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Supporting Information

An Unexpected Photoinduced Cyclization to Synthesize Fully Substituted γ-Spirolactones via Intramolecular Hydrogen Abstraction with Allyl Acrylates

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Contents of Supporting Information

Experiment Section.

1. NMR spectra were recorded on Bruker DPX-400, DRX-600 and Bruker Ascend IIITM 600 MHz NMR spectrometer instruments and calibrated using residual solvent peaks as internal reference, such as $CDCl_3$ solutions. High resolution mass spectra were performed on API STAR Pulsar and Thermo Q Exactive. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel $60F_{254}$. Silica gel (Wakogel 300 - 400 mesh) was used for column chromatography. The photo-promoted reactions were run in Perfectlight PLMR Low Temperature Photosynthetic System (Instrument model : PLMR254-XXYY; Low Voltage Mercury Lamp Source, Main Wave Peak 254 nm, Electric Power 8-40W Optional, Low Voltage Mercury Lamp , AC 220 Regulator).

Figure **S1**. Photos of Photosynthetic reactor

2.Reagent: Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Unsaturated ketenes were purchased from Accela ChemBio Co., Ltd and Shanghai Titan Scientific Co., Ltd.. Cinnamic acids were purchased from Energy-Chemical Co., Ltd.. Other reagents were purchased from Thermo Fisher Scientific Co., Ltd. and Shanghai Aladdin Biochemical Technology Co., Ltd.. Solvents were purchased from Shanghai Titan Scientific Co., Ltd. and Thermo Fisher Scientific Co., Ltd..

All reactions were carried out under N_2 atmosphere.

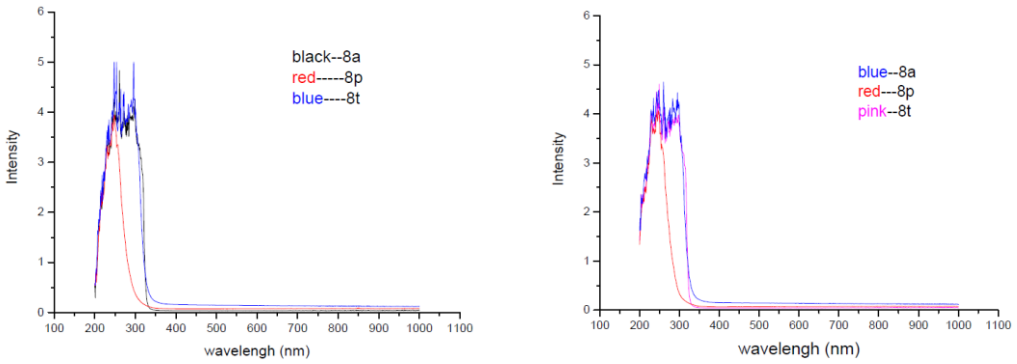
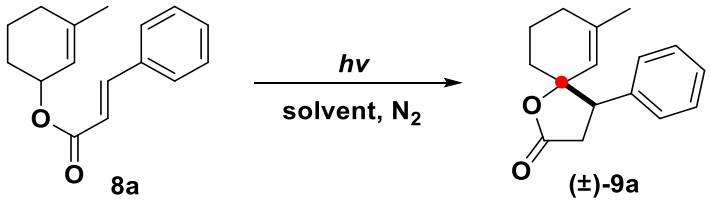


Figure S2. Original UV absorption spectra of **8a**, **8p** and **8t** in MeOH (left); Original UV absorption spectra of **8a**, **8p** and **8t** in MeCN (right)

Table S1. Screening for the optimal reaction conditions with **8a** [a].



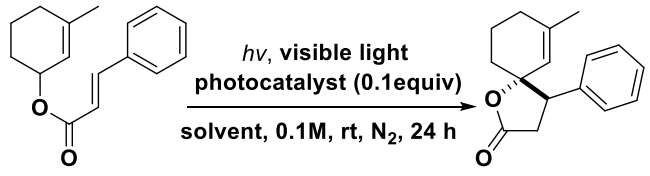
entry	solvent	λ (nm)	additive (equiv.)	temp. (°C)	time (h)	conv. (%)	yield (%)[b]
1	MeCN	254	-	r.t.	31	100	36
2	MeOH	254	-	r.t.	34	100	46
3	EtOH	254	-	r.t.	35	100	30
4	^{n}PrOH	254	-	r.t.	38	100	20
5[c]	TFE	254	-	r.t.	12	100	8
6[d]	HFIP	254	-	r.t.	4	100	trace
7	CH_2Cl_2	254	-	r.t.	6	100	10
8	DCE	254	-	r.t.	10	100	trace
9	toluene	254	-	r.t.	16	100	9
10	$PhCF_3$	254	-	r.t.	10	100	10
11	PhF	254	-	r.t.	12	100	8
12	PhCl	254	-	r.t.	12	100	6
13	THF	254	-	r.t.	6	100	trace
14	2-MeTHF	254	-	r.t.	9	100	trace
15[e]	CPME	254	-	r.t.	8.5	100	trace
16	1,4-dioxane	254	-	r.t.	12	100	6
17[f]	DME	254	-	r.t.	3	100	0
18	butyl ether	254	-	r.t.	14	100	8
19	Acetone	254	-	r.t.	6	100	trace

20	ethyl acetate	254	-	r.t.	4	100	0
21	DMF	254	-	r.t.	12	100	0
22	DMSO	254	-	r.t.	12	100	0
23	MeOH	185	-	r.t.	26	100	36
24	MeOH	310	-	r.t.	34	100	36
25	MeOH	365	-	r.t.	35	100	38
26[g]	MeOH	blue LEDs	-	r.t.	24	trace	0
27[h]	MeOH	purple LEDs	-	r.t.	24	trace	trace
28	MeOH	254	PhSSPh	r.t.	24	100	4
29	MeOH	254	PhSeSePh	r.t.	12	100	trace
30[i]	MeOH	254	TBADT	r.t.	12	100	trace
31	MeOH	sunlight	TBADT	r.t.	12	trace	trace
32	MeOH	254	AIBN	r.t.	12	100	10
33	MeOH	254	DTBP	r.t.	12	100	5
34	MeOH	254	TBHP	r.t.	12	100	trace
35[j]	MeOH	254	DLP	r.t.	12	100	9
37	MeOH	254	TBPB	r.t.	12	100	10
38[k]	MeOH	254	TEMPO	r.t.	12	100	26
39	MeOH	254	-	0	48	100	33
40[l]	MeOH	254	-	r.t.	34	100	40
41[m]	MeOH	254	-	r.t.	34	100	43

[a] *typical reaction conditions*: **8a** (0.1 mmol), *hv* (254 nm), solvent (10 mL), N_2, rt;

[b] isolated yield;[c]TFE: 2,2,2-trifluoroethanol; [d]HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol; [e]CPME: cyclopentyl methyl ether; [f]DME: 1,2-dimethoxyethane; [g](λ= 455-460 nm, 60W); [h](λ= 405-410 nm, 60W); [i]TBADT tetrabutylammonium decatungstate; [j]DLP: dilauroyl peroxide; [k]TEMPO: 2,2,6,6-tetramethylpiperidinooxy [l] :the reaction was run at 0.1M; [m] the reaction was run at 0.05M.

Table S2. Screening for the optimal reaction conditions of **8a** in the presence of organic photosensitizer [a]

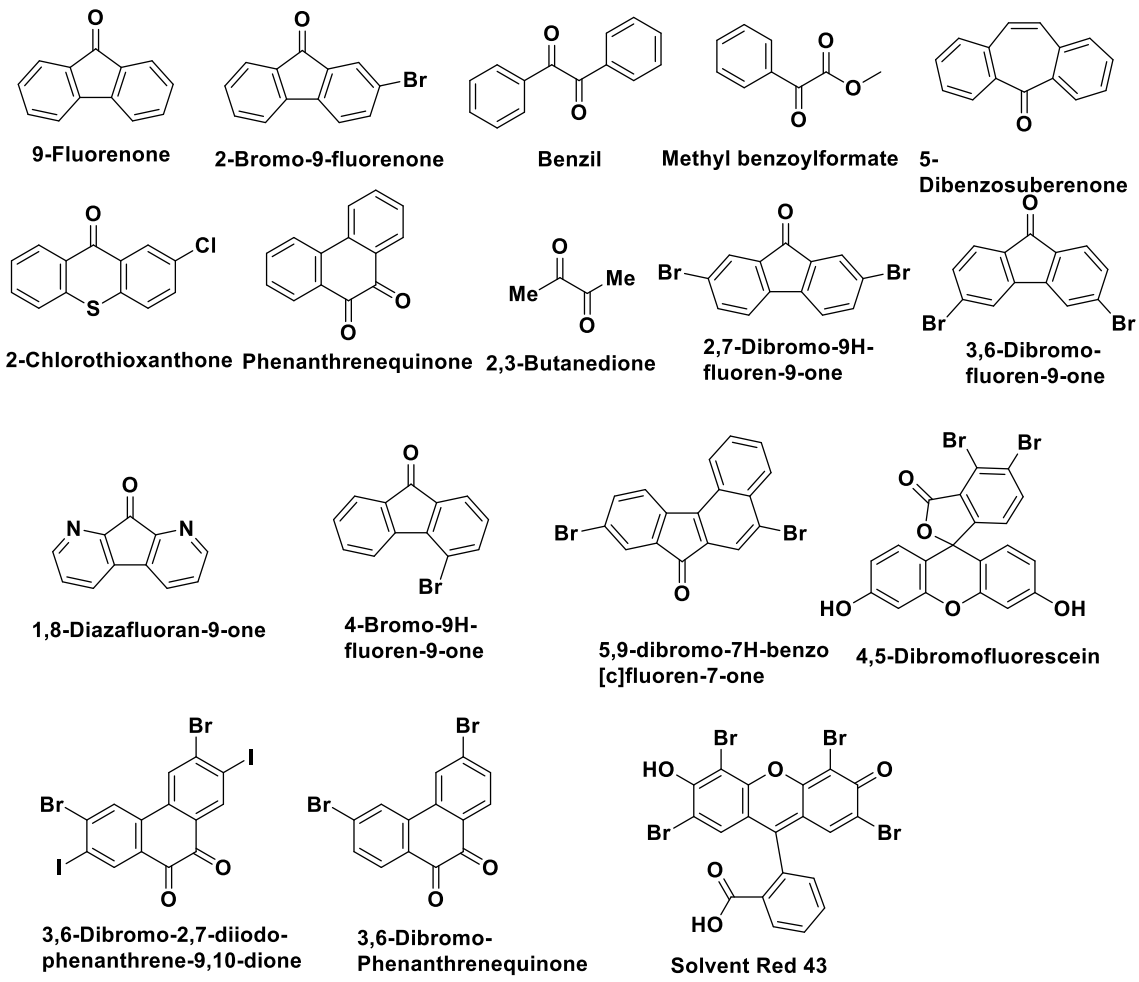


8a **9a**

entry	Solvent	Photocatalyst	nm	conversion	yield[b]
1	CH_3OH	9-Fluorenone	400	trace	0
2	CH_3CN	9-Fluorenone	400	trace	0
3	CH_3OH	2-Bromo-9-fluorenone	400	30	0
4	CH_3CN	2-Bromo-9-fluorenone	400	20	0
5	CH_3OH	Benzil	400-435	trace	0
6	CH_3CN	Benzil	400-435	trace	0
7	CH_3OH	Methyl benzoylformate	400	<5	0
8	CH_3CN	Methyl benzoylformate	400	<5	0

9	CH_3OH	5-Dibenzosuberenone	400	trace	0
10	CH_3CN	5-Dibenzosuberenone	400	trace	0
11	CH_3OH	2-Chlorothioxanthone	400	50	0
12	CH_3CN	2-Chlorothioxanthone	400	70	0
13	CH_3OH	Phenanthrenequinone	400	<10	0
14	CH_3CN	Phenanthrenequinone	400	<10	0
15	CH_3OH	Benzil	400	40	0
16	CH_3CN	Benzil	400	<30	0
17	CH_3OH	2,3-Butanedione	400	<20	0
18	CH_3CN	2,3-Butanedione	400	<10	0
19	CH_3OH	2,7-Dibromo-9H-fluoren-9-one	400	<30	0
20	CH_3CN	2,7-Dibromo-9H-fluoren-9-one	400	<30	0
21	CH_3OH	3,6-Dibromo-fluoren-9-one	400	<20	0
22	CH_3CN	3,6-Dibromo-fluoren-9-one	400	<20	0
23	CH_3OH	1,8-Diazafluoran-9-one	400	trace	0
24	CH_3CN	1,8-Diazafluoran-9-one	400	trace	0
25	CH_3OH	Solvent Red 43	400	<10	0
26	CH_3CN	Solvent Red 43	400	<10	0
27	CH_3OH	4-Bromo-9H-fluoren-9-one	400	90	0
28	CH_3CN	4-Bromo-9H-fluoren-9-one	400	<20	0
29	CH_3OH	5,9-dibromo-7H-benzo [c]fluoren-7-one	400	<5	0
30	CH_3CN	5,9-dibromo-7H-benzo [c]fluoren-7-one	400	90	0
31	CH_3OH	4,5-Dibromofluorescein	400	80	0
32	CH_3CN	4,5-Dibromofluorescein	400	80	0
33	CH_3OH	3,6-Dibromo-2,7-diiodo-phenanthrene-9,10-dione	400-435	70	0
34	CH_3CN	3,6-Dibromo-2,7-diiodo-phenanthrene-9,10-dione	400-435	80	0
35	CH_3OH	3,6-Dibromo-Phenanthrenequinone	400-435	80	0
36	CH_3CN	3,6-Dibromo-phenanthrenequinone	400-435	80	0
37	CH_3OH	3,6-Dibromo-2,7-diiodo-phenanthrene-9,10-dione	400	>60	0
38	CH_3CN	3,6-Dibromo-2,7-diiodo-phenanthrene-9,10-dione	400	>90	0
39	CH_3OH	3,6-Dibromo-Phenanthrenequinone	400	>80	0
40	CH_3CN	3,6-Dibromo-Phenanthrenequinone	400	trace	0

[a] *typical reaction conditions*: **8a** (0.1 mmol), Photocatalyst (0.1 equiv), *hv* (400 nm), solvent (10 mL), N_2, rt, 24 h; [b] NMR yield



Scheme S1. List of organic photocatalyst

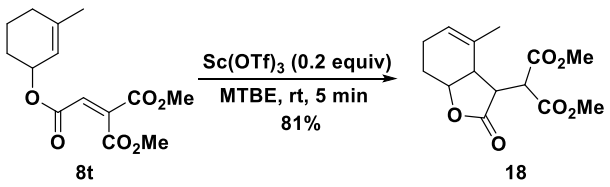


Figure S3. [Ref. 16] A Lewis acid-catalyzed intramolecular Michael addition reaction with 8t was carried out as following, which was consistent with the result of Snider, see: Snider, B. B.; Roush, D. M. *J. Org. Chem*, **1979**, *44*, 4229.

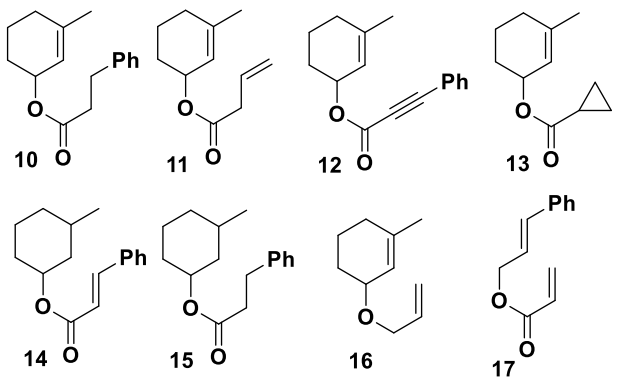


Figure S4. Structurally similar unreactive substrates for control experiments.

Deuterium Experiments

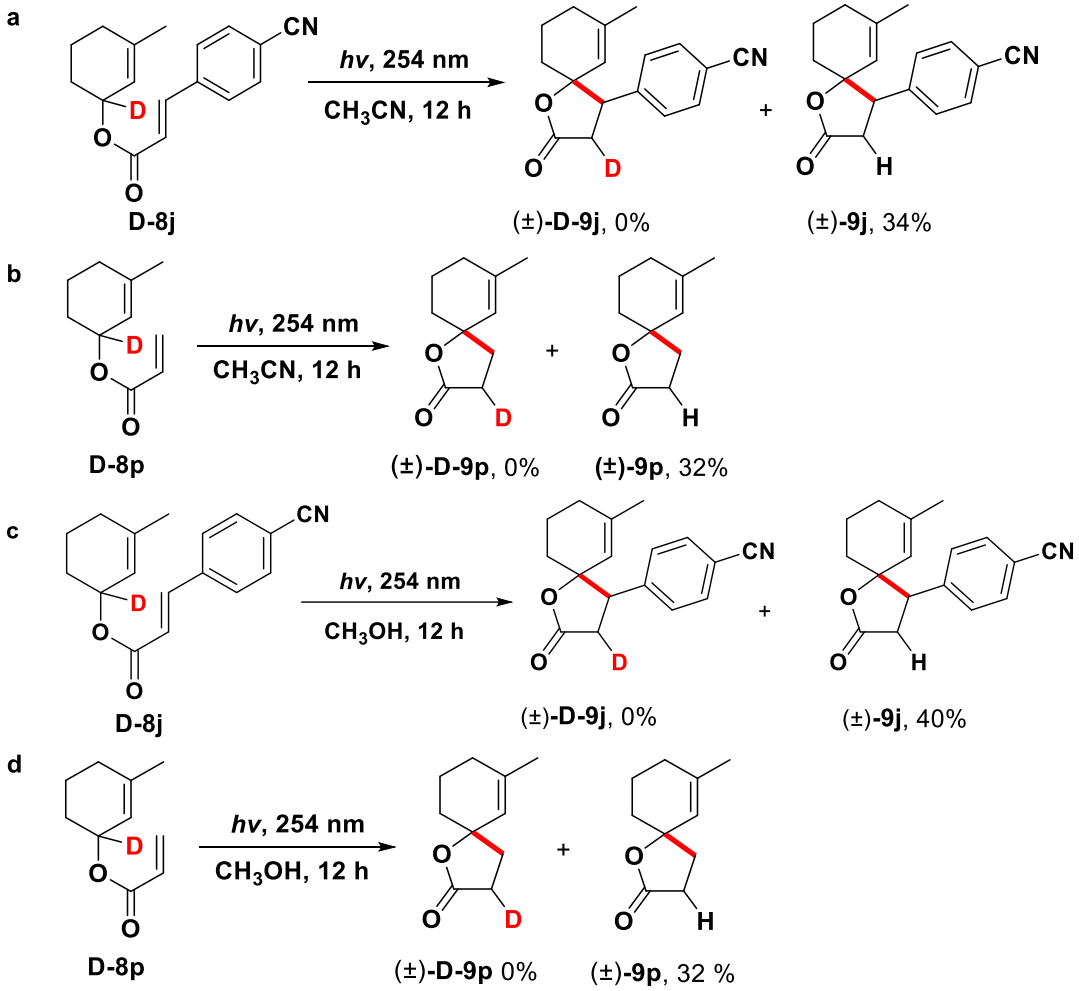


Figure S5. Deuterium experiments **D-8j/D-8p** in CH_3OH/ CH_3CN.

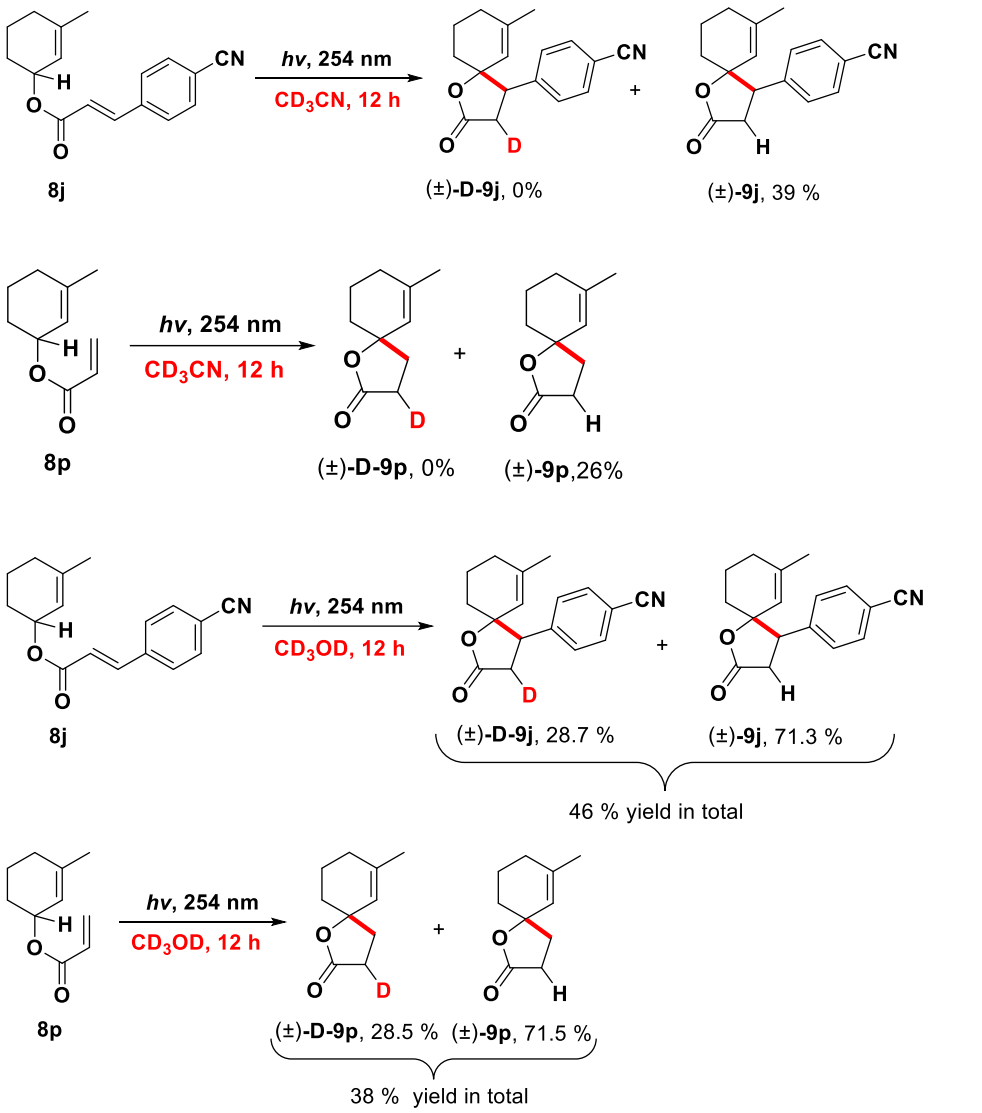
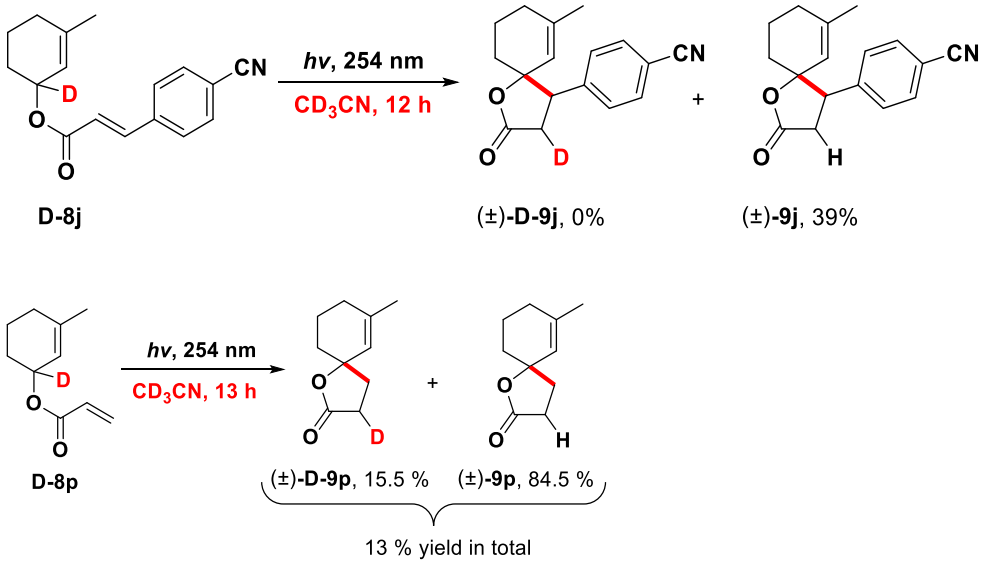


Figure S6. Deuterium experiments **8j/8p** in CD_3OD/ CD_3CN.



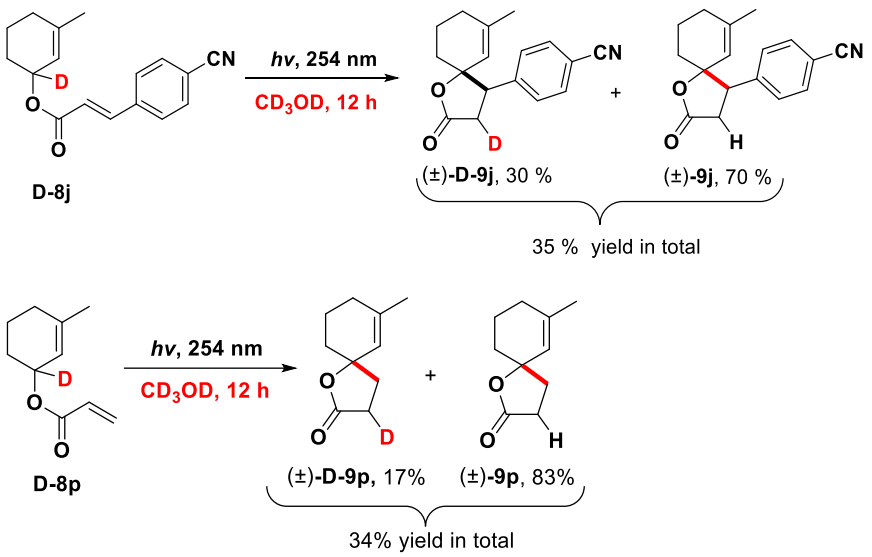


Figure S7. Deuterium experiments **D-8j/D-8p** in CD_3OD/ CD_3CN.

Computational Studies

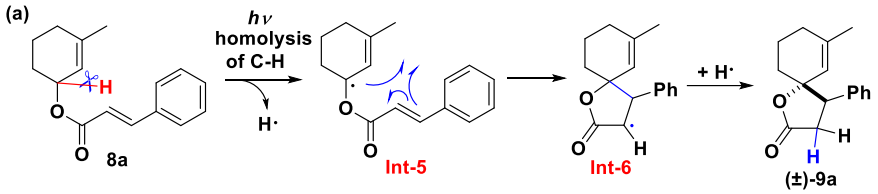


Figure S8. Mechanistic investigations: a radical is produced via homolytic bond cleavage (***sequence a***)

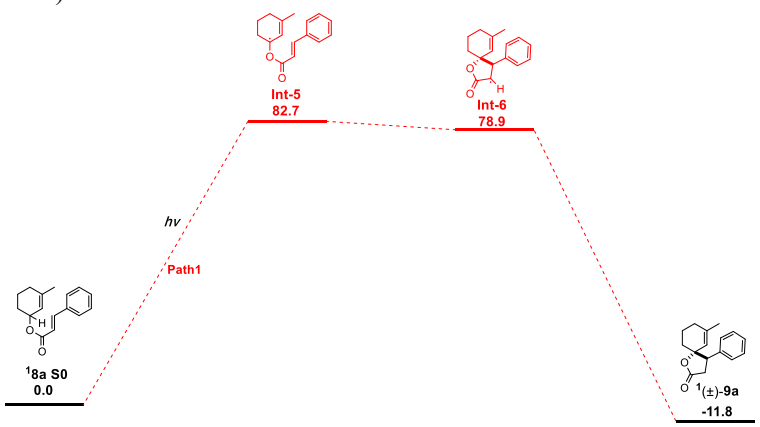


Figure S9. DFT (M06-2X/6-311G(d)) computational studies of ***sequences a*** (***Path 1***).

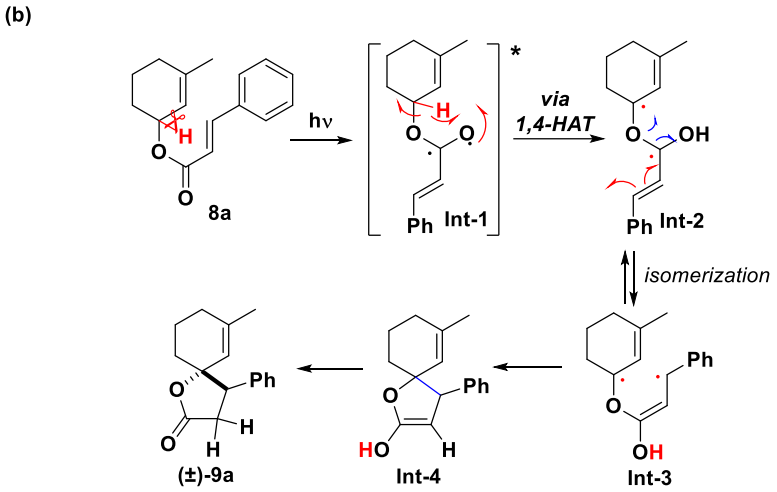


Figure S10. Mechanistic investigations: a radical is produced via intramolecular hydrogen abstraction (***sequence b***)

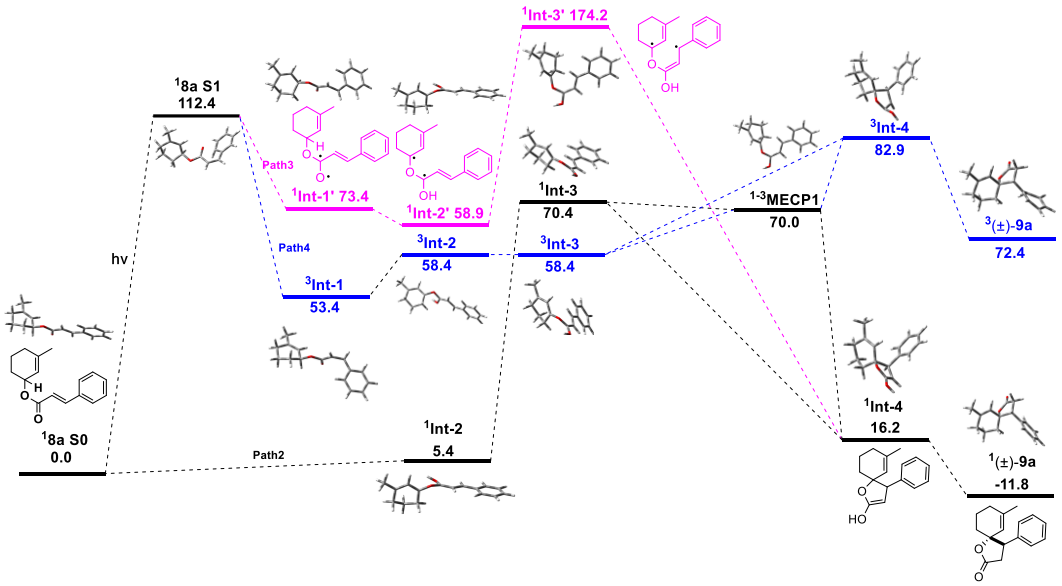


Figure S11. DFT(M06-2X/6-311G(d)) computational studies of ***sequences b*** (***Path 2***, ***Path 3*** and ***Path 4***).

Computational Methods.

All the DFT calculations were performed on the GAUSSIAN 16 C01 series of programs.

Density functional theory M06-2X with a standard /6-311G (d) basis set was used for primary geometry optimizations.

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

^{1}8a S0

Final structure in terms of initial Cartesian coordinates:

C -4.779588 -1.423013 -0.475574
C -3.287329 -1.698570 -0.314136
C -2.496995 -0.437850 -0.617569
C -3.067526 0.770001 0.074800
C -4.290504 0.810763 0.602270
C -5.233797 -0.366843 0.531169
C -4.818539 2.028609 1.304919
O -1.148680 -0.685787 -0.160151
C -0.186906 0.109114 -0.654989
C 1.139337 -0.281146 -0.123810
O -0.392012 1.010144 -1.427478
C 2.223886 0.398744 -0.502827
C 3.610903 0.156600 -0.092270
C 4.611134 1.009340 -0.568930
C 5.940484 0.822448 -0.210757
C 6.290357 -0.225550 0.631678
C 5.303820 -1.084184 1.113156
C 3.978359 -0.896044 0.755497
H -5.353705 -2.343616 -0.348624
H -4.975470 -1.063385 -1.491819
H -3.072410 -1.993375 0.718305
H -2.952075 -2.509635 -0.964360
H -2.443177 -0.255664 -1.695794
H -2.424508 1.644687 0.112167
H -5.317311 -0.810716 1.532160
H -6.238550 -0.007731 0.282448
H -4.067837 2.816593 1.372212
H -5.693785 2.429012 0.783751
H -5.143398 1.775425 2.319354
H 1.160751 -1.120281 0.560772
H 2.062216 1.223621 -1.194196
H 4.337932 1.828201 -1.226754
H 6.701299 1.494888 -0.590371
H 7.326399 -0.376740 0.912619
H 5.572878 -1.905129 1.768073
H 3.223719 -1.575518 1.135318

^{1}8a S1

Final structure in terms of initial Cartesian coordinates:
C -4.106030 -0.217101 -1.405089
C -2.986991 -1.208980 -1.093824
C -1.771595 -0.456482 -0.578001

C -2.142325 0.531430 0.498305
C -3.387654 0.961428 0.715000
C -4.552556 0.499975 -0.130289
C -3.719474 1.927934 1.817366
O -0.866957 -1.449723 -0.064681
C 0.365474 -1.021672 0.301390
C 1.197635 -1.925070 0.995368
O 0.811003 0.117131 -0.134710
C 2.548325 -1.653057 1.122229
C 3.143911 -0.573195 0.379125
C 4.251432 0.150587 0.811157
C 4.645189 1.316661 0.155908
C 3.943830 1.779587 -0.978434
C 2.897394 1.048317 -1.491720
C 2.445424 -0.141985 -0.837621
H -4.953675 -0.728212 -1.871881
H -3.741476 0.523351 -2.128897
H -3.312322 -1.907030 -0.312794
H -2.712222 -1.799567 -1.973115
H -1.266078 0.062099 -1.402262
H -1.322247 0.899411 1.112664
H -5.183158 -0.167019 0.476312
H -5.184604 1.362965 -0.377774
H -2.838040 2.181532 2.411310
H -4.140686 2.854834 1.409661
H -4.477438 1.503827 2.487576
H 0.746884 -2.816236 1.417463
H 3.164800 -2.234039 1.802165
H 4.774747 -0.171048 1.708049
H 5.492564 1.882213 0.530298
H 4.265288 2.691551 -1.471715
H 2.407340 1.350222 -2.412049
H 2.096015 -0.938388 -1.495089

^{1}Int-1'

Final structure in terms of initial Cartesian coordinates:
C -4.319682 -1.273634 -1.104079
C -2.881365 -1.322806 -0.577654
C -2.458810 0.047270 -0.150716
C -3.362254 1.027461 0.215134
C -4.723170 0.789610 0.272952
C -5.246794 -0.567084 -0.111041

C -5.699594 1.815702 0.747615
O -1.130612 0.427591 -0.246264
C -0.164879 -0.400113 0.227179
C 1.169546 0.159272 -0.070086
O -0.389484 -1.428054 0.804810
C 2.260326 -0.504032 0.323435
C 3.657660 -0.108712 0.122898
C 4.668354 -0.962103 0.575943
C 6.008149 -0.635463 0.407247
C 6.357729 0.555095 -0.217949
C 5.360688 1.416282 -0.672292
C 4.024835 1.088842 -0.504081
H -4.677518 -2.285881 -1.305072
H -4.335937 -0.726310 -2.051497
H -2.801536 -2.020622 0.262657
H -2.198549 -1.695793 -1.346854
H -2.967173 2.003316 0.483272
H -5.357351 -1.184394 0.793060
H -6.252466 -0.471340 -0.534134
H -5.207448 2.750615 1.020054
H -6.449112 2.035414 -0.021687
H -6.253205 1.457823 1.624322
H 1.195827 1.100861 -0.604289
H 2.095252 -1.443510 0.847500
H 4.395359 -1.891379 1.065638
H 6.777396 -1.310206 0.765028
H 7.401835 0.814082 -0.351655
H 5.629085 2.346542 -1.159863
H 3.261864 1.770953 -0.861882

[1]Int-1"

Final structure in terms of initial Cartesian coordinates:
C -4.086315 -1.373554 -1.050264
C -2.784424 -1.438611 -0.255189
C -2.132263 -0.062854 -0.242236
C -3.112179 1.012938 0.130388
C -4.435115 0.868627 0.073145
C -5.077860 -0.420988 -0.382037
C -5.381301 1.966452 0.467772
O -1.073557 -0.002229 0.723555
C 0.123920 -0.521929 0.327348
C 1.132363 -0.357741 1.329322

O 0.287357 -1.039514 -0.764813
C 2.433243 -0.911157 1.111579
C 3.503923 -0.250045 0.458728
C 4.760387 -0.886933 0.322605
C 5.799179 -0.252014 -0.326851
C 5.606471 1.025490 -0.860480
C 4.372854 1.666260 -0.744356
C 3.326853 1.039739 -0.093323
H -4.525842 -2.368695 -1.152283
H -3.870222 -1.018862 -2.064256
H -2.990975 -1.724463 0.782210
H -2.086770 -2.163831 -0.676303
H -1.693868 0.138493 -1.226020
H -2.676492 1.951788 0.464164
H -5.537916 -0.905072 0.490090
H -5.905987 -0.190348 -1.061900
H -4.852265 2.842441 0.845304
H -5.995462 2.275467 -0.384188
H -6.071132 1.620190 1.244439
H 0.877972 0.128250 2.265873
H 2.652781 -1.934511 1.440208
H 4.894197 -1.881067 0.737019
H 6.760788 -0.741203 -0.428586
H 6.423098 1.520655 -1.374226
H 4.234331 2.652554 -1.171588
H 2.354946 1.510084 0.003211

^{3}Int-1

Final structure in terms of initial Cartesian coordinates:
C -4.164280 -1.367126 -0.983155
C -2.832830 -1.437739 -0.238967
C -2.158515 -0.074069 -0.288978
C -3.100431 1.033309 0.084804
C -4.426758 0.910916 0.087516
C -5.109464 -0.380307 -0.298888
C -5.335245 2.038995 0.483951
O -1.064584 -0.008442 0.649117
C 0.090100 -0.587628 0.260280
C 1.130334 -0.423691 1.273223
O 0.242042 -1.157440 -0.793805
C 2.464825 -0.977479 1.074508
C 3.523382 -0.276087 0.443465

C 4.800142 -0.872788 0.312126
C 5.839195 -0.199237 -0.300511
C 5.645193 1.088035 -0.804465
C 4.393431 1.692957 -0.688828
C 3.346449 1.027429 -0.078326
H -4.623183 -2.356682 -1.040719
H -3.983770 -1.042711 -2.014010
H -3.005183 -1.691874 0.812649
H -2.169497 -2.190191 -0.667686
H -1.737112 0.092020 -1.286482
H -2.634065 1.974998 0.363537
H -5.536101 -0.830688 0.607355
H -5.963764 -0.154932 -0.946891
H -4.775136 2.917407 0.806697
H -5.980575 2.329155 -0.351014
H -5.995113 1.731662 1.301599
H 0.863545 0.108732 2.181269
H 2.650958 -1.989765 1.425806
H 4.953398 -1.874251 0.701425
H 6.809449 -0.674753 -0.392305
H 6.461519 1.612825 -1.287097
H 4.237730 2.690377 -1.084812
H 2.374061 1.502784 0.001657

[1]Int-2

Final structure in terms of initial Cartesian coordinates:
C -3.523170 1.899941 -0.642580
C -2.265068 1.059751 -0.847631
C -2.108395 0.095116 0.319131
C -3.383321 -0.637121 0.621163
C -4.583874 -0.236938 0.205360
C -4.766194 1.011297 -0.626437
C -5.837827 -0.998929 0.525074
O -1.119015 -0.910327 0.015037
C 0.169301 -0.539635 0.143785
C 1.044596 -1.674573 -0.233393
O 0.505806 0.561026 0.496459
C 2.378053 -1.674737 -0.367095
C 3.399948 -0.644702 -0.112069
C 4.528191 -0.638037 -0.942228
C 5.542969 0.291282 -0.761693

C 5.461779 1.209312 0.279970
C 4.364640 1.187140 1.134772
C 3.338530 0.272099 0.942062
H -3.608592 2.657688 -1.424746
H -3.446979 2.436528 0.309608
H -2.353432 0.469235 -1.766101
H -1.373820 1.683566 -0.928800
H -1.754742 0.638451 1.202016
H -3.281142 -1.537884 1.221420
H -5.028447 0.709323 -1.649208
H -5.631733 1.569652 -0.252647
H -5.625634 -1.923312 1.063442
H -6.514221 -0.392056 1.135207
H -6.379741 -1.250821 -0.391953
H 0.502293 -2.574108 -0.499919
H 2.793993 -2.600437 -0.762359
H 4.600944 -1.364551 -1.745954
H 6.400217 0.292260 -1.425289
H 6.254750 1.933362 0.430511
H 4.304055 1.890359 1.957579
H 2.486945 0.269544 1.606076

[1]Int-2"

Final structure in terms of initial Cartesian coordinates:
C 3.788700 1.493810 1.031714
C 2.460366 0.734396 1.100807
C 2.409798 -0.283241 0.004243
C 3.551795 -0.850856 -0.536674
C 4.820223 -0.500167 -0.116769
C 4.981024 0.535234 0.963196
C 6.053397 -1.147895 -0.656948
O 1.194816 -0.825504 -0.367737
C 0.153530 0.024306 -0.565796
C -1.115464 -0.328609 -0.214775
O 0.440362 1.206864 -1.147919
C -2.240270 0.451733 -0.502004
C -3.596382 0.128179 -0.155192
C -4.634432 1.002833 -0.537839
C -5.957107 0.732898 -0.229636
C -6.294208 -0.421428 0.474192
C -5.283750 -1.298733 0.864599
C -3.959834 -1.033349 0.558794

H 3.883592 2.160493 1.891194
H 3.787105 2.122126 0.135133
H 2.365083 0.221364 2.068233
H 1.619986 1.429230 1.033491
H 1.286856 1.143685 -1.611247
H 3.418977 -1.615570 -1.297316
H 5.104009 0.029677 1.932411
H 5.906944 1.097889 0.802858
H 5.821397 -1.906777 -1.405660
H 6.722098 -0.409699 -1.114645
H 6.627156 -1.628522 0.144622
H -1.196960 -1.272873 0.309049
H -2.077772 1.382268 -1.036490
H -4.381545 1.903882 -1.088146
H -6.732492 1.424797 -0.540287
H -7.329128 -0.634788 0.715751
H -5.534067 -2.199317 1.415044
H -3.196974 -1.733411 0.879779

^{3}Int-2

Final structure in terms of initial Cartesian coordinates:
C -1.735189 -1.191034 1.598008
C -1.698393 0.332439 1.434137
C -2.000337 0.683134 0.010887
C -2.777698 -0.123837 -0.805739
C -3.306711 -1.325019 -0.368660
C -3.029383 -1.787734 1.036629
C -4.181071 -2.175715 -1.233498
O -1.632963 1.916570 -0.496888
C -0.429411 2.468868 -0.208209
C 0.788025 1.845596 -0.108823
O -0.516590 3.810504 -0.102726
C 1.048680 0.484599 -0.305634
C 2.340681 -0.141802 -0.209069
C 2.455056 -1.522899 -0.478413
C 3.674597 -2.177165 -0.398676
C 4.827690 -1.476647 -0.044467
C 4.736657 -0.111011 0.228132
C 3.519434 0.547807 0.148957
H -1.618806 -1.454809 2.653265
H -0.878666 -1.618138 1.061737
H -2.447765 0.800200 2.092353

H -0.720966 0.717008 1.737919
H -1.454177 4.049788 -0.160794
H -2.973703 0.221988 -1.818325
H -3.875175 -1.509319 1.686391
H -2.980630 -2.883855 1.064822
H -4.339031 -1.724957 -2.217047
H -3.745918 -3.173436 -1.380480
H -5.164970 -2.332458 -0.770147
H 1.597547 2.528400 0.128970
H 0.222829 -0.167032 -0.579678
H 1.561114 -2.075924 -0.757809
H 3.728605 -3.240403 -0.614029
H 5.783511 -1.986695 0.019799
H 5.626840 0.445708 0.506461
H 3.480013 1.609856 0.370113

[1]Int-3

Final structure in terms of initial Cartesian coordinates:
C -1.979308 -1.423451 1.404034
C -1.617781 0.065335 1.359193
C -1.879206 0.596238 -0.008406
C -2.892600 0.040328 -0.832323
C -3.613881 -1.051531 -0.482040
C -3.379060 -1.703554 0.854730
C -4.685280 -1.629833 -1.350907
O -1.495723 1.849497 -0.347589
C -0.334809 2.371133 0.003425
C 0.871383 1.708505 0.172747
O -0.345521 3.724230 -0.008863
C 1.138913 0.358042 0.081281
C 2.471342 -0.206428 -0.052469
C 2.603327 -1.602284 -0.154889
C 3.846353 -2.204862 -0.272635
C 5.001760 -1.429132 -0.284900
C 4.892251 -0.043876 -0.183821
C 3.650280 0.560403 -0.075239
H -1.889642 -1.792107 2.427980
H -1.247215 -1.973586 0.802246
H -2.227104 0.638447 2.076668
H -0.580859 0.185462 1.686822
H -1.220490 4.023990 -0.280033
H -3.078650 0.536980 -1.781108

H -4.135449 -1.340921 1.566327
H -3.539773 -2.784495 0.776976
H -4.824924 -1.051561 -2.265428
H -4.450477 -2.662830 -1.633935
H -5.644007 -1.665857 -0.819881
H 1.692480 2.407751 0.285922
H 0.331537 -0.358203 0.021422
H 1.706771 -2.215120 -0.141632
H 3.915154 -3.284298 -0.352794
H 5.975733 -1.896174 -0.375495
H 5.785558 0.571236 -0.196678
H 3.599199 1.641266 -0.012448

[1]Int-3"

Final structure in terms of initial Cartesian coordinates:
C -1.735189 -1.191034 1.598008
C -1.698393 0.332439 1.434137
C -2.000337 0.683134 0.010887
C -2.777698 -0.123837 -0.805739
C -3.306711 -1.325019 -0.368660
C -3.029383 -1.787734 1.036629
C -4.181071 -2.175715 -1.233498
O -1.632963 1.916570 -0.496888
C -0.429411 2.468868 -0.208209
C 0.788025 1.845596 -0.108823
O -0.516590 3.810504 -0.102726
C 1.048680 0.484599 -0.305634
C 2.340681 -0.141802 -0.209069
C 2.455056 -1.522899 -0.478413
C 3.674597 -2.177165 -0.398676
C 4.827690 -1.476647 -0.044467
C 4.736657 -0.111011 0.228132
C 3.519434 0.547807 0.148957
H -1.618806 -1.454809 2.653265
H -0.878666 -1.618138 1.061737
H -2.447765 0.800200 2.092353
H -0.720966 0.717008 1.737919
H -1.454177 4.049788 -0.160794
H -2.973703 0.221988 -1.818325
H -3.875175 -1.509319 1.686391
H -2.980630 -2.883855 1.064822

H -4.339031 -1.724957 -2.217047
H -3.745918 -3.173436 -1.380480
H -5.164970 -2.332458 -0.770147
H 1.597547 2.528400 0.128970
H 0.222829 -0.167032 -0.579678
H 1.561114 -2.075924 -0.757809
H 3.728605 -3.240403 -0.614029
H 5.783511 -1.986695 0.019799
H 5.626840 0.445708 0.506461
H 3.480013 1.609856 0.370113

^{1}Int-2'

Final structure in terms of initial Cartesian coordinates:
C 2.505392 -1.018019 -1.385491
C 2.401388 0.357363 -0.732400
C 1.087573 0.492845 0.035149
C 0.831150 -0.711675 0.891118
C 1.449796 -1.881961 0.744456
C 2.494935 -2.112079 -0.319634
C 1.162058 -3.050785 1.641745
O 1.196815 1.636947 0.912784
C 0.634511 2.747952 0.355669
C -0.103403 2.336000 -0.829555
O 0.745094 3.842173 0.834581
C -0.093968 0.856782 -0.942347
C -1.422567 0.214201 -0.581059
C -1.797529 -0.976096 -1.201509
C -2.976238 -1.621278 -0.848667
C -3.796921 -1.080429 0.135412
C -3.430941 0.106343 0.760342
C -2.250650 0.750985 0.404904
H 3.412668 -1.082129 -1.990337
H 1.662859 -1.171721 -2.069849
H 3.215229 0.492845 -0.014159
H 2.481011 1.162318 -1.470895
H 0.082031 -0.580521 1.667433
H 3.476455 -2.170304 0.169293
H 2.334871 -3.093835 -0.778578
H 0.461298 -2.790280 2.435119
H 0.739742 -3.882083 1.068490
H 2.084621 -3.419093 2.101611
H -0.655912 3.028776 -1.446645

H 0.170709 0.532534 -1.954226
H -1.154130 -1.404890 -1.964345
H -3.254691 -2.545202 -1.343045
H -4.717611 -1.580965 0.412704
H -4.066381 0.534553 1.527408
H -1.975542 1.676149 0.902303

^{3}Int-3

Final structure in terms of initial Cartesian coordinates:
C -1.617182 -1.083753 1.698125
C -1.737167 0.423754 1.453762
C -1.999636 0.663416 0.002585
C -2.653686 -0.253011 -0.798779
C -3.081688 -1.476406 -0.316613
C -2.817994 -1.838138 1.120444
C -3.839525 -2.450986 -1.158330
O -1.704129 1.901413 -0.555810
C -0.515645 2.504890 -0.295471
C 0.711125 1.914480 -0.218520
O -0.656042 3.835050 -0.164752
C 0.985994 0.563520 -0.484066
C 2.253870 -0.081238 -0.284226
C 2.417501 -1.420438 -0.697744
C 3.618948 -2.086823 -0.528009
C 4.703598 -1.442177 0.063979
C 4.561641 -0.121229 0.486030
C 3.362068 0.549941 0.319508
H -1.519642 -1.283216 2.767167
H -0.700058 -1.439284 1.217421
H -2.562931 0.838988 2.049662
H -0.825490 0.934652 1.771960
H -1.597679 4.041486 -0.156103
H -2.832765 0.019253 -1.835441
H -3.715303 -1.619873 1.718744
H -2.659308 -2.918464 1.207175
H -4.004865 -2.074046 -2.168787
H -3.309841 -3.407711 -1.233403
H -4.818213 -2.674080 -0.716248
H 1.506615 2.594536 0.063841
H 0.195470 -0.053206 -0.898471
H 1.578904 -1.928243 -1.165126
H 3.714171 -3.114848 -0.860381

H 5.645276 -1.961497 0.198325
H 5.396748 0.387881 0.955298
H 3.276942 1.571175 0.672817

$^{1\text{-}3}$MECP1

C -1.972314 -1.354517 1.481163
C -1.622720 0.133983 1.373532
C -1.871372 0.604434 -0.017615
C -2.881047 0.010212 -0.823470
C -3.590926 -1.075476 -0.438479
C -3.359308 -1.678191 0.922462
C -4.637618 -1.704717 -1.302121
O -1.486250 1.839128 -0.406186
C -0.332242 2.381524 -0.073811
C 0.872435 1.723168 0.140242
O -0.334910 3.731334 -0.177432
C 1.126877 0.369499 0.117228
C 2.454749 -0.210465 -0.012795
C 2.564927 -1.575330 -0.330088
C 3.801746 -2.183342 -0.483527
C 4.970260 -1.448128 -0.309486
C 4.880838 -0.098820 0.026037
C 3.645777 0.513560 0.170159
H -1.898823 -1.672866 2.523335
H -1.221551 -1.923008 0.920940
H -2.245745 0.735717 2.054801
H -0.590854 0.273148 1.710621
H -1.184845 4.012178 -0.535753
H -3.068378 0.469807 -1.790739
H -4.131056 -1.309011 1.613546
H -3.498013 -2.764172 0.878178
H -4.772369 -1.160032 -2.237719
H -4.373035 -2.740477 -1.547221
H -5.605164 -1.745006 -0.787562
H 1.701527 2.420755 0.191078
H 0.312270 -0.339521 0.071998
H 1.657604 -2.154758 -0.474840
H 3.853551 -3.235025 -0.743024

H 5.939226 -1.918938 -0.432539
H 5.785729 0.480590 0.174415
H 3.608846 1.562548 0.442844

[1]Int-4

Final structure in terms of initial Cartesian coordinates:
C 2.374000 -1.274801 -1.395516
C 2.396588 0.111339 -0.758191
C 1.107548 0.364204 0.020788
C 0.755456 -0.805126 0.890179
C 1.272841 -2.024774 0.752111
C 2.289451 -2.350957 -0.315453
C 0.886682 -3.159711 1.656003
O 1.344677 1.505344 0.895892
C 0.851543 2.582952 0.263407
C 0.096533 2.337947 -0.811485
O 1.217067 3.725238 0.857951
C -0.046374 0.844082 -0.943446
C -1.419139 0.304119 -0.583585
C -1.869096 -0.885884 -1.156448
C -3.095337 -1.433140 -0.799119
C -3.892946 -0.794798 0.145275
C -3.453790 0.390529 0.724251
C -2.226787 0.935621 0.360646
H 3.262283 -1.423431 -2.014018
H 1.509622 -1.362744 -2.063482
H 3.228421 0.180254 -0.050666
H 2.530110 0.899239 -1.505001
H 0.794122 4.460376 0.403222
H 0.016168 -0.607863 1.662047
H 3.268189 -2.478610 0.166136
H 2.048802 -3.323445 -0.759089
H 0.204993 -2.836530 2.443053
H 0.400900 -3.958530 1.086684
H 1.773921 -3.598337 2.123897
H -0.407492 3.073462 -1.420586
H 0.197062 0.491575 -1.951169
H -1.245536 -1.391943 -1.888729
H -3.430039 -2.357118 -1.258113
H -4.850670 -1.218190 0.426719
H -4.069656 0.894879 1.460920
H -1.888192 1.862703 0.810921

^{3}Int-4

Final structure in terms of initial Cartesian coordinates:

C 2.888275 -0.147257 -1.288629
C 2.260490 1.093842 -0.661156
C 0.934011 0.751618 0.016516
C 1.052631 -0.489046 0.852028
C 2.053334 -1.364645 0.761197
C 3.192584 -1.186780 -0.212803
C 2.125829 -2.582158 1.636896
O 0.575278 1.834725 0.909458
C -0.207678 2.752710 0.283048
C -0.600352 2.183663 -1.046132
O -1.216073 3.143090 1.141349
C -0.241042 0.729835 -1.031804
C -1.367531 -0.214450 -0.652747
C -1.437033 -1.473613 -1.246841
C -2.425544 -2.380352 -0.881071
C -3.356389 -2.037608 0.092865
C -3.290679 -0.785000 0.694262
C -2.305024 0.123441 0.324447
H 3.798549 0.119262 -1.830816
H 2.200538 -0.580910 -2.023568
H 2.924838 1.498538 0.108461
H 2.101015 1.883978 -1.402437
H -1.672969 3.890509 0.743305
H 0.247660 -0.648392 1.564119
H 4.087391 -0.893348 0.352357
H 3.433613 -2.152986 -0.669403
H 1.302792 -2.616759 2.350991
H 2.096971 -3.494713 1.033196
H 3.068288 -2.600341 2.193670
H -0.698201 2.770684 -1.948661
H 0.152043 0.416734 -2.002823
H -0.705249 -1.748482 -2.001433
H -2.468509 -3.354054 -1.356804
H -4.128952 -2.741669 0.381100
H -4.011466 -0.511089 1.456939
H -2.257280 1.095331 0.804906

^{1}(±)-9a

Final structure in terms of initial Cartesian coordinates:

C 1.835754 -1.338612 1.714024
C 0.577306 -1.069834 0.895789
C 0.760145 0.153004 0.011010
C 2.107179 0.153637 -0.668372
C 3.117541 -0.651222 -0.341468
C 3.009285 -1.644702 0.787999
O 0.677193 1.329748 0.863222
C 0.106033 2.368554 0.217703
C -0.355419 1.908394 -1.156676
C -0.374405 0.382733 -1.040659
C 4.428664 -0.625268 -1.072752
O -0.009831 3.450385 0.705176
H 0.373402 2.257732 -1.892097
H -1.316156 2.358697 -1.401040
C -1.716416 -0.159410 -0.600207
C -2.171306 -1.379043 -1.102474
C -3.381209 -1.920387 -0.682428
C -4.157390 -1.246208 0.252888
C -3.716909 -0.027791 0.758629
C -2.507960 0.511745 0.335484
H 1.669168 -2.166789 2.406386
H 2.063839 -0.452832 2.313975
H -0.292155 -0.912231 1.536698
H 0.353561 -1.930623 0.254602
H 2.242418 0.874057 -1.473878
H 2.904750 -2.651042 0.359894
H 3.951049 -1.655294 1.346639
H -0.086548 -0.105037 -1.974092
H 4.414550 0.067240 -1.914977
H 5.237504 -0.330670 -0.397405
H 4.679043 -1.622045 -1.449514
H -1.570368 -1.909432 -1.835562
H -3.719117 -2.867272 -1.088876
H -5.101822 -1.664072 0.582634
H -4.316614 0.508243 1.485485
H -2.190759 1.466748 0.743020

^{3}(±)-9a

Final structure in terms of initial Cartesian coordinates:

C 2.039432 -1.282063 1.698969
C 0.752555 -1.136267 0.894014
C 0.804150 0.102409 0.013556
C 2.134774 0.223716 -0.688448
C 3.218708 -0.486903 -0.378937
C 3.224230 -1.477406 0.758479
O 0.612744 1.269537 0.856001
C -0.042182 2.252954 0.190702
C -0.464695 1.733199 -1.175728
C -0.362567 0.210983 -1.021519
C 4.507473 -0.350080 -1.137075
O -0.226805 3.333007 0.656866
H 0.230035 2.121064 -1.924336
H -1.461373 2.098407 -1.419184
C -1.654638 -0.357202 -0.512951
C -2.212371 -1.503173 -0.982564
C -3.527026 -1.891564 -0.583492
C -4.371066 -0.957797 0.117981
C -3.852469 0.186981 0.609612
C -2.378098 0.325884 0.600505
H 1.962014 -2.120689 2.394471
H 2.187718 -0.376353 2.294399
H -0.118726 -1.079341 1.549064
H 0.609651 -2.009791 0.246833
H 2.189798 0.947370 -1.500133
H 3.214259 -2.492825 0.339019
H 4.170368 -1.390158 1.302862
H -0.072352 -0.296803 -1.943643
H 4.416216 0.335971 -1.979788
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H 4.835565 -1.322771 -1.517025
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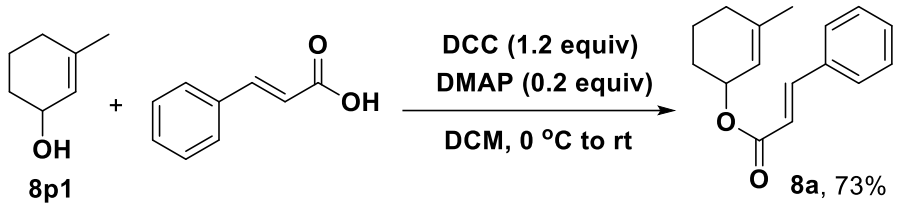
H -1.891768 0.293515 1.579577

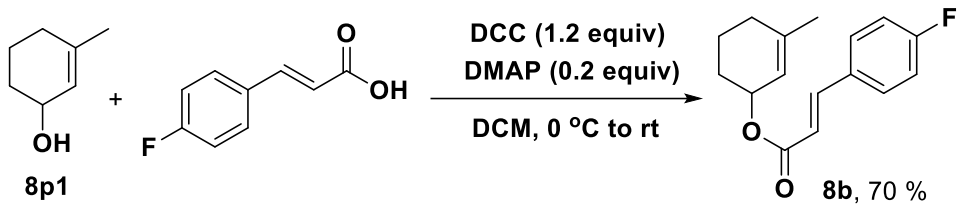
Preparation of Starting Materials Allyl Acrylic Esters.

1.Preparation of compound 8a to 8o.

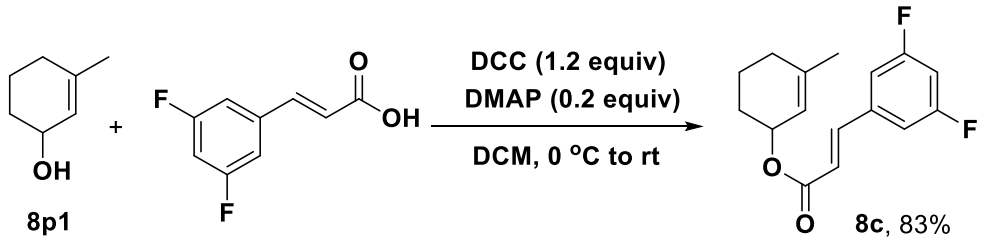
To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), cinnamic acid (2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ^{o}C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8a** to **8o.**



***(E)*-3-Methylcyclohex-2-en-1-yl cinnamate (8a)**: To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-cinnamic acid (356 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ^{o}C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8a** (354 mg, 73% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.53-7.50 (m, 2H), 7.38 – 7.36 (m, 3H), 6.45 (d, *J* = 16.0 Hz, 1H), 5.55 (s, 1H), 5.40 (s, 1H), 2.05 – 1.96 (m, 2H), 1.86 – 1.78 (m, 3H), 1.74 (s, 3H), 1.70-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 144.4, 141.2, 134.5, 130.1, 128.8, 128.0, 120.0, 118.7, 68.9, 29.9, 28.1, 23.8, 19.1; HRMS(EI) Calcd for $C_{16}H_{19}O_2$ $[M + H]^+$: 242.1385, Found 243.1379; IR (KBr) ν(cm^{-1}) : 3350, 2947, 2833, 1651, 1451, 1115, 1032.

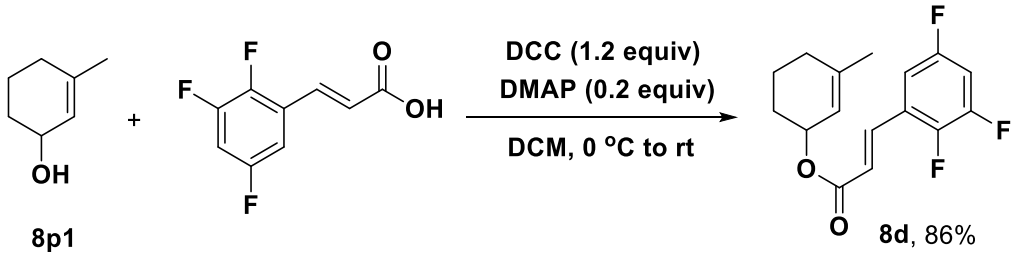


(*E*)-3-Methylcyclohex-2-en-1-yl 3-(4-fluorophenyl)acrylate (8b): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-fluorophenyl)acrylic acid (399 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8b** (364 mg, 70% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.49 (dd, *J* = 8.6 and 5.4 Hz, 2H), 7.05 (t, *J* = 8.6 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 5.53 (s, 1H), 5.38 (s, 1H), 2.04 – 1.95 (m, 2H), 1.85-1.76 (m, 3H), 1.72 (s, 3H), 1.68 – 1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 163.7 (d, J_{C-F} = 249.5 Hz), 143.0, 141.2, 130.8 (d, J_{C-F} = 3.3 Hz), 129.8 (d, J_{C-F} = 8.5 Hz), 120.0, 118.5 (d, J_{C-F} = 2.3 Hz), 116.0, 115.8, 68.9, 29.9, 28.0, 23.7, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.88; HRMS(EI) Calcd for $C_{16}H_{17}FO_2$ [M^+]: 260.1213, Found 260.1209; IR (KBr) ν (cm^{-1}) : 2937, 1708, 1639, 1601, 1510, 1233, 1161, 981, 917, 832.



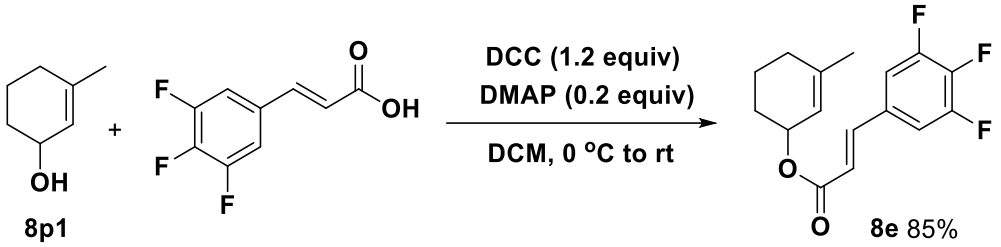
(*E*)-3-Methylcyclohex-2-en-1-yl 3-(3,5-difluorophenyl)acrylate (8c): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(3,5-difluorophenyl)acrylic acid (442 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by

column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8c**. (463 mg, 83% yield). White solid; mp 39.1-39.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 16.0 Hz, 1H), 7.04-6.99 (m, 2H), 6.81 (tt, *J* = 8.7 and 2.2 Hz, 1H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.53 (s, 1H), 5.38 (s, 1H), 2.05 – 1.96 (m, 2H), 1.84-1.76 (m, 3H), 1.73 (s, 3H), 1.70-1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 163.2 (d, $J_{C–F}$ = 247.6 Hz), 163.1 (d, $J_{C–F}$ = 247.7 Hz), 141.7 (t, $J_{C–F}$ = 2.9 Hz), 141.5, 137.8 (t, $J_{C–F}$ = 9.5 Hz), 121.5, 119.7, 110.62 (d, $J_{C–F}$ = 25.7 Hz), 110.58 (d, $J_{C–F}$ = 11.6 Hz), 105.2 (t, $J_{C–F}$ = 25.4 Hz), 69.3, 29.9, 28.0, 23.7, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.15; HRMS(EI) Calcd for $C_{16}H_{16}F_2O_2$ [M^+]: 278.1118, Found 278.1124; IR (KBr) (cm^{-1}) : 2938, 1711, 1592, 1440, 1277, 1181, 1122, 980, 915, 851.

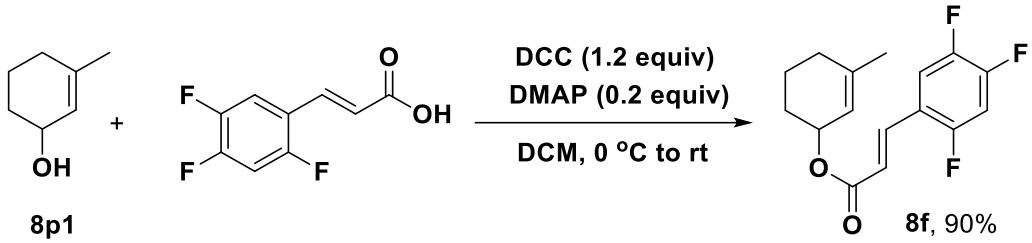


***(E)*-3-Methylcyclohex-2-en-1-yl 3-(2,3,5-trifluorophenyl)acrylate (8d)**: To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(2,3,5-trifluorophenyl)acrylic acid (485 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8d** (510 mg, 86% yield). White solid; mp 66.8-67.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 16.2 Hz, 1H), 7.05-6.90 (m, 2H), 6.52 (d, *J* = 16.2 Hz, 1H), 5.53 (s, 1H), 5.38 (s, 1H), 2.06 – 1.92(m, 2H), 1.85 – 1.76 (m, 3H), 1.73 (s, 3H), 1.69 – 1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 157.5 (ddd, J_{C-F} = 244.4, 10.6 and 3.2 Hz), 150.6 (ddd, J_{C-F} = 250.1, 14.6 and 12.9 Hz), 145.8 (ddd, J_{C-F} = 250.1, 13.3 and 4.0 Hz), 141.4, 134.3 (q, J_{C-F} = 2.8 Hz), 125.2-125.0 (m, 1C), 123.7 (d, J_{C-F} = 6.1 Hz), 119.7, 109.3 (ddd, J_{C-F} = 24.3, 3.6 and 1.3 Hz), 106.5 (dd, J_{C-F} = 27.5 and 22.0 Hz), 69.4, 29.8, 27.9,

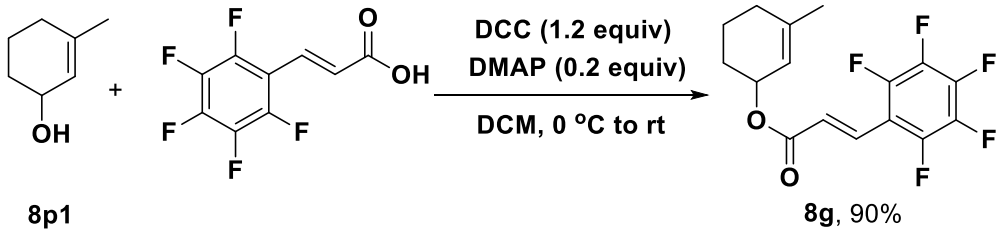
23.6, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.79 (dd, *J* = 14.8 and 3.4 Hz), -132.57 (dd, *J* = 19.9 and 3.4 Hz), -144.70 (dd, *J* = 19.9 and 14.8 Hz); HRMS(EI) Calcd for $C_{16}H_{16}F_3O_2$ [M + H]$^+$: 297.1102, Found 297.1097; IR (KBr) ν (cm^{-1}) : 3433, 2938, 1706, 1640, 1597, 1494, 1445, 1280, 1198, 1164, 1128,
1051, 1000, 987.



(*E*)-3-Methylcyclohex-2-en-1-yl 3-(3,4,5-trifluorophenyl)acrylate (8e): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(3,4,5-trifluorophenyl)acrylic acid (485 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ºC. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8e** (504 mg, 85% yield). White solid; mp 81.6-81.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 15.9 Hz, 1H), 7.23 – 6.99 (m, 2H), 6.35 (d, *J* = 15.9 Hz, 1H), 5.52 (s, 1H), 5.37 (s, 1H), 2.06 – 1.90 (m, 2H), 1.85-1.75 (m, 3H), 1.73 (s, 3H), 1.69-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 151.3 (ddd, J_{C-F} = 249.5, 10.3 and 4.1 Hz), 141.4, 140.5 (dt, J_{C-F} = 245.6 and 15.4 Hz), 140.8 (d, J_{C-F} = 2.3 Hz), 130.7 (td, J_{C-F} = 7.8 and 4.8 Hz), 121.2 (d, J_{C-F} = 2.4 Hz), 119.7, 111.8 (dd, J_{C-F} = 15.8 and 6.0 Hz), 69.3, 29.8, 27.9, 23.7, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -133.33 (d, J_{C-F} =20.1 Hz), -157.09 (t, J_{C-F} = 20.0 Hz); HRMS(EI) Calcd for $C_{16}H_{16}F_3O_2$ [M + H]$^+$: 297.1102, Found 297.1094; IR (KBr) ν (cm^{-1}) : 2940, 1711, 1645, 1529, 1442, 1329, 1308, 1277, 1184, 1166, 1046, 991.

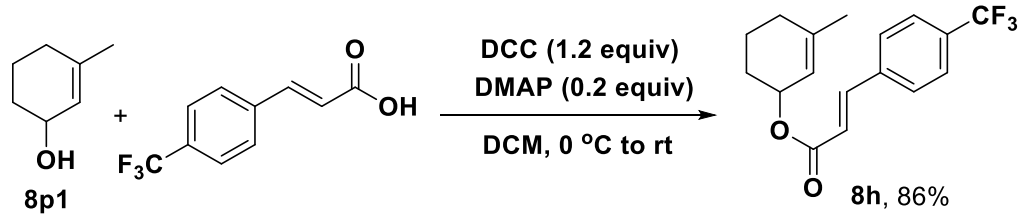


(*E*)-3-Methylcyclohex-2-en-1-yl 3-(2,4,5-trifluorophenyl)acrylate (8f): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(2,4,5-trifluorophenyl)acrylic acid (485 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8f** (533 mg, 90 % yield). White solid; mp 77.9-78.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 16.1 Hz, 1H), 7.35-7.25 (m, 1H), 6.96 (td, J = 9.8 and 6.6 Hz, 1H), 6.44 (d, J = 16.1 Hz, 1H), 5.52 (s, 1H), 5.38 (s, 1H), 2.04 – 1.95 (m, 2H), 1.91-1.76(m, 3H), 1.72 (s, 3H), 1.69 – 1.63 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.0, 156.4 (ddd, J_{C-F} = 251.6, 9.2 and 2.2 Hz), 150.9 (ddd, J_{C-F} = 254.5, 14.8 and 12.5 Hz), 149.5 (ddd, J_{C-F} = 244.6, 13.0 and 3.5 Hz), 141.5, 134.7 (d, J_{C-F} = 2.0 Hz), 122.1 (dd, J_{C-F} = 6.0 and 2.4 Hz), 119.8, 119.2 (dt, J_{C-F} = 13.8 and 5.2 Hz), 116.0 (ddd, J_{C-F} = 19.6, 4.5 and 1.5 Hz), 106.3 (dd, J_{C-F} = 28.0 and 21.0 Hz), 69.2, 29.8, 27.9, 23.6, 18.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.68 (dd, J_{C-F} = 15.0 and 5.3 Hz), -129.67 (dd, J_{C-F} = 21.4 and 5.3 Hz) -141.63 (dd, J_{C-F} = 21.4 and 15.0 Hz); HRMS(EI) Calcd for $C_{16}H_{15}F_3O_2$ [M^+]: 296.1024, Found 296.1019; IR (KBr) ν (cm^{-1}) : 3059, 2953, 1697, 1519, 1433, 1336, 1284, 1187.



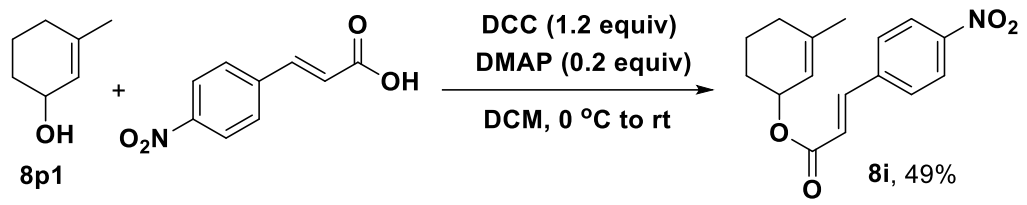
(*E*)-3-Methylcyclohex-2-en-1-yl 3-(perfluorophenyl)acrylate (8g): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(perfluorophenyl)acrylic acid (571 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2

equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ºC. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8g** (598 mg, 90% yield). White solid; m.p. 56.0-56.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.4 Hz, 1H), 6.74 (d, *J* = 16.4 Hz, 1H), 5.53 (s, 1H), 5.39 (s, 1H), 2.06-1.96 (m, 2H), 1.86-1.76 (m, 3H), 1.73 (s, 3H), 1.70 – 1.64 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 146.4-144.6 (m, 1C), 142.4-140.5 (m, 1C), 141.4, 138.6-136.7 (m, 1C), 127.5, 126.7 (t, $J_{C\text{-}F}$ = 7.9 Hz), 119.5, 109.8 (td, $J_{C\text{-}F}$ = 13.4 and 3.9 Hz), 69.5, 29.7, 27.8, 23.4, 18.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -139.50--139.57(m), -151.45 (tt, $J_{C–F}$ = 20.8 and 2.7 Hz), -161.62--161.76 (m); HRMS(EI) Calcd for $C_{16}H_{13}F_5O_2$ [M^+]: 332.0836, Found 332.0841; IR (KBr) ν(cm^{-1}) : 3429, 2939, 1716, 1524, 1500, 1293,1263, 1189, 1151,1018, 984, 962, 913.

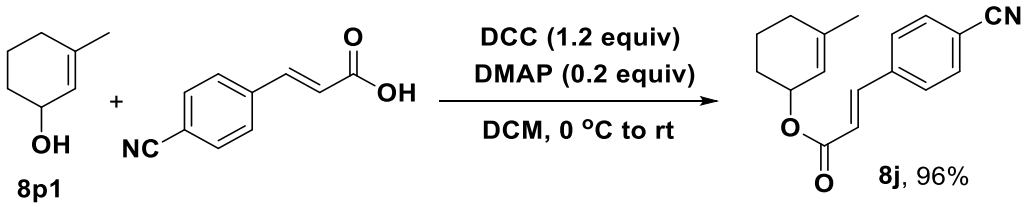


(*E*)-3-Methylcyclohex-2-en-1-yl 3-(4-(trifluoromethyl)phenyl)acrylate (8h): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-(trifluoromethyl)phenyl)acrylic acid (519 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ºC. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8h** (534 mg, 86% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 16.0 Hz, 1H), 7.64-7.59 (m, 4H), 6.51 (d, *J* = 16.0 Hz, 1H), 5.54 (s, 1H), 5.39 (s, 1H), 2.04 – 1.91 (m, 2H), 1.86-1.76 (m, 3H), 1.73 (s, 3H), 1.69 – 1.62 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 142.4, 141.4, 137.9 (d, $J_{C\text{-}F}$ = 1.2 Hz), 131.5(q, $J_{C\text{-}F}$ = 32.5 Hz), 128.1, 125.8 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 270.5 Hz), 121.3, 119.8, 69.2, 29.9, 28.0, 23.7, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.87; HRMS(EI) Calcd for

$C_{17}H_{17}F_3O_2$ [M^+]: 310.1181, Found 310.1174; IR (KBr) ν(cm^{-1}) : 2938, 1711, 1642, 1325, 1173, 1129, 1068, 981, 917, 834.



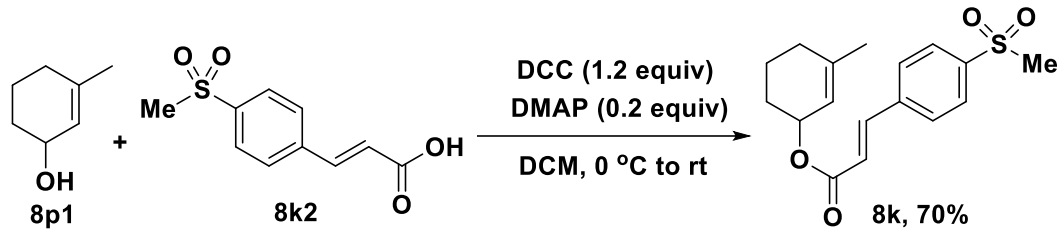
***(E)*-3-Methylcyclohex-2-en-1-yl 3-(4-nitrophenyl)acrylate (8i)**: To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-nitrophenyl)acrylic acid (464 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8i** (141 mg, 49% yield). White solid; mp 117.8-118.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.7 Hz, 1H), 7.71 – 7.65 (m, 3H), 6.56 (d, *J* = 16.0 Hz, 1H), 5.54 (s, 1H), 5.40 (s, 1H), 2.06 – 1.93 (m, 2H), 1.86 – 1.77 (m, 3H), 1.74 (s, 3H), 1.70 – 1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 148.4, 141.7, 141.3, 140.7, 128.5, 124.1, 123.1, 119.6, 69.5, 29.9, 28.0, 23.8, 19.0; HRMS(EI) Calcd for $C_{16}H_{17}NO_4$ [M^+]: 287.1158, Found; 287.1161; IR (KBr) ν(cm^{-1}) : 2939, 2869, 1704, 1640, 1600, 1520, 1347, 1206, 1180, 1165, 1110, 984.



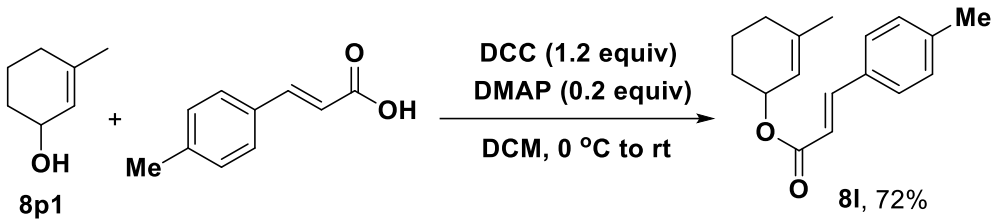
(*E*)-3-Methylcyclohex-2-en-1-yl 3-(4-cyanophenyl)acrylate (8j): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-cyanophenyl)acrylic acid (416 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent

was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8j**

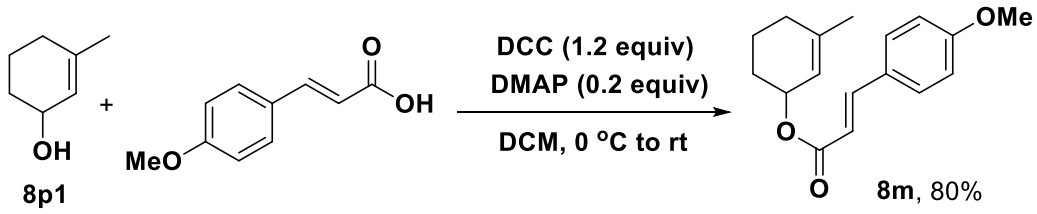
(513 mg, 96% yield). White solid; mp 83.5-83.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.55 (m, 5H), 6.52 (d, *J* = 16.0 Hz, 1H), 5.53 (s, 1H), 5.39 (s, 1H), 2.07 – 1.92 (m, 2H), 1.86 – 1.76 (m, 3H), 1.73 (s, 3H), 1.70 – 1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 141.8, 141.6, 138.8, 132.6, 128.3, 122.4, 119.7, 118.4, 113.2, 69.4, 29.9, 28.0, 23.8, 19.0; HRMS(EI) Calcd for $C_{17}H_{17}NO_2$ [M^+]: 267.1259, Found; 267.1247; IR (KBr) (cm^{-1}) : 3432, 2938, 2229, 1707, 1639, 1329, 1306, 1279, 1254, 1205, 1181, 985, 915, 831.



3-Methylcyclohex-2-en-1-yl (E)-3-(4-(methylsulfonyl)phenyl)acrylate (8k): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-(methylsulfonyl) -phenyl)acrylic acid (**8k2**) (543 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ºC. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 20/1) to give **8k** (448 mg, 70% yield). White solid; mp 195.2-195.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 15.8 Hz, 1H), 6.55 (d, *J* = 16.1 Hz, 1H), 5.53 (s, 1H), 5.38 (s, 1H), 3.06 (s, 3H), 2.05 – 1.92 (m, 2H), 1.85-1.77 (m, 3H), 1.73 (s, 3H), 1.70-1.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 141.7, 141.6, 141.3, 139.8, 128.6, 127.9, 122.6, 119.7, 69.4, 44.4, 29.9, 28.0, 23.7, 19.0; HRMS(EI) Calcd for $C_{17}H_{20}O_4S$ [M + Na]$^+$: 343.0980, Found 343.0972; IR (KBr) (cm^{-1}): 1707, 1642, 1301, 1142, 960, 831,774.

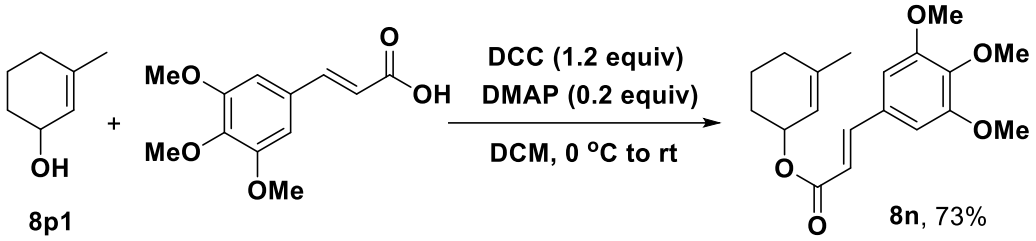


(*E*)-3-Methylcyclohex-2-en-1-yl 3-(p-tolyl)acrylate (8l): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(p-tolyl)acrylic acid (389 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8l** (369 mg, 72% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 5.55 (s, 1H), 5.39 (s, 1H), 2.36 (s, 3H), 2.06-1.96 (m, 2H), 1.91 – 1.76 (m, 3H), 1.73 (s, 3H), 1.69 – 1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 144.3, 141.0, 140.4, 131.7, 129.5, 127.9, 120.1, 117.6, 68.7, 29.9, 28.0, 23.7, 21.4, 19.0; HRMS(EI) Calcd for $C_{17}H_{20}O_2$ [M^+]: 256.1463, Found 256.1452; IR (KBr) ν(cm^{-1}) : 2936, 1707, 1636, 1304, 1253, 1164, 983, 918, 813.

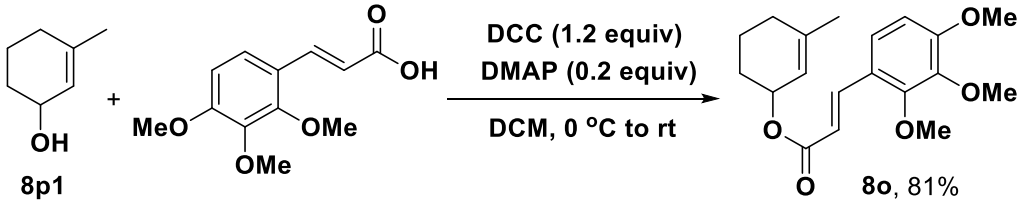


(*E*)-3-Methylcyclohex-2-en-1-yl 3-(4-methoxyphenyl)acrylate (8m): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-methoxyphenyl)acrylic acid (428 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8m (**436 mg, 80% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 5.53 (s,

1H), 5.37 (s, 1H), 3.80 (s, 3H), 2.04 – 1.94 (m, 2H), 1.84 – 1.74 (m, 3H), 1.71 (s, 3H), 1.67 – 1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 161.1, 143.9, 140.9, 129.5, 127.1, 120.1, 116.1, 114.1, 68.5, 55.2, 29.8, 28.0, 23.7, 19.0; HRMS(EI) Calcd for $C_{17}H_{20}O_3$ [M^+]: 272.1412, Found 272.1417; IR (KBr) ν (cm^{-1}) : 2937, 2836, 1705, 1634, 1604, 1513, 1252, 1171, 1031, 982, 918, 829.



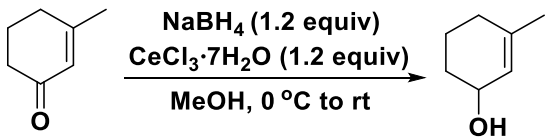
(*E*)-3-Methylcyclohex-2-en-1-yl 3-(3,4,5-trimethoxyphenyl)acrylate (8n): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(3,4,5-trimethoxyphenyl)acrylic acid (572 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8n** (486 mg, 73% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.9 Hz, 1H), 6.72 (s, 2H), 6.33 (d, *J* = 15.9 Hz, 1H), 5.51 (s, 1H), 5.36 (s, 1H), 3.84 (s, 9H), 2.02-1.89 (m, 2H), 1.83-1.74 (m,3H), 1.70 (s, 3H), 1.67 – 1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 153.2, 144.2, 141.2, 139.8, 129.9, 119.9, 117.9, 105.0, 68.7, 60.8, 56.0, 29.8, 28.0, 23.7, 18.9; HRMS(EI) Calcd for $C_{19}H_{24}O_5$ [M^+]: 332.1624, Found 332.1629; IR (KBr) ν(cm^{-1}) : 2938, 1704, 1636, 1582, 1505, 1455, 1419, 1317, 1246, 1152, 1005, 917, 828.



