# **Electronic Supplementary Information**

for

## AlCl<sub>3</sub>-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

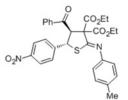
### **Content**

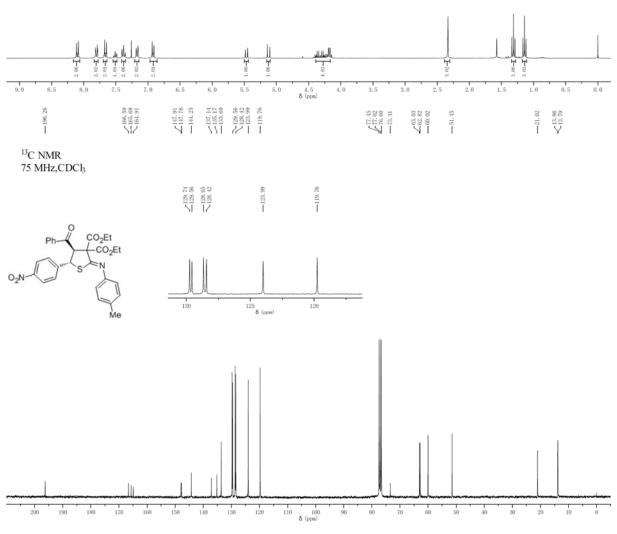
<sup>1</sup> H, <sup>13</sup> C NMR Spectra of all products	S2–S39
X-ray crystallographic analysis of <b>3ck</b>	S40–S41

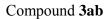
### <sup>1</sup>H, <sup>13</sup>C NMR Spectra of all products

#### Compound 3aa

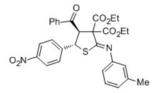
8, 1200 8, 1200 8, 1020 8, 1020 8, 1020 8, 1020 1, 28, 1021 1, 28, 10, 1021 1, 28, 10, 1021 1, 28, 10, 1021 1, 28, 10, 1021	5.4490	<sup>5</sup> , 1411 <sup>5</sup> , 1042 <sup>5</sup> , 1042	4, 3424 4, 2325 4, 2387 4, 2522 4, 2522 4, 2522 4, 2522 4, 1552 4, 1555 4, 1555 4, 1656 4, 1656 4, 1656 4, 1656 4, 1656 4, 1656 4, 1656	2. 3322		$\frac{\swarrow^{1.3138}}{\eqsim^{1.1659}}$	0.0004
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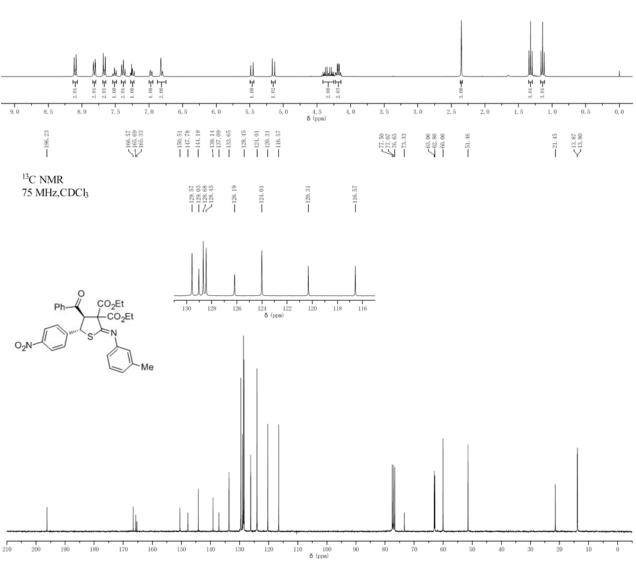






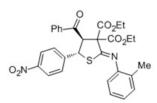
Control (C)     Contro     Control (C)     Control (C)     Control (C)     Control (C)	-0.0006
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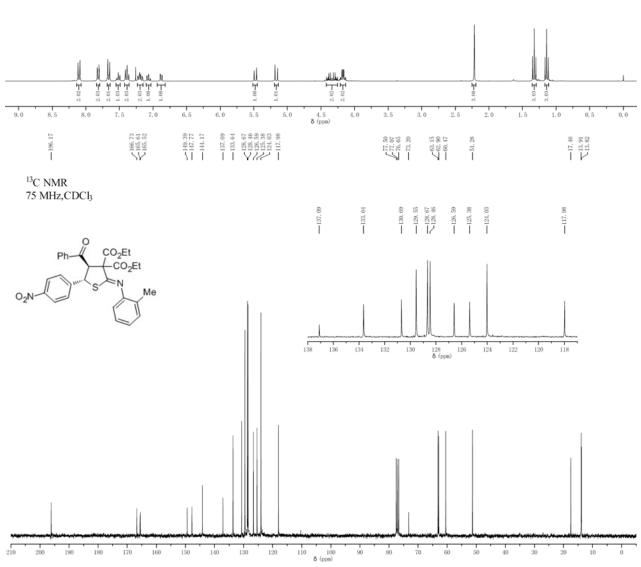




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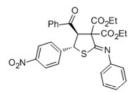
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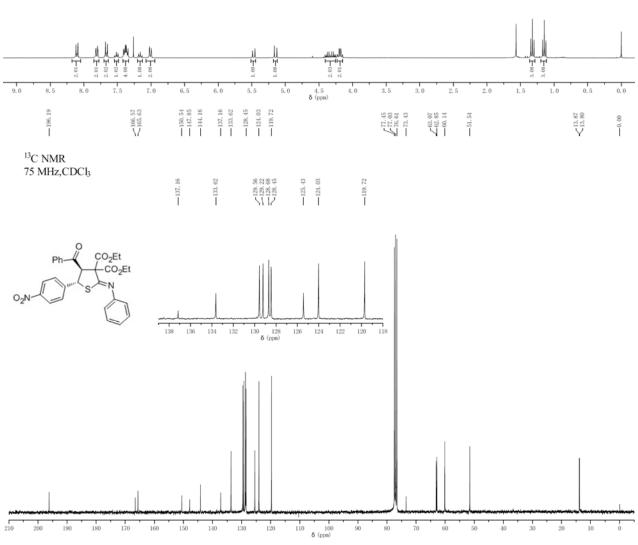


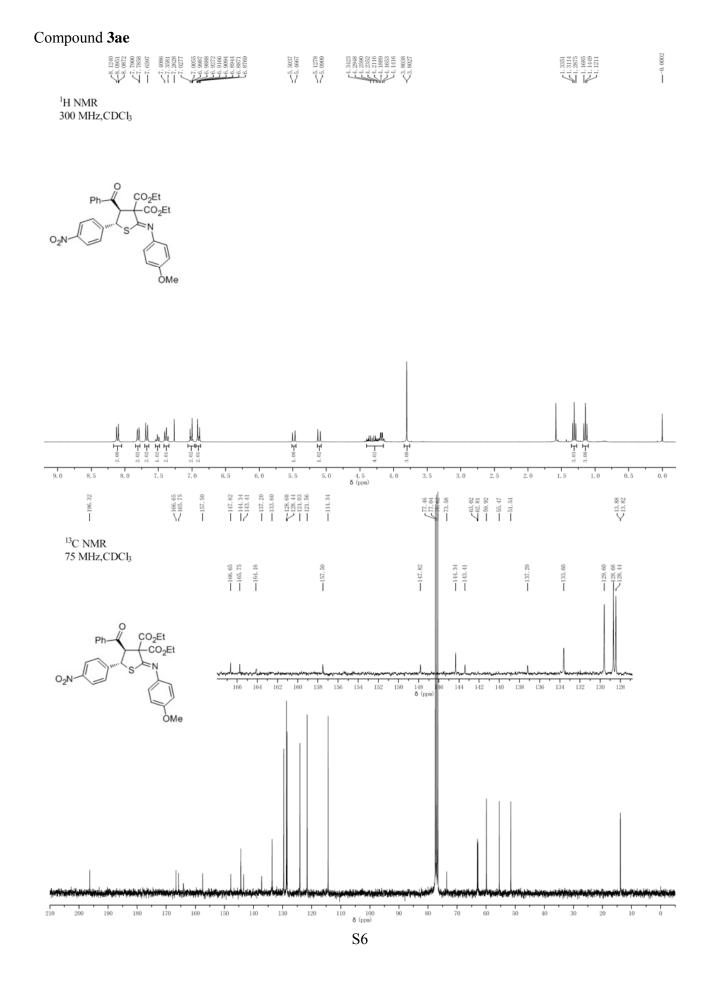


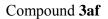
#### Compound 3ad

8, 11170 8, 11170 8, 11170 8, 11170 9, 11170 1,		∆5. 1632 ∆5. 1263	14, 4066 14, 4066 14, 5285 14, 5285 14, 5285 14, 5285 14, 5285 14, 5285 14, 5285 14, 2581 14, 2581 14, 2581 14, 2581 14, 2581 14, 2581 14, 2581 14, 2581 14, 2585 14,	1, 2015 1, 2016 1, 2019 1, 2019 1, 2019 1, 1, 2019	
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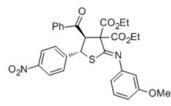


