Supplementary Information

Enantioselective One-Pot Synthesis of 4H-Chromene Derivatives Catalyzed by A Chiral Ni(II) Complex

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1. General information.

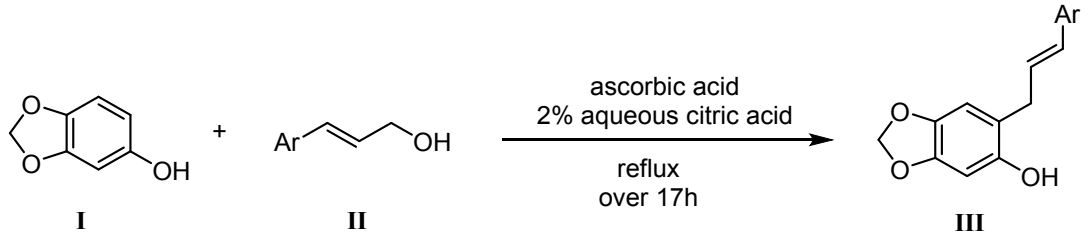
The ^{1}H, ^{13}C NMR spectra were recorded on a Bruker Avance DPX300 or Bruker Avance III 500 instrument with TMS as internal standard. Optical rotations were measured on an Insmark IP-digi300E8 polarimeter. The enantiomeric excesses of (*R*)- and (*S*)-enantiomer were determined by Agilent 1260 HPLC analysis over a chiral column (Daicel Chiralcel OD-H, AD-H, AS-H or OJ-H; eluted with hexane/iso-propanol; UV detector). Infrared Radiation were determined by NICOLET iS10. Solvents were purified and dried by standard procedures. The high-resolution mass spectra (HRMS) were measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI.

2. General procedure for the synthesis of substrates

2.1 Syntheses of o-quinone methides (*o*-QMs)

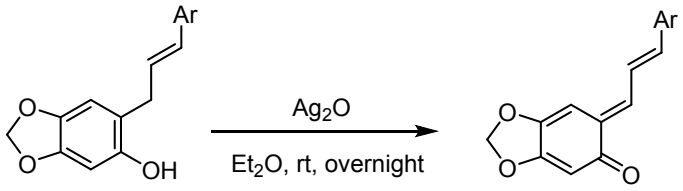
Most of *o*-QMs were synthesized according to Jurd's procedure.[1]

Synthetic procedure for vinyl o-quinone methide.



I **II** **III**

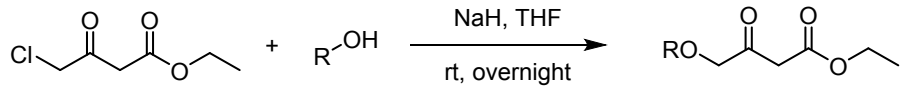
According to Jurd's method[1]: A suspension of sesame phenol **I**(2.76 g, 20.0 mmol) and (E)-3-argioprop-2-en-1-ol **II** (1 eq. 20 mmol) in 2% aqueous citric acid (100 mL) containing ascorbic acid (1.0 g, 5.6 mmol) was refluxed for 17 hours, then cooling to room temperature, the oily product was crystallized. After filtration, the crude product was recrystallized from toluene and afforded **III**, which was directly used in the next step



III **1c-1k**

The solid III(1g) was dissolved in diethyl ether (50 mL), followed by addition of silver oxide (1.5 g), and stirred for 12h at room temperature (RT). The solution was filtered, the residue was washed with dichloromethane until the liquid flowing down became colorless. Then the solution was concentrated to 10 mL, and crystals were collected. The product is acid and heat sensitive.[2]

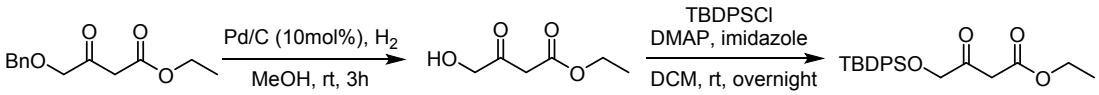
2.2 Synthesis procedure for ethyl 4-methoxyacetoacetate, ethyl 4-benzyloxyacetoacetate (2f, 2g).



IV **2f or 2g**

The methanol or benzyl alcohol (30mmol, 1.5eq) was added dropwise to a stirred suspension of 60% sodium hydride (60mmol, 3eq) in THF (20 mL) at 0℃. The mixture was stirred at RT for 2 h, then cooled to 0℃. Subsequently a solution of ethyl 4-chloroacetoacetate **IV** (20 mmol, 1.0 eq.) in THF (5mL) was added dropwise over 15 min. The mixture was stirred at 0℃ for 30min and then warmed to room temperature for overnight. The reaction mixture was carefully quenched with 1N HCl solution at 0°C and extracted with EtOAc (20mL×3). The organic layers were washed with saturated aq. $NaHCO_3$ (20mL×2) and then saturated aq. NaCl (20mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography to give ethyl 4-methoxyacetoacetate **2f** (colorless oil, 2.71g, 85% yield) (^{1}H NMR (300 MHz, $CDCl_3$) δ 4.15 (q, *J* = 7.1 Hz, 2H), 4.04 (s, 2H), 3.46 (s, 2H), 3.38 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H))or ethyl 4-benzyloxyacetoacetate **2g** (slight yellow oil, 4.25g, 90% yield) (^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.30 (m, 5H), 4.74 (s, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.17(s, 2H), 3.56 (s, 2H), 1.28 (t, J = 7.1 Hz, 3H)).

2.3 Synthesis procedure for ethyl 4-(tert-butyldiphenylsilyl)oxyacetoacetate.

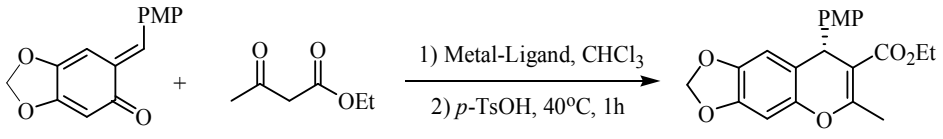


2g **V** **2k**

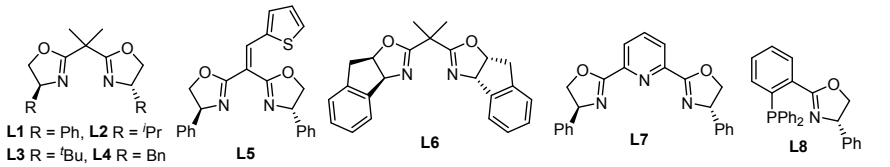
10% palladium on activated charcoal (0.21g) was added to a stirred solution of ethyl 4-(benzyloxy)-3-oxobutanoate **2g** (2g, 8 mmol) in anhydrous methanol (50mL) and the mixture was stirred under a hydrogen atmosphere for 3 h. The solution was filtered through a short pad of Celite®, the filtrate was concentrated in vacuo, and yielded the colorless oil and directly used in the next step.

Imidazole (12mmol, 1.5eq) and DMAP (5mol%) was added to a solution of **V** (8mmol, 1eq. in CH_2Cl_2(30mL), the mixture was stirred at 0℃ for 15min, then a solution of TBDPSCl (8.8mmol, 1.1eq) in CH_2Cl_2(10mL) was added dropwise, then warmed to RT and stirred for 8h. The reaction mixture was washed in sequence with HCl(1N, 20 mL), saturated aq. $NaHCO_3$ (20 mL × 2) and then a solution of saturated aq. NaCl (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography (PE: EtOAc = 20:1) to give ethyl 4-(*tert*-butyldiphenylsilyl)oxyacetoacetate **2k**(2.3g, 75% yield). ^{1}HNMR (300 MHz, $CDCl_3$) δ 7.76-7.64 (m, 4H), 7.51-7.39 (m, 6H), 4.29 (s, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.68 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.15 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.07, 167.04, 135.40, 132.17, 130.02, 127.86, 69.40, 61.25, 45.69, 26.68, 19.09, 13.98.

3. Optimization of the Reaction Conditions[a]



1a **2a** PMP = *p*-methoxyphenyl **3aa**



entry	metal	ligand	solvent	T (℃)	time	yield (%)[b]	ee (%)[c]
1	$Cu(OTf)_2$	--	$CHCl_3$	25	30min	51	--
2	$Cu(OTf)_2$	**L1**	$CHCl_3$	0	5min	77	30
3	$Mg(OTf)_2$	**L1**	$CHCl_3$	0	5min	65	6
4	$Zn(OTf)_2$	**L1**	$CHCl_3$	0	5min	84	-36
5	$Ni(OTf)_2$	**L1**	$CHCl_3$	0	5min	81	90
6	$Ni(ClO_4)_2$	**L1**	$CHCl_3$	0	5min	54	67
7	$Ni(OTf)_2$	**L1**	PhMe	0	5min	56	90
8	$Ni(OTf)_2$	**L1**	CH_2Cl_2	0	5min	73	69
9	$Ni(OTf)_2$	**L1**	THF	0	5min	trace	--
10	$Ni(OTf)_2$	**L1**	EtOAc	0	5min	46	88
11	$Ni(OTf)_2$	**L2**	$CHCl_3$	0	5min	67	60
12	$Ni(OTf)_2$	**L3**	$CHCl_3$	0	5min	79	20
13	$Ni(OTf)_2$	**L4**	$CHCl_3$	0	5min	66	55
14	$Ni(OTf)_2$	**L5**	$CHCl_3$	0	5min	88	52
15	$Ni(OTf)_2$	**L6**	$CHCl_3$	0	5min	75	26
16	$Ni(OTf)_2$	**L7**	$CHCl_3$	25	8h	trace	--
17	$Ni(OTf)_2$	**L8**	$CHCl_3$	0	5min	75	-22
18	$Ni(OTf)_2$	**Ll**	$CHCl_3$	25	5min	69	65
19	$Ni(OTf)_2$	**L1**	$CHCl_3$	-20	1h	87	92
20	$Ni(OTf)_2$	**L1**	$CHCl_3$	-40	3h	90	95
21[d]	$Ni(OTf)_2$	**L1**	$CHCl_3$	-40	5h	78	95
22[e]	$Ni(OTf)_2$	**L1**	$CHCl_3$	-40	12h	68	91

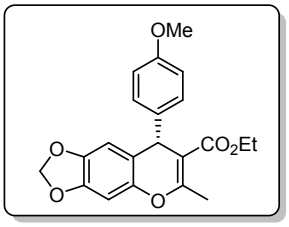
[a] Unless indicated otherwise, reactions of **1a** (0.15 mmol) and **2a** (0.1 mmol), were carried out under nitrogen in the presence of metal salt (0.01 mmol), chiral ligand (0.011 mmol) in solvent(1.5 mL); [b] Isolated yield; [c] Determined by chiral HPLC analysis; [d]5 mol% catalyst; [e]2.5 mol% catalyst.

4. The synthesis of 4*H*-chromenes

4.1 The typical asymmetric catalytic procedure

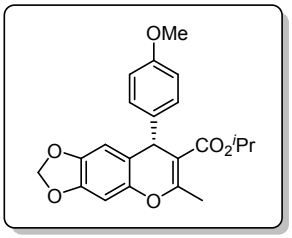
In a nitrogen-filled flask, a solution of ligand **L1**(3.67mg, 0.011mmol) and $Ni(OTf)_2$ (3.57mg, 0.01mmol) in $CHCl_3$ (1mL) was stirred at room temperature for 30min, then β-dicarbonyls (0.1mmol, 1.0eq) was added and stirred for another 30 min. The mixture was cooled to -40℃, and a solution of *o*-QMs (0.15mmol, 1.5eq, in 0.5mL of $CHCl_3$) was added by syringe and stirred at -40℃. After completion(TLC monitoring), the solution was heated to 40°C and then *p*-TsOH (3.5mg, 0.02mmol, 0.20 equiv) was added, and stirred for 1 h, the solution was concentrated and purified by silica gel chromatography.

Ethyl (*S*)-8-(4-methoxyphenyl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3aa).



The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product, slight yellow oil, 90% yield. $[\alpha]_D^{20}$ = -50.7 (c = 0.41, CH_2Cl_2); 95% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95 : 5, 0.5 mL/min, 254 nm; t (major) = 13.17 min, t (minor) = 12.40 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.06 (m, 2H), 6.84 – 6.72 (m, 2H), 6.52 (s, 1H), 6.42 (s, 1H), 5.86 (dd, *J* = 16.7, 1.4 Hz, 2H), 4.84 (s, 1H), 4.08 (qq, *J* = 7.1, 3.7 Hz, 2H), 3.74 (s, 3H), 2.44(s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.94, 159.26, 157.81, 146.28, 143.94, 143.53, 138.85, 128.37, 116.83, 113.41, 107.12, 105.30, 100.94, 97.55, 59.74, 54.84, 40.54, 19.07, 13.81. IR (film): ν = 3360, 2922, 2851, 1708, 1608, 1507, 1479, 1369, 1250, 1150, 1066, 1035, 936, 845, 705, 656, 554, 457 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{21}H_{20}O_6^+$ $[M-H]^+$: 367.1176; found: 367.1176.

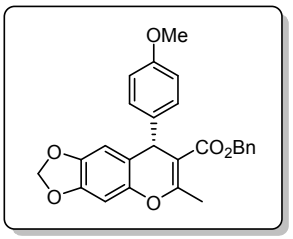
Isopropyl (*S*)-8-(4-methoxyphenyl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ab).



The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product, colorless oil, 84% yield. $[\alpha]_D^{20}$ = -10.1 (c = 1.43, CH_2Cl_2); 91% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 12.00 min, t (minor) = 11.00 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.06 (m, 2H), 6.84 – 6.70 (m, 2H), 6.51 (s, 1H), 6.42 (s, 1H), 5.85 (dd, *J* = 17.5, 1.4 Hz, 2H), 4.95 (m, 1H), 4.83 (s, 1H), 3.74 (s, 3H), 2.43 (s, 3H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.04 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.71, 159.22, 158.11, 146.56, 144.19, 143.77, 139.22, 128.74, 117.07, 113.66, 107.46, 105.76, 101.22, 97.82, 67.38, 55.15, 40.85, 21.99, 21.59, 19.29. IR (film): ν =2953, 2921, 2852, 2360, 1712, 1508, 1480, 1457, 1377, 1231, 1199, 1151, 1061, 1040 cm^{-1}; HRMS (ESI): m/z: calcd. for

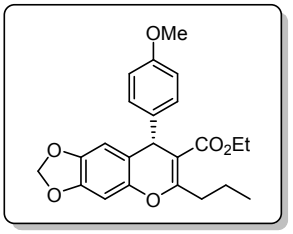
$C_{22}H_{22}O_6^+$ [M-H]$^+$: 381.1333; found: 381.1332.

Benzyl (*S*)-8-(4-methoxyphenyl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ac).



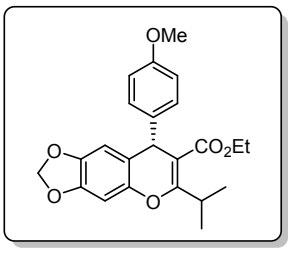
The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product, colorless oil, 85% yield. $[\alpha]_D^{20}$ = -43.1 (c = 1.08, CH_2Cl_2); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 20.09 min, t (minor) = 18.97 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31-7.27 (m, 3H), 7.17-7.14 (m, 2H), 7.09 – 7.02 (m, 2H), 6.77 – 6.69 (m, 2H), 6.51 (s, 1H), 6.40 (s, 1H), 5.83 (dd, *J* = 17.3, 1.3 Hz, 2H), 5.06 (q, *J* = 10.3 Hz, 2H), 4.85 (s, 1H), 3.74 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.02, 160.25, 158.14, 146.60, 144.29, 143.67, 139.03, 136.08, 128.66, 128.34, 128.05, 127.90, 117.06, 113.77, 107.38, 105.21, 101.25, 97.86, 65.99, 55.15, 40.77, 19.51. IR (film): ν = 2920, 2359, 1706, 1651,1608, 1507, 1477, 1378, 1321, 1231, 1192, 1147, 1033, 935, 843, 785, 697, 593, 545, 490 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{26}H_{22}O_6^+$ [M+H]$^+$: 431.1489; found: 431.1491.

Ethyl (*S*)-8-(4-methoxyphenyl)-6-propyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ad).



The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product: slightly yellow oil, 78% yield. $[\alpha]_D^{20}$ = -45.2 (c = 1.36, CH_2Cl_2); 93% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 11.70 min, t (minor) = 10.68 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 –7.06 (m, 2H), 6.84 – 6.73 (m, 2H), 6.53 (s, 1H), 6.43 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 5.83 (d, *J* = 1.4 Hz, 1H), 4.85 (s, 1H), 4.08 (qd, *J* = 7.1, 3.0 Hz, 2H), 3.74 (s, 3H), 2.94 – 2.71 (m, 2H), 1.78-1.65 (m, 2H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.00 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.07, 163.14, 158.13, 146.60, 144.21, 143.97, 139.18, 128.62, 117.23, 113.76, 107.41, 105.62, 101.23, 97.86, 60.05, 55.15, 41.01, 34.16, 21.01, 14.10, 13.88. IR (film): ν = 3054, 2962, 2930, 1706, 1651, 1610, 1508, 1479, 1328, 1264, 1191, 1069, 1035, 939, 845, 735, 562 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{28}H_{24}O_6^+$ [M-H]$^+$: 395.1489; found: 395.1488.

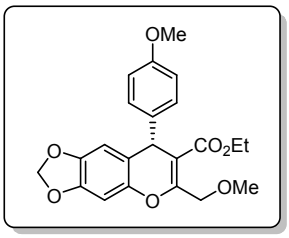
Ethyl (*S*)-6-isopropyl-8-(4-methoxyphenyl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ae).



The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product, colorless oil, 65% yield. $[\alpha]_D^{20}$ = -72.0 (c = 0.40, CH_2Cl_2); 92% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH =90:10, 1.0

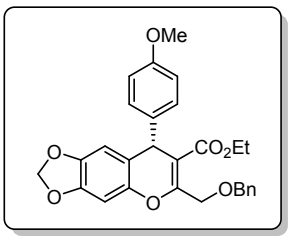
mL/min, 254 nm; t (major) = 4.79 min, t (minor) = 4.25 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.06 (m, 2H), 6.84 –6.72 (m, 2H), 6.55 (s, 1H), 6.44 (s, 1H), 5.86 (dd, *J* = 15.1, 1.4 Hz, 2H), 4.83 (s, 1H), 4.07 (q, *J* = 6.9 Hz, 2H), 3.98-3.89 (m, 1H), 3.74 (s, 3H), 1.28 (t, *J* = 6.9 Hz, 3H), 1.18 (dt, *J* = 7.1, 3.7 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.15, 166.40, 158.15, 146.62, 144.18, 144.06, 139.17, 128.51, 117.27, 113.80, 107.32, 104.20, 101.23, 97.80, 60.06, 55.16, 41.15, 29.58, 19.90, 19.40, 14.08. IR (film): ν = 2964, 2929, 1706, 1650, 1611, 1507, 1479, 1440, 1320, 1247, 1150, 1081, 1034, 938, 843, 786, 583 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{28}H_{24}O_6^+$ $[M-H]^+$: 396.1489; found: 395.1487.

Ethyl (S)-6-(methoxymethyl)-8-(4-methoxyphenyl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3af).



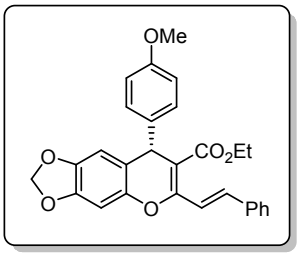
The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product: slight yellow oil, 62% yield. $[\alpha]_D^{20}$ = -55.37 (c =0.91, CH_2Cl_2); 86% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 11.05 min, t (minor) = 9.34 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 2H), 6.83 – 6.73 (m, 2H), 6.62 (s, 1H), 6.41 (s, 1H), 5.87 (dd, *J* = 15.5, 1.2 Hz, 1H)., 4.89 (s, 1H), 4.62 (dd, *J* = 17.6 Hz, 12.6 Hz, 2H), 4.14-4.06 (m, 2H), 3.74 (s, 3H), 3.46 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.44, 158.32, 157.03, 146.77, 144.52, 143.77, 138.40, 128.80, 116.59, 113.86, 108.77, 107.36, 101.34, 98.18, 69.27, 60.50, 58.71, 55.17, 41.05, 14.06. IR (film): ν = 2929, 2360, 1706, 1654, 1609, 1508, 1479, 1440, 1324, 1245, 1192, 1148, 1095, 1060, 1035, 936, 846, 790, 565 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{22}H_{23}O_7^+$ $[M+H]^+$: 399.1438; found: 399.1436.

Ethyl (*S*)-6-((benzyloxy)methyl)-8-(4-methoxyphenyl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ag).



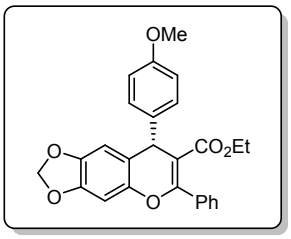
The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product: slight yellow oil, 63% yield. $[\alpha]_D^{20}$ = -67.2 (c =0.96, CH_2Cl_2); 91% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90:10, 0.8 mL/min, 254 nm; t (major) = 12.37 min, t (minor) = 11.19 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 7.16 – 7.08 (m, 2H), 6.84 – 6.73 (m, 2H), 6.61 (s, 1H), 6.41 (s, 1H), 5.86 (dd, *J* = 16.2, 1.4 Hz, 2H), 4.89 (s, 1H), 4.73(dd, *J* = 44.7, 12.9 Hz), 4.63(s, 2H), 4.06 (qd, *J* = 7.1, 1.4 Hz, 2H), 3.74 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.42, 158.30, 157.15, 146.76, 144.49, 143.80, 138.37, 138.08, 128.79, 128.31, 127.85, 127.82, 127.65, 125.75, 116.60, 113.85, 108.77, 107.36, 101.32, 98.15, 72.85, 67.08, 60.47, 55.15, 41.08, 14.02. IR (film): ν = 2922, 2359, 1704, 1653, 1609, 1507, 1478, 1439, 1367, 1324, 1243, 1192, 1148, 1060, 1034, 936, 846, 789, 698, 586 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{28}H_{27}O_7^+$ $[M+H]^+$: 475.1751; found: 475.1751.

Ethyl (*S*)-8-(4-methoxyphenyl)-6-styryl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ah).



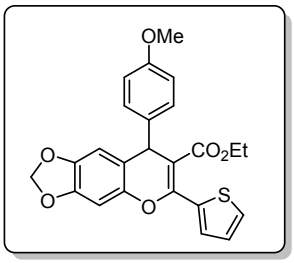
The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product: slightly yellow solid, 95% yield. Mp. 90-94℃, $[\alpha]_D^{30}$ = 0.049 (c = 0.38, CH_2Cl_2); 85% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90 : 10, 1.0 mL/min, 254 nm; t (major) = 10.69 min, t (minor) = 21.11 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.43 –7.28 (m, 3H), 7.19–7.12 (m, 2H), 6.82 –6.74 (m, 2H), 6.70 (s, 1H), 6.49 (s, 1H), 5.89 (dd, *J* = 15.6, 1.4 Hz, 2H), 4.97 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.74 (s, 3H), 1.27 (t, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.46, 157.97, 155.24, 146.51, 144.04, 143.56, 138.39, 136.12, 134.56, 128.49, 127.20, 119.83, 116.97, 113.56, 107.03, 101.04, 97.72, 60.15, 54.86, 41.23, 13.89. IR (film): $\tilde{\nu}$ = 3025, 2922, 2851, 1697, 1584, 1508, 1479, 1441, 1341, 1239, 1195, 1150, 1075, 1036, 971, 939, 844, 792, 559 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{28}H_{24}O_6^+$ $[M]^+$: 455.1489; found: 455.1490.

Ethyl (*S*)-8-(4-methoxyphenyl)-6-phenyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ai).



The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product: white solid, 60% yield. Mp. 60-62℃, $[\alpha]_D^{20}$ = -8.8 (c = 0.79, CH_2Cl_2); 70% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 20.22 min, t (minor) = 19.21 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 –7.39 (m, 5H), 7.27 – 7.22 (m, 3H), 6.85 – 6.78 (m, 2H), 6.60 (s, 1H), 6.49 (s, 1H), 5.89 (dd, *J* = 15.4, 1.4 Hz, 2H), 4.97 (s, 1H), 3.86 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 0.84 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.18, 158.34, 158.05, 146.79, 144.52, 144.47, 138.50, 135.25, 129.42, 128.79, 128.71, 127.82, 116.97, 113.96, 107.47, 107.07, 101.35, 98.16, 60.13, 55.19, 41.73, 13.51. IR (film): ν = 2919, 2849, 1695, 1608, 1508, 1478, 1442, 1369, 1338, 1243, 1161, 1076, 1034, 936, 843, 787, 698, 550 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{26}H_{23}O_6^+$ $[M+H]^+$: 431.1489; found: 431.1491.

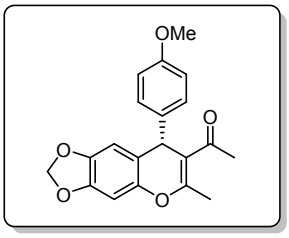
Ethyl (S)-8-(4-methoxyphenyl)-6-(thiophen-2-yl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3aj).



