

Electronic Supplementary Information

for

AlCl₃-promoted [3 + 2] annulation of *cis*-2,3-disubstituted cyclopropane 1,1-diesters with isothiocyanates: stereoselective synthesis of densely substituted 2-iminodihydrothiophenes

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Key Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui key Laboratory of
Molecule-Based Materials, Institute of Organic Chemistry, College of Chemistry and Materials Science,
Anhui Normal University, Wuhu, 241000, China

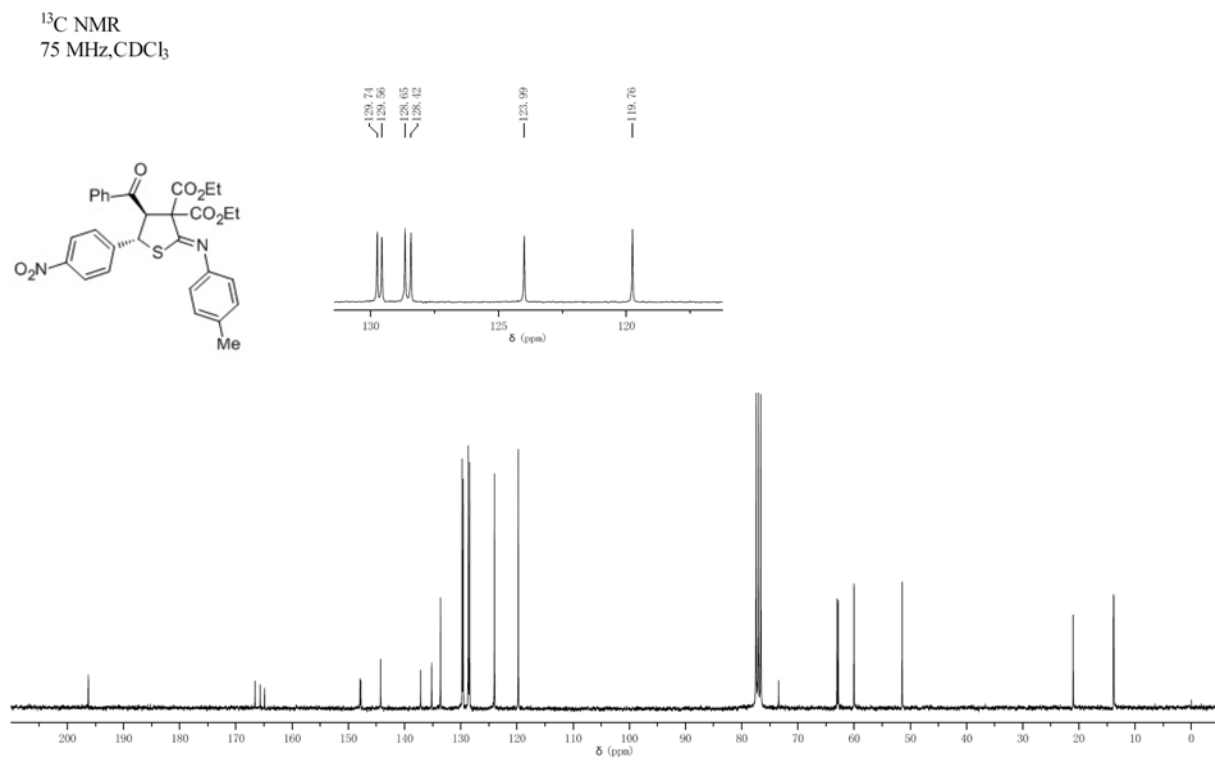
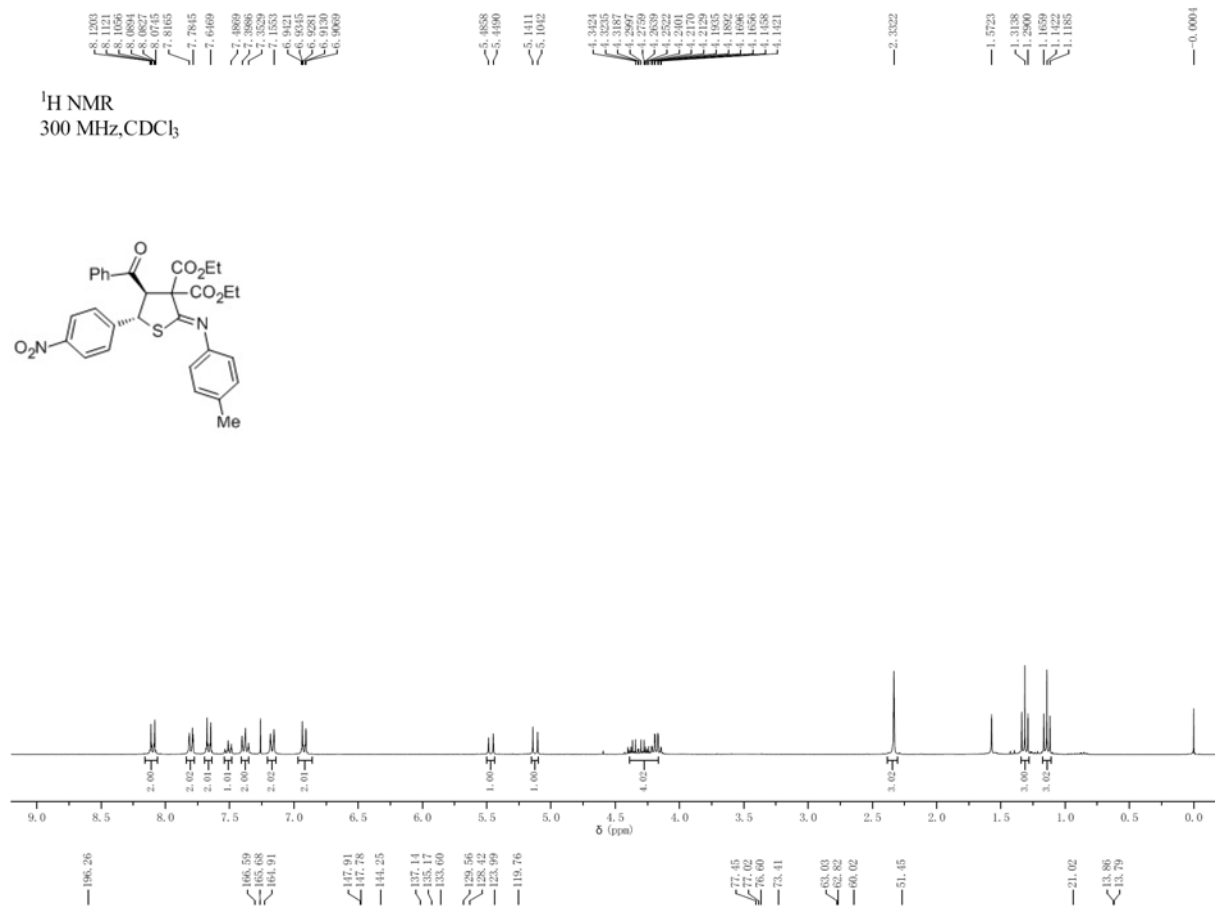
gshyang@mail.ahnu.edu.cn; chaizhuo@mail.ahnu.edu.cn

Content

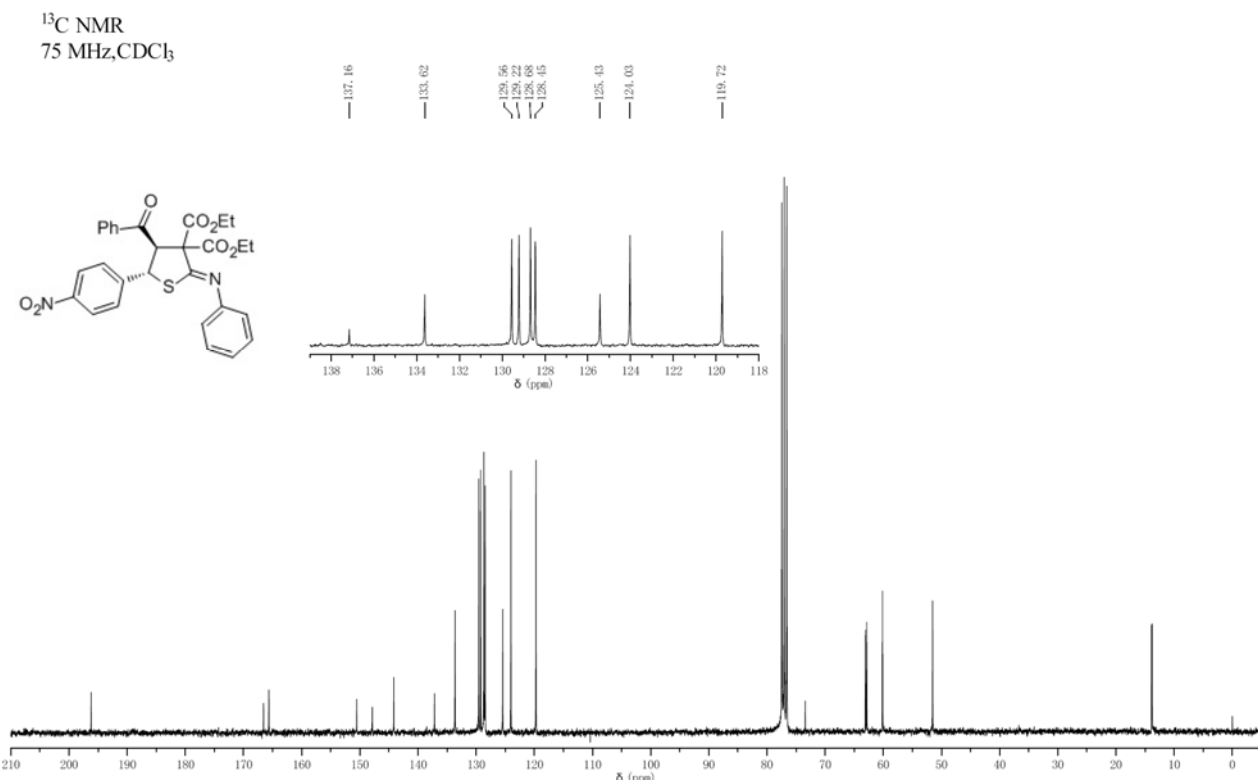
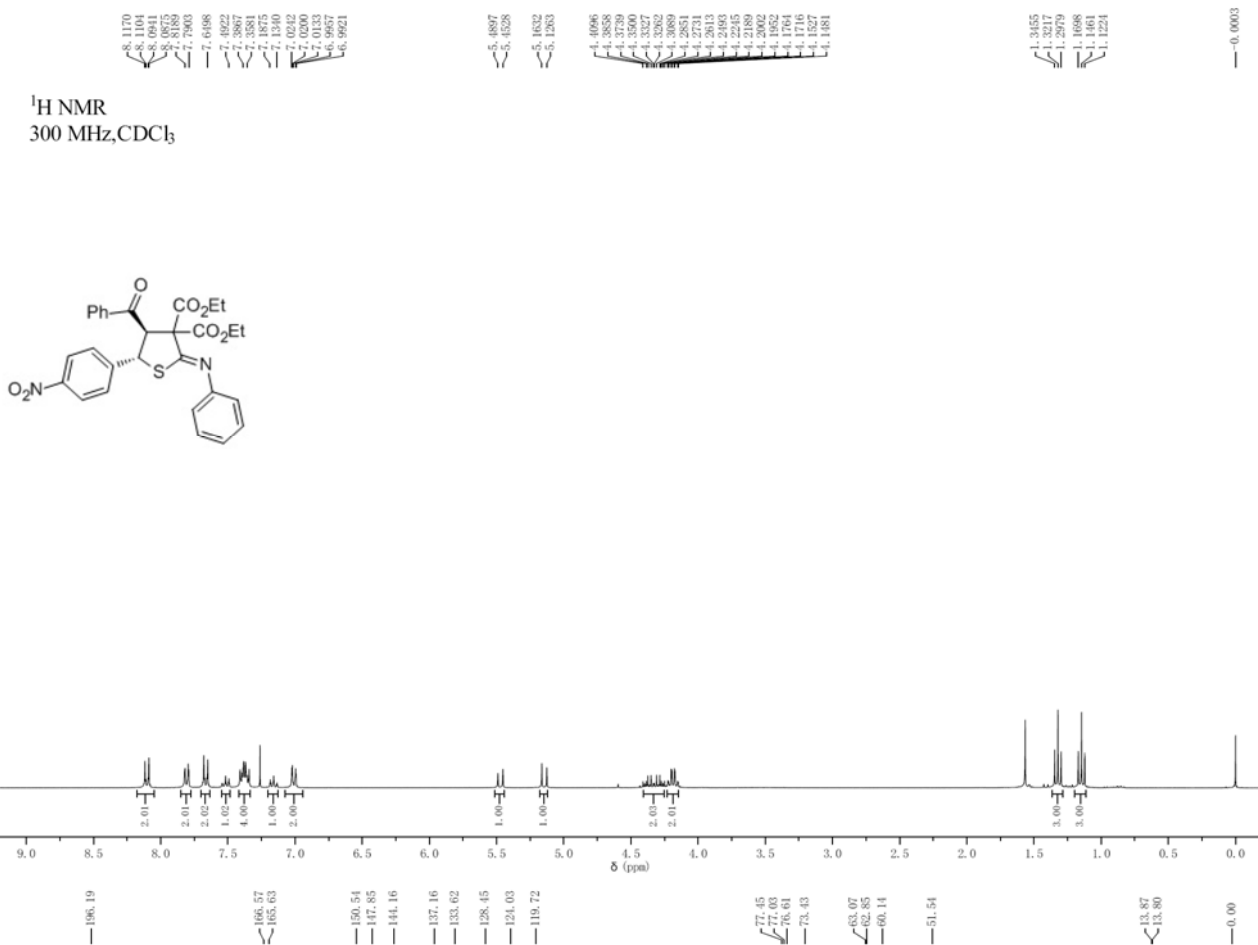
¹ H, ¹³ C NMR Spectra of all products.....	S2–S39
X-ray crystallographic analysis of 3ck	S40–S41

¹H, ¹³C NMR Spectra of all products

Compound 3aa



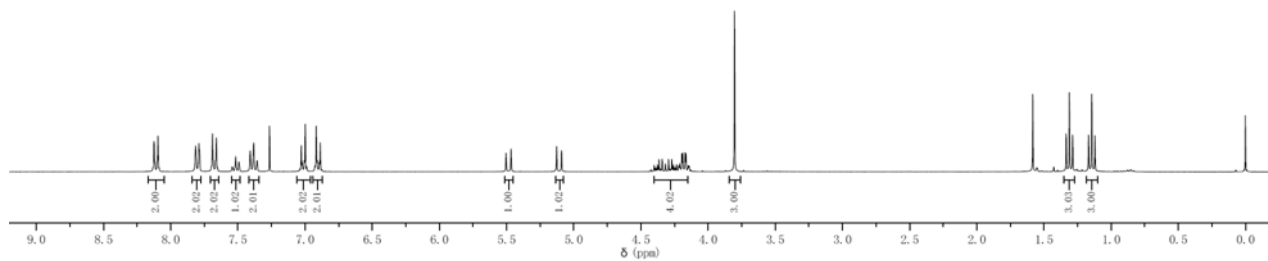
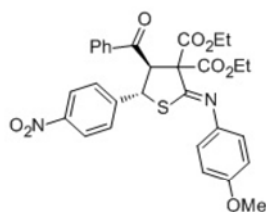
Compound 3ad



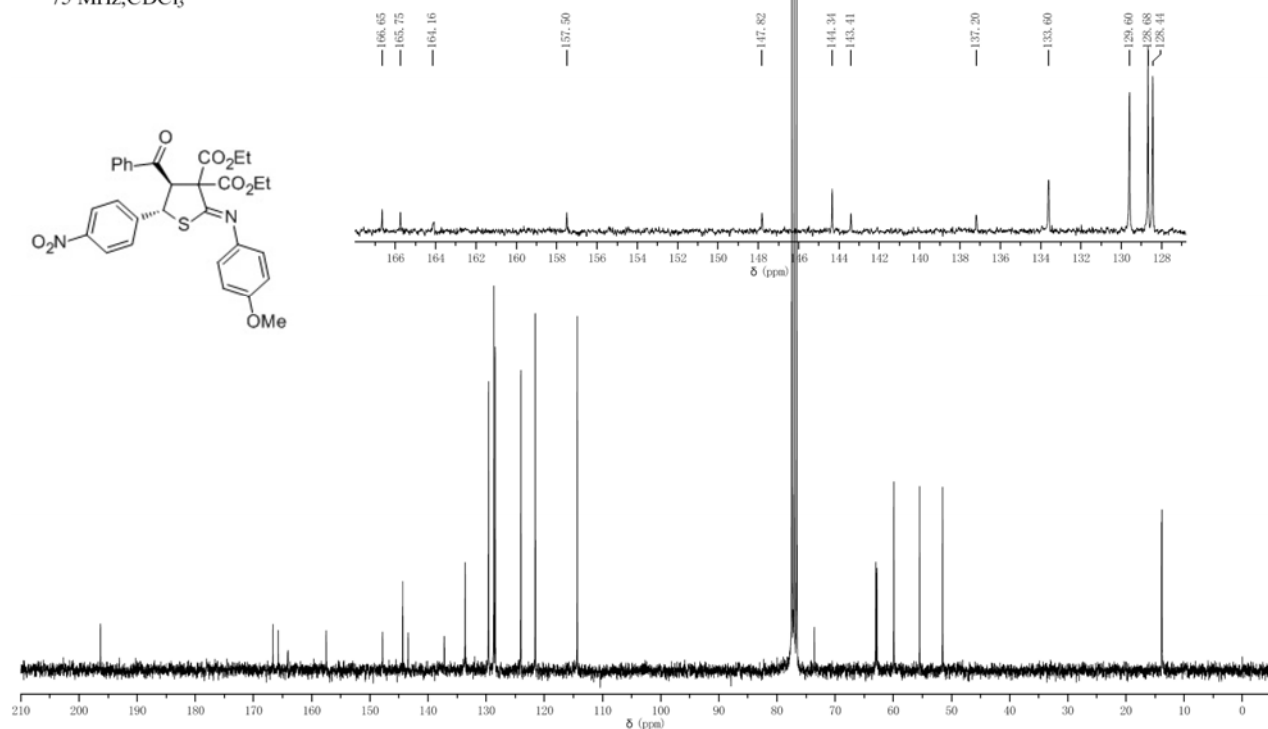
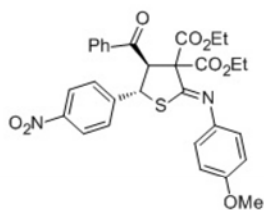
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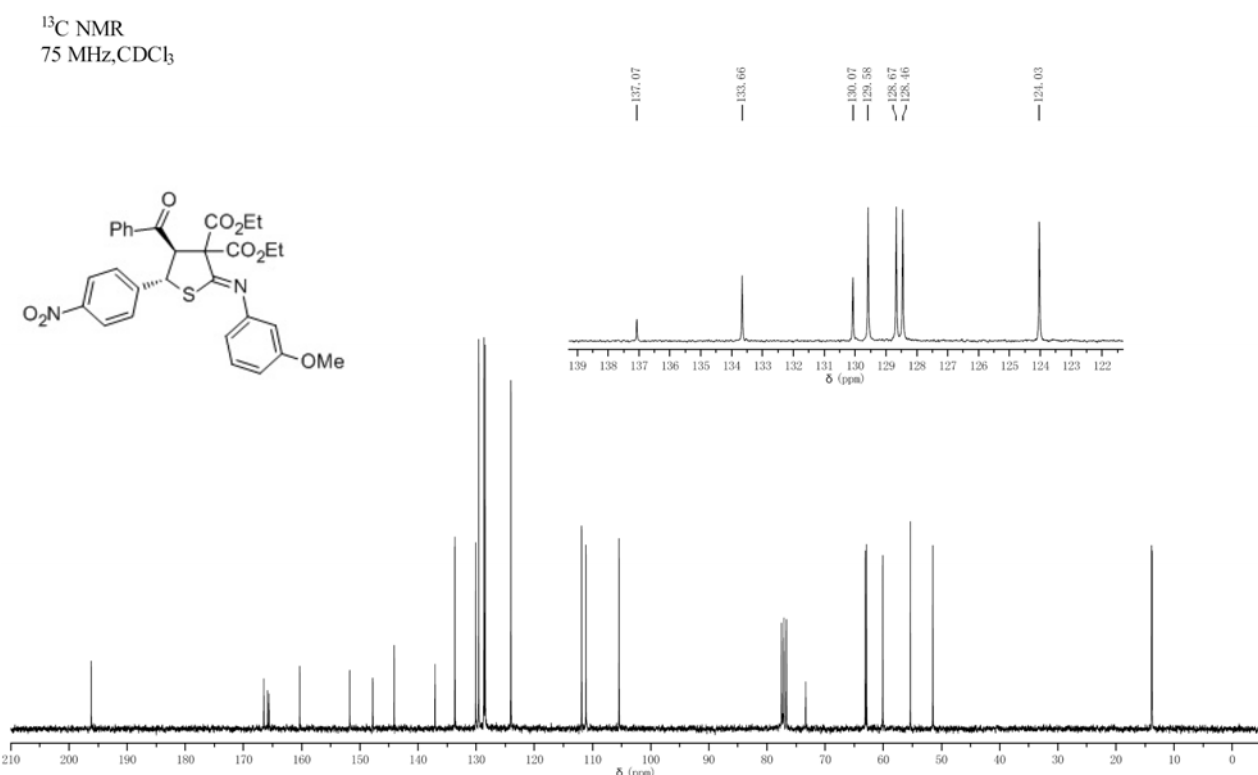
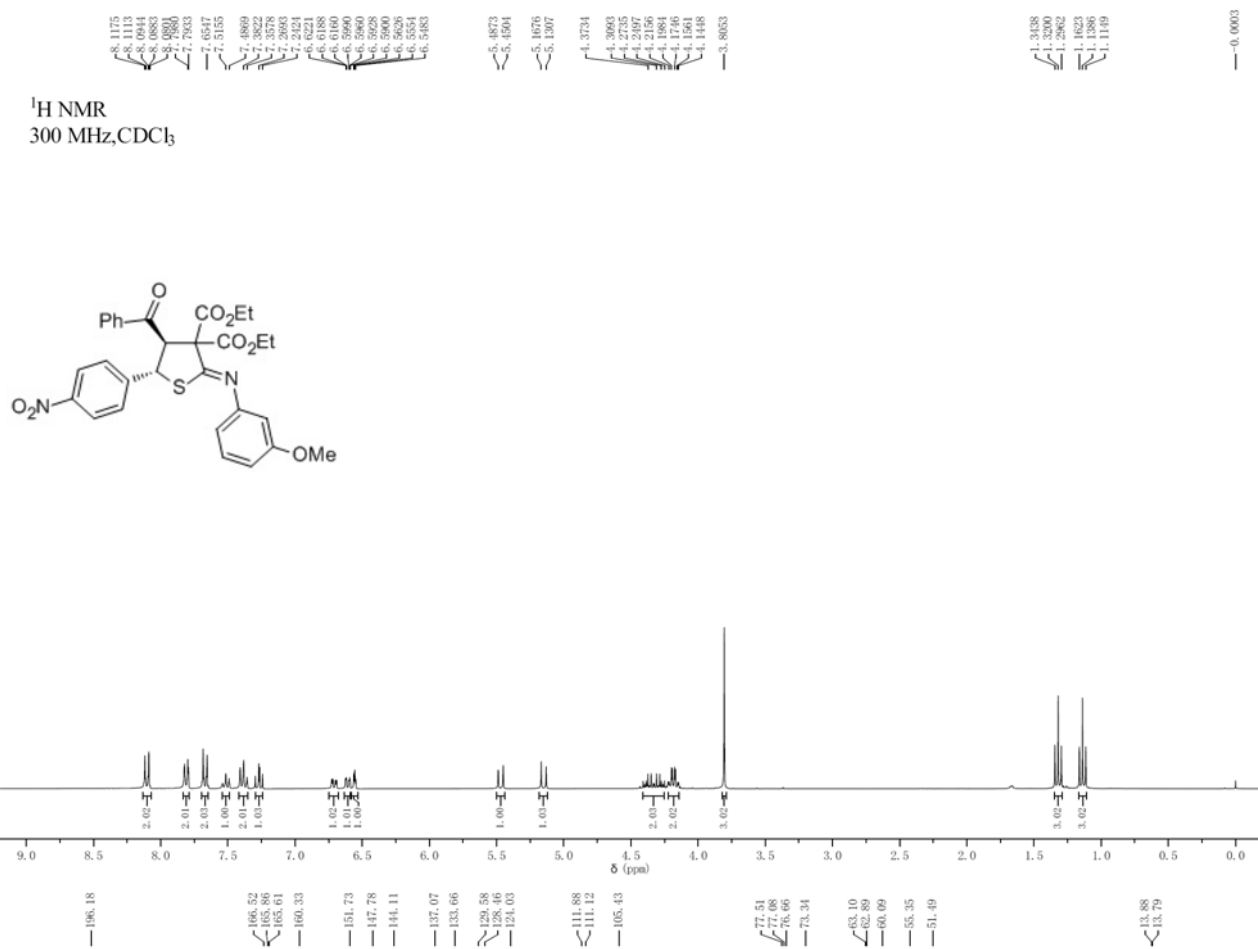
¹H NMR
 300 MHz, CDCl₃



