Unified Approach to Synthesize Diverse Heterocyclic: Metal-Free Visible-Light-Promoted Cyclization Reaction to Acquire Sulfonylated Spiro-trienones, Coumarins and Their Derivatives

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Contents of Supporting Information

Experiment Section.

1. NMR spectra were recorded on Bruker DPX-400 MHz and DPX-600 MHz NMR spectrometer instruments and calibrated using residual solvent peaks as internal reference, such as $CDCl_3$ solutions. High resolution mass spectra were performed on API STAR Pulsar and Thermo Q Exactive. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F254. Silica gel (200-300 mesh) was used for column chromatography.

2.Reagent: Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Aromatic amines and benzylamines were purchased from Accela ChemBio Co., Ltd and Shanghai Titan Scientific Co., Ltd.. Phenylpropiolic acids were purchased from Energy-Chemical Co., Ltd.. Other reagents were purchased from Energy-Chemical Co., Ltd. and Bidepharm Co., Ltd.. Solvents were purchased from Shanghai Titan Scientific Co., Ltd.. The preparation of spirotrienones, coumarins and their derivatives reactions were carried out under N_2 atmosphere.

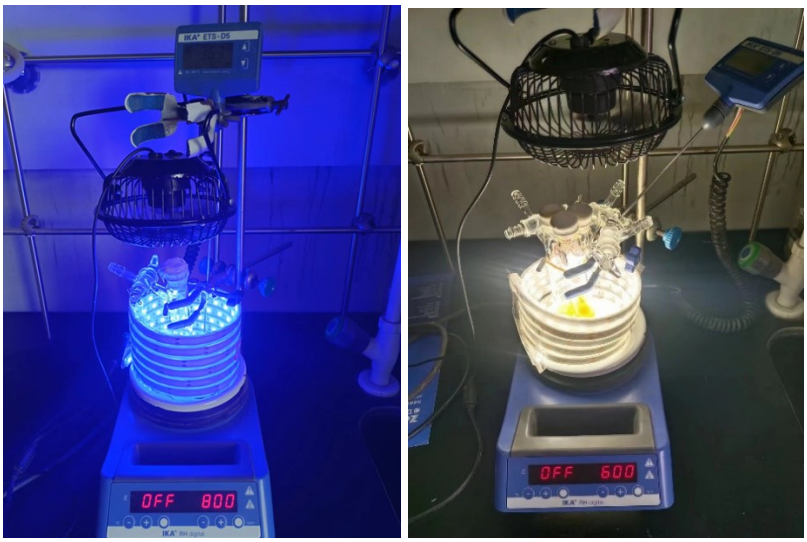


Figure S1. Photos of photochemical reaction devices

1. Preparation of Substrates

The starting materials were synthesized followed by the following procedures, and used directly after purification through silica gel column chromatography with petroleum ether/ethyl acetate as eluent.

1) Preparation of Substrates 5 and 9

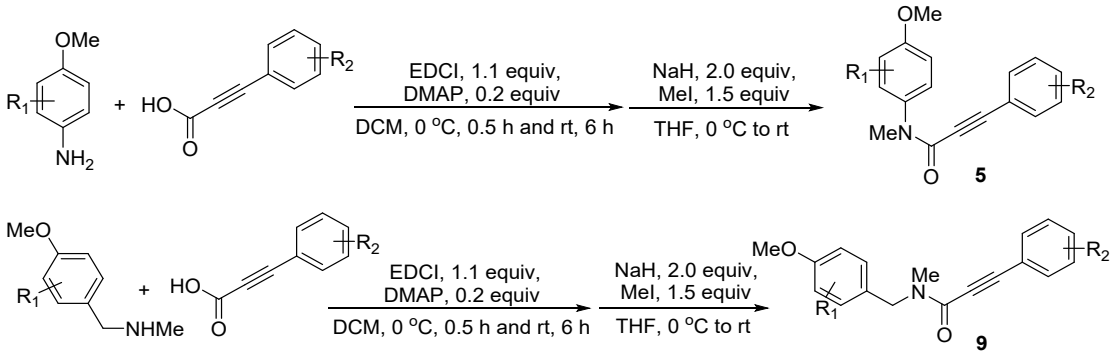


Figure S2 Preparation of Substrates **5** and **9**

To the mixture of aniline derivatives (or benzylamine) (5.0 mmol, 1.0 equiv), phenylpropiolic acid (5.0 mmol, 1.0 equiv) and 4-Dimethylaminopyridine (DMAP, 0.2 equiv) in dichloromethane (DCM, 40.0 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 5.5 mmol, 1.1 equiv) in portions at 0 °C, the resulting mixture was stirred at room temperature until the anilines totally consumed. The reaction mixture was then quenched with water (3.0 mL) and saturated $NaHCO_3$ (3.0 mL), and then extracted with dichloromethane (DCM, 10.0 mL×3), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford *N*-(4-methoxyphenyl)-3-phenylpropiolamide product.

The above mentioned *N*-(4-methoxyphenyl)-3-phenylpropiolamide (5.0 mmol, 1.0 equiv) was dissolved in anhydrous THF (20.0 mL), then NaH (10 mmol, 2.0 equiv) was added into the solvent in portions under N_2 atmosphere at 0 °C. After 30 min, CH_3I (7.5 mmol, 1.5 equiv) was added dropwise into the solution, the resulting mixture was stirred at room temperature until *N*-(4-methoxyphenyl)-3-phenylpropiolamide totally consumed. The reaction mixture was quenched with water (3.0 mL) and saturated

NH_4Cl (3.0 mL) and extracted with dichloromethane (DCM, 10.0 mL×3), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired *N*-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide product **5** or *N*-(4-methoxybenzyl)-N-methyl-3-phenylpropiolamide product **9**.

2) Preparation of Substrates 7 and 11

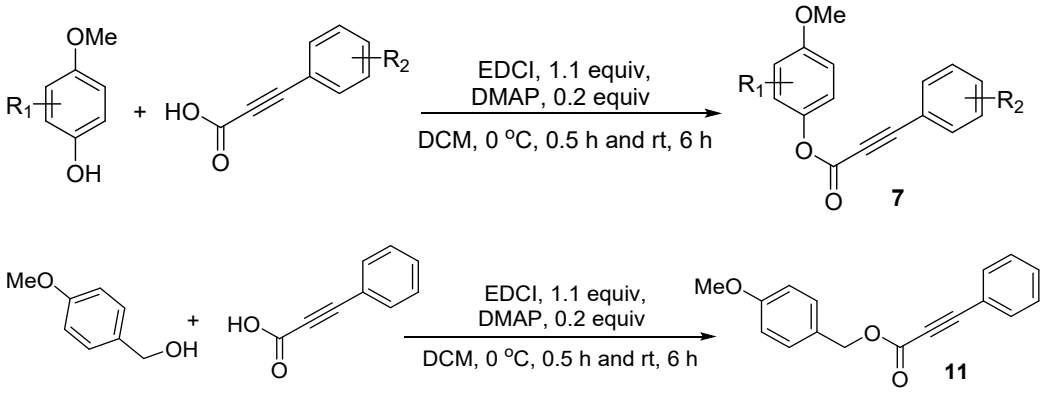
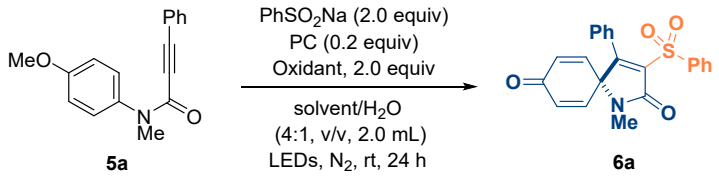


Figure S3 Preparation of Substrates **7** and **11**

To the mixture of phenol (or benzyl alcohol) (5.0 mmol, 1.0 equiv), phenylpropiolic acid (5.0 mmol, 1.0 equiv) and 4-Dimethylaminopyridine (DMAP, 0.2 equiv) in dichloromethane (DCM, 40.0 mL) was added 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDCI, 5.5 mmol, 1.1 equiv) in portions at 0 °C, the resulting mixture was stirred at room temperature until the aniline totally consumed. The reaction mixture was quenched with water (3.0 mL) and saturated $NaHCO_3$ (3.0 mL), and then extracted with dichloromethane (DCM, 10.0 mL×3), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford 4-methoxyphenyl 3-phenylpropiolate product **7** or 4-methoxybenzyl 3-phenylpropiolate product **11**.

Table S1. Screening of Reaction Conditions of Spiro[4.5]trienone **6**



Entry	Solvent/H_2O	(v/v)	PC	Oxidant	Yield[a](%)
1	CH_3OH	neat	PC-1	$K_2S_2O_8$	40
2	DMF	neat	PC-1	$K_2S_2O_8$	38
3	CH_3CN	neat	PC-1	$K_2S_2O_8$	31
4	CH_3CN/H_2O	4/1	PC-1	$K_2S_2O_8$	65
5	dioxane/H_2O	4/1	PC-1	$K_2S_2O_8$	50
6	CH_3OH/H_2O	4/1	PC-1	$K_2S_2O_8$	27
7	DMF/H_2O	4/1	PC-1	$K_2S_2O_8$	0
8	DMSO/H_2O	4/1	PC-1	$K_2S_2O_8$	0
9	CH_3CN/H_2O	4/1	PC-2	$K_2S_2O_8$	63
10	CH_3CN/H_2O	4/1	PC-3	$K_2S_2O_8$	66
11	CH_3CN/H_2O	4/1	PC-4	$K_2S_2O_8$	84
12	CH_3CN/H_2O	4/1	PC-5	$K_2S_2O_8$	65
13	CH_3CN/H_2O	4/1	PC-6	$K_2S_2O_8$	66
14	CH_3CN/H_2O	4/1	PC-7	$K_2S_2O_8$	59
15	CH_3CN/H_2O	4/1	PC-8	$K_2S_2O_8$	73
16	CH_3CN/H_2O	4/1	PC-9	$K_2S_2O_8$	69
17	CH_3CN/H_2O	4/1	PC-10	$K_2S_2O_8$	72
18	CH_3CN/H_2O	4/1	PC-4	$Na_2S_2O_8$	58
19	CH_3CN/H_2O	4/1	PC-4	$(NH_4)_2S_2O_8$	65
20	CH_3CN/H_2O	4/1	PC-4	$H_3K_5O_{18}S_4$	0
21[b]	CH_3CN/H_2O	4/1	PC-4	$K_2S_2O_8$	72
22[c]	CH_3CN/H_2O	4/1	PC-4	$K_2S_2O_8$	95
23[d]	CH_3CN/H_2O	4/1	PC-4	$K_2S_2O_8$	62
24[e]	CH_3CN/H_2O	4/1	none	$K_2S_2O_8$	85
25[f]	CH_3CN/H_2O	4/1	PC-4	none	0
26[g]	CH_3CN/H_2O	4/1	PC-4	$K_2S_2O_8$	90
27[h]	CH_3CN/H_2O	4/1	PC-4	$K_2S_2O_8$	0

[a] Isolated yield.[b] The reaction was run in green light.[c] The reaction was run in blue light.[d] The reaction was run in purple light.[e] The reaction was run in blue light.[f] The reaction was run in blue light.[g] The reaction was run in dark.[h] The reaction was run in air.

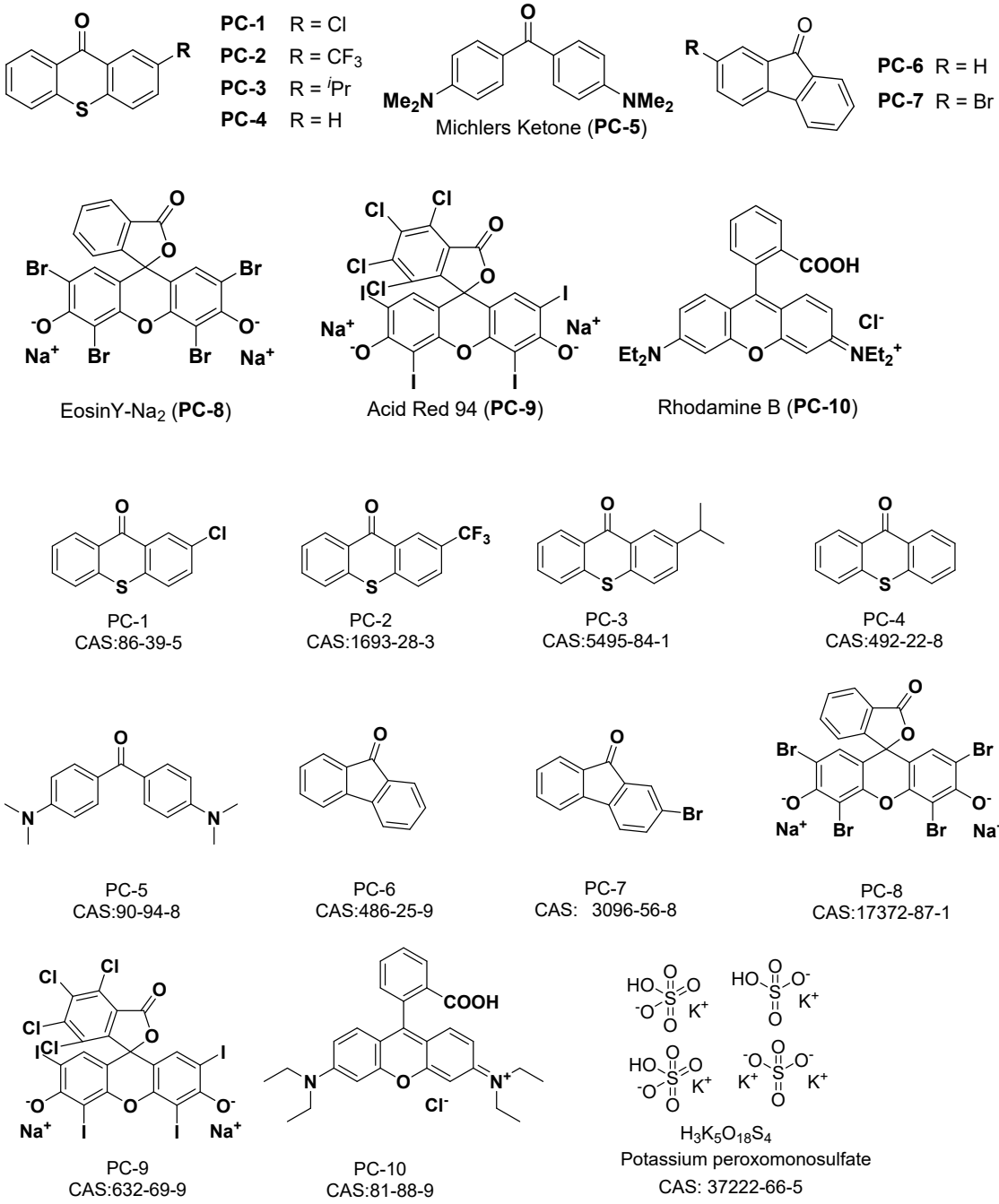
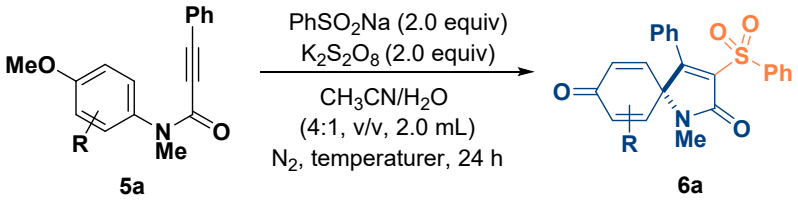


Figure S4 Structures of Photosensitizer (PCs)

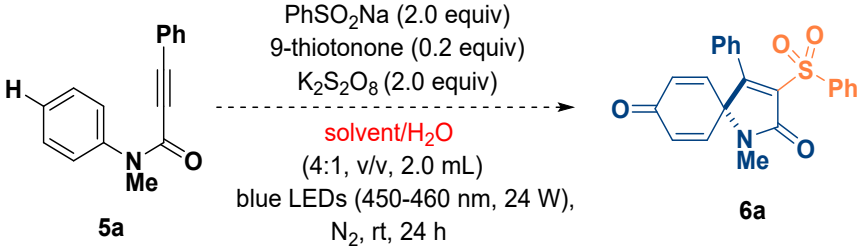
Table S2 Control experiment of reaction condition.



5a 6a

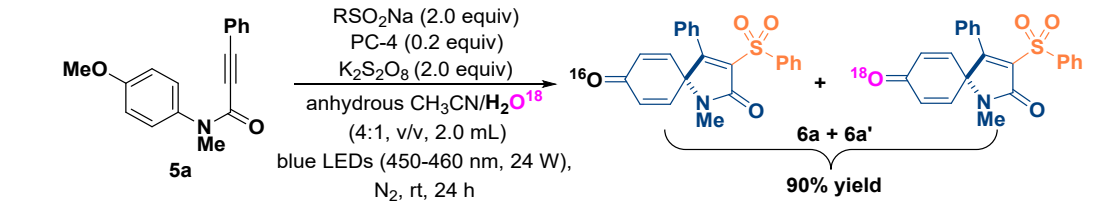
Entry	substrate	$K_2S_2O_8$, rt	$K_2S_2O_8$, 90 °C	$AgNO_3$, $K_2S_2O_8$, rt	$AgNO_3$, $K_2S_2O_8$, 90 °C
1	6b	28%	71%	--	--
2	6d	7%	16%	24%	64%
3	6f	6%	69%	--	--
4	6h	5%	38%	--	--
5	6i	16%	30%	--	--

Table S3 Control experiment of reaction condition.



5a 6a

entry	**solvent/H_2O**	**yield (%)**
1	CH_3CN/H_2O	0
2	CH_3OH/H_2O	0
3	dioxane/H_2O	0



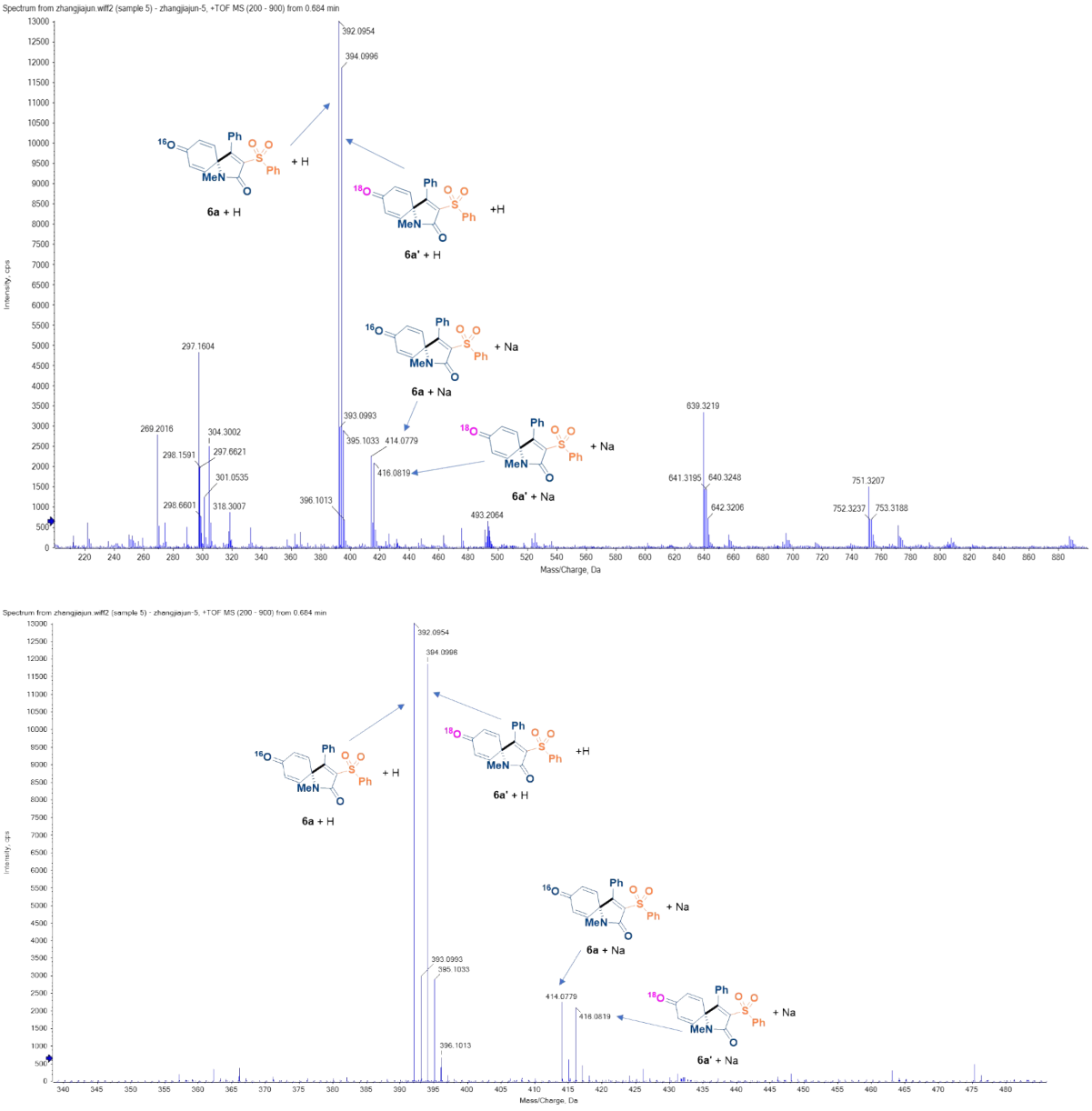
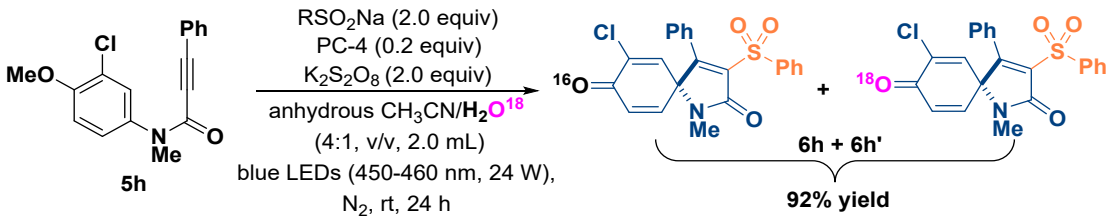


Figure S5 Isotope experiment (^{18}O) of preparation of Spiro[4.5]trienone **6a**

[Note: anhydrous CH_3CN (H_2O content≤50ppm)**]**



[Note: anhydrous CH_3CN (H_2O content≤50ppm)**]**

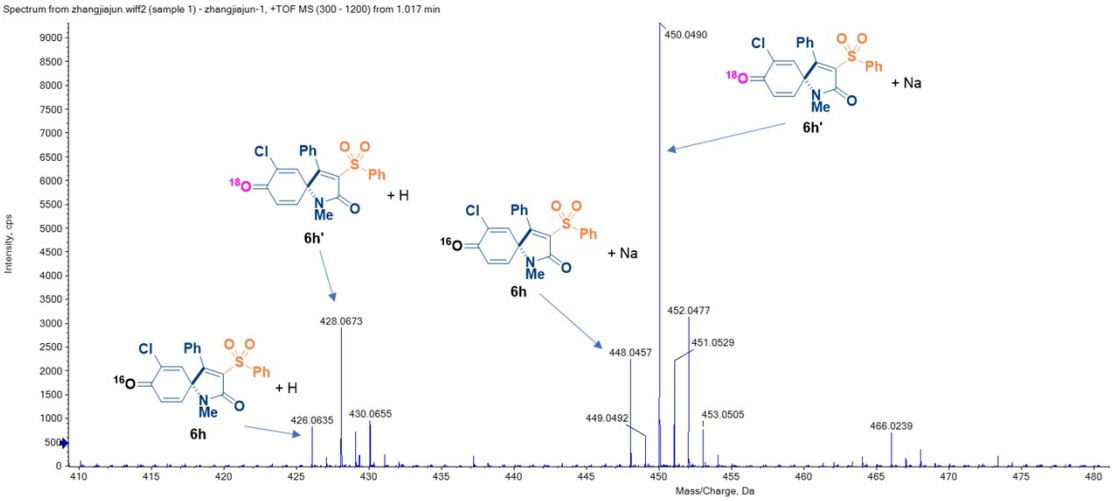


Figure S6 Isotope experiment (^{18}O) of preparation of Spiro[4.5]trienone **6h**

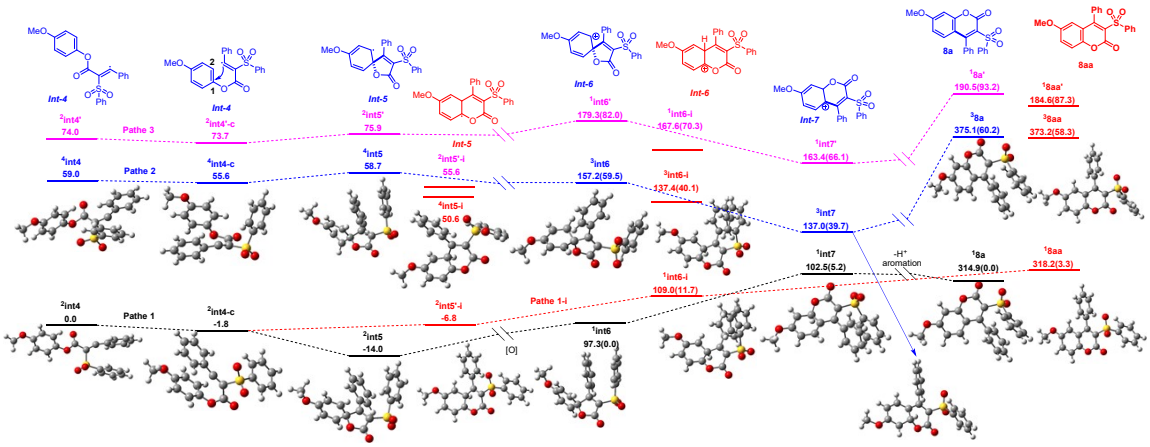


Figure S7 DFT (M06-2X/6-311G(d)) computational studies of the formation of coumarin **8a**.

We have modified the excitation energy on the pink line **^{1}Int6'**(82.0kcal/mol), **^{1}Int6-i**(70.3), **^{1}Int7'** (66.1), **^{1}8a'** (93.2), **^{1}8aa'** (87.3) to **^{1}Int6'**(82.0+97.3=179.3 kcal/mol), **^{1}Int6-i**(82.0+70.3=167.3), **^{1}Int7'** (66.1+97.3=163.4), **^{1}8a'** (93.2+97.3=190.5), **^{1}8aa'** (87.3+97.3=184.6)，respectively. For example, the excitation energy of ^{1}Int6' was 82.0 kcal/mol, which is relative to the energy of the ground state ^{1}Int6 at 0 kcal/mol.

Description of DFT calculation method

The geometries were full optimized using M06−2X[S1]/6−311G(d)[S2] due to the reduced cost of DFT. Harmonic frequency calculations were performed at the same level to characterize the nature of the stationary points. TDDFT[S3] calculation are performed with M06−2X/6−311G(d) based on the geometries optimized at M06−2X/6−311G(d) level. All calculations have been performed by the Gaussian 16 Program[S4].

Table S4 The M06−2X/6−311G(d) level predicted optimized geometries in terms of Cartesian coordinates for the reactants, products, and intermediates for reactions presented.

^{2}Int4

Final structure in terms of initial Cartesian coordinates:

C -5.994655 0.395375 0.038625

C -5.366660 -0.671857 -0.603080

C -3.982943 -0.813900 -0.508428

C -3.251158 0.098903 0.223146

C -3.862194 1.164454 0.873131

C -5.233762 1.310555 0.776208

O -1.872443 -0.111976 0.345747

C -1.038197 0.774346 -0.221440

O -1.368338 1.774942 -0.784033

C 0.386210 0.344797 -0.032091

C 1.391510 1.149693 -0.205893

S 0.666976 -1.398612 0.475001

O 0.375151 -1.529593 1.898604

O -0.025559 -2.258266 -0.479945

O -7.328871 0.627815 0.009525

C -8.141998 -0.285405 -0.711860

C 2.711019 1.577678 -0.243584

C 3.293904 2.191564 0.893694

C 4.618055 2.581480 0.857042

C 5.383161 2.381783 -0.294488

C 4.811229 1.794501 -1.424255

C 3.487112 1.398951 -1.415044

C 2.416843 -1.584425 0.228760

C 2.869864 -2.022354 -1.010333

C 4.240902 -2.101669 -1.222425

C 5.124782 -1.729840 -0.212703

C 4.650103 -1.289962 1.020617

C 3.281880 -1.217672 1.252702

H -5.930361 -1.394963 -1.175477

H -3.475785 -1.635767 -0.998702

H -3.268257 1.864908 1.446544

H -5.743880 2.128415 1.269615

H -9.162164 0.073951 -0.605699

H -7.869102 -0.302490 -1.770568

H -8.063316 -1.293242 -0.295233

H 2.695385 2.334163 1.784835

H 5.063964 3.040796 1.730530

H 6.422253 2.686385 -0.311926

H 5.406854 1.640897 -2.315768

H 3.037964 0.934901 -2.284221

H 2.162290 -2.298654 -1.782328

H 4.617601 -2.447864 -2.176737

H 6.192452 -1.782299 -0.388195

H 5.342952 -1.000823 1.800821

H 2.889986 -0.875880 2.203512

^{4}Int4

Final structure in terms of initial Cartesian coordinates:

C 4.244201 -1.942106 0.076021

C 4.389467 -0.549011 -0.174593

C 3.312266 0.157948 -0.615656

C 2.054909 -0.484837 -0.816213

C 1.911025 -1.881955 -0.565361

C 2.986447 -2.587570 -0.129466

O 1.077873 0.281297 -1.214833

C -0.230294 -0.327200 -1.548229

O -0.269438 -0.948754 -2.581098

C -1.211621 -0.002693 -0.603971

C -2.577153 -0.221374 -0.853829

S -0.759034 0.814695 0.899555

O -1.979336 0.938156 1.698737

O 0.399877 0.152239 1.511293

O 5.207237 -2.717098 0.498120

C 6.518083 -2.177937 0.748735

C -3.594672 -1.060114 -0.352423

C -3.320982 -2.026666 0.647881

C -4.328242 -2.840664 1.136934

C -5.631535 -2.727232 0.648439

C -5.918092 -1.785164 -0.341162

C -4.920661 -0.961658 -0.835396

C -0.242145 2.470776 0.469623

C 1.078959 2.848310 0.664151

C 1.460359 4.144502 0.329871

C 0.524910 5.032564 -0.191906

C -0.798032 4.635888 -0.380379

C -1.191950 3.346297 -0.047025

H 5.338927 -0.055519 -0.023299

H 3.377594 1.217483 -0.828472

H 0.953962 -2.361932 -0.719523

H 2.925713 -3.647464 0.080465

H 7.112198 -3.021165 1.083253

H 6.928979 -1.765304 -0.172341

H 6.460661 -1.418863 1.528532

H -2.307215 -2.117816 1.022532

H -4.101923 -3.572600 1.903945

H -6.414912 -3.367650 1.034815

H -6.927596 -1.694204 -0.724911

H -5.141108 -0.226019 -1.600740

H 1.784517 2.138321 1.078666

H 2.486422 4.458093 0.477254

H 0.825903 6.039630 -0.453981

H -1.522069 5.332018 -0.785377

H -2.216706 3.020527 -0.187744

^{2}Int4-c

Final structure in terms of initial Cartesian coordinates:

C 3.664577 -0.993606 0.788961

C 3.376078 -1.592800 -0.439566

C 2.125306 -2.163912 -0.649505

C 1.179940 -2.124786 0.360351

C 1.476194 -1.593587 1.611640

C 2.717332 -1.023381 1.820298

O -0.083260 -2.672205 0.138456

C -1.109975 -1.929895 -0.323155

O -2.191581 -2.429822 -0.433347

C -0.860855 -0.492385 -0.674107

C 0.211169 0.215553 -0.517343

S -2.325568 0.371715 -1.380322

O -1.872052 1.729583 -1.661666

O -2.889017 -0.423293 -2.464875

O 4.827967 -0.368346 1.076697

C 5.806815 -0.292325 0.050448

C 1.223532 1.141627 -0.390351

C 2.177124 1.330621 -1.423732

C 3.227944 2.207166 -1.231353

C 3.362517 2.903727 -0.028149

C 2.420342 2.732434 0.989558

C 1.358763 1.865707 0.823465

C -3.484405 0.446828 -0.033286

C -4.520003 -0.476467 0.036165

C -5.414558 -0.384938 1.096464

C -5.256119 0.606370 2.061500

C -4.206165 1.517706 1.976753

C -3.307083 1.444333 0.920627

H 4.100324 -1.603733 -1.242111

H 1.872925 -2.610298 -1.603777

H 2.973578 -0.571942 2.770637

H 6.639763 0.264285 0.472103

H 6.144399 -1.289666 -0.243795

H 5.413764 0.237930 -0.821133

H 2.075653 0.775069 -2.347559

H 3.955089 2.348719 -2.021956

H 4.194336 3.582115 0.113966

H 2.521759 3.278185 1.919557

H 0.630006 1.716596 1.610828

H -4.613245 -1.243163 -0.721617

H -6.234144 -1.088643 1.169065

H -5.956189 0.669953 2.885618

H -4.089684 2.287887 2.728745

H -2.491623 2.151712 0.827929

H 0.725108 -1.603728 2.392440

^{4}Int4-c

Final structure in terms of initial Cartesian coordinates:

C 2.801455 -2.022662 -0.222887

C 3.314342 -1.053202 -1.129241

C 2.444529 -0.211880 -1.755294

C 1.045974 -0.285150 -1.487181

C 0.527323 -1.302885 -0.630636

C 1.393510 -2.150267 -0.015765

O 0.304730 0.639572 -2.040623

C -1.078644 0.861542 -1.573417

O -1.939889 0.652779 -2.392343

C -1.108233 1.323023 -0.241934

C -0.054096 1.328197 0.679539

S -2.729284 1.393480 0.460172

O -2.585670 1.843819 1.845833

O -3.660315 2.111826 -0.407273

O 3.543317 -2.851634 0.463248

C 4.976868 -2.794754 0.358076

C 1.305505 1.678736 0.756012

C 1.899372 2.557289 -0.188449

C 3.263406 2.797499 -0.167504

C 4.077046 2.188990 0.788782

C 3.504874 1.344348 1.745122

C 2.144464 1.091552 1.736336

C -3.214837 -0.322360 0.491464

C -4.001264 -0.831884 -0.534236

C -4.290464 -2.193538 -0.537790

C -3.787216 -3.017630 0.463803

C -2.996016 -2.489767 1.483213

C -2.702916 -1.132016 1.503089

H 4.376252 -0.969757 -1.311754

H 2.788319 0.558239 -2.433285

H 1.050388 -2.928796 0.653309

H 5.343070 -3.552360 1.042180

H 5.281847 -3.025041 -0.662468

H 5.328187 -1.807764 0.659639

H 1.269246 3.024103 -0.937154

H 3.698986 3.463653 -0.903546

H 5.143862 2.375060 0.795193

H 4.131391 0.876212 2.495687

H 1.704065 0.418171 2.463496

H -4.369112 -0.170499 -1.307591

H -4.907194 -2.609187 -1.324961

H -4.013368 -4.077013 0.453370

H -2.611528 -3.135219 2.263117

H -2.091327 -0.700819 2.287438

H -0.541819 -1.384633 -0.472748

^{2}Int5

Final structure in terms of initial Cartesian coordinates:

C -3.883661 -1.070804 0.582779

C -2.570403 -1.226267 0.911982

C -1.467545 -1.110887 -0.091809

C -1.954735 -0.845719 -1.481591

C -3.264693 -0.687917 -1.761140

C -4.263418 -0.777584 -0.745418

O -0.714631 -2.369241 -0.084701

C 0.550906 -2.180049 0.328030

C 0.718725 -0.731329 0.615356

C -0.414492 -0.078499 0.333647

O 1.354645 -3.064559 0.402062

S 2.210260 -0.108949 1.351948

O 1.970553 1.263443 1.774026

O 2.622004 -1.098384 2.338422

O -5.524252 -0.584772 -1.158205

C -6.568666 -0.643771 -0.191351

C 3.393302 -0.095803 0.025783

C 3.953815 -1.303167 -0.381071

C 4.873225 -1.283101 -1.422396

C 5.218368 -0.077079 -2.028025

C 4.651416 1.119982 -1.599817

C 3.724874 1.119208 -0.563432

C -0.699973 1.361651 0.273044

C -1.802071 1.924752 0.921097

C -2.054206 3.286279 0.796032

C -1.229097 4.083867 0.009436

C -0.141407 3.520819 -0.653061

C 0.126757 2.166198 -0.517954

H -4.631553 -1.181427 1.357318

H -2.273118 -1.457390 1.928285

H -1.199065 -0.776158 -2.255759

H -3.596416 -0.490595 -2.773840

H -7.486253 -0.432458 -0.732757

H -6.625380 -1.638576 0.255881

H -6.416883 0.108478 0.585964

H 3.667732 -2.228691 0.103481

H 5.322715 -2.208861 -1.758892

H 5.936870 -0.070113 -2.838601

H 4.931080 2.054495 -2.069421

H 3.278921 2.038854 -0.203885

H -2.444196 1.308979 1.537579

H -2.899717 3.723550 1.312618

H -1.435069 5.142631 -0.090891

H 0.497406 4.136223 -1.274735

H 0.960090 1.717665 -1.047072

^{4}Int5

Final structure in terms of initial Cartesian coordinates:

C -3.227139 -0.542850 1.290139

C -2.041716 -1.309739 1.315523

C -1.340167 -1.731065 0.057479

C -2.312435 -1.718445 -1.101308

C -3.146015 -0.525231 -1.162277

C -3.793210 -0.141216 0.102912

O -0.772558 -3.037999 0.236816

C 0.576910 -3.016047 0.106513

C 0.965455 -1.607456 -0.155557

C -0.134743 -0.849614 -0.241042

O 1.245289 -4.002409 0.182726

S 2.650274 -1.071753 -0.317696

O 3.462302 -1.960015 0.503882

O 2.967144 -0.927455 -1.734247

O -4.877485 0.625352 -0.046759

C -5.524304 1.091448 1.134494

C 2.640955 0.542893 0.430210

C 2.817394 1.663324 -0.370114

C 2.782005 2.916853 0.230765

C 2.565151 3.026693 1.600897

C 2.395504 1.888666 2.387077

C 2.436803 0.629482 1.803307

C -0.273560 0.559994 -0.636917

C -0.702117 1.534828 0.266679

C -0.837886 2.850312 -0.157859

C -0.568203 3.191906 -1.480873

C -0.147679 2.218596 -2.381923

C 0.009999 0.903259 -1.961961

H -3.670915 -0.262960 2.236640

H -1.577756 -1.599264 2.249597

H -2.694470 -2.692477 -1.392794

H -3.035848 0.227696 -1.937052

H -6.365967 1.690665 0.799952

H -5.879734 0.249161 1.732401

H -4.838846 1.703851 1.725184

H 2.967462 1.550873 -1.436601

H 2.912307 3.805408 -0.374225

H 2.527274 4.006567 2.061297

H 2.232567 1.982107 3.453349

H 2.308620 -0.266894 2.399332

H -0.907120 1.265047 1.295646

H -1.155180 3.610320 0.545822

H -0.682657 4.218090 -1.808566

H 0.065389 2.482389 -3.410720

H 0.346940 0.138115 -2.652450

^{2}Int5'-i

Final structure in terms of initial Cartesian coordinates:

C -3.722087 -0.790439 -0.048252

C -4.153987 0.308699 -0.833241

C -3.454596 1.534710 -0.750501

C -2.394410 1.665990 0.077112

C -1.880039 0.584516 0.961359

C -2.646845 -0.687634 0.789938

O -1.740384 2.876924 0.157785

C -0.397777 2.898481 0.344361

O 0.154790 3.944225 0.516327

C 0.283349 1.575131 0.356096

C -0.361546 0.462507 0.739454

S 2.035988 1.653584 -0.066887

O 2.164001 2.705601 -1.068701

O 2.833388 1.732052 1.151765

O -4.342863 -2.000449 -0.077400

C -5.469528 -2.156606 -0.927556

C 0.315362 -0.808577 1.079846

C 0.132841 -1.964292 0.315346

C 0.801083 -3.129398 0.664218

C 1.621264 -3.158381 1.791100

C 1.784197 -2.015321 2.564201

C 1.142200 -0.834755 2.204528

C 2.379316 0.114207 -0.892852

C 3.284704 -0.774404 -0.331775

C 3.567407 -1.949617 -1.020286

C 2.943783 -2.214322 -2.235325

C 2.040319 -1.304694 -2.782636

C 1.756712 -0.121733 -2.114159

H -4.996991 0.229088 -1.502149

H -3.754897 2.381294 -1.355519

H -2.371339 -1.542015 1.393872

H -5.802284 -3.182638 -0.792835

H -6.275967 -1.474491 -0.645374

H -5.200859 -1.997455 -1.975286

H -0.502649 -1.937413 -0.562405

H 0.682346 -4.018023 0.056213

H 2.134248 -4.073244 2.062250

H 2.418941 -2.034438 3.441772

H 1.281389 0.067718 2.787847

H 3.744000 -0.552167 0.623276

H 4.267407 -2.661215 -0.600094

H 3.162146 -3.135619 -2.761557

H 1.561295 -1.514027 -3.730762

H 1.061805 0.599825 -2.528147

H -1.966191 0.916240 2.015033

^{1}Int6

Final structure in terms of initial Cartesian coordinates:

C -3.133236 -0.372106 1.375797

C -2.065344 -1.181571 1.435143

C -1.442442 -1.736598 0.201130

C -2.323375 -1.729182 -1.003850

C -3.391228 -0.926283 -1.066400

C -3.765457 -0.156011 0.096887

O -0.891731 -3.014878 0.432772

C 0.465176 -3.018795 0.238150

C 0.853232 -1.621798 -0.108807

C -0.216995 -0.833084 -0.149473

O 1.115198 -4.004095 0.340429

S 2.547055 -1.143580 -0.449364

O 3.388318 -2.064789 0.295922

O 2.682936 -1.035458 -1.893390

O -4.714973 0.675148 -0.085048

C -5.209788 1.526587 0.983723

C 2.681250 0.472022 0.268657

C 2.754043 1.578868 -0.567634

C 2.843040 2.837839 0.014517

C 2.854619 2.966028 1.400461

C 2.786167 1.841247 2.220130

C 2.702230 0.575195 1.655735

C -0.351089 0.585069 -0.517006

C -0.549804 1.565347 0.459213

C -0.641788 2.898926 0.080336

C -0.554452 3.251742 -1.263020

C -0.361109 2.273263 -2.233671

C -0.251785 0.938403 -1.865474

H -3.534349 0.087598 2.267845

H -1.561618 -1.395450 2.371794

H -2.002085 -2.329524 -1.847825

H -4.007021 -0.830491 -1.950537

H -5.953987 2.154815 0.509067

H -5.661878 0.904209 1.753126

H -4.386754 2.123558 1.372228

H 2.731562 1.452977 -1.642728

H 2.893571 3.716847 -0.615759

H 2.918736 3.950906 1.846944

H 2.802676 1.949474 3.297077

H 2.657703 -0.311365 2.277633

H -0.594875 1.292594 1.507247

H -0.775970 3.661496 0.837518

H -0.631046 4.292347 -1.553760

H -0.288706 2.547889 -3.278605

H -0.088029 0.171337 -2.614176

^{3}Int6

Final structure in terms of initial Cartesian coordinates:

C -4.076698 -0.451875 0.652168

C -2.785016 -0.183297 0.969568

C -1.658157 -0.389772 -0.015921

C -2.181183 -0.068940 -1.371679

C -3.491856 -0.580582 -1.714236

C -4.445035 -0.777894 -0.690103

O -1.284577 -1.780992 0.061926

C 0.012128 -1.898620 0.462092

C 0.547169 -0.524025 0.644454

C -0.386164 0.379154 0.318643

O 0.547193 -2.953848 0.592353

S 2.157847 -0.260387 1.361215

O 2.273229 1.151179 1.688542

O 2.281127 -1.260396 2.410058

O -5.601658 -1.247199 -1.067905

C -6.601345 -1.561056 -0.078759

C 3.300106 -0.643451 0.059172

C 3.530763 -1.980497 -0.253034

C 4.427010 -2.271170 -1.273469

C 5.074962 -1.240018 -1.950128

C 4.838540 0.089783 -1.613020

C 3.940525 0.401268 -0.599061

C -0.309920 1.833137 0.138637

C -1.296232 2.689451 0.638899

C -1.210355 4.055295 0.402058

C -0.164111 4.569171 -0.357377

C 0.804908 3.716773 -0.879917

C 0.737372 2.354574 -0.628692

H -4.831066 -0.416224 1.427698

H -2.525419 0.113583 1.979674

H -1.670857 0.618438 -2.034747

H -3.750026 -0.826750 -2.738511

H -7.413401 -2.019737 -0.631240

H -6.187966 -2.258188 0.649959

H -6.937221 -0.641886 0.401400

H 3.019843 -2.766197 0.289693

H 4.624255 -3.302846 -1.535825

H 5.774297 -1.475307 -2.743048

H 5.355065 0.885329 -2.134901

H 3.753387 1.427352 -0.306241

H -2.115120 2.308382 1.236144

H -1.965190 4.716961 0.807569

H -0.107862 5.633722 -0.548715

H 1.611194 4.111891 -1.484958

H 1.473559 1.683255 -1.054951

^{1}Int6-i

Final structure in terms of initial Cartesian coordinates:

C -3.864466 -0.808098 -0.083063

C -4.368704 0.398489 -0.661895

C -3.676717 1.591450 -0.645082

C -2.429279 1.633022 -0.048771

C -1.881891 0.467645 0.660789

C -2.642454 -0.788860 0.514886

O -1.755867 2.761708 -0.072535

C -0.399301 2.835278 0.301431

O 0.039861 3.908022 0.523004

C 0.301837 1.538617 0.362910

C -0.359930 0.398935 0.607778

S 2.104219 1.660467 0.150081

O 2.306923 2.801871 -0.728315

O 2.729910 1.635625 1.462456

O -4.533330 -1.968787 -0.103617

C -5.774945 -2.038916 -0.806533

C 0.291305 -0.889409 0.926351

C 0.198842 -1.974395 0.049212

C 0.841738 -3.161527 0.365736

C 1.541204 -3.280728 1.566281

C 1.609278 -2.208615 2.447346

C 0.994774 -1.002793 2.125790

C 2.551017 0.197701 -0.751230

C 3.382482 -0.738593 -0.152588

C 3.747088 -1.859496 -0.890240

C 3.274034 -2.025232 -2.188276

C 2.444114 -1.068656 -2.770255

C 2.081667 0.063697 -2.054129

H -5.338007 0.389385 -1.145944

H -4.073075 2.481329 -1.114170

H -2.255191 -1.685850 0.980925

H -6.100507 -3.070328 -0.713357

H -6.517366 -1.379694 -0.352276

H -5.637577 -1.792282 -1.861499

H -0.343989 -1.876935 -0.885337

H 0.796742 -3.995531 -0.323485

H 2.033286 -4.213899 1.811829

H 2.147318 -2.302551 3.382338

H 1.056300 -0.155103 2.797563

H 3.722622 -0.594453 0.865107

H 4.391872 -2.606519 -0.444545

H 3.553392 -2.906346 -2.753107

H 2.084352 -1.200903 -3.782617

H 1.445638 0.821842 -2.495862

H -2.103441 0.735758 1.726512

^{3}Int6-i

Final structure in terms of initial Cartesian coordinates:

