Supporting Information

Synthesis of Methylene Cyclopropane-Fused Chromenes and Dihydroquinolines by Sequential [4 + 2]- and [1 + 2]-Annulation

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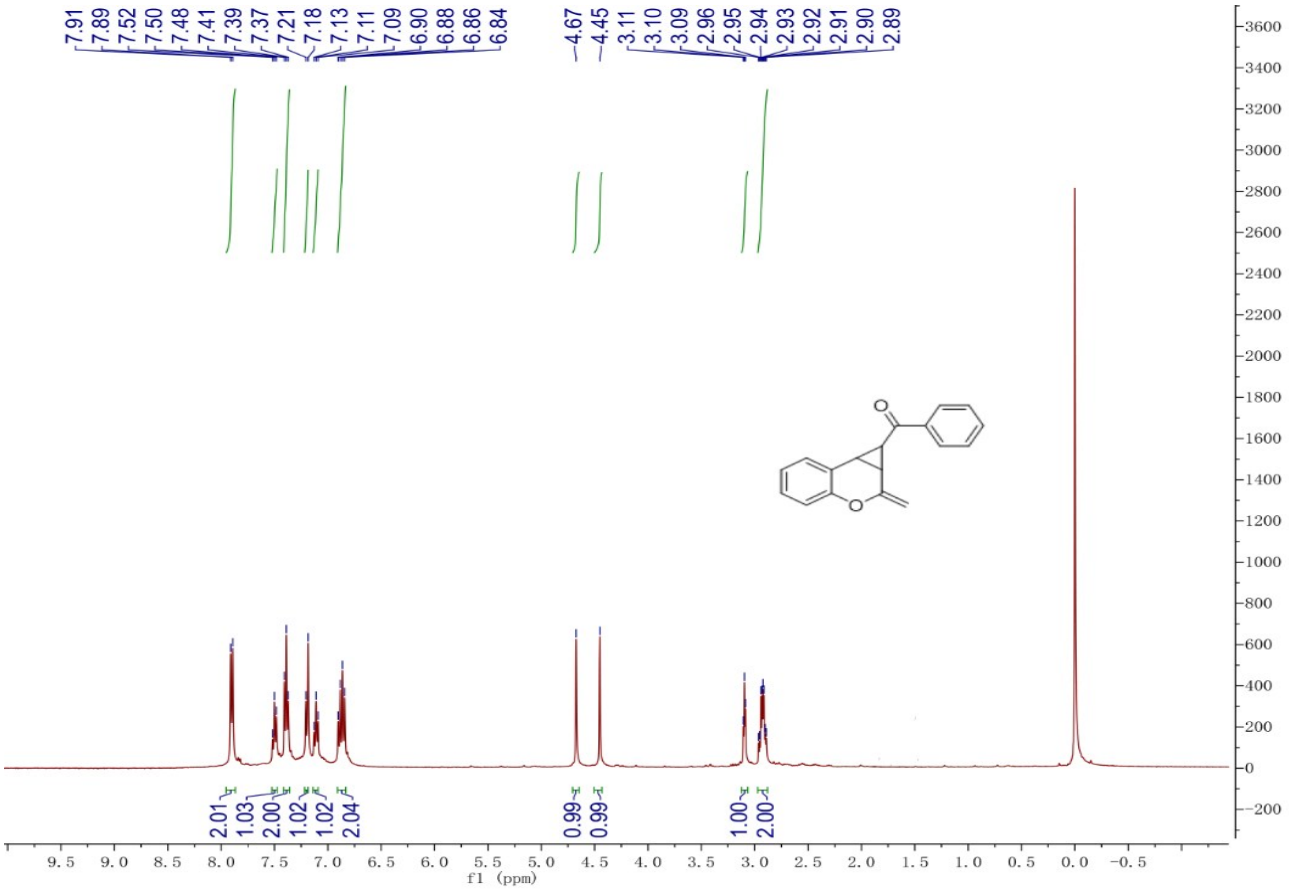
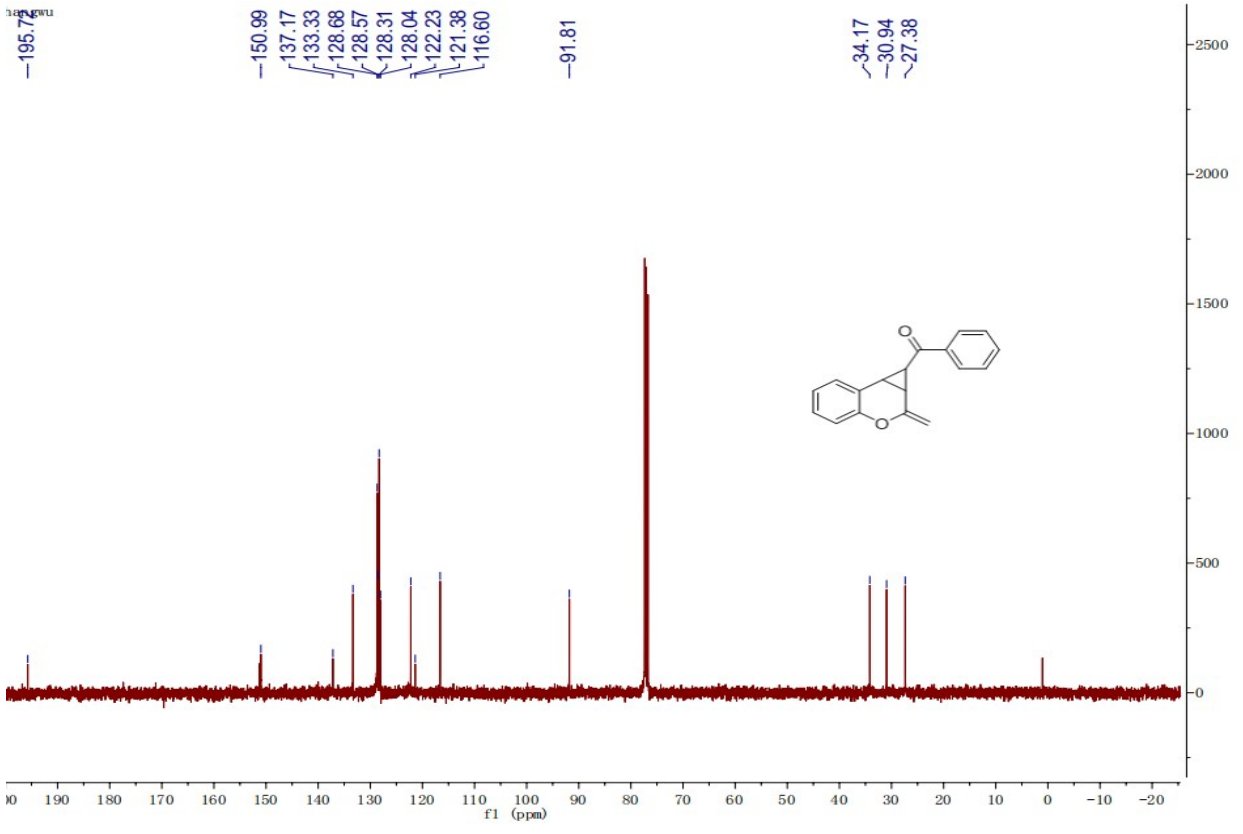
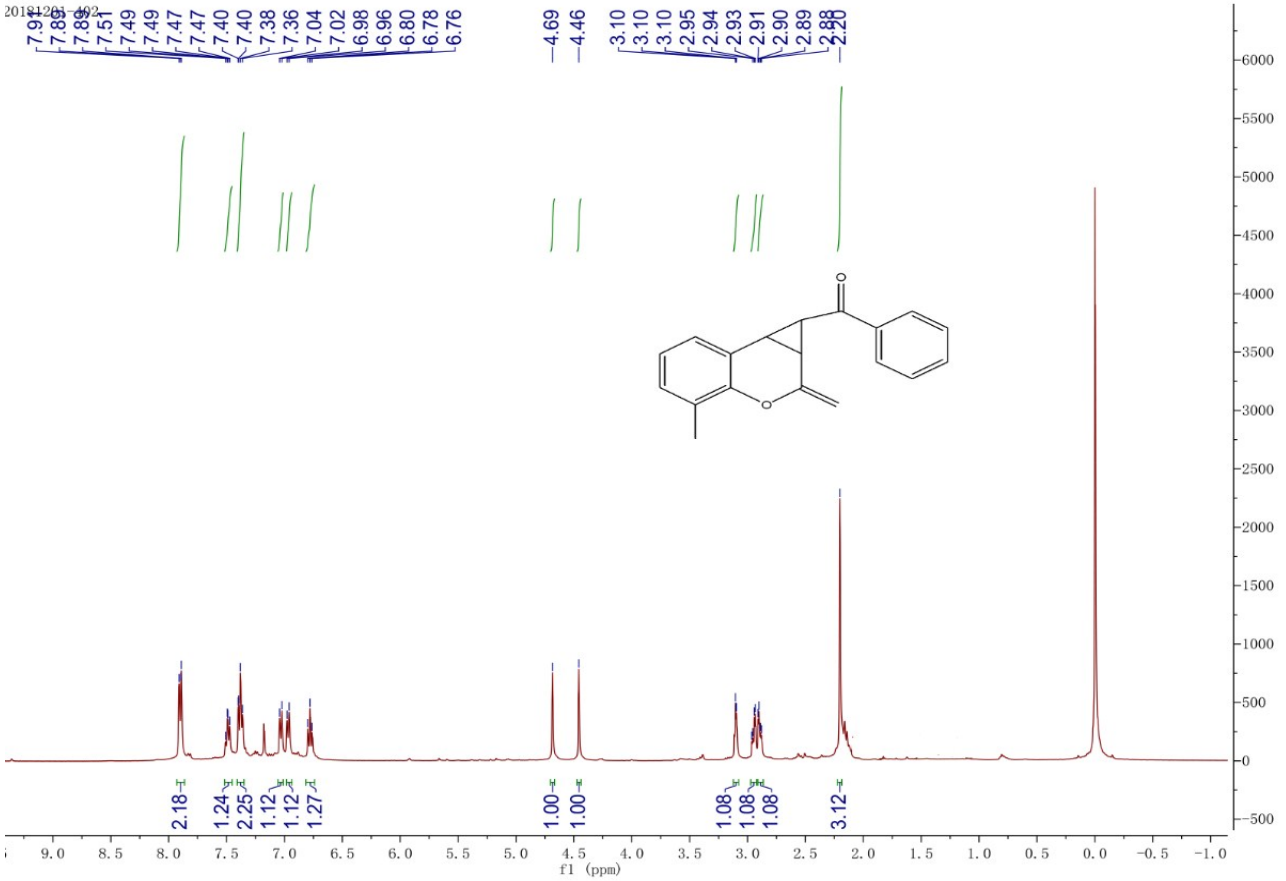
Copies of ^{1}H NMR and ^{13}C NMR spectra of **3a-3z**:

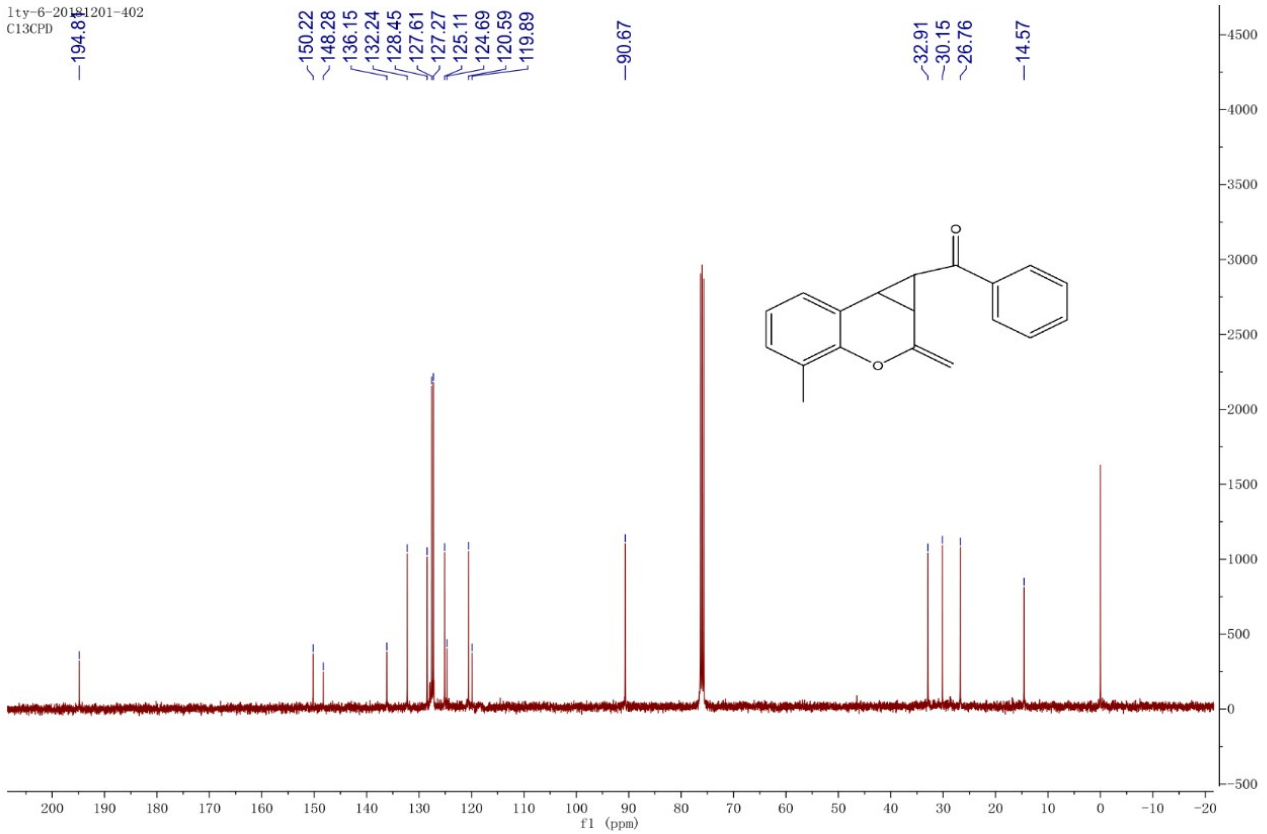
(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3a)



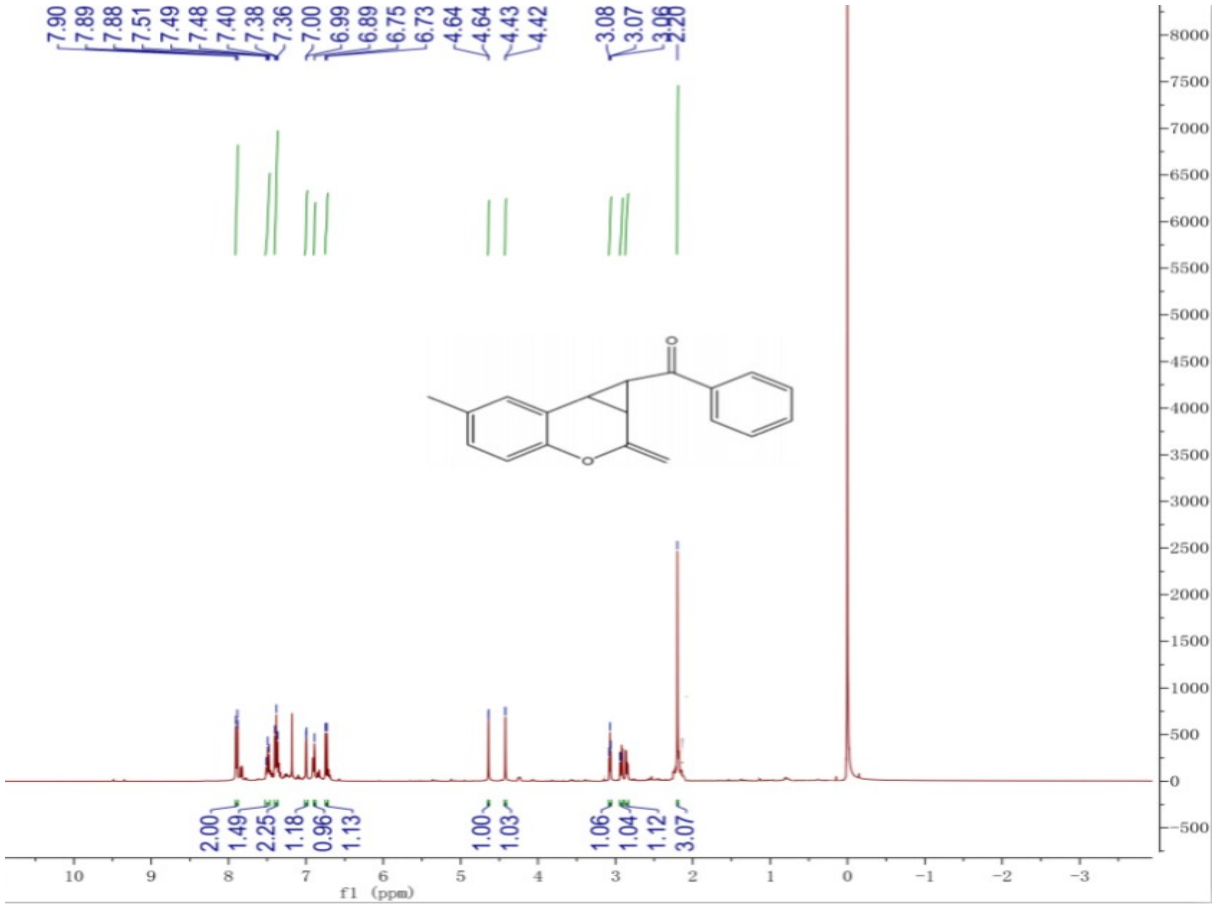


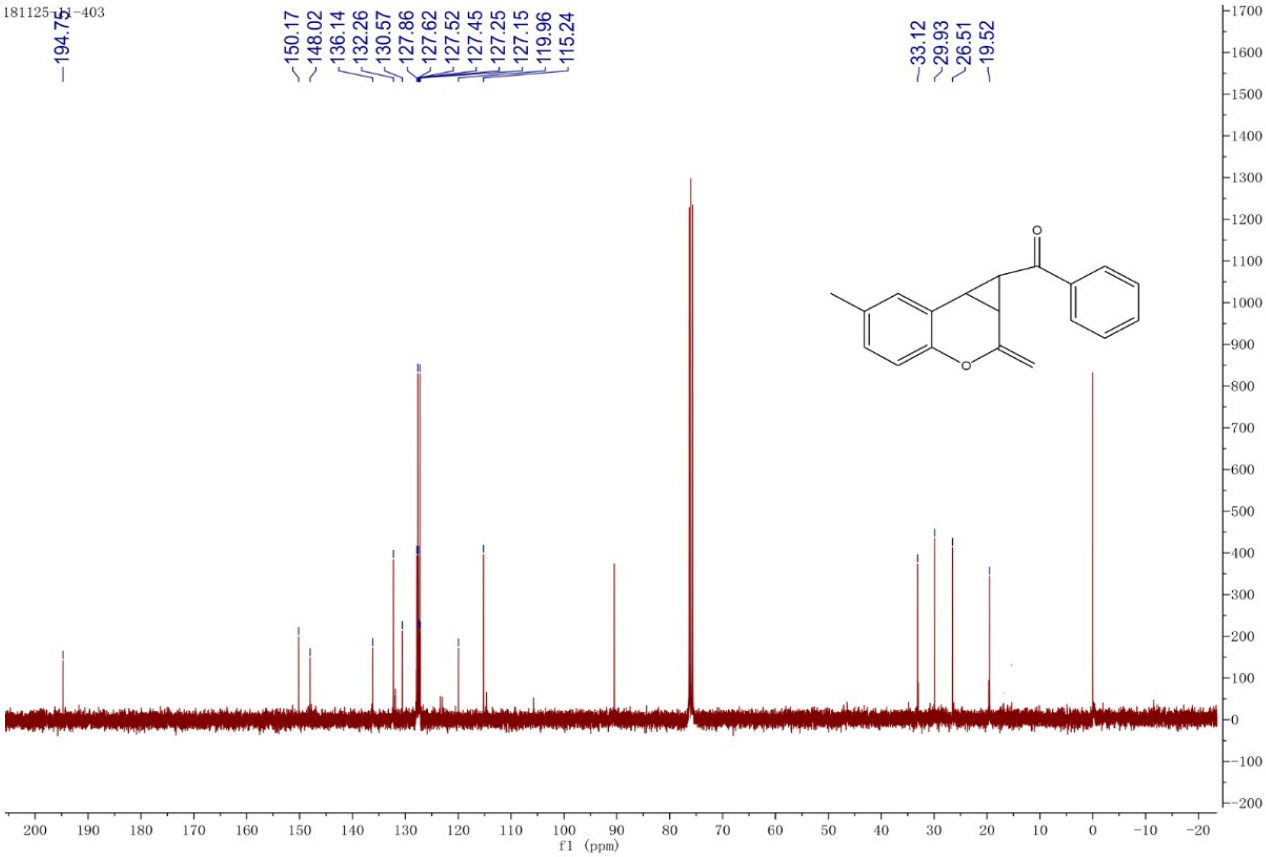
(4-Methyl-2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone(3b)



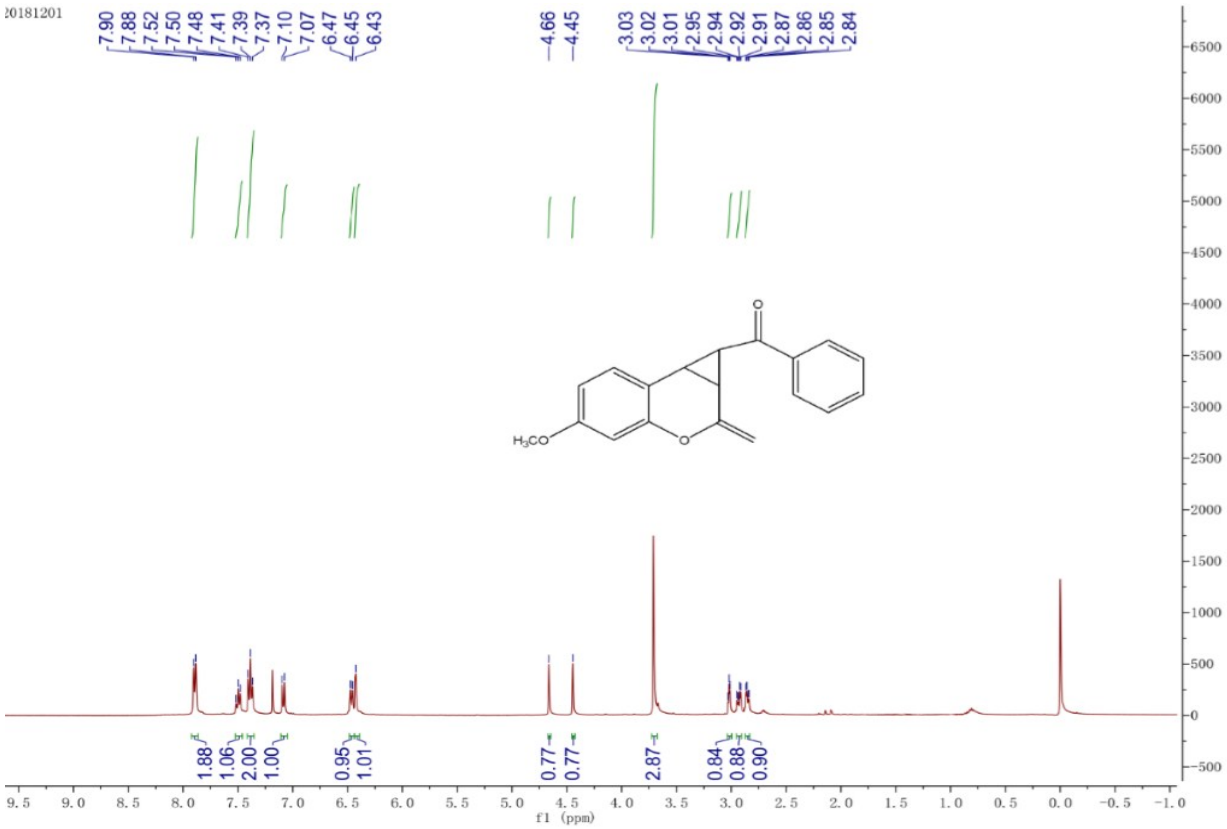


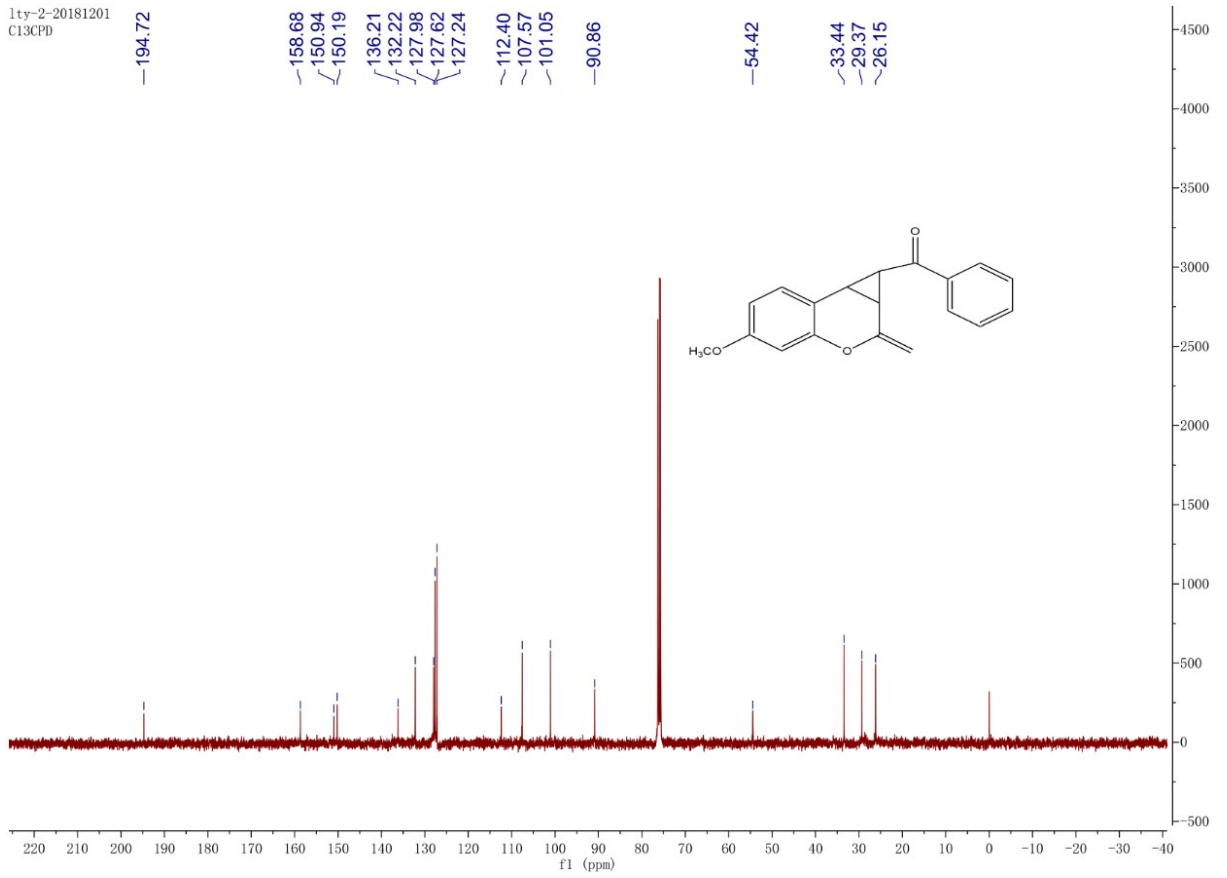
(6-Methyl-2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3c)





(5-Methoxy-2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3d)





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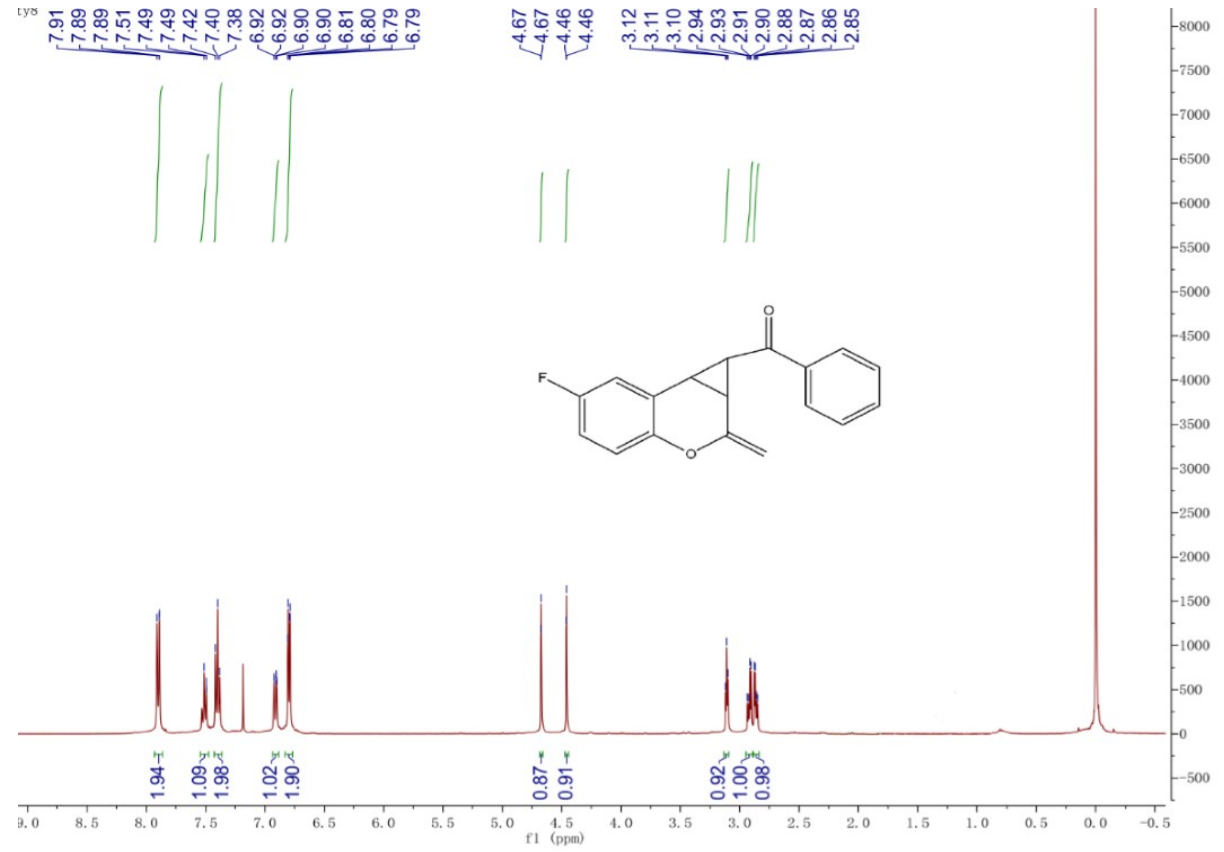