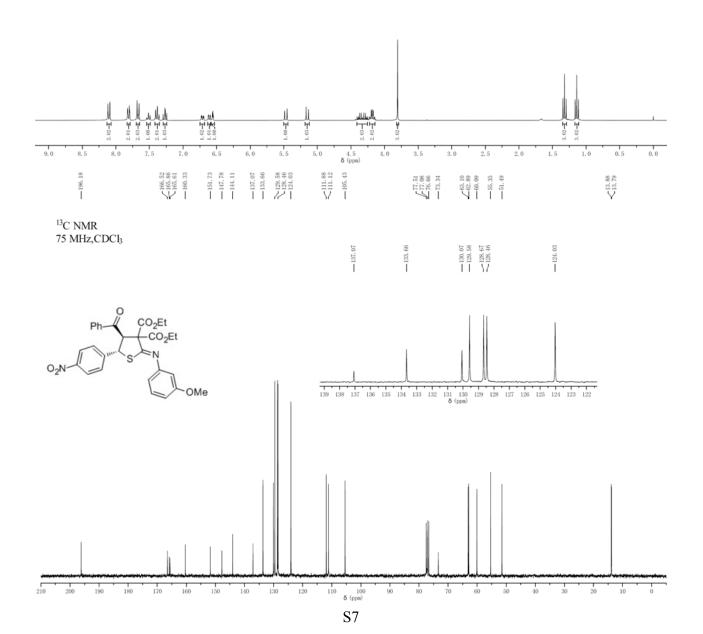


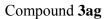




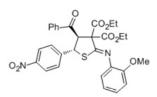
			-1, 3734 -1, 2796 -1,	$\underbrace{\underbrace{I}_{11,296}^{11,3138}}_{11,1149}$	
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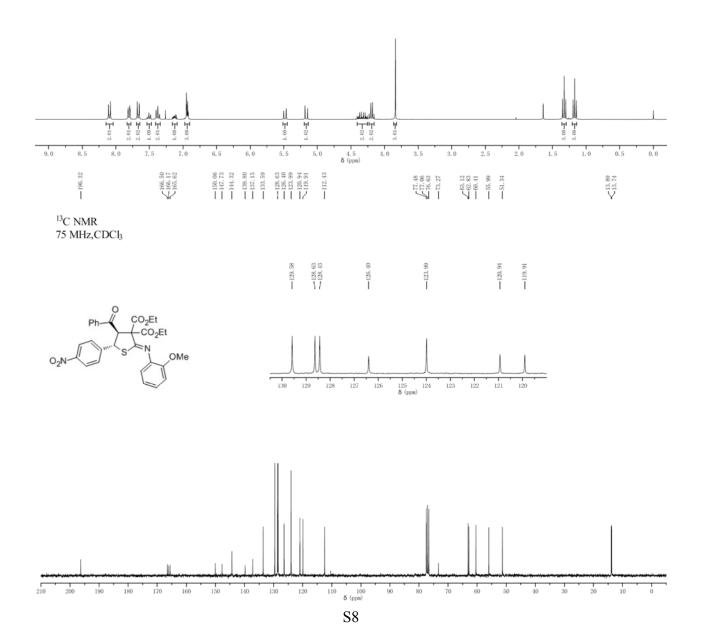






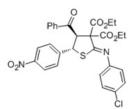
8, 1196 8, 1196 8, 1101 8, 8, 8, 8, 8, 8, 8, 8, 8, 8, 8, 8, 8, 8	0,000 1,	1. 3468 1. 2568 1. 2568 1. 1807 1. 1807 1. 1463
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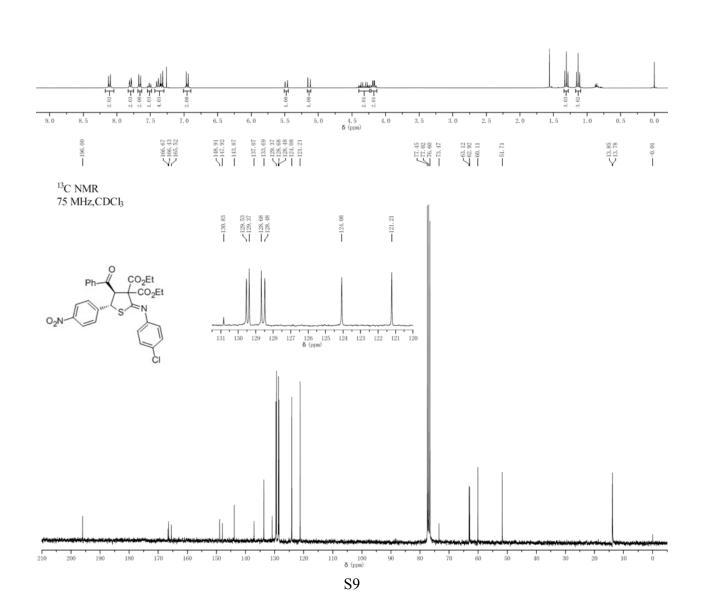


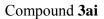


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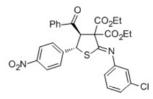
8, 11180 8,	5,4967 5,4967 5,1198 5,	2.1. 3333 2.1. 28767 1.1. 28767 1.1. 28767 1.1. 15869 1.1. 15869 1
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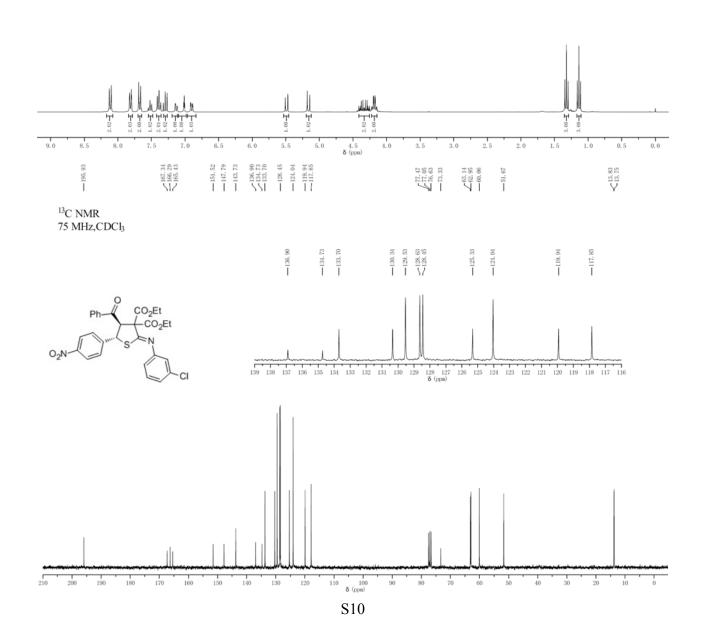






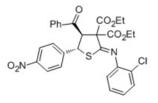
Section 2015     S	
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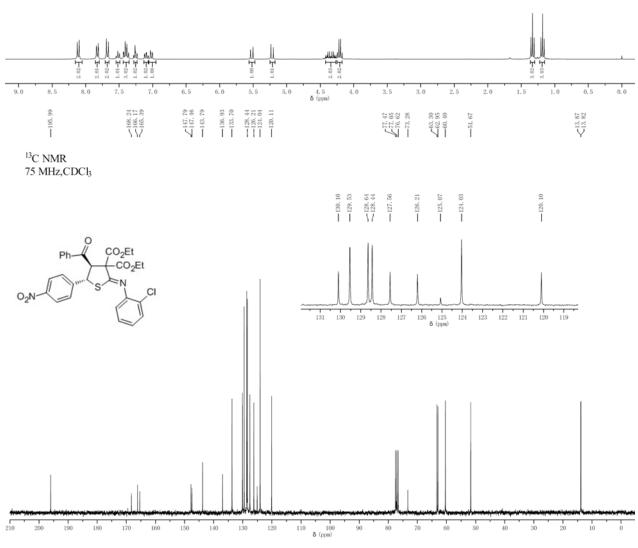






