Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supplementary Information

Lewis Acids Catalyzed Asymmetric [4+2] Cycloaddition of Cyclobutenones to Synthesize *α,β*-Unsaturated *δ*-Lactones

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Contents

(A) General Information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublets), coupling constants (Hz), integration. ^{13}C{^{1}H} NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. The enantiomeric excesses were determined by HPLC analysis on chiral DAICEL CHIRALPAK IA or CHIRALPAK IB or CHIRALPAK IC or CHIRALPAK IE or CHIRALPAK ADH column at 254 nm. Optical rotations were measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^T$ (*c* = g/100 mL, CH_2Cl_2). HRMS was recorded on a commercial apparatus (ESI Source). Solvents were dried according to standard procedures. Racemic samples were prepared by using the racemic *N,N'*-dioxdes as the ligand. All reactions were performed in sealed oven-dried glass tubes under an atmosphere of nitrogen unless otherwise noted. The *N,N'*-dioxdes were prepared according to the previous reports.[1] Starting materials of cyclobutenones,[2] *α*-ketoesters[3] and *α*-ketoamide[4] were prepared according to the previous reports.

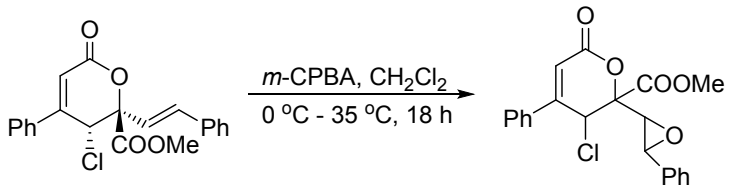
(B) General procedure for the asymmetric [4+2] cycloaddition

a) Preparing chiral catalyst: *N,N'*-dioxide **L-Pi*t*Bu** (15.4 mg, 0.035 mmol), $Yb(OTf)_3$ (21.7 mg, 0.035 mmol), 5 Å molecular sieves (350 mg) and $LiNTf_2$ (30.1 mg, 0.105 mmol) were stirred in 3.5 mL CH_2Cl_2 at 30 ^{o}C for 3 hours. After the solvent was removed in vacuo, the solid of the chiral catalyst was obtained.

b) Catalytic reaction: A dry reaction tube was charged with the prepared chiral catalyst (119.2 mg, 0.01 mmol, 10 mol%), *α*-keto carbonyl compounds (**1**) (0.10 mmol) and cyclobutenones (**2**) (0.12 mmol) under an N_2 atmosphere. Then, $CHCl_3$ (1.0 mL) were added and the mixture was stirred at 50 ºC for 48 hours. The products were purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/6).

(C) Transformation of 3aa

a) The oxidant *m*-CPBA (0.2 mmol, 34.4 mg) was added to a solution of **3aa** (0.10 mmol, 36.8 mg) in CH_2Cl_2 (1 mL) at 0 ºC. Then, the reaction mixture was stirred at 35 ºC for 18 hours.[5] The product was purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/6).



3aa: 95% ee, 17/1 dr

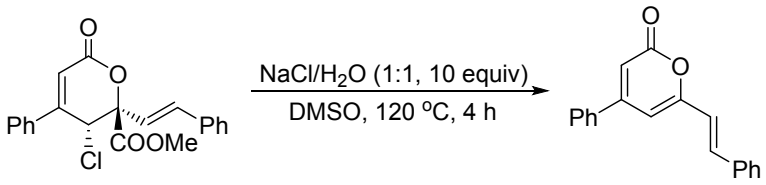
4aa: 68% yield
95% ee, >19/1 dr

b) To a dry Schlenk tube was added **3aa** (0.1 mmol, 36.8 mg), NaCl (1 mmol, 58.4 mg), H_2O (1 mmol, 18 mg) and DMSO (1.5 mL). The reaction was stirred at 120 °C for 4 hours. The solution was then cooled to room temperature, diluted with water and extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na_2SO_4, concentrated and the product was purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/6).

5aa: **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.70 – 7.55 (m, 12H), 7.55 – 7.48 (m, 5H), 7.46 – 7.30 (m, 3H), 6.73 (d, *J* = 16.0, 1H), 6.46 (dd, *J* = 24.0, 1.2, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 162.6, 159.1, 155.6, 135.9, 135.6, 135.5, 130.8, 129.6, 129.3, 129.1, 127.6, 126.8, 119.1, 109.5, 105.3.

HRMS (ESI-FT): calcd for $C_{19}H_{14}NaO_2^+$ ([M + Na]$^+$) 297.0891, found 297.0890.



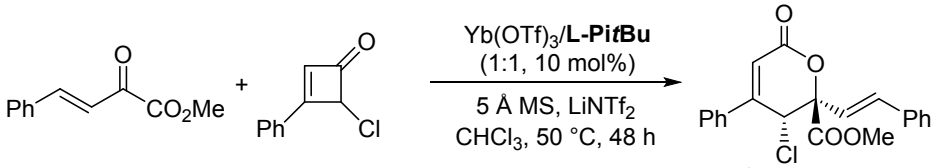
3aa: 95% ee, 17/1 dr

5aa: 70% yield.

(D) Control experiments

a) Cyclobutenones are known to undergo ring opening to form vinylketenes at high temperature (≥ 80 °C). Under our catalytic conditions, no product was detected when the reaction was carried out at 0 °C. However, the reaction could occur at lower temperatures (50 °C), which indicated in our system the thermal conditions might be not the only factor to cause such ring opening.

It showed that the thermal conditions were benefit for the reaction.

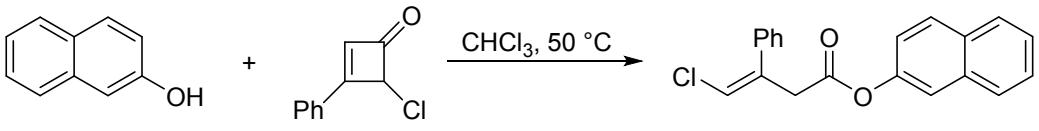


1a **2a**

3aa: 0% yield
(0% conversion)

General procedure for the reaction: a dry reaction tube was charged with the prepared chiral catalyst (119.2 mg, 0.01 mmol, 10 mol%), *α*-keto carbonyl compound **1a** (0.10 mmol, 19.0 mg) and cyclobutenone **2a** (0.12 mmol, 21.4 mg) under an N_2 atmosphere. Then, $CHCl_3$ (1.0 mL) were added and the mixture was stirred at 0 °C for 48 hours.

b) In order to gain insight into the influence of our catalytic condition on the ring opening of cyclobutenones, we selected 2-naphthol **6a**, which was weakly coordinated with Lewis acid, to trap the vinylketenes.



6a + **2a**

Conditions	**7aa**
5 Å MS	trace
$Yb(OTf)_3$	trace
$LiNTf_2$	trace
$LiNTf_2$, 5 Å MS	trace
$Yb(OTf)_3$, 5 Å MS	40% yield
$Yb(OTf)_3$, $LiNTf_2$	55% yield
$Yb(OTf)_3$, $LiNTf_2$ 5 Å MS,	85% yield

The results above suggested that the Lewis acid [$Yb(OTf)_3$] might participate in the activation of cyclobutanone to generate the active vinylketene intermediate assisted by $LiNTf_2$ and 5 Å molecular series under the thermal condition.

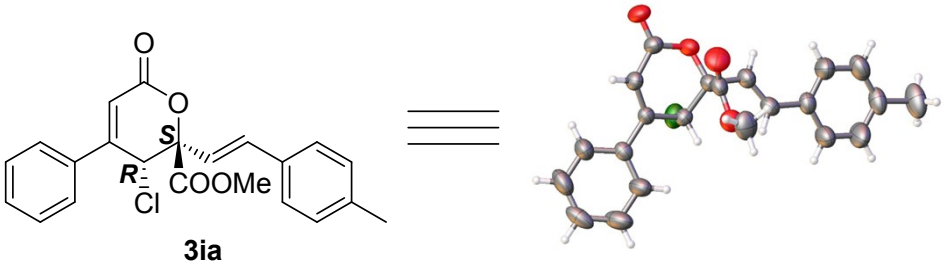
General procedure for the reaction: a dry reaction tube was charged with $Yb(OTf)_3$ (6.2 mg, 0.01 mmol), 5 Å molecular sieves (100 mg) and $LiNTf_2$ (8.6 mg, 0.03 mmol), cyclobutenone **2a** (0.10 mmol, 17.8 mg) and 2-naphthol **6a** (0.1 mmol, 14.4 mg) under an N_2 atmosphere. Then, $CHCl_3$ (1.0 mL) were added and the mixture was stirred at 50 ºC for 48 hours. The product was purified by silica gel column chromatographic (ethyl acetate/petroleum ether 1/20 to 1/9).

7aa: **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.80 – 7.71 (m, 3H), 7.49 – 7.30 (m, 8H), 7.04 – 6.91 (m, 1H), 6.43 (d, *J* = 1.2, 1H), 3.70 (s, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.9, 148.2, 136.6, 135.4, 133.7, 131.6, 129.5, 128.6, 128.5, 128.4, 127.9, 127.7, 126.7, 125.9, 120.8, 118.4, 118.4, 42.6.

HRMS (ESI-FT): calcd for $C_{20}H_{16}{}^{34.9689}ClKO_2^+$ ([M + K]$^+$) 323.0839, found 323.0837, calcd for $C_{20}H_{16}{}^{36.9659}ClKO_2^+$ ([M + K]$^+$) 325.0809, found 325.0809.

(E) The X-ray structure for 3ia (CCDC 1560408)



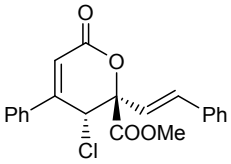
3ia

The compound **3ia** was recrystallized from CH_2Cl_2 and petroleum ether.

CCDC 1560408 contains the supplementary crystallographic data of the adduct **3ia** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(F) The analytical and spectral characterization data for the compounds

Methyl (*E*)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-*2H*-pyran-2-carboxylate (3aa)

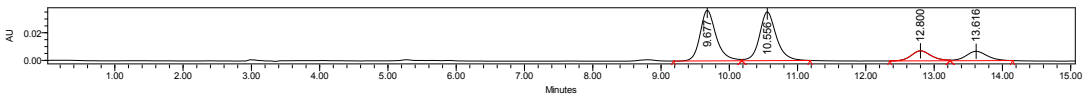


White solid, 92% yield (1.19 g). 17/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 9.7 min, 10.6 min, 12.8 min, 13.6 min. $[\alpha]_D^{20}$ = −240.31 (*c* = 0.52).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H), 7.54 – 7.44 (m, 5H), 7.40 – 7.30 (m, 3H), 7.17 (d, *J* = 16.0, 1H), 6.42 (s, 1H), 6.30 (d, *J* = 16.0, 1H), 5.53 (s, 1H), 3.77 (s, 3H).

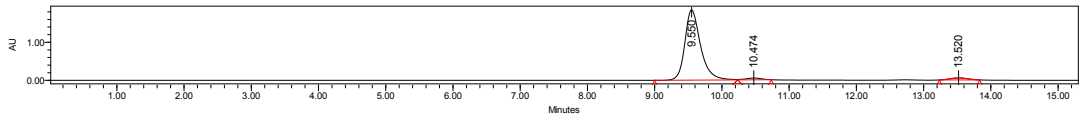
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 161.9, 153.3, 135.3, 134.7, 133.2, 131.6, 129.5, 129.0, 128.9, 127.2, 126.7, 121.7, 116.6, 85.5, 54.5, 54.2.

HRMS (ESI-TOF): calcd for $C_{21}H_{17}{}^{34.9689}ClKO_4^+$ ([M + K]$^+$) 407.0452, found 407.0448, calcd for $C_{21}H_{17}{}^{36.9659}ClKO_4^+$ ([M + K]$^+$) 409.0423, found 409.0424.



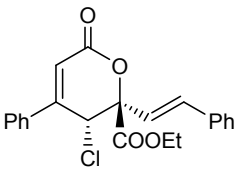
	Retention Time	Area	% Area
1	9.677	601262	40.03
2	10.556	604814	40.27
3	12.800	147979	9.85

4	13.616	147869	9.85



	Retention Time	Area	% Area
1	9.550	29985632	94.59
2	10.474	766232	2.42
3	13.520	947398	2.99

Ethyl (*E*)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-2*H*-pyran-2-carboxylate (3ba)

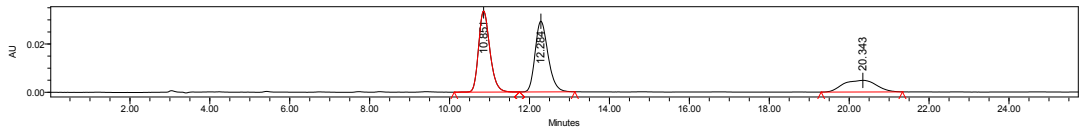


White solid, 87% yield (33.2 mg). 16/1 dr determined by ^{1}H NMR, 94% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.0 min, 12.5 min, 20.4 min. $[\alpha]_D^{20}$ = −259.89 (*c* = 0.53).

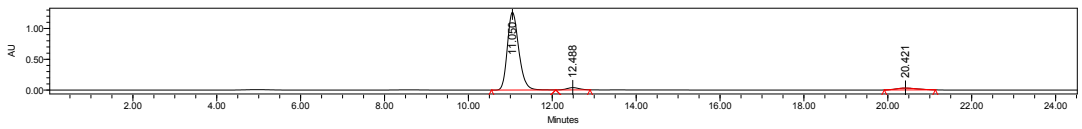
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H), 7.54 – 7.44 (m, 5H), 7.41 – 7.31 (m, 3H), 7.18 (d, *J* = 16.0, 1H), 6.42 (s, 1H), 6.31 (d, *J* = 16.0, 1H), 5.53 (s, 1H), 4.23 (dd, *J* = 14.0, 6.8, 2H), 1.20 (t, *J* = 6.8, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.8, 162.0, 153.2, 135.4, 134.7, 133.3, 131.6, 129.5, 128.9, 128.9, 127.2, 126.7, 121.7, 116.7, 85.4, 63.5, 54.6, 14.1.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 405.0870, found 405.0864, calcd for $C_{22}H_{19}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 407.0840, found 407.0850.

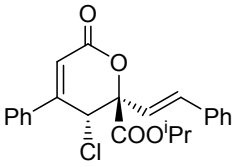


	Retention Time	Area	% Area
1	10.851	658734	41.31
2	12.284	656987	41.21
3	20.343	278710	17.48



	Retention Time	Area	% Area
1	11.050	23819289	93.00
2	12.488	739739	2.89
3	20.421	1052883	4.11

Isopropyl (*E*)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ca)

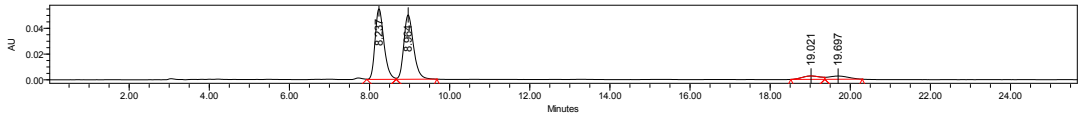


White solid, 83% yield (32.7 mg). 16/1 dr determined by ^{1}H NMR, 93% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 8.4 min, 9.1 min, 19.7 min, 20.2 min. $[\alpha]_D^{20}$ = −200.19 (*c* = 0.54).

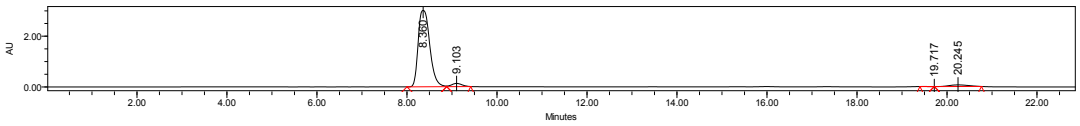
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.60 (m, 2H), 7.53 – 7.45 (m, 5H), 7.41 – 7.31 (m, 3H), 7.17 (d, *J* = 16.0, 1H), 6.42 (s, 1H), 6.31 (d, *J* = 16.0, 1H), 5.51 (s, 1H), 5.12 – 4.96 (m, 1H), 1.21 (d, *J* = 6.0, 3H), 1.16 (d, *J* = 6.0, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 168.2, 162.1, 153.1, 135.5, 134.6, 133.4, 131.6, 129.5, 128.9, 127.2, 126.6, 121.7, 116.8, 85.3, 71.8, 54.8, 21.6, 21.5.

HRMS (ESI-TOF): calcd for $C_{23}H_{21}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 419.1026, found 419.1028, calcd for $C_{23}H_{21}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 421.0997, found 421.1006.

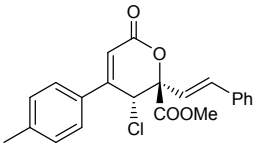


	Retention Time	Area	% Area
1	8.237	842624	45.50
2	8.964	841735	45.45
3	19.021	82616	4.46
4	19.697	85117	4.60



	Retention Time	Area	% Area
1	8.360	53721747	93.21
2	9.103	2014865	3.50
3	19.717	16588	0.03
4	20.245	1883949	3.27

Methyl (*E*)-3-chloro-6-oxo-2-styryl-4-(*p*-tolyl)-3,6-dihydro-*2H*-pyran-2-carboxylate (3ab)

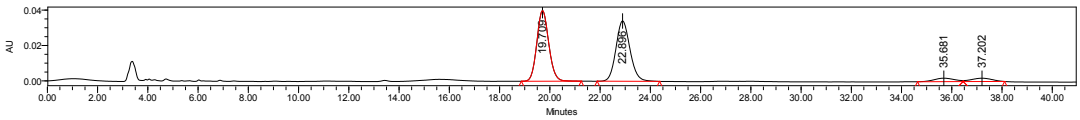


White solid, 82% yield (31.5 mg). 17/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IC** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 19.4 min, 22.6 min, 35.1 min, 36.6 min. $[\alpha]_D^{20}$ = −227.30 (*c* = 0.63).

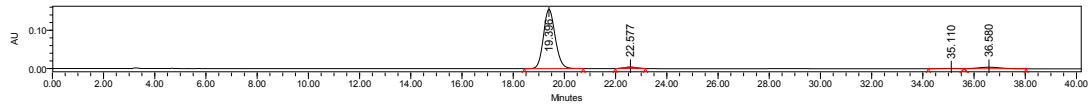
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.46 (m, 4H), 7.39 – 7.29 (m, 5H), 7.17 (d, *J* = 16.0, 1H), 6.40 (s, 1H), 6.30 (d, *J* = 16.0, 1H), 5.53 (s, 1H), 3.76 (s, 3H), 2.42 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 162.1, 153.2, 142.4, 135.3, 134.6, 130.2, 128.9, 128.9, 127.2, 126.6, 121.8, 115.5, 85.4, 54.4, 54.2, 21.6.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 405.0870, found 405.0869, calcd for $C_{22}H_{19}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 407.0840, found 407.0861.

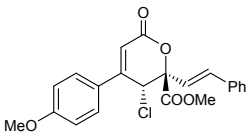


	Retention Time	Area	% Area
1	19.709	1310869	46.01
2	22.896	1320951	46.36
3	35.681	110360	3.87
4	37.202	107145	3.76



	Retention Time	Area	% Area
1	19.396	4931045	92.13
2	22.577	126996	2.37
3	35.110	41149	0.77
4	36.580	253273	4.73

Methyl (*E*)-3-chloro-4-(4-methoxyphenyl)-6-oxo-2-styryl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ac)

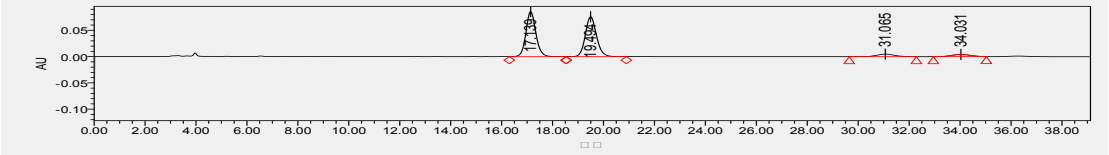


White solid, 56% yield (22.5 mg). 15/1 dr determined by ^{1}H NMR, 93% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.0 min, 19.4 min, 31.0 min, 33.9 min. $[\alpha]_D^{20}$ = −260.67 (*c* = 0.45).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 – 7.58 (m, 2H), 7.50 – 7.45 (m, 2H), 7.39 – 7.30 (m, 3H), 7.16 (d, *J* = 16.0, 1H), 7.02 – 6.98 (m, 2H), 6.35 (s, 1H), 6.30 (d, *J* = 15.6, 1H), 5.52 (s, 1H), 3.87 (s, 3H), 3.76 (s, 3H).

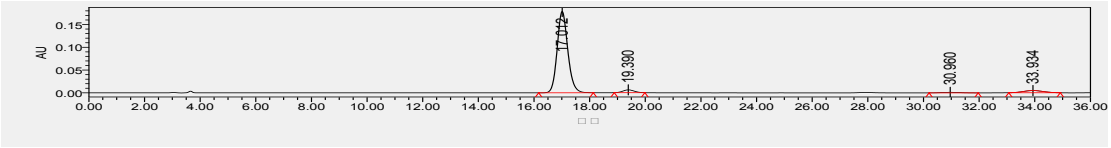
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.5, 162.5, 162.3, 152.6, 135.4, 134.6, 128.9, 128.9, 128.4, 127.2, 125.2, 121.9, 115.0, 114.0, 85.3, 55.7, 54.3, 54.1.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}^{34.9689}ClNaO_5^+$ ([M + Na]$^+$) 421.0819, found 421.0815, calcd for $C_{22}H_{19}^{36.9659}ClNaO_5^+$ ([M + Na]$^+$) 423.0789, found 423.0801.



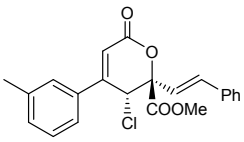
	Retention Time	Area	% Area
1	17.139	2333527	45.79
2	19.494	2313473	45.40
3	31.065	233654	4.58

4	34.031	215549	4.23



	Retention Time	Area	% Area
1	17.012	4754442	91.07
2	19.390	174274	3.34
3	30.960	51294	0.98
4	33.934	240905	4.61

Methyl (*E*)-3-chloro-6-oxo-2-styryl-4-(*m*-tolyl)-3,6-dihydro-*2H*-pyran-2-carboxylate (3ad)

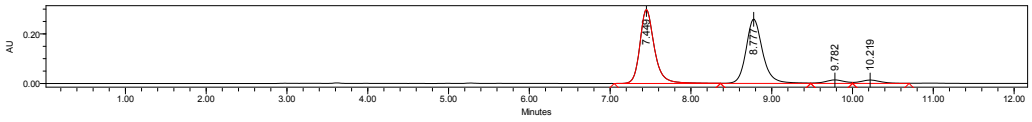


White solid, 78% yield (30.0 mg). >19/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 7.4 min, 8.7 min, 9.7 min, 10.1 min. $[\alpha]_D^{20}$ = −279.83 (*c* = 0.60).

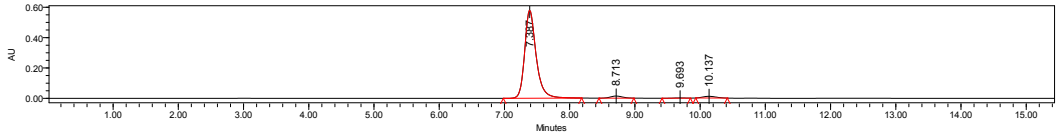
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50 – 7.46 (m, 2H), 7.44 – 7.31 (m, 7H), 7.17 (d, *J* = 16.0, 1H), 6.41 (s, 1H), 6.31 (d, *J* = 16.0, 1H), 5.53 (s, 1H), 3.77 (s, 3H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.5, 162.0, 153.5, 139.3, 135.3, 134.7, 133.2, 132.5, 129.4, 129.0, 128.9, 127.3, 127.2, 123.9, 121.8, 116.4, 85.5, 54.5, 54.2, 21.6.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 405.0870, found 405.0873, calcd for $C_{22}H_{19}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 407.0840, found 407.0853.

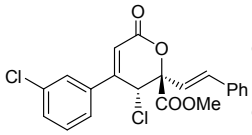


	Retention Time	Area	% Area
1	7.449	3714879	47.04
2	8.777	3704849	46.91
3	9.782	234068	2.96
4	10.219	243485	3.08



	Retention Time	Area	% Area
1	7.387	7056205	95.29
2	8.713	173281	2.34
3	9.693	19059	0.26
4	10.137	156737	2.12

Methyl (*E*)-3-chloro-4-(3-chlorophenyl)-6-oxo-2-styryl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ae)

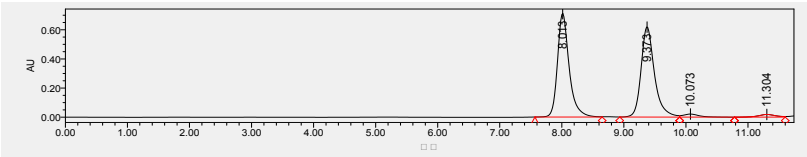


White solid, 53% yield (10.7 mg). 16/1 dr determined by ^{1}H NMR, 93% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 7.9 min, 9.3 min, 10.0 min, 11.2 min. $[\alpha]_D^{20}$ = −316.36 (*c* = 0.21).

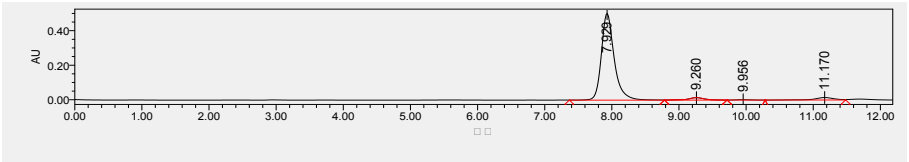
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (t, *J* = 2.0, 1H), 7.53 – 7.43 (m, 5H), 7.41 – 7.32 (m, 3H), 7.16 (d, *J* = 16.0, 1H), 6.41 (s, 1H), 6.28 (d, *J* = 16.0, 1H), 5.45 (s, 1H), 3.79 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.3, 161.4, 152.1, 135.7, 135.2, 135.2, 134.9, 131.6, 130.8, 129.1, 128.9, 127.2, 126.8, 124.9, 121.4, 117.7, 85.5, 54.4, 54.3.

HRMS (ESI-FT): calcd for $C_{21}H_{16}{}^{34.9689}Cl_2NaO_4^+$ ([M + Na]$^+$) 425.0323, found 425.0321, calcd for $C_{21}H_{16}{}^{36.9659}Cl_2NaO_4^+$ ([M + Na]$^+$) 427.0294, found 427.0294.

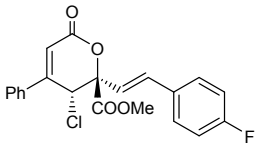


	Retention Time	Area	% Area
1	8.013	9313360	48.21
2	9.373	9298383	48.13
3	10.073	356584	1.85
4	11.304	350304	1.81



	Retention Time	Area	% Area
1	7.929	6666177	92.06
2	9.260	245460	3.39
3	9.956	31839	0.44
4	11.170	297515	4.11

Methyl (*E*)-3-chloro-2-(4-fluorostyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3da)

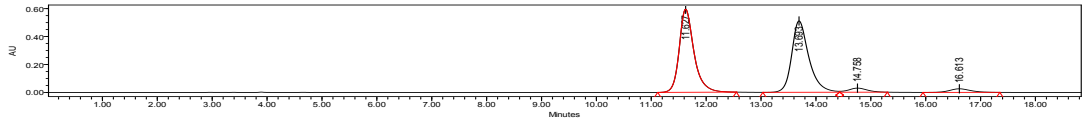


White solid, 86% yield (33.1 mg). 19/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.6 min, 13.7 min, 14.7 min, 16.5 min. $[\alpha]_D^{20}$ = −254.98 (*c* = 0.66).

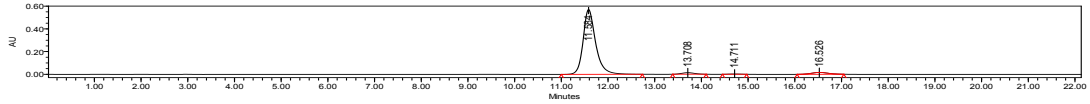
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.59 (m, 2H), 7.53 – 7.43 (m, 5H), 7.13 (d, *J* = 15.6, 1H), 7.09 – 7.02 (m, 2H), 6.42 (s, 1H), 6.21 (d, *J* = 16.0, 1H), 5.52 (s, 1H), 3.77 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 167.9 (d, *J* = 502.0), 161.9 (d, *J* = 90.9), 153.3, 133.6, 133.2, 131.7, 131.5 (d, *J* = 3.0), 129.5, 128.9 (d, *J* = 8.1), 126.7, 121.4, 116.6, 116.0, 115.8, 85.4, 54.5, 54.2.

HRMS (ESI-TOF): calcd for $C_{21}H_{17}{}^{34.9689}ClFO_4^+$ ([M + H]$^+$) 387.0799, found 387.0792, calcd for $C_{21}H_{17}{}^{36.9659}ClFO_4^+$ ([M + H]$^+$) 389.0770, found 389.0771.

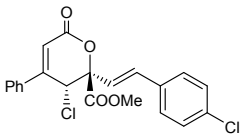


	Retention Time	Area	% Area
1	11.627	11069788	47.09
2	13.693	11060353	47.05
3	14.758	696122	2.96
4	16.613	679360	2.89



	Retention Time	Area	% Area
1	11.584	10602850	93.74
2	13.708	258149	2.28
3	14.711	40547	0.36
4	16.526	409288	3.62

Methyl (*E*)-3-chloro-2-(4-chlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ea)

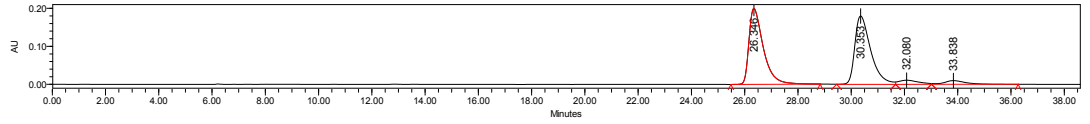


White solid, 90% yield (36.0 mg). >19/1 dr determined by ^{1}H NMR, 93% ee determined by **HPLC** (chiral **IA-IB** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 26.3 min, 30.4 min, 32.1 min, 33.8 min. $[\alpha]_D^{20}$ = −181.39 (*c* = 0.72).

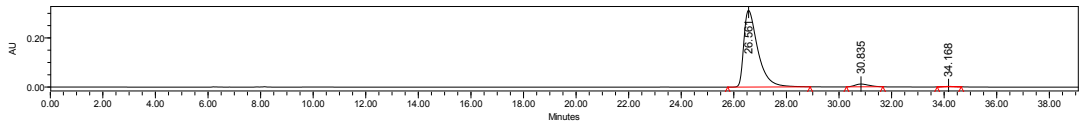
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J* = 8.0, 2H), 7.55 – 7.47 (m, 3H), 7.37 (dd, *J* = 26.0, 8.0, 4H), 7.12 (d, *J* = 16.0, 1H), 6.42 (s, 1H), 6.27 (d, *J* = 15.6, 1H), 5.51 (s, 1H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.3, 161.8, 153.3, 134.8, 133.8, 133.5, 133.2, 131.7, 129.5, 129.1, 128.4, 126.7, 122.3, 116.6, 85.4, 54.4, 54.3.

