Supporting information

Photoinduced synthesis of functionalized oxetanes via diradical-mediated ring contraction

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General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents were dried and purified according to the procedure from "Purification of Laboratory Chemicals book". Column chromatography was performed using silica gel. Reactions were monitored by TLC and visualized by UV lamp (254 nm) and stained with ethanolic solution of concentrated potassium permanganate. Yields generally referred to chromatographically isolated yields, unless otherwise noted. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra are recorded on a Bruker AV-400 spectrometer in $CDCl_3$ with TMS as internal standard. For ^{1}H NMR (400 MHz), $CDCl_3$ (δ = 7.26 ppm) served as internal standard and data are reported as follows: chemical shift (in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet), coupling constant (in Hz), and integration. GC-MS analysis was performed on 7890A-5975C/Agilent. HR-MS spectra were recorded on a Waters Xevo G2QTOF/UPLC mass spectrometer using TOF as the mass analyzer type. The photoreaction instrument (WPP-TEC-1020SL) was purchased from WATTCAS, China.

SPECTROPHOTOCOLORMETER ANALYSIS REPORT

Color Parameters:

CIE(1931:) x =0.1776 y =0.0296

CIE(1960:) u =0.2367 v =0.0592

CIE (1976:) u' =0.2367 v' =0.0888

Color Temperature： Tc=25000K Dominant Wave: WL.D=435.20nm Purity: PUR=93.54

Peak Wave: WL.P=392.5nm Delta Wave: WL.H=18.0nm

Color Tolerance: SDCM=186.7 Ra:Ra=15.0

CRI1=56.1 CRI2=16.3 CRI3=0.0 CRI4=0.0 CRI5=47.6

CRI6=0.0 CRI7=0.0 CRI8=0.0 CRI9=0.0 CRI10=0.0

CRI11=0.0 CRI12=0.0 CRI13=42.0 CRI14=6.3 CRI15=66.7

Photology Parameters:

Lum Flux: Φ(lm)=4.75lm Optical Power: Φe(mW)=2769.6mW η(lm/W)=0.4lm/W

Eletric Parameters:

Forward Voltage: VF = 22.68 V Forward Current: IF = 498.9 mA Power = 11.32 W

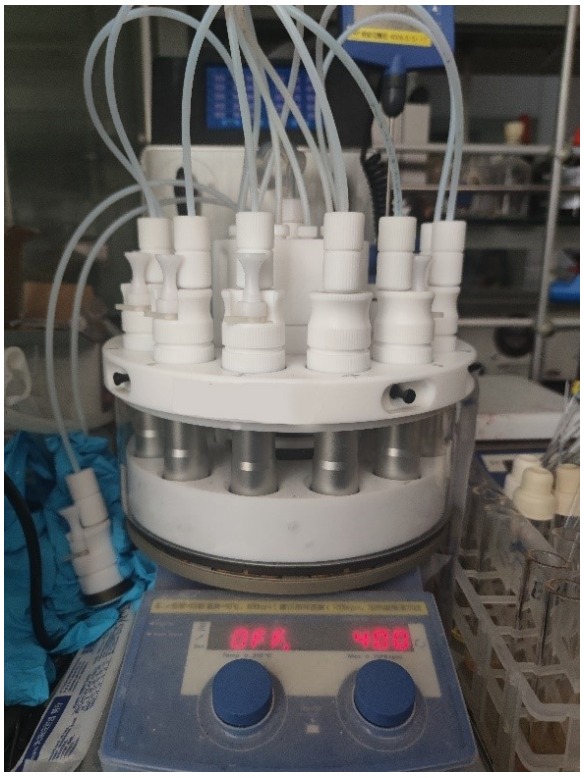


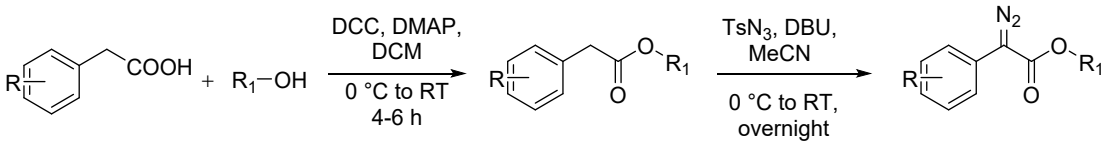
Figure S1. Photoreactor for photoreaction

Important Safety Note

Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

Synthesis of starting materials

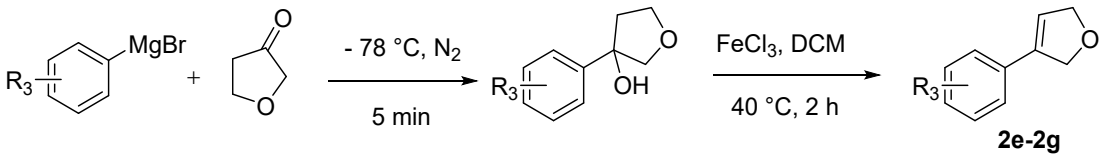
Synthesis of diazoacetates 1a-1x[1]



Step-I: To a stirred, ice cooled solution of the phenylacetic acid derivatives (10 mmol, 1 equiv.), and alcohol (12 mmol, 1.2 equiv.) in 20 mL DCM was added a solution of DCC (13 mmol, 1.3 equiv.) and DMAP (1 mmol, 0.1 equiv.) in 10 mL DCM at once. The solution was stirred 4-6 h while slowly warming up to room temperature. After finishing the reaction, the solid was filtered off and washed with Et_2O. The solvent was evaporated, and the residue was purified by silica gel column chromatography (pentane : ethyl acetate = 20:1) provided the desired ester.

Step-II: To a stirred, ice cooled solution of the ester (5 mmol, 1 equiv.) and p-Tosyl azide (5.5 mmol, 1.1 equiv.) in 10 mL MeCN were added DBU (7 mmol, 1.4 equiv.) dropwise. The solution was stirred over night while slowly warming up to room temperature. DCM was added, and the organic layer was washed two times with sat. aq. NH_4Cl solution. The organic layer was dried over $MgSO_4$ and the solvent was removed in vacuum. The crude product was purified by silica gel column chromatography using (pentane : ethyl acetate = 10:1) provided the desired diazo compound as a orange oil.

Synthesis of furan 2e-2g[2]

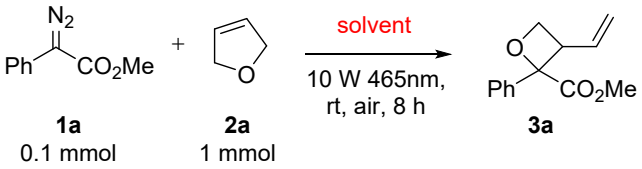


Step-I: In a dry round bottomed flask, dihydrofuran-3(2*H*)-one (2 mL, 10.0 mmol) was added dropwise to Grignard (1.0 M in THF, 5.0 mL, 12.0 mmol). Following a further 5 min at –78 °C the reaction mixture was warmed to rt and water (50 mL) was added. The layers were separated and the aqueous portion extracted with diethylether (3 × 50 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by flash column chromatography (Et_2O : pentane = 3 : 2) afforded tetrahydrofuran-3-ol as a clear oil. R_f = 0.26.

Step-II: $FeCl_3$ (0.125 mmol) was added to a solution of tetrahydrofuranol (2.5 mmol) in dichloromethane (5 mL). The reaction mixture was stirred at 40 °C for 2 h then sat. aq. $NaHCO_3$ (15 mL) was added followed by dichloromethane (15 mL). The layers were separated and the aqueous portion was extracted with dichloromethane (2 × 15 mL). The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by flash column chromatography (Et_2O : pentane = 5 : 1) afforded dihydrofuran as a yellow solid. R_f = 0.50.

Reaction Optimization

Table S1. Solvent optimization[a]



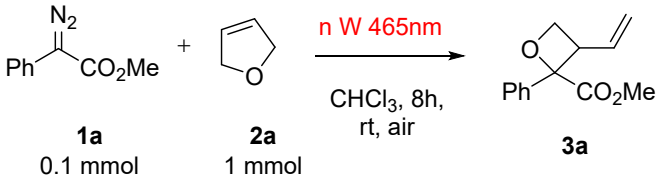
1a 0.1 mmol **2a** 1 mmol **3a**

Entry	solvent	Yield(%)
1	$CHCl_3$	70
2	DCM	55
3	MeCN	trace
4	EA	trace
5	Et_2O	trace

6	DMSO	trace
7	DMF	n.r.
8	MeOH	n.r.
9	PhMe	trace
10	acetone	trace

[a] Yields of isolated products.

Table S2. LEDs irradiation optimization[a]

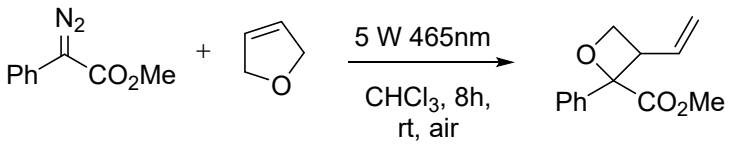


1a 0.1 mmol **2a** 1 mmol **3a**

Entry	n W	Yield(%)
1	1	33
2	2	39
3	3	41
4	4	49
5	5	70
6	6	40
7	7	38
8	8	39
9	9	37
10	10	30

[a] Yields of isolated products.

Table S3. Radio of 1a:2a optimization[a]

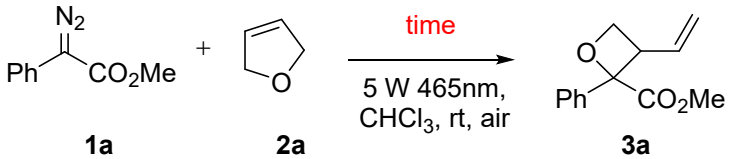


1a 0.1 mmol **2a** **3a**

Entry	Radio(1a:2a)	Yield(%)
1	1:1	<5
2	1:2	<10
3	1:5	40
4	1:10	70
5	1:15	42

[a] Yields of isolated products.

Table S4. Reaction time optimization[a]

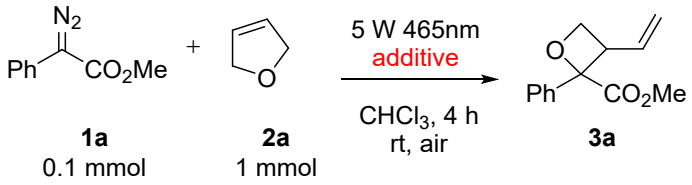


1a 0.1 mmol **2a** 1 mmol **3a**

Entry	Time	Yield(%)
1	1	57
2	2	55
3	3	79
4	4	92
5	5	79
6	6	75
7	7	74
8	8	70

[a] Yields of isolated products.

Table S5. Additive optimization[a]

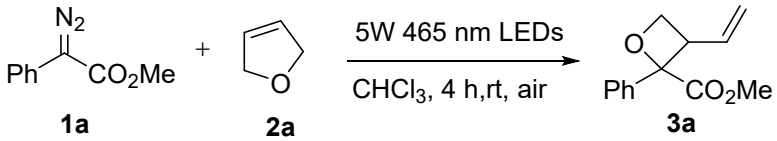


1a 0.1 mmol **2a** 1 mmol **3a**

Entry	additive	Yield(%)
1	KH_2PO_4	64
2	NH_4Cl	68
3	$FeCl_3$	trace
4	$AgBF_4$	trace
5	$NaHCO_3$	71
6	DABCO	55
7	Li_2CO_3	67
8	K_3PO_4	60

[a] Yields of isolated products.

General procedure for the multicomponent synthesis of vinyloxetane



1a **2a** **3a**

An oven dried 50 mL reaction vial was charged with a stir bar. Substrate **1a** (0.1 mmol, 1 eq), **2a** (1 mmol, 10 eq) was added with 1 mL $CHCl_3$. The reaction mixture was stirred and irradiated with 5 W blue LEDs lamp (WATTCAS：WPTEC-1020SL) for 4 hours until the reaction was

completed(monitored by TLC). After reaction, the solvent was removed by rotary evaporation. Purified by flash column chromatography on silica gel(petroleum ether: ethyl acetate = 10:1) afforded vinyloxetane as a yellow oil liquid. R_f = 0.2

General procedure for the gram-scale flow reaction

An oven dried 250 mL erlenmeyer flask was charged with a stir bar. Substrate **1a** (1.0 g, 5.7 mmol, 1 eq), **2a** (4 g, 57 mmol, 10 eq) was added with 20 mL $CHCl_3$.The reaction mixture was stirred and irradiated with commercially available blue light bulbs and flow pump for 4 hours. After reaction, the solvent was removed by rotary evaporation. Purified by flash column chromatography on silica gel(petroleum ether: ethyl acetate = 10:1) afforded vinyloxetane(0.66g, 54% yield) as a colorless oil. R_f= 0.2

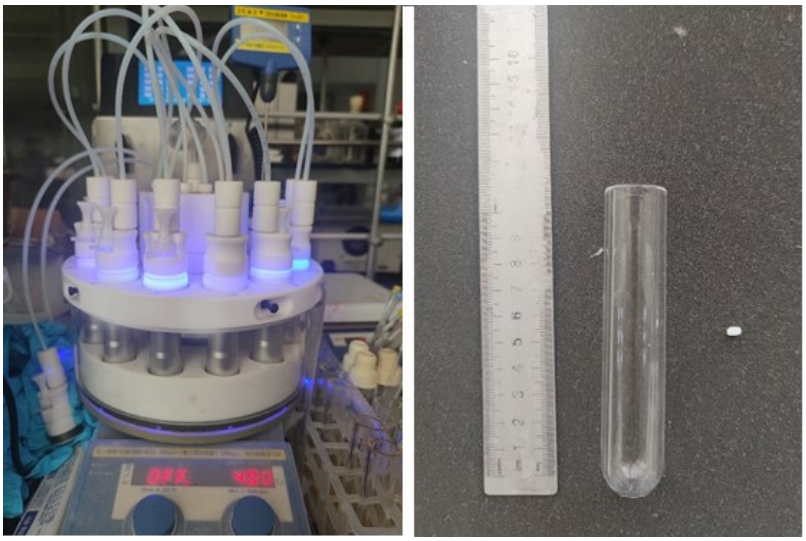


Figure S2. Reaction setup for general photoreactions

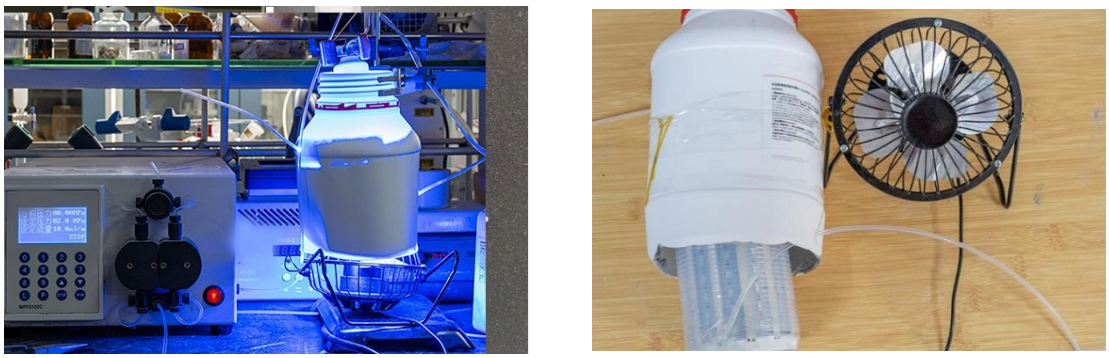


Figure S3. Flow reactor of photoreactions

UV-vis absorbance spectra of diazoacetates 1

Before the quenching experiments, the emission spectrum of methyl 2-diazo-2-phenylacetate (0.002 mM in $CHCl_3$, 1 mL) was measured after added 2 mL $CHCl_3$ to serve as the background experiment, in which the emission maximum λ_{max} was determined at 430 nm (Figure S4).

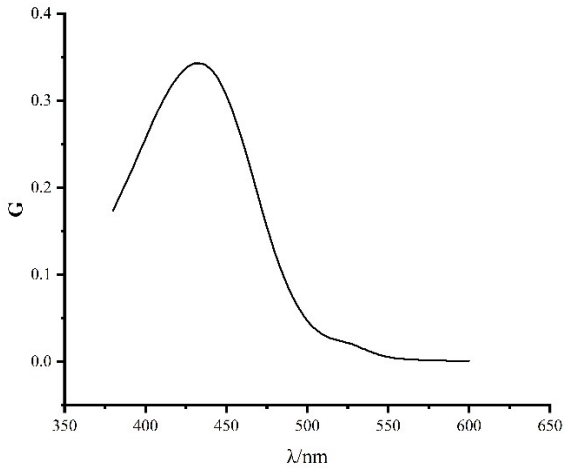
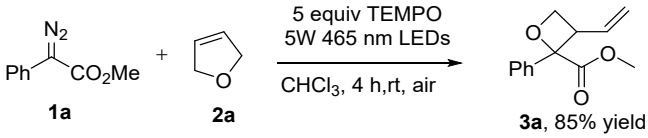
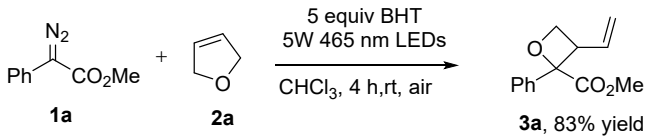


Figure S4. Emission spectrum of methyl 2-diazo-2-phenylacetate. Concentration = 6.67×10^{-4}mM (0.002/3 mM)

Control experiments

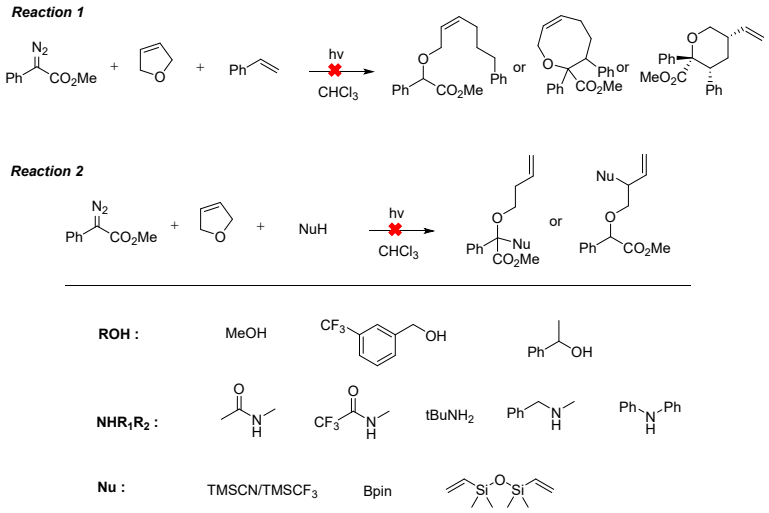


An oven dried 50 mL reaction vial was charged with a stir bar. Substrate **1a** (0.1 mmol, 1 eq), **2a** (1 mmol, 10 eq) , TEMPO (0.5 mmol, 5 eq) was added with 1 mL $CHCl_3$. The reaction mixture was stirred and irradiated with 5 W blue LEDs lamp (WATTCAS：WPTEC-1020SL) for 4 hours until the reaction was completed(monitored by TLC). After reaction, the solvent was removed by rotary evaporation. Purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) afforded vinyloxetane(85% yield) as a colorless oil.



An oven dried 50 mL reaction vial was charged with a stir bar. Substrate **1a** (0.1 mmol, 1 eq), **2a** (1 mmol, 10 eq) , BHT (0.5 mmol, 5 eq) was added with 1 mL $CHCl_3$. The reaction mixture was stirred and irradiated with 5 W blue LEDs lamp (WATTCAS：WPTEC-1020SL) for 4 hours until the reaction was completed(monitored by TLC). After reaction, the solvent was removed by rotary

evaporation. Purified by flash column chromatography on silica gel (petroleum ether: ethyl acetate = 10:1) afforded vinyloxetane (83% yield) as a colorless oil.



An oven dried 50 mL reaction vial was charged with a stir bar. Substrate **1a** (0.1 mmol, 1eq), **2a** (1 mmol, 10 eq) , nucleophile (0.12 mmol, 1.2 eq) was added with 1 mL $CHCl_3$. The reaction mixture was stirred and irradiated with 5 W blue LEDs lamp (WATTCAS：WPTEC-1020SL) for 4 hours until the reaction was completed(monitored by TLC). After reaction, the solvent was removed by rotary evaporation. Target product cannot be obtained.

DFT Calculations

Computational Details and Discussion

All the calculations were performed with the Gaussian 16 program.[3] DFT Method (U)B3LYP with a standard basis set 6-31G(d)[4,5] were applied for the optimization of all structures. Frequency calculations were performed to confirm that each stationary point is either a minimum or a transition structure. Key transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations. single-point energies calculations in the chloroform were computed at the (U)B3LYP level of theory with the 6-311+G(d,p) basis set in the chloroform with SMD solvation model.[6] Singlet diradical intermediates and transition states were located with UB3LYP/6-31G(d), where the keyword guess=mix was used. Gibbs free energies in solution were used in the paper.

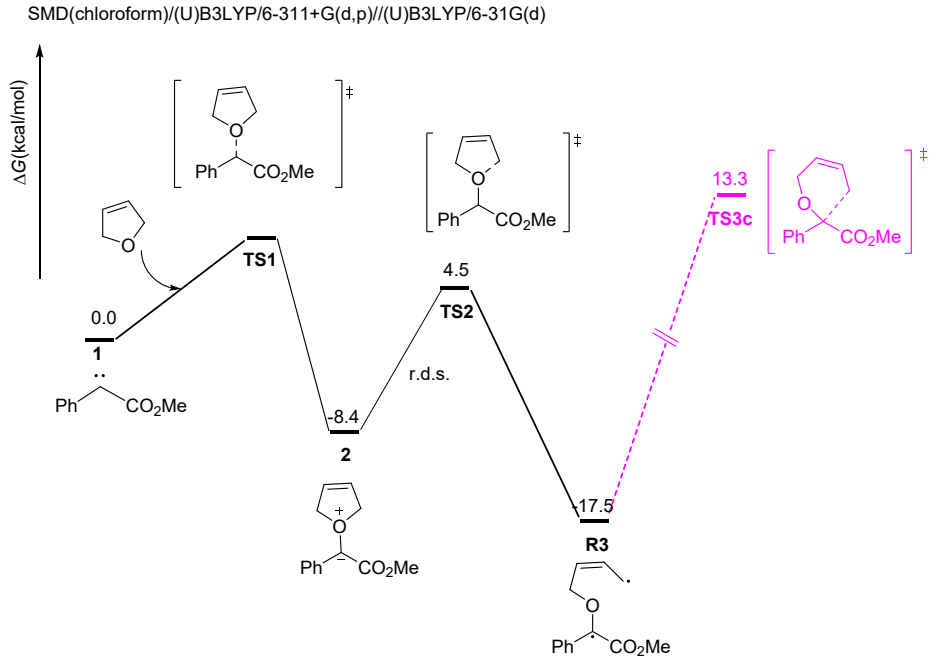


Figure S5. Free energy profiles for the concerted rearrangement process.

We have considered the selectivity for the products and the corresponding DFT calculation results are shown in Figure S5. These similar ring expansion processes involve the ylide formation, homolytic cleavage of C-O bond, rearrangement and intramolecular radical-radical coupling.

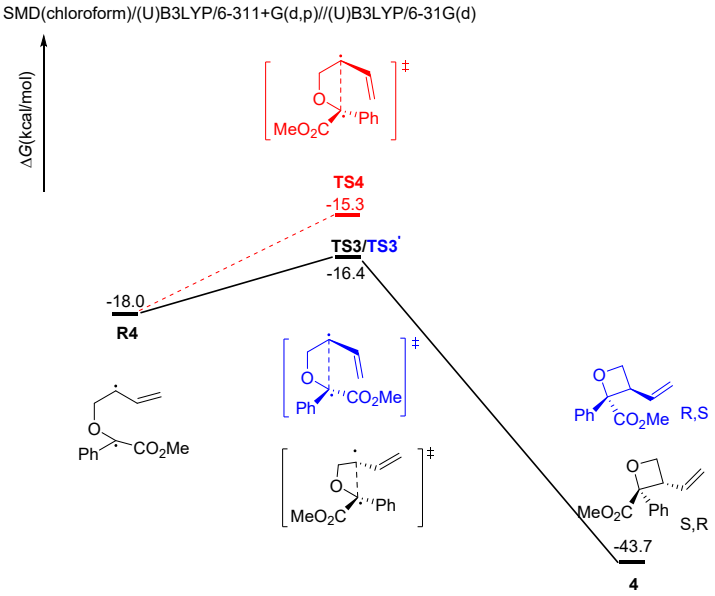


Figure S6. The stereoselective step.

Furthermore, we have computed several other substrates (Figure S7), e.g., naphthyl substituted carbene and 5,6-dihydro-2H-pyran. The low energy barrier of naphthyl substituted carbene (13.0

kcal mol^{-1}) and high energy barrier of 5,6-dihydro-2H-pyran (33.0 kcal mol^{-1}) in the rate-determining step is consistent with the observed reactivity in experiment.

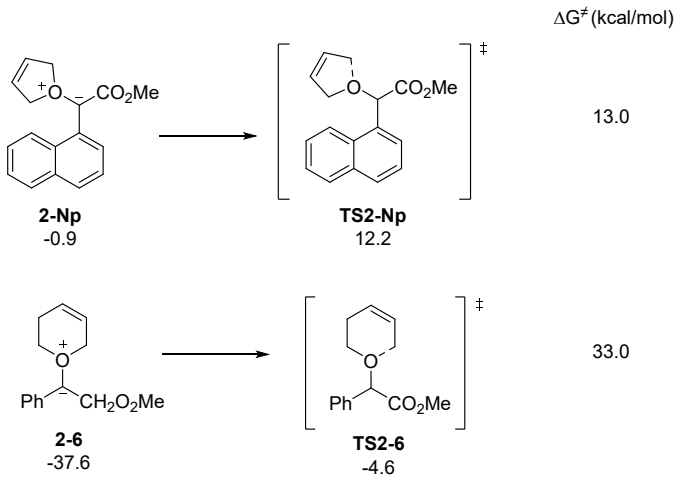


Figure S7. Computed energy barrier for other substrates.

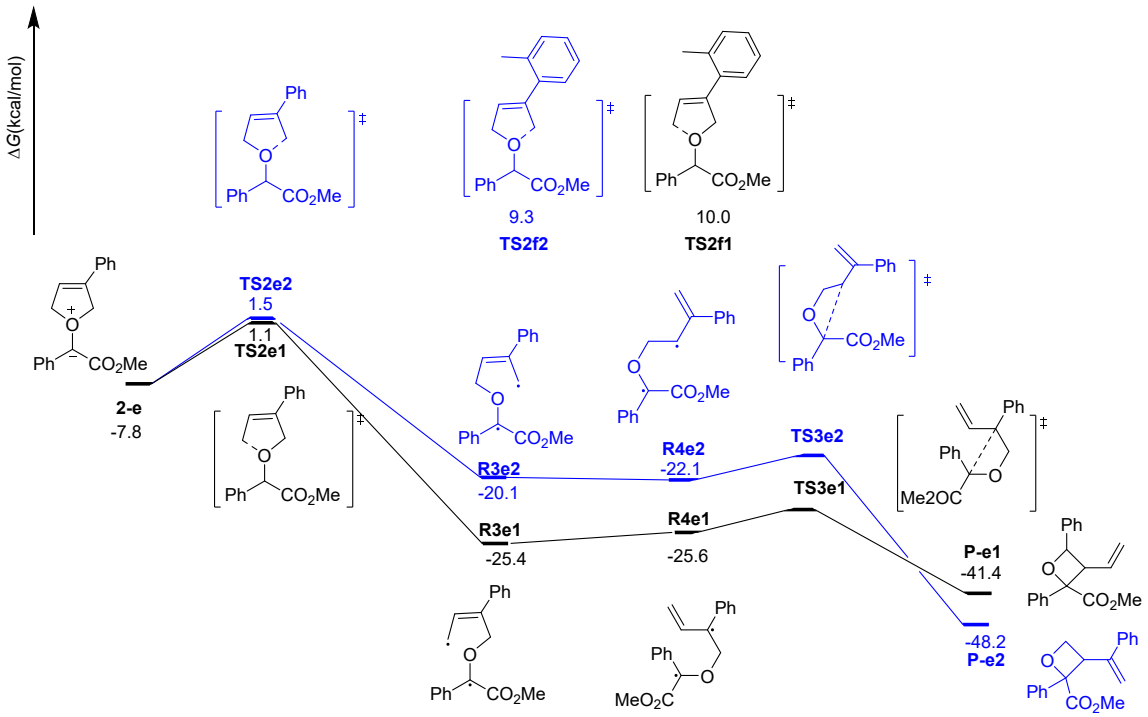


Figure S8. Free energy profiles for substrate **2e** and **2f**.

Computed Energies of All Stationary Points

	ΔG	E(gas)	G	E(sol)
1	0.10979	-498.15135	-498.04156	-498.3007883
2	0.201738	-729.417888	-729.21615	-729.6489636
TS2	0.19998	-729.401843	-729.20186	-729.6265603
I3	0.196164	-729.439201	-729.24304	-729.6340021
R3	0.195225	-729.438334	-729.24311	-729.656889
R4	0.19622	-729.440047	-729.24383	-729.6587491
TS3	0.198767	-729.439396	-729.24063	-729.6586507
TS3b	0.203409	-729.43891	-729.2355	-729.657751
TS3c	0.196804	-729.391403	-729.1946	-729.609379
TS3-pri	0.198754	-729.439322	-729.24057	-729.6587897
4	0.200651	-729.484653	-729.284	-729.7041749

1

C	2.564496	1.321868	-0.000241
C	1.210955	1.022262	-0.000292
C	0.779004	-0.337916	-0.000097
C	1.768419	-1.360281	0.000197
C	3.116683	-1.039224	0.000251
C	3.523388	0.300950	0.000016
H	2.881217	2.361139	-0.000407
H	0.458694	1.801557	-0.000421
H	1.446385	-2.396815	0.000363
H	3.859363	-1.831831	0.000487

H	4.580962	0.547935	0.000041
C	-0.579334	-0.687578	-0.000231
C	-1.813732	0.049849	0.000056
O	-1.884222	1.274696	0.000604
O	-2.897249	-0.758845	-0.000550
C	-4.160044	-0.077611	0.000131
H	-4.914608	-0.864364	0.002405
H	-4.258386	0.552338	0.888609
H	-4.260867	0.549322	-0.890246

2

C	-3.688894	0.943909	-0.000159
C	-2.320046	1.181462	0.000135
C	-1.401690	0.103644	0.000311
C	-1.932837	-1.206511	0.000193
C	-3.308253	-1.426634	-0.000107
C	-4.202557	-0.357039	-0.000286
H	-4.368180	1.793193	-0.000287
H	-1.930657	2.191942	0.000206
H	-1.261742	-2.061362	0.000376
H	-3.680232	-2.448756	-0.000193
H	-5.274640	-0.530740	-0.000514
C	0.016916	0.344536	0.000668
C	0.757210	1.540615	0.000180

O	0.329721	2.692451	0.000035
O	2.145371	1.289627	-0.000068
C	2.943239	2.473091	-0.000348
H	3.980585	2.130581	-0.001260
H	2.744346	3.083150	-0.886347
H	2.745775	3.082603	0.886362
C	1.513338	-1.319776	1.224907
C	2.480637	-2.309673	-0.666487
C	1.512726	-1.319567	-1.224869
H	0.739971	-1.727286	1.880061
H	1.977118	-0.435190	1.666577
H	3.103947	-2.924381	-1.305202
H	0.738846	-1.726795	-1.879574
H	1.976236	-0.434823	-1.666511
O	0.812318	-0.869193	0.000337
C	2.480992	-2.309816	0.665832
H	3.104654	-2.924666	1.304053

TS2

C	-3.684275	0.871986	0.081845
C	-2.325108	1.146024	-0.024103
C	-1.385110	0.093206	-0.106203
C	-1.874120	-1.233195	-0.074078
C	-3.235920	-1.491849	0.038073

C	-4.154487	-0.443287	0.116583
H	-4.386464	1.699851	0.140001
H	-1.969180	2.167468	-0.050767
H	-1.172332	-2.057651	-0.139188
H	-3.582261	-2.522200	0.061980
H	-5.218109	-0.647326	0.200708
C	0.041723	0.333025	-0.213071
C	0.693331	1.608109	-0.081814
O	0.185298	2.719710	-0.158668
O	2.056276	1.460619	0.145751
C	2.767459	2.697203	0.260803
H	3.810883	2.422160	0.424121
H	2.665655	3.292248	-0.650927
H	2.390334	3.284819	1.102269
C	1.741268	-1.539111	1.379562
C	2.406512	-2.383868	-0.730083
C	1.828295	-1.090176	-1.185731
H	0.996982	-1.750873	2.143584
H	2.290183	-0.611693	1.506682
H	2.738983	-3.123522	-1.449621
H	1.305905	-1.152903	-2.144802
H	2.526072	-0.248631	-1.193012
O	0.810934	-0.785793	-0.150426
C	2.299541	-2.618814	0.593343
H	2.468632	-3.603548	1.024952

R3

C	-3.940590	0.518593	0.136383
C	-2.608828	0.903381	0.066091
C	-1.580436	-0.075112	0.045983
C	-1.957522	-1.442411	0.110644
C	-3.292770	-1.809334	0.182716
C	-4.295260	-0.833355	0.194502
H	-4.713655	1.281911	0.147272
H	-2.339906	1.949219	0.016662
H	-1.178663	-2.195074	0.111394
H	-3.557839	-2.861884	0.231290
H	-5.340601	-1.123319	0.249970
C	-0.181465	0.246166	-0.031348
C	0.351023	1.610080	-0.096812
O	-0.295261	2.629745	-0.292531
O	1.702086	1.640844	0.097378
C	2.287978	2.947487	0.040504
H	3.356029	2.792515	0.195726
H	2.102180	3.412909	-0.931176
H	1.874035	3.588830	0.823056
C	3.710557	-1.021237	1.077422
C	2.475545	-2.190131	-0.714012
C	1.565297	-1.055960	-1.057831

H	4.509975	-1.046290	1.810822
H	3.110698	-0.119908	1.015389
H	2.353496	-3.117878	-1.265096
H	0.939245	-1.299913	-1.923339
H	2.130126	-0.144149	-1.275568
O	0.685110	-0.796774	0.073165
C	3.457466	-2.115546	0.271625
H	4.073432	-3.003216	0.414305

I3

C	-3.938117	0.492938	0.061028
C	-2.610853	0.898547	0.032179
C	-1.567432	-0.062769	0.078118
C	-1.924433	-1.434105	0.164625
C	-3.255389	-1.822024	0.192468
C	-4.272916	-0.863012	0.139578
H	-4.723324	1.242848	0.022221
H	-2.355850	1.947086	-0.032531
H	-1.133613	-2.172476	0.218465
H	-3.505501	-2.877277	0.258656
H	-5.314859	-1.169203	0.162211
C	-0.171311	0.278002	0.043042
C	0.350017	1.645267	-0.048923
O	-0.306664	2.663805	-0.213200

O	1.708786	1.676874	0.079267
C	2.288217	2.984980	-0.002828
H	3.362694	2.833178	0.103351
H	2.057101	3.451174	-0.964441
H	1.908517	3.624503	0.798391
C	3.759349	-1.085105	0.972067
C	2.383484	-2.232398	-0.721296
C	1.518583	-1.059640	-1.023570
H	4.587624	-1.128438	1.671835
H	3.197944	-0.158944	0.913206
H	2.168218	-3.168026	-1.228605
H	0.828455	-1.273134	-1.846481
H	2.109871	-0.172839	-1.270981
O	0.715319	-0.741262	0.167483
C	3.419775	-2.186482	0.210019
H	3.999363	-3.098975	0.347260

R4

C	-3.234943	-1.365111	0.673319
C	-1.855599	-1.348970	0.511216
C	-1.234368	-0.330792	-0.255204
C	-2.066312	0.648546	-0.856020
C	-3.443006	0.616649	-0.687858
C	-4.039859	-0.387845	0.080574

H	-3.688464	-2.151123	1.270915
H	-1.240150	-2.103654	0.980032
H	-1.610173	1.419911	-1.463703
H	-4.057470	1.378708	-1.159542
H	-5.117722	-0.409367	0.213421
C	0.191091	-0.257267	-0.460033
C	1.141248	-1.237718	0.063682
O	0.921829	-2.052255	0.949762
O	2.350095	-1.170632	-0.567892
C	3.332578	-2.086786	-0.071920
H	4.227538	-1.905225	-0.668186
H	3.531857	-1.904548	0.988016
H	2.993755	-3.119046	-0.192345
C	0.118008	2.866005	1.085900
C	2.174206	1.659961	0.428271
C	1.837600	1.481053	-1.018058
H	-0.454440	3.353018	1.867707
H	-0.331157	2.819772	0.100675
H	3.114016	1.238921	0.771261
H	2.648738	0.977743	-1.543978
H	1.640719	2.443169	-1.503385
O	0.600372	0.748641	-1.269144
C	1.352970	2.307238	1.350164
H	1.722914	2.365908	2.373109

TS3

C	-2.603142	-1.974987	0.568392
C	-1.262933	-1.659158	0.457030
C	-0.852726	-0.542613	-0.323230
C	-1.855657	0.230926	-0.965209
C	-3.205386	-0.121567	-0.859834
C	-3.584865	-1.212178	-0.090970
H	-2.900666	-2.829025	1.170572
H	-0.509426	-2.244848	0.965255
H	-1.546340	1.023131	-1.631088
H	-3.952499	0.466846	-1.385069
H	-4.633481	-1.481390	-0.000433
C	0.504136	-0.109253	-0.419920
C	1.663298	-0.905185	0.025881
O	1.631515	-1.858517	0.788788
O	2.824376	-0.436960	-0.503900
C	3.998712	-1.138077	-0.078424
H	4.829073	-0.652579	-0.592074
H	4.121833	-1.066592	1.006174
H	3.939959	-2.194006	-0.355123
C	-1.454347	2.521901	0.647187
C	0.868724	1.773504	0.971210
C	1.298344	2.021203	-0.473194
H	-2.451863	2.655384	1.050261

H	-1.286937	2.875534	-0.362990
H	1.645183	1.560458	1.699589
H	2.389520	2.011298	-0.551498
H	0.930959	2.973476	-0.878774
O	0.740834	0.972129	-1.275231
C	-0.430721	2.062000	1.428263
H	-0.649738	1.810006	2.464853

TS3b

C	-2.474586	-2.053240	0.489528
C	-1.154626	-1.738971	0.357486
C	-0.753324	-0.539934	-0.335225
C	-1.808036	0.356402	-0.825124
C	-3.183488	-0.096003	-0.746842
C	-3.509295	-1.235933	-0.083959
H	-2.756155	-2.956679	1.023784
H	-0.382989	-2.372247	0.772532
H	-1.536749	0.931954	-1.703568
H	-3.950958	0.518753	-1.209903
H	-4.545312	-1.551455	0.001551
C	0.554862	-0.120072	-0.472482
C	1.740168	-0.878920	-0.034501
O	1.743823	-1.915292	0.611267
O	2.889939	-0.272973	-0.434939

C	4.089281	-0.945392	-0.034786
H	4.907047	-0.343871	-0.433050
H	4.153053	-1.009363	1.055291
H	4.120511	-1.957563	-0.446843
C	-1.723209	2.055902	0.382978
C	0.638236	1.902879	1.100120
C	1.200253	2.111747	-0.290770
H	-2.743446	2.113420	0.750768
H	-1.518121	2.749685	-0.429033
H	1.348763	1.778349	1.912930
H	2.293809	2.130387	-0.262514
H	0.850059	3.048186	-0.744501
O	0.765721	1.061068	-1.169836
C	-0.688666	1.896690	1.372777
H	-1.000805	1.647089	2.385420

TS3c

C	0.838086	-0.664574	1.681030
C	2.182308	-1.064685	1.538896
C	2.447428	-2.137304	0.583612
C	2.006885	-1.888742	-0.827589
C	0.288223	-0.246546	-0.216249
H	2.950087	-3.067271	0.836851
H	2.972305	-0.340058	1.755448