¹³C NMR
 75 MHz, CDCl₃



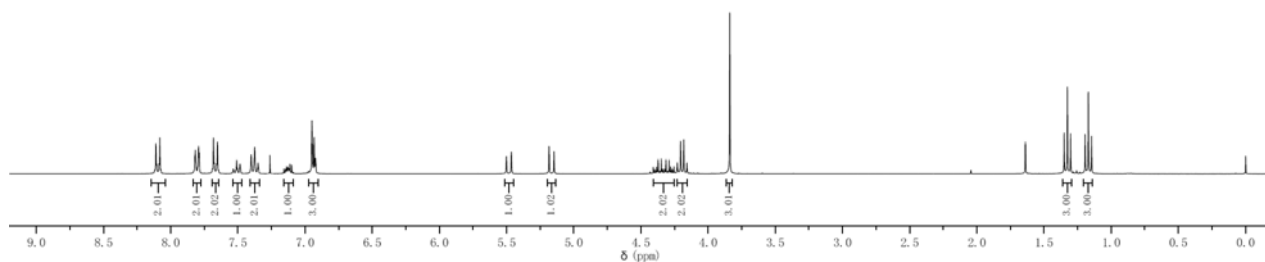
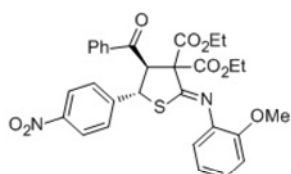
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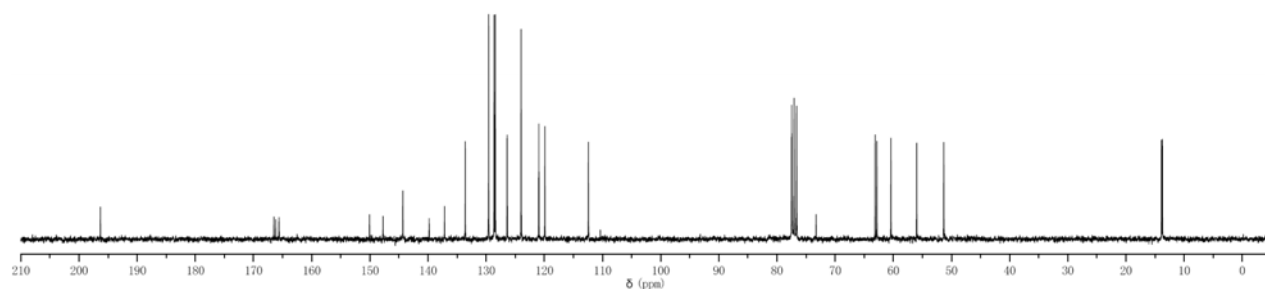
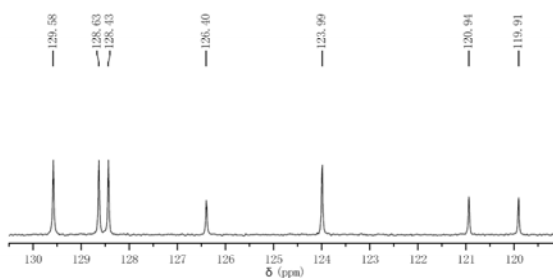
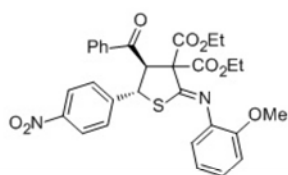
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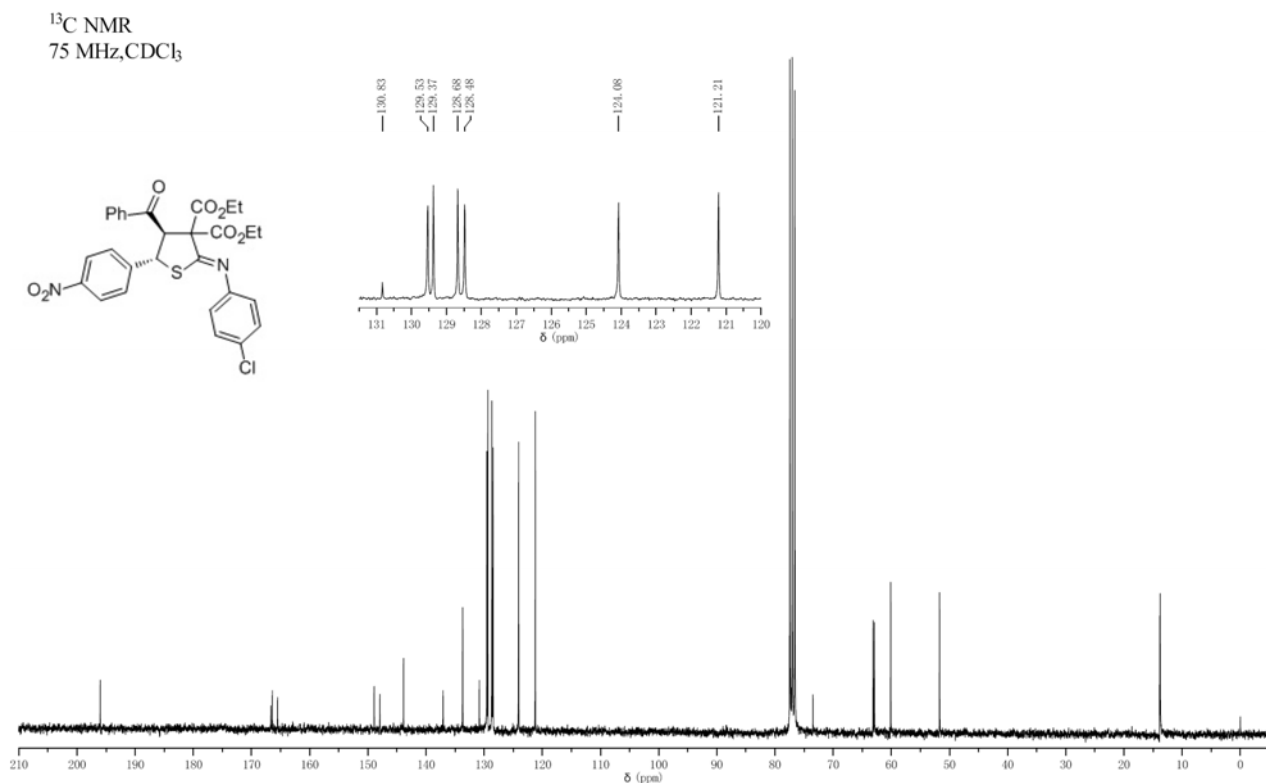
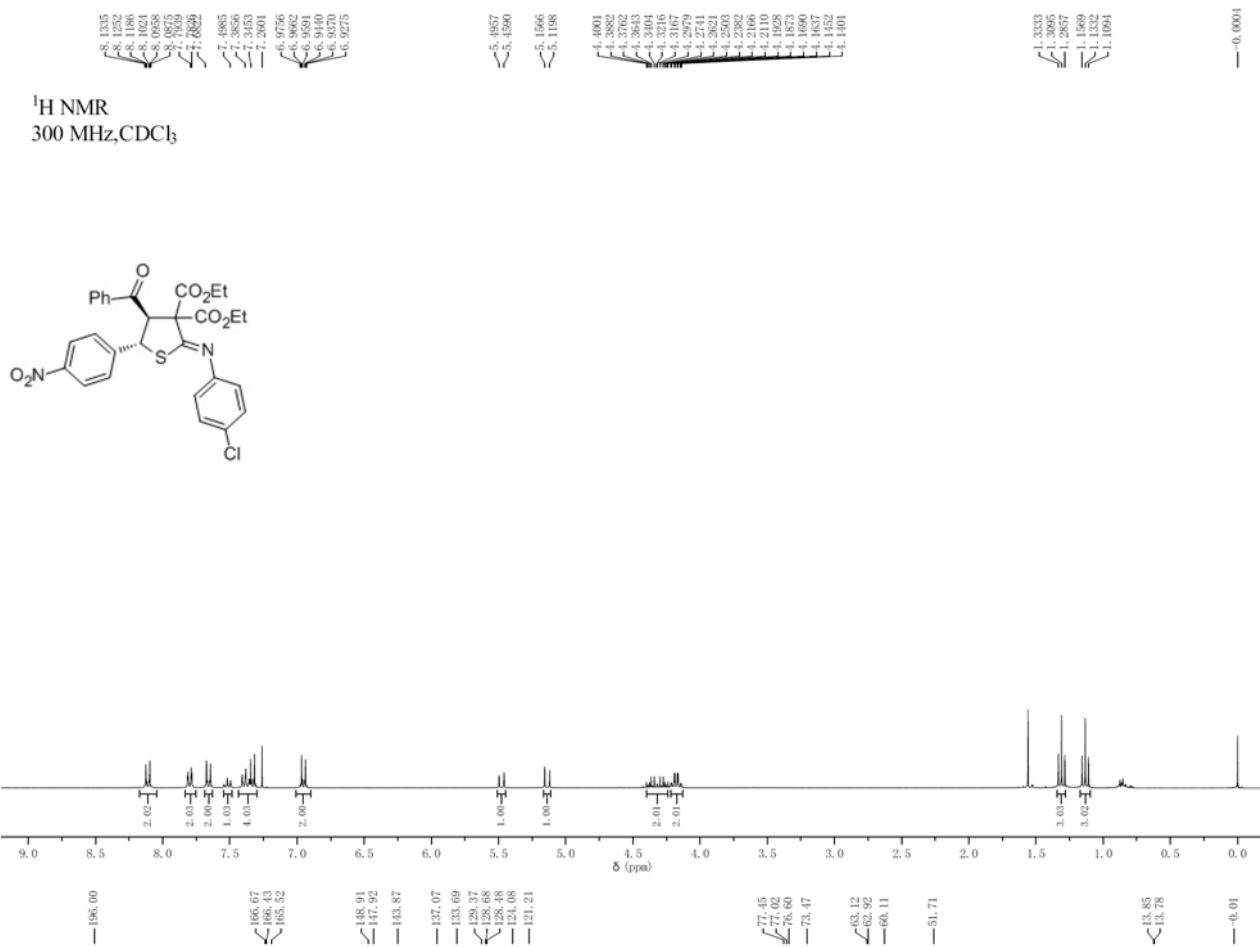
¹H NMR
 300 MHz, CDCl₃



¹³C NMR
 75 MHz, CDCl₃



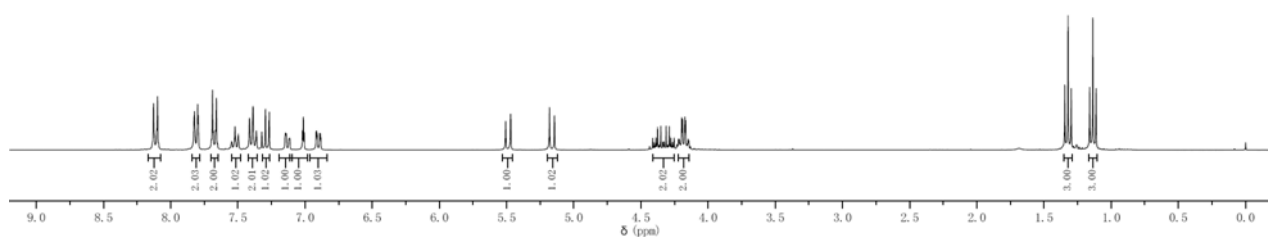
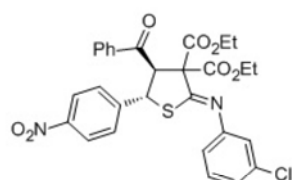
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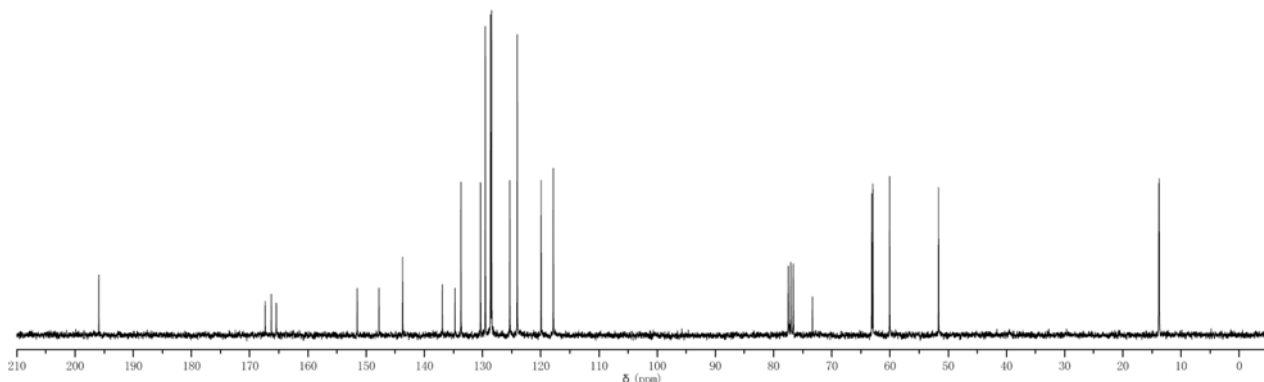
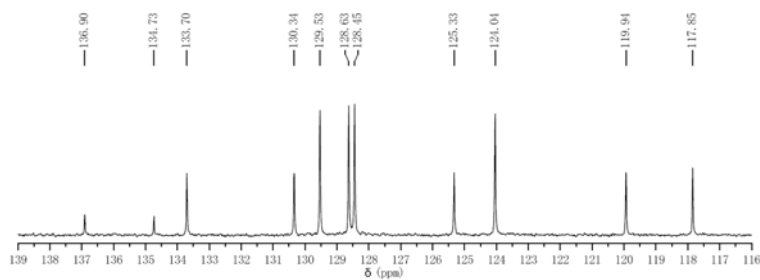
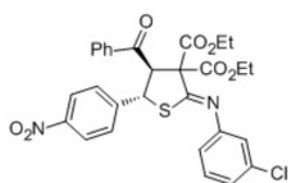
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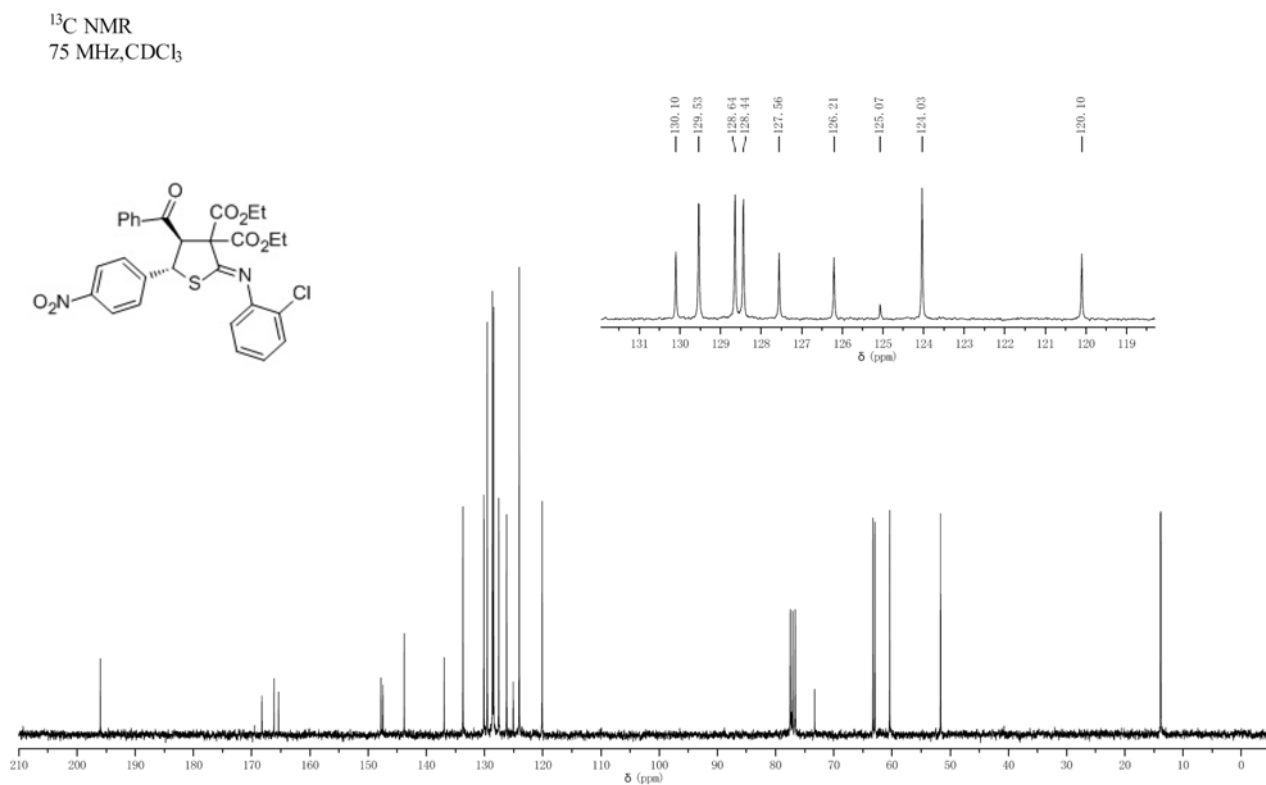
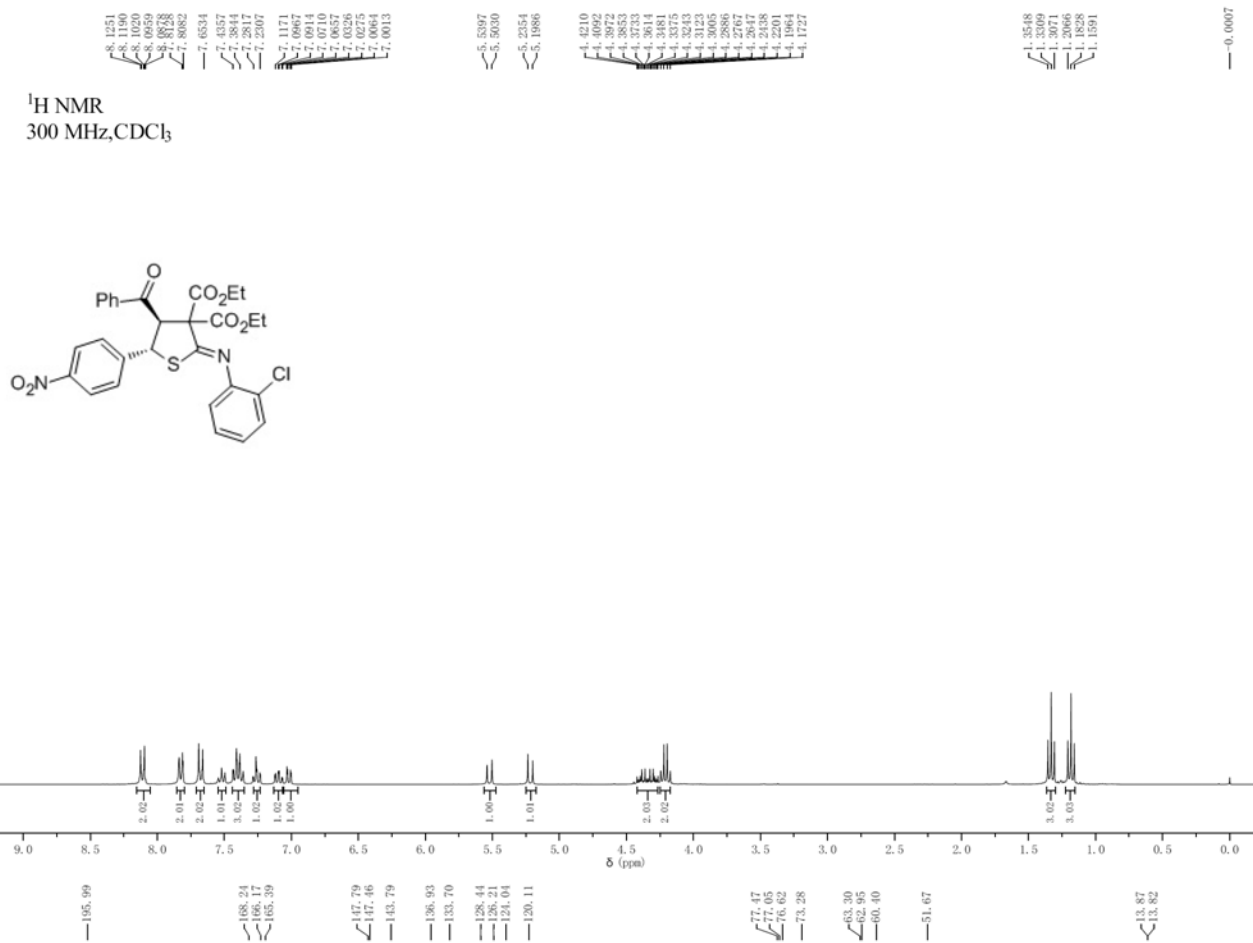
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 300 MHz, CDCl₃