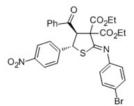
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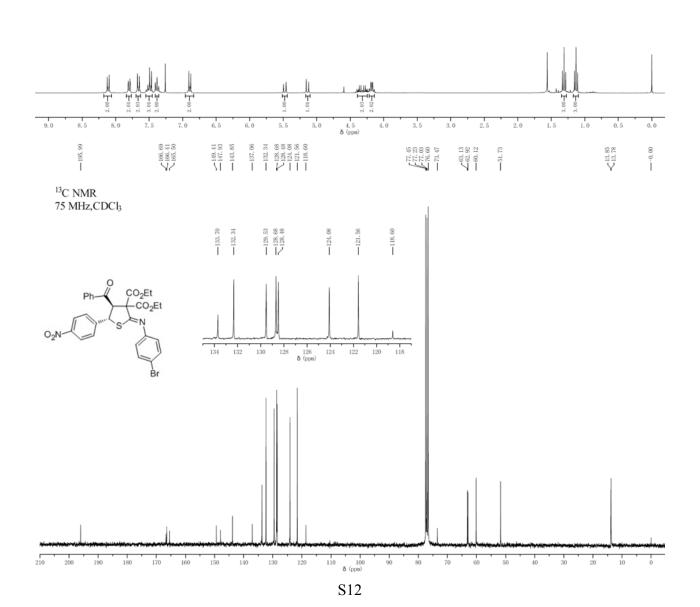


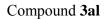


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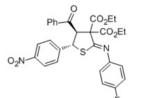
	~5. 4574		2015 2015 2015 2015 2015 2015 2015 2015	1.3326 1.3088 1.2849 1.1545 1.1545 1.1308 1.1071	
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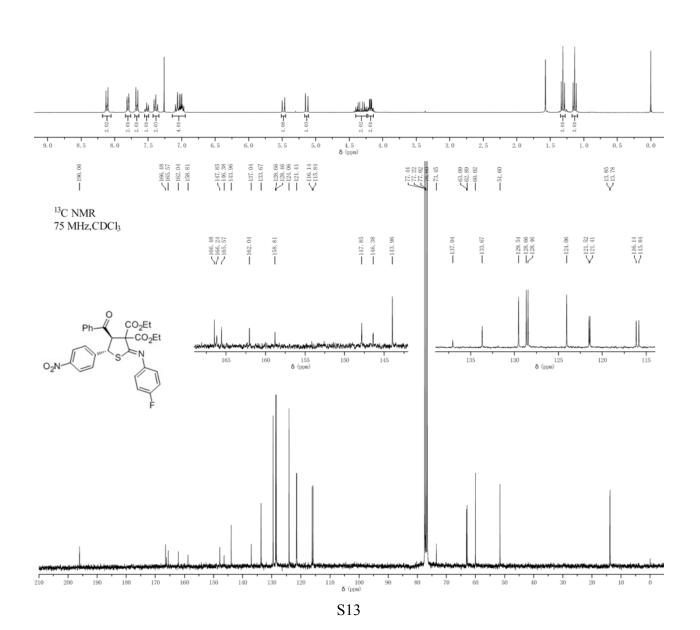




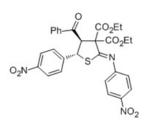


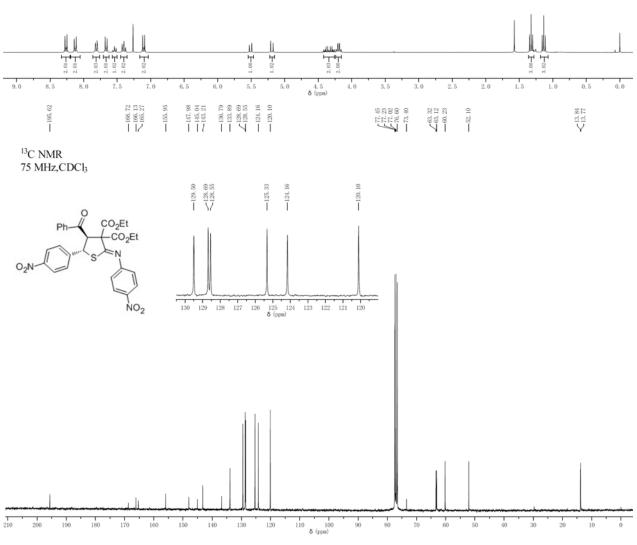
8, 1000 8, 10000 8, 10000 8, 10000	A 1000 C	L 3366 L 318 L 1389 L 15896 L 15866 L 15866
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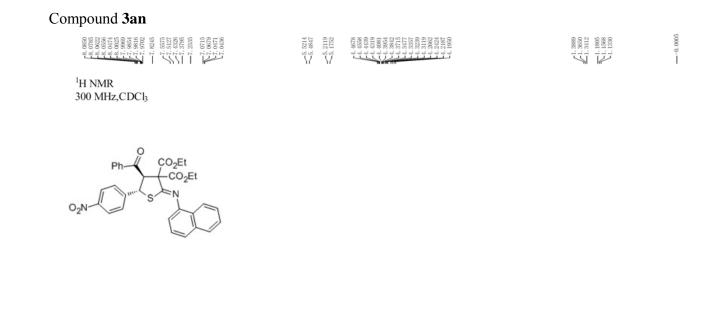