The title compound was purified by silica gel chromatography (PE: EtOAc = 30: 1) to afford the product, slightly yellow oil, 90% yield., $[\alpha]_D^{30}$ =0.023 (c = 0.6, CH_2Cl_2); 37% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90 : 10, 0.8 mL/min, 254 nm; t (major) = 12.92 min, t (minor) = 10.85 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 4.3 Hz), 7.24 – 7.15 (m), 7.10 – 7.00 (m), 6.87 – 6.76 (m), 6.63, 6.50 – 6.42 (m), 5.89 (dd, *J* = 13.8, 1.4 Hz), 4.95, 4.00 (q, *J* =

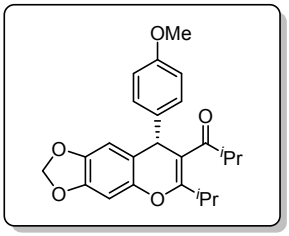
7.1 Hz), 3.76, 1.03 (t, J = 7.1 Hz).. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.12, 158.46, 150.52, 146.88, 144.57, 137.84, 135.45, 129.96, 128.87, 128.04, 126.60, 116.91, 114.00, 107.55, 107.31, 101.39, 60.48, 55.21, 42.26, 13.76. IR (film): ν = 3104, 2978, 2902, 1708, 1666, 1609, 1508, 1479, 1368, 1224, 1192, 1152, 1072, 1035, 936, 854, 795, 557 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{24}H_{21}O_6^+$ $[M+H]^+$: 437.1503; found: 437.1504.

(*S*)-1-(8-(4-methoxyphenyl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)ethan-1-one (3ak).



The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product, slight yellow oil, 90% yield. $[\alpha]_D^{20}$ = -59.7 (c = 1.43, CH_2Cl_2); 89% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 26.25 min, t (minor) = 15.19 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 2H), 6.86 – 6.77 (m, 2H), 6.51 (s, 1H), 6.49 (s, 1H), 5.86 (dd, J = 18.7, 1.4 Hz, 2H), 4.84 (s, 1H), 3.75 (s, 3H), 2.41 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.04, 158.61, 158.45, 146.72, 144.29, 143.52, 138.31, 128.46, 117.23, 114.23, 113.73, 107.21, 101.31, 97.97, 55.20, 41.63, 30.04, 19.94. IR (film): ν = 2902, 2359, 1681, 1644, 1606, 1582, 1506, 1476, 1428, 1377, 1322, 1230, 1197, 1149, 1031, 930, 82, 794, 609, 554, 450 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{20}H_{19}O_5^+$ $[M+H]^+$: 339.1227; found: 339.1227.

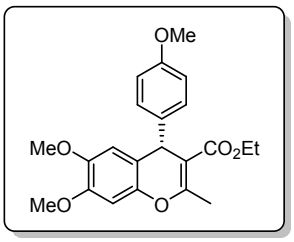
(*S*)-1-(6-isopropyl-8-(4-methoxyphenyl)-8H-[1,3]dioxolo[4,5-g]chromen-7-yl)-2-methylpropan-1-one (3al).



The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product, slight yellow oil, 80% yield. $[\alpha]_D^{20}$ = -48.3 (c = 0.60, CH_2Cl_2); 93% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 12.76 min, t (minor) = 6.27 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.06 (m, 2H), 6.86 – 6.74 (m, 2H), 6.52 (s, 1H), 6.42 (s, 1H), 5.85 (dd, J = 15.1, 1.4 Hz, 2H), 4.81 (s, 1H), 3.75 (s, 3H), 3.26-3.17 (m, 1H), 2.93-2.84 (m, 1H), 1.31 (d, J = 6.8 Hz, 3H), 1.16 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 7.0 Hz, 3H), 0.79 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.79, 161.67, 158.46, 146.73, 144.13, 143.95, 137.88, 128.76, 116.74, 114.21, 111.97, 107.26, 101.24, 97.85, 55.19, 41.86, 37.69, 30.03, 20.32, 19.71, 19.24, 17.69. IR (film): ν = 2965, 2929, 2360, 1683, 1608,1507, 1478, 1438, 1303, 1235, 1141, 1034, 934, 870, 835, 795, 559 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{24}H_{27}O_5^+$ $[M+H]^+$: 395.1853; found: 395.1857.

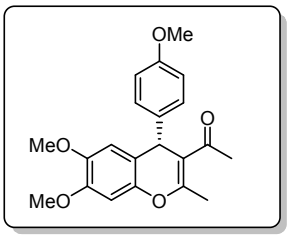
Ethyl (*S*)-6,7-dimethoxy-4-(4-methoxyphenyl)-2-methyl-4H-chromene-3-carboxylate (3ba).

The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product, slight yellow oil, 87% yield. $[\alpha]_D^{20}$ = -16.8 (c = 1.16, CH_2Cl_2); 84% ee, determined by



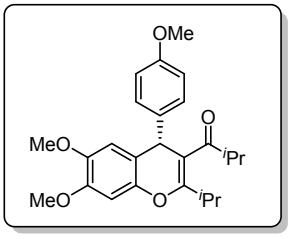
HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 9.19 min, t (minor) = 10.42 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 –7.07 (m, 2H), 6.82 – 6.73 (m, 2H), 6.58 (s, 1H), 6.44 (s, 1H), 4.90 (s, 1H), 4.09 (qd, J = 7.1, 2.5 Hz, 2H), 3.85 (s, 3H), 3.75 (s, 3H), 3.74 (s, 3H), 2.45 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.36, 159.53, 158.06, 148.32, 146.06, 143.19, 139.16, 128.75, 115.87, 113.70, 110.79, 105.94, 100.07, 60.03, 56.17, 55.99, 55.15, 40.49, 19.47, 14.15. IR (film): ν = 2932, 2834, 1707, 1643, 1600, 1508, 1463, 1379, 1322, 1254, 1225, 1211, 1172, 1121, 1068, 1034, 970, 844, 767, 606, 554 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{22}H_{24}O_6^+$ $[M-H]^+$: 383.1489; found: 383.1488.

(*S*)-1-(6,7-dimethoxy-4-(4-methoxyphenyl)-2-methyl-4H-chromen-3-yl)ethan-1-one (3bi).



The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product: slight yellow oil, 79% yield. $[\alpha]_D^{20}$ = -22.5 (c = 0.80, CH_2Cl_2); 63% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 12.16 min, t (minor) = 12.32 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 – 7.11 (m, 2H), 6.85 – 6.73 (m, 2H), 6.56 (s, 1H), 6.50 (s, 1H), 4.90 (s, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 3.75 (s, 3H), 2.41 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.20, 158.45, 158.38, 148.46, 146.04, 142.80, 138.33, 128.51, 115.89, 114.20, 114.03, 110.66, 100.18, 77.25, 77.00, 76.75, 56.23, 56.00, 55.19, 41.27, 30.05, 20.00. IR (film): ν = 2999, 2930, 2835, 1680, 1629, 1582, 1507, 1441, 1378, 1356, 1322, 1252, 1211, 1173, 1121, 1033, 936, 871, 842, 762, 651, 599, 557 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{21}H_{23}O_5^+$ $[M+H]^+$: 355.1540; found: 355.1539.

(*S*)-1-(2-isopropyl-6,7-dimethoxy-4-(4-methoxyphenyl)-4H-chromen-3-yl)-2-methylpropan-1-one (3bj).



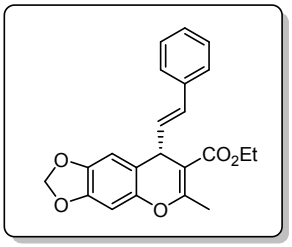
The title compound was purified by silica gel chromatography (PE: EtOAc = 10: 1) to afford the product, slight yellow oil, 55% yield. $[\alpha]_D^{20}$ = -32.1 (c = 1.27, CH_2Cl_2); 74% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 6.96 min, t (minor) = 8.08 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 – 7.04 (m, 2H), 6.86 – 6.76 (m, 2H), 6.56 (s, 1H), 6.43 (s, 1H), 4.87 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H), 3.73 (s, 3H), 3.22 (m, 1H), 2.91 (m, 1H), 1.33 (d, J = 6.8 Hz, 3H), 1.18 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 7.0 Hz, 3H), 0.80 (d, J = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.95, 161.38, 158.39, 148.56, 145.72, 143.35, 137.93, 128.83, 115.35, 114.17, 112.18, 110.92, 100.06, 56.29, 56.01, 55.16, 41.49, 37.72, 30.08,

20.37, 19.78, 19.26, 17.64. IR (film): ν = 2966, 2933, 1682, 1608, 1508, 1465, 1303, 1264, 1225, 1192, 1129, 1056, 1033, 944, 842, 732, 560 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{25}H_{31}O_5^+$ $[M+H]^+$: 411.2166; found: 411.2164.

4.2 The reaction of vinyl o-quinone methide with β-keto esters.

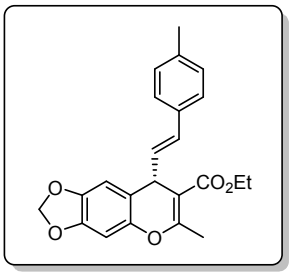
In the nitrogen-filled flask, a solution of ligand **L1**(3.67mg, 0.011mmol) and $Ni(OTf)_2$ (3.57mg, 0.01mmol) in $CHCl_3$(1.5mL) was stirred at room temperature for 30min, ethyl acetoacetate (0.1mmol, 1.0eq) were added and stirred at room temperature for another 30 min. The mixture was cooled to -20 ℃ followed by addition of vinyl *o*-QMs (0.15mmol, 1.5eq), subsequently stirred at -20℃. After completion of the reaction, the solution was warmed to 40 °C and *p*-TsOH (3.5mg, 0.02mmol, 0.20 eq.) was added. After stirring for 1h, the solution was concentrated and purified by silica gel chromatography.

Ethyl (*S*, *E*)-6-methyl-8-styryl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ca).



The title compound was purified by silica gel chromatography (Petroleum: EtOAc = 50: 1) to afford the product as a slight yellow oil, 74% yield. $[\alpha]_D^{20}$ =-176.5 (c = 0.84, CH_2Cl_2); 88% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 12.22 min, t (minor) = 11.37 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.13 (m, 5H), 6.59 (s, 1H), 6.52 (s, 1H), 6.31 (d, *J* = 15.7 Hz, 1H), 6.13 (dd, *J* = 15.7, 7.6 Hz, 1H), 5.92 (dd, *J* = 3.4, 1.3 Hz2H), 4.51 (d, *J* = 7.6 Hz, 1H), 4.31 – 4.10 (m, 2H), 2.40 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.25, 160.52, 146.94, 144.53, 144.29, 137.09, 132.83, 129.09, 128.42, 127.25, 126.32, 115.21, 107.57, 103.85, 101.36, 98.03, 60.35, 60.17, 39.05, 19.46, 14.36. IR (film): ν = 2916, 1707, 1651, 1618, 1500, 1480, 1441, 1379, 1324, 1231, 1193, 1150, 1066, 1037, 963, 938, 857, 781, 748, 693, 500 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{22}H_{21}O_5^+$ $[M+H]^+$: 365.1284, found: 365.1287.

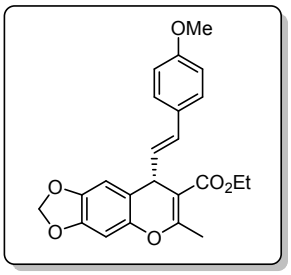
Ethyl (*S*, *E*)-6-methyl-8-(4-methylstyryl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3da).



The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product, white solid, 70% yield. Mp. 48-52℃, $[\alpha]_D^{20}$ = -137.4(c = 0.73, CH_2Cl_2); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 22.37 min, t (minor) = 20.35 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 7.9 Hz, 2H), 6.58 (s, 1H), 6.52 (s, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 6.07 (dd, *J* = 15.7, 7.7 Hz, 1H), 5.2 (dd, *J* = 3.2, 1.3Hz, 2H), 4.49 (d, *J* = 7.7 Hz, 1H), 4.32 – 4.10 (m, 2H), 2.40 (s, 3H), 2.30 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 167.30, 160.37, 146.89, 144.51,

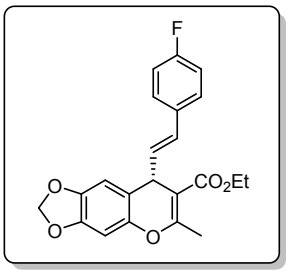
144.26, 137.03, 134.29, 131.84, 129.11, 128.96, 126.22, 115.36, 107.61, 103.96, 101.34, 98.00, 60.14, 39.05, 21.11, 19.43, 14.36. IR (film): ν = 2918, 1708, 1652, 1619, 1501, 1480, 1379, 1323, 1231, 1194, 1151, 1067, 1038, 972, 938, 857, 810, 780, 507, 456 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{23}H_{23}O_5^+$ $[M+H]^+$: 379.1540; found: 379.1539.

Ethyl (*S*, *E*)-8-(4-methoxystyryl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ea).



The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product: white solid, 58% yield. Mp. 78-81℃, $[\alpha]_D^{20}$ = -86.8 (c = 0.80, CH_2Cl_2); 80% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 19.66 min, t (minor) = 10.59 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.19 (m, 2H), 6.83 – 6.76 (m, 2H), 6.59 (s, 1H), 6.52 (s, 1H), 6.25 (d, *J* = 15.6 Hz, 1H), 5.99 (dd, *J* = 15.6, 7.7 Hz, 1H), 5.92 (dd, *J* = 3.0, 1.3 Hz, 2H), 4.48 (d, *J* = 7.7 Hz, 1H), 4.32 – 4.09 (m, 2H), 3.78 (s, 3H), 2.39 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.33, 160.31, 159.02, 146.87, 144.52, 144.26, 130.81, 129.90, 128.51, 127.45, 115.48, 113.89, 107.60, 104.07, 101.34, 97.99, 60.14, 55.27, 39.03, 19.44, 14.37. IR (film): ν = 2916, 2848, 1706, 1651, 1607, 1510, 1480, 1440, 1379, 1263, 1193, 1150, 1067, 1036, 937, 895, 823, 732, 522 cm^{-1};HRMS (ESI): m/z: calcd. for $C_{23}H_{23}O_6^+$ $[M+H]^+$: 395.1489; found: 395.1490.

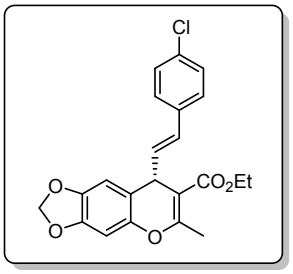
Ethyl (*S*, *E*)-8-(4-fluorostyryl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3fa).



The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product: white solid, 82% yield. Mp. 43-45℃, $[\alpha]_D^{20}$ = -116.4 (c = 0.97, CH_2Cl_2); 92% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 12.49 min, t (minor) = 7.81 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 –7.21 (m, 2H), 6.99 – 6.89 (m, 2H), 6.58 (s, 1H), 6.53 (s, 1H), 6.26 (d, *J* = 15.7 Hz, 1H), 6.05 (dd, *J* = 15.7, 7.6 Hz, 1H), 5.92 (dd, *J* = 2.9, 1.3 Hz, 2H), 4.50 (d, *J* = 7.6 Hz, 1H), 4.32 – 4.11 (m, 2H), 2.40 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.22, 162.12 (d, J = 246.8 Hz), 160.62, 146.97, 144.55, 144.32, 133.23 (d, J = 3.3 Hz), 132.60 (d, J = 2.2 Hz), 127.89, 127.77 (d, J = 7.9 Hz), 115.28 (d, J = 21.6 Hz), 107.49, 103.80, 101.38, 98.05, 60.19, 38.98, 19.49, 14.36. IR (film): ν = 2980, 2917, 2849, 1707, 1652, 1619, 1507, 1480, 1441, 1379, 1324, 1228, 1194, 1151, 1067, 1038, 972, 938, 824, 780, 514 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{22}H_{20}FO_5^+$ $[M+H]^+$: 383.1289; found: 383.1288.

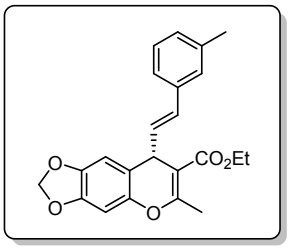
Ethyl (*S*,*E*)-8-(4-chlorostyryl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ga).

The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the



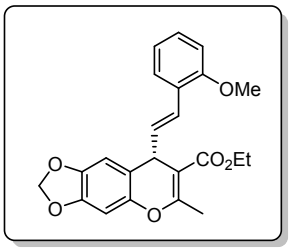
product, colorless oil, 82% yield. $[\alpha]_D^{20}$ = -125.3 (c = 0.83, CH_2Cl_2); 88% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 13.39 min, t (minor) = 8.54 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (s, 4H), 6.57 (s, 1H), 6.53 (s, 1H), 6.25 (d, *J* = 15.7 Hz, 1H), 6.11 (dd, *J* = 15.7, 7.4 Hz, 1H), 5.93 (dd, *J* = 2.8, 1.3 Hz, 2H), 4.50 (d, *J* = 7.4 Hz, 1H), 4.32 – 4.11 (m, 2H), 2.40 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.18, 160.74, 147.02, 144.57, 144.35, 135.61, 133.50, 132.85, 128.55, 127.88, 127.52, 114.96, 107.48, 103.68, 101.40, 98.09, 60.21, 39.01, 19.51, 14.37. IR (film): ν =2980, 2918, 2849, 1707, 1652, 1619, 1480, 1441, 1379, 1324, 1231, 1195, 1151, 1067, 1038, 972, 938, 857, 817, 735, 503 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{22}H_{19}ClO_5^+$ [M-H]$^+$: 397.0837; found: 397.0837.

Ethyl (*S*, *E*)-6-methyl-8-(3-methylstyryl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ha).



The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product as a slight yellow oil, 59% yield. $[\alpha]_D^{20}$ = -139.6 (c = 0.42, CH_2Cl_2); 91% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 98: 2, 0.3 mL/min, 254 nm; t (major) = 22.12 min, t (minor) = 20.12 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.07 (m, 3H), 7.04 – 6.96 (m, 1H), 6.58 (s, 1H), 6.52 (s, 1H), 6.28 (d, *J* = 15.7 Hz, 1H), 6.11 (dd, *J* = 15.7, 7.7 Hz, 1H), 5.92 (dd, *J* = 3.4, 1.3 Hz, 2H), 4.50 (d, *J* = 7.6 Hz, 1H), 4.21 (qq, *J* = 10.8, 7.1 Hz, 2H), 2.40 (s, 3H), 2.29 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.26, 160.44, 146.91, 144.52, 144.28, 137.95, 137.01, 132.62, 129.14, 128.32, 128.05, 126.96, 123.53, 115.27, 107.58, 103.89, 101.34, 98.00, 60.16, 39.06, 21.30, 19.44, 14.36. IR (film): ν = 2917, 2849, 1708, 1652, 1619, 1480, 1440, 1379, 1323, 1231, 1194, 1151, 1068, 1038, 973, 938, 859, 780, 439 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{23}H_{22}O_5^+$ [M-H]$^+$: 377.1384; found: 377.1383.

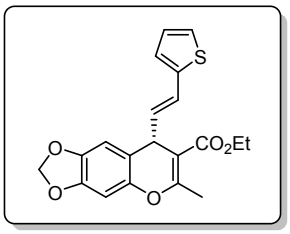
Ethyl (*S*, *E*)-8-(2-methoxystyryl)-6-methyl-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ia).



The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product as a slight yellow oil, 60% yield. $[\alpha]_D^{20}$ = -62.5 (c = 0.56, CH_2Cl_2); 87% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 8.71 min, t (minor) = 7.32 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.23–7.11 (m, 1H), 6.90 – 6.79 (m, 2H), 6.73 (d, J = 15.7 Hz, 1H), 6.61 (s, 1H), 6.51 (s, 1H), 6.07 (dd, *J* = 15.8, 8.3 Hz, 1H), 5.91 (dd, *J* = 4.1, 1.3 Hz, 2H), 4.52 (d, *J* = 8.3 Hz, 1H), 4.30 – 4.09 (m, 2H), 3.82 (s, 3H), 2.40 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.34, 160.07,

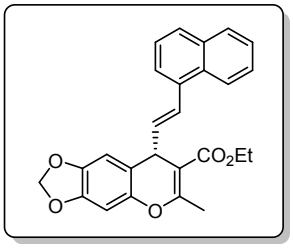
156.70, 146.83, 144.37, 144.21, 133.16, 128.25, 126.66, 126.09, 123.89, 120.49, 115.52, 110.82, 107.72, 104.01, 101.29, 97.95, 60.12, 55.37, 39.66, 19.32, 14.16. IR (film): ν = 2918, 2849, 1707, 1652, 1619, 1480, 1438, 1379, 1323, 1244, 1194, 1151, 1067, 1037, 973, 937, 857, 708, 752, 582 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{23}H_{23}O_6^+$ $[M+H]^+$: 395.1489; found: 395.1489.

Ethyl (*S*, *E*)-6-methyl-8-(2-(thiophen-2-yl)vinyl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ja).



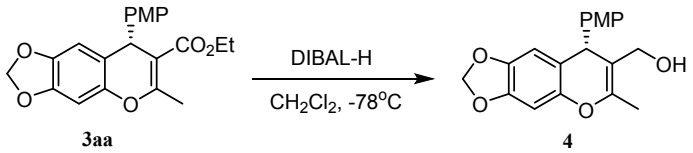
The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product, white solid, 56% yield. Mp. 67-70℃, $[\alpha]_D^{20}$ = -164.0 (c = 0.71, CH_2Cl_2); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 13.04 min, t (minor) = 12.36 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (dt, *J* = 5.0, 0.9 Hz, 1H), 6.97 – 6.84 (m, 2H), 6.58 (s, 1H), 6.52 (s, 1H), 6.41 (d, *J* = 15.6 Hz, 1H), 5.99 (dd, *J* = 15.5, 7.6 Hz, 1H), 5.93 (dd, *J* = 1.7, 1.3 Hz, 2H), 4.47 (d, *J* = 7.6 Hz, 1H), 4.36 –4.09 (m, 2H), 2.40 (d, *J* = 0.7 Hz, 3H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.15, 160.72, 146.98, 144.54, 144.31, 142.22, 132.57, 127.17, 125.29, 123.75, 122.41, 114.91, 107.51, 103.61, 101.37, 98.03, 60.19, 38.78, 19.49, 14.34. IR (film): ν = 2917, 2849, 1708, 1651, 1619, 1480, 1441, 1379, 1333, 1231, 1196, 1151, 1067, 1037, 938, 855, 780, 423 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{20}H_{18}O_5S^+$ $[M-H]^+$: 369.0791; found: 369.0789.

Ethyl (*S*, *E*)-6-methyl-8-(2-(naphthalen-1-yl)vinyl)-8H-[1,3]dioxolo[4,5-g]chromene-7-carboxylate (3ka).



The title compound was purified by silica gel chromatography (PE: EtOAc = 50: 1) to afford the product as a colorless oil, 52% yield. $[\alpha]_D^{20}$ = -73.2 (c = 0.96, CH_2Cl_2); 92% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 10.18 min, t (minor) = 8.41 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.47 (m, 3H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 15.3 Hz, 1H), 6.68 (s, 1H), 6.55 (s, 1H), 6.16 (dd, *J* = 15.4, 7.7 Hz, 1H), 5.92 (d, *J* = 8.1 Hz, 2H), 4.65 (d, *J* = 7.7 Hz, 1H), 4.25 (qq, *J* = 11.0, 7.2 Hz, 2H), 2.43 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.31, 160.53, 146.97, 144.56, 144.35, 135.97, 134.80, 133.57, 131.20, 128.46, 127.61, 126.30, 125.87, 125.63, 125.51, 123.71, 115.21, 107.55, 103.89, 101.38, 98.10, 60.25, 39.43, 19.49, 14.41. IR (film): ν = 2925, 1707, 1652, 1619, 1501, 1480, 1440, 1379, 1332, 1231, 1194, 1151, 1065, 1037, 972, 938, 859, 799, 779, 410 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{26}H_{23}O_5^+$ $[M+H]^+$: 415.1540; found: 415.1543.

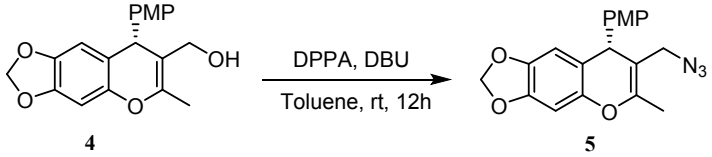
4.3 Synthesis of (8-(4-methoxyphenyl)-8H-[1, 3]dioxolo[4,5-g]chromen-7-yl)methanol (4).