HRMS (ESI-TOF): calcd for $C_{21}H_{16}{}^{34.9689}Cl_2NaO_4^+$ ([M + Na]$^+$) 425.0323, found 425.0329, calcd for $C_{21}H_{16}{}^{36.9659}Cl_2NaO_4^+$ ([M + Na]$^+$) 427.0294, found 427.0302.

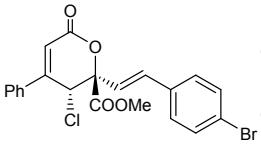


	Retention Time	Area	% Area
1	26.346	7442649	46.47
2	30.353	7452310	46.53
3	32.080	568758	3.55
4	33.838	553674	3.46



	Retention Time	Area	% Area
1	26.561	11579598	96.06
2	30.835	422880	3.51
3	34.168	52333	0.43

Methyl (*E*)-2-(4-bromostyryl)-3-chloro-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3fa)

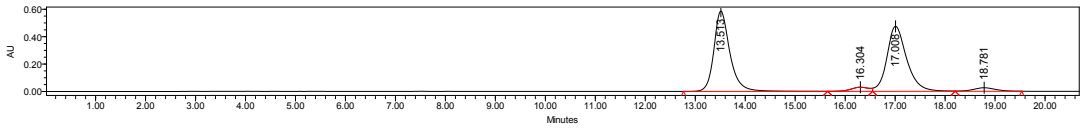


White solid, 85% yield (38.0 mg). >19/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 13.5 min, 16.3 min, 17.1 min, 18.8 min. $[\alpha]_D^{20}$ = −207.76 (*c* = 0.76).

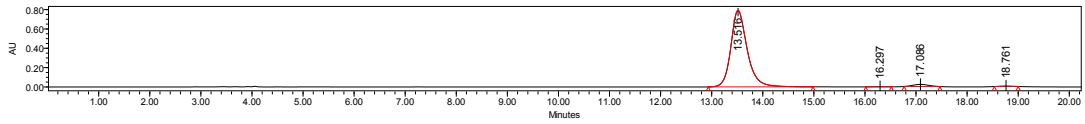
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.59 (m, 2H), 7.56 – 7.44 (m, 5H), 7.34 (d, *J* = 8.8, 2H), 7.11 (d, *J* = 16.0, 1H), 6.42 (s, 1H), 6.29 (d, *J* = 16.0, 1H), 5.51 (s, 1H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.2, 161.7, 153.2, 134.2, 133.6, 133.2, 132.1, 131.7, 129.5, 128.7, 126.7, 123.0, 122.4, 116.6, 85.4, 54.4, 54.3.

HRMS (ESI-TOF): calcd for $C_{21}H_{17}Br^{34.9689}ClO_4^+$ ([M + H]$^+$) 446.9999, found 446.9994, calcd for $C_{21}H_{17}Br^{36.9659}ClO_4^+$ ([M + H]$^+$) 448.9978, found 448.9957.

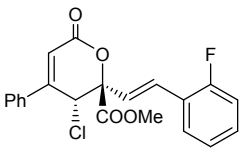


	Retention Time	Area	% Area
1	13.513	13059748	47.24
2	16.304	758525	2.74
3	17.008	13035980	47.15
4	18.781	792017	2.86



	Retention Time	Area	% Area
1	13.516	17524641	96.89
2	16.297	21643	0.12
3	17.086	466305	2.58
4	18.761	74887	0.41

Methyl (*E*)-3-chloro-2-(2-fluorostyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ga)

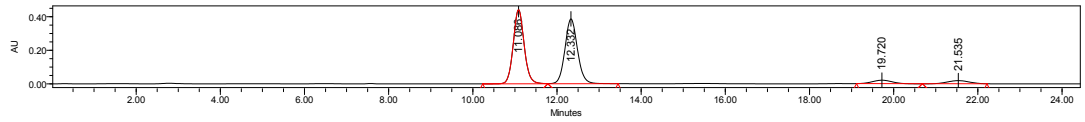


White solid, 80% yield (30.9 mg). 11/1 dr determined by ^{1}H NMR, 86% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.9 min, 12.2 min, 19.4 min, 21.2 min. $[\alpha]_D^{20}$ = −250.81 (*c* = 0.62).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.60 (m, 2H), 7.55 – 7.47 (m, 4H), 7.32 – 7.22 (m, 2H), 7.18 – 7.12 (m, 1H), 7.11 – 7.05 (m, 1H), 6.49 – 6.42 (m, 2H), 5.54 (s, 1H), 3.78 (s, 3H).

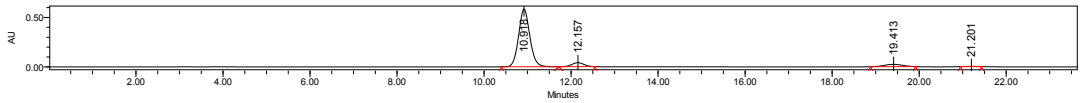
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.3, 162.0 (d, *J* = 35.4), 159.7, 153.3, 133.2, 131.7, 130.3 (d, *J* = 8.1), 129.5, 128.9 (d, *J*=3.0), 128.0 (d, *J* = 3.0), 126.7, 124.6 (d, *J* = 7.1), 124.4 (d, *J* = 4.0), 123.2 (d, *J* = 11.1), 116.6, 116.1 (d, *J* = 22.2), 85.5, 54.4, 54.2.

HRMS (ESI-TOF): calcd for $C_{21}H_{17}^{34.9689}ClFO_4^+$ ([M + H]$^+$) 387.0799, found 387.0800, calcd for $C_{21}H_{17}^{36.9659}ClFO_4^+$ ([M + H]$^+$) 389.0770, found 389.0772.



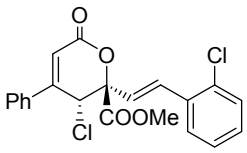
	Retention Time	Area	% Area
1	11.086	7965866	46.11
2	12.332	7979677	46.19
3	19.720	666447	3.86

4	21.535	664689	3.85



	Retention Time	Area	% Area
1	10.918	10494433	87.24
2	12.157	793779	6.60
3	19.413	707189	5.88
4	21.201	33352	0.28

Methyl (*E*)-3-chloro-2-(2-chlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ha)

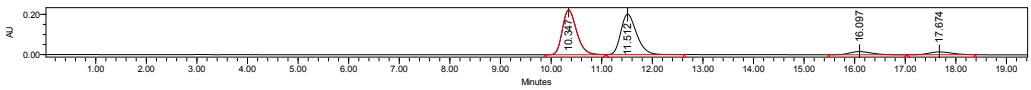


White solid, 85% yield (34.4 mg). 8/1 dr determined by ^{1}H NMR, 86% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.3 min, 11.4 min, 16.0 min, 17.5 min. $[\alpha]_D^{20}$ = −209.16 (*c* = 0.69).

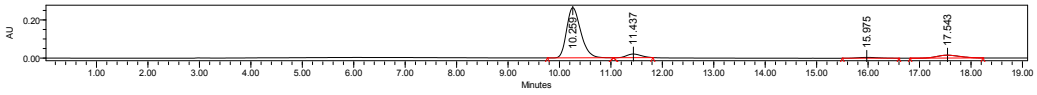
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.61 (m, 2H), 7.59 – 7.56 (m, 1H), 7.54 – 7.48 (m, 4H), 7.42 – 7.37 (m, 1H), 7.28 – 7.24 (m, 2H), 6.43 (s, 1H), 6.32 (d, *J* = 16.0, 1H), 5.53 (s, 1H), 3.79 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.2, 161.8, 153.2, 134.0, 133.7, 133.2, 131.7, 131.2, 130.1, 129.9, 129.5, 127.4, 127.1, 126.7, 124.9, 116.7, 85.5, 54.5, 54.3.

HRMS (ESI-TOF): calcd for $C_{22}H_{16}{}^{34.9689}Cl_2NaO_4^+$ ([M + Na]$^+$) 425.0323, found 425.0320, calcd for $C_{22}H_{16}{}^{36.9659}Cl_2NaO_4^+$ ([M + Na]$^+$) 427.0294, found 427.0289.

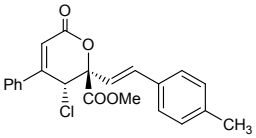


	Retention Time	Area	% Area
1	10.347	4347268	45.24
2	11.512	4351249	45.28
3	16.097	468523	4.88
4	17.674	442086	4.60



	Retention Time	Area	% Area
1	10.259	5000377	84.01
2	11.437	367222	6.17
3	15.975	113990	1.92
4	17.543	470419	7.90

Methyl (*E*)-3-chloro-2-(4-methylstyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ia)

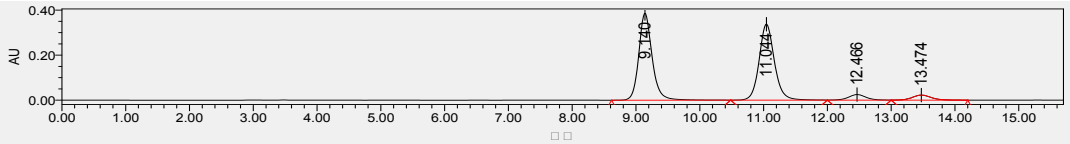


White solid, 91% yield (34.8 mg). >19/1 dr determined by ^{1}H NMR, 97% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 9.1 min, 11.0 min, 12.5 min, 13.5 min. $[\alpha]_D^{20}$ = −293.65 (*c* = 0.63).

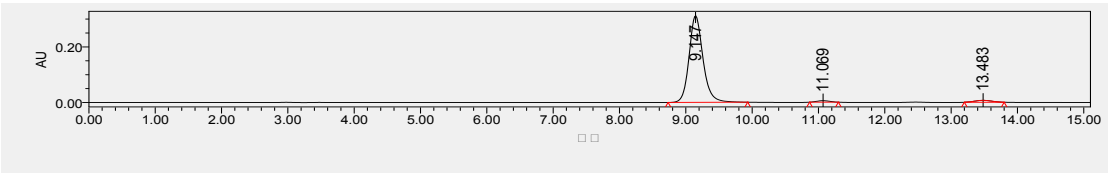
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H), 7.54 – 7.46 (m, 3H), 7.41 – 7.32 (m, 2H), 7.20 – 7.09 (m, 3H), 6.42 (s, 1H), 6.25 (d, *J* = 16.0, 1H), 5.52 (s, 1H), 3.77 (s, 3H), 2.36 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.5, 162.0, 153.4, 139.0, 134.6, 133.3, 132.5, 131.6, 129.6, 129.5, 127.1, 126.7, 120.6, 116.6, 85.5, 54.6, 54.1, 27.0, 21.4.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 405.0870, found 405.0872, calcd for $C_{22}H_{19}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 407.0840, found 407.0828.

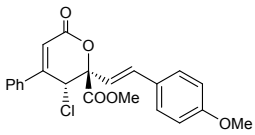


	Retention Time	Area	% Area
1	9.140	5615290	46.06
2	11.044	5624776	46.13
3	12.466	482829	3.96
4	13.474	469648	3.85



	Retention Time	Area	% Area
1	9.147	4544933	95.92
2	11.069	71068	1.50
3	13.483	122119	2.58

Methyl (*E*)-3-chloro-2-(4-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ja)

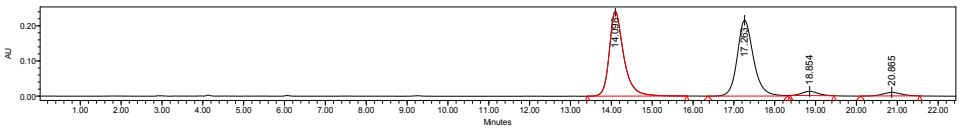


White solid, 80% yield (31.9 mg). >19/1 dr determined by ^{1}H NMR, 98% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.0 min, 17.3 min, 18.7 min, 20.8 min. $[\alpha]_D^{20}$ = −264.89 (*c* = 0.64).

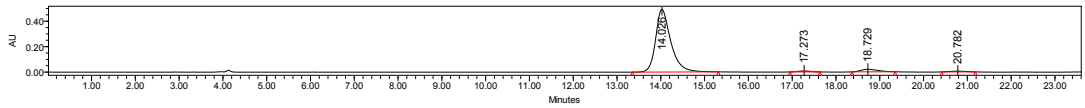
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.59 (m, 2H), 7.53 – 7.46 (m, 3H), 7.45 – 7.38 (m, 2H), 7.10 (d, *J* = 16.0, 1H), 6.90 (dd, *J* = 8.8, 2.8, 2H), 6.41 (s, 1H), 6.16 (d, *J* = 16.0, 1H), 5.51 (s, 1H), 3.82 (s, 3H), 3.76 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.6, 162.0, 160.3, 153.4, 134.1, 133.3, 131.6, 129.5, 128.5, 128.0, 126.7, 119.3, 116.6, 114.3, 85.5, 55.5, 54.6, 54.1.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}^{34.9689}ClNaO_5^+$ ([M + Na]$^+$) 421.0819, found 421.0819, calcd for $C_{22}H_{19}^{36.9659}ClNaO_5^+$ ([M + Na]$^+$) 423.0789, found 423.0799.

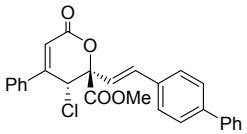


	Retention Time	Area	% Area
1	14.098	5918043	47.38
2	17.263	5925465	47.44
3	18.854	328293	2.63
4	20.865	319745	2.56



	Retention Time	Area	% Area
1	14.026	11848007	93.55
2	17.273	133888	1.06
3	18.729	536099	4.23
4	20.782	146345	1.16

Methyl (*E*)-2-(2-([1,1'-biphenyl]-4-yl)vinyl)-3-chloro-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ka)

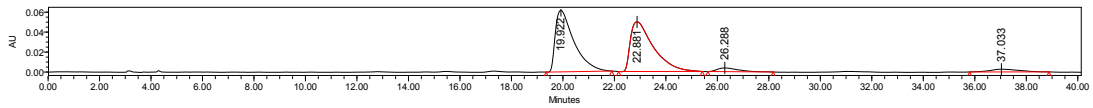


White solid, 79% yield (34.9 mg). 17/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IB** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 20.4 min, 22.6 min, 26.4 min, 37.1 min. $[\alpha]_D^{20}$ = −223.50 (*c* = 0.70).

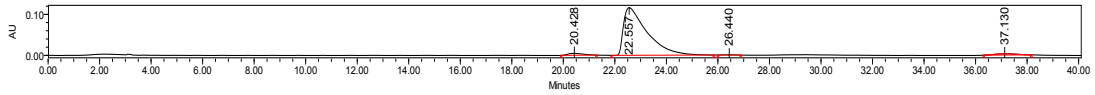
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 – 7.60 (m, 6H), 7.58 – 7.45 (m, 7H), 7.39 – 7.35 (m, 1H), 7.22 (d, *J* = 16.0, 1H), 6.44 (s, 1H), 6.35 (d, *J* = 16.0, 1H), 5.55 (s, 1H), 3.79 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 161.9, 153.4, 141.8, 140.5, 134.3, 134.3, 133.3, 131.6, 129.5, 129.0, 127.7, 127.7, 127.6, 127.1, 126.7, 121.7, 116.6, 85.5, 54.5, 54.2.

HRMS (ESI-TOF): calcd for $C_{27}H_{21}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 467.1026, found 467.1026, calcd for $C_{27}H_{21}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 469.0997, found 469.1119.

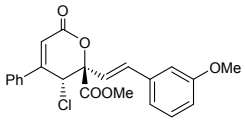


	Retention Time	Area	% Area
1	19.922	3099852	46.90
2	22.881	3086532	46.69
3	26.288	211278	3.20
4	37.033	212411	3.21



	Retention Time	Area	% Area
1	20.428	187703	2.42
2	22.557	7382342	95.00
3	26.440	17142	0.22
4	37.130	184060	2.37

Methyl (*E*)-3-chloro-2-(3-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3la)

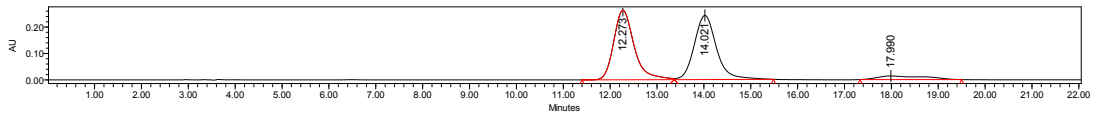


White solid, 85% yield (33.7 mg). 17/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.2 min, 14.0 min, 17.9 min. $[\alpha]_D^{20}$ = −247.92 (*c* = 0.67).

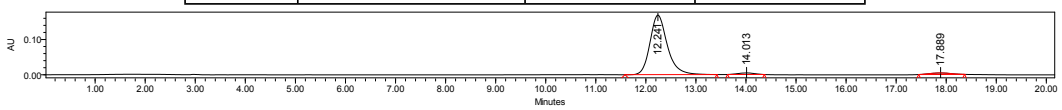
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 – 7.60 (m, 2H), 7.54 – 7.47 (m, 3H), 7.29 (t, *J* = 8.0, 1H), 7.14 (d, *J* = 16.0, 1H), 7.08 (d, *J* = 7.6, 1H), 7.00 (s, 1H), 6.88 (dd, *J* = 8.4, 2.4, 1H), 6.42 (s, 1H), 6.29 (d, *J* = 16.0, 1H), 5.53 (s, 1H), 3.84 (s, 3H), 3.77 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 161.9, 160.0, 153.3, 136.7, 134.6, 133.2, 131.7, 129.9, 129.5, 126.7, 122.0, 119.8, 116.6, 114.8, 112.4, 85.4, 55.4, 54.4, 54.2.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}^{34.9689}ClNaO_5^+$ ([M + Na]$^+$) 421.0819, found 421.0812, calcd for $C_{22}H_{19}^{36.9659}ClNaO_5^+$ ([M + Na]$^+$) 423.0789, found 423.0799.

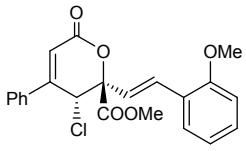


	Retention Time	Area	% Area
1	12.273	7979801	47.09
2	14.021	7980952	47.10
3	17.990	983804	5.81



	Retention Time	Area	% Area
1	12.241	4050086	94.79
2	14.013	99674	2.33
3	17.889	123045	2.88

Methyl (*E*)-3-chloro-2-(2-methoxystyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3ma)

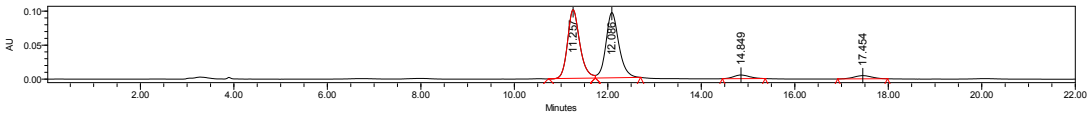


White solid, 77% yield (30.6 mg). 14/1 dr determined by ^{1}H NMR, 94% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.2 min, 12.1 min, 14.8 min, 17.4 min. $[\alpha]_D^{20}$ = −261.76 (*c* = 0.61).

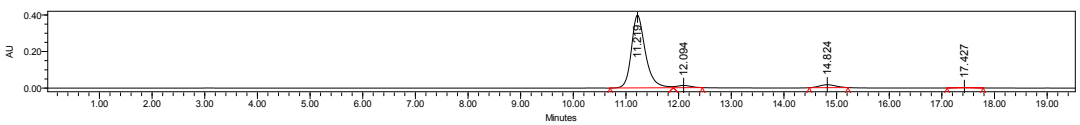
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 – 7.61 (m, 2H), 7.53 – 7.45 (m, 4H), 7.41 (d, *J* = 16.0, 1H), 7.32 – 7.27 (m, 1H), 7.01 – 6.88 (m, 2H), 6.47 – 6.36 (m, 2H), 5.54 (s, 1H), 3.88 (s, 3H), 3.76 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.6, 162.1, 157.6, 153.5, 133.3, 131.6, 130.1, 130.0, 129.5, 128.2, 126.7, 124.2, 122.4, 120.7, 116.6, 111.2, 85.8, 55.5, 54.7, 54.1.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}^{34.9689}ClNaO_5^+$ ([M + Na]$^+$) 421.0819, found 421.0823, calcd for $C_{22}H_{19}^{36.9659}ClNaO_5^+$ ([M + Na]$^+$) 423.0789, found 423.0760.



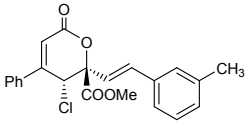
	Retention Time	Area	% Area
1	11.257	1840441	46.71
2	12.086	1845689	46.84
3	14.849	126916	3.22
4	17.454	127478	3.24



	Retention Time	Area	% Area

1	11.219	7345576	92.26
2	12.094	230132	2.89
3	14.824	338579	4.25
4	17.427	47186	0.59

Methyl (*E*)-3-chloro-2-(3-methylstyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3na)

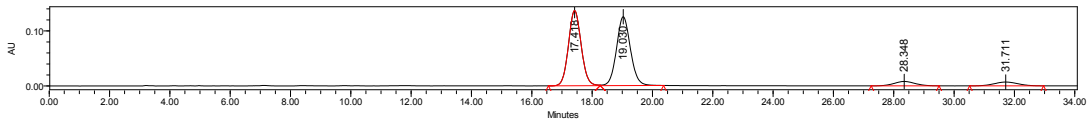


White solid, 83% yield (31.7 mg). 17/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IC** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.2 min, 18.8 min, 28.1 min, 31.4 min. $[\alpha]_D^{20}$ = −267.03 (*c* = 0.63).

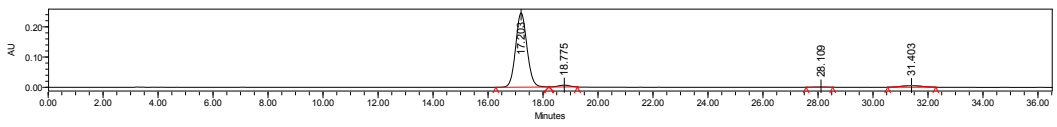
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (dd, *J* = 7.2, 1.6, 2H), 7.54 – 7.47 (m, 3H), 7.32 – 7.25 (m, 3H), 7.13 (dd, *J* = 10.4, 4.4, 2H), 6.42 (s, 1H), 6.28 (d, *J* = 16.0, 1H), 5.52 (s, 1H), 3.77 (s, 3H), 2.37 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.5, 161.9, 153.3, 138.5, 135.2, 134.8, 133.3, 131.6, 129.8, 129.5, 128.8, 127.8, 126.7, 124.4, 121.5, 116.6, 85.5, 54.5, 54.2, 21.5.

HRMS (ESI-TOF): calcd for $C_{22}H_{19}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 405.0870, found 405.0873, calcd for $C_{22}H_{19}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 407.0840, found 407.0853.



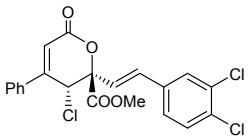
	Retention Time	Area	% Area
1	17.418	3996921	45.57
2	19.030	4012108	45.75
3	28.348	383815	4.38
4	31.711	377405	4.30



	Retention Time	Area	% Area

1	17.203	7026800	93.54
2	18.775	186130	2.48
3	28.109	24909	0.33
4	31.403	273867	3.65

Methyl (*E*)-3-chloro-2-(3,4-dichlorostyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3oa)

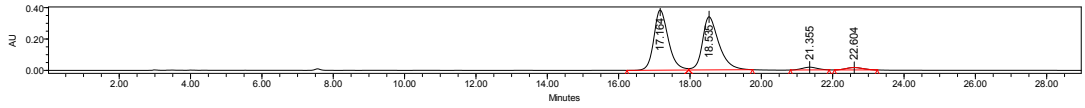


White solid, 73% yield (31.7 mg). >19/1 dr determined by ^{1}H NMR, 90% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.2 min, 18.5 min, 21.4 min, 22.6 min. $[\alpha]_D^{20}$ = −216.72 (*c* = 0.63).

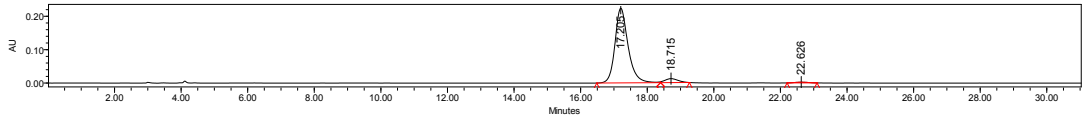
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.59 (m, 2H), 7.56 (d, *J* = 1.6, 1H), 7.54 – 7.46 (m, 3H), 7.44 (d, *J* = 8.0, 1H), 7.28 (dd, *J* = 8.0, 1.6, 1H), 7.09 (d, *J* = 16.0, 1H), 6.42 (s, 1H), 6.29 (d, *J* =16.0, 1H), 5.51 (s, 1H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.1, 161.6, 153.1, 135.4, 133.1, 132.8, 132.5, 131.7, 130.9, 129.5, 128.7, 126.7, 126.6, 123.7, 116.6, 85.3, 54.3, 54.3.

HRMS (ESI-TOF): calcd for $C_{21}H_{15}{}^{34.9689}Cl_3NaO_4^+$ ([M + Na]$^+$) 458.9934, found 458.9932, calcd for $C_{21}H_{15}{}^{36.9659}Cl_3NaO_4^+$ ([M + Na]$^+$) 460.9904, found 461.0035.



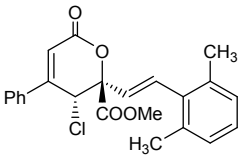
	Retention Time	Area	% Area
1	17.164	10776032	47.65
2	18.535	10825634	47.87
3	21.355	510725	2.26
4	22.604	501064	2.22



	Retention Time	Area	% Area
1	17.205	6130370	94.12

2	18.715	324232	4.98
3	22.626	58980	0.91

Methyl (*E*)-3-chloro-2-(2,6-dimethylstyryl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3pa)

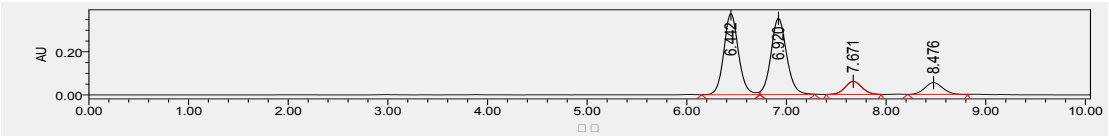


White solid, 82% yield (32.6 mg). >19/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 6.4 min, 6.9 min, 7.7 min, 8.5 min. $[\alpha]_D^{20}$ = −227.45 (*c* = 0.65).

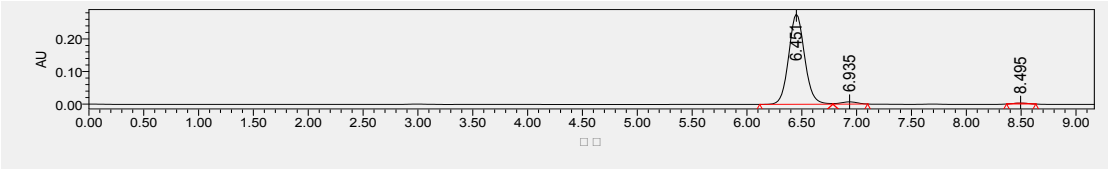
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 – 7.61 (m, 2H), 7.55 – 7.47 (m, 3H), 7.19 (d, *J* = 16.4, 1H), 7.14 – 7.04 (m, 3H), 6.44 (s, 1H), 5.85 (d, *J* = 16.0, 1H), 5.52 (s, 1H), 3.79 (s, 3H), 2.33 (s, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 162.0, 153.2, 136.2, 135.3, 133.4, 133.2, 131.6, 129.5, 128.0, 127.5, 127.2, 126.7, 116.7, 85.5, 54.3, 54.1, 20.9.

HRMS (ESI-TOF): calcd for $C_{23}H_{22}^{34.9689}ClO_4^+$ ([M + H]$^+$) 397.1207, found 397.1201, calcd for $C_{23}H_{22}^{36.9659}ClO_4^+$ ([M + H]$^+$) 399.1177, found 399.1152.



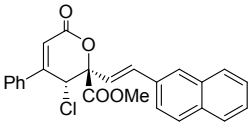
	Retention Time	Area	% Area
1	6.442	3855992	42.33
2	6.920	3861456	42.39
3	7.671	709876	7.79
4	8.476	682112	7.49



	Retention Time	Area	% Area
1	6.451	2789342	96.62

2	6.935	71588	2.48
3	8.495	25902	0.90

Methyl (*E*)-3-chloro-2-(2-(naphthalen-2-yl)vinyl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3qa)

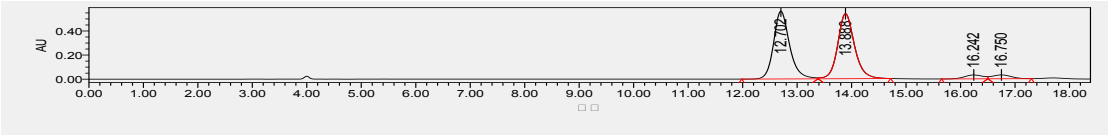


White solid, 80% yield (33.4 mg). 17/1 dr determined by ^{1}H NMR, 96% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.7 min, 13.9 min, 16.2 min, 16.8 min. $[\alpha]_D^{20}$ = −221.41 (*c* = 0.67).

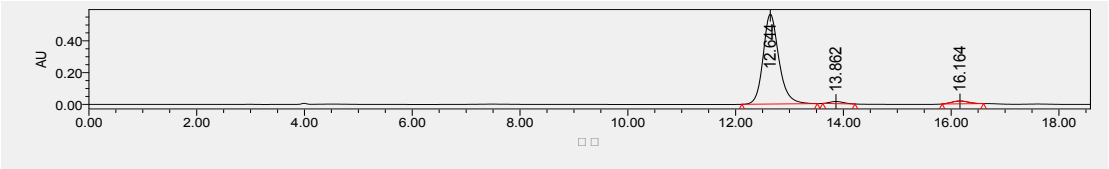
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 – 7.80 (m, 4H), 7.67 – 7.61 (m, 3H), 7.53 – 7.46 (m, 5H), 7.33 (d, *J* = 16.0, 1H), 6.46 – 6.38 (m, 2H), 5.57 (s, 1H), 3.78 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 161.9, 153.4, 134.8, 133.6, 133.6, 133.3, 132.7, 131.6, 129.5, 128.6, 128.4, 128.1, 127.8, 126.7, 126.7, 123.5, 122.0, 116.6, 85.6, 54.6, 54.2.

HRMS (ESI-TOF): calcd for $C_{25}H_{19}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 441.0870, found 441.0873, calcd for $C_{25}H_{19}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 443.0840, found 443.0854.