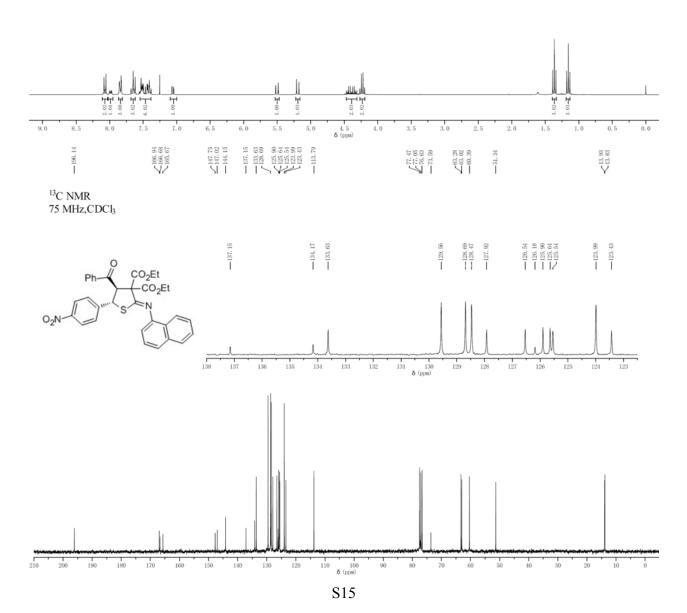




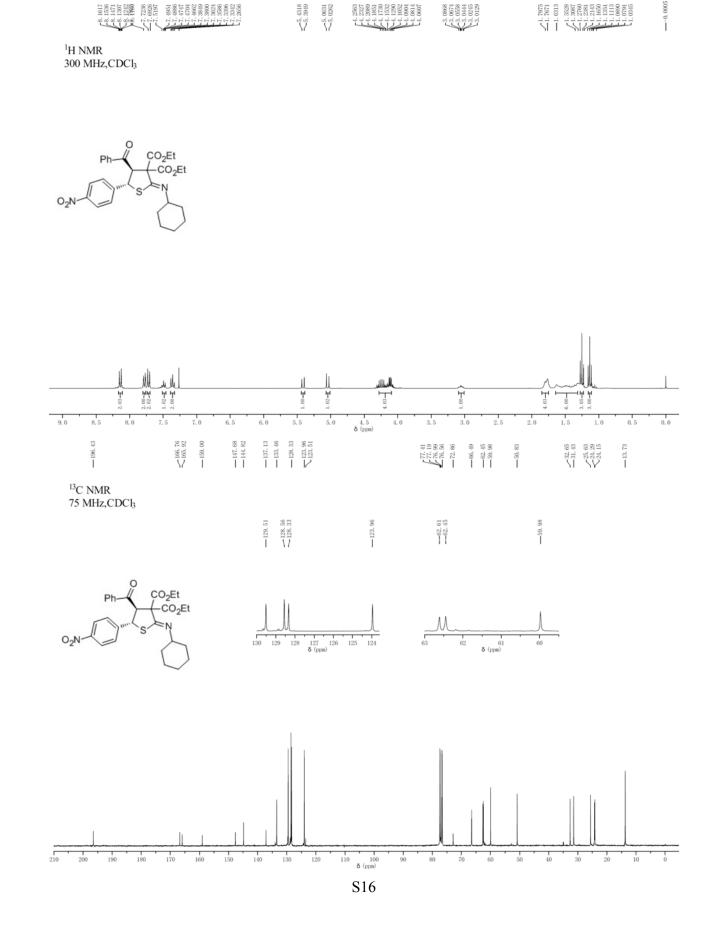


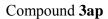




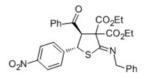


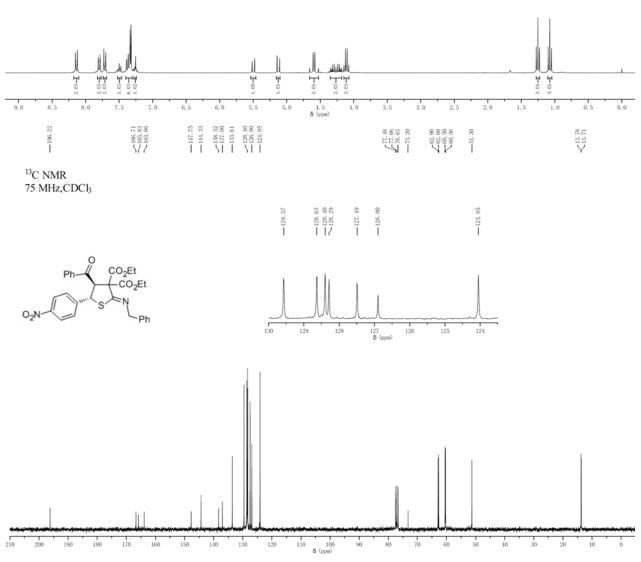
Compound 3ao



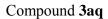


1879 1512 1512 1512 1512 1512 1512 1512 1528 1528	5157 4788	1433	6585 6060 5795 5269 3487	3248 3248 3129 3129 3129 3129 2891 1816 1574 1816 1578 1816 1578 1816 1578 1816 1578 0987 0987 0749	2756 2518 2250 0988 0748 0507	000.0
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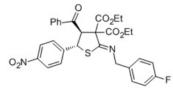


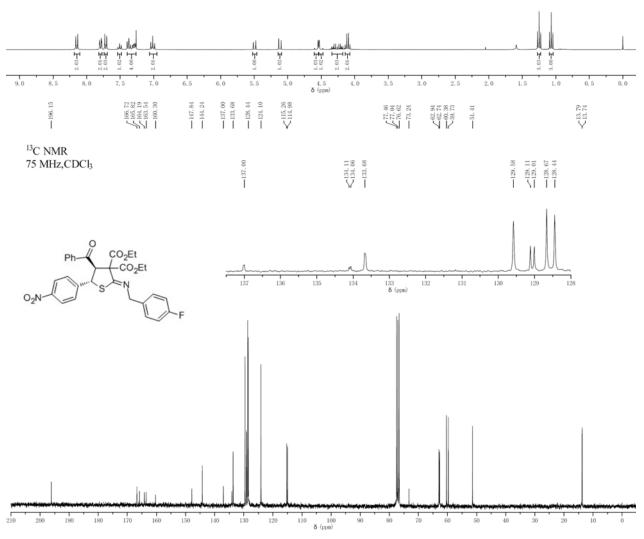


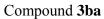
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry This journal is The Royal Society of Chemistry 2013



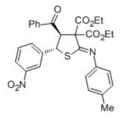
8801 8 1811 8 18	5, 132 5, 1763 5, 1341 5, 134155555555555555555555555555555555555	1. 2716 <u>1. 2778</u> <u>1. 0807</u> <u>1. 0807</u> <u>1. 0432</u>
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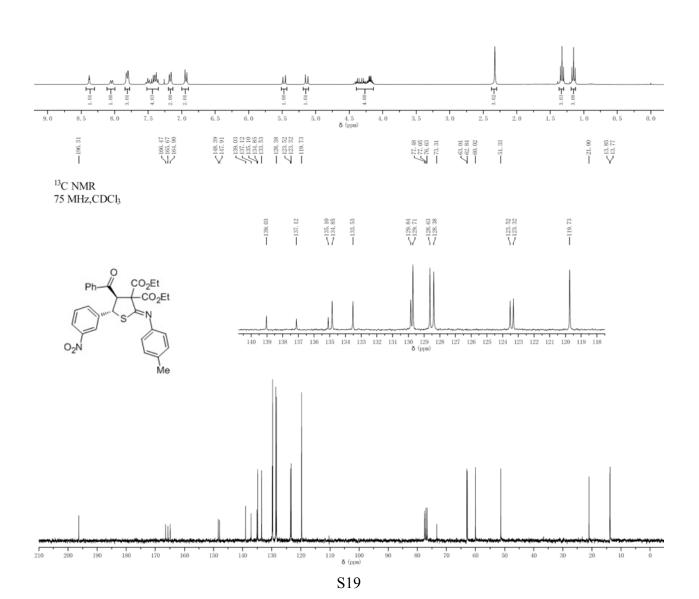


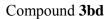




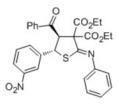
A 2019 A 2019	5,4896	∧5, 1529 ∧5, 1160	4.3531 4.3138 4.3138 4.2125 4.2562 4.2512 4.2512 4.2512 4.1315 4.	2.3272	$\underbrace{\underbrace{\swarrow}_{1.3485}^{1.3485}}_{1.3247}$
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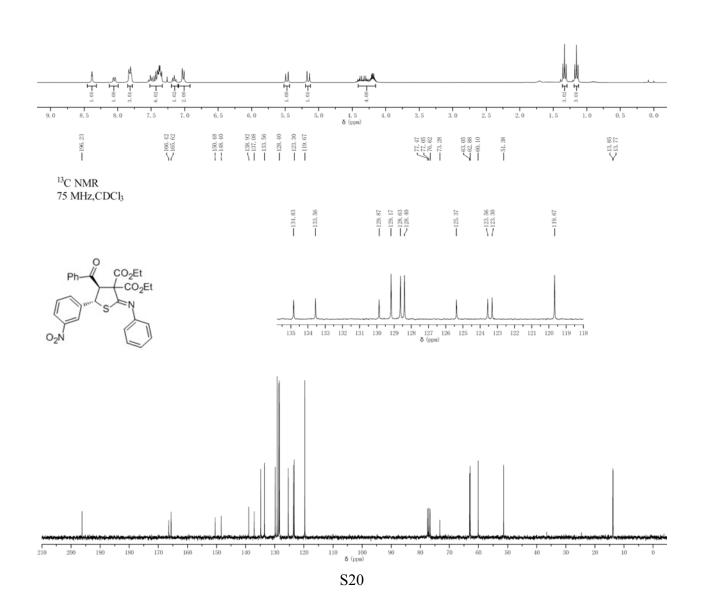


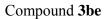




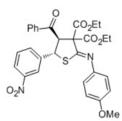
1100 11 1100 1100		5. 1741 5. 1372	-4, 38/9 -4, 37/8 -4, 27/8 -4, 22/9 -4,	1315 1351 1315 11115 11115 11115	<b>—</b> -0. 0006
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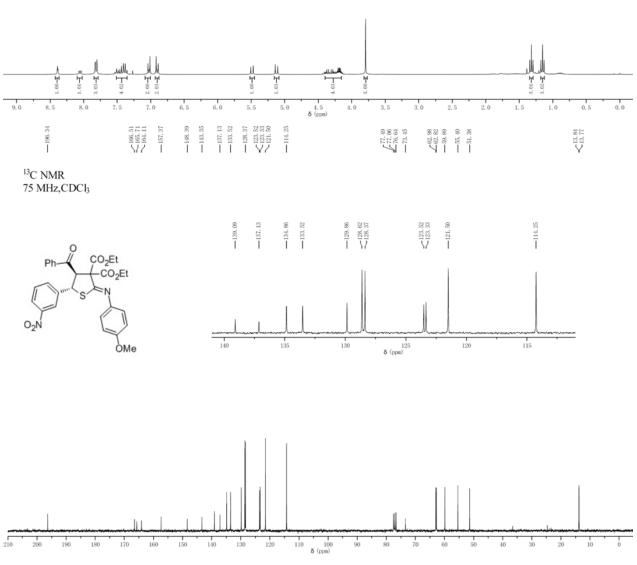






