Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enantioselective Construction of Branched 1,3-Dienyl Substituted Quaternary Carbon Stereocenters by Asymmetric Allenyl Claisen Rearrangement

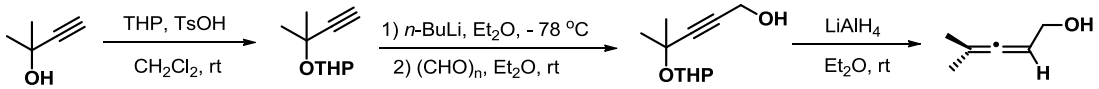
Yangbin Liu, Haipeng Hu, Lili Lin, Xiaoyu Hao, Xiaohua Liu,* Xiaoming Feng*

I. General information

^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26; DMSO, δ = 2.49). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; DMSO, δ = 39.6). Enantiomeric excesses (ee) were determined by HPLC analysis using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 ^{o}C. Optical rotations were reported as follows: $[a]^{T}_{D}$ (*c* g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All reagents and solvents were obtained from commercial suppliers and used without further purification except as indicated below. All catalytic reactions were run in dried glassware. THF and toluene were distilled from sodium benzophenone ketyl. CH_2Cl_2 and CH_2ClCH_2Cl were distilled over CaH_2.

II. Procedure of allenyl vinyl ethers preparation

1) General procedure for the synthesis of the allenols



A **B** **C** **D**

The procedures were further modified according to Giovanni Poli's report. Please see: A. Boutier, C. Kammerer-Pentier, N. Krause, G. Prestat, G. Poli, *Chem. Eur. J.* **2012**, *18*, 3840.

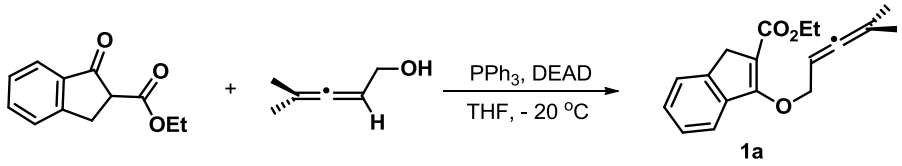
3,4-Dihydro-2*H*-pyran (1.1 equiv.) was added dropwise to a solution of 3-methylbut-1-yn-3-ol (1.0 equiv.) and *p*-toluenesulfonic acid (*p*-TSOH) (1 mol%) in dichloromethane (1 M). The resulting pink mixture was stirred at room temperature for 24 h and solid K_2CO_3 was then introduced. Dichloromethane was evaporated under reduced pressure and the residue was purified.

n-Butyllithium (1.1 equiv., 2.5 M solution in hexanes) was added dropwise to a solution of protected propargyl alcohol (1.0 equiv.) in distilled diethyl ether (1 M), cooled to -78 ℃. The temperature of the solution was carefully maintained below −50 ℃ during the addition. The reaction mixture was stirred at −78 ℃ during 45 min and paraformaldehyde (3.0 equiv.) was then added. The reaction was vigorously stirred and allowed to slowly reach room temperature overnight. The reaction medium was smoothly quenched with a mixture of ice and water, and the aqueous layer was extracted with diethyl ether. The combined organic layers were washed with

brine, dried on $MgSO_4$ and concentrated in vacuum. The crude product was purified by flash chromatography on silica gel.

Propargyl alcohol (1.0 equiv.) diluted in diethyl ether (1 M) was added dropwise to a suspension of powdered lithium and aluminium hydride $LiAlH_4$ (3.0 equiv.) in distilled diethyl ether (0.25 M), cooled to 0 ℃. The resulting reaction mixture was allowed to reach room temperature over 5 h (the completion of the reaction was monitored by ^1H NMR). The excess lithium and aluminium hydride was hydrolyzed at 0 ℃ by adding successively water, an aqueous NaOH solution (15% w/w) and water again. The biphasic mixture was then stirred vigorously during 1 h. The resulting white suspension was filtered on celatom and washed several times with diethyl ether. The combined organic layers were dried on Na_2SO_4 and concentrated in vacuum. The crude product was purified by flash chromatography on silica gel to afford the expected allenol.

2) General procedure for the synthesis of the allenyl vinyl ethers

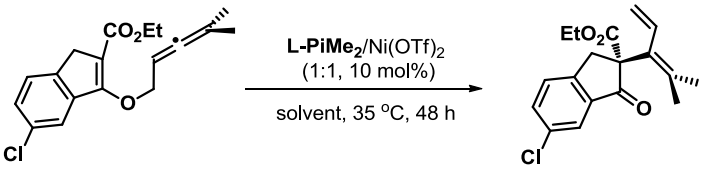


1a

PPh_3 (7.5 mmol) was dissolved in THF (10 mL), and the solution was cooled to –20 ^oC. DEAD (7.5 mmol), the allenic alcohol (6.0 mmol), and the β-ketoester (5.0 mmol) were added successively. The reaction was allowed to warm to room temperature over 2 h and continued stirring at room temperature until the β-ketoester was consumed as judged by TLC. Then, the reaction mixture was concentrated and chromatographed on SiO_2 column using 2–5% ethyl acetate/petroleum ether to afford the allenyl vinyl ethers.

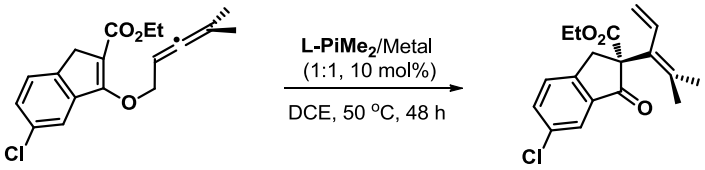
III. Optimization of reaction condition

Table S1: Screen of organic solvent



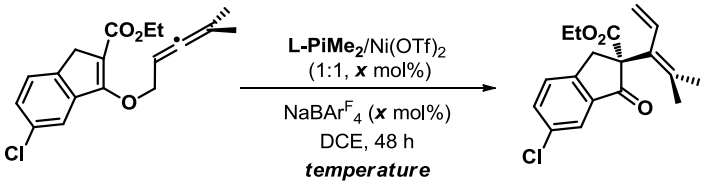
Entry	solvent	isolated yield (%)	*ee* (%)
1	toluene	12	96
2	CH_2Cl_2	57	99
3	Et_2O	40	98
4	THF	trace	--
5	CH_3CN	trace	--

Table S2: Screen of metal precursors



Entry	metal	isolated yield (%)	*ee* (%)
1	$Sc(OTf)_3$	<5	60
2	$Yb(OTf)_3$	35	58
3	$Cu(OTf)_2$	10	67
4	$NiCl_2$	trace	--
5	$Ni(OAc)_2$	trace	--
6	$Ni(ClO_4)_2$	<5	63

Table S3: Screen of catalyst loading and temperature

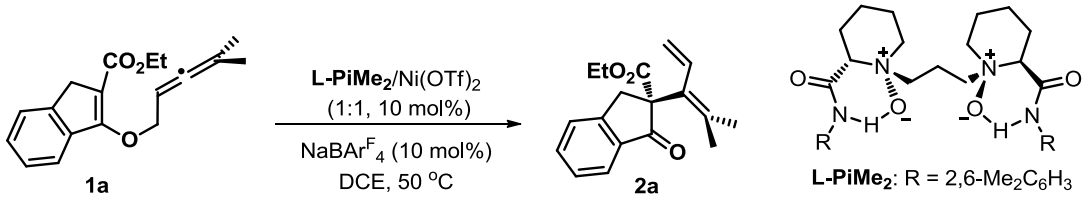


Entry	catalyst loading	temp.	isolated yield (%)	*ee* (%)
1[a]	10 mol%	50	80	99
2	5 mol%	50	82	86
3	3 mol%	50	84	85
4	1 mol%	50	41	80

5	10 mol%	35	54	95
6	10 mol%	70	82	89

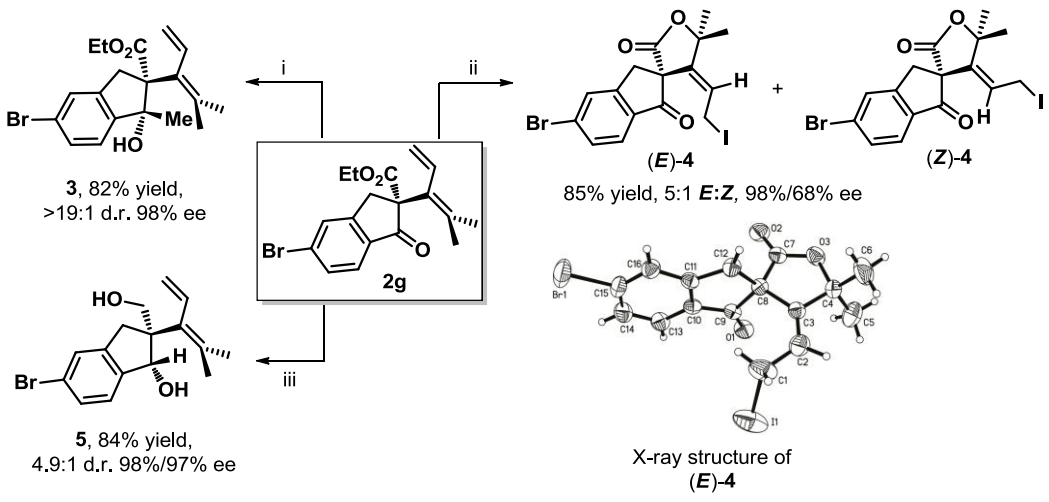
[a] The reaction mixture was stirred at 50 ℃ for 30 h.

IV. Procedure of catalytic asymmetric allenyl Claisen rearrangement



A dry reaction tube was charged with $Ni(OTf)_2$ (3.5 mg, 10 mol%), ligand **L-PiMe$_2$** (5.3 mg, 10 mol%) and $NaBAr^F_4$ (8.8 mg, 10 mol%). Then CH_2Cl_2 (0.5 mL) was added and the mixture was stirred at 35 ^oC for 0.5 h. After removing CH_2Cl_2 from tube under vacuum, the substrate **1a** (0.1 mmol) and CH_2ClCH_2Cl (1.0 mL) was added. The reaction mixture continued stirring at 50 ^oC for the indicated time. The residue was purified by flash chromatography on silica gel (1/15, EA/petroleum ether) to afford the desired product **2a**.

V. Procedure for the transformation of the rearrangement product



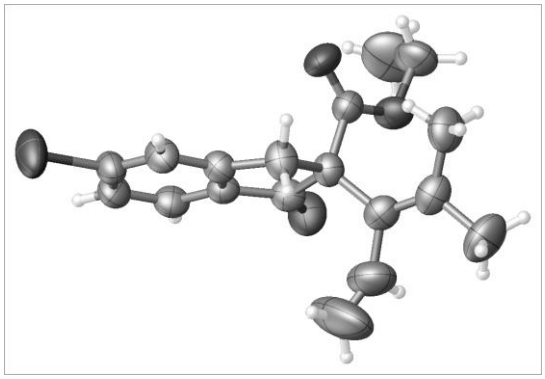
For compound **3**: To a flame-dried tube were charged with **2g** (0.1 mmol) and Et_2O (2.0 mL) under nitrogen atmosphere. The mixture was stirred at 0 ^oC and MeMgBr (0.4 mL, 1 M in THF) was added slowly. The reaction was allowed to warm to room temperature over 2 h and continued stirring at room temperature until the starting material was consumed as judged by TLC. The reaction was quenched with water and the aqueous layer was extracted with diethyl ether. The

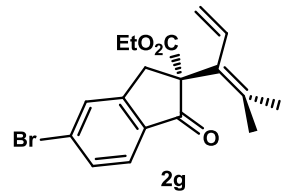
combined organic layers were washed with brine, dried on Na_2SO_4 and concentrated in vacuum. The crude product was purified by flash chromatography on silica gel eluting with PE/EA = 10/1 to afford the product **3** in 82% yield with19:1 d.r., 98% ee.

For compound **4**: The rearrangement product **2g** (25 mg, 0.07 mmol) was dissolved in $CHCl_3$ (1.0 mL) in a flame-dried tube. The reaction vessel was covered with foil and iodine (52.5 mg, 3.0 eq) was added. After stirring for 24 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 and washed with $Na_2S_2O_3$ (aq) and brine. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The crude reaction mixture was isolated via column chromatography with PE/EA = 7/1 to give spirolactone **4** in 85% yield. And the product **4** was analyzed by ^1H NMR and shown to be a 5:1 mixture of *E/Z*-isomers. The mixture was recrystallized from Et_2O/PE to obtain single crystal for X-ray analysis. Based on the crystal structure, the major isomer was determined to be *E*-configuration.

For compound **5**: To a solution of **2g** (0.1 mmol) in toluene (0.5 mL) was added DIBAL-H (0.6 mmol, 1.2 M in toluene) at –78 ℃. After ambient temperature was reached, the reaction mixture was stirred overnight. The mixture was diluted with water and 1 M HCl (aq) to get weak-acidic solution. The aqueous layer was extracted with CH_2Cl_2 (3×10 mL) and the combined organic layers were washed with brined, dried over anhydrous Na_2SO_4 and concentrated and purified through flash chromatograph (PE/EA =4/1) to give 1,3-diol **5** (84% yield, 4.9:1 d.r., 98%/97% ee).

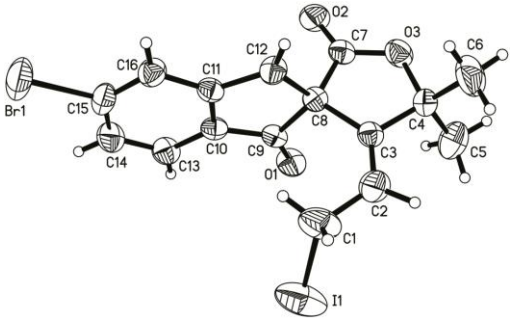
VI. X-ray structure of compound 2g and *E*-4

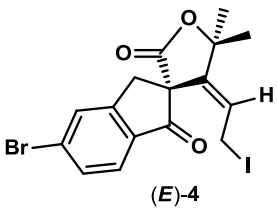




2g

(*R*)-ethyl 5-bromo-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate
CCDC 1479692



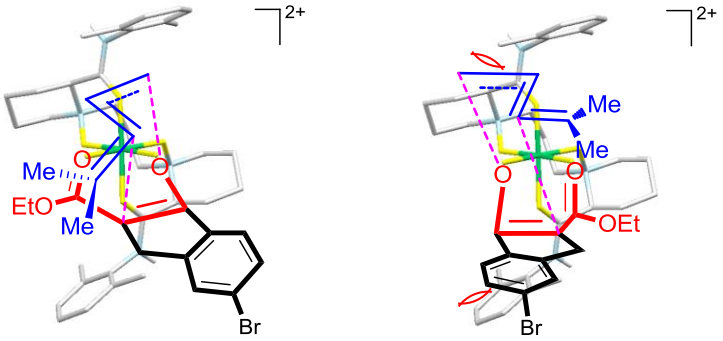


(*E*)-**4**

(*R*,*E*)-5'-bromo-4-(2-iodoethylidene)-5,5-dimethyl-4,5-dihydro-2*H*-spiro[furan-3,2'-indene]-1',2(3'*H*)-dione
CCDC 1480048

The supplementary crystallographic data can be obtained free of charge from the Cambrige Crystallographic Data Centere via www.ccdc.cam.ac.uk/data_request/cif.

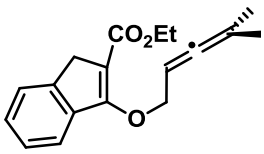
VII. Proposed stereochemical model



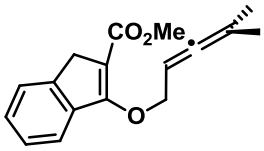
A1 *Re*-face favored **A2** *Si*-face disfavored

Based on the X-ray crystal structure of the *N,N'*-dioxide/ metal complexes,[18] the absolute configuration of the product **2g**, and our previous reports,[7] a possible stereochemical model was proposed. The 1*H*-indone-derived allenyl vinyl ether **1g** could be activated through coordination to the nickel atom in a bidentate fashion, which might result in two possible chairlike transition states. We postulate two adverse factors lead to the intermediate **A2** disfavorable: the steric hindrance between the 1*H*-indone backbone and the downward amide group of the ligand; the possible repulsive interaction of allenyl unit with the upward amide group ligand. Therefore, the allenyl would preferentially approach the enolate ether from the *Re* face to afford exclusive (*R*)-product (model **A1**).

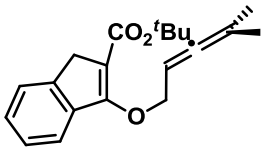
VIII. Spectral data of typical substrate



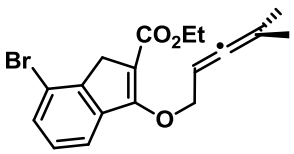
1a, colorless oil. 1H NMR (400 MHz, CDCl3) δ = 7.59 (dd, J=6.0, 2.3, 1H), 7.37 (ddt, J=12.1, 9.5, 4.3, 3H), 5.23 (qt, J=5.8, 2.8, 1H), 5.00 (d, J=6.7, 2H), 4.27 (q, J=7.1, 2H), 3.66 (s, 2H), 1.61 (d, J=2.8, 6H), 1.35 (t, J=7.1, 3H). 13C NMR (100 MHz, CDCl3) δ = 203.26, 164.64, 163.83, 141.97, 140.59, 128.30, 126.56, 124.08, 121.03, 110.84, 96.95, 86.05, 72.33, 59.94, 36.38, 20.23, 14.46.



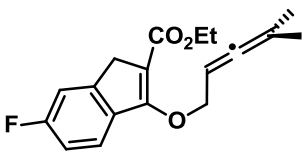
1b, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.48 (m, 1H), 7.37 – 7.32 (m, 1H), 7.31 – 7.24 (m, 2H), 5.22 – 5.09 (m, 1H), 4.94 (d, *J*=6.7, 2H), 3.73 (s, 3H), 3.58 (s, 2H), 1.53 (d, *J*=2.8, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.26, 165.01, 164.10, 141.98, 140.46, 128.40, 126.60, 124.12, 121.11, 110.20, 97.01, 86.02, 72.35, 51.27, 36.34, 20.23.



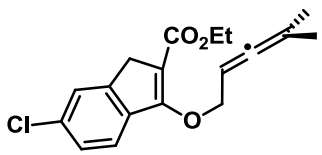
1c, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 – 7.47 (m, 1H), 7.33 (dd, *J*=5.0, 3.0, 1H), 7.29 – 7.20 (m, 2H), 5.20 – 5.10 (m, 1H), 4.86 (d, *J*=6.8, 2H), 3.53 (s, 2H), 1.53 (d, *J*=2.8, 6H), 1.49 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.35, 164.20, 162.87, 141.85, 140.76, 128.00, 126.48, 124.03, 120.90, 113.61, 96.85, 86.08, 80.03, 72.13, 36.56, 28.42, 20.26.



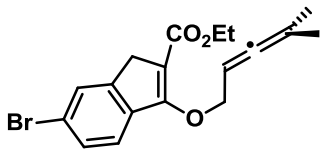
1d, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 – 7.40 (m, 2H), 7.19 – 7.13 (m, 1H), 5.16 – 5.10 (m, 1H), 4.93 (d, *J*=6.7, 2H), 4.23 – 4.18 (m, 2H), 3.53 (d, *J*=3.3, 2H), 1.53 (d, *J*=2.8, 6H), 1.29 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.35, 164.24, 162.84, 142.24, 141.75, 131.29, 128.51, 120.09, 119.04, 111.33, 97.08, 85.84, 72.49, 60.17, 37.69, 20.24, 14.46.



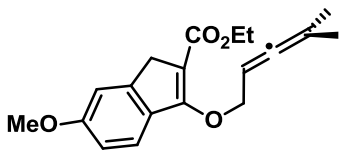
1e, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.45 (dd, *J*=8.4, 5.1, 1H), 7.04 (dd, *J*=8.5, 2.0, 1H), 6.96 (td, *J*=9.2, 2.3, 1H), 5.20 – 5.05 (m, 1H), 4.93 (d, *J*=6.7, 2H), 4.22 – 4.15 (m, 2H), 3.56 (s, 2H), 1.53 (d, *J*=2.8, 6H), 1.27 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.27, 163.62 (d, *J*=246), 164.31, 163.07, 144.08 (d, *J*=10), 136.62 (d, *J*=2), 122.24 (d, *J*=9), 114.08 (d, *J*=24), 111.50 (d, *J*=24), 110.15 (d, *J*=3), 97.04, 85.93, 72.40, 59.98, 36.32 (d, *J*=2), 20.22, 14.44.



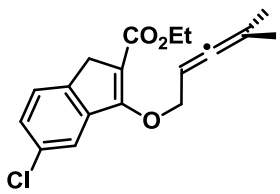
1f, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.43 (d, *J*=8.1, 1H), 7.32 (d, *J*=1.2, 1H), 7.24 (dd, *J*=8.2, 1.8, 1H), 5.18 – 5.08 (m, 1H), 4.92 (d, *J*=6.7, 2H), 4.19 (q, *J*=7.1, 2H), 3.57 (s, 2H), 1.54 (d, *J*=2.8, 6H), 1.28 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.31, 164.34, 162.87, 143.35, 139.18, 134.52, 127.07, 124.44, 121.97, 110.77, 97.09, 85.87, 72.42, 60.09, 36.21, 20.23, 14.44.



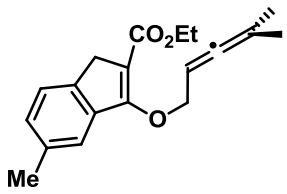
1g, light red solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, *J*=0.8, 1H), 7.39 (dt, *J*=14.0, 4.8, 2H), 5.17 – 5.07 (m, 1H), 4.92 (d, *J*=6.7, 2H), 4.19 (dt, *J*=7.1, 5.8, 2H), 3.55 (s, 2H), 1.53 (d, *J*=2.8, 6H), 1.28 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.32, 164.31, 162.90, 143.62, 139.63, 129.89, 127.35, 122.77, 122.28, 110.74, 97.09, 85.86, 72.43, 60.11, 36.22, 20.24, 14.44.



1h, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J*=8.4, 1H), 6.90 (d, *J*=1.8, 1H), 6.82 (dd, *J*=8.4, 2.2, 1H), 5.15 (td, *J*=6.5, 3.3, 1H), 4.92 (d, *J*=6.7, 2H), 4.18 (q, *J*=7.1, 2H), 3.78 (s, 3H), 3.55 (s, 2H), 1.55 (d, *J*=2.8, 6H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.22, 164.59, 164.17, 160.75, 144.27, 133.40, 121.99, 113.13, 109.55, 108.79, 96.92, 86.09, 72.31, 59.76, 55.54, 36.21, 20.26, 14.50.

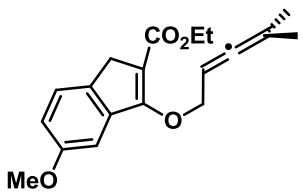


1i, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.52 – 7.45 (m, 1H), 7.25 (d, *J*=1.6, 2H), 5.21 – 5.06 (m, 1H), 4.91 (d, *J*=6.6, 2H), 4.20 (q, *J*=7.1, 2H), 3.56 (s, 2H), 1.54 (t, *J*=2.8, 6H), 1.28 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.27, 164.31, 162.47, 142.38, 139.93, 132.77, 128.31, 125.12, 121.13, 112.11, 97.23, 85.89, 72.40, 60.14, 36.06, 20.23, 14.43.

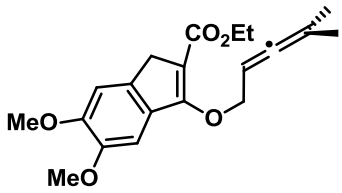


1j, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, *J*=0.6, 1H), 7.22 (d, *J*=7.6, 1H), 7.09 (dd, *J*=7.6, 0.8, 1H), 5.16 (qt, *J*=5.7, 2.8, 1H), 4.91 (d, *J*=6.7, 2H), 4.18 (q, *J*=7.1, 2H), 3.53 (s, 2H), 2.33 (s, 3H), 1.55 (d, *J*=2.8, 6H), 1.27 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.25, 164.68, 163.93, 140.73, 139.16, 136.29, 129.37, 123.80,

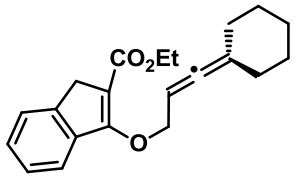
121.39, 111.04, 96.92, 86.12, 72.31, 59.90, 35.97, 21.46, 20.26, 14.47.



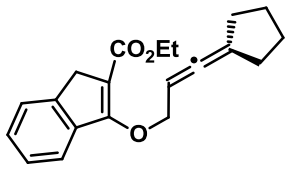
1k, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.22 (d, *J*=8.2, 1H), 7.01 (dd, *J*=8.5, 2.4, 1H), 6.86 (dd, *J*=8.2, 2.5, 1H), 5.16 (pd, *J*=5.7, 2.8, 1H), 4.93 (d, *J*=6.7, 2H), 4.18 (dt, *J*=7.1, 6.1, 2H), 3.77 (s, 3H), 3.51 (s, 2H), 1.54 (d, *J*=2.8, 6H), 1.27 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.28, 164.57, 163.57, 159.02, 141.90, 134.16, 124.71, 115.78, 111.83, 104.97, 96.96, 86.03, 72.33, 59.94, 55.57, 35.68, 20.26, 14.45.



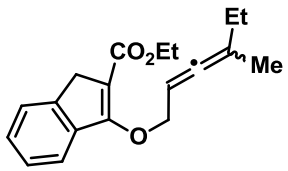
1l, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.00 (s, 1H), 6.88 (s, 1H), 5.16 (qt, *J*=5.7, 2.8, 1H), 4.95 (d, *J*=6.7, 2H), 4.18 (q, *J*=7.1, 2H), 3.86 (d, *J*=3.4, 6H), 3.52 (s, 2H), 1.55 (d, *J*=2.8, 6H), 1.27 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.22, 164.44, 164.16, 150.49, 148.67, 135.34, 133.07, 108.91, 107.10, 103.33, 96.92, 86.09, 72.34, 59.74, 56.14, 36.20, 20.27, 14.49.



1m, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 – 7.50 (m, 1H), 7.36 – 7.33 (m, 1H), 7.27 (tt, *J*=7.2, 5.8, 2H), 5.22 – 5.10 (m, 1H), 4.94 (d, *J*=6.8, 2H), 4.20 (q, *J*=7.1, 2H), 3.58 (s, 2H), 2.00 – 1.90 (m, 4H), 1.48 – 1.35 (m, 6H), 1.28 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.14, 164.65, 163.79, 141.98, 140.59, 128.30, 126.56, 124.09, 121.09, 110.83, 103.94, 85.81, 72.63, 59.94, 36.37, 31.11, 27.13, 25.97, 14.49.

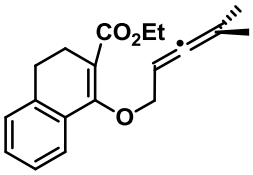


1n, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.60 (d, *J*=6.4, 1H), 7.41 (d, *J*=6.8, 1H), 7.33 (d, *J*=5.7, 2H), 5.33 (s, 1H), 5.03 (d, *J*=6.6, 2H), 4.29 – 4.24 (m, 2H), 3.66 (s, 2H), 2.33 – 2.3 (m, 4H), 1.63 –1.57 (m, 4H), 1.35 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.60, 164.64, 163.87, 141.96, 140.57, 128.30, 126.54, 124.07, 121.06, 110.62, 105.45, 88.48, 72.41, 59.93, 36.41, 31.14, 27.01, 14.47.

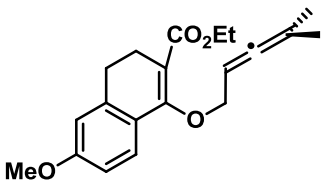


1o, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 (ddd, *J*=7.1, 4.0, 2.8, 1H), 7.29 (dd, *J*=5.7, 2.3, 1H), 7.24 – 7.18 (m, 2H), 5.24 (ddt, *J*=9.6, 6.2, 3.0, 1H), 4.96 – 4.87 (m, 2H), 4.15 (dt, *J*=7.1, 5.5, 2H), 3.53 (s, 2H), 1.76 (tt, *J*=7.3, 3.7, 2H), 1.51 (d, *J*=2.8, 3H), 1.24 (t,

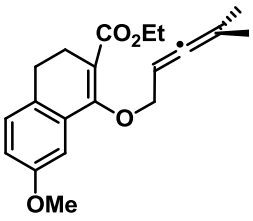
J=7.1, 3H), 0.81 (t, *J*=7.4, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 202.48, 164.56, 163.94, 141.95, 140.59, 128.31, 126.54, 124.05, 120.99, 110.81, 103.12, 88.08, 72.55, 59.89, 36.38, 26.69, 18.72, 14.46, 12.01.



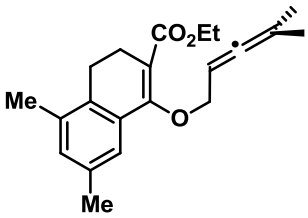
1p, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.57 (m, 1H), 7.26 – 7.20 (m, 2H), 7.17 – 7.12 (m, 1H), 5.28 (ddd, *J*=9.7, 6.8, 3.0, 1H), 4.41 (d, *J*=7.0, 2H), 4.27 (tt, *J*=7.1, 3.5, 2H), 2.77 (t, *J*=7.7, 2H), 2.66 – 2.60 (m, 2H), 1.66 (dd, *J*=2.8, 1.0, 6H), 1.35 (td, *J*=7.1, 1.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.42, 167.22, 158.56, 138.93, 131.58, 129.40, 127.32, 126.47, 124.46, 114.93, 96.35, 85.99, 72.41, 60.29, 27.80, 24.23, 20.25, 14.35.



1q, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.46 (d, *J*=8.5, 1H), 6.68 (dd, *J*=8.6, 2.5, 1H), 6.62 (d, *J*=2.3, 1H), 5.32 – 5.07 (m, 1H), 4.32 (d, *J*=7.1, 2H), 4.18 (q, *J*=7.1, 2H), 3.73 (s, 3H), 2.69 – 2.64 (m, 2H), 2.56 – 2.51 (m, 2H), 1.58 (d, *J*=2.8, 6H), 1.27 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.37, 167.35, 160.67, 159.23, 141.25, 126.26, 124.44, 113.18, 112.29, 111.47, 96.35, 85.99, 72.48, 60.20, 55.27, 28.29, 24.18, 20.31, 14.38.



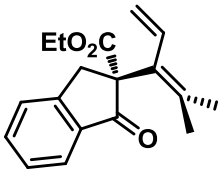
1r, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, *J*=2.3, 1H), 7.07 (d, *J*=8.2, 1H), 6.81 (dd, *J*=8.2, 2.4, 1H), 5.28 (dd, *J*=6.1, 3.1, 1H), 4.41 (d, *J*=7.1, 2H), 4.28 (q, *J*=7.1, 2H), 3.80 (s, 3H), 2.75 – 2.67 (m, 2H), 2.65 – 2.55 (m, 2H), 1.66 (d, *J*=2.7, 6H), 1.36 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.43, 167.30, 158.46, 158.29, 132.63, 131.07, 128.13, 115.50, 114.95, 109.89, 96.43, 85.89, 72.50, 60.35, 55.34, 55.32, 26.88, 24.59, 20.26, 14.34.



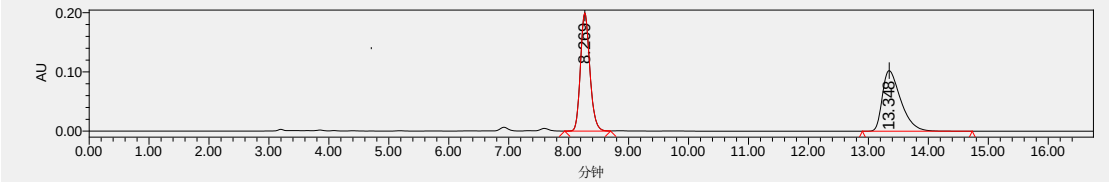
1s, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (s, 1H), 6.91 (s, 1H), 5.31 – 5.10 (m, 1H), 4.29 (d, *J*=7.1, 2H), 4.20 (q, *J*=7.1, 2H), 2.63 – 2.58 (m, 2H), 2.55 – 2.49 (m, 2H), 2.24 (s, 3H), 2.19 (s, 3H), 1.61 (d, *J*=2.8, 6H), 1.29 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 203.38, 167.45, 158.94, 135.24, 134.76, 134.43, 132.30, 131.32, 122.98, 114.41, 96.34, 85.96, 72.31, 60.33, 23.90, 23.51, 21.21, 20.35, 19.34, 14.38.

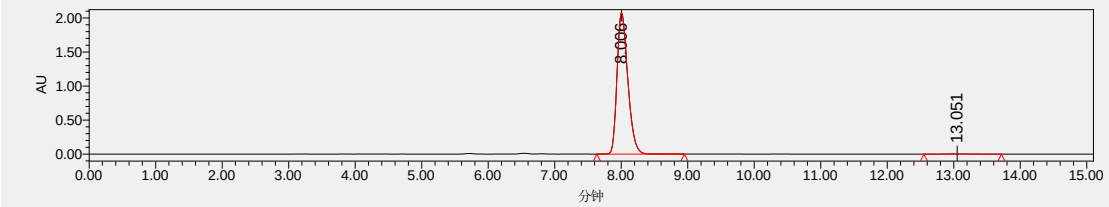
IX. Spectral data of rearrangement product

(*R*)-ethyl 2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2a).



Reaction time: 48 h; Yield: 90%; $[\alpha]^{15}_{D}$ = −9.9 (*c* 1.53, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 8.00 min, $t_{R(minor)}$ = 13.05 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 1H), 6.43 (dd, *J* = 17.8, 11.3 Hz, 1H), 5.03 (dd, *J* = 11.3, 1.4 Hz, 1H), 4.79 (dd, *J* = 17.8, 1.3 Hz, 1H), 4.28 (d, *J* = 17.1 Hz, 1H), 4.22 – 4.10 (m, 2H), 3.22 (d, *J* = 17.1 Hz, 1H), 1.80 (s, 3H), 1.57 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.49, 170.27, 153.03, 136.67, 135.28, 135.01, 133.70, 131.92, 127.68, 126.14, 124.88, 116.00, 67.09, 62.18, 40.44, 23.10, 22.74, 13.98. ESI-HRMS calcd for [$C_{18}H_{20}O_3$+Na^+]: 307.1310, found 307.1314.

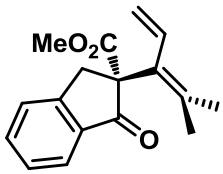




	Retention Time	Area	% Area
1	8.269	2174107	49.88
2	13.348	2184193	50.12

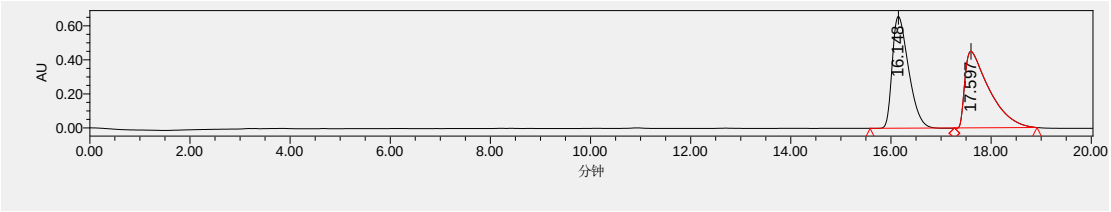
	Retention Time	Area	% Area
1	8.006	23347533	99.75
2	13.051	57868	0.25

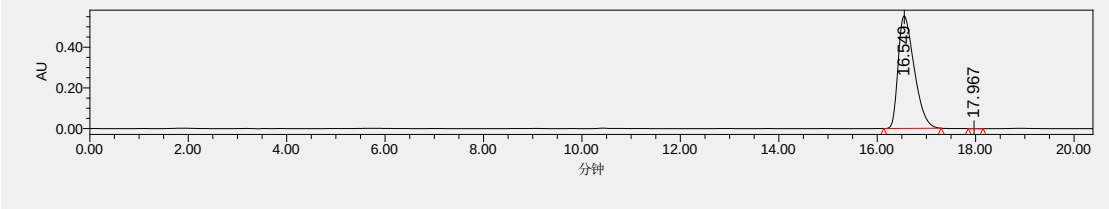
(*R*)-methyl 2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2b).



Reaction time: 34 h; Yield: 85%; $[\alpha]^{25}_{D}$ = −382.8 (*c* 0.46, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $t_{R(major)}$ = 16.55 min, $t_{R(minor)}$ = 17.97 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (t, *J*=10.8, 1H), 7.54 (t, *J*=7.4, 1H), 7.41 (d, *J*=7.7, 1H), 7.31 (t, *J*=7.5, 1H), 6.36 (dd, *J*=17.8, 11.3, 1H), 4.96 (dd, *J*=11.3, 1.2, 1H), 4.71 (dd, *J*=17.8, 1.1, 1H), 4.22 (d, *J*=17.1, 1H), 3.63 (s, 3H), 3.14 (d, *J*=17.1, 1H), 1.74 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.49, 170.92, 153.07, 136.56, 135.41, 134.92, 134.02, 131.78, 127.76, 126.19, 125.01, 115.94,

67.06, 53.30, 40.32, 23.02, 22.78. ESI-HRMS calcd for [$C_{17}H_{18}O_3$+Na^+]: 293.1154, found 293.1150.

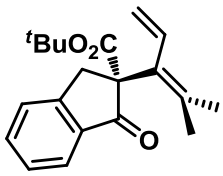




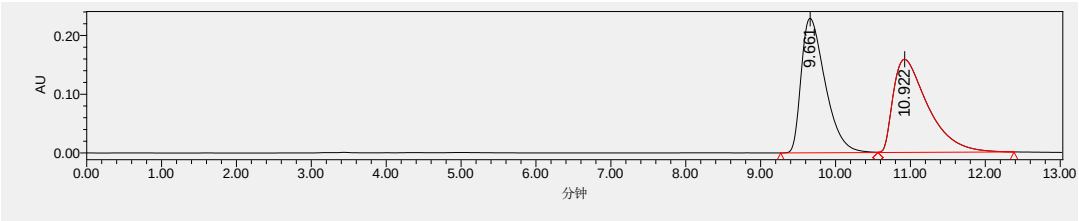
	Retention Time	Area	% Area
1	16.148	14903821	49.57
2	17.597	15160423	50.43

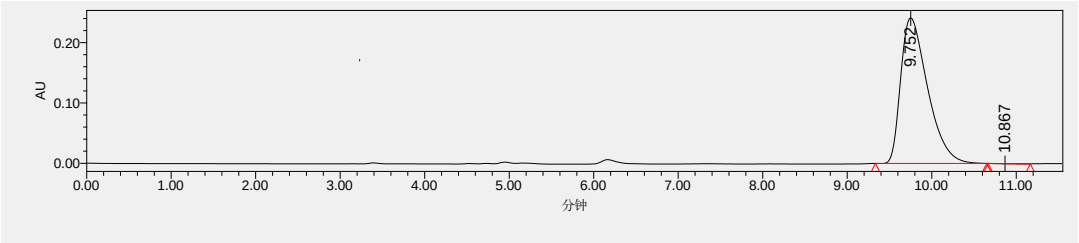
	Retention Time	Area	% Area
1	16.549	12558767	100.00
2	17.967	42	0.00

(*R*)-*tert*-butyl 2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2c).



Reaction time: 48 h; Yield: 90%; $[\alpha]^{25}_D$ = −253.1 (*c* 0.57, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 99/1, 1.0 mL/min, $t_{R(major)}$ = 9.75 min, $t_{R(minor)}$ = 10.87 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J*=7.7, 1H), 7.62 – 7.55 (m, 1H), 7.45 (d, *J*=7.7, 1H), 7.36 (t, *J*=7.4, 1H), 6.36 (dd, *J*=17.8, 11.2, 1H), 5.04 (dd, *J*=11.2, 1.7, 1H), 4.77 (dd, *J*=17.8, 1.6, 1H), 4.16 (d, *J*=17.1, 1H), 3.21 (d, *J*=17.1, 1H), 1.79 (s, 3H), 1.61 (s, 3H), 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.96, 169.21, 153.03, 136.88, 135.32, 135.03, 133.03, 132.44, 127.54, 126.03, 124.73, 116.36, 81.99, 67.68, 40.73, 27.68, 23.16, 22.71. ESI-HRMS calcd for [$C_{20}H_{24}O_3$+Na^+]: 335.1623, found 335.1619.

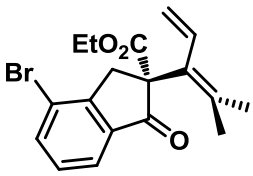




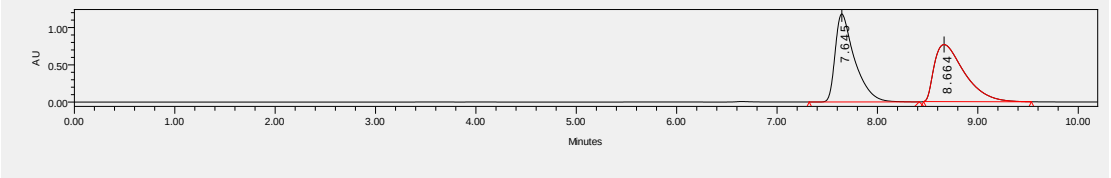
	Retention Time	Area	% Area
1	9.661	5095969	49.97
2	10.922	5102855	50.03

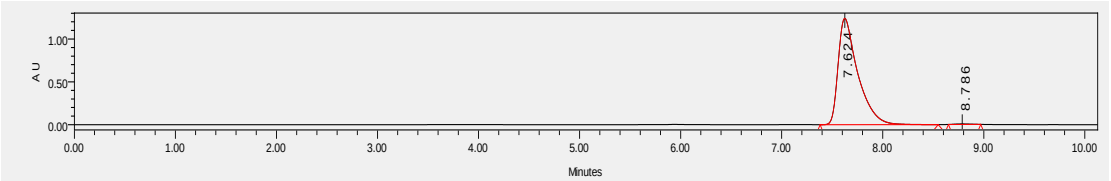
	Retention Time	Area	% Area
1	9.752	5321073	99.92
2	10.867	4067	0.08

(*R*)-ethyl 4-bromo-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2d).



