Synthesis of aryl-fused 1,4-oxathiepines from pyridinium 1,4-zwitterionic thiolates and vinyliene *ortho*-quinone methides

Yixuan He,[ab†] Ping Wu,[c†] Xiang Zhang,[d†] Taimin Wang*[b] Qingqing Tao,[b] Kang Zhou,[b] Zijun Ouyang,[b] Hongbin Zhai,[be] Dao-Juan Cheng,*[d] and Bin Cheng,*[ab]

[a.] *State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China*

[b.] *Institute of Marine Biomedicine, Shenzhen Polytechnic, Shenzhen 518055, China; e-mail: chengbin@szpt.edu.cn, wangtm@szpt.edu.cn*

[c.] *Key Laboratory of Coordination Chemistry and Functional Materials in Universities of Shandong, Dezhou College, Dezhou 253023, China*

[d.] *School of Pharmacy, Anhui University of Chinese Medicine, Hefei 230012, China; chengdj614@ahtcm.edu.cn*

[e.] *State Key Laboratory of Chemical Oncogenomics, Shenzhen Engineering Laboratory of Nano Drug Slow-Release, Peking University Shenzhen Graduate School, Shenzhen 518055, China*

[†] *These authors contributed equally to this work*

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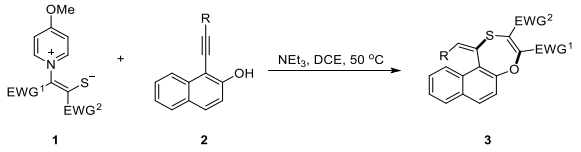
1. General Information

All isolated compounds were characterized on JEOL 400 MHz spectrometer in $(CD_3)_2CO$ and $CDCl_3$. Chemical shifts were reported as δ values relative to internal chloroform (δ 7.26 for ^{1}H NMR and 77.16 for ^{13}C NMR) and $(CH_3)_2CO$ (δ 2.05 for ^{1}H NMR and δ 29.84 for ^{13}C NMR). ^{19}F NMR chemical shifts were determined as δ values relative to external standard $PhCF_3$ at −63.0. High-resolution mass spectra (HRMS) were recorded on a 4G mass spectrometer using electrospray ionization (ESI) analyzed by a quadrupole time-of-flight (QTof) instrument. All melting points were measured with the samples after column chromatography and uncorrected. Column chromatography was performed on silica gel. All solvents and reagents were used as obtained from commercial sources without further purification. High pressure liquid chromatography (HPLC) analyses were performed on a waters 1525 instrument equipped with an isostatic pump, using a chiral stationary phase column (Daicel Co. CHIRALPAK). The chiral HPLC methods were calibrated with the corresponding racemic mixtures. α-Alkynyl naphthalen-2-ols are all known and prepared according to the literature.[1] (2-(Bromomethyl)phenoxy)(*tert*-butyl)dimethylsilane **6a** is known and prepared according to the literature.[2] 2-Alkynylphenols were prepared according to the literature.[3,4,5] **4a**, **4f**, **4g**, and **4h** are known.

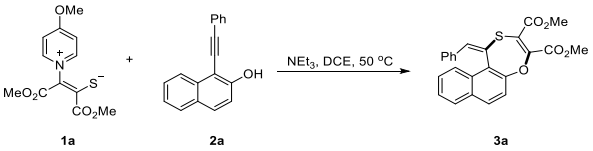
2. Experimental Procedure

(1) General procedure for the synthesis of naphthalene-fused 1,4-oxathiepines 3a−3r



To a solution of α-alkynyl naphthalen-2-ol **2** (0.1 mmol, 1.0 equiv) in DCE (2 mL) were added 1,4-zwitterionic thiolate (1.05 equiv) and NEt_3 (1.05 equiv), and then the mixture was stirred at 50 ℃. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography (eluent: 2% EtOAc in petroleum ether for **3g** and 10% for other products) to afford the corresponding naphthalene-fused 1,4-oxathiepines **3a−3r**.

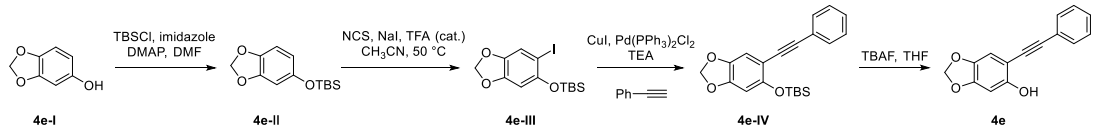
(2) Scale-up experiment of 3a



To a solution of 1-(phenylethynyl)naphthalen-2-ol (**2a**, 1.0 g, 4.1 mmol, 1.0 equiv) in DCE (40 mL) were added 1,4-zwitterionic thiolate **1a** (1.2 g, 4.3 mmol, 1.05 equiv) and NEt_3 (0.60 mL, 4.3 mmol, 1.05 equiv), and then the mixture was stirred at 50 ℃. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography (eluent: 10% EtOAc in petroleum ether) to afford **3a** (1.68 g, yield = 98%)

as a yellow oil.

(3) Procedure for the synthesis of 2-alkynylphenol 4e



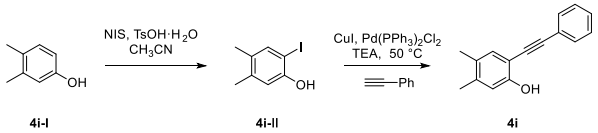
To a solution of sesamol (1.38 g, 10.0 mmol) in DMF (20 mL) was added imidazole (680 mg, 1.0 equiv), DMAP (12 mg, 0.01 equiv), and TBSCl (1.81 g, 1.2 equiv), and then the mixture was stirred for 1 h. After the consumption of sesamol monitored by TLC, the solution was quenched by icy water, extracted three times with petroleum ether. The combined organic layers were concentrated under reduced pressure to give crude TBS-protected sesamol.

To a solution of silane (**4e–II**) in CH_3CN (20 mL) was added NaI (1.68 g, 1.12 equiv), NCS (1.55 g, 1.16 equiv) and TFA (cat.), and then the mixture was stirred at 50 ℃ in the dark. After the consumption of the silane monitored by TLC, the solution was quenched with aqueous sodium thiosulfate and extracted three times with ethyl acetate. Removal of the solvent gave an oil, which was purified by chromatography (eluent: petroleum ether) to give an iodinated silyl ether (**4e–III**).

To a solution of above-mentioned iodinated silyl ether in TEA (10 mL) was added ethynylbenzene (1.2 g, 1.2 equiv), CuI (95 mg, 0.05 equiv), and $Pd(PPh_3)_2Cl_2$ (70 mg, 0.01 equiv). The mixture was degassed and refilled with nitrogen, and then it was stirred at 50 ℃ overnight. After the coupling reaction was finished, removal of the solvent gave a residue, which was purified directly by silica gel column chromatography (eluent: petroleum ether) to give 2-alkynylphenol **4e–IV** (1.51 g, yield = 43% for 3 steps) as a brown solid.

To a solution of 2-alkynylphenol **4e–IV** (352 mg, 1 mmol) in THF (10 mL) was added TBAF $3H_2O$ (473 mg, 1.5 equiv) at 0 ℃ directly and stirred for 30 mins. Then, the solution was quenched with icy water and extracted with ethyl acetate three times. Removal of the solvent gave a residue, which was purified by chromatography (eluent: 5% ethyl acetate in petroleum ether) to give 2-alkynylphenol **4e** as a white solid (233 mg, yield = 98%).

(4) Procedure for the synthesis of 2-alkynylphenol 4i

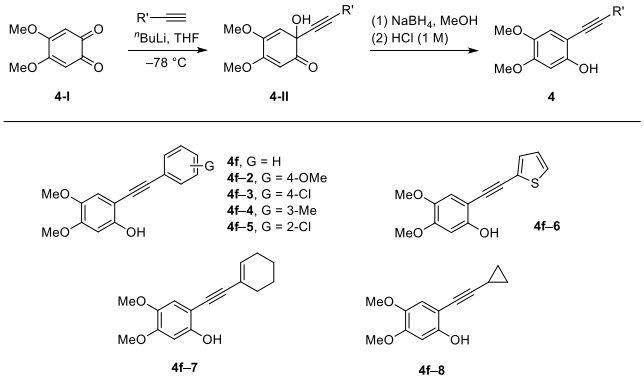


To a solution of 3,4-dimethylphenol (1.22 g, 10.0 mmol) and *p*-toluenesulfonic acid monohydrate (2.00 g, 1.05 equiv) in CH_3CN (100 mL) was slowly added NIS (2.36 g, 1.05 equiv), and then the mixture was stirred for 0.5 h. After the consumption of 3,4-dimethylphenol monitored by TLC, the

solution was quenched by saturated sodium thiosulfate aqueous solution, extracted three times with ethyl acetate. The combined organic layers were concentrated under reduced pressure to give 2-iodo-4,5-dimethylphenol.

To a solution of 2-iodo-4,5-dimethylphenol obtained aforementioned in TEA (10 mL) was added ethynylbenzene (2.04 g, 2.0 equiv), CuI (95 mg, 0.05 equiv), and $Pd(PPh_3)_2Cl_2$ (70 mg, 0.01 equiv). The mixture was degassed and refilled with nitrogen, and then it was stirred at 50 ℃ overnight. After the coupling reaction was finished, removal of the solvent gave a residue, which was purified directly by silica gel column chromatography (eluent: 5% ethyl acetate in petroleum ether) to give 4,5-dimethyl-2-(phenylethynyl)phenol **4i** (1.62 g, yield = 73% for 2 steps) as a white solid.

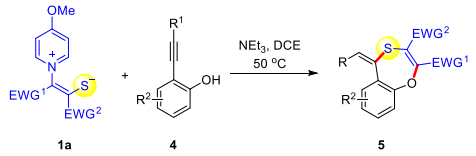
(5) Procedure for the synthesis of 2-alkynylphenols (4f, 4f–2, 4f–3, 4f–4, 4f–5, 4f–6, 4f–7, and 4f–8)



To a solution of ethynylbenzene (245 mg, 2.4 mmol) in THF (20 mL) at –78 ℃ was added *n*-butyllithium (1.6 M in hexane, 1.44 mL) and then the solution was stirred for 20 min. To a solution of 4,5-dimethoxycyclohexa-3,5-diene-1,2-dione (336 mg, 2.0 mmol) in THF (130 mL) at –78 ℃ was added the above-mentioned solution dropwise. The stirring was continued at –78 ℃ for 1 h and the reaction was quenched with saturated aqueous ammonium chloride. The organic layer was removed in vacuum and the aqueous layer was extracted with dichloromethane. The organic layers were combined, dried, and concentrated. The residual oil was dissolved in methanol (50 mL) and sodium borohydride (151 mg, 4 mmol) was added slowly at 0 ℃. After l h, HCl (1 M) was added to quenched the reduction reaction and most of the methanol was removed under reduced pressure. The aqueous solution was extracted with dichloromethane and the organic layers were combined and dried with Na_2SO_4. Removal of the solvent gave an oil, which was purified by chromatography (eluent: 10% to 20% ethyl acetate in petroleum ether) to give **4f** (270 mg, yield = 53% for 2 steps) as a brown solid.

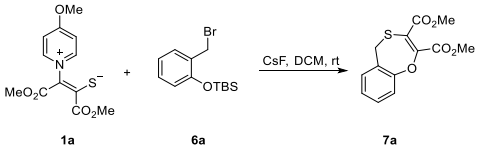
The other 2-alkynylphenols were prepared followed the same procedure with 4,5-dimethoxycyclohexa-3,5-diene-1,2-dione (336 mg, 2.0 mmol).

(6) General procedure for the synthesis of benzene-fused 1,4-oxathiepines 5b−5l



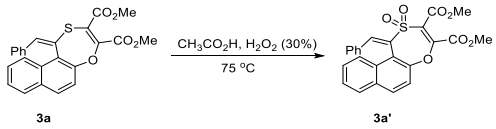
To a solution of 2-alkynylphenol **4** (0.2 mmol, 1.0 equiv) in DCE (2 mL) were added 1,4-zwitterionic thiolate (1.20 equiv) and NEt_3 (1.20 equiv), and then the mixture was stirred at 50 ℃. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography (eluent: 10% to 20% ethyl acetate in petroleum ether) to afford the corresponding 1,4-oxathiepines **5b−5l**.

(7) Synthesis of 7a



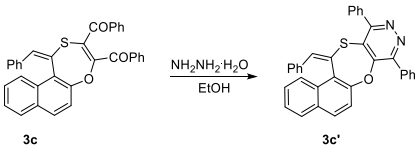
To a solution of (2-(bromomethyl)phenoxy)(*tert*-butyl)dimethylsilane (**6a**, 90 mg, 0.30 mmol, 1.0 equiv) in DCM (2 mL) was added 1,4-zwitterionic thiolate **1a** (102 mg, 0.360 mmol, 1.2 equiv) and CsF (68 mg, 0.45 mmol, 1.5 equiv), and then the mixture was stirred at room temperature. After completion of the annulation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography (eluent: 10% EtOAc in petroleum ether) to afford **7a** (43 mg, yield = 51%) as a pale red oil.

(8) Synthesis of 3a'



To a solution of naphthalene-fused 1,4-oxathiepines **3a** (84 mg, 0.20 mmol, 1.0 equiv) in CH_3CO_2H (2 mL) was added H_2O_2 (30%, 91 mg, 0.80 mmol, 4 equiv), and then the mixture was stirred at 75 ℃. After completion of the oxidation reaction as monitored by TLC, the reaction mixture was diluted with DCM and quenched with cold aqueous Na_2CO_3 solution. To the mixture saturated aqueous sodium thiosulfate solution was added and then it was extracted with DCM. The combined organic layers were dried with Na_2SO_4, filtered, and evaporated, and the resulting residue was purified by silica gel column chromatography (eluent: 20–50% EtOAc in petroleum ether) to afford **3a'** (81 mg, yield = 90%) as a colorless oil.

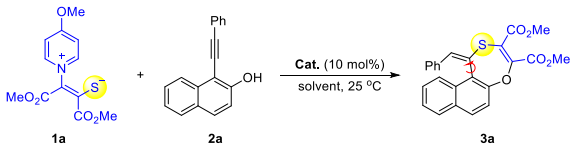
(9) Synthesis of 3c'



3c 3c'

To a solution of naphthalene-fused 1,4-oxathiepines **3c** (102 mg, 0.200 mmol, 1.0 equiv) in EtOH (2 mL) was added $NH_2NH_2{\cdot}H_2O$ (80%, 31 mg, 0.50 mmol, 2.5 equiv), and then the mixture was stirred at reflux. After completion of the condensation reaction as monitored by TLC, the solvent was evaporated and the resulting residue was purified directly by silica gel column chromatography (eluent: 10% EtOAc in petroleum ether) to afford **3c'** (82 mg, yield = 81%) as a white solid.

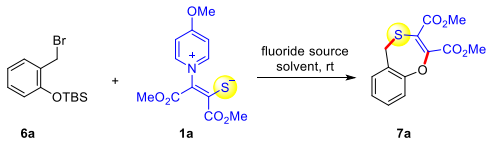
(10) General Procedure for the Organocatalytic Asymmetric (3 + 4) Reaction



1a 2a 3a

To a tube equipped with a magnetic stirring bar were added catalyst **Cat.** (0.005 mmol), pyridinium 1,4-zwitterionic thiolate **1a** (17.0 mg, 0.060 mmol, 1.2 equiv), 1-(phenylethynyl)naphthalen-2-ol **2a** (12.2 mg, 0.050 mmol) and solvent (0.5 mL) successively. The resulting mixture was stirred at 25 ℃ for 2-4 d, and directly charged onto silica gel. Products **3a** were isolated using petroleum ether/ethyl acetate (10:1) as eluent.

3. Table S1 Optimization of the Reaction Conditions for the Formation of **7a**.[a]

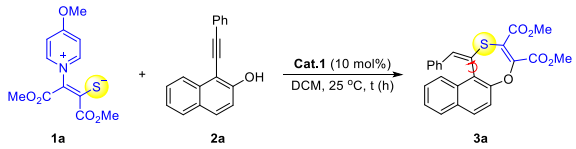


Entry	**6a**:**1a**	Solvent	Fluoride source	Isolated Yield (%)	NMR Yield (%)[b]
1	1:1.2	THF	CsF/18-C-6		trace
2	1:1.2	DCM	CsF/18-C-6	52%	
3	1:1.2	DCM	KF/18-C-6	27%	
4	1:1.2	DCM	KF	50%	
5	1:1.2	DCM	CsF	51%	55%
6	1:1.2	DCM	TBAF		trace
7	1:1.2	MeCN	KF		26%
8	1:1.2	Acetone	KF		25%
9	1:1.2	DCE	KF		21%
10	1:1.2	MeCN	CsF		33%
11	1:1.2	Acetone	CsF		31%
12	1:1.2	DCE	CsF		30%
13	1:1.2	$CHCl_3$	CsF		49%
14	1:1.5	DCM	CsF		47%
15	1.2:1	DCM	CsF		42%
16	1:1	DCM	CsF		34%

[a] Reaction conditions: **6a** (0.3 mmol), **1a**, and fluoride source in solvent (2 mL) in air.

[b] The yield was determined by ^{1}H-NMR spectra using 1,3,5-trimethoxybenzene as the internal standard.

4. Table S2 Optimization of the Catalytic Asymmetric Version of (3 + 4) Reaction between **1a** and **2a** with Bifunctional Organocatalysts.[a]



Entry	Solvent	Time (h)	Yield (%)	ee (%)
1	DCE	48	86	56
2	**DCM**	**48**	**82**	**67**
3	CH_3CN	72	71	39
4	1,4-dioxane	48	38	40
5	$CHCl_3$	48	81	63
6	acetone	48	48	41
7	CH_3OH	72	34	13
8	$PhCF_3$	48	32	15
9	CH_2Br_2	72	37	35
10	MTBE	48	trace	-
11	toluene	48	trace	-
12	MTBE:DCM=1:1	96	33	55

[a] All reactions were carried out with pyridinium 1,4-zwitterionic thiolate **1a** (17.0 mg, 0.060 mmol), 1-(phenylethynyl)naphthalen-2-ol **2a** (12.2 mg, 0.050 mmol), catalyst **Cat.1** (10 mol%) and solvent (0.5 mL) at 25 ℃ in a sealed tube for 2-4 d. Yields refer to isolated pure compound. The ee values were determined by chiral stationary phase HPLC analysis [Daicel Chiralpak OD-H, isopropanol/hexane (22:78), 1.0 mL/min, λ = 254 nm].

5. Investigation on the Racemization Barrier of 3a

The reaction was conducted at 1 mg/mL concentration in a sealed tube and heated at the specified temperature. The change in enantiomeric excess over time was determined by HPLC. The barrier to rotation for **3a** was obtained by kinetic of racemization of an enantiomer.

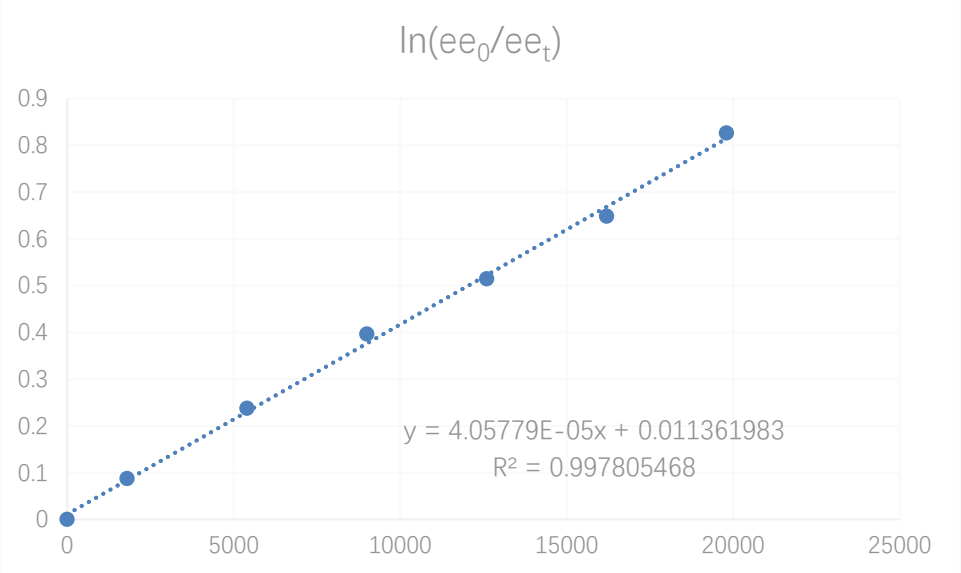
This data was plotted as ($In[ee_0/ee_t]$) versus time (seconds). The gradient of this graph gives the racemization constant ($k_{racemization} = 2 \times k_{enantiomerization}$) at the specified temperature. The barrier to rotation, $\Delta G^{\neq}_{enantiomerization}$, was calculated using the following Eyring equation, R = Gas constant = 8.3145 J K^{-1} mol^{-1}, h = Planck constant = 6.62608 x 10^{-34} J s, k_B = Boltzmann constant = 1.38066 x 10^{-23} J K^{-1}, and T_1 = temperature racemization study was conducted at, in Kelvin.

$$\Delta G^{\neq}_{enantiomerization} = RT_1 \ln \frac{k_B T_1}{h k_{enantiomerization}}$$

Racemization of **3a** in *i*-PrOH at 60 ℃

Table S3 Investigation on the racemization barrier of 3a

Time (seconds)	Enantiomeric Excess (ee)	First Order Racemization ($ln[ee_0/ee_t]$)
0	58.7	0.00000
1800	53.8	0.08717
5400	46.3	0.23730
9000	39.5	0.39614
12600	35.1	0.51424
16200	30.7	0.64818
19800	25.7	0.82595

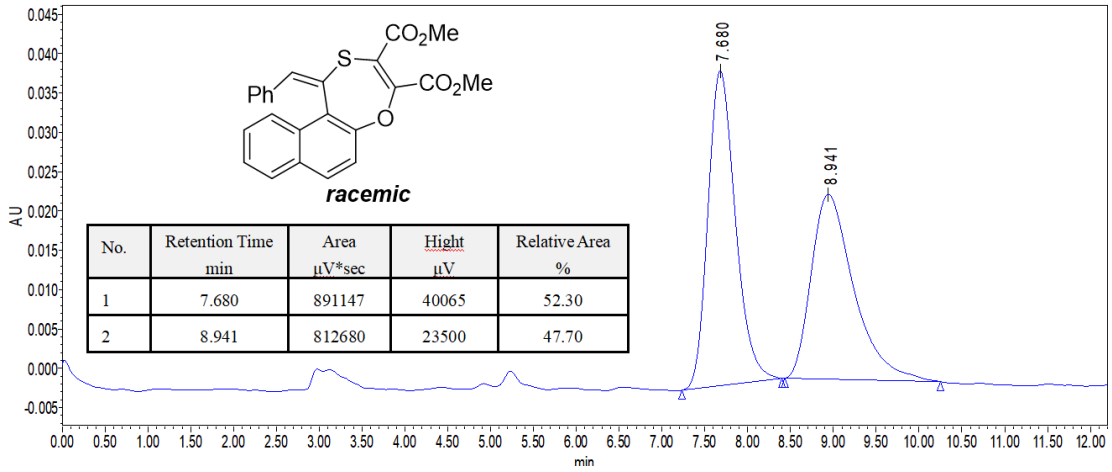


$k_{racemization}$ (60 ℃) = 4.0578 $\times 10^{-5}$ s^{-1}

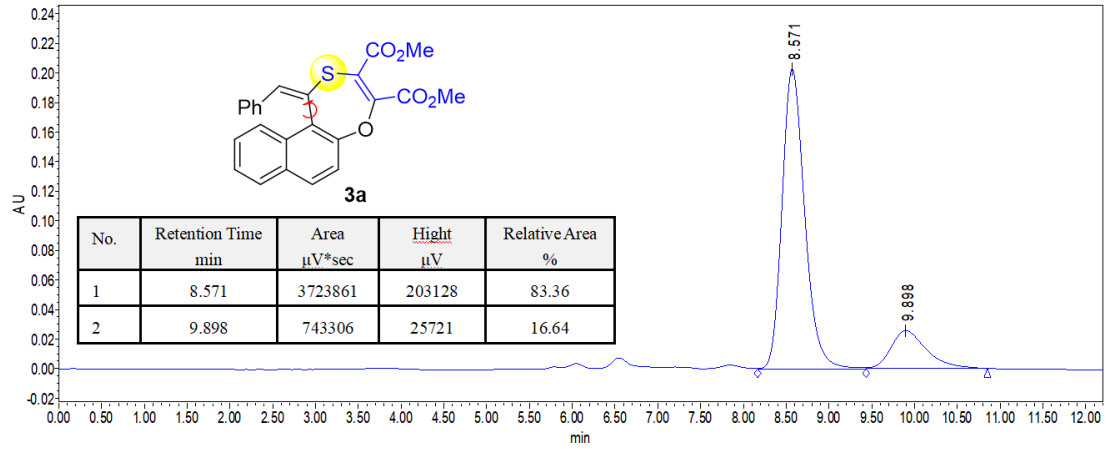
$k_{enantiomerization}$ (60 ℃) = 2.0289 $\times 10^{-5}$ s^{-1}

$\Delta G^{\neq}_{enantiomerization}$ = $RT_1 \ln \frac{k_B T_1}{h k_{enantiomerization}}$ = 112.73 KJ/mol = 26.9 kcal/mol

6. HPLC Traces



No.	Retention Time min	Area μV*sec	Hight μV	Relative Area %
1	7.680	891147	40065	52.30
2	8.941	812680	23500	47.70



No.	Retention Time min	Area μV*sec	Hight μV	Relative Area %
1	8.571	3723861	203128	83.36
2	9.898	743306	25721	16.64

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8. Computation Details

All the calculations were carried out using Gaussian 16 software package[1]. In present work, M06-2X density functional combined with 6-311G(d,p) basis set were employed for geometry optimizations and vibrational frequency calculations. Given the solvent effect, the self-consistent reaction field (SCRF) method and SMD model[2] in dichloroethane solvent were used in geometry optimization and vibrational frequencies calculations. vibrational frequencies calculations were performed at 50 ℃ and 1 atm to characterize stationary point (no imaginary frequency) and transition state (only one imaginary frequency). Intrinsic reaction coordinate (IRC)[3] calculations were performed to verify transition-state structures connected to their corresponding stationary points.

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Table S4 The Gibbs free energies (G) and relative Gibbs free energies (ΔG relative to reactants) for **2a** (1-(phenylethynyl)naphthalen-2-ol), **4a** (2-phenylethynyl-phenol) with **1a**

substrates	**2a**		**4a**	
Species	G (a.u.)	ΔG (kcal/mol)	G (a.u.)	ΔG (kcal/mol)
Reactant **2**	-768.028789		-614.449954	
Reactant **1a**	-1293.854956		-1293.854956	
Et_3N	-292.176323		-292.176323	
Et_3NH^+	-292.627925		-292.627925	
Complex	-1060.204423	0.4	-906.627408	-0.7
IM1	-767.554647	14.1	-613.970632	17.4
TS1	-1060.16472	25.3	-906.574514	32.5
IM2	-768.012891	10.0	-614.421062	18.1
TS2	-2061.838485	28.4	-1908.241132	40.0
IM3	-2061.855951	17.4	-1908.275224	18.6
TS3	-2061.844985	24.3	-1908.265549	24.7
IM4	-2061.864525	12.1	-1908.287532	10.9
TS4	-2061.852039	19.9	-1908.27553	18.4
Product	-1699.214584	-1.4	-1545.636783	-2.1
4-methoxypyridine	-362.67144		-362.67144	

*values given in solvent dichloroethane at 50 ℃ and 1 atm

Table S5 The Gibbs free energies (G for substrates **4b**–**4h** and **IM2**) and relative Gibbs free energies (ΔG) of **IM2** relative to corresponding substrate.

Species	G (a.u.) for substrate	G (a.u.) for **IM2**	ΔG (kcal/mol)
4b	-728.932524	-728.903918	18.0
4c	-818.937223	-818.907958	18.4
4d	-422.784012	-422.752759	19.6
4e	-802.955803	-802.939357	10.3
4f	-843.408806	-843.38965	12.0
4g	-843.417305	-843.397439	12.5
4h	-728.933294	-728.905973	17.1
4i	-693.014802	-692.988250	16.7

*values given in solvent dichloroethane at 50 ℃ and 1 atm

Cartesian coordinates for reaction of substrate 2-phenylethynyl-phenol

Reactant 4a (2-phenylethynyl-phenol)

C	3.974928	0.913145	0.000011
C	2.581681	0.920602	0.000005
C	1.87437	-0.296186	-0.000005
C	2.587833	-1.503624	-0.000002
C	3.972677	-1.505472	-0.000009
C	4.661977	-0.29169	-0.000008

H	4.497411	1.862184	0.000042
H	2.031885	-2.433569	0.000001
H	4.514172	-2.443029	-0.000019
H	5.745724	-0.284121	-0.000001
O	1.955784	2.117027	-0.000069
H	0.996841	1.984664	0.00044
C	0.446879	-0.266798	-0.000003
C	-0.759663	-0.191299	0.000031
C	-2.189166	-0.123235	0.000029
C	-2.949455	-1.300783	0.000012
C	-2.837926	1.119263	0.00001
C	-4.335937	-1.231087	-0.000014
H	-2.445285	-2.259719	0.000019
C	-4.225013	1.17782	-0.000009
H	-2.248778	2.02874	0.00002
C	-4.976609	0.005472	-0.00002
H	-4.918185	-2.14494	-0.000031
H	-4.720457	2.141464	-0.000025
H	-6.059068	0.055339	-0.00004

Zero-point correction =	0.197001 (Hartree/Particle)
Thermal correction to Energy =	0.211129
Thermal correction to Enthalpy =	0.212153
Thermal correction to Gibbs Free Energy =	0.151807
Sum of electronic and zero-point Energies =	-614.404760
Sum of electronic and thermal Energies =	-614.390632
Sum of electronic and thermal Enthalpies =	-614.389608
Sum of electronic and thermal Free Energies =	-614.449954
SCF Done: E(RM062X) =	-614.601761089 A.U.

Complex for substrate 2-phenylethynyl-phenol

C	0.777211	1.397237	-0.033547
C	-0.480461	2.035132	-0.126129
C	-0.544686	3.428728	-0.258008
C	0.609463	4.196035	-0.297164
C	1.849033	3.56426	-0.203933
C	1.935557	2.18502	-0.072748
H	2.759929	4.151546	-0.231952
H	2.903979	1.702573	0.000988
O	0.808082	0.071088	0.093906
C	-1.672573	1.250459	-0.086186
C	-2.690286	0.599998	-0.052302
C	-3.885865	-0.185392	-0.009476

C	-5.141614	0.422906	-0.145033
C	-3.809873	-1.574203	0.168703
C	-6.296558	-0.346818	-0.102595
H	-5.199952	1.496027	-0.283164
C	-4.970253	-2.335413	0.210027
H	-2.838295	-2.04247	0.273877
C	-6.215195	-1.725737	0.074598
H	-7.26318	0.131561	-0.208543
H	-4.902618	-3.408098	0.348693
H	-7.118656	-2.323242	0.10702
H	-1.519808	3.896823	-0.328625
H	0.545786	5.272075	-0.399392
H	1.76727	-0.299496	0.111826
N	3.157283	-1.103136	0.104567
C	4.064747	-0.606363	1.155056
C	2.720981	-2.483352	0.394926
C	3.736064	-0.945216	-1.243095
H	4.549364	0.294031	0.767934
H	4.858405	-1.339574	1.352512
C	3.335734	-0.266409	2.449125
H	2.206417	-2.460341	1.357506
H	3.594793	-3.139443	0.51147
C	1.774189	-3.048499	-0.655062
H	2.945737	-1.141922	-1.971064
H	4.002055	0.109736	-1.348423
C	4.952456	-1.816646	-1.543523
H	2.900719	-1.148412	2.921919
H	4.038798	0.175122	3.158684
H	2.536178	0.456431	2.26783
H	2.279498	-3.243582	-1.603017
H	1.364142	-3.994602	-0.296402
H	0.942383	-2.36414	-0.838675
H	5.319255	-1.593805	-2.547828
H	5.767135	-1.627358	-0.840627
H	4.706611	-2.880567	-1.507571

Zero-point correction =	0.405294 (Hartree/Particle)
Thermal correction to Energy =	0.431592
Thermal correction to Enthalpy =	0.432615
Thermal correction to Gibbs Free Energy =	0.341626
Sum of electronic and zero-point Energies =	-906.563741
Sum of electronic and thermal Energies =	-906.537443
Sum of electronic and thermal Enthalpies =	-906.536420
Sum of electronic and thermal Free Energies =	-906.627408

E(UM062X) = -906.969034799 A.U.

IM1 for substrate 2-phenylethynyl-phenol

C	2.366248	1.048489	0.162548
C	1.643925	-0.133254	-0.432624
C	2.314719	-1.428623	-0.518662
C	3.573458	-1.573369	-0.071402
C	4.285286	-0.445024	0.504303
C	3.733571	0.778803	0.617969
H	5.300026	-0.607793	0.852104
H	4.272384	1.614682	1.048828
O	1.848452	2.146315	0.25697
C	0.406255	0.032593	-0.864945
C	-0.80921	0.209577	-1.294388
C	-2.039585	0.041042	-0.494293
C	-1.997918	-0.28857	0.865151
C	-3.27722	0.21762	-1.116817
C	-3.175395	-0.439973	1.5829
H	-1.04008	-0.42101	1.357264
C	-4.456217	0.064942	-0.394166
H	-3.311805	0.475508	-2.169793
C	-4.408674	-0.264459	0.955931
H	-3.133326	-0.693653	2.635724
H	-5.410927	0.204366	-0.887711
H	-5.326364	-0.382739	1.519989
H	-0.933133	0.507347	-2.335316
H	1.764462	-2.255354	-0.952319
H	4.075688	-2.530632	-0.133553

Zero-point correction =	0.183500 (Hartree/Particle)
Thermal correction to Energy =	0.197299
Thermal correction to Enthalpy =	0.198322
Thermal correction to Gibbs Free Energy =	0.138830
Sum of electronic and zero-point Energies =	-613.925963
Sum of electronic and thermal Energies =	-613.912164
Sum of electronic and thermal Enthalpies =	-613.911141
Sum of electronic and thermal Free Energies =	-613.970632
SCF Done: E(RM062X) =	-614.109462779 A.U.

TS1 for substrate 2-phenylethynyl-phenol

C	2.664451	-0.78684	1.039765
C	1.998051	-1.031918	-0.2566

C	2.768925	-1.35396	-1.430974
C	4.115205	-1.499611	-1.362115
C	4.778766	-1.325807	-0.099386
C	4.107859	-0.996492	1.033076
H	5.85536	-1.459328	-0.059136
H	4.622696	-0.858229	1.977412
O	2.058425	-0.399179	2.04283
C	0.651798	-0.897809	-0.323655
C	-0.581858	-0.599438	-0.366853
C	-1.827457	-1.373391	-0.289873
C	-1.819185	-2.772069	-0.20417
C	-3.054687	-0.703081	-0.298967
C	-3.012328	-3.477409	-0.130678
H	-0.870604	-3.297935	-0.195062
C	-4.249241	-1.411921	-0.222575
H	-3.067154	0.379907	-0.367781
C	-4.231125	-2.800183	-0.138715
H	-2.993627	-4.559192	-0.064703
H	-5.193031	-0.879162	-0.229932
H	-5.160668	-3.354235	-0.080134
H	-0.700907	0.692972	-0.289914
N	-0.71542	2.089426	0.020527
H	2.237323	-1.487649	-2.367159
H	4.694247	-1.751064	-2.241634
C	-1.464764	2.292051	1.279636
H	-2.528016	2.274142	1.026917
H	-1.236502	3.289315	1.674129
C	0.729671	2.342314	0.209136
H	1.095614	1.567831	0.890242
H	0.867036	3.308961	0.709182
C	-1.323076	2.819587	-1.108755
H	-0.820408	2.495708	-2.021763
H	-2.359819	2.480903	-1.178085
C	1.532285	2.29664	-1.084943
H	1.367784	3.181295	-1.703449
H	2.595351	2.250464	-0.838445
H	1.289373	1.41128	-1.676481
C	-1.275522	4.338626	-0.986248
H	-1.721046	4.786291	-1.877044
H	-1.836882	4.691065	-0.118666
H	-0.249062	4.703784	-0.905205
C	-1.174989	1.237407	2.340904
H	-0.115867	1.177968	2.595525
H	-1.726783	1.495695	3.247233

H	-1.50055	0.246481	2.019562

Zero-point correction =	0.401213 (Hartree/Particle)
Thermal correction to Energy =	0.426683
Thermal correction to Enthalpy =	0.427706
Thermal correction to Gibbs Free Energy =	0.342978
Sum of electronic and zero-point Energies =	-906.516279
Sum of electronic and thermal Energies =	-906.490810
Sum of electronic and thermal Enthalpies =	-906.489786
Sum of electronic and thermal Free Energies =	-906.574514
SCF Done: E(RM062X) =	-906.917492221 A.U.

IM2 for substrate 2-phenylethynyl-phenol

C	2.588526	1.034817	0.000032
C	1.882514	-0.239549	-0.000005
C	2.571313	-1.463577	0.00005
C	3.954212	-1.522442	0.000095
C	4.671173	-0.310156	0.000069
C	4.028045	0.906828	0.00002
H	5.757617	-0.335318	0.000081
H	4.594134	1.833619	-0.000017
O	2.005463	2.143388	-0.000138
C	0.462258	-0.218132	-0.000094
C	-0.750548	-0.191787	-0.000131
C	-2.177246	-0.12438	-0.000046
C	-2.956911	-1.291825	-0.000041
C	-2.823722	1.122501	0.000009
C	-4.343323	-1.209861	0.000017
H	-2.464353	-2.257144	-0.000089
C	-4.210067	1.194511	0.000068
H	-2.223389	2.024699	0
C	-4.976343	0.030874	0.000075
H	-4.932575	-2.119791	0.000018
H	-4.694761	2.164165	0.000109
H	-6.058379	0.090732	0.000121
H	1.98862	-2.380372	0.000044
H	4.470093	-2.474629	0.000129

Zero-point correction =	0.195911 (Hartree/Particle)
Thermal correction to Energy =	0.209990
Thermal correction to Enthalpy =	0.211013
Thermal correction to Gibbs Free Energy =	0.150210
Sum of electronic and zero-point Energies =	-614.375362

Sum of electronic and thermal Energies =	-614.361282
Sum of electronic and thermal Enthalpies =	-614.360259
Sum of electronic and thermal Free Energies =	-614.421062
SCF Done: E(RM062X) =	-614.571272293 A.U.

TS2 for substrate 2-phenylethynyl-phenol

C	1.470516	-0.233665	-1.267785
C	2.824416	-0.326966	-1.422535
C	3.661617	-0.060519	-0.32543
C	3.081229	0.292855	0.901376
C	1.712079	0.366913	0.984251
N	0.928347	0.112733	-0.078184
H	0.769095	-0.424756	-2.068371
H	3.252535	-0.602426	-2.376457
H	3.669156	0.507262	1.781548
H	1.198005	0.628019	1.899937
O	4.96194	-0.165575	-0.536066
C	5.856506	0.097231	0.551786
H	6.854388	-0.048598	0.147925
H	5.741375	1.125953	0.898936
H	5.678676	-0.604882	1.368569
C	-0.507411	0.200011	0.05066
C	-1.209289	-0.962484	0.219683
C	-0.99456	1.576579	-0.011117
O	-0.270979	2.540001	-0.140748
O	-2.324911	1.667015	0.097107
C	-2.709437	-0.882751	0.370384
O	-3.280485	-0.879552	1.426264
O	-3.309281	-0.892842	-0.816894
C	-2.86317	2.993106	0.059968
H	-2.452771	3.593019	0.872585
H	-2.638376	3.468001	-0.895551
H	-3.937163	2.877858	0.181856
C	-4.7388	-0.813221	-0.775225
H	-5.153926	-1.678016	-0.256496
H	-5.048627	0.101355	-0.267707
H	-5.064497	-0.801259	-1.812112
S	-0.567422	-2.535349	0.301201

Zero-point correction =	0.442975 (Hartree/Particle)
Thermal correction to Energy =	0.474648
Thermal correction to Enthalpy =	0.475592
Thermal correction to Gibbs Free Energy =	0.377590

Sum of electronic and zero-point Energies =	-1908.175746
Sum of electronic and thermal Energies =	-1908.144073
Sum of electronic and thermal Enthalpies =	-1908.143129
Sum of electronic and thermal Free Energies =	-1908.241132
SCF Done: E(RM062X) =	-1908.61872113 A.U.

IM3 for substrate 2-phenylethynyl-phenol

C	1.5583	2.613398	1.095102
C	1.591431	2.176814	-0.282929
C	2.592002	2.619418	-1.162089
C	3.598696	3.476045	-0.754646
C	3.597082	3.915446	0.581818
C	2.622186	3.510112	1.465485
H	4.375955	4.59123	0.92326
H	2.625626	3.856406	2.494381
O	0.691824	2.224804	1.931449
C	0.581643	1.247359	-0.805019
C	0.772227	0.109712	-1.498242
C	2.003785	-0.686763	-1.617715
C	2.023055	-1.707512	-2.579377
C	3.106152	-0.568352	-0.755258
C	3.101432	-2.577076	-2.684996
H	1.170688	-1.822078	-3.24153
C	4.176976	-1.447459	-0.854186
H	3.116484	0.200859	0.006951
C	4.183154	-2.453846	-1.817632
H	3.09291	-3.356368	-3.438486
H	5.011667	-1.348876	-0.168865
H	5.022775	-3.13519	-1.890294
H	-0.087688	-0.330818	-1.999288
C	-0.477169	-2.358934	0.213833
C	0.701763	-2.881061	0.648618
C	1.510442	-2.130422	1.526912
C	1.054854	-0.879675	1.960597
C	-0.156527	-0.419472	1.508185
N	-0.902519	-1.136397	0.643031
H	-1.114031	-2.870201	-0.494897
H	1.041209	-3.843015	0.28952
H	1.618982	-0.233255	2.617202
H	-0.51207	0.562984	1.792306
O	2.664116	-2.669199	1.868132
C	3.558227	-1.900816	2.6833
H	4.453519	-2.50797	2.784239

H	3.798654	-0.954571	2.193998
H	3.115624	-1.720658	3.664859
C	-2.127523	-0.592073	0.14308
C	-2.235097	0.662058	-0.350762
C	-3.281765	-1.522442	0.315197
O	-3.277804	-2.426583	1.109755
O	-4.278246	-1.257459	-0.521308
C	-3.626547	1.219827	-0.609706
O	-3.997874	1.611213	-1.678445
O	-4.318388	1.278704	0.51934
C	-5.492936	-1.992443	-0.299834
H	-5.303867	-3.062024	-0.385618
H	-5.889829	-1.762318	0.68974
H	-6.178521	-1.663336	-1.07563
C	-5.67726	1.725251	0.378348
H	-6.212289	1.068239	-0.30864
H	-6.106933	1.672434	1.374564
H	-5.699436	2.748877	0.004657
S	-1.085207	1.921982	-0.700856
H	4.357498	3.811804	-1.450451
H	2.563491	2.266519	-2.189387

Zero-point correction=	0.444774 (Hartree/Particle)
Thermal correction to Energy=	0.480932
Thermal correction to Enthalpy=	0.481956
Thermal correction to Gibbs Free Energy=	0.372837
Sum of electronic and zero-point Energies=	-1908.203287
Sum of electronic and thermal Energies=	-1908.167128
Sum of electronic and thermal Enthalpies=	-1908.166105
Sum of electronic and thermal Free Energies=	-1908.275224
SCF Done: E(RM062X) =	-1908.64806044 A.U.

TS3 for substrate 2-phenylethynyl-phenol

C	-0.879149	-1.042757	1.164682
C	-1.626281	-1.000646	-0.038471
C	-2.654607	-1.913453	-0.270287
C	-2.970911	-2.885209	0.672235
C	-2.244681	-2.939399	1.864228
C	-1.211555	-2.04616	2.101144
H	-2.484183	-3.691592	2.608537
H	-0.634585	-2.085794	3.018662
O	0.069932	-0.173648	1.396123
C	-1.348637	0.070631	-1.035408

C	-2.079597	1.174058	-1.240825
C	-3.302335	1.577816	-0.521115
C	-3.508735	1.322262	0.841361
C	-4.286392	2.287043	-1.222746
C	-4.678033	1.737093	1.468191
H	-2.741469	0.817766	1.415248
C	-5.457418	2.695967	-0.595833
H	-4.128919	2.509194	-2.273243
C	-5.660166	2.417703	0.752969
H	-4.818609	1.533609	2.523682
H	-6.210162	3.23504	-1.159721
H	-6.570948	2.737559	1.245773
H	-1.780036	1.840972	-2.04687
C	2.662527	1.260872	-1.12818
C	3.12721	2.535298	-1.262421
C	2.913649	3.460788	-0.226219
C	2.249309	3.029118	0.929825
C	1.80464	1.732194	1.002849
N	1.97955	0.868055	-0.020272
H	2.826602	0.502108	-1.878275
H	3.665458	2.828774	-2.153151
H	2.072461	3.679133	1.774013
H	1.282556	1.346003	1.862818
O	3.376336	4.681225	-0.418081
C	3.189154	5.659154	0.613489
H	3.632089	6.573392	0.228979
H	2.125185	5.810592	0.804037
H	3.702225	5.350664	1.526183
C	1.584828	-0.53591	0.069383
C	1.076004	-1.163514	-1.034883
C	2.366553	-1.253607	1.14563
O	3.409724	-0.82667	1.571368
O	1.763653	-2.346368	1.564711
C	1.355249	-2.589452	-1.288362
O	2.364976	-3.158162	-0.934907
O	0.404956	-3.190592	-2.010891
C	2.50843	-3.157778	2.476371
H	2.719359	-2.606206	3.393171
H	1.875495	-4.016051	2.686814
H	3.442511	-3.478262	2.013115
C	0.659201	-4.558207	-2.340175
H	0.728527	-5.161514	-1.434159
H	-0.188113	-4.878193	-2.941609
H	1.585454	-4.6503	-2.908952

S	0.0239	-0.247815	-2.136203
H	-3.212724	-1.849784	-1.199128
H	-3.773577	-3.588165	0.48403

Zero-point correction =	0.444840 (Hartree/Particle)
Thermal correction to Energy =	0.480196
Thermal correction to Enthalpy =	0.481220
Thermal correction to Gibbs Free Energy =	0.372243
Sum of electronic and zero-point Energies =	-1908.192952
Sum of electronic and thermal Energies =	-1908.157596
Sum of electronic and thermal Enthalpies =	-1908.156572
Sum of electronic and thermal Free Energies =	-1908.265549
SCF Done: E(RM062X) =	-1908.63779192 A.U.