<ul> <li>第3853</li> <li>第3853</li> <li>第3853</li> <li>第3853</li> <li>第3854</li> <li>第3854</li> <li>第3854</li> <li>第3854</li> <li>第3855</li> <li>11,28825</li> <li>12,28825</li> <li>12,28825</li> <li>12,28825</li> <li>14,2825</li> <li>14,282</li></ul>		5.1414	4, 3493 4, 2825 4, 2828 4, 22588 4, 22586 4, 1277 4, 1317 4, 1377 4, 13777 4, 13777 4, 137777 4, 13777777777777777777777777777777777777	1, 1304 1. 1755 1. 175
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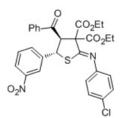


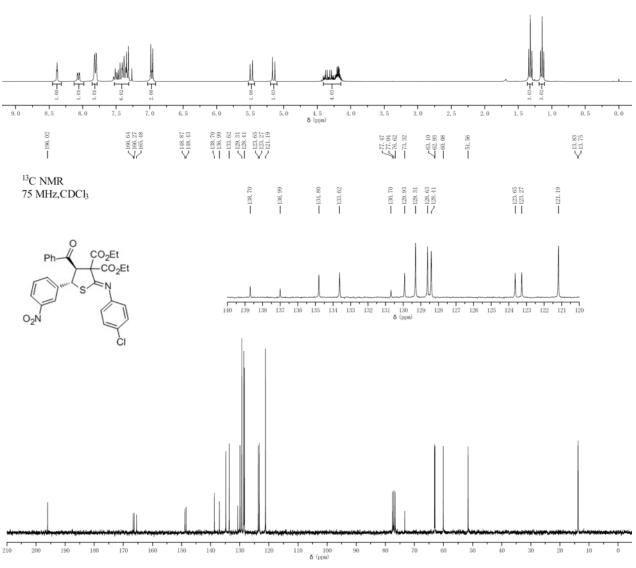


#### Compound 3bh

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<sup>1</sup>H NMR 300 MHz,CDCl<sub>3</sub>

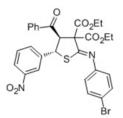


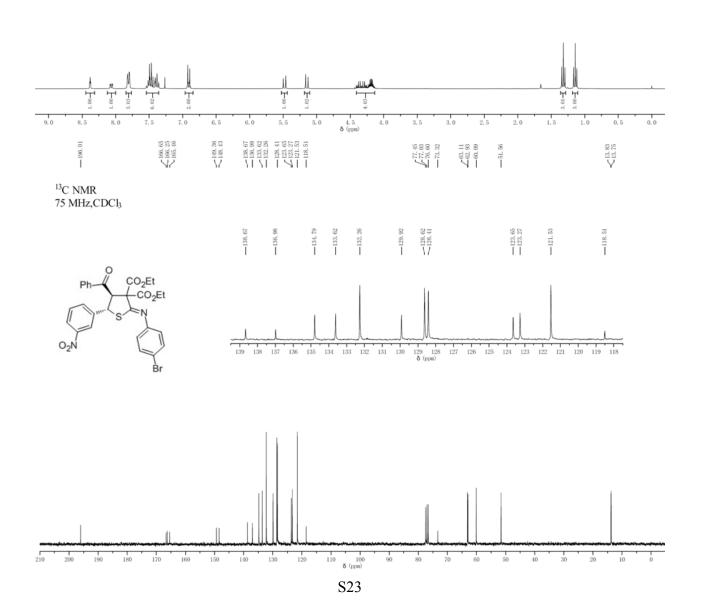


S22

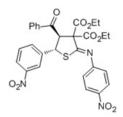
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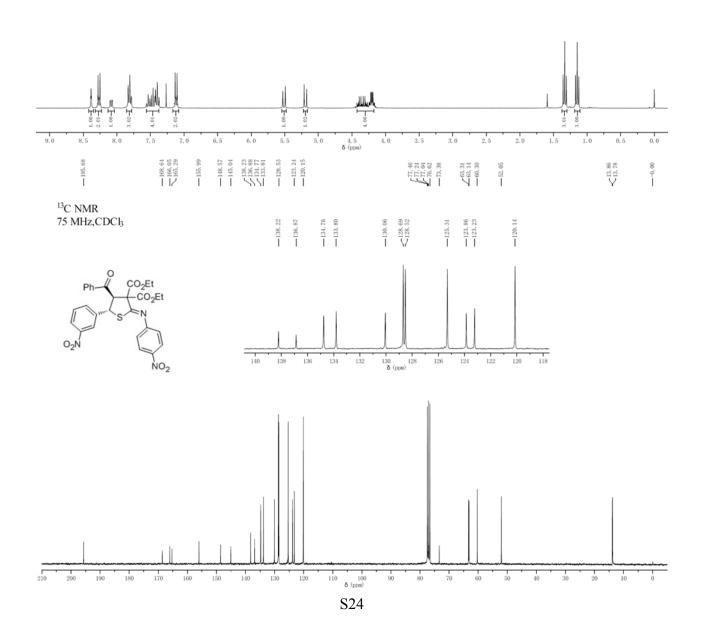
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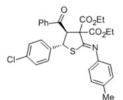


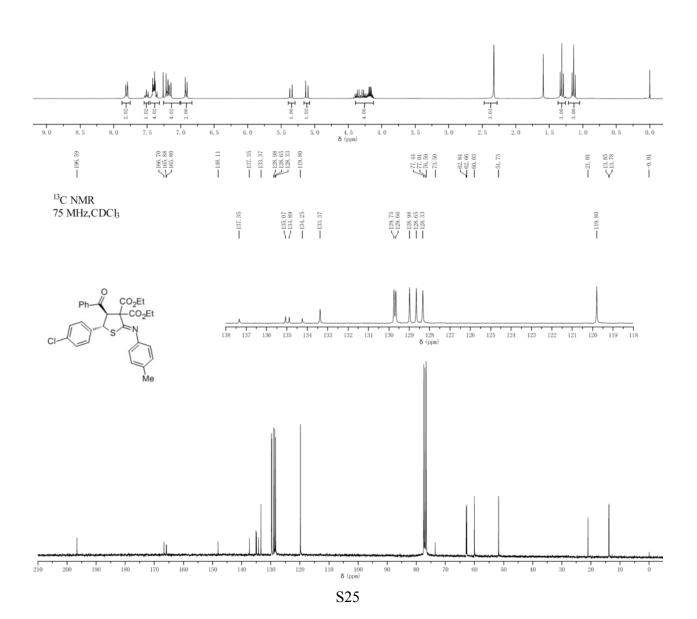




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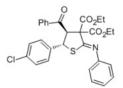
1006 9 9962 9 9962 9 9962 9 9962 1 2241 1 2241 1 2241 1 2241 1 2011 1 20	5. 3731 5. 3361 5. 0989	4, 1382 4, 1382 4, 1383 4, 1383 4, 1384 4, 1384 4, 1386 4, 13866 4, 138666 4, 138666666666666666666666666666666666666	2. 3269	L. 3369 L. 3131 L. 1597 L. 1597 L. 1123	0.0003
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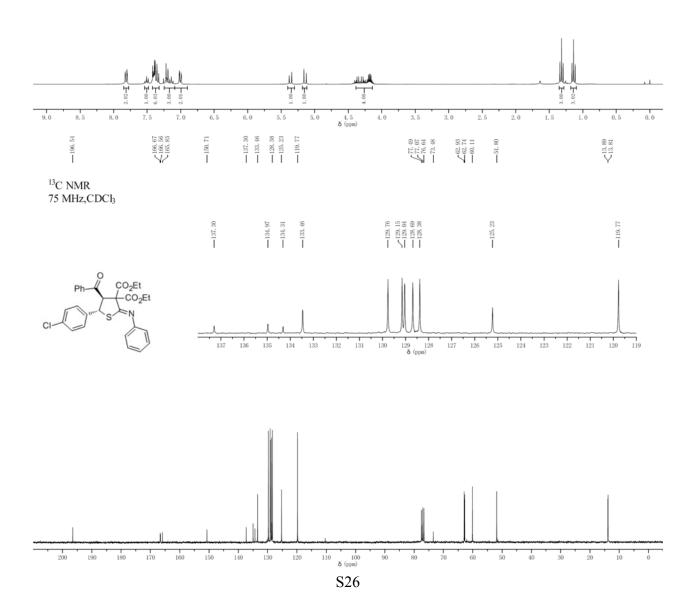




