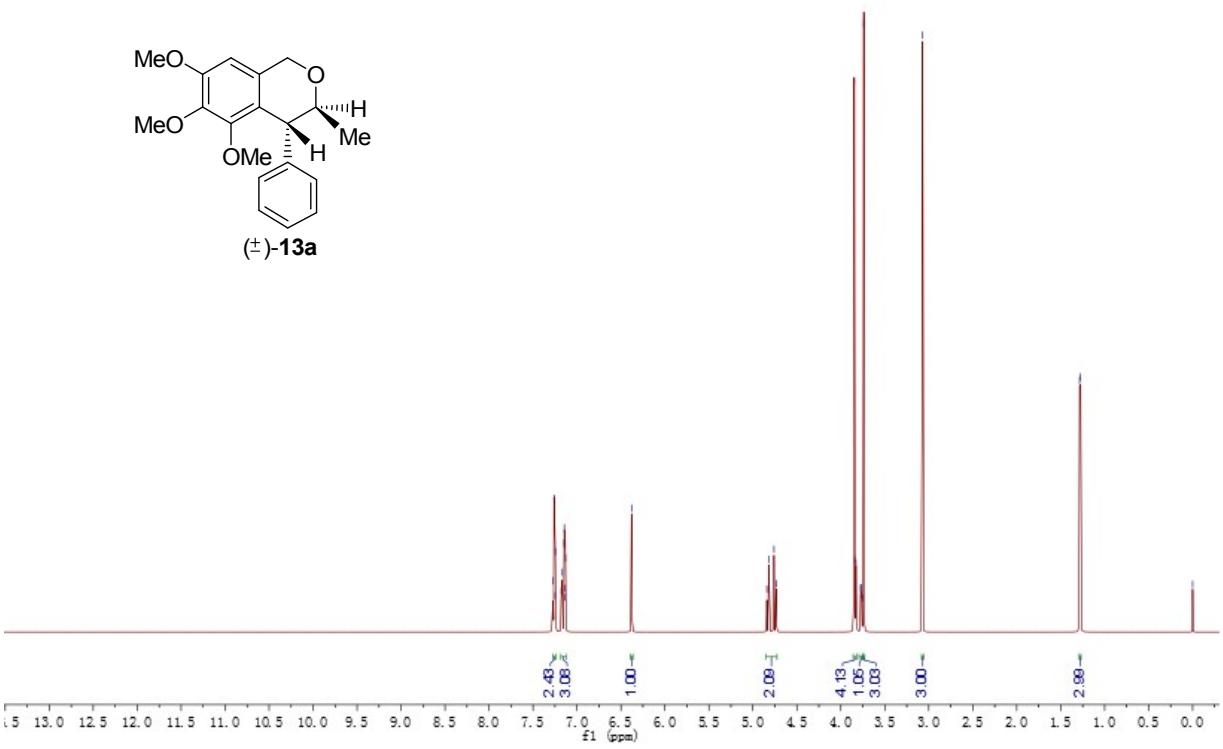


20121130087.141.1.1r
20151116-qie

12k



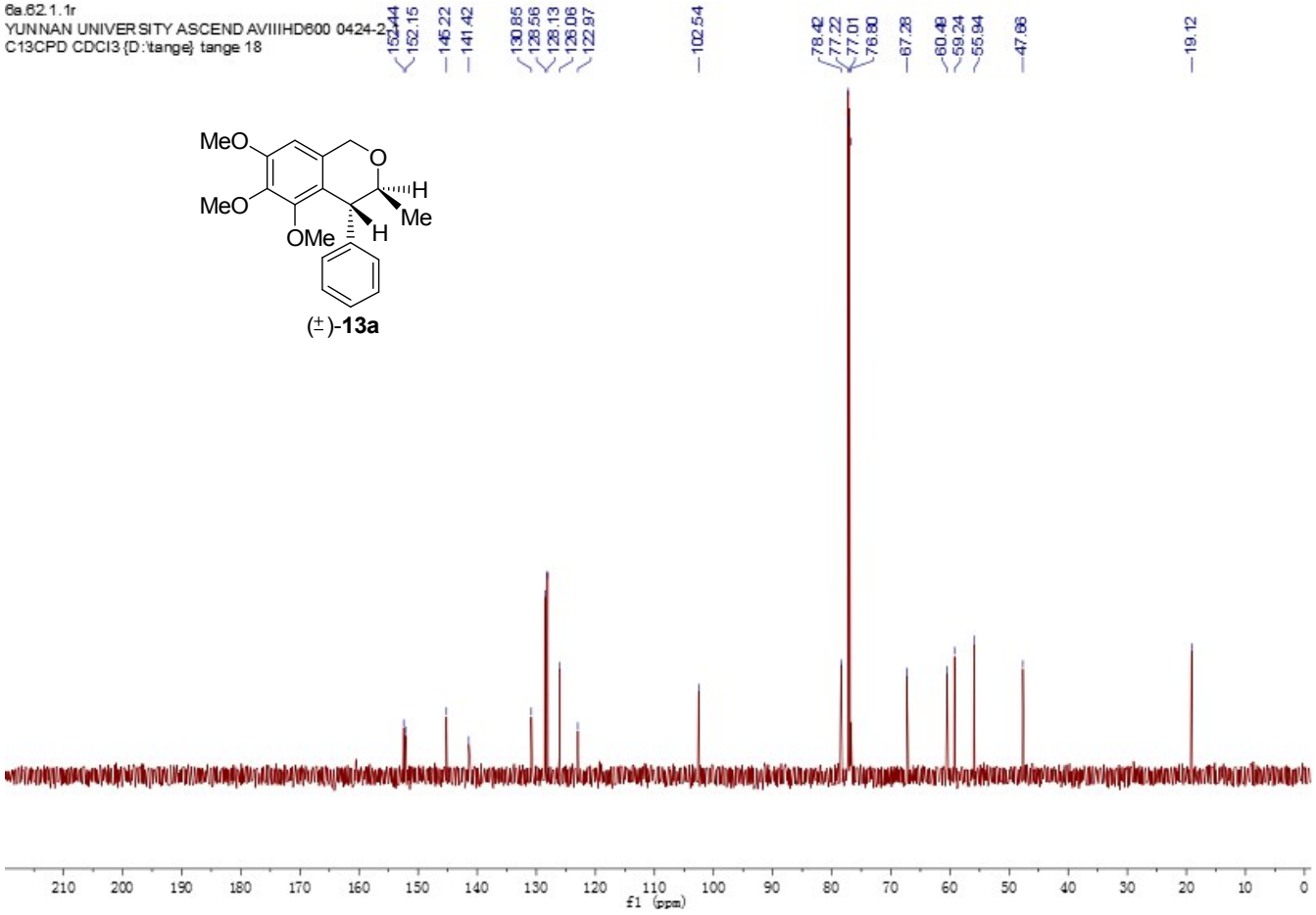
6a.61.1.1r
YUNNAN UNIVERSITY ASCEND AVIIIHD600 0424-2-1
PROTON CDCI3 {D:\tange} tange 18