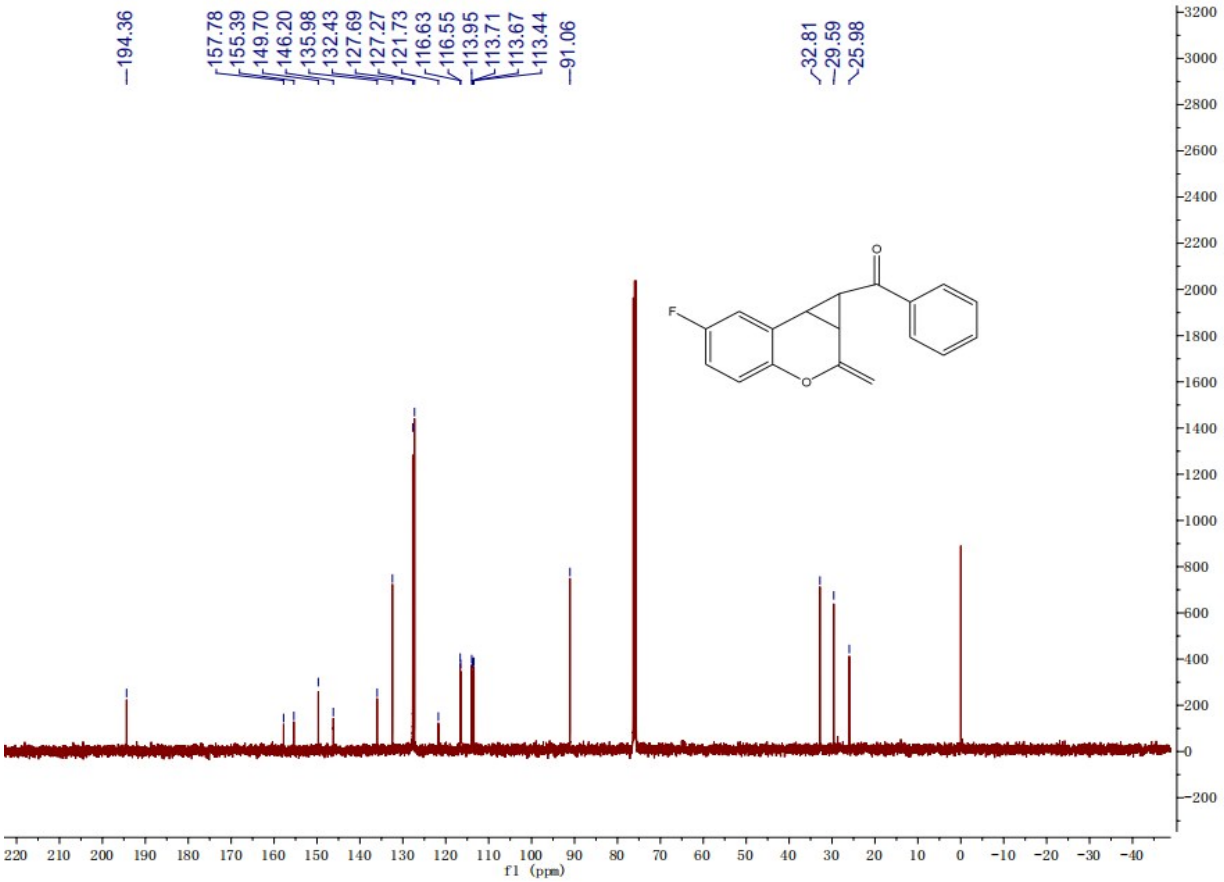

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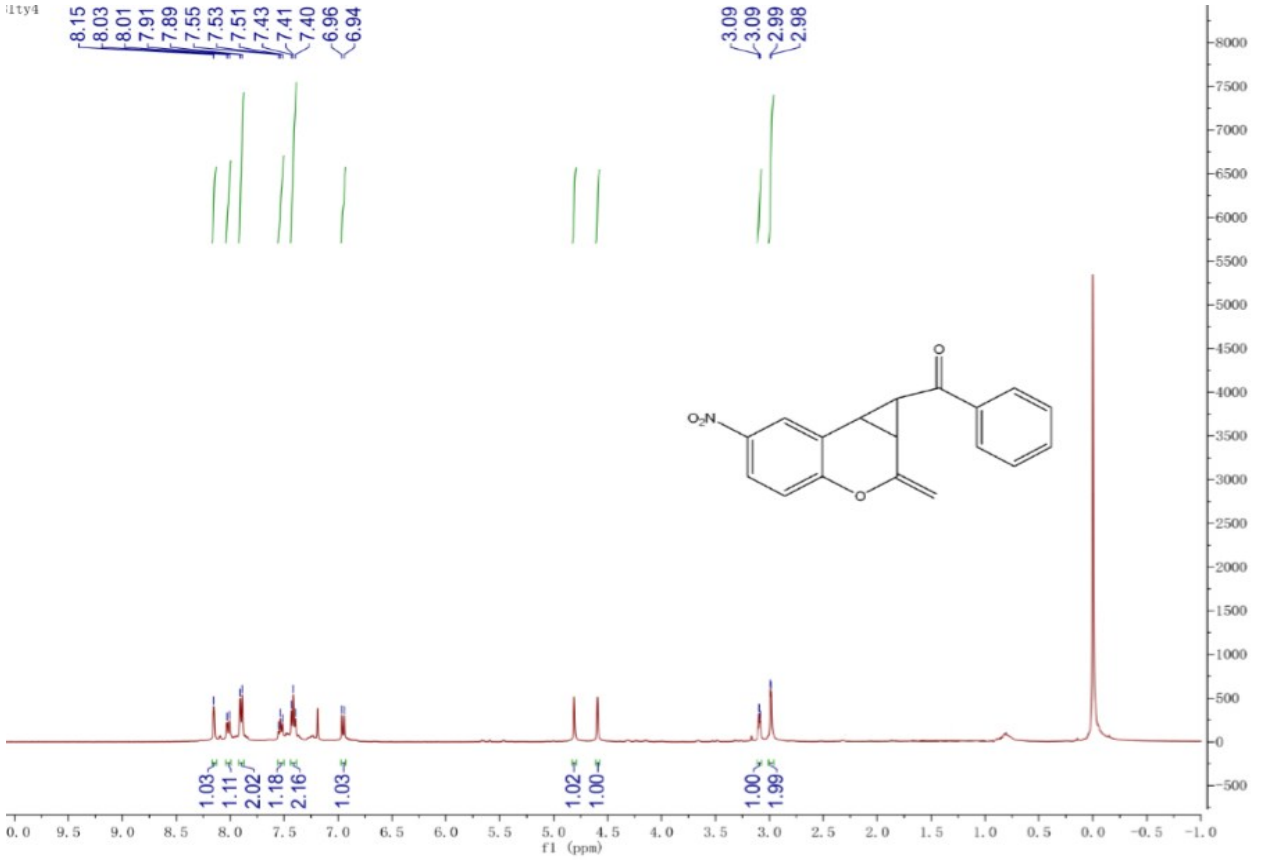

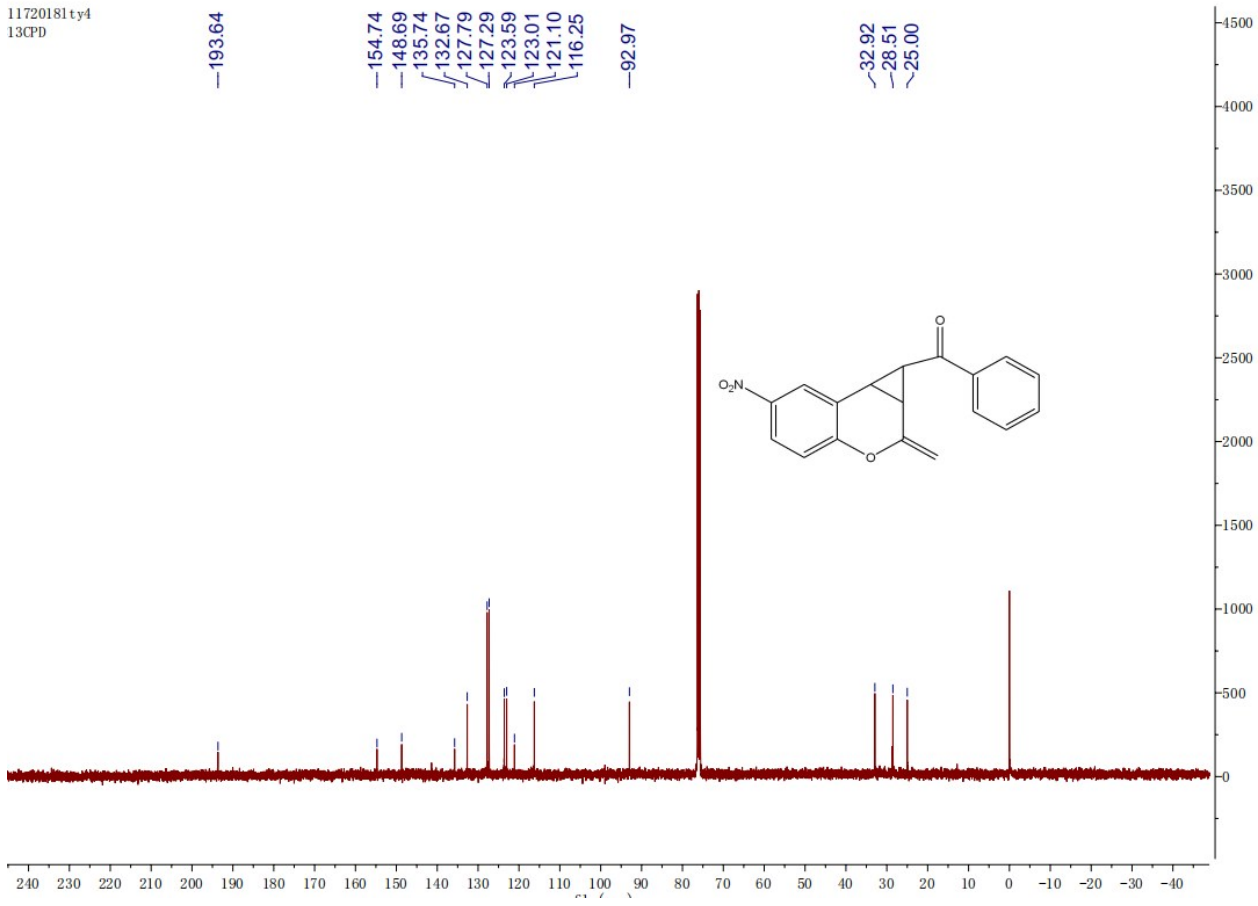

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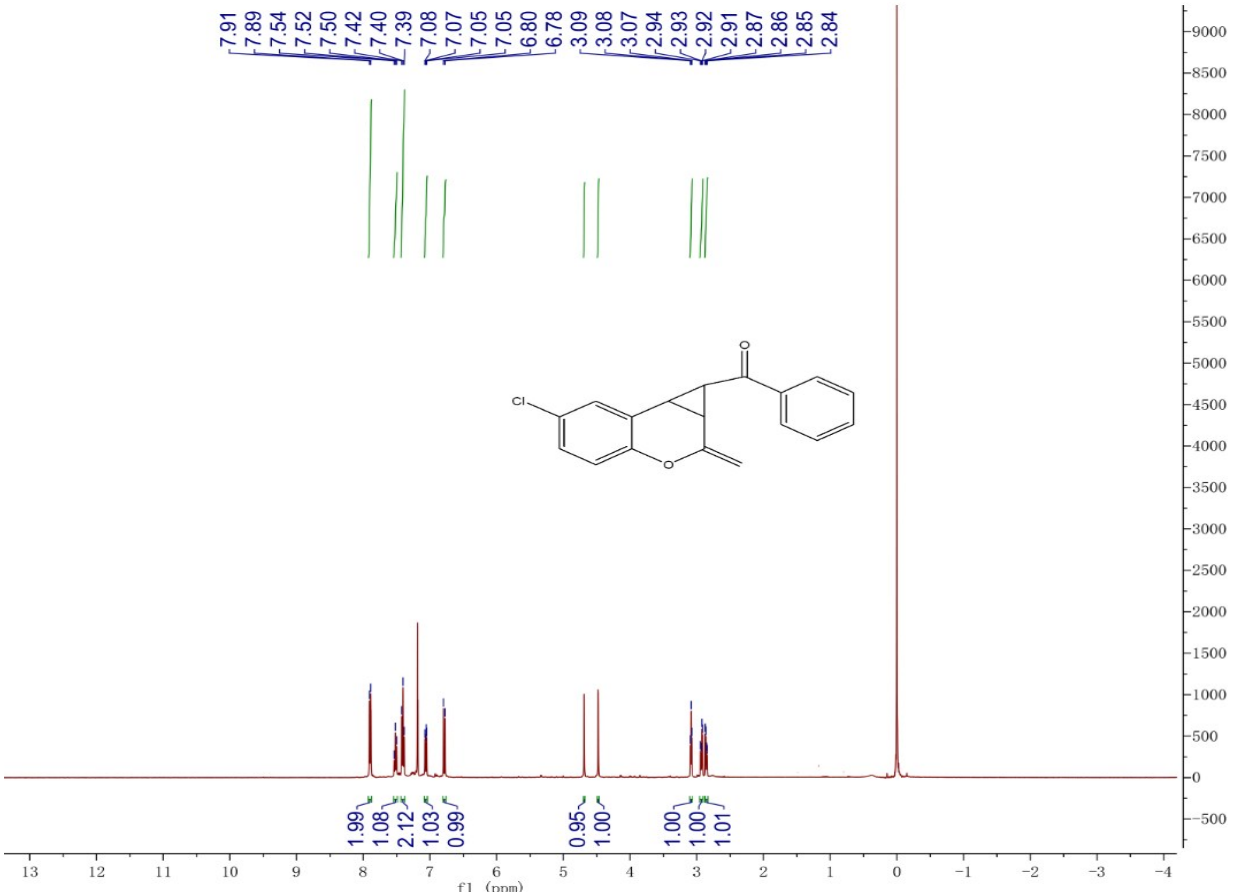
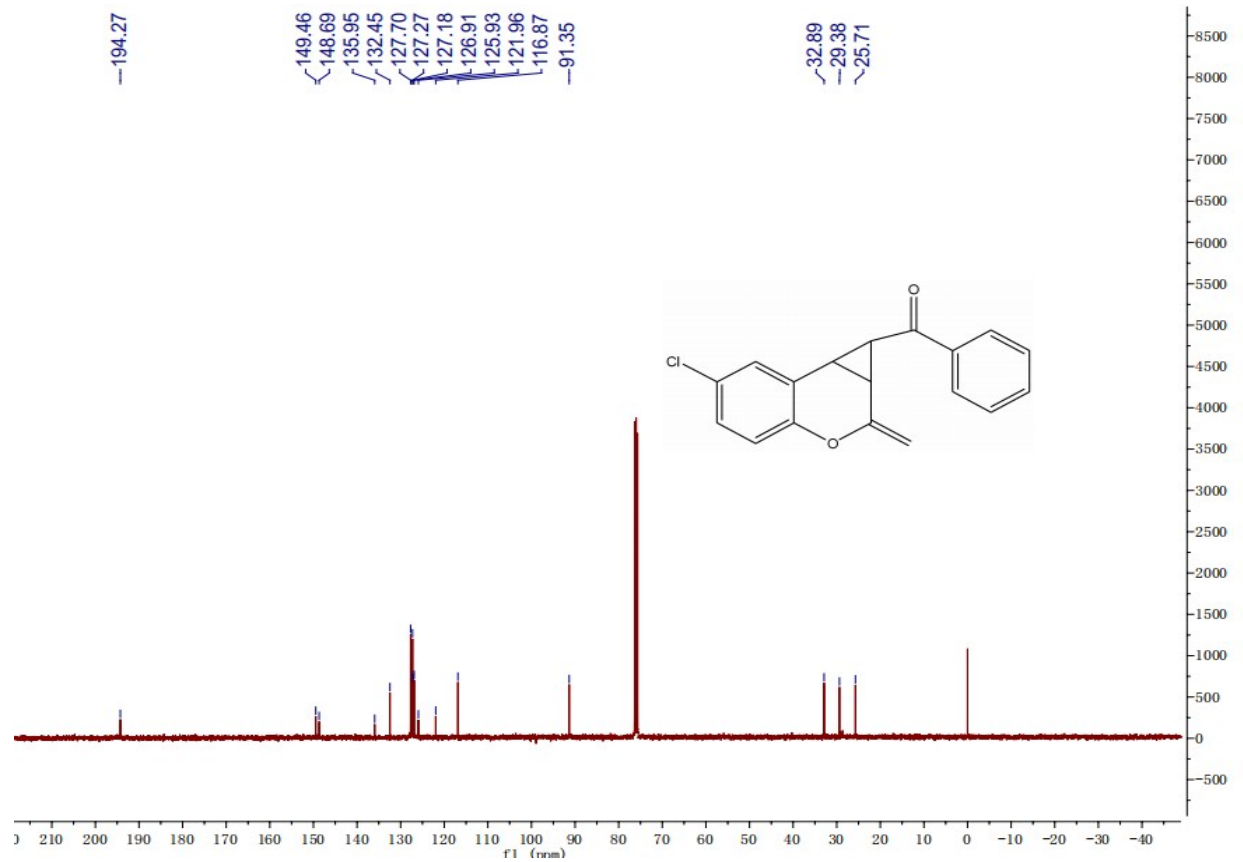
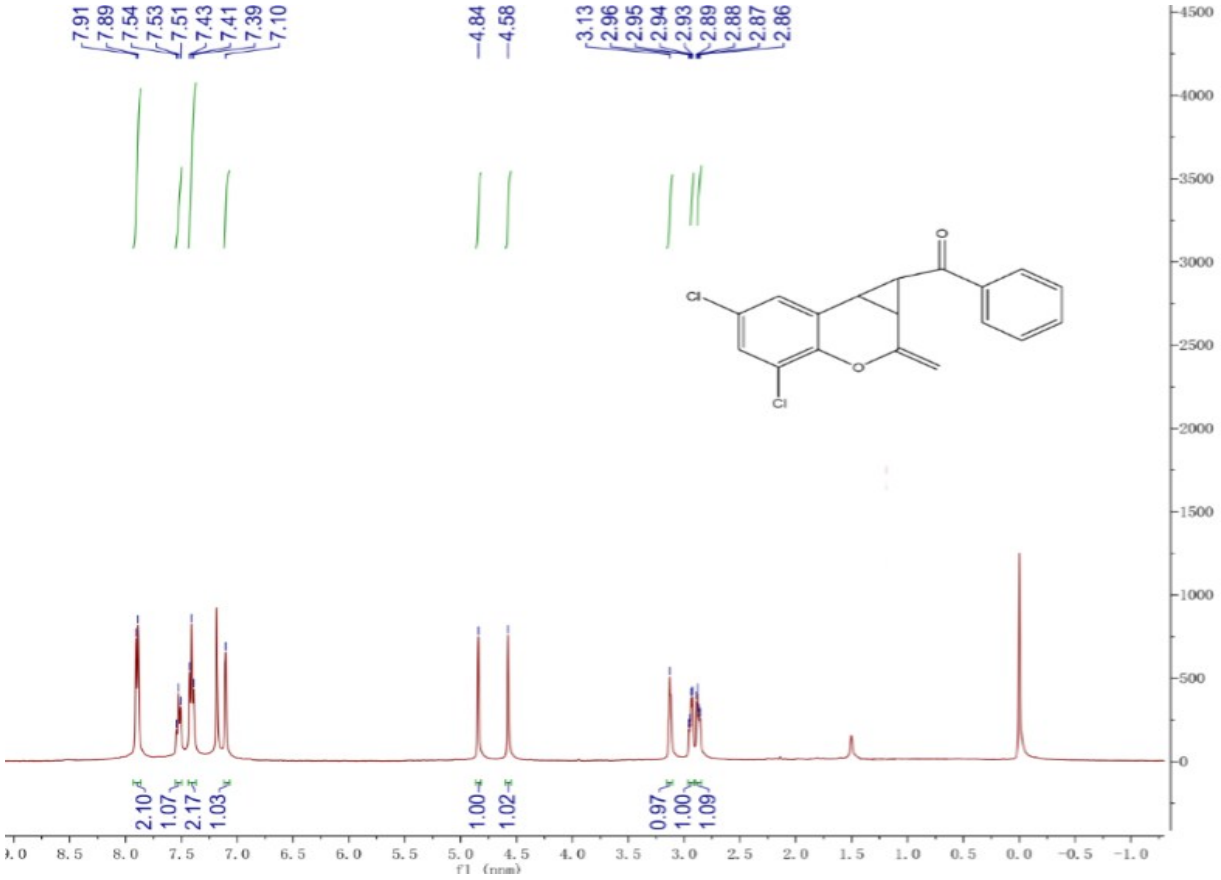
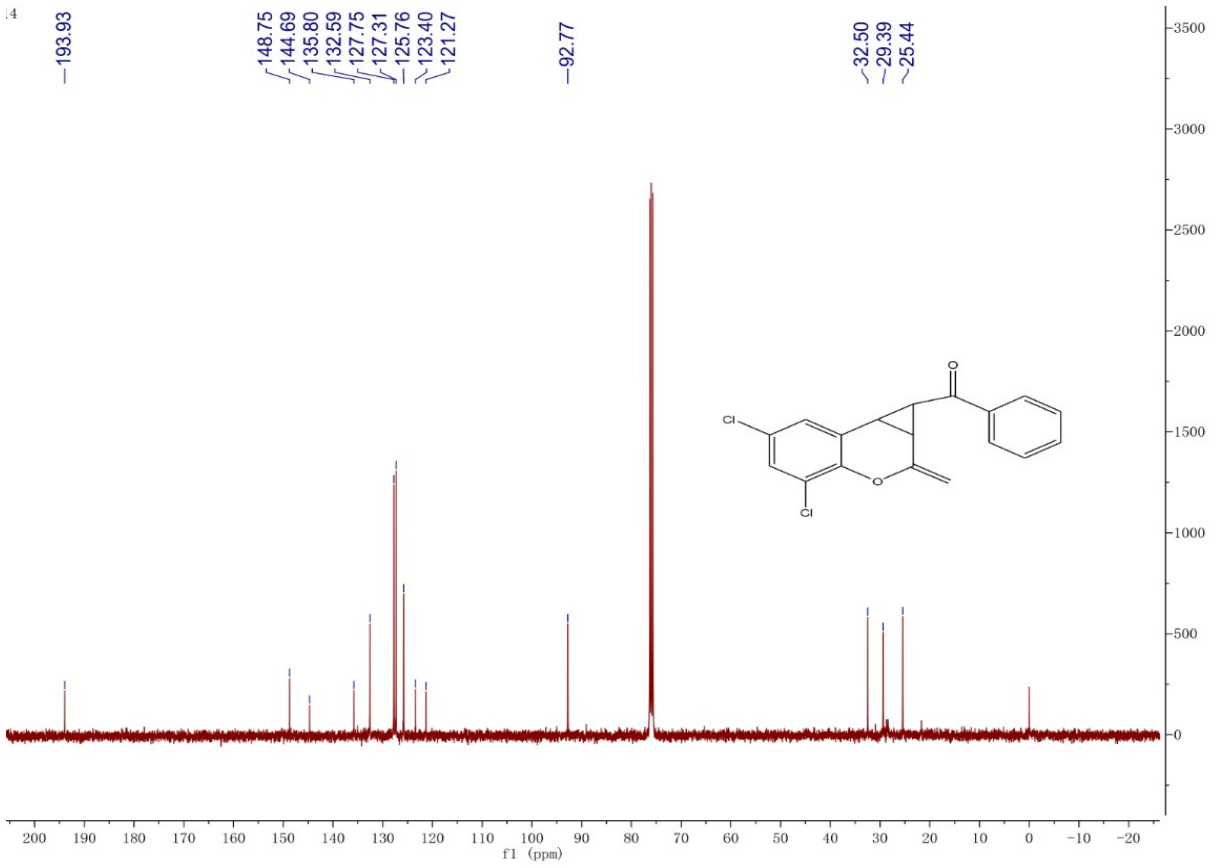


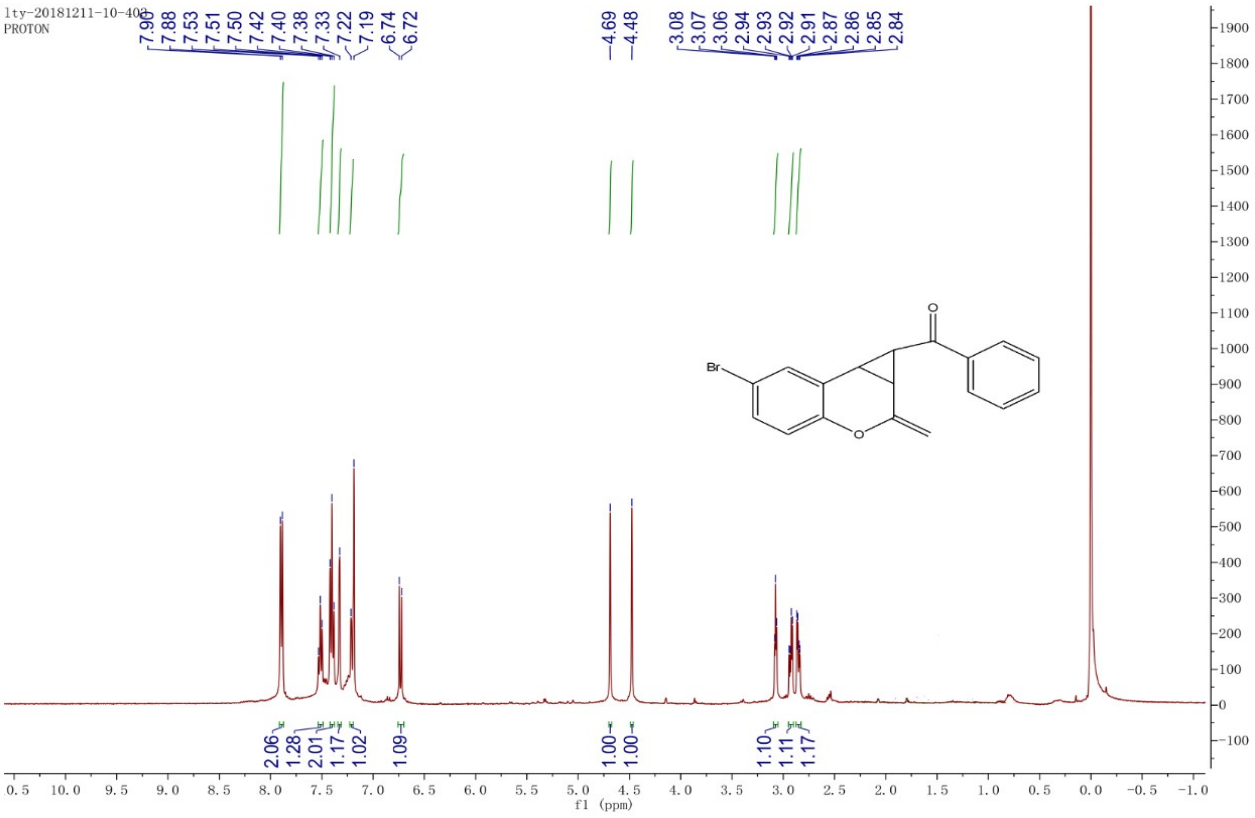


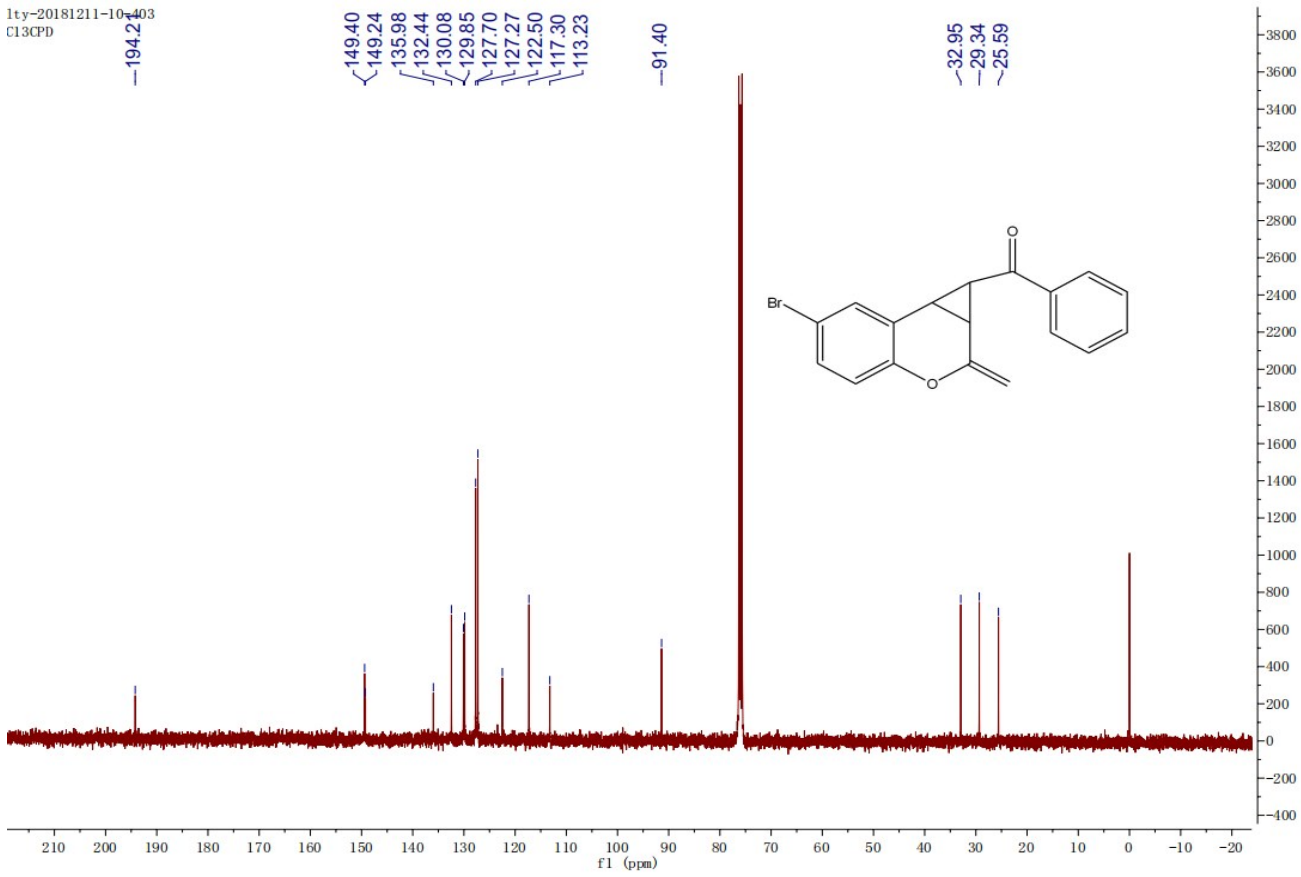
(4,6-Dichloro-2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3h)