Reaction time: 48 h; Yield: 84%; $[\alpha]^{25}_{D}$ = −266.0 (*c* 0.60, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $t_{R(major)}$ = 7.62 min, $t_{R(minor)}$ = 8.79 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.71 (d, *J*=7.7, 1H), 7.64 (d, *J*=7.6, 1H), 7.24 – 7.19 (m, 1H), 6.33 (dd, *J*=17.7, 11.3, 1H), 5.05 – 4.93 (m, 1H), 4.72 (d, *J*=17.8, 1H), 4.21 – 4.03 (m, 3H), 3.05 (d, *J*=17.6, 1H), 1.74 (s, 3H), 1.50 (s, 3H), 1.17 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.93, 169.85, 152.66, 138.08, 136.94, 136.42, 134.19, 131.56, 129.50, 123.74, 121.65, 116.42, 67.13, 62.46, 41.41, 23.20, 22.77, 13.99. ESI-HRMS calcd for $[C_{18}H_{19}{}^{79}BrO_3+Na^+]$: 385.0415, found 385.0415； $[C_{18}H_{19}{}^{81}BrO_3+Na^+]$: 387.0355, found 387.0399.



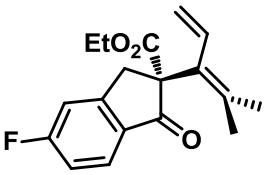


	Retention Time	Area	% Area
1	7.645	15846082	49.86
2	8.664	15932530	50.14

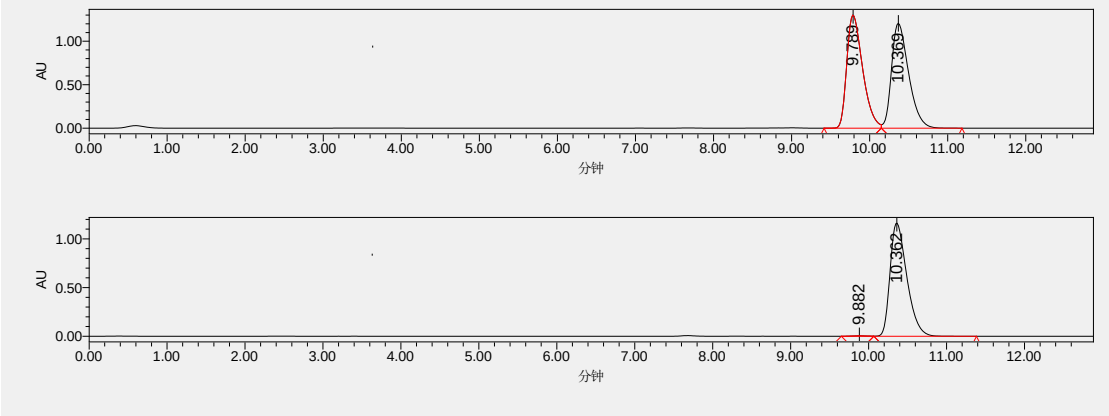
	Retention Time	Area	% Area
1	7.624	16698612	99.62
2	8.786	63058	0.38

(*R*)-ethyl 5-fluoro-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-

carboxylate (2e).



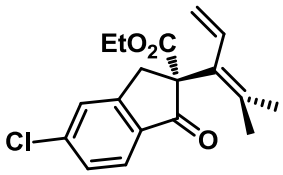
Reaction time: 36 h; Yield: 83%; $[\alpha]^{25}_{D}$ = −333.6 (*c* 0.50, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $t_{R(major)}$ = 10.36 min, $t_{R(minor)}$ = 9.88 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 (dd, *J*=8.4, 5.3, 1H), 7.14 (d, *J*=8.3, 1H), 7.11 – 7.02 (m, 1H), 6.43 (dd, *J*=17.8, 11.3, 1H), 5.04 (d, *J*=11.3, 1H), 4.78 (d, *J*=17.8, 1H), 4.26 (d, *J*=17.3, 1H), 4.21 – 4.10 (m, 2H), 3.19 (d, *J*=17.3, 1H), 1.80 (s, 3H), 1.56 (s, 3H), 1.24 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.66, 170.13, 167.43 (d, *J*=256), 156.00 (d, *J*=10), 136.58, 133.99, 131.68, 131.37 (d, *J*=2), 127.30 (d, *J*=11), 116.12 (d, *J*=24), 116.11, 112.87 (d, *J*=22), 67.40, 62.38, 40.23, 23.08, 22.76, 13.99. ESI-HRMS calcd for $[C_{18}H_{19}FO_3+Na^+]$: 325.1216, found 325.1214.



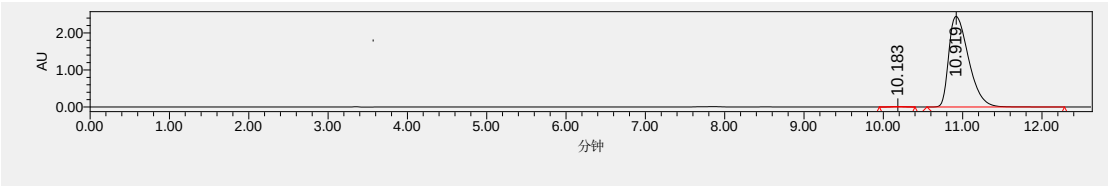
	Retention Time	Area	% Area
1	9.789	18336749	50.02
2	10.369	18323519	49.98

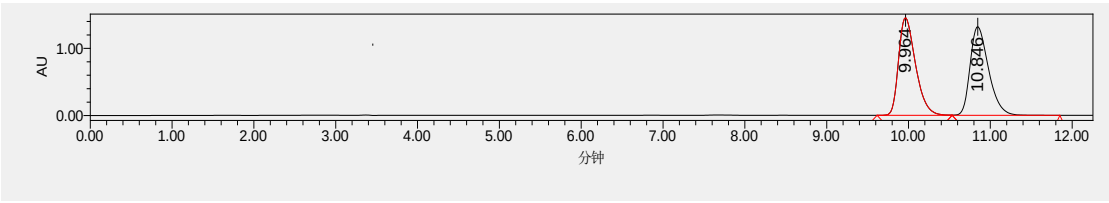
	Retention Time	Area	% Area
1	9.882	63313	0.36
2	10.362	17443364	99.64

(*R*)-ethyl 5-chloro-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2f).



Reaction time: 120 h; Yield: 74%; $[\alpha]^{17}_{D}$ = −328.6 (*c* 0.47, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $t_{R(major)}$ = 10.92 min, $t_{R(minor)}$ = 10.18 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J*=8.2, 1H), 7.40 (d, *J*=0.9, 1H), 7.33 – 7.24 (m, 1H), 6.35 (dd, *J*=17.8, 11.3, 1H), 4.96 (dd, *J*=11.3, 1.5, 1H), 4.70 (dd, *J*=17.8, 1.4, 1H), 4.18 (d, *J*=17.3, 1H), 4.14 – 4.04 (m, 2H), 3.10 (d, *J*=17.3, 1H), 1.72 (s, 3H), 1.48 (d, *J*=0.9, 3H), 1.16 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.11, 169.98, 154.46, 141.90, 136.53, 134.07, 133.44, 131.56, 128.58, 126.40, 126.03, 116.15, 67.30, 62.42, 40.05, 23.15, 22.74, 13.99. ESI-HRMS calcd for $[C_{18}H_{19}{}^{35}ClO_3+Na^+]$: 341.0920, found 341.0917; $[C_{18}H_{19}{}^{37}ClO_3+Na^+]$: 343.0891, found 343.0862.

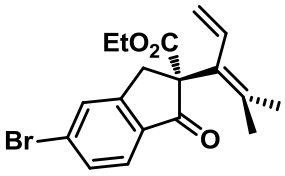




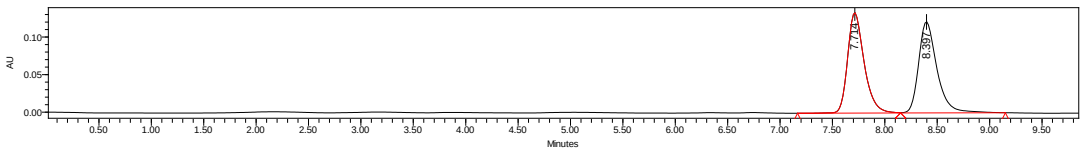
	Retention Time	Area	% Area
1	9.964	20874454	50.35
2	10.846	20584849	49.65

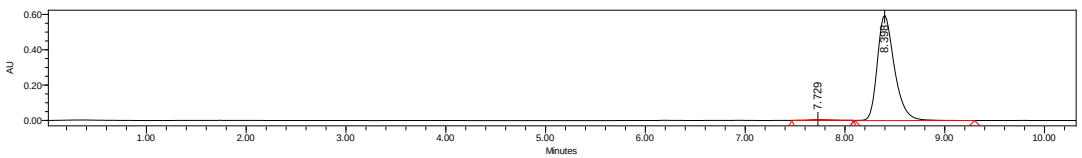
	Retention Time	Area	% Area
1	10.183	113458	0.27
2	10.919	42547760	99.73

(*R*)-ethyl 5-bromo-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2g).



Reaction time: 53 h; Yield: 87%; $[\alpha]^{25}_{D}$ = −286.5 (*c* 0.51, CH_2Cl_2, 98% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 8.40 min, $t_{R(minor)}$ = 7.73 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (s, 1H), 7.62 (d, *J*=8.2, 1H), 7.52 (d, *J*=8.2, 1H), 6.41 (dd, *J*=17.8, 11.3, 1H), 5.04 (dd, *J*=11.3, 1.3, 1H), 4.77 (dd, *J*=17.8, 1.1, 1H), 4.25 (d, *J*=17.3, 1H), 4.21 – 4.10 (m, 2H), 3.18 (d, *J*=17.3, 1H), 1.80 (s, 3H), 1.55 (s, 3H), 1.23 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.36, 169.94, 154.57, 136.53, 134.10, 133.85, 131.52, 131.43, 130.83, 129.49, 126.11, 116.19, 67.23, 62.44, 40.00, 23.16, 22.75, 13.99. ESI-HRMS calcd for $[C_{18}H_{19}{}^{79}BrO_3+Na^+]$: 385.0415, found 385.0417; $[C_{18}H_{19}{}^{81}BrO_3+Na^+]$: 387.0395, found 387.0400.

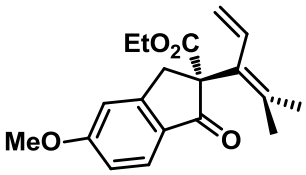




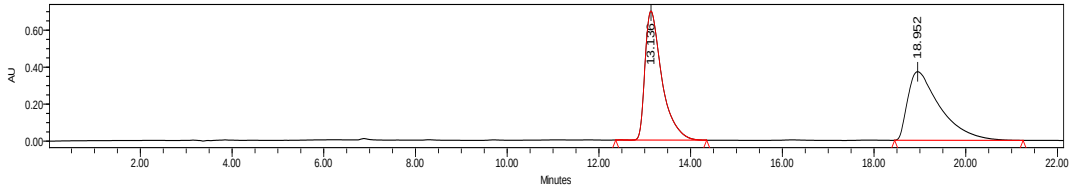
	Retention Time	Area	% Area
1	7.714	1464629	49.87
2	8.397	1472532	50.13

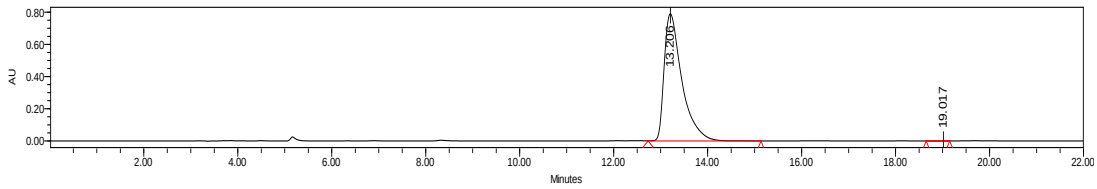
	Retention Time	Area	% Area
1	7.729	51630	0.72
2	8.398	7087878	99.28

(*R*)-ethyl 5-methoxy-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2h).



Reaction time: 48 h; Yield: 77%; $[\alpha]^{17}_{D}$ = −359.7 (*c* 0.49, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, $t_{R(major)}$ = 13.21 min, $t_{R(minor)}$ = 19.02 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.62 (d, *J*=9.2, 1H), 6.90 – 6.76 (m, 2H), 6.39 (dd, *J*=17.8, 11.3, 1H), 4.95 (dd, *J*=11.3, 1.5, 1H), 4.72 (dd, *J*=17.9, 1.5, 1H), 4.15 (t, *J*=9.6, 1H), 4.13 – 3.97 (m, 2H), 3.82 (s, 3H), 3.06 (d, *J*=17.1, 1H), 1.73 (s, 3H), 1.50 (d, *J*=0.9, 3H), 1.16 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.57, 170.61, 165.77, 156.14, 136.81, 133.69, 132.02, 128.19, 126.70, 115.86, 115.69, 109.16, 67.37, 62.21, 55.71, 40.40, 23.04, 22.78, 14.03. ESI-HRMS calcd for [$C_{19}H_{22}O_4$+Na^+]: 337.1416, found 337.1412.

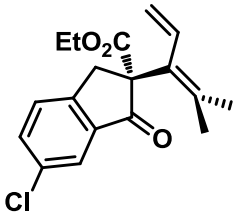




	Retention Time	Area	% Area
1	13.136	17812167	49.54
2	18.952	18140863	50.46

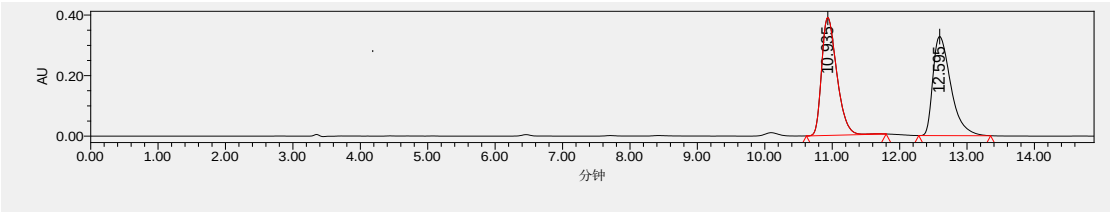
	Retention Time	Area	% Area
1	13.206	20636015	100.00
2	19.017	673	0.00

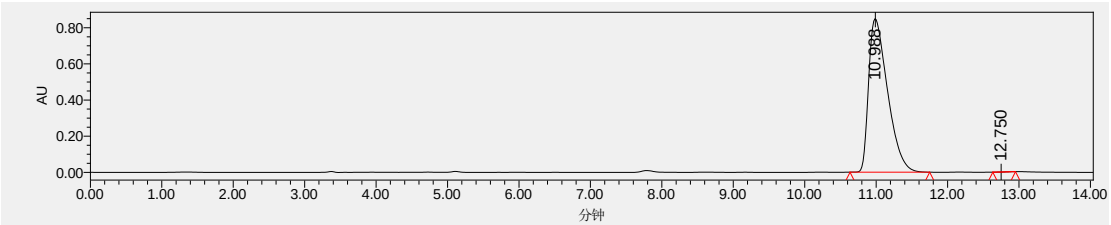
(*R*)-ethyl 6-chloro-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2i).



Reaction time: 30 h; Yield: 80%; $[\alpha]^{17}_{D}$ = −331.1 (*c* 0.51, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $t_{R(major)}$ = 10.99 min, $t_{R(minor)}$ = 12.75 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ

= 7.65 (d, *J*=1.9, 1H), 7.49 (dd, *J*=8.1, 2.0, 1H), 7.36 (d, *J*=8.2, 1H), 6.34 (dd, *J*=17.8, 11.3, 1H), 4.97 (dd, *J*=11.3, 1.4, 1H), 4.70 (dd, *J*=17.8, 1.4, 1H), 4.16 (d, *J*=17.2, 1H), 4.13 – 4.04 (m, 2H), 3.10 (d, *J*=17.2, 1H), 1.73 (s, 3H), 1.48 (d, *J*=0.9, 3H), 1.16 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.29, 169.92, 151.10, 136.52, 136.47, 135.31, 134.08, 134.07, 131.52, 127.41, 124.65, 116.18, 67.73, 62.43, 39.97, 23.21, 22.74, 13.99. ESI-HRMS calcd for [$C_{18}H_{19}{}^{35}ClO_3$+Na^+]: 341.0920, found 341.0915; [$C_{18}H_{19}{}^{37}ClO_3$+Na^+]: 343.0891, found 343.0857.

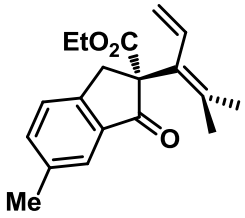




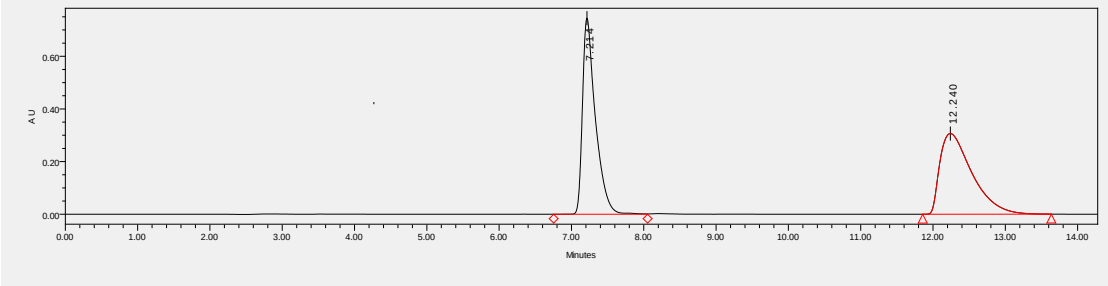
	Retention Time	Area	% Area
1	10.935	6093028	50.17
2	12.595	6052192	49.83

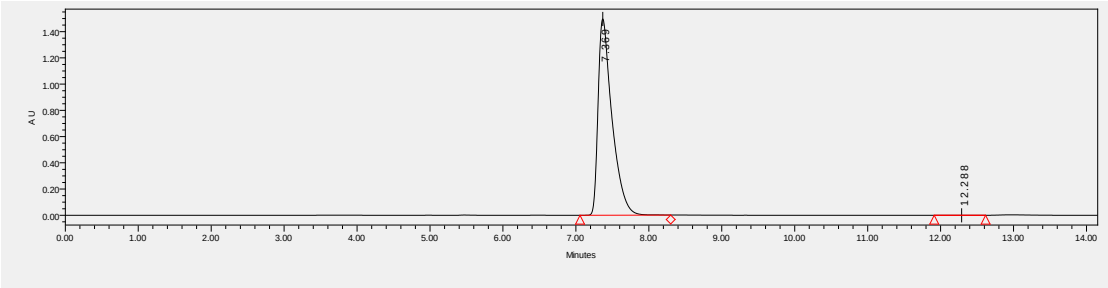
	Retention Time	Area	% Area
1	10.988	15612661	99.97
2	12.750	4308	0.03

(*R*)-ethyl 6-methyl-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2j).



Reaction time: 24 h; Yield: 86%; $[\alpha]^{25}_D$ = −281.4 (*c* 0.42, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $t_{R(major)}$ = 7.37 min, $t_{R(minor)}$ = 12.29 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (s, 1H), 7.40 (dd, *J*=26.1, 7.7, 2H), 6.44 (dd, *J*=17.8, 11.3, 1H), 5.02 (dd, *J*=11.3, 1.2, 1H), 4.79 (dd, *J*=17.8, 1.1, 1H), 4.22 (d, *J*=16.9, 1H), 4.15 (qd, *J*=7.1, 1.6, 2H), 3.15 (d, *J*=16.9, 1H), 2.39 (s, 3H), 1.80 (s, 3H), 1.55 (s, 3H), 1.23 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.62, 170.37, 150.48, 137.67, 136.74, 136.60, 135.15, 133.69, 131.95, 125.82, 124.84, 115.80, 67.54, 62.20, 40.11, 23.17, 22.74, 21.06, 14.00. ESI-HRMS calcd for [$C_{19}H_{22}O_3$+Na^+]: 321.1467, found 321.1468.

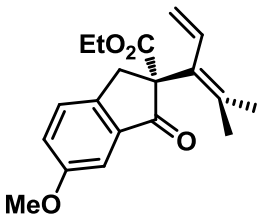




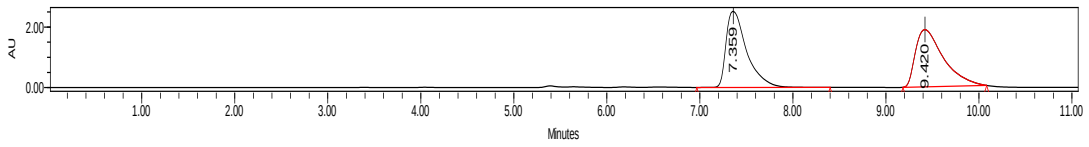
	Retention Time	Area	% Area
1	7.214	9288209	49.53
2	12.240	9466130	50.47

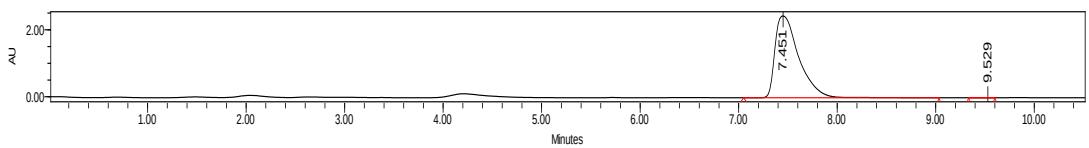
	Retention Time	Area	% Area
1	7.369	19870291	99.99
2	12.288	2122	0.01

(*R*)-ethyl 6-methoxy-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2k).



Reaction time: 30 h; Yield: 88%; $[\alpha]^{17}_{D}$ = −332.5 (*c* 0.55, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, $t_{R(major)}$ = 7.45 min, $t_{R(minor)}$ = 9.53 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J*=8.0, 1H), 7.19 – 7.08 (m, 2H), 6.38 (dd, *J*=17.8, 11.3, 1H), 4.96 (dd, *J*=11.3, 1.4, 1H), 4.72 (dd, *J*=17.9, 1.3, 1H), 4.15 – 4.03 (m, 3H), 3.75 (s, 3H), 3.05 (d, *J*=16.8, 1H), 1.73 (s, 3H), 1.52 – 1.45 (m, 3H), 1.16 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.56, 170.26, 159.61, 146.06, 136.69, 136.10, 133.79, 131.82, 126.88, 124.92, 115.79, 105.84, 68.02, 62.25, 55.59, 39.78, 23.18, 22.74, 14.02. ESI-HRMS calcd for [$C_{19}H_{22}O_4$+Na^+]: 337.1416, found 337.1410.



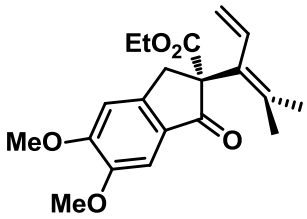


	Retention Time	Area	% Area

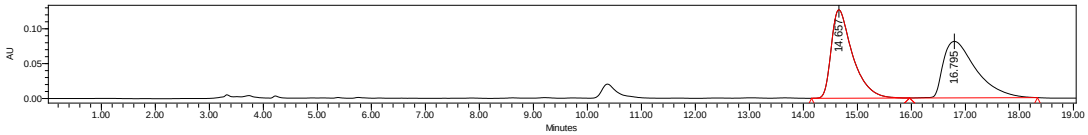
1	7.359	38856068	49.49
2	9.420	39653823	50.51

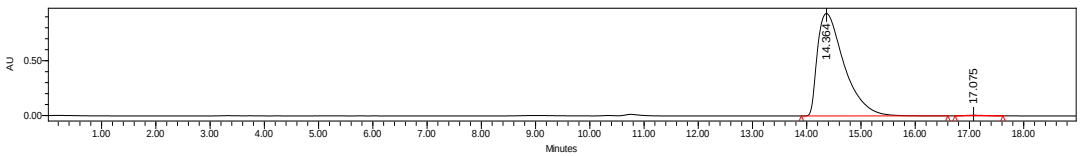
	Retention Time	Area	% Area
1	7.451	40931137	100.00
2	9.529	1942	0.00

(*R*)-ethyl 5,6-dimethoxy-2-(4-methylpenta-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2l).



Reaction time: 24 h; Yield: 65%; $[\alpha]^{30}_{D}$ = −370.7 (*c* 0.60, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, $t_{R(major)}$ = 14.36 min, $t_{R(minor)}$ = 17.08 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (s, 1H), 6.90 (s, 1H), 6.47 (dd, *J*=17.8, 11.3, 1H), 5.03 (dd, *J*=11.3, 1.4, 1H), 4.80 (dd, *J*=17.9, 1.3, 1H), 4.22 – 4.12 (m, 3H), 3.98 (s, 3H), 3.90 (s, 3H), 3.10 (d, *J*=16.8, 1H), 1.81 (s, 3H), 1.57 (s, 3H), 1.24 (t, *J*=7.1, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 199.04, 170.60, 155.98, 149.68, 148.66, 136.82, 133.70, 131.89, 127.63, 115.62, 106.99, 105.22, 67.52, 62.20, 56.28, 56.09, 40.14, 22.98, 22.77, 14.02. ESI-HRMS calcd for [$C_{20}H_{24}O_5$+Na^+]: 367.1521, found 367.1522.

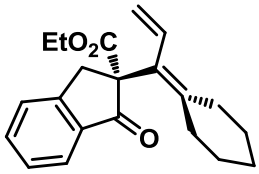




	Retention Time	Area	% Area
1	14.657	3485505	50.46
2	16.795	3422258	49.54

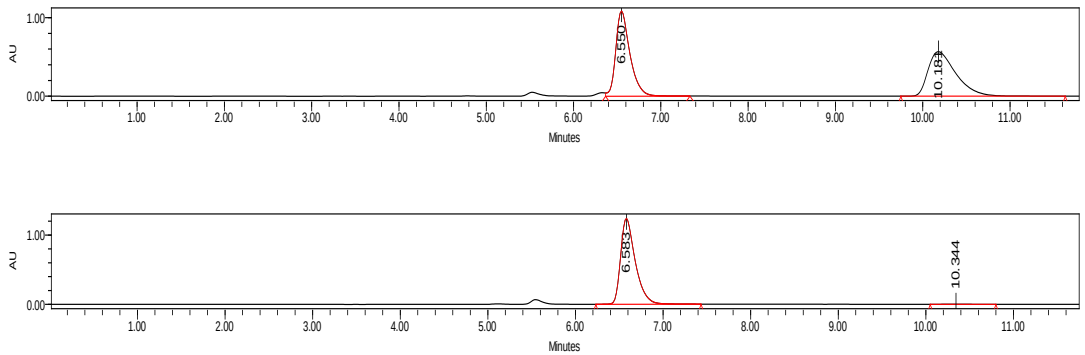
	Retention Time	Area	% Area
1	14.364	31940786	99.63
2	17.075	119727	0.37

(*R*)-ethyl 2-(1-cyclohexylideneallyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2m).



Reaction time: 48 h; Yield: 90%; $[\alpha]^{17}_{D}$ = −287.3 (*c* 0.64, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, $t_{R(major)}$ = 6.58 min, $t_{R(minor)}$ = 10.34 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J*=7.7, 1H), 7.53 (td, *J*=7.6, 1.1, 1H), 7.39 (d, *J*=7.7, 1H), 7.30 (dd, *J*=11.0, 3.9, 1H), 6.29 (dd, *J*=17.7, 11.1, 1H), 4.95 (dd, *J*=11.1, 2.0, 1H), 4.69 (dd, *J*=17.7, 2.0,

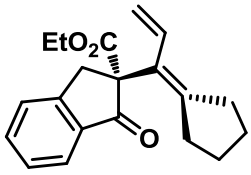
1H), 4.17 (d, *J*=17.1, 1H), 4.09 (q, *J*=7.1, 2H), 3.13 (d, *J*=17.1, 1H), 2.22 (s, 2H), 1.97 – 1.81 (m, 2H), 1.46 (s, 6H), 1.17 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.89, 170.73, 152.91, 141.06, 136.43, 135.25, 135.14, 129.41, 127.65, 126.14, 124.86, 117.13, 66.71, 62.17, 41.01, 33.00, 32.40, 28.10, 27.29, 26.41, 14.04. ESI-HRMS calcd for [$C_{21}H_{24}O_3$+Na^+]: 347.1623, found 347.1618.



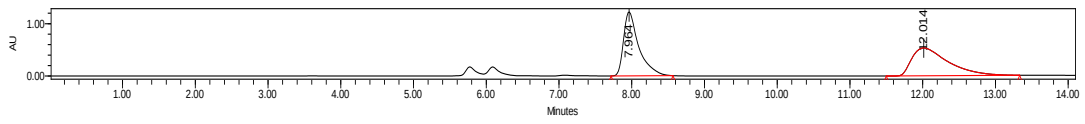
	Retention Time	Area	% Area
1	6.550	12285036	49.56
2	10.181	12501852	50.44

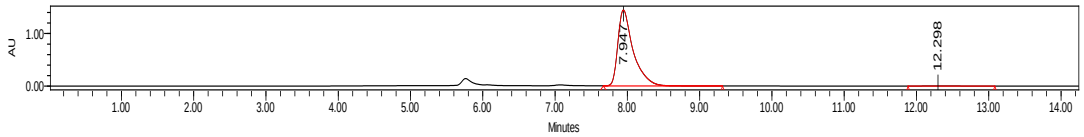
	Retention Time	Area	% Area
1	6.583	14373486	99.72
2	10.344	39740	0.28

(*R*)-ethyl 2-(1-cyclopentylideneallyl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2n).



Reaction time: 52 h; Yield: 80%; $[\alpha]^{25}_D$ = −428.2 (*c* 0.54, CH_2Cl_2, 99% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $t_{R(major)}$ = 7.95 min, $t_{R(minor)}$ = 12.30 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (d, *J*=7.7, 1H), 7.62 (td, *J*=7.6, 1.1, 1H), 7.50 (d, *J*=7.7, 1H), 7.39 (dd, *J*=11.4, 4.1, 1H), 6.51 (dd, *J*=18.0, 11.6, 1H), 4.96 (d, *J*=11.6, 1H), 4.83 (d, *J*=18.0, 1H), 4.32 (d, *J*=17.2, 1H), 4.20 – 4.10 (m, 2H), 3.21 (t, *J*=14.7, 1H), 2.64 – 2.42 (m, 1H), 2.27 (ddd, *J*=22.6, 15.8, 7.7, 2H), 1.69 – 1.52 (m, 4H), 1.45 – 1.36 (m, 1H), 1.22 (dd, *J*=11.3, 4.2, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.21, 170.09, 153.57, 147.07, 136.68, 135.27, 134.97, 128.73, 127.74, 126.19, 124.94, 112.39, 67.13, 62.34, 40.15, 33.37, 33.09, 27.31, 25.72, 13.97. ESI-HRMS calcd for [$C_{20}H_{22}O_3$+Na^+]: 333.1467, found 333.1468.

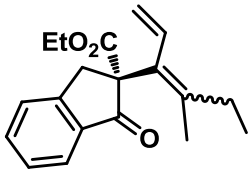




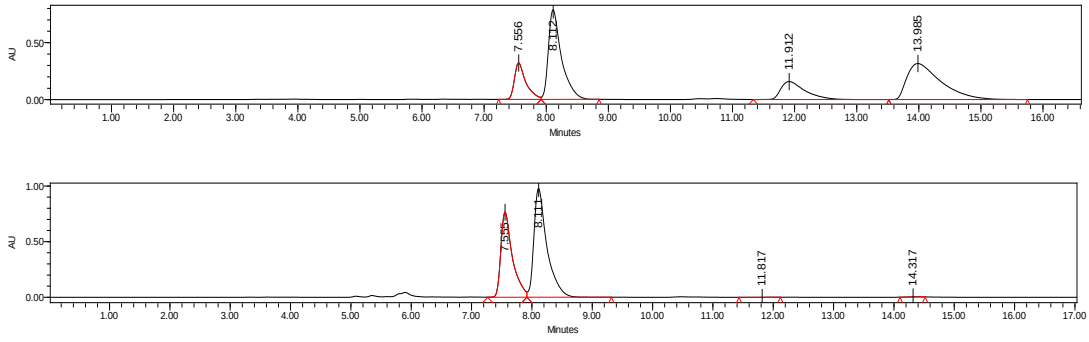
	Retention Time	Area	% Area
1	7.964	17820606	49.12
2	12.014	18457150	50.88

	Retention Time	Area	% Area
1	7.947	21382098	99.48
2	12.298	111098	0.52

(*R*)-ethyl 2-(4-methylhexa-1,3-dien-3-yl)-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (2o).



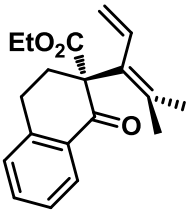
Reaction time: 52 h; Yield: 85%; mixture of *Z*/*E* isomer, *Z*/*E* = 1/1.5; The *Z* isomer was determined to be 99% ee by HPLC (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH 90/10 1.0 mL/min, $t_{R(major)}$ = 7.56 min, $t_{R(minor)}$ = 11.82 min). The *E* isomer was determined to be 99% ee ($t_{R(major)}$ = 8.11 min, $t_{R(minor)}$ = 14.32 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J*=7.7, 1H), 7.65 – 7.58 (m, 1H), 7.51 – 7.45 (m, 1H), 7.37 (t, *J*=7.5, 1H), 6.58 – 6.34 (m, 1H), 5.01 (ddd, *J*=20.6, 11.3, 1.6, 1H), 4.77 (dd, *J*=17.9, 1.6, 1H), 4.28 (dd, *J*=17.1, 7.3, 1H), 4.21 – 4.10 (m, 2H), 3.20 (d, *J*=17.1, 1H), 2.23 (tt, *J*=15.0, 7.5, 0.6H), 2.13 – 2.04 (m, 0.6H), 1.86 (ddd, *J*=14.6, 7.3, 1.9, 0.8H), 1.76 (d, *J*=0.9, 1.2H), 1.54 (d, *J*=1.2, 1.8H), 1.23 (td, *J*=7.1, 4.2, 3H), 0.97 (td, *J*=7.4, 2.6, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 200.57, 200.51, 170.50, 170.32, 153.07, 152.81, 139.23, 138.37, 137.10, 136.44, 135.27, 135.25, 135.08, 135.06, 131.87, 131.51, 127.68, 126.16, 126.14, 124.91, 124.85, 116.16, 115.61, 67.11, 67.05, 62.19, 62.18, 41.05, 40.60, 29.20, 28.98, 20.09, 19.22, 14.00, 13.97, 12.72, 11.20. ESI-HRMS calcd for [$C_{19}H_{22}O_3$+Na^+]: 321.1467, found 321.1465.



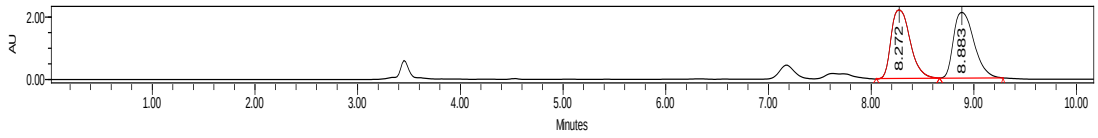
	Retention Time	Area	% Area
1	7.556	4117385	12.90
2	8.112	11557215	36.20
3	11.912	4275291	13.39
4	13.985	11973868	37.51

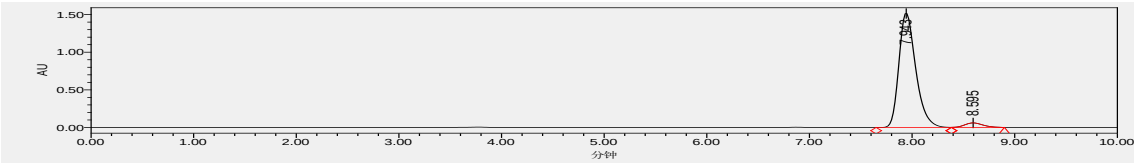
	Retention Time	Area	% Area
1	7.555	10149905	40.71
2	8.111	14743870	59.13
3	11.817	9726	0.04
4	14.317	30755	0.12

(*R*)-ethyl 2-(4-methylpenta-1,3-dien-2-yl)-1-oxo-1,2,3,4-tetrahydro-naphthalene-2-carboxylate (2p).



Reaction time: 72 h; Yield: 91%; $[\alpha]^{30}_{D}$ = −72.1 (*c* 0.39, CH_2Cl_2, 92% ee); HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 7.94 min, $t_{R(minor)}$ = 8.60 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (d, *J*=7.8, 1H), 7.47 – 7.39 (m, 1H), 7.28 (t, *J*=7.5, 1H), 7.18 (d, *J*=7.6, 1H), 6.01 (dd, *J*=17.6, 11.1, 1H), 5.06 (dd, *J*=11.1, 2.1, 1H), 4.93 (dd, *J*=17.6, 2.1, 1H), 4.22 (qd, *J*=7.1, 1.2, 2H), 3.02 – 2.89 (m, 2H), 2.67 – 2.54 (m, 2H), 1.79 (s, 3H), 1.63 (d, *J*=1.1, 3H), 1.24 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.14, 172.07, 142.99, 136.57, 134.15, 133.21, 133.07, 129.06, 128.37, 128.16, 126.63, 118.81, 63.52, 61.41, 32.87, 26.12, 23.73, 22.49, 14.06. ESI-HRMS calcd for $[C_{19}H_{22}O_3+Na^+]$: 321.1467, found 321.1466.

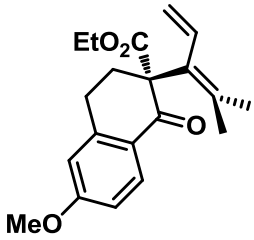




	Retention Time	Area	% Area
1	8.272	28412665	49.22
2	8.883	29308136	50.78

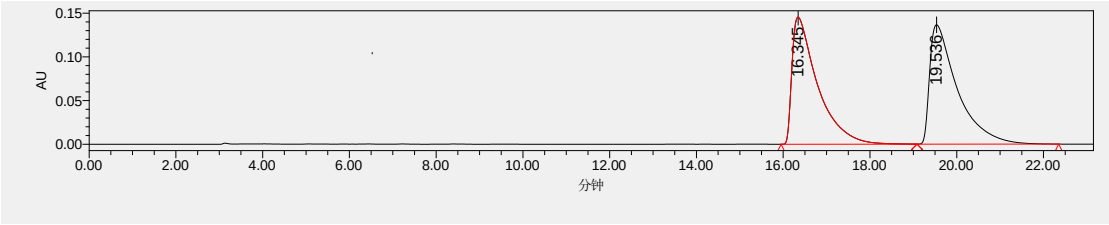
	Retention Time	Area	% Area
1	7.943	17297983	95.94
2	8.595	732187	4.06

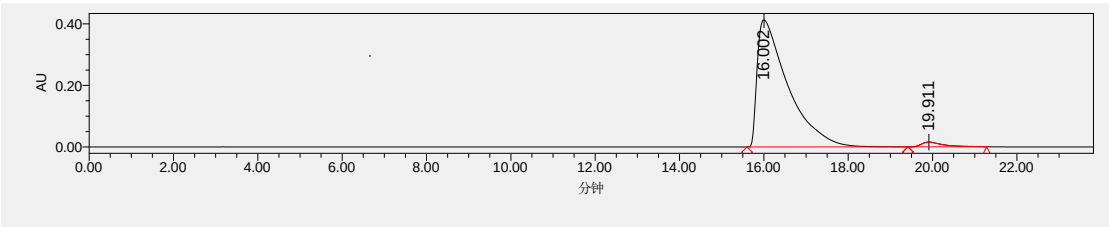
(*R*)-ethyl 6-methoxy-2-(4-methylpenta-1,3-dien-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2q).



Reaction time: 32 h; Yield: 90%; $[\alpha]^{25}_{D}$ = −112.2 (*c* 0.62, CH_2Cl_2, 95% ee); HPLC (Daicel chiralpak IB, *n*-hexane/*i*-PrOH 99/1, 1.0 mL/min, $t_{R(major)}$ = 16.00 min, $t_{R(minor)}$ = 19.91 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.90 (d, *J*=8.8, 1H), 6.74 (dd, *J*=8.8, 2.5, 1H), 6.56 (d, *J*=2.4, 1H), 5.94 (dd, *J*=17.6, 11.1, 1H), 4.99 (dd, *J*=11.1, 2.2, 1H), 4.86 (dd, *J*=17.6, 2.2, 1H), 4.14 (q, *J*=7.1, 2H), 3.77 (s, 3H), 2.85 (t, *J*=6.1, 2H), 2.61 – 2.52 (m, 1H), 2.46 (dt, *J*=13.7, 5.9, 1H), 1.72 (s, 3H), 1.55 (d, *J*=1.3, 3H), 1.17 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 193.70, 172.15, 163.38, 145.58, 136.68, 133.85, 130.66, 129.55, 126.62, 118.66, 113.31, 112.08, 63.35, 61.41, 55.42, 32.93, 26.56, 23.74, 22.61, 14.10. ESI-HRMS calcd for

[$C_{20}H_{24}O_4$+Na^+]: 351.1572, found 351.1573.