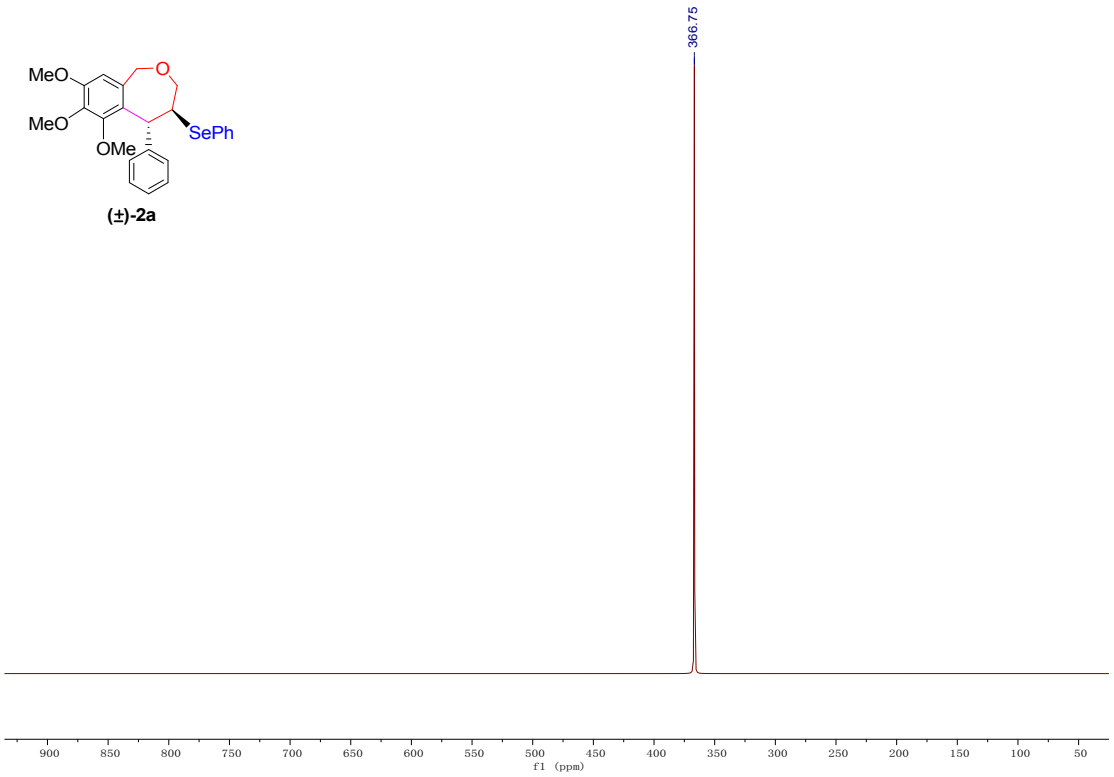
(±)-**13a**

6a.62.1.1r
YUNNAN UNIVERSITY ASCEND AVIIIHD600 0424-2
C13CPD CDCI3 {D:\tange} tange 18