3aa **4**

In the nitrogen-filled flask, a solution of **3aa** (2 mmol) in CH_2Cl_2 was stirred at -78℃ for 30min, added DIBAL-H (4.4 mL, 2.2eq, 1.0M in hexane) then stirred at -78℃ for 1h. After completion, the solution was quenched with 15% NaOH(aq.) at 0℃, and extracted with CH_2Cl_2 (5mL × 3). The organic layers were washed with H_2O (5 mL× 2) and then saturated NaCl (5 mL), dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude product was purified by silica gel chromatography to give compound **4** (0.55g, 85% yield) as colorless oil. $[\alpha]_D^{25}$ = -49.2 (c = 0.96, CH_2Cl_2); 95% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 80: 20, 1.0 mL/min, 254 nm; t (major) = 7.55 min, t (minor) = 11.91 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.12 (m, 2H), 6.93–6.79 (m, 2H), 6.51 (s, 1H), 6.37 (s, 1H), 5.87 (dd, J = 14.0, 1.4 Hz, 2H), 4.59 (s, 1H), 4.06 (dd, J = 69.6, 12.1 Hz, 2H), 3.79 (s, 3H), 2.07 (s, 3H), 1.35 (br, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.37, 146.47, 146.00, 144.80, 143.36, 138.34, 129.05, 116.32, 114.07, 109.27, 107.77, 100.99, 97.60, 61.12, 55.16, 42.23, 15.84. IR (film): ν = 3370, 2894, 1747, 1692, 1607, 1506, 1477, 1438, 1383, 1302, 1247, 1196, 1172, 1033, 981, 935, 873, 832, 802, 735, 663, 584, 552 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{19}H_{19}O_5^+$ $[M+H]^+$: 327.1227; found: 327.1228.

4.4 Synthesis of 7-(azidomethyl)-8-(4-methoxyphenyl)-6-methyl-8H-[1,3]dioxolo[-4, 5-g]chromene (5)

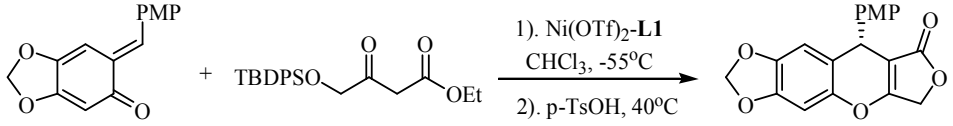


4 **5**

Compound **4** (0.3mmol, 1eq.) and DPPA (0.45mmol, 1.5eq.) was dissolved in toluene (2mL), then DBU(0.45mmol, 1.5eq.) was added, and stirred at room temperature for 12h. After completion of the reaction, the solution was concentrated and purified by silica gel chromatography to give compound **5** (64mg, 61% yield) as a slight yellow oil. $[\alpha]_D^{25}$ =20.9 (c 1.68, CH_2Cl_2); 90% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90:10, 0.8 mL/min, 254 nm; t (major) = 9.50 min, t (minor) = 8.00 min]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 – 7.07 (m, 2H), 6.87– 6.78 (m, 2H), 6.47 (s, 1H), 6.31 (s, 1H), 5.85 (dd, J = 12.1, 1.4 Hz, 2H), 4.48 (s, 1H), 3.77 (s, 3H), 3.69(dd, J = 135.3, 13.5Hz), 2.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.53, 147.16, 146.64, 144.55, 143.60, 137.47, 129.18, 115.78, 114.07, 107.88, 104.68, 101.10, 97.65, 55.19, 50.75, 42.61, 16.27; IR (film): ν = 3002, 2953, 2900, 2836, 2094, 1689, 1608, 1506, 1477, 1438, 1200, 1172, 1034, 937, 880, 734, 585 cm^{-1};HRMS (ESI): m/z: calcd. for $C_{19}H_{18}NO_4^+$ $[M+H-N_2]^+$: 324.1236, found: 324.1232.

4.5 Synthesis of 9-(4-methoxyphenyl)-6,9-dihydro-8H-[1,3]dioxolo[4,5-g]furo-

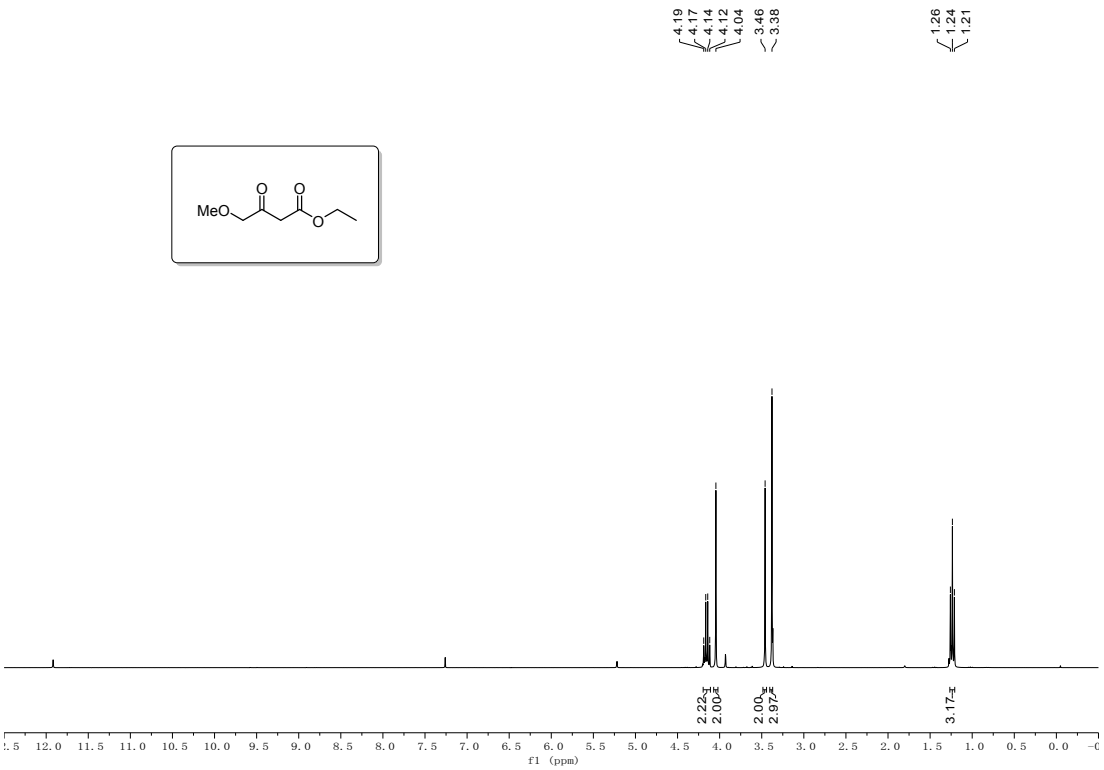
[3,4-b]chromen-8-one (3ak).

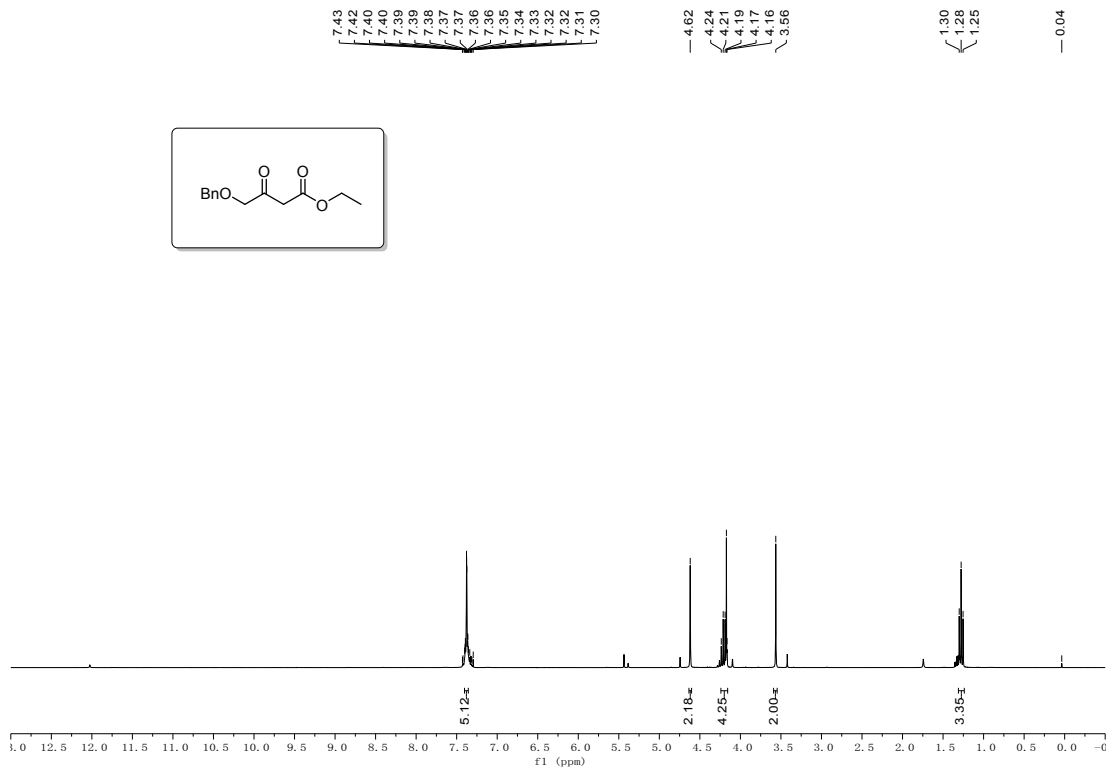


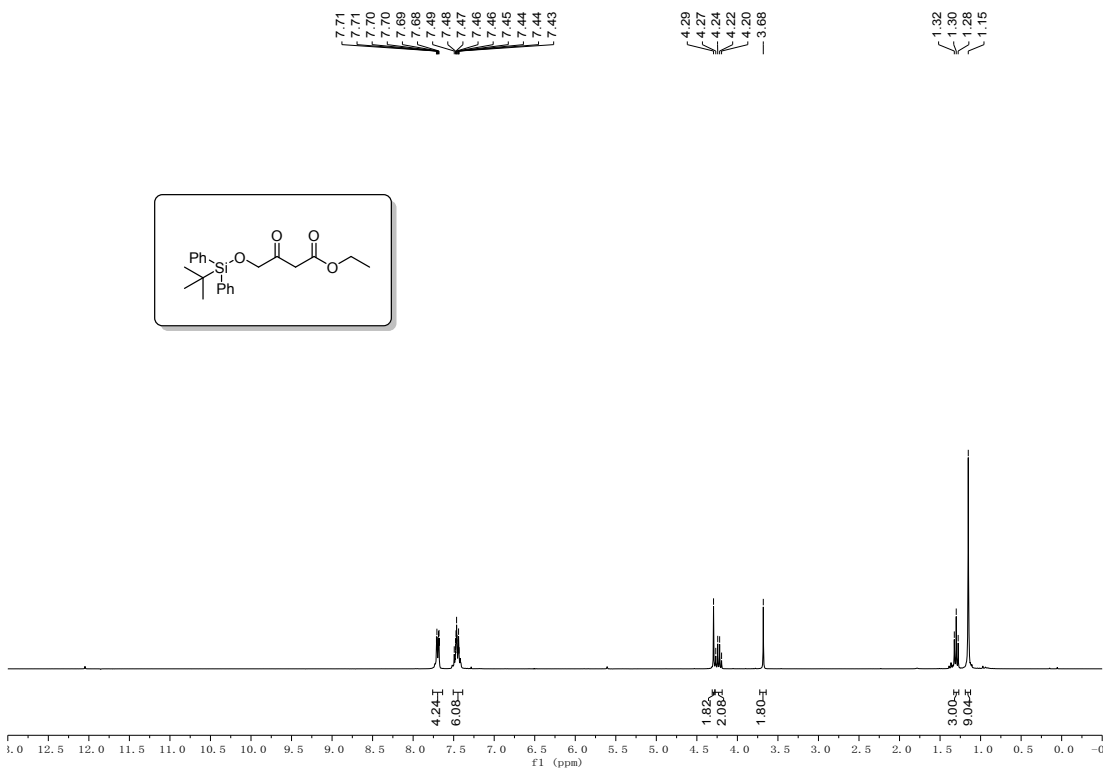
1a **2k** **3ak**

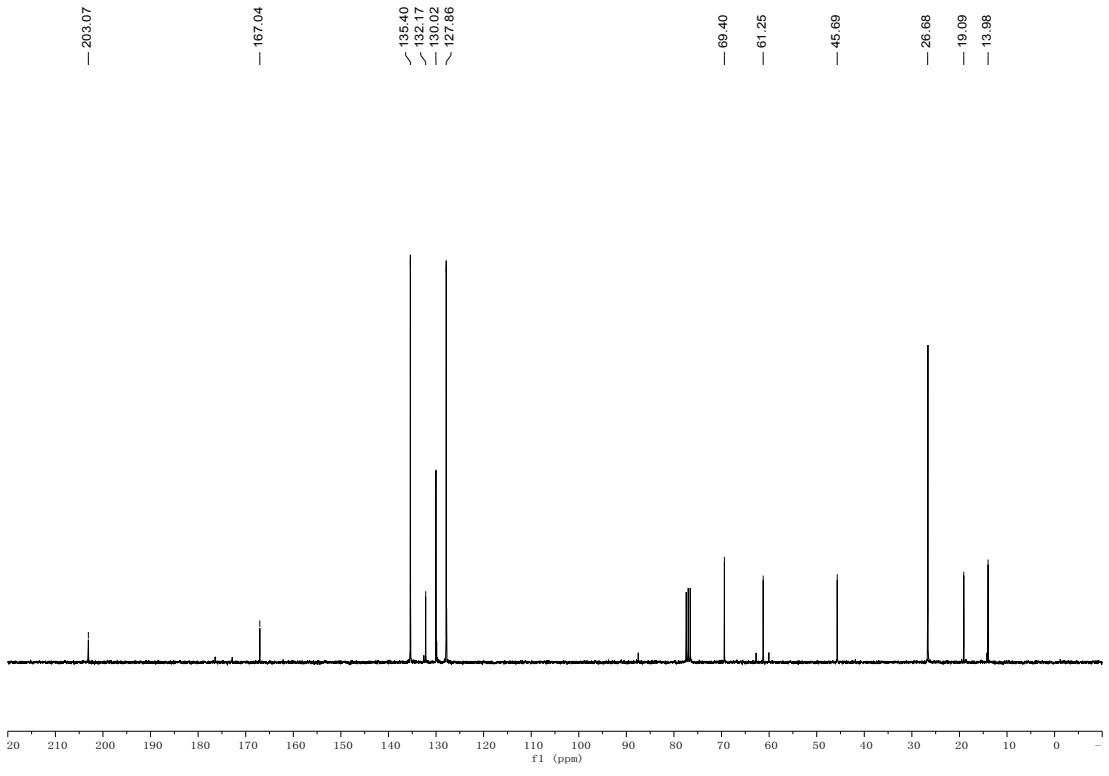
In the nitrogen-filled flask, a solution of ligand L1 (3.67mg, 0.011mmol) and $Ni(OTf)_2$ (3.57mg, 0.01mmol) in $CHCl_3$(1mL) was stirred at room temperature for 30min, followed by added **2k** (0.1mmol, 1.0eq) and stirred for another 30 min. After the mixture was cooled to -55℃, a solution of *o*-QMs **1a** (0.15mmol, 1.5eq.) in $CHCl_3$ (0.5mL) was added over 10min, and stirred at -55℃. After completion of the reaction, the solution was heated to 40°C and *p*-TsOH (3.5mg, 0.02mmol, 0.20eq.) was added. After stirring for 12h at this temperature, the solution was concentrated and purified by silica gel chromatography to afford **3ak** (25.4mg, 75% yield) as slight yellow solid. $[\alpha]_D^{25}$ = –97.4 (c 1.02, CH_2Cl_2); 92% ee, determined by HPLC analysis [Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 254 nm; t (major) = 19.29 min, t (minor) = 27.36 min]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16–7.07 (m, 2H), 6.87–6.78 (m, 2H), 6.63 (s, 1H), 6.45 (s, 1H), 5.94 (dd, *J* = 14.8, 1.3 Hz, 2H), 4.81 (dd, J = 15.2, 7.8 Hz, 2H), 4.80 (s, 1H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.82, 167.90, 158.74, 147.43, 145.55, 144.66, 135.22, 129.30, 115.75, 114.10, 108.97, 103.59, 101.91, 98.49, 65.50, 55.24, 37.52; IR (film): ν = 2921, 1760, 1694, 1609, 1508, 1480, 1405, 1346, 1303, 1245, 1174, 1137, 1030, 1009, 933, 867, 849, 788, 767, 735, 608, 570, 526 cm^{-1}; HRMS (ESI): m/z: calcd. for $C_{19}H_{15}O_6^+$ $[M+H]^+$: 339.0863, found: 339.0851.