IM4 for substrate 2-phenylethynyl-phenol

C	0.79603	-1.150243	-1.01192
C	1.70753	-0.877178	0.012085
C	2.854531	-1.667613	0.111614
C	3.104304	-2.677852	-0.808935
C	2.202044	-2.912239	-1.84298
C	1.041784	-2.152089	-1.941677
H	2.393898	-3.694093	-2.568312
H	0.314039	-2.321701	-2.724056
O	-0.327313	-0.356262	-1.176127
C	1.464027	0.215073	0.981449
C	2.260515	1.276666	1.174611
C	3.49042	1.634767	0.443587
C	4.493591	2.334204	1.128093
C	3.688423	1.354156	-0.916308
C	5.670203	2.709498	0.489833
H	4.345722	2.576819	2.175437
C	4.862443	1.734588	-1.554623
H	2.913282	0.849862	-1.481052
C	5.862091	2.406859	-0.854807
H	6.435768	3.241836	1.042792
H	4.994166	1.511536	-2.607359
H	6.776666	2.700532	-1.356675
H	1.99426	1.959932	1.979446
C	-2.967394	0.986203	0.836498
C	-3.595466	2.188463	0.994812
C	-3.259372	3.260888	0.152635
C	-2.286652	3.057712	-0.83409
C	-1.700379	1.818453	-0.946456

N	-2.031575	0.807084	-0.125486
H	-3.163861	0.129729	1.463328
H	-4.337695	2.319404	1.770176
H	-1.975026	3.837977	-1.512414
H	-0.94721	1.610148	-1.689574
O	-3.894597	4.401409	0.361145
C	-3.572296	5.526743	-0.464591
H	-4.209518	6.334398	-0.115461
H	-2.522856	5.80064	-0.341178
H	-3.790215	5.30665	-1.511443
C	-1.397631	-0.570036	-0.248881
C	-0.985899	-1.076722	1.077717
C	-2.496213	-1.447621	-0.909376
O	-3.629066	-1.457163	-0.509823
O	-2.056935	-2.097899	-1.969732
C	-0.984074	-2.48691	1.268244
O	-1.530361	-3.308048	0.532347
O	-0.332024	-2.900143	2.38698
C	-2.957269	-3.089361	-2.47944
H	-3.189383	-3.802369	-1.687982
H	-3.872585	-2.622928	-2.844182
H	-2.428585	-3.578385	-3.293625
C	-0.317358	-4.307621	2.594458
H	0.175176	-4.821317	1.766545
H	0.243778	-4.465226	3.513934
H	-1.329193	-4.701974	2.704711
S	0.0086	0.008685	2.018385
H	3.555094	-1.470388	0.915341
H	4.002467	-3.277516	-0.721765

Zero-point correction =	0.446326 (Hartree/Particle)
Thermal correction to Energy =	0.481623
Thermal correction to Enthalpy =	0.482646
Thermal correction to Gibbs Free Energy =	0.374578
Sum of electronic and zero-point Energies =	-1908.215784
Sum of electronic and thermal Energies =	-1908.180487
Sum of electronic and thermal Enthalpies =	-1908.179464
Sum of electronic and thermal Free Energies =	-1908.287532
SCF Done: E(RM062X) =	-1908.66211014 A.U.

TS4 for substrate 2-phenylethynyl-phenol (4a)

C	1.10537	-0.668952	-1.265763
C	2.063315	-0.671516	-0.253898

C	3.259107	-1.359121	-0.478641
C	3.499031	-1.981045	-1.696626
C	2.546465	-1.921629	-2.711698
C	1.33744	-1.271887	-2.492948
H	2.737191	-2.394393	-3.667723
H	0.569041	-1.228306	-3.256273
O	-0.10244	-0.009049	-1.052085
C	1.843288	0.089643	0.993758
C	2.695062	1.005866	1.480342
C	3.934921	1.507509	0.857248
C	5.017911	1.831706	1.683898
C	4.058644	1.730028	-0.52138
C	6.202643	2.325753	1.149262
H	4.926892	1.685666	2.75526
C	5.240685	2.229162	-1.053642
H	3.219666	1.525511	-1.176565
C	6.320636	2.521754	-0.223249
H	7.032063	2.561363	1.806244
H	5.316235	2.398998	-2.121647
H	7.241321	2.910444	-0.642476
H	2.464419	1.444194	2.44971
C	-3.054028	0.872705	0.846398
C	-3.97853	1.876863	1.040473
C	-4.142923	2.838279	0.035855
C	-3.365404	2.74088	-1.122773
C	-2.466762	1.689655	-1.219224
N	-2.317124	0.784736	-0.257861
H	-2.883624	0.107406	1.598895
H	-4.57019	1.93367	1.944626
H	-3.444033	3.451304	-1.933532
H	-1.841917	1.568545	-2.096946
O	-5.047802	3.795772	0.265808
C	-5.23853	4.792681	-0.736117
H	-6.003562	5.45957	-0.346561
H	-4.315762	5.352159	-0.907465
H	-5.583862	4.342874	-1.670104
C	-1.004449	-0.781759	-0.322655
C	-0.70012	-1.177222	0.954299
C	-1.814098	-1.690852	-1.254383
O	-2.828069	-1.401378	-1.822671
O	-1.134827	-2.817099	-1.450476
C	-1.499822	-2.244452	1.553064
O	-2.481689	-2.738173	1.033134
O	-1.063107	-2.623317	2.760998

C	-1.757577	-3.762806	-2.328391
H	-2.724572	-4.062729	-1.922854
H	-1.891188	-3.330869	-3.320789
H	-1.082131	-4.613126	-2.370485
C	-1.831299	-3.646937	3.400109
H	-1.817656	-4.561846	2.806994
H	-1.353491	-3.814376	4.362205
H	-2.862437	-3.320499	3.540253
S	0.392879	-0.245094	1.985476
H	4.00528	-1.382797	0.307318
H	4.433749	-2.504281	-1.85825

Zero-point correction =	0.444093 (Hartree/Particle)
Thermal correction to Energy =	0.479679
Thermal correction to Enthalpy =	0.480702
Thermal correction to Gibbs Free Energy =	0.370022
Sum of electronic and zero-point Energies =	-1908.201458
Sum of electronic and thermal Energies =	-1908.165873
Sum of electronic and thermal Enthalpies =	-1908.164850
Sum of electronic and thermal Free Energies =	-1908.275530
SCF Done: E(RM062X) =	-1908.64555155 A.U.

Product for substrate 2-phenylethynyl-phenol

C	-0.194313	1.376084	0.186487
C	-1.054382	0.452926	0.774462
C	-1.878749	0.875913	1.817648
C	-1.843828	2.200118	2.238597
C	-0.986076	3.110511	1.624651
C	-0.147844	2.699545	0.592964
H	-0.965355	4.142872	1.952532
H	0.532923	3.381731	0.098392
O	0.599238	0.941302	-0.867473
C	-1.07336	-0.932416	0.254941
C	-2.127004	-1.569839	-0.26962
C	-3.47689	-1.020964	-0.497268
C	-4.569629	-1.889518	-0.390231
C	-3.708121	0.311602	-0.863078
C	-5.864813	-1.431623	-0.6007
H	-4.396382	-2.929342	-0.133568
C	-5.002884	0.764047	-1.083932
H	-2.873895	0.990029	-0.995513
C	-6.085365	-0.101368	-0.944649
H	-6.700038	-2.115358	-0.503424

H	-5.16651	1.795698	-1.372972
H	-7.093765	0.257211	-1.115146
H	-2.003044	-2.61432	-0.545464
C	1.749708	0.305766	-0.468708
C	1.757159	-0.902939	0.108725
C	3.020036	1.055131	-0.689356
O	4.112778	0.61786	-0.423497
O	2.801625	2.25889	-1.20246
C	3.051532	-1.561349	0.53391
O	3.448995	-1.558224	1.664608
O	3.606611	-2.206401	-0.479696
C	3.978213	3.046672	-1.439748
H	4.513056	3.215152	-0.504918
H	4.631169	2.541072	-2.151346
H	3.621626	3.986926	-1.851046
C	4.877332	-2.810867	-0.193269
H	4.771334	-3.562311	0.58936
H	5.199291	-3.270764	-1.12332
H	5.585138	-2.043199	0.12058
S	0.39411	-1.922217	0.532678
H	-2.489404	2.523999	3.045908
H	-2.550212	0.164066	2.284291

Zero-point correction =	0.320790 (Hartree/Particle)
Thermal correction to Energy =	0.347717
Thermal correction to Enthalpy =	0.348741
Thermal correction to Gibbs Free Energy =	0.258646
Sum of electronic and zero-point Energies =	-1545.574639
Sum of electronic and thermal Energies =	-1545.547711
Sum of electronic and thermal Enthalpies =	-1545.546688
Sum of electronic and thermal Free Energies =	-1545.636783
SCF Done: E(RM062X) =	-1545.89542880 A.U.

Et_3N

N	-0.18598	0.014731	0.421796
C	0.237754	1.12019	-0.439469
C	-1.37172	-0.651809	-0.119231
C	0.889379	-0.9387	0.712614
C	1.440079	1.878871	0.106666
H	0.454206	0.769599	-1.463502
H	-0.601014	1.814567	-0.519683
C	-2.635442	0.192021	0.008842
H	-1.22996	-0.938104	-1.17506

H	-1.511046	-1.578251	0.444951
C	1.538293	-1.616811	-0.497335
H	1.65832	-0.422077	1.292312
H	0.468797	-1.702342	1.372776
H	2.359916	1.292843	0.049795
H	1.271494	2.154461	1.151006
H	1.593546	2.793932	-0.469222
H	-2.618913	1.06617	-0.644609
H	-2.754248	0.534661	1.039606
H	-3.510969	-0.403045	-0.261426
H	0.804279	-2.165789	-1.092524
H	2.032918	-0.892428	-1.149549
H	2.294467	-2.329888	-0.159967

Zero-point correction =	0.206950 (Hartree/Particle)
Thermal correction to Energy =	0.217524
Thermal correction to Enthalpy =	0.218547
Thermal correction to Gibbs Free Energy =	0.169715
Sum of electronic and zero-point Energies =	-292.139089
Sum of electronic and thermal Energies =	-292.128515
Sum of electronic and thermal Enthalpies =	-292.127491
Sum of electronic and thermal Free Energies =	-292.176323
SCF Done: E(RM062X) =	-292.346038241 A.U.

Et_3NH^+

N	-0.177986	0.004951	0.409923
C	0.27209	1.14599	-0.461312
C	-1.412266	-0.658478	-0.140851
C	0.911659	-0.99116	0.713086
C	1.50664	1.839337	0.078585
H	0.432681	0.731618	-1.456686
H	-0.565188	1.839577	-0.506571
C	-2.63592	0.2307	-0.031649
H	-1.193957	-0.920304	-1.175497
H	-1.549134	-1.574164	0.434015
C	1.503406	-1.623273	-0.530419
H	1.668099	-0.461036	1.28945
H	0.453981	-1.739052	1.36004
H	2.400525	1.220574	-0.005154
H	1.369879	2.128456	1.1238
H	1.670472	2.747568	-0.502718
H	-2.580474	1.101801	-0.684103
H	-2.786619	0.562778	0.998445

H	-3.509688	-0.351699	-0.327216
H	0.749484	-2.142879	-1.123702
H	2.011955	-0.890956	-1.159781
H	2.242691	-2.359342	-0.211476
H	-0.442451	0.413704	1.313053

Zero-point correction =	0.223502 (Hartree/Particle)
Thermal correction to Energy =	0.233898
Thermal correction to Enthalpy =	0.234922
Thermal correction to Gibbs Free Energy =	0.186783
Sum of electronic and zero-point Energies =	-292.591206
Sum of electronic and thermal Energies =	-292.580810
Sum of electronic and thermal Enthalpies =	-292.579786
Sum of electronic and thermal Free Energies =	-292.627925
SCF Done: E(RM062X) =	-292.814707991 A.U.

Reactant 1a

C	1.470516	-0.233665	-1.267785
C	2.824416	-0.326966	-1.422535
C	3.661617	-0.060519	-0.32543
C	3.081229	0.292855	0.901376
C	1.712079	0.366913	0.984251
N	0.928347	0.112733	-0.078184
H	0.769095	-0.424756	-2.068371
H	3.252535	-0.602426	-2.376457
H	3.669156	0.507262	1.781548
H	1.198005	0.628019	1.899937
O	4.96194	-0.165575	-0.536066
C	5.856506	0.097231	0.551786
H	6.854388	-0.048598	0.147925
H	5.741375	1.125953	0.898936
H	5.678676	-0.604882	1.368569
C	-0.507411	0.200011	0.05066
C	-1.209289	-0.962484	0.219683
C	-0.99456	1.576579	-0.011117
O	-0.270979	2.540001	-0.140748
O	-2.324911	1.667015	0.097107
C	-2.709437	-0.882751	0.370384
O	-3.280485	-0.879552	1.426264
O	-3.309281	-0.892842	-0.816894
C	-2.86317	2.993106	0.059968
H	-2.452771	3.593019	0.872585

H	-2.638376	3.468001	-0.895551
H	-3.937163	2.877858	0.181856
C	-4.7388	-0.813221	-0.775225
H	-5.153926	-1.678016	-0.256496
H	-5.048627	0.101355	-0.267707
H	-5.064497	-0.801259	-1.812112
S	-0.567422	-2.535349	0.301201

Zero-point correction =	0.245986 (Hartree/Particle)
Thermal correction to Energy =	0.267897
Thermal correction to Enthalpy =	0.268921
Thermal correction to Gibbs Free Energy =	0.190224
Sum of electronic and zero-point Energies =	-1293.799195
Sum of electronic and thermal Energies =	-1293.777283
Sum of electronic and thermal Enthalpies =	-1293.776260
Sum of electronic and thermal Free Energies =	-1293.854956
SCF Done: E(RM062X) =	-1294.04518054 A.U

Product 4-methoxypyridine

C	1.857674	-0.913996	-0.000026
C	0.526702	-1.285702	0.000009
C	-0.448808	-0.283345	0.000013
C	-0.028345	1.04678	-0.00002
C	1.340741	1.29723	-0.000054
N	2.283427	0.356809	-0.000057
H	2.628348	-1.678647	-0.000029
H	0.230079	-2.326888	0.000034
H	-0.723988	1.874488	-0.000022
H	1.687754	2.326279	-0.000079
O	-1.730239	-0.684067	0.00005
C	-2.738297	0.321934	0.000061
H	-3.687473	-0.208698	0.000096
H	-2.667377	0.945482	0.89493
H	-2.667426	0.945453	-0.894833

Zero-point correction =	0.122609 (Hartree/Particle)
Thermal correction to Energy =	0.130290
Thermal correction to Enthalpy =	0.131314
Thermal correction to Gibbs Free Energy =	0.088455
Sum of electronic and zero-point Energies =	-362.637286
Sum of electronic and thermal Energies =	-362.629605
Sum of electronic and thermal Enthalpies =	-362.628582
Sum of electronic and thermal Free Energies =	-362.671440

SCF Done: E(RM062X) = -362.759895294 A.U.

Cartesian coordinates for reaction of substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

1-(phenylethynyl)naphthalen-2-ol (2a)

O	0.579926	3.013016	-0.000013
H	-0.325588	2.66838	-0.000024
C	-0.332	0.364442	-0.000011
C	-1.525657	0.169043	0.000007
C	-2.934079	-0.081623	0.000005
C	-3.415034	-1.398455	-0.000081
C	-3.842183	0.986218	0.00009
C	-4.782497	-1.637349	-0.000081
H	-2.711295	-2.222486	-0.000147
C	-5.20769	0.736197	0.000087
H	-3.469155	2.003606	0.000158
C	-5.681277	-0.573394	0.000002
H	-5.147827	-2.657482	-0.000148
H	-5.904009	1.566488	0.000152
H	-6.747873	-0.764527	0.000001
C	1.061504	0.660613	-0.000008
C	2.052372	-0.376334	-0.000002
C	1.456766	1.990264	-0.000009
C	1.706502	-1.75009	-0.000001
C	3.425706	-0.01699	0.000001
C	2.829	2.336891	-0.000005
C	2.682608	-2.714954	0.000005
H	0.659321	-2.030812	-0.000003
C	4.410428	-1.035969	0.000007
C	3.781845	1.360156	0
H	3.089421	3.388376	-0.000006
C	4.049914	-2.358768	0.000008
H	2.403113	-3.762168	0.000006
H	5.455649	-0.745324	0.000009
H	4.833517	1.625363	0.000003
H	4.807945	-3.13293	0.000012

Zero-point correction =	0.244182 (Hartree/Particle)
Thermal correction to Energy =	0.261363
Thermal correction to Enthalpy =	0.262387
Thermal correction to Gibbs Free Energy =	0.195141
Sum of electronic and zero-point Energies =	-767.979748
Sum of electronic and thermal Energies =	-767.962566
Sum of electronic and thermal Enthalpies =	-767.961543

Sum of electronic and thermal Free Energies = -768.028789

SCF Done: E(RM062X) = -768.223929678 A.U.

Complex for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	0.781942	0.767988	-0.020813
C	-0.539496	1.210497	-0.046156
C	1.575611	3.059709	-0.078759
C	1.839624	1.721323	-0.038292
H	2.39109	3.775287	-0.092017
H	2.862624	1.3622	-0.022873
O	1.031074	-0.53695	0.024293
C	-1.589947	0.248821	-0.028353
C	-2.488007	-0.560495	-0.011992
C	-3.534701	-1.535224	0.009024
C	-4.879153	-1.137759	-0.009316
C	-3.222463	-2.901999	0.048553
C	-5.887966	-2.091614	0.012168
H	-5.120592	-0.081688	-0.039949
C	-4.238145	-3.848197	0.069754
H	-2.18286	-3.207369	0.063009
C	-5.571924	-3.447461	0.051705
H	-6.924441	-1.775516	-0.002035
H	-3.987814	-4.902187	0.100437
H	-6.362154	-4.188807	0.068597
H	2.040273	-0.754748	0.05795
N	3.519271	-1.343499	0.09324
C	4.309129	-0.739175	1.182752
C	3.27235	-2.776229	0.353639
C	4.123182	-1.08784	-1.228706
H	4.665771	0.231319	0.827226
H	5.196192	-1.350987	1.394528
C	3.499374	-0.538163	2.457693
H	2.720769	-2.840456	1.293361
H	4.225714	-3.30191	0.501179
C	2.459065	-3.454821	-0.740065
H	3.396133	-1.378468	-1.990266
H	4.24829	-0.005177	-1.312416
C	5.457806	-1.781087	-1.488205
H	3.193713	-1.484092	2.907567
H	4.105635	-0.004681	3.192882
H	2.602809	0.055551	2.262061
H	3.024026	-3.560981	-1.668199

H	2.175624	-4.455263	-0.40741
H	1.544886	-2.89476	-0.951086
H	5.831958	-1.489171	-2.471856
H	6.20929	-1.498141	-0.747509
H	5.357587	-2.868956	-1.479785
C	0.240723	3.546394	-0.103903
C	-0.040221	4.934866	-0.144576
C	-0.830807	2.613781	-0.089434
C	-1.33343	5.388973	-0.169301
H	0.79272	5.630332	-0.155328
C	-2.158801	3.112228	-0.115723
C	-2.400672	4.462502	-0.154487
H	-1.541781	6.451796	-0.199999
H	-2.984993	2.410651	-0.104433
H	-3.422407	4.824207	-0.173902

Zero-point correction =	0.452455 (Hartree/Particle)
Thermal correction to Energy =	0.481800
Thermal correction to Enthalpy =	0.482823
Thermal correction to Gibbs Free Energy =	0.386522
Sum of electronic and zero-point Energies =	-1060.138490
Sum of electronic and thermal Energies =	-1060.109146
Sum of electronic and thermal Enthalpies =	-1060.108123
Sum of electronic and thermal Free Energies =	-1060.204423
SCF Done: E(RM062X) =	-1060.59094545 A.U.

IM1 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	1.25029	2.135694	-0.052136
C	0.870528	0.717668	-0.395712
C	1.849426	-0.378739	-0.220765
C	3.136819	-0.066382	0.250176
C	3.482877	1.315279	0.561064
C	2.622988	2.336969	0.42807
H	0.537761	-1.956051	-0.860706
C	1.531421	-1.709188	-0.50294
C	4.079311	-1.086655	0.422909
H	4.491398	1.499235	0.919558
H	2.900991	3.35637	0.668998
C	3.754087	-2.40307	0.1366
C	2.474616	-2.711788	-0.326504
H	5.068889	-0.830425	0.786013
H	4.488626	-3.187553	0.273093
H	2.212158	-3.739201	-0.549743

O	0.467814	3.058569	-0.169578
C	-0.349271	0.508337	-0.84762
C	-1.556187	0.30936	-1.294319
C	-2.733442	-0.012605	-0.461755
C	-2.636507	-0.164613	0.926212
C	-3.97467	-0.175482	-1.080874
C	-3.762995	-0.471474	1.675495
H	-1.67542	-0.040307	1.41441
C	-5.102714	-0.482936	-0.326709
H	-4.052349	-0.058623	-2.156461
C	-5.000151	-0.631824	1.051989
H	-3.678102	-0.587061	2.749762
H	-6.060685	-0.606021	-0.818321
H	-5.877872	-0.871809	1.640521
H	-1.716467	0.381589	-2.369592

Zero-point correction =	0.230671 (Hartree/Particle)
Thermal correction to Energy =	0.247609
Thermal correction to Enthalpy =	0.248632
Thermal correction to Gibbs Free Energy =	0.181579
Sum of electronic and zero-point Energies =	-767.505555
Sum of electronic and thermal Energies =	-767.488617
Sum of electronic and thermal Enthalpies =	-767.487594
Sum of electronic and thermal Free Energies =	-767.554647
SCF Done: E(RM062X) =	-767.736226577 A.U.

TS1 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	-1.767041	-0.086002	2.029991
C	-1.518345	0.405016	0.662566
C	-4.175951	-0.067017	1.516556
C	-3.177001	-0.275176	2.393933
H	-5.207239	-0.228497	1.817583
H	-3.370008	-0.607735	3.40779
O	-0.86612	-0.355623	2.823036
C	-0.233961	0.597227	0.296354
C	0.984906	0.601143	-0.065663
C	2.020497	1.64247	-0.109656
C	1.786756	2.934513	0.382004
C	3.276686	1.342818	-0.646587
C	2.785065	3.897372	0.332566
H	0.816702	3.172729	0.805055
C	4.276709	2.309224	-0.69511

H	3.462136	0.346729	-1.034977
C	4.033785	3.588205	-0.205711
H	2.591586	4.892508	0.716502
H	5.244546	2.062698	-1.116246
H	4.811569	4.342081	-0.242151
H	1.389625	-0.652377	-0.257099
N	1.759409	-1.98739	-0.250507
C	2.92651	-2.141385	0.644544
H	3.77135	-1.662043	0.143836
H	3.162117	-3.206655	0.749307
C	0.54835	-2.63121	0.3069
H	0.26953	-2.049865	1.191399
H	0.79746	-3.645287	0.642539
C	2.079975	-2.365767	-1.641145
H	1.239733	-2.060264	-2.26703
H	2.937066	-1.756268	-1.938849
C	-0.627212	-2.661223	-0.661284
H	-0.488406	-3.394594	-1.457923
H	-1.529964	-2.930672	-0.108614
H	-0.797125	-1.683002	-1.116256
C	2.390287	-3.843531	-1.850625
H	2.553869	-4.027676	-2.914422
H	3.292558	-4.148238	-1.317449
H	1.564389	-4.479378	-1.523745
C	2.723975	-1.522571	2.021047
H	1.983103	-2.064512	2.61055
H	3.671136	-1.56055	2.562673
H	2.412144	-0.478433	1.952999
C	-3.943073	0.365496	0.15218
C	-2.621316	0.604641	-0.279243
C	-5.0147	0.545929	-0.735958
C	-2.41484	1.019873	-1.60528
C	-4.793193	0.952798	-2.038674
H	-6.023085	0.358695	-0.381113
C	-3.482453	1.18828	-2.469941
H	-1.404271	1.21281	-1.948915
H	-5.624799	1.08937	-2.719413
H	-3.299115	1.508407	-3.489358

Zero-point correction =	0.448292 (Hartree/Particle)
Thermal correction to Energy =	0.477006
Thermal correction to Enthalpy =	0.478029
Thermal correction to Gibbs Free Energy =	0.385298
Sum of electronic and zero-point Energies =	-1060.101726

Sum of electronic and thermal Energies =	-1060.073012
Sum of electronic and thermal Enthalpies =	-1060.071989
Sum of electronic and thermal Free Energies =	-1060.164720
SCF Done: E(RM062X) =	-1060.55001791 A.U.

IM2 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	-1.443507	2.09886	-0.000002
C	-1.059918	0.708719	0.000005
C	-2.02777	-0.345969	0.000009
C	-3.417645	-0.032737	0.000004
C	-3.805654	1.347057	-0.000006
C	-2.886953	2.342846	-0.00001
H	-0.619085	-1.988808	0.000022
C	-1.670065	-1.721495	0.000018
C	-4.376235	-1.065972	0.000009
H	-4.86751	1.579073	-0.000011
H	-3.191274	3.384963	-0.000018
C	-3.999876	-2.391047	0.000018
C	-2.627066	-2.710473	0.000023
H	-5.427503	-0.792705	0.000005
H	-4.744674	-3.178036	0.000022
H	-2.318991	-3.750676	0.00003
O	-0.636202	3.050747	-0.000009
C	0.323805	0.414788	0.000013
C	1.513254	0.16881	0.000012
C	2.919631	-0.071752	-0.000002
C	3.43319	-1.379133	-0.000006
C	3.819715	1.007535	-0.000009
C	4.804899	-1.595469	-0.000016
H	2.74605	-2.217452	0
C	5.189135	0.781124	-0.000019
H	3.427206	2.017732	-0.000005
C	5.689562	-0.519351	-0.000023
H	5.185423	-2.610626	-0.000019
H	5.869685	1.625018	-0.000024
H	6.759279	-0.692507	-0.000031

Zero-point correction =	0.243333 (Hartree/Particle)
Thermal correction to Energy =	0.260400
Thermal correction to Enthalpy =	0.261423
Thermal correction to Gibbs Free Energy =	0.193743
Sum of electronic and zero-point Energies =	-767.963301
Sum of electronic and thermal Energies =	-767.946234

Sum of electronic and thermal Enthalpies =	-767.945211
Sum of electronic and thermal Free Energies =	-768.012891
SCF Done: E(RM062X) =	-768.206634002 A.U.

TS2 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	-1.595259	-1.426582	1.882287
C	-1.876527	-1.340956	0.448633
C	-2.927875	-2.153749	-0.163153
C	-3.715086	-2.985858	0.664938
C	-3.441368	-3.037955	2.085049
C	-2.457571	-2.319455	2.659344
H	-2.613689	-1.502091	-2.194716
C	-3.2097	-2.128652	-1.541302
C	-4.749566	-3.755724	0.108518
H	-4.064268	-3.691076	2.689611
H	-2.258723	-2.373722	3.723849
C	-5.011759	-3.716127	-1.24717
C	-4.230485	-2.896386	-2.071529
H	-5.340211	-4.385491	0.766015
H	-5.810721	-4.313549	-1.669525
H	-4.425228	-2.861252	-3.137415
O	-0.691606	-0.78376	2.426952
C	-1.103654	-0.519649	-0.320712
C	-1.010704	0.530789	-1.110456
C	-2.017576	1.614083	-1.145525
C	-1.878359	2.612381	-2.117097
C	-3.06218	1.71601	-0.219594
C	-2.760112	3.685493	-2.164941
H	-1.064861	2.543601	-2.832268
C	-3.942073	2.790545	-0.269051
H	-3.179647	0.956309	0.545409
C	-3.794393	3.780181	-1.237993
H	-2.637078	4.449659	-2.923838
H	-4.744352	2.858432	0.457116
H	-4.480935	4.618088	-1.270585
H	-0.15697	0.65174	-1.767888
C	1.761783	2.362411	-0.588807
C	0.848563	3.326619	-0.283306
C	0.033887	3.17097	0.856131
C	0.209522	2.042491	1.663045
C	1.155079	1.110876	1.303715
N	1.904932	1.262473	0.197032
H	2.400144	2.411355	-1.460133

H	0.728767	4.192943	-0.919417
H	-0.388869	1.845705	2.539916
H	1.307221	0.204924	1.871385
O	-0.862533	4.11807	1.069971
C	-1.710307	4.004666	2.218141
H	-2.384648	4.855435	2.167325
H	-2.281872	3.075845	2.18232
H	-1.11486	4.052235	3.132472
C	2.905577	0.276623	-0.131854
C	2.542092	-1.000466	-0.424038
C	4.273127	0.817861	-0.027943
O	4.513341	1.947366	0.330148
O	5.212429	-0.061126	-0.375331
C	3.620316	-2.023441	-0.713743
O	3.950201	-2.34916	-1.819774
O	4.075783	-2.559885	0.41214
C	6.567285	0.395366	-0.267521
H	6.801384	0.639708	0.768883
H	7.182728	-0.431417	-0.611926
H	6.72139	1.271787	-0.896911
C	5.105306	-3.543635	0.243098
H	4.733731	-4.384592	-0.342967
H	5.967208	-3.098888	-0.256077
H	5.371132	-3.866803	1.245952
S	0.978117	-1.711288	-0.503853

Zero-point correction =	0.489770 (Hartree/Particle)
Thermal correction to Energy =	0.529592
Thermal correction to Enthalpy =	0.530616
Thermal correction to Gibbs Free Energy =	0.411346
Sum of electronic and zero-point Energies =	-2061.760060
Sum of electronic and thermal Energies =	-2061.720238
Sum of electronic and thermal Enthalpies =	-2061.719215
Sum of electronic and thermal Free Energies =	-2061.838485
SCF Done: E(RM062X) =	-2062.24983064 A.U.

IM3 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	-1.422414	-1.682722	1.844195
C	-1.617395	-1.494948	0.437559
C	-2.842189	-1.881995	-0.205429
C	-3.904082	-2.428699	0.573557
C	-3.707354	-2.604747	1.980187
C	-2.539536	-2.26673	2.576174

H	-2.290611	-1.371164	-2.24092
C	-3.074548	-1.760305	-1.604039
C	-5.120175	-2.804566	-0.035609
H	-4.522801	-3.024467	2.56292
H	-2.388689	-2.405447	3.641952
C	-5.315603	-2.661234	-1.389318
C	-4.26857	-2.138698	-2.173327
H	-5.903274	-3.216033	0.594312
H	-6.253306	-2.950305	-1.848695
H	-4.401834	-2.033368	-3.244644
O	-0.378781	-1.347406	2.467073
C	-0.525345	-0.910677	-0.347251
C	-0.531895	0.134943	-1.195622
C	-1.566824	1.166066	-1.343611
C	-1.490522	2.012759	-2.459151
C	-2.57241	1.408123	-0.394056
C	-2.384701	3.062389	-2.627496
H	-0.709466	1.845958	-3.194293
C	-3.457773	2.466219	-0.558449
H	-2.648955	0.77572	0.481938
C	-3.37127	3.296716	-1.673334
H	-2.30797	3.701194	-3.499888
H	-4.221475	2.643559	0.190589
H	-4.067728	4.117669	-1.797825
H	0.331165	0.272756	-1.844107
C	1.557629	2.421161	-0.251243
C	0.615901	3.321966	0.139235
C	-0.231234	3.01407	1.224109
C	-0.047302	1.801835	1.900147
C	0.935594	0.943654	1.471516
N	1.712743	1.239189	0.410375
H	2.203901	2.586591	-1.102427
H	0.485482	4.249009	-0.402148
H	-0.657797	1.489144	2.735165
H	1.071248	-0.022841	1.940522
O	-1.156249	3.906738	1.516204
C	-2.08196	3.608116	2.568526
H	-2.778517	4.441704	2.587866
H	-2.613662	2.679033	2.353838
H	-1.55752	3.535781	3.523285
C	2.687418	0.294599	-0.044539
C	2.407399	-1.007451	-0.282059
C	4.05408	0.886561	-0.134022
O	4.370034	1.890186	0.451179

O	4.85281	0.206394	-0.948551
C	3.570429	-1.961645	-0.511358
O	3.711307	-2.614579	-1.504915
O	4.340192	-2.017002	0.566446
C	6.232749	0.606077	-0.951095
H	6.319521	1.651531	-1.245373
H	6.662497	0.461478	0.041045
H	6.720815	-0.036004	-1.679034
C	5.51837	-2.828659	0.432142
H	6.1237	-2.464785	-0.399237
H	6.053353	-2.72476	1.371847
H	5.241268	-3.868825	0.261123
S	0.94801	-1.954699	-0.302372

Zero-point correction =	0.491947 (Hartree/Particle)
Thermal correction to Energy =	0.531284
Thermal correction to Enthalpy =	0.532308
Thermal correction to Gibbs Free Energy =	0.415747
Sum of electronic and zero-point Energies =	-2061.779751
Sum of electronic and thermal Energies =	-2061.740414
Sum of electronic and thermal Enthalpies =	-2061.739390
Sum of electronic and thermal Free Energies =	-2061.855951
SCF Done: E(RM062X) =	-2062.27169804 A.U.

TS3 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	-0.634506	-0.387122	1.284284
C	-1.372734	-0.042864	0.150021
C	-2.737961	-0.434877	0.013894
C	-3.360636	-1.168038	1.063859
C	-2.599174	-1.490833	2.224112
C	-1.289159	-1.131862	2.322144
H	-3.054599	0.433405	-1.945865
C	-3.513921	-0.121528	-1.135962
C	-4.716546	-1.555466	0.937227
H	-3.083125	-2.04192	3.024565
H	-0.696062	-1.388505	3.192919
C	-5.440139	-1.238323	-0.184953
C	-4.825681	-0.514337	-1.231264
H	-5.173105	-2.111023	1.750387
H	-6.477396	-1.539792	-0.272541
H	-5.397572	-0.266998	-2.118574
O	0.619091	-0.048901	1.414785
C	-0.738253	0.82656	-0.879891

C	-0.968088	2.13354	-1.066614
C	-1.918439	2.996275	-0.342088
C	-2.287448	2.805409	0.997288
C	-2.468382	4.085595	-1.032846
C	-3.197907	3.660571	1.607276
H	-1.848468	1.997496	1.568373
C	-3.381735	4.936475	-0.422502
H	-2.177342	4.256264	-2.064347
C	-3.754791	4.723899	0.901415
H	-3.468669	3.497726	2.644305
H	-3.799935	5.766717	-0.980156
H	-4.465451	5.386093	1.38214
H	-0.447943	2.624737	-1.886927
C	3.426033	0.024688	-1.235184
C	4.4508	0.910798	-1.389227
C	4.800294	1.755334	-0.321592
C	4.088359	1.643439	0.880597
C	3.064701	0.733686	0.97028
N	2.718033	-0.045158	-0.077195
H	3.142403	-0.672878	-2.008601
H	5.001278	0.951859	-2.318848
H	4.316472	2.245686	1.747531
H	2.481141	0.607107	1.867264
O	5.799823	2.59077	-0.529348
C	6.211274	3.451659	0.540832
H	7.035022	4.036231	0.141382
H	5.392125	4.110793	0.833334
H	6.550924	2.860434	1.393202
C	1.691575	-1.078315	0.038084
C	0.881199	-1.353673	-1.031938
C	2.096769	-2.131681	1.045935
O	3.246722	-2.315654	1.353197
O	1.061226	-2.771064	1.548873
C	0.432192	-2.729928	-1.301834
O	1.040482	-3.724137	-0.967234
O	-0.696498	-2.78395	-2.016259
C	1.365615	-3.900504	2.371127
H	1.940635	-3.593377	3.245206
H	0.404527	-4.309057	2.672736
H	1.92814	-4.636679	1.795331
C	-1.150228	-4.097168	-2.350712
H	-1.371256	-4.666051	-1.44675
H	-2.055603	-3.954564	-2.935623
H	-0.397735	-4.626169	-2.937197

S	0.32563	-0.006024	-2.04785

Zero-point correction =	0.492066 (Hartree/Particle)
Thermal correction to Energy =	0.530572
Thermal correction to Enthalpy =	0.531596
Thermal correction to Gibbs Free Energy =	0.415970
Sum of electronic and zero-point Energies =	-2061.768890
Sum of electronic and thermal Energies =	-2061.730383
Sum of electronic and thermal Enthalpies =	-2061.729360
Sum of electronic and thermal Free Energies =	-2061.844985
SCF Done: E(RM062X) =	-2062.26095552 A.U.

IM4 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	0.628406	-0.734708	-1.046458
C	1.405258	-0.174828	-0.057983
C	2.782048	-0.552859	0.037655
C	3.325449	-1.440878	-0.932103
C	2.488074	-1.951974	-1.957843
C	1.163721	-1.617506	-2.008322
H	3.228568	0.599238	1.816865
C	3.635215	-0.065779	1.064768
C	4.697592	-1.798938	-0.856544
H	2.914425	-2.623428	-2.695182
H	0.500287	-2.007897	-2.768267
C	5.496607	-1.305609	0.139376
C	4.954297	-0.433394	1.112721
H	5.096965	-2.474264	-1.605913
H	6.542826	-1.583643	0.189887
H	5.589882	-0.054973	1.904888
O	-0.698519	-0.368062	-1.189596
C	0.797215	0.783311	0.895397
C	1.11438	2.080556	1.017234
C	2.132172	2.833033	0.261997
C	2.802498	3.878958	0.910682
C	2.452825	2.568196	-1.076902
C	3.785592	4.613947	0.258458
H	2.552279	4.106569	1.941863
C	3.431972	3.307347	-1.729399
H	1.924393	1.790409	-1.615064
C	4.108177	4.327674	-1.064697
H	4.298084	5.41188	0.783626
H	3.664127	3.088705	-2.765512
H	4.873195	4.899421	-1.576935

H	0.606688	2.647485	1.795929
C	-3.587168	0.03599	0.8894
C	-4.561342	0.974777	1.075354
C	-4.60371	2.103656	0.240735
C	-3.64621	2.221949	-0.774495
C	-2.697674	1.235685	-0.913023
N	-2.66603	0.170227	-0.093955
H	-3.484411	-0.841302	1.509935
H	-5.286445	0.859306	1.869146
H	-3.620151	3.060653	-1.45453
H	-1.936198	1.279918	-1.675528
O	-5.557916	2.985753	0.484054
C	-5.623651	4.165991	-0.324884
H	-6.464642	4.735382	0.060716
H	-4.704508	4.746542	-0.225782
H	-5.80029	3.903147	-1.369609
C	-1.621428	-0.924193	-0.244111
C	-1.040496	-1.274916	1.069343
C	-2.385915	-2.110331	-0.892987
O	-3.427158	-2.512049	-0.448629
O	-1.805988	-2.552614	-1.992519
C	-0.533003	-2.596594	1.2174
O	-0.757491	-3.53663	0.455424
O	0.232364	-2.781598	2.324617
C	-2.343126	-3.780033	-2.501131
H	-2.277589	-4.547166	-1.729082
H	-3.380329	-3.645318	-2.808427
H	-1.72421	-4.042085	-3.355354
C	0.761485	-4.092614	2.484033
H	1.397104	-4.364561	1.639103
H	1.353097	-4.063879	3.397376
H	-0.035904	-4.831781	2.580728
S	-0.435183	0.076636	1.998999

Zero-point correction =	0.493523 (Hartree/Particle)
Thermal correction to Energy =	0.531963
Thermal correction to Enthalpy =	0.532987
Thermal correction to Gibbs Free Energy =	0.418007
Sum of electronic and zero-point Energies =	-2061.789009
Sum of electronic and thermal Energies =	-2061.750569
Sum of electronic and thermal Enthalpies =	-2061.749545
Sum of electronic and thermal Free Energies =	-2061.864525
SCF Done: E(RM062X) =	-2062.24868169 A.U.

TS4 for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	0.817181	-0.62217	-1.140337
C	1.658237	-0.341692	-0.093943
C	3.005428	-0.819116	-0.139141
C	3.449844	-1.504446	-1.303672
C	2.548053	-1.718478	-2.380118
C	1.249328	-1.299624	-2.298794
H	3.586036	-0.114742	1.824737
C	3.920842	-0.623388	0.928748
C	4.794084	-1.956658	-1.371662
H	2.905366	-2.231813	-3.266059
H	0.542006	-1.466773	-3.101356
C	5.657	-1.744904	-0.330282
C	5.210869	-1.075242	0.833643
H	5.120255	-2.475116	-2.267043
H	6.681602	-2.092575	-0.390253
H	5.897522	-0.921165	1.65783
O	-0.488735	-0.146059	-1.10049
C	1.139815	0.481878	1.020407
C	1.600081	1.692743	1.36872
C	2.713347	2.43816	0.754063
C	3.513845	3.234278	1.583708
C	2.998483	2.407171	-0.617808
C	4.59012	3.947077	1.06857
H	3.290441	3.282418	2.644552
C	4.071202	3.125006	-1.132075
H	2.370361	1.831905	-1.287529
C	4.876563	3.890451	-0.292111
H	5.203132	4.548935	1.729626
H	4.27578	3.090817	-2.196047
H	5.713983	4.44627	-0.697465
H	1.143656	2.175019	2.230636
C	-3.565086	0.562431	0.699532
C	-4.550578	1.51374	0.845264
C	-4.65587	2.523097	-0.120574
C	-3.756897	2.526565	-1.191324
C	-2.801627	1.522987	-1.245511
N	-2.712379	0.57113	-0.323026
H	-3.437351	-0.239133	1.422108
H	-5.235332	1.494378	1.682855
H	-3.784273	3.278029	-1.967517
H	-2.080952	1.48036	-2.053995
O	-5.626255	3.424593	0.058905

C	-5.761293	4.464196	-0.908634
H	-6.597497	5.072326	-0.573079
H	-4.85583	5.074322	-0.950783
H	-5.980578	4.048876	-1.895212
C	-1.362833	-0.922005	-0.33674
C	-1.063056	-1.277669	0.956081
C	-2.127849	-1.890171	-1.247235
O	-3.244048	-1.753632	-1.657679
O	-1.295493	-2.858375	-1.618729
C	-1.731156	-2.436155	1.535821
O	-2.522468	-3.152759	0.953616
O	-1.396471	-2.642064	2.819698
C	-1.858437	-3.855724	-2.480118
H	-2.692532	-4.347228	-1.978266
H	-2.201079	-3.405636	-3.412335
H	-1.057578	-4.565283	-2.670623
C	-2.023155	-3.762483	3.449288
H	-1.757993	-4.687597	2.936475
H	-1.645251	-3.775462	4.468651
H	-3.107513	-3.645292	3.448832
S	-0.128805	-0.231657	2.04983

Zero-point correction =	0.491327 (Hartree/Particle)
Thermal correction to Energy =	0.530018
Thermal correction to Enthalpy =	0.531041
Thermal correction to Gibbs Free Energy =	0.414203
Sum of electronic and zero-point Energies =	-2061.774915
Sum of electronic and thermal Energies =	-2061.736224
Sum of electronic and thermal Enthalpies =	-2061.735201
Sum of electronic and thermal Free Energies =	-2061.852039
SCF Done: E(RM062X) =	-2062.26624224 A.U.

Product for substrate 1-(phenylethynyl)naphthalen-2-ol (2a)

C	0.122424	1.099419	-0.562809
C	-0.7378	0.331775	0.179583
C	-1.734681	0.977462	0.974808
C	-1.825062	2.397078	0.929647
C	-0.920532	3.137029	0.121846
C	0.048528	2.504809	-0.607505
H	-2.569447	-0.81982	1.850023
C	-2.640003	0.260055	1.799888
C	-2.824017	3.051708	1.697348

H	-1.008264	4.217637	0.098365
H	0.754653	3.045209	-1.225839
C	-3.689528	2.333305	2.477578
C	-3.59093	0.922915	2.530704
H	-2.883688	4.133902	1.652447
H	-4.449629	2.840426	3.059973
H	-4.274508	0.362873	3.158011
O	1.077968	0.453114	-1.33643
C	-0.586959	-1.139481	0.108032
C	-1.484881	-2.018446	-0.354182
C	-2.822601	-1.71676	-0.893565
C	-3.842258	-2.652427	-0.680768
C	-3.113989	-0.553991	-1.618266
C	-5.131421	-2.4154	-1.142236
H	-3.618276	-3.566241	-0.140356
C	-4.401187	-0.324463	-2.08739
H	-2.33036	0.162784	-1.831603
C	-5.415323	-1.247443	-1.843566
H	-5.911861	-3.14479	-0.959507
H	-4.612212	0.576984	-2.650796
H	-6.418734	-1.061966	-2.208633
H	-1.237395	-3.075697	-0.295613
C	2.207147	0.1011	-0.636496
C	2.218184	-0.854885	0.301593
C	3.444973	0.865353	-0.962396
O	4.524412	0.631872	-0.476381
O	3.214384	1.832172	-1.841307
C	3.481177	-1.19526	1.06159
O	3.728603	-0.759715	2.150321
O	4.197144	-2.095637	0.407248
C	4.360584	2.617698	-2.2027
H	4.76726	3.116516	-1.322881
H	5.124313	1.982641	-2.651726
H	3.999578	3.346678	-2.92272
C	5.44944	-2.439855	1.020312
H	5.282214	-2.868928	2.008372
H	5.90841	-3.16941	0.359015
H	6.073712	-1.549581	1.10178
S	0.877277	-1.829465	0.876737

Zero-point correction =	0.367849 (Hartree/Particle)
Thermal correction to Energy =	0.397946
Thermal correction to Enthalpy =	0.398969
Thermal correction to Gibbs Free Energy =	0.301685

Sum of electronic and zero-point Energies =	-1699.148420
Sum of electronic and thermal Energies =	-1699.118323
Sum of electronic and thermal Enthalpies =	-1699.117300
Sum of electronic and thermal Free Energies =	-1699.214584
SCF Done: E(RM062X) =	-1699.51626903 A.U.

Cartesian coordinates for other substrates

4b

C	-4.923909	0.838195	0.000158
C	-3.531514	0.875369	0.000135
C	-2.796836	-0.325317	-0.000062
C	-3.484458	-1.547351	-0.000233
C	-4.869499	-1.579098	-0.000184
C	-5.585408	-0.381278	0.000007
H	-5.466569	1.77591	0.000296
H	-2.909257	-2.46554	-0.000398
O	-2.930335	2.084982	0.000308
H	-1.969089	1.970939	-0.000008
C	-1.370192	-0.260212	-0.000081
C	-0.16591	-0.148697	-0.00007
C	1.258072	-0.027659	-0.000068
C	2.07237	-1.163708	0.0003
C	1.865381	1.239922	-0.000407
C	3.457729	-1.052569	0.000387
H	1.615762	-2.146327	0.000529
C	3.240161	1.358001	-0.000323
H	1.246287	2.129384	-0.00075
C	4.048438	0.213454	0.00011
H	4.060135	-1.951027	0.000665
H	3.719085	2.329741	-0.000607
H	-5.390055	-2.528493	-0.000303
H	-6.669053	-0.396981	0.000035
O	5.379953	0.433328	0.000291
C	6.241276	-0.697248	-0.000205
H	7.253918	-0.300211	-0.000659
H	6.089269	-1.30743	0.894351
H	6.088427	-1.307267	-0.894715

Zero-point correction =	0.230096 (Hartree/Particle)
Thermal correction to Energy =	0.247042
Thermal correction to Enthalpy =	0.248065
Thermal correction to Gibbs Free Energy =	0.181684
Sum of electronic and zero-point Energies =	-728.884112

Sum of electronic and thermal Energies =	-728.867167
Sum of electronic and thermal Enthalpies =	-728.866143
Sum of electronic and thermal Free Energies =	-728.932524
SCF Done: E(RM062X) =	-729.114208479 A.U.