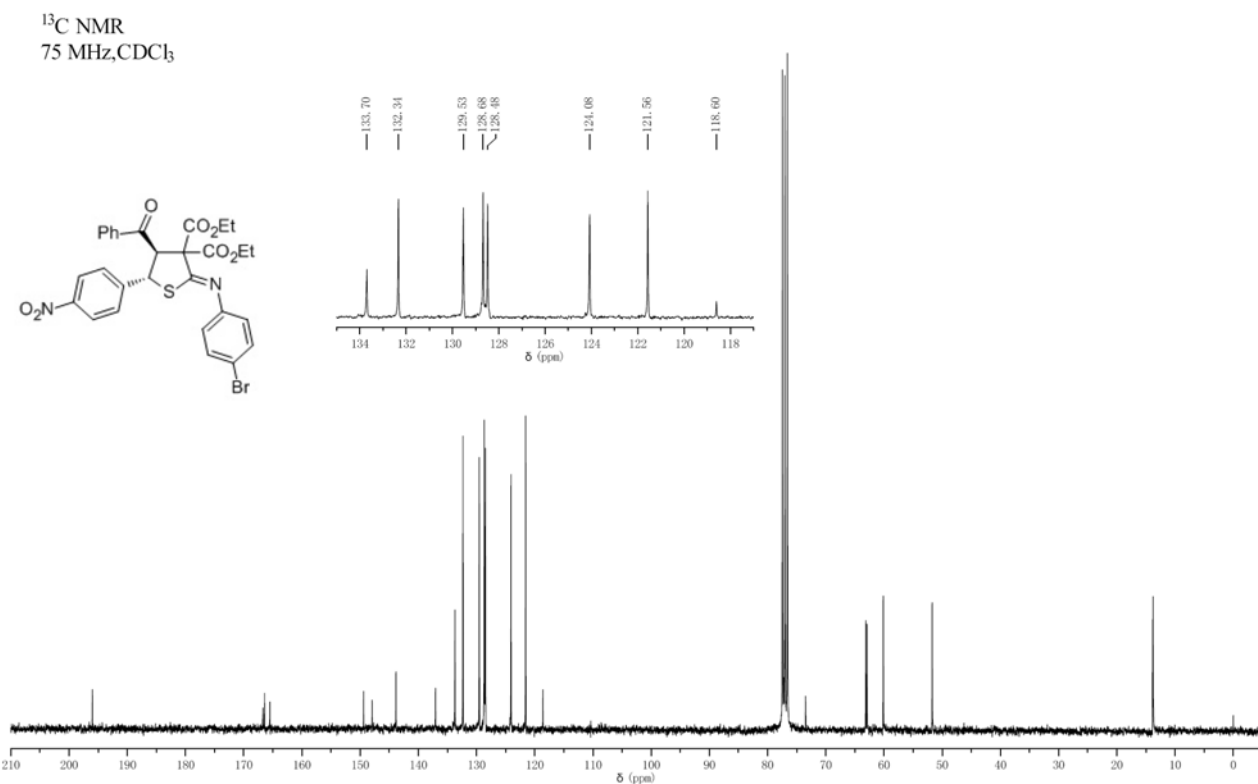
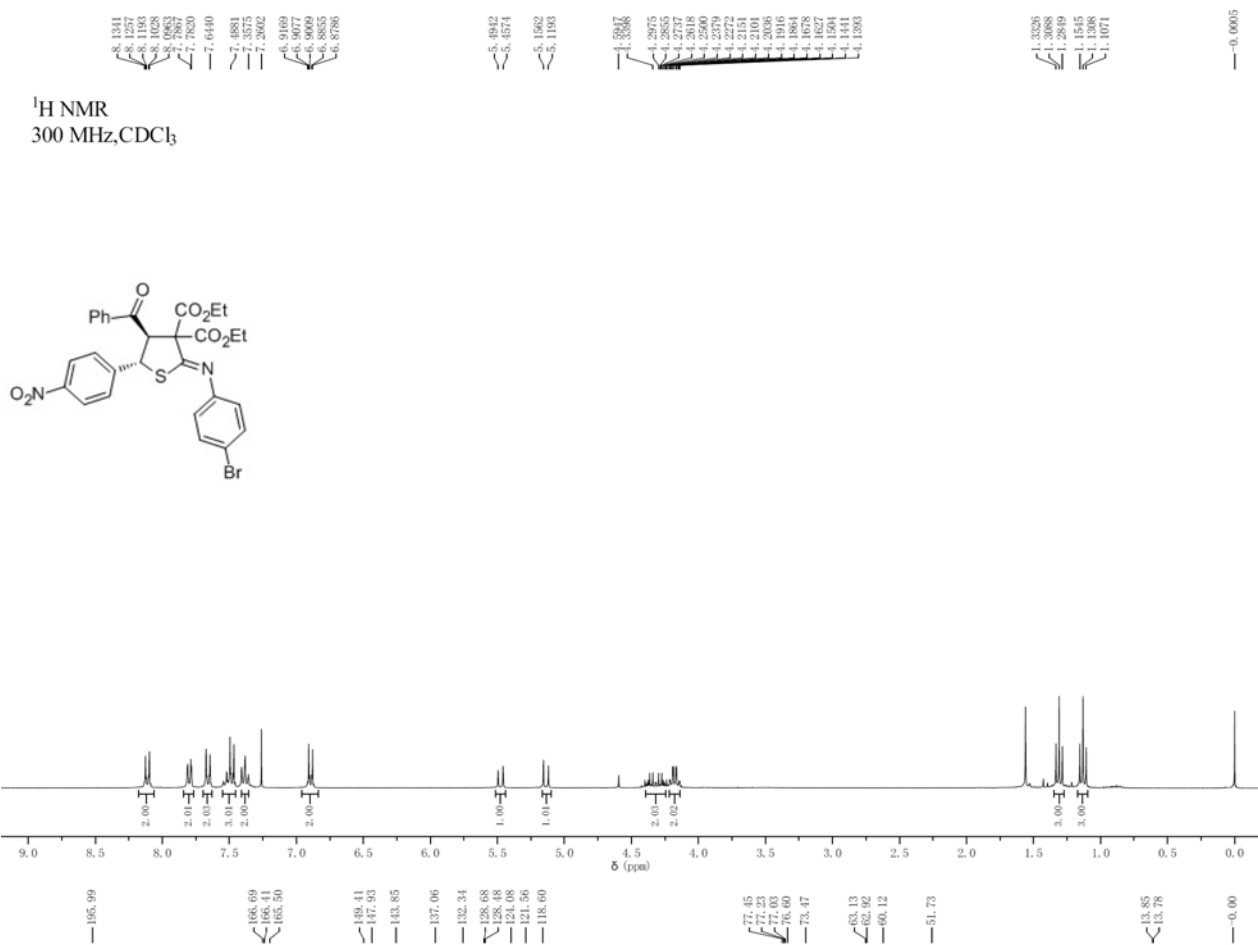
¹³C NMR
 75 MHz, CDCl₃



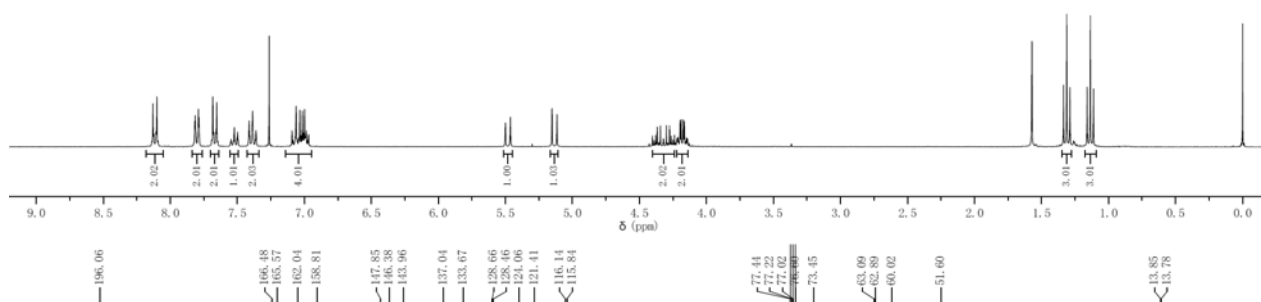
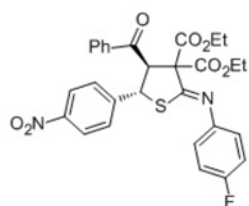
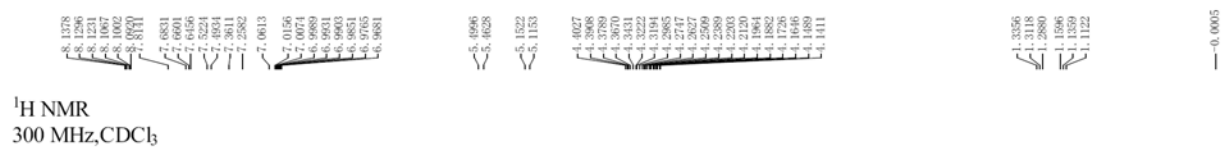
Compound 3aj



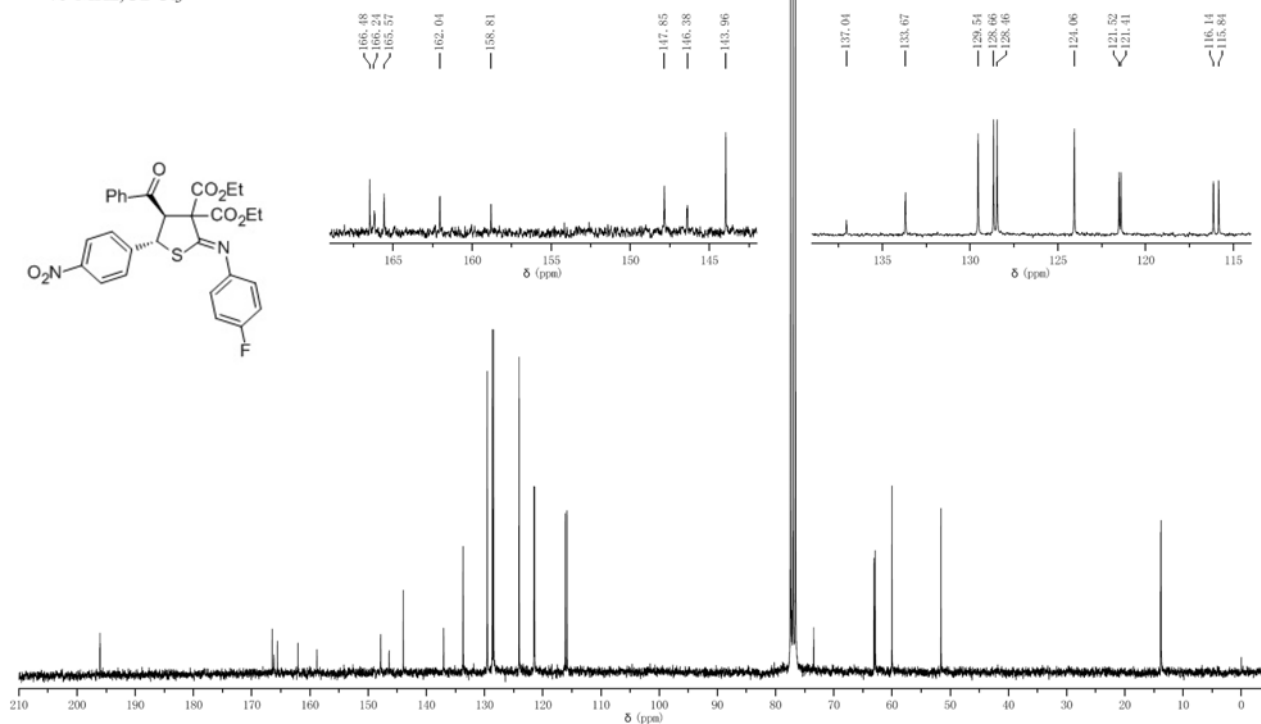
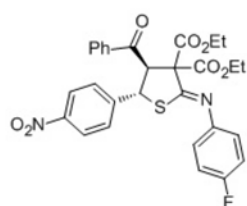
Compound 3ak



Compound 3al



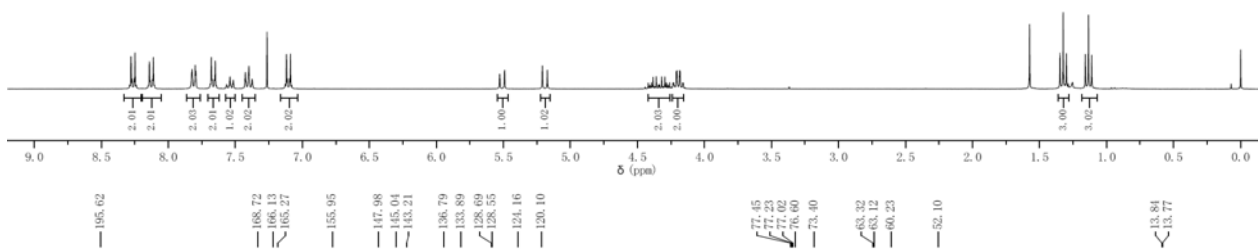
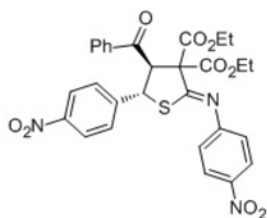
¹³C NMR
 75 MHz, CDCl₃



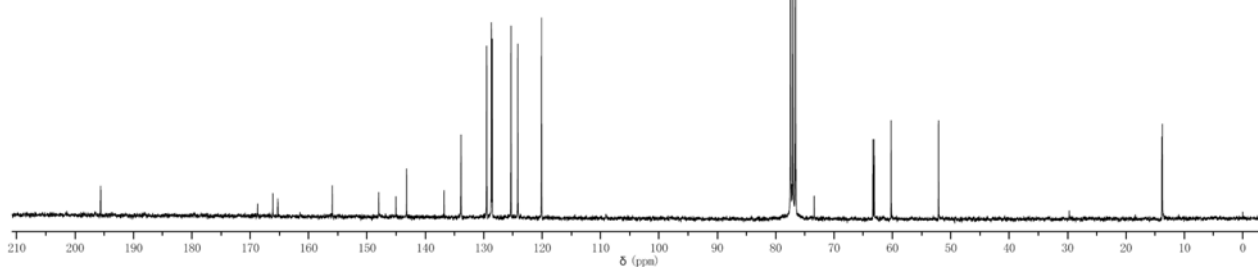
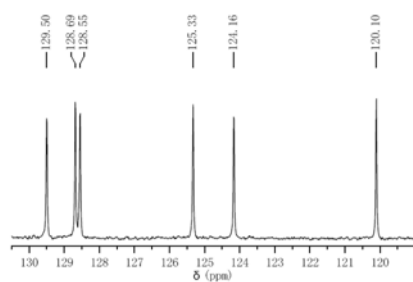
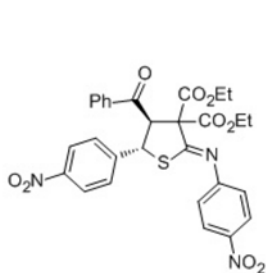
Compound 3am



¹H NMR
 300 MHz, CDCl₃



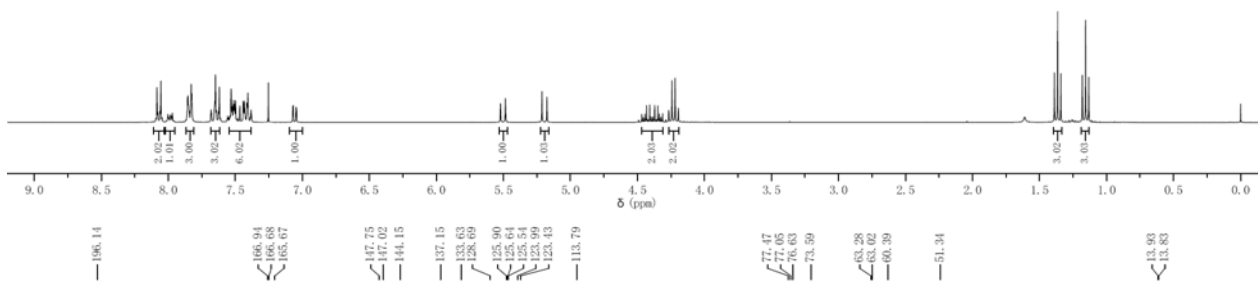
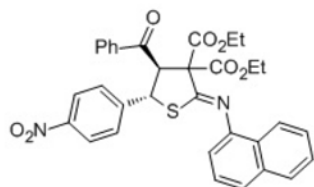
¹³C NMR
 75 MHz, CDCl₃