C -3.810972 -0.703075 -0.080803

C -4.247613 0.404563 -0.845773

C -3.496033 1.570225 -0.792234

C -2.361497 1.677914 -0.007647

C -1.855122 0.615128 0.911901

C -2.643864 -0.640153 0.758631

O -1.686935 2.832143 -0.035672

C -0.344602 2.883703 0.326630

O 0.139680 3.946589 0.522851

C 0.336975 1.568979 0.399823

C -0.338707 0.460002 0.726492

S 2.121964 1.630178 0.087147

O 2.324927 2.749537 -0.820832

O 2.820156 1.600252 1.363829

O -4.393369 -1.855798 -0.060052

C -5.578370 -2.106918 -0.851856

C 0.274854 -0.854009 1.013910

C 0.075638 -1.933091 0.146991

C 0.666332 -3.155888 0.431517

C 1.424870 -3.314033 1.589741

C 1.603228 -2.245402 2.460494

C 1.036700 -1.007972 2.172193

C 2.471026 0.137278 -0.811131

C 3.295791 -0.819380 -0.236136

C 3.580956 -1.967280 -0.966946

C 3.038763 -2.138523 -2.237016

C 2.217375 -1.161559 -2.796674

C 1.932768 -0.003385 -2.086365

H -5.123422 0.346619 -1.473020

H -3.775189 2.431854 -1.386301

H -2.403689 -1.510748 1.352464

H -5.837896 -3.138223 -0.643518

H -6.370847 -1.433138 -0.530279

H -5.338438 -1.970350 -1.905385

H -0.502364 -1.804276 -0.762333

H 0.536267 -3.984880 -0.252954

H 1.879080 -4.272594 1.809492

H 2.190042 -2.367890 3.362435

H 1.183941 -0.165680 2.837380

H 3.691779 -0.669526 0.760428

H 4.218839 -2.729735 -0.537815

H 3.258380 -3.039438 -2.796903

H 1.803542 -1.298337 -3.787736

H 1.303299 0.769941 -2.510838

H -1.971391 0.969013 1.955084

^{1}10a

Final structure in terms of initial Cartesian coordinates:

C -3.764035 -1.481854 0.020728

C -2.415320 -1.340648 -0.232115

C -1.788012 -0.085187 -0.188772

C -2.594580 1.030764 0.082849

C -3.944280 0.918117 0.347595

C -4.535463 -0.345236 0.323708

C -0.371728 0.121427 -0.389118

C 0.118984 1.392311 -0.325157

C -0.774481 2.554437 -0.263420

O -2.077500 2.288644 0.063478

O -0.480609 3.694613 -0.480692

S 1.874696 1.791006 -0.373997

O 2.348201 1.736505 -1.753929

O 2.059680 3.023257 0.383215

O -5.849337 -0.378067 0.587849

C -6.516064 -1.637039 0.552594

C 0.481832 -1.058214 -0.682402

C 0.689397 -2.045778 0.284192

C 1.497947 -3.134957 -0.008002

C 2.071411 -3.260824 -1.272150

C 1.839895 -2.293138 -2.242441

C 1.052700 -1.183943 -1.948150

C 2.685549 0.509827 0.564523

C 2.421130 0.424160 1.927651

C 3.092274 -0.536669 2.671968

C 4.019656 -1.374014 2.054389

C 4.283429 -1.256540 0.693645

C 3.611331 -0.306313 -0.067793

H -4.210471 -2.464504 -0.021288

H -1.828595 -2.218004 -0.471881

H -4.538768 1.797358 0.556503

H -7.555513 -1.425396 0.786244

H -6.445815 -2.084581 -0.441253

H -6.101518 -2.317027 1.299938

H 0.239746 -1.941865 1.265631

H 1.679485 -3.887089 0.750201

H 2.696973 -4.115761 -1.499298

H 2.278468 -2.393798 -3.227858

H 0.883544 -0.415786 -2.693032

H 1.703431 1.089753 2.393479

H 2.896700 -0.628197 3.732963

H 4.540897 -2.121802 2.639660

H 5.005437 -1.909912 0.219643

H 3.787949 -0.203223 -1.131000

^{3}10a

Final structure in terms of initial Cartesian coordinates:

C -3.484063 -1.615586 -0.051827

C -2.151604 -1.460126 -0.351029

C -1.531780 -0.178526 -0.453457

C -2.421456 0.940322 -0.325736

C -3.745133 0.801544 -0.015178

C -4.293737 -0.482513 0.152571

C -0.180190 0.060601 -0.755377

C 0.225290 1.460718 -0.515575

C -0.711736 2.567397 -0.689957

O -2.024395 2.228688 -0.630995

O -0.407262 3.714228 -0.863607

S 1.703180 1.895257 0.406572

O 2.740411 2.254752 -0.554772

O 1.322763 2.868861 1.425127

O -5.590212 -0.521772 0.469207

C -6.213055 -1.794476 0.636992

C 0.830450 -0.885167 -1.224151

C 0.979609 -2.177752 -0.696564

C 1.996372 -3.010475 -1.145019

C 2.888569 -2.575271 -2.120370

C 2.763558 -1.287777 -2.639187

C 1.753013 -0.449915 -2.192291

C 2.155225 0.381899 1.216504

C 1.301988 -0.103566 2.202185

C 1.627996 -1.300442 2.824903

C 2.793204 -1.976085 2.465859

C 3.638101 -1.464964 1.485052

C 3.318740 -0.274924 0.840714

H -3.896397 -2.612329 0.016426

H -1.559209 -2.344297 -0.531376

H -4.381471 1.673594 0.058805

H -7.245656 -1.583205 0.898486

H -6.176401 -2.366037 -0.292469

H -5.732874 -2.352924 1.442907

H 0.351958 -2.505716 0.122005

H 2.106988 -3.996748 -0.709456

H 3.683332 -3.226657 -2.462804

H 3.457305 -0.934514 -3.392904

H 1.666752 0.553390 -2.596209

H 0.404303 0.440973 2.473069

H 0.977057 -1.702876 3.590638

H 3.042724 -2.909249 2.956125

H 4.539924 -1.998000 1.211188

H 3.944193 0.132919 0.056353

[1]8a

Final structure in terms of initial Cartesian coordinates:

C 4.099613 -0.881071 0.423514

C 3.973134 -2.267554 0.255144

C 2.751303 -2.816734 -0.101340

C 1.656917 -1.989271 -0.289258

C 1.758287 -0.604963 -0.125894

C 2.995841 -0.060305 0.231555

O 0.477700 -2.582437 -0.640017

C -0.661796 -1.880738 -0.857619

O -1.657321 -2.488565 -1.142783

C -0.575553 -0.418657 -0.709653

C 0.571134 0.210547 -0.349220

S -2.126898 0.427460 -1.055252

O -1.940980 1.852009 -0.819992

O -2.593030 -0.009766 -2.364227

O 5.250442 -0.259033 0.768825

C 6.409012 -1.060895 0.953208

C 0.723532 1.681483 -0.170965

C 1.072014 2.476686 -1.259439

C 1.268855 3.840637 -1.079709

C 1.124814 4.407360 0.183633

C 0.793379 3.605675 1.271756

C 0.600397 2.239243 1.099323

C -3.232923 -0.181851 0.199646

C -4.135072 -1.192173 -0.108859

C -5.008058 -1.622877 0.883374

C -4.960597 -1.051794 2.152226

C -4.048497 -0.039597 2.441312

C -3.175597 0.408773 1.458061

H 4.818296 -2.926096 0.399233

H 2.635605 -3.884268 -0.236837

H 3.111556 1.007938 0.362173

H 7.208552 -0.372485 1.213127

H 6.265616 -1.777248 1.766302

H 6.668846 -1.591780 0.033526

H 1.178304 2.030059 -2.241650

H 1.533956 4.460574 -1.927575

H 1.276544 5.471103 0.321297

H 0.687023 4.042093 2.257568

H 0.348171 1.608295 1.944567

H -4.139945 -1.627721 -1.098894

H -5.723314 -2.406251 0.666333

H -5.641417 -1.396435 2.921147

H -4.020460 0.404645 3.428183

H -2.472275 1.209014 1.656306

^{3}8a

Final structure in terms of initial Cartesian coordinates:

C 3.988207 -1.196361 0.321783

C 3.751766 -2.559811 -0.012699

C 2.505717 -2.881748 -0.484437

C 1.495903 -1.906587 -0.608268

C 1.683887 -0.529202 -0.206290

C 2.969466 -0.205346 0.207587

O 0.359483 -2.315142 -1.157660

C -0.789680 -1.466742 -1.269980

O -1.761426 -2.026997 -1.707249

C -0.628356 -0.129391 -0.829225

C 0.603860 0.382769 -0.331178

S -2.159932 0.740617 -0.728355

O -1.938604 2.005913 -0.030439

O -2.809588 0.785930 -2.038196

O 5.135337 -0.741570 0.746663

C 6.260781 -1.625280 0.906151

C 0.849041 1.822466 -0.084771

C 0.725882 2.740581 -1.131743

C 0.983981 4.088282 -0.920702

C 1.367266 4.538347 0.341049

C 1.495053 3.631216 1.387945

C 1.240961 2.279855 1.175641

C -3.179595 -0.256721 0.349421

C -4.183268 -1.053998 -0.183399

C -4.979979 -1.792136 0.686388

C -4.759244 -1.730402 2.058938

C -3.743994 -0.927627 2.575879

C -2.946075 -0.180467 1.719229

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H 3.243269 0.808880 0.464576

H 7.068094 -0.993714 1.259999

H 6.024942 -2.392068 1.643345

H 6.517619 -2.070578 -0.054588

H 0.420926 2.388502 -2.111546

H 0.886185 4.790298 -1.740311

H 1.565518 5.590605 0.506404

H 1.789281 3.974495 2.372632

H 1.328445 1.574381 1.995362

H -4.328147 -1.089401 -1.254936

H -5.770884 -2.417057 0.290524

H -5.381636 -2.309820 2.730210

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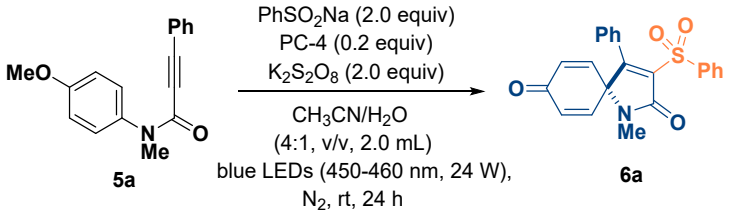
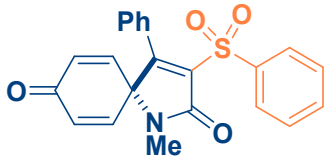
H -2.161208 0.461022 2.103117

General Procedure for Preparation of Spiro[4.5]trienone 6

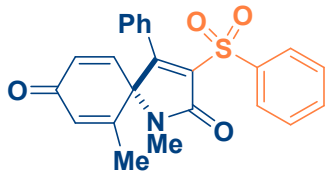


N-(4-methoxyphenyl)-N-methyl-3-phenylpropiolamide **5** (0.1 mmol, 1.0 equiv), $PhSO_2Na$ (0.2 mmol, 2.0 equiv), 9-thioxanthone (PC-4) (0.02 mmol, 0.2 equiv) and $K_2S_2O_8$ (0.2 mmol, 2.0 equiv) in CH_3CN/H_2O (4:1, v/v, 2.0 mL) and then irradiation under blue light in a nitrogen atmosphere for corresponding hours until the starting materials **5** totally consumed or left maintain without change (A fan is used to cool down the reaction temperature). The reaction mixture was filtrated and the filtrate was extracted with dichloromethane (DCM, 5.0 mL×3), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired 1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **6**.



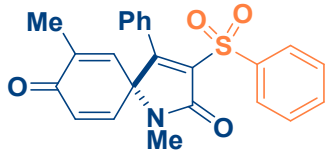
6a, 96 %

1-Methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione(**6a**): 26.8 mg, 96% yield. Yellow solid; mp 216.6-217.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.65 (tt, *J* = 6.9 and 1.1 Hz, 1H), 7.54 (d, *J* = 15.5 Hz, 2H), 7.46-7.41 (m, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.44 (s, 4H), 2.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 163.4, 162.0, 142.1, 139.1, 136.6, 134.3, 130.3, 129.1, 129.0, 128.4, 127.9, 127.7, 68.2, 26.3. The NMR spectra data are consistent with previously reported [S5].



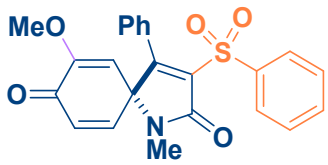
6b, 93%

1,6-Dimethyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6b)** : 37.8 mg, 93% yield. Yellow solid, 203.2-204.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.39 (d, *J* = 4.0 Hz, 2H), 6.28 (s, 1H), 2.71 (s, 3H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 163.7, 162.2, 150.5, 142.2, 139.1, 136.9, 134.2, 133.7, 132.8, 130.5, 128.9, 128.8, 127.9, 127.6, 70.4, 25.9, 17.5. The NMR spectra data are consistent with previously reported [S5].



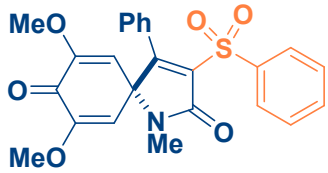
6c, 66%

1,7-Dimethyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6c**) **:** 26.9 mg, 66% yield. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 -7.91 (m, 2H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.41-7.35 (m, 3H), 7.10 (d, *J* = 7.0 Hz, 2H), 6.40 (s, 2H), 6.20 (s, 1H), 2.81 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 163.4, 162.6, 142.0, 141.9, 139.2, 136.8, 136.2, 134.2, 134.0, 130.1, 129.1, 129.0, 127.8, 127.7, 68.8, 26.3, 15.8. The NMR spectra data are consistent with previously reported [S5].



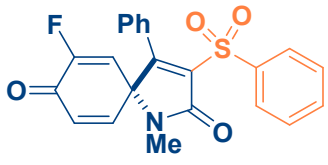
6d, 72 %

7-Methoxy-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6d**) : 30.1 mg, 72% yield. Yellow solid, mp 239.2-240.6 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.7 Hz, 2H), 7.63 (t, *J* = 7.1 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.10 (d, *J* = 7.4 Hz, 2H), 6.41 (t, *J* = 7.4 Hz, 2H), 5.31 (s, 1H), 3.64 (s, 3H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 163.1, 163.0, 154.4, 142.8, 139.1, 135.8, 134.2, 133.6, 130.1, 129.0, 128.9, 128.5, 127.8, 127.6, 108.4, 69.6, 55.6, 26.0. The NMR spectra data are consistent with previously reported [S6].



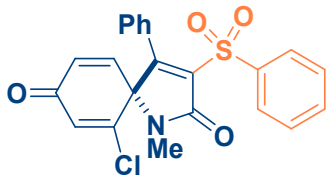
6e, 80%

7,9-Dimethoxy-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6e**) **:** 36.2 mg, 80% yield. Brown solid; mp 123.4-123.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.98 (m, 2H), 7.64 (t, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.44 – 7.36 (m, 1H), 7.32 (t, *J* = 7.3 Hz, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 5.33 (s, 2H), 3.65 (s, 6H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5, 164.6, 162.9, 154.0, 139.3, 135.3, 134.1, 130.0, 129.1, 128.9, 128.7, 127.8, 127.5, 109.1, 68.3, 56.0, 25.8. HRMS(EI) Calcd for $C_{24}H_{21}NO_6S$ $[M + H]^+$: 452.11624, Found 452.1162; IR (KBr) ν (cm^{-1}): 1711, 1688, 1651, 1619, 1447, 1376, 1327, 1153, 1108, 775, 593.



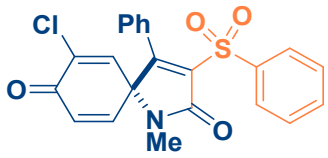
6f, 89%

7-Fluoro-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6f**) : 36.6 mg, 89% yield. Yellow solid; mp 179.1-180.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 8.2 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.53 (t, J = 7.2 Hz, 2H), 7.49 – 7.41 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 6.58 – 6.37 (m, 2H), 6.08 (d, J = 10.9 Hz, 1H), 2.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ176.2 (d, J_{C-F} = 22.2 Hz), 163.0, 161.5, 156.1 (d, J_{C-F} = 272.1 Hz), 143.6, 138.9, 136.7, 134.4, 133.4 (d, J_{C-F} =3.9 Hz), 130.4, 129.1 (d, J_{C-F} = 3.4 Hz), 128.0, 127.7, 118.6 (d, J_{C-F} = 15.3 Hz), 69.6 (d, J_{C-F} = 8.4 Hz), 26.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ 119.4 (q, J_{C-F} = 1.1 Hz). HRMS(EI) Calcd for $C_{22}H_{16}FNO_4S$ $[M + H]^+$: 410.08568, Found 410.0851; IR (KBr) ν (cm^{-1}): 1714, 1690, 1662, 1447, 1373, 1329, 1170, 1154, 1086, 1037, 879, 808, 715, 686, 592.



6g, 82%

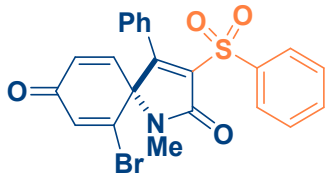
6-Chloro-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6g)** : 35.1 mg, 82% yield. Yellow solid, mp 198.0-199.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.74 – 7.60 (m, 1H), 7.53 (t, J = 7.0 Hz, 2H), 7.48 – 7.42 (m, 1H), 7.38 (t, J = 6.8 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 6.62 (s, 1H), 6.57 – 6.37 (m, 2H), 2.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 163.7, 160.4, 148.3, 141.5, 139.0, 137.9, 134.3, 133.7, 133.3, 130.6, 129.0, 128.9, 128.1, 127.6, 71.3, 25.9. The NMR spectra data are consistent with previously reported [S5].



6h, 92%

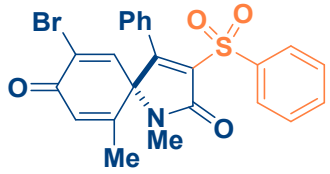
7-Chloro-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6h):** 39.1 mg, 92% yield. Brown solid, mp 183.5-185.0 °C; ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.11 – 7.86 (m, 2H), 7.74 – 7.60 (m, 1H), 7.53 (d, *J* = 6.9 Hz, 2H), 7.47 – 7.32 (m, 3H), 7.12 (s, 2H), 6.83 – 6.63 (m, 1H), 6.50 (d, *J* = 6.0 Hz, 2H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.3, 163.1, 161.1, 142.9, 138.0, 134.4, 133.1, 130.4, 129.0, 128.0, 127.6, 69.9, 26.5. The NMR spectra data are consistent with previously reported [S5].



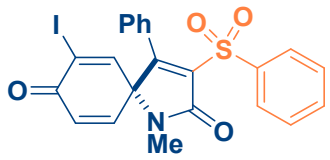
6i, 93%

6-Bomo-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (**6i**): 43.9 mg, 93% yield. Brown solid, mp 200.9-202.1 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.64 (t, *J* = 7.0 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.42 (s, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.97 (s, 1H), 6.51 (q, *J* = 9.9 Hz, 2H), 2.85 (s, 3H). ^{13}C NMR (100MHz, $CDCl_3$) δ 176.2, 163.1, 160.8, 142.8, 142.3, 138.8, 136.7, 134.3, 132.6, 130.4, 129.3, 129.05, 129.02, 128.0, 127.6, 70.6, 26.6. The NMR spectra data are consistent with previously reported [S5].



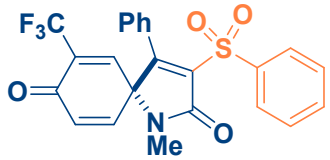
6j, 64%

9-Bromo-1,6-dimethyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6j)**: 31.1 mg, 64% yield. Yellow solid; mp 200.5-201.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.66 (t, *J* = 7.0 Hz, 1H), 7.55 (t, *J* = 7.3 Hz, 2H), 7.50 -7.42 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.86 (s, 1H), 6.36 (s, 1H), 2.77 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 163.6, 161.2, 151.6, 141.9, 139.0, 137.3, 134.4, 131.2, 130.8, 129.1, 129.0, 128.2, 127.5, 72.9, 26.2, 17.4. HRMS(EI) Calcd for $C_{23}H_{18}BrNO_4S$ $[M + H]^+$: 484.02127, Found 484.0209; IR (KBr) ν (cm^{-1}): , 1672, 1606, 1446, 1371, 1329, 1180, 1154, 1086, 812, 718, 687, 594.



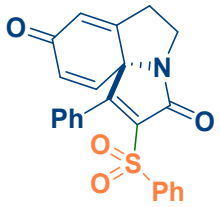
6k, 86%

7-Iodo-1-methyl-4-phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6k)** : 44.4 mg, 86% yield. Yellow solid; mp 103.3-103.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 2.7 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 2H), 6.55-6.48 (m, 2H), 2.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 163.2, 160.7, 149.9, 142.9, 138.9, 136.7, 134.4, 131.0, 130.4, 129.1, 129.0, 128.0, 127.7, 109.4, 71.4, 26.6. HRMS(EI) Calcd for $C_{22}H_{16}INO_4S$ $[M + H]^+$: 517.99176, Found 517.9911; IR (KBr) ν (cm^{-1}): 1713, 1667, 1591, 1447, 1368, 1328, 1179, 1154, 1087, 1038, 814, 716, 686, 594.



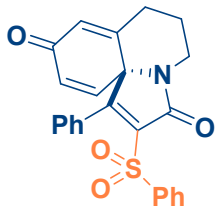
6l, 28%

1-Methyl-4-phenyl-3-(phenylsulfonyl)-7-(trifluoromethyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6l)** : 12.9 mg, 28% yield. Yellow solid, mp 193.8-195.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.0 Hz, 2H), 7.51 – 7.43 (m, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.98 (s, 1H), 6.50 (q, *J* = 10.0 Hz, 2H), 2.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 163.2, 160.5, 143.7 (q, J_{C-F} = 5.1 Hz), 142.0, 138.7, 137.6, 134.6, 134.3 130.7, 129.3, 129.2, 128.2, 127.6, 67.9, 26.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -66.07. HRMS(EI) Calcd for $C_{23}H_{16}F_3NO_4S$ $[M + H]^+$: 460.08304, Found 460.0810; IR (KBr) ν (cm^{-1}): 1717, 1689, 1384, 1301, 1153, 1086, 1002, 982, 835.



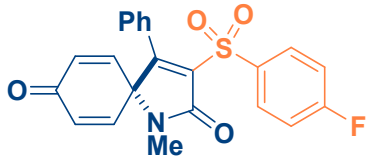
6m, 66%

1-Phenyl-2-(phenylsulfonyl)-5,6-dihydro-3H,8H-pyrrolo[2,1-i]indole-3,8-dione **(6m)** : 12.2 mg, 30% yield (50% yield based on the recovered 5m). Yellow solid; mp 214.2-215.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 7.3 Hz, 2H), 6.68 (d, *J* = 9.6 Hz, 1H), 6.24 (s, 1H), 6.07 (d, *J* = 10.4 Hz, 1H), 4.25 (dd, *J* = 11.6 and 7.4 Hz, 1H), 3.32 (td, *J* = 11.7 and 4.7 Hz, 1H), 2.71-2.58 (m, 1H), 2.54 (dd, *J* = 14.3 and 4.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 173.7, 169.6, 157.3, 144.2, 139.3, 137.4, 134.3, 132.7, 130.3, 129.1, 128.8, 128.2, 127.8, 127.6, 127.2, 99.9, 75.3, 49.9, 33.6. HRMS(EI) Calcd for $C_{23}H_{17}NO_4S$ $[M + H]^+$: 404.09511, Found 404.0952; IR (KBr) ν (cm^{-1}): 1730, 1672, 1463, 1372, 1280, 1180, 1135, 960, 900, 759, 683.



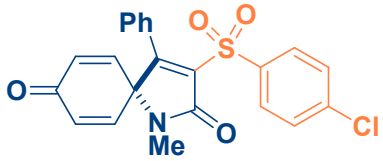
6n, 30%

1-Phenyl-2-(phenylsulfonyl)-6,7-dihydro-3H-pyrrolo[2,1-j]quinoline-3,9(5H)-dione **(6n)** : 27.5 mg, 66% yield. Yellow solid, mp 208.2-209.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.4 Hz, 2H), 7.70 – 7.37 (m, 4H), 7.33 (t, *J* = 6.7 Hz, 2H), 6.95 (d, *J* = 7.1 Hz, 2H), 6.49 (d, *J* = 9.7 Hz, 1H), 6.38 – 6.07 (m, 2H), 4.13 (dd, *J* = 13.6 and 9.7 Hz, 1H), 2.76 (dt, *J* = 16.4 and 8.4 Hz, 1H), 2.52 – 2.24 (m, 2H), 1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.5, 167.1, 163.6, 155.8, 143.5, 139.3, 136.9, 134.3, 133.4, 130.2, 129.8, 129.0, 128.8, 128.0, 127.6, 71.9, 36.6, 26.4, 26.1. HRMS(EI) Calcd for $C_{24}H_{19}NO_4S$ $[M + H]^+$: 418.11076, Found 418.1109; IR (KBr) ν (cm^{-1}): 1713, 1669, 1642, 1448, 1330, 1157, 1086, 898, 687, 599.



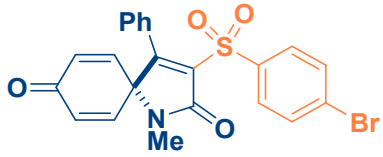
6o, 98%

3-((4-Fluorophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6o)** : 40.1 mg, 98% yield. Yellow solid, mp 210.1-212.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (dd, J = 8.9 and 5.1 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 8.6 Hz, 2H), 7.15 (d, J = 7.2 Hz, 2H), 6.44 (d, J = 2.1 Hz, 4H), 2.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 163.4, 162.1, 142.0, 136.5, 135.0, 134.4, 132.3 (d, $J_{C\text{-}F}$ = 9.8 Hz), 130.5, 128.4, 128.0, 127.7, 116.4 (d, $J_{C\text{-}F}$ = 22.5 Hz), 68.3, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.02. HRMS(EI) Calcd for $C_{22}H_{17}FNO_4S$ $[M + H]^+$: 410.08568, Found 410.08470; $C_{22}H_{16}FNaNO_4S$ $[M + Na]^+$: 432.06763, Found 432.06680; IR (KBr) ν (cm^{-1}): 1712, 1672, 1632, 1590, 1493, 1333, 1237, 1150, 846, 806, 581.



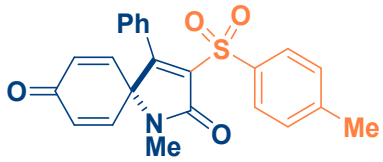
6p, 83%

3-((4-Chlorophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6p) :** 35.4 mg, 83% yield. Yellowish brown solid, mp 253.9-254.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 8.5 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.49 – 7.42 (m, 1H), 7.39 (t, J = 6.8 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.45 (s, 4H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 163.3, 162.4, 141.9, 141.3, 137.4, 136.3, 134.4, 130.8, 130.5, 129.4, 128.0, 127.7, 68.3, 26.4. The NMR spectra data are consistent with previously reported [S5].



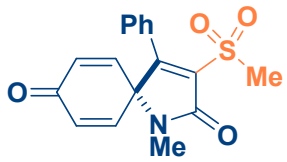
6q, 84%

3-((4-Bromophenyl)sulfonyl)-1-methyl-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6q)** : 39.7 mg, 84% yield. Yellow solid, mp 220.1-222.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.68 (d, *J* = 8.6 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 6.44 (s, 4H), 2.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.9, 163.3, 162.4, 141.9, 138.0, 136.2, 134.4, 132.4, 130.8, 130.5, 130.0, 128.3, 128.0, 127.7, 68.3, 26.4. The NMR spectra data are consistent with previously reported [S5].



6r, 93%

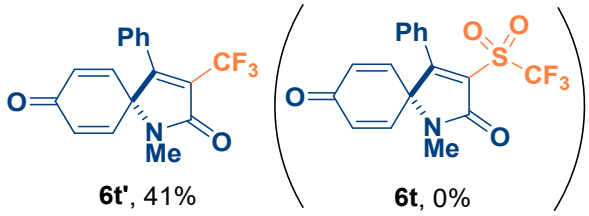
1-Methyl-4-phenyl-3-tosyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6r)** : 37.7 mg, 93% yield. Yellow solid, mp 276.9-278.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.9 Hz, 2H), 7.45 – 7.43 (m, 1H), 7.42 – 7.33 (m, 4H), 7.14 (d, *J* = 7.1 Hz, 2H), 6.43 (s, 4H), 2.82 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.1, 163.5, 161.5, 145.5, 142.2, 136.1, 134.3, 130.3, 129.7, 129.3, 127.9, 127.8, 68.2, 26.3, 21.8. The NMR spectra data are consistent with previously reported [S5].



6s, 64%

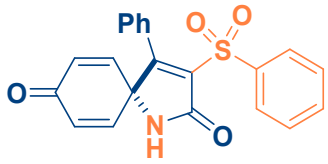
1-Methyl-3-(methylsulfonyl)-4-phenyl-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6s)** : 20.9 mg, 64% yield. Yellow solid; mp 109.6-110.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.1 Hz, 2H),

6.49 (d, J = 1.7 Hz, 4H), 3.30 (s, 3H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.0, 164.0, 161.8, 142.0, 135.6, 134.3, 130.7, 128.1, 128.01, 127.95, 68.1, 42.4, 26.3. HRMS(EI) Calcd for $C_{17}H_{16}NO_4S$ [M + H]$^+$: 330.07946, Found 330.0789; $C_{17}H_{15}NNaO_4S$ [M + Na]$^+$: 352.0614, Found 352.0606; IR (KBr) ν (cm^{-1}): 3052, 3018, 2925, 1706, 1670, 1631, 1426, 1390, 1319, 1178, 1138, 954, 874, 812, 720.



6t', 41% **6t**, 0%

1-Methyl-4-phenyl-3-((trifluoromethyl)sulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6t')**: 13.2 mg, 41% yield. Yellow solid, mp 166.9-168.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (t, J = 7.4 Hz, 1H), 7.35 (t, J = 7.5 Hz, 2H), 7.11 (d, J = 7.3 Hz, 2H), 6.57-6.40 (m, 4H), 2.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 164.5, 159.4, 142.6, 134.2, 130.4, 128.3, 127.5, 120.3 (d, $J_{C\text{-}F}$ = 270.8 Hz), 67.9, 26.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -60.66. HRMS(EI) Calcd for $C_{17}H_{13}F_3NO_2$ [M + H]$^+$: 320.08984, Found 320.0902; $C_{17}H_{12}F_3NNaO_2$ [M + Na]$^+$: 342.07178, Found 342. 0722; IR (KBr) ν (cm^{-1}): 1710, 1666, 1626, 1391, 1377, 1170, 1132, 1044, 993, 878, 856, 698; The NMR spectra data are consistent with previously reported [S6].

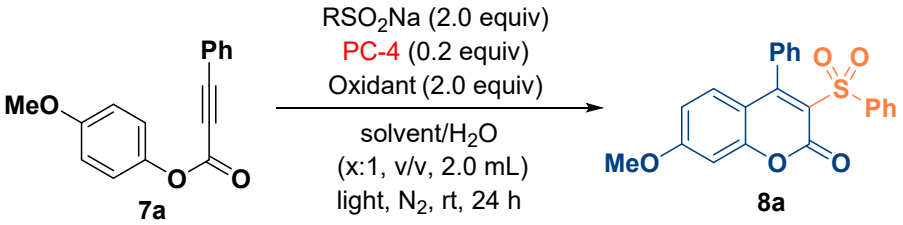


6u, 19%

4-Phenyl-3-(phenylsulfonyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione **(6u)** : 7.2 mg, 19% yield. Yellow solid, mp 186.6-187.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.5 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.52 (t, J = 7.8 Hz, 2H), 7.44 (t, J = 7.4 Hz, 1H), 7.37 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.76 (s, 1H), 6.56 (d, J = 10.1 Hz, 2H), 6.31 (d, J = 10.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.2, 165.5, 165.1, 142.4, 139.1, 136.0, 134.4, 132.6, 130.5, 129.1, 129.0, 128.2, 127.9, 127.7, 64.1. HRMS(EI) Calcd for $C_{21}H_{16}NO_4S$ [M + H]$^+$: 378.08000, Found 378.0799; $C_{21}H_{15}NNaO_4S$ [M + Na]$^+$: 400.06195, Found 400.0621; IR (KBr) ν (cm^{-1}): 1701,

1686, 1668, 1443, 1328, 1295, 1165, 1074, 855, 755, 732, 711, 694, 694.

Table S5 Screening of Reaction Conditions of Coumarin **8**



Entry	Solvent/H_2O	(v/v)	PC	Oxidant	Yield[a](%)
1	CH_3CN	neat	PC-1	$K_2S_2O_8$	trace
2	CH_3CN/H_2O	1:1	PC-1	$K_2S_2O_8$	50
3	CH_3CN/H_2O	3:1	PC-1	$K_2S_2O_8$	63
4	CH_3CN/H_2O	4:1	None	$K_2S_2O_8$	11
5	CH_3CN/H_2O	4:1	PC-1	None	0
6	CH_3CN/H_2O	4:1	PC-1	$K_2S_2O_8$	44
7[b]	DMSO/H_2O	4:1	PC-1	$K_2S_2O_8$	0
8[b]	CH_3CN/H_2O	4:1	PC-1	$K_2S_2O_8$	14
9[b]	CH_3OH/H_2O	4:1	PC-1	$K_2S_2O_8$	0
10	CH_3CN/H_2O	5:1	PC-1	$K_2S_2O_8$	60
11	CH_3CN/H_2O	7:1	PC-1	$K_2S_2O_8$	77
12	CH_3CN/H_2O	9:1	PC-1	$K_2S_2O_8$	49
13	CH_3OH/H_2O	7:1	PC-1	$K_2S_2O_8$	28
14	dioxane/H_2O	7:1	PC-1	$K_2S_2O_8$	59
15	DMF/H_2O	7:1	PC-1	$K_2S_2O_8$	0
16	$phCF_3/H_2O$	7:1	PC-1	$K_2S_2O_8$	trace
17	DCE/H_2O	7:1	PC-1	$K_2S_2O_8$	0
18	DMSO/H_2O	7:1	PC-1	$K_2S_2O_8$	29
19	CH_3CN/H_2O	7:1	PC-2	$K_2S_2O_8$	28
20	CH_3CN/H_2O	7:1	PC-3	$K_2S_2O_8$	29
20	CH_3CN/H_2O	7:1	PC-4	$K_2S_2O_8$	29
22	CH_3CN/H_2O	7:1	PC-5	$K_2S_2O_8$	31
23	CH_3CN/H_2O	7:1	PC-6	$K_2S_2O_8$	36
24	CH_3CN/H_2O	7:1	PC-7	$K_2S_2O_8$	25
25	CH_3CN/H_2O	7:1	PC-9	$K_2S_2O_8$	37
26	CH_3CN/H_2O	7:1	PC-10	$K_2S_2O_8$	60
27	CH_3CN/H_2O	7:1	PC-11	$K_2S_2O_8$	31
28	CH_3CN/H_2O	7:1	PC-12	$K_2S_2O_8$	34
29	CH_3CN/H_2O	7:1	PC-13	$K_2S_2O_8$	23
30	CH_3CN/H_2O	7:1	PC-14	$K_2S_2O_8$	44
31	CH_3CN/H_2O	7:1	PC-1	$Na_2S_2O_8$	31
32	CH_3CN/H_2O	7:1	PC-1	$Ce(NH_4)_2(NO_3)_6$	22
33	CH_3CN/H_2O	7:1	PC-1	$(NH_4)_2S_2O_8$	trace

34	CH_3CN/H_2O	7:1	PC-1	HKO_6S^1	trace
35	CH_3CN/H_2O	7:1	PC-1	HKO_6S^2	trace
36	CH_3CN/H_2O	7:1	PC-1	$H_3KO_{13}S_3^{(-4)}$	0
37[c]	CH_3CN/H_2O	7:1	PC-1	$K_2S_2O_8$	48
38[d]	CH_3CN/H_2O	7:1	PC-1	$K_2S_2O_8$	46
39[e]	CH_3CN/H_2O	7:1	PC-1	$K_2S_2O_8$	25
40	CH_3CN/H_2O	7:1	none	$K_2S_2O_8$	28
41	CH_3CN/H_2O	7:1	PC-1	none	0
42[f]	CH_3CN/H_2O	7:1	PC-1	$K_2S_2O_8$	26

[a]Isolated yield. [b]The reaction was run in dark. [c]The reaction was run in blue light. [d]The reaction was run in purple light. [e]The reaction was run in green light. [f]The reaction was run in dark.

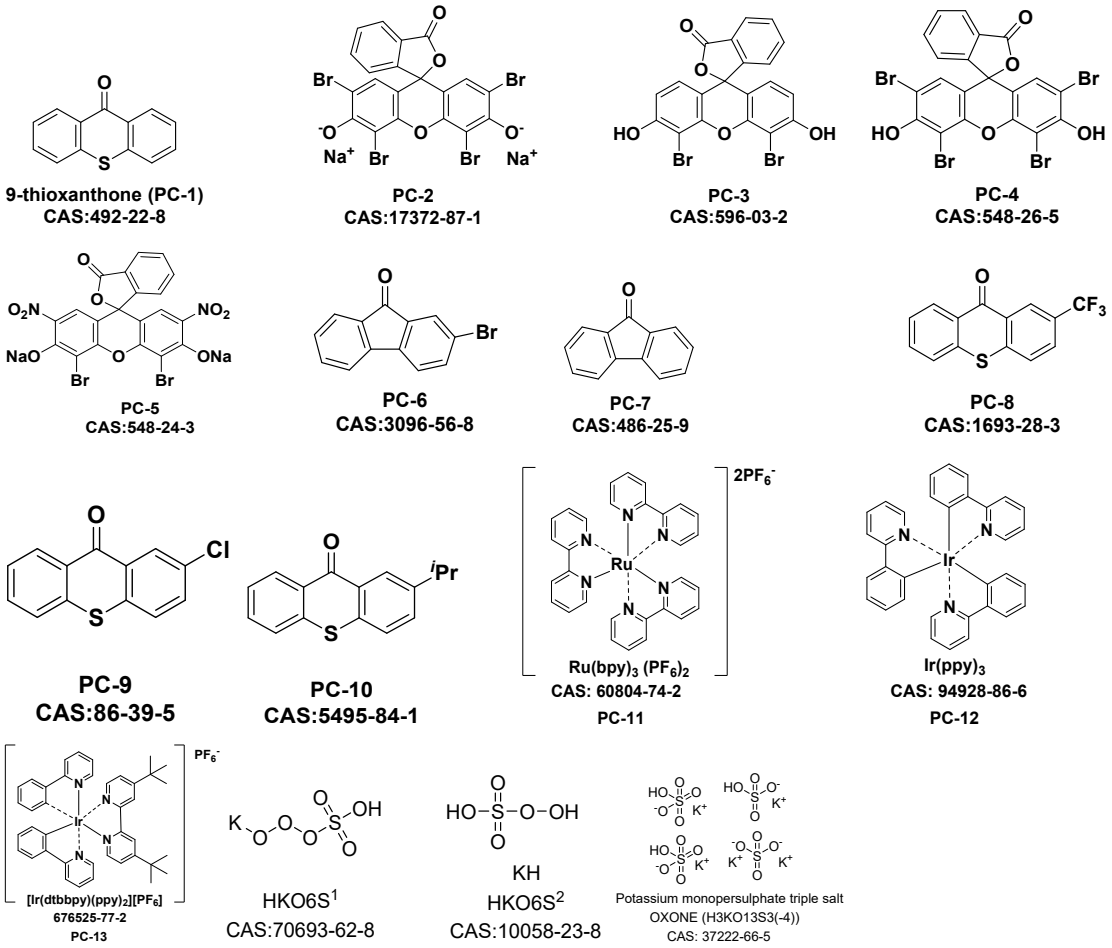


Figure S8 Structures of Photosensitizer (PCs)

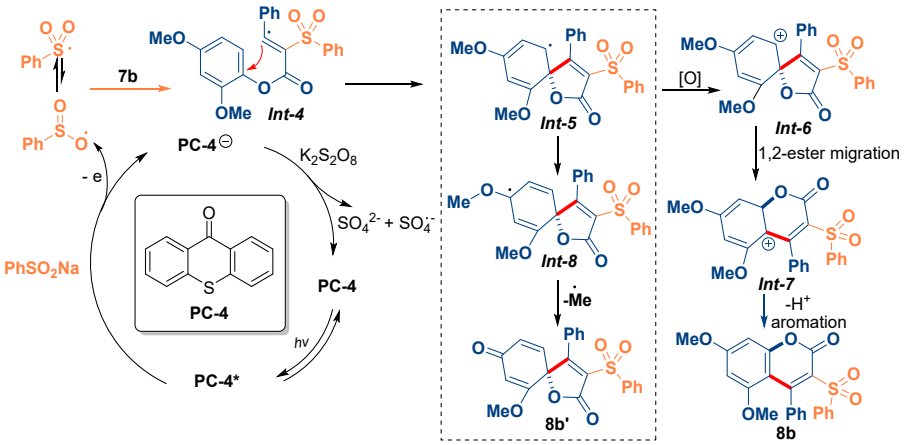
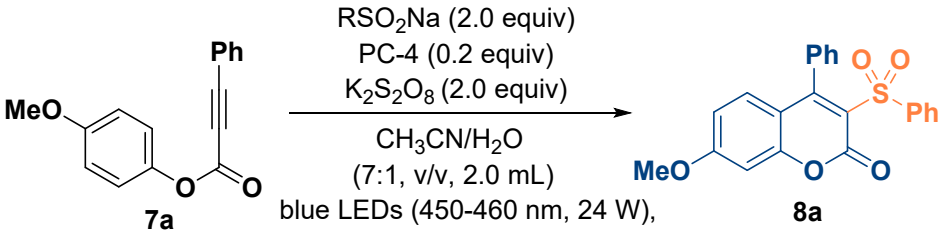
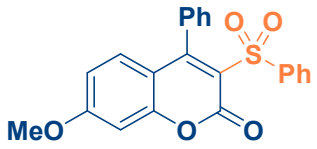


Figure S9 Formation of **8b'**

General procedure for Preparation of Coumarin 8

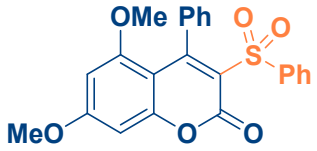


4-methoxyphenyl 3-phenylpropiolate **7** (0.1 mmol, 1.0 equiv), $PhSO_2Na$ (0.2 mmol, 2.0 equiv), 9-thioxanthone (PC-4, 0.02 mmol, 0.2 equiv) and $K_2S_2O_8$ (0.2 mmol, 2.0 equiv) in CH_3CN/H_2O (7:1, v/v, 2.0 mL) and then irradiation under blue light in a nitrogen atmosphere for corresponding hours until the starting materials **7** totally consumed or left maintain without change (A fan is used to cool down the reaction temperature). The reaction mixture was filtrated and the filtrate was extracted with dichloromethane (DCM, 5.0 mL×3), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired 7-methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **8**.



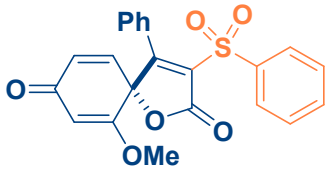
8a, 77%

7-Methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8a)**: 30.2 mg, 77% yield. Light yellow-white solid, m.p. 213.6-214.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.37 – 7.29 (m, 2H), 6.90 (d, *J* = 9.1 Hz, 1H), 6.79 (d, *J* = 2.1 Hz, 1H), 6.73 (dd, *J* = 9.1 and 2.2 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 159.7, 156.1, 156.0, 140.5, 133.4, 132.9, 131.2, 129.1, 129.0, 128.5, 128.1, 127.3, 122.2, 113.6, 113.5, 100.2, 56.1. The NMR spectra data are consistent with previously reported [S7].



8b, 62%

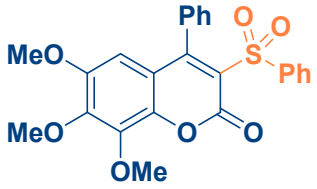
5,7-Dimethoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8b)**: 26.2 mg, 62% yield. Light yellow-white solid, mp 221.7-222.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 2H), 7.71 – 7.66 (m, 3H), 7.60 (t, *J* = 5.8 Hz, 2H), 7.54 (d, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 6.65 (s, 1H), 3.89 (s, 3H), 3.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 153.7, 140.6, 138.0, 135.7, 133.7, 133.3, 130.8, 128.7, 128.5, 128.1, 105.3, 103.9, 56.1, 55.9. HRMS(EI) Calcd for $C_{23}H_{18}O_6S$ $[M + K]^+$: 461.04612, Found 461.0465; IR (KBr) ν (cm^{-1}): 1473, 1384, 1320, 1194, 1171, 1161, 1050, 866, 836.



8b'

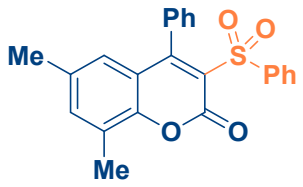
6-Methoxy-4-phenyl-3-(phenylsulfonyl)-1-oxaspiro[4.5]deca-3,6,9-triene-2,8-dione **(8b')**: 6.9 mg, 17% yield. Light yellow viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.98

(d, J = 7.6 Hz, 2H), 7.69 (t, J = 6.9 Hz, 1H), 7.56 (t, J = 7.1 Hz, 2H), 7.51 – 7.48 (m, 1H), 7.41 (t, J = 6.8 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 6.49 – 6.15 (q, J = 9.9 Hz, 2H), 5.61 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.9, 170.0, 164.8, 164.4, 138.5, 135.4, 134.7, 132.7, 131.4, 129.2, 129.0, 128.4, 127.2, 126.9, 105.3, 82.2, 56.6. HRMS(EI) Calcd for $C_{22}H_{16}O_6S$ $[M + H]^+$: 409.07458, Found 409.0734; $C_{22}H_{16}O_6NaS$ $[M + Na]^+$: 431.05653, Found 431.0567; IR (KBr) ν (cm^{-1}): 1783, 1668, 1384, 1227, 1202, 1160, 1093, 1086, 1000, 993.



8c, 56%

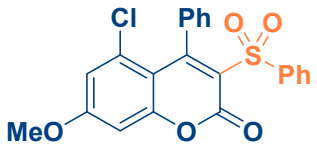
6,7,8-Trimethoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8c):** 25.3 mg, 56% yield. Light yellow-white solid, mp 213.6-214.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.61– 7.57 (m, 4H), 7.49 (td, J = 8.3 and 7.0 Hz, 2H), 7.34 (dd, J = 3.2 and 0.9 Hz, 1H), 7.33 (d, J = 2.1 Hz, 1H), 6.12 (s, 1H), 4.02 (s, 3H), 3.97 (s, 3H), 3.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 155.4, 149.7, 148.4, 143.9, 140.3, 133.5, 132.9, 129.2, 129.1, 128.5, 128.1, 127.3, 124.0, 115.1, 105.2, 62.0, 61.6, 56.0. HRMS(EI) Calcd for $C_{24}H_{21}O_7S$ $[M + H]^+$: 453.10025, Found 453.09950; $C_{24}H_{20}O_7NaS$ $[M + Na]^+$: 475.0822, Found 475.0811; IR (KBr) ν (cm^{-1}): 3065, 2927, 1736, 1516, 1447, 1330, 1247, 1156, 1081, 1033, 812, 686.



