SUPPORTING INFORMATION

Phosphine-catalysed one-pot domino sequence to access cyclopentene-fused coumarins

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1. General Information

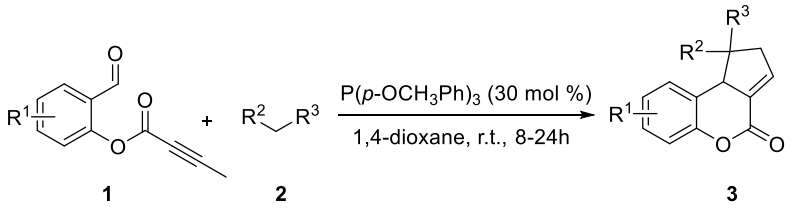
Unless otherwise noted, all the starting reagents were obtained from commercial suppliers and used without further purification. And it also includes all the solvents that were used. Yields refer to isolated compounds through flash column chromatography performed using 300-400 mesh silica gel. ^{1}H NMR spectra were recorded at 400 MHz. The chemical shifts were recorded in *ppm* relative to tetramethylsilane and with the solvent resonance as the internal standard. Data were reported as follows: chemical shift (δ *ppm*), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *dd* = doublet of doublets, *dt* = doublet of triplets, *td* = triplets of doublet, *ddd* = doublet doublet of doublets, *m* = multiplet), coupling constants (Hz), integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift and multiplicities, with coupling constants (Hz) in the case of J_{CF} coupling. High resolution mass spectroscopy (HRMS) was recorded on TOF MS ES+ Mass spectrometer and acetonitrile was used to dissolve the sample. Infrared spectra (IR) were measured by FT-IR apparatus.

2. General Procedure for the Preparation of 2-formylphenyl but-2-ynoate 1

2-formylphenyl but-2-ynoates **1** are prepared according to literatures procedure with minor modification[1]. To a stirred solution of but-2-ynoic acid (10 mmol, 1.0 equiv) in anhydrous CH_2Cl_2 (10 mL) is added DMAP (40 mg, 0.03 equiv) and *o*-hydroxyl arylaldehyde (10 mmol, 1.0 equiv). Dicyclohexylcarbodiimide (10 mmol) in 10 mL of anhydrous CH_2Cl_2 is added slowly (within 20 minutes) to the reaction mixture at 0 ℃, which is then stirred for 10 minutes at 0 ℃ and 3 h at room temperature (monitored by TLC). When the reaction reaches a certain limit, precipitated urea was then filtered off and the filtrate evaporated down in vacuum. Column chromatography of the residue (petroleum ether/ethyl acetate = 19/1) gave the crude alkynoates **1** and the pure ones can be obtained by recrystallization from hexanes and CH_2Cl_2.

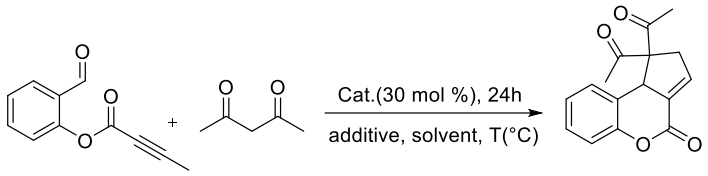
3. Synthesis of Cyclopenta[*c*]chromenone 3

3.1 General Procedure



The mixture of alkynoates **1** (0.15 mmol), active methylene compounds **2** (0.3 mmol), P(*p*-OCH_3Ph)$_3$ (30 mol%) were combined in 1,4-dioxane (1 mL) at room temperature for 8 - 24h. After the reaction, the solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 17/3) to give the desired products.

Table S1. Optimization of Reaction Conditions[a]

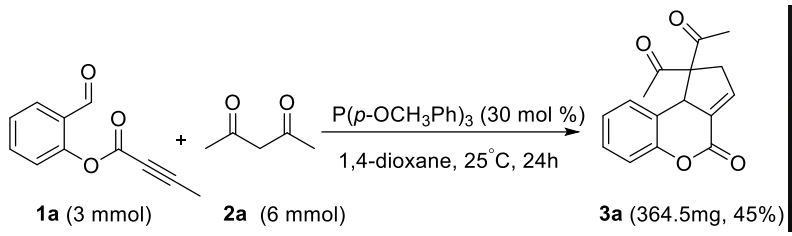


1a 2a 3a

entry	catalyst	T(℃)	solvent	additive[c]	yield (%)[b]
1	PPh_3	r.t.	toulene	-	50
2	P(*p*-FPh_3)	r.t.	toulene	-	trace
3	PBu_3	r.t.	toulene	-	trace
4	PPh_2CH_3	r.t.	toulene	-	trace
5	P(*p*-CH_3Ph)$_3$	r.t.	toulene	-	53
6	P(*p*-OCH_3Ph)$_3$	r.t.	toulene	-	55
7	P(*p*-OCH_3Ph)$_3$	30	toulene	-	50
8	P(*p*-OCH_3Ph)$_3$	50	toulene	-	32
9	P(*p*-OCH_3Ph)$_3$	80	toulene	-	29
10	P(*p*-OCH_3Ph)$_3$	r.t.	CH_3CN	-	44
11	P(*p*-OCH_3Ph)$_3$	r.t.	acetone	-	43
12	P(*p*-OCH_3Ph)$_3$	r.t.	DMSO	-	50
13	**P(*p*-OCH_3Ph)$_3$**	**r.t.**	**1,4-dioxane**	-	**72**
14	P(*p*-OCH_3Ph)$_3$	r.t.	isopropanol	-	trace
15	P(*p*-OCH_3Ph)$_3$	r.t.	THF	-	49
16	P(*p*-OCH_3Ph)$_3$	r.t.	ether	-	51
17	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	$NaHCO_3$	52
18	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	K_2CO_3	54
19	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	$PhCO_2H$	70
20	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	Na_2CO_3	56
21	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	DIPEA	60
22	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	AcOH/AcONa	57
23[d]	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	-	70
24[e]	P(*p*-OCH_3Ph)$_3$	r.t.	1,4-dioxane	-	53

[a]The reaction was carried out with compound **1a** (0.15 mmol), **2a** (0.3 mmol, 2equiv), PR_3 (0.3 equiv) at room temperature for 24h; [b]Isolated yield; [c]0.5 equiv of additive was added; [d]1.0 equiv of H_2O was added; [e]under anhydrous conditions.

3.2 *Scale-up synthesis of 3a*



The mixture of alkynoates **1a** (3.0 mmol, 564.54mg), active methylene compounds **2a** (6.0 mmol, 1.2 mL), P(*p*-$OCH_3Ph)_3$ (0.9 mmol, 318 mg, 30 mol%) were combined in 1,4-dioxane (20 mL) at room temperature for 24 h. After the reaction, the solvent was evaporated under reduced pressure. The crude product was purified by silica gel chromatography (petroleum ether/ethyl acetate = 17/3) to give the desired products **3a** (364.5 mg, 45%).

4. Mechanistic Studies

4.1 HRMS studies

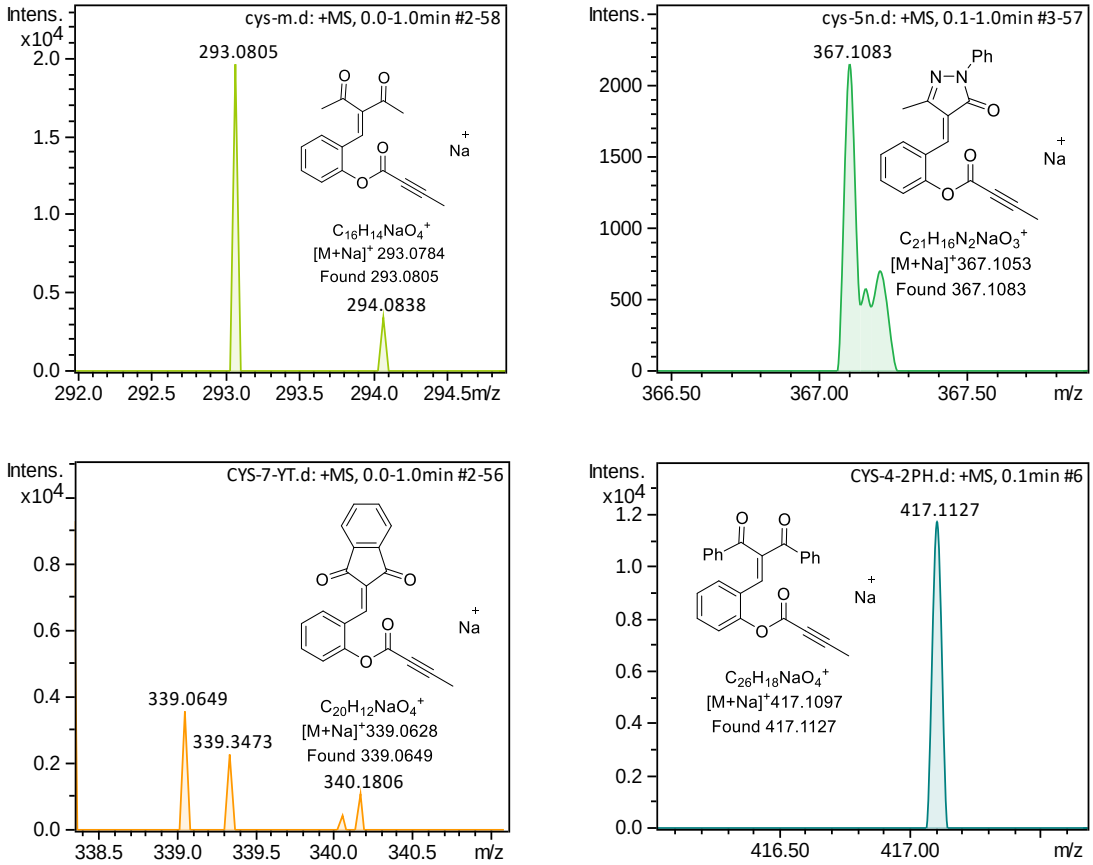
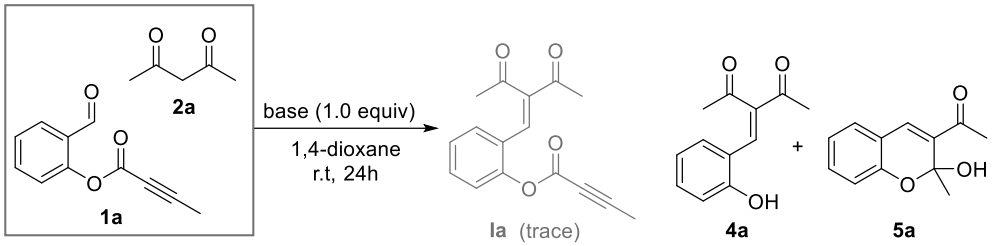


Figure S1 ESI-MS of the corresponding adducts

4.2 Control Experiments



The mixture of alkynoates **1a** (0.15 mmol), active methylene compounds **2a** (0.3 mmol), base (Et_3N, K_2CO_3, or Na_2CO_3) (1.0 equiv), were combined in 1,4-dioxane (1 mL) at room temperature for 24h. The solvent was then removed under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 17/3) to afford a mixture of **4a** and **5a**.[2]

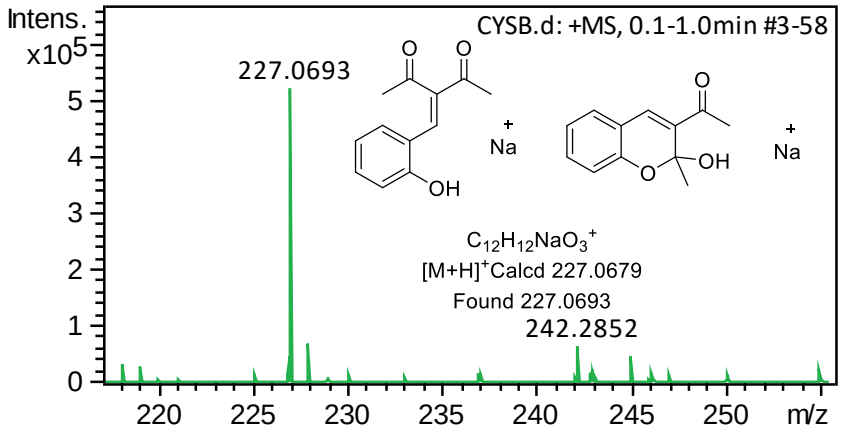
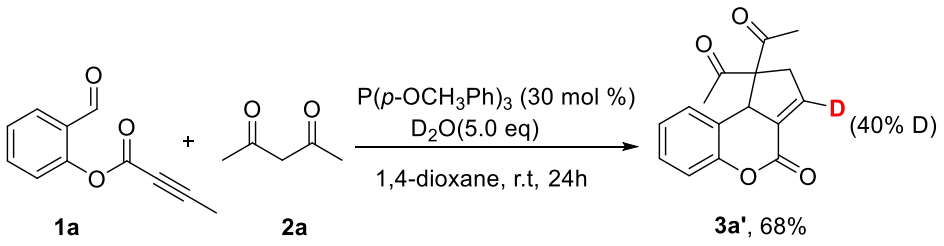
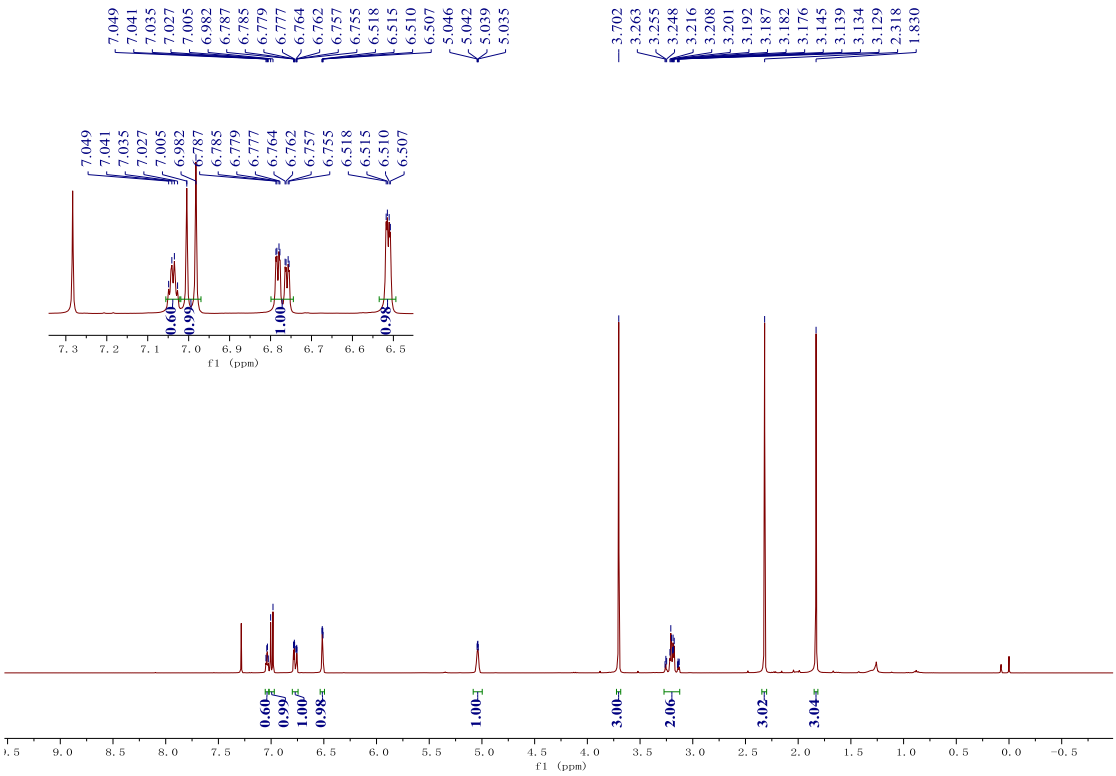


Figure S2 ESI-MS of the corresponding adducts

4.3 Deuterium Labeling Experiments

The mixture of alkynoates **1a** (0.15 mmol), active methylene compounds **2a** (0.3 mmol), P(*p*-$OCH_3Ph)_3$ (30mol%), D_2O (0.75 mmol, 5 equiv) were combined in 1,4-dioxane (1 mL) at room temperature for 24 h. The solvent was then removed under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate = 17/3) to afford product **3a'** in 68% yield with 40% deuterium. The ^1H NMR spectra copies of the products above are provided as follows.