7-Methyl-4-(2,3,4-trimethoxyphenyl)-1-oxaspiro[4.5]dec-6-en-2-one (8o): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(2,3,4-trimethoxyphenyl)acrylic acid (572 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4

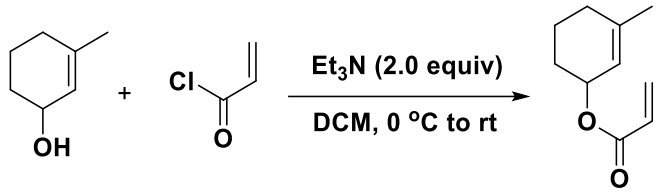
mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 ºC. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give **8o** (539 mg, 81% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 16.1 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 6.66 (d, *J* = 8.8 Hz, 1H), 6.40 (d, *J* = 16.1 Hz, 1H), 5.52 (s, 1H), 5.36 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 2.02-1.89 (m, 2H), 1.83 – 1.75 (m, 3H), 1.71 (s, 3H), 1.67 – 1.61(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 155.3, 153.2, 142.2, 140.9, 139.3, 123.0, 121.5, 120.2, 117.5, 107.5, 68.6, 61.3, 60.8, 55.9, 29.9, 28.1, 23.7, 19.1; HRMS(EI) Calcd for $C_{19}H_{24}O_5$ [M^+]: 332.1624, Found 332.1618; IR (KBr) ν(cm^{-1}) : 2938, 1704, 1630, 1594, 1496, 1465, 1415, 1296, 1256, 1159, 1098.

2 . Preparation of compound 8p, 8q and 8r



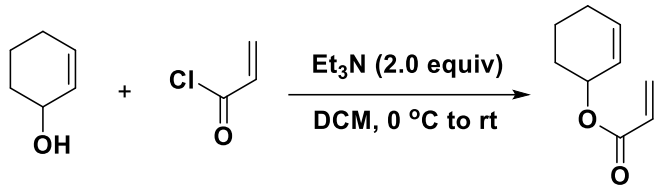
8p1, 98%

3-Methylcyclohex-2-en-1-ol[1] (8p1): To the solution of 3-Methyl-2-cyclohexen-1-one (2.2 g, 20 mmol, 1.0 equiv) and Cerium(III) chloride heptahydrate (8.94 g, 24 mmol, 1.2 equiv) in MeOH (50 mL) was added $NaBH_4$ (908 mg, 24 mmol, 1.2 equiv) at 0 ºC, the reaction was stirred at room temperature for 30 min. The reaction mixture was extracted by DCM (15 mL x 3), the combined organic phase was dried over anhydrous Na_2SO_4, After evaporation of the solvent under reduced pressure (the temperature should be kept below 20 ºC), the residue light yellow oil was pure enough for next step without further purification **8p1 (**2.2 g, 98% yield). The data is consistent with the literature **[1]**. Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.48 (s, 1H), 4.15 (s, 1H), 1.95 – 1.87 (m, 2H), 1.78 – 1.72 (m, 3H), 1.67 (s, 3H), 1.58-1.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 124.2, 65.8, 31.6, 30.0, 23.6, 19.0.



8p1 **8p**, 47 %

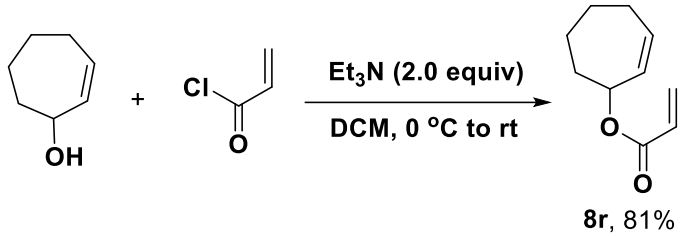
3-Methylcyclohex-2-en-1-yl acrylate (8p): Acryloyl chloride (1.2 equiv) was added dropwise into the mixture of 3-Methyl-2-cyclohexen-1-ol (1.0 equiv) and Et_3N (2.0 equiv) in DCM (20 mL) under 0 °C. After 30 minutes, the reaction mixture was extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure , the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to give **8p** (772 mg, 47% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (dd, *J* = 17.3 and 1.4 Hz, 1H), 6.10 (dd, *J* = 17.3 and 10.4 Hz, 1H), 5.78 (dd, *J* = 10.4 and 1.4 Hz, 1H), 5.49 (s, 1H), 5.32 (s, 1H), 2.02-1.89 (m, 2H), 1.83 – 1.73 (m, 3H), 1.71 (s, 3H), 1.67-1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 141.2, 130.2, 129.0, 119.9, 68.9, 29.9, 28.0, 23.7, 19.0; HRMS(EI) Calcd for $C_{10}H_{14}O_2$ [M^+]: 166.0994, Found 166.0993; IR (film) ν(cm^{-1}): 2938, 1721, 1406, 1270, 1043, 982, 914, 811.



8q, 78%

Cyclohex-2-en-1-yl acrylate (8q): Acryloyl chloride (1.2 equiv) was added dropwise into the mixture of 2-cyclohexen-1-ol (1.0 equiv) and Et_3N (2.0 equiv) in DCM (20 mL) under 0 °C. After 30 minutes, the reaction mixture was extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to give **8q** (237 mg, 78% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, *J* = 17.3 and 1.2 Hz, 1H), 6.11 (dd, *J* = 17.3 and 10.4 Hz, 1H), 6.03-5.88 (m, 1H), 5.79 (dd, *J* = 10.4 and 1.2 Hz, 1H), 5.72 (dd, *J* = 6.0 and 1.6 Hz, 1H), 5.33 (s, 1H), 2.12-1.99 (m, 2H), 1.92-1.86 (m, 1H), 1.80-1.73 (m, 2H), 1.68 – 1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 132.7, 130.3, 128.9,

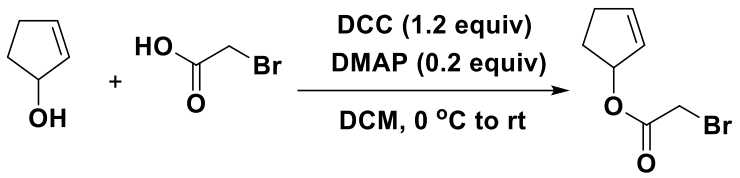
125.5, 68.2, 28.2, 24.8, 18.8; HRMS(EI) Calcd for $C_9H_{12}O_2$ [M^+]: 152.0837, Found 152.0839; IR (KBr) ν(cm-1) : 3445, 1723, 1635, 1407, 1385, 1269, 1193, 1048, 941, 908.



8r, 81%

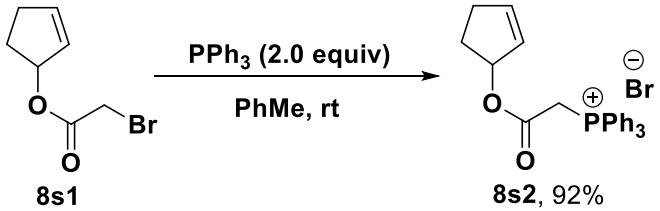
Cyclohept-2-en-1-yl acrylate (8r): To the solution of cyclopent-2-en-1-one (1.0 equiv) in MeOH was added $NaBH_4$ (1.2 equiv) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue light yellow oil was used for next step directly without further purification. Acryloyl chloride (1.2 equiv) was added dropwise into the mixture of cyclohept-2-en-1-ol (1.0 equiv) and Et_3N (2.0 equiv) in DCM (20 mL) under 0 °C. After 30 minutes, the reaction mixture was extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate = 20/1) to give **8r** (269 mg, 81% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, *J* = 17.3 and 1.3 Hz, 1H), 6.12 (dd, *J* = 17.3 and 10.4 Hz, 1H), 5.86 – 5.83 (m, 1H), 5.80 (dd, *J* = 10.3 and 1.3 Hz, 1H), 5.66 (d, *J* = 11.6 Hz,1H), 5.47 (d, *J* = 8.7 Hz, 1H), 2.24 – 2.17 (m, 1H), 2.12-2.05 (m, 1H), 1.96-1.87 (m, 2H), 1.75 – 1.62 (m, 3H), 1.46-1.37 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 133.4, 131.7, 130.4, 128.9, 74.3, 32.7, 28.4, 26.6, 26.5; HRMS(EI) Calcd for $C_{10}H_{14}O_2$ [M^+]: 166.0994, Found 166.0995; IR (film) (cm^{-1}): 2927, 1729, 1457, 1262, 1098, 1028, 800.

3. Preparation of compound 8s, 8t, 8u and 8v.



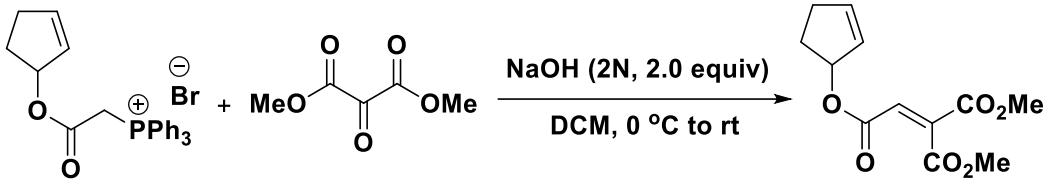
8s1, 86%

Cyclopent-2-en-1-yl 2-bromoacetate (8s1): To the solution of cyclopent-2-en-1-one (1.0 equiv) in MeOH was added $NaBH_4$ (1.2 equiv) at 0 °C. The reaction was stirred at 0 °C for 30 min. The reaction mixture was extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure (the temperature should be kept below 20 °C), the residue light yellow oil was used for next step without further purification. To the mixture of cyclopent-2-en-1-ol (561 mg, 5.0 mmol, 1.0 equiv), bromoacetic acid (834 mg, 6.0 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 122 mg, 1.0 mmol, 0.2 equiv) in DCM (30 mL) was added dicyclohexylcarbodiimide (DCC, 1.24 g, 6.0 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give the desired ester products **8s1** (886 mg, 86% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.20-6.12 (m, 1H), 5.82 (dd, *J* = 5.4 and 2.1 Hz, 1H), 5.74 (dd, *J* = 5.4 and 2.1 Hz, 1H), 3.79 (s, 2H), 2.55 – 2.51 (m, 1H), 2.35 – 2.26 (m, 2H), 1.87 – 1. 82 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.1, 138.6, 128.4, 82.6, 31.0, 29.5, 26.3; HRMS(EI) Calcd for $C_7H_9BrO_2$ [M^+]: 203.9786, Found 203.9783; IR (film) ν (cm^{-1}):
2931, 1732, 1421, 1279, 1171, 1028, 874, 739.



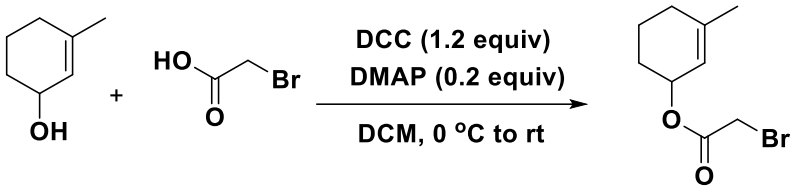
(2-(Cyclopent-2-en-1-yloxy)-2-oxoethyl)triphenylphosphonium bromide (8s2): The obtained ester **8s1** (1.0 g, 4.29 mmol, 1.0 equiv) and PPh_3 (2.25 g, 8.58 mmol, 2.0 equiv) were stirred in toluene (30 mL) at room temperature for 48 h. A white precipitate was formed from the reaction mixture. After filtered, the white solid was collected and dried at room

temperature to give the desired product **8s2** (1.84 g, 92%).White solid; mp 127.5-127.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76-7.72 (m, 6H), 7.68 (t, *J* = 7.2 Hz, 3H), 7.56 (br, 6H), 5.89 (s, 1H), 5.35 (s, 2H), 5.23 (d, *J* = 14.0 Hz, 2H), 2.17 – 2.05 (m, 2H), 1.94-1.88 (m, 1H), 1.38 – 1.34 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 163.5(d, $J_{c\text{-}p}$ = 4.0 Hz), 138.8, 134.9 (d, $J_{c\text{-}p}$ = 2.8 Hz), 133.6 (d, $J_{c\text{-}p}$ = 10.7 Hz), 129.9 (d, $J_{c\text{-}p}$ = 13.1 Hz), 127.3, 117.8, 117.2, 83.1, 32.9 (d, $J_{c\text{-}p}$ = 54.0 Hz), 30.6, 28.8; ^{31}P NMR (242 MHz, $CDCl_3$) δ 20.86; HRMS(EI) Calcd for $C_{25}H_{24}BrO_2P$ [M^+]: 466.0697, Found 466.0709; IR (film) ν (cm^{-1}): 1705, 1585, 1435, 1309, 1196, 1153, 1028, 868 .



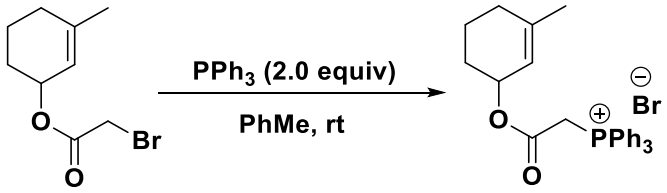
8s2 **8s**, 80%

2-(Cyclopent-2-en-1-yl) 1,1-dimethyl ethene-1,1,2-tricarboxylate (8s): 8s2 (1.49 g, 3.0 mmol, 1.0 equiv) and dimethyl keto malonate (439 mg, 3.0 mmol, 1.0 equiv) were dissolved in DCM (30 mL), and then cooled to 0 ºC. A aqueous solution of NaOH (240 mg, 6.0 mmol, 2.0 equiv, 2N) was added dropwise into the solution. The reaction was stirred at 0 ºC for 30 min, and then extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give the desired esters **8s** (610 mg, 80%). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.20-6.10 (m, 1H), 5.90-5.75 (m, 1H), 5.70-5.60 (m, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 2.55 – 2.45 (m, 1H), 2.36 – 2.23 (m, 2H), 1.89 – 1.81 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 163.3, 162.6, 138.6, 137.8, 131.1, 128.4, 82.2, 53.2, 52.8, 31.0, 29.5; HRMS(EI) Calcd for $C_{12}H_{15}O_6$ [M + H]$^+$: 255.0869, Found 255.0864; IR (film) ν (cm^{-1}): 2956, 1720, 1456, 1070, 1028, 920, 777.



8p1 **8t1**, 86%

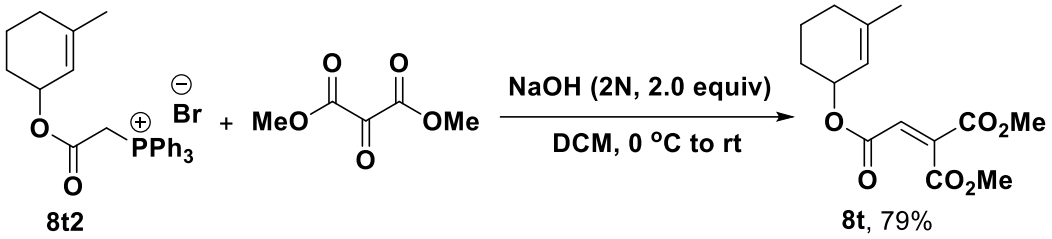
Cyclohex-2-en-1-yl 2-bromoacetate (8t1): To the mixture of **8p1** (561 mg, 5.0 mmol, 1.0 equiv), bromoacetic acid (834 mg, 6.0 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 122 mg, 1.0 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 1.24 g, 6.0 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give the desired ester products **8t1** (1.0 g, 86% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 1H), 5.28 (s, 1H), 3.80 (s, 2H), 2.01-1.93(m, 2H), 1.78-1.73 (m, 3H), 1.70 (s, 3H), 1.67-1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 142.1, 119.0, 71.0, 29.8, 27.6, 26.5, 23.7, 18.7; HRMS(EI) Calcd for $C_9H_{13}BrO_2$ [M^+]: 233.0177, Found 233.0171; IR (KBr) ν(cm^{-1}) : 3368, 2945, 2833, 1728, 1450, 1285, 1032.



8t1 **8t2**, 98%

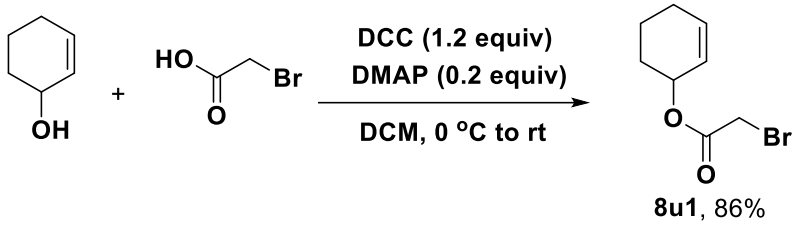
(2-(Cyclohex-2-en-1-yloxy)-2-oxoethyl)triphenylphosphonium bromide (8t2): The obtained ester **8t1** (1.0 g, 4.29 mmol, 1.0 equiv) and PPh_3 (2.25 g, 8.58 mmol, 2.0 equiv) were stirred in toluene (30 mL) at room temperature for 48 h. A white precipitate was formed from the reaction mixture. After filtered, the white solid was collected and dried at room temperature to give the desired product **8t2** (2.08g, 98%). White solid; mp 129.6-129.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 13.4 and 7.5 Hz, 6H), 7.79 – 7.74 (m, 3H), 7.66 (tt, J = 7.7 and 3.5 Hz, 6H), 5.54-5.41 (m, 2H), 5.12 (s, 1H), 5.05 (s, 1H), 1.88 – 1.83 (m, 2H), 1.72 (s, 3H), 1.60 – 1.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4 (d, $J_{c\text{-}p}$ = 4.1 Hz), 142.2, 134.9 (d, $J_{c\text{-}p}$ = 3.0 Hz), 133.7 (d, $J_{c\text{-}p}$ = 10.7 Hz), 130.0 (d, $J_{c\text{-}p}$ = 13.1 Hz), 118.1, 117.9, 117.2, 71.7, 33.0 (d, $J_{c\text{-}p}$ = 53.7 Hz), 29.3,

27.0, 23.4, 18.1; ^{31}P NMR (242 MHz, $CDCl_3$) δ 20.92; HRMS(EI) Calcd for $C_{27}H_{28}BrO_2P$ [M^+]: 494.1010, Found 494.1015; IR (KBr) ν(cm^{-1}) : 3422, 2915, 2871, 1715, 1587, 1485, 1438, 1326, 1270, 1113.



8t2 **8t**, 79%

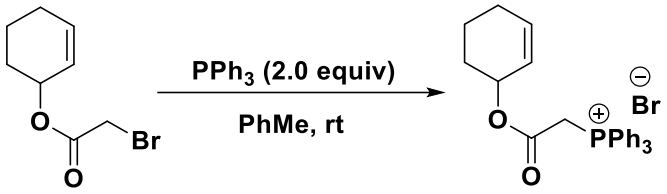
1,1-Dimethyl 2-(3-methylcyclohex-2-en-1-yl) ethene-1,1,2-tricarboxylate (8t): **8t2** (1.49 g, 3.0 mmol, 1.0 equiv) and dimethyl keto malonate (439 mg, 3.0 mmol, 1.0 equiv) were mixed in DCM (30 mL), and then cooled to 0 °C. A aqueous solution of NaOH (240 mg, 6.0 mmol, 2.0 equiv, 2N) was added dropwise into the solution. The reaction was stirred at 0 °C for 30 min, and then extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give the desired esters **8t (**670 mg, 79% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (s, 1H), 5.47 (s, 1H), 5.31 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.03– 1.89 (m, 2H), 1.78-1.75 (s, 3H), 1.70 (s, 3H), 1.65 – 1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 163.1, 162.7, 142.2, 137.7, 131.4, 118.9, 70.6, 53.2, 52.8, 29.8, 27.7, 23.7, 18.7; HRMS(EI) Calcd for $C_{14}H_{18}O_6$ [M^+]: 282.1103, Found 282.1106; IR (KBr) ν(cm^{-1}) : 2953, 1742, 1721, 1437, 1266, 1174.



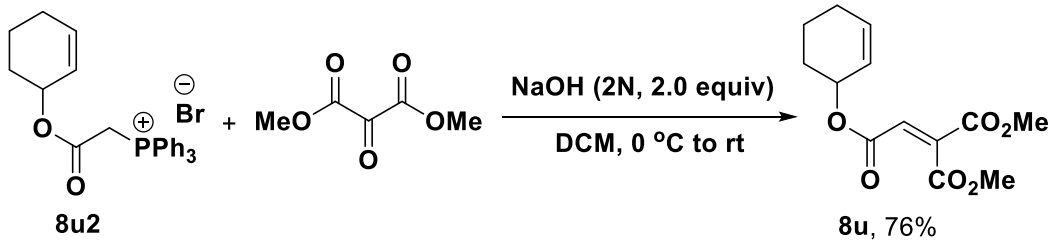
8u1, 86%

Cyclohex-2-en-1-yl 2-bromoacetate (8u1): To the mixture of 2-Cyclohexen-1-ol (491 mg, 5.0 mmol, 1.0 equiv), bromoacetic acid (834 mg, 6.0 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 122 mg, 1.0 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 1.24 g, 6.0 mmol, 1.2 equiv) in portions at 0 °C. After 30 min, the reaction mixture was filtered. The solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on silica

gel (Petroleum ether/ EtOAc = 50/1) to give the desired ester products **8u1** (942 mg, 86% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (d, *J* = 10.0 Hz, 1H), 5.70 (d, *J* = 8.8 Hz, 1H), 5.29 (s, 1H), 3.81 (s, 2H), 2.11 – 1.96 (m, 2H), 1.90 – 1.82 (m, 1H), 1.79-1.70 (m, 2H), 1.65-1.61 (m, 1H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 133.5, 124.6, 70.1, 27.9, 26.3, 24.7, 18.5; HRMS(EI) Calcd for $C_8H_{11}BrO_2$ [M^+]: 217.9942, Found 217.9950; IR (film) ν(cm^{-1}) : 3427, 2926, 2857, 1711, 1633, 1458, 1385, 1282, 1029.

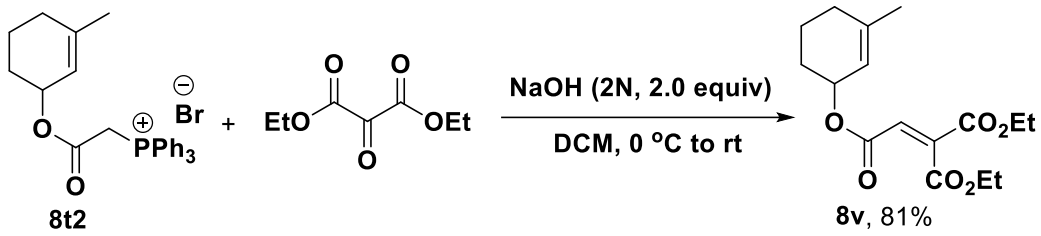


(2-(Cyclohex-2-en-1-yloxy)-2-oxoethyl)triphenylphosphonium bromide (8u2): The obtained ester **8u1** (0.8 g, 3.65 mmol, 1.0 equiv) and PPh_3 (1.92 g, 7.3 mmol, 2.0 equiv) were stirred in toluene (30 mL) at room temperature for 48 h. A white precipitate was formed from the reaction mixture. After filtered, the white solid was collected and dried at room temperature to give the desired product **8u2** (1.69 g, 96% yield). White solid; mp 137.1-137.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 6H), 7.80 – 7.76 (m, 3H), 7.69-7.65 (m, 6H), 5.85 (dt, *J* = 10.2 and 3.9 Hz, 1H), 5.64 – 5.50 (m, 2H), 5.40 – 5.36 (m, 1H), 5.08 (d, *J* = 4.7 Hz, 1H), 2.00 – 1.86 (m, 2H), 1.68-1.64 (m, 1H), 1.56-1.53 (m,1H), 1.50-1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.8 (d, $J_{c\text{-}p}$ = 3.9 Hz), 135.1(d, $J_{c\text{-}p}$ = 2.9 Hz), 134.0 (d, $J_{c\text{-}p}$ = 10.6 Hz), 130.2 (d, $J_{c\text{-}p}$ = 13.1 Hz), 123.7, 118.4, 117.5, 71.0, 33.4 (d, $J_{c\text{-}p}$ = 54.0 Hz), 27.6, 24.5, 18.2; ^{31}P NMR (242 MHz, $CDCl_3$) δ 20.83; HRMS(EI) Calcd for $C_{26}H_{26}BrO_2P$ [M^+]: 480.0854, Found 480.0838; IR (KBr) (cm^{-1}) : 3436, 3011, 2873, 2832, 1738, 1439, 1247, 1111, 1002, 915, 869.



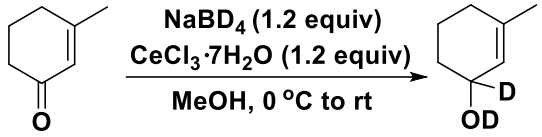
2-Cyclohex-2-en-1-yl 1,1-dimethyl ethene-1,1,2-tricarboxylate (8u): **8u2** (1.49 g, 3.1 mmol, 1.0 equiv) and dimethyl keto malonate (453 mg, 3.1 mmol, 1.0 equiv) were

mixed in DCM (30 mL), and then cooled to 0 °C. A aqueous solution of NaOH (240 mg, 6.0 mmol, 2.0 equiv, 2N) was added dropwise into the solution. The reaction was stirred at 0 °C for 30 min, and then extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4, After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give the desired esters **8u** (632 mg, 76% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.02 – 5.98 (m, 1H), 5.73 – 5.69 (m, 1H), 5.34 (d, *J* = 3.1Hz, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 2.13 – 1.96 (m, 2H), 1.92-1.84 (m, 1H), 1.81 – 1.71 (m, 2H), 1.68 – 1.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 163.1, 162.7, 137.9, 133.7, 131.3, 124.6, 69.8, 53.2, 52.9, 28.0, 24.8, 18.5; HRMS(EI) Calcd for $C_{13}H_{16}O_6$ [M^+]: 268.0947, Found 268.0960; IR (KBr) (cm^{-1}) : 3425, 2953, 1744, 1723, 1438, 1367, 1268, 1173, 1069, 1011, 910.



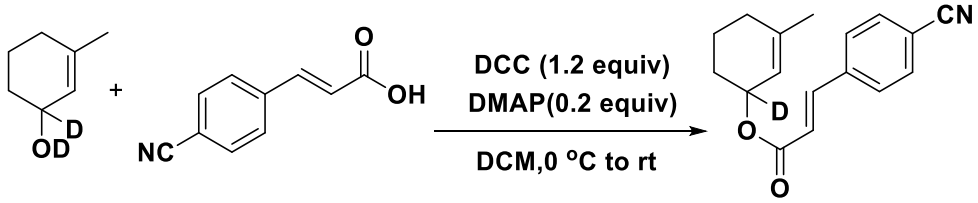
1,1-Diethyl 2-(3-methylcyclohex-2-en-1-yl) ethene-1,1,2-tricarboxylate (8v): **8t2** (1.49 g, 3.0 mmol, 1.0 equiv) and diethyl keto malonate (522 mg, 3.0 mmol, 1.0 equiv) were mixed in DCM (30 mL), and then cooled to 0 °C. A aqueous solution of NaOH (240 mg, 6.0 mmol, 2.0 equiv, 2N) was added dropwise into the solution. The reaction was stirred at 0 °C for 30 min, and then extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 30/1) to give the desired esters **8v** (754 mg, 81% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 1H), 5.46 (s, 1H), 5.31 (s, 1H), 4.35-4.24 (m, 4H), 2.02 – 1.93 (m, 2H), 1.88-1.74 (m, 3H), 1.69 (s, 3H), 1.33 (t, *J* = 7.1Hz, 3H), 1.29 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 163.2, 162.3, 142.1, 138.4, 130.6, 119.0, 70.5, 62.3, 61.9, 29.8, 27.7, 23.7, 18.7, 13.9, 13.8; HRMS(EI) Calcd for $C_{16}H_{22}O_6$ [M^+]: 310.1416, Found 310.1405; IR (film) ν(cm^{-1}) : 2940, 1721, 1376, 1254, 1183, 1164, 1067, 1023, 913.

4. Preparation of deuterated substrates D-8p and D-8j



D-8p1, 87%

Deuterated-3-Methylcyclohex-2-enol (D-8p1): To the solution of 3-Methyl-2-cyclohexen-1-one (330 mg, 3.0 mmol, 1.0 equiv) and Cerium(III) chloride heptahydrate (1.34 g, 3.6 mmol, 1.2 equiv) in MeOH (20 mL)was added $NaBD_4$ (151 mg, 3.6 mmol, 1.2 equiv) at 0 °C, the reaction was stirred at 0 °C for 30 min. The reaction mixture was extracted by DCM (15 mL x 3), the combined organic phase was dried over anhydrous Na_2SO_4, After evaporation of the solvent under reduced pressure (the temperature should be kept below 20 °C), the residue light yellow oil was pure enough used for next step without further purification (994 mg, 87% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 (s, 1H), 1.96-1.87 (m, 2H), 1.78-1.71 (m, 3H), 1.67 (s, 3H), 1.57-1.55 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 124.1, 65.79, 65.54, 65.32, 65.11, 31.4, 30.0, 23.6, 18.9; HRMS(EI) Calcd for $C_7H_{10}D_2O$ [M^+]: 114.1014, Found 114.1013; IR (film) (cm^{-1}): 3331, 2934, 1447, 1339, 1171, 1095, 1069, 1005, 942.



D-8p1 **D-8j**, 89%

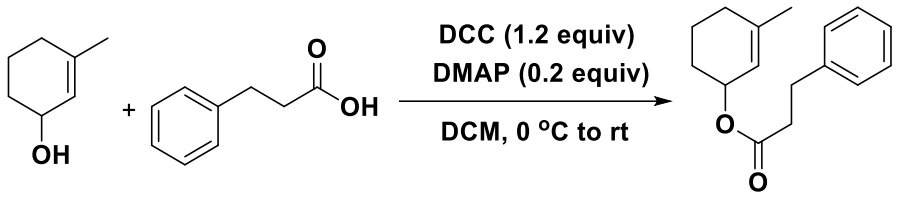
Deuterated-(*E*)-3-Methylcyclohex-2-en-1-yl 3-(4-cyanophenyl)acrylate (D-8j): To the mixture of **D-8p1** (228 mg, 2.0 mmol, 1.0 equiv), *(E)*-3-(4-cyanophenyl)acrylic acid (416 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica

gel (Petroleum ether/ EtOAc = 30/1) to give **D-8j** (478 mg, 89 % yield). White solid; mp 82.4-82.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68– 7.66 (m, 3H), 7.63-7.59 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 5.54 (s, 1H), 2.06 – 1.93 (m, 2H), 1.84-1.78 (m, 3H), 1.74 (s, 3H), 1.70-1.65 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 141.8, 141.6, 138.8, 132.5, 128.3, 122.4, 119.5, 118.3, 113.2, 69.4, 69.2, 69.0, 68.7, 29.9, 27.8, 23.7, 18.9; HRMS(EI) Calcd for $C_{17}H_{16}DNO_2$ [M^+]: 268.1322, Found 268.1313; IR (KBr) ν(cm^{-1}) : 2938, 2227, 1708, 1638, 1329, 1319, 1207, 1165, 1085, 901, 829.

D-8p1 **D-8p**, 93%

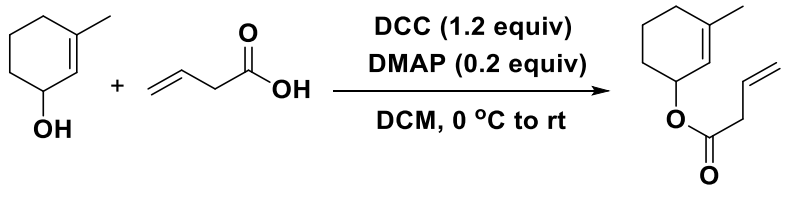
Deuterated-3-Methylcyclohex-2-en-1-yl acrylate (D-8p): To the mixture of **D-8p1** (228 mg, 2.0 mmol, 1.0 equiv) and Et_3N (405 mg, 4.0 mmol, 2.0 equiv) in DCM (20 mL) was added acryloyl chloride (217 mg, 2.4 mmol, 1.2 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 30 min. Then the reaction was quenched by water, extracted by DCM (15 mL x 3), the combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **D-8p** (311 mg, 93% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.38 (dd, *J* = 17.3 and 1.1 Hz, 1H), 6.11 (dd, *J* = 17.3, 10.4 Hz, 1H), 5.78 (dd, *J* = 10.4 and 1.2 Hz, 1H), 5.49 (s, 1H), 2.03 – 1.89 (m, 2H), 1.80 – 1.72 (m, 3H), 1.71 (s, 3H), 1.66-1.59 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 141.3, 130.2, 129.1, 119.8, 68.92, 68.77, 68.54, 68.31, 29.9, 27.9, 23.7, 19.0; HRMS(EI) Calcd for $C_{10}H_{13}DO_2$ [M^+]: 167.1057, Found 167.1051; IR (film) ν(cm^{-1}): 2935, 1720, 1405, 1296, 1209, 1167, 1042, 927.

5. Preparation of structurally similar substrates (10-17)



8p1 **10**, 86%

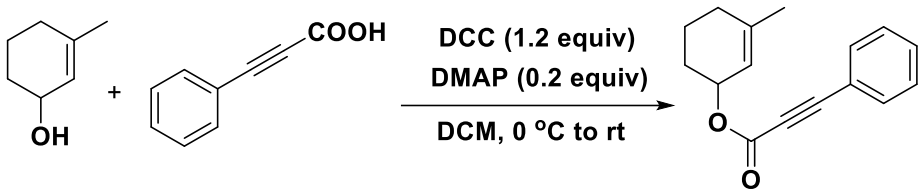
3-Methylcyclohex-2-en-1-yl 3-phenylpropanoate (10): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), 3-phenylpropanoic acid (360 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **10** (420 mg, 86% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.30-7.28 (m, 3H), 5.52 (s, 1H), 5.34 (s, 1H), 3.04 (t, *J* = 7.9 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.09-1.96 (m, 2H), 1.87-1.81 (m, 2H), 1.79 (s, 3H), 1.75 – 1.67(m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 141.0, 140.5, 128.4, 128.3, 126.1, 119.9, 68.8, 36.2, 31.1, 29.8, 27.9, 23.7, 19.0; HRMS(EI) Calcd for $C_{16}H_{20}O_2$ [M^+]: 244.1463, Found 244.1460; IR (KBr) ν (cm^{-1}) : 2936, 2867, 1729, 1497, 1452, 1377, 1288, 1180, 1160, 1074, 976, 914.



8p1 **11**, 51%

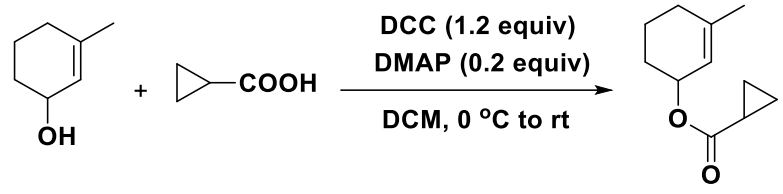
Cyclohex-2-en-1-yl but-3-enoate (11): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), but-3-enoic acid (207 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give

11(185 mg, 51% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99-5.84 (m, 1H), 5.44 (s, 1H), 5.24 (s, 1H), 5.15 (d, *J* = 4.0 Hz, 1H), 5.11 (s, 1H), 3.05 (d, *J* = 4.0 Hz, 2H), 1.99-1.83 (m, 2H), 1.77-1.70 (m, 3H), 1.68 (s, 3H), 1.66 – 1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 141.1, 130.5, 119.8, 118.2, 69.0, 39.4, 29.8, 27.9, 23.7, 18.9; HRMS(EI) Calcd for $C_{11}H_{16}O_2$ [M^+]: 180.1150, Found 180.1148; IR (film) ν(cm^{-1}): 2938, 1732, 1440, 1253, 1180, 988, 916.



8p1 **12**, 62%

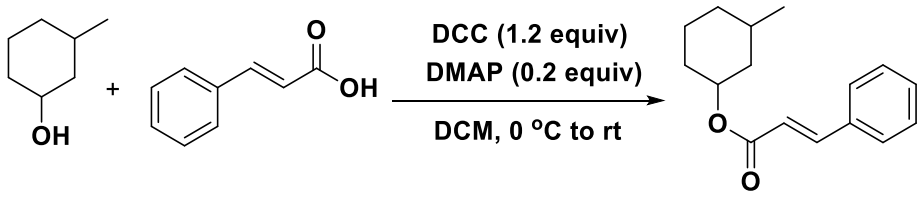
3-Methylcyclohex-2-en-1-yl 3-phenylpropiolate (12): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), 3-phenylpropiolic acid (351 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **12** (298 mg, 62% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.56 (m, 2H), 7.45-7.41 (m, 1H), 7.37-7.33 (m, 2H), 5.54 (s, 1H), 5.39 (s, 1H), 2.04-1.91 (m, 2H), 1.85-1.79 (m, 3H), 1.73 (s, 3H), 1.69-1.63 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 142.2, 132.9, 130.4, 128.5, 119.8, 119.1, 85.7, 81.0, 70.9, 29.8, 27.8, 23.7, 18.8; HRMS(EI) Calcd for $C_{16}H_{16}O_2$ [M^+]: 240.1150, Found 240.1153; IR (KBr) ν(cm^{-1}) : 2936, 2216, 1704, 1491, 1444, 1282, 1192, 1069, 972, 907, 757, 690.



8p1 **13**, 89%

3-Methylcyclohex-2-en-1-yl cyclopropanecarboxylate (13): To the mixture of **8p1** (224 mg, 2.0 mmol, 1.0 equiv), cyclopropanecarboxylic acid (207 mg, 2.4 mmol, 1.2

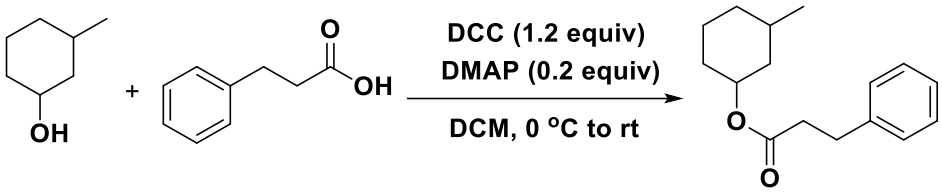
equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **13** (321mg, 89% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.43 (s, 1H), 5.21 (s, 1H), 1.98-1.88 (m, 2H), 1.75-1.70 (m, 2H), 1.68 (s, 3H), 1.66-1.63 (m, 1H), 1.62-1.58 (m, 1H), 1.57 – 1.53 (m, 1H), 0.96-0.93 (m, 2H), 0.81-0.78 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 140.8, 120.0, 68.5, 29.8, 27.9, 23.7, 18.9, 13.1, 8.3, 8.2; HRMS(EI) Calcd for $C_{11}H_{16}O_2$ [M^+]: 180.1150, Found 180.1151; IR (KBr) ν (cm^{-1}) : 3339, 2943, 2832, 1454, 1115, 1032.



14 , 80%

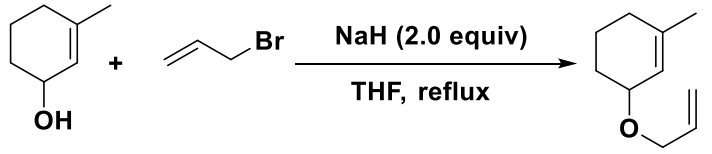
3-Methylcyclohexyl cinnamate (14): To the mixture of 3-methylcyclohexan-1-ol (228 mg, 2.0 mmol, 1.0 equiv), cinnamic acid (356 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **14** (391 mg, 80% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69-7.65 (m, 1.70 H), 7.54-7.51 (m, 3.47 H), 7.39-7.36 (m, 5.00 H), 6.47-6.41 (m, 1.61 H), 5.21-5.20 (m, 0.57 H), 4.86-4.81 (m, 1.00 H), 2.05-2.03 (d, *J* = 12.2 Hz, 2.14 H), 1.91 – 1.78 (m, 3.26 H), 1.73-1.46 (m, 4.92 H), 1.41-1.20 (m, 3.03 H), 1.06 (q, *J* = 11.6 Hz, 1.27 H), 1.03-0.96 (m, 1.01 H), 0.95 (d, *J* = 6.5 Hz, 3.15 H), 0.91 (d, *J* = 6.7 Hz, 1.82 H), 0.85 (qd, *J* = 12.7 and 3.6 Hz, 1.29 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.37, 166.36, 144.2, 144.1, 134.44, 134.42, 130.0, 128.8, 128.0, 118.9, 118.7, 73.3, 70.3, 40.5, 38.4,

34.1, 33.9, 31.5, 31.3, 29.9, 27.1, 23.9, 22.2, 22.1, 20.7; HRMS(EI) Calcd for $C_{16}H_{20}O_2$ [M^+]: 244.1463, Found 244.1457; IR (KBr) (cm^{-1}) : 2932, 2864, 1710, 1639, 1451, 1309, 1276, 1201, 1176, 1002, 979, 767.



15 , 93%

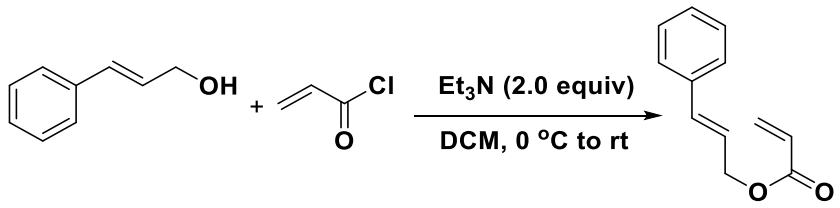
3-Methylcyclohexyl 3-phenylpropanoate (15): To the mixture of 3-methylcyclohexan-1-ol (228 mg, 2.0 mmol, 1.0 equiv), 3-phenylpropanoic acid (360 mg, 2.4 mmol, 1.2 equiv) and 4-dimethylaminopyridine (DMAP, 49 mg, 0.4 mmol, 0.2 equiv) in DCM (20 mL) was added dicyclohexylcarbodiimide (DCC, 495 mg, 2.4 mmol, 1.2 equiv) in portions at 0 °C. The reaction was stirred at room temperature for 30 min. The reaction mixture was filtered, after evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **15** (458 mg, 93% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 3.22 H), 7.30-7.28 (m, 4.03 H), 5.16 – 5.14 (m, 0.6 H), 4.82 – 4.74 (m, 1.01 H), 3.07-3.01 (m, 4.01 H), 2.74-2.66 (m, 4.06 H), 2.01-1.98 (d, *J* = 11.9 Hz, 2.55 H), 1.86 – 1.69 (m, 6.04 H), 1.62-1.53 (m, 2.78 H), 1.52-1.45 (m, 0.68 H), 1.44-1.35 (m, 1.65 H), 1.31-1.18 (m, 2.27 H), 1.07-1.04 (m, 1.34 H), 1.00 (d, *J* = 6.6 Hz, 3.84 H), 0.94 (d, *J* = 6.4 Hz, 1.77 H), 0.91-0.84 (m, 1.57 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.34, 172.32, 140.6, 140.5, 128.4, 128.3, 128.2, 126.1, 73.2, 70.3, 40.4, 38.3, 36.2, 34.1, 33.9, 31.4, 31.3, 31.1, 31.0, 29.8, 27.0, 23.9, 22.2, 22.1, 20.6; HRMS(EI) Calcd for $C_{16}H_{22}O_2$ [M^+]: 246.1620, Found 246.1614; IR (KBr) ν(cm^{-1}) : 2932, 2864, 1732, 1496, 1453, 1360, 1259, 1238, 1178, 1093, 1042, 989, 920.



8p1 **16**, 79%

3-(Allyloxy)-1-methylcyclohex-1-ene (16): NaH (160 mg, 60%, 4.0 mmol, 2.0 equiv) was added into the solution of **8p1** (224.3 mg, 2.0 mmol, 1.0 equiv) in THF (20 mL),

the mixture was reflux for 30 min. 3-Bromoprop-1-ene (484 mg, 4.0 mmol, 2.0 equiv) was added into the reaction mixture and reflux for additional 2 hours. Then the reaction mixture was quenched by saturated NH_4Cl (aq), and extracted by DCM (15 mL×3). The combined organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **16** (240 mg, 79% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97-5.87 (m, 1H), 5.50 (d, *J* = 1.1Hz, 1H), 5.25 (dd, *J* = 17.2 and 1.4 Hz, 1H), 5.12 (dd, *J* = 10.3 and 0.7 Hz, 1H), 4.06-3.95 (m, 2 H), 3.85 (s, 1H), 1.97-1.85 (m, 2H), 1.78 – 1.71 (m, 2H), 1.67 (s, 3H), 1.64 – 1.59 (m, 1H), 1.56-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 135.5, 122.1, 116.2, 72.6, 69.0, 30.1, 27.9, 23.6, 19.2; HRMS(EI) Calcd for $C_{10}H_{17}O$ $[M+H]^+$: 153.1279, Found 153.1274 ; IR (KBr) ν (cm^{-1}) : 3468, 2936, 1639, 1449, 1082, 1016, 916.



17, 93%

Cinnamyl acrylate[2] (17): To the mixture of Cinnamyl alcohol (268 mg, 2.0 mmol, 1.0 equiv) and Et_3N (405 mg, 4.0 mmol, 2.0 equiv) in DCM (30 mL) was added acryloyl chloride (217 mg, 2.4 mmol, 1.2 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 30 min. Then the reaction was quenched by water, extracted by DCM (15 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (Petroleum ether/ EtOAc = 50/1) to give **17** (350 mg, 93% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 15.9 Hz, 1H), 6.48 (dd, *J* = 17.3 and 1.2 Hz, 1H), 6.34 (dt, *J* = 15.9 and 6.4 Hz, 1H), 6.19 (dd, *J* = 17.3 and 10.4 Hz, 1H), 5.86 (dd, *J* = 10.4 and 1.2 Hz, 1H), 4.84 (dd, *J* = 6.4 and 1.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 136.1, 134.2, 130.9, 128.5, 128.3, 128.0, 126.5, 123.0, 65.0.

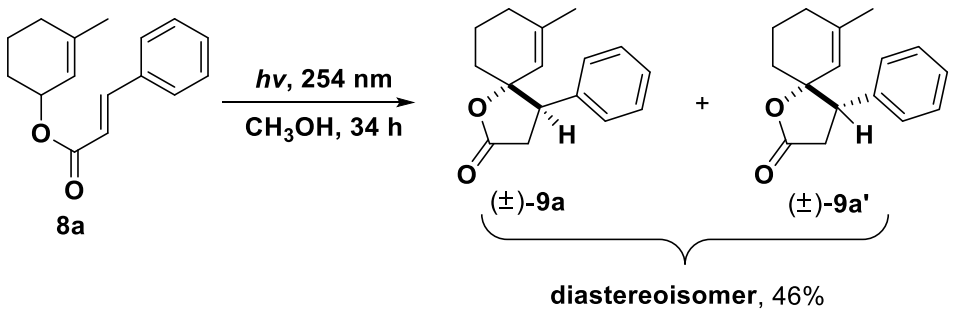
Reference:

1. *a*) Klaus Daniel Umland, Adeline Palisse, Timm T. Haug, Stefan F. Kirsch. *Angewandte Chemie, International Edition.* **2011**, *50*, 9965-9968; *b*) Monica Nardi,Giovanni Sindona, Paola Costanzo, Manuela Oliverio, Antonio Procopio. *Tetrahedron*. **2015**, *71*, 1132-1135; *c*) Gary B. Fisher, Joseph C. Fuller, John Harrison, Salvador G. Alvarez, Elizabeth R. Burkhardt, Christian T. Goralski, and Bakthan Singaram. *Journal of Organic Chemistry*. **1994**, *59*, 6378-6385.
2. *a)* Maria Kalyva, Alexandros L. Zografos, Era Kapourani, Evaggelos Giambazolias, Laurent Devel, Athanasios Papakyriakou, Vincent Dive, Yannis G. Lazarou, and Dimitris Georgiadis. *Chemistry - A European Journal*, **2015**, 21, 3278-3289;

   b) Daiki Nakatake, Ryo Yazaki, and Takashi Ohshima. *Eur. J. Org. Chem.* **2016**, 3696–3699.

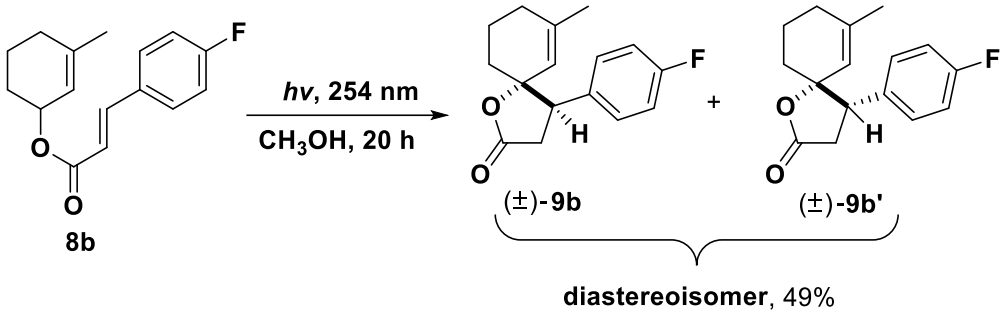
Typical Procedure for Photo-Promoted Hydrogen Abstraction and Cyclization of Allyl Acrylic Esters

To a quartz Schlenk tube (15 mL) was added allyl acrylic esters **8** (0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9**.

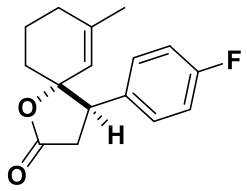


7-Methyl-4-phenyl-1-oxaspiro[4.5]dec-6-en-2-one (±)-9a and (±)-9a': To a quartz Schlenk tube (15 mL) was added **8a** (24.2 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to

ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9a and (±)-9a' (**11.1 mg, 46% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.31 (m, 3.88 H), 7.30-7.27 (m, 2.01 H), 7.18-7.17 (m, 4.17 H), 5.54 (s, 1.00 H), 5.14 (s, 0.67 H), 3.58 (t, *J* = 8.6 Hz, 1.05 H), 3.48 (t, *J* = 8.6 Hz, 0.73 H), 3.02 – 2.91 (m, 3.80 H), 2.05 – 2.02 (m, 0.79 H), 1.95 – 1.88 (m, 2.36 H), 1.88-1.84 (m, 1.08 H), 1.83-1.79 (m, 1.04 H), 1.77 (s, 3.78 H), 1.75-1.74 (m, 0.54 H), 1.72-1.64 (m, 2.22 H), 1.62-1.58 (m, 1.31 H), 1.54 (s, 2.39 H), 1.40-1.35 (m, 1.30 H), 1.33-1.28 (m, 0.83 H), 1.24-1.19 (m, 1.34 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 175.7, 143.8, 142.2, 137.3, 136.8, 128.6, 128.5, 128.2, 127.8, 127.53, 127.47, 122.8, 119.3, 87.4, 87.2, 50.954, 50.950, 35.4, 34.4, 34.2, 29.8, 29.6, 29.5, 23.8, 23.7, 19.6, 18.7; HRMS(EI) Calcd for $C_{16}H_{18}O_2$ [M^+]: 242.1307, Found 242.1311; IR (KBr) ν(cm^{-1}) : 3429, 2936, 1768, 1453, 1270, 1240, 1230, 1155, 1078, 937.

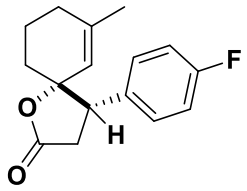


4-(4-Fluorophenyl)-7-methyl-1-oxaspiro[4.5]dec-6-en-2-one (±)-9b and (±)-9b' : To a quartz Schlenk tube (15 mL) was added 8**b** (26.0 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9b and (±)-9b' (**12.7 mg, 49% yield).



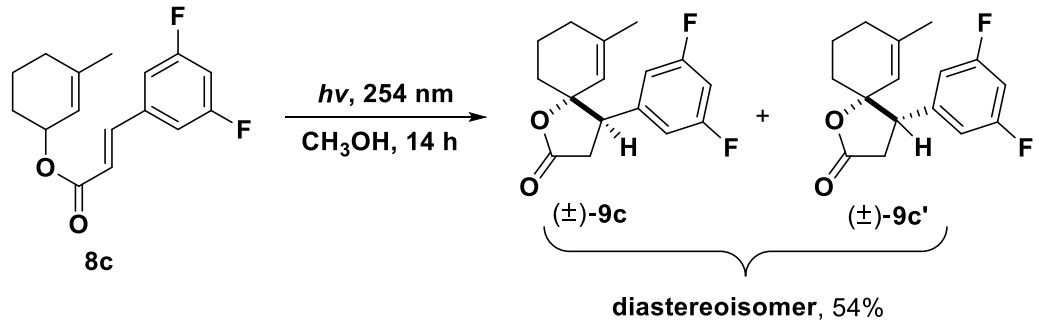
(±)-**9b**

(±)-9b: White solid; mp 64.9-65.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.4 and 5.4 Hz, 2H), 7.02 (t, *J* = 8.5 Hz, 2H), 5.10 (s, 1H), 3.47 (t, *J* = 8.5 Hz, 1H), 3.00-2.90 (m, 2H), 2.04 – 2.01 (m, 1H), 1.94 – 1.91 (m, 1H), 1.86-1.77 (m, 2H), 1.71 – 1.66 (m, 1H), 1.65-1.61 (s, 1H), 1.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.6, 162.0 (d, J_{C-F} = 244.9 Hz), 142.6, 133.1 (d, J_{C-F} = 3.2 Hz), 129.6 (d, J_{C-F} = 8.0 Hz), 119.2, 115.4 (d, J_{C-F} = 21.2 Hz), 87.3, 50.3, 35.5, 34.4, 29.5, 23.8, 19.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.81; HRMS(EI) Calcd for $C_{16}H_{18}FO_2$ $[M + H]^+$: 261.1291, Found 261.1285; IR (KBr) ν(cm^{-1}) : 2933, 1770, 1606, 1512, 1429, 1379, 1228, 1163, 1082, 937.

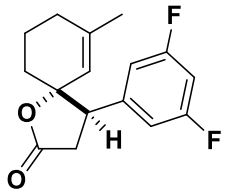


(±)-**9b'**

(±)-9b': White solid; mp 85.2-85.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 8.4 and 5.4 Hz, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 5.51 (s, 1H), 3.56 (t, *J* = 9.1 Hz, 1H), 2.93 (d, *J* = 9.1 Hz, 2H), 1.96-1.92 (m, 1H), 1.77 (s, 3H), 1.70-1.65 (m, 1H), 1.62-1.58 (m, 1H) 1.42 – 1.37 (m, 1H),1.33-1.28 (m, 1H), 1.23 – 1.16 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.3, 162.1(d, J_{C-F} = 245.1 Hz), 144.1, 132.6 (d, J_{C-F} = 3.2 Hz), 129.3 (d, J_{C-F} = 8.0 Hz), 122.6, 115.5 (d, J_{C-F} = 21.2 Hz), 87.0, 50.3, 34.3, 29.72, 29.66, 23.8, 18.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.63; HRMS(EI) Calcd for $C_{16}H_{18}FO_2$ $[M + H]^+$: 261.1291, Found 261.1285; IR (KBr) ν(cm^{-1}) : 2920, 1770, 1606, 1514, 1427, 1228, 1076, 931.

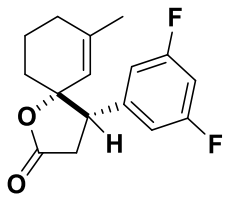


4-(3,5-Difluorophenyl)-7-methyl-1-oxaspiro[4.5]dec-6-en-2-one (±)-9c and (±)-9c': To a quartz Schlenk tube (15 mL) was added 8**c** (27.8 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9c and (±)-9c'** (15.0 mg, 54% yield).



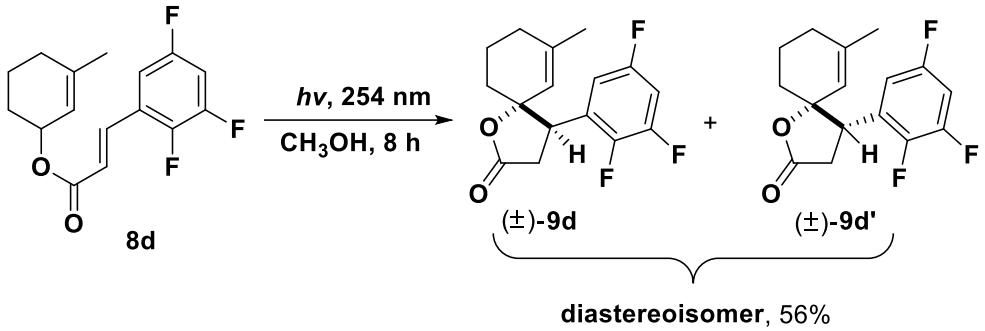
(±)-9c

(±)-9c: White solid; mp 113.2-113.5 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.77 – 6.68 (m, 3H), 5.09 (s, 1H), 3.46 (t, *J* = 8.4 Hz, 1H), 3.00 (dd, *J* = 17.7 and 8.4 Hz, 1H), 2.89 (dd, *J* = 17.6 and 8.3 Hz, 1H), 2.04 – 2.01 (m, 1H), 1.97 – 1.94 (m, 1H), 1.91 – 1.83 (m, 3H), 1.72-1.67 (m, 1H), 1.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 162.9 (dd, J_{C-F} = 247.6 and 12.7 Hz), 143.2, 141.5 (t, J_{C-F} = 4.0 Hz), 118.8, 111.2 (dd, J_{C-F} = 20.1 and 5.2 Hz), 103.1 (t, J_{C-F} = 25.0 Hz), 87.0, 50.6, 35.2, 34.5, 29.5, 23.8, 19.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -109.06; HRMS(EI) Calcd for $C_{16}H_{17}F_2O_2$ [M + H]$^+$: 279.1197, Found 279.1191; IR (KBr) (cm^{-1}) : 2922, 1755, 1599, 1456, 1363, 1246, 1163, 1117, 931 .

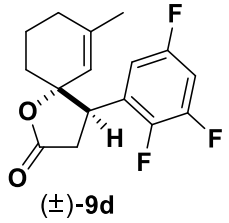


(±)-9c'

(±)-9c': White solid; mp128.0-128.2 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.78-6.69 (m, 3H), 5.50 (s, 1H), 3.56 (t, *J* = 9.1 Hz, 1H), 2.96-2.88 (m, 2H), 1.99-1.95 (m, 1H),1.85-1.82 (m, 1H), 1.79 (s, 3H), 1.74 – 1.67 (m, 1H), 1.64 – 1.62 (m, 1H), 1.48 – 1.43 (m, 1H), 1.20 (td, *J* = 3.2 and 0.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 163.0 (dd, J_{C-F} =247.8 and 12.9 Hz), 144.8, 140.8 (t, J_{C-F} = 8.9 Hz), 122.3, 110.8 (dd, J_{C-F} = 20.0 and 5.3 Hz), 103.2 (t, J_{C-F} = 25.1 Hz), 86.6, 50.7, 33.9, 29.7, 23.9, 18.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -108.80; HRMS(EI) Calcd for $C_{16}H_{16}F_2O_2$ [M^+] : 278.1118, Found 278.1117; IR (KBr) ν(cm^{-1}) : 3427, 2926, 1768, 1626, 1599, 1458, 1242, 1116, 954, 926.

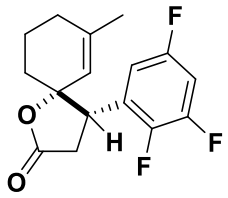


7-Methyl-4-(2,3,5-trifluorophenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9d and (±)-9d': To a quartz Schlenk tube (15 mL) was added 8**d** (29.6 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9d and (±)-9d'** (17.2 mg, 56% yield).



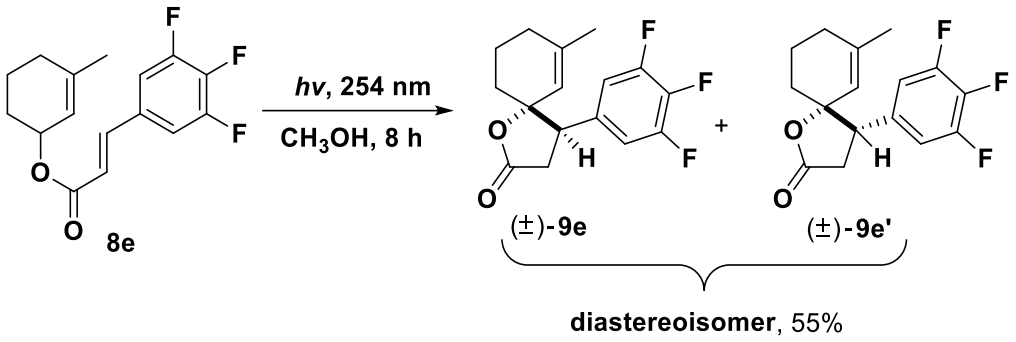
(±)-9d : White solid; mp 106.1-106.4 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.90 – 6.85 (m, 1H), 6.72-6.69 (m, 1H), 5.01 (s, 1H), 3.86 (dd, *J* = 8.8 and 6.2 Hz, 1H), 3.06 (dd, *J* =

17.9 and 8.9 Hz, 1H), 2.84 (dd, *J* = 17.9 and 6.2 Hz, 1H), 2.02-1.95 (m, 2H), 1.92-1.86 (m, 3H), 1.77-1.69 (m, 1H), 1.59 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.89, 157.6 (ddd, J_{C-F} = 244.7, 10.6 and 3.2 Hz), 150.5 (ddd, J_{C-F} = 250.2, 15.4 and 13.0 Hz), 144.4 (ddd, J_{C-F} =241.9, 12.8 and 4.0 Hz), 143.3, 128.9 (dd, J_{C-F} = 12.3 and 8.3 Hz), 118.9, 109.8 (dt, J_{C-F} = 23.9 and 3.3 Hz), 104.8 (dd, J_{C-F} = 27.1 and 20.8 Hz), 87.1, 43.2, 34.7, 34.5, 29.4, 23.7, 19.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.20 (dd, J_{C-F} = 14.6 and 3.3 Hz), -132.59 (dd, J_{C-F} = 20.9 and 3.3 Hz), -145.25 (dd, J_{C-F} = 20.9 and 14.6 Hz); HRMS(EI) Calcd for $C_{16}H_{16}F_3O_2$ [M + H]$^+$: 297.1102, Found 297.1096; IR (KBr) ν(cm^{-1}) : 2935, 1778, 1635, 1500, 1346, 1232, 1011.

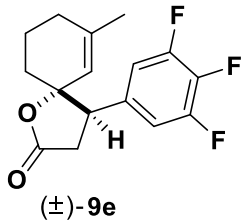


(±)-**9d'**

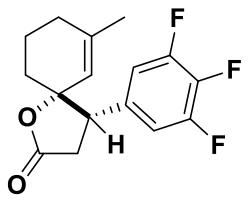
(±)-9d' : White solid; mp 93.7-94.0 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.91-6.85 (m, 1H), 6.79 – 6.60 (m, 1H), 5.52 (s, 1H), 3.86 (t, *J* = 8.1 Hz, 1H), 3.05 (dd, *J* = 17.7 and 8.6 Hz, 1H), 2.86 (dd, *J* = 17.7 and 7.5 Hz, 1H), 1.98-1.95 (m, 1H), 1.87 – 1.81 (m, 1H), 1.75 (s, 3H), 1.73-1.71 (m, 1H), 1.69-1.66 (m, 1H), 1.56-1.52 (m, 1H), 1.27 – 1.22 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 157.6 (ddd, J_{C-F} = 245.0, 10.5 and 2.9 Hz), 149.8 (ddd, J_{C-F} = 250.4, 15.2 and 12.9 Hz), 145.6 (ddd, J_{C-F} = 242.9, 13.0 and 4.1 Hz), 143.7, 128.1(dd, J_{C-F} = 12.9 and 8.4 Hz), 122.0, 110.2 (dt, J_{C-F} = 24.0 and 3.2 Hz), 104.9 (dd, J_{C-F} = 27.1 and 20.8 Hz), 86.3, 44.0, 34.5, 30.2, 29.6, 23.7, 18.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.10 (dd, J_{C-F} = 14.6 and 3.4 Hz), -132.08 (dd, J_{C-F} = 20.9 and 3.4 Hz), -144.70 (dd, J_{C-F} = 20.9 and 14.7 Hz); HRMS(EI) Calcd for $C_{16}H_{15}F_3O_2$ [M$^+$]: 296.1024, Found 296.1028; IR (KBr) ν(cm^{-1}) : 2941, 1774, 1608, 1496, 1369, 1234, 1126, 1003, 926.



7-Methyl-4-(3,4,5-trifluorophenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9e and (±) -9e': To a quartz Schlenk tube (15 mL) was added 8**e** (29.6 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9e and (±)-9e'** (16.3 mg, 55% yield).

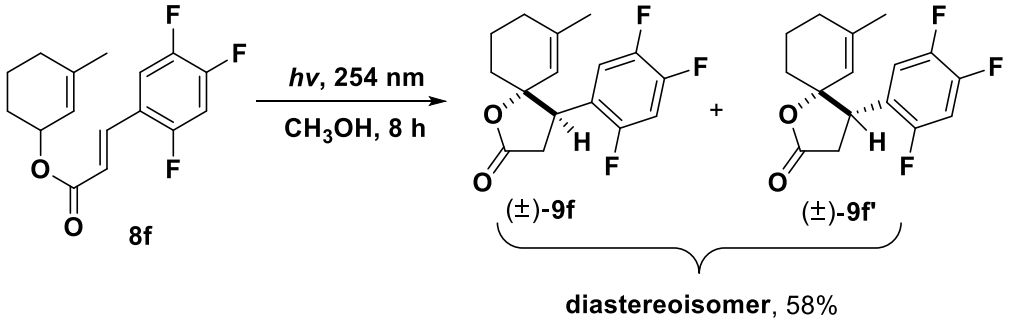


(±)-9e: White solid; mp 106.3-106.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83-6.78 (m, 2H), 5.06 (s, 1H), 3.41 (t, *J* = 8.4 Hz, 1H), 2.99 (dd, *J* = 17.6 and 8.5 Hz, 1H), 2.84 (dd, *J* = 17.6 and 8.3 Hz, 1H), 2.04 – 1.94 (m, 2H), 1.88-1.81 (m, 3H), 1.71 – 1.67 (m, 1H), 1.61 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.62, 151.0 (ddd, J_{C-F} = 249.2 and 9.8 and 4.1 Hz), 143.5, 139.0 (dt, J_{C-F} = 250.9 and 15.1 Hz), 134.0-133.9 (m, 1C), 118.5, 112.3 (dd, J_{C-F} = 16.8 and 4.5 Hz), 86.8, 50.2, 35.2, 34.4, 29.5, 23.8, 19.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -133.37 (dd, *J*= 20.2 and 8.2 Hz), -161.05 (t, *J*= 20.2 Hz); HRMS(EI) Calcd for $C_{16}H_{16}F_3O_2$ $[M + H]^+$: 297.1102, Found 297.1096; IR (KBr) ν(cm^{-1}) : 2945, 1755, 1620, 1533, 1452, 1338, 1246, 1039, 931.

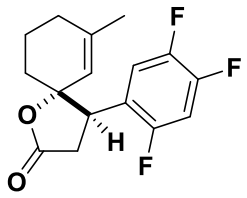


(±)-9e'

(±)-9e': White solid; mp 144.3-144.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83-6.80 (m, 2H), 5.48 (s, 1H), 3.51 (t, *J* = 2.2Hz, 1H), 2.95-2.83 (m, 2H), 1.99-1.96 (m, 1H), 1.85 – 1.82 (m, 1H), 1.79 (s, 3H), 1.75-1.67 (m, 1H), 1.62-1.61 (m, 1H), 1.49-1.44 (m, 1H), 1.20-1.15 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.3, 151.1 (ddd, J_{C-F} = 249.5, 9.9 and 4.2 Hz), 145.1, 139.0 (dt, J_{C-F} = 250.9 and 15.1 Hz), 133.3-133.2 (m, 1C), 122.0, 112.0 (dd, J_{C-F} = 16.7 and 4.5 Hz), 86.4, 50.3, 33.9, 29.66, 29.65, 23.8, 18.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -133.12 (dd, *J*= 19.2 and 7.3 Hz), -160.95 (t, *J*= 19.9 Hz); HRMS(EI) Calcd for $C_{16}H_{16}F_3O_2$ $[M + H]^+$: 297.1102, Found 297.1096; IR (KBr) ν(cm^{-1}) : 2947, 1763, 1620, 1533, 1448, 1365, 1336, 1240, 1038.

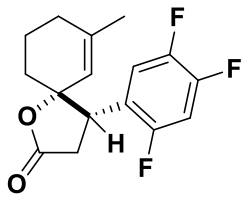


7-Methyl-4-(2,4,5-trifluorophenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9f and (±)-9f': To a quartz schlenk tube (15 mL) was added **8f** (29.6 mg, 0.1 mmol) and CH_3OH (10 mL), the schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9f and (±)-9f'** (17.2 mg, 58% yield).



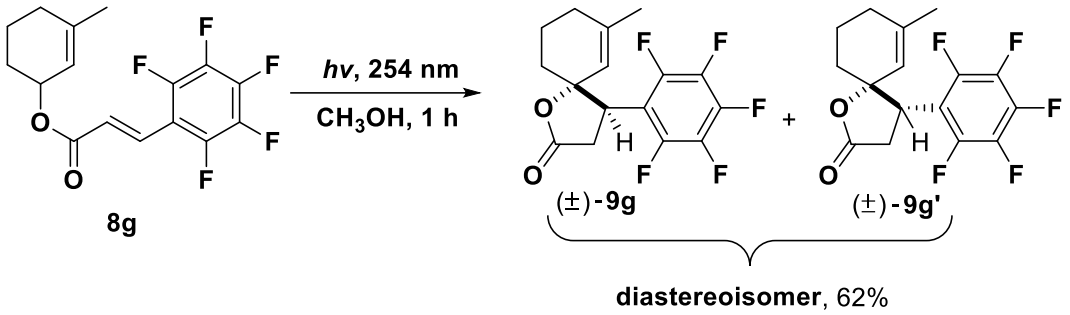
(±)-**9f**

(±)-9f: White solid; mp 113.6-113.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 – 6.99 (m, 1H), 6.95-6.91 (m, 1H), 5.03 (s, 1H), 3.77 (d, *J* = 8.2 Hz, 1H), 3.04 (dd, *J* = 17.8 and 8.9 Hz, 1H), 2.83 (dd, *J* = 17.8 and 6.6 Hz, 1H), 2.00-1.95 (m, 2H), 1.87 – 1.84 (m, 3H), 1.74 – 1.68 (m, 1H), 1.59 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 155.7 (ddd, J_{C-F} = 243.5, 9.2 and 2.4 Hz) ,149.2 (dt, J_{C-F} = 250.5 and 13.7 Hz), 146.8 (ddd, J_{C-F} = 244.1, 12.2 and 3.4 Hz) , 143.2, 121.9 (dt, J_{C-F} = 19.8 and 5.4 Hz), 118.9, 116.5 (dd, J_{C-F} = 19.8 and 5.4 Hz), 105.8 (dd, J_{C-F} = 29.1 and 20.5 Hz), 87.2, 43.0, 34.7, 34.4, 29.4, 23.7, 19.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.79, -133.90 (t, *J*= 10.3 Hz), -141.45 (d, *J*= 8.9 Hz); HRMS(EI) Calcd for $C_{16}H_{16}F_3O_2$ $[M + H]^+$: 297.1102, Found 297.1096; IR (film) ν(cm^{-1}): 2939, 1751, 1630, 1508, 1427, 1336, 1242, 1163, 1080, 937.

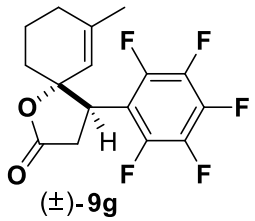


(±)-**9f'**

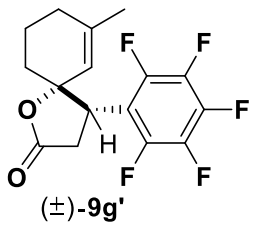
(±)-9f': White solid; mp 100.6-100.9 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03-6.99 (m, 1H), 6.97-6.92 (m, 1H), 5.50 (s, 1H), 3.78 (t, *J* = 8.1 Hz, 1H), 3.03 (dd, *J* = 17.6 and 8.6 Hz, 1H), 2.85 (dd, *J* = 17.6 and 7.7 Hz, 1H), 1.98-1.94 (m,1H), 1.88-1.80 (m, 1H), 1.74 (s, 3H), 1.68-1.65 (m, 1H), 1.55 – 1.50 (m, 1H), 1.26 – 1.21 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 155.9 (ddd, J_{C-F} = 244.3, 9.1 and 2.6 Hz), 149.3 (ddd, J_{C-F} = 250.9, 14.1 and 13.0 Hz), 146.8 (ddd, J_{C-F} = 244.5, 12.5 and 3.6 Hz), 143.5, 122.1, 121.2 (dt, J_{C-F} = 16.4 and 4.6 Hz), 116.8 (dd, J_{C-F} = 19.9 and 6.1 Hz), 106.0 (dd, J_{C-F} = 29.0 and 20.5 Hz), 86.4, 43.9, 34.5, 30.2, 29.6, 23.7, 18.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.18, -133.65 (t, *J*= 10.2 Hz), -141.32 (d, *J*= 7.5 Hz); HRMS(EI) Calcd for $C_{16}H_{15}F_3O_2$ $[M^+]$: 296.1024, Found 296.1023; IR (film) ν(cm^{-1}): 3428, 2929, 1768, 1630, 1519, 1427, 1334, 1217, 1152, 940, 841.



7-Methyl-4-(perfluorophenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9g and (±)-9g': To a quartz Schlenk tube (15 mL) was added 8**g** (33.2 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl = acetate 20/1) to give product **(±)-9g and (±)-9g'** (20.6 mg, 62% yield).

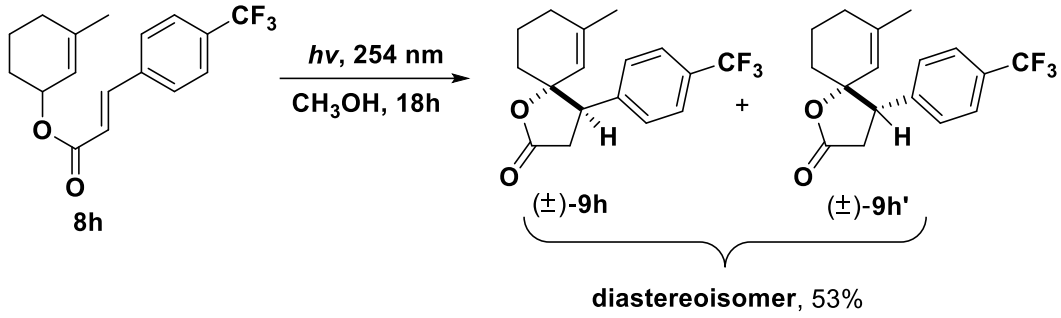


(±)-9g: White solid; mp136.6-136.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.13 (s, 1H), 3.91 (dd, *J* = 9.4 and 5.8 Hz, 1H), 3.09 – 2.99 (m, 2H), 2.00 – 1.96 (m, 2H), 1.89-1.87 (m, 3H), 1.72 – 1.70 (m, 1H), 1.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.5, 146.2-145.9 (m, 1C), 143.7, 141.4-141.1(m, 1C), 138.9-136.7 (m, 1C), 119.0, 112.6 (td, J_{C-F} = 16.8 and 4.3 Hz), 85.6, 40.6, 34.9, 33.6, 29.3, 23.7, 19.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -139.49 (d, *J* = 18.5 Hz) , -153.83 (t, *J* = 20.9 Hz)., -160.97 (td, *J* = 22.0 and 4.0 Hz); HRMS(EI) Calcd for $C_{16}H_{14}F_5O_2$ $[M + H]^+$: 333.0914, Found 333.0907; IR (film) ν(cm^{-1}): 2931, 1770, 1657, 1498, 1300, 1211, 1119, 985.

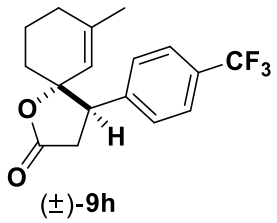


(±)-9g': White solid; mp 122.5-122.8 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.47 (s, 1H),

3.92 (dd, J = 9.2 and 7.4 Hz, 1H), 3.11 – 3.02 (m, 2H), 2.00 – 1.96 (m, 1H), 1.89 – 1.80 (m, 2H), 1.75 (s, 3H), 1.62-1.60 (m, 1H), 1.28 – 1.23 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 146.5-144.6 (m, 1C), 143.8, 141.5-139.6 (m, 1C), 138.7-136.8 (m, 1C), 121.8, 111.6-111.4 (m, 1C), 85.6, 41.3, 33.3, 30.5, 29.5, 23.7, 18.9; ^{19}F NMR (565MHz, $CDCl_3$) δ -138.91, -153.53 (t, J = 20.9 Hz), -160.73 (td, J = 21.0 and 6.0 Hz); HRMS(EI) Calcd for $C_{16}H_{13}F_5O_2$ [M^+]: 332.0836, Found 332.0844; IR (film) ν(cm^{-1}): 2935, 1774, 1529, 1499, 1426, 1245, 1211, 1192, 1120, 993, 967, 938, 893, 805.

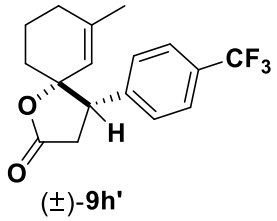


7-Methyl-4-(4-(trifluoromethyl)phenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9h and (±)-9h': To a quartz Schlenk tube (15 mL) was added 8**h** (31.0 mg, 0.1 mmol) and CH_3CN (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9h and (±)-9h'** (16.4 mg, 53% yield).



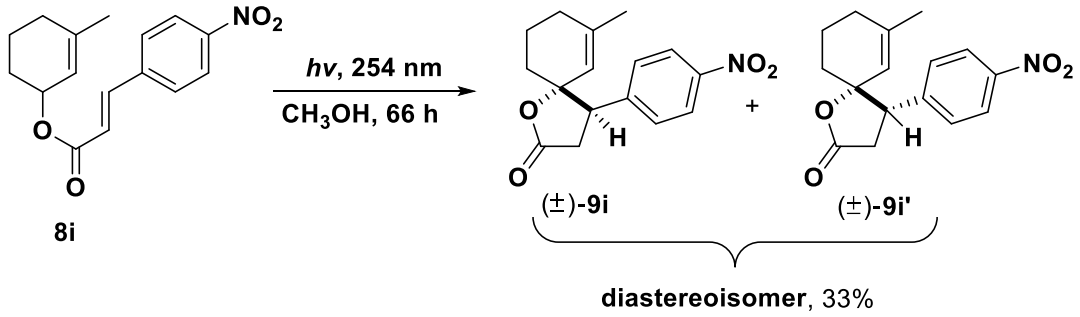
(±)-9h: White solid; 75.9-76.1 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 5.09 (s, 1H), 3.55 (t, J = 8.4 Hz, 1H), 3.05 – 2.94 (m, 2H), 2.07-2.04 (m, 1H), 1.96-1.92 (m, 1H), 1.88 – 1.85 (m, 2H), 1.84-1.80 (m, 1H), 1.73 – 1.68 (m, 1H), 1.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.2, 143.0, 141.6, 129.8 (q, J_{C-F} = 32.3 Hz), 128.6, 125.5 (q, J_{C-F} = 3.6 Hz), 124.2 (q, J_{C-F} = 270.5 Hz),

118.9, 87.1, 50.8, 35.3, 34.5, 29.5, 23.8, 19.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.55; HRMS(EI) Calcd for $C_{17}H_{18}F_3O_2$ $[M + H]^+$: 311.1259, Found 311.1252; IR (KBr) ν(cm^{-1}) : 2924, 1770, 1620, 1429, 1327, 1124, 1070, 939.



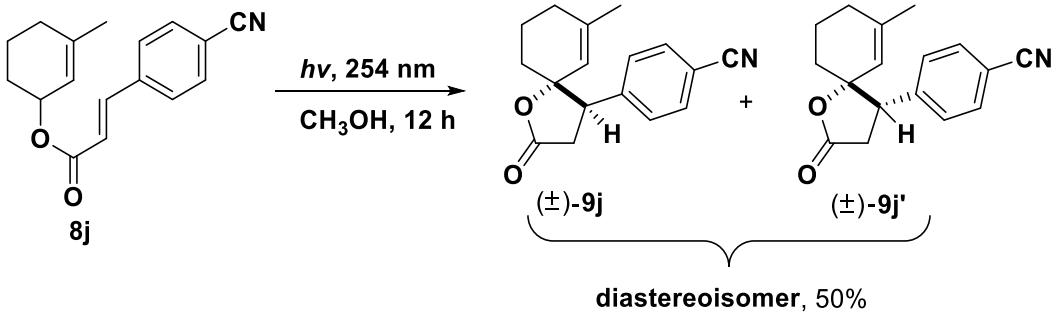
(±)-**9h'**

(±)-9h': White solid; 84.5-84.7 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.54 (s, 1H), 3.64 (t, *J* = 9.0 Hz, 1H), 3.02-2.94 (m, 2H), 1.95 (dt, *J* = 17.6 and 4.1 Hz, 1H), 1.78 (s, 3H), 1.72-1.66 (m, 1H), 1.63 – 1.59 (m, 2H), 1.44-1.39 (m, 1H), 1.18-1.11 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.0, 144.5, 141.0, 129.9 (q, J_{C-F} = 32.5 Hz), 128.5, 128.2, 125.5 (q, J_{C-F} = 3.7 Hz), 123.9 (q, J_{C-F} = 270.3 Hz), 122.4, 111.6, 86.7, 50.8, 34.1, 29.8, 29.6, 23.8, 18.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.58 ; HRMS(EI) Calcd for $C_{17}H_{18}F_3O_2$ $[M + H]^+$: 311.1259, Found 311.1252; IR (KBr) ν(cm^{-1}) : 2941, 1770, 1620, 1439, 1332, 1120, 1070, 935.

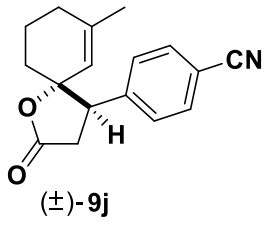


7-Methyl-4-(4-nitrophenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9i and (±)-9i': To a quartz Schlenk tube (15 mL) was added 8**i** (28.7 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9i and (±)-9i' (**9.5 mg, 33% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 – 7.19 (m, 3.01 H), 7.37-7.35 (m, 3.16 H), 5.55 (s, 0.49 H), 5.04 (s, 1.00 H), 3.69 (t, *J* = 9.0 Hz, 0.51 H), 3.61 (t, *J* = 8.2

Hz, 1.04 H), 3.09 – 2.95 (m, 3.23 H), 2.08 – 2.05 (m, 1.16 H), 1.98 – 1.94 (m, 1.80 H), 1.91-1.86 (m, 2.22 H), 1.84-1.81 (m, 0.82 H), 1.79 (s, 3.28 H), 1.72-1.68 (m, 2.00 H), 1.63-1.60 (m, 3.33 H), 1.56 (s, 3.60 H), 1.42-1.39 (m, 0.93 H), 1.15-1.10 (m, 0.81H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.9, 174.5, 147.4, 147.3, 145.2, 144.9, 144.4, 143.5, 129.1, 128.7, 123.8, 123.7, 122.1, 118.8, 87.0, 86.6, 50.9, 50.8, 35.3, 34.5, 34.0, 29.9, 29.6, 29.5, 23.84, 23.77, 19.6, 18.6; HRMS(EI) Calcd for $C_{16}H_{17}NO_4$ [M^+]: 287.1158, Found 287.1164; IR (film) ν(cm^{-1}): 3433, 2924, 1759, 1632, 1604, 1519, 1350, 1229,1109, 1077, 936.

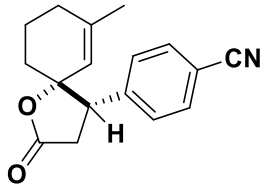


4-(7-Methyl-2-oxo-1-oxaspiro[4.5]dec-6-en-4-yl)benzonitrile (±)-9j and (±)-9j': To a quartz Schlenk tube (15 mL) was added 8**j** (26.7 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9j and (±)-9j'** (13.4 mg, 50% yield).



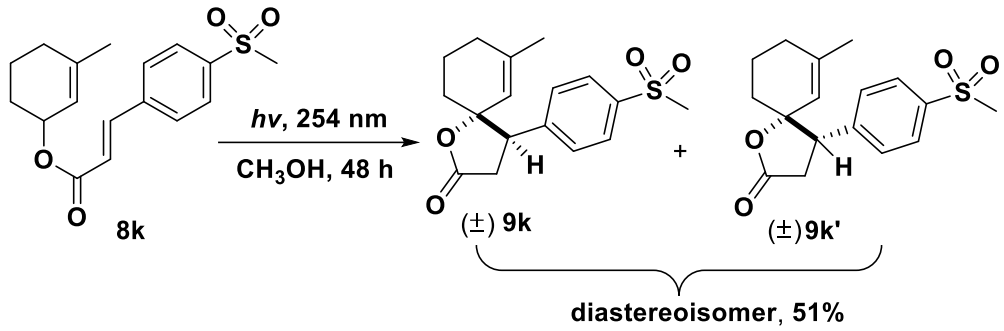
(±)-9j : White solid; mp 125.5-125.6 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 5.02 (s, 1H), 3.54 (t, *J* = 8.2 Hz, 1H), 3.04 (dd, *J* = 17.7 and 8.4 Hz, 1H), 2.93 (dd, *J* = 17.6 and 8.0 Hz, 1H), 2.06-2.03 (m, 1H), 1.96-1.93 (m, 1H), 1.88-1.85 (m, 2H), 1.83 – 1.78 (m, 1H), 1.71 – 1.66 (m, 1H), 1.56 (s, 3H); ^{13}C

NMR (150 MHz, $CDCl_3$) δ 174.9, 143.3, 143.1, 132.3, 129.0, 118.9, 118.4, 111.6, 87.0, 50.9, 35.2, 34.5, 29.5, 23.8, 19.6; HRMS(EI) Calcd for $C_{17}H_{17}NO_2$ [M^+] : 267.1259, Found 267.1263; IR (KBr) ν(cm^{-1}) : 2945, 2225, 1766, 1608, 1431, 1232, 1074, 933.