8d, 64%

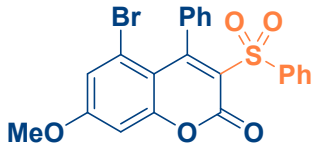
5,7-Dimethyl-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8d)**: 25.0 mg, 64% yield. Light yellow-white solid; mp 208.1-209.0°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 7.4 Hz, 2H), 7.59-7.57 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.33 (dd, J = 6.4 and 2.9 Hz, 2H), 7.28 (s, 1H), 6.60 (s, 1H), 2.39 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 155.8, 150.4, 140.3, 137.2, 134.0, 133.5, 132.9, 129.1, 128.5, 128.0,

127.4, 127.1, 126.0, 125.2, 119.6, 20.8, 15.3. The NMR spectra data are consistent with previously reported [S7].



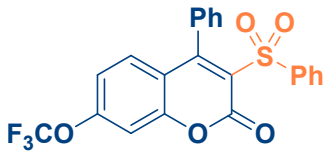
8e, 48%

5-Chloro-7-methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8e):** 20.5 mg, 48% yield. Light yellow-white solid; mp 179.8-180.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.7 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 3H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 2H), 6.65 (d, *J* = 9.9 Hz, 1H), 6.56 (s, 1H), 6.39 (d, *J* = 10.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.72, 146.62, 139.09, 138.24, 134.89, 132.21, 131.68, 129.31, 129.05, 128.49, 127.34, 83.26. HRMS(EI) Calcd for $C_{22}H_{15}ClO_5NaS$ $[M + Na]^+$: 449.02264, Found 449.0172; IR (KBr) ν (cm^{-1}): 3064, 2925, 2854, 1789, 1667, 1606, 1447, 1335, 1271, 1197, 1160, 995, 773, 686.



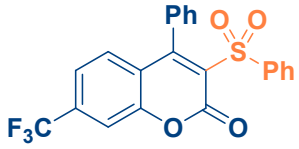
8f, 52%

5-Bromo-7-methoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8f):** 24.5 mg, 52% yield. Light yellow-white solid; mp 160.6-161.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.9 Hz, 2H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.0 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 (t, *J* = 6.8 Hz, 2H), 7.29 – 7.17 (m, 2H), 6.81 (s, 1H), 6.73 (dd, *J* = 9.9 and 2.3 Hz, 1H), 6.48 – 6.31 (d, *J* = 9.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.68, 139.49, 139.17, 138.26, 136.36, 134.86, 132.85, 132.04, 131.67, 129.28, 129.08, 128.43, 127.43, 126.33, 83.5. HRMS(EI) Calcd for $C_{22}H_{15}BrO_5S$ $[M + H]^+$: 469.98236, Found 470.9526; IR (KBr) ν (cm^{-1}): 3062, 2921, 2851, 1788, 1675, 1447, 1334, 1267, 1197, 1159, 1068, 994, 771, 685.



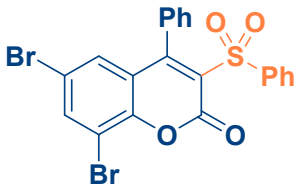
8g, 60%

4-Phenyl-3-(phenylsulfonyl)-7-(trifluoromethoxy)-2H-chromen-2-one **(8g)**: 26.8 mg, 60% yield. Light yellow-white solid; mp 181.5-182.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.63-7.59 (m, 4H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.35-7.33 (m, 2H), 7.19 (s, 1H), 7.09-7.02 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 155.0, 154.6, 153.2, 139.8, 133.8, 132.1, 131.7, 129.5, 129.2, 128.7, 128.3, 127.3, 125.8, 120.0 (d, $J_{C\text{-}F}$ = 259.2 Hz), 118.4, 116.7, 108.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.69. HRMS(EI) Calcd for $C_{22}H_{13}F_3O_5S_1$ $[M + H]^+$: 485.00996, Found 485.0073; IR (KBr) ν (cm^{-1}): 38, 1604, 1544, 1448, 1322, 1252, 1215, 1158, 1085, 1020, 848, 775, 686.



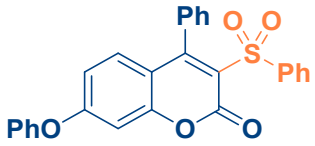
8h, 50%

4-Phenyl-3-(phenylsulfonyl)-7-(trifluoromethyl)-2H-chromen-2-one **(8h)**: 21.5 mg, 50% yield. Light yellow-white solid; mp 225.1-226.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (*J* = 7.8 Hz, 2H), 7.61 (dd, *J* = 6.9 and 4.0 Hz, 5H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.35 (dd, *J* = 6.1 and 2.7 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 154.7, 153.4, 139.6, 135.9, 135.6, 134.0, 131.8, 130.9, 129.7, 129.3, 128.8, 128.4, 127.3, 122.8, 121.2 (d, $J_{C\text{-}F}$ = 3.4 Hz), 114.2 (d, $J_{C\text{-}F}$ = 3.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.32. HRMS(EI) Calcd for $C_{22}H_{13}F_3O_4S$ $[M + H]^+$: 431.05594, Found 431.0559; IR (KBr) ν (cm^{-1}): 1739, 1545, 1500, 1327, 1237, 1133, 1008, 850, 744, 688.



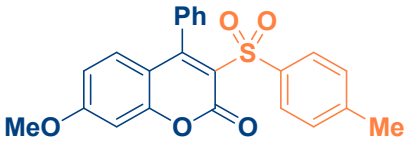
8i, 58%

6,8-Dibromo-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8i)**: 31.2 mg, 58% yield. Light yellow-white solid; mp 228.0-230.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.95 (d, *J* = 2.2 Hz, 1H), 7.63 (q, *J* = 4.5 and 3.8 Hz, 4H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.32 (dd, *J* = 6.4 and 2.6 Hz, 2H), 7.06 (d, *J* = 2.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 157.8, 154.0, 149.6, 144.6, 139.9, 134.0, 131.2, 129.9, 129.4, 128.7, 128.5, 127.4, 122.6, 117.5, 111.6. HRMS(EI) Calcd for $C_{21}H_{12}Br_2O_4$ Na S $[M + Na]^+$: 540.87207, Found 540.8709; IR (KBr) ν (cm^{-1}): 1751, 1537, 1446, 1330, 1258, 1174, 1156, 1003, 777, 688.



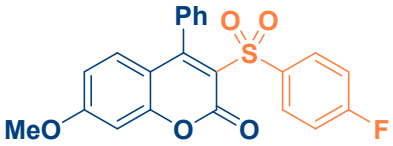
8j, 46%

7-Phenoxy-4-phenyl-3-(phenylsulfonyl)-2H-chromen-2-one **(8j)**: 20.9 mg, 46% yield. Light yellow-white solid; mp 174.3-174.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.5 Hz, 2H), 7.57 (dd, *J* = 6.3 and 3.1 Hz, 4H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.34 (dd, *J* = 6.0 and 2.5 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.9 Hz, 1H), 6.80 (dd, *J* = 11.6, and 2.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 159.5, 155.7, 154.0, 140.3, 133.5, 132.8, 131.6, 130.3, 129.1, 129.0, 128.5, 128.1, 127.3, 125.7, 123.0, 120.6, 114.8, 114.6, 103.9. HRMS(EI) Calcd for $C_{27}H_{18}O_5S$ $[M + H]^+$: 454.0875, Found 455.09532; $C_{27}H_{18}O_5$ Na S $[M + Na]^+$: 477.07726, Found 477.0755; IR (KBr) ν (cm^{-1}): 1743, 1615, 1586, 1534, 1485, 1354, 1327, 1275, 1163, 1017, 851, 775, 687.



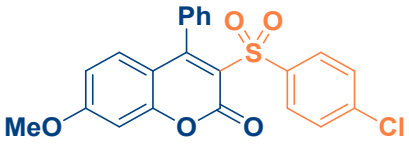
8k, 71%

7-Methoxy-4-phenyl-3-tosyl-2H-chromen-2-one **(8k)**: 28.9 mg, 71% yield. Light yellow-white solid; mp 124.3-124.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 8.2 Hz, 2H), 7.56-7.55 (m, 3H), 7.32 – 7.27 (m, 4H), 6.89 (d, J = 9.1 Hz, 1H), 6.78 (d, J = 2.1 Hz, 1H), 6.72 (dd, J = 9.1, 2.2 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 159.3, 156.0, 144.4, 137.5, 133.0, 131.1, 129.2, 129.1, 129.0, 128.0, 127.3, 122.5, 113.6, 113.5, 100.1, 56.1, 21.6. HRMS(EI) Calcd for $C_{23}H_{18}O_5S$ $[M + H]^+$: 407.09477, Found 407.0948; IR (KBr) ν (cm^{-1}): 1734, 1613, 1585, 1527, 1487, 1362, 1339, 1329, 1295, 1289, 1260, 1160, 1085, 1031, 849, 775, 704, 659.



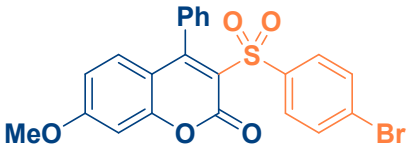
8l, 63%

3-((4-Fluorophenyl)sulfonyl)-7-methoxy-4-phenyl-2H-chromen-2-one**(8l)**: 25.9 mg, 63% yield. Light yellow-white solid; mp 108.9-109.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.8 and 5.1 Hz, 2H), 7.57-7.56 (m, 3H), 7.31 (dd, J = 6.6 and 2.9 Hz, 2H), 7.16 (t, J = 8.6 Hz, 2H), 6.91 (d, J = 9.1 Hz, 1H), 6.80 (d, J = 2.4 Hz, 1H), 6.74 (dd, J = 9.1 and 2.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 165.3, 164.4, 159.8, 156.1 (d, $J_{C\text{-}F}$ = 8.1 Hz), 136.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 132.9, 132.0 (d, $J_{C\text{-}F}$ =9.7 Hz), 131.2, 129.2, 128.1, 127.3, 122.1, 115.8 (d, $J_{C\text{-}F}$ = 22.5 Hz), 113.7, 113.5, 100.2, 56.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.80. HRMS(EI) Calcd for $C_{22}H_{15}FO_5S$ $[M + H]^+$: 411.0697, Found 411.0700; IR (KBr) ν (cm^{-1}): 1733, 1613, 1586, 1528, 1492, 1364, 1289, 1215, 1165, 1147, 1084, 836, 774, 702.



8m, 68%

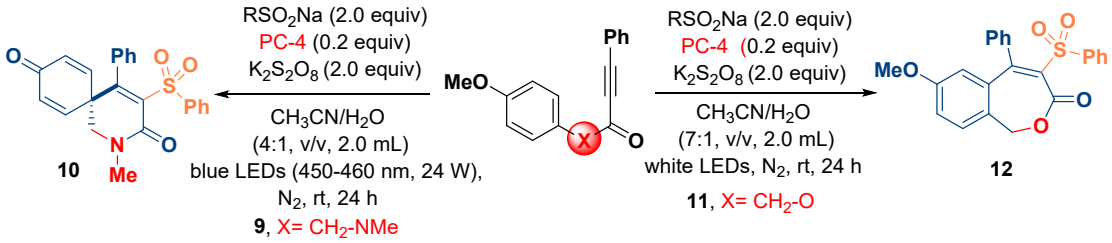
3-((4-Chlorophenyl)sulfonyl)-7-methoxy-4-phenyl-2H-chromen-2-one**(8m)**: 29.0 mg, 68% yield. Light yellow-white solid; mp 99.1-99.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.56 (s, 3H), 7.46 (d, *J* = 7.4 Hz, 2H), 7.31 (s, 2H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.80 (s, 1H), 6.75 (d, *J* = 9.1 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 160.0, 156.2, 156.0, 140.1, 138.9, 132.8, 131.2, 130.5, 129.2, 128.8, 128.1, 127.3, 121.8, 113.7, 113.5, 100.2, 56.1. HRMS(EI) Calcd for $C_{22}H_{15}ClO_5S$ [M + H]$^{+}$: 427.04015, Found 427.0400; IR (KBr) ν (cm^{-1}): 1732, 1613, 1584, 1526, 1363, 1340, 1295, 1260, 1162, 1087, 1031, 848, 777, 704, 623.



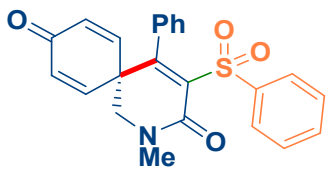
8n, 55%

3-((4-Bromophenyl)sulfonyl)-7-methoxy-4-phenyl-2H-chromen-2-one **(8n)**: 25.9 mg, 55% yield. Light yellow-white solid; mp 154.1-155.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.32 – 7.29 (m, 3H), 7.31 (dd, *J* = 6.5 and 2.9 Hz, 2H), 6.91 (d, *J* = 9.1 Hz, 1H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.74 (dd, *J* = 9.1 and 2.4 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 160.1, 156.2, 156.0, 139.5, 132.8, 131.8, 131.2, 130.6, 129.2, 128.8, 128.1, 127.3, 113.7, 113.5, 100.2, 56.1.HRMS(EI) Calcd for $C_{22}H_{15}BrO_5S$ [M + H]$^{+}$: 470.98963, Found 470.9894; IR (KBr) ν (cm^{-1}): 1736, 1723, 1617, 1582, 1498, 1453, 1355, 1288, 1249, 1054, 817, 709.

General procedure for Preparation of Spiro[5.5]trienone (10) and 5-Phenyl-4-(phenylsulfonyl)benzo[c]oxepin-3(1H)-one (12)



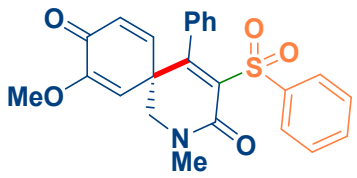
N-(4-methoxybenzyl)-*N*-methyl-3-phenylpropiolamide **9** or 4-methoxybenzyl 3-phenylpropiolate **11** (0.1 mmol, 1.0 equiv), $PhSO_2Na$ (0.2 mmol, 2.0 equiv), 9-thioxanthone (0.02 mmol, 0.2 equiv) and $K_2S_2O_8$ (0.2 mmol, 2.0 equiv) in CH_3CN/H_2O (4:1, v/v, 2.0 mL or 7:1, v/v, 2.0 mL) and then irradiation under blue light in a nitrogen atmosphere for corresponding hours until the starting materials **9** or **11** totally consumed or left maintain without change (A fan is used to cool down the reaction temperature). The reaction mixture was filtrated and the filtrate was extracted with dichloromethane (DCM, 5.0 mL×3), the combined organic phase was dried over anhydrous Na_2SO_4. The solvent was removed by rotary evaporation, the residual was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to afford desired 2-methyl-5-phenyl-4-(phenylsulfonyl)-2-azaspiro[5.5]undeca-4,7,10-triene-3,9-dione (**10**) or 7-methoxy-5-phenyl-4-(phenylsulfonyl)benzo[c]oxepin-3(1H)-one **(12)**.



10a, 62%

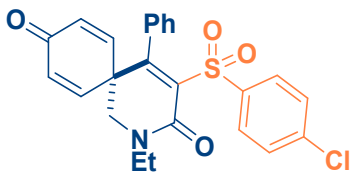
2-Methyl-5-phenyl-4-(phenylsulfonyl)-2-azaspiro[5.5]undeca-4,7,10-triene-3,9-dione **(10a)**: 25.1 mg, 62% yield. Light yellow-white solid; mp 108.3-108.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.1

Hz, 2H), 7.33 (q, J = 8.9 and 8.3 Hz, 3H), 6.99 (d, J = 7.7 Hz, 2H), 6.78 (d, J = 8.8 Hz, 2H), 6.24 (d, J = 9.5 Hz, 2H), 3.63 (d, J = 1.7 Hz, 2H), 3.06 (d, J = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 159.4, 158.8, 144.4, 141.2, 136.4, 133.5, 133.1, 132.3, 129.1, 129.0, 128.5, 127.6, 126.3, 54.9, 47.9, 34.9. HRMS(EI) Calcd for $C_{23}H_{20}NO_4S$ [M + H]$^+$: 406.11076, Found 406.1098; $C_{23}H_{19}NNaO_4S$ [M + Na]$^+$: 428.0927, Found 428.0914; IR (KBr) ν (cm^{-1}): 3064, 3034, 2927, 1661, 1489, 1384, 1317, 1167, 1149, 1081, 867, 689, 597.



10b, 58%

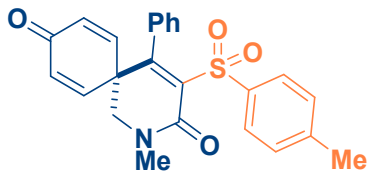
8-Methoxy-2-methyl-5-phenyl-4-(phenylsulfonyl)-2-azaspiro[5.5]undeca-4,7,10-triene-3,9-dione **(10b)**: 25.3 mg, 58% yield. Light yellow-white solid; mp 126.6-127.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 7.6 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.32 (dt, J = 14.1, 6.8 Hz, 3H), 6.97 (d, J = 6.8 Hz, 2H), 6.82 (dd, J = 10.0, 2.6 Hz, 1H), 6.28 (d, J = 10.0 Hz, 1H), 5.59 (d, J = 2.6 Hz, 1H), 3.64 (d, J = 3.4 Hz, 2H), 3.56 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.1, 160.4, 159.1, 153.4, 144.5, 141.2, 136.0, 133.5, 133.1, 131.9, 129.02, 129.00, 128.5, 127.4, 111.3, 55.8, 55.3, 48.5, 35.0. HRMS(EI) Calcd for $C_{24}H_{22}NO_5S$ [M + H]$^+$: 436.12132, Found 436.1197; $C_{24}H_{21}NNaO_5S$ [M + Na]$^+$: 458.10327, Found 458.1018; IR (KBr) ν (cm^{-1}): 1665, 1641, 1612, 1488, 1447, 1321, 1211, 1164, 1149, 1083, 764, 597.



10c, 49%

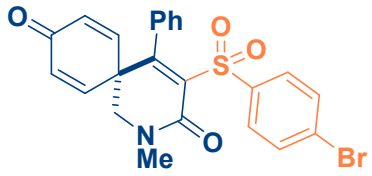
4-((4-Chlorophenyl)sulfonyl)-2-ethyl-5-phenyl-2-azaspiro[5.5]undeca-4,7,10-triene-3,9-dione **(10c)**: 22.2 mg, 49% yield. Light yellow-white solid; mp 140.8-141.6 °C;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.60 (t, J = 7.9 Hz, 1H), 7.49 (t, J

= 7.7 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6.28 (d, *J* = 9.7 Hz, 2H), 5.30 (s, 1H), 3.61 (s, 2H), 3.51 (q, *J* = 7.0 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ 183.6, 157.9, 157.7, 144.2, 141.0, 137.3, 135.3, 133.6, 132.5, 131.6, 129.0, 128.6, 128.0, 127.8, 52.3, 47.8, 41.8, 12.3. HRMS(EI) Calcd for $C_{24}H_{21}ClNO_4S$ $[M + H]^+$: 454.08743, Found 454.0867; $C_{24}H_{20}ClNaNO_4S$ $[M + Na]^+$: 476.06938, Found 476.0685; IR (KBr) ν (cm^{-1}): 1663, 1485, 1448, 1319, 1148, 1086, 1016, 823, 763, 687, 598.



10d, 55%

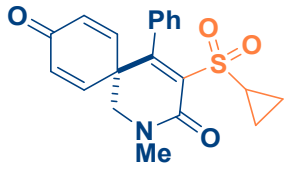
2-Methyl-5-phenyl-4-tosyl-2-azaspiro[5.5]undeca-4,7,10-triene-3,9-dione **(10d)**: 23.1 mg, 55% yield. Light yellow-white solid; mp 115.8-116.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.36-7.33 (m, 2H), 7.32-7.31 (m, 1H), 7.26 (s, 1H), 6.98 (dd, *J* = 8.0 and 1.5 Hz, 2H), 6.78 (d, *J* = 10.2 Hz, 2H), 6.24 (d, *J* = 10.2 Hz, 2H), 3.62 (s, 2H), 3.06 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.9, 158.9, 144.55, 144.50, 133.2, 132.2, 129.2, 129.1, 129.0, 127.5, 126.3, 54.9, 47.9, 35.0, 21.7. HRMS(EI) Calcd for $C_{24}H_{22}NO_4S$ $[M + H]^+$: 420.12641, Found 420.1252; $C_{24}H_{21}NNaO_4S$ $[M + Na]^+$: 442.10835, Found 442.1069; IR (KBr) ν (cm^{-1}): 2927, 1663, 1596, 1491, 1384, 1319, 1260, 1148, 1083, 862, 811.



10e, 52%

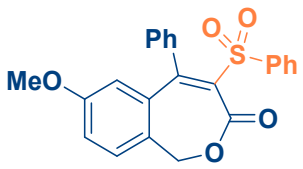
4-((4-Bromophenyl)sulfonyl)-2-methyl-5-phenyl-2-azaspiro[5.5]undeca-4,7,10 triene-3,9-dione **(10e)**: 25.2 mg, 52% yield. Light yellow-white solid; mp 119.5-119.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.37-7.30 (m, 3H), 6.97 (dd, *J* = 8.0 and 1.3 Hz, 2H), 6.77 (d, *J* = 10.2 Hz, 2H), 6.25 (d, *J* = 10.2

Hz, 2H), 3.63 (s, 2H), 3.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.7, 159.9, 158.8, 144.2, 140.1, 136.1, 133.0, 132.4, 131.9, 130.7, 129.2, 129.0, 127.6, 126.2, 54.8, 47.9, 35.0. HRMS(EI) Calcd for $C_{23}H_{19}BrNO_4S$ $[M + H]^+$: 484.02127, Found 484.0198; $C_{23}H_{18}BrNNaO_4S$ $[M + Na]^+$: 506.00321, Found 506.0018; IR (KBr) ν (cm^{-1}): 3086, 3061, 2927, 1662, 1573, 1490, 1394, 1324, 1150, 1068, 1010, 862, 733.



10f, 60%

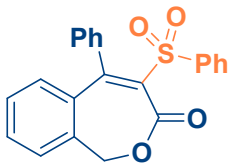
4-(Cyclopropylsulfonyl)-2-methyl-5-phenyl-2-azaspiro[5.5]undeca-4,7,10-triene-3,9-dione **(10f)**: 22.2 mg, 60% yield. Light yellow-white solid; mp 126.6-126.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 4H), 6.93 (dd, J = 7.9 and 1.1 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 6.28 (d, J = 10.1 Hz, 2H), 3.66 (s, 2H), 3.16 (s, 3H), 1.28-1.25 (m, 1H), 1.08-1.03 (m, 2H), 0.99-0.96 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.8, 159.6, 157.7, 144.6, 133.1, 132.3, 129.0, 127.4, 126.2, 110.0, 55.1, 47.5, 35.0, 33.1, 5.7. HRMS(EI) Calcd for $C_{20}H_{19}NO_4S$ $[M + H]^+$: 370.11076, Found 370.1096; $C_{20}H_{19}NO_4S$ $[M + H]^+$: 392.0927, Found 392.0914; IR (KBr) ν (cm^{-1}): 3073, 3037, 2925, 2854, 1657, 1624, 1491, 1403, 1316, 1264, 1139, 864, 804, 701.



12a, 56%

7-Methoxy-5-phenyl-4-(phenylsulfonyl)benzo[c]oxepin-3(1H)-one **(12a)**: 22.8 mg, 56% yield. Colorless viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.58 (m, 1H), 7.53-7.49 (m, 2H), 7.47 (dd, J = 8.5 and 1.2 Hz, 2H), 7.37 – 7.33 (m, 3H), 7.29 (d, J = 7.2 Hz, 2H), 7.07 (t, J = 7.9 Hz, 2H), 6.97 (d, J = 8.7 Hz, 2H), 6.60 (d, J = 7.4 Hz, 2H), 5.44 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.6, 149.8, 145.0, 142.7, 134.6, 134.2, 131.1, 130.8, 129.9, 129.3, 129.0, 128.8, 128.5, 127.3, 114.0, 69.2,

55.3. HRMS(EI) Calcd for $C_{23}H_{18}O_5S$ $[M+H]^+$: 407.09532, Found 407.0759; IR (KBr) ν (cm^{-1}): 1735, 1613, 1516, 1448, 1331, 1248, 1157, 1081, 1033, 813, 688.



12b, 46%

5-phenyl-4-(phenylsulfonyl)benzo[c]oxepin-3(1H)-one **(12b)**: 17.3 mg, 46% yield. Colorless viscous oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.30 (d, *J* = 5.7 Hz, 4H), 7.25 (t, *J* = 7.7 Hz, 2H), 7.09 (d, *J* = 4.9 Hz, 2H), 7.03 (d, *J* = 7.1 Hz, 2H), 5.04 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ163.6, 154.7, 136.9, 134.0, 129.6, 129.5, 129.0, 128.9, 128.5, 128.4, 128.2, 127.9, 126.7, 67.1. HRMS(EI) Calcd for $C_{22}H_{16}O_4S$ $[M+H]^+$: 377.08475, Found 377.0820; IR (KBr) ν (cm^{-1}): 3473, 3416, 3068, 2925, 1725, 1448, 1384, 1330, 1258, 1159, 1082, 813, 686, 552.

[Reference]

[**S1**] Zhao, Y., and Truhlar, D. G. (2008). The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.*, **2007**, 120, 215–241. DOI: 10.1007/s00214-007-0310-x.

[**S2**] a) Hariharan, P. C.; Pople, J. A. Chem. Phys. Lett. 1972, 66, 217-219; b) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.*, **1982**, 77, 3654-3665.

[**S3**] a) Rüdiger Bauernschmitt, Reinhart Ahlrichs, Treatment of electronic excitations within the adiabatic approximation of time dependent density functional theory, *Chem. Phys. Lett.*, **1996**, 256, 454-464. DOI: 10.1016/0009-2614(96)00440-X; b) R. Eric Stratmann and Gustavo E. Scuseria, An efficient implementation of time-dependent density-functional theory for the calculation of excitation energies of large

molecules, *J. Chem. Phys.*, **1998**, 109, 8218. DOI: 10.1063/1.477483; c) Giovanni Scalmania, Michael J. Frisch, Geometries and properties of excited states in the gas phase and in solution: Theory and application of a time-dependent density functional theory polarizable continuum model, *J. Chem. Phys.*, **2006**, 124, 094107. DOI: 10.1063/1.2173258

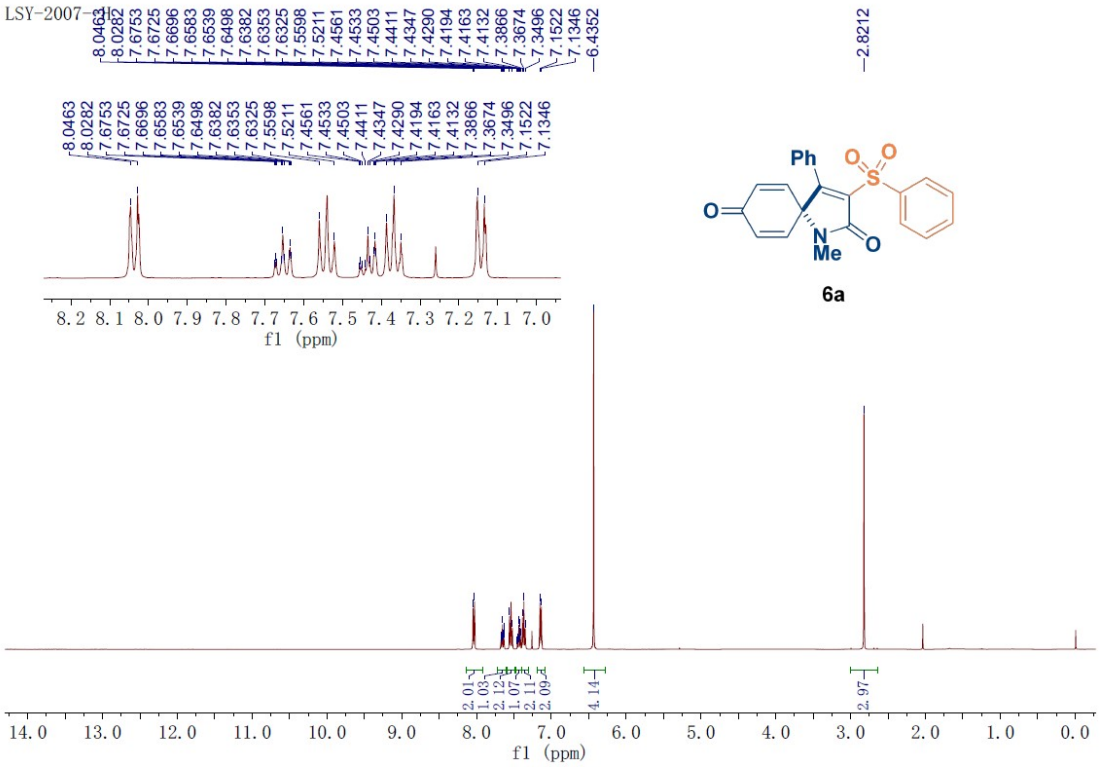
[**S4**] Frisch M J, Trucks G W, Schlegel H B, et al. Gaussian 16, Revision C. 01; Gaussian, Inc. Wallingford, CT, 2019.

[**S5**] Metal-Free Oxidative Spirocyclization of Alkynes with Sulfonylhydrazides Leading to 3-Sulfonated Azaspiro[4,5]trienones. Jiangwei Wen, Wei Wei, Shengnan Xue, Daoshan Yang, Yu Lou, Chaoyang Gao and Hua Wang. *J. Org. Chem*., **2015**, 80, 10, 4966-4972.

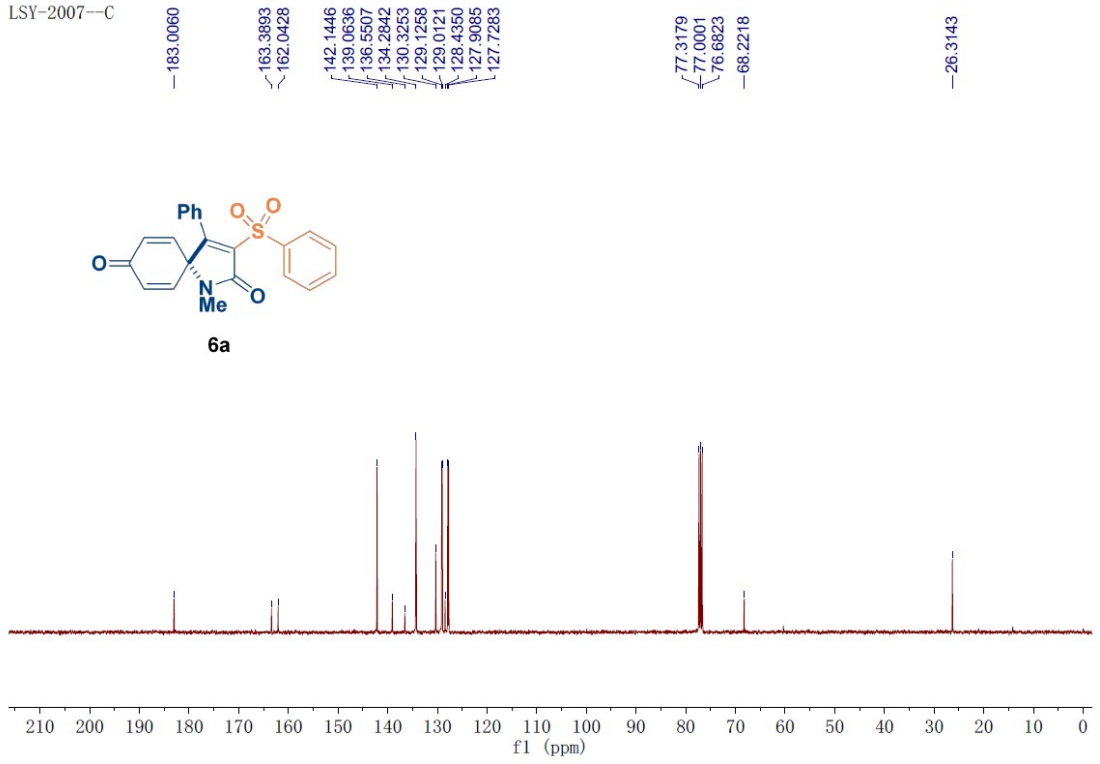
[**S6**] Visible-light-enabled spirocyclization of alkynes leading to 3-sulfonyl and 3-sulfenyl azaspiro[4,5]trienones. Wei Wei, Huanhuan Cui, Daoshan Yang, Huilan Yue, Chenglong He, Yulong Zhang and Hua Wang. *Green Chem*., **2017**,19, 5608-5613.

[**S7**] Visible-light mediated 3-component synthesis of sulfonylated coumarins from sulfur dioxide. Zhengkai Chen, Nai-Wei Liu, Michael Bolte, Hongjun Rena and Georg Manolikakes. *Green Chem*., **2018**,20, 3059-3070.

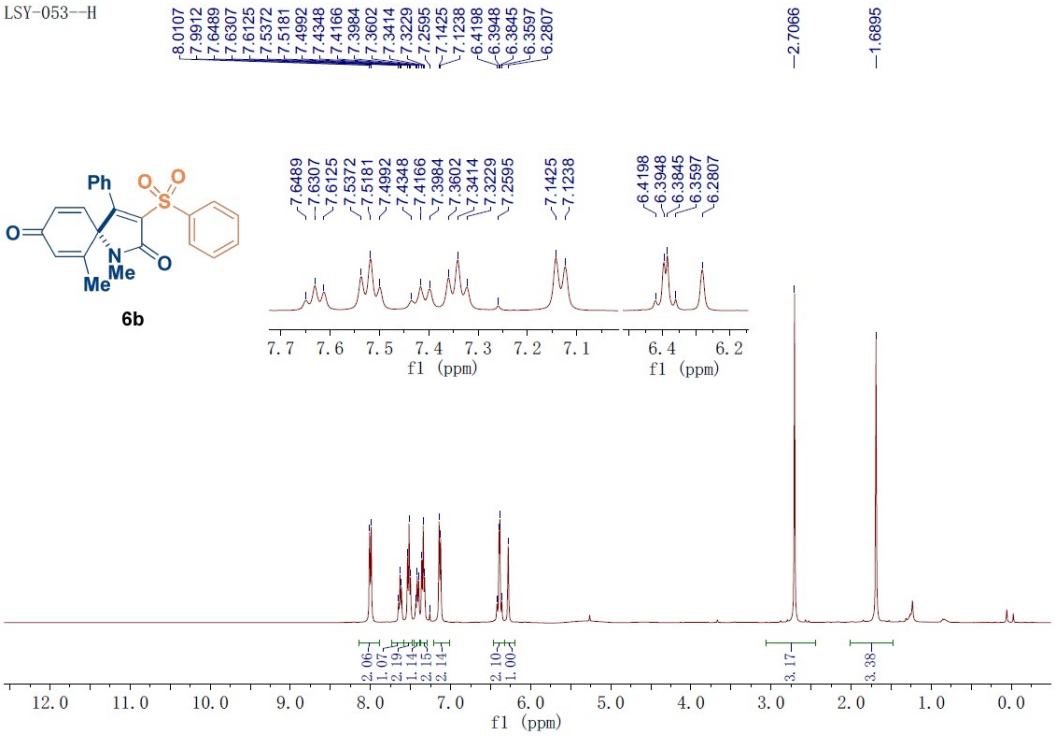
^{1}H NMR of **6a** (400 M, $CDCl_3$)



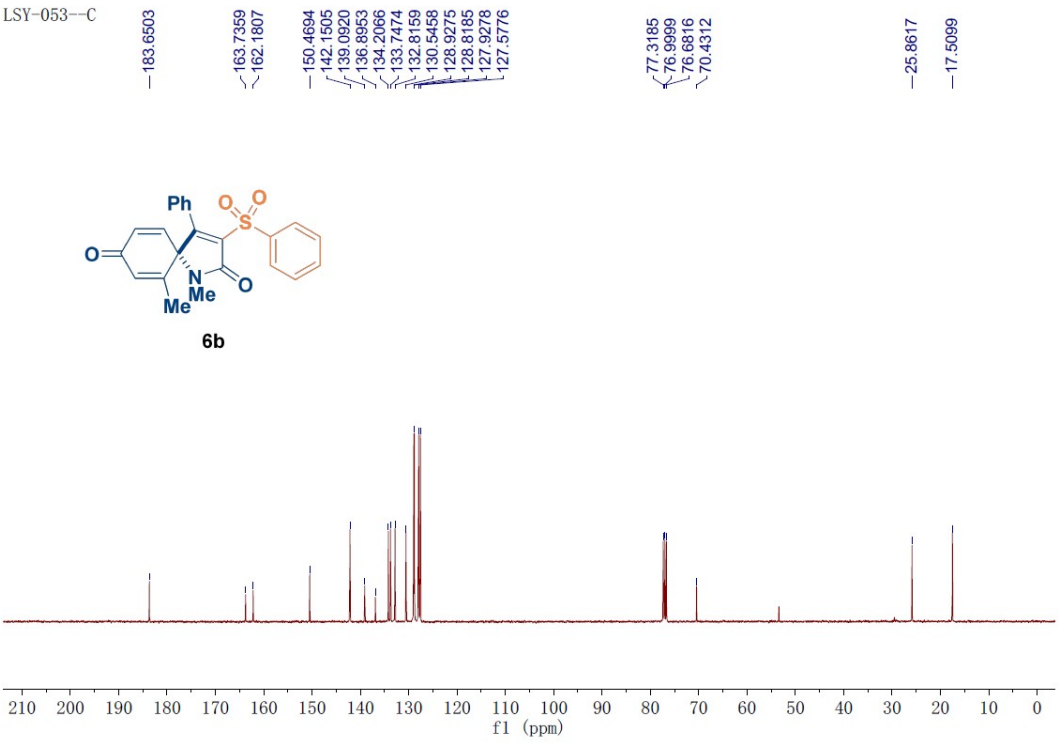
^{13}C NMR of **6a** (100 M, $CDCl_3$)



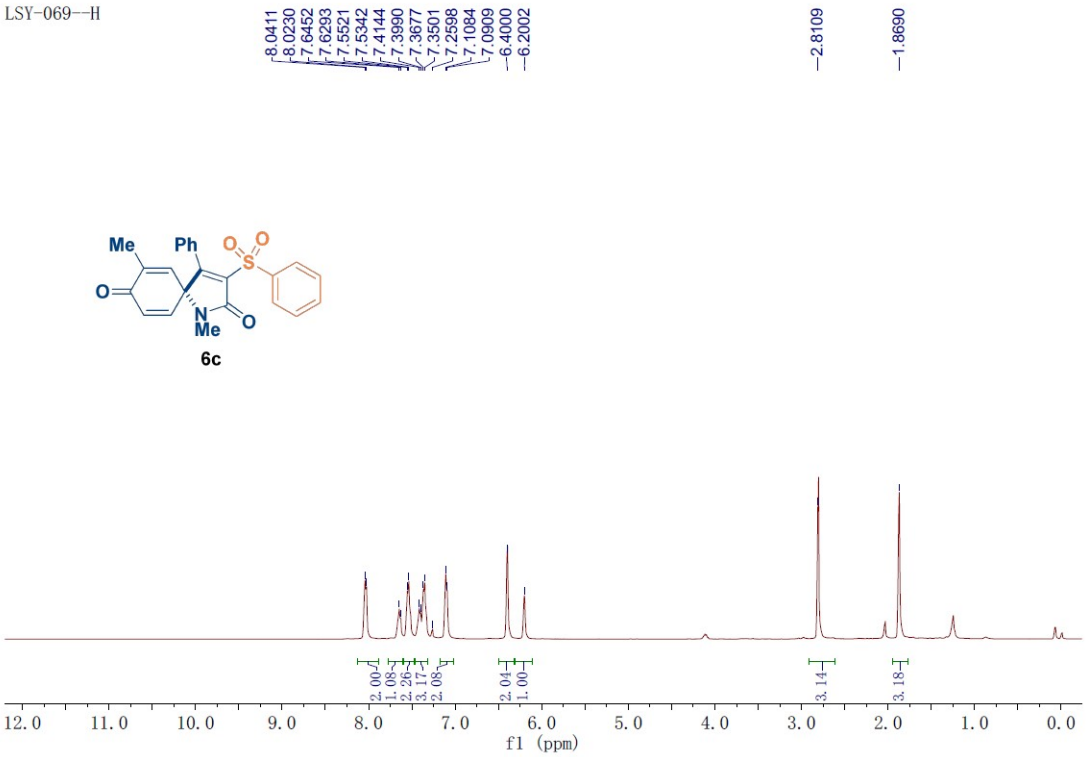
^{1}H NMR of **6b** (400 M, $CDCl_3$)



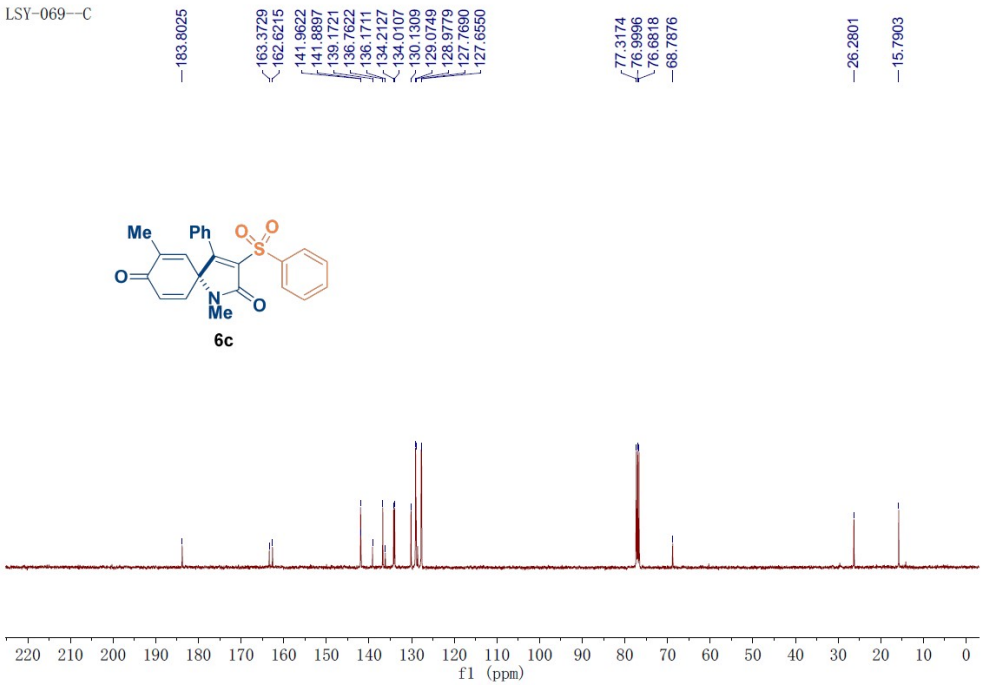
^{13}C NMR of **6b** (100 M, $CDCl_3$)



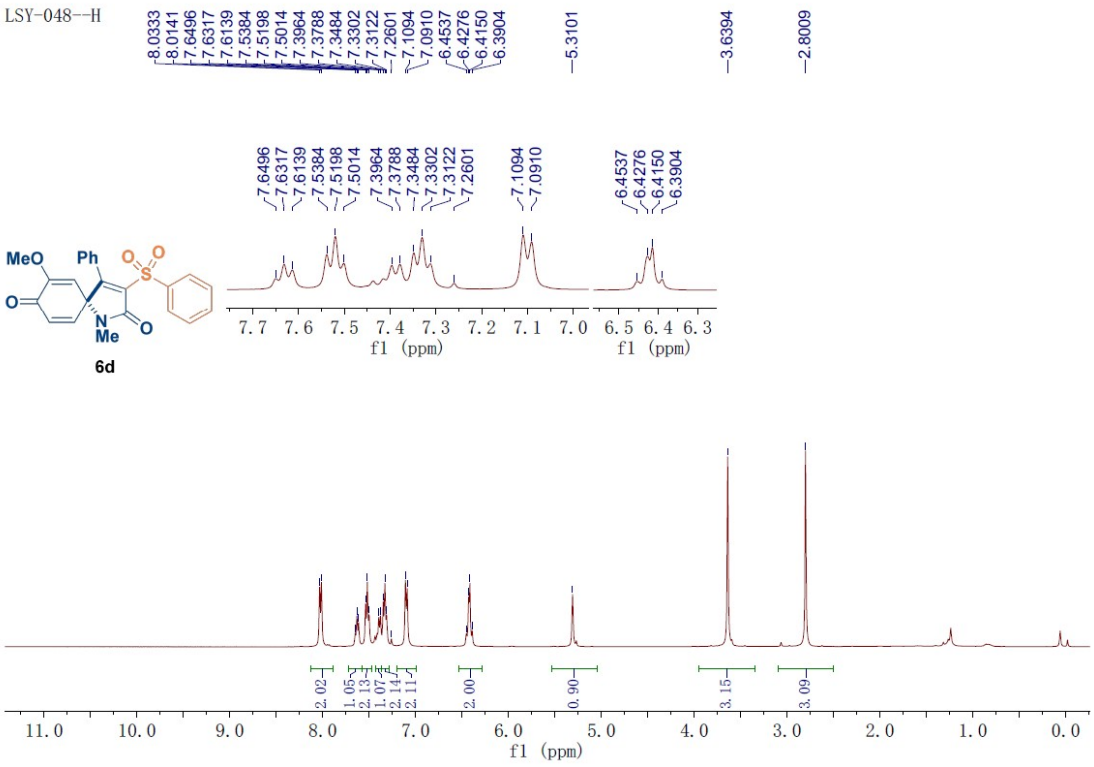
^{1}H NMR of **6c** (400 M, $CDCl_3$)



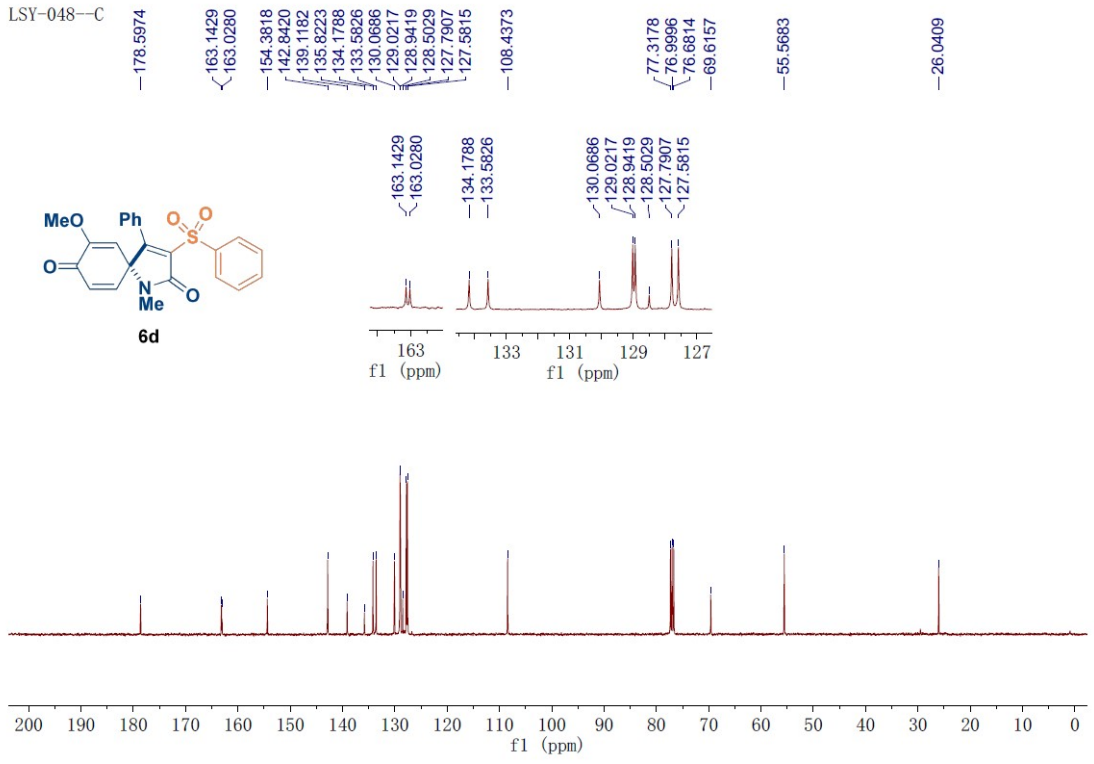
^{13}C NMR of **6c** (100 M, $CDCl_3$)