IM2 for substrate 4b

C	3.239726	0.323264	1.006089
C	2.543775	0.269739	-0.32956
C	3.196815	-0.381048	-1.463231
C	4.414962	-0.931375	-1.324364
C	5.100648	-0.887662	-0.044322
C	4.563267	-0.30706	1.046307
H	5.082385	-0.279245	1.99733
O	2.736434	0.850594	1.981652
C	1.346748	0.819256	-0.445752
C	0.175319	1.377047	-0.550383
C	-1.123069	0.720894	-0.312366
C	-1.21658	-0.612026	0.116105
C	-2.298903	1.438296	-0.515997
C	-2.446967	-1.19843	0.32743
H	-0.312446	-1.1869	0.28741
C	-3.548468	0.858493	-0.306954
H	-2.243355	2.470622	-0.844594
C	-3.625428	-0.467586	0.116495
H	-2.529769	-2.226506	0.659549
H	-4.441169	1.445378	-0.476081
H	0.151598	2.427253	-0.841028
H	2.666501	-0.401208	-2.408093
H	4.90262	-1.414037	-2.16206
H	6.082795	-1.343798	0.022372
O	-4.779601	-1.131291	0.349581
C	-5.997888	-0.429155	0.148301
H	-6.791806	-1.134322	0.38437
H	-6.068315	0.43504	0.814898
H	-6.097463	-0.102579	-0.890713

Zero-point correction =	0.228883 (Hartree/Particle)
Thermal correction to Energy =	0.245836
Thermal correction to Enthalpy =	0.246859
Thermal correction to Gibbs Free Energy =	0.179401
Sum of electronic and zero-point Energies =	-728.854436
Sum of electronic and thermal Energies =	-728.837483
Sum of electronic and thermal Enthalpies =	-728.836460

Sum of electronic and thermal Free Energies =	-728.903918
SCF Done: E(RM062X) =	-729.083318949 A.U.

4c

C	5.181792	0.920535	0.010122
C	3.788189	0.928069	0.014395
C	3.083019	-0.290102	-0.00232
C	3.796453	-1.498413	-0.023095
C	5.180212	-1.499081	-0.027476
C	5.868152	-0.283796	-0.010691
H	5.704299	1.869364	0.023529
H	3.240258	-2.428047	-0.036025
O	3.164275	2.124018	0.034881
H	2.204786	1.996326	0.035637
C	1.657307	-0.265866	0.001171
C	0.450545	-0.19859	0.004018
C	-0.976178	-0.140896	0.004038
C	-1.724766	-1.326985	0.028746
C	-1.63095	1.099432	-0.022127
C	-3.108179	-1.277091	0.026449
H	-1.215181	-2.281708	0.049166
C	-3.014098	1.156572	-0.024431
H	-1.050511	2.013051	-0.041011
C	-3.725826	-0.034482	-0.000513
H	-3.701911	-2.180579	0.044801
H	-3.536475	2.102972	-0.044564
H	5.723022	-2.435608	-0.043984
H	6.951888	-0.275702	-0.013917
N	-5.196808	0.023238	-0.00424
O	-5.720849	1.116908	-0.027454
O	-5.805495	-1.025746	0.015865

Zero-point correction =	0.199844 (Hartree/Particle)
Thermal correction to Energy =	0.216877
Thermal correction to Enthalpy =	0.217900
Thermal correction to Gibbs Free Energy =	0.149087
Sum of electronic and zero-point Energies =	-818.886465
Sum of electronic and thermal Energies =	-818.869433
Sum of electronic and thermal Enthalpies =	-818.868410
Sum of electronic and thermal Free Energies =	-818.937223
SCF Done: E(RM062X) =	-819.086309600 A.U.

IM2 for substrate 4c

C	3.434503	-0.00869	1.05855
C	2.771616	0.341162	-0.251984
C	3.411269	-0.023961	-1.51462
C	4.593343	-0.661511	-1.513687
C	5.251672	-0.998031	-0.26185
C	4.722349	-0.698863	0.939886
H	5.220194	-0.954673	1.867949
O	2.930411	0.26455	2.131509
C	1.616324	0.977232	-0.22095
C	0.481286	1.613452	-0.17324
C	-0.84676	0.973675	-0.120268
C	-0.992518	-0.417672	-0.052674
C	-1.983557	1.786963	-0.134944
C	-2.251375	-0.988677	-0.004968
H	-0.114754	-1.053276	-0.032519
C	-3.252136	1.228528	-0.087395
H	-1.871233	2.863575	-0.183744
C	-3.3607	-0.151748	-0.024675
H	-2.380577	-2.06079	0.049033
H	-4.139562	1.846245	-0.097698
H	0.508001	2.702154	-0.172387
H	2.903144	0.238497	-2.434924
H	5.074767	-0.933147	-2.444799
H	6.206238	-1.510945	-0.31242
N	-4.701859	-0.754818	0.02543
O	-5.659928	-0.010697	0.010573
O	-4.778622	-1.964488	0.07797

Zero-point correction =	0.198912 (Hartree/Particle)
Thermal correction to Energy =	0.215813
Thermal correction to Enthalpy =	0.216837
Thermal correction to Gibbs Free Energy =	0.148740
Sum of electronic and zero-point Energies =	-818.857787
Sum of electronic and thermal Energies =	-818.840885
Sum of electronic and thermal Enthalpies =	-818.839862
Sum of electronic and thermal Free Energies =	-818.907958
SCF Done: E(RM062X) =	-819.056698645 A.U.

4d

C	-2.105866	0.973108	-0.000002
C	-0.713517	0.923934	0.000005
C	-0.053481	-0.318266	-0.000001

C	-0.81404	-1.494665	-0.000002
C	-2.199275	-1.442645	0.000006
C	-2.840723	-0.203781	0.000006
H	-2.589778	1.94249	-0.000022
H	-0.296199	-2.446465	-0.000006
O	-0.036388	2.093135	0.000024
H	0.915155	1.913044	-0.000176
C	1.378979	-0.338569	-0.000025
C	2.584877	-0.298443	-0.000032
H	-2.776584	-2.358713	0.000021
H	-3.923338	-0.15345	0.000002
C	4.043617	-0.273231	0.000026
H	4.438486	-1.290847	-0.000788
H	4.419984	0.24282	-0.885425
H	4.419957	0.241397	0.886316

Zero-point correction =	0.143190 (Hartree/Particle)
Thermal correction to Energy =	0.153932
Thermal correction to Enthalpy =	0.154956
Thermal correction to Gibbs Free Energy =	0.104243
Sum of electronic and zero-point Energies =	-422.745065
Sum of electronic and thermal Energies =	-422.734323
Sum of electronic and thermal Enthalpies =	-422.733300
Sum of electronic and thermal Free Energies =	-422.784012
SCF Done: E(RM062X) =	-422.888255519 A.U.

IM2 for substrate 4d

C	0.698432	1.058221	-0.042212
C	-0.029551	-0.250199	-0.174596
C	0.712101	-1.505426	-0.111532
C	2.044923	-1.503765	0.066939
C	2.764166	-0.249913	0.199237
C	2.147876	0.947972	0.149999
H	2.694014	1.878976	0.249211
O	0.125745	2.133358	-0.090561
C	-1.343903	-0.234859	-0.346097
C	-2.628563	-0.205921	-0.507725
H	-3.005057	-0.166297	-1.529376
H	0.153016	-2.428474	-0.212569
H	2.59905	-2.432794	0.114699
H	3.838846	-0.291881	0.34313
C	-3.632583	-0.217674	0.615155
H	-4.248672	0.682797	0.566532
H	-4.294145	-1.080533	0.512004
H	-3.140403	-0.259276	1.585854

Zero-point correction =	0.142305 (Hartree/Particle)
Thermal correction to Energy =	0.152879
Thermal correction to Enthalpy =	0.153902
Thermal correction to Gibbs Free Energy =	0.103652
Sum of electronic and zero-point Energies =	-422.714106
Sum of electronic and thermal Energies =	-422.703532
Sum of electronic and thermal Enthalpies =	-422.702508
Sum of electronic and thermal Free Energies =	-422.752759
SCF Done: E(RM062X) =	-422.856410928 A.U.

4e

C	2.805691	1.560745	-0.020942
C	1.415851	1.368637	-0.011931
C	0.858244	0.079083	-0.016314
C	1.694224	-1.064726	-0.032947
C	3.043744	-0.855624	-0.040996
C	3.585216	0.431429	-0.034383
H	3.223704	2.558558	-0.019227
H	1.266286	-2.058417	-0.045894
O	0.65013	2.482406	0.006539
H	-0.28542	2.233928	0.01879
C	-0.560824	-0.049082	-0.009705

C	-1.76908	-0.102755	-0.001172
C	-3.197527	-0.182744	0.004237
C	-3.835224	-1.431226	-0.009144
C	-3.969903	0.986997	0.022493
C	-5.221712	-1.502367	-0.004333
H	-3.236983	-2.334407	-0.023313
C	-5.35571	0.904585	0.027109
H	-3.476205	1.951582	0.032784
C	-5.985027	-0.337641	0.013727
H	-5.707835	-2.470749	-0.014952
H	-5.946114	1.813136	0.041056
H	-7.066931	-0.397827	0.017292
O	4.939429	0.349108	-0.073938
O	4.062583	-1.768732	-0.101597
C	5.238849	-1.024771	0.2011
H	6.053592	-1.351815	-0.439407
H	5.477911	-1.129501	1.264053

Zero-point correction =	0.213174 (Hartree/Particle)
Thermal correction to Energy =	0.229810
Thermal correction to Enthalpy =	0.230833
Thermal correction to Gibbs Free Energy =	0.164618
Sum of electronic and zero-point Energies =	-802.907247
Sum of electronic and thermal Energies =	-802.890611
Sum of electronic and thermal Enthalpies =	-802.889588
Sum of electronic and thermal Free Energies =	-802.955803
SCF Done: E(RM062X) =	-803.120421028 A.U.

IM2 for substrate 4e

C	1.225601	1.554492	0.097494
C	0.665665	0.28737	-0.531222
C	1.496288	-0.909794	-0.686502
C	2.75776	-0.829356	-0.259067
C	3.312417	0.375874	0.332583
C	2.624144	1.515716	0.516794
H	3.062753	2.398138	0.963105
O	0.534585	2.547026	0.236462
C	-0.592482	0.306763	-0.925248
C	-1.835582	0.33953	-1.313566
C	-3.003661	-0.012047	-0.479538
C	-2.873058	-0.334785	0.875982
C	-4.27302	-0.018698	-1.062229
C	-3.992343	-0.661098	1.627936

H	-1.891278	-0.322126	1.337698
C	-5.393874	-0.346735	-0.306011
H	-4.377874	0.234657	-2.111774
C	-5.256818	-0.669261	1.039672
H	-3.881138	-0.907392	2.677549
H	-6.373588	-0.348483	-0.769417
H	-6.129135	-0.923449	1.630302
H	-2.039544	0.650121	-2.337751
H	1.081851	-1.807945	-1.124197
O	4.588639	0.129937	0.658557
O	3.722019	-1.78294	-0.252041
C	4.937136	-1.157735	0.13901
H	5.58456	-1.025453	-0.729555
H	5.412407	-1.74166	0.923701

Zero-point correction =	0.212380 (Hartree/Particle)
Thermal correction to Energy =	0.228965
Thermal correction to Enthalpy =	0.229988
Thermal correction to Gibbs Free Energy =	0.163071
Sum of electronic and zero-point Energies =	-802.890048
Sum of electronic and thermal Energies =	-802.873463
Sum of electronic and thermal Enthalpies =	-802.872439
Sum of electronic and thermal Free Energies =	-802.939357
SCF Done: E(RM062X) =	-803.102427686 A.U.

4f

C	-2.553409	-1.497061	0.000015
C	-1.161271	-1.373246	0.000019
C	-0.56937	-0.109573	-0.000005
C	-1.3949	1.037859	-0.000028
C	-2.767453	0.924219	-0.000026
C	-3.35631	-0.368807	-0.000011
H	-2.975806	-2.49236	0.000042
H	-0.918664	2.008892	-0.000056
O	-0.442104	-2.520016	0.000071
H	0.502109	-2.307638	0.000106
C	0.851577	-0.006293	0.000006
C	2.061142	0.018883	0.000004
C	3.491214	0.060753	-0.000002
C	4.164171	1.290707	0.0001
C	4.231172	-1.130092	-0.000107
C	5.552191	1.323006	0.000097
H	3.591527	2.210454	0.00018

C	5.618743	-1.0867	-0.000106
H	3.710554	-2.080493	-0.000189
C	6.282833	0.137392	-0.000004
H	6.065306	2.277448	0.000177
H	6.183474	-2.01155	-0.000185
H	7.366031	0.167168	-0.000003
O	-4.701147	-0.392213	-0.00002
O	-3.640424	1.961657	-0.000031
C	-3.084531	3.265566	-0.000037
H	-2.476845	3.436573	0.893943
H	-2.476758	3.436544	-0.893966
H	-3.929003	3.951623	-0.000064
C	-5.336362	-1.66362	0.000036
H	-5.072142	-2.234439	-0.894498
H	-5.072042	-2.234413	0.894553
H	-6.404962	-1.461193	0.000093

Zero-point correction =	0.262915 (Hartree/Particle)
Thermal correction to Energy =	0.282958
Thermal correction to Enthalpy =	0.283982
Thermal correction to Gibbs Free Energy =	0.210052
Sum of electronic and zero-point Energies =	-843.355943
Sum of electronic and thermal Energies =	-843.335900
Sum of electronic and thermal Enthalpies =	-843.334876
Sum of electronic and thermal Free Energies =	-843.408806
SCF Done: E(RM062X) =	-843.618858062 A.U.

IM2 for substrate 4f

C	-0.986479	-1.531287	-0.405307
C	-0.388323	-0.16604	-0.635641
C	-1.206822	1.028633	-0.449803
C	-2.494143	0.923049	-0.071794
C	-3.094773	-0.405753	0.161239
C	-2.380674	-1.548718	0.002746
H	-2.817288	-2.523474	0.170779
O	-0.335592	-2.552296	-0.552653
C	0.8772	-0.093846	-0.999567
C	2.128859	-0.046119	-1.359125
C	3.282355	0.027015	-0.437946
C	3.118277	0.038037	0.951929
C	4.572109	0.083743	-0.97119
C	4.224307	0.106449	1.786592
H	2.119777	-0.011139	1.373641

C	5.679864	0.152144	-0.131973
H	4.703681	0.072102	-2.047847
C	5.509483	0.164232	1.248011
H	4.086013	0.113101	2.861555
H	6.675498	0.194821	-0.558049
H	6.371287	0.216314	1.902969
H	2.35416	-0.063322	-2.424939
H	-0.74389	1.989812	-0.625058
O	-4.369992	-0.340237	0.530212
O	-3.352524	1.937421	0.131175
C	-2.848376	3.249023	-0.077298
H	-2.515689	3.377692	-1.111474
H	-3.675096	3.924329	0.129939
H	-2.019074	3.45965	0.604295
C	-5.053059	-1.567384	0.777062
H	-4.575226	-2.115126	1.592787
H	-6.065282	-1.289513	1.059068
H	-5.072832	-2.183421	-0.125146

Zero-point correction =	0.262824 (Hartree/Particle)
Thermal correction to Energy =	0.282408
Thermal correction to Enthalpy =	0.283432
Thermal correction to Gibbs Free Energy =	0.210867
Sum of electronic and zero-point Energies =	-843.337692
Sum of electronic and thermal Energies =	-843.318108
Sum of electronic and thermal Enthalpies =	-843.317084
Sum of electronic and thermal Free Energies =	-843.389650
SCF Done: E(RM062X) =	-843.600516210 A.U.

4g

C	3.966958	1.031343	-0.000089
C	3.235301	-0.164765	-0.000021
C	3.917027	-1.389775	0.000039
C	5.305323	-1.412994	0.000032
C	6.027715	-0.222444	-0.000034
C	5.354777	0.996971	-0.000094
H	7.111115	-0.244725	-0.000039
H	5.91315	1.92573	-0.000146
C	1.805307	-0.129829	-0.000011
C	0.596925	-0.07223	-0.000003
C	-0.823941	-0.088357	-0.000007
C	-1.581448	1.108587	-0.000005
C	-1.507861	-1.31161	-0.000007

C	-2.96427	1.067652	0.000002
C	-2.901345	-1.368807	0
C	-3.615649	-0.17642	0.000007
H	-3.570828	1.961795	0.000008
H	-3.377414	-2.338661	-0.000004
H	3.351686	-2.314315	0.000093
H	5.824805	-2.364032	0.000079
O	-0.846979	-2.486482	-0.000017
O	-0.858955	2.243426	-0.000011
C	-1.563646	3.479065	0.000036
H	-2.184218	3.57518	-0.894743
H	-2.184207	3.575116	0.894829
H	-0.801049	4.254616	0.000058
O	-4.961904	-0.112599	0.000011
C	-5.687348	-1.335678	0.00011
H	-6.738857	-1.057518	0.00017
H	-5.464997	-1.923168	-0.894568
H	-5.464874	-1.923094	0.894805
H	0.107665	-2.322726	0.000009
H	3.437786	1.976796	-0.000136

Zero-point correction =	0.262999 (Hartree/Particle)
Thermal correction to Energy =	0.282994
Thermal correction to Enthalpy =	0.284018
Thermal correction to Gibbs Free Energy =	0.210395
Sum of electronic and zero-point Energies =	-843.364700
Sum of electronic and thermal Energies =	-843.344705
Sum of electronic and thermal Enthalpies =	-843.343682
Sum of electronic and thermal Free Energies =	-843.417305
SCF Done: E(RM062X) =	-843.627699859 A.U.

IM2 for substrate 4g

C	-2.863167	-0.322071	0.964342
C	-3.01919	-0.145348	-0.415196
C	-4.306098	-0.09112	-0.955016
C	-5.420625	-0.211211	-0.130973
C	-5.259096	-0.3865	1.238973
C	-3.976299	-0.441481	1.783401
H	-6.126381	-0.480476	1.881877
H	-3.845413	-0.579281	2.850416
C	-1.859003	-0.015104	-1.31948
C	-0.611207	-0.031494	-0.950988
C	0.651032	-0.082656	-0.580859

C	1.380252	1.137126	-0.202518
C	1.355115	-1.422484	-0.536825
C	2.67227	1.064007	0.182438
C	2.734964	-1.399114	-0.110667
C	3.339004	-0.222567	0.221947
H	3.252748	1.928527	0.47116
H	3.248448	-2.349185	-0.073565
H	-4.429282	0.045527	-2.023992
H	-6.414466	-0.168122	-0.561054
O	0.764892	-2.445073	-0.848719
O	0.648279	2.252558	-0.280222
C	1.284294	3.477429	0.072656
H	1.618926	3.451307	1.112735
H	2.133415	3.674284	-0.586829
H	0.530949	4.250881	-0.053995
O	4.609102	-0.110531	0.623066
C	5.393658	-1.297453	0.708108
H	6.376163	-0.978863	1.047447
H	4.960192	-1.995068	1.4286
H	5.475847	-1.775629	-0.270756
H	-2.068494	0.107716	-2.381242
H	-1.866271	-0.367004	1.390135

Zero-point correction =	0.262527 (Hartree/Particle)
Thermal correction to Energy =	0.282195
Thermal correction to Enthalpy =	0.283218
Thermal correction to Gibbs Free Energy =	0.210257
Sum of electronic and zero-point Energies =	-843.345170
Sum of electronic and thermal Energies =	-843.325502
Sum of electronic and thermal Enthalpies =	-843.324478
Sum of electronic and thermal Free Energies =	-843.397439
SCF Done: E(RM062X) =	-843.607696271 A.U.

4h

C	3.018335	1.207199	0.000109
C	1.63619	1.123633	0.0001
C	0.998091	-0.136295	-0.000022
C	1.793427	-1.286077	-0.000129
C	3.177717	-1.214889	-0.00012
C	3.791022	0.044712	-0.000003
H	3.502402	2.175831	0.00021
H	1.306023	-2.253693	-0.00022
O	0.935062	2.276488	0.000218

H	-0.012986	2.079688	0.000246
C	-0.426152	-0.19191	-0.000031
C	-1.635565	-0.177111	-0.000029
C	-3.066428	-0.176056	-0.000024
C	-3.773831	-1.386291	0.000209
C	-3.771293	1.035695	-0.000247
C	-5.16216	-1.37884	0.000214
H	-3.227407	-2.32183	0.000384
C	-5.159594	1.032042	-0.000233
H	-3.223518	1.970712	-0.000432
C	-5.858264	-0.172621	-0.000004
H	-5.702622	-2.318052	0.000395
H	-5.697689	1.972605	-0.000406
H	-6.94189	-0.171392	0.000005
O	5.126191	0.235631	0.000021
H	3.760254	-2.12529	-0.00021
C	5.965101	-0.912163	-0.000064
H	5.801415	-1.518839	0.894543
H	5.801424	-1.518697	-0.894769
H	6.985008	-0.534171	-0.000024

Zero-point correction =	0.229954 (Hartree/Particle)
Thermal correction to Energy =	0.246987
Thermal correction to Enthalpy =	0.248010
Thermal correction to Gibbs Free Energy =	0.181082
Sum of electronic and zero-point Energies =	-728.884422
Sum of electronic and thermal Energies =	-728.867389
Sum of electronic and thermal Enthalpies =	-728.866366
Sum of electronic and thermal Free Energies =	-728.933294
SCF Done: E(RM062X) =	-729.114375561 A.U.

IM2 for substrate 4h

C	1.445194	1.317177	0.366893
C	0.793137	0.304289	-0.544536
C	1.566462	-0.831027	-1.032148
C	2.854083	-0.993677	-0.687471
C	3.49824	-0.022325	0.189995
C	2.831896	1.058991	0.681403
H	3.34532	1.75746	1.330767
O	0.824857	2.278082	0.797568
C	-0.47349	0.463069	-0.880411
C	-1.722671	0.634023	-1.202755
C	-2.881416	0.113336	-0.448459

C	-2.727265	-0.558201	0.769681
C	-4.164518	0.301814	-0.96667
C	-3.838638	-1.034315	1.449821
H	-1.734163	-0.698771	1.183429
C	-5.277108	-0.176833	-0.282072
H	-4.287176	0.825349	-1.908625
C	-5.117453	-0.84617	0.926201
H	-3.709633	-1.551165	2.393645
H	-6.268026	-0.024518	-0.693666
H	-5.983404	-1.217965	1.461208
H	-1.934777	1.208827	-2.103628
H	1.071473	-1.541524	-1.683444
O	4.781762	-0.161273	0.548082
H	3.412697	-1.841093	-1.05919
C	5.54206	-1.269444	0.066574
H	5.117053	-2.215955	0.406676
H	5.612626	-1.254567	-1.02295
H	6.533983	-1.144807	0.494293

Zero-point correction =	0.229044 (Hartree/Particle)
Thermal correction to Energy =	0.245994
Thermal correction to Enthalpy =	0.247017
Thermal correction to Gibbs Free Energy =	0.179933
Sum of electronic and zero-point Energies =	-728.856861
Sum of electronic and thermal Energies =	-728.839912
Sum of electronic and thermal Enthalpies =	-728.838889
Sum of electronic and thermal Free Energies =	-728.905973
SCF Done: E(RM062X) =	-729.085905610 A.U.

4i

C	-3.102517	1.383024	0.000053
C	-1.713789	1.279273	0.000091
C	-1.114	0.011197	0.000071
C	-1.93708	-1.126537	0.000027
C	-3.319161	-1.030242	-0.000005
C	-3.909364	0.251864	0.000001
H	-3.542891	2.374079	0.000072
H	-1.464329	-2.102726	0.000014
O	-0.992842	2.423501	0.000146
H	-0.048489	2.211576	0.000168
C	0.309621	-0.08481	0.000111
C	1.518742	-0.10626	0.000118
C	2.94921	-0.146199	0.000011
C	3.622371	-1.375855	-0.000189

C	3.687409	1.045401	0.000116
C	5.010396	-1.407138	-0.000282
H	3.050029	-2.295768	-0.000268
C	5.075016	1.003104	0.00002
H	3.165727	1.995189	0.000275
C	5.739651	-0.220675	-0.00018
H	5.524467	-2.361023	-0.000438
H	5.639243	1.928215	0.000102
H	6.822886	-0.249574	-0.000254
C	-4.177449	-2.267114	-0.000005
H	-4.826719	-2.299398	0.879875
H	-4.827102	-2.299153	-0.879605
H	-3.560082	-3.16598	-0.000252
C	-5.406101	0.39303	-0.000058
H	-5.843467	-0.088888	-0.879367
H	-5.843609	-0.089388	0.8789
H	-5.700664	1.442458	0.000207

Zero-point correction =	0.252157 (Hartree/Particle)
Thermal correction to Energy =	0.270128
Thermal correction to Enthalpy =	0.271151
Thermal correction to Gibbs Free Energy =	0.202508
Sum of electronic and zero-point Energies =	-692.965153
Sum of electronic and thermal Energies =	-692.947182
Sum of electronic and thermal Enthalpies =	-692.946158
Sum of electronic and thermal Free Energies =	-693.014802
SCF Done: E(RM062X) =	-693.217309819 A.U.

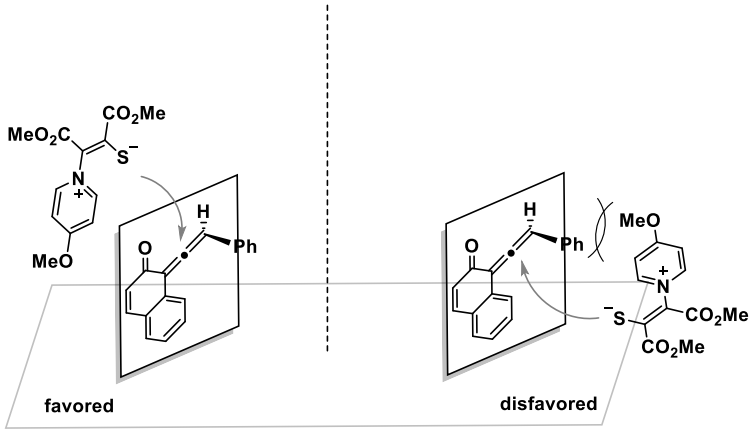
IM2 for substrate 4i

C	1.529388	1.475636	-0.02298
C	0.910563	0.206868	-0.543155
C	1.709953	-1.013531	-0.589674
C	2.99095	-1.04043	-0.177523
C	3.613154	0.193723	0.335388
C	2.920753	1.353175	0.401474
H	3.384066	2.258318	0.77972
O	0.912293	2.525241	0.038019
C	-0.348555	0.228204	-0.940074
C	-1.590551	0.260437	-1.329803
C	-2.765657	0.001218	-0.472211
C	-2.637084	-0.262411	0.896218
C	-4.03861	0.019127	-1.046621
C	-3.762736	-0.506485	1.669472

H	-1.651886	-0.271466	1.35069
C	-5.16575	-0.226087	-0.268554
H	-4.14193	0.226139	-2.106384
C	-5.031152	-0.490253	1.089947
H	-3.65303	-0.709025	2.728533
H	-6.148326	-0.209761	-0.725543
H	-5.908173	-0.681454	1.697088
H	-1.785205	0.495697	-2.375611
H	1.23263	-1.909952	-0.97078
C	3.802769	-2.304665	-0.226932
H	4.693011	-2.179141	-0.849284
H	4.144443	-2.593961	0.770929
H	3.209359	-3.122148	-0.636843
C	5.04384	0.133889	0.783051
H	5.168203	-0.605117	1.579576
H	5.691893	-0.174659	-0.042408
H	5.378966	1.104116	1.148026

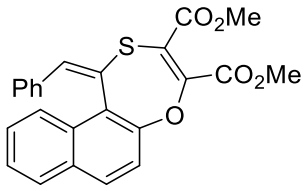
Zero-point correction =	0.251532 (Hartree/Particle)
Thermal correction to Energy =	0.269225
Thermal correction to Enthalpy =	0.270248
Thermal correction to Gibbs Free Energy =	0.201820
Sum of electronic and zero-point Energies =	-692.938538
Sum of electronic and thermal Energies =	-692.920845
Sum of electronic and thermal Enthalpies =	-692.919822
Sum of electronic and thermal Free Energies =	-692.988250
SCF Done: E(RM062X) = ……	-693.190070319 A.U.

9. Figure S1 Steric selectivity of the addition of *S*-anion to allene moiety

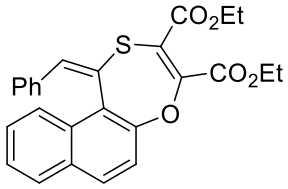


The transition state TS2 for nucleophilic addition of S-anion to allene moiety is the rate-determining transition state. As shown in Figure S1, steric hindrance makes reaction attacked from phenyl side (transition state TS2') less favorable.

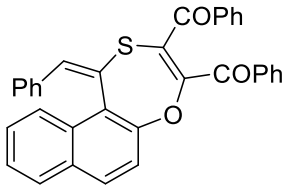
10. **Characterization Data**



Dimethyl (*E*)-1-benzylidene-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3a** (41 mg, Yield = 98%, R_f = 0.25 (PE/EA = 5:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.09 (d, J = 9.2 Hz, 1H), 7.96 (d, J = 8.0 Hz, 1H), 7.65–7.60 (m, 2H), 7.58 (s, 1H), 7.47–7.41 (m, 1H), 7.36–7.31 (m, 1H), 7.13–6.96 (m, 5H), 3.88 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.6, 162.8, 155.1, 141.6, 139.9, 135.7, 133.0, 132.3, 130.8, 129.6, 129.5, 129.4, 129.1, 129.0, 128.9, 128.4, 127.0, 125.4, 123.2, 121.5, 53.6, 53.3; ESI-HRMS *m/z* calcd for $C_{24}H_{19}O_5S$ $[M + H]^+$ 419.0948, found 419.0944.

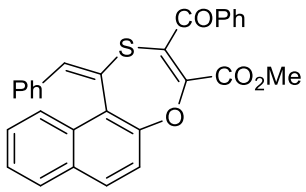


Diethyl (*E*)-1-benzylidene-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3b** (44 mg, Yield = 98%, R_f = 0.12 (PE/EA = 10:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.10 (d, J = 9.2 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.66–7.60 (m, 2H), 7.58 (s, 1H), 7.48–7.43 (m, 1H), 7.38–7.32 (m, 1H), 7.12–7.01 (m, 3H), 7.00–6.96 (m, 2H), 4.40–4.26 (m, 2H), 4.20 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.0, 162.3, 155.2, 141.8, 139.7, 135.7, 132.9, 132.3, 130.6, 129.6, 129.5, 129.3, 129.1, 129.0 (2C), 128.3, 126.9, 125.4, 123.4, 121.5, 63.1, 62.7, 14.4, 14.0; ESI-HRMS *m/z* calcd for $C_{26}H_{23}O_5S$ $[M + H]^+$ 447.1261, found 447.1260.

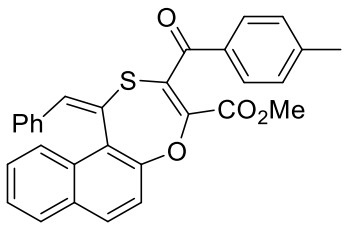


(*E*)-(1-Benzylidene-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-diyl)bis(phenylmethanone). Compound **3c** (50 mg, Yield = 98%, R_f = 0.17 (PE/EA = 10:1)) was isolated as a yellow solid; mp 178–179 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.89–7.86 (m, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 9.2 Hz, 1H), 7.64–7.56 (m, 2H), 7.52–7.44 (m, 4H), 7.43–7.33 (m, 3H), 7.32–7.27 (m, 1H), 7.12–7.07 (m, 1H), 7.06–7.00 (m, 2H), 6.97–6.93 (m,2H), 6.91 (d, J = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.2, 187.8, 154.0, 144.9, 139.9, 138.8, 136.5, 135.6, 134.6, 133.6, 132.9, 131.9, 131.4,

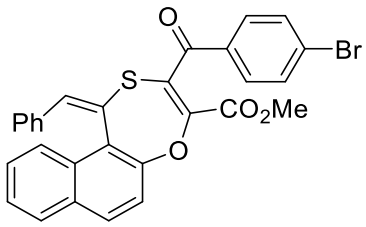
130.1, 129.0, 128.8, 128.7, 128.6, 128.4, 128.3, 127.5, 126.1, 125.0, 123.5, 120.4, (3C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{34}H_{23}O_3S$ $[M + H]^+$ 511.1362, found 511.1364.



Methyl (*E*)-3-benzoyl-1-benzylidene-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-4-carboxylate. Compound **3d** (46 mg, Yield = 99%, R_f = 0.18 (PE/EA = 10:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.15 (d, J = 8.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.85–7.81 (m, 2H), 7.70–7.59 (m, 4H), 7.50–7.44 (m, 3H), 7.38–7.32 (m, 1H), 7.14–6.99 (m, 5H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 188.6, 162.5, 155.4, 139.9, 139.4, 137.9, 136.3, 135.7, 134.6, 133.0, 132.5, 129.7, 129.6 (2C), 129.4, 129.2, 129.1, 129.0, 128.4, 127.0, 125.4, 123.6, 121.5, 52.8, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{29}H_{21}O_4S$ $[M + H]^+$ 465.1155, found 465.1152.

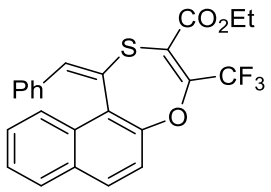


Methyl (*E*)-1-benzylidene-3-(4-methylbenzoyl)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-4-carboxylate. Compound **3e** (46 mg, Yield = 96%, R_f = 0.12 (PE/EA = 10:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.14 (d, J = 8.4 Hz, 1H), 8.01 (d, J = 8.8 Hz, 1H), 7.72–7.62 (m, 4H), 7.58 (s, 1H), 7.49–7.44 (m, 1H), 7.37–7.31 (m, 1H), 7.28–7.24 (m, 2H), 7.14–6.99 (m, 5H), 3.66 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 188.2, 162.5, 155.4, 145.7, 139.7, 139.6, 137.8, 135.8, 133.8, 133.0, 132.4, 130.3, 129.9, 129.6, 129.6, 129.4, 129.2, 129.1, 128.9, 128.3, 126.9, 125.4, 123.8, 121.5, 52.7, 21.6; ESI-HRMS *m/z* calcd for $C_{30}H_{23}O_4S$ $[M + H]^+$ 479.1312, found 479.1318.

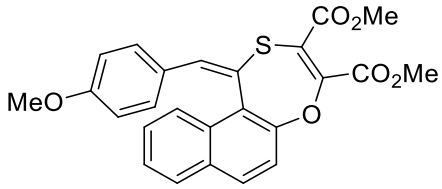


Methyl (*E*)-1-benzylidene-3-(4-bromobenzoyl)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-4-carboxylate. Compound **3f** (53 mg, Yield = 97%, R_f = 0.26 (PE/EA = 10:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.13 (d, J = 9.2 Hz, 1H), 8.00 (d, J = 8.4 Hz, 1H), 7.80–7.75 (m, 2H), 7.70–7.63 (m, 4H), 7.61 (s, 1H), 7.49–7.43 (m, 1H), 7.37–7.31 (m, 1H), 7.14–6.99 (m, 5H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 187.8, 162.6, 155.2, 140.2, 138.9, 137.8, 135.7, 135.3, 133.0, 132.5,

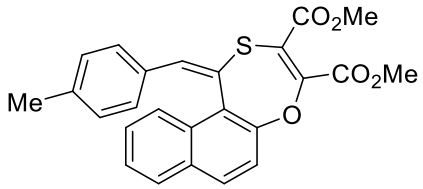
131.4, 129.6 (2C), 129.5, 129.2, 129.0, 128.4, 127.0, 125.4, 123.3, 121.5, 53.0, (3C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{29}H_{20}BrO_4S$ $[M + H]^+$ 543.0260, found 543.0264.



Ethyl (*E*)-1-benzylidene-4-(trifluoromethyl)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3-carboxylate. Compound **3g** (41 mg, Yield = 93%, R_f = 0.49 (PE/EA = 10:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 9.2 Hz, 1H), 7.48 (s, 1H), 7.45–7.39 (m, 2H), 7.34–7.28 (m, 1H), 7.10–7.04 (m, 1H), 7.03–6.97 (m, 2H), 6.91–6.85 (m, 2H), 4.29–4.20 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 153.6, 139.9, 137.4 (q, *J* = 36.2 Hz), 134.5, 132.0, 131.3, 129.0, 128.7, 128.6, 128.5, 128.4, 128.2, 127.7, 126.3, 125.3 (q, *J* = 2.9 Hz), 124.8, 121.9, 120.5, 120.1 (q, *J* = 272.9 Hz), 63.2, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.9 (s, 1F); ESI-HRMS *m/z* calcd for $C_{24}H_{18}F_3O_3S$ $[M + H]^+$ 443.0923, found 443.0926.

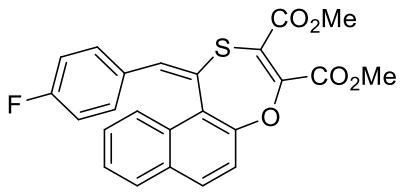


Dimethyl (*E*)-1-(4-methoxybenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3h** (42 mg, Yield = 94%, R_f = 0.22 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.10 (d, *J* = 8.8 Hz, 1H), 8.02–7.98 (m, 1H), 7.68–7.64 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.51–7.45 (m, 2H), 7.41–7.36 (m, 1H), 6.94–6.89 (m, 2H), 6.63–6.58 (m, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.7, 162.9, 160.8, 154.9, 141.3, 139.8, 133.0, 132.1, 131.3, 131.1, 129.6, 129.3, 129.2, 128.4, 128.2, 127.0, 125.5, 121.6 119.7, 114.6, 55.4, 53.6, 53.2; ESI-HRMS *m/z* calcd for $C_{25}H_{21}O_6S$ $[M + H]^+$ 449.1053, found 449.1052.

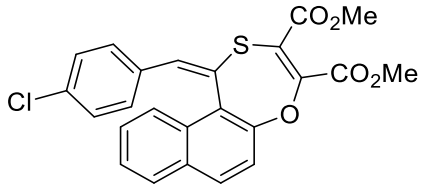


Dimethyl (*E*)-1-(4-methylbenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3i** (41 mg, Yield = 95%, R_f = 0.28 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.10 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.66–7.63 (m, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.53 (s, 1H), 7.49–7.44 (m, 1H), 7.40–7.34 (m,1H), 6.86 (s, 4H), 3.88 (s, 3H), 3.73 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.6, 162.8, 155.0, 141.5, 140.0, 139.5, 133.0,

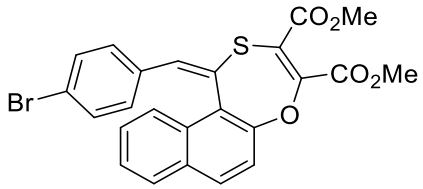
132.9, 132.2, 130.9, 129.8, 129.7, 129.6, 129.2, 129.1, 128.4, 127.0, 125.4, 121.8, 121.5, 53.6, 53.2, 21.1; ESI-HRMS *m/z* calcd for $C_{25}H_{21}O_5S$ $[M + H]^+$ 433.1104, found 433.1107.



Dimethyl (*E*)-1-(4-fluorobenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3j** (43 mg, Yield = 98%, R_f = 0.14 (PE/EA = 10:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 1H), 7.56–7.50 (m, 2H), 7.43–7.38 (m, 2H), 7.33–7.28 (m, 1H), 6.89–6.83 (m, 2H), 6.71–6.64 (s, 2H), 3.90 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 162.5 (d, *J* = 248.8 Hz), 162.4, 154.1, 139.9, 138.0, 132.0, 131.4, 130.9 (d, *J* = 3.3 Hz), 130.7 (d, *J* = 8.6 Hz), 128.7, 128.2, 128.0, 127.6, 126.2, 124.7, 122.3 (2C), 120.9, 115.5 (d, *J* = 21.5 Hz), 53.6, 53.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.6 (s, 1F); ESI-HRMS *m/z* calcd for $C_{24}H_{18}FO_5S$ $[M + H]^+$ 437.0853, found 437.0853.

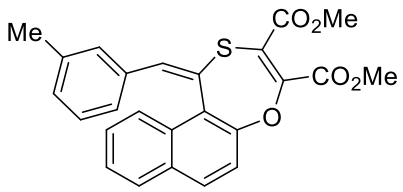


Dimethyl (*E*)-1-(4-chlorobenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3k** (43 mg, Yield = 95%, R_f = 0.16 (PE/EA = 10:1)) was isolated as a yellow solid; mp 79–80 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.11 (d, *J* = 9.2 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.57 (s, 1H), 7.49–7.43 (m, 1H), 7.40–7.34 (m, 1H), 7.10–7.05 (m, 2H), 7.00–6.95 (m, 2H), 3.89 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.5, 162.8, 155.3, 141.8, 138.3, 134.6, 134.5, 133.0, 132.5, 131.1, 130.6, 129.6, 129.3, 128.8, 128.5, 128.4, 127.1, 125.2, 124.4, 121.5, 53.7, 53.3; ESI-HRMS *m/z* calcd for $C_{24}H_{18}ClO_5S$ $[M + H]^+$ 453.0558, found 453.0564.

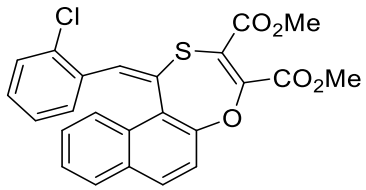


Dimethyl (*E*)-1-(4-bromobenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3l** (48 mg, Yield = 97%, R_f = 0.34 (PE/EA = 5:1)) was isolated as a yellow solid; mp 82–83 ℃. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.10 (d, *J* = 8.8 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.55 (s, 1H), 7.49–7.43 (m, 1H), 7.39–7.34 (m, 1H), 7.25–7.20 (m, 2H), 6.93–6.88 (m, 2H), 3.89 (s, 3H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.5, 162.8, 155.3, 141.8, 138.4,

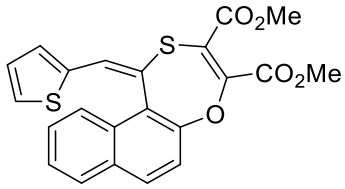
134.9, 133.0, 132.5, 132.3, 131.3, 130.6, 129.6, 128.8, 128.5, 128.4, 127.1, 125.2, 124.6, 123.0, 121.5, 53.7, 53.3. ESI-HRMS *m/z* calcd for $C_{24}H_{18}BrO_5S$ $[M + H]^+$ 497.0053, found 497.0060.



Dimethyl (*E*)-1-(3-methylbenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3m** (42 mg, Yield = 97%, R_f = 0.35 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.10 (d, J = 8.8 Hz, 1H), 7.98 (d, J = 8.4 Hz, 1H), 7.65–7.59 (m, 2H), 7.53 (s, 1H), 7.48–7.43 (m, 1H), 7.38–7.32 (m, 1H), 6.93–6.83 (m, 3H), 6.72–6.63 (m, 1H), 3.88 (s, 3H), 3.73 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.6, 162.8, 155.1, 141.6, 140.0, 138.6, 135.6, 132.9, 132.2, 130.9, 130.6, 130.1, 129.5, 129.1, 129.0 (2C), 128.3, 126.9, 126.5, 125.4, 122.9, 121.4, 53.6, 53.2, 21.1. ESI-HRMS *m/z* calcd for $C_{25}H_{21}O_5S$ $[M + H]^+$ 433.1104, found 433.1105.

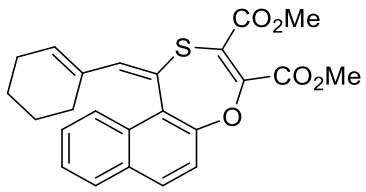


Dimethyl (*E*)-1-(2-chlorobenzylidene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3n** (44 mg, Yield = 97%, R_f = 0.11 (PE/EA = 10:1)) was isolated as a white solid; mp 79–80 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.8 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.66 (s, 1H), 7.57–7.49 (m, 2H), 7.37–7.25 (m, 3H), 6.97–6.91 (m, 1H), 6.67–6.58 (m, 2H), 3.93 (s, 3H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 162.3, 154.8, 140.1, 135.6, 133.4, 133.2, 131.9, 131.3, 130.7, 129.8, 129.5, 129.3, 128.4, 128.3, 127.5, 127.4, 126.3, 126.0, 125.7, 124.4, 120.6, 53.6, 53.1. ESI-HRMS *m/z* calcd for $C_{24}H_{18}ClO_5S$ $[M + H]^+$ 453.0558, found 453.0558.

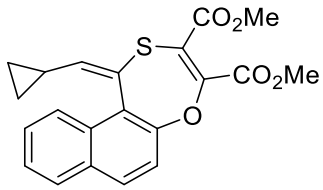


Dimethyl (*E*)-1-(thiophen-2-ylmethylene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3o** (42 mg, Yield = 99%, R_f = 0.32 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 8.14 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.81 (s, 1H), 7.80–7.76 (m, 1H), 7.60 (d, J = 9.2 Hz, 1H), 7.56–7.51 (m, 1H), 7.50–7.45 (m, 1H), 7.23–7.20 (m, 1H), 7.15–7.12 (m, 1H), 6.89 (dd, J = 5.2, 4.0 Hz, 1H), 3.86 (s, 3H), 3.73 (s,3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.6, 162.8, 155.3, 142.0, 138.2, 133.9, 133.1, 132.6, 132.0, 130.4, 130.2, 130.1, 129.7, 128.6, 128.3, 127.3,

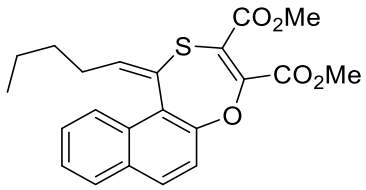
127.1, 125.3, 121.5, 119.4, 53.6, 53.2. ESI-HRMS *m/z* calcd for $C_{22}H_{17}O_5S_2$ $[M + H]^+$ 425.0512, found 425.0511.



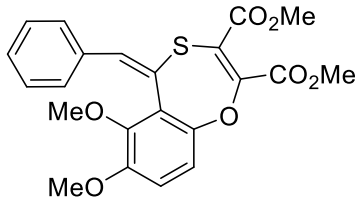
Dimethyl (*E*)-1-(cyclohex-1-en-1-ylmethylene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3p** (34 mg, Yield = 80%, R_f = 0.15 (PE/EA = 10:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.82 (m, 2H), 7.79–7.75 (m, 1H), 7.55–7.45 (m, 2H), 7.41 (d, *J* = 8.8 Hz, 1H), 6.99 (s, 1H), 5.90 (t, *J* = 3.6 Hz, 1H), 3.88 (s, 3H), 3.77 (s, 3H), 2.11–1.92 (m, 2H), 1.55–1.36 (m, 2H), 1.27–1.08 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.5, 153.0, 144.4, 139.3, 136.5, 135.2, 131.5, 131.3, 130.6, 130.5, 129.6, 128.5, 127.4, 126.0, 125.0, 120.6, 116.8, 53.5, 53.0, 26.3, 25.9, 22.4, 21.5. ESI-HRMS *m/z* calcd for $C_{24}H_{23}O_5S$ $[M + H]^+$ 423.1261, found 423.1261.