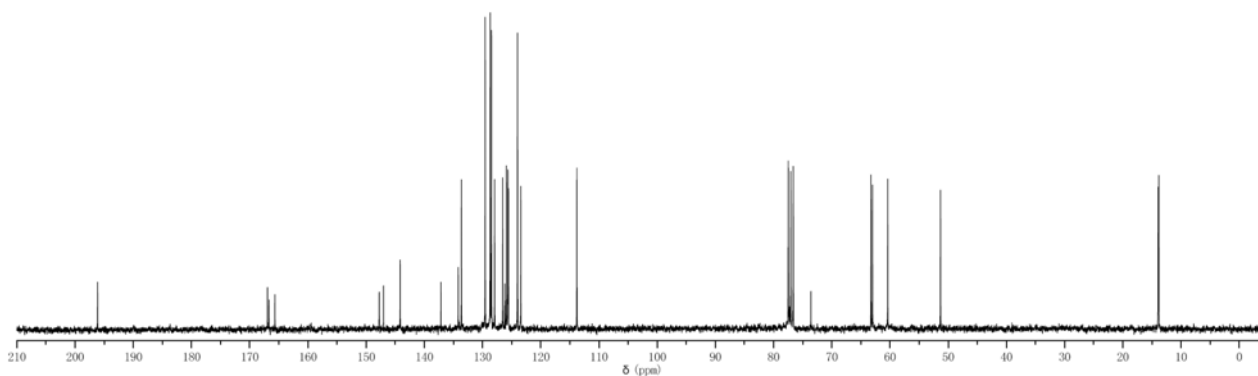
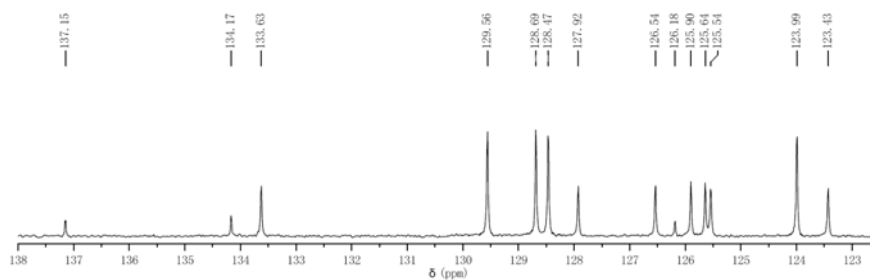
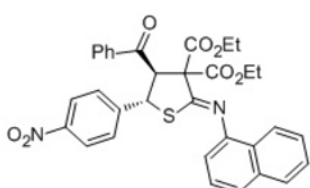
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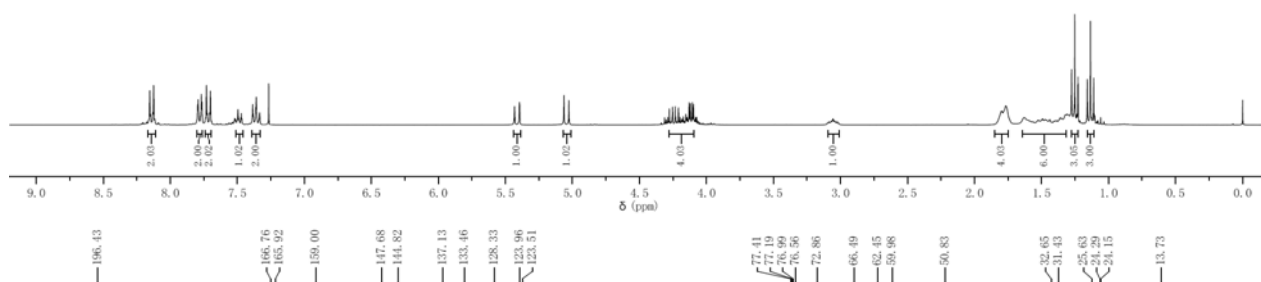
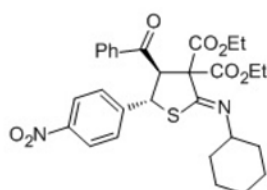
¹H NMR
300 MHz, CDCl₃



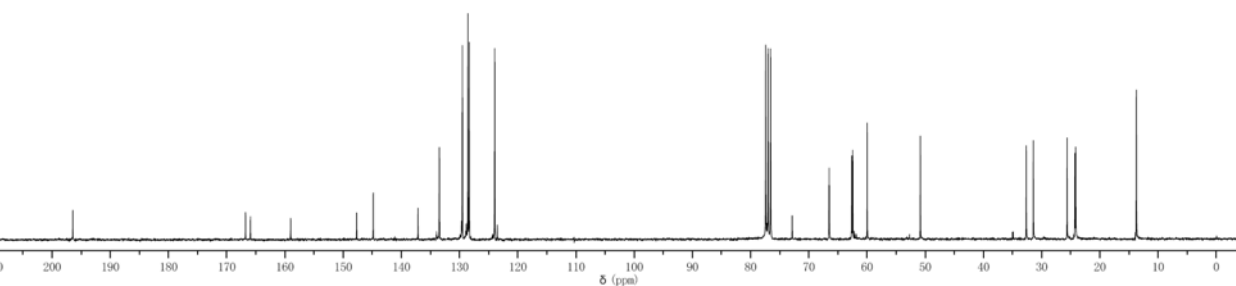
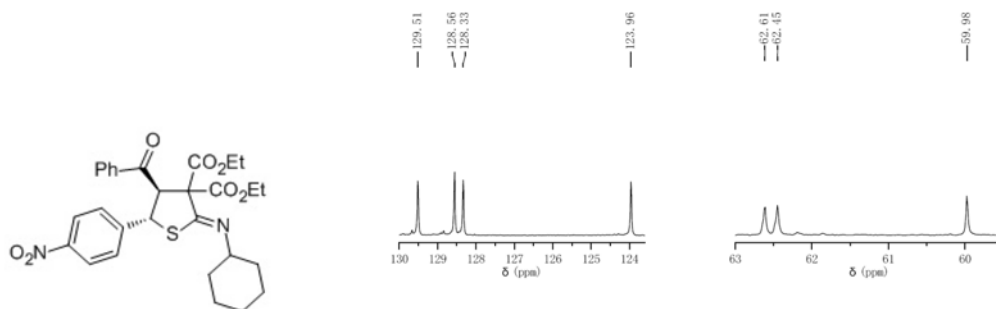
¹³C NMR
75 MHz, CDCl₃



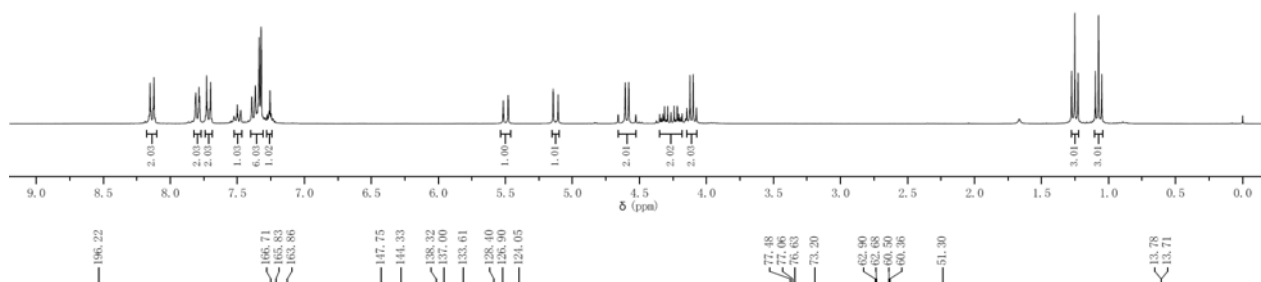
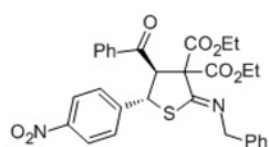
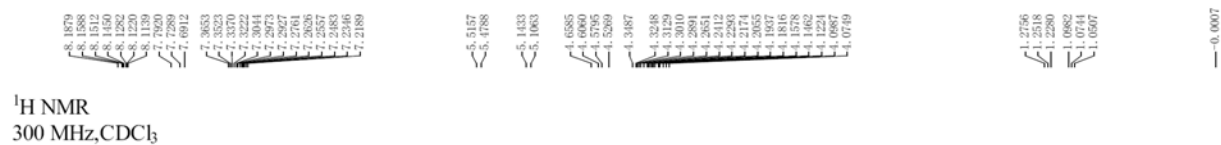
Compound 3ao



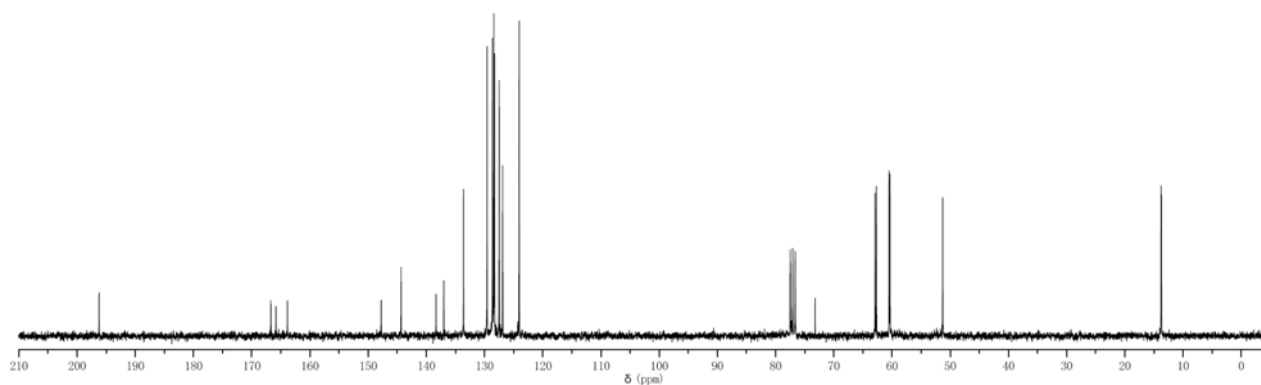
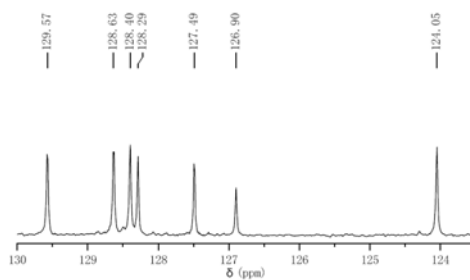
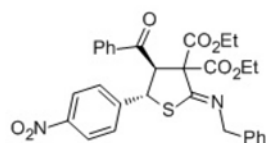
¹³C NMR
 75 MHz, CDCl₃



Compound 3ap



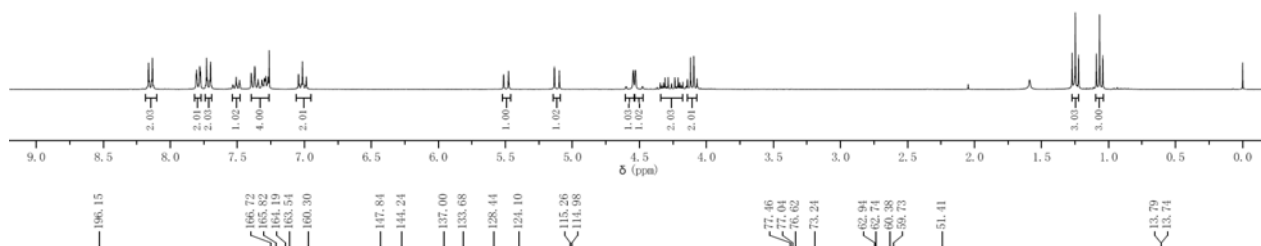
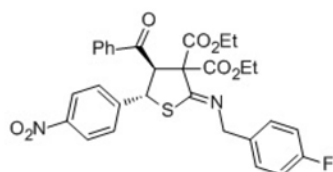
¹³C NMR
 75 MHz, CDCl₃



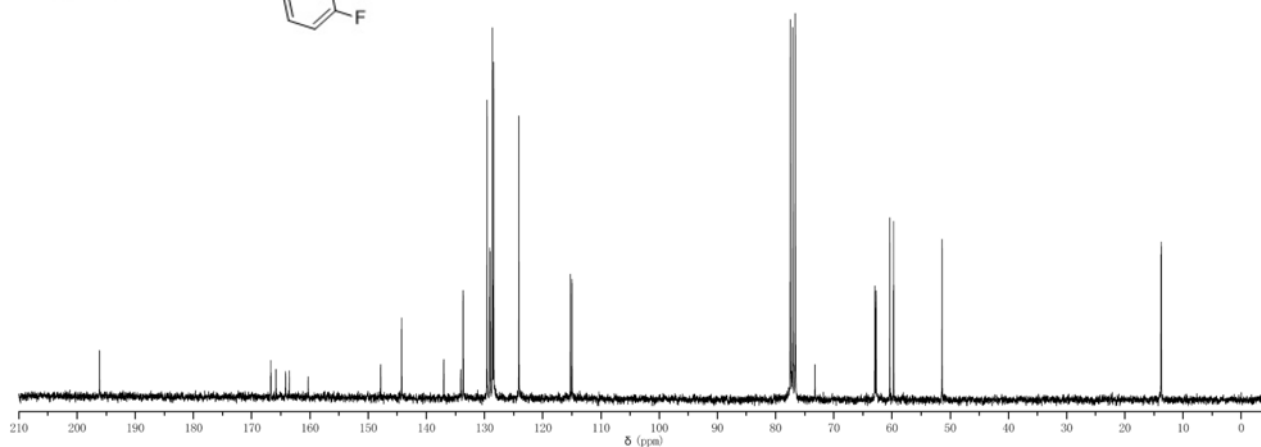
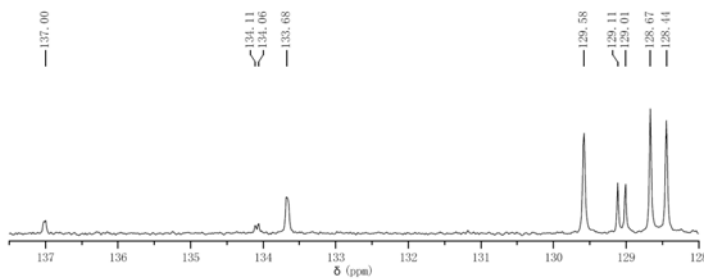
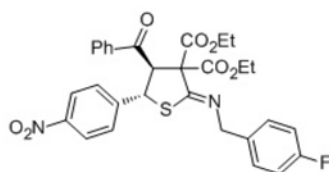
Compound 3aq



¹H NMR
 300 MHz, CDCl₃



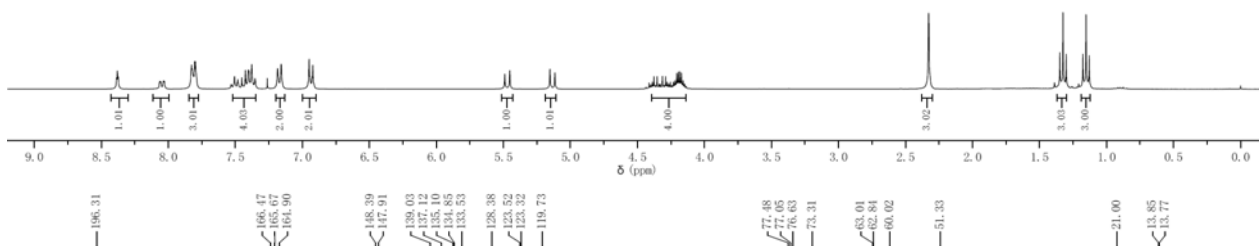
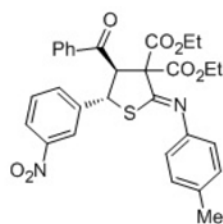
¹³C NMR
 75 MHz, CDCl₃



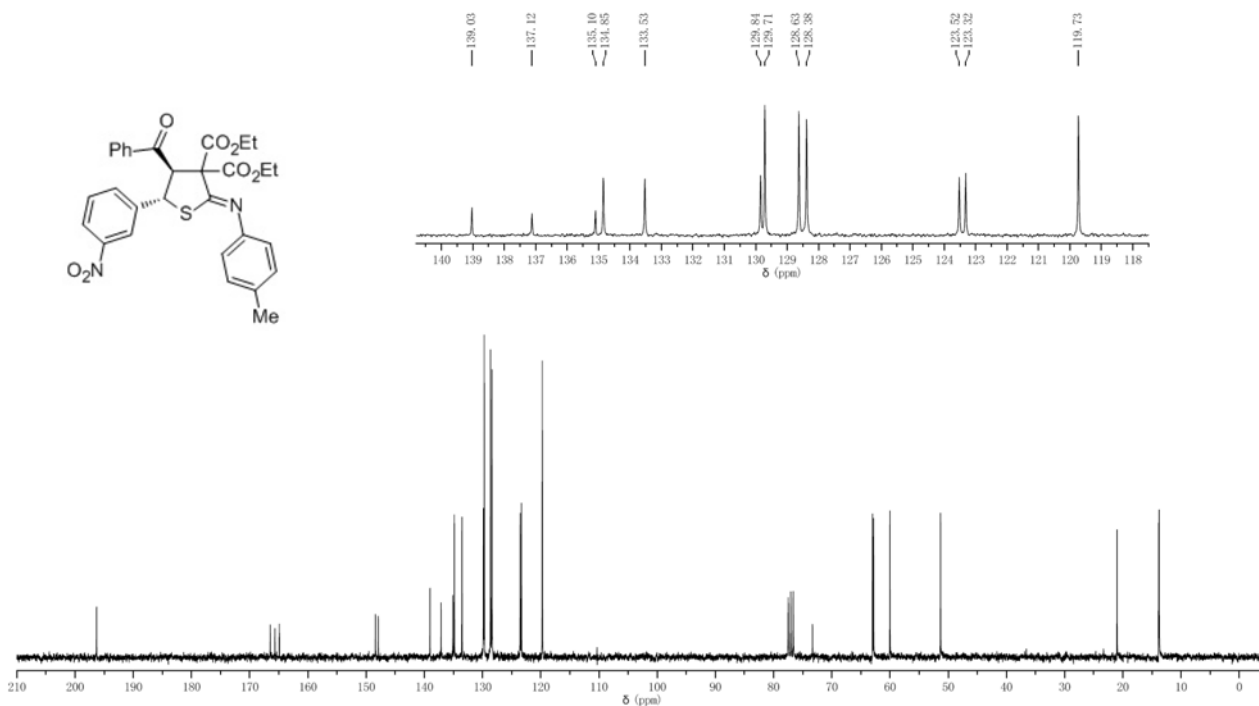
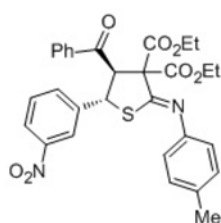
Compound **3ba**



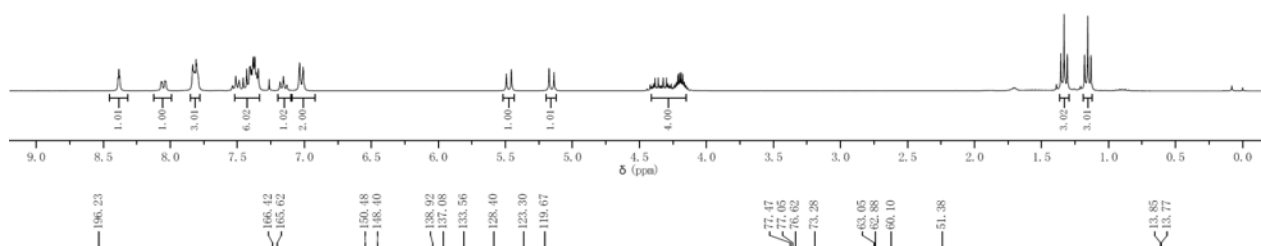
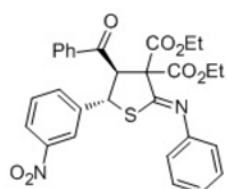
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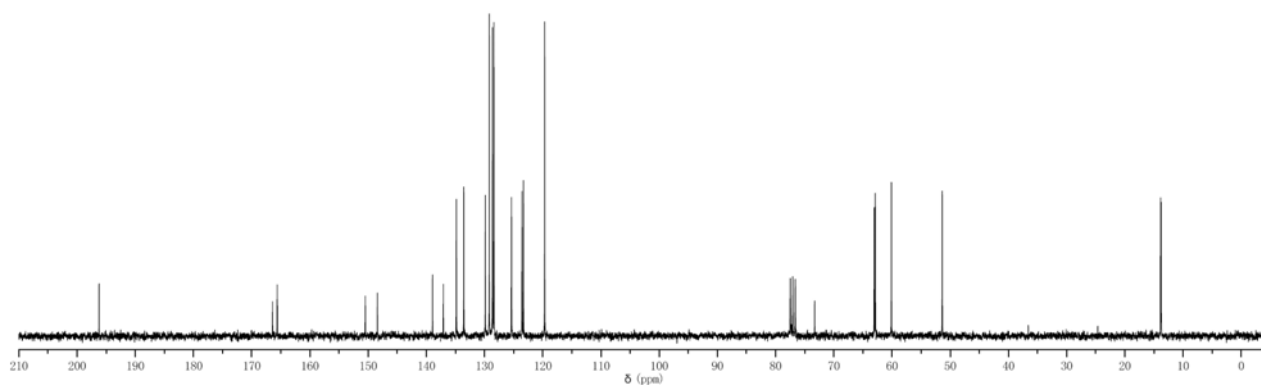
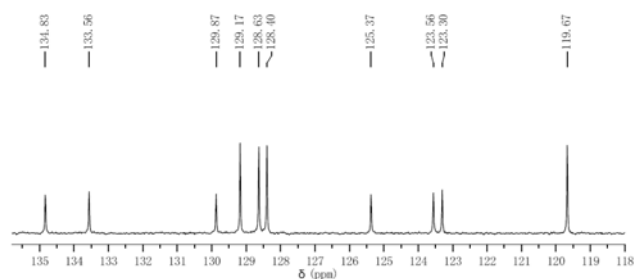
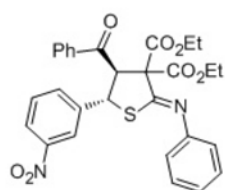
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75 MHz, CDCl₃