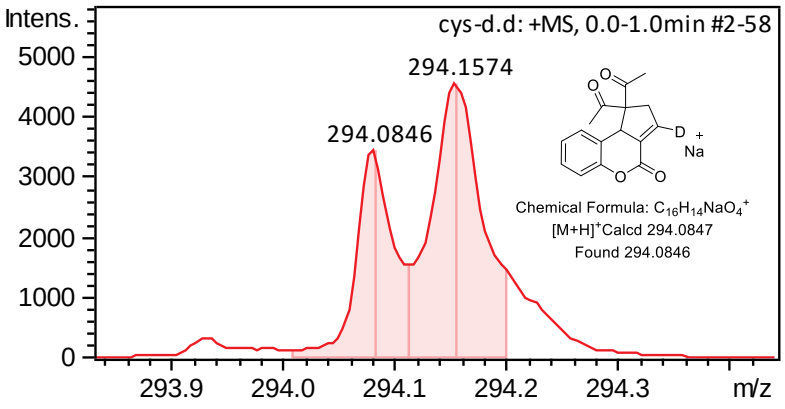
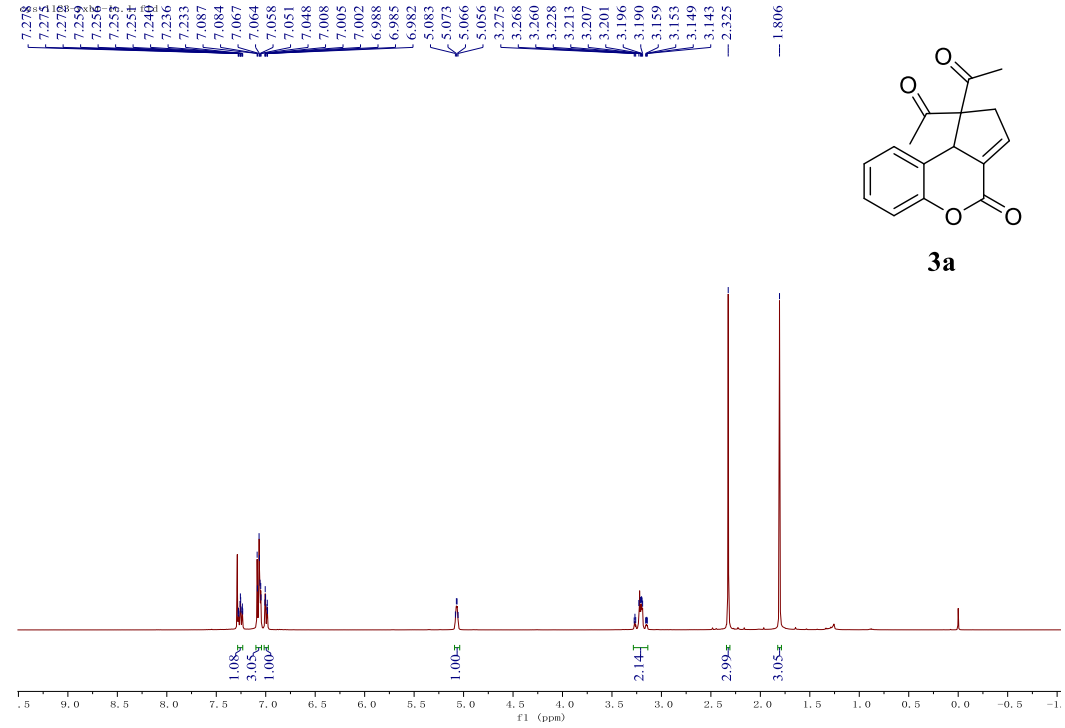


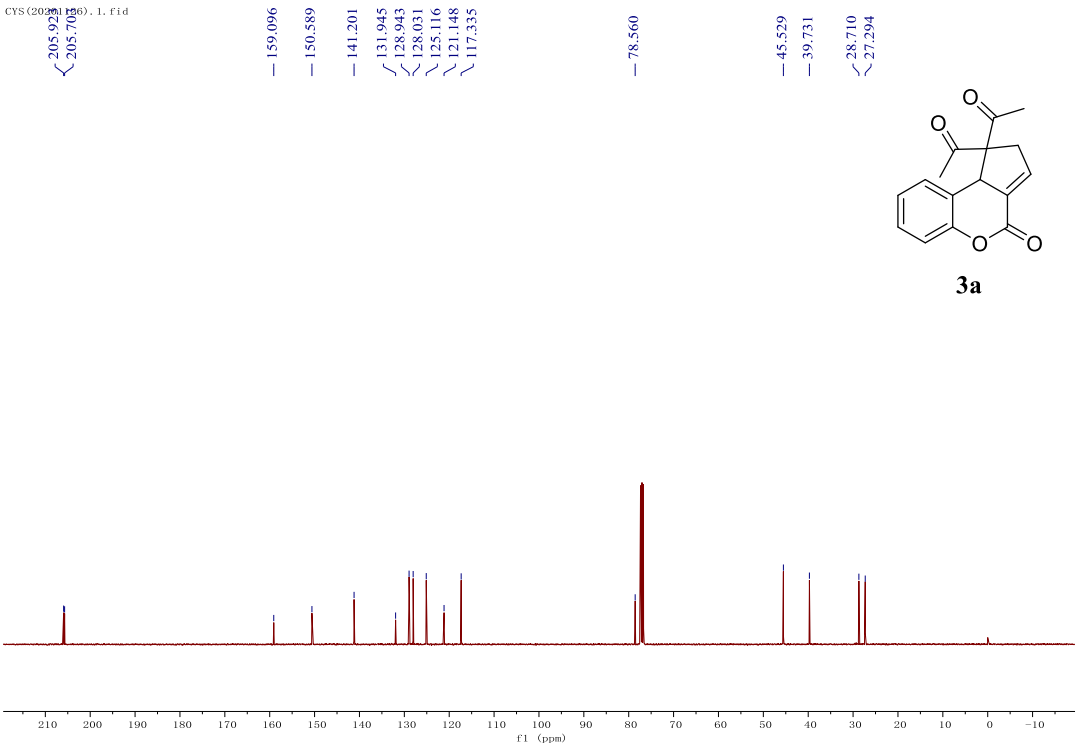
Figure S3 ^{1}H NMR and HRMS for deuterated product **3a'**

5. NMR Spectra Copies for New Compounds of 3

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3a**

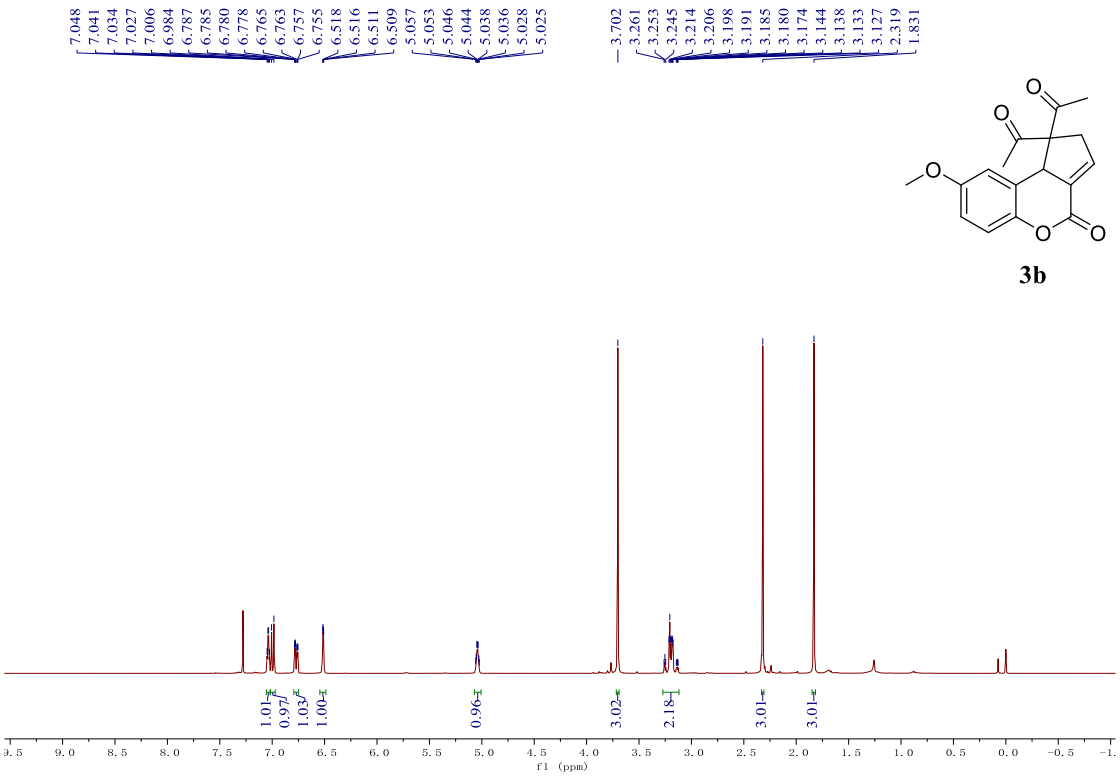


3a

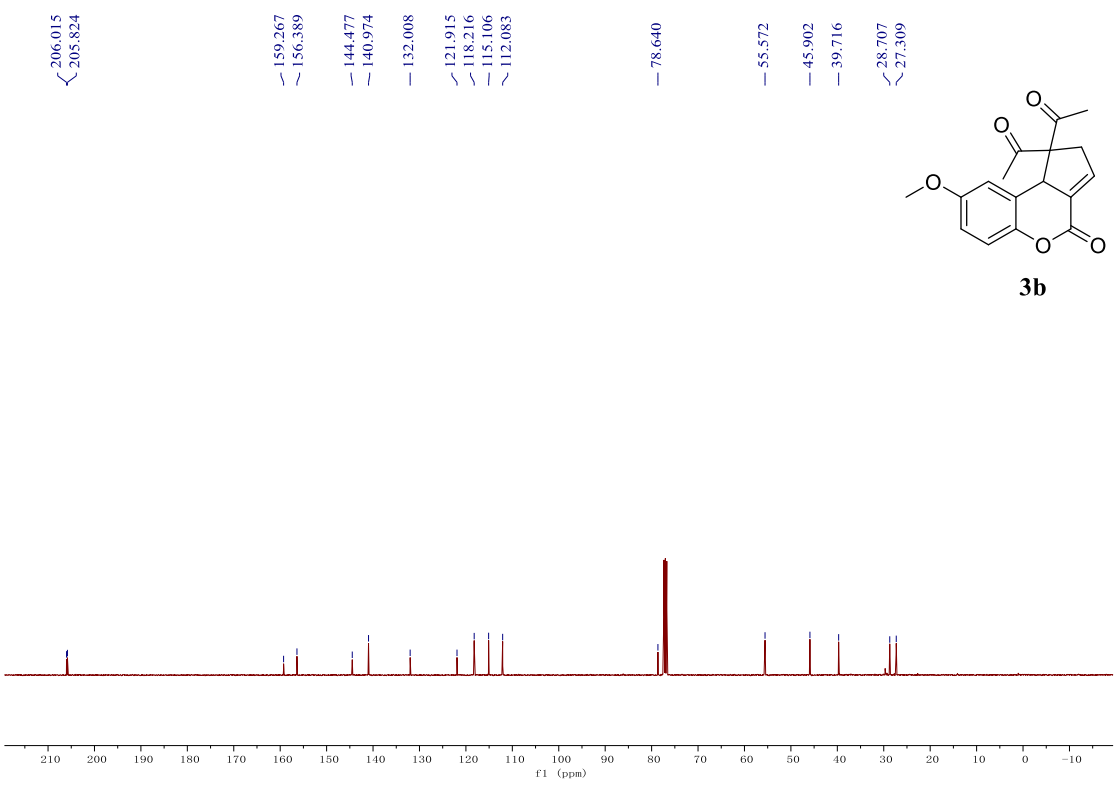


3a

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3b**

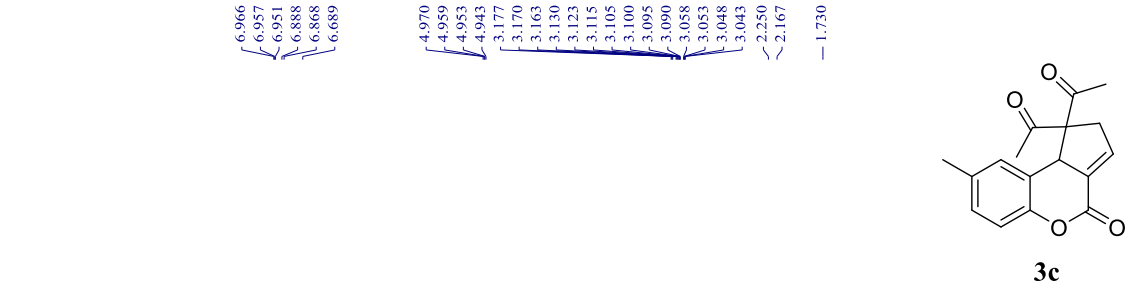


3b



3b

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3c**



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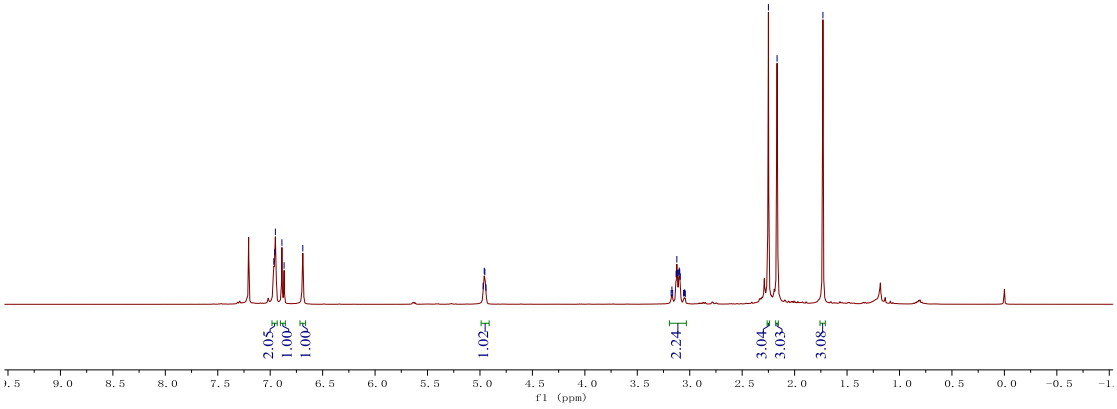

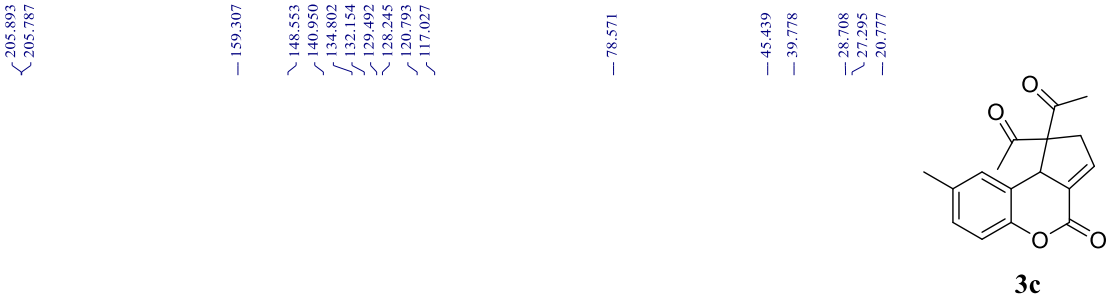

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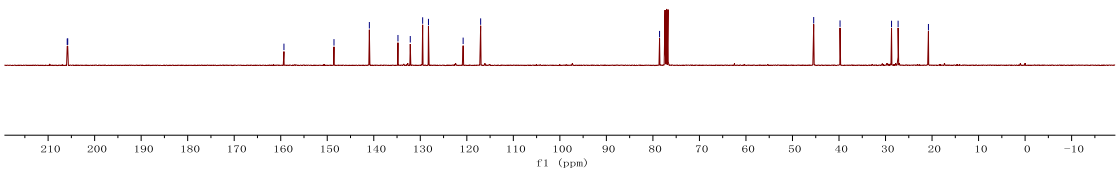
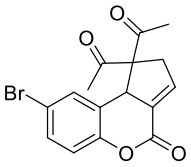
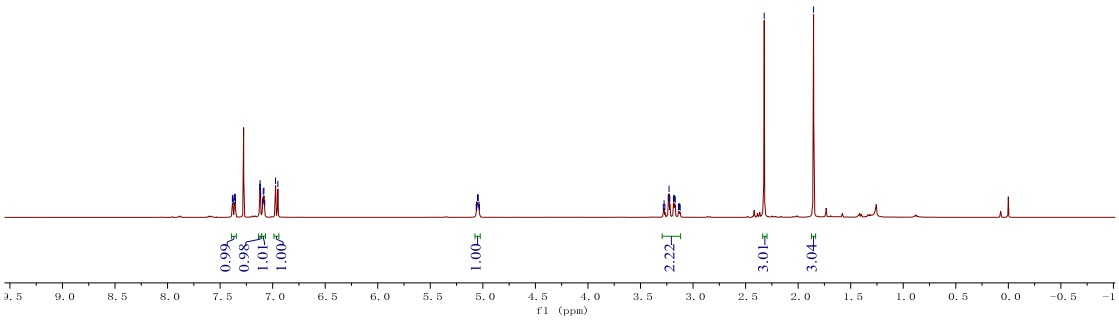
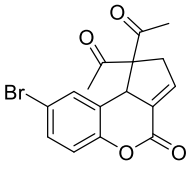


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3d**

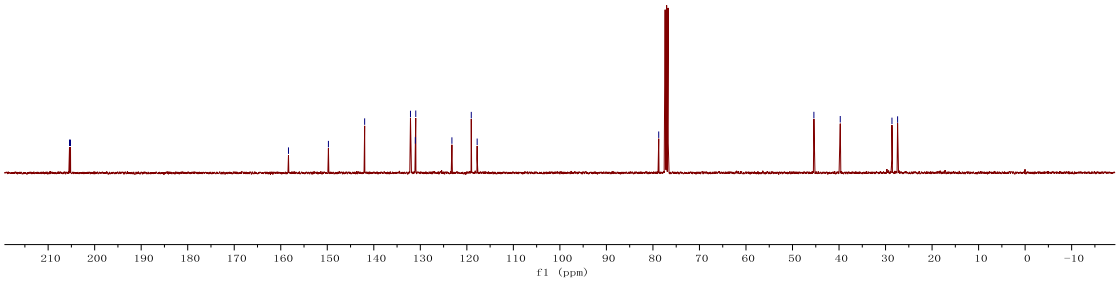


3d

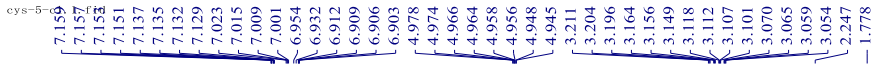


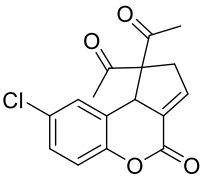


3d



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3e**





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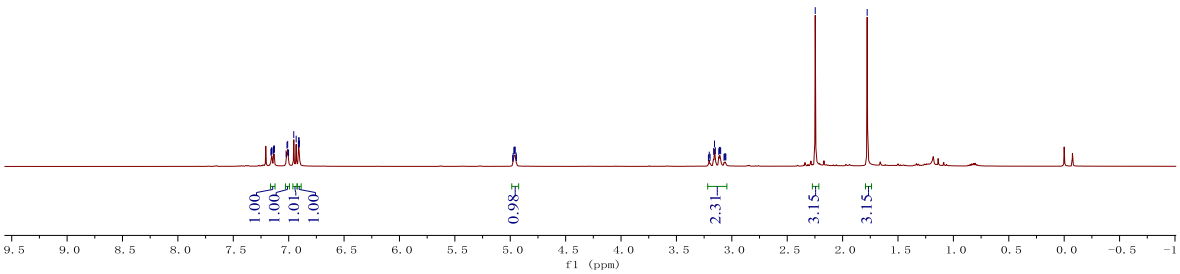