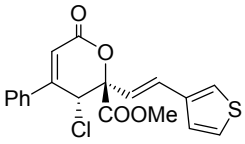
	Retention Time	Area	% Area
1	12.702	11503906	46.75
2	13.888	11551890	46.94
3	16.242	771967	3.14
4	16.750	780688	3.17



	Retention Time	Area	% Area
1	12.644	11488517	94.94

2	13.862	239665	1.98
3	16.164	373169	3.08

Methyl (*E*)-3-chloro-6-oxo-4-phenyl-2-(2-(thiophen-3-yl)vinyl)-3,6-dihydro-*2H*-pyran-2-carboxylate (3ra)

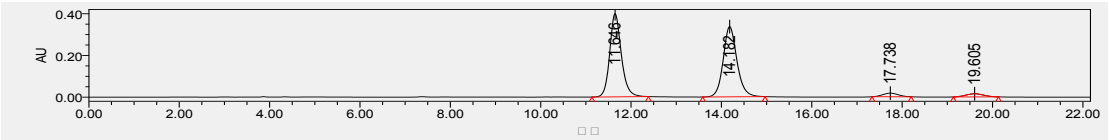


White solid, 91% yield (33.9 mg). 19/1 dr determined by ^{1}H NMR, 96% ee determined by **HPLC** (chiral **IA** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.6 min, 14.2 min, 17.7 min, 19.6 min. $[\alpha]_D^{20}$ = −248.23 (*c* = 0.68).

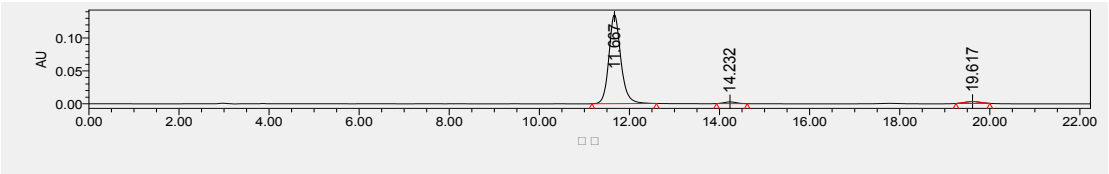
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.59 (m, 2H), 7.56 – 7.47 (m, 3H), 7.35 – 7.26 (m, 3H), 7.16 (d, *J* = 15.6, 1H), 6.41 (s, 1H), 6.15 (d, *J* = 15.6, 1H), 5.50 (s, 1H), 3.76 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 161.9, 153.4, 138.0, 133.2, 131.6, 129.5, 128.8, 126.7, 126.7, 125.1, 124.9, 121.4, 116.6, 85.3, 54.5, 54.2.

HRMS (ESI-TOF): calcd for $C_{19}H_{15}{}^{34.9689}ClNaO_4S^+$ ([M + Na]$^+$) 397.0277, found 397.0282, calcd for $C_{19}H_{15}{}^{36.9659}ClNaO_4S^+$ ([M + Na]$^+$) 399.0248, found 399.0238.



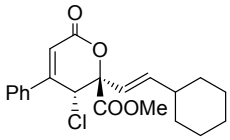
	Retention Time	Area	% Area
1	11.646	7132975	47.28
2	14.182	7129962	47.26
3	17.738	416243	2.76
4	19.605	408011	2.70



	Retention Time	Area	% Area
1	11.667	2488590	95.53
2	14.232	49727	1.91

3	19.617	66737	2.56

Methyl (*E*)-3-chloro-2-(2-cyclohexylvinyl)-6-oxo-4-phenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3sa)

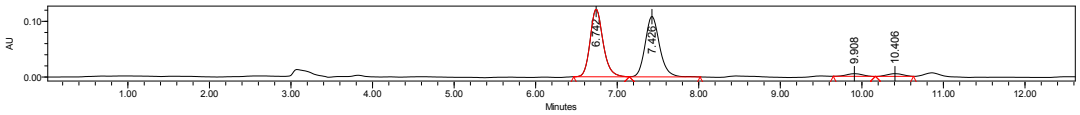


Colorless oil, 64% yield (24.1 mg). 9/1 dr determined by ^{1}H NMR, 93% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 6.7 min, 7.4 min, 9.8 min, 10.3 min. $[\alpha]_D^{20}$ = −286.31 (*c* = 0.48).

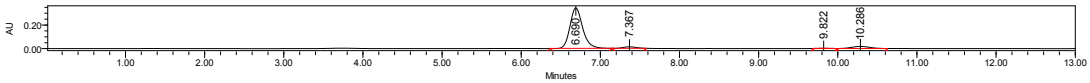
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.59 (dd, *J* = 7.2, 1.2, 2H), 7.49 (t, *J* = 4.2, 3H), 6.36 (s, 1H), 6.21 (dd, *J* = 15.6, 6.4, 1H), 5.57 (dd, *J* = 16.0, 1.2, 1H), 5.38 (s, 1H), 3.73 (s, 3H), 2.14 – 2.06 (m, 1H), 1.81 – 1.71 (m, 4H), 1.34 – 1.09 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.8, 162.2, 153.5, 142.5, 133.4, 131.5, 129.4, 126.7, 120.6, 116.5, 85.2, 54.5, 54.0, 40.6, 32.4, 26.1, 25.9.

HRMS (ESI-TOF): calcd for $C_{21}H_{23}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 397.1183, found 397.1186, calcd for $C_{21}H_{23}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 399.1153, found 399.1161.

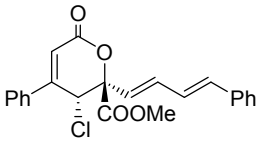


	Retention Time	Area	% Area
1	6.742	1340089	47.88
2	7.426	1333382	47.64
3	9.908	62401	2.23
4	10.406	63025	2.25



	Retention Time	Area	% Area
1	6.690	3816652	90.03
2	7.367	136063	3.21
3	9.822	14071	0.33
4	10.286	272603	6.43

Methyl 3-chloro-6-oxo-4-phenyl-2-((*1E*,*3E*)-4-phenylbuta-1,3-dien-1-yl)-3,6-dihydro-*2H*-pyran-2-carboxylate (3ta)

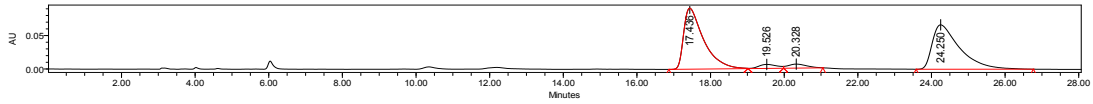


White solid, 77% yield (30.2 mg). 14/1 dr determined by ^{1}H NMR, 96% ee determined by **HPLC** (chiral **IB** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.4 min, 19.5 min, 20.3 min, 24.3 min. $[\alpha]_D^{20}$ = −256.29 (*c* = 0.60).

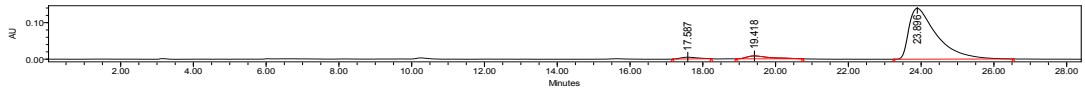
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 – 7.58 (m, 2H), 7.52 – 7.47 (m, 3H), 7.46 – 7.40 (m, 2H), 7.34 (t, *J* = 7.2, 2H), 7.29 – 7.24 (m, 1H), 6.95 (dd, *J* = 14.8, 10.0, 1H), 6.84 (dd, *J* = 15.6, 10.4, 1H), 6.74 (d, *J* = 15.2, 1H), 6.40 (s, 1H), 5.89 (d, *J* = 14.8, 1H), 5.46 (s, 1H), 3.76 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.4, 161.9, 153.3, 136.6, 136.5, 135.1, 133.3, 131.6, 129.5, 128.8, 128.4, 126.9, 126.7, 126.7, 124.8, 116.6, 85.4, 54.5, 54.2.

HRMS (ESI-TOF): calcd for $C_{23}H_{20}{}^{34.9689}ClO_4^+$ ([M + H]$^+$) 395.1050, found 395.1052, calcd for $C_{23}H_{20}{}^{36.9659}ClO_4^+$ ([M + H]$^+$) 397.1021, found 397.1019.



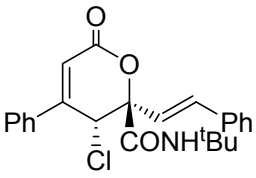
	Retention Time	Area	% Area
1	17.436	3431446	47.14
2	19.526	204632	2.81
3	20.328	209926	2.88
4	24.250	3432859	47.16



	Retention Time	Area	% Area
1	17.587	152117	1.93
2	19.418	357494	4.54
3	23.896	7369302	93.53

(*E*)-N-(*tert*-butyl)-3-chloro-6-oxo-4-phenyl-2-styryl-3,6-dihydro-*2H*-pyran-2-

carboxamide (3ua)

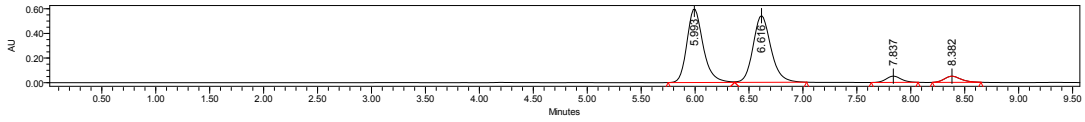


White solid, 59% yield (24.1 mg). 11/1 dr determined by ^{1}H NMR, 94% ee determined by **HPLC** (chiral **ADH** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 6.0 min, 6.6 min, 7.8 min, 8.4 min. $[\alpha]_D^{20}$ = −292.53 (*c* = 0.48).

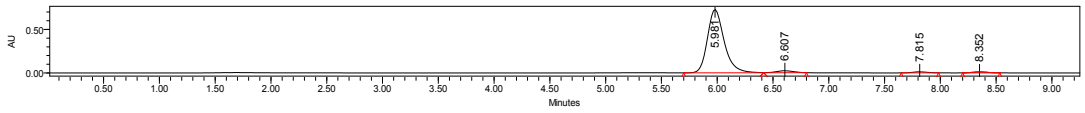
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 – 7.63 (m, 2H), 7.52 – 7.44 (m, 5H), 7.40 – 7.31 (m, 3H), 7.05 (d, *J* = 16.0, 1H), 6.35 (d, *J* = 15.6, 1H), 6.33 (s, 1H), 6.14 (s, 1H), 5.78 (s, 1H), 1.28 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 167.9, 162.4, 156.5, 135.6, 133.8, 133.0, 131.5, 129.4, 128.9, 128.8, 127.1, 127.0, 123.5, 114.8, 86.8, 54.9, 52.4, 28.5.

HRMS (ESI-TOF): calcd for $C_{24}H_{24}{}^{34.9689}ClNNaO_3^+$ ([M + Na]$^+$) 432.1342, found 432.1347, calcd for $C_{24}H_{24}{}^{36.9659}ClNNaO_3^+$ ([M + Na]$^+$) 434.1313, found 434.1319.

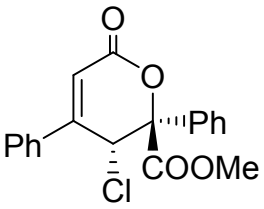


	Retention Time	Area	% Area
1	5.993	6222598	46.21
2	6.616	6224287	46.22
3	7.837	492315	3.66
4	8.382	527360	3.92



	Retention Time	Area	% Area
1	5.981	7553299	94.51
2	6.607	239798	3.00
3	7.815	101507	1.27
4	8.352	97821	1.22

Methyl 3-chloro-6-oxo-2,4-diphenyl-3,6-dihydro-*2H*-pyran-2-carboxylate (3va)

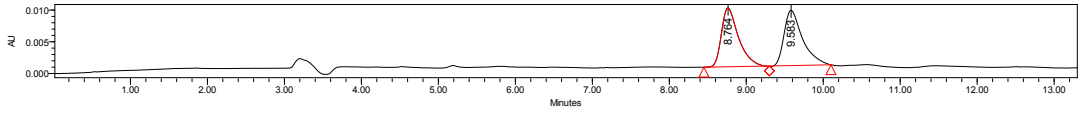


White solid, 63% yield (21.6 mg). >19/1 dr determined by ^{1}H NMR, 96% ee determined by **HPLC** (chiral **IB** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 8.7 min, 9.6 min. $[\alpha]_D^{20}$ = −321.43 (*c* = 0.42).

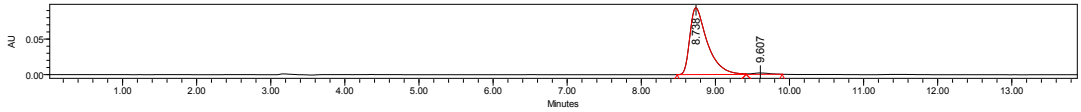
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 – 7.75 (m, 2H), 7.71 – 7.64 (m, 2H), 7.55 – 7.40 (m, 6H), 6.43 (s, 1H), 5.79 (s, 1H), 3.71 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ = 169.9, 161.8, 154.7, 134.0, 133.5, 131.7, 129.5, 129.5, 128.9, 126.8, 125.6, 116.4, 86.4, 55.3, 54.2.

HRMS (ESI-TOF): calcd for $C_{19}H_{15}{}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 365.0557, found 365.0561, calcd for $C_{19}H_{15}{}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 367.0527, found 367.0544.

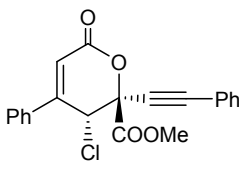


	Retention Time	Area	% Area
1	8.764	143164	49.65
2	9.583	145188	50.35



	Retention Time	Area	% Area
1	8.738	1536461	98.09
2	9.607	29927	1.91

Methyl 3-chloro-6-oxo-4-phenyl-2-(phenylethynyl)-3,6-dihydro-*2H*-pyran-2-carboxylate (3wa)



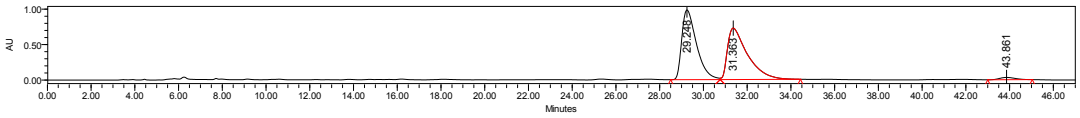
White solid, 38% yield (13.8 mg). >19/1 dr determined by ^{1}H NMR, 64% ee determined by **HPLC** (chiral **IE** column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 29.5 min, 31.8 min, 44.6 min. $[\alpha]_D^{20}$ = −101.34 (*c* = 0.22).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.0, 2H), 7.58 – 7.46 (m, 5H), 7.45 – 7.31 (m,

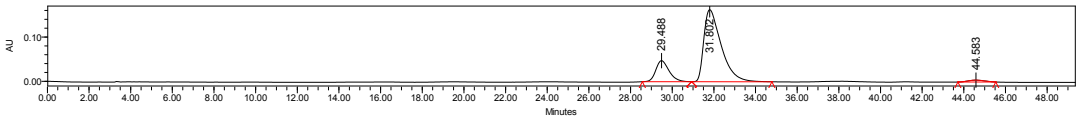
3H), 6.38 (s, 1H), 5.59 (s, 1H), 3.86 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 166.8, 161.0, 152.9, 133.1, 132.4, 131.8, 129.9, 129.6, 128.6, 126.7, 120.7, 116.2, 89.7, 80.5, 80.4, 54.8, 54.4.

HRMS (ESI-TOF): calcd for $C_{21}H_{15}^{34.9689}ClNaO_4^+$ ([M + Na]$^+$) 389.0557, found 389.0558, calcd for $C_{21}H_{15}^{36.9659}ClNaO_4^+$ ([M + Na]$^+$) 391.0527, found 391.0544.

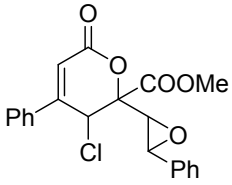


	Retention Time	Area	% Area
1	29.248	45976132	49.15
2	31.363	45977972	49.15
3	43.861	1584417	1.69



	Retention Time	Area	% Area
1	29.488	2109182	17.93
2	31.802	9422443	80.11
3	44.583	230855	1.96

Methyl 3-chloro-6-oxo-4-phenyl-2-(3-phenyloxiran-2-yl)-3,6-dihydro-*2H*-pyran-2-carboxylate (4aa)

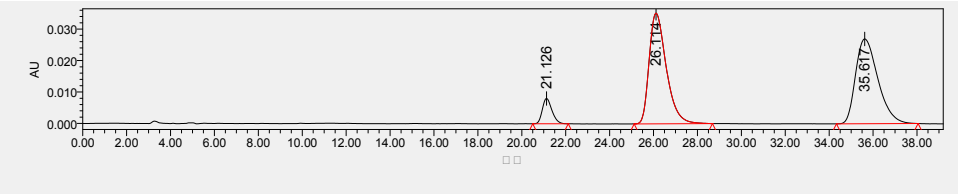


White solid, 68% yield (26.1 mg). >19/1 dr determined by ^{1}H NMR, 95% ee determined by **HPLC** (chiral **IE** column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 21.3 min, 26.4 min, 36.5 min. $[\alpha]_D^{20}$ = −736.78 (*c* = 0.52, λ = 405 nm).

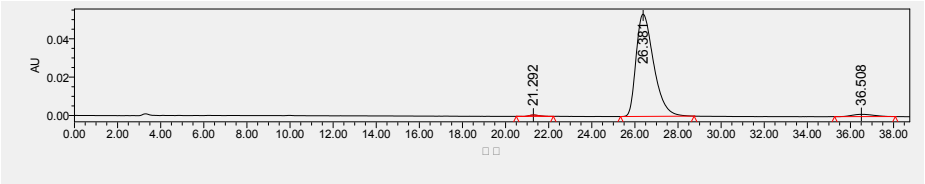
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 – 7.55 (m, 2H), 7.54 – 7.45 (m, 3H), 7.44 – 7.27 (m, 5H), 6.44 (s, 1H), 5.53 (s, 1H), 4.40 (s, 1H), 3.85 (s, 3H), 3.61 (d, *J* = 1.2, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ = 168.2, 161.0, 152.0, 135.4, 132.7, 131.8, 129.6, 128.9, 128.8, 126.7, 126.0, 117.0, 83.2, 63.0, 56.5, 54.5, 52.6.

HRMS (ESI-FT): calcd for $C_{21}H_{17}{}^{34.9689}ClNaO_5^+$ ([M + Na]$^+$) 407.0662, found 407.0661, calcd for $C_{21}H_{17}{}^{36.9659}ClNaO_5^+$ ([M + Na]$^+$) 409.0633, found 409.0630.



	Retention Time	Area	% Area
1	21.126	244528	6.04
2	26.114	1902771	46.98
3	35.617	1902498	46.98



	Retention Time	Area	% Area
1	21.292	21962	0.70
2	26.381	3015253	96.57
3	36.508	85062	2.72

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3678.

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[3] a) E. D. Secher and H. F. Ryder, *J. Am. Chem. Soc*., 1952, **74**, 4392; b) H. Audrain, J. Thorhauge, R. G. Hazell and K. A. Jørgensen, *J. Org. Chem*., 2000, **65**, 4487; c) K. B. Jensen, J. Thorhauge, R. G.Hazell and K. A. Jørgensen, *Angew. Chem. Int. Ed*., 2001, **40**, 160; d) M. Guo, D. Li and Z. Zhang, *J. Org. Chem.*, 2003, **68**, 10172.

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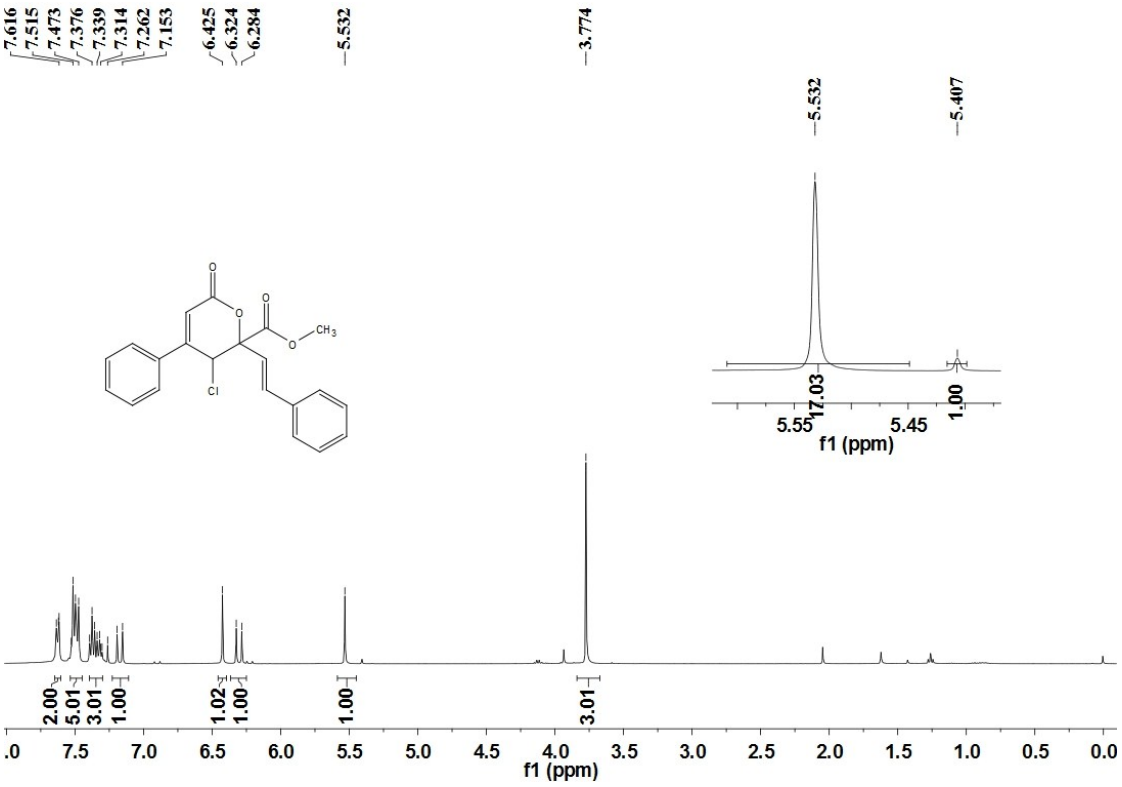
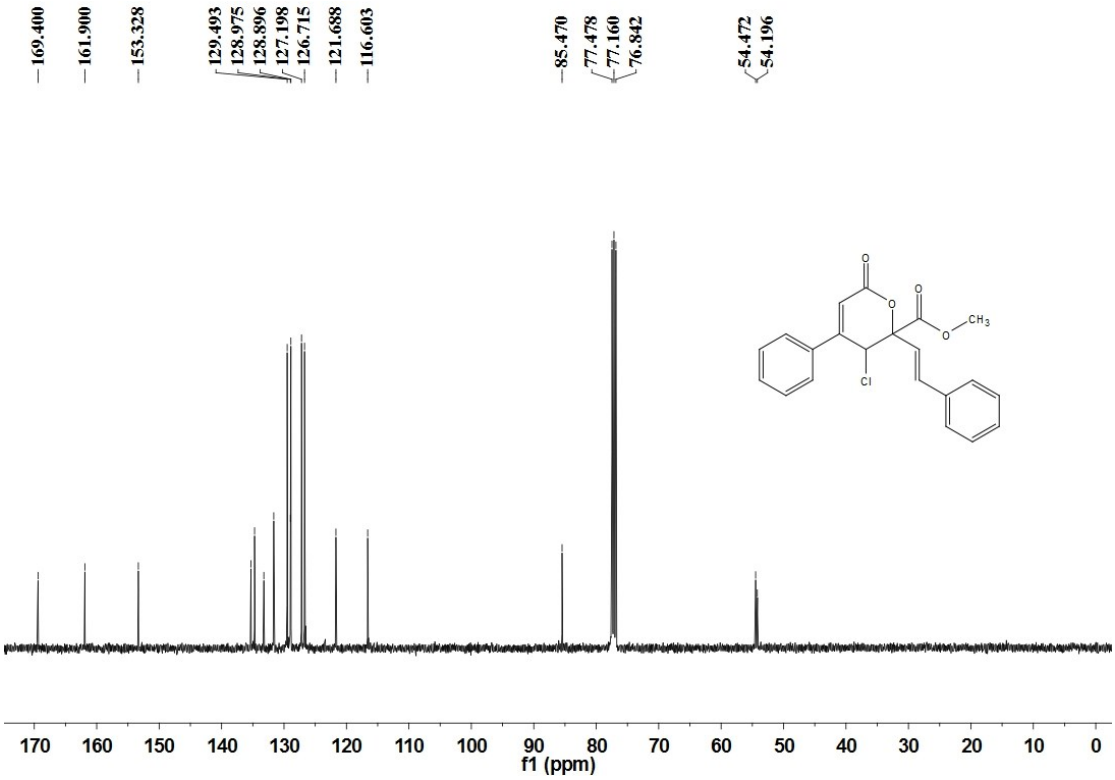
[5] J. Mo, L. Shen, Y. R. Chi, *Angew. Chem. Int. Ed.* **2013**, *52*, 8588.