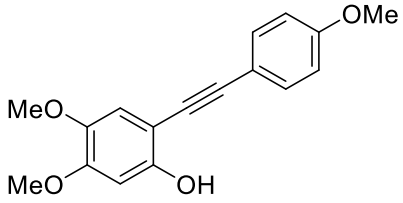
Dimethyl (*E*)-1-(cyclopropylmethylene)-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3q** (25 mg, Yield = 65%, R_f = 0.15 (PE/EA = 10:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.84 (m, 3H), 7.59–7.53 (m, 1H), 7.52–7.45 (m, 2H), 5.91 (d, *J* = 10.0 Hz, 1H), 3.89 (s, 3H), 3.77 (s, 3H), 1.14–1.03 (m, 1H), 0.79–0.57 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.6, 154.4, 146.7, 139.5, 131.8, 131.1, 130.6, 130.0, 128.6, 128.0, 127.3, 125.9, 125.4, 121.0, 117.5, 53.5, 53.0, 13.8, 8.4, 7.6. ESI-HRMS *m/z* calcd for $C_{21}H_{19}O_5S$ $[M + H]^+$ 383.0948, found 383.0952.



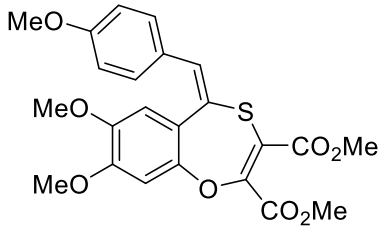
Dimethyl (*E*)-1-pentylidene-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate. Compound **3r** (28 mg, Yield = 70%, R_f = 0.15 (PE/EA = 10:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.84 (m, 2H), 7.74–7.70 (m, 1H), 7.57–7.47 (m, 2H), 7.45 (d, *J* = 8.8 Hz, 1H), 6.56 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.88 (s, 3H), 3.78 (s, 3H), 2.00–1.90 (m, 1H), 1.85–1.74 (m, 1H), 1.40–1.31 (m, 2H), 1.29–1.05 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.5, 154.3, 143.2, 139.6, 131.7, 131.3, 130.7, 129.8, 128.7, 127.7, 127.4, 125.9, 124.9, 120.9, 120.8, 53.5, 53.0, 30.7, 30.5, 22.1, 13.9. ESI-HRMS *m/z* calcd for $C_{22}H_{23}O_5S$ $[M + H]^+$ 399.1261, found 399.1264.



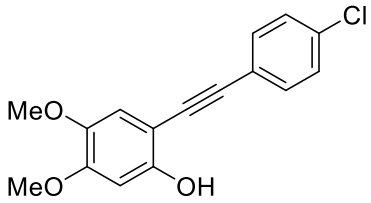
Dimethyl (*E*)-5-benzylidene-6,7-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5b** (79 mg, Yield = 92%, R_f = 0.36 (PE/EA = 3:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.26–7.21 (m, 3H), 7.15–7.10 (m, 3H), 6.99 (s, 1H), 6.56 (s, 1H), 3.87 (s, 3H), 3.85 (s, 3H), 3.76 (s, 3H), 3.52 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.6, 162.7, 152.0, 151.2, 148.4, 142.0, 135.9, 135.3, 130.3, 129.9, 129.1, 129.0, 127.6, 123.8, 112.2, 106.4, 56.4, 56.3, 53.6, 53.1; ESI-HRMS *m/z* calcd for $C_{22}H_{21}O_7S$ $[M + H]^+$ 429.1003, found 429.1004.



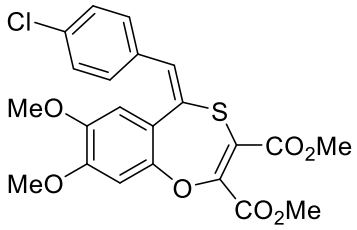
4,5-Dimethoxy-2-((4-methoxyphenyl)ethynyl)phenol. Compound **4f–2** (272 mg, Yield = 48%, R_f = 0.36 (PE/EA = 3:1)) was isolated as a yellow solid; mp 91−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.43 (m, 2H), 6.91–6.86 (m, 3H), 6.55 (s, 1H), 5.62 (s, 1H) 3.87 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 152.1, 151.2, 143.0, 133.1, 114.9, 114.3, 113.5, 100.1, 99.3, 95.3, 82.0, 56.6, 56.1, 55.5; ESI-HRMS *m/z* calcd for $C_{17}H_{17}O_4$ $[M + H]^+$ 285.1121, found 285.1121.



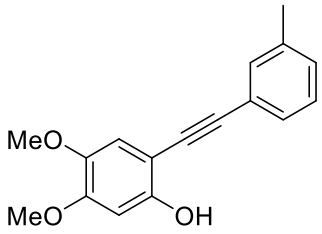
Dimethyl
(*E*)-7,8-dimethoxy-5-(4-methoxybenzylidene)-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate.
Compound **5c** (84 mg, Yield = 92%, R_f = 0.29 (PE/EA = 3:1)) was isolated as a pale-yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.11–7.06 (m, 2H), 7.05 (s, 1H),7.10–7.04 (m, 3H), 6.98 (s, 1H), 6.83–6.78 (m, 2H), 6.64 (s, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.76 (s, 3H), 3.76 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.7, 162.8, 160.7, 151.9, 151.0, 148.5, 141.6, 135.5, 131.4, 130.5, 128.3, 124.3 (2C), 114.6, 112.0, 106.4, 56.5, 56.3, 55.6, 53.6, 53.1; ESI-HRMS *m/z* calcd for $C_{23}H_{23}O_8S$ $[M + H]^+$ 459.1108, found 459.1105.



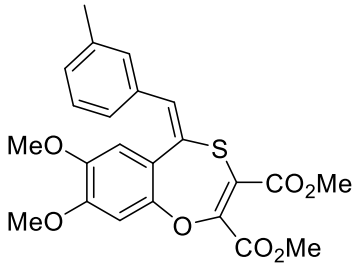
2-((4-Chlorophenyl)ethynyl)-4,5-dimethoxyphenol. Compound **4f–3** (243 mg, Yield = 42%, R_f = 0.37 (PE/EA = 3:1)) was isolated as a yellow solid; mp 162−163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.40 (m, 2H), 7.34–7.29 (m, 2H), 6.85 (s, 1H), 6.54 (s, 1H), 5.62 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.6, 143.1, 134.6, 132.7, 128.9, 121.3, 113.4, 99.4, 94.1, 84.6, 56.5, 56.1, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{16}H_{14}ClO_3$ $[M + H]^+$ 289.0626, found 289.0623.



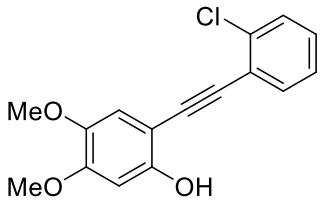
Dimethyl (*E*)-5-(4-chlorobenzylidene)-7,8-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5d** (79 mg, Yield = 85%, R_f = 0.37 (PE/EA = 3:1)) was isolated as a white solid; mp 69−70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16–7.12 (m, 2H), 6.98–6.93 (m, 3H), 6.88 (s, 1H), 6.38 (s, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 162.3, 150.7, 150.2, 147.2, 140.6, 134.0, 133.6, 133.3, 130.4, 129.8, 128.6, 127.6, 123.1, 110.4, 105.6, 56.4, 56.3, 53.6, 53.1; ESI-HRMS *m/z* calcd for $C_{22}H_{20}ClO_7S$ $[M + H]^+$ 463.0613, found 463.0606.



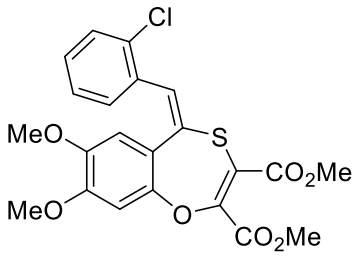
4,5-Dimethoxy-2-(*m*-tolylethynyl)phenol. Compound **4f–4** (148 mg, Yield = 28%, R_f = 0.46 (PE/EA = 3:1)) was isolated as a yellow solid; mp 110−111 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 2H), 7.27–7.22 (m, 1H), 7.18–7.14 (m, 1H), 6.87 (s, 1H), 6.55 (s, 1H), 5.66 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 151.4, 143.0, 138.3, 132.1, 129.5, 128.6, 128.5, 122.6, 113.4, 99.8, 99.3, 95.5, 83.1, 56.5, 56.1, 21.3; ESI-HRMS *m/z* calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1172, found 269.1172.



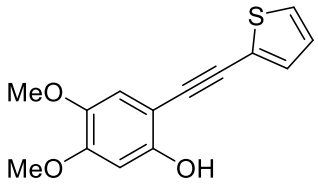
Dimethyl (*E*)-7,8-dimethoxy-5-(3-methylbenzylidene)-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5e** (78 mg, Yield = 88%, R_f = 0.38 (PE/EA = 3:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07–7.02 (m, 1H), 7.01–6.97 (m, 2H), 6.89–6.87 (m, 2H), 6.83–6.79 (m, 1H), 6.43 (s, 1H), 3.91(s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.57 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 162.4, 150.5, 150.1, 147.1, 140.3, 138.0, 135.4, 134.8, 130.2, 130.1, 129.1, 128.2, 126.2, 123.7, 110.8, 105.5, 56.4, 56.3, 53.6, 53.0, 21.4, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{23}H_{23}O_7S$ $[M + H]^+$ 443.1159, found 443.1166.



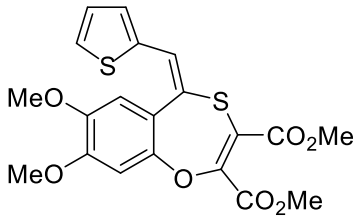
2-((2-Chlorophenyl)ethynyl)-4,5-dimethoxyphenol. Compound **4f–5** (173 mg, Yield = 30%, R_f = 0.46 (PE/EA = 3:1)) was isolated as a yellow solid; mp 87−88 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.51 (m, 1H), 7.48–7.42 (m, 1H), 7.30–7.24 (m, 2H), 6.88 (s, 1H), 6.57 (s, 1H), 6.00 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 151.9, 143.0, 135.1, 132.4, 129.3 (2C), 126.9, 122.9, 112.9, 99.3, 99.2, 92.5, 89.6, 56.6, 56.1; ESI-HRMS *m/z* calcd for $C_{16}H_{14}ClO_3$ $[M + H]^+$ 289.0626, found 289.0625.



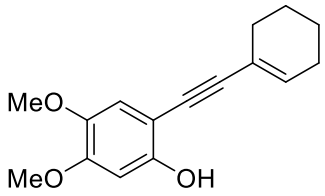
Dimethyl (*E*)-5-(2-chlorobenzylidene)-7,8-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5f** (75 mg, Yield = 81%, R_f = 0.35 (PE/EA = 3:1)) was isolated as a white solid; mp 65−66 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, J = 8.0, 1.2 Hz, 1H), 7.17 (s, 1H), 7.14–7.09 (m, 1H), 6.97–6.92 (m, 1H), 6.86 (s, 1H), 6.84 (dd, J = 8.0, 1.6 Hz, 1H), 6.24 (s, 1H), 3.88 (s, 6H), 3.83 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 162.2, 150.6, 150.5, 146.9, 140.8, 133.7, 133.6, 131.1, 131.0, 129.9, 129.8, 129.5, 129.2, 126.5, 122.7, 110.9, 105.4, 56.2 (2C), 53.6, 53.1; ESI-HRMS *m/z* calcd for $C_{22}H_{20}ClO_7S$ $[M + H]^+$ 463.0613, found 463.0616.



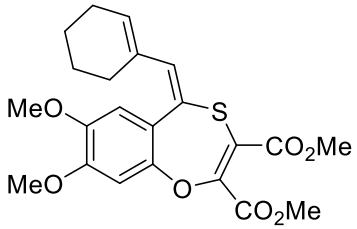
4,5-Dimethoxy-2-(thiophen-2-ylethynyl)phenol. Compound **4f–6** (150 mg, Yield = 29%, R_f = 0.35 (PE/EA = 3:1)) was isolated as a yellow solid; mp 78–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, J = 5.2, 1.2 Hz, 1H), 7.28 (dd, J = 3.6, 1.2 Hz, 1H), 7.02 (dd, J = 5.2, 3.6 Hz, 1H), 6.86 (s, 1H), 6.54 (s, 1H), 5.60 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 151.7, 143.1, 132.3, 127.8, 127.3, 122.8, 113.4, 99.5, 99.4, 88.2, 87.2, 56.5, 56.1; ESI-HRMS *m/z* calcd for $C_{14}H_{13}O_3S$ $[M + H]^+$ 261.0580, found 261.0578.



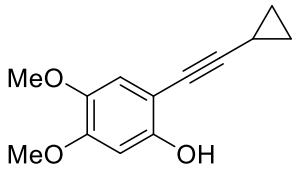
Dimethyl
(*E*)-7,8-dimethoxy-5-(thiophen-2-ylmethylene)-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate.
Compound **5g** (72 mg, Yield = 83%, R_f = 0.34 (PE/EA = 3:1)) was isolated as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.38 (m, 1H), 7.38–7.36 (m, 1H), 7.19–7.17 (m, 1H), 7.01– 6.97 (m, 3H), 3.89 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.9, 152.4, 151.0, 148.5, 142.2, 138.5, 132.0, 130.2, 130.0, 129.1, 127.4, 123.4, 123.3, 112.8, 106.5, 56.6, 56.3, 53.6, 53.1; ESI-HRMS *m/z* calcd for $C_{20}H_{19}O_7S_2$ $[M + H]^+$ 435.0567, found 435.0566.



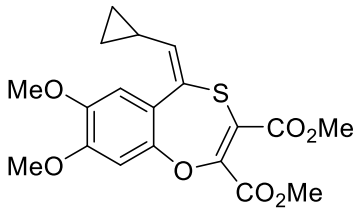
2-(Cyclohex-1-en-1-ylethynyl)-4,5-dimethoxyphenol. Compound **4f–7** (150 mg, Yield = 29%, R_f = 0.47 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.78 (s, 1H), 6.51 (s, 1H), 6.22–6.18 (m, 1H), 5.53 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 2.25–2.19 (m, 2H), 2.18–2.11 (m, 2H), 1.72–1.58 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.9, 151.1, 143.0, 135.6, 120.5, 113.7, 100.4, 99.3, 97.3, 80.6, 56.6, 56.1, 29.5, 25.9, 22.4, 21.6; ESI-HRMS *m/z* calcd for $C_{16}H_{19}O_3$ $[M + H]^+$ 259.1329, found 259.1329.



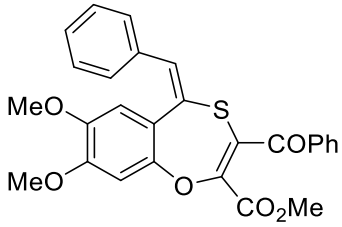
Dimethyl (*E*)-5-(cyclohex-1-en-1-ylmethylene)-7,8-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5h** (71 mg, Yield = 82%, R_f = 0.45 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 6.87 (s, 1H), 6.83 (s, 1H), 6.61 (s, 1H), 5.90–5.86 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 2.14–2.07 (m, 2H), 1.83–1.77 (m, 2H), 1.54–1.42 (m, 4H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.8, 162.9, 151.6, 150.4, 147.7, 141.4, 140.5, 135.5, 135.4, 130.6, 124.9, 122.6, 112.9, 105.8, 56.7, 56.2, 53.5, 53.0, 28.4, 26.7, 23.3, 22.4; ESI-HRMS *m/z* calcd for $C_{22}H_{25}O_7S$ $[M + H]^+$ 433.1316, found 433.1312.



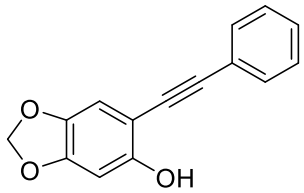
2-(Cyclopropylethynyl)-4,5-dimethoxyphenol. Compound **4f–8** (157 mg, Yield = 36%, R_f = 0.32 (PE/EA = 3:1)) was isolated as a pale-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 1H), 6.50 (s, 1H), 5.55 (s, 1 H), 3.84 (s, 3H), 3.79 (s, 3H), 1.53–1.45 (m, 1H), 0.94–0.88 (m, 2H), 0.84–0.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 150.7, 142.8, 113.8, 100.2, 99.7, 99.0, 69.8, 56.5, 56.0, 9.1, 0.3; ESI-HRMS *m/z* calcd for $C_{13}H_{15}O_3$ $[M + H]^+$ 219.1016, found 219.1016.



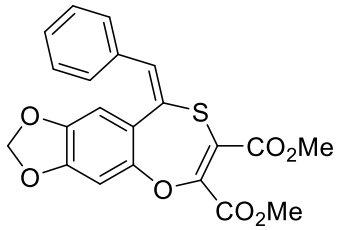
Dimethyl (*E*)-5-(cyclopropylmethylene)-7,8-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5i** (46 mg, Yield = 59%, R_f = 0.29 (PE/EA = 3:1)) was isolated as a pale-yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.82 (s, 1H), 5.52 (d, *J* = 10.0 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.79 (s, 3H), 1.61–1.51 (m, 1H), 0.85–0.79 (m, 2H), 0.60–0.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.6, 150.2, 150.0, 146.6, 142.9, 139.9, 130.2, 123.6, 121.2, 111.2, 105.7, 56.5, 56.3, 53.5, 53.0, 12.8, 8.2; ESI-HRMS *m/z* calcd for $C_{19}H_{21}O_7S$ $[M + H]^+$ 393.1003, found 393.1001.



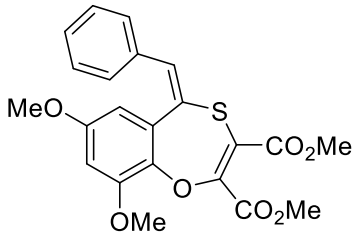
Methyl (*E*)-3-benzoyl-5-benzylidene-7,8-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2-carboxylate. Compound **5j** (86 mg, Yield = 91%, R_f = 0.38 (PE/EA = 3:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.88–7.84 (m, 2H), 7.68–7.62 (m, 1H), 7.55–7.49 (m, 2H), 7.29–7.23 (m, 3H), 7.17–7.13 (m, 2H), 7.12 (s, 1H), 7.05 (s, 1H), 6.61 (s, 1H), 3.89 (s, 3H), 3.63 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 188.6, 162.5, 152.1, 151.5, 148.3, 138.8, 138.5, 136.4, 136.0, 135.1, 134.6, 129.9, 129.8, 129.7, 129.2, 129.0, 128.2, 123.7, 112.3, 106.3, 56.4, 56.3, 52.7; ESI-HRMS *m/z* calcd for $C_{27}H_{23}O_6S$ $[M + H]^+$ 475.1210, found 475.1209.



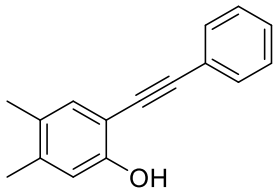
6-(Phenylethynyl)benzo[*d*][1,3]dioxol-5-ol. Compound **4e** (233 mg, Yield = 98%, R_f = 0.38 (PE/EA = 3:1)) was isolated as a yellow solid; mp 88−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.49 (m, 2H), 7.38–7.34 (m, 3H), 6.83 (s, 1H), 6.54 (s, 1H), 5.94 (s, 2H), 5.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 149.7, 141.3, 131.6, 128.7, 128.6, 122.7, 109.6, 101.6, 100.6, 97.3, 95.5, 83.5; ESI-HRMS *m/z* calcd for $C_{15}H_{11}O_3$ $[M + H]^+$ 239.0703, found 239.0703.



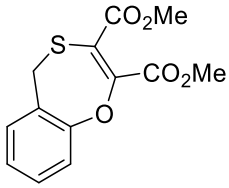
Dimethyl (*E*)-9-benzylidene-9*H*-[1,3]dioxolo[4',5':4,5]benzo[1,2-*f*][1,4]oxathiepine-6,7-dicarboxylate. Compound **5k** (75 mg, Yield = 91%, R_f = 0.38 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ 7.28–7.22 (m, 3H), 7.16–7.12 (m. 3H), 6.95 (s, 1H), 6.49 (s, 1H), 6.06 (s, 2H), 3.86 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $(CD_3)_2CO$) δ 164.5, 162.6, 151.9, 150.1, 146.7, 141.5, 136.3, 135.7, 131.1, 129.9, 129.2, 129.1, 127.1, 125.5, 108.0, 104.0, 103.3, 53.7, 53.2; ESI-HRMS *m/z* calcd for $C_{22}H_{17}O_7S$ $[M + H]^+$ 413.0690, found 413.0693.



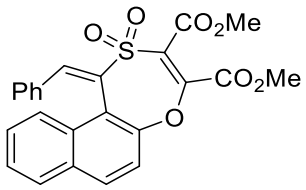
Dimethyl (*E*)-5-benzylidene-7,9-dimethoxy-5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **5l** (75 mg, Yield = 88%, R_f = 0.36 (PE/EA = 3:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18–7.13 (m, 3H), 7.10 (s, 1H), 7.04–7.00 (m, 2H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.25 (d, *J* = 2.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.82 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 162.3, 162.0, 157.8, 156.1, 139.1, 137.8, 136.2, 131.7, 128.1 (2C), 121.1, 114.8, 98.8, 97.4, 55.8, 55.7, 53.6, 53.0, (1C peak was merged with other peaks); ESI-HRMS *m/z* calcd for $C_{22}H_{21}O_7S$ $[M + H]^+$ 429.1003, found 429.1004.



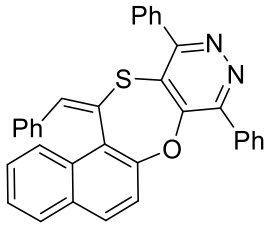
4,5-Dimethyl-2-(phenylethynyl)phenol. Compound **4i** (1.62 g, Yield = 73%, R_f = 0.60 (PE/EA = 20:1)) was isolated as a white solid; mp 100−101 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56–7.50 (m, 2H), 7.40–7.33 (m, 3H), 7.18 (s, 1H), 6.79 (s, 1H), 5.63 (s, 1H), 2.25 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 139.9, 132.2, 131.6, 128.7, 128.6, 122.9, 116.0, 106.6, 95.7, 83.6, 20.3, 18.8, (1C peak is merged with other peaks); ESI-HRMS *m/z* calcd for $C_{16}H_{15}O$ $[M + H]^+$ 223.1117, found 223.1119.



Dimethyl 5*H*-benzo[*f*][1,4]oxathiepine-2,3-dicarboxylate. Compound **7a** (43 mg, Y = 51%, R_f = 0.41 (PE/EA = 5:1)) was isolated as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.27 (m, 1H), 7.25–7.14 (m, 3H), 4.31 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 162.8, 157.4, 139.8, 132.3, 129.8, 128.0, 127.6, 126.3, 121.8, 53.5, 53.0, 31.3. ESI-HRMS *m/z* calcd for $C_{13}H_{13}O_5S$ $[M + H]^+$ 281.0478, found 281.0478.

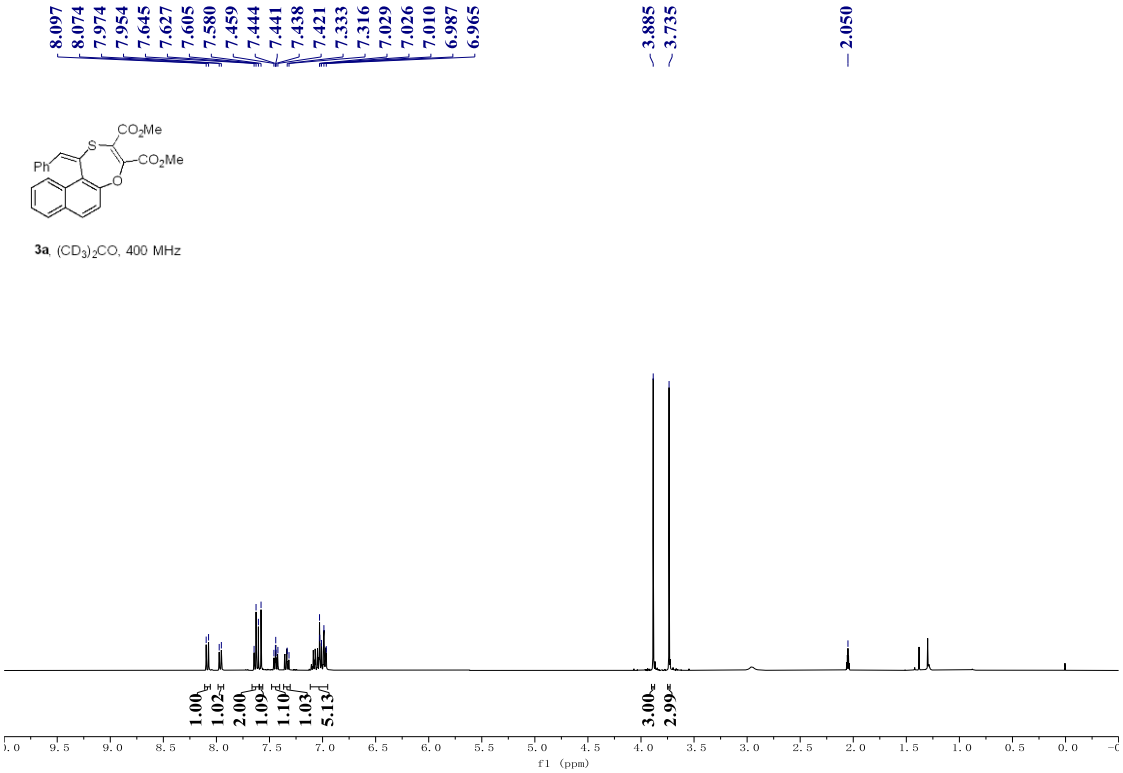


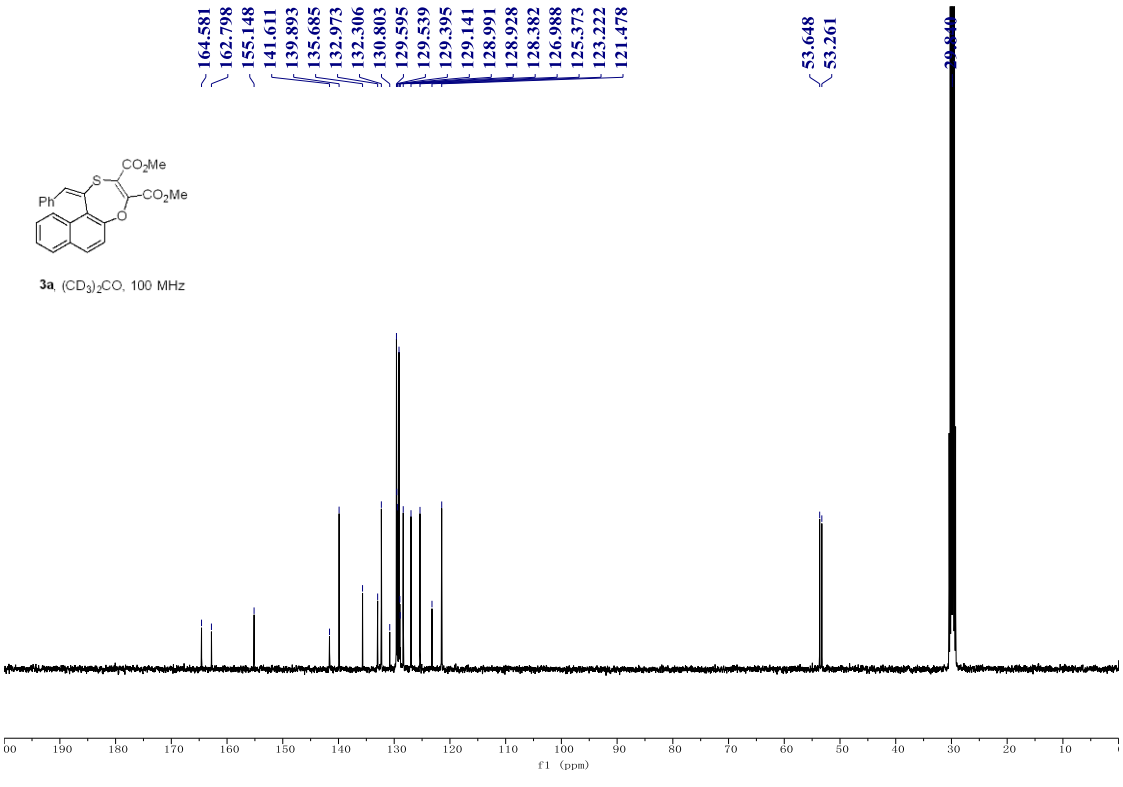
Dimethyl (*E*)-1-benzylidene-1*H*-naphtho[1,2-*f*][1,4]oxathiepine-3,4-dicarboxylate 2,2-dioxide. Compound **3a'** (81 mg, Yield = 90%, R_f = 0.19 (PE/EA = 5:1)) was isolated as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 8.00 (d, *J* = 9.2 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.55–7.51 (m, 1H), 7.49–7.42 (m, 2H), 7.30–7.24 (m, 1H), 7.16–7.07 (m, 4H), 3.96 (s, 3H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 161.1, 152.4, 152.0, 144.1, 132.4, 132.3, 131.7, 131.4, 130.9, 130.7, 130.5, 129.0, 128.7 (2C), 127.3, 125.0, 124.7, 119.8, 118.8, 53.9 (2C). ESI-HRMS *m/z* calcd for $C_{24}H_{19}O_7S$ $[M + H]^+$ 451.0846, found 451.0847.

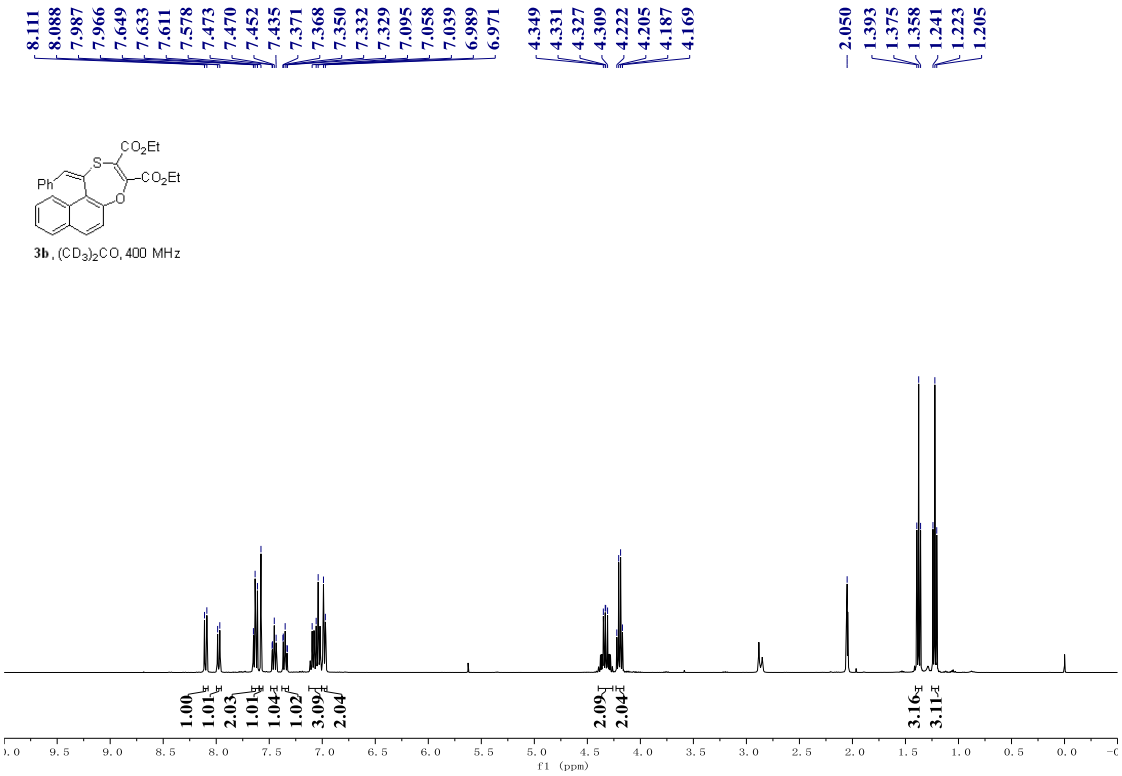


(*E*)-13-Benzylidene-8,11-diphenyl-13*H*-naphtho[1',2':6,7][1,4]oxathiepino[2,3-*d*]pyridazine.
Compound **3c'** (99 mg, Yield = 98%, R_f = 0.25 (PE/EA = 5:1)) was isolated as a white solid; mp 138–149 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.12 (m, 2H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.71 (d, *J* = 8.8 Hz, 1H), 7.66–7.59 (m, 5H), 7.56–7.52 (m, 1H), 7.52–7.47 (m, 3H), 7.46 (s, 1H), 7.40–7.34 (m, 1H), 7.29–7.24 (m, 1H), 7.09–7.04 (m, 1H), 7.03–6.97 (m, 2H), 6.91–6.86 (m, 2H), 6.70 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 154.1, 152.9, 149.6, 138.7, 135.6, 134.7, 134.5, 132.6, 132.0, 131.3, 130.6, 129.8, 129.7, 129.4, 128.9, 128.6 (2C), 128.5 (3C), 128.4, 128.2, 127.6, 126.3, 124.9, 123.6, 120.5. ESI-HRMS *m/z* calcd for $C_{34}H_{23}N_2OS$ $[M + H]^+$ 507.1526, found 507.1522.

11. NMR Spectra



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7.350
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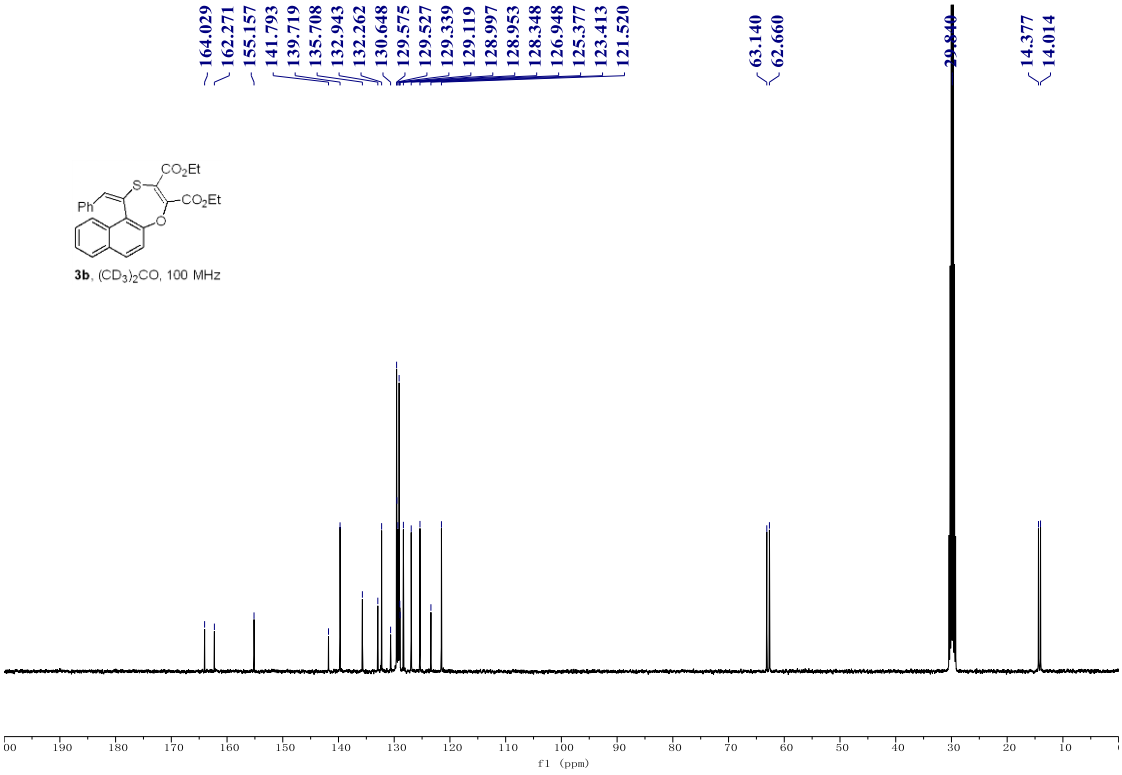
4.309
4.222
4.205
4.187
4.169
2.050
1.393
1.375
1.358
1.241
1.223
1.205
CO2Et
S
Ph
CO2Et
O
3b, (CD3)2CO, 400 MHz
1.00
1.01
2.03
1.01
1.04
1.02
3.09
2.04
2.09
2.04
3.16
3.11
f1 (ppm)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128.997
128.953
128.348
126.948
125.377
123.413
121.520
63.140
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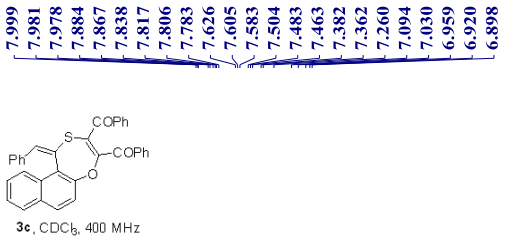
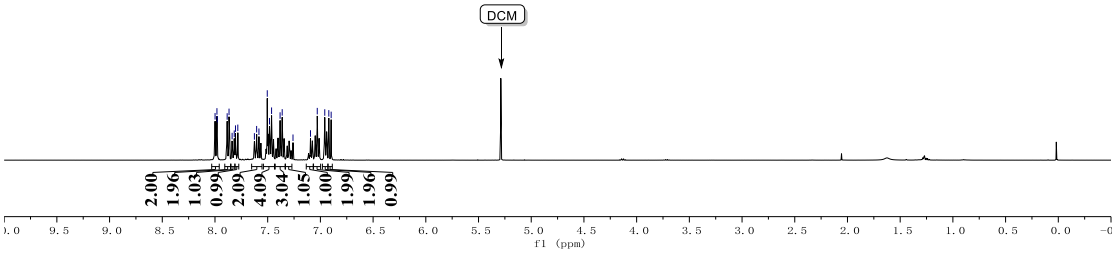
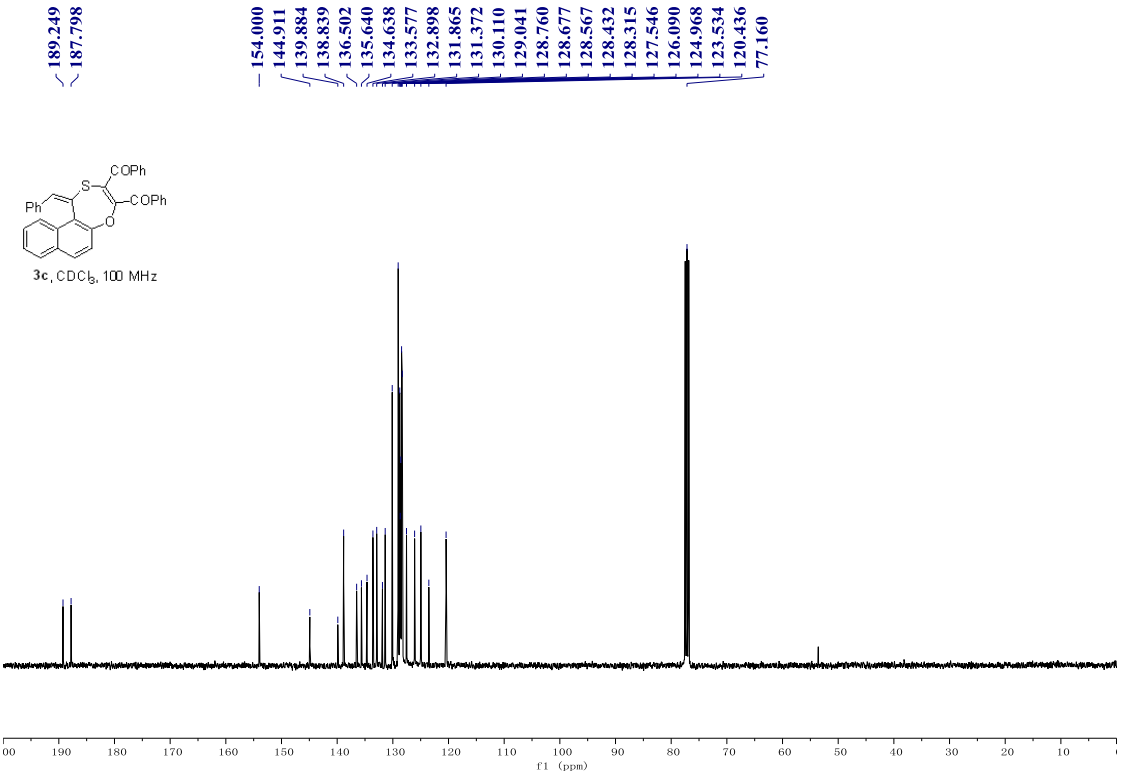
29.840
14.377
14.014
CO2Et
S
Ph
CO2Et
O
3b, (CD3)2CO, 100 MHz
f1 (ppm)