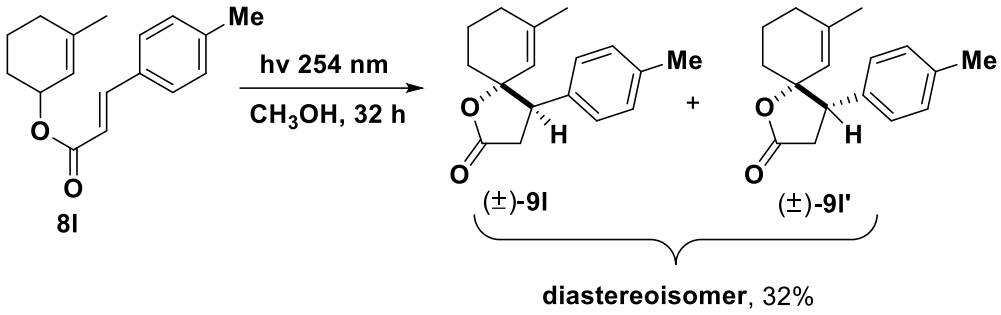
(±)-9j'

(±)-9j' : White solid; mp 139.0-139.2 °C; ^1H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 5.53 (s, 1H), 3.63 (t, *J* = 9.0 Hz, 1H), 2.97 (dd, *J* = 9.0 and 1.5 Hz, 2H), 1.98 – 1.94 (m, 1H), 1.85-1.74 (m, 4H), 1.72 – 1.65 (m, 1H), 1.61 – 1.58 (m, 1H), 1.43 – 1.38 (m, 1H), 1.14 – 1.09 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.6, 144.7, 142.4, 132.4, 128.6, 122.2, 118.4, 111.6, 86.6, 51.0, 33.9, 29.9, 29.6, 23.8, 18.6; HRMS(EI) Calcd for $C_{17}H_{17}NO_2$ [M^+]: 267.1259, Found 267.1258; IR (KBr) ν(cm^{-1}) : 3430, 2943, 2917, 2226, 1762, 1668, 1609, 1508, 1429, 1233, 1076, 959, 934.

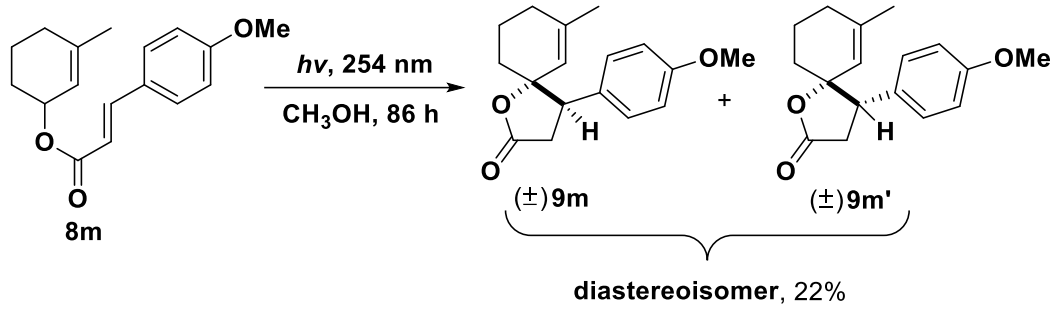


7-Methyl-4-(4-(methylsulfonyl)phenyl)-1-oxaspiro[4.5]dec-6-en-2-one (9k) : To a quartz Schlenk tube (15 mL) was added 8**k** (32.0 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give product **(±)-9k and (±)-9k'** (15.4 mg, 51% yield). Colorless oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 8.4 and 2.8 Hz, 3.54 H), 7.39 (dd, *J* = 8.4 and 2.5 Hz, 3.70 H), 5.54 (s, 1.02 H), 5.06 (s, 1 H), 3.66 (t, *J* = 9.0 Hz, 1.18

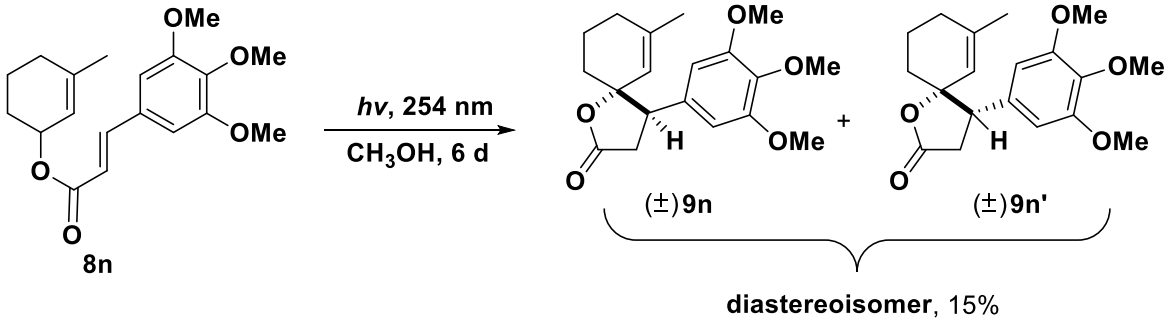
H), 3.58 (t, *J* = 8.3 Hz, 1.16 H), 3.06 (s, 5.37 H), 3.07 – 2.92 (m, 3.42 H), 2.06-2.03 (m, 1H), 1.97-1.90 (m, 2.13 H), 1.89 – 1.82 (m, 2.72 H), 1.78 (s, 3.31 H), 1.72-1.59 (m, 3.79 H), 1.55 (s, 2.75 H), 1.44-1.38 (m, 1.5 H), 1.58-1.09 (m, 1.27 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.8, 174.5, 144.7, 144.1, 143.4, 143.3, 139.9, 139.8, 129.2, 128.8, 127.7, 127.6, 122.3, 118.8, 87.0, 86.6, 50.94, 50.88, 44.4, 35.4, 34.5, 34.1, 29.9, 29.6, 29.5, 23.8, 23.7, 19.6, 18.6; HRMS(EI) Calcd for $C_{17}H_{20}O_4S$ $[M + H]^+$: 321.1161, Found 321.1151; IR (KBr) (cm^{-1}): 1760, 1305, 1233, 1092, 933, 912, 728.



7-Methyl-4-(p-tolyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9l and (±)-9l': To a quartz schlenk tube (15 mL) was added **8l** (25.6 mg, 0.1 mmol) and CH_3OH (10 mL), the schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9l and (±)-9l'** (8.2 mg, 32% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.14-7.11 (m, 4.07 H), 7.06 – 7.05 (m, 4.28 H), 5.52 (s, 1.00 H), 5.17 (s, 0.86 H), 3.54 (t, *J* = 9.1 Hz, 1.03 H), 3.45 (t, *J* = 8.7 Hz, 1.01H), 2.99-2.88 (m, 4.30 H), 2.33 (s, 6.33 H), 2.03-1.99 (m, 1.12 H), 1.93 – 1.83 (m, 4.17 H), 1.82-1.78 (m, 1.36 H), 1.76 (s, 3.85 H), 1.70-1.62 (m, 2.62 H), 1.61-1.58 (m, 1.20 H), 1.55 (s, 3.00 H), 1.421– 1.36 (m, 1.21 H), 1.25 – 1.19 (m, 1.80 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 175.8, 143.6, 142.1, 137.2, 137.1, 134.1, 133.7, 129.2, 129.1, 128.0, 127.6, 122.9, 119.3, 87.4, 87.2, 50.6, 35.4, 34.3, 34.2, 29.7, 29.6, 29.5, 23.8, 23.7, 21.0, 19.6, 18.7; HRMS(EI) Calcd for $C_{17}H_{21}O_2$ $[M + H]^+$: 257.1542, Found 257.1534; IR (film) ν (cm^{-1}): 2934, 1771, 1518, 1233, 934.

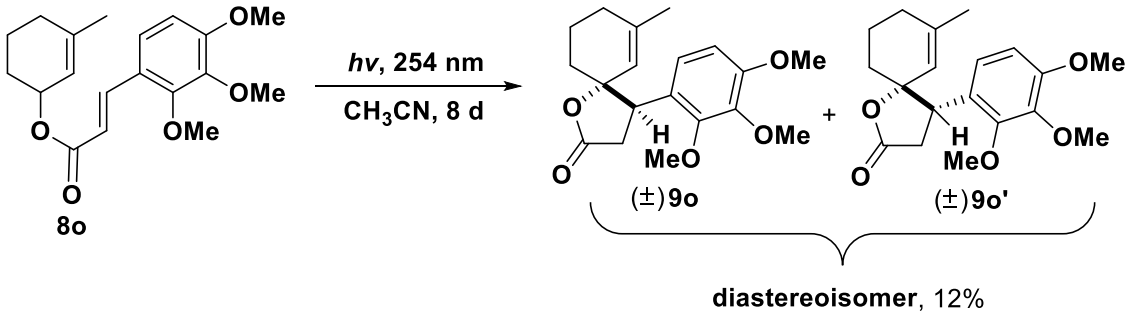


(4R,5R)-4-(4-methoxyphenyl)-7-methyl-1-oxaspiro[4.5]dec-6-en-2-one (±)-9m and (±)-9m': To a quartz Schlenk tube (15 mL) was added **8m** (27.2 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9m and (±)-9m'** (6.0 mg, 22% yield). Colorless oil; ^{1}H NMR (600 MHz, , $CDCl_3$) δ 7.10-7.08 (m, 2.66 H), 6.86-6.84 (m, 2.81H), 5.51 (s, 1H), 5.16 (s, 0.59 H), 3.86-3.74 (m, 3.78 H), 3.53 (t, *J* = 9.2 Hz, 0.88 H), 3.44 (t, *J* = 8.7 Hz, 0.51 H), 2.97 – 2.88 (m, 2.53 H), 2.03-1.98 (m, 0.55 H), 1.94 – 1.91 (m, 1.3 H), 1.87 – 1.83 (m, 0.91 H),1.81- 1.79 (m, 0.72 H), 1.76 (s, 3.21 H), 1.70-1.64 (m, 1.57 H), 1.63-1.61 (m, 1.56 H), 1.59-1.58 (s, 0.66 H), 1.56 (s, 1.27 H), 1.41-1.35 (m, 1.05 H), 1.25 – 1.20 (m, 1.68 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.9, 175.8, 143.6, 142.1, 137.2, 137.1,134.1, 133.7, 129.2, 129.1, 128.0, 127.6, 122.9, 119.3, 87.4, 87.2, 50.6, 35.4, 34.3, 34.2, 29.7, 29.6, 29.5, 23.8, 23.7, 21.0, 19.6, 18.7; HRMS(EI) Calcd for $C_{17}H_{21}O_3$ $[M+H]^+$: 273.1491, Found 273.1485; IR (film) ν (cm^{-1}): 2933, 1770, 1612, 1516, 1442, 1250, 1034, 933, 833.



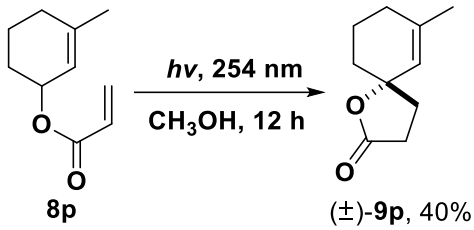
7-Methyl-4-(3,4,5-trimethoxyphenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9n and

(±)-9n': To a quartz Schlenk tube (15 mL) was added **8n** (33.2 mg, 0.1 mmol) and CH_3OH (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9n and (±)-9n'** (5.0 mg, 15% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.35 (s, 2.79 H), 5.53 (s, 1.0 H), 5.17 (s, 0.73 H), 3.84 – 3.83 (m, 11.7 H), 3.50 (t, *J* = 8.9 Hz, 0.96 H), 3.39 (t, *J* = 8.2 Hz, 0.65 H), 3.02 – 2.88 (m, 3.00 H), 2.04 – 1.94 (m, 2.20 H), 1.87-1.81 (m, 2.38 H), 1.78 (s, 3.05 H), 1.72-1.63 (m, 3.83 H), 1.59 (s, 2.19 H), 1.49-1.41 (s, 1.27 H), 1.29-1.24 (s, 2.20 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.8, 175.5, 153.15, 153.07, 143.7, 142.4, 137.29, 137.25, 133.3, 132.7, 122.9, 119.4, 105.2, 104.7, 87.4, 87.1, 60.9, 56.2, 56.1, 51.3, 51.0, 35.8, 34.5, 34.3, 29.71, 29.67, 29.56, 23.9, 23.8, 19.6, 18.8; HRMS(EI) Calcd for $C_{19}H_{25}O_5$ $[M + H]^+$: 333.1702, Found 333.1694; IR (film) ν (cm^{-1}): 2935, 1770, 1589, 1508, 1460, 1240, 1128, 1009, 924.



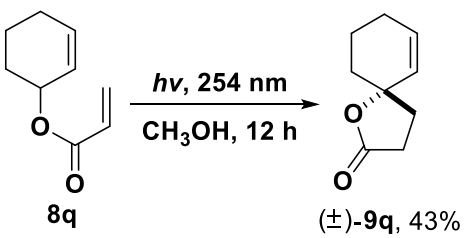
7-Methyl-4-(2,3,4-trimethoxyphenyl)-1-oxaspiro[4.5]dec-6-en-2-one (±)-9o and (±)-9o': To a quartz Schlenk tube (15 mL) was added **8o** (33.2 mg, 0.1 mmol) and CH_3CN (10 mL), the Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9o and (±)-9o'** (4.0 mg, 12% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.79-6.75 (m, 2.04 H), 6.62- 6.60 (m, 2.15 H), 5.53 (s, 1.00 H), 4.94 (s, 1.14 H), 3.86-3.85 (m, 8.53 H), 3.84-3.82 (m,

8.23 H), 3.79-3.77 (m, 2.37 H), 3.07-2.99 (m, 2.22 H), 2.80-2.71 (m, 2.30 H), 1.97 – 1.94 (m, 2.23 H), 1.90-1.83 (m, 4.13 H), 1.73 (s, 3.26 H), 1.67-1.60 (s, 3.23 H), 1.53 (s, 3.13 H), 1.50-1.48 (m, 1.02 H), 1.27-1.23 (m, 2.13 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.9, 176.4, 153.1, 152.9, 152.1, 151.8, 141.9, 141.8, 141.4, 141.2, 124.9, 123.63, 123.55, 123.2, 122.4, 120.8, 106.7, 106.6, 87.9, 87.0, 60.9, 60.59, 60.58, 60.55, 55.89, 55.87, 44.9, 43.9, 35.9, 35.6, 34.9, 30.5, 29.591, 29.585, 23.74, 23.71, 19.7, 19.1; HRMS(EI) Calcd for $C_{19}H_{25}O_5$ $[M + H]^+$: 333.1702, Found 333.1694; IR (film) ν (cm^{-1}): 1759, 1601, 1466, 1101, 926.



8p (±)-**9p**, 40%

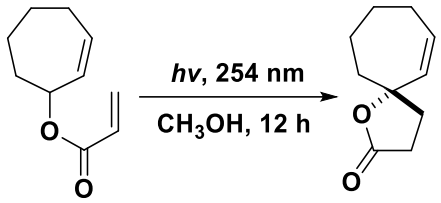
7-Methyl-1-oxaspiro[4.5]dec-6-en-2-one (±)-9p: To a quartz Schlenk tube (15 mL) was added **8p** (16.6 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9p** (6.6 mg, 40% yield). Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 2.59 (t, J = 8.2 Hz, 2H), 2.07 (t, J = 8.2 Hz, 2H), 1.99-1.87 (m, 3H), 1.83-1.79 (m, 1H), 1.70 (s, 3H), 1.67-1.61 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 141.2, 123.1, 84.6, 34.3, 29.6, 28.9, 23.5, 19.6; HRMS(EI) Calcd for $C_{10}H_{14}O_2$ $[M^+]$: 166.0994, Found 166.0995; IR (film) ν(cm^{-1}): 3436, 2937, 1769, 1451, 1238, 1193, 1164, 941, 914.



8q (±)-**9q**, 43%

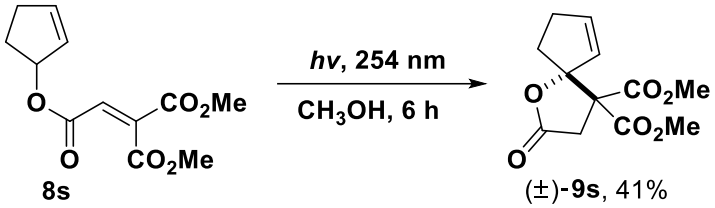
Oxaspiro[4.5]dec-6-en-2-one (±)-9q: To a quartz Schlenk tube (15 mL) was added **8q**

(15.2 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9q** (6.5 mg, 43% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.96 (dt, *J* = 10.0 and 3.7 Hz, 1H), 5.64 (d, *J* = 10.0 Hz, 1H), 2.62 (t, *J* = 8.2 Hz, 2H), 2.11 (t, *J* = 8.2 Hz, 2H), 2.03 – 1.97 (m, 3H), 1.87-1.80 (m, 1H), 1.76-1.72 (m, 1H), 1.68-1.64 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 132.6, 128.4, 83.7, 34.5, 34.0, 28.8, 24.6, 19.3; HRMS(EI) Calcd for $C_9H_{12}O_2$ [M^+]: 152.0837, Found 152.0834; IR (KBr) ν(cm^{-1}) : 2936, 1771, 1728, 1455, 1242, 1188, 1162, 1072, 1043, 1010.

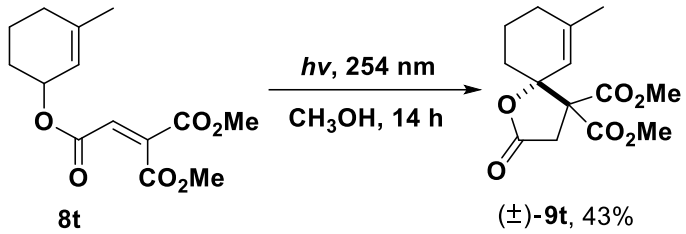


8r (±)-**9r**, 29%

1-Oxaspiro[4.6]undec-6-en-2-one (±)-9r: To a quartz Schlenk (15 mL) tube was added 8**r** (16.6 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9r** (4.8 mg, 29% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.86-5.82 (m, 1H), 5.71 (d, *J* = 11.9 Hz, 1H), 2.63-2.52 (m, 2H), 2.27-2.17 (m, 2H), 2.15-2.09 (m, 1H), 2.06-2.01 (m, 1H), 1.95-1.90 (m, 1H), 1.86-1.82 (m, 1H), 1.71-1.64 (m, 2H), 1.63-1.57 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 176.8, 135.1, 132.9, 89.4, 37.4, 33.8, 29.1, 27.8, 26.9, 24.1; HRMS(EI) Calcd for $C_{10}H_{14}O_2$ [M^+]: 166.0994, Found 166.0993; IR (KBr) ν(cm^{-1}) : 2931, 2860, 1773, 1451, 1263, 1223, 1181, 1160, 1020, 971, 916.

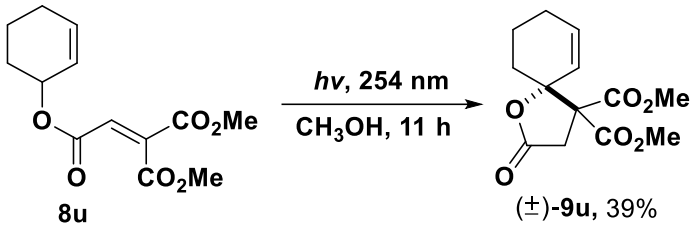


Dimethyl 2-oxo-1-oxaspiro[4.4]non-6-ene-4,4-dicarboxylate (±)-9s: To a quartz Schlenk tube (15 mL) was added 8**s** (25.4 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9s** (10.4 mg, 41% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.36 – 6.08 (m, 1H), 5.77 – 5.40 (m, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.27 (d, *J* = 17.7 Hz, 1H), 2.97 (d, *J* = 17.7 Hz, 1H), 2.62 – 2.57 (m, 1H), 2.46 – 2.41 (m, 1H), 2.40 – 2.28 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 168.6, 167.4, 140.3, 127.5, 98.5, 63.2, 53.2, 53.1, 37.3, 32.8, 31.5; HRMS(EI) Calcd for $C_{12}H_{15}O_6$ $[M+H]^+$: 255.0869, Found 255.0863; IR (KBr) ν(cm^{-1}) : 1766, 1739, 1437, 1267, 1038, 937.

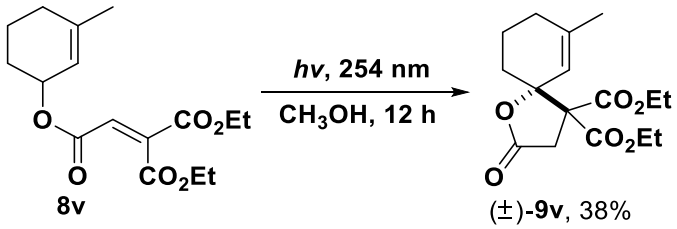


Dimethyl 7-methyl-2-oxo-1-oxaspiro[4.5]dec-6-ene-4,4-dicarboxylate (±)-9t: To a quartz Schlenk tube (15 mL) was added 8**t** (28.2 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9t** (12.1mg, 43% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.21 (s, 1H), 3.76 (s, 3H), 3.71 (s, 3H), 3.25 (d, *J* = 17.7 Hz,

1H), 2.92 (d, *J* = 17.7 Hz, 1H), 2.03-1.98 (m, 1H), 1.95-1.91 (m, 3H), 1.77-1.75 (m, 2H), 1.69 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.3, 168.5, 167.4, 144.5, 117.6, 85.0, 63.5, 53.1, 52.8, 36.3, 29.9, 29.3, 23.8, 19.1; HRMS(EI) Calcd for $C_{14}H_{19}O_6$ [M + H]$^+$: 283.1182, Found 283.1174; IR (KBr) ν(cm^{-1}) : 2954, 1776, 1739, 1437, 1267, 1070, 945, 768, 650, 550.



Dimethyl 2-oxo-1-oxaspiro[4.5]dec-6-ene-4,4-dicarboxylate (±)-9u: To a quartz Schlenk tube (15 mL) was added 8**u** (26.8 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product **(±)-9u** (10.5 mg, 39% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.16- 6.08 (m, 1H), 5.51 (d, *J* = 10.0 Hz, 1H), 3.80 (s, 3H), 3.76 (s, 3H), 3.26 (d, *J* = 17.7 Hz, 1H), 2.98 (d, *J* = 17.7 Hz, 1H), 2.16 – 2.11 (m, 2H), 2.04 – 1.98 (m, 2H), 1.80 – 1.75 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.2, 168.5, 167.3, 135.7, 123.1, 83.9, 63.5, 53.2, 53.1, 36.3, 30.4, 24.3, 18.8; HRMS(EI) Calcd for $C_{13}H_{17}O_6$ [M + H]$^+$: 269.1025, Found 269.1018 ; IR (KBr) ν(cm^{-1}) : 2956, 1739, 1437, 1265, 1068, 945, 756.

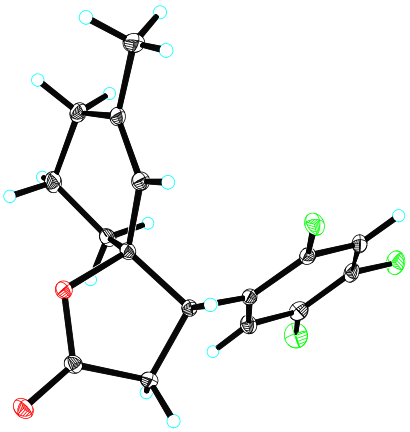


Diethyl 7-methyl-2-oxo-1-oxaspiro[4.5]dec-6-ene-4,4-dicarboxylate (±)-9v: To a quartz Schlenk tube (15 mL) was added 8**v** (31.0 mg, 0.1 mmol) and CH_3OH (10 mL). The Schlenk tube was refilled with N_2, and then the reaction mixture was exposed to

ultraviolet light (254 nm). The reaction was monitored by TLC. When the starting material was completely consumed, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give product (±)-**9v** (11.8 mg, 38% yield). Colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.25 (s, 1H), 4.29-4.22 (m, 3H), 4.20 – 4.14 (m, 1H), 3.29 (d, *J* = 18.5 Hz, 1H), 2.93 (d, *J* = 17.7 Hz, 1H), 2.10 – 2.02 (m, 2H), 1.98 – 1.91 (m, 2H), 1.81 – 1.79 (m, 2H), 1.72 (s, 3H), 1.29 (td, *J* = 7.6 and 0.8 Hz, 3H), 1.23 (td, *J* = 7.5 and 0.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.6, 168.2, 167.1, 144.2, 118.0, 85.1, 63.6, 62.5, 62.0, 36.5, 30.0, 29.5, 23.9, 19.3, 13.94, 13.92; HRMS(EI) Calcd for $C_{16}H_{22}O_6$ [M^+]: 310.1416, Found 310.1409; IR (KBr) ν(cm^{-1}) : 2937, 1790, 1736, 1444, 1370, 1303, 1258, 1233, 1172, 932, 906, 858.

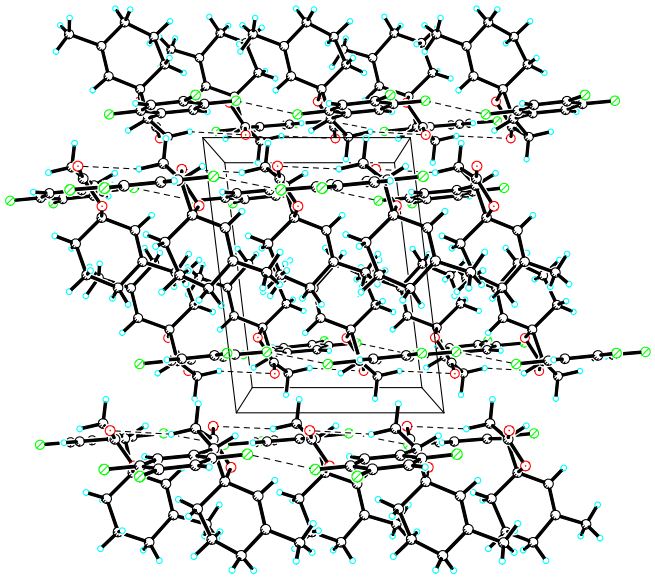
X-ray data of **(±)-9f' (CCDC 1911404)**

Crystal data for mo_**(±)-9f'**: $C_{16}H_{15}F_3O_2$, M = 296.28, a = 10.5914(10) Å, b = 16.4477(16) Å, c = 7.9363(8) Å, α = 90°, β = 96.959(2)°, γ = 90°, V = 1372.4(2) Å^3, T = 100(2) K, space group $P2_1/c$, Z = 4, μ(MoKα) = 0.120 mm^{-1}, 15271 reflections measured, 4091 independent reflections (R_{int} = 0.0359). The final R_1 values were 0.0452 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1209 ($I > 2\sigma(I)$). The final R_1 values were 0.0654 (all data). The final $wR(F^2)$ values were 0.1335 (all data). The goodness of fit on F^2 was 1.049.



View of a molecule of **(±)-9f'** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.+



View of the pack drawing of **(±)-9f'**.

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for mo_**(±)-9f'**_0m.

Identification code	mo_**(±)-9f'**_0m	
Empirical formula	C16 H15 F3 O2	
Formula weight	296.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.5914(10) Å	α= 90°.
	b = 16.4477(16) Å	β= 96.959(2)°.
	c = 7.9363(8) Å	γ = 90°.
Volume	1372.4(2) $Å^3$	
Z	4	
Density (calculated)	1.434 Mg/m^3	
Absorption coefficient	0.120 mm^{-1}	
F(000)	616	
Crystal size	0.300 x 0.220 x 0.150 mm^3	
Theta range for data collection	1.937 to 30.986°.	

Index ranges	-15<=h<=14, -22<=k<=23, -11<=l<=11
Reflections collected	15271
Independent reflections	4091 [R(int) = 0.0359]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4091 / 0 / 191
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0452, wR2 = 0.1209
R indices (all data)	R1 = 0.0654, wR2 = 0.1335
Extinction coefficient	n/a
Largest diff. peak and hole	0.390 and -0.231 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_**(±)-9f'**_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
F(1)	8020(1)	12041(1)	5435(1)	34(1)
F(2)	8052(1)	10703(1)	3489(1)	38(1)
F(3)	8557(1)	10418(1)	10335(1)	25(1)
O(1)	7655(1)	7674(1)	9131(1)	21(1)
O(2)	9123(1)	6826(1)	8366(1)	25(1)
C(1)	8155(1)	11305(1)	6188(2)	23(1)
C(2)	8291(1)	11244(1)	7924(2)	22(1)
C(3)	8418(1)	10473(1)	8618(2)	18(1)
C(4)	8423(1)	9763(1)	7672(2)	16(1)
C(5)	8545(1)	8946(1)	8555(2)	16(1)
C(6)	7259(1)	8539(1)	8848(2)	17(1)
C(7)	6771(1)	8823(1)	10440(2)	20(1)
C(8)	5532(1)	8875(1)	10622(2)	21(1)
C(9)	4506(1)	8643(1)	9228(2)	26(1)
C(10)	8165(1)	10618(1)	5191(2)	24(1)
C(11)	8303(1)	9851(1)	5908(2)	21(1)
C(12)	8708(1)	7508(1)	8383(2)	19(1)
C(13)	9217(1)	8277(1)	7679(2)	19(1)
C(14)	6235(1)	8548(1)	7322(2)	21(1)
C(15)	5011(1)	8167(1)	7797(2)	27(1)
C(16)	5104(2)	9186(1)	12241(2)	29(1)

Table 3. Bond lengths [Å] and angles [°] for mo_**(±)-9f'**_0m.

F(1)-C(1)	1.3506(15)
F(2)-C(10)	1.3487(16)
F(3)-C(3)	1.3560(15)
O(1)-C(12)	1.3525(16)
O(1)-C(6)	1.4923(15)
O(2)-C(12)	1.2054(16)
C(1)-C(2)	1.372(2)
C(1)-C(10)	1.381(2)
C(2)-C(3)	1.3829(18)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3887(17)
C(4)-C(11)	1.3983(17)
C(4)-C(5)	1.5124(17)
C(5)-C(13)	1.5246(17)
C(5)-C(6)	1.5604(18)
C(5)-H(3)	1.0000
C(6)-C(7)	1.4964(18)
C(6)-C(14)	1.5243(19)
C(7)-C(8)	1.3402(19)
C(7)-H(6)	0.9500
C(8)-C(9)	1.503(2)
C(8)-C(16)	1.503(2)
C(9)-C(15)	1.528(2)
C(9)-H(1)	0.9900
C(9)-H(10)	0.9900
C(10)-C(11)	1.3832(19)
C(11)-H(15)	0.9500
C(12)-C(13)	1.5077(19)
C(13)-H(5)	0.9900
C(13)-H(4)	0.9900
C(14)-C(15)	1.528(2)
C(14)-H(14)	0.9900
C(14)-H(13)	0.9900
C(15)-H(11)	0.9900
C(15)-H(12)	0.9900
C(16)-H(7)	0.9800

C(16)-H(8)	0.9800
C(16)-H(9)	0.9800

C(12)-O(1)-C(6)	111.00(10)
F(1)-C(1)-C(2)	120.16(13)
F(1)-C(1)-C(10)	119.23(13)
C(2)-C(1)-C(10)	120.61(12)
C(1)-C(2)-C(3)	117.37(12)
C(1)-C(2)-H(2)	121.3
C(3)-C(2)-H(2)	121.3
F(3)-C(3)-C(2)	117.06(11)
F(3)-C(3)-C(4)	118.67(11)
C(2)-C(3)-C(4)	124.27(12)
C(3)-C(4)-C(11)	116.60(11)
C(3)-C(4)-C(5)	120.13(11)
C(11)-C(4)-C(5)	123.27(11)
C(4)-C(5)-C(13)	116.66(11)
C(4)-C(5)-C(6)	115.05(10)
C(13)-C(5)-C(6)	102.83(10)
C(4)-C(5)-H(3)	107.2
C(13)-C(5)-H(3)	107.2
C(6)-C(5)-H(3)	107.2
O(1)-C(6)-C(7)	106.83(10)
O(1)-C(6)-C(14)	106.76(10)
C(7)-C(6)-C(14)	112.53(11)
O(1)-C(6)-C(5)	101.35(9)
C(7)-C(6)-C(5)	112.89(11)
C(14)-C(6)-C(5)	115.28(11)
C(8)-C(7)-C(6)	123.61(13)
C(8)-C(7)-H(6)	118.2
C(6)-C(7)-H(6)	118.2
C(7)-C(8)-C(9)	122.31(13)
C(7)-C(8)-C(16)	120.99(14)
C(9)-C(8)-C(16)	116.69(13)
C(8)-C(9)-C(15)	112.97(12)
C(8)-C(9)-H(1)	109.0
C(15)-C(9)-H(1)	109.0
C(8)-C(9)-H(10)	109.0

C(15)-C(9)-H(10)	109.0
H(1)-C(9)-H(10)	107.8
F(2)-C(10)-C(1)	118.89(12)
F(2)-C(10)-C(11)	119.90(13)
C(1)-C(10)-C(11)	121.20(12)
C(10)-C(11)-C(4)	119.94(12)
C(10)-C(11)-H(15)	120.0
C(4)-C(11)-H(15)	120.0
O(2)-C(12)-O(1)	120.94(12)
O(2)-C(12)-C(13)	128.91(13)
O(1)-C(12)-C(13)	110.14(11)
C(12)-C(13)-C(5)	103.23(10)
C(12)-C(13)-H(5)	111.1
C(5)-C(13)-H(5)	111.1
C(12)-C(13)-H(4)	111.1
C(5)-C(13)-H(4)	111.1
H(5)-C(13)-H(4)	109.1
C(6)-C(14)-C(15)	110.08(11)
C(6)-C(14)-H(14)	109.6
C(15)-C(14)-H(14)	109.6
C(6)-C(14)-H(13)	109.6
C(15)-C(14)-H(13)	109.6
H(14)-C(14)-H(13)	108.2
C(9)-C(15)-C(14)	110.96(11)
C(9)-C(15)-H(11)	109.4
C(14)-C(15)-H(11)	109.4
C(9)-C(15)-H(12)	109.4
C(14)-C(15)-H(12)	109.4
H(11)-C(15)-H(12)	108.0
C(8)-C(16)-H(7)	109.5
C(8)-C(16)-H(8)	109.5
H(7)-C(16)-H(8)	109.5
C(8)-C(16)-H(9)	109.5
H(7)-C(16)-H(9)	109.5
H(8)-C(16)-H(9)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_**(±)-9f'**_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F(1)	35(1)	20(1)	45(1)	14(1)	1(1)	-1(1)
F(2)	53(1)	40(1)	20(1)	10(1)	2(1)	0(1)
F(3)	33(1)	24(1)	18(1)	-5(1)	3(1)	-3(1)
O(1)	18(1)	15(1)	29(1)	3(1)	5(1)	2(1)
O(2)	24(1)	18(1)	32(1)	1(1)	2(1)	5(1)
C(1)	19(1)	16(1)	34(1)	8(1)	2(1)	-1(1)
C(2)	20(1)	16(1)	30(1)	-2(1)	3(1)	-2(1)
C(3)	16(1)	19(1)	19(1)	-1(1)	2(1)	-2(1)
C(4)	15(1)	15(1)	18(1)	1(1)	2(1)	-1(1)
C(5)	15(1)	14(1)	18(1)	0(1)	2(1)	0(1)
C(6)	16(1)	13(1)	23(1)	1(1)	2(1)	2(1)
C(7)	19(1)	18(1)	22(1)	2(1)	3(1)	1(1)
C(8)	20(1)	13(1)	31(1)	4(1)	6(1)	1(1)
C(9)	16(1)	21(1)	42(1)	2(1)	4(1)	-2(1)
C(10)	25(1)	28(1)	19(1)	6(1)	3(1)	-1(1)
C(11)	25(1)	20(1)	18(1)	-1(1)	2(1)	-2(1)
C(12)	17(1)	18(1)	20(1)	-1(1)	-1(1)	2(1)
C(13)	18(1)	17(1)	23(1)	0(1)	5(1)	2(1)
C(14)	19(1)	17(1)	24(1)	-4(1)	-1(1)	2(1)
C(15)	19(1)	21(1)	39(1)	-4(1)	-2(1)	-3(1)
C(16)	28(1)	24(1)	38(1)	1(1)	14(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_**(±)-9f'**_0m.

	x	y	z	U(eq)
H(2)	8298	11714	8623	27
H(3)	9037	9035	9696	19
H(6)	7373	8973	11374	24
H(1)	4080	9143	8752	31
H(10)	3862	8309	9714	31
H(15)	8317	9386	5202	26
H(5)	9004	8304	6431	23
H(4)	10152	8314	7964	23
H(14)	6534	8239	6375	25
H(13)	6068	9114	6938	25
H(11)	4361	8162	6790	32
H(12)	5178	7598	8162	32
H(7)	5846	9355	13020	43
H(8)	4650	8754	12769	43
H(9)	4535	9652	11989	43

Table 6. Torsion angles [°] for mo_**(±)-9f'**_0m.

F(1)-C(1)-C(2)-C(3)	179.69(12)
C(10)-C(1)-C(2)-C(3)	-0.9(2)
C(1)-C(2)-C(3)-F(3)	179.79(12)
C(1)-C(2)-C(3)-C(4)	0.3(2)
F(3)-C(3)-C(4)-C(11)	-178.73(11)
C(2)-C(3)-C(4)-C(11)	0.7(2)
F(3)-C(3)-C(4)-C(5)	1.64(19)
C(2)-C(3)-C(4)-C(5)	-178.90(13)
C(3)-C(4)-C(5)-C(13)	-148.82(13)
C(11)-C(4)-C(5)-C(13)	31.57(18)
C(3)-C(4)-C(5)-C(6)	90.58(15)
C(11)-C(4)-C(5)-C(6)	-89.02(15)
C(12)-O(1)-C(6)-C(7)	-143.33(11)
C(12)-O(1)-C(6)-C(14)	96.06(12)
C(12)-O(1)-C(6)-C(5)	-24.96(13)
C(4)-C(5)-C(6)-O(1)	160.81(10)
C(13)-C(5)-C(6)-O(1)	32.90(12)
C(4)-C(5)-C(6)-C(7)	-85.27(13)
C(13)-C(5)-C(6)-C(7)	146.82(11)
C(4)-C(5)-C(6)-C(14)	45.97(15)
C(13)-C(5)-C(6)-C(14)	-81.94(13)
O(1)-C(6)-C(7)-C(8)	-100.60(14)
C(14)-C(6)-C(7)-C(8)	16.26(18)
C(5)-C(6)-C(7)-C(8)	148.86(13)
C(6)-C(7)-C(8)-C(9)	0.6(2)
C(6)-C(7)-C(8)-C(16)	-178.36(12)
C(7)-C(8)-C(9)-C(15)	13.43(19)
C(16)-C(8)-C(9)-C(15)	-167.54(12)
F(1)-C(1)-C(10)-F(2)	0.6(2)
C(2)-C(1)-C(10)-F(2)	-178.76(13)
F(1)-C(1)-C(10)-C(11)	179.85(13)
C(2)-C(1)-C(10)-C(11)	0.5(2)
F(2)-C(10)-C(11)-C(4)	179.87(13)
C(1)-C(10)-C(11)-C(4)	0.6(2)
C(3)-C(4)-C(11)-C(10)	-1.2(2)
C(5)-C(4)-C(11)-C(10)	178.42(13)

C(6)-O(1)-C(12)-O(2)	-174.67(12)
C(6)-O(1)-C(12)-C(13)	6.38(14)
O(2)-C(12)-C(13)-C(5)	-163.22(14)
O(1)-C(12)-C(13)-C(5)	15.63(14)
C(4)-C(5)-C(13)-C(12)	-156.63(11)
C(6)-C(5)-C(13)-C(12)	-29.74(13)
O(1)-C(6)-C(14)-C(15)	70.89(13)
C(7)-C(6)-C(14)-C(15)	-46.00(14)
C(5)-C(6)-C(14)-C(15)	-177.42(11)
C(8)-C(9)-C(15)-C(14)	-43.69(17)
C(6)-C(14)-C(15)-C(9)	60.68(15)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_**(±)-9f’** _0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(13)-H(5)...O(2)#1	0.99	2.46	3.4169(17)	162.2
C(7)-H(6)...O(2)#2	0.95	2.64	3.3665(18)	133.9
C(2)-H(2)...F(1)#3	0.95	2.54	3.4848(16)	173.0
C(13)-H(5)...O(2)#1	0.99	2.46	3.4169(17)	162.2
C(7)-H(6)...O(2)#2	0.95	2.64	3.3665(18)	133.9
C(2)-H(2)...F(1)#3	0.95	2.54	3.4848(16)	173.0
C(2)-H(2)...F(1)#3	0.95	2.54	3.4848(16)	173.0
C(7)-H(6)...O(2)#2	0.95	2.64	3.3665(18)	133.9
C(13)-H(5)...O(2)#1	0.99	2.46	3.4169(17)	162.2
C(2)-H(2)...F(1)#3	0.95	2.54	3.4848(16)	173.0
C(7)-H(6)...O(2)#2	0.95	2.64	3.3665(18)	133.9
C(13)-H(5)...O(2)#1	0.99	2.46	3.4169(17)	162.2
C(2)-H(2)...F(1)#3	0.95	2.54	3.4848(16)	173.0
C(7)-H(6)...O(2)#2	0.95	2.64	3.3665(18)	133.9
C(13)-H(5)...O(2)#1	0.99	2.46	3.4169(17)	162.2

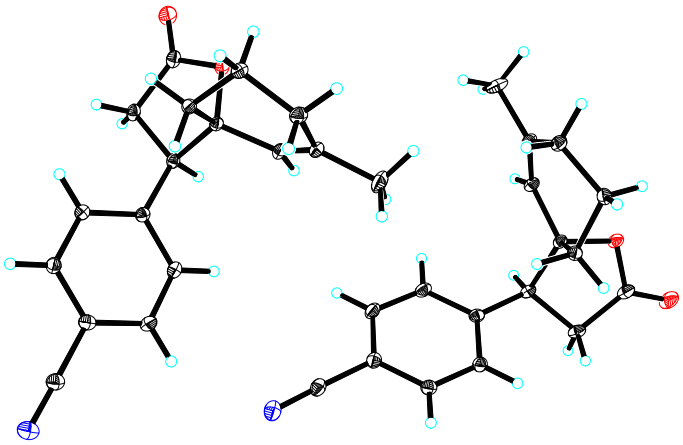
Symmetry transformations used to generate equivalent atoms:

#1 x,-y+3/2,z-1/2 #2 x,-y+3/2,z+1/2 #3 x,-y+5/2,z+1/2

X-ray data of (±)-**9j' (CCDC 1911403)**

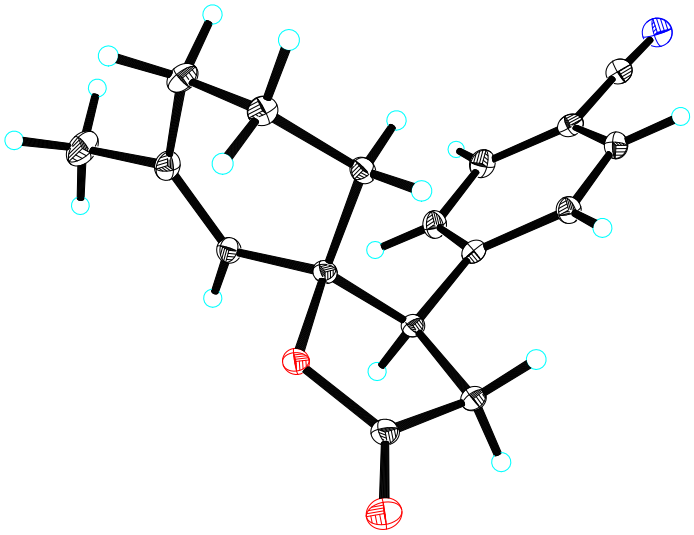
Original name：**_mo_9j'_0m-data_mo_bwsx1094_0m_a_file002**

Crystal data for mo_bwsx1094_0m_a: $C_{17}H_{17}NO_2$, M = 267.31, a = 13.9466(16) Å, b = 23.367(3) Å, c = 8.8425(10) Å, α = 90°, β = 90°, γ = 90°, V = 2881.7(6) Å^3, T = 100(2) K, space group $Pba2$, Z = 8, μ(MoKα) = 0.081 mm^{-1}, 31450 reflections measured, 8481 independent reflections (R_{int} = 0.0361). The final R_1 values were 0.0406 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0968 ($I > 2\sigma(I)$). The final R_1 values were 0.0528 (all data). The final $wR(F^2)$ values were 0.1036 (all data). The goodness of fit on F^2 was 1.016. Flack parameter = 0.2(4).



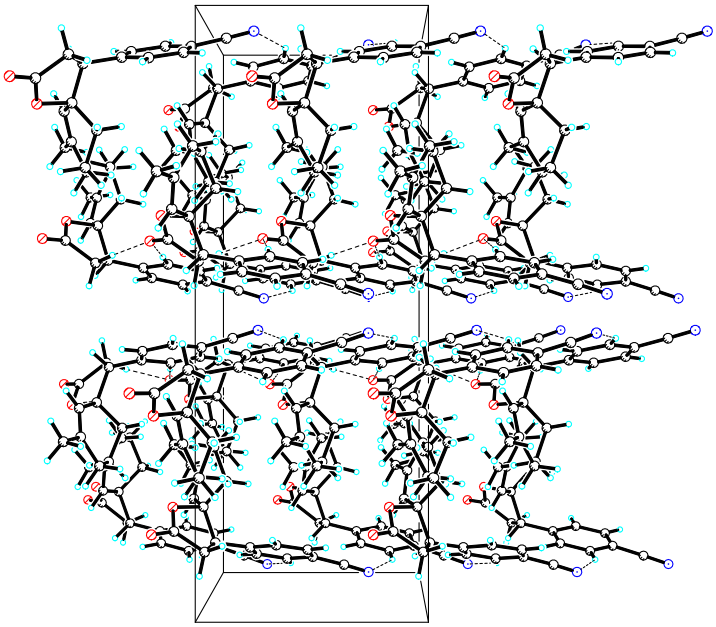
View of the molecules in an asymmetric unit.

Displacement ellipsoids are drawn at the 30% probability level.



View of a molecule of **(±)-9j'** with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **(±)-9j'**

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for **(±)-9j'** （mo_bwsx1094_0m_a.）

Identification code	mo_bwsx1094_0m_a

Empirical formula	C17 H17 N O2	
Formula weight	267.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pba2	
Unit cell dimensions	a = 13.9466(16) Å	α= 90°.
	b = 23.367(3) Å	β= 90°.
	c = 8.8425(10) Å	γ = 90°.
Volume	2881.7(6) $Å^3$	
Z	8	
Density (calculated)	1.232 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	1136	
Crystal size	1.800 x 0.320 x 0.100 mm^3	
Theta range for data collection	1.700 to 31.054°.	
Index ranges	-19<=h<=19, -31<=k<=33, -12<=l<=12	
Reflections collected	31450	
Independent reflections	8481 [R(int) = 0.0361]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8481 / 1 / 363	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0406, wR2 = 0.0968	
R indices (all data)	R1 = 0.0528, wR2 = 0.1036	
Absolute structure parameter	0.2(4)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.274 and -0.208 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for **(±)-9j' –(**mo_bwsx1094_0m_a). U (eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(001)	4460(1)	6630(1)	3362(1)	20(1)
O(002)	10938(1)	6621(1)	-1618(1)	22(1)
O(003)	3042(1)	6292(1)	2627(2)	31(1)
O(004)	12314(1)	6232(1)	-2360(2)	35(1)
N(005)	8818(1)	5319(1)	7421(2)	30(1)
N(006)	6514(1)	5283(1)	12368(2)	31(1)
C(007)	4642(1)	5874(1)	8064(2)	20(1)
C(008)	9410(1)	5638(1)	4774(2)	21(1)
C(009)	6120(1)	6645(1)	4098(2)	19(1)
C(00A)	5237(1)	5820(1)	6798(2)	17(1)
C(00B)	5928(1)	5585(1)	9703(2)	20(1)
C(00C)	9276(1)	6674(1)	-889(2)	19(1)
C(00D)	6633(1)	7123(1)	4287(2)	21(1)
C(00E)	4981(1)	5761(1)	9504(2)	20(1)
C(00F)	10455(1)	5968(1)	280(2)	18(1)
C(00G)	10691(1)	5941(1)	3140(2)	20(1)
C(00H)	10110(1)	5860(1)	1868(2)	18(1)
C(00I)	9073(1)	5472(1)	6251(2)	24(1)
C(00J)	11520(1)	5880(1)	-75(2)	22(1)
C(00K)	4904(1)	5948(1)	5210(2)	17(1)
C(00L)	3834(1)	5886(1)	4855(2)	20(1)

C(00M)	10271(1)	6589(1)	-302(2)	18(1)
C(00N)	10346(1)	5835(1)	4582(2)	21(1)
C(00O)	5121(1)	6571(1)	4678(2)	16(1)
C(00P)	6262(1)	5423(1)	11184(2)	23(1)
C(00Q)	3700(1)	6274(1)	3508(2)	22(1)
C(00R)	10563(1)	7057(1)	808(2)	18(1)
C(00S)	11666(1)	6246(1)	-1456(2)	24(1)
C(00T)	8814(1)	5562(1)	3519(2)	24(1)
C(00U)	8784(1)	7159(1)	-727(2)	21(1)
C(00V)	6538(1)	5533(1)	8458(2)	24(1)
C(00W)	5149(1)	7621(1)	5248(2)	20(1)
C(00X)	10285(1)	7646(1)	201(2)	21(1)
C(00Y)	6188(1)	5650(1)	7022(2)	22(1)
C(00Z)	4852(1)	7032(1)	5820(2)	18(1)
C(010)	9168(1)	5675(1)	2088(2)	24(1)
C(011)	9199(1)	7680(1)	10(2)	23(1)
C(012)	6235(1)	7644(1)	5055(2)	23(1)
C(013)	7656(1)	7166(1)	3754(3)	33(1)
C(014)	7765(1)	7211(1)	-1260(3)	34(1)

Table 3. Bond lengths [Å] and angles [°] for **(±)-9j'** (mo_bwsx1094_0m_a).

O(001)-C(00Q)	1.354(2)
O(001)-C(00O)	1.491(2)
O(002)-C(00S)	1.348(2)
O(002)-C(00M)	1.491(2)
O(003)-C(00Q)	1.204(2)
O(004)-C(00S)	1.208(2)
N(005)-C(00I)	1.151(3)
N(006)-C(00P)	1.152(3)
C(007)-C(00E)	1.383(2)
C(007)-C(00A)	1.399(2)
C(007)-H(007)	0.9500
C(008)-C(00N)	1.394(3)
C(008)-C(00T)	1.398(3)
C(008)-C(00I)	1.442(3)
C(009)-C(00D)	1.337(2)
C(009)-C(00O)	1.494(2)
C(009)-H(009)	0.9500
C(00A)-C(00Y)	1.398(2)
C(00A)-C(00K)	1.509(2)
C(00B)-C(00E)	1.394(2)
C(00B)-C(00V)	1.397(3)
C(00B)-C(00P)	1.441(3)
C(00C)-C(00U)	1.333(2)
C(00C)-C(00M)	1.495(2)
C(00C)-H(00C)	0.9500
C(00D)-C(012)	1.501(3)
C(00D)-C(013)	1.505(3)

C(00E)-H(00E)	0.9500
C(00F)-C(00H)	1.506(2)
C(00F)-C(00J)	1.532(2)
C(00F)-C(00M)	1.560(2)
C(00F)-H(00F)	1.0000
C(00G)-C(00N)	1.386(3)
C(00G)-C(00H)	1.399(2)
C(00G)-H(00G)	0.9500
C(00H)-C(010)	1.397(3)
C(00J)-C(00S)	1.505(3)
C(00J)-H(00A)	0.9900
C(00J)-H(00B)	0.9900
C(00K)-C(00L)	1.532(2)
C(00K)-C(00O)	1.558(2)
C(00K)-H(00K)	1.0000
C(00L)-C(00Q)	1.509(3)
C(00L)-H(00D)	0.9900
C(00L)-H(00H)	0.9900
C(00M)-C(00R)	1.526(2)
C(00N)-H(00N)	0.9500
C(00O)-C(00Z)	1.524(2)
C(00R)-C(00X)	1.527(2)
C(00R)-H(00J)	0.9900
C(00R)-H(00L)	0.9900
C(00T)-C(010)	1.384(3)
C(00T)-H(00T)	0.9500
C(00U)-C(011)	1.497(3)
C(00U)-C(014)	1.501(3)
C(00V)-C(00Y)	1.387(3)

C(00V)-H(00V)	0.9500
C(00W)-C(00Z)	1.524(2)
C(00W)-C(012)	1.525(3)
C(00W)-H(00M)	0.9900
C(00W)-H(00O)	0.9900
C(00X)-C(011)	1.526(3)
C(00X)-H(00Q)	0.9900
C(00X)-H(00R)	0.9900
C(00Y)-H(00Y)	0.9500
C(00Z)-H(00S)	0.9900
C(00Z)-H(00U)	0.9900
C(010)-H(010)	0.9500
C(011)-H(01A)	0.9900
C(011)-H(01B)	0.9900
C(012)-H(01C)	0.9900
C(012)-H(01D)	0.9900
C(013)-H(01E)	0.9800
C(013)-H(01F)	0.9800
C(013)-H(01G)	0.9800
C(014)-H(01H)	0.9800
C(014)-H(01I)	0.9800
C(014)-H(01J)	0.9800

C(00Q)-O(001)-C(00O)	110.70(13)
C(00S)-O(002)-C(00M)	110.71(13)
C(00E)-C(007)-C(00A)	121.10(16)
C(00E)-C(007)-H(007)	119.5
C(00A)-C(007)-H(007)	119.5
C(00N)-C(008)-C(00T)	120.16(17)

C(00N)-C(008)-C(00I)	120.29(17)
C(00T)-C(008)-C(00I)	119.39(16)
C(00D)-C(009)-C(00O)	123.59(16)
C(00D)-C(009)-H(009)	118.2
C(00O)-C(009)-H(009)	118.2
C(00Y)-C(00A)-C(007)	118.36(16)
C(00Y)-C(00A)-C(00K)	118.70(16)
C(007)-C(00A)-C(00K)	122.93(15)
C(00E)-C(00B)-C(00V)	120.22(16)
C(00E)-C(00B)-C(00P)	119.90(17)
C(00V)-C(00B)-C(00P)	119.76(16)
C(00U)-C(00C)-C(00M)	123.75(16)
C(00U)-C(00C)-H(00C)	118.1
C(00M)-C(00C)-H(00C)	118.1
C(009)-C(00D)-C(012)	122.39(16)
C(009)-C(00D)-C(013)	121.60(17)
C(012)-C(00D)-C(013)	116.01(16)
C(007)-C(00E)-C(00B)	119.73(17)
C(007)-C(00E)-H(00E)	120.1
C(00B)-C(00E)-H(00E)	120.1
C(00H)-C(00F)-C(00J)	118.59(15)
C(00H)-C(00F)-C(00M)	114.27(14)
C(00J)-C(00F)-C(00M)	102.47(14)
C(00H)-C(00F)-H(00F)	106.9
C(00J)-C(00F)-H(00F)	106.9
C(00M)-C(00F)-H(00F)	106.9
C(00N)-C(00G)-C(00H)	120.91(16)
C(00N)-C(00G)-H(00G)	119.5
C(00H)-C(00G)-H(00G)	119.5

C(010)-C(00H)-C(00G)	118.39(17)
C(010)-C(00H)-C(00F)	118.83(16)
C(00G)-C(00H)-C(00F)	122.78(15)
N(005)-C(00I)-C(008)	177.5(2)
C(00S)-C(00J)-C(00F)	102.75(14)
C(00S)-C(00J)-H(00A)	111.2
C(00F)-C(00J)-H(00A)	111.2
C(00S)-C(00J)-H(00B)	111.2
C(00F)-C(00J)-H(00B)	111.2
H(00A)-C(00J)-H(00B)	109.1
C(00A)-C(00K)-C(00L)	118.16(14)
C(00A)-C(00K)-C(00O)	113.95(13)
C(00L)-C(00K)-C(00O)	102.49(13)
C(00A)-C(00K)-H(00K)	107.2
C(00L)-C(00K)-H(00K)	107.2
C(00O)-C(00K)-H(00K)	107.2
C(00Q)-C(00L)-C(00K)	103.05(14)
C(00Q)-C(00L)-H(00D)	111.2
C(00K)-C(00L)-H(00D)	111.2
C(00Q)-C(00L)-H(00H)	111.2
C(00K)-C(00L)-H(00H)	111.2
H(00D)-C(00L)-H(00H)	109.1
O(002)-C(00M)-C(00C)	107.48(14)
O(002)-C(00M)-C(00R)	107.38(13)
C(00C)-C(00M)-C(00R)	112.02(14)
O(002)-C(00M)-C(00F)	101.68(12)
C(00C)-C(00M)-C(00F)	113.08(14)
C(00R)-C(00M)-C(00F)	114.28(14)
C(00G)-C(00N)-C(008)	119.78(17)

C(00G)-C(00N)-H(00N)	120.1
C(008)-C(00N)-H(00N)	120.1
O(001)-C(00O)-C(009)	107.31(14)
O(001)-C(00O)-C(00Z)	107.37(13)
C(009)-C(00O)-C(00Z)	112.03(13)
O(001)-C(00O)-C(00K)	101.65(12)
C(009)-C(00O)-C(00K)	113.15(14)
C(00Z)-C(00O)-C(00K)	114.37(14)
N(006)-C(00P)-C(00B)	178.4(2)
O(003)-C(00Q)-O(001)	120.93(17)
O(003)-C(00Q)-C(00L)	128.80(16)
O(001)-C(00Q)-C(00L)	110.27(14)
C(00M)-C(00R)-C(00X)	110.63(14)
C(00M)-C(00R)-H(00J)	109.5
C(00X)-C(00R)-H(00J)	109.5
C(00M)-C(00R)-H(00L)	109.5
C(00X)-C(00R)-H(00L)	109.5
H(00J)-C(00R)-H(00L)	108.1
O(004)-C(00S)-O(002)	120.78(18)
O(004)-C(00S)-C(00J)	128.50(17)
O(002)-C(00S)-C(00J)	110.72(15)
C(010)-C(00T)-C(008)	119.27(16)
C(010)-C(00T)-H(00T)	120.4
C(008)-C(00T)-H(00T)	120.4
C(00C)-C(00U)-C(011)	122.54(16)
C(00C)-C(00U)-C(014)	121.55(18)
C(011)-C(00U)-C(014)	115.91(16)
C(00Y)-C(00V)-C(00B)	119.34(16)
C(00Y)-C(00V)-H(00V)	120.3

C(00B)-C(00V)-H(00V)	120.3
C(00Z)-C(00W)-C(012)	109.84(14)
C(00Z)-C(00W)-H(00M)	109.7
C(012)-C(00W)-H(00M)	109.7
C(00Z)-C(00W)-H(00O)	109.7
C(012)-C(00W)-H(00O)	109.7
H(00M)-C(00W)-H(00O)	108.2
C(011)-C(00X)-C(00R)	109.78(14)
C(011)-C(00X)-H(00Q)	109.7
C(00R)-C(00X)-H(00Q)	109.7
C(011)-C(00X)-H(00R)	109.7
C(00R)-C(00X)-H(00R)	109.7
H(00Q)-C(00X)-H(00R)	108.2
C(00V)-C(00Y)-C(00A)	121.24(17)
C(00V)-C(00Y)-H(00Y)	119.4
C(00A)-C(00Y)-H(00Y)	119.4
C(00W)-C(00Z)-C(00O)	110.63(14)
C(00W)-C(00Z)-H(00S)	109.5
C(00O)-C(00Z)-H(00S)	109.5
C(00W)-C(00Z)-H(00U)	109.5
C(00O)-C(00Z)-H(00U)	109.5
H(00S)-C(00Z)-H(00U)	108.1
C(00T)-C(010)-C(00H)	121.47(17)
C(00T)-C(010)-H(010)	119.3
C(00H)-C(010)-H(010)	119.3
C(00U)-C(011)-C(00X)	112.96(15)
C(00U)-C(011)-H(01A)	109.0
C(00X)-C(011)-H(01A)	109.0
C(00U)-C(011)-H(01B)	109.0

C(00X)-C(011)-H(01B)	109.0
H(01A)-C(011)-H(01B)	107.8
C(00D)-C(012)-C(00W)	112.97(15)
C(00D)-C(012)-H(01C)	109.0
C(00W)-C(012)-H(01C)	109.0
C(00D)-C(012)-H(01D)	109.0
C(00W)-C(012)-H(01D)	109.0
H(01C)-C(012)-H(01D)	107.8
C(00D)-C(013)-H(01E)	109.5
C(00D)-C(013)-H(01F)	109.5
H(01E)-C(013)-H(01F)	109.5
C(00D)-C(013)-H(01G)	109.5
H(01E)-C(013)-H(01G)	109.5
H(01F)-C(013)-H(01G)	109.5
C(00U)-C(014)-H(01H)	109.5
C(00U)-C(014)-H(01I)	109.5
H(01H)-C(014)-H(01I)	109.5
C(00U)-C(014)-H(01J)	109.5
H(01H)-C(014)-H(01J)	109.5
H(01I)-C(014)-H(01J)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **(±)-9j'** (mo_bwsx1094_0m_a). The anisotropic

displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(001)	16(1)	29(1)	16(1)	1(1)	-3(1)	-5(1)
O(002)	16(1)	34(1)	16(1)	0(1)	2(1)	5(1)
O(003)	22(1)	47(1)	26(1)	2(1)	-8(1)	-9(1)
O(004)	21(1)	58(1)	26(1)	-2(1)	6(1)	11(1)
N(005)	26(1)	31(1)	33(1)	0(1)	5(1)	-1(1)
N(006)	32(1)	30(1)	30(1)	3(1)	-5(1)	2(1)
C(007)	17(1)	22(1)	20(1)	1(1)	1(1)	1(1)
C(008)	19(1)	16(1)	26(1)	0(1)	3(1)	2(1)
C(009)	14(1)	23(1)	18(1)	-2(1)	2(1)	-1(1)
C(00A)	16(1)	16(1)	21(1)	0(1)	-1(1)	-2(1)
C(00B)	21(1)	17(1)	23(1)	1(1)	-4(1)	-2(1)
C(00C)	14(1)	26(1)	18(1)	-3(1)	-2(1)	1(1)
C(00D)	13(1)	25(1)	23(1)	2(1)	0(1)	-1(1)
C(00E)	19(1)	21(1)	21(1)	1(1)	2(1)	0(1)
C(00F)	14(1)	20(1)	20(1)	-5(1)	-3(1)	2(1)
C(00G)	18(1)	19(1)	23(1)	1(1)	-2(1)	-2(1)
C(00H)	18(1)	16(1)	22(1)	-1(1)	-2(1)	2(1)
C(00I)	19(1)	20(1)	31(1)	-1(1)	4(1)	1(1)
C(00J)	18(1)	28(1)	20(1)	-5(1)	-3(1)	7(1)
C(00K)	15(1)	19(1)	16(1)	-2(1)	1(1)	-2(1)
C(00L)	15(1)	27(1)	19(1)	-2(1)	0(1)	-6(1)
C(00M)	14(1)	24(1)	15(1)	-2(1)	0(1)	2(1)
C(00N)	21(1)	18(1)	23(1)	1(1)	-3(1)	-1(1)

C(00O)	13(1)	22(1)	14(1)	-1(1)	-2(1)	-1(1)
C(00P)	23(1)	21(1)	25(1)	1(1)	-3(1)	0(1)
C(00Q)	18(1)	28(1)	18(1)	-4(1)	0(1)	-4(1)
C(00R)	18(1)	22(1)	16(1)	0(1)	-1(1)	-1(1)
C(00S)	17(1)	35(1)	19(1)	-6(1)	-2(1)	5(1)
C(00T)	15(1)	26(1)	32(1)	1(1)	0(1)	-2(1)
C(00U)	14(1)	28(1)	22(1)	1(1)	0(1)	2(1)
C(00V)	16(1)	27(1)	28(1)	3(1)	-2(1)	2(1)
C(00W)	17(1)	20(1)	23(1)	0(1)	-1(1)	1(1)
C(00X)	21(1)	21(1)	20(1)	1(1)	1(1)	-2(1)
C(00Y)	17(1)	26(1)	24(1)	1(1)	3(1)	1(1)
C(00Z)	16(1)	22(1)	15(1)	0(1)	0(1)	1(1)
C(010)	16(1)	25(1)	29(1)	0(1)	-6(1)	-2(1)
C(011)	18(1)	23(1)	28(1)	1(1)	3(1)	3(1)
C(012)	18(1)	20(1)	30(1)	1(1)	-4(1)	-3(1)
C(013)	17(1)	33(1)	48(1)	-1(1)	6(1)	-6(1)
C(014)	18(1)	39(1)	46(1)	-3(1)	-9(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **(±)-9j'** (mo_bwsx1094_0m_a).

	x	y	z	U(eq)
H(007)	3995	5990	7933	23
H(009)	6405	6335	3566	22
H(00C)	8979	6366	-1408	23
H(00E)	4570	5804	10353	24
H(00F)	10088	5704	-397	22
H(00G)	11332	6070	3013	24
H(00A)	11929	6011	773	27
H(00B)	11662	5473	-292	27
H(00K)	5257	5684	4517	20
H(00D)	3670	5485	4602	24
H(00H)	3435	6012	5720	24
H(00N)	10745	5897	5437	25
H(00J)	11265	7043	973	22
H(00L)	10244	6992	1793	22
H(00T)	8172	5433	3647	29
H(00V)	7185	5418	8593	28
H(00M)	4943	7918	5979	24
H(00O)	4833	7700	4268	24
H(00Q)	10502	7946	912	25
H(00R)	10602	7712	-786	25
H(00Y)	6603	5614	6175	27

H(00S)	4150	7026	5991	21
H(00U)	5173	6953	6796	21
H(010)	8761	5625	1236	28
H(01A)	8900	7731	1016	27
H(01B)	9040	8020	-609	27
H(01C)	6404	7987	4454	27
H(01D)	6537	7683	6062	27
H(01E)	7837	6810	3240	49
H(01F)	8078	7227	4625	49
H(01G)	7718	7488	3051	49
H(01H)	7574	6856	-1768	51
H(01I)	7713	7532	-1970	51
H(01J)	7345	7279	-391	51

Table 6. Torsion angles [°] for **(±)-9j' (**mo_bwsx1094_0m_a).

C(00E)-C(007)-C(00A)-C(00Y)	-0.2(3)
C(00E)-C(007)-C(00A)-C(00K)	-178.93(16)
C(00O)-C(009)-C(00D)-C(012)	-2.5(3)
C(00O)-C(009)-C(00D)-C(013)	176.67(18)
C(00A)-C(007)-C(00E)-C(00B)	-0.6(3)
C(00V)-C(00B)-C(00E)-C(007)	1.2(3)
C(00P)-C(00B)-C(00E)-C(007)	-175.00(16)
C(00N)-C(00G)-C(00H)-C(010)	0.6(2)
C(00N)-C(00G)-C(00H)-C(00F)	-179.87(16)
C(00J)-C(00F)-C(00H)-C(010)	-150.34(17)
C(00M)-C(00F)-C(00H)-C(010)	88.64(19)
C(00J)-C(00F)-C(00H)-C(00G)	30.1(2)
C(00M)-C(00F)-C(00H)-C(00G)	-90.90(19)
C(00H)-C(00F)-C(00J)-C(00S)	-157.22(14)
C(00M)-C(00F)-C(00J)-C(00S)	-30.36(17)
C(00Y)-C(00A)-C(00K)-C(00L)	154.72(16)
C(007)-C(00A)-C(00K)-C(00L)	-26.6(2)
C(00Y)-C(00A)-C(00K)-C(00O)	-84.87(19)
C(007)-C(00A)-C(00K)-C(00O)	93.85(19)
C(00A)-C(00K)-C(00L)-C(00Q)	156.16(14)
C(00O)-C(00K)-C(00L)-C(00Q)	29.99(16)
C(00S)-O(002)-C(00M)-C(00C)	-143.44(15)
C(00S)-O(002)-C(00M)-C(00R)	95.87(16)
C(00S)-O(002)-C(00M)-C(00F)	-24.44(17)
C(00U)-C(00C)-C(00M)-O(002)	-104.3(2)
C(00U)-C(00C)-C(00M)-C(00R)	13.4(3)
C(00U)-C(00C)-C(00M)-C(00F)	144.33(18)

C(00H)-C(00F)-C(00M)-O(002)	162.68(13)
C(00J)-C(00F)-C(00M)-O(002)	33.09(15)
C(00H)-C(00F)-C(00M)-C(00C)	-82.39(18)
C(00J)-C(00F)-C(00M)-C(00C)	148.02(15)
C(00H)-C(00F)-C(00M)-C(00R)	47.35(19)
C(00J)-C(00F)-C(00M)-C(00R)	-82.24(16)
C(00H)-C(00G)-C(00N)-C(008)	0.8(3)
C(00T)-C(008)-C(00N)-C(00G)	-1.7(3)
C(00I)-C(008)-C(00N)-C(00G)	173.71(16)
C(00Q)-O(001)-C(00O)-C(009)	144.71(14)
C(00Q)-O(001)-C(00O)-C(00Z)	-94.68(15)
C(00Q)-O(001)-C(00O)-C(00K)	25.72(16)
C(00D)-C(009)-C(00O)-O(001)	103.56(19)
C(00D)-C(009)-C(00O)-C(00Z)	-14.1(2)
C(00D)-C(009)-C(00O)-C(00K)	-145.15(17)
C(00A)-C(00K)-C(00O)-O(001)	-162.39(13)
C(00L)-C(00K)-C(00O)-O(001)	-33.54(15)
C(00A)-C(00K)-C(00O)-C(009)	82.87(18)
C(00L)-C(00K)-C(00O)-C(009)	-148.28(15)
C(00A)-C(00K)-C(00O)-C(00Z)	-47.05(19)
C(00L)-C(00K)-C(00O)-C(00Z)	81.81(16)
C(00O)-O(001)-C(00Q)-O(003)	173.65(16)
C(00O)-O(001)-C(00Q)-C(00L)	-6.81(19)
C(00K)-C(00L)-C(00Q)-O(003)	163.95(19)
C(00K)-C(00L)-C(00Q)-O(001)	-15.54(18)
O(002)-C(00M)-C(00R)-C(00X)	72.60(16)
C(00C)-C(00M)-C(00R)-C(00X)	-45.2(2)
C(00F)-C(00M)-C(00R)-C(00X)	-175.45(14)
C(00M)-O(002)-C(00S)-O(004)	-175.40(17)

C(00M)-O(002)-C(00S)-C(00J)	5.20(19)
C(00F)-C(00J)-C(00S)-O(004)	-162.55(19)
C(00F)-C(00J)-C(00S)-O(002)	16.80(19)
C(00N)-C(008)-C(00T)-C(010)	1.0(3)
C(00I)-C(008)-C(00T)-C(010)	-174.39(17)
C(00M)-C(00C)-C(00U)-C(011)	2.8(3)
C(00M)-C(00C)-C(00U)-C(014)	-176.40(18)
C(00E)-C(00B)-C(00V)-C(00Y)	-0.9(3)
C(00P)-C(00B)-C(00V)-C(00Y)	175.30(17)
C(00M)-C(00R)-C(00X)-C(011)	61.65(18)
C(00B)-C(00V)-C(00Y)-C(00A)	0.0(3)
C(007)-C(00A)-C(00Y)-C(00V)	0.5(3)
C(00K)-C(00A)-C(00Y)-C(00V)	179.28(16)
C(012)-C(00W)-C(00Z)-C(00O)	-61.94(18)
O(001)-C(00O)-C(00Z)-C(00W)	-71.78(16)
C(009)-C(00O)-C(00Z)-C(00W)	45.80(19)
C(00K)-C(00O)-C(00Z)-C(00W)	176.26(14)
C(008)-C(00T)-C(010)-C(00H)	0.4(3)
C(00G)-C(00H)-C(010)-C(00T)	-1.2(3)
C(00F)-C(00H)-C(010)-C(00T)	179.20(16)
C(00C)-C(00U)-C(011)-C(00X)	13.6(3)
C(014)-C(00U)-C(011)-C(00X)	-167.11(17)
C(00R)-C(00X)-C(011)-C(00U)	-45.0(2)
C(009)-C(00D)-C(012)-C(00W)	-13.5(3)
C(013)-C(00D)-C(012)-C(00W)	167.29(17)
C(00Z)-C(00W)-C(012)-C(00D)	44.8(2)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **(±)-9j'** (mo_bwsx1094_0m_a) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(00L)-H(00H)...O(004)#1	0.99	2.36	3.348(2)	172.1
C(00L)-H(00D)...N(006)#2	0.99	2.68	3.540(2)	145.3
C(00J)-H(00A)...O(003)#3	0.99	2.35	3.337(2)	173.8
C(00C)-H(00C)...N(005)#4	0.95	2.67	3.561(2)	157.0
C(009)-H(009)...N(006)#4	0.95	2.68	3.574(3)	156.5
C(00L)-H(00H)...O(004)#1	0.99	2.36	3.348(2)	172.1
C(00L)-H(00D)...N(006)#2	0.99	2.68	3.540(2)	145.3
C(00J)-H(00A)...O(003)#3	0.99	2.35	3.337(2)	173.8
C(00C)-H(00C)...N(005)#4	0.95	2.67	3.561(2)	157.0
C(009)-H(009)...N(006)#4	0.95	2.68	3.574(3)	156.5
C(009)-H(009)...N(006)#4	0.95	2.68	3.574(3)	156.5
C(00C)-H(00C)...N(005)#4	0.95	2.67	3.561(2)	157.0
C(00J)-H(00A)...O(003)#3	0.99	2.35	3.337(2)	173.8
C(00L)-H(00D)...N(006)#2	0.99	2.68	3.540(2)	145.3
C(00L)-H(00H)...O(004)#1	0.99	2.36	3.348(2)	172.1

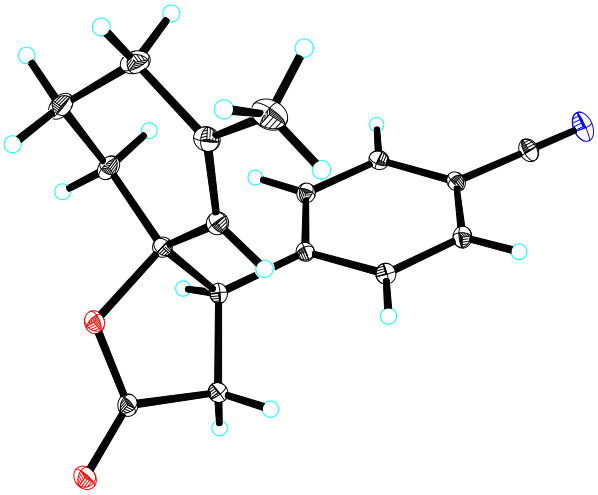
Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z+1 #2 -x+1,-y+1,z-1 #3 x+1,y,z

#4 x,y,z-1

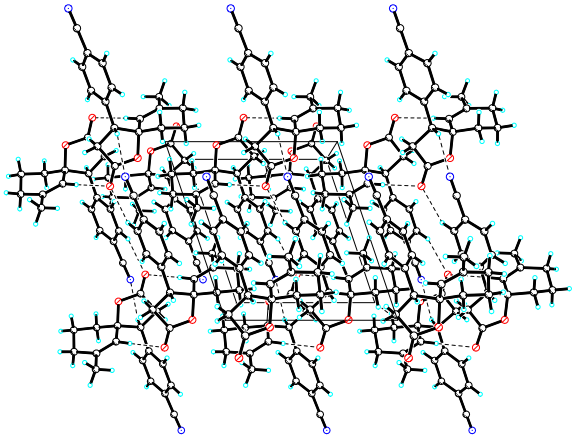
X-ray data of 9j —CCDC2111150 (Original name: **mo_bwsx01093_0m)**

Crystal data for mo_bwsx01093_0m: $C_{17}H_{17}NO_2$, M = 267.31, a = 9.5290(10) Å, b = 17.7336(19) Å, c = 8.6854(9) Å, α = 90°, β = 108.621(2)°, γ = 90°, V = 1390.9(3) Å^3, T = 100(2) K, space group $P21/c$, Z = 4, μ(MoKα) = 0.084 mm^{-1}, 15426 reflections measured, 4108 independent reflections (R_{int} = 0.0263). The final R_1 values were 0.0398 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.1016 ($I > 2\sigma(I)$). The final R_1 values were 0.0489 (all data). The final $wR(F^2)$ values were 0.1082 (all data). The goodness of fit on F^2 was 1.042.



View of a molecule of **9j** (bwsx01093) with the atom-labelling scheme.

Displacement ellipsoids are drawn at the 30% probability level.



View of the pack drawing of **9j (**bwsx01093).

Hydrogen-bonds are shown as dashed lines.

Table 1. Crystal data and structure refinement for **9j** (mo_bwsx01093_0m).

Identification code	mo_bwsx01093_0m	
Empirical formula	C17 H17 N O2	
Formula weight	267.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.5290(10) Å	α= 90°.
	b = 17.7336(19) Å	β= 108.621(2)°.
	c = 8.6854(9) Å	γ = 90°.
Volume	1390.9(3) $Å^3$	
Z	4	
Density (calculated)	1.277 Mg/m^3	
Absorption coefficient	0.084 mm^{-1}	
F(000)	568	
Crystal size	0.870 x 0.350 x 0.260 mm^3	
Theta range for data collection	2.255 to 30.942°.	
Index ranges	-13<=h<=12, -25<=k<=24, -12<=l<=12	
Reflections collected	15426	
Independent reflections	4108 [R(int) = 0.0263]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4108 / 0 / 182	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR2 = 0.1016	
R indices (all data)	R1 = 0.0489, wR2 = 0.1082	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.391 and -0.237 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9j** (mo_bwsx01093_0m). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	10491(1)	795(1)	7620(1)	18(1)
O(2)	12224(1)	656(1)	10031(1)	23(1)
N(1)	1776(1)	2509(1)	8486(1)	29(1)
C(1)	7339(1)	393(1)	3686(1)	26(1)
C(2)	7297(1)	30(1)	5241(1)	21(1)
C(3)	8000(1)	328(1)	6697(1)	17(1)
C(4)	8910(1)	1033(1)	6948(1)	15(1)
C(5)	8740(1)	1555(1)	8322(1)	15(1)
C(6)	7168(1)	1695(1)	8295(1)	14(1)
C(7)	6415(1)	1222(1)	9062(1)	16(1)
C(8)	4998(1)	1399(1)	9077(1)	17(1)
C(9)	4320(1)	2063(1)	8330(1)	16(1)
C(10)	2892(1)	2295(1)	8411(1)	20(1)
C(11)	6439(1)	2339(1)	7498(1)	16(1)
C(12)	5032(1)	2530(1)	7517(1)	17(1)
C(13)	10992(1)	862(1)	9244(1)	17(1)
C(14)	9814(1)	1202(1)	9857(1)	17(1)
C(15)	8646(1)	929(1)	3969(1)	25(1)
C(16)	8736(1)	1460(1)	5381(1)	21(1)
C(17)	6438(1)	-691(1)	5089(2)	30(1)

Table 3. Bond lengths [Å] and angles [°] for **9j** (mo_bwsx01093_0m).

O(1)-C(13)	1.3417(12)
O(1)-C(4)	1.4926(11)
O(2)-C(13)	1.2110(12)
N(1)-C(10)	1.1498(14)
C(1)-C(2)	1.5084(15)
C(1)-C(15)	1.5219(17)
C(1)-H(1)	0.9900
C(1)-H(8)	0.9900
C(2)-C(3)	1.3373(13)
C(2)-C(17)	1.5005(15)
C(3)-C(4)	1.4977(13)
C(3)-H(16)	0.9500
C(4)-C(16)	1.5194(13)
C(4)-C(5)	1.5584(12)
C(5)-C(6)	1.5116(12)
C(5)-C(14)	1.5318(13)
C(5)-H(17)	1.0000
C(6)-C(11)	1.3993(13)
C(6)-C(7)	1.4032(13)
C(7)-C(8)	1.3911(13)
C(7)-H(3)	0.9500
C(8)-C(9)	1.3991(13)
C(8)-H(2)	0.9500
C(9)-C(12)	1.3960(13)
C(9)-C(10)	1.4446(13)
C(11)-C(12)	1.3878(13)
C(11)-H(5)	0.9500
C(12)-H(4)	0.9500
C(13)-C(14)	1.5125(13)
C(14)-H(7)	0.9900
C(14)-H(6)	0.9900
C(15)-C(16)	1.5272(14)
C(15)-H(9)	0.9900
C(15)-H(10)	0.9900
C(16)-H(11)	0.9900
C(16)-H(12)	0.9900

C(17)-H(13)	0.9800
C(17)-H(15)	0.9800
C(17)-H(14)	0.9800
C(13)-O(1)-C(4)	111.22(7)
C(2)-C(1)-C(15)	112.13(9)
C(2)-C(1)-H(1)	109.2
C(15)-C(1)-H(1)	109.2
C(2)-C(1)-H(8)	109.2
C(15)-C(1)-H(8)	109.2
H(1)-C(1)-H(8)	107.9
C(3)-C(2)-C(17)	120.98(10)
C(3)-C(2)-C(1)	121.93(10)
C(17)-C(2)-C(1)	117.09(9)
C(2)-C(3)-C(4)	124.07(9)
C(2)-C(3)-H(16)	118.0
C(4)-C(3)-H(16)	118.0
O(1)-C(4)-C(3)	106.59(7)
O(1)-C(4)-C(16)	107.45(7)
C(3)-C(4)-C(16)	113.15(8)
O(1)-C(4)-C(5)	101.97(7)
C(3)-C(4)-C(5)	114.22(7)
C(16)-C(4)-C(5)	112.41(7)
C(6)-C(5)-C(14)	117.64(8)
C(6)-C(5)-C(4)	115.48(7)
C(14)-C(5)-C(4)	102.68(7)
C(6)-C(5)-H(17)	106.8
C(14)-C(5)-H(17)	106.8
C(4)-C(5)-H(17)	106.8
C(11)-C(6)-C(7)	118.38(8)
C(11)-C(6)-C(5)	118.30(8)
C(7)-C(6)-C(5)	123.30(8)
C(8)-C(7)-C(6)	120.89(8)
C(8)-C(7)-H(3)	119.6
C(6)-C(7)-H(3)	119.6
C(7)-C(8)-C(9)	119.52(9)
C(7)-C(8)-H(2)	120.2
C(9)-C(8)-H(2)	120.2
C(12)-C(9)-C(8)	120.38(8)

C(12)-C(9)-C(10)	118.33(9)
C(8)-C(9)-C(10)	121.27(9)
N(1)-C(10)-C(9)	177.20(11)
C(12)-C(11)-C(6)	121.43(9)
C(12)-C(11)-H(5)	119.3
C(6)-C(11)-H(5)	119.3
C(11)-C(12)-C(9)	119.31(9)
C(11)-C(12)-H(4)	120.3
C(9)-C(12)-H(4)	120.3
O(2)-C(13)-O(1)	121.46(9)
O(2)-C(13)-C(14)	128.03(9)
O(1)-C(13)-C(14)	110.50(8)
C(13)-C(14)-C(5)	102.79(7)
C(13)-C(14)-H(7)	111.2
C(5)-C(14)-H(7)	111.2
C(13)-C(14)-H(6)	111.2
C(5)-C(14)-H(6)	111.2
H(7)-C(14)-H(6)	109.1
C(1)-C(15)-C(16)	110.38(8)
C(1)-C(15)-H(9)	109.6
C(16)-C(15)-H(9)	109.6
C(1)-C(15)-H(10)	109.6
C(16)-C(15)-H(10)	109.6
H(9)-C(15)-H(10)	108.1
C(4)-C(16)-C(15)	111.94(8)
C(4)-C(16)-H(11)	109.2
C(15)-C(16)-H(11)	109.2
C(4)-C(16)-H(12)	109.2
C(15)-C(16)-H(12)	109.2
H(11)-C(16)-H(12)	107.9
C(2)-C(17)-H(13)	109.5
C(2)-C(17)-H(15)	109.5
H(13)-C(17)-H(15)	109.5
C(2)-C(17)-H(14)	109.5
H(13)-C(17)-H(14)	109.5
H(15)-C(17)-H(14)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9j (**mo_bwsx01093_0m). The anisotropic

displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	16(1)	20(1)	20(1)	2(1)	8(1)	4(1)
O(2)	16(1)	27(1)	27(1)	10(1)	7(1)	4(1)
N(1)	19(1)	23(1)	46(1)	0(1)	13(1)	0(1)
C(1)	29(1)	33(1)	16(1)	-4(1)	5(1)	10(1)
C(2)	19(1)	21(1)	21(1)	-4(1)	5(1)	6(1)
C(3)	18(1)	16(1)	17(1)	0(1)	6(1)	2(1)
C(4)	16(1)	16(1)	15(1)	2(1)	6(1)	3(1)
C(5)	14(1)	15(1)	16(1)	-1(1)	6(1)	0(1)
C(6)	14(1)	14(1)	14(1)	-3(1)	5(1)	-1(1)
C(7)	16(1)	14(1)	18(1)	0(1)	6(1)	0(1)
C(8)	17(1)	17(1)	19(1)	-2(1)	7(1)	-2(1)
C(9)	13(1)	18(1)	17(1)	-3(1)	4(1)	-1(1)
C(10)	17(1)	18(1)	26(1)	-1(1)	7(1)	-2(1)
C(11)	17(1)	16(1)	17(1)	-1(1)	6(1)	-1(1)
C(12)	17(1)	16(1)	18(1)	0(1)	4(1)	1(1)
C(13)	16(1)	16(1)	20(1)	4(1)	7(1)	0(1)
C(14)	14(1)	21(1)	16(1)	0(1)	5(1)	1(1)
C(15)	32(1)	30(1)	17(1)	4(1)	13(1)	12(1)
C(16)	26(1)	21(1)	18(1)	5(1)	11(1)	7(1)
C(17)	27(1)	24(1)	32(1)	-11(1)	3(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9j** (mo_bwsx01093_0m).

	x	y	z	U(eq)
H(1)	6407	675	3191	32
H(8)	7405	-4	2913	32
H(16)	7916	78	7631	20
H(17)	9162	2057	8178	18
H(3)	6880	773	9579	19
H(2)	4494	1072	9590	21
H(5)	6918	2652	6931	20
H(4)	4559	2973	6984	21
H(7)	10239	1589	10699	21
H(6)	9318	810	10309	21
H(9)	8530	1227	2972	30
H(10)	9574	635	4214	30
H(11)	9588	1805	5545	25
H(12)	7825	1771	5107	25
H(13)	6400	-842	6161	44
H(15)	6923	-1087	4657	44
H(14)	5428	-614	4351	44

Table 6. Torsion angles [°] for **9j (**mo_bwsx01093_0m).