5. NMR Spectra






7.71
7.71
7.70
7.70
7.69
7.68
7.49
7.48
7.47
7.46
7.46
7.45
7.44
7.44
7.43
4.29
4.27
4.24
4.22
4.20
3.68
1.32
1.30
1.28
1.15
Ph
Si
O
Ph
O
O
O
4.24
6.08
1.82
2.08
1.80
3.00
9.04
f1 (ppm)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61.25
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26.68
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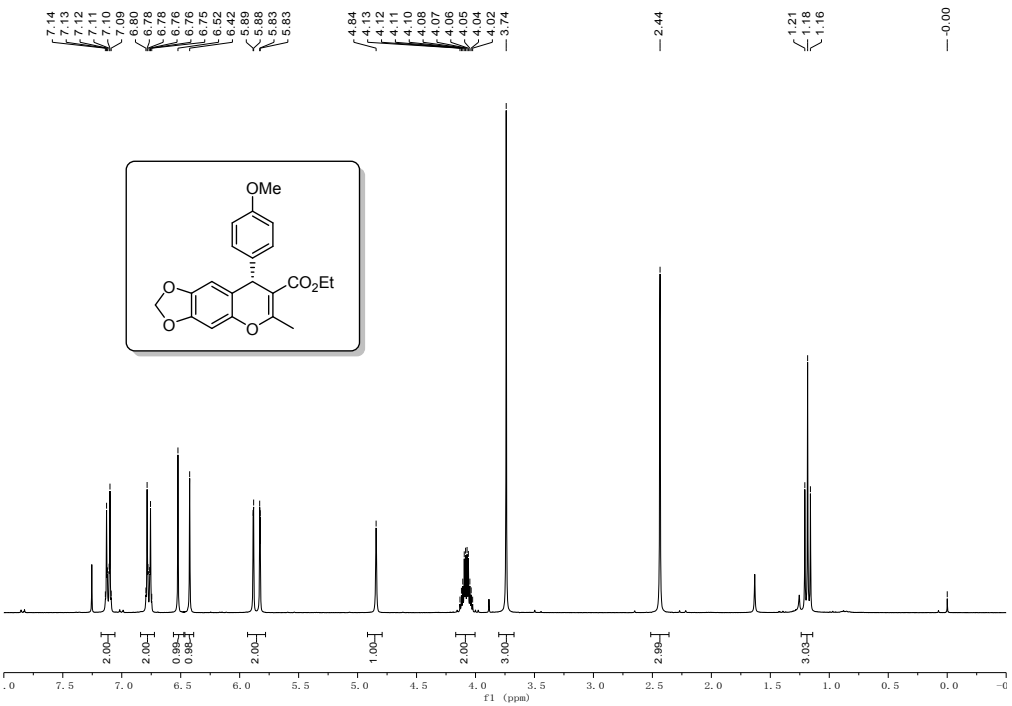
f1 (ppm)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6.76
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6.52
6.42
5.89
5.88
5.83
5.83
4.84
4.13
4.12
4.11
4.10
4.08
4.07
4.06
4.05
4.04
4.02
3.74
2.44
1.21
1.18
1.16
-0.00
OMe
CO2Et
O
O
O
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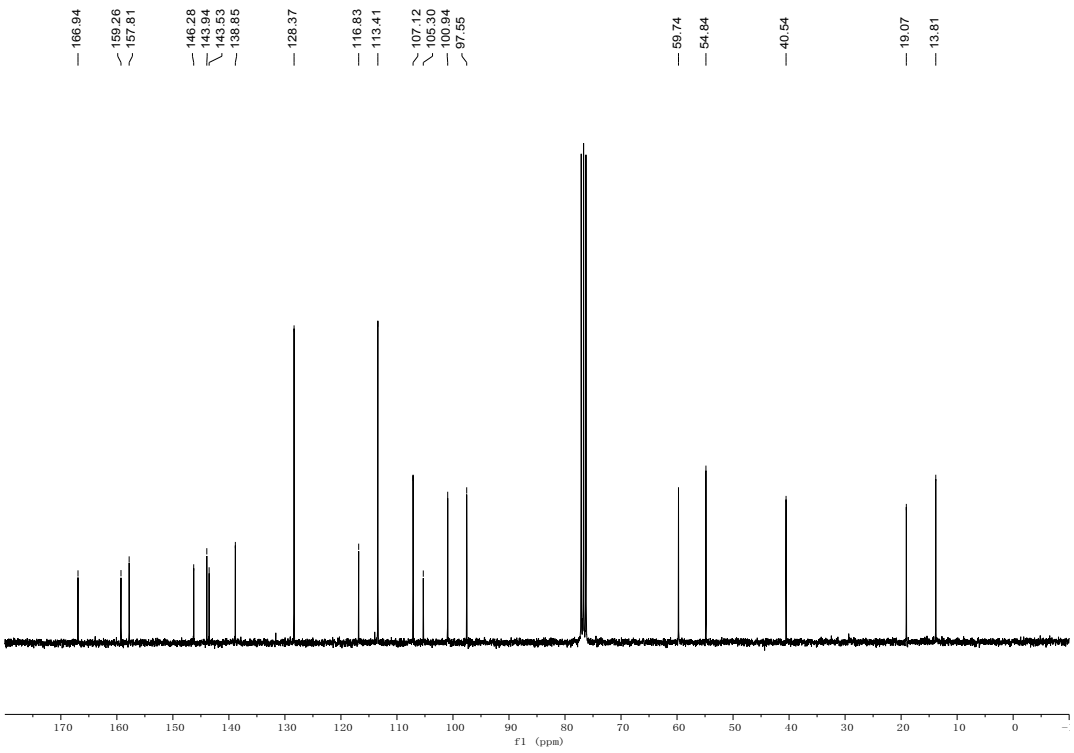
0.98
2.00
1.00
2.00
3.00
2.89
3.03
f1 (ppm)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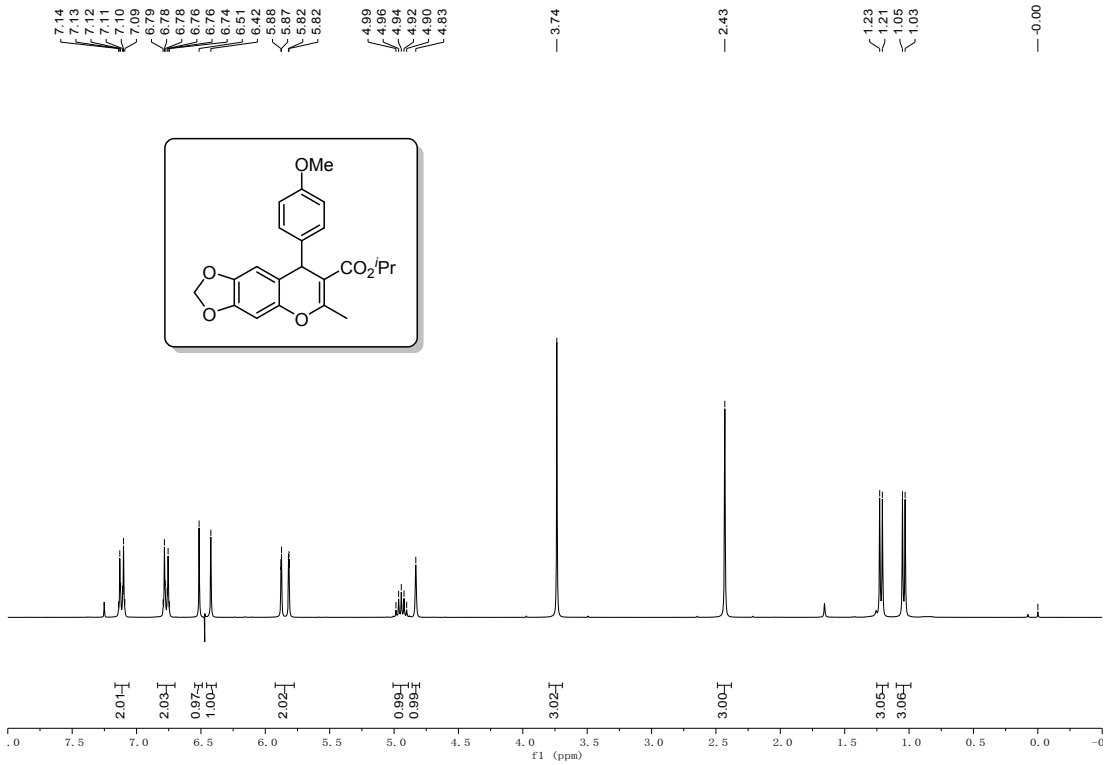
59.74
54.84
40.54
19.07
13.81
f1 (ppm)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6.51
6.42
5.88
5.87
5.82
5.82
4.99
4.96
4.94
4.92
4.90
4.83
3.74
2.43
1.23
1.21
1.05
1.03
0.00
OMe
CO2iPr
O
O
O
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2.03
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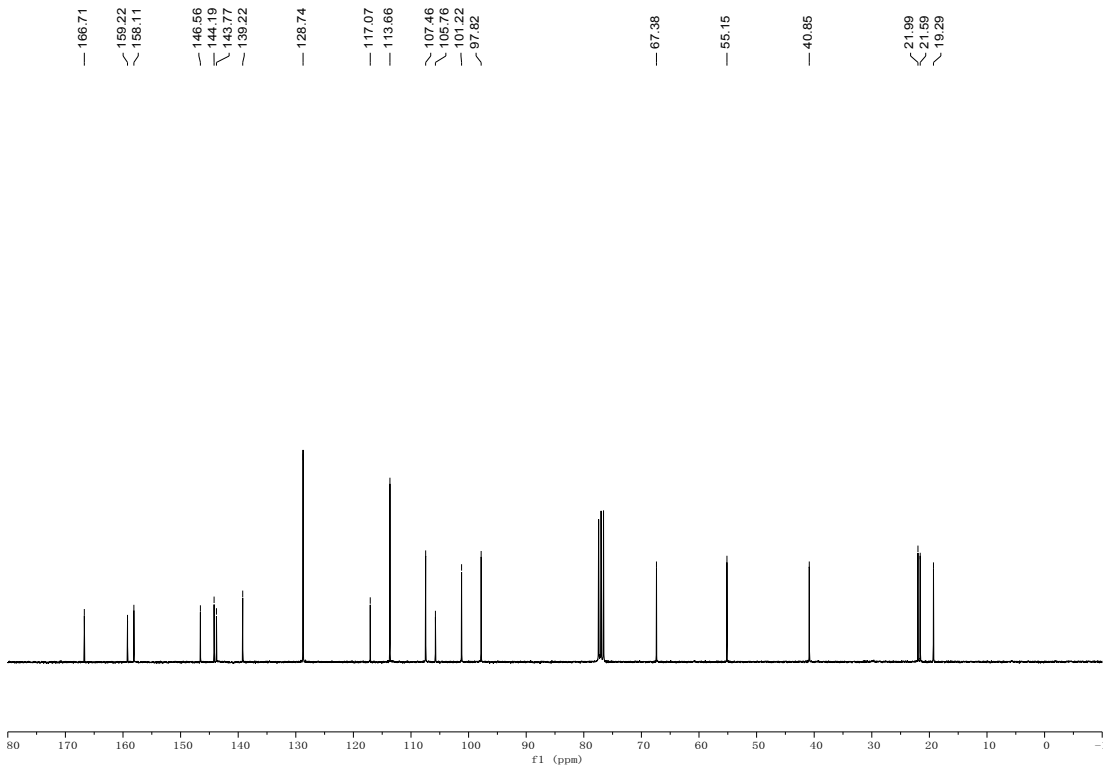
1.00
2.02
0.99
0.99
3.02
3.00
3.05
3.06
f1 (ppm)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97.82
67.38
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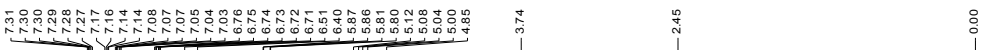
40.85
21.99
21.59
19.29
f1 (ppm)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7.07
7.05
7.04
7.03
6.76
6.75
6.74
6.73
6.72
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6.40
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5.04
5.00
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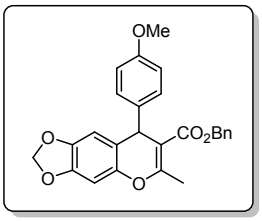
3.74
2.45
0.00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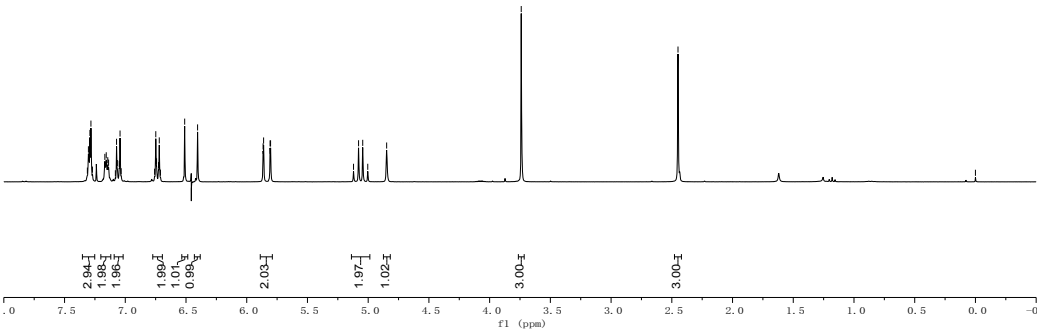
CO2Bn
O
O
O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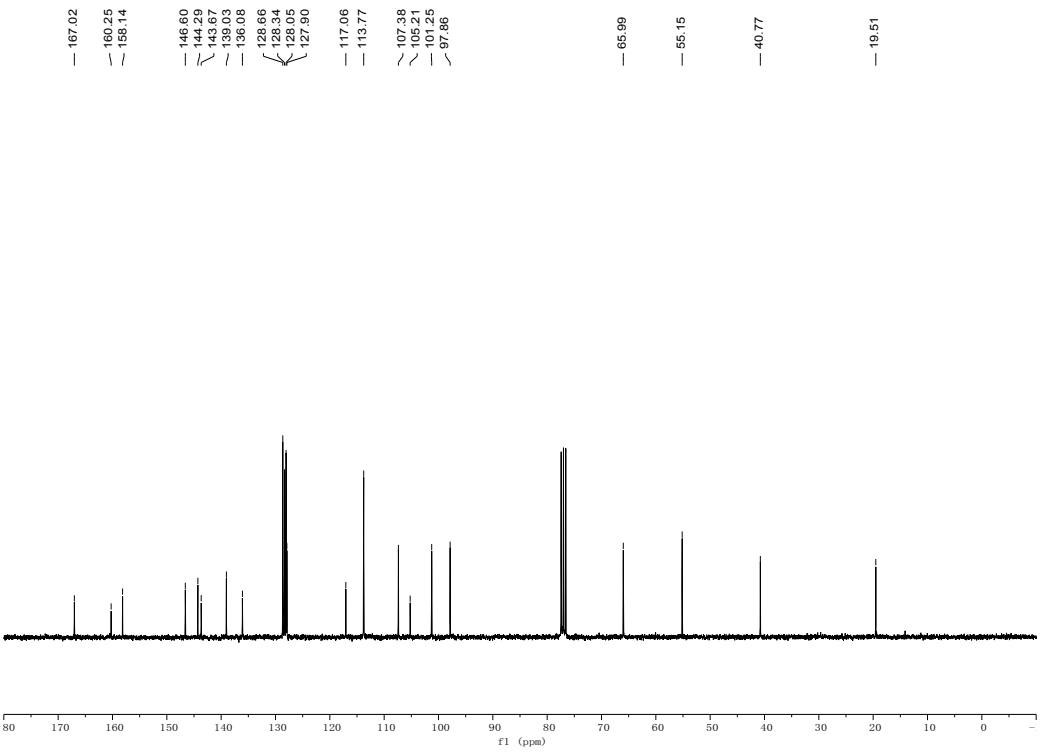
0.99
2.03
1.97
1.02
3.00
3.00
f1 (ppm)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139.03
136.08
128.86
128.34
128.05
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117.06
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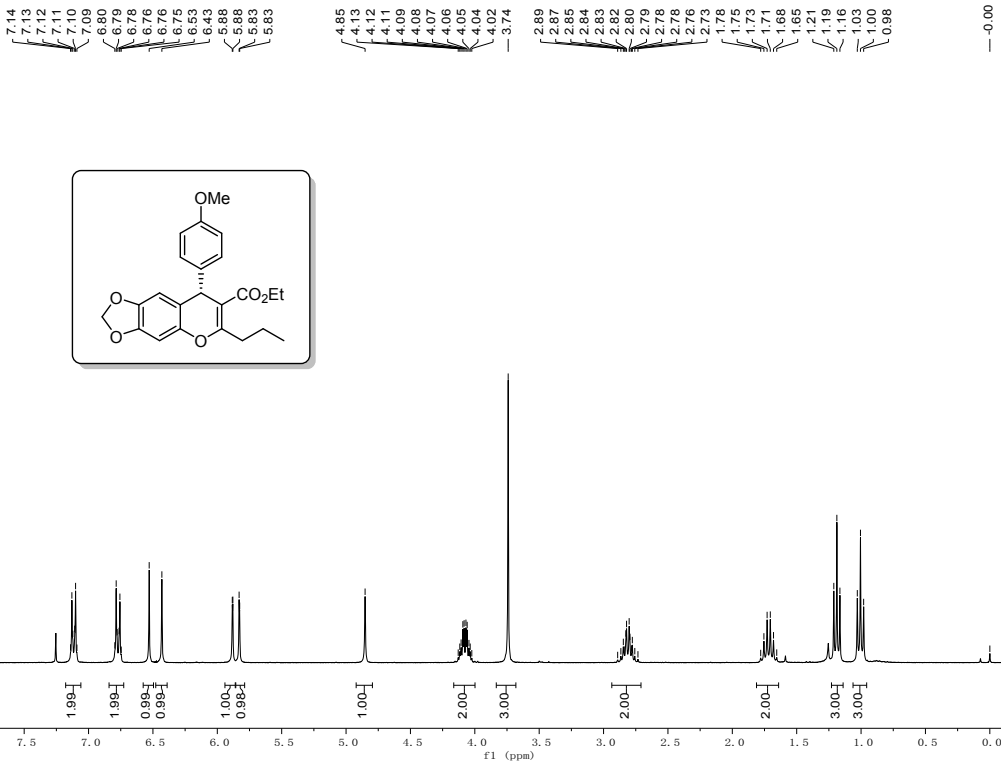
107.38
105.21
101.25
97.86
65.99
55.15
40.77
19.51
f1 (ppm)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6.76
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6.75
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6.43
5.88
5.88
5.83
5.83
4.85
4.13
4.12
4.11
4.09
4.08
4.07
4.06
4.05
4.04
4.02
3.74
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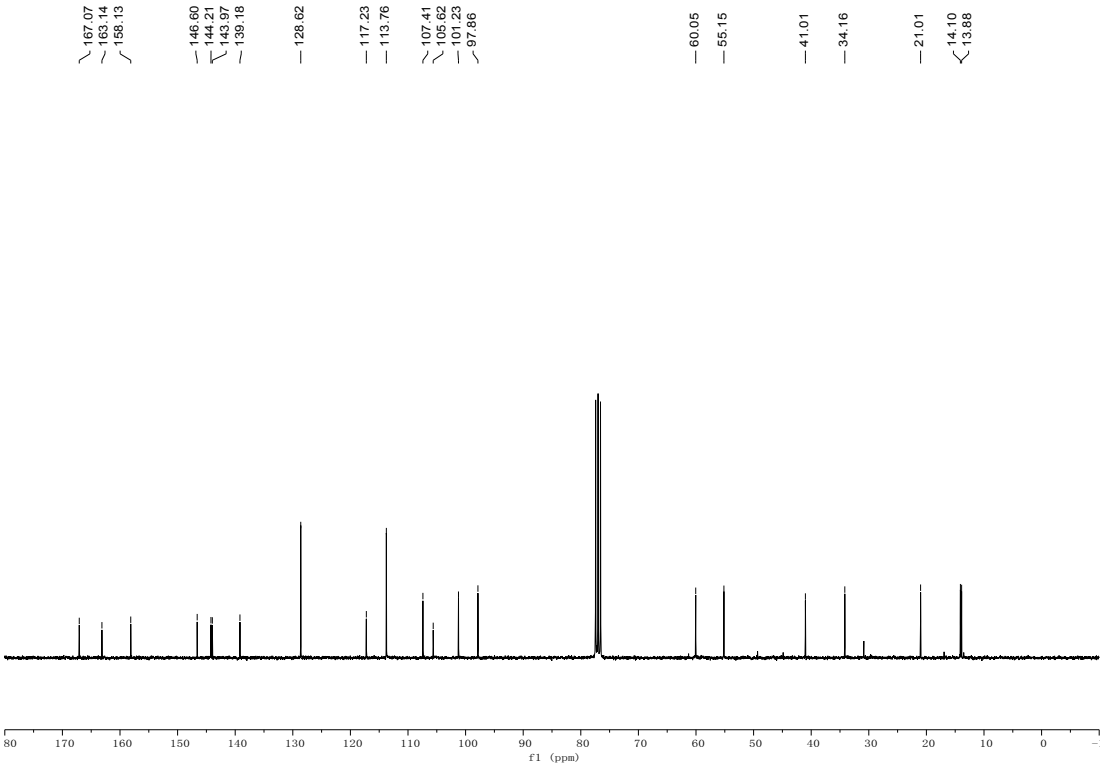
2.73
1.78
1.75
1.73
1.71
1.68
1.65
1.21
1.19
1.16
1.03
1.00
0.98
0.00
OMe
CO2Et
O
O
O
1.99
1.99
0.99
0.99
1.00
0.98
1.00
2.00
3.00
2.00
2.00
3.00
3.00
f1 (ppm)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139.18
128.62
117.23
113.76
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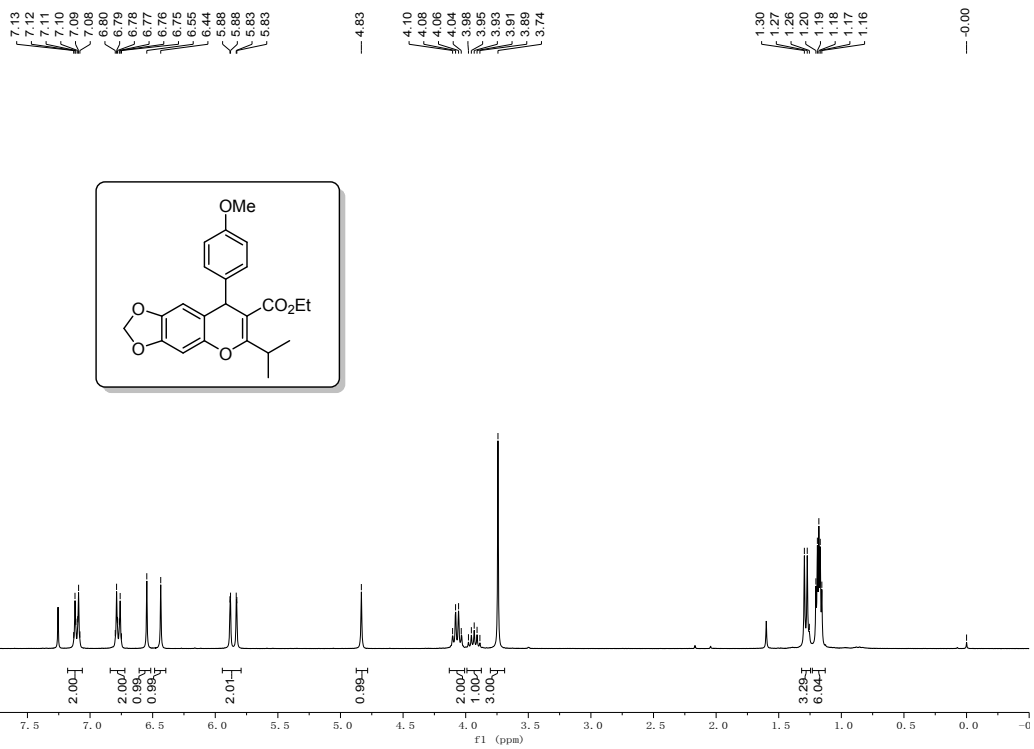
105.62
101.23
97.86
60.05
55.15
41.01
34.16
21.01
14.10
13.88
f1 (ppm)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6.78
6.77
6.76
6.75
6.55
6.44
5.88
5.83
5.83
4.83
4.10
4.08
4.06
4.04
3.98
3.95
3.93
3.91
3.89
3.74
1.30
1.27
1.26
1.20
1.19
1.18
1.17
1.16
-0.00
OMe
CO2Et
O
O
O
2.00
2.00
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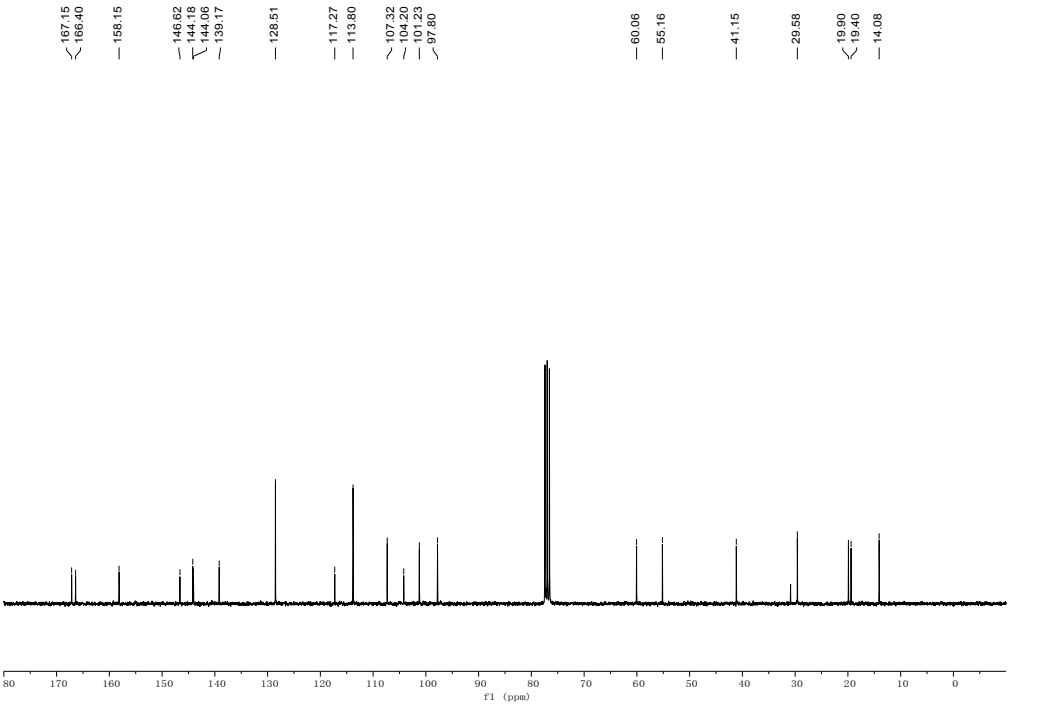
0.99
2.01
0.99
2.00
1.00
3.00
3.29
6.04
f1 (ppm)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104.20
101.23
97.80
60.06
55.16
41.15
29.58
19.90
19.40
14.08
f1 (ppm)


7.14
7.13
7.12
7.11
6.79
6.78
6.77
6.76
6.62
6.48
6.48
6.41
5.89
5.89
5.84
5.84
4.69
4.65
4.59
4.55
4.14
4.13
4.11
4.11
4.09
4.08
4.07
4.06
3.74
3.46
1.22
1.19
1.17
0.00
OMe
CO2Et
OMe
O
O
O
2.04
2.01
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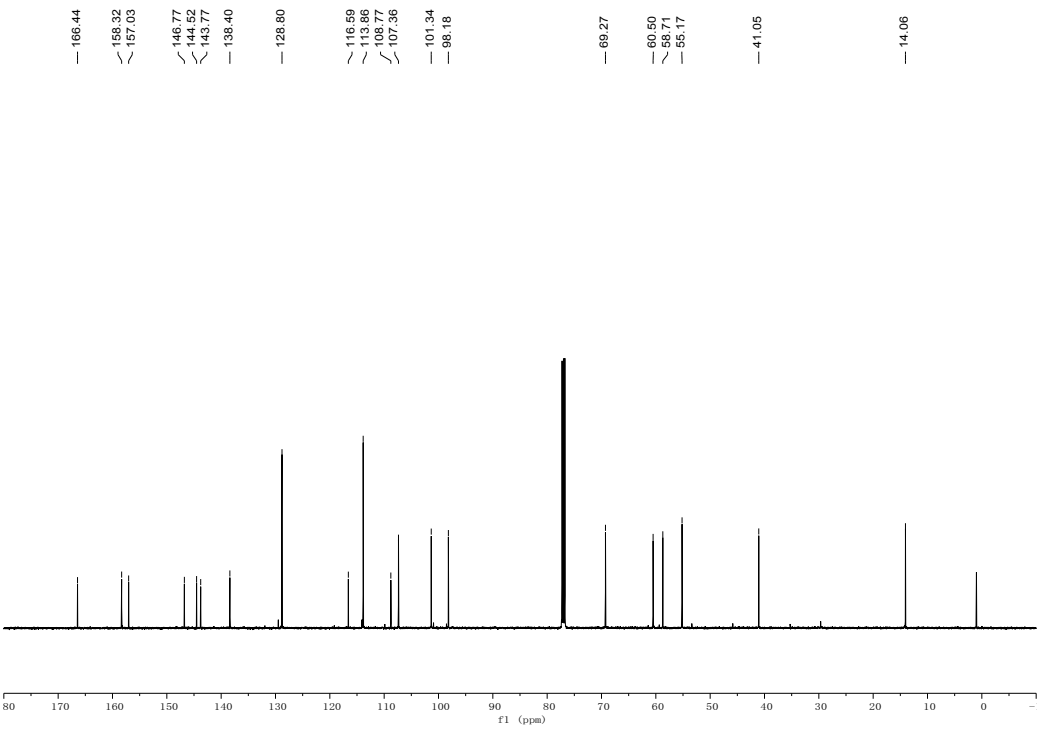
1.10
2.10
1.00
2.05
2.11
2.98
2.93
3.00
f1 (ppm)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113.86
108.77
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101.34
98.18
69.27
60.50
58.71
55.17
41.05
14.06
f1 (ppm)


7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.33
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7.29
7.28
7.15
7.13
7.13
7.11
7.11
7.10
6.80
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6.78
6.76
6.76
6.75
6.61
6.41
5.89
5.88
5.83
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4.89
4.85
4.81
4.66
4.63
4.62
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4.55
4.10
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4.02
3.74
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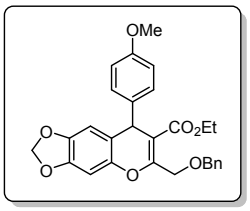
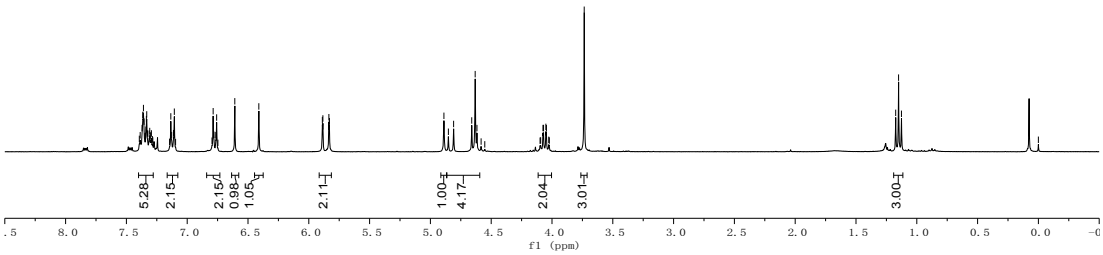
1.13
0.00