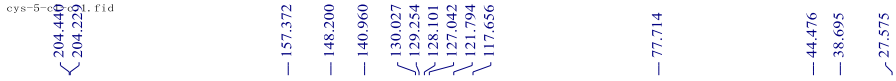

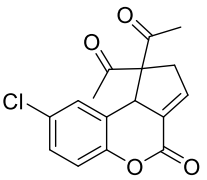

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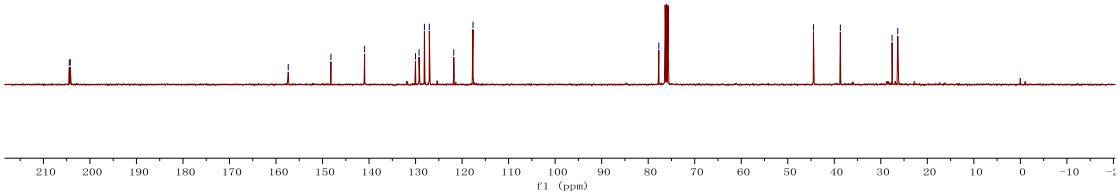
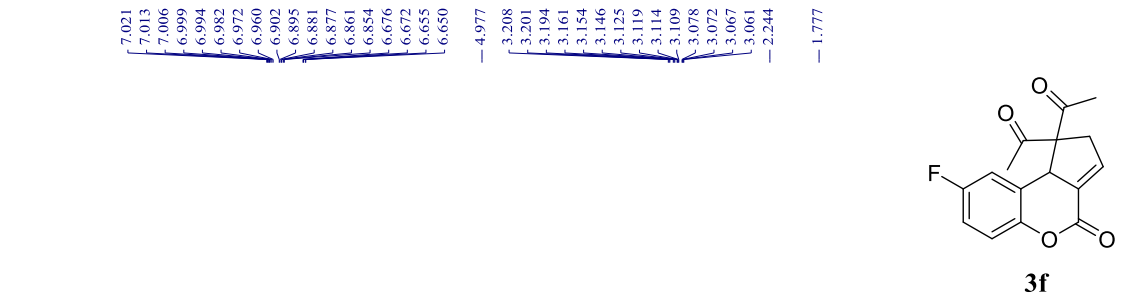


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3f**



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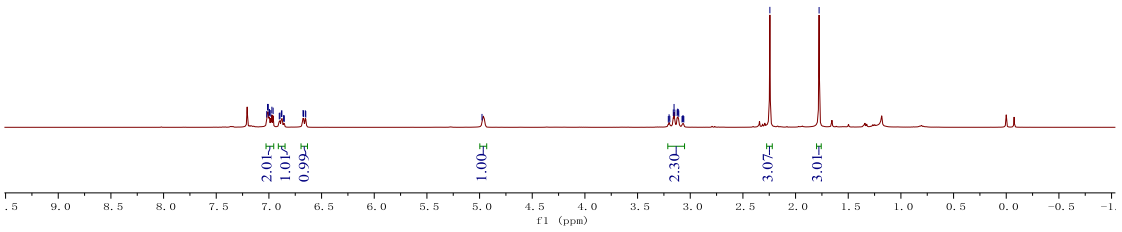
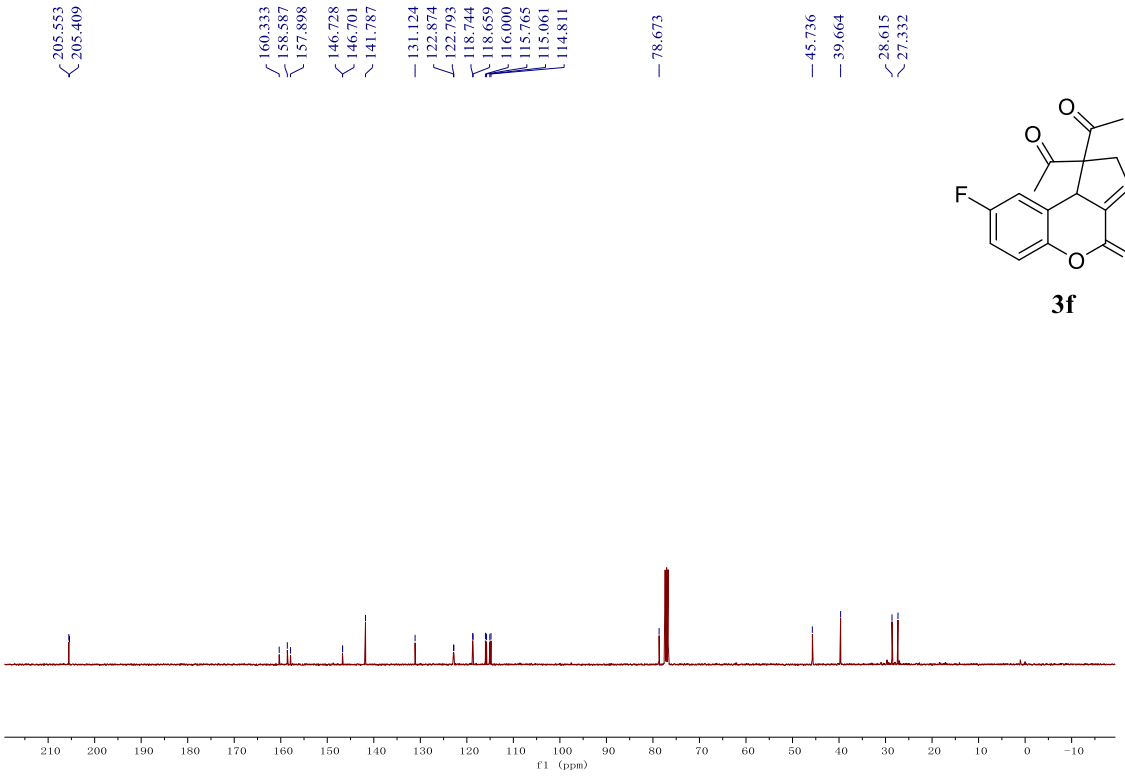
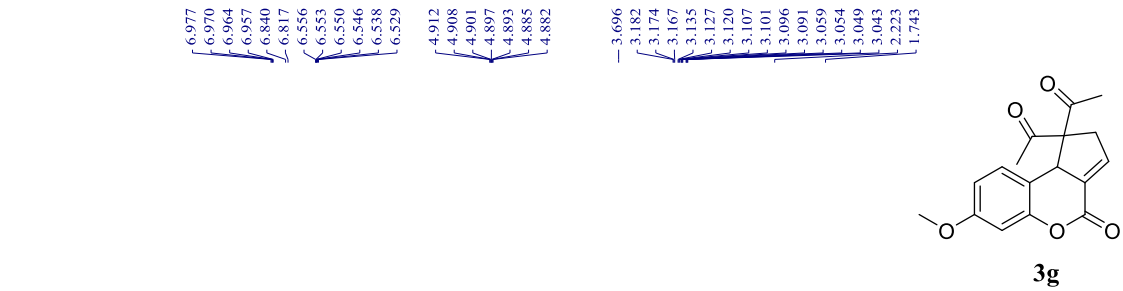




3f

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3g**



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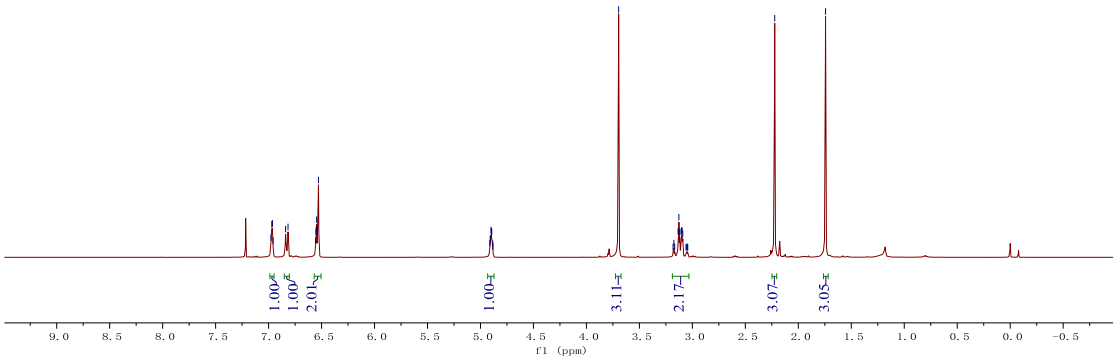

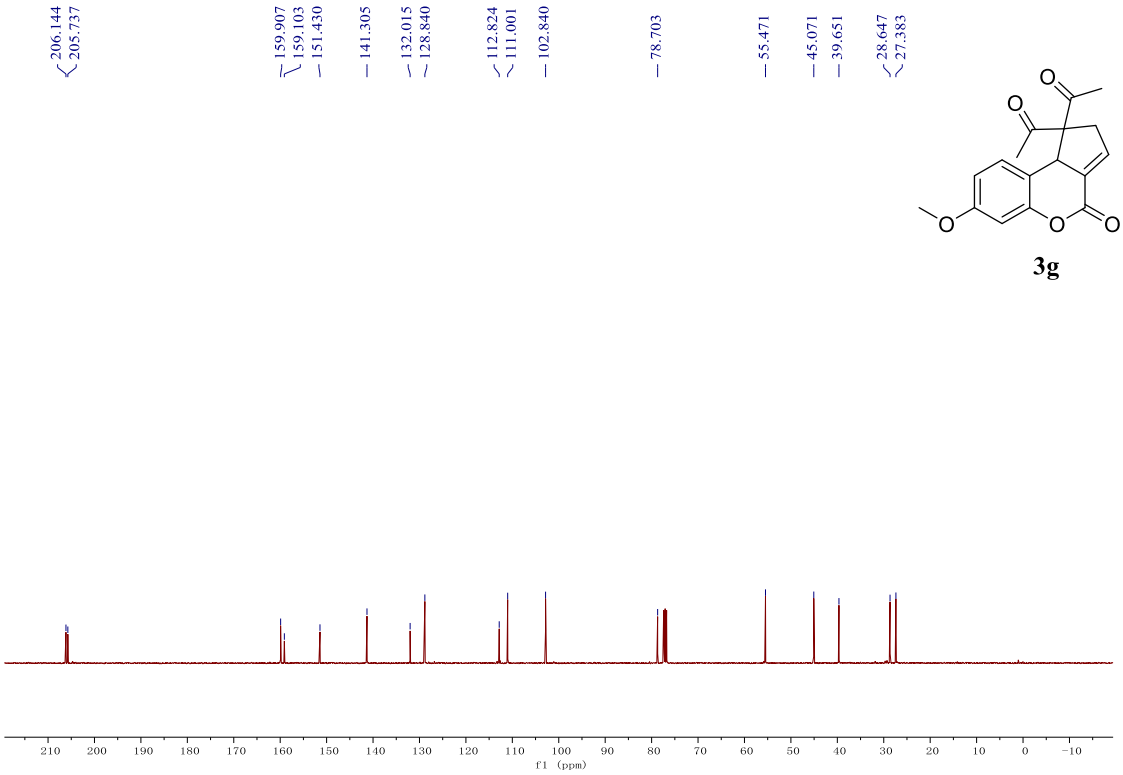

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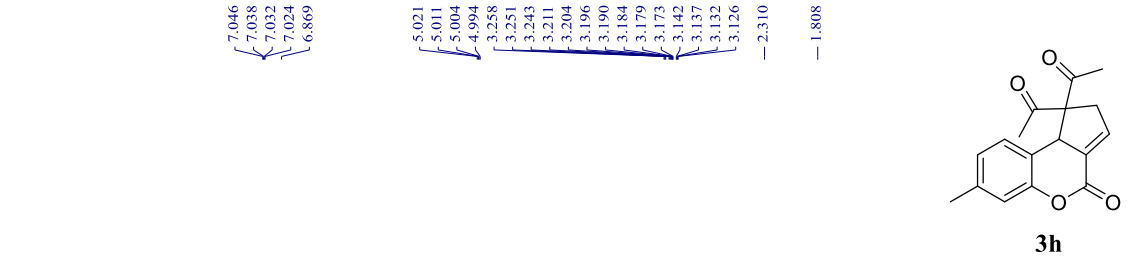
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3h**



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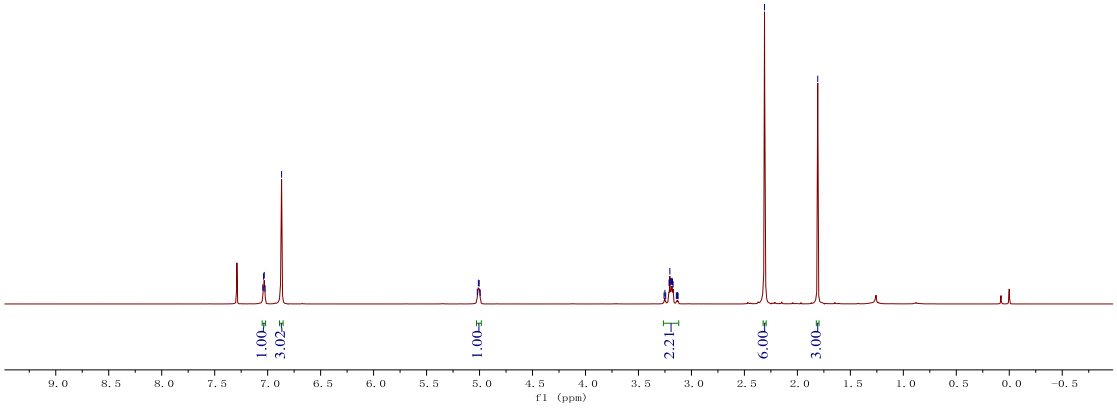

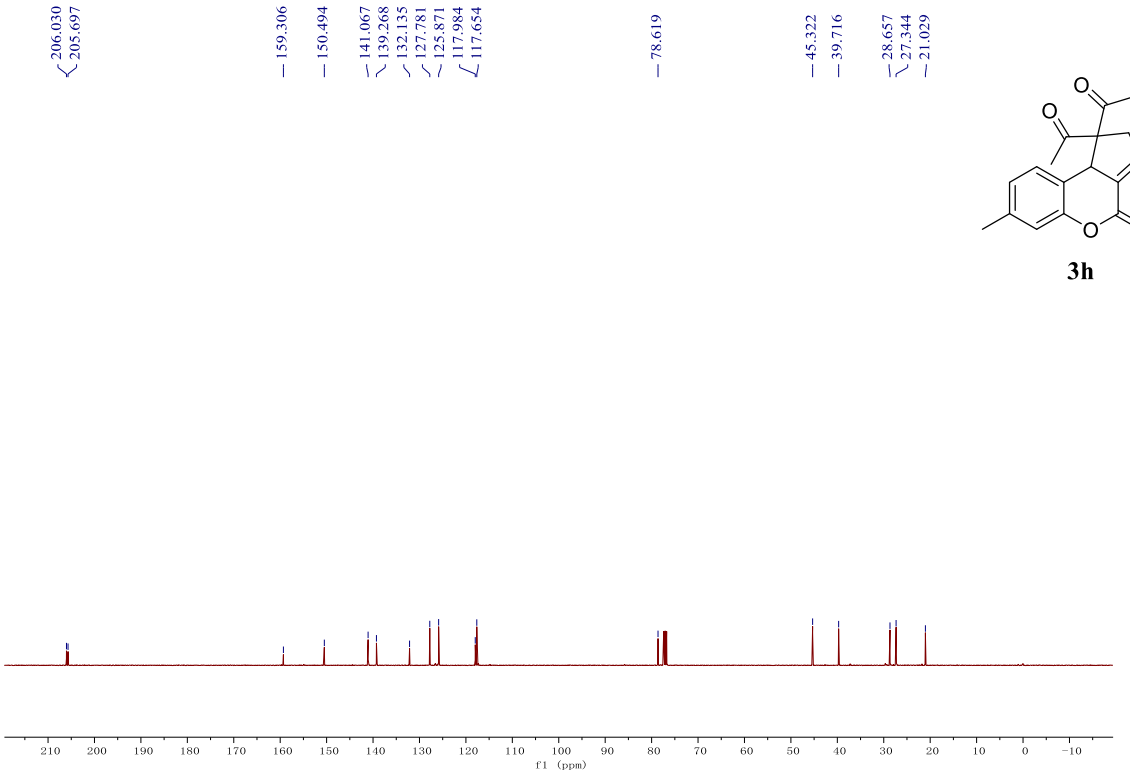

3h

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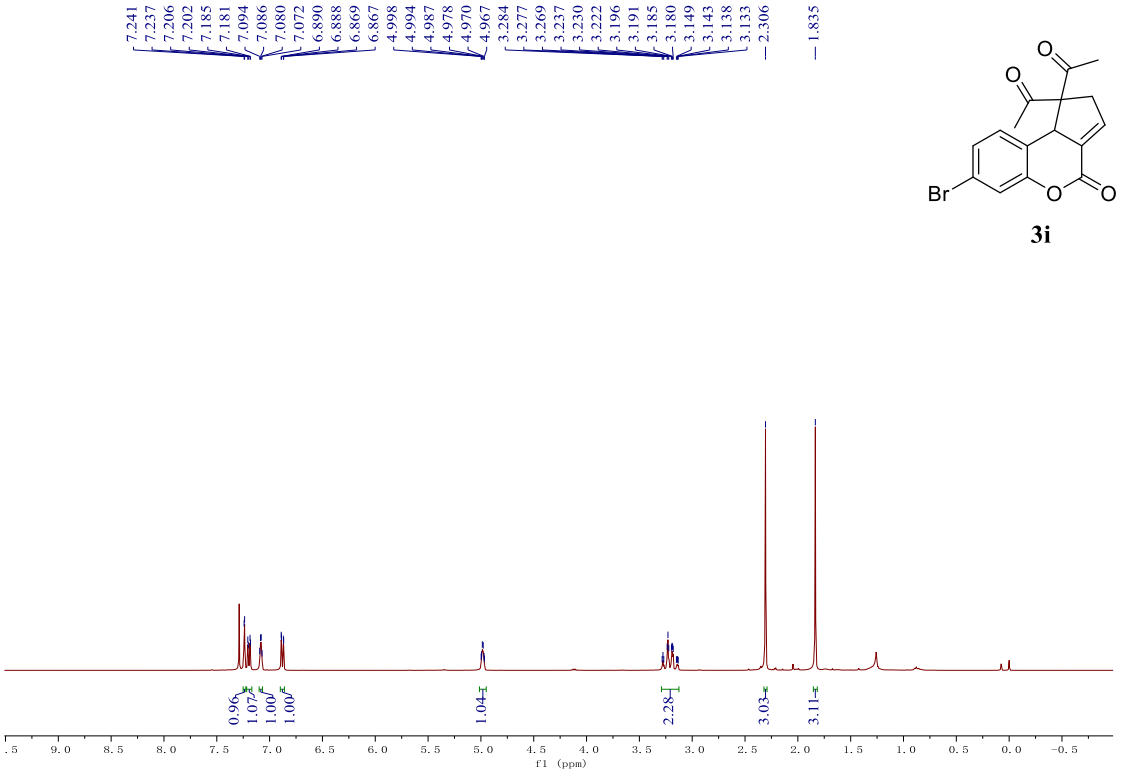