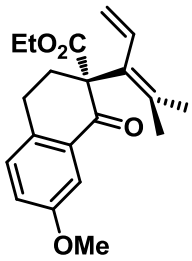




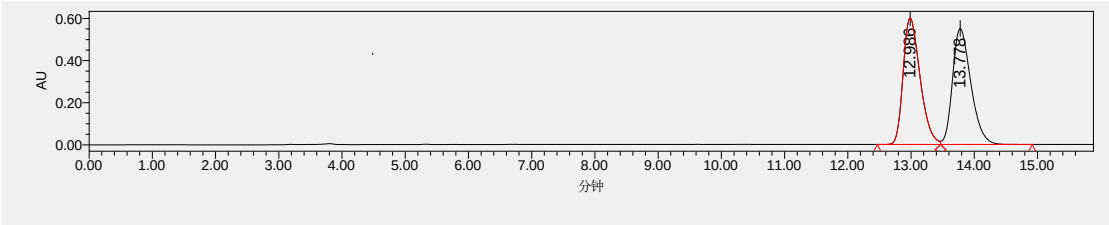
	Retention Time	Area	% Area
1	16.345	5948001	49.60
2	19.536	6043842	50.40

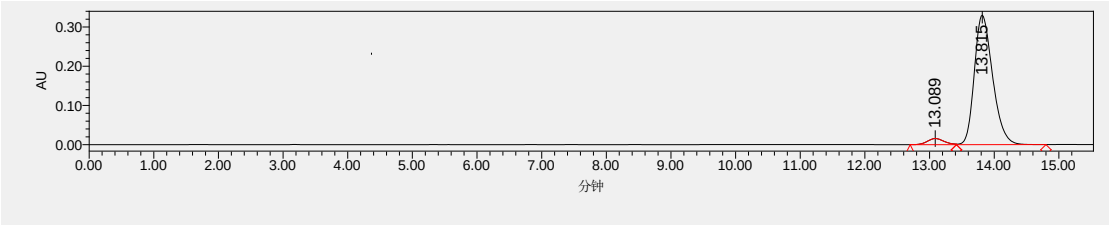
	Retention Time	Area	% Area
1	16.002	20892718	97.50
2	19.911	536093	2.50

(*R*)-ethyl 7-methoxy-2-(4-methylpenta-1,3-dien-2-yl)-1-oxo-1,2,3,4-tetrahydro-naphthalene-2-carboxylate (2r).



Reaction time: 48 h; Yield: 80%; $[\alpha]^{25}_D$ = −108.5 (*c* 0.54, CH_2Cl_2, 92% ee); HPLC (Daicel chiralpak IE, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 13.82 min, $t_{R(minor)}$ = 13.09 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 (d, *J*=2.7, 1H), 7.02 (d, *J*=8.4, 1H), 6.95 (dd, *J*=8.4, 2.8, 1H), 5.93 (dd, *J*=17.6, 11.1, 1H), 5.01 (dd, *J*=11.1, 2.2, 1H), 4.86 (dd, *J*=17.6, 2.2, 1H), 4.22 – 4.03 (m, 2H), 3.75 (s, 3H), 2.89 – 2.71 (m, 2H), 2.59 – 2.38 (m, 2H), 1.72 (s, 3H), 1.56 (d, *J*=1.2, 3H), 1.17 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.04, 172.15, 158.29, 136.58, 135.65, 134.09, 133.90, 129.60, 129.11, 121.54, 118.89, 110.01, 63.34, 61.44, 55.44, 33.23, 25.39, 23.73, 22.54, 14.09. ESI-HRMS calcd for [$C_{20}H_{24}O_4$+Na^+]: 351.1572, found 351.1574.

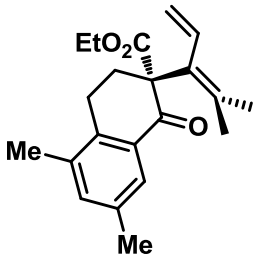




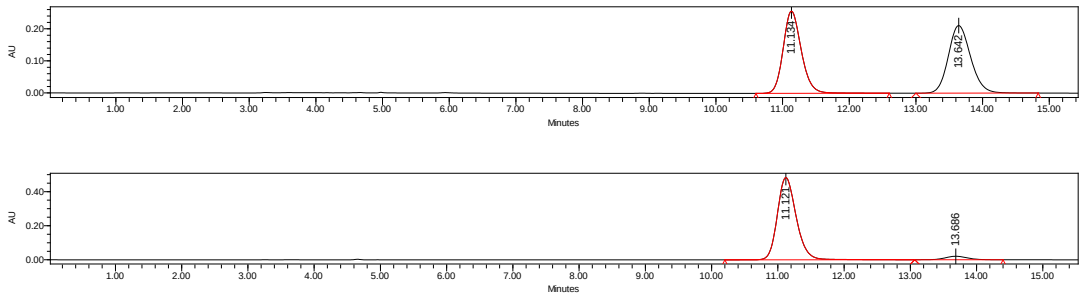
	Retention Time	Area	% Area
1	12.986	11165257	50.21
2	13.778	11073825	49.79

	Retention Time	Area	% Area
1	13.089	276315	4.09
2	13.815	6479634	95.91

(*R*)-ethyl 6,7-dimethyl-2-(4-methylpenta-1,3-dien-2-yl)-1-oxo-1,2,3,4-tetrahydronaphthal ene-2-carboxylate (2s).



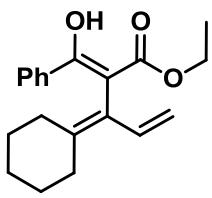
Reaction time: 96 h; Yield: 78%; $[\alpha]^{25}_{D}$ = −113.7 (*c* 0.52, CH_2Cl_2, 90% ee); HPLC (Daicel chiralpak IC, *n*-hexane/*i*-PrOH 99/1, 1.0 mL/min, $t_{R(major)}$ = 11.12 min, $t_{R(minor)}$ = 13.69 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.58 (s, 1H), 7.07 (s, 1H), 5.92 (dd, *J*=17.6, 11.1, 1H), 4.98 (dd, *J*=11.1, 2.2, 1H), 4.85 (dd, *J*=17.6, 2.1, 1H), 4.21 – 4.05 (m, 2H), 2.69 (t, *J*=6.0, 2H), 2.57 – 2.46 (m, 2H), 2.24 (s, 3H), 2.16 (s, 3H), 1.71 (s, 3H), 1.55 (d, *J*=1.2, 3H), 1.17 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 195.97, 172.21, 138.48, 136.57, 135.76, 135.73, 135.52, 134.11, 133.26, 128.95, 126.11, 118.58, 63.05, 61.35, 32.12, 23.76, 23.26, 22.46, 20.90, 19.11, 14.10. ESI-HRMS calcd for [$C_{21}H_{26}O_3$+Na^+]: 349.1780, found 349.1778.



	Retention Time	Area	% Area
1	11.134	4837151	49.68
2	13.642	4898795	50.32

	Retention Time	Area	% Area
1	11.121	9579969	95.15
2	13.686	488452	4.85

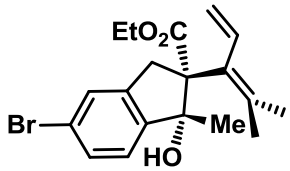
ethyl 3-cyclohexylidene-2-(hydroxy(phenyl)methylene)pent-4-enoate (2t).



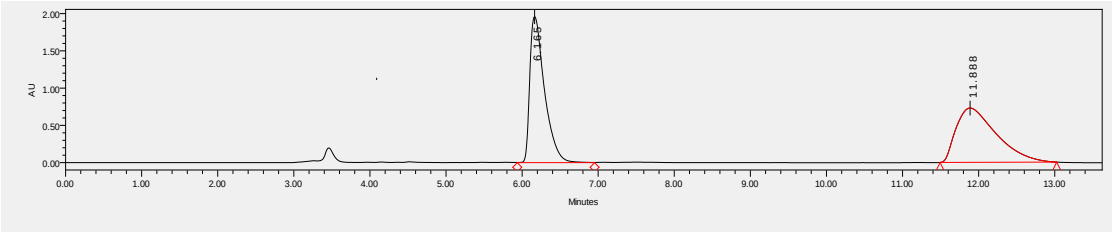
Reaction time: 11 h; Temperature: 35 ^{o}C; Yield: 87%; ^{1}H NMR (400 MHz,

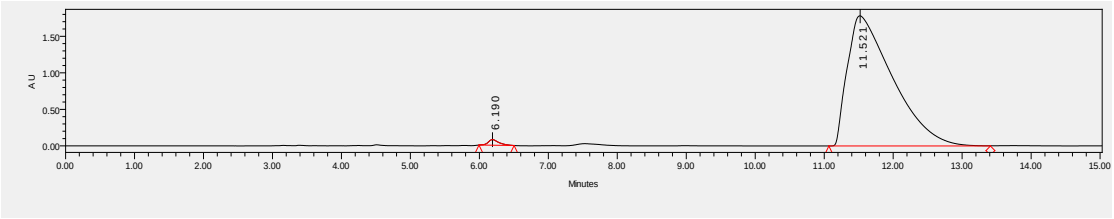
$CDCl_3$) δ = 13.53 (s, 1H), 7.68 – 7.51 (m, 2H), 7.36 – 7.24 (m, 3H), 6.90 (dd, *J*=17.0, 10.6, 1H), 5.15 – 4.97 (m, 2H), 4.22 (q, *J*=7.1, 2H), 2.36 – 2.20 (m, 2H), 2.04 – 1.88 (m, 2H), 1.56 – 1.48 (m, 1H), 1.44 – 1.28 (m, 4H), 1.24 (t, *J*=7.1, 3H), 0.83 – 0.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 173.90, 170.58, 143.90, 135.25, 134.76, 129.84, 128.02, 127.50, 124.88, 113.59, 99.96, 60.63, 32.89, 30.18, 27.28, 26.76, 26.64, 14.25. ESI-HRMS calcd for [$C_{20}H_{24}O_3$+Na^+]: 335.1623, found 335.1622.

(1*R*,2*R*)-ethyl 5-bromo-1-hydroxy-1-methyl-2-(4-methylpenta-1,3-dien-3-yl)-2,3-dihydro-1*H*-indene-2-carboxylate (3).



Yield: 82%; 19:1 d.r.; 98% ee; HPLC (Daicel chiralpak ID, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 11.52 min, $t_{R(minor)}$ = 6.19 min); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, *J*=8.0, 1H), 7.26 (s, 1H), 7.14 (d, *J*=8.0, 1H), 5.96 (dd, *J*=17.7, 11.0, 1H), 5.14 (dd, *J*=11.0, 2.4, 1H), 4.79 (dd, *J*=17.8, 2.4, 1H), 4.28 – 4.12 (m, 2H), 3.64 (d, *J*=15.9, 1H), 3.24 (s, 1H), 3.14 (d, *J*=15.9, 1H), 1.72 (dd, *J*=6.4, 1.0, 6H), 1.43 (s, 3H), 1.29 (t, *J*=7.1, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 174.51, 147.51, 140.83, 139.12, 134.18, 133.56, 130.29, 127.71, 123.24, 121.45, 120.14, 84.07, 67.00, 60.94, 41.76, 26.47, 24.22, 22.08, 14.24. ESI-HRMS calcd for [$C_{19}H_{23}{}^{79}BrO_3$+K^+]: 417.0468, found 417.0466; calcd for [$C_{19}H_{23}{}^{81}BrO_3$+K^+]: 419.0447, found 419.0446;

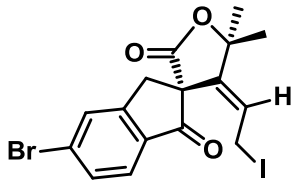




	Retention Time	Area	% Area
1	6.165	26273886	49.57
2	11.888	26729499	50.43

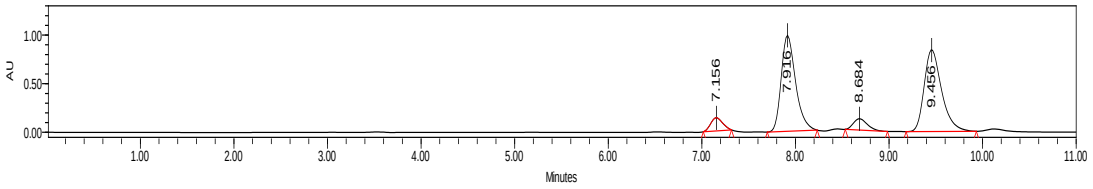
	Retention Time	Area	% Area
1	6.190	835821	1.02
2	11.521	81141157	98.98

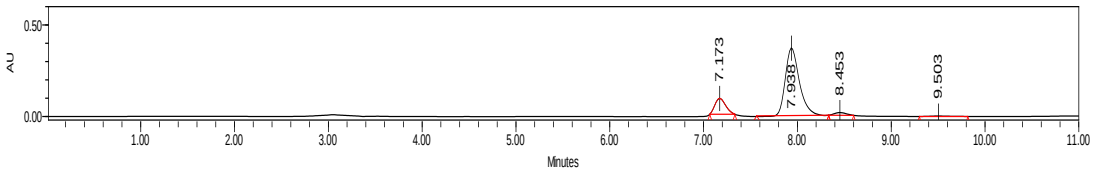
(*R*,*E*)-5'-bromo-4-(2-iodoethylidene)-5,5-dimethyl-4,5-dihydro-2*H*-spiro[furan-3,2'-indene]-1',2(3'*H*)-dione (4).



Yield: 85%; 5:1 mixture of *E/Z*-isomoers; The *E*-isomer was determined to be 98% ee by HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 7.94 min, $t_{R(minor)}$ = 9.50 min). The *Z*-isomer was determined to be 68% ee by HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $t_{R(major)}$ = 7.17 min, $t_{R(minor)}$ = 8.45 min).

for the *E*-isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.79 (s, 1H), 7.71 – 7.60 (m, 2H), 5.79 (dd, *J*=11.0, 7.4, 1H), 3.72 (dd, *J*=43.0, 17.8, 2H), 3.55 (dd, *J*=9.9, 7.4, 1H), 3.13 (dd, *J*=10.9, 10.0, 1H), 1.68 (s, 3H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 198.93, 174.22, 155.10, 148.16, 134.39, 133.62, 133.32, 131.10, 127.75, 123.84, 87.99, 62.36, 38.05, 29.92, 29.33, 0.00. ESI-HRMS calcd for $[C_{16}H_{14}{}^{79}BrIO_3+Na^+]$: 482.9069, found 482.9065; calcd for $[C_{16}H_{14}{}^{81}BrIO_3+Na^+]$: 484.9048, found 484.9044.

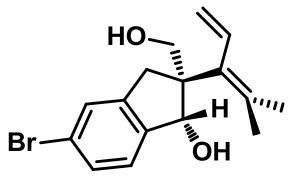




	Retention Time	Area	% Area
1	7.156	1196703	5.03
2	7.916	10501527	44.18
3	8.684	1211236	5.10
4	9.456	10859045	45.69

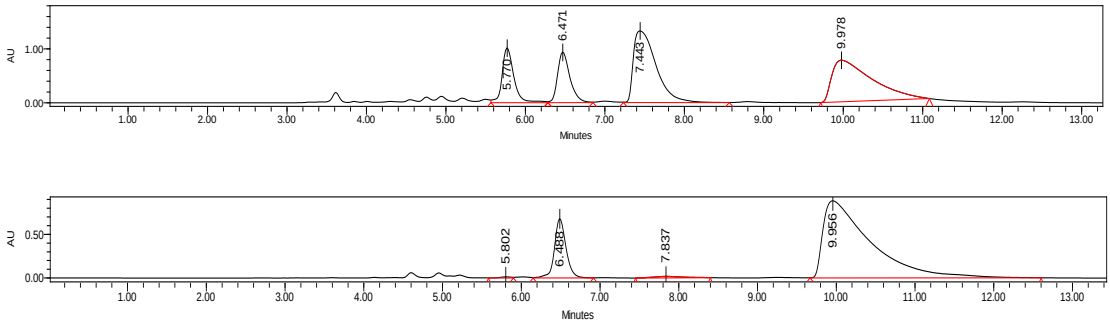
	Retention Time	Area	% Area
1	7.173	688103	14.65
2	7.938	3851013	81.98
3	8.453	130174	2.77
4	9.503	28236	0.60

(1*R*,2*S*)-5-bromo-2-(hydroxymethyl)-2-(4-methylpenta-1,3-dien-3-yl)-2,3-dihydro-1*H*-inden-1-ol (5).



Yield: 82%; 4.9:1 d.r.; The major diastereomer was determined to be

98% ee by HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $t_{R(major)}$ = 9.96 min, $t_{R(minor)}$ = 7.84 min). The minor diastereomer was determined to be 97% ee ($t_{R(major)}$ = 6.49 min, $t_{R(minor)}$ = 5.80 min). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.27 (m, 2.46H), 7.26 – 7.13 (m, 0.58H), 6.45 (dd, *J*=17.8, 11.1, 0.17H), 6.33 (dd, *J*=17.7, 11.1, 0.83H), 5.45 (s, 0.17H), 5.35 (ddd, *J*=11.1, 6.6, 2.3, 1H), 5.03 (ddd, *J*=17.7, 9.7, 2.3, 1H), 4.93 (s, 0.83H), 3.89 (d, *J*=11.5, 0.17H), 3.71 (d, *J*=11.4, 0.17H), 3.62 (d, *J*=10.9, 0.83H), 3.40 (dd, *J*=16.1, 0.7, 0.83H), 3.26 (dd, *J*=26.1, 13.7, 1H), 3.16 (s, 0.17H), 3.03 (d, *J*=16.2, 0.83H), 2.17 (s, 1H), 2.01 (d, *J*=1.4, 2.49H), 1.91 (d, *J*=0.9, 2.50H), 1.88 (d, *J*=1.5, 0.51H), 1.79 (d, *J*=1.0, 0.51H), 1.66 – 1.55 (br, 1H).^{13}C NMR (100 MHz, $CDCl_3$) δ = 144.89, 142.34, 141.60, 139.29, 138.99, 135.03, 134.10, 132.02, 131.80, 130.04, 129.90, 128.38, 127.19, 126.99, 125.17, 122.92, 121.76, 118.68, 81.38, 77.45, 66.98, 66.65, 59.75, 57.06, 41.47, 39.51, 25.20, 24.75, 22.33, 22.29. ESI-HRMS calcd for [$C_{16}H_{19}{}^{79}BrO_2$+Na^+]: 345.0466, found 345.0464; calcd for [$C_{16}H_{19}{}^{81}BrO_2$+Na^+]: 347.0446, found 347.0453.

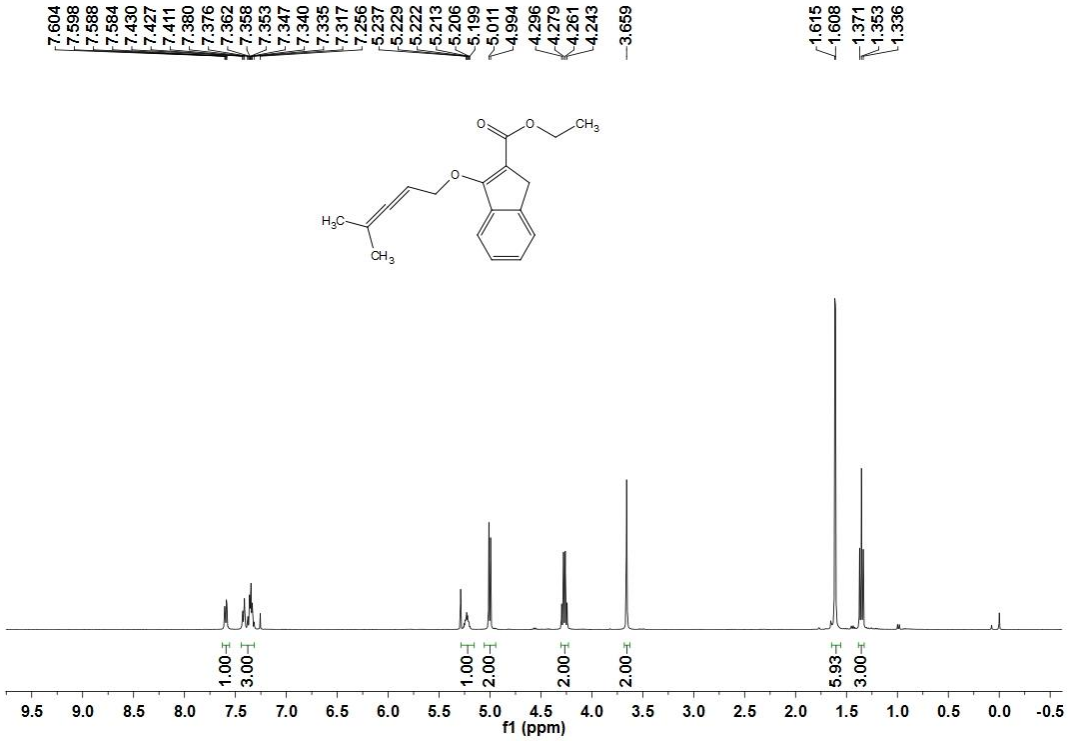


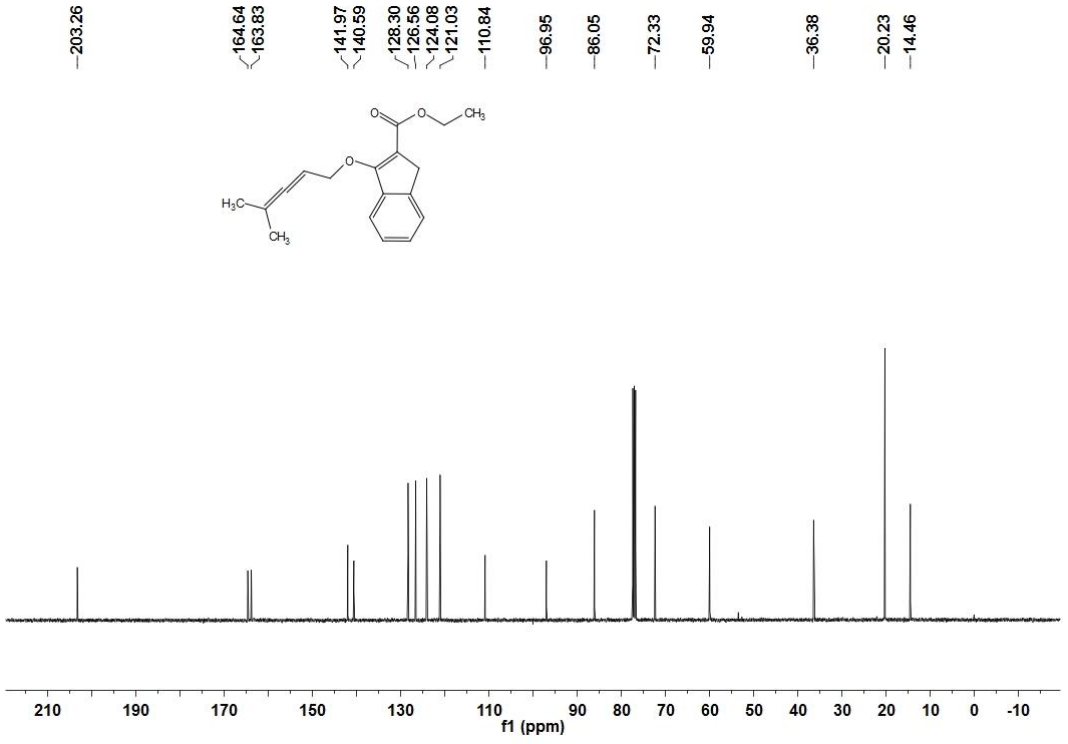
	Retention Time	Area	% Area
1	5.770	10472851	14.14
2	6.471	10149362	13.70
3	7.443	26360194	35.59
4	9.978	27076700	36.56

	Retention Time	Area	% Area
1	5.802	105366	0.24
2	6.488	6924894	15.61
3	7.837	326145	0.74
4	9.956	37000784	83.42

X. Copies of NMR spectral for substrate and product

1a





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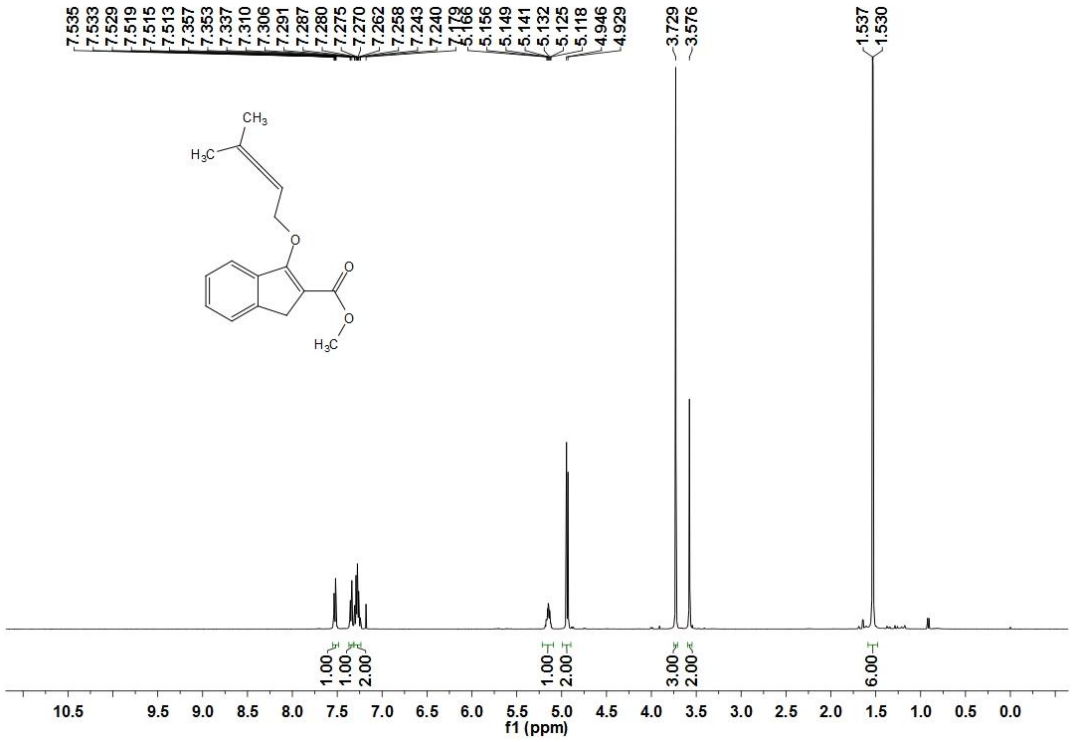
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7.258
7.243
7.240
7.179
5.166
5.156
5.149
5.141
5.132
5.125
5.118
4.946
4.929
3.729
3.576
1.537
1.530
1.00
1.00
2.00
1.00
2.00
3.00
2.00
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
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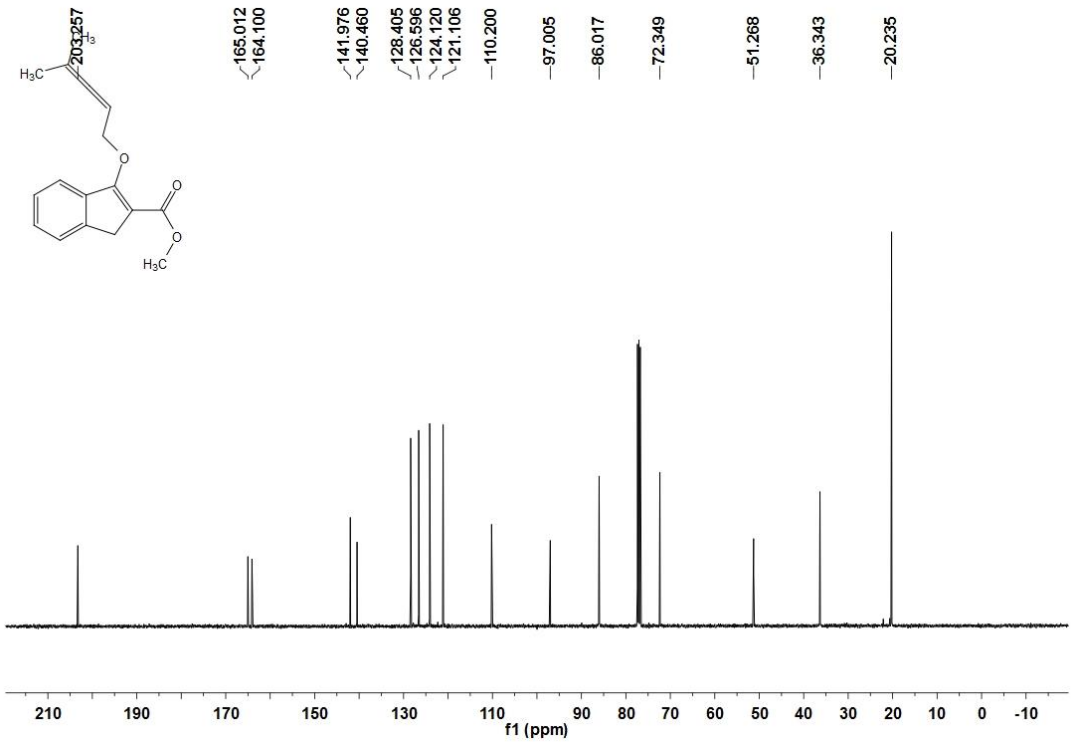
0.0
f1 (ppm)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140.460
128.405
126.596
124.120
121.106
110.200
97.005
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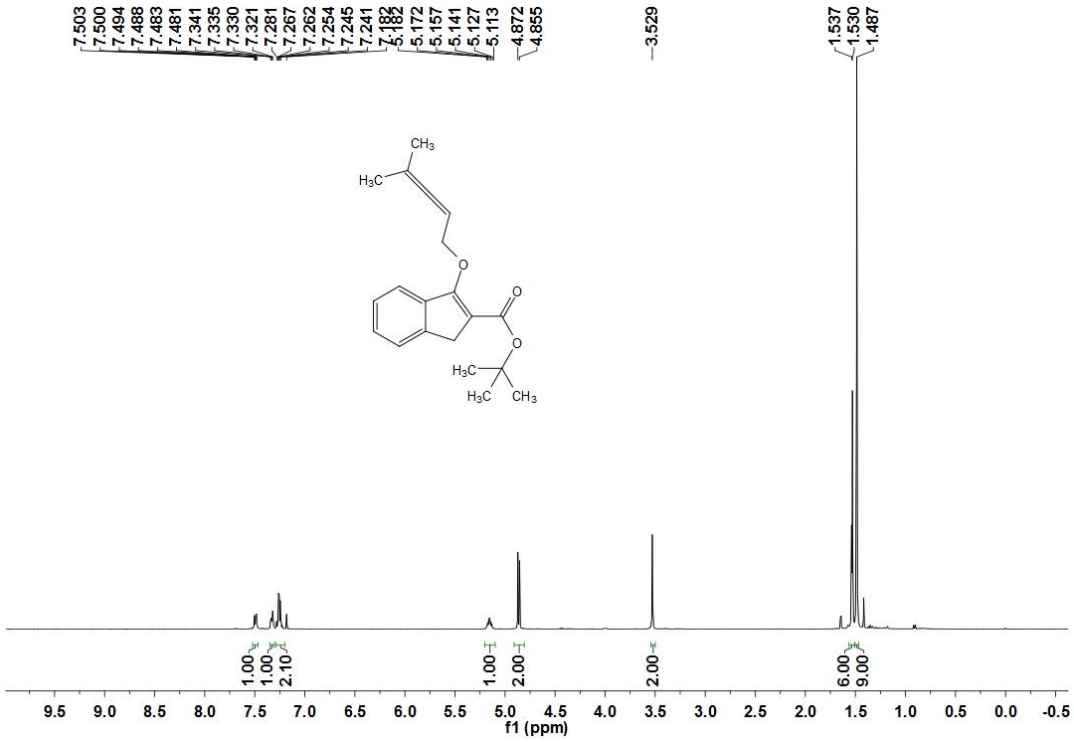
72.349
51.268
36.343
20.235
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1c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7.262
7.254
7.245
7.241
5.172
5.157
5.141
5.127
5.113
4.872
4.855
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1.537
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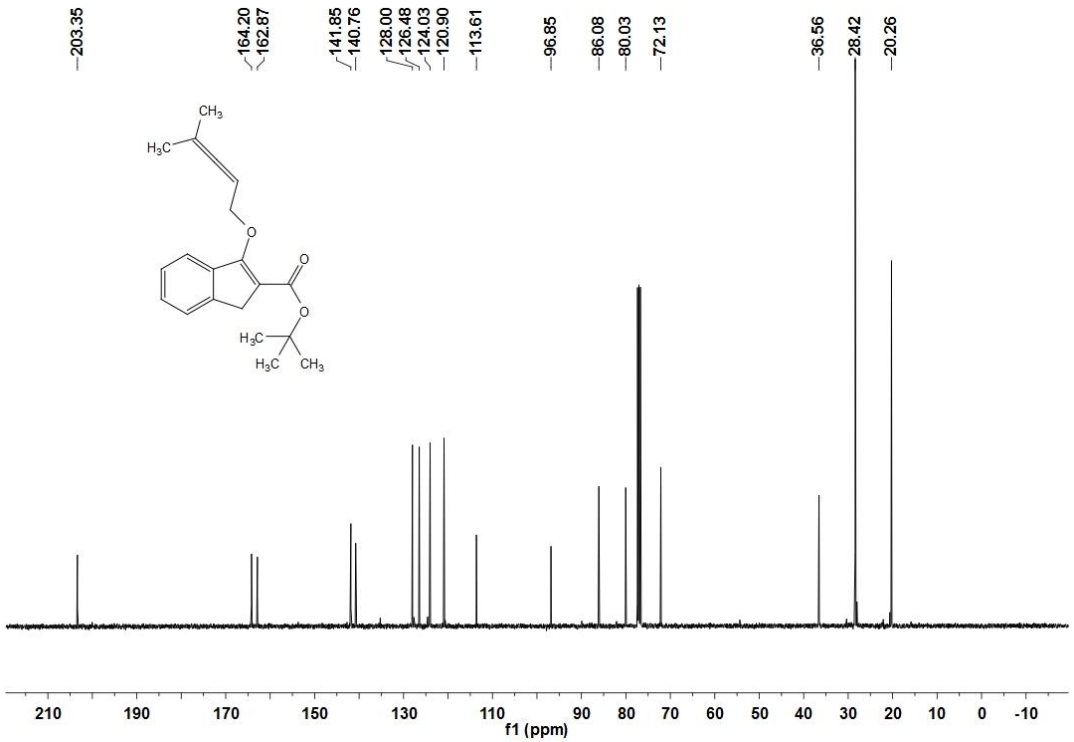
1.00
1.00
2.10
1.00
2.00
2.00
6.00
9.00
f1 (ppm)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36.56
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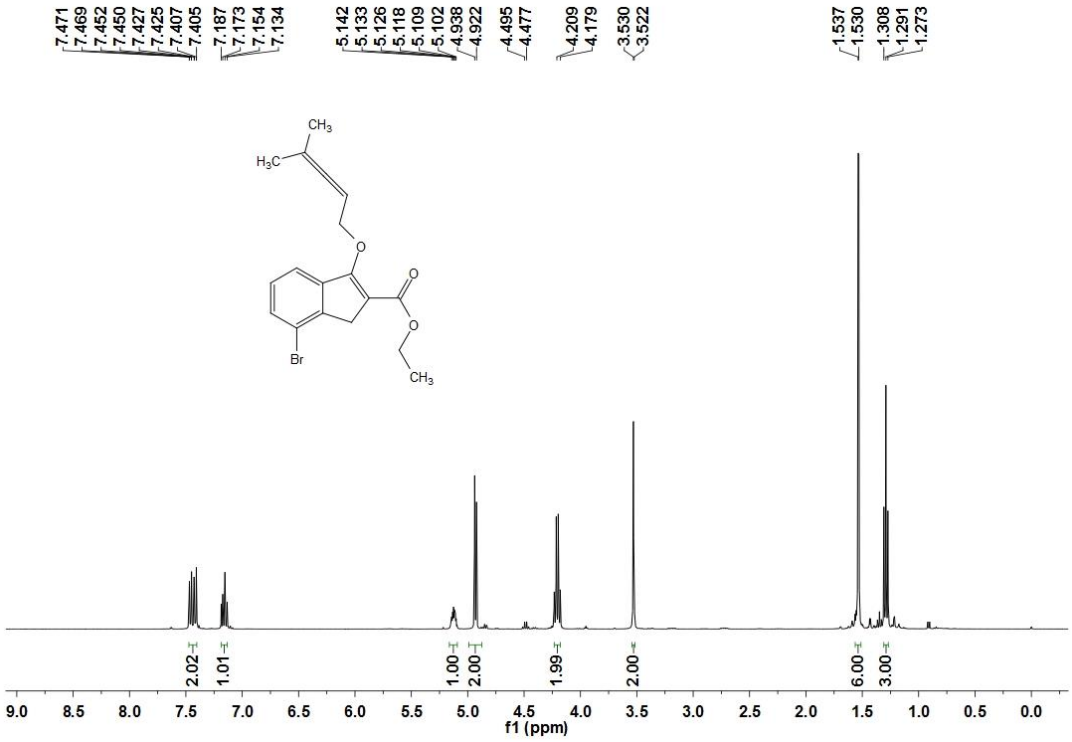
20.26
f1 (ppm)

1d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5.142
5.133
5.126
5.118
5.109
5.102
4.938
4.922
4.495
4.477
4.209
4.179
3.530
3.522
1.537
1.530
1.308
1.291
1.273
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H3C
O
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O
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Br
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1.00
2.00
1.99
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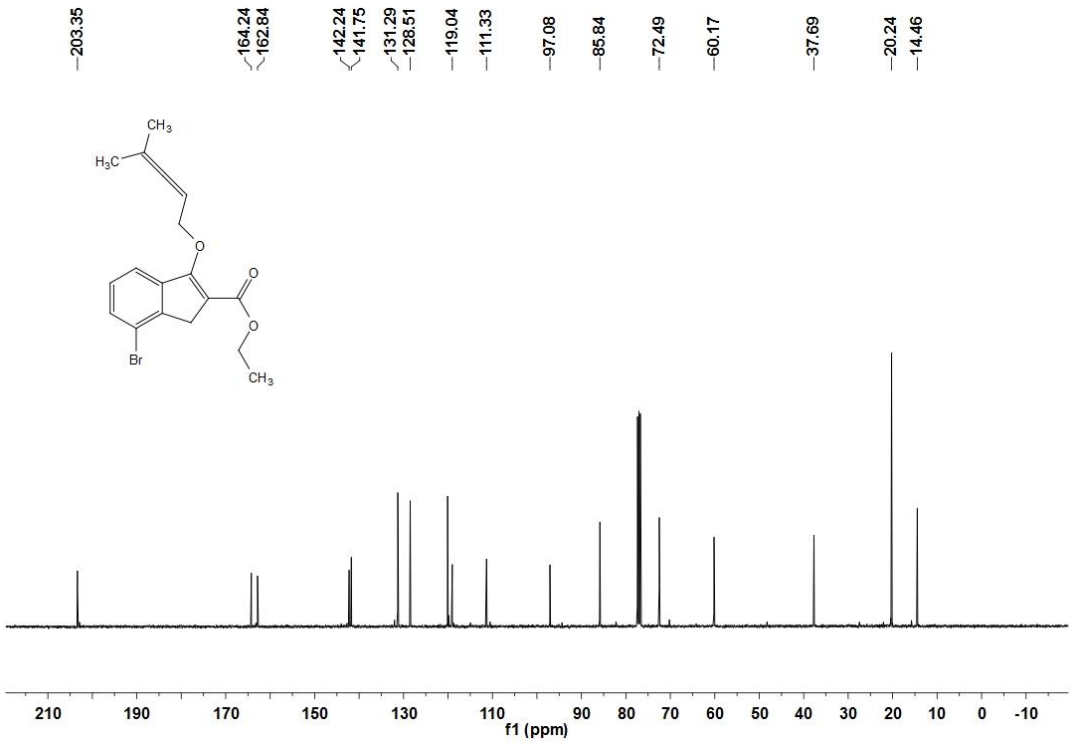
3.00
f1 (ppm)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119.04
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97.08
85.84
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20.24
14.46
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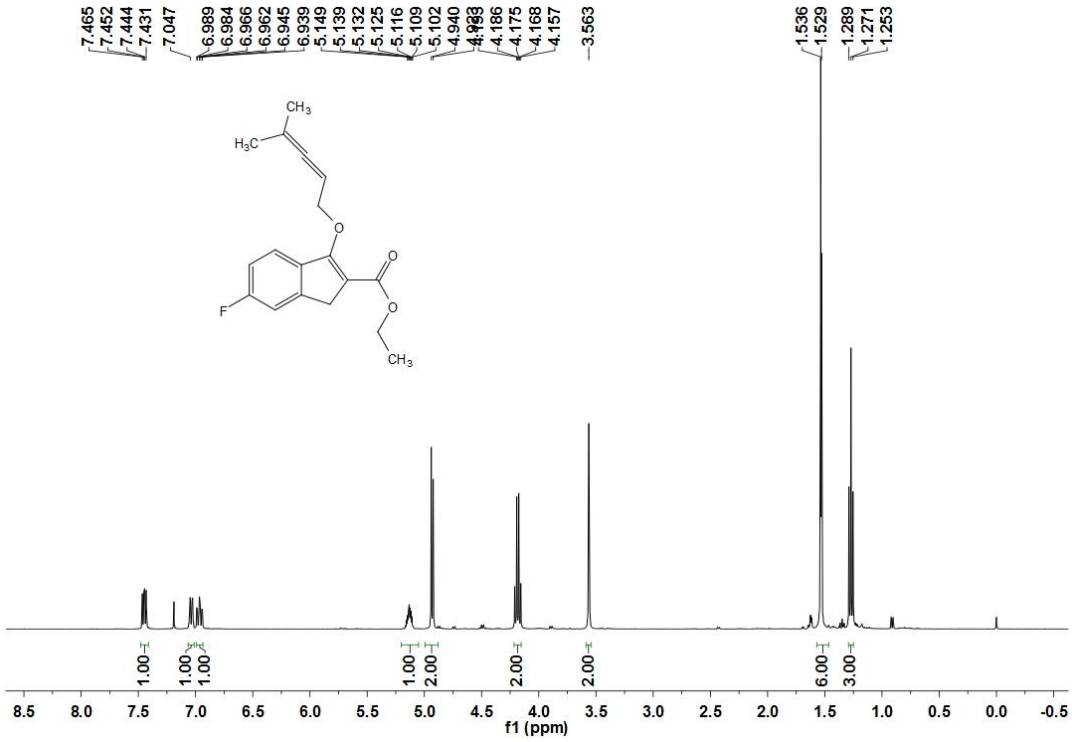
H3C
O
O
O
CH3
Br
f1 (ppm)