OMe
CO2Et
OBn
O
O
O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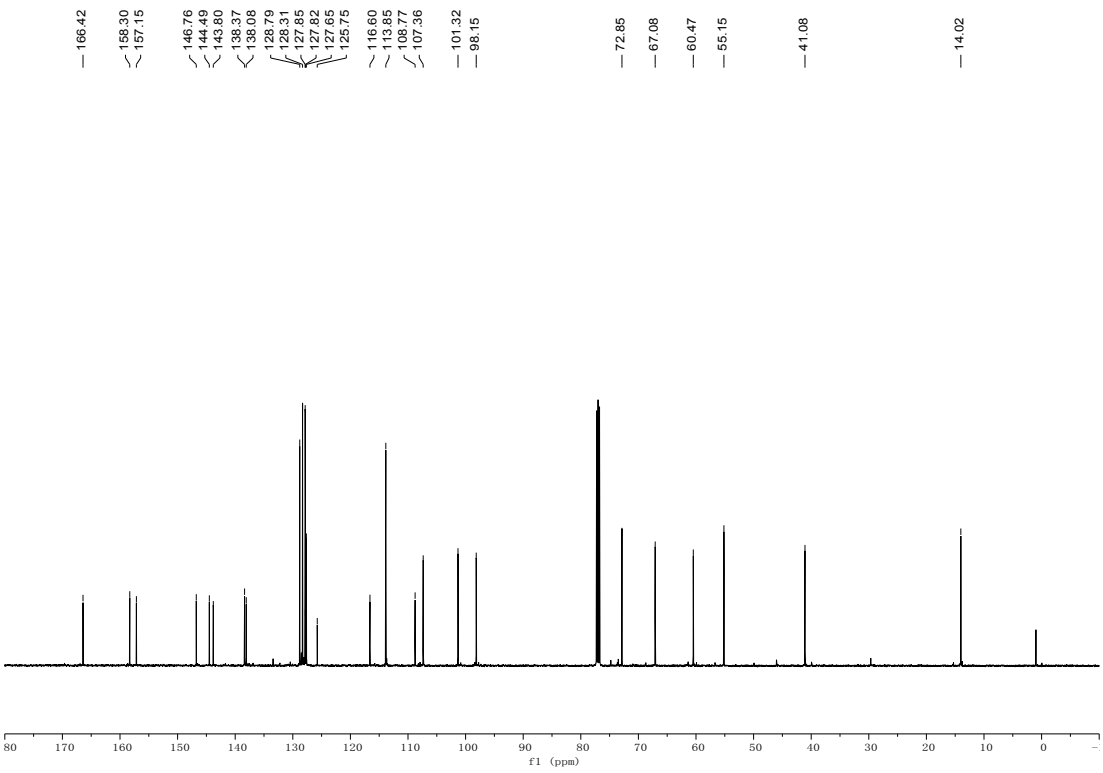
3.00
f1 (ppm)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127.65
125.75
116.60
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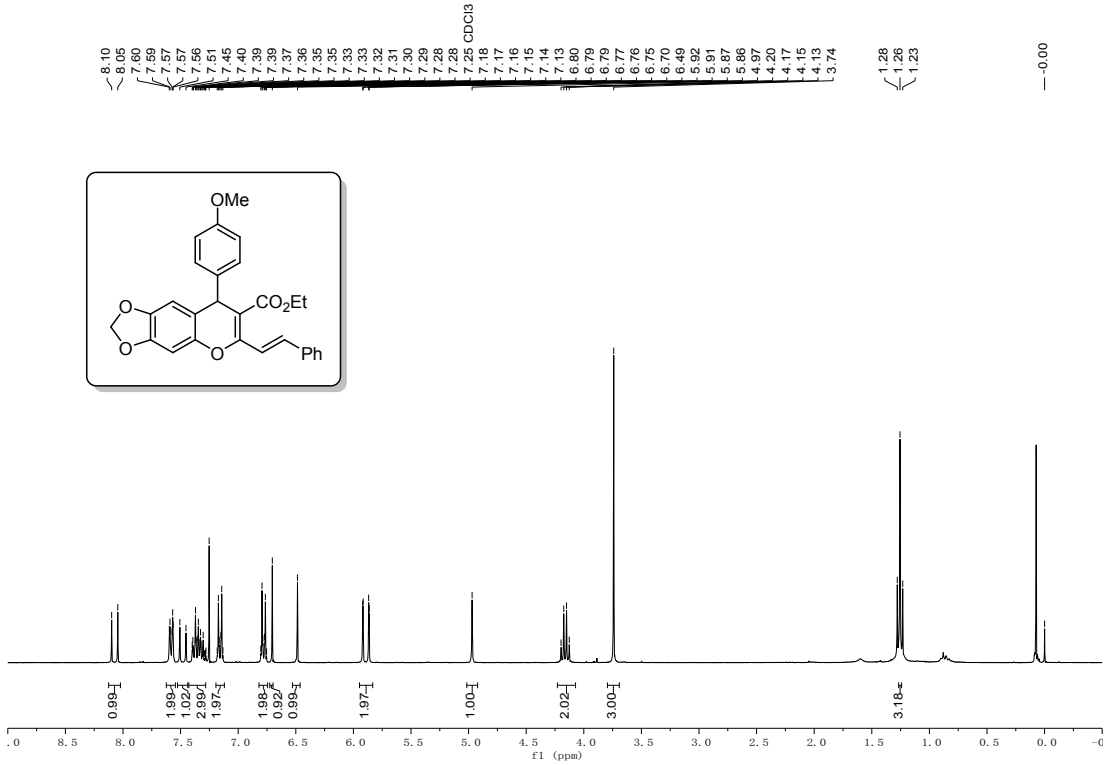
72.85
67.08
60.47
55.15
41.08
14.02
f1 (ppm)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7.33
7.32
7.31
7.30
7.29
7.28
7.28
7.25 CDCl3
7.18
7.17
7.16
7.15
7.14
7.13
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6.79
6.77
6.76
6.75
6.70
6.49
5.92
5.91
5.87
5.86
4.97
4.20
4.17
4.15
4.13
3.74
1.28
1.26
1.23
-0.00
OMe
CO2Et
O
O
O
Ph
0.99
1.99
1.02
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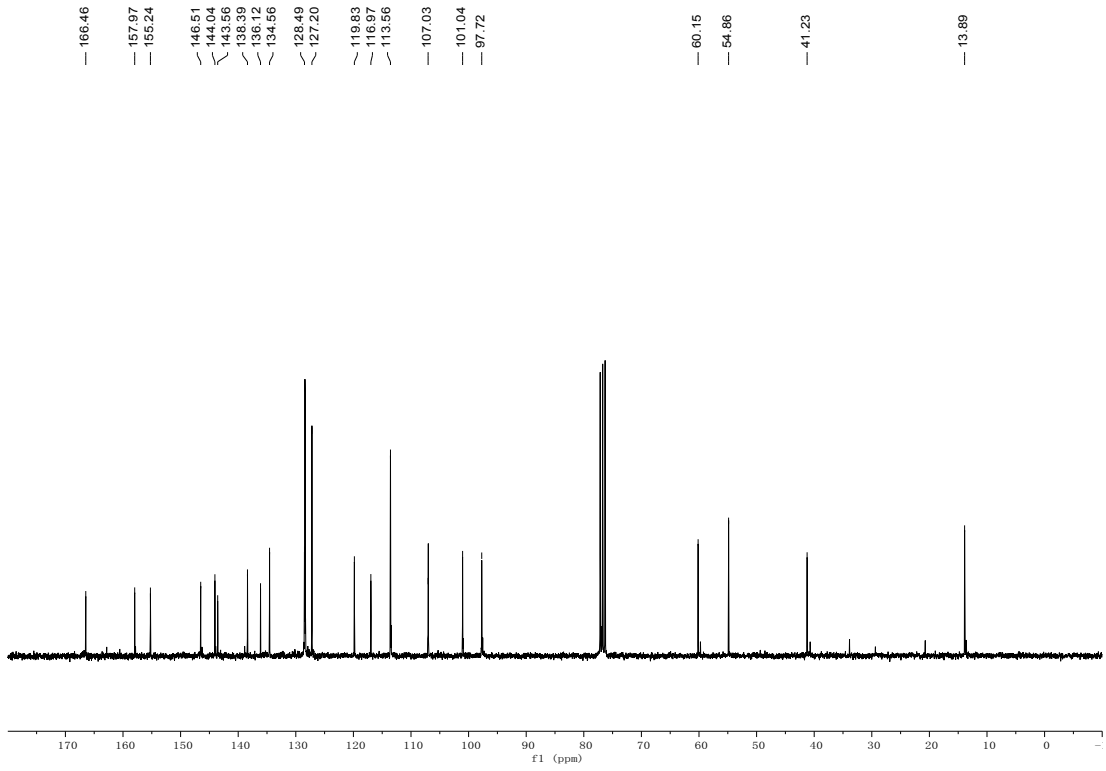
0.92
0.99
1.97
1.00
2.02
3.00
3.18
f1 (ppm)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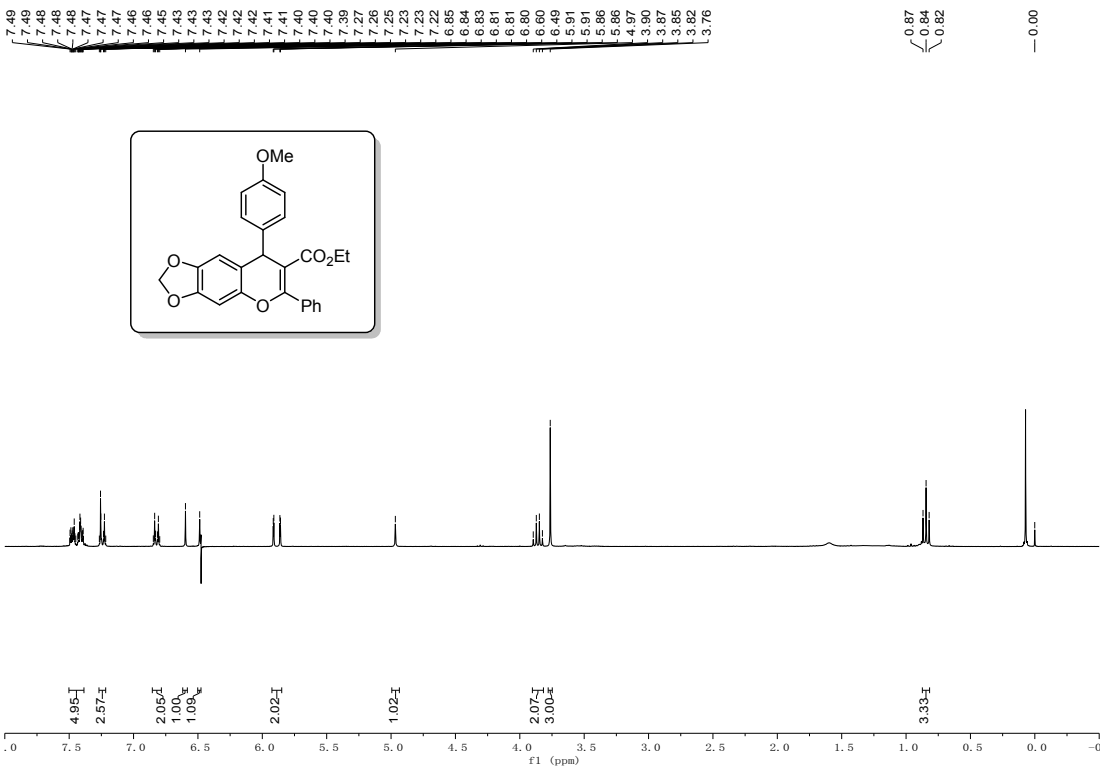
101.04
97.72
60.15
54.86
41.23
13.89
f1 (ppm)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7.41
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7.40
7.40
7.39
7.27
7.26
7.25
7.23
7.23
7.22
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6.84
6.83
6.81
6.81
6.80
6.60
6.49
5.91
5.91
5.86
5.86
4.97
3.90
3.87
3.85
3.82
3.76
0.87
0.84
0.82
0.00
OMe
CO2Et
O
O
O
O
Ph
4.95
2.57
2.05
1.00
1.09
2.02
1.02
2.07
3.00
3.33
f1 (ppm)
167.18
158.34
158.05
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144.52
144.47
138.50
135.25
129.42
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128.71
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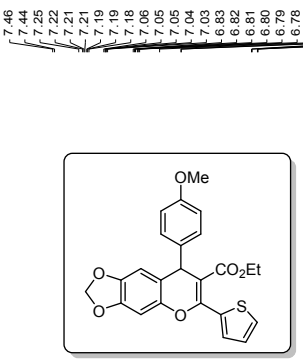
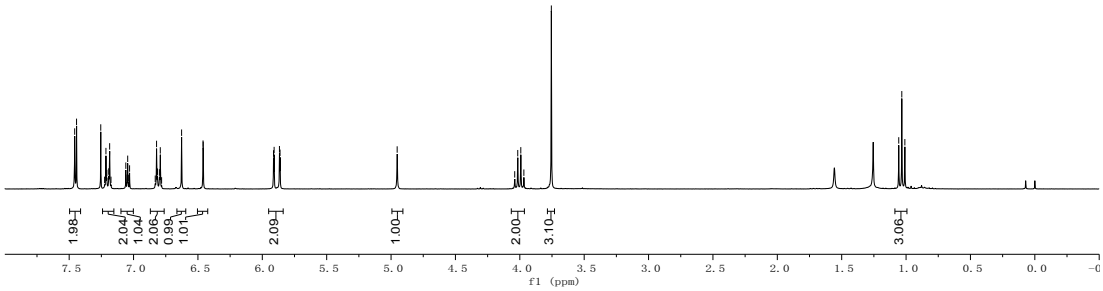
55.19
41.73
13.51
f1 (ppm)