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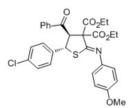
8257 8061 77970 33979 33799 33799 33799 33799 11256 11779 11	3799 3429 1611 1241	4040 3921 3921 3923 3923 3923 3924 39263 3026 32638 3026 32638 3025 11716 1171	3418 31800 1545 11375 11375	0006
	12	444493333333333333333333333333		Ì

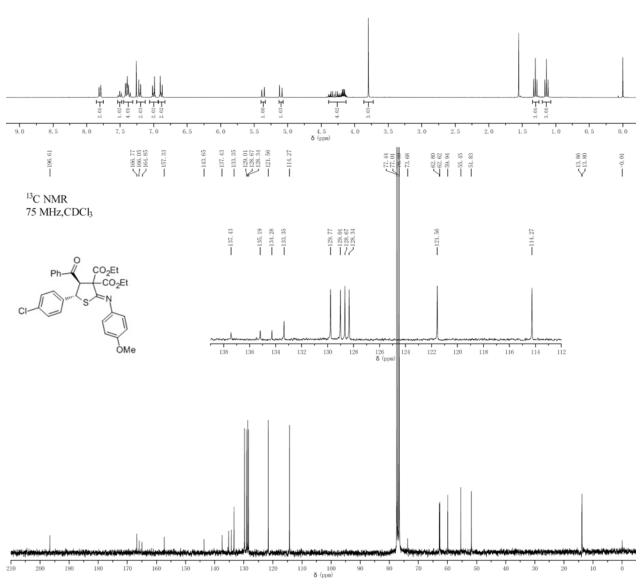




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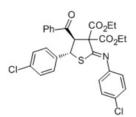
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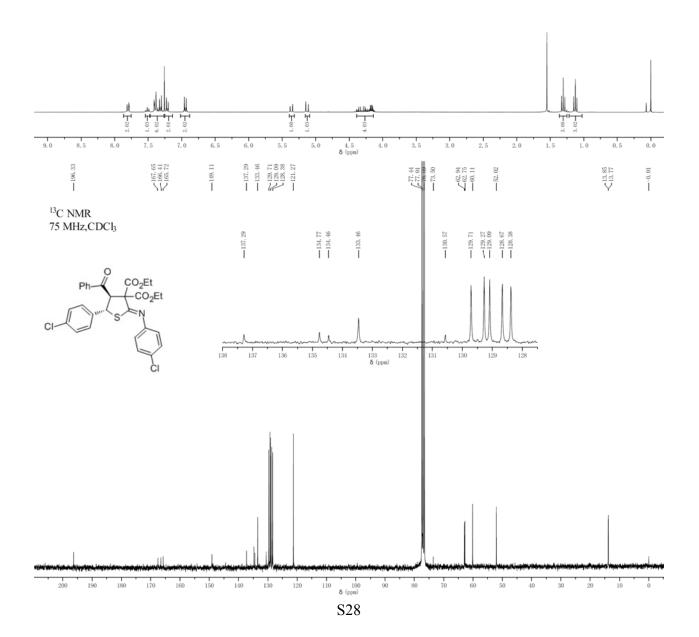




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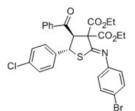
7,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1,1	5, 3450 5, 3450 6, 1472 5, 3450 6, 1472 5, 3450 6, 1472 6, 147	1. 1031 1. 1031 1. 1031	
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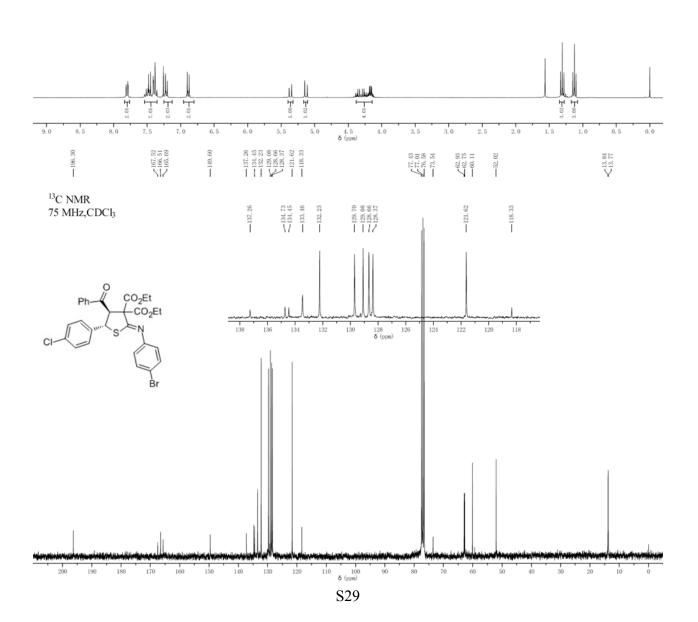




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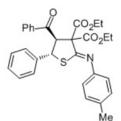
7, 1952 1, 7952 1, 7052 1, 705		9195. 44.3881 44.3887 44.3887 44.3887 44.3887 44.3887 44.3887 44.1373 44.1373 44.1573 44.1573 44.1573 44.1573 44.1573 44.1573 44.1573 44.1573 44.1573 44.1573 44.1573 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.15744 44.1574444 44.15744 44.15744 44.15744 44.1574444 44.15744 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.1574444 44.15744 44.1574444 44.1574444 44.15744 44.1574444 44.1574444 44.15744 44.1574444 44.1574444 44.15744 44.1574444 44.15744 44.1574444 44.1574444 44.1574444 44.15744 44.1574444 44.1574444 44.1574444 44.1574444 44.1574444 44.1574444 44.1574444 44.15744444 44.1574444 44.15744444 44.15744444 44.157444	1. 3292 1. 3053 1. 2815 1. 1483 1. 1483 1. 1009	-0.0006
<b>1 1 1 1</b>	• 11		101 107	

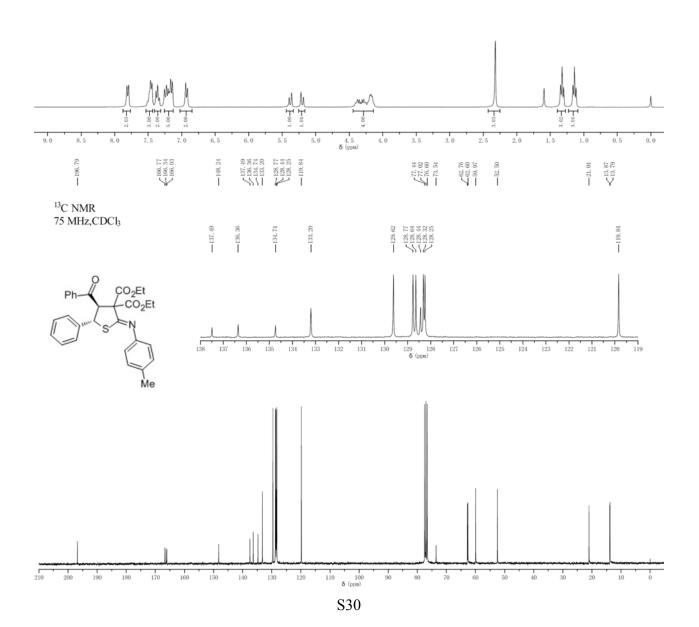




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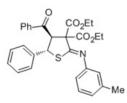
7, 18163 7, 1722 7, 1672 7, 18163 7, 18263 7, 19263 7, 192657 7, 1926577 7, 19265777 7, 19265777777777777777777777777777	5, 2963 5, 3963 5, 3969 5, 3964 5, 3969 5, 3965 5, 396	2. 3207	L 3469 L 322 L 2294 L 1620 L 1620 L 1147	-0.0004
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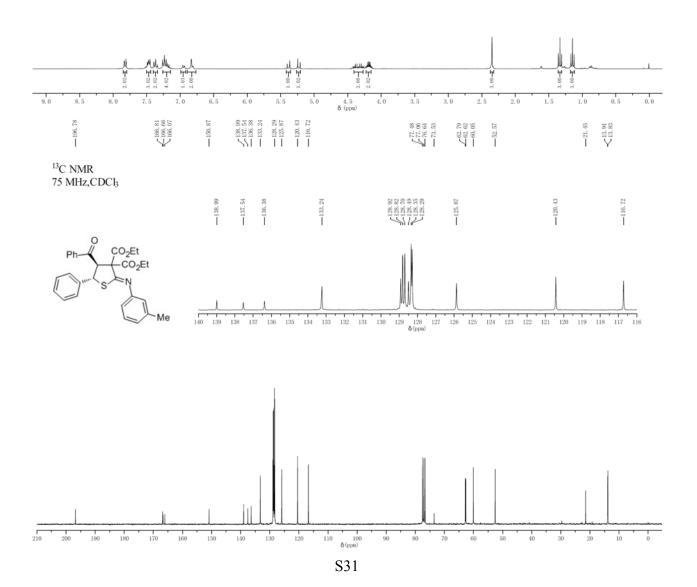