1e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6.966
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5.149
5.139
5.132
5.125
5.116
5.109
5.102
4.940
4.186
4.175
4.168
4.157
3.563
1.536
1.529
1.289
1.271
1.253
CH3
H3C
O
O
F
O
CH3
1.00
1.00
1.00
1.00
2.00
2.00
2.00
6.00
3.00
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8.0
7.5
7.0
6.5
6.0
5.5
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2.0
1.5
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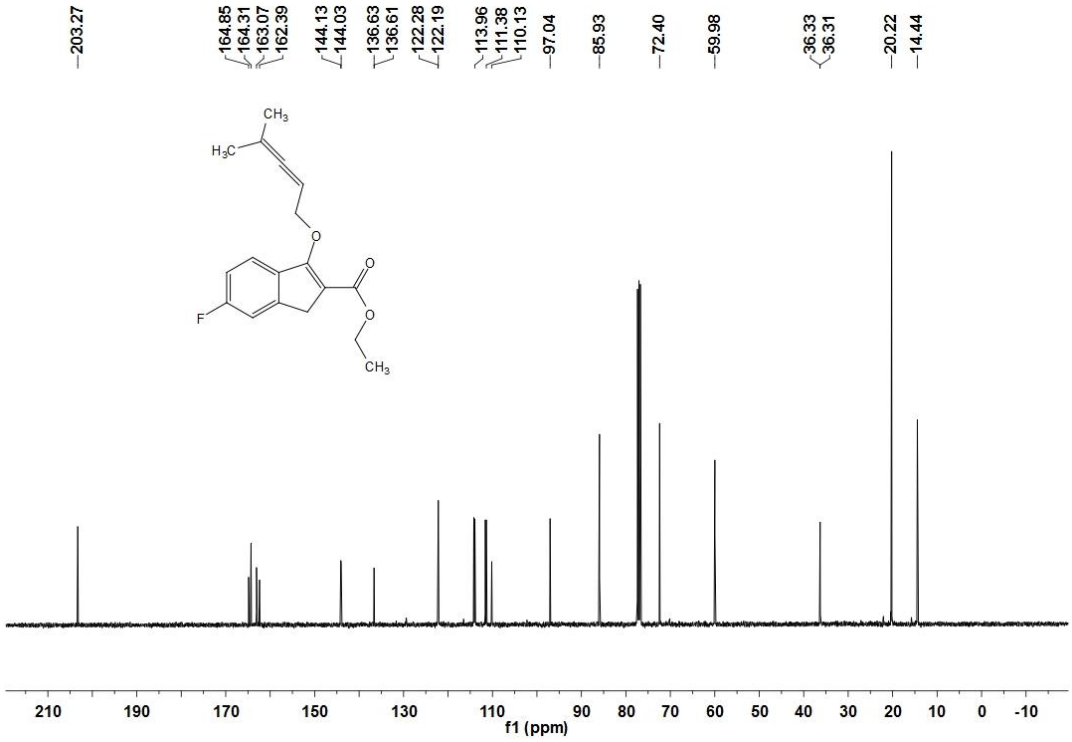
f1 (ppm)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122.19
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111.38
110.13
97.04
85.93
72.40
59.98
36.33
36.31
20.22
14.44
CH3
H3C
O
O
F
O
CH3
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150
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110
90
80
70
60
50
40
30
20
10
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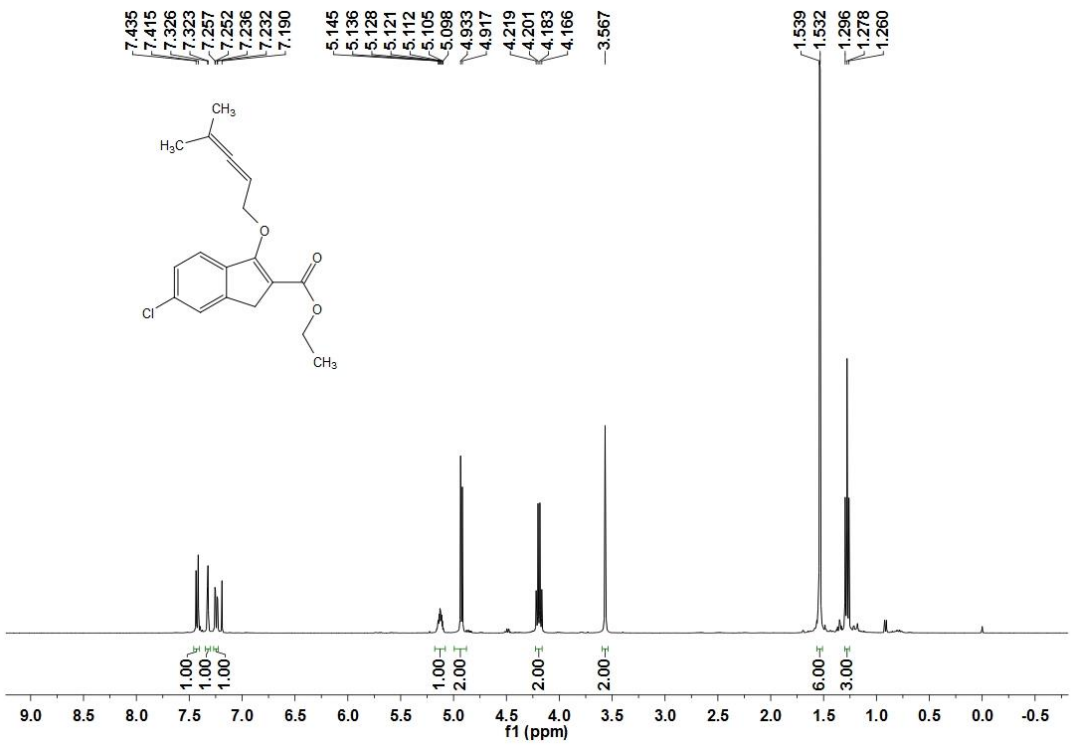
-10
f1 (ppm)

1f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7.232
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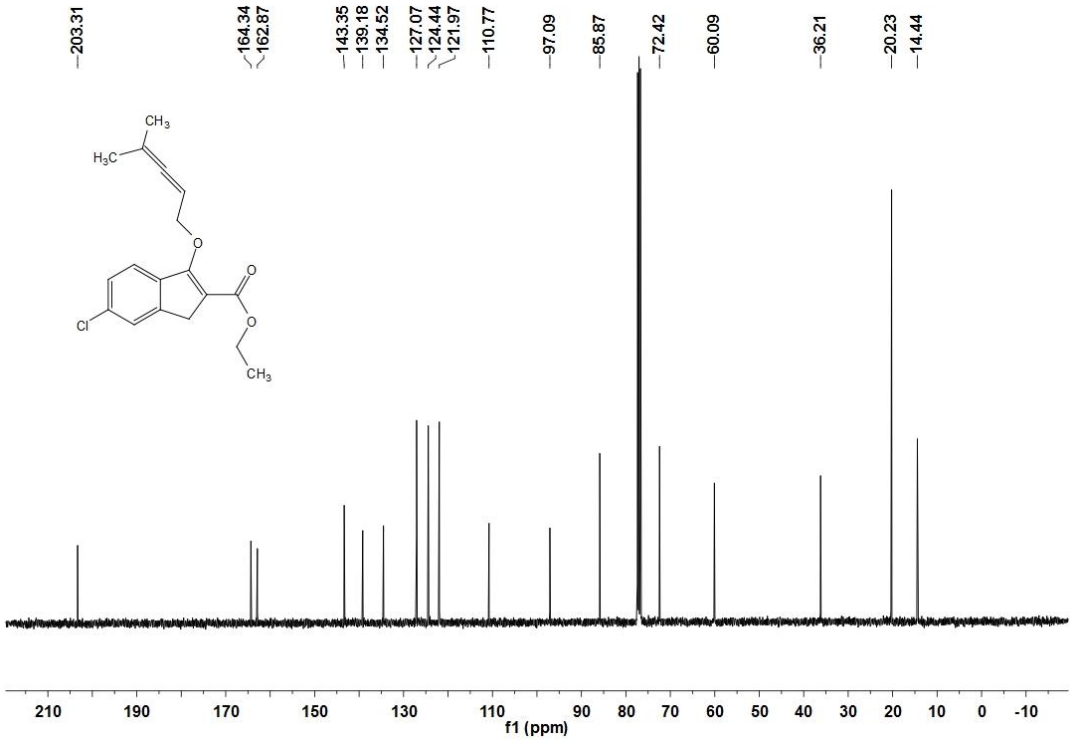
5.136
5.128
5.121
5.112
5.105
5.098
4.933
4.917
4.219
4.201
4.183
4.166
3.567
1.539
1.532
1.296
1.278
1.260
CH3
H3C
O
O
O
Cl
CH3
1.00
1.00
1.00
1.00
2.00
2.00
2.00
6.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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110.77
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72.42
60.09
36.21
20.23
14.44
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O
O
O
Cl
CH3
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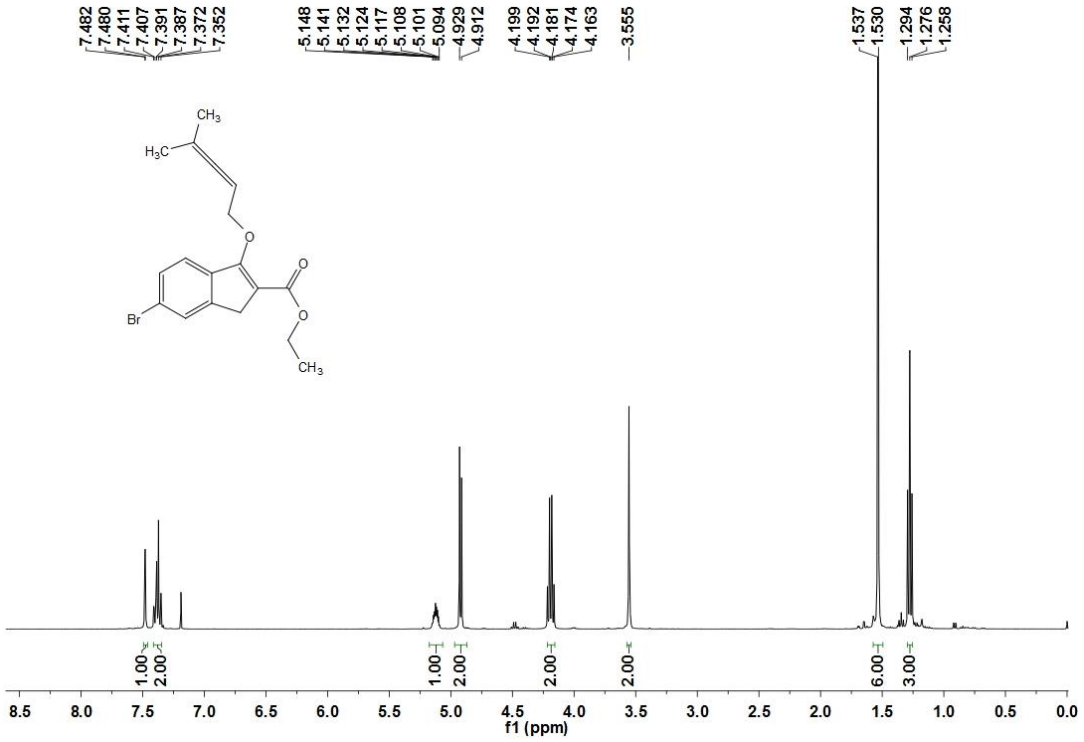
f1 (ppm)

1g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5.101
5.094
4.929
4.912
4.199
4.192
4.181
4.174
4.163
3.555
1.537
1.530
1.294
1.276
1.258
CH3
H3C
O
Br
O
O
CH3
1.00
2.00
1.00
2.00
2.00
2.00
6.00
3.00
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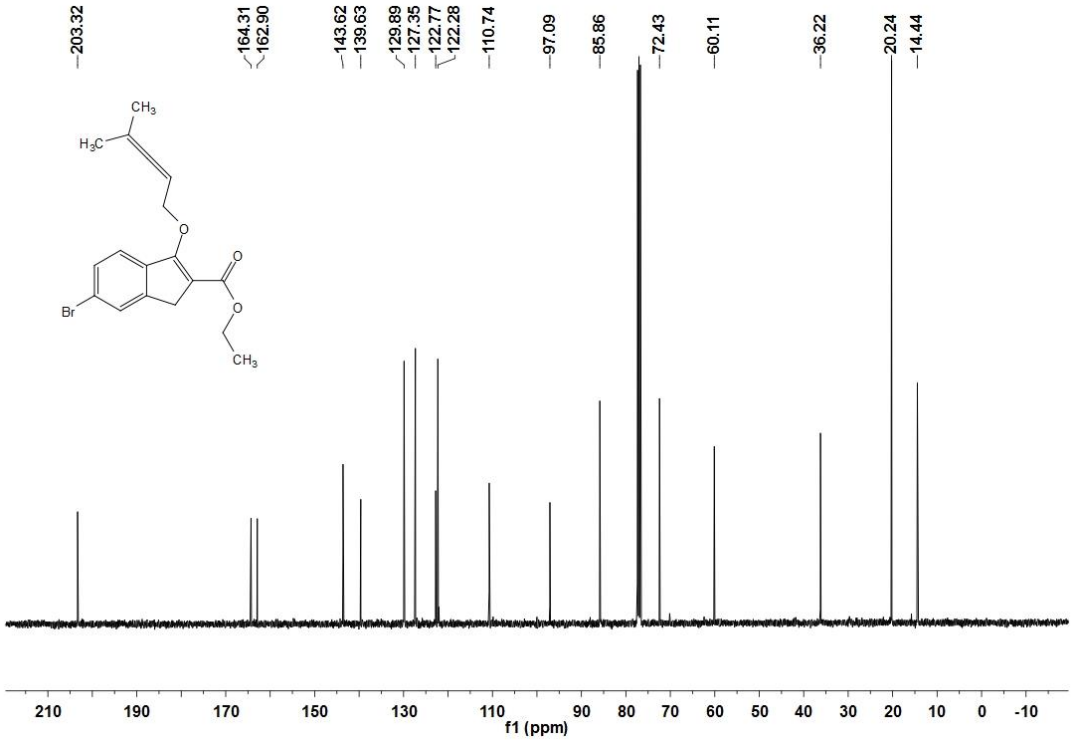
f1 (ppm)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110.74
97.09
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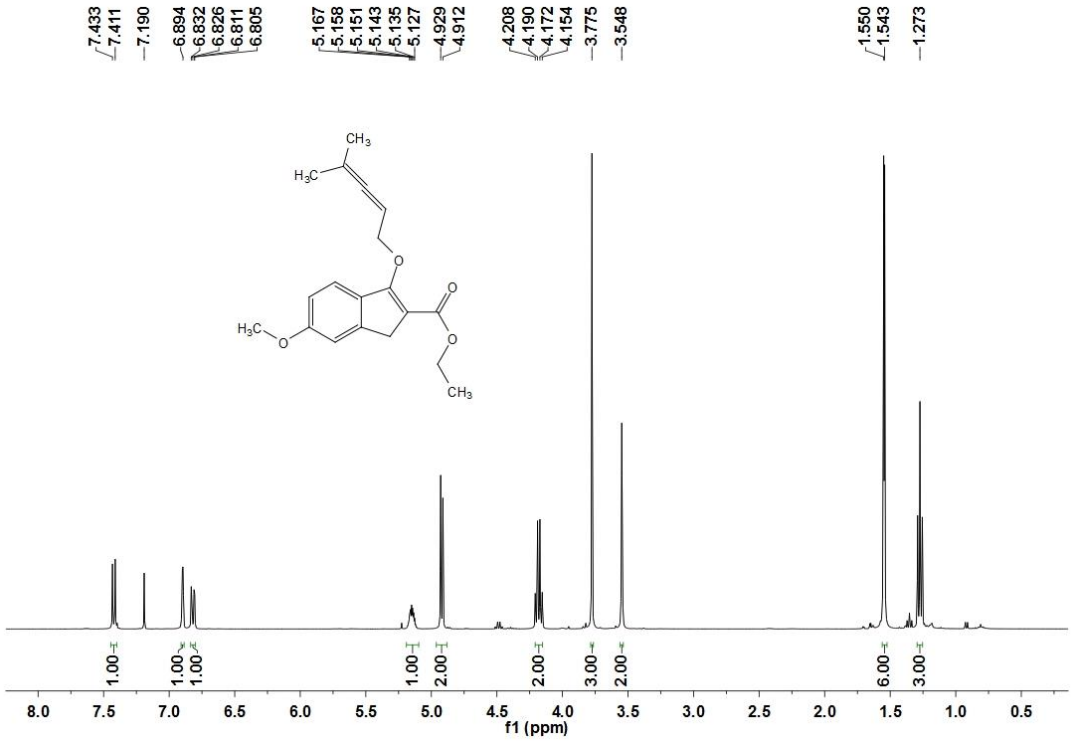
72.43
60.11
36.22
20.24
14.44
CH3
H3C
O
Br
O
O
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1h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5.135
5.127
4.929
4.912
4.208
4.190
4.172
4.154
3.775
3.548
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1.543
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2.00
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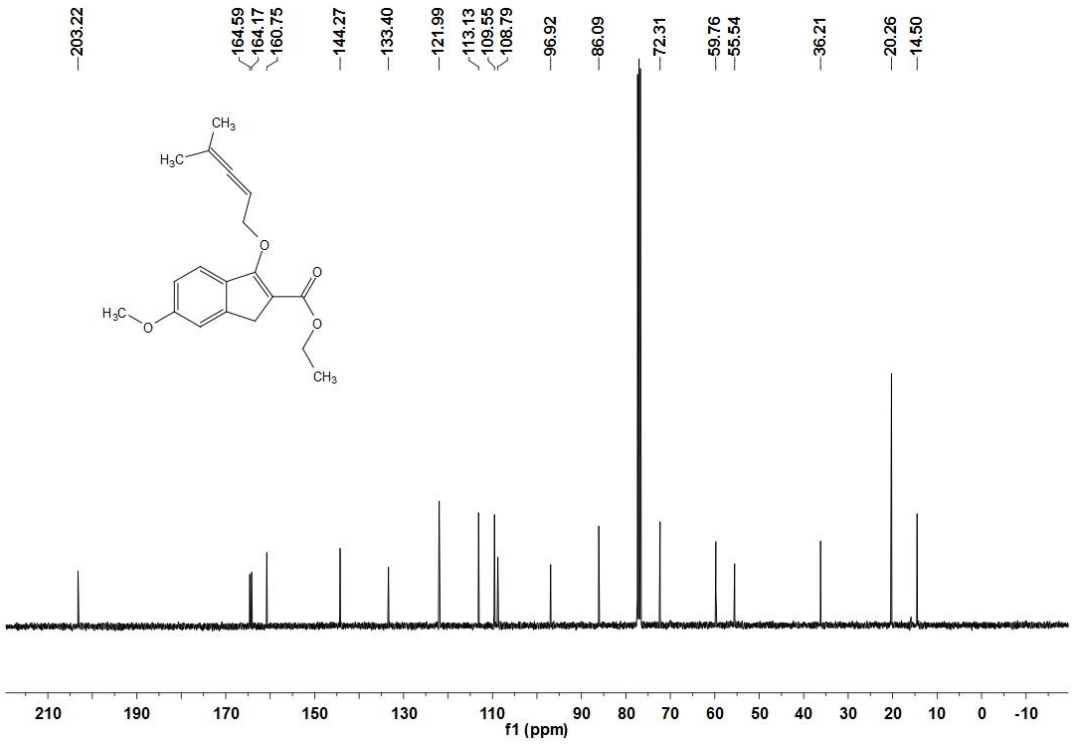
3.00
f1 (ppm)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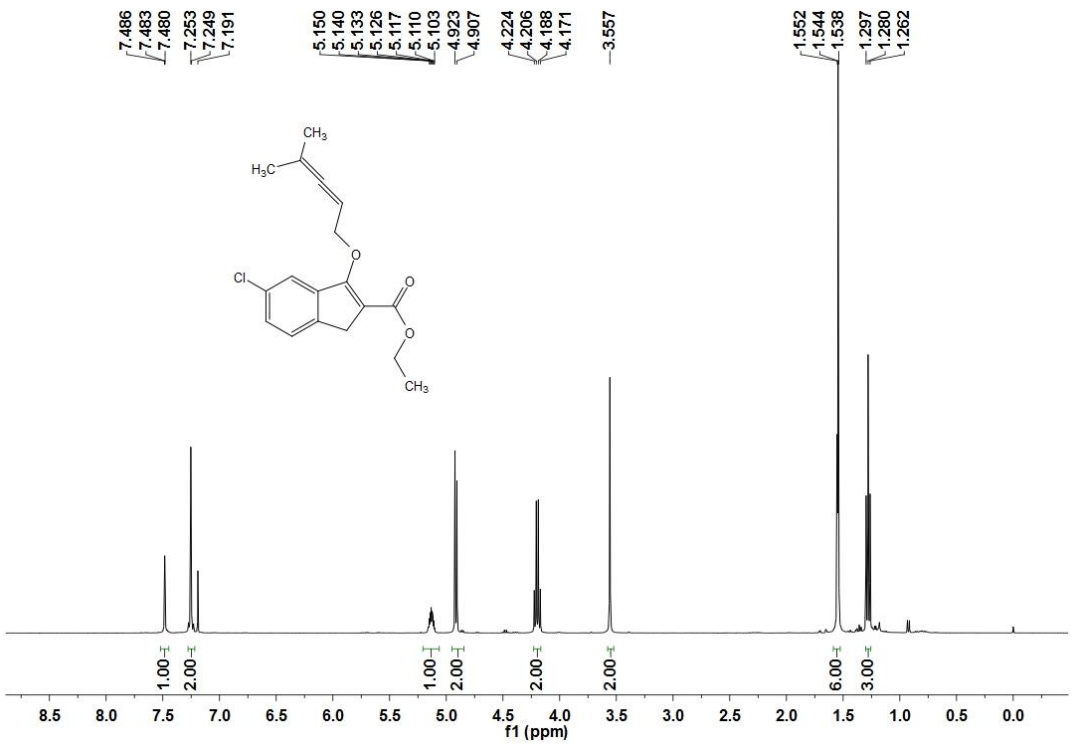
59.76
55.54
36.21
20.26
14.50
f1 (ppm)

1i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CH3
H3C
O
Cl
O
O
CH3
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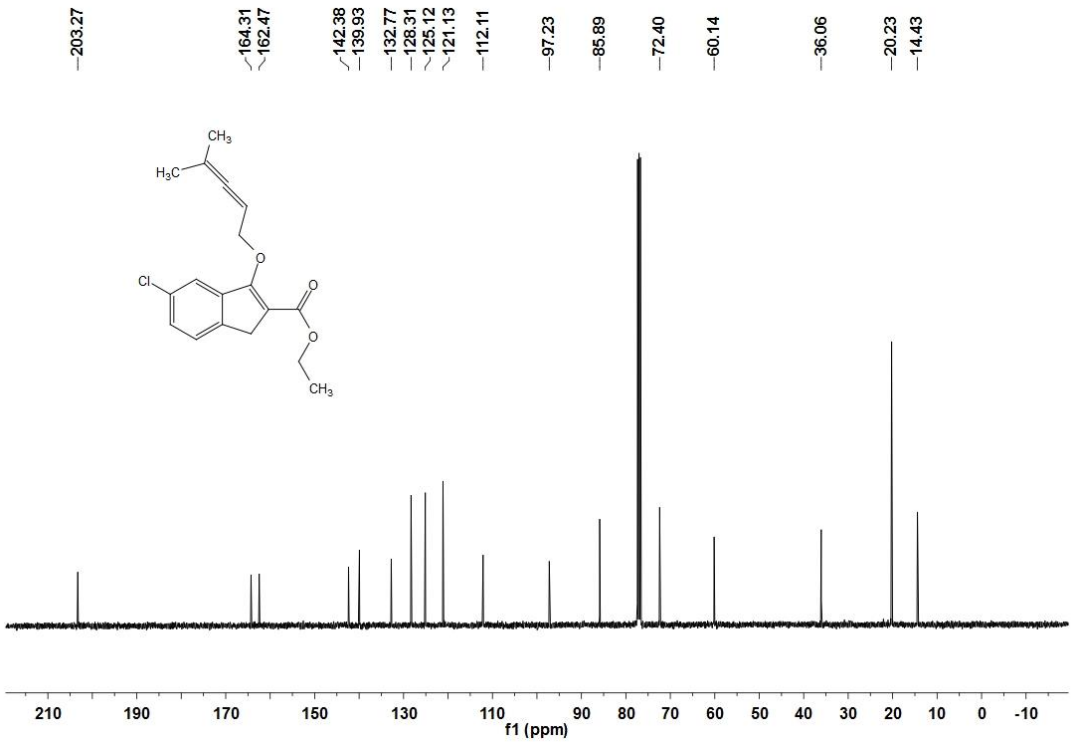
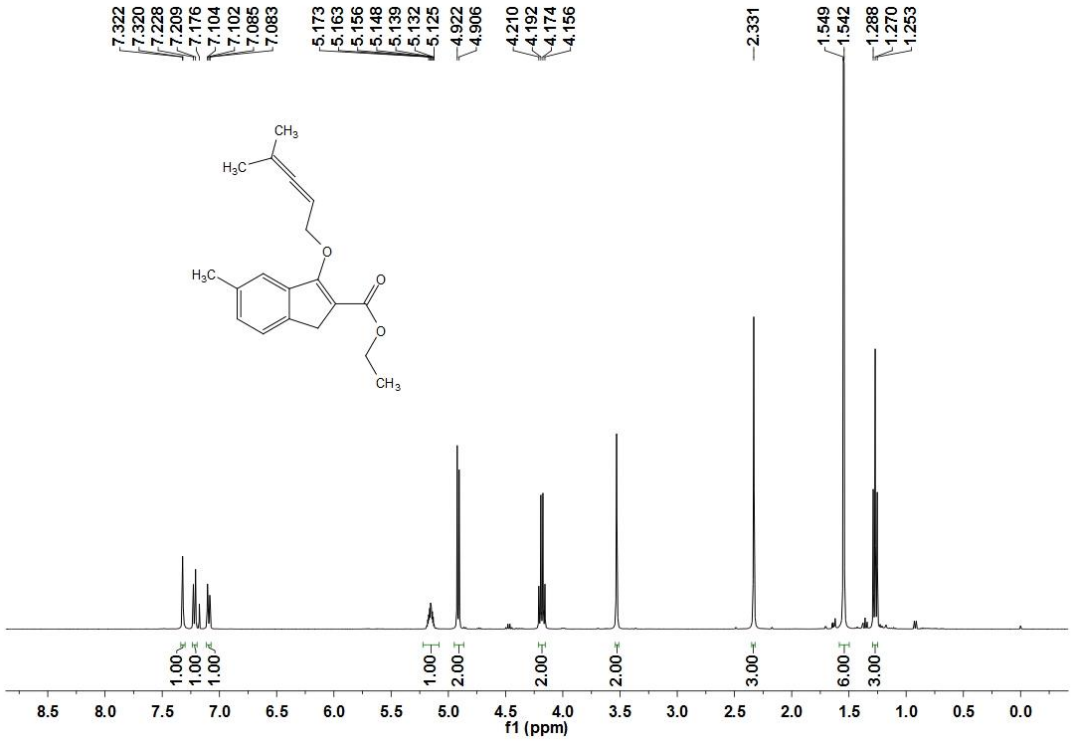
2.00
1.00
2.00
2.00
2.00
6.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.27
164.31
162.47
142.38
139.93
132.77
128.31
125.12
121.13
112.11
97.23
85.89
72.40
60.14
36.06
20.23
14.43
CH3
H3C
O
Cl
O
O
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1j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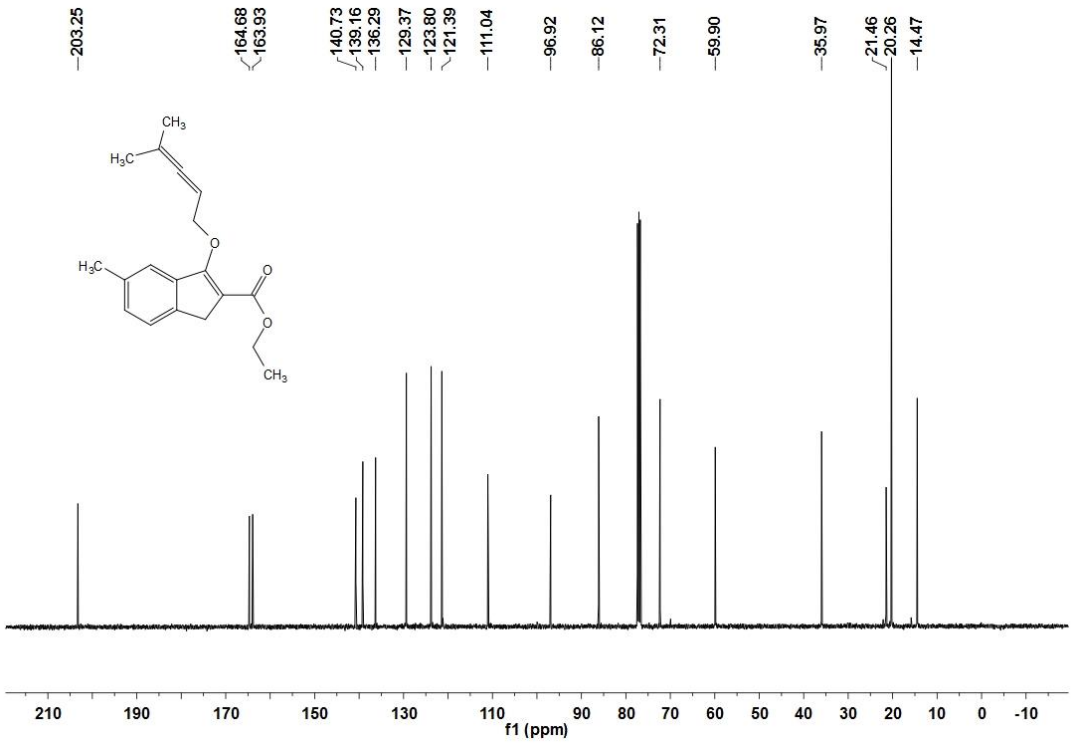
7.320
7.228
7.209
7.176
7.104
7.102
7.085
7.083
5.173
5.163
5.156
5.148
5.139
5.132
5.125
4.922
4.906
4.210
4.192
4.174
4.156
2.331
1.549
1.542
1.288
1.270
1.253
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
6.00
3.00
f1 (ppm)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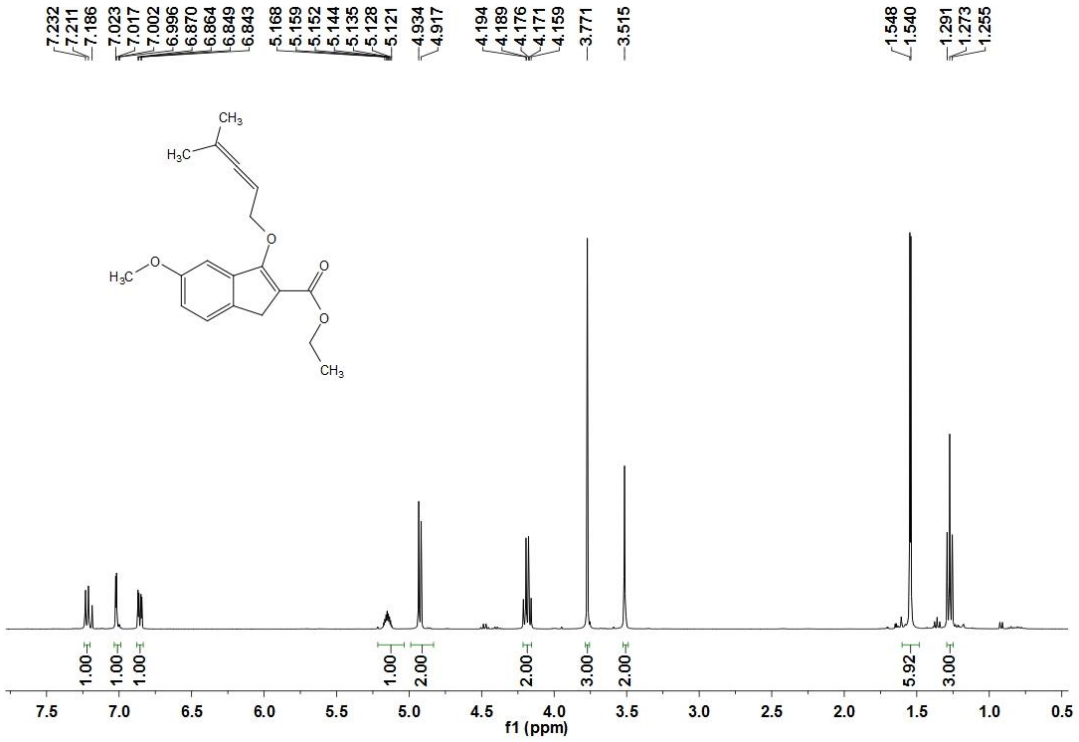
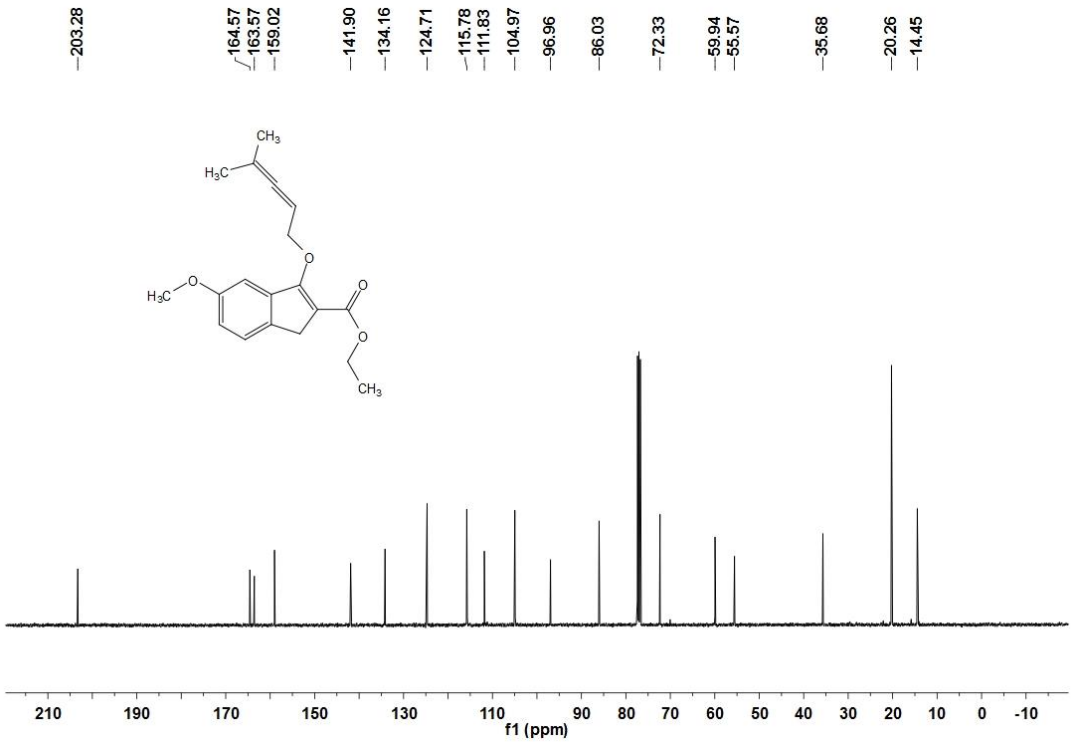
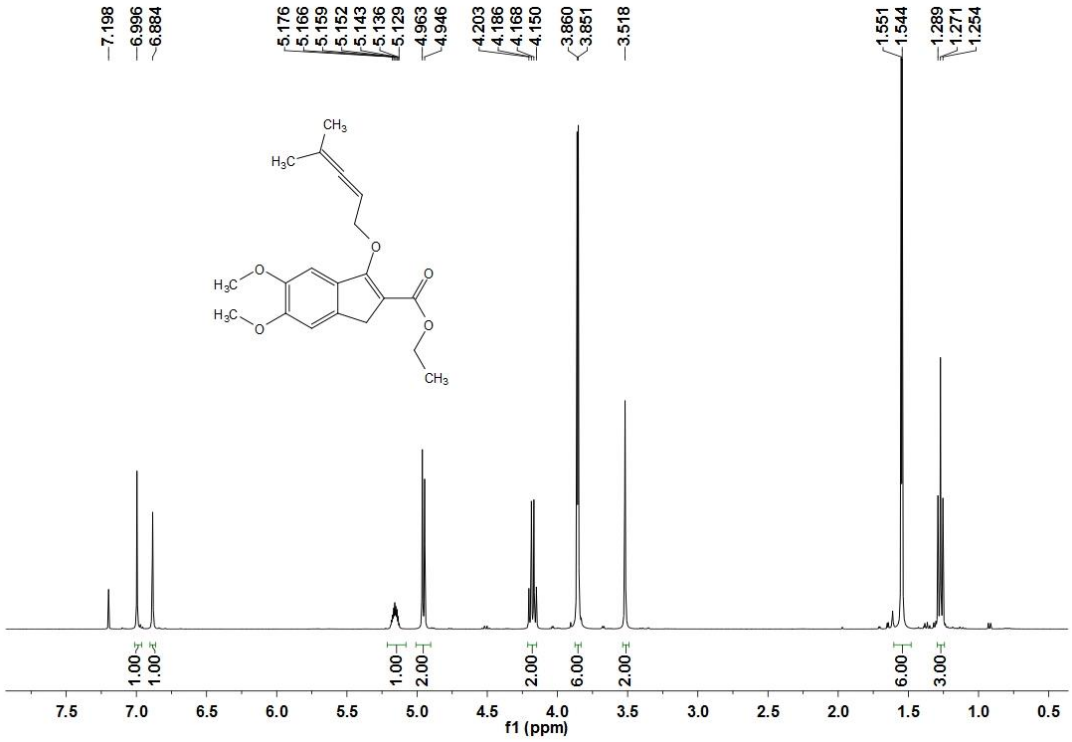
164.68
163.93
140.73
139.16
136.29
129.37
123.80
121.39
111.04
96.92
86.12
72.31
59.90
35.97
21.46
20.26
14.47
f1 (ppm)

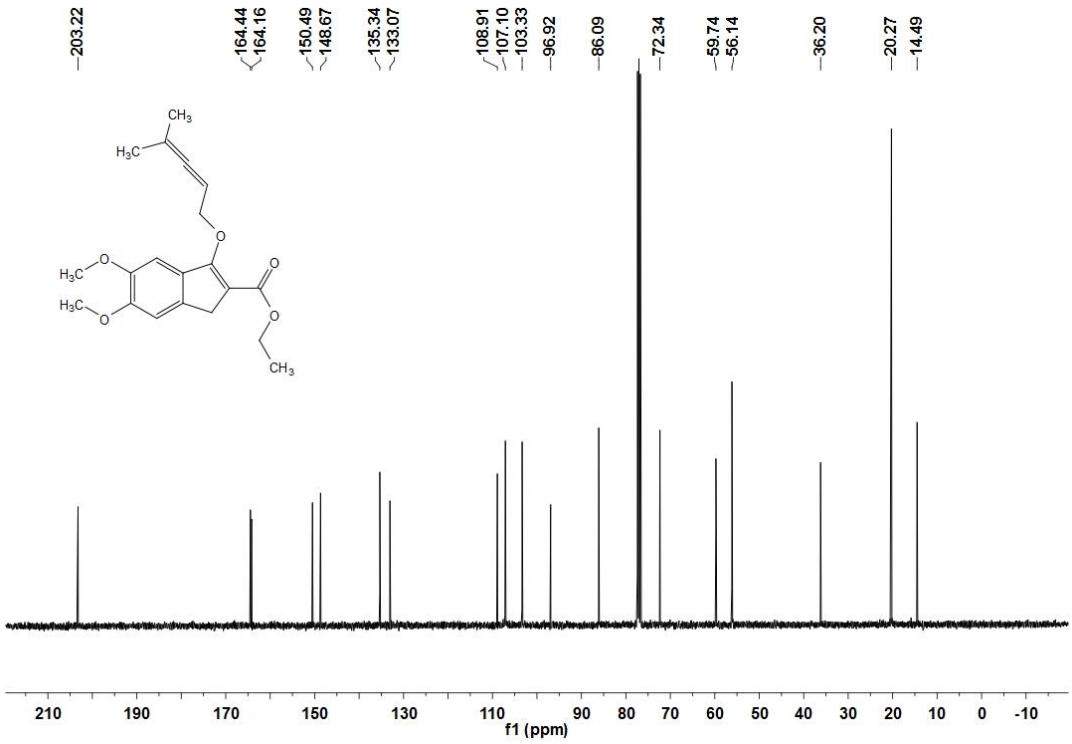
1k


7.232
7.211
7.186
7.023
7.017
7.002
6.996
6.870
6.864
6.849
6.843
5.168
5.159
5.152
5.144
5.135
5.128
5.121
4.934
4.917
4.194
4.189
4.176
4.171
4.159
3.771
3.515
1.548
1.540
1.291
1.273
1.255
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
5.92
3.00
f1 (ppm)