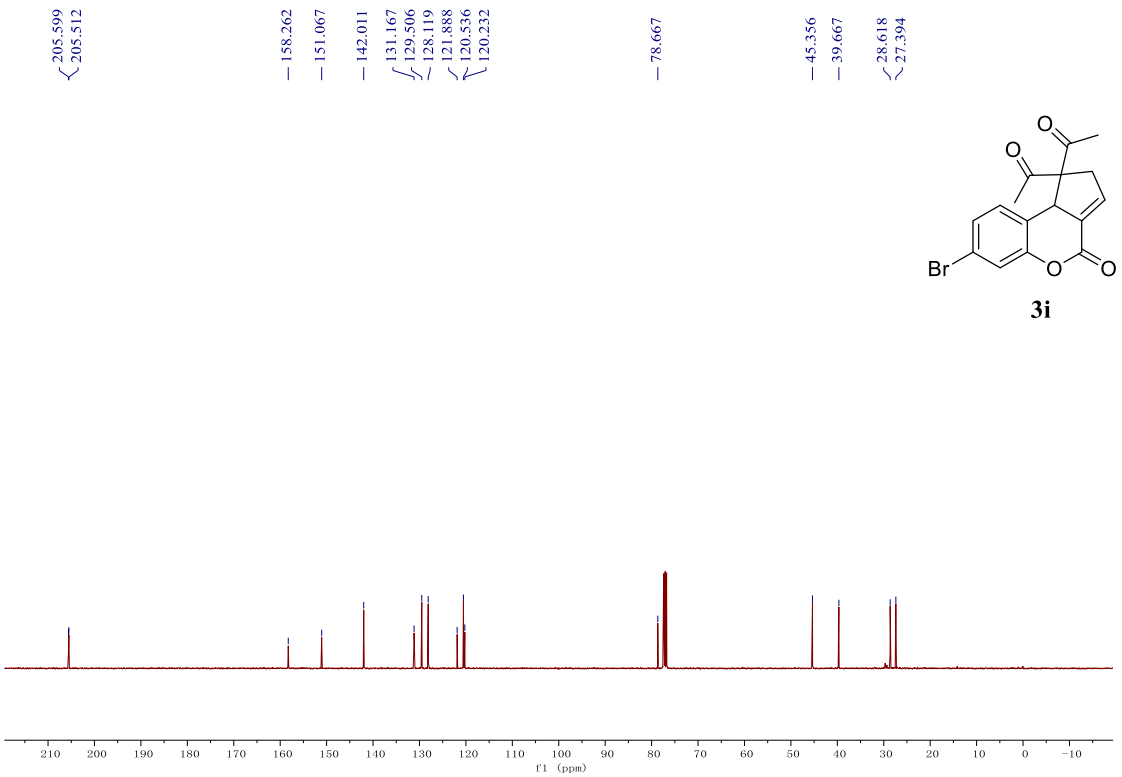

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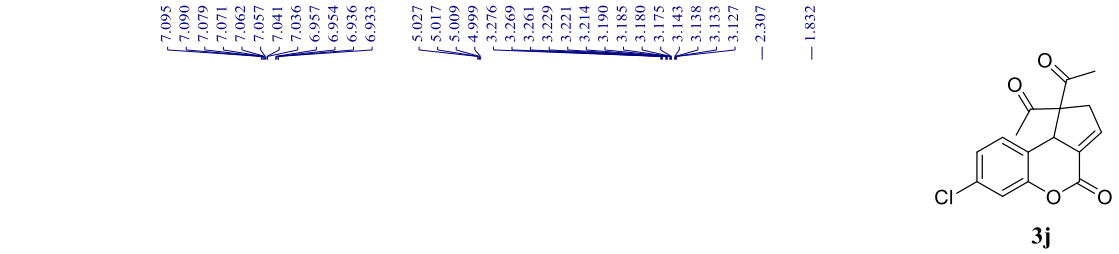

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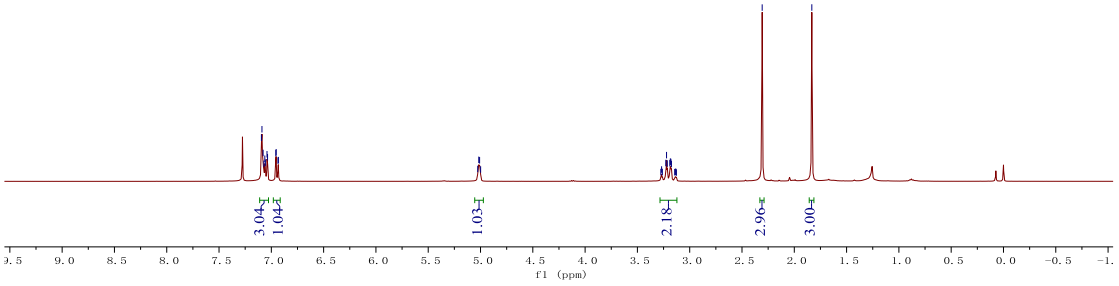
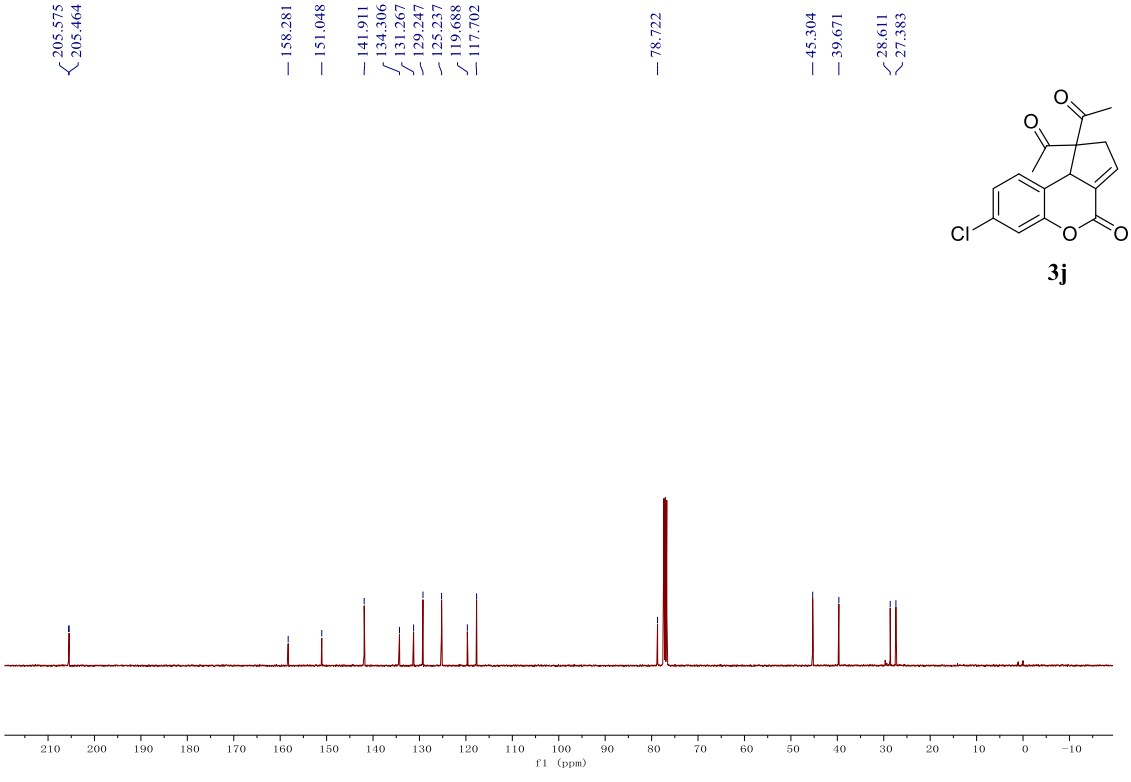
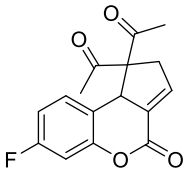


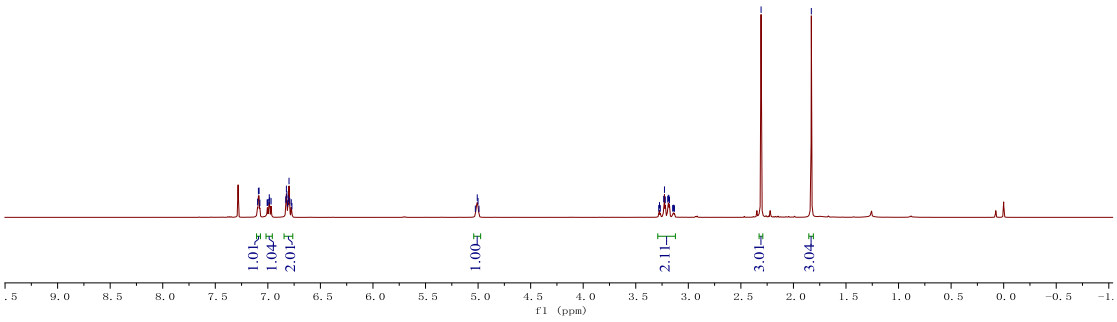


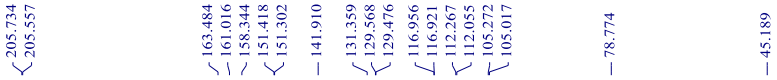
3j

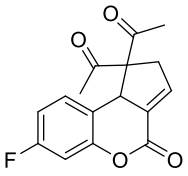
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3k**



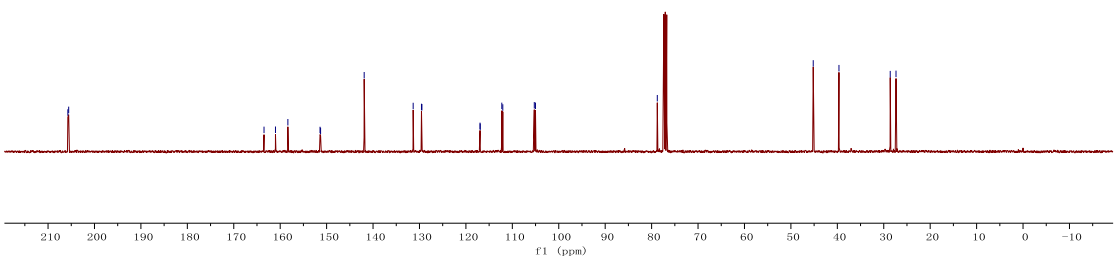
3k



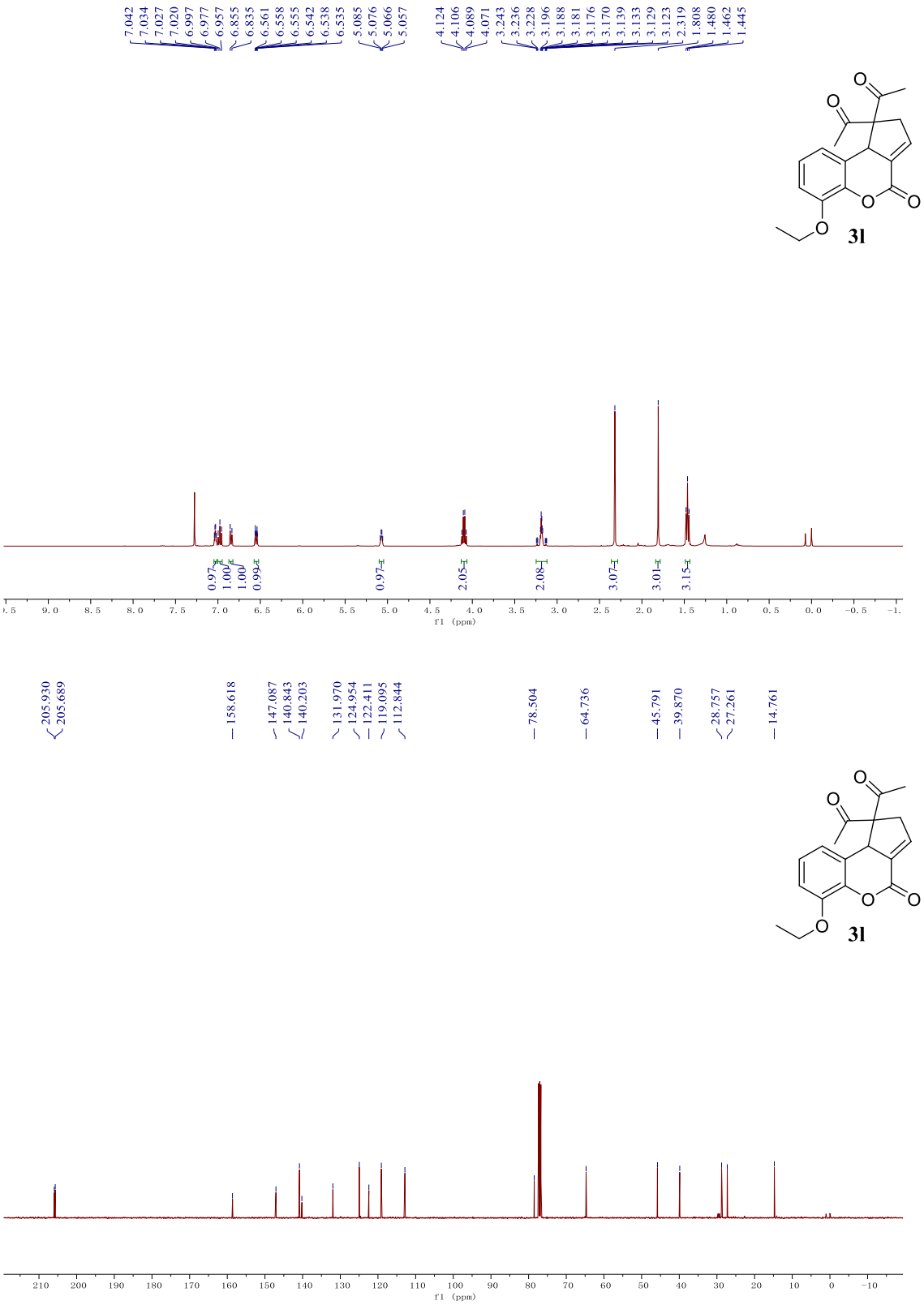




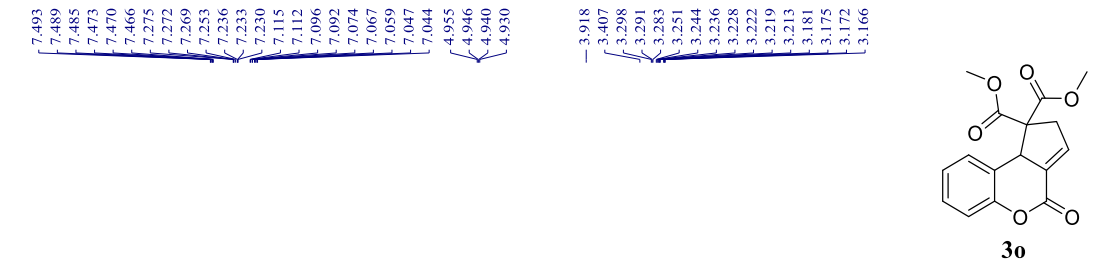
3k



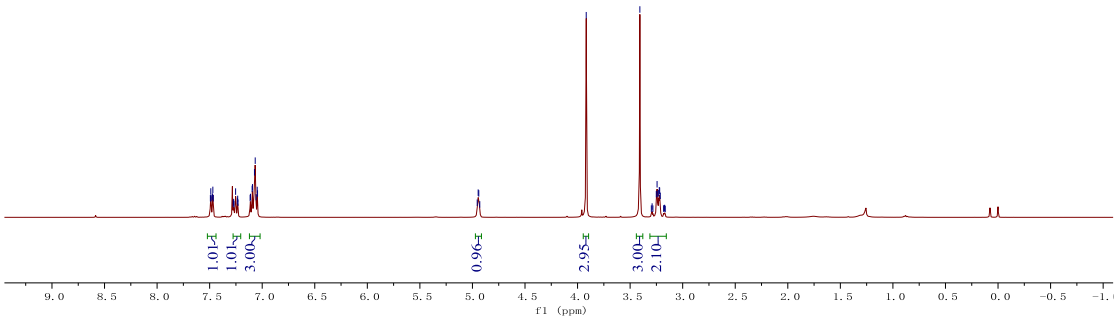
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3l**

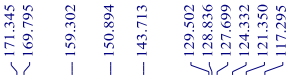


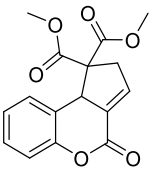
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3o**