H	0.085263	-1.447784	1.752642
H	0.604326	0.234317	2.247110
H	2.660651	-1.170659	-1.336942
H	1.976980	-2.813495	-1.409315
C	-1.193483	-0.120947	-0.138430
C	-1.846746	1.068007	0.233431
C	-1.978278	-1.263013	-0.386120
C	-3.234728	1.109922	0.340054
H	-1.267787	1.957134	0.442949
C	-3.365038	-1.212703	-0.276960
H	-1.486510	-2.183404	-0.674391
C	-4.003939	-0.026343	0.085969
H	-3.717094	2.041073	0.624907
H	-3.948986	-2.106503	-0.479405
H	-5.086198	0.012166	0.170702
C	1.131427	0.951598	-0.554071
O	1.978168	0.971422	-1.425163
O	0.924726	1.996673	0.282474
C	1.738611	3.151526	0.021567
H	1.442241	3.889223	0.767328
H	2.797359	2.901278	0.124401
H	1.559183	3.528685	-0.988280
O	0.646312	-1.389582	-0.900416

TS3-pri

C	-3.427417	-1.133069	0.829289
C	-2.070170	-1.140341	0.536360
C	-1.490806	-0.072795	-0.194763
C	-2.333848	0.986569	-0.614610
C	-3.689462	0.977044	-0.317658
C	-4.246557	-0.080939	0.407335
H	-3.853392	-1.958562	1.392773
H	-1.438287	-1.952030	0.869181
H	-1.900547	1.801954	-1.180580
H	-4.317594	1.798225	-0.651738
H	-5.307329	-0.085176	0.641293
C	-0.088971	-0.008278	-0.523346
C	0.871211	-1.082852	-0.227820
O	0.717247	-1.972882	0.594988
O	1.997000	-0.977179	-0.982593
C	2.987597	-1.978583	-0.713165
H	3.828534	-1.736437	-1.363926
H	3.289368	-1.947828	0.336088
H	2.599120	-2.973942	-0.944542
C	3.536988	0.986004	1.253734
C	1.218016	1.671830	0.689716
C	1.352955	1.772678	-0.804407
H	4.251540	0.720600	2.025464
H	3.890996	0.961702	0.228998

H	0.271672	2.015616	1.097359
H	2.310832	1.390193	-1.161826
H	1.225870	2.798561	-1.173049
O	0.280605	1.001942	-1.381346
C	2.248257	1.338089	1.579357
H	1.983643	1.339936	2.635990

4

C	-2.065398	-1.975550	1.114838
C	-0.955272	-1.136250	1.047516
C	-0.626719	-0.500937	-0.156657
C	-1.410994	-0.720326	-1.289854
C	-2.520280	-1.563713	-1.219545
C	-2.852084	-2.191054	-0.018625
H	-2.314940	-2.463336	2.053031
H	-0.337592	-0.975169	1.926182
H	-1.136006	-0.231879	-2.217604
H	-3.125039	-1.731303	-2.106583
H	-3.716902	-2.846419	0.034606
C	0.554503	0.448183	-0.224822
C	1.783948	-0.230038	0.366902
O	2.100377	-0.136118	1.536071
O	2.433388	-0.968715	-0.540038
C	3.573933	-1.688180	-0.041620

H	3.979530	-2.220732	-0.901385
H	4.312871	-0.995319	0.368651
H	3.269000	-2.388925	0.739915
C	-1.918997	2.986242	0.735144
C	0.316777	1.899703	0.321855
C	0.423261	2.303006	-1.158017
H	-2.783606	3.142439	1.373330
H	-1.911864	3.528346	-0.206702
H	1.190440	2.211284	0.903491
H	1.203033	3.028263	-1.412212
H	-0.521689	2.600854	-1.625259
O	0.794174	0.959217	-1.553838
C	-0.926772	2.176400	1.101735
H	-0.986179	1.661901	2.059884

2e

C	3.178027	0.700207	0.000285
C	0.923362	0.095358	-0.000000
C	1.767460	-1.161608	-0.000281
H	3.731549	1.052178	-0.885784
H	3.731206	1.051486	0.886868
H	1.576856	-1.786343	-0.887406
H	1.576990	-1.786557	0.886710
O	3.123711	-0.726448	-0.000342

C	1.748751	1.150786	0.000292
H	1.466681	2.197539	0.000641
C	-0.542371	0.061616	-0.000003
C	-1.222064	-1.168024	0.000200
C	-1.308829	1.241293	-0.000255
C	-2.615447	-1.218247	0.000237
H	-0.658926	-2.096156	0.000311
C	-2.697871	1.191425	-0.000216
H	-0.808952	2.205077	-0.000516
C	-3.359845	-0.039955	0.000045
H	-3.118025	-2.181373	0.000415
H	-3.268745	2.115812	-0.000407
H	-4.445351	-0.077179	0.000072

2-e

C	4.953583	-1.362056	-0.631856
C	4.039252	-0.322649	-0.514122
C	2.722248	-0.569793	-0.056371
C	2.384327	-1.902953	0.271255
C	3.313599	-2.933066	0.147162
C	4.607485	-2.677220	-0.304960
H	5.957321	-1.139484	-0.986461
H	4.315129	0.692886	-0.769646
H	1.383865	-2.134795	0.626697

H	3.017461	-3.946557	0.408429
H	5.330546	-3.481939	-0.400853
C	1.771458	0.503061	0.066263
C	1.879286	1.877780	-0.211338
O	2.861624	2.488924	-0.625385
O	0.668664	2.554066	0.045873
C	0.724695	3.955422	-0.218141
H	-0.269354	4.341037	0.019517
H	1.480142	4.444449	0.403942
H	0.966573	4.150263	-1.267088
C	-0.676033	-0.028444	-0.378403
C	-1.435881	0.110090	1.825402
C	0.027200	0.367287	1.924176
H	-0.499079	-0.922067	-0.980470
H	-0.665742	0.871833	-0.995645
H	-2.070773	0.138546	2.702533
H	0.589903	-0.311021	2.570606
H	0.293909	1.407686	2.125066
O	0.470075	0.072738	0.543341
C	-1.842689	-0.111826	0.565840
C	-3.196720	-0.380704	0.071421
C	-3.453696	-0.393304	-1.309220
C	-4.262226	-0.631794	0.953294
C	-4.736962	-0.639833	-1.793914
C	-5.541447	-0.877750	0.468887

C	-5.785174	-0.882048	-0.907594
H	-2.650775	-0.200495	-2.014863
H	-4.084270	-0.646116	2.024139
H	-4.915073	-0.642231	-2.865070
H	-6.351504	-1.072254	1.165619
H	-6.785008	-1.076763	-1.283767

TS2e1

C	-4.438756	-2.183446	-0.394564
C	-3.781435	-0.959940	-0.460828
C	-2.431056	-0.848863	-0.056534
C	-1.782795	-2.013896	0.415932
C	-2.454680	-3.229101	0.481084
C	-3.787876	-3.326551	0.076436
H	-5.475902	-2.243724	-0.714482
H	-4.291402	-0.079532	-0.828763
H	-0.746772	-1.951318	0.730375
H	-1.931766	-4.108122	0.849559
H	-4.310163	-4.277760	0.125703
C	-1.703790	0.404533	-0.107223
C	-2.262865	1.690627	-0.438965
O	-3.336356	1.921181	-0.980610
O	-1.411187	2.722235	-0.072971
C	-1.897907	4.028548	-0.398039

H	-1.125505	4.721935	-0.061412
H	-2.059791	4.127442	-1.474919
H	-2.842393	4.228510	0.115178
C	0.217568	0.954387	2.160625
C	1.878606	0.449438	0.536791
C	0.728421	0.808846	-0.345129
H	-0.348507	0.509396	2.976112
H	-0.096778	1.953154	1.876417
H	0.697632	0.278396	-1.298273
H	0.601059	1.880979	-0.515022
O	-0.461470	0.365561	0.430829
C	1.526919	0.475843	1.861766
H	2.106091	-0.060603	2.609294
C	3.151816	-0.044295	0.017377
C	3.292687	-0.535437	-1.295082
C	4.295179	-0.035968	0.842825
C	4.515181	-1.021505	-1.750179
H	2.440102	-0.557396	-1.965424
C	5.514512	-0.521878	0.385964
H	4.223619	0.381013	1.842541
C	5.632209	-1.020696	-0.913795
H	4.594330	-1.402769	-2.764229
H	6.380271	-0.500905	1.041826
H	6.586352	-1.394405	-1.273234

TS2e2

C	-4.081325	2.550135	-0.462766
C	-3.632550	1.241793	-0.316071
C	-2.305390	0.974211	0.090516
C	-1.460124	2.083338	0.333166
C	-1.919143	3.385801	0.176309
C	-3.234399	3.633853	-0.221777
H	-5.108575	2.723502	-0.773420
H	-4.304868	0.417810	-0.509711
H	-0.437426	1.906702	0.645875
H	-1.242815	4.214804	0.369037
H	-3.592707	4.652292	-0.340914
C	-1.773133	-0.367754	0.255449
C	-2.343545	-1.646265	-0.078322
O	-1.670460	-2.675802	-0.209829
O	-3.698728	-1.659641	-0.212484
C	-4.257789	-2.931769	-0.555208
H	-5.332312	-2.763598	-0.638407
H	-3.851789	-3.293713	-1.503948
H	-4.045414	-3.671456	0.221644
C	1.015438	-0.870655	-0.772755
C	1.552232	-1.087702	1.510077
C	0.086970	-1.281204	1.607165
H	1.009259	-0.133273	-1.571223

H	0.487052	-1.797533	-0.969819
H	2.161364	-1.039369	2.405370
H	-0.348433	-0.920212	2.544002
H	-0.272724	-2.290842	1.385972
O	-0.442851	-0.415650	0.506865
C	2.020603	-0.790212	0.267858
C	3.369867	-0.257633	-0.016088
C	3.941926	-0.434156	-1.285816
C	4.109448	0.429251	0.960720
C	5.215605	0.054361	-1.570304
H	3.387418	-0.976777	-2.046634
C	5.385342	0.909219	0.679881
H	3.667173	0.611288	1.935343
C	5.943697	0.724707	-0.587212
H	5.641709	-0.095154	-2.558291
H	5.940167	1.442675	1.446586
H	6.936873	1.105681	-0.806822

R3e1

C	-3.702310	-2.879738	0.034152
C	-3.370273	-1.540862	-0.122146
C	-2.064378	-1.084749	0.195532
C	-1.127930	-2.031161	0.689713
C	-1.477457	-3.364662	0.842036

C	-2.765242	-3.801217	0.513184
H	-4.705384	-3.210538	-0.220467
H	-4.096546	-0.833919	-0.498090
H	-0.135984	-1.691051	0.959152
H	-0.743919	-4.069981	1.222726
H	-3.036083	-4.846419	0.631771
C	-1.645266	0.283182	0.046048
C	-2.519345	1.373206	-0.395854
O	-3.626028	1.250471	-0.901848
O	-1.963465	2.599629	-0.169777
C	-2.772839	3.708359	-0.582825
H	-2.187819	4.597948	-0.347757
H	-2.983008	3.656427	-1.654498
H	-3.720592	3.716197	-0.038198
C	1.283318	3.296984	1.365869
C	1.890482	1.243234	0.114176
C	0.530276	1.164342	-0.512122
H	1.584880	4.071489	2.063354
H	0.254420	3.315433	1.022608
H	0.534026	0.542282	-1.411598
H	0.166707	2.156397	-0.780734
O	-0.380612	0.567103	0.453258
C	2.165603	2.319029	0.992398
H	3.153569	2.347398	1.445966
C	2.855345	0.187230	-0.144770

C	2.436865	-1.079920	-0.617924
C	4.242895	0.371419	0.065958
C	3.349761	-2.102384	-0.849909
H	1.381576	-1.276536	-0.769639
C	5.151781	-0.650789	-0.174662
H	4.613238	1.337854	0.390732
C	4.713860	-1.897389	-0.631740
H	2.992748	-3.067180	-1.199433
H	6.211452	-0.472982	-0.013268
H	5.426686	-2.695133	-0.818357

R3e2

C	-5.274081	1.563533	-0.303552
C	-4.403737	0.486720	-0.205948
C	-3.007961	0.704220	-0.064703
C	-2.539625	2.044345	-0.038234
C	-3.422788	3.108511	-0.139197
C	-4.796542	2.877999	-0.270918
H	-6.339337	1.377118	-0.407722
H	-4.777986	-0.527190	-0.227083
H	-1.474697	2.219203	0.053818
H	-3.041740	4.125741	-0.116595
H	-5.486505	3.713317	-0.348799
C	-2.047067	-0.358905	0.047366

C	-2.385316	-1.784679	0.028780
O	-3.507821	-2.262359	0.114204
O	-1.277355	-2.571237	-0.106702
C	-1.539466	-3.980131	-0.129697
H	-0.562587	-4.454533	-0.227061
H	-2.032768	-4.296900	0.793107
H	-2.179186	-4.238193	-0.977705
C	1.930817	-1.430609	-0.779921
C	1.450551	0.126741	1.043197
C	0.042597	-0.325749	1.244940
H	2.615006	-1.800148	-1.535834
H	0.932984	-1.851312	-0.752365
H	1.827372	0.899124	1.705871
H	-0.410182	0.181179	2.104185
H	-0.014225	-1.407270	1.405054
O	-0.737996	0.009941	0.062823
C	2.312737	-0.407538	0.077975
C	3.692122	0.152812	-0.023670
C	4.798385	-0.692125	-0.194359
C	3.912932	1.535883	0.048451
C	6.087335	-0.170538	-0.288597
H	4.644715	-1.766704	-0.232071
C	5.201502	2.059179	-0.046460
H	3.063528	2.204407	0.154354
C	6.294158	1.207771	-0.214662

H	6.932237	-0.842371	-0.412640
H	5.350823	3.134291	0.002682
H	7.298599	1.614846	-0.288548

R4e1

C	-4.299051	-1.287662	1.132759
C	-2.979617	-1.315762	0.700519
C	-2.493077	-0.322755	-0.187362
C	-3.399248	0.676511	-0.626527
C	-4.715635	0.688141	-0.189174
C	-5.177021	-0.290500	0.697188
H	-4.647577	-2.053900	1.819855
H	-2.304389	-2.084271	1.050136
H	-3.051833	1.426113	-1.326297
H	-5.389856	1.463737	-0.542344
H	-6.207316	-0.277279	1.040975
C	-1.137002	-0.302577	-0.670115
C	-0.150227	-1.344516	-0.373009
O	-0.178416	-2.104709	0.584933
O	0.831183	-1.395963	-1.312933
C	1.867869	-2.350719	-1.043569
H	2.585920	-2.234272	-1.854820
H	2.341719	-2.139917	-0.082839
H	1.457063	-3.363703	-1.031260

C	-0.892220	2.839134	0.725654
C	1.026782	1.494601	-0.101018
C	0.459946	1.365828	-1.489877
H	-1.338122	3.398783	1.540710
H	-1.451819	2.789089	-0.200133
H	1.133681	0.817603	-2.145734
H	0.242663	2.344304	-1.928896
O	-0.840920	0.705839	-1.527721
C	0.316891	2.215851	0.885297
H	0.799033	2.305035	1.856559
C	2.295532	0.847622	0.225438
C	2.526604	0.313575	1.511599
C	3.328414	0.724587	-0.728503
C	3.730970	-0.308003	1.826399
C	4.534887	0.111453	-0.408378
C	4.744662	-0.410185	0.870624
H	1.731056	0.341629	2.248605
H	3.193189	1.137715	-1.723138
H	3.873384	-0.727347	2.818340
H	5.317324	0.043024	-1.159102
H	5.684346	-0.895430	1.117482

R4e2

C	-3.550612	-1.789936	-1.553112

C	-2.734496	-0.682156	-1.363473
C	-2.415165	-0.241274	-0.054209
C	-2.968712	-0.954754	1.039875
C	-3.785808	-2.056707	0.833913
C	-4.081420	-2.486847	-0.463620
H	-3.775593	-2.114461	-2.565395
H	-2.321329	-0.153984	-2.211088
H	-2.754073	-0.616722	2.045905
H	-4.197564	-2.584990	1.689559
H	-4.718862	-3.351861	-0.622744
C	-1.568199	0.894898	0.209789
C	-0.990454	1.742252	-0.833223
O	-0.905553	1.466252	-2.021825
O	-0.546993	2.934268	-0.337245
C	0.076063	3.786033	-1.305631
H	0.375121	4.680188	-0.757483
H	0.947626	3.294925	-1.747937
H	-0.625693	4.041438	-2.103791
C	0.549620	-1.281081	1.789662
C	1.071813	1.063459	1.320482
C	-0.106176	1.632213	2.040886
H	0.814616	-2.329930	1.721925
H	-0.361435	-1.030962	2.317923
H	1.709543	1.761438	0.789087
H	-0.078982	2.721629	2.019356

H	-0.146689	1.295218	3.082065
O	-1.402402	1.197622	1.519649
C	1.350943	-0.305165	1.215341
C	2.550997	-0.720536	0.433023
C	2.470745	-1.780888	-0.480636
C	3.776553	-0.057218	0.586851
C	3.587241	-2.169550	-1.218864
C	4.894195	-0.446449	-0.149531
C	4.803201	-1.504351	-1.055274
H	1.518709	-2.282045	-0.628628
H	3.855871	0.754426	1.304626
H	3.504475	-2.986935	-1.929732
H	5.838490	0.072833	-0.010962
H	5.673381	-1.806999	-1.630826

Pe1

C	3.403792	-0.521409	-1.931307
C	2.148787	-0.641406	-1.336706
C	1.978338	-0.337893	0.021555
C	3.083541	0.088758	0.765468
C	4.339349	0.197899	0.169735
C	4.504173	-0.103368	-1.181755
H	3.520970	-0.761480	-2.984485
H	1.309463	-0.996339	-1.920109

H	2.944654	0.331420	1.811748
H	5.188595	0.524070	0.763896
H	5.481301	-0.013212	-1.648241
C	0.624028	-0.367858	0.688743
C	-0.199852	-1.626704	0.383540
O	-0.108733	-2.307329	-0.615434
O	-1.126073	-1.829392	1.335523
C	-2.097769	-2.842189	1.028426
H	-2.763786	-2.875704	1.890335
H	-2.647194	-2.566963	0.124212
H	-1.610495	-3.807918	0.876635
C	0.787951	3.245706	0.483565
C	-0.299015	0.948797	0.535684
C	-0.292371	0.899532	2.077657
H	1.301207	4.019603	-0.079141
H	0.572039	3.472325	1.523351
H	-1.228884	0.545246	2.516237
H	0.047907	1.794610	2.604317
O	0.706388	-0.137690	2.105174
C	0.450085	2.095168	-0.094700
H	0.695488	1.939684	-1.143369
C	-1.628446	0.784430	-0.177141
C	-2.834518	1.131607	0.440470
C	-1.663117	0.314292	-1.497066
C	-4.047635	0.992723	-0.233633

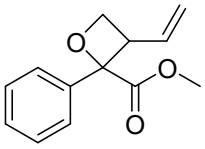
C	-2.874488	0.167779	-2.170481
C	-4.073153	0.503906	-1.539854
H	-2.832157	1.517778	1.454987
H	-0.738604	0.047988	-1.998413
H	-4.973374	1.266542	0.264802
H	-2.879870	-0.210498	-3.188718
H	-5.017987	0.389496	-2.063344

Pe2

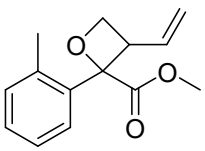
C	-0.991085	2.421873	1.000977
C	-0.081653	1.604787	0.335119
C	0.494458	0.509669	0.987213
C	0.165926	0.253731	2.320180
C	-0.742146	1.074532	2.988266
C	-1.327124	2.156536	2.329384
H	-1.444434	3.258574	0.477881
H	0.149611	1.798705	-0.707445
H	0.632000	-0.583940	2.826539
H	-0.992091	0.868098	4.025340
H	-2.039209	2.791562	2.849066
C	1.386432	-0.457659	0.244626
C	2.182764	0.246220	-0.856004
O	2.005558	0.096707	-2.048541
O	3.107486	1.058979	-0.330296

C	3.919737	1.767052	-1.280658
H	4.610878	2.362771	-0.685099
H	4.463288	1.064006	-1.916891
H	3.297485	2.409544	-1.909246
C	-1.220828	-3.026533	0.694638
C	0.744069	-1.807037	-0.238907
C	1.751565	-2.460907	0.721758
H	-2.289908	-3.189101	0.786842
H	-0.579667	-3.745993	1.192611
H	0.995277	-1.979010	-1.288688
H	2.510987	-3.095005	0.250552
H	1.325280	-2.983289	1.583650
O	2.294523	-1.178775	1.117053
C	-0.734161	-2.007064	-0.025363
C	-1.636639	-1.021806	-0.675212
C	-1.334396	-0.472889	-1.931177
C	-2.794265	-0.582851	-0.014477
C	-2.173820	0.476988	-2.511104
C	-3.629314	0.368644	-0.592290
C	-3.323412	0.902802	-1.845399
H	-0.427461	-0.762921	-2.449667
H	-3.005946	-0.955052	0.982593
H	-1.922337	0.889626	-3.484289
H	-4.510401	0.708246	-0.054839
H	-3.970548	1.651355	-2.294054

Characterization Data of Products

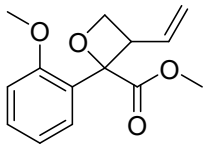


Compound 3a major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 7H), 5.94 (dd, J = 12.5, 6.4 Hz, 1H), 5.89 (d, J = 6.3 Hz, 1H), 5.53 (d, J = 6.2 Hz, 1H), 5.44 (tt, J = 7.6, 4.6 Hz, 1H), 4.66 – 4.58 (m, 3H), 3.73 (s, 4H), 3.71 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.57, 135.92, 128.84, 128.52, 128.20 , 127.85 , 127.56 , 87.77 , 75.71 , 58.30 , 52.20. **Compound 3a minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.30 (m, 5H), 5.94 (dd, J = 12.5, 6.4 Hz, 1H), 5.53 (d, J = 6.2 Hz, 1H), 5.44 (tt, J = 7.6, 4.6 Hz, 1H), 4.74 – 4.67 (m, 2H), 3.75 (s, 3H), 3.71 (d, J = 8.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.26, 135.07, 128.76, 128.52, 128.31, 127.80 , 87.33 , 75.66 , 57.20 , 52.09. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{14}O_3$: 219.1015; Found: 219.1007.

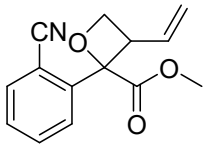


Compound 3b major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 1H), 7.21 (d, J = 2.7 Hz, 3H), 6.02 – 5.96 (m, 1H), 5.93 (dt, J = 6.4, 1.8 Hz, 1H), 5.56 – 5.46 (m, 1H), 4.80 – 4.65 (m, 3H), 4.02 (s, 1H), 3.73 (s, 3H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.91, 136.47, 133.76, 130.73, 128.23, 127.50, 127.38, 127.29, 126.42, 88.05, 75.74, 53.02, 52.15, 20.27. **Compound 3b minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 – 7.42 (m, 1H), 7.21 (d, J = 2.7 Hz, 3H), 6.02 – 5.96 (m, 1H), 5.56 – 5.46 (m, 1H), 5.43 (dd, J = 8.2, 4.7 Hz, 1H), 4.62 – 4.59 (m, 2H),

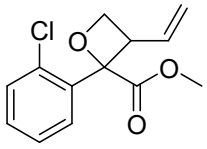
3.99 (d, *J* = 1.7 Hz, 1H), 3.70 (s, 3H), 2.41 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.91, 136.47, 133.76, 130.73, 128.23, 127.50, 127.38, 127.29, 126.42, 88.05, 75.74, 53.02, 52.15, 20.27. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_3$: 233.1172; Found: 233.1173.



Compound 3c major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.43 (d, *J* = 1.7 Hz, 1H), 7.32 – 7.22 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.88 (m, 1H), 5.87 (dd, *J* = 6.2, 1.8 Hz, 1H), 5.55 – 5.50 (m, 1H), 5.46 (m, 1H), 4.66 (dt, *J* = 4.1, 1.9 Hz, 2H), 4.24 (d, *J* = 8.6 Hz, 1H), 3.83 (s, 4H), 3.72 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.94 , 156.96, 129.28 , 128.75 , 127.70 , 127.49 , 124.01 , 120.82 , 111.06 , 87.39 , 75.70 , 55.70 , 52.01 , 49.95 . **Compound 3c minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.41 (d, *J* = 1.6 Hz, 1H), 7.32 – 7.22 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.88 (m, 1H), 5.94 – 5.89 (m, 1H), 5.87 (dd, *J* = 6.2, 1.8 Hz, 1H), 5.46 (m, 1H), 4.60 – 4.45 (m, 2H), 4.32 (d, *J* = 6.2 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.70, 157.14, 129.95 , 128.51 , 128.05 , 127.60 , 124.33, 120.62 , 110.66 , 86.40 , 75.62 , 55.61 , 51.95 , 49.00 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_4$: 249.1121; Found: 249.1123.

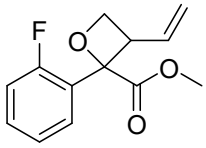


Compound 3d major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.73 – 7.66 (m, 2H), 7.61 (td, *J* = 7.8, 7.0, 4.8 Hz, 1H), 7.47 – 7.37 (m, 1H), 6.01 (d, *J* = 6.3 Hz, 1H), 5.95 (s, 1H), 5.47 (m, 1H), 4.69 – 4.63 (m, 2H), 4.20 (d, *J* = 6.8 Hz, 1H), 3.77 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ*171.04 , 139.52 , 132.97 , 132.79 , 129.06 , 128.96 , 127.89 , 127.11 , 117.99 , 114.35, 87.16 , 75.90 , 54.67 , 52.51 . **Compound 3d minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.73 – 7.66 (m, 2H), 7.61 (td, *J* = 7.8, 7.0, 4.8 Hz, 1H), 7.47 – 7.37 (m, 1H), 5.95 (s, 1H), 5.59 – 5.54 (m, 1H), 5.47 (m, 1H), 4.60 – 4.56 (m, 2H), 4.28 (d, *J* = 8.2 Hz, 1H), 3.77 (d, *J* = 1.8 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 171.25, 138.38, 133.22 , 132.60 , 129.59 , 128.87 , 128.20 , 126.07 , 117.64 , 113.56, 87.55 , 75.92 , 55.08 , 52.51 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}O_3N$: 244.0968; Found: 244.0971.

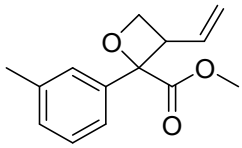


Compound 3e major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.59 (ddd, *J* = 7.5, 3.4, 1.9 Hz, 1H), 7.42 (ddd, *J* = 13.8, 7.6, 1.8 Hz, 1H), 7.30 – 7.22 (m, 2H), 6.00 – 5.96 (m, 1H), 5.94 – 5.85 (m, 1H), 5.59 – 5.52 (m, 1H), 4.64 – 4.47 (m, 2H), 4.45 (d, *J* = 6.0 Hz, 1H), 3.75 (s, 3H).. **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 171.84, 134.48, 133.54, 131.69, 130.30, 129.38, 128.66, 128.29, 127.28, 126.85, 86.85, 75.87, 52.94, 52.24. **Compound 3e minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ*

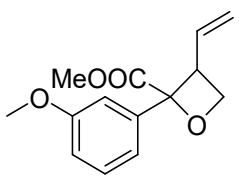
7.59 (ddd, *J* = 7.5, 3.4, 1.9 Hz, 1H), 7.42 (ddd, *J* = 13.8, 7.6, 1.8 Hz, 1H), 7.30 – 7.22 (m, 2H), 5.94 – 5.85 (m, 1H), 5.59 – 5.52 (m, 1H), 5.49 – 5.42 (m, 1H), 4.80 – 4.67 (m, 2H), 4.40 (d, *J* = 8.8 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.13, 134.29, 133.06, 130.64, 129.92, 128.88, 128.46, 127.18, 126.93, 87.74, 75.90, 52.35, 52.32. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}O_3Cl$: 253.0626; Found: 253.0624.



Compound 3f major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (q, *J* = 8.6, 7.7 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.20 – 7.03 (m, 2H), 5.97 – 5.92 (m, 1H), 5.89 (d, *J* = 1.6 Hz, 1H), 5.55 – 5.44 (m, 1H), 4.65 (s, 3H), 4.13 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 1.7 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.98, 161.53 , 161.45 , 137.30, 137.22, 130.15 , 130.06 , 128.50 , 126.97 , 124.60 , 124.29 , 114.58 (dd, *J* = 25.7, 21.1 Hz). 87.51 , 75.68 , 57.80 , 52.25 . **^{19}F NMR (376 MHz, CDCl3)** δ -116.83. **Compound 3f minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 (q, *J* = 8.6, 7.7 Hz, 1H), 7.29 (d, *J* = 7.0 Hz, 1H), 7.20 – 7.03 (m, 2H), 5.89 (d, *J* = 1.6 Hz, 1H), 5.65 – 5.59 (m, 1H), 5.55 – 5.44 (m, 1H), 4.59 (dd, *J* = 12.8, 3.4 Hz, 1H), 4.47 (dd, *J* = 13.0, 6.2 Hz, 1H), 4.17 (d, *J* = 6.0 Hz, 1H), 3.76 (d, *J* = 1.7 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.66, 163.98 , 163.90 , 138.22 , 138.14 , 129.82 , 129.73 , 128.48 , 127.48 , 124.58 , 124.26 , 115.68 (dd, *J* = 37.7, 22.1 Hz), 87.12 , 75.68 , 56.82 , 52.17 . **^{19}F NMR (376 MHz, CDCl3)** δ -118.03. **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{13}H_{13}O_3F$: 275.0480; Found: 275.0477.

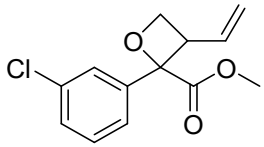


Compound 3g major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 8H), 5.92 (m, 2H), 5.52 (m, 2H), 5.48 – 5.38 (m, 2H), 4.76 – 4.64 (m, 4H), 3.75 (s, 6H), 3.62 (d, *J* = 9.5 Hz, 2H), 2.38 (d, *J* = 2.4 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.68, 138.48 , 134.97 , 129.10 , 128.57 , 128.44 , 128.23 , 127.55 , 125.53 , 87.77 , 87.35 , 75.69 , 58.27 , 52.18 , 21.46 . **Compound 3g minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 – 7.10 (m, 4H), 5.97 (dt, *J* = 6.3, 1.7 Hz, 1H), 5.92 (m, 1H), 5.48 – 5.38 (m, 1H), 4.63 – 4.58 (m, 2H), 3.72 (s, 3H), 3.66 (d, *J* = 7.8 Hz, 1H), 2.38 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.36, 138.16, 135.88, 129.41 , 128.64 , 128.41 , 128.07 , 127.98 , 125.79 , 87.77 , 87.35 , 75.61 , 57.22 , 52.06 , 21.53 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_3$: 233.1172; Found: 233.1173.

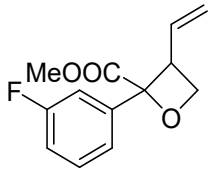


Compound 3h major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 2.9 Hz,

1H), 6.97 (t, *J* = 8.5 Hz, 1H), 6.92 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.96 (dd, *J* = 15.4, 6.1 Hz, 1H), 5.57 – 5.52 (m, 1H), 5.44 (m, 1H), 4.76 – 4.64 (m, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 3.63 (d, J = 9.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.48, 159.81, 136.50 , 129.76 , 128.16 , 127.47 , 120.87 , 114.12 , 113.21 , 87.72 , 75.72 , 58.32 , 55.29 , 52.24 . **Compound 3h minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.26 (d, *J* = 2.9 Hz, 1H), 6.97 (t, *J* = 8.5 Hz, 1H), 6.92 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.96 (dd, *J* = 15.4, 6.1 Hz, 1H), 5.57 – 5.52 (m, 1H), 5.44 (m, 1H), 4.64 – 4.60 (m, 2H), 3.84 (s, 3H), 3.73 (s, 3H), 3.68 (d, *J* = 7.6 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.15, 159.62 , 137.43 , 129.49 , 128.32 , 127.88 , 121.20 , 114.55 , 112.99 , 87.32 , 75.66 , 57.22 , 55.24 , 52.12 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_4$: 249.1121; Found: 249.1123.

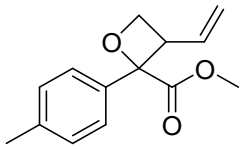


Compound 3i major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39 (d, *J* = 10.0 Hz, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.00 – 5.93 (m, 1H), 5.58 – 5.53 (m, 1H), 5.42 (dt, *J* = 4.1, 1.7 Hz, 1H), 4.73 – 4.63 (m, 3H), 3.77 (s, 4H), 3.67 (dd, *J* = 8.0, 6.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.02 , 136.91 , 134.55 , 129.96 , 128.70 , 128.65 , 128.05 , 127.14 , 126.80 , 87.56 , 75.78 , 57.80 , 52.38 . **Compound 3i minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.39 (d, *J* = 10.0 Hz, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.30 – 7.23 (m, 2H), 6.00 – 5.93 (m, 1H), 5.88 – 5.84 (m, 1H), 5.42 (dt, *J* = 4.1, 1.7 Hz, 1H), 4.60 (q, *J* = 3.9, 3.0 Hz, 2H), 3.75 (s, 3H), 3.67 (dd, *J* = 8.0, 6.3 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 171.70 , 137.81 , 134.28, 129.68 , 129.12 , 128.60 , 127.79 , 127.53 , 127.00 , 87.13 , 75.78 , 56.85 , 52.30 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}O_3Cl$: 253.0626; Found: 253.0624.

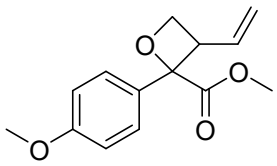


Compound 3j major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.36 – 7.29 (m, 1H), 7.17 – 7.09 (m, 2H), 7.01 (m, 1H), 5.96 (m, 1H), 5.55 (m, 1H), 5.45 – 5.38 (m, 1H), 4.73 – 4.62 (m, 3H), 3.76 (s, 4H), 3.69 (dd, *J* = 9.3, 8.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.06 , 164.06 , 163.97, 137.38 , 137.31, 130.22 , 130.14 , 128.58 , 127.05 , 124.70 , 124.37 , 114.65 (dd, *J* = 26.4, 21.0 Hz), 87.59 , 75.74 , 57.87 , 52.31 . **^{19}F NMR (376 MHz, CDCl3)** *δ* -112.40 . **Compound 3j minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.36 – 7.29 (m, 1H), 7.17 – 7.09 (m, 2H), 7.01 (m, 1H), 5.96 (m, 1H), 5.86 (m, 1H), 5.45 – 5.38 (m, 1H), 4.62 – 4.58 (m, 2H), 3.74 (s, 3H), 3.69 (dd, *J* = 9.3, 8.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 171.73 , 161.61, 161.53, 138.81, 138.23, 129.89 , 129.81 , 128.55 , 127.56 , 124.67 , 124.35 , 115.76 (dd, *J* = 38.3, 22.1 Hz), 87.19 , 75.74 , 56.89 , 52.23 . **^{19}F NMR (376 MHz, CDCl3)** *δ* -113.02 . **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{13}H_{13}O_3F$:

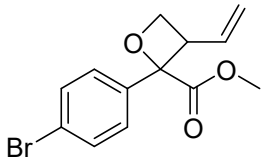
275.0480; Found: 275.0477.



Compound 3k major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 14.9 Hz, 3H), 7.17 (d, J = 8.1 Hz, 3H), 5.98 – 5.91 (m, 2H), 5.56 – 5.51 (m, 2H), 5.42 (m, 2H), 4.74 – 4.62 (m, 3H), 3.74 (s, 5H), 3.63 (d, J = 9.4 Hz, 2H), 2.36 (d, J = 3.2 Hz, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.75, 137.52, 132.06 , 129.46 , 128.34 , 128.09 , 127.52 , 87.77 , 75.69 , 57.90 , 52.16 , 21.14 . **Compound 3k minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.27 (d, J = 14.9 Hz, 2H), 7.17 (d, J = 8.1 Hz, 2H), 5.98 – 5.91 (m, 1H), 5.91 – 5.86 (m, 1H), 5.56 – 5.51 (m, 1H), 4.62 – 4.58 (m, 2H), 3.72 (s, 3H), 3.67 (d, J = 7.6 Hz, 1H), 2.36 (d, J = 3.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.41, 137.21, 132.94, 129.28 , 128.63 , 128.24 , 127.94 , 87.36 , 75.59 , 56.83 , 52.16 , 21.16 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_3$: 233.1172; Found: 233.1173.

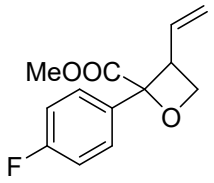


Compound 3l major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 4H), 6.90 (dd, J = 8.8, 3.0 Hz, 4H), 5.94 (m, 2H), 5.57 – 5.52 (m, 2H), 5.41 (m, 2H), 4.68 (m, 4H), 3.83 (s, 6H), 3.74 (s, 6H), 3.61 (d, J = 9.3 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.86 , 159.20, 129.54 , 128.14 , 127.88 , 127.51 , 114.31 , 114.14 , 113.97 , 87.82 , 75.70 , 57.40 , 55.30 , 52.14 . **Compound 3l minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33 – 7.25 (m, 2H), 6.90 (dd, J = 8.8, 3.0 Hz, 2H), 5.94 (m, 1H), 5.89 – 5.85 (m, 1H), 5.41 (m, 1H), 4.59 (dt, J = 3.9, 2.0 Hz, 2H), 3.82 (s, 3H), 3.72 (s, 3H), 3.66 (d, J = 7.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.54, 158.99, 129.86 , 128.24 , 128.00, 127.18 , 114.31 , 114.14 , 113.97 , 87.38 , 75.63 , 56.33 , 55.26 , 52.06 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_4$: 249.1121; Found: 249.1123.

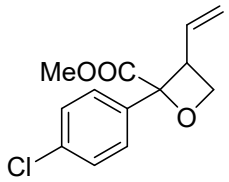


Compound 3m major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 3H), 7.29 – 7.22 (m, 3H), 5.95 (dd, J = 4.3, 2.0 Hz, 2H), 5.58 – 5.53 (m, 2H), 5.41 (m, 2H), 4.66 (dt, J = 4.5, 2.0 Hz, 3H), 3.75 (s, 4H), 3.68 – 3.64 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.13, 134.02 , 131.83 , 130.30 , 128.64 , 126.99 , 121.91, 87.51 , 75.75 , 57.53 , 52.31. **Compound 3m minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.51 – 7.46 (m, 2H), 7.29 – 7.22 (m, 2H), 5.95 (dd, J = 4.3, 2.0 Hz, 1H), 5.85 (ddt, J = 6.1, 3.6, 1.9 Hz, 1H), 5.41 (m, 1H), 4.63 – 4.52 (m, 2H), 3.74 (s, 3H), 3.68 – 3.64 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.81, 134.87, 131.58 , 130.68 , 128.56 ,

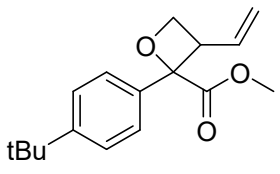
127.54 , 121.70, 87.10 , 75.75 , 56.59 , 52.25 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}O_3Br$: 297.0121; Found: 297.0127.



Compound 3n major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 5H), 7.08 – 7.01 (m, 5H), 5.95 (m, 3H), 5.85 (m, 1H), 5.54 (m, 2H), 5.44 – 5.37 (m, 3H), 4.66 (m, 3H), 4.58 (m, 2H), 3.75 (s, 5H), 3.74 (s, 3H), 3.71 – 3.66 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.45 , 163.64, 163.51, 130.85 , 130.81, 130.21 , 130.13 , 128.51 , 127.64 , 127.12 , 115.61 (d, J = 21.3 Hz), 87.70 , 75.74 , 57.33 , 52.25 . **^{19F} NMR (376 MHz, CDCl3)** δ -114.60 . **Compound 3n minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 5H), 7.08 – 7.01 (m, 5H), 5.95 (m, 3H), 5.85 (m, 1H), 5.54 (m, 2H), 5.44 – 5.37 (m, 3H), 4.66 (m, 3H), 4.58 (m, 2H), 3.75 (s, 5H), 3.74 (s, 3H), 3.71 – 3.66 (m, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.13, 161.19, 161.07, 131.63, 131.59, 130.54 , 130.46 , 128.45 , 127.64 , 127.12 , 115.36 (d, J = 21.4 Hz), 87.26 , 75.71 , 56.36 , 52.18 . **^{19}F NMR (376 MHz, CDCl3)** δ -115.22 . **HRMS (ESI)** m/z: $[M + K]^+$ Calcd for $C_{13}H_{13}O_3F$: 275.0480; Found: 275.0477.