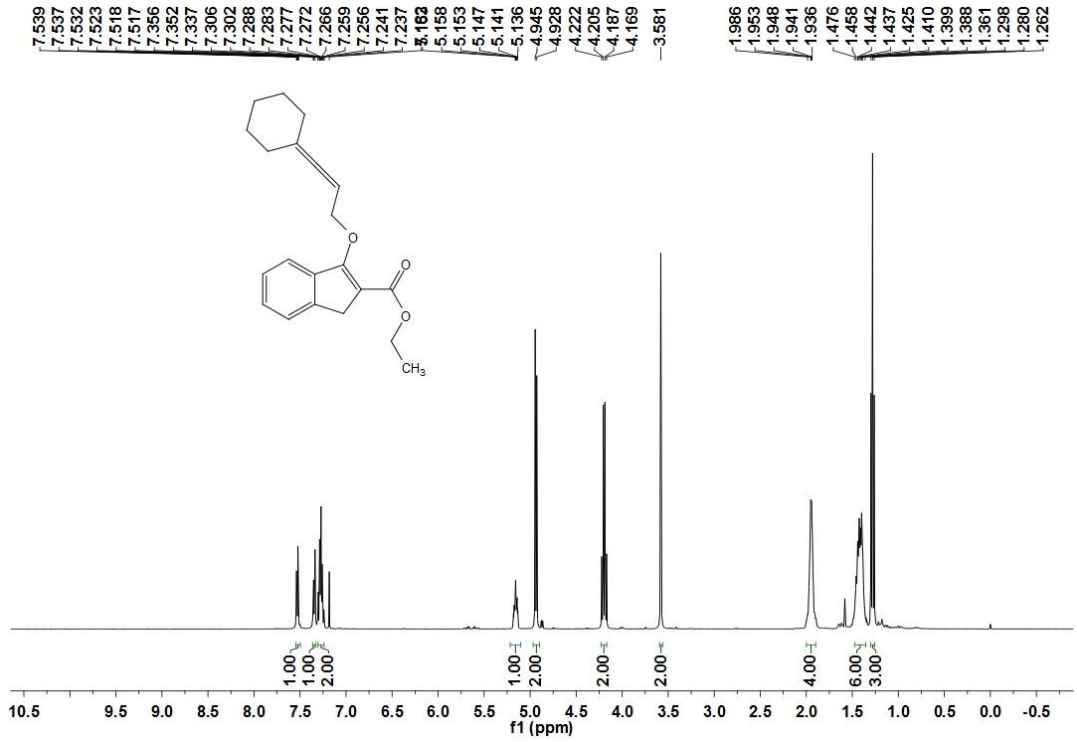

203.28
164.57
163.57
159.02
141.90
134.16
124.71
115.78
111.83
104.97
96.96
86.03
72.33
59.94
55.57
35.68
20.26
14.45
f1 (ppm)

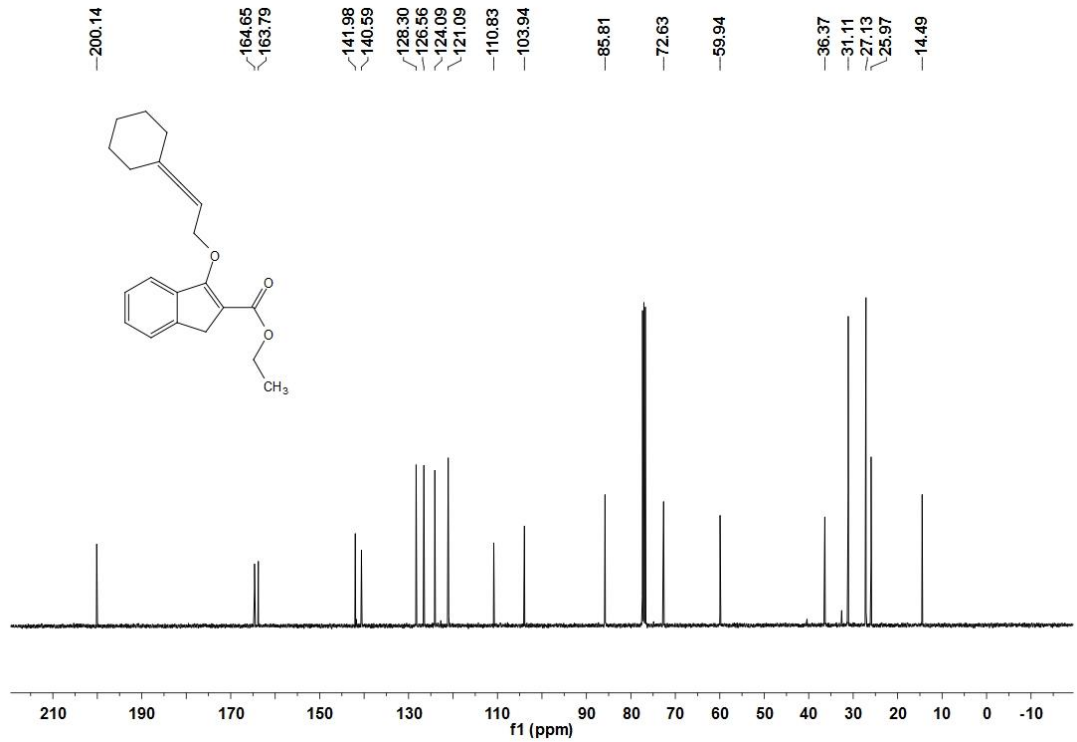
1l


7.198
6.996
6.884
5.176
5.166
5.159
5.152
5.143
5.136
5.129
4.963
4.946
4.203
4.186
4.168
4.150
3.860
3.851
3.518
1.551
1.544
1.289
1.271
1.254
1.00
1.00
1.00
2.00
2.00
6.00
2.00
6.00
3.00
f1 (ppm)

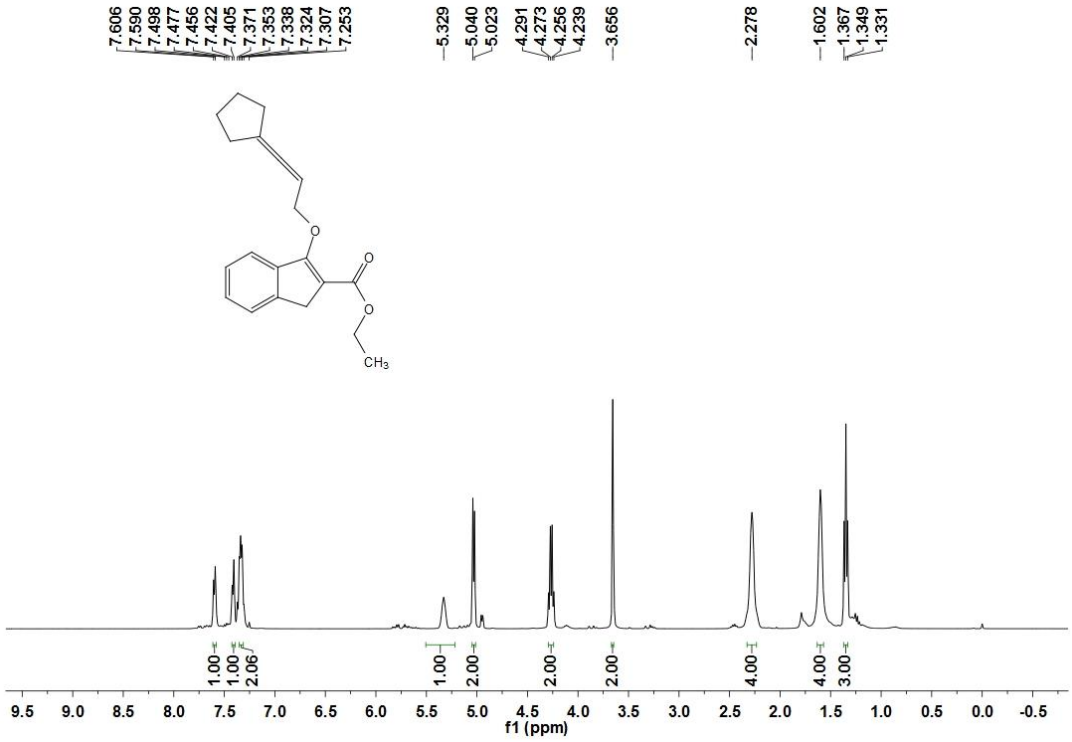

203.22
164.44
164.16
150.49
148.67
135.34
133.07
108.91
107.10
103.33
96.92
86.09
72.34
59.74
56.14
36.20
20.27
14.49
f1 (ppm)

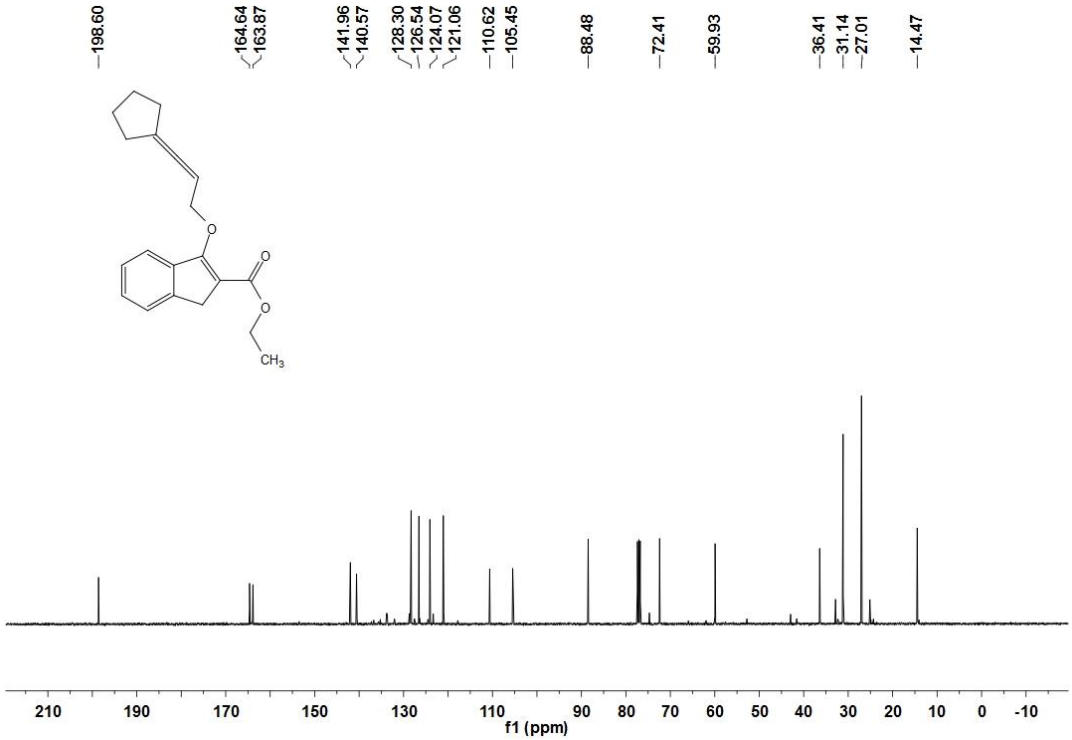
1m


7.539
7.537
7.532
7.523
7.518
7.517
7.356
7.352
7.337
7.306
7.302
7.288
7.283
7.277
7.272
7.266
7.259
7.256
7.241
7.237
5.158
5.153
5.147
5.141
5.136
4.945
4.928
4.222
4.205
4.187
4.169
3.581
1.986
1.953
1.948
1.941
1.936
1.476
1.458
1.442
1.437
1.425
1.410
1.399
1.388
1.361
1.298
1.280
1.262
O
O
O
CH3
1.00
1.00
2.00
1.00
2.00
2.00
2.00
4.00
6.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

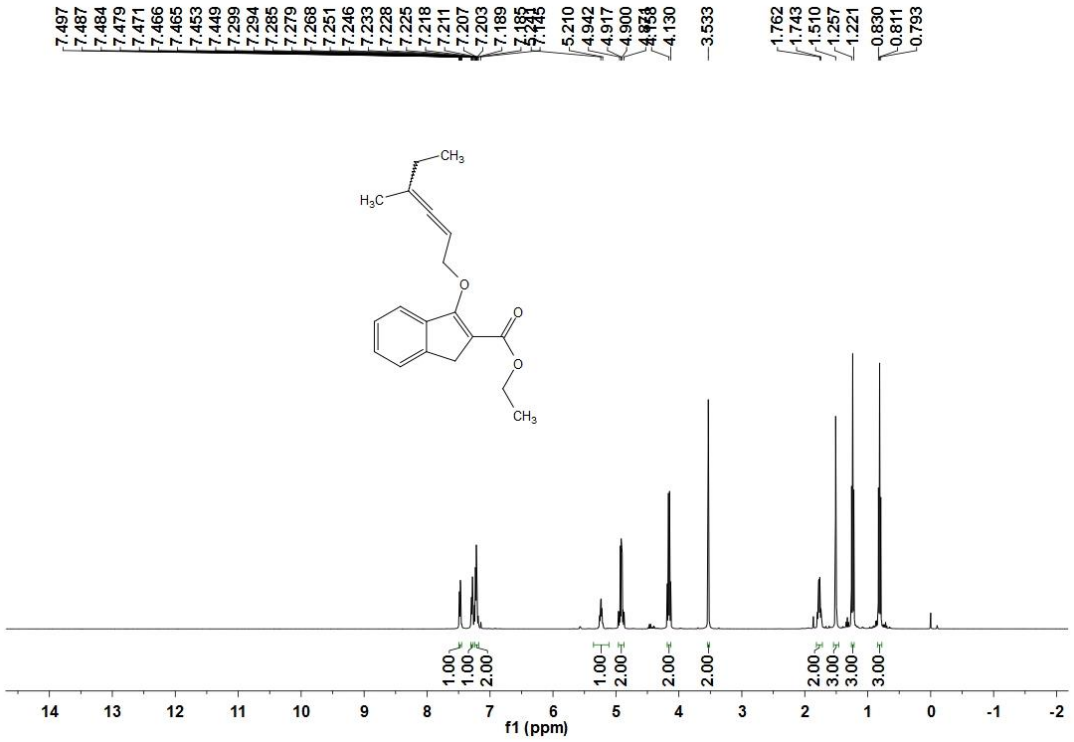

200.14
164.65
163.79
141.98
140.59
128.30
126.56
124.09
121.09
110.83
103.94
85.81
72.63
59.94
36.37
31.11
27.13
25.97
14.49
O
O
O
CH3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1n


7.606
7.590
7.498
7.477
7.456
7.422
7.405
7.371
7.353
7.338
7.324
7.307
7.253
5.329
5.040
5.023
4.291
4.273
4.256
4.239
3.656
2.278
1.602
1.367
1.349
1.331
O
O
O
CH3
1.00
1.00
2.06
1.00
2.00
2.00
2.00
4.00
4.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


198.60
164.64
163.87
141.96
140.57
128.30
126.54
124.07
121.06
110.62
105.45
88.48
72.41
59.93
36.41
31.14
27.01
14.47
O
O
O
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1o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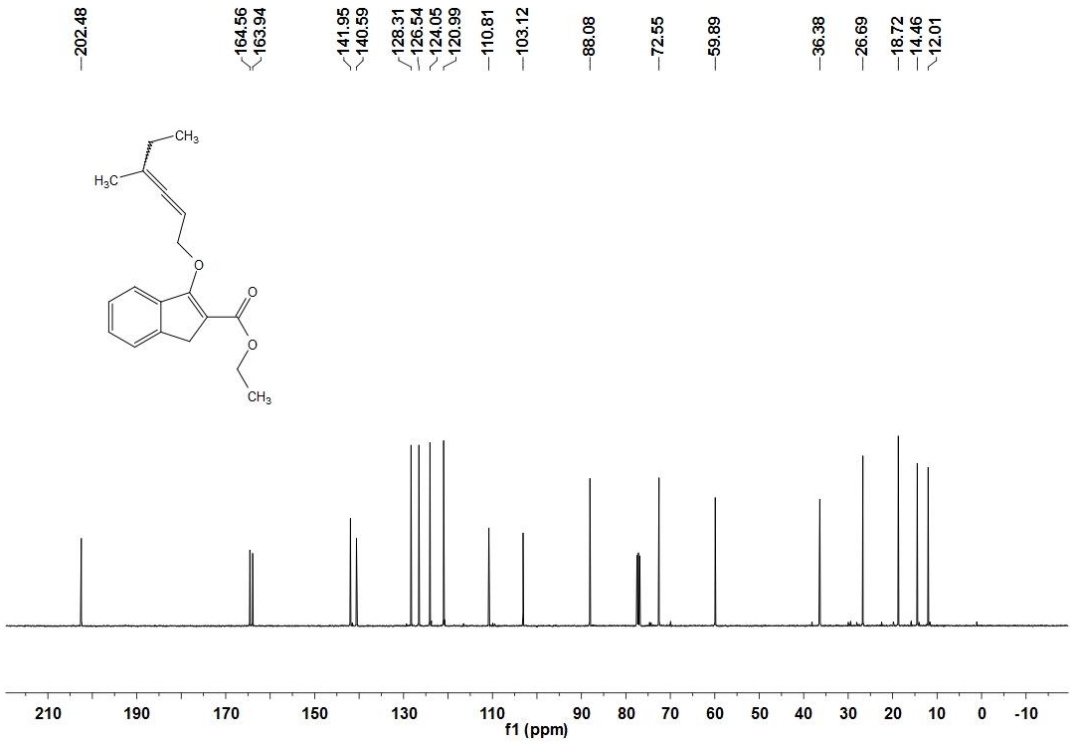
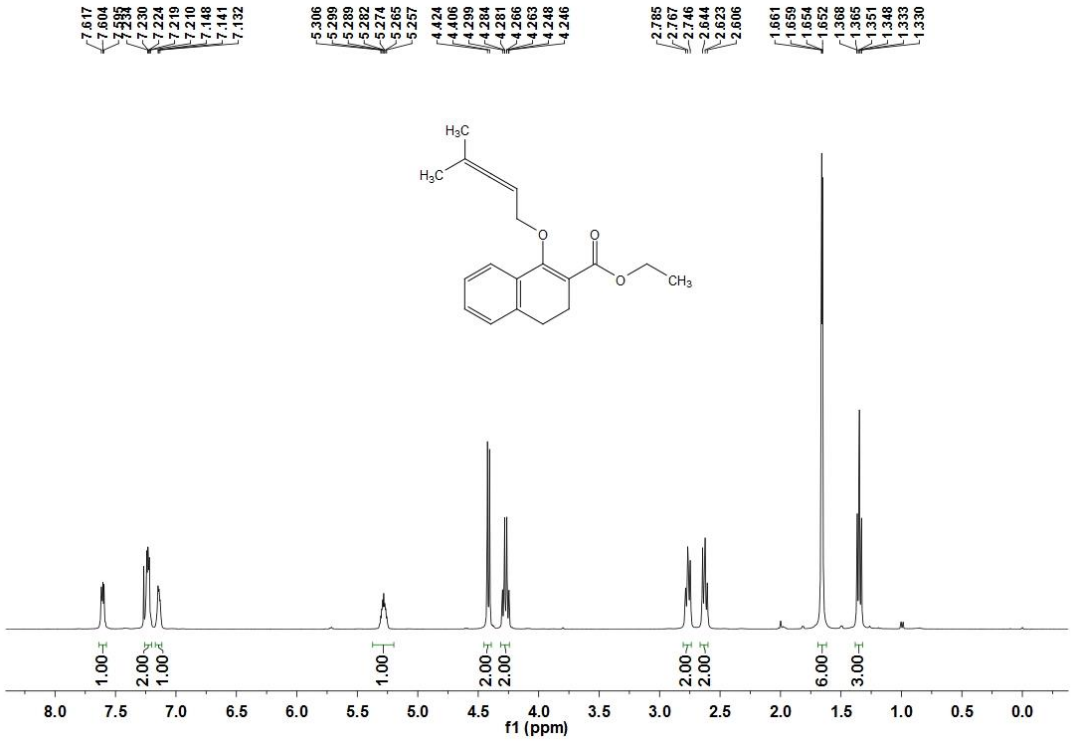
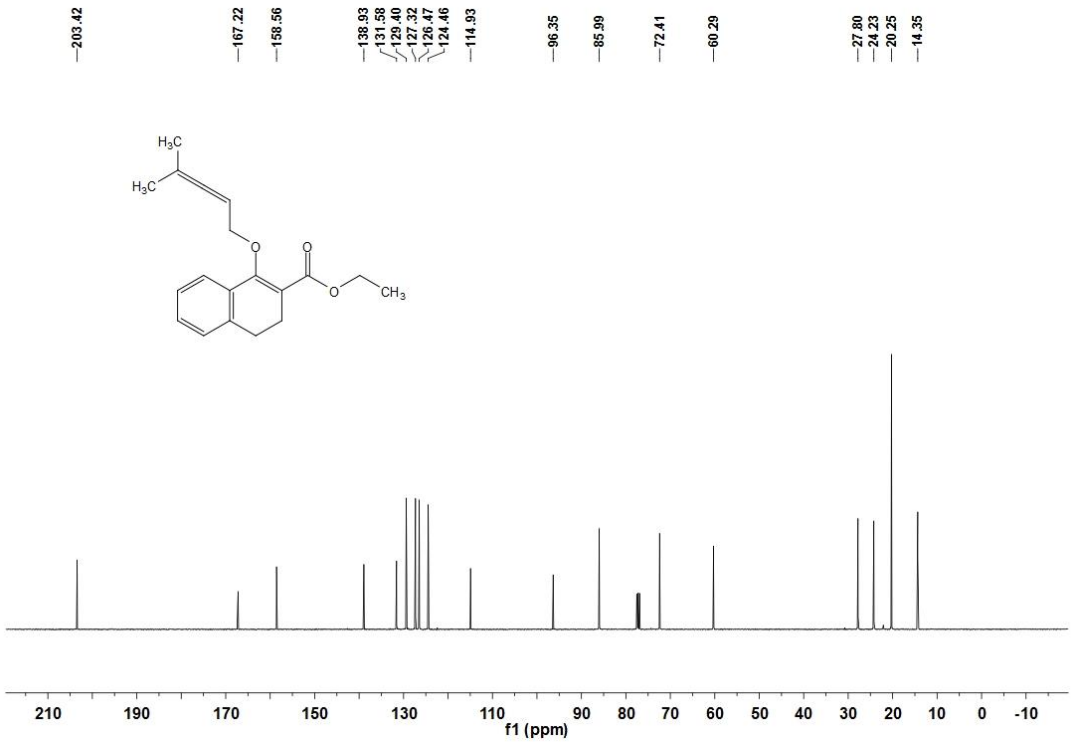
7.487
7.484
7.479
7.471
7.466
7.465
7.453
7.449
7.299
7.294
7.285
7.279
7.268
7.251
7.246
7.233
7.228
7.225
7.218
7.211
7.207
7.203
7.189
5.210
4.942
4.917
4.900
4.130
3.533
1.762
1.743
1.510
1.257
1.221
0.830
0.811
0.793
CH3
H3C
O
O
O
CH3
1.00
1.00
2.00
1.00
2.00
2.00
2.00
2.00
3.00
3.00
3.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)

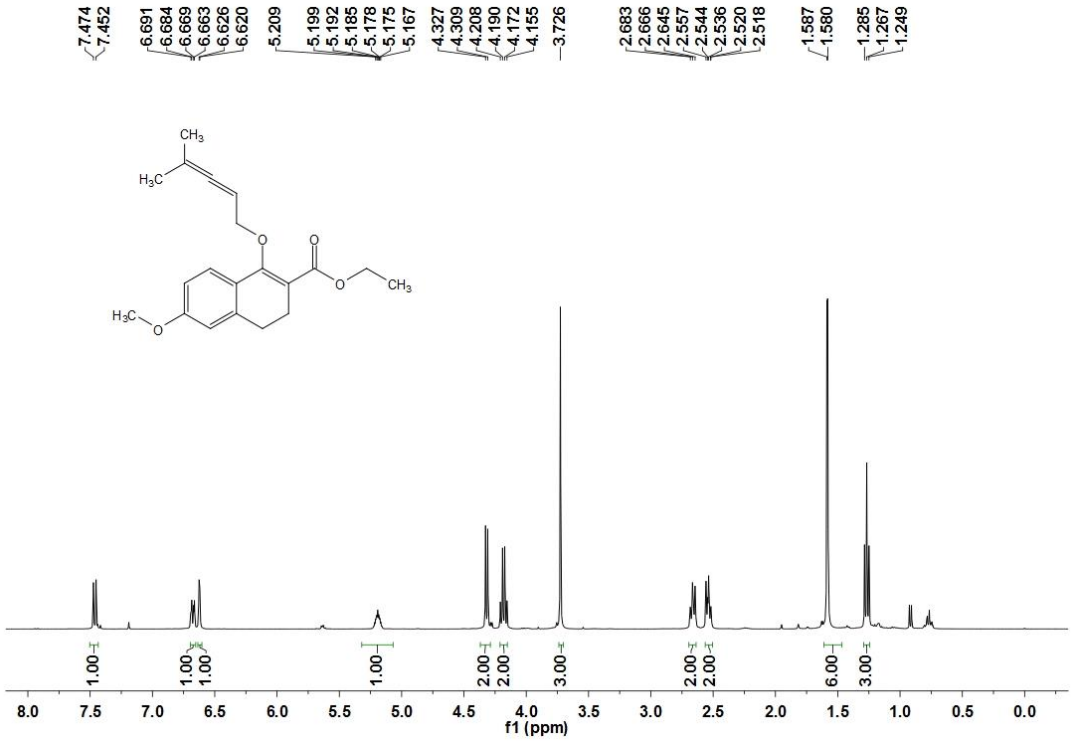

202.48
164.56
163.94
141.95
140.59
128.31
126.54
124.05
120.99
110.81
103.12
88.08
72.55
59.89
36.38
26.69
18.72
14.46
12.01
CH3
H3C
O
O
O
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

1p


7.617
7.604
7.230
7.224
7.219
7.210
7.148
7.141
7.132
5.306
5.299
5.289
5.282
5.274
5.265
5.257
4.424
4.406
4.299
4.284
4.281
4.266
4.263
4.248
4.246
2.785
2.767
2.746
2.644
2.623
2.606
1.661
1.659
1.654
1.652
1.368
1.365
1.351
1.348
1.333
1.330
H3C
H3C
O
O
O
CH3
1.00
2.00
1.00
1.00
2.00
2.00
2.00
2.00
6.00
3.00
f1 (ppm)


203.42
167.22
158.56
138.93
131.58
129.40
127.32
126.47
124.46
114.93
96.35
85.99
72.41
60.29
27.80
24.23
20.25
14.35
H3C
H3C
O
O
O
CH3
f1 (ppm)

1q


7.474
7.452
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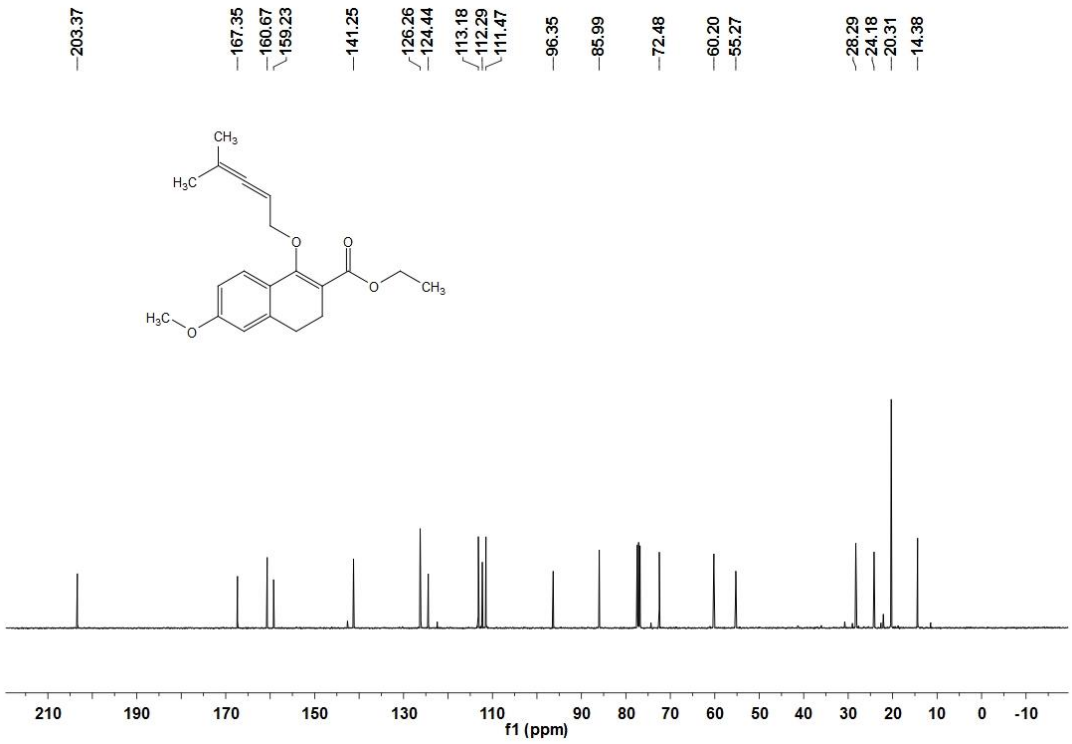
6.684
6.669
6.663
6.626
6.620
5.209
5.199
5.192
5.185
5.178
5.175
5.167
4.327
4.309
4.208
4.190
4.172
4.155
3.726
2.683
2.666
2.645
2.557
2.544
2.536
2.520
2.518
1.587
1.580
1.285
1.267
1.249
CH3
H3C
O
O
O
CH3
H3C
O
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
2.00
6.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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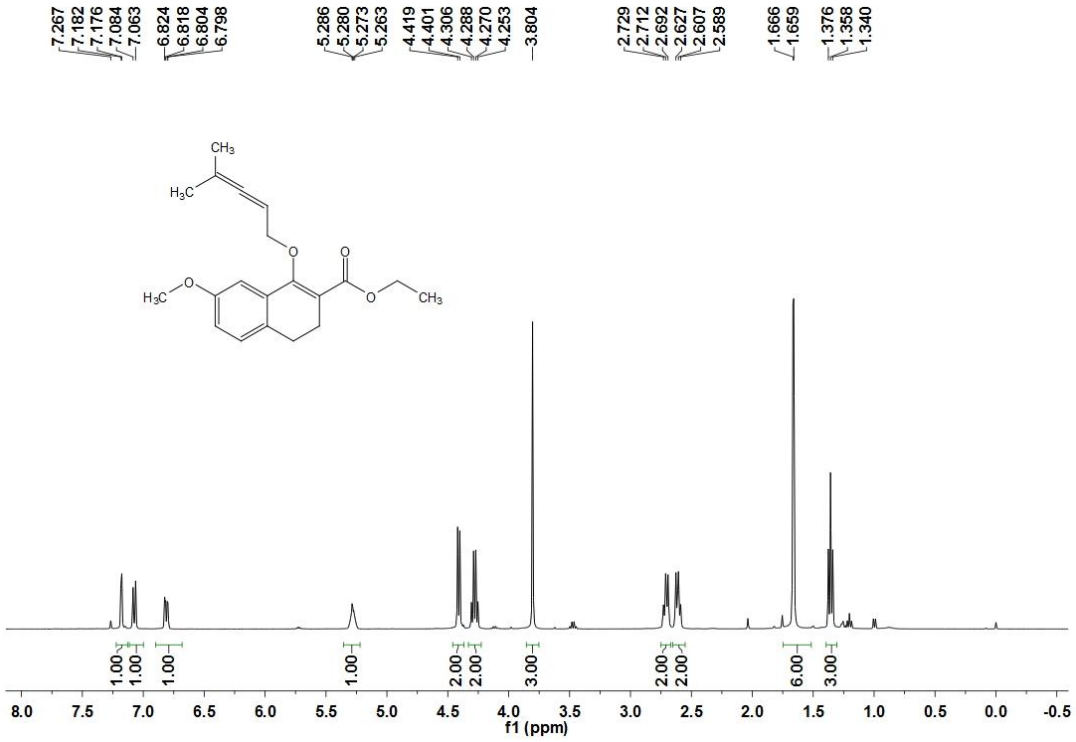
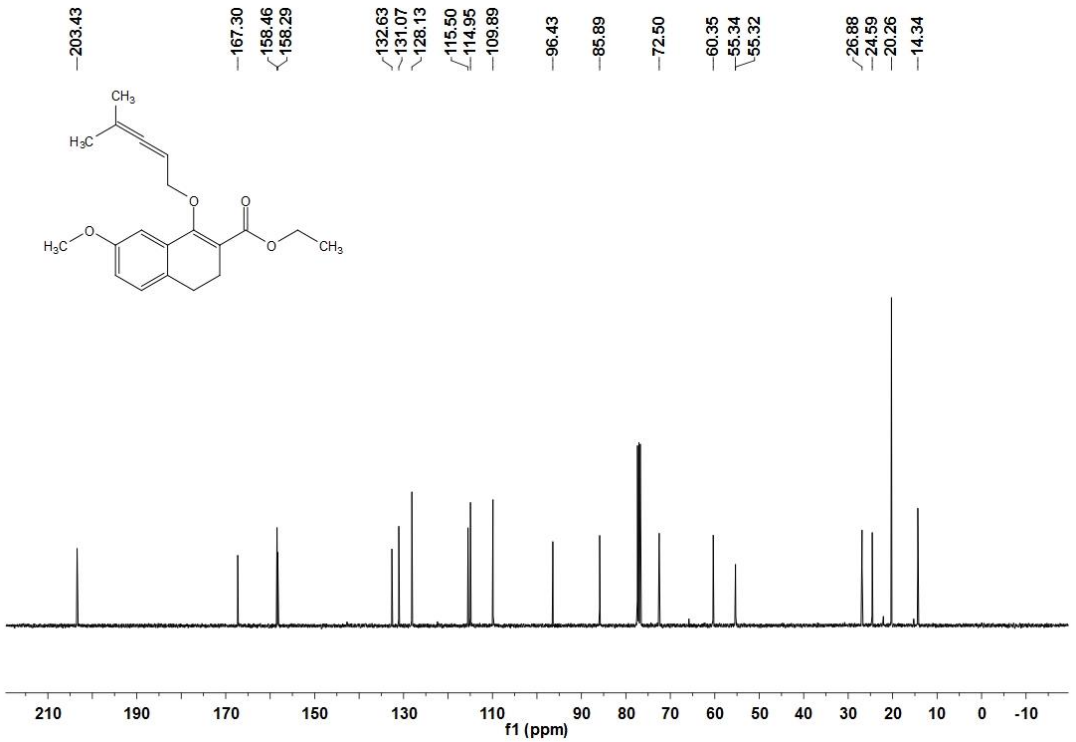
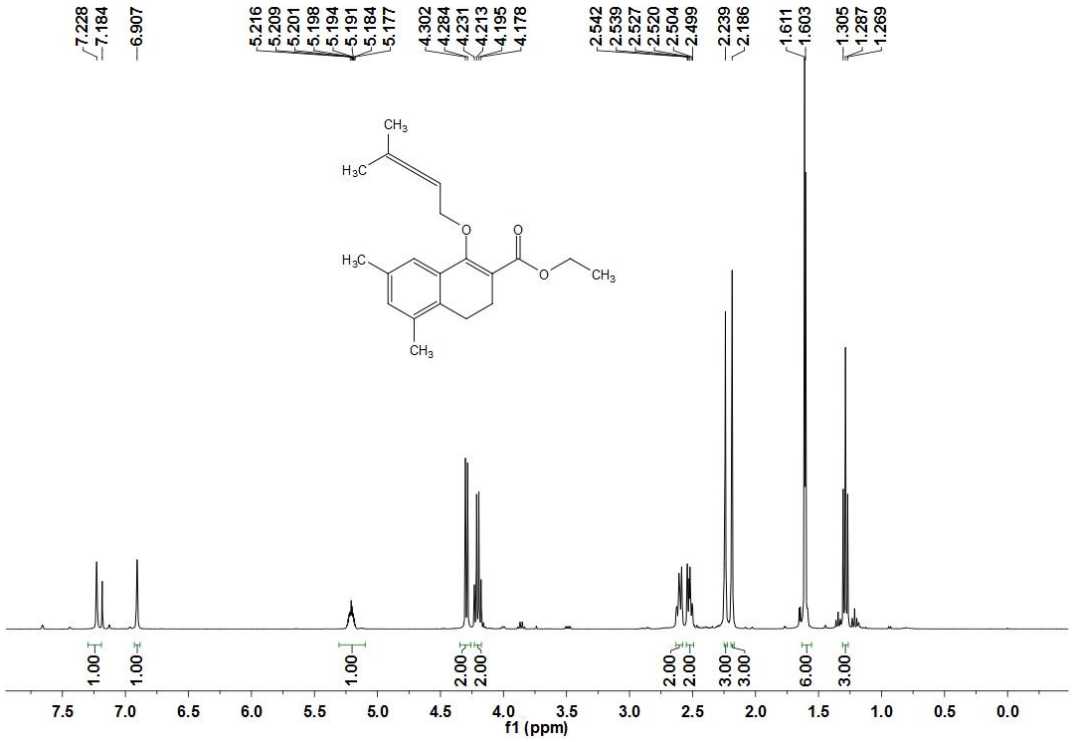
160.67
159.23
141.25
126.26
124.44
113.18
112.29
111.47
96.35
85.99
72.48
60.20
55.27
28.29
24.18
20.31
14.38
CH3
H3C
O
O
O
CH3
H3C
O
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

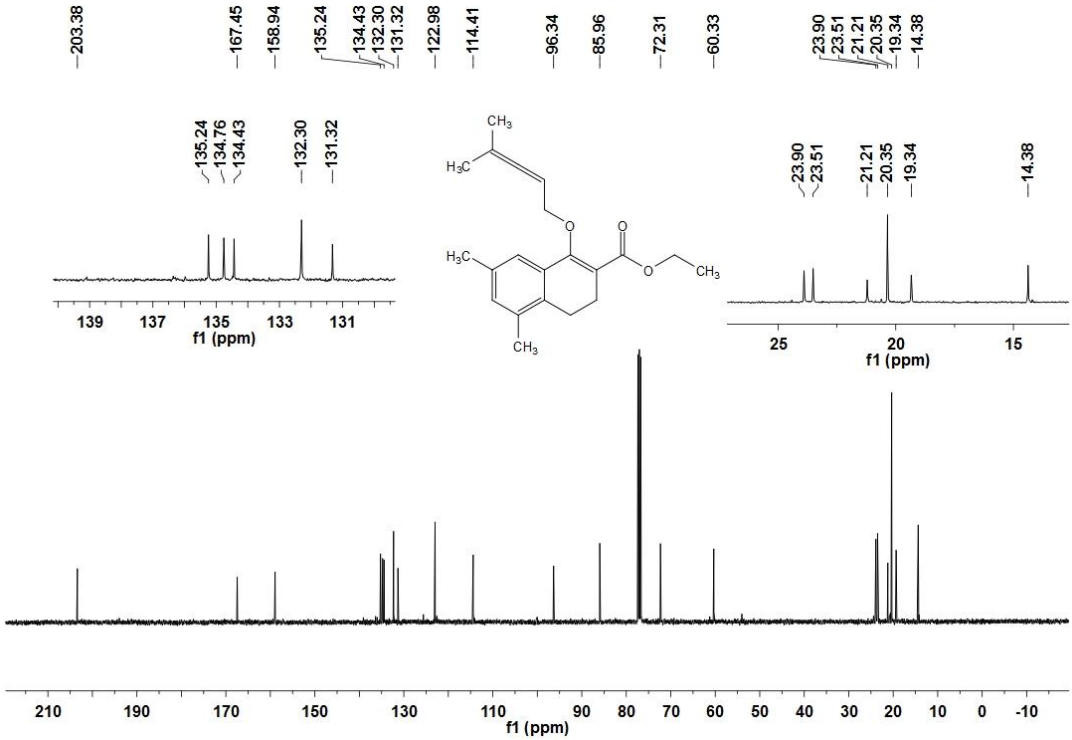
1r


7.267
7.182
7.176
7.084
7.063
6.824
6.818
6.804
6.798
5.286
5.280
5.273
5.263
4.419
4.401
4.306
4.288
4.270
4.253
3.804
2.729
2.712
2.692
2.627
2.607
2.589
1.666
1.659
1.376
1.358
1.340
CH3
H3C
O
O
H3C
O
O
CH3
1.00
1.00
1.00
1.00
2.00
2.00
3.00
2.00
2.00
6.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

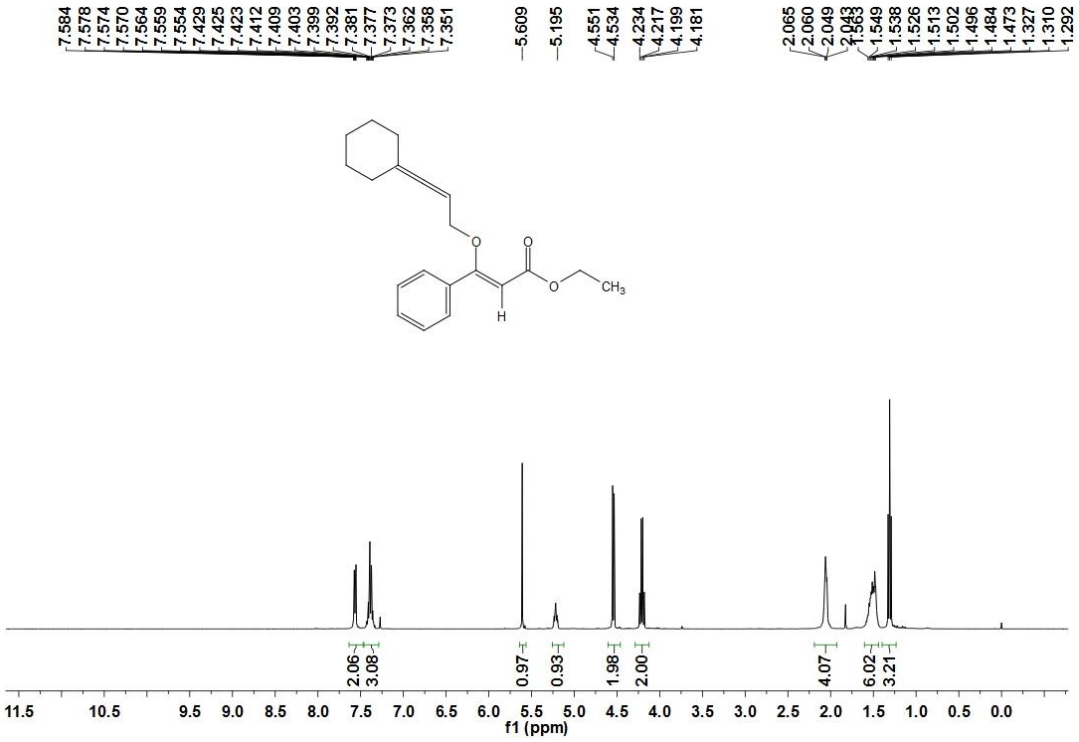

203.43
167.30
158.46
158.29
132.63
131.07
128.13
115.50
114.95
109.89
96.43
85.89
72.50
60.35
55.34
55.32
26.88
24.59
20.26
14.34
CH3
H3C
O
O
H3C
O
O
CH3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