C(15)-C(1)-C(2)-C(3)	20.64(13)
C(15)-C(1)-C(2)-C(17)	-158.88(9)
C(17)-C(2)-C(3)-C(4)	178.36(9)
C(1)-C(2)-C(3)-C(4)	-1.14(15)
C(13)-O(1)-C(4)-C(3)	-97.64(8)
C(13)-O(1)-C(4)-C(16)	140.78(8)
C(13)-O(1)-C(4)-C(5)	22.41(9)
C(2)-C(3)-C(4)-O(1)	-107.28(10)
C(2)-C(3)-C(4)-C(16)	10.61(13)
C(2)-C(3)-C(4)-C(5)	140.93(9)
O(1)-C(4)-C(5)-C(6)	-160.99(7)
C(3)-C(4)-C(5)-C(6)	-46.44(11)
C(16)-C(4)-C(5)-C(6)	84.24(10)
O(1)-C(4)-C(5)-C(14)	-31.64(8)
C(3)-C(4)-C(5)-C(14)	82.90(9)
C(16)-C(4)-C(5)-C(14)	-146.42(8)
C(14)-C(5)-C(6)-C(11)	144.18(9)
C(4)-C(5)-C(6)-C(11)	-94.22(10)
C(14)-C(5)-C(6)-C(7)	-34.21(12)
C(4)-C(5)-C(6)-C(7)	87.40(11)
C(11)-C(6)-C(7)-C(8)	-2.02(13)
C(5)-C(6)-C(7)-C(8)	176.37(8)
C(6)-C(7)-C(8)-C(9)	-0.64(14)
C(7)-C(8)-C(9)-C(12)	2.59(14)
C(7)-C(8)-C(9)-C(10)	-175.76(9)
C(7)-C(6)-C(11)-C(12)	2.82(13)
C(5)-C(6)-C(11)-C(12)	-175.64(8)
C(6)-C(11)-C(12)-C(9)	-0.94(14)
C(8)-C(9)-C(12)-C(11)	-1.81(14)
C(10)-C(9)-C(12)-C(11)	176.59(9)
C(4)-O(1)-C(13)-O(2)	175.70(8)
C(4)-O(1)-C(13)-C(14)	-3.34(10)
O(2)-C(13)-C(14)-C(5)	163.43(10)
O(1)-C(13)-C(14)-C(5)	-17.61(10)
C(6)-C(5)-C(14)-C(13)	157.89(8)
C(4)-C(5)-C(14)-C(13)	29.90(9)

C(2)-C(1)-C(15)-C(16)	-48.52(11)
O(1)-C(4)-C(16)-C(15)	78.13(10)
C(3)-C(4)-C(16)-C(15)	-39.24(11)
C(5)-C(4)-C(16)-C(15)	-170.47(8)
C(1)-C(15)-C(16)-C(4)	59.09(11)

Symmetry transformations used to generate equivalent atoms:

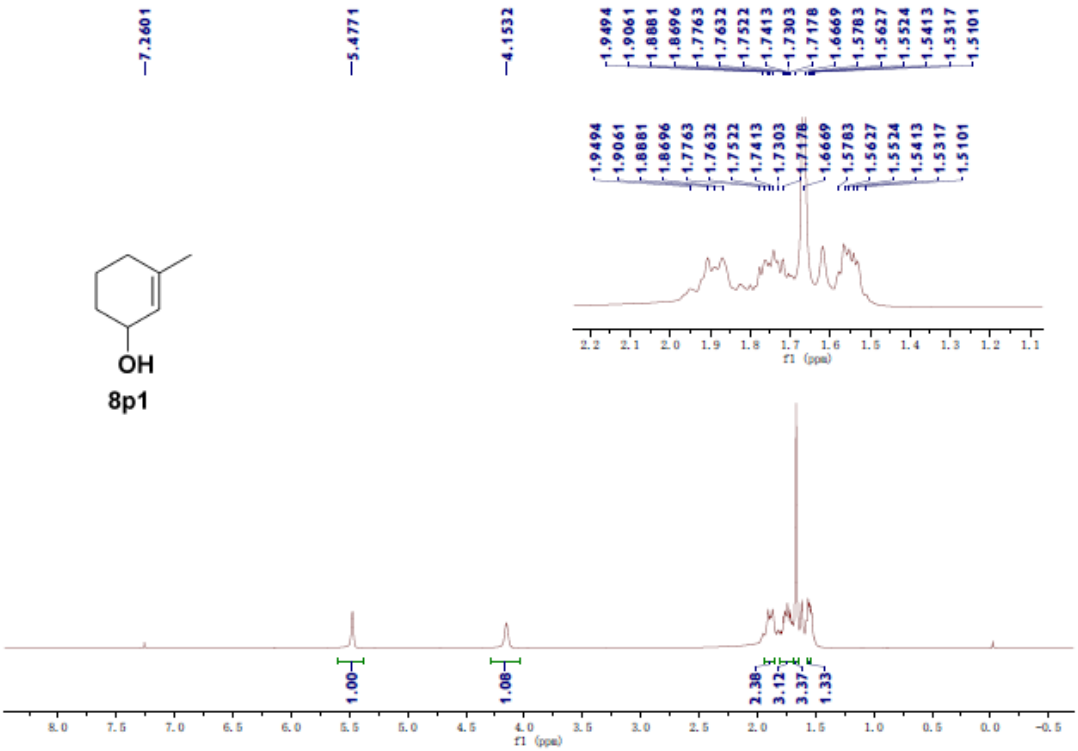
Table 7. Hydrogen bonds for **9j** (mo_bwsx01093_0m) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3
C(3)-H(16)...O(2)#2	0.95	2.45	3.3987(12)	175.6
C(5)-H(17)...N(1)#1	1.00	2.55	3.3143(13)	133.3

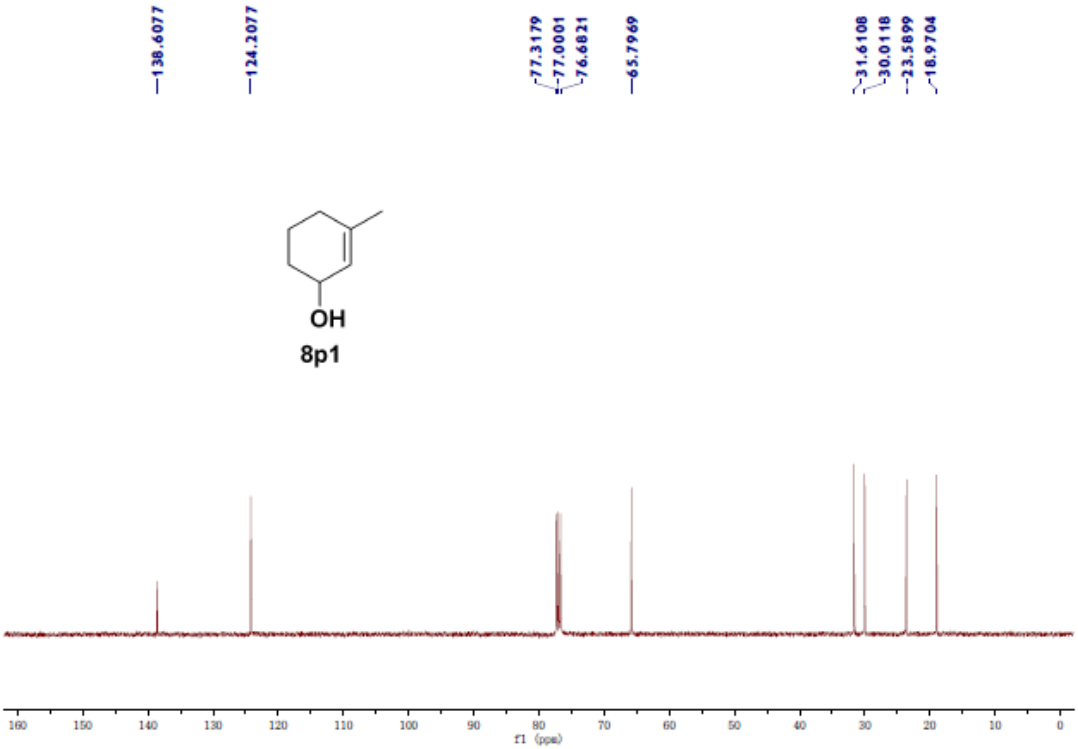
Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 -x+2,-y,-z+2

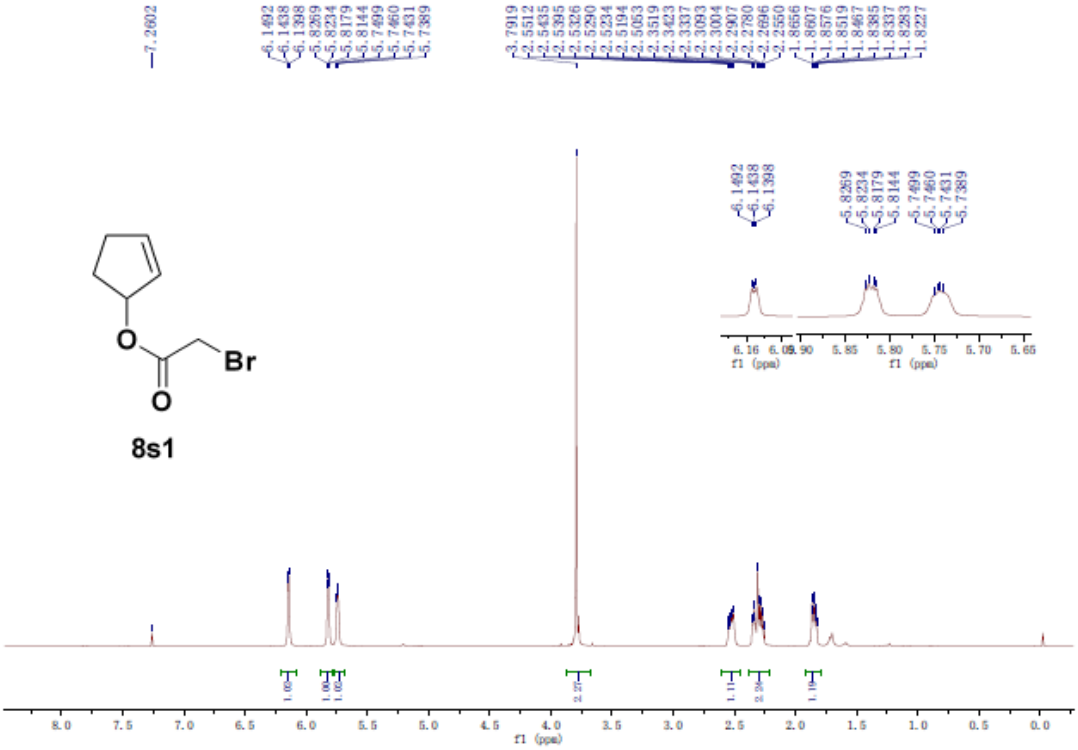
^{1}H NMR of **8p1** (400 M, $CDCl_3$)



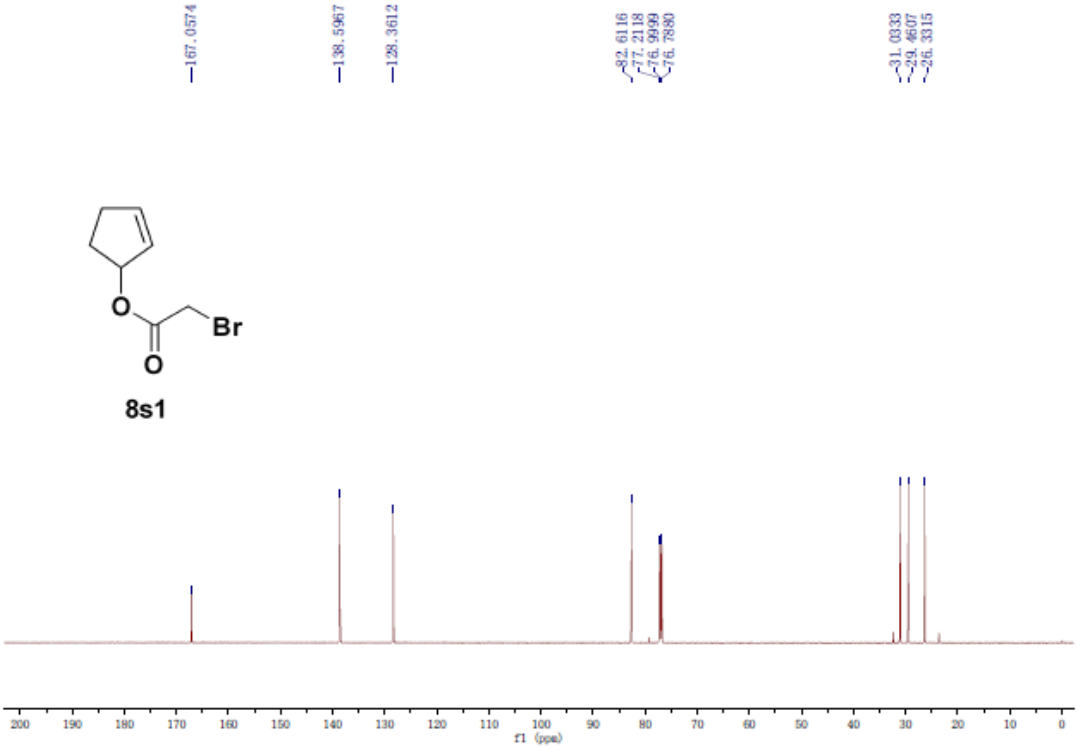
^{13}C NMR of **8p1** (100 M, $CDCl_3$)



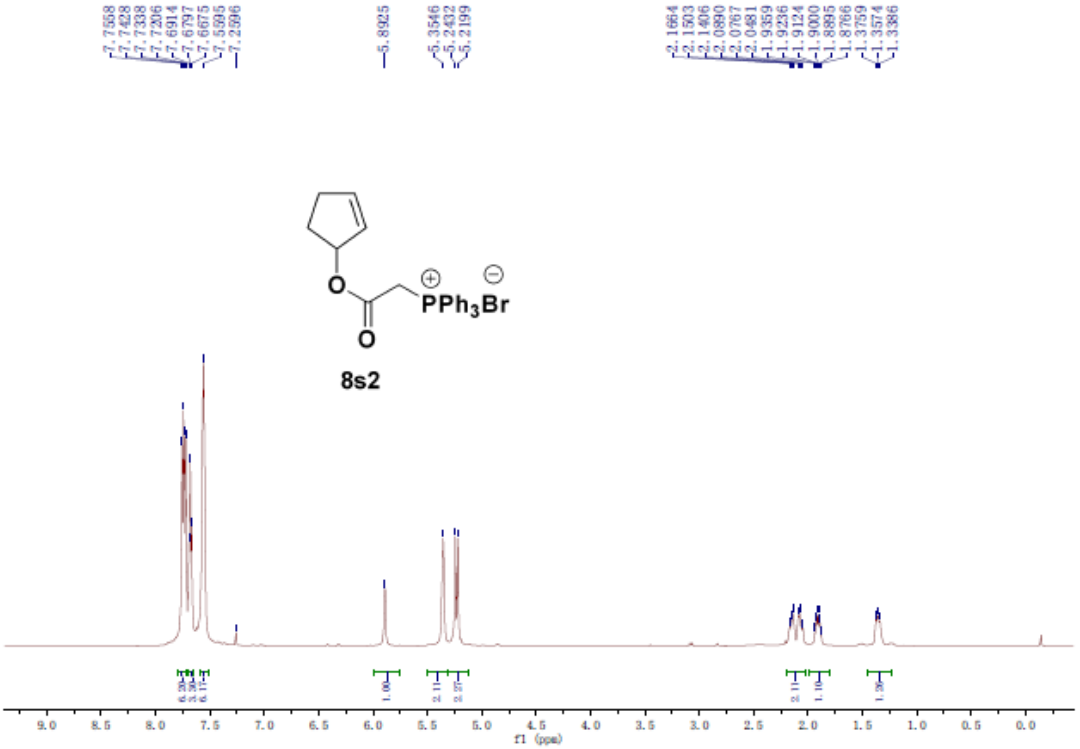
^{1}H NMR of **8s1** (600 M, $CDCl_3$)



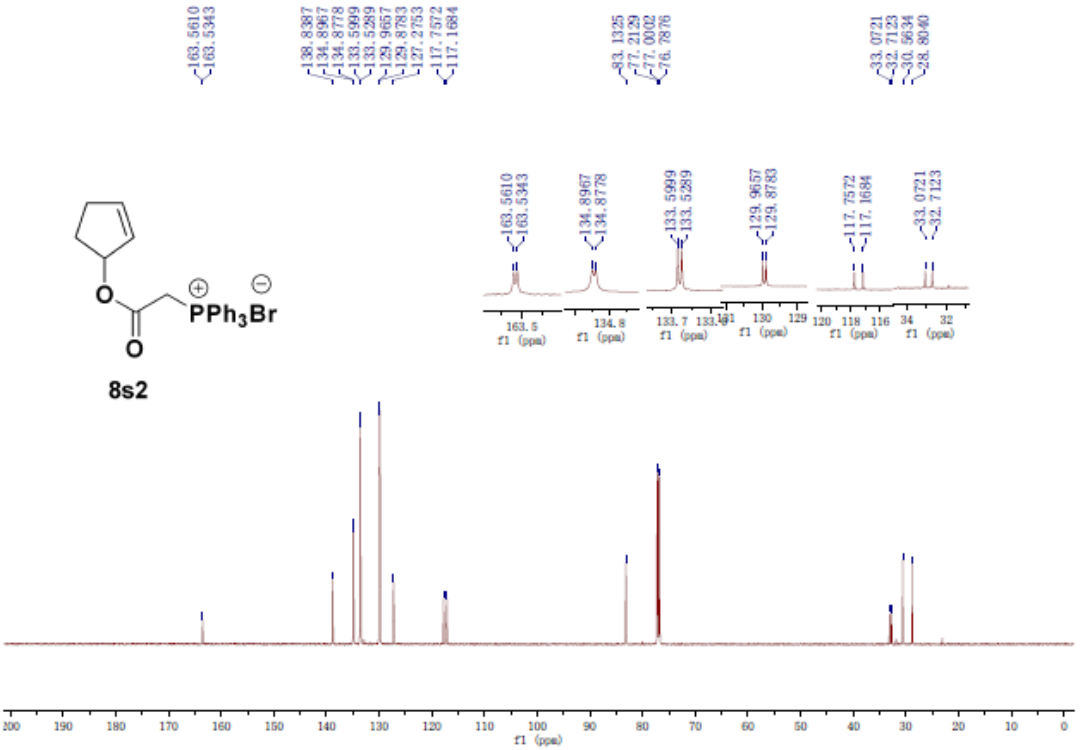
^{13}C NMR of **8s1** (150 M, $CDCl_3$)



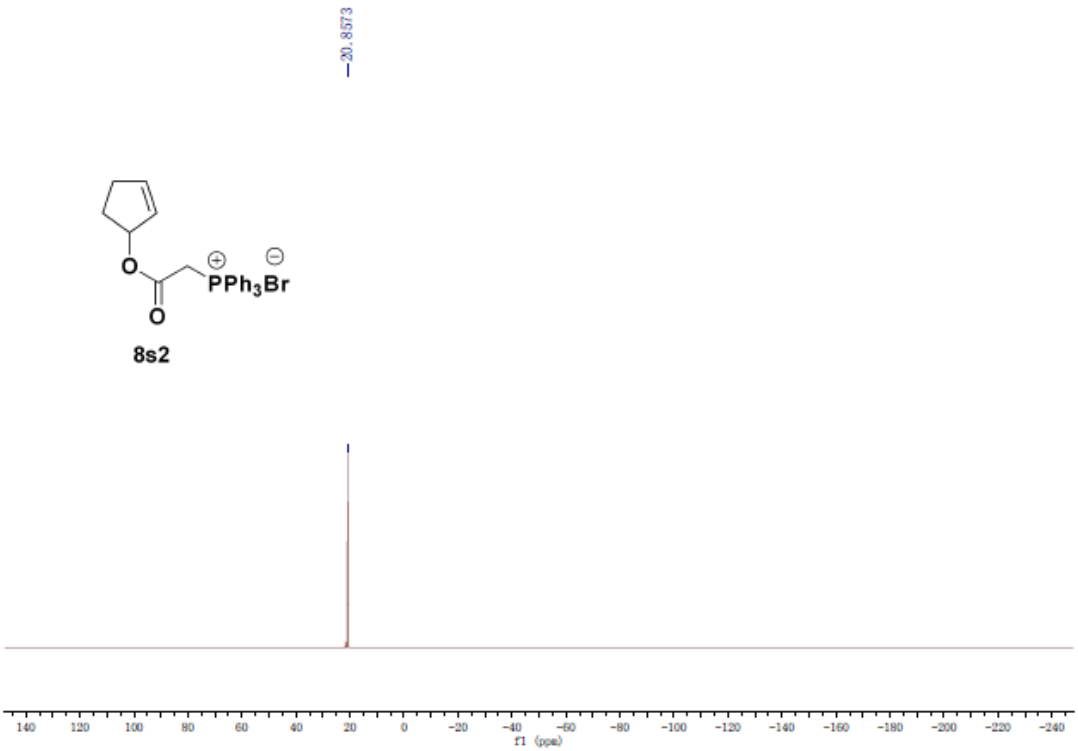
^{1}H NMR of **8s2** (600 M, $CDCl_3$)



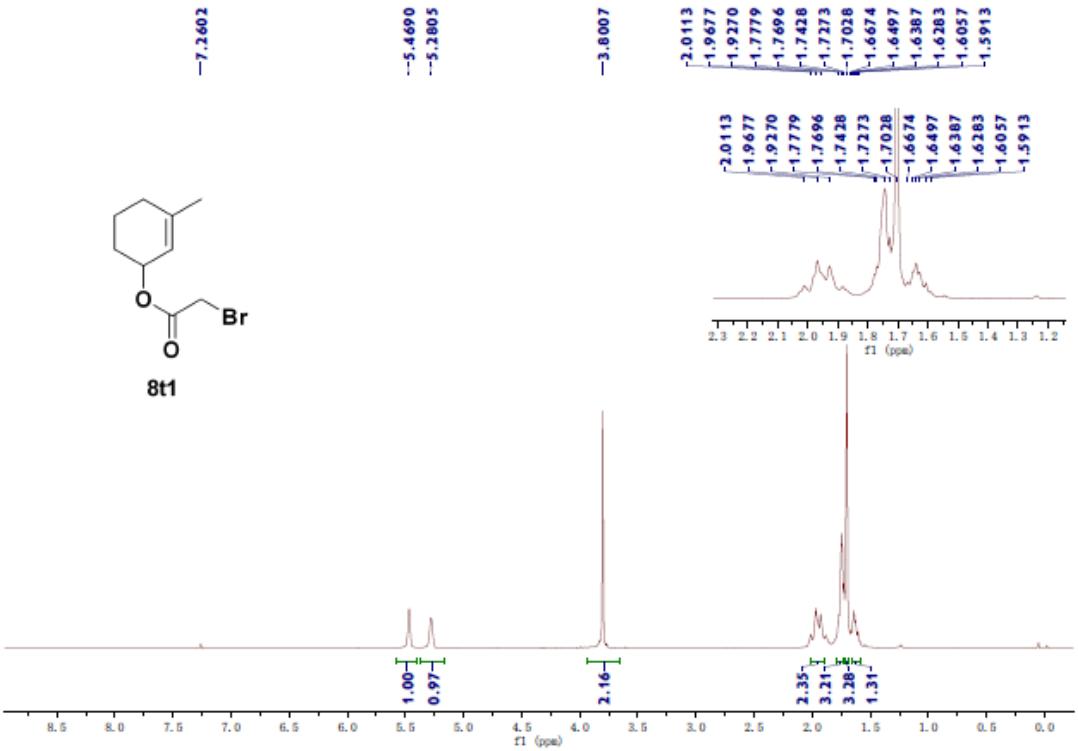
^{13}C NMR of **8s2** (150 M, $CDCl_3$)



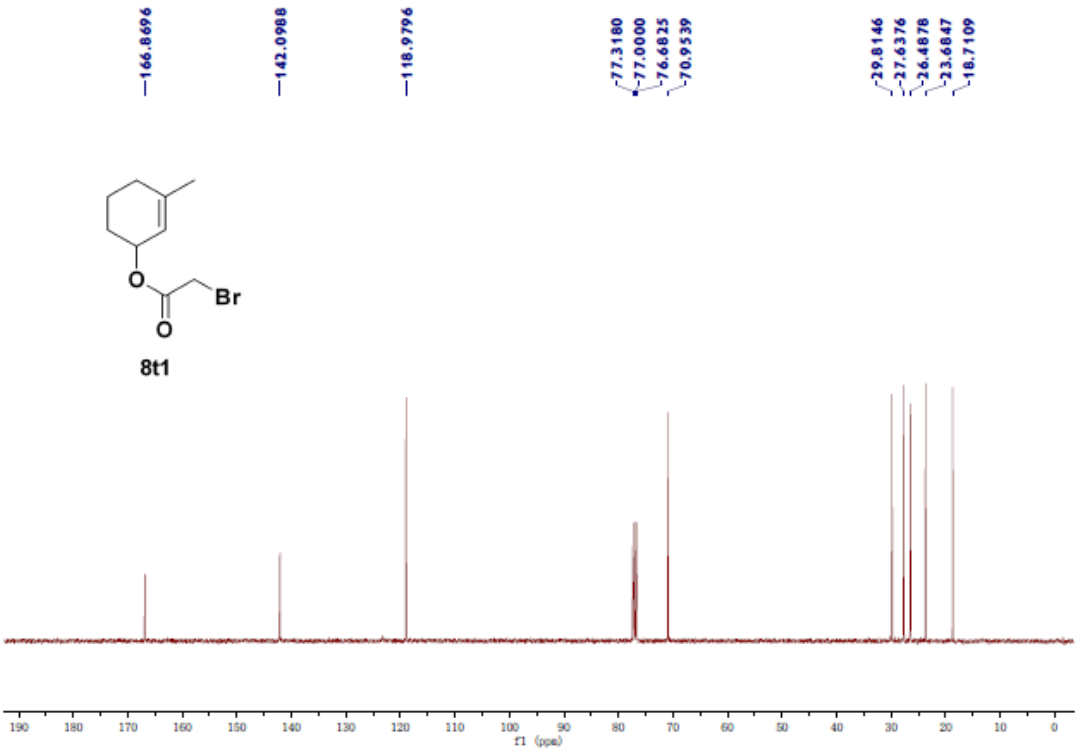
^{31}P NMR of **8s2** (242 M, $CDCl_3$)



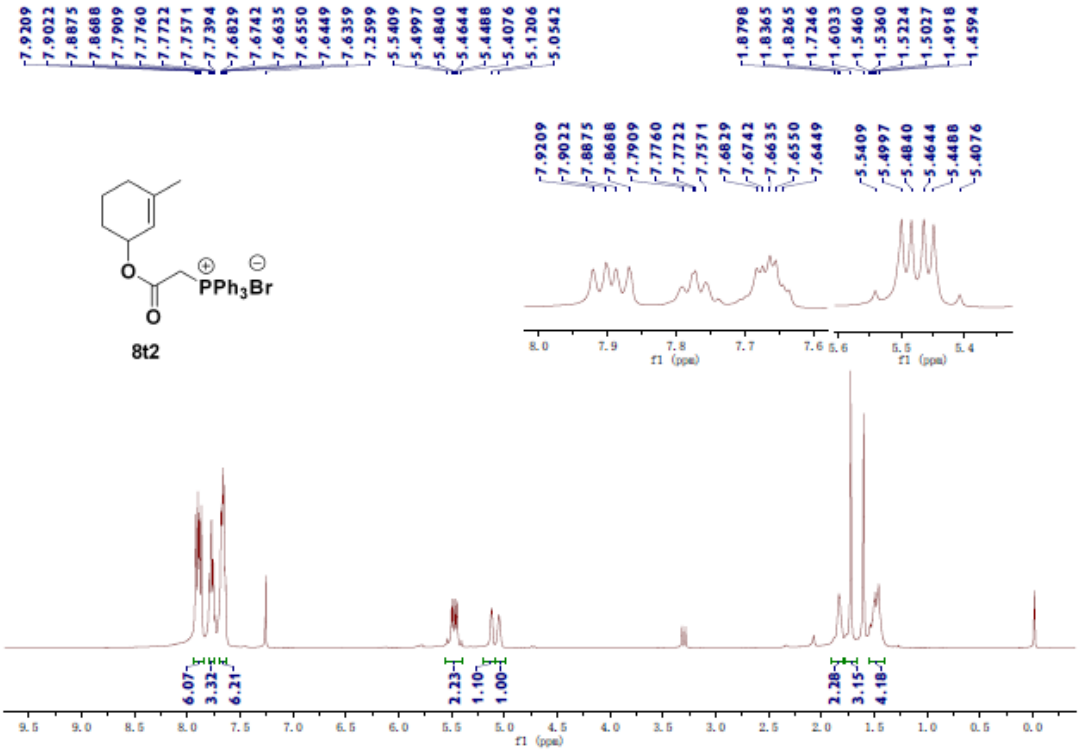
^{1}H NMR of **8t1** (400 M, $CDCl_3$)



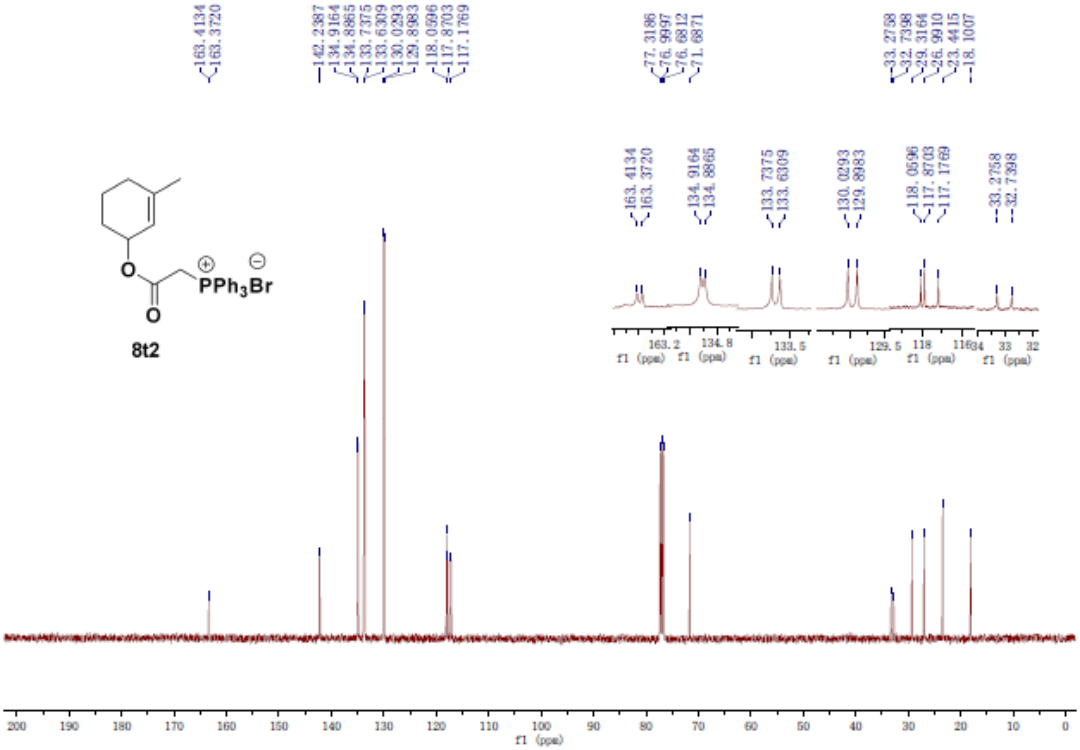
^{13}C NMR of **8t1** (100 M, $CDCl_3$)



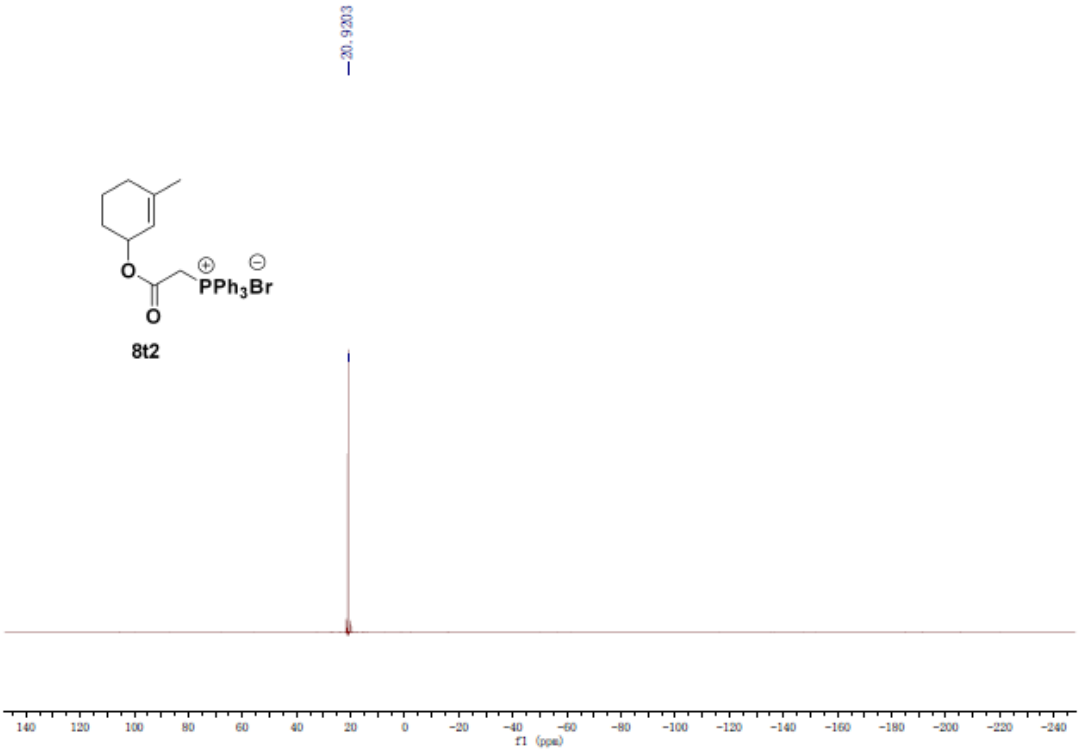
^{1}H NMR of **8t2** (400 M, $CDCl_3$)



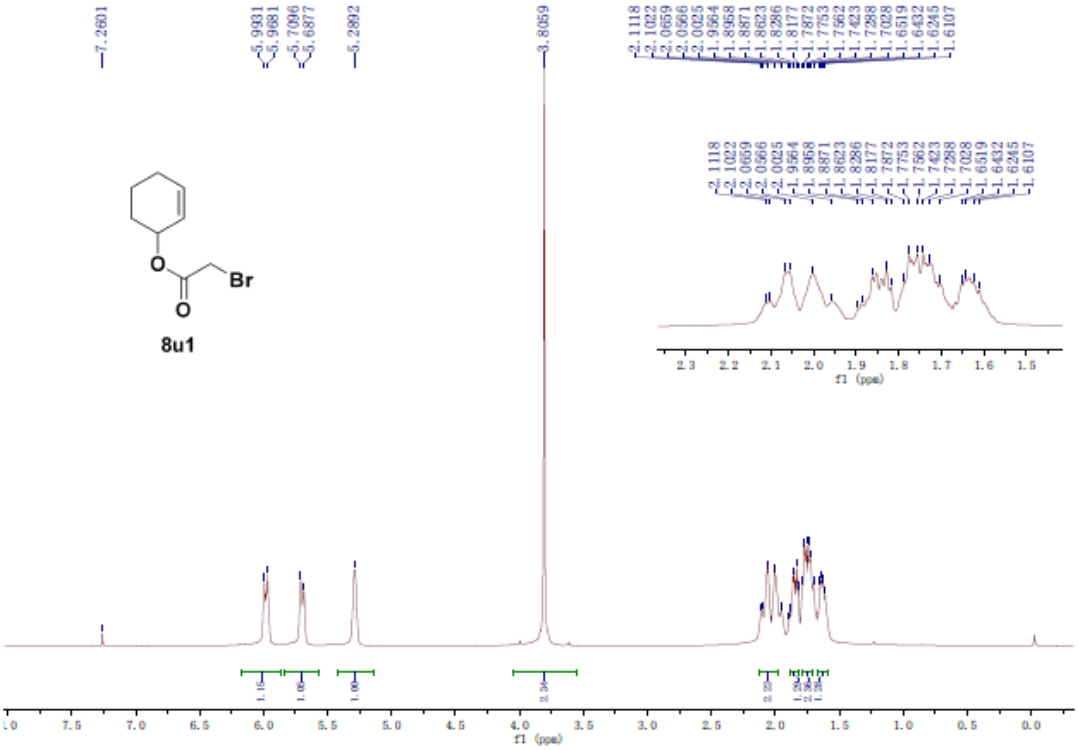
^{13}C NMR of **8t2** (100 M, $CDCl_3$)



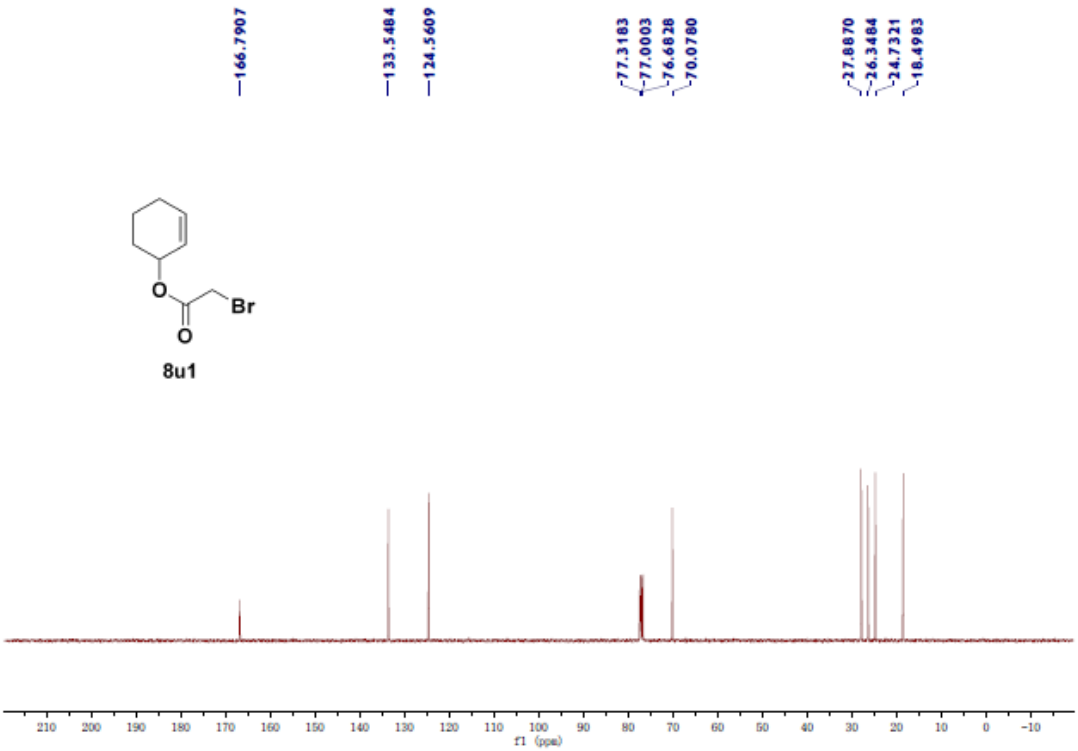
^{31}P NMR of **8t2** (242 M, $CDCl_3$)



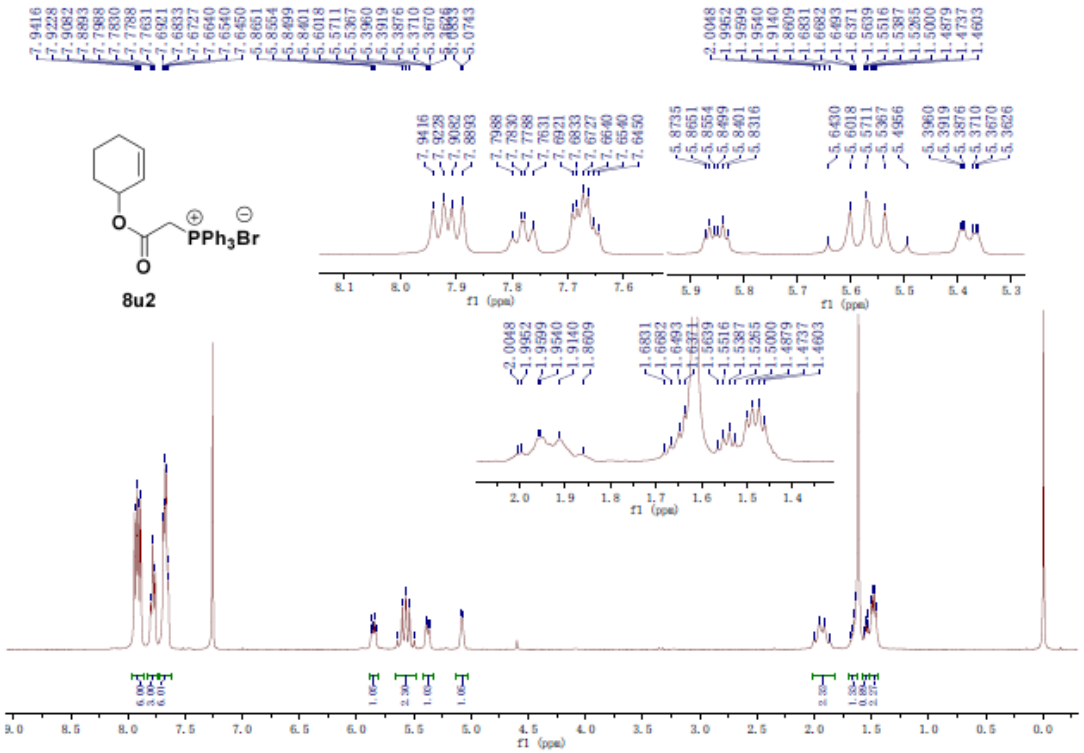
^{1}H NMR of **8u1** (400 M, $CDCl_3$)



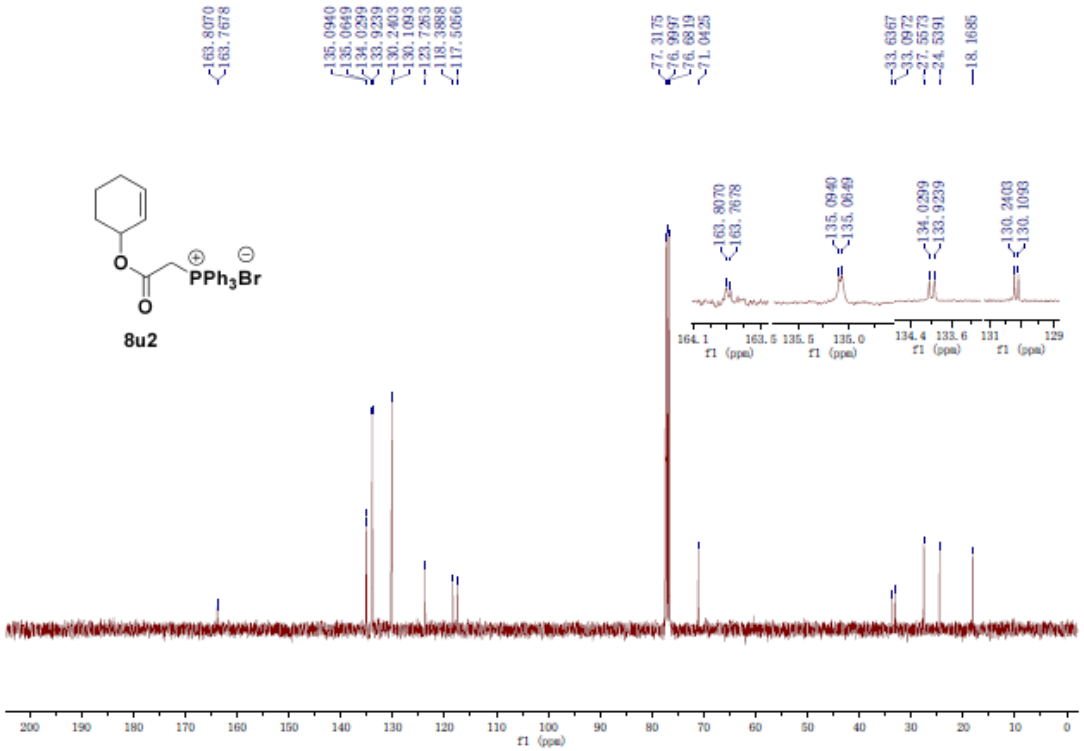
^{13}C NMR of **8u1** (100 M, $CDCl_3$)



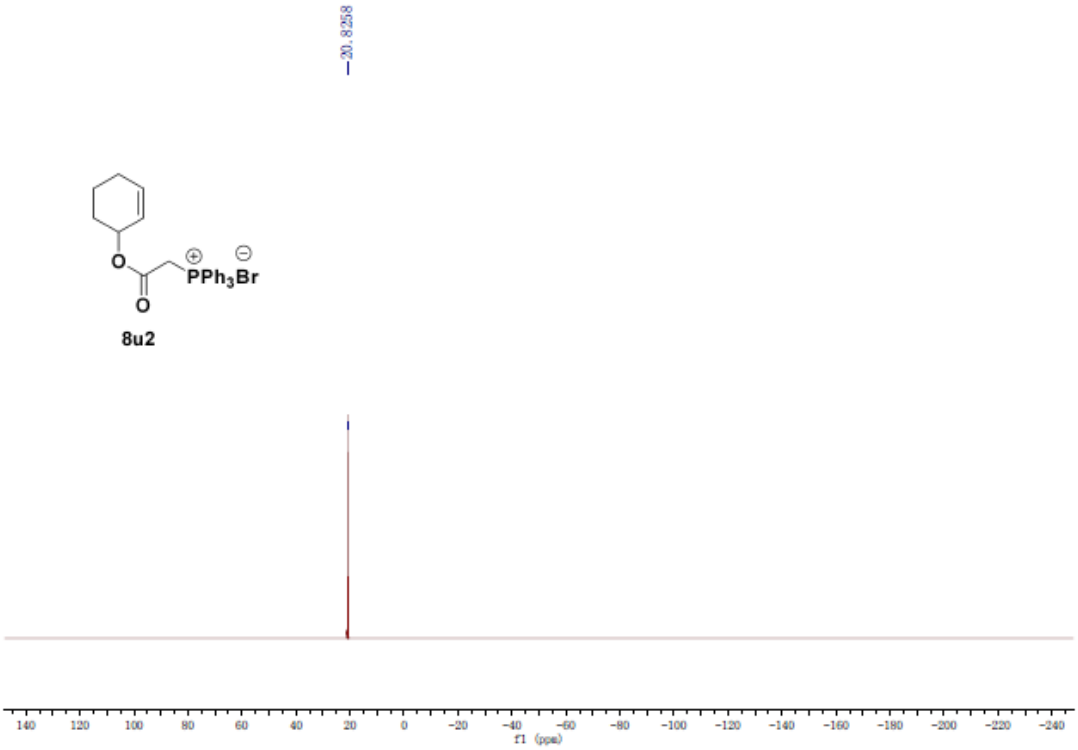
^{1}H NMR of **8u2** (400 M, $CDCl_3$)



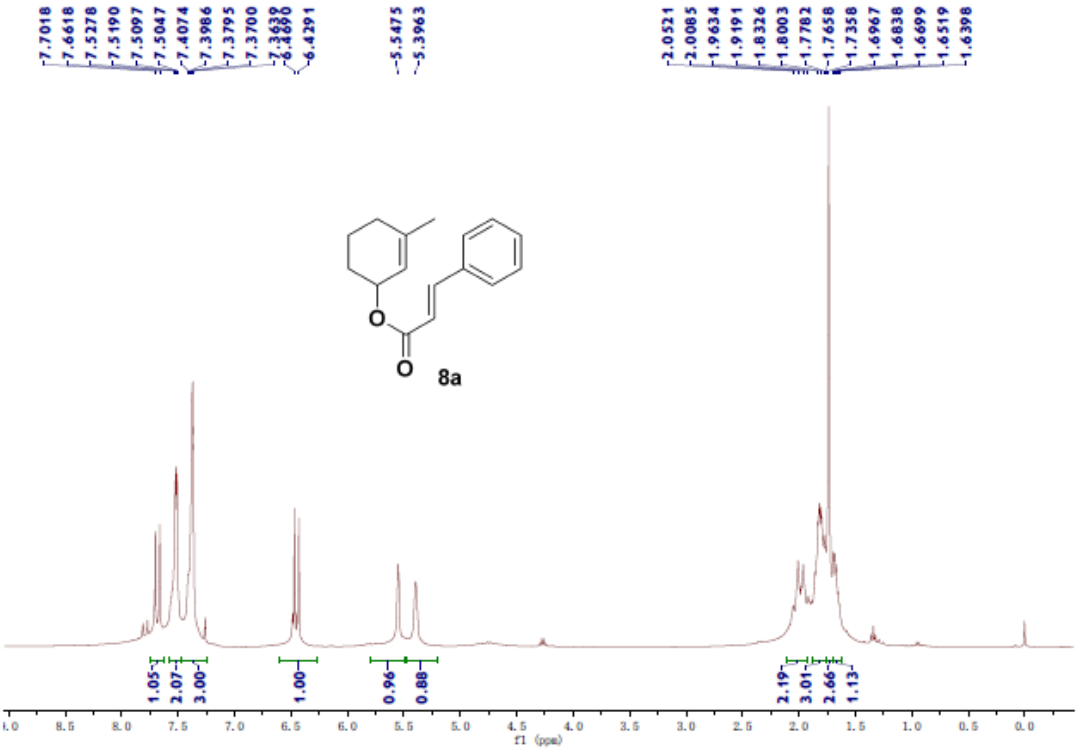
^{13}C NMR of **8u2** (100 M, $CDCl_3$)



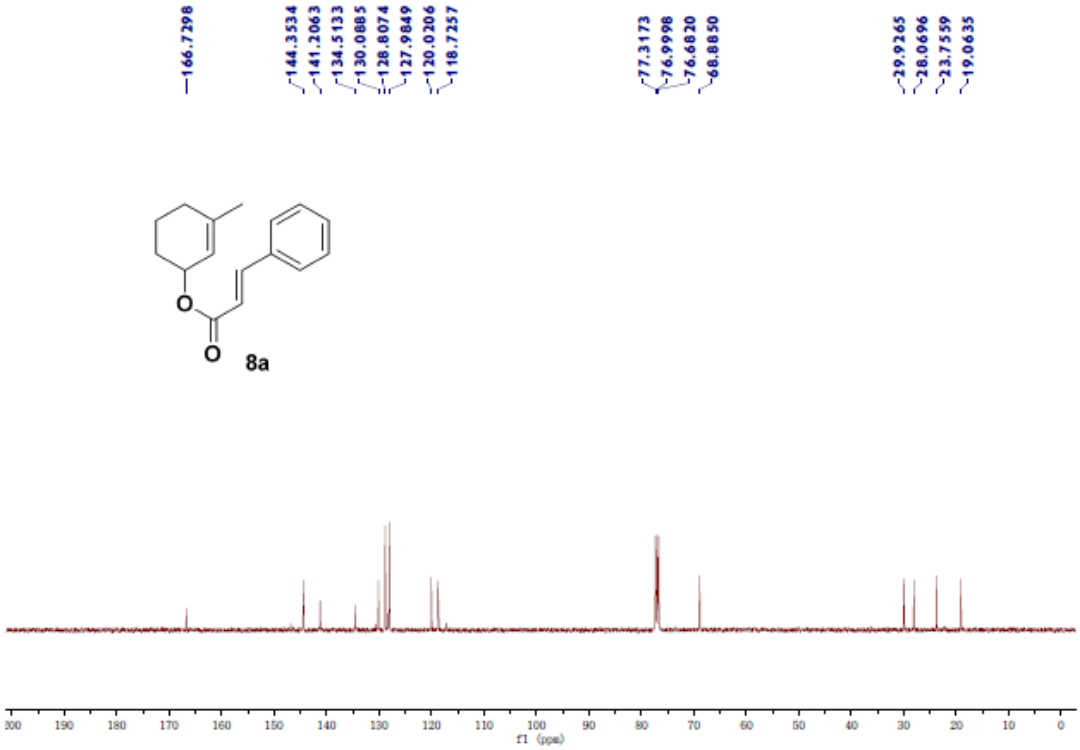
^{31}P NMR of **8u2** (242 M, $CDCl_3$)



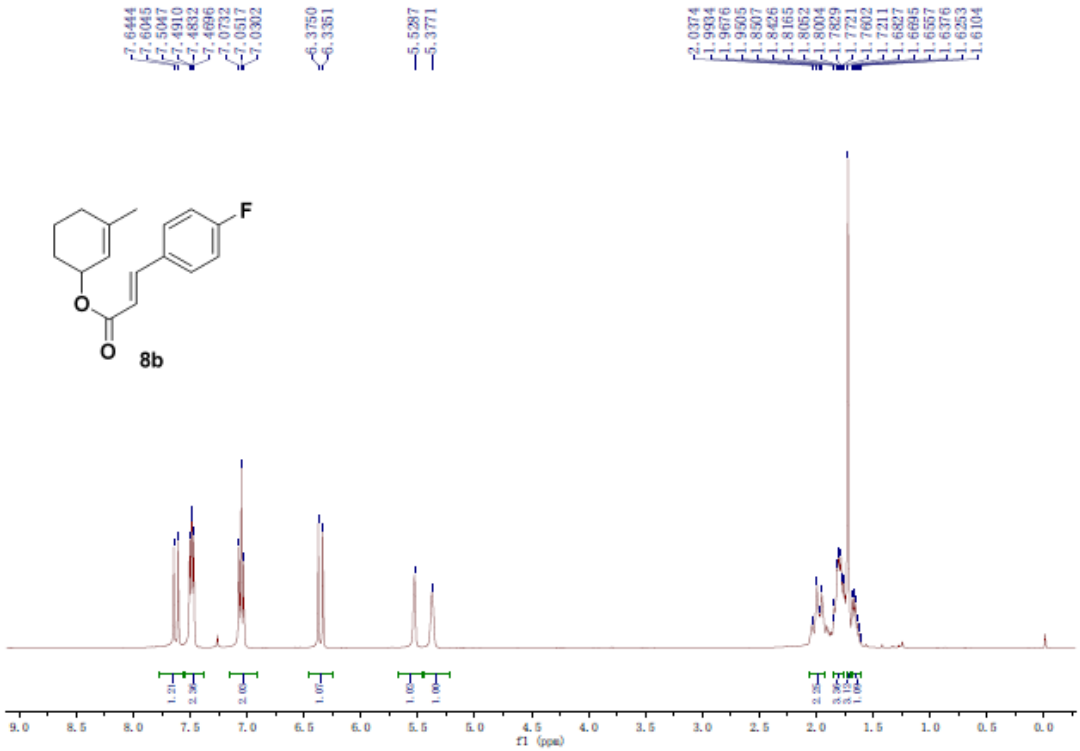
^{1}H NMR of **8a** (400 M, $CDCl_3$)



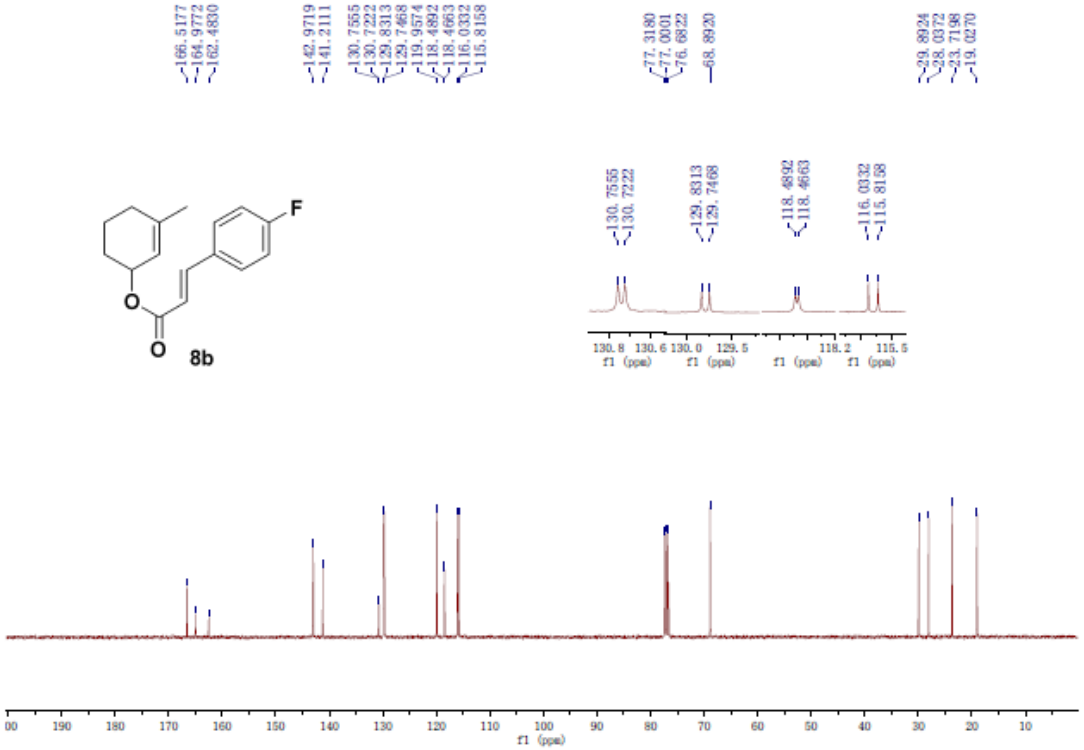
^{13}C NMR of **8a** (100 M, $CDCl_3$)



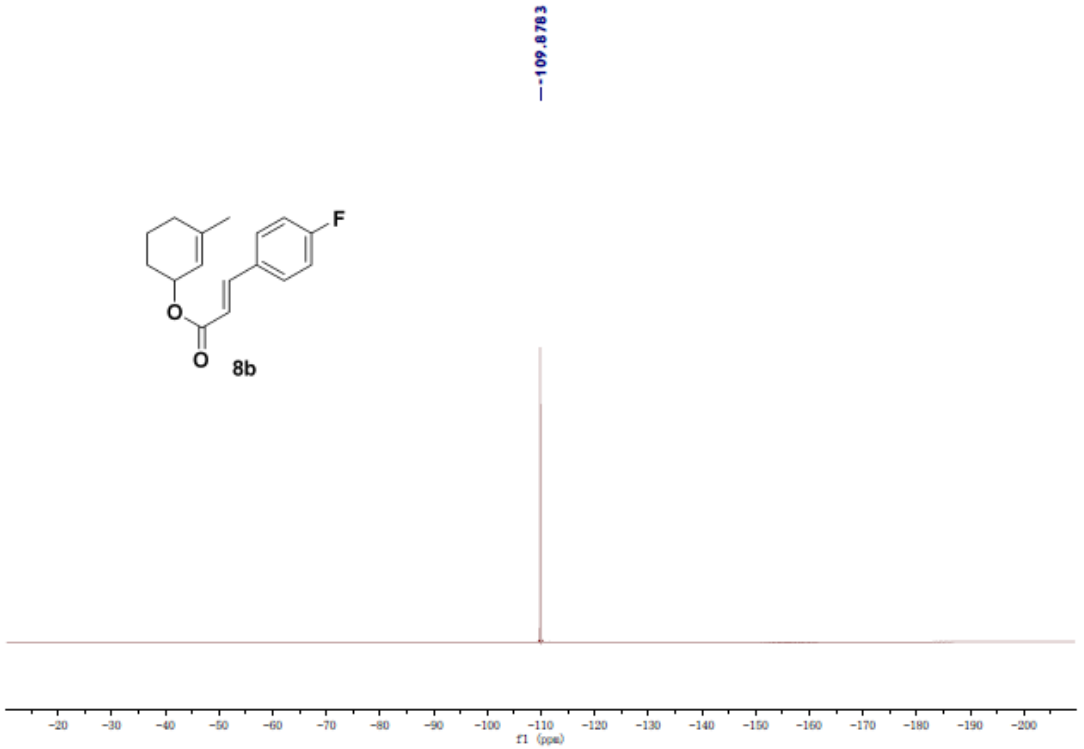
^{1}H NMR of **8b** (400 M, $CDCl_3$)



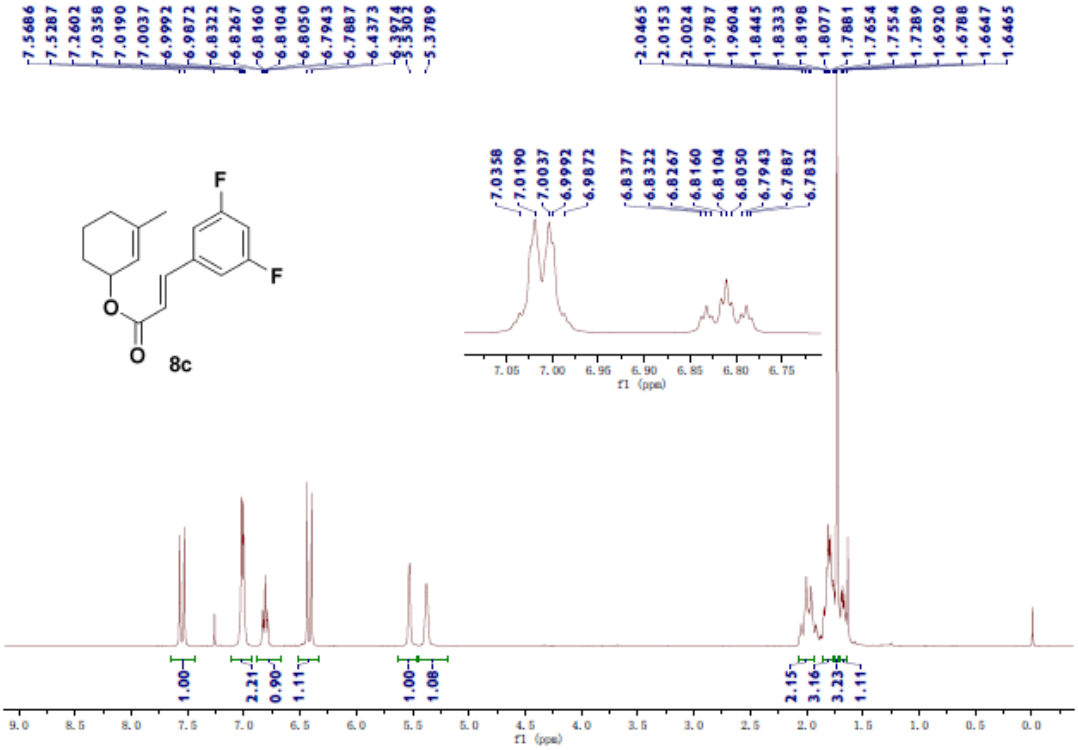
^{13}C NMR of **8b** (100 M, $CDCl_3$)



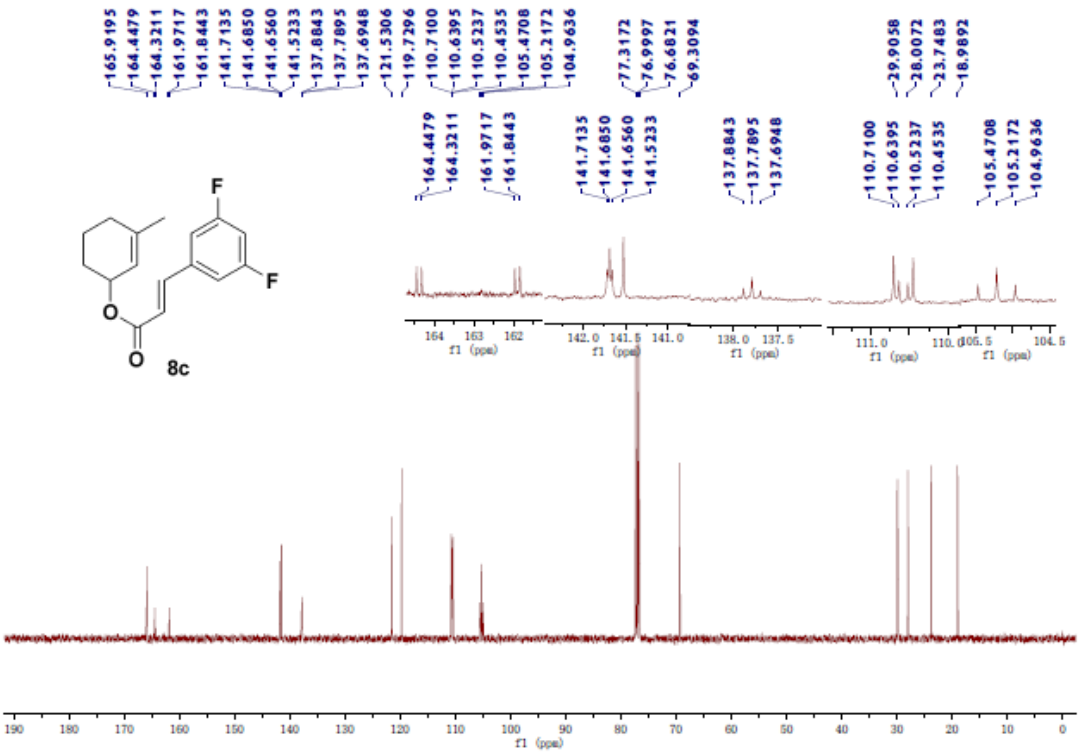
^{19}F NMR of **8b** (376 M, $CDCl_3$)



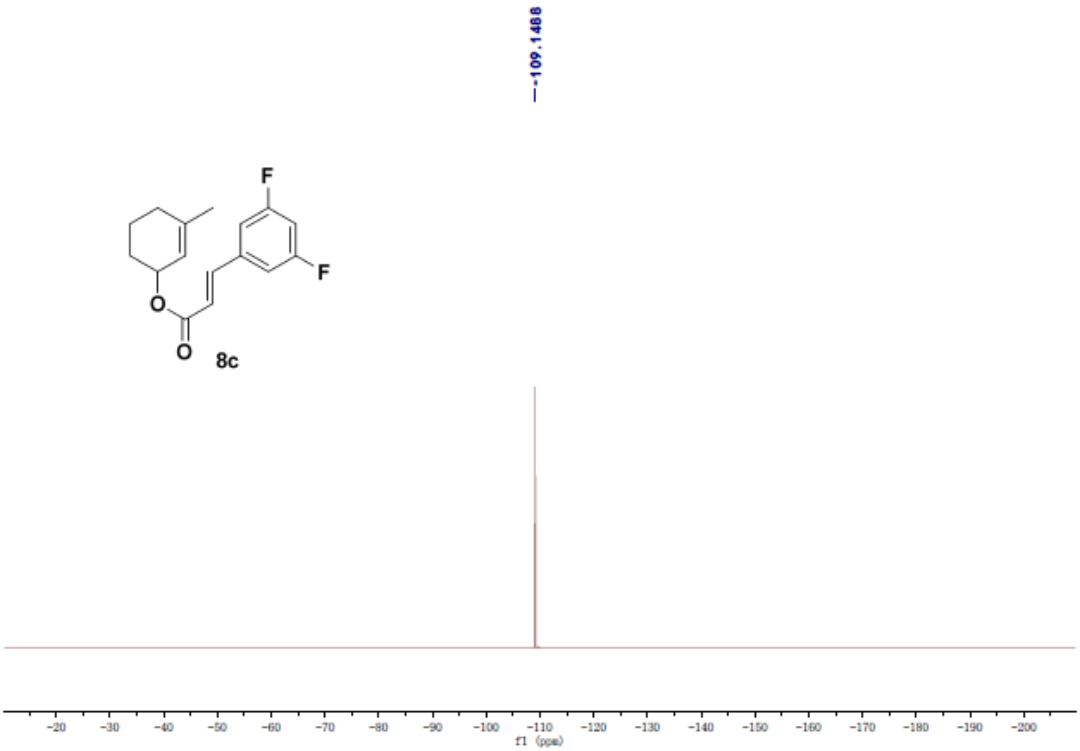
^{1}H NMR of **8c** (400 M, $CDCl_3$)



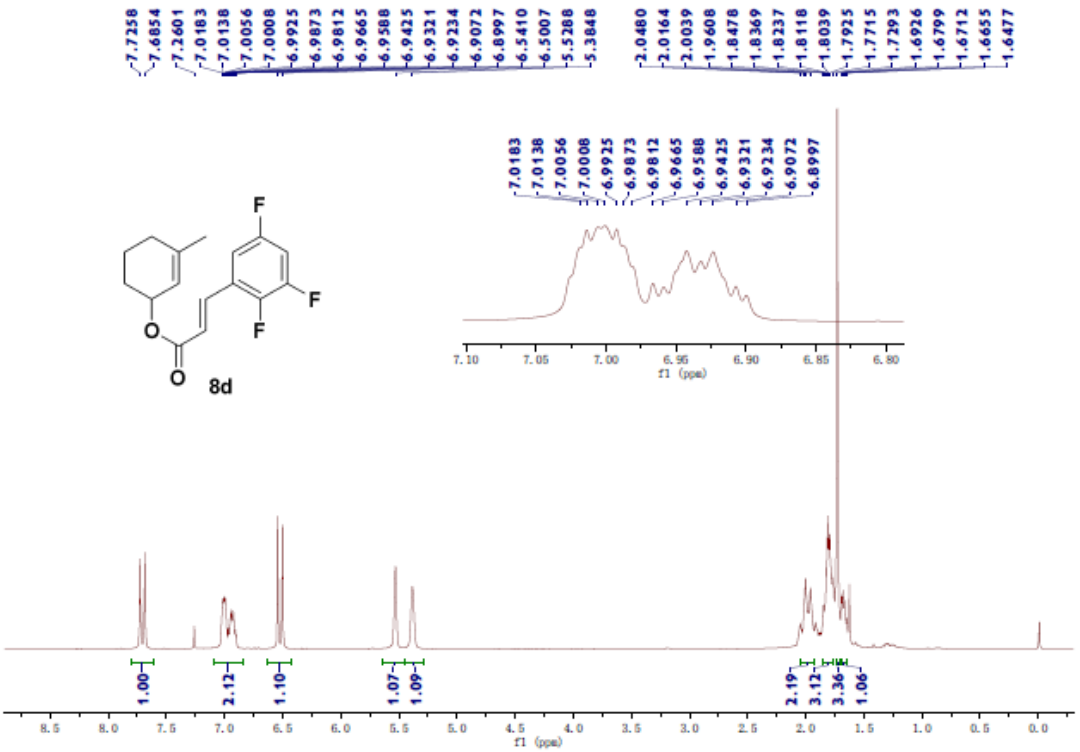
^{13}C NMR of **8c** (100 M, $CDCl_3$)



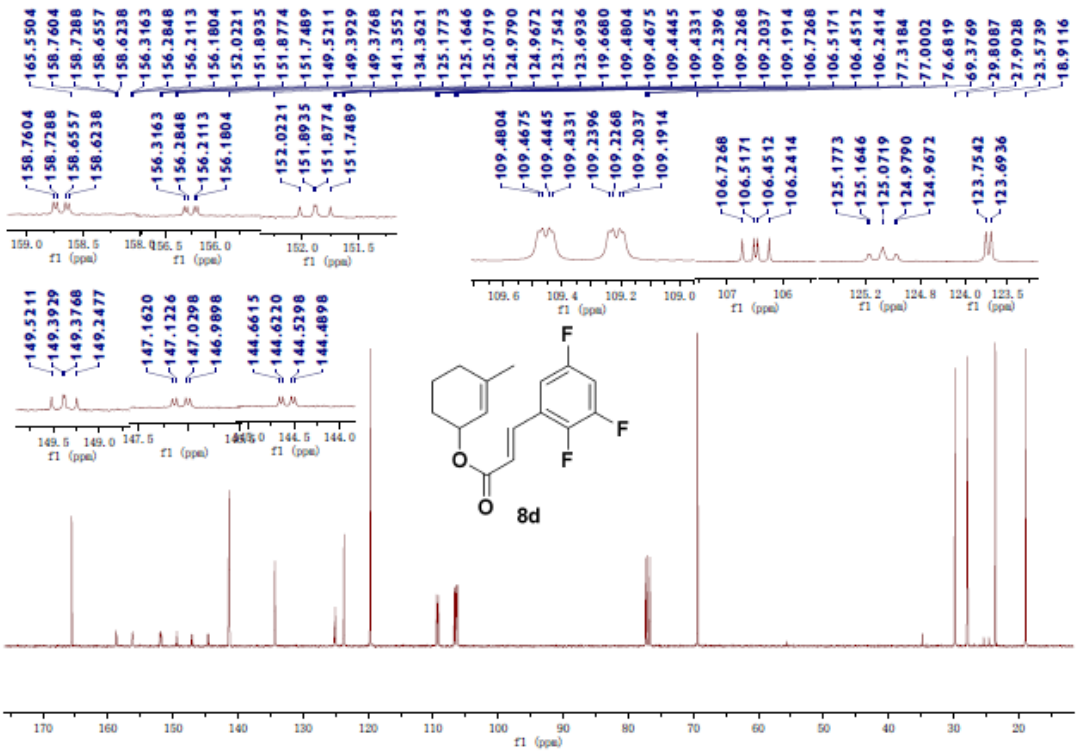
^{19}F NMR of **8c** (376 M, $CDCl_3$)



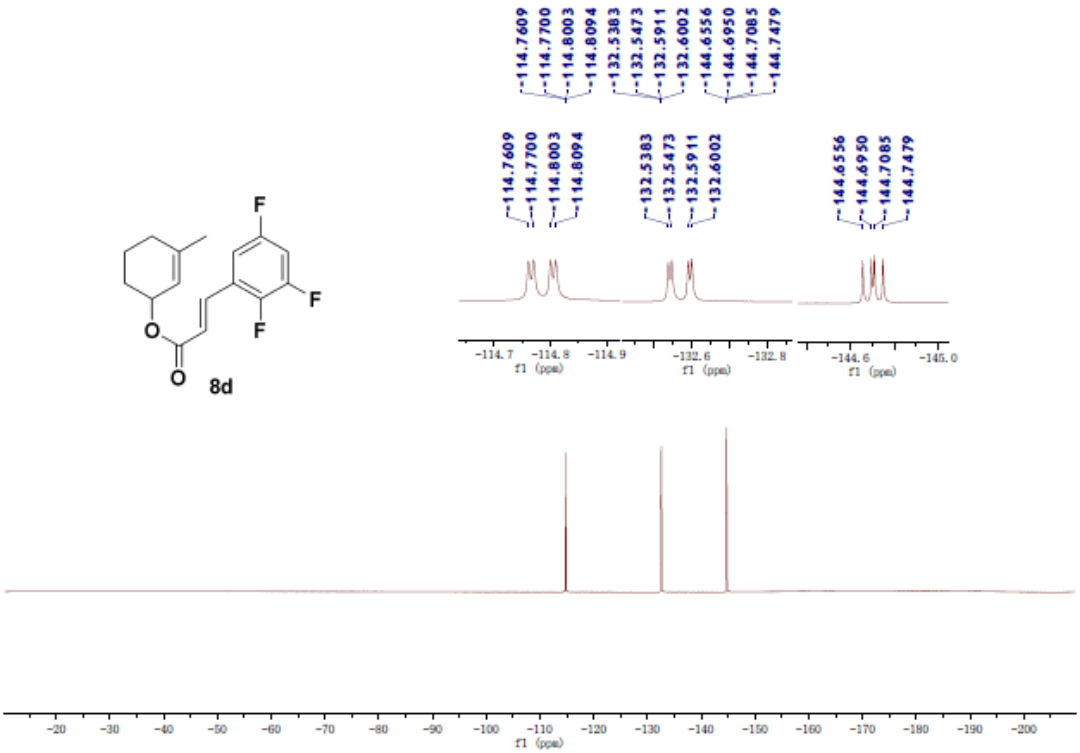
^{1}H NMR of **8d** (400 M, $CDCl_3$)



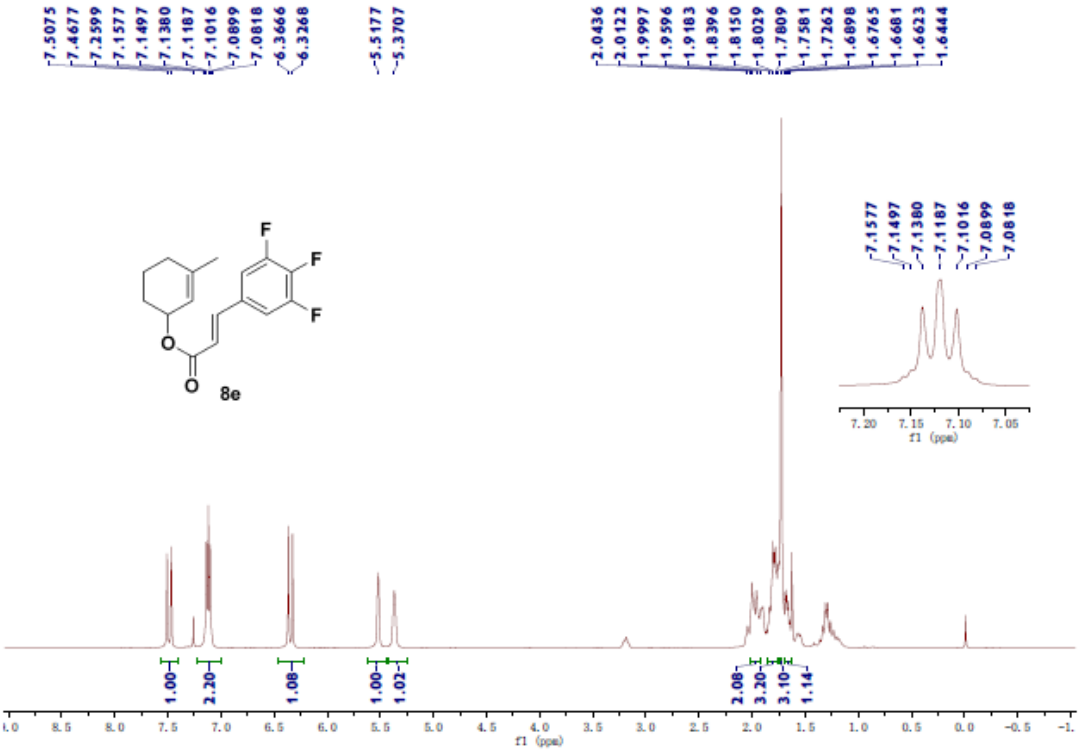
^{13}C NMR of **8d** (100 M, $CDCl_3$)



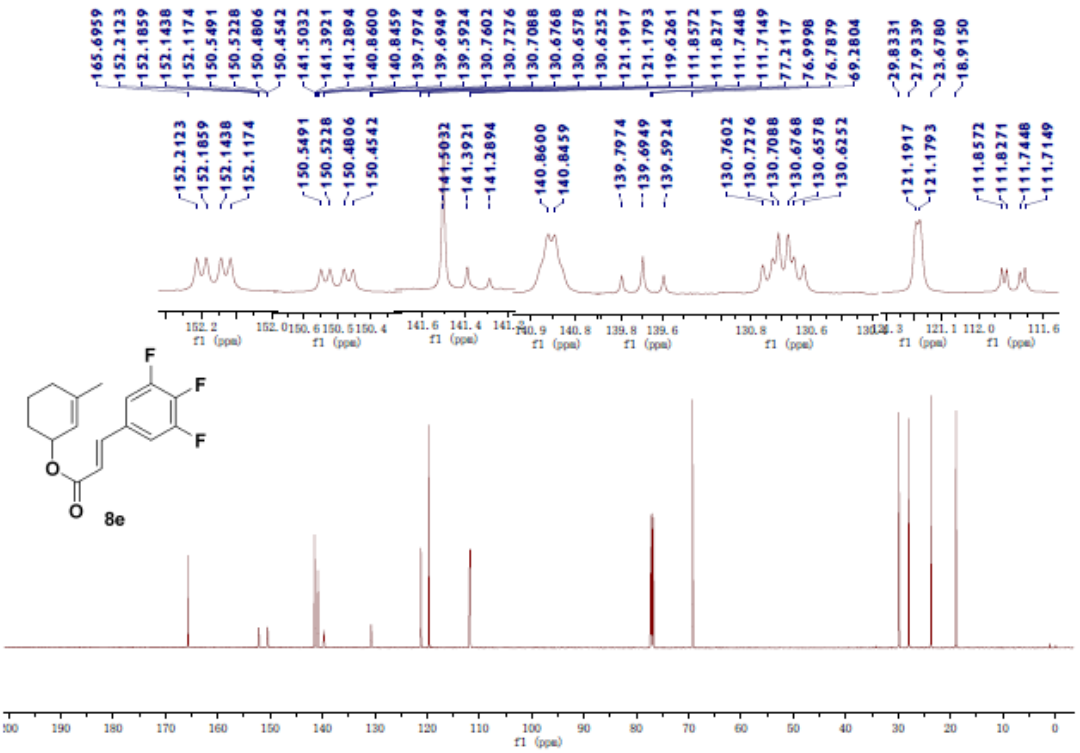
^{19}F NMR of **8d** (376 M, $CDCl_3$)



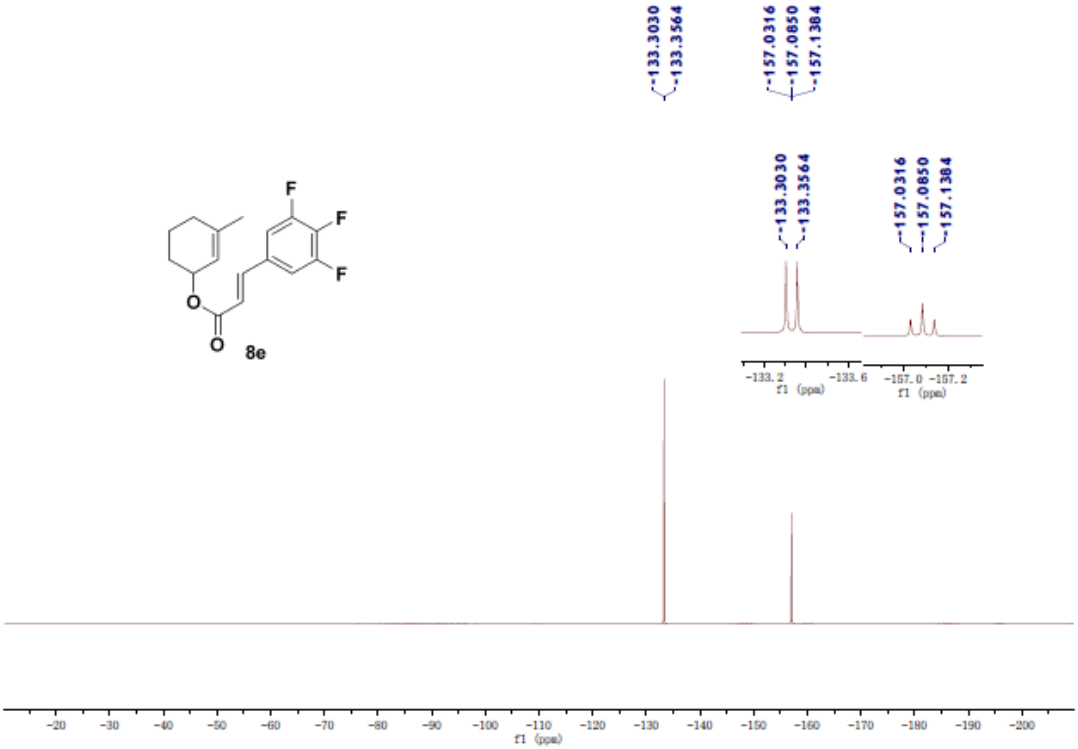
^{1}H NMR of **8e** (400 M, $CDCl_3$)



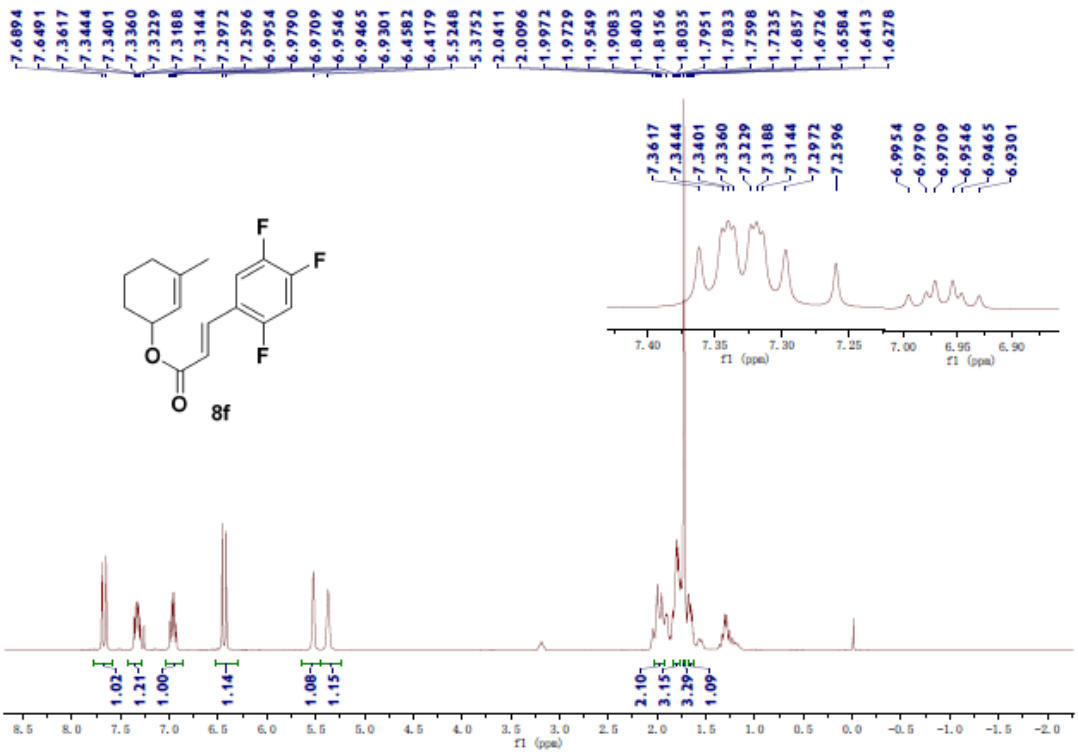
^{13}C NMR of **8e** (100 M, $CDCl_3$)



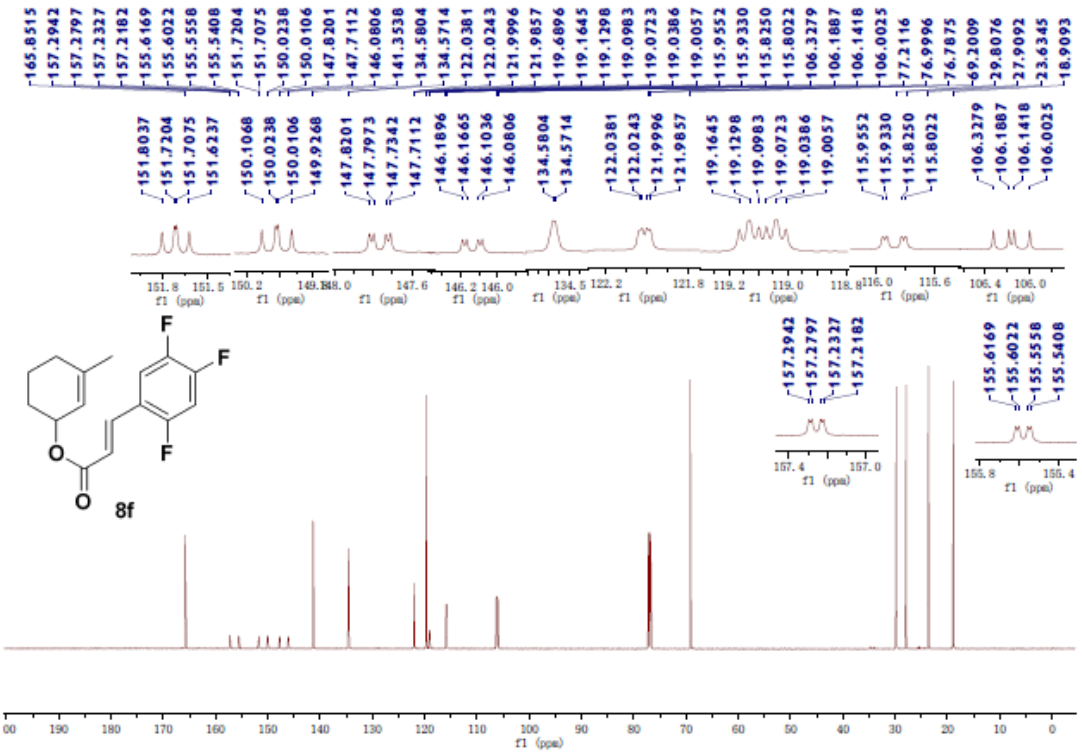
^{19}F NMR of **8e** (376 M, $CDCl_3$)