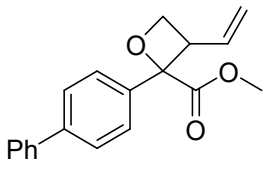


Compound 3o major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 7.5 Hz, 6H), 5.97 – 5.92 (m, 1H), 5.55 (dh, J = 4.9, 1.4 Hz, 1H), 5.41 (m, 1H), 4.65 (dt, J = 4.5, 2.0 Hz, 3H), 3.75 (s, 4H), 3.68 (dd, J = 7.9, 3.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.20 , 134.36, 133.52 , 129.96 , 128.62 , 128.54 , 127.02 , 87.58 , 75.74 , 57.47 , 52.28 . **Compound 3o minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32 (d, J = 7.5 Hz, 4H), 5.97 – 5.92 (m, 1H), 5.84 (m, 1H), 5.41 (m, 1H), 4.63 – 4.53 (m, 2H), 3.74 (s, 3H), 3.68 (dd, J = 7.9, 3.4 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.89, 134.36, 133.77, 130.33 , 128.87 , 128.54 , 127.56 , 87.16 , 75.74 , 56.52 , 52.22 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{13}O_3Cl$: 253.0626; Found: 253.0624.

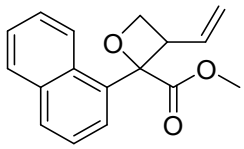


Compound 3p major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, J = 8.2, 5.5 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H). 5.92 (td, J = 6.2, 1.8 Hz, 2H), 5.55 (dd, J = 6.4, 1.6 Hz, 2H), 5.43 (m, 2H), 4.71 (m, 4H), 3.75 (s, 6H), 3.63 (d, J = 9.5 Hz, 2H), 1.34 (d, J = 1.9 Hz, 18H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.75, 150.67, 131.96 , 128.06 , 127.99 , 125.68 , 87.86 , 75.69 , 57.92 , 52.15 , 34.54 , 31.36 . **Compound 3p minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (dd, J = 8.2,

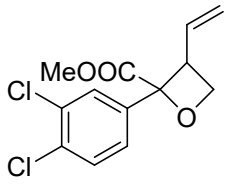
5.5 Hz, 2H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.01 – 5.97 (m, 1H), 5.92 (td, *J* = 6.2, 1.8 Hz, 1H), 5.43 (m, 1H), 4.65 – 4.61 (m, 2H), 3.72 (s, 3H), 3.69 (d, *J* = 8.0 Hz, 1H), 1.34 (d, *J* = 1.9 Hz, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.44 , 150.23, 132.89 , 128.22 , 127.66 , 125.56 , 87.44 , 75.60 , 56.87 , 52.02 , 34.54 , 31.36 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{22}O_3Cl$: 275.1642; Found: 275.1645.



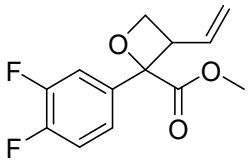
Compound 3q major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.66 – 7.55 (m, 6H), 7.51 – 7.34 (m, 7H), 5.98 – 5.90 (m, 1H), 5.60 (dq, *J* = 6.3, 2.1 Hz, 1H), 5.48 (d, *J* = 1.6 Hz, 1H), 4.71 (m, 3H), 3.78 (s, 4H), 3.72 (d, *J* = 9.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.56, 140.71, 140.59 , 135.00, 128.93 , 128.85 , 128.41 , 128.30 , 127.86 , 127.45 , 127.32 , 127.09 , 87.79 , 75.76 , 57.96 , 52.27. **Compound 3q minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 7.66 – 7.55 (m, 4H), 7.51 – 7.34 (m, 5H), 5.99 (dd, *J* = 6.2, 1.9 Hz, 1H), 5.98 – 5.90 (m, 2H), 5.48 (d, *J* = 1.6 Hz, 1H), 4.64 (dt, *J* = 4.1, 1.9 Hz, 2H), 3.76 (s, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 172.25, 140.86 , 140.47 , 134.07, 129.19 , 128.77 , 128.41 , 128.30 , 127.86 , 127.15 , 87.36 , 75.70 , 56.97 , 52.17. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{19}H_{18}O_3$: 295.1328; Found: 295.1330.



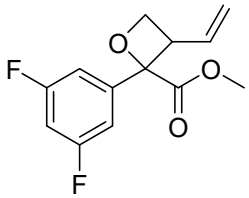
Compound 3r major: ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.17 (dd, *J* = 14.0, 8.4 Hz, 3H), 7.94 – 7.88 (m, 3H), 7.84 (dd, *J* = 8.2, 2.6 Hz, 3H), 7.71 (t, *J* = 7.5 Hz, 3H), 7.54 (tt, *J* = 15.4, 7.8 Hz, 9H), 6.04 – 5.97 (m, 2H), 5.90 (dq, *J* = 6.0, 1.8 Hz, 2H), 5.74 – 5.62 (m, 3H), 5.39 – 5.33 (m, 2H), 4.80 (dt, *J* = 6.4, 1.9 Hz, 1H), 4.73 (m, 2H), 4.65 – 4.60 (m, 3H), 4.58 (d, *J* = 9.2 Hz, 2H), 3.74 (s, 5H), 3.71 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* 173.03, 172.68, 134.22, 134.13, 132.30 , 131.80, 131.53, 129.16 , 129.07 , 128.41 , 128.36 , 128.26 , 128.21 , 127.71 , 126.67 , 126.45 , 125.94 , 125.90 , 125.69 , 125.59 , 123.53 , 123.29 , 88.33 , 87.36 , 75.90 , 75.74 , 52.40 , 52.25 , 52.02 . **Compound 3r minor: ^{1}H NMR (400 MHz, $CDCl_3$)** *δ* 8.17 (dd, *J* = 14.0, 8.4 Hz, 3H), 7.94 – 7.88 (m, 3H), 7.84 (dd, *J* = 8.2, 2.6 Hz, 3H), 7.71 (t, *J* = 7.5 Hz, 3H), 7.54 (tt, *J* = 15.4, 7.8 Hz, 9H), 6.04 – 5.97 (m, 2H), 5.90 (dq, *J* = 6.0, 1.8 Hz, 2H), 5.74 – 5.62 (m, 3H), 5.39 – 5.33 (m, 2H), 4.80 (dt, *J* = 6.4, 1.9 Hz, 1H), 4.73 (m, 2H), 4.65 – 4.60 (m, 3H), 4.58 (d, *J* = 9.2 Hz, 2H), 3.74 (s, 5H), 3.71 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** *δ* **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{17}H_{16}O_3$: 269.1172; Found: 269.1173.



Compound 3s major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 6.5 Hz, 1H), 7.43 (dt, J = 8.5, 1.7 Hz, 1H), 7.22 (t, J = 8.6 Hz, 1H), 6.00 – 5.94 (m, 1H), 5.58 (dq, J = 6.9, 1.6 Hz, 1H), 5.39 (dt, J = 15.0, 4.9 Hz, 1H), 4.68 – 4.62 (m, 3H), 3.76 (s, 4H), 3.65 (t, J = 7.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.72 , 135.13 , 132.74, 132.06, 130.61 , 130.57 , 128.99 , 128.06 , 126.71 , 87.40 , 75.81 , 57.07 , 52.43 . **Compound 3s minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.48 (d, J = 6.5 Hz, 1H), 7.43 (dt, J = 8.5, 1.7 Hz, 1H), 7.22 (t, J = 8.6 Hz, 1H), 6.00 – 5.94 (m, 1H), 5.82 (m, 1H), 5.39 (dt, J = 15.0, 4.9 Hz, 1H), 4.61 – 4.52 (m, 2H), 3.75 (s, 3H), 3.65 (t, J = 7.0 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.40 , 136.00 , 132.45, 131.77, 131.05 , 130.31 , 128.78 , 128.43 , 127.31 , 87.02 , 75.83 , 56.28 , 52.39 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}O_3Cl_2$: 287.0236; Found: 287.0237.

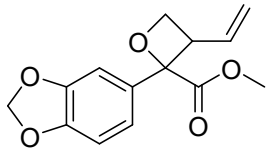


Compound 3t major: ^{1}H NMR (400 MHz, $CDCl_3$) δ7.25 (dddd, J = 11.3, 9.6, 7.6, 2.2 Hz, 1H), 7.19 – 7.04 (m, 2H), 5.96 (dq, J = 5.3, 1.7 Hz, 1H), 5.56 (dq, J = 6.3, 2.2 Hz, 1H), 5.37 (dddd, J = 13.4, 8.9, 4.0, 2.0 Hz, 1H), 4.65 (ddt, J = 4.3, 2.8, 1.4 Hz, 2H), 3.76 (s, 3H), 3.65 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.97, 149.05, 148.92, 148.83, 148.71, 148.58, 131.94, 131.90, 131.88, 131.84, 128.88, 126.76, 124.84 (dd, J = 6.4, 3.6 Hz), 117.82 (dd, J = 39.9, 17.9 Hz), 87.54, 75.81, 57.12, 52.39. **^{19}F NMR (376 MHz, CDCl3)** δ -109.14 , -109.16 , -109.18. **Compound 3t minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.25 (dddd, J = 11.3, 9.6, 7.6, 2.2 Hz, 1H), 7.19 – 7.04 (m, 2H), 5.96 (dq, J = 5.3, 1.7 Hz, 1H), 5.82 (dq, J = 6.2, 2.2 Hz, 1H), 5.37 (dddd, J = 13.4, 8.9, 4.0, 2.0 Hz, 1H), 4.61 – 4.53 (m, 2H), 3.75 (s, 3H), 3.67 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.63, 151.52, 151.40, 151.30, 151.18, 151.05, 132.79, 132.76, 132.74, 132.69, 128.69, 127.35, 125.16 (dd, J = 6.3, 3.6 Hz), 117.24 (dd, J = 33.3, 17.2 Hz), 87.15, 75.81, 56.24, 52.35. **^{19}F NMR (376 MHz, CDCl3)** δ -109.88 , -109.90 , -109.92 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}O_3F_2$: 255.0827; Found: 255.0829.

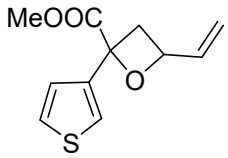


Compound 3u major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (td, J = 7.9, 2.1 Hz, 2H), 6.77 (m, 1H), 5.98 (dt, J = 6.3, 1.8 Hz, 1H), 5.58 (dq, J = 6.3, 2.3 Hz, 1H), 5.38 (m, 1H),

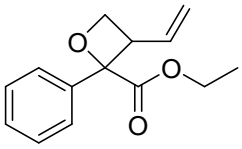
4.66 (dt, *J* = 4.4, 2.0 Hz, 2H), 3.77 (s, 3H), 3.68 (s, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** δ 171.53 , 161.67 (t, *J* = 13.1 Hz), 138.56 (t, *J* = 9.2 Hz), 128.95 , 126.70 , 111.89 (dd, *J* = 34.3, 25.7 Hz), 87.41 , 75.80 , 57.66 , 52.44 . **^{19}F NMR (376 MHz, CDCl3)** δ-108.42 , -108.44 , -108.46 , -109.14 , -109.17 , -109.19 . **Compound 3u minor: ^{1}H NMR (400 MHz, CDCl$_3$)** *δ* 6.93 (td, *J* = 7.9, 2.1 Hz, 2H), 6.77 (m, 1H), 5.98 (dt, *J* = 6.3, 1.8 Hz, 1H), 5.83 (dq, *J* = 6.3, 2.3 Hz, 1H), 5.38 (m, 1H), 4.62 (dt, *J* = 4.0, 2.1 Hz, 2H), 3.76 (s, 3H), 3.66 (s, 1H). **^{13}C NMR (101 MHz, CDCl$_3$)** *δ* 171.19 , 164.14 (t, *J* = 13.5 Hz), 139.45 (d, *J* = 9.5 Hz), 128.80 , 127.29 , 103.22 (q, *J* = 25.1 Hz). 87.06 , 75.80 , 56.83 , 52.38 . **^{19}F NMR (376 MHz, CDCl3)** δ -108.33 , -108.36 , -108.38 , -109.89 , -109.91 , -109.93 . **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{13}H_{12}O_3F_2$: 255.0827; Found: 255.0829. 13C NMR (101 MHz, Chloroform-d) δ



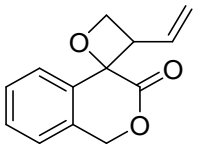
Compound 3v major: ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 6.89 (d, *J* = 1.3 Hz, 1H), 6.79 (d, *J* = 1.4 Hz, 3H), 6.00 – 5.92 (m, 4H), 5.57 (m, 1H), 5.38 (m, 1H), 4.70 (dp, *J* = 8.3, 1.8 Hz, 3H), 3.76 (s, 4H), 3.57 (dd, *J* = 9.3, 1.1 Hz, 1H). **13C NMR (101 MHz, CDCl3)** *δ* 172.65, 147.90, 147.22, 129.64, 128.25, 127.40, 121.96, 108.72, 108.48, 101.20, 87.77, 57.81, 52.24. **Compound 3v minor: ^{1}H NMR (400 MHz, CDCl$_3$)** *δ* 6.94 (d, *J* = 1.7 Hz, 1H), 6.81 (q, *J* = 1.3 Hz, 2H), 6.00 – 5.92 (m, 3H), 5.87 (m, 1H), 5.38 (m, 1H), 4.64 – 4.59 (m, 2H), 3.73 (s, 3H), 3.61 (dd, *J* = 7.6, 1.2 Hz, 1H). **13C NMR (101 MHz, CDCl3)** *δ* 172.31, 147.77, 147.06, 128.72, 128.34, 127.81, 122.27, 109.08, 108.30, 101.12, 87.38, 75.66, 75.73, 56.81, 52.15. **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{14}H_{14}O_5$: 263.0914; Found: 263.0913.



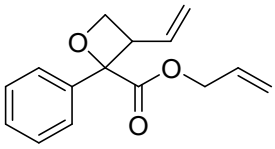
Compound 3w major: ^{1}H NMR (400 MHz, CDCl$_3$) *δ* 7.25 (m, 2H), 7.10 (dd, *J* = 4.9, 1.3 Hz, 2H), 5.95 (dt, *J* = 6.4, 1.7 Hz, 1H), 5.61 (m, 1H), 5.39 (m, 1H), 4.73 – 4.64 (m, 3H), 3.84 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 5H). **^{13}C NMR (101 MHz, CDCl$_3$)** *δ* 172.29 , 135.04 , 128.34 , 127.64 , 127.45 , 125.86 , 122.94 , 87.56 , 75.76 , 53.71 , 52.24 . **Compound 3w minor: ^{1}H NMR (400 MHz, CDCl$_3$)** *δ* 7.32 (dt, *J* = 4.8, 2.4 Hz, 2H), 7.14 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.95 (dt, *J* = 6.4, 1.7 Hz, 1H), 5.83 (m, 1H), 5.39 (m, 1H), 4.63 – 4.60 (m, 2H), 3.92 (d, *J* = 6.5 Hz, 1H), 3.75 (s, 3H). **^{13}C NMR (101 MHz, CDCl$_3$)** *δ* 171.94 , 135.69 , 128.39 , 128.07 , 127.49 , 125.39 , 123.18 , 87.29 , 75.83 , 52.55 , 52.17 . **HRMS (ESI)** m/z: [M + H]$^+$ Calcd for $C_{11}H_{12}O_3S$: 225.0580; Found: 225.0580.



Compound 3x major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.30 (m, 7H), 5.92 (d, J = 7.2 Hz, 3H), 5.54 (d, J = 6.3 Hz, 2H), 5.44 (dp, J = 10.3, 5.2 Hz, 2H), 4.69 (d, J = 3.8 Hz, 3H), 4.29 – 4.13 (m, 3H), 3.66 (d, J = 9.2 Hz, 2H), 1.27 (t, J = 7.2 Hz, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.12, 135.23, 128.69, 128.54, 128.12, 127.50, 87.81, 75.69, 61.01, 58.43, 14.14. **Compound 3x minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.41 – 7.30 (m, 5H), 5.97 (d, J = 6.5 Hz, 1H), 5.92 (d, J = 7.2 Hz, 1H), 5.44 (dp, J = 10.3, 5.2 Hz, 1H), 4.60 (d, J = 2.8 Hz, 2H), 4.29 – 4.13 (m, 2H), 3.69 (d, J = 7.6 Hz, 1H), 1.27 (t, J = 7.2 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.78, 136.10, 128.80, 128.49, 128.25, 127.92, 127.70, 87.42, 75.62, 60.90, 57.41, 14.18 . **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_3$: 233.1172; Found: 233.1174.

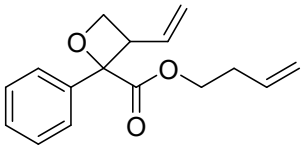


Compound 3y major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 9H), 5.93 (tt, J = 6.4, 1.8 Hz, 2H), 5.55 (dq, J = 6.4, 2.3 Hz, 2H), 5.46 (m, 2H), 5.21 – 5.13 (m, 4H), 4.69 (dt, J = 4.1, 2.0 Hz, 3H), 3.74 (d, J = 9.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.96, 135.89, 134.99, 128.72, 128.61, 128.50, 128.10, 127.99, 127.44, 87.77, 75.71, 66.67, 58.38. **Compound 3y minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.37 – 7.34 (m, 5H), 5.93 (tt, J = 6.4, 1.8 Hz, 1H), 5.85 (dq, J = 6.4, 2.3 Hz, 1H), 5.46 (m, 1H), 5.29 – 5.22 (m, 2H), 4.58 (dq, J = 5.7, 2.0 Hz, 2H), 3.77 (d, J = 7.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.58, 135.82, 134.99, 128.87, 128.55, 128.35, 128.25, 127.78, 127.57, 87.37, 75.65, 66.59, 57.34. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_3$: 233.1172; Found: 233.1174. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}O_3$: 217.0859; Found: 217.0863.

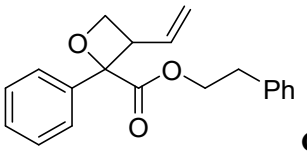


Compound 3z major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.31 (m, 7H), 5.99 – 5.85 (m, 4H), 5.54 (h, J = 3.7 Hz, 2H), 5.45 (m, 2H), 5.28 (d, J = 17.2 Hz, 2H), 5.22 (dd, J = 10.4, 7.0 Hz, 2H), 4.75 – 4.58 (m, 6H), 3.70 (d, J = 9.2 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.76, 135.04, 132.03, 128.73, 128.55, 128.22, 127.79, 127.43, 118.14, 87.78, 75.70, 65.55, 58.39, 57.33. **Compound 3z minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.31 (m, 5H), 5.99 – 5.85 (m, 3H), 5.45 (m, 1H), 5.28 (d, J = 17.2 Hz, 1H), 5.22 (dd, J = 10.4, 7.0 Hz, 1H), 4.75 – 4.58 (m, 4H), 3.74 (d, J = 7.5 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.42, 135.89, 131.91, 128.84, 128.51, 128.33, 127.83, 127.56, 118.38, 87.37, 75.65, 65.43, 58.39, 57.33. **HRMS (ESI)**

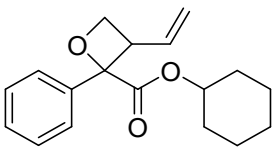
m/z: $[M + H]^+$ Calcd for $C_{15}H_{16}O_3$: 245.1172; Found: 245.1174.



Compound 3aa major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.30 (m, 8H), 5.92 (ddt, J = 9.1, 6.3, 1.7 Hz, 2H), 5.75 (ddtd, J = 17.1, 10.3, 6.8, 1.5 Hz, 2H), 5.54 (ddt, J = 6.4, 4.0, 1.9 Hz, 2H), 5.44 (tddt, J = 8.1, 4.8, 3.5, 1.8 Hz, 2H), 5.11 – 5.00 (m, 2H), 4.69 (dq, J = 6.2, 1.9 Hz, 3H), 4.26 – 4.16 (m, 3H), 3.66 (d, J = 9.3 Hz, 2H), 2.39 (dtq, J = 8.6, 6.7, 1.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.06, 135.13, 133.87, 128.70, 128.58, 128.18, 127.74, 127.47, 117.28, 87.76, 75.70, 64.01, 58.44, 33.02. **Compound 3aa minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.30 (m, 5H), 5.96 (dt, J = 5.3, 1.8 Hz, 1H), 5.92 (ddt, J = 9.1, 6.3, 1.7 Hz, 1H), 5.75 (ddtd, J = 17.1, 10.3, 6.8, 1.5 Hz, 1H), 5.44 (tddt, J = 8.1, 4.8, 3.5, 1.8 Hz, 1H), 5.11 – 5.00 (m, 2H), 4.61 (dt, J = 4.9, 2.0 Hz, 2H), 4.26 – 4.16 (m, 2H), 3.69 (d, J = 7.7 Hz, 1H), 2.39 (dtq, J = 8.6, 6.7, 1.6 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.74, 136.02, 133.81, 128.82, 128.50, 128.28, 127.92, 127.53, 117.42, 87.31, 75.64, 63.93, 57.42, 33.06. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}O_3$: 259.1329; Found: 259.1328.

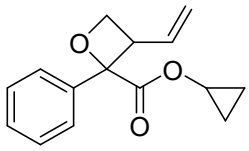


Compound 3bb major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.31 (m, 8H), 7.29 – 7.23 (m, 8H), 5.92 (dd, J = 6.3, 1.8 Hz, 2H), 5.55 – 5.50 (m, 2H), 5.48 – 5.37 (m, 2H), 4.68 (dt, J = 4.1, 2.0 Hz, 3H), 4.37 (dt, J = 8.8, 6.9 Hz, 3H), 3.66 (t, J = 8.4 Hz, 2H), 2.95 (td, J = 7.0, 2.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.02, 137.81, 135.10, 129.01, 128.76, 128.55, 128.49, 128.21, 127.76, 127.48, 126.51, 87.75, 75.70, 65.49, 58.48, 35.03. **Compound 3bb minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 – 7.31 (m, 5H), 7.18 – 7.13 (m, 5H), 5.92 (dd, J = 6.3, 1.8 Hz, 1H), 5.80 (dq, J = 6.3, 2.2 Hz, 1H), 5.48 – 5.37 (m, 1H), 4.61 – 4.57 (m, 2H), 4.37 (dt, J = 8.8, 6.9 Hz, 2H), 3.66 (t, J = 8.4 Hz, 1H), 2.95 (td, J = 7.0, 2.0 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.70, 137.70, 136.01, 128.99, 128.86, 128.59, 128.49, 128.25, 127.92, 127.54, 126.60, 87.28, 75.63, 65.37, 57.46, 35.06. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}O_3$: 309.1485; Found: 309.1481.

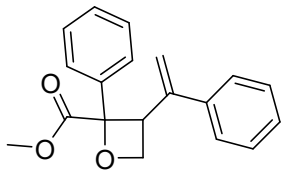


Compound 3cc major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 8H), 5.91 (dq, J = 5.7, 1.8 Hz, 2H), 5.43 (m, 2H), 4.67 (dq, J = 3.7, 1.9 Hz, 3H), 3.66 (dd, J = 8.5, 6.9 Hz, 2H), 1.58 – 1.20 (m, 17H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.49, 135.47, 128.58, 128.45,

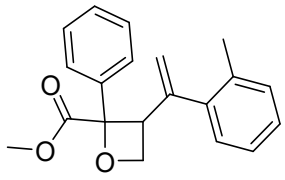
128.07, 127.57, 127.40, 87.78, 75.64, 73.07, 58.63, 31.54, 31.30, 25.43, 23.70, 23.57. **Compound 3cc minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 – 7.30 (m, 5H), 5.97 (dt, J = 5.5, 1.8 Hz, 1H), 5.91 (dq, J = 5.7, 1.8 Hz, 1H), 5.43 (m, 1H), 4.61 (dd, J = 4.8, 2.2 Hz, 2H), 3.66 (dd, J = 8.5, 6.9 Hz, 1H), 1.96 – 1.70 (m, 11H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.18, 136.37, 128.73, 128.20, 128.02, 127.62, 126.82, 87.46, 75.58, 73.14, 57.77, 31.54, 31.30, 25.38, 23.65, 23.57. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{18}H_{22}O_3$: 287.1641; Found: 287.1640.



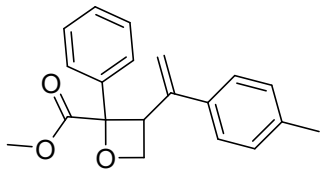
Compound 3dd major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 10H), 5.93 (dq, J = 6.4, 1.7 Hz, 2H), 5.55 (dt, J = 6.3, 2.0 Hz, 2H), 5.45 (m, 2H), 4.69 (m, 4H), 4.07 – 3.92 (m, 6H), 3.71 (dd, J = 10.6, 8.4 Hz, 2H), 1.14 (m, 2H), 0.56 (m, 4H), 0.31 – 0.25 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.24, 135.27, 128.67, 128.60, 128.14, 128.09, 127.69, 127.51, 87.82, 75.70, 69.72, 58.42, 9.72, 3.24. **Compound 3dd minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.31 (m, 15H), 6.01 – 5.96 (m, 1H), 5.93 (dq, J = 6.4, 1.7 Hz, 1H), 5.45 (m, 1H), 4.61 (dt, J = 4.9, 2.0 Hz, 2H), 4.07 – 3.92 (m, 2H), 3.71 (dd, J = 10.6, 8.4 Hz, 1H), 1.14 (m, 1H), 0.56 (m, 2H), 0.31 – 0.25 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.91, 136.14, 128.83, 128.48, 128.28, 127.93, 127.49, 87.46, 75.64, 69.60, 57.48, 9.83, 3.29. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{16}H_{18}O_3$: 259.1329; Found: 259.1327.



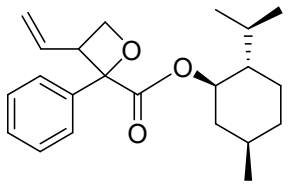
Compound 3ee major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 12H), 5.87 (q, J = 2.1 Hz, 1H), 5.70 – 5.55 (m, 1H), 5.15 – 5.01 (m, 2H), 3.79 (s, 1H), 3.78 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.56, 140.28, 135.08, 132.14, 128.70, 128.68, 128.55, 127.92, 127.68, 125.97, 121.25, 89.03, 75.55, 58.38, 52.30. **Compound 3ee minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.45 – 7.34 (m, 10H), 6.27 (t, J = 2.1 Hz, 1H), 5.70 – 5.55 (m, 1H), 4.98 (p, J = 2.4 Hz, 2H), 3.77 (s, 1H), 3.75 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 172.34, 140.37, 135.96, 132.09, 128.89, 128.68, 128.43, 128.01, 127.48, 125.94, 121.90, 88.54, 75.41, 57.43, 52.19. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}O_3$: 317.1148; Found: 317.1146.



Compound 3ff major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (M, 6H), 7.23 – 7.15 (m, 4H), 7.07 (dd, J = 13.6, 7.1 Hz, 1H), 5.70 – 5.62 (m, 1H), 5.60 (d, J = 2.0 Hz, 1H), 4.99 – 4.92 (m, 1H), 3.85 (dd, J = 7.8, 5.9 Hz, 1H), 3.78 (s, 4H), 2.29 (s, 4H). **^{13}C NMR (101 MHz, CDCl3)** δ 172.56, 140.55, 136.06, 135.06, 132.51, 130.91, 128.81, 128.60, 127.91, 127.87, 125.88, 125.01, 89.18, 58.41, 52.29, 21.35. **Compound 3ff minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (M, 5H), 7.23 – 7.15 (m, 3H), 7.07 (dd, J = 13.6, 7.1 Hz, 1H), 5.88 (q, J = 2.1 Hz, 1H), 5.70 – 5.62 (m, 1H), 4.99 – 4.92 (m, 1H), 3.85 (dd, J = 7.8, 5.9 Hz, 1H), 3.76 (s, 3H), 2.27 (s, 3H). **^{13}C NMR (101 MHz, CDCl3)** δ 172.29, 140.71, 136.16, 135.74, 132.58, 130.84, 129.11, 128.55, 127.99, 127.64, 125.84, 125.34, 88.71, 57.28, 52.22, 21.12. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}O_3$: 309.1485; Found: 309.1484.

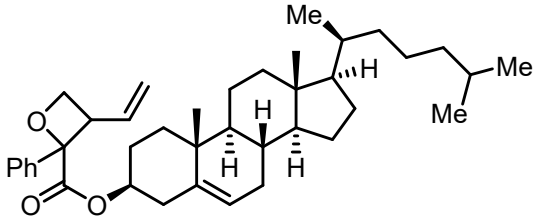


Compound 3gg major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 10H), 7.19 – 7.15 (m, 9H), 6.20 (d, J = 2.1 Hz, 1H), 5.80 (d, J = 2.1 Hz, 2H), 5.62 (dq, J = 12.8, 4.1 Hz, 2H), 5.10 – 4.99 (m, 3H), 4.94 (d, J = 2.1 Hz, 1H), 3.77 (s, 3H), 3.74 (d, J = 5.8 Hz, 3H), 3.70 (d, J = 8.4 Hz, 0H), 2.38 (s, 4H), 2.37 (s, 5H). **^{13}C NMR (101 MHz, CDCl3)** δ 172.60, 140.13, 135.14, 129.34, 128.70, 128.56, 127.88, 125.84, 120.22, 89.03, 75.60, 58.44, 52.29, 21.34. **Compound 3gg minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.36 (m, 10H), 7.19 – 7.15 (m, 9H), 6.20 (d, J = 2.1 Hz, 1H), 5.80 (d, J = 2.1 Hz, 2H), 5.62 (dq, J = 12.8, 4.1 Hz, 2H), 5.10 – 4.99 (m, 3H), 4.94 (d, J = 2.1 Hz, 1H), 3.77 (s, 3H), 3.74 (d, J = 5.8 Hz, 3H), 3.70 (d, J = 8.4 Hz, 0H), 2.38 (s, 4H), 2.37 (s, 5H). **^{13}C NMR (101 MHz, CDCl3)** δ 172.38, 140.24, 138.40, 128.86, 128.65, 128.02, 127.65, 125.87, 120.89, 88.52, 75.46, 57.51, 52.17, 21.34. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{20}H_{20}O_3$: 309.1485; Found: 309.1484.



Compound 3hh major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 8H), 6.01 – 5.93 (m, 2H), 5.92 – 5.88 (m, 2H), 5.49 – 5.37 (m, 2H), 4.72 (ddd, J = 21.2, 10.5, 5.6 Hz, 1H), 4.61 (dt, J = 4.2, 2.0 Hz, 4H), 3.64 (dd, J = 8.8, 1.8 Hz, 2H), 2.06 – 2.00 (m, 1H), 1.93 – 1.83 (m, 2H), 1.68 – 1.60 (m, 3H), 1.49 (tq, J = 9.3, 2.7 Hz, 3H), 1.34 (ddd, J = 14.7, 7.3, 3.2 Hz, 2H), 1.09 – 0.96 (m, 3H), 0.91 (d, J = 7.4 Hz, 4H), 0.87 – 0.80 (m, 1H), 0.74 (d, J = 7.0 Hz, 4H), 0.58 (d, J = 7.0 Hz, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.43, 136.35, 128.67, 128.60, 128.56,

128.52, 128.48, 127.98, 127.61, 127.42, 87.25, 75.56, 74.79, 57.76, 47.06, 40.88, 34.26, 31.49, 31.46, 25.75, 23.25, 22.04, 20.82, 16.05. **Compound 3hh minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 – 7.32 (m, 5H), 6.01 – 5.93 (m, 1H), 5.56 (dq, J = 6.3, 2.2 Hz, 1H), 5.49 – 5.37 (m, 1H), 4.72 (ddd, J = 21.2, 10.5, 5.6 Hz, 1H), 4.68 – 4.65 (m, 2H), 3.64 (dd, J = 8.8, 1.8 Hz, 1H), 2.16 – 2.09 (m, 1H), 1.68 – 1.60 (m, 2H), 1.49 (tq, J = 9.3, 2.7 Hz, 2H), 1.34 (ddd, J = 14.7, 7.3, 3.2 Hz, 1H), 1.09 – 0.96 (m, 2H), 0.88 (d, J = 6.5 Hz, 3H), 0.87 – 0.80 (m, 1H), 0.70 (d, J = 7.0 Hz, 3H), 0.54 (d, J = 6.9 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.71, 135.44, 128.43, 128.26, 128.21, 128.14, 128.09, 127.98, 127.56, 127.42, 87.46, 75.63, 74.92, 58.55, 47.21, 40.98, 34.34, 31.41, 26.13, 23.39, 22.09, 20.64, 15.97. **HRMS (ESI)** m/z: $[M + Na]^+$ Calcd for $C_{22}H_{30}O_3$: 365.2087; Found: 365.2084.



Compound 3ii major: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.30 (m, 9H), 5.91 (dd, J = 6.4, 2.1 Hz, 2H), 5.55 (dp, J = 5.7, 1.9 Hz, 2H), 5.47 – 5.33 (m, 4H), 4.68 (dq, J = 4.4, 2.3 Hz, 4H), 3.68 – 3.60 (m, 2H), 2.46–2.18 (m, 4H), 2.08 – 1.77 (m, 6H), 1.62 – 0.80 (m, 39H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.55, 139.69, 135.43, 128.69, 128.63, 128.15, 127.68, 127.64, 122.74, 87.88, 75.74, 74.60, 58.63, 56.23, 50.08, 42.42, 39.63, 37.08, 37.01, 36.69, 36.29, 35.92, 31.95, 28.36, 28.14, 27.84, 23.95, 22.96, 22.69, 21.14, 18.83, 11.97. **Compound 3ii minor: ^{1}H NMR (400 MHz, $CDCl_3$)** δ7.45 – 7.30 (m, 5H), 5.91 (dd, J = 6.4, 2.1 Hz, 1H), 5.55 (dp, J = 5.7, 1.9 Hz, 2H), 5.47 – 5.33 (m, 2H), 4.61 (t, J = 3.5 Hz, 2H), 3.68 – 3.60 (m, 1H), 2.46–2.18 (m, 2H), 2.08 – 1.77 (m, 10H), 1.62 – 0.80 (m, 71H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.23, 139.78, 136.31, 128.81, 128.54, 128.31, 128.03, 127.50, 122.87, 87.60, 75.67, 74.65, 57.70, 56.79, 50.08, 42.42, 39.83, 38.12, 37.86, 36.69, 36.29, 35.92, 32.01, 24.40, 22.96, 22.69, 21.14, 19.45, 11.97. **HRMS (ESI)** m/z: $[M + H]^+$ Calcd for $C_{39}H_{56}O_3$: 573.4302; Found: 573.4308.