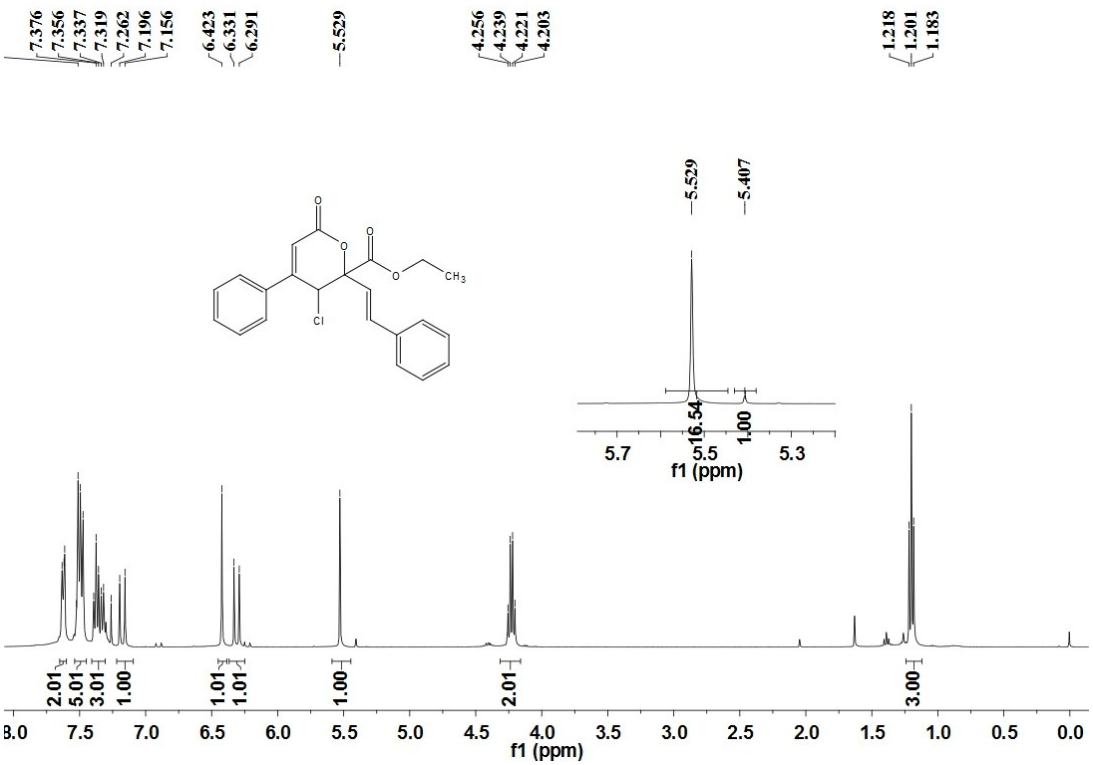
(H) Copies of the NMR spectra

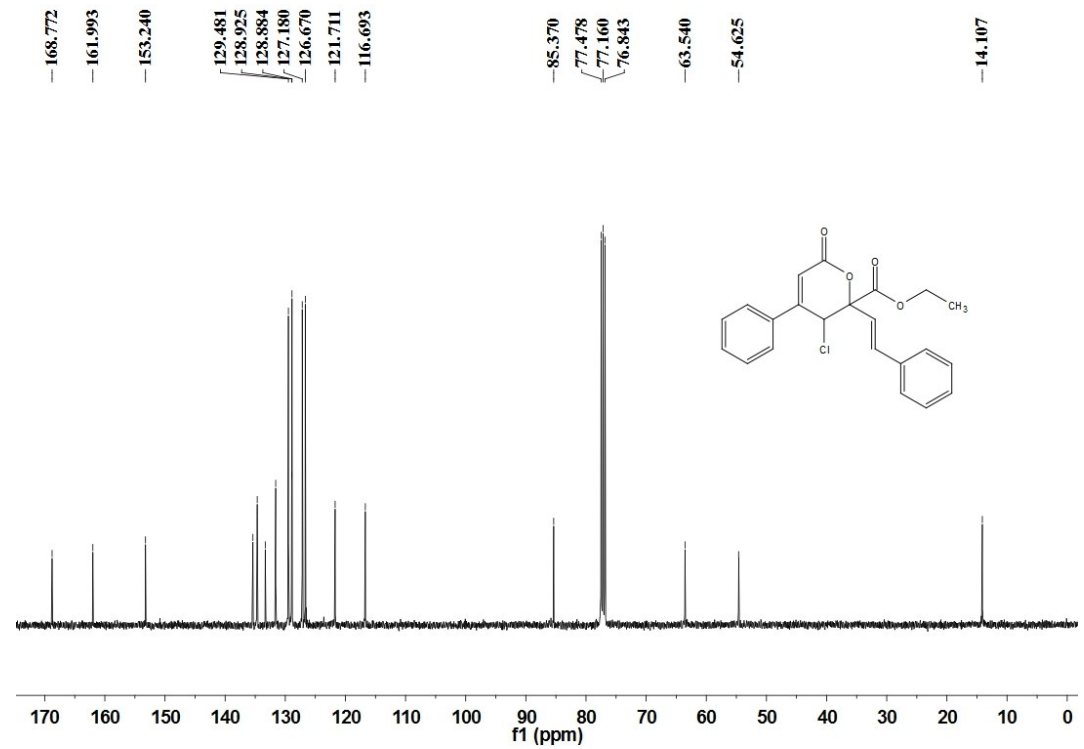
Compound 3aa



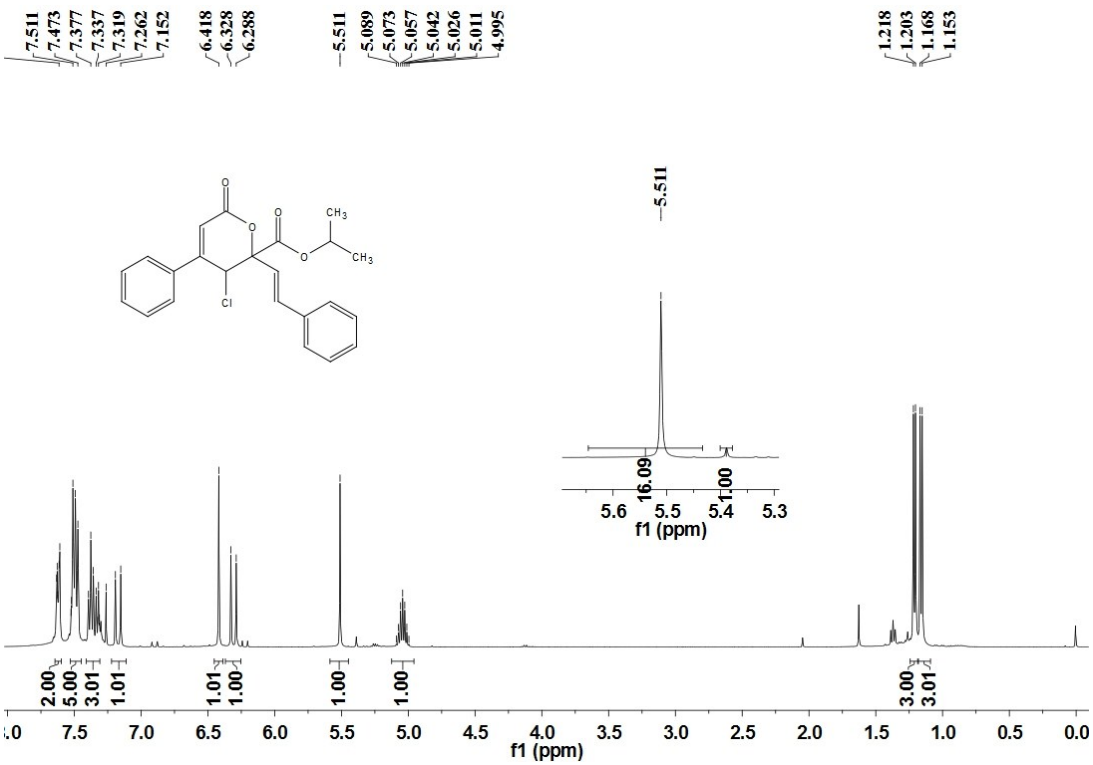


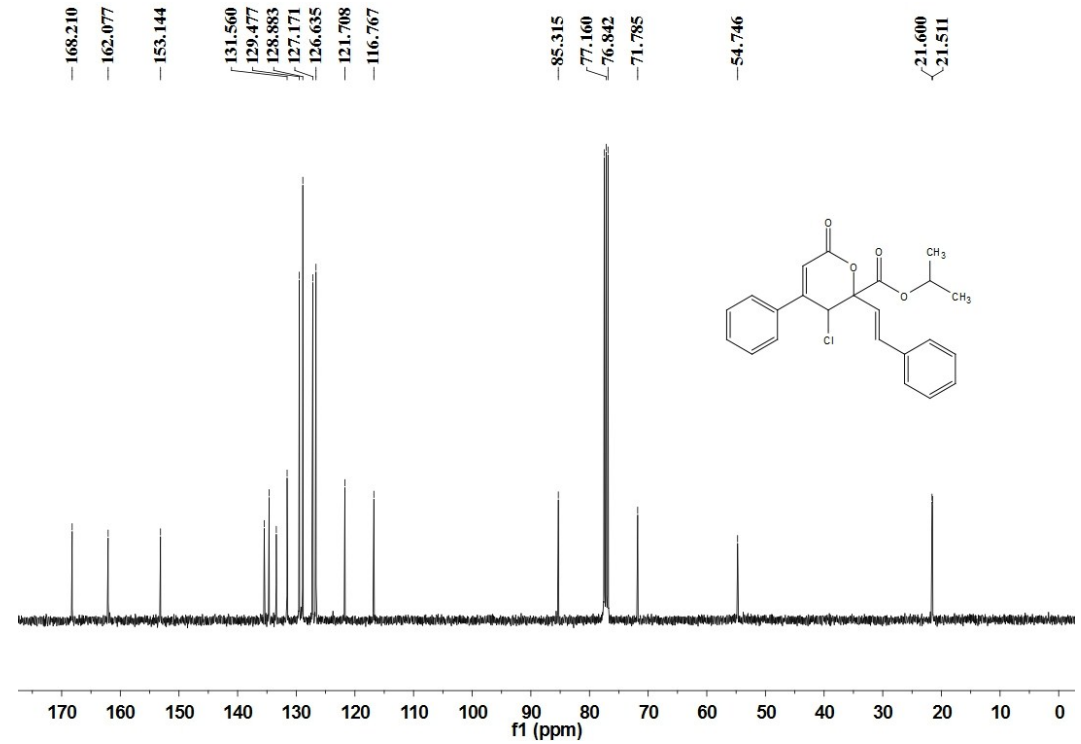
Compound 3ba





Compound 3ca





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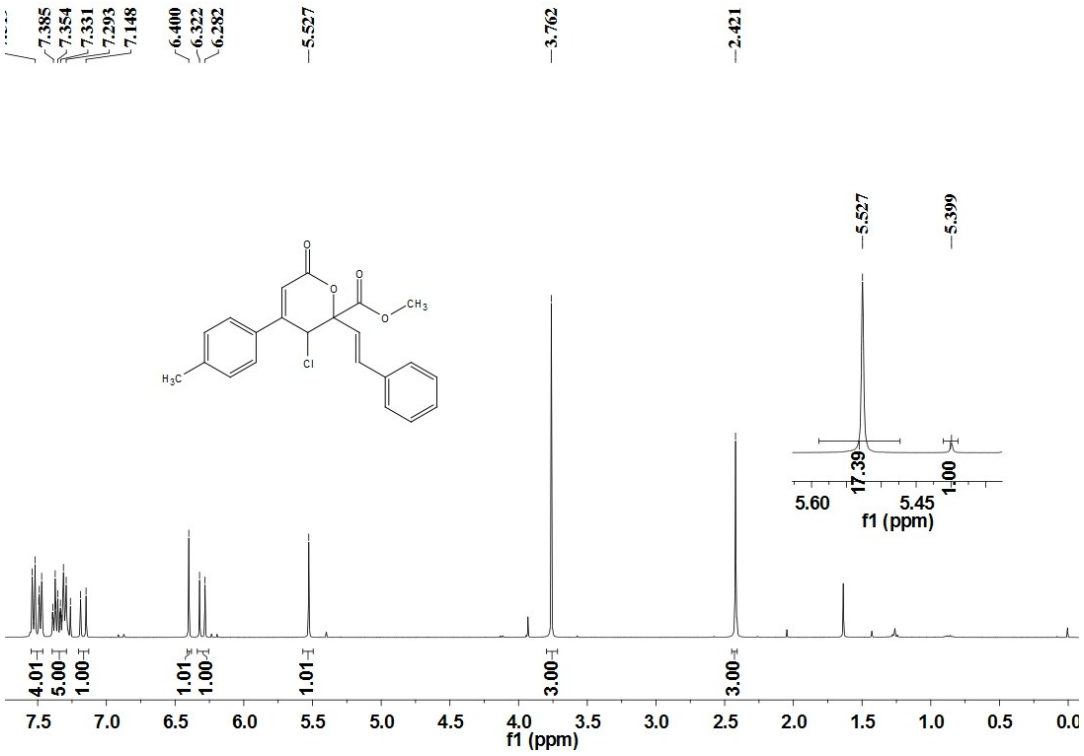

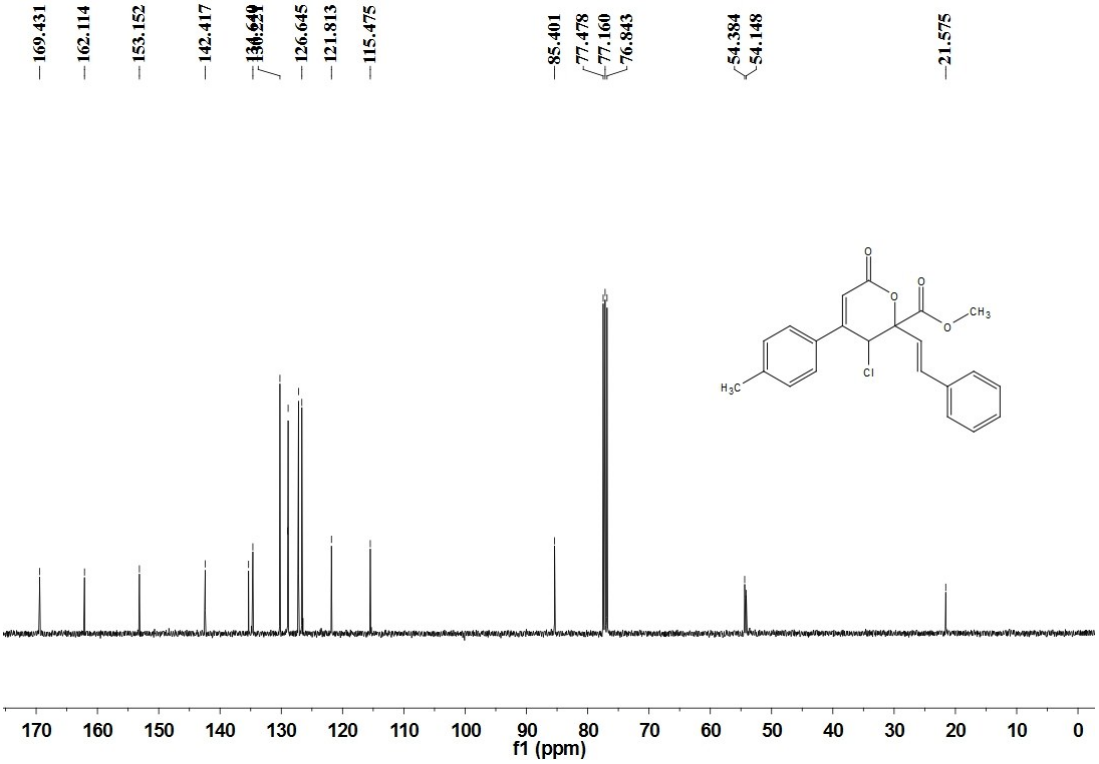

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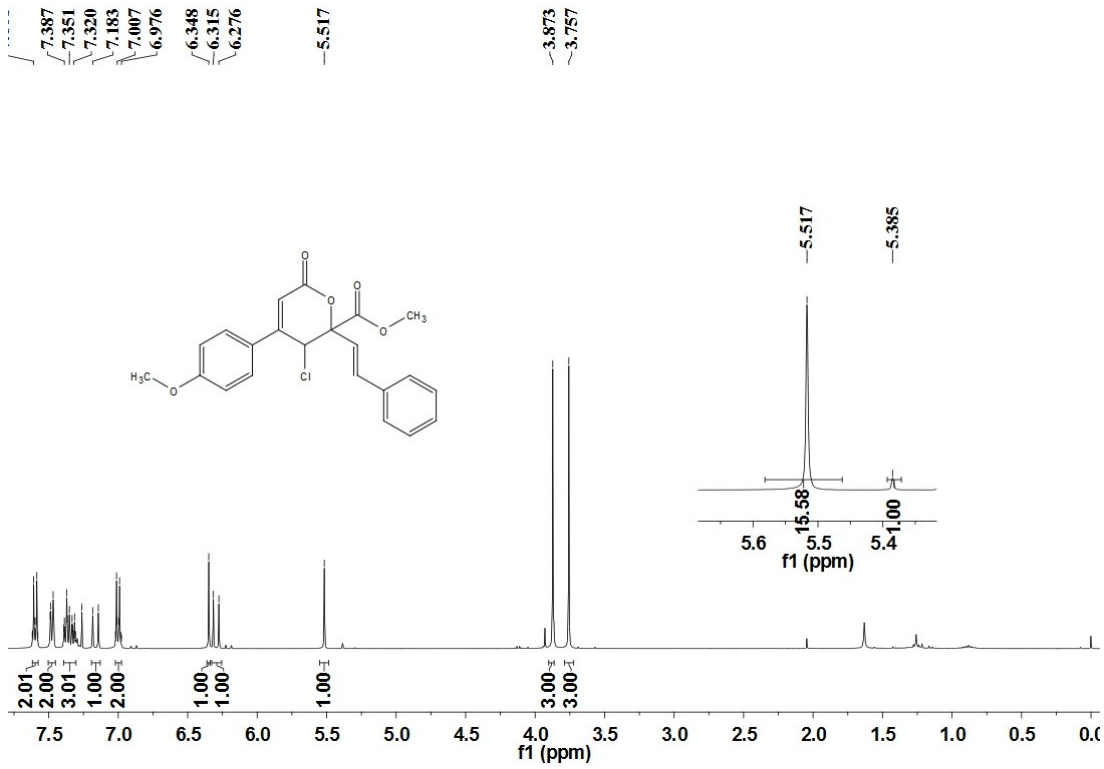

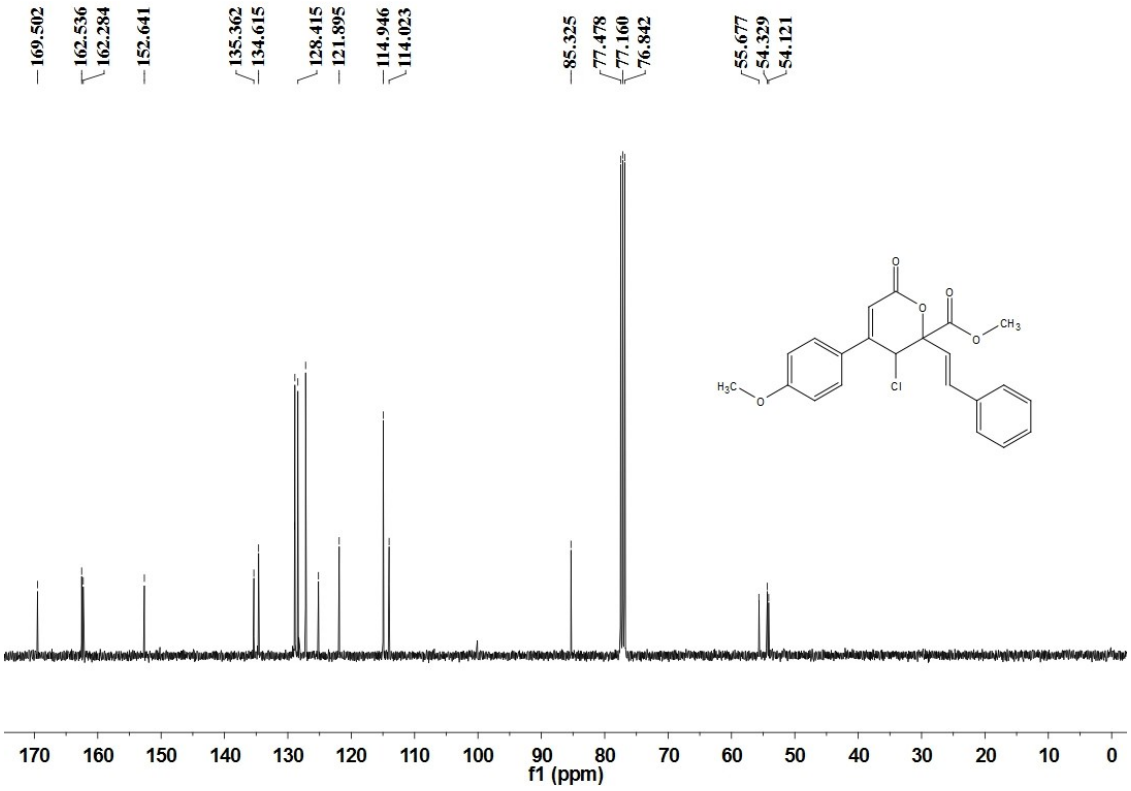

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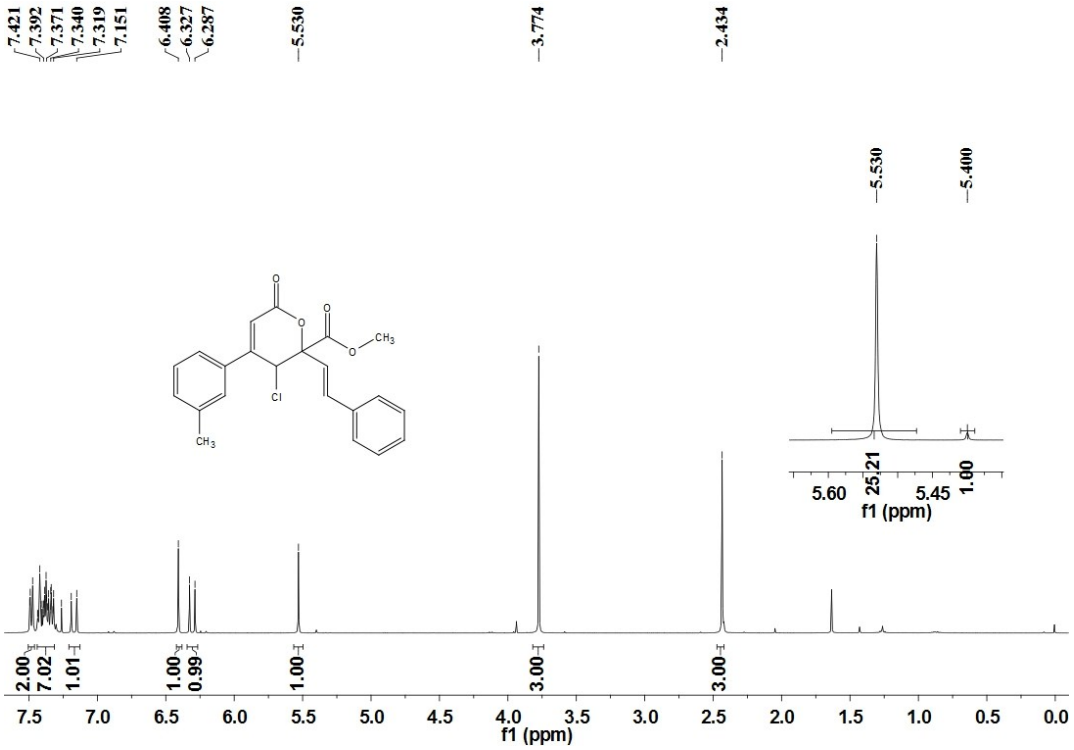

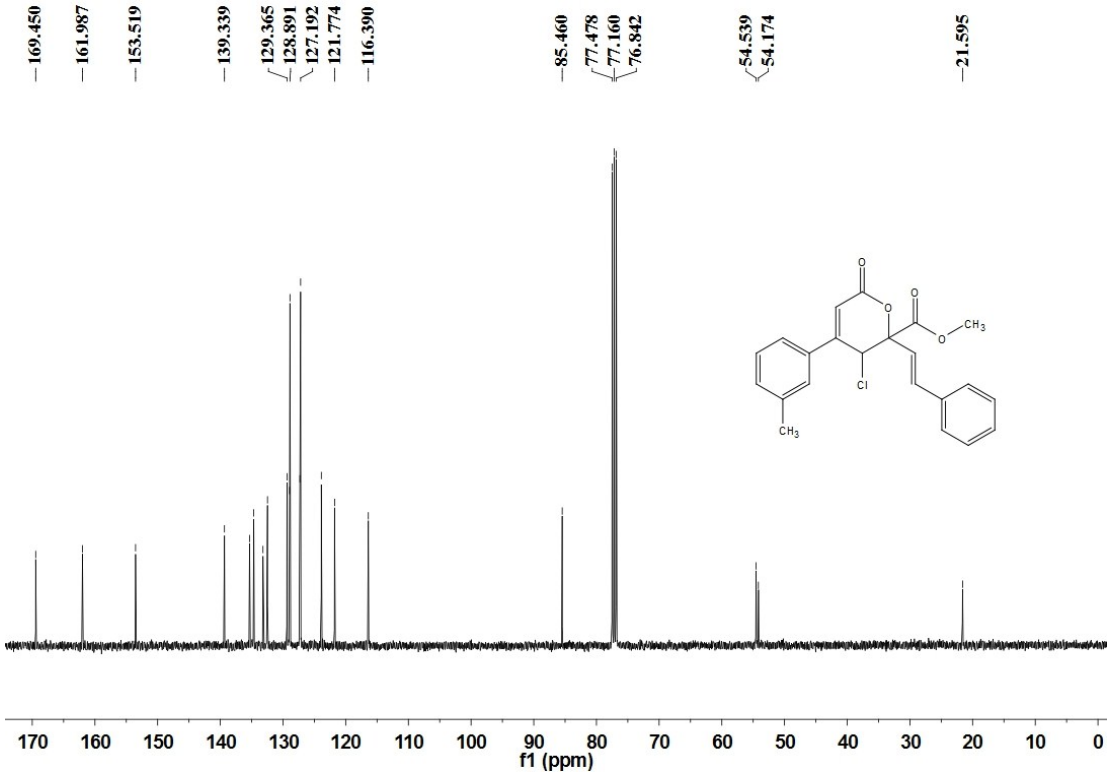

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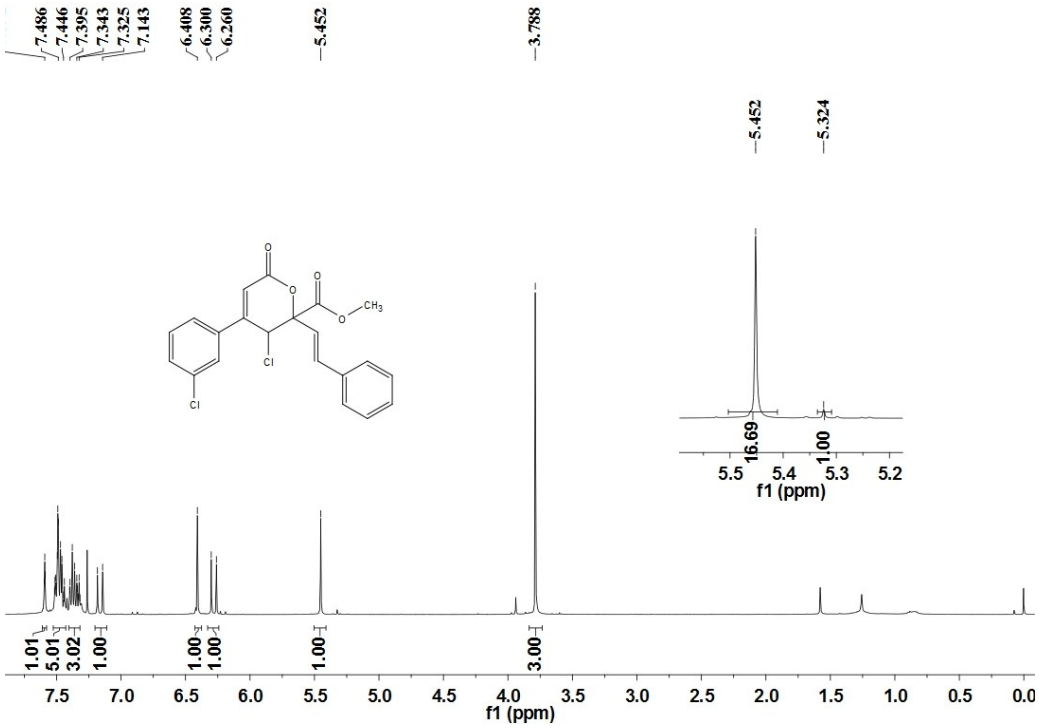

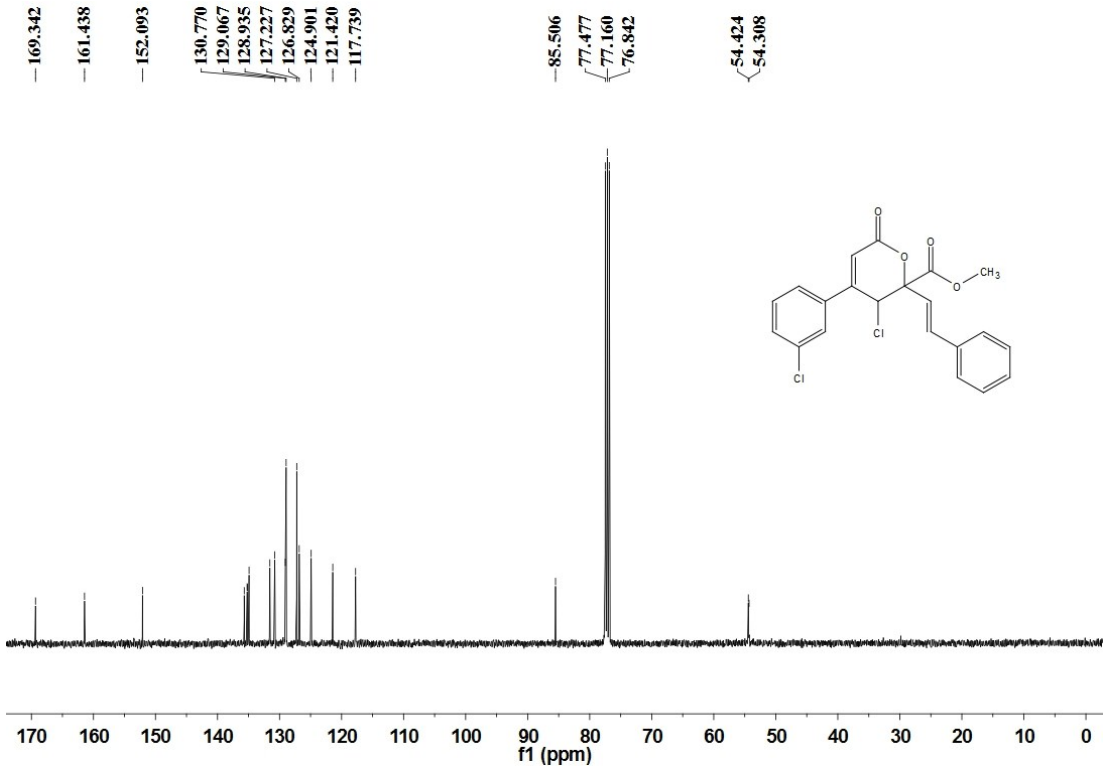

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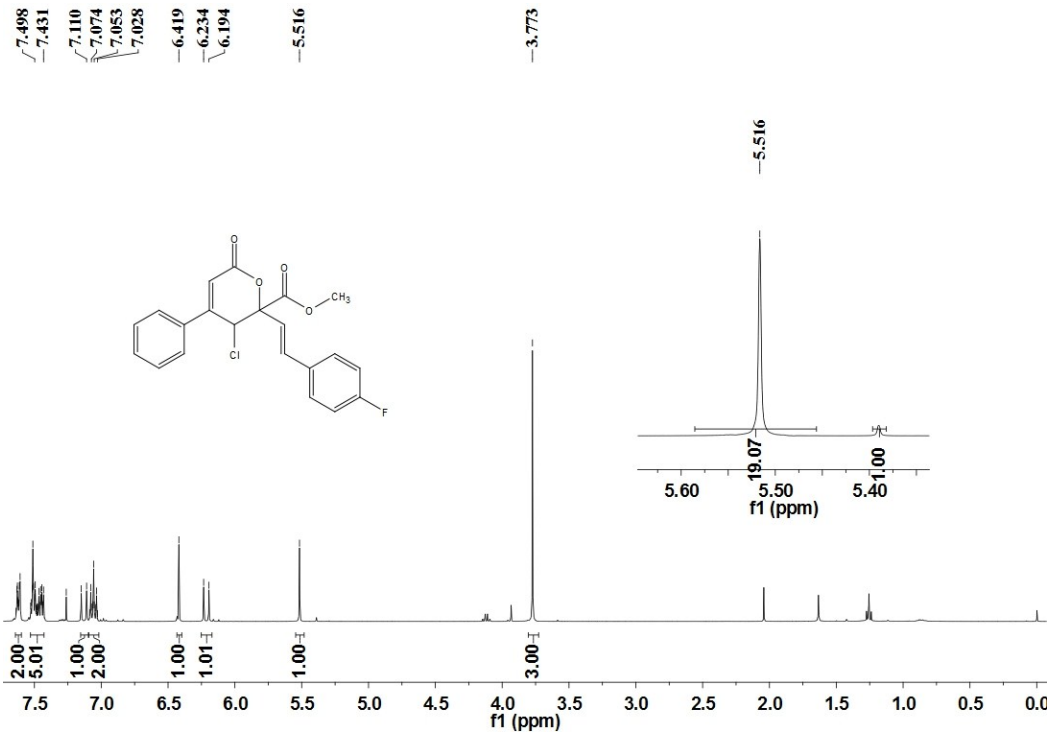