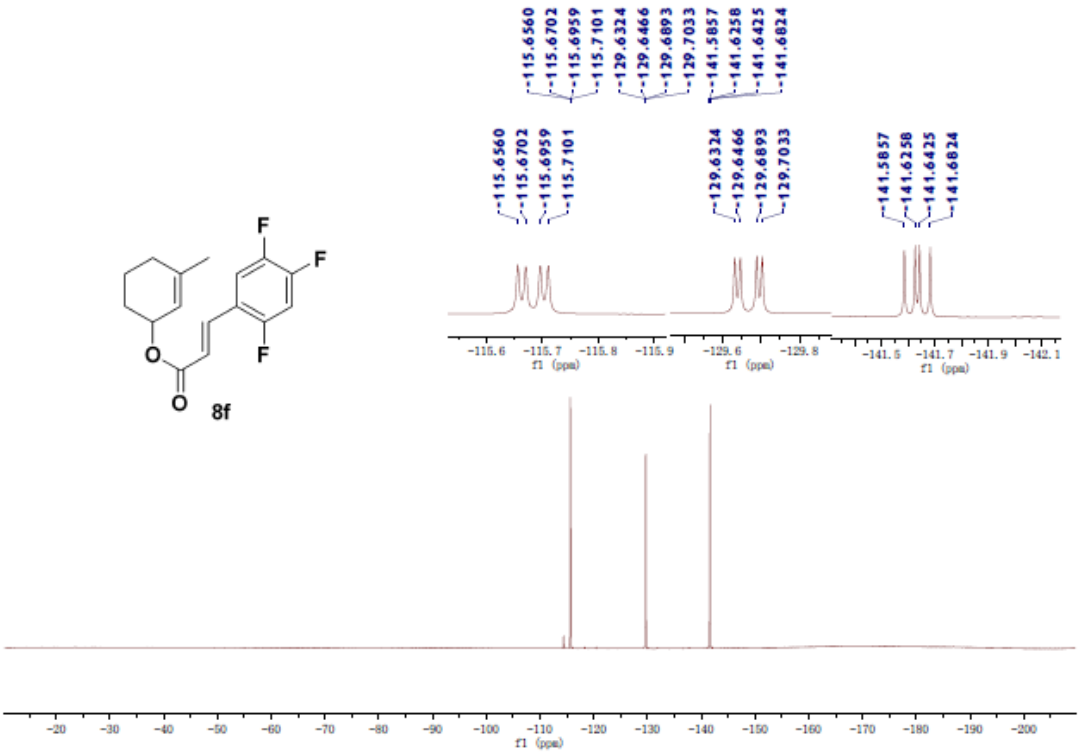
^{1}H NMR of **8f** (400 M, $CDCl_3$)



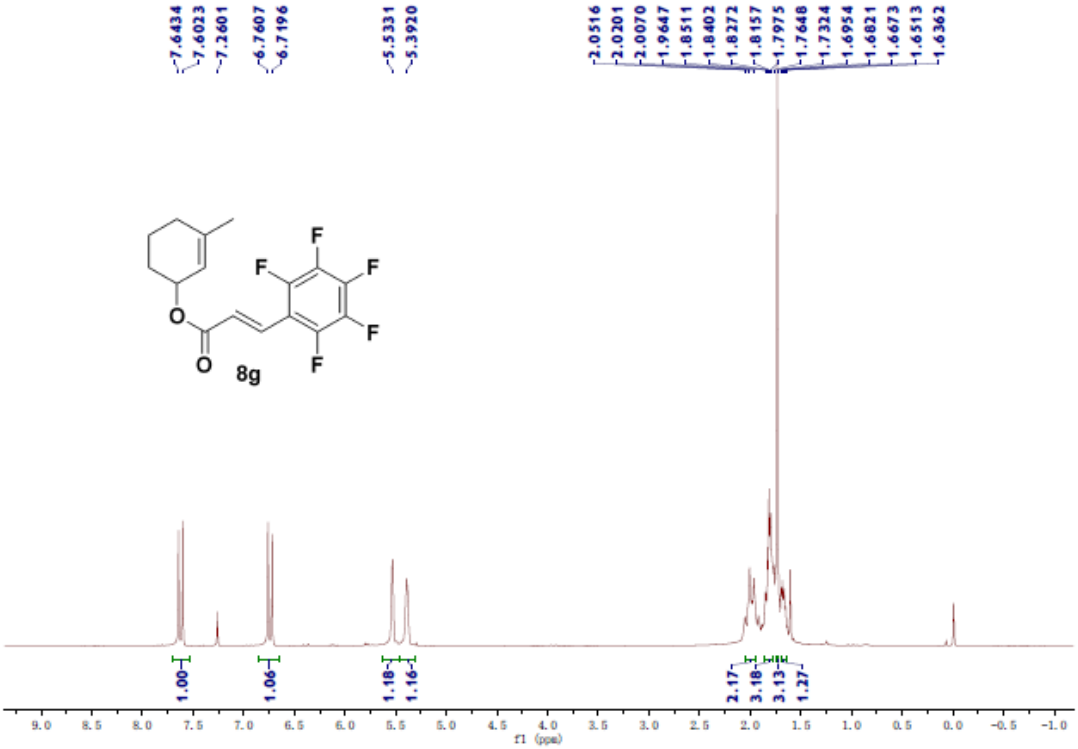
^{13}C NMR of **8f** (100 M, $CDCl_3$)



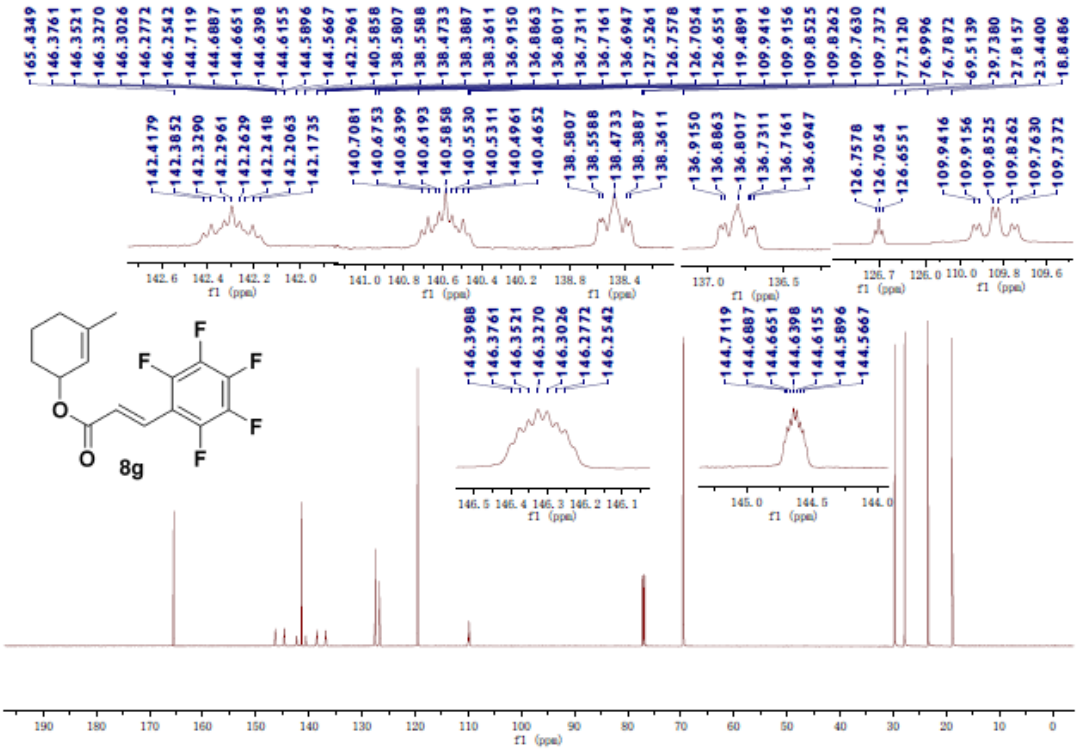
^{19}F NMR of **8f** (376 M, $CDCl_3$)



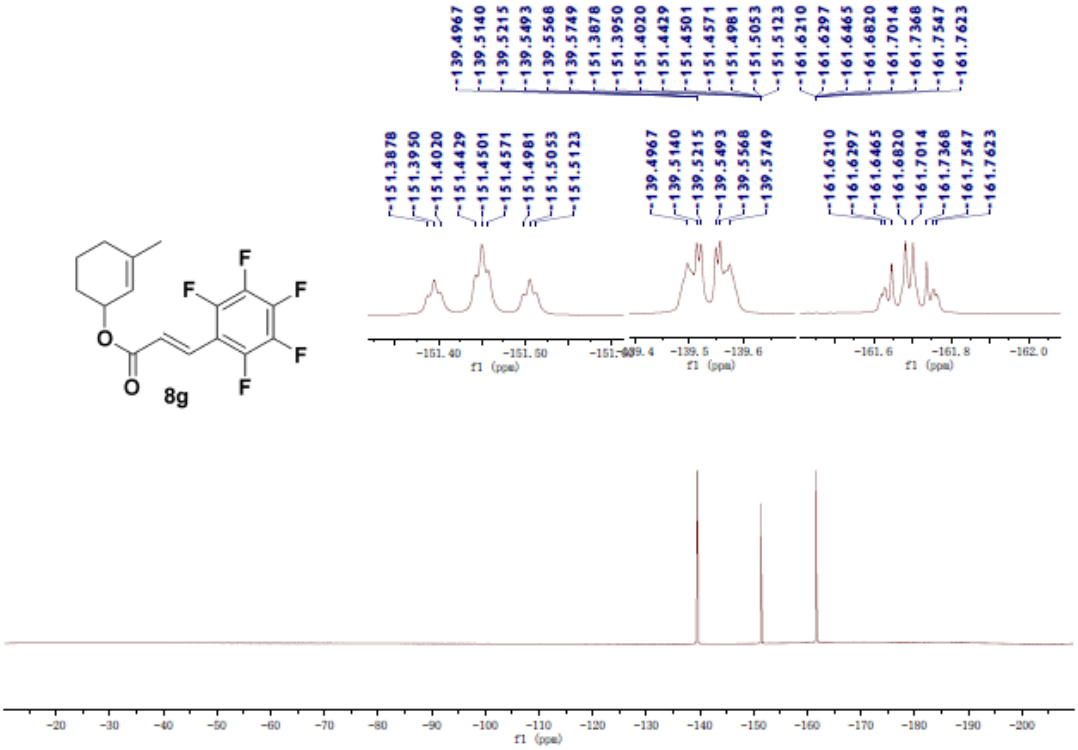
^{1}H NMR of **8g** (400 M, $CDCl_3$)



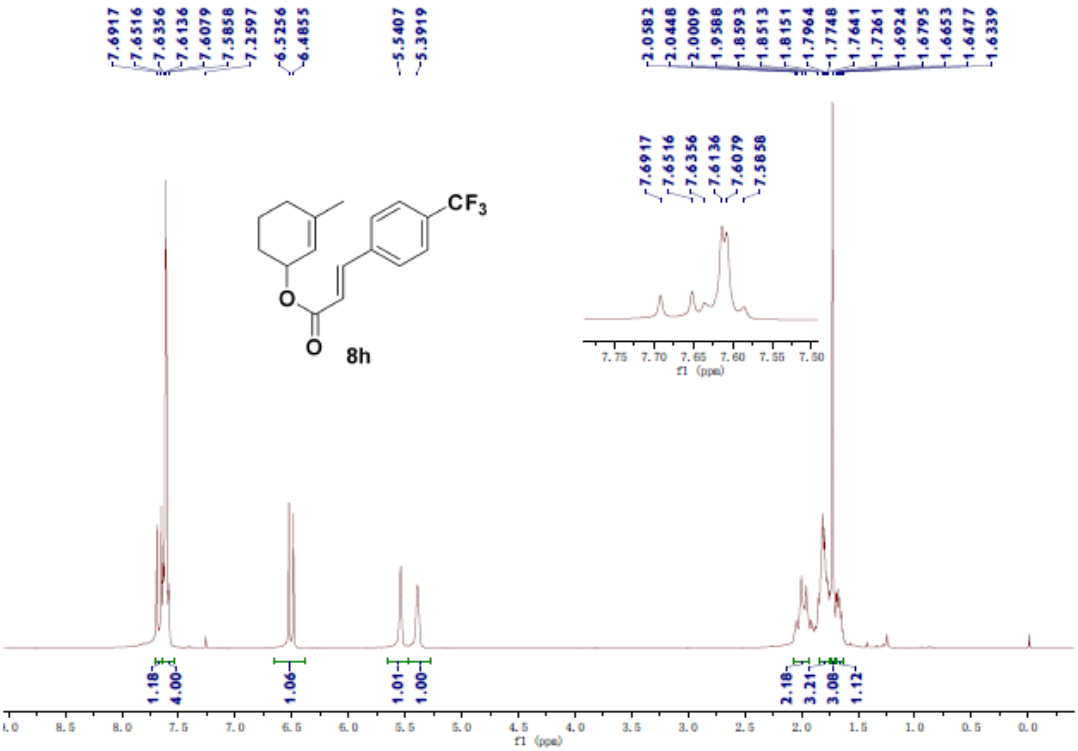
^{13}C NMR of **8g** (100 M, $CDCl_3$)



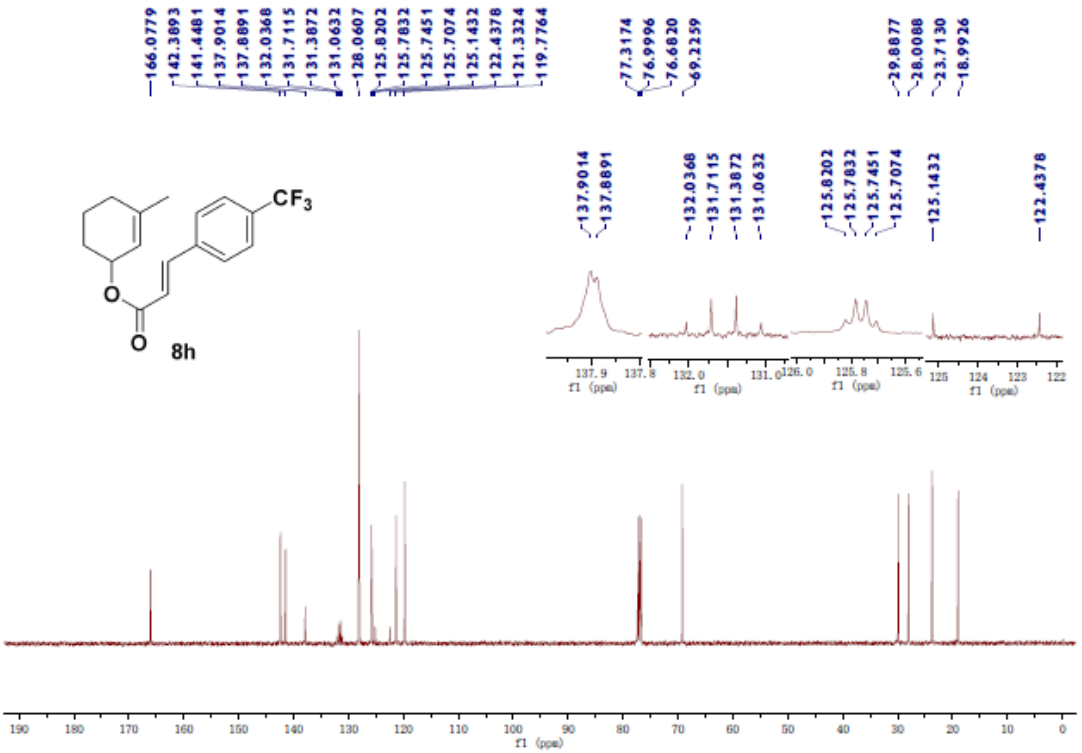
^{19}F NMR of **8g** (376 M, $CDCl_3$)



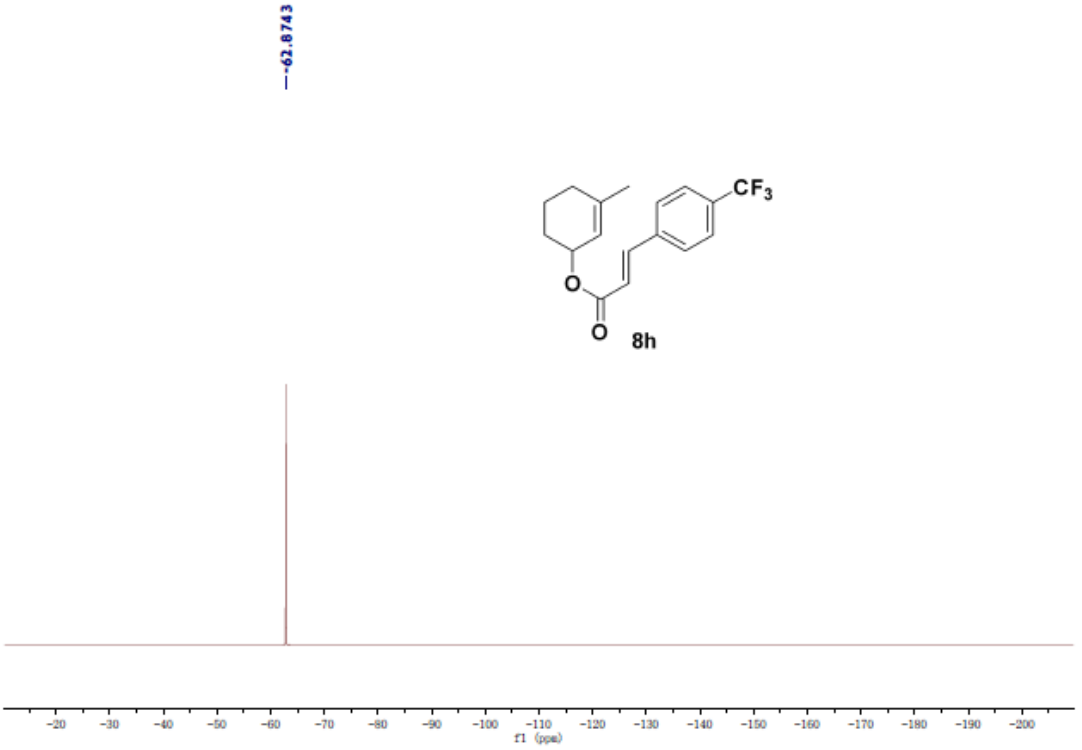
^{1}H NMR of **8h** (400 M, $CDCl_3$)



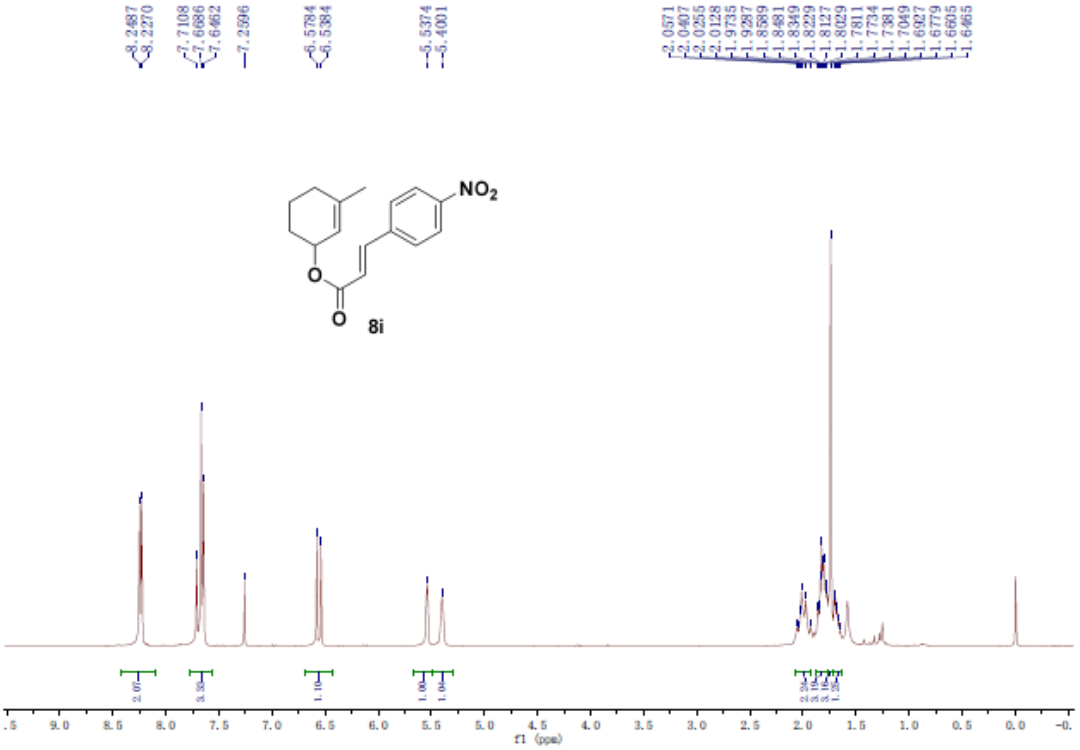
^{13}C NMR of **8h** (100 M, $CDCl_3$)



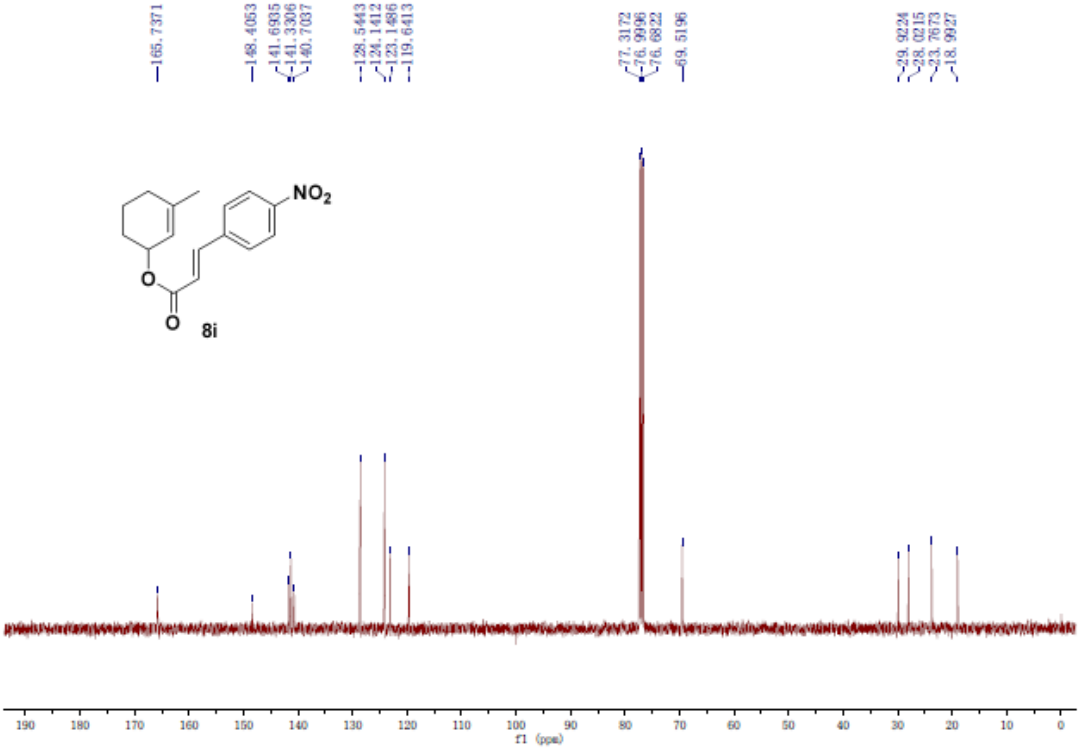
^{19}F NMR of **8h** (376 M, $CDCl_3$)



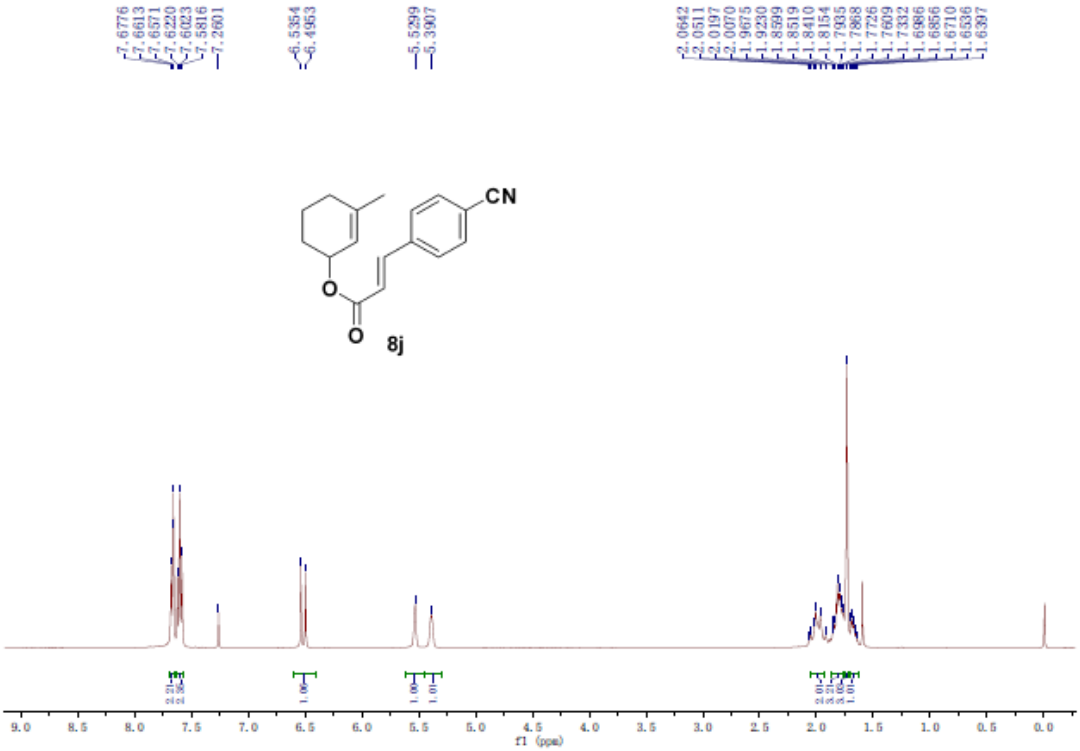
^{1}H NMR of **8i** (400 M, $CDCl_3$)



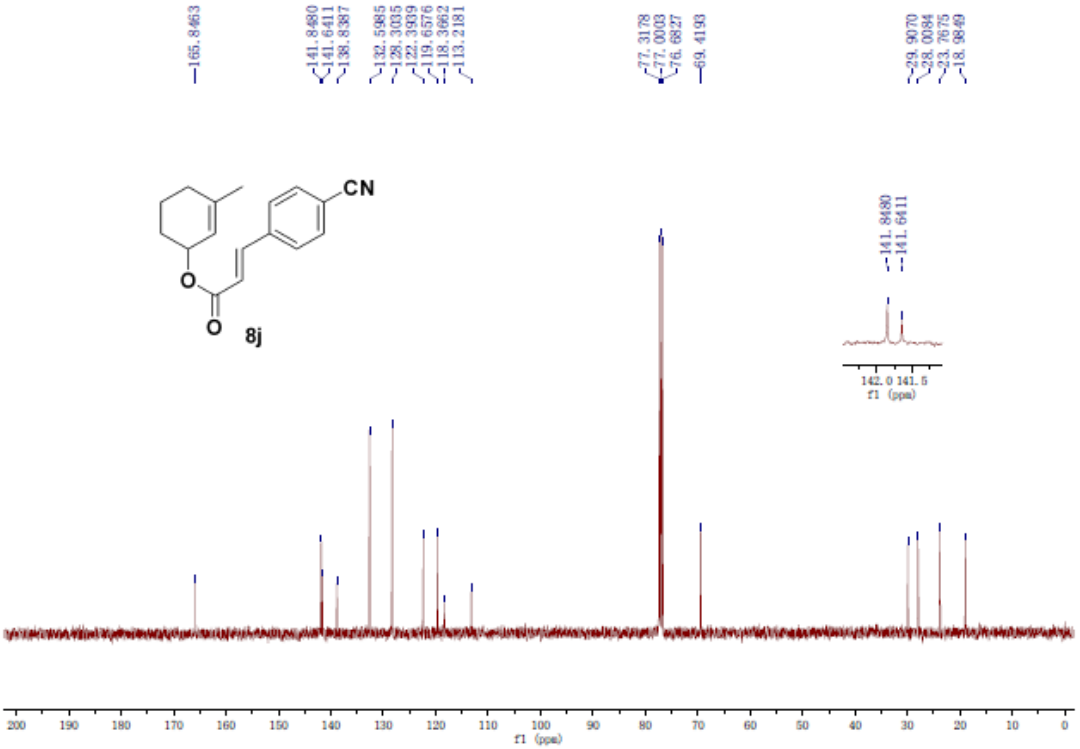
^{13}C NMR of **8i** (100 M, $CDCl_3$)



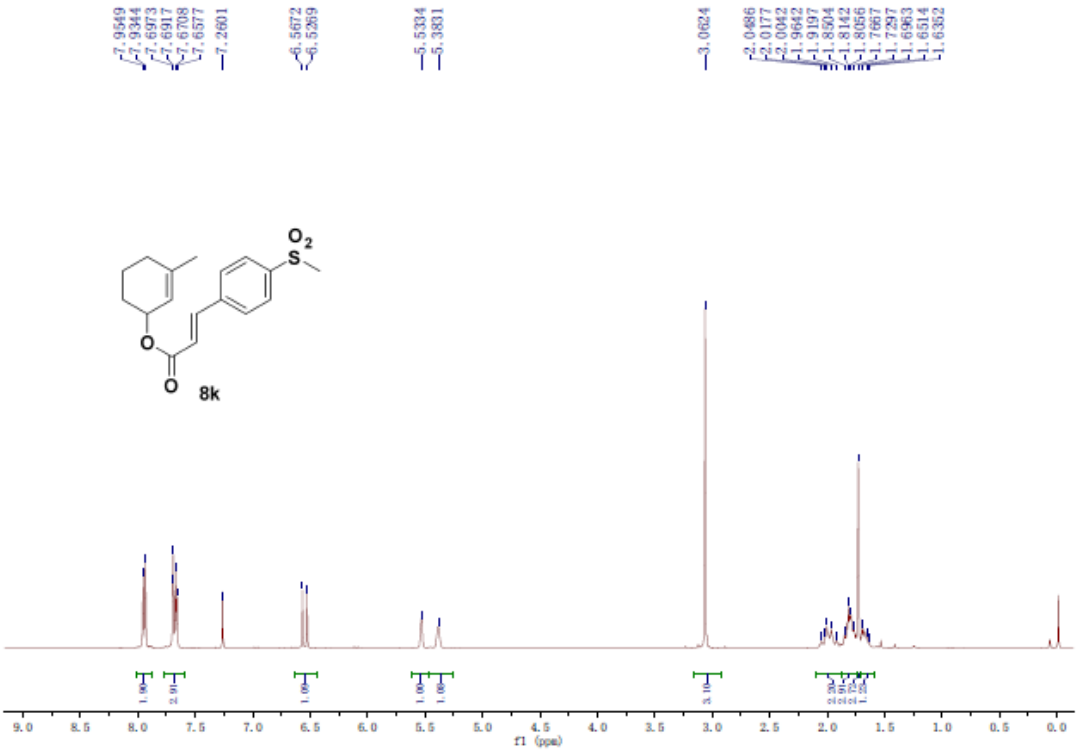
^{1}H NMR of **8j** (400 M, $CDCl_3$)



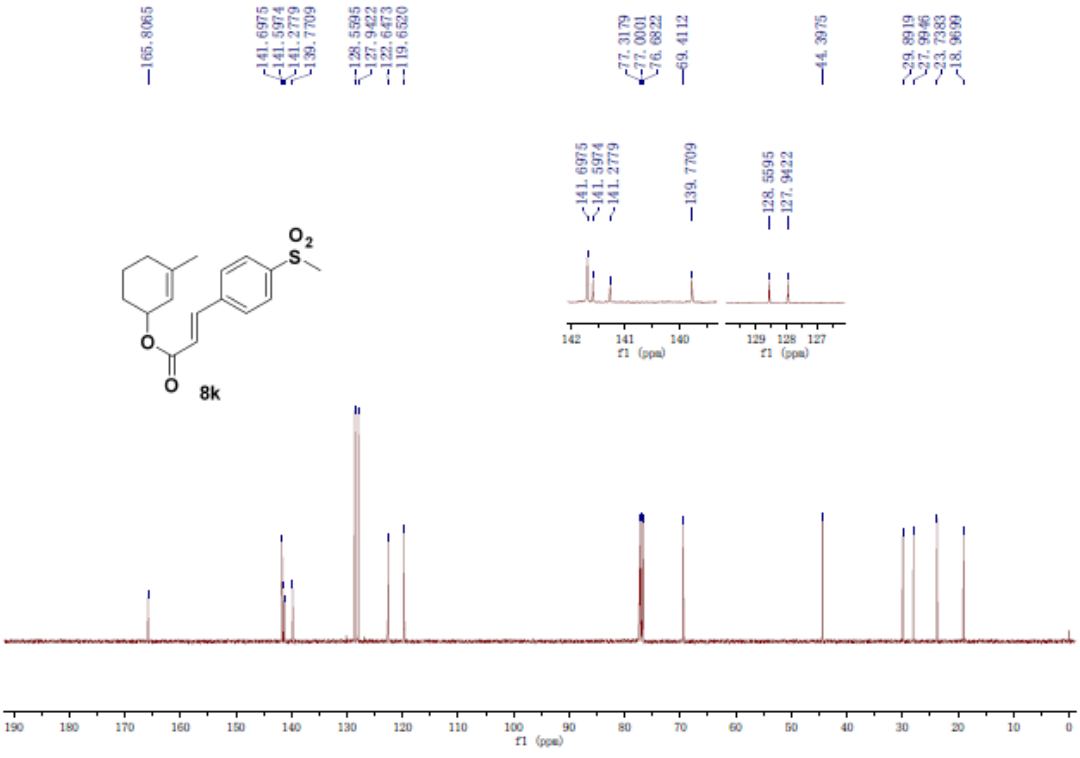
^{13}C NMR of **8j** (150 M, $CDCl_3$)



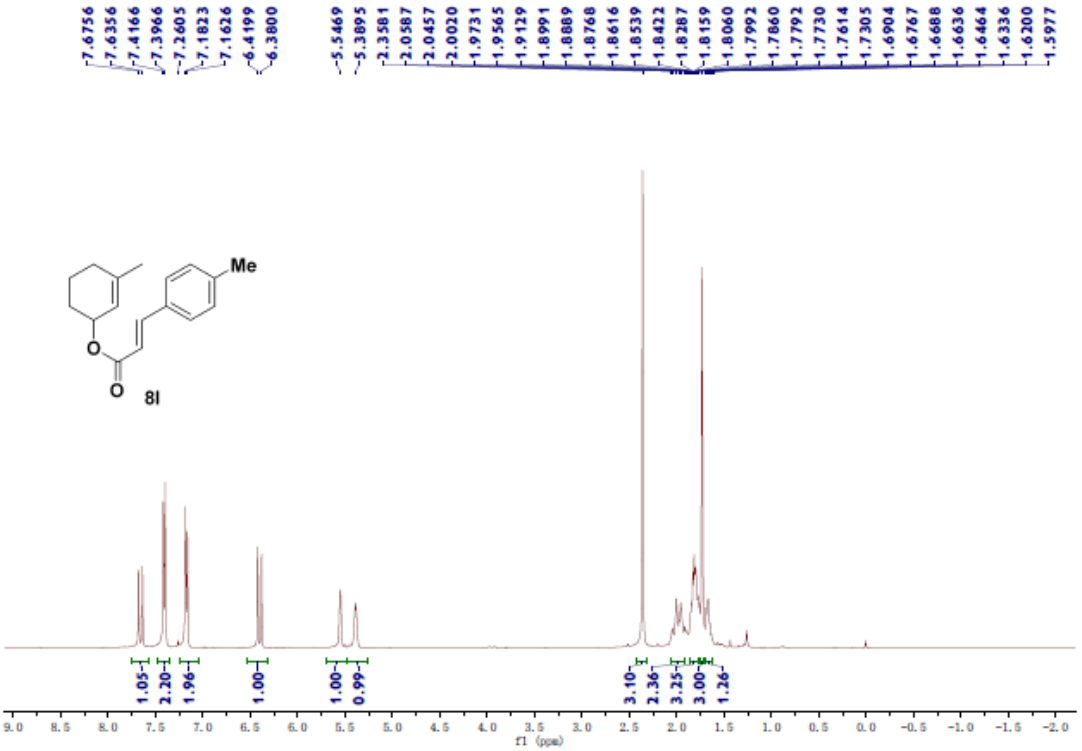
^{1}H NMR of **8k** (400 M, $CDCl_3$)



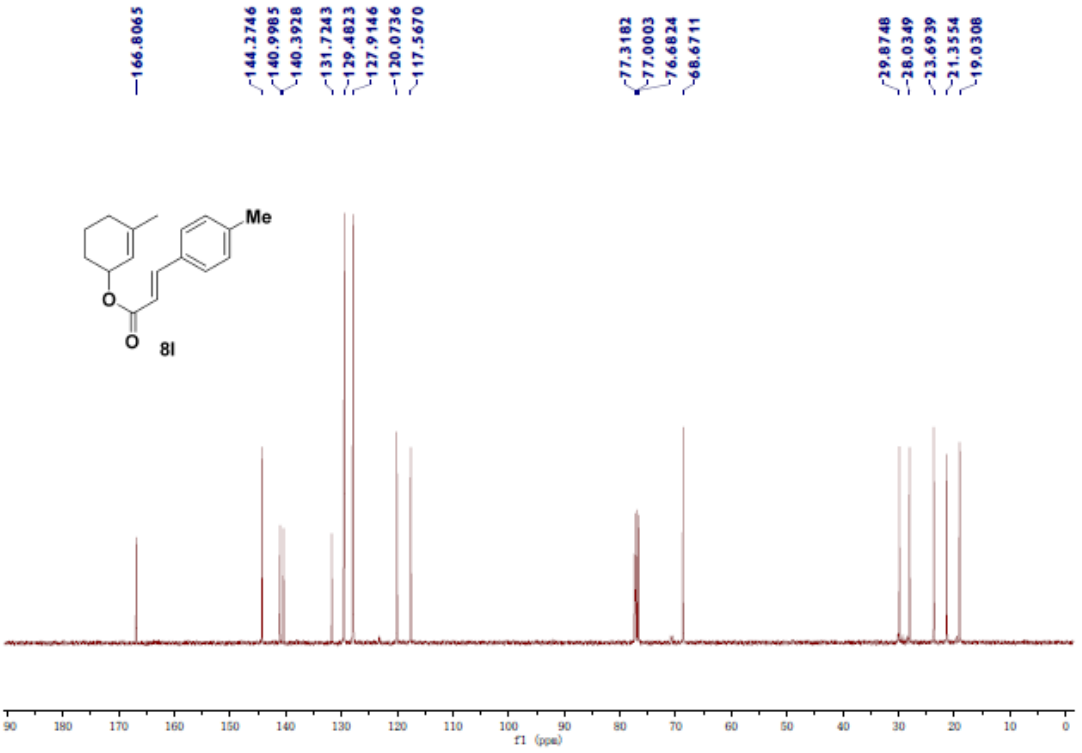
^{13}C NMR of **8k** (100 M, $CDCl_3$)



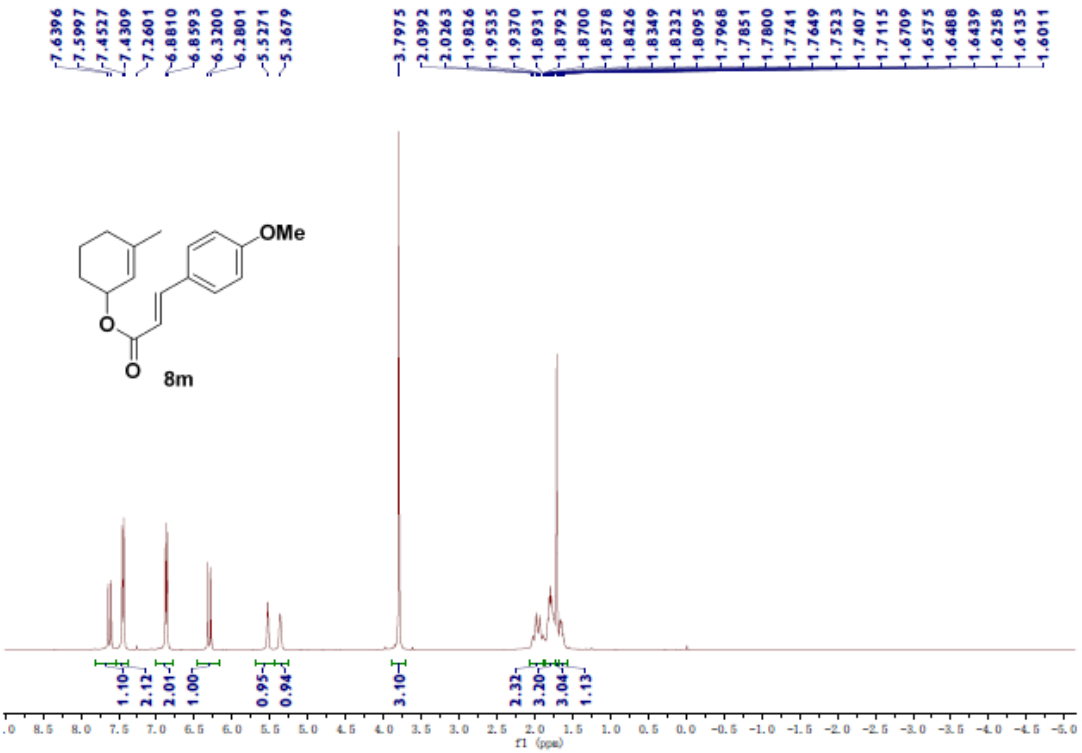
^{1}H NMR of **8l** (400 M, $CDCl_3$)



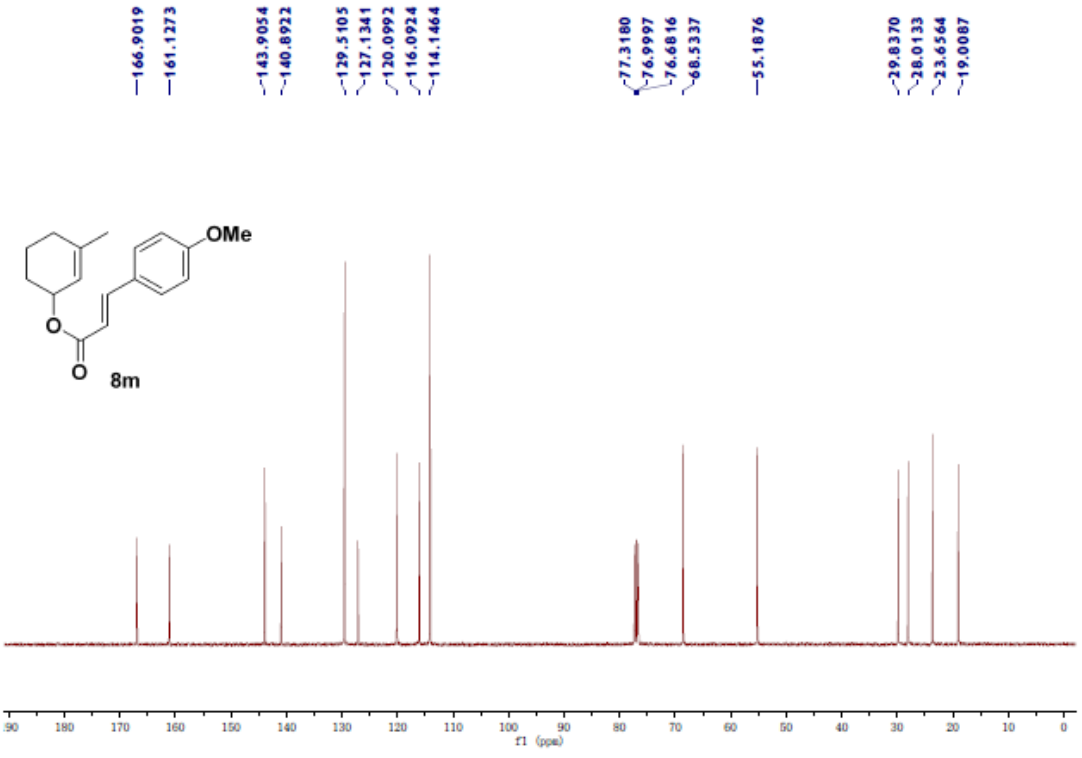
^{13}C NMR of **8l** (100 M, $CDCl_3$)



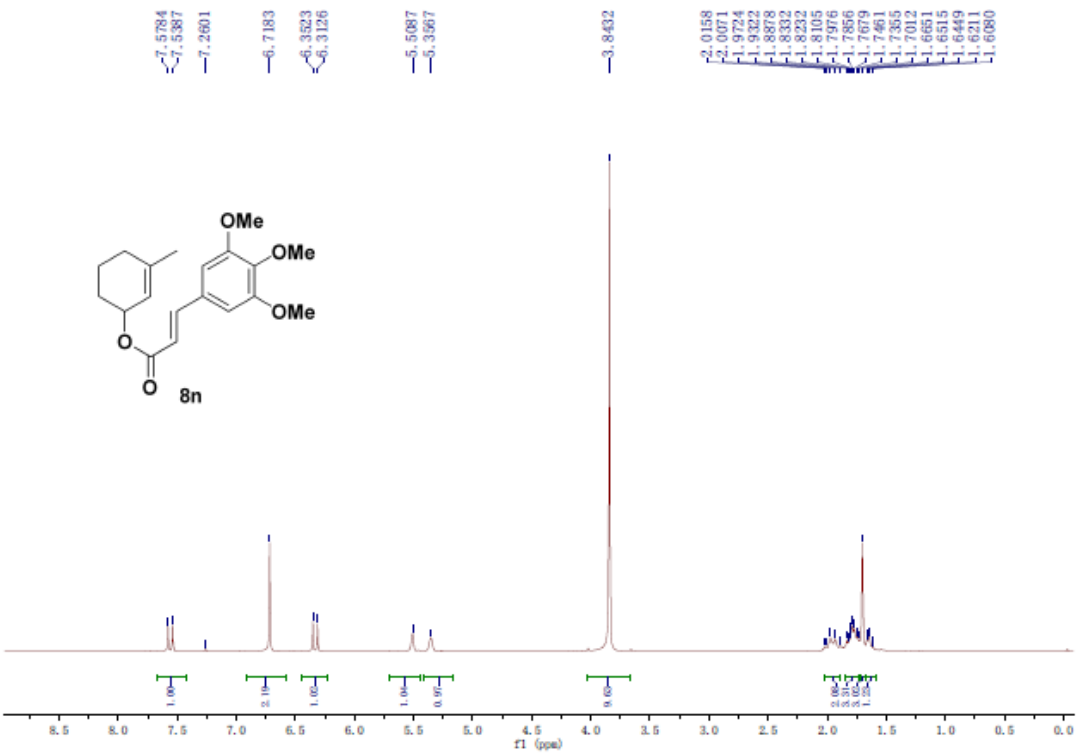
^{1}H NMR of **8m** (400 M, $CDCl_3$)



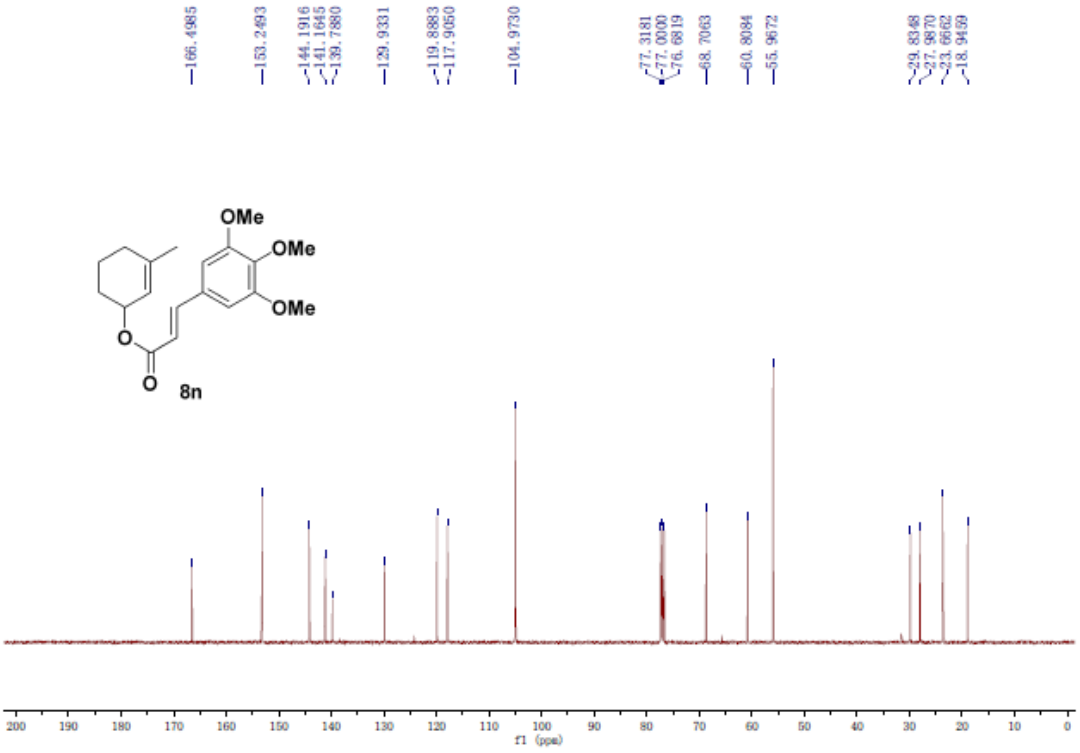
^{13}C NMR of **8m** (150 M, $CDCl_3$)



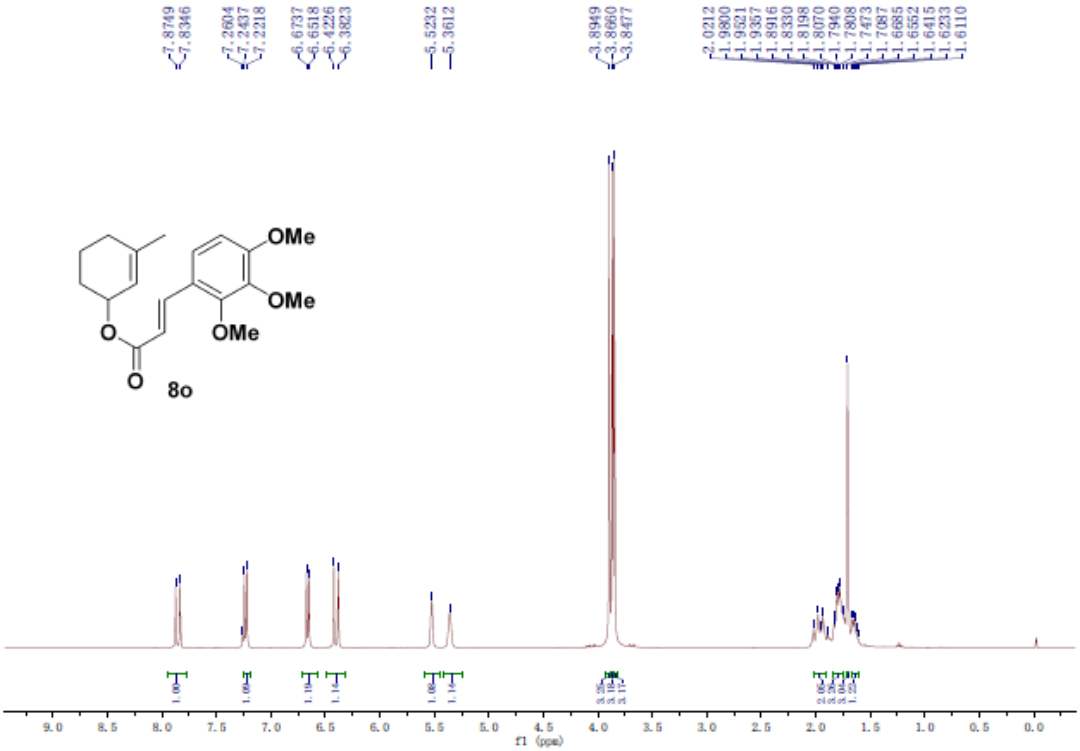
^{1}H NMR of **8n** (400 M, $CDCl_3$)



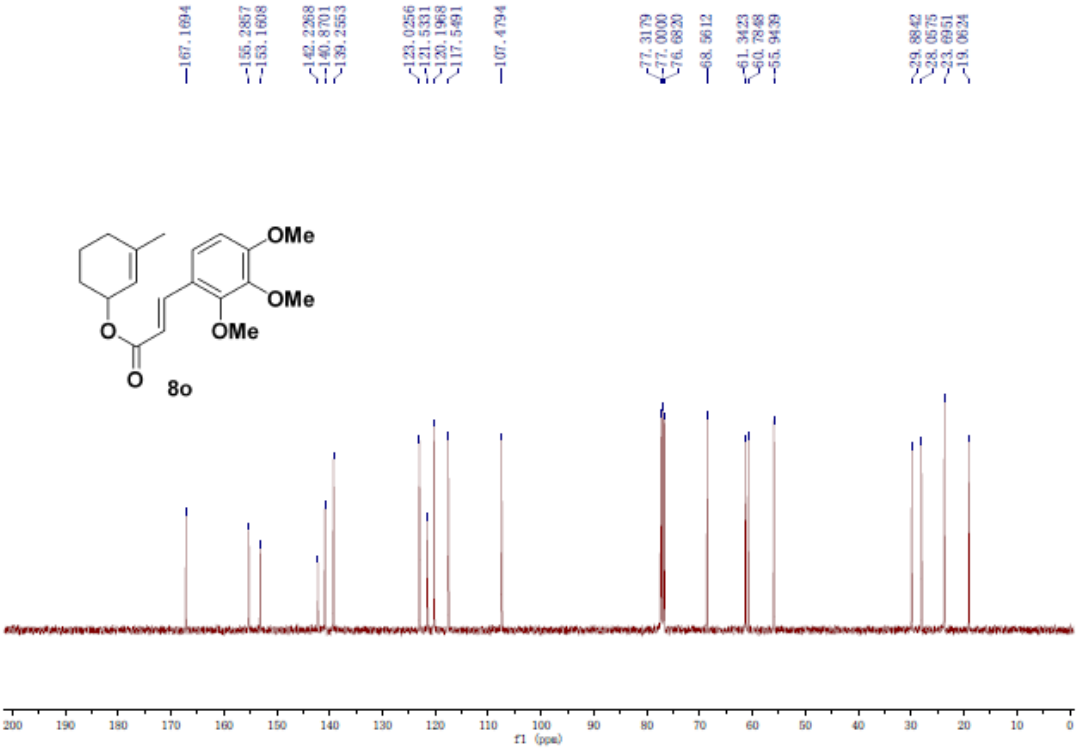
^{13}C NMR of **8n** (100 M, $CDCl_3$)



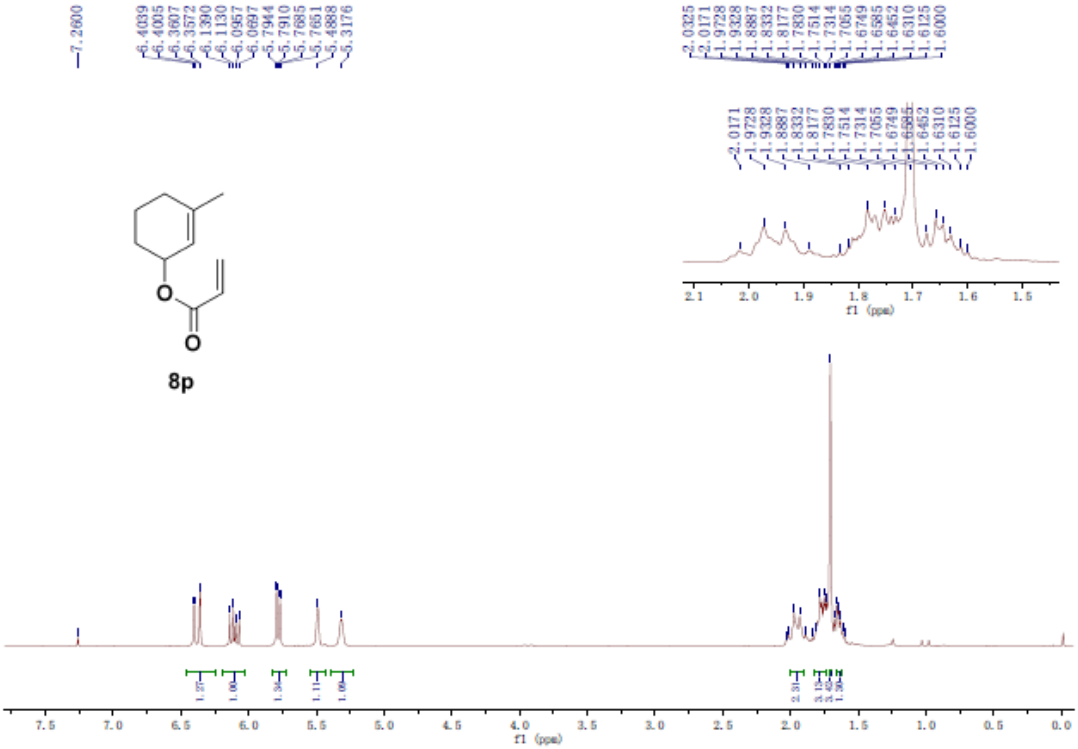
^{1}H NMR of **8o** (400 M, $CDCl_3$)



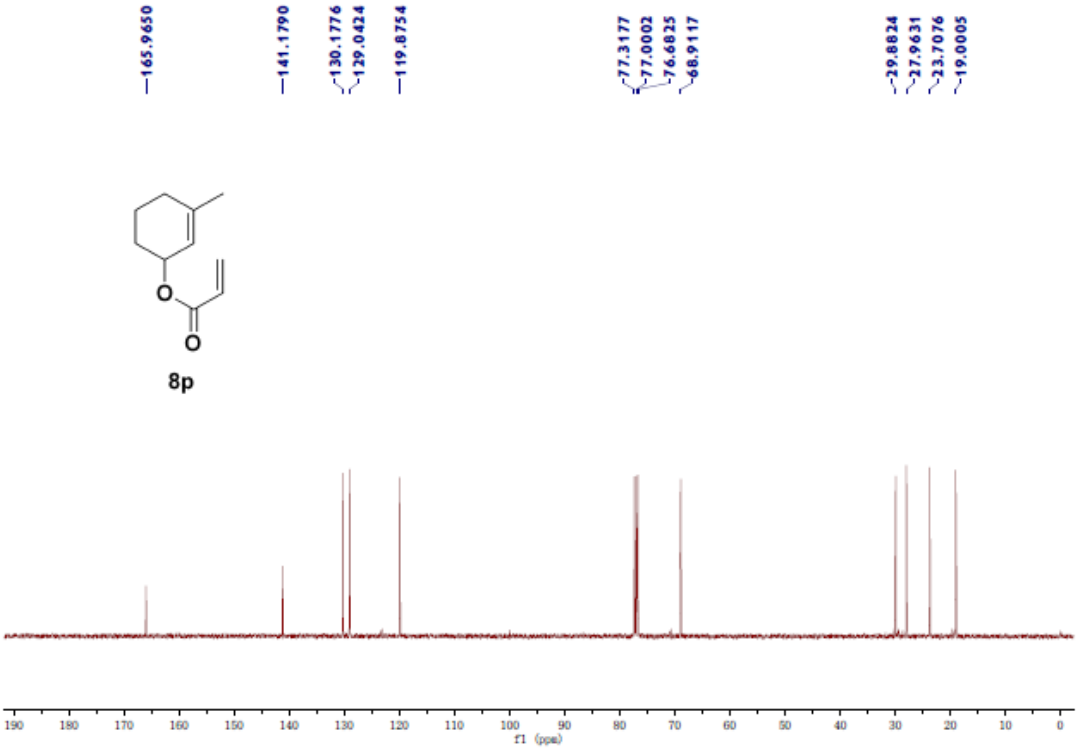
^{13}C NMR of **8o** (100 M, $CDCl_3$)



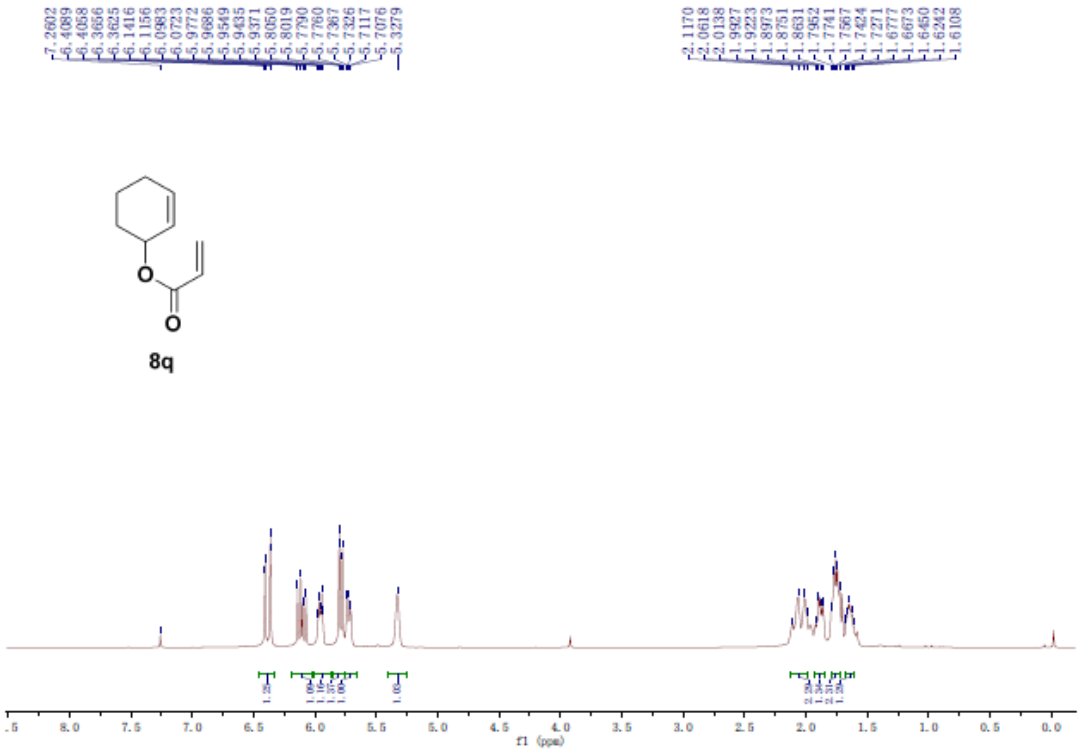
^{1}H NMR of **8p** (400 M, $CDCl_3$)



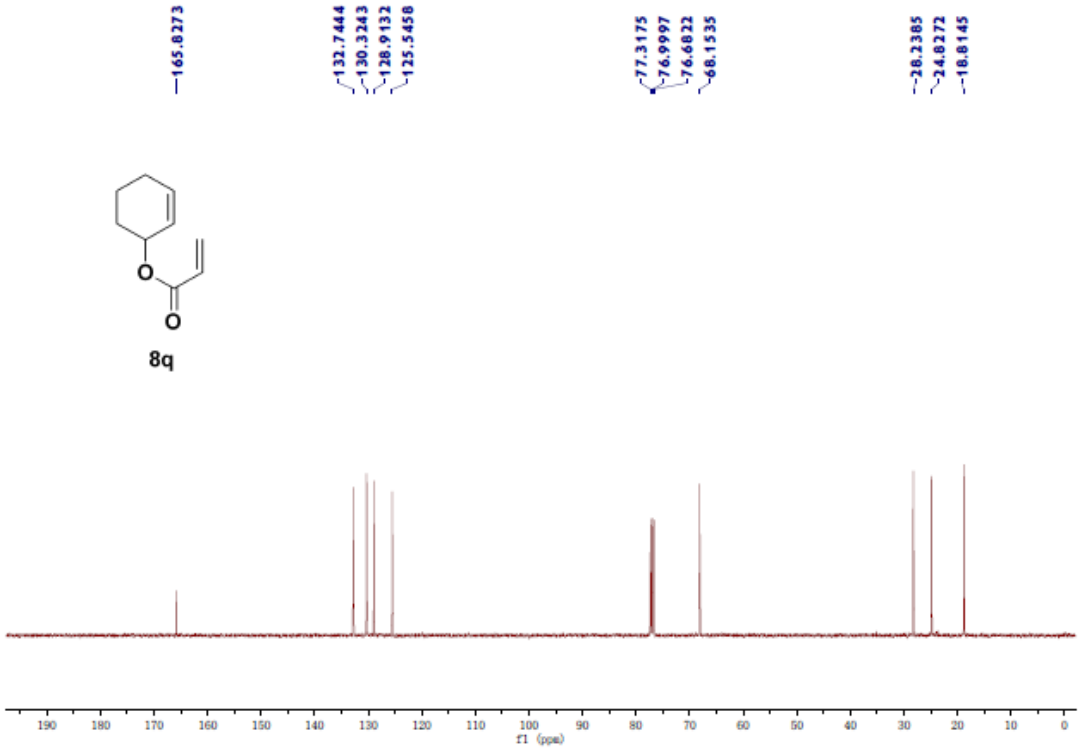
^{13}C NMR of **8p** (100 M, $CDCl_3$)



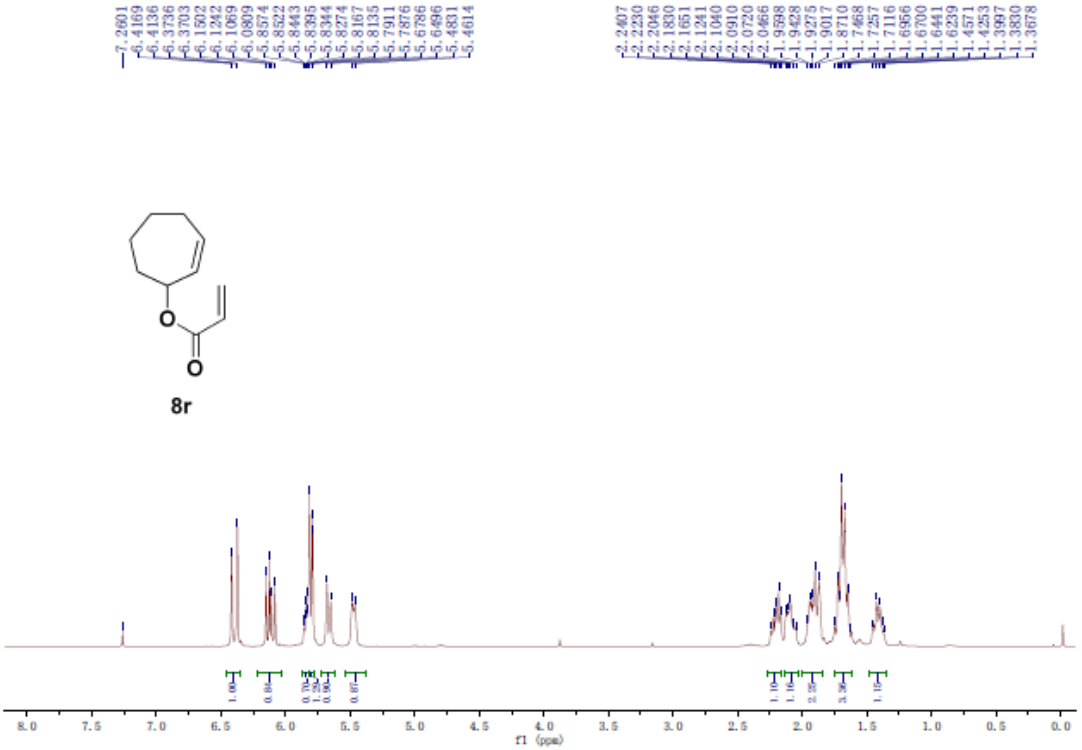
^{1}H NMR of **8q** (400 M, $CDCl_3$)



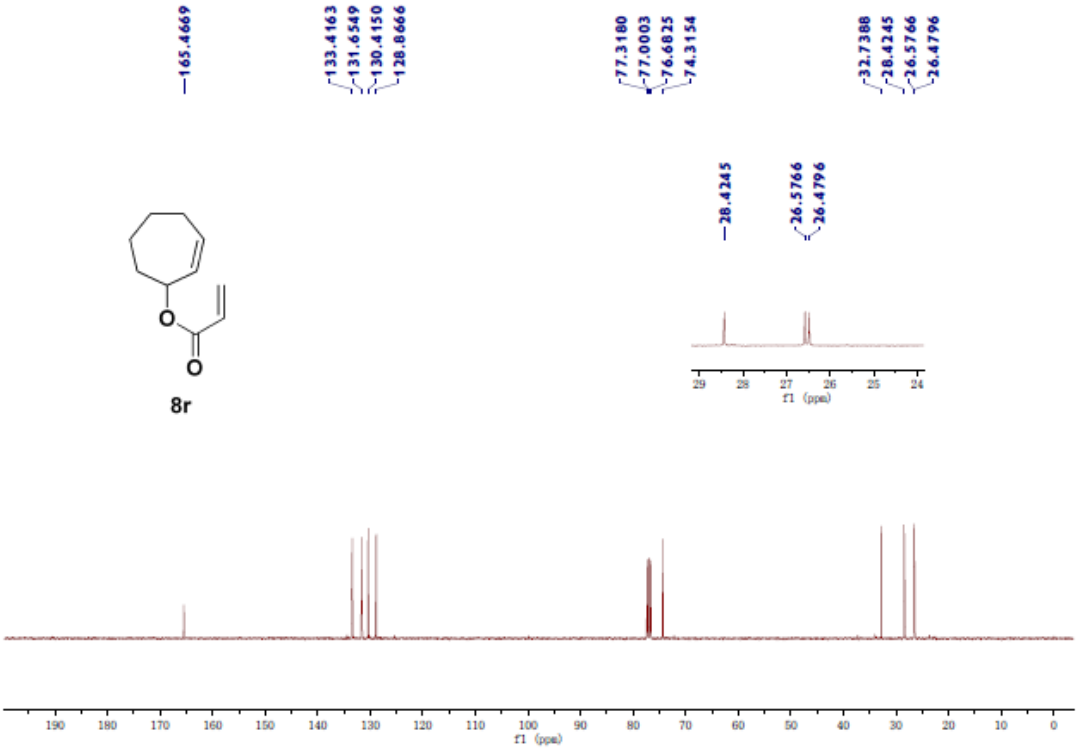
^{13}C NMR of **8q** (100 M, $CDCl_3$)



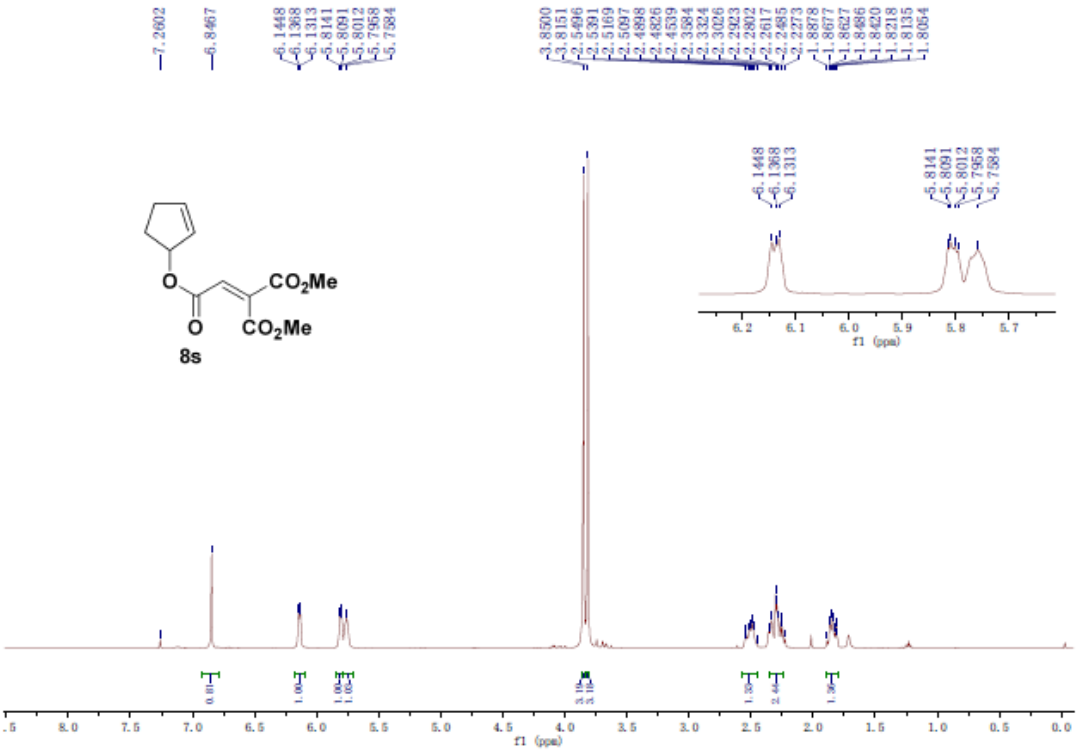
^{1}H NMR of **8r** (400 M, $CDCl_3$)



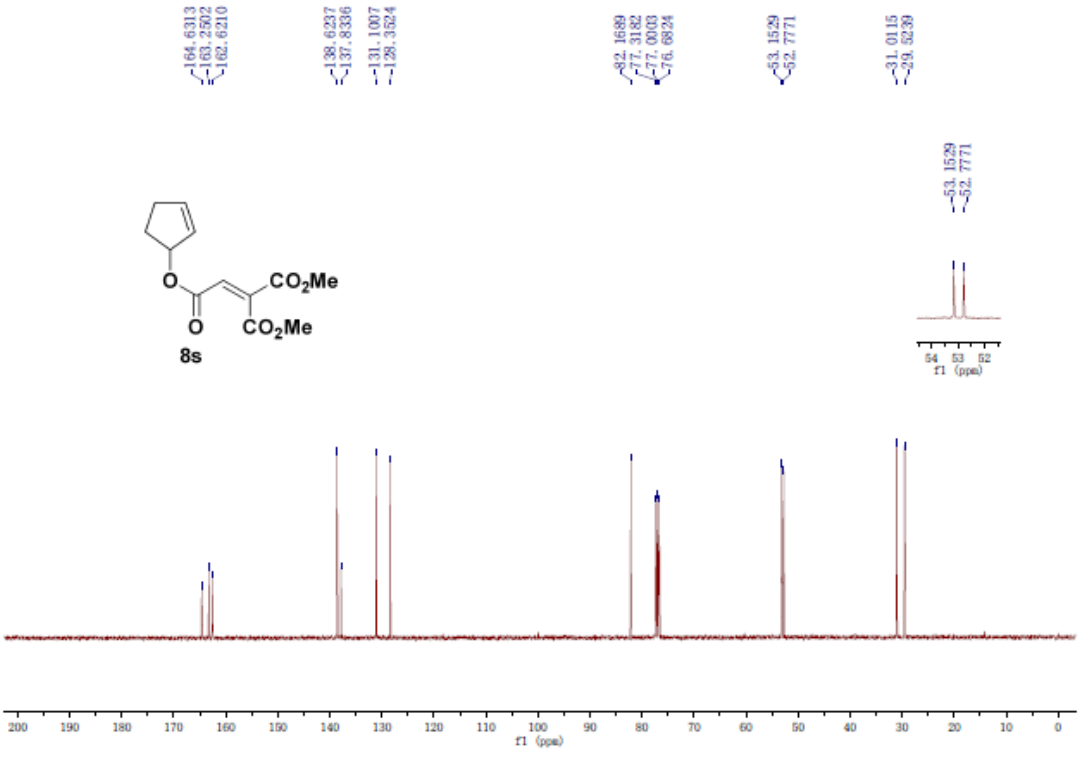
^{13}C NMR of **8r** (100 M, $CDCl_3$)



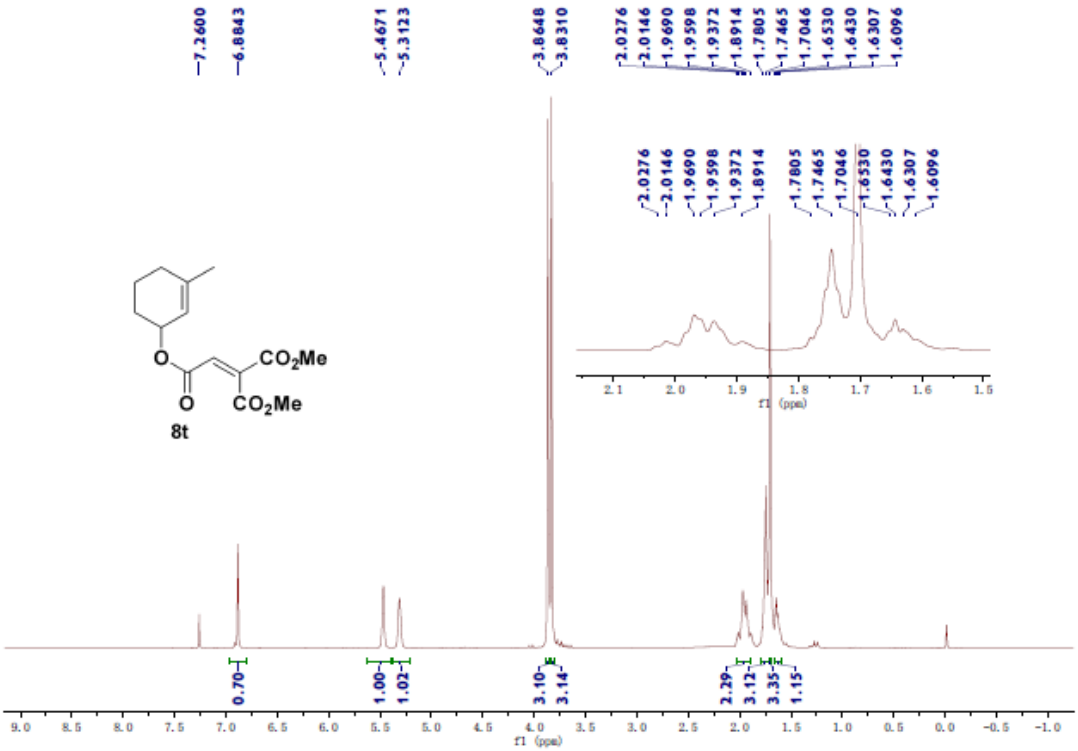
^{1}H NMR of **8s** (600 M, $CDCl_3$)



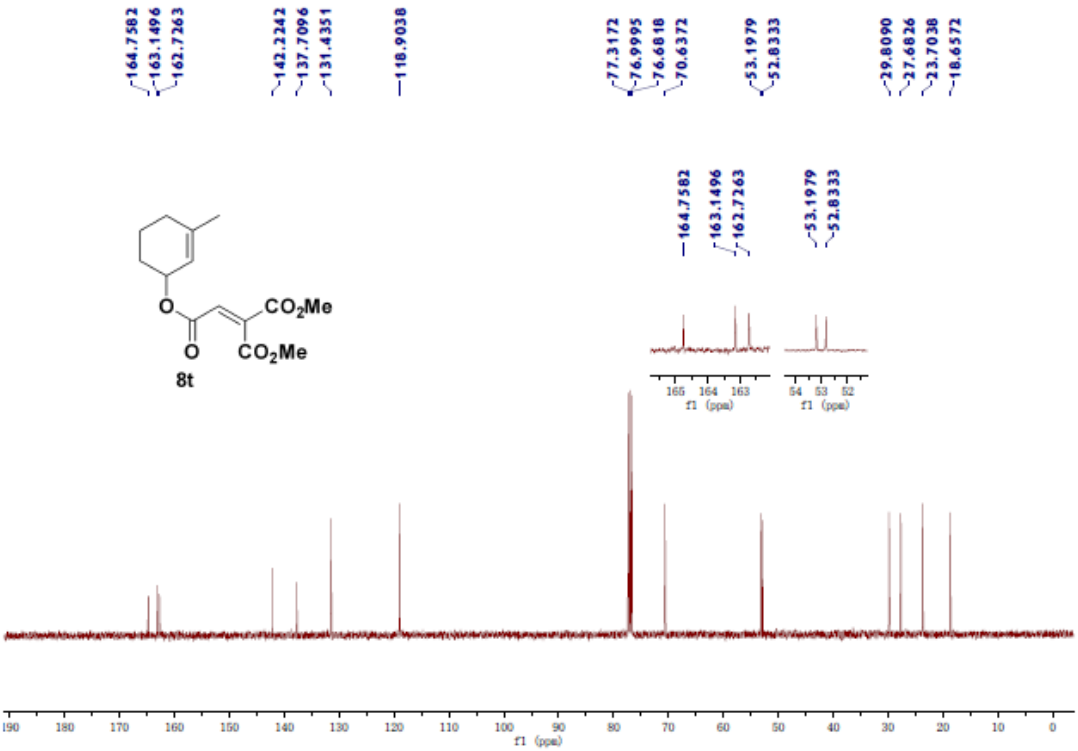
^{13}C NMR of **8s** (150 M, $CDCl_3$)



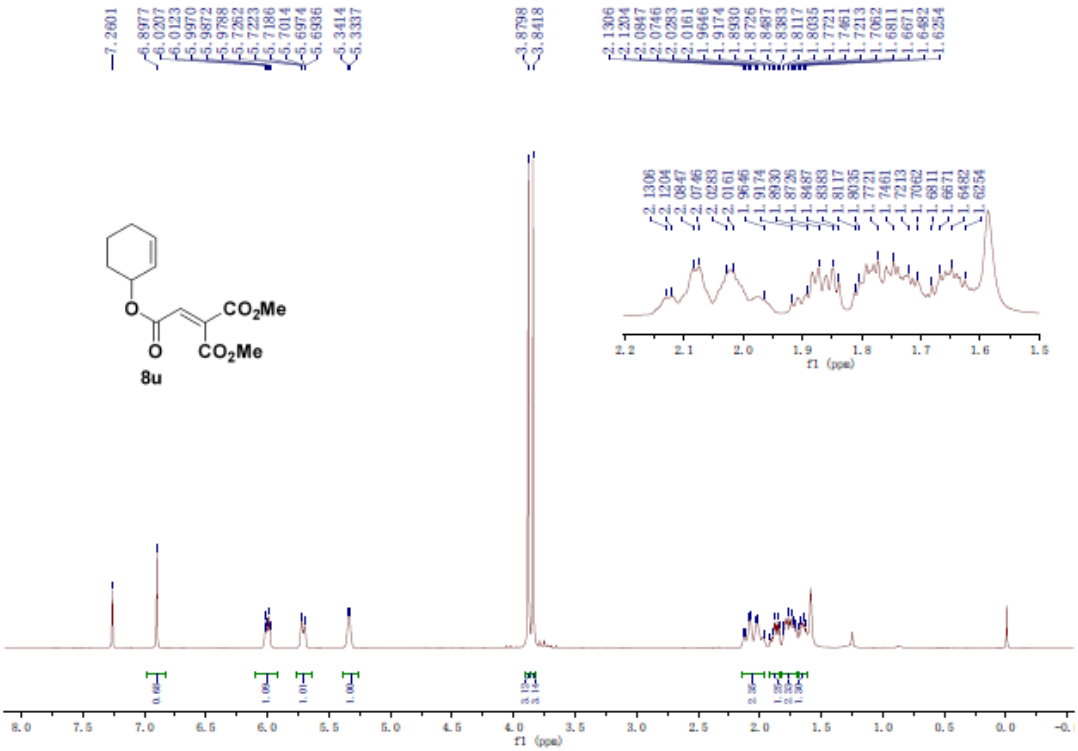
^{1}H NMR of **8t** (400 M, $CDCl_3$)



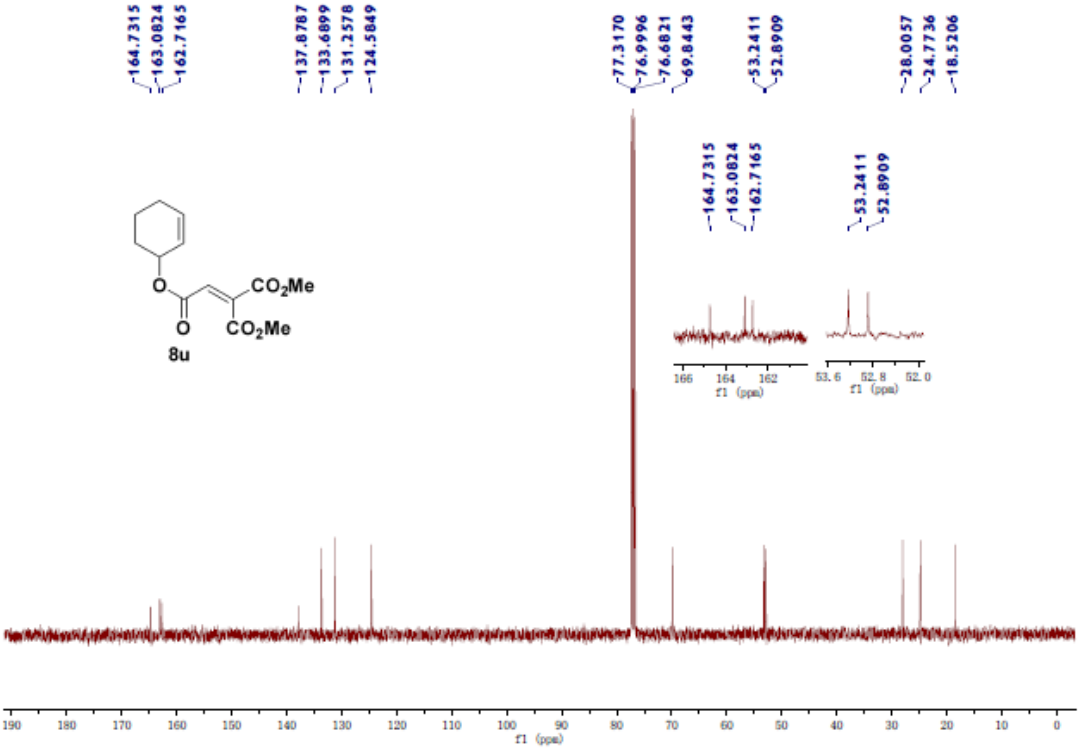
^{13}C NMR of **8t** (100 M, $CDCl_3$)