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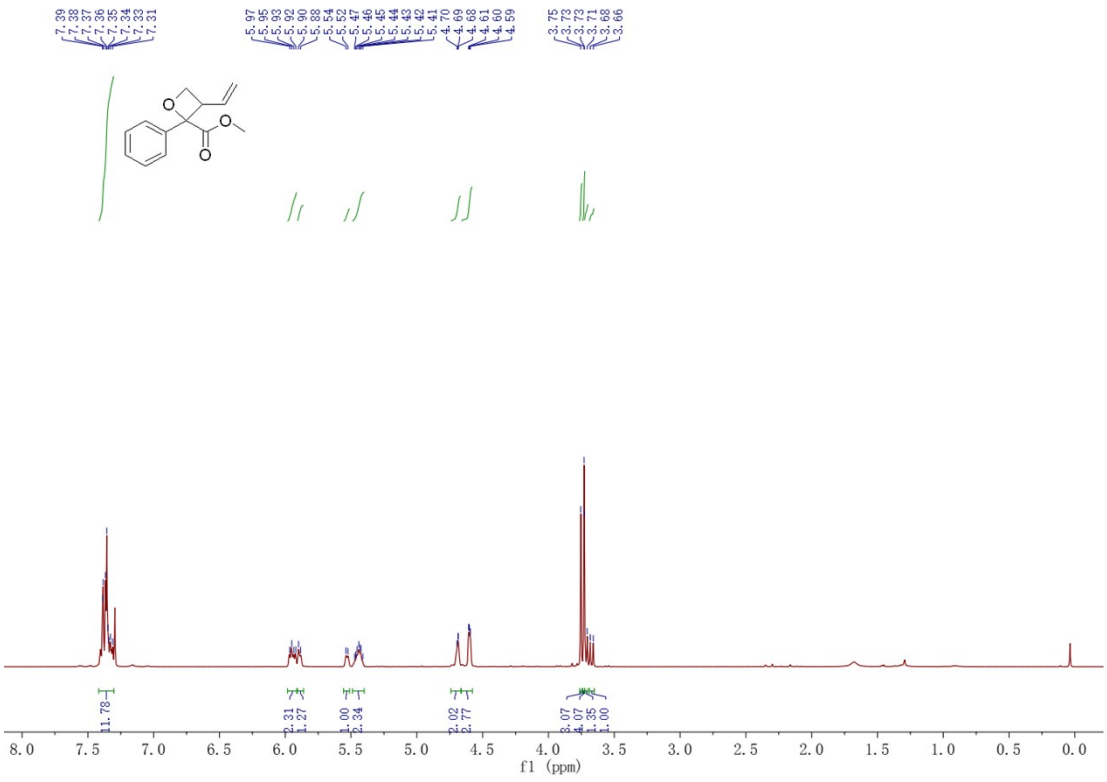
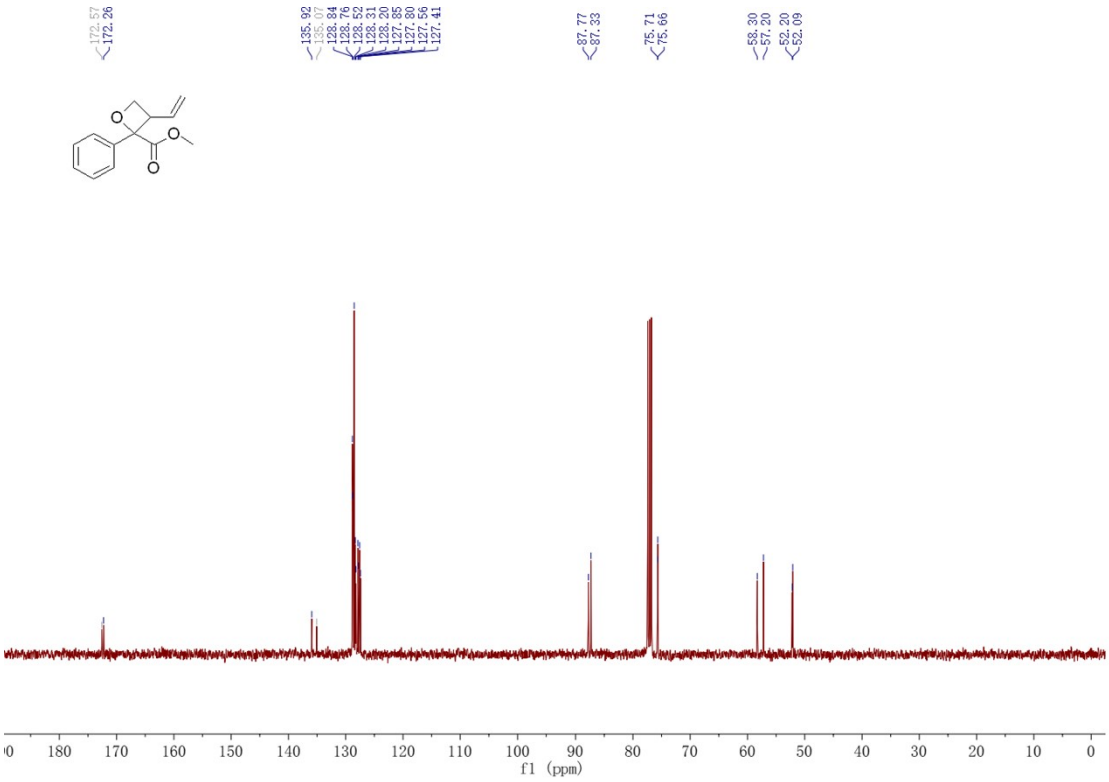
^{1}H NMR and ^{13}C NMR Spectra for Products

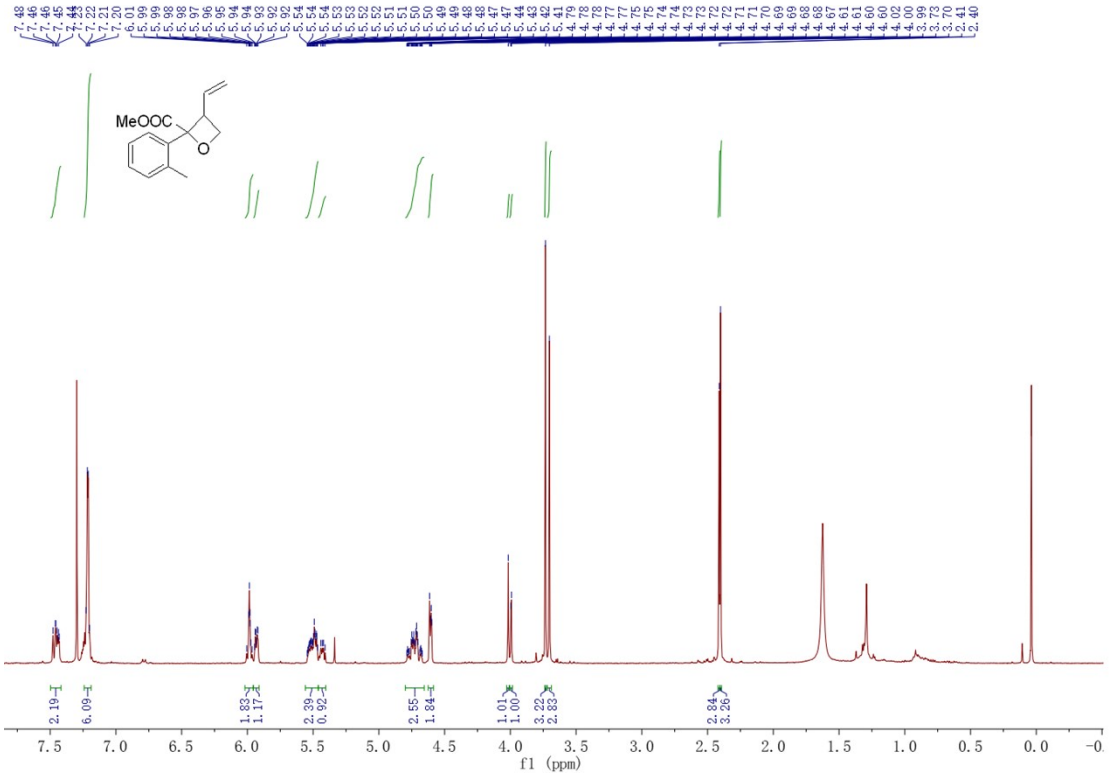
3a: ^{1}H NMR (400 MHz, $CDCl_3$)



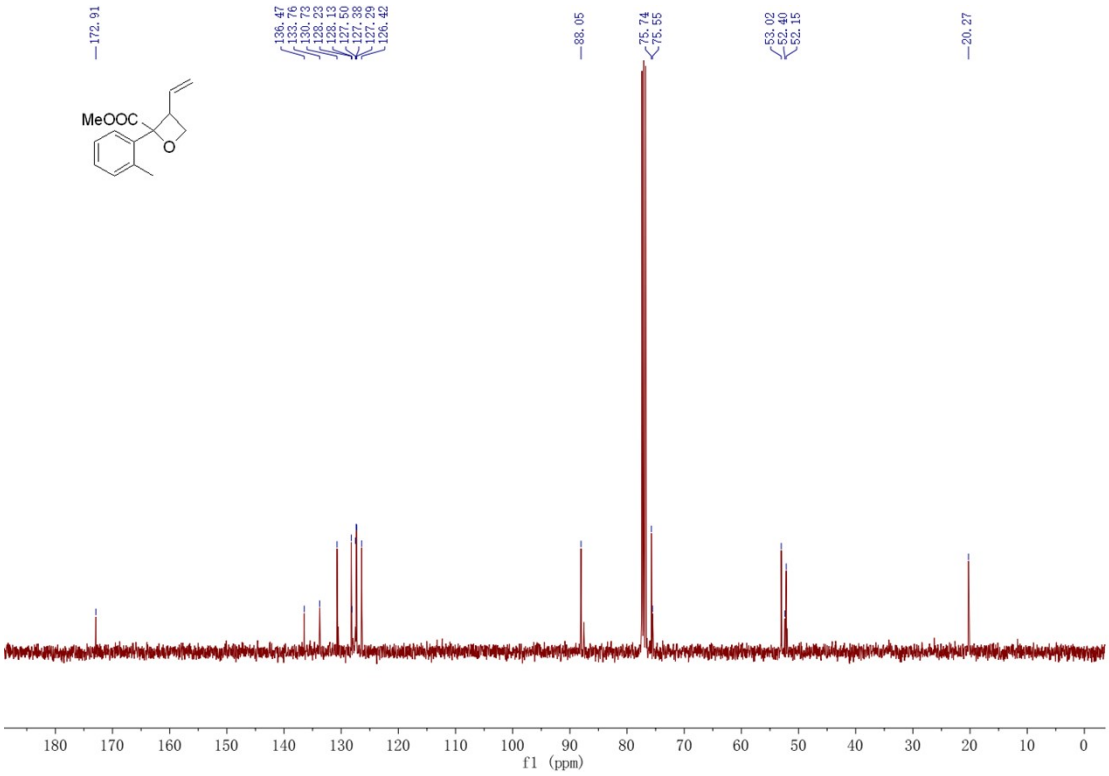
^{13}C NMR (101 MHz, CDCl3)



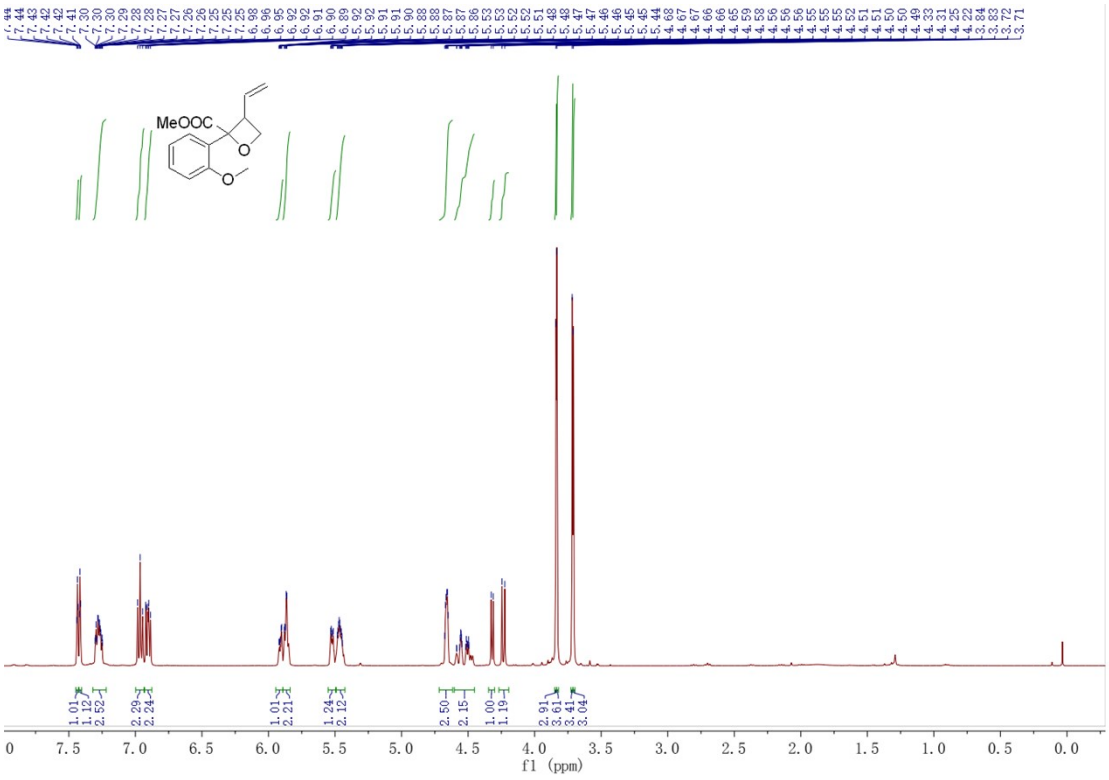
3b: ^{1}H NMR (400 MHz, $CDCl_3$)



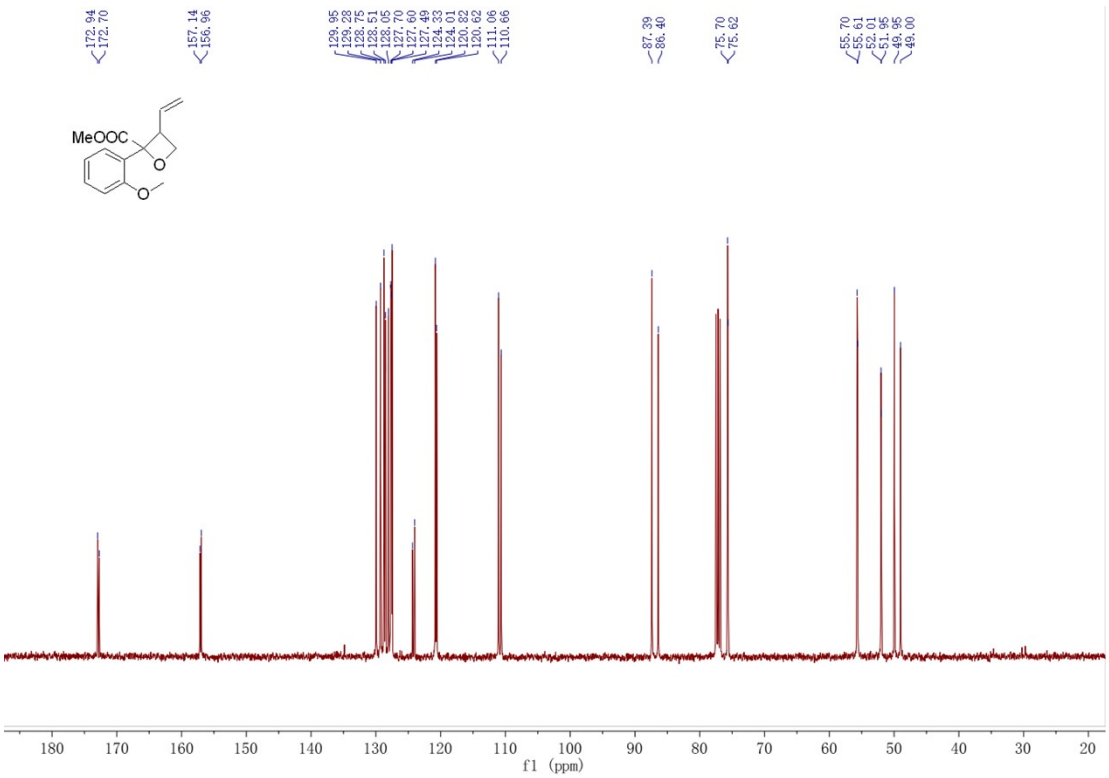
^{13}C NMR (101 MHz, CDCl3)



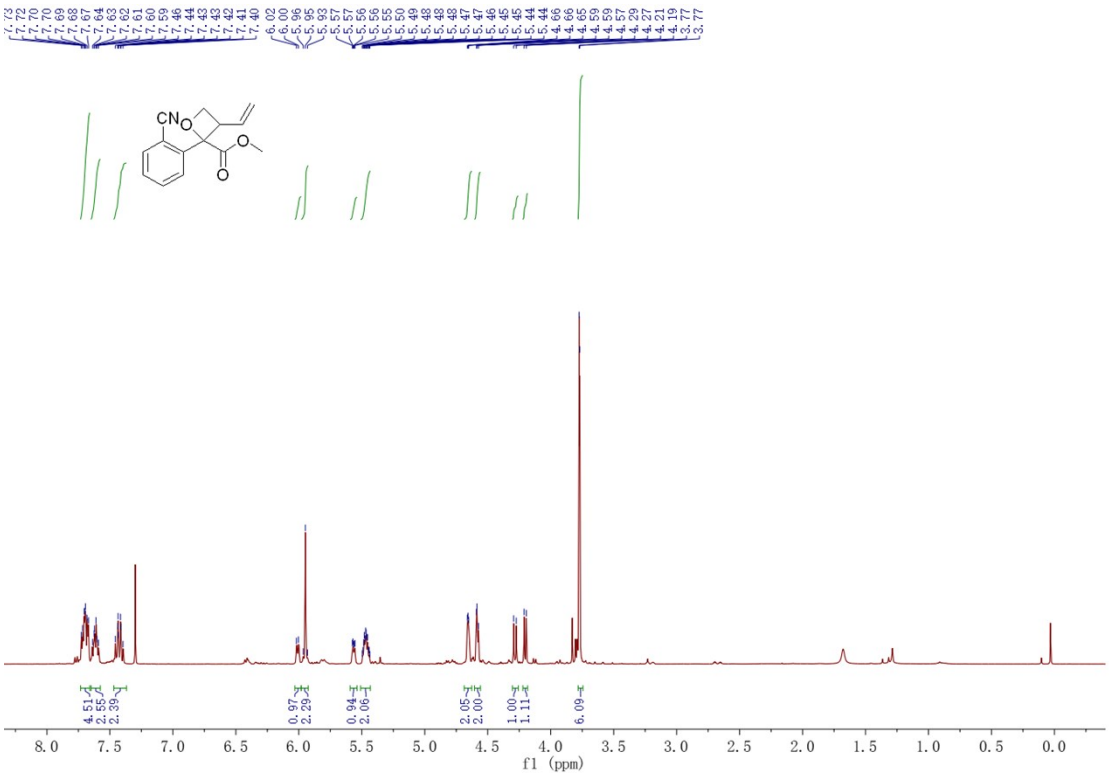
3c: ^{1}H NMR (400 MHz, $CDCl_3$)



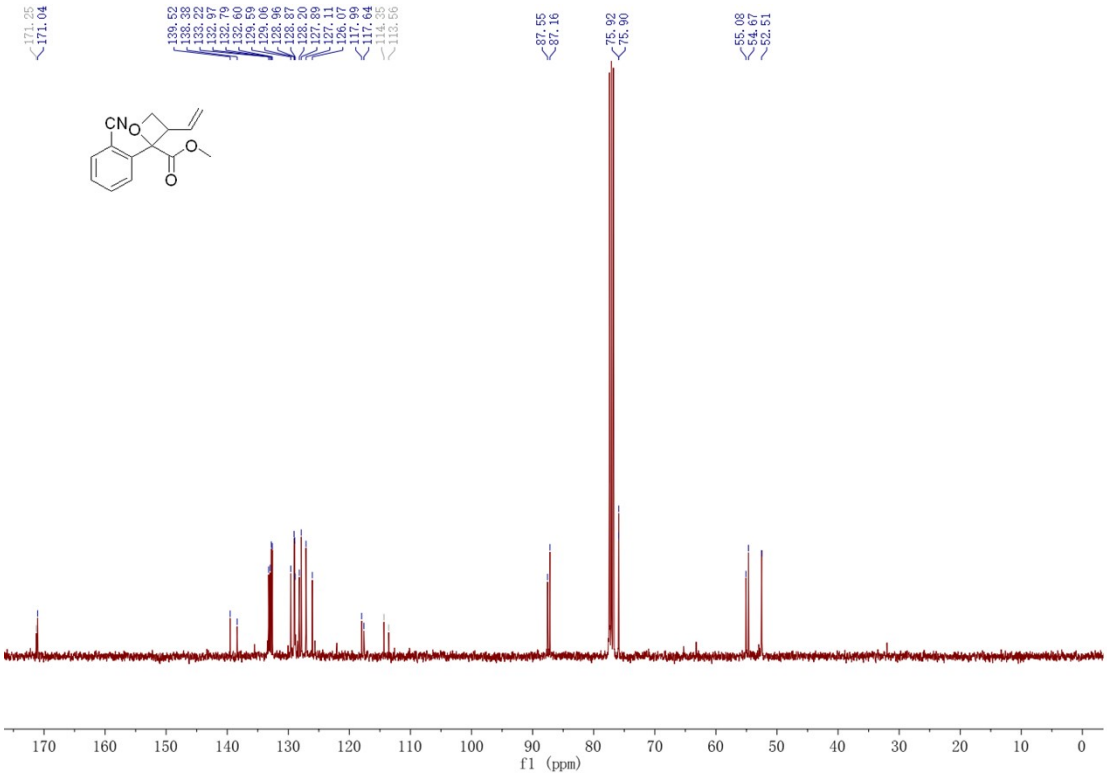
^{13}C NMR (101 MHz, CDCl3)



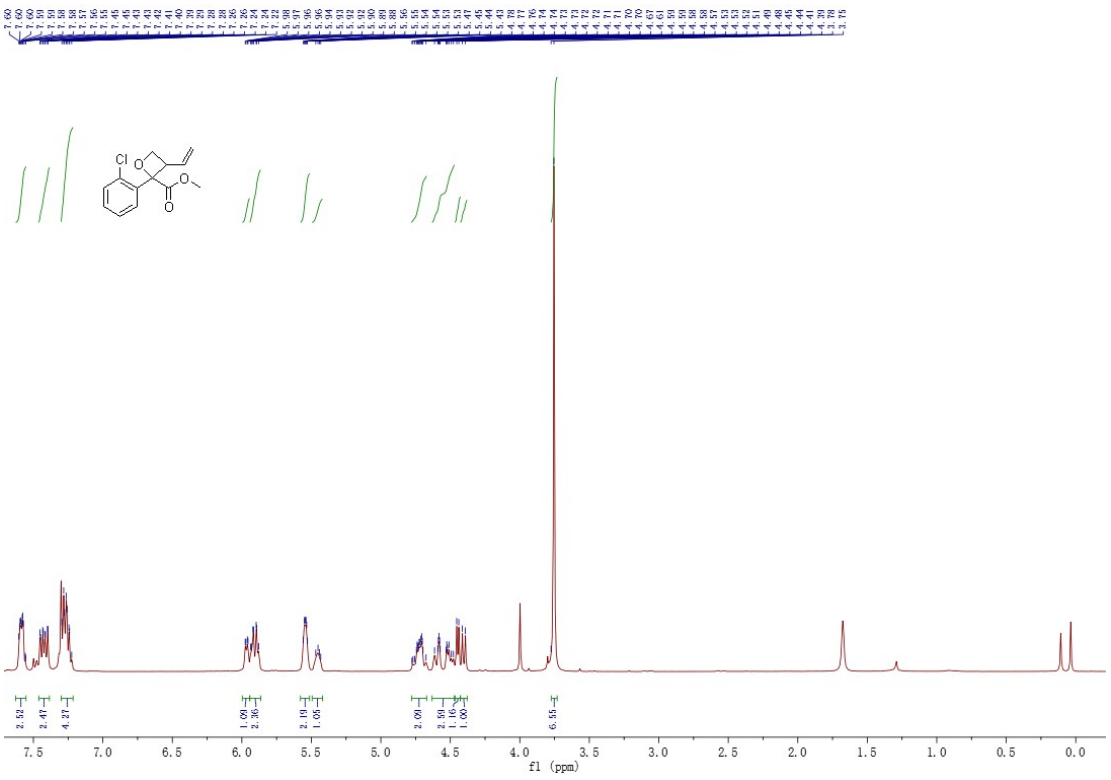
3d: ^{1}H NMR (400 MHz, $CDCl_3$)



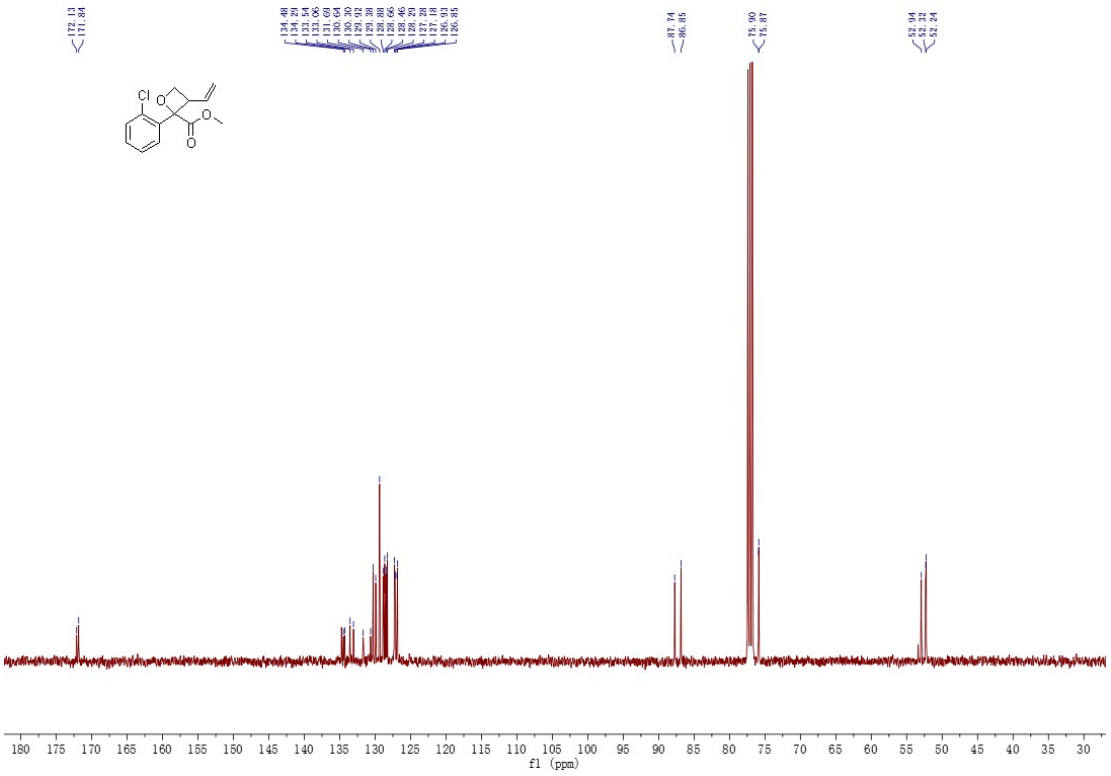
^{13}C NMR (101 MHz, CDCl3)



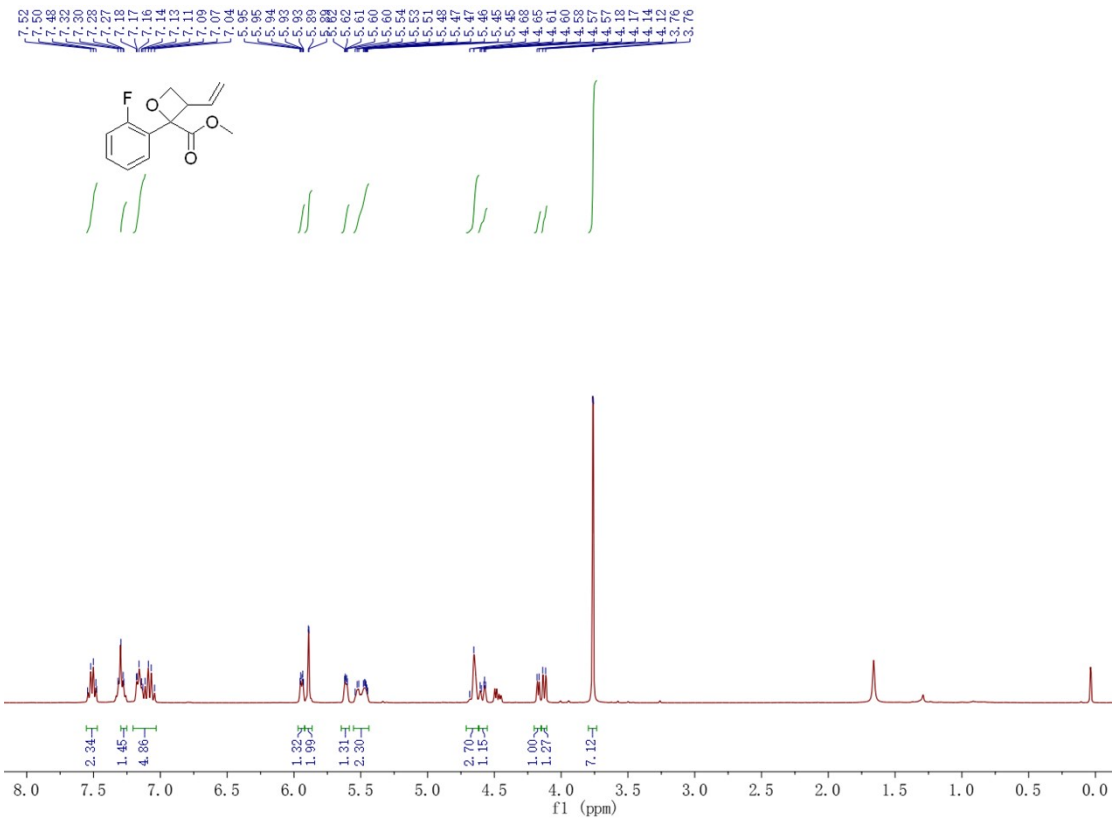
3e: ^{1}H NMR (400 MHz, $CDCl_3$)



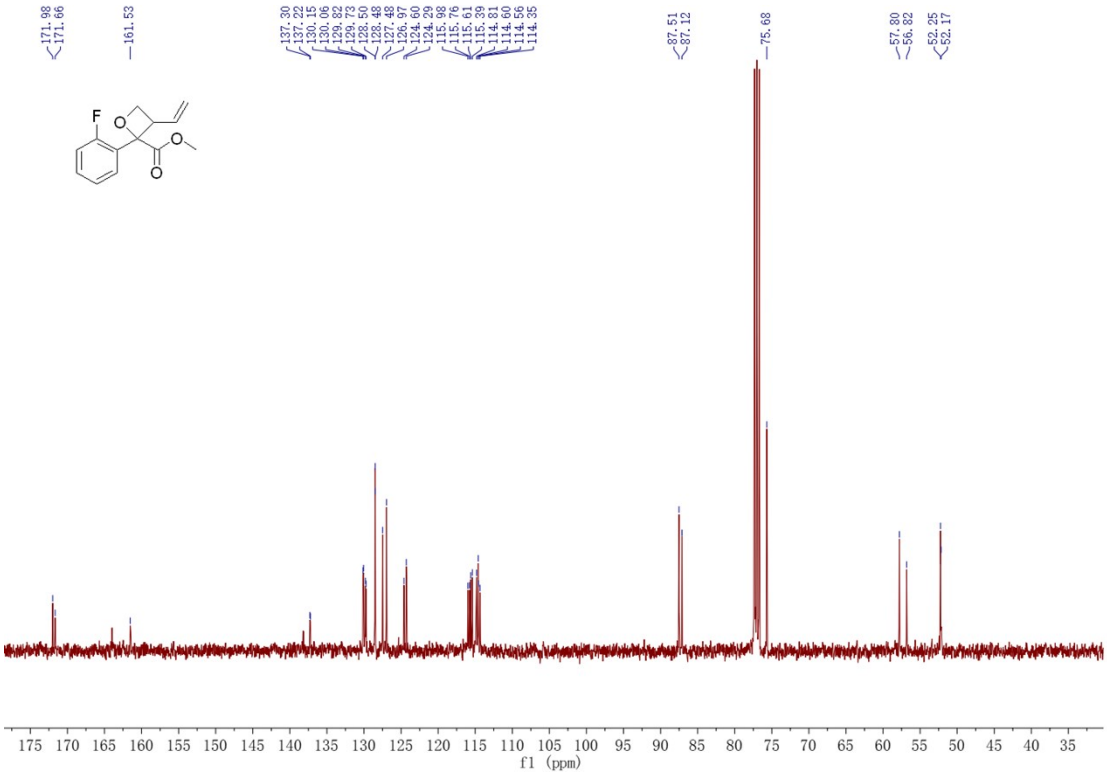
^{13}C NMR (101 MHz, CDCl3)



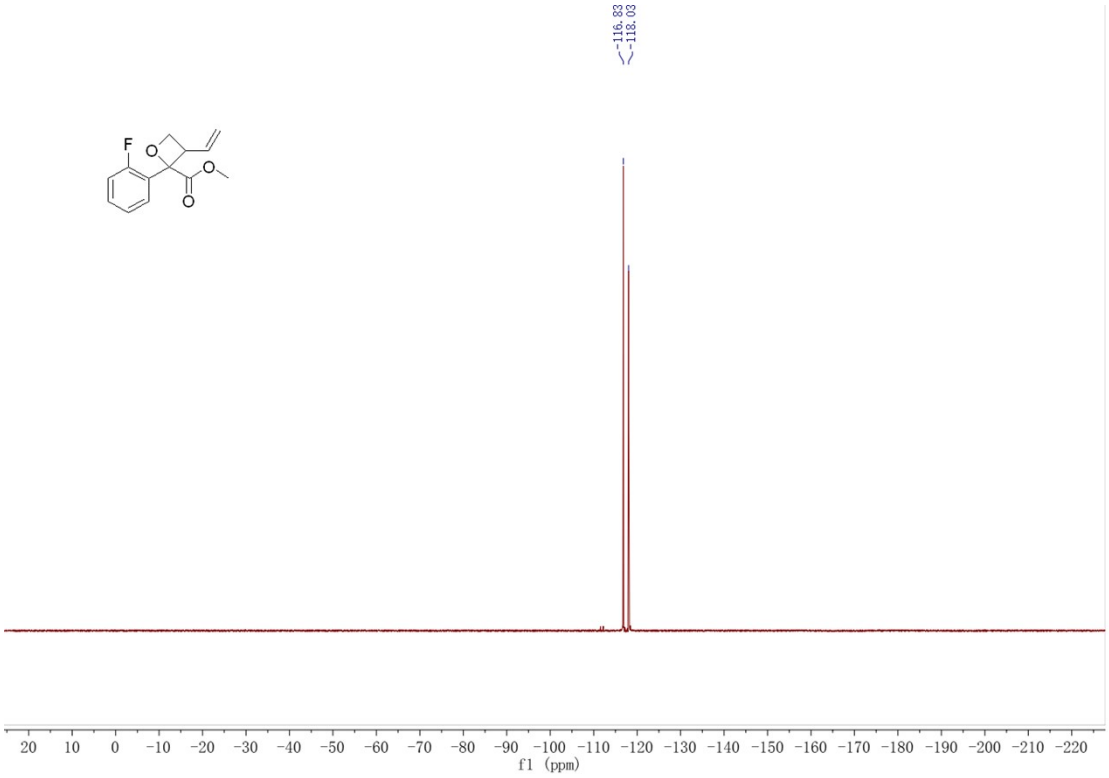
3f: ^{1}H NMR (400 MHz, $CDCl_3$)



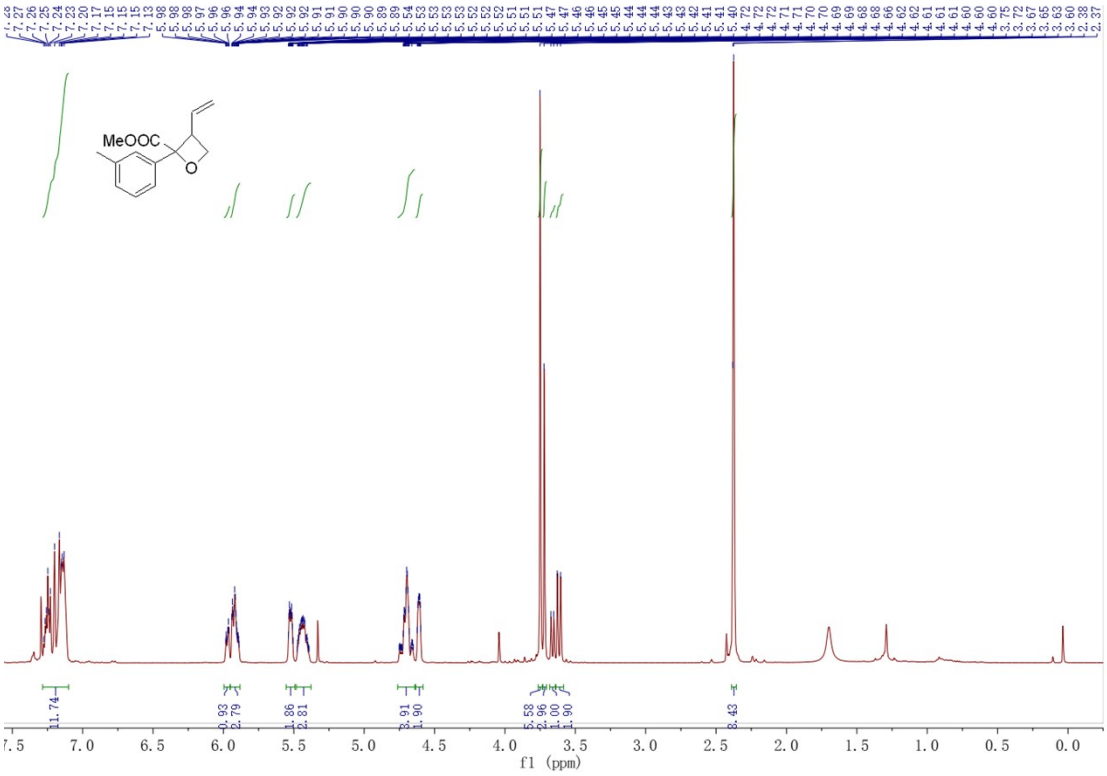
^{13}C NMR (101 MHz, CDCl3)



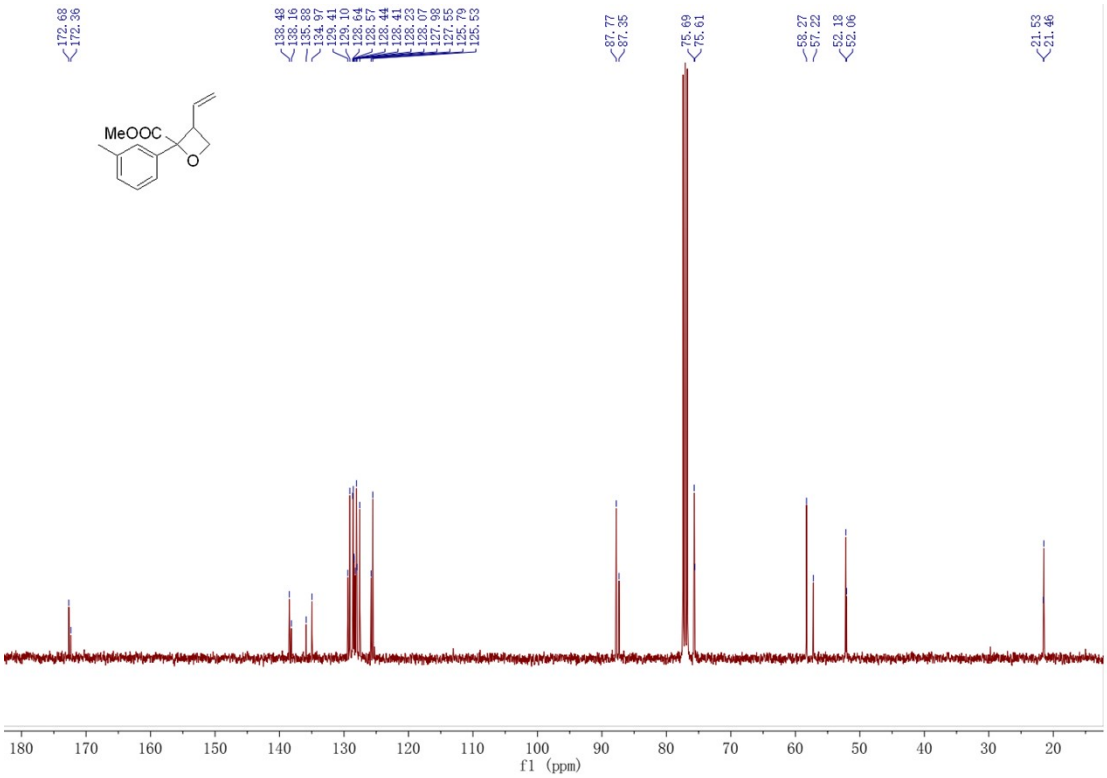
^{19}F NMR (376 MHz, CDCl3)



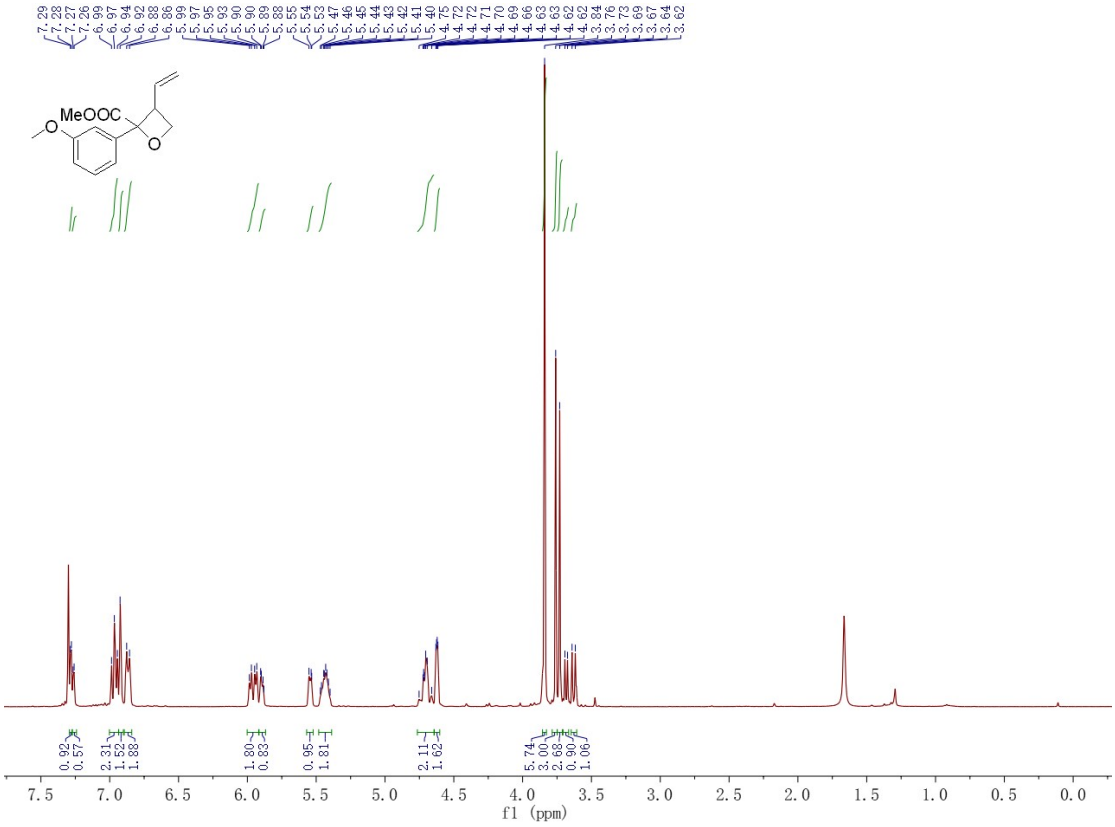
3g: ^{1}H NMR (400 MHz, $CDCl_3$)