#### Compound 3db

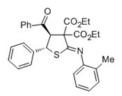
8355 8321 8321 8036 8036 8036 8036 147 1431 1431 1431 1431 1431 1431 1431	4023 3653 2963 2093	3603	3365 3365 3070 3070 3070 22596 22596 22596 22596 22561 22561 22561 22561 22561 22561 1550 11568 11650 11650 11650 11650	3469	3564 3326 3087 1691 1691 1691 1691 1691	5700
		4	4444444444444444	\$ V		0.

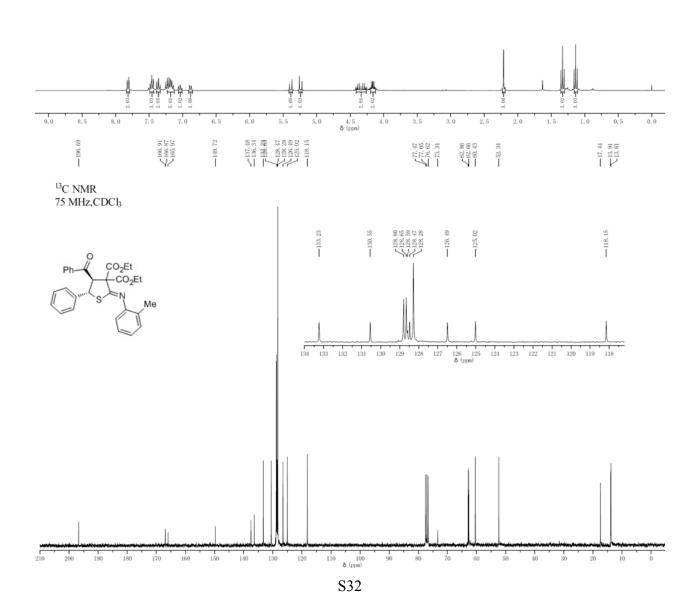




#### Compound 3dc

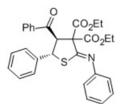
10000 100000 100000 100000 10000 10000 10000 10000 10000 100000	-5, 4063 -5, 3695 -5, 2575 -5, 2207	4, 3860 4, 3821 4, 3821 4, 3823 4, 3828 4, 3828 4, 1857 4, 18574, 1056 4, 10564, 1056 4, 1056 4, 1056 4, 10564, 1056 4, 1056 4, 1056 4, 10564, 105	-2.2115	$\underbrace{\swarrow_{1.3549}^{1.3549}}_{1.1125}$	
--	--	---	---------	--	--

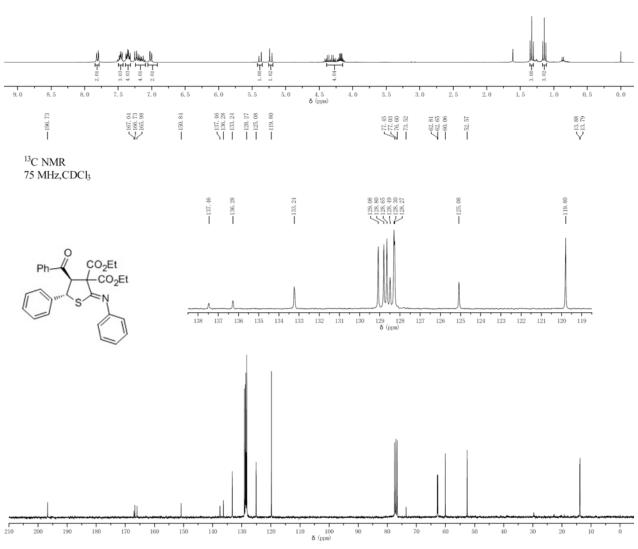




#### Compound 3dd

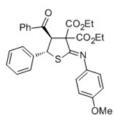
8310 8310 8245 8245 8205 8005 8105 17921 1591 14593 3382 3382 3382 3382 3382 3382 1951 1479 1479 1479 1479 1479 1479 1479 147	4004 3634 2413 2043	3910 3751 3652 3652 3652 3314 3652 3314 3652 3314 3652 3314 3652 3314 1733 1666 11733 1971 11733 1971 11733 1971 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 11733 1972 1972 1972 1972 1972 1972 1972 1972	3521 3283 3045 11407 1170	. 0005
		444444444444444444444444444444444444444		ļ

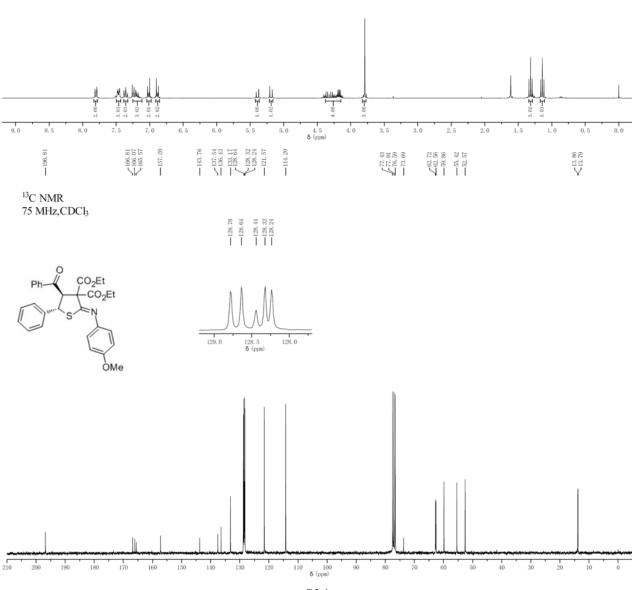




#### Compound 3de

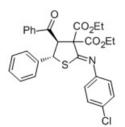
11111111111111111111111111111111111111	-4, 1258 4, 1258 3, 7580 3, 7580 5, 7681 4, 1287 1, 1400 1, 14
--	---