OMe
CO2Et
O
O
O
S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1.01
2.09
1.00
2.00
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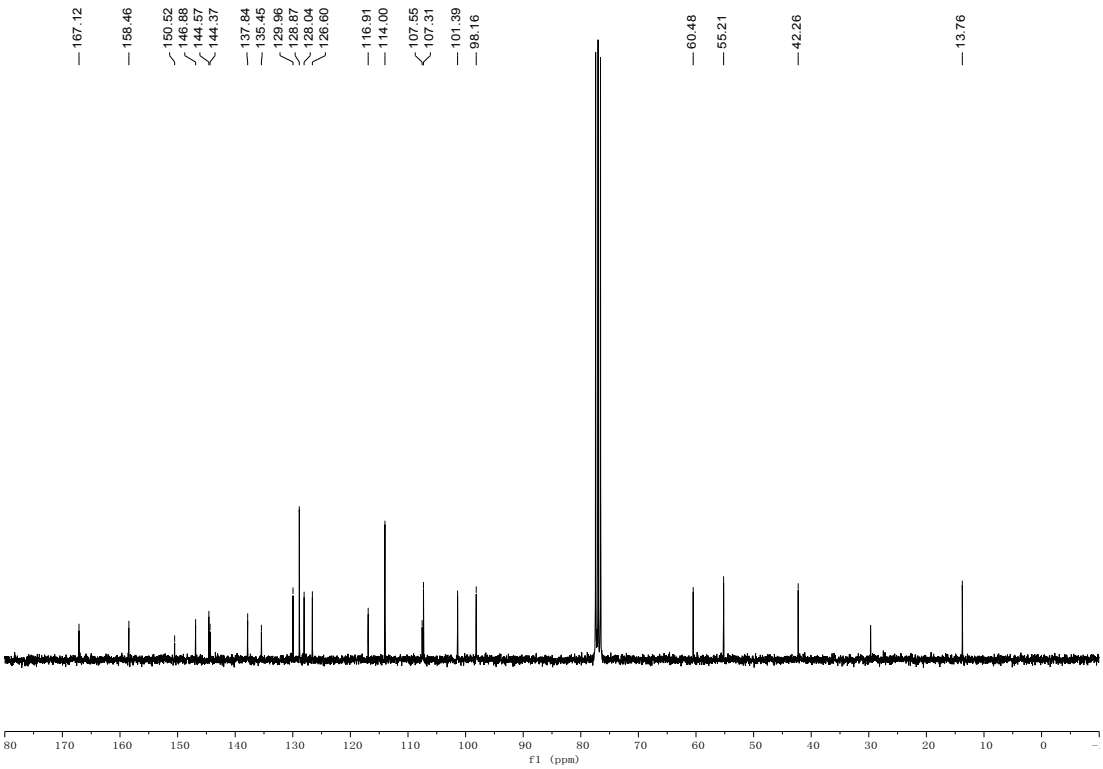
3.06
f1 (ppm)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128.87
128.04
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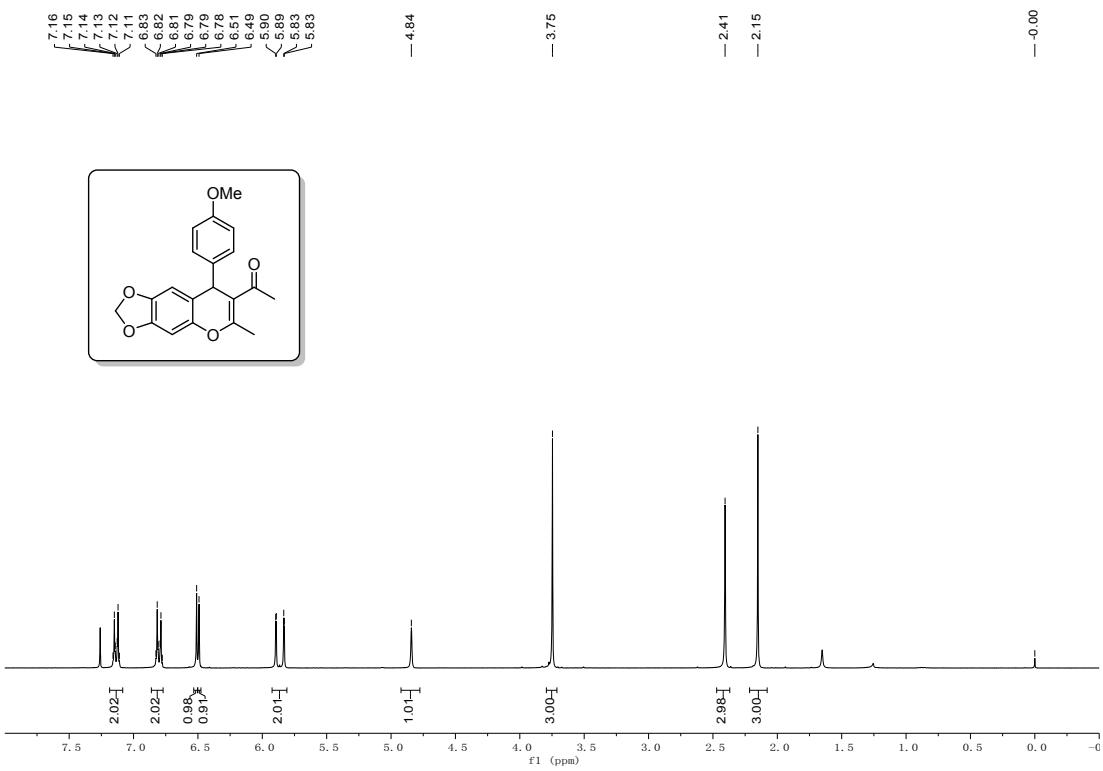
107.55
107.31
101.39
98.16
60.48
55.21
42.26
13.76
f1 (ppm)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6.79
6.78
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6.49
5.90
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5.83
5.83
4.84
3.75
2.41
2.15
0.00
OMe
O
O
O
O
2.02
2.02
0.98
0.91
2.01
1.01
3.00
2.98
3.00
7.5
7.0
6.5
6.0
5.5
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4.5
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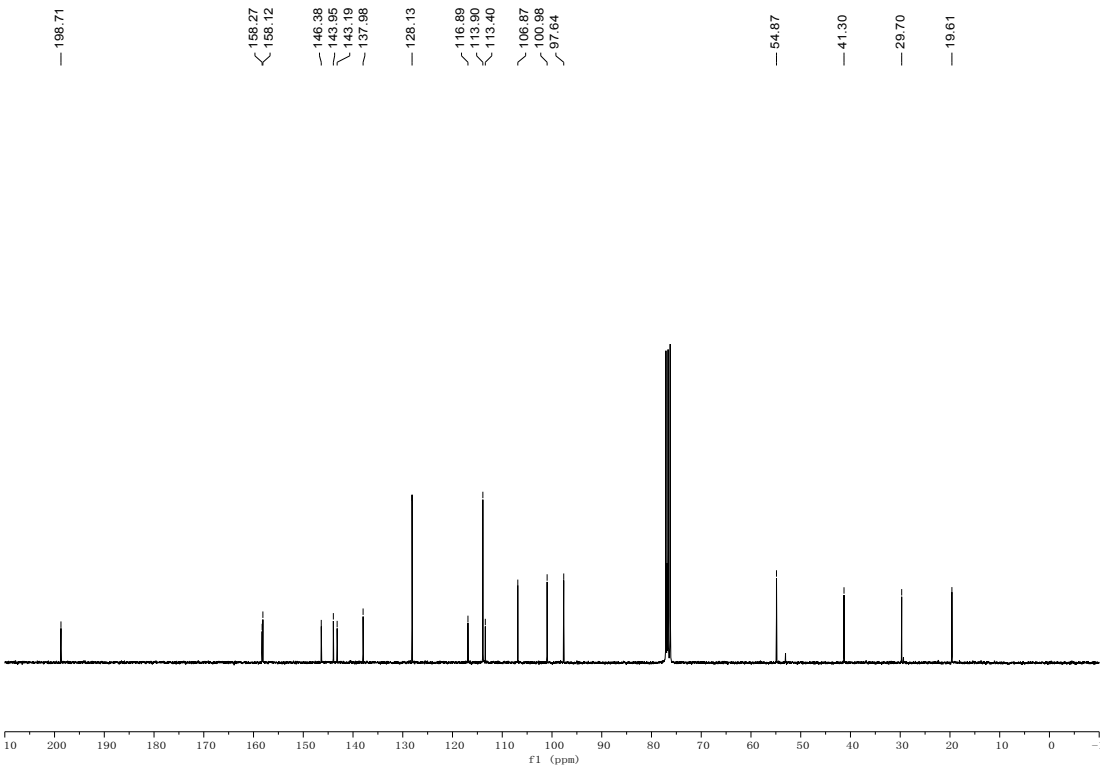
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.13
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106.87
100.98
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54.87
41.30
29.70
19.61
10
200
190
180
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160
150
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130
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100
90
80
70
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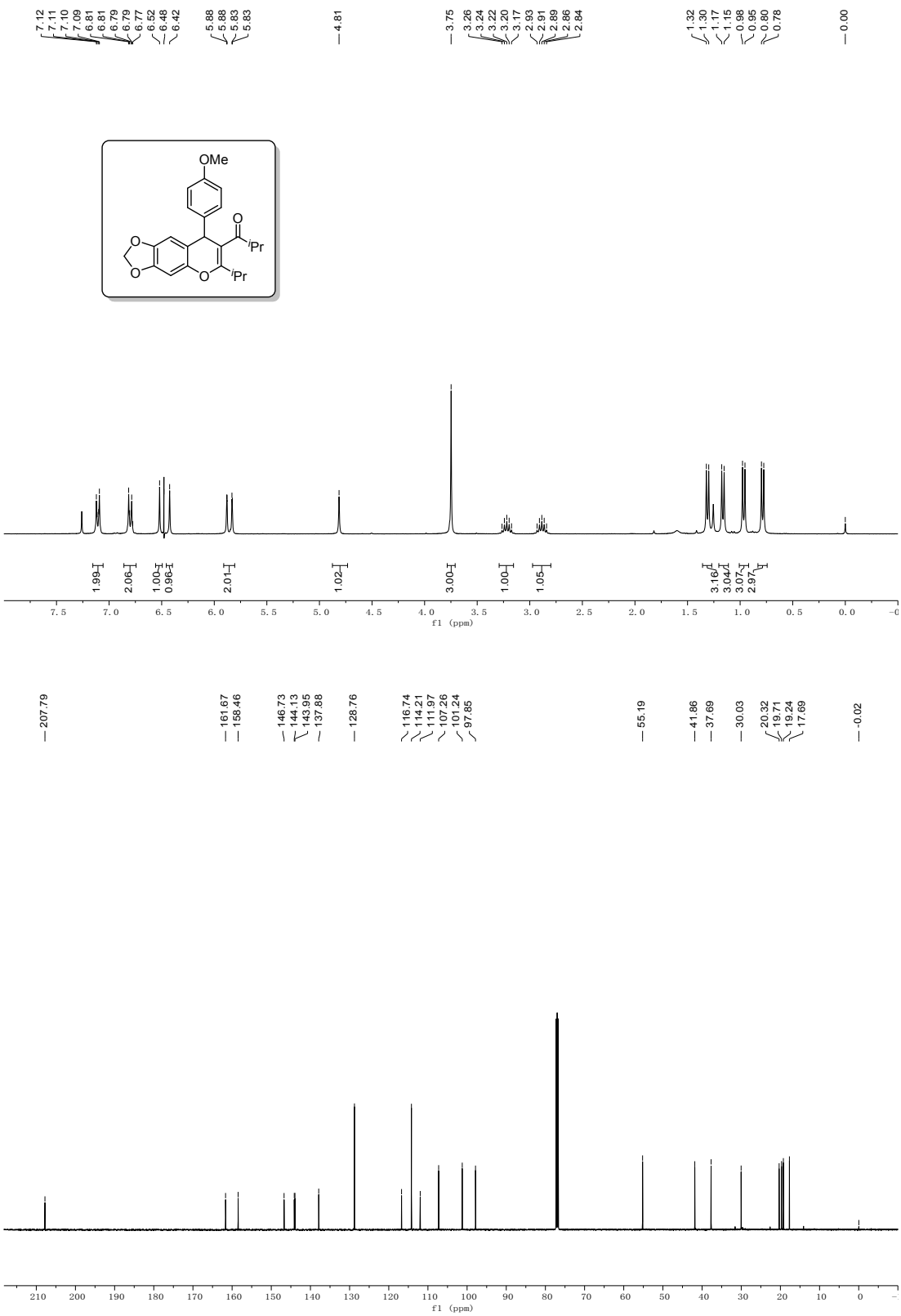
50
40
30
20
10
0
f1 (ppm)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6.77
6.52
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5.88
5.83
5.83
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3.22
3.20
3.17
2.93
2.91
2.89
2.86
2.84
1.32
1.30
1.17
1.15
0.98
0.95
0.80
0.78
0.00
OMe
O
iPr
O
O
O
iPr
1.99
2.06
1.00
0.96
2.01
1.02
3.00
1.00
1.05
3.16
3.04
3.07
2.97
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)
207.79
161.67
158.46
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114.21
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107.26
101.24
97.85
55.19
41.86
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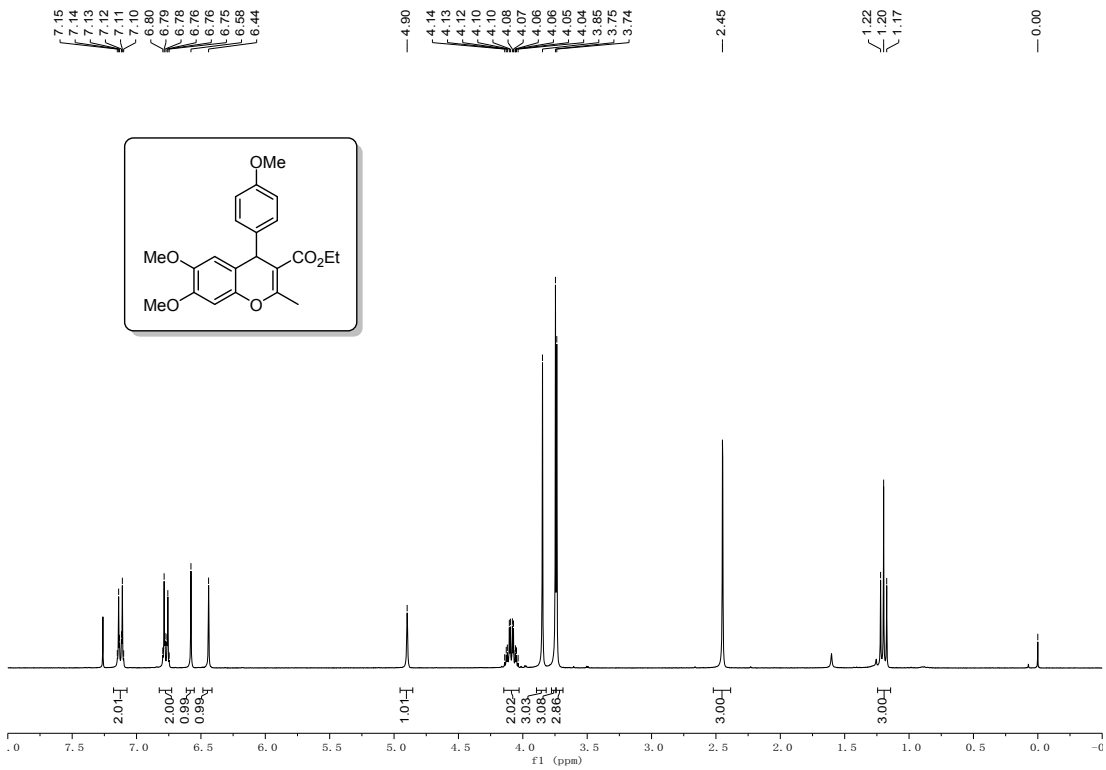
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4.12
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4.10
4.08
4.07
4.06
4.06
4.05
4.04
3.85
3.75
3.74
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1.17
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MeO
MeO
CO2Et
O
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0.99
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2.02
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3.00
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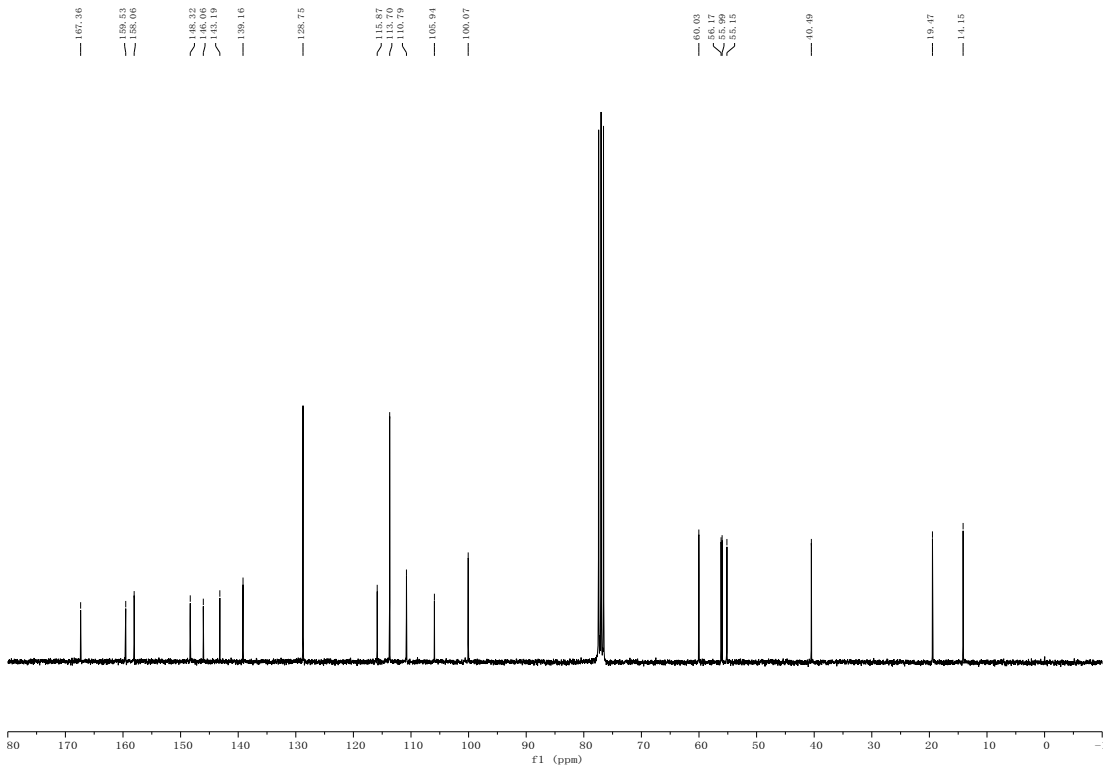
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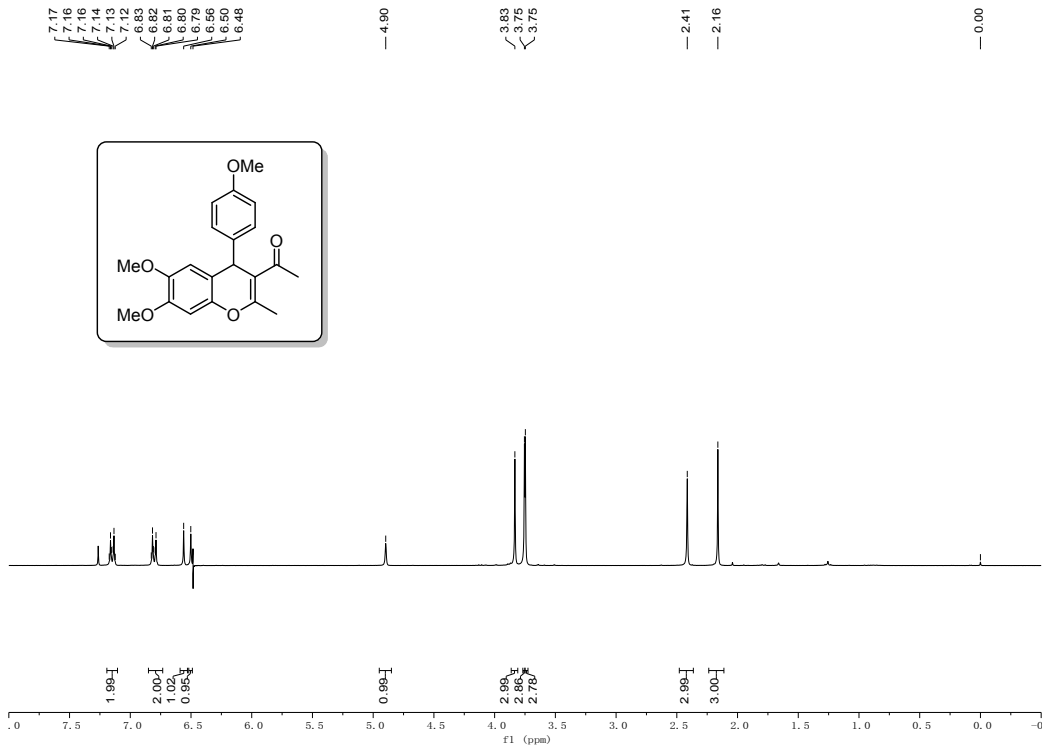
f1 (ppm)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6.48
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3.75
3.75
2.41
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0.00
OMe
MeO
MeO
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3.00
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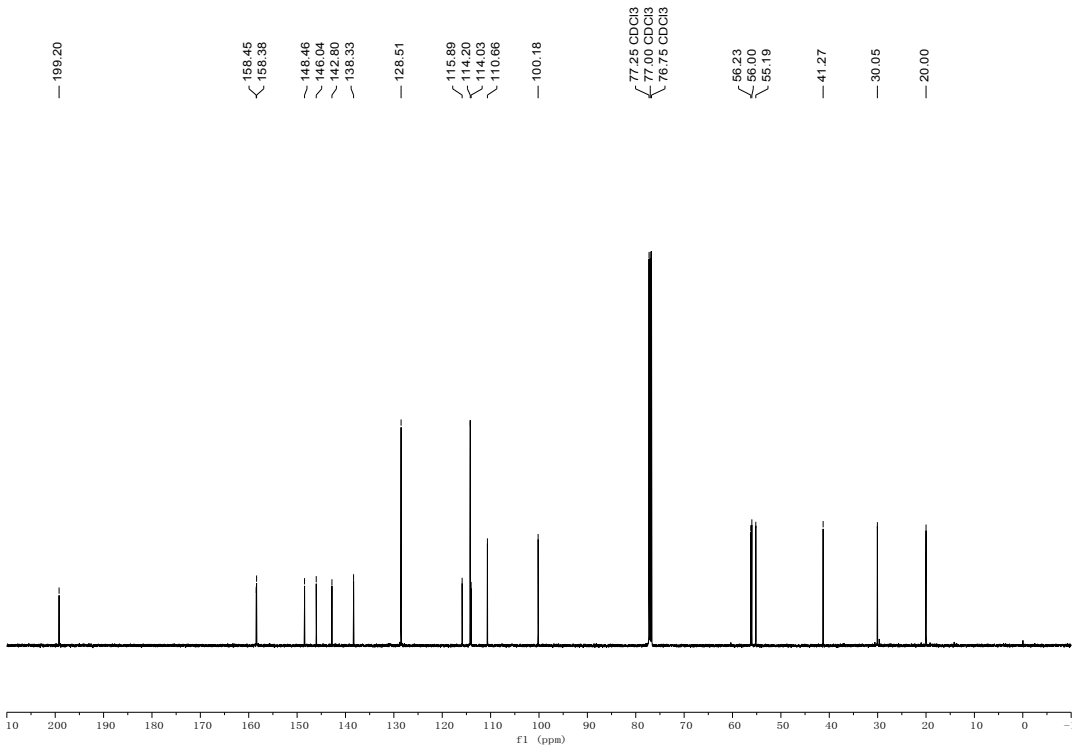
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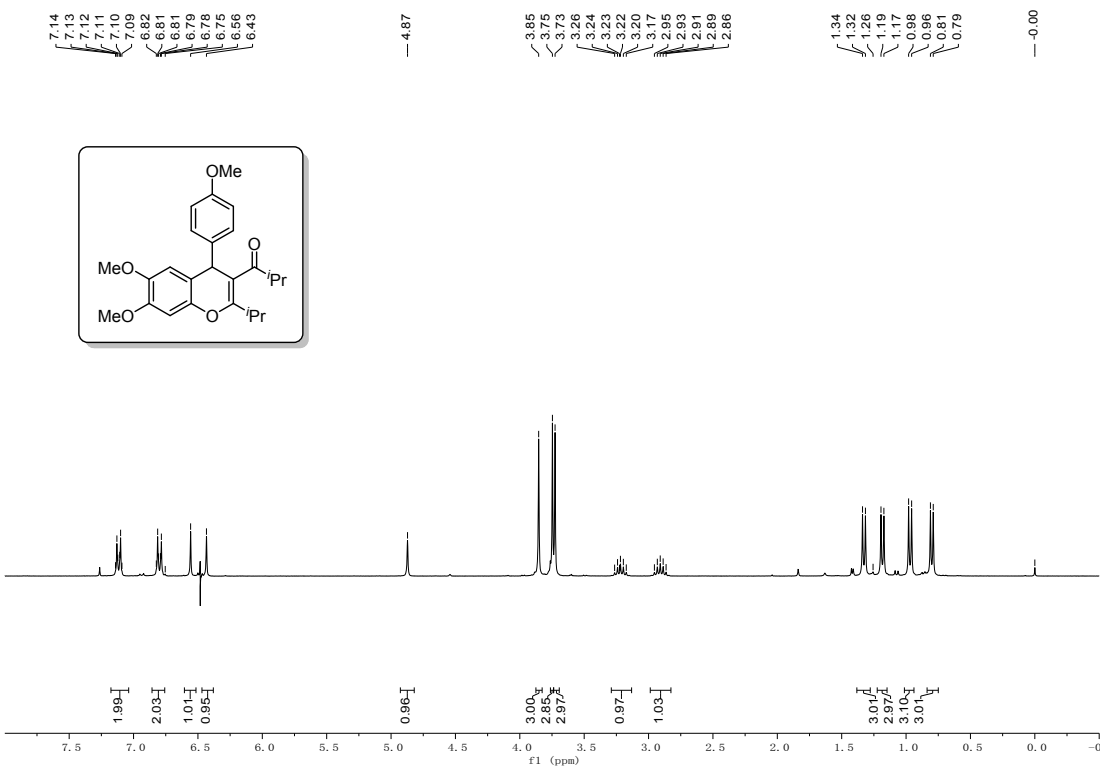
20.00
f1 (ppm)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2.91
2.89
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1.32
1.26
1.19
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0.96
0.81
0.79
0.00
OMe
MeO
MeO
O
iPr
O
iPr
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1.01
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0.96
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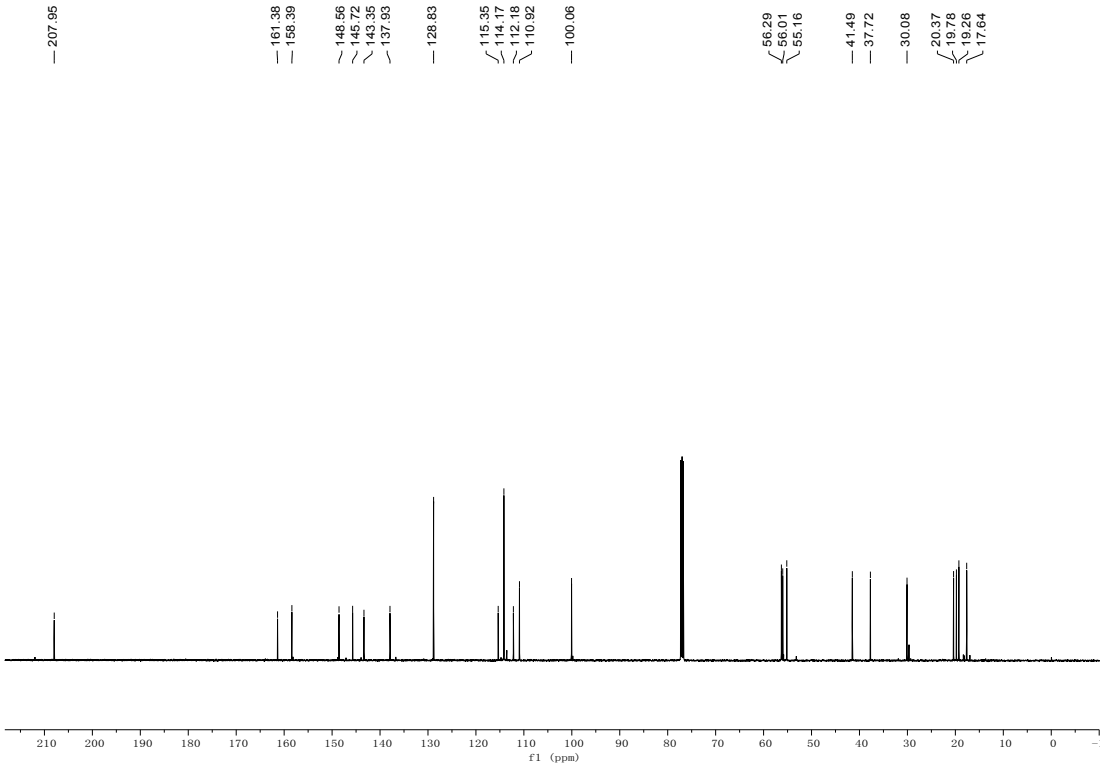
f1 (ppm)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180
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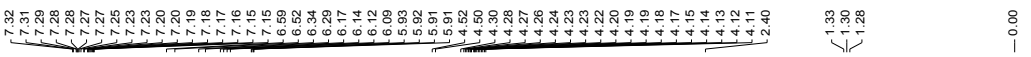
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7.17
7.16
7.15
7.15
6.59
6.52
6.34
6.29
6.17
6.14
6.12
6.09
5.93
5.92
5.91
5.91
4.52
4.50
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4.23
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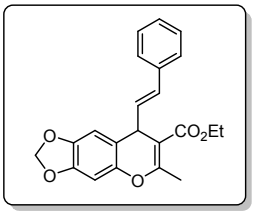