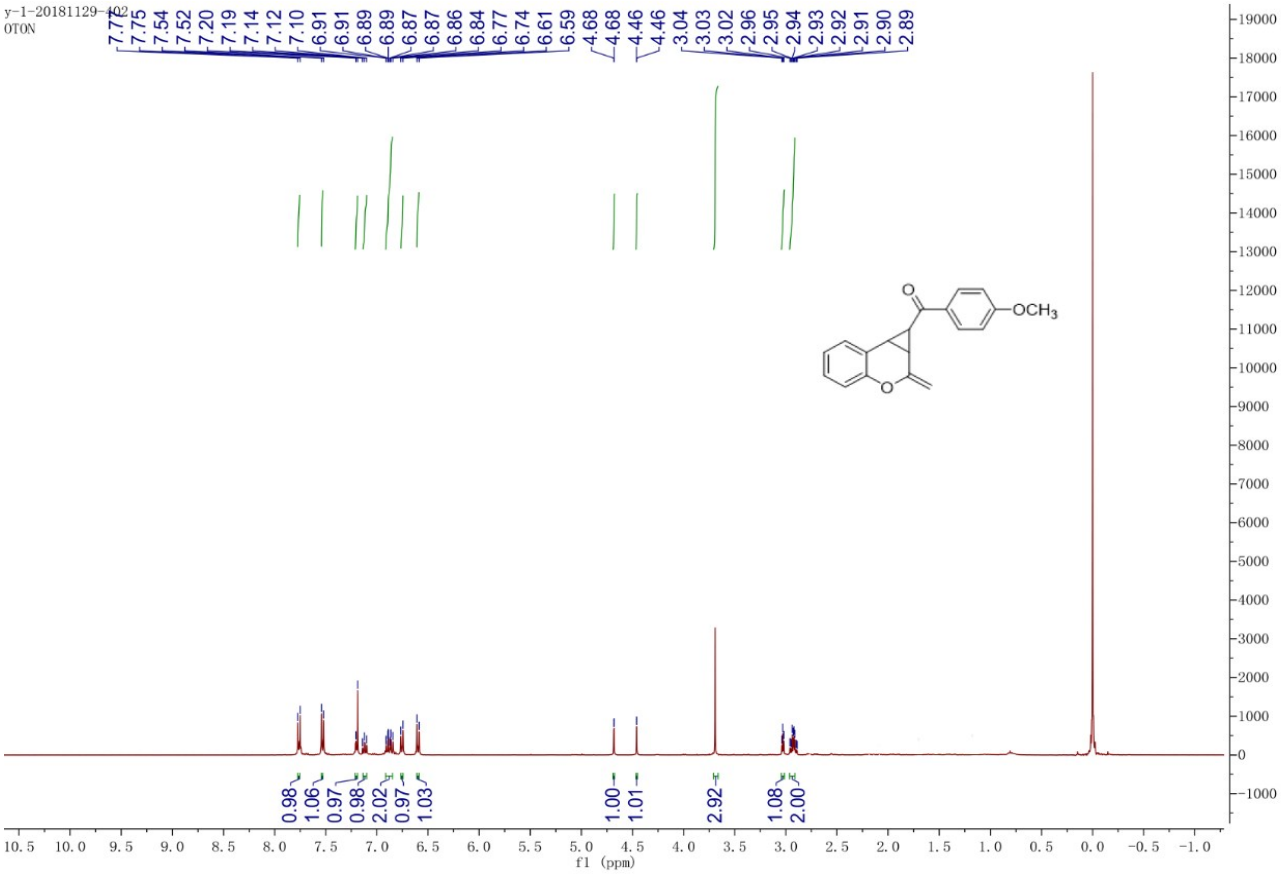


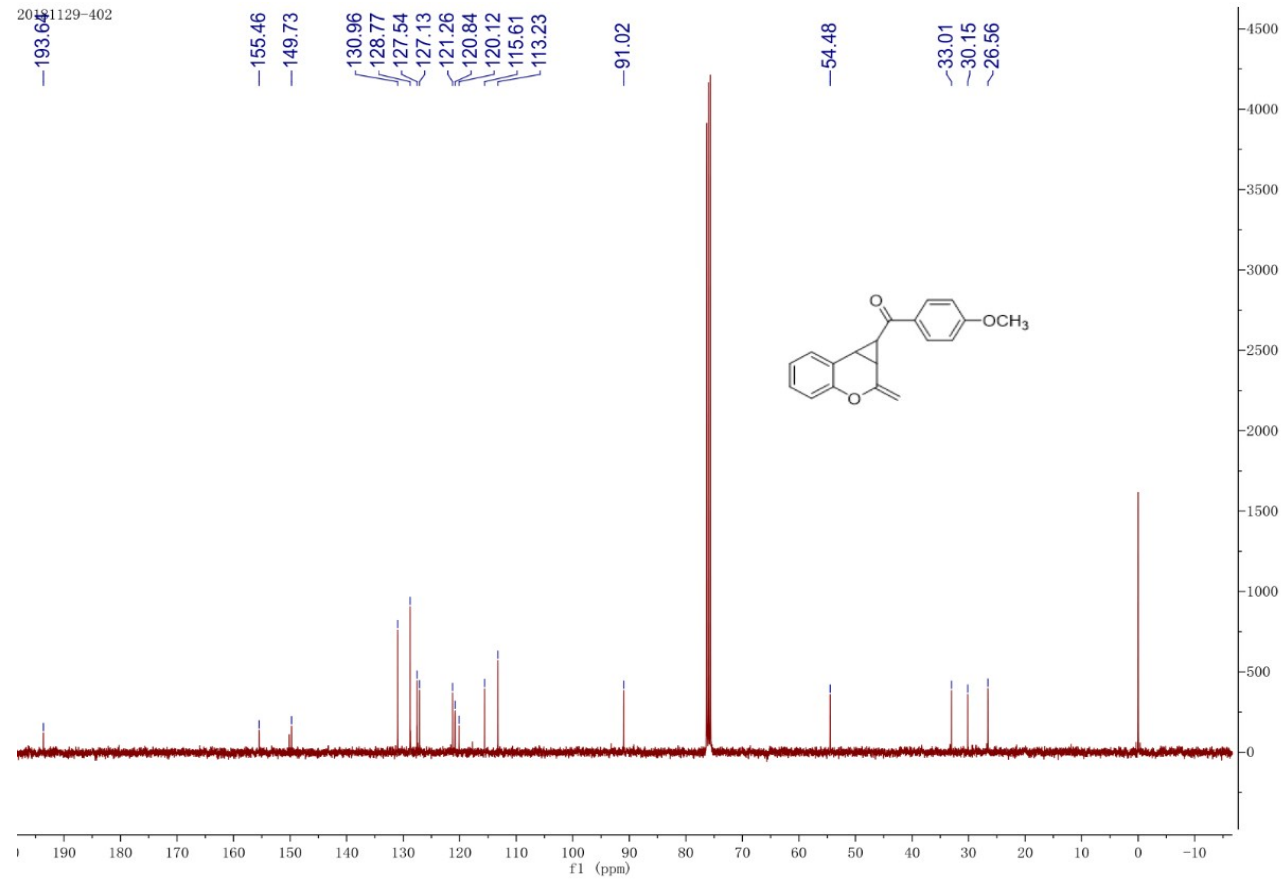
(6-Bromo-2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3i)



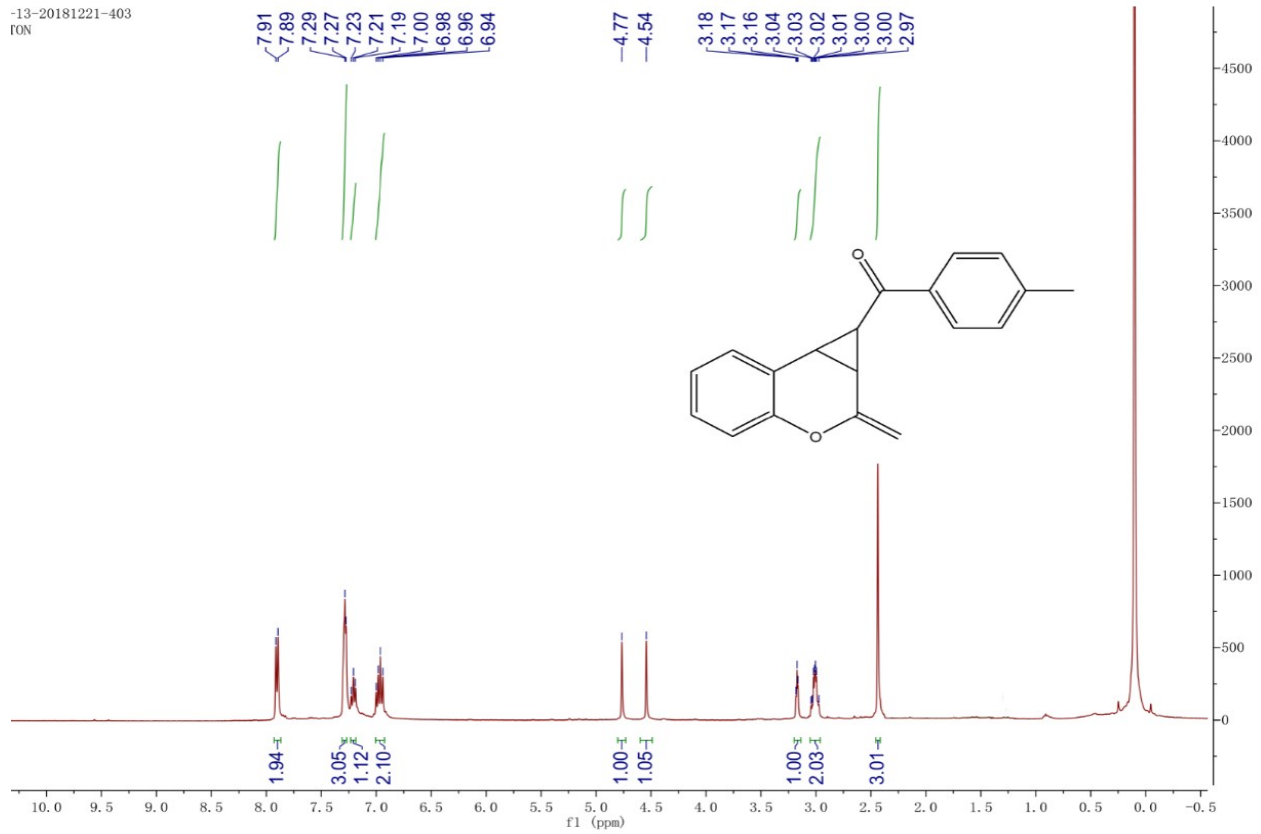


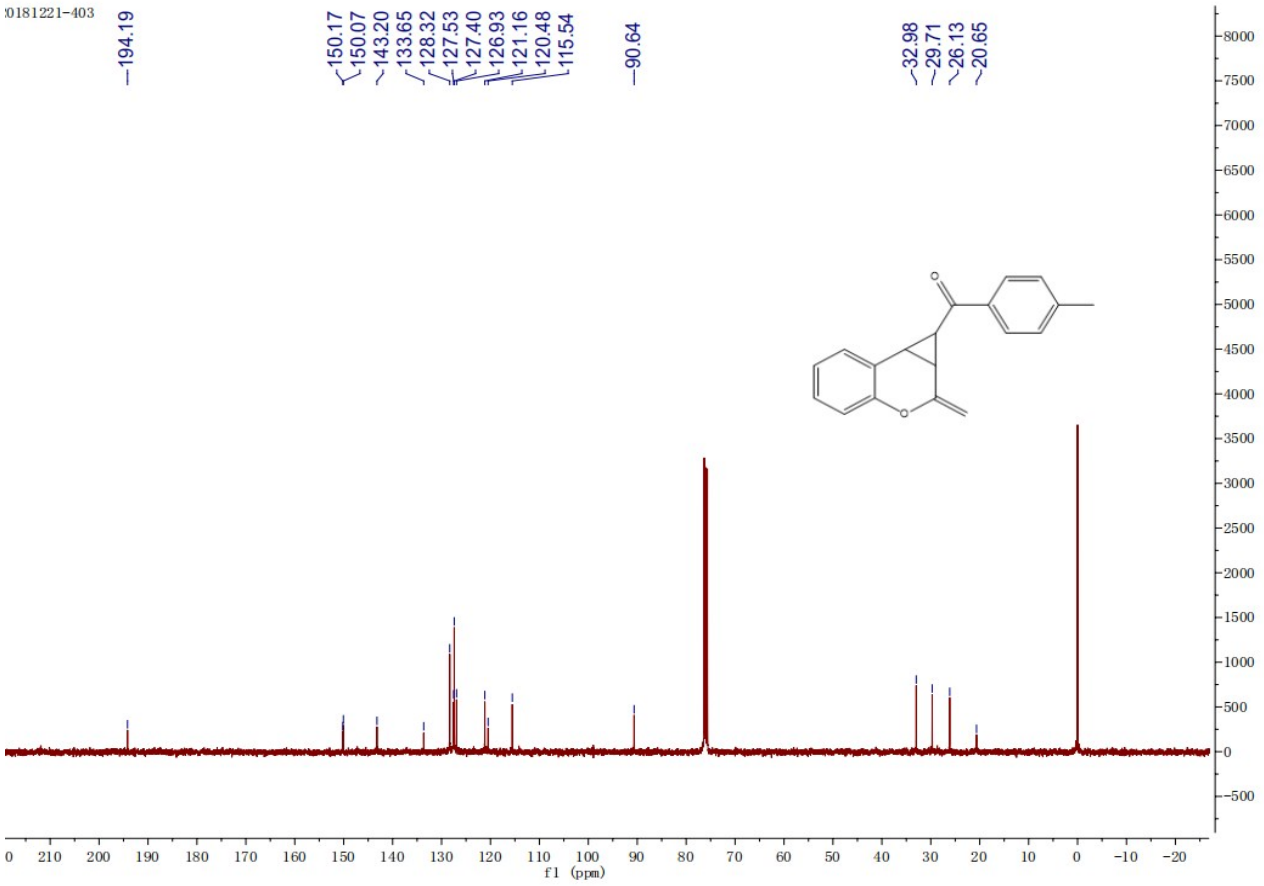
(4-Methoxyphenyl)(2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)methanone (3j)



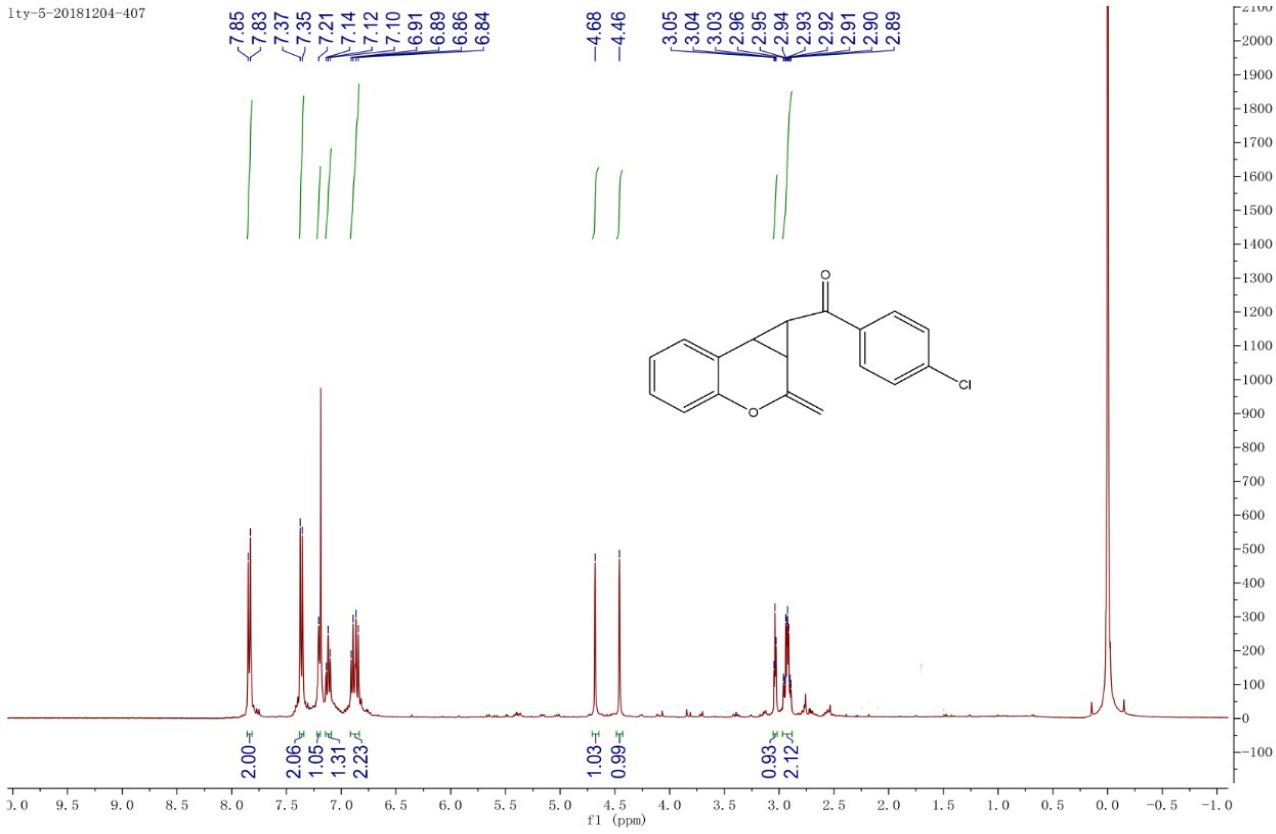


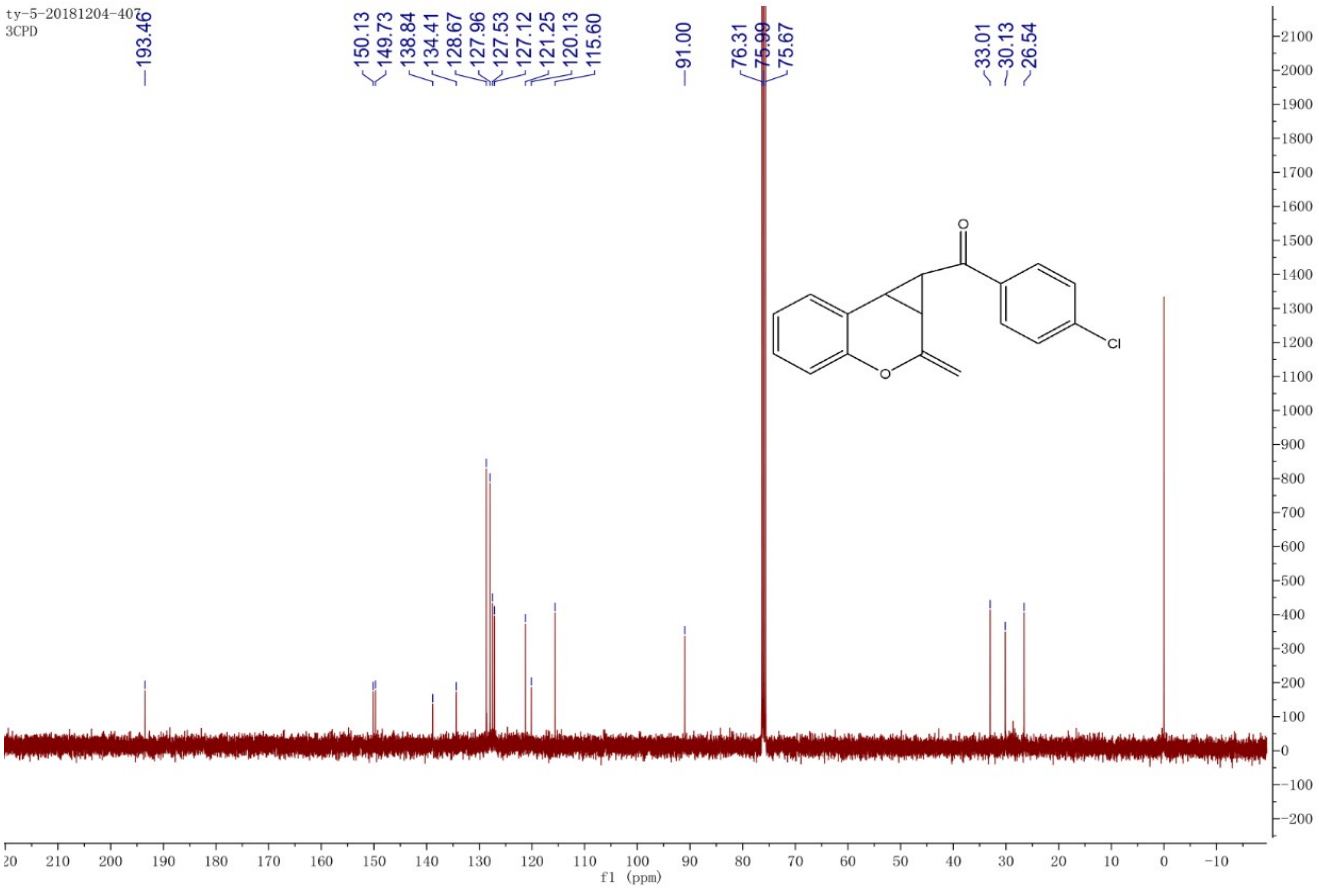
(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(p-tolyl)methanone (3k)



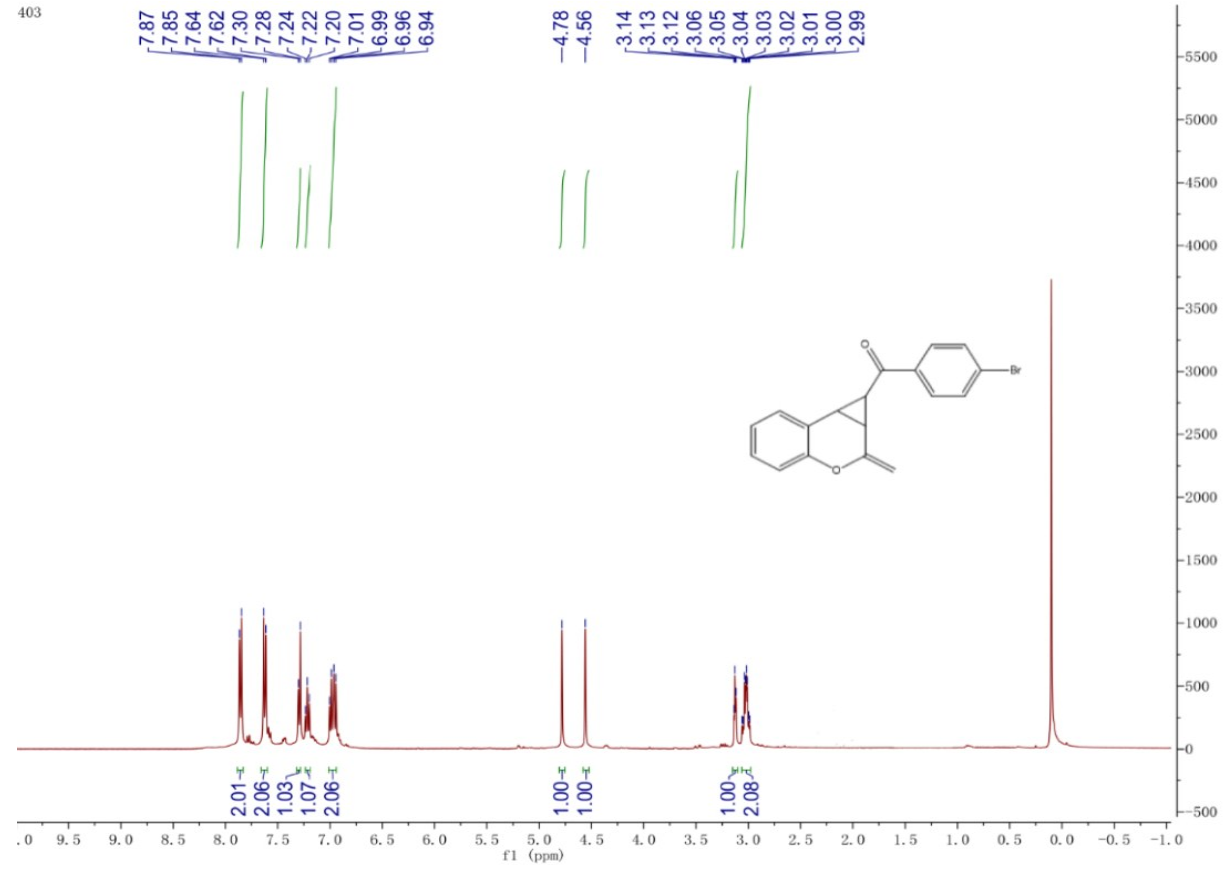


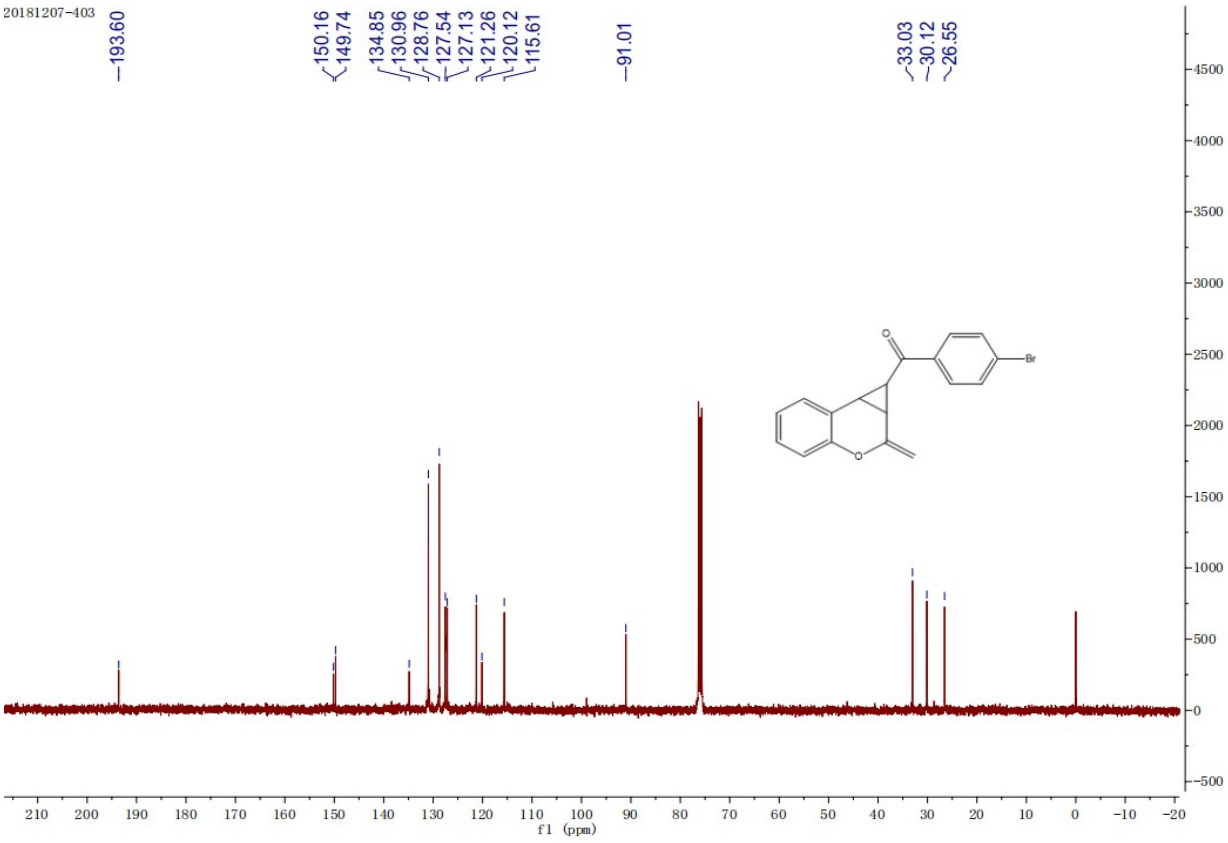
(4-Chlorophenyl)(2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)methanone (3l)