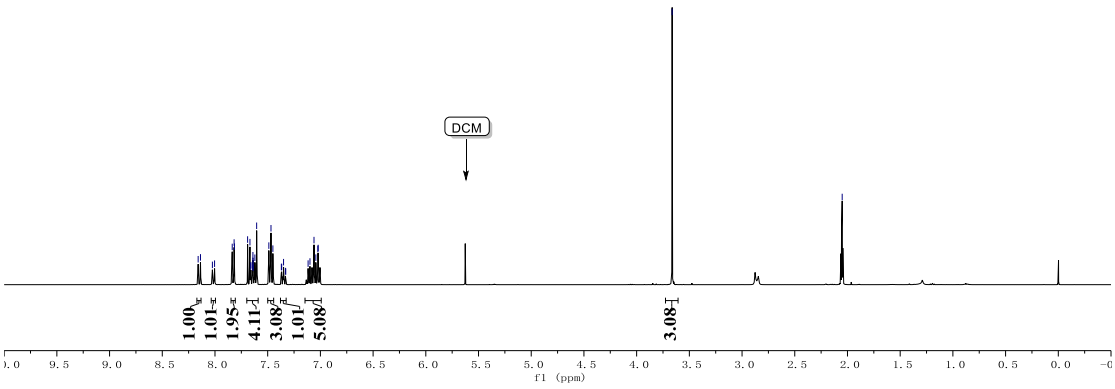
3c, $CDCl_3$, 400 MHz

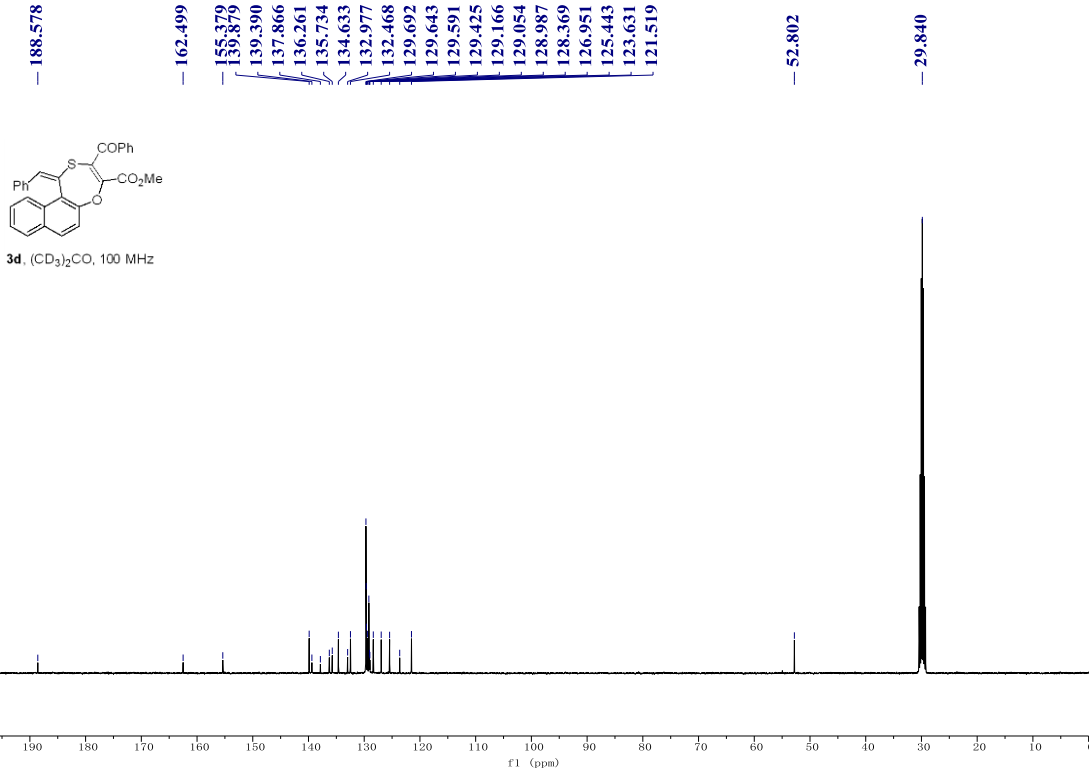




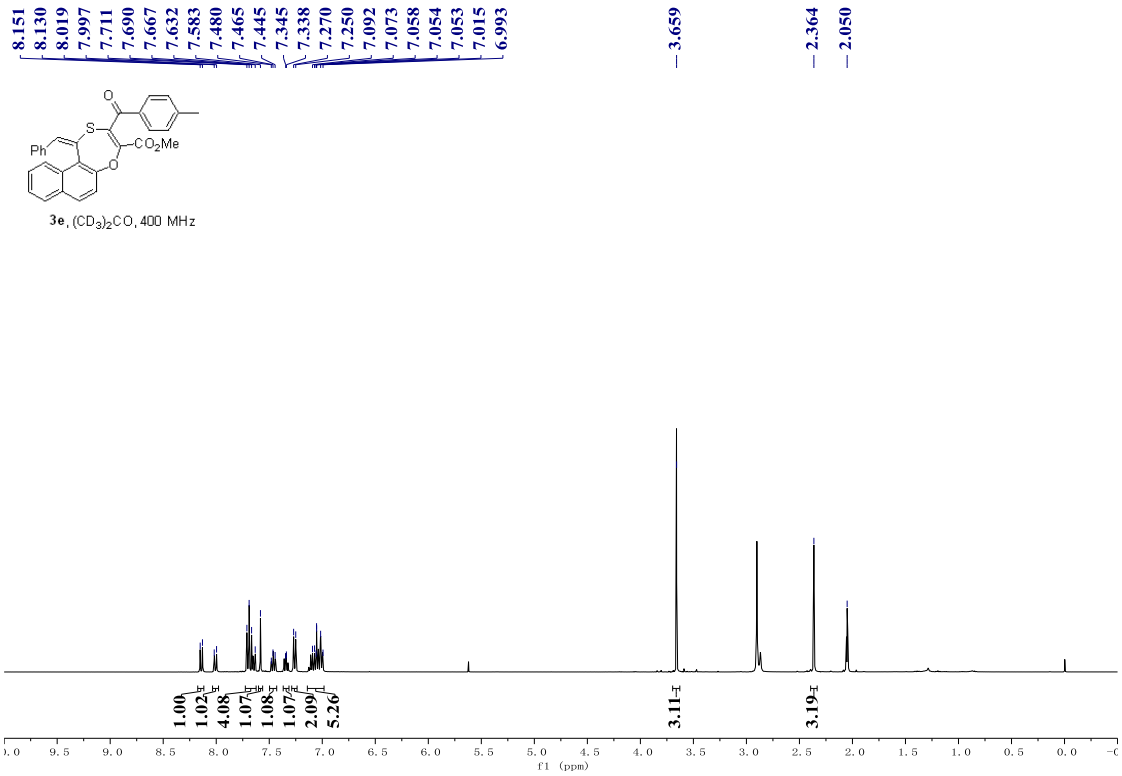
3c, $CDCl_3$, 100 MHz

3d, $(CD_3)_2CO$, 400 MHz

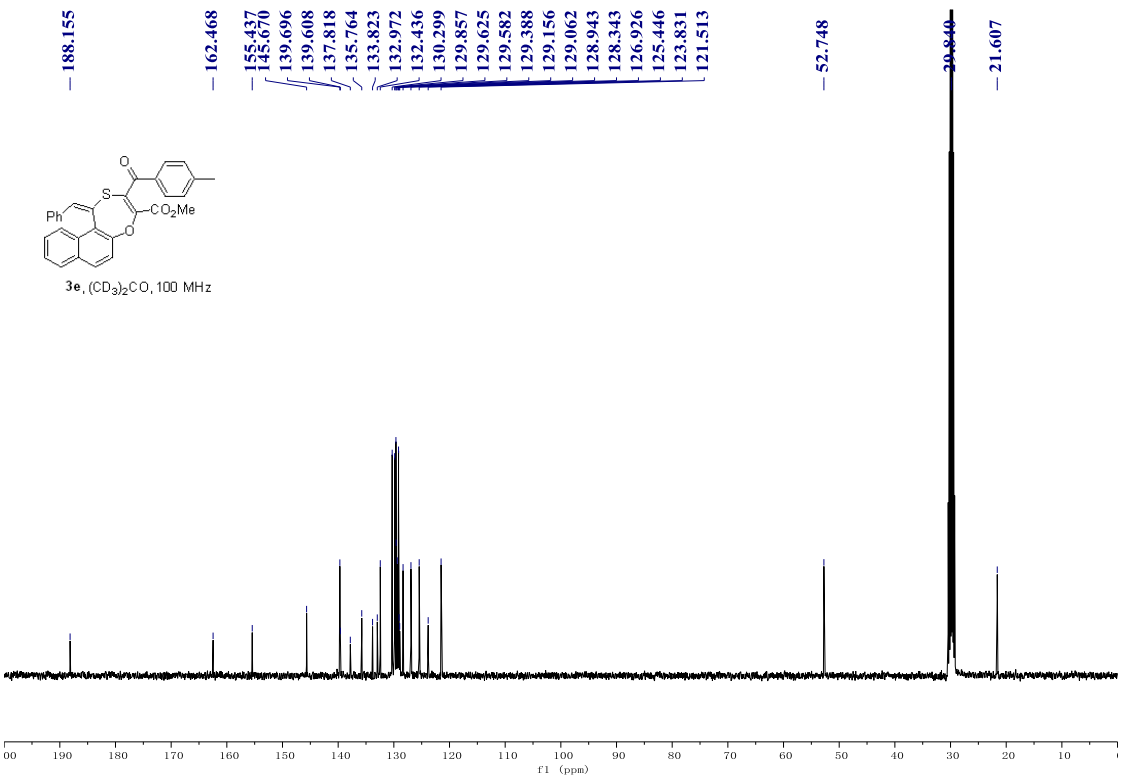




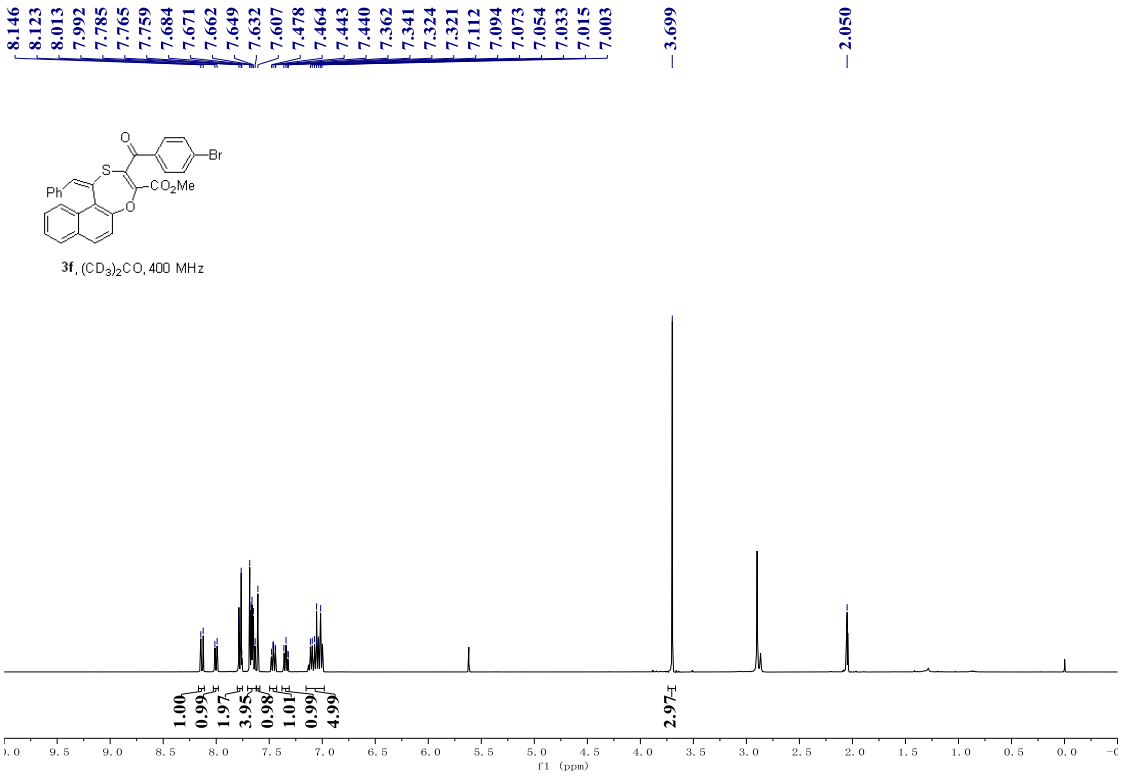
3d, $(CD_3)_2CO$, 100 MHz



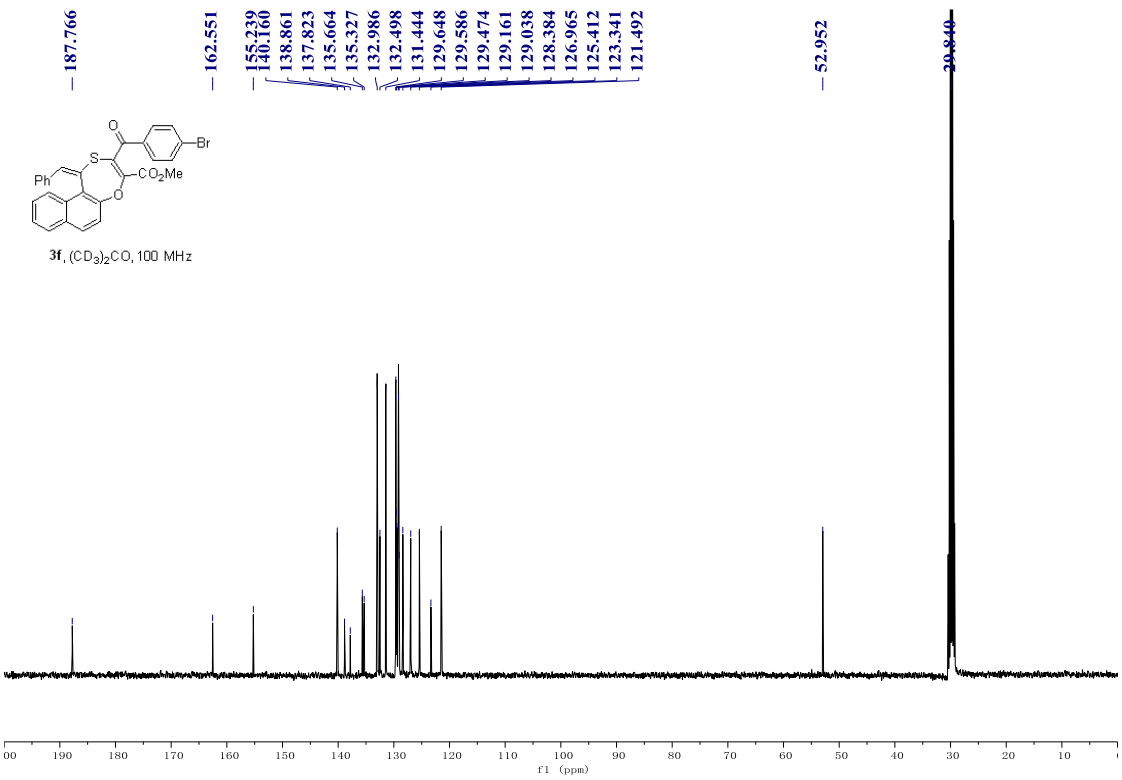
3e, $(CD_3)_2CO$, 400 MHz



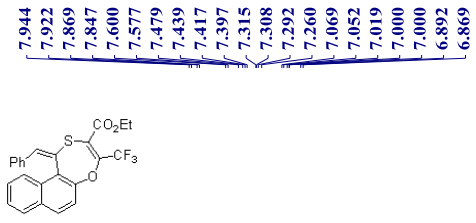
3e, $(CD_3)_2CO$, 100 MHz



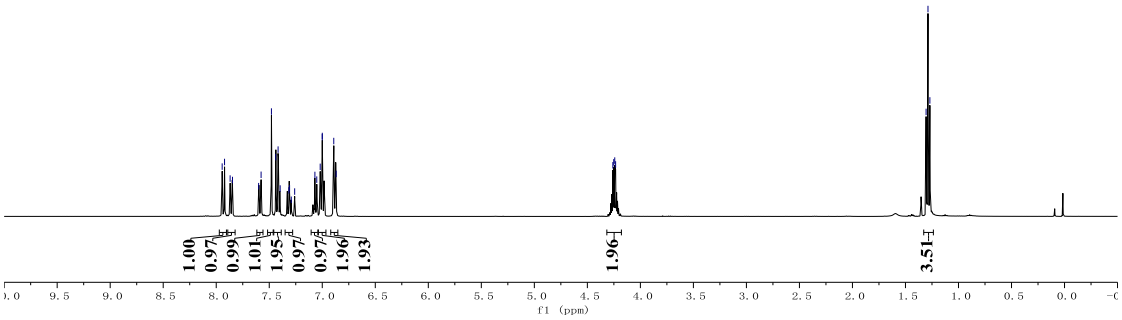
3f, $(CD_3)_2CO$, 400 MHz

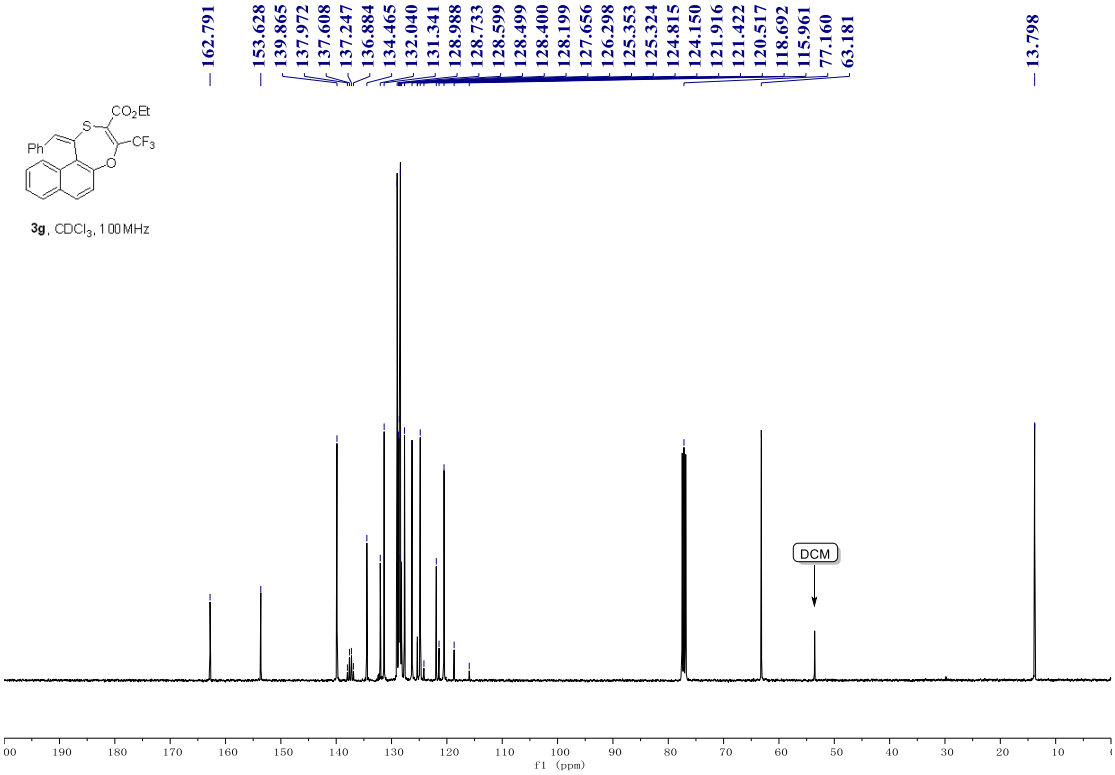


3f, $(CD_3)_2CO$, 100 MHz

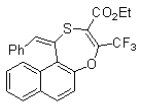


3g, $CDCl_3$, 400MHz

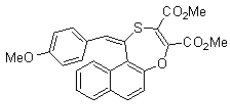




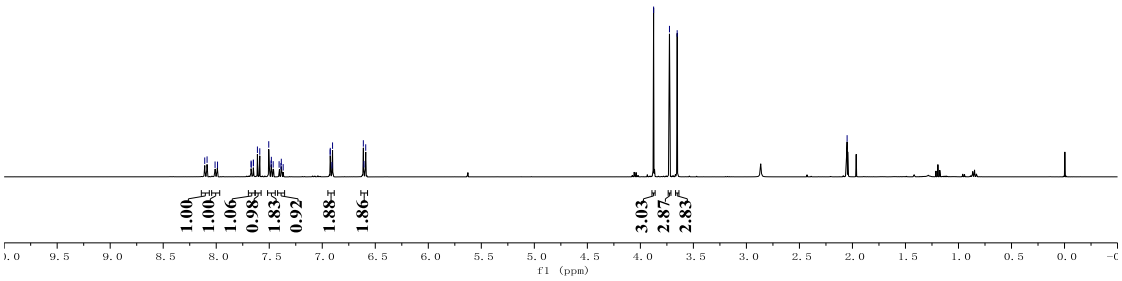
3g, $CDCl_3$, 100MHz

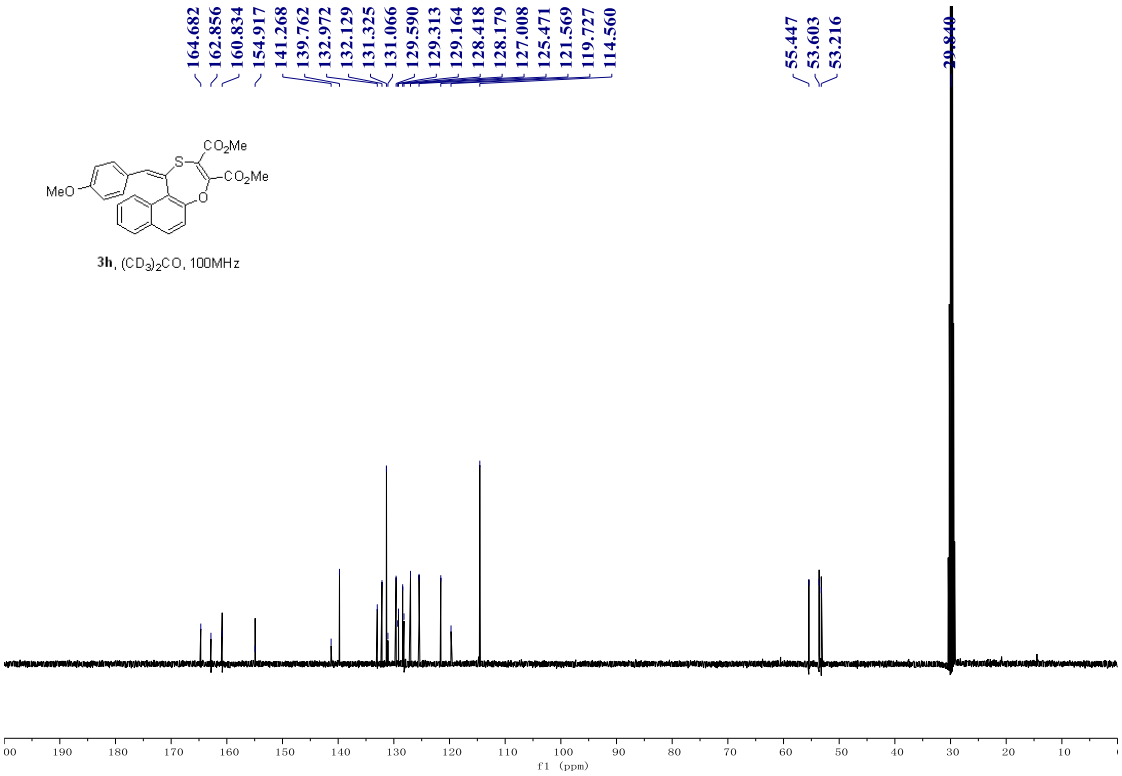


3g, $CDCl_3$, 376MHz

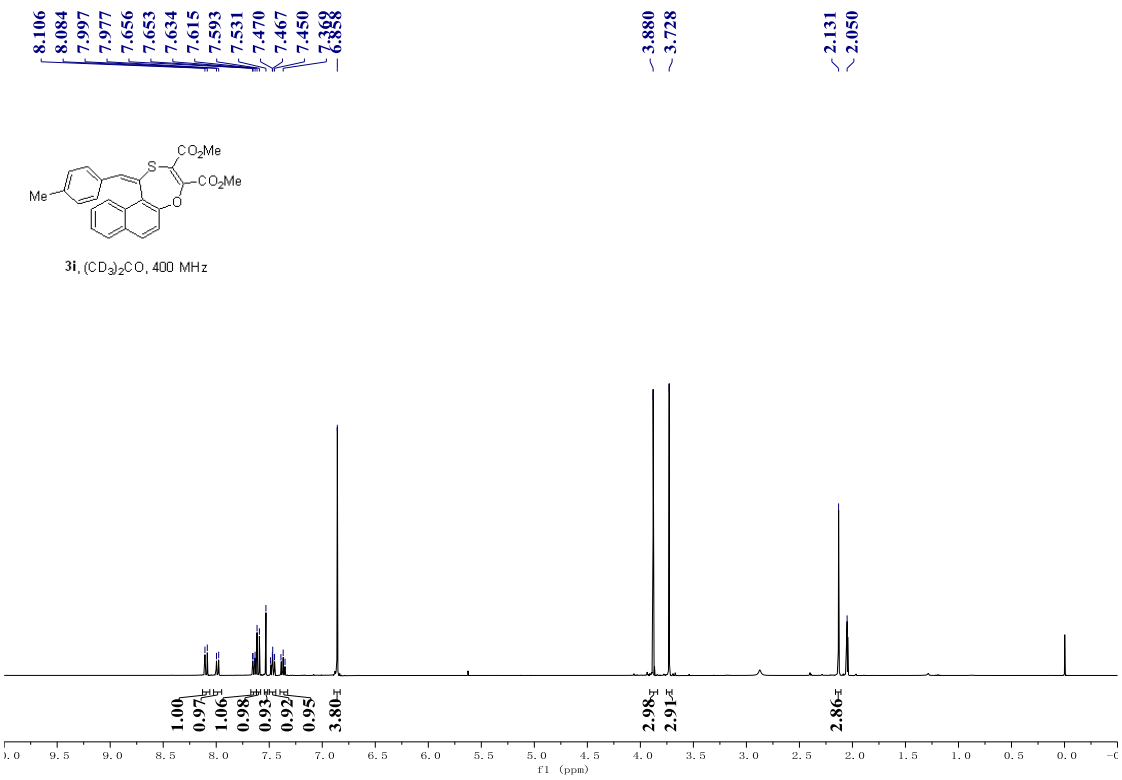


3h, $(CD_3)_2CO$, 400MHz

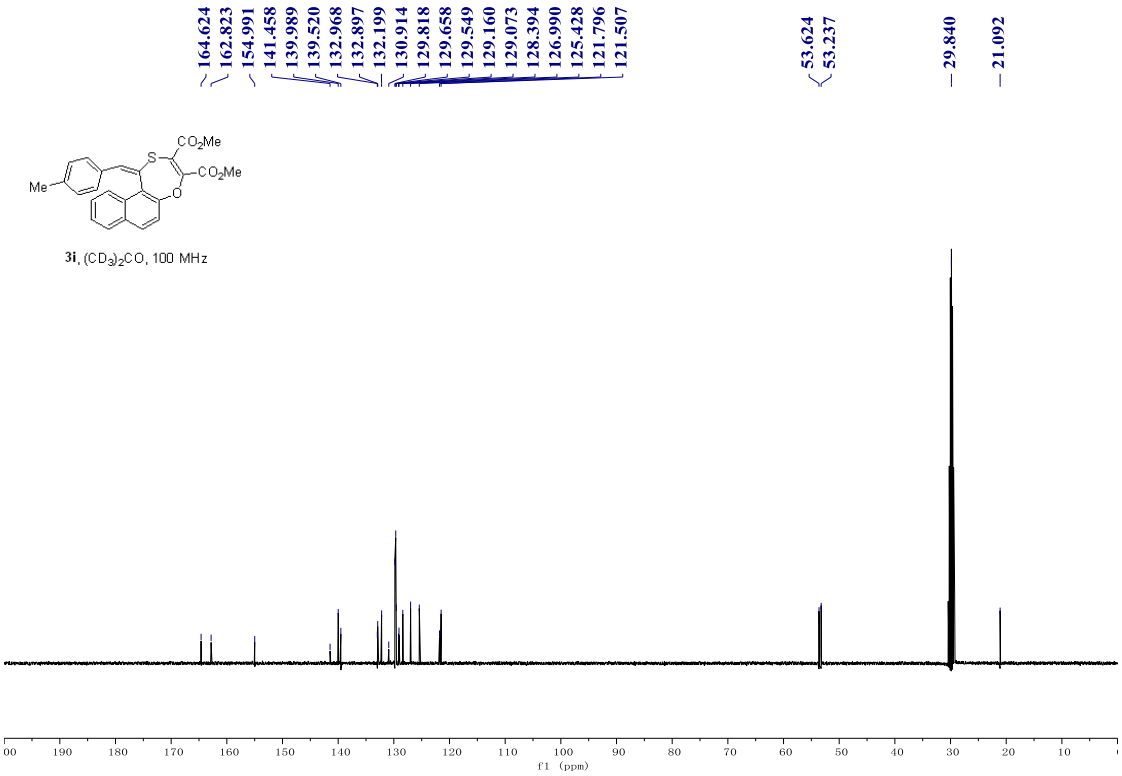




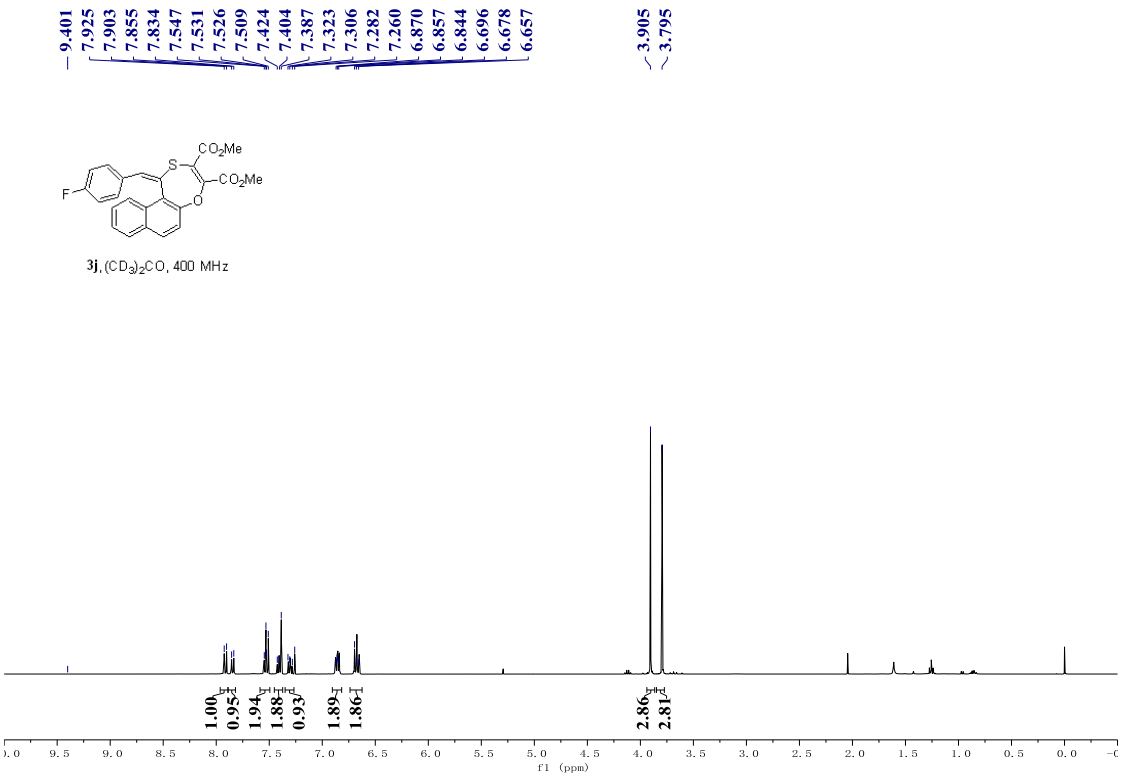
3h, $(CD_3)_2CO$, 100MHz



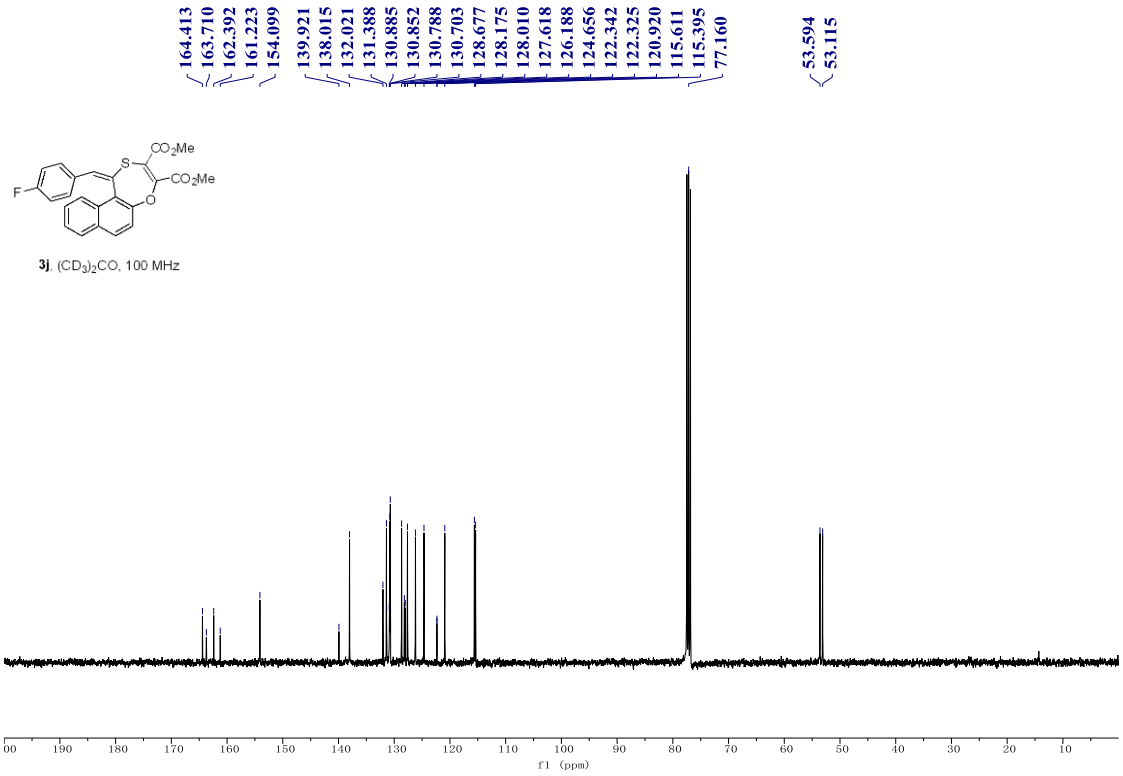
3i, $(CD_3)_2CO$, 400 MHz

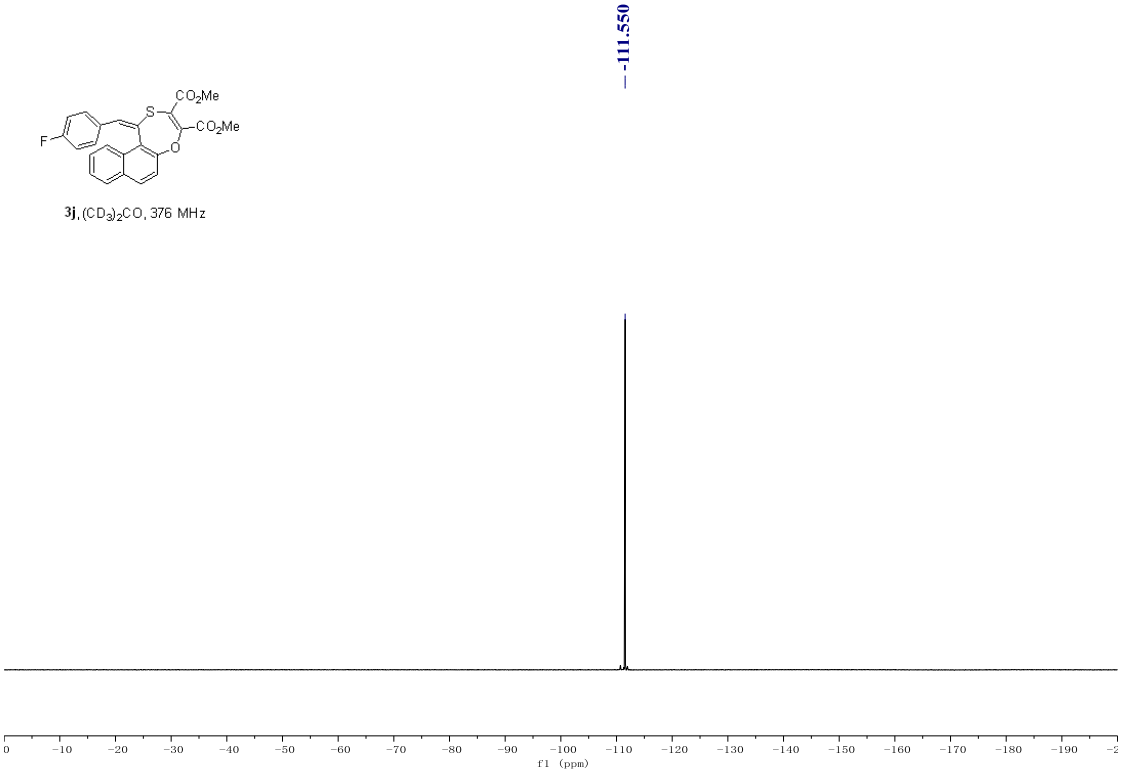


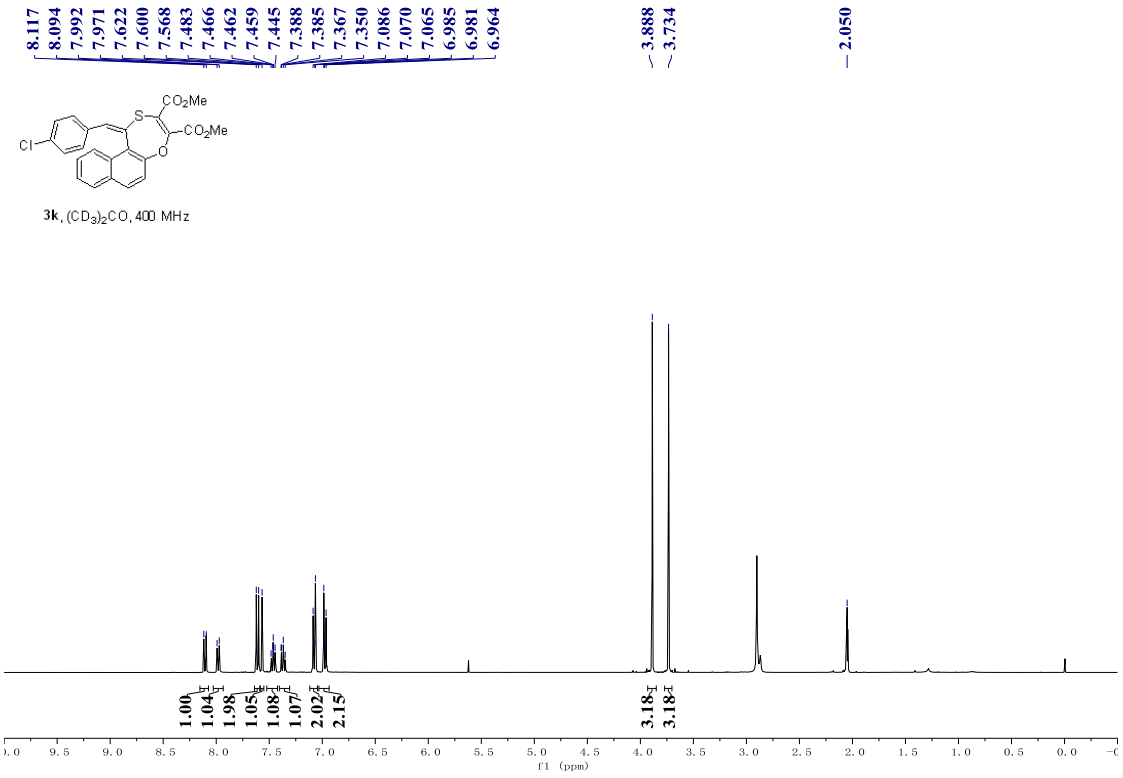
3i, $(CD_3)_2CO$, 100 MHz



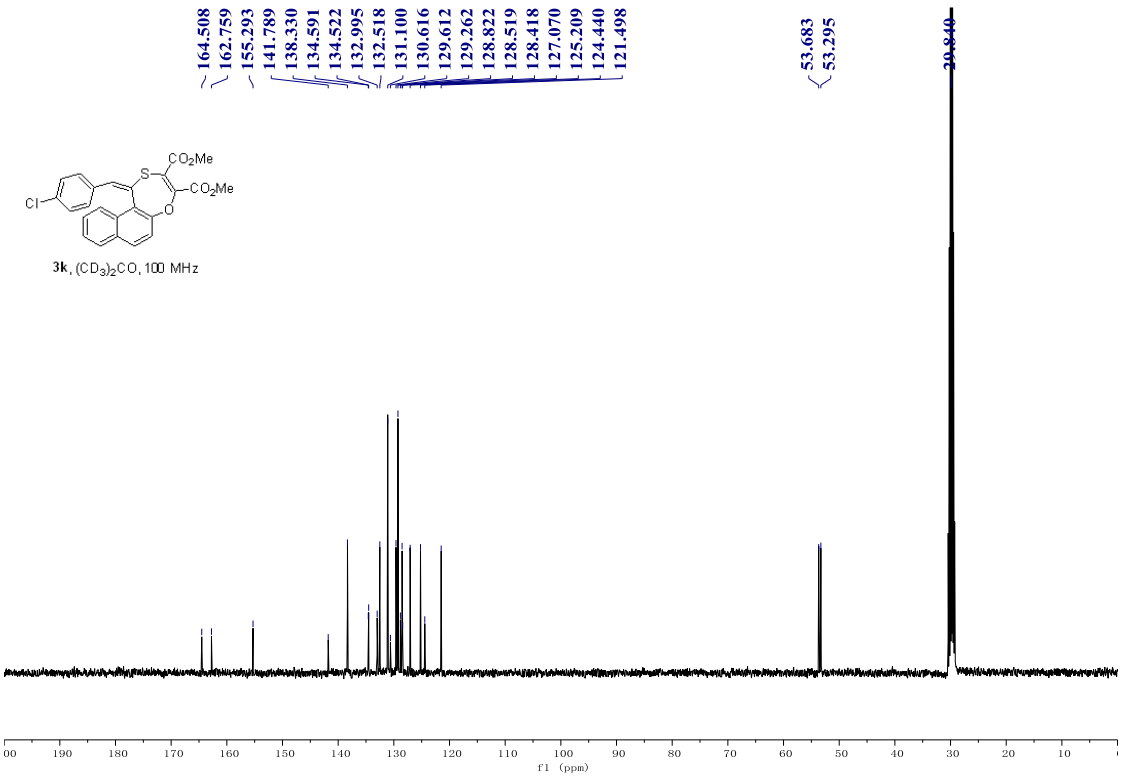
3j, $(CD_3)_2CO$, 400 MHz


164.413
163.710
162.392
161.223
154.099
139.921
138.015
132.021
131.388
130.885
130.852
130.788
130.703
128.677
128.175
128.010
127.618
126.188
124.656
122.342
122.325
120.920
115.611
115.395
77.160
53.594
53.115
CO2Me
CO2Me
S
O
F
3j, (CD3)2CO, 100 MHz
f1 (ppm)

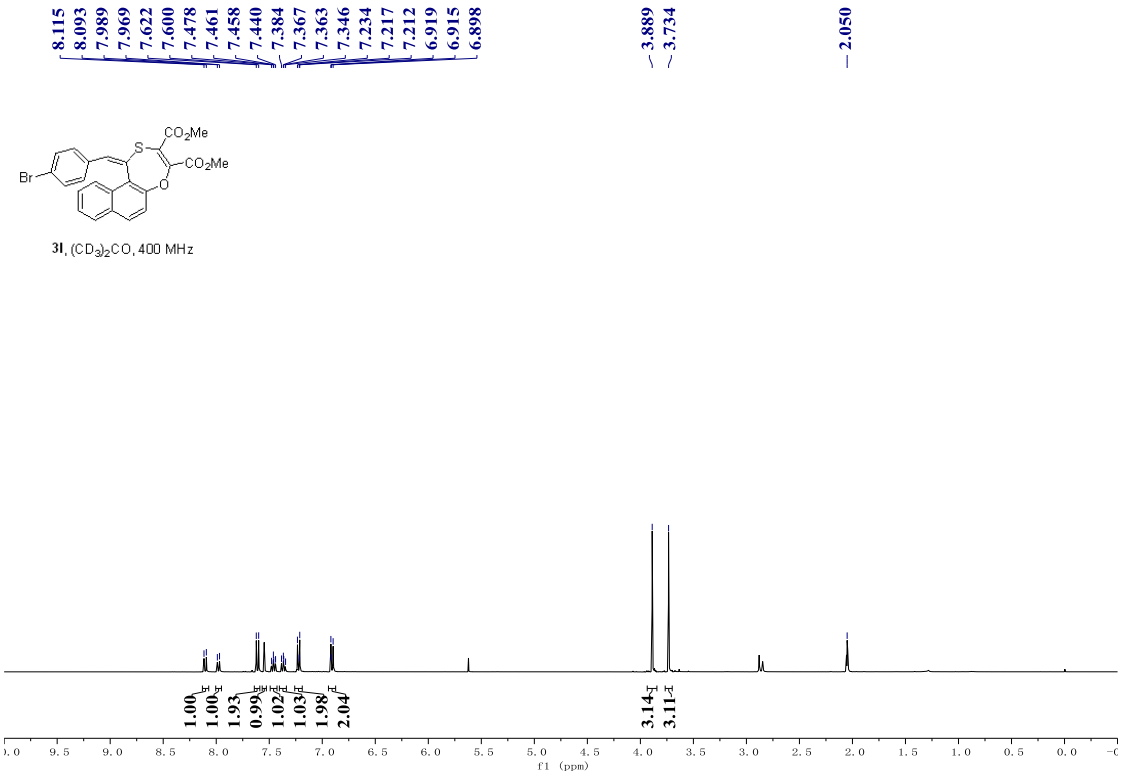

-111.550
CO2Me
CO2Me
S
O
F
3j, (CD3)2CO, 376 MHz
f1 (ppm)



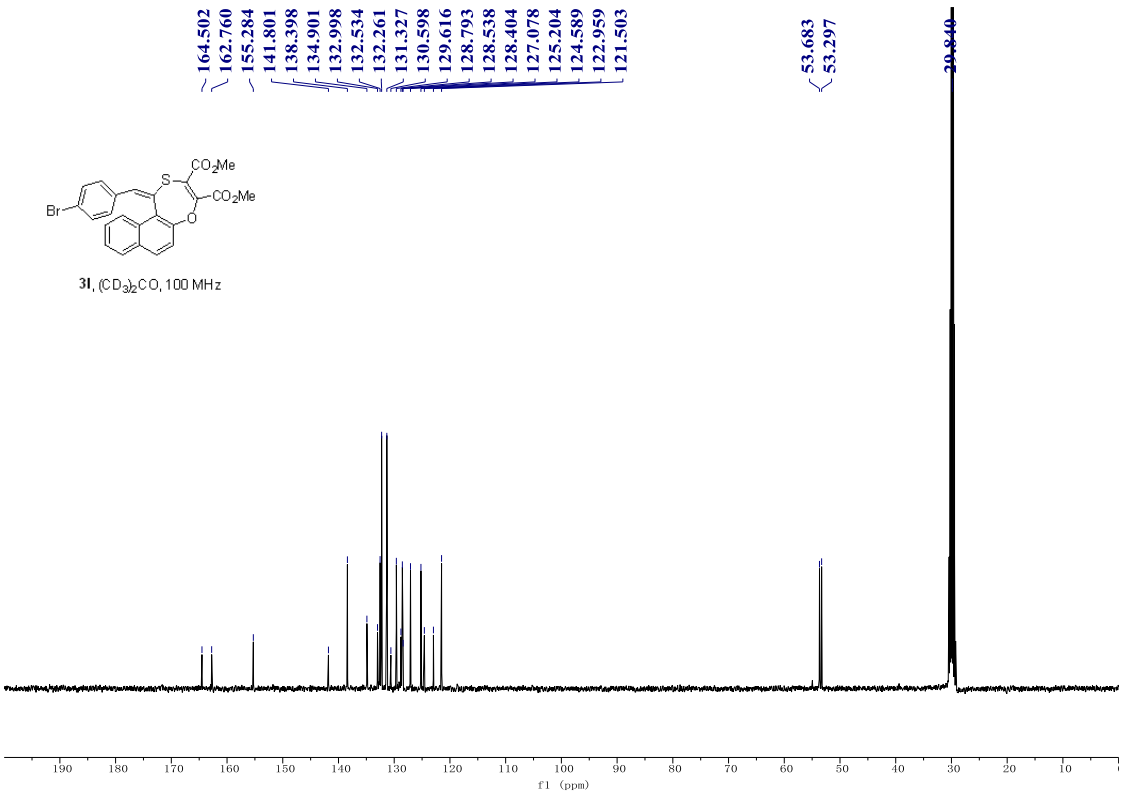
3k, $(CD_3)_2CO$, 400 MHz



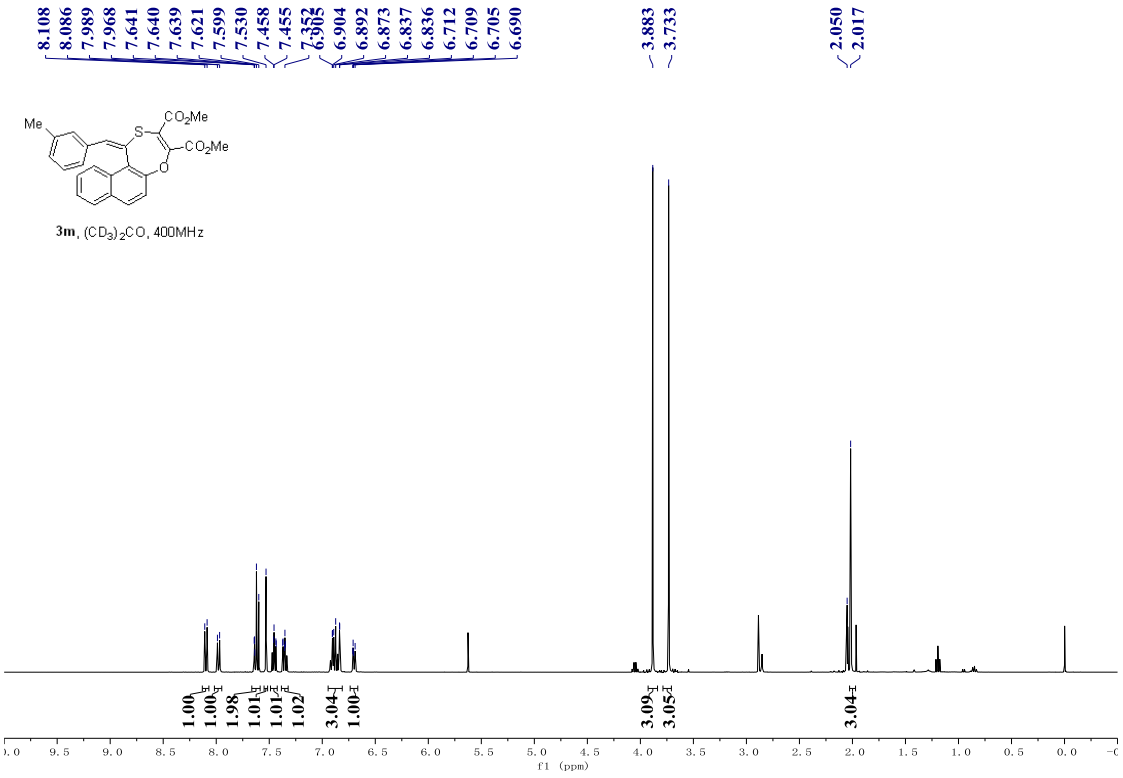
3k, $(CD_3)_2CO$, 100 MHz

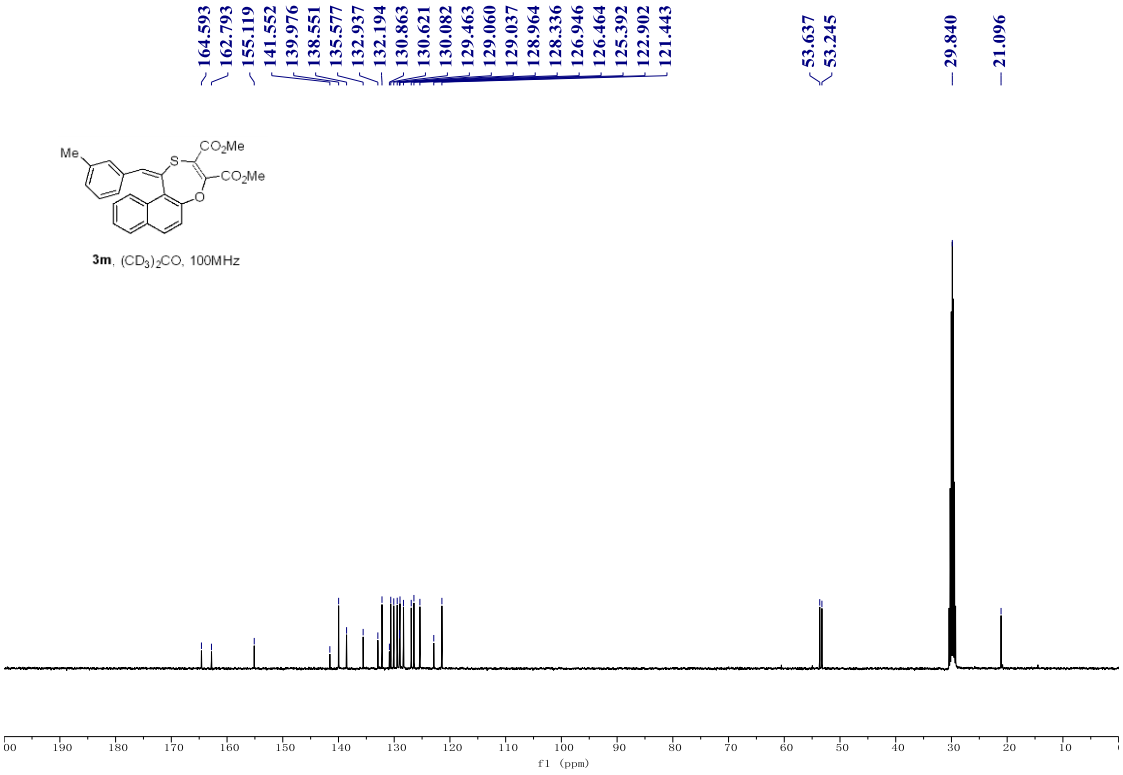


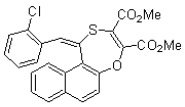
3l, $(CD_3)_2CO$, 400 MHz



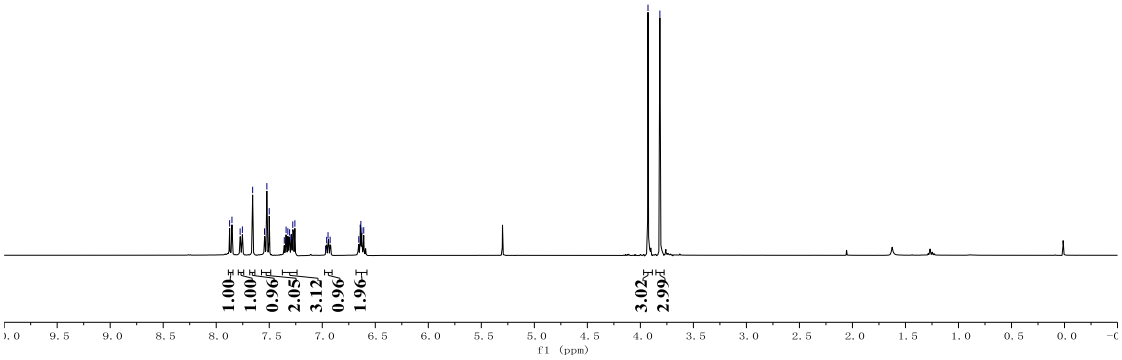
3l, $(CD_3)_2CO$, 100 MHz

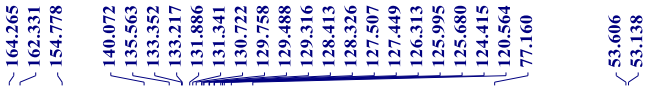

8.108
8.086
7.989
7.968
7.641
7.640
7.639
7.621
7.599
7.530
7.458
7.455
7.352
6.904
6.892
6.873
6.837
6.836
6.712
6.709
6.705
6.690
3.883
3.733
2.050
2.017
Me
CO2Me
CO2Me
S
O
3m, (CD3)2CO, 400MHz
1.00
1.00
1.98
1.01
1.01
1.02
3.04
1.00
3.09
3.05
3.04
f1 (ppm)