1s


7.228
7.184
6.907
5.216
5.209
5.201
5.198
5.194
5.191
5.184
5.177
4.302
4.284
4.231
4.213
4.195
4.178
2.542
2.539
2.527
2.520
2.504
2.499
2.239
2.186
1.611
1.603
1.305
1.287
1.269
1.00
1.00
1.00
2.00
2.00
2.00
2.00
3.00
3.00
6.00
3.00
f1 (ppm)


203.38
167.45
158.94
135.24
134.43
132.30
131.32
122.98
114.41
96.34
85.96
72.31
60.33
23.90
23.51
21.21
20.35
19.34
14.38
f1 (ppm)

1u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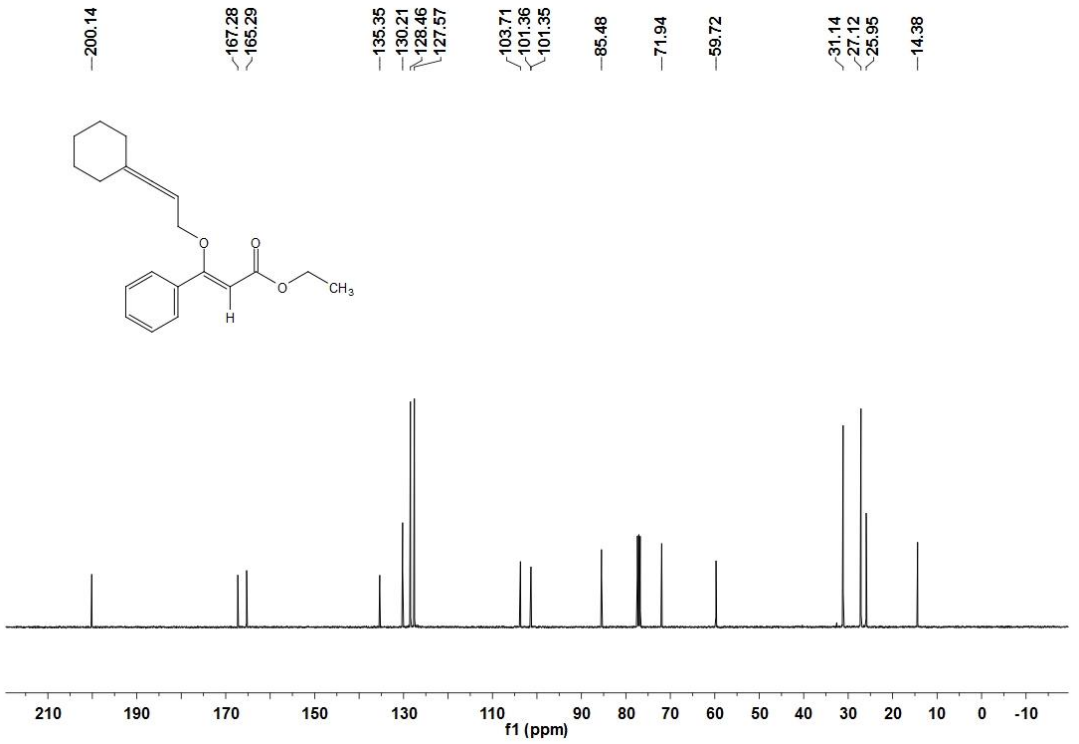
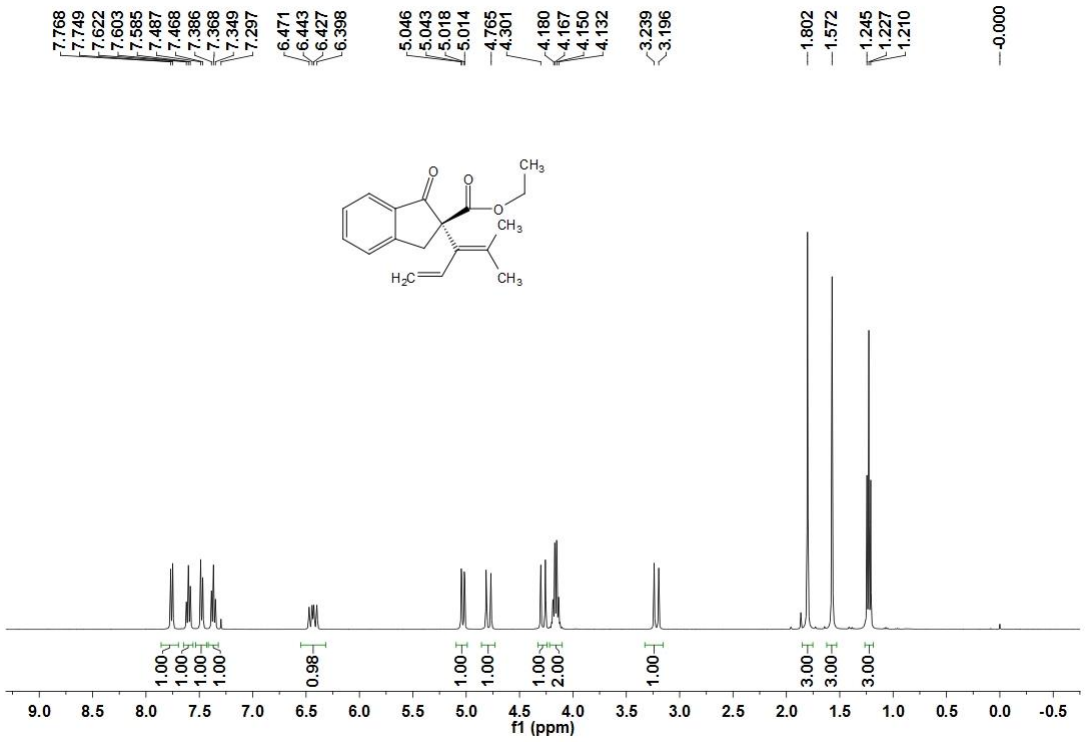
7.574
7.570
7.564
7.559
7.554
7.429
7.425
7.423
7.412
7.409
7.403
7.399
7.392
7.381
7.377
7.373
7.362
7.358
7.351
5.609
5.195
4.551
4.534
4.234
4.217
4.199
4.181
2.065
2.060
2.049
2.043
1.583
1.549
1.538
1.526
1.513
1.502
1.496
1.484
1.473
1.327
1.310
1.292
O
O
O
CH3
H
2.06
3.08
0.97
0.93
1.98
2.00
4.07
6.02
3.21
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


200.14
167.28
165.29
135.35
130.21
128.46
127.57
103.71
101.36
101.35
85.48
71.94
59.72
31.14
27.12
25.95
14.38
O
O
O
CH3
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2a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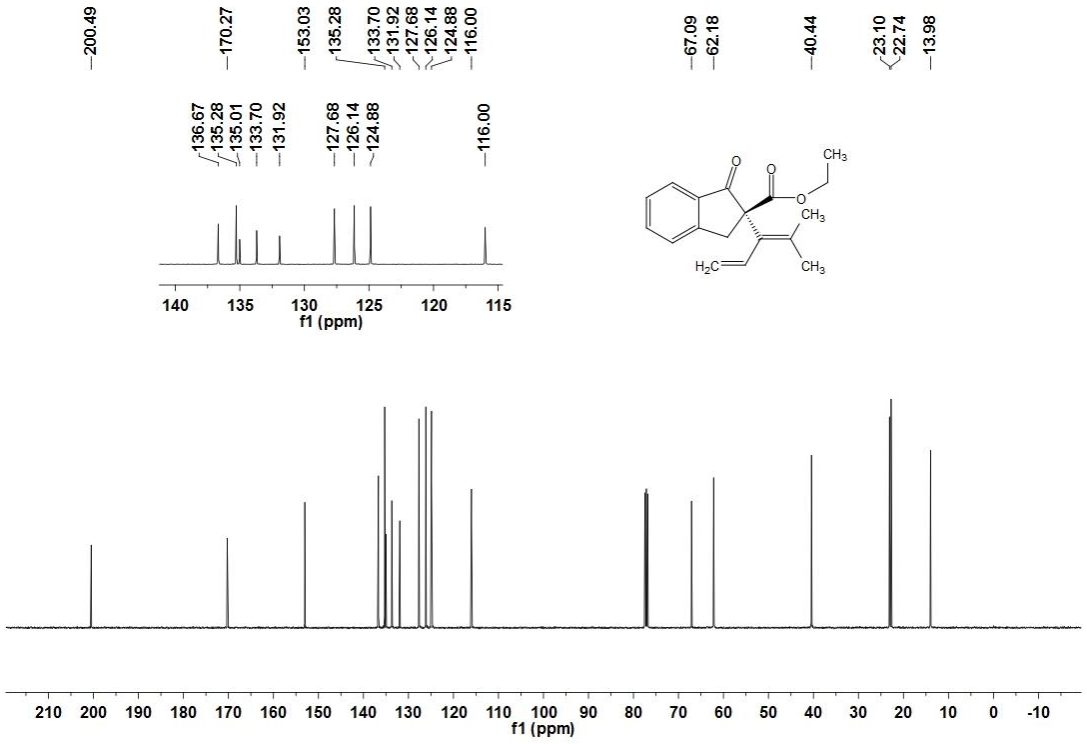
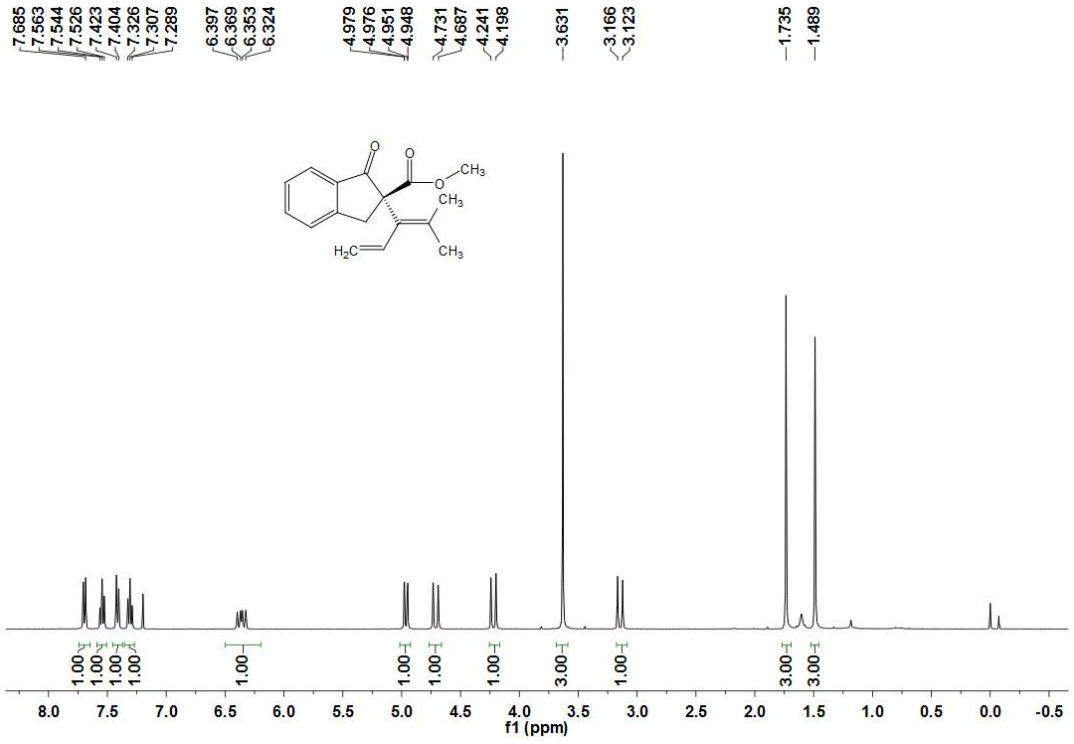
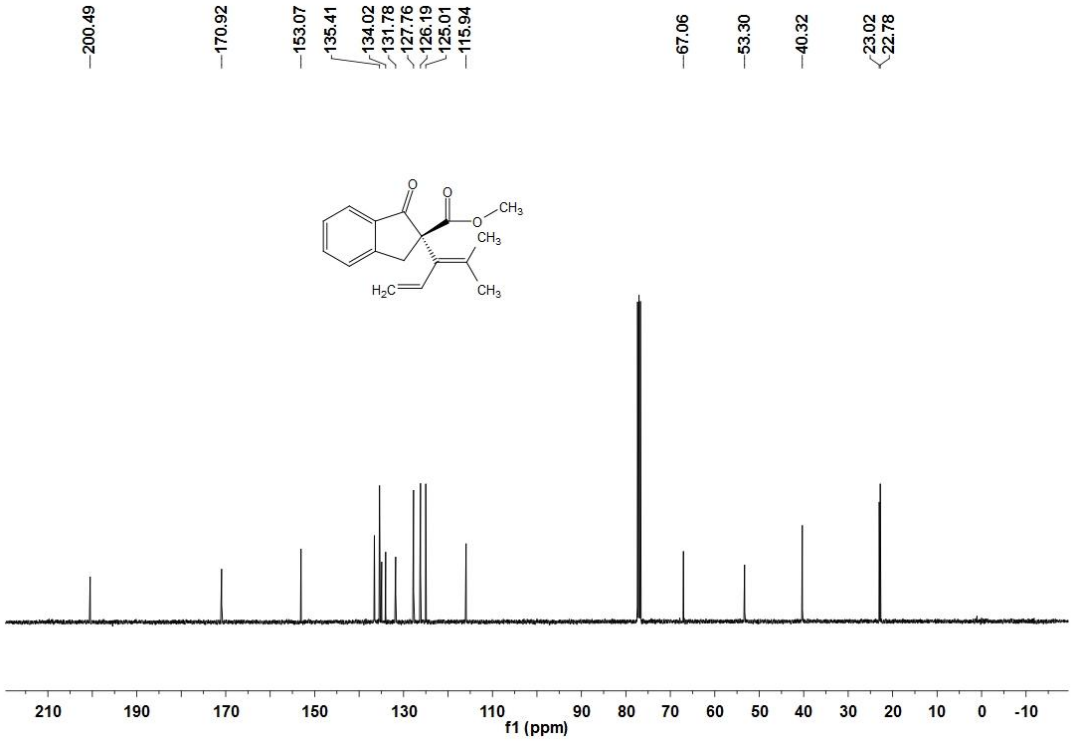
7.622
7.603
7.585
7.487
7.468
7.386
7.368
7.349
7.297
6.471
6.443
6.427
6.398
5.046
5.043
5.018
5.014
4.765
4.301
4.180
4.167
4.150
4.132
3.239
3.196
1.802
1.572
1.245
1.227
1.210
-0.000
1.00
1.00
1.00
1.00
0.98
1.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
f1 (ppm)

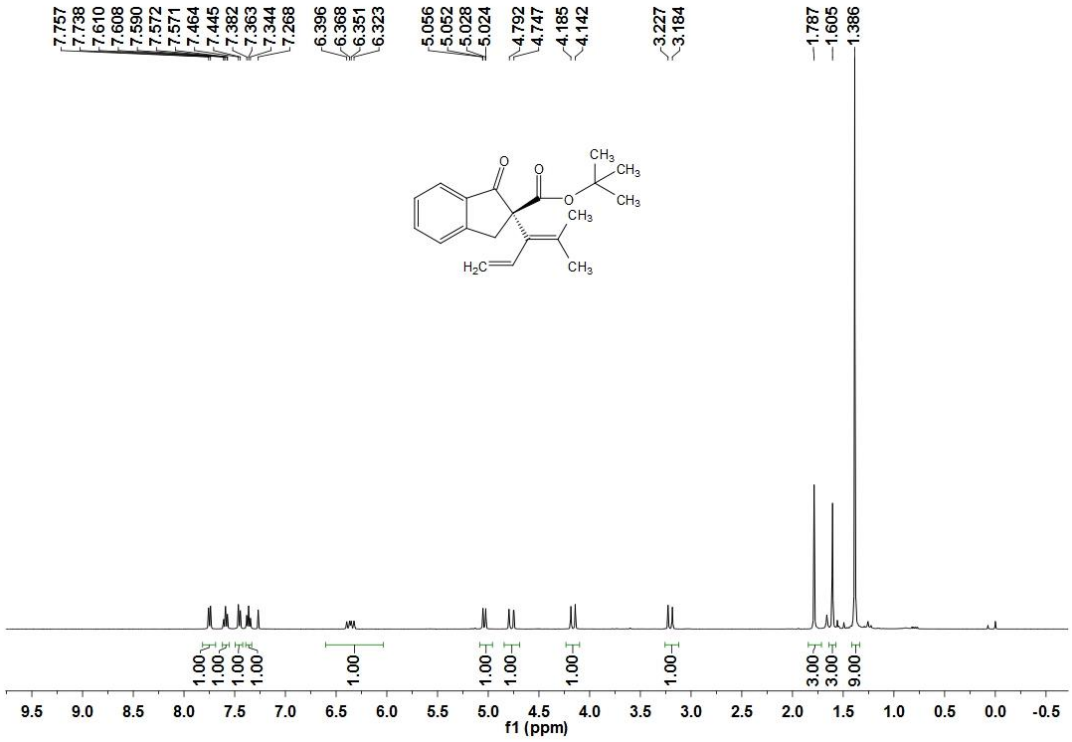

200.49
170.27
153.03
135.28
133.70
131.92
127.68
126.14
124.88
116.00
67.09
62.18
40.44
23.10
22.74
13.98
136.67
135.28
135.01
133.70
131.92
127.68
126.14
124.88
116.00
f1 (ppm)
f1 (ppm)

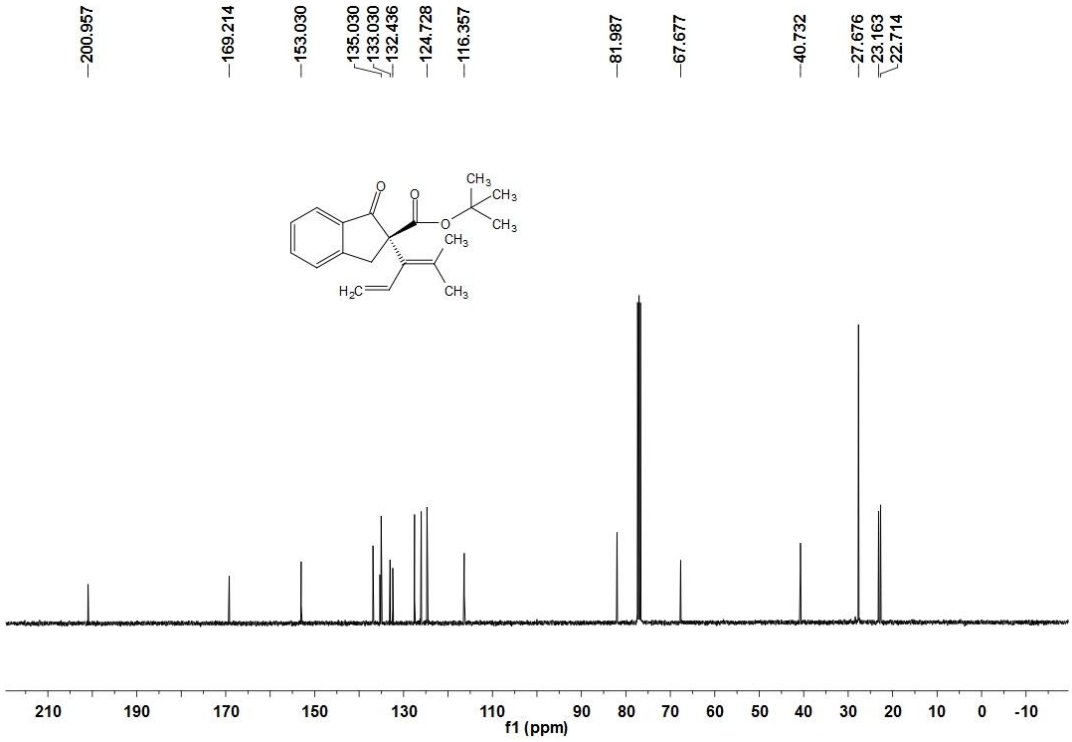
2b


7.685
7.563
7.544
7.526
7.423
7.404
7.326
7.307
7.289
6.397
6.369
6.353
6.324
4.979
4.976
4.951
4.948
4.731
4.687
4.241
4.198
3.631
3.166
3.123
1.735
1.489
O
O
O
CH3
CH3
H2C
CH3
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
1.00
3.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

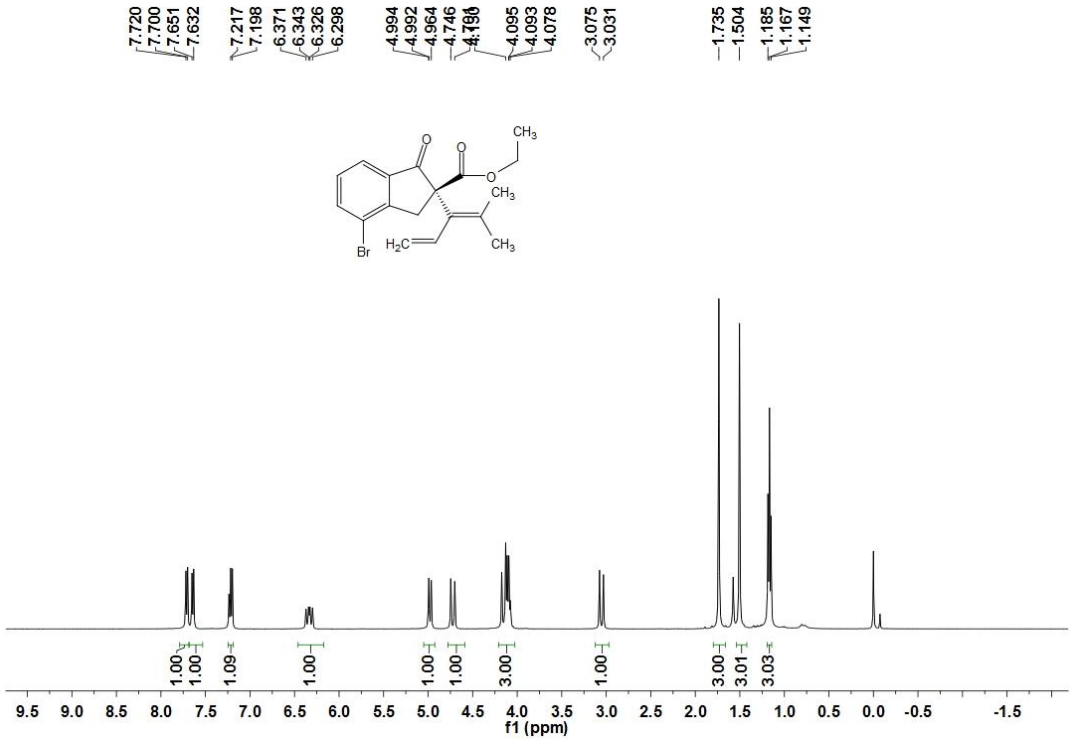

200.49
170.92
153.07
135.41
134.02
131.78
127.76
126.19
125.01
115.94
67.06
53.30
40.32
23.02
22.78
O
O
O
CH3
CH3
H2C
CH3
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

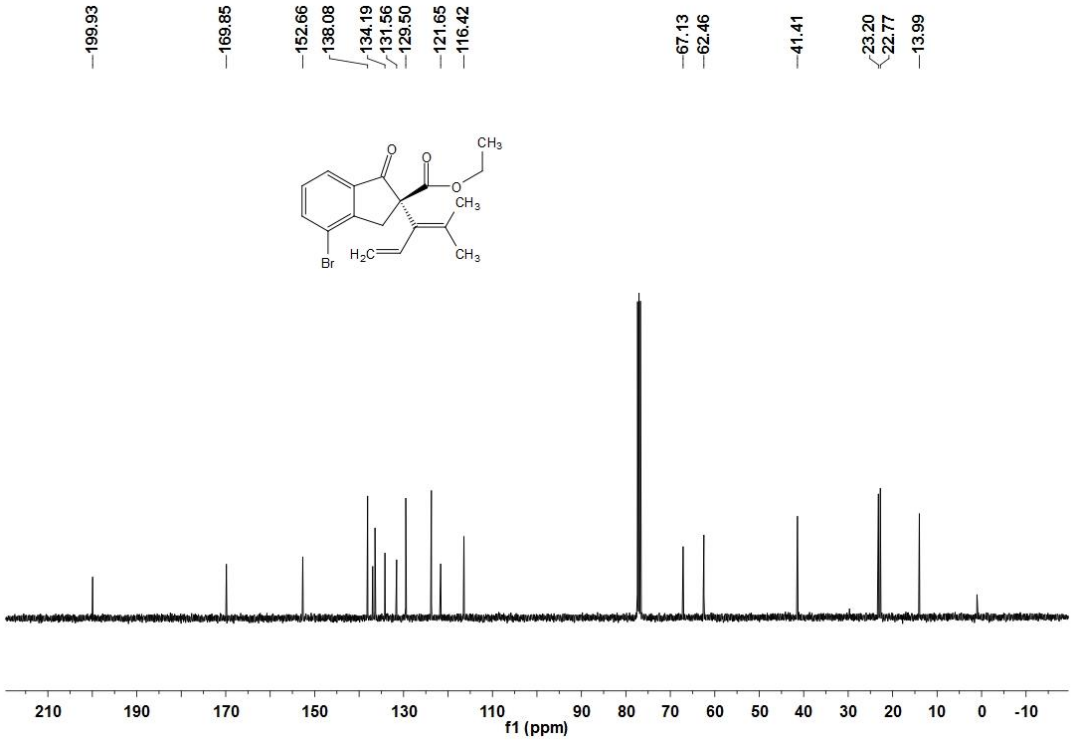
2c


7.757
7.738
7.610
7.608
7.590
7.572
7.571
7.464
7.445
7.382
7.363
7.344
7.268
6.396
6.368
6.351
6.323
5.056
5.052
5.028
5.024
4.792
4.747
4.185
4.142
3.227
3.184
1.787
1.605
1.386
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
3.00
3.00
9.00
f1 (ppm)

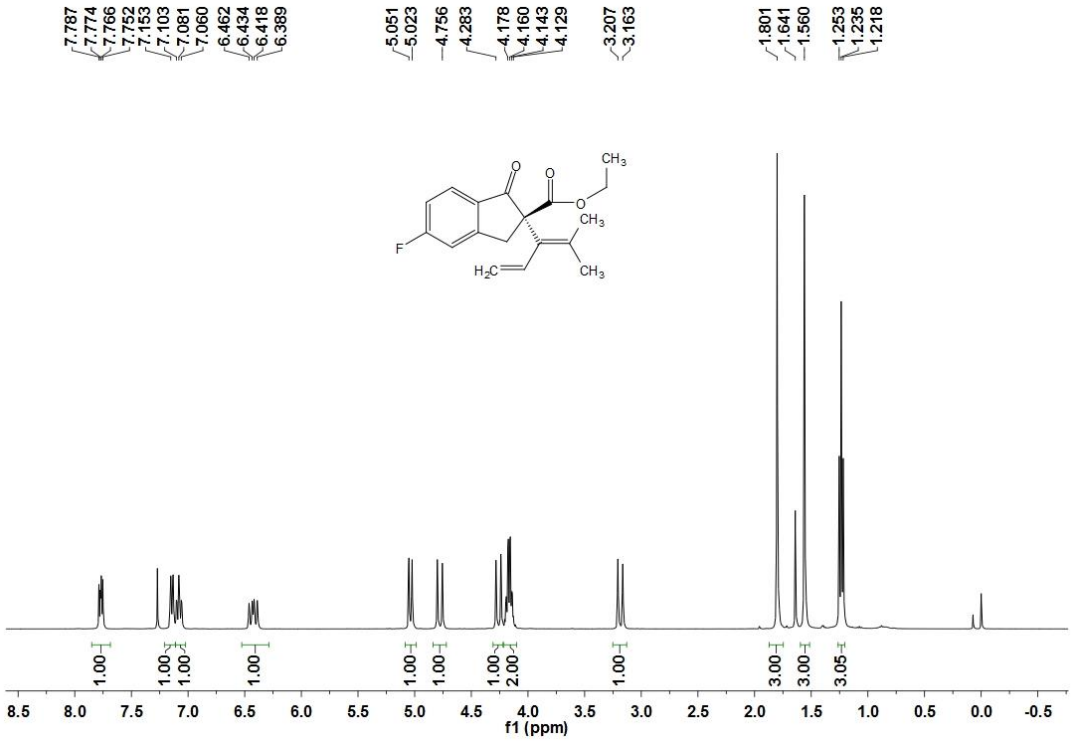

200.957
169.214
153.030
135.030
133.030
132.436
124.728
116.357
81.987
67.677
40.732
27.676
23.163
22.714
f1 (ppm)

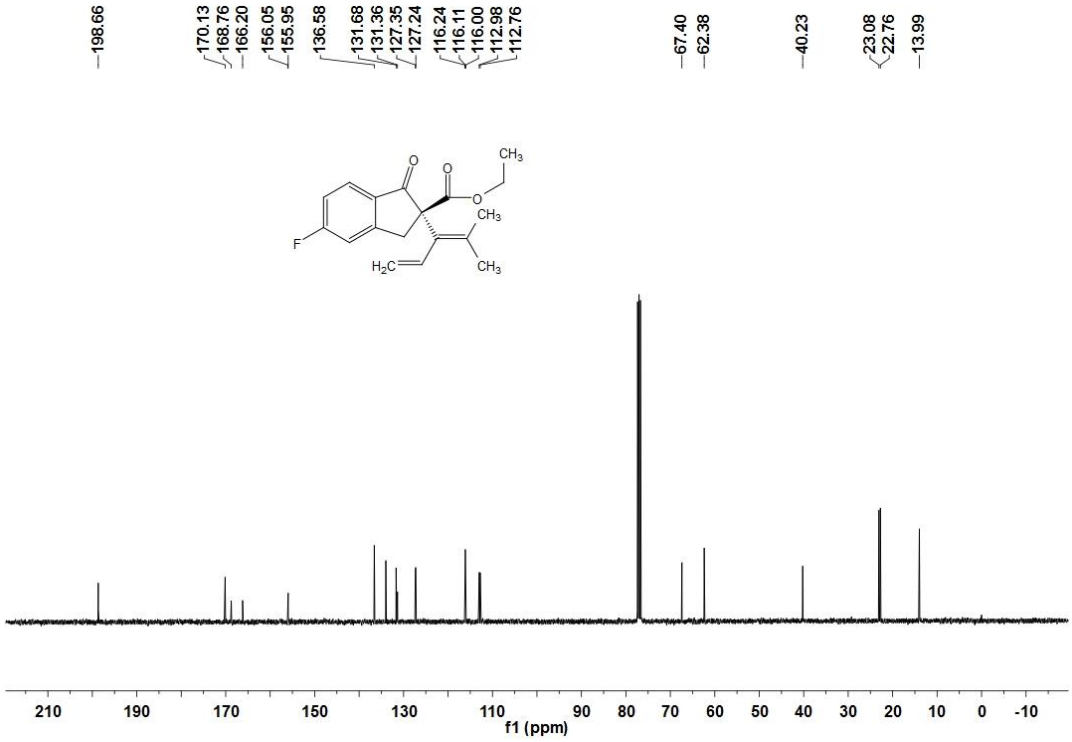
2d


7.720
7.700
7.651
7.632
7.217
7.198
6.371
6.343
6.326
6.298
4.994
4.992
4.964
4.746
4.095
4.093
4.078
3.075
3.031
1.735
1.504
1.185
1.167
1.149
1.00
1.00
1.09
1.00
1.00
1.00
3.00
1.00
3.00
3.01
3.03
f1 (ppm)

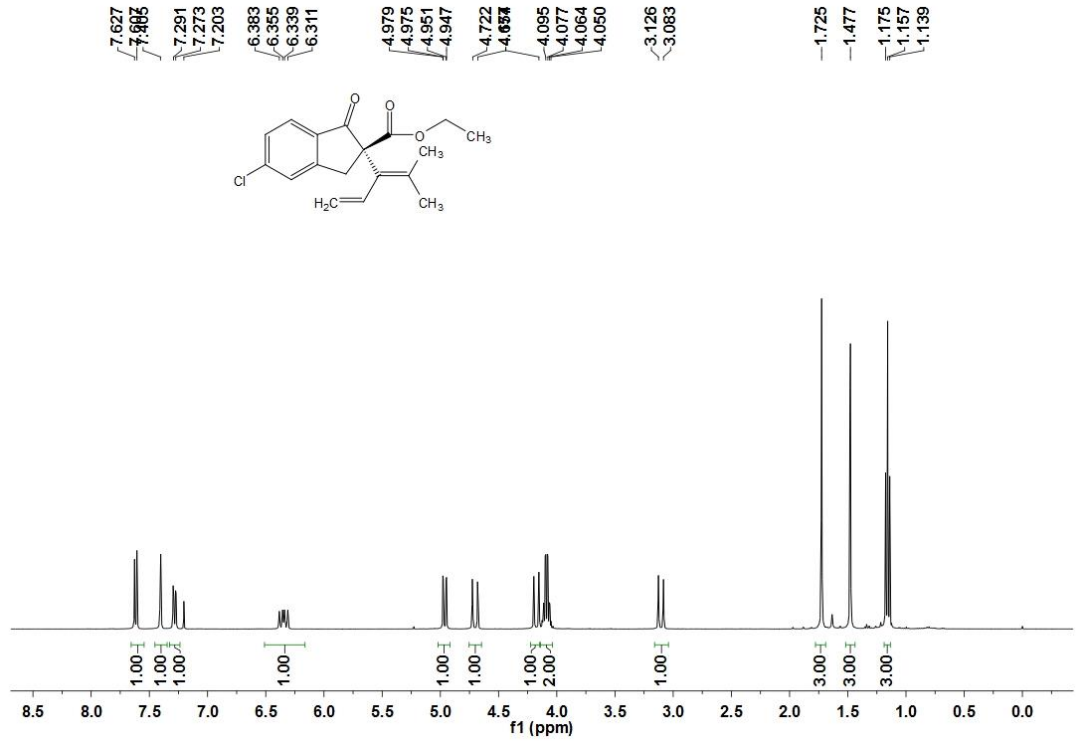

199.93
169.85
152.66
138.08
134.19
131.56
129.50
121.65
116.42
67.13
62.46
41.41
23.20
22.77
13.99
f1 (ppm)

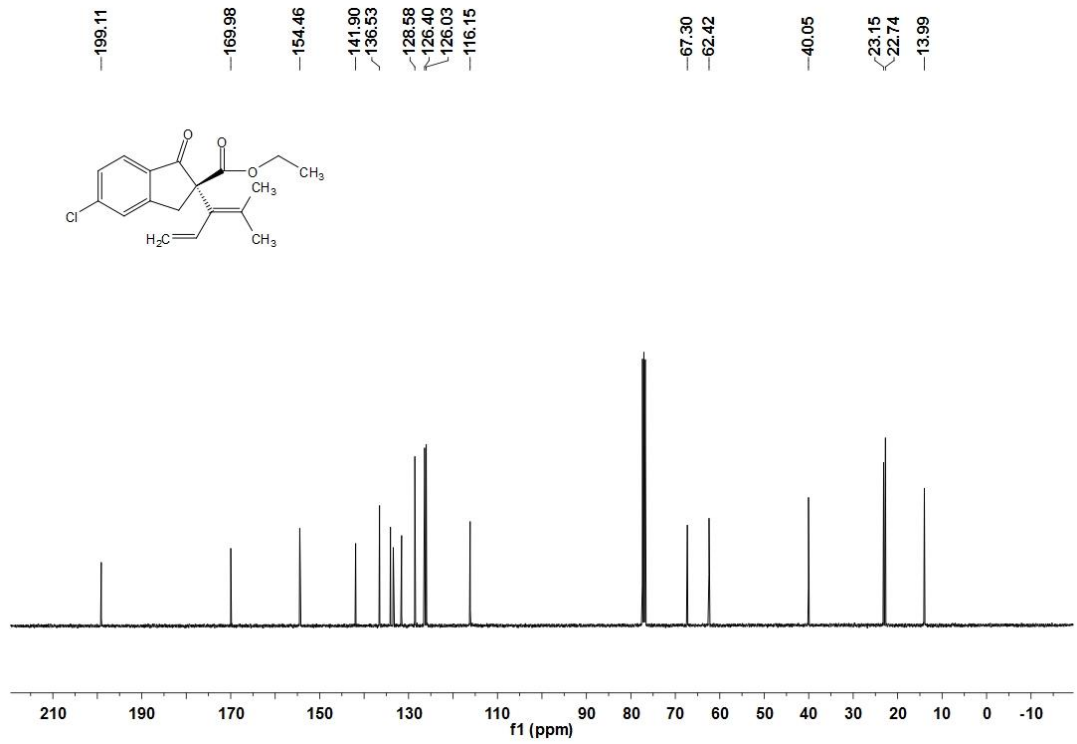
2e


7.787
7.774
7.766
7.752
7.153
7.103
7.081
7.060
6.462
6.434
6.418
6.389
5.051
5.023
4.756
4.283
4.178
4.160
4.143
4.129
3.207
3.163
1.801
1.641
1.560
1.253
1.235
1.218
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
3.00
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

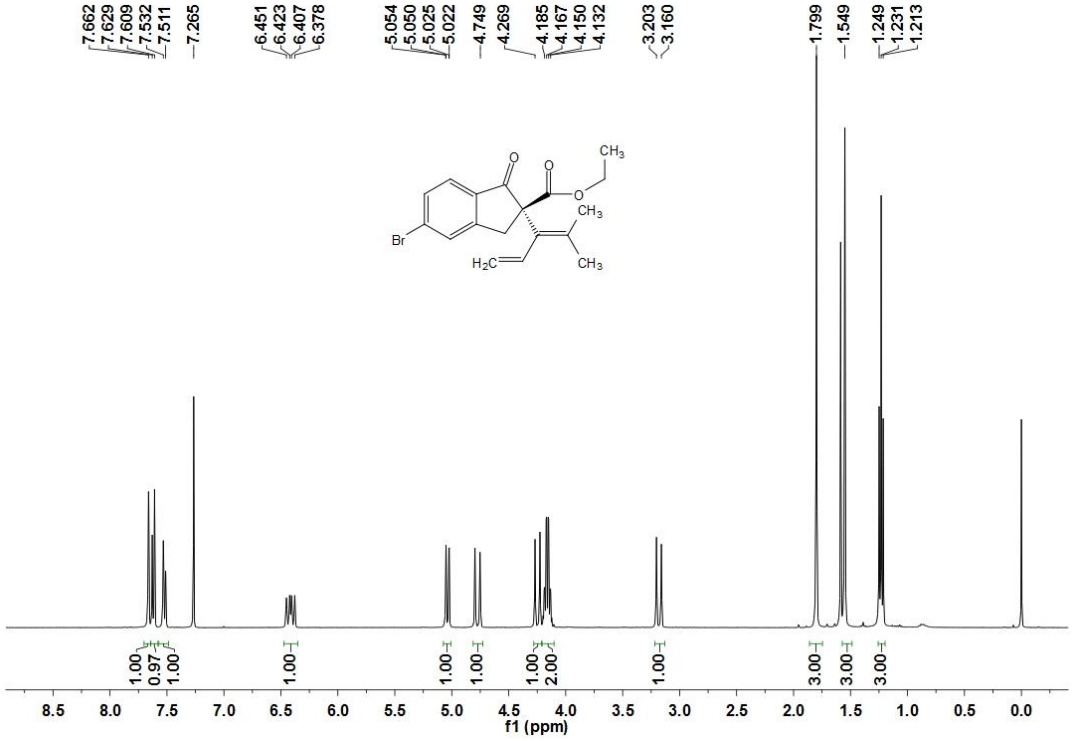

198.66
170.13
168.76
166.20
156.05
155.95
136.58
131.68
131.36
127.35
127.24
116.24
116.11
116.00
112.98
112.76
67.40
62.38
40.23
23.08
22.76
13.99
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

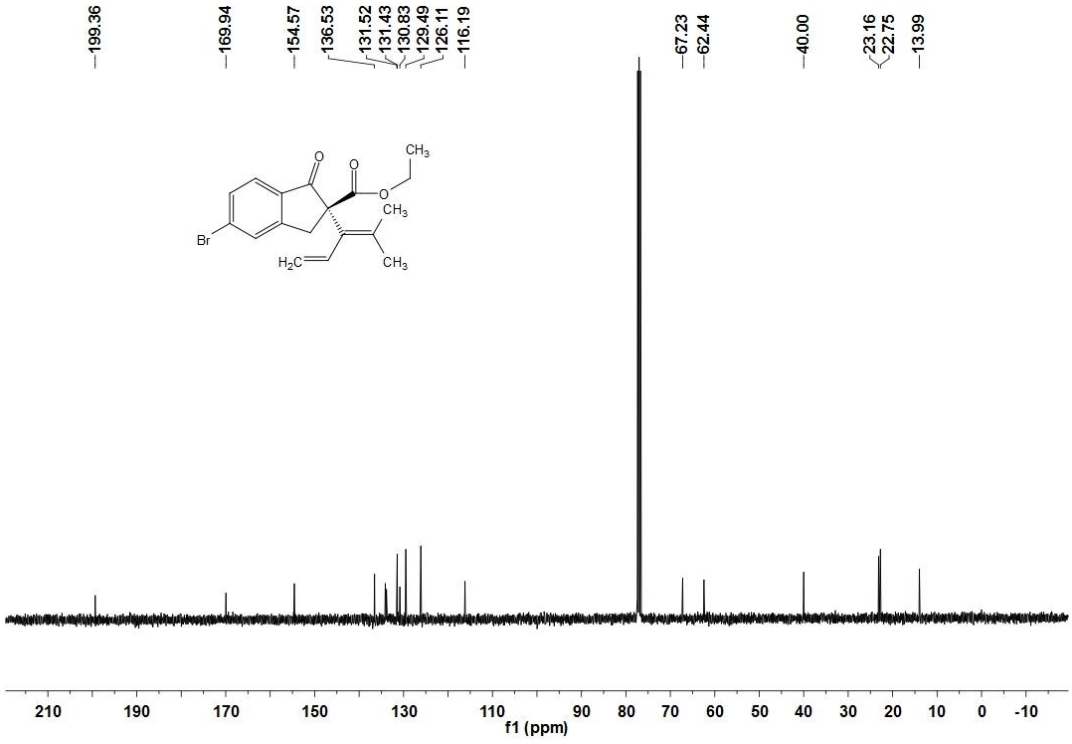
2f


7.627
7.291
7.273
7.203
6.383
6.355
6.339
6.311
4.979
4.975
4.951
4.947
4.095
4.077
4.064
4.050
3.126
3.083
1.725
1.477
1.175
1.157
1.139
Cl
O
O
CH3
CH3
H2C
CH3
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
f1 (ppm)