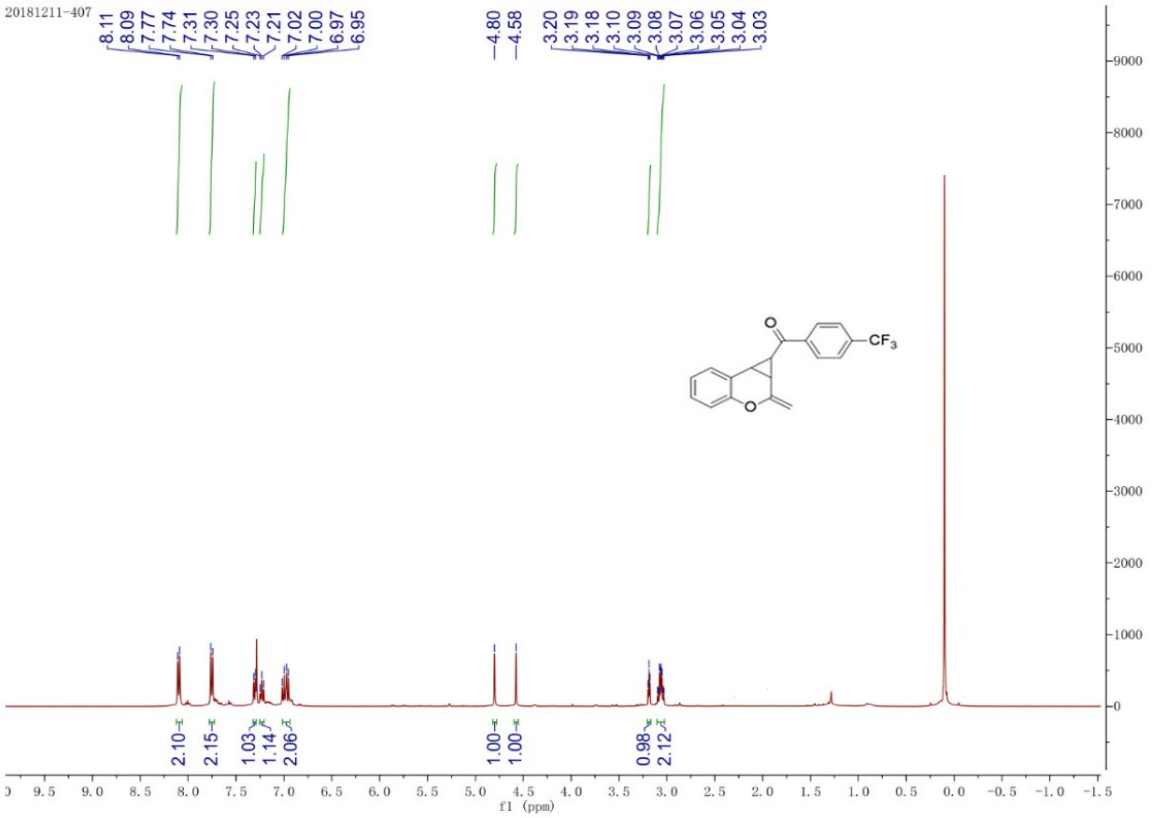


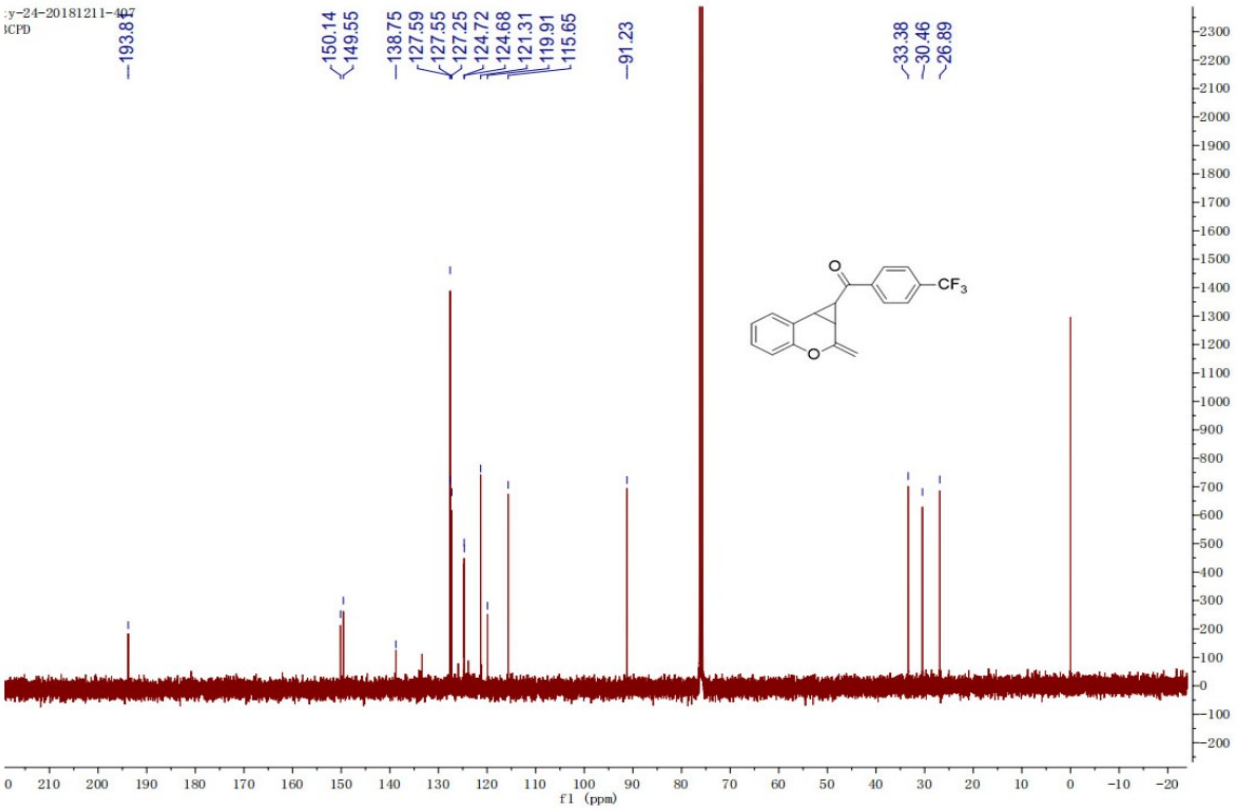
(4-Bromophenyl)(2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)methanone (3m)



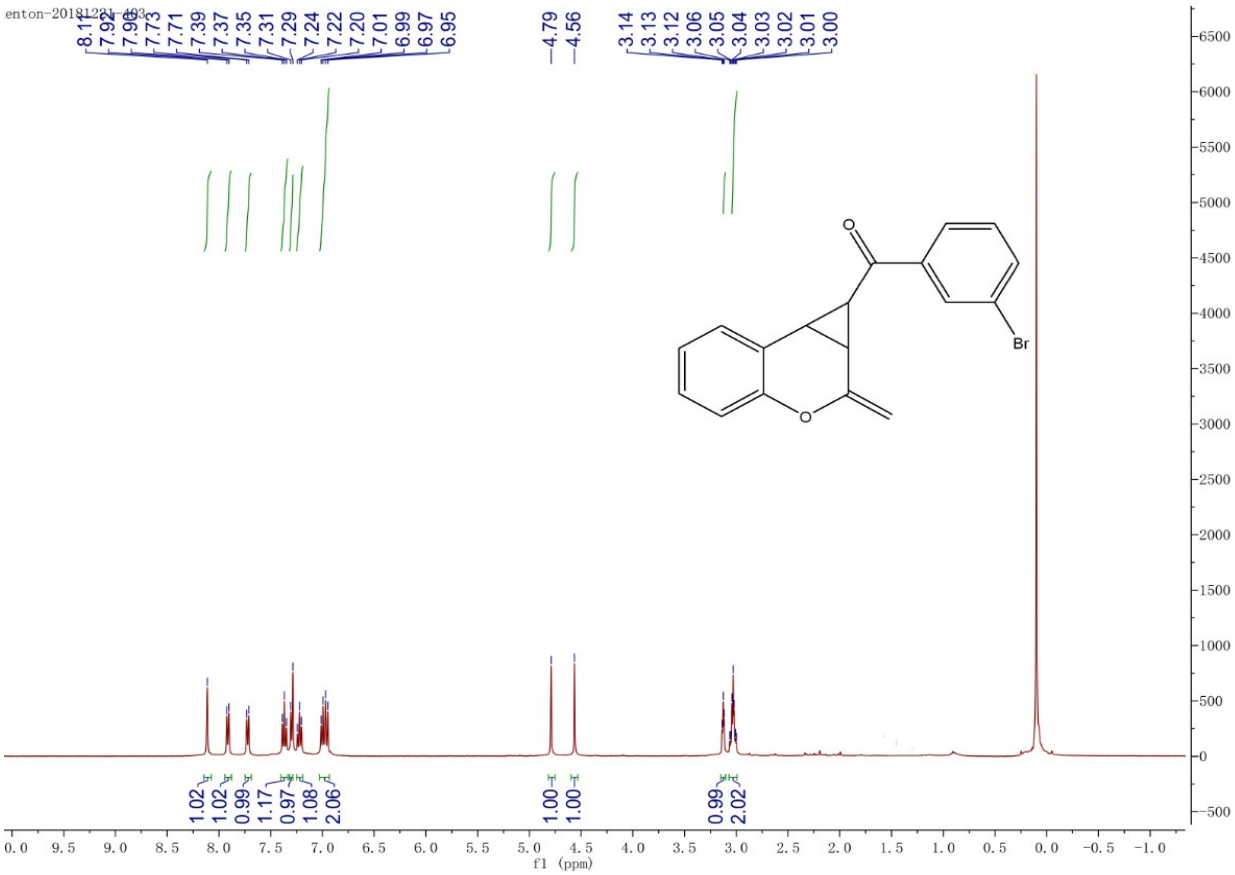


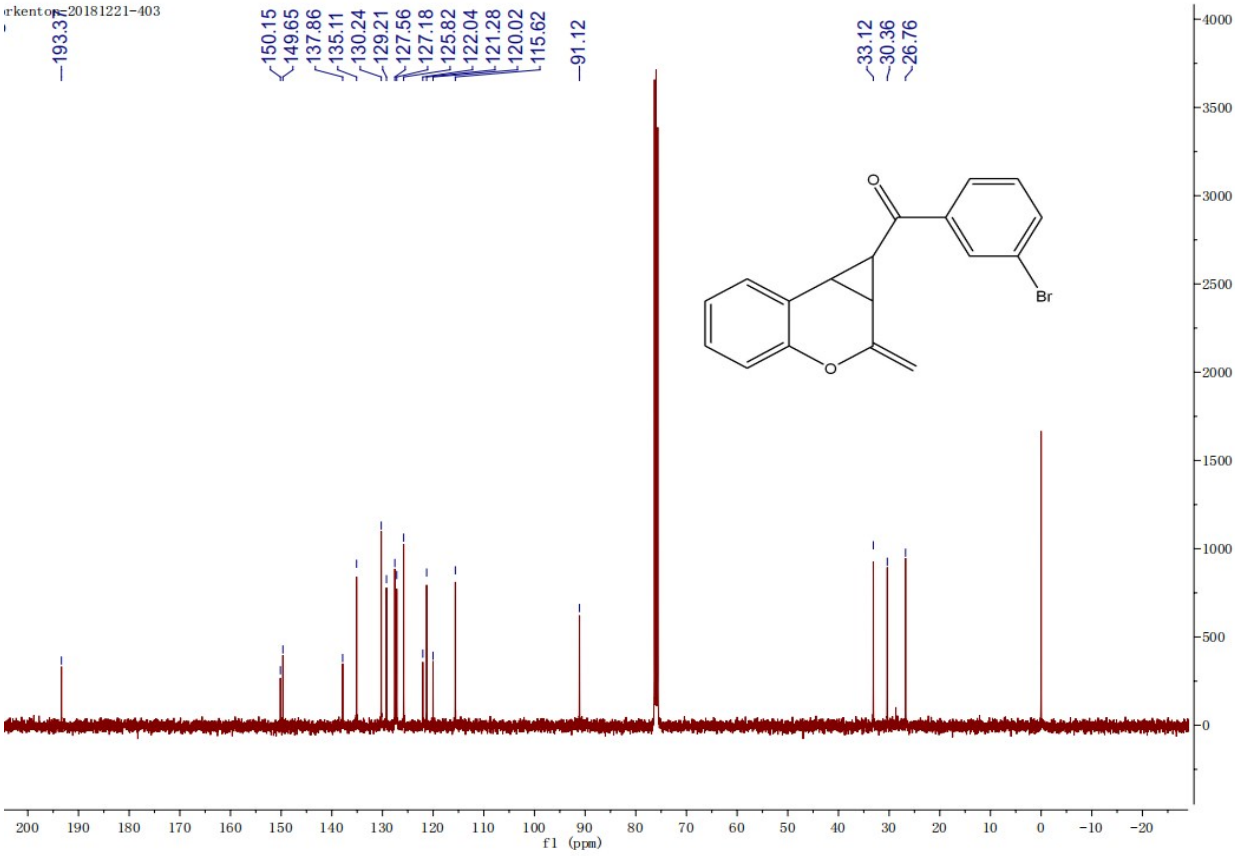
(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(4-(trifluoromethyl)phenyl) methanone (3n)



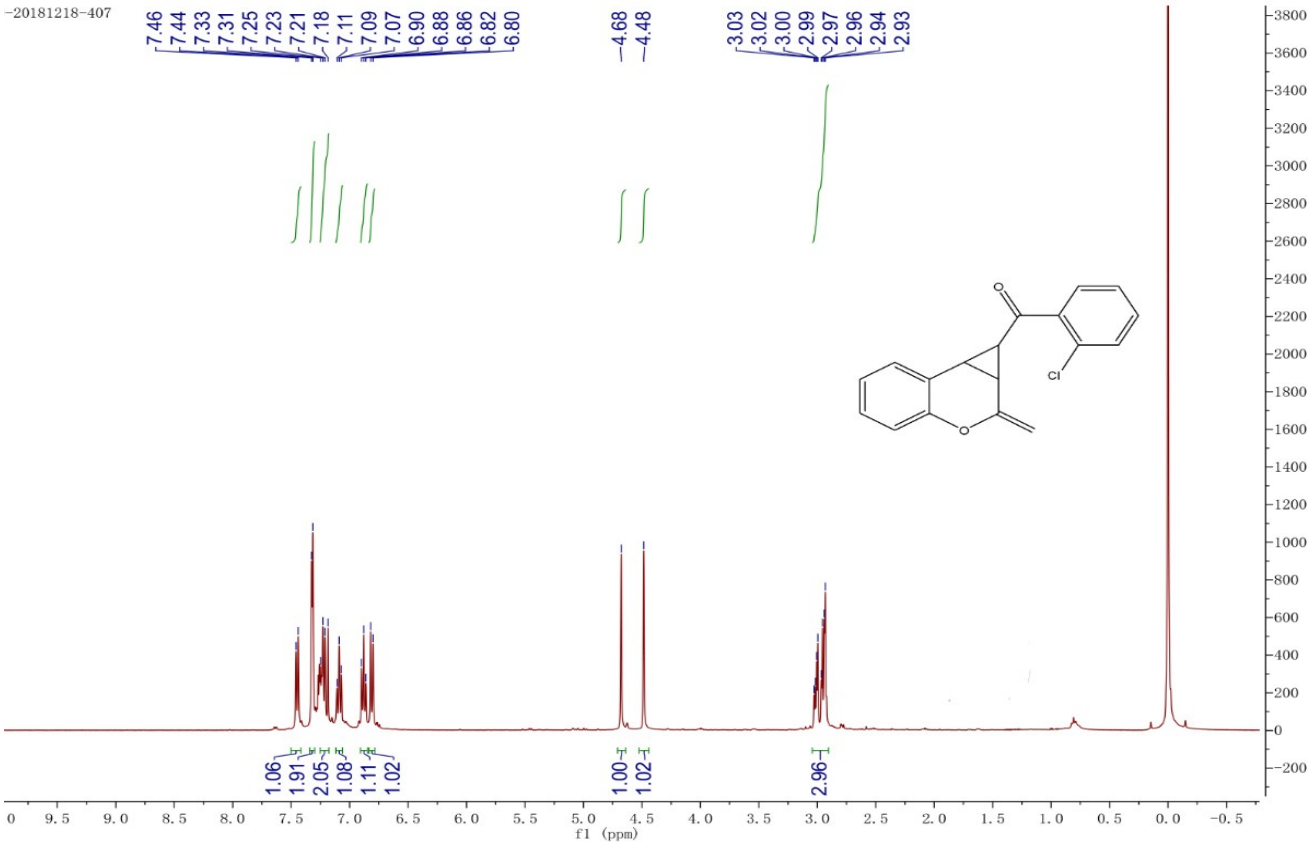


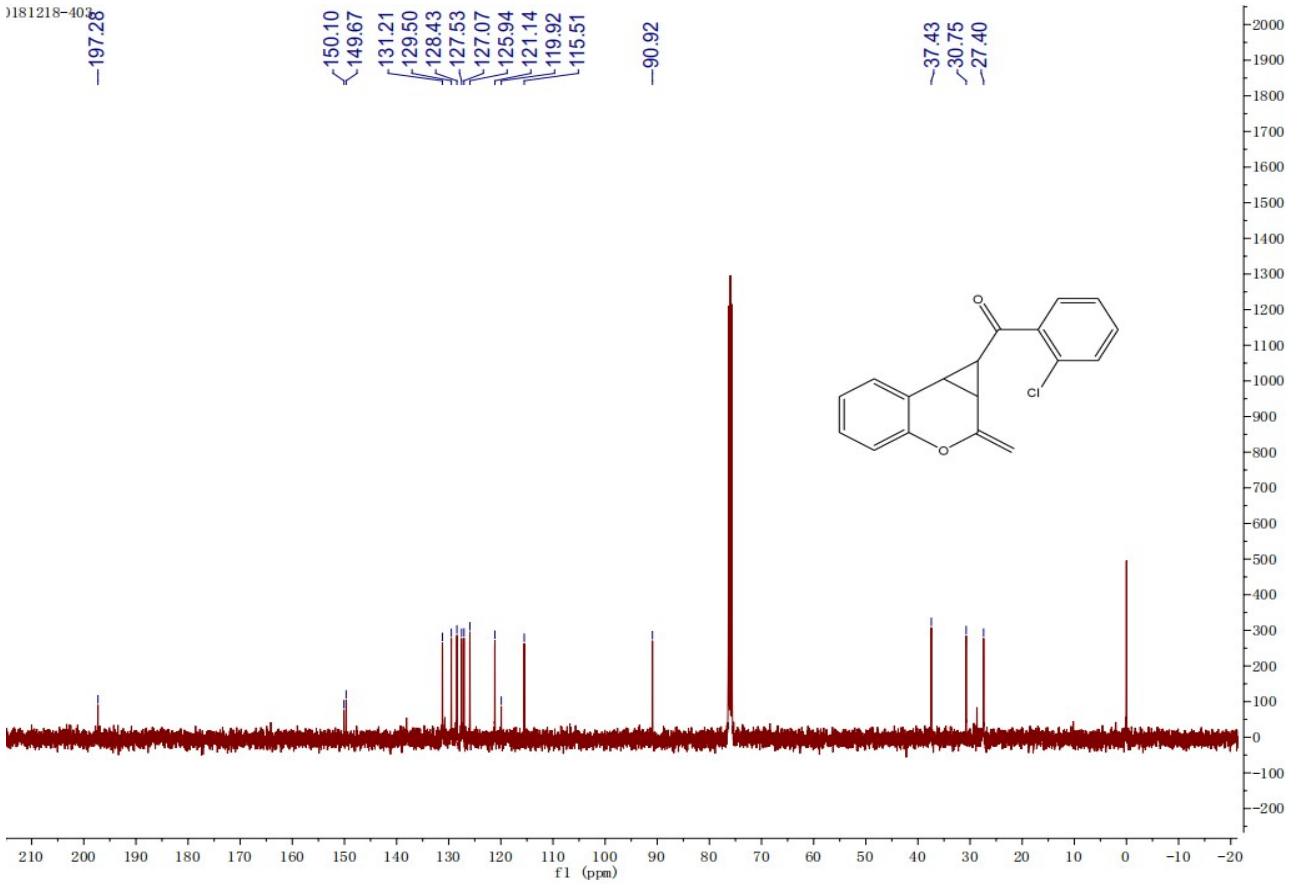
(3-Bromophenyl)(2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)methanone (3o)



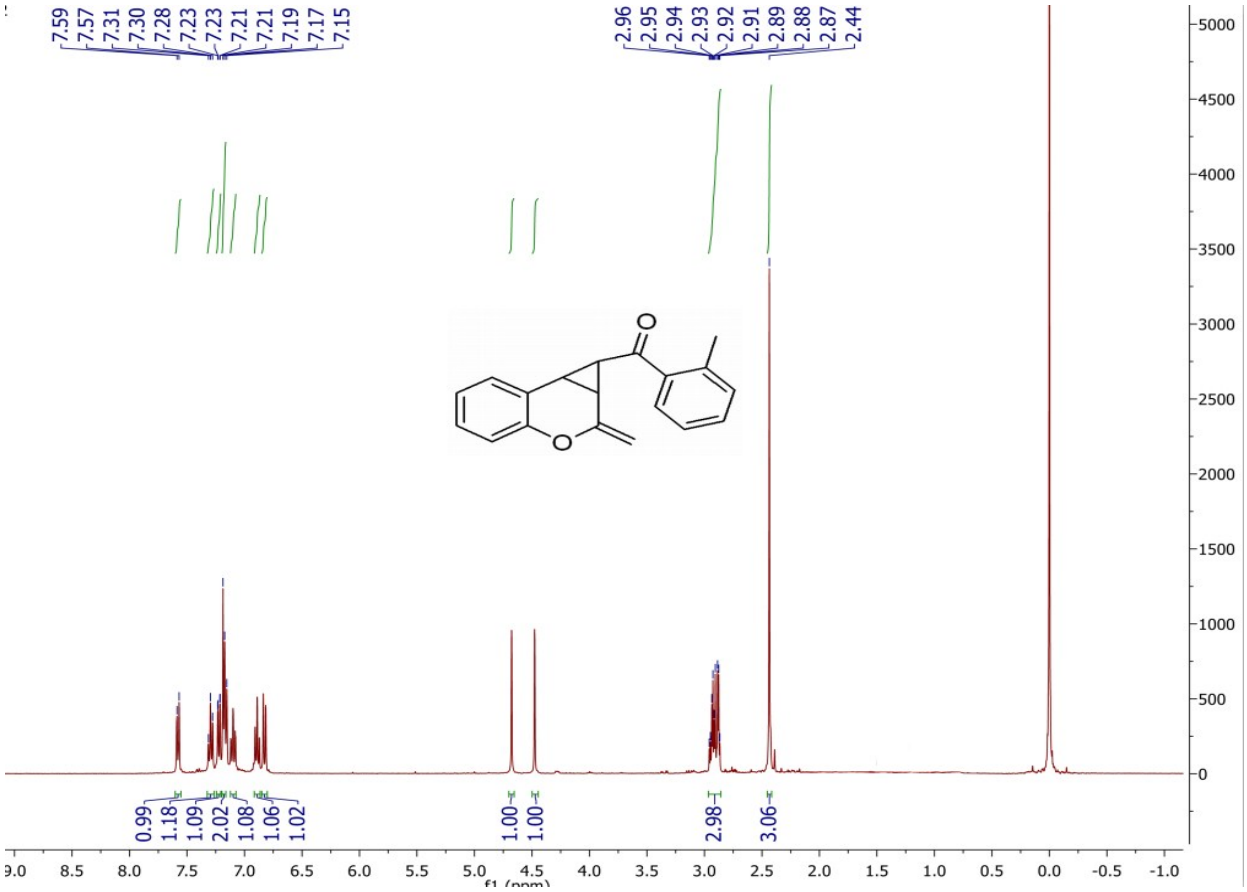


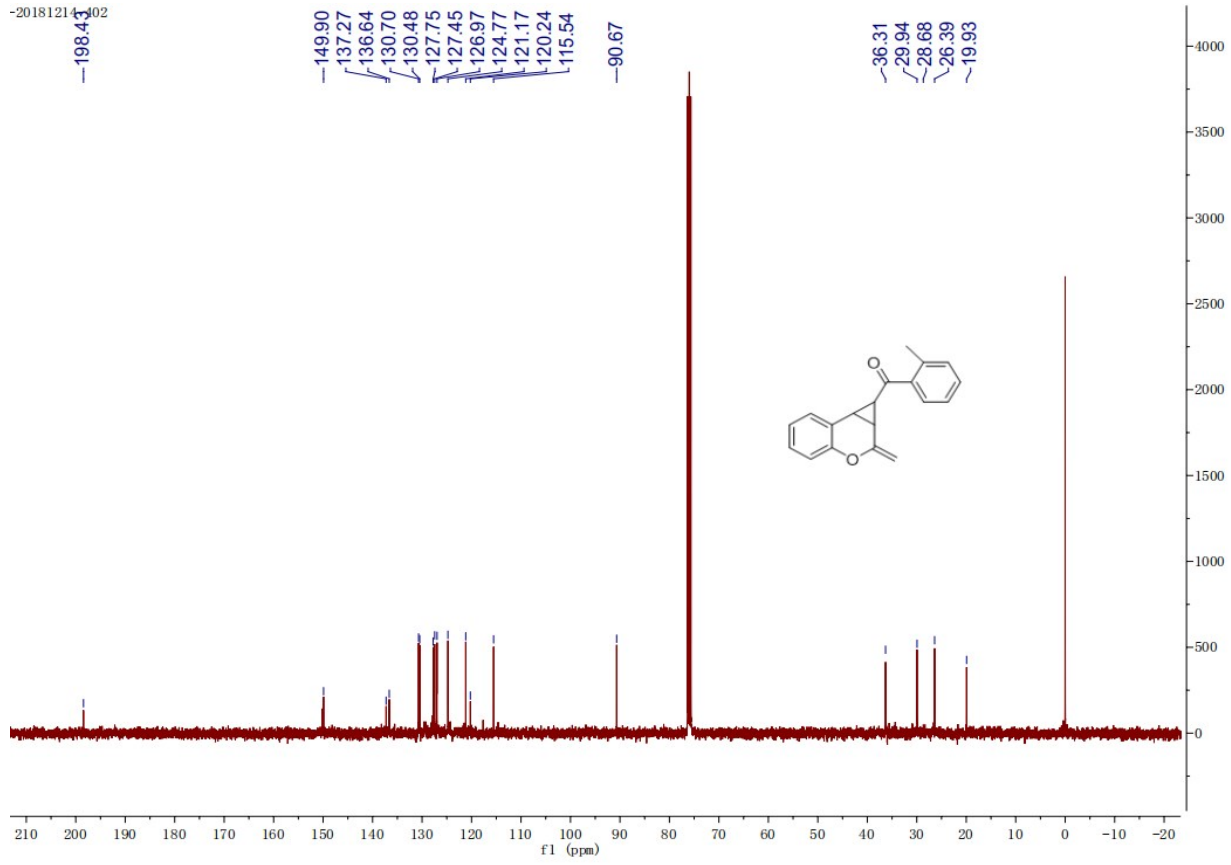
(2-Chlorophenyl)(2-methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)methanone (3p)



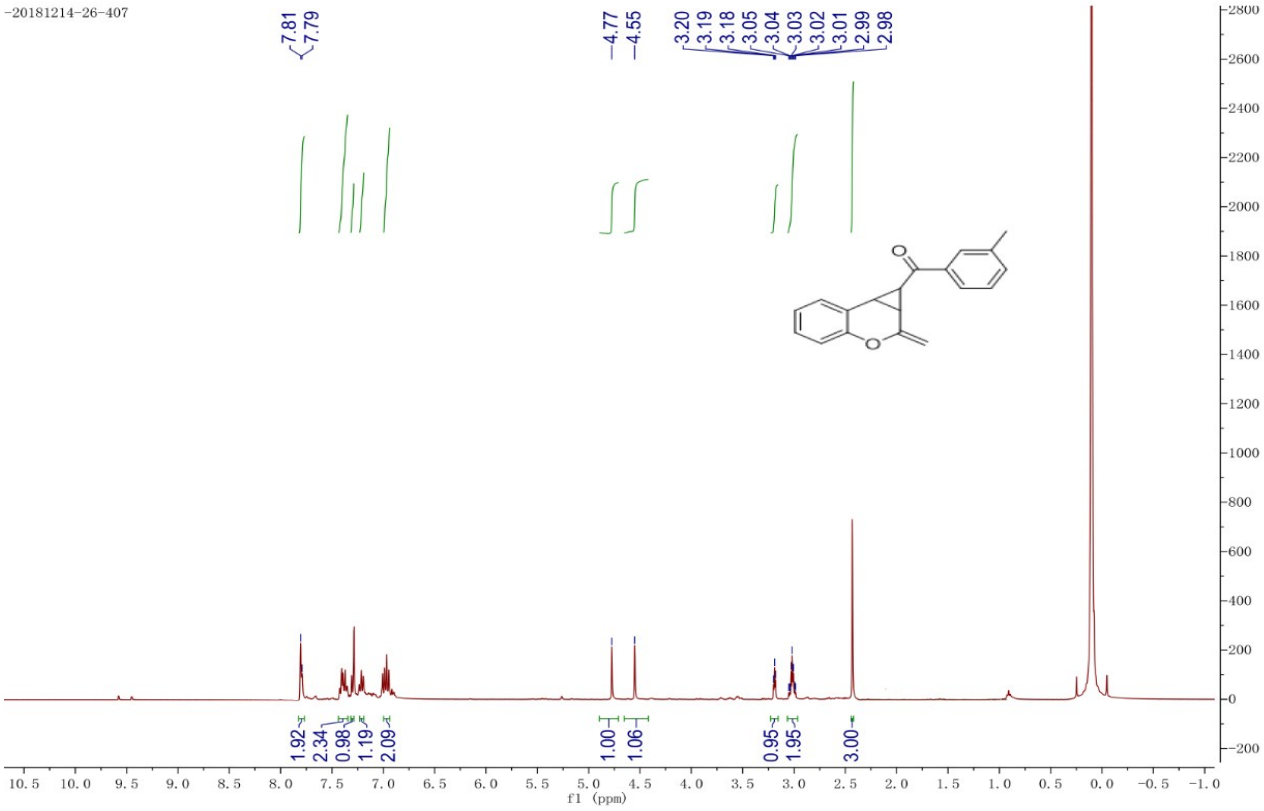


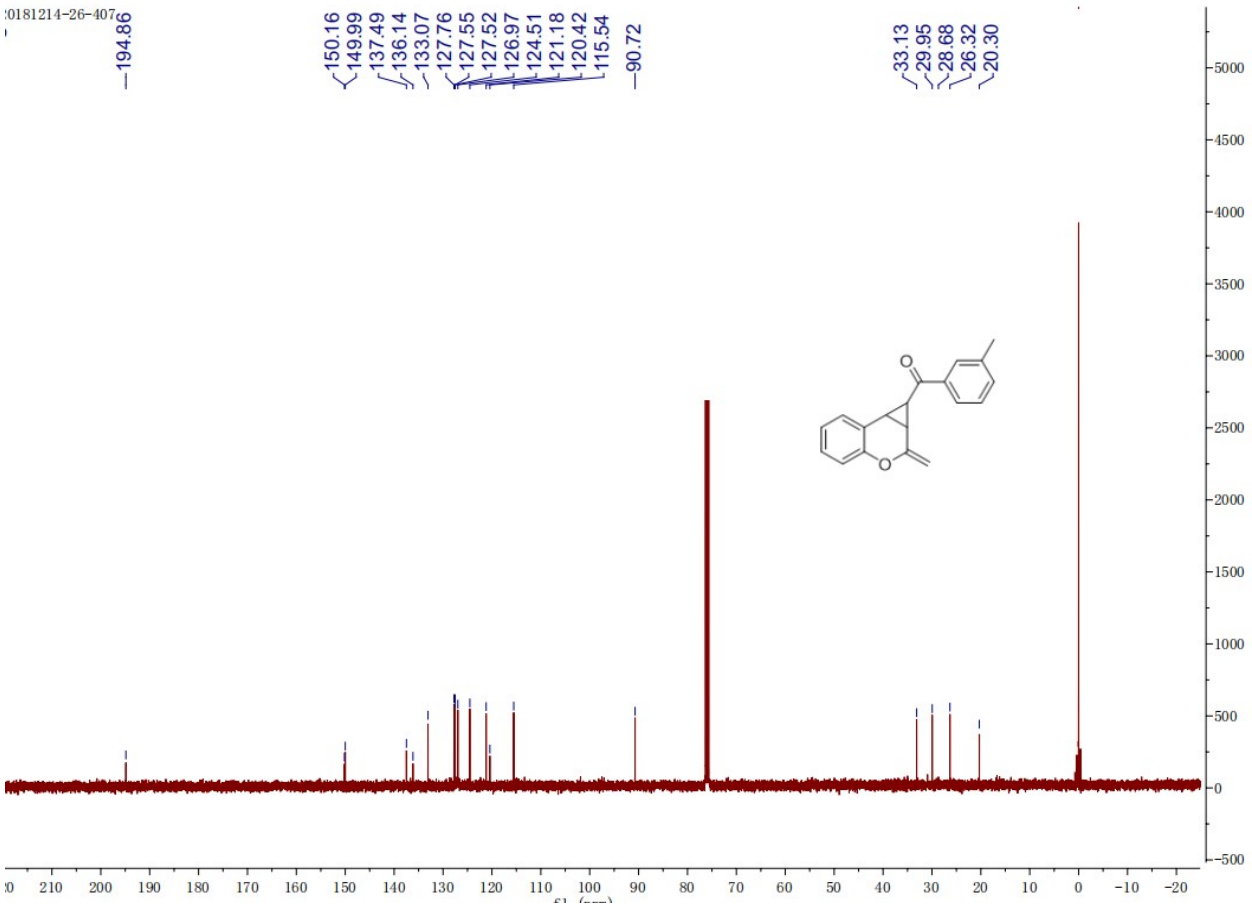
(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(o-tolyl)methanone (3q)