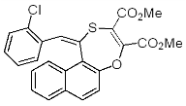

164.593
162.793
155.119
141.552
139.976
138.551
135.577
132.937
132.194
130.863
130.621
130.082
129.463
129.060
129.037
128.964
128.336
126.946
126.464
125.392
122.902
121.443
53.637
53.245
29.840
21.096
Me
CO2Me
CO2Me
S
O
3m, (CD3)2CO, 100MHz
f1 (ppm)



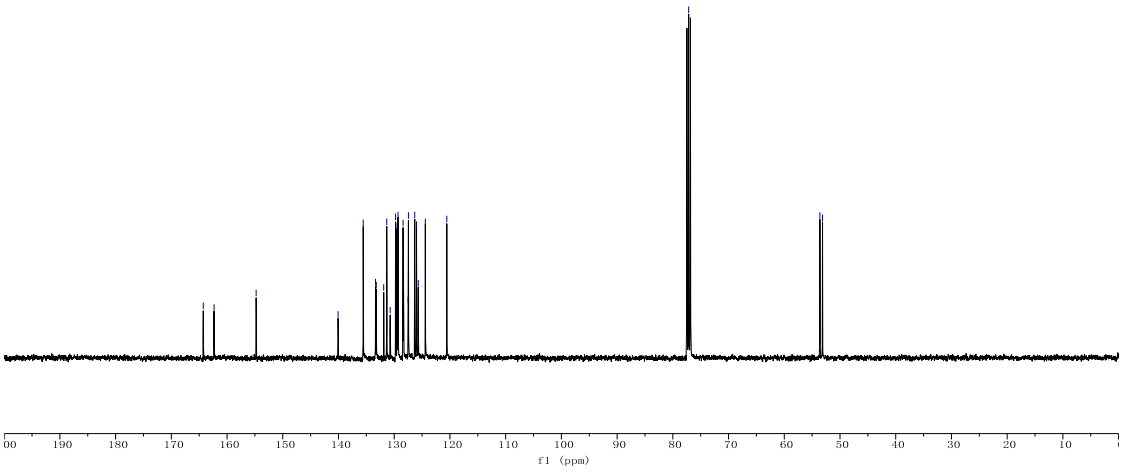
3n, $CDCl_3$, 400MHz

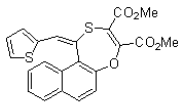




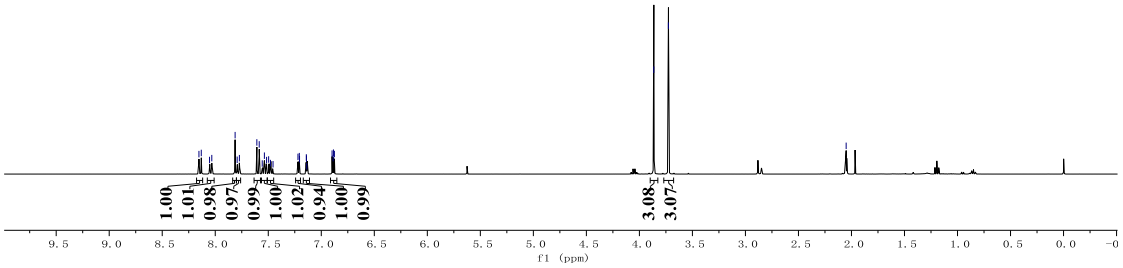


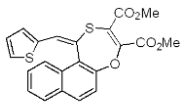
3n, $CDCl_3$, 100MHz



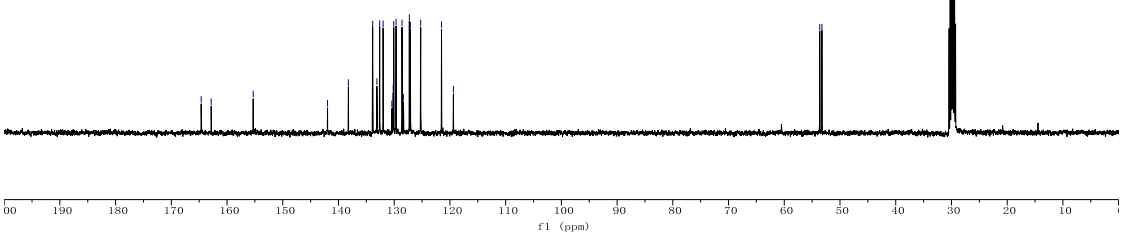


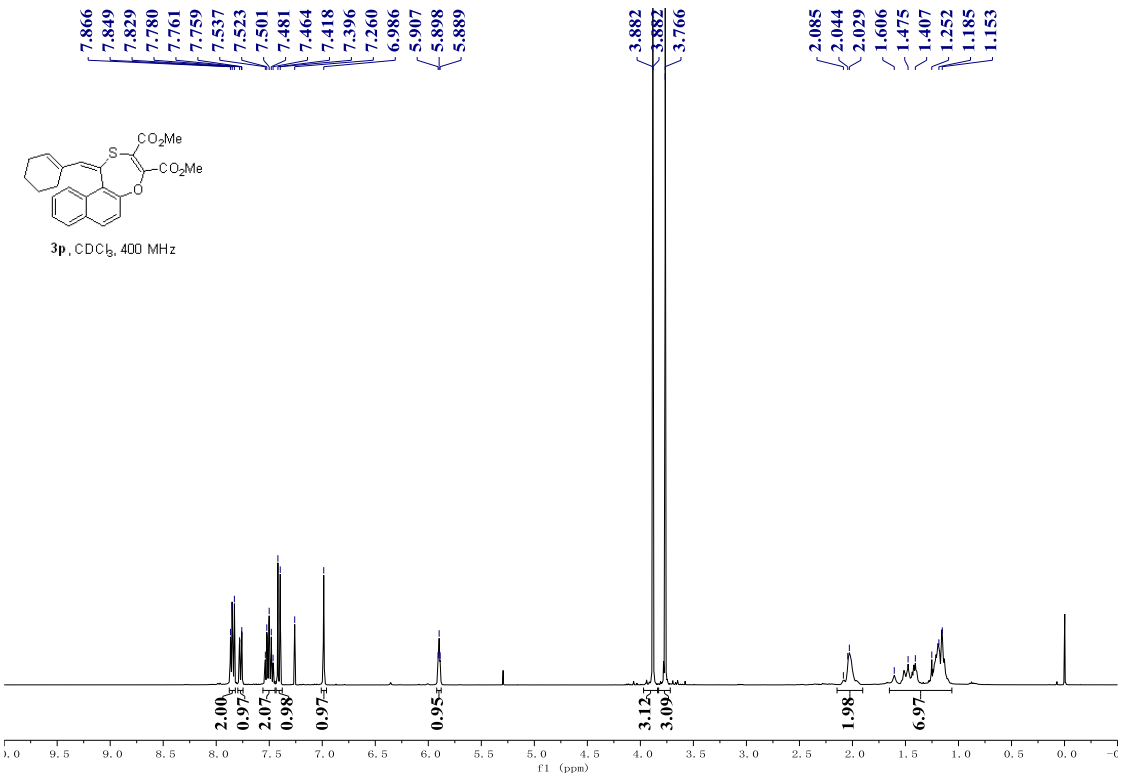
3o, $(CD_3)_2CO$, 400MHz



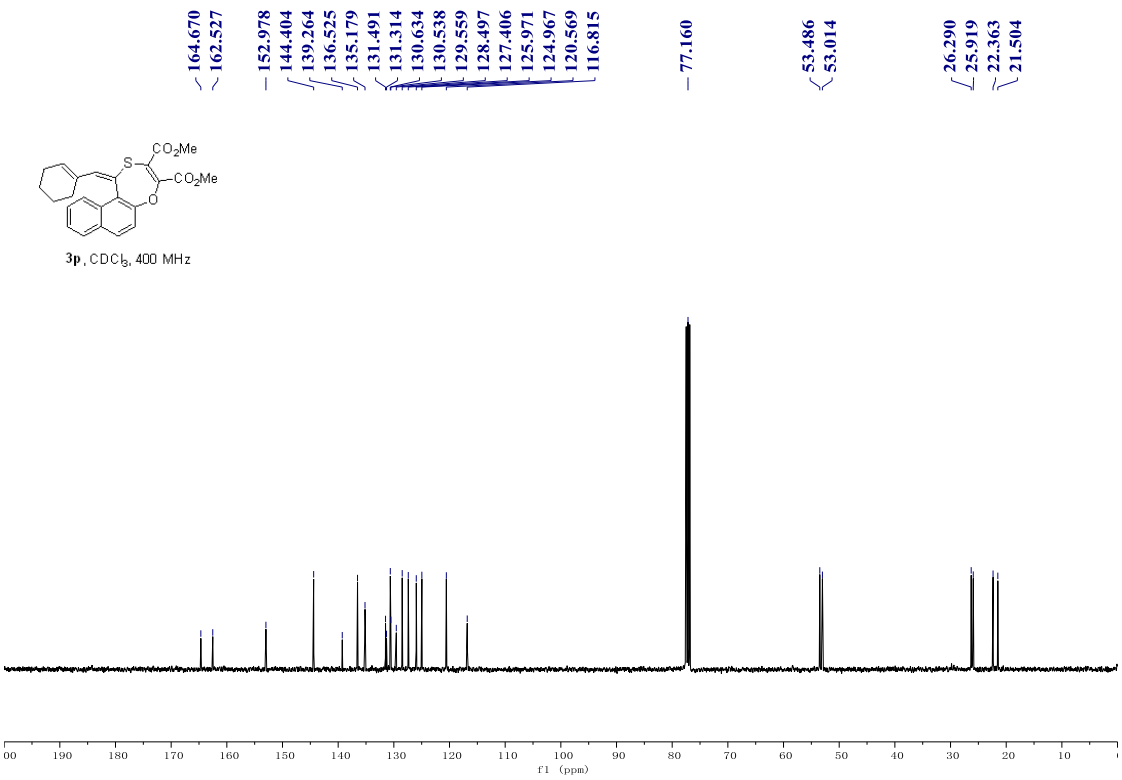


3o, $(CD_3)_2CO$, 100MHz

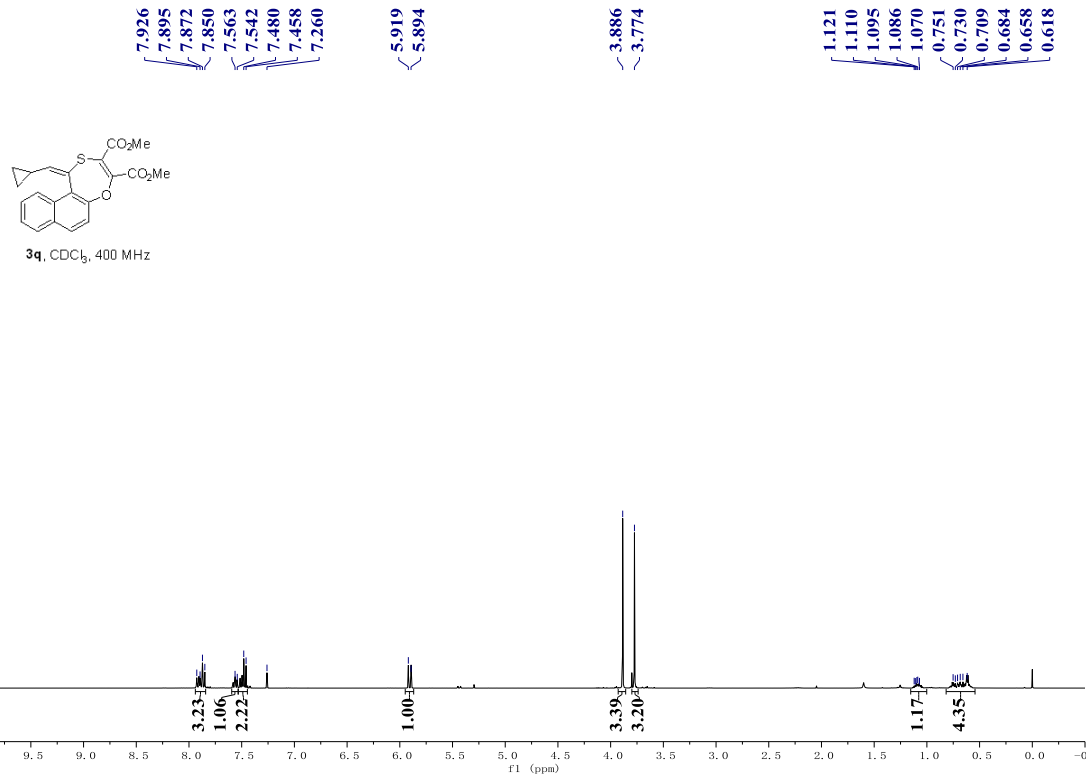


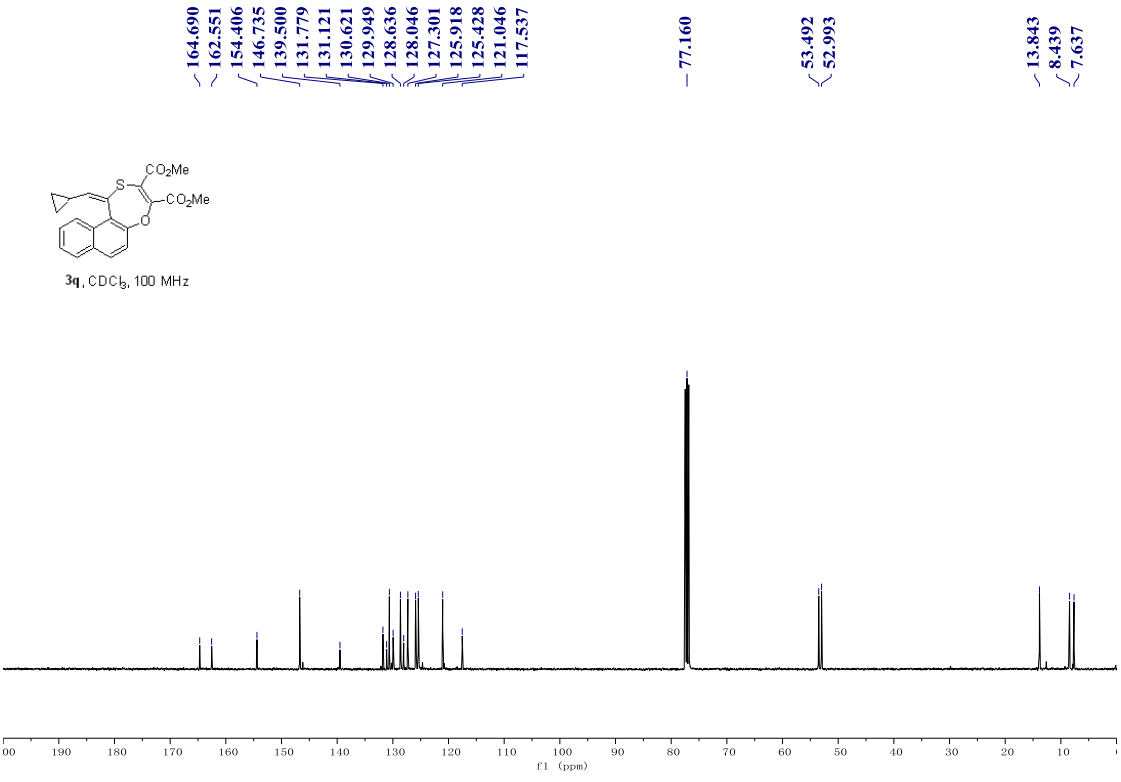


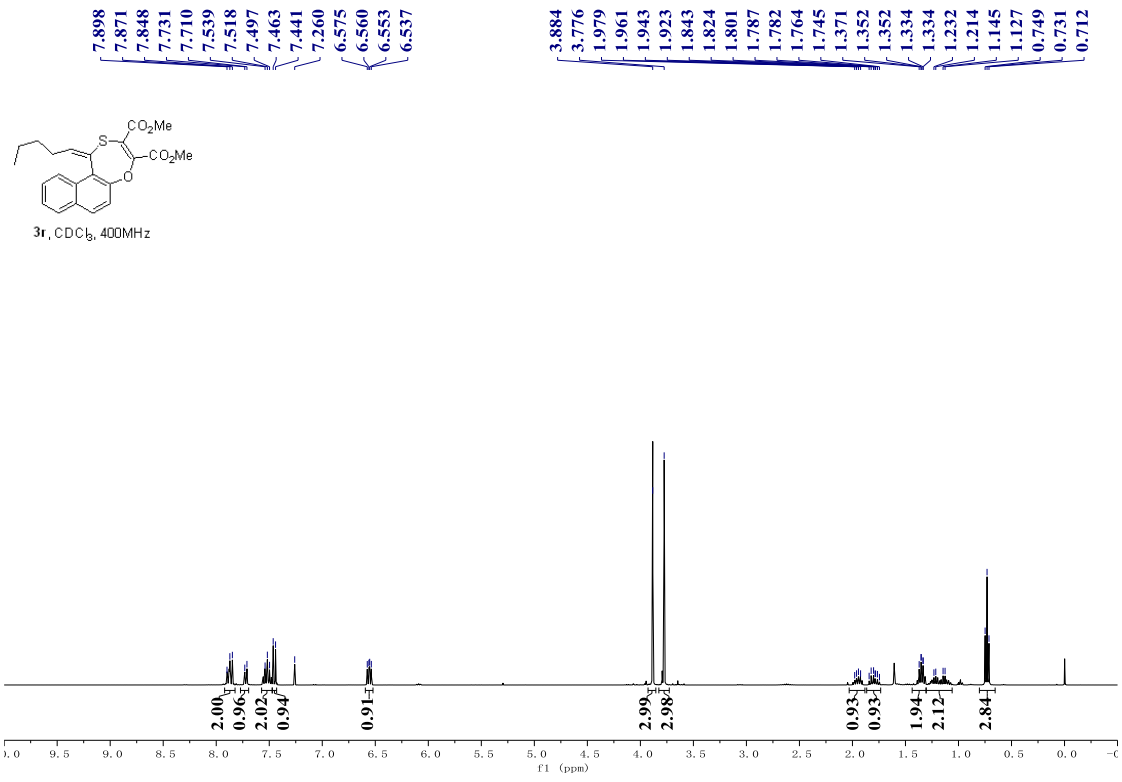
3p, $CDCl_3$, 400 MHz

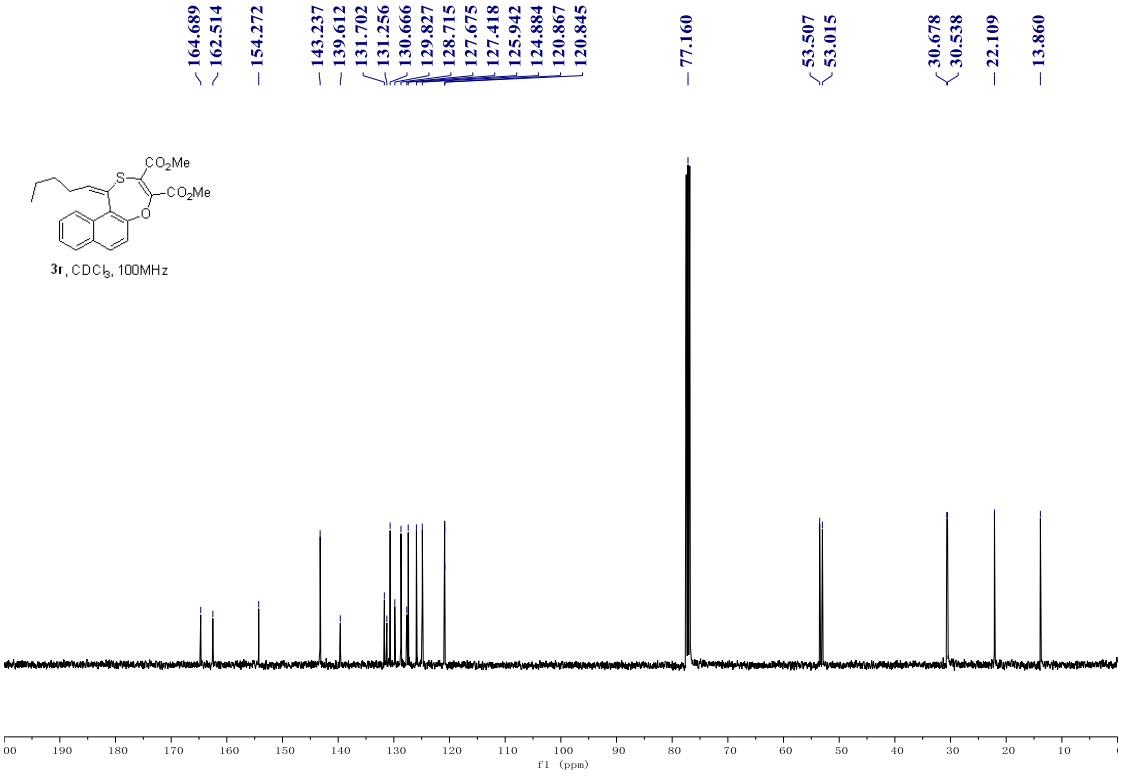


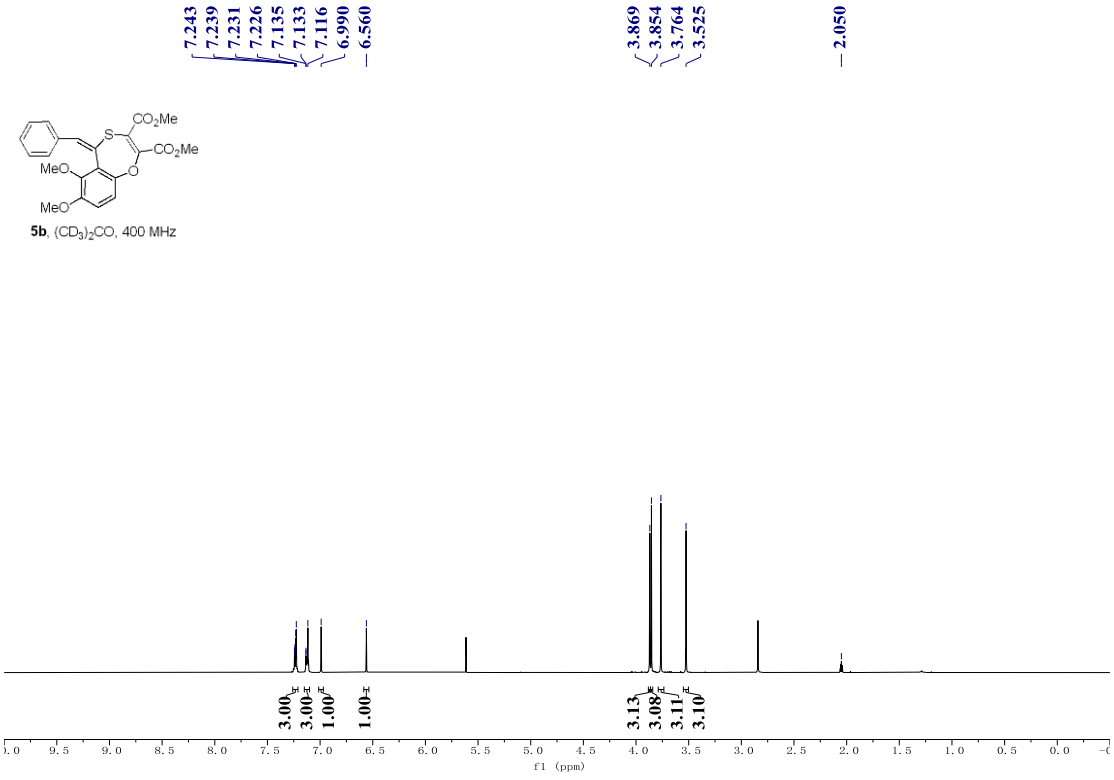
3p, $CDCl_3$, 400 MHz


7.926
7.895
7.872
7.850
7.563
7.542
7.480
7.458
7.260
5.919
5.894
3.886
3.774
1.121
1.110
1.095
1.086
1.070
0.751
0.730
0.709
0.684
0.658
0.618
CO2Me
CO2Me
S
O
3q, CDCl3, 400 MHz
3.23
1.06
2.22
1.00
3.39
3.20
1.17
4.35
f1 (ppm)

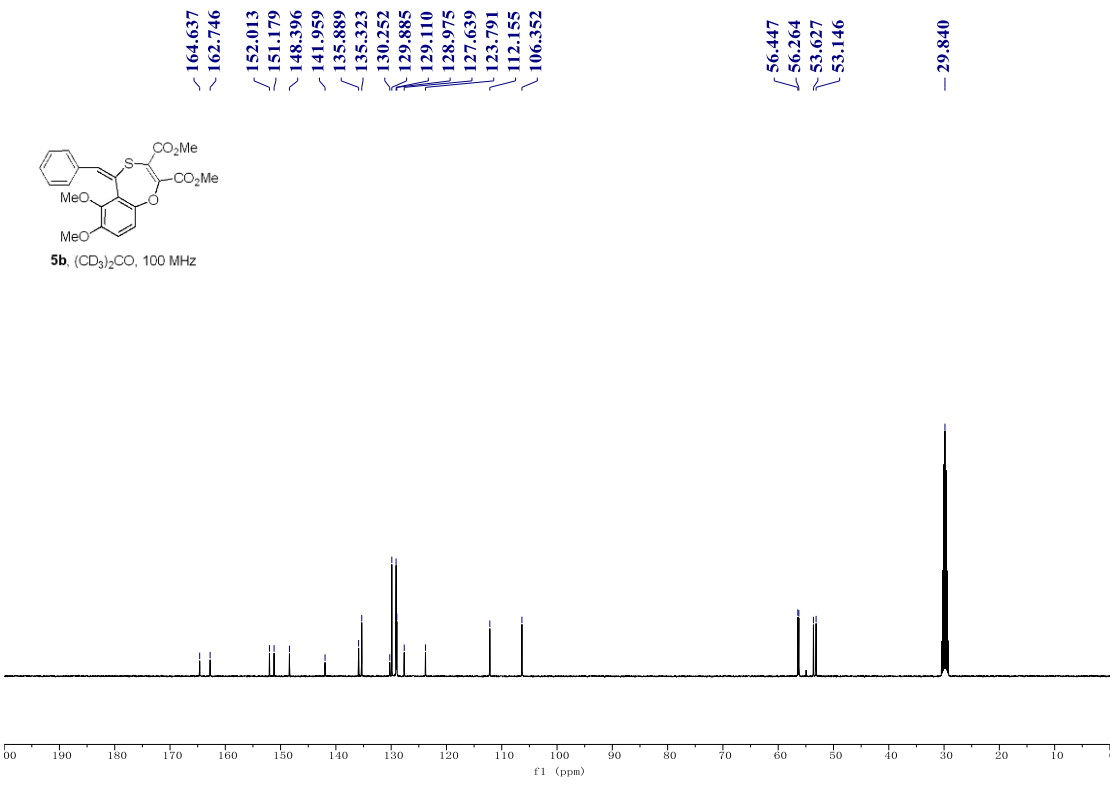

164.690
162.551
154.406
146.735
139.500
131.779
131.121
130.621
129.949
128.636
128.046
127.301
125.918
125.428
121.046
117.537
77.160
53.492
52.993
13.843
8.439
7.637
CO2Me
CO2Me
S
O
3q, CDCl3, 100 MHz
f1 (ppm)


7.898
7.871
7.848
7.731
7.710
7.539
7.518
7.497
7.463
7.441
7.260
6.575
6.560
6.553
6.537
3.884
3.776
1.979
1.961
1.943
1.923
1.843
1.824
1.801
1.787
1.782
1.764
1.745
1.371
1.352
1.352
1.334
1.334
1.232
1.214
1.145
1.127
0.749
0.731
0.712
CO2Me
CO2Me
S
O
3r, CDCl3, 400MHz
2.00
0.96
2.02
0.94
0.91
2.99
2.98
0.93
0.93
1.94
2.12
2.84
f1 (ppm)

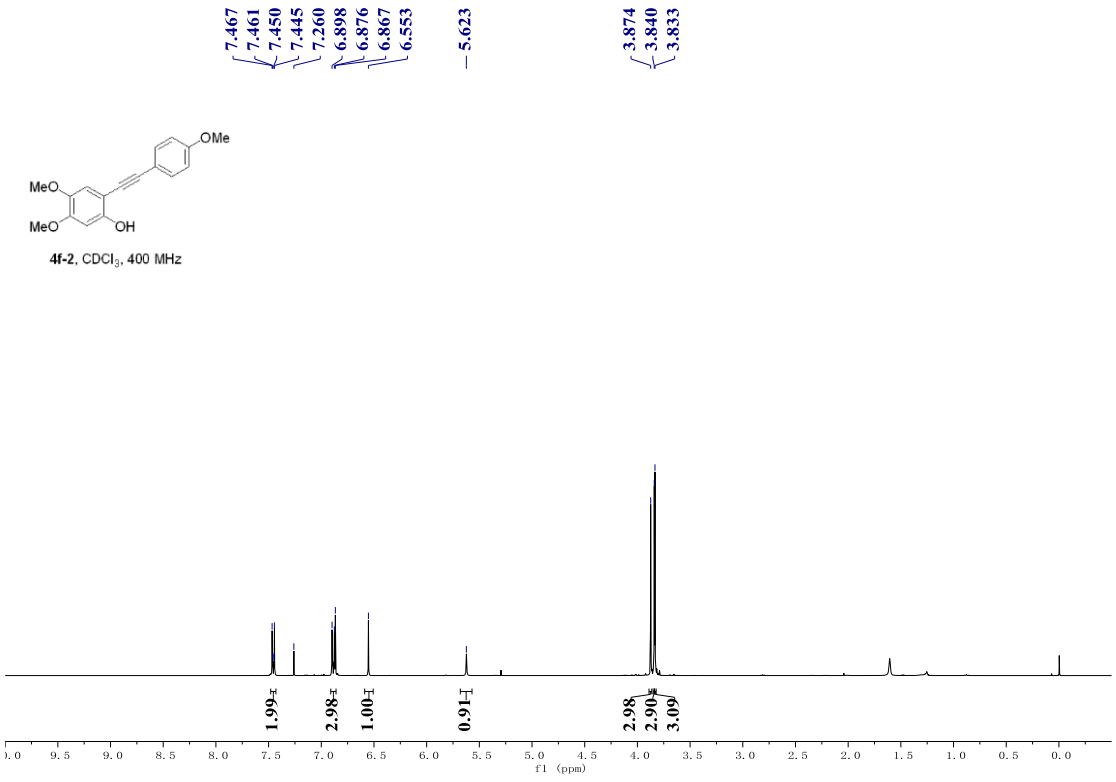

164.689
162.514
154.272
143.237
139.612
131.702
131.256
130.666
129.827
128.715
127.675
127.418
125.942
124.884
120.867
120.845
77.160
53.507
53.015
30.678
30.538
22.109
13.860
CO2Me
CO2Me
S
O
3r, CDCl3, 100MHz
f1 (ppm)

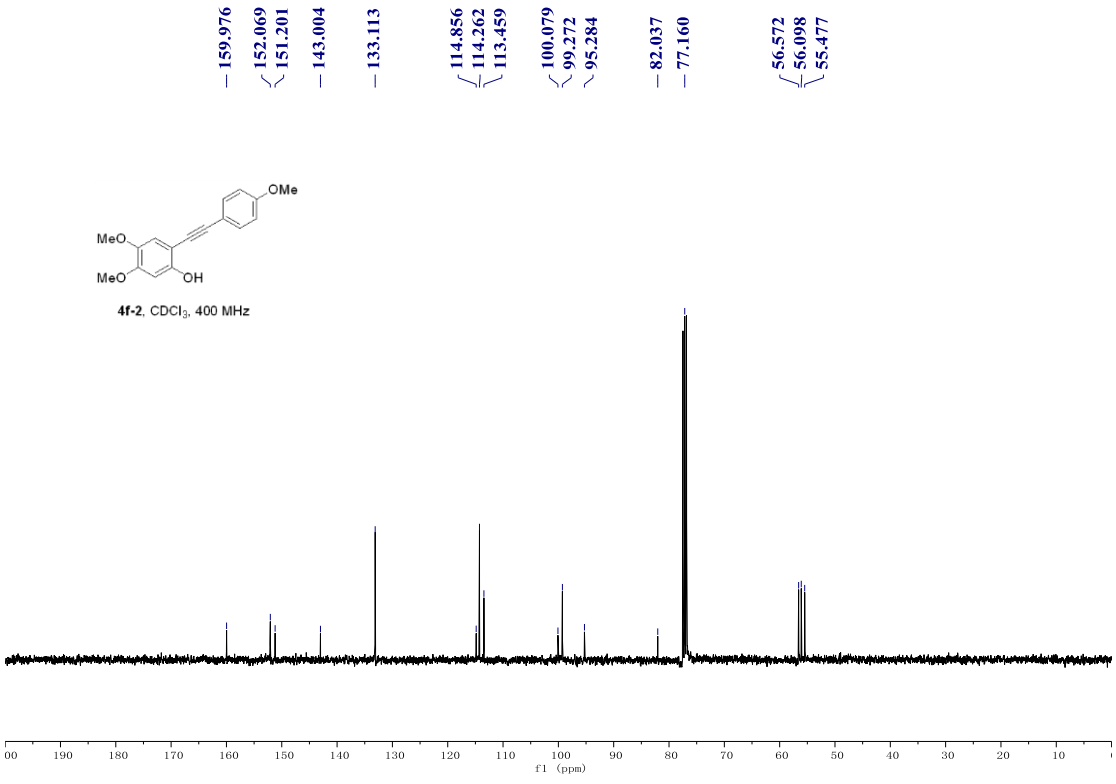


5b, $(CD_3)_2CO$, 400 MHz

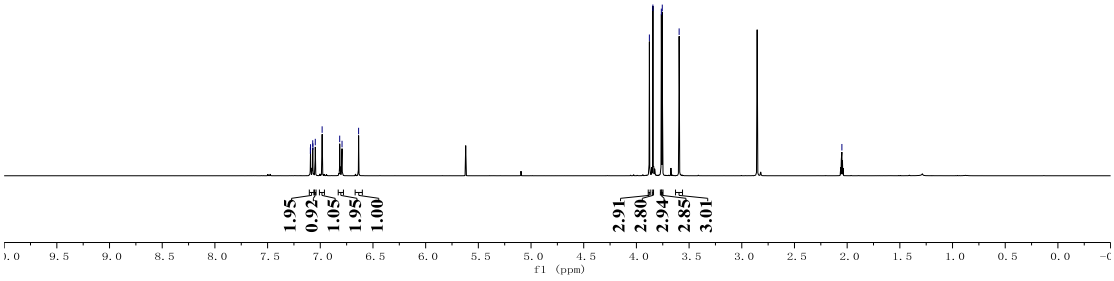


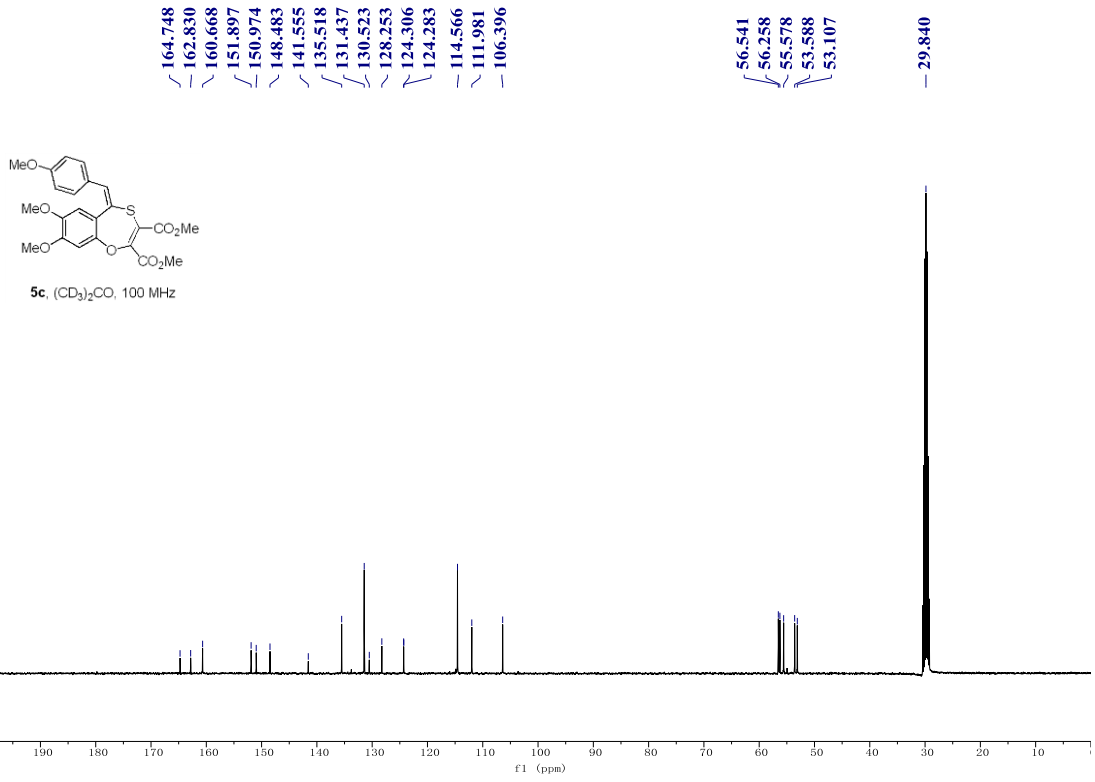
5b, $(CD_3)_2CO$, 100 MHz


7.467
7.461
7.450
7.445
7.260
6.898
6.876
6.867
6.553
5.623
3.874
3.840
3.833
OMe
MeO
MeO
OH
4f-2, CDCl3, 400 MHz
1.99
2.98
1.00
0.91
2.98
2.90
3.09
f1 (ppm)

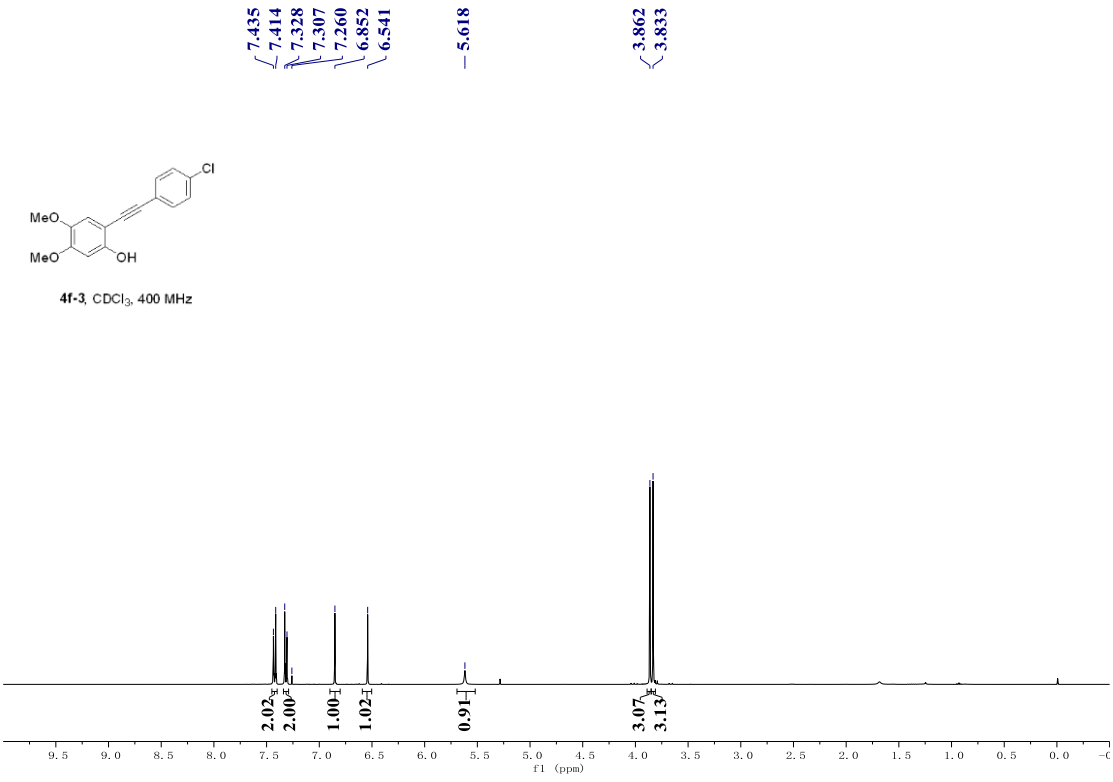

159.976
152.069
151.201
143.004
133.113
114.856
114.262
113.459
100.079
99.272
95.284
82.037
77.160
56.572
56.098
55.477
OMe
MeO
MeO
OH
4f-2, CDCl3, 400 MHz
f1 (ppm)