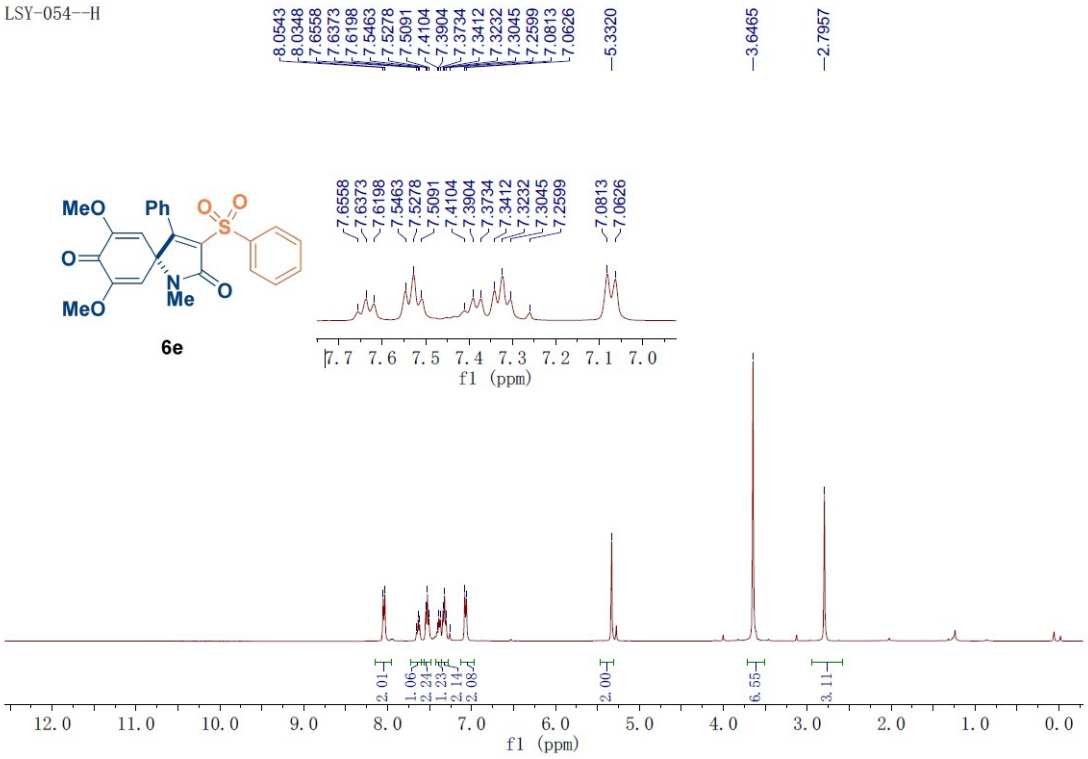
^{1}H NMR of **6d** (400 M, $CDCl_3$)



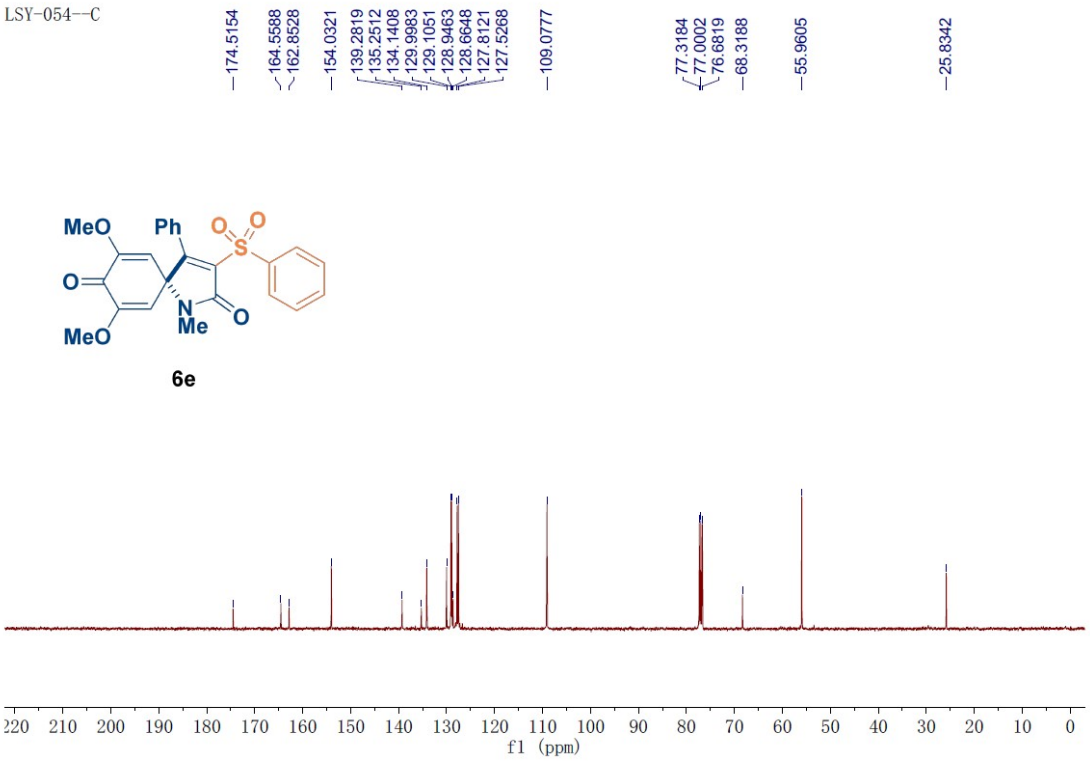
^{13}C NMR of **6d** (100 M, $CDCl_3$)



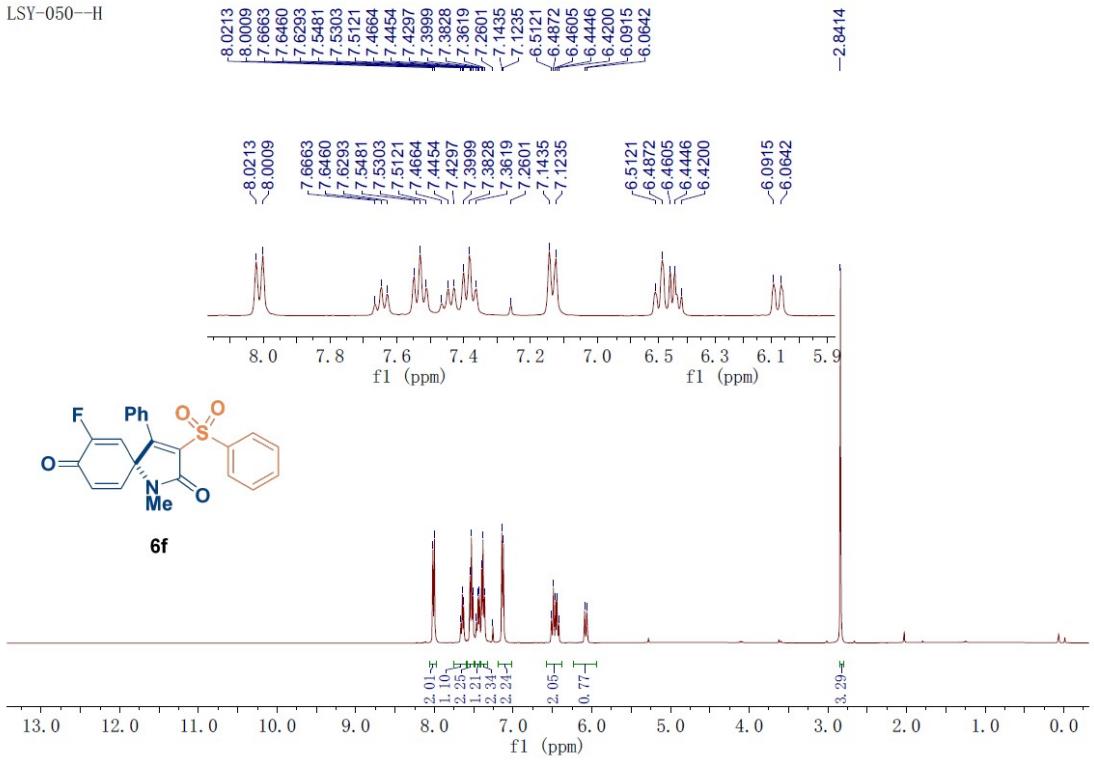
^{1}H NMR of **6e** (400 M, $CDCl_3$)



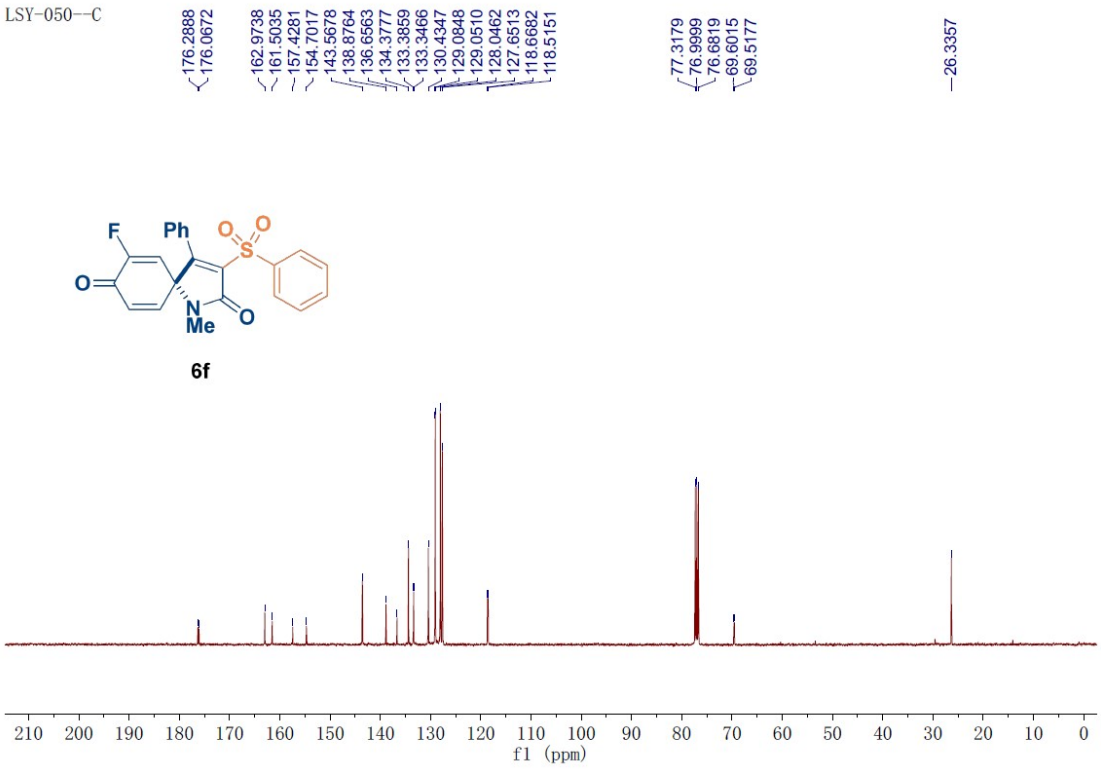
^{13}C NMR of **6e** (100 M, $CDCl_3$)



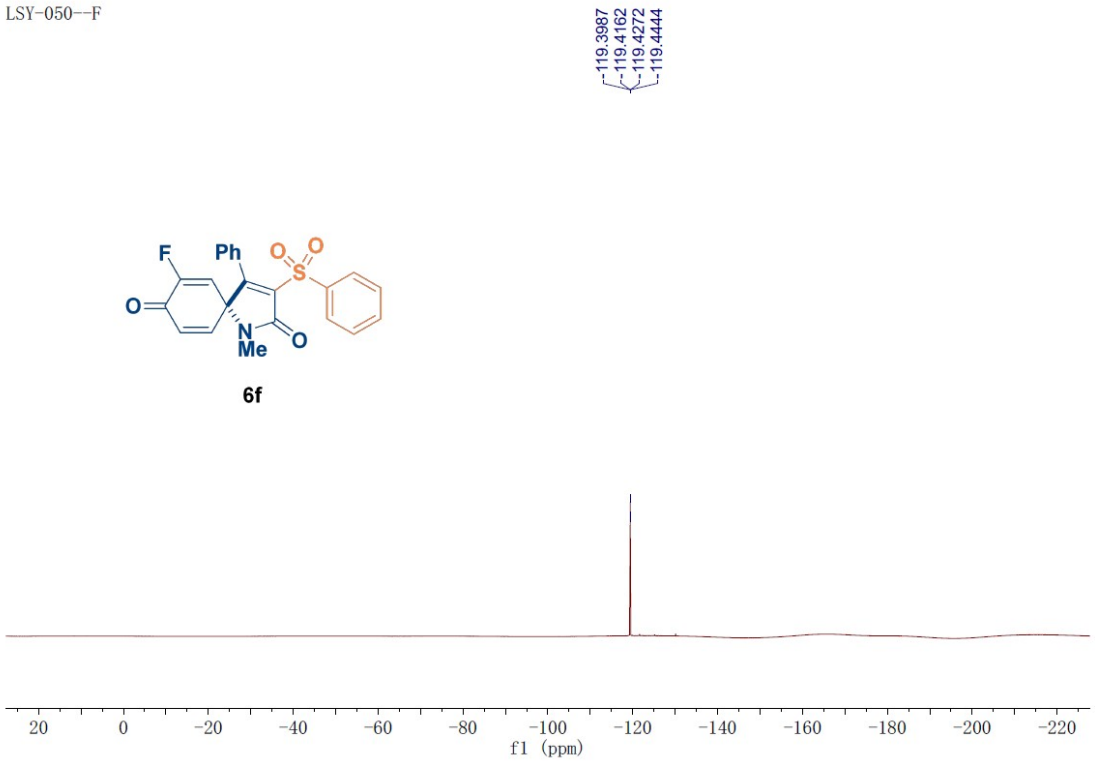
^{1}H NMR of **6f** (400 M, $CDCl_3$)



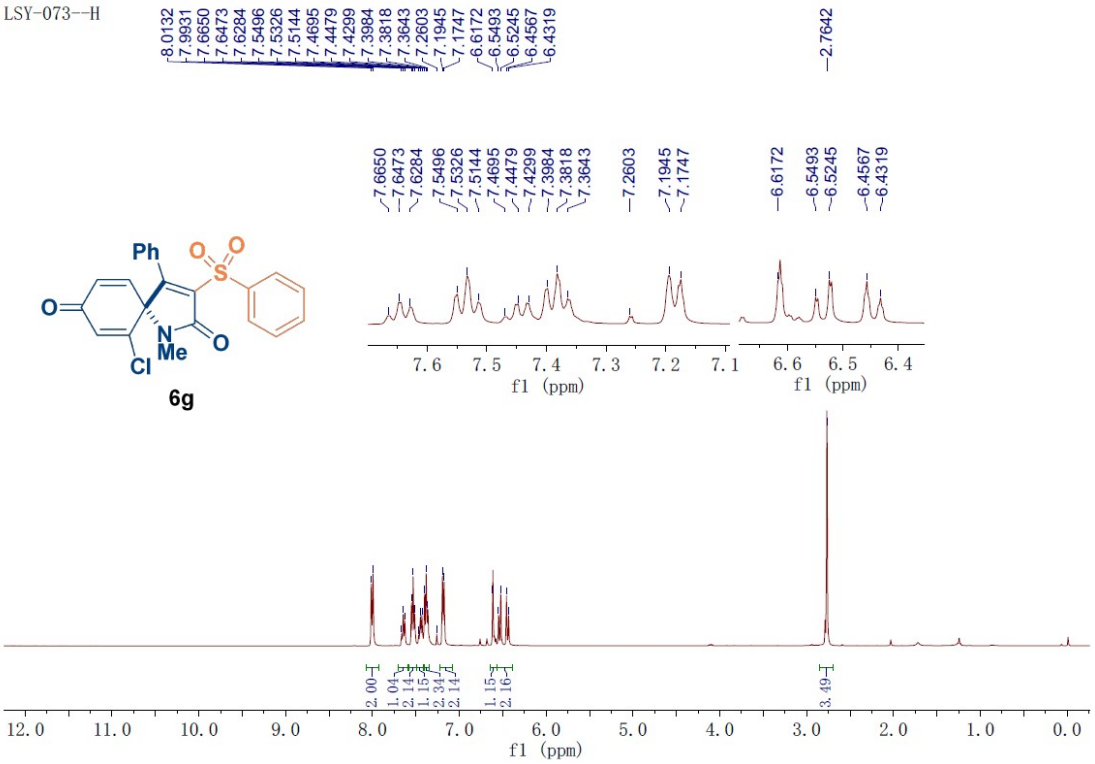
^{13}C NMR of **6f** (100 M, $CDCl_3$)



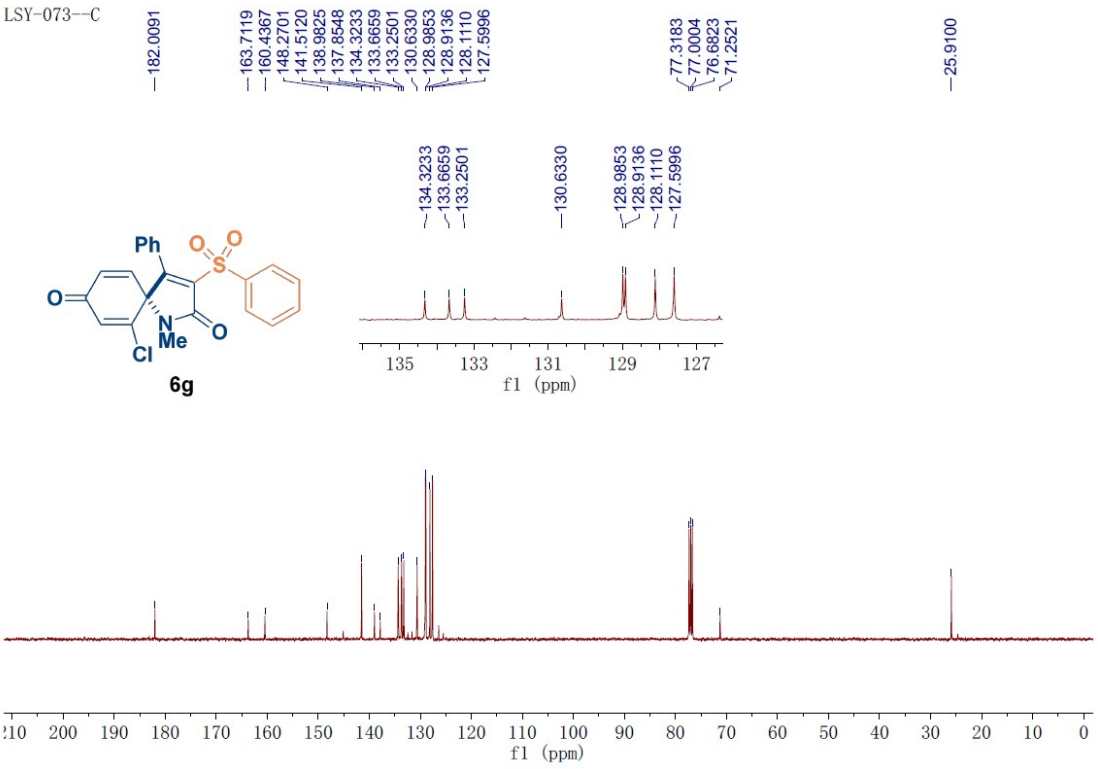
^{19}F NMR of **6f** (376 M, $CDCl_3$)



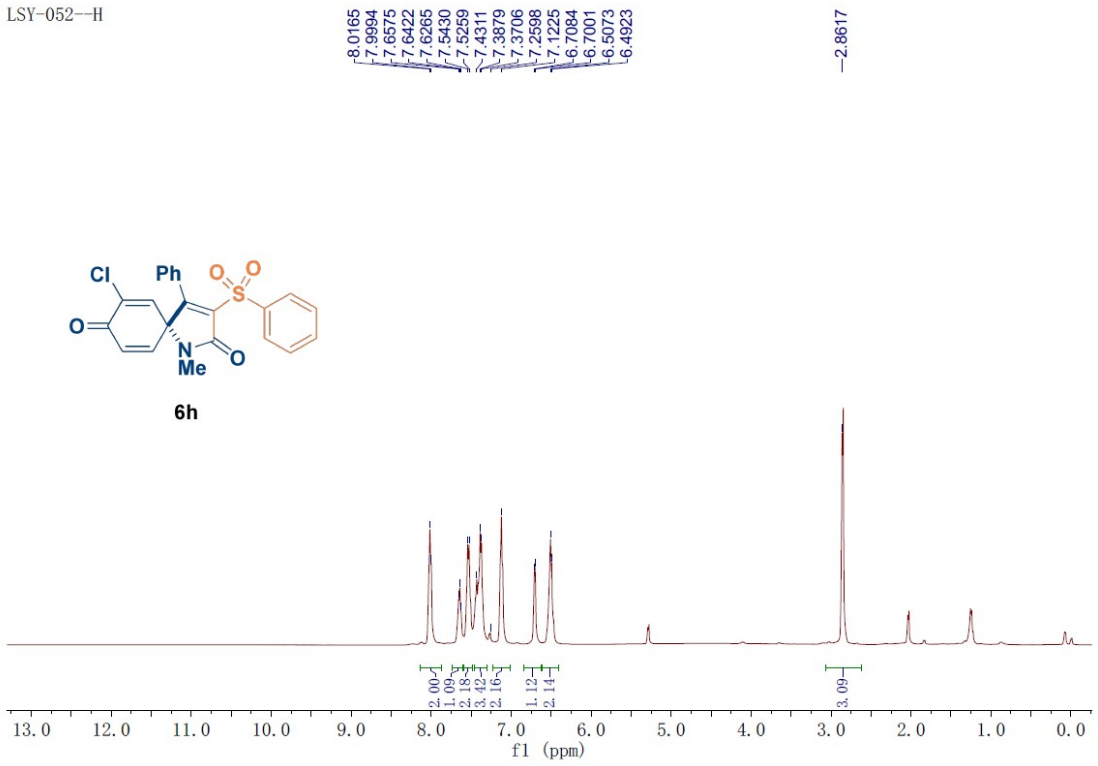
^{1}H NMR of **6g** (400 M, $CDCl_3$)



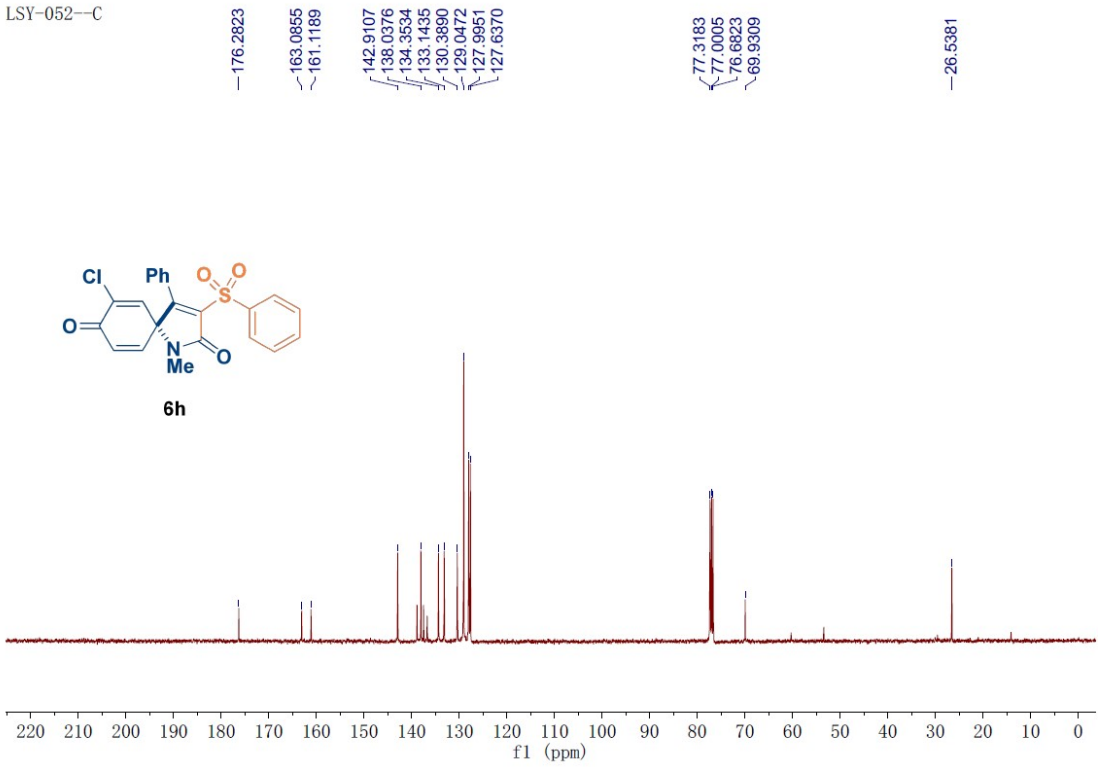
^{13}C NMR of **6g** (100 M, $CDCl_3$)



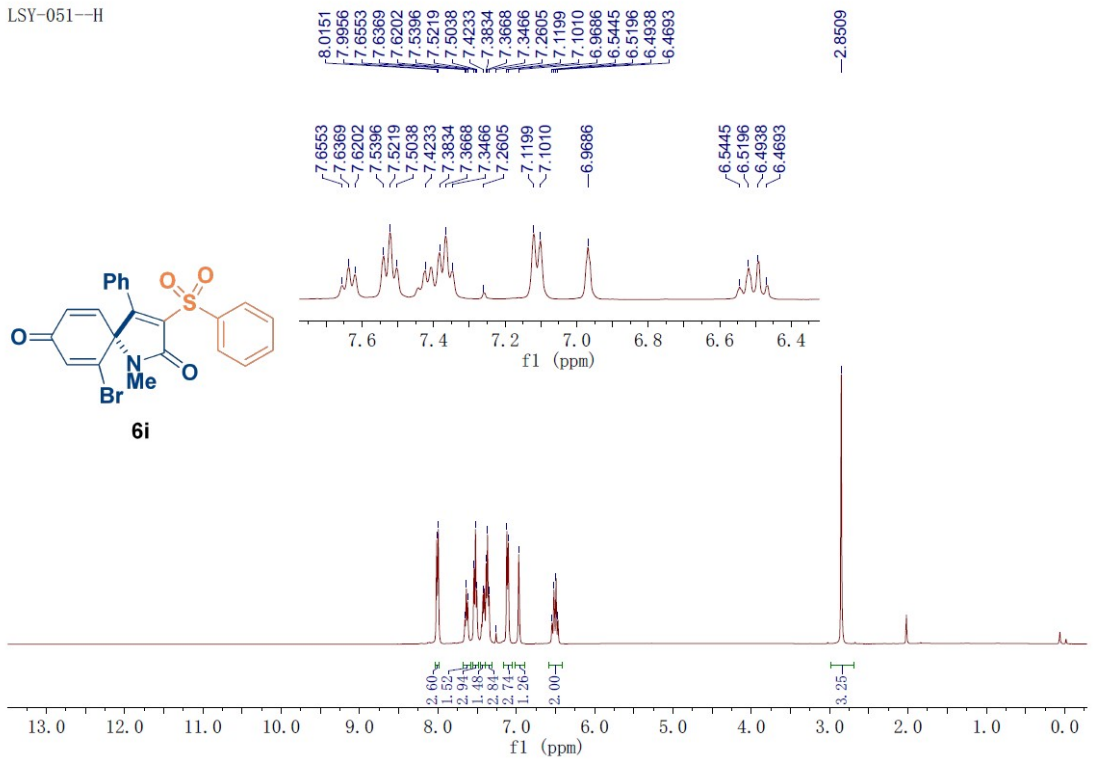
^{1}H NMR of **6h** (400 M, $CDCl_3$)



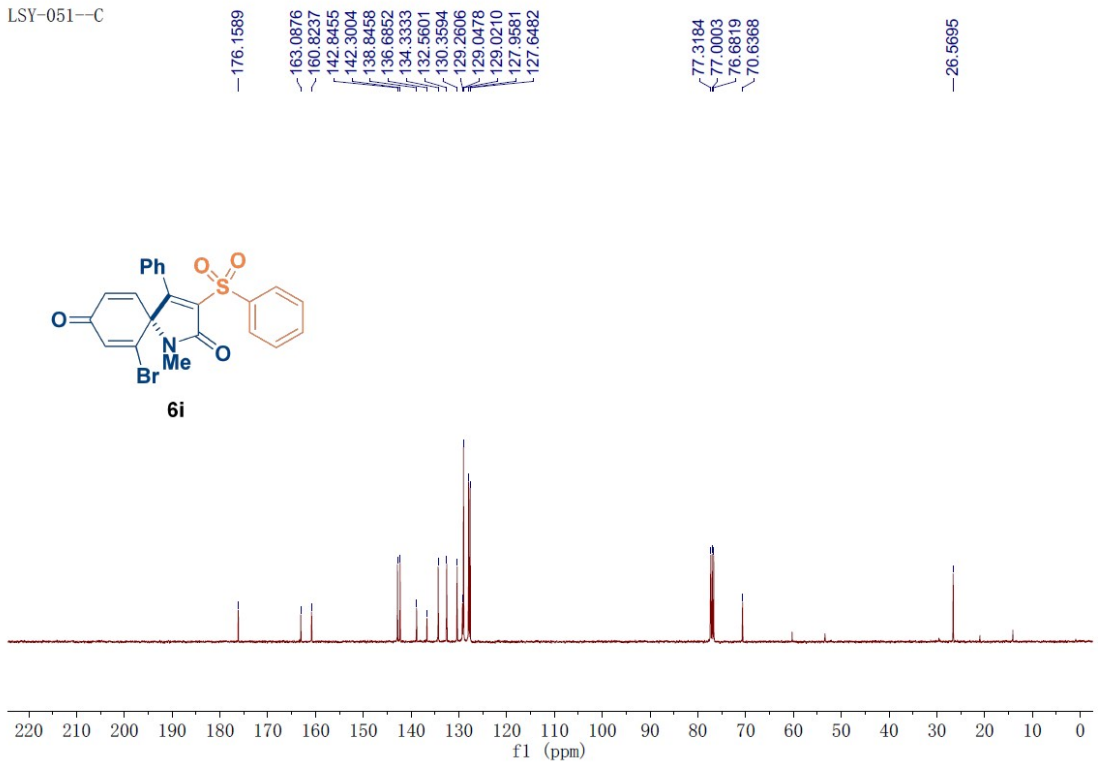
^{13}C NMR of **6h** (100 M, $CDCl_3$)



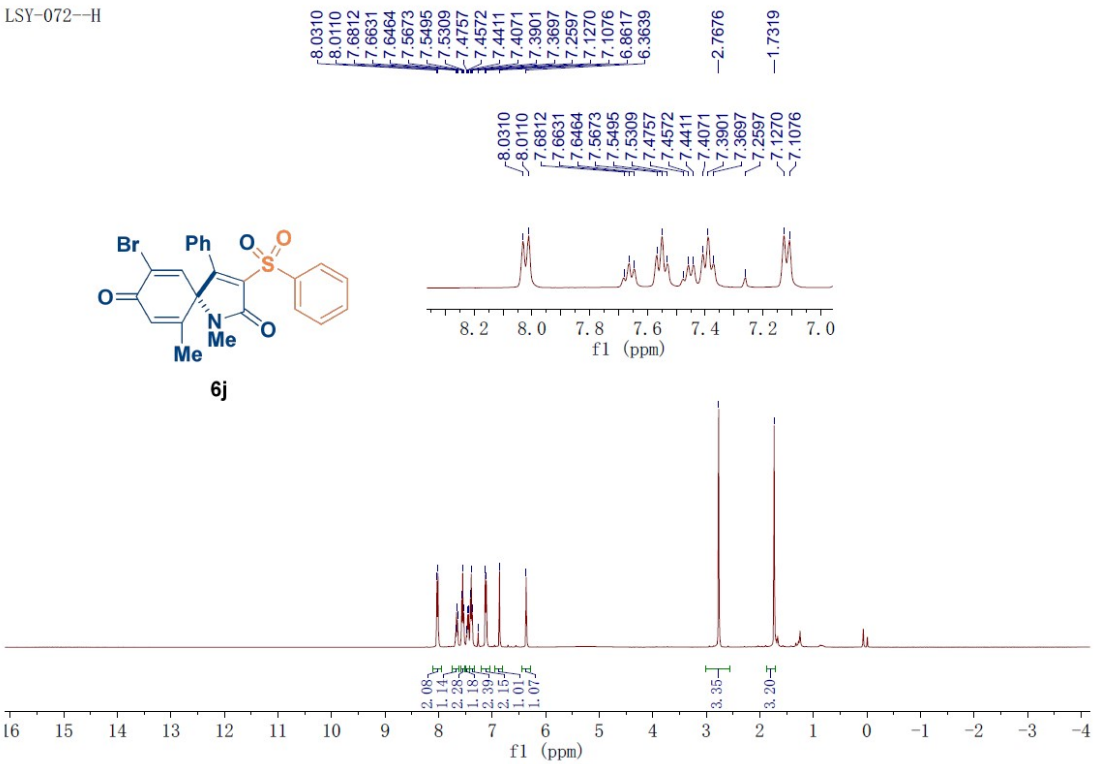
^{1}H NMR of **6i** (400 M, $CDCl_3$)



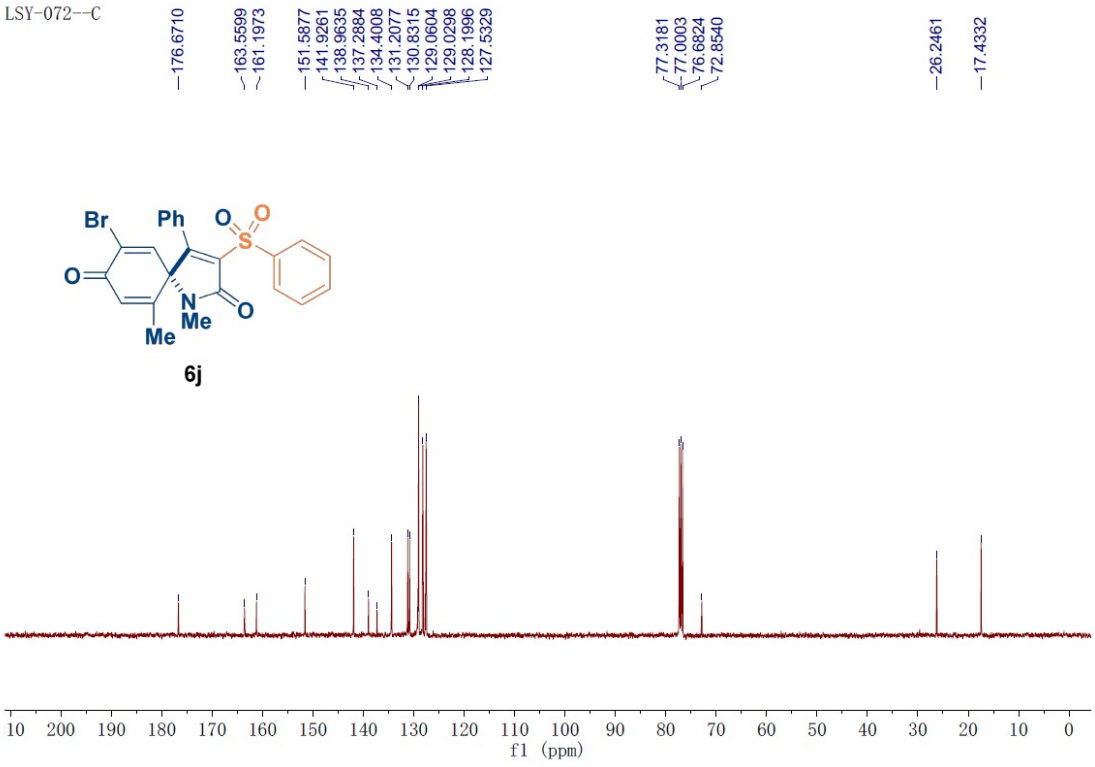
^{13}C NMR of **6i** (100 M, $CDCl_3$)



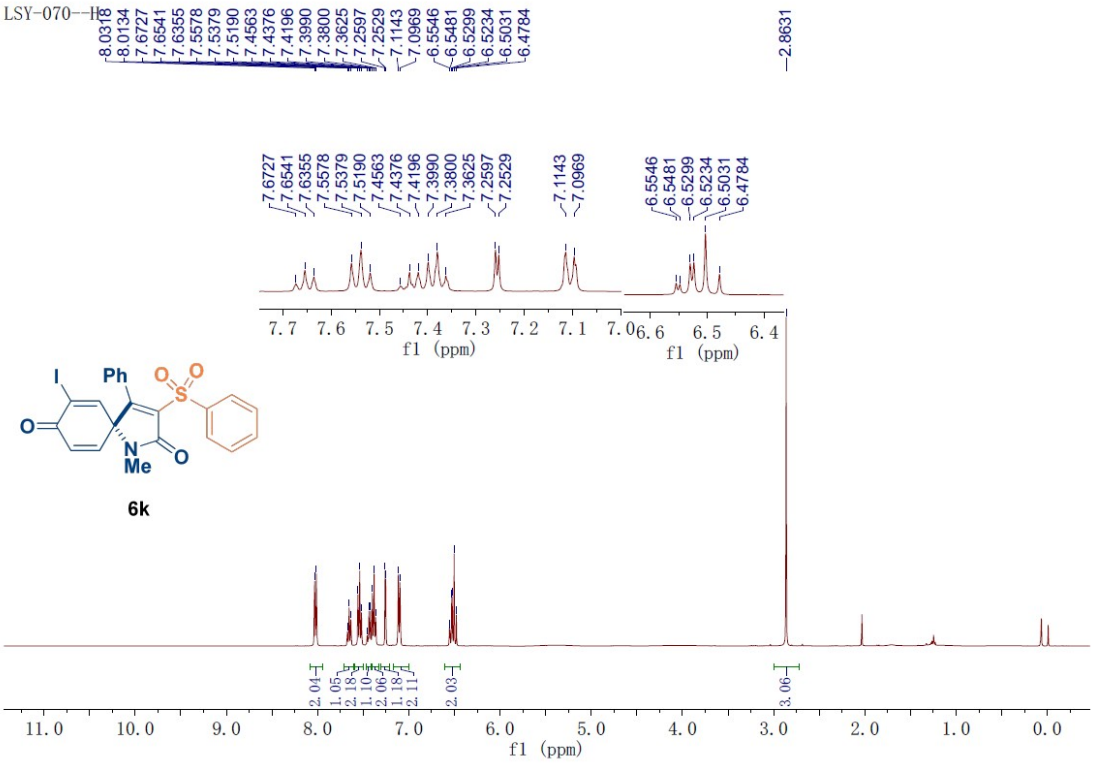
^{1}H NMR of **6j** (400 M, $CDCl_3$)



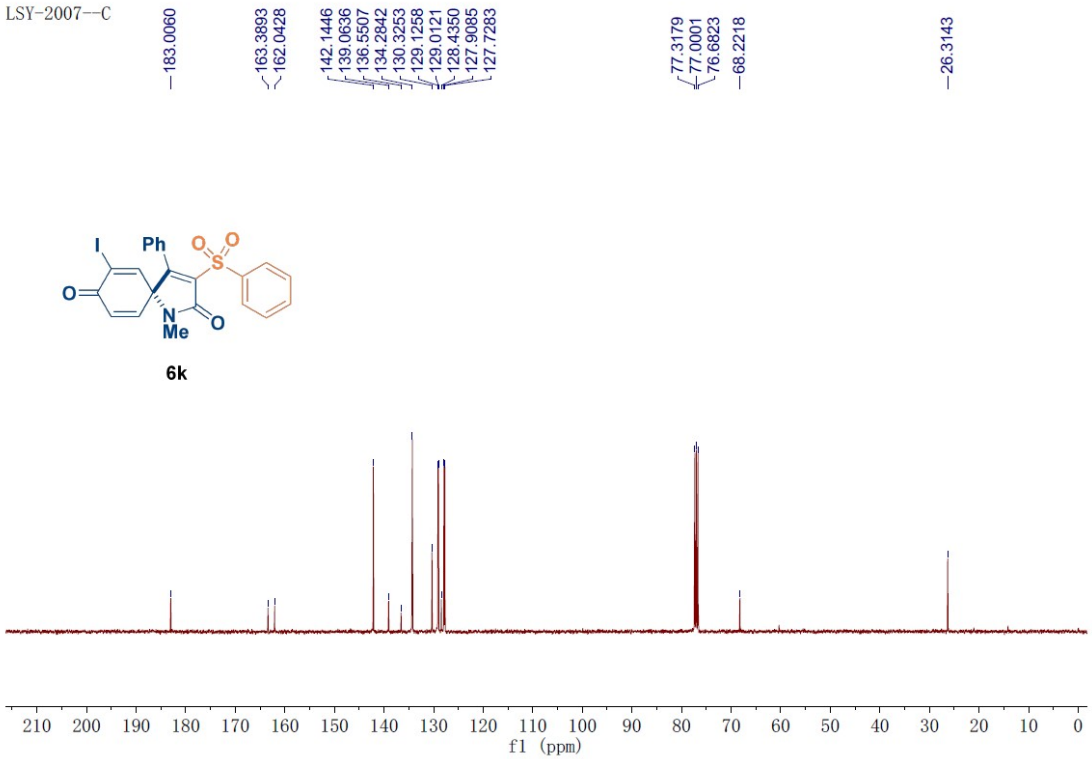
^{13}C NMR of **6j** (100 M, $CDCl_3$)



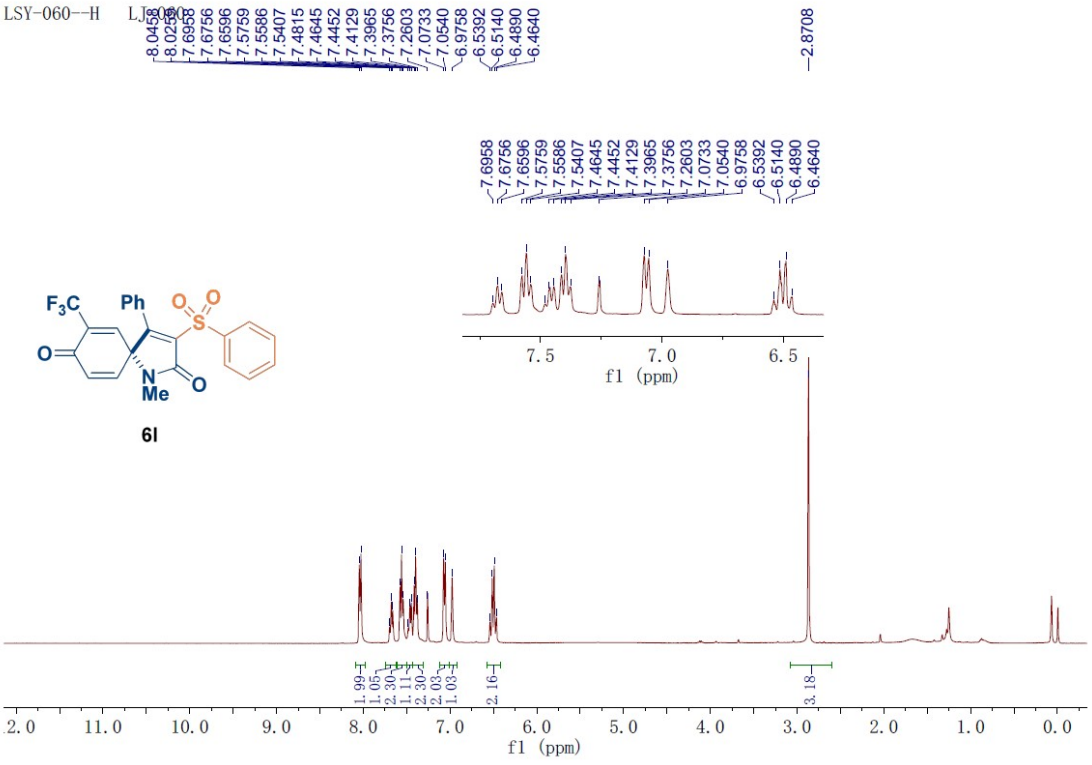
^{1}H NMR of **6k** (400 M, $CDCl_3$)



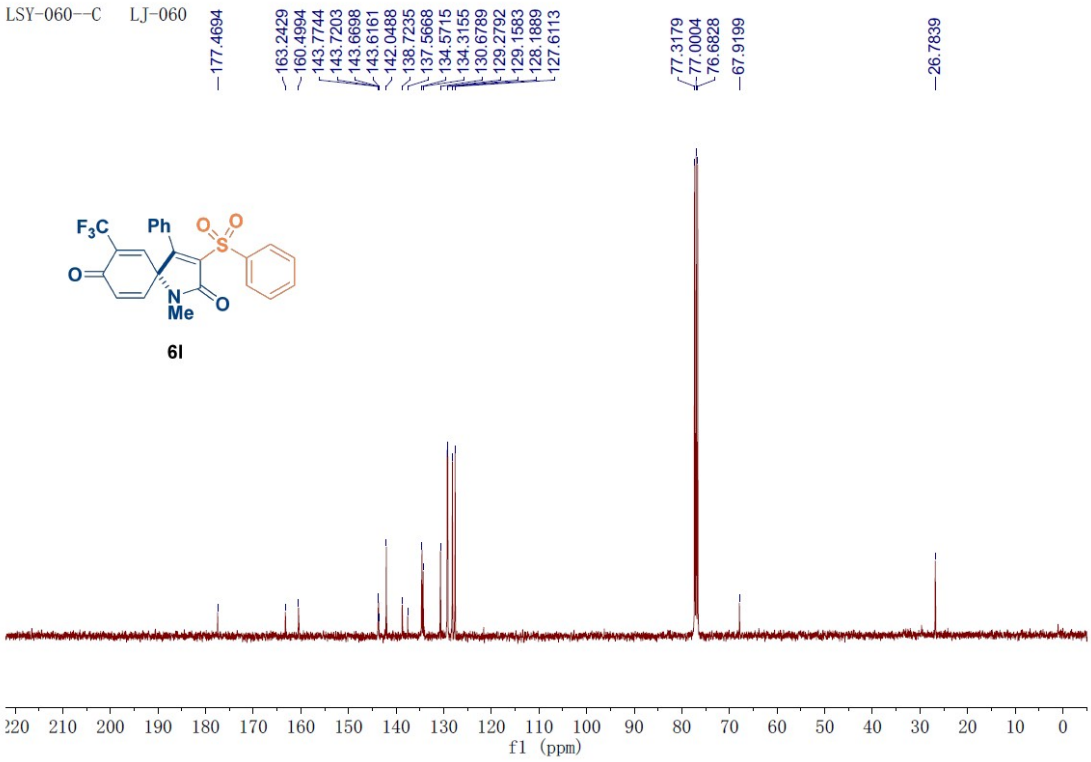
^{13}C NMR of **6k** (100 M, $CDCl_3$)