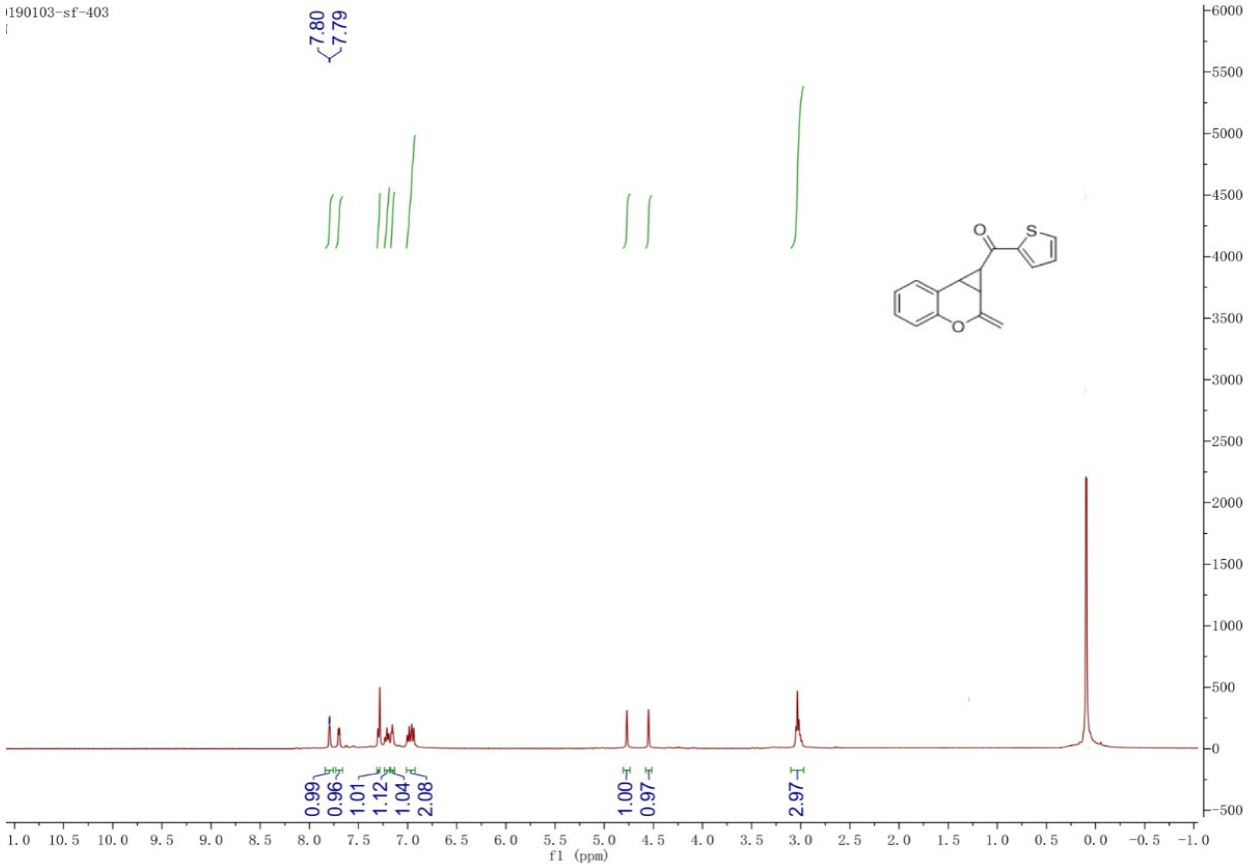


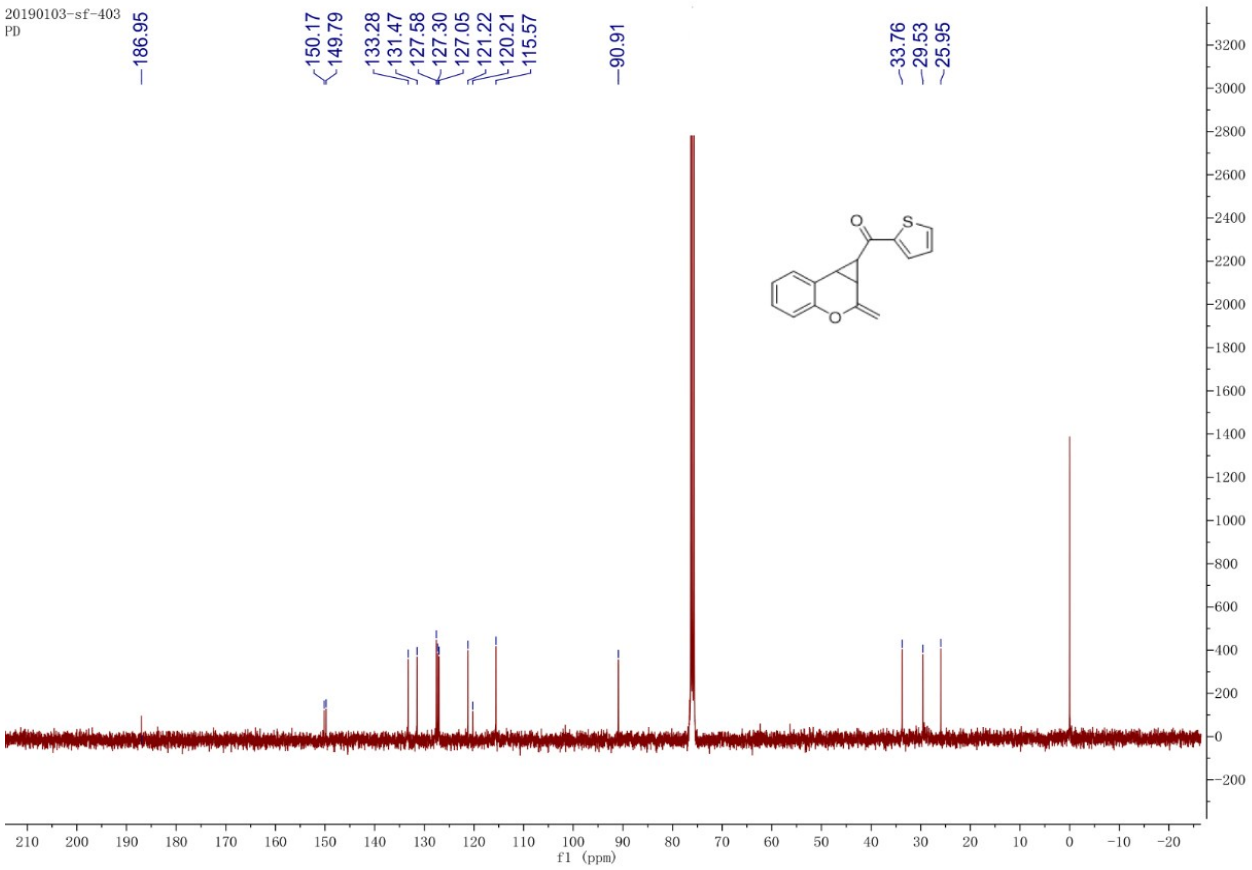
(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(m-tolyl)methanone (3r)





(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(thiophen-2-yl)methanone (3s)





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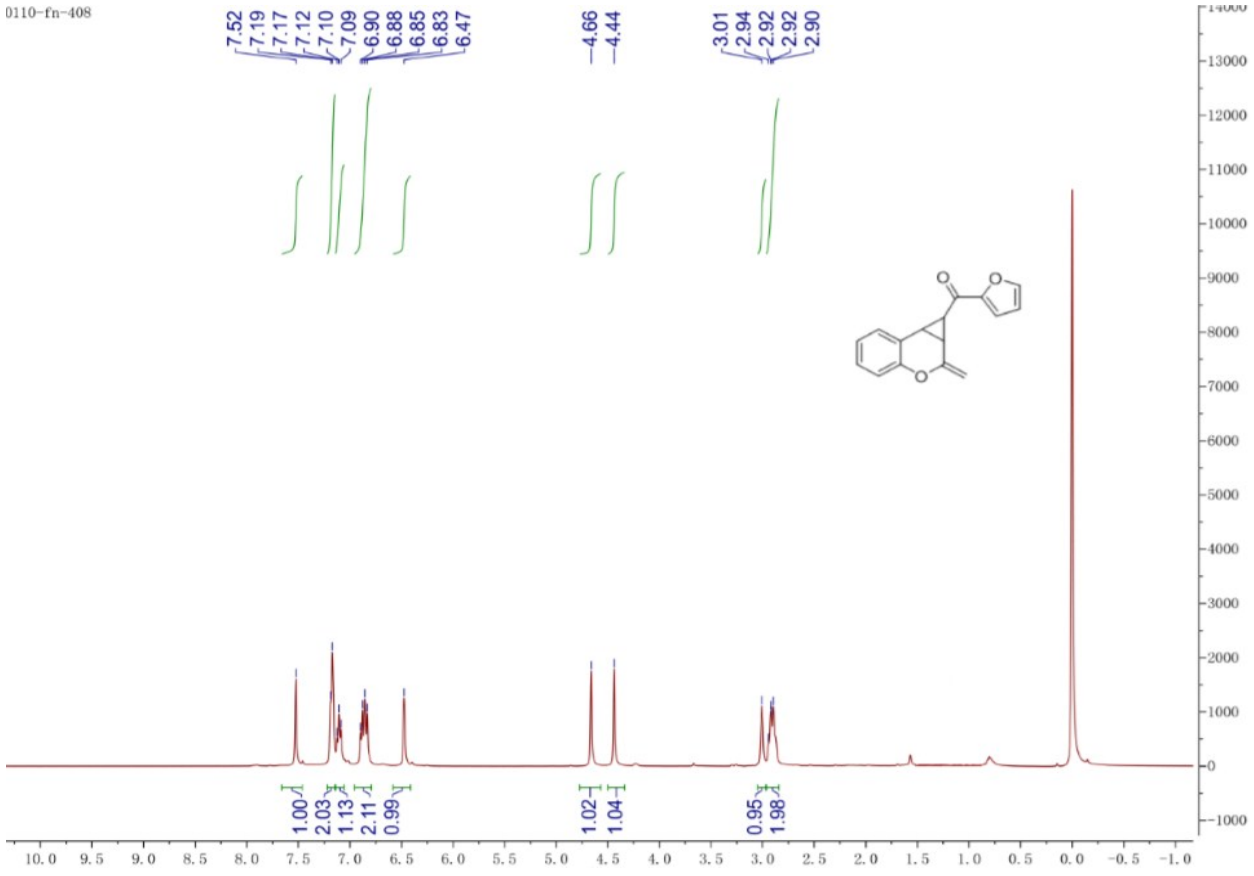
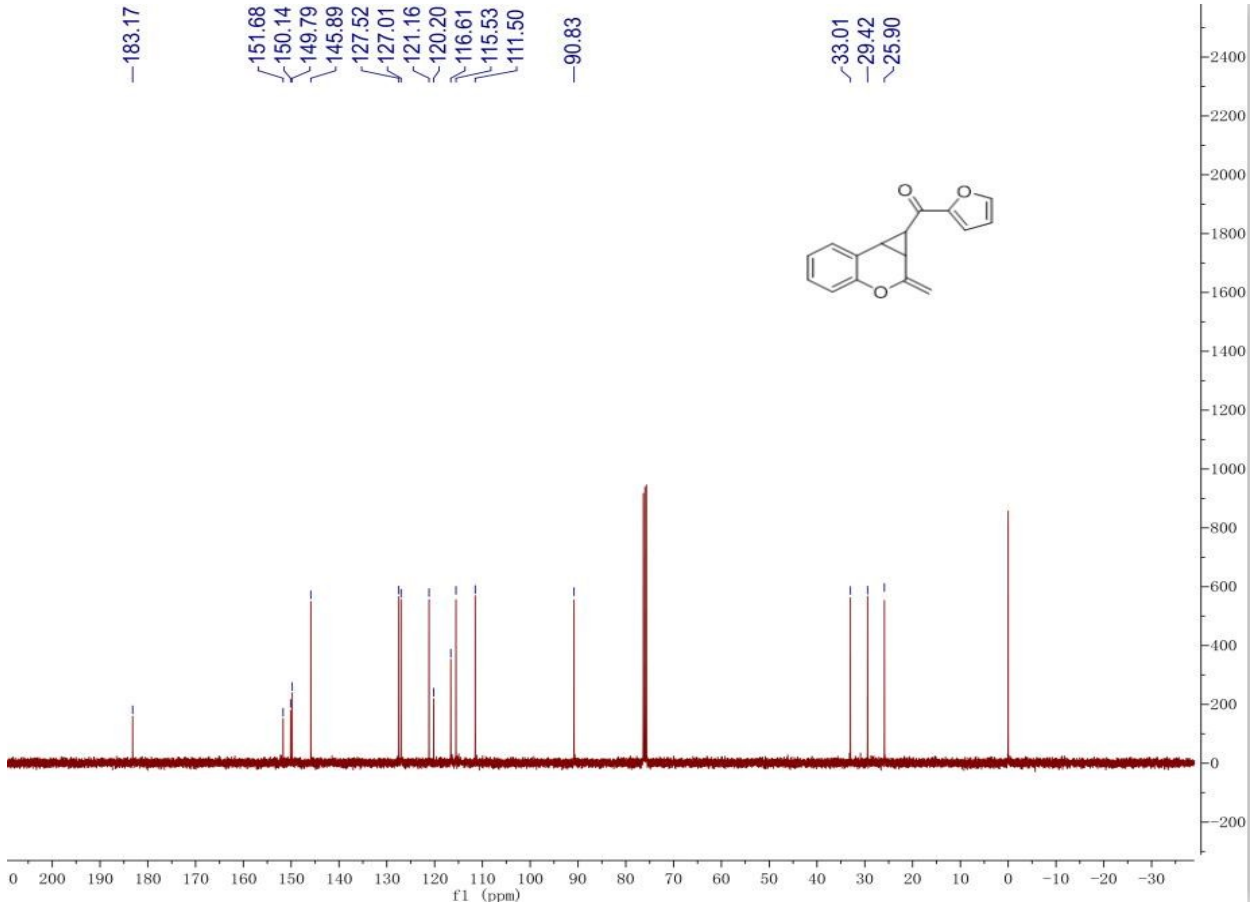
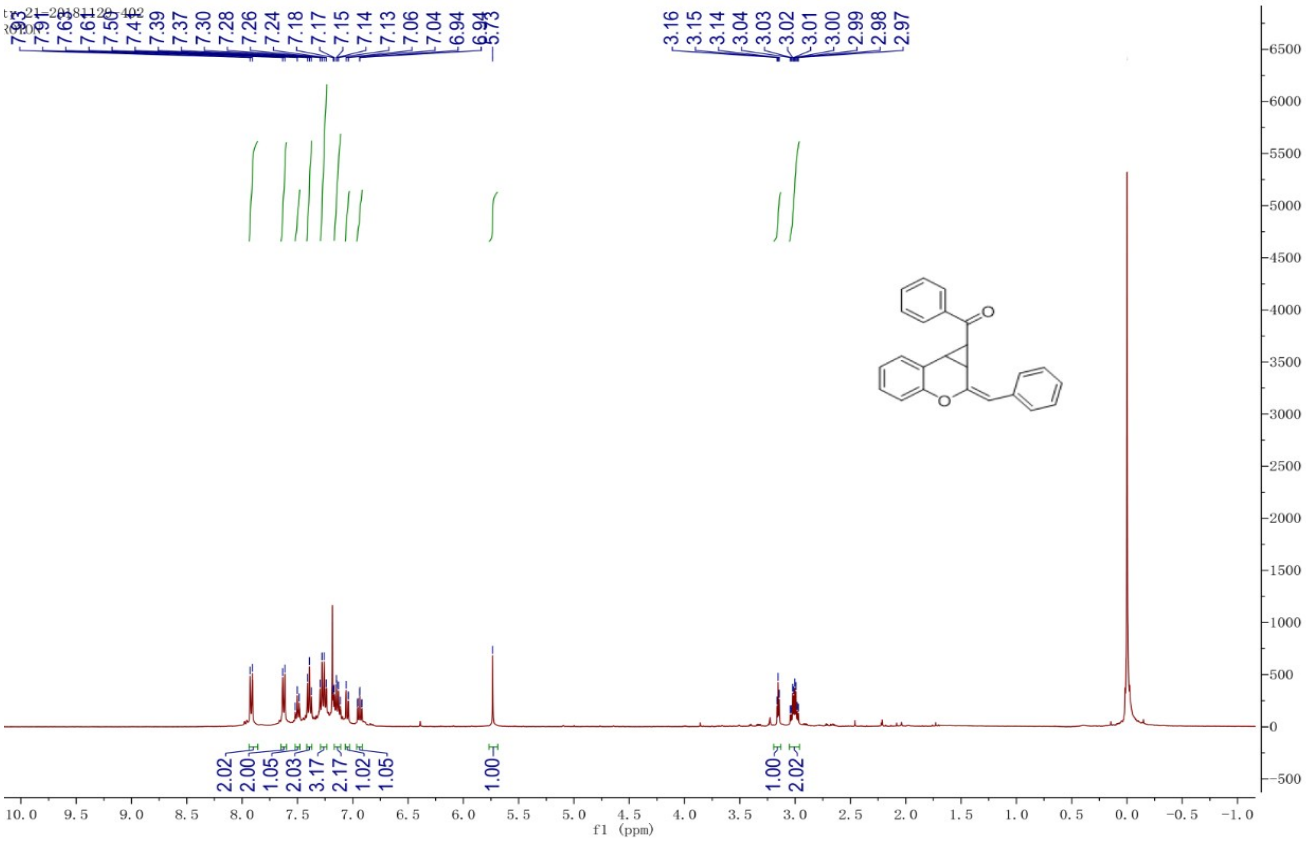
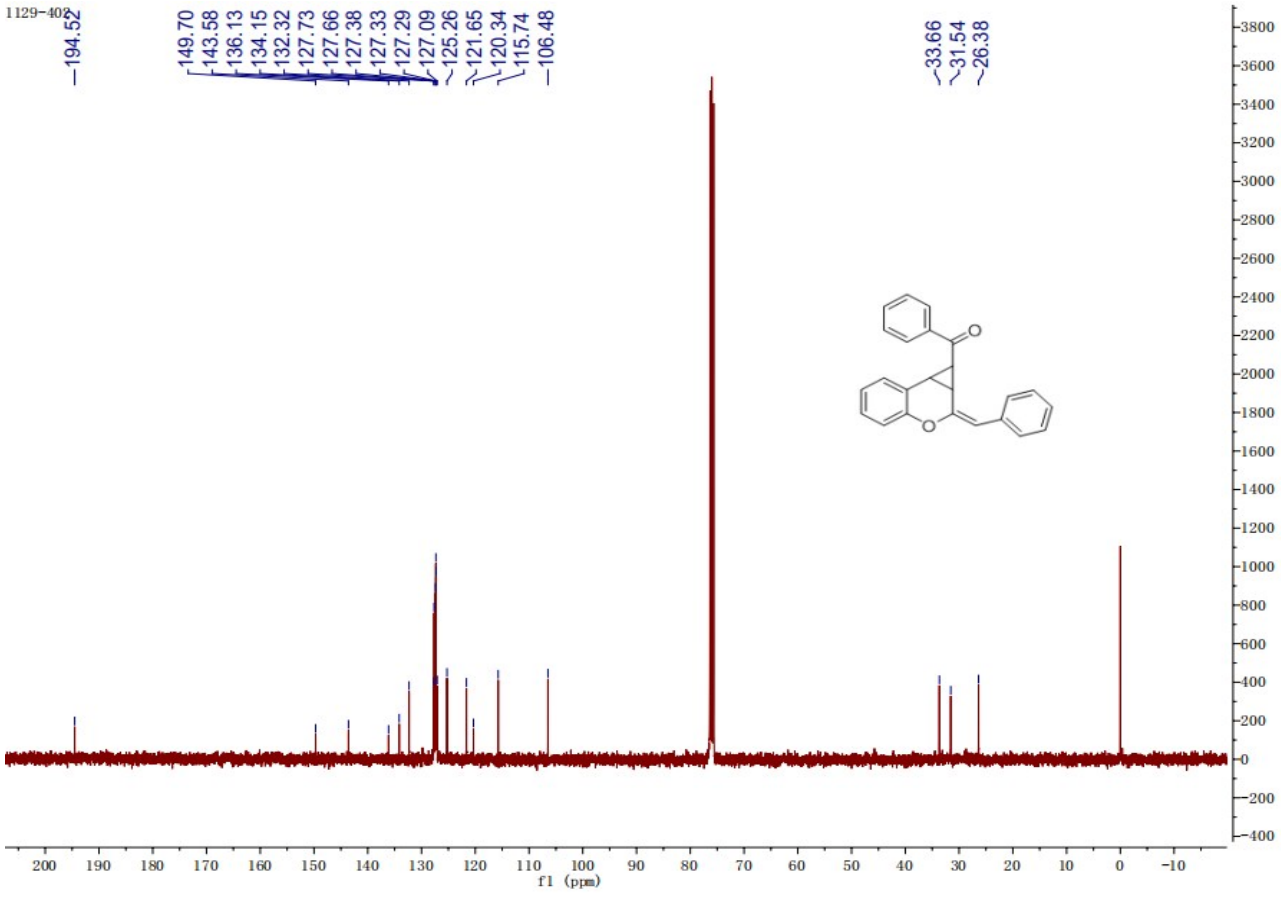


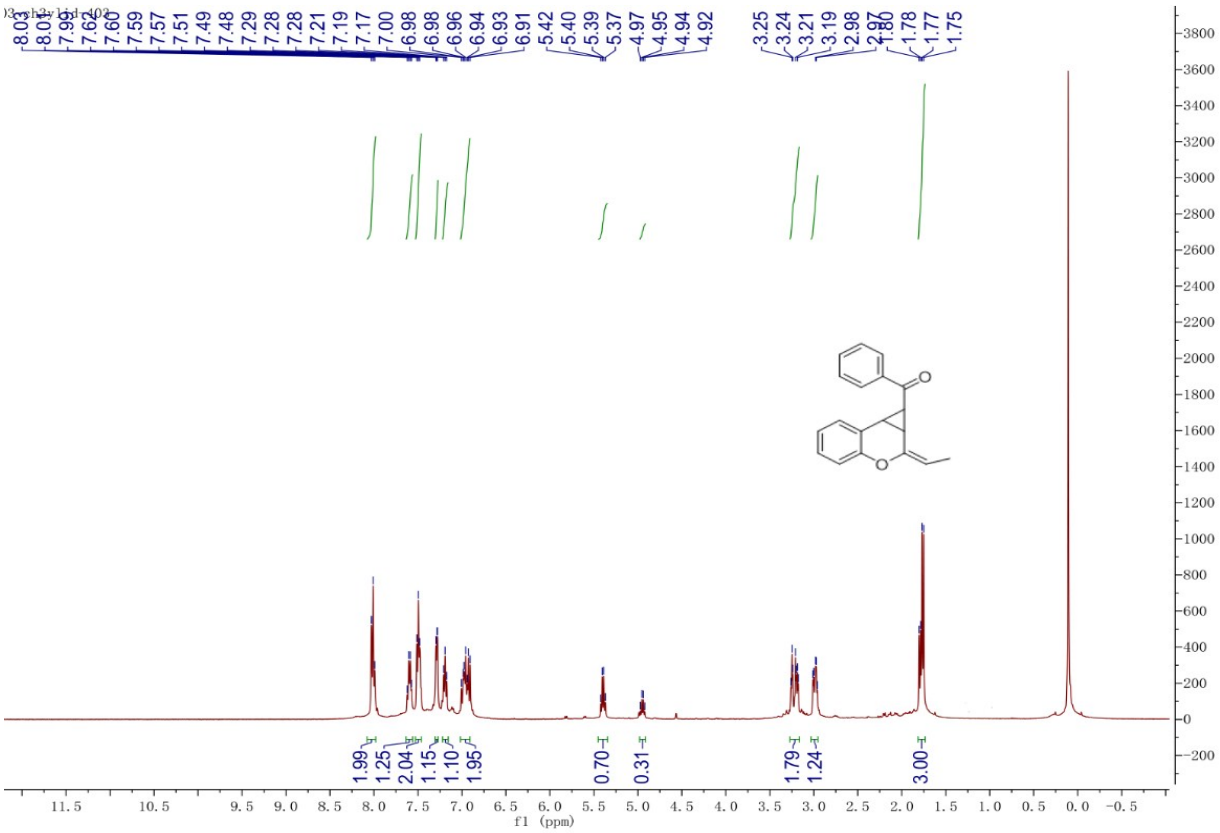


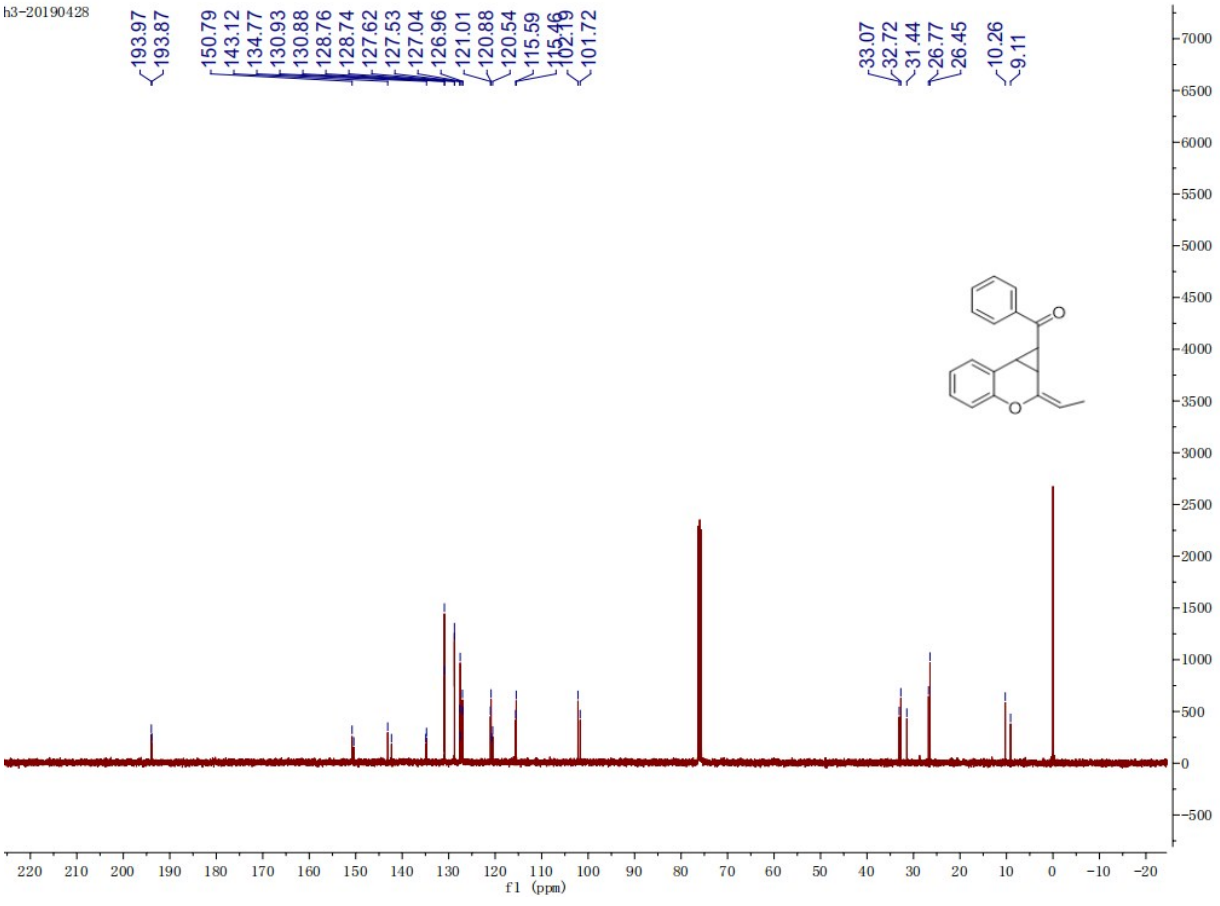
(2-Benzylidene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3u)