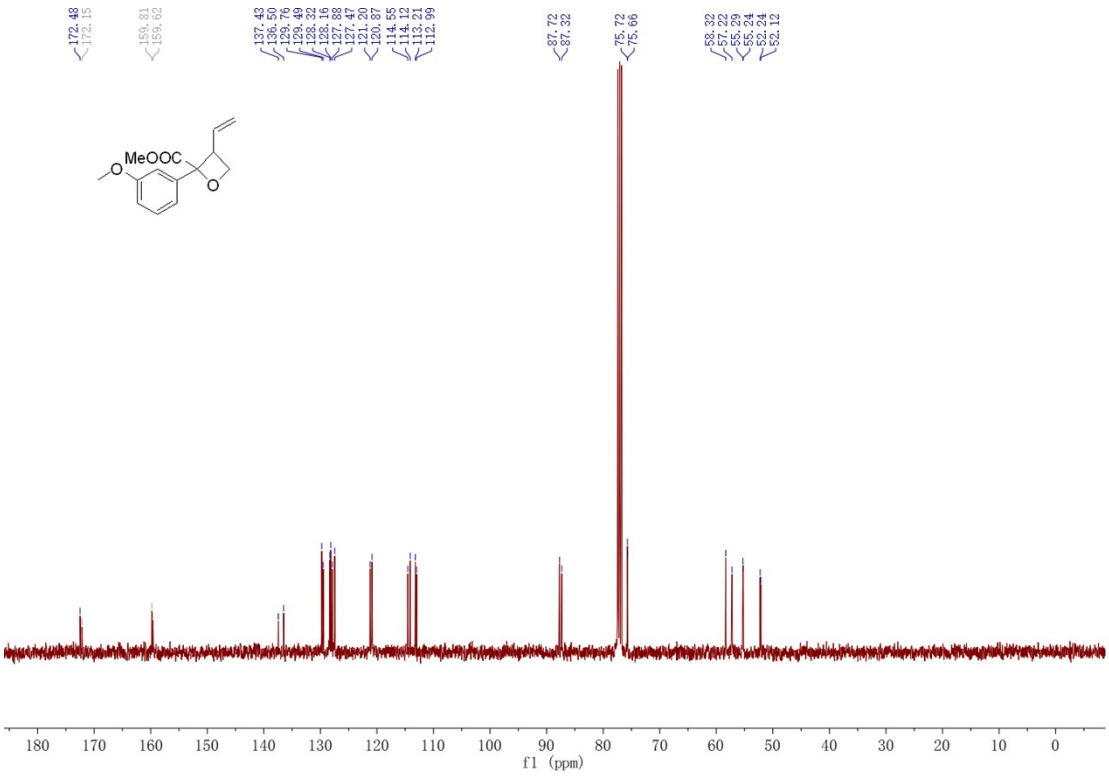
^{13}C NMR (101 MHz, CDCl3)



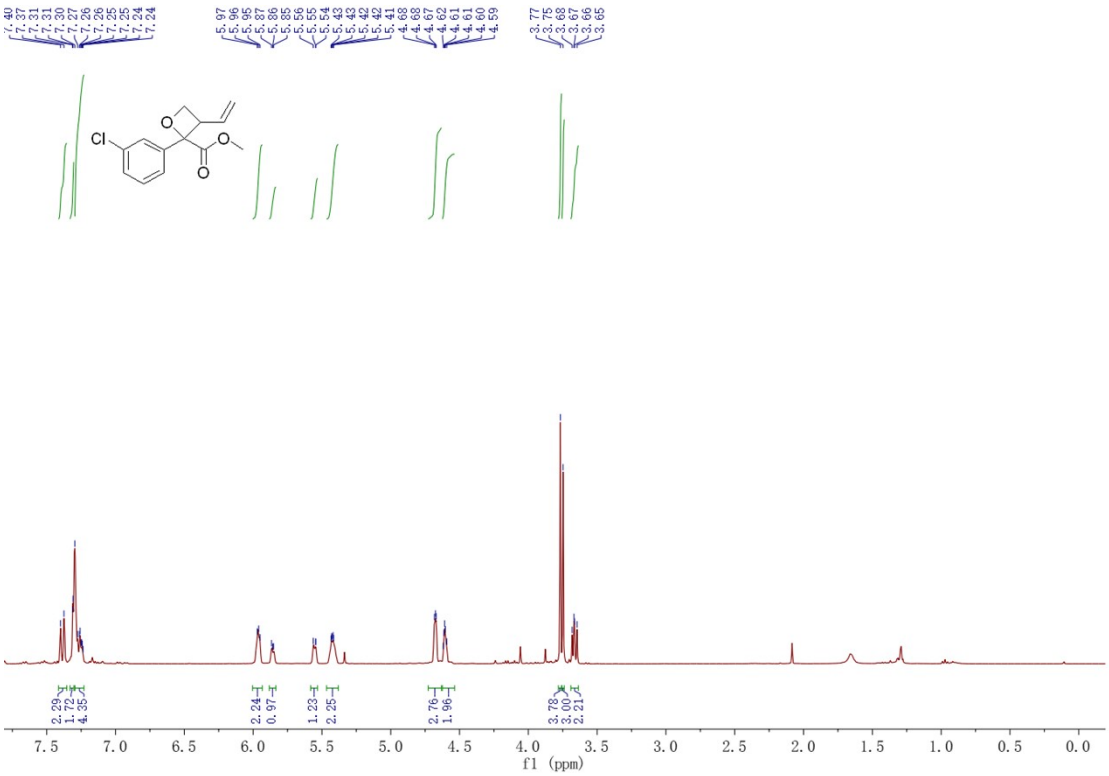
3h: ^{1}H NMR (400 MHz, $CDCl_3$)



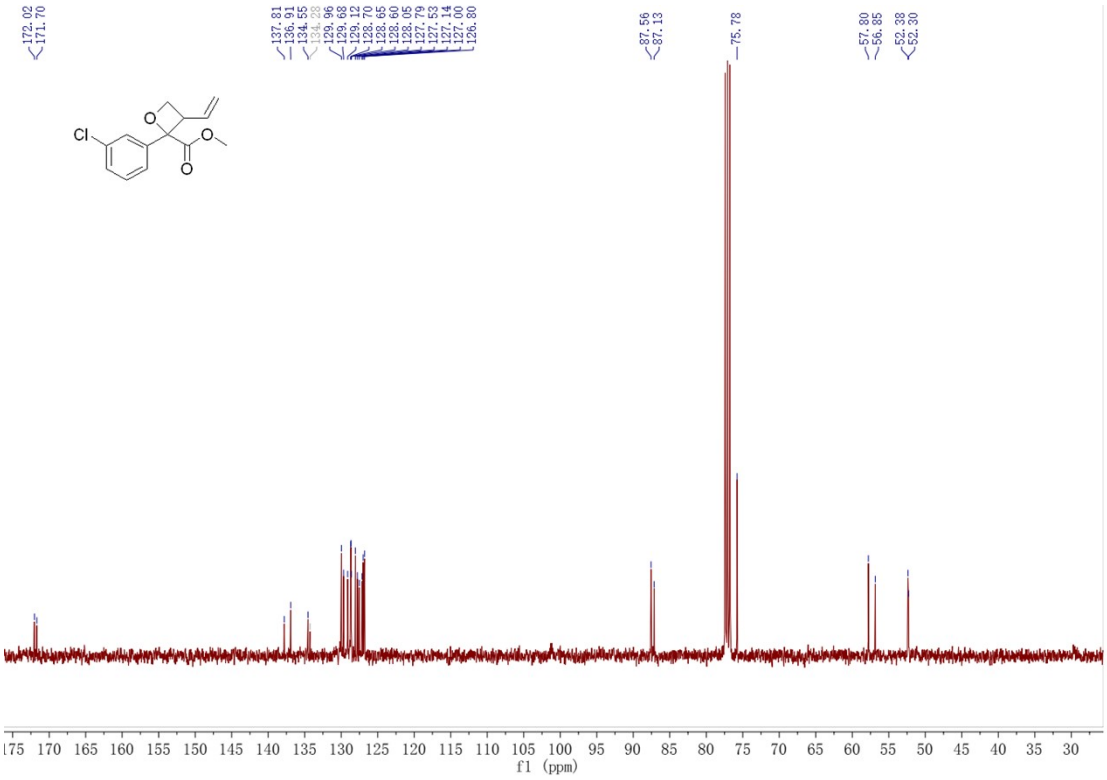
^{13}C NMR (101 MHz, CDCl3)



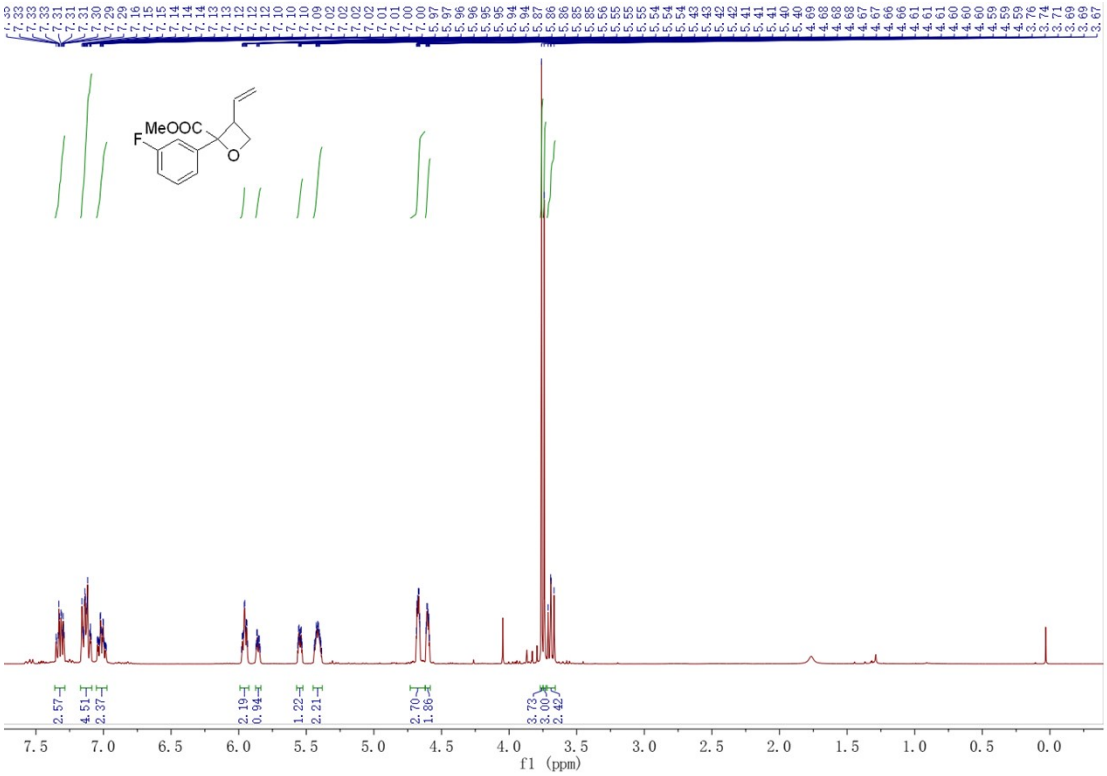
3i: ^{1}H NMR (400 MHz, $CDCl_3$)



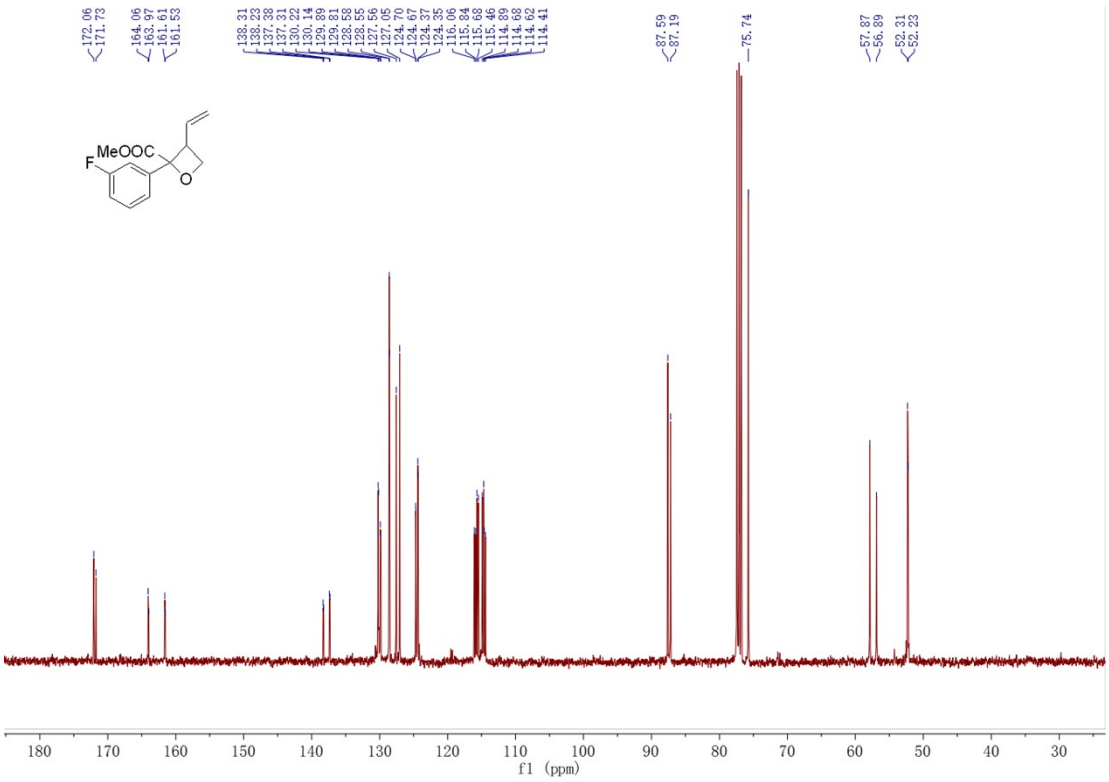
^{13}C NMR (101 MHz, CDCl3)



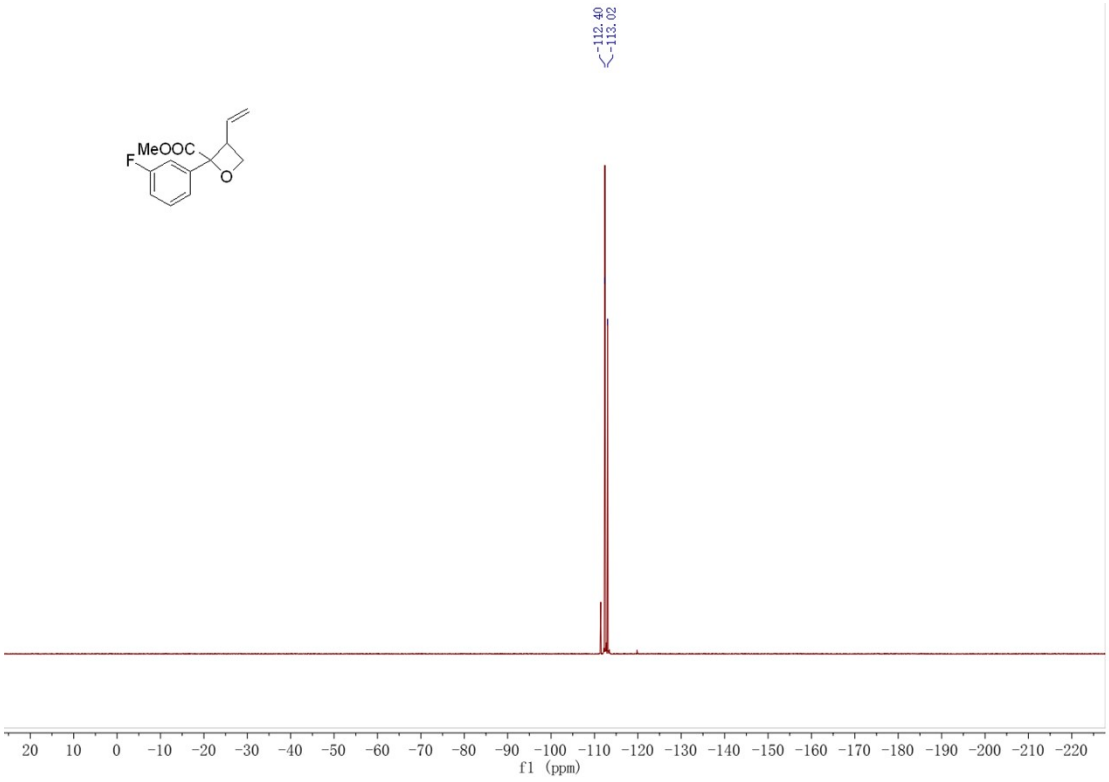
3j: ^{1}H NMR (400 MHz, $CDCl_3$)



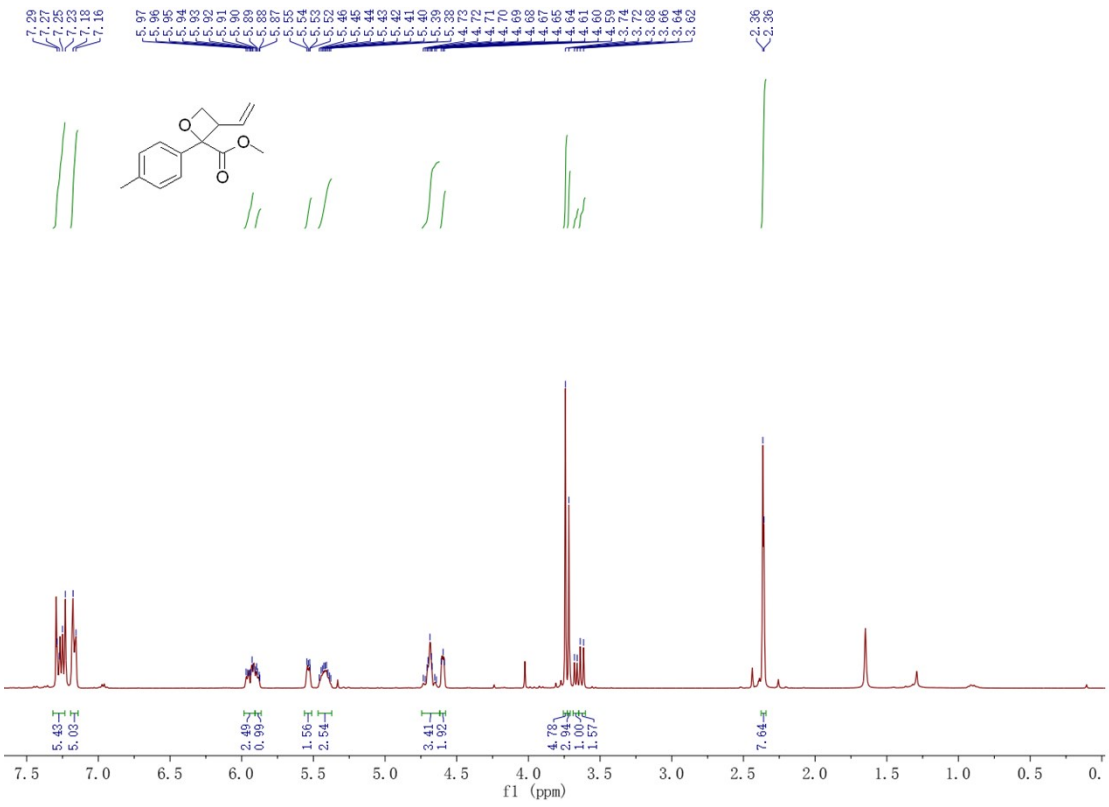
^{13}C NMR (101 MHz, CDCl3)



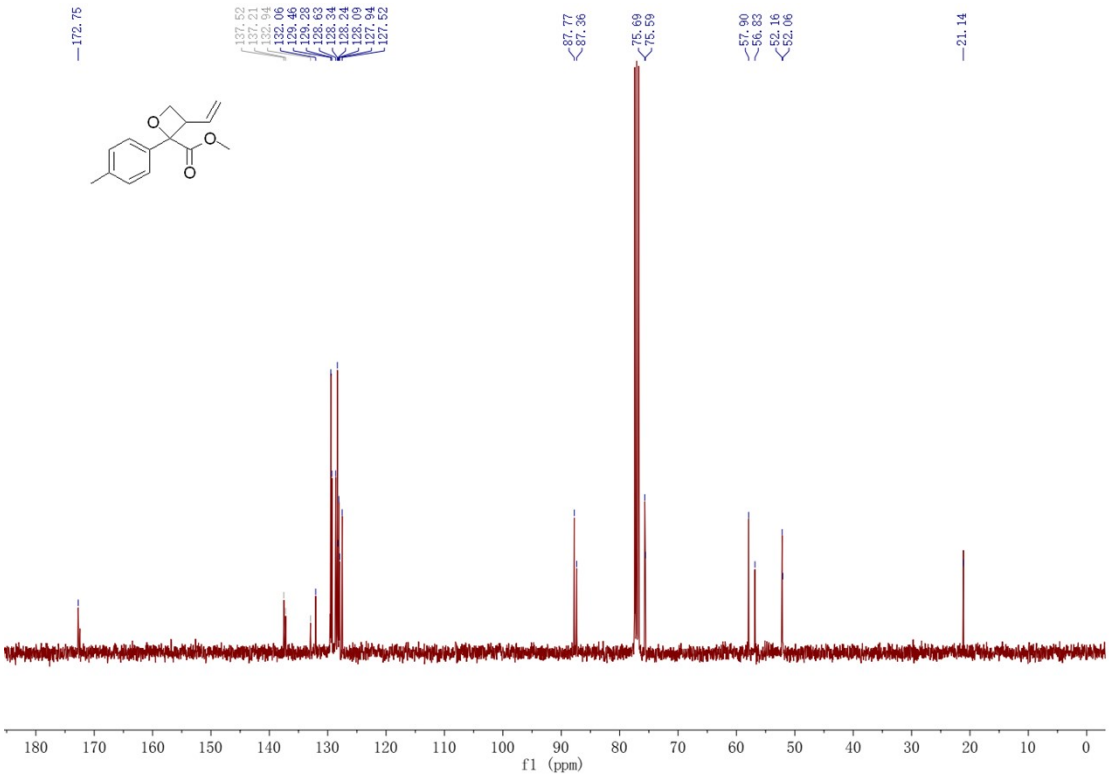
^{19}F NMR (376 MHz, CDCl3)



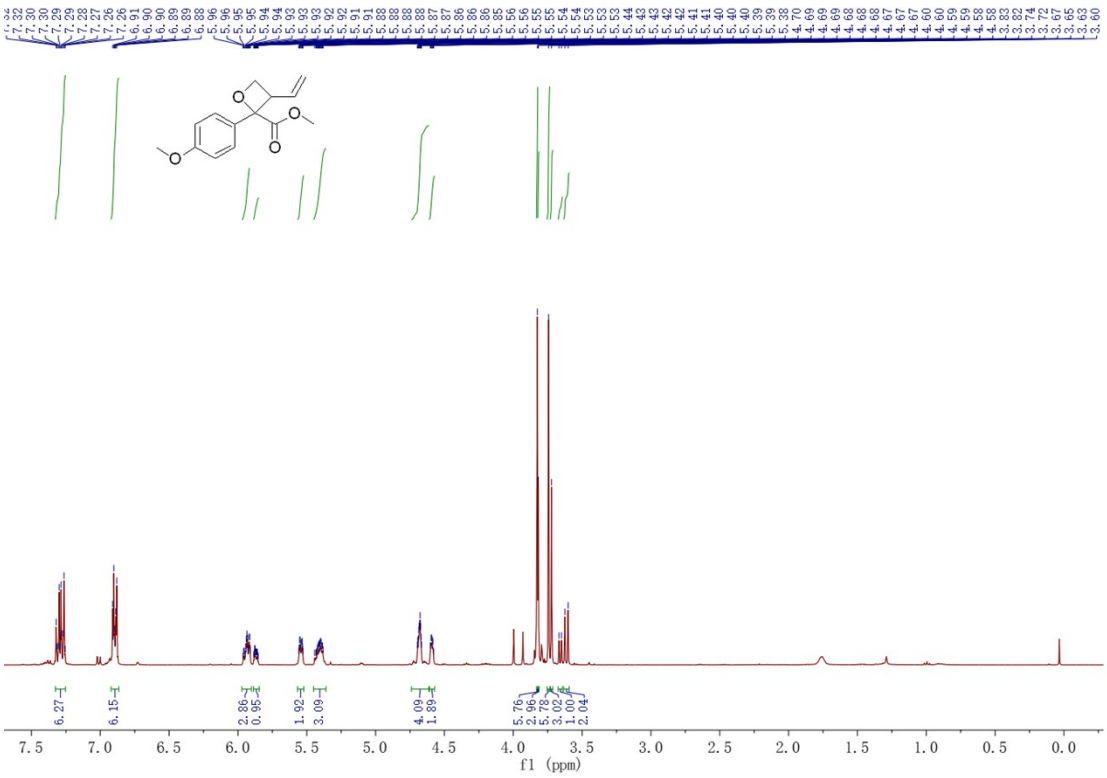
3k: ^{1}H NMR (400 MHz, $CDCl_3$)



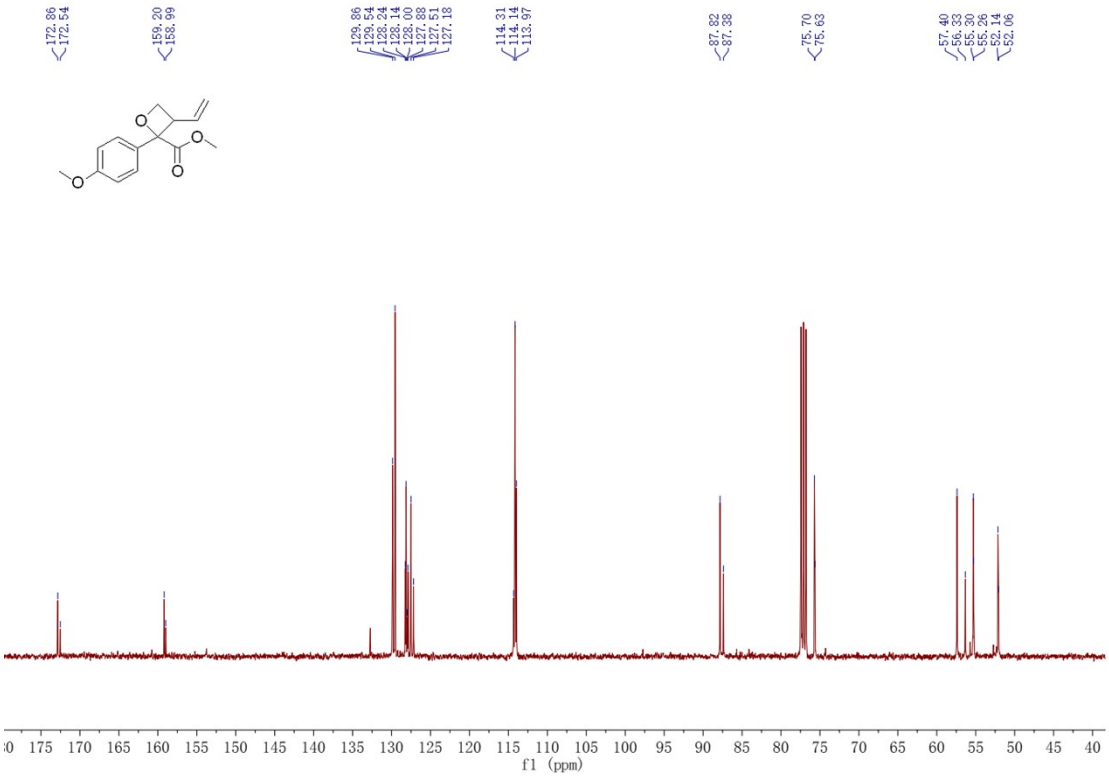
^{13}C NMR (101 MHz, CDCl3)



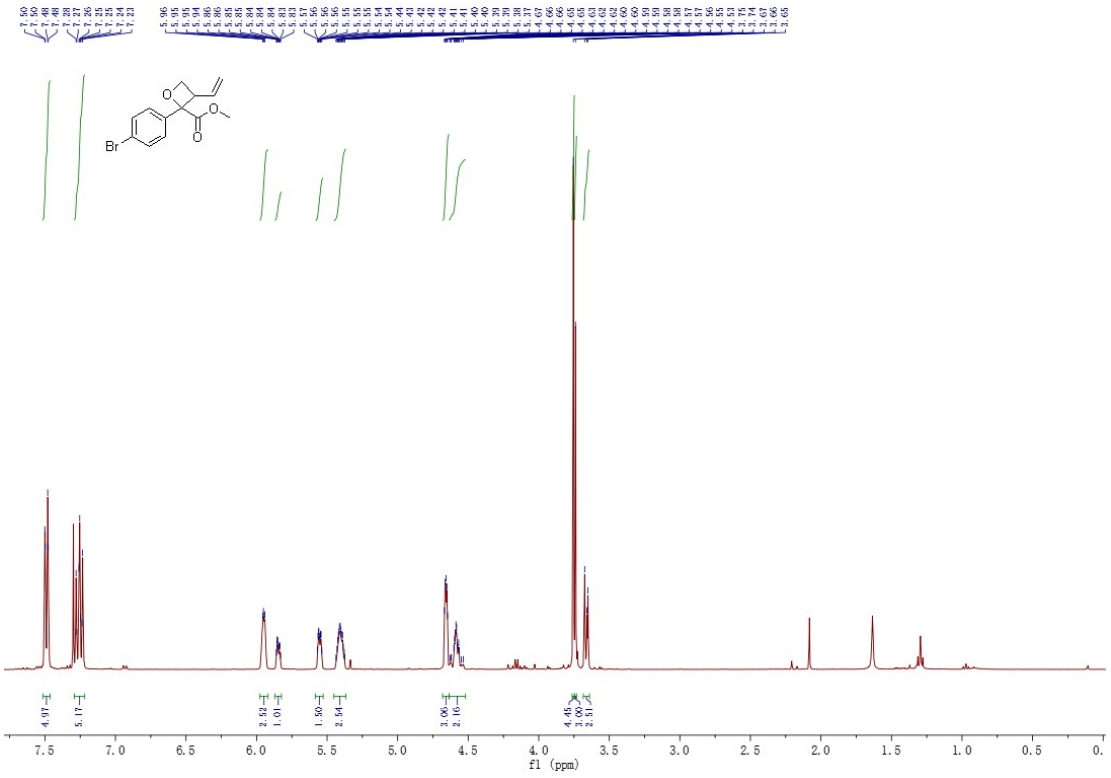
3l: ^{1}H NMR (400 MHz, $CDCl_3$)



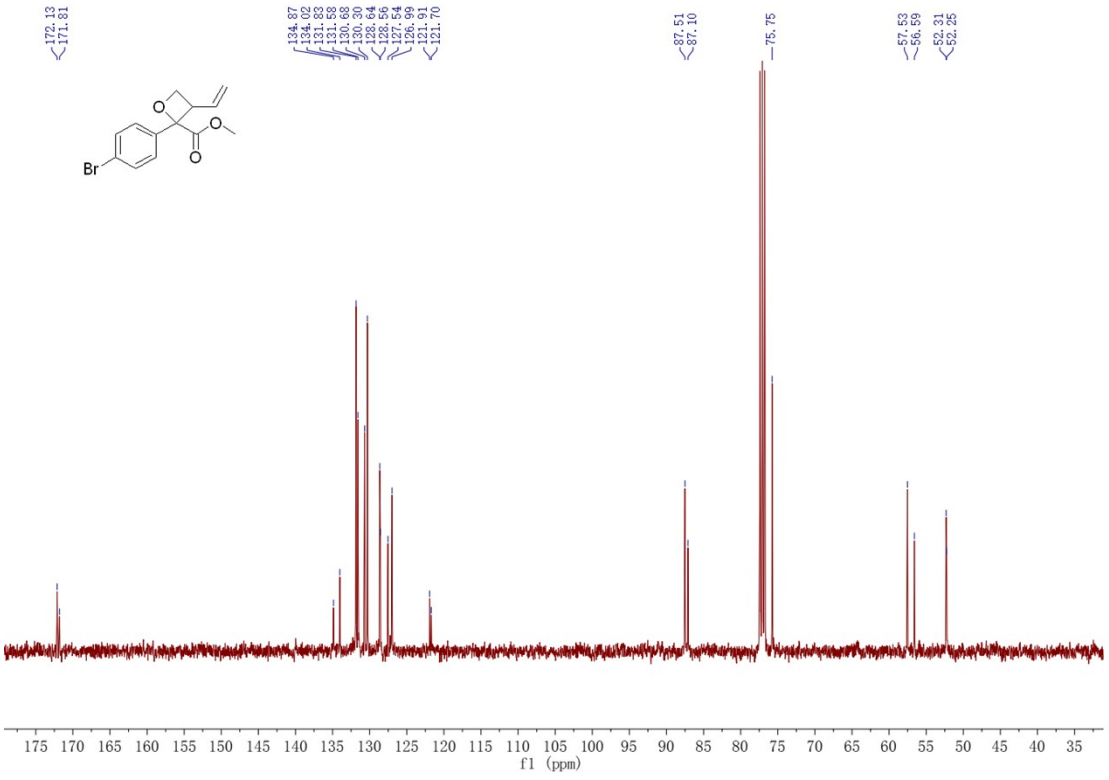
^{13}C NMR (101 MHz, CDCl3)



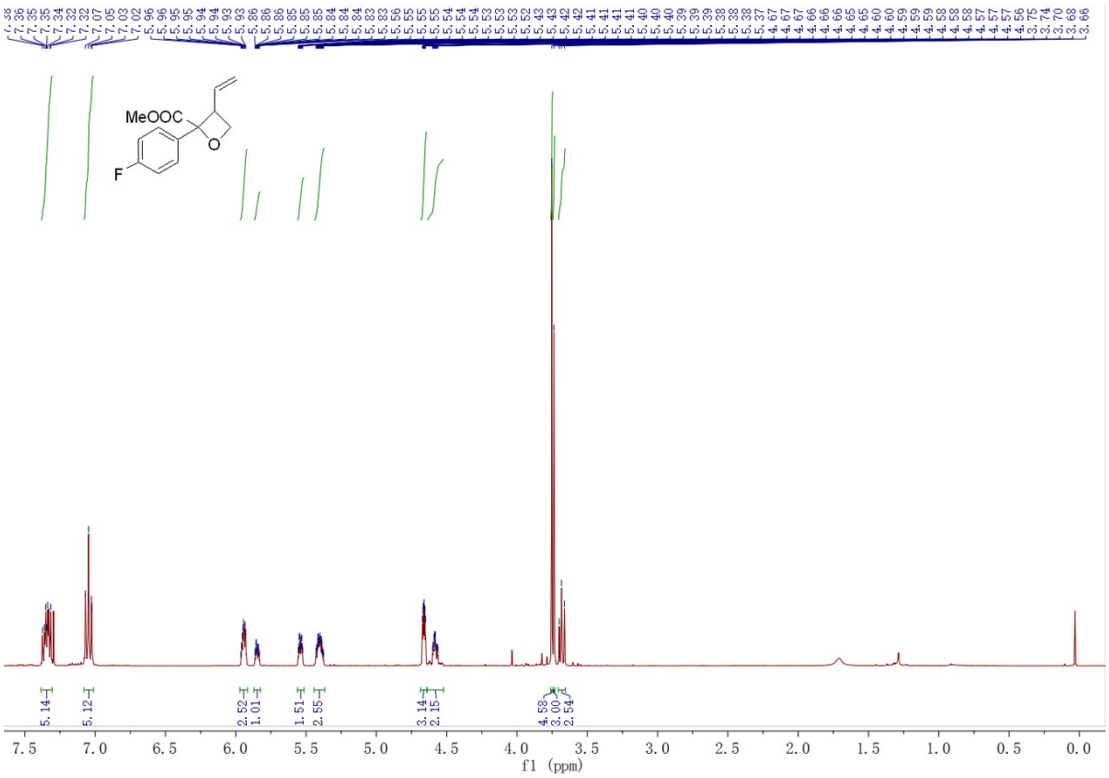
3m: ^{1}H NMR (400 MHz, $CDCl_3$)



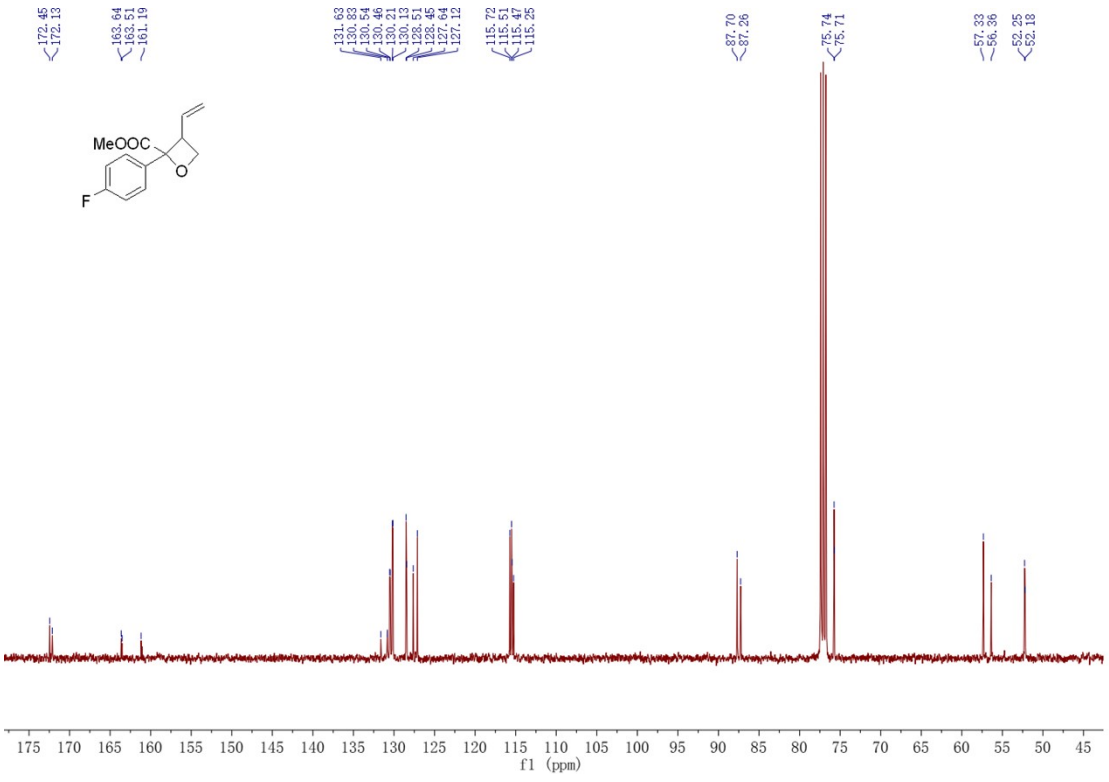
^{13}C NMR (101 MHz, CDCl3)



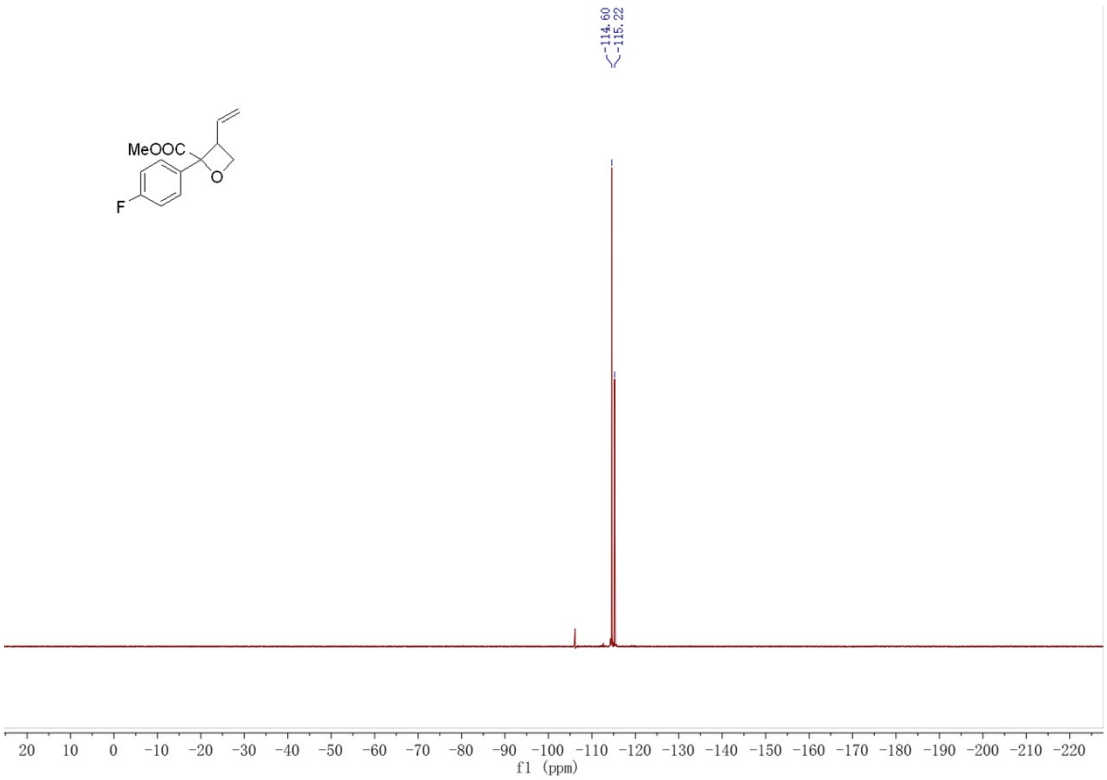
3n: ^{1}H NMR (400 MHz, $CDCl_3$)