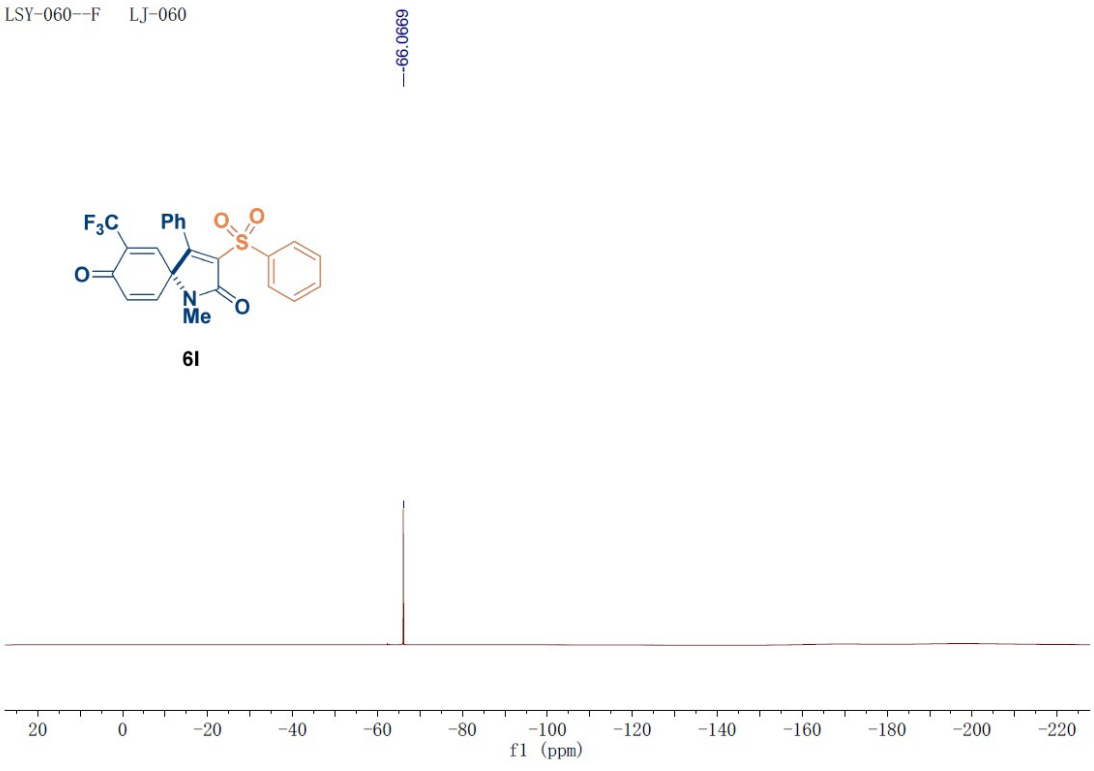
^{1}H NMR of **6l** (400 M, $CDCl_3$)



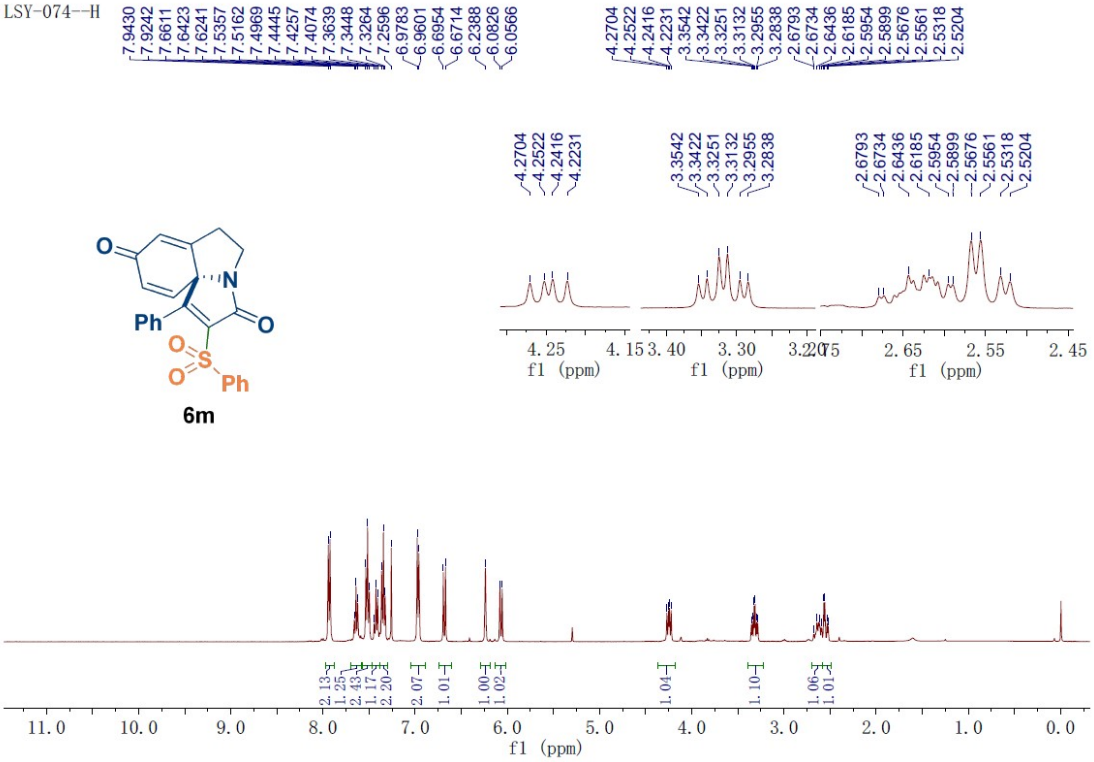
^{13}C NMR of **6l** (100 M, $CDCl_3$)



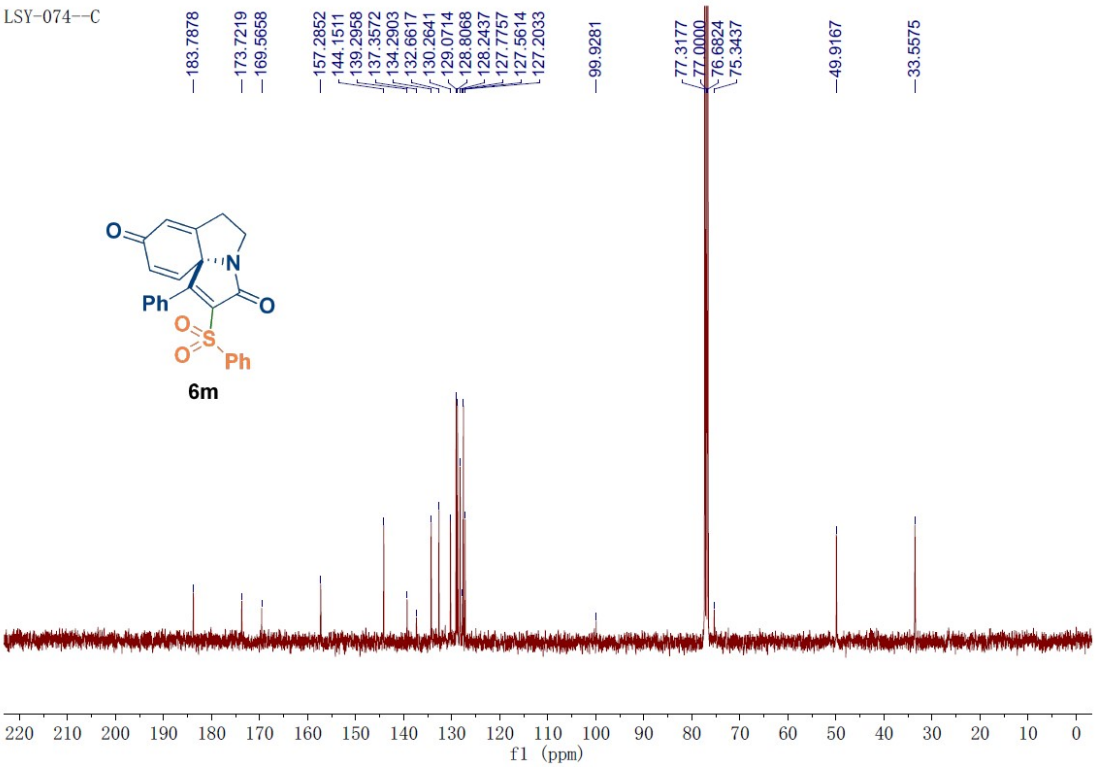
^{19}F NMR of **6l** (376 M, $CDCl_3$)



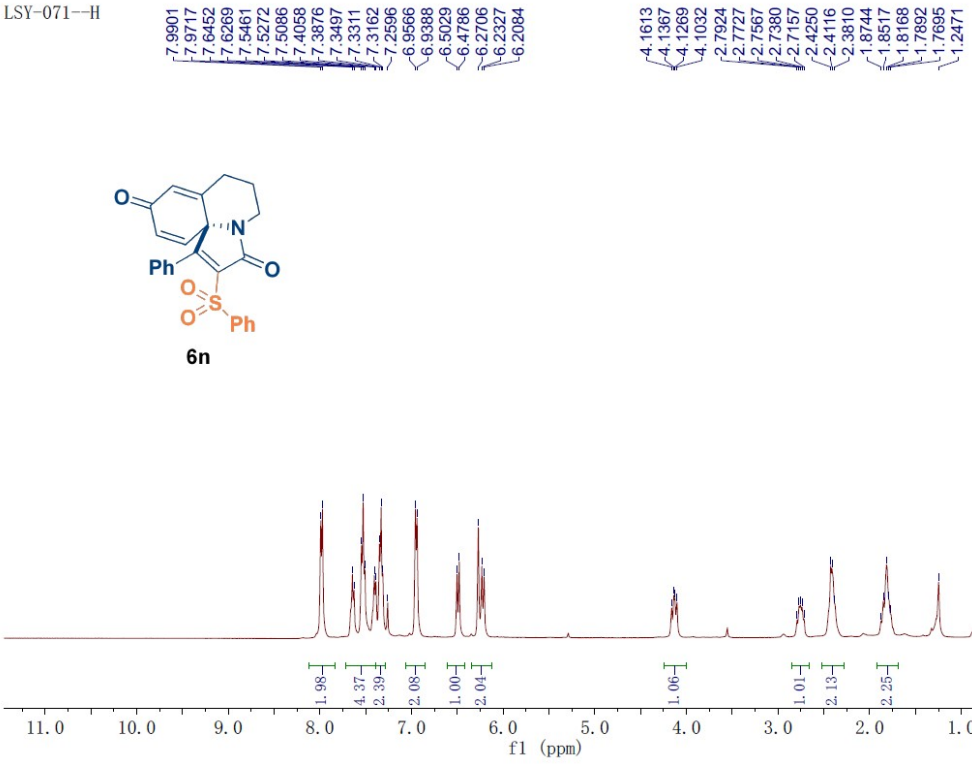
^{1}H NMR of **6m** (400 M, $CDCl_3$)



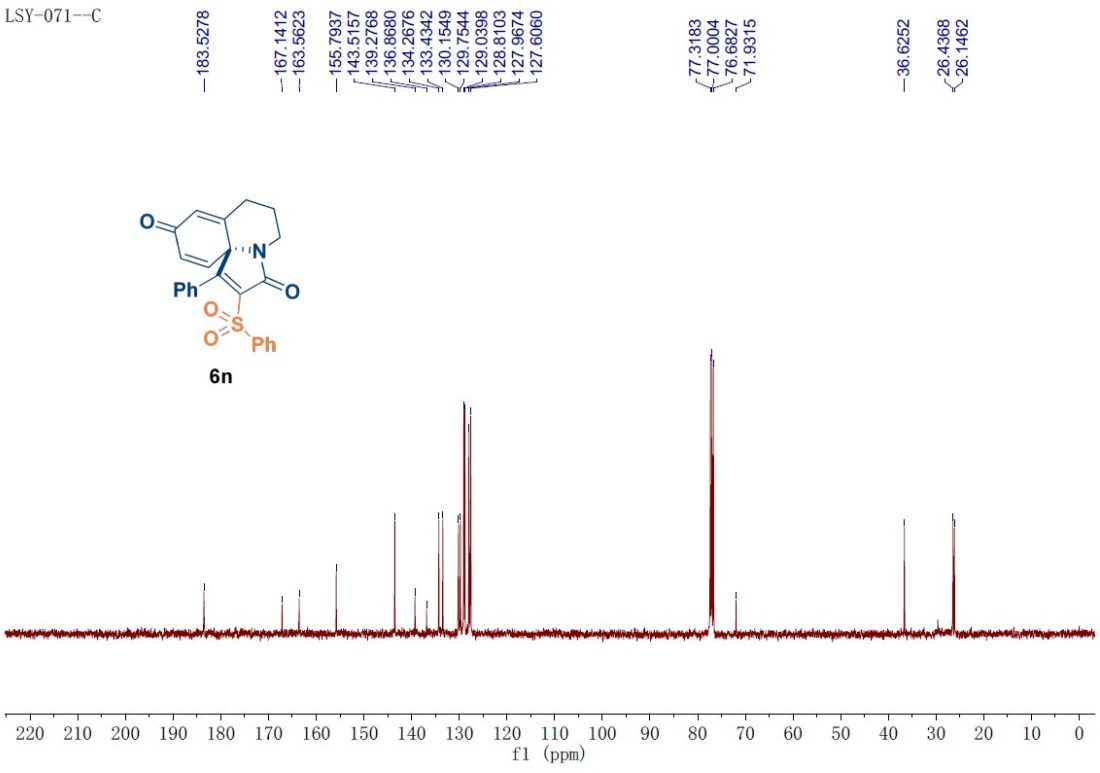
^{13}C NMR of **6m** (100 M, $CDCl_3$)



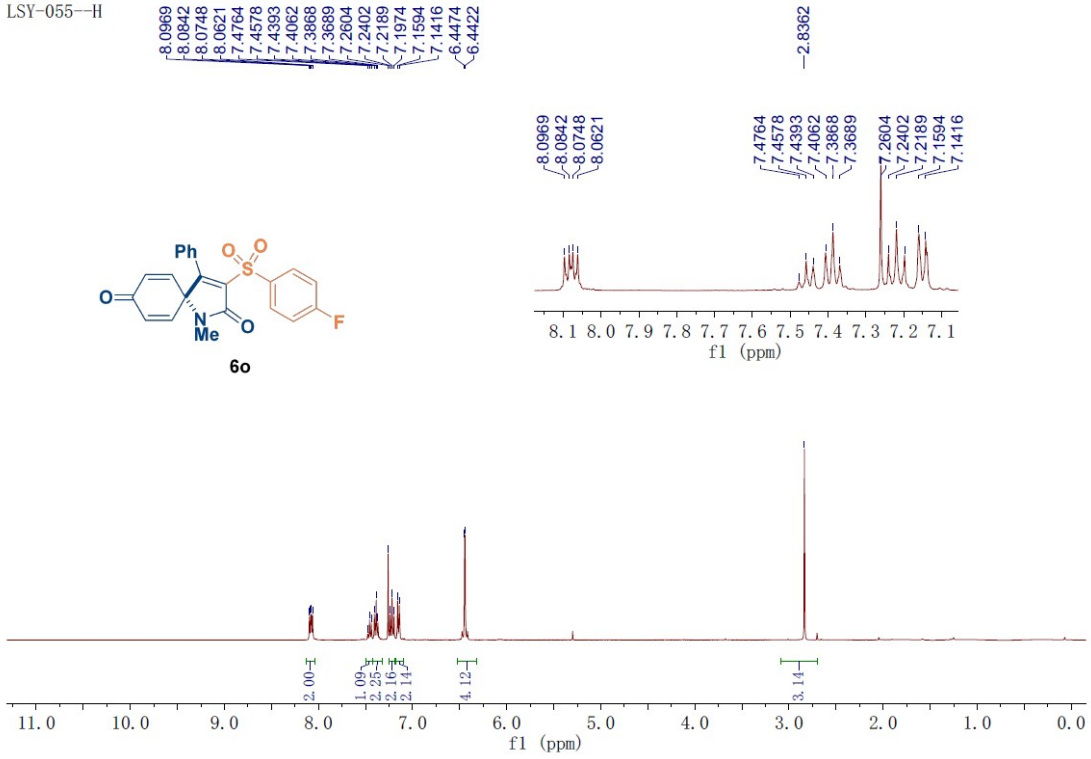
^{1}H NMR of **6n** (400 M, $CDCl_3$)



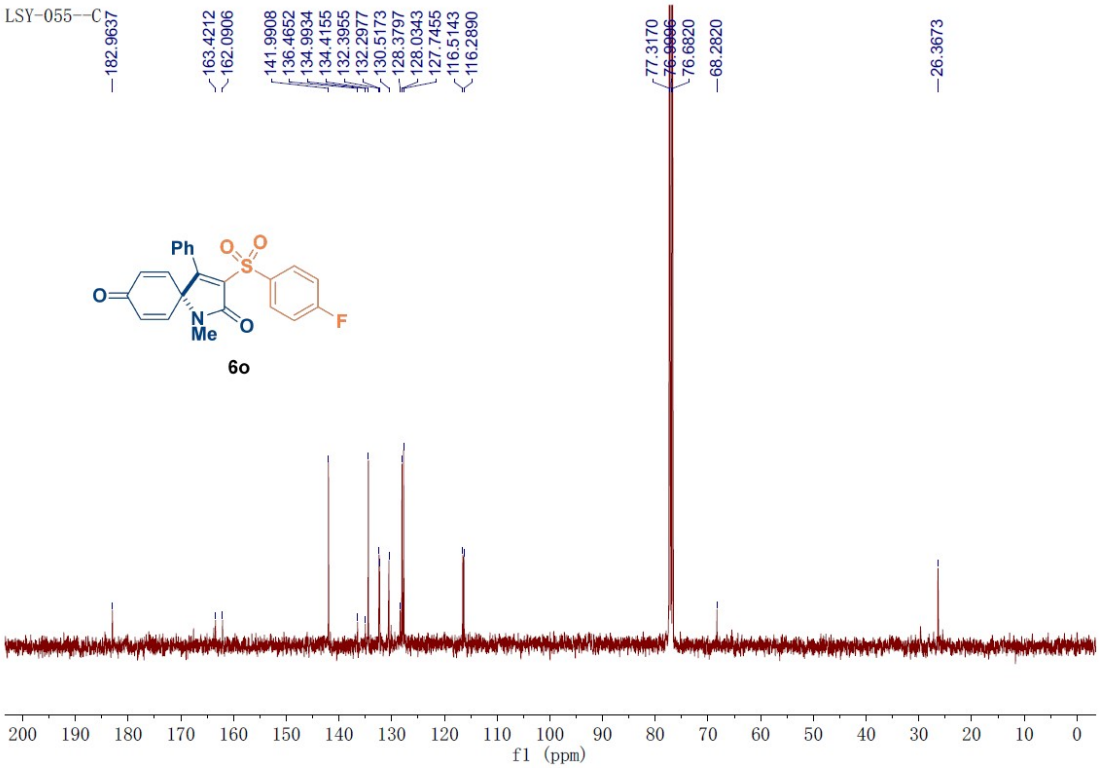
^{13}C NMR of **6n** (100 M, $CDCl_3$)



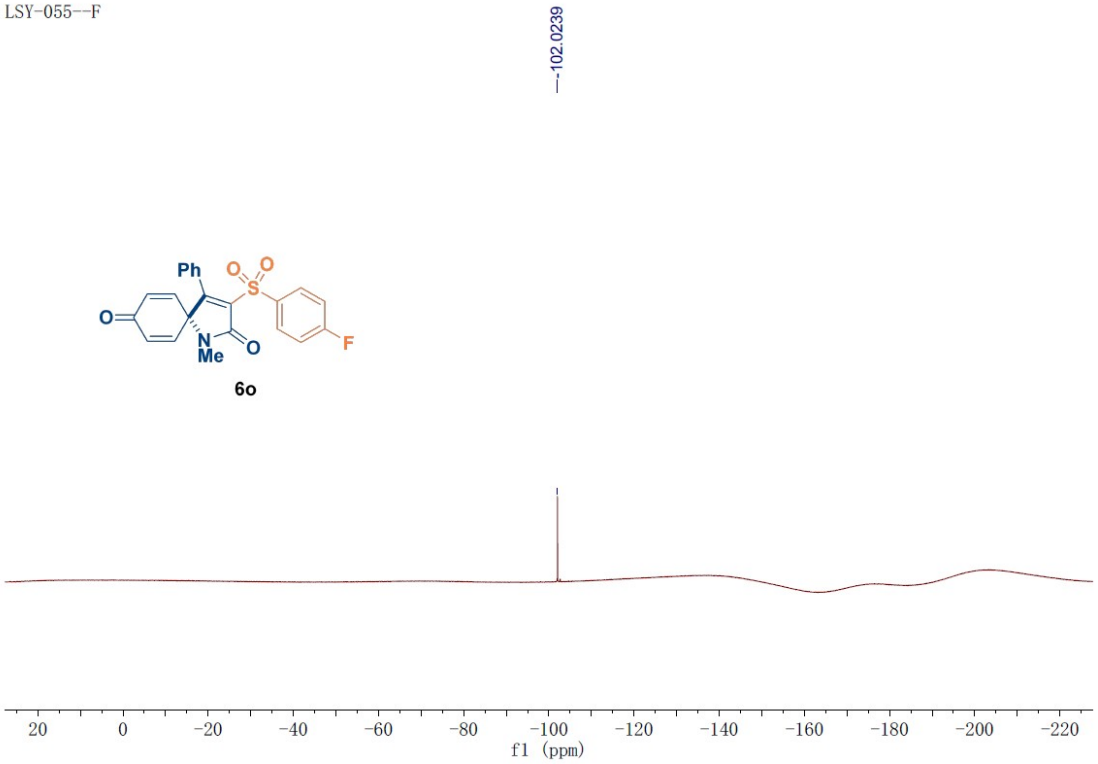
^{1}H NMR of **6o** (400 M, $CDCl_3$)



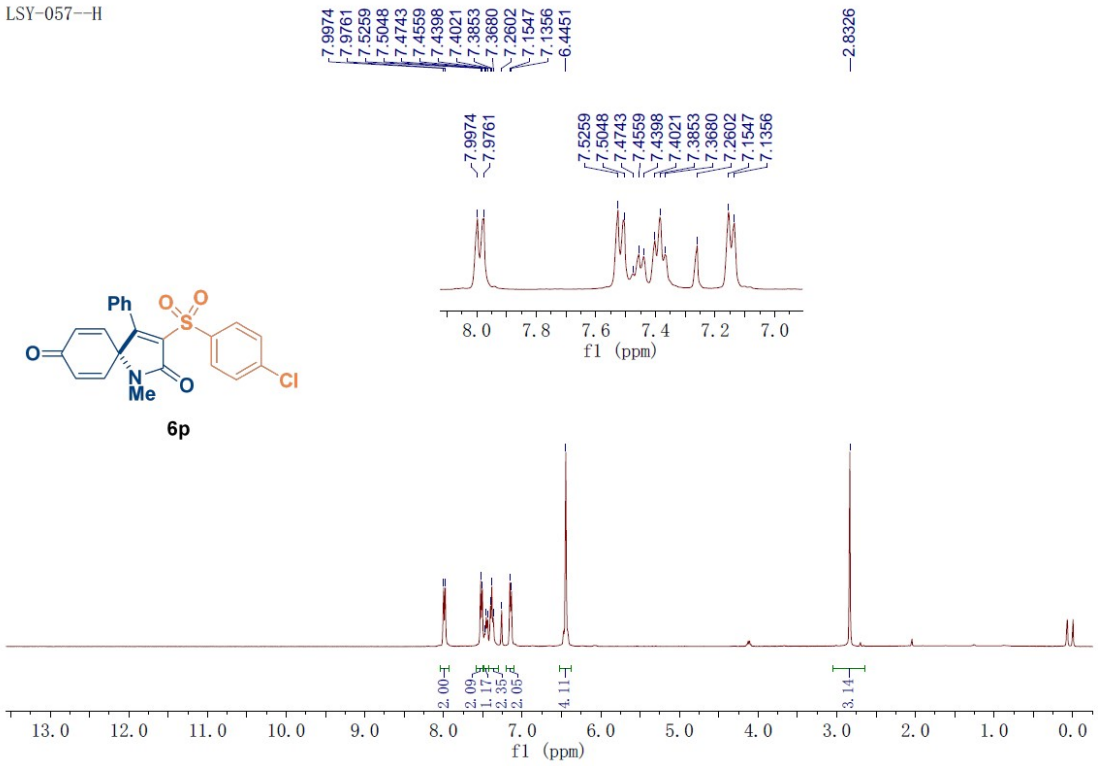
^{13}C NMR of **6o** (100 M, $CDCl_3$)



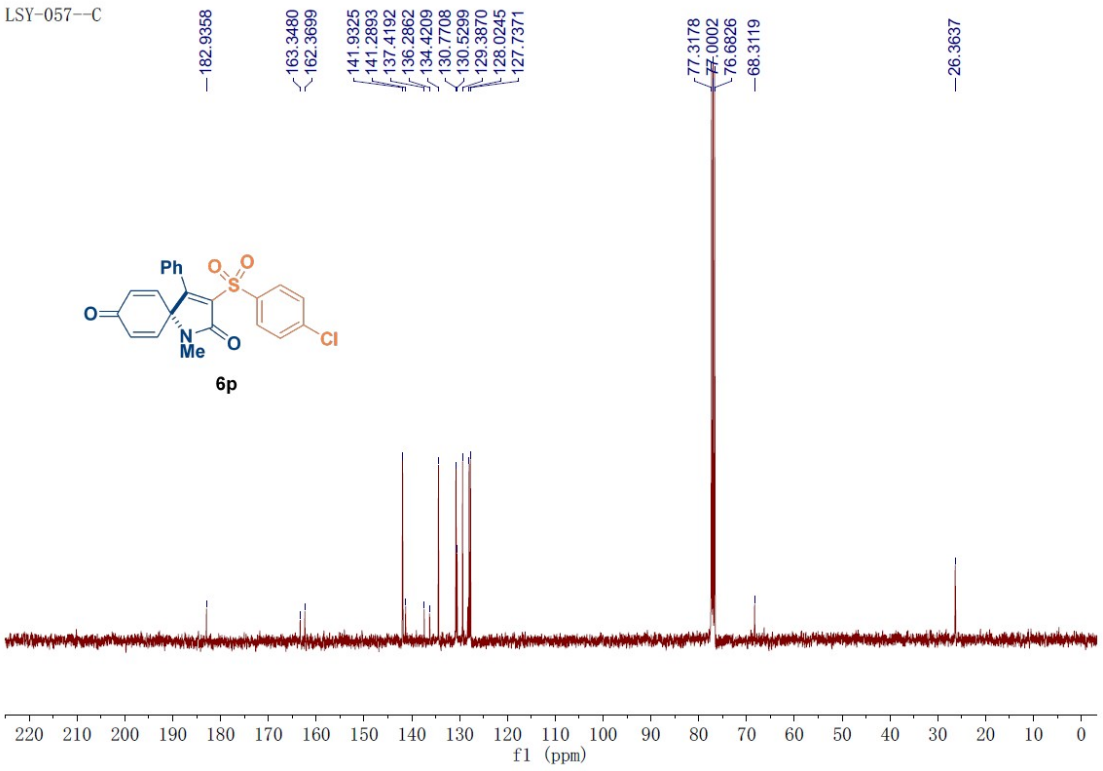
^{19}F NMR of **6o** (376 M, $CDCl_3$)



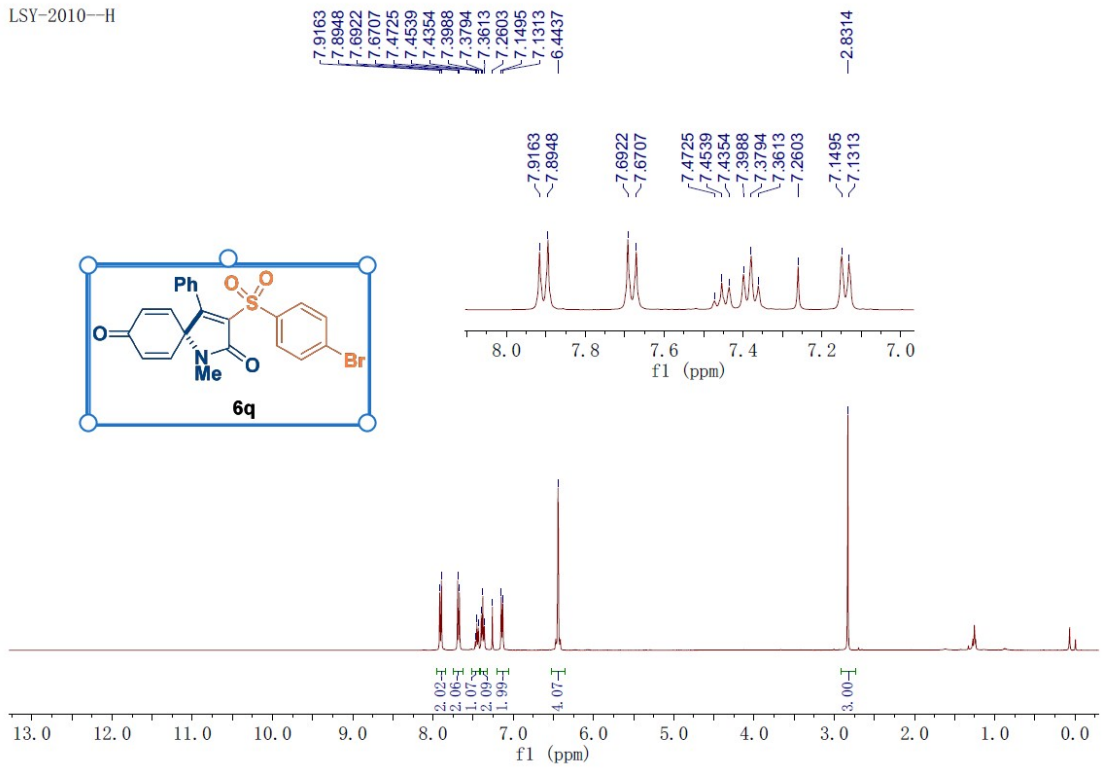
^{1}H NMR of **6p** (400 M, $CDCl_3$)



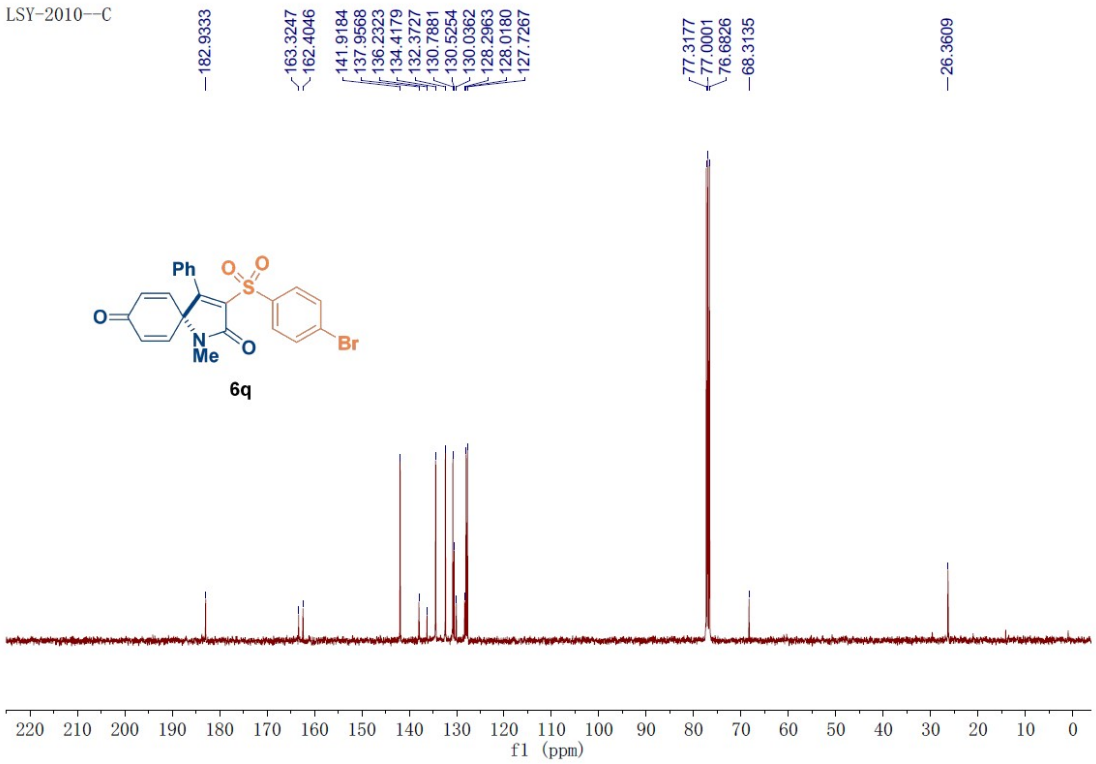
^{13}C NMR of **6p** (100 M, $CDCl_3$)



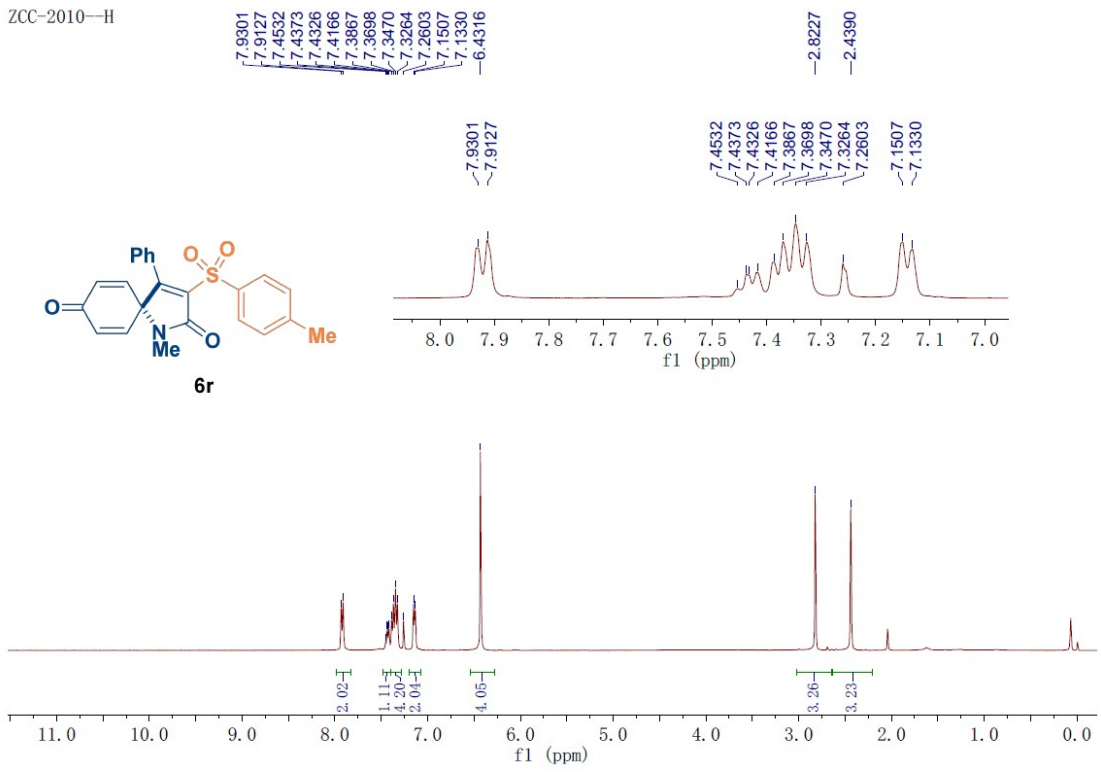
^{1}H NMR of **6q** (400 M, $CDCl_3$)



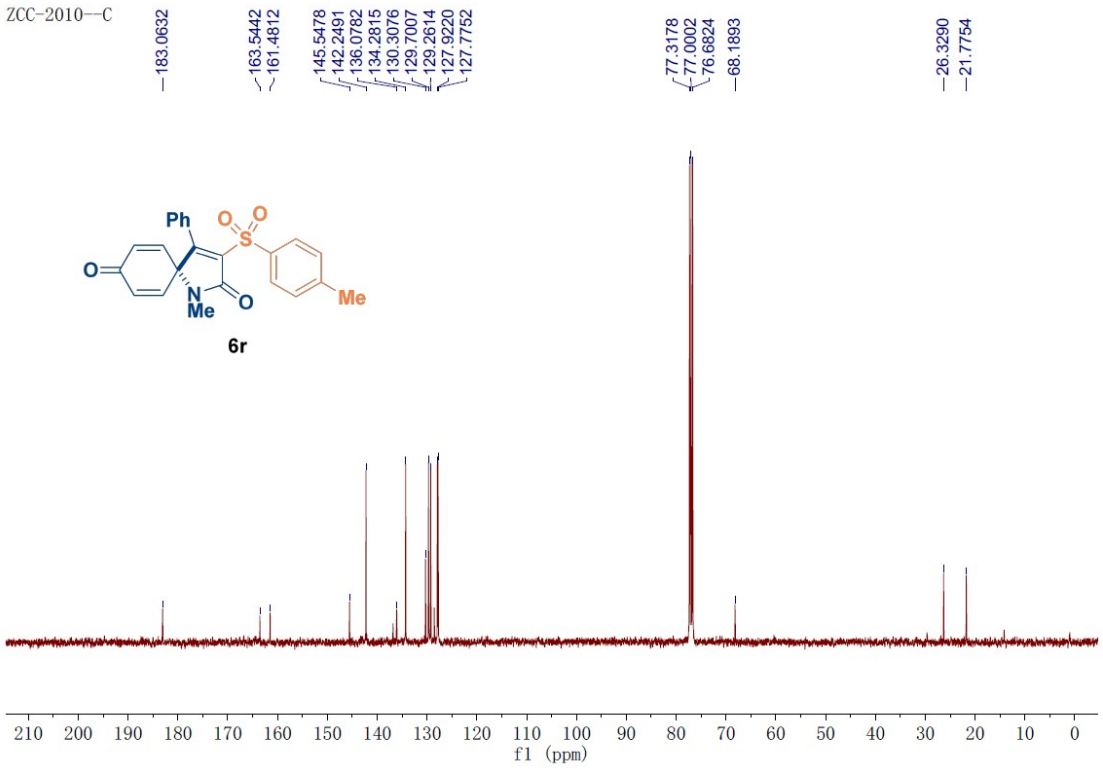
^{13}C NMR of **6q** (100 M, $CDCl_3$)



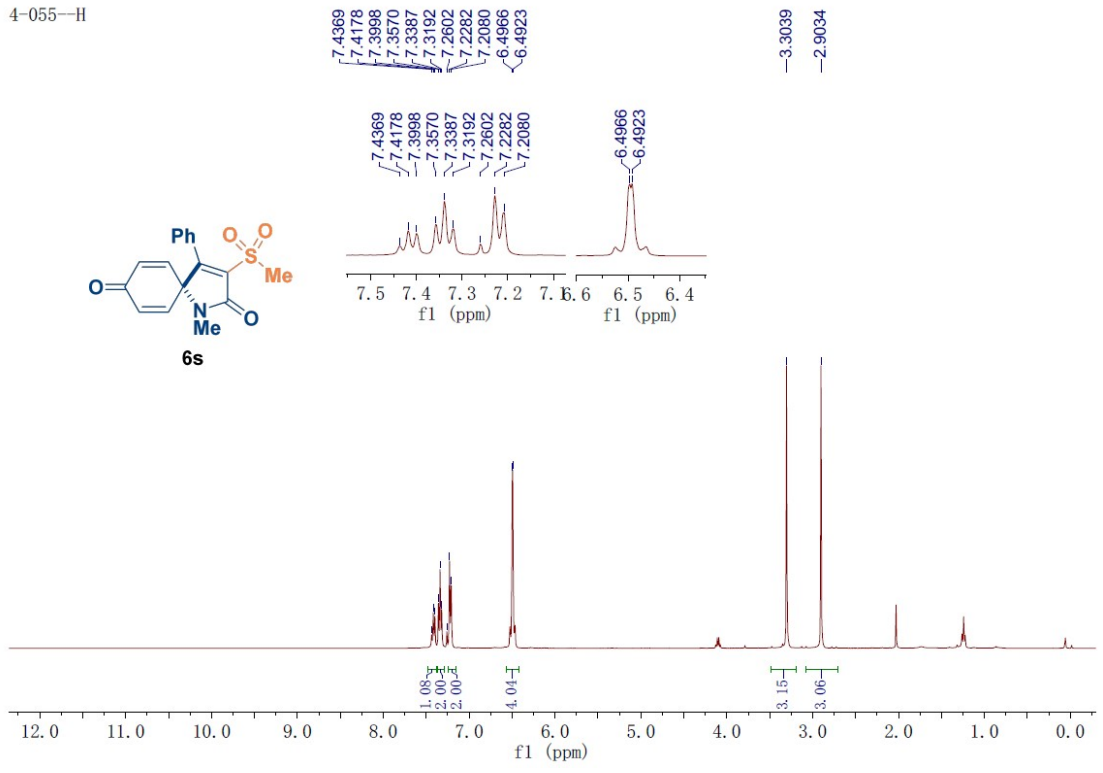
^{1}H NMR of **6r** (400 M, $CDCl_3$)



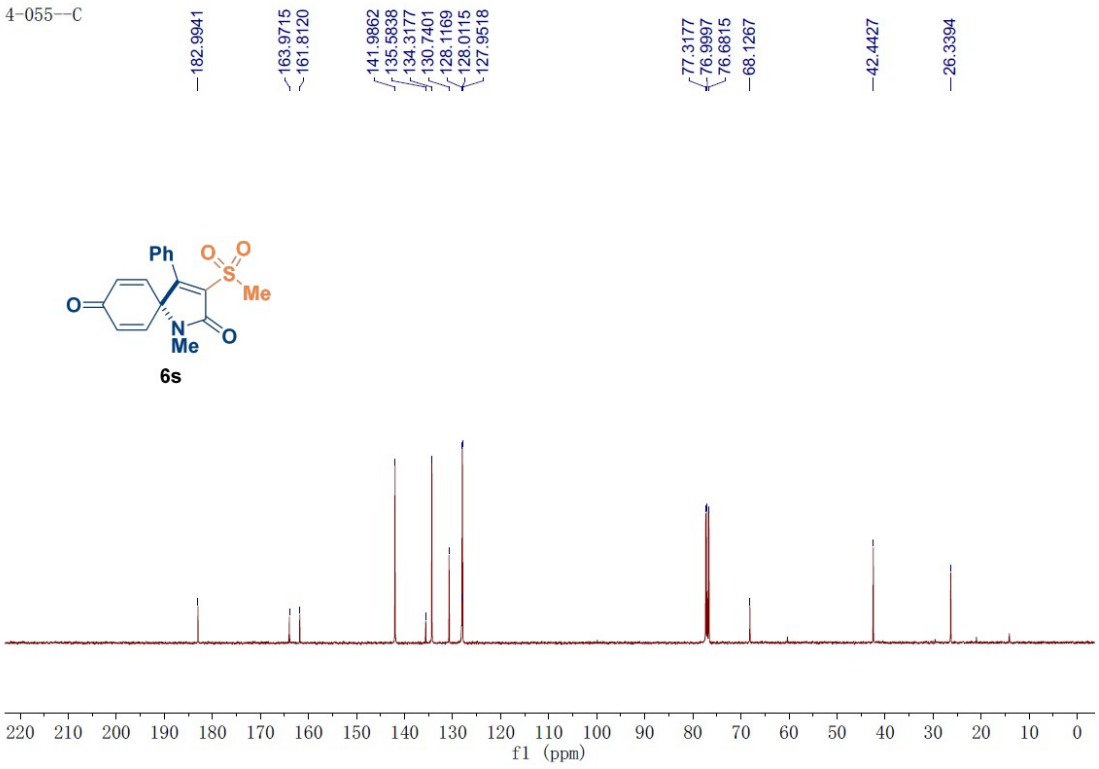
^{13}C NMR of **6r** (100 M, $CDCl_3$)



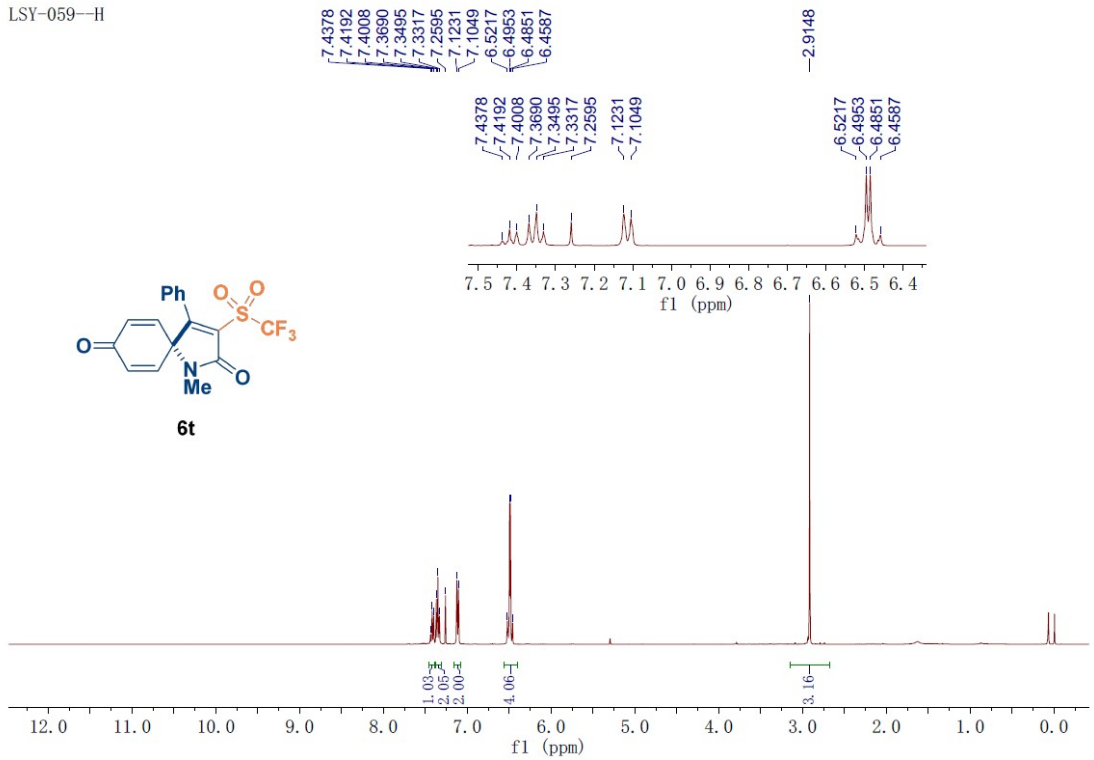
^{1}H NMR of **6s** (400 M, $CDCl_3$)