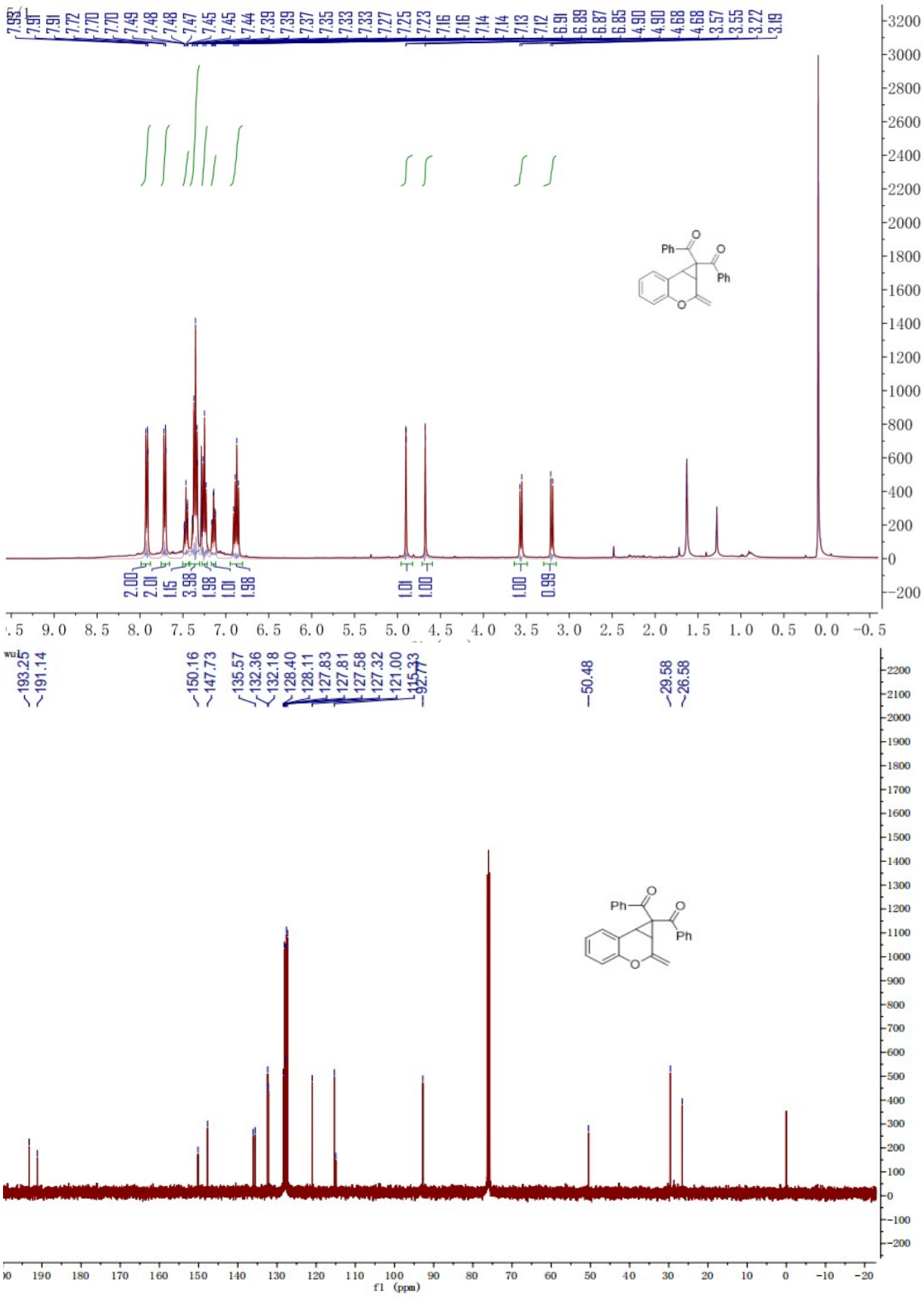
(2-Ethylidene-1,1a,2,7b-tetrahydrocyclopropa[c]chromen-1-yl)(phenyl)methanone (3v)



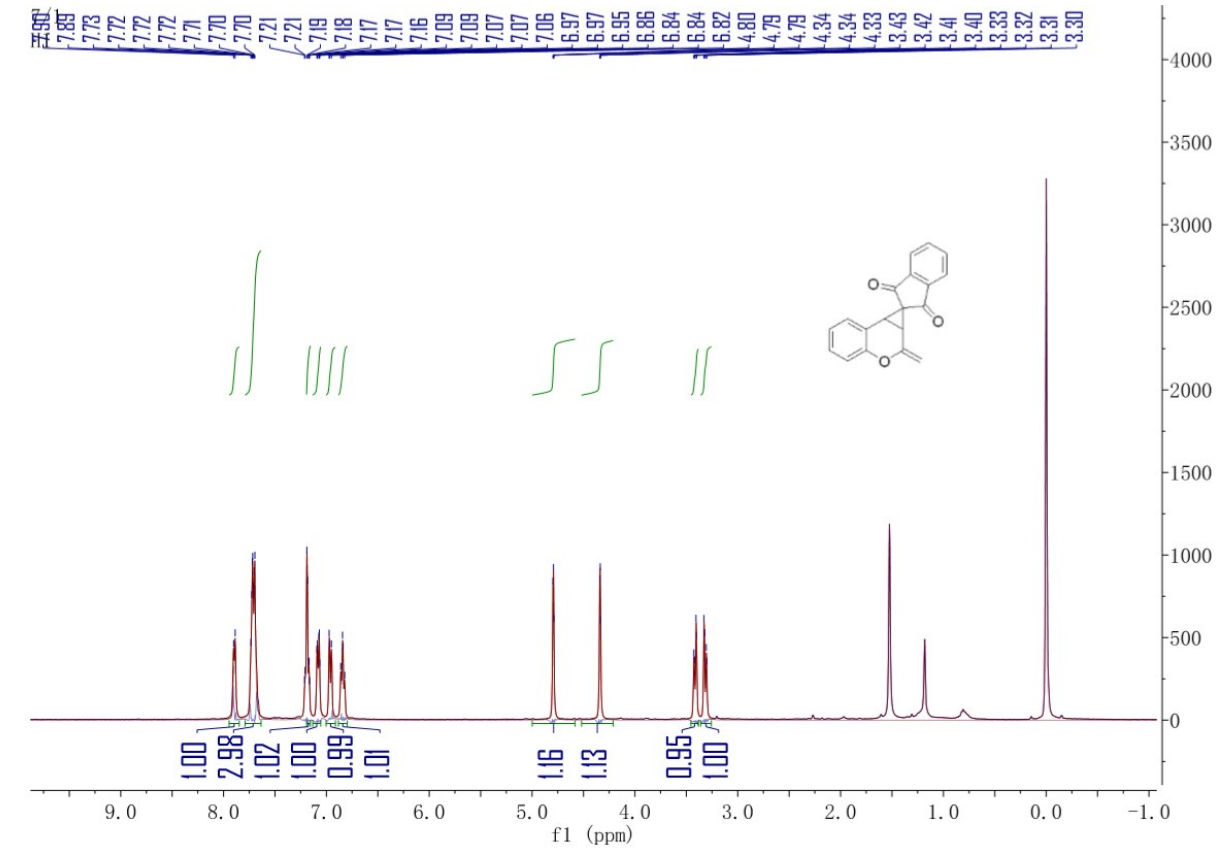


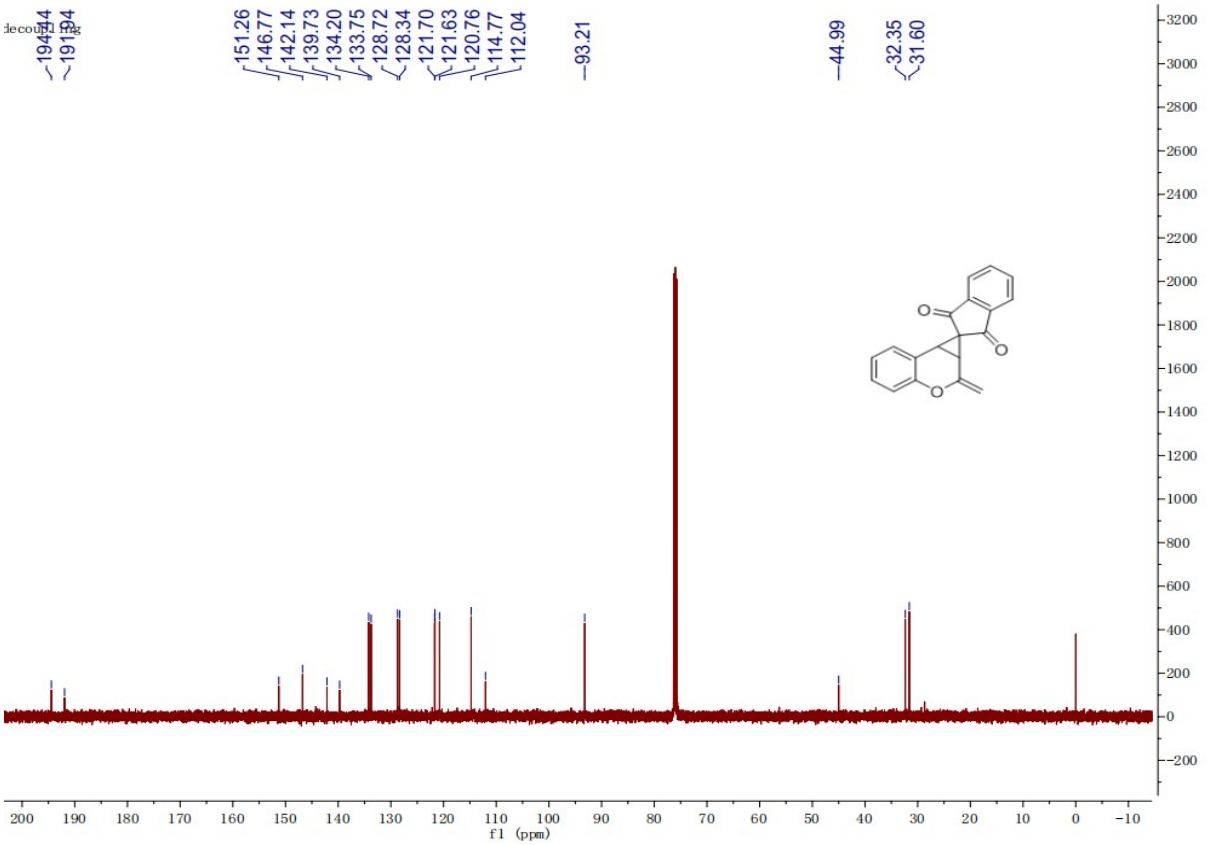
Copy of ^{1}H NMR and ^{13}C NMR spectra of **5** and **7**

(2-Methylene-1,1a,2,7b-tetrahydrocyclopropa[c]chromene-1,1-diyl)bis(phenylmethanone) (5)



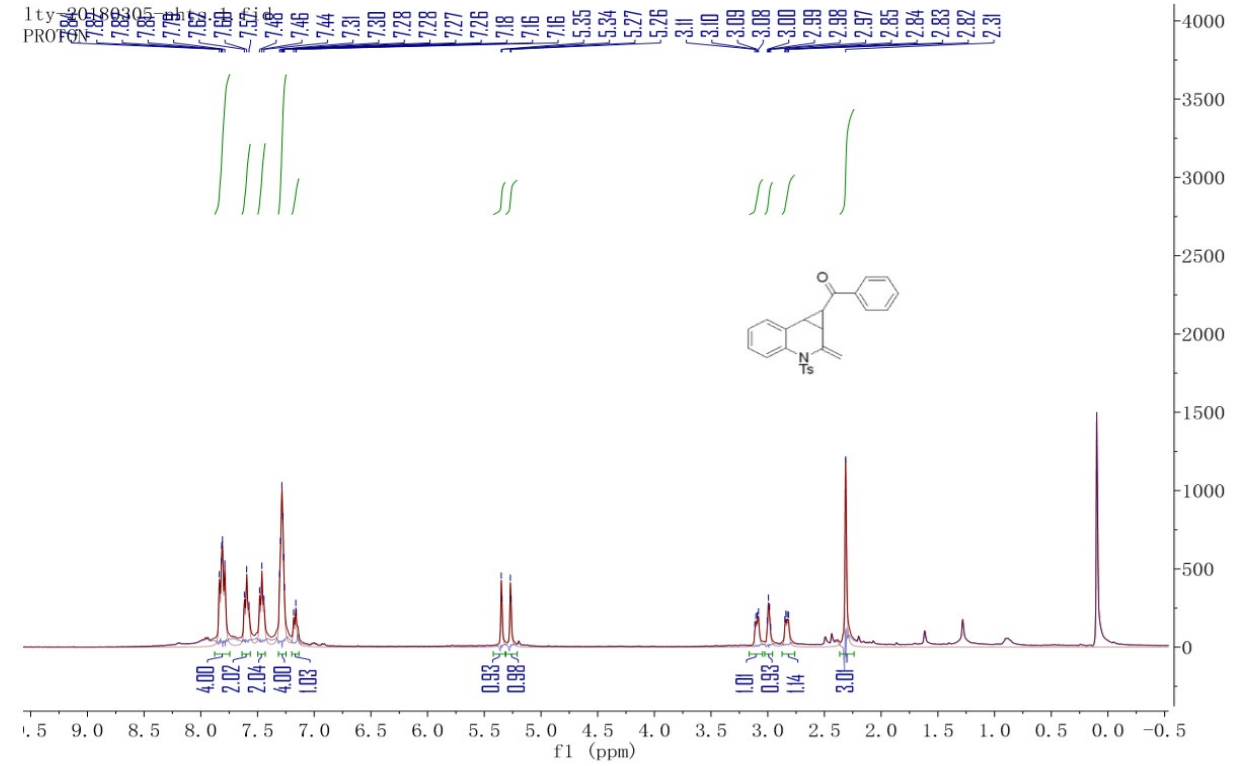
2-Methylene-1a,7b-dihydro-2H-spiro[cyclopropa[c]chromene-1,2'-indene]-1',3'-dione (7)

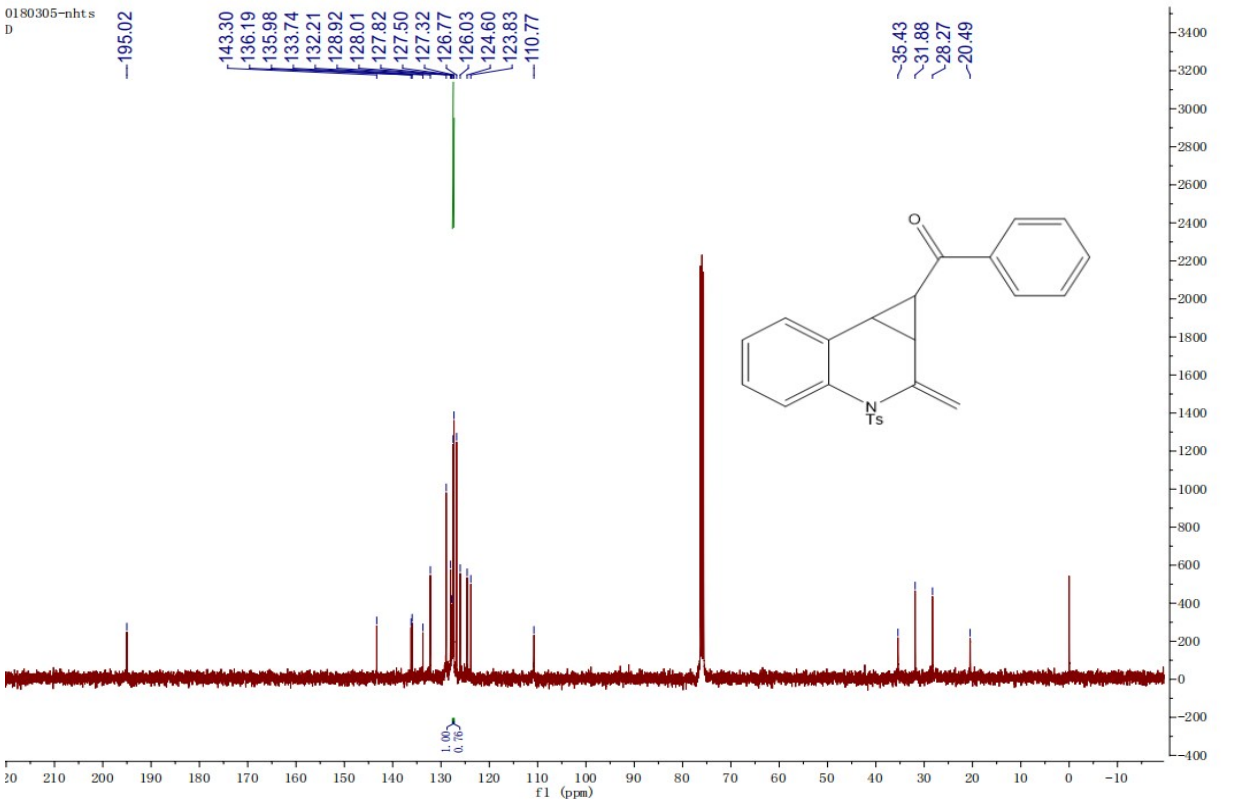




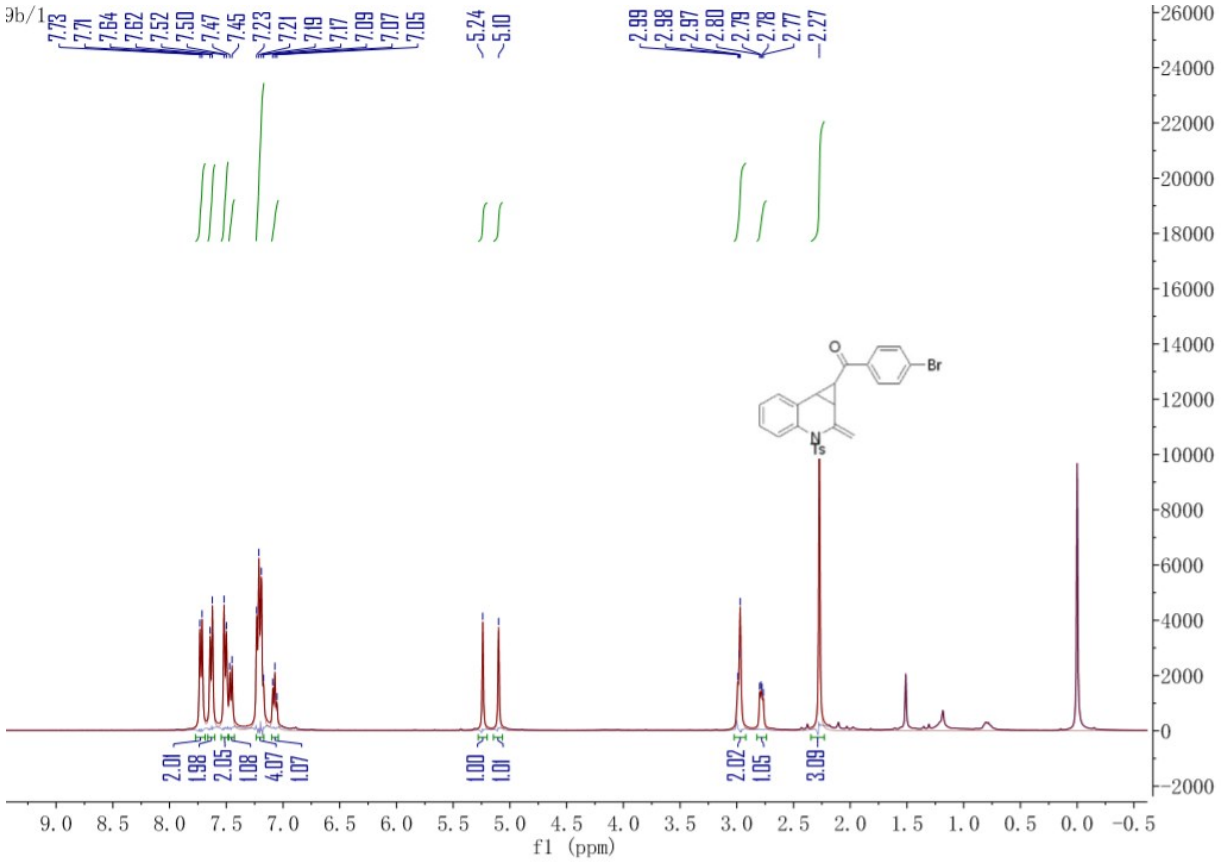
Copy of ^{1}H NMR and ^{13}C NMR spectra of **9a-9l**

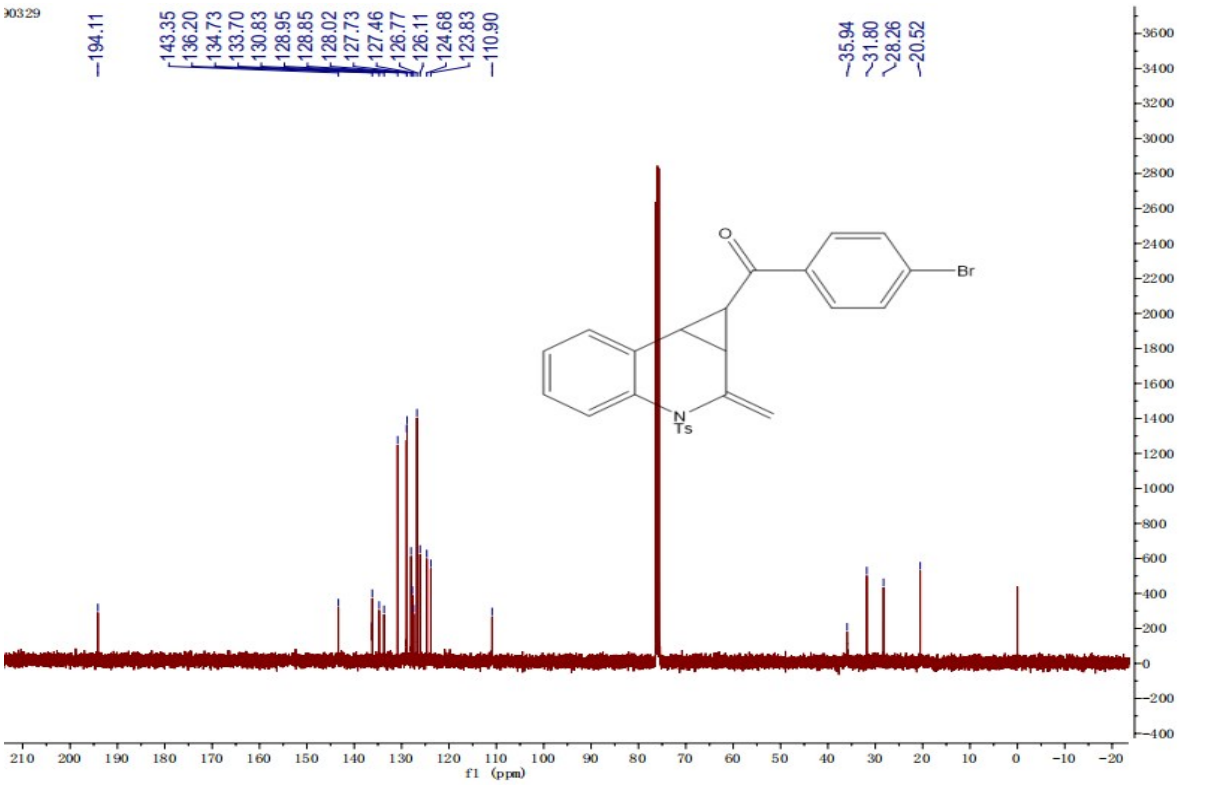
(2-Methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl)(phenyl) methanone (9a)



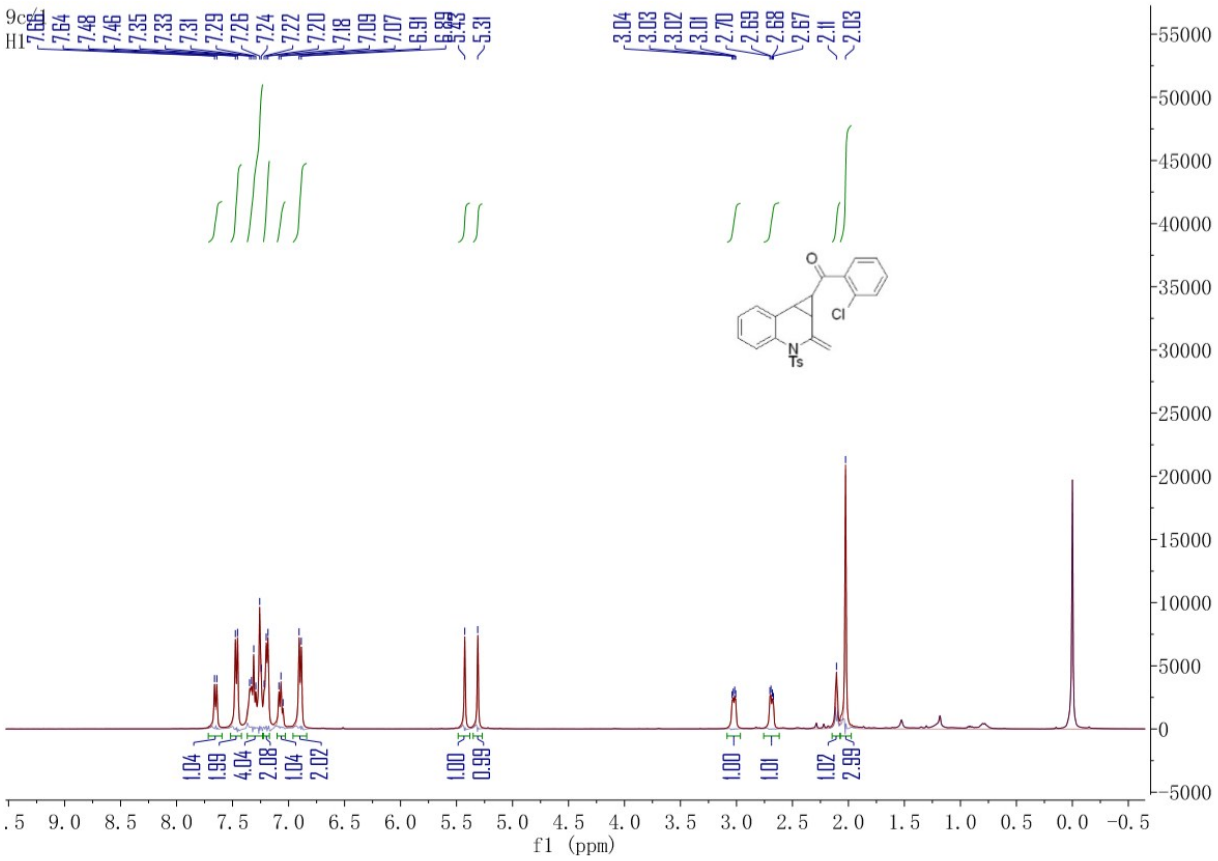


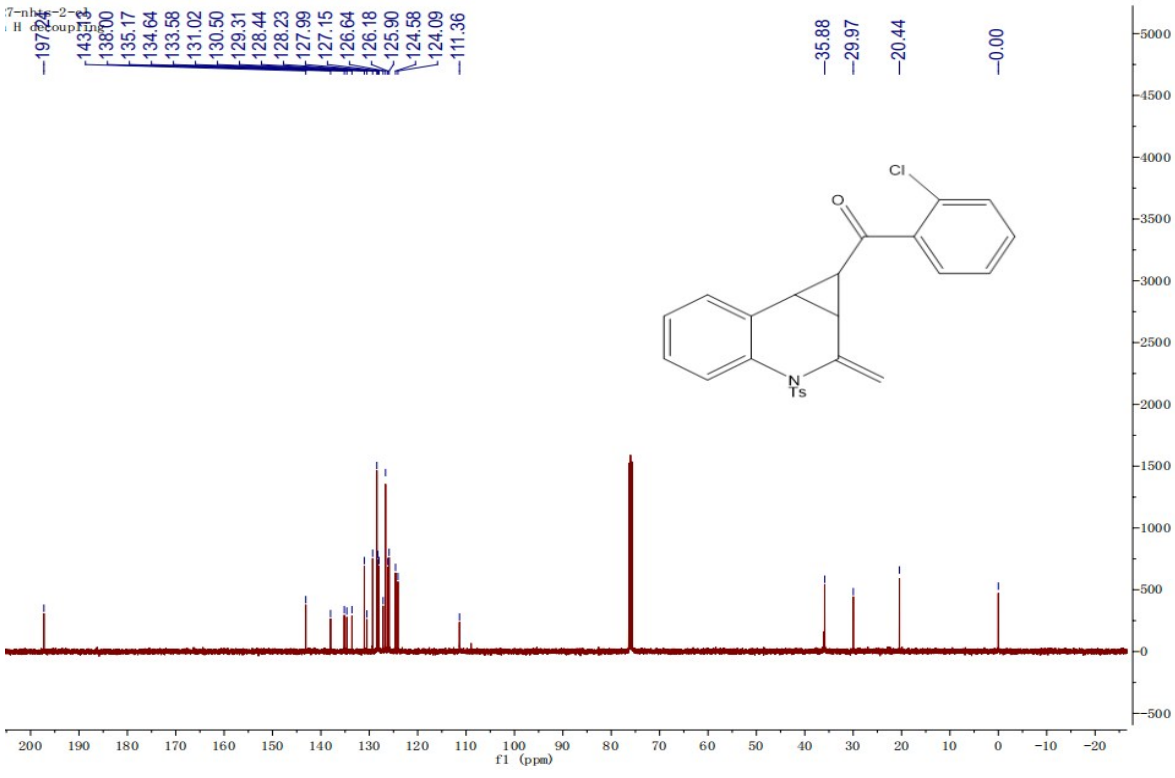
(4-Bromophenyl)(2-methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) methanone (9b)



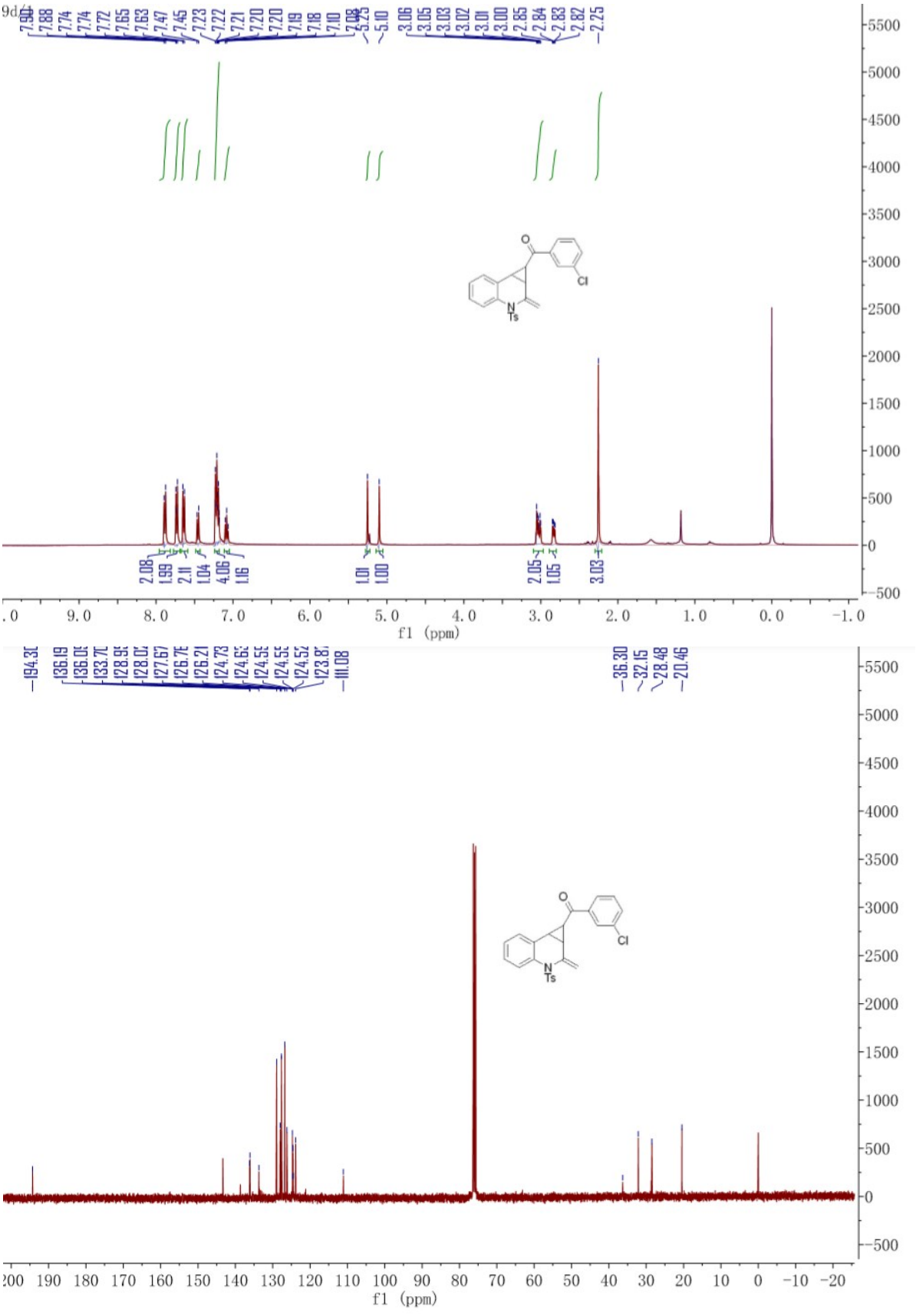


(2-Chlorophenyl)(2-methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) methanone (9c)