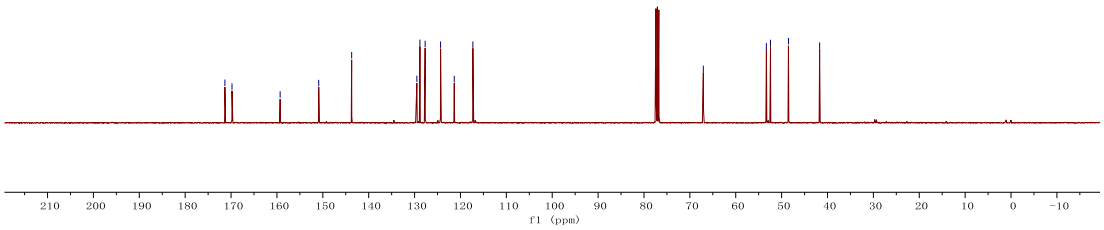
3o



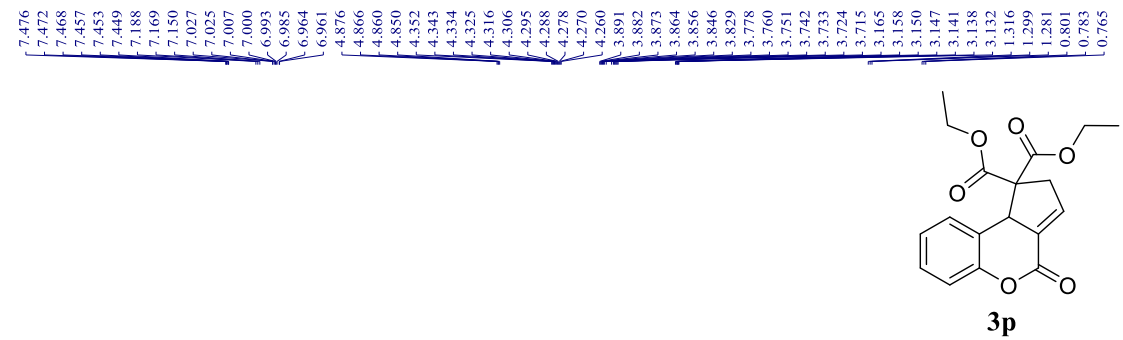




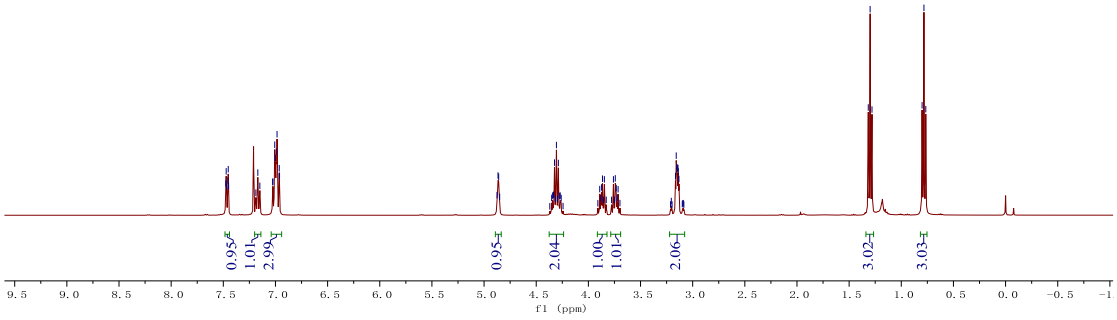
3o

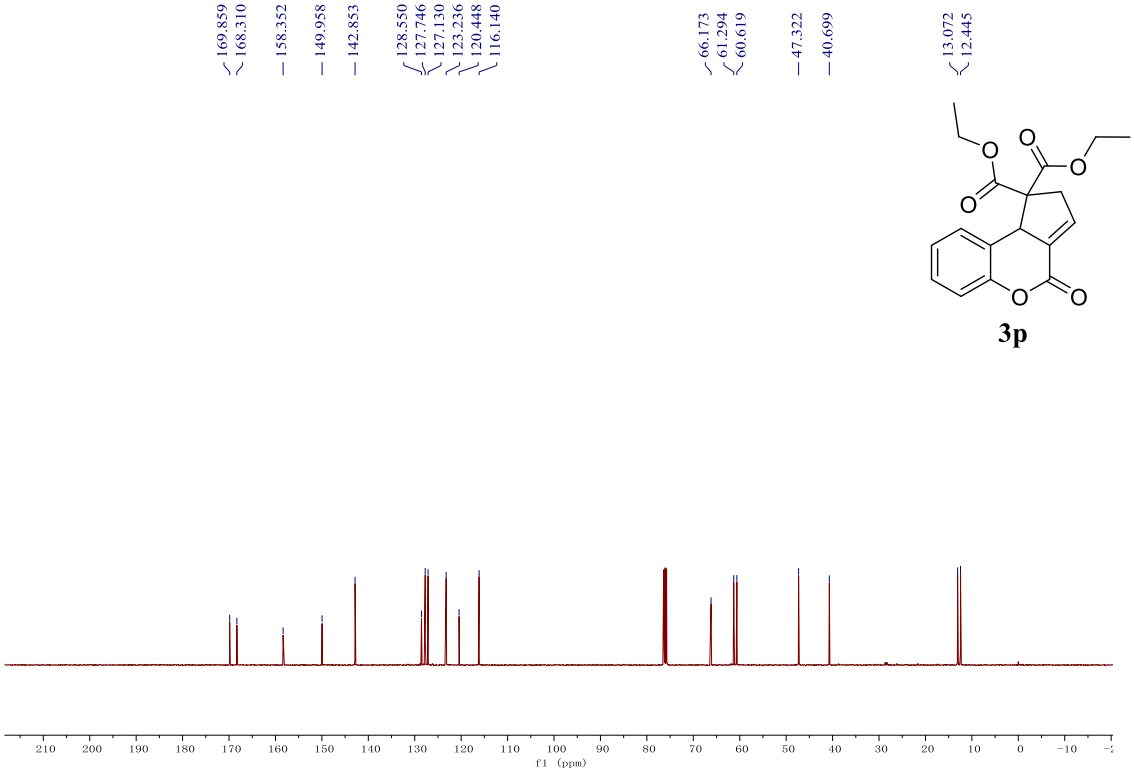


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3p**



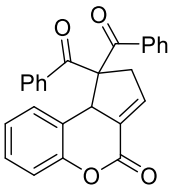
3p



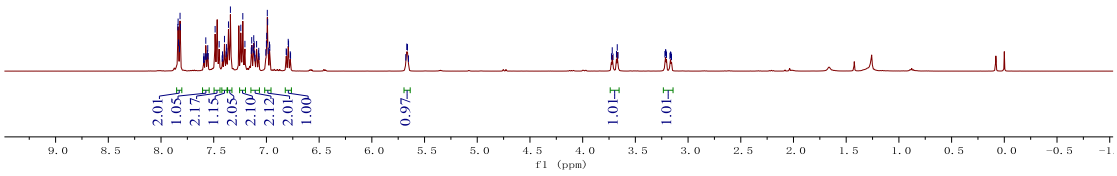


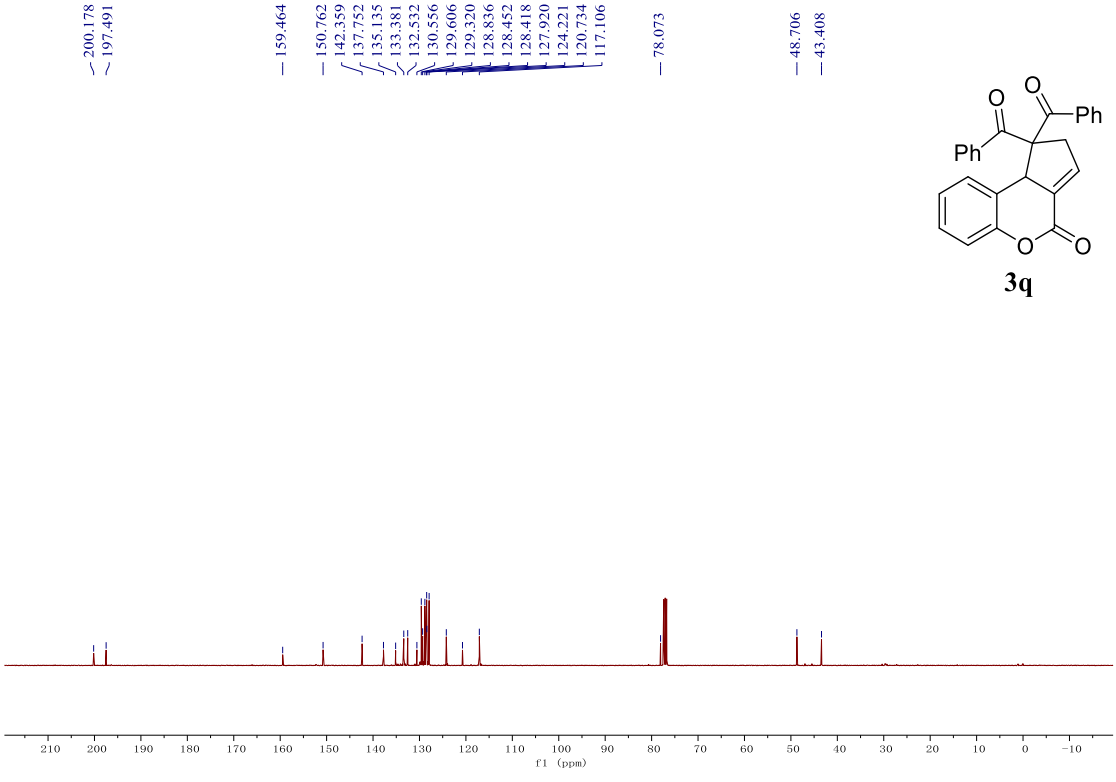
3p

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3q**



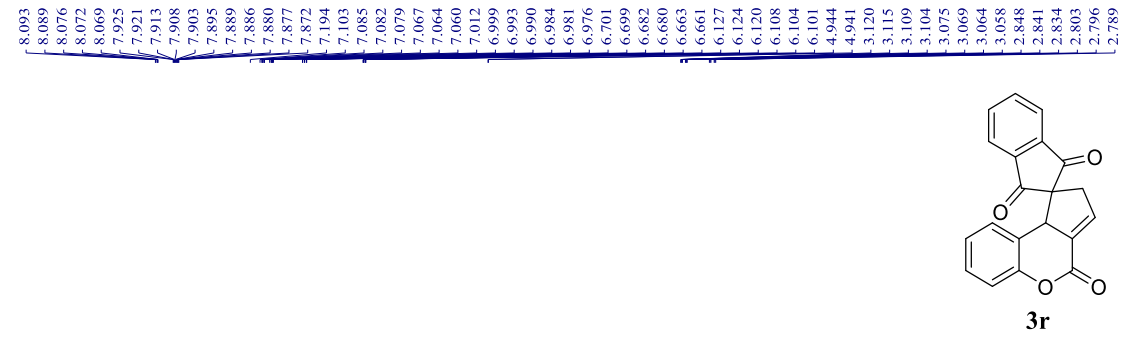
3q



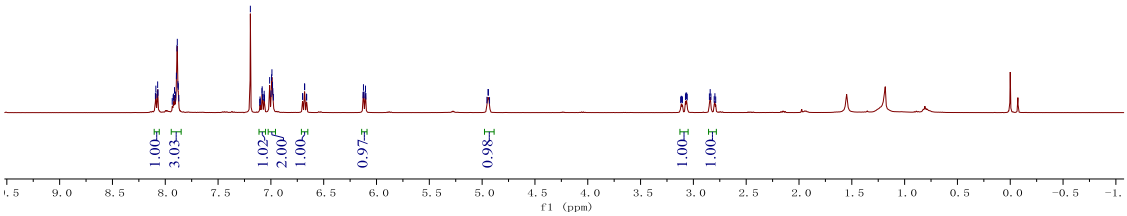


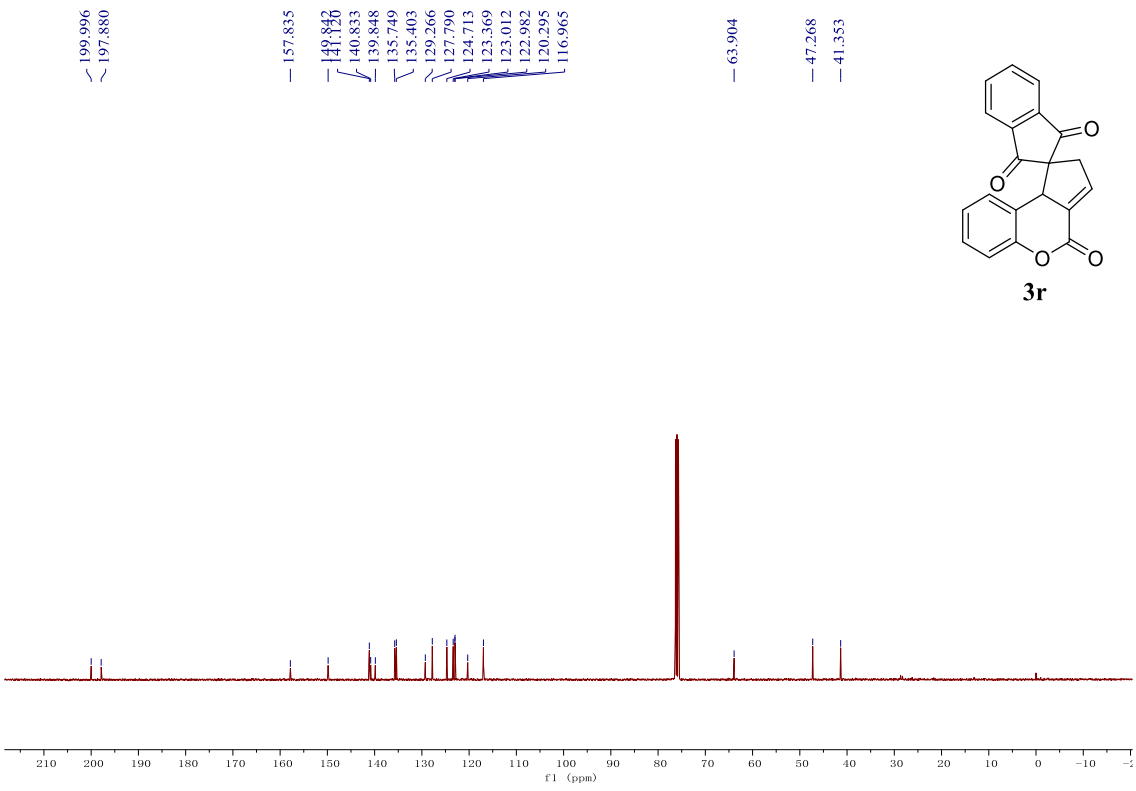
3q

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3r**



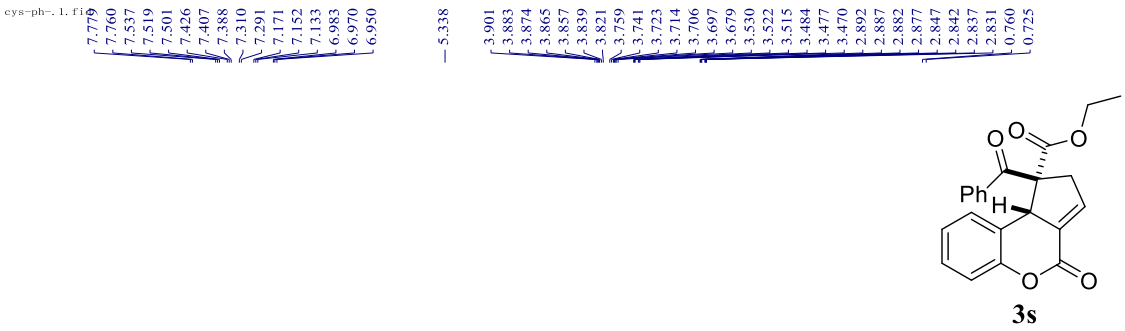
3r



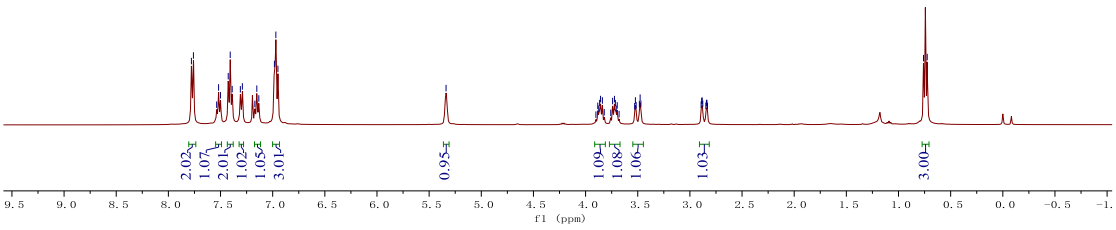


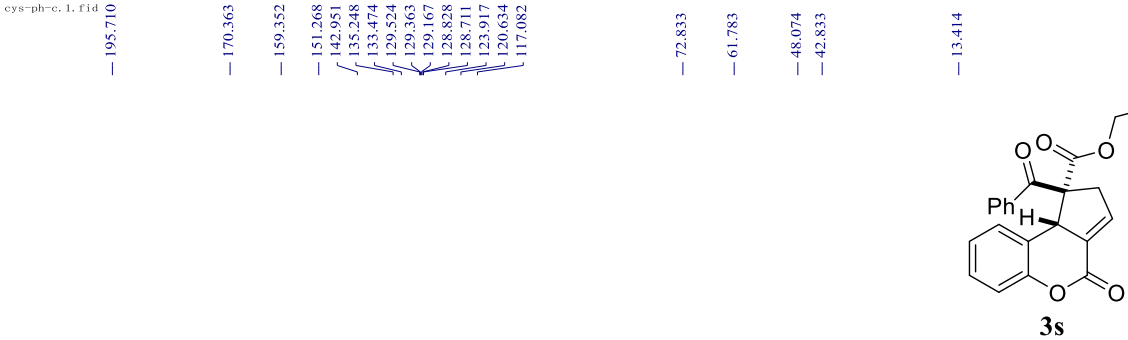
3r

^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3s**

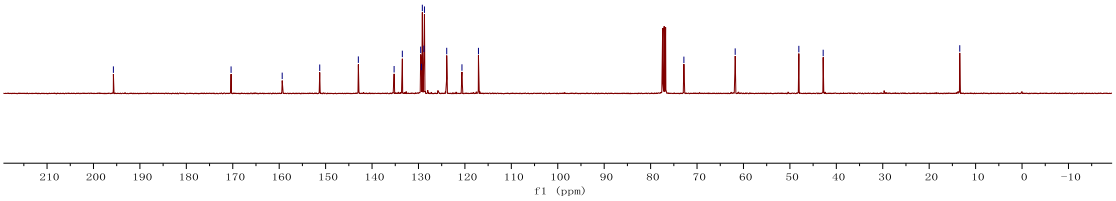


3s

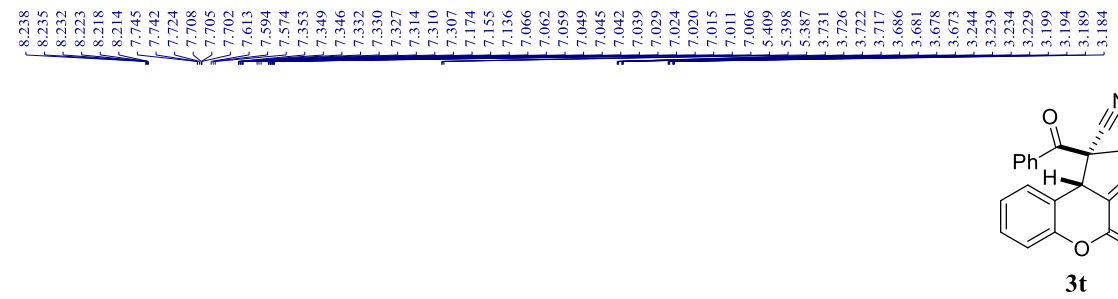




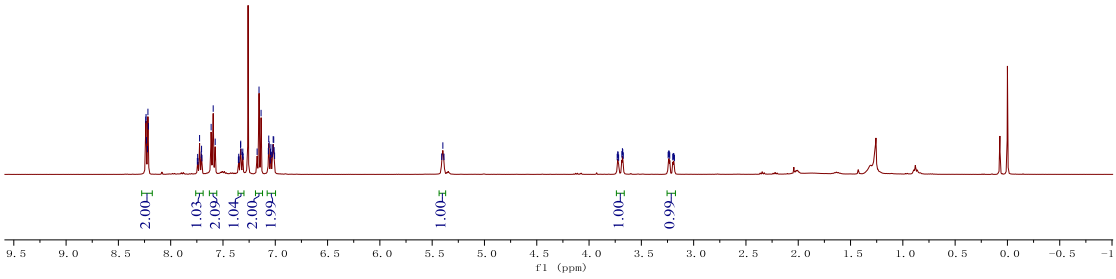
3s

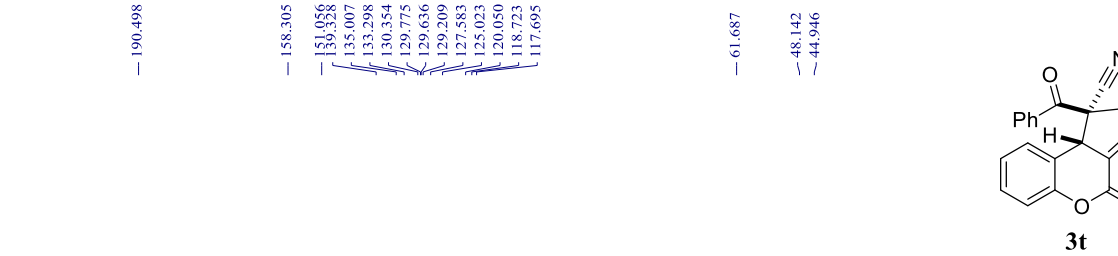


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3t**

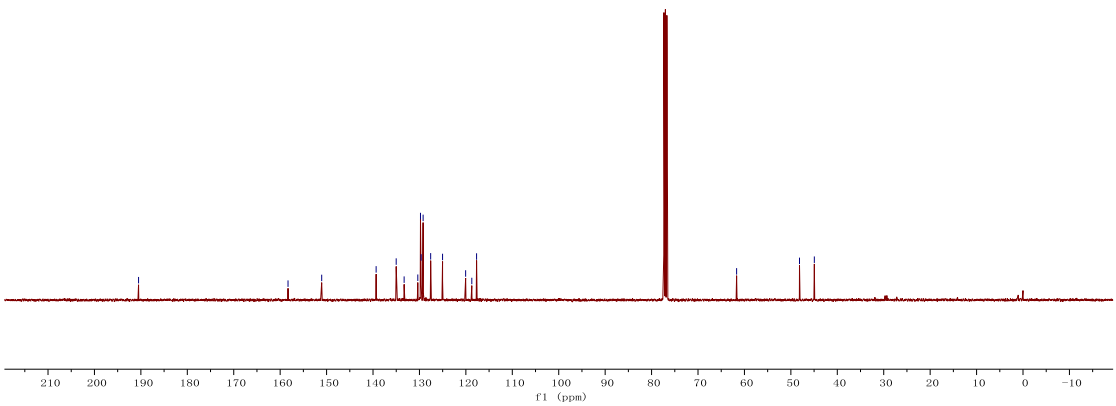