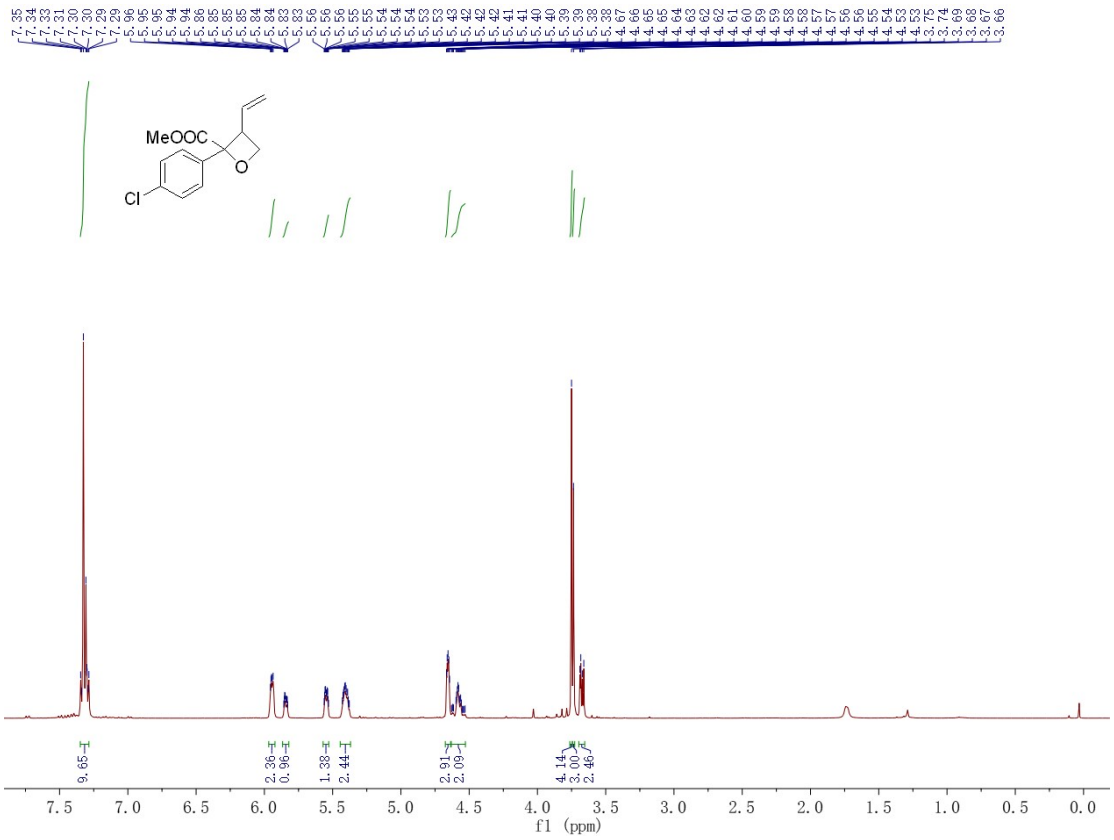
^{13}C NMR (101 MHz, CDCl3)



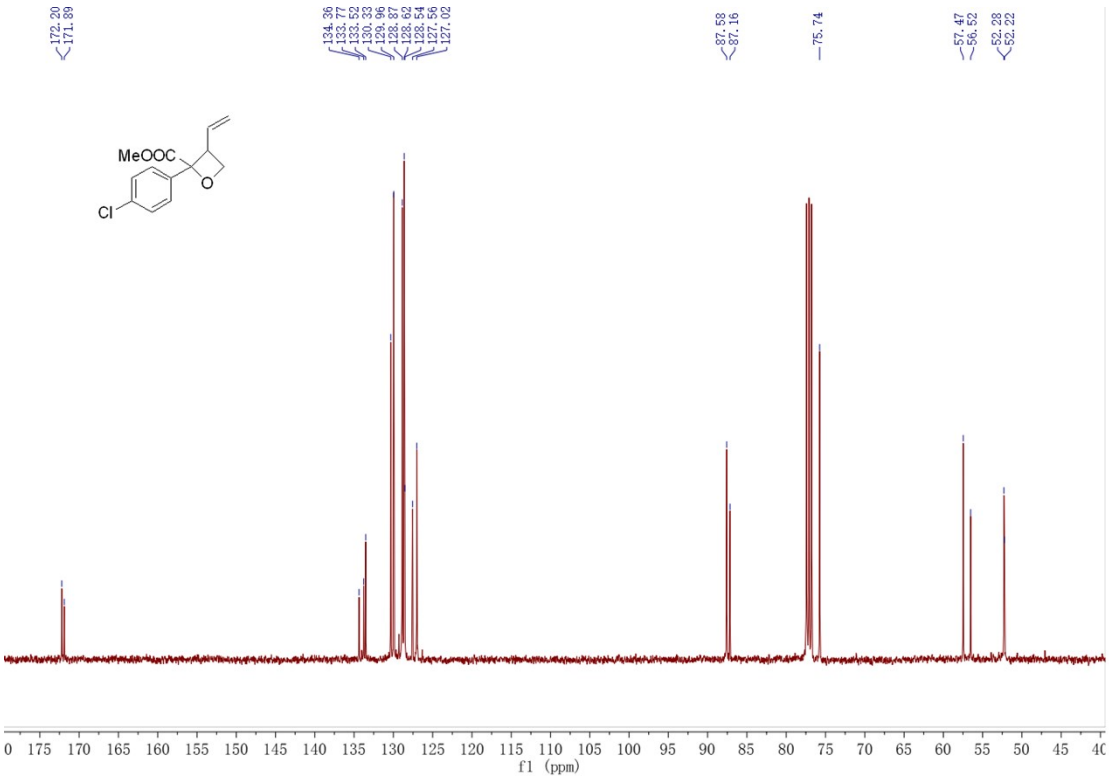
^{19}F NMR (376 MHz, CDCl3)



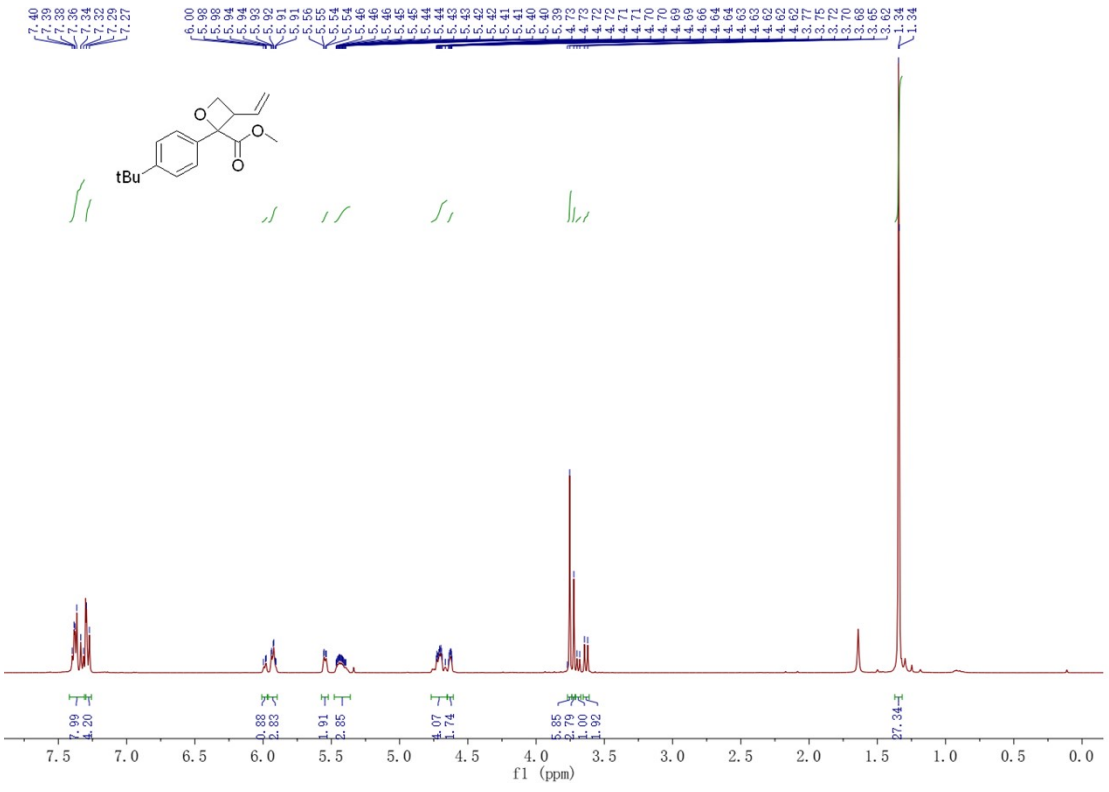
3o: ^{1}H NMR (400 MHz, $CDCl_3$)



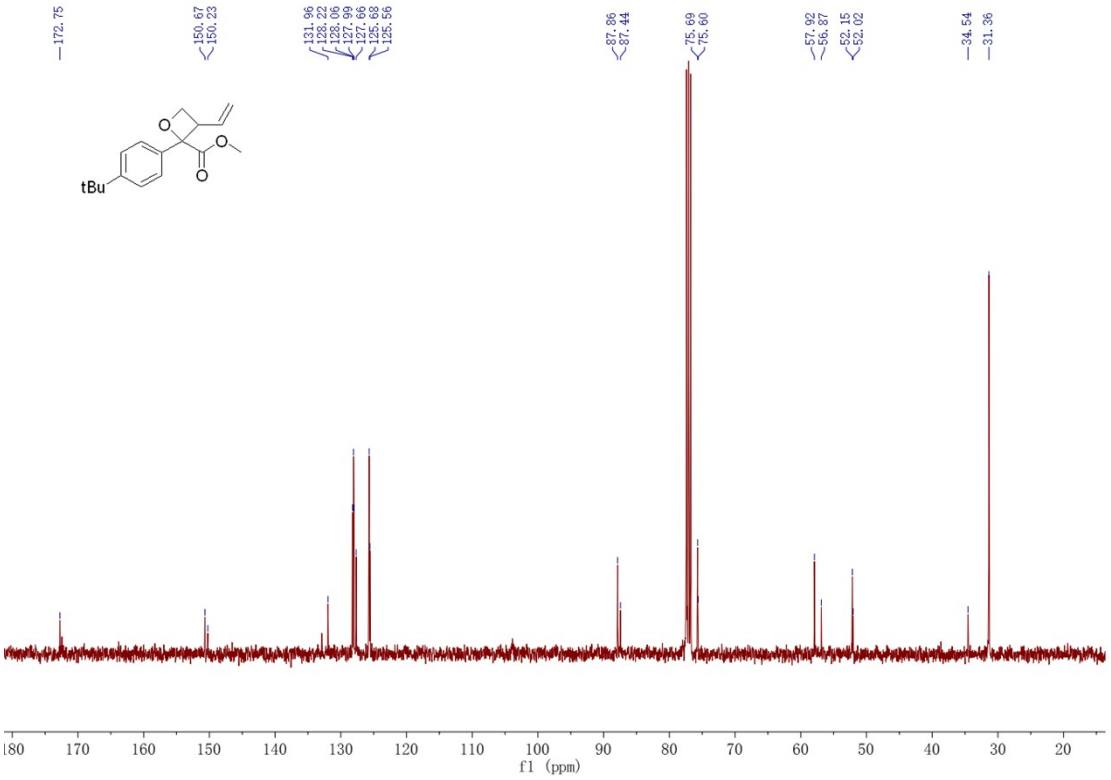
^{13}C NMR (101 MHz, CDCl3)



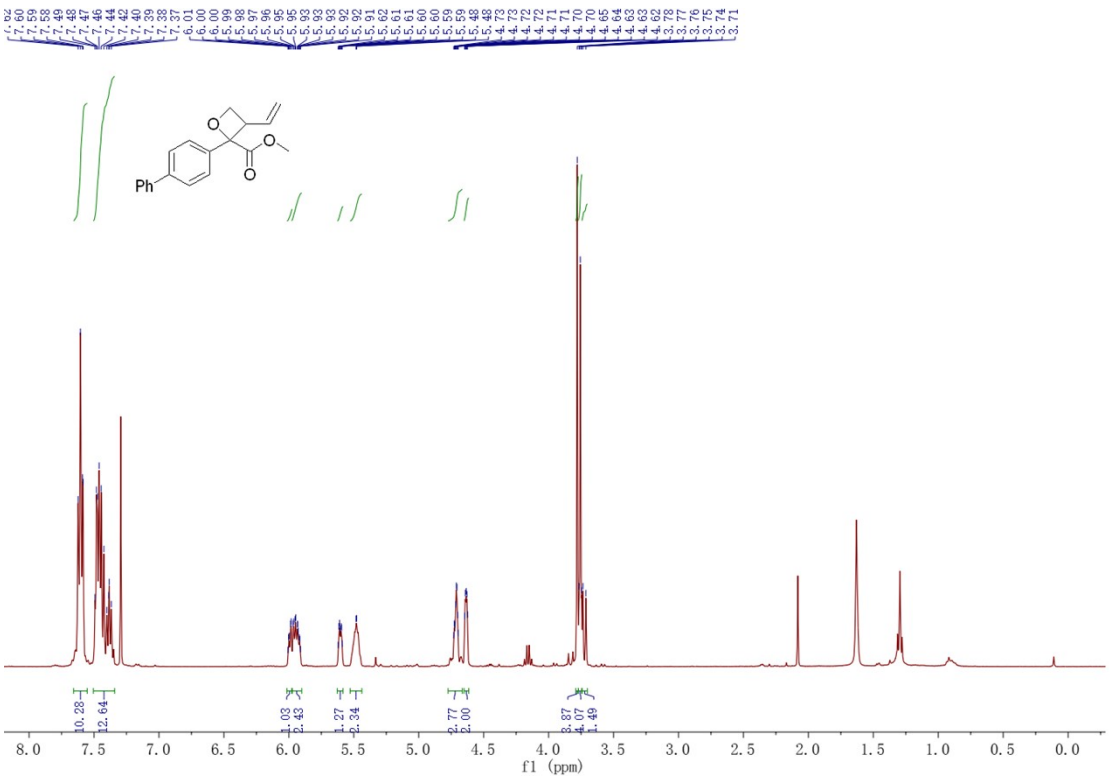
3p: ^{1}H NMR (400 MHz, $CDCl_3$)



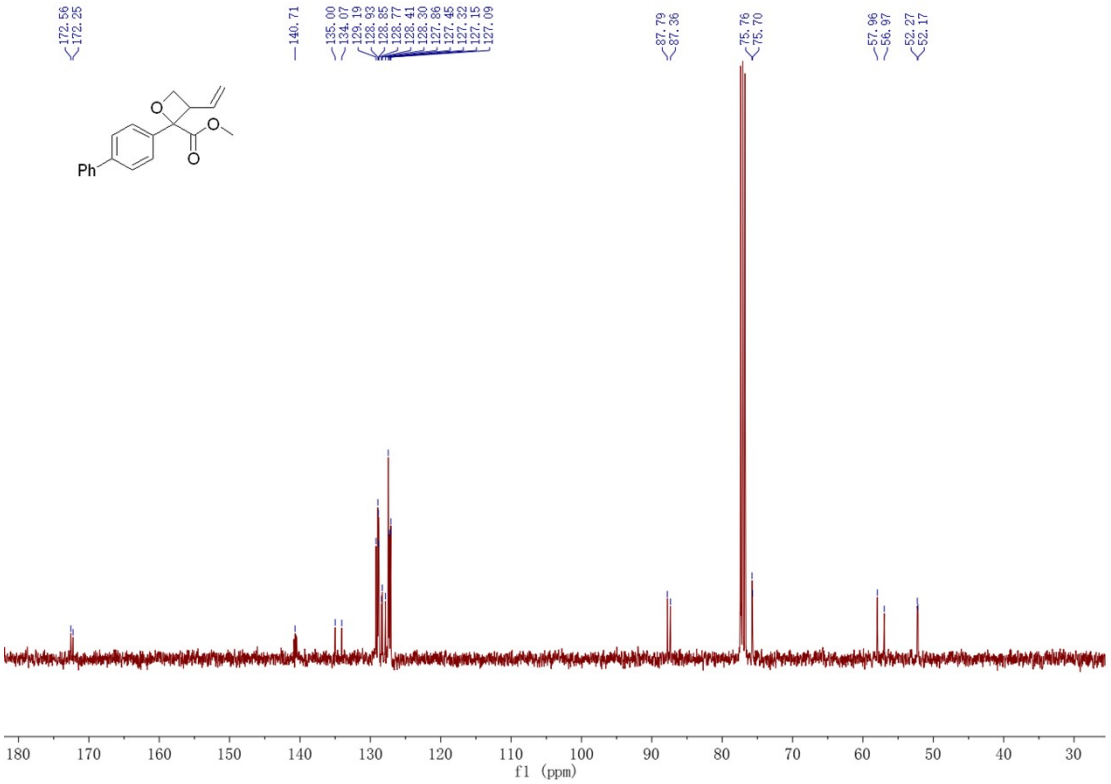
^{13}C NMR (101 MHz, CDCl3)



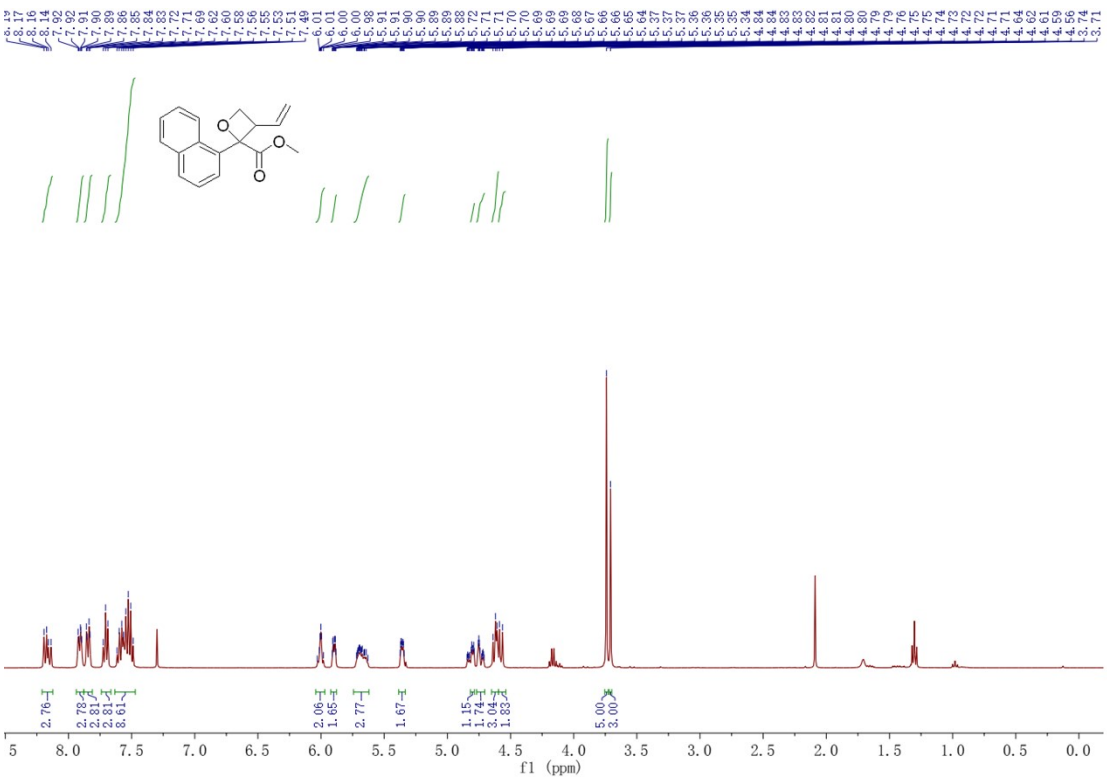
3q: ^{1}H NMR (400 MHz, $CDCl_3$)



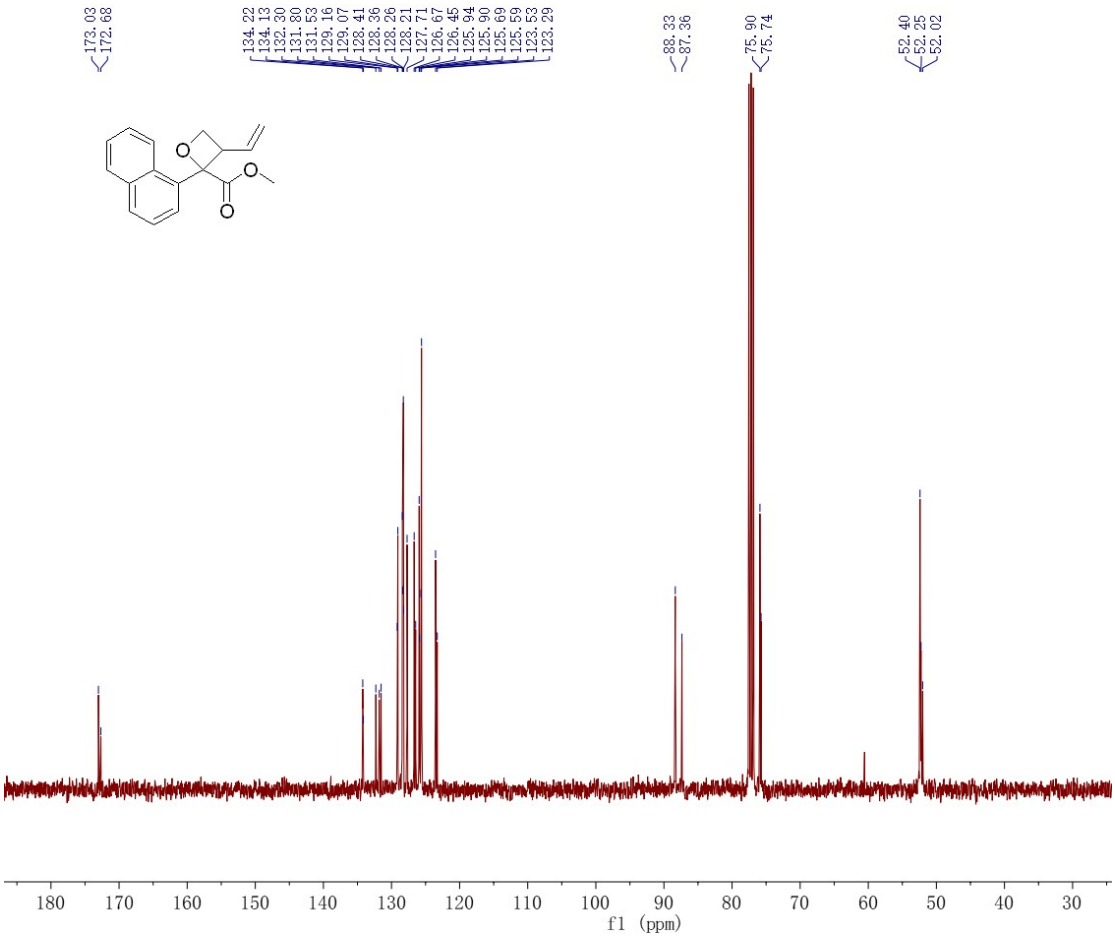
^{13}C NMR (101 MHz, CDCl3)



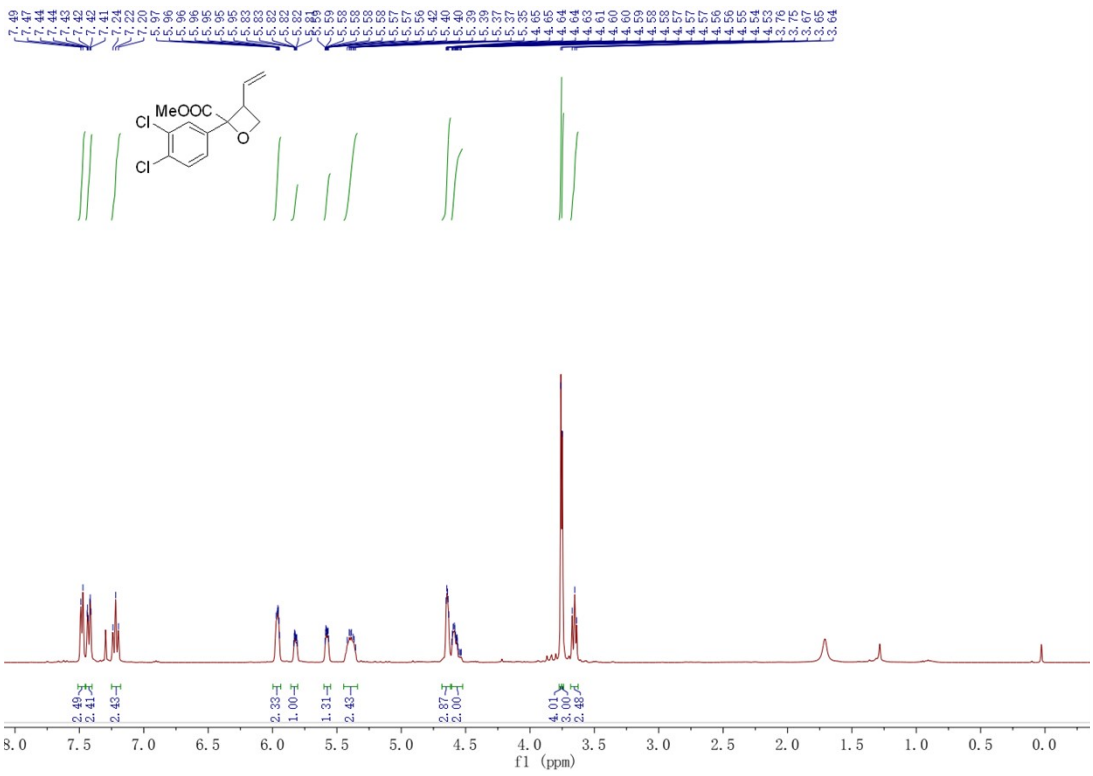
3r: ^{1}H NMR (400 MHz, $CDCl_3$)



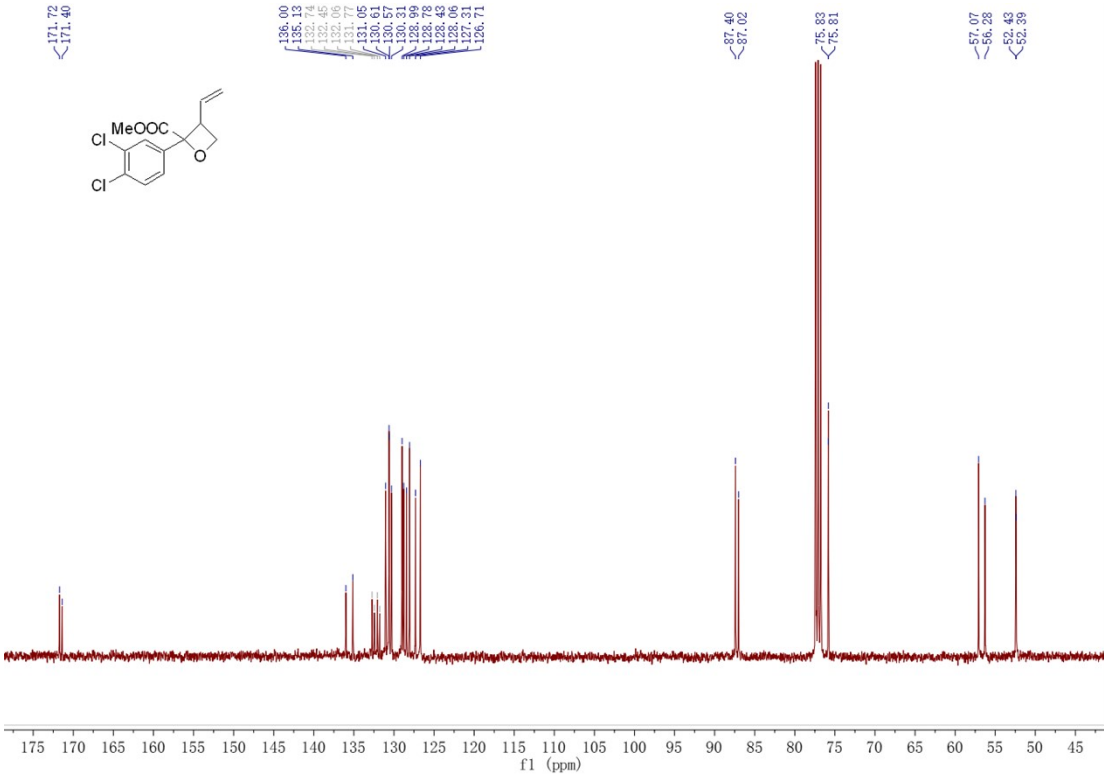
^{13}C NMR (101 MHz, CDCl3)



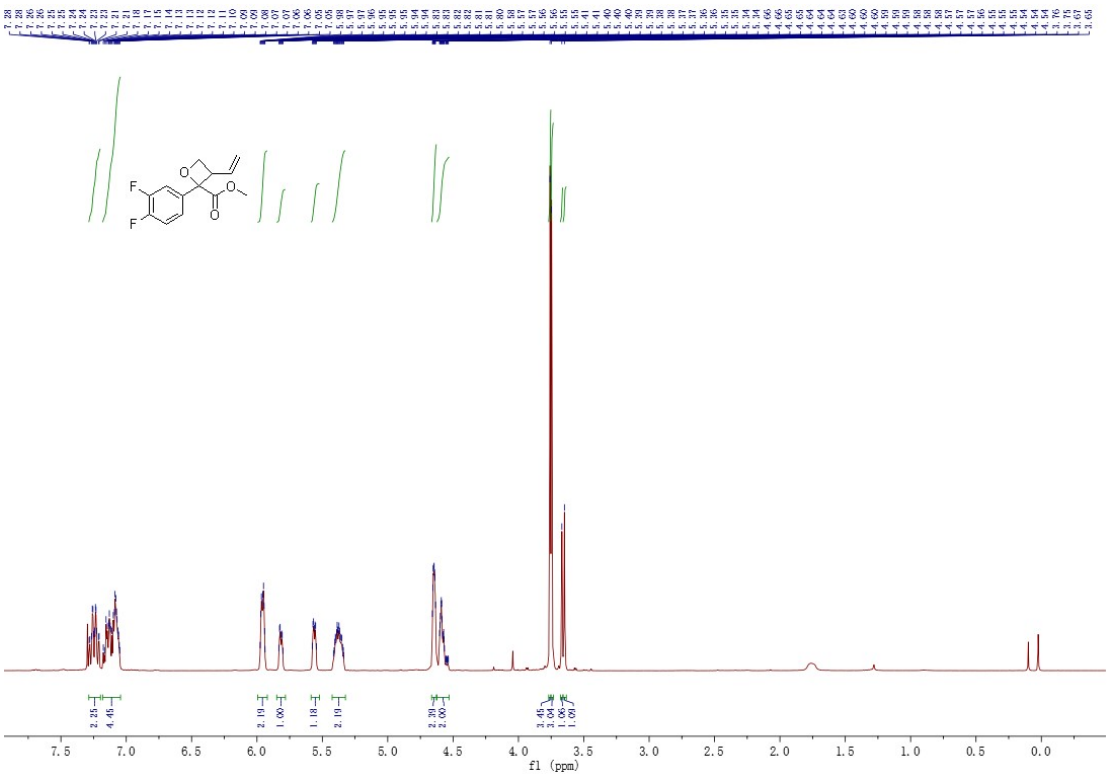
3s: ^{1}H NMR (400 MHz, $CDCl_3$)



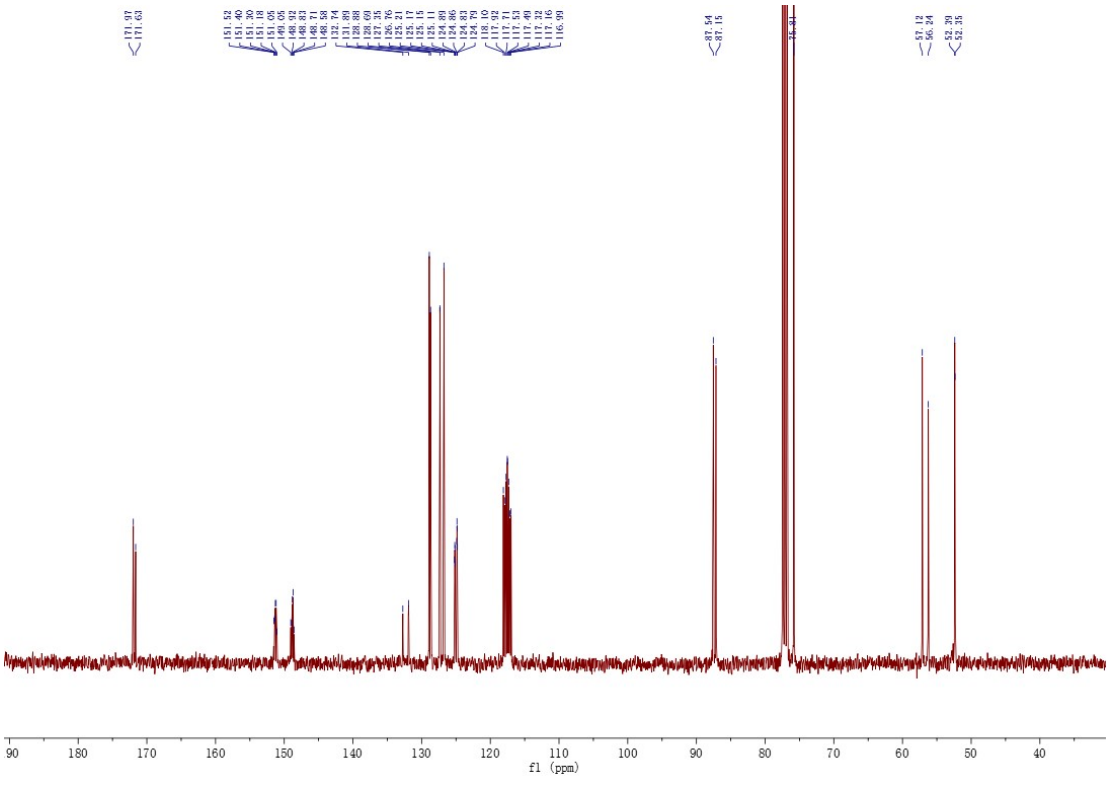
^{13}C NMR (101 MHz, CDCl3)



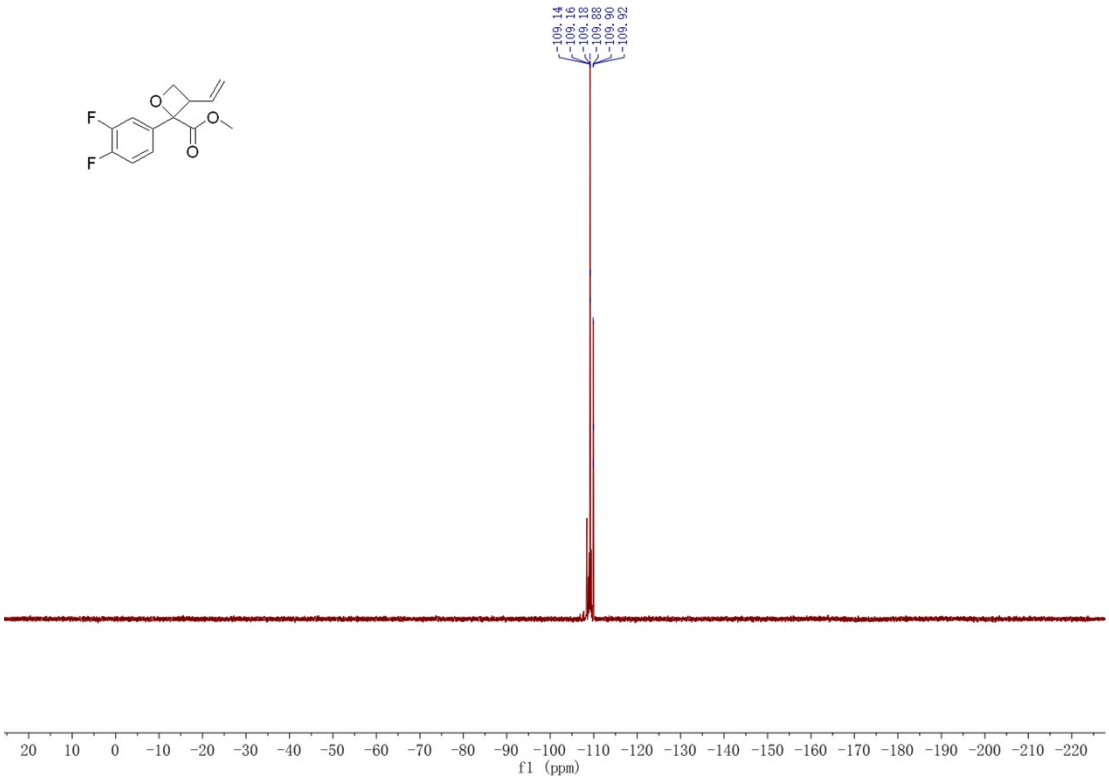
3t: ^{1}H NMR (400 MHz, $CDCl_3$)



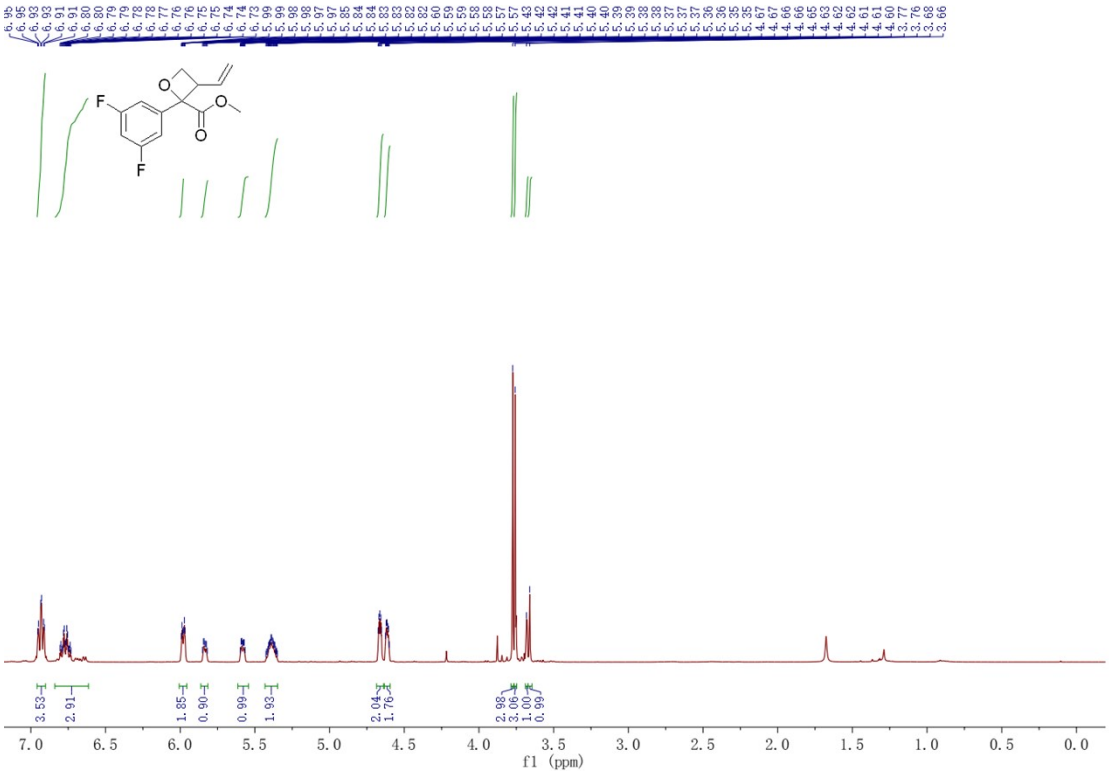
^{13}C NMR (101 MHz, CDCl3)