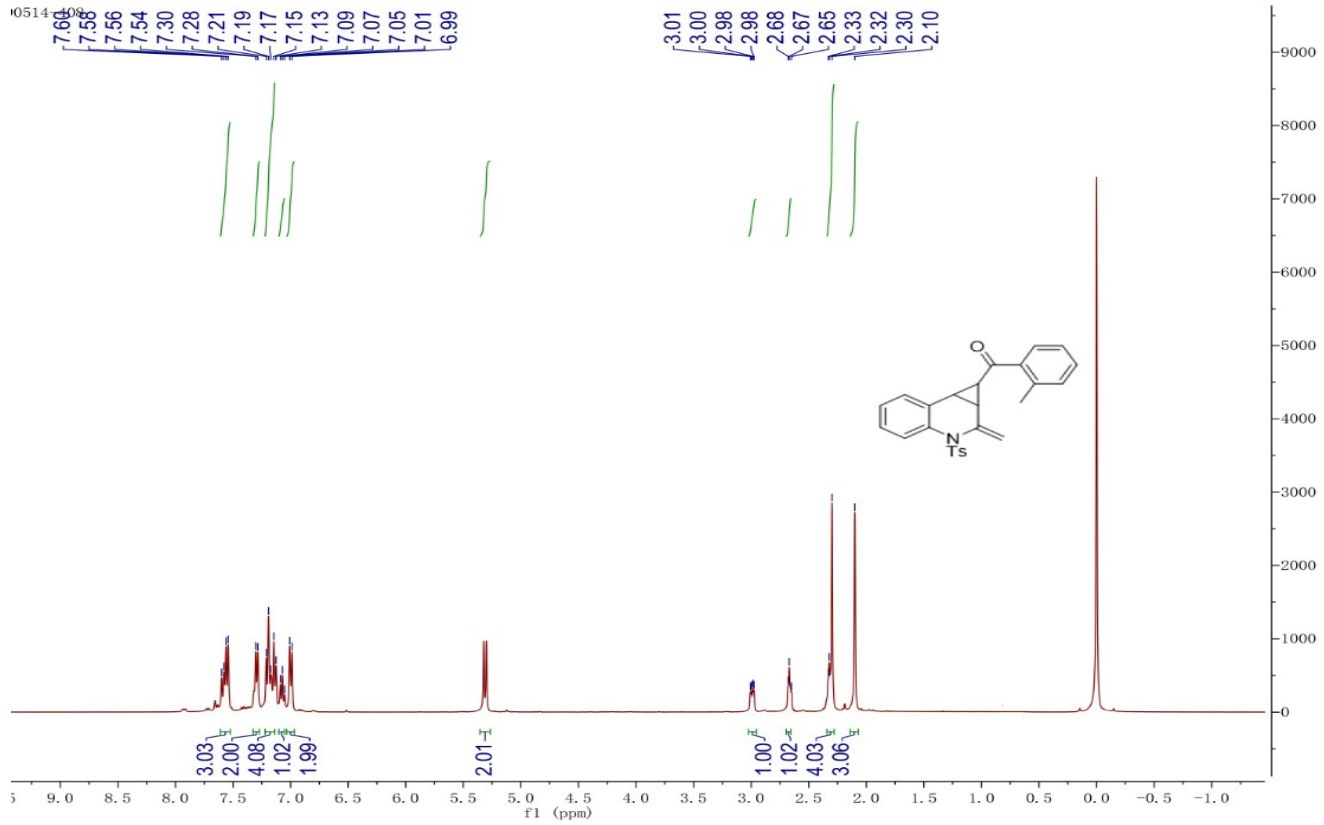


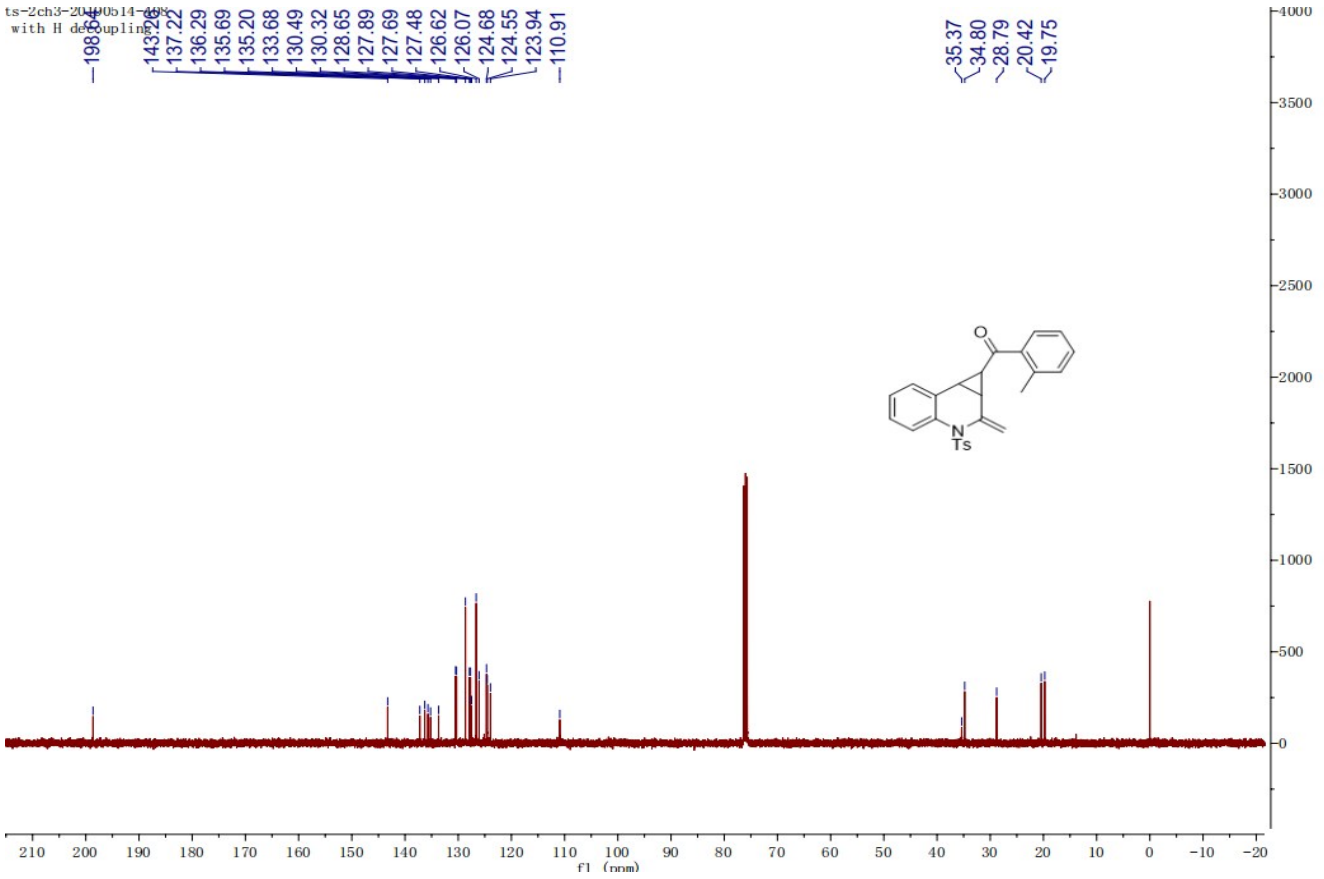


(3-chlorophenyl)(2-methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl)methanone (9d)

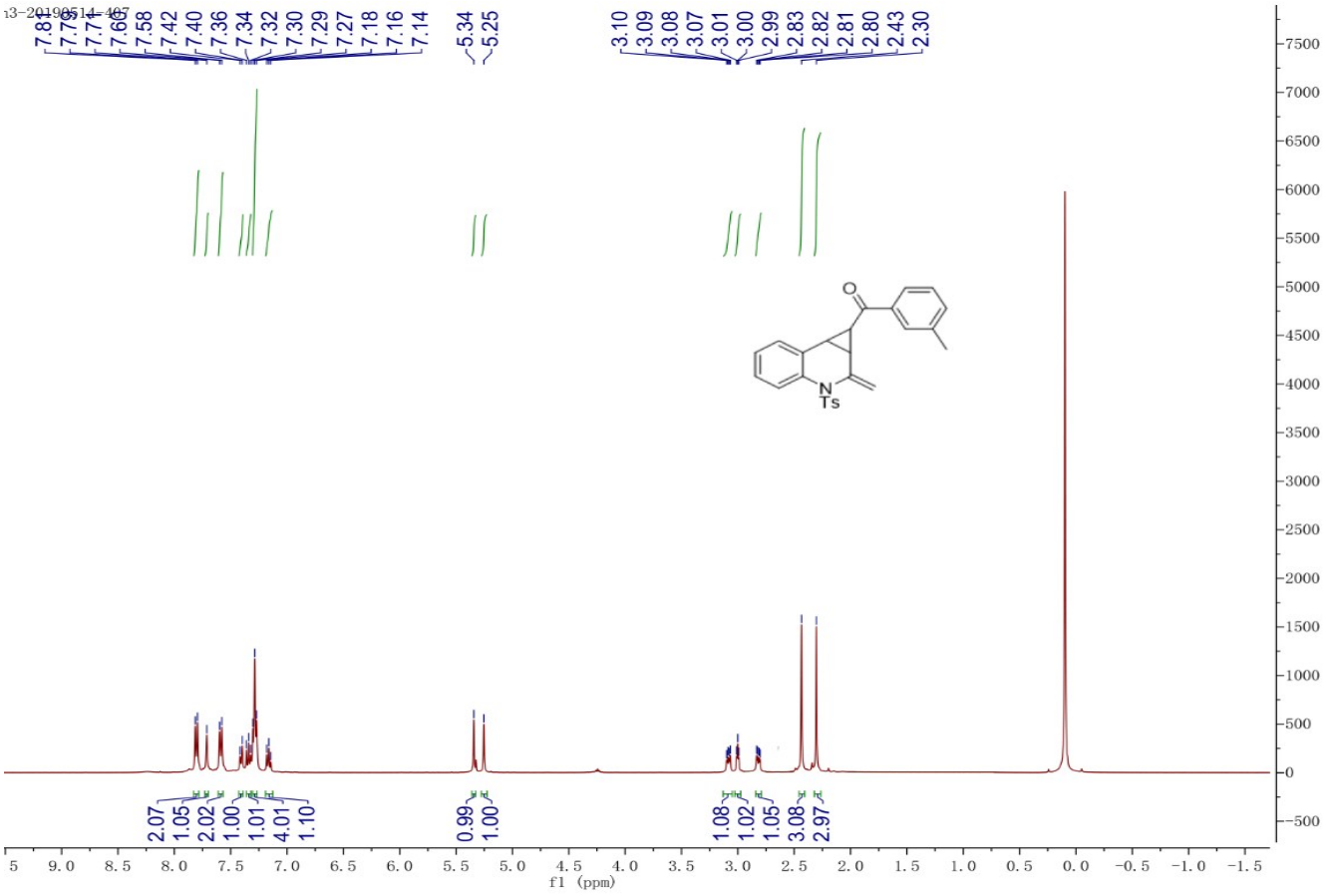


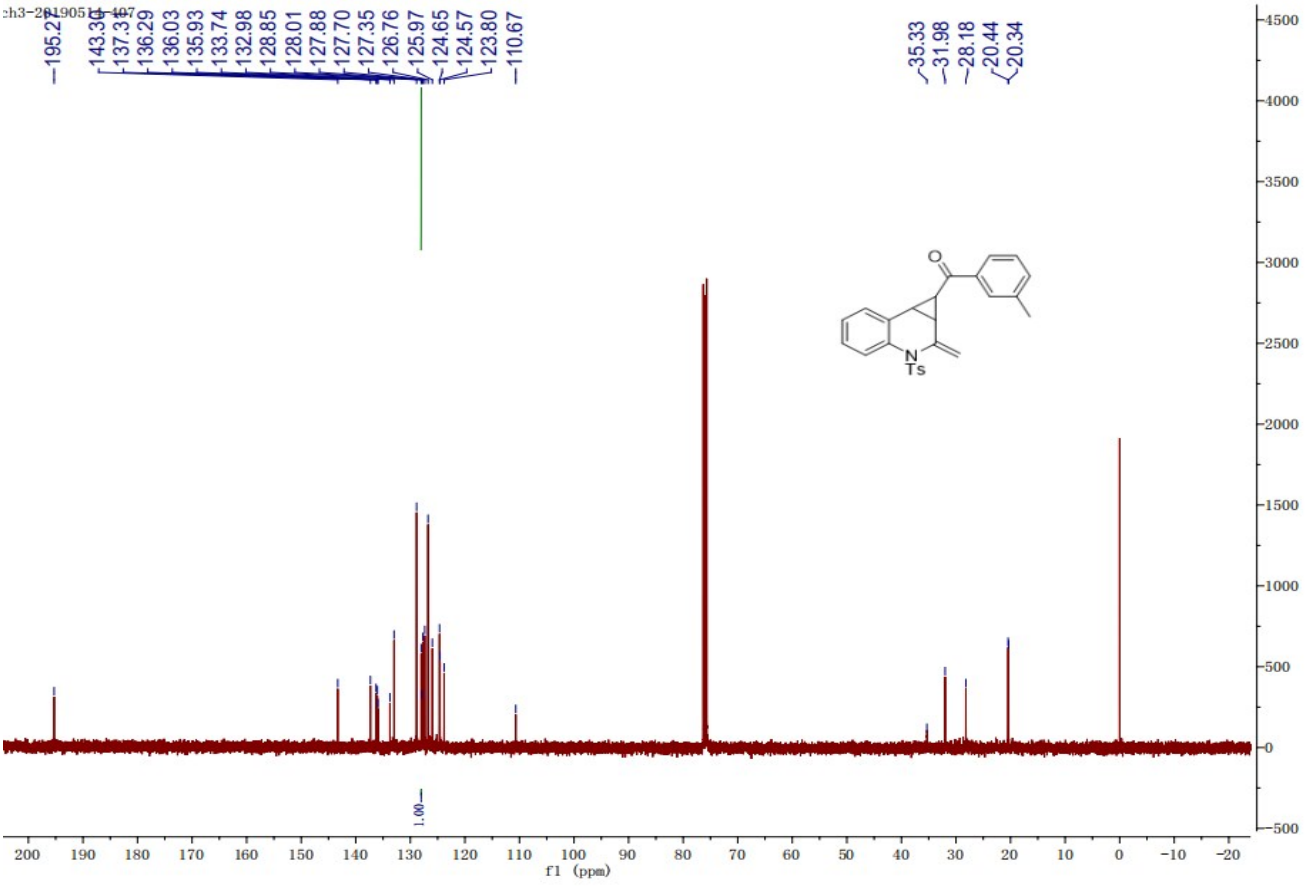
(2-Methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl)(o-tolyl) methanone (9e)



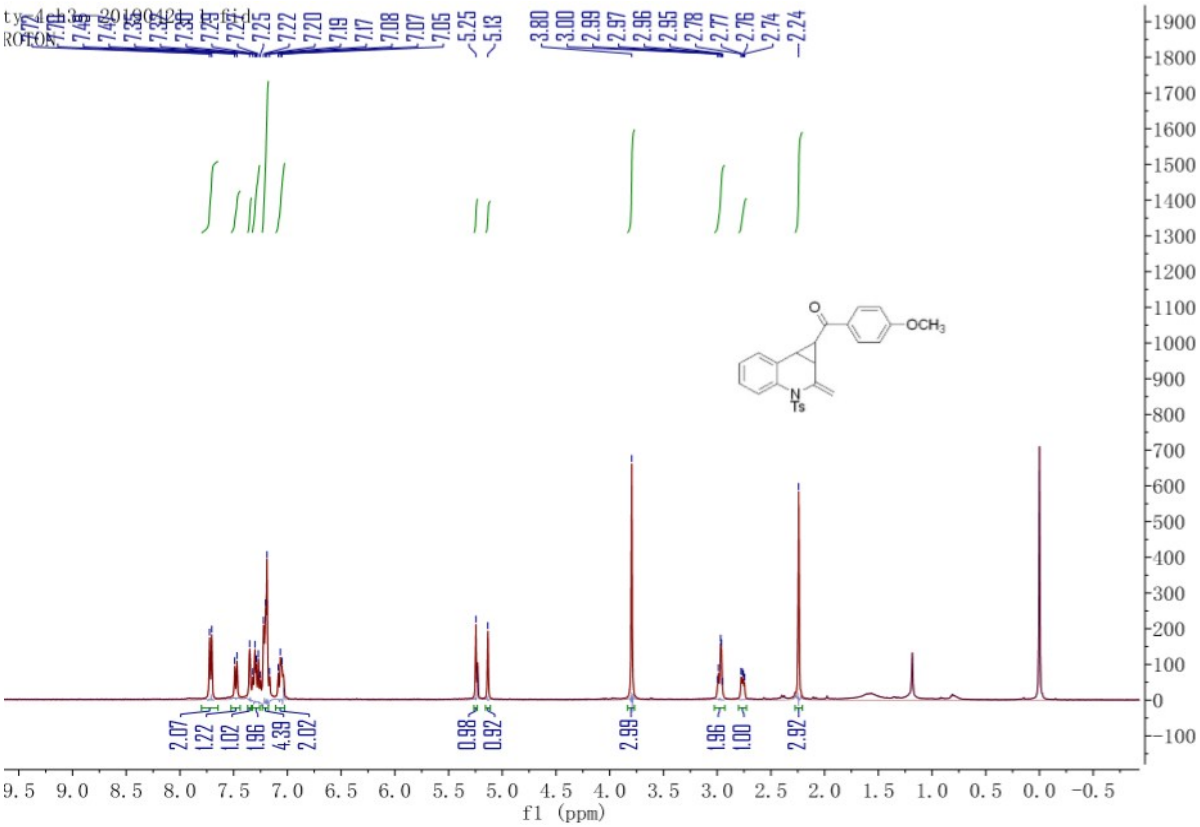


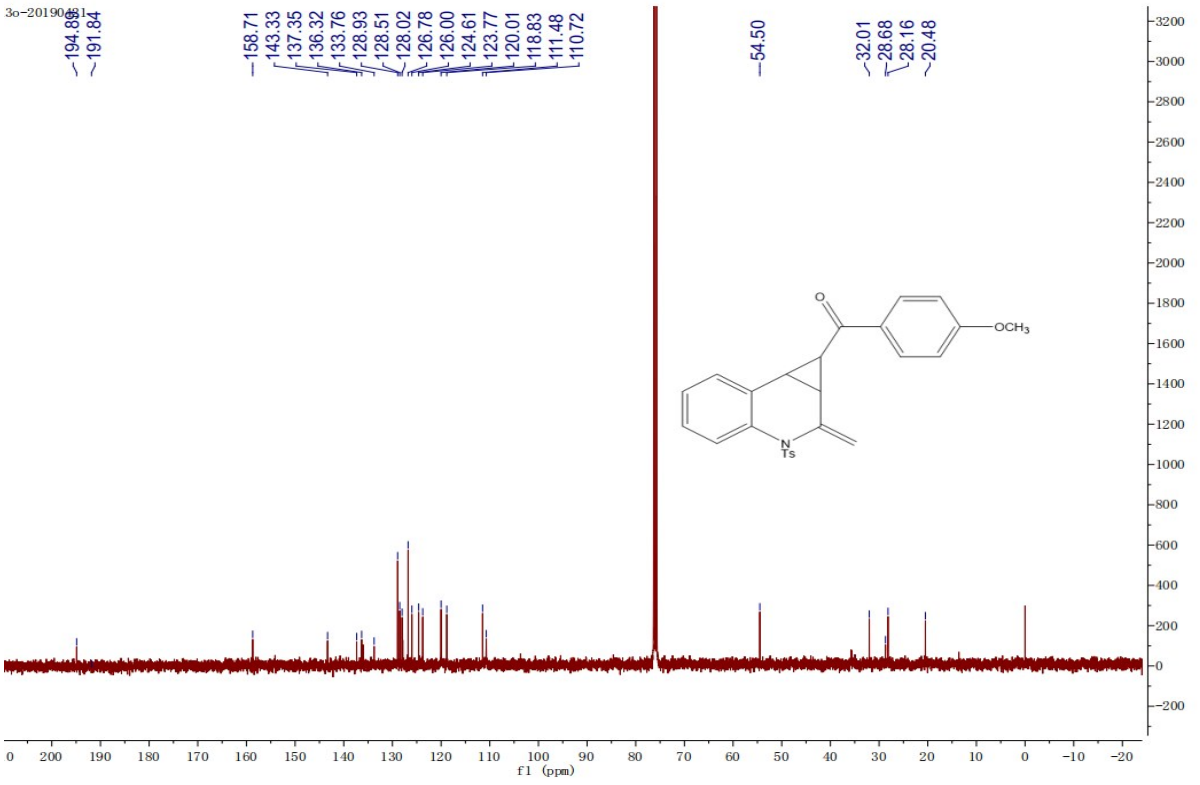
(2-Methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl)(m-tolyl) methanone (9f)



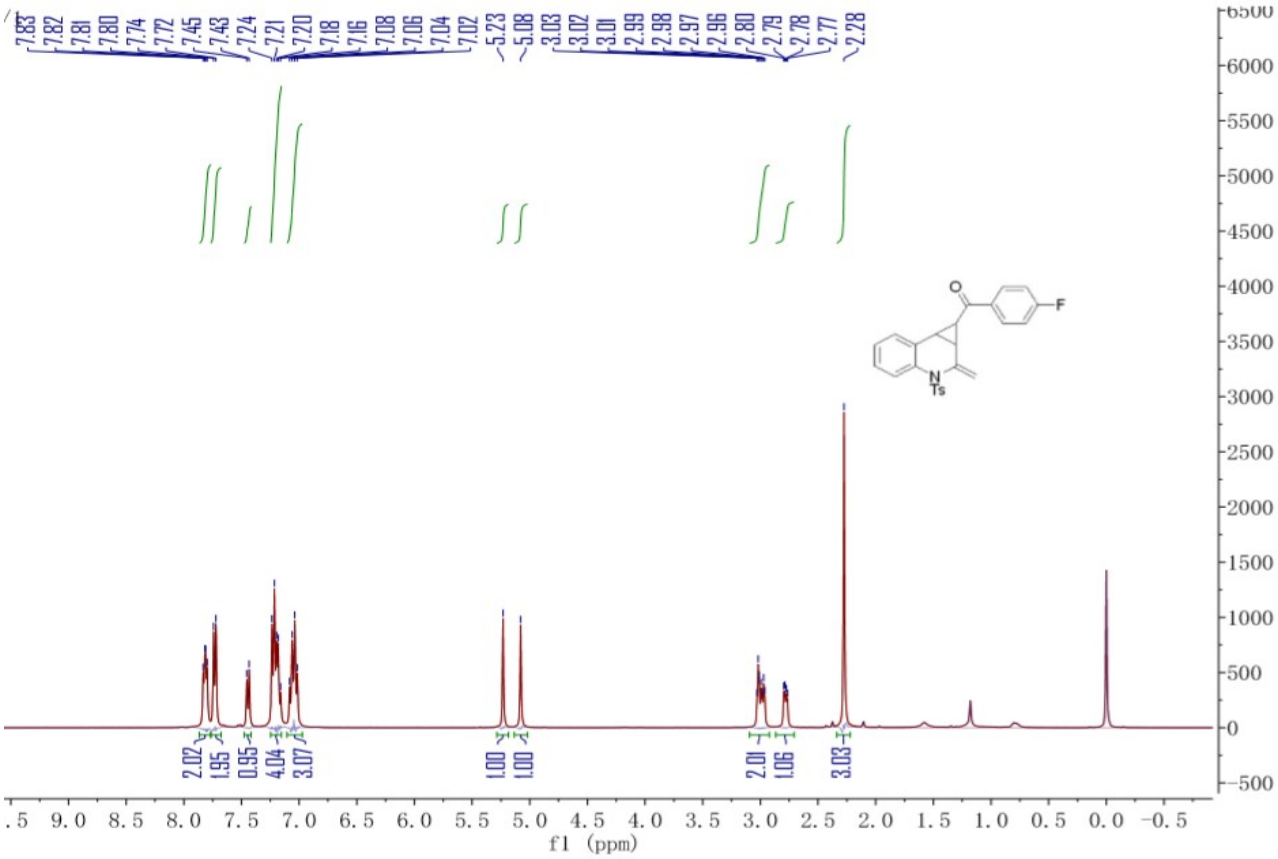


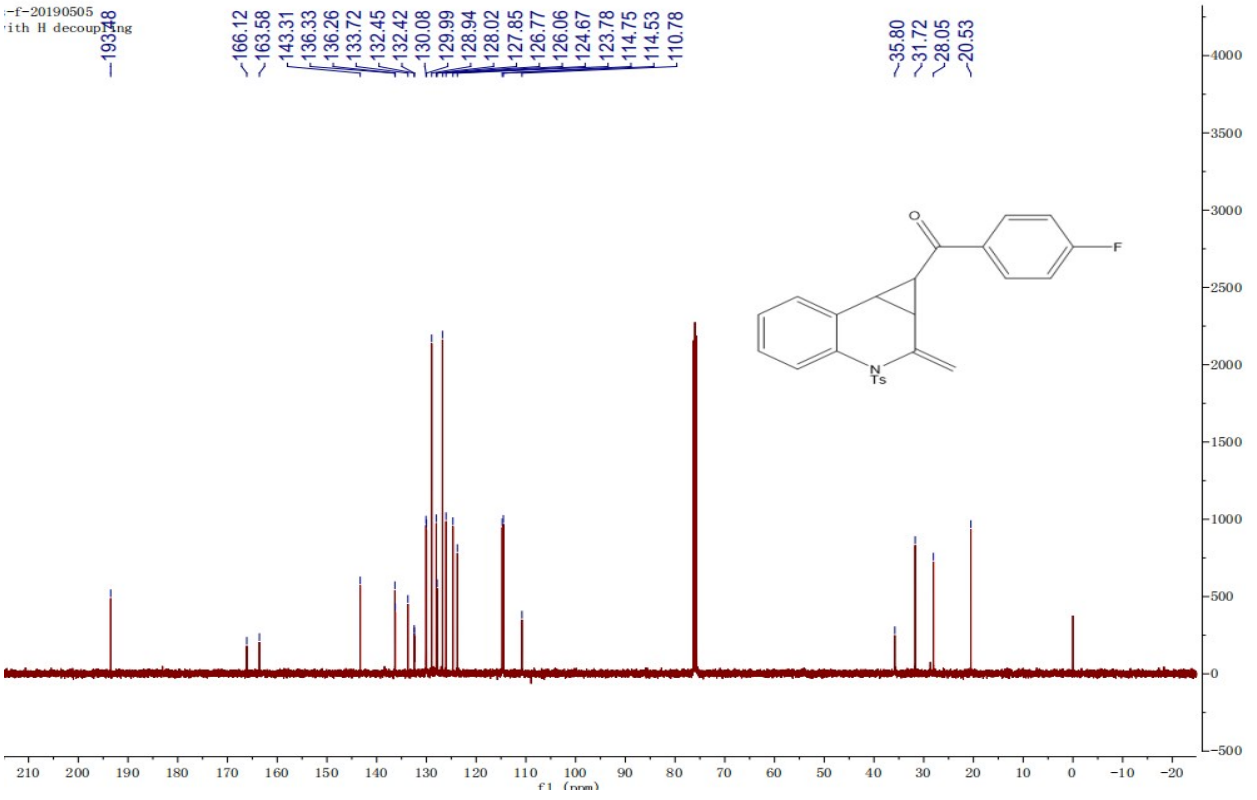
(4-Methoxyphenyl)(2-methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) methanone (9g)