Compound 3bd



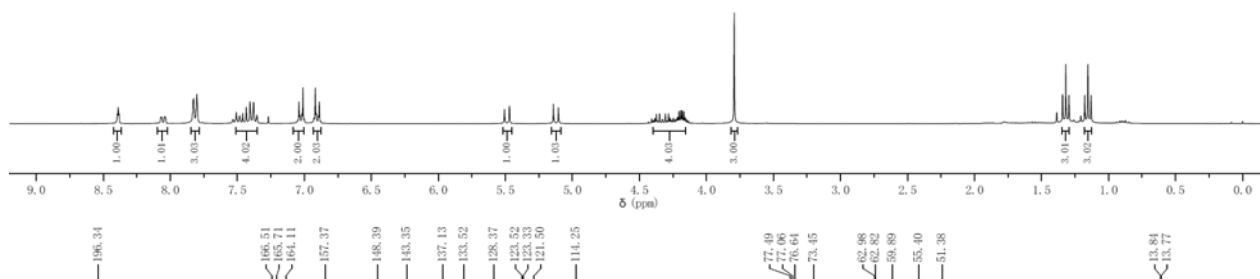
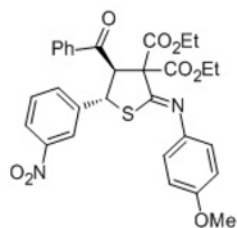
¹³C NMR
 75 MHz, CDCl₃



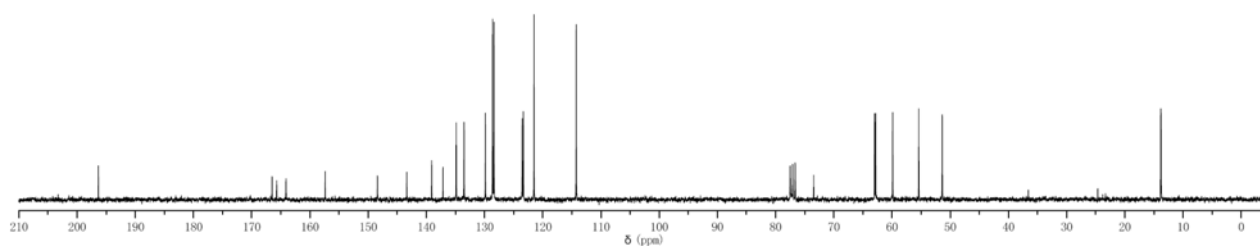
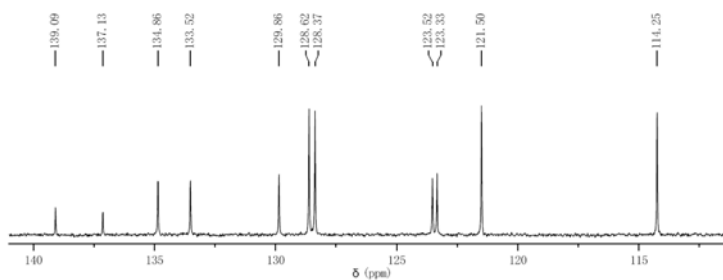
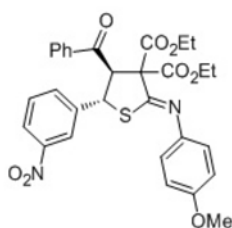
Compound 3be



¹H NMR
300 MHz, CDCl₃



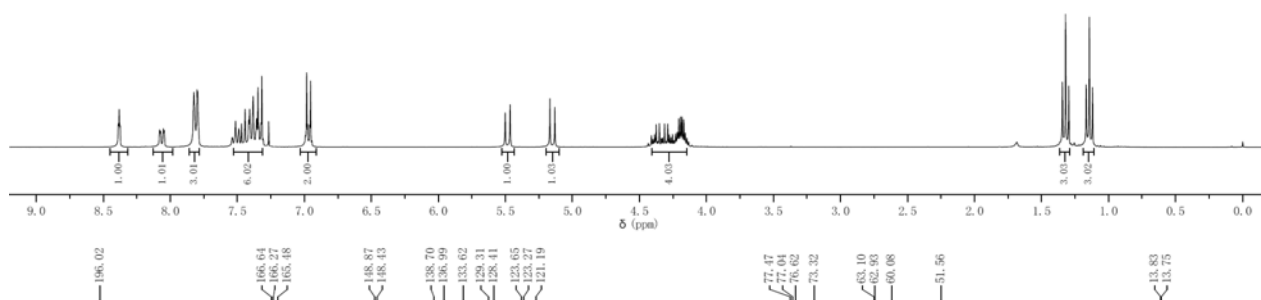
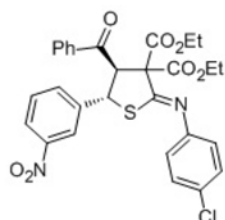
¹³C NMR
75 MHz, CDCl₃



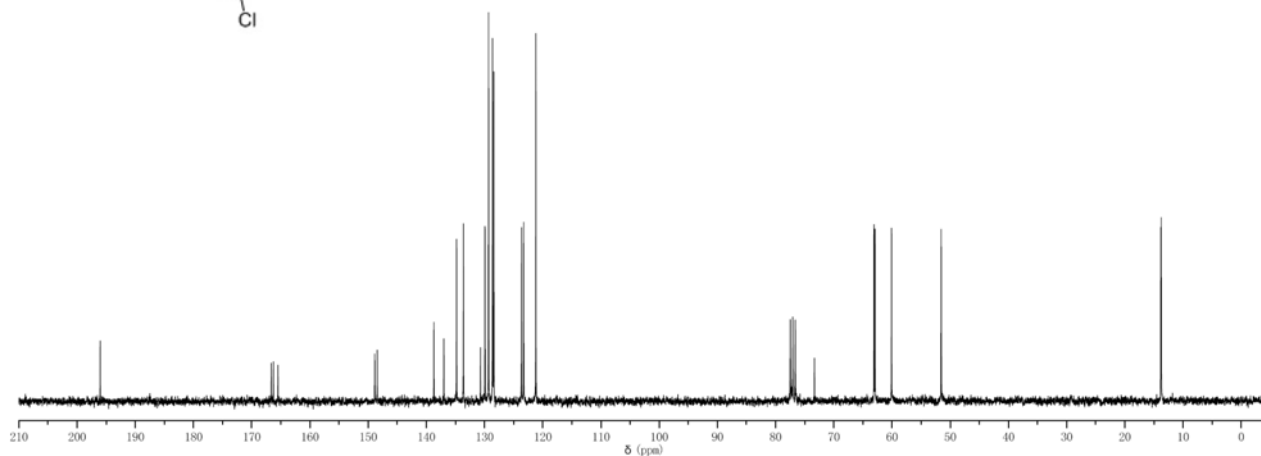
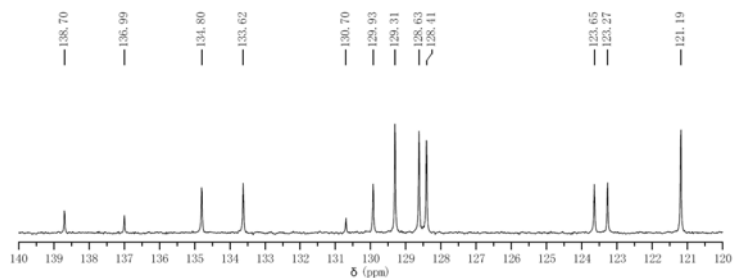
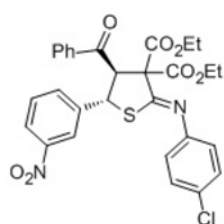
Compound 3bh



¹H NMR
300 MHz, CDCl₃



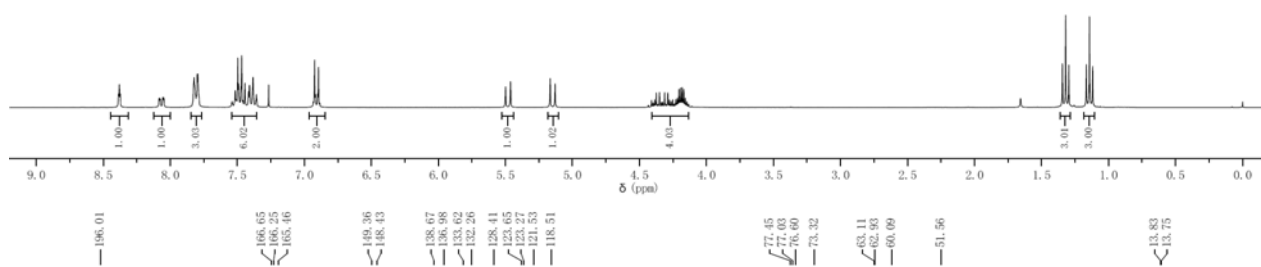
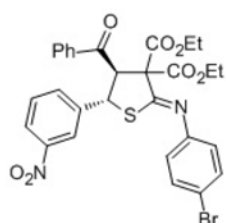
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75 MHz, CDCl₃



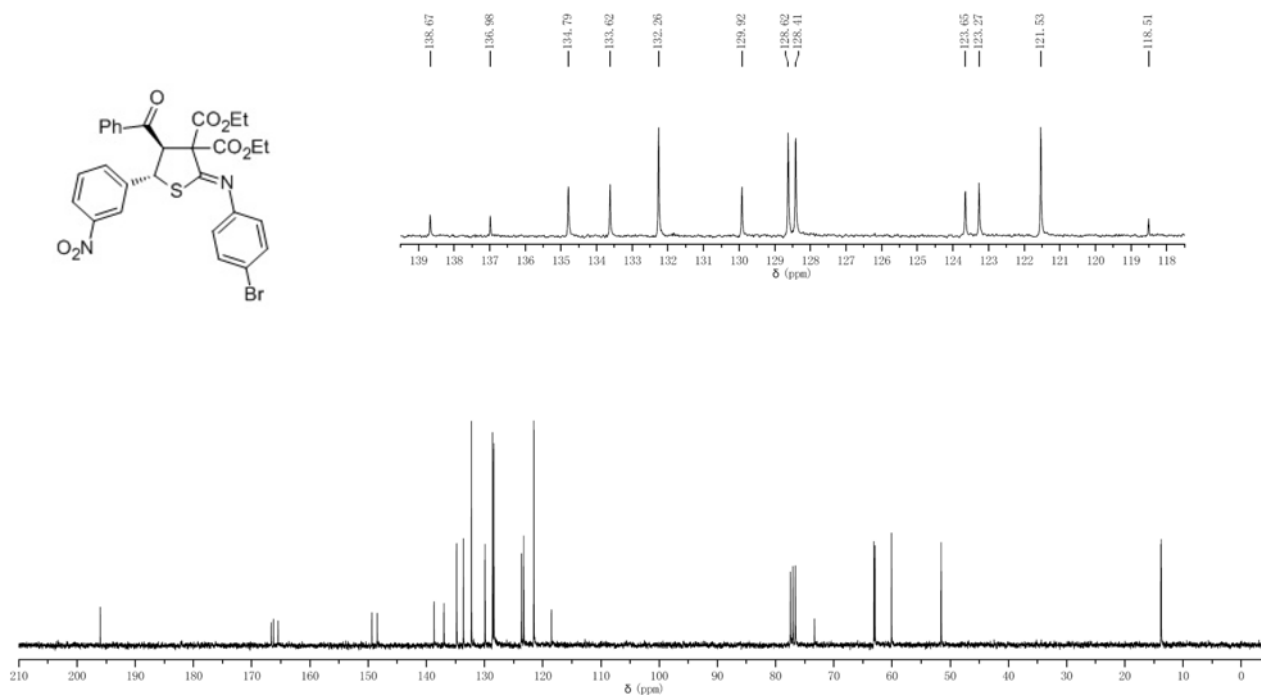
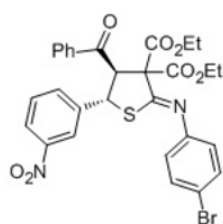
Compound 3bk



¹H NMR
 300 MHz, CDCl₃



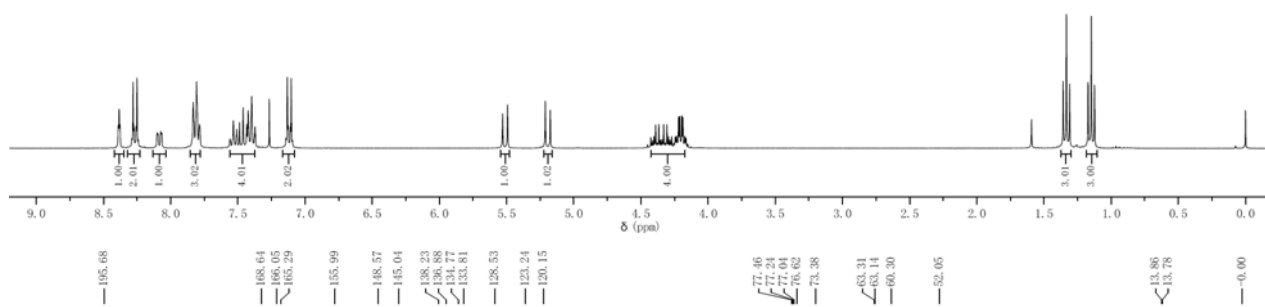
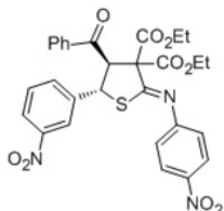
¹³C NMR
 75 MHz, CDCl₃



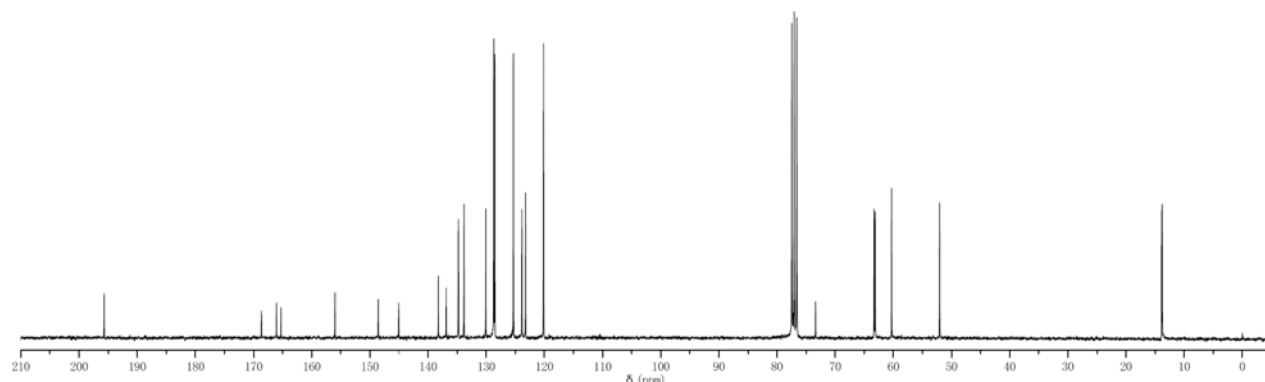
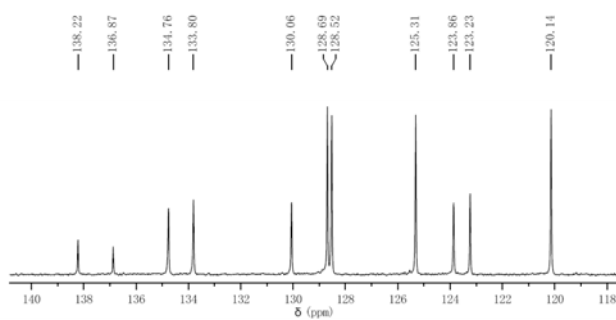
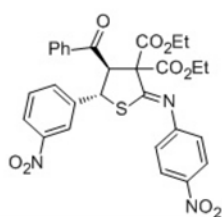
Compound 3bm



¹H NMR
300 MHz, CDCl₃



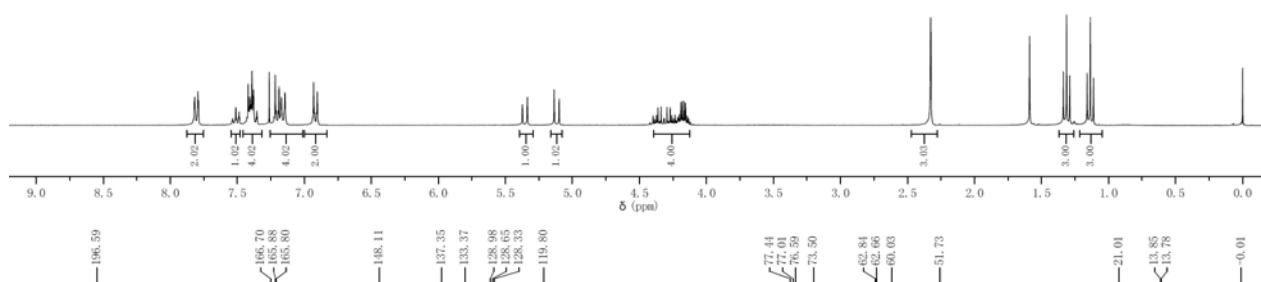
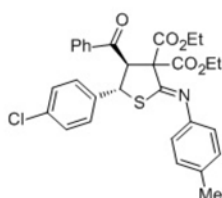
¹³C NMR
75 MHz, CDCl₃



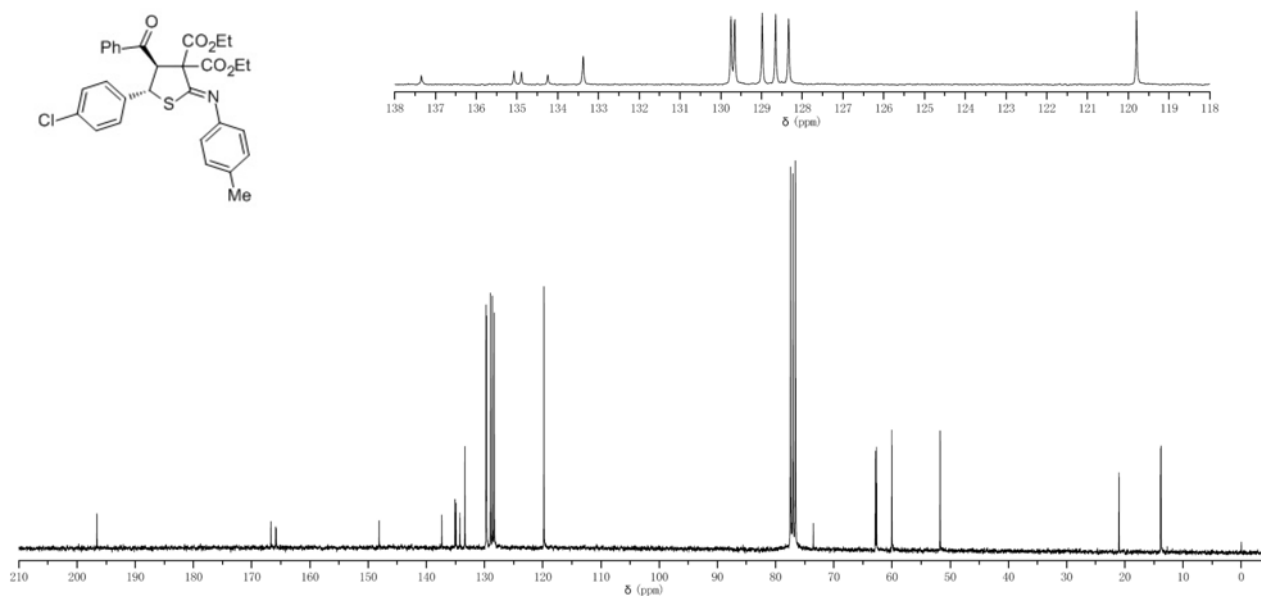
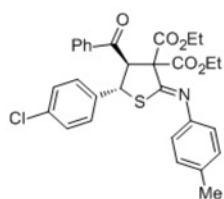
Compound 3ca



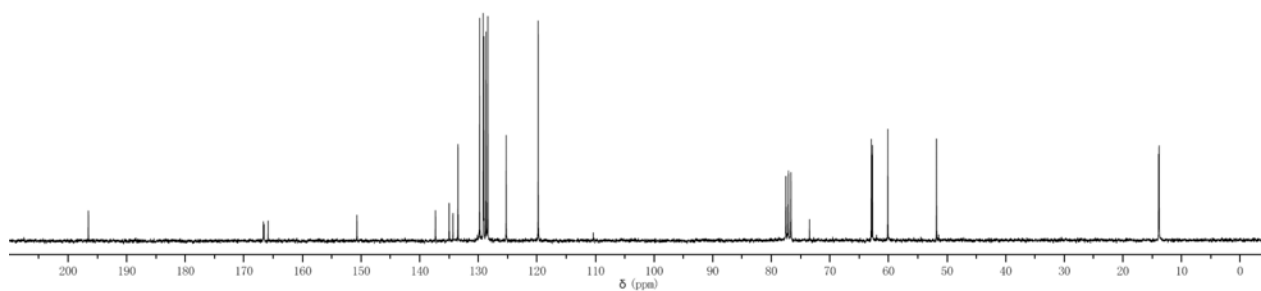
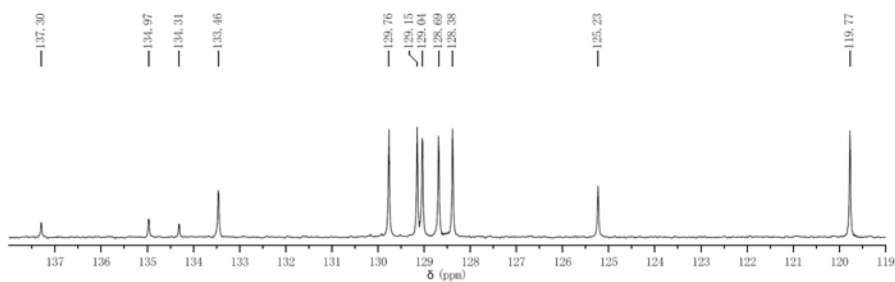
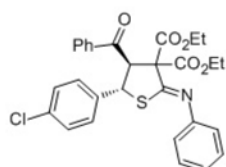
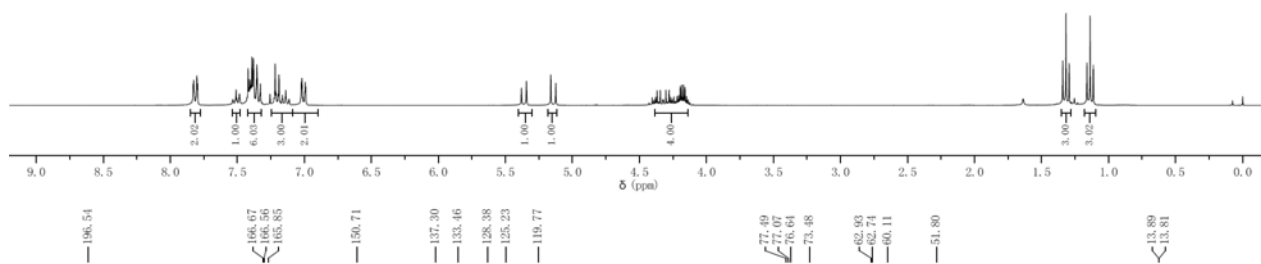
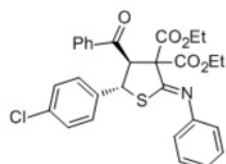
¹H NMR
300 MHz, CDCl₃