3t



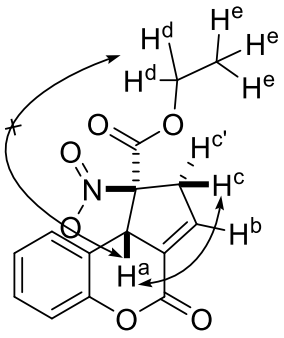


3t

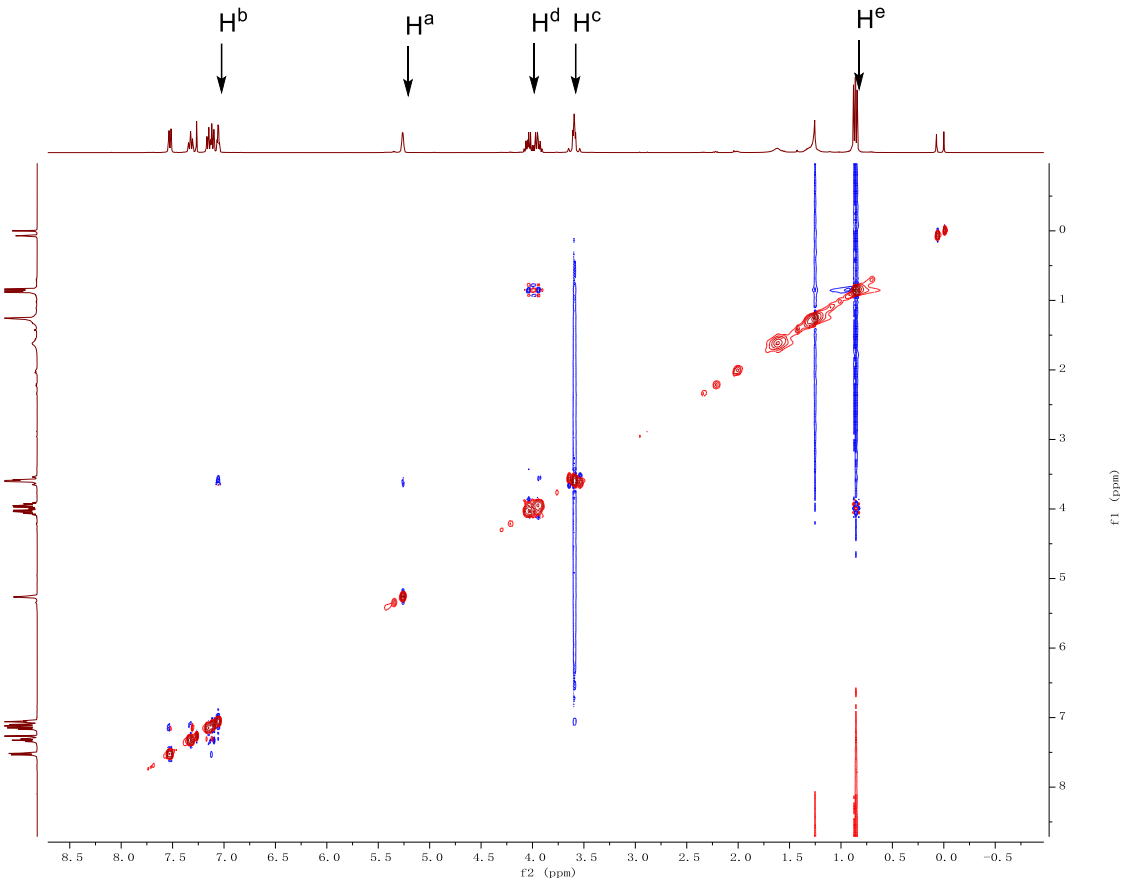


The relative stereochemistry of **3u** was assigned based on its 2D-NMR spectra and comparison with the spectra of **3w** (*major diastereomer*) crystal structures. The NOESY and the 1D ^{1}H and ^{13}C NMR spectra are provided below.

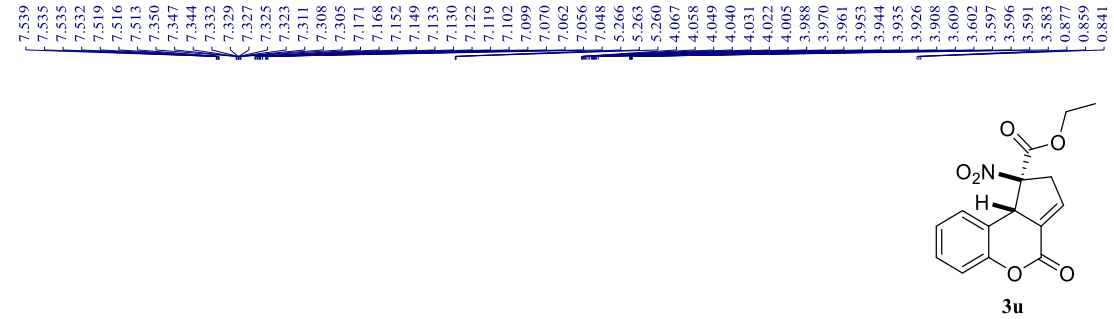
NOESY



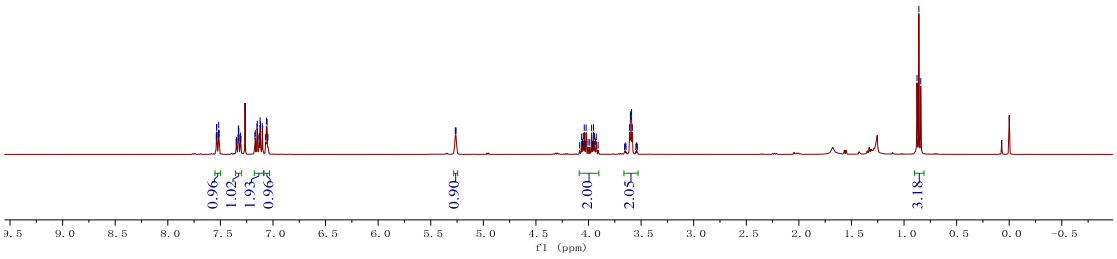
3u

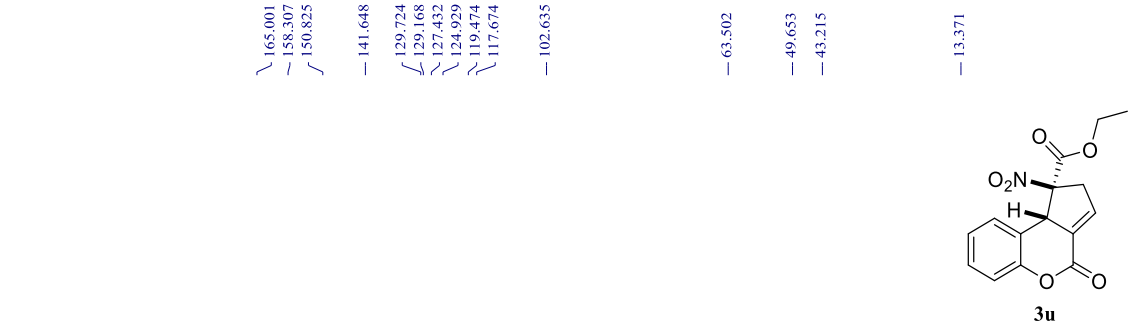


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3u**

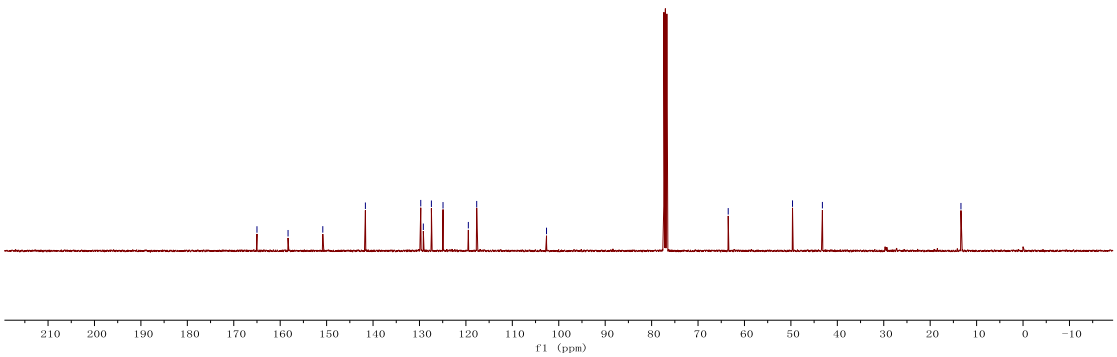


3u

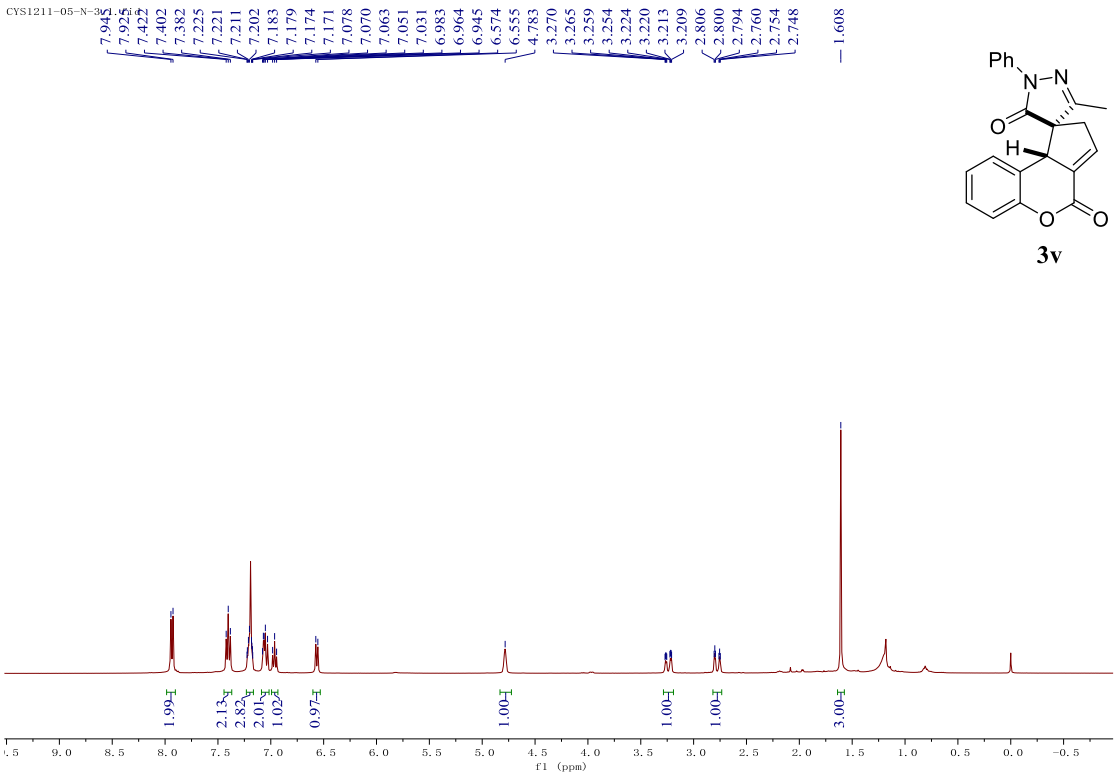




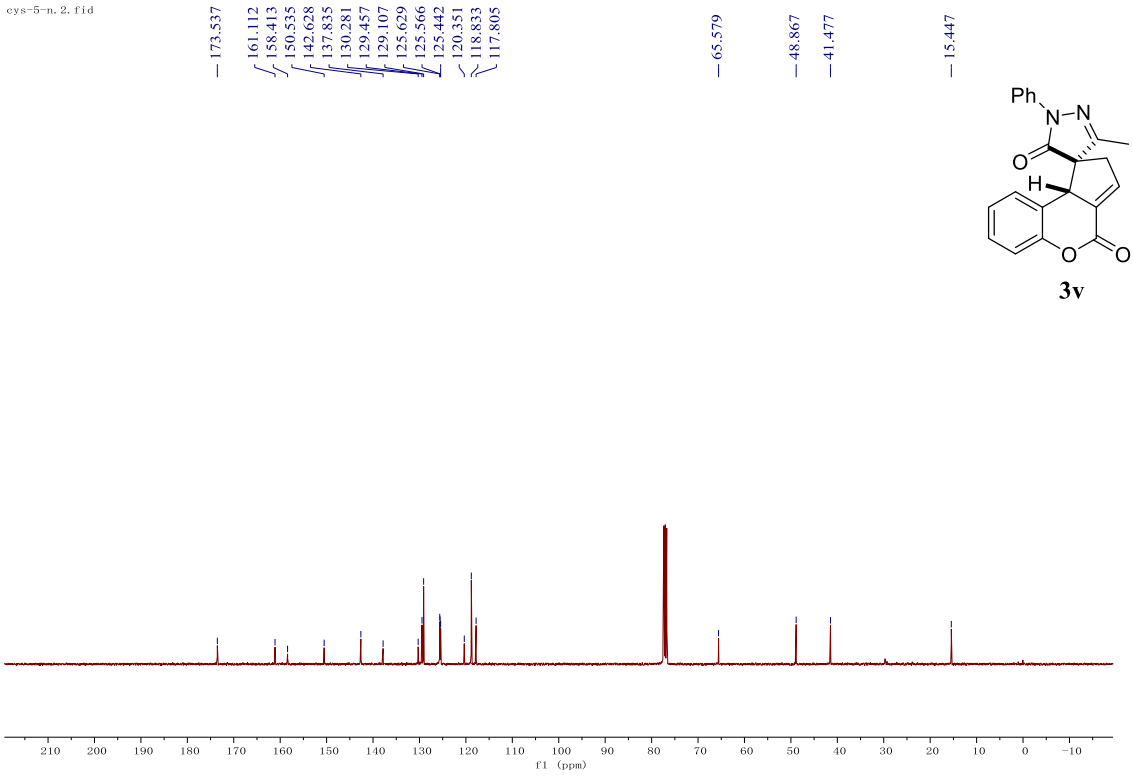
3u



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3v**

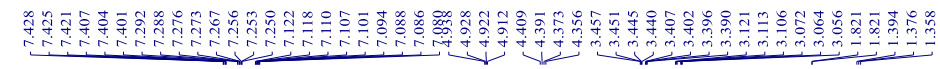


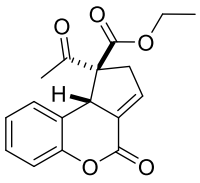
3v



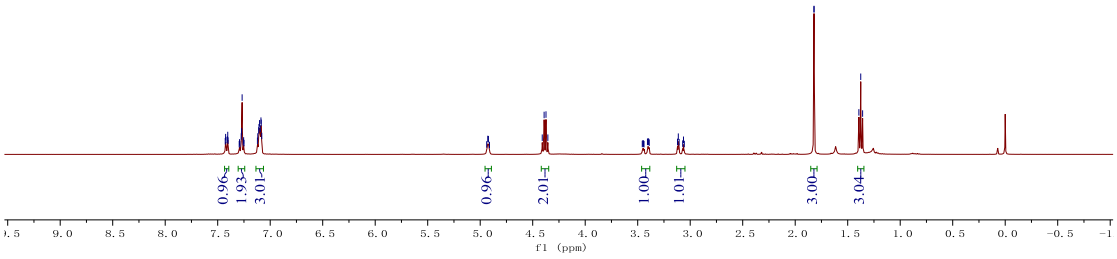
3v

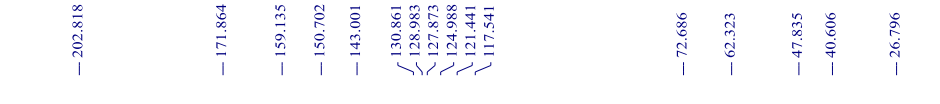
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3w (*minor diastereomer*).**

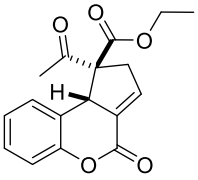




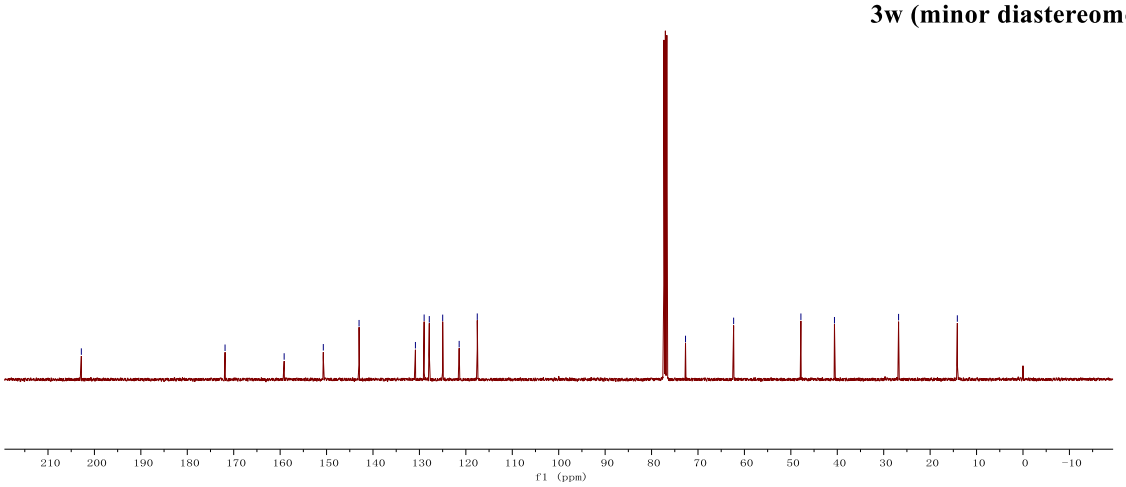
3w (minor diastereomer).