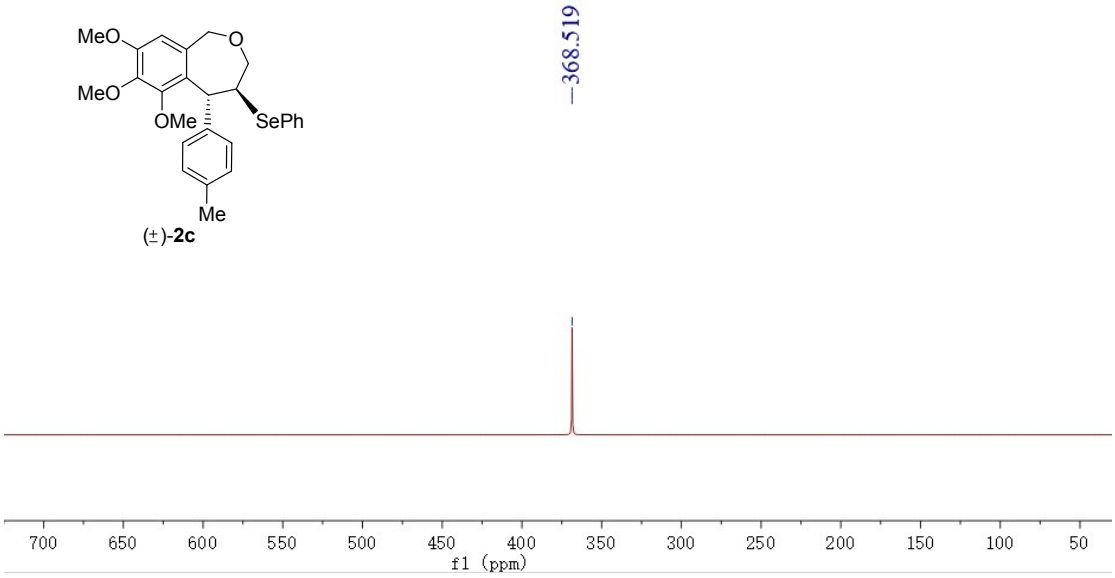
(±)-**13a**



8. Copies of ^{77}Se NMR Spectra for compounds (±)-2a, (±)-2c, (±)-2g, (±)-2h, (±)-2l, (±)-2n, and (±)-3a



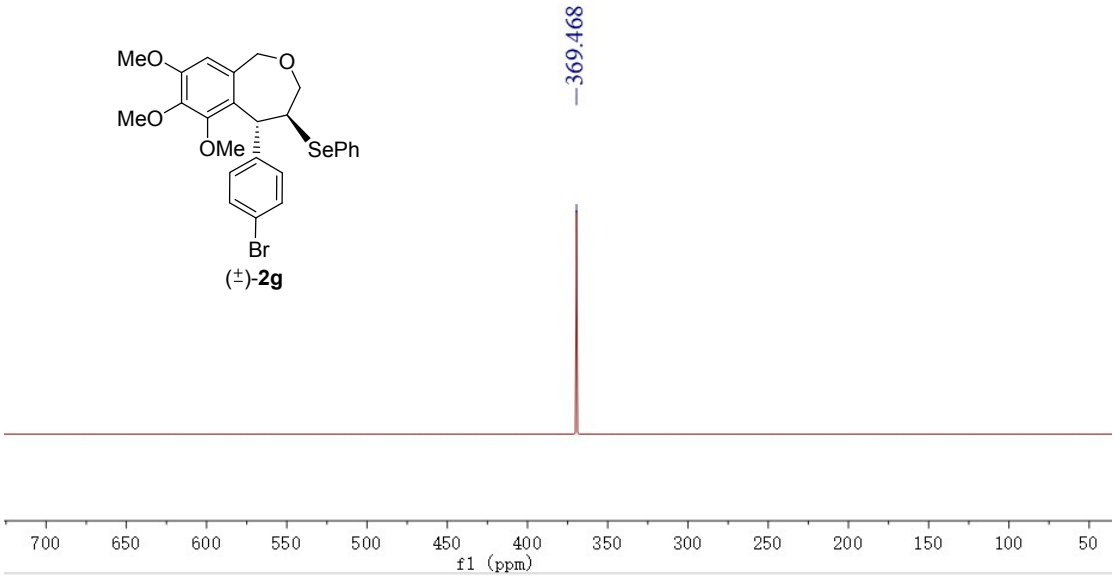
(±)-2a



(±)-2c

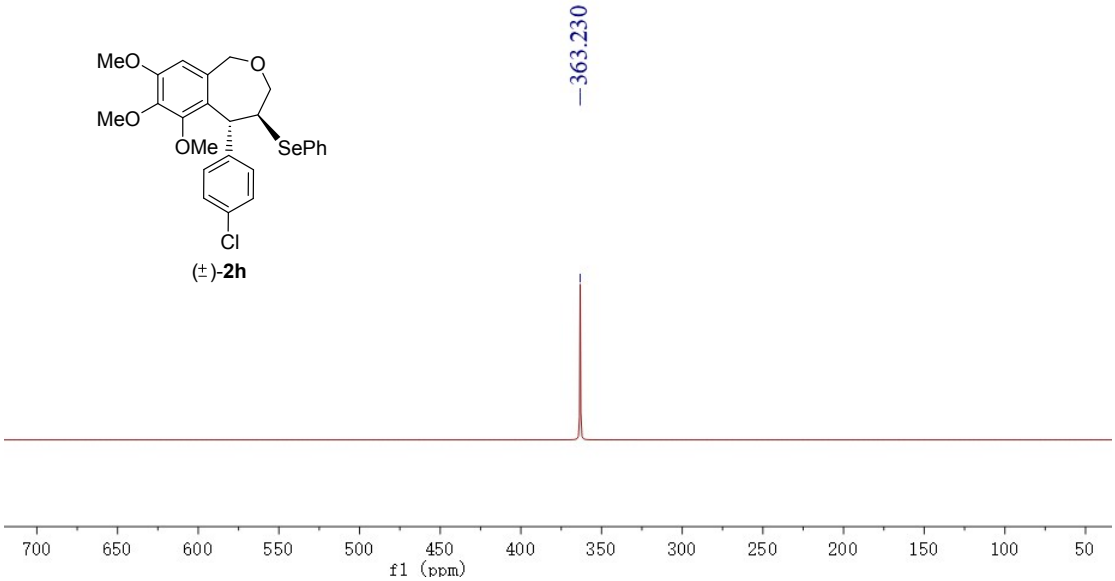
MeO
MeO
OMe
O
SePh
Br

(±)-**2g**


369.468
700
650
600
550
500
450
400
350
300
250
200
150
100
50
f1 (ppm)