¹³C NMR
75 MHz, CDCl₃

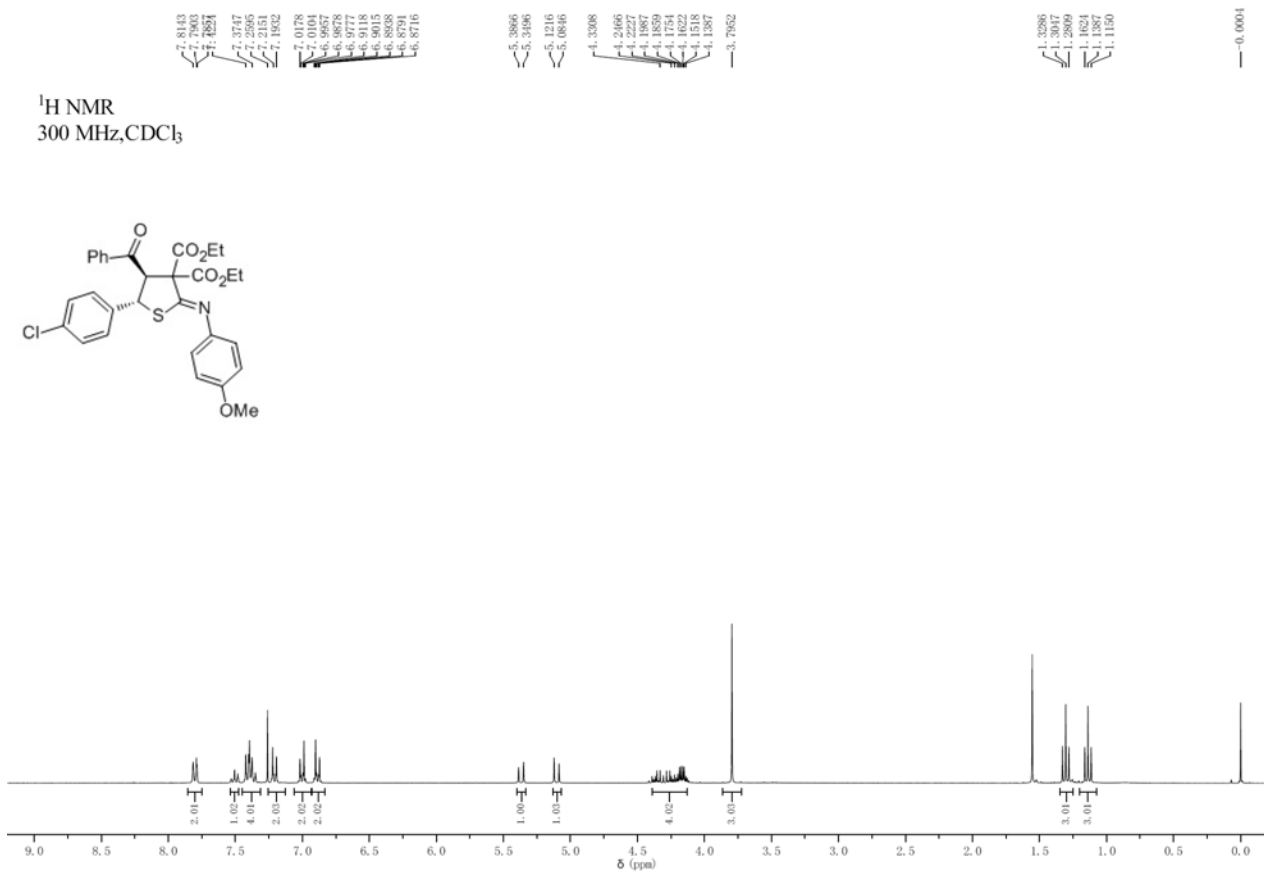
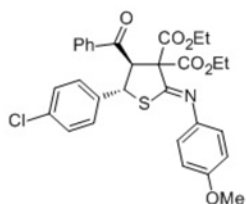


Compound 3cd

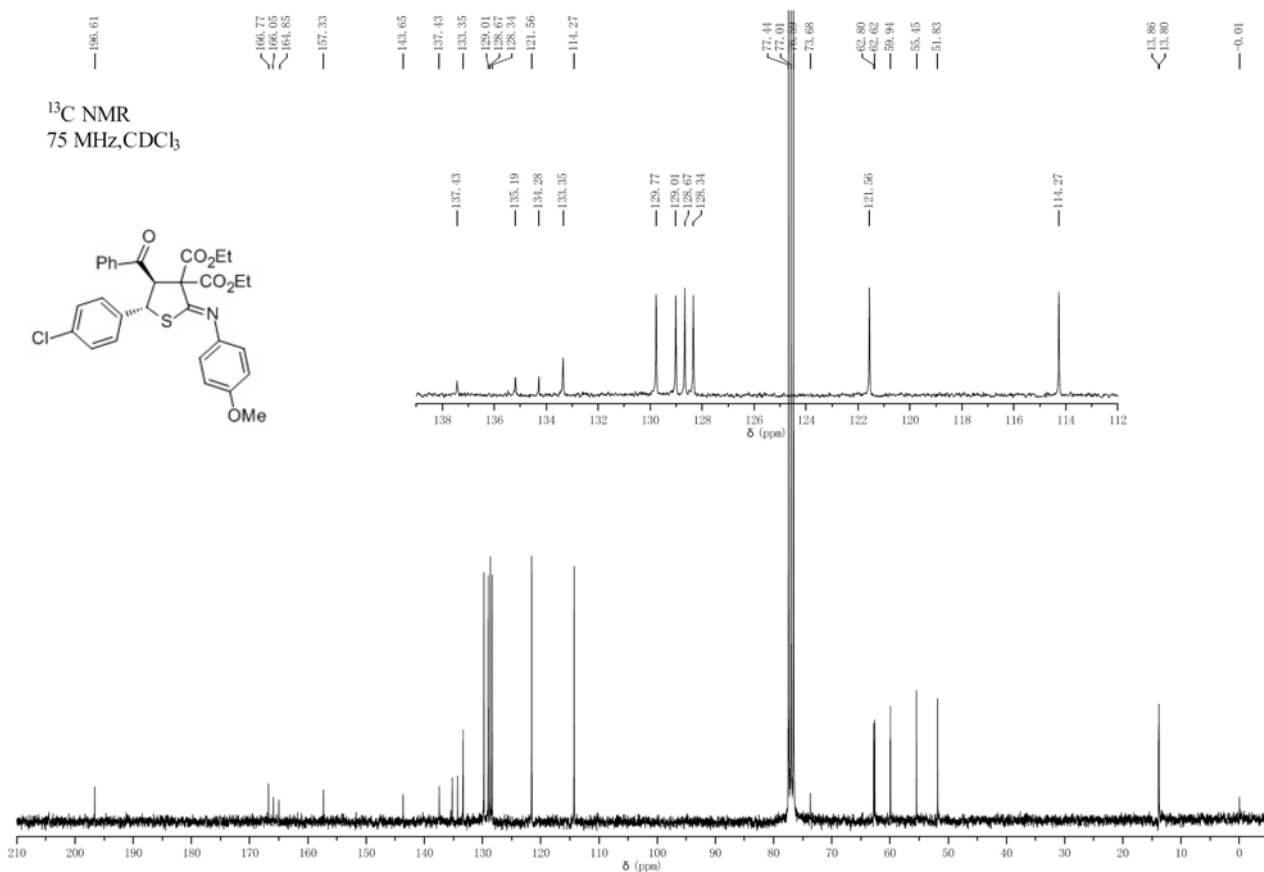
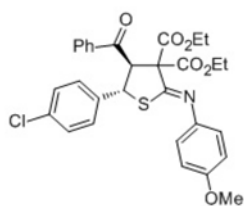


Compound 3ce

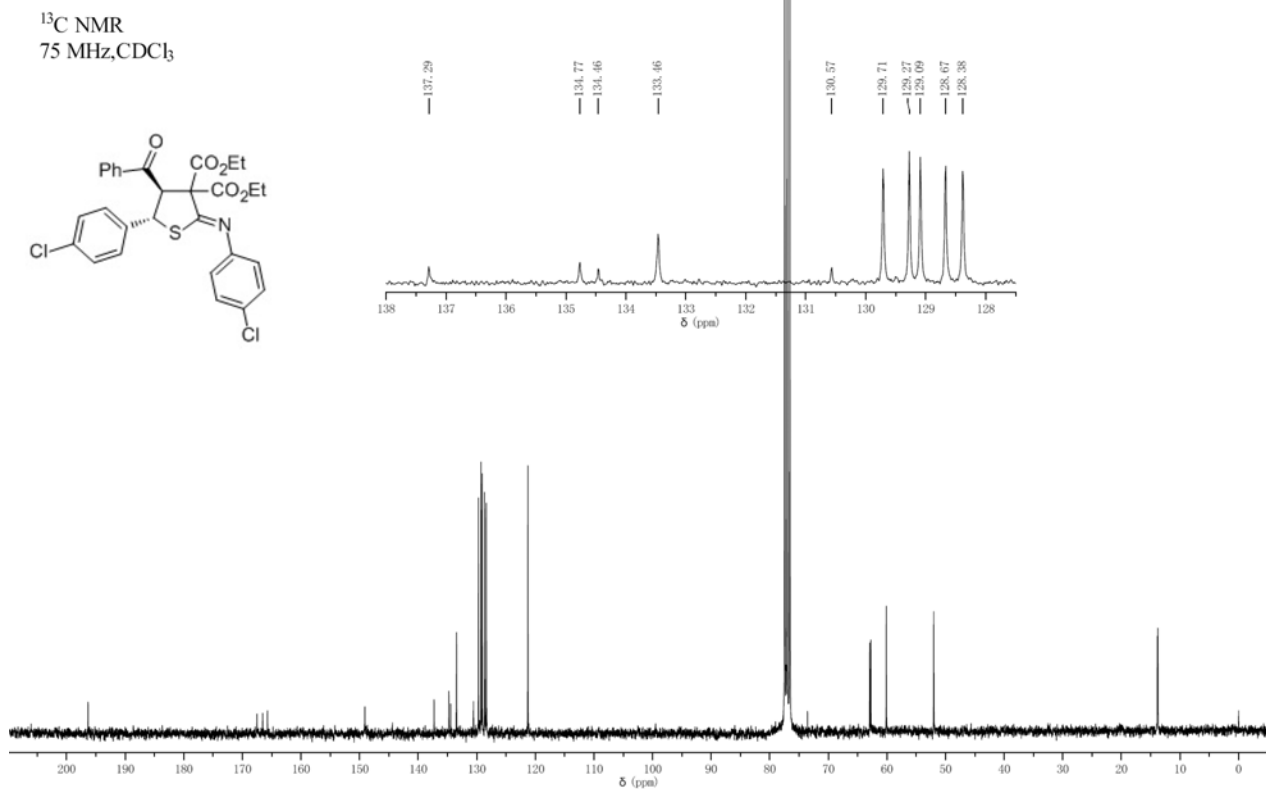
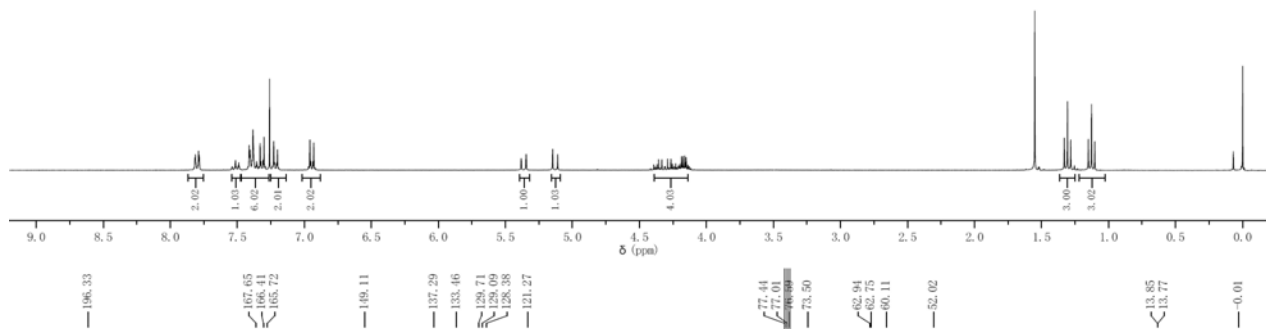
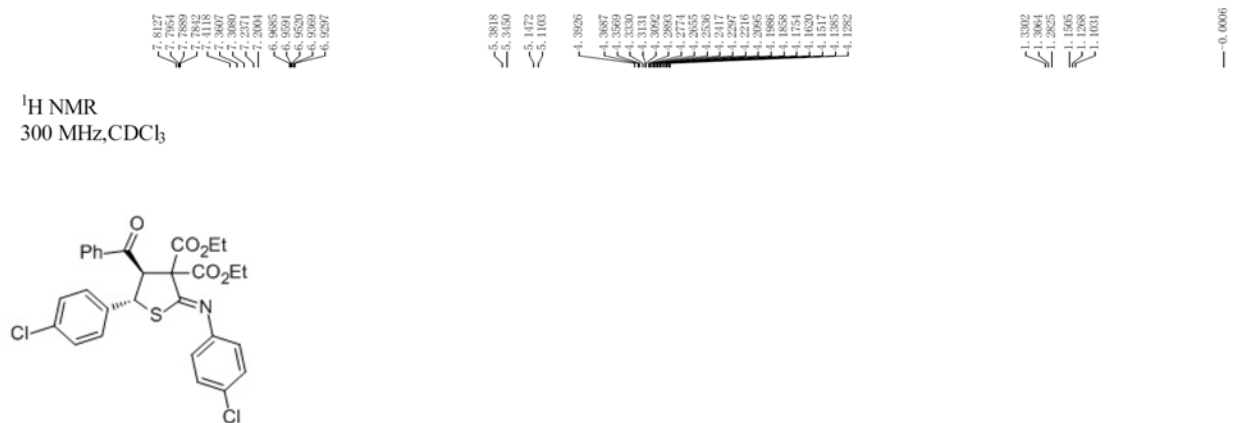
¹H NMR
300 MHz, CDCl₃



¹³C NMR
75 MHz, CDCl₃



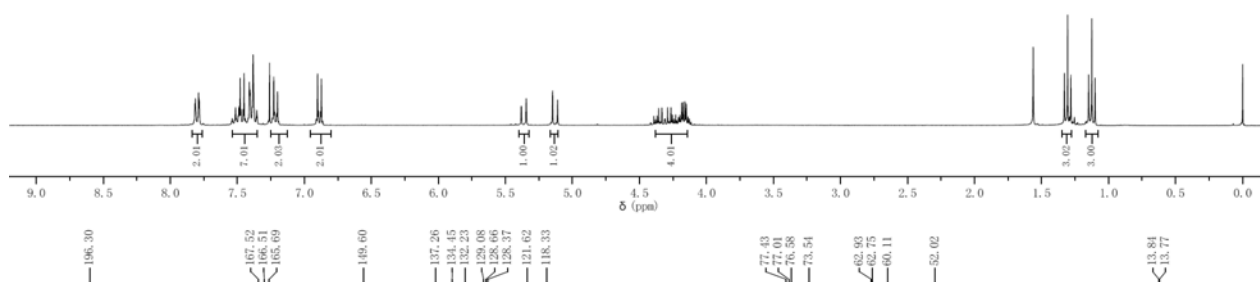
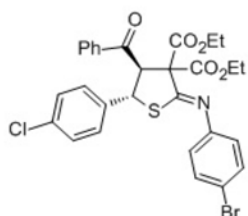
Compound 3ch



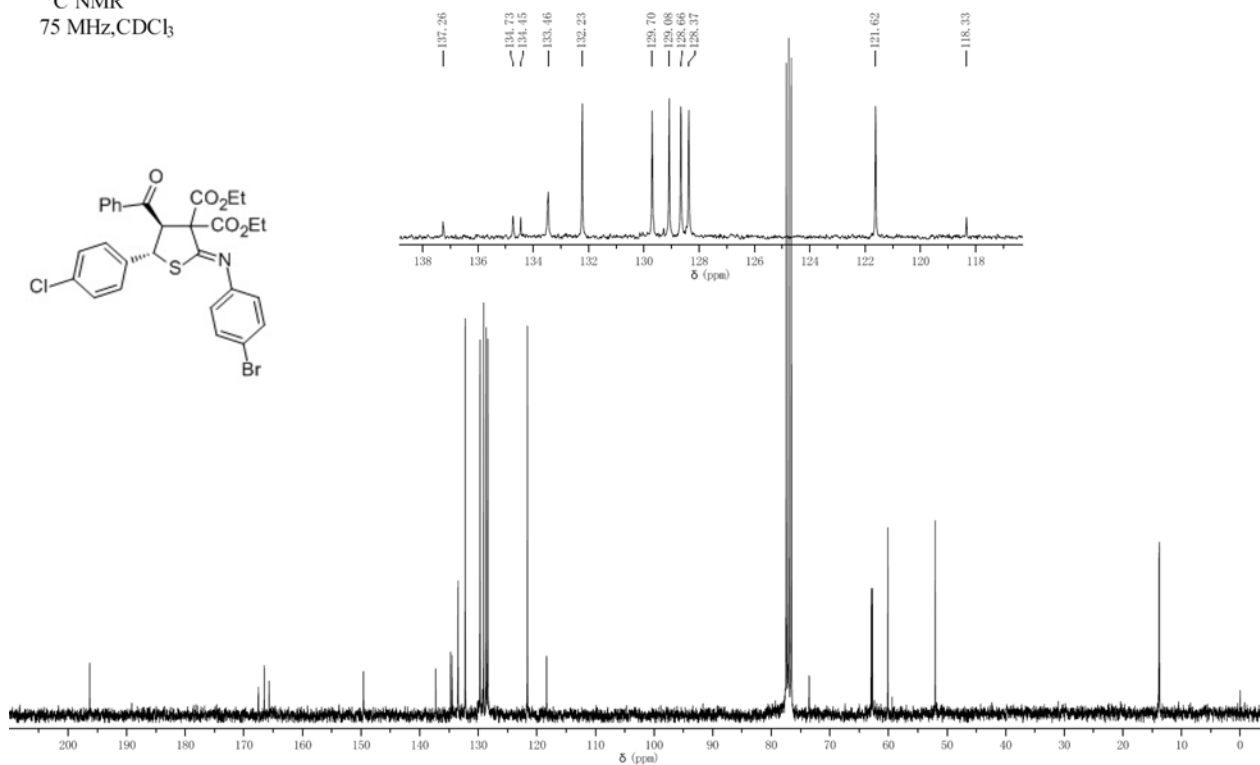
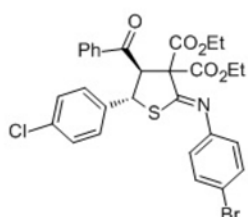
Compound 3ck



¹H NMR
300 MHz, CDCl₃



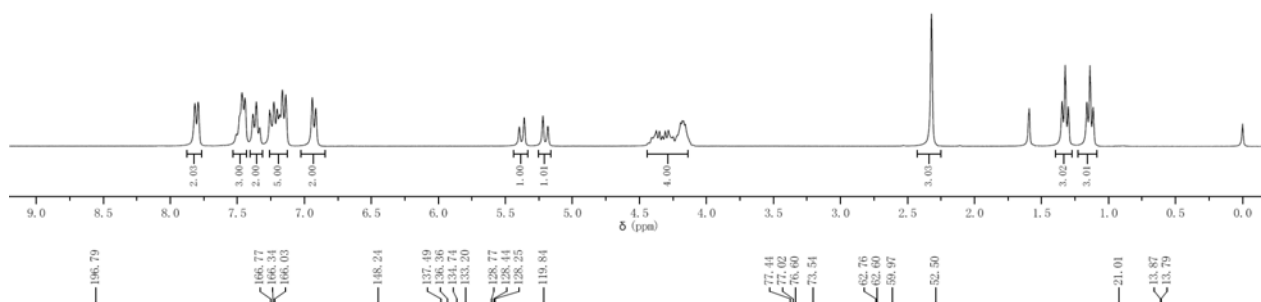
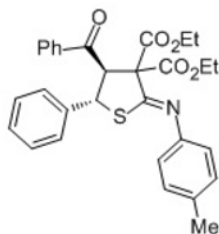
¹³C NMR
75 MHz, CDCl₃