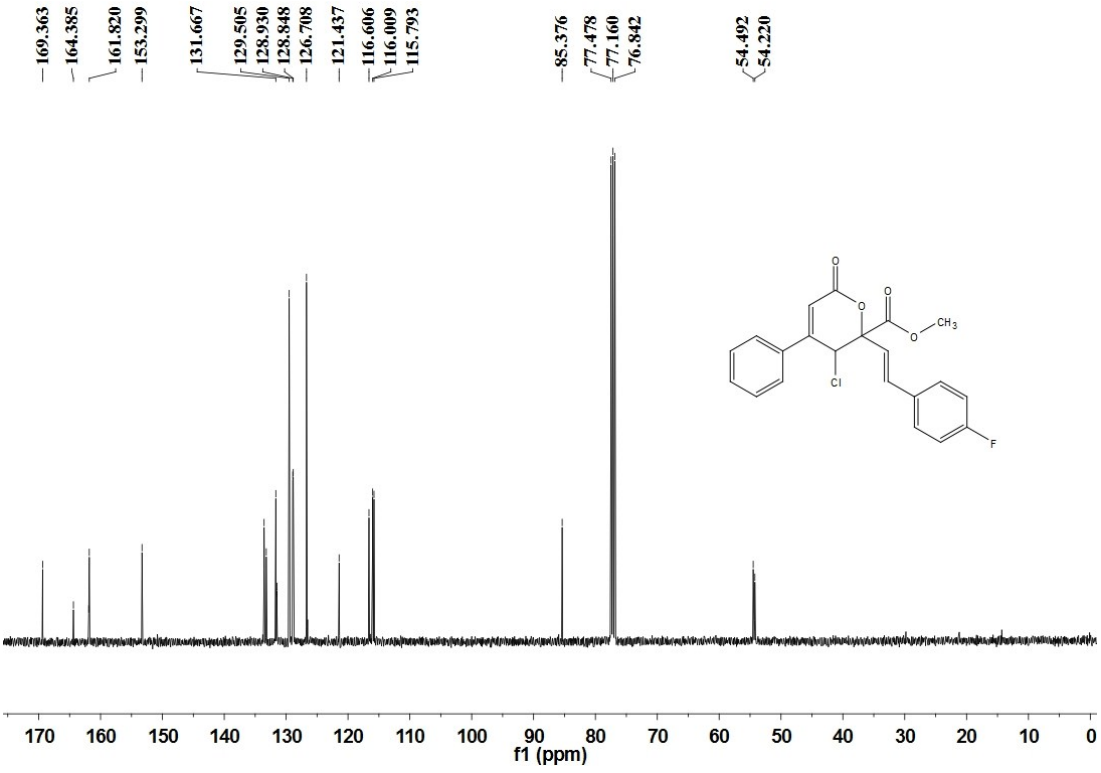

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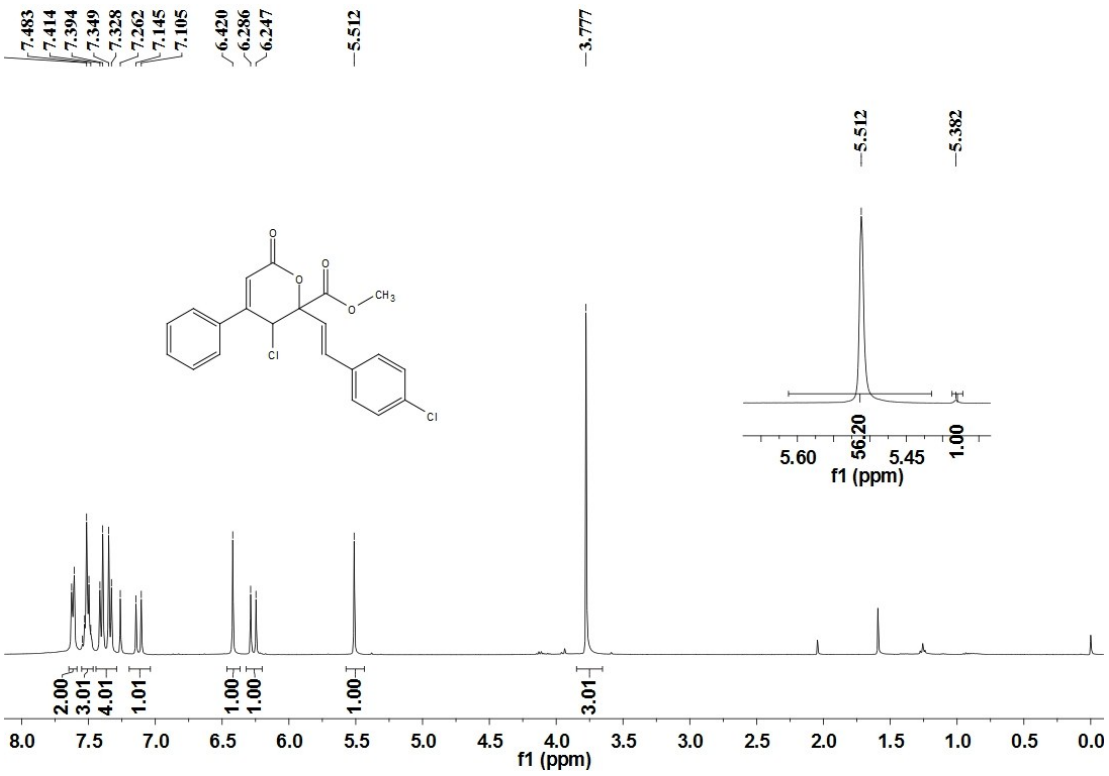

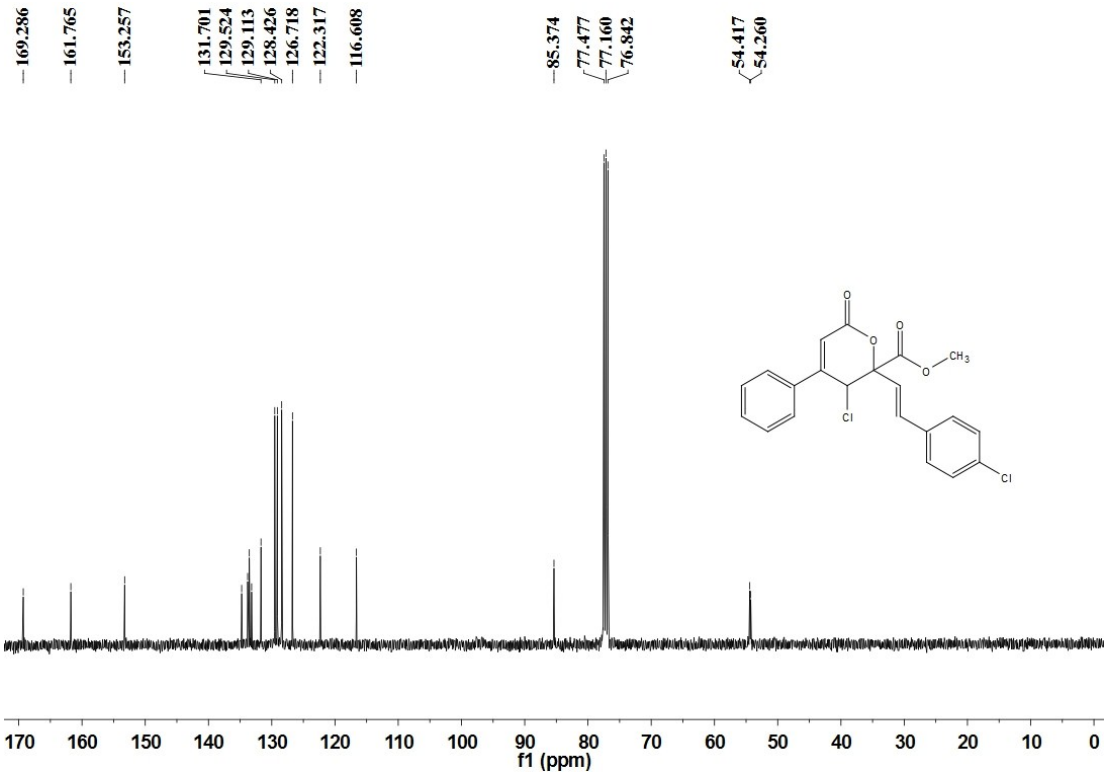

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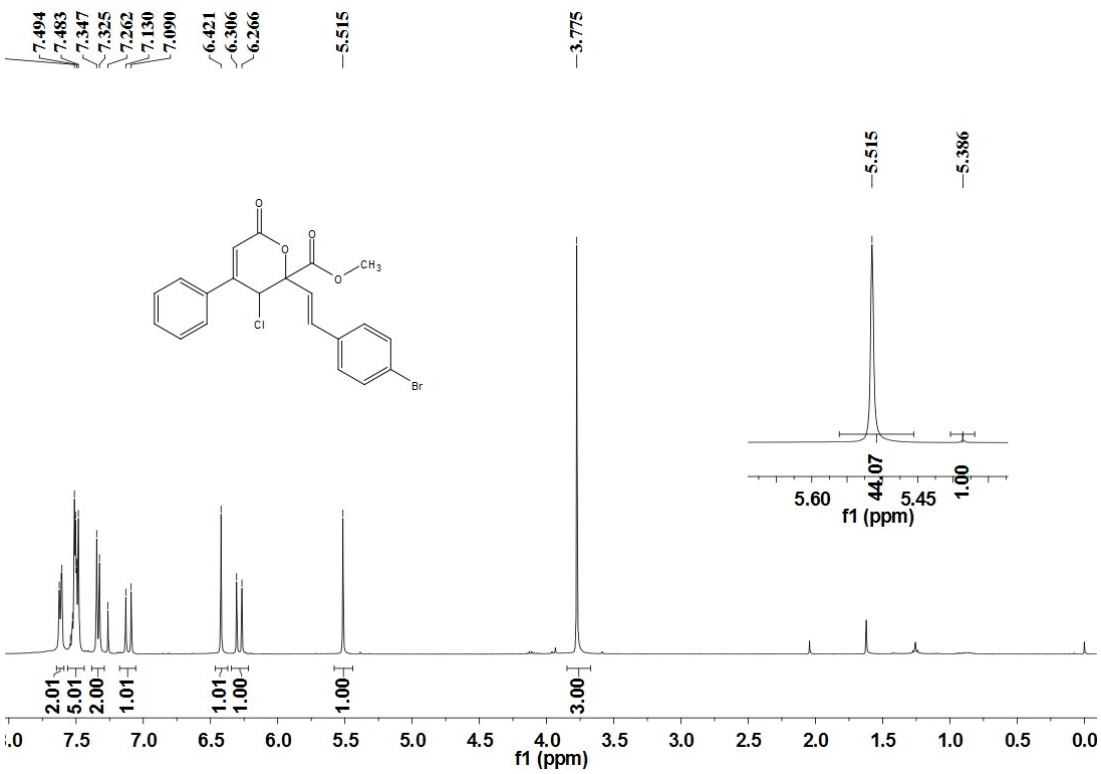

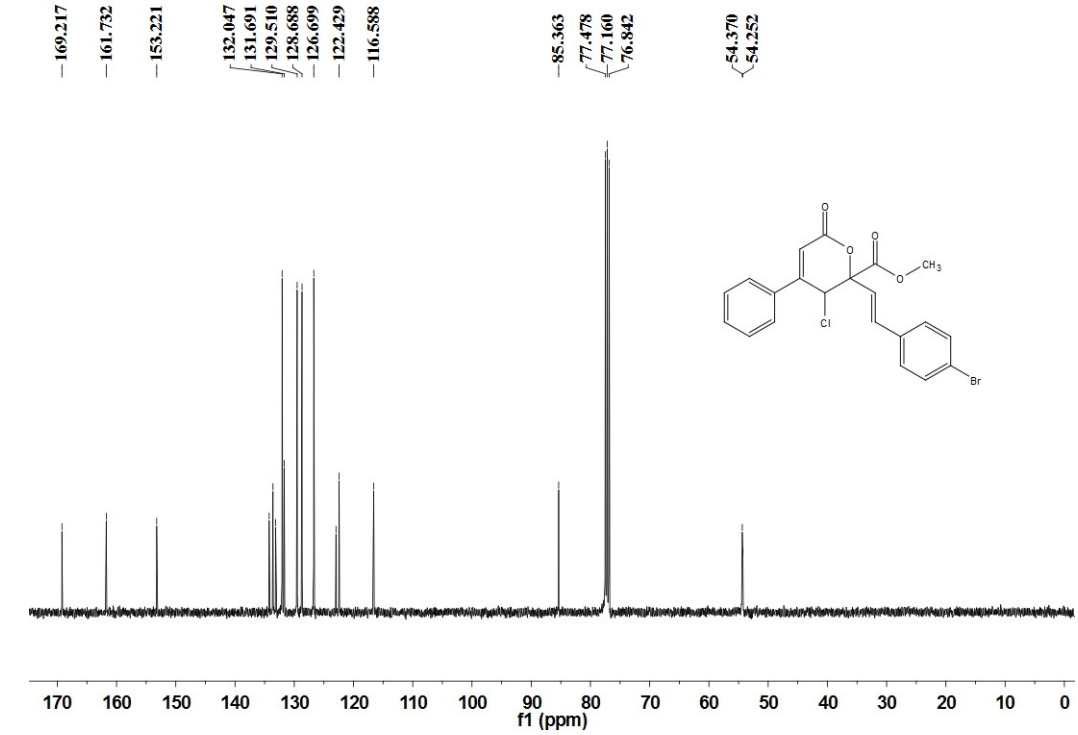

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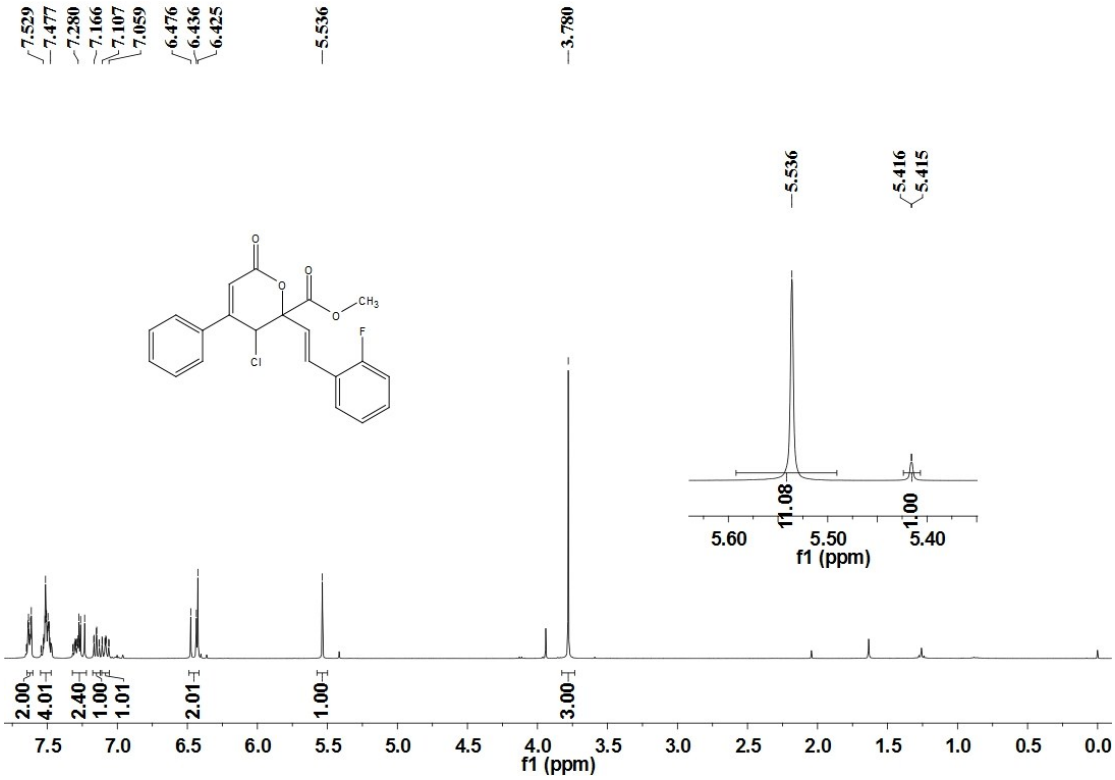

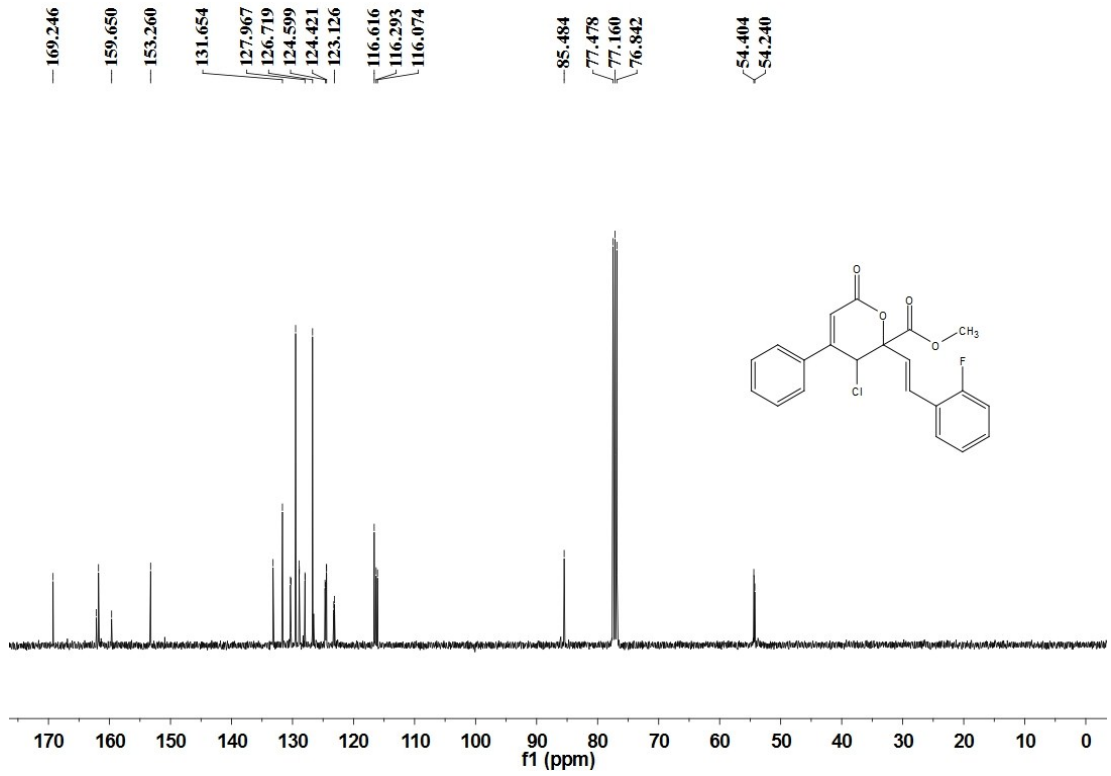

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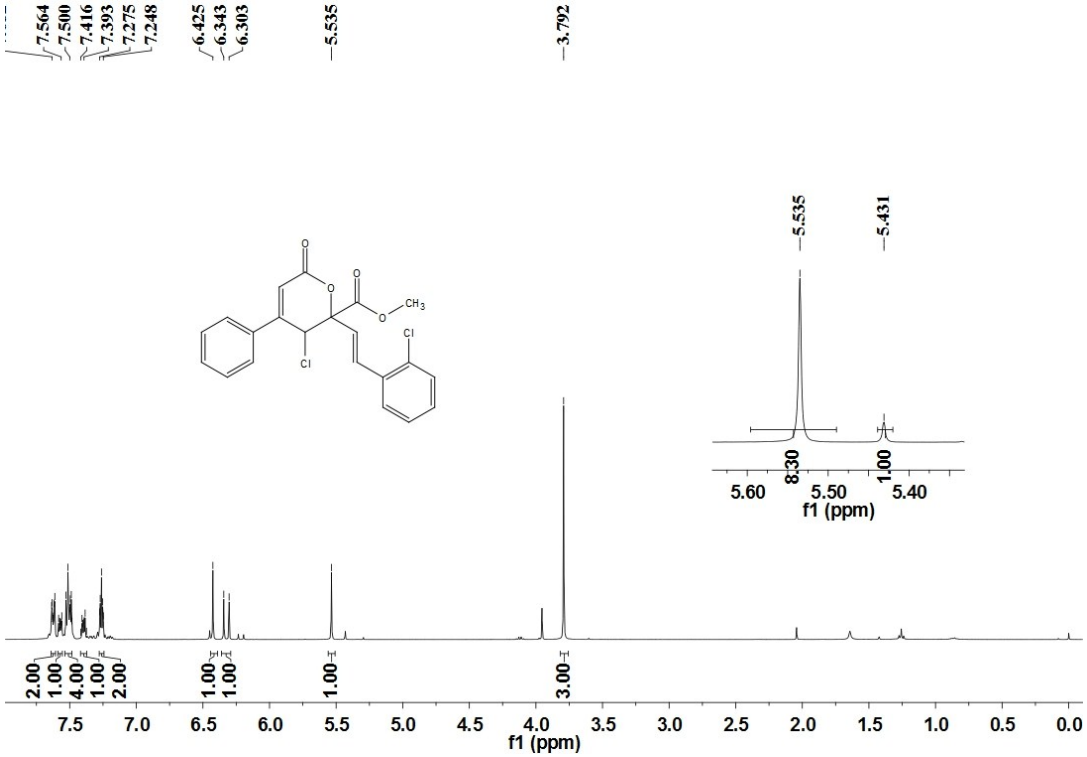

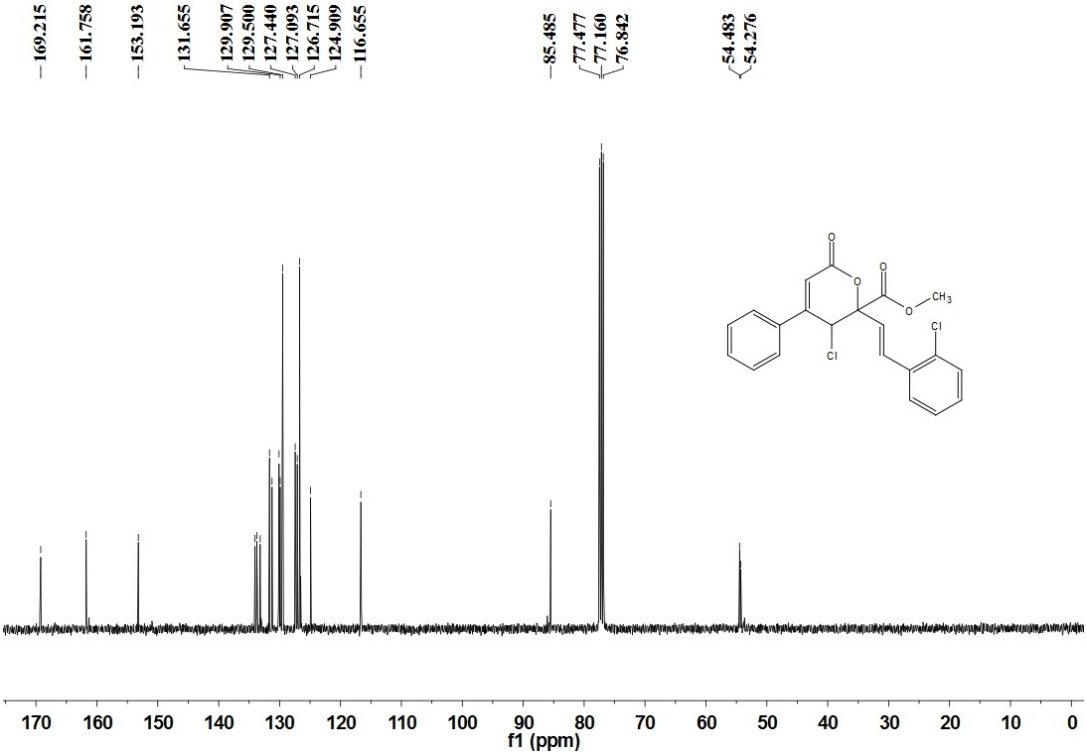

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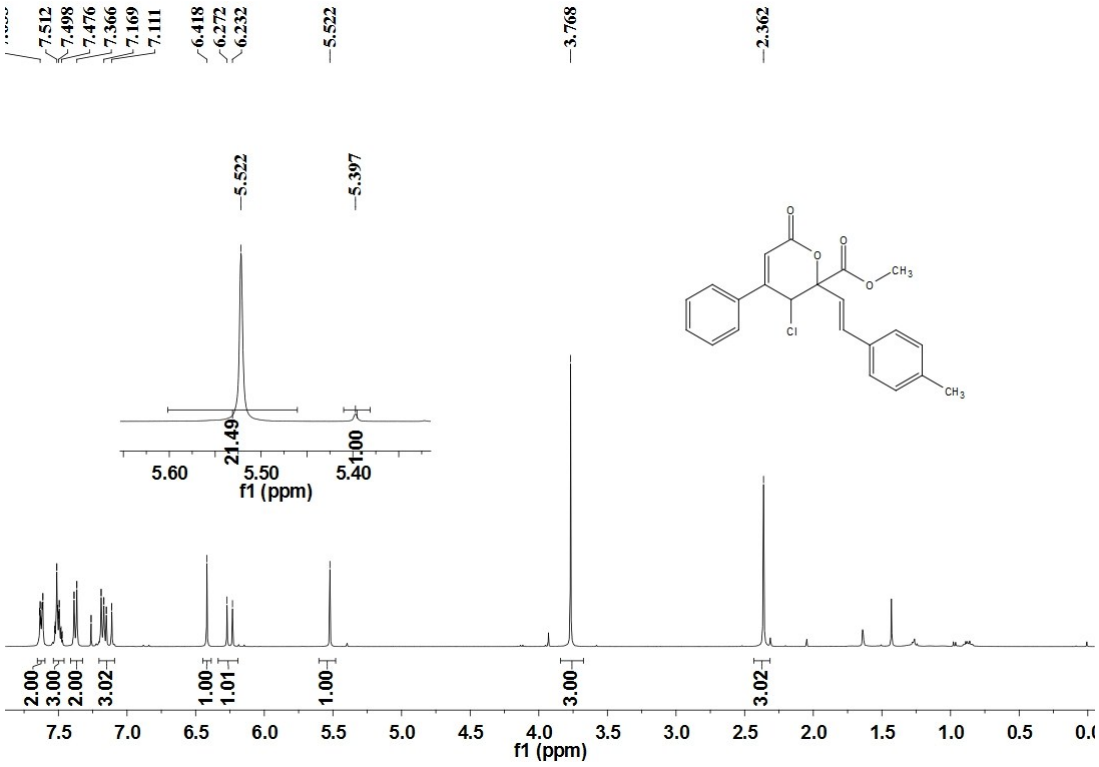

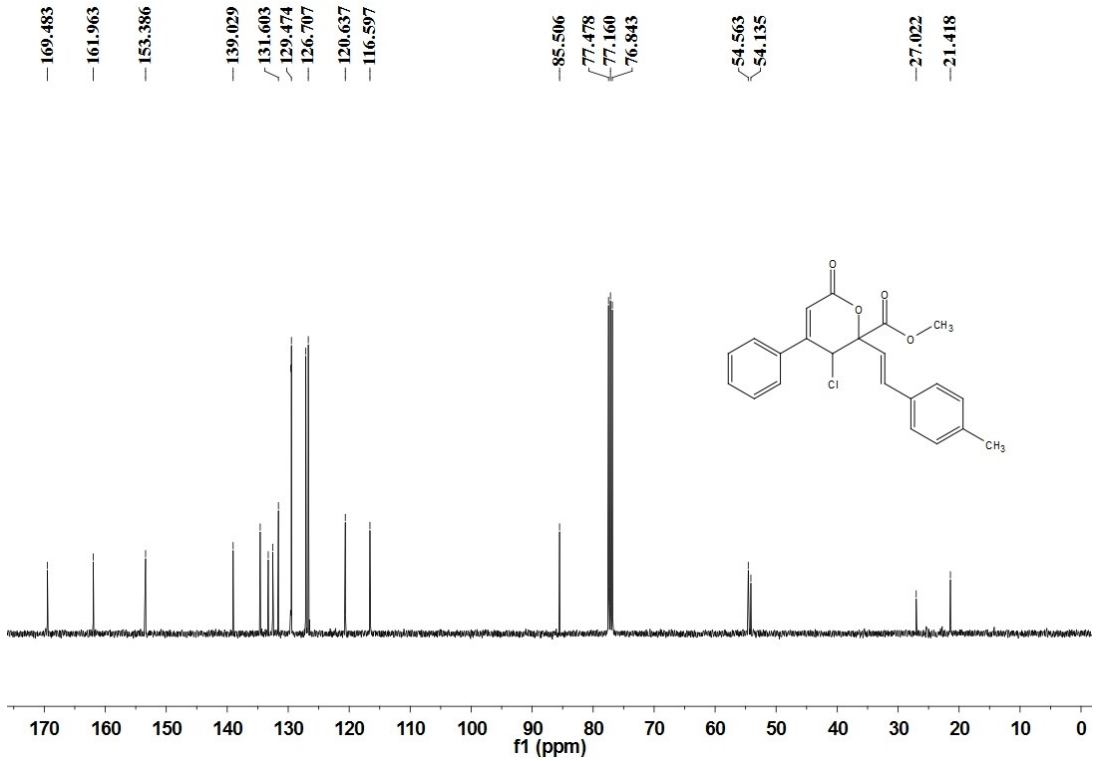

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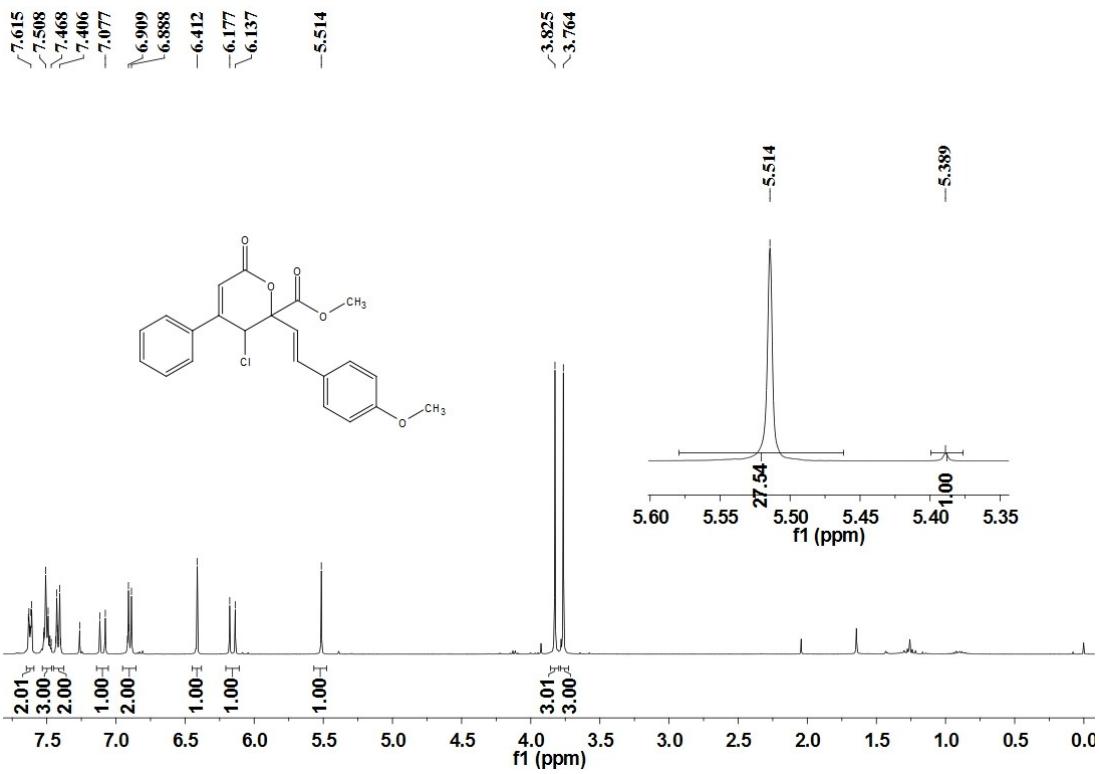