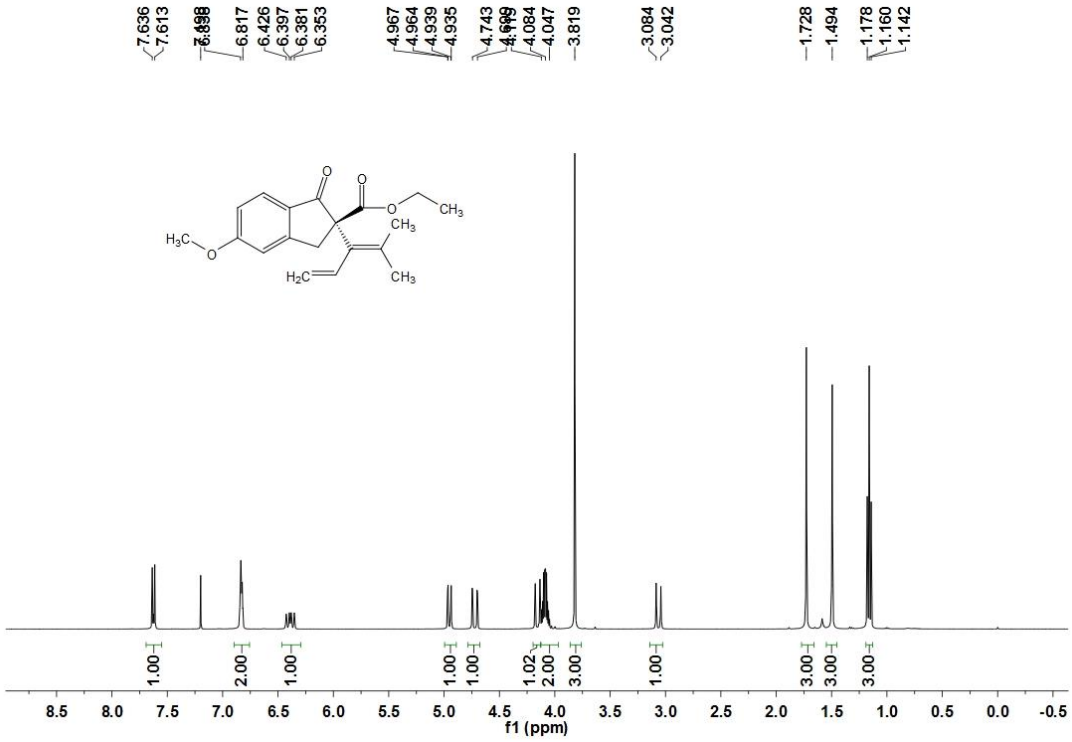

199.11
169.98
154.46
141.90
136.53
128.58
126.40
126.03
116.15
67.30
62.42
40.05
23.15
22.74
13.99
Cl
O
O
CH3
CH3
H2C
CH3
f1 (ppm)

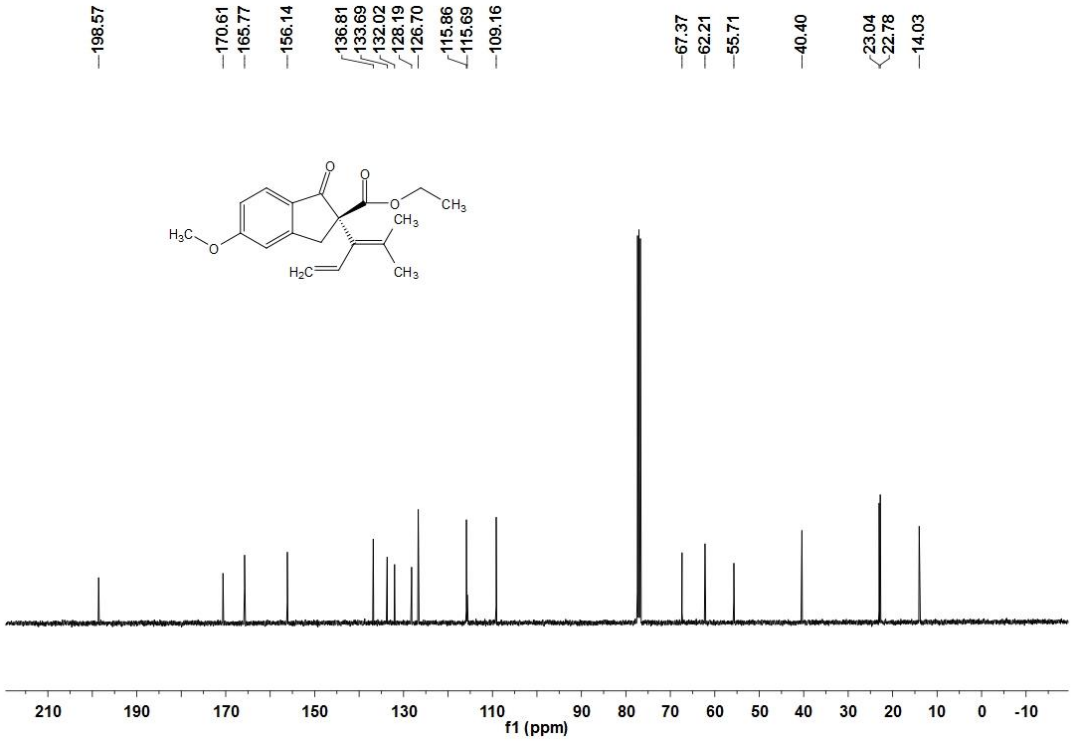
2g


7.662
7.629
7.609
7.532
7.511
7.265
6.451
6.423
6.407
6.378
5.054
5.050
5.025
5.022
4.749
4.269
4.185
4.167
4.150
4.132
3.203
3.160
1.799
1.549
1.249
1.231
1.213
Br
O
O
O
CH3
CH3
H2C
CH3
1.00
0.97
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
f1 (ppm)

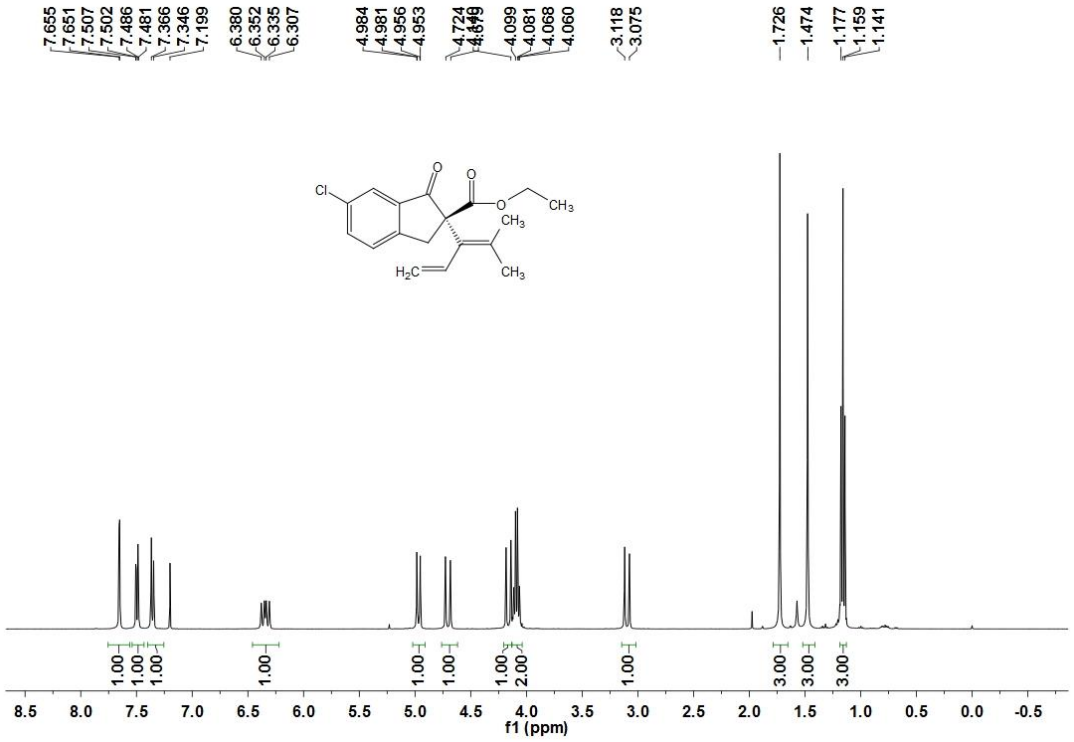

199.36
169.94
154.57
136.53
131.52
131.43
130.83
129.49
126.11
116.19
67.23
62.44
40.00
23.16
22.75
13.99
Br
O
O
O
CH3
CH3
H2C
CH3
f1 (ppm)

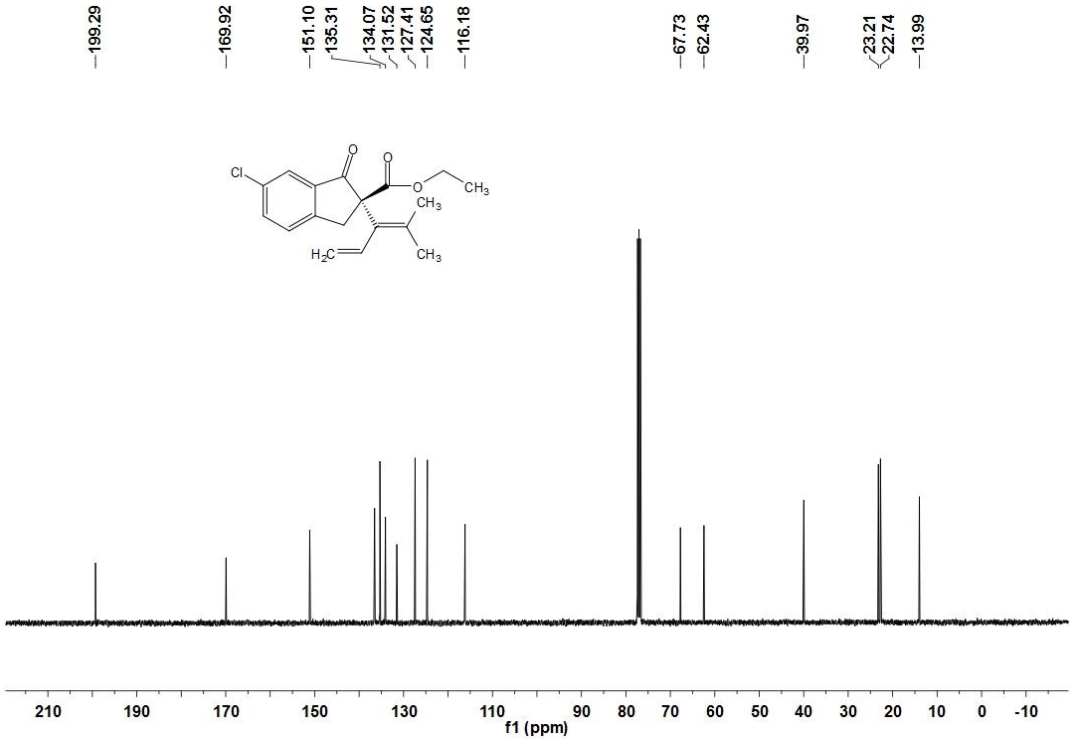
2h


7.636
7.613
6.817
6.426
6.397
6.381
6.353
4.967
4.964
4.939
4.935
4.743
4.084
4.047
3.819
3.084
3.042
1.728
1.494
1.178
1.160
1.142
1.00
2.00
1.00
1.00
1.00
1.02
2.00
3.00
1.00
3.00
3.00
3.00
f1 (ppm)

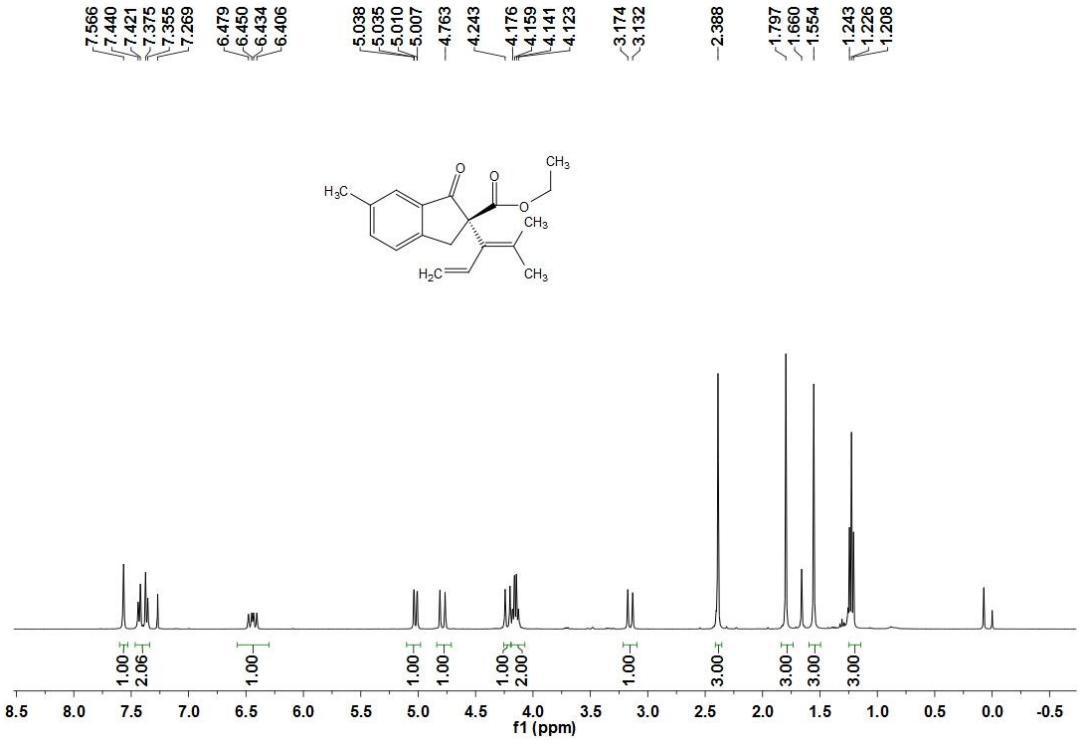

198.57
170.61
165.77
156.14
136.81
133.69
132.02
128.19
126.70
115.86
115.69
109.16
67.37
62.21
55.71
40.40
23.04
22.78
14.03
f1 (ppm)

2i


7.655
7.651
7.507
7.502
7.486
7.481
7.366
7.346
7.199
6.380
6.352
6.335
6.307
4.984
4.981
4.956
4.953
4.724
4.099
4.081
4.068
4.060
3.118
3.075
1.726
1.474
1.177
1.159
1.141
Cl
O
O
O
CH3
CH3
H2C
CH3
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


199.29
169.92
151.10
135.31
134.07
131.52
127.41
124.65
116.18
67.73
62.43
39.97
23.21
22.74
13.99
Cl
O
O
O
CH3
CH3
H2C
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2j


7.566
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7.421
7.375
7.355
7.269
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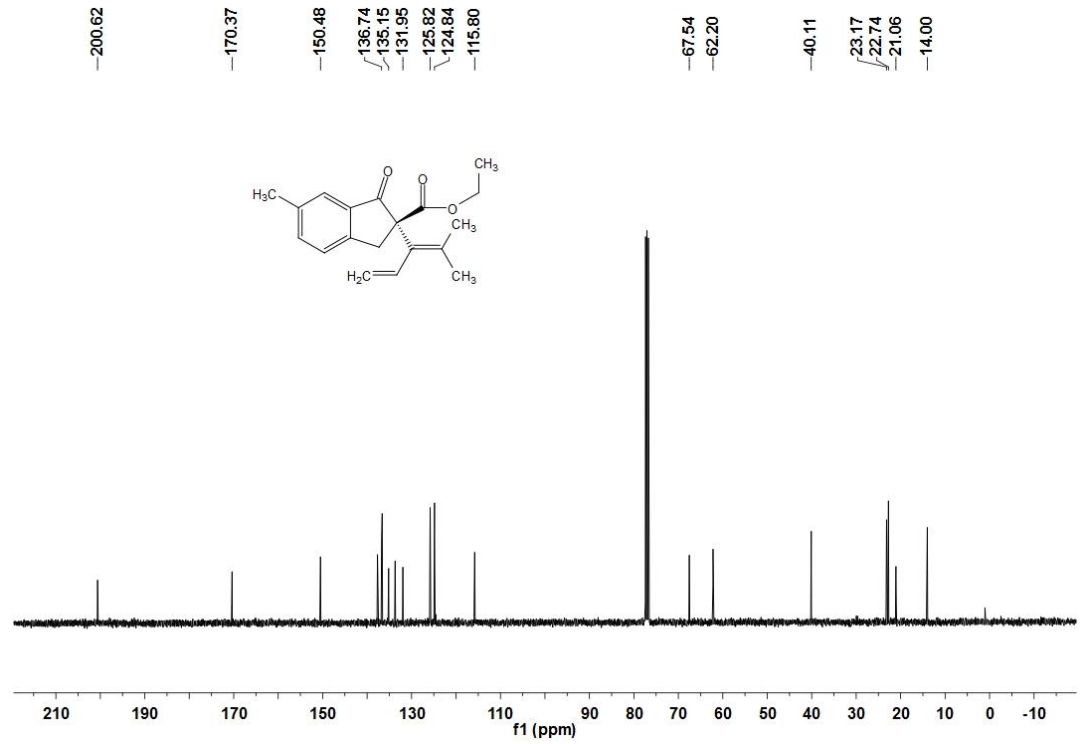
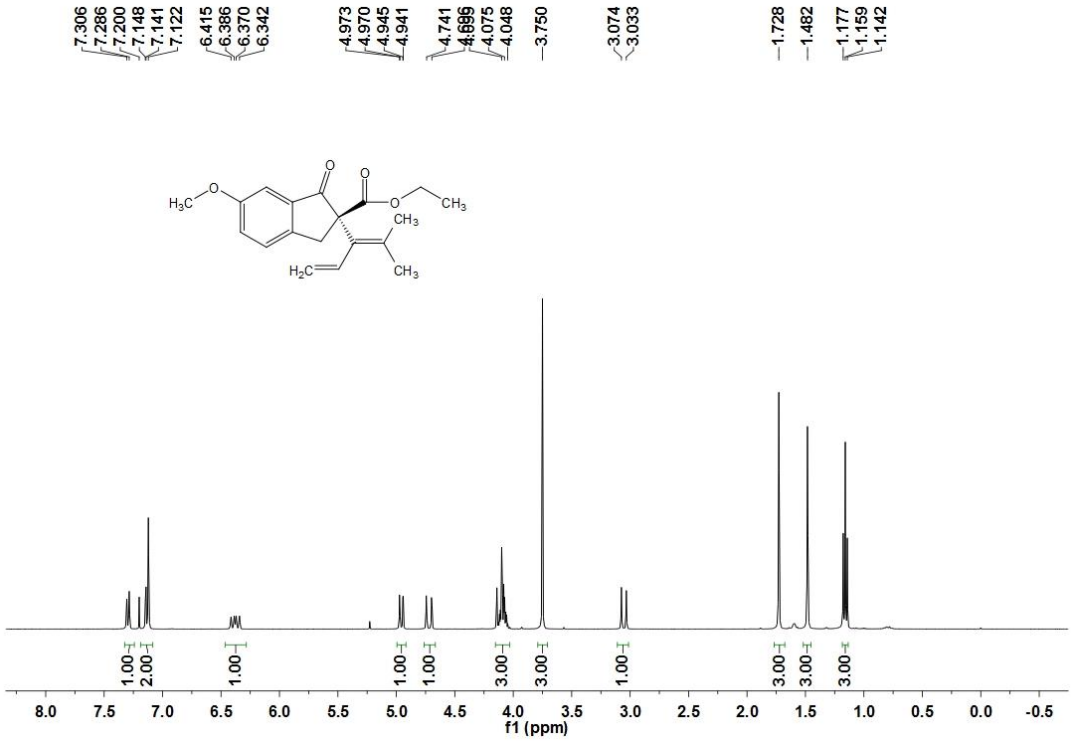
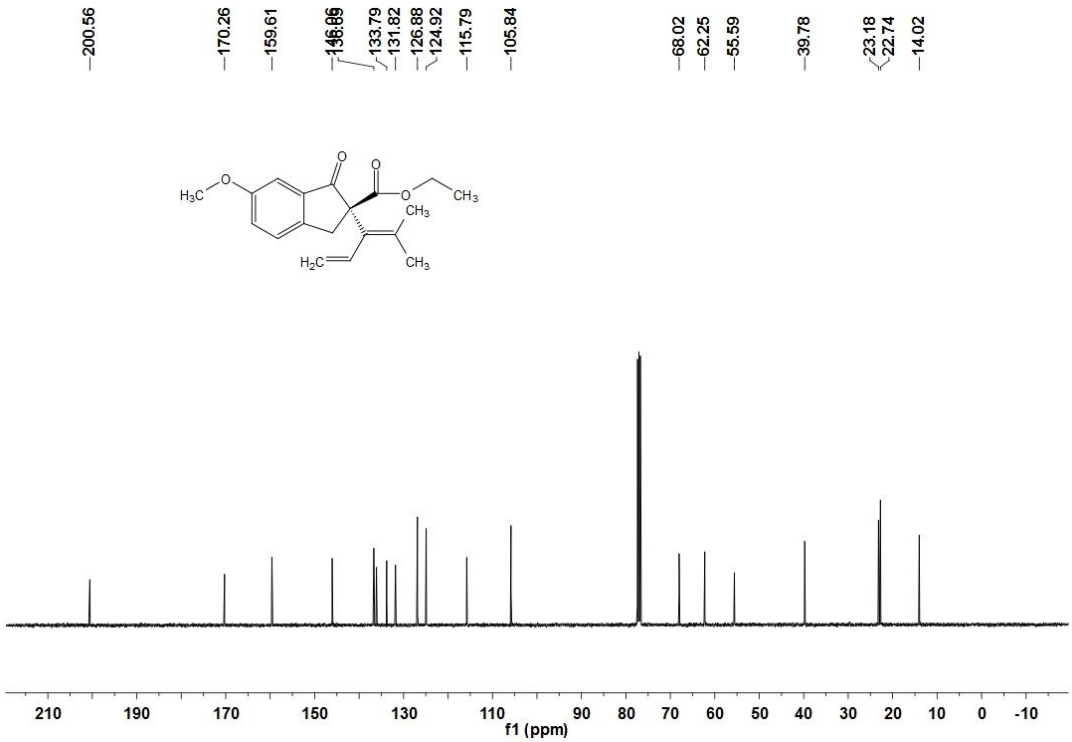
6.450
6.434
6.406
5.038
5.035
5.010
5.007
4.763
4.243
4.176
4.159
4.141
4.123
3.174
3.132
2.388
1.797
1.660
1.554
1.243
1.226
1.208
1.00
2.06
1.00
1.00
1.00
1.00
2.00
1.00
3.00
3.00
3.00
3.00
f1 (ppm)

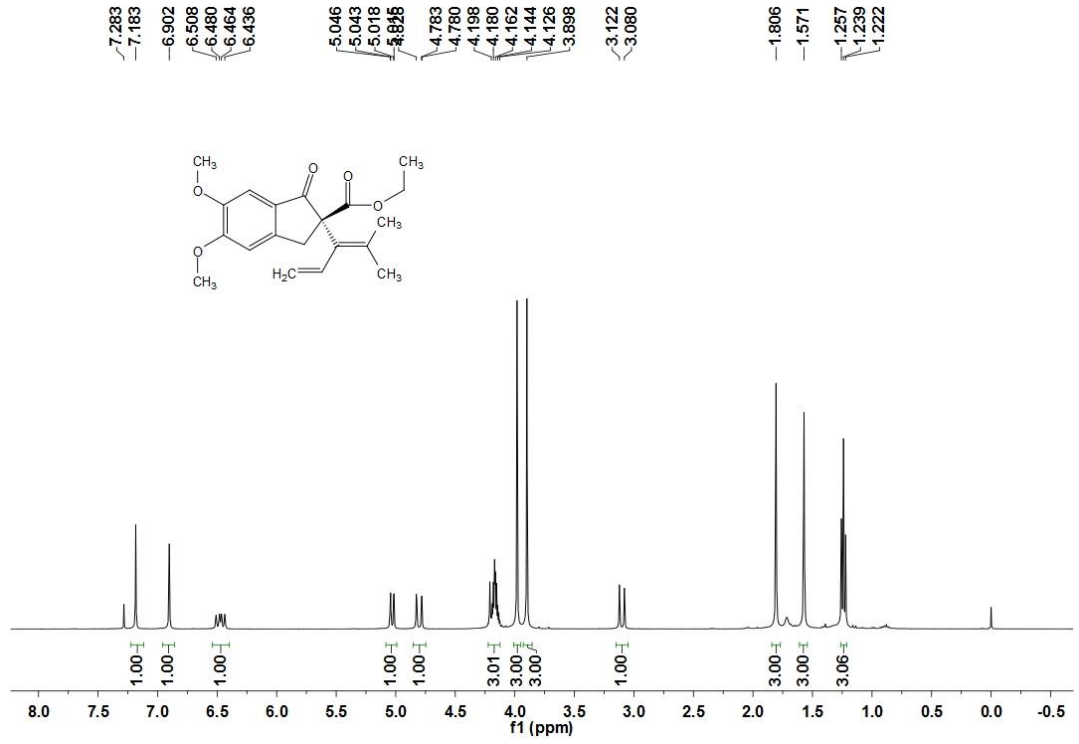

200.62
170.37
150.48
136.74
135.15
131.95
125.82
124.84
115.80
67.54
62.20
40.11
23.17
22.74
21.06
14.00
f1 (ppm)

2k


7.306
7.286
7.200
7.148
7.141
7.122
6.415
6.386
6.370
6.342
4.973
4.970
4.945
4.941
4.741
4.075
4.048
3.750
3.074
3.033
1.728
1.482
1.177
1.159
1.142
1.00
2.00
1.00
1.00
1.00
3.00
3.00
1.00
3.00
3.00
3.00
f1 (ppm)


200.56
170.26
159.61
133.79
131.82
126.88
124.92
115.79
105.84
68.02
62.25
55.59
39.78
23.18
22.74
14.02
f1 (ppm)

2l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7.183
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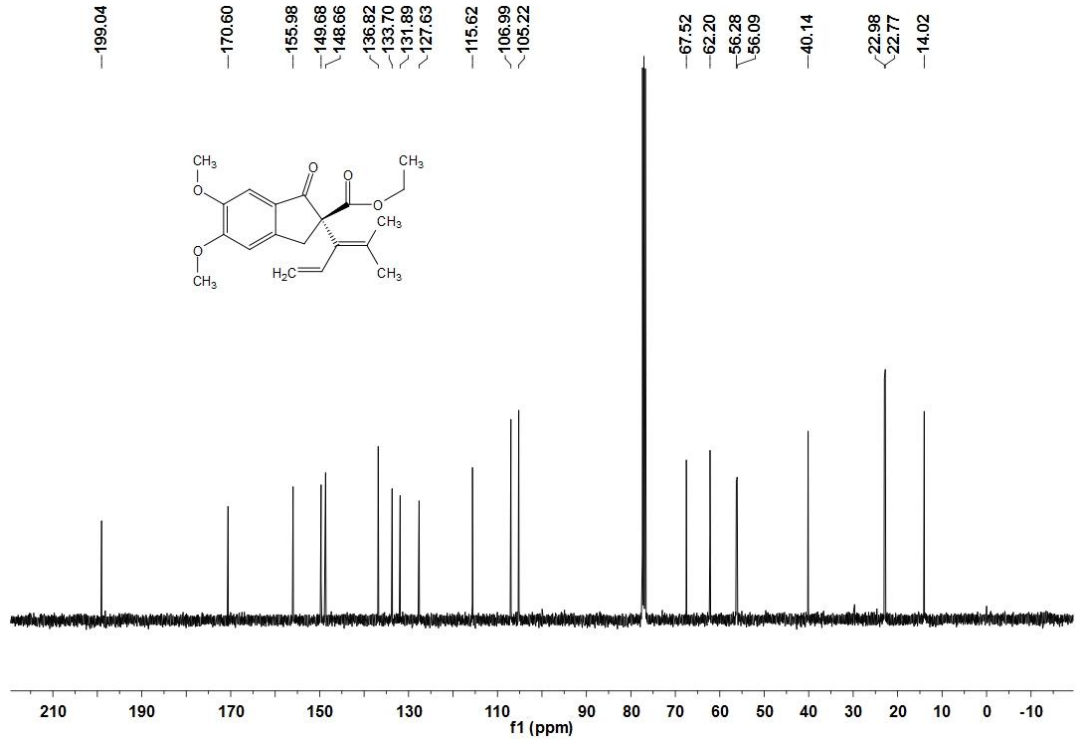
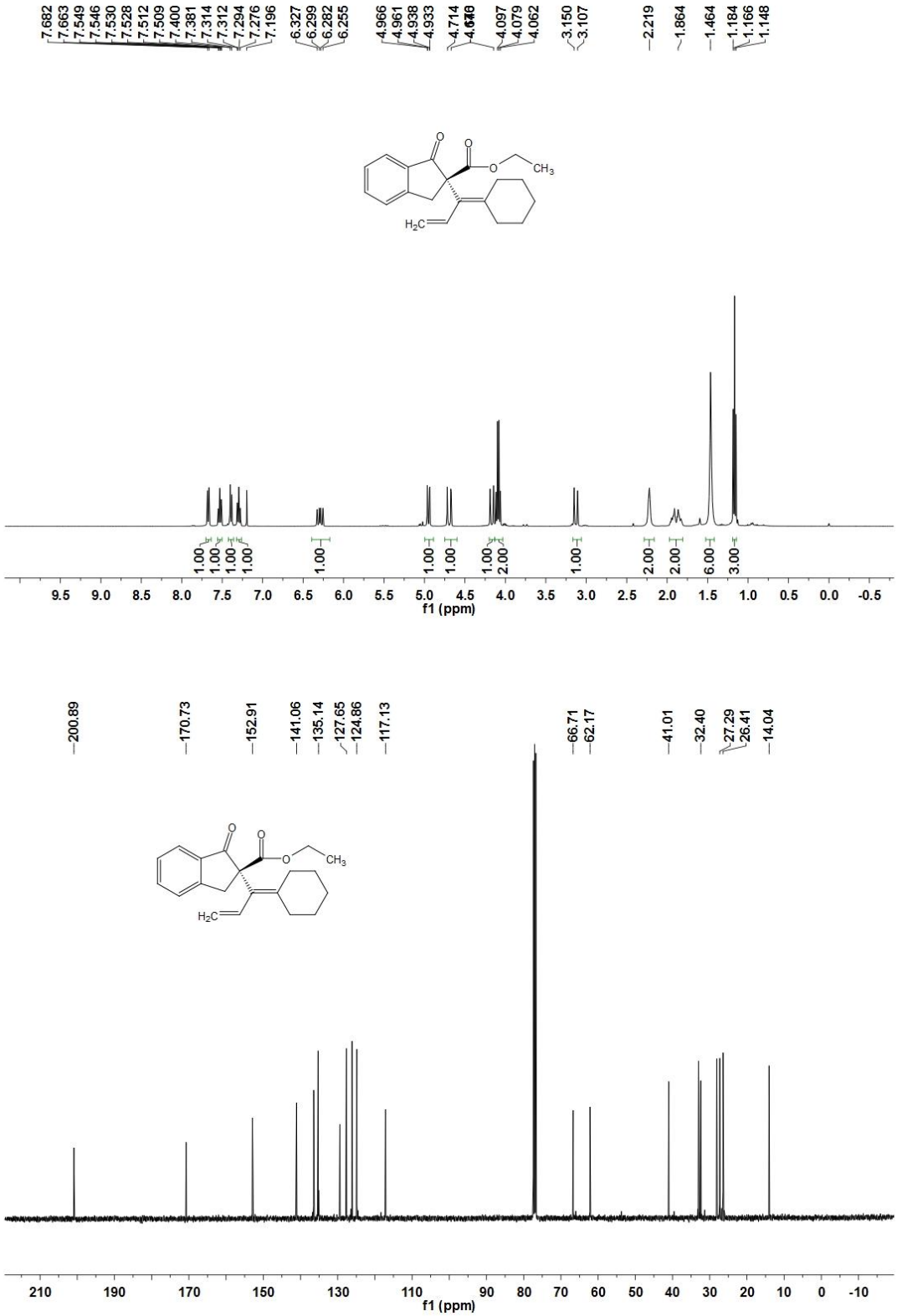
6.508
6.480
6.464
6.436
5.046
5.043
5.018
4.783
4.780
4.198
4.180
4.162
4.144
4.126
3.898
3.122
3.080
1.806
1.571
1.257
1.239
1.222
1.00
1.00
1.00
1.00
1.00
3.01
3.00
3.00
1.00
3.00
3.00
3.06
f1 (ppm)


199.04
170.60
155.98
149.68
148.66
136.82
133.70
131.89
127.63
115.62
106.99
105.22
67.52
62.20
56.28
56.09
40.14
22.98
22.77
14.02
f1 (ppm)

2m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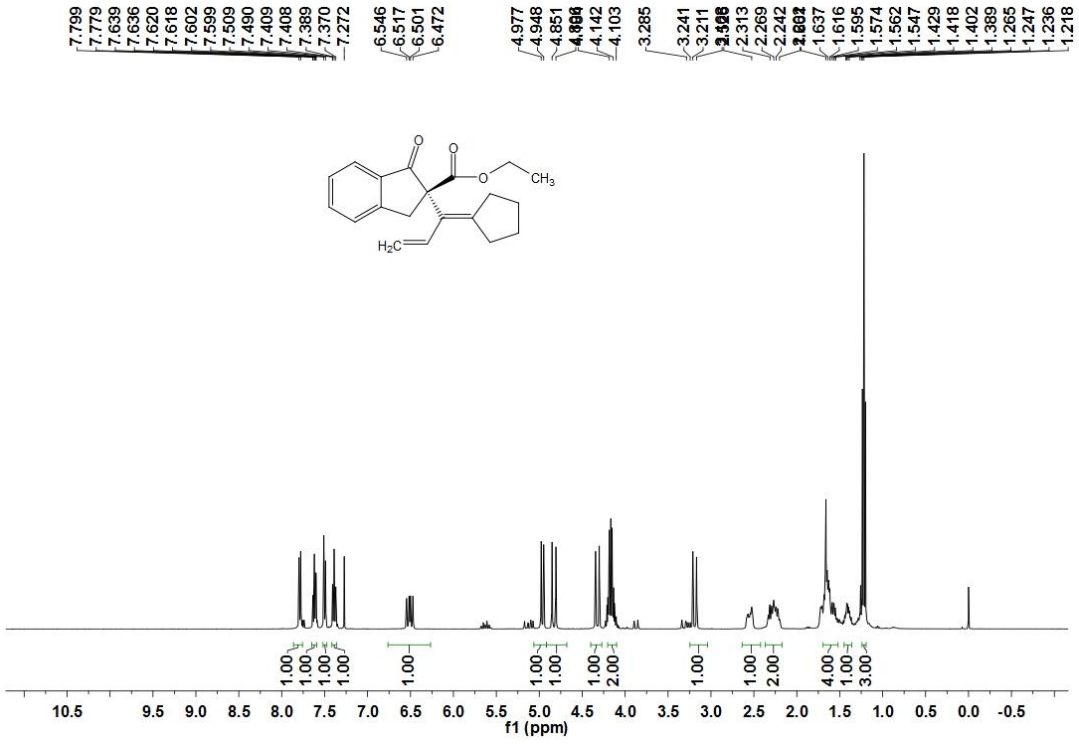
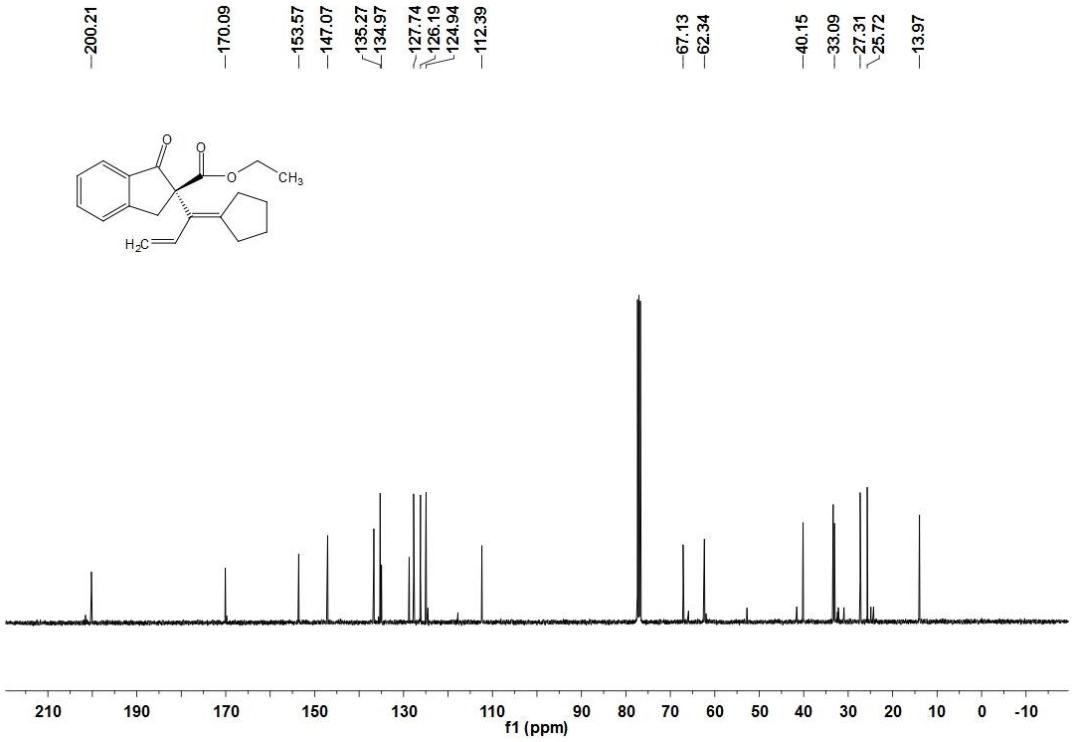
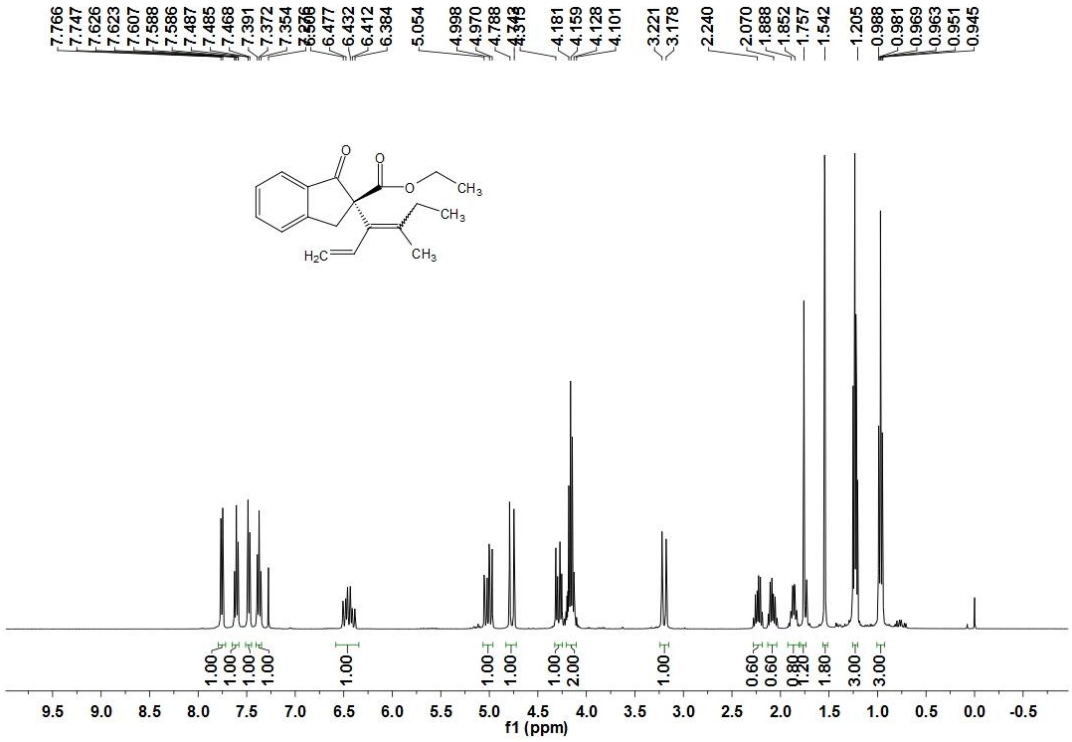
7.549
7.546
7.530
7.528
7.512
7.509
7.400
7.381
7.314
7.312
7.294
7.276
7.196
6.327
6.299
6.282
6.255
4.966
4.961
4.938
4.933
4.714
4.097
4.079
4.062
3.150
3.107
2.219
1.864
1.464
1.184
1.166
1.148
O
O
O
CH3
H2C
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
2.00
2.00
6.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
200.89
170.73
152.91
141.06
135.14
127.65
124.86
117.13
66.71
62.17
41.01
32.40
27.29
26.41
14.04
O
O
O
CH3
H2C
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