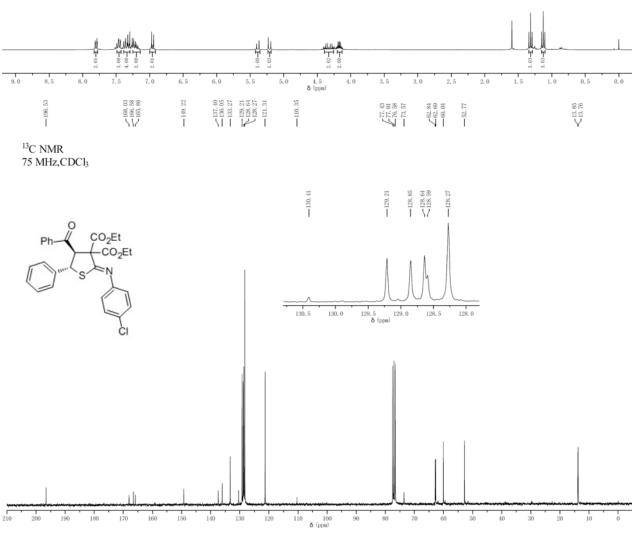




#### Compound 3dh

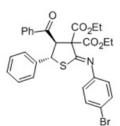
11118 1720 1700 17200 1720 1720 1720 1720 1720 1720 1720 1720 1720 1720	-5,4051 -5,3083 -5,1932	4, 4063 4, 4063 4, 8345 4, 8345 4, 8365 4, 8365 4, 8367 4, 836	L1. 3416 1. 3178 1. 2239 1. 1516 1. 1011	
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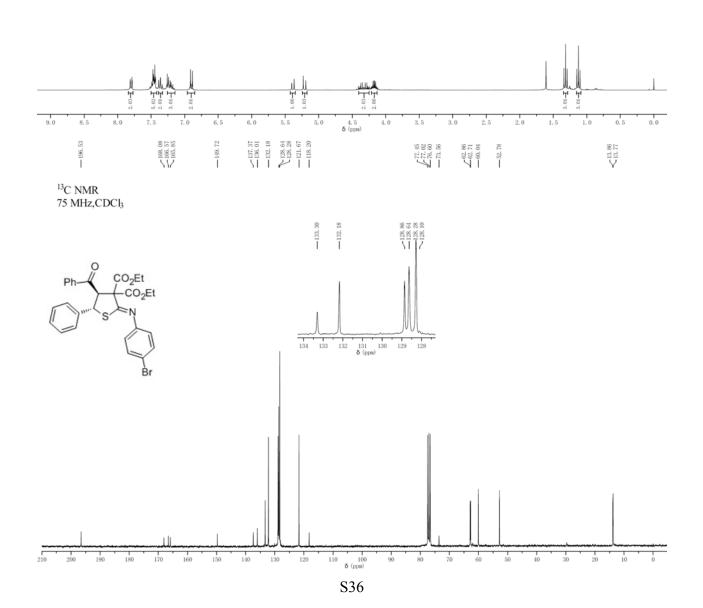




#### Compound 3dk

7, 1, 17, 18108 1, 17, 17, 17, 17, 17, 17, 17, 17, 17, 1	5. 4035 5. 3666 €. 1929	2012 100 100 100 100 100 100 100 100 100	$\int_{-1.1246}^{1.3174} \frac{1.3412}{1.2806}$	
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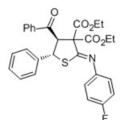


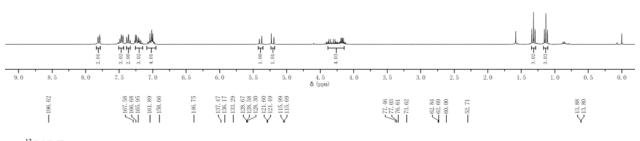


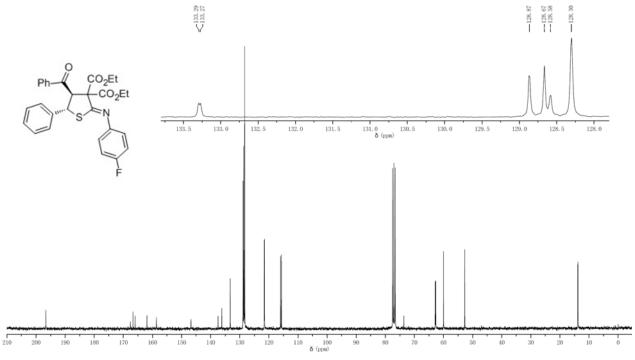
#### Compound **3dl**

11,12,000 11,12,000	L. 1086	-0.000
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<sup>1</sup>H NMR 300 MHz,CDCl<sub>3</sub>

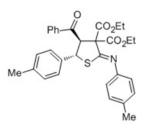


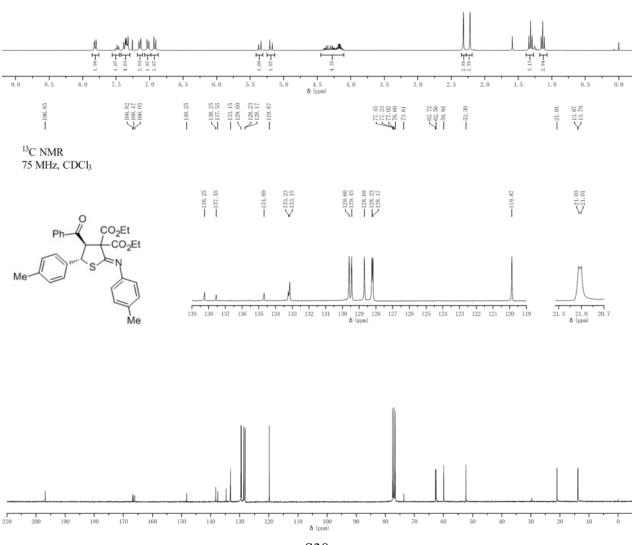




#### Compound 3ea

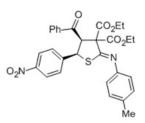
7, 8248 1, 2006 1, 2008 1,			-1.5885 -1.5885 -1.3170 -1.1317 -1.1345 -1.1109	$<^{0.0006}_{-0.0007}$
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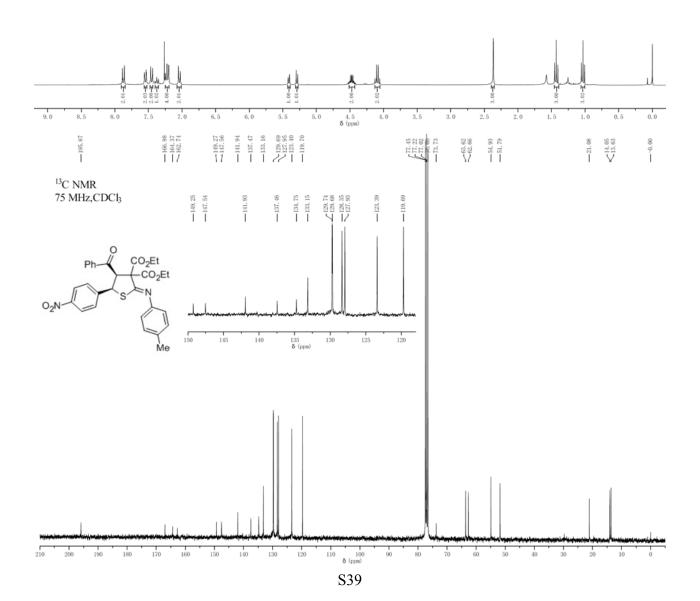




#### Compound 4aa

7, 8881 7, 9881 7, 9882 7, 9882 7, 9882 7, 9882 7, 9882 1, 9872 7, 9772 7, 977	$\sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{j=1}^{2} \sum_{i=1}^{2} \sum_{j=1}^{2} \sum_{j=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{i=1}^{2} \sum_{i$	-2, 3662 -2, 1623 -1, 1623 -1, 10545 -1, 10545 -1, 10545	
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#### 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 monchromated Mo K<sub> $\alpha$ </sub> radiation ( $\lambda = 0.71073$  Å) at room temperature. Saint program and SADABS program carried out the data integration. The structure was solved by a direct method and refined on F<sup>2</sup> 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.

Compound	3ck
Formula	C <sub>29</sub> H <sub>25</sub> BrClNO <sub>5</sub> S
Formula weight	614.92
Temperature/K	293(2)
Crystal system	Triclinic
Space group	P-1
<i>a</i> , Å	9.740(1)
b, Å	12.565(1)
<i>c</i> , Å	13.024(1)
$\alpha$ , deg	90.176(1)
$\beta$ , deg	108.720(1)
γ, deg	109.614(1)
V / Å <sup>3</sup>	1411.1(2)
Ζ	2
$\mu$ (Mo Ka), mm <sup>-1</sup>	1.664
$\theta$ range for data collection, deg	1.7 to 27.6
Calculated density/(g·cm <sup>-3</sup> )	1.447
Reflections collected	12325
Unique reflections/R <sub>int</sub>	6387 / R(int) = 0.022
F (000)	628
Goodness-of-fit on F <sup>2</sup>	0.98
Crystal dimension/mm <sup>3</sup>	0.18×0.22×0.28
$\mathbf{R}, \mathbf{R}_{w} \left[\mathbf{I} > 2\sigma(\mathbf{I})\right]$	0.0709, 0.2751
Residual $\rho/(e \cdot \text{\AA}^{-3})$	1.39, -0.65

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

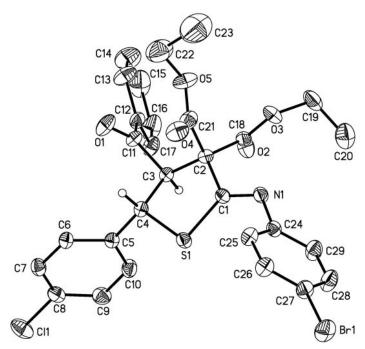


Figure S1 X-ray structure (50 % probability ellipsoids) of 3ck.