CO2Et
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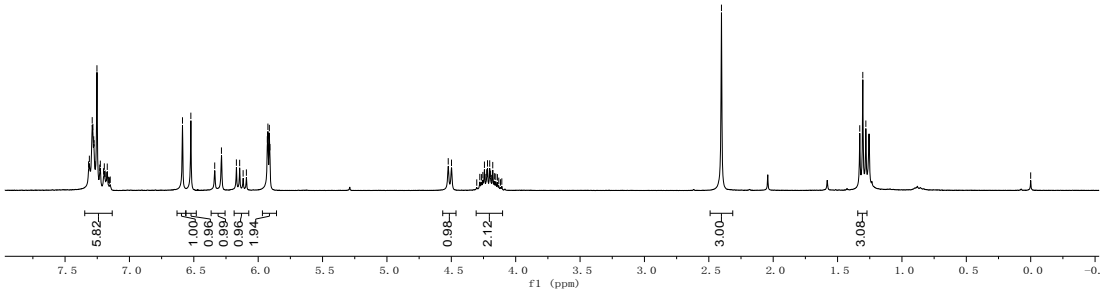
O
O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6.0
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2.0
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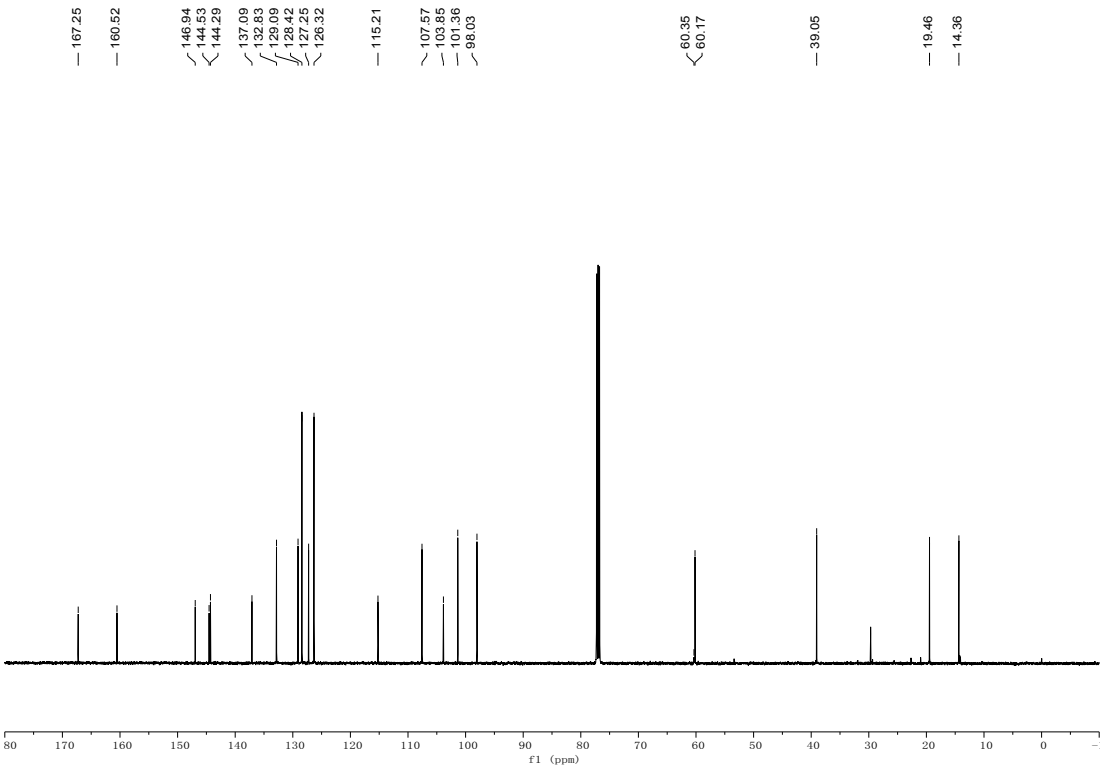
0.0
f1 (ppm)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14.36
80
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120
110
100
90
80
70
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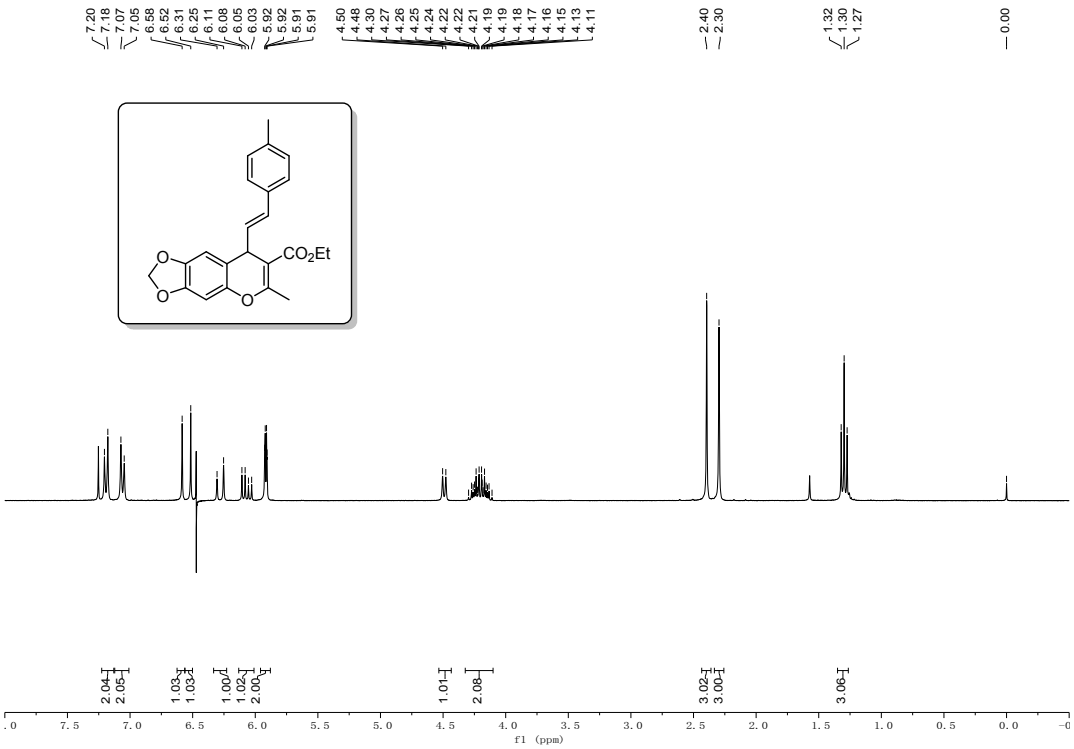
50
40
30
20
10
0
f1 (ppm)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6.03
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5.92
5.91
5.91
5.91
4.50
4.48
4.30
4.27
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4.25
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4.22
4.21
4.19
4.19
4.18
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4.16
4.15
4.13
4.11
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2.30
1.32
1.30
1.27
0.00
CO2Et
O
O
O
2.04
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1.03
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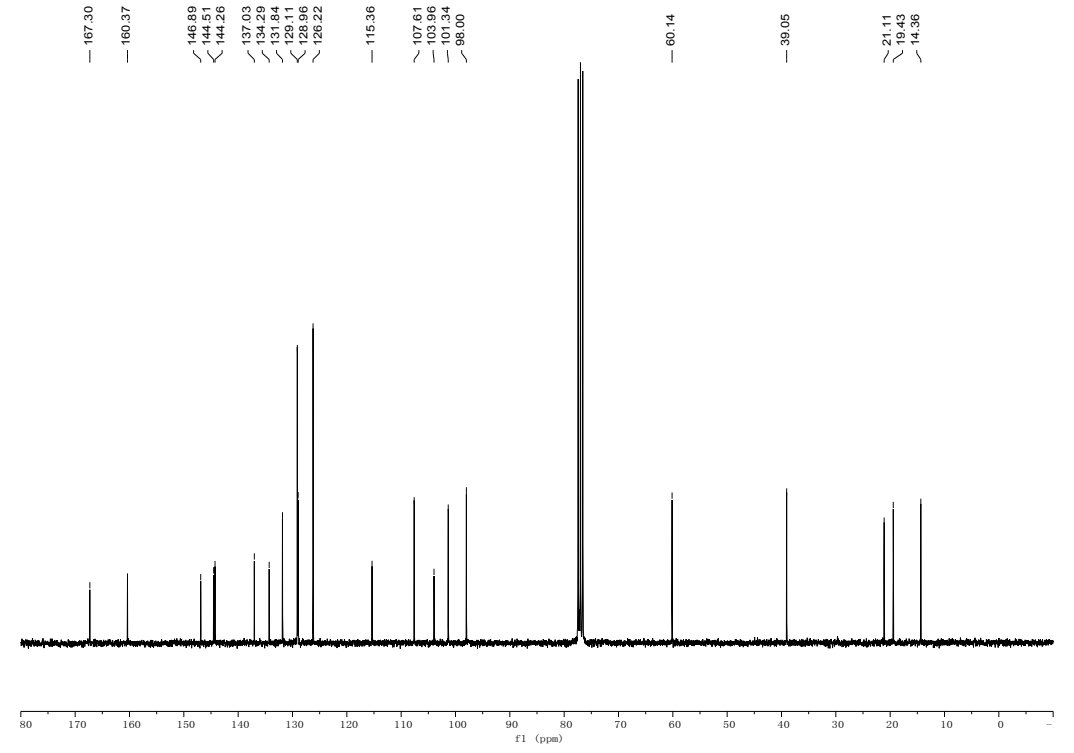
1.00
1.02
2.00
1.01
2.08
3.02
3.00
3.06
f1 (ppm)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39.05
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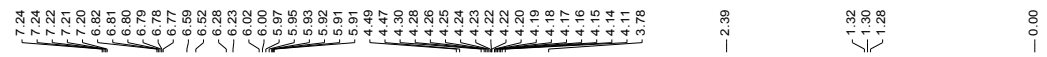
19.43
14.36
f1 (ppm)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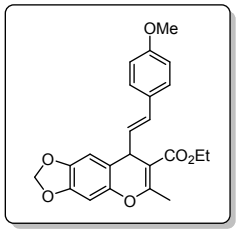
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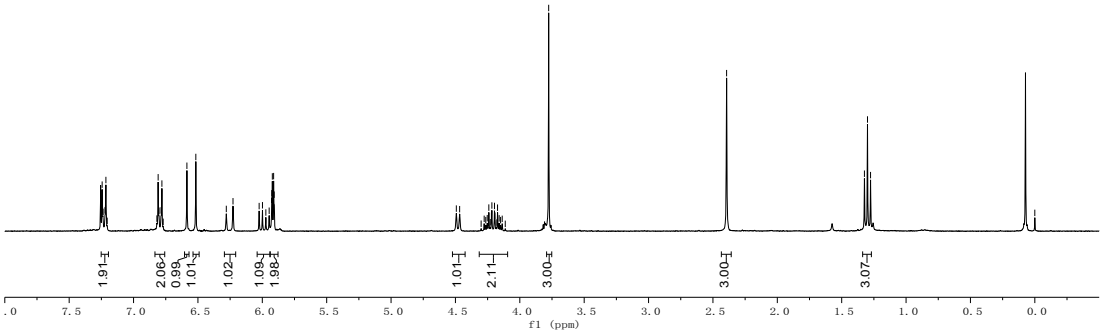
CO2Et
O
O
O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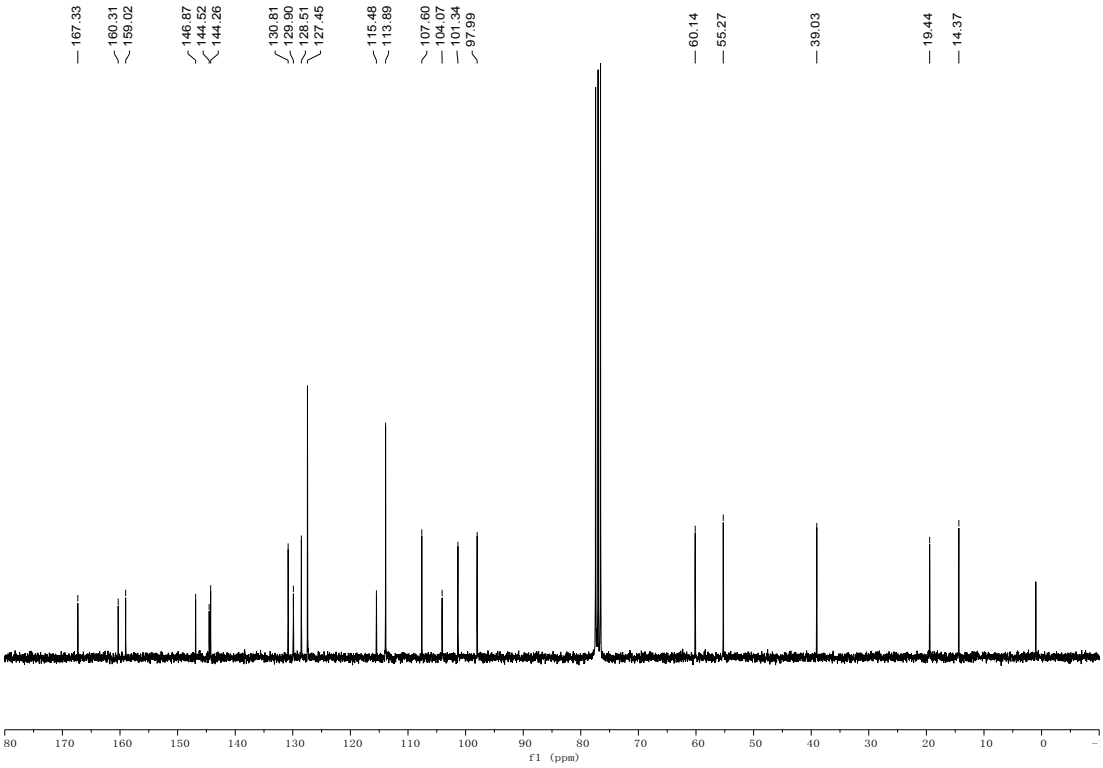
3.07
f1 (ppm)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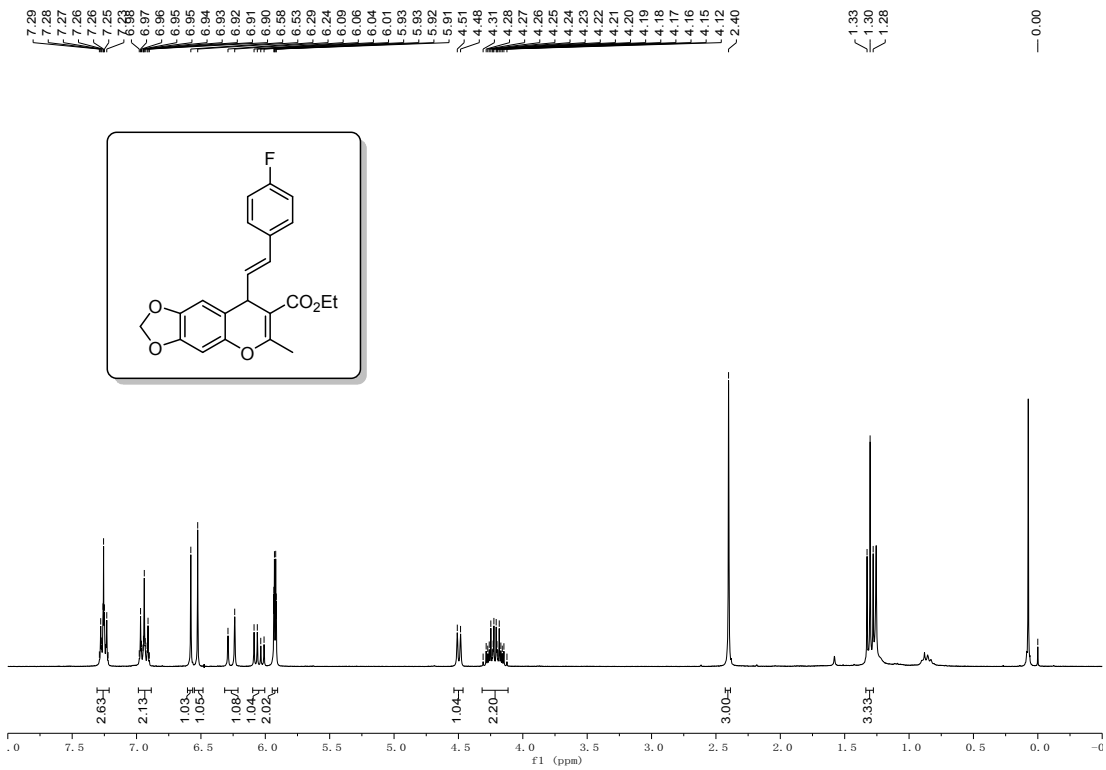
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1.28
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F
CO2Et
O
O
O
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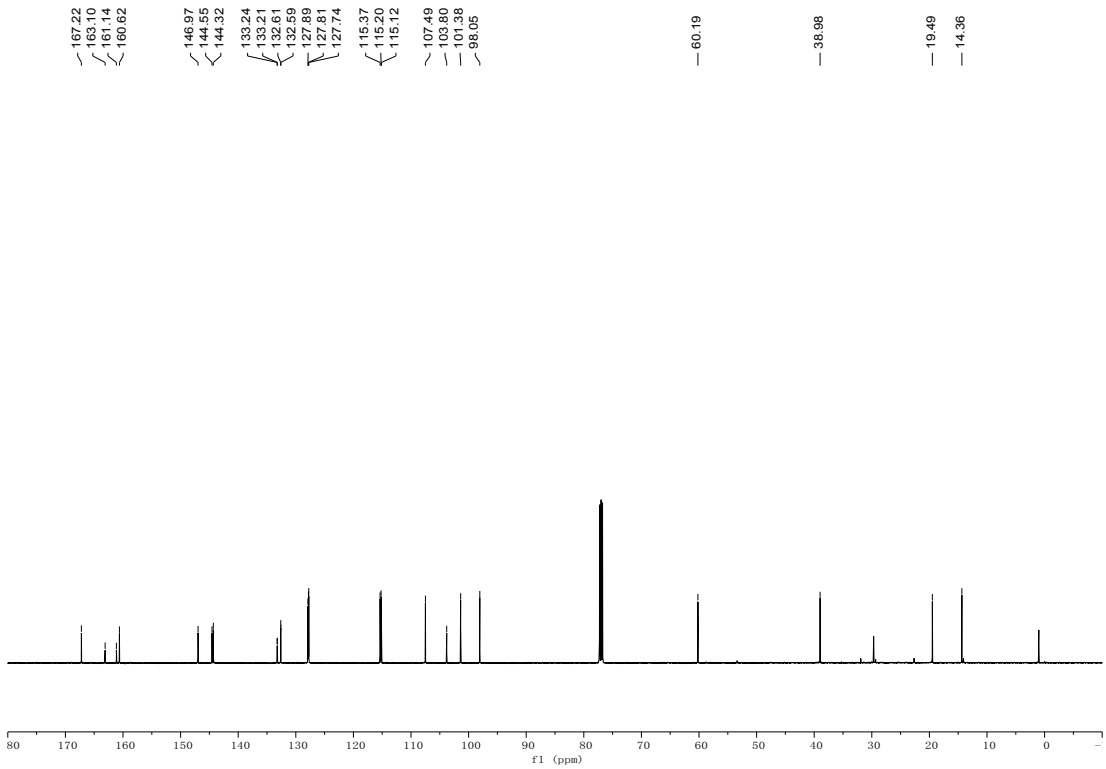
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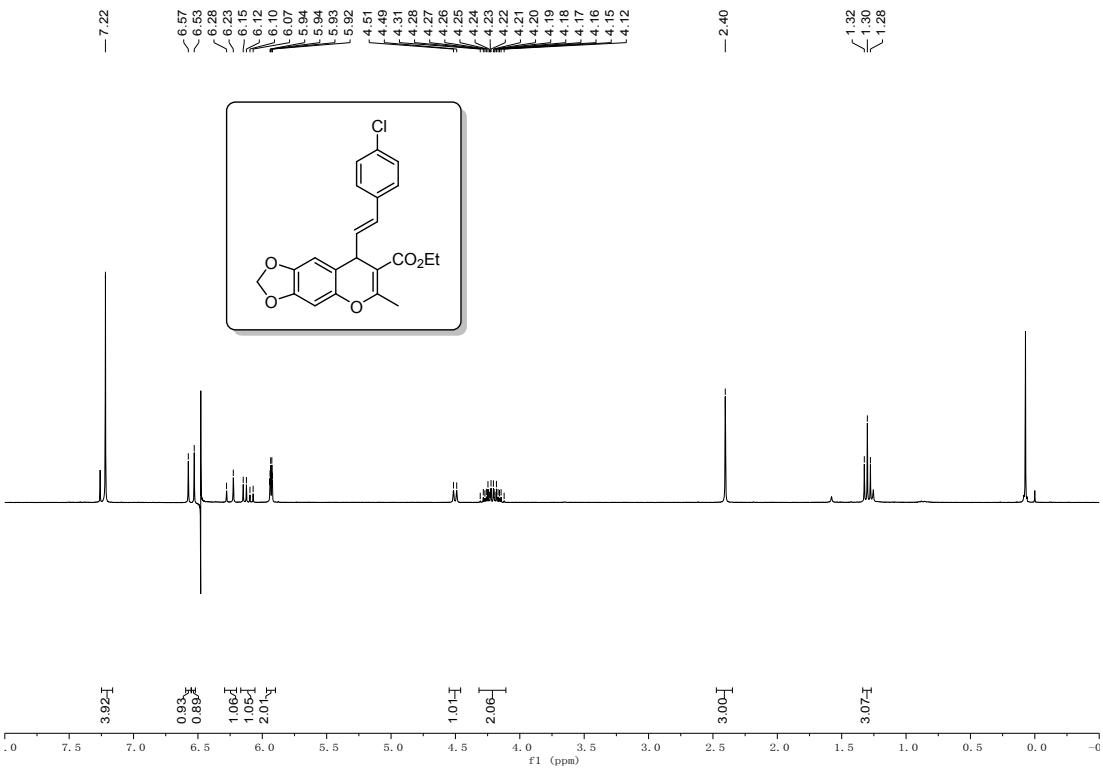
f1 (ppm)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4.19
4.18
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4.15
4.12
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1.30
1.28
Cl
CO2Et
O
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1.05
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2.06
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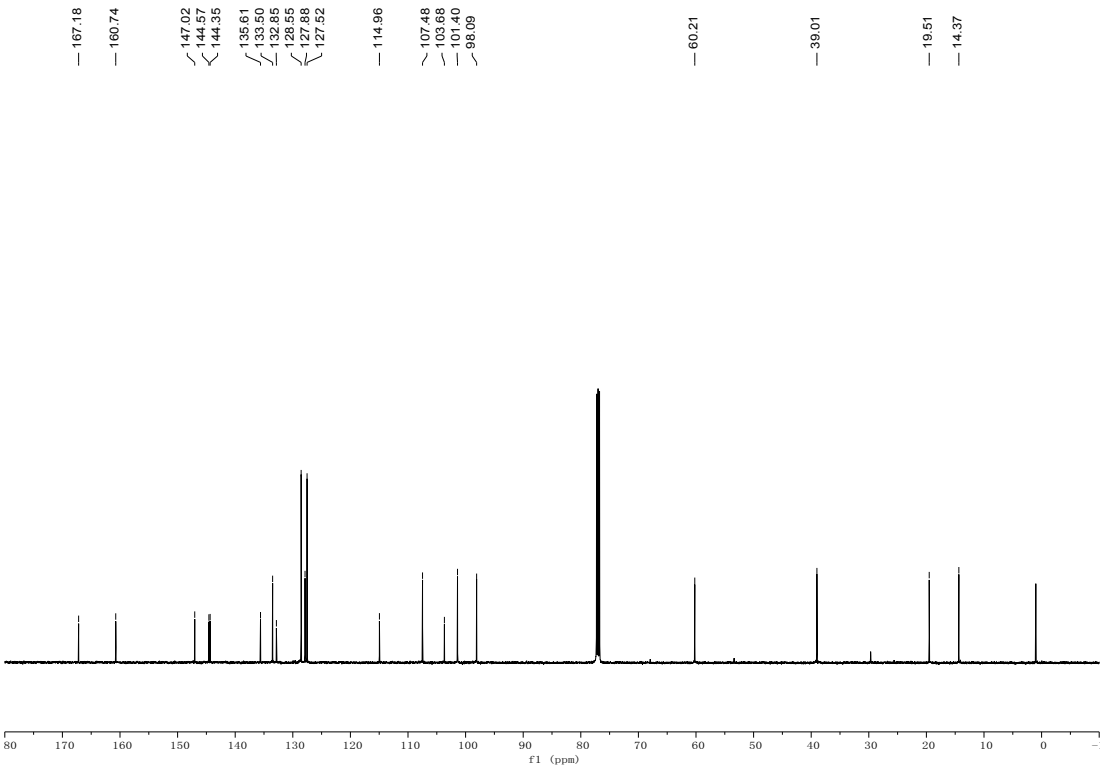
f1 (ppm)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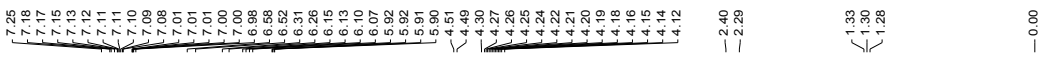
f1 (ppm)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7.00
7.00
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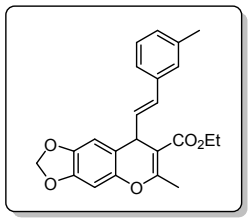
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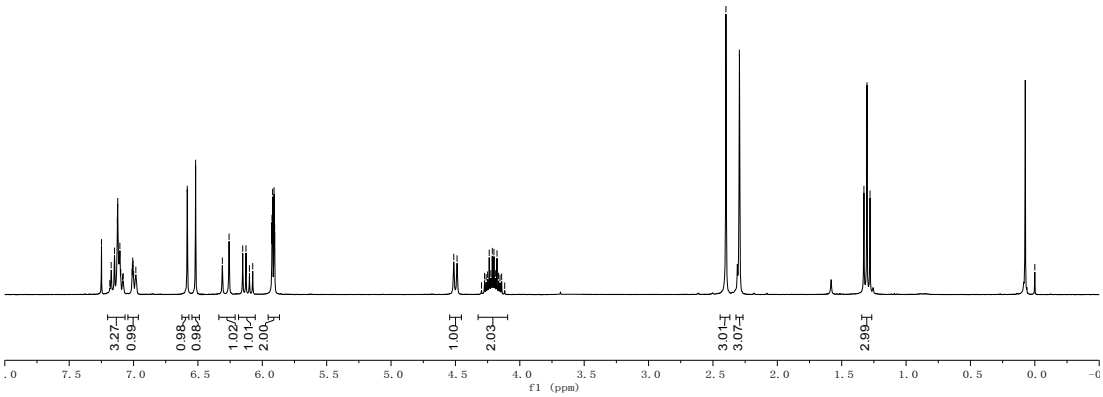
O
CO2Et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2.99
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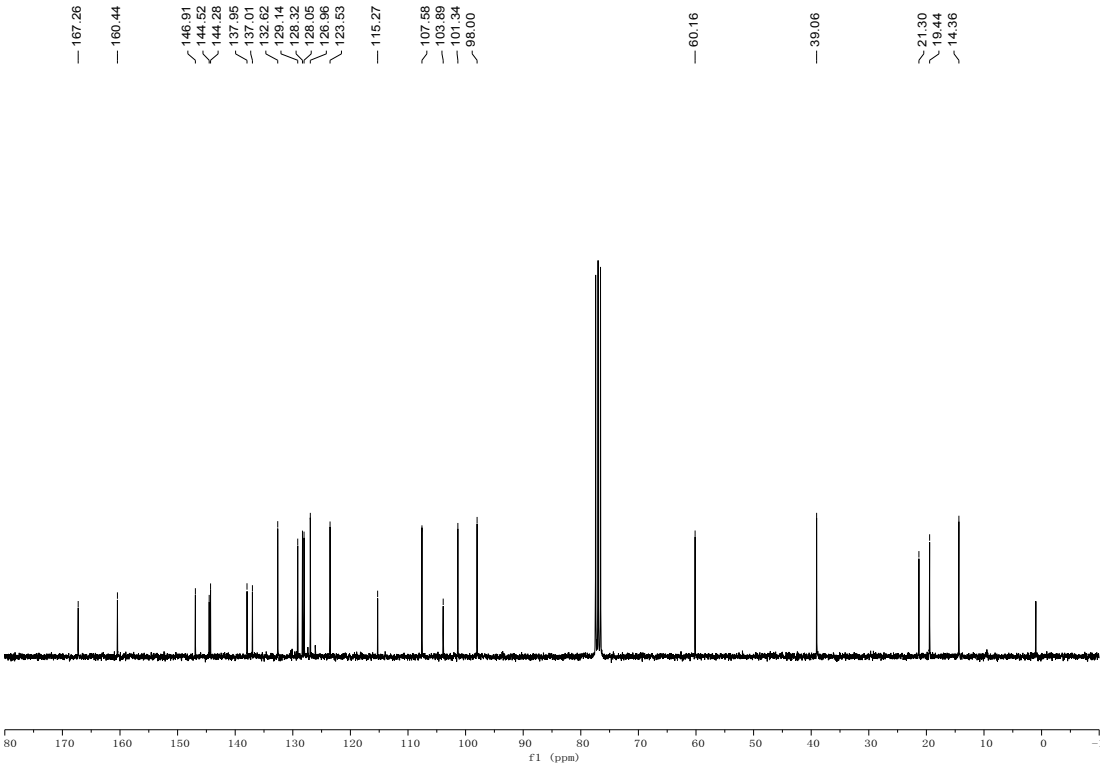
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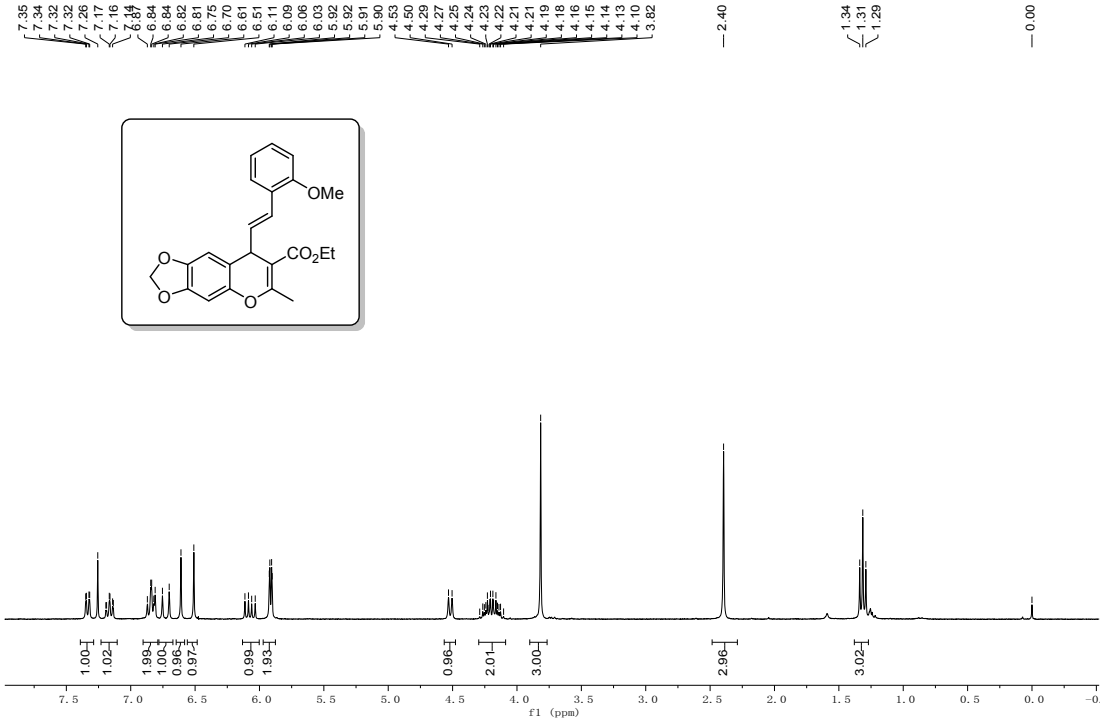
14.36
f1 (ppm)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CO2Et
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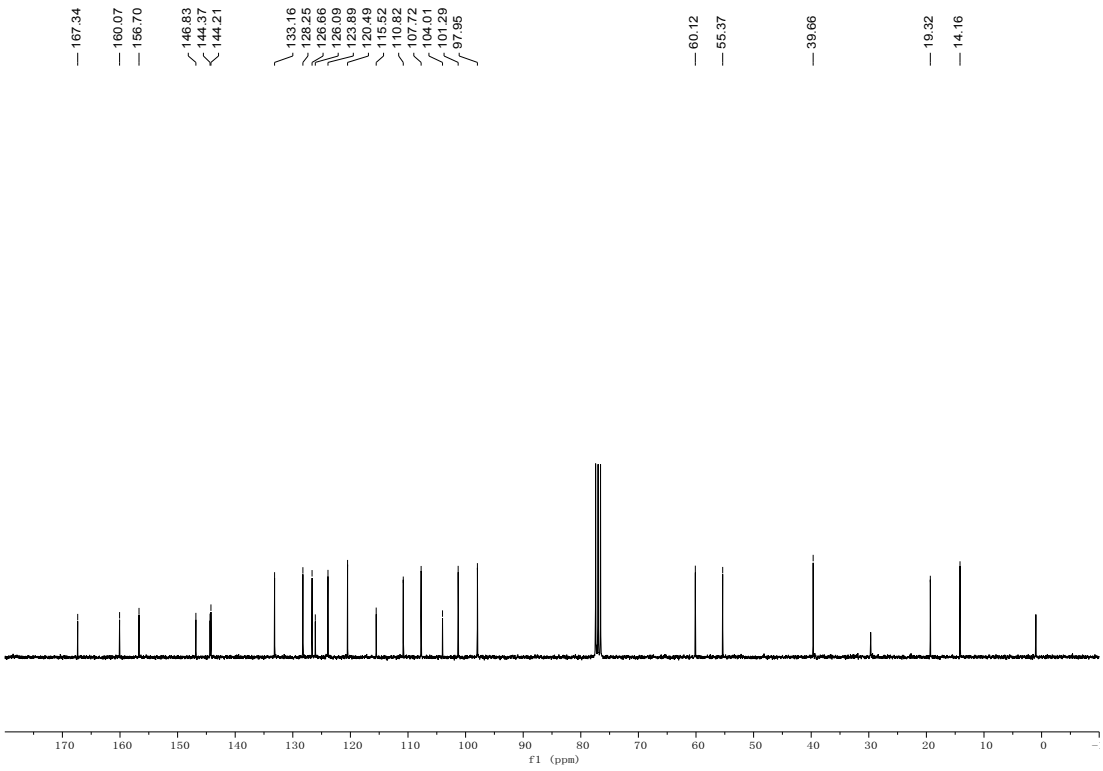
f1 (ppm)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60
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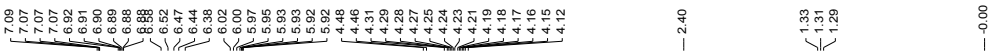
40
30
20
10
0
f1 (ppm)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7.07
7.07
7.07
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6.90
6.89
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6.88
6.52
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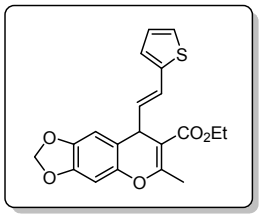
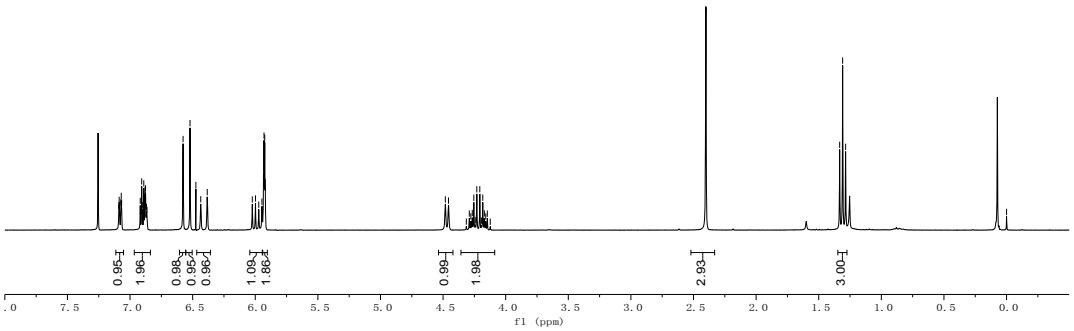
6.44
6.38
6.02
6.00
5.97
5.95
5.93
5.93
5.92
5.92
4.48
4.46
4.31
4.29
4.28
4.27
4.25
4.24
4.23
4.21
4.19
4.18
4.17
4.16
4.15
4.12
2.40
1.33
1.31
1.29
0.00