5c, $(CD_3)_2CO$, 400 MHz

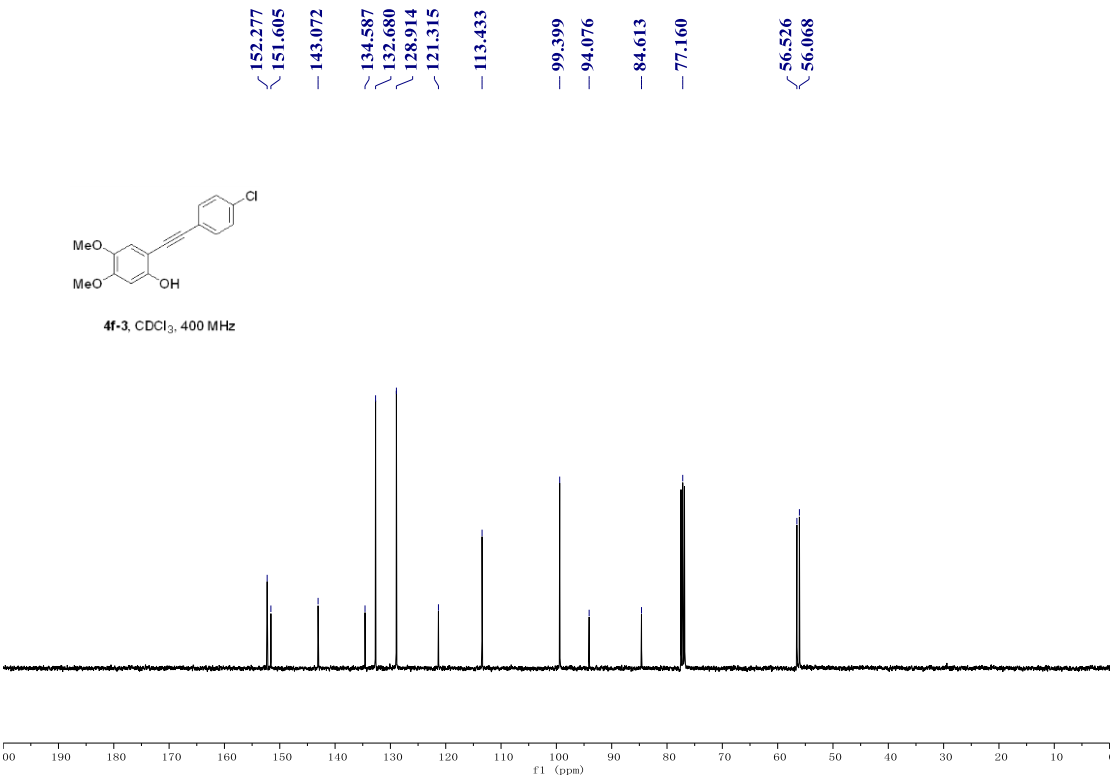




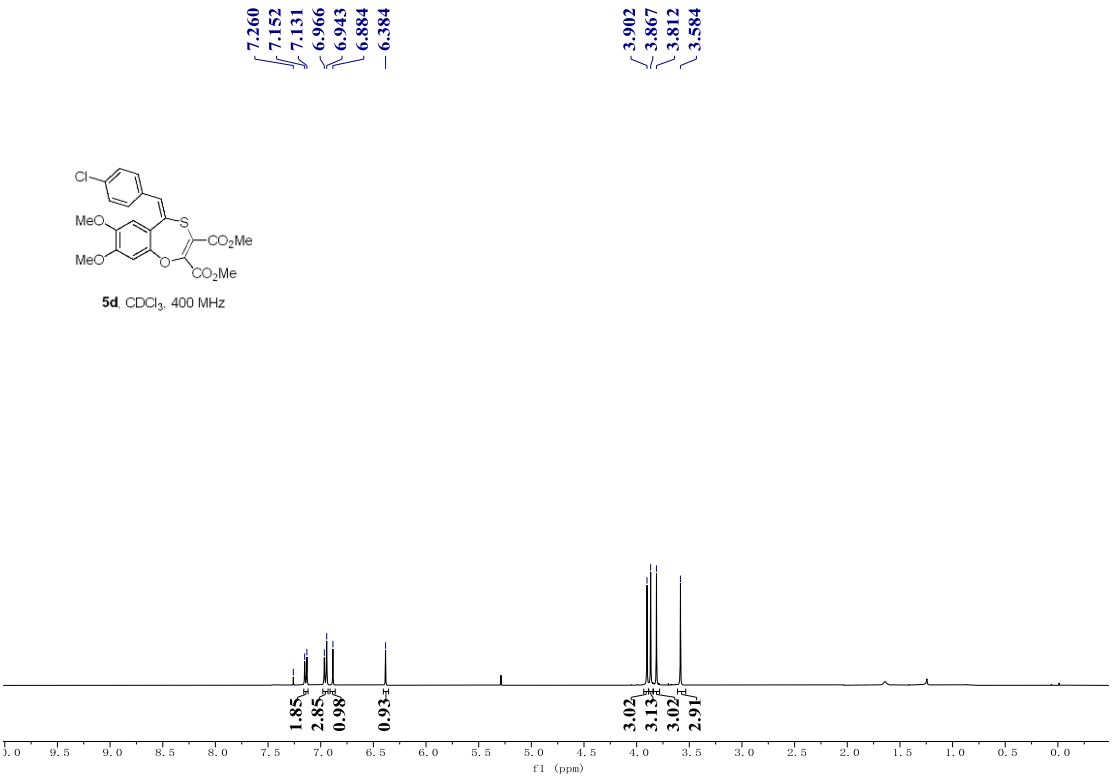
5c, $(CD_3)_2CO$, 100 MHz



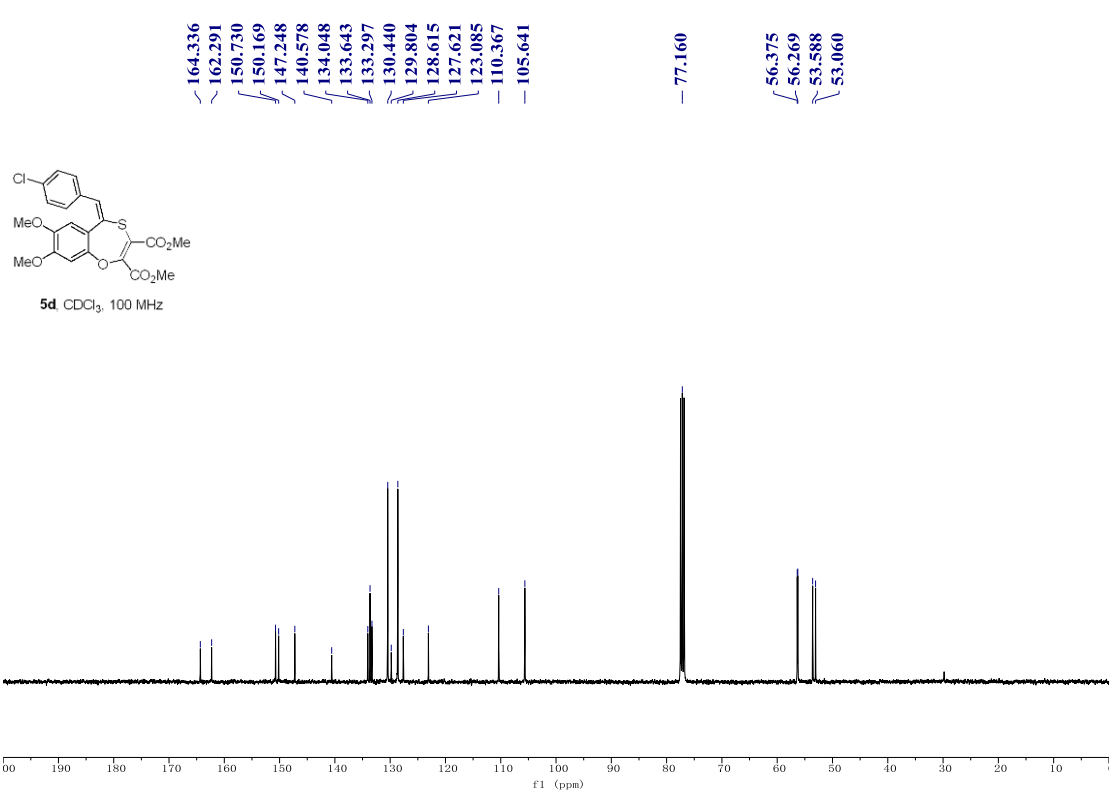
4f-3, $CDCl_3$, 400 MHz



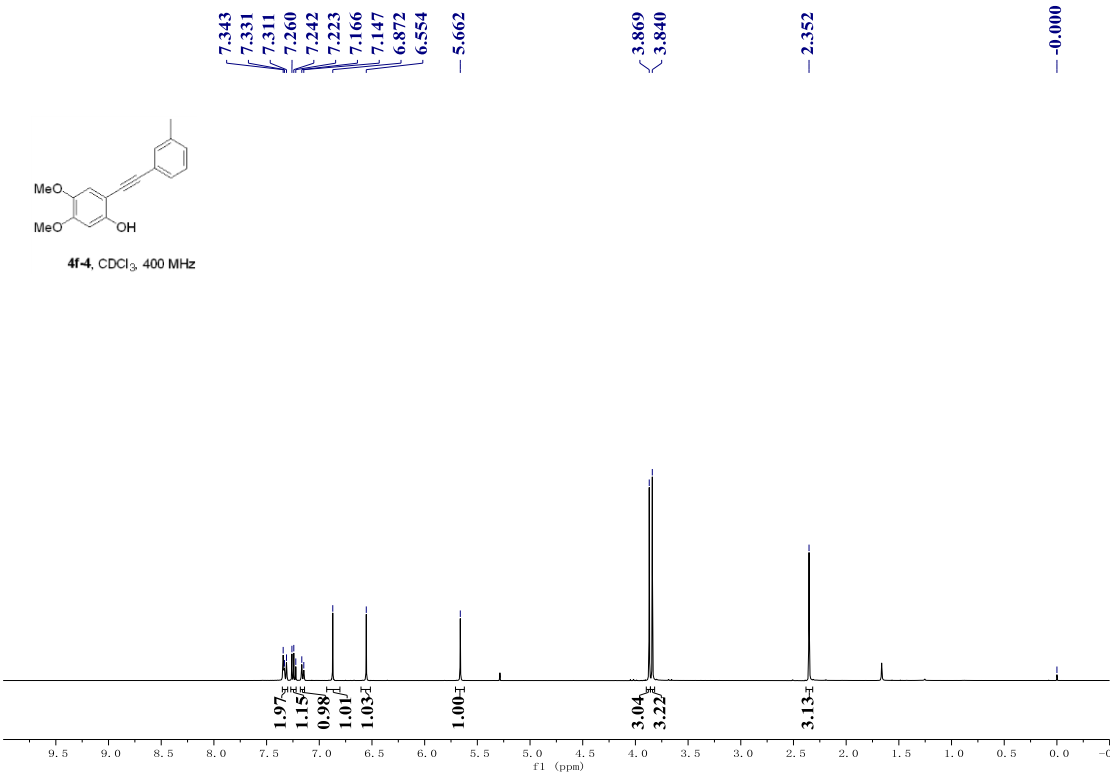
4f-3, $CDCl_3$, 400 MHz



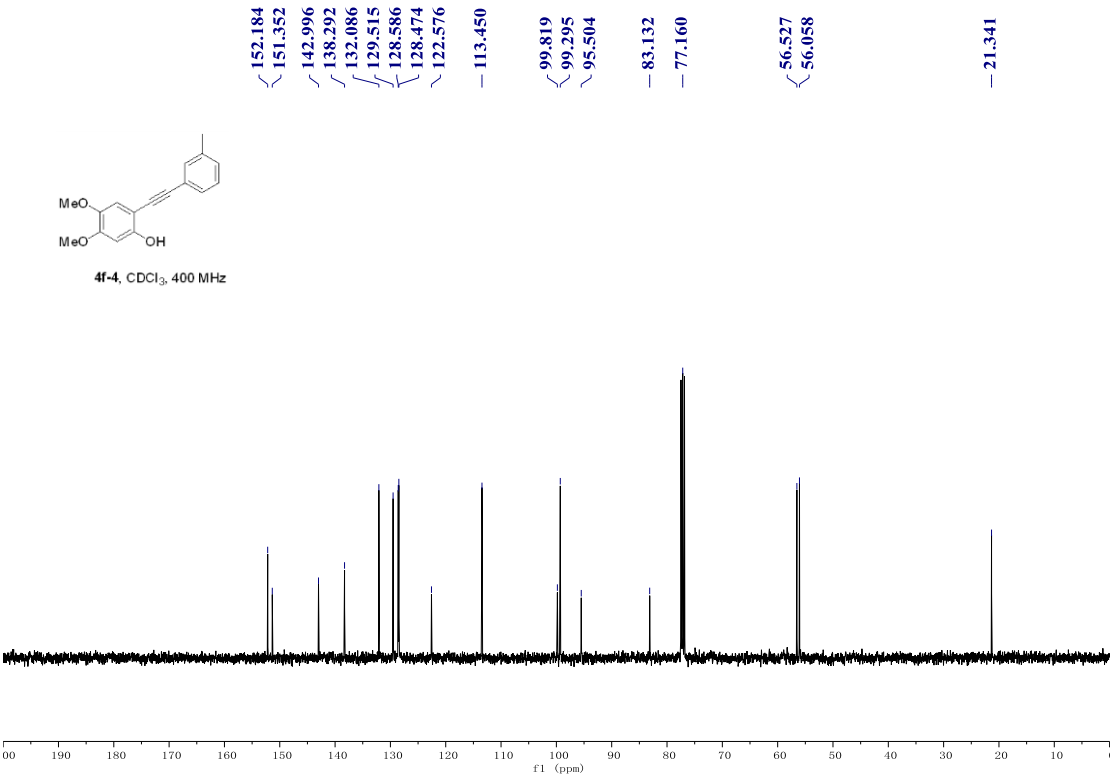
5d, $CDCl_3$, 400 MHz



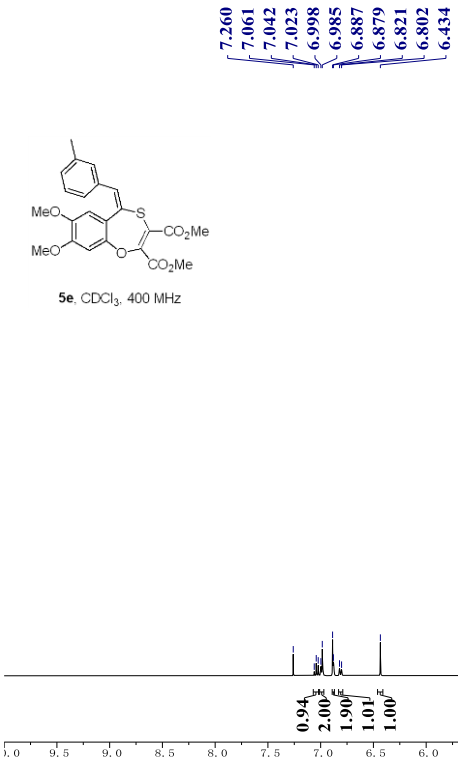
5d, $CDCl_3$, 100 MHz



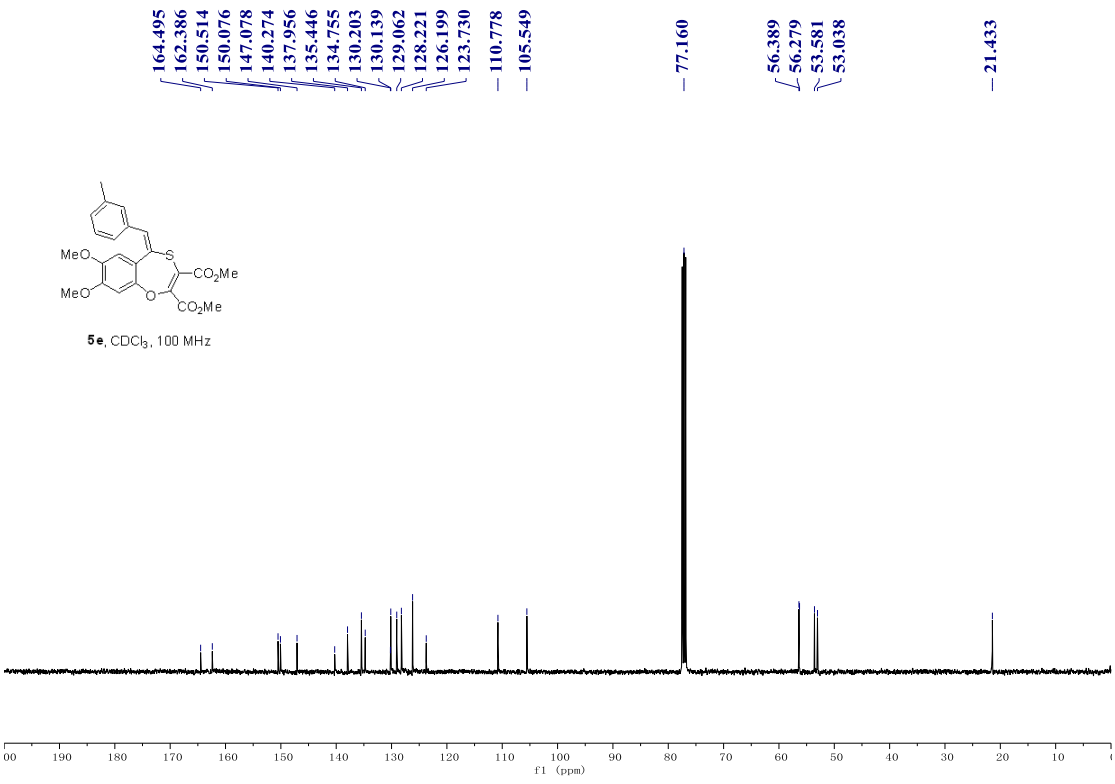
4f-4, $CDCl_3$, 400 MHz



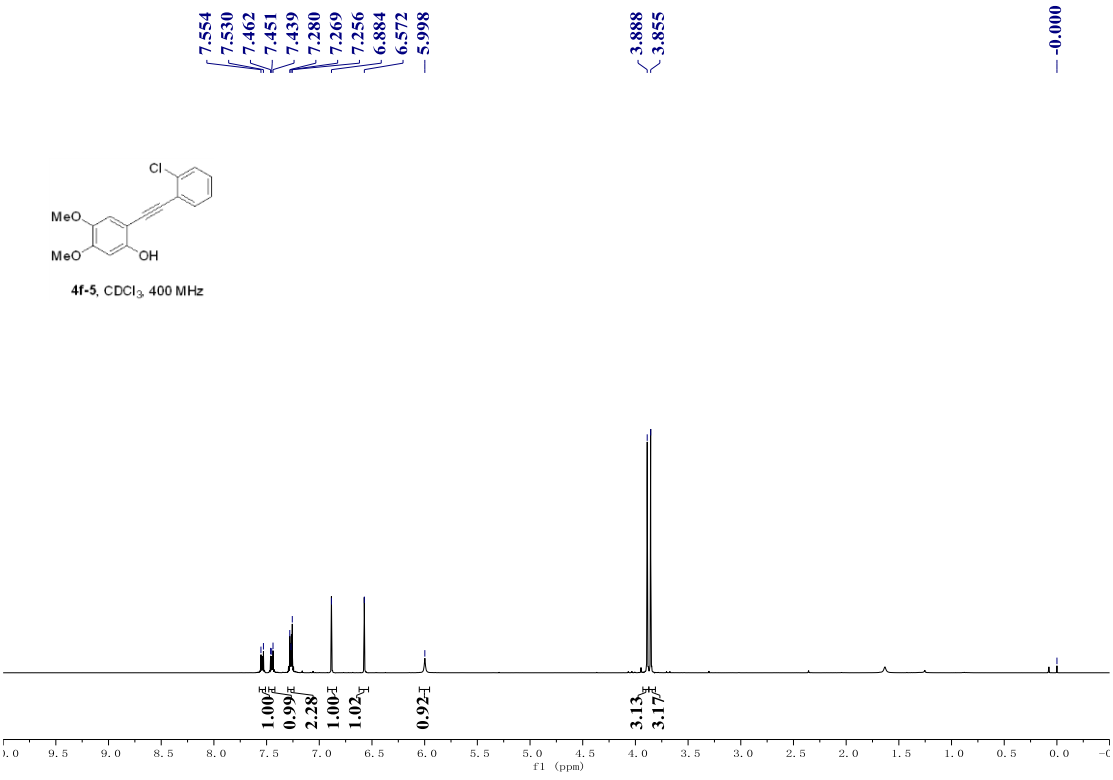
4f-4, $CDCl_3$, 400 MHz



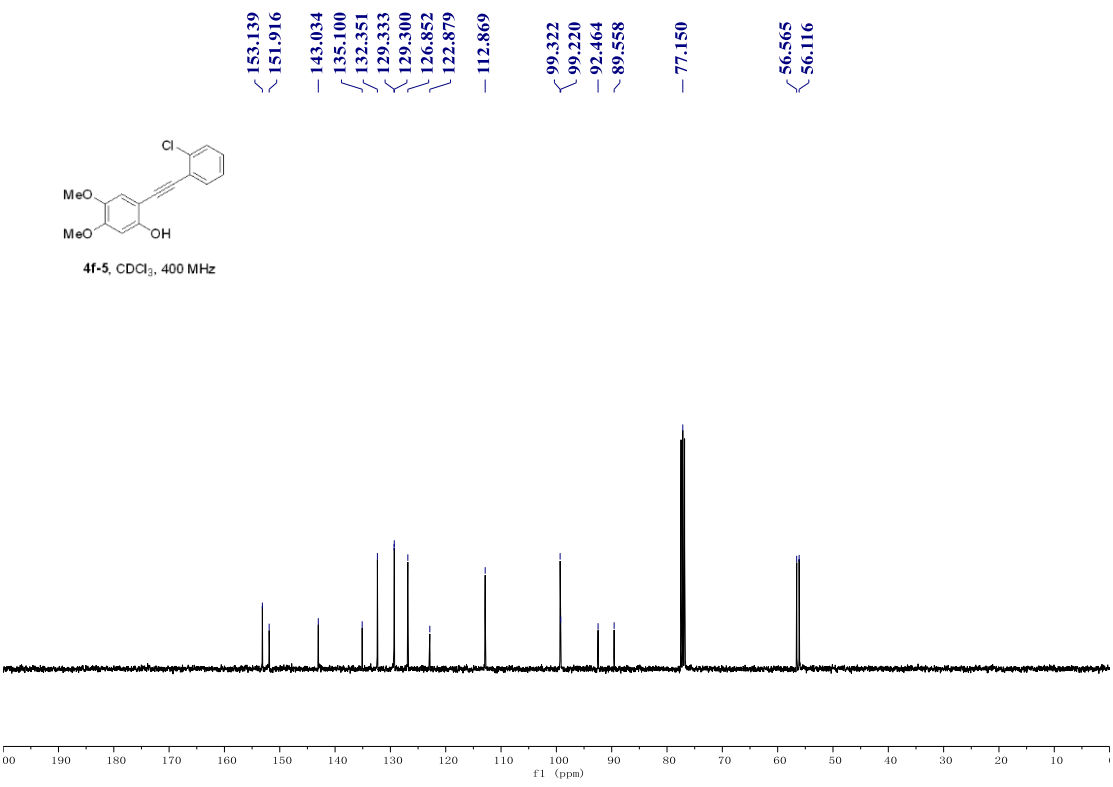
5e, $CDCl_3$, 400 MHz



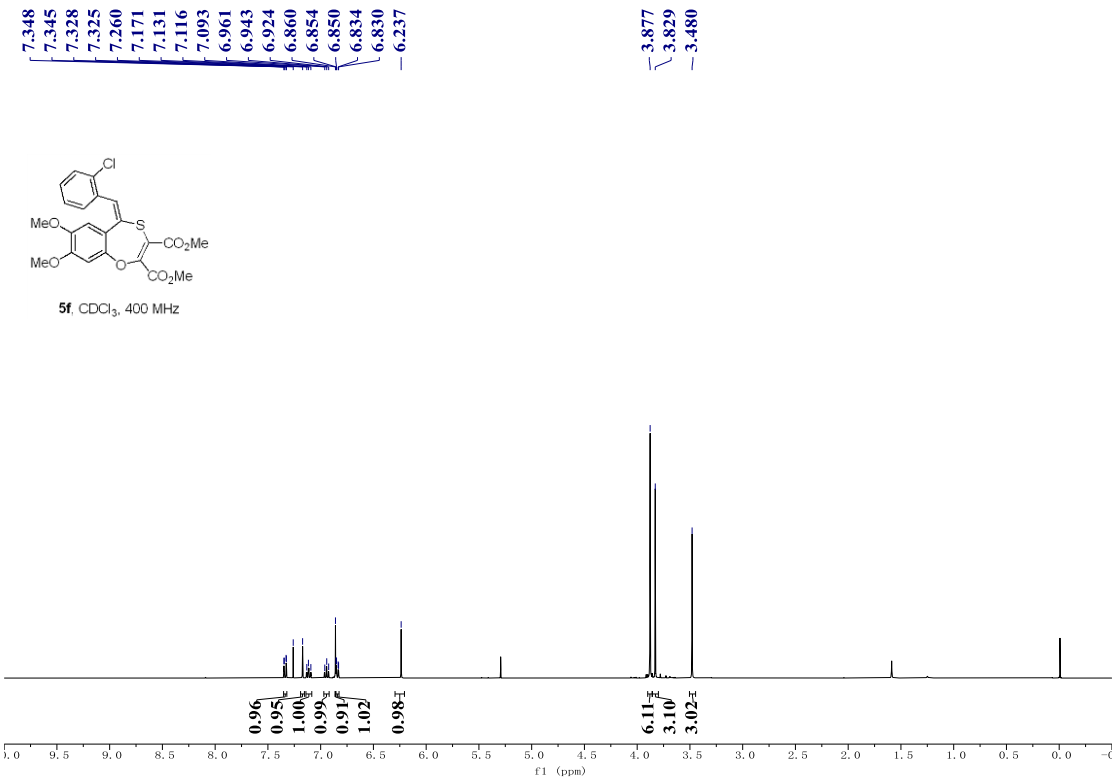
5e, $CDCl_3$, 100 MHz



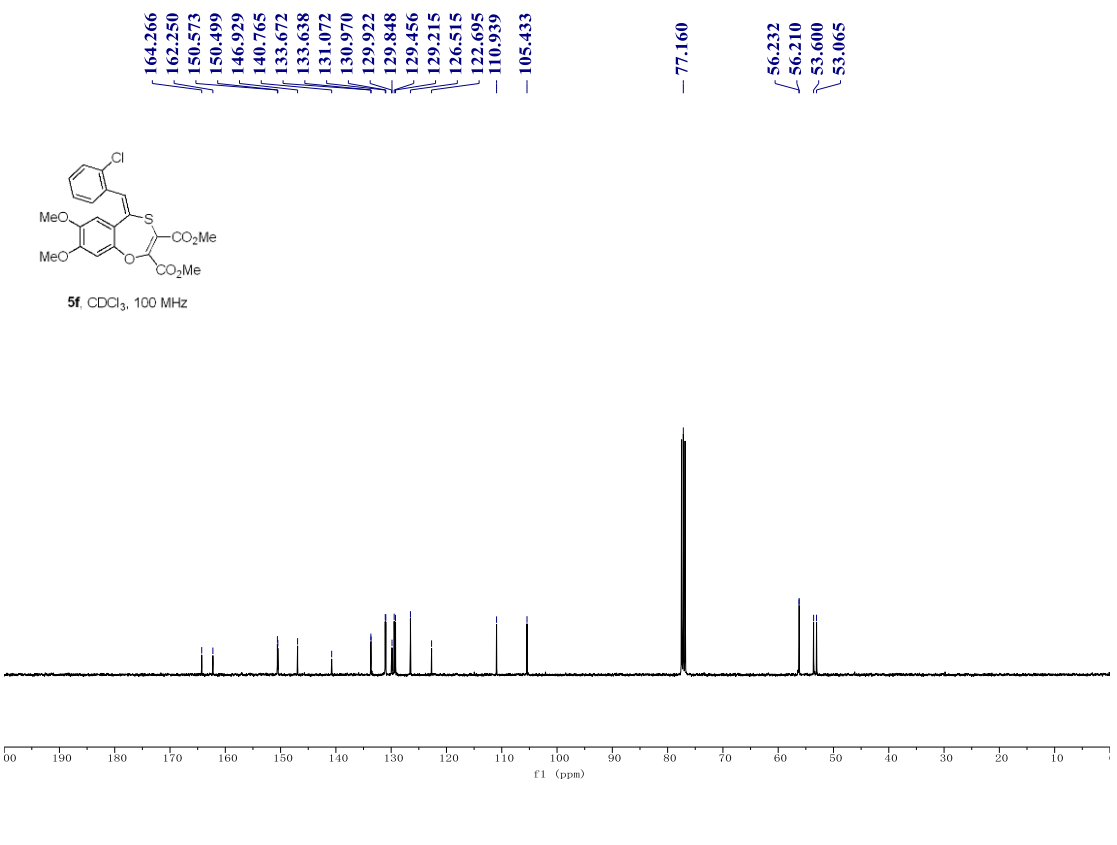
4f-5, $CDCl_3$, 400 MHz



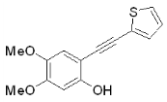
4f-5, $CDCl_3$, 400 MHz



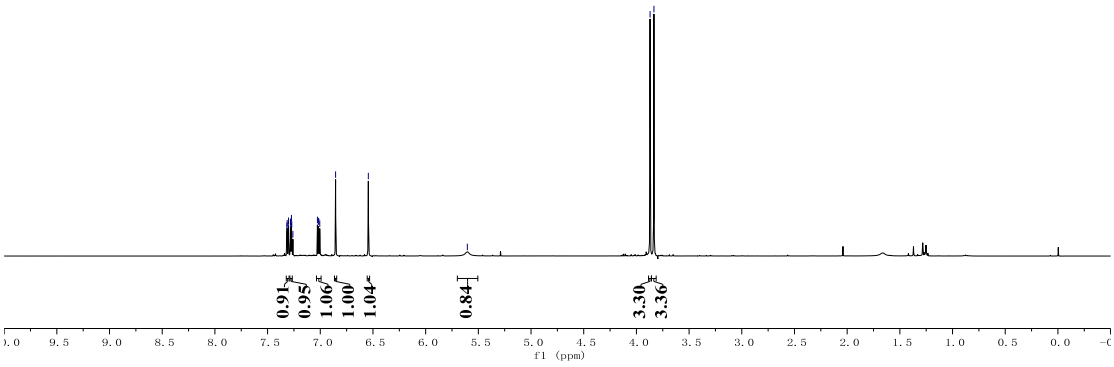
5f, $CDCl_3$, 400 MHz

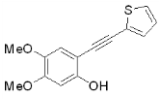


5f, $CDCl_3$, 100 MHz

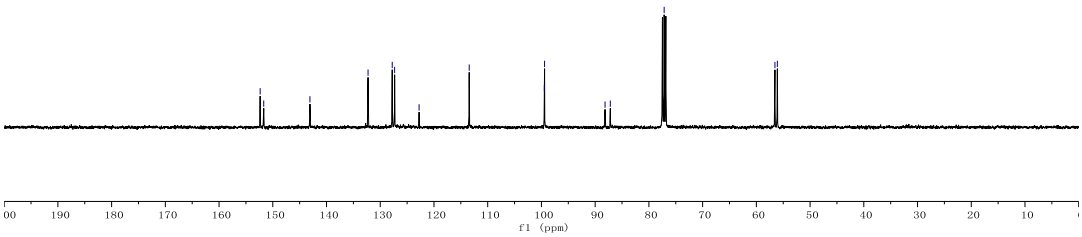


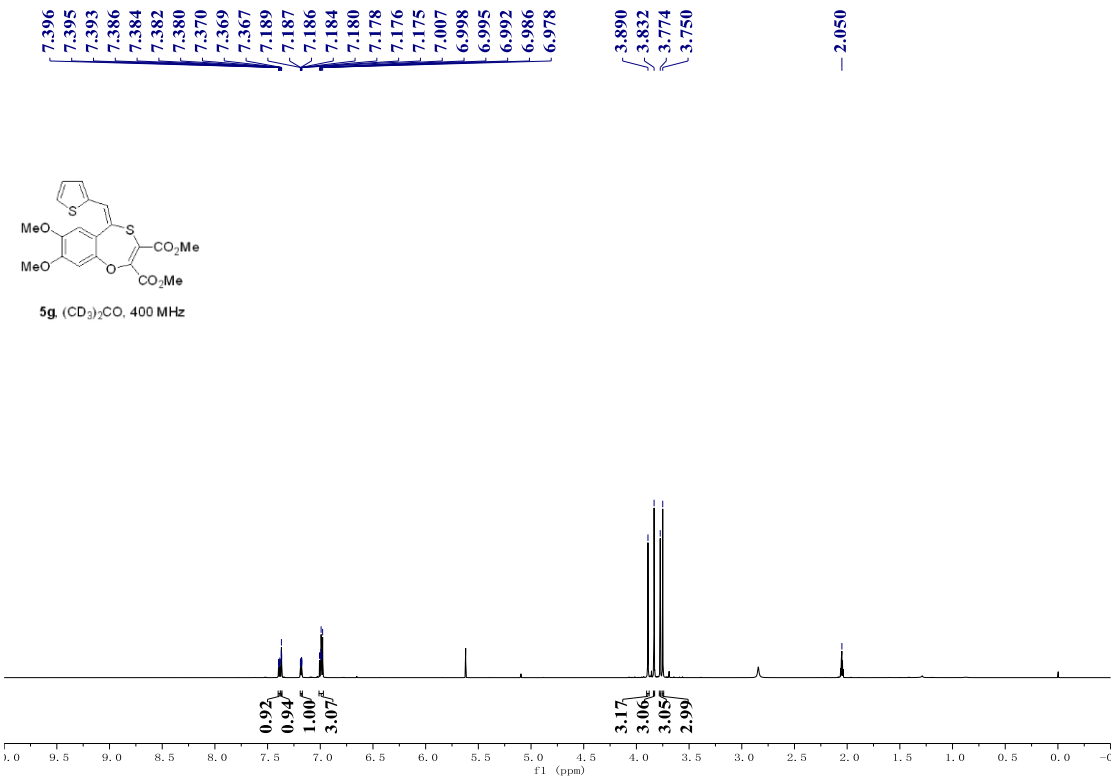
4f-6, $CDCl_3$, 400 MHz

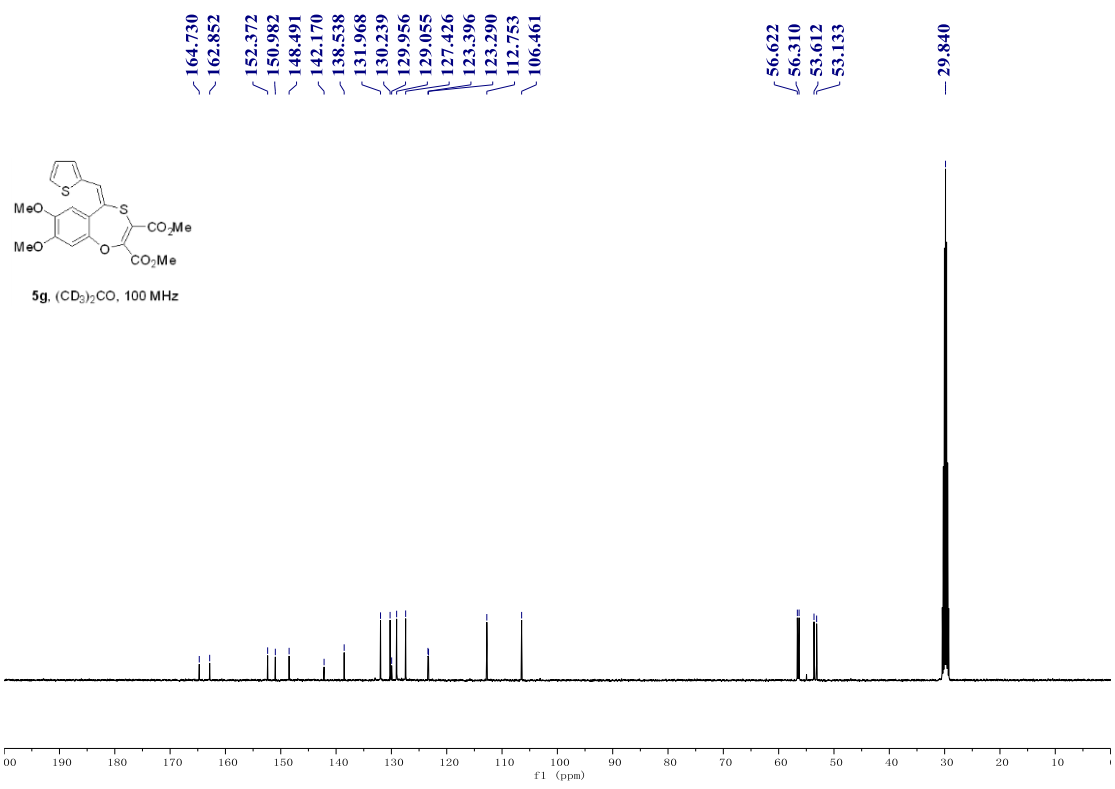


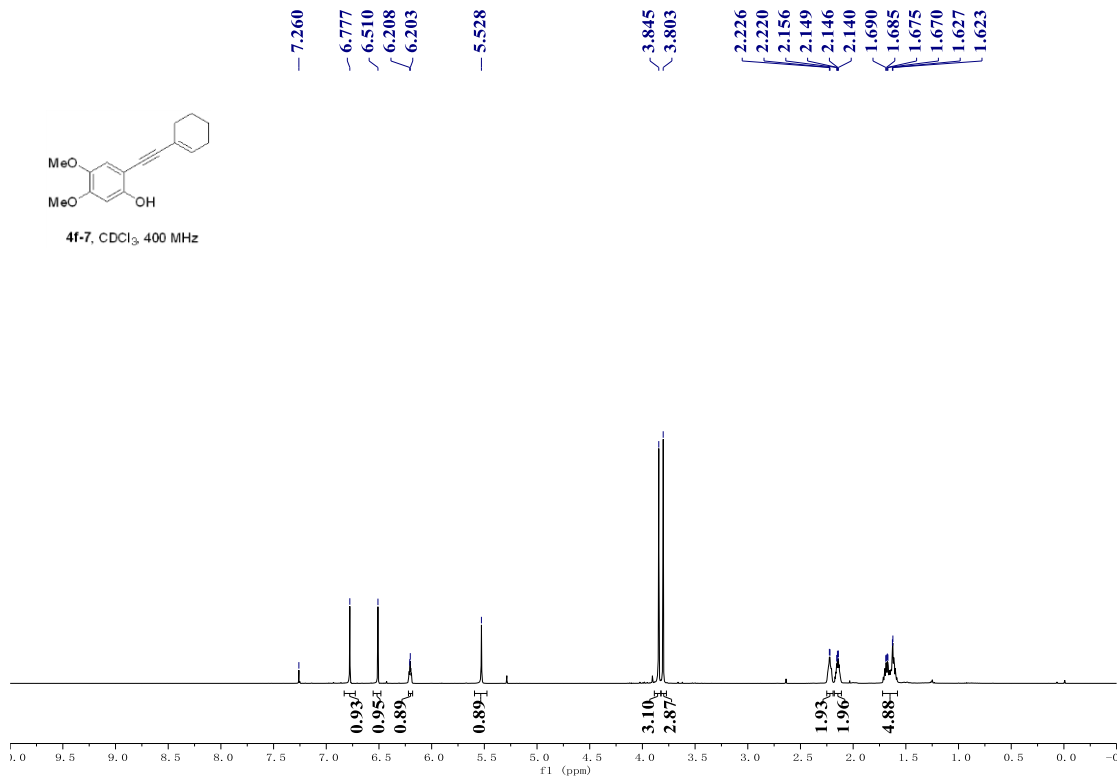


4f-6, $CDCl_3$, 400 MHz

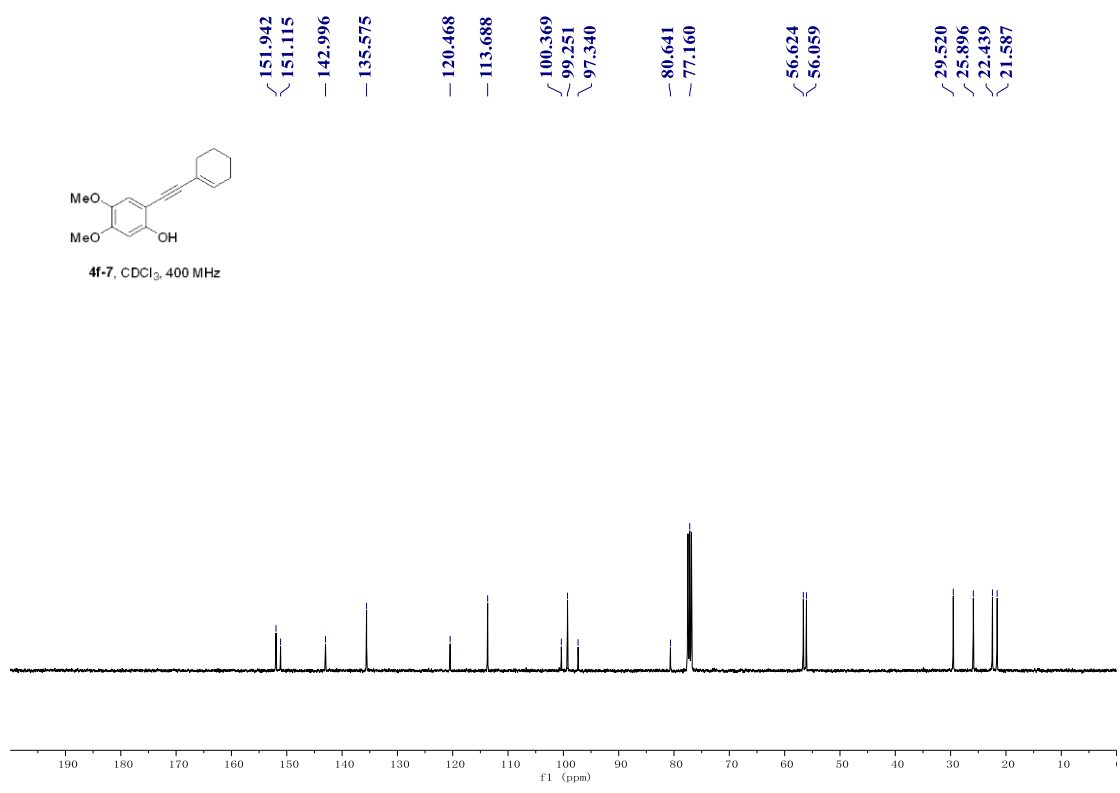



7.396
7.395
7.393
7.386
7.384
7.382
7.380
7.370
7.369
7.367
7.189
7.187
7.186
7.184
7.180
7.178
7.176
7.175
7.007
6.998
6.995
6.992
6.986
6.978
3.890
3.832
3.774
3.750
2.050
MeO
MeO
CO2Me
CO2Me
5g, (CD3)2CO, 400 MHz
0.92
0.94
1.00
3.07
3.17
3.06
3.05
2.99
f1 (ppm)

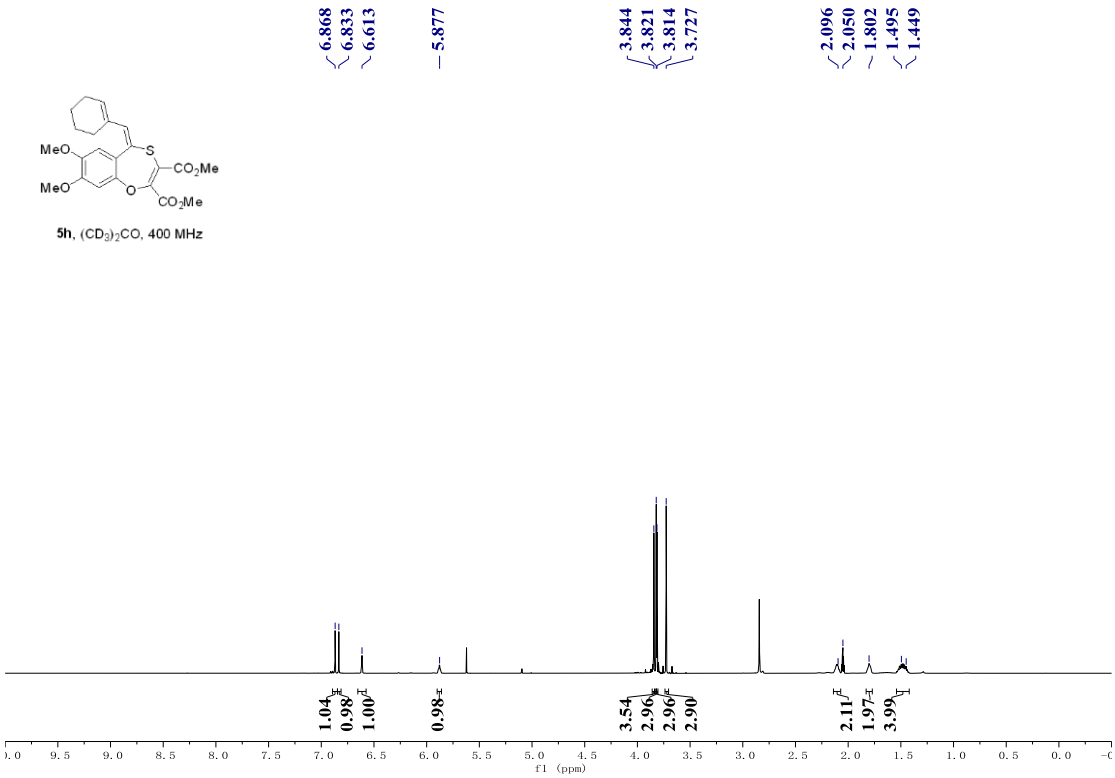

164.730
162.852
152.372
150.982
148.491
142.170
138.538
131.968
130.239
129.956
129.055
127.426
123.396
123.290
112.753
106.461
56.622
56.310
53.612
53.133
29.840
MeO
MeO
CO2Me
CO2Me
5g, (CD3)2CO, 100 MHz
f1 (ppm)