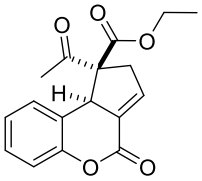




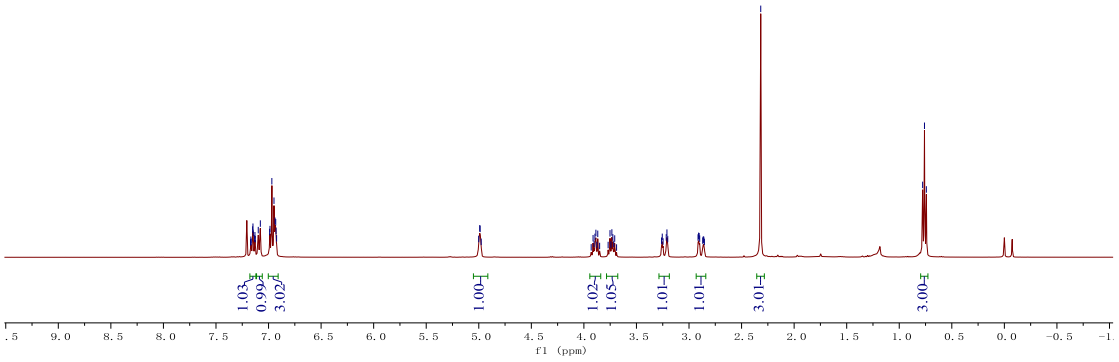
3w (minor diastereomer).

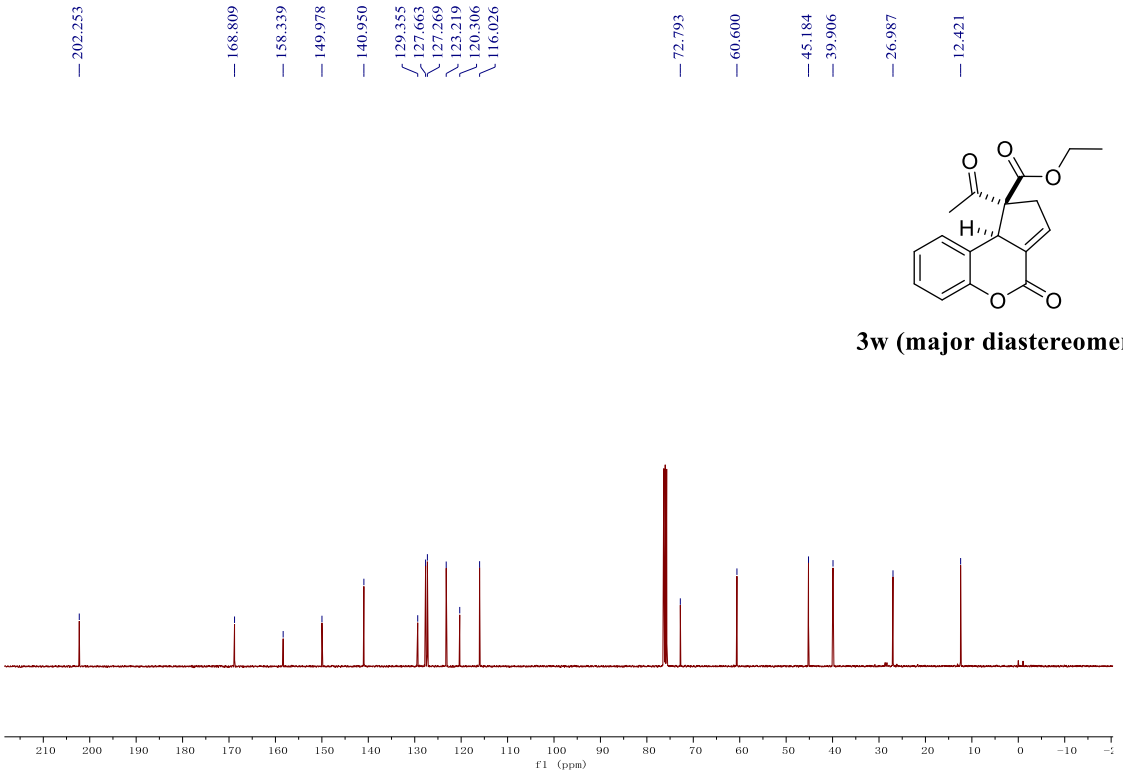


^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product **3w (*major diastereomer*)**.



3w (major diastereomer).





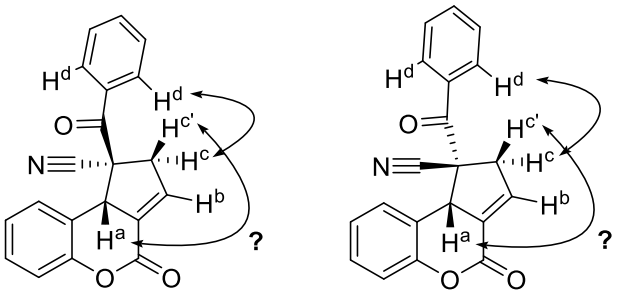
3w (major diastereomer).

6. Assignment of the Relative Stereochemistry of 3t

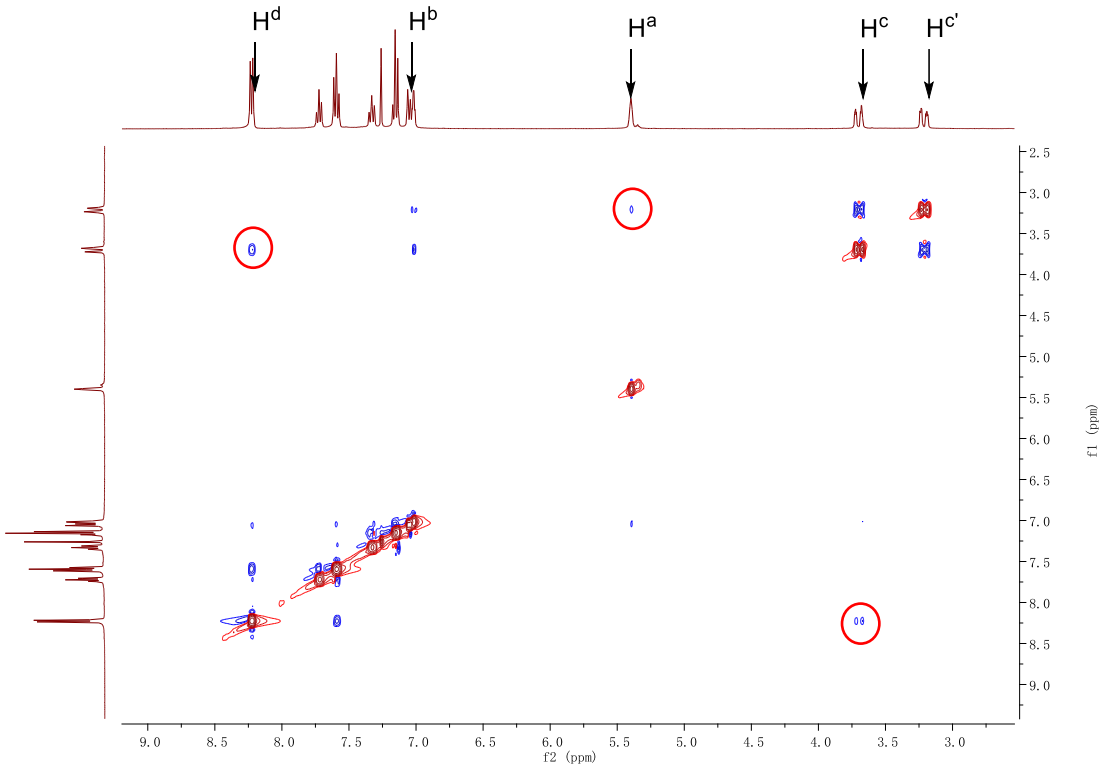
The relative stereochemistry of **3t** was assigned based on its 2D-NMR spectra and DFT calculations.

NOESY

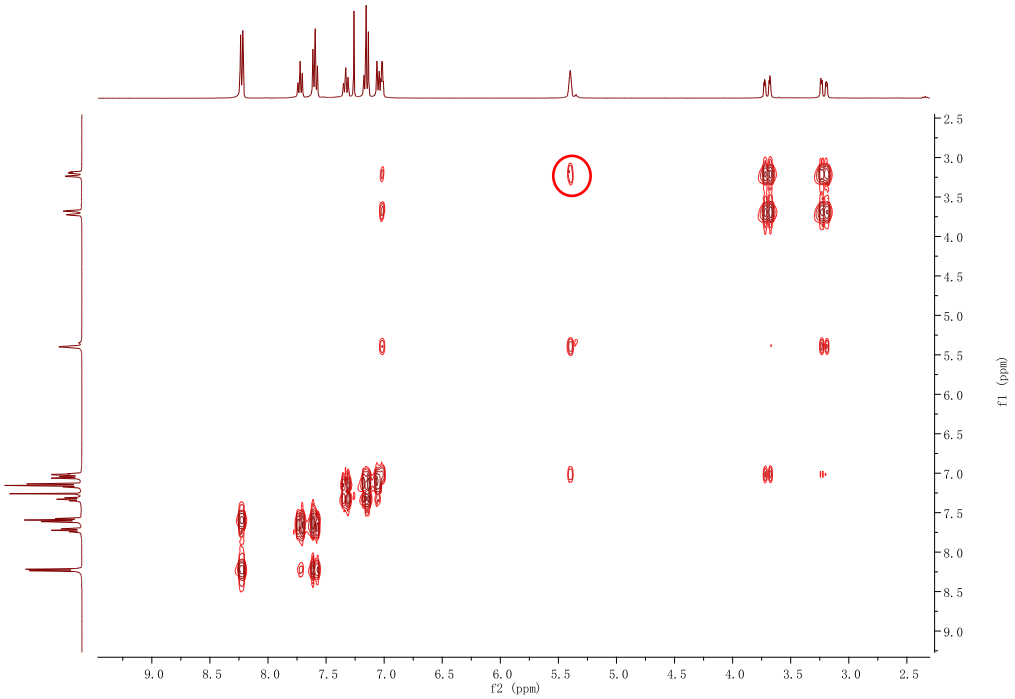
In the ^{1}H-^{1}H NOESY spectrum, H^{a}-$H^{c'}$ and H^{c}-H^{d} cross signals could be observed. However, there is also a cross signal between H^{a} and $H^{c'}$ in the COSY spectrum. Since it is difficult to completely remove unwanted COSY-like cross-peaks in NOE spectroscopy, the relative stereochemistry could not be unequivocally assigned by 2D NMR experiments.



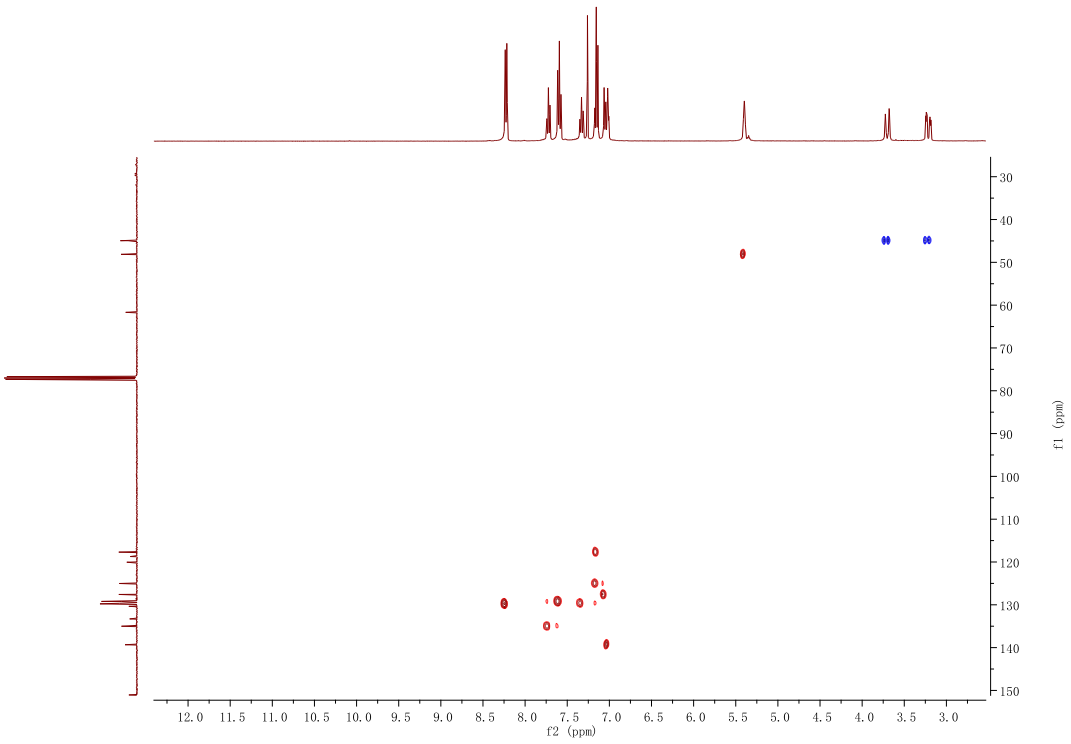
3t-isomer-1 **3t-isomer-2**



COSY



HSQC



To solve the challenge involved in the stereoassignment of **3t**, GIAO NMR shift calculations were then conducted to provide helpful assistance in the structural elucidation.[3] First, the most stable conformations of isomers **1** and **2** were obtained after a comprehensive conformational search. Actually, it was found that the distance between H^c and H^d in **3t-isomer-1** is 2.26 **Å**, even shorter than that in **3t-isomer-2**, 2.41 Å (Figure S4).

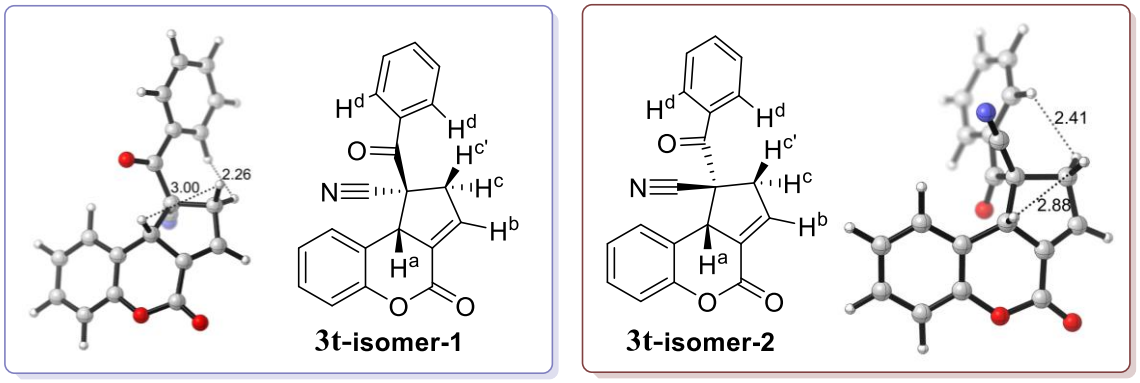
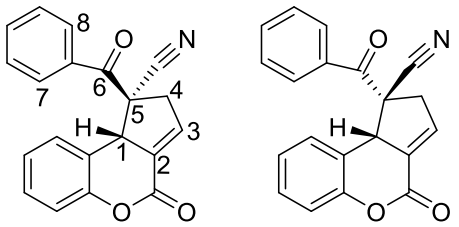


Figure S4. The most stable conformations of **3t-isomer-1** and **3t-isomer-2**. Structures are optimized at M062X/6-311+G(2d,p) theoretical level using Gaussian09 software.[4] Distances were given in angstrom.

Comparing the experimental and calculated isotropic magnetic shielding values, it is suggested that **3t-isomer-1** is assigned to be the plausible configuration (Table S2). To be noted, the NMR chemical shifts for C^1, C^5, H^1, and H^8 of **3t-isomer-1** are obviously closer to the corresponding experimental values than those of **3t-isomer-2**. What is more, the RMSDs with respect to experimental NMR chemical shifts for **3t-isomer-1** are 3.90 and 0.181 *ppm* for ^{13}C and ^{1}H, respectively, lower than the corresponding values for **3t-isomer-2**.

Table S2. Comparison of the Boltzmann averaged GIAO isotropic magnetic shielding values and experimental results.[5]



Nuclei	**3t-isomer-1**	**3t-isomer-2**	Exp (^{13}C)
^{13}C			
1	**49.56**	**53.35**	**48.10**
3	143.19	144.58	158.30
4	47.38	46.17	44.90
5	**61.94**	**56.35**	**61.70**
6	189.83	187.90	190.50

Table S2 continued.

	156.07	155.50	
	150.70	150.11	151.10
	135.32	133.96	139.30
	132.52	132.81	135.00
	132.14	129.72	133.30
	130.78	129.55	130.40
	129.97	131.89	
	128.65	128.72	129.80
	128.47	127.96	129.60
	128.19	126.67	129.20
	127.39	125.62	127.60
	123.58	123.52	125.00
	121.60	123.17	120.10
	120.88	121.30	118.70
	116.80	116.93	117.70
RMSD	3.90	4.31	

Nuclei	**3t-isomer-1**	**3t-isomer-2**	Exp (^{1}H)
^{1}H			
1	**5.07**	**4.88**	**5.40**
3	6.77	6.76	7.02
4	3.51	3.56	3.70
4	3.00	3.42	3.21
7	8.38	8.24	8.23
8	**8.10**	**7.51**	**8.23**
	7.57	7.50	7.72
	7.46	7.26	7.60
	7.39	7.33	7.60
	7.15	7.15	7.33
	7.14	7.07	7.15
	7.04	6.92	7.15
	6.99	6.76	7.05
RMSD	0.181	0.320	

[a]The GIAO isotropic magnetic shielding values were calculated at the mPW1PW91/6-311+G(2d,p) theoretical level in chloroform with IEFPCM solvent model using G09 software.[6] The contributions of different conformations were taken into account according to the Boltzmann distribution principle.