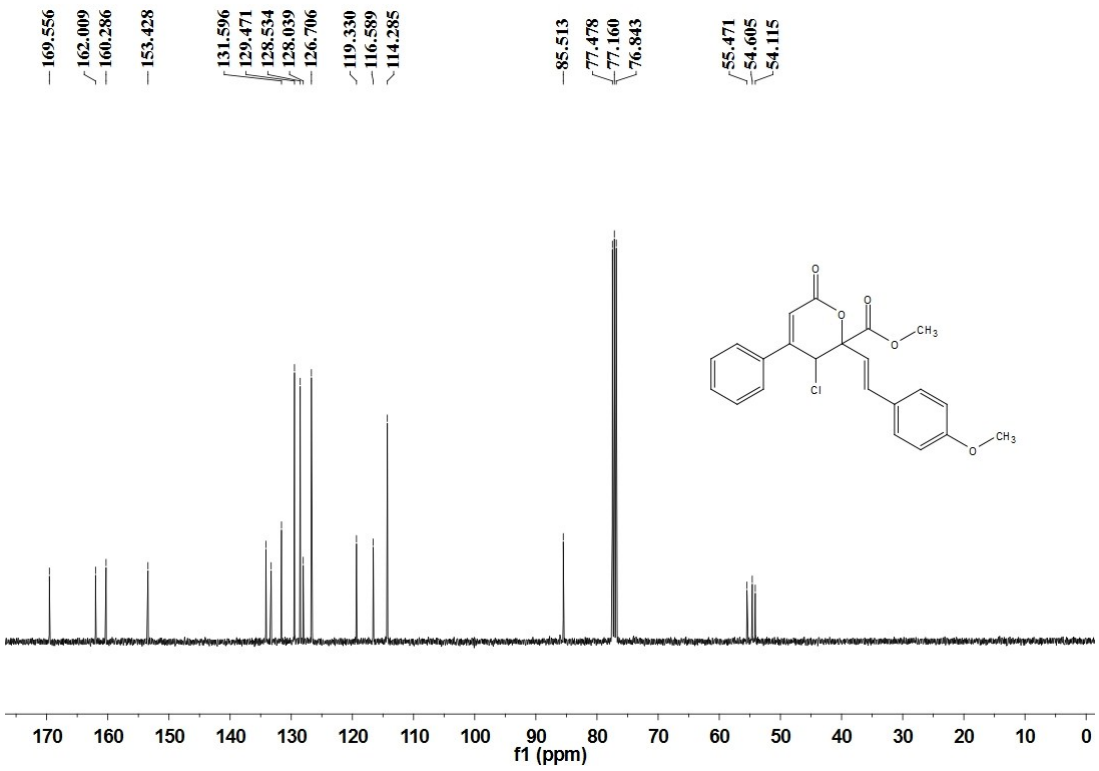

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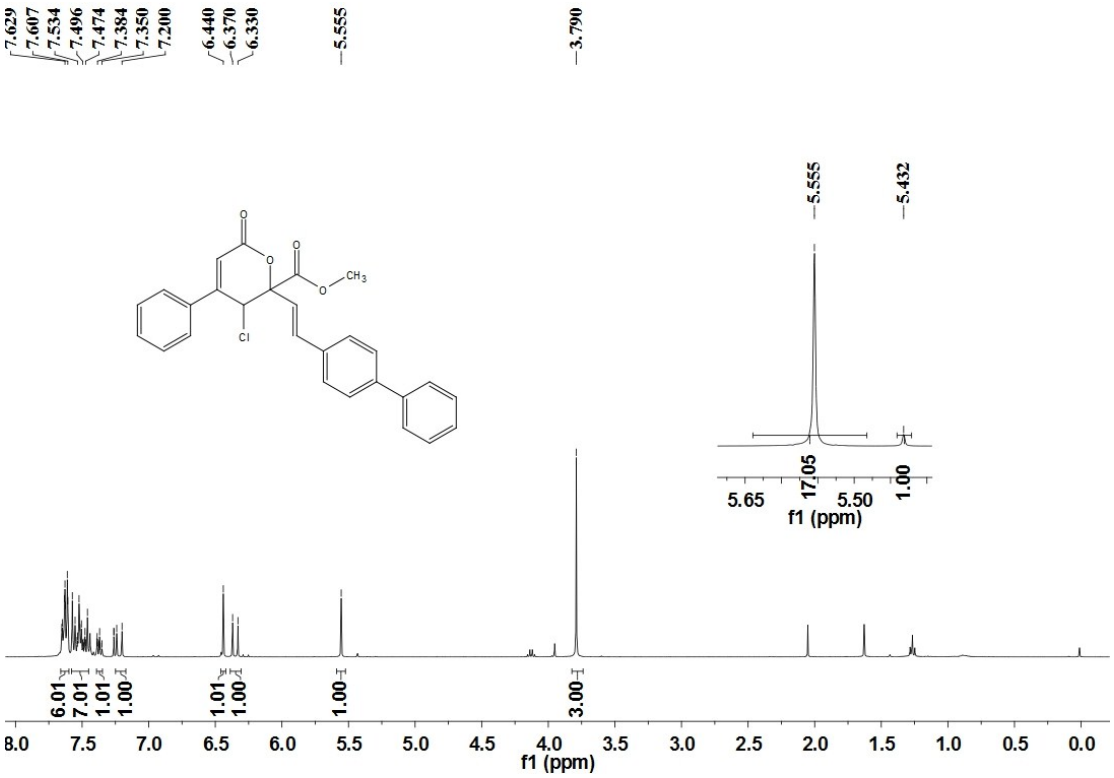

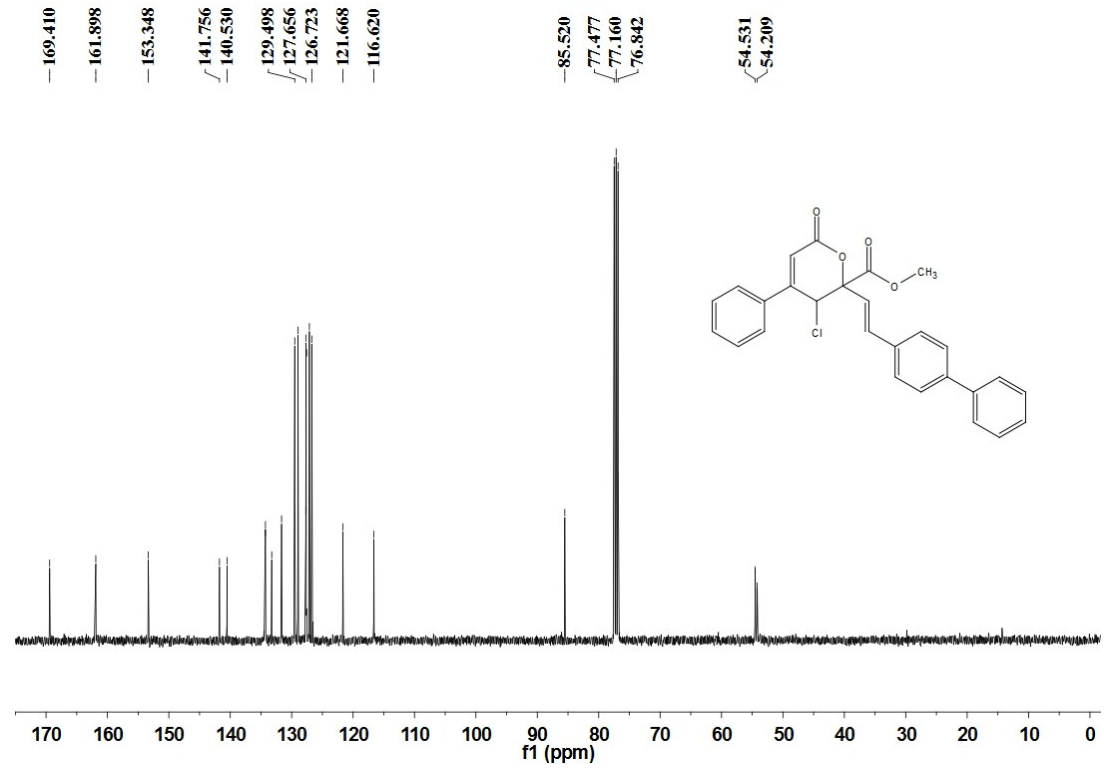

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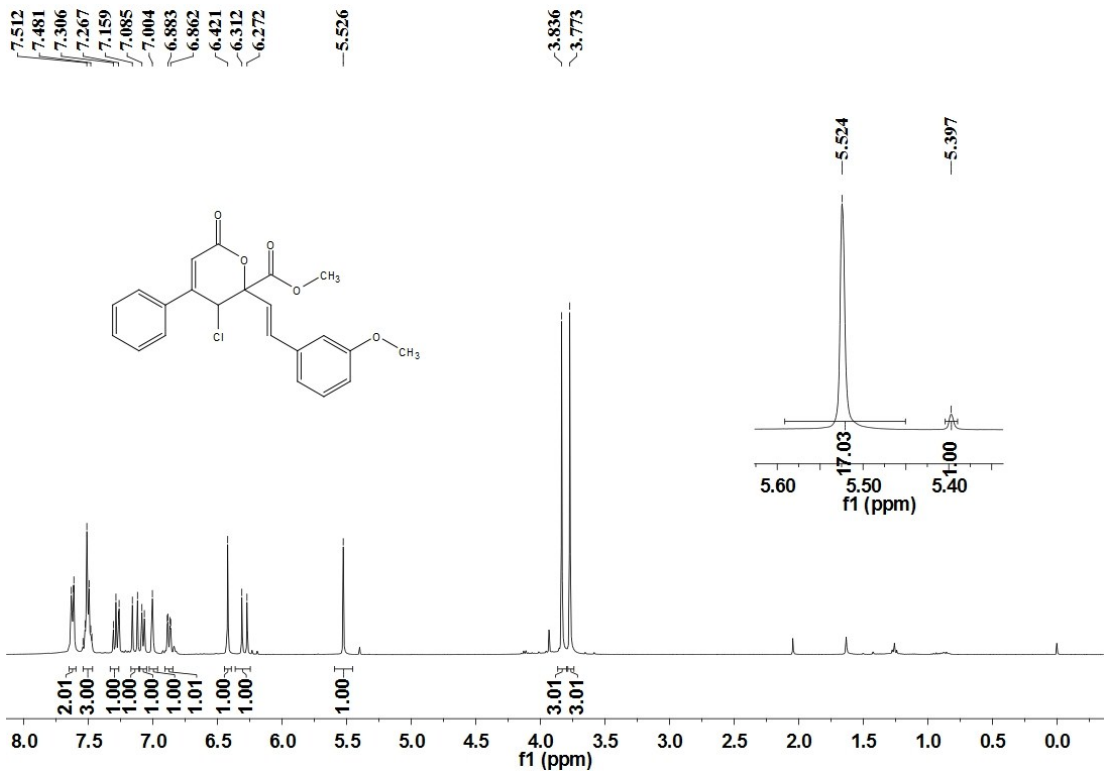

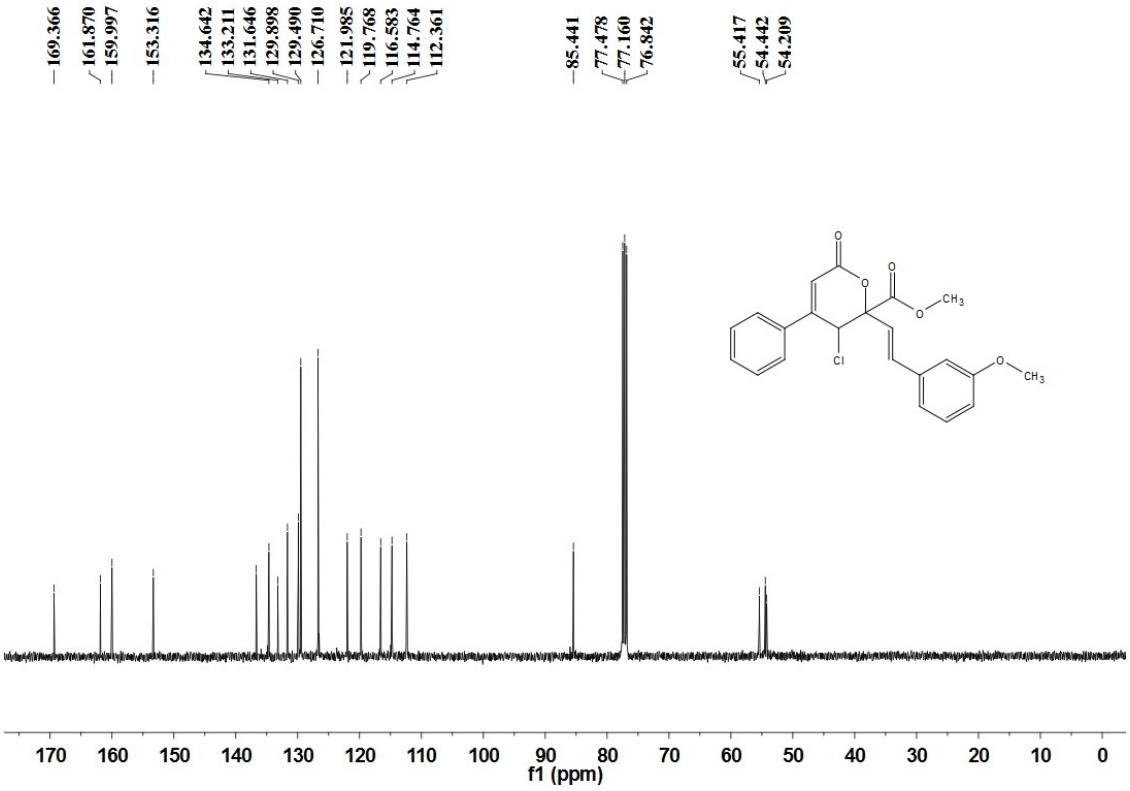

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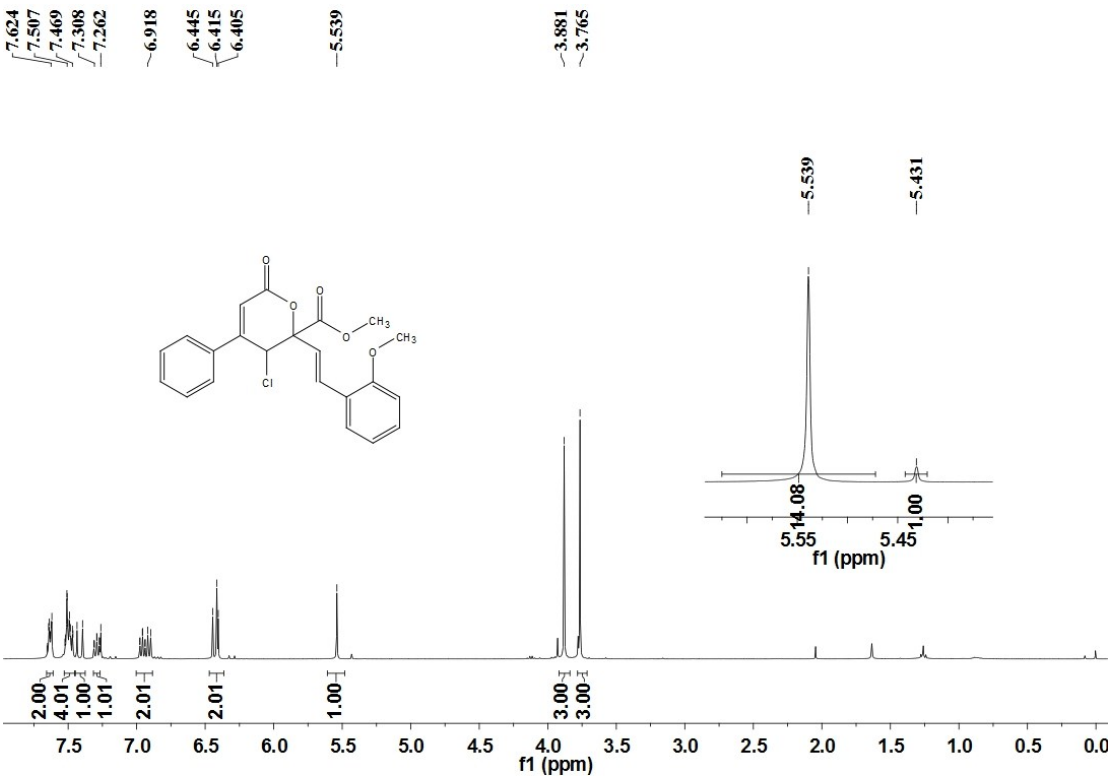

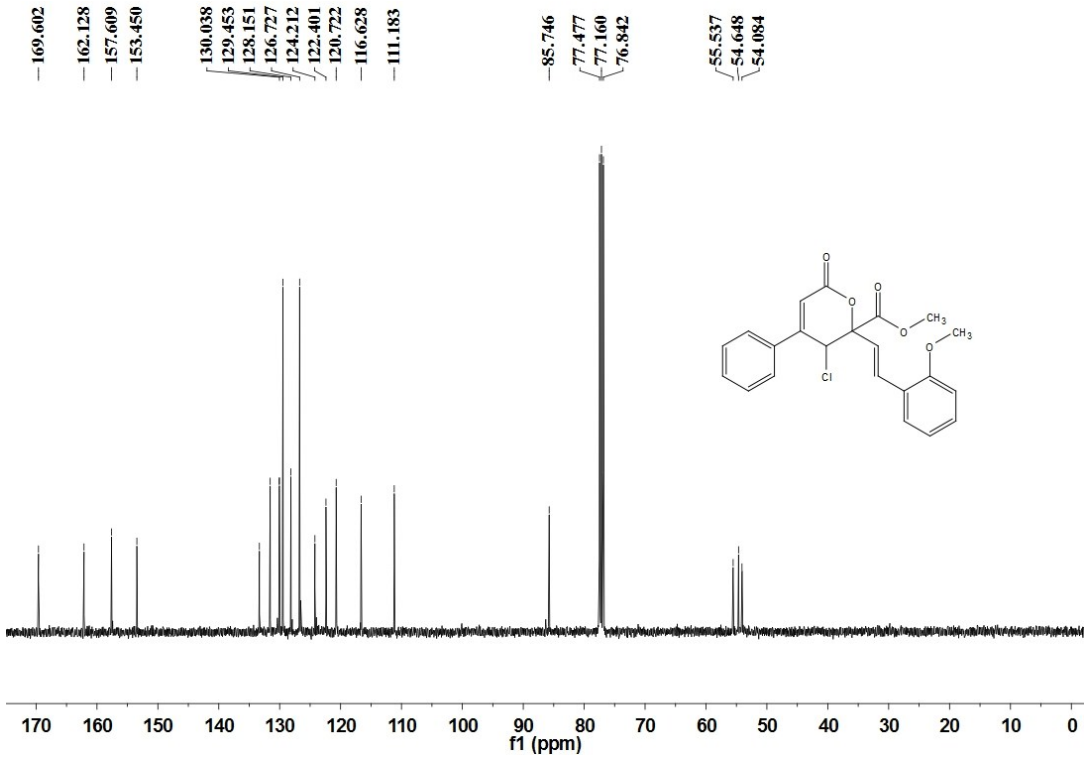

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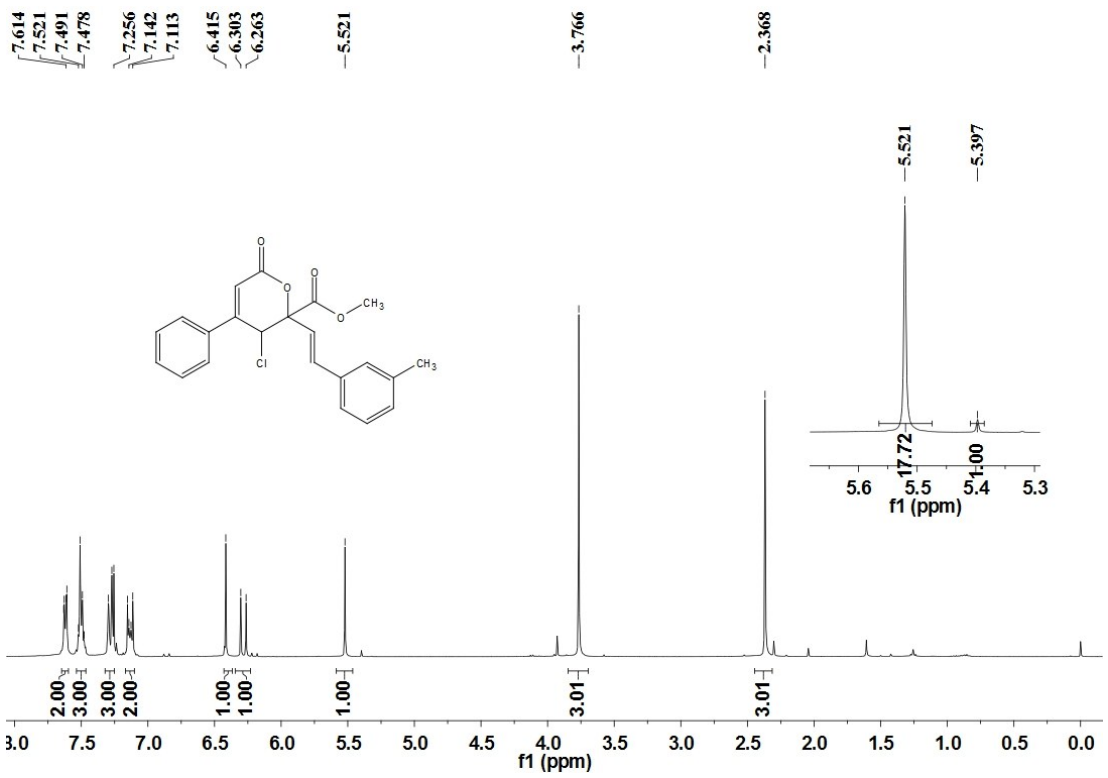

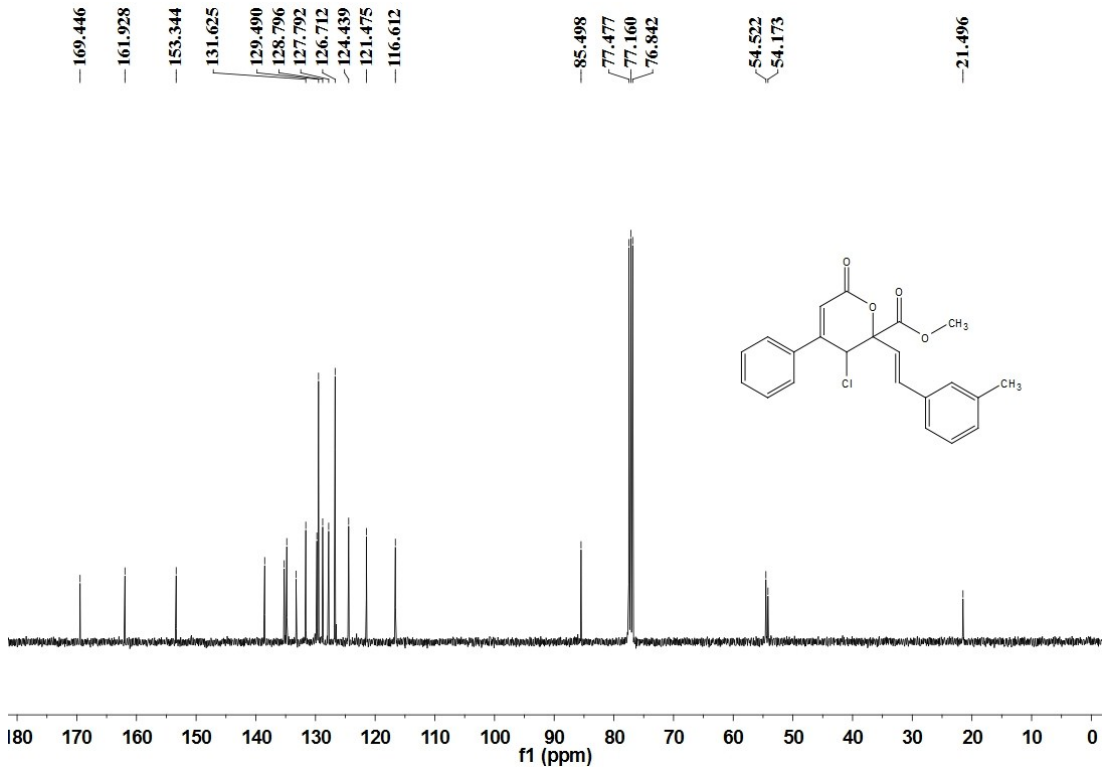

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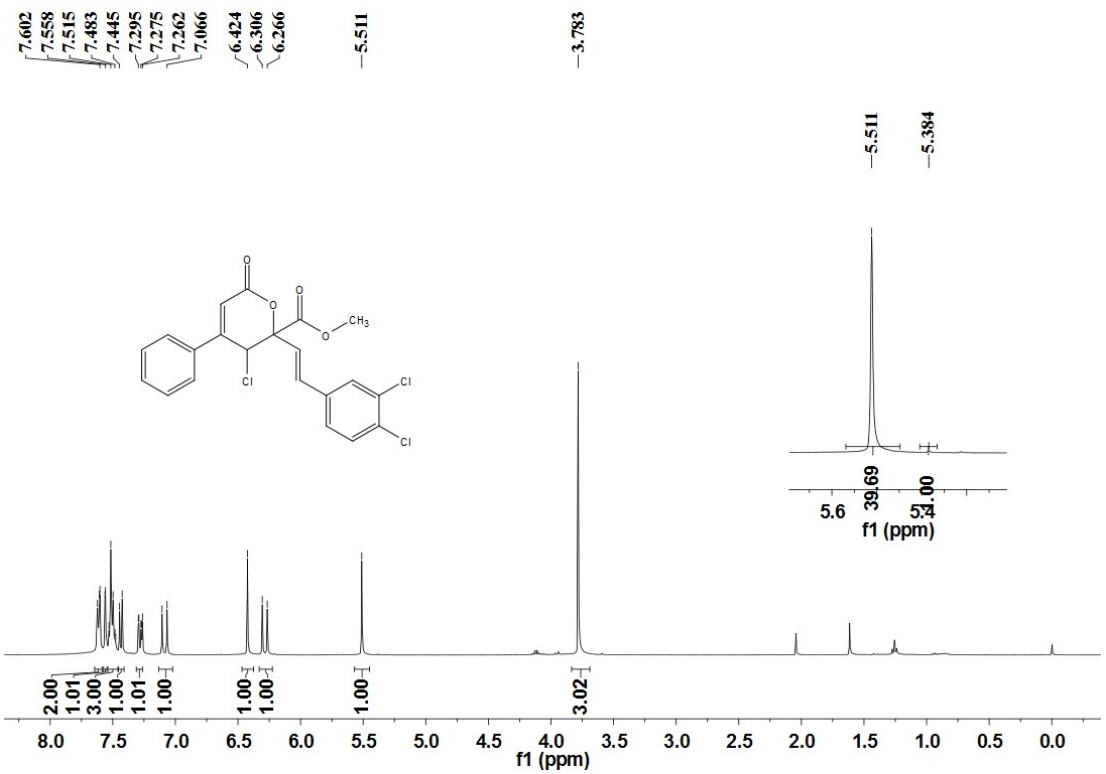

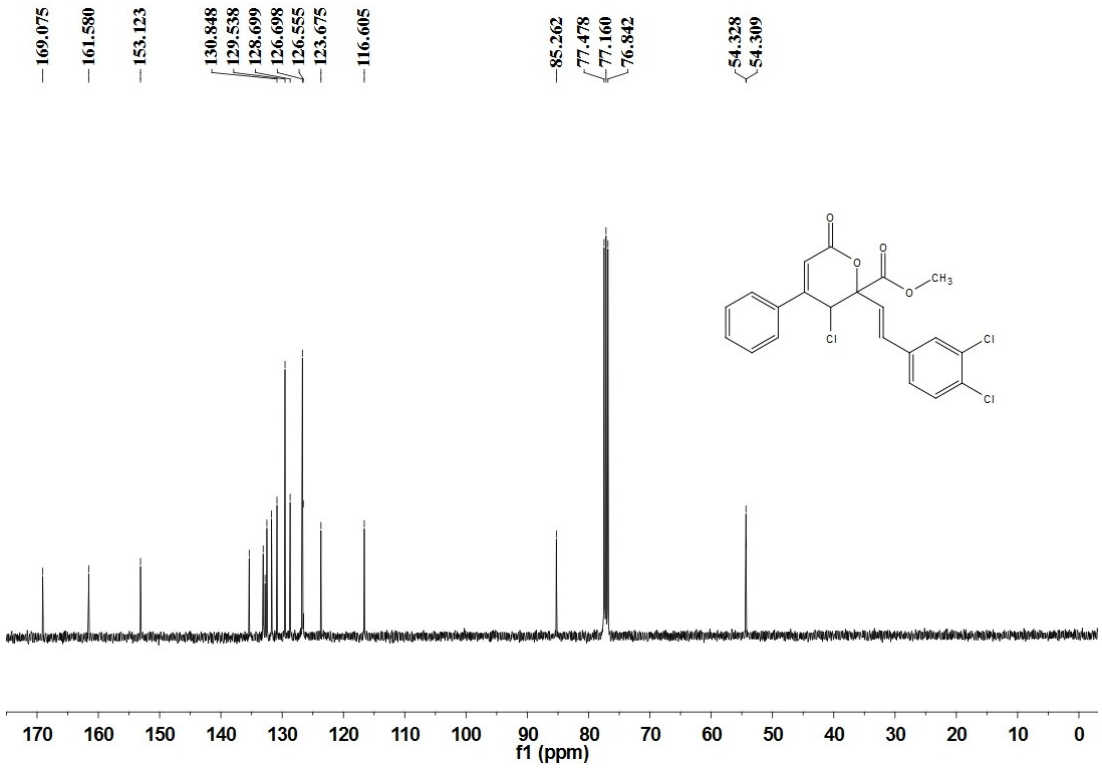

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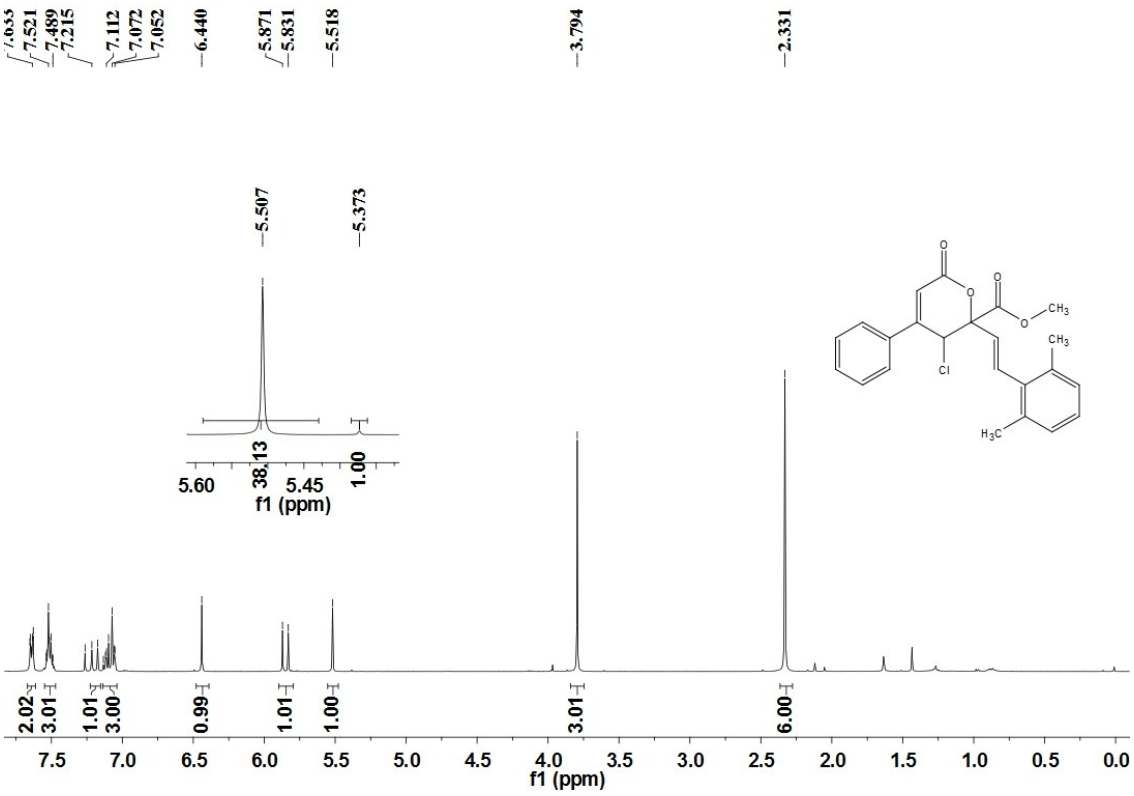