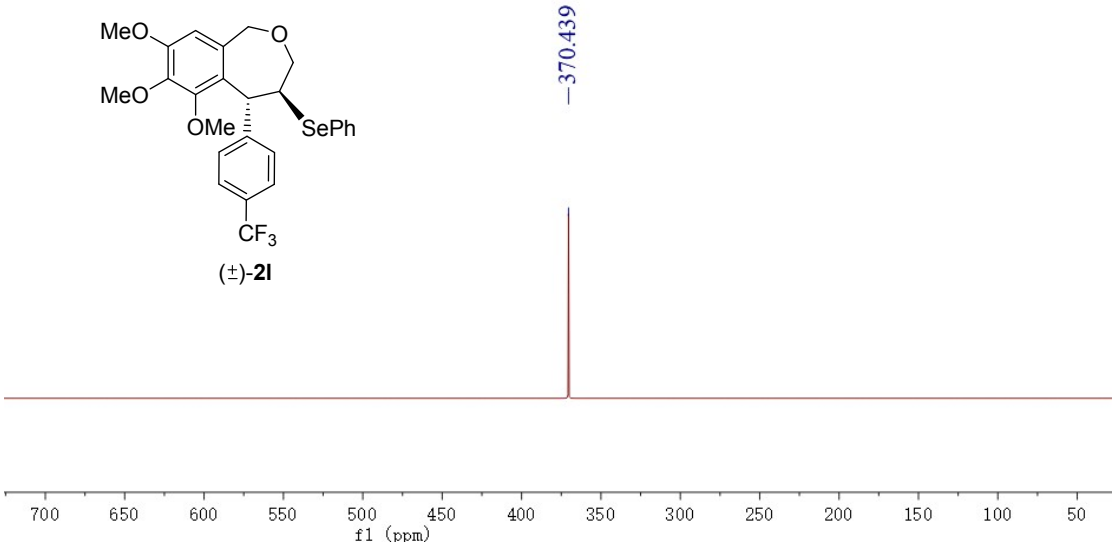
MeO
MeO
OMe
O
SePh
Cl

(±)-**2h**


363.230
700
650
600
550
500
450
400
350
300
250
200
150
100
50
f1 (ppm)