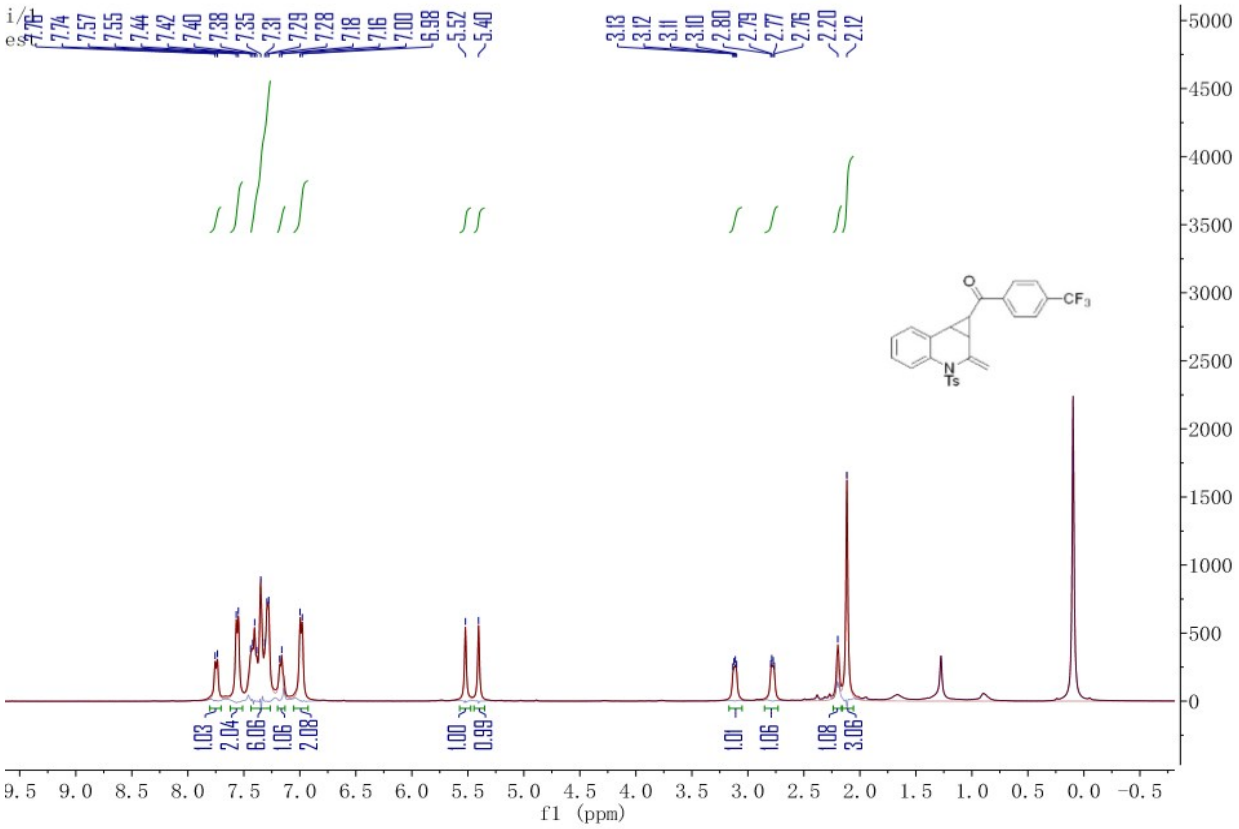


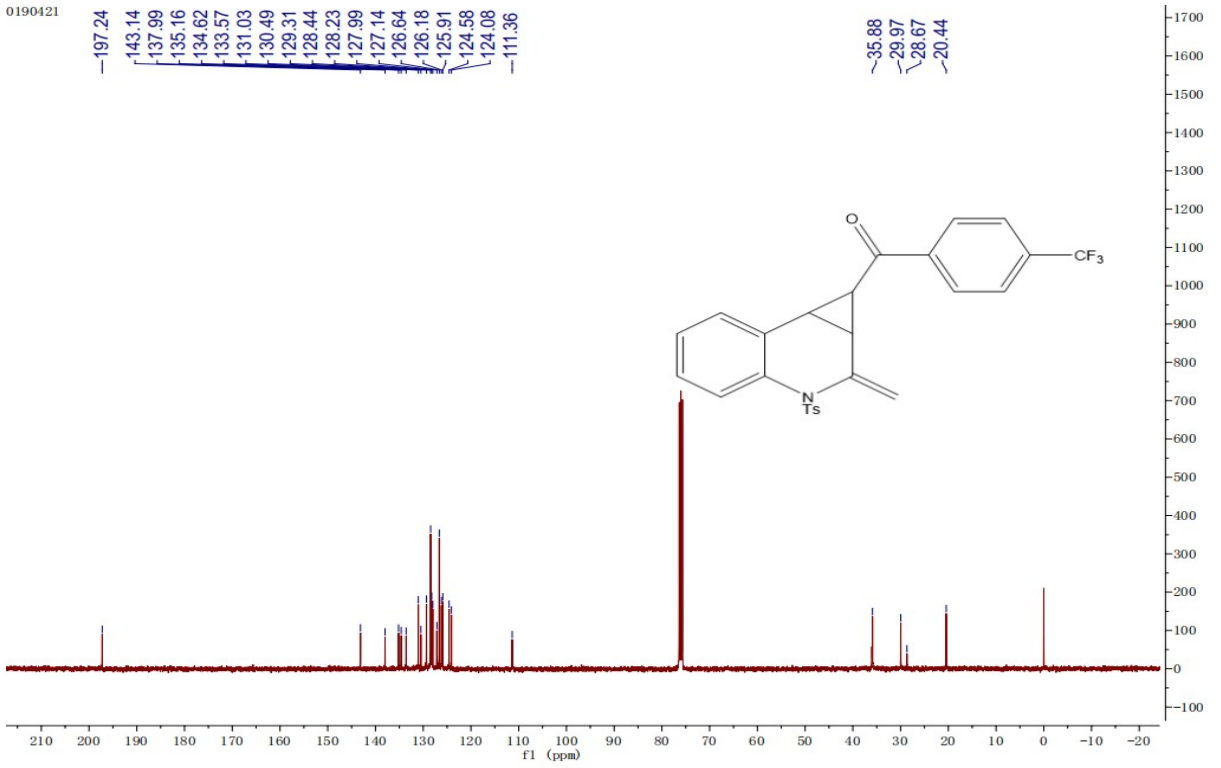
(4-Fluorophenyl)(2-methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) methanone (9h)



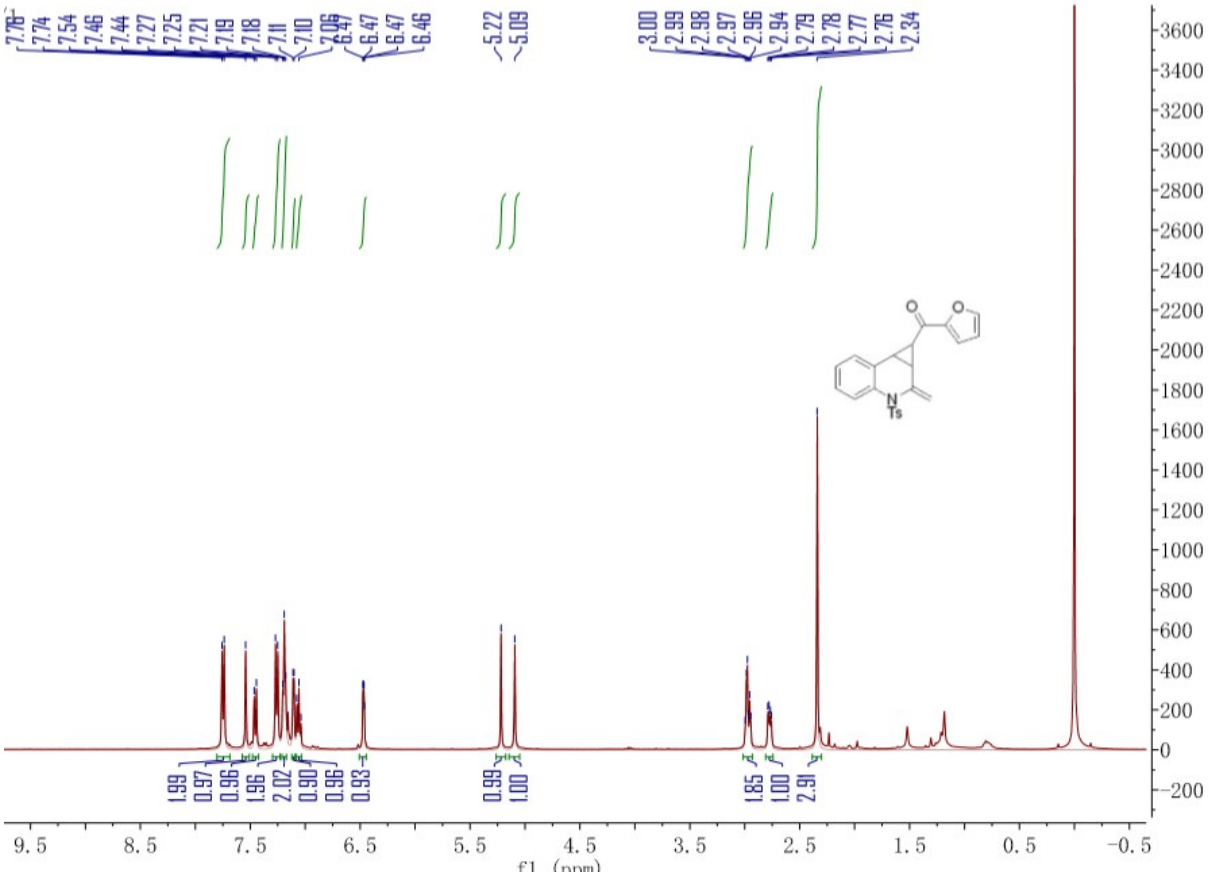


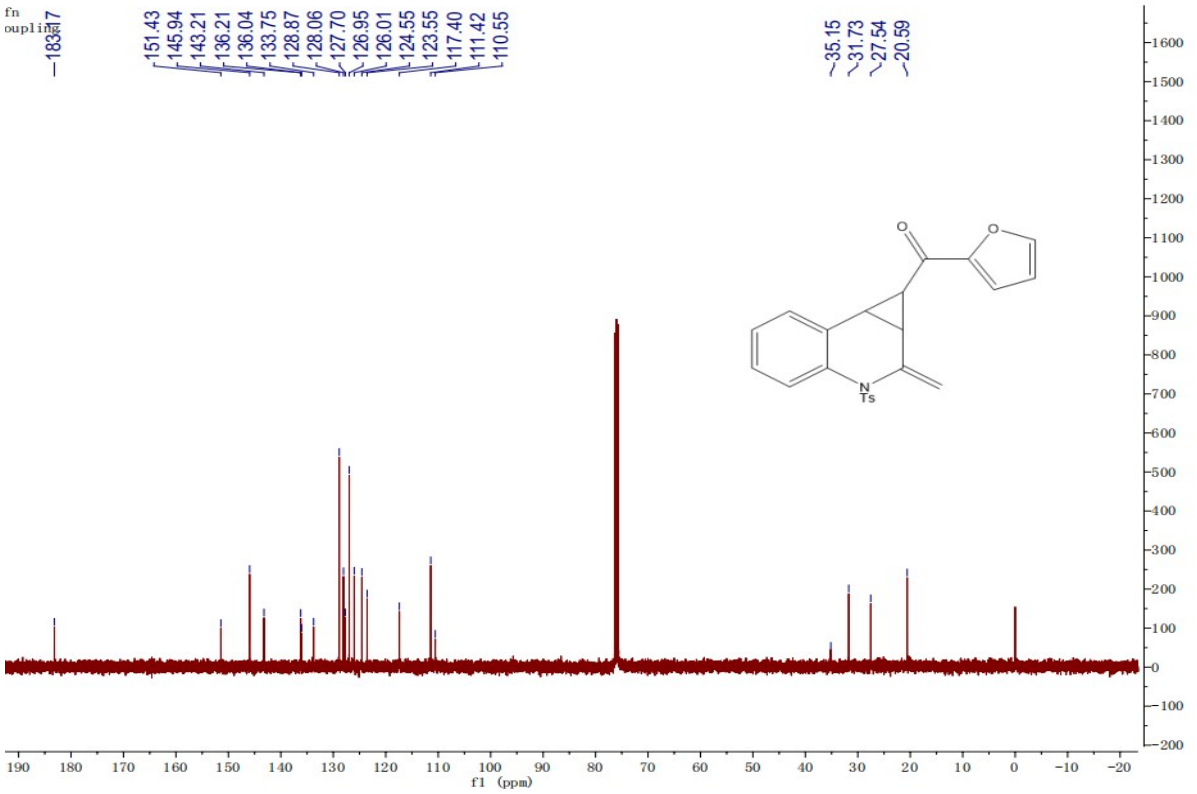
(2-Methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl)(4-(trifluoromethyl) phenyl)methanone (9i)



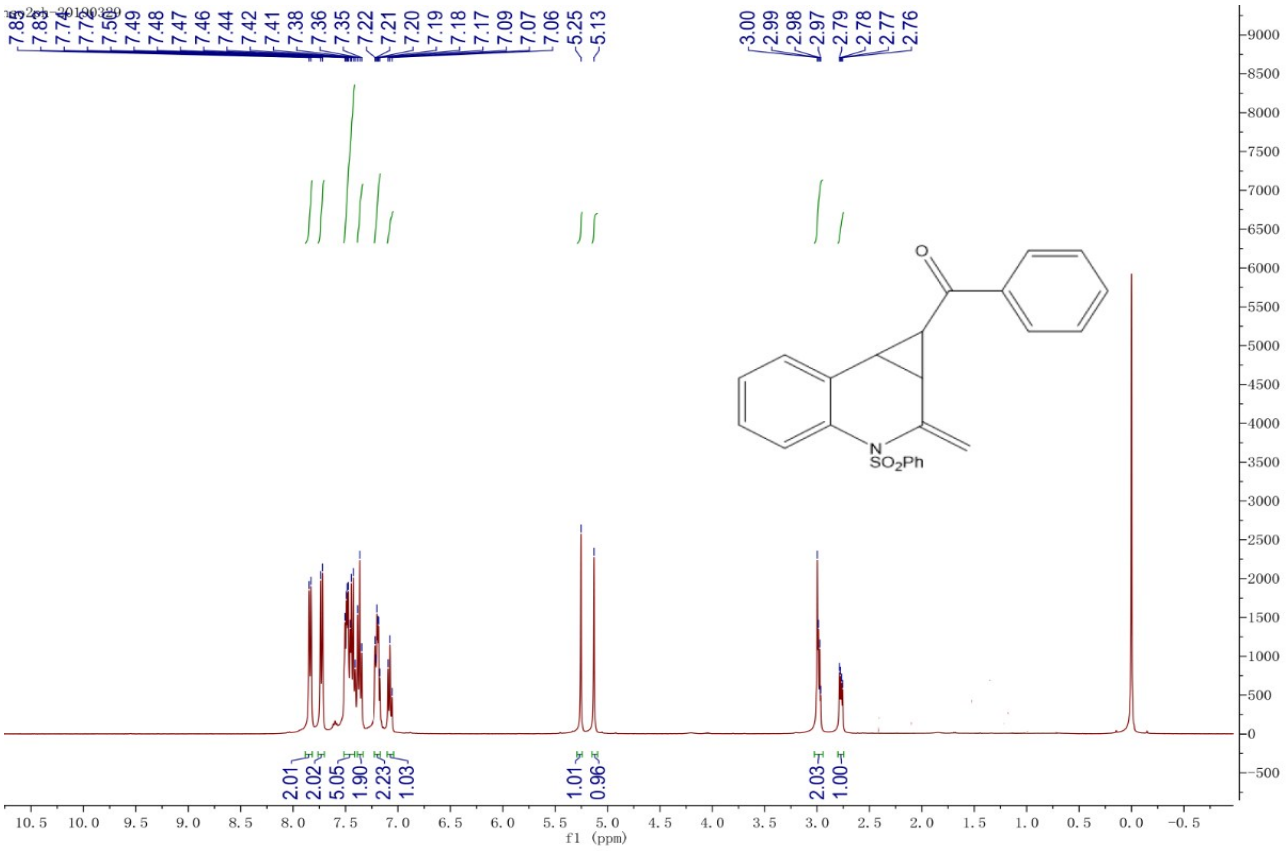


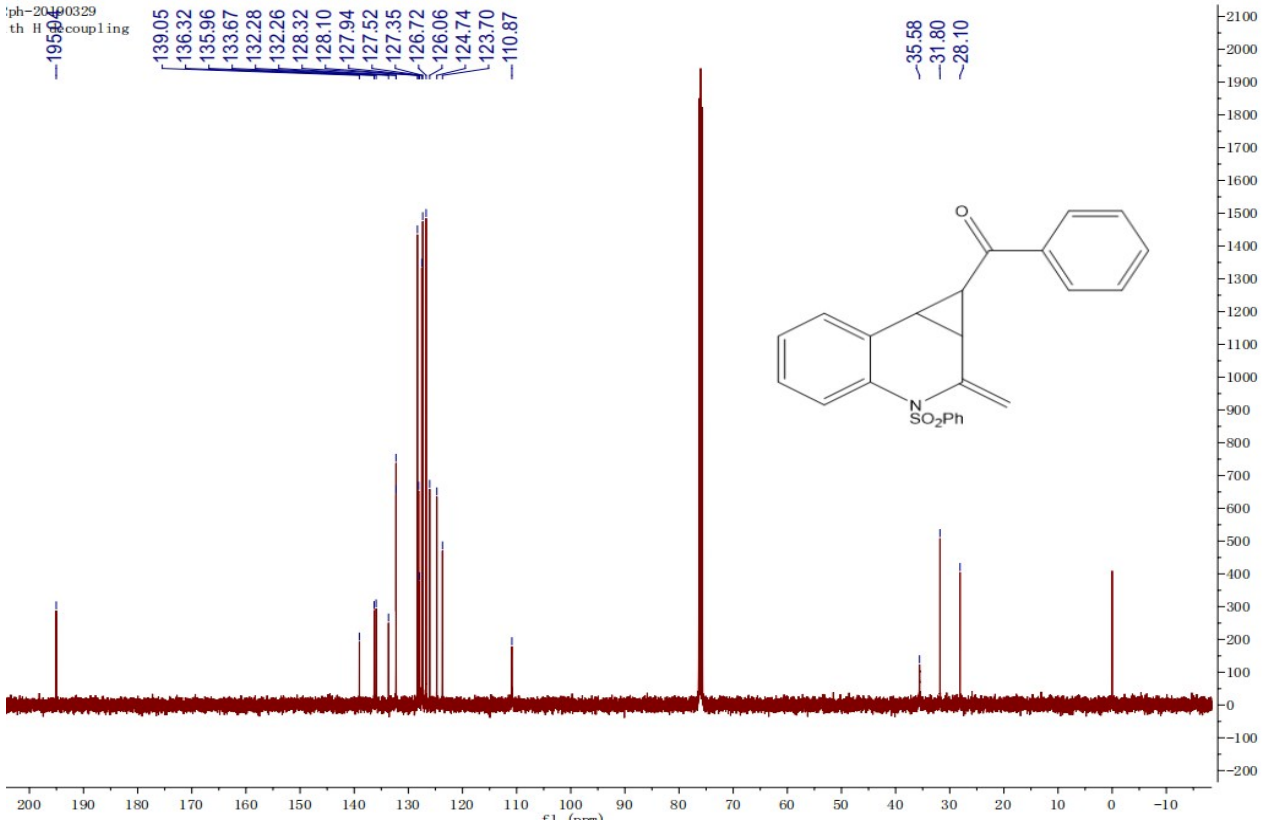
Furan-2-yl(2-methylene-3-tosyl-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) methanone (9j)



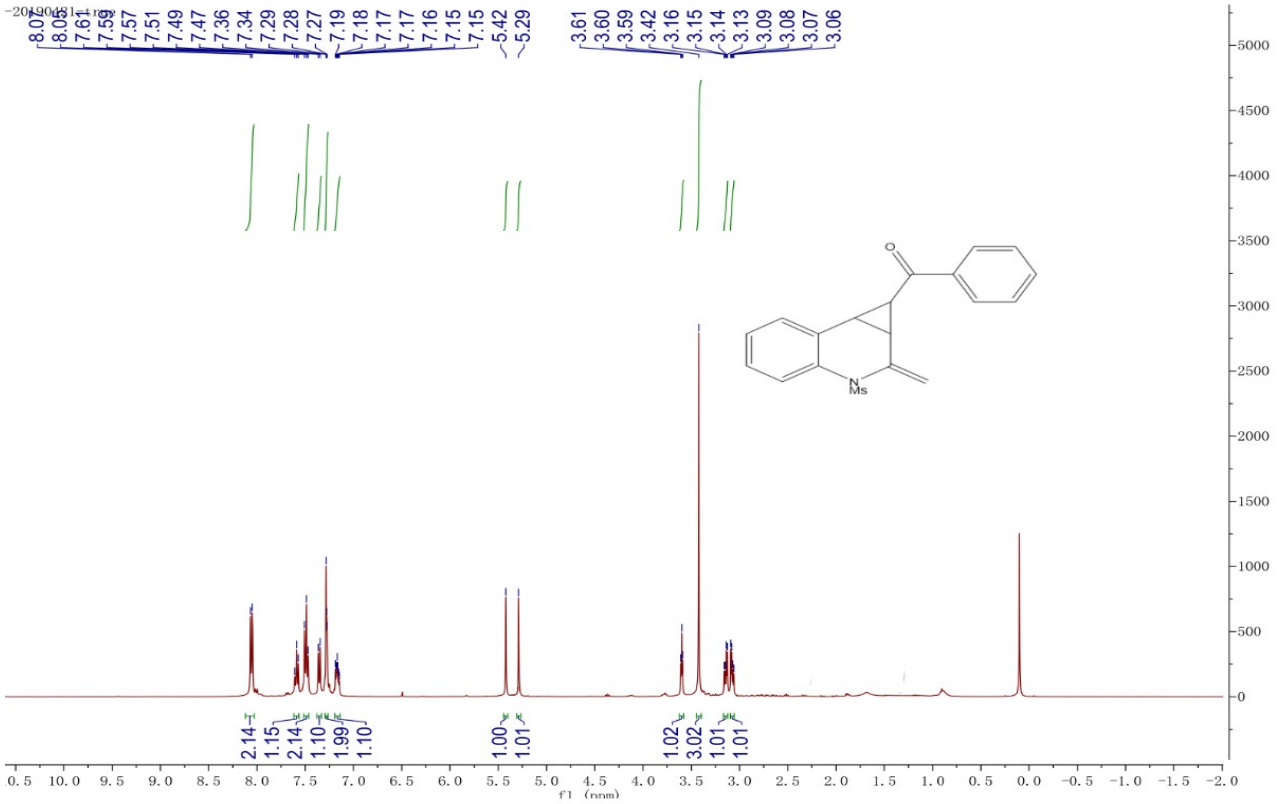


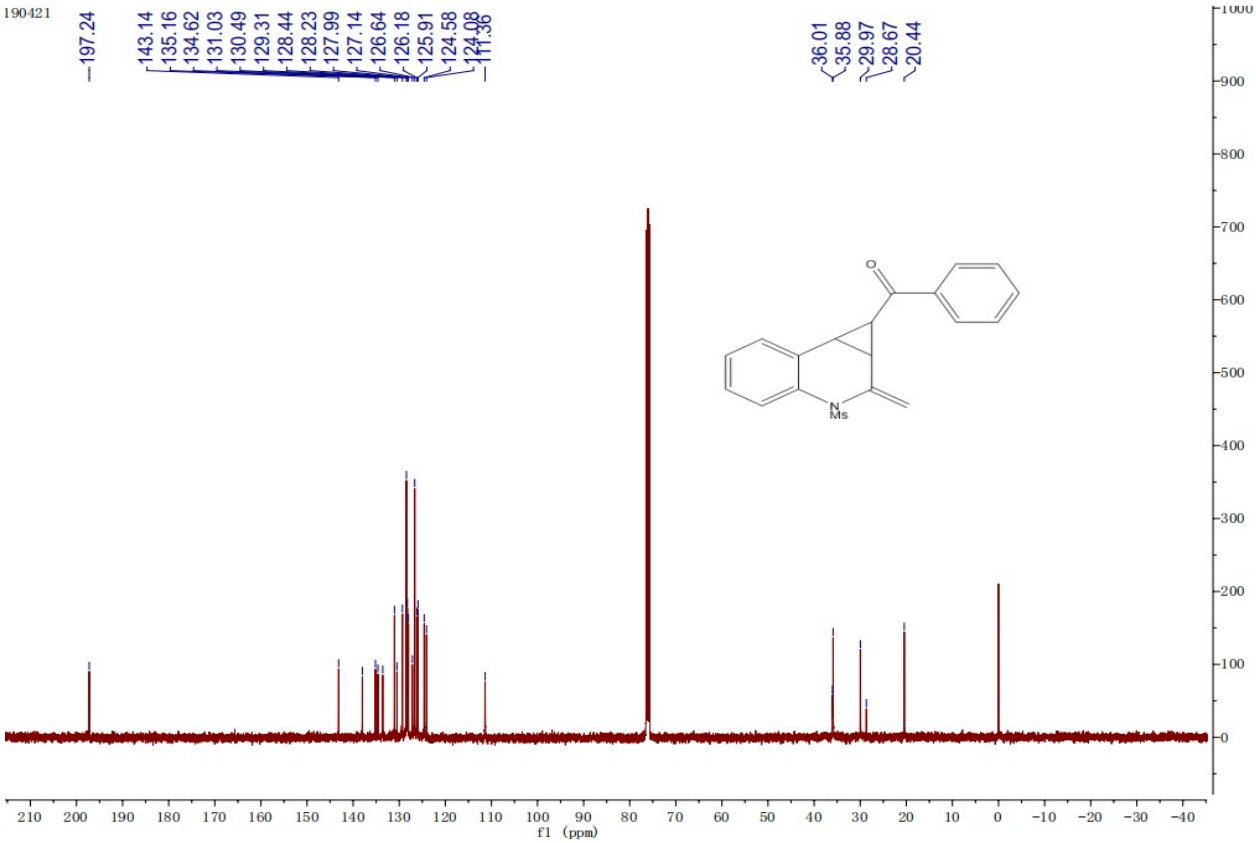
(2-Methylene-3-(phenylsulfonyl)-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) (phenyl) methanone (9k)





(2-Methylene-3-(methylsulfonyl)-1a,2,3,7b-tetrahydro-1H-cyclopropa[c]quinolin-1-yl) (phenyl) methanone (9l)





X-ray crystallographic data of compound 5

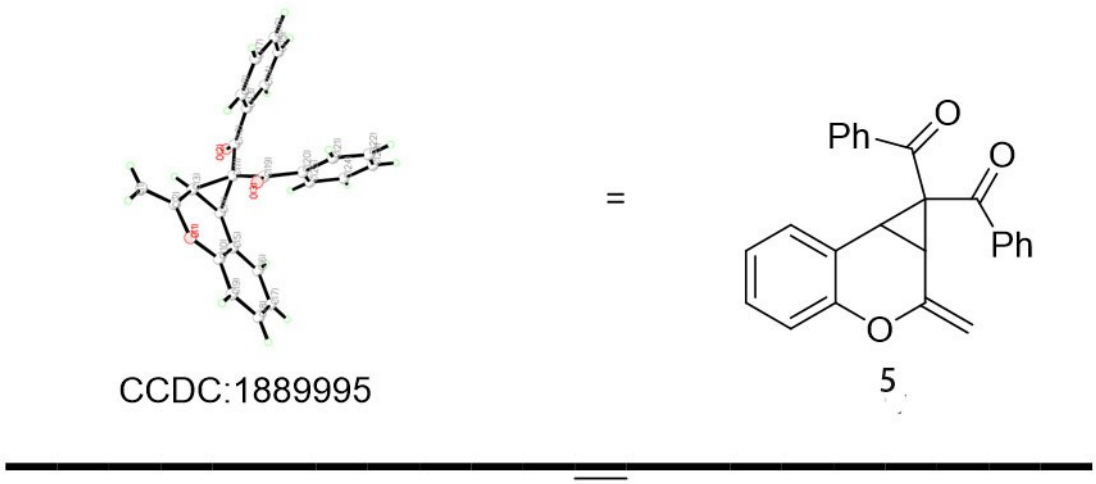


Figure S1 X-ray crystal structure of **5**

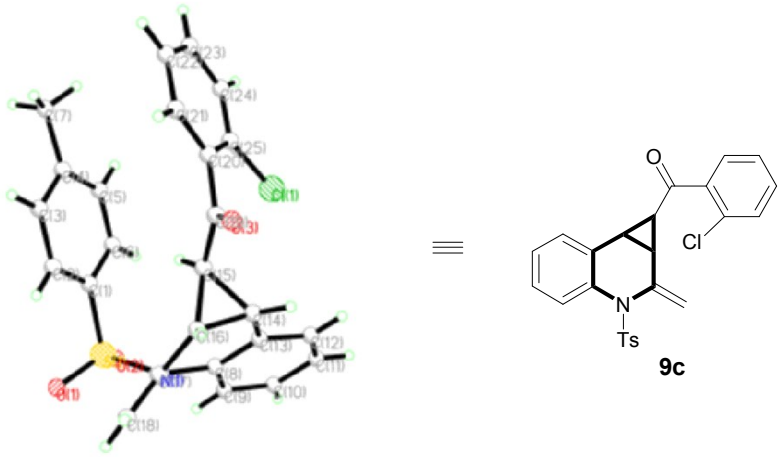
Displacement ellipsoids are shown at the 50% probability level.

Table S1 Crystal data and structure refinement for compound **5**

Identification code	shelxl
Empirical formula	C25 H18 O3
Formula weight	366.39
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.5548(19) A alpha = 100.86(3) deg.
	b = 10.071(2) A beta = 104.43(3) deg.
	c = 10.634(2) A gamma = 105.69(3) deg.
Volume	917.4(4) A^3
Z, Calculated density	2, 1.326 Mg/m^3
Absorption coefficient	0.086 mm^-1
F(000)	384
Crystal size	0.200 x 0.180 x 0.120 mm
Theta range for data collection	2.184 to 27.895 deg.

Limiting indices	-12<=h<=12, -13<=k<=12, -13<=l<=13
Reflections collected / unique	11084 / 4356 [R(int) = 0.0387]
Completeness to theta = 25.242	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.7810
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4356 / 0 / 253
Goodness-of-fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0563, wR2 = 0.1485
R indices (all data)	R1 = 0.0779, wR2 = 0.1687
Extinction coefficient	n/a
Largest diff. peak and hole	0.305 and -0.354 e.A^-3

X-ray crystallographic data of compound 9c



CCDC: 1916597

Figure S2 X-ray crystal structure of **9c**

Displacement ellipsoids are shown at the 50% probability level.

Table S2 Crystal data and structure refinement for compound **9c**

Identification code	shelxl
Empirical formula	C25 H20 Cl N O3 S
Formula weight	449.93
Temperature	113(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.132(3) A alpha = 90 deg.
	b = 8.2538(17) A beta = 105.43(3) deg.
	c = 20.537(4) A gamma = 90 deg.
Volume	2145.7(8) A^3
Z, Calculated density	4, 1.393 Mg/m^3
Absorption coefficient	0.303 mm^-1
F(000)	936
Crystal size	0.200 x 0.180 x 0.120 mm
Theta range for data collection	1.609 to 27.835 deg.

Limiting indices	-16<=h<=17, -10<=k<=10, -26<=l<=26
Reflections collected / unique	24767 / 5069 [R(int) = 0.0431]
Completeness to theta = 25.242	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1 and 0.8498
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5069 / 0 / 281
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.1089
R indices (all data)	R1 = 0.0491, wR2 = 0.1297
Extinction coefficient	n/a
Largest diff. peak and hole	0.397 and -0.487 e.A^-3