S
CO2Et
O
O
O
O


0.95
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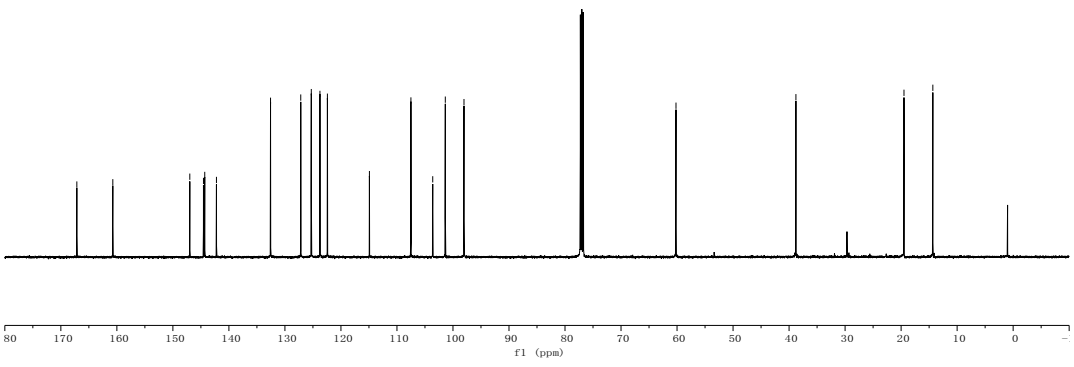
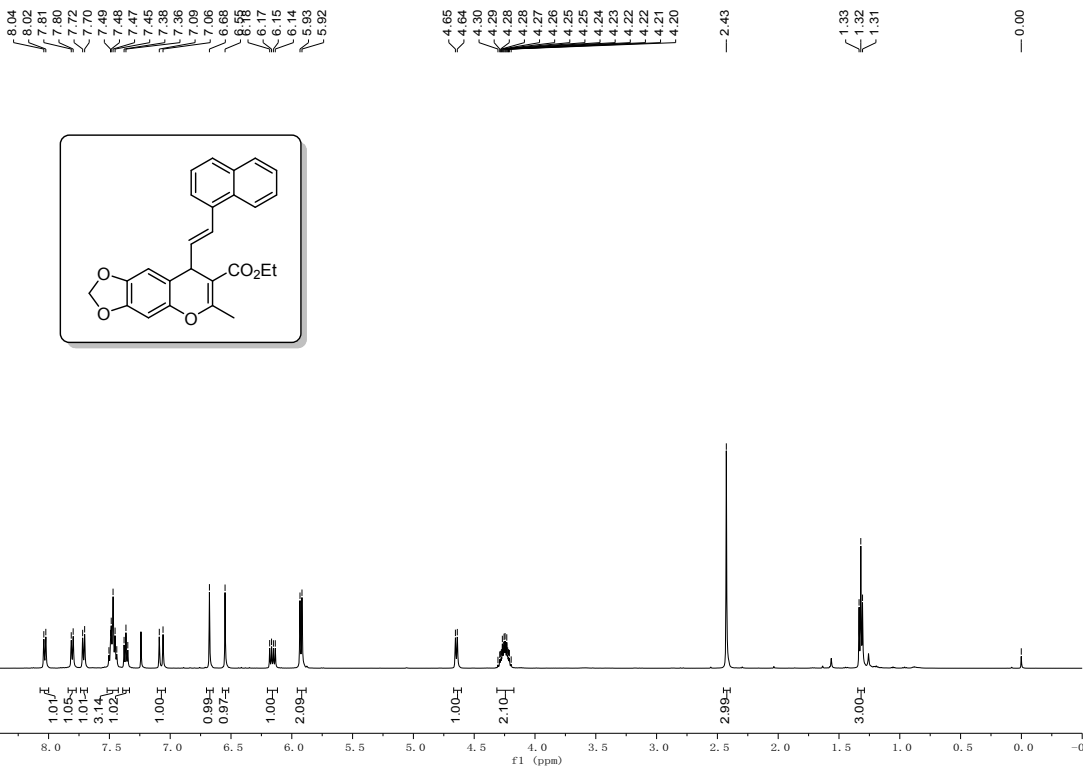
0.98
0.95
0.96
1.09
1.86
0.99
1.98
2.93
3.00
f1 (ppm)


167.15
160.72
146.98
144.54
144.31
142.22
132.57
127.17
125.29
123.75
122.41
114.91
107.51
103.61
101.37
98.03
60.19
38.78
19.49
14.34


f1 (ppm)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8.02
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7.80
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7.70
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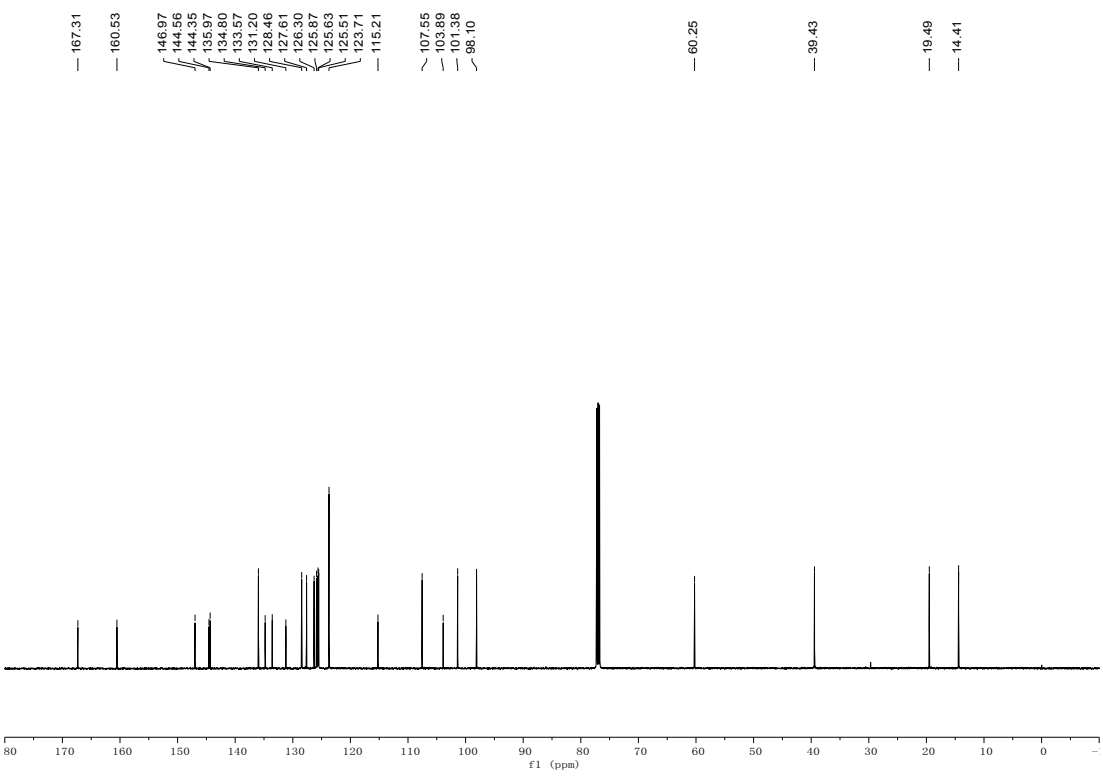
7.48
7.47
7.45
7.38
7.36
7.09
7.06
6.68
6.55
6.18
6.17
6.15
6.14
5.93
5.92
4.65
4.64
4.30
4.29
4.28
4.28
4.27
4.26
4.25
4.25
4.24
4.23
4.22
4.22
4.21
4.20
2.43
1.33
1.32
1.31
0.00
CO2Et
O
O
O
1.01
1.05
1.01
3.14
1.02
1.00
0.99
0.97
1.00
2.09
1.00
2.10
2.99
3.00
f1 (ppm)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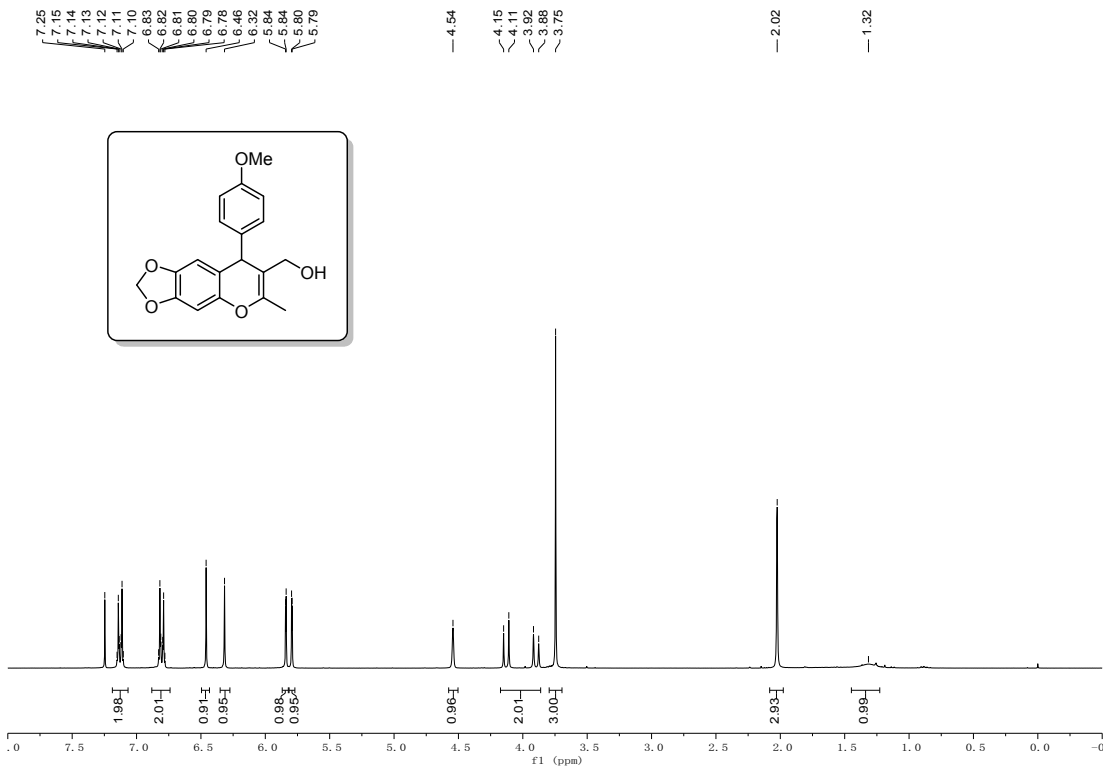
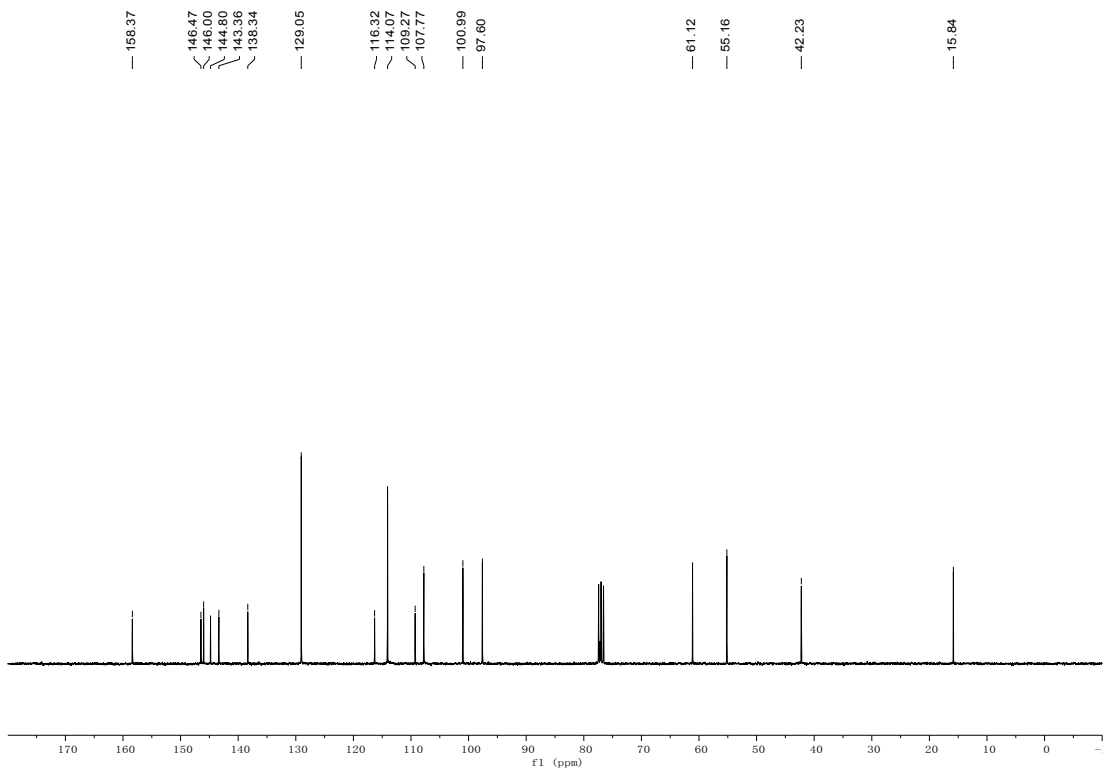
135.97
134.80
133.57
131.20
128.46
127.61
126.30
125.87
125.63
125.51
123.71
115.21
107.55
103.89
101.38
98.10
60.25
39.43
19.49
14.41
f1 (ppm)


7.25
7.15
7.14
7.13
7.12
7.11
7.10
6.83
6.82
6.81
6.80
6.79
6.78
6.46
6.32
5.84
5.84
5.80
5.79
4.54
4.15
4.11
3.92
3.88
3.75
2.02
1.32
OMe
OH
O
O
O
1.98
2.01
0.91
0.95
0.98
0.95
0.96
2.01
3.00
2.93
0.99
f1 (ppm)


158.37
146.47
146.00
144.80
143.36
138.34
129.05
116.32
114.07
109.27
107.77
100.99
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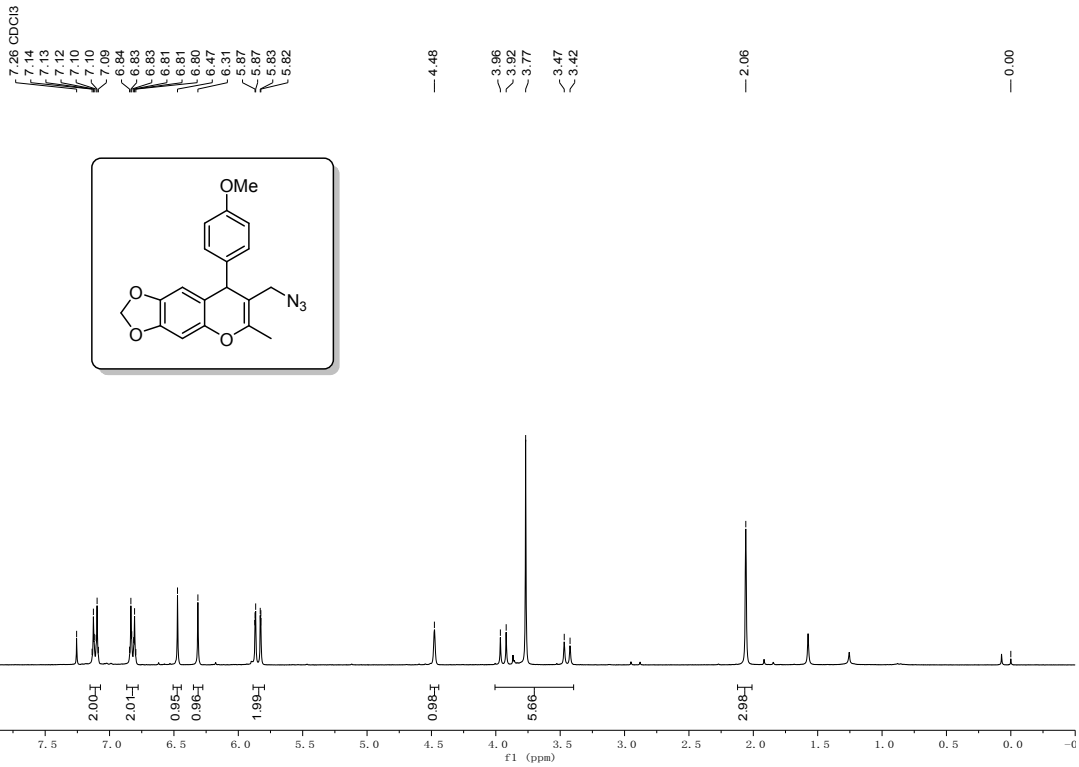
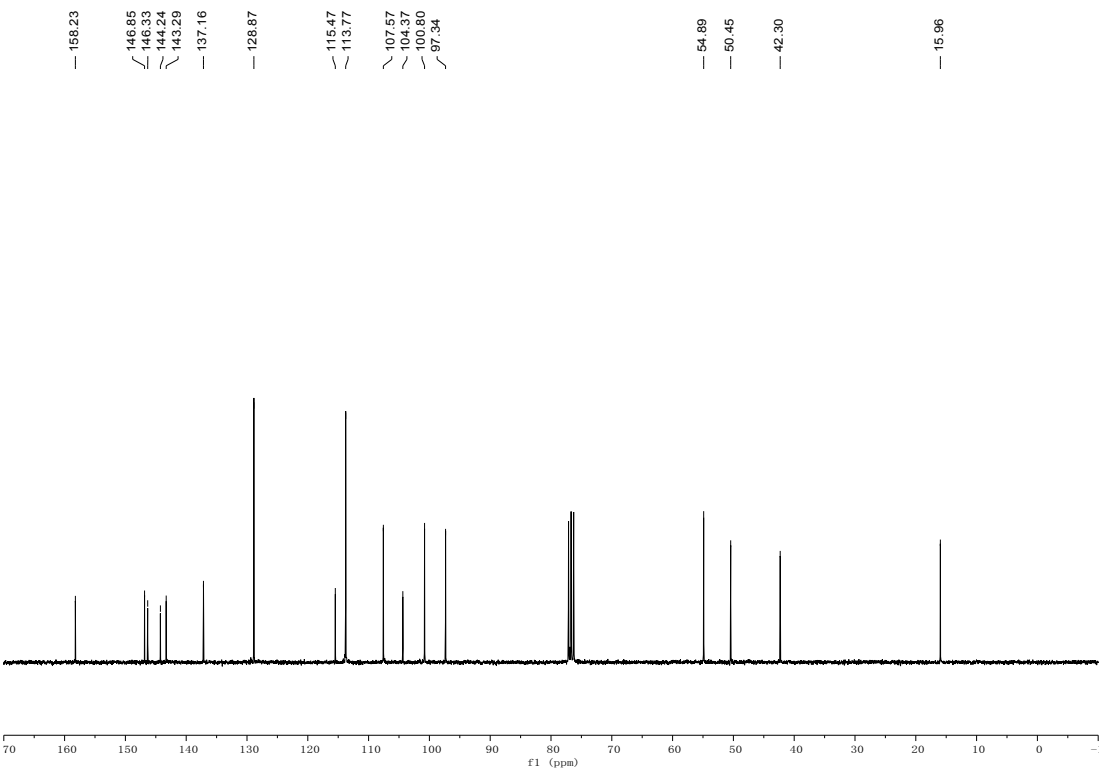
61.12
55.16
42.23
15.84
f1 (ppm)


7.26 CDCl3
7.14
7.13
7.12
7.10
7.10
7.09
6.84
6.83
6.83
6.81
6.81
6.80
6.47
6.31
5.87
5.87
5.83
5.82
4.48
3.96
3.92
3.77
3.47
3.42
2.06
0.00
OMe
N3
O
O
O
2.00
2.01
0.95
0.96
1.99
0.98
5.66
2.98
f1 (ppm)


158.23
146.85
146.33
144.24
143.29
137.16
128.87
115.47
113.77
107.57
104.37
100.80
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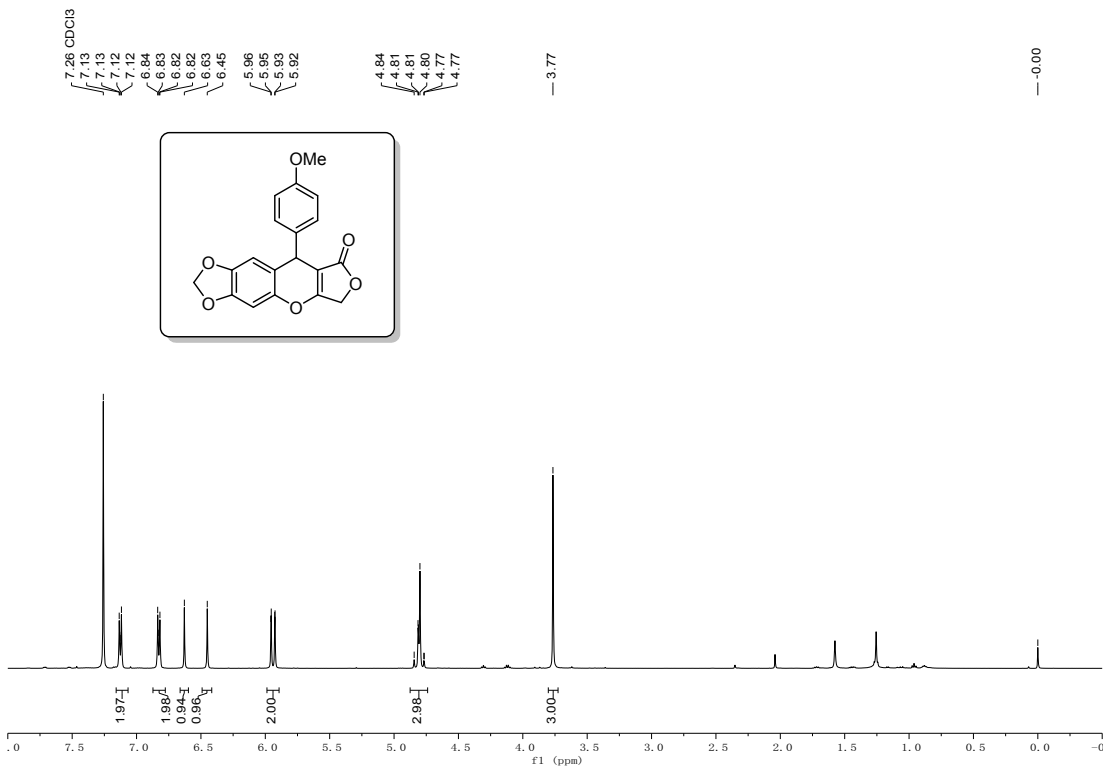