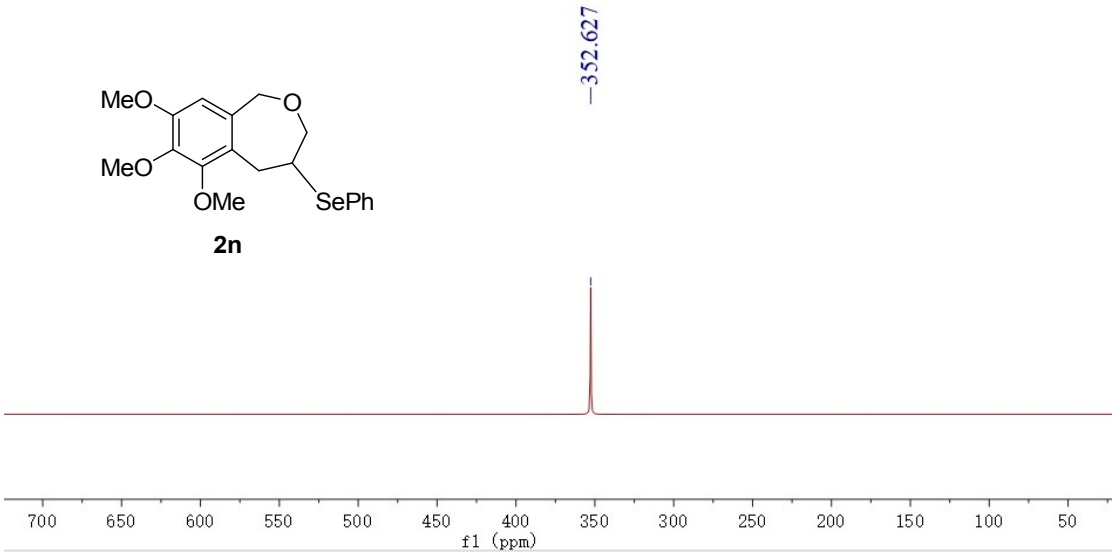
MeO
MeO
OMe
O
SePh
CF3

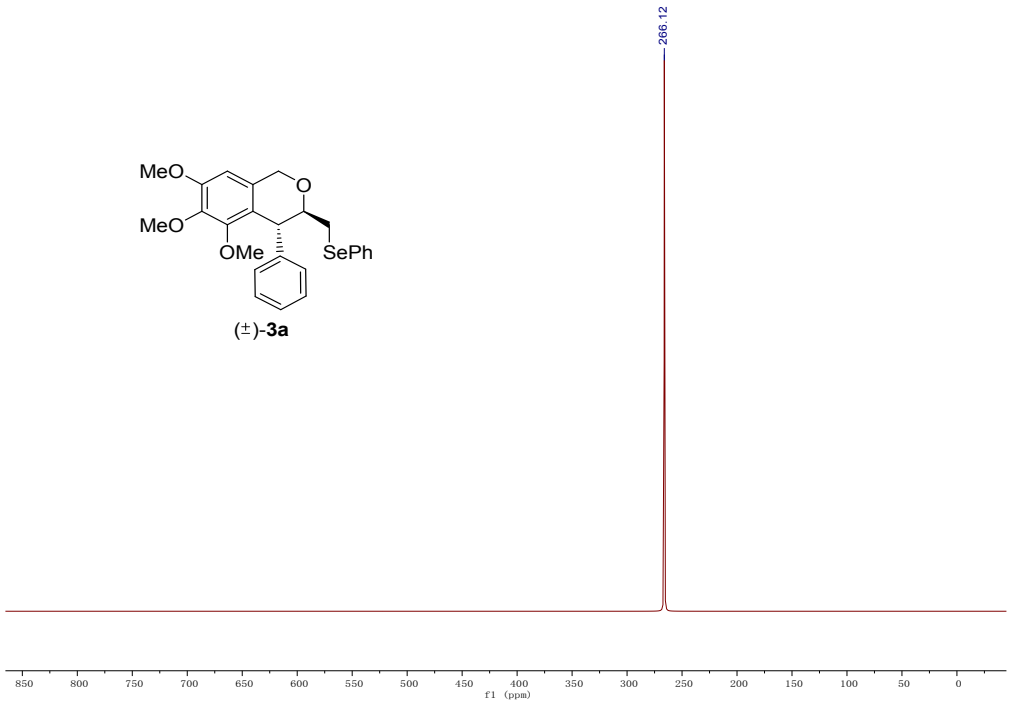
(±)-**2l**


-370.439
700
650
600
550
500
450
400
350
300
250
200
150
100
50
f1 (ppm)