Table S3. Energies and thermodynamic parameters.

Structure	E_{ele}	E_0	E	H	G
3t-isomer-1-conf1	-1050.252201	-1049.969899	-1049.951444	-1049.950500	-1050.017370
3t-isomer-1-conf2	-1050.247515	-1049.964792	-1049.946444	-1049.945500	-1050.012241
3t-isomer-1-conf3	-1050.242860	-1049.960956	-1049.942426	-1049.941482	-1050.008714
3t-isomer-2-conf1	-1050.249093	-1049.967053	-1049.948632	-1049.947688	-1050.014426
3t-isomer-2-conf2	-1050.248106	-1049.966421	-1049.948103	-1049.947159	-1050.013104
3t-isomer-2-conf3	-1050.244905	-1049.963098	-1049.944685	-1049.943741	-1050.009951
3t-isomer-2-conf4	-1050.243597	-1049.961704	-1049.943134	-1049.942190	-1050.009585

Notes: E_{ele}, E_0, E, H, and G were the electronic energies, sum of electronic and zero-point energies, sum of electronic and thermal energies, sum of electronic and thermal enthalpies, and sum of electronic and thermal free energies, respectively, which were given at the M062X/6-311+G(2d,p) theoretical level using Gaussian09 software

Coordinates of all stationary points.

3t-isomer-1-conf1

0 imaginary frequency

C	-4.201050	-1.390231	0.180528
C	-3.260090	-0.417514	-0.118990
C	-1.910866	-0.730795	-0.256534
C	-1.524993	-2.057965	-0.097272
C	-2.453821	-3.040555	0.204049
C	-3.794541	-2.703313	0.343617
H	-5.237454	-1.095648	0.278705
H	-0.480904	-2.320241	-0.219205
H	-2.132215	-4.065892	0.328475
H	-4.527093	-3.464648	0.578831
C	-0.959333	0.376414	-0.611198
H	-0.770158	0.340145	-1.690529
C	-1.538860	1.714502	-0.243928
C	-2.991265	1.968522	-0.296224
O	-3.774230	0.857638	-0.304567
O	-3.499569	3.047930	-0.320453
C	0.437559	0.428168	0.080241
C	-0.622424	2.584580	0.155313
H	-0.825042	3.609650	0.435530
C	0.746188	1.963226	0.156316
H	1.337228	2.226602	1.031949
H	1.317626	2.271584	-0.726402
C	1.518845	-0.337518	-0.722233
O	1.188698	-0.949789	-1.705669
C	0.340544	-0.106425	1.445322
N	0.278779	-0.503266	2.519129
C	2.954024	-0.240586	-0.317945
C	3.901568	-0.647300	-1.259701
C	3.378873	0.227087	0.925829
C	5.252179	-0.575020	-0.968520
H	3.555086	-1.014043	-2.217267
C	4.734033	0.287369	1.218167
H	2.668412	0.516445	1.687933
C	5.669873	-0.107032	0.272637
H	5.981159	-0.885479	-1.706089
H	5.057439	0.638538	2.189440
H	6.726612	-0.054071	0.503405

3t-isomer-1-conf2

0 imaginary frequency

C	3.959035	0.349863	-1.324124
C	2.815880	-0.256418	-0.828330
C	1.703313	0.491883	-0.456089
C	1.753344	1.874277	-0.605287
C	2.890545	2.493282	-1.098567
C	3.993731	1.727894	-1.456671
H	4.800620	-0.272448	-1.598355
H	0.894122	2.470970	-0.318614
H	2.916426	3.570039	-1.199082
H	4.886464	2.204396	-1.840530
C	0.484773	-0.255298	0.012457
H	-0.161897	-0.392033	-0.861934

C	0.872949	-1.596631	0.565827
C	1.977378	-2.370898	-0.036463
O	2.855654	-1.643130	-0.775925
O	2.142575	-3.545863	0.089324
C	-0.387142	0.350894	1.175575
C	0.198769	-1.942686	1.654325
H	0.341625	-2.873913	2.186944
C	-0.762233	-0.873319	2.085817
H	-0.638906	-0.617971	3.138495
H	-1.802716	-1.176772	1.954649
C	-1.590251	1.137312	0.616558
O	-1.629458	2.332938	0.751088
C	0.423826	1.253600	2.003593
N	1.063419	1.896805	2.702871
C	-2.685307	0.415167	-0.116483
C	-3.792983	1.183182	-0.480373
C	-2.654254	-0.938085	-0.461649
C	-4.848947	0.613205	-1.170545
H	-3.803724	2.231164	-0.210471
C	-3.710700	-1.505304	-1.159755
H	-1.814505	-1.570011	-0.202035
C	-4.808661	-0.732993	-1.512929
H	-5.703937	1.218229	-1.444019
H	-3.673754	-2.553397	-1.427685
H	-5.632318	-1.181007	-2.054684

3t-isomer-1-conf3

0 imaginary frequency

C	-3.507071	-1.849445	-0.320493
C	-2.620164	-0.810770	-0.554661
C	-1.387024	-0.752776	0.088419
C	-1.071264	-1.755350	1.000423
C	-1.948089	-2.800492	1.245203
C	-3.165264	-2.847310	0.577199
H	-4.453969	-1.850919	-0.843951
H	-0.133825	-1.704272	1.545585
H	-1.688018	-3.567126	1.962712
H	-3.858807	-3.656636	0.765200
C	-0.474155	0.387951	-0.255102
H	0.205562	0.082344	-1.058953
C	-1.262035	1.570424	-0.755842
C	-2.498730	1.384033	-1.536560
O	-3.039880	0.133043	-1.477860
O	-3.028167	2.220397	-2.201317
C	0.381829	1.022505	0.874514
C	-0.705211	2.727669	-0.426918
H	-1.079148	3.700361	-0.716747
C	0.545801	2.502357	0.377918
H	0.679505	3.186134	1.214907
H	1.429905	2.581021	-0.266517
C	1.801037	0.491843	1.178141
O	2.291487	0.762457	2.241914
C	-0.390433	1.051816	2.126207
N	-1.018591	1.087357	3.083257
C	2.620182	-0.177989	0.117130
C	2.195375	-1.292687	-0.603981
C	3.910098	0.316740	-0.074171
C	3.053150	-1.896015	-1.513334
H	1.213034	-1.719179	-0.440100
C	4.752514	-0.270634	-1.004085
H	4.240544	1.161004	0.518598
C	4.324467	-1.379059	-1.723977
H	2.726452	-2.772828	-2.057639
H	5.746339	0.129385	-1.159480
H	4.984972	-1.844843	-2.444491

3t-isomer-2-conf1

0 imaginary frequency

C	-3.595360	1.823652	-0.570974
C	-2.927703	0.653957	-0.242601
C	-1.782097	0.674797	0.544286
C	-1.320371	1.900620	1.010626
C	-1.975116	3.078296	0.687412
C	-3.115386	3.036632	-0.106033
H	-4.480878	1.760127	-1.189615
H	-0.434832	1.929085	1.637035
H	-1.599585	4.023943	1.055627
H	-3.634818	3.950536	-0.363491
C	-1.141505	-0.634604	0.898557
H	-1.449107	-0.895039	1.921093
C	-1.571950	-1.744490	-0.017268
C	-2.872522	-1.715308	-0.712988
O	-3.501416	-0.509683	-0.733023
O	-3.381894	-2.652104	-1.249059
C	0.408574	-0.774854	0.857103
C	-0.643154	-2.680223	-0.148090
H	-0.748862	-3.580816	-0.737414
C	0.600153	-2.316477	0.621904

H	1.518823	-2.537509	0.076868
H	0.647639	-2.844889	1.579790
C	1.016260	-0.066189	-0.383310
O	0.286663	0.244375	-1.286637
C	0.993146	-0.307772	2.114835
N	1.402830	0.060219	3.120747
C	2.495373	0.142092	-0.476679
C	2.946422	0.967723	-1.507738
C	3.421274	-0.457419	0.376818
C	4.300275	1.200009	-1.675748
H	2.215370	1.418725	-2.166320
C	4.778638	-0.232599	0.197977
H	3.105856	-1.102449	1.186134
C	5.218648	0.597659	-0.823217
H	4.641897	1.849007	-2.471822
H	5.491789	-0.702830	0.862523
H	6.278478	0.776847	-0.955111

3t-isomer-2-conf2

0 imaginary frequency

C	-0.167381	3.143026	0.278786
C	-0.927972	1.979918	0.317615
C	-0.441682	0.825931	0.921261
C	0.798287	0.883616	1.556050
C	1.564332	2.034100	1.527786
C	1.081387	3.163073	0.871838
H	-0.583292	4.015415	-0.207758
H	1.169345	-0.000726	2.062050
H	2.532563	2.051971	2.010395
H	1.673430	4.068871	0.839128
C	-1.282856	-0.416474	0.911742
H	-1.603997	-0.633006	1.939148
C	-2.493570	-0.272726	0.027544
C	-3.043709	1.036034	-0.362909
O	-2.190866	2.092908	-0.234903
O	-4.129117	1.219420	-0.822041
C	-0.680730	-1.770662	0.355938
C	-2.887389	-1.434981	-0.476727
H	-3.729510	-1.565823	-1.142431
C	-1.968991	-2.543970	-0.041235
H	-1.775151	-3.271072	-0.827019
H	-2.376048	-3.069198	0.828837
C	0.150778	-1.483225	-0.932913
O	-0.387449	-1.636885	-1.997566
C	0.068966	-2.475800	1.393561
N	0.608325	-3.033877	2.238106
C	1.520975	-0.890458	-0.857984
C	1.752143	0.221411	-1.668836
C	2.543078	-1.388249	-0.053896
C	2.979836	0.859631	-1.639006
H	0.951370	0.586885	-2.299843
C	3.782086	-0.760869	-0.051305
H	2.391138	-2.264574	0.560161
C	3.996781	0.368940	-0.827545
H	3.146008	1.738770	-2.248553
H	4.579589	-1.157985	0.563658
H	4.959524	0.864480	-0.807015

3t-isomer-2-conf3

0 imaginary frequency

C	2.061900	-2.433078	0.450085
C	1.114024	-1.558576	0.960256
C	-0.171456	-1.503908	0.431047
C	-0.504681	-2.374168	-0.603332
C	0.432515	-3.255154	-1.119642
C	1.719604	-3.276334	-0.594242
H	3.052527	-2.436201	0.885340
H	-1.507122	-2.345030	-1.017017
H	0.160009	-3.919396	-1.928930
H	2.459251	-3.958452	-0.993707
C	-1.145595	-0.517515	1.007500
H	-1.853700	-1.055627	1.650517
C	-0.449974	0.538946	1.819259
C	0.835359	0.284083	2.495046
O	1.537202	-0.787174	2.029395
O	1.299884	0.952675	3.366636
C	-2.000902	0.348057	0.012288
C	-1.051410	1.718016	1.746750
H	-0.721452	2.608561	2.265658
C	-2.238245	1.661904	0.822198
H	-2.343597	2.534237	0.176827
H	-3.169406	1.578683	1.391113
C	-1.235625	0.555831	-1.326352
O	-1.694708	0.097093	-2.337447
C	-3.274020	-0.315262	-0.288326
N	-4.279166	-0.840333	-0.450978
C	0.122129	1.198339	-1.341435
C	1.152263	0.445305	-1.903904

C	0.387976	2.485582	-0.880812
C	2.439189	0.957559	-1.964464
H	0.937592	-0.550580	-2.273278
C	1.671424	3.005059	-0.967859
H	-0.399363	3.104137	-0.473084
C	2.700943	2.237770	-1.495596
H	3.236421	0.355476	-2.381381
H	1.866729	4.010838	-0.618698
H	3.704740	2.640208	-1.545987
H	-0.207185	1.393390	-0.108774
C	-3.320660	2.648851	-0.478578
H	-5.079213	1.498376	-0.926681
H	-1.403491	3.526355	-0.076486
H	-3.845640	3.595684	-0.463764

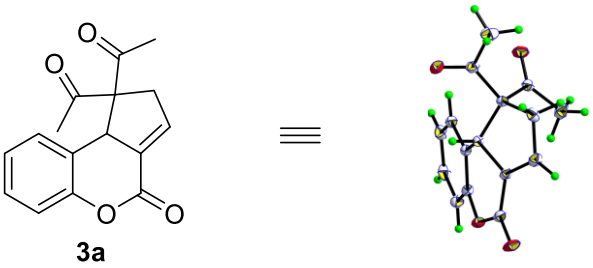
3t-isomer-2-conf4

0 imaginary frequency

C	2.983239	1.391732	-1.365809
C	2.349725	0.763373	-0.305415
C	1.605307	-0.398380	-0.493872
C	1.524633	-0.935047	-1.775378
C	2.152759	-0.314745	-2.844741
C	2.880060	0.850455	-2.637203
H	3.546906	2.294876	-1.172038
H	0.962524	-1.848710	-1.933432
H	2.074344	-0.741657	-3.835637
H	3.371926	1.341090	-3.467229
C	0.976656	-1.031926	0.714498
H	1.651379	-1.823052	1.065375
C	0.794616	-0.033103	1.822775
C	1.750427	1.073113	2.015509
O	2.528830	1.362944	0.932313
O	1.867177	1.723061	3.008285
C	-0.449579	-1.678875	0.588414
C	-0.323491	-0.214658	2.510358
H	-0.630783	0.391381	3.352574
C	-1.124600	-1.361759	1.967071
H	-2.181831	-1.115301	1.850279
H	-1.066631	-2.229602	2.629544
C	-1.341826	-1.147902	-0.574720
O	-1.639005	-1.895846	-1.467213
C	-0.305727	-3.127186	0.398239
N	-0.144824	-4.257886	0.308177
C	-1.967176	0.214929	-0.505587
C	-3.337946	0.263827	-0.766460
C	-1.276233	1.397484	-0.255992
C	-4.013635	1.472803	-0.737904
H	-3.861000	-0.657045	-0.993027
C	-1.952142	2.610039	-0.252710

7. X-ray Crystallographic Data of Compound

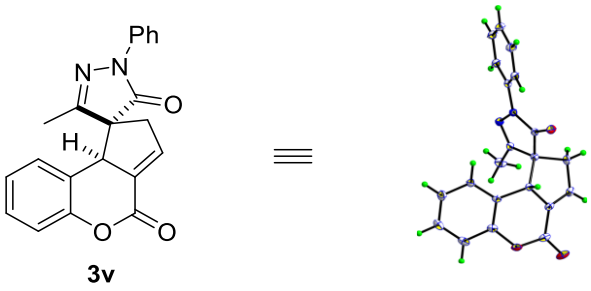
X-Ray crystallographic analysis of **3a** (CCDC 2080977) showing the thermal ellipsoids at 30% probability level.



3a

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71076

Cell:          a=10.2334(13)      b=12.1426(15)    c=12.2272(15)
               alpha=115.446(4)   beta=93.730(4)   gamma=103.262(4)
Temperature:   293 K

                 Calculated                Reported
Volume           1312.0(3)                 1312.0(3)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C16 H14 O4                2(C16 H14 O4)
Sum formula      C16 H14 O4                C32 H28 O8
Mr               270.27                    540.54
Dx,g cm-3        1.368                     1.368
Z                4                         2
Mu (mm-1)        0.098                     0.098
F000             568.0                     568.0
F000'            568.32
h,k,lmax         13,15,15                  13,15,15
Nref             6056                      6038
Tmin,Tmax        0.964,0.994               0.707,0.746
Tmin'            0.961

Correction method= # Reported T Limits: Tmin=0.707 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.997          Theta(max)= 27.560

R(reflections)= 0.0494( 3735)     wR2(reflections)= 0.1323( 6038)

S = 1.017                 Npar= 366
```

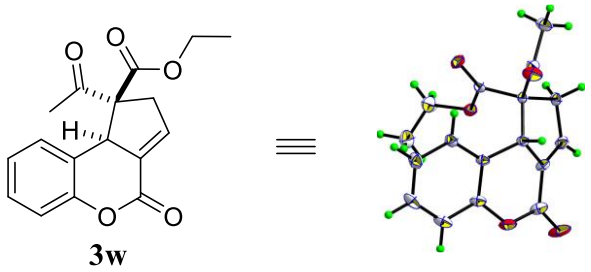
X-Ray crystallographic analysis of **3v** (CCDC 2081221) showing the thermal ellipsoids at 30% probability level.



3v

```
Bond precision:  C-C = 0.0020 A          Wavelength=0.71076

Cell:            a=8.9293(5)    b=10.0916(6)         c=18.8422(10)
                 alpha=90       beta=96.1923(16)     gamma=90
Temperature:     293 K

                 Calculated                 Reported
Volume           1687.98(16)                1687.98(16)
Space group      P 21/n                     P 1 21/n 1
Hall group       -P 2yn                     -P 2yn
Moiety formula   C21 H16 N2 O3              C21 H16 N2 O3
Sum formula      C21 H16 N2 O3              C21 H16 N2 O3
Mr               344.36                     344.36
Dx,g cm-3        1.355                      1.355
Z                4                          4
Mu (mm-1)        0.092                      0.092
F000             720.0                      720.0
F000'            720.33
h,k,lmax         11,13,24                   11,13,24
Nref             3905                       3883
Tmin,Tmax        0.978,0.990                0.702,0.746
Tmin'            0.972

Correction method= # Reported T Limits: Tmin=0.702 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.994          Theta(max)= 27.560

R(reflections)= 0.0454( 3020)     wR2(reflections)= 0.1149( 3883)

S = 1.056                 Npar= 236
```

X-Ray crystallographic analysis of **3w** ***(major diastereomer)*** (CCDC 2080106) showing the thermal ellipsoids at 30% probability level.



3w

Bond precision: C-C = 0.0025 A Wavelength=0.71073

Cell: a=9.9700(3) b=11.9190(3) c=12.5827(4)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1495.23(8)	1495.23(8)
Space group	P n a 21	Pna2(1)
Hall group	P 2c -2n	?
Moiety formula	C17 H16 O5	?
Sum formula	C17 H16 O5	C1.55 H1.45 O0.45
Mr	300.30	27.30
Dx,g cm-3	1.334	1.334
Z	4	44
Mu (mm-1)	0.098	0.098
F000	632.0	632.0
F000'	632.37	
h,k,lmax	13,15,16	13,15,15
Nref	3548[1854]	3498
Tmin,Tmax	0.977,0.981	
Tmin'	0.971	

Correction method= Not given

Data completeness= 1.89/0.99 Theta(max)= 27.830

R(reflections)= 0.0407(3242) wR2(reflections)= 0.1239(3498)

S = 1.018 Npar= 199

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