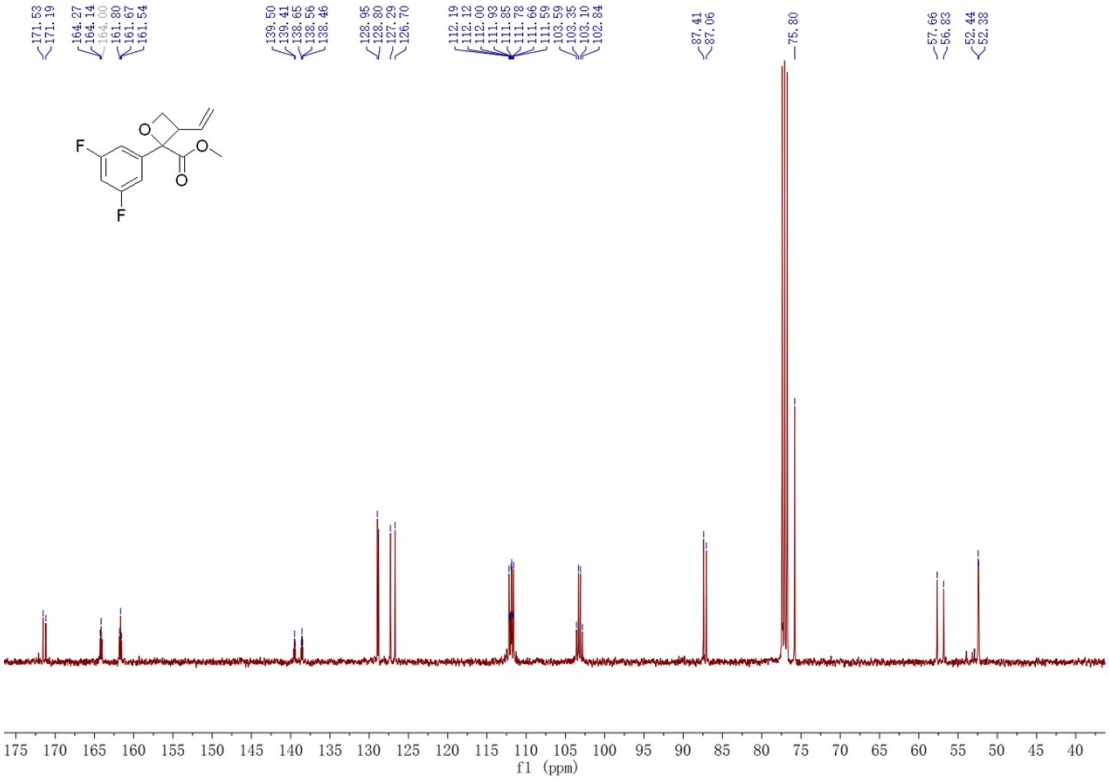
^{19}F NMR (376 MHz, CDCl3)



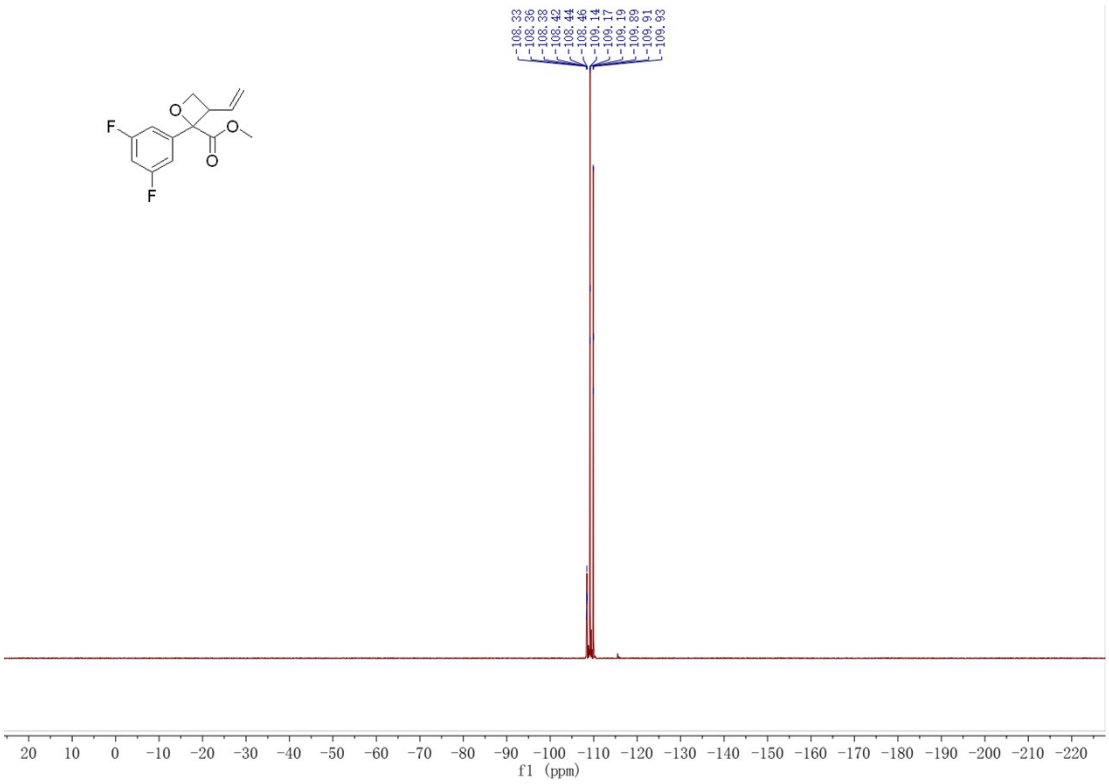
3u: ^{1}H NMR (400 MHz, $CDCl_3$)



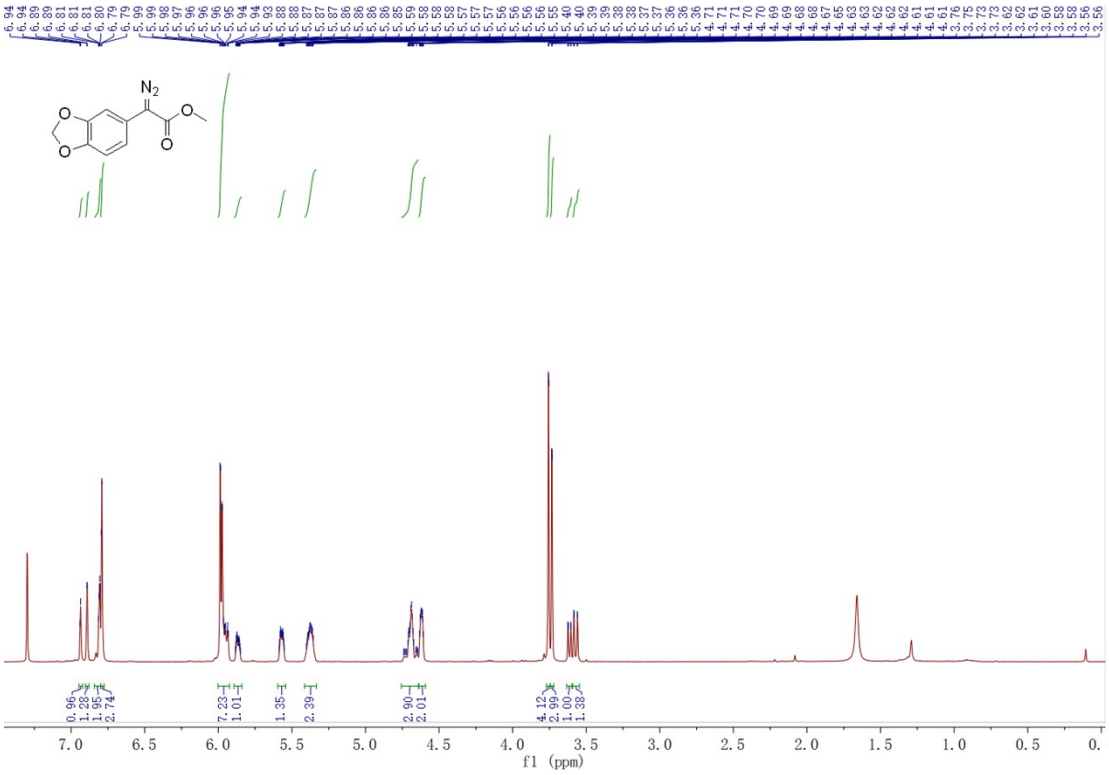
^{13}C NMR (101 MHz, CDCl3)



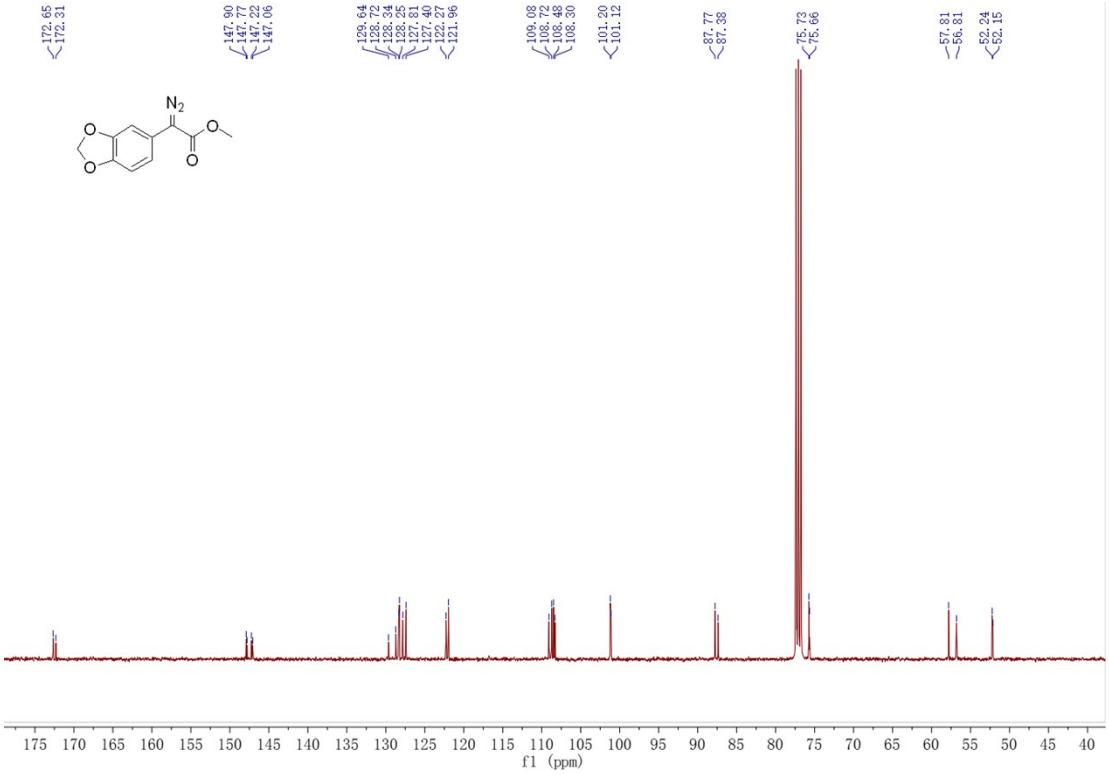
^{19}F NMR (376 MHz, CDCl3)



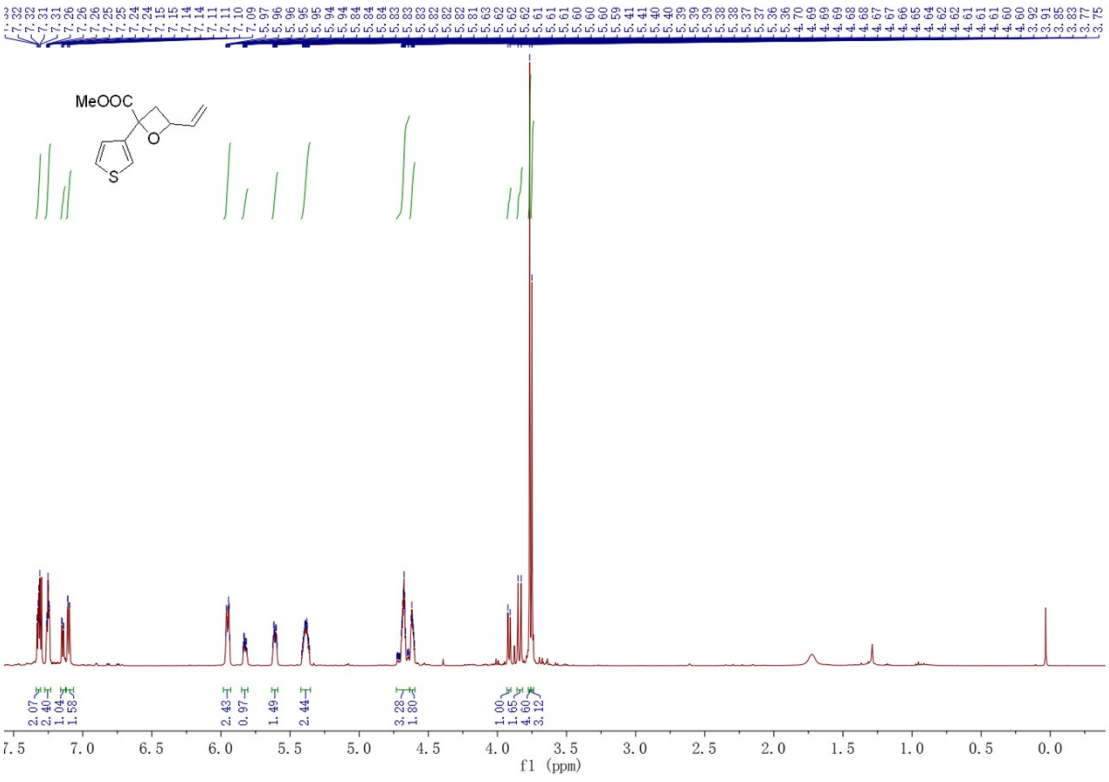
3v: ^{1}H NMR (400 MHz, $CDCl_3$)



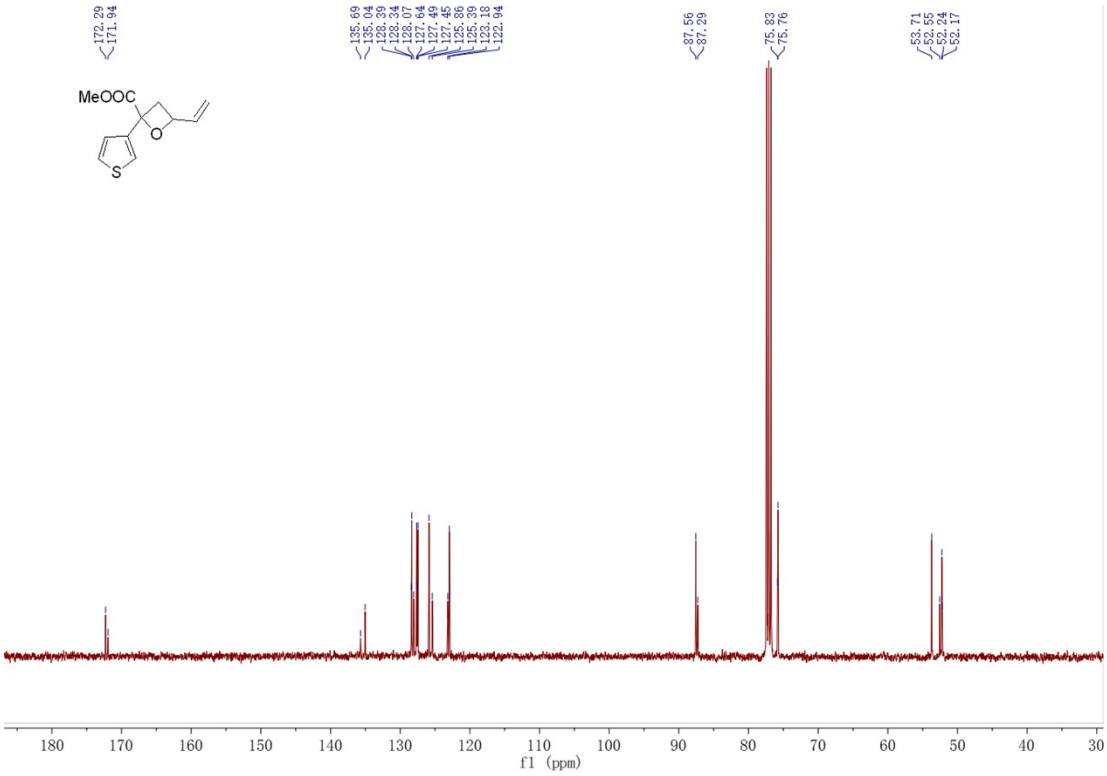
^{13}C NMR (101 MHz, CDCl3)



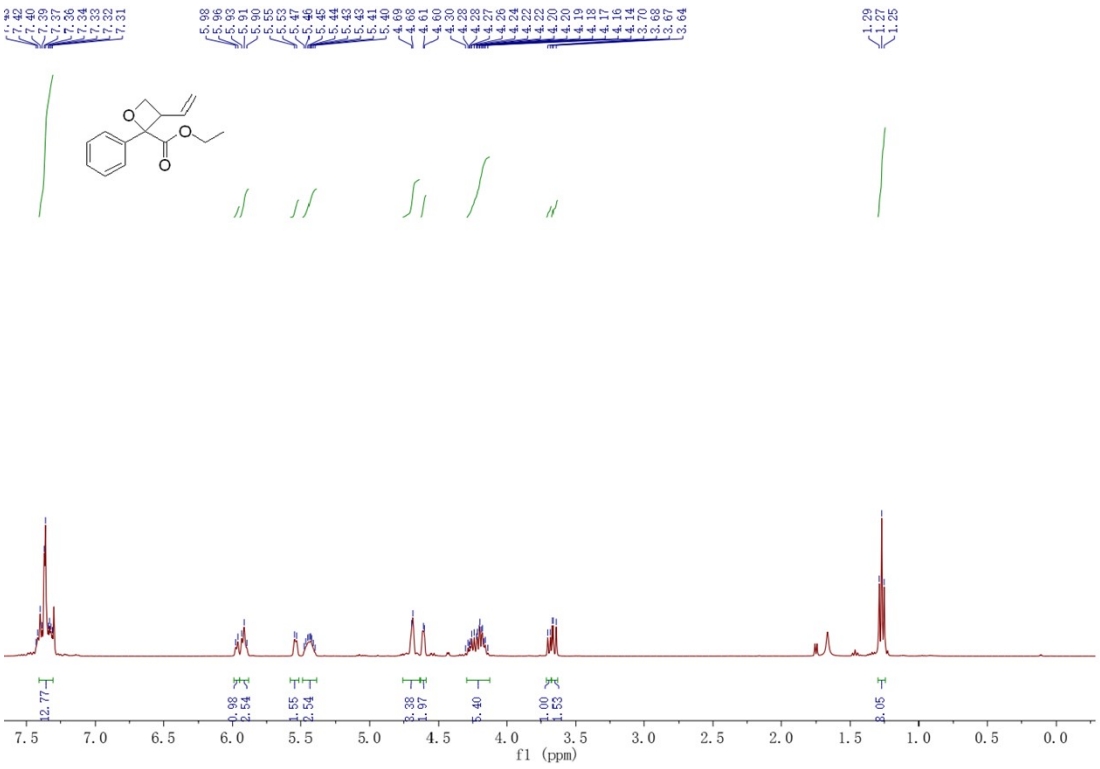
3w: ^{1}H NMR (400 MHz, $CDCl_3$)



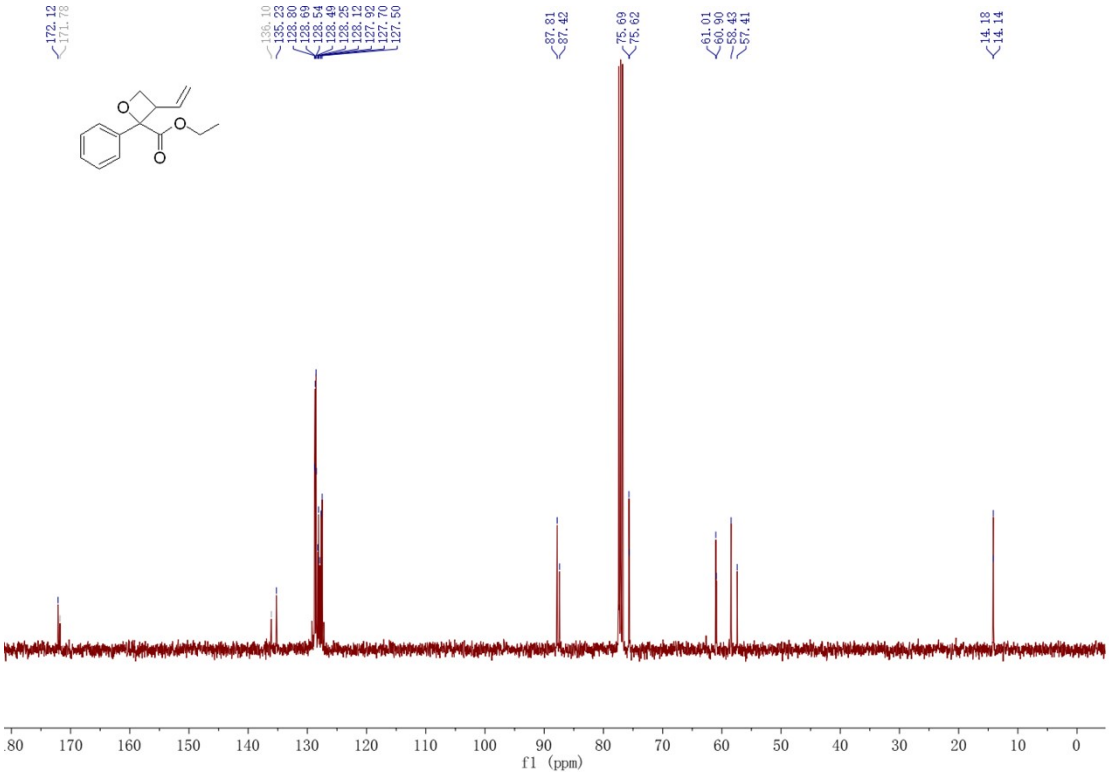
^{13}C NMR (101 MHz, CDCl3)



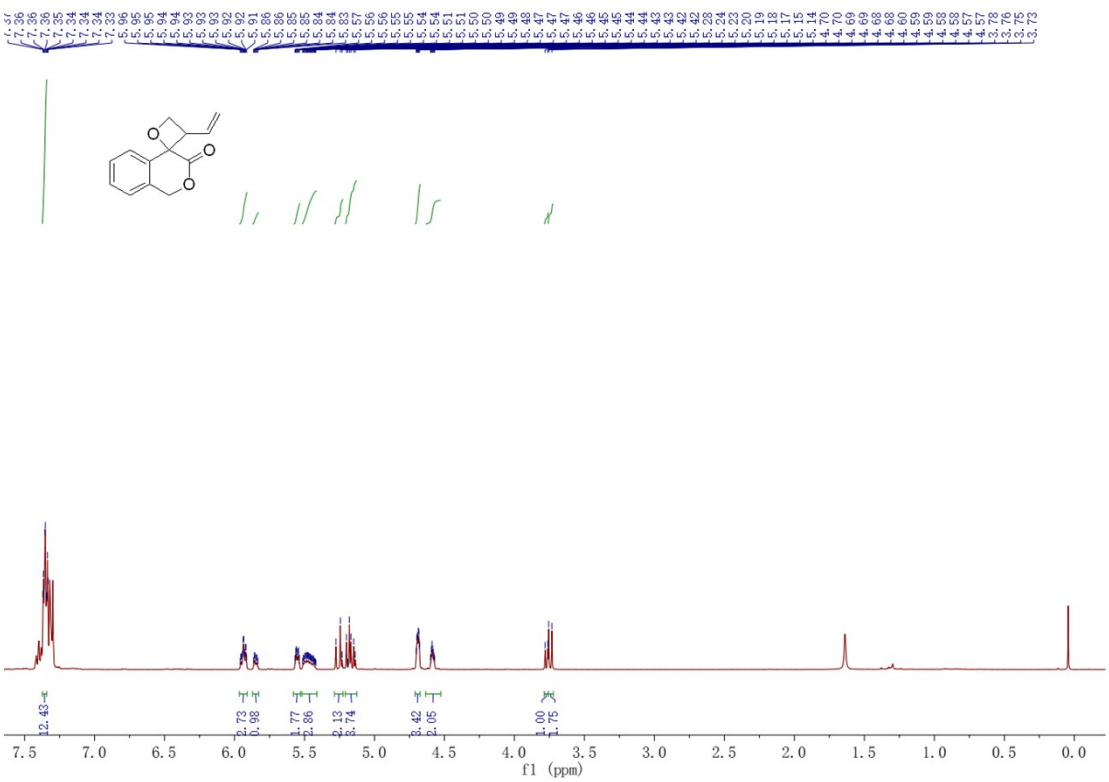
3x: ^{1}H NMR (400 MHz, $CDCl_3$)



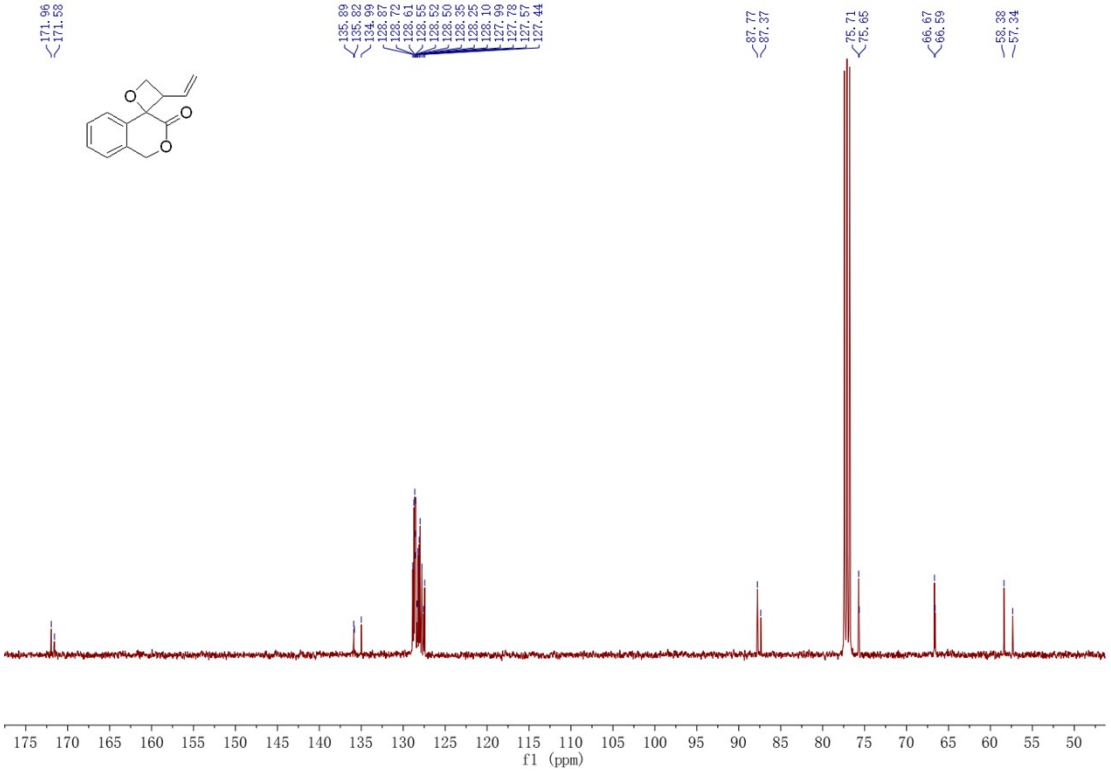
^{13}C NMR (101 MHz, CDCl3)



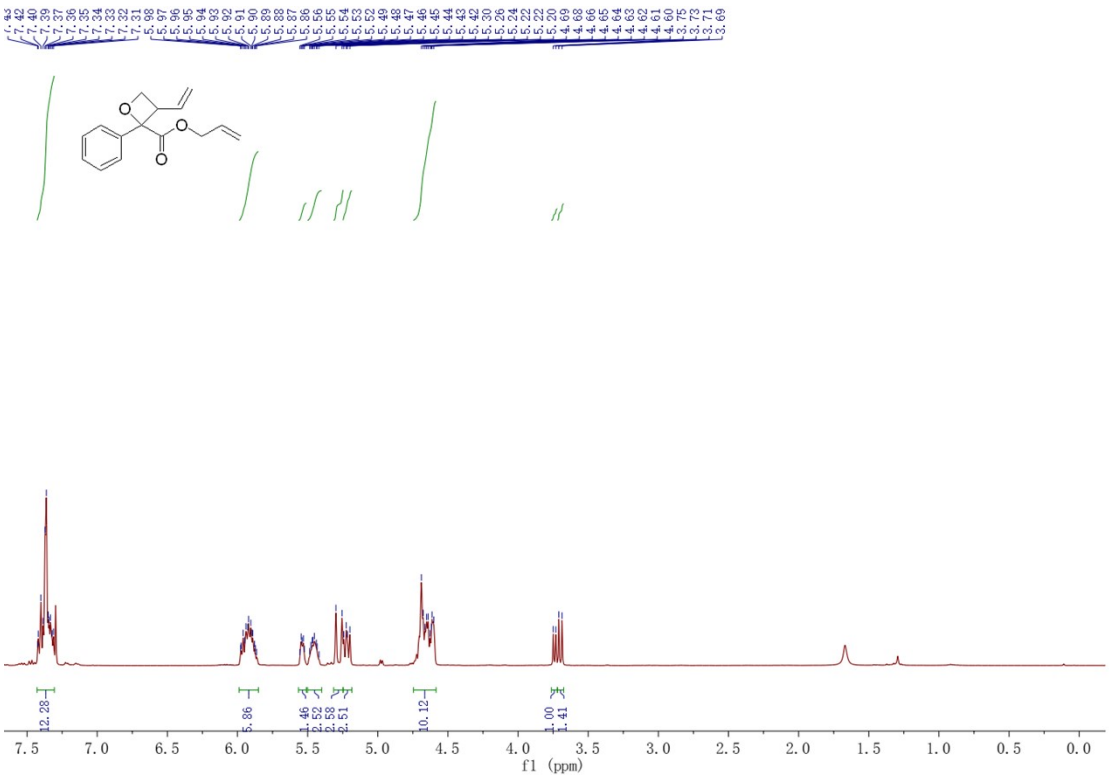
3y: ^{1}H NMR (400 MHz, $CDCl_3$)



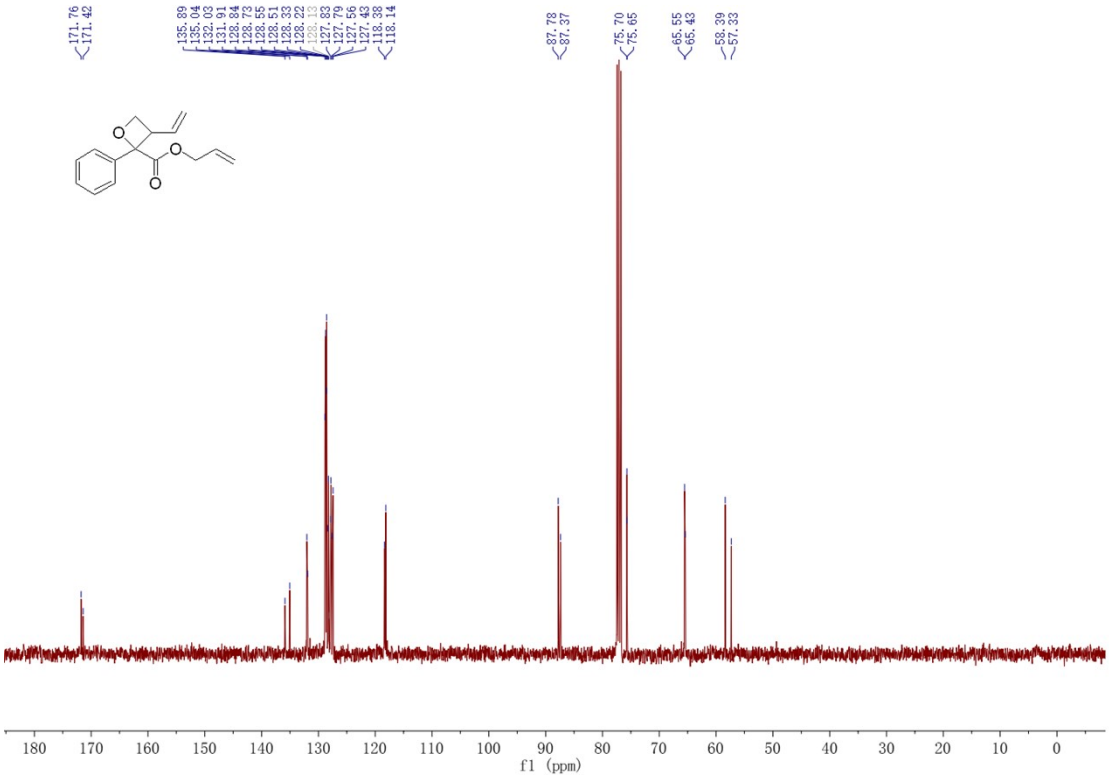
^{13}C NMR (101 MHz, CDCl3)



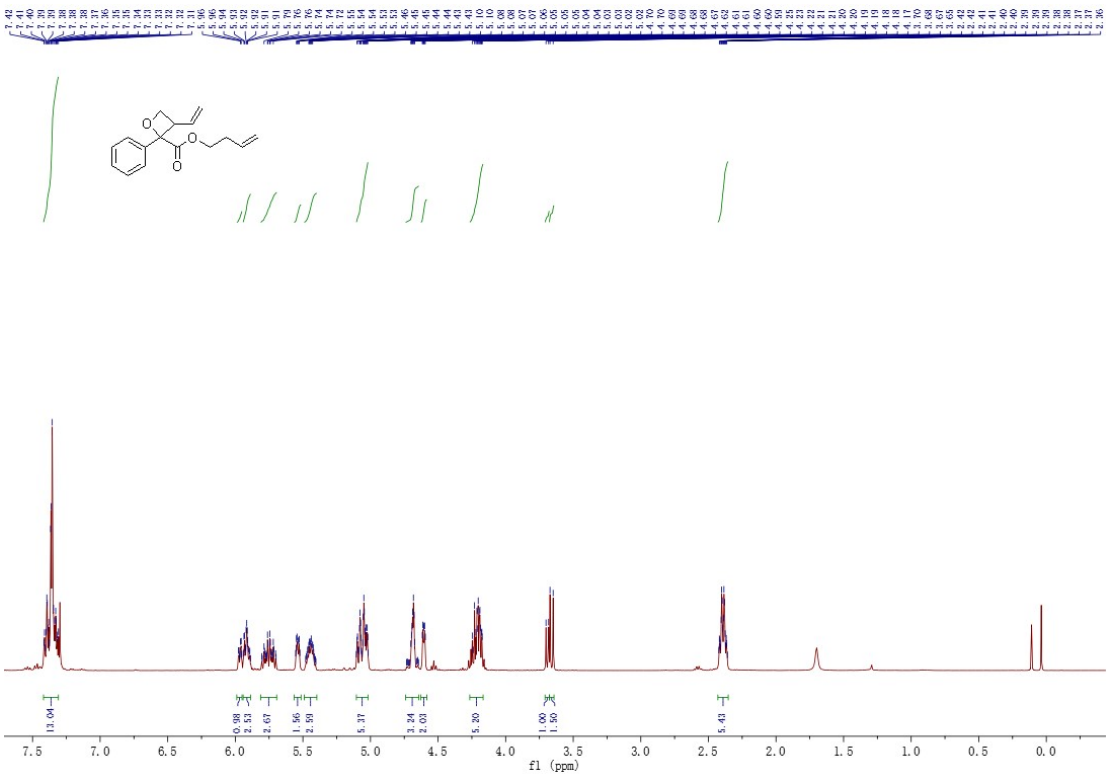
3z: ^{1}H NMR (400 MHz, $CDCl_3$)



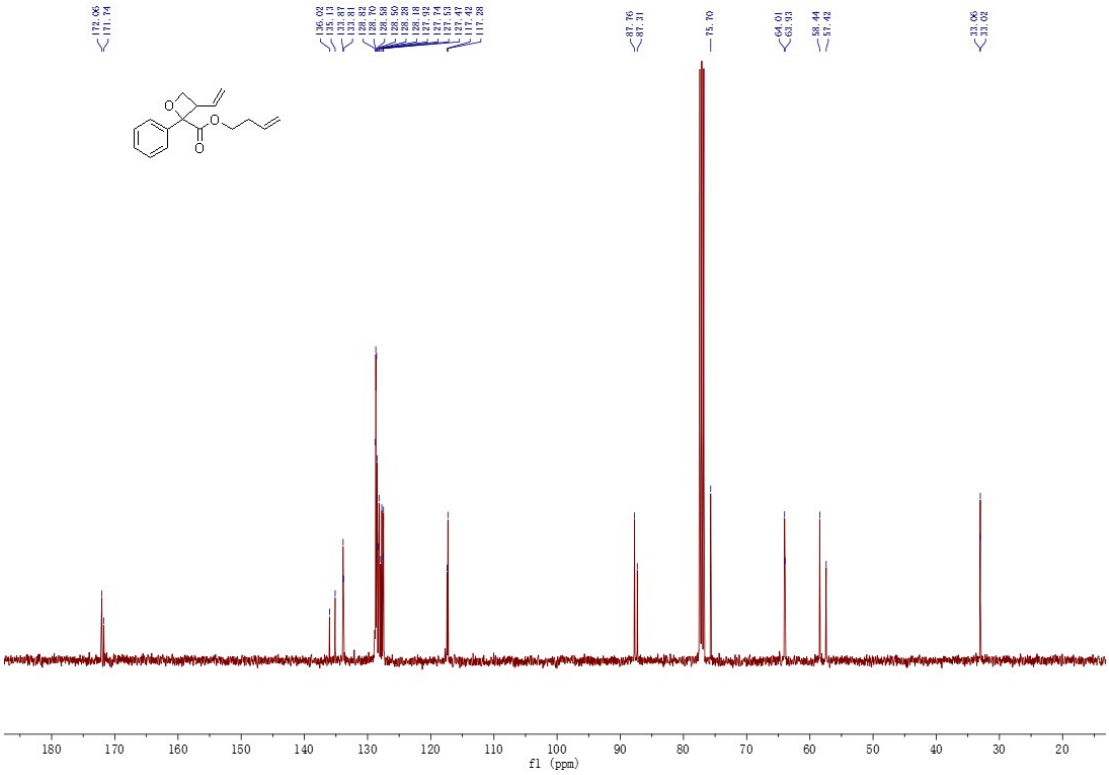
^{13}C NMR (101 MHz, CDCl3)