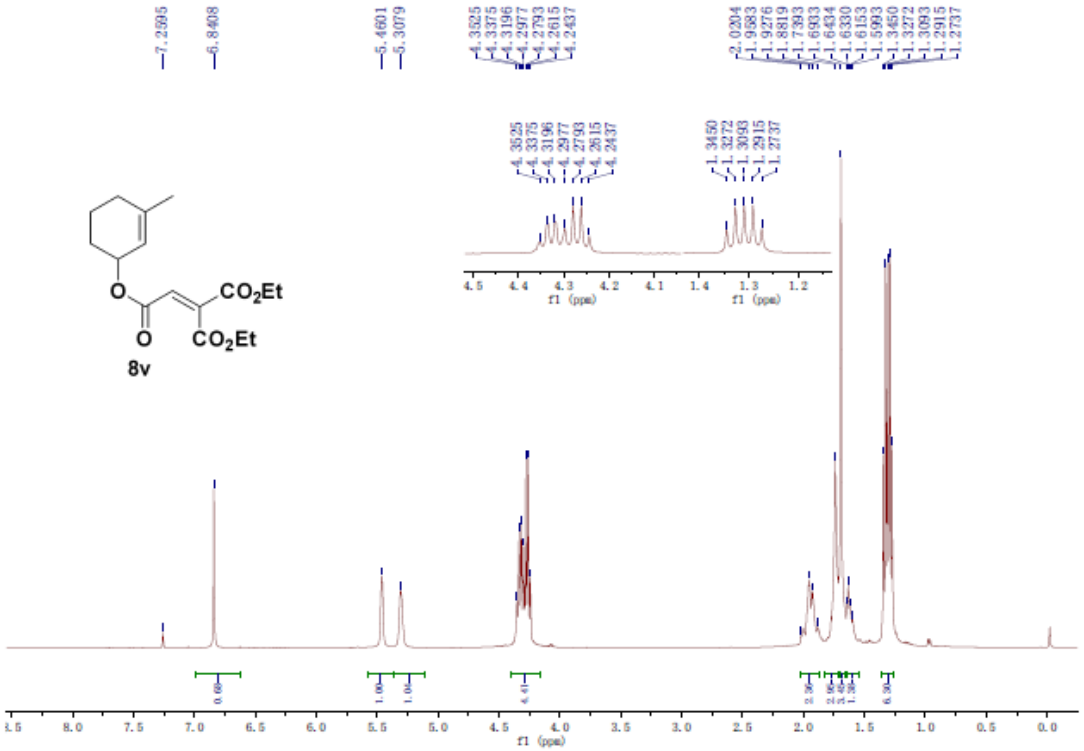
^{1}H NMR of **8u** (400 M, $CDCl_3$)



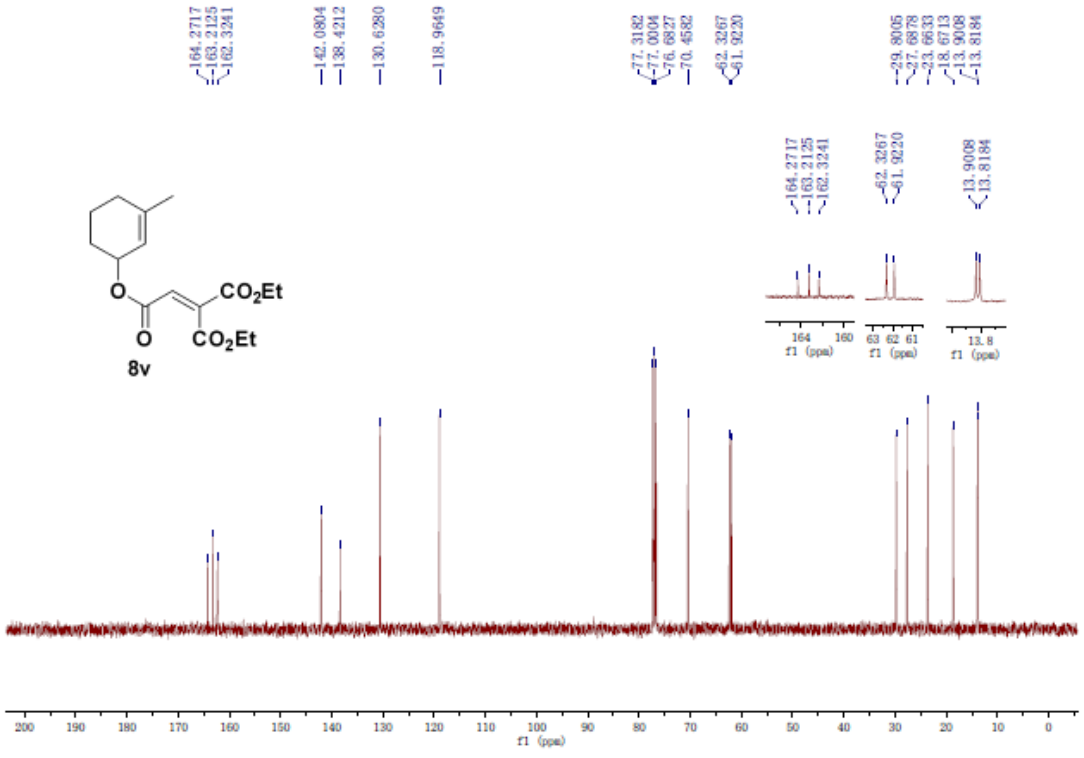
^{13}C NMR of **8u** (100 M, $CDCl_3$)



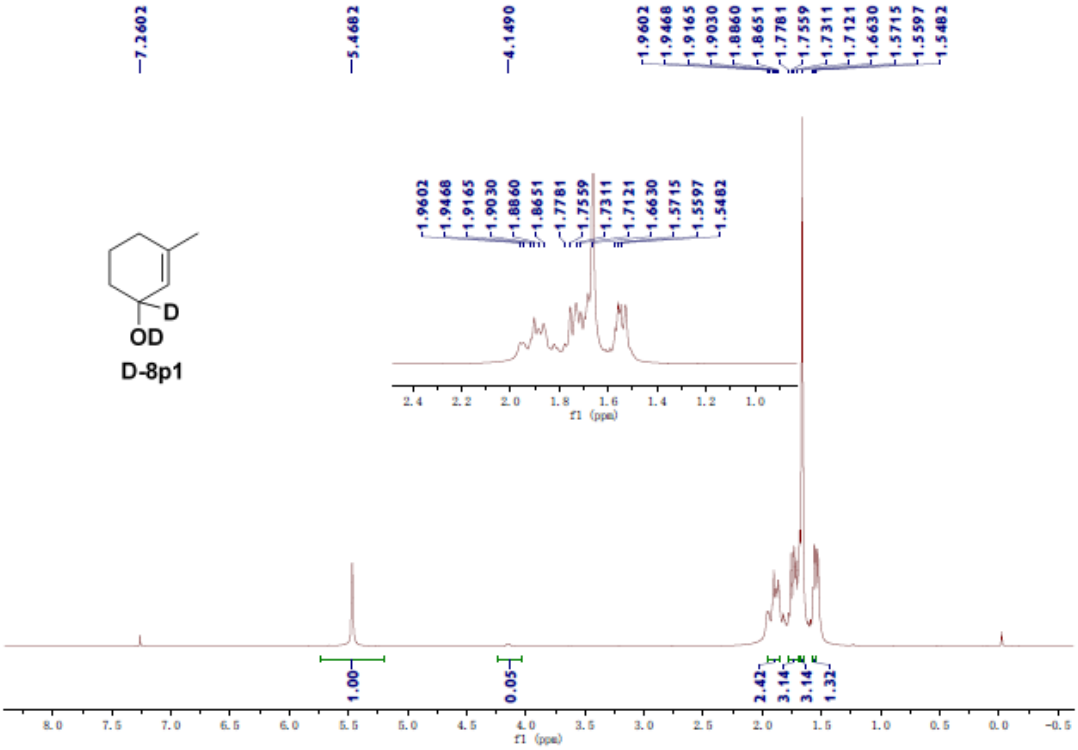
^{1}H NMR of **8v** (400 M, $CDCl_3$)



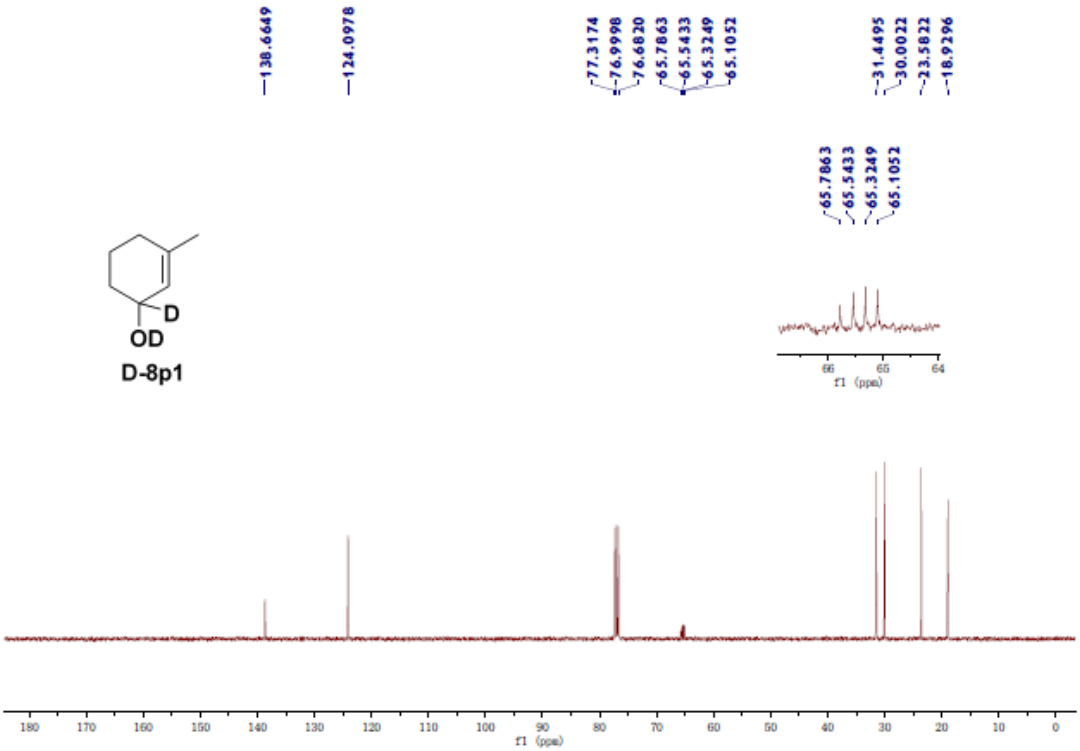
^{13}C NMR of **8v** (100 M, $CDCl_3$)



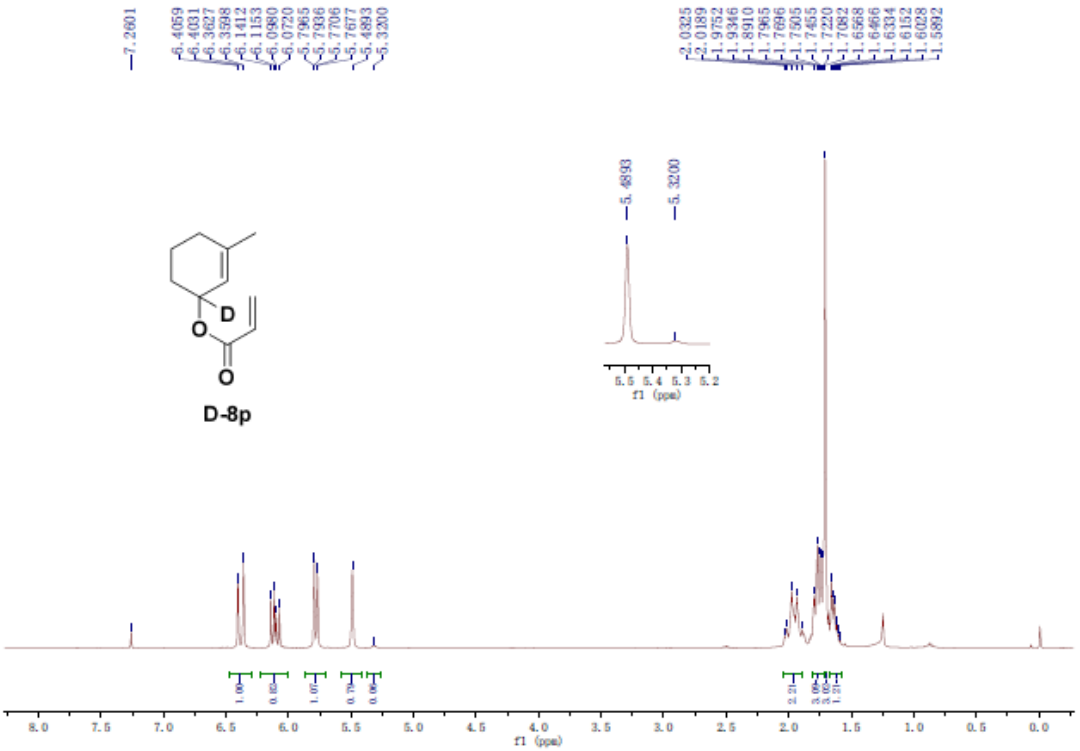
^{1}H NMR of **D-8p1** (400 M, $CDCl_3$)



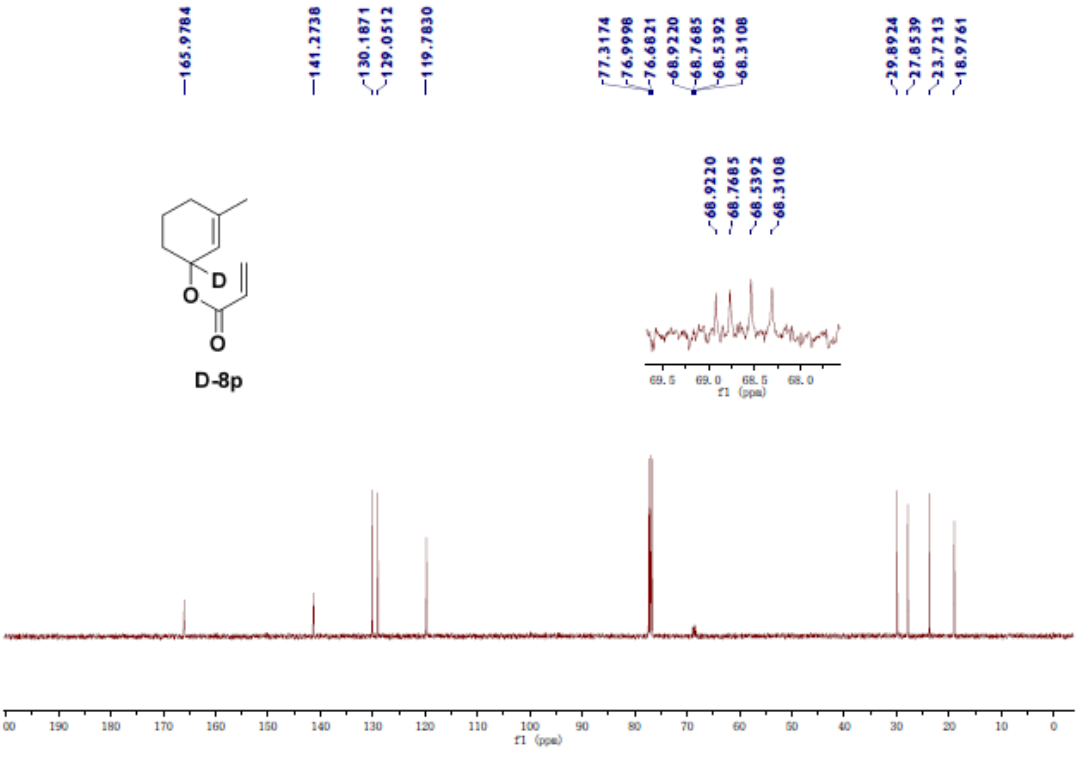
^{13}C NMR of **D-8p1** (100 M, $CDCl_3$)



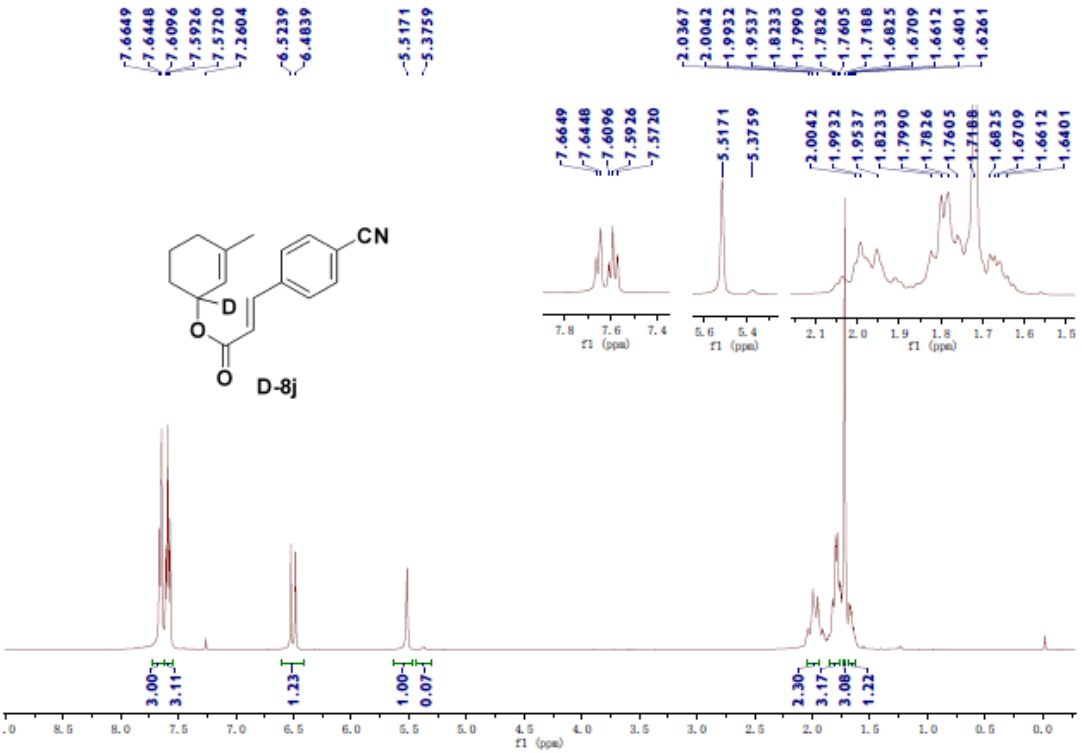
^{1}H NMR of **D-8p** (400 M, $CDCl_3$)



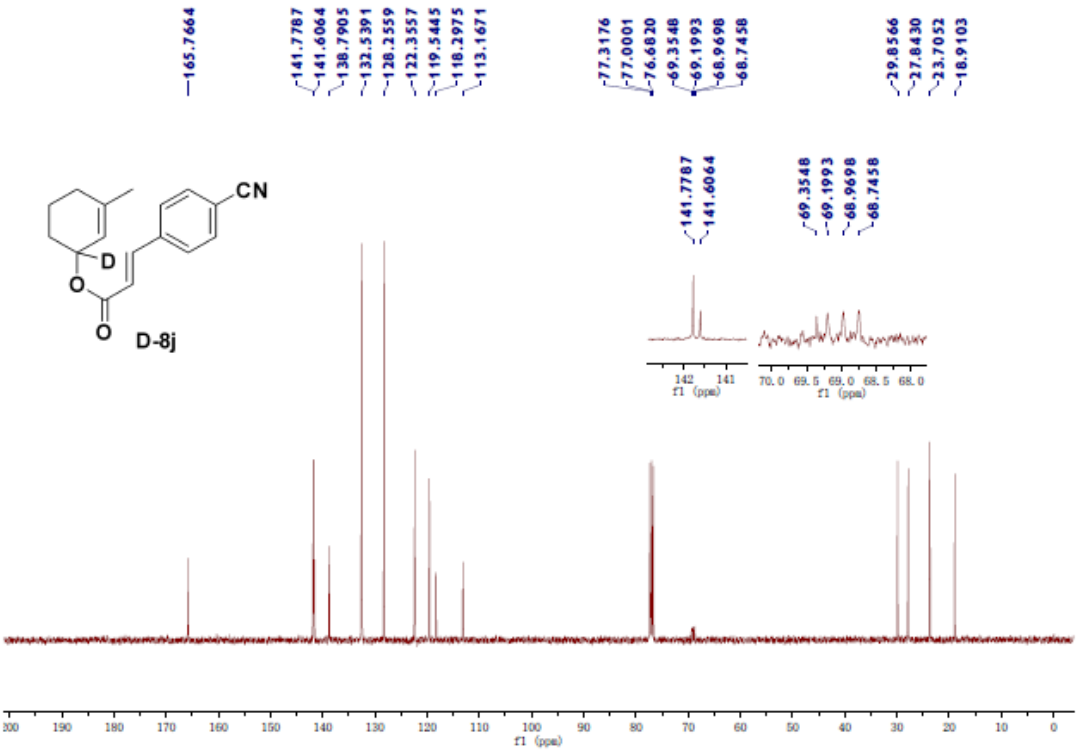
^{13}C NMR of **D-8p** (100 M, $CDCl_3$)



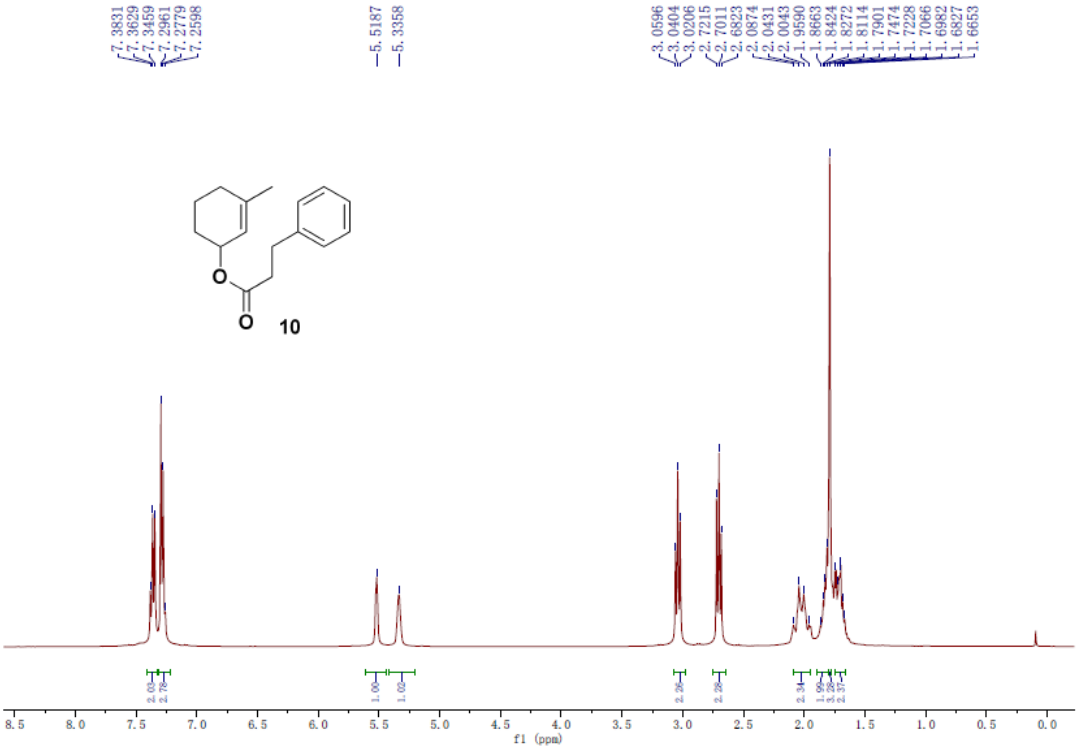
^{1}H NMR of **D-8j** (400 M, $CDCl_3$)



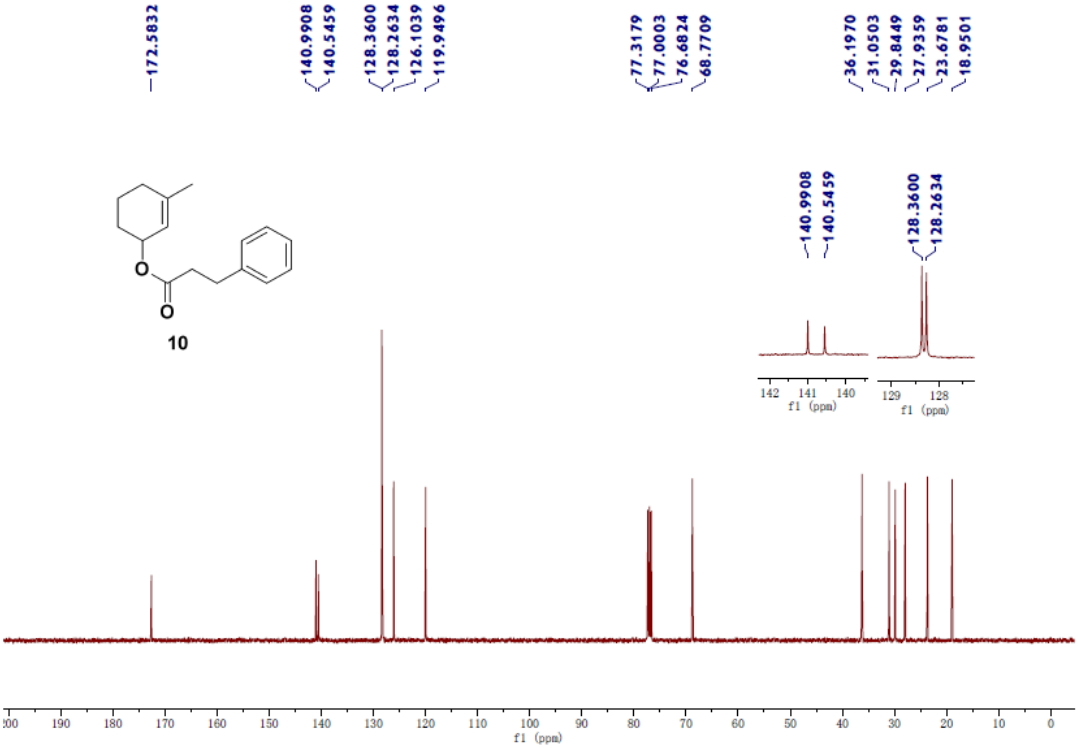
^{13}C NMR of **D-8j** (100 M, $CDCl_3$)



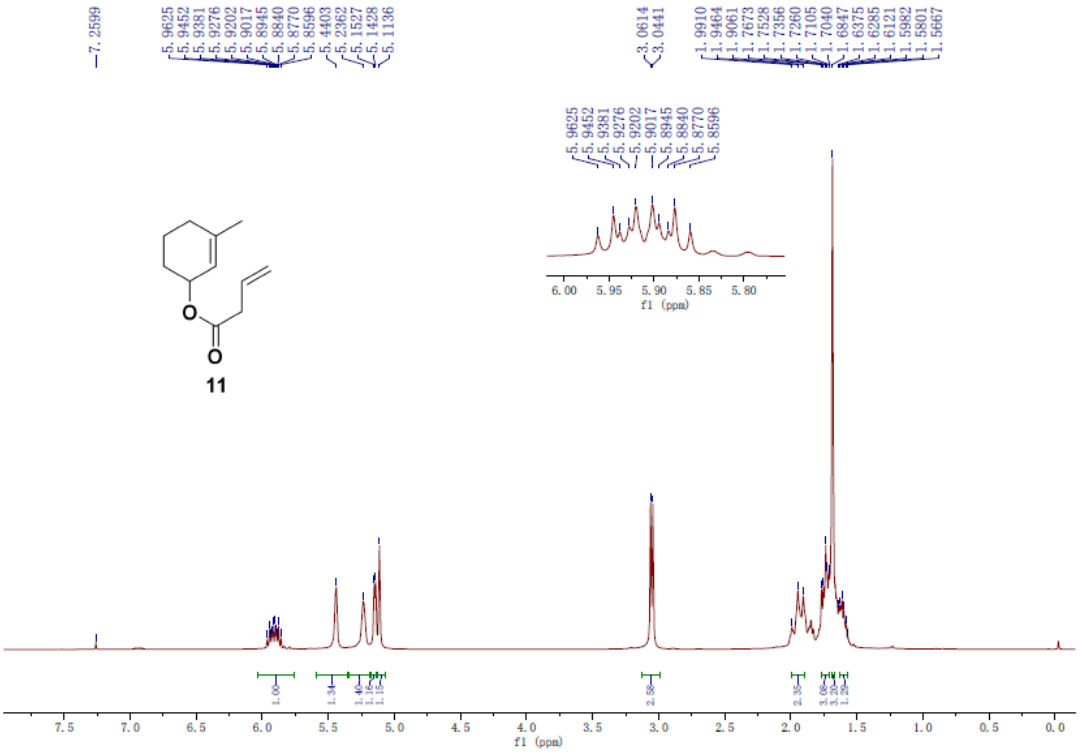
^{1}H NMR of **10** (400 M, $CDCl_3$)



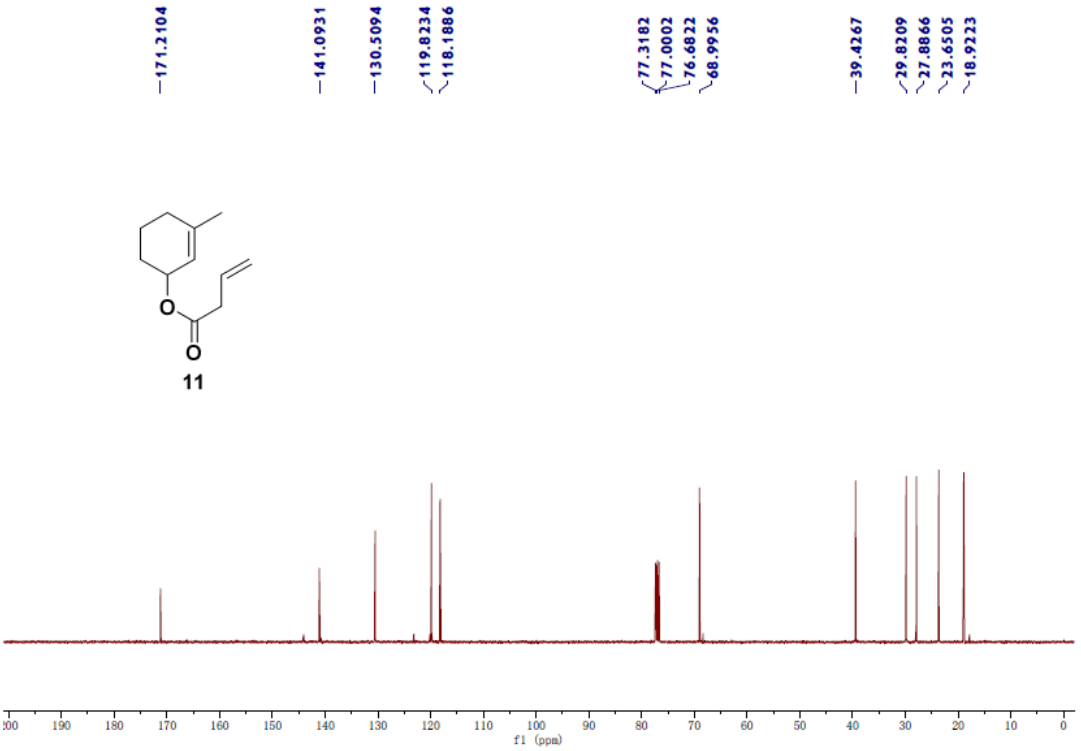
^{13}C NMR of **10** (100 M, $CDCl_3$)



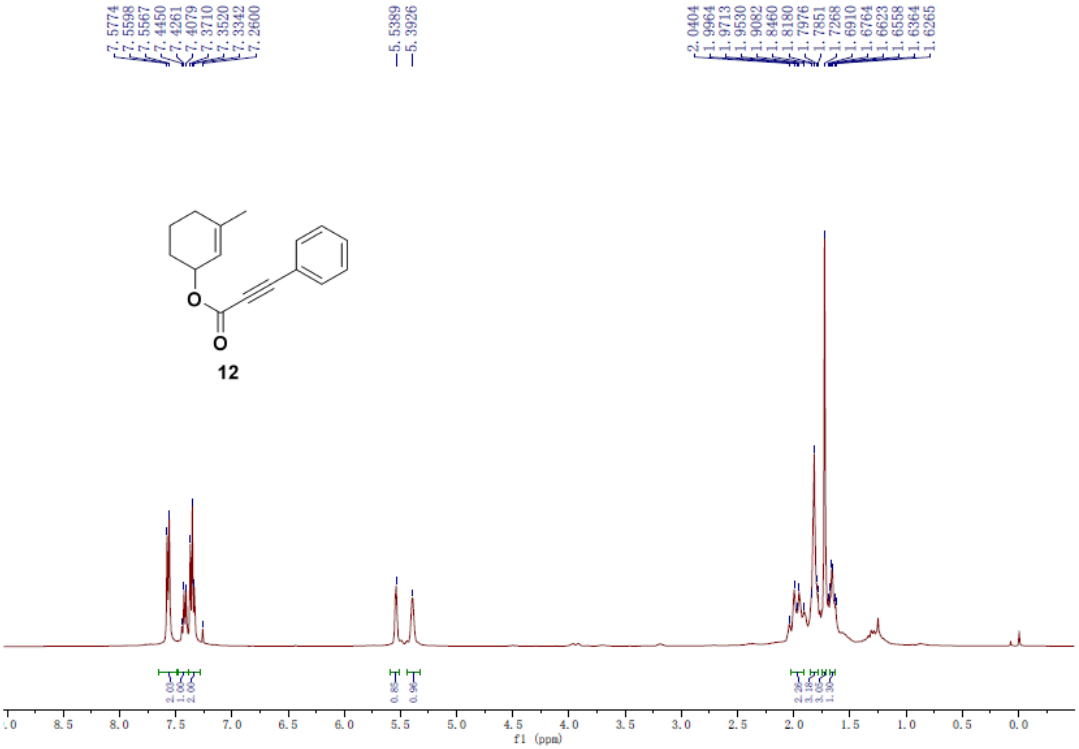
^{1}H NMR of **11** (400 M, $CDCl_3$)



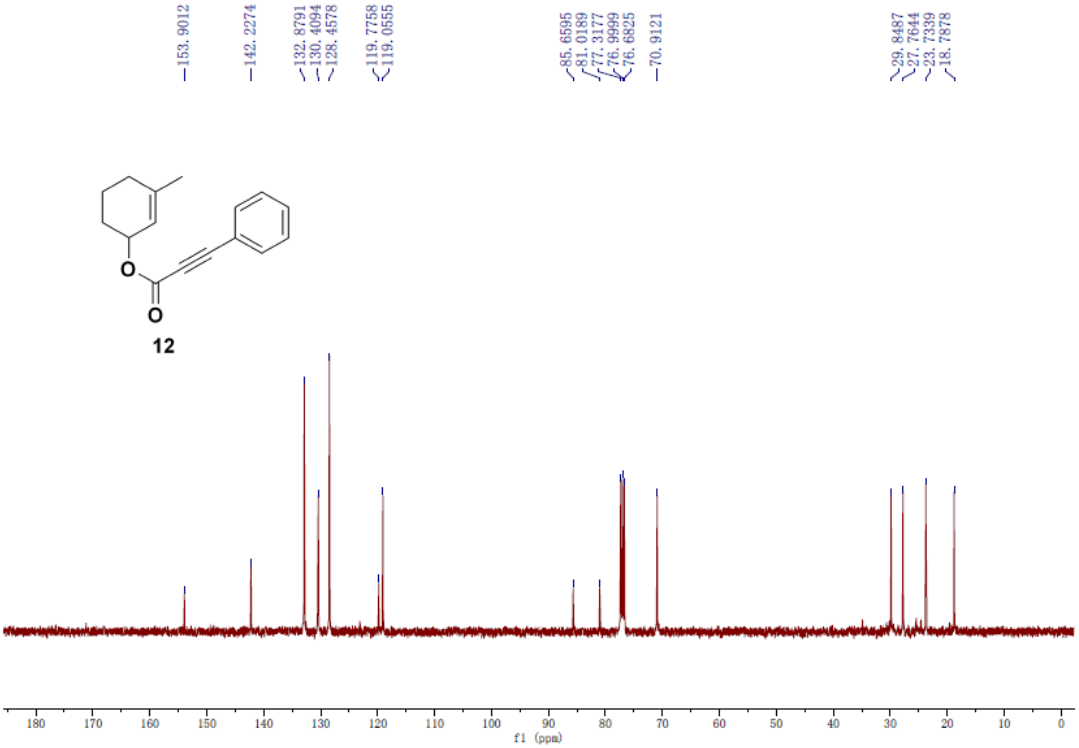
^{13}C NMR of **11** (100 M, $CDCl_3$)



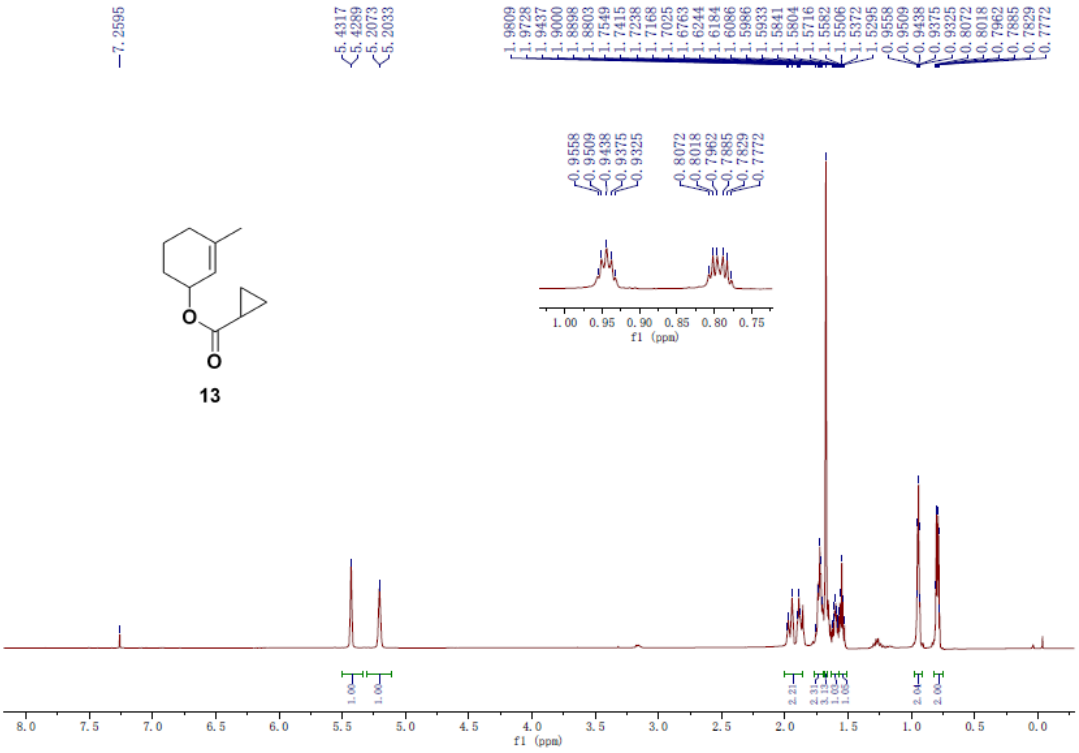
^{1}H NMR of **12** (400 M, $CDCl_3$)



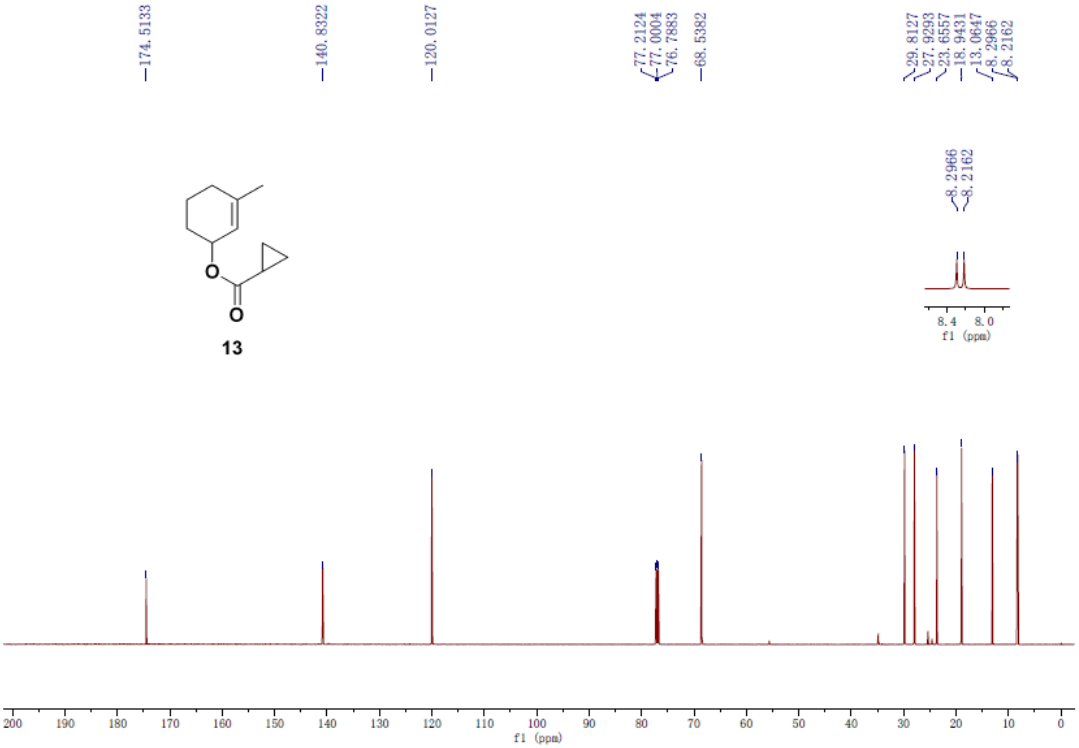
^{13}C NMR of **12** (100 M, $CDCl_3$)



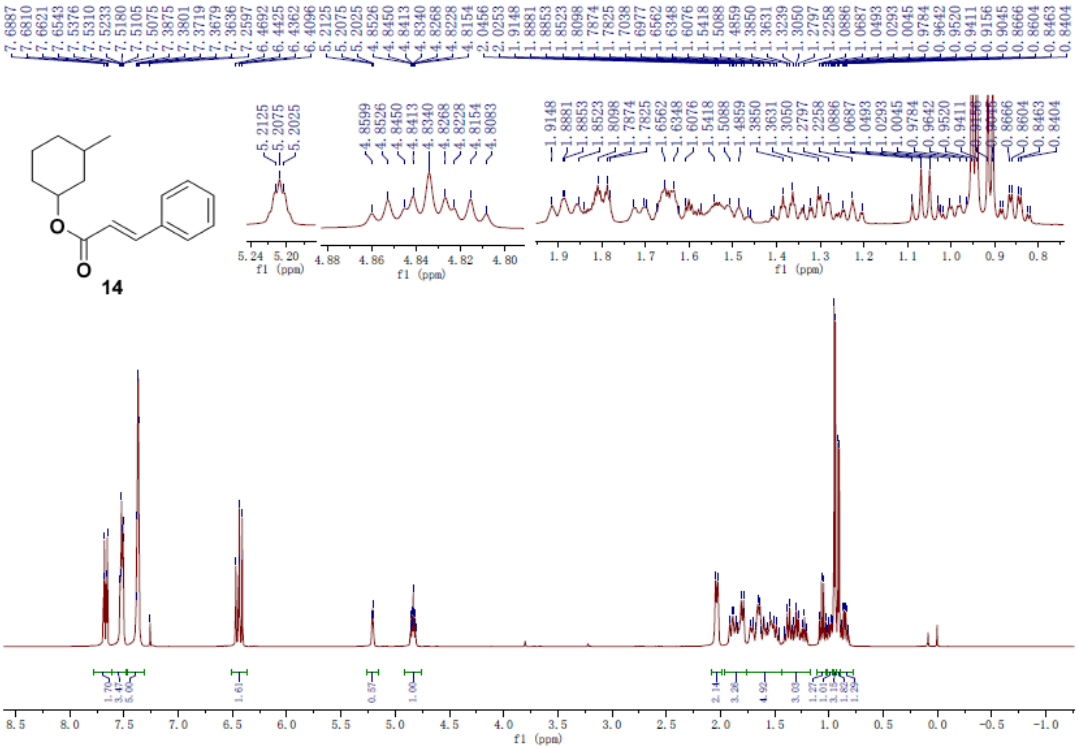
^{1}H NMR of **13** (600 M, $CDCl_3$)



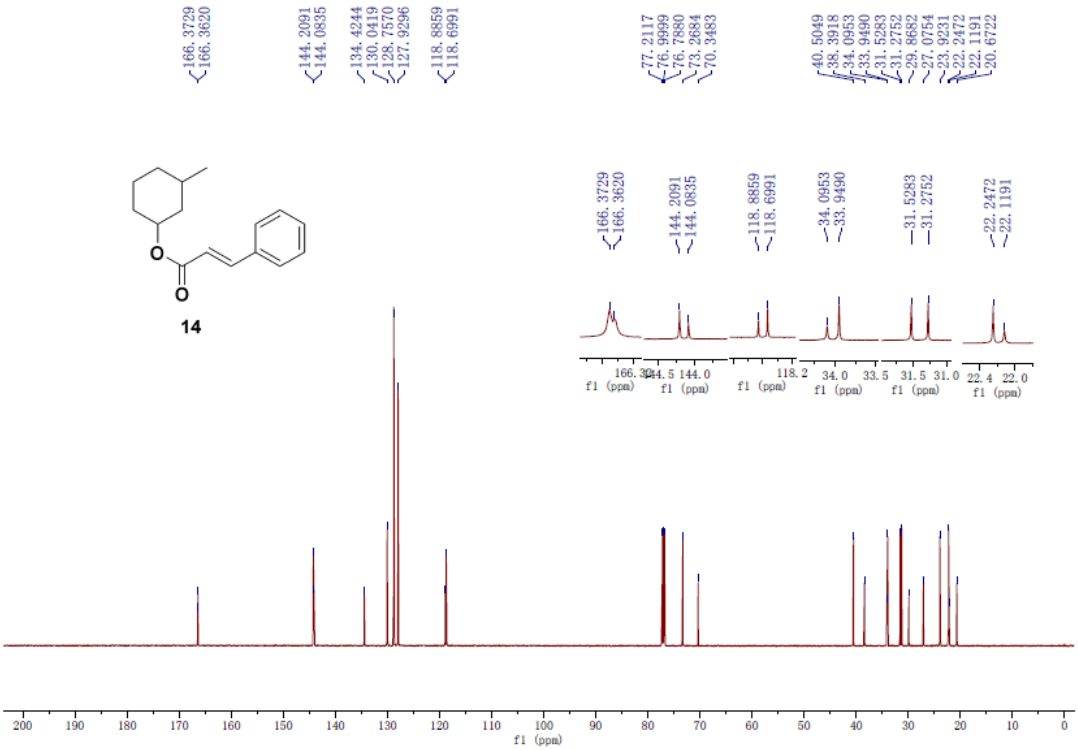
^{13}C NMR of **13** (150 M, $CDCl_3$)



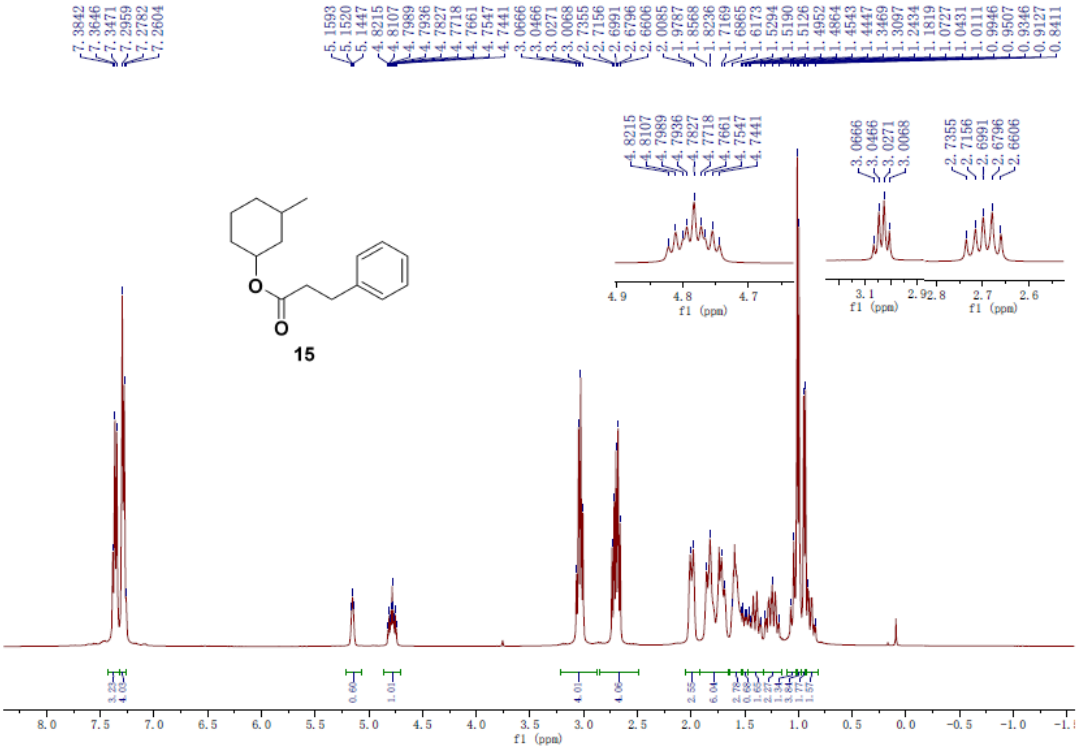
^{1}H NMR of **14** (600 M, $CDCl_3$)



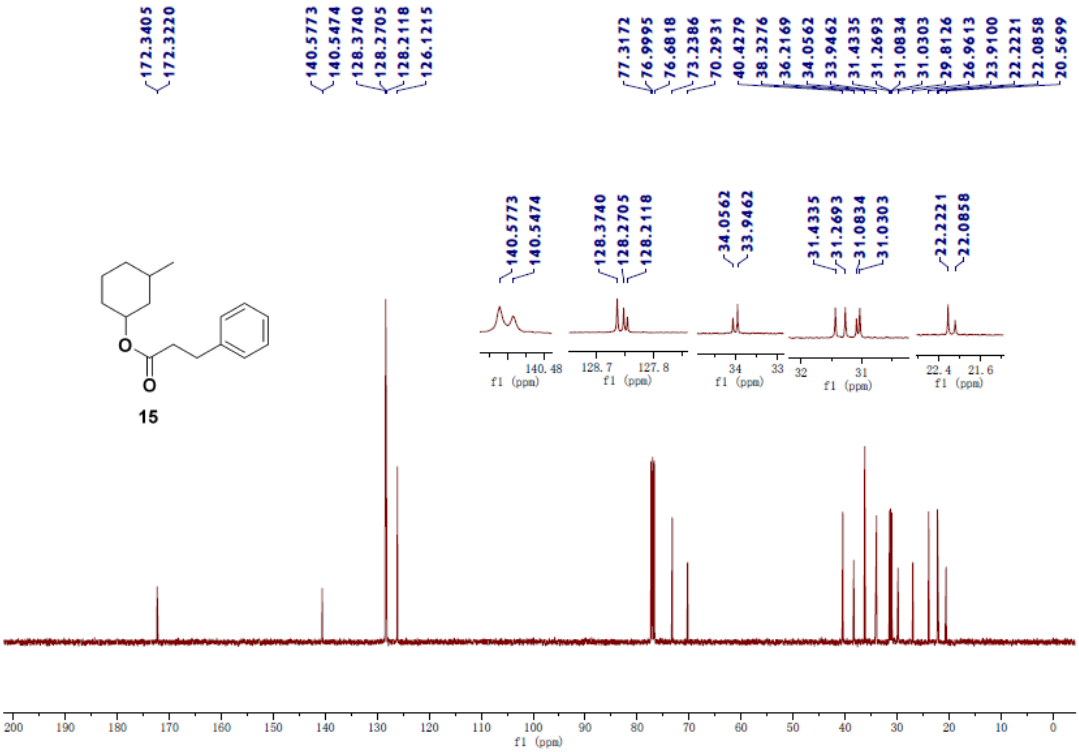
^{13}C NMR of **14** (150 M, $CDCl_3$)



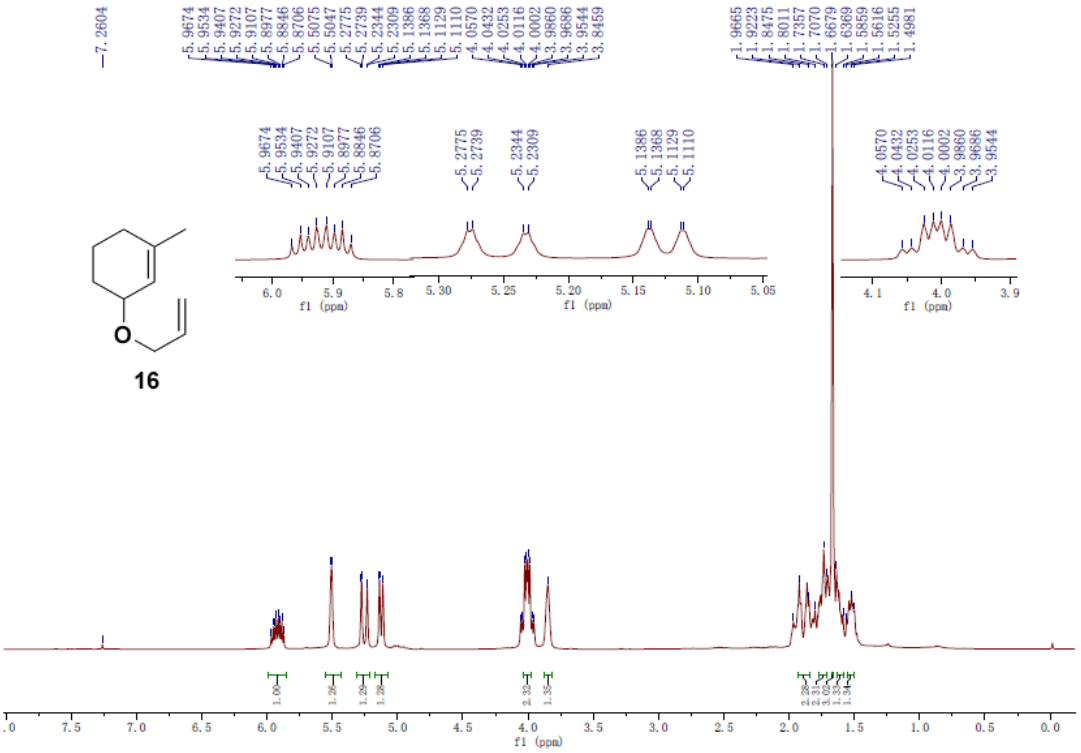
^{1}H NMR of **15** (400 M, $CDCl_3$)



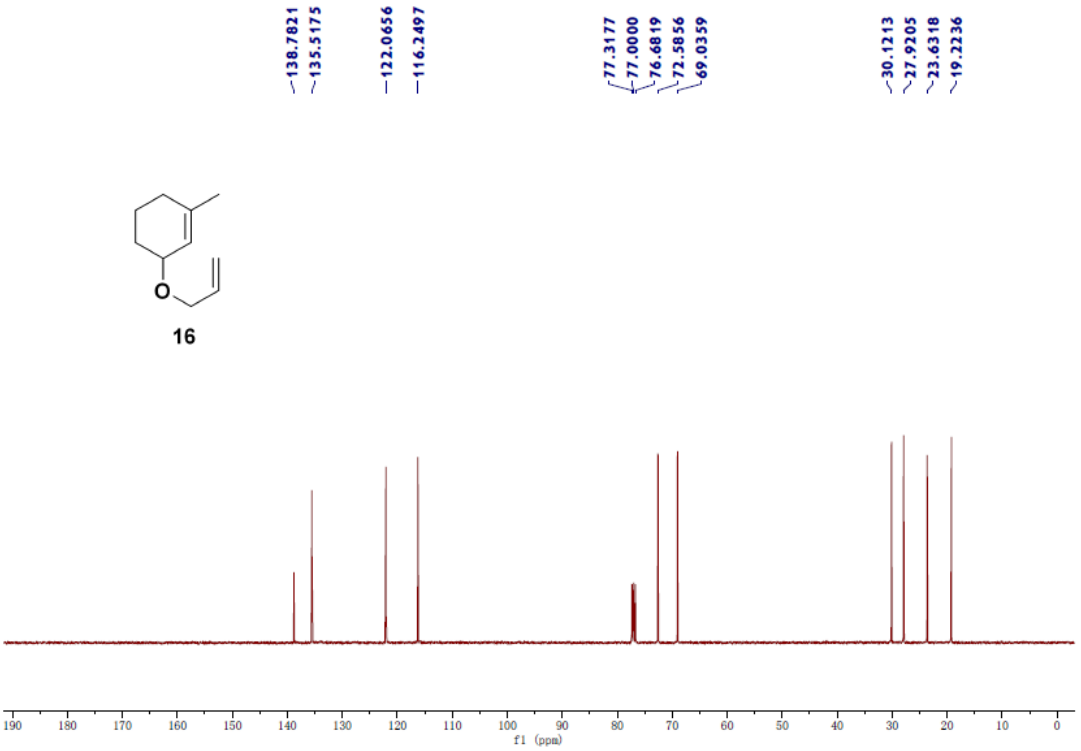
^{13}C NMR of **15** (100 M, $CDCl_3$)



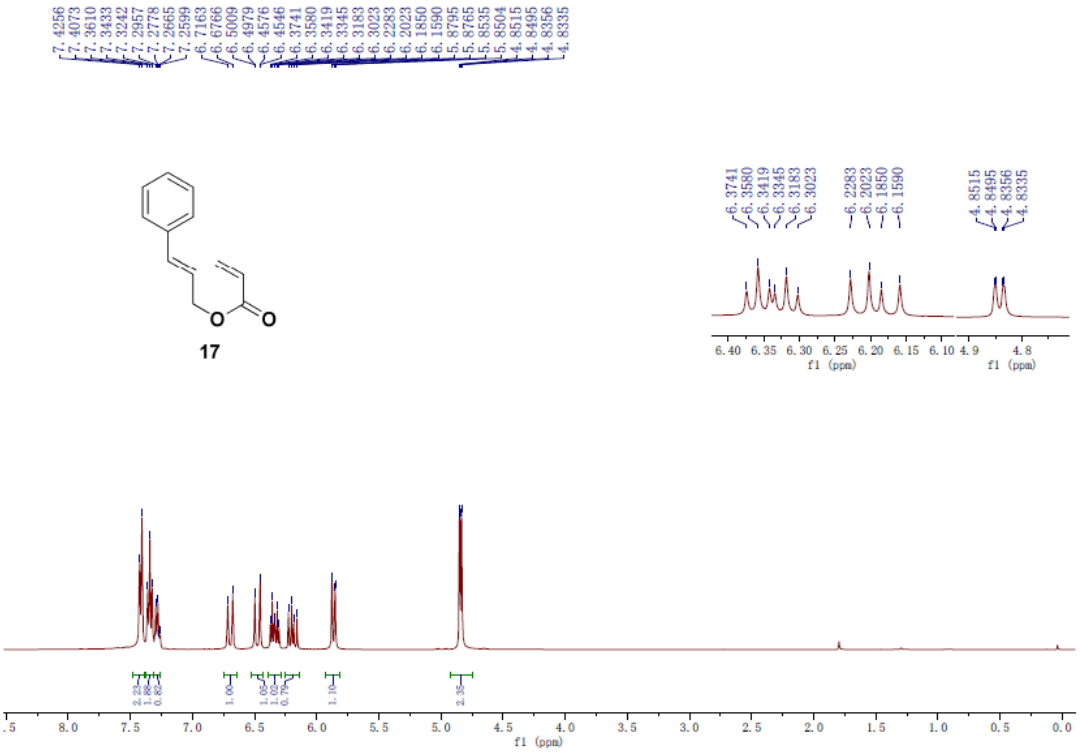
^{1}H NMR of **16** (400 M, $CDCl_3$)



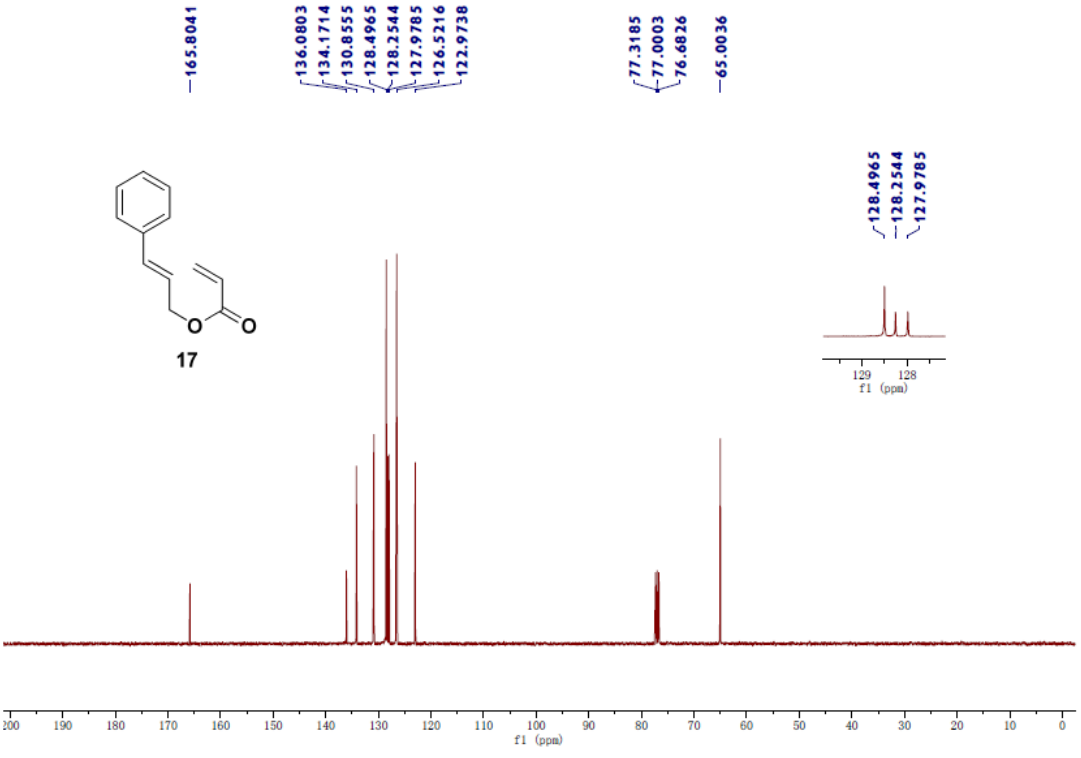
^{13}C NMR of **16** (100 M, $CDCl_3$)



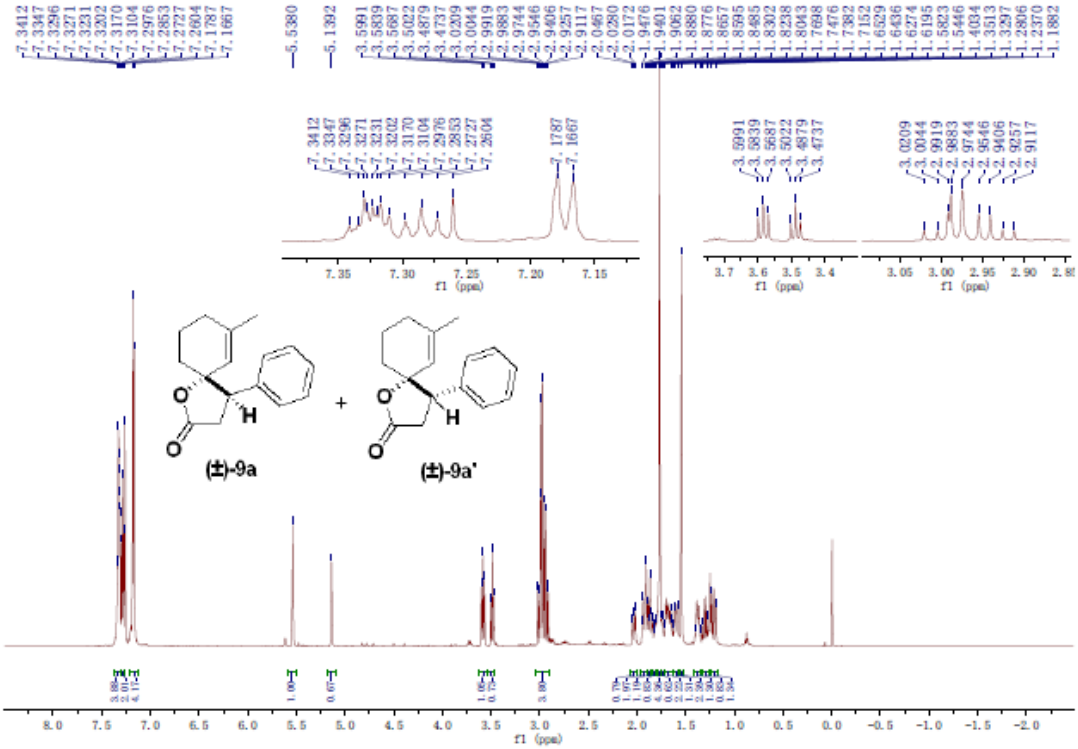
^{1}H NMR of **17**(400 M, $CDCl_3$)



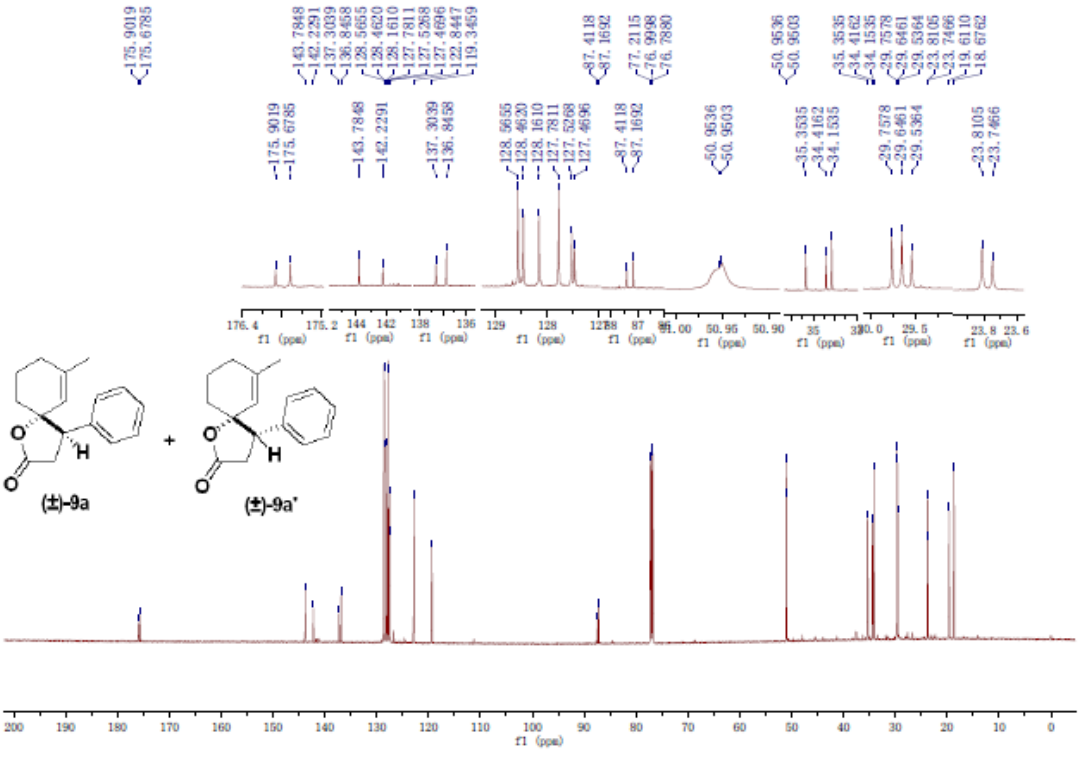
^{13}C NMR of **17** (100 M, $CDCl_3$)



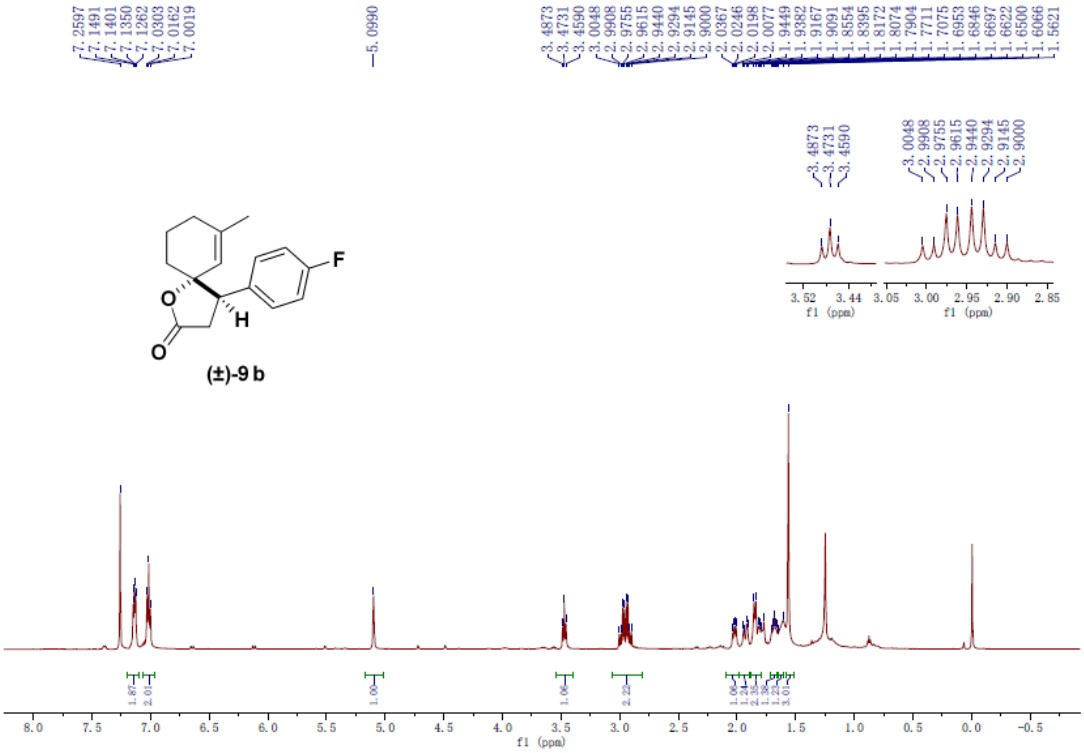
^{1}H NMR of (±)-**9a** (400 M, $CDCl_3$)



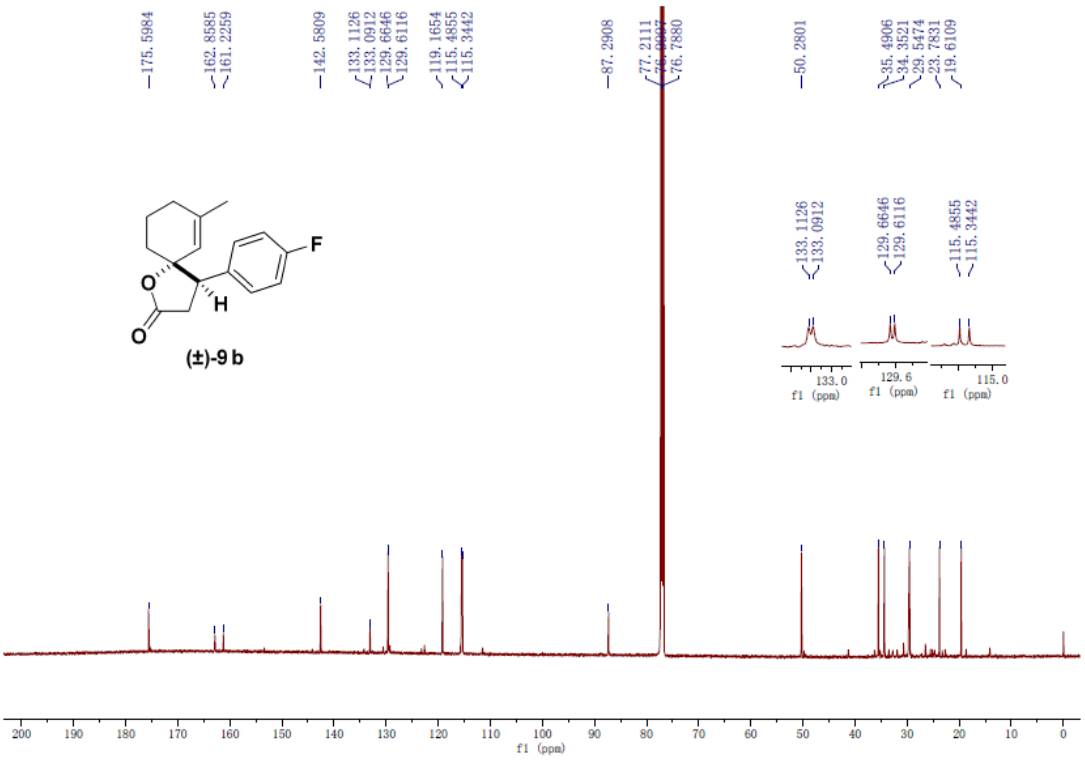
^{13}C NMR of (±)-**9a** (100 M, $CDCl_3$)



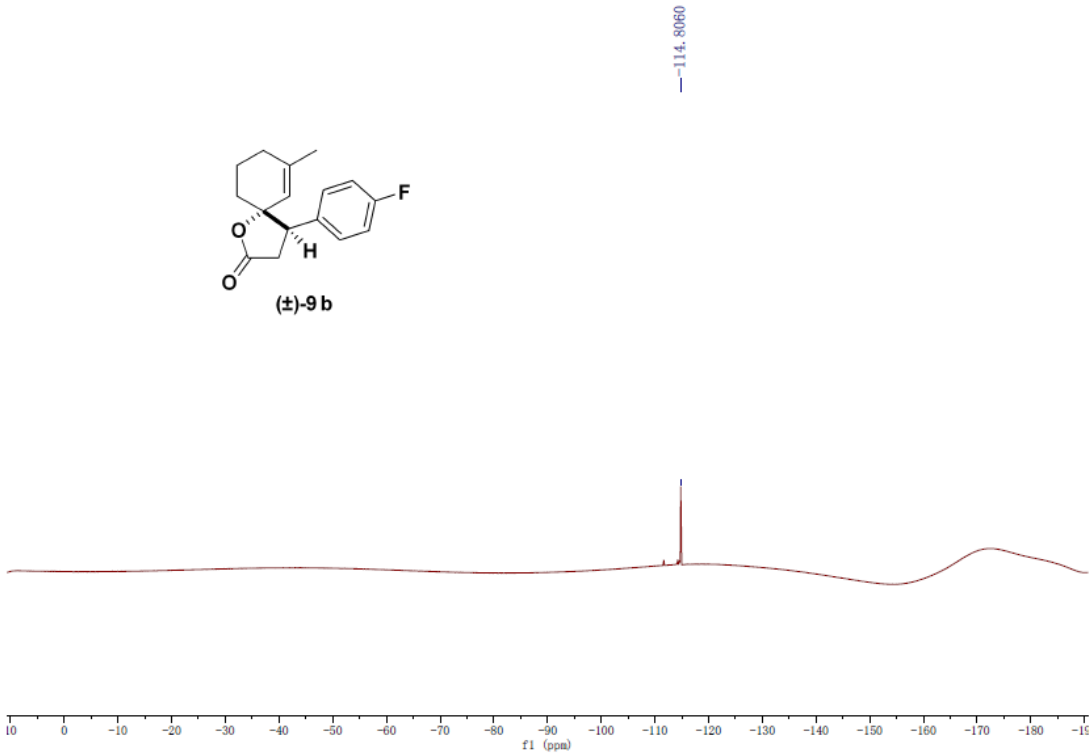
^{1}H NMR of **(±)-9b** (600 M, $CDCl_3$)



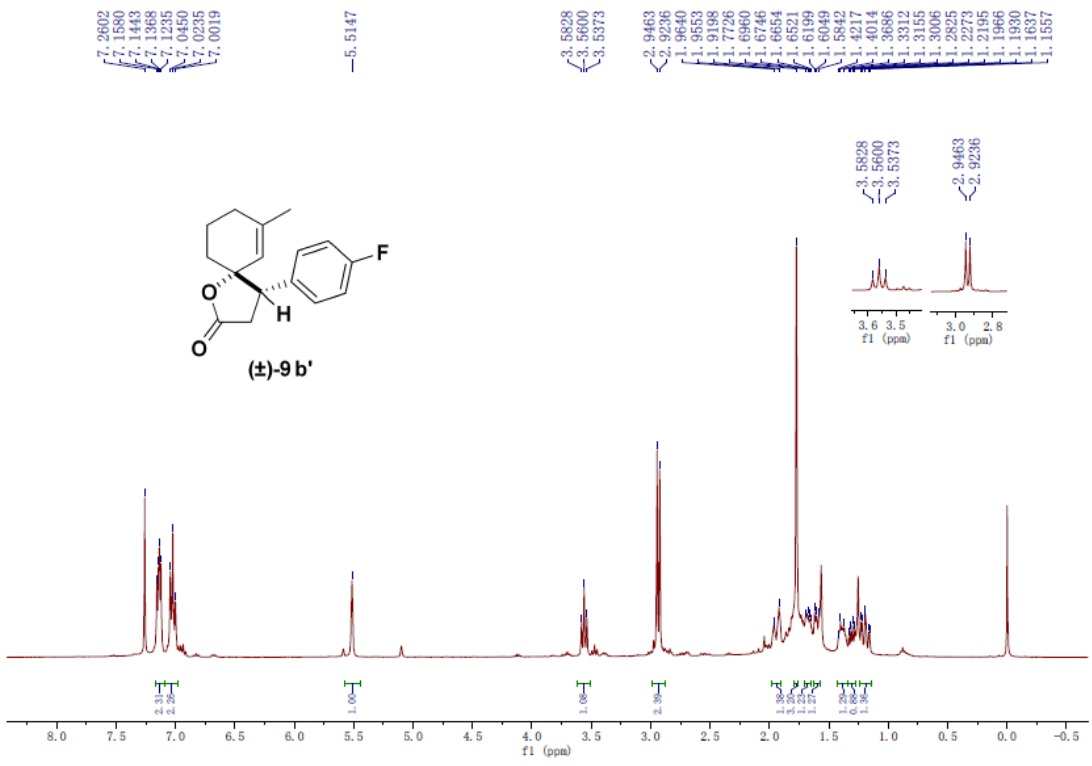
^{13}C NMR of **(±)-9b** (150 M, $CDCl_3$)



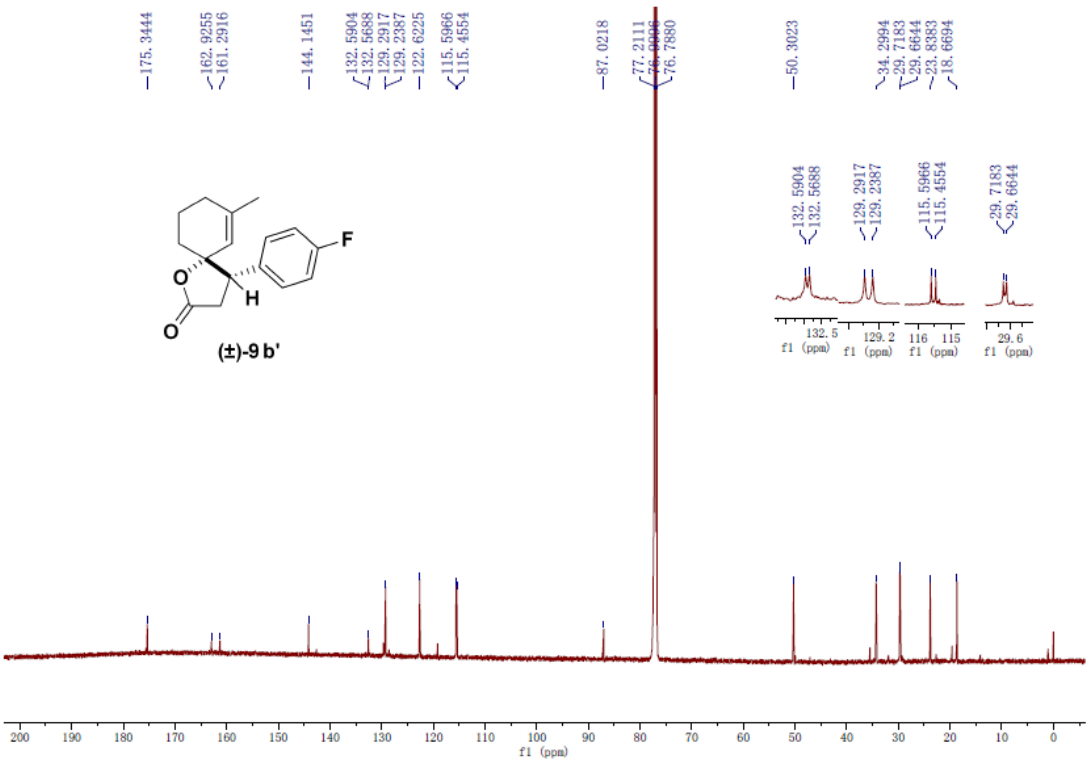
^{19}F NMR of **(±)-9b** (565 M, $CDCl_3$)



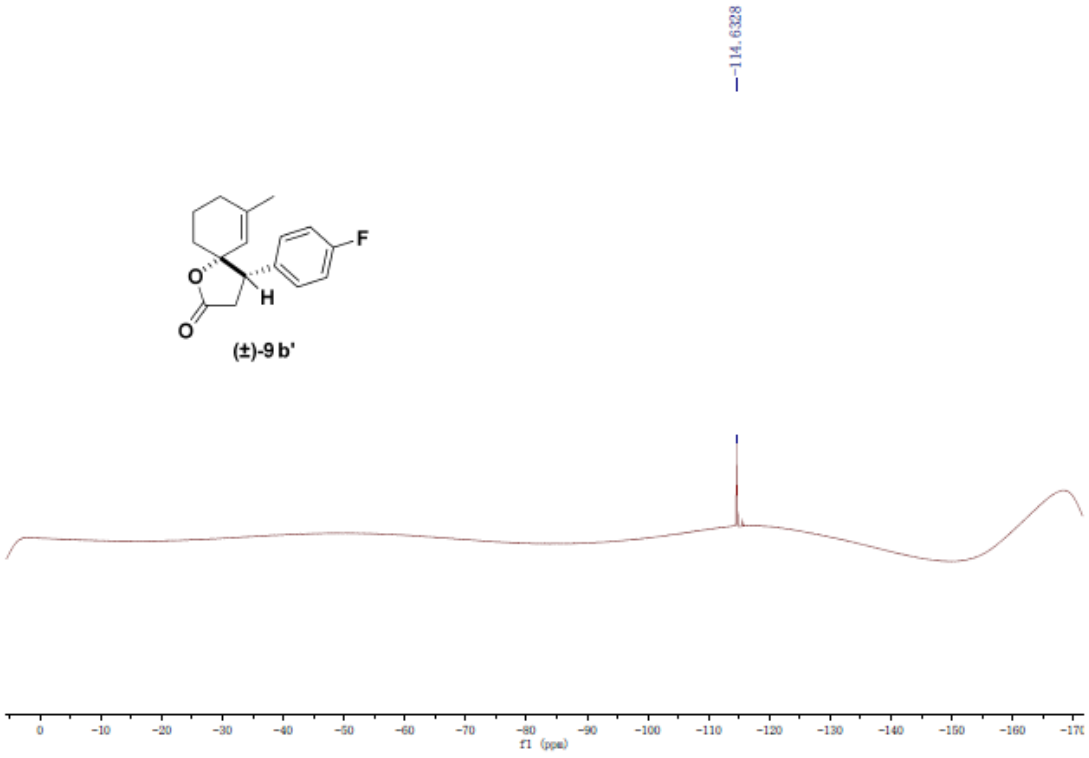
^{1}H NMR of **(±)-9b'** (600 M, $CDCl_3$)



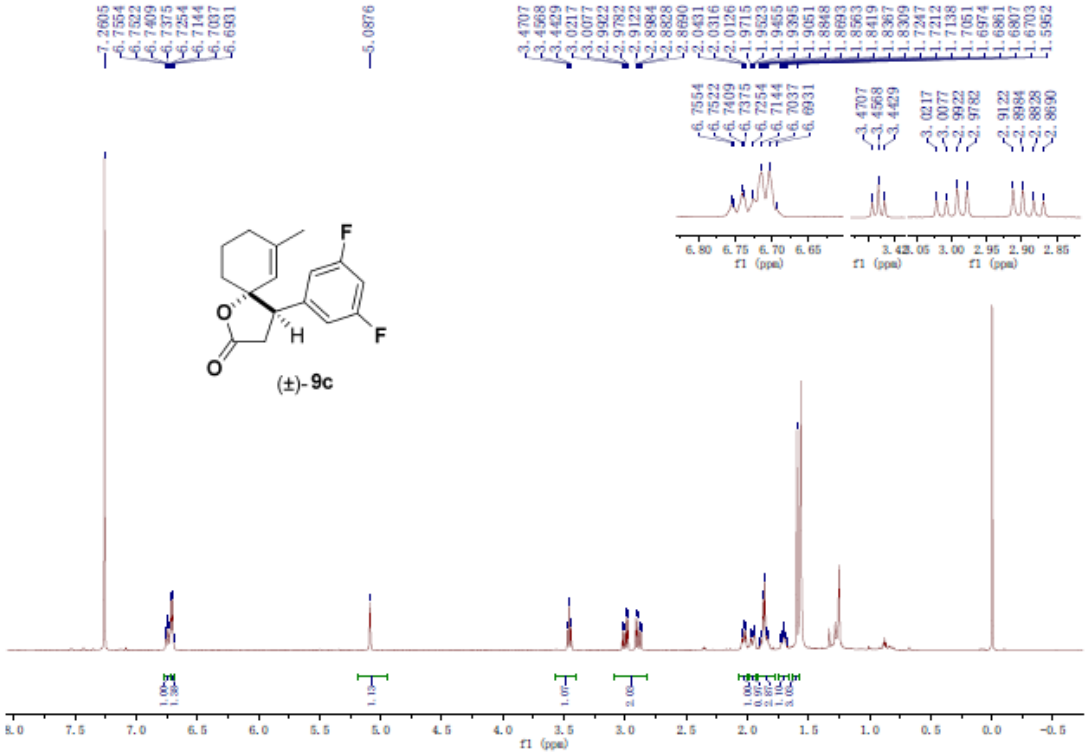
^{13}C NMR of **(±)-9b'** (150 M, $CDCl_3$)



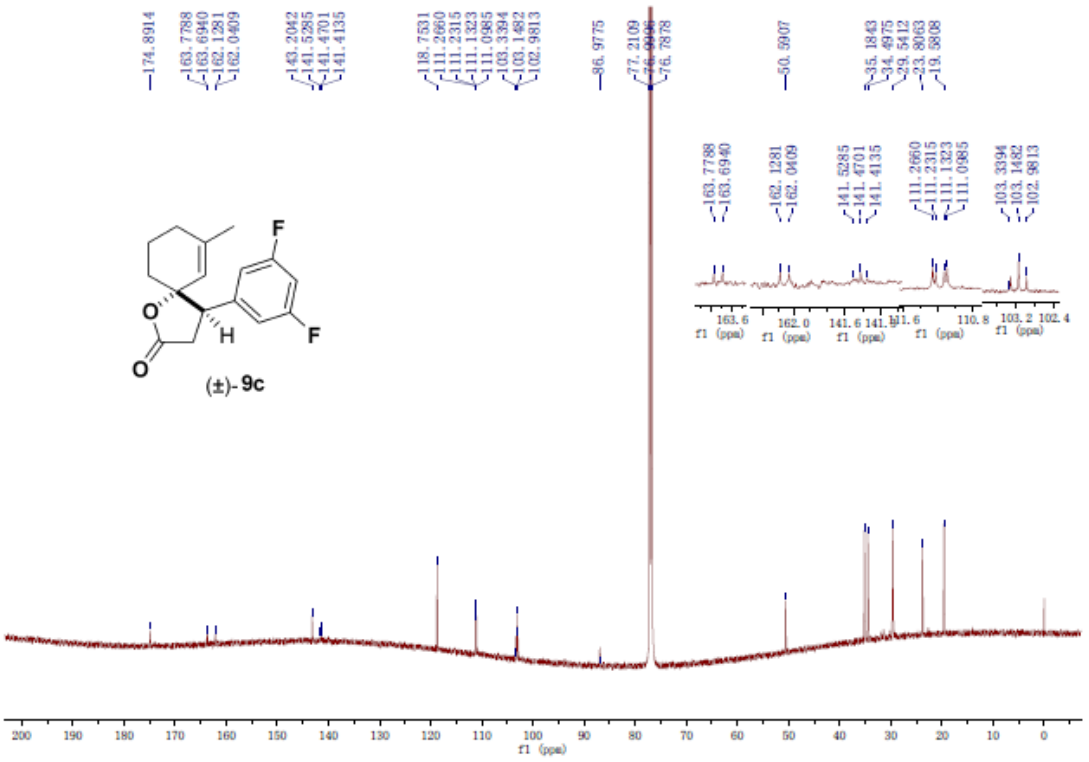
^{19}F NMR of **(±)-9b'** (565 M, $CDCl_3$)