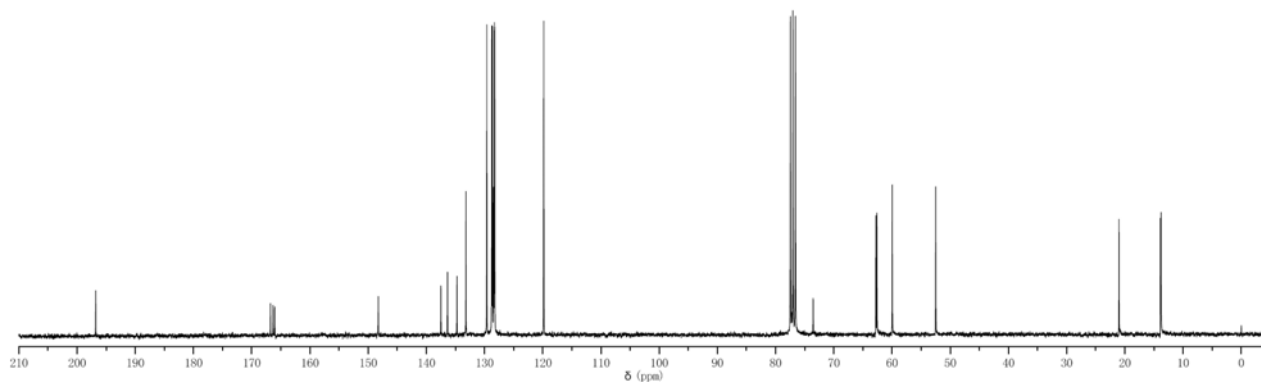
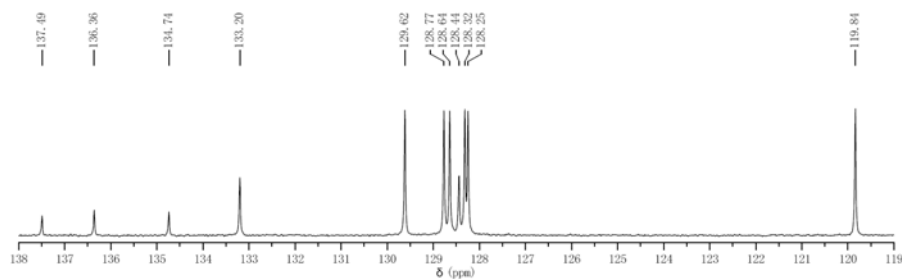
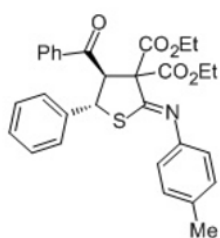
Compound 3da



¹H NMR
300 MHz, CDCl₃



¹³C NMR
75 MHz, CDCl₃



Compound 3db

7.8355
7.8311
7.8267
7.8084
7.8038
7.4222
7.3657
7.3510
7.1831
7.1831
6.9348
6.8344
6.8105

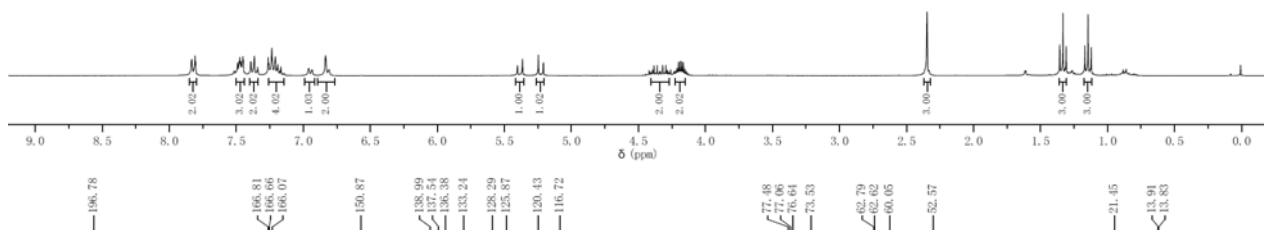
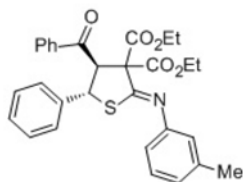
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5.3653
5.2463
5.2063
4.3603
4.3365
4.3171
4.3070
4.2953
4.2833
4.2715
4.2596
4.2474
4.2124
4.2007
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4.1768
4.1650
4.1530
4.1414

2.3469
2.3325

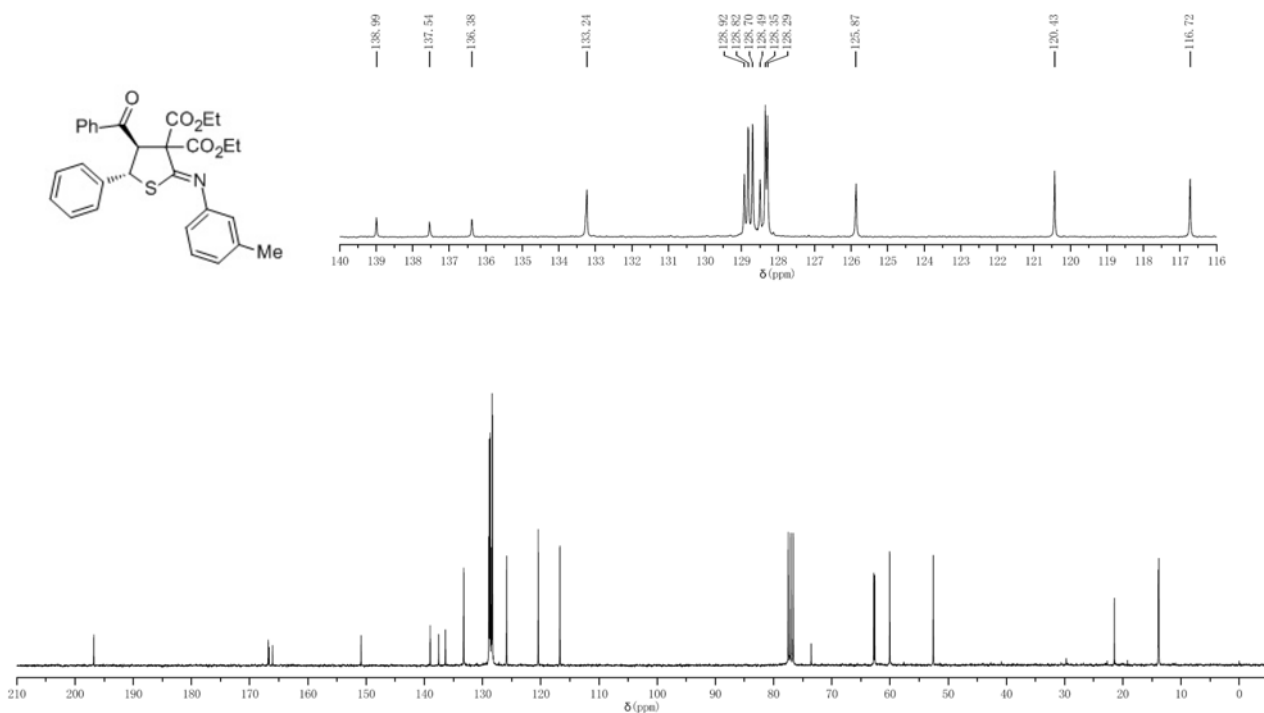
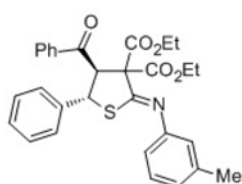
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1.3226
1.3087
1.0714
1.1514
1.1216

-0.0075

¹H NMR
300 MHz, CDCl₃



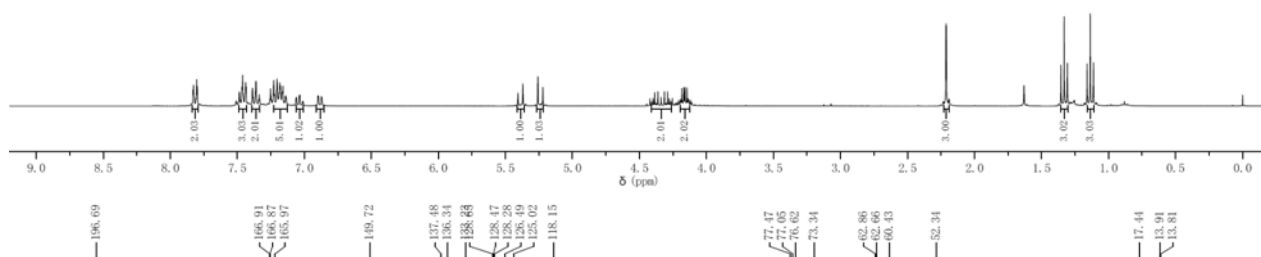
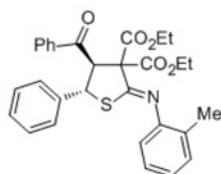
¹³C NMR
75 MHz, CDCl₃



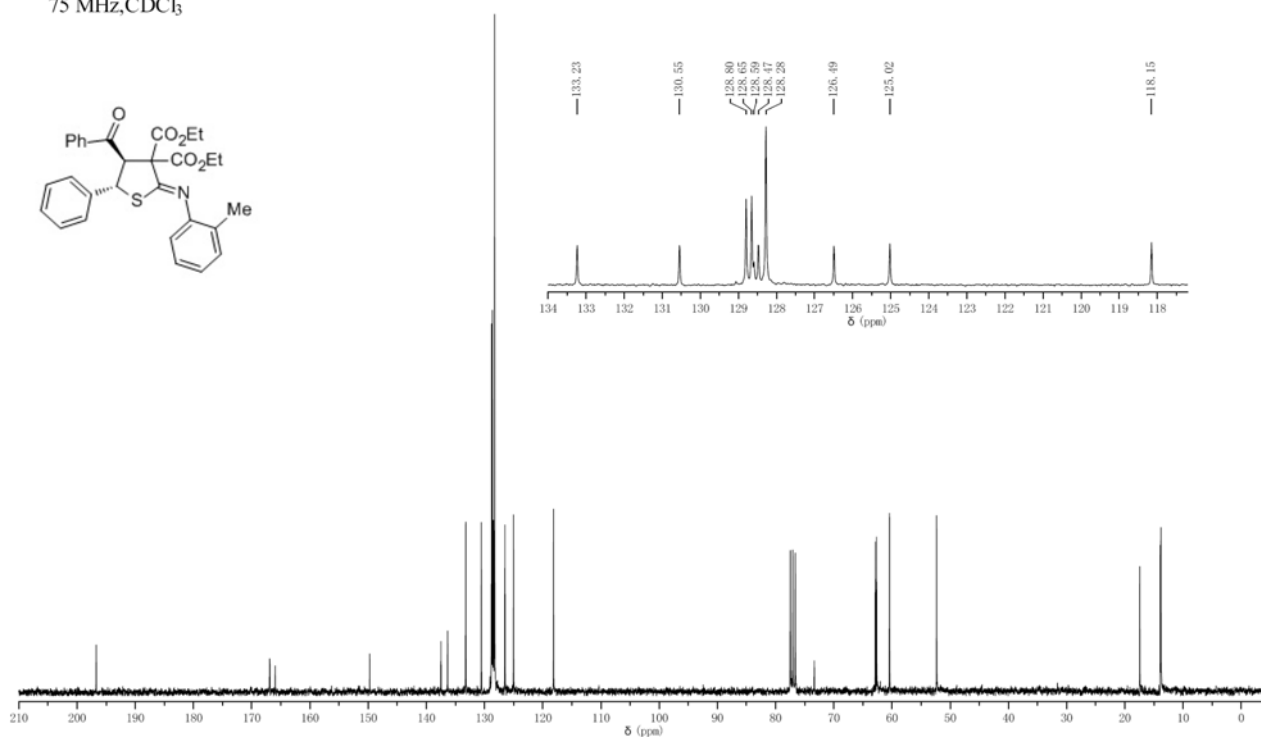
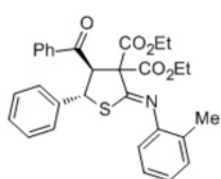
Compound 3dc



¹H NMR
300 MHz, CDCl₃



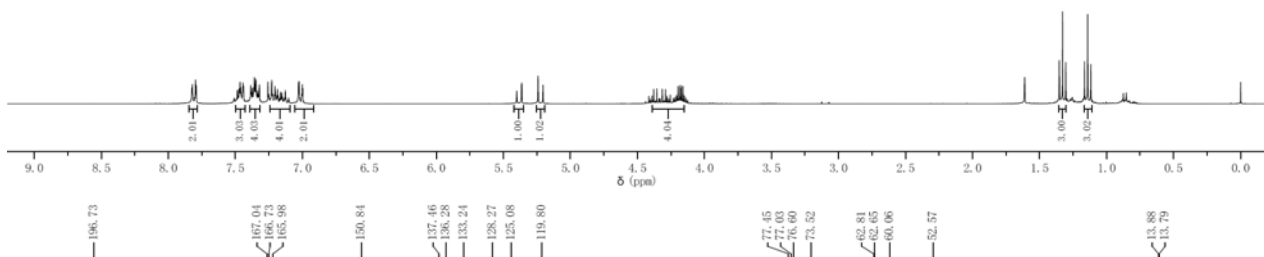
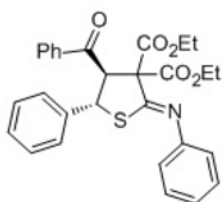
¹³C NMR
75 MHz, CDCl₃



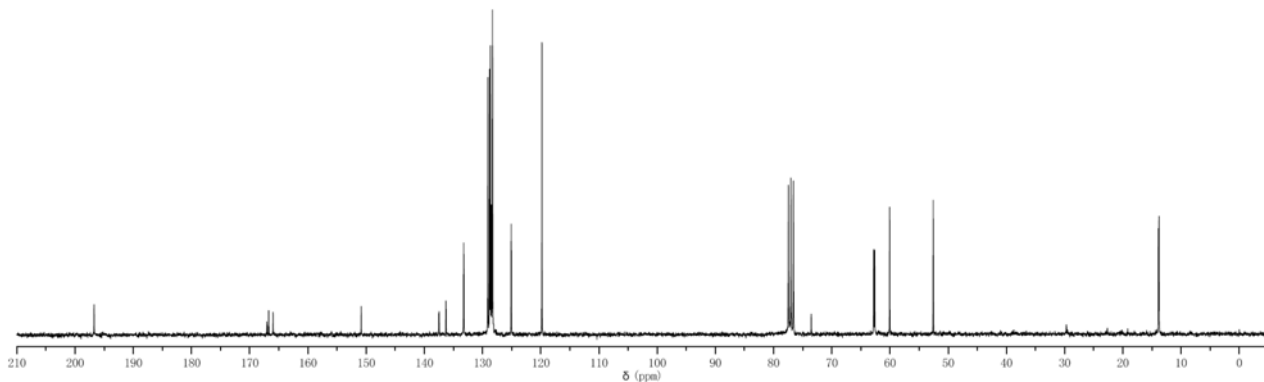
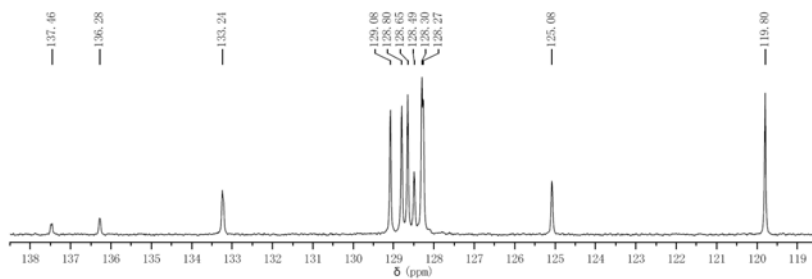
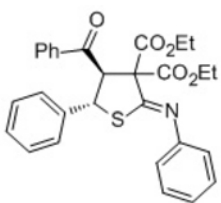
Compound 3dd



¹H NMR
300 MHz, CDCl₃



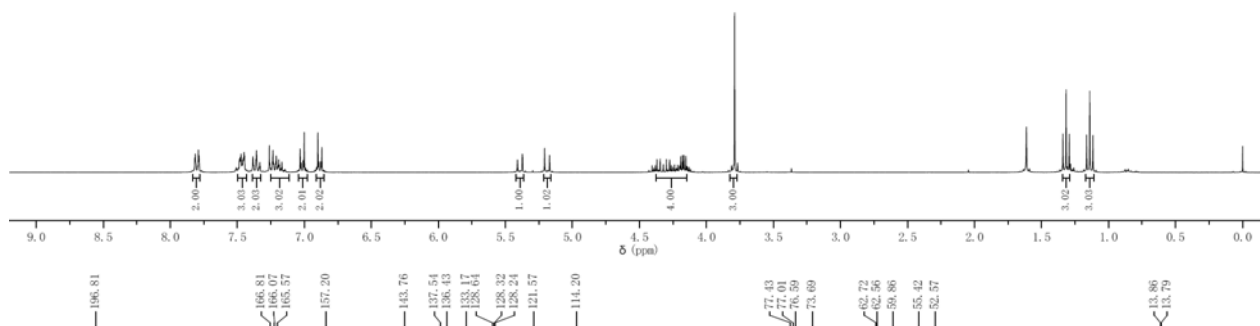
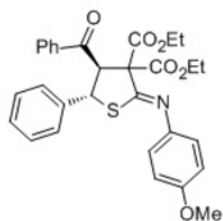
¹³C NMR
75 MHz, CDCl₃



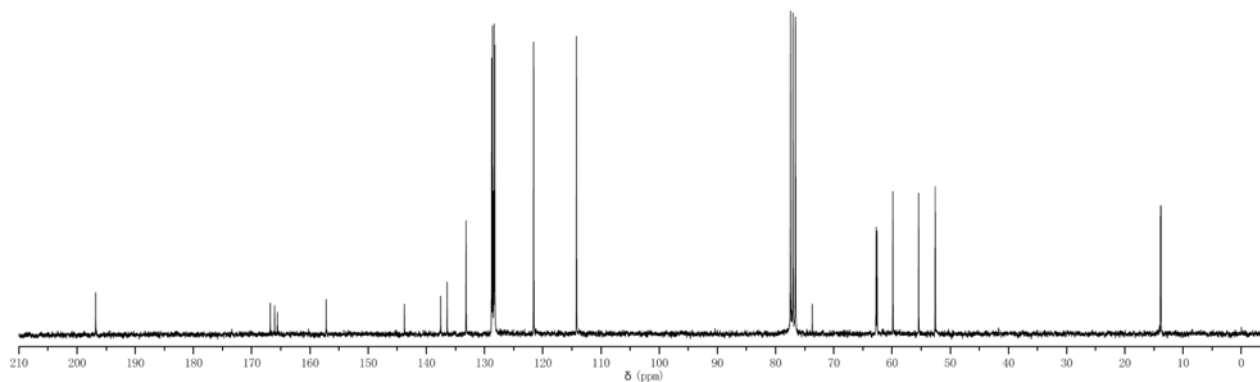
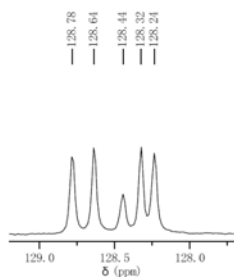
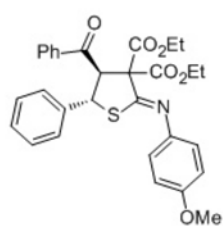
Compound 3de



¹H NMR
300 MHz, CDCl₃



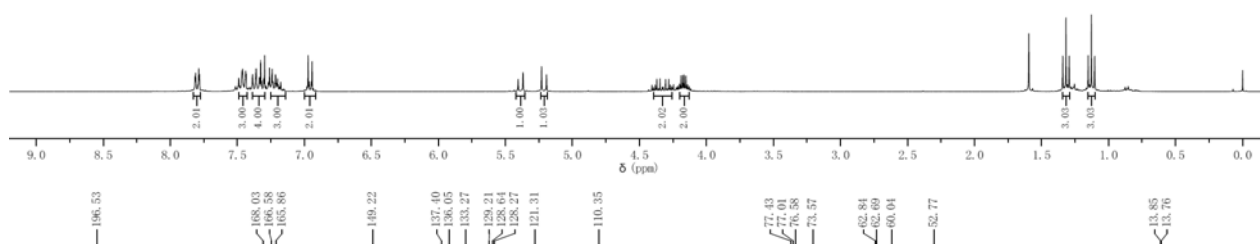
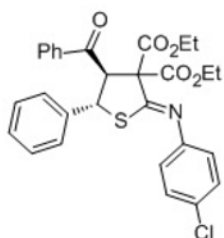
¹³C NMR
75 MHz, CDCl₃