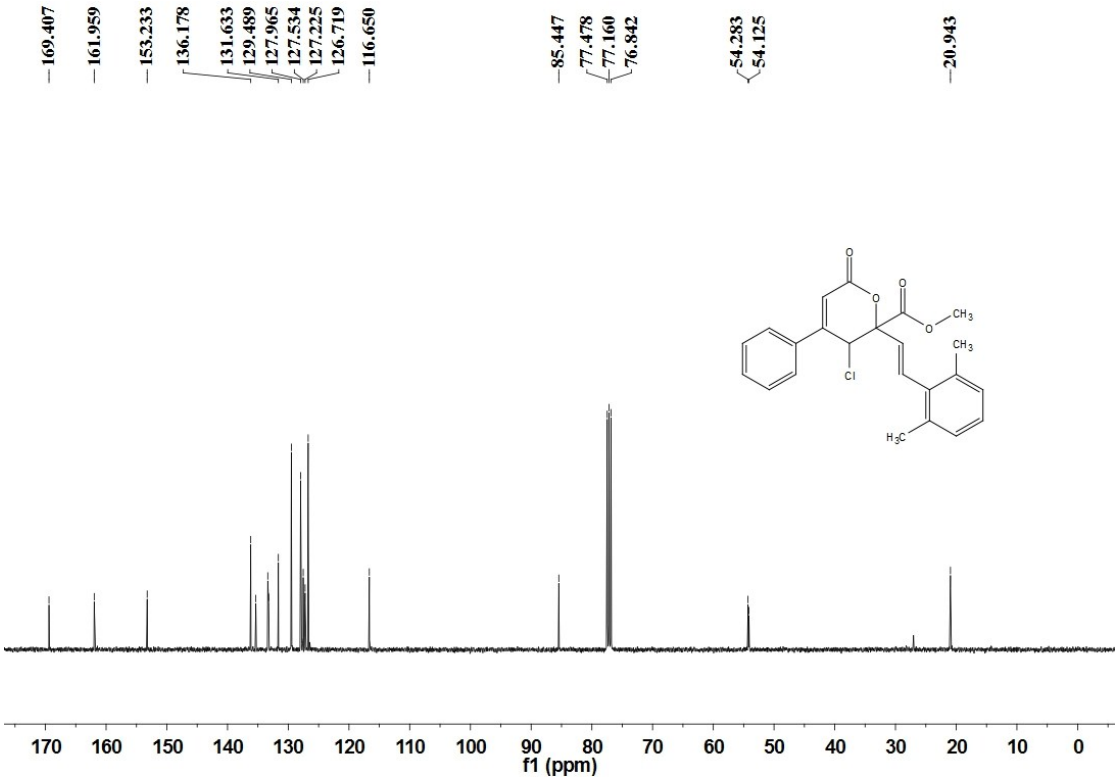

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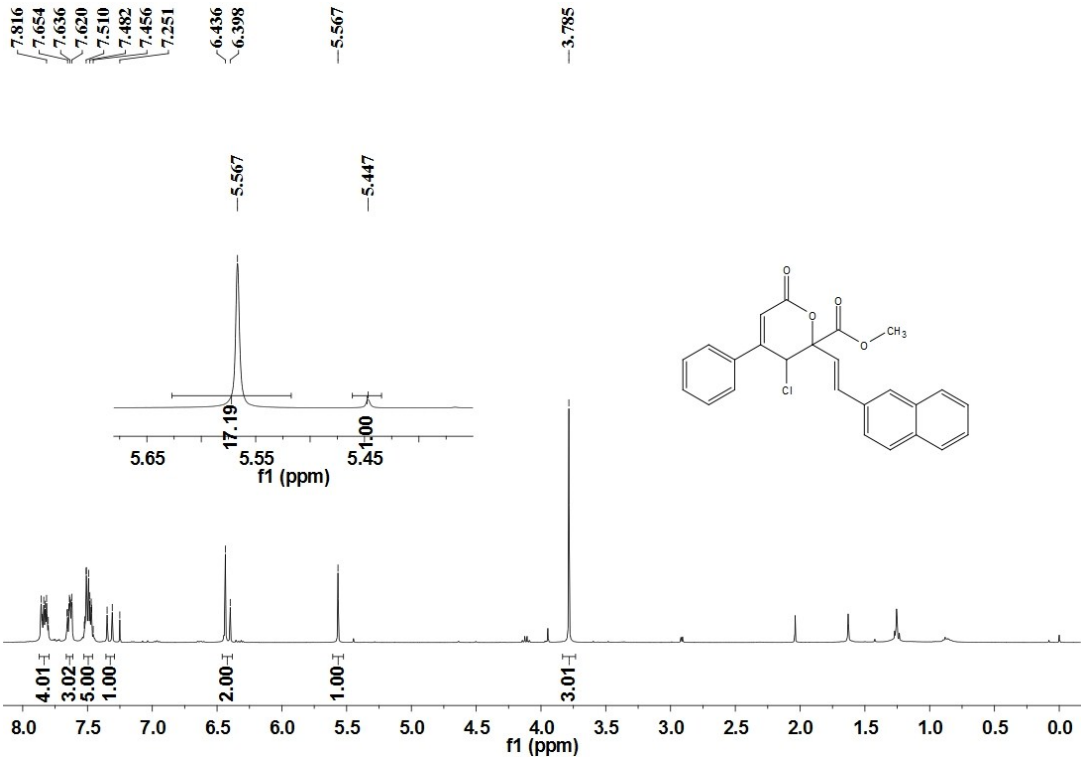

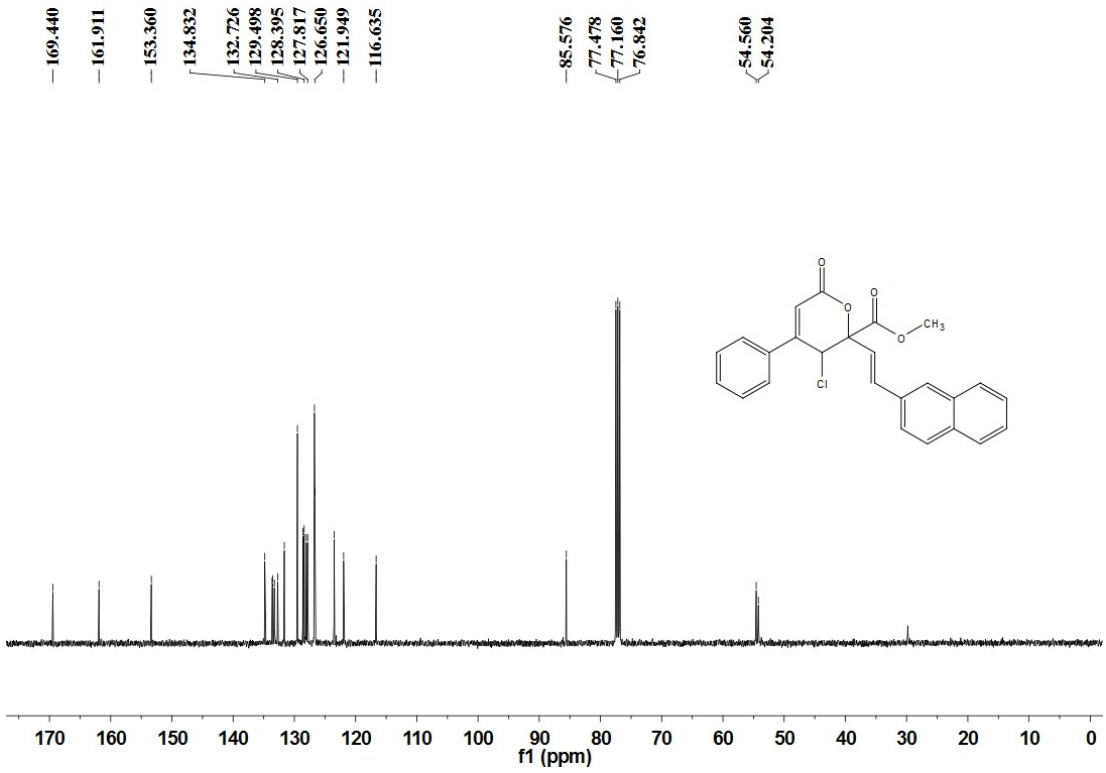

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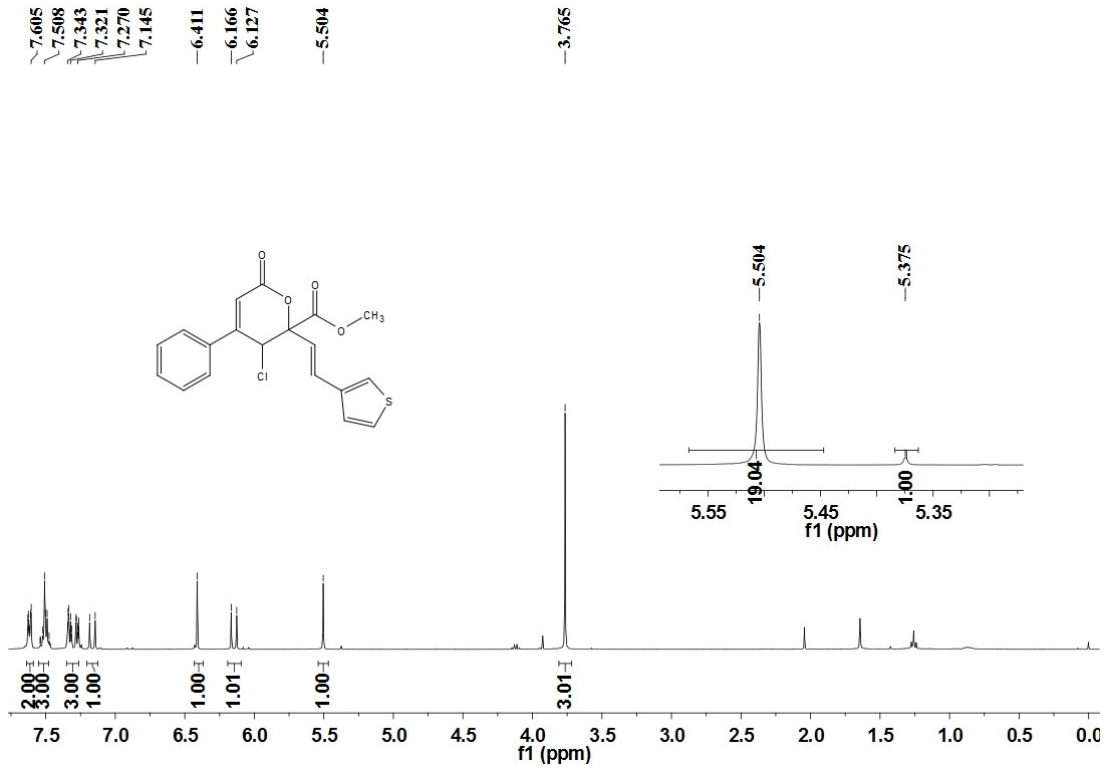

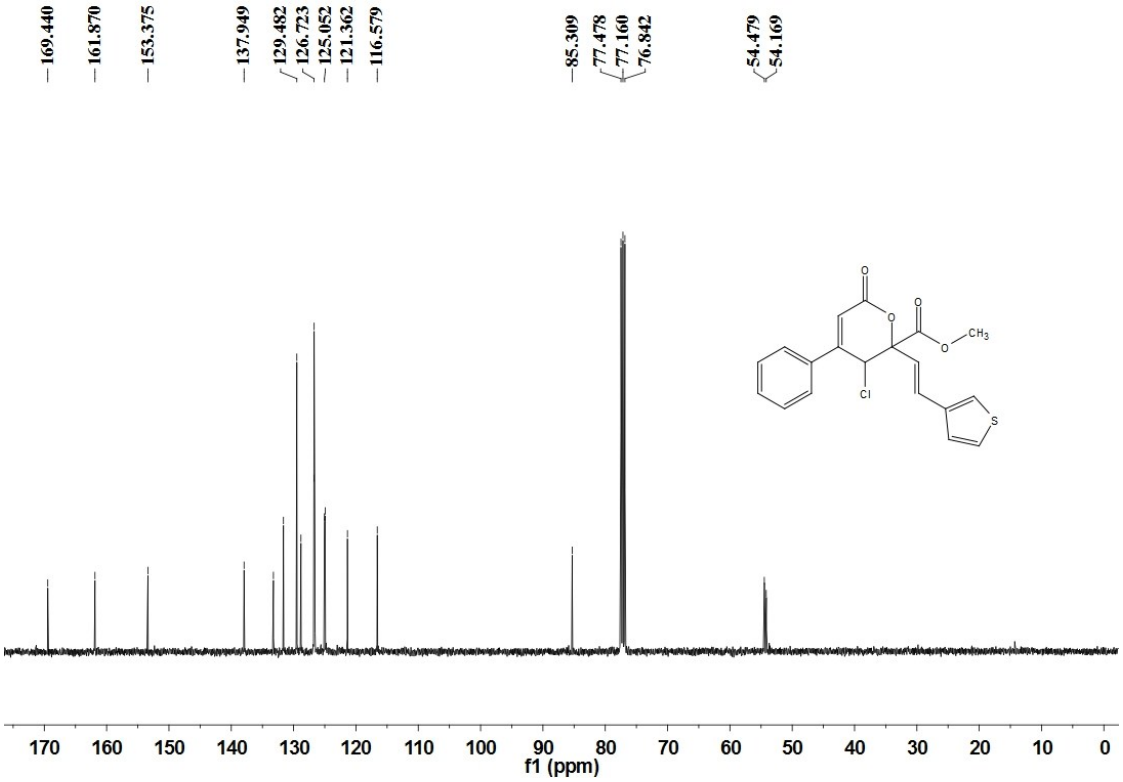

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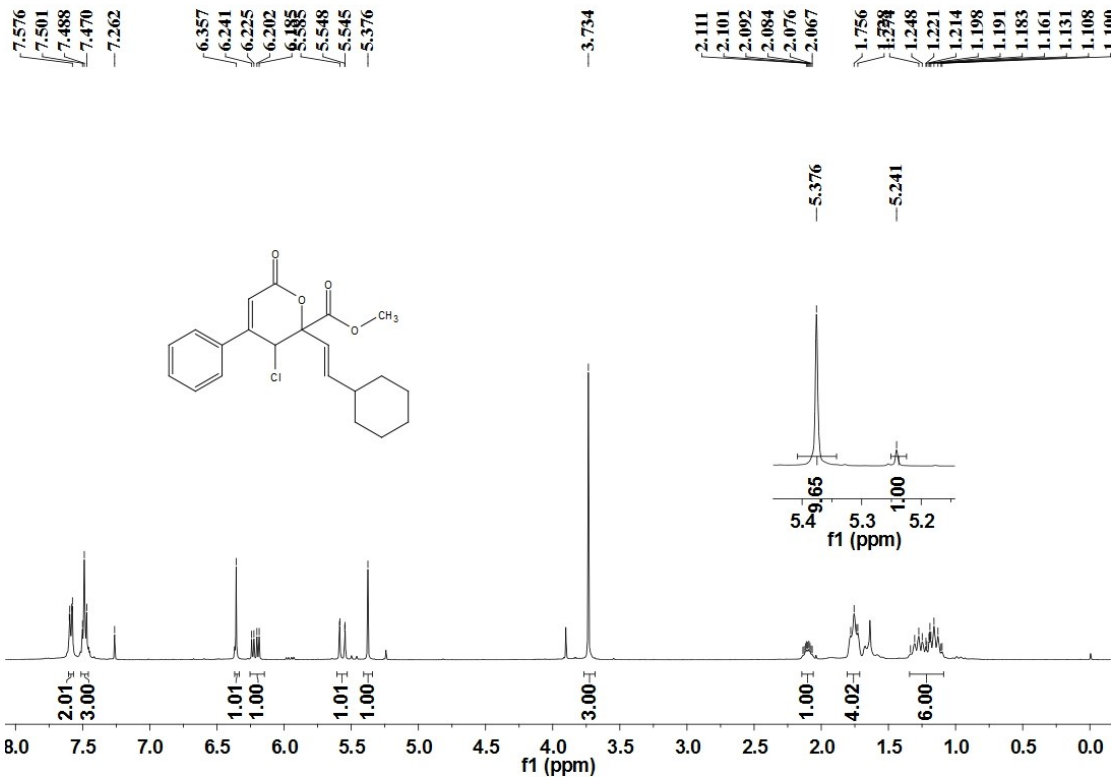

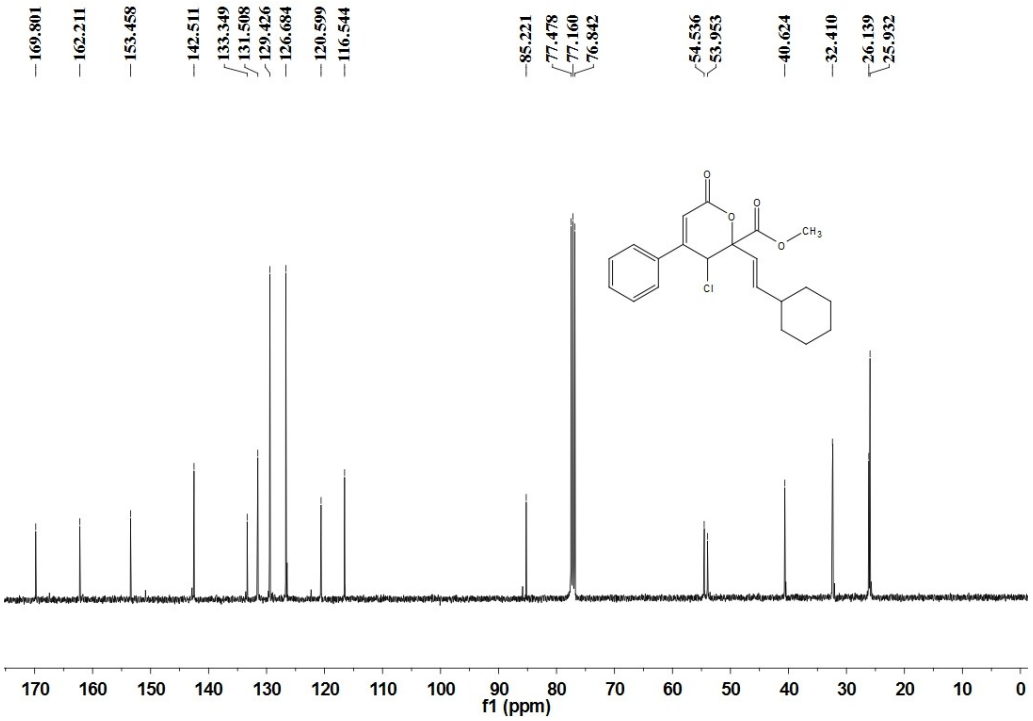

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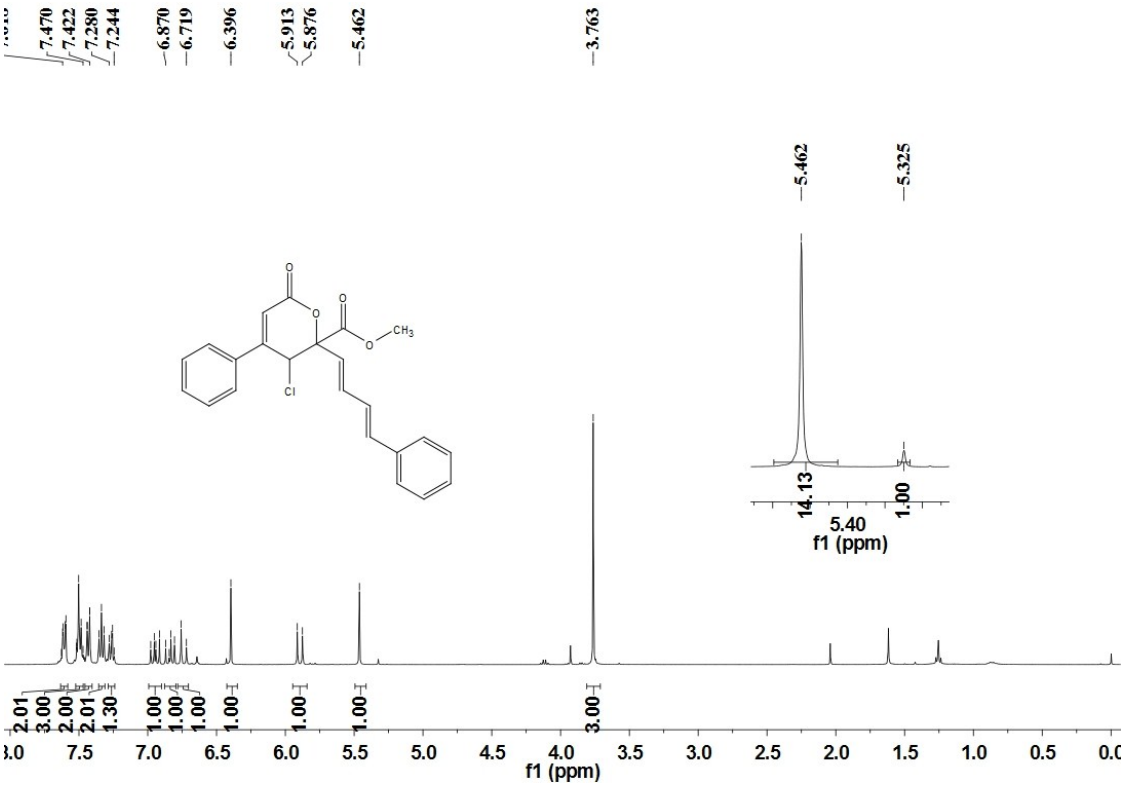

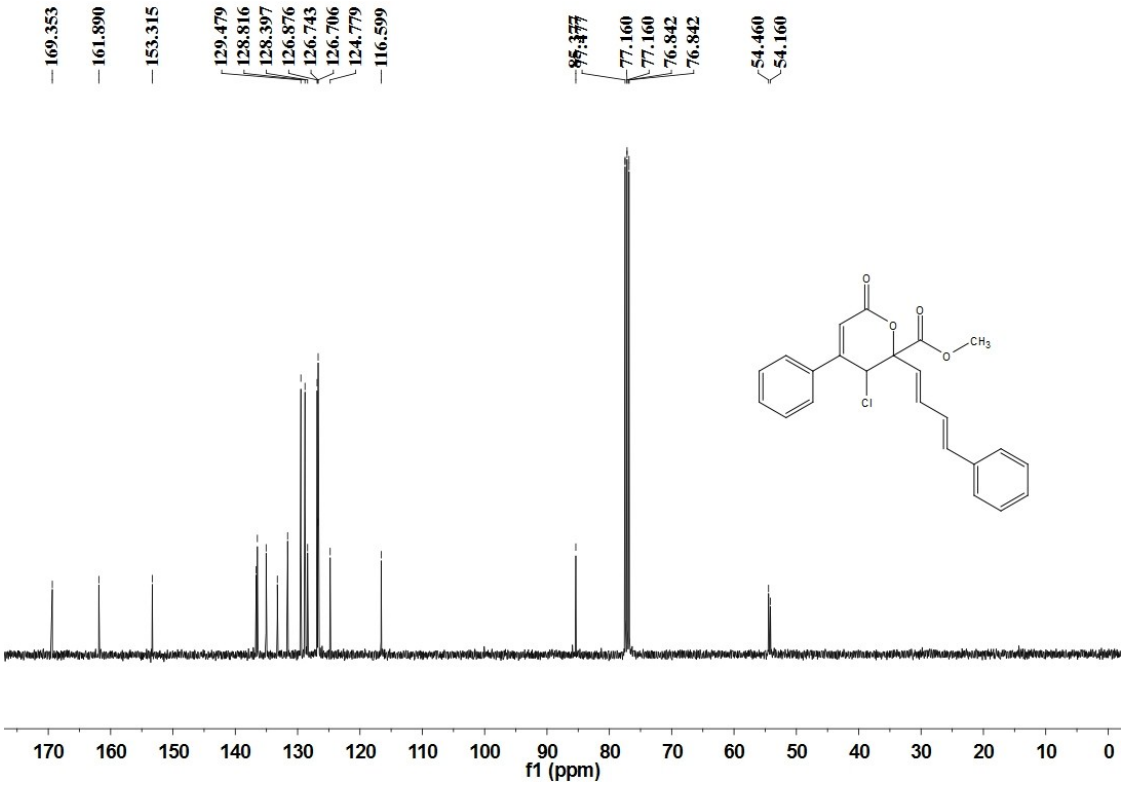

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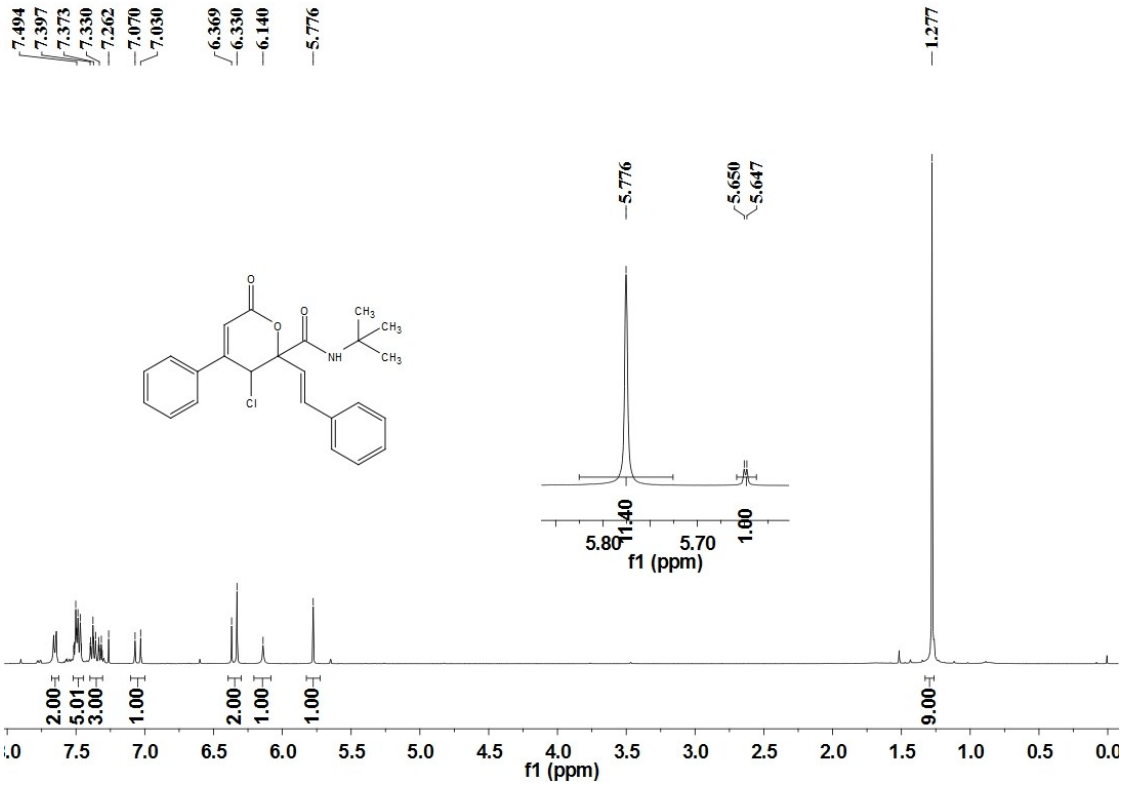

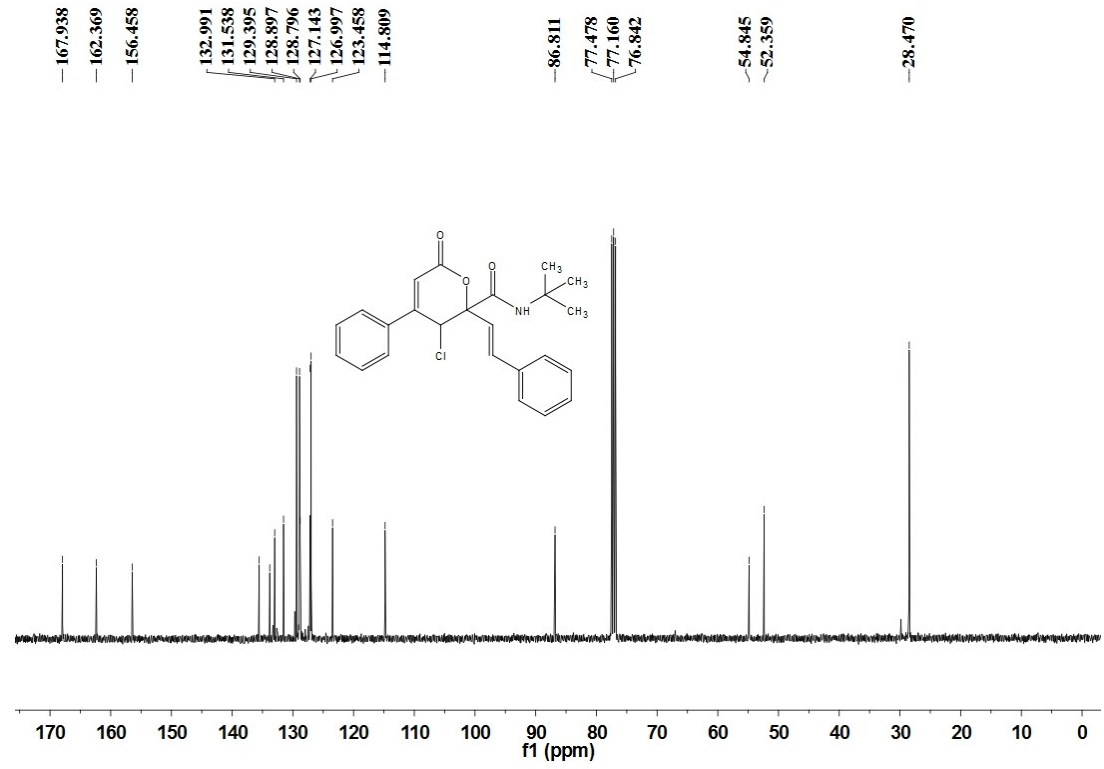

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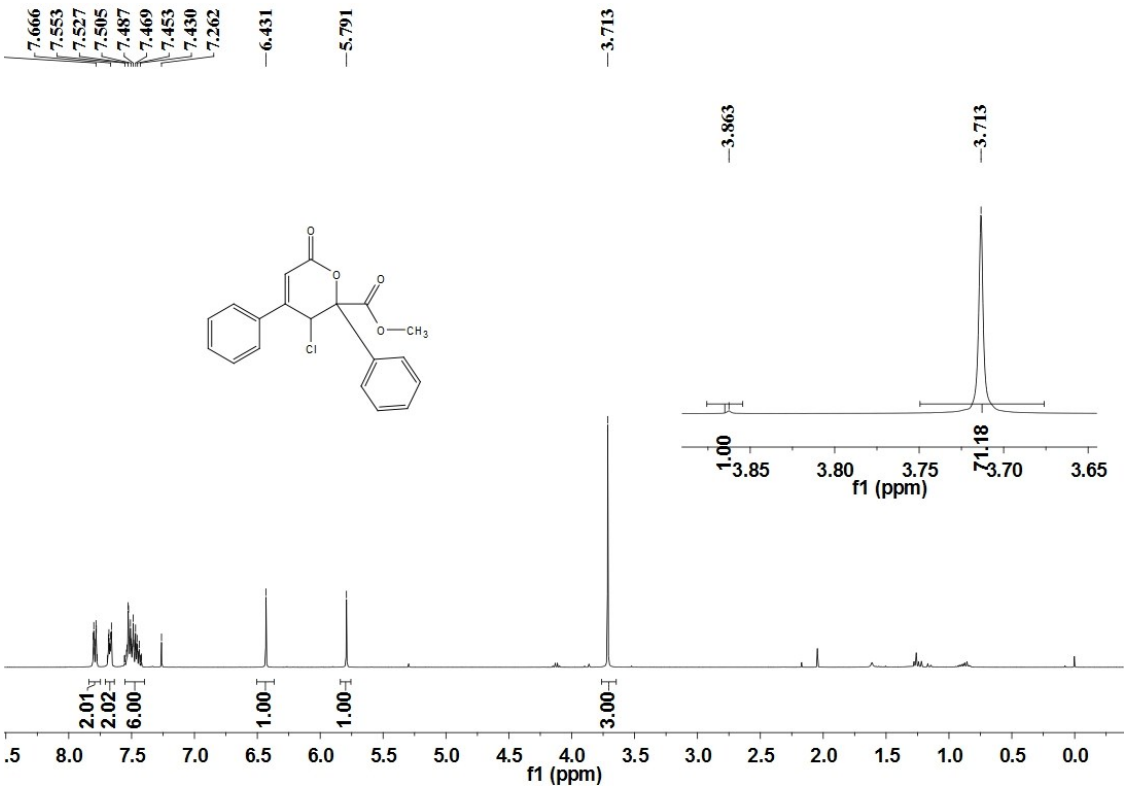