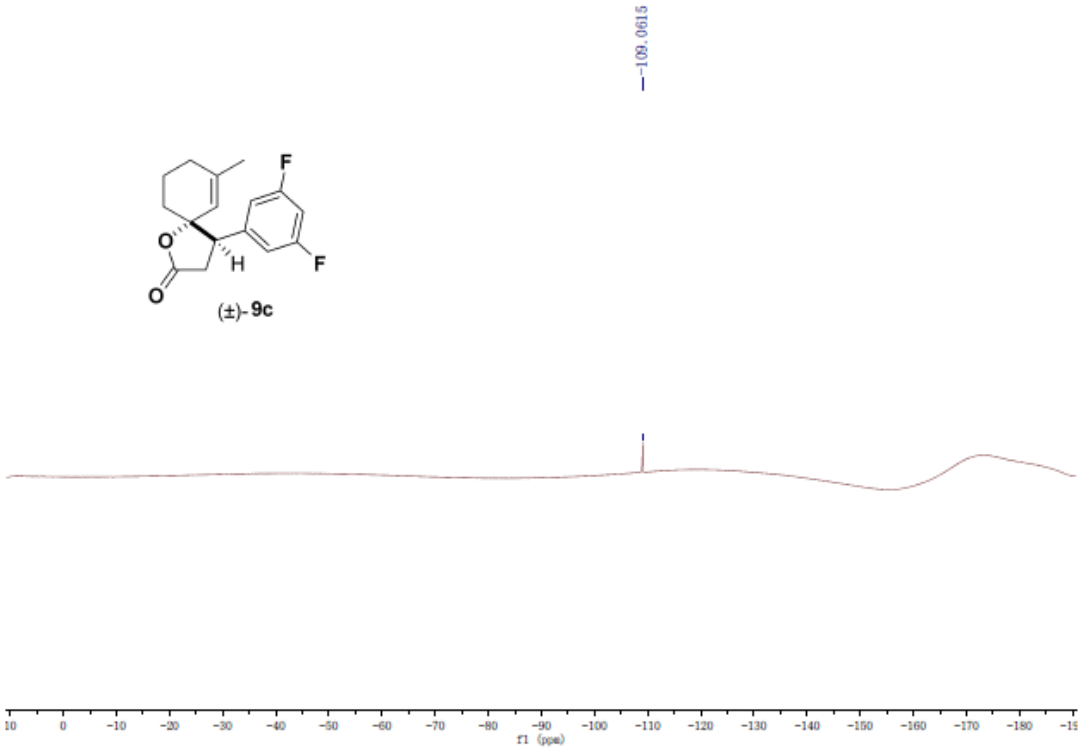
^{1}H NMR of **(±)-9c** (600 M, $CDCl_3$)



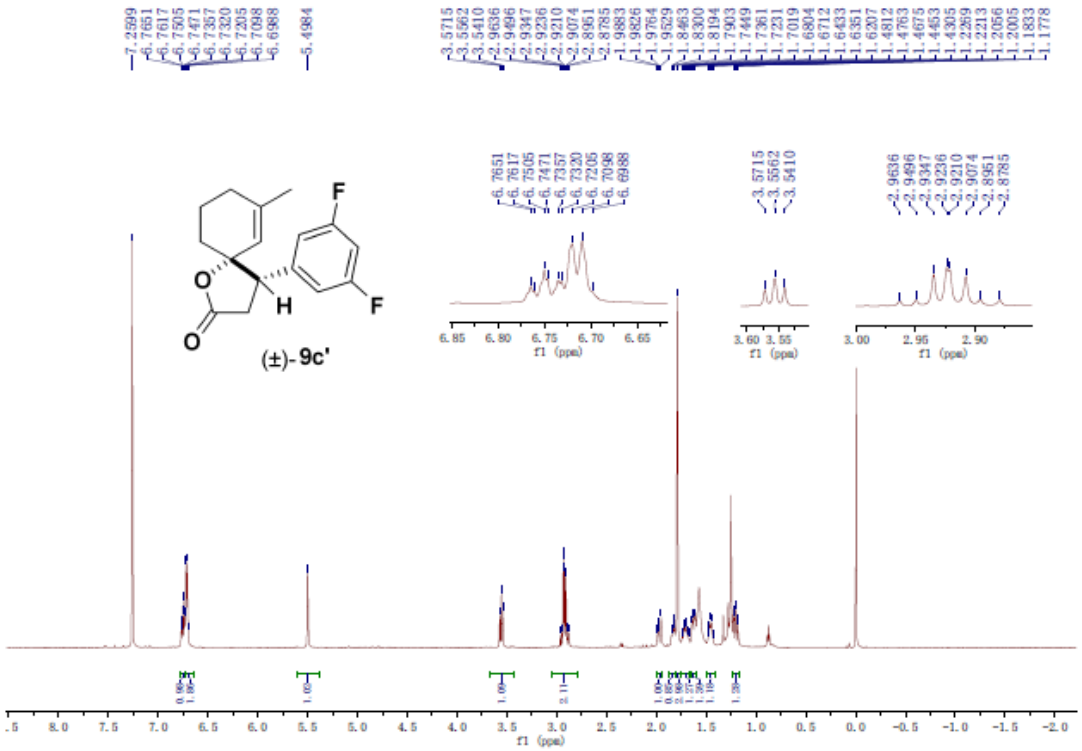
^{13}C NMR of **(±)-9c** (150 M, $CDCl_3$)



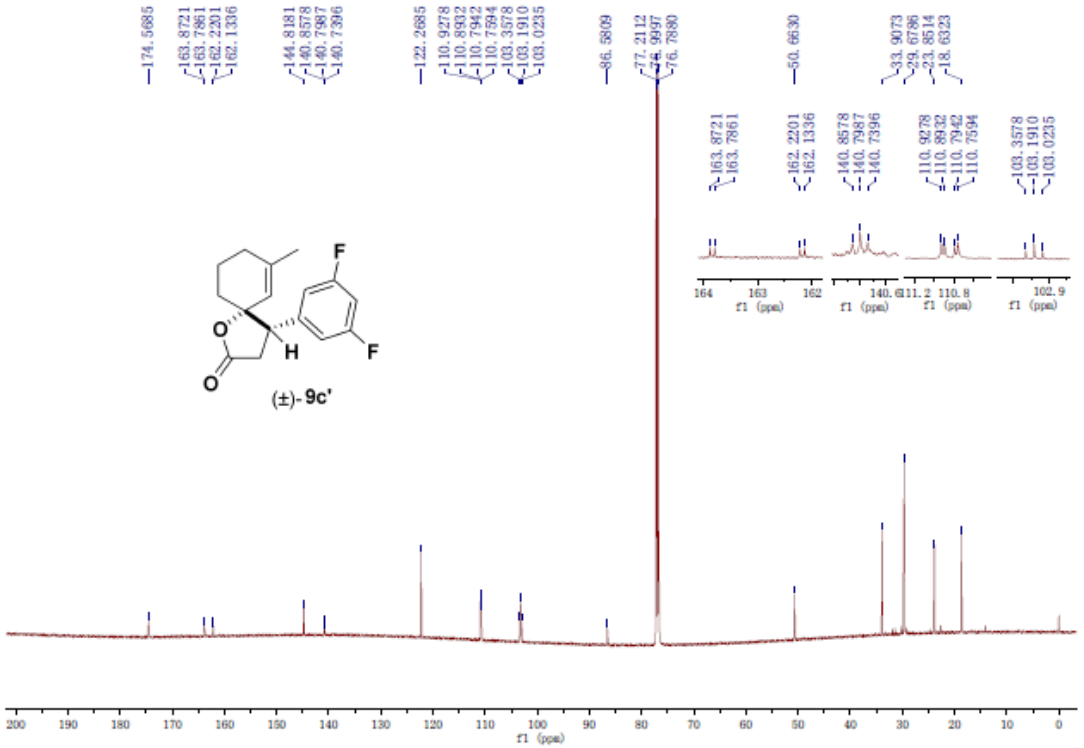
^{19}F NMR of **(±)-9c** (565 M, $CDCl_3$)



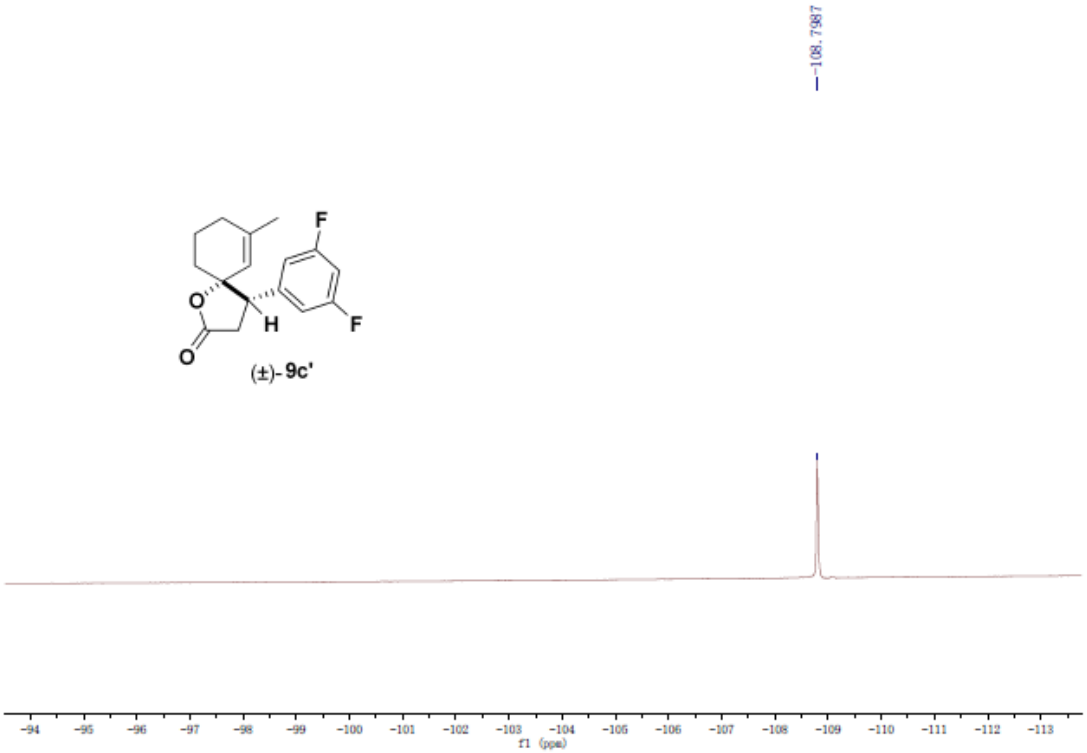
^{1}H NMR of **(±)-9c'** (600 M, $CDCl_3$)



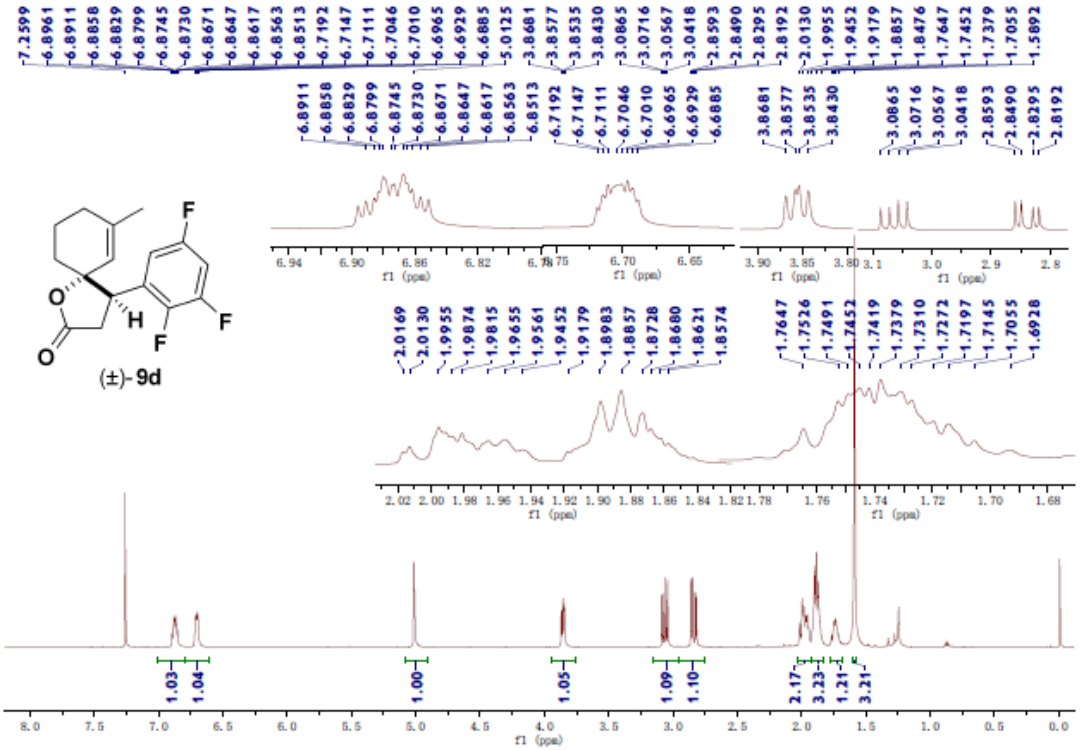
^{13}C NMR of **(±)-9c'** (150 M, $CDCl_3$)



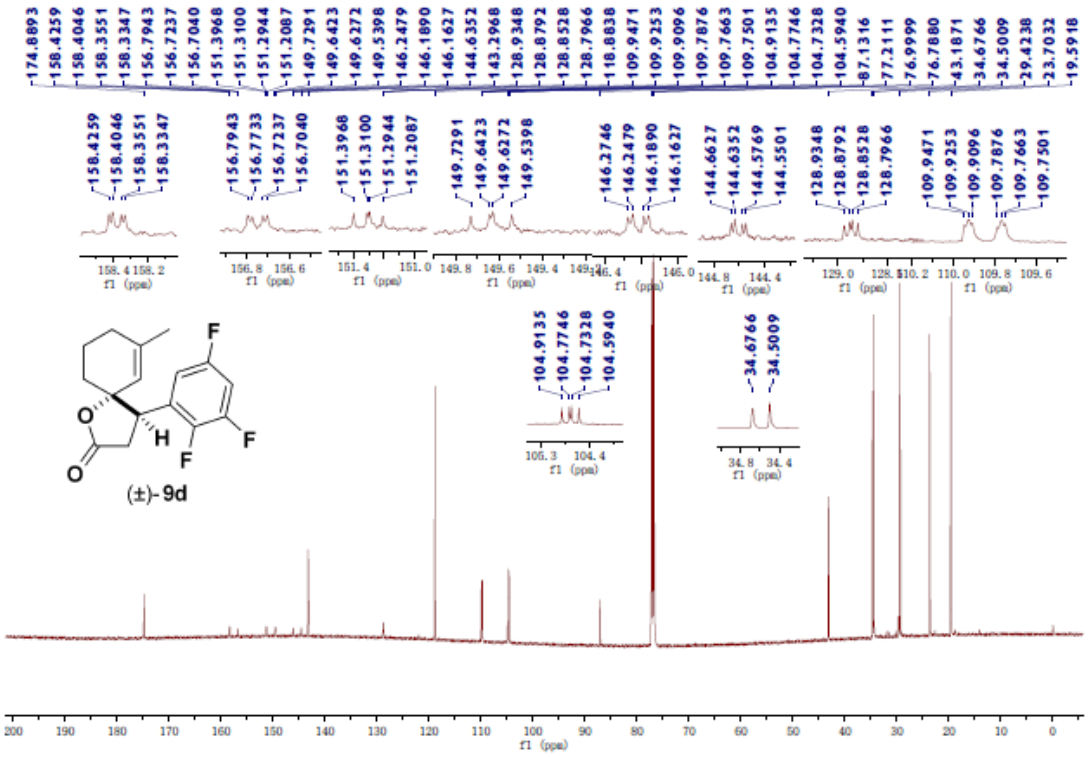
^{19}F NMR of **(±)-9c'** (565 M, $CDCl_3$)



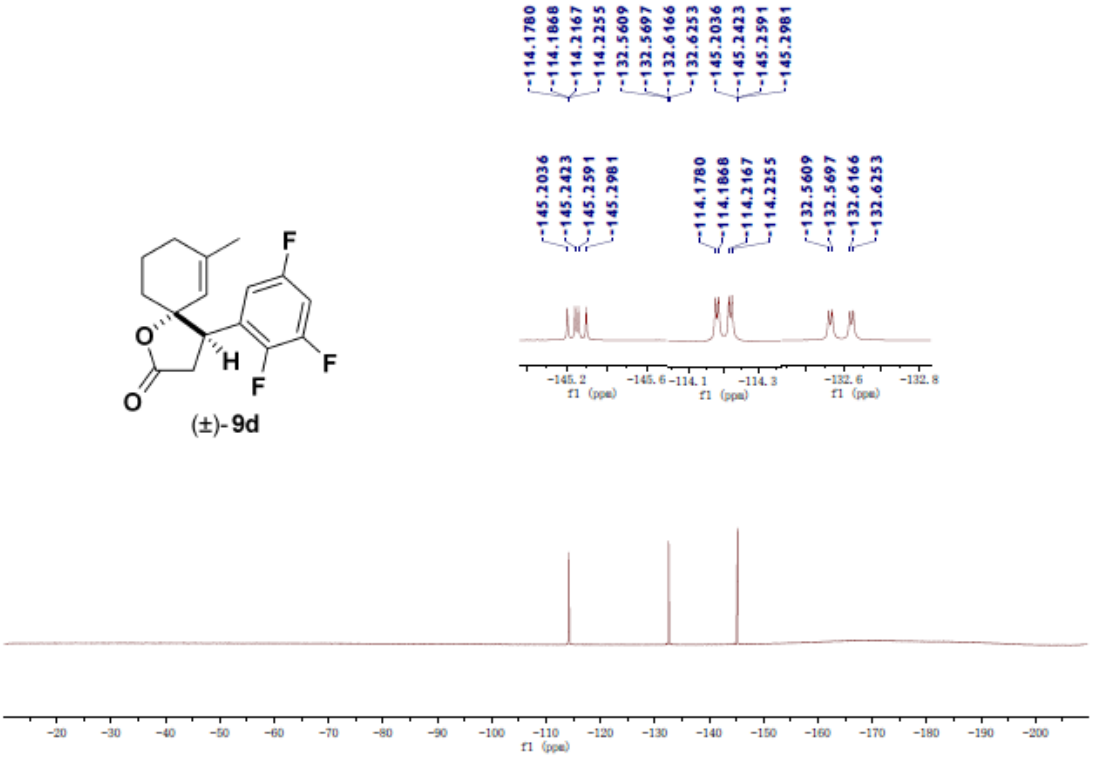
^{1}H NMR of **(±)-9d** (600 M, $CDCl_3$)



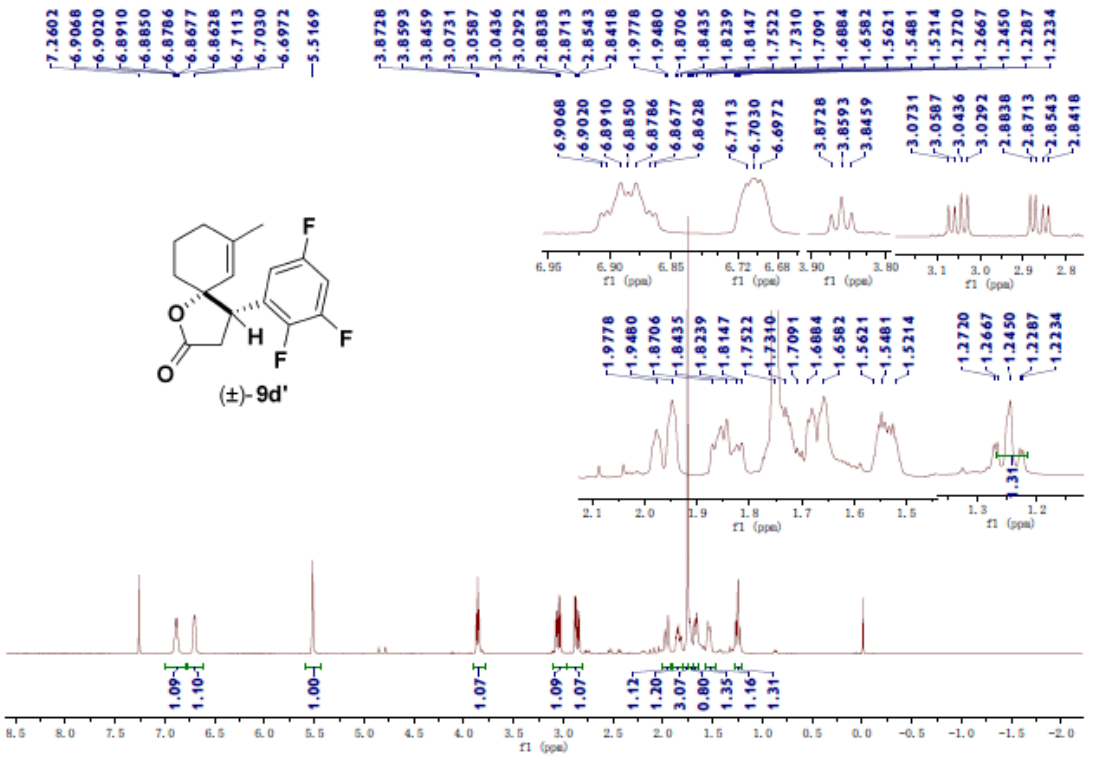
^{13}C NMR of **(±)-9d** (150 M, $CDCl_3$)



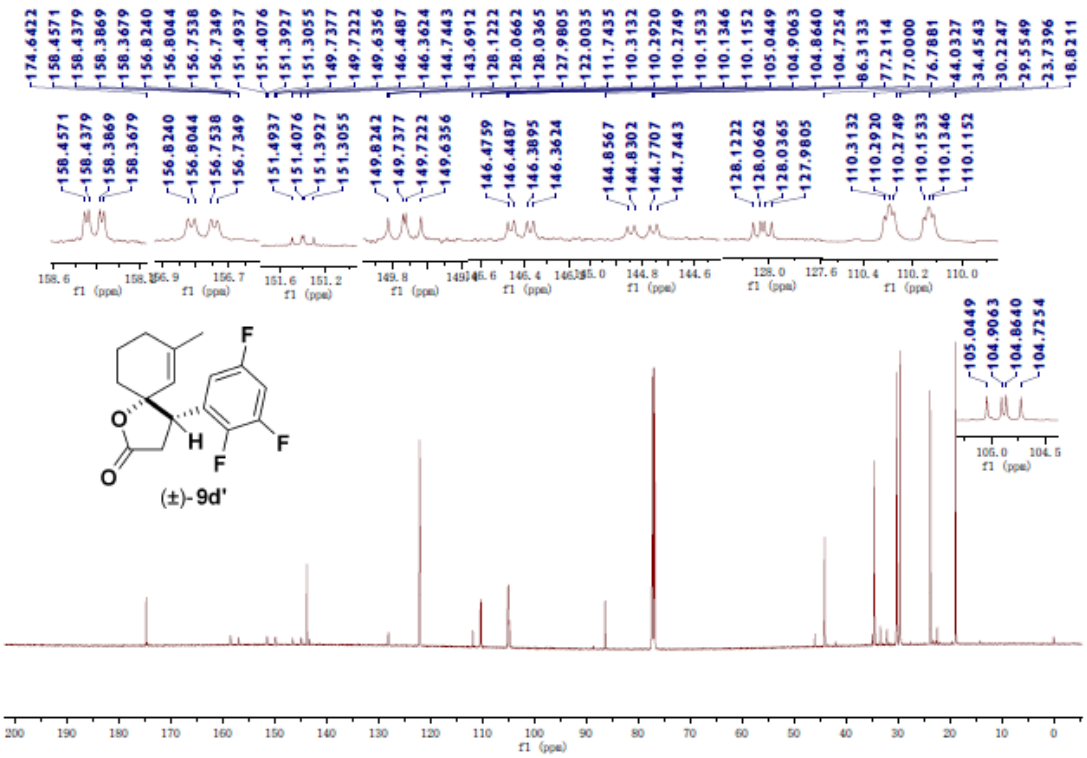
^{19}F NMR of **(±)-9d** (565 M, $CDCl_3$)



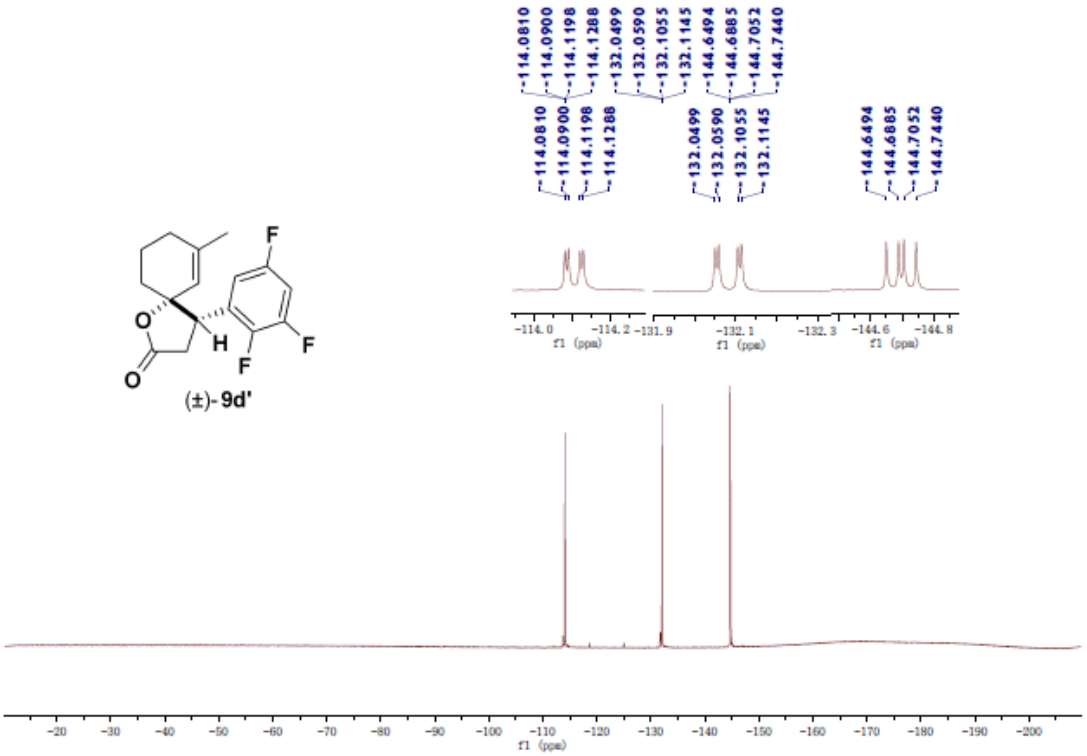
^{1}H NMR of **(±)-9d'** (600 M, $CDCl_3$)



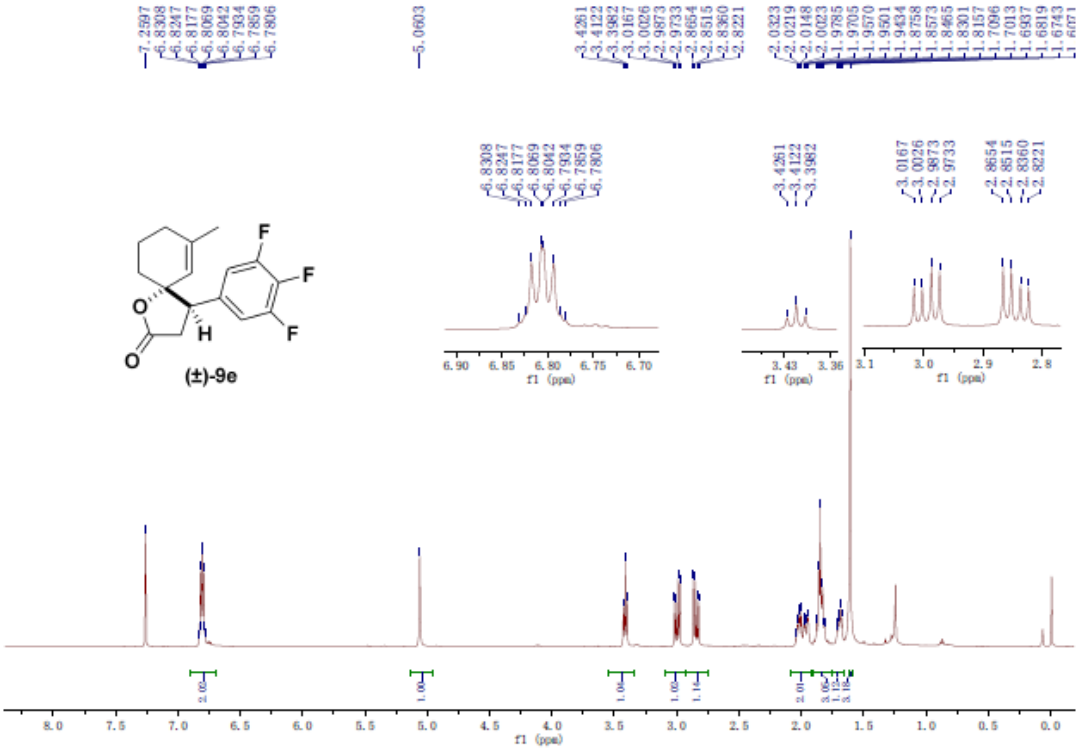
^{13}C NMR of **(±)-9d'** (150 M, $CDCl_3$)



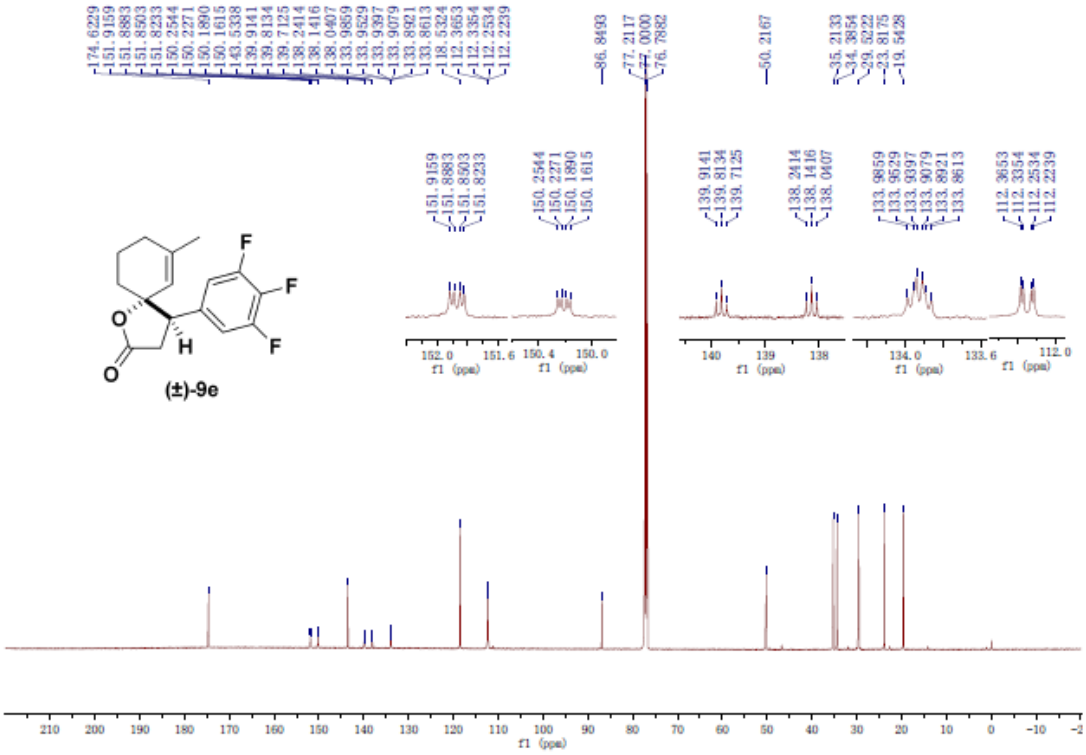
^{19}F NMR of **(±)-9d'** (565 M, $CDCl_3$)



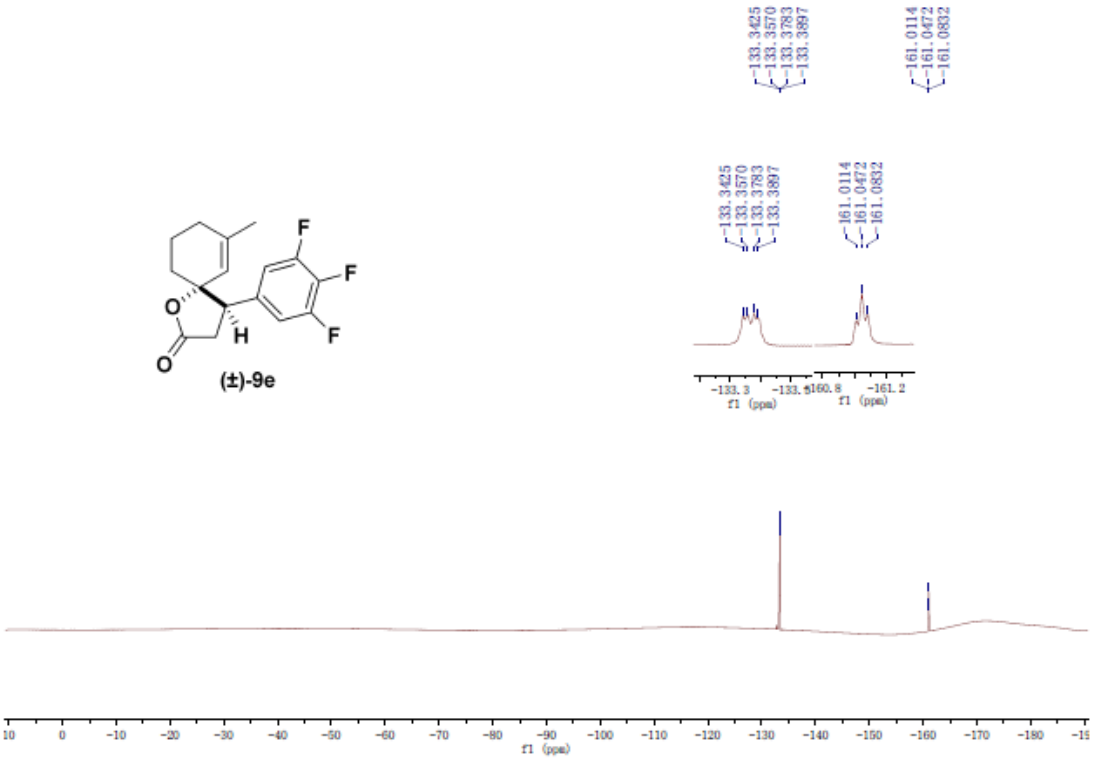
^{1}H NMR of **(±)-9e** (600 M, $CDCl_3$)



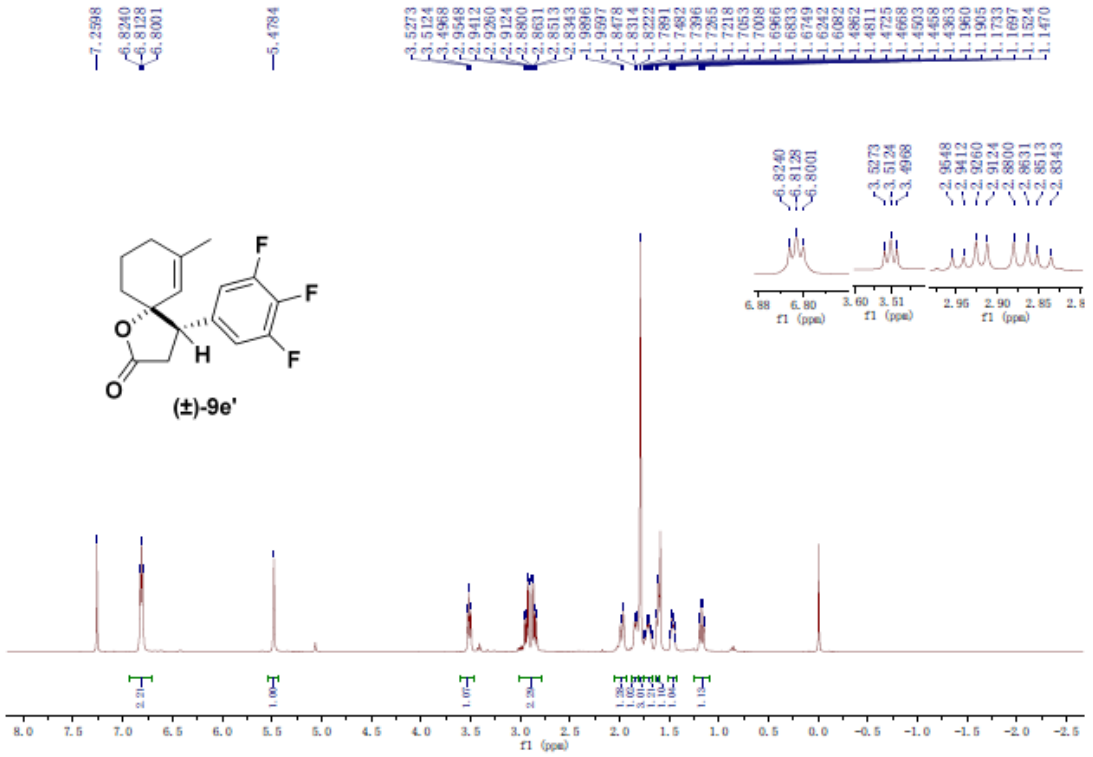
^{13}C NMR of **(±)-9e** (150 M, $CDCl_3$)



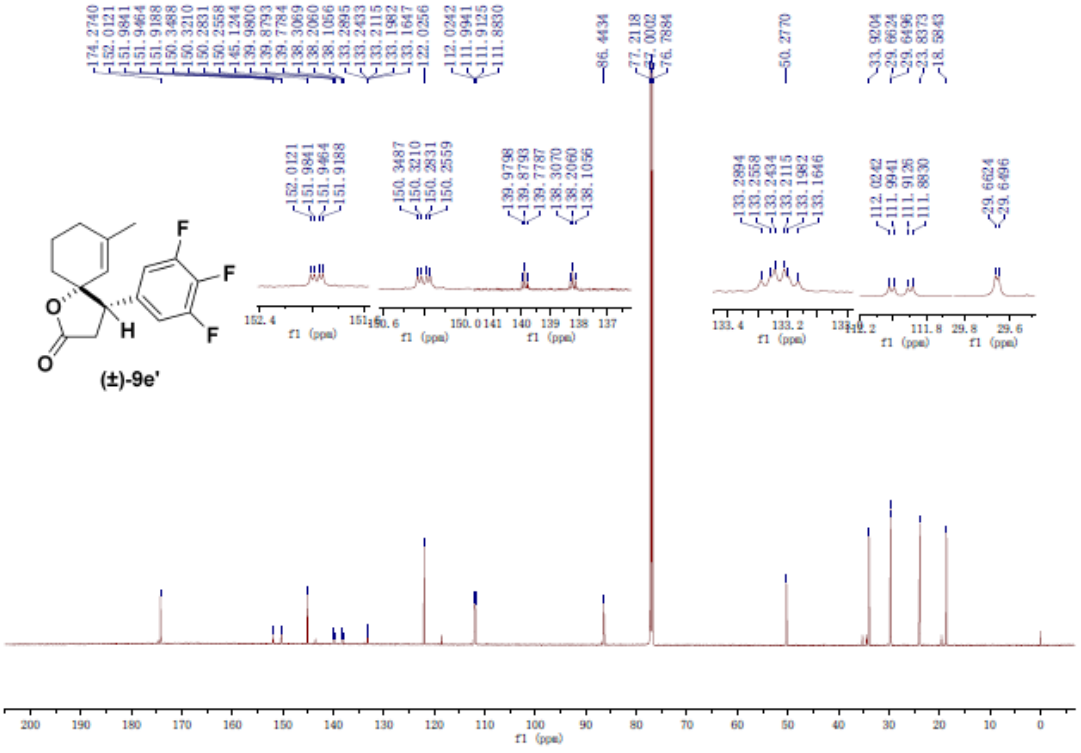
^{19}F NMR of **(±)-9e** (376 M, $CDCl_3$)



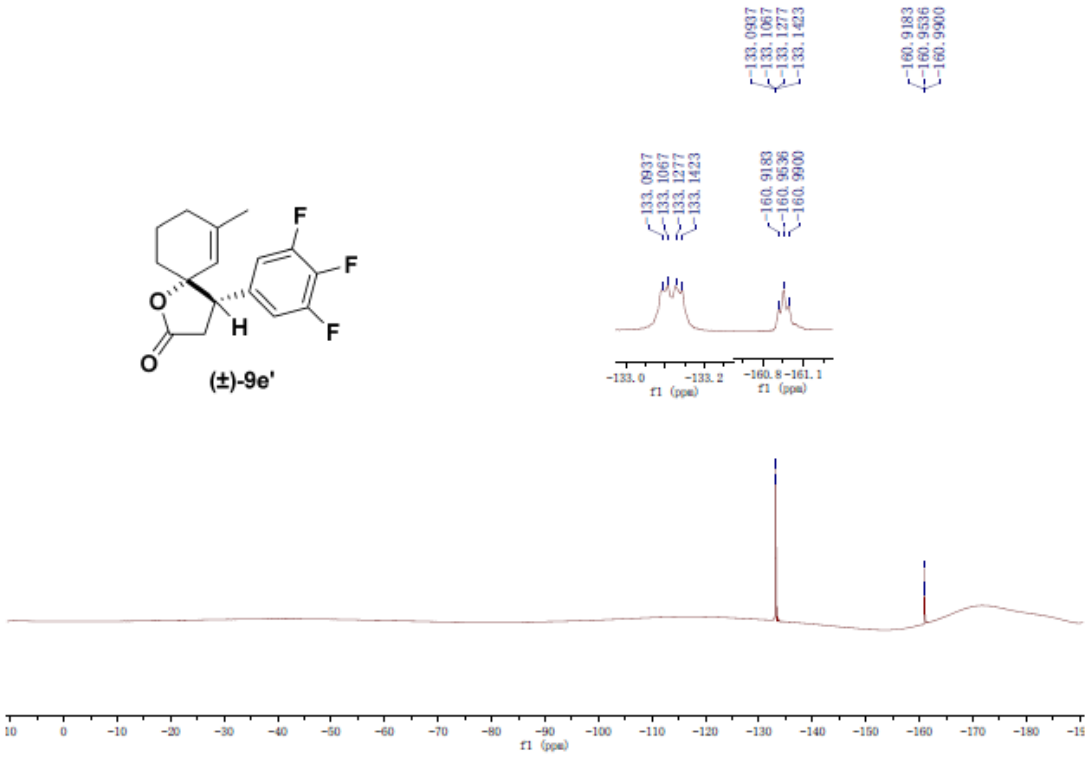
^{1}H NMR of **(±)-9e'** (600 M, $CDCl_3$)



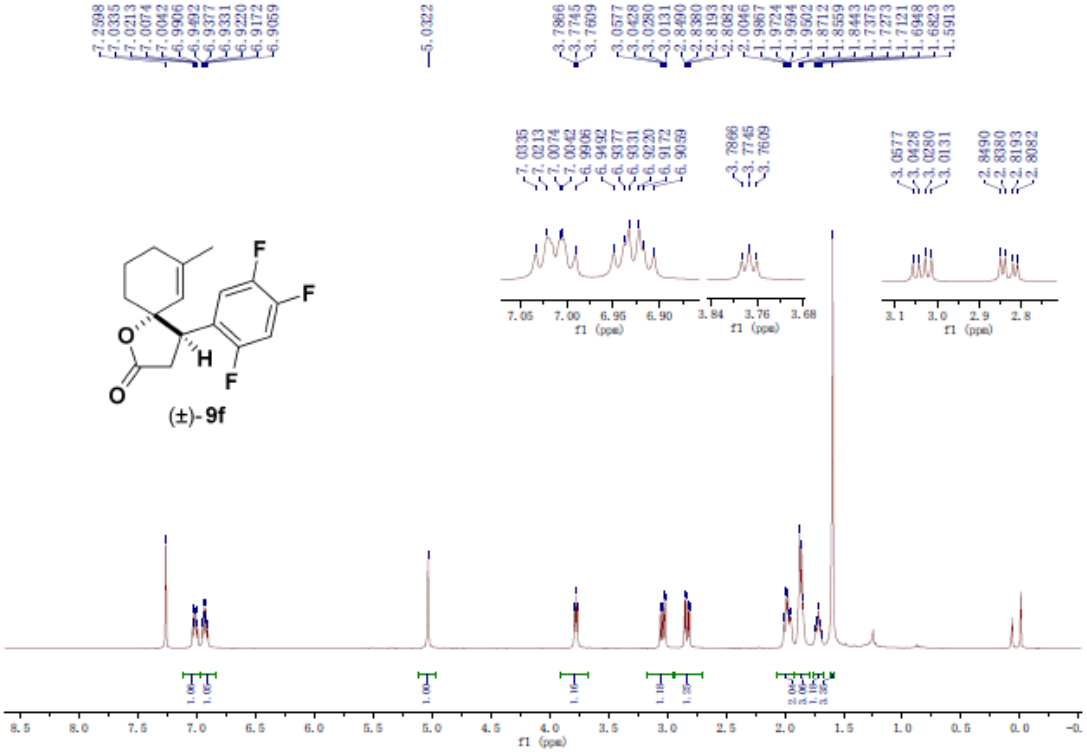
^{13}C NMR of **(±)-9e'** (150 M, $CDCl_3$)



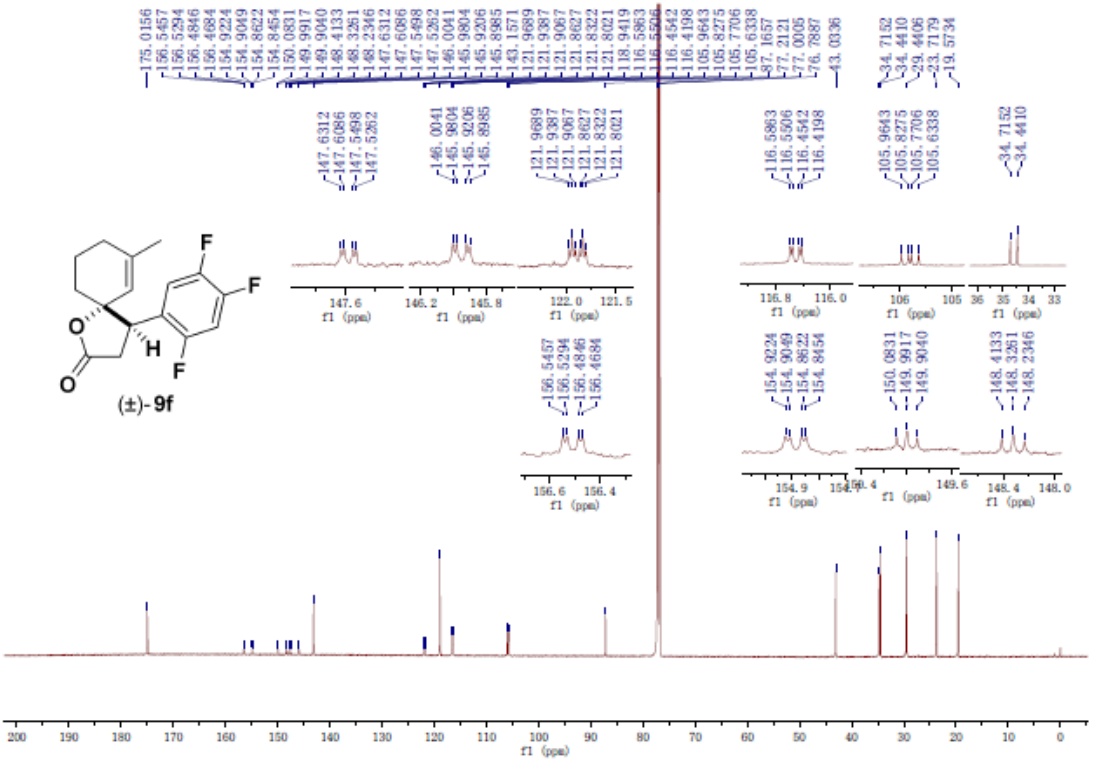
^{19}F NMR of **(±)-9e'** (376 M, $CDCl_3$)



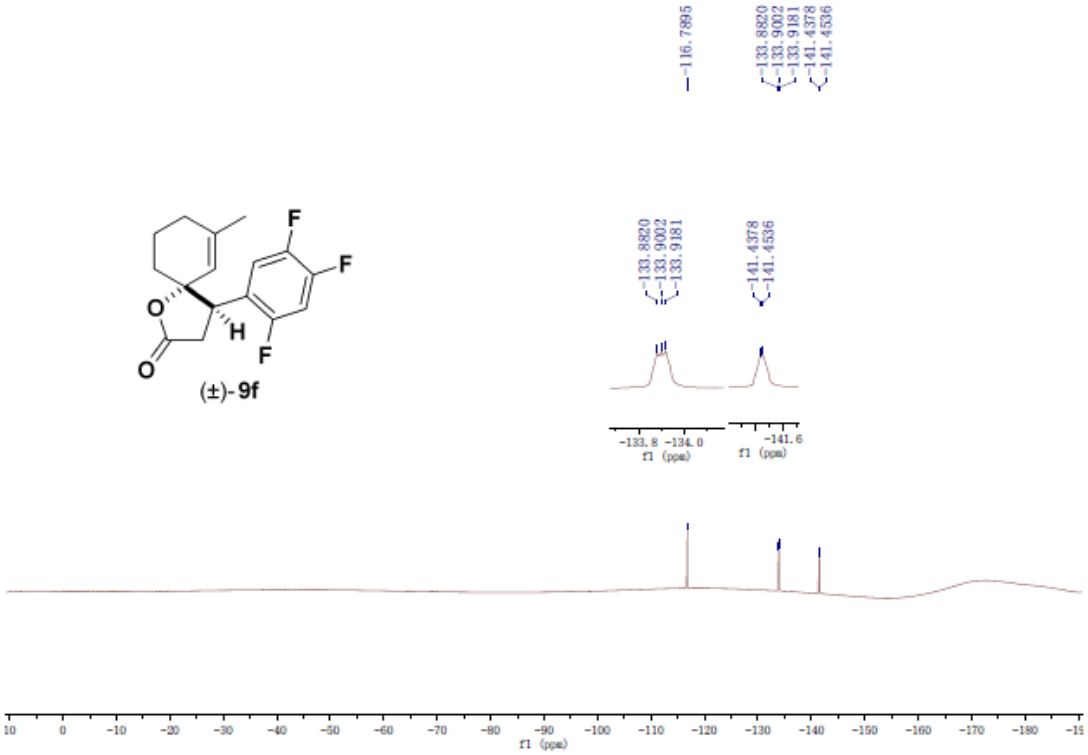
^{1}H NMR of **(±)-9f** (600 M, $CDCl_3$)



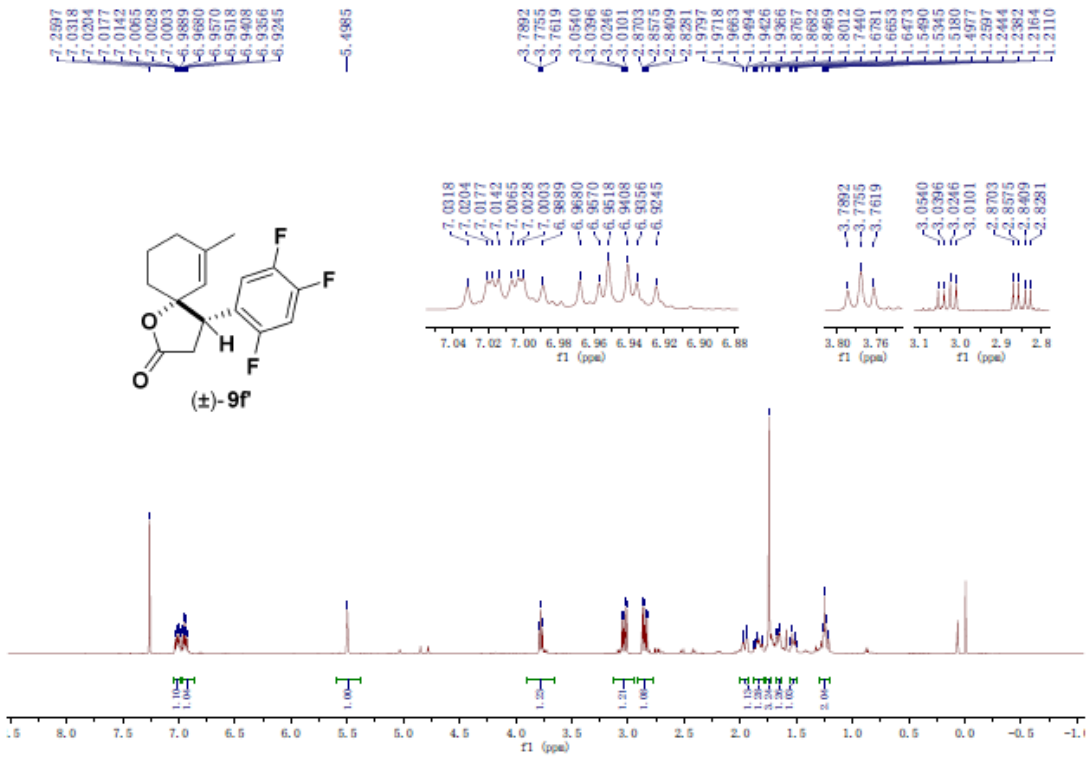
^{13}C NMR of **(±)-9f** (150 M, $CDCl_3$)



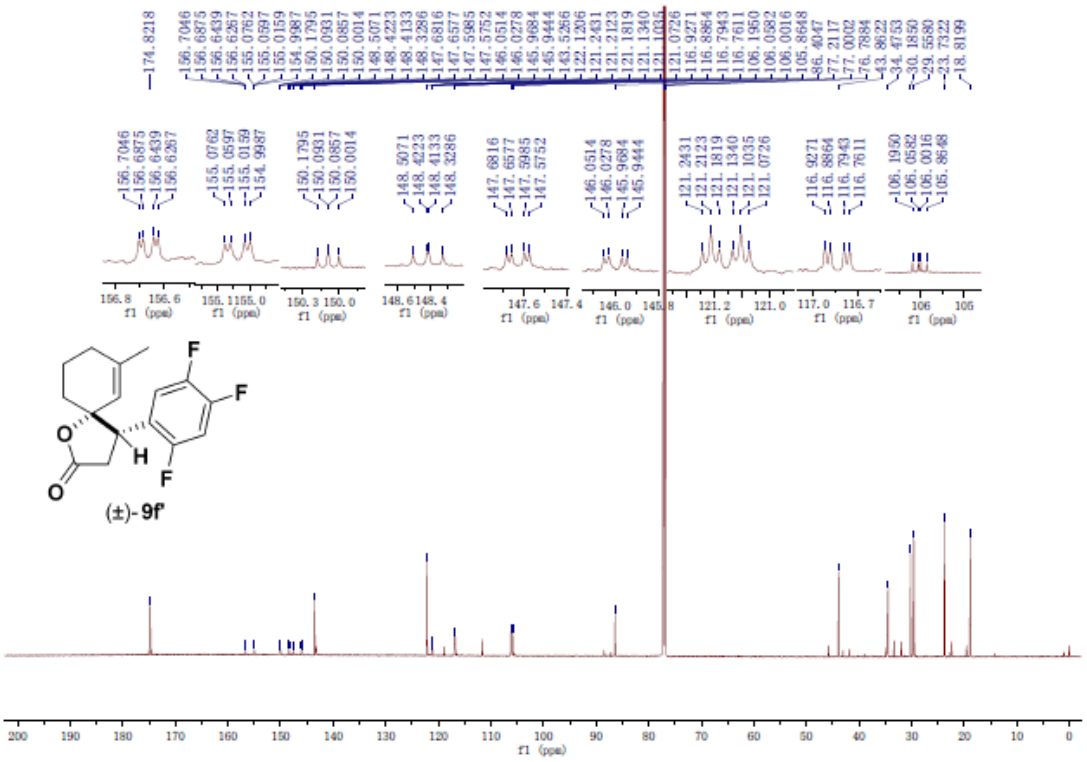
^{19}F NMR of **(±)-9f** (565 M, $CDCl_3$)



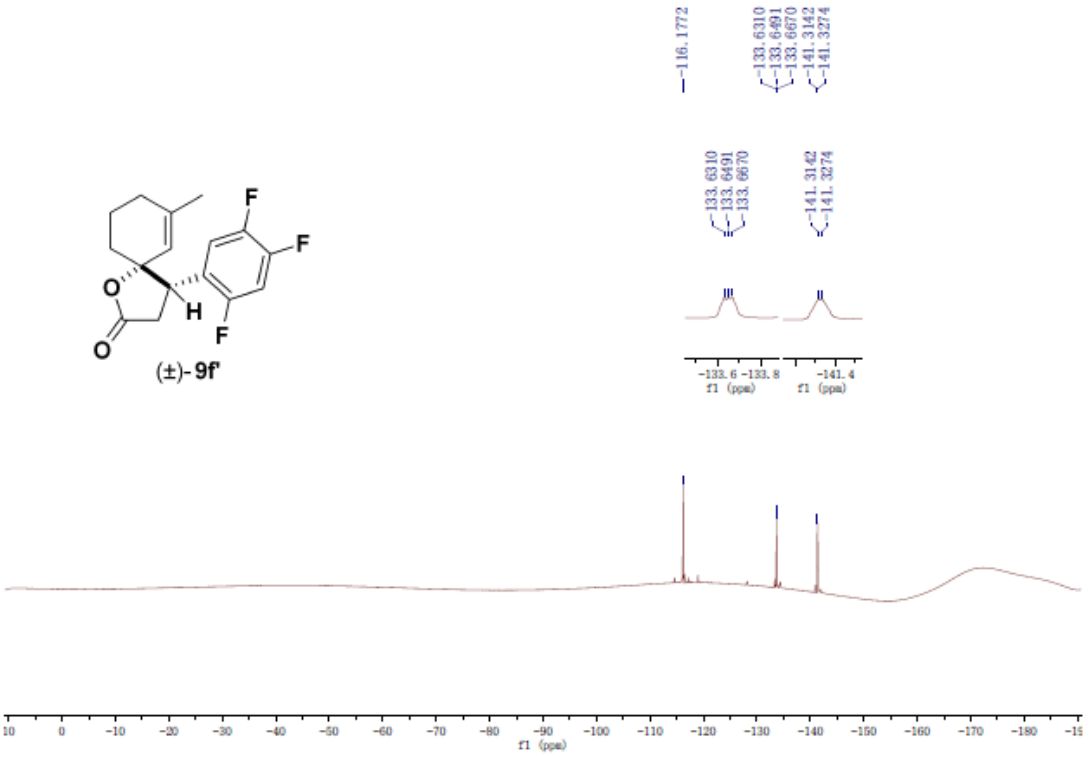
^{1}H NMR of **(±)-9f'** (600 M, $CDCl_3$)



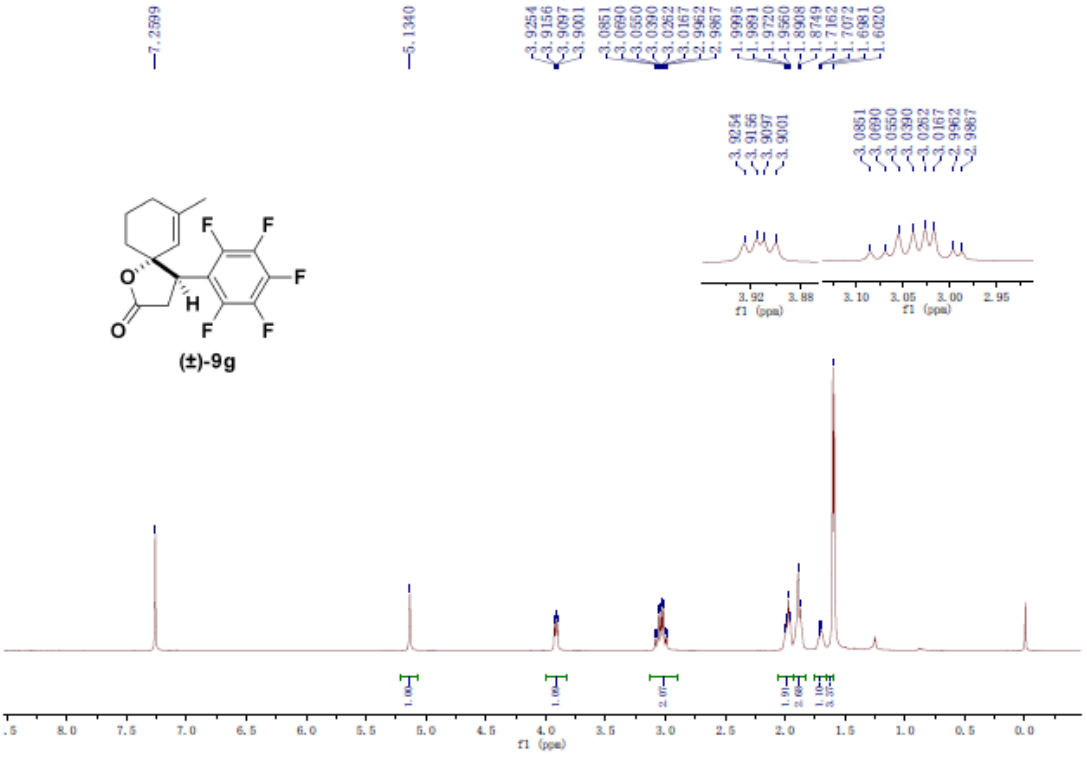
^{13}C NMR of **(±)-9f'** (150 M, $CDCl_3$)



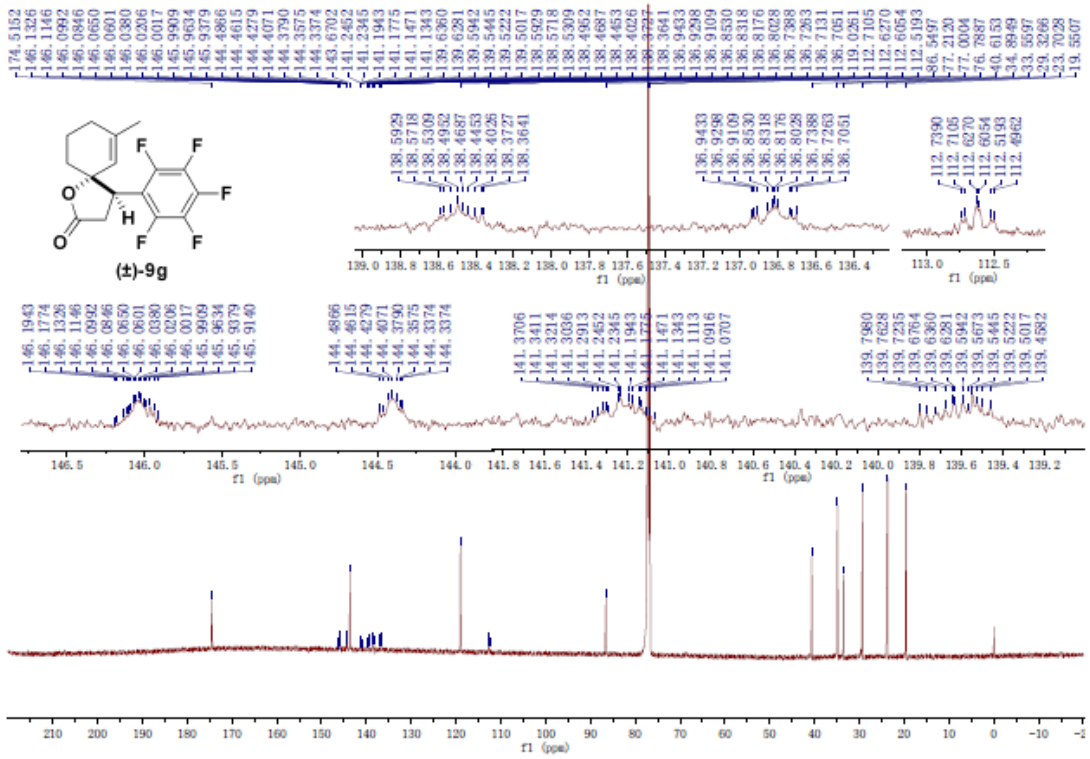
^{19}F NMR of **(±)-9f'** (565 M, $CDCl_3$)



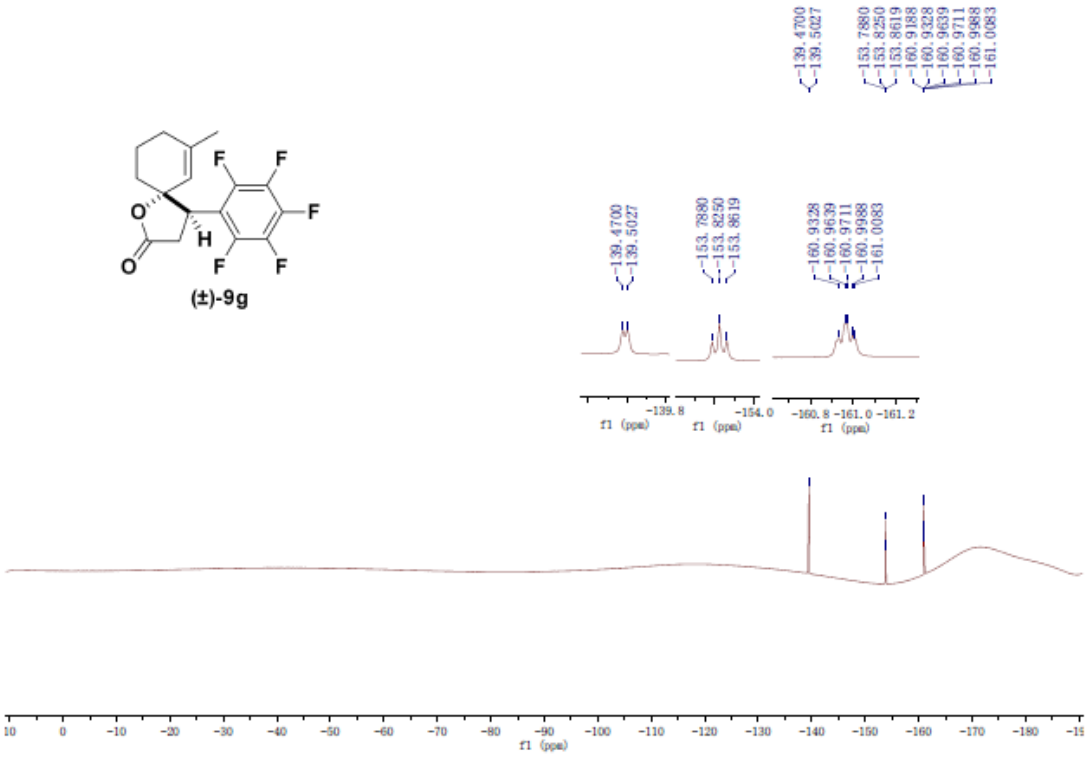
^{1}H NMR of (±)-**9g** (600 M, $CDCl_3$)



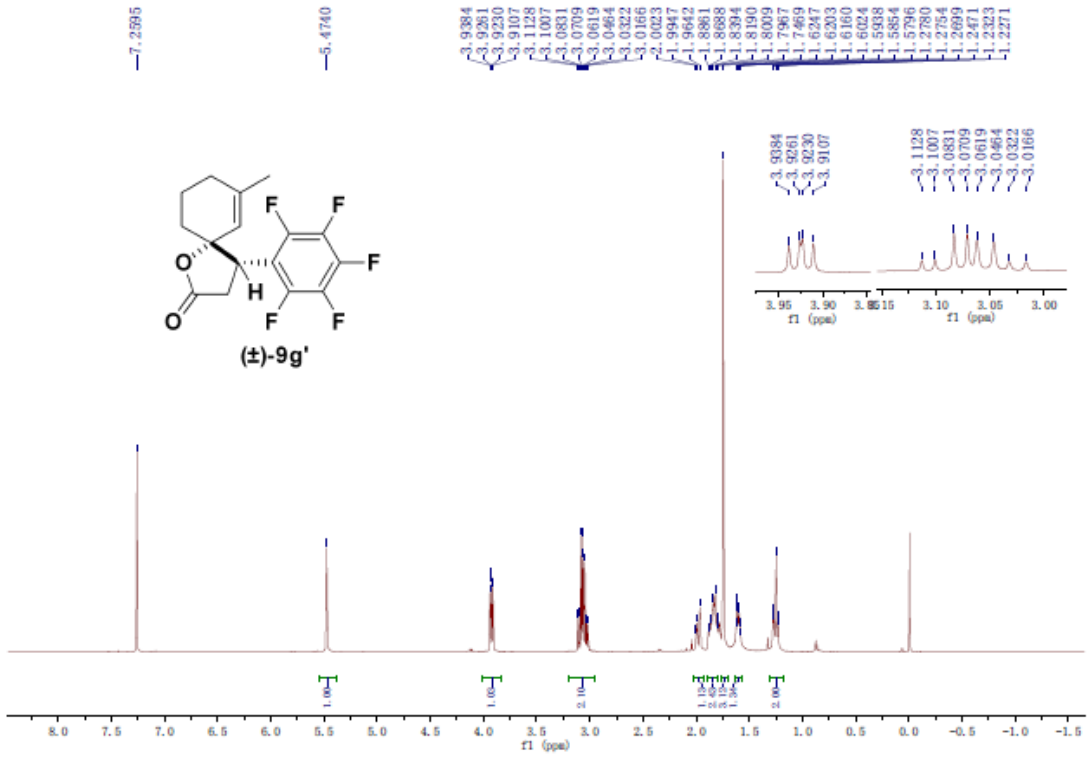
^{13}C NMR of (±)-**9g** (150 M, $CDCl_3$)



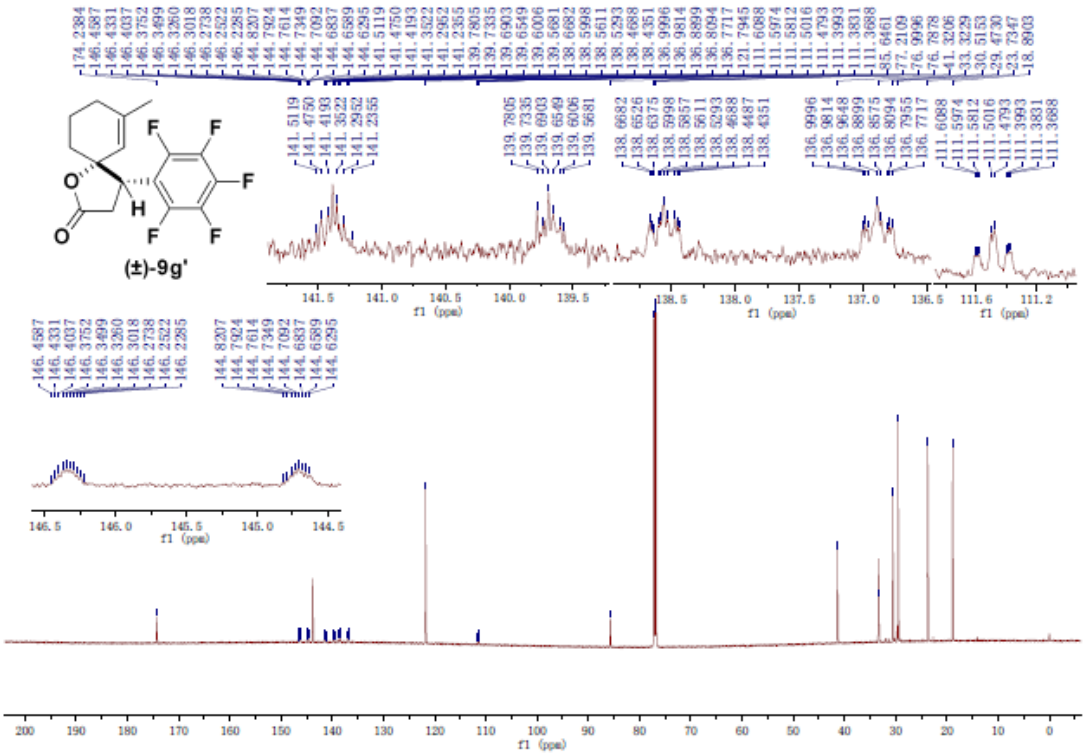
^{19}F NMR of **(±)-9g** (565 M, $CDCl_3$)



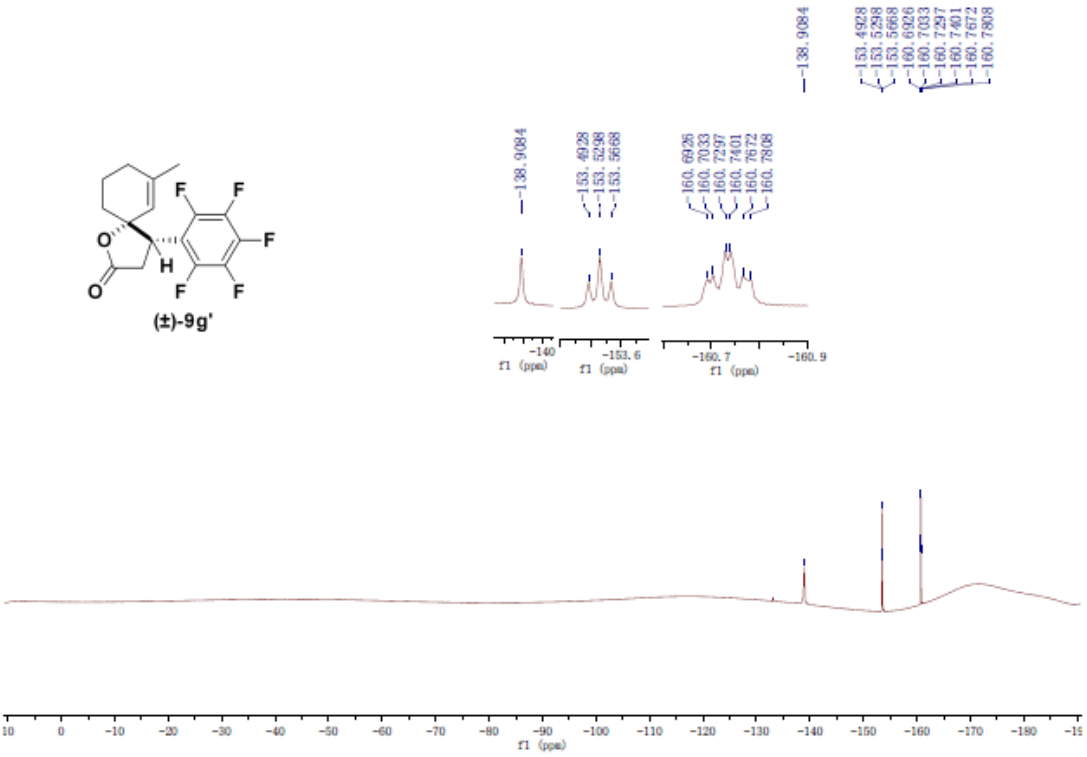
^{1}H NMR of **(±)-9g'** (600 M, $CDCl_3$)



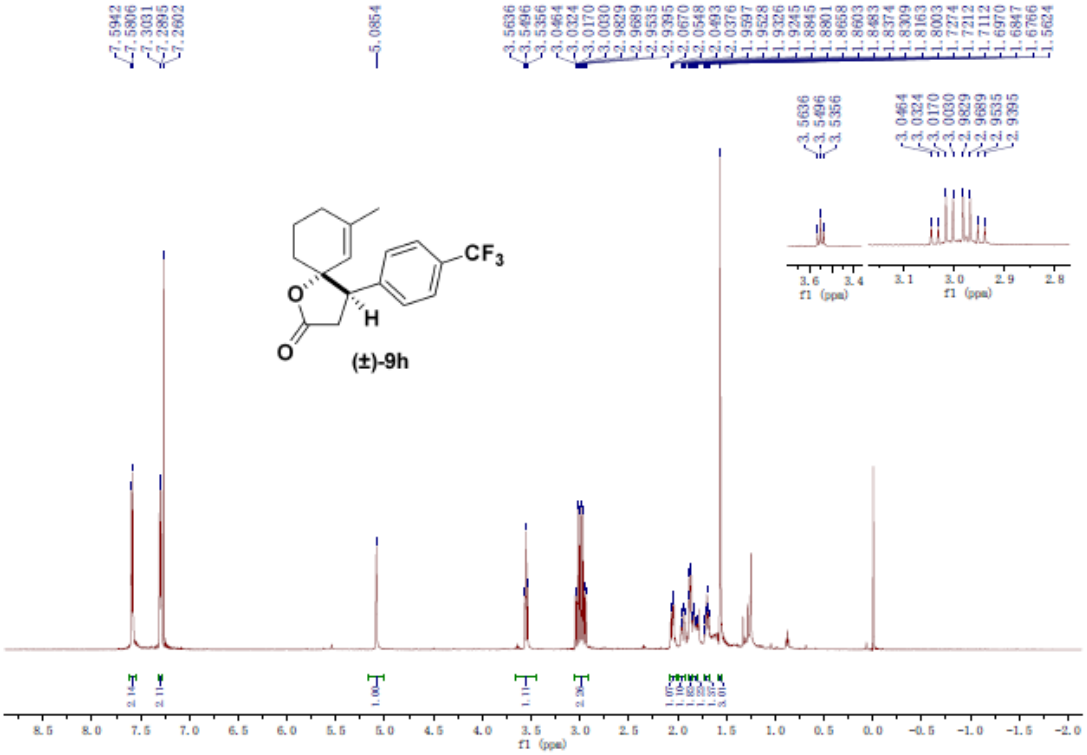
^{13}C NMR of **(±)-9g'** (150 M, $CDCl_3$)



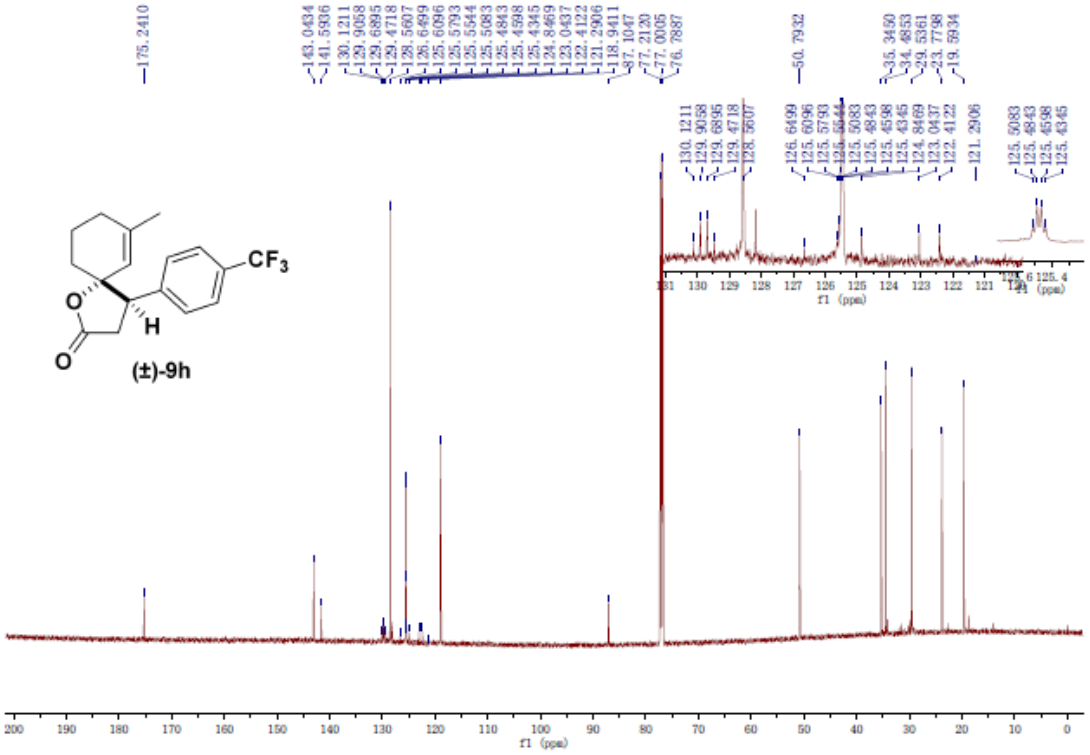
^{19}F NMR of **(±)-9g'** (565 M, $CDCl_3$)



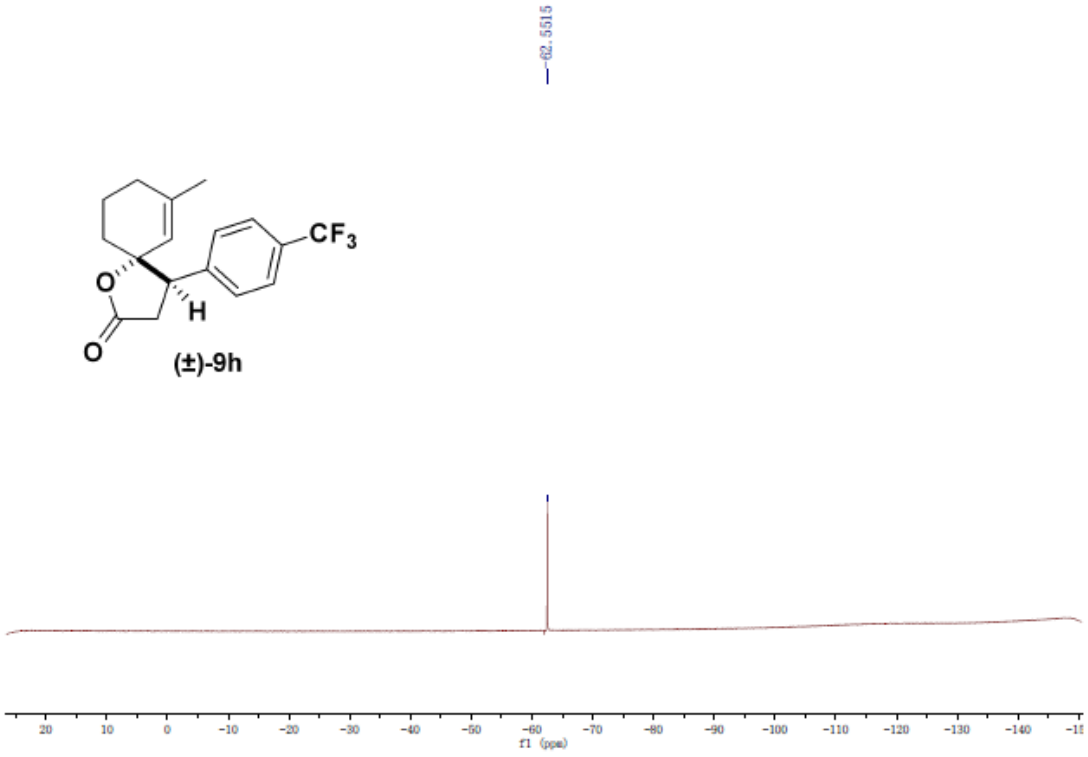
^{1}H NMR of (±)-**9h** (600 M, $CDCl_3$)



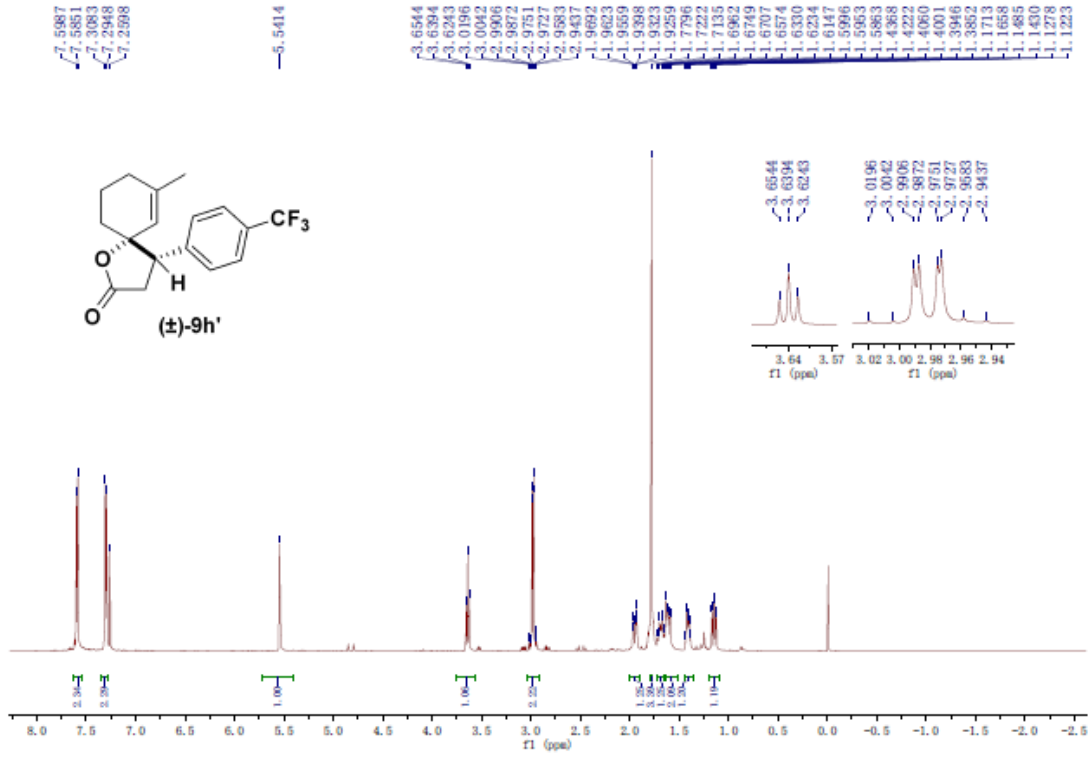
^{13}C NMR of (±)-**9h** (150 M, $CDCl_3$)