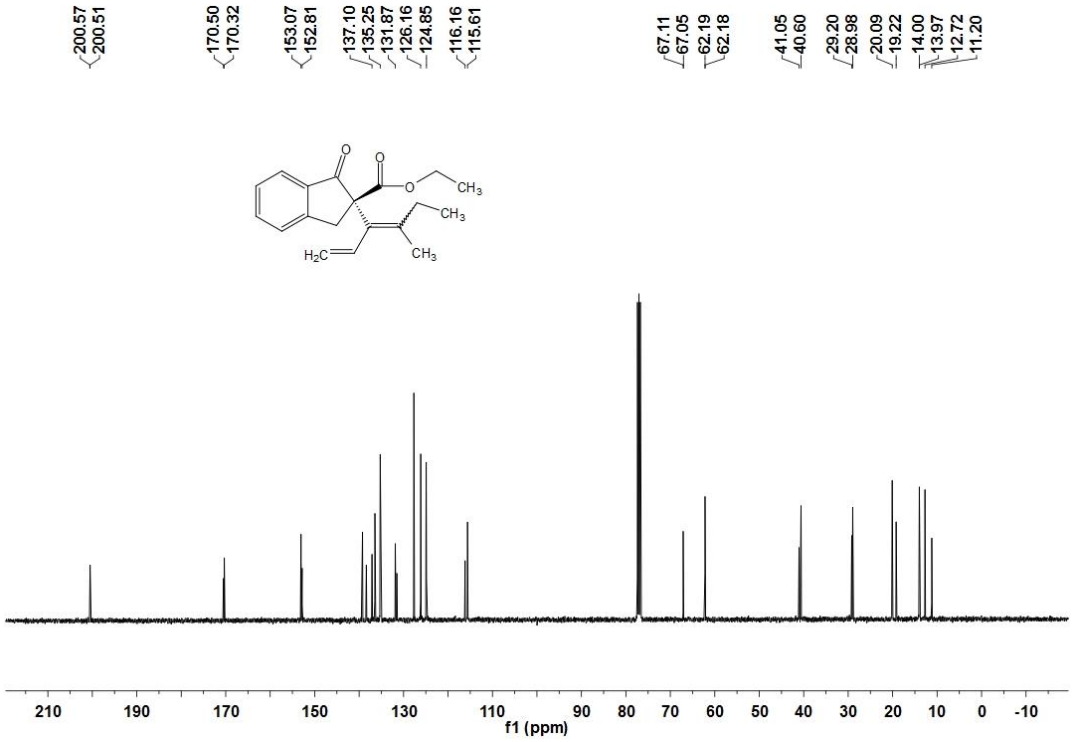
2n


7.799
7.779
7.639
7.636
7.620
7.618
7.602
7.599
7.509
7.490
7.409
7.408
7.389
7.370
7.272
6.546
6.517
6.501
6.472
4.977
4.948
4.851
4.142
4.103
3.285
3.241
3.211
2.313
2.269
2.242
1.637
1.616
1.595
1.574
1.562
1.547
1.429
1.418
1.402
1.389
1.265
1.247
1.236
1.218
O
O
O
CH3
H2C
1.00
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
2.00
4.00
1.00
3.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

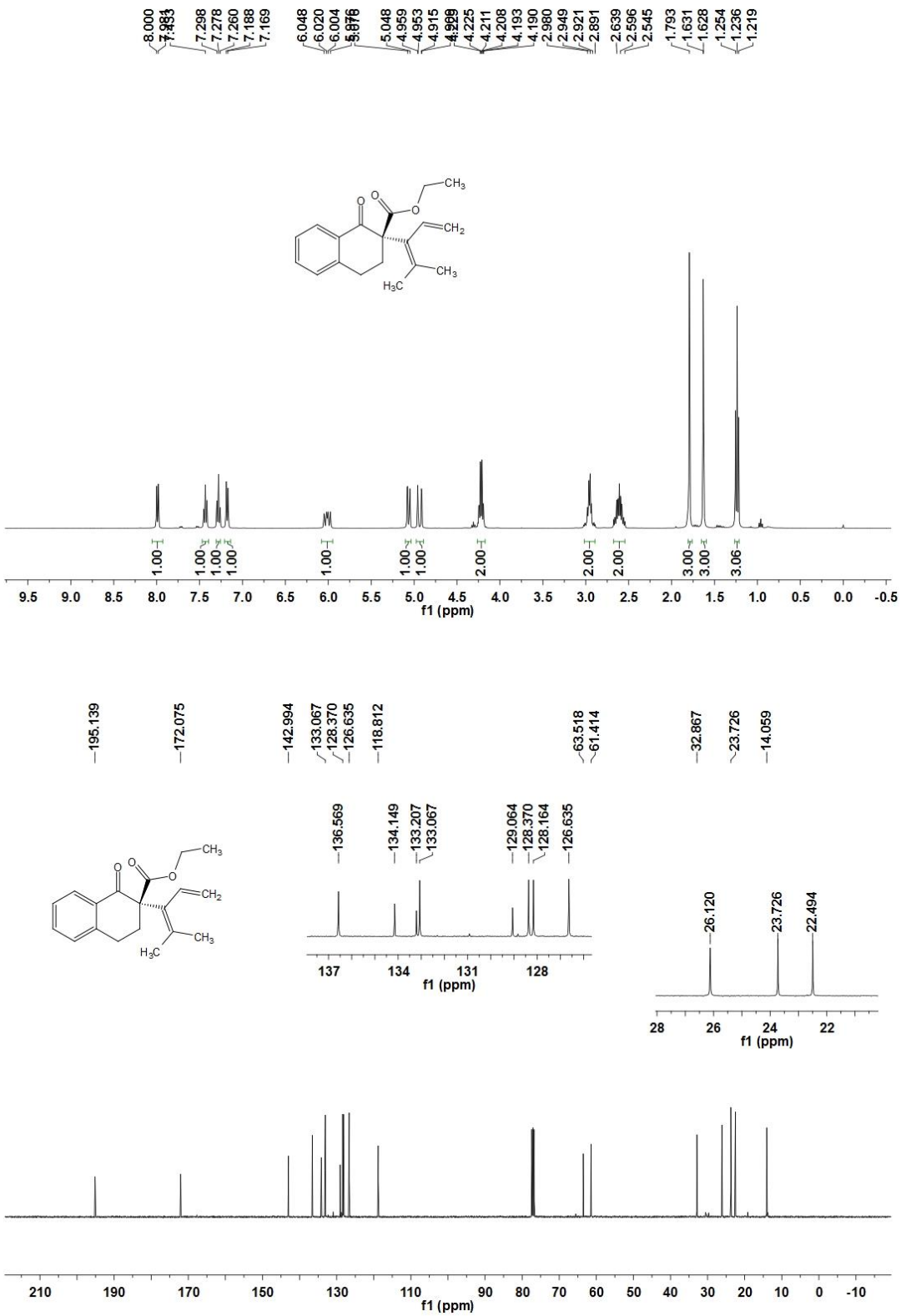

200.21
170.09
153.57
147.07
135.27
134.97
127.74
126.19
124.94
112.39
67.13
62.34
40.15
33.09
27.31
25.72
13.97
O
O
O
CH3
H2C
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

2o

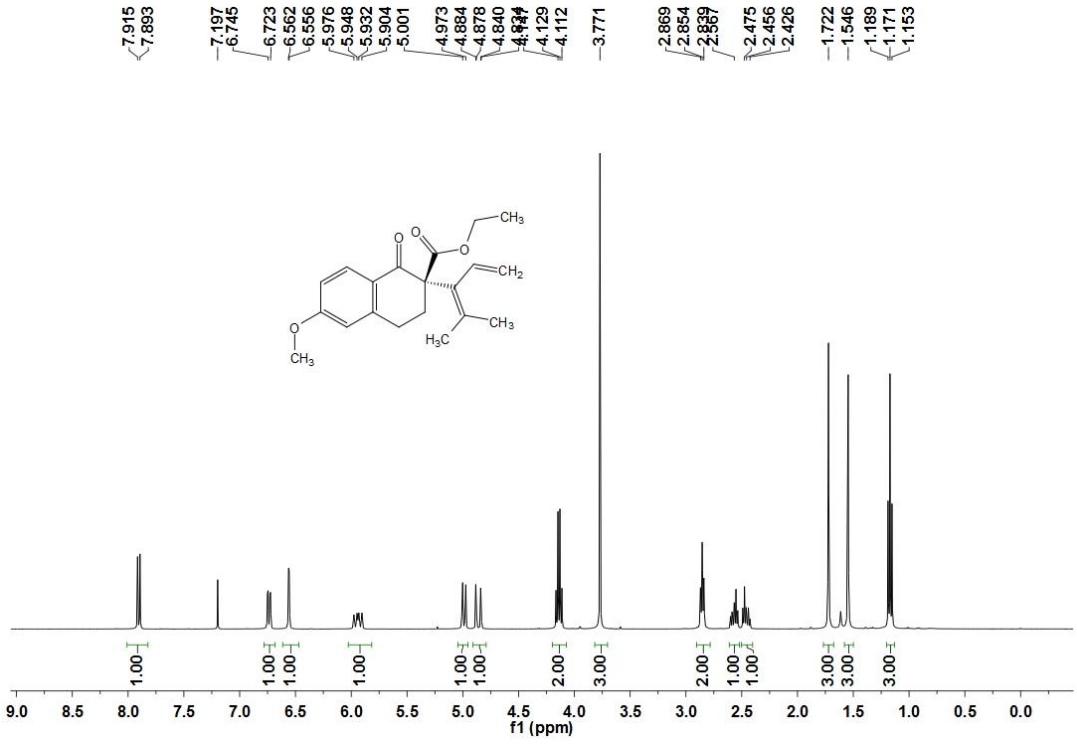

7.766
7.747
7.626
7.623
7.607
7.588
7.586
7.487
7.485
7.468
7.391
7.372
7.354
6.506
6.477
6.432
6.412
6.384
5.054
4.998
4.970
4.788
4.181
4.159
4.128
4.101
3.221
3.178
2.240
2.070
1.888
1.852
1.757
1.542
1.205
0.988
0.981
0.969
0.963
0.951
0.945
O
O
O
CH3
CH3
H2C
CH3
1.00
1.00
1.00
1.00
1.00
1.00
1.00
2.00
1.00
0.60
0.60
1.80
3.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

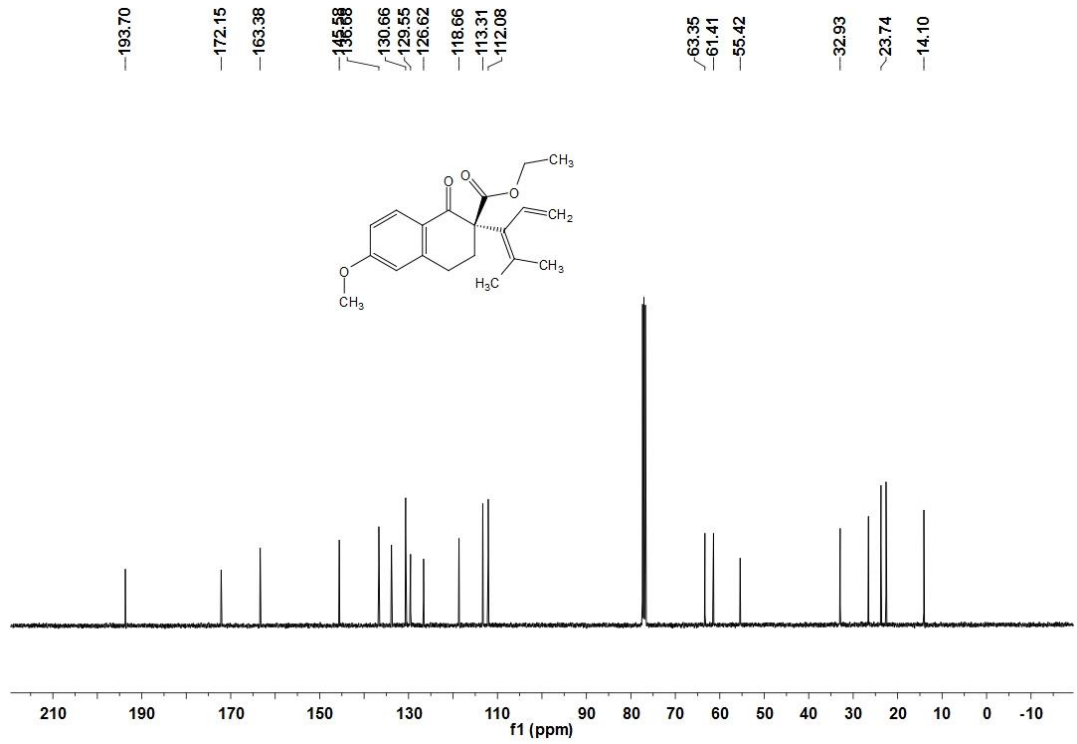

200.57
200.51
170.50
170.32
153.07
152.81
137.10
135.25
131.87
126.16
124.85
116.16
115.61
67.11
67.05
62.19
62.18
41.05
40.60
29.20
28.98
20.09
19.22
14.00
13.97
12.72
11.20
O
O
O
CH3
CH3
H2C
CH3
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2p

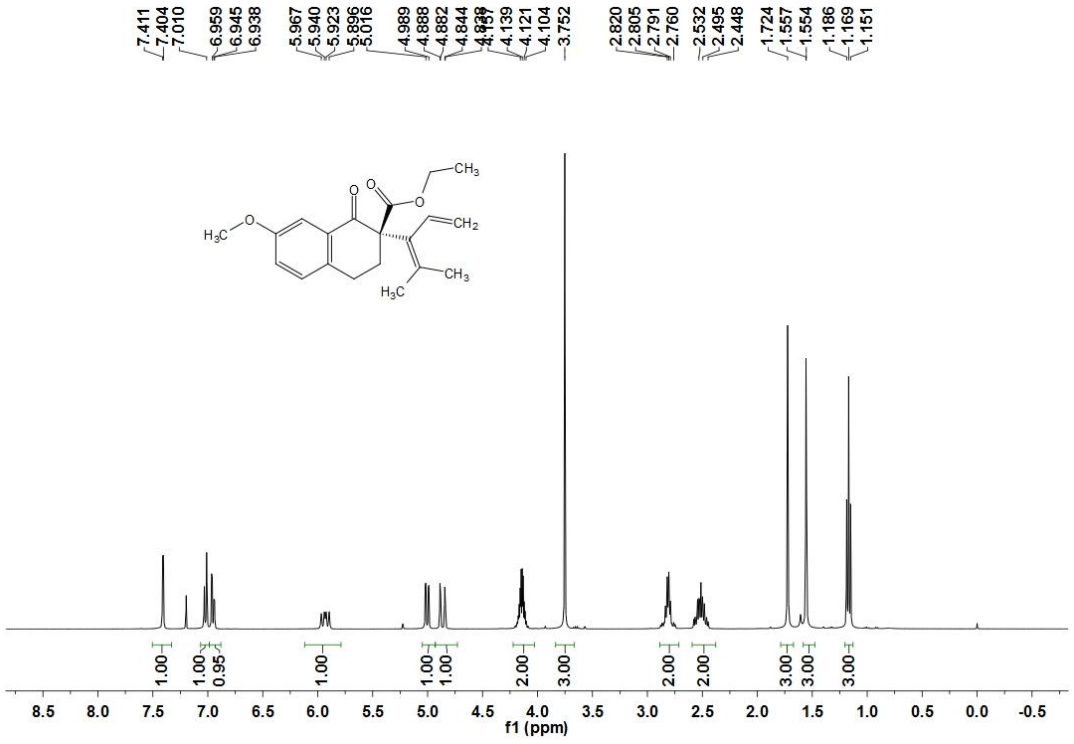

8.000
7.298
7.278
7.260
7.188
7.169
6.048
6.020
6.004
5.048
4.959
4.953
4.915
4.225
4.211
4.208
4.193
4.190
2.980
2.949
2.921
2.891
2.639
2.596
2.545
1.793
1.631
1.628
1.254
1.236
1.219
1.00
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
3.00
3.06
f1 (ppm)
195.139
172.075
142.994
133.067
128.370
126.635
118.812
63.518
61.414
32.867
23.726
14.059
136.569
134.149
133.207
133.067
129.064
128.370
128.164
126.635
26.120
23.726
22.494
f1 (ppm)
f1 (ppm)

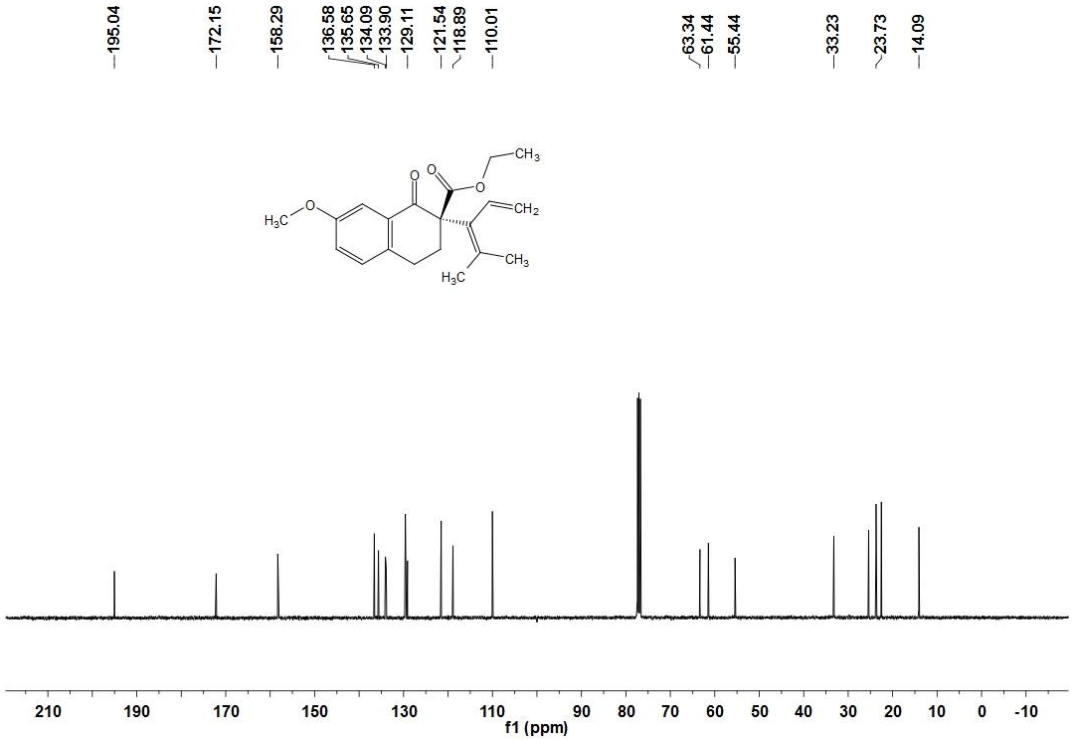
2q


7.915
7.893
7.197
6.745
6.723
6.562
6.556
5.976
5.948
5.932
5.904
5.001
4.973
4.884
4.878
4.840
4.129
4.112
3.771
2.869
2.854
2.475
2.456
2.426
1.722
1.546
1.189
1.171
1.153
1.00
1.00
1.00
1.00
1.00
1.00
2.00
3.00
2.00
1.00
1.00
3.00
3.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

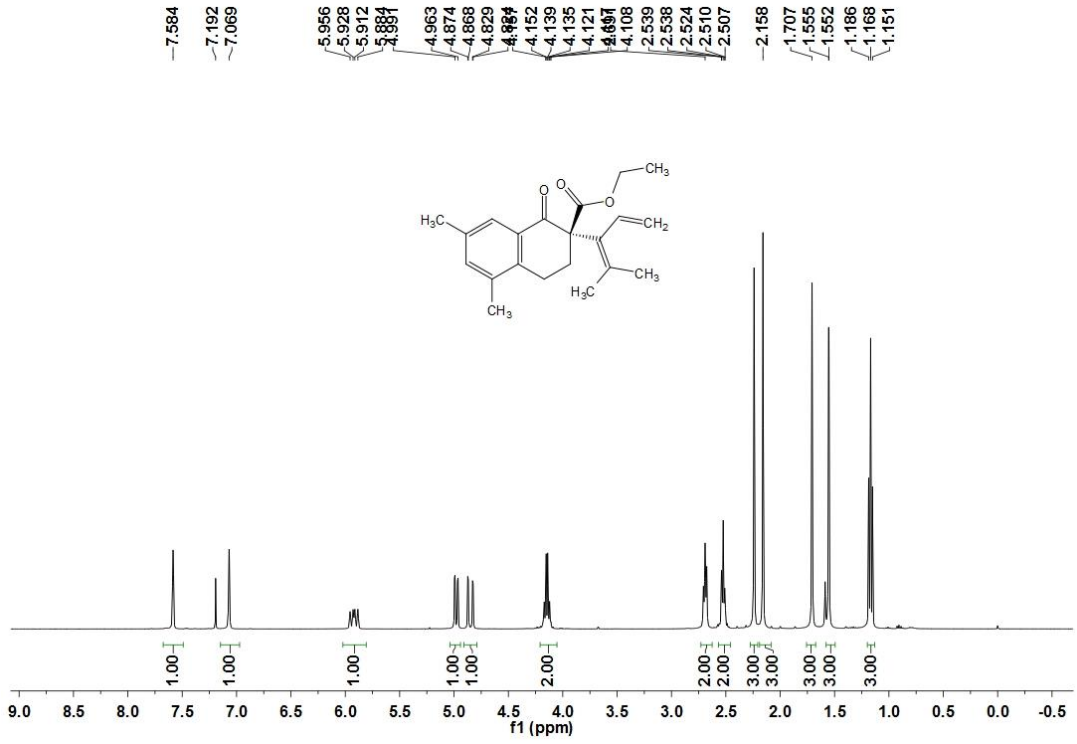

193.70
172.15
163.38
130.66
129.55
126.62
118.66
113.31
112.08
63.35
61.41
55.42
32.93
23.74
14.10
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

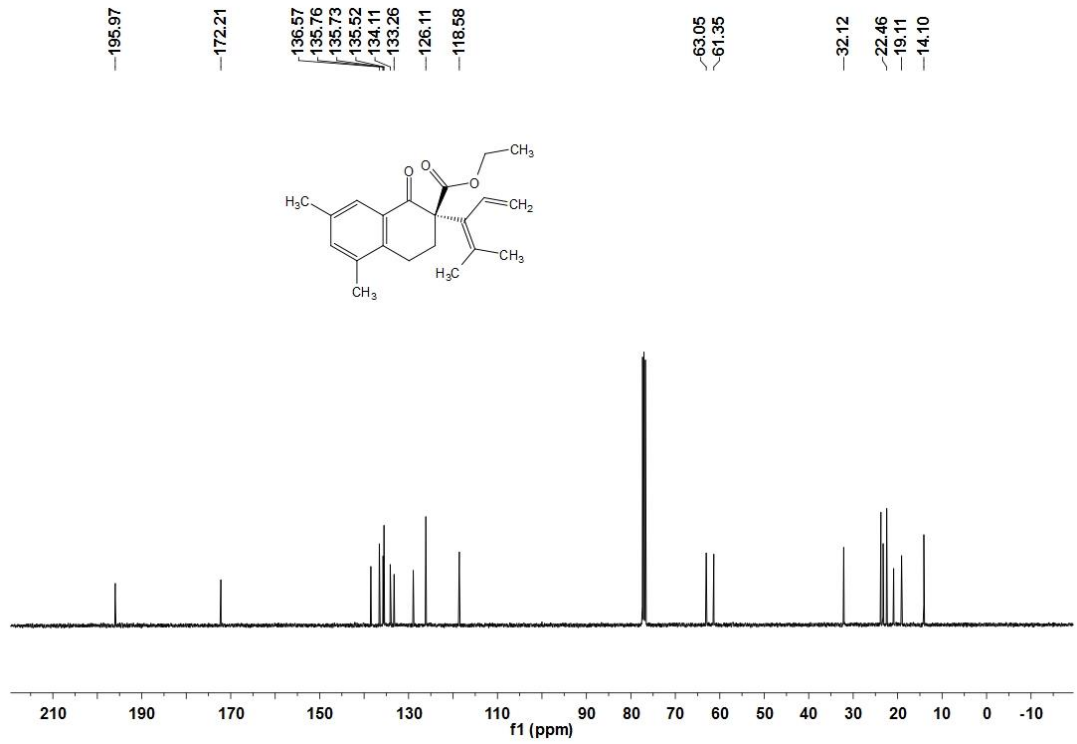
2r


7.411
7.404
7.010
6.959
6.945
6.938
5.967
5.940
5.923
5.896
5.016
4.989
4.888
4.882
4.844
4.139
4.121
4.104
3.752
2.820
2.805
2.791
2.760
2.532
2.495
2.448
1.724
1.557
1.554
1.186
1.169
1.151
1.00
1.00
0.95
1.00
1.00
1.00
2.00
3.00
2.00
2.00
3.00
3.00
3.00
f1 (ppm)

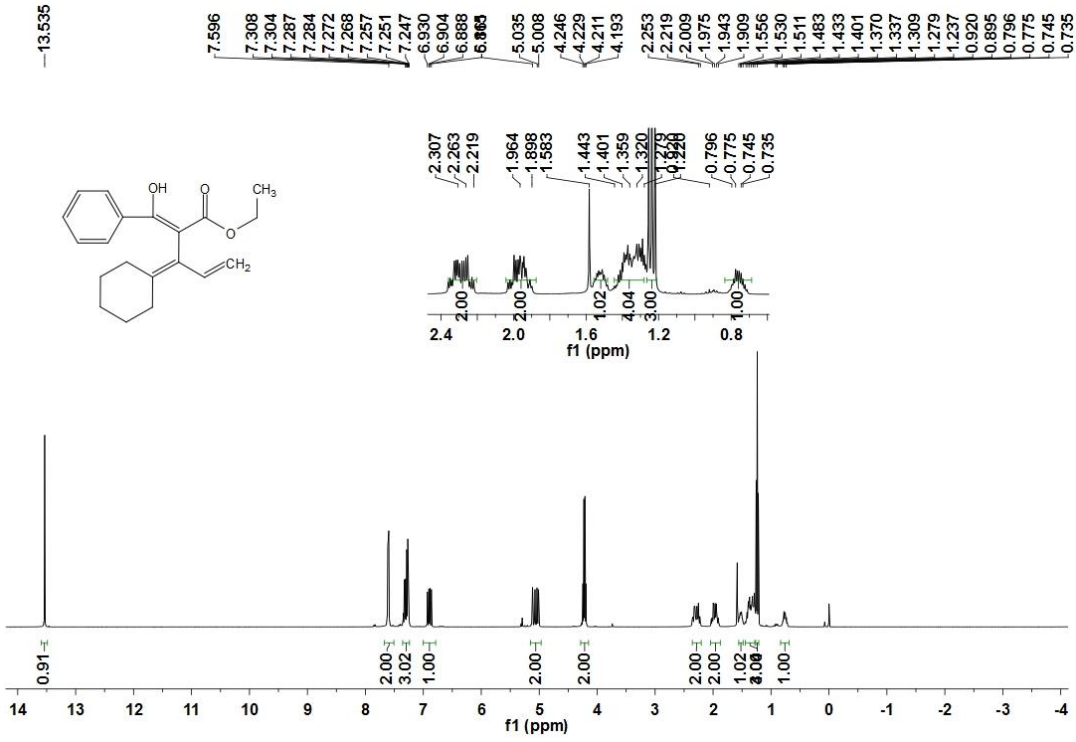

195.04
172.15
158.29
136.58
135.65
134.09
133.90
129.11
121.54
118.89
110.01
63.34
61.44
55.44
33.23
23.73
14.09
f1 (ppm)

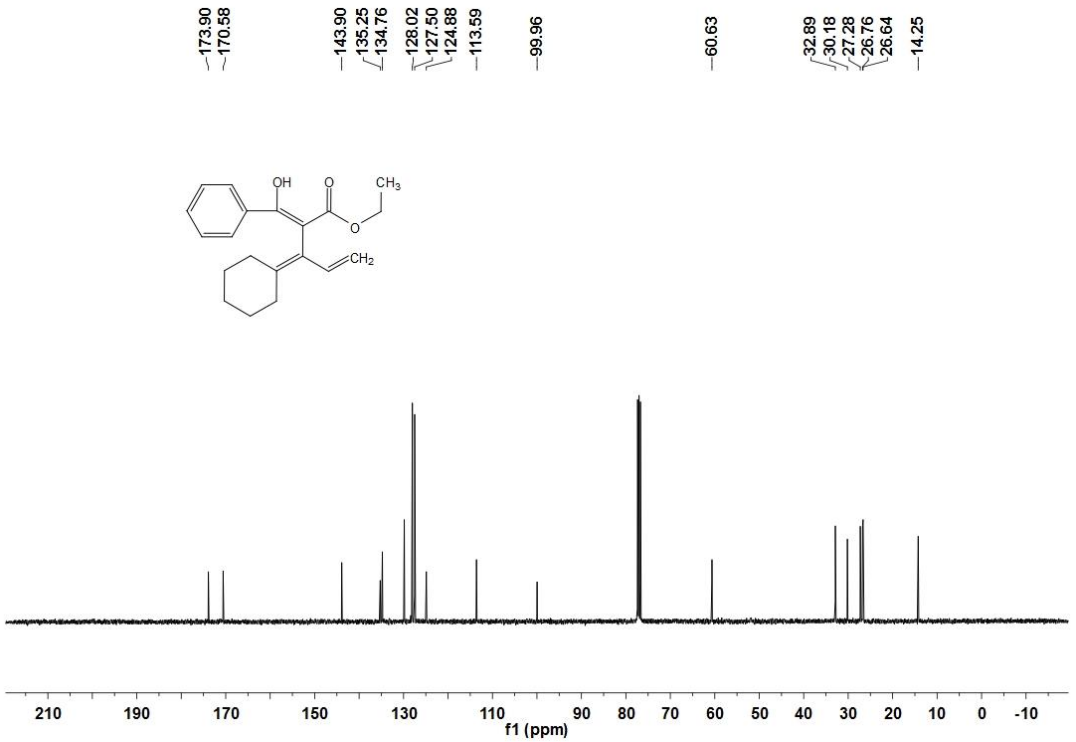
2s


7.584
7.192
7.069
5.956
5.928
5.912
4.963
4.874
4.868
4.829
4.152
4.139
4.135
4.121
4.108
2.539
2.538
2.524
2.510
2.507
2.158
1.707
1.555
1.552
1.186
1.168
1.151
1.00
1.00
1.00
1.00
1.00
2.00
2.00
2.00
3.00
3.00
3.00
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

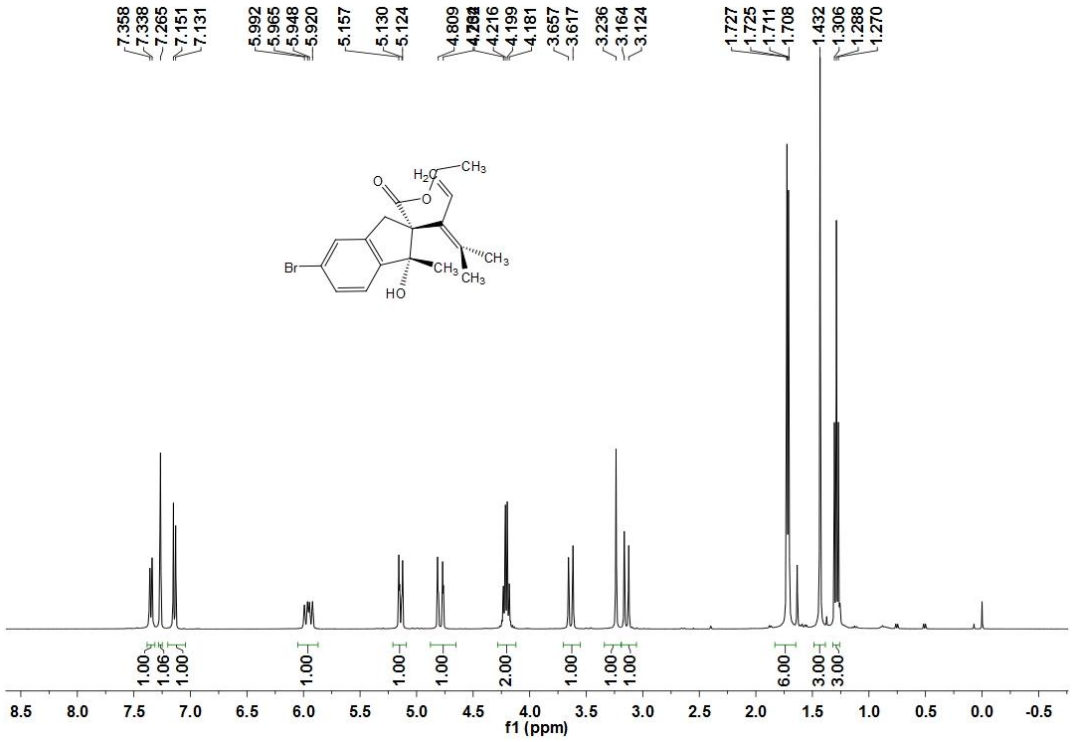

195.97
172.21
136.57
135.76
135.73
135.52
134.11
133.26
126.11
118.58
63.05
61.35
32.12
22.46
19.11
14.10
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

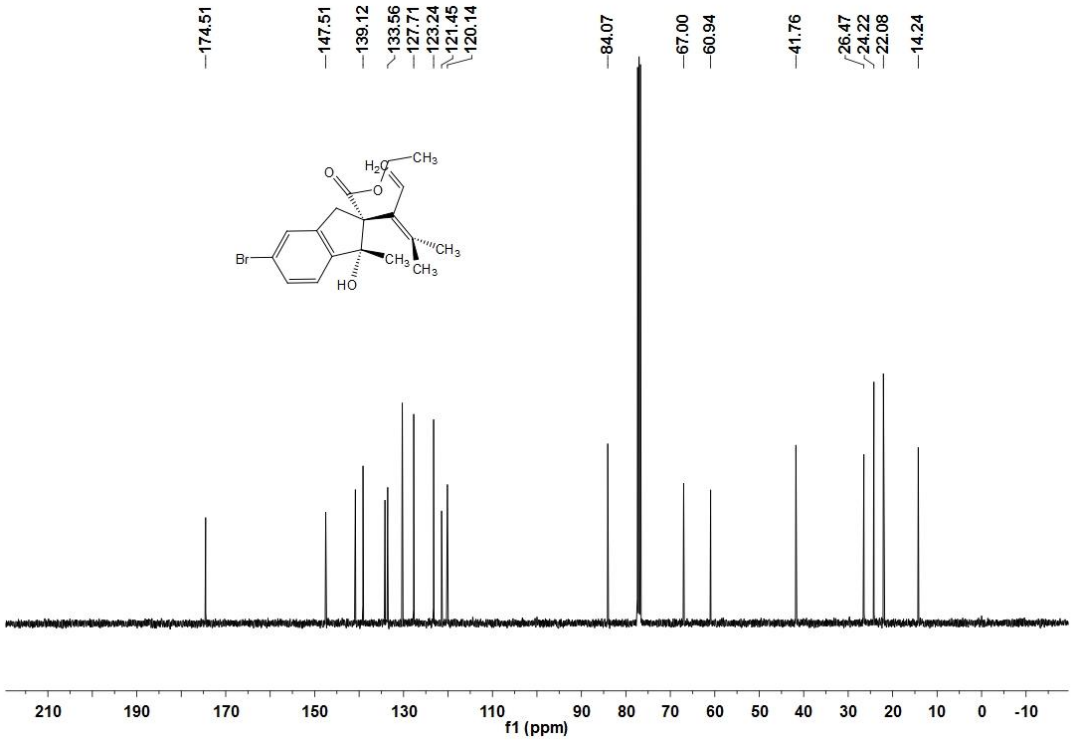
2t


13.535
7.596
7.308
7.304
7.287
7.284
7.272
7.268
7.257
7.251
7.247
6.930
6.904
6.888
5.035
5.008
4.246
4.229
4.211
4.193
2.253
2.219
2.009
1.975
1.943
1.909
1.556
1.530
1.511
1.483
1.433
1.401
1.370
1.337
1.309
1.279
1.237
0.920
0.895
0.796
0.775
0.745
0.735
OH
O
CH3
O
CH2
f1 (ppm)

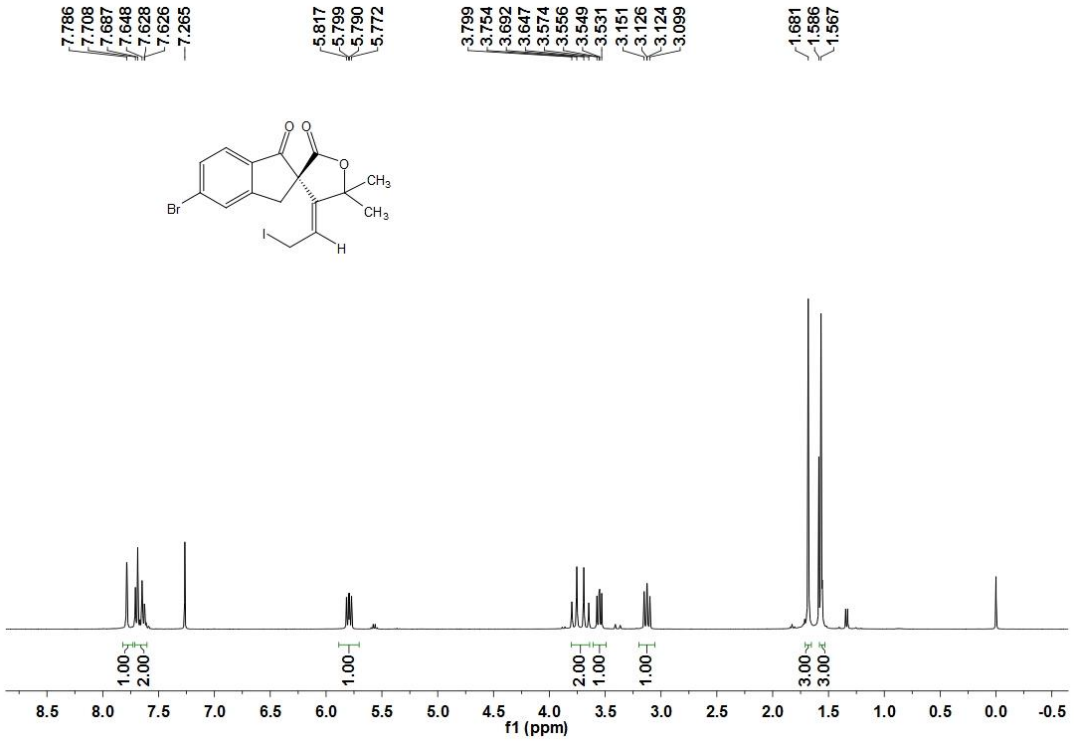

173.90
170.58
143.90
135.25
134.76
128.02
127.50
124.88
113.59
99.96
60.63
32.89
30.18
27.28
26.76
26.64
14.25
OH
O
CH3
O
CH2
f1 (ppm)

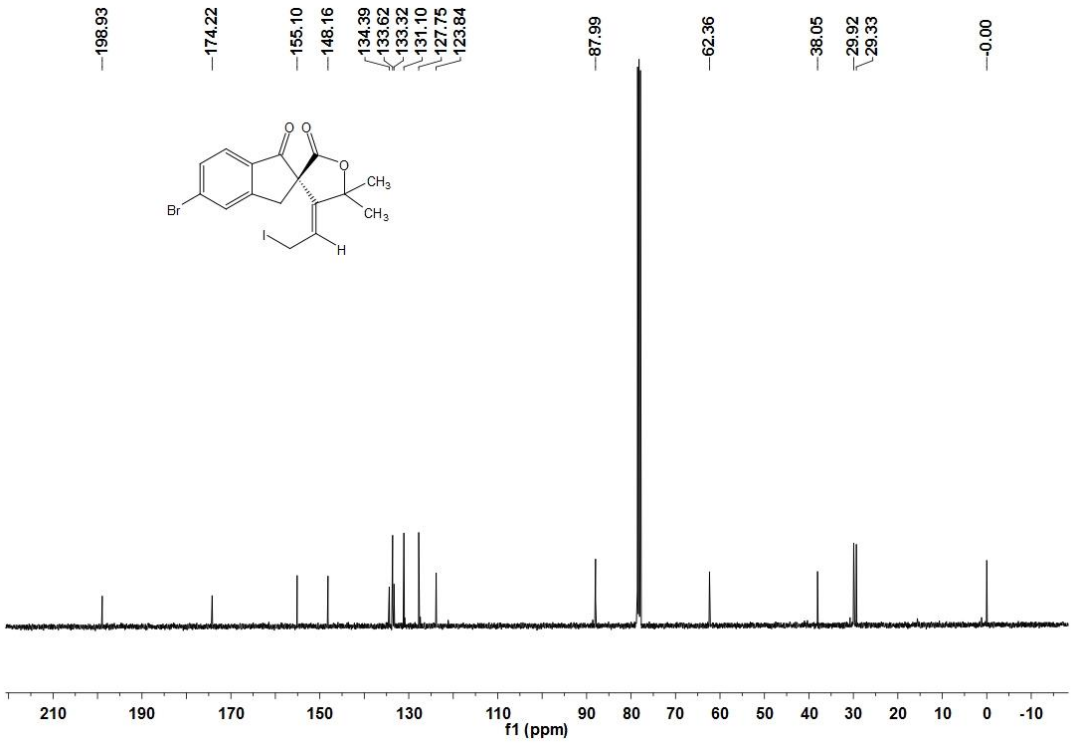
3


7.358
7.338
7.265
7.151
7.131
5.992
5.965
5.948
5.920
5.157
5.130
5.124
4.809
4.216
4.199
4.181
3.657
3.617
3.236
3.164
3.124
1.727
1.725
1.711
1.708
1.432
1.306
1.288
1.270
1.00
1.06
1.00
1.00
1.00
1.00
2.00
1.00
1.00
1.00
6.00
3.00
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.51
147.51
139.12
133.56
127.71
123.24
121.45
120.14
84.07
67.00
60.94
41.76
26.47
24.22
22.08
14.24
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

***E*-4**


7.786
7.708
7.687
7.648
7.628
7.626
7.265
5.817
5.799
5.790
5.772
3.799
3.754
3.692
3.647
3.574
3.556
3.549
3.531
3.151
3.126
3.124
3.099
1.681
1.586
1.567
O
O
O
CH3
CH3
Br
I
H
1.00
2.00
1.00
2.00
1.00
1.00
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


198.93
174.22
155.10
148.16
134.39
133.62
133.32
131.10
127.75
123.84
87.99
62.36
38.05
29.92
29.33
0.00
O
O
O
CH3
CH3
Br
I
H
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

5