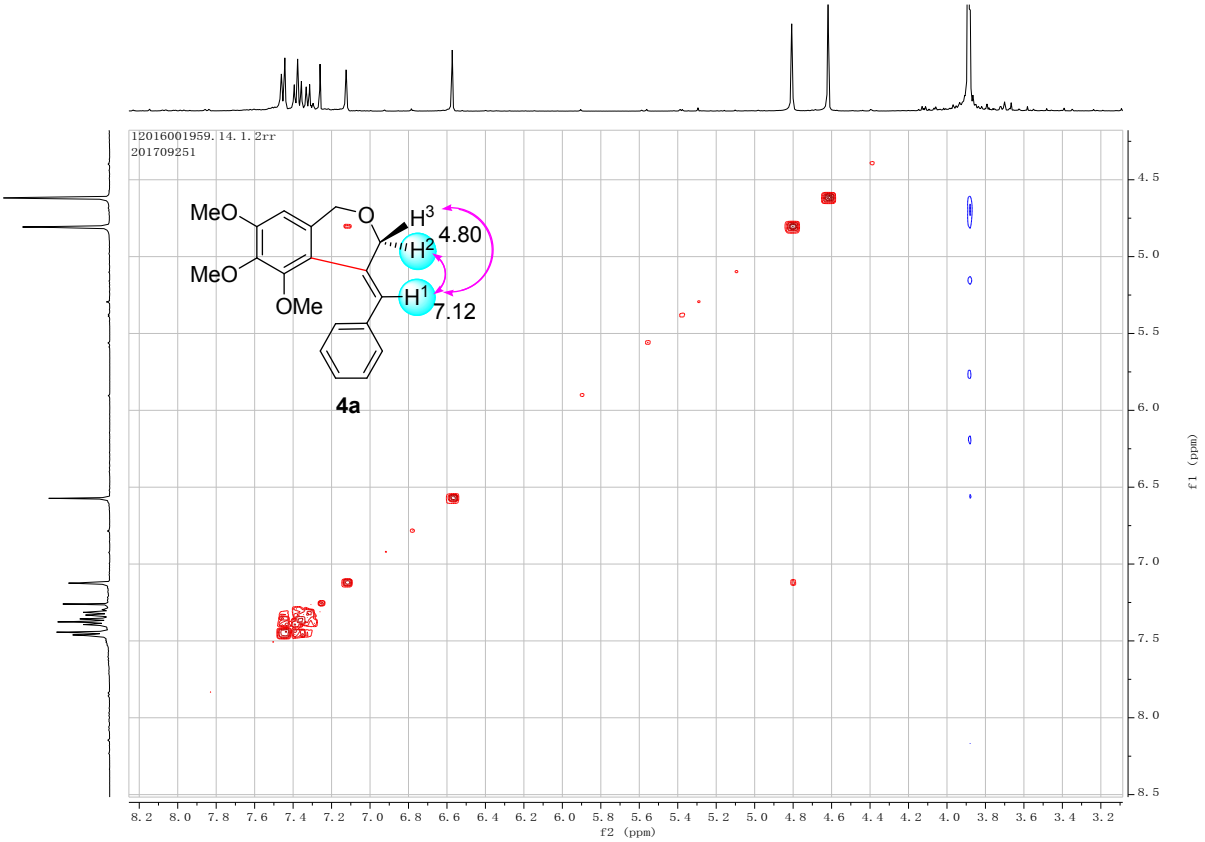
MeO
MeO
OMe
O
SePh

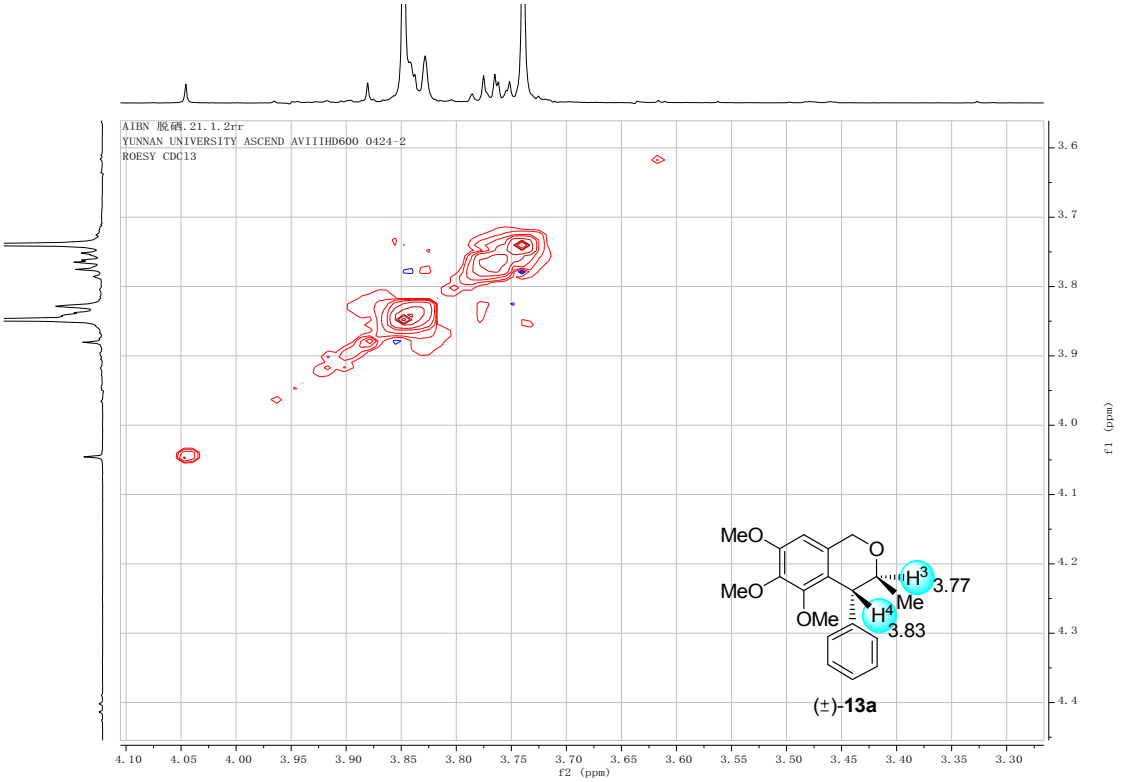
2n


-352.627
700
650
600
550
500
450
400
350
300
250
200
150
100
50
f1 (ppm)



9. Copies of ROESY Spectra for compounds 4a and (±)-13a.




AIBN 脱硒.21.1.2rr
YUNNAN UNIVERSITY ASCEND AVIIIHD600 0424-2
ROESY CDCl3
f2 (ppm)
f1 (ppm)
MeO
MeO
OMe
O
H3
3.77
Me
H4
3.83
(±)-13a