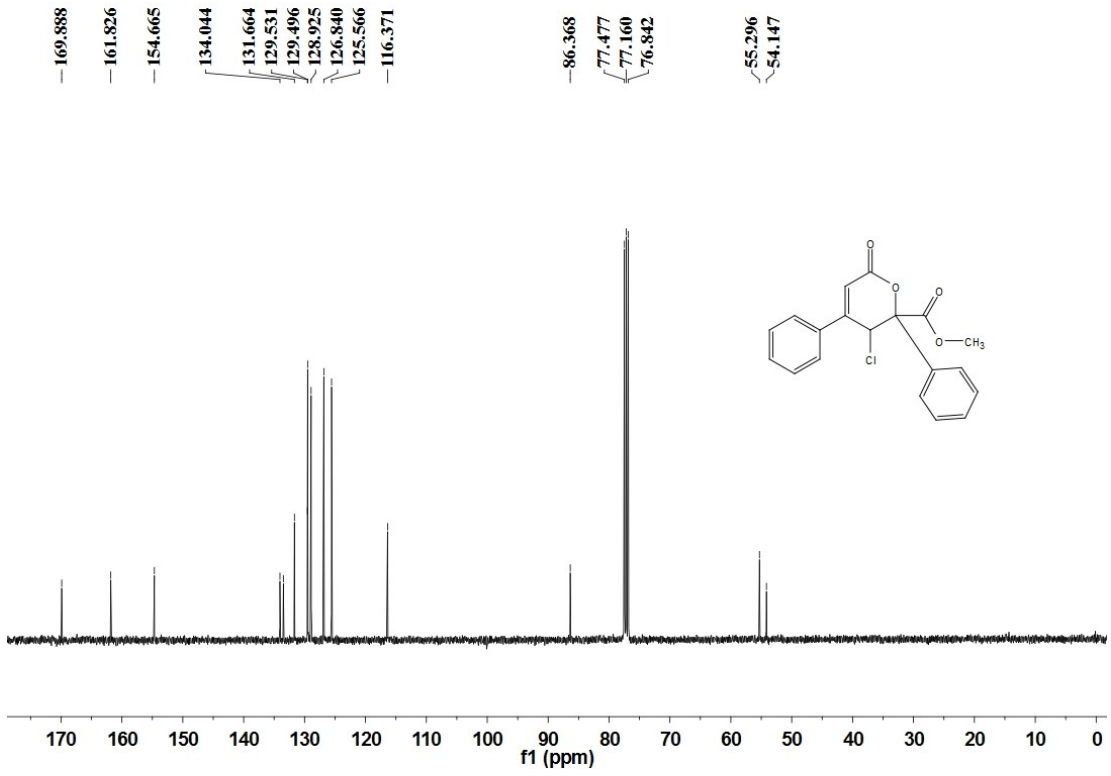

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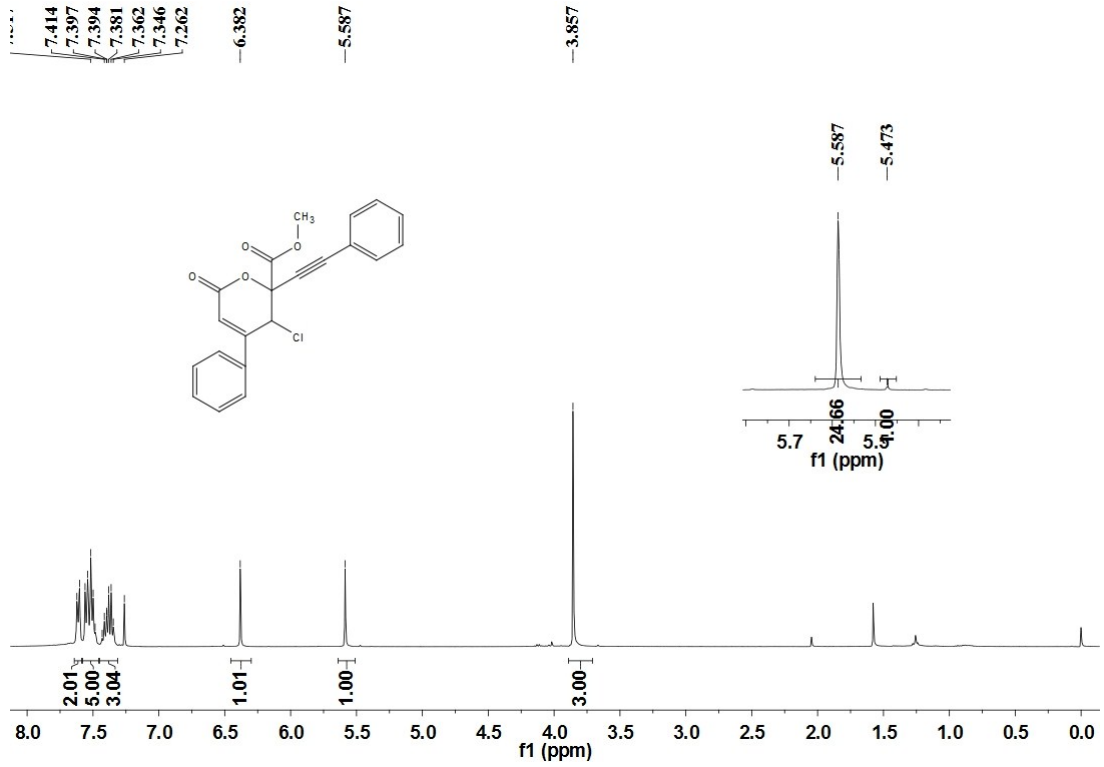

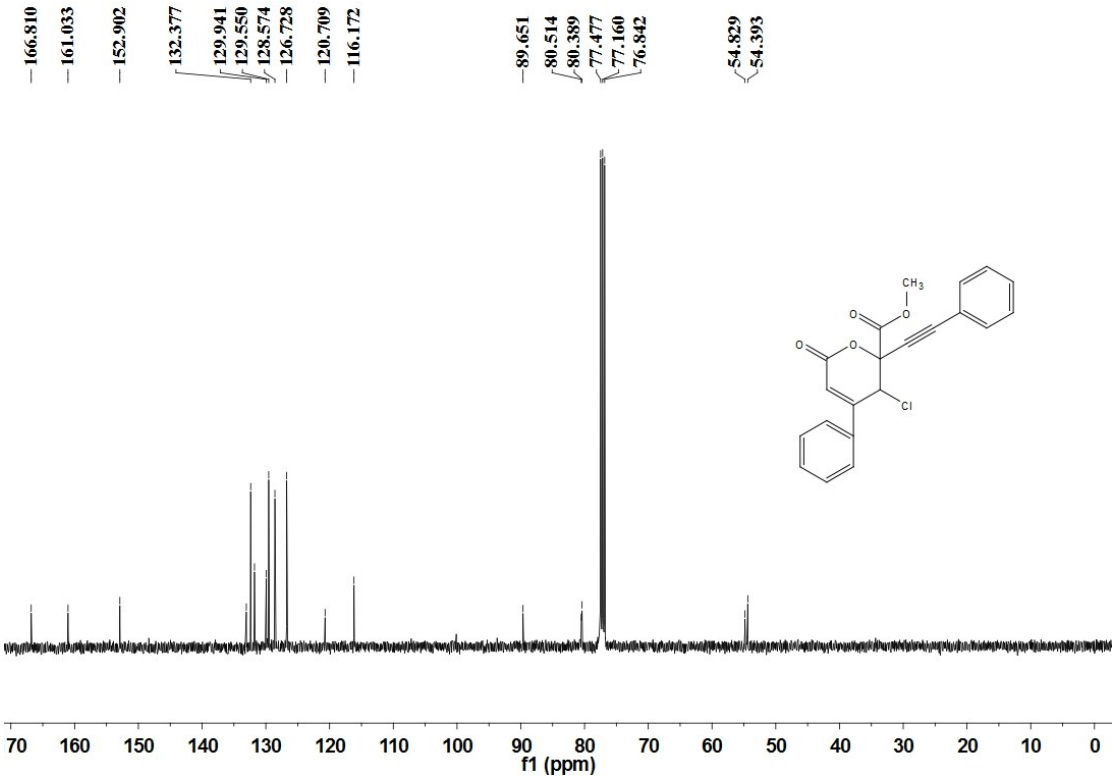

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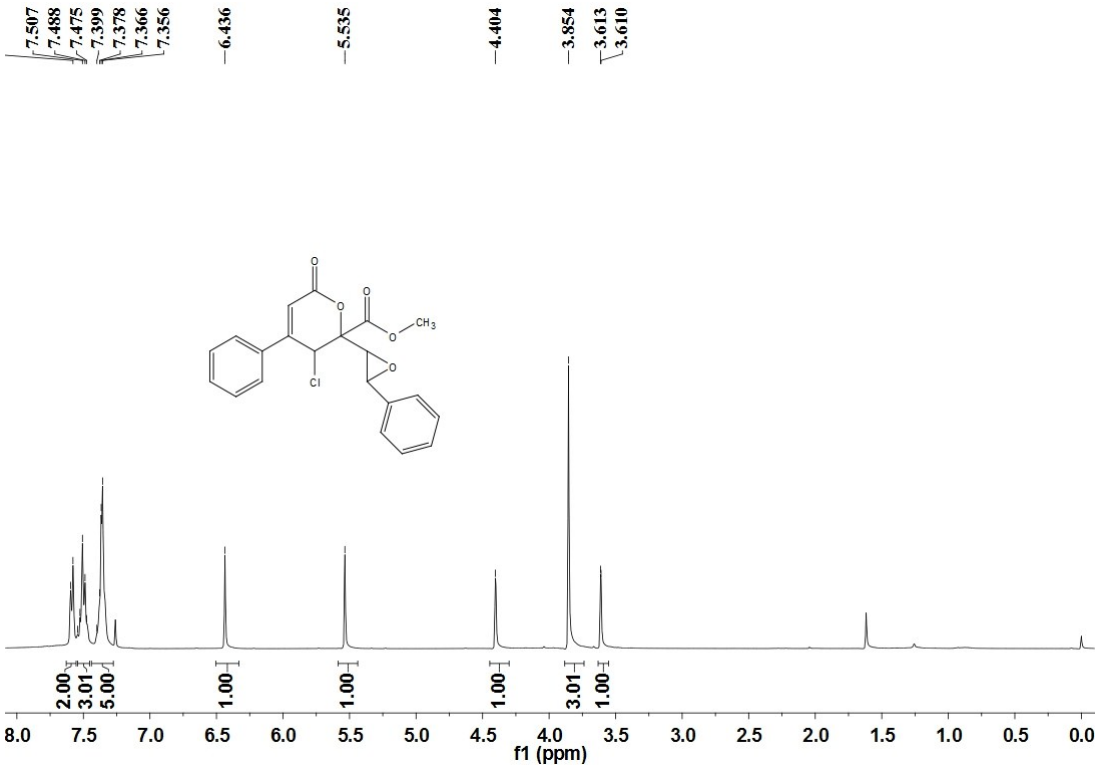

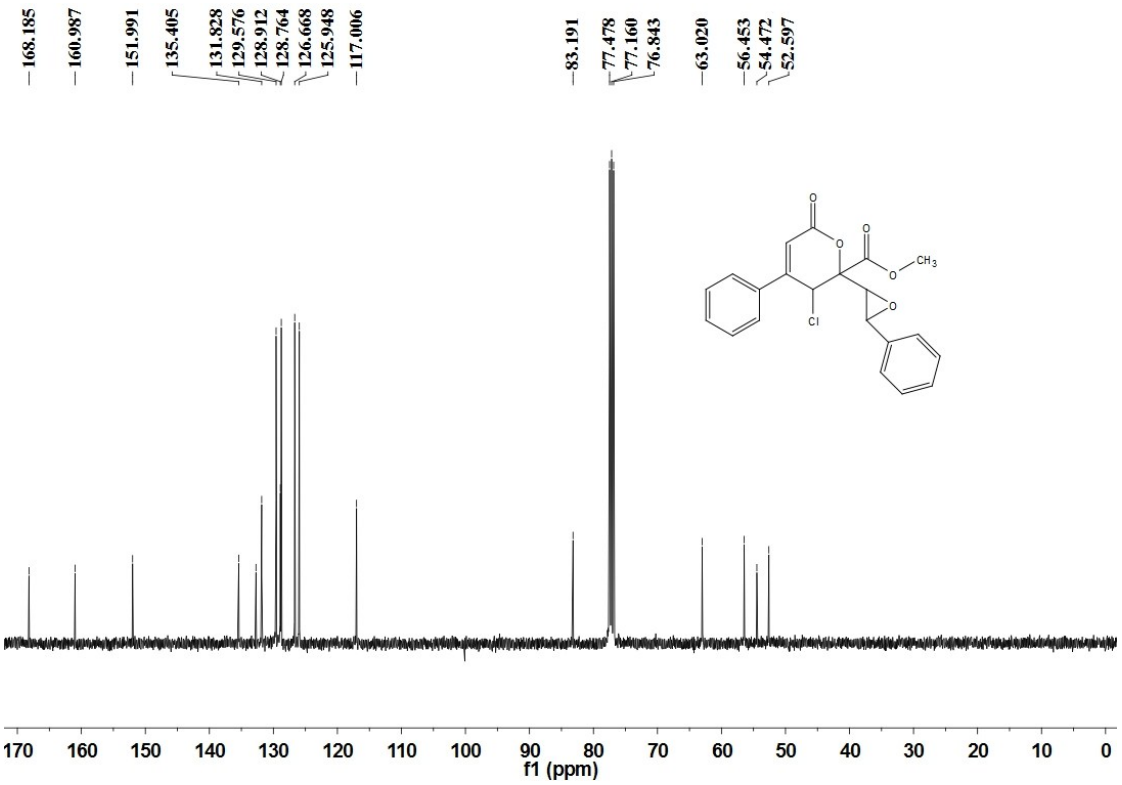

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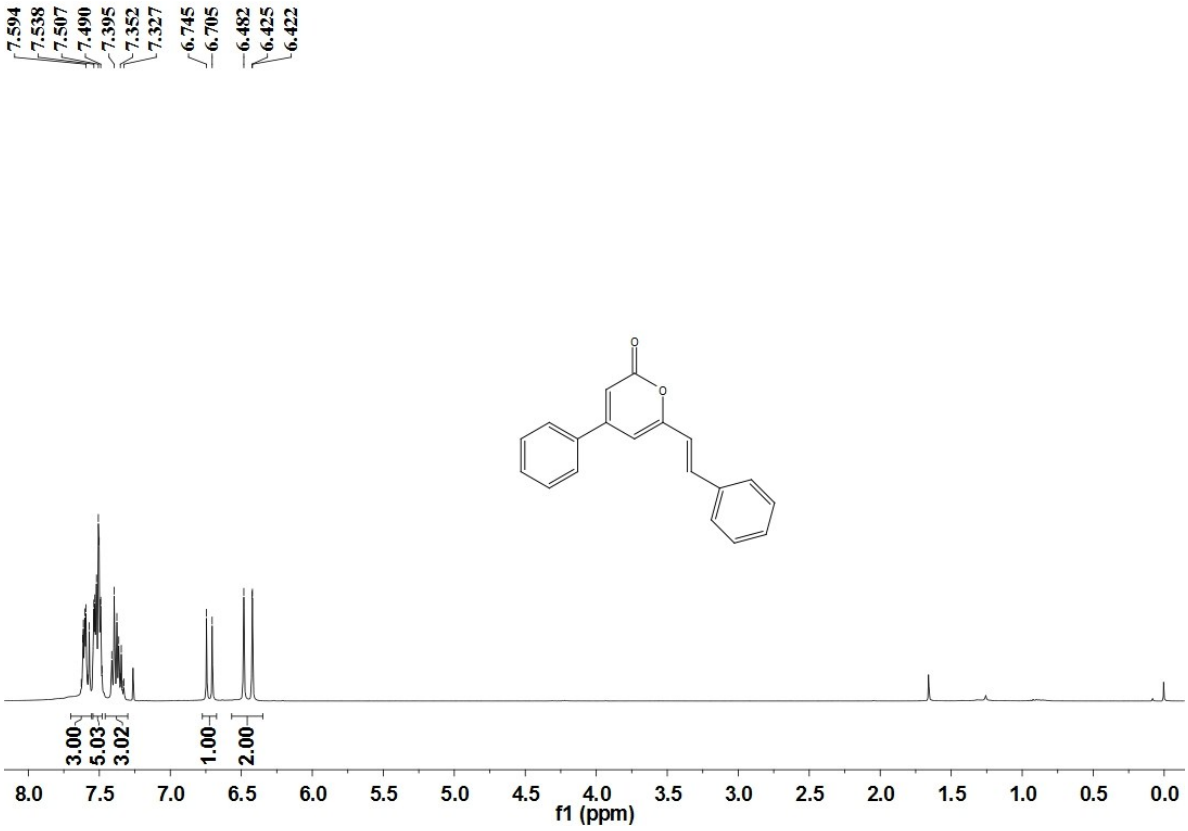

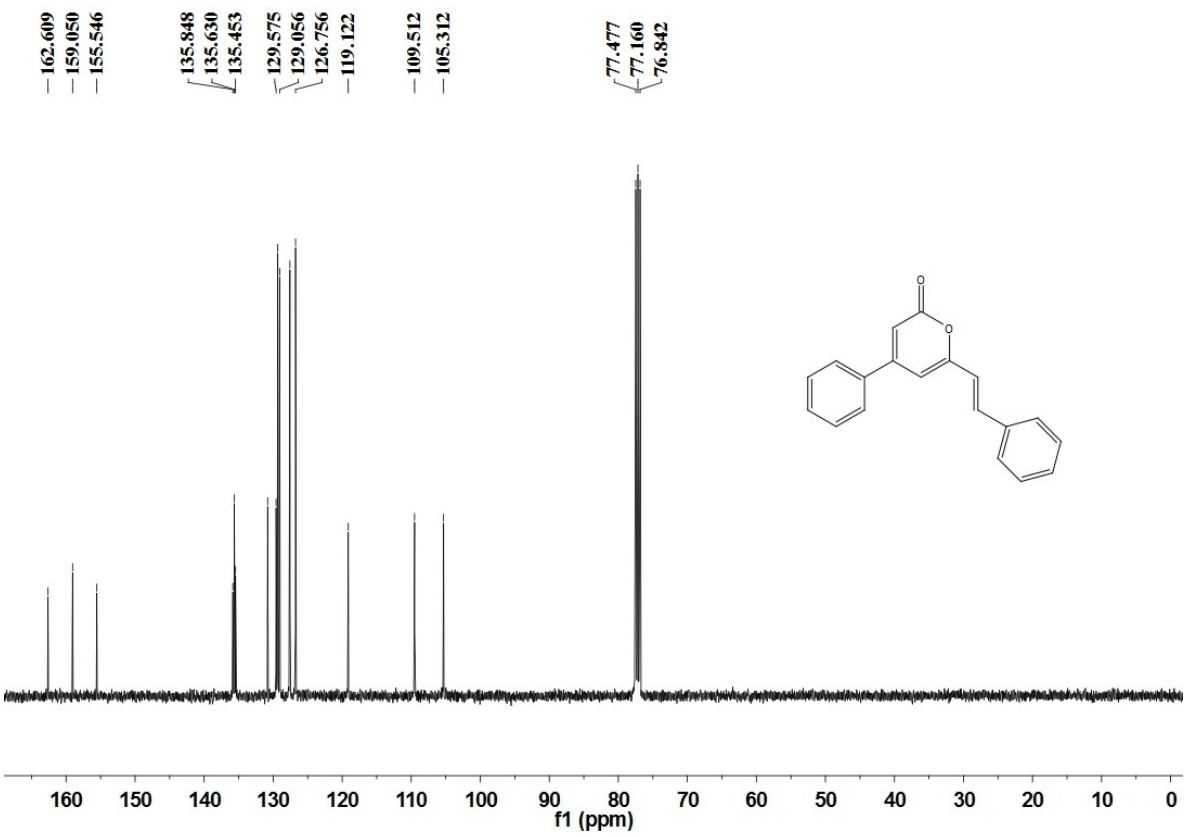

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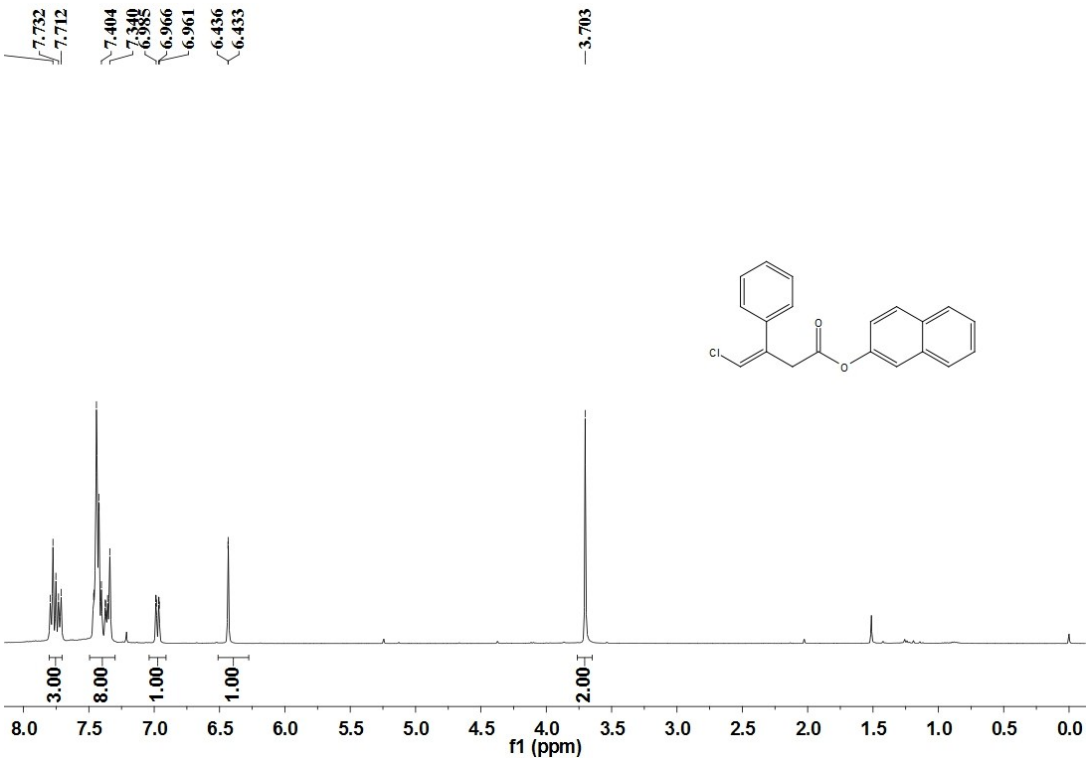
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6.433
3.703
Cl
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O
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8.00
1.00
1.00
2.00
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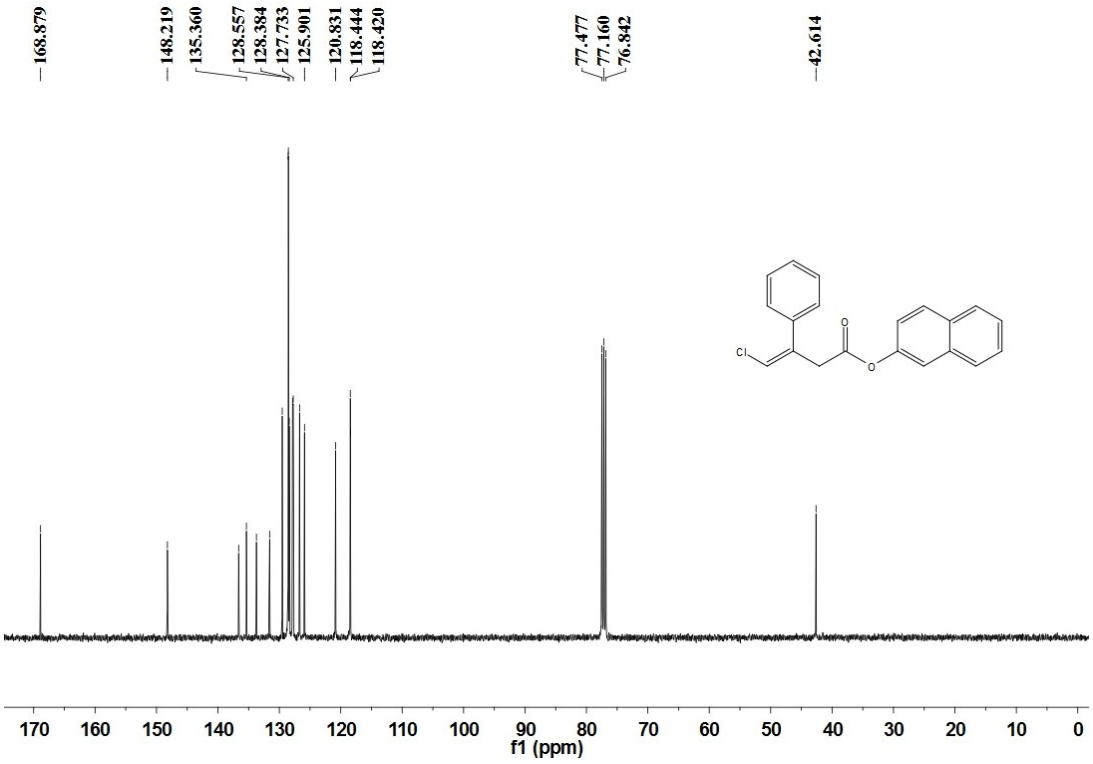
f1 (ppm)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Cl
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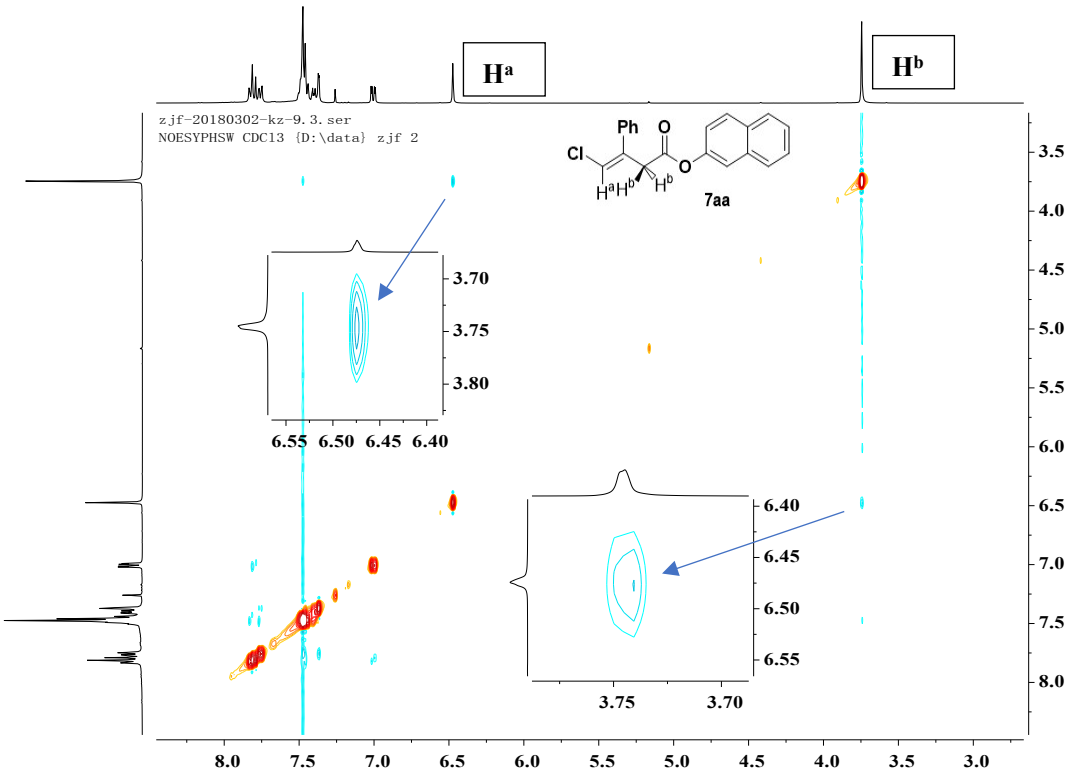
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O
Cl
HaHb
Hb
O
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3.75
3.80
6.55 6.50 6.45 6.40
6.40
6.45
6.50
6.55
3.75
3.70
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0
3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0