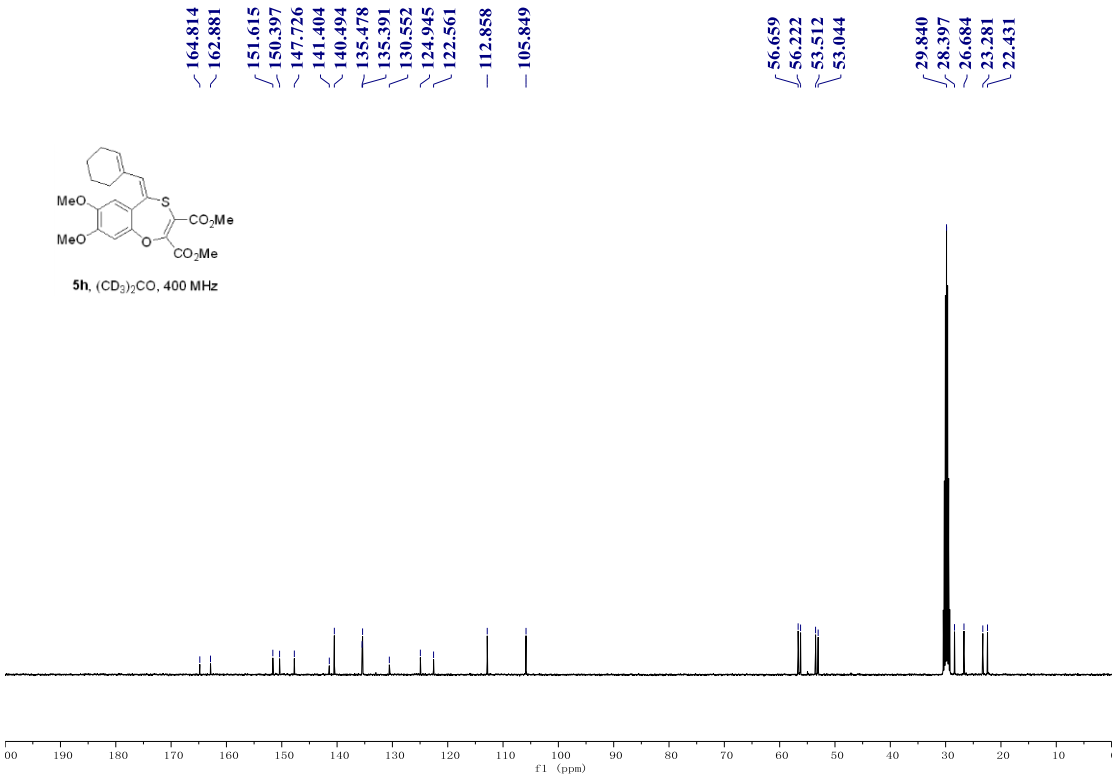


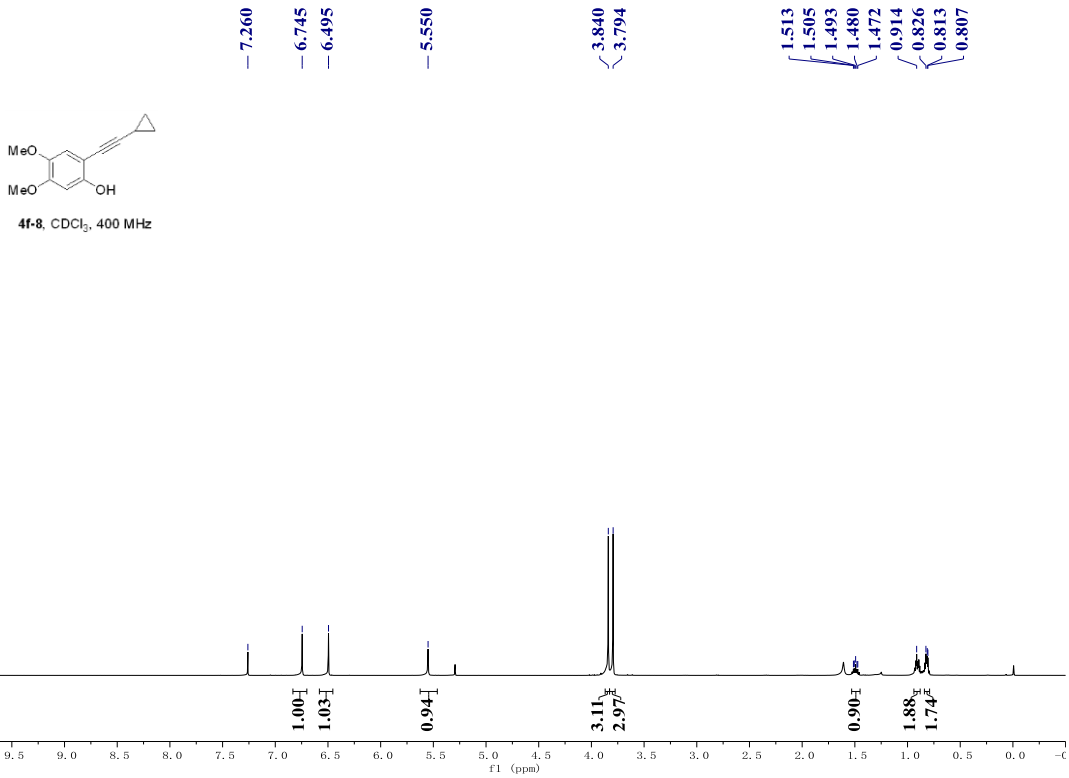
4f-7, $CDCl_3$, 400 MHz

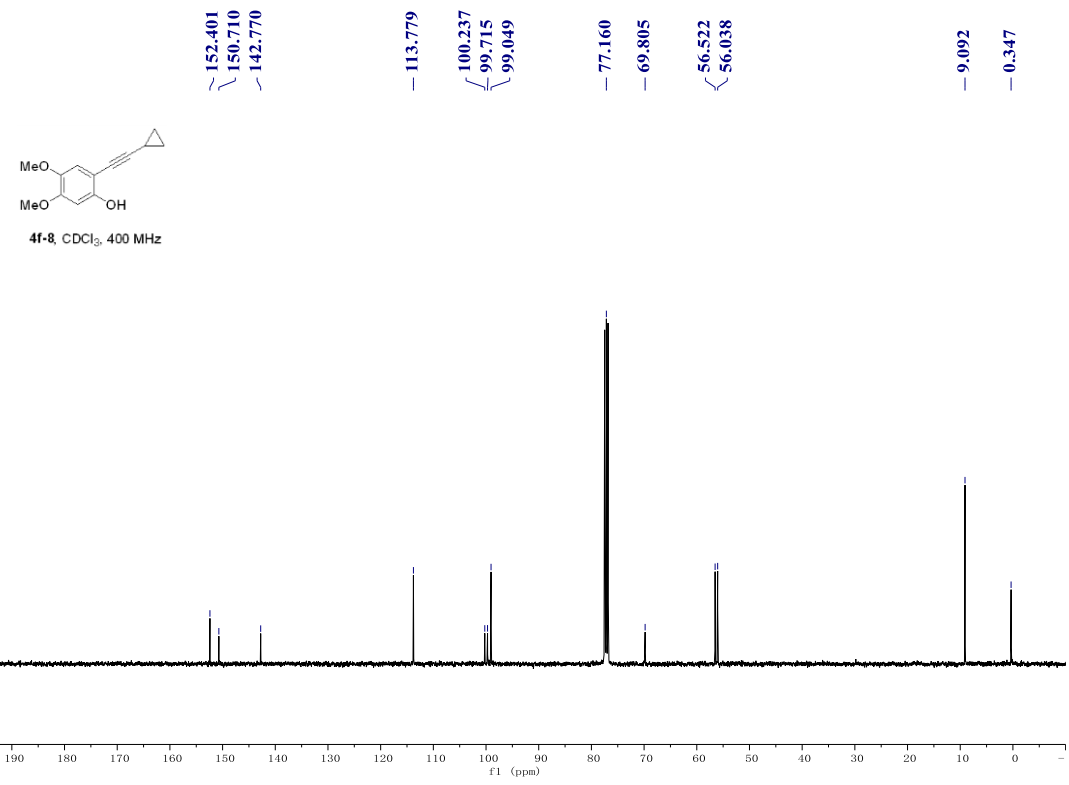


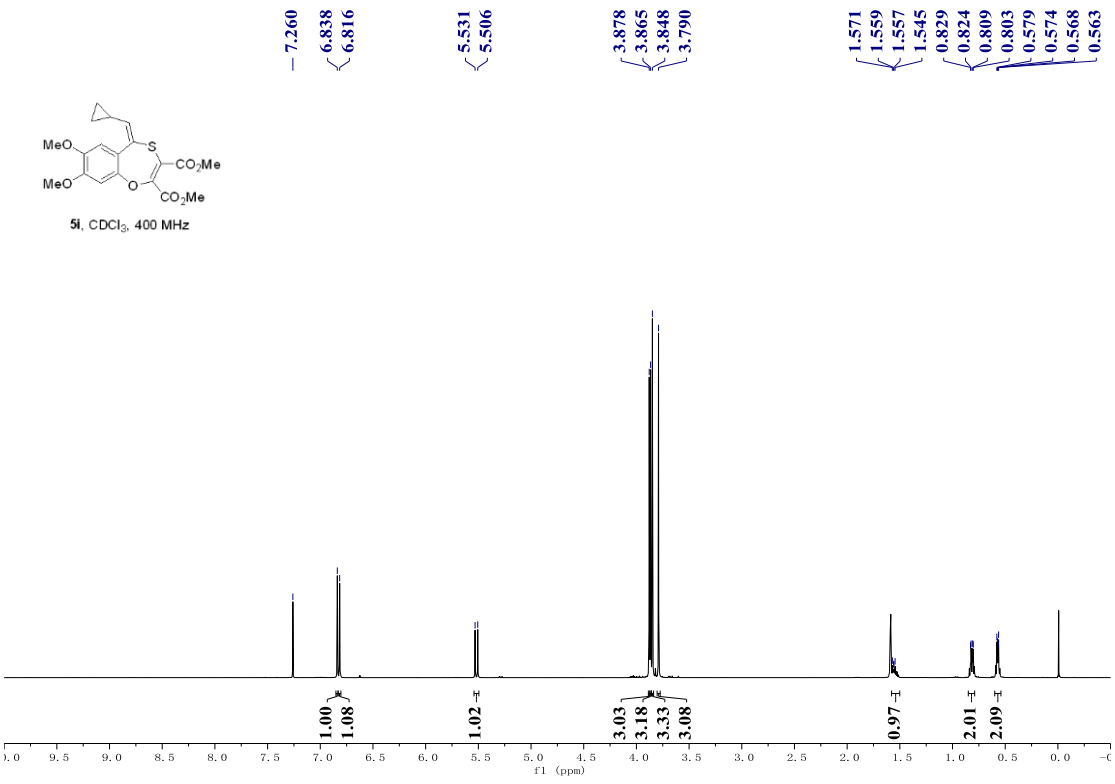
4f-7, $CDCl_3$, 400 MHz

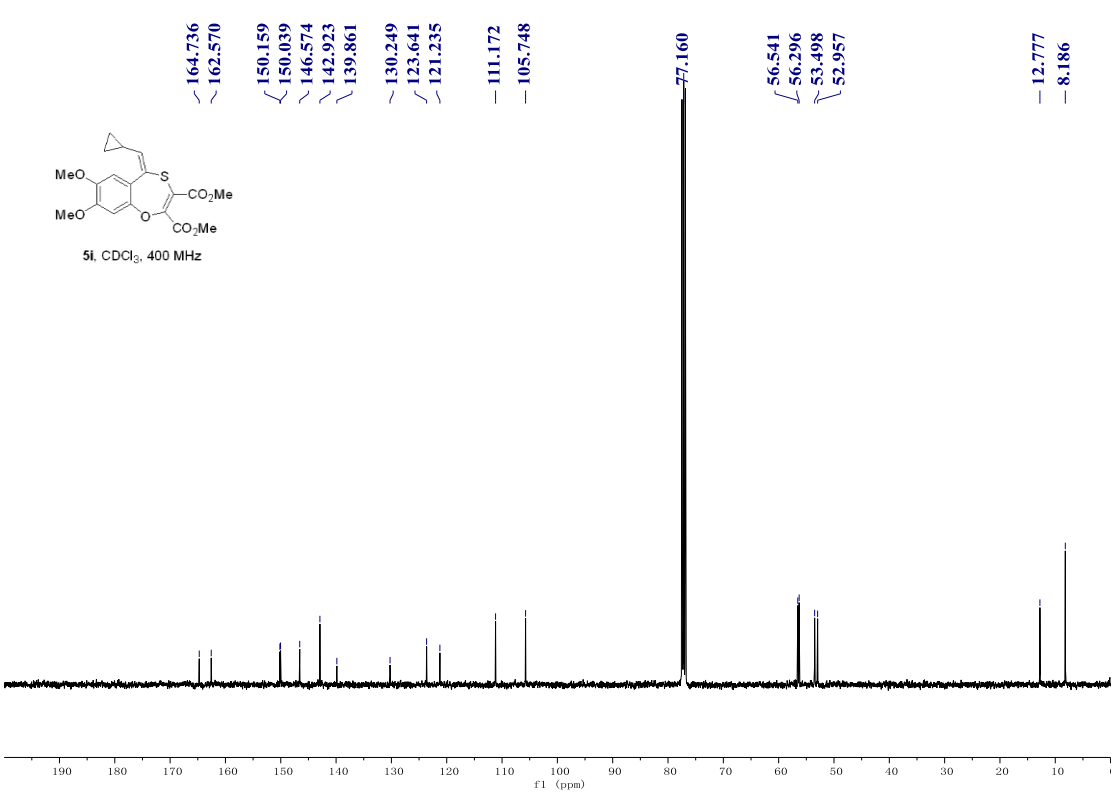

6.868
6.833
6.613
5.877
3.844
3.821
3.814
3.727
2.096
2.050
1.802
1.495
1.449
MeO
MeO
S
O
CO2Me
CO2Me
5h, (CD3)2CO, 400 MHz
1.04
0.98
1.00
0.98
3.54
2.96
2.96
2.90
2.11
1.97
3.99
f1 (ppm)

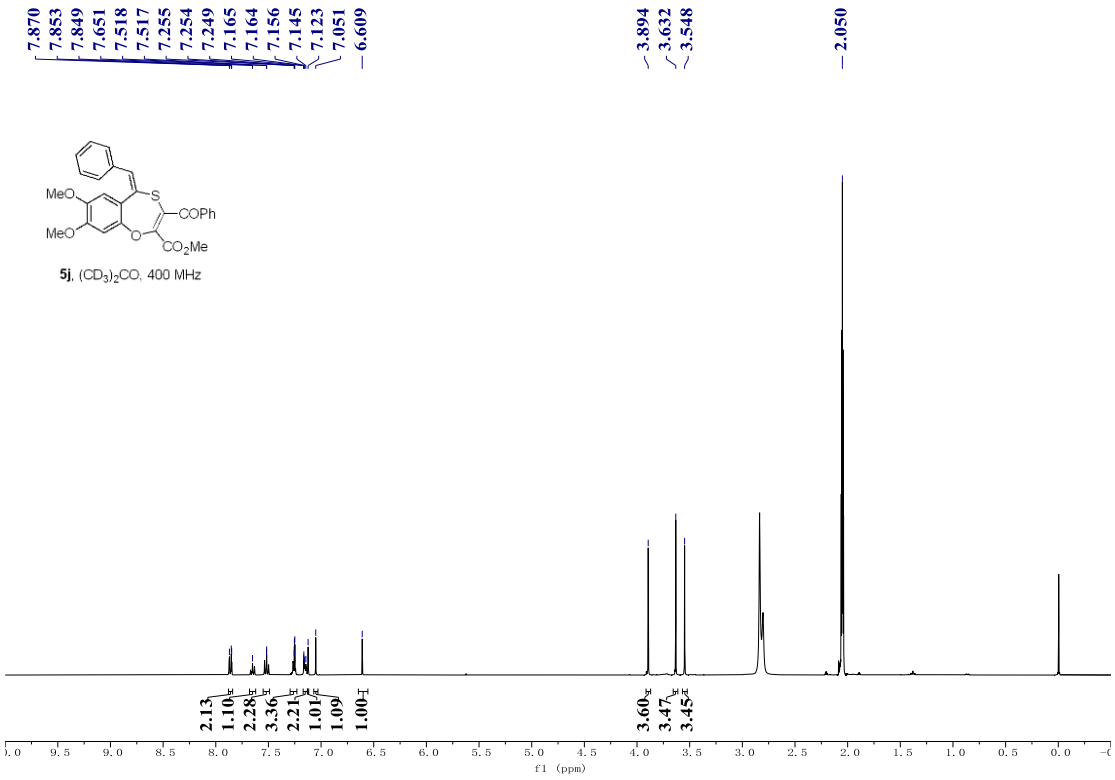

164.814
162.881
151.615
150.397
147.726
141.404
140.494
135.478
135.391
130.552
124.945
122.561
112.858
105.849
56.659
56.222
53.512
53.044
29.840
28.397
26.684
23.281
22.431
MeO
MeO
S
O
CO2Me
CO2Me
5h, (CD3)2CO, 400 MHz
f1 (ppm)

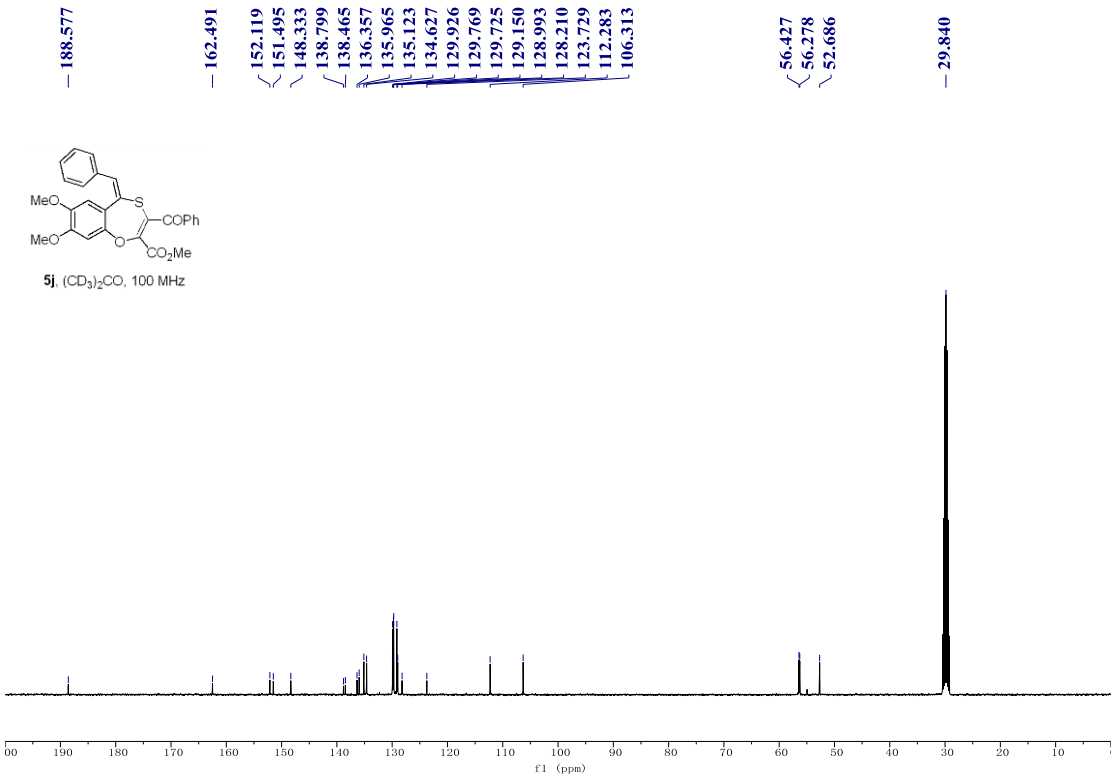

7.260
6.745
6.495
5.550
3.840
3.794
1.513
1.505
1.493
1.480
1.472
0.914
0.826
0.813
0.807
MeO
MeO
OH
4f-8, CDCl3, 400 MHz
1.00
1.03
0.94
3.11
2.97
0.90
1.88
1.74
f1 (ppm)

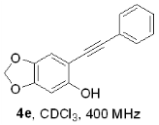

152.401
150.710
142.770
113.779
100.237
99.715
99.049
77.160
69.805
56.522
56.038
9.092
0.347
MeO
MeO
OH
4f-8, CDCl3, 400 MHz
f1 (ppm)


7.260
6.838
6.816
5.531
5.506
3.878
3.865
3.848
3.790
1.571
1.559
1.557
1.545
0.829
0.824
0.809
0.803
0.579
0.574
0.568
0.563
MeO
MeO
S
O
CO2Me
CO2Me
5i, CDCl3, 400 MHz
1.00
1.08
1.02
3.03
3.18
3.33
3.08
0.97
2.01
2.09
f1 (ppm)

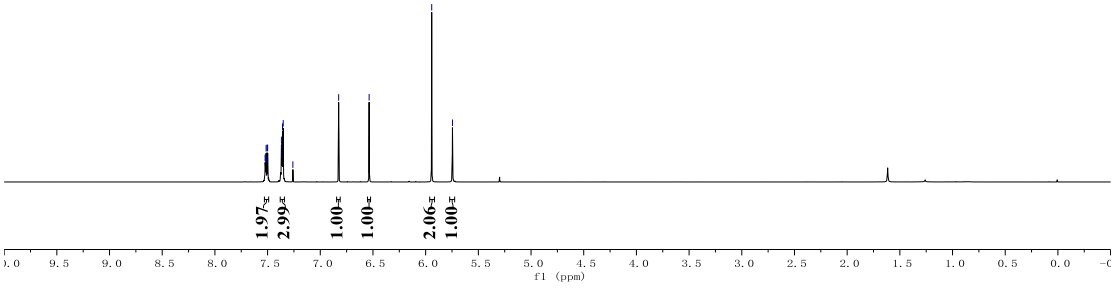

164.736
162.570
150.159
150.039
146.574
142.923
139.861
130.249
123.641
121.235
111.172
105.748
77.160
56.541
56.296
53.498
52.957
12.777
8.186
MeO
MeO
S
O
CO2Me
CO2Me
5i, CDCl3, 400 MHz
f1 (ppm)

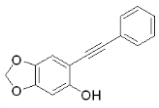

7.870
7.853
7.849
7.651
7.518
7.517
7.255
7.254
7.249
7.165
7.164
7.156
7.145
7.123
7.051
6.609
3.894
3.632
3.548
2.050
MeO
MeO
S
COPh
O
CO2Me
5j, (CD3)2CO, 400 MHz
2.13
1.10
2.28
3.36
2.21
1.01
1.09
1.00
3.60
3.47
3.45
f1 (ppm)


188.577
162.491
152.119
151.495
148.333
138.799
138.465
136.357
135.965
135.123
134.627
129.926
129.769
129.725
129.150
128.993
128.210
123.729
112.283
106.313
56.427
56.278
52.686
29.840
MeO
MeO
S
COPh
O
CO2Me
5j, (CD3)2CO, 100 MHz
f1 (ppm)

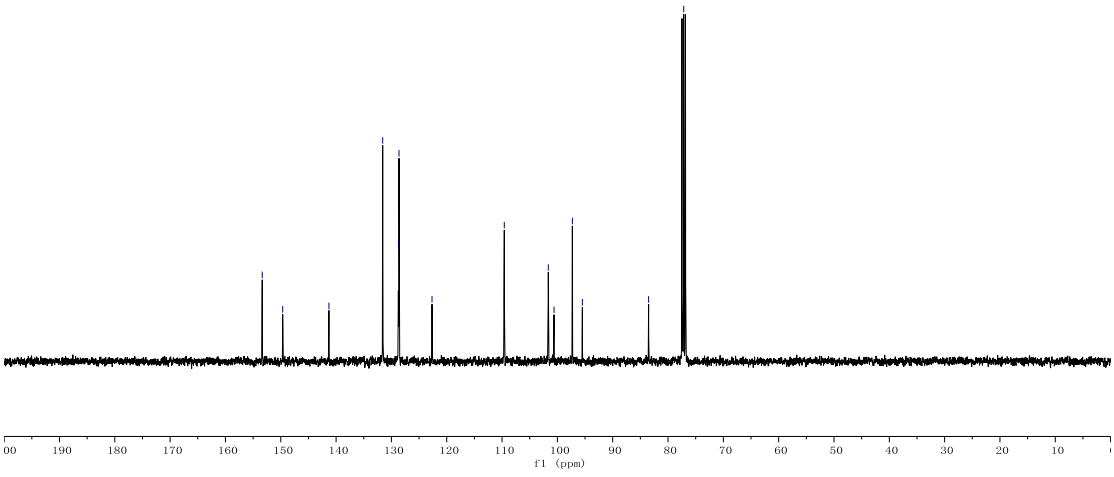


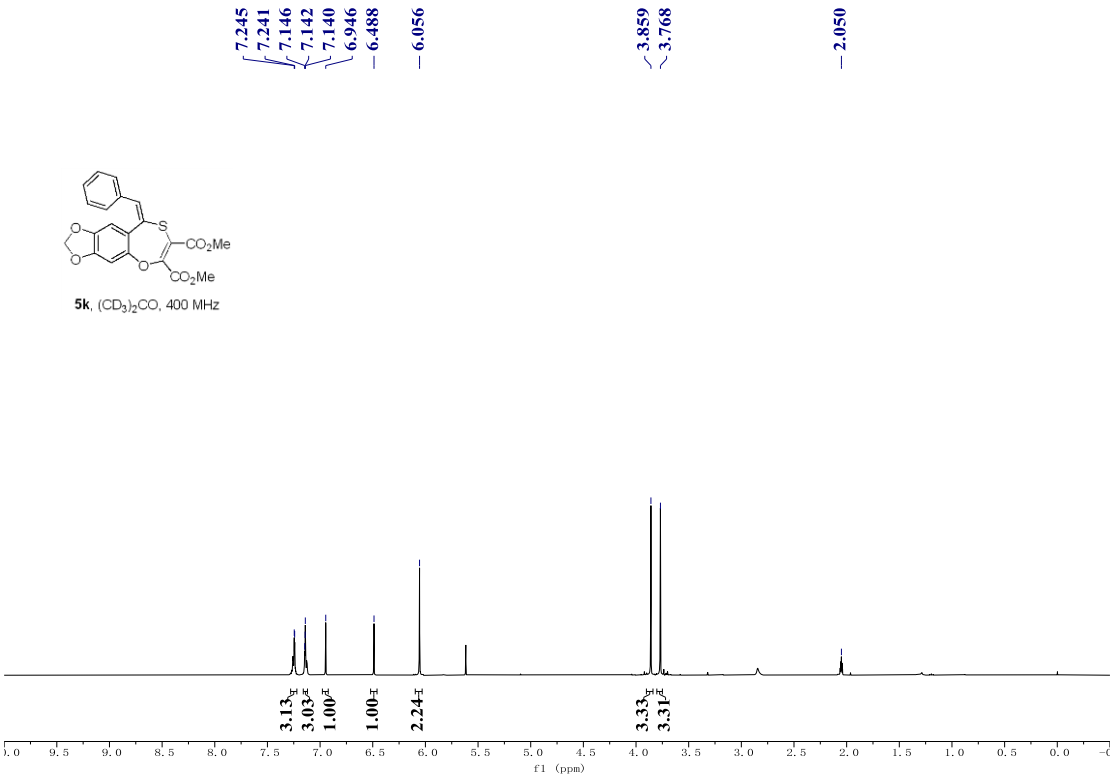
4e, $CDCl_3$, 400 MHz

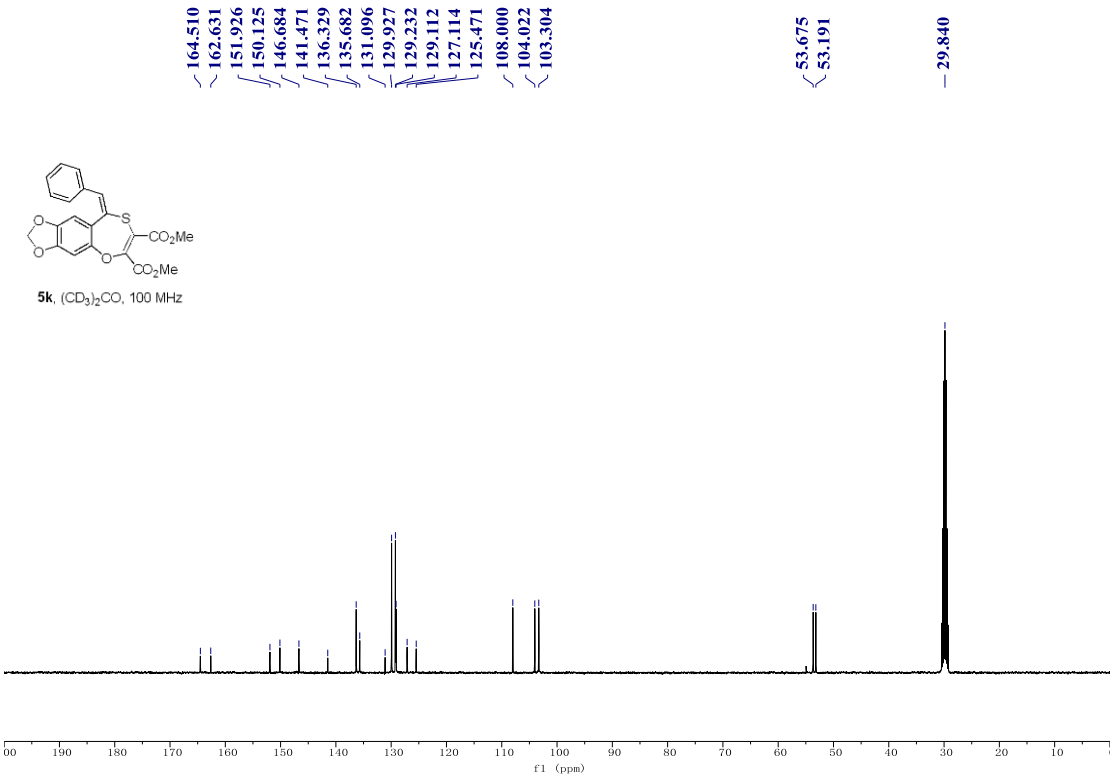


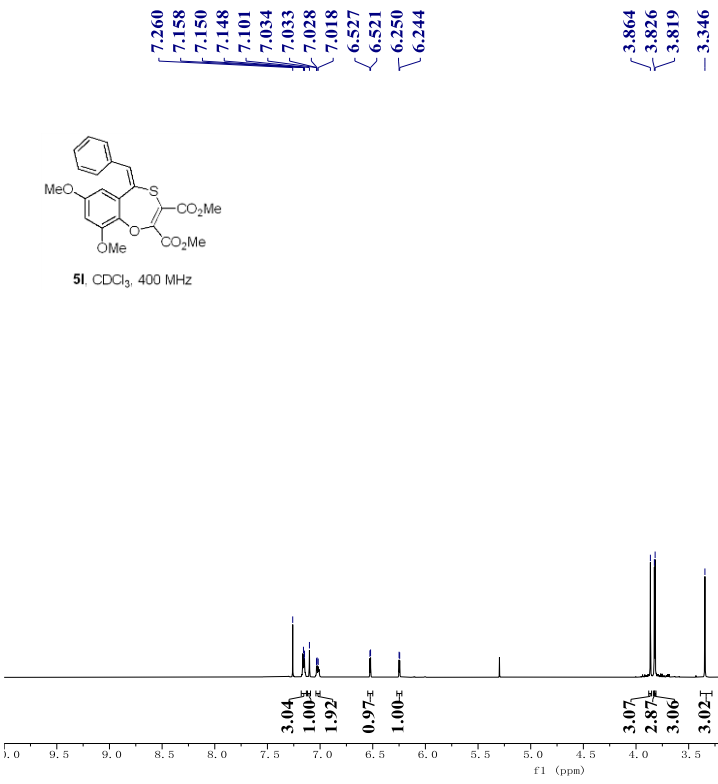


4e, $CDCl_3$, 400 MHz

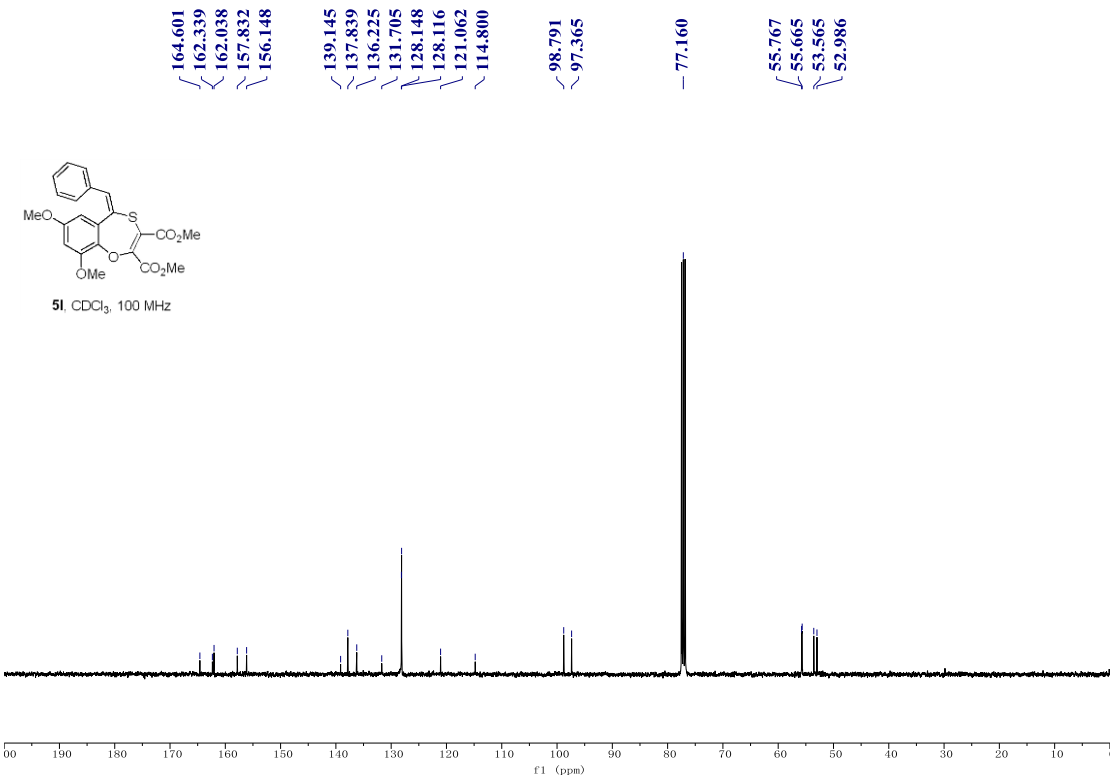



7.245
7.241
7.146
7.142
7.140
6.946
6.488
6.056
3.859
3.768
2.050
CO2Me
CO2Me
5k, (CD3)2CO, 400 MHz
3.13
3.03
1.00
1.00
2.24
3.33
3.31
f1 (ppm)

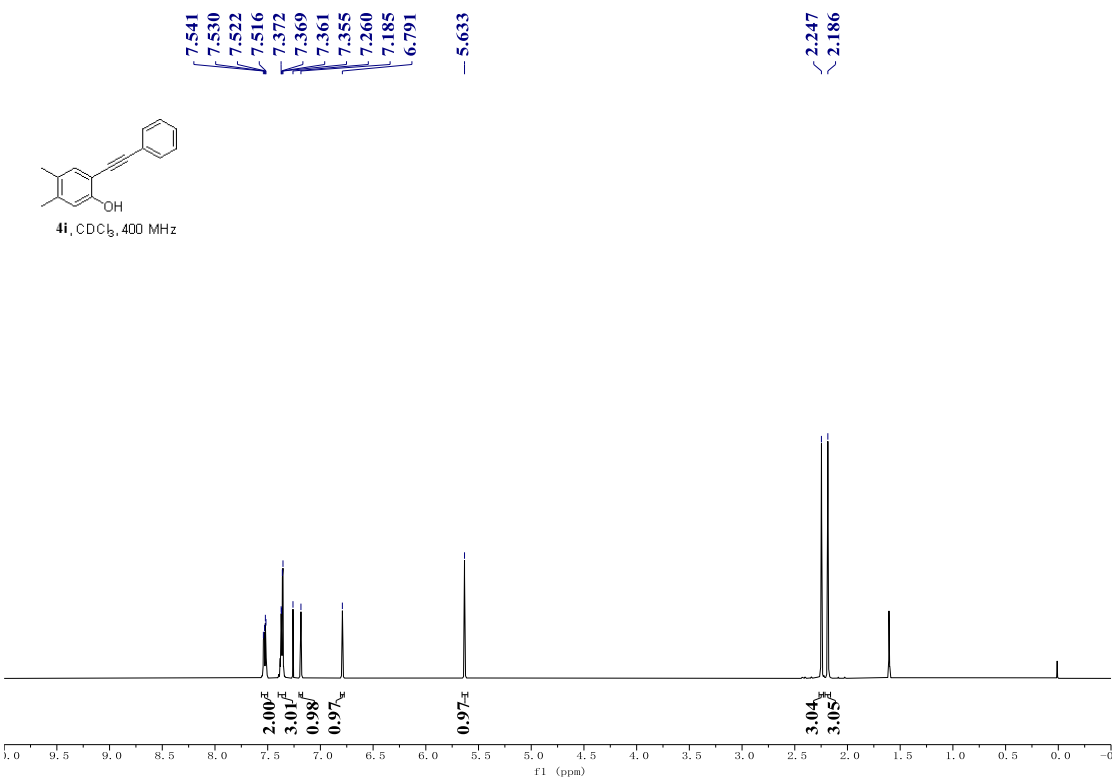

164.510
162.631
151.926
150.125
146.684
141.471
136.329
135.682
131.096
129.927
129.232
129.112
127.114
125.471
108.000
104.022
103.304
53.675
53.191
29.840
CO2Me
CO2Me
5k, (CD3)2CO, 100 MHz
f1 (ppm)

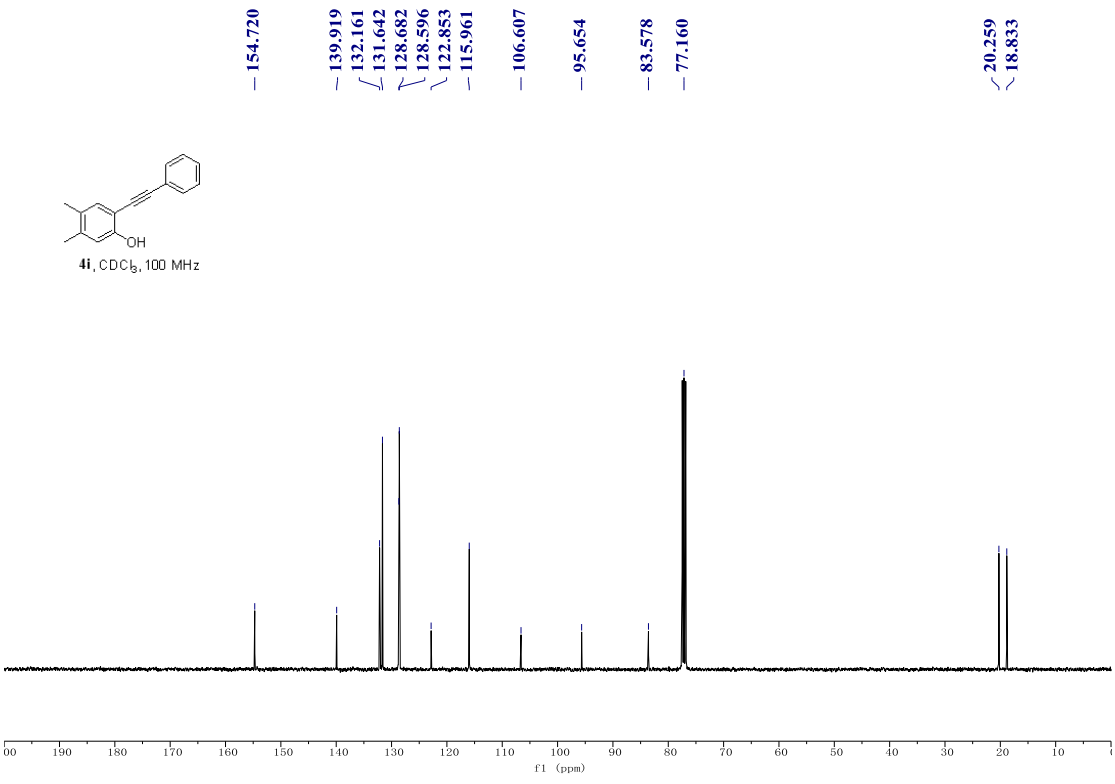


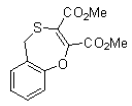
5l, $CDCl_3$, 400 MHz



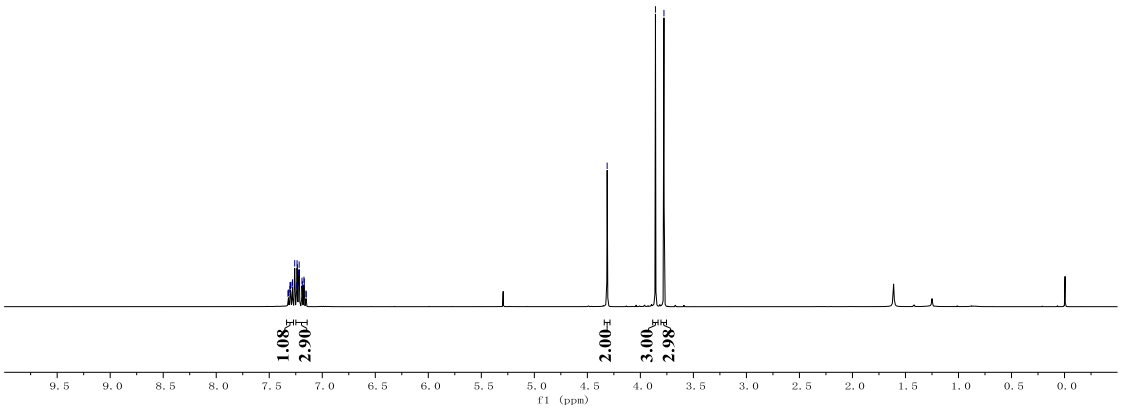
5l, $CDCl_3$, 100 MHz

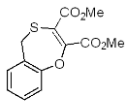

7.541
7.530
7.522
7.516
7.372
7.369
7.361
7.355
7.260
7.185
6.791
5.633
2.247
2.186
OH
4i, CDCl3, 400 MHz
2.00
3.01
0.98
0.97
0.97
3.04
3.05
f1 (ppm)


154.720
139.919
132.161
131.642
128.682
128.596
122.853
115.961
106.607
95.654
83.578
77.160
20.259
18.833
OH
4i, CDCl3, 100 MHz
f1 (ppm)

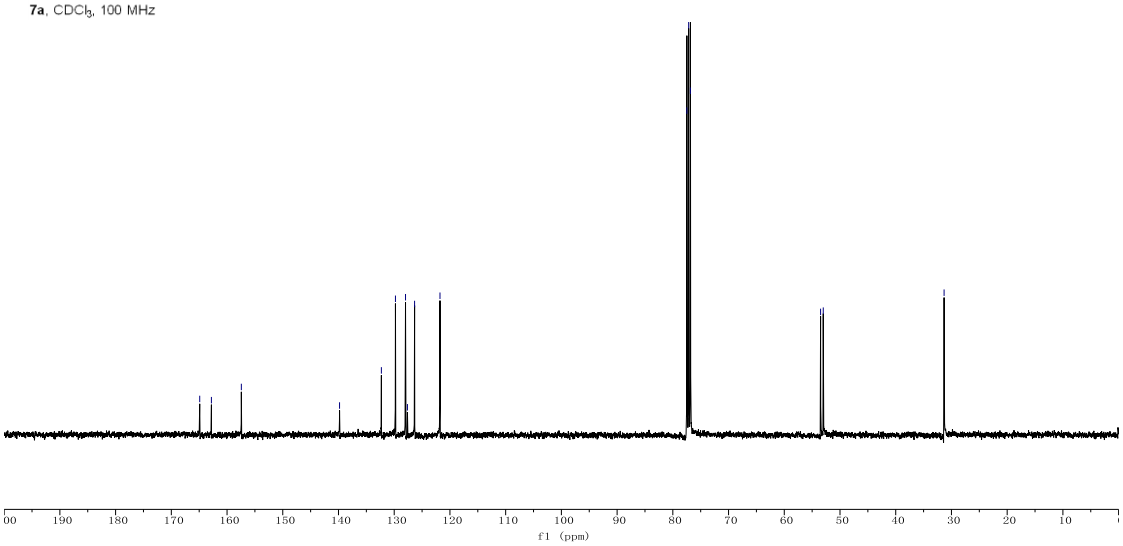


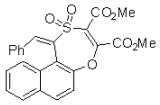
7a, $CDCl_3$, 400 MHz



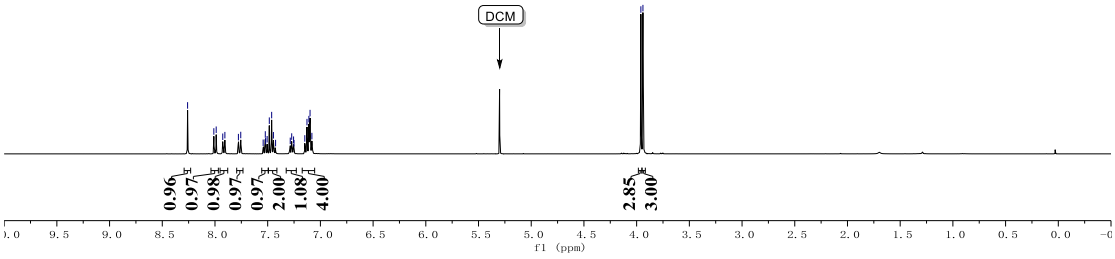


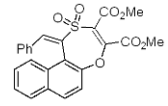
7a, $CDCl_3$, 100 MHz



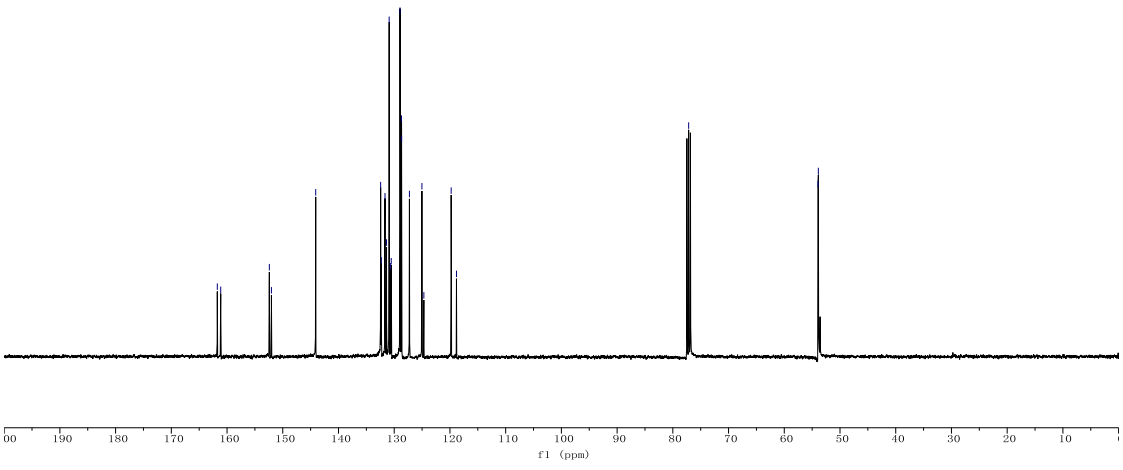


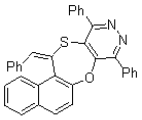
3a', $CDCl_3$, 400 MHz



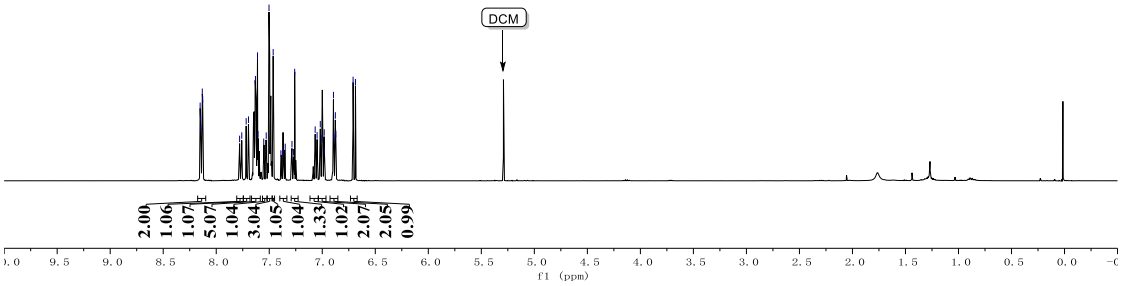


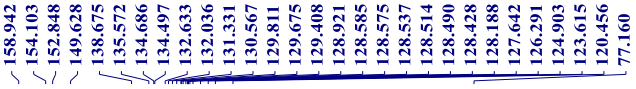
3a', $CDCl_3$, 100 MHz

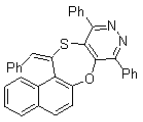




3c', $CDCl_3$, 400MHz







3c', $CDCl_3$, 100MHz