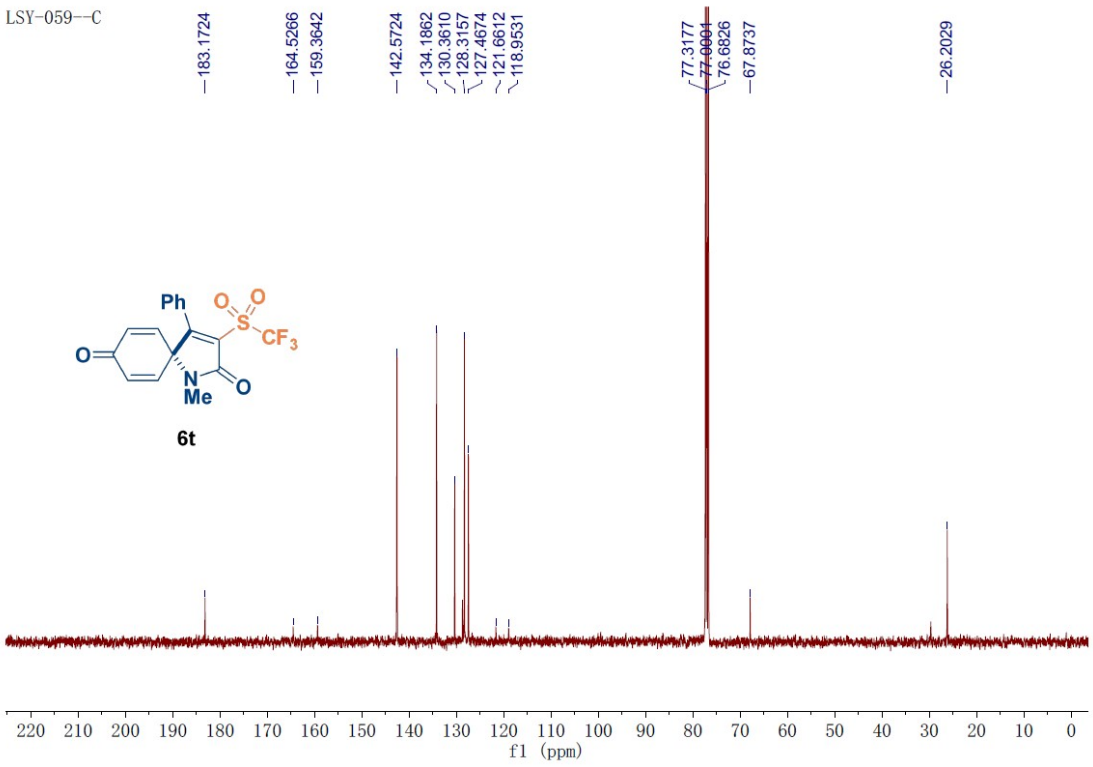
^{13}C NMR of **6s** (100 M, $CDCl_3$)



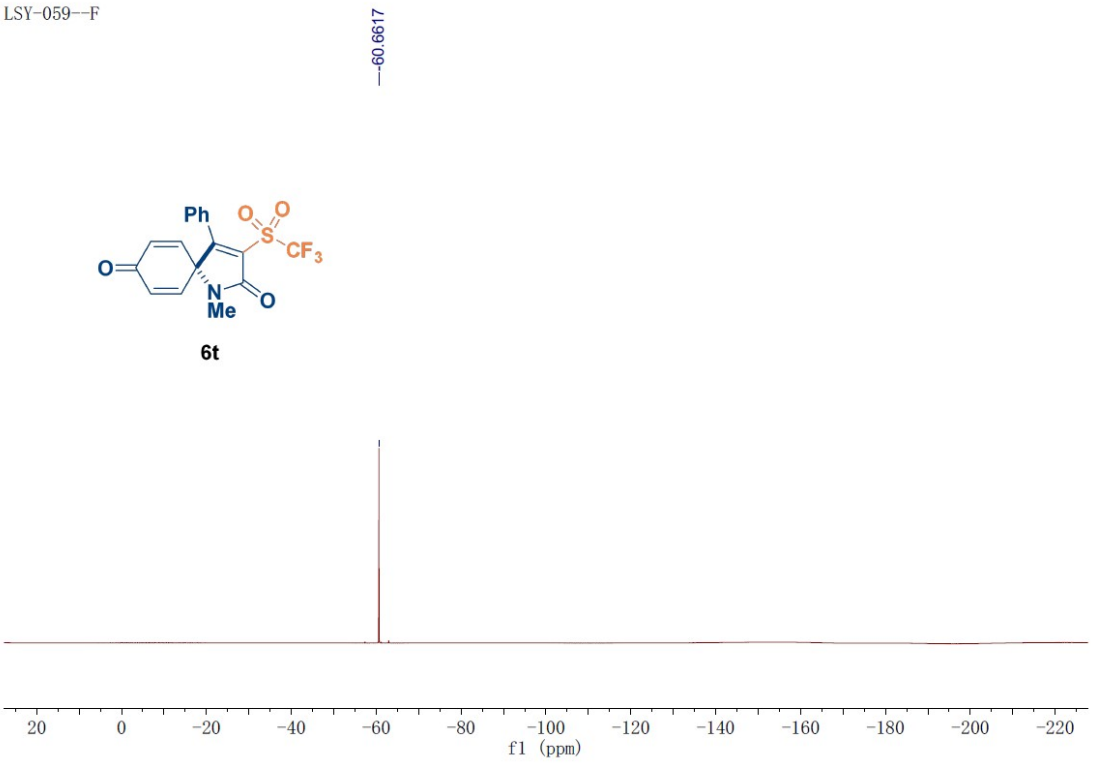
^{1}H NMR of **6t** (400 M, $CDCl_3$)



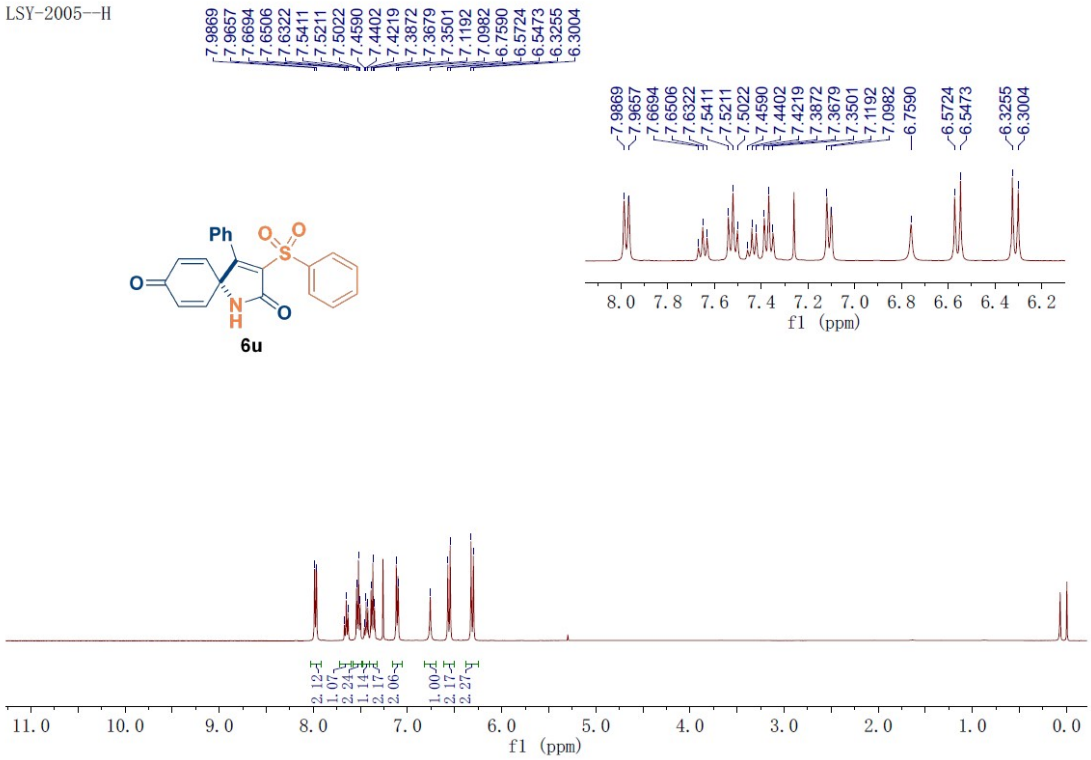
^{13}C NMR of **6t** (100 M, $CDCl_3$)



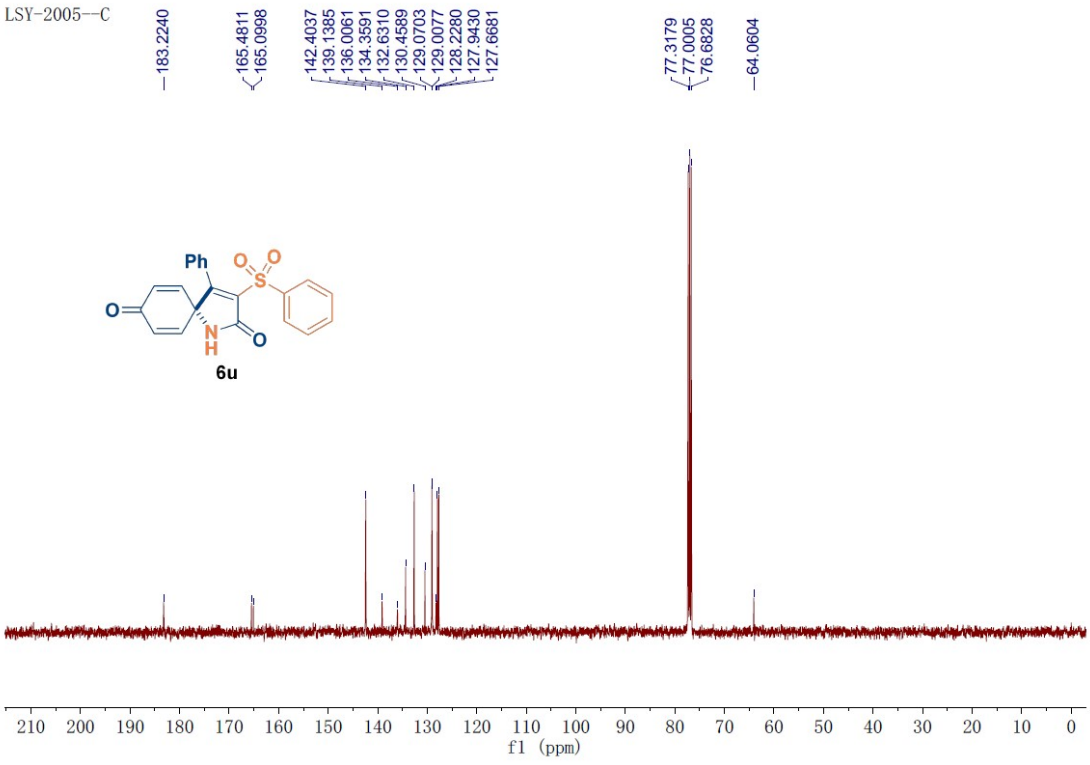
^{19}F NMR of **6t** (376 M, $CDCl_3$)



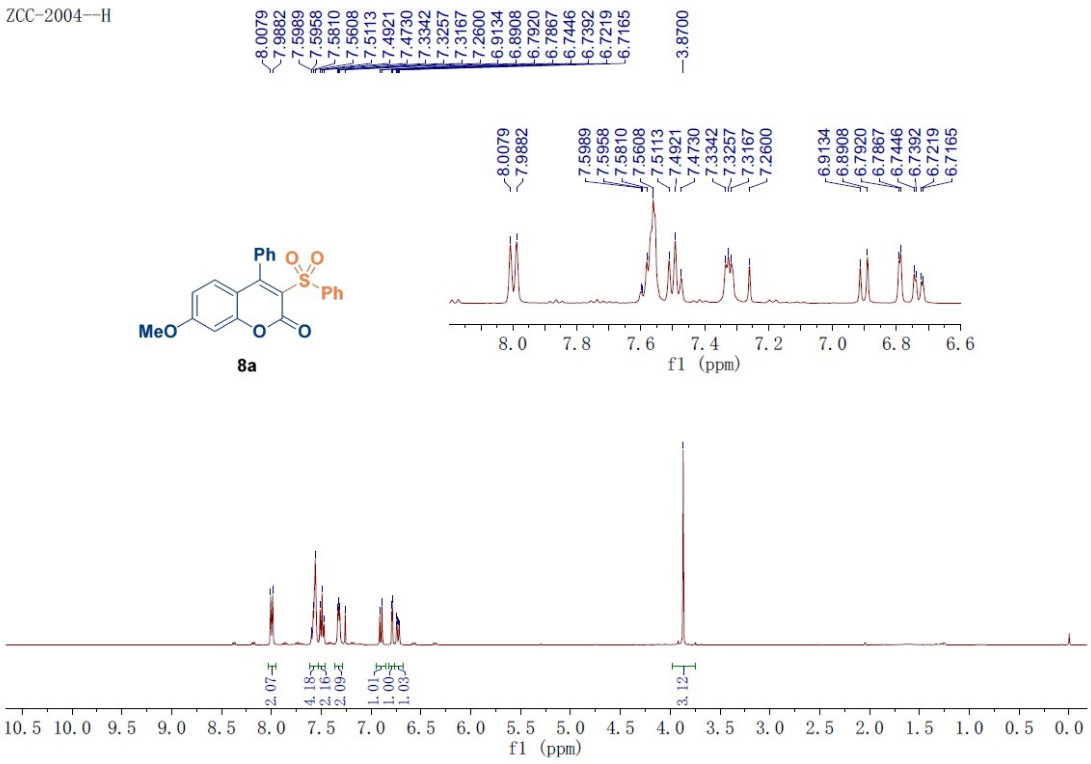
^{1}H NMR of **6u** (400 M, $CDCl_3$)



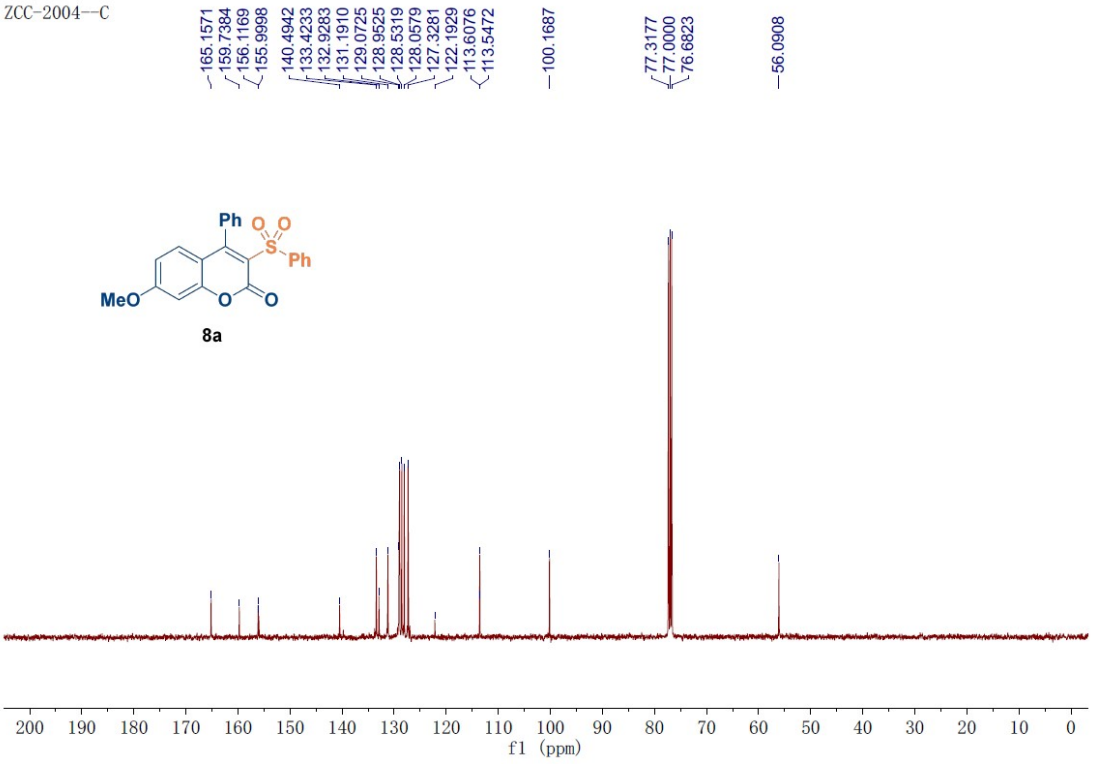
^{13}C NMR of **6u** (100 M, $CDCl_3$)



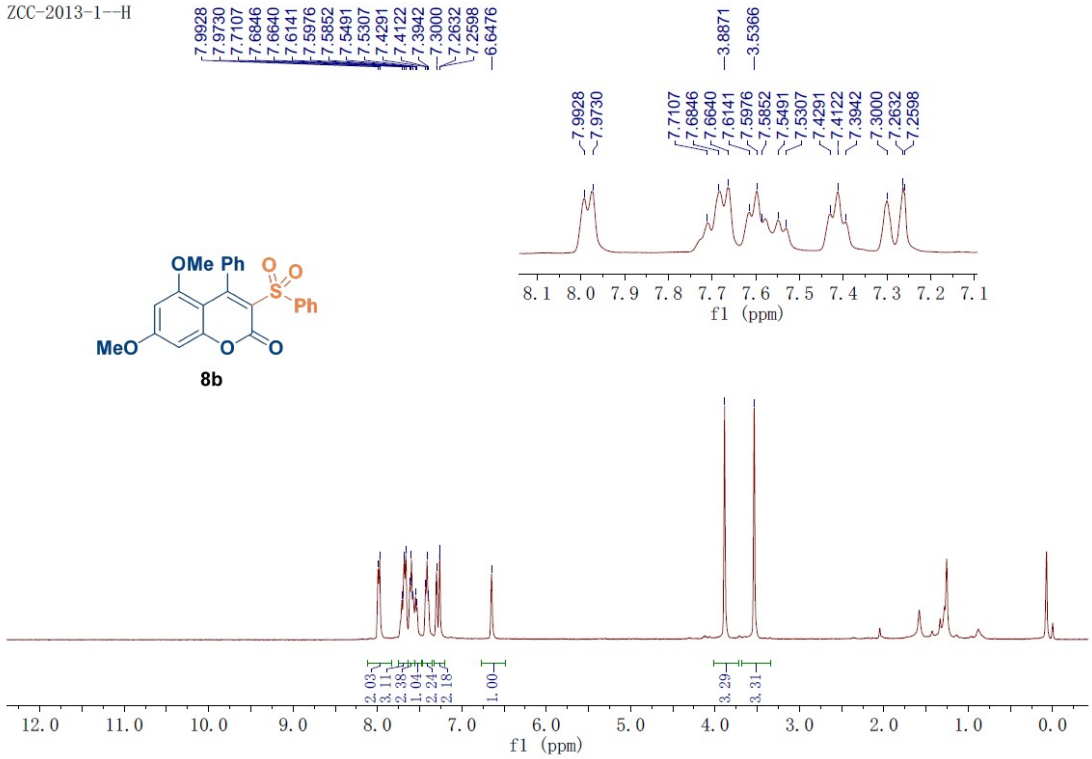
^{1}H NMR of **8a** (400 M, $CDCl_3$)



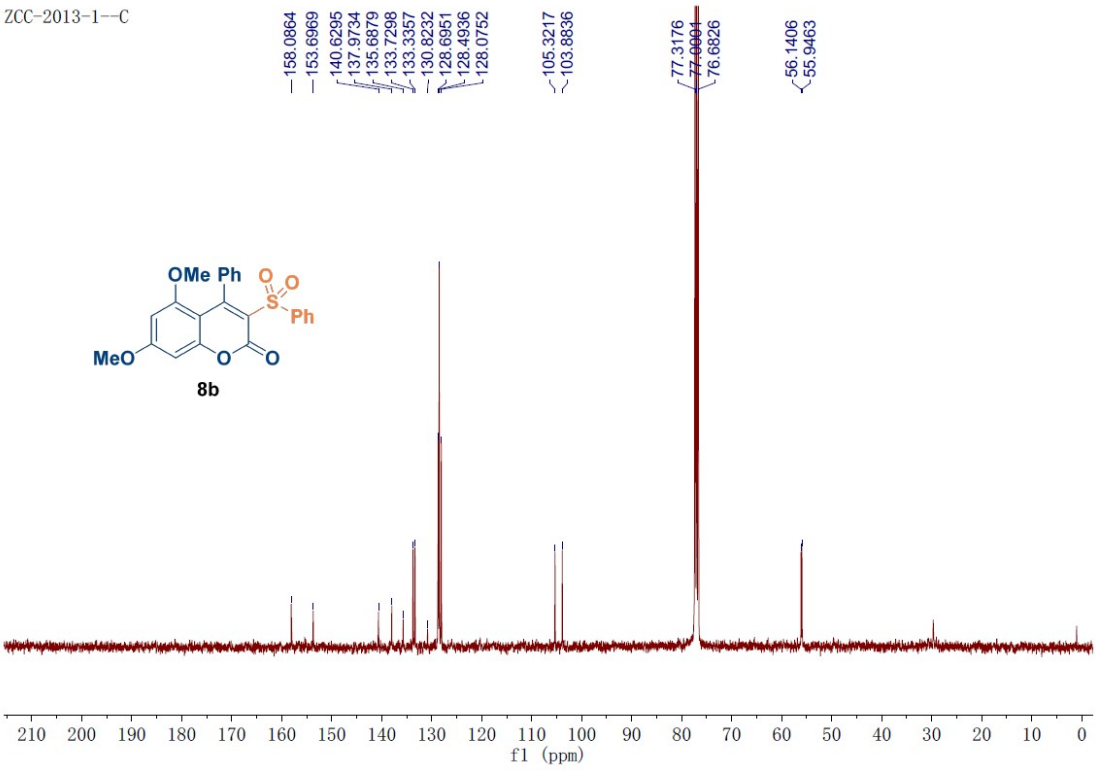
^{13}C NMR of **8a** (100 M, $CDCl_3$)



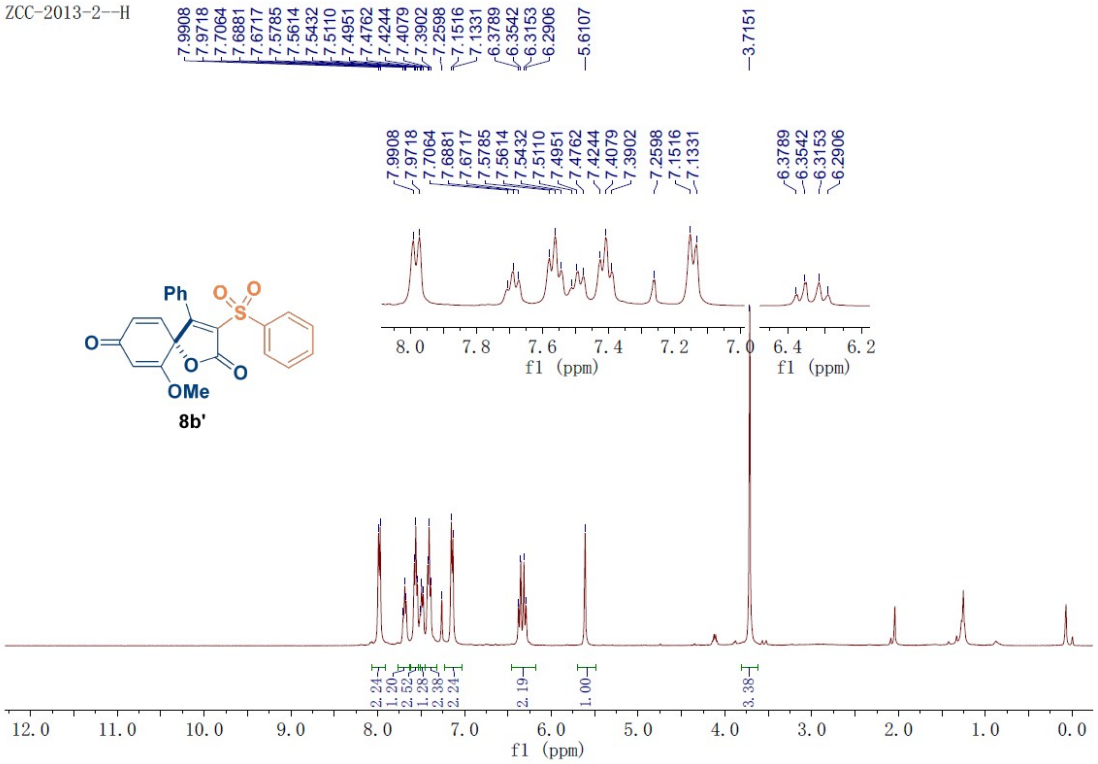
^{1}H NMR of **8b** (400 M, $CDCl_3$)



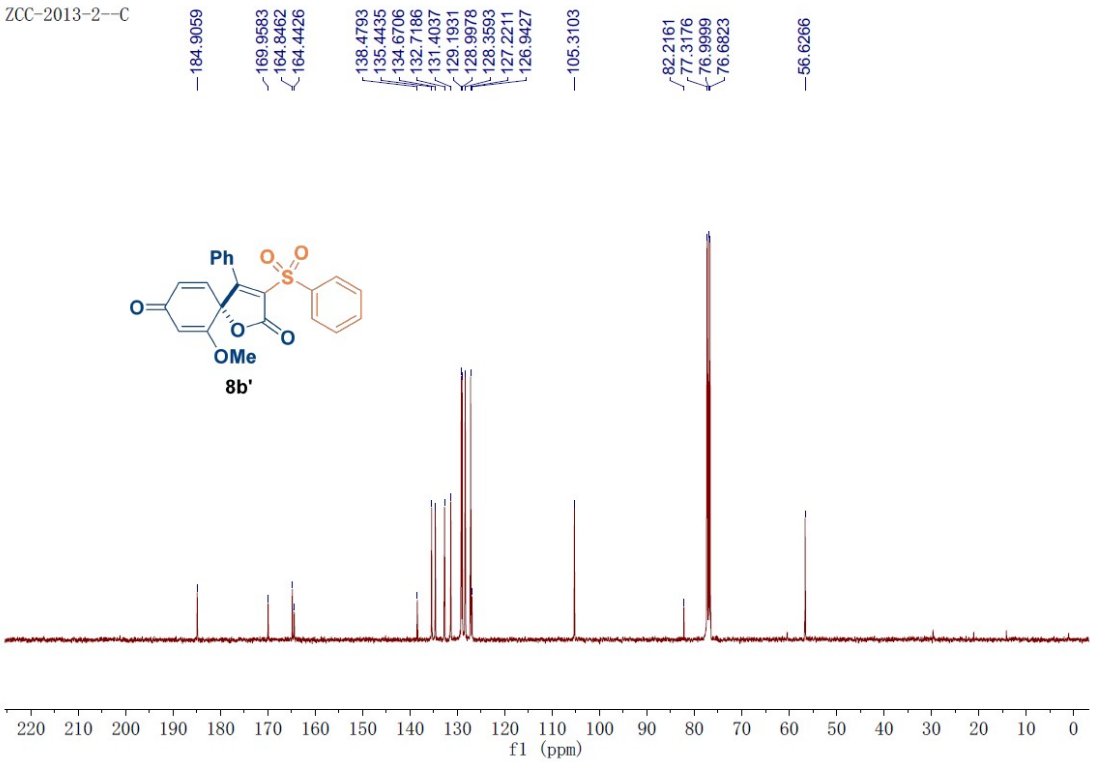
^{13}C NMR of **8b** (100 M, $CDCl_3$)



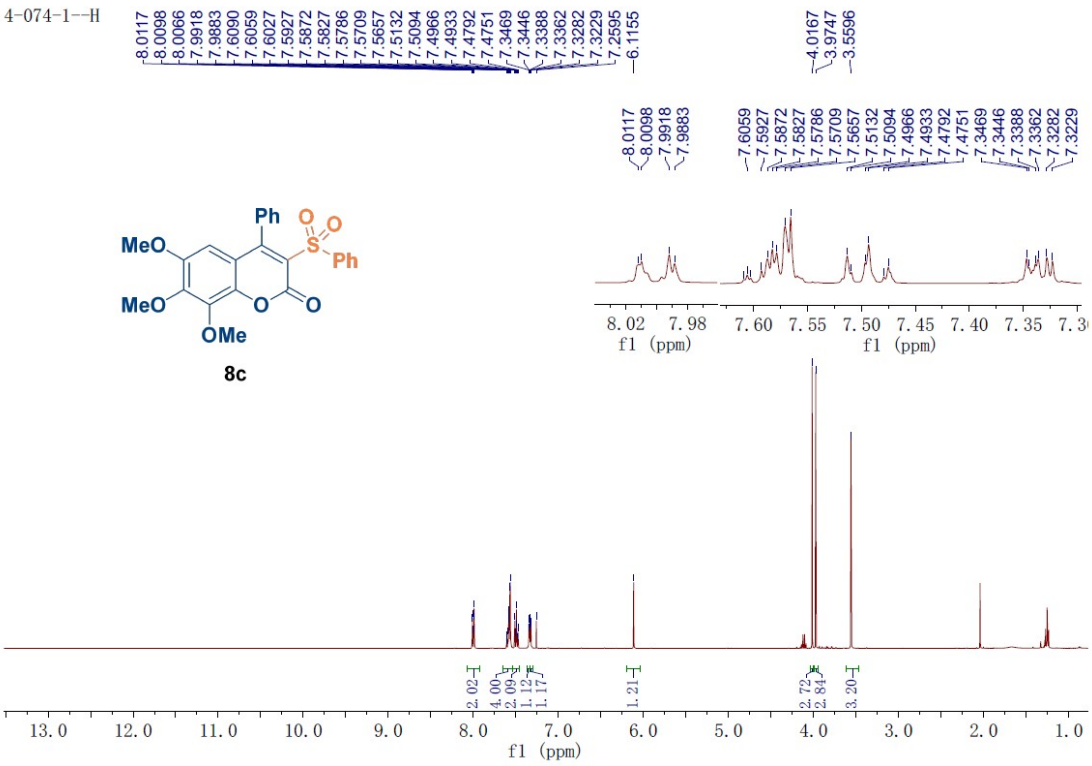
^{1}H NMR of **8b'** (400 M, $CDCl_3$)



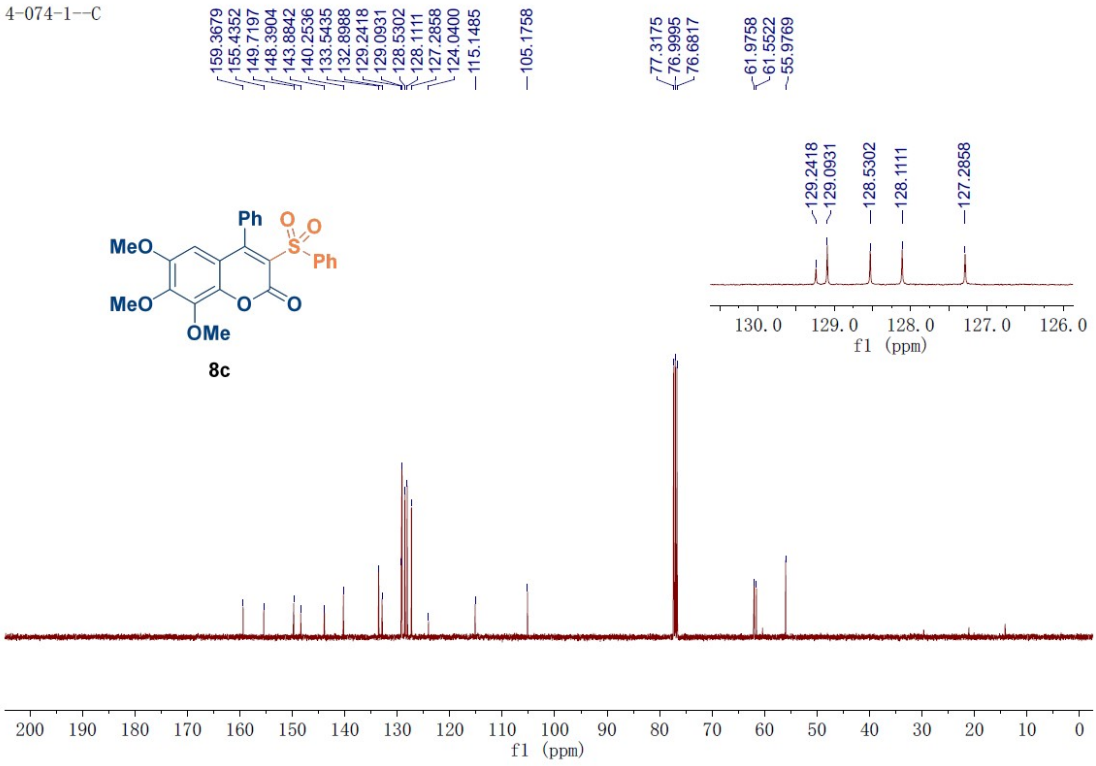
^{13}C NMR of **8b'** (100 M, $CDCl_3$)



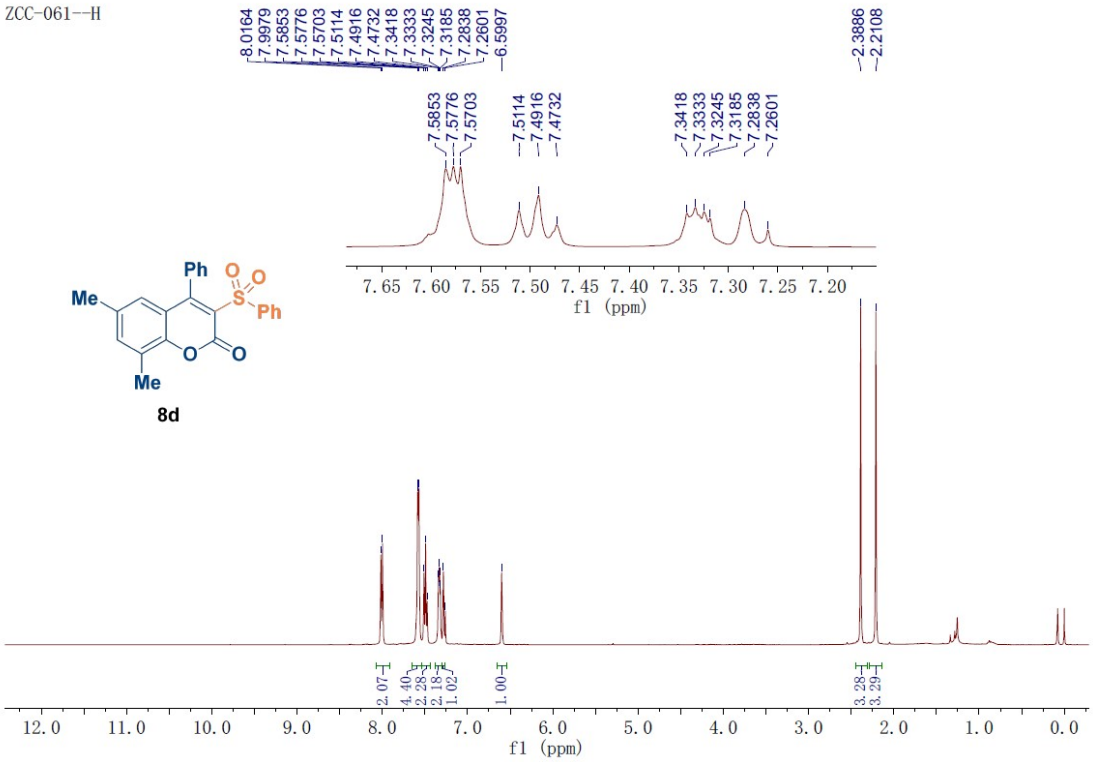
^{1}H NMR of **8c** (400 M, $CDCl_3$)



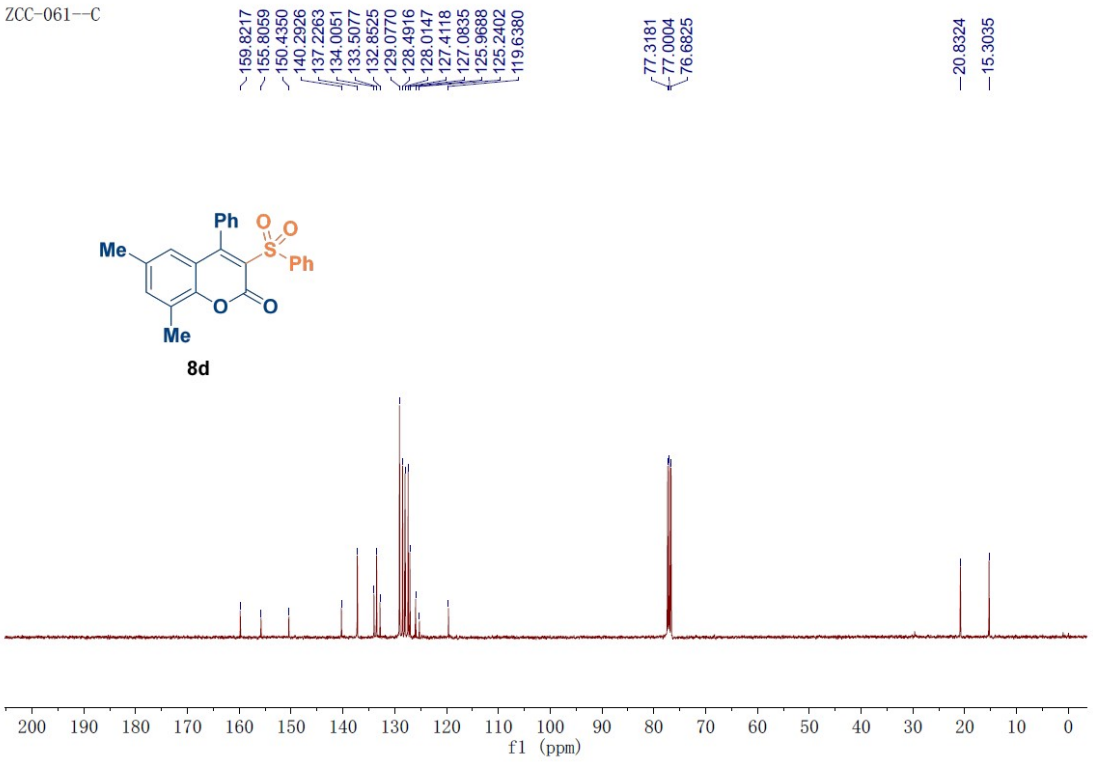
^{13}C NMR of **8c** (100 M, $CDCl_3$)



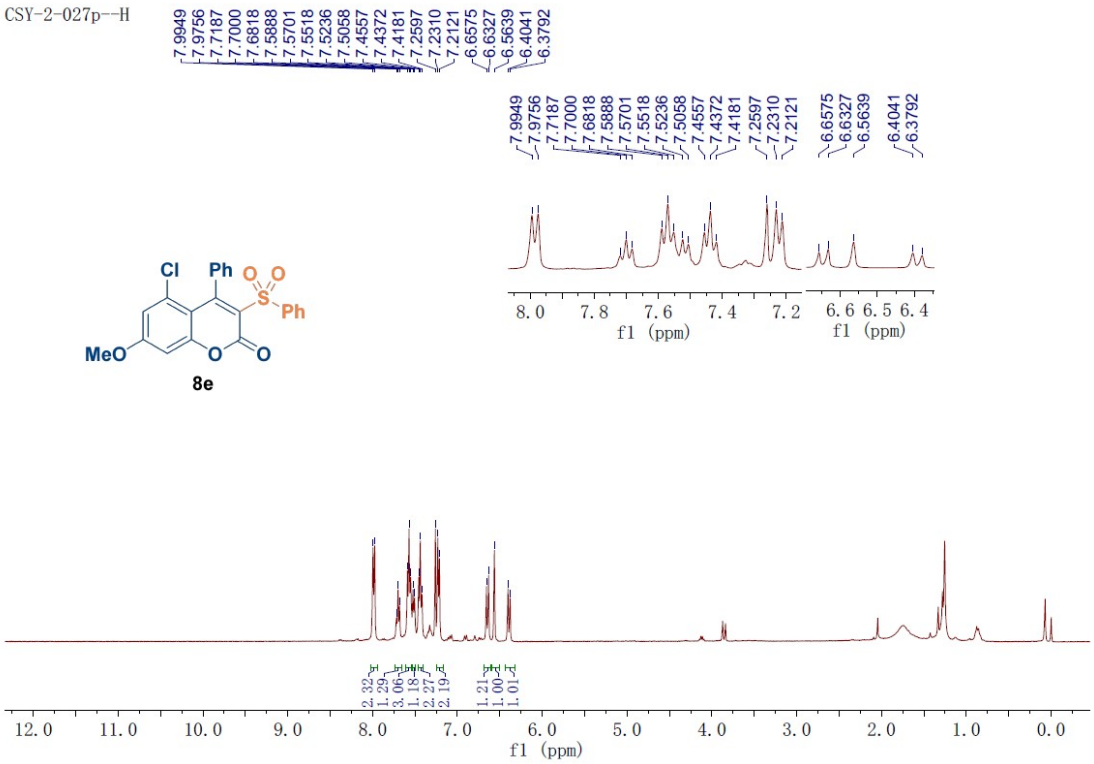
^{1}H NMR of **8d** (400 M, $CDCl_3$)



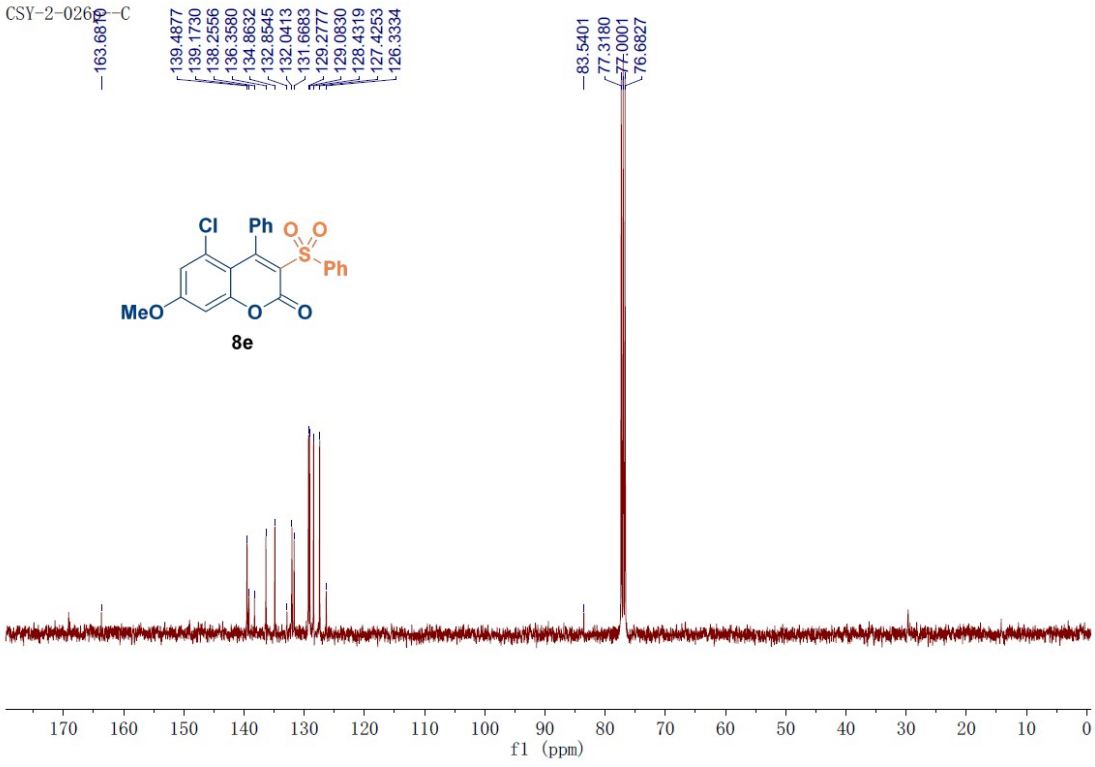
^{13}C NMR of **8d** (100 M, $CDCl_3$)



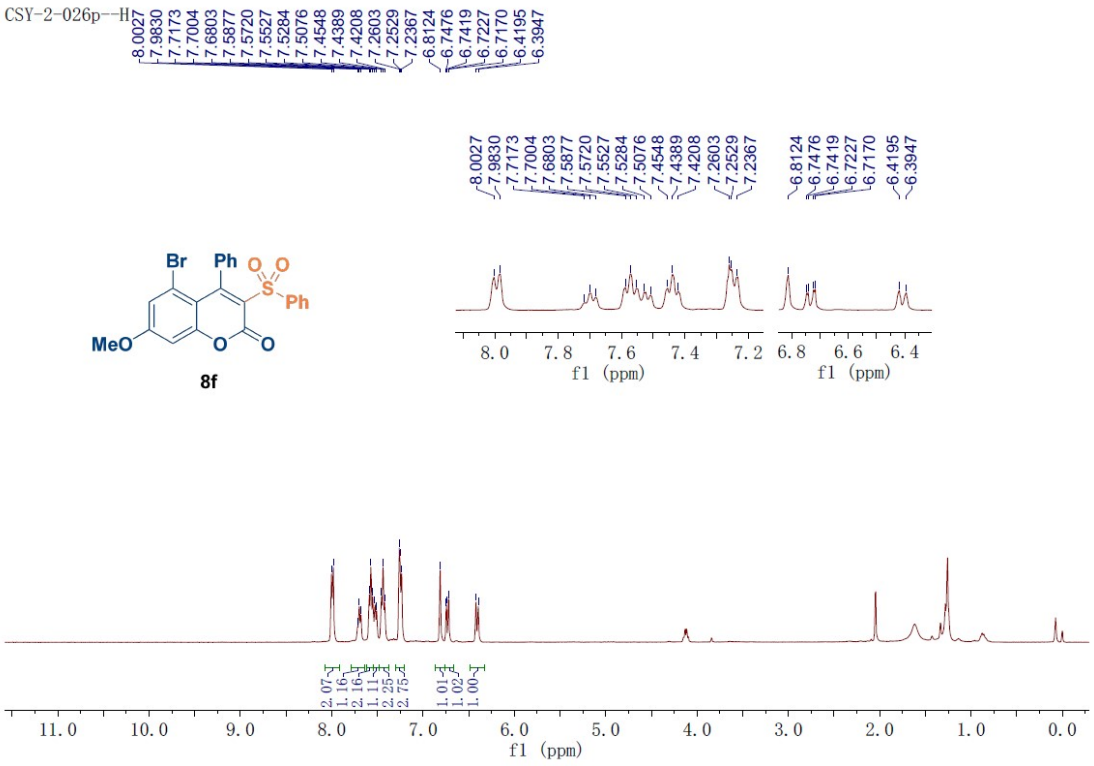
^{1}H NMR of **8e** (400 M, $CDCl_3$)



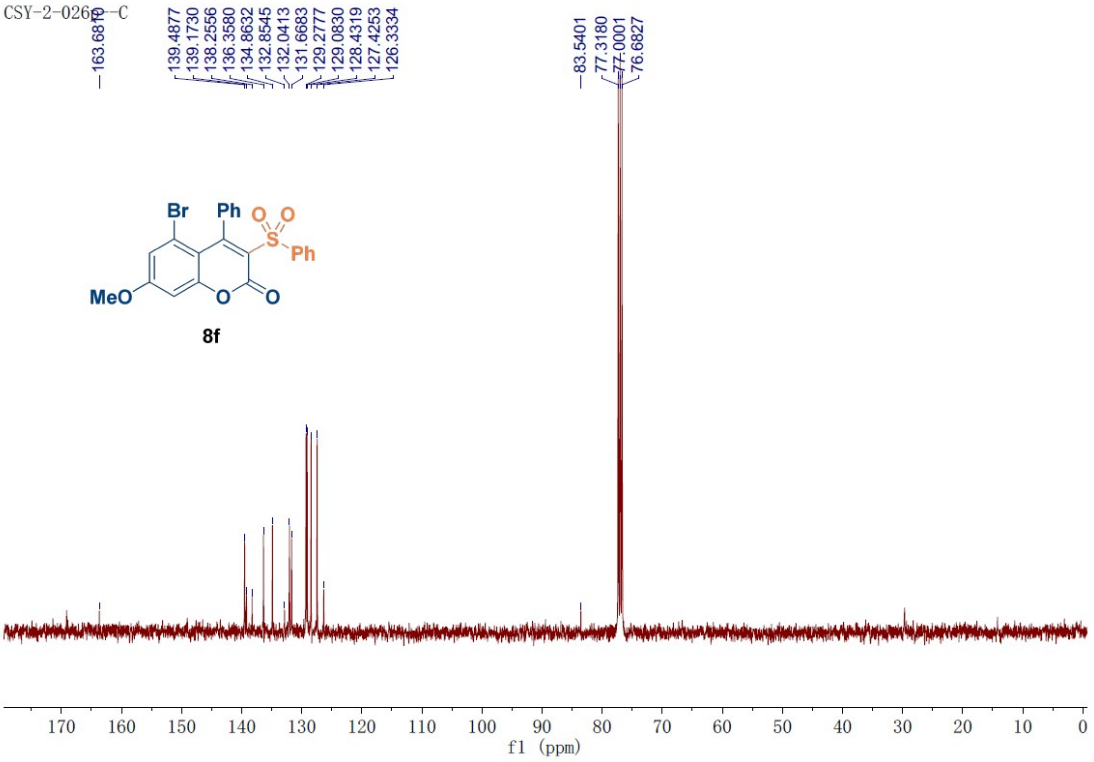
^{13}C NMR of **8e** (100 M, $CDCl_3$)