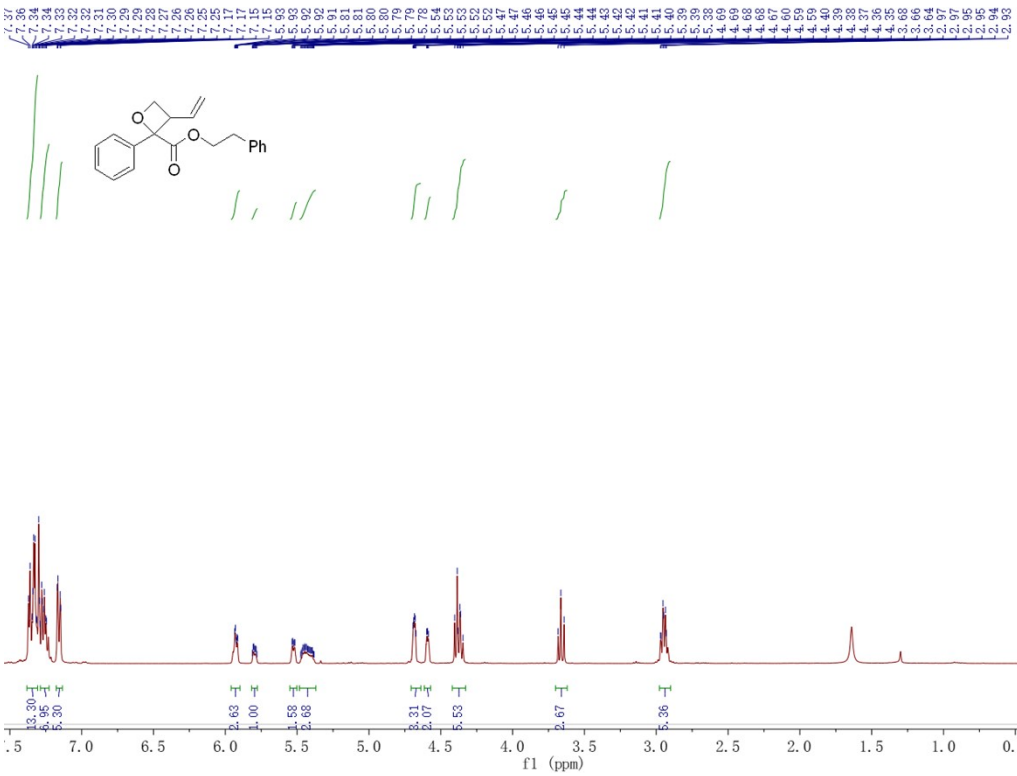
3aa: ^{1}H NMR (400 MHz, $CDCl_3$)



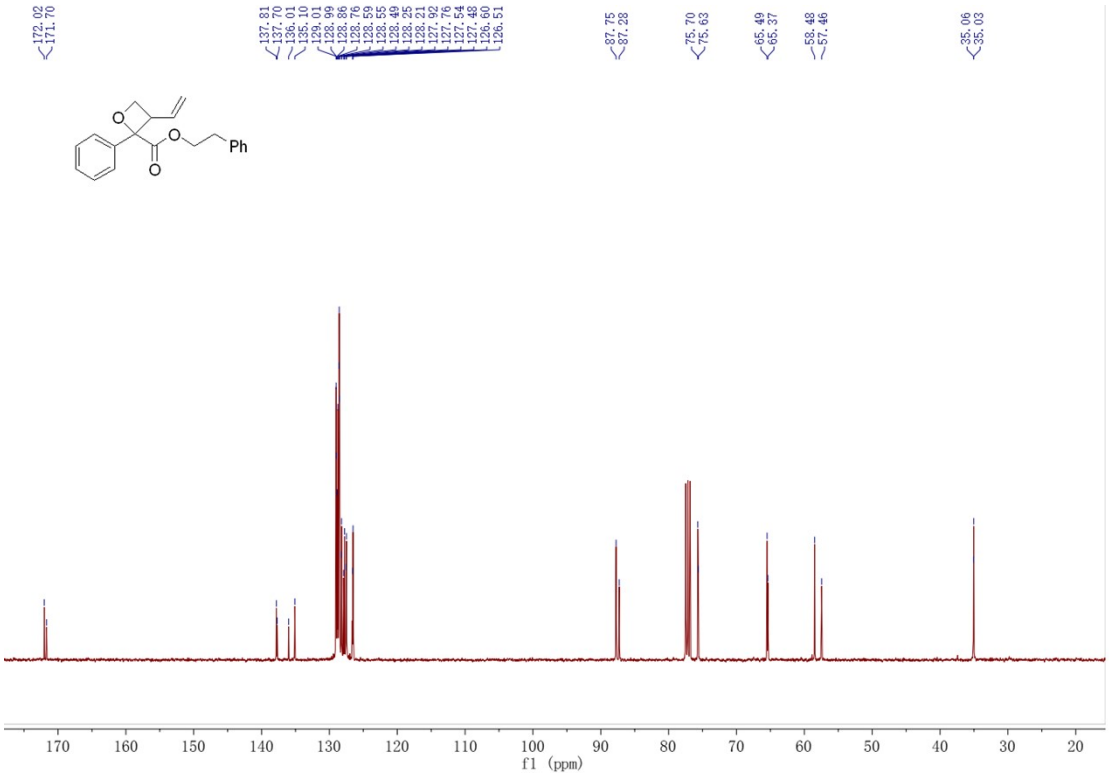
^{13}C NMR (101 MHz, CDCl3)



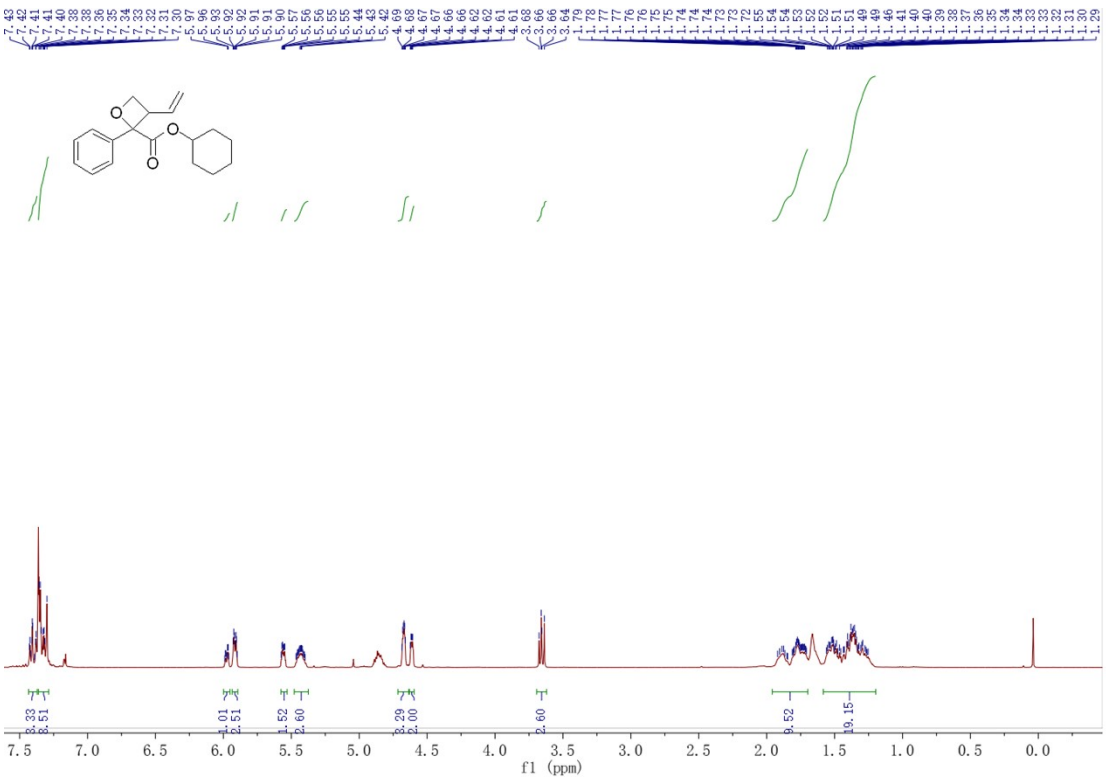
3bb: ^{1}H NMR (400 MHz, $CDCl_3$)



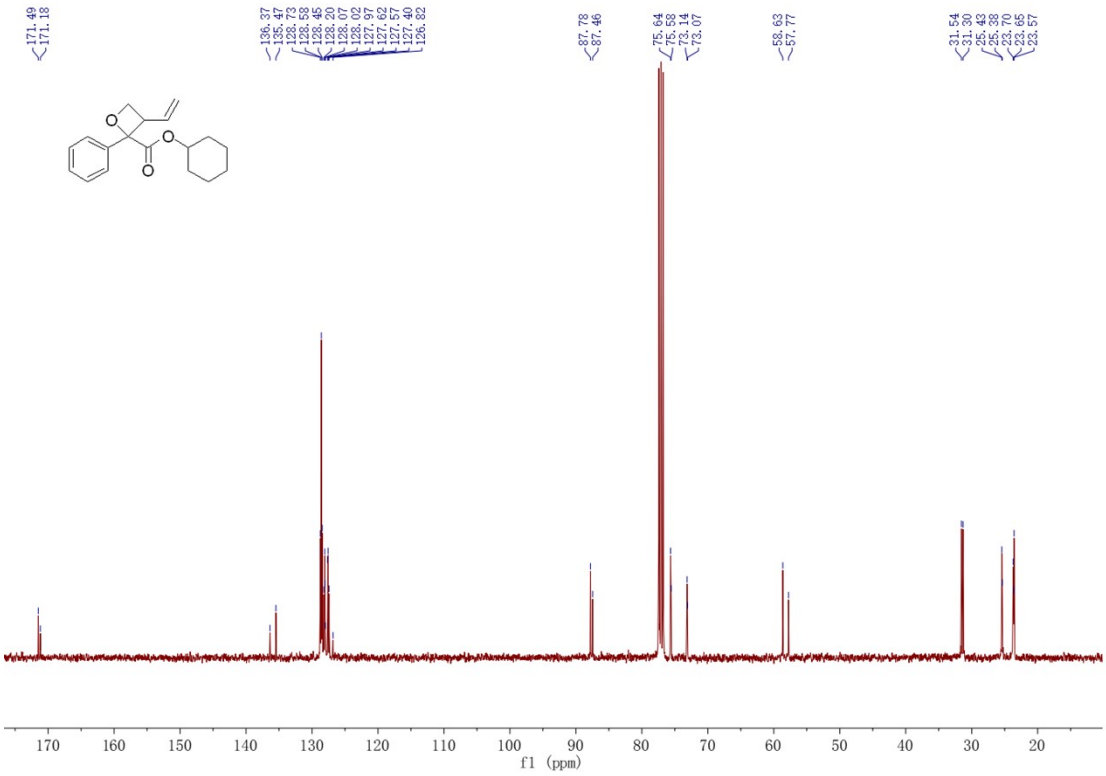
^{13}C NMR (101 MHz, CDCl3)



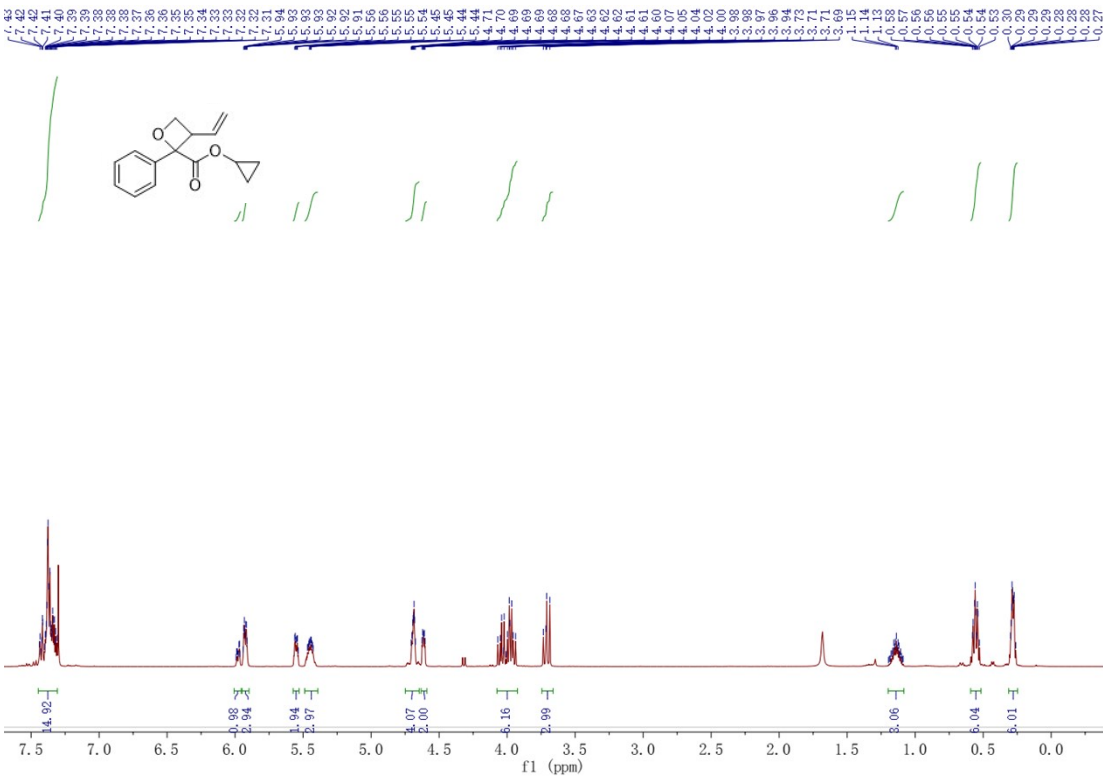
3cc: ^{1}H NMR (400 MHz, $CDCl_3$)



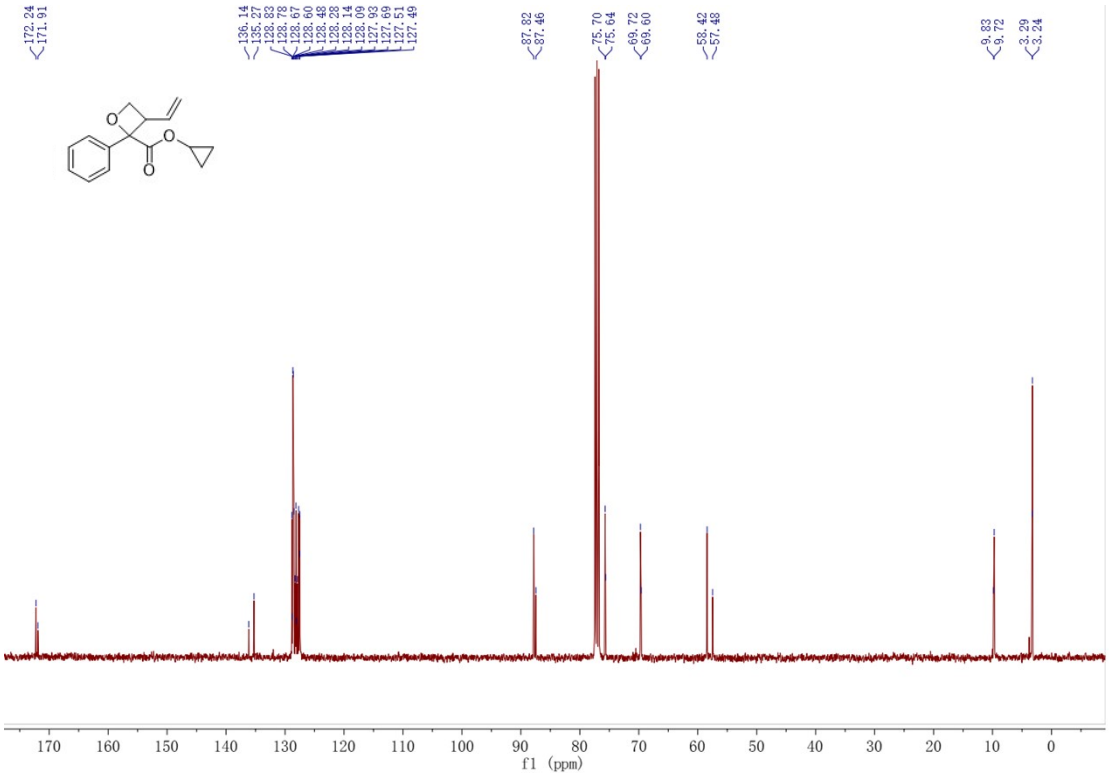
^{13}C NMR (101 MHz, CDCl3)



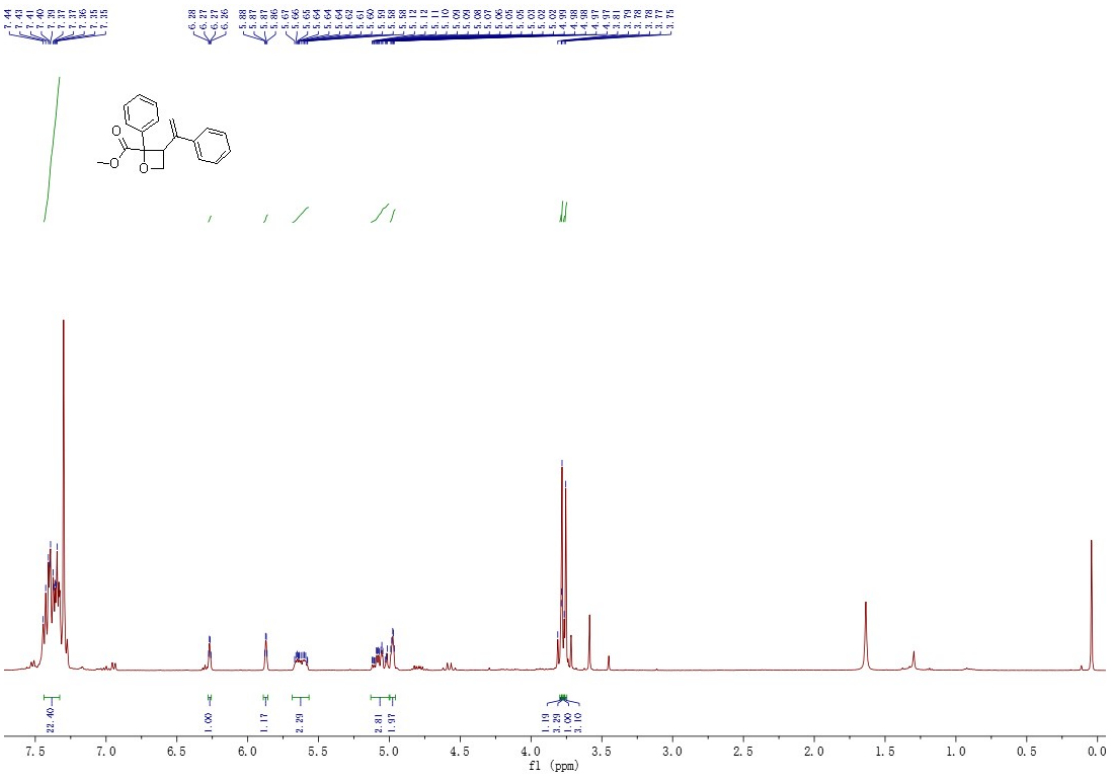
3dd: ^{1}H NMR (400 MHz, $CDCl_3$)



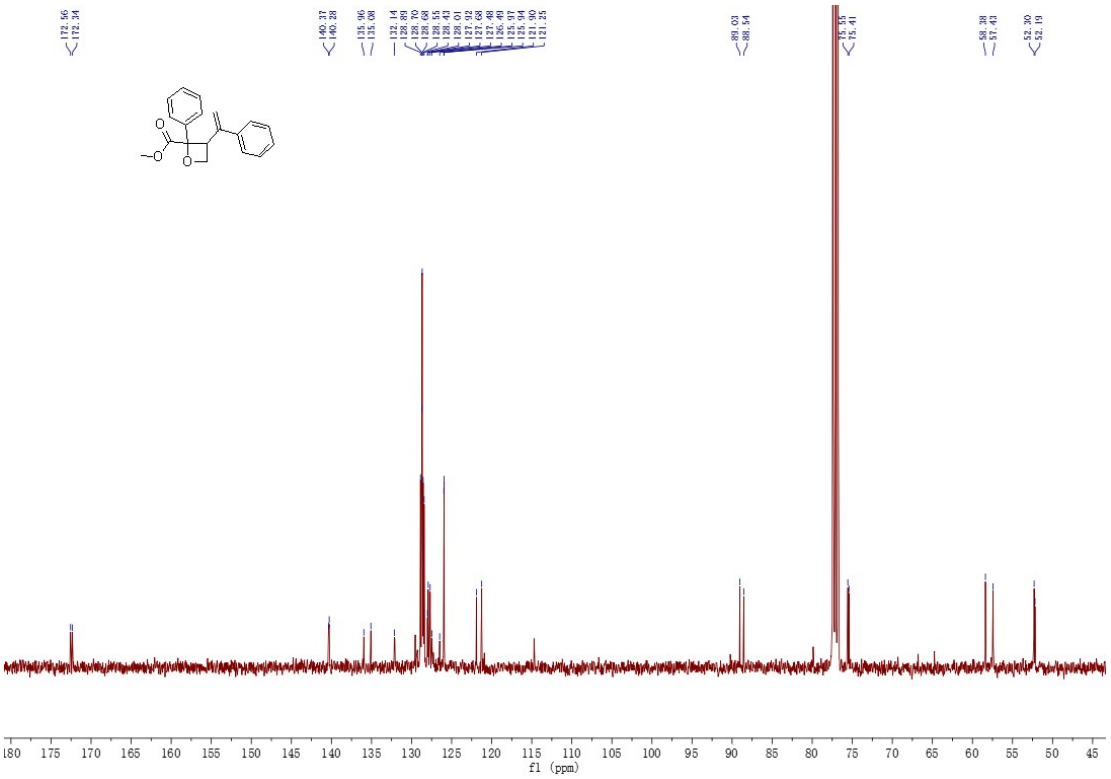
^{13}C NMR (101 MHz, CDCl3)



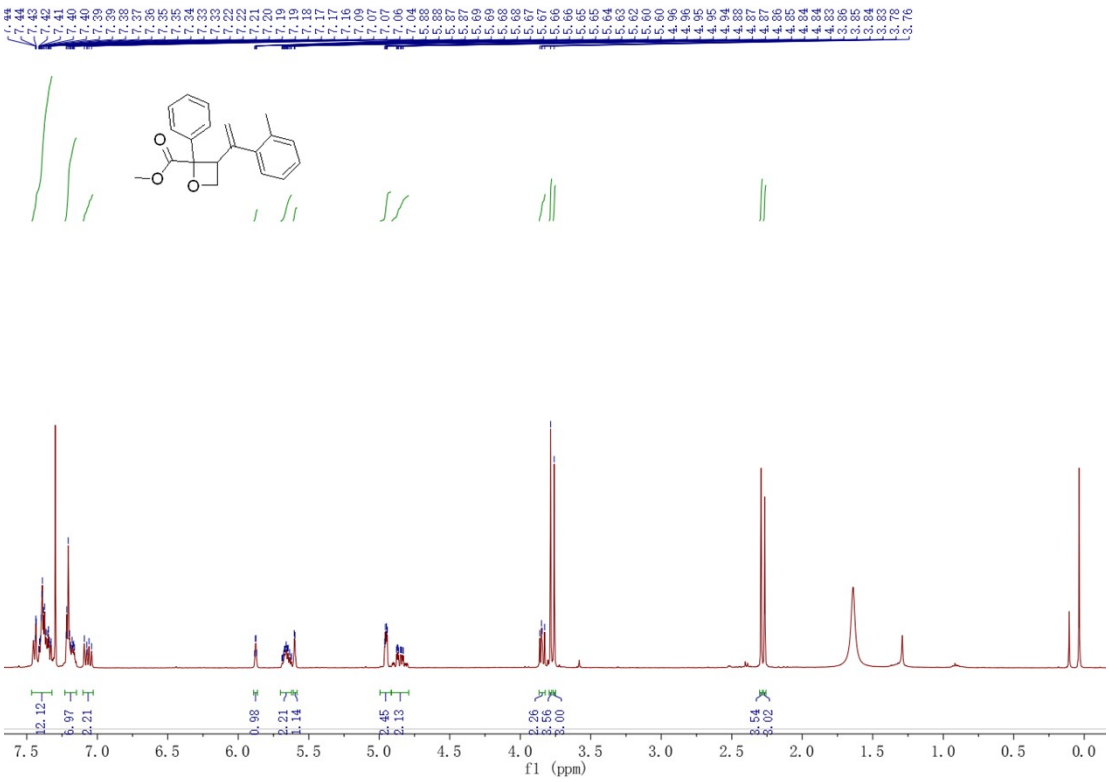
3ee: ^{1}H NMR (400 MHz, $CDCl_3$)



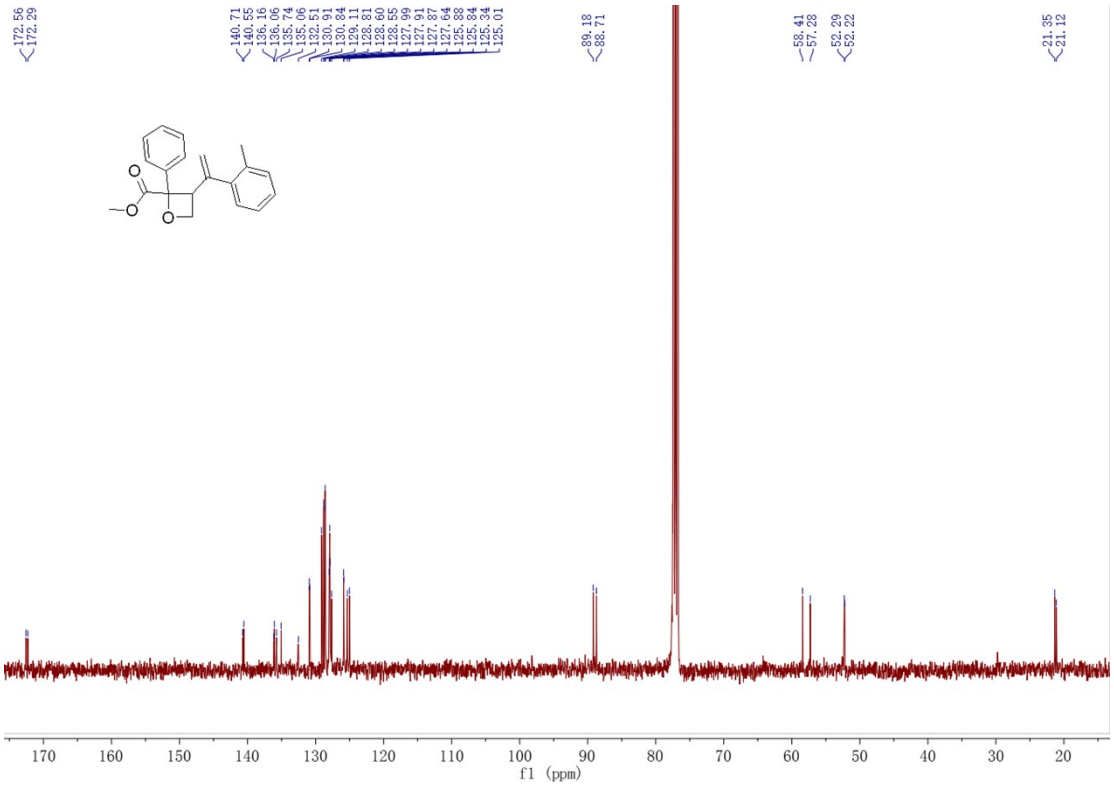
^{13}C NMR (101 MHz, CDCl3)



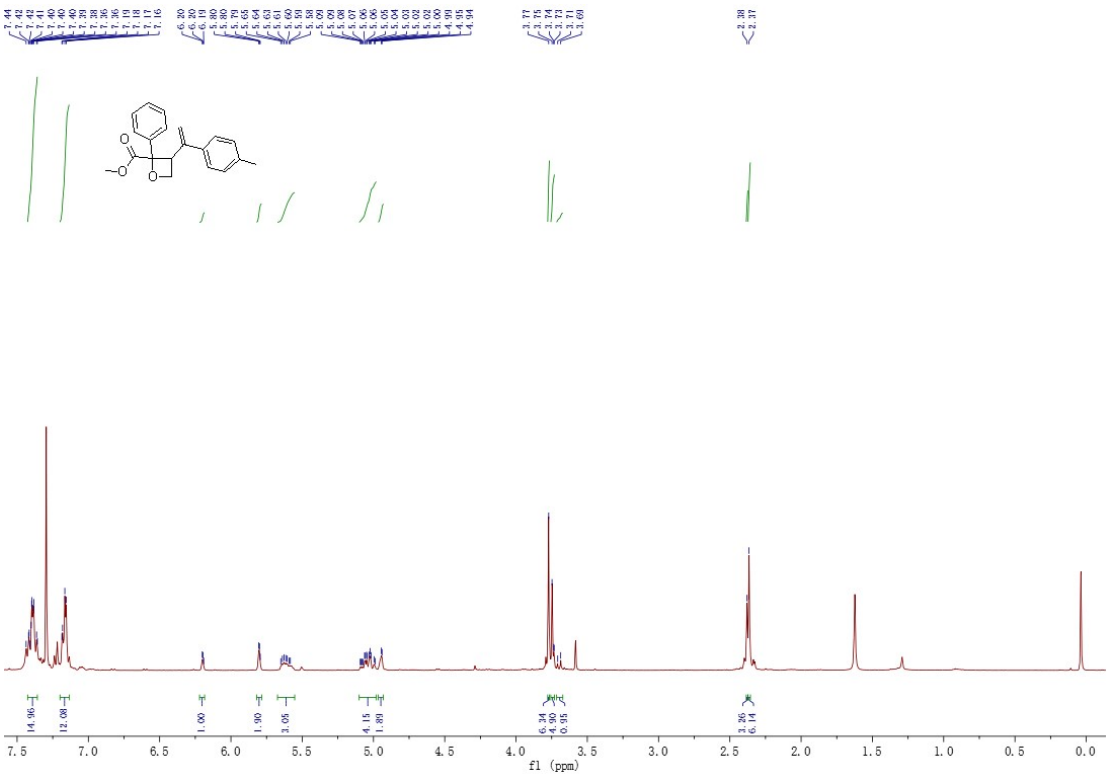
3ff: ^{1}H NMR (400 MHz, $CDCl_3$)



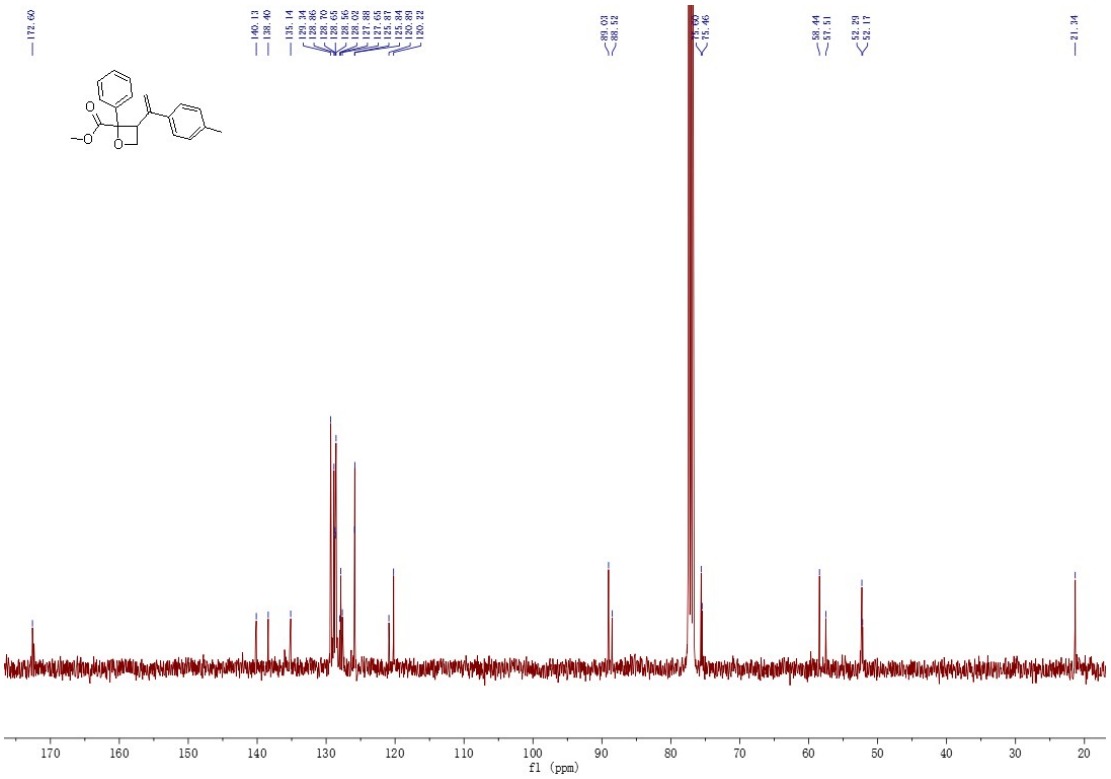
^{13}C NMR (101 MHz, CDCl3)



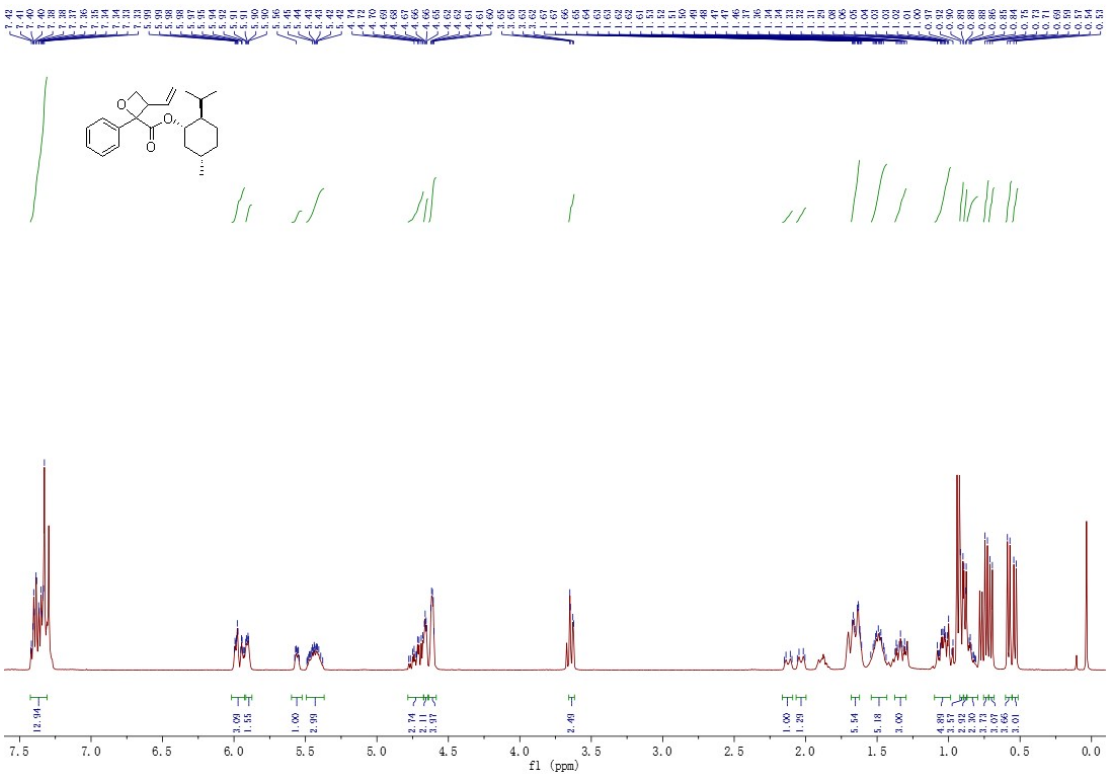
3gg: ^{1}H NMR (400 MHz, $CDCl_3$)



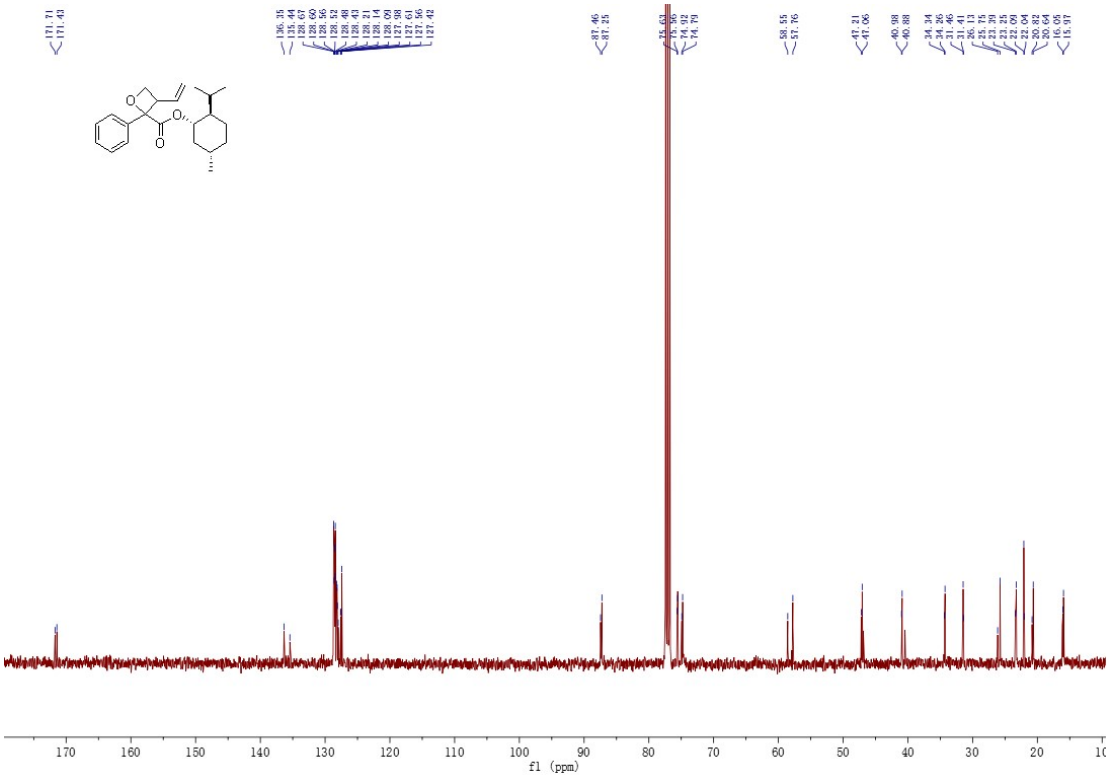
^{13}C NMR (101 MHz, CDCl3)



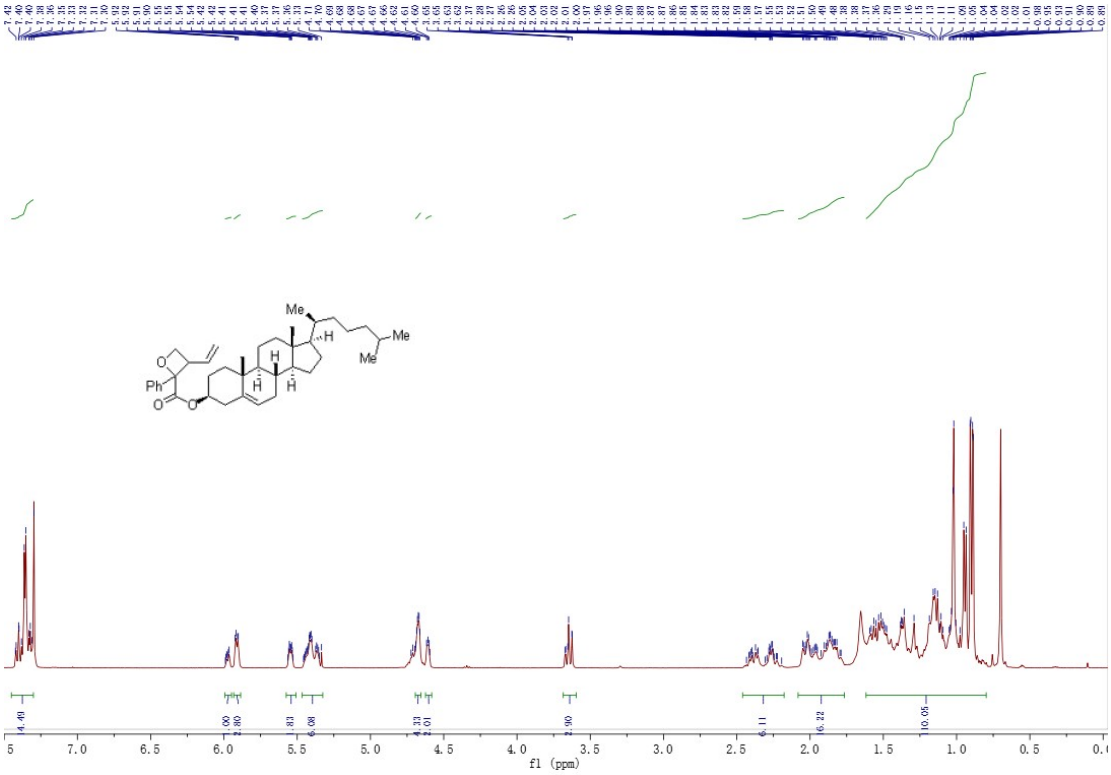
3hh: ^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, CDCl3)



3ii: ^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, CDCl3)