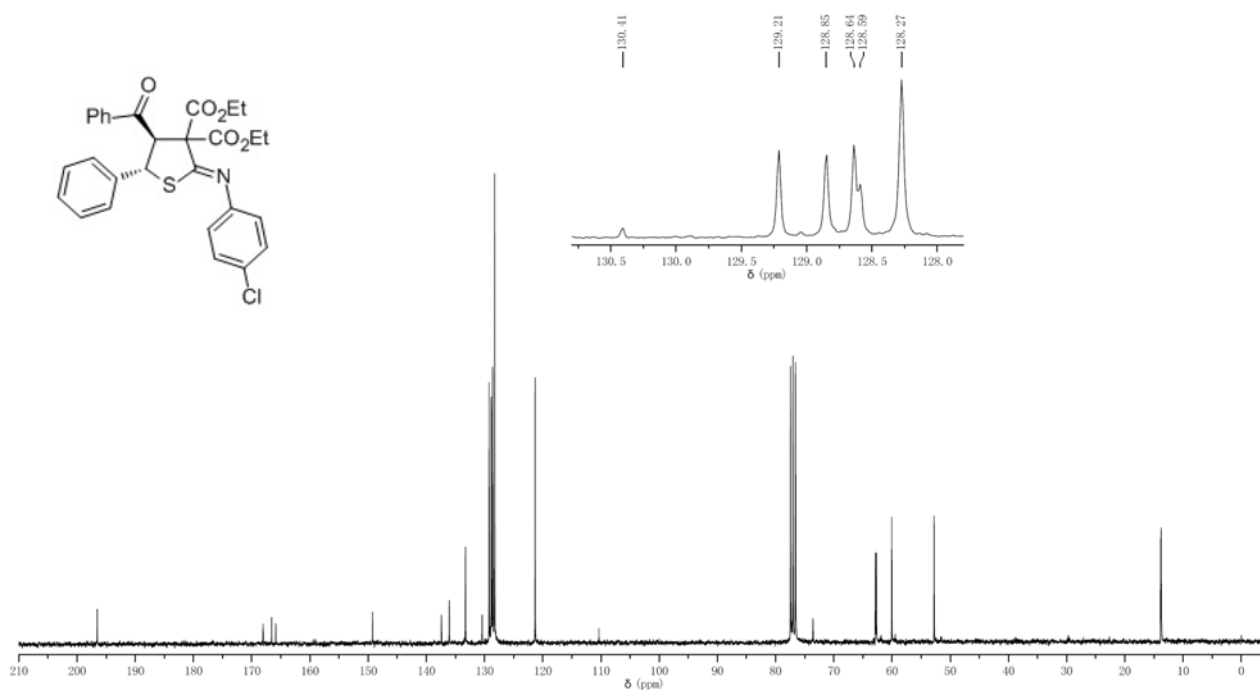
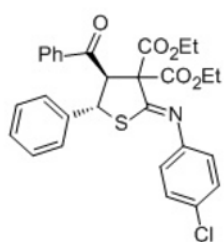
Compound 3dh



¹H NMR
300 MHz, CDCl₃



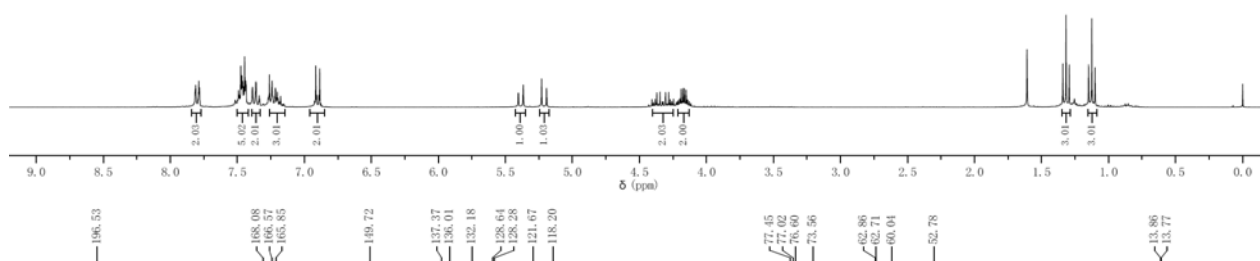
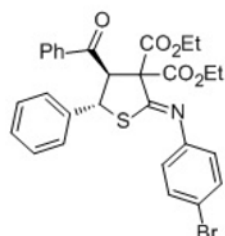
¹³C NMR
75 MHz, CDCl₃



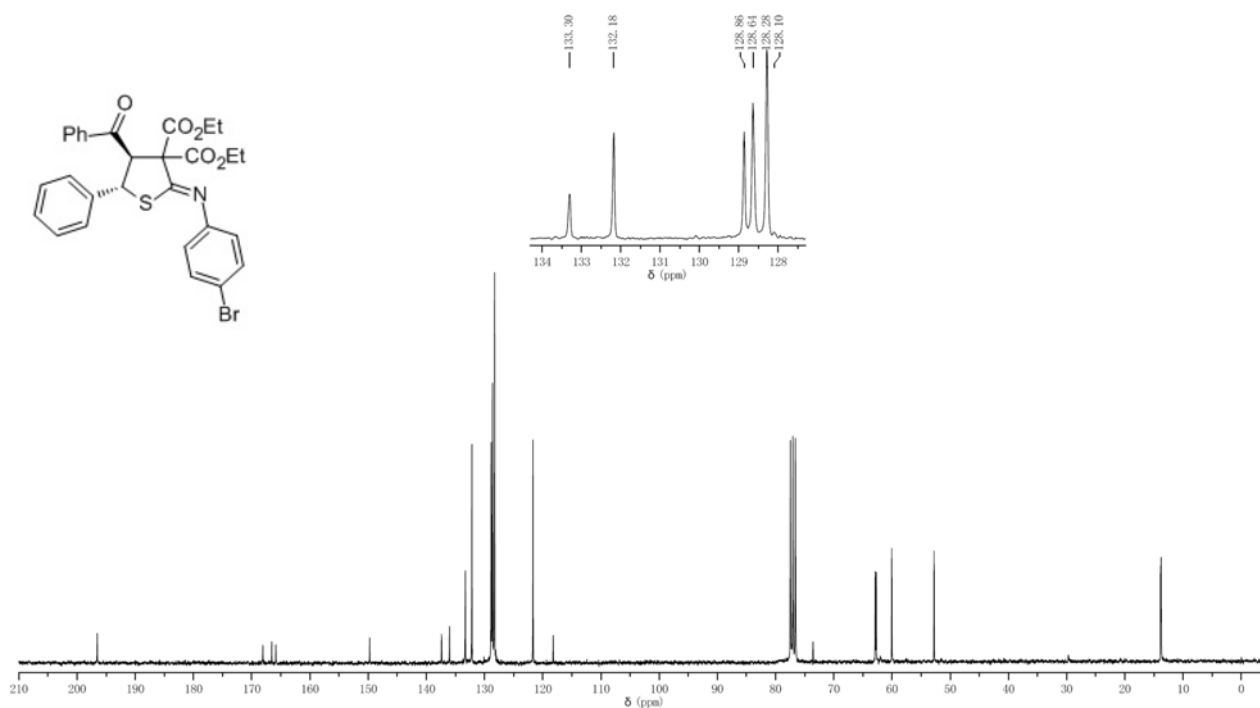
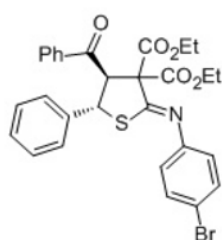
Compound 3dk



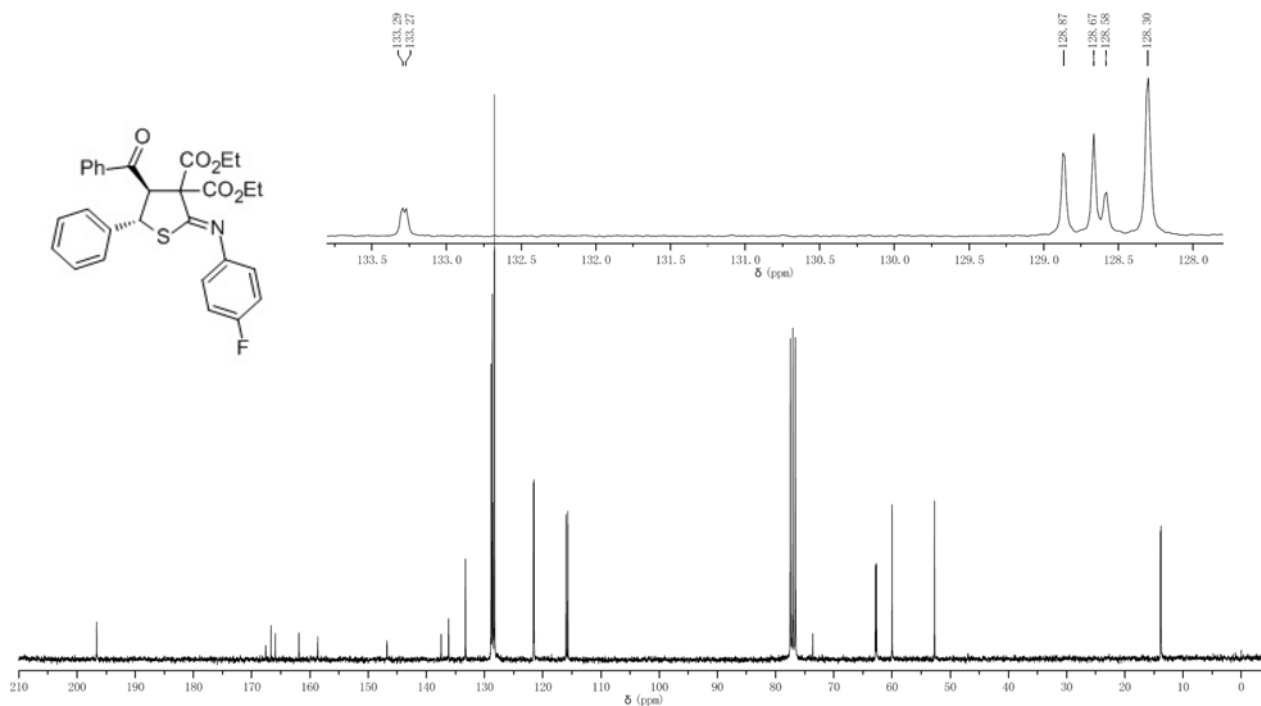
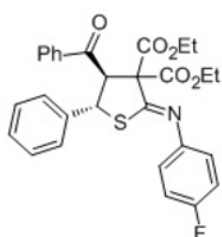
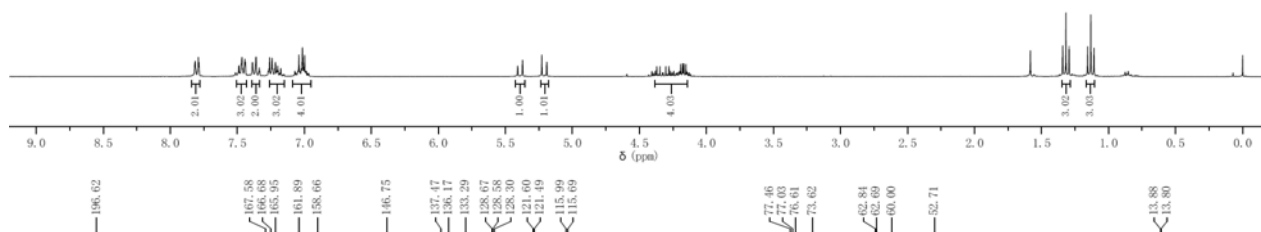
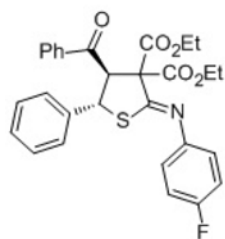
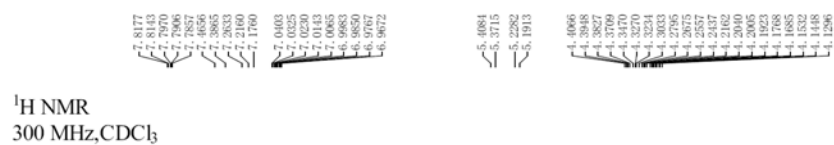
¹H NMR
 300 MHz, CDCl₃



¹³C NMR
 75 MHz, CDCl₃



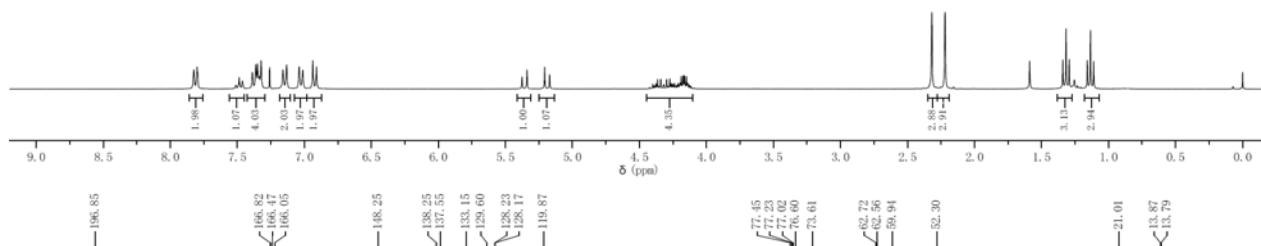
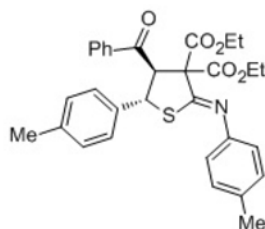
Compound 3dl



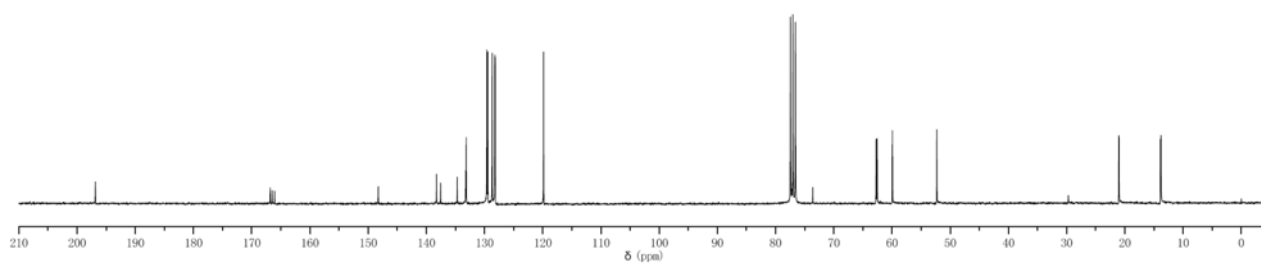
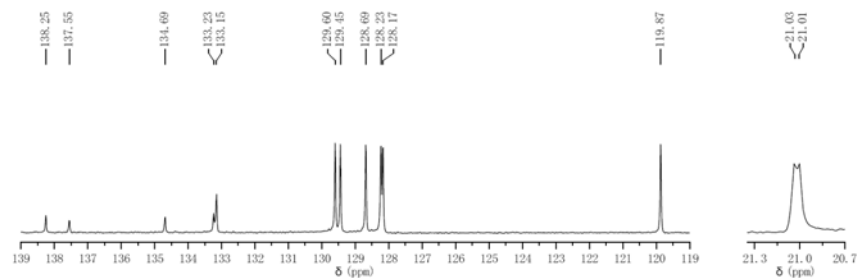
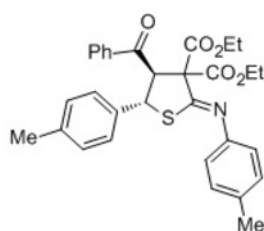
Compound 3ea



¹H NMR
300 MHz, CDCl₃



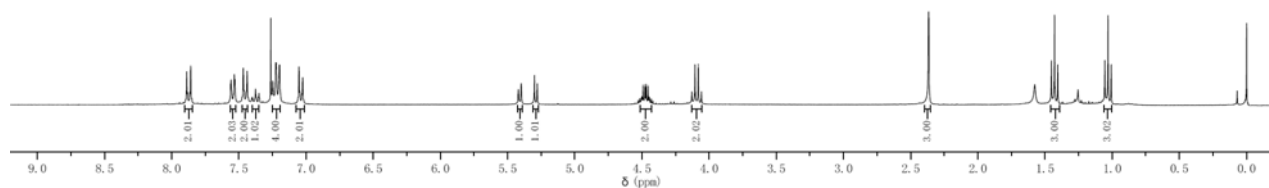
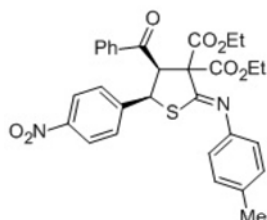
¹³C NMR
75 MHz, CDCl₃



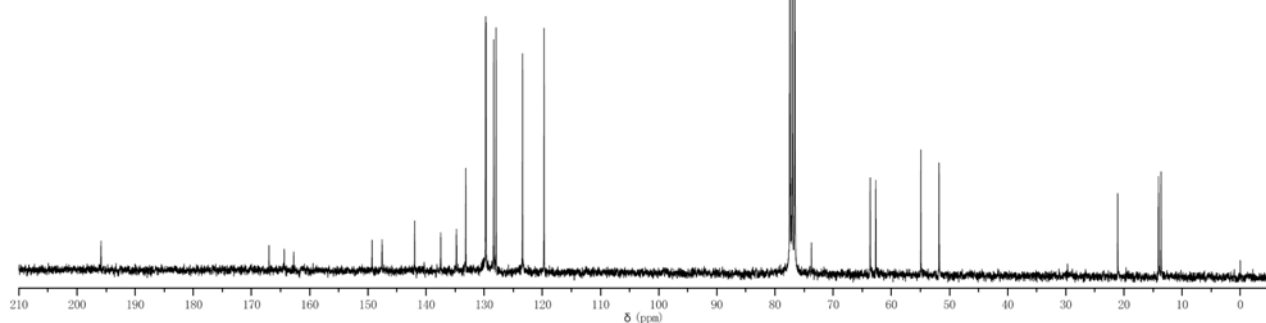
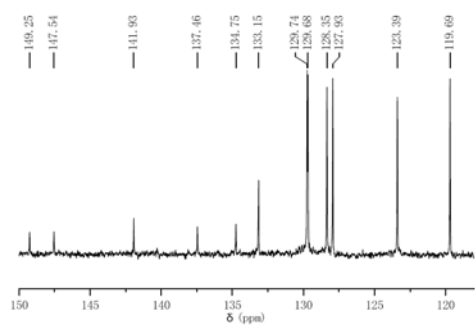
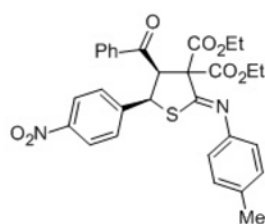
Compound 4aa



¹H NMR
 300 MHz, CDCl₃



¹³C NMR
 75 MHz, CDCl₃



X-ray crystallographic analysis of **3ck**

The single crystal of **3ck** suitable for X-ray crystallographic analysis was obtained by recrystallization from a mixed solvent of dichloromethane and petroleum ether. The single crystal X-ray diffraction data for the **3ck** was collected on a diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) at room temperature. Saint program and SADABS program carried out the data integration. The structure was solved by a direct method and refined on F² using SHELXTL suite of program. All non-hydrogen atoms were anisotropically refined by full-matrix least squares methods. All hydrogen atoms were geometrically generated and isotropically refined using a riding model. The details of the X-ray data collection, structure solution and structure refinements are given in Table S1. The crystal structure of **3ck** is given in Figure S1.

Table S1 Crystallographic data and structural refinement details for compound **3ck**.

Compound	3ck
Formula	C ₂₉ H ₂₅ BrClNO ₅ S
Formula weight	614.92
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
<i>a</i> , Å	9.740(1)
<i>b</i> , Å	12.565(1)
<i>c</i> , Å	13.024(1)
α , deg	90.176(1)
β , deg	108.720(1)
γ , deg	109.614(1)
<i>V</i> / Å ³	1411.1(2)
<i>Z</i>	2
μ (Mo K α), mm ⁻¹	1.664
θ range for data collection, deg	1.7 to 27.6
Calculated density/(g·cm ⁻³)	1.447
Reflections collected	12325
Unique reflections/R _{int}	6387 / R(int) = 0.022
<i>F</i> (000)	628
Goodness-of-fit on F ²	0.98
Crystal dimension/mm ³	0.18×0.22×0.28
R, R _w [<i>I</i> > 2 σ (<i>I</i>)]	0.0709, 0.2751
Residual ρ /(e·Å ⁻³)	1.39, -0.65

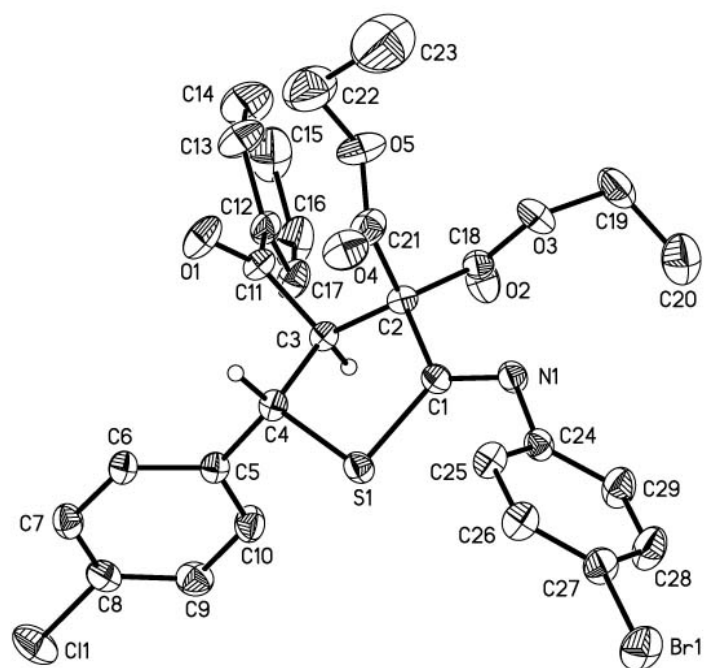


Figure S1 X-ray structure (50 % probability ellipsoids) of **3ck**.