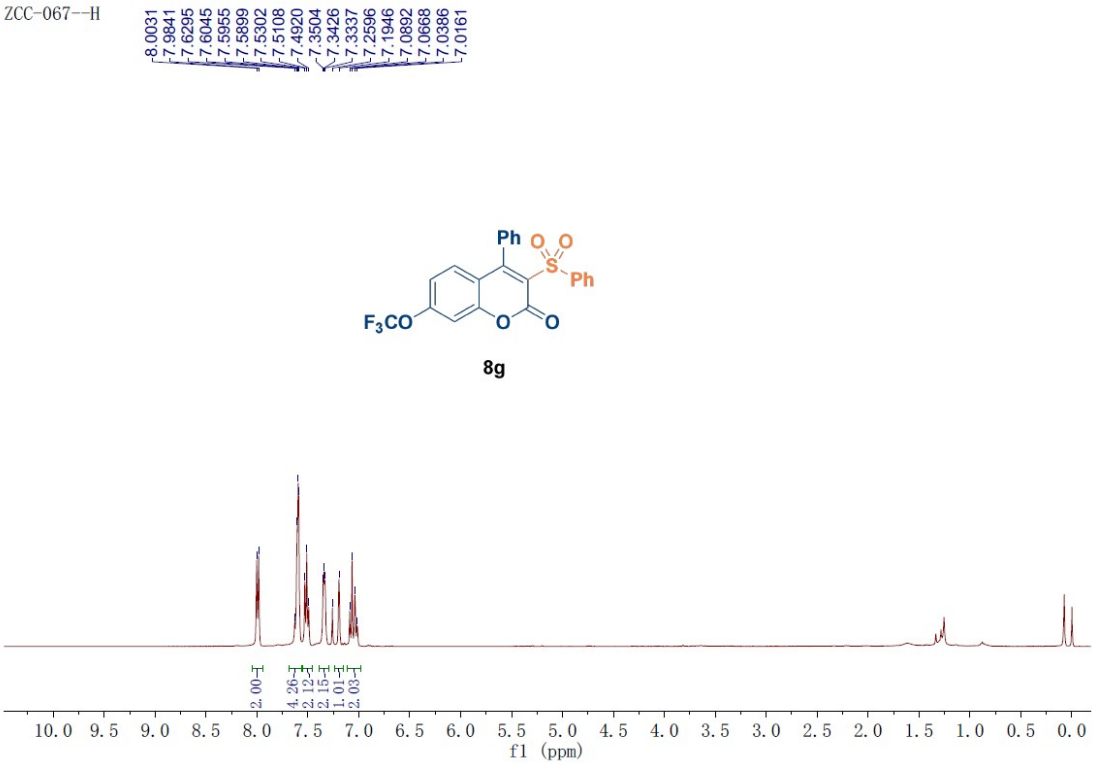
^{1}H NMR of **8f** (400 M, $CDCl_3$)



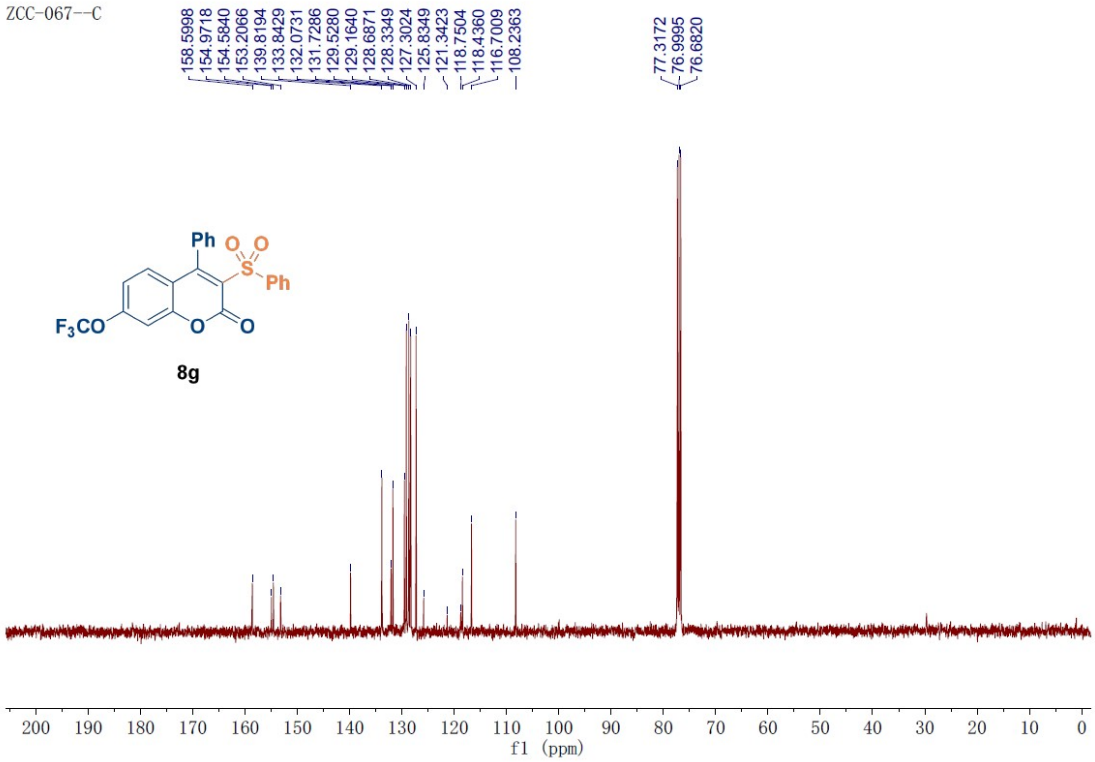
^{13}C NMR of **8f** (100 M, $CDCl_3$)



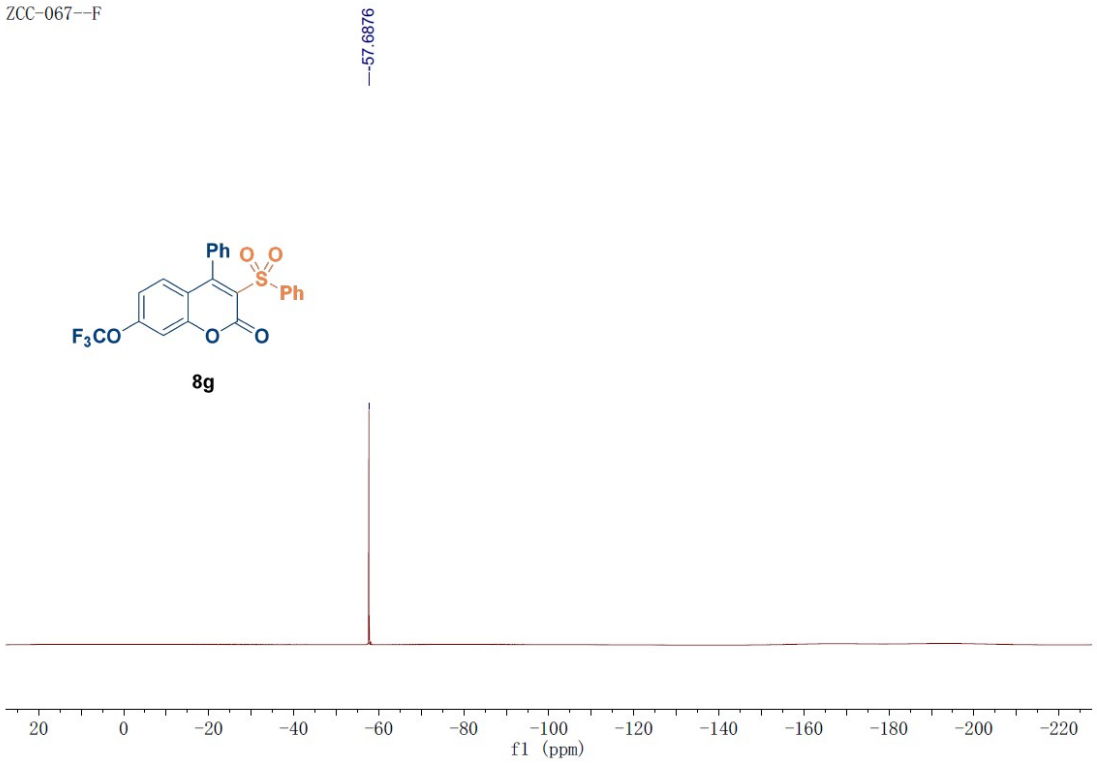
^{1}H NMR of **8g** (400 M, $CDCl_3$)



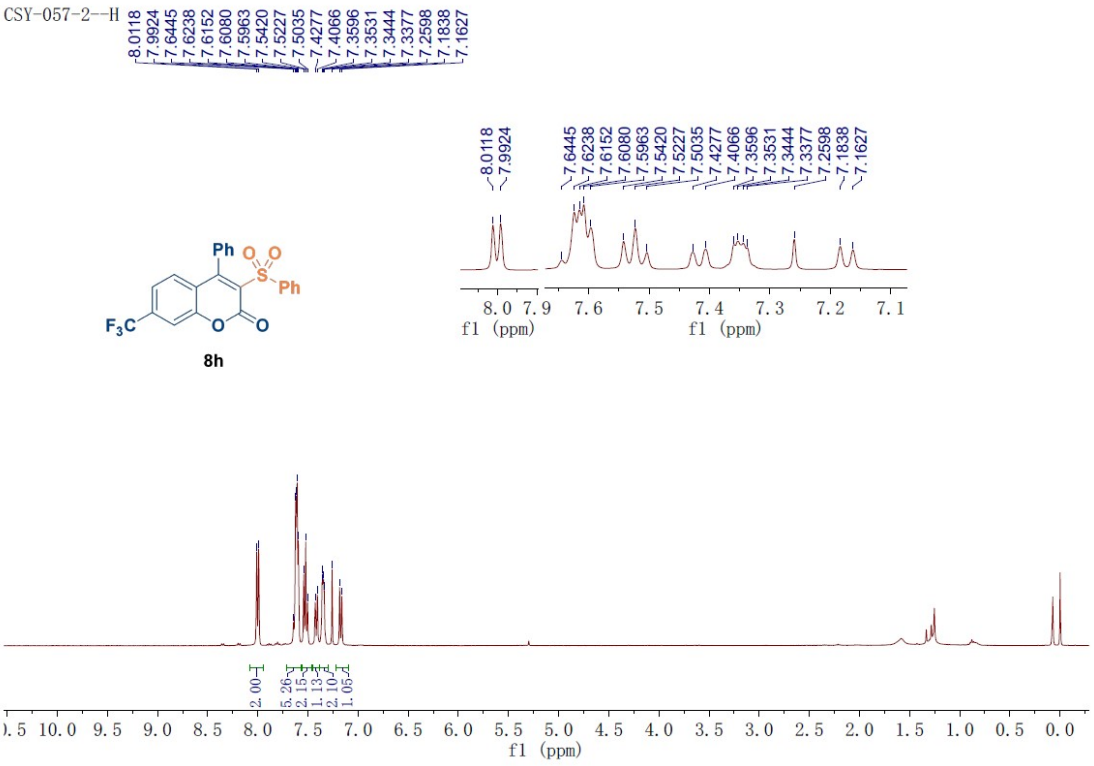
^{13}C NMR of **8g** (100 M, $CDCl_3$)



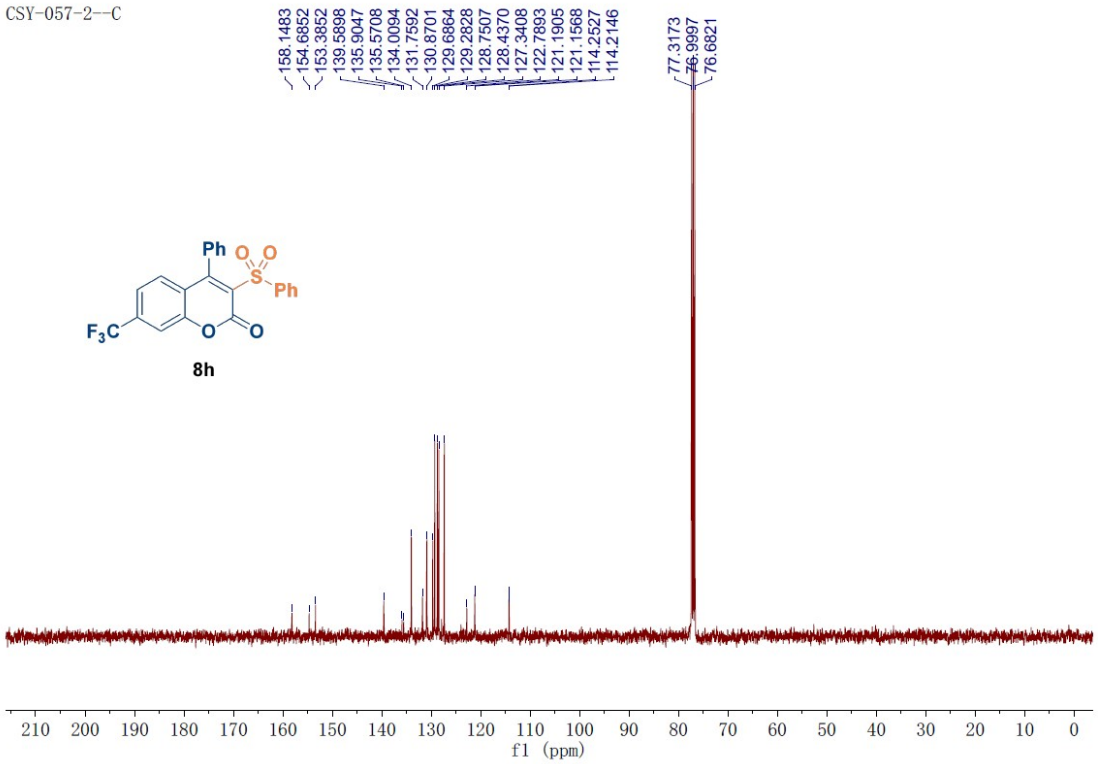
^{19}F NMR of **8g** (376 M, $CDCl_3$)



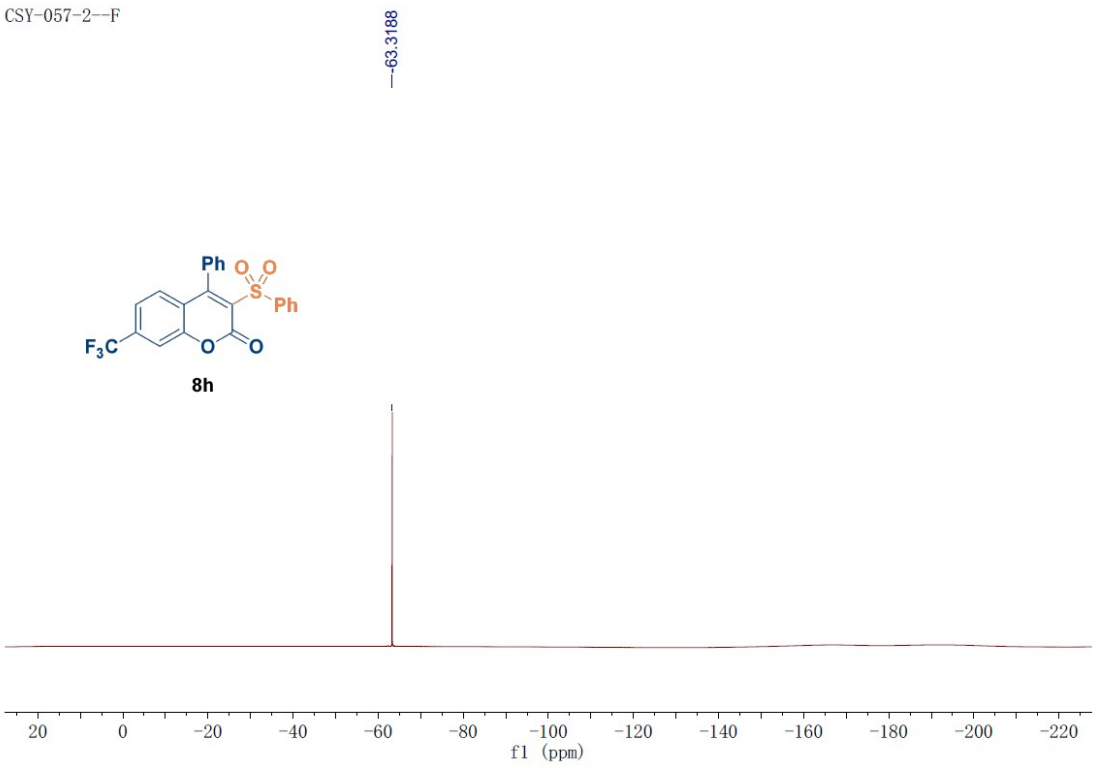
^{1}H NMR of **8h** (400 M, $CDCl_3$)



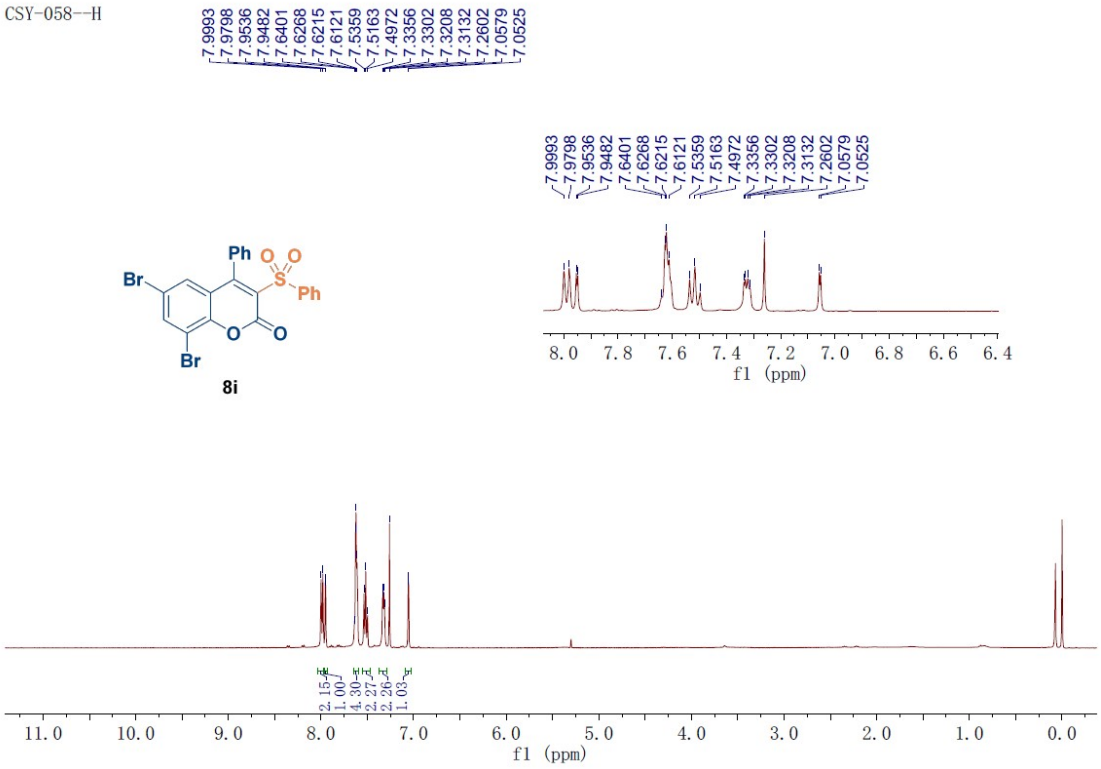
^{13}C NMR of **8h** (100 M, $CDCl_3$)



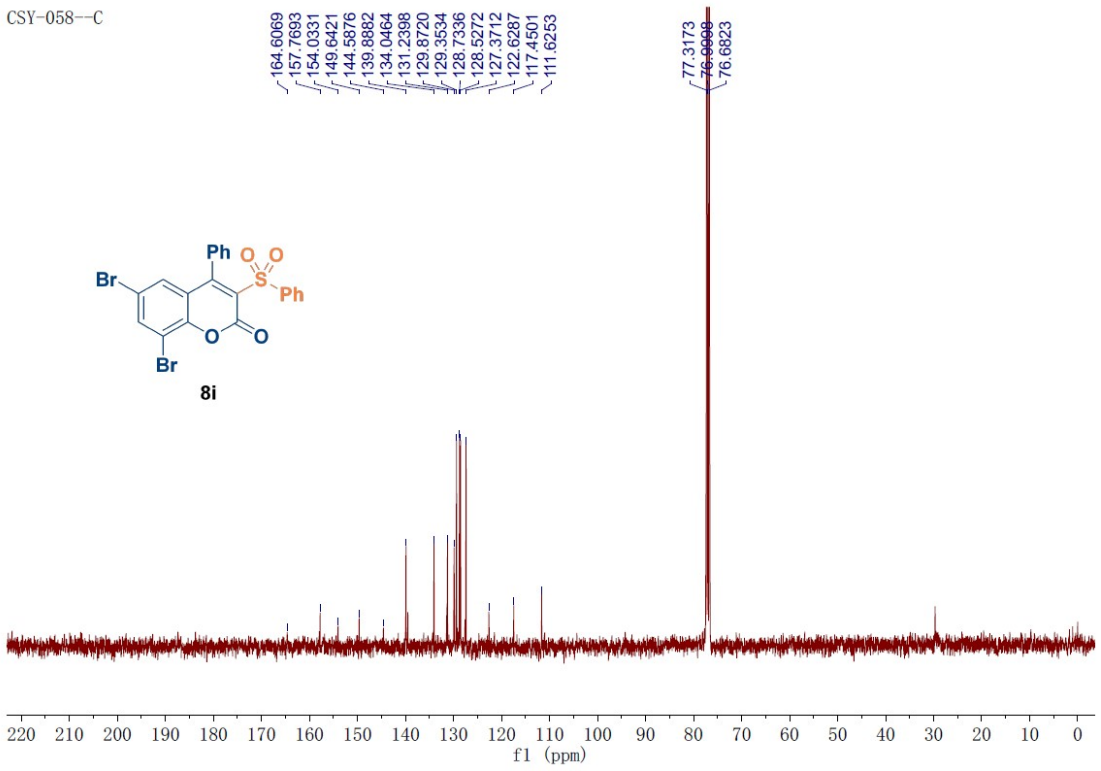
^{19}F NMR of **8h** (376 M, $CDCl_3$)



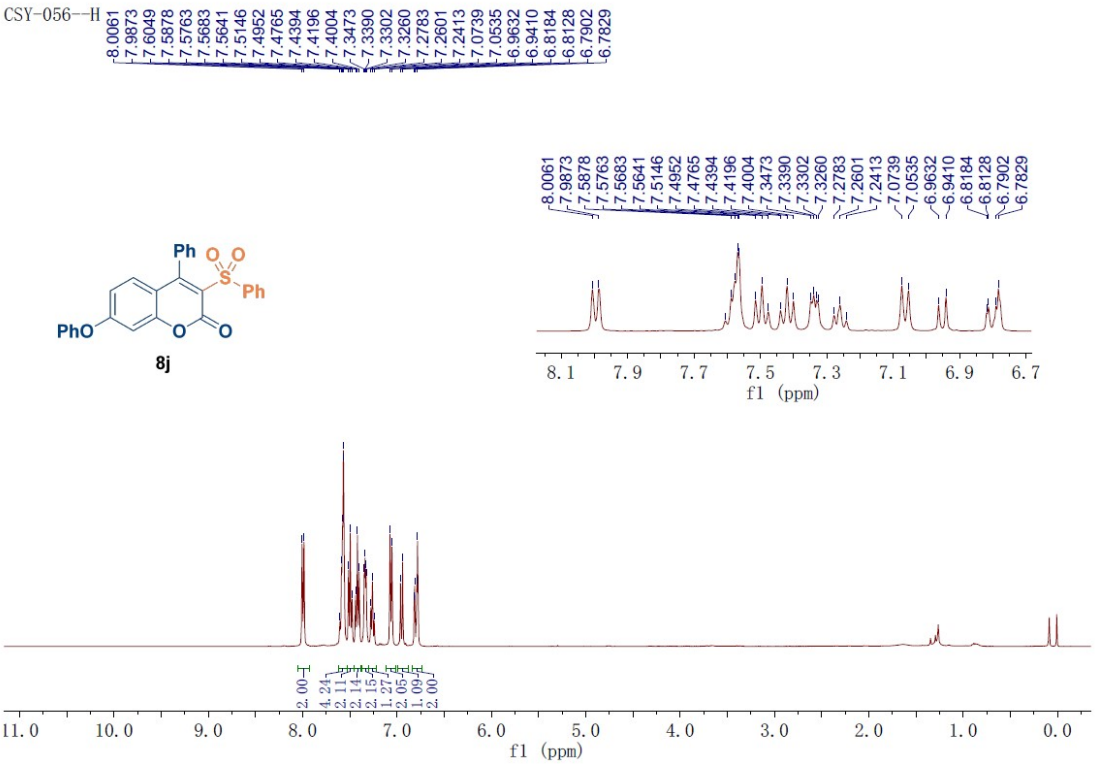
^{1}H NMR of **8i** (400 M, $CDCl_3$)



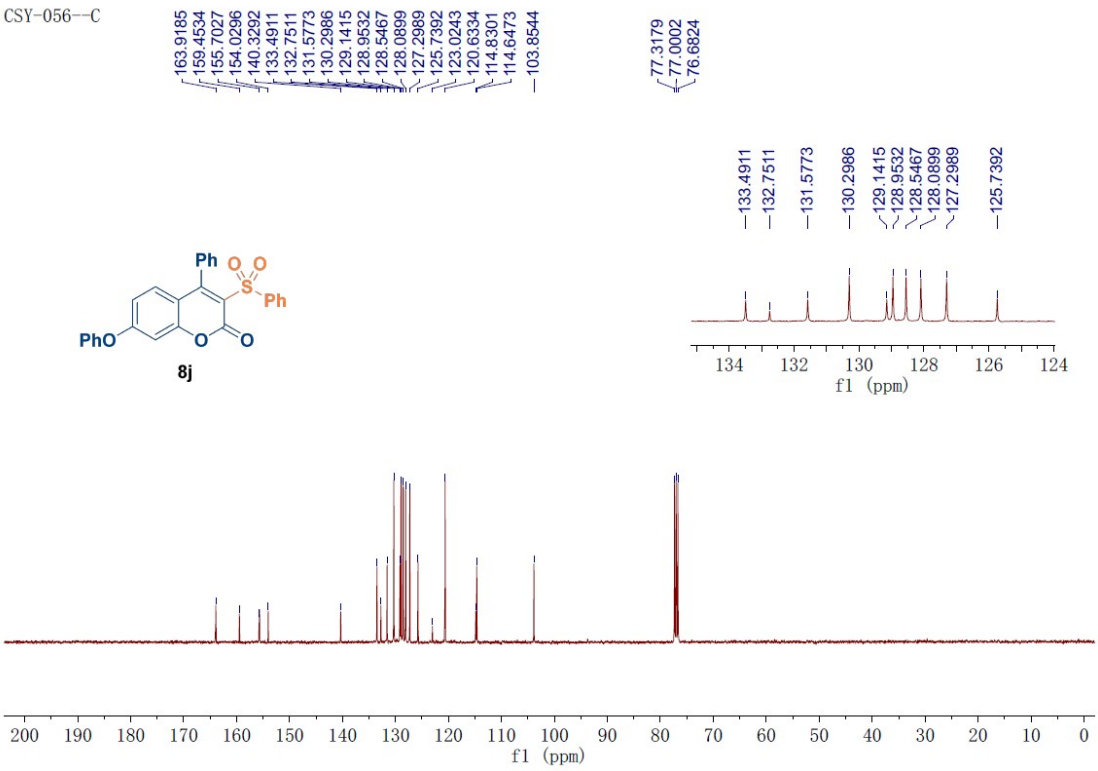
^{13}C NMR of **8i** (100 M, $CDCl_3$)



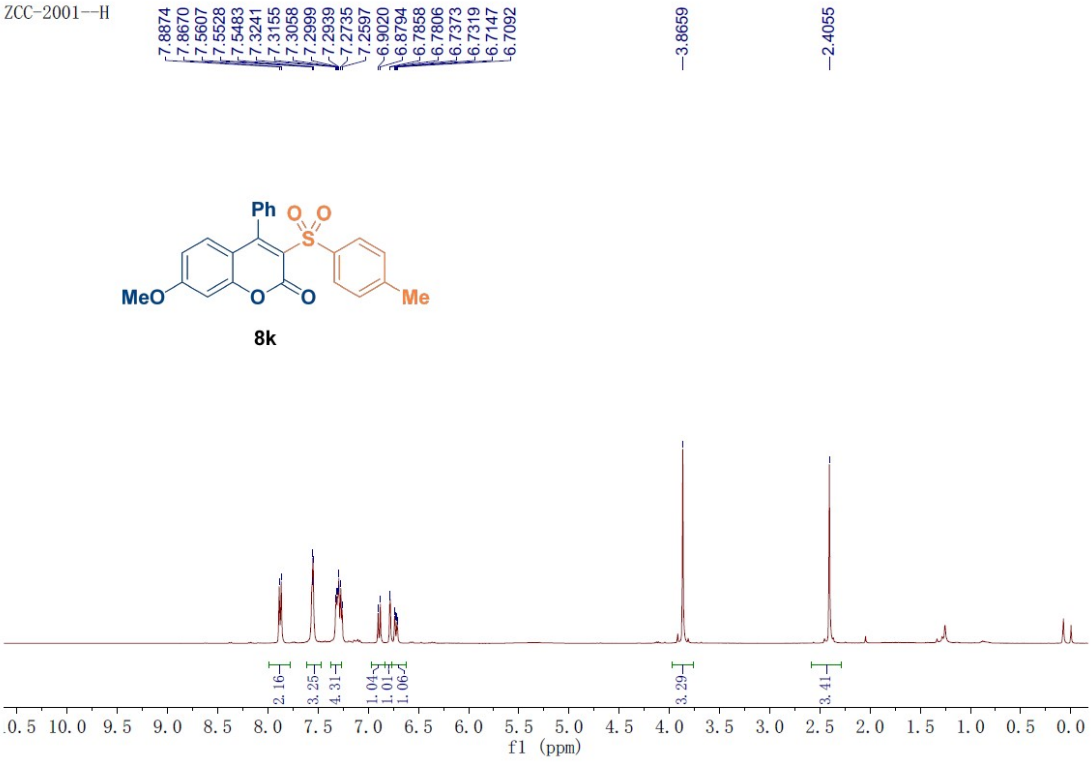
^{1}H NMR of **8j** (400 M, $CDCl_3$)



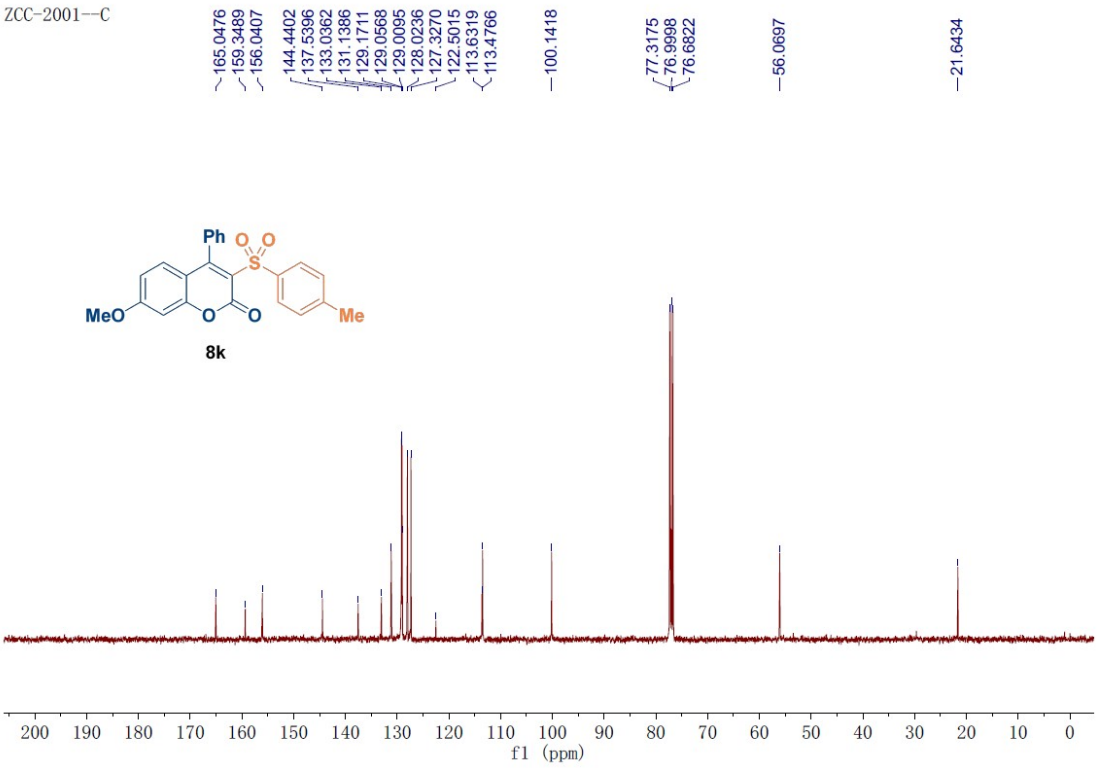
^{13}C NMR of **8j** (100 M, $CDCl_3$)



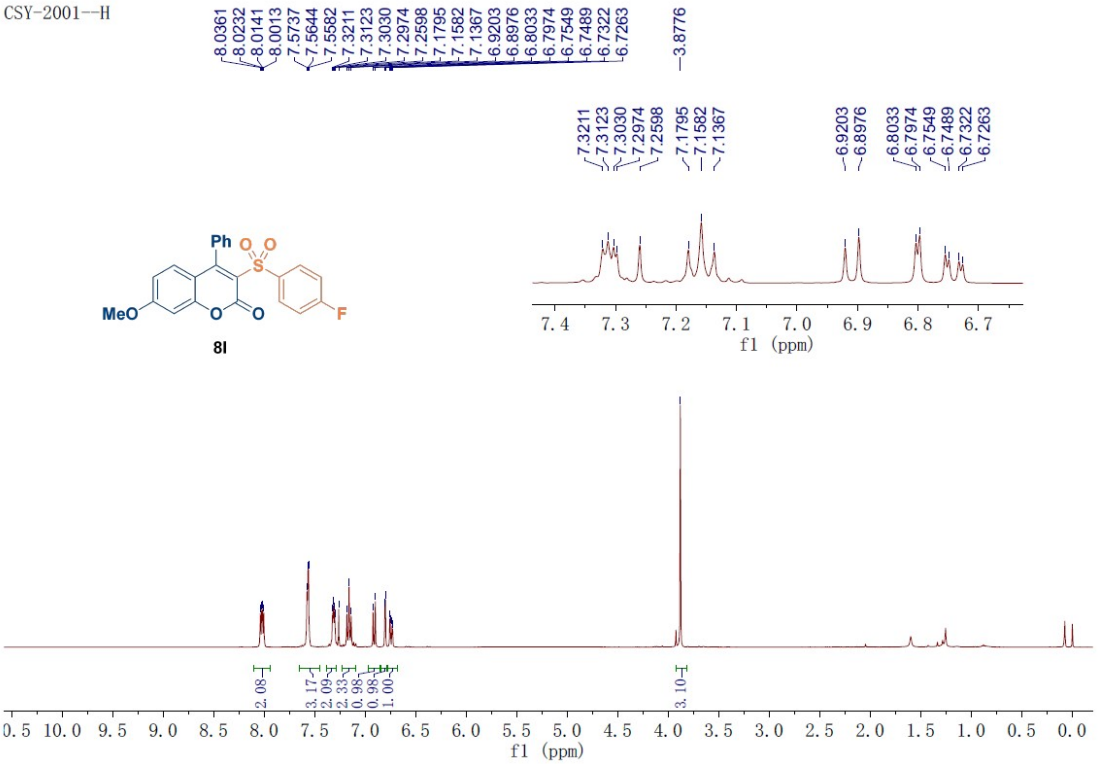
^{1}H NMR of **8k** (400 M, $CDCl_3$)



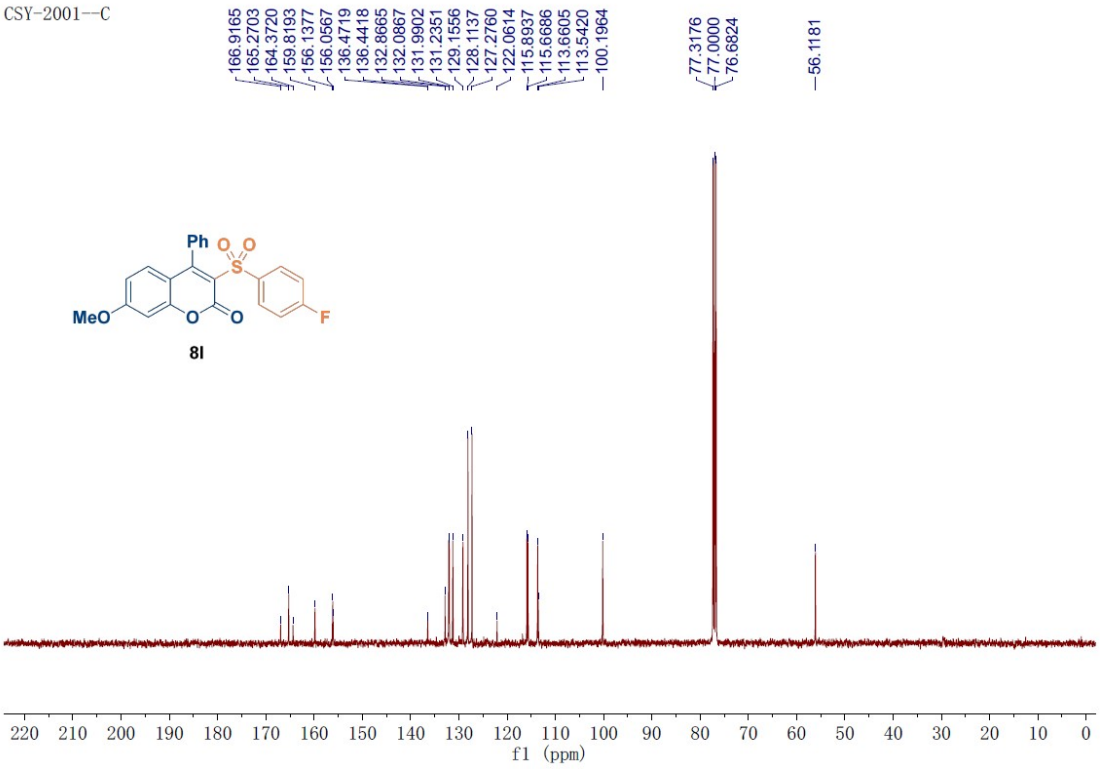
^{13}C NMR of **8k** (100 M, $CDCl_3$)



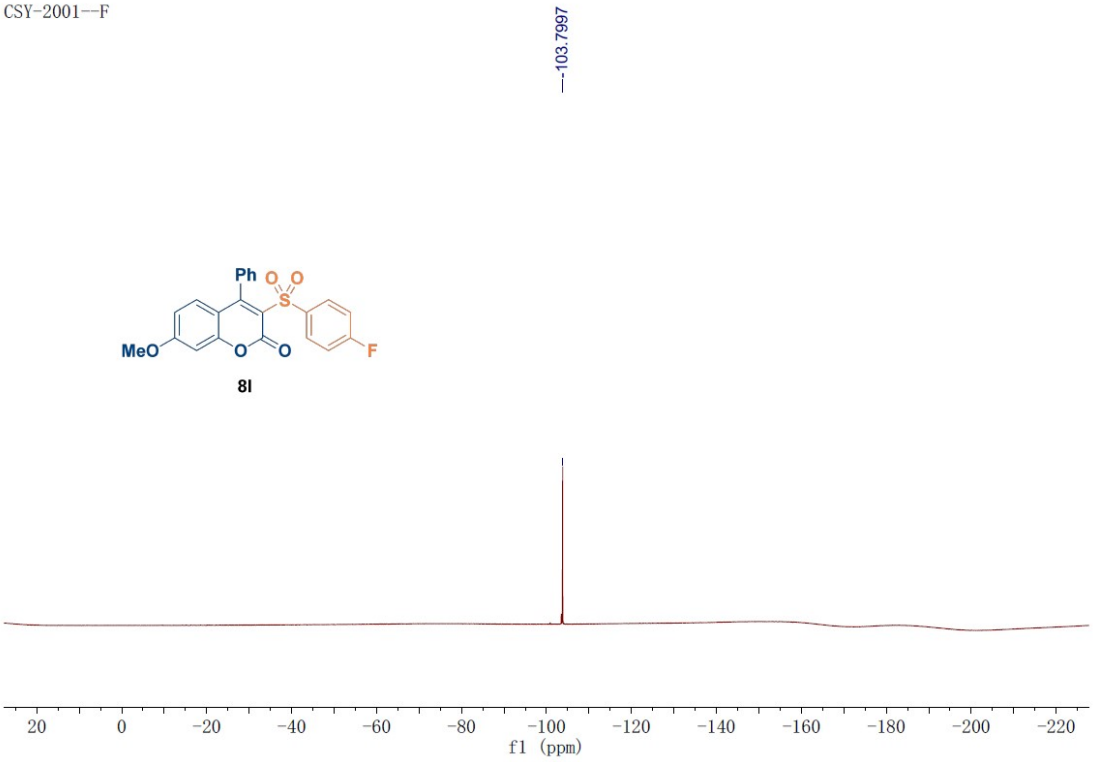
^{1}H NMR of **8l** (400 M, $CDCl_3$)



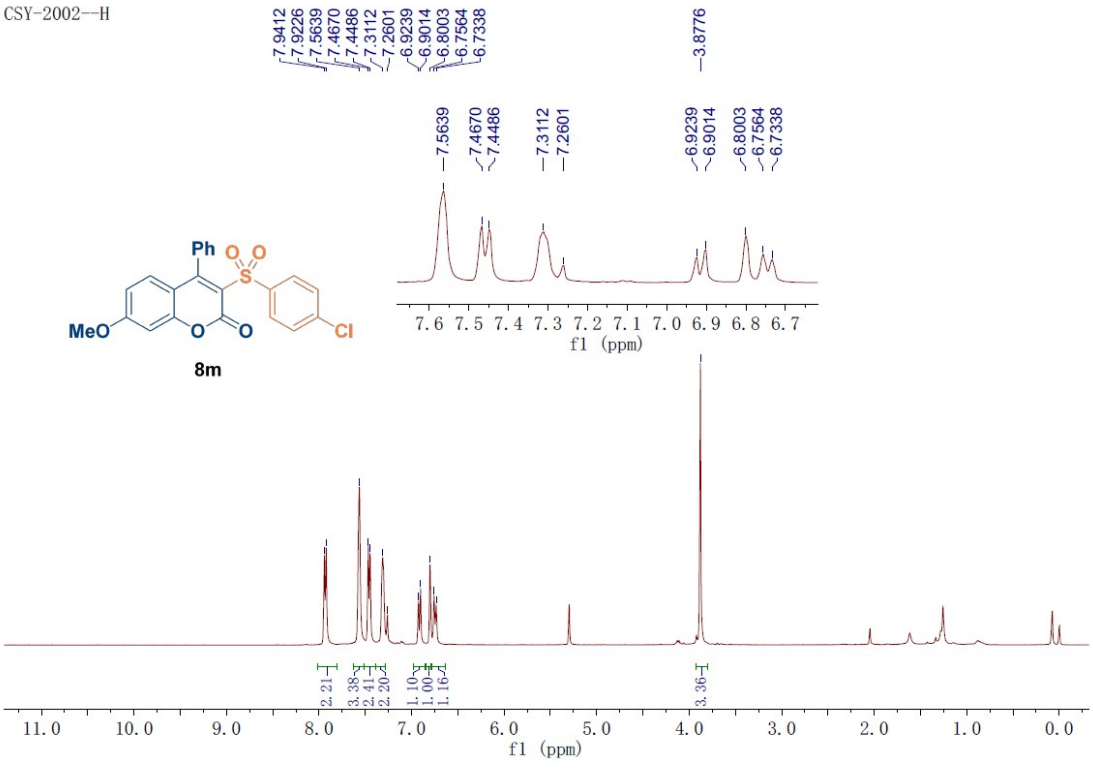
^{13}C NMR of **8l** (100 M, $CDCl_3$)



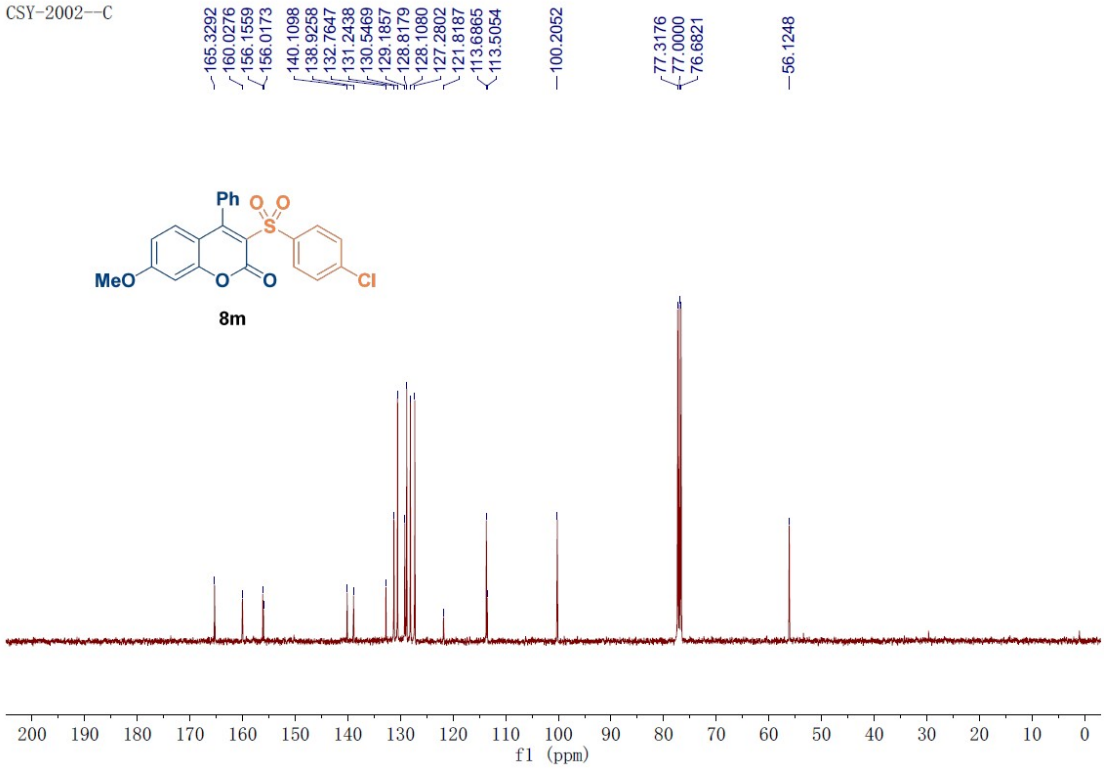
^{19}F NMR of **8l** (376 M, $CDCl_3$)