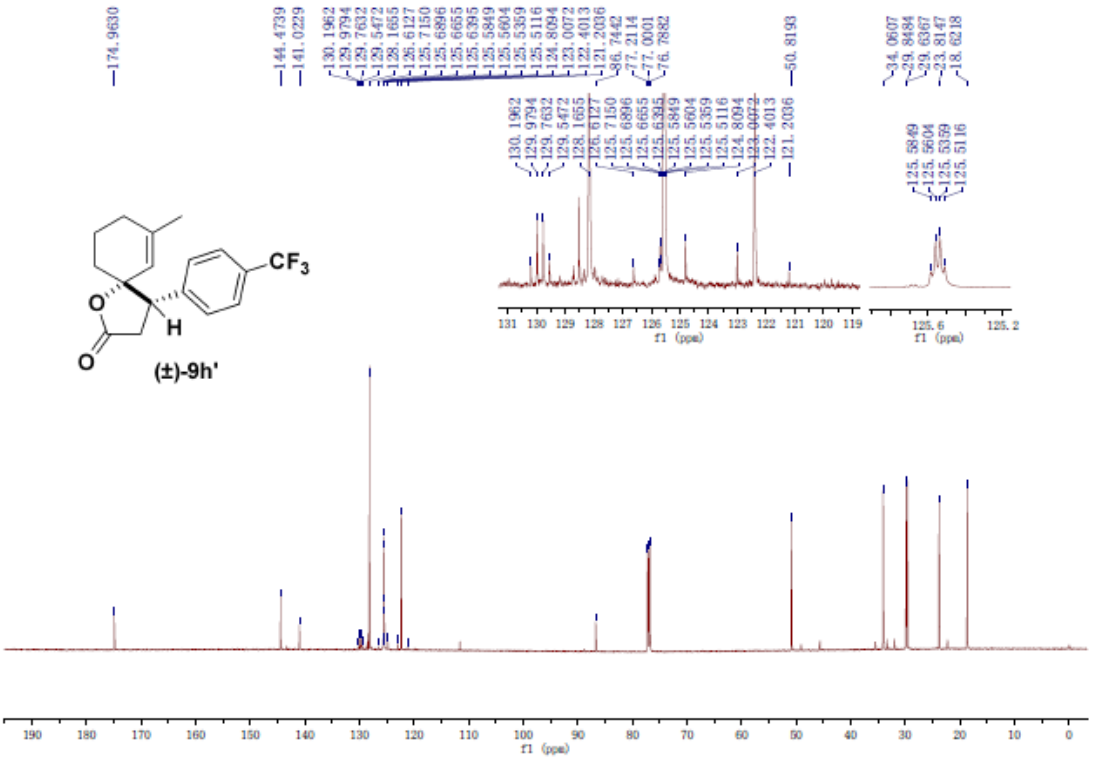
^{19}F NMR of **(±)-9h** (565 M, $CDCl_3$)



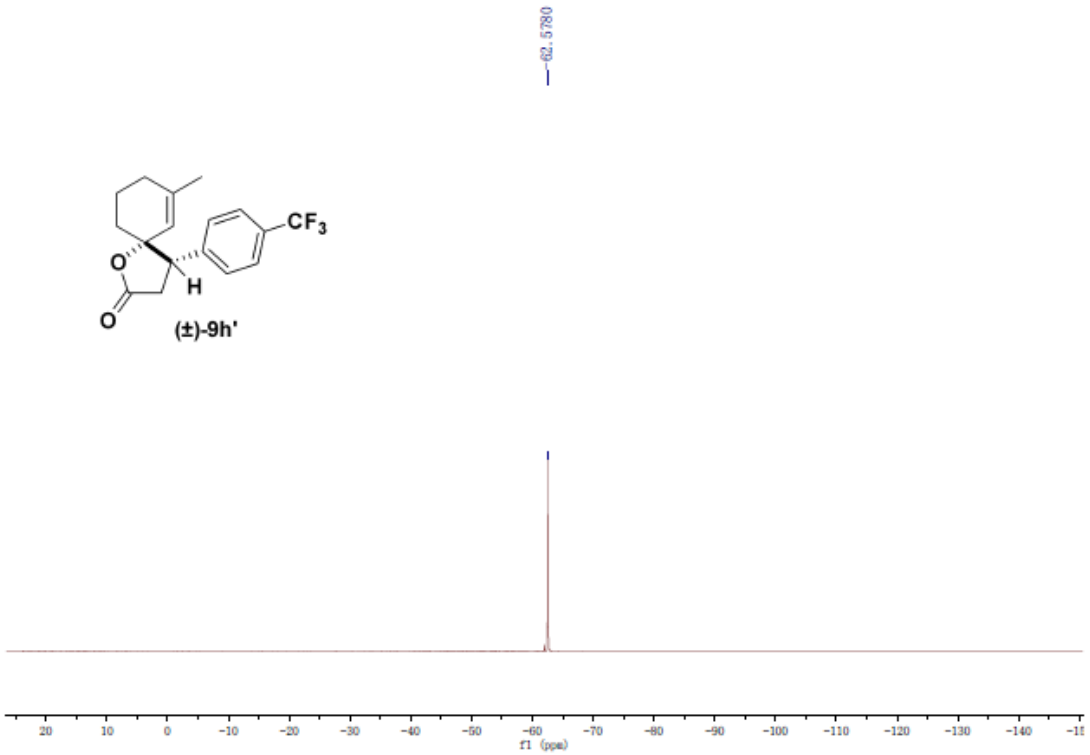
^{1}H NMR of **(±)-9h'** (600 M, $CDCl_3$)



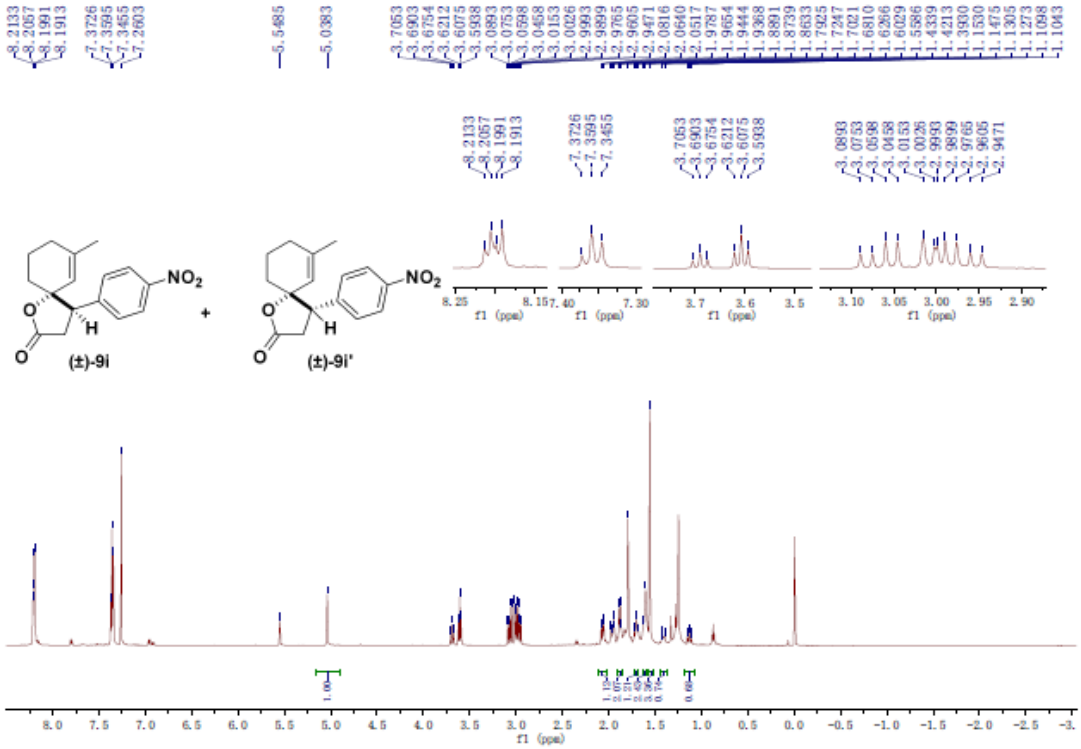
^{13}C NMR of **(±)-9h'** (150 M, $CDCl_3$)



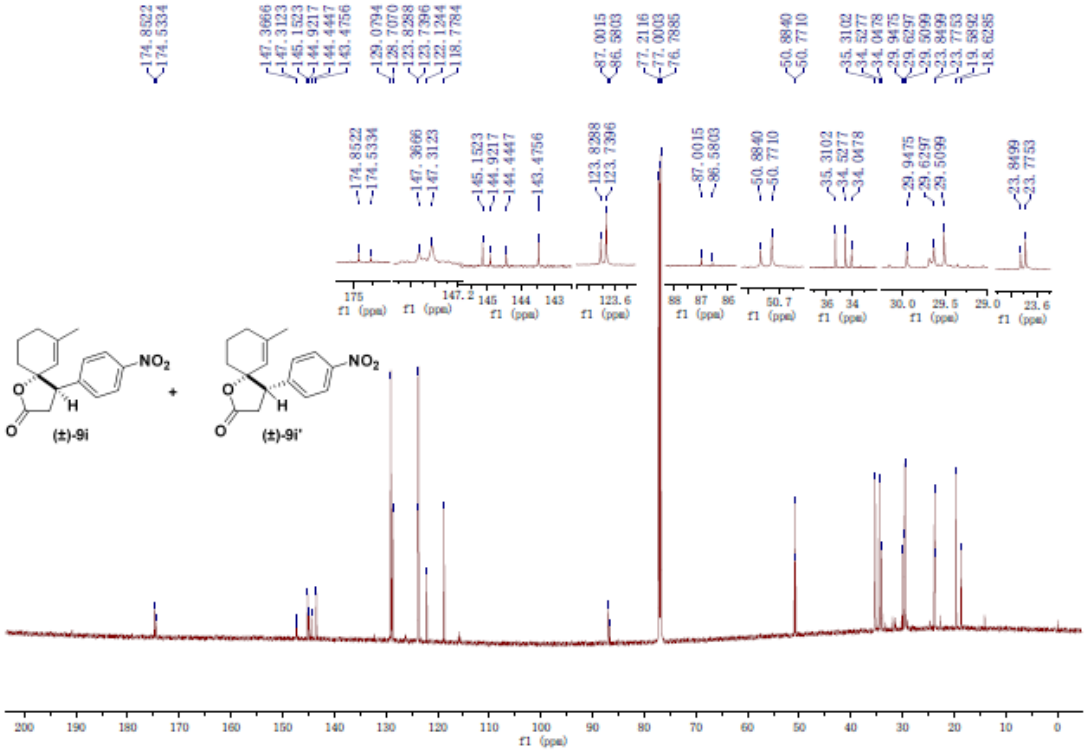
^{19}F NMR of **(±)-9h'** (565 M, $CDCl_3$)



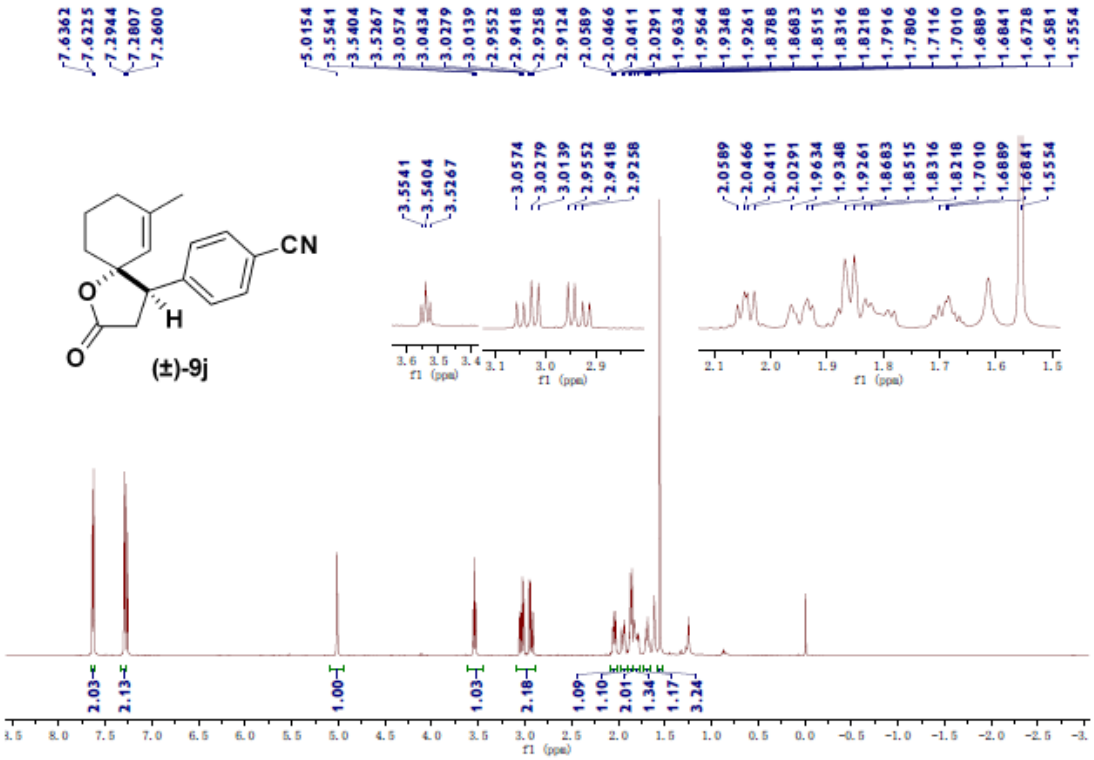
^{1}H NMR of **(±)-9i and (±)-9i'** (600 M, $CDCl_3$)



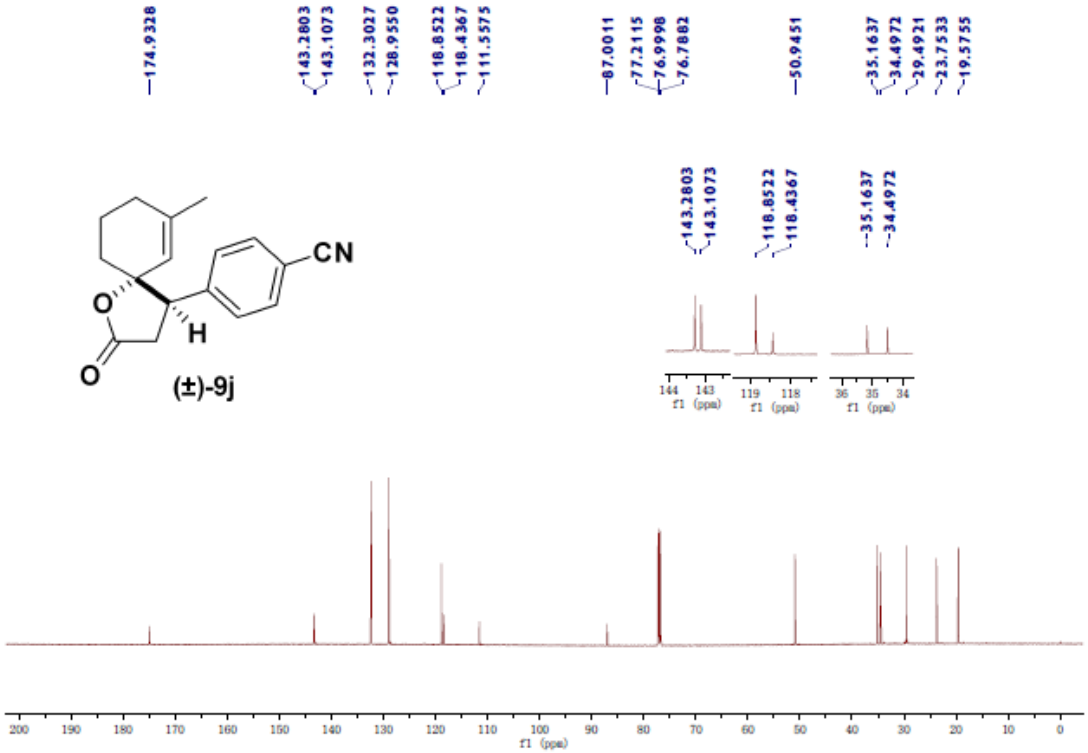
^{13}C NMR of **(±)-9i and (±)-9i'** (150 M, $CDCl_3$)



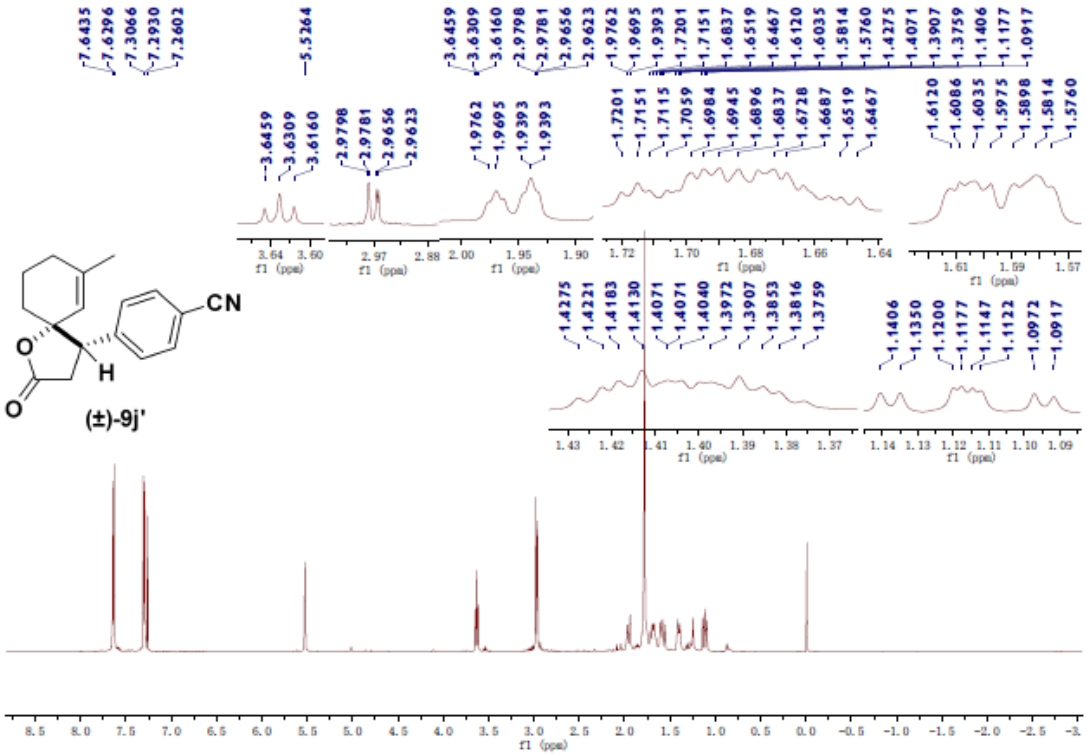
^{1}H NMR of (±)-**9j** (600 M, $CDCl_3$)



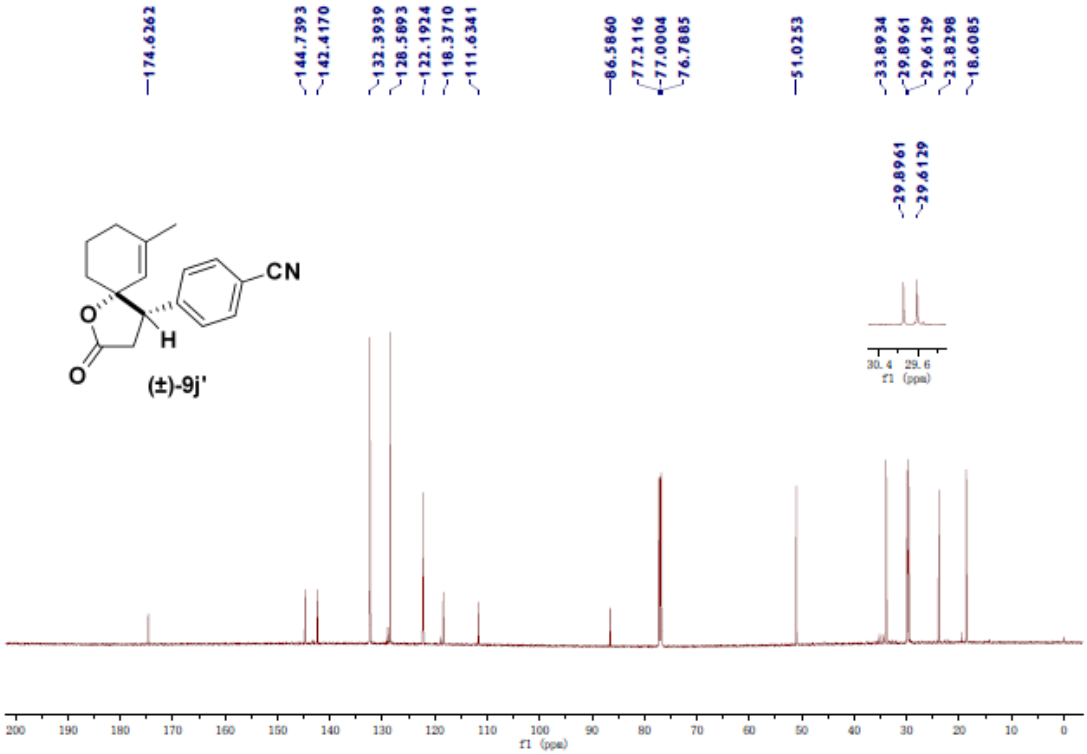
^{13}C NMR of (±)-**9j** (150 M, $CDCl_3$)



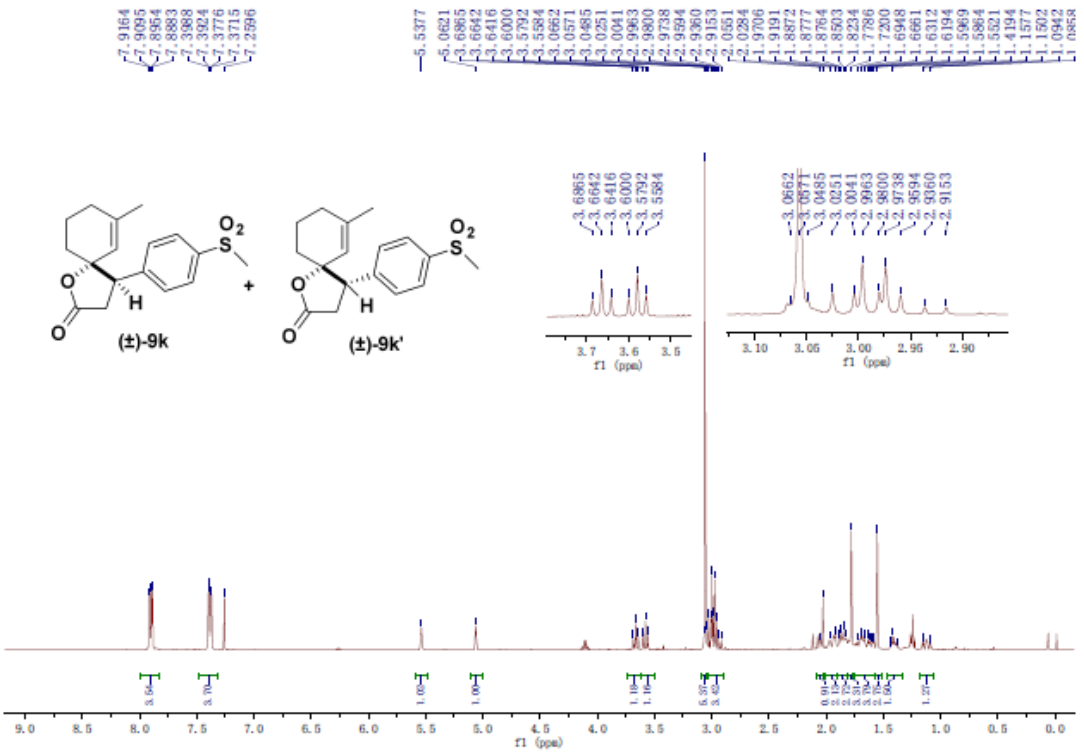
^{1}H NMR of **(±)-9j'** (600 M, $CDCl_3$)



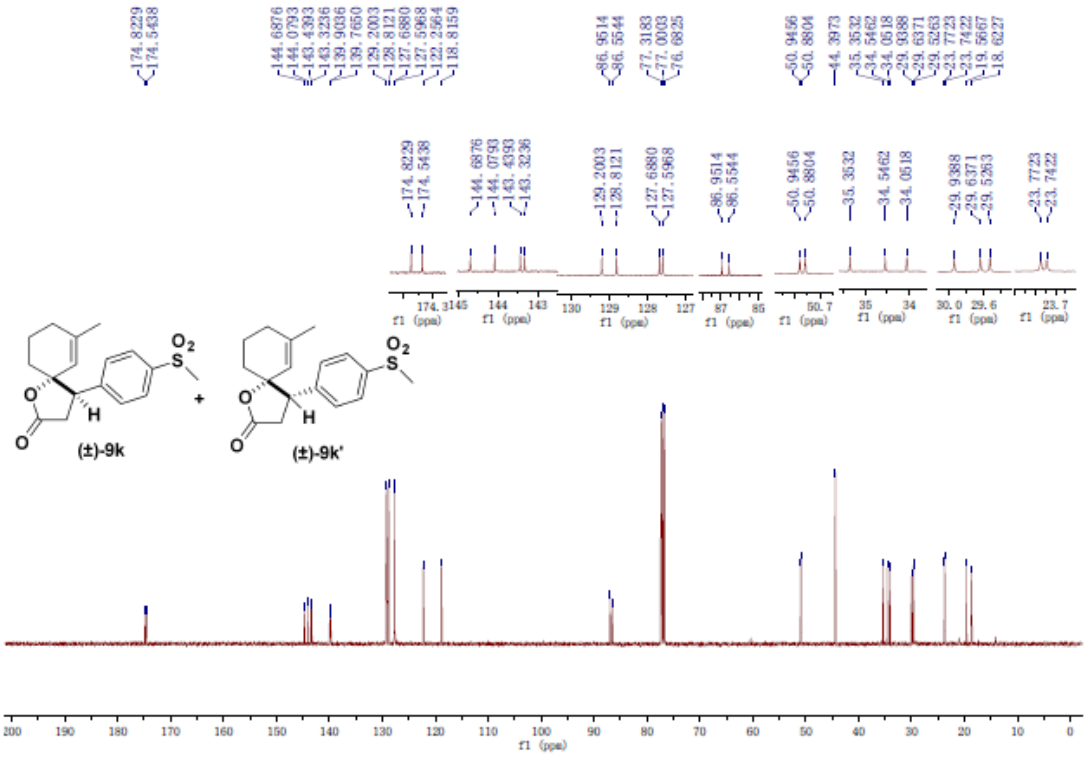
^{13}C NMR of **(±)-9j'** (150 M, $CDCl_3$)



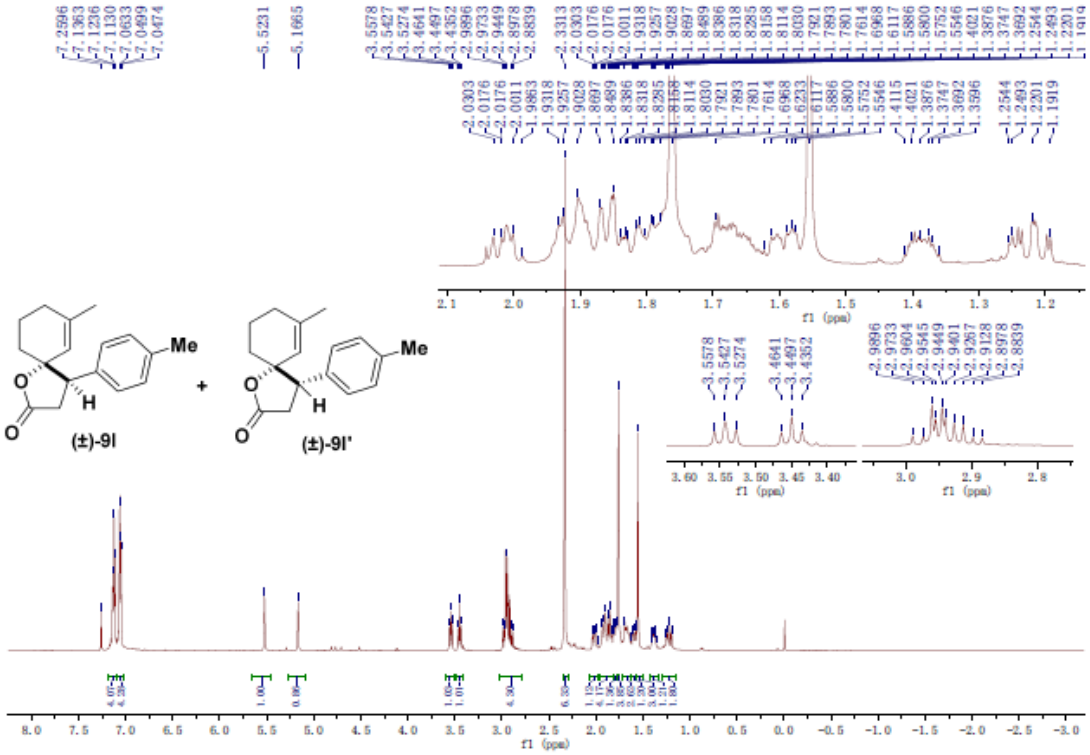
^{1}H NMR of **(±)-9k and (±)-9k'** (400 M, $CDCl_3$)



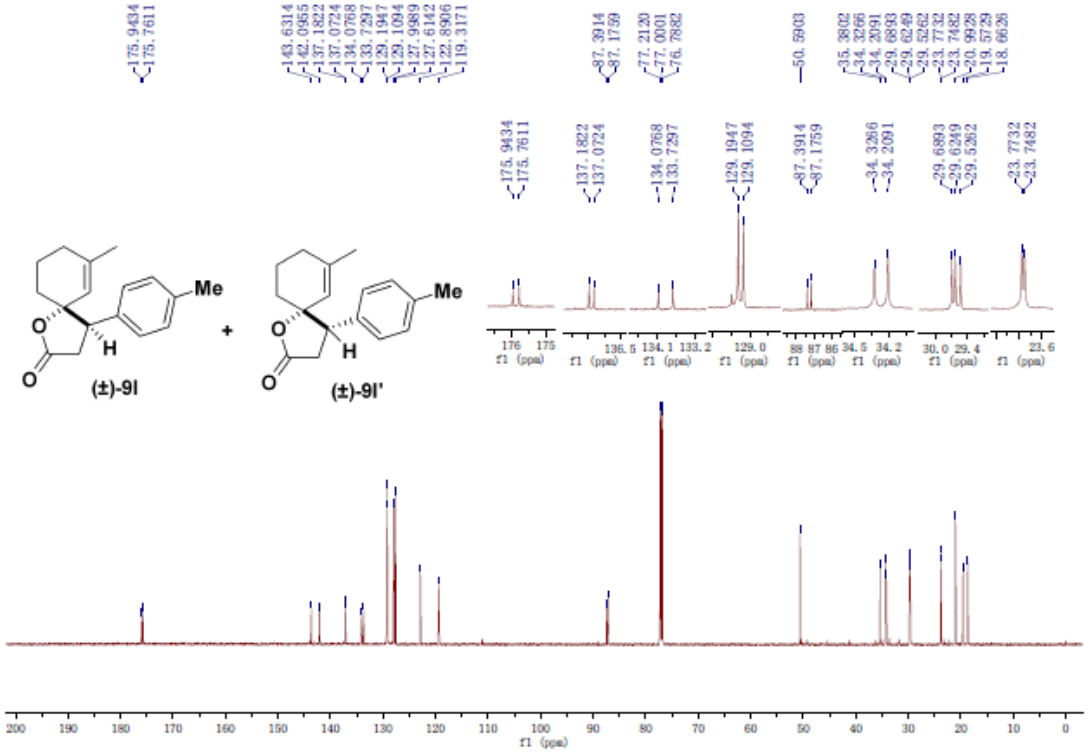
^{13}C NMR of **(±)-9k and (±)-9k'** (100 M, $CDCl_3$)



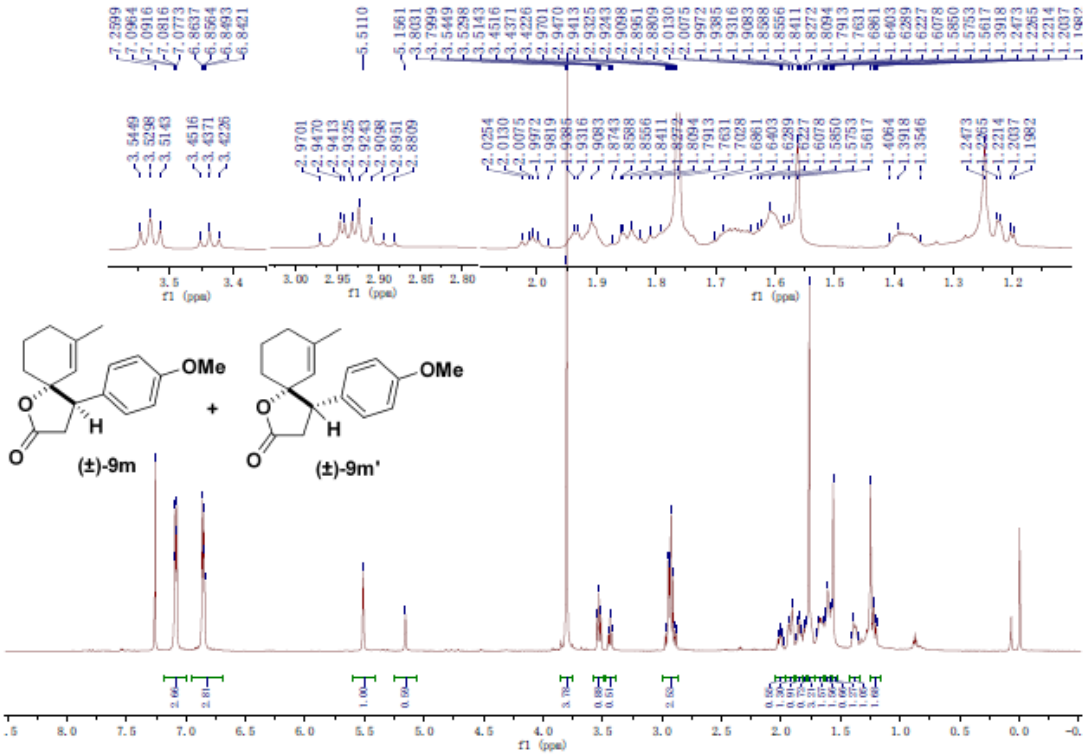
^{1}H NMR of **(±)-9l and (±)-9l'** (600 M, $CDCl_3$)



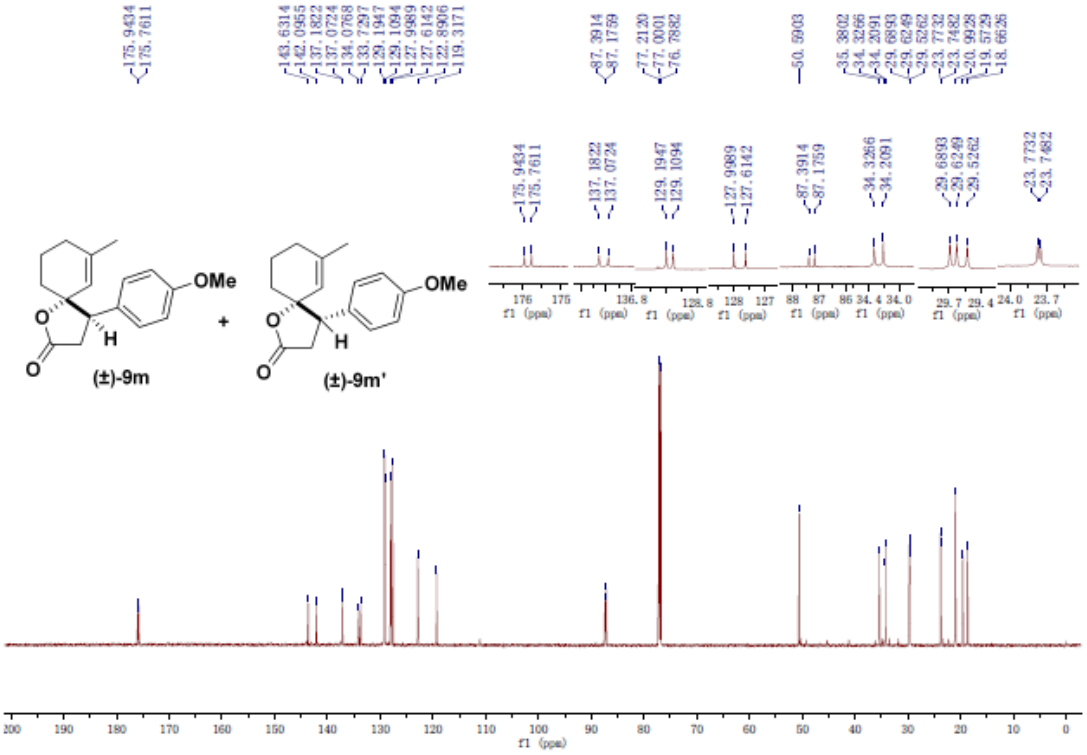
^{13}C NMR of **(±)-9l and (±)-9l'** (150 M, $CDCl_3$)



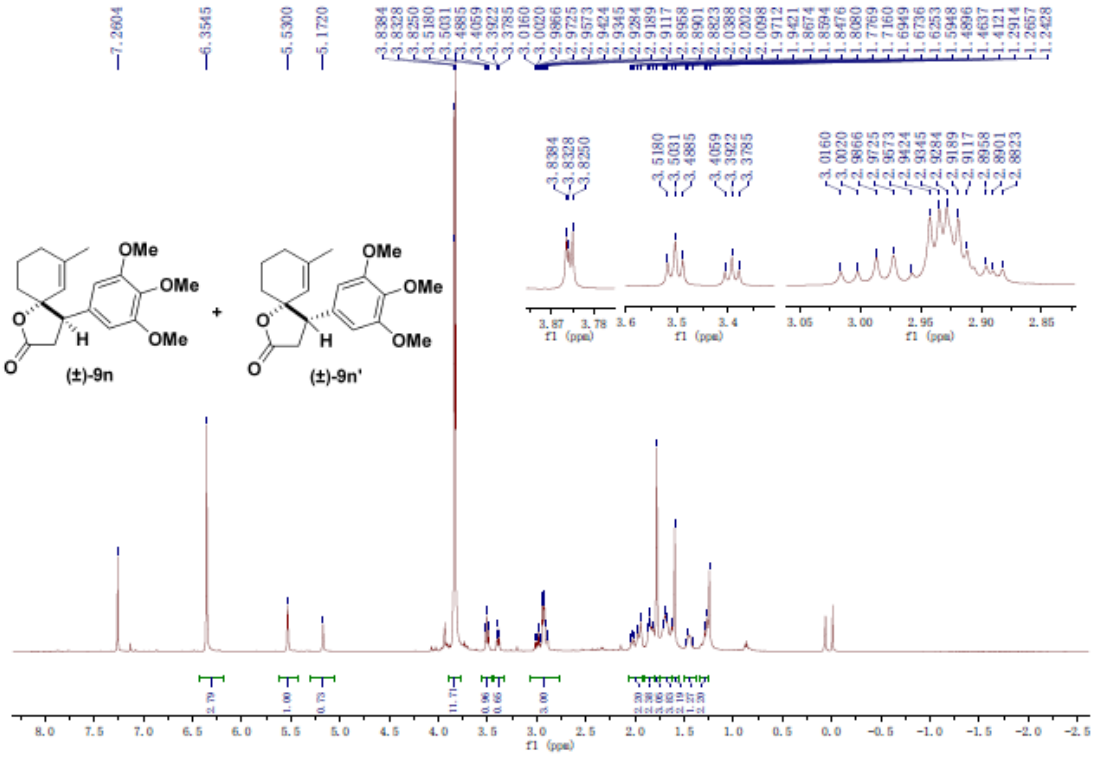
^{1}H NMR of **(±)-9m and (±)-9m'** (600 M, $CDCl_3$)



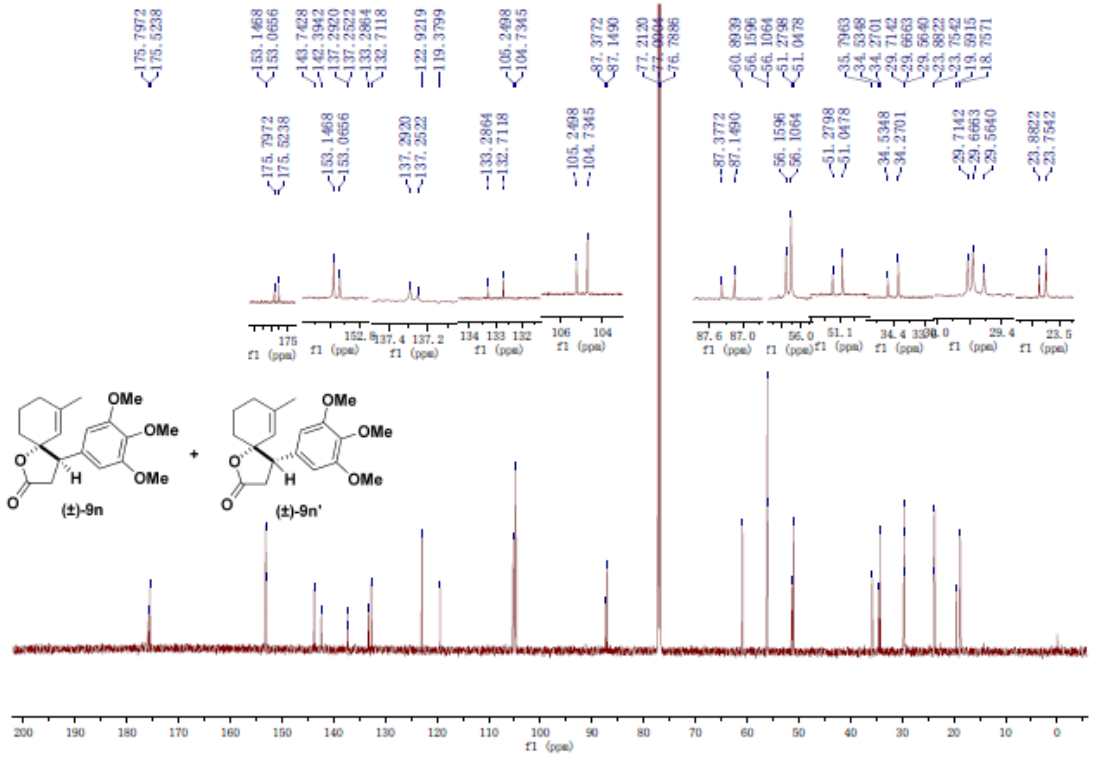
^{13}C NMR of **(±)-9m and (±)-9m'** (150 M, $CDCl_3$)



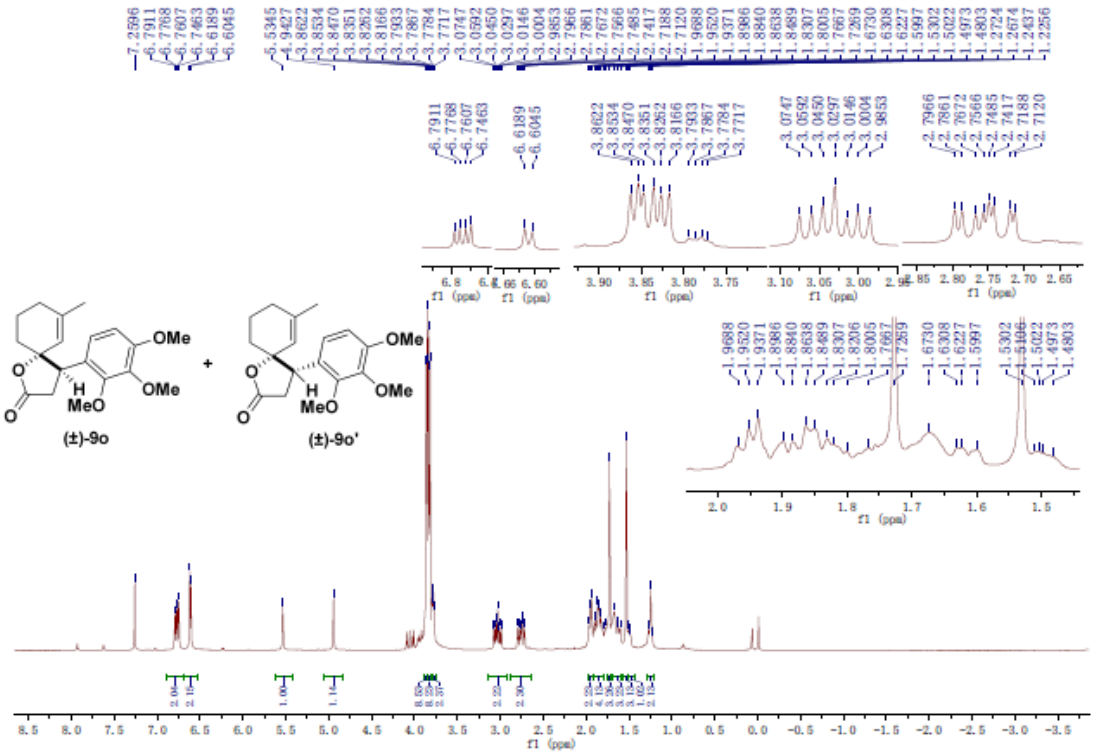
^{1}H NMR of **(±)-9n and (±)-9n'** (600 M, $CDCl_3$)



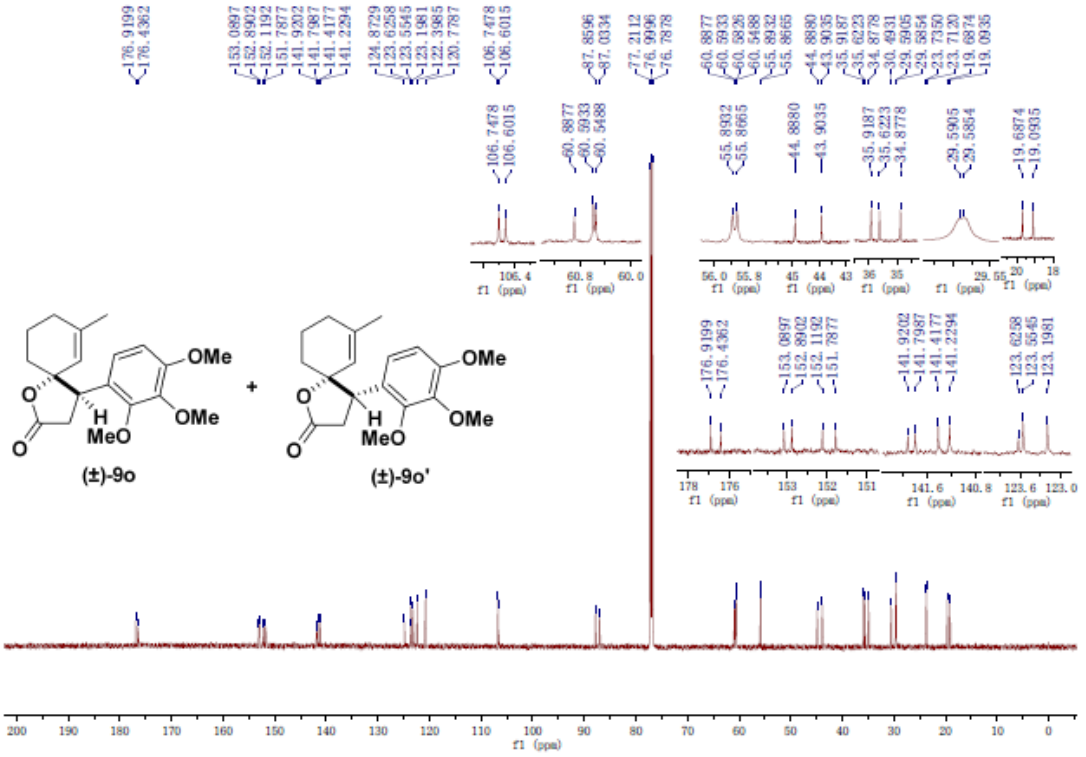
^{13}C NMR of **(±)-9n and (±)-9n'** (150 M, $CDCl_3$)



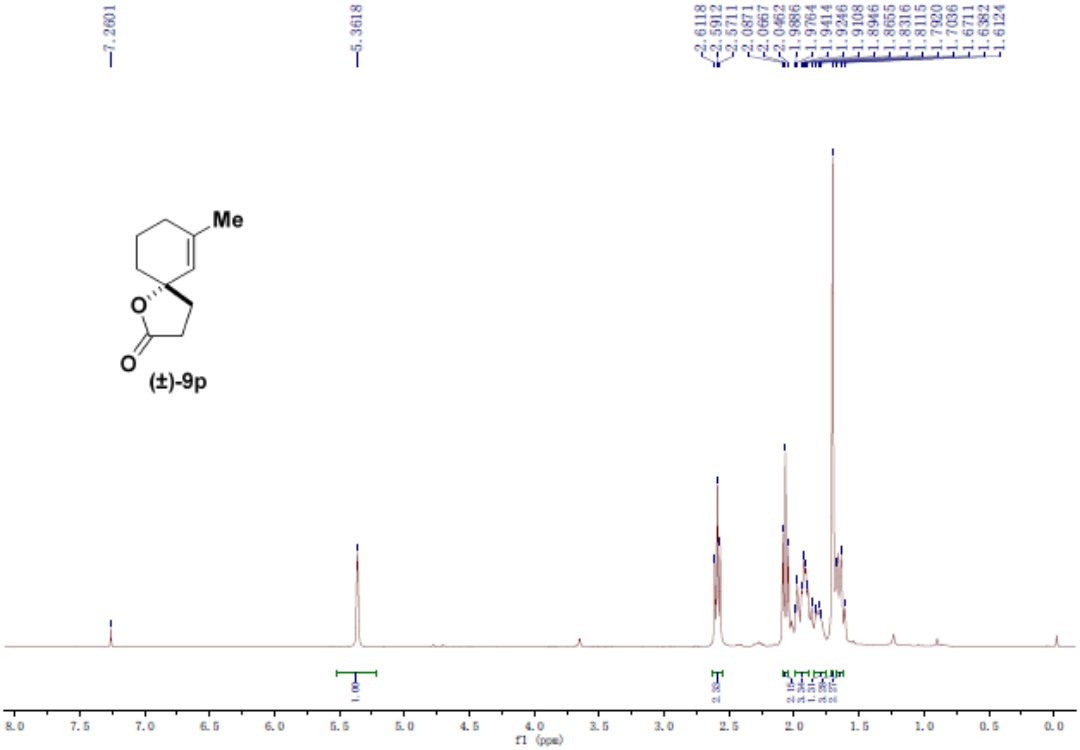
^{1}H NMR of **(±)-9o and (±)-9o'** (600 M, $CDCl_3$)



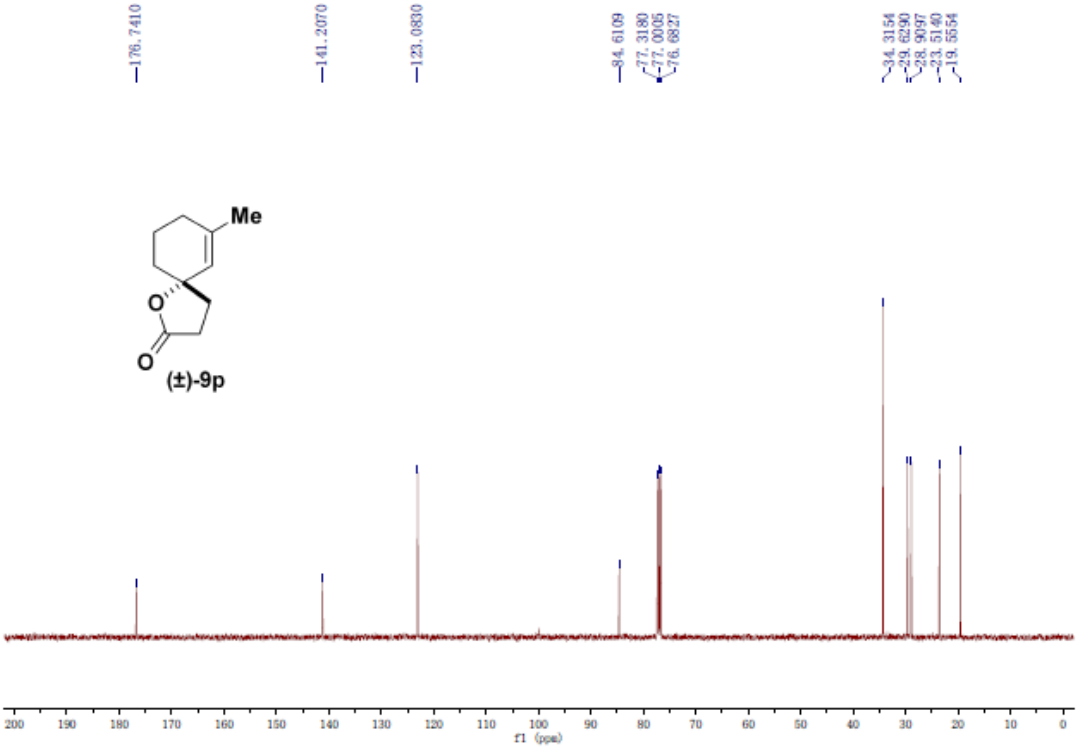
^{13}C NMR of **(±)-9o and (±)-9o'** (150 M, $CDCl_3$)



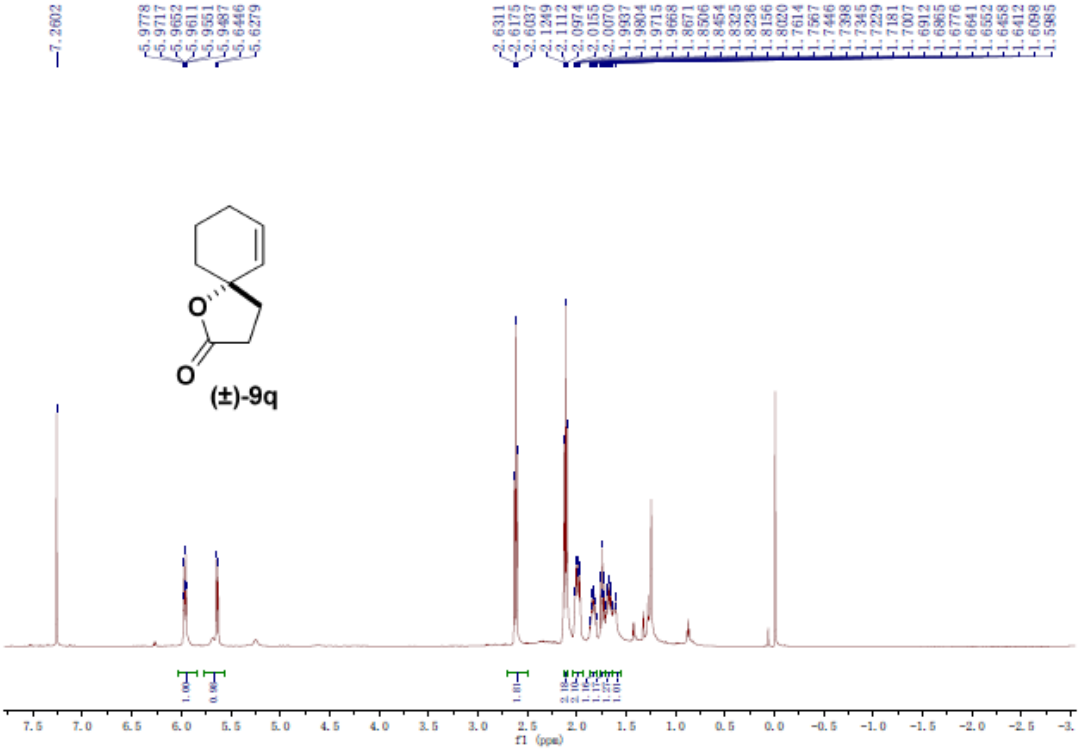
^{1}H NMR of (±)-**9p** (400 M, $CDCl_3$)



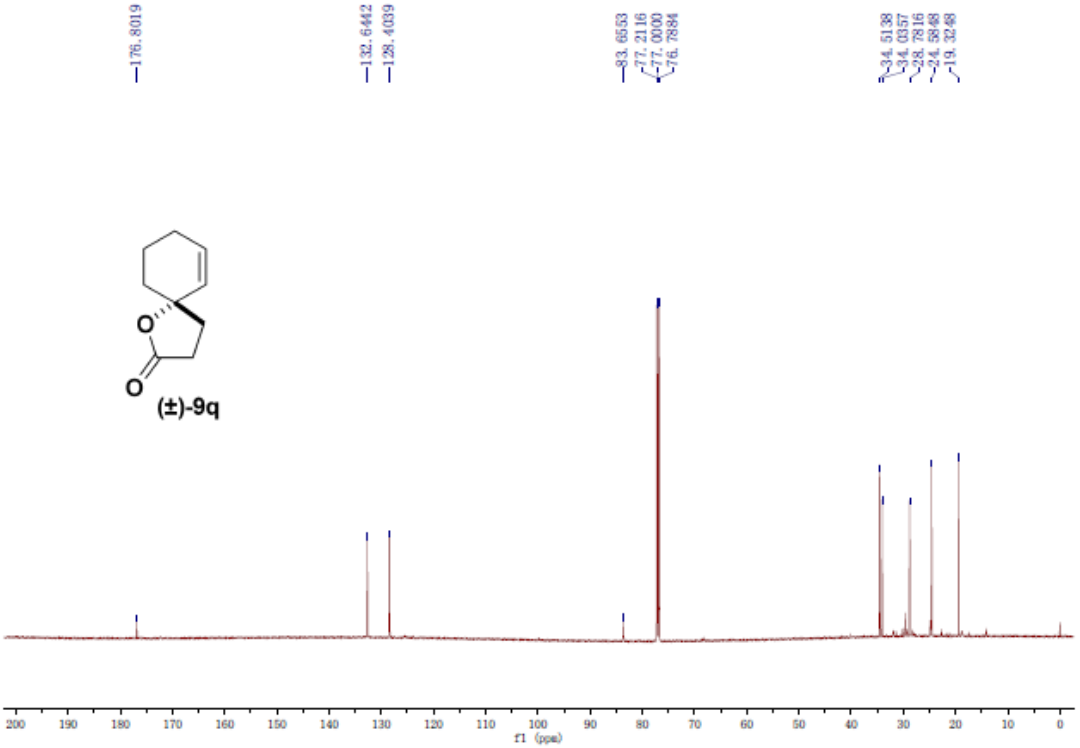
^{13}C NMR of (±)-**9p** (100 M, $CDCl_3$)



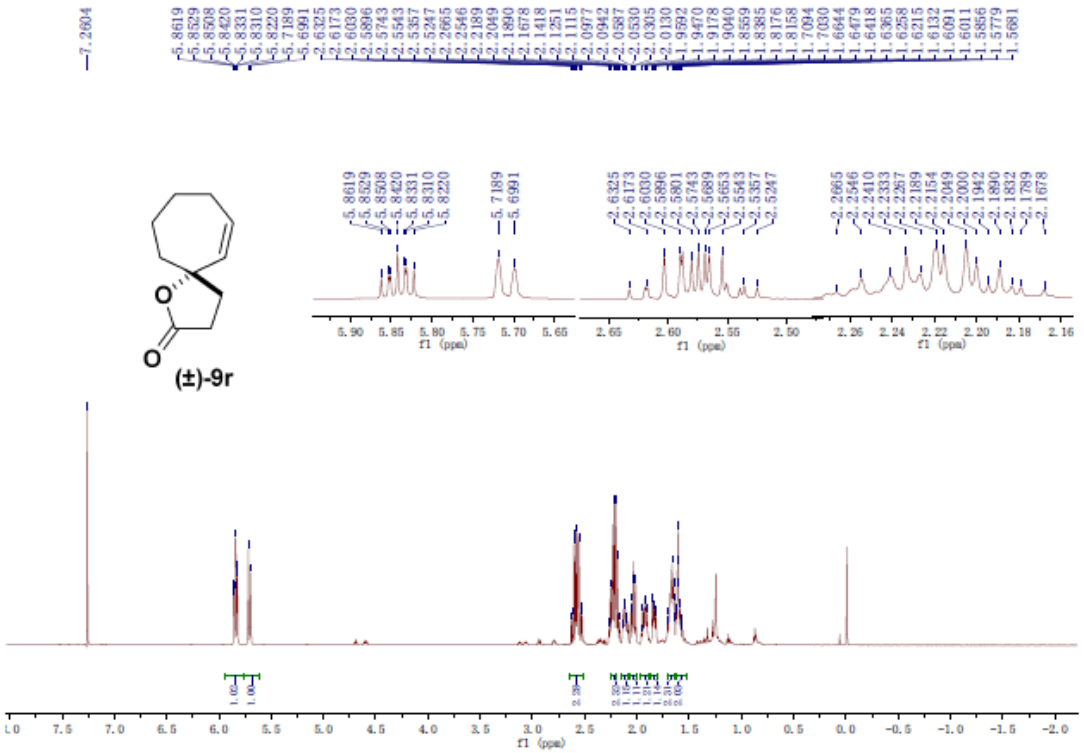
^{1}H NMR of (±)-**9q** (400 M, $CDCl_3$)



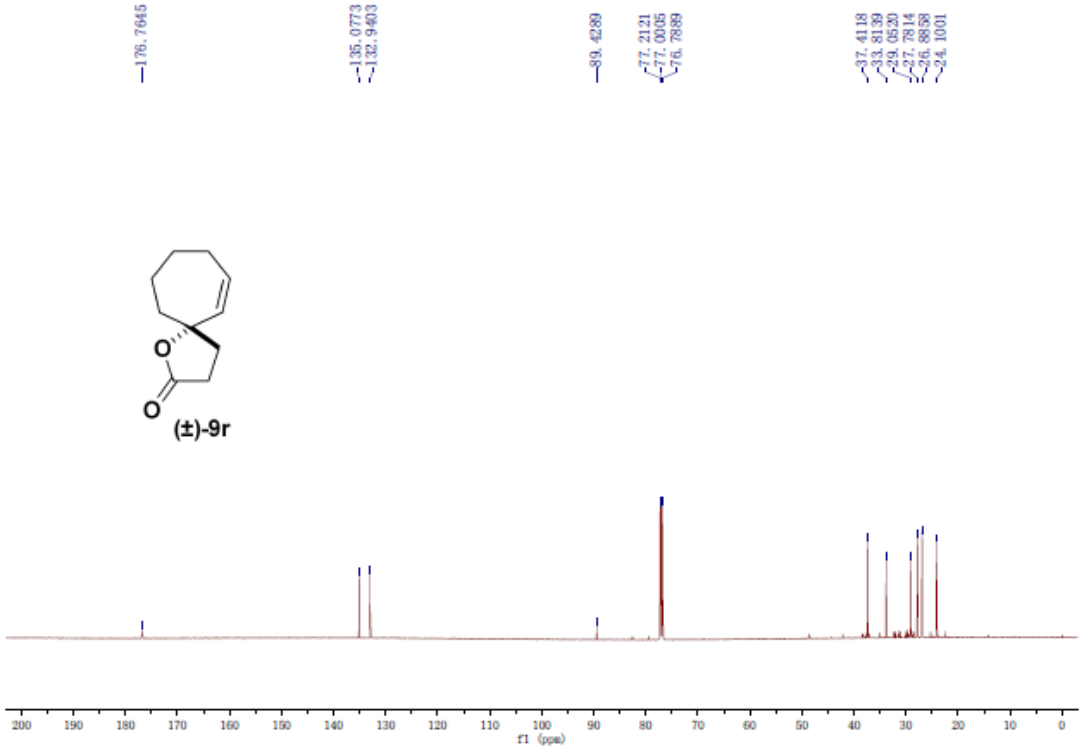
^{13}C NMR of (±)-**9q** (100 M, $CDCl_3$)



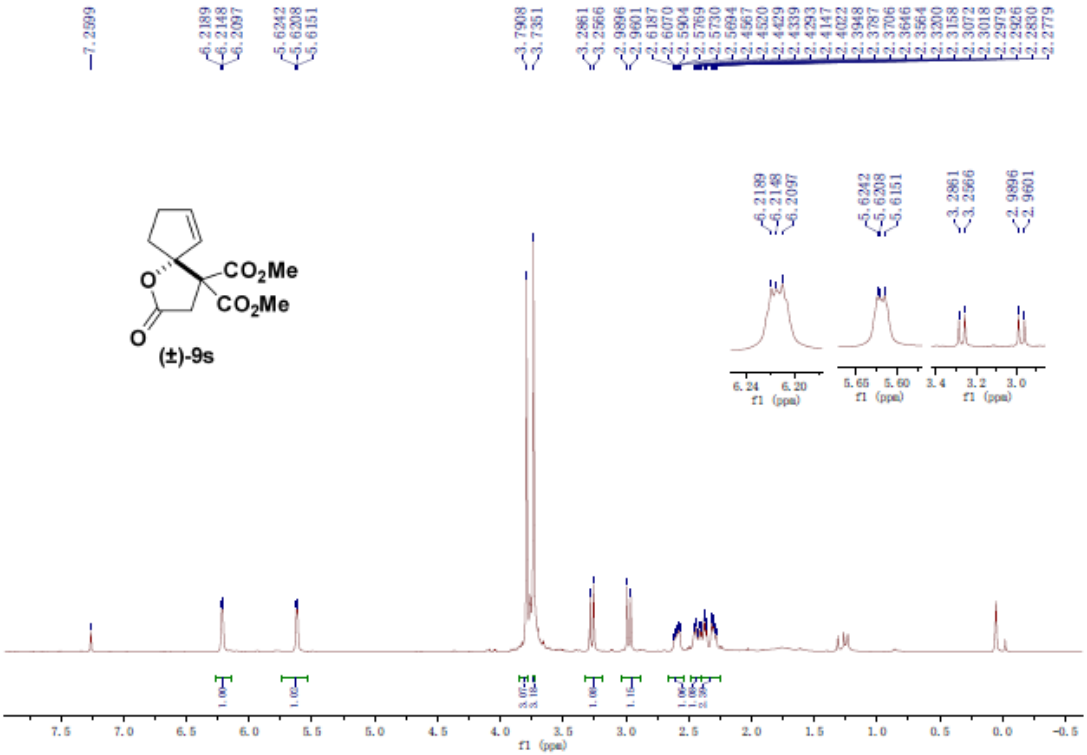
^{1}H NMR of (±)-**9r** (400 M, $CDCl_3$)



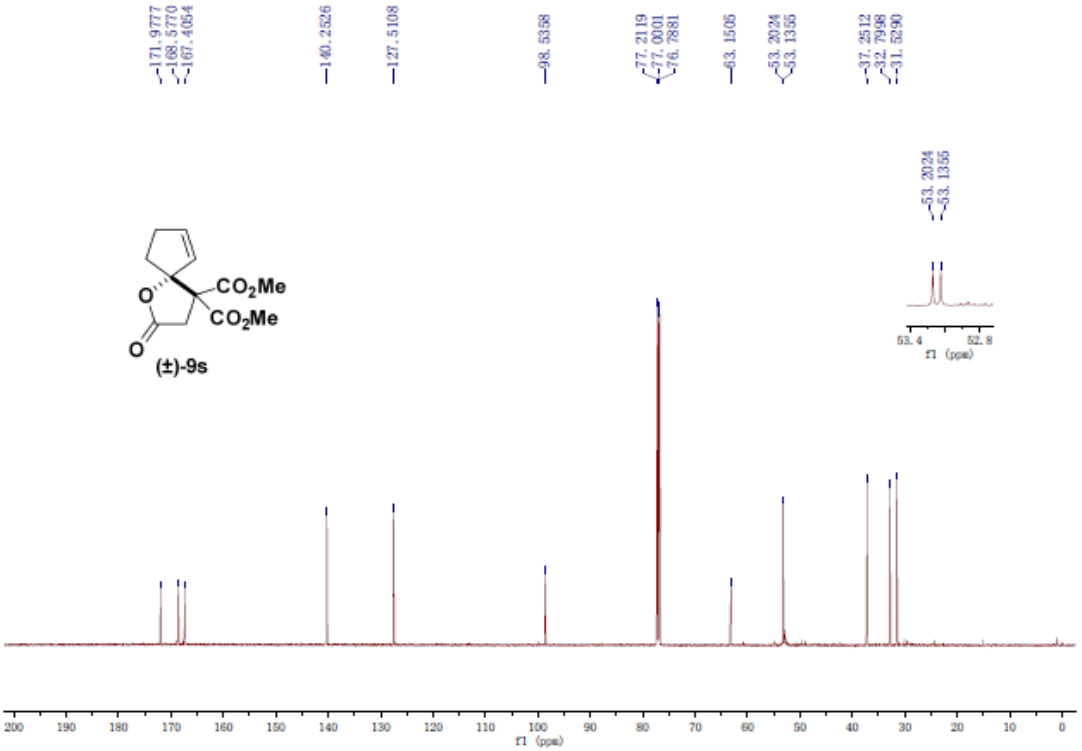
^{13}C NMR of (±)-**9r** (100 M, $CDCl_3$)



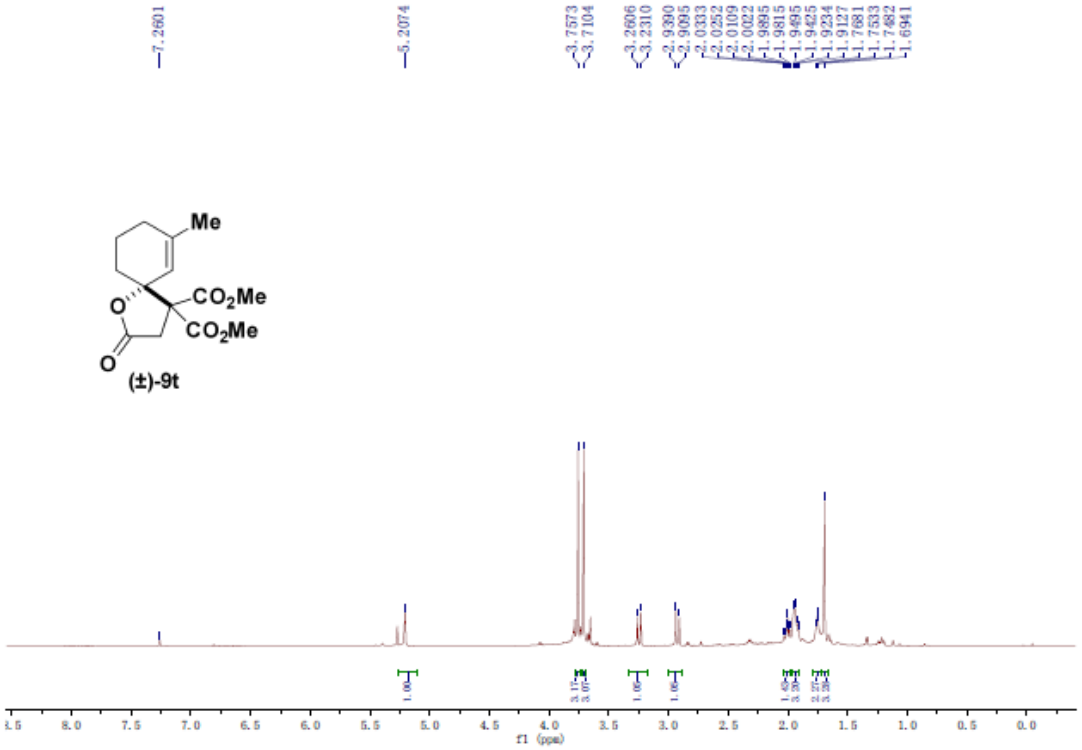
^{1}H NMR of **(±)-9s** (400 M, $CDCl_3$)



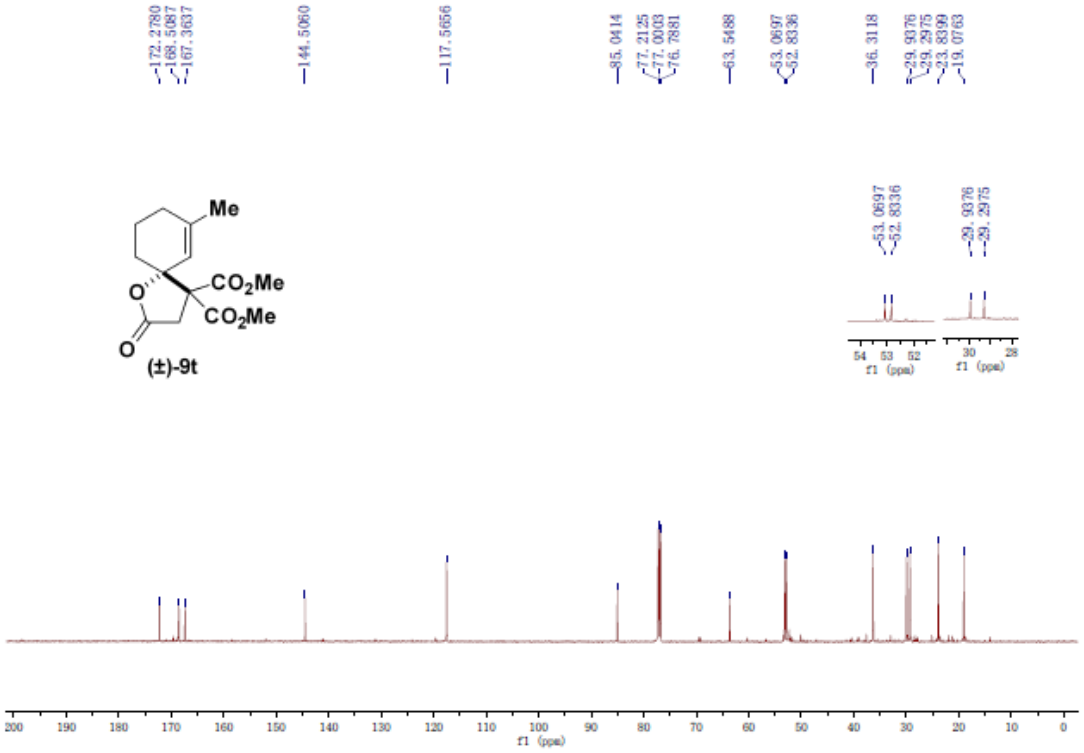
^{13}C NMR of **(±)-9s** (100 M, $CDCl_3$)



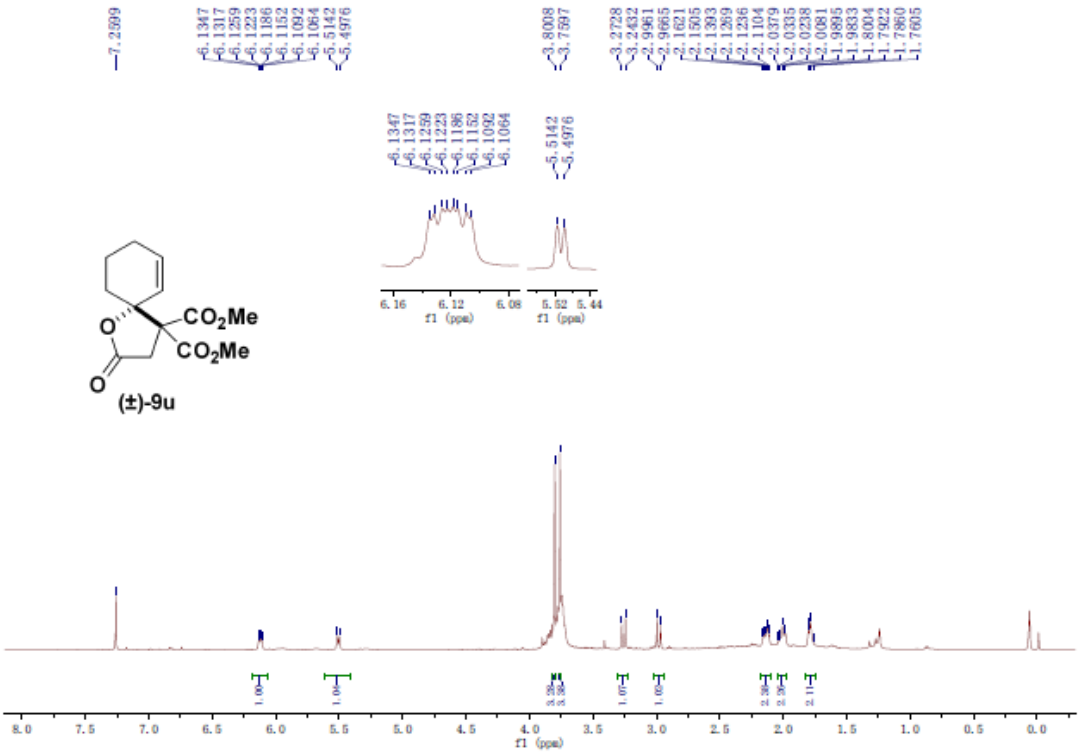
^{1}H NMR of **(±)-9t** (600 M, $CDCl_3$)



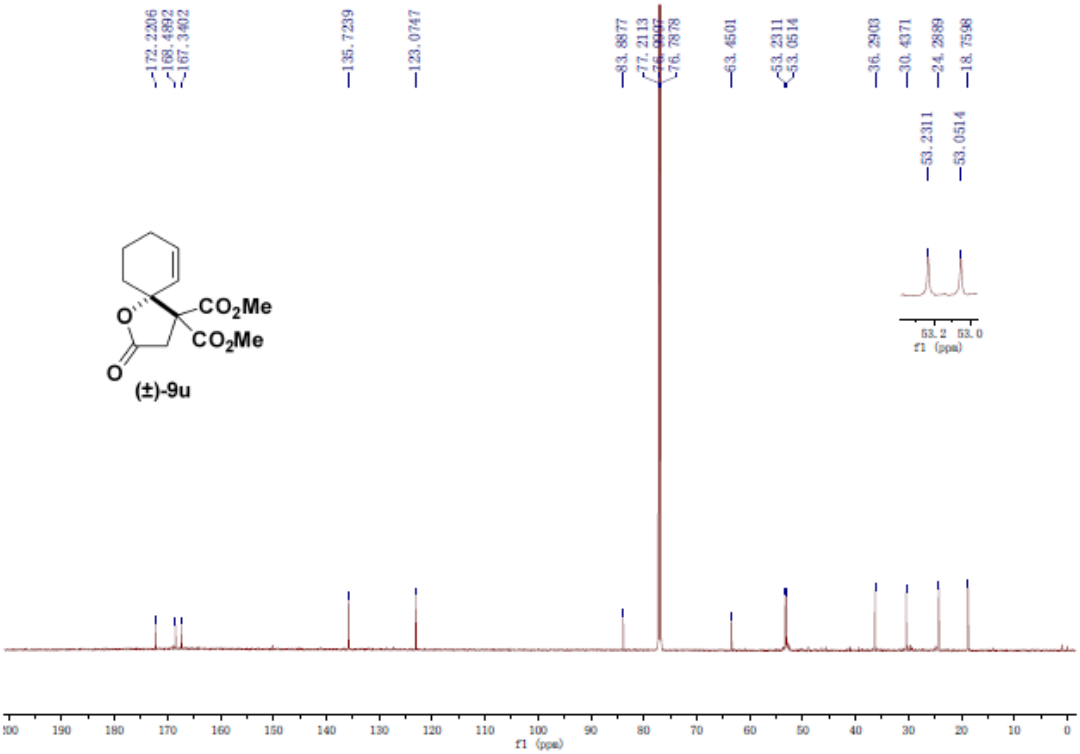
^{13}C NMR of **(±)-9t** (150 M, $CDCl_3$)



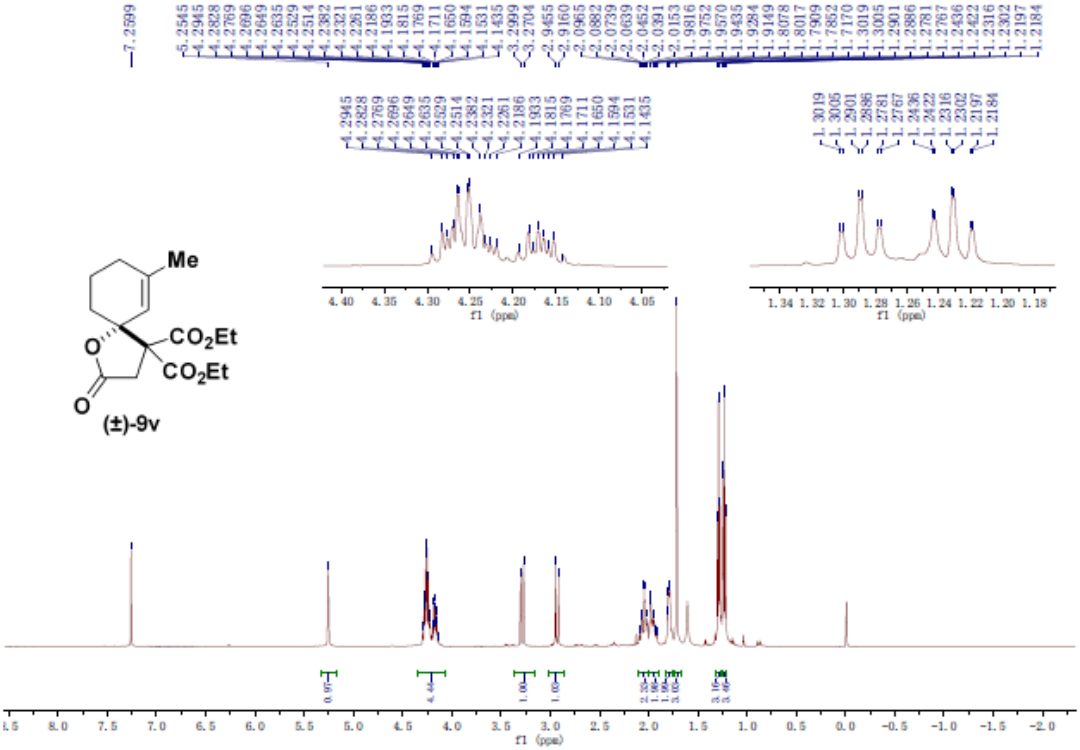
^{1}H NMR of (±)-**9u** (400 M, $CDCl_3$)



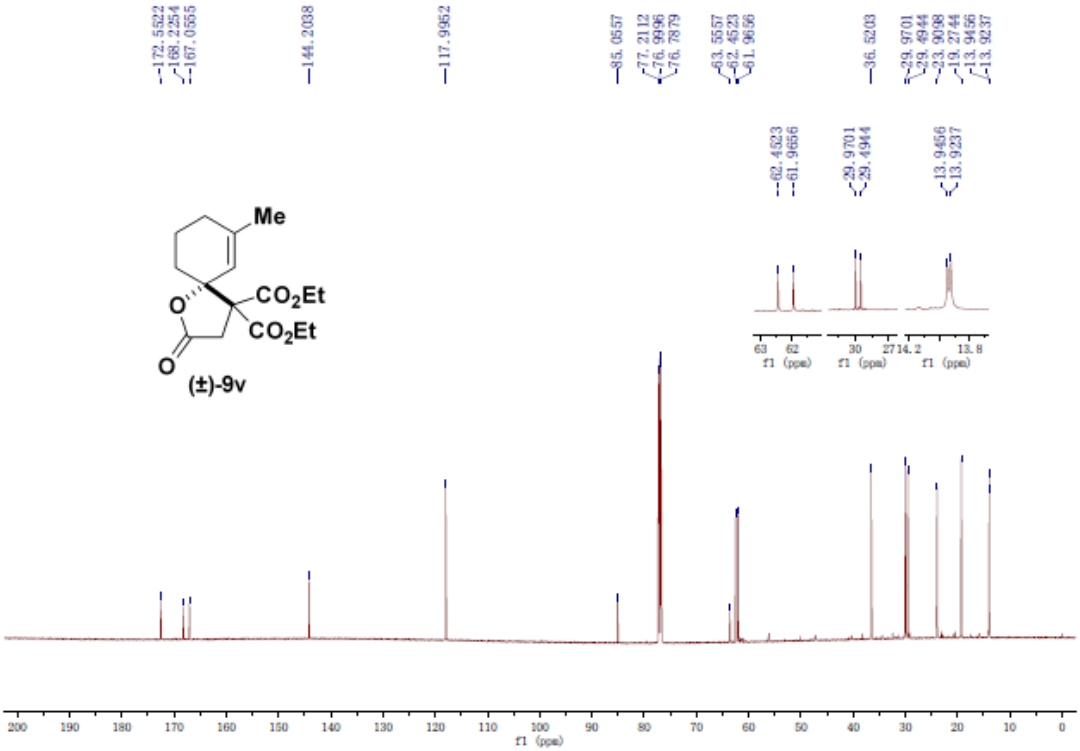
^{13}C NMR of (±)-**9u** (100 M, $CDCl_3$)



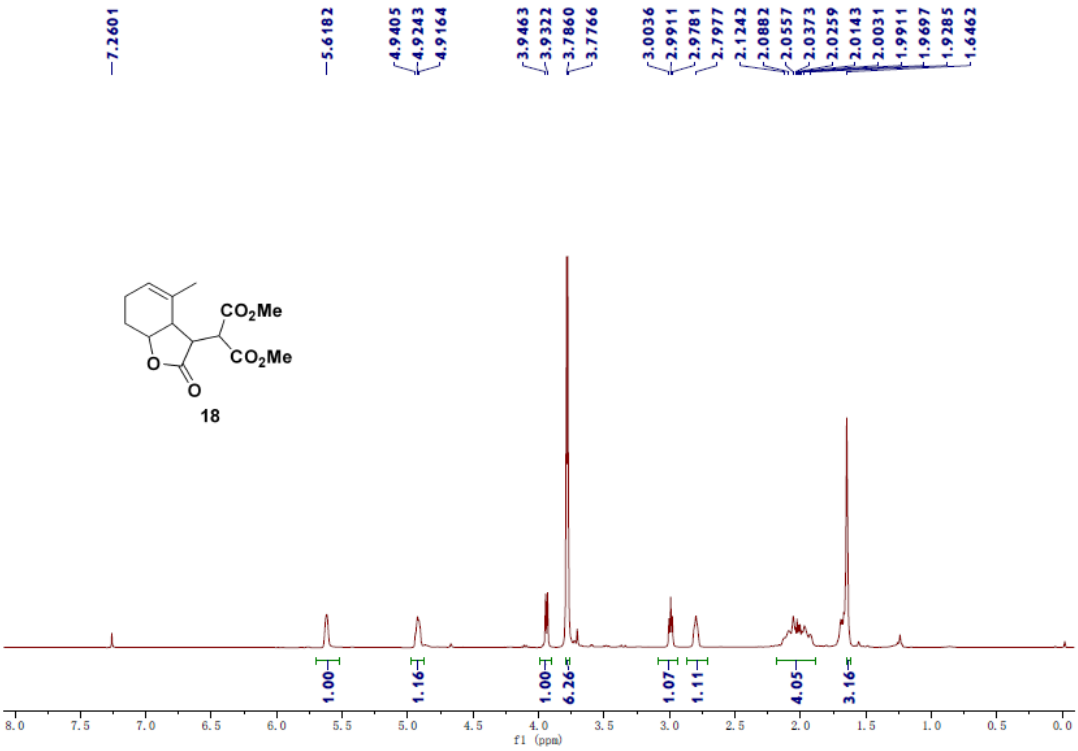
^{1}H NMR of (±)-**9v** (400 M, $CDCl_3$)



^{13}C NMR of (±)-**9v** (100 M, $CDCl_3$)



^{1}H NMR of **18** (400 M, $CDCl_3$)



^{13}C NMR of **18** (100 M, $CDCl_3$)