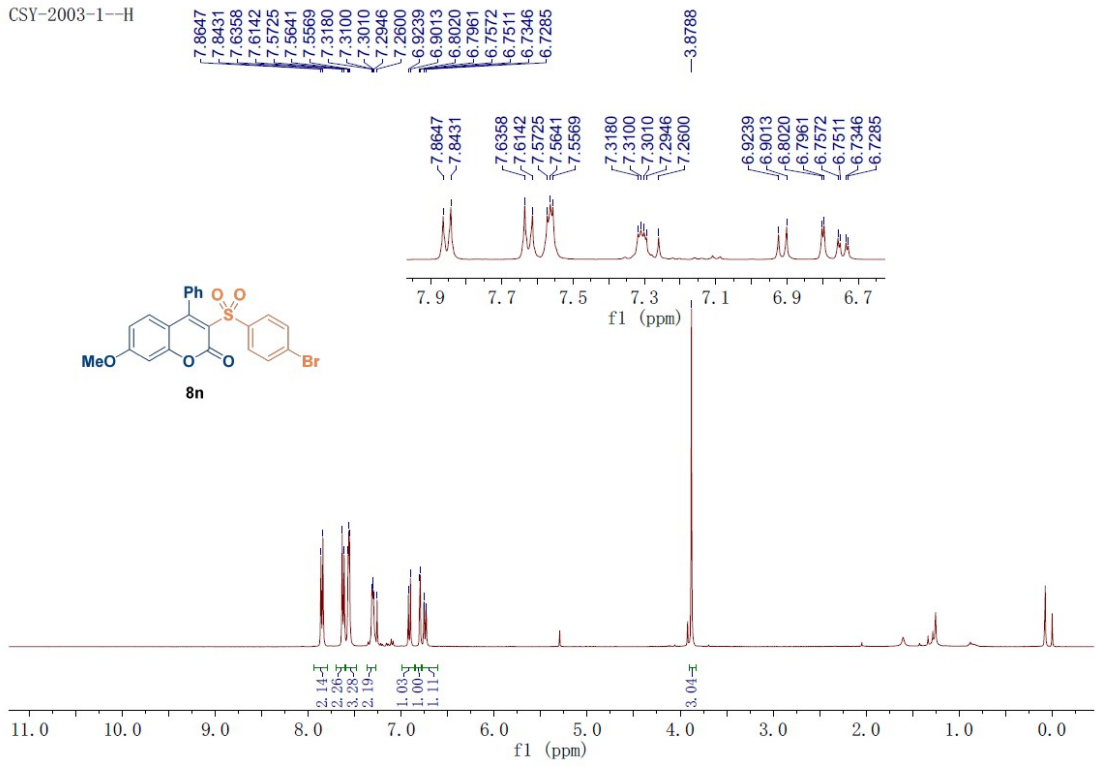
^{1}H NMR of **8m** (400 M, $CDCl_3$)



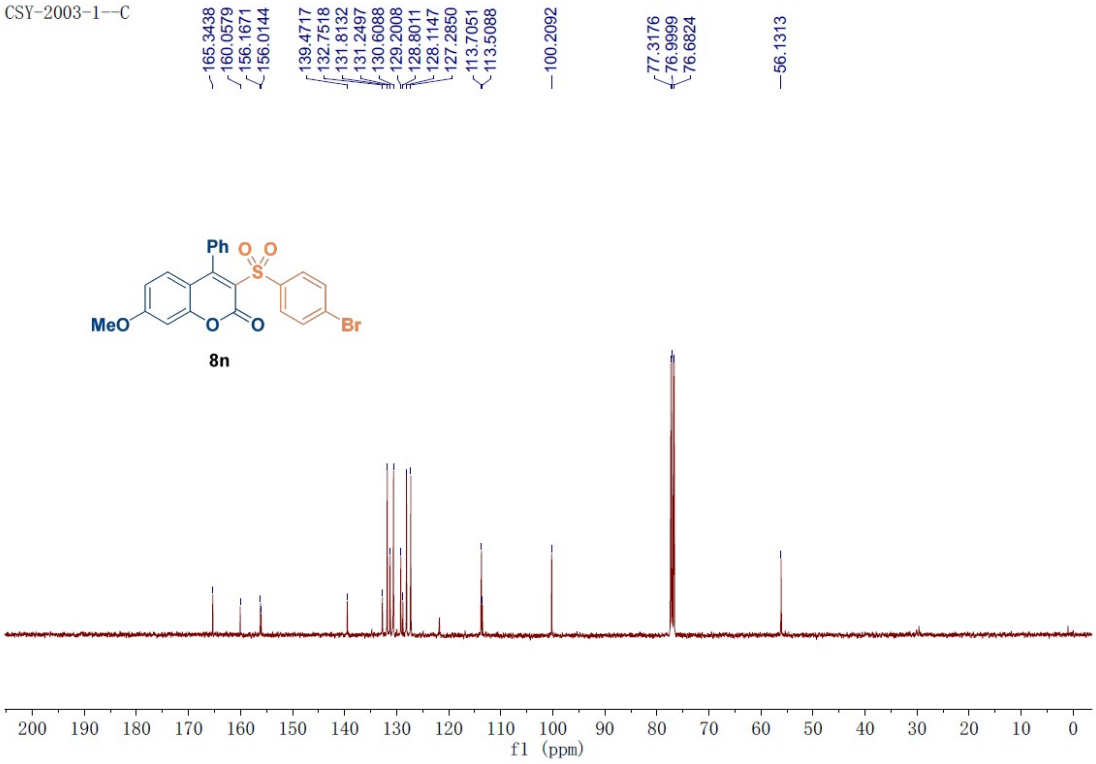
^{13}C NMR of **8m** (100 M, $CDCl_3$)



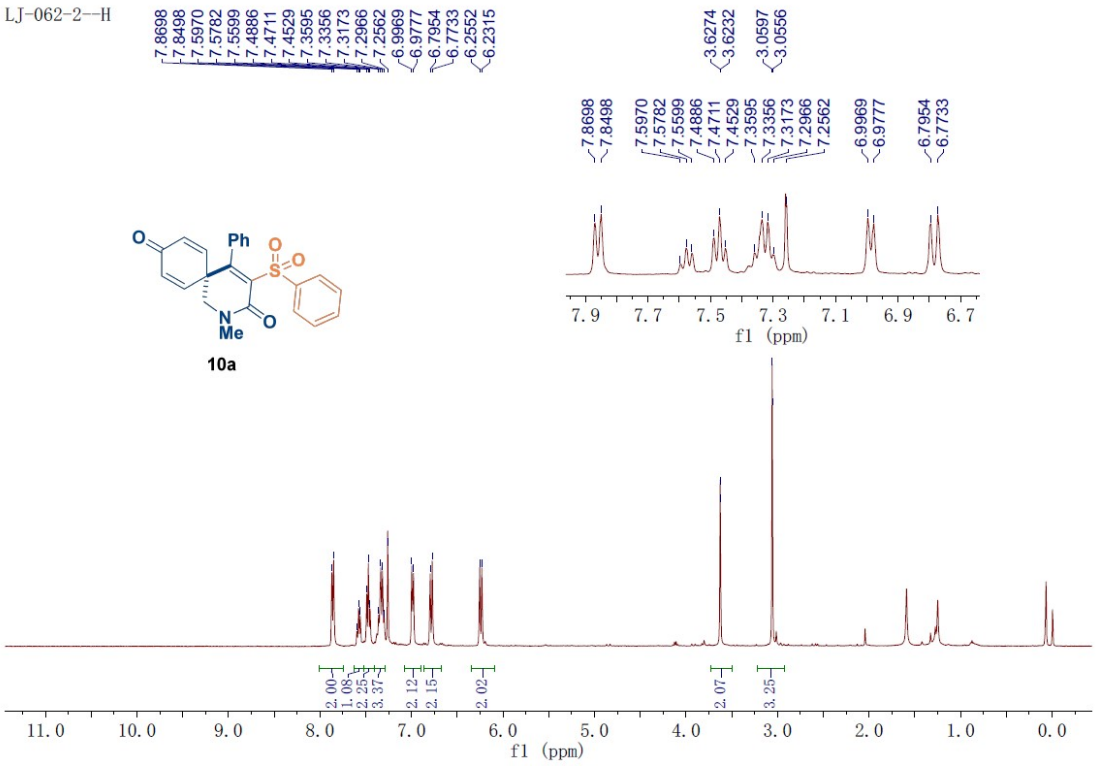
^{1}H NMR of **8n** (400 M, $CDCl_3$)



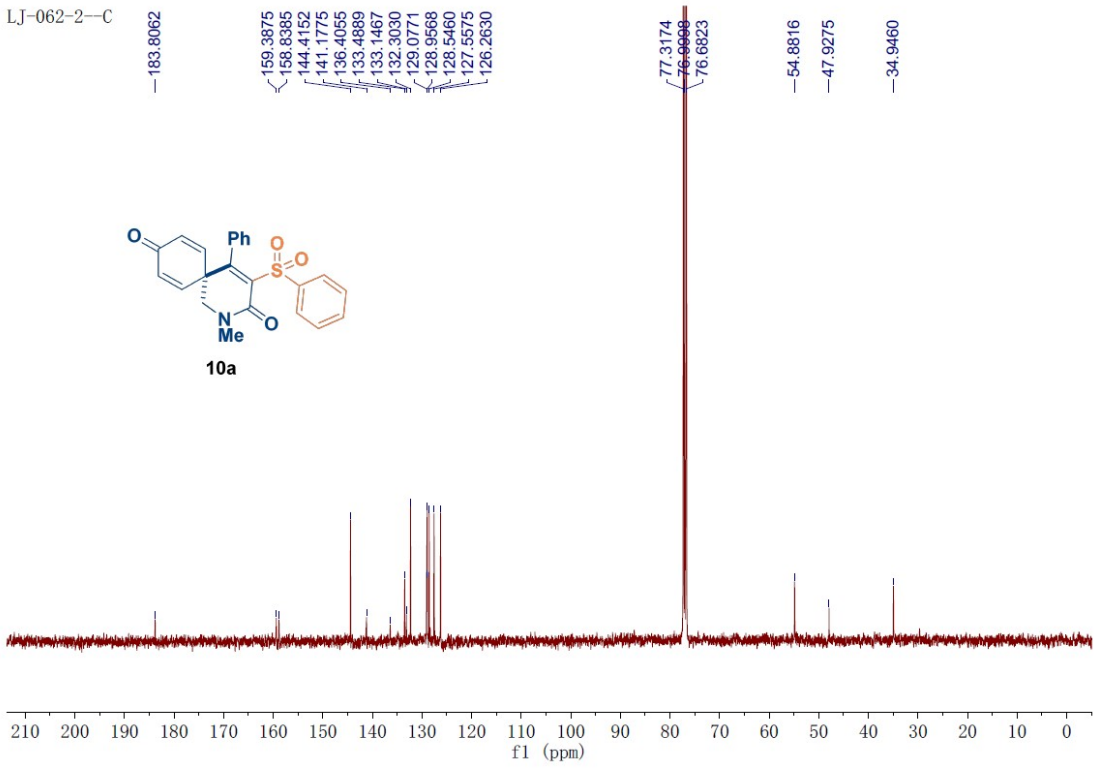
^{13}C NMR of **8n** (100 M, $CDCl_3$)



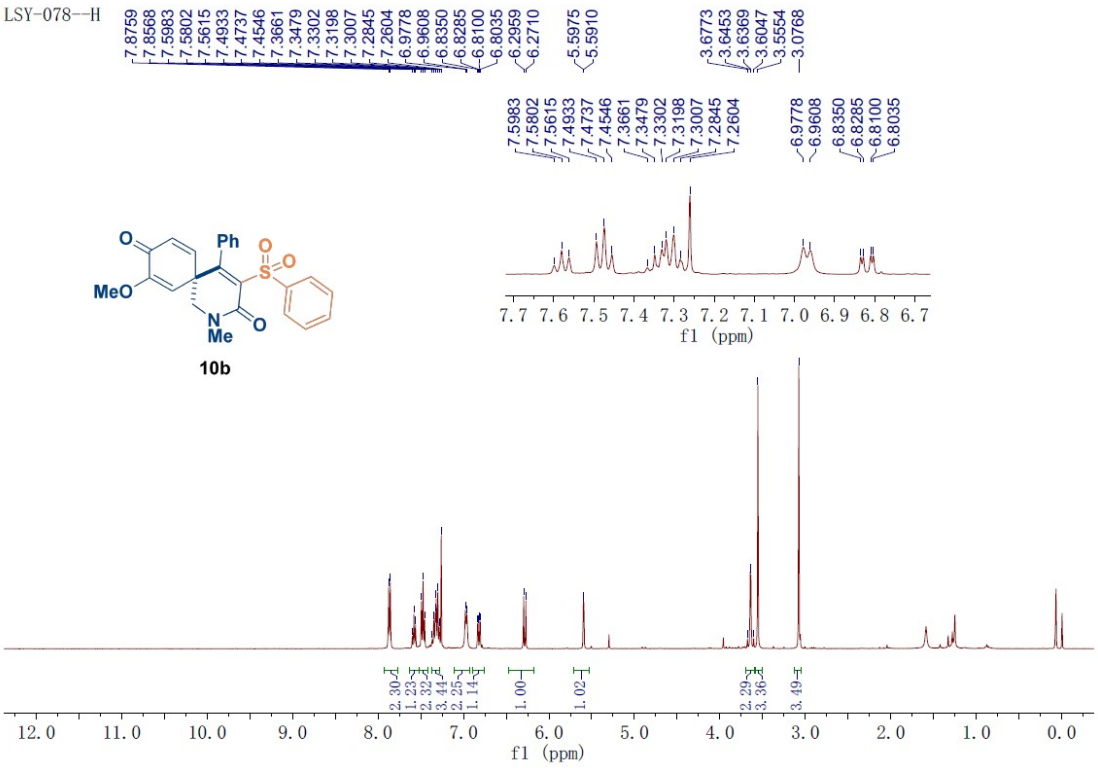
^{1}H NMR of **10a** (400 M, $CDCl_3$)



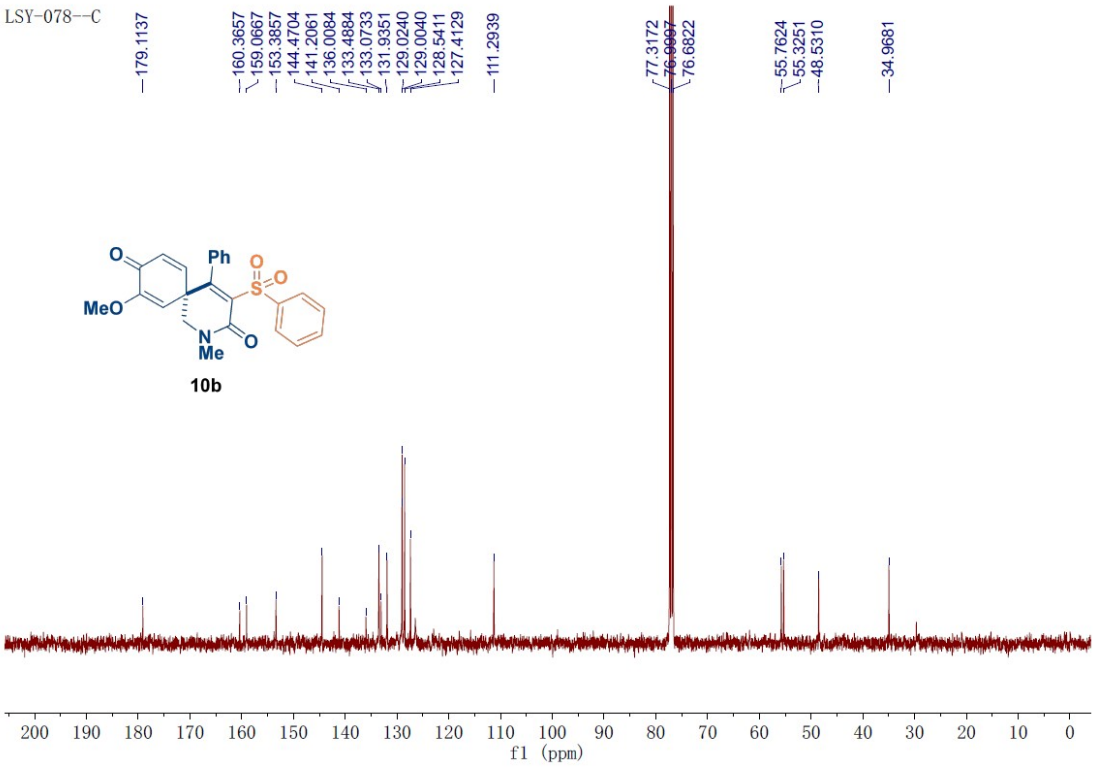
^{13}C NMR of **10a** (100 M, $CDCl_3$)



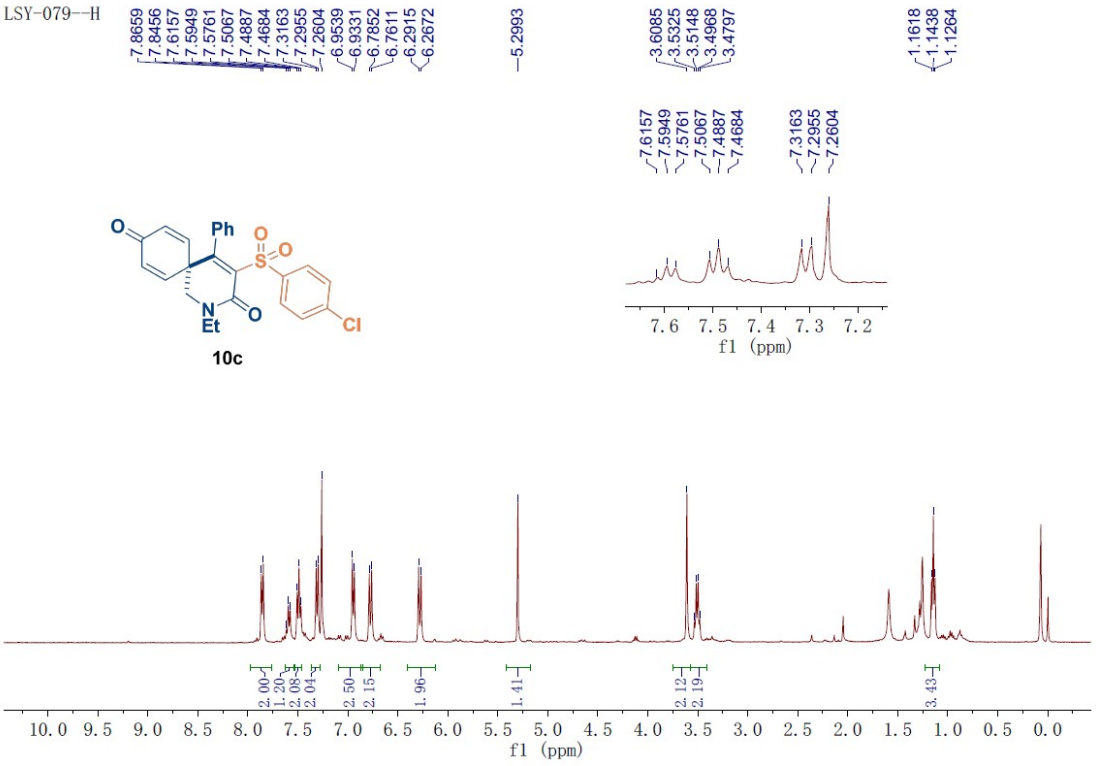
^{1}H NMR of **10b** (400 M, $CDCl_3$)



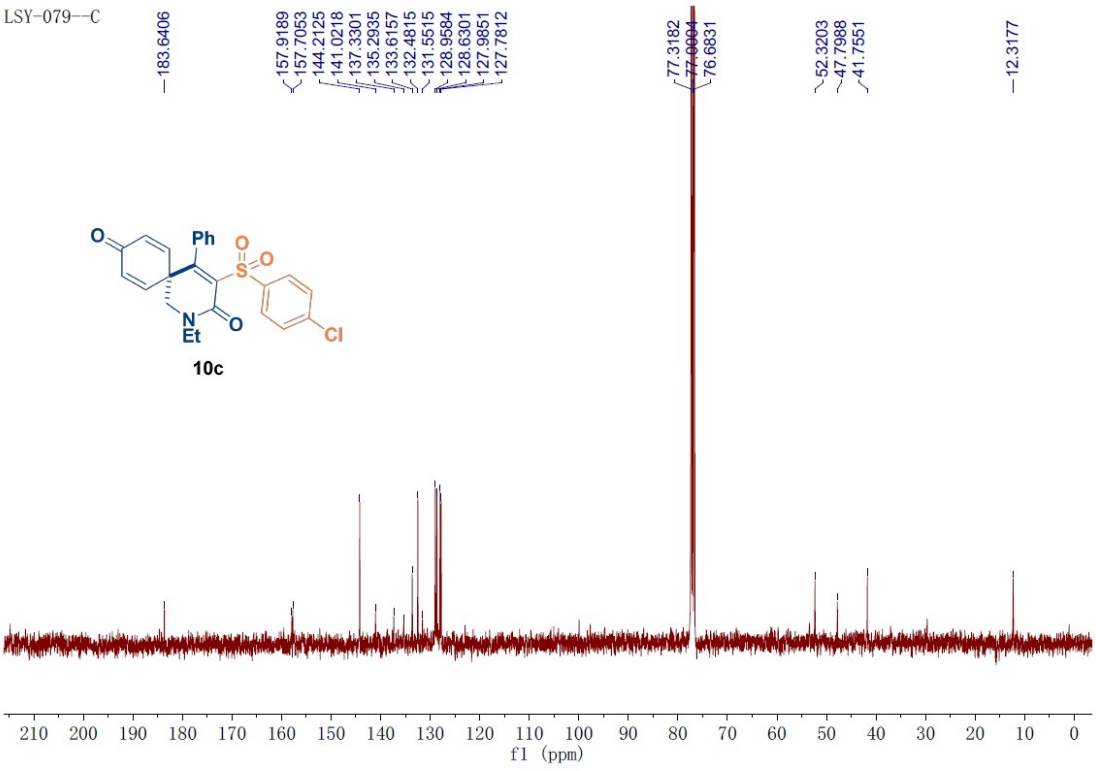
^{13}C NMR of **10b** (100 M, $CDCl_3$)



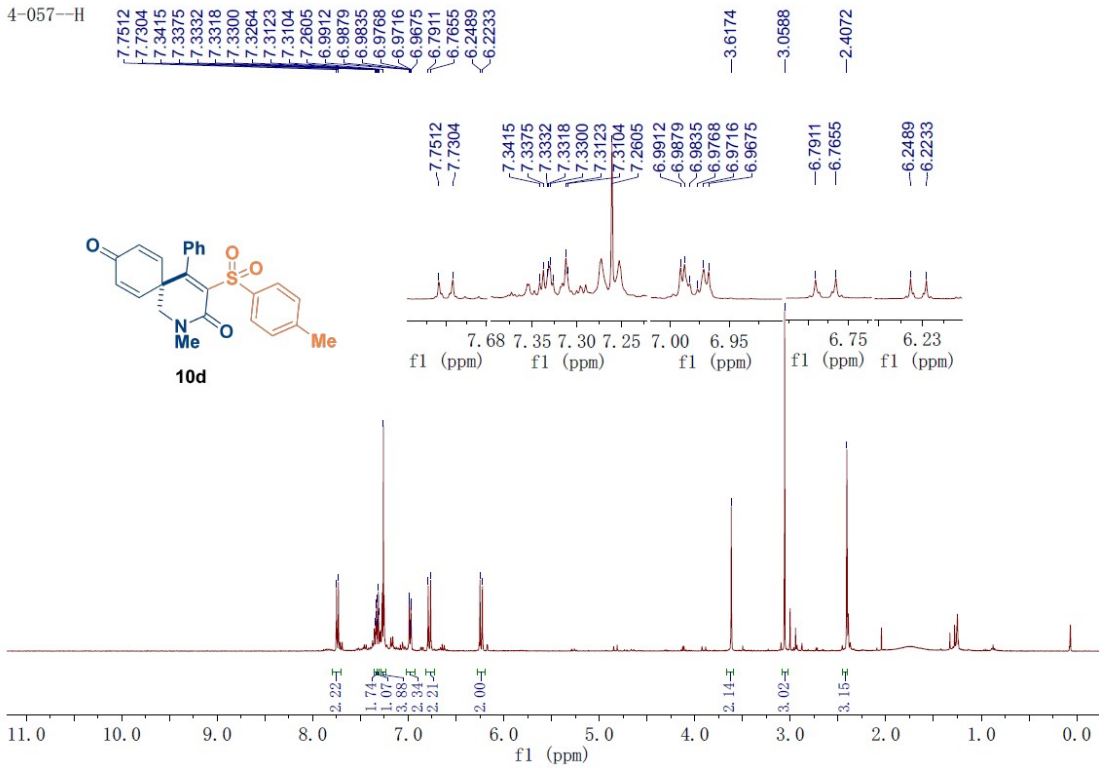
^{1}H NMR of **10c** (400 M, $CDCl_3$)



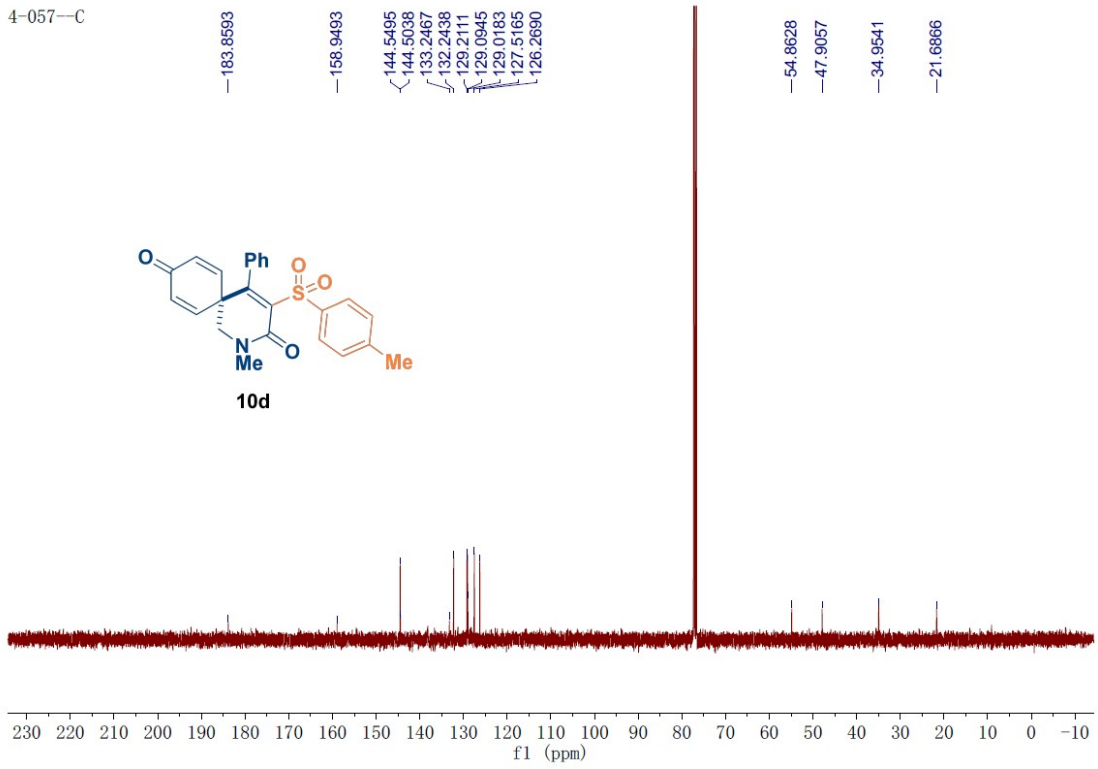
^{13}C NMR of **10c** (100 M, $CDCl_3$)



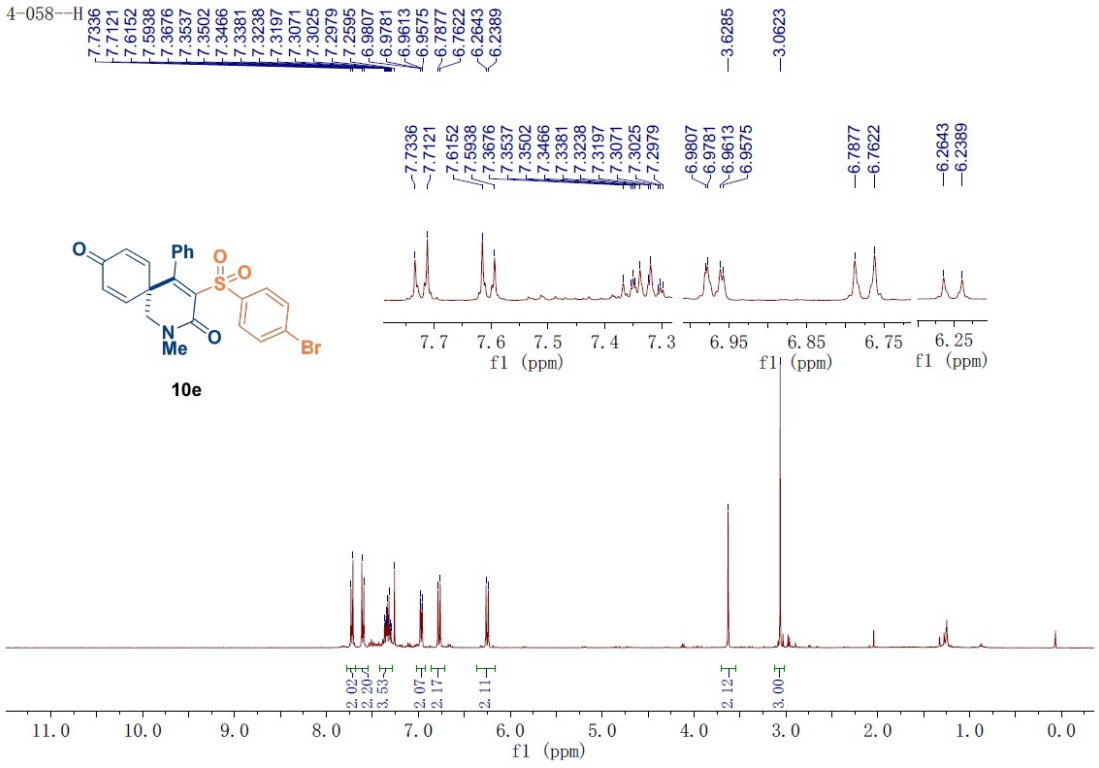
^{1}H NMR of **10d** (400 M, $CDCl_3$)



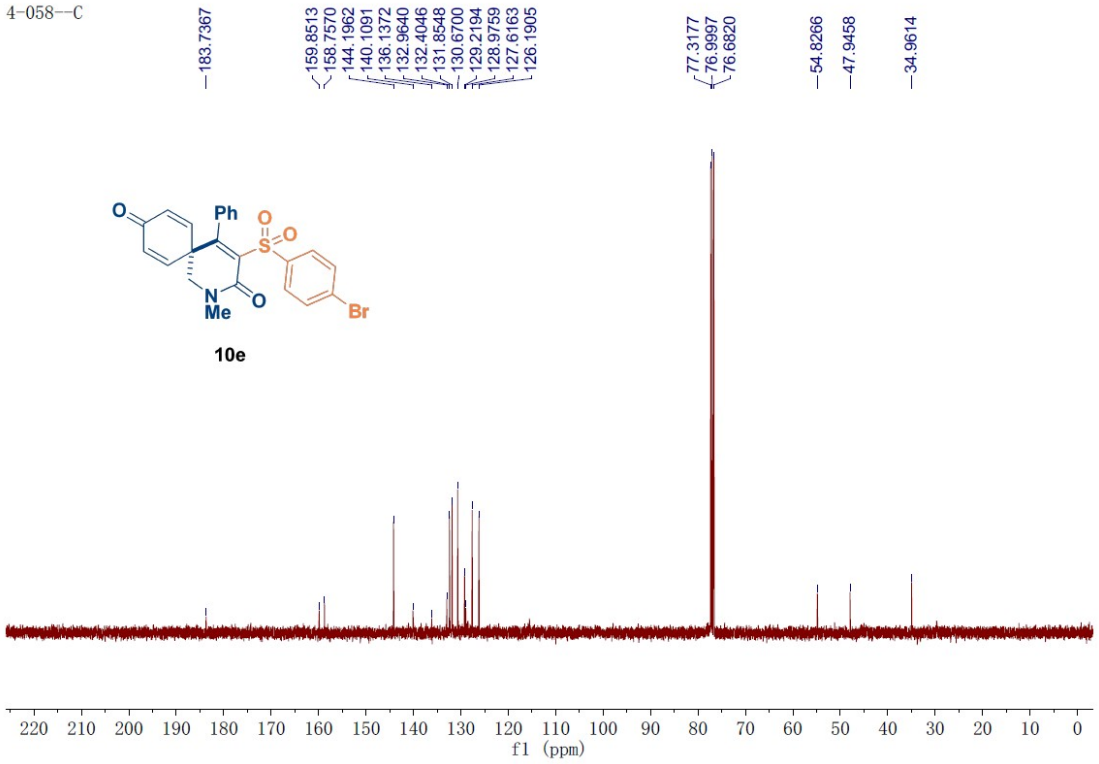
^{13}C NMR of **10d** (100 M, $CDCl_3$)



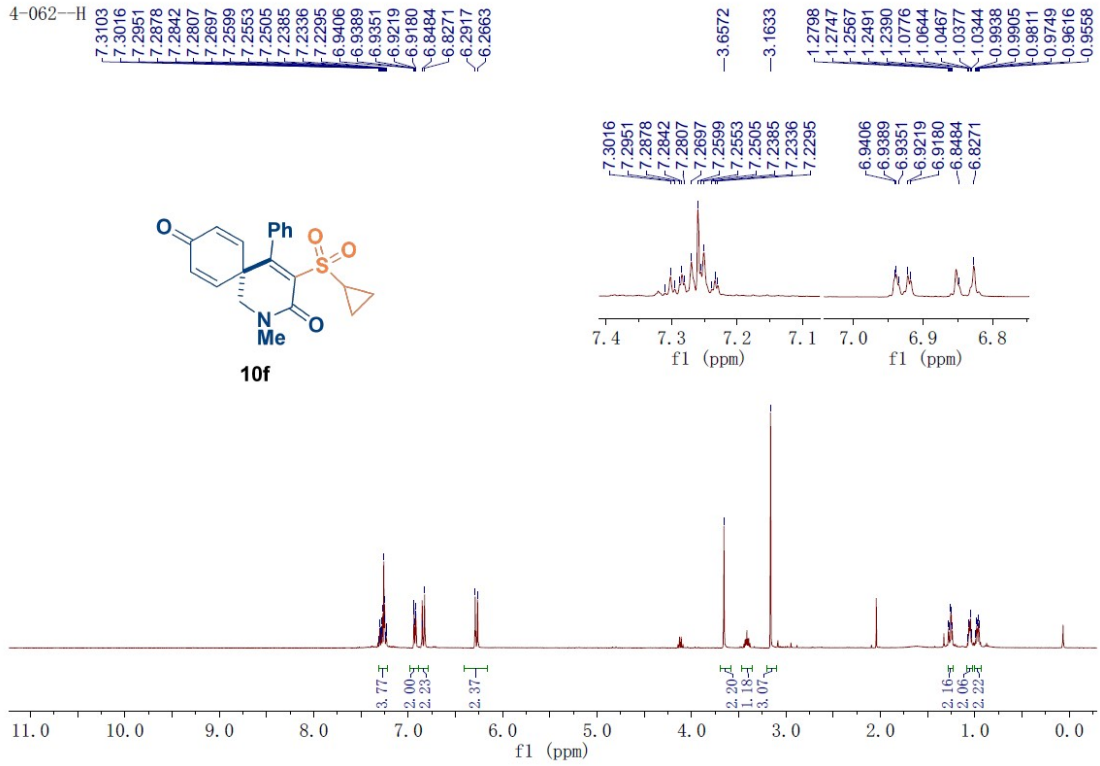
^{1}H NMR of **10e** (400 M, $CDCl_3$)



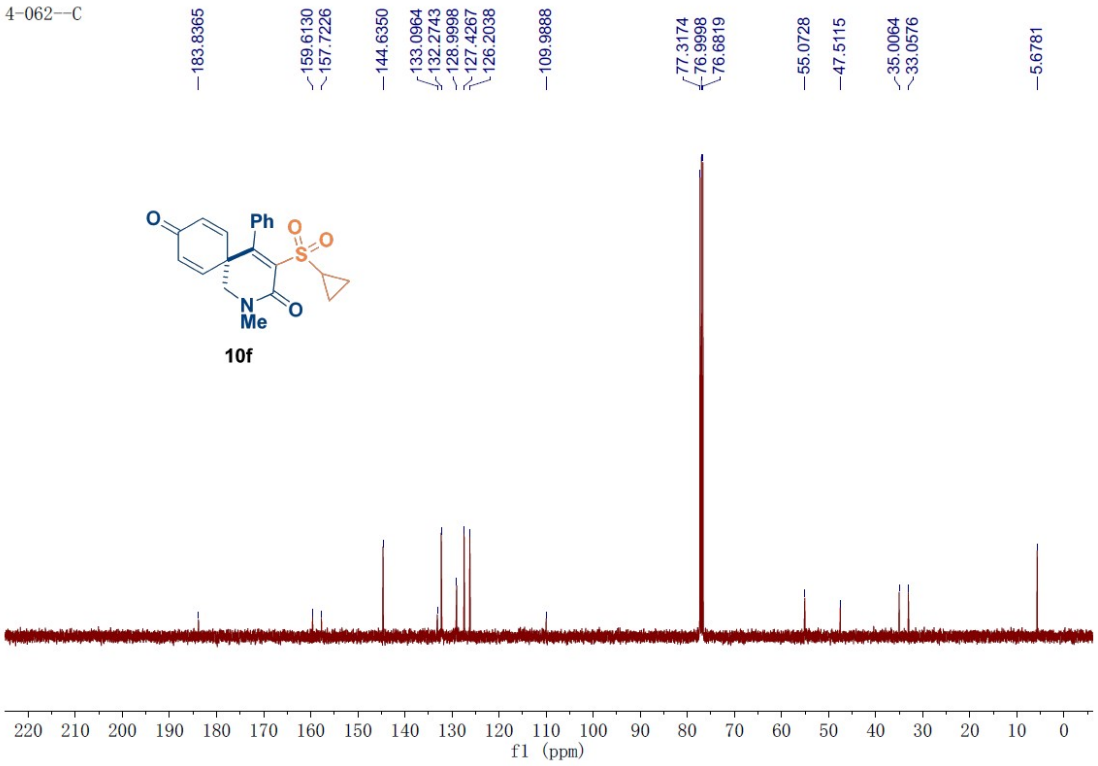
^{13}C NMR of **10e** (100 M, $CDCl_3$)



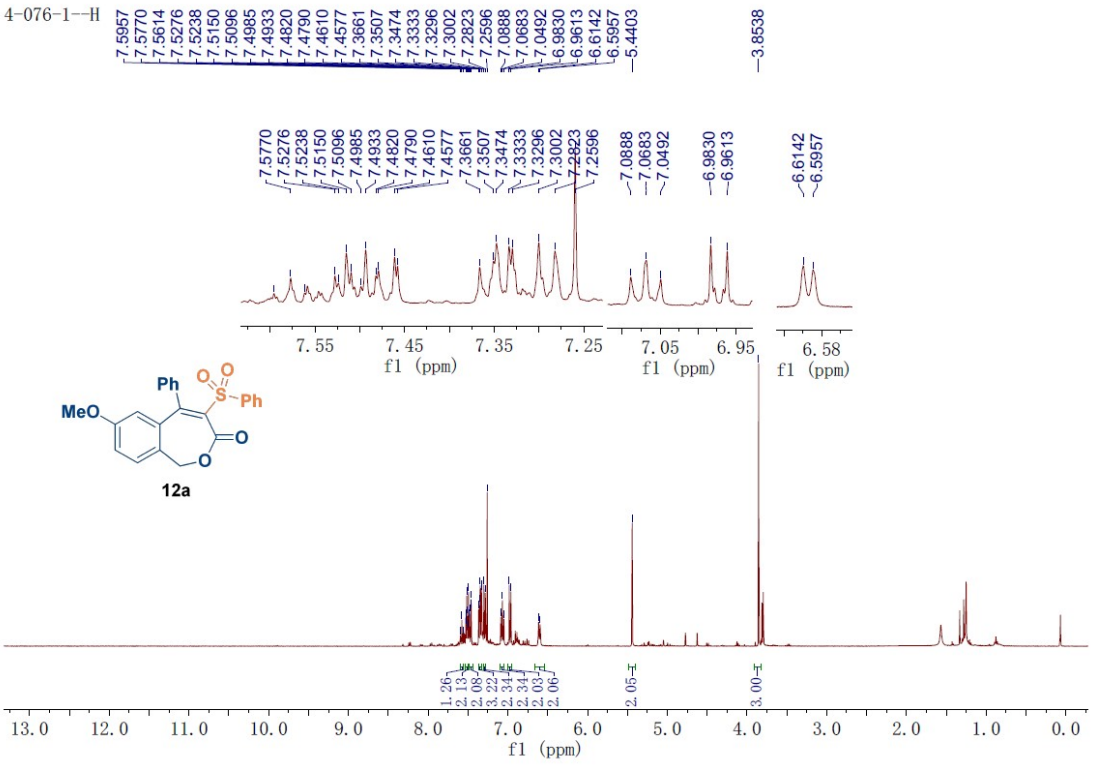
^{1}H NMR of **10f** (400 M, $CDCl_3$)



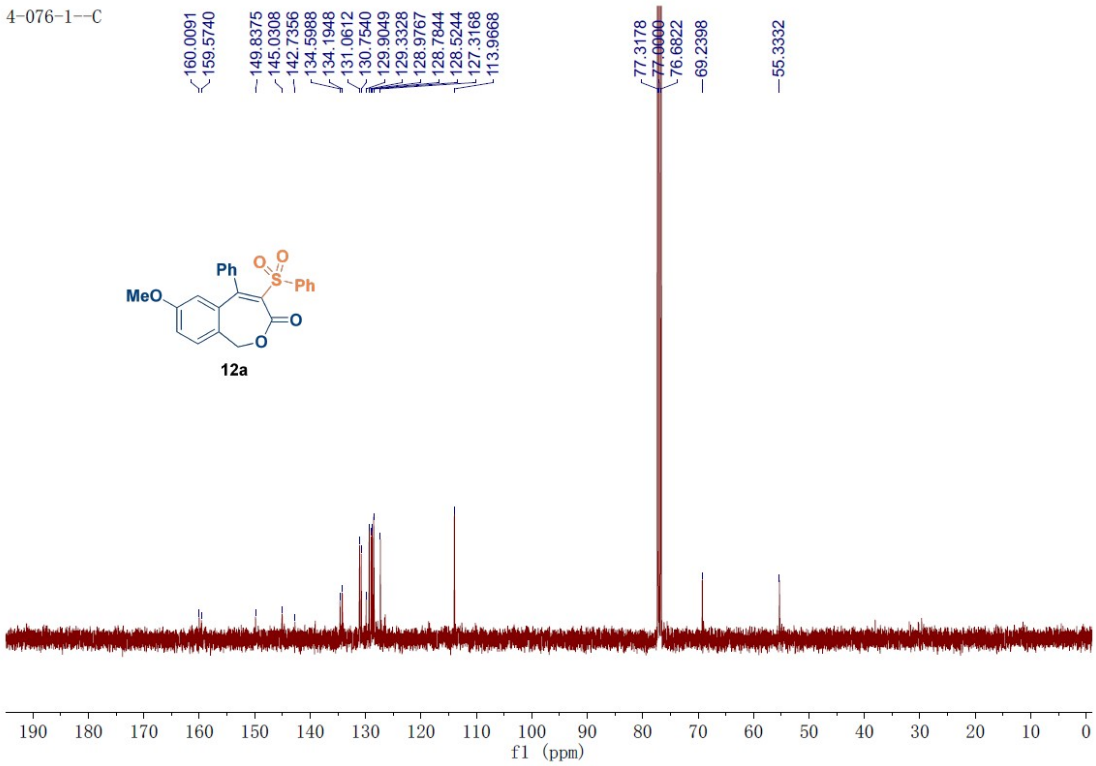
^{13}C NMR of **10f** (100 M, $CDCl_3$)



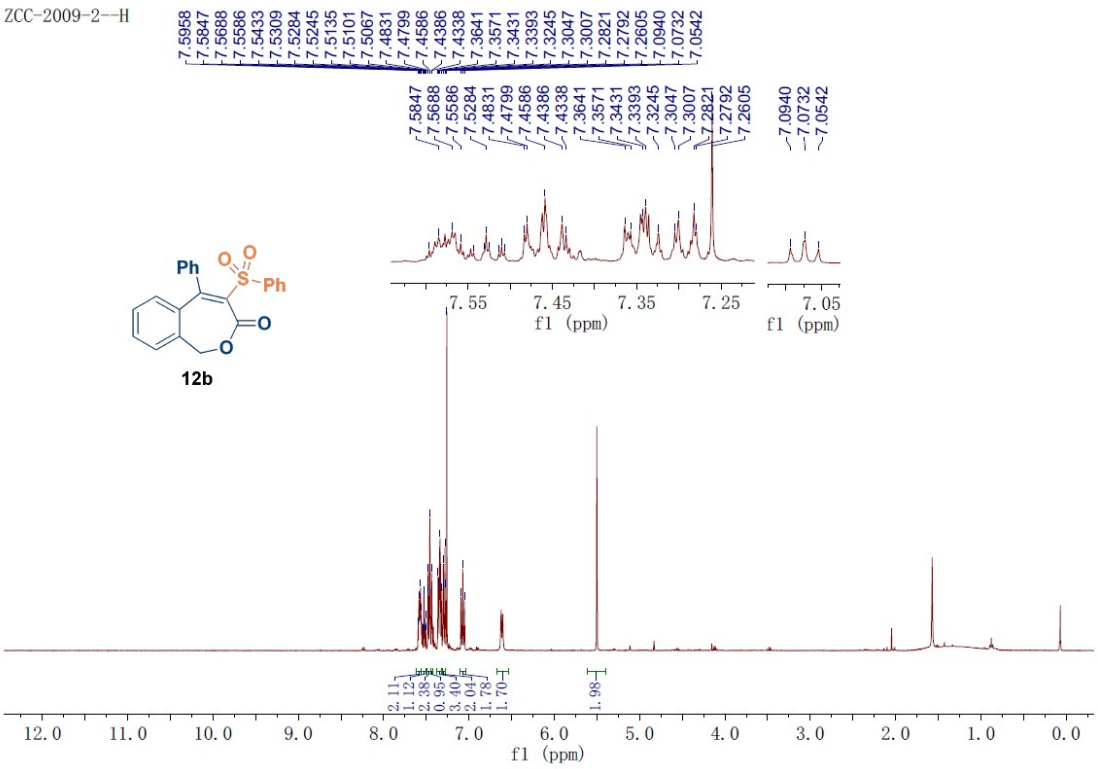
^{1}H NMR of **12a** (400 M, $CDCl_3$)



^{13}C NMR of **12a** (100 M, $CDCl_3$)



^{1}H NMR of **12b** (400 M, $CDCl_3$)



^{13}C NMR of **12b** (100 M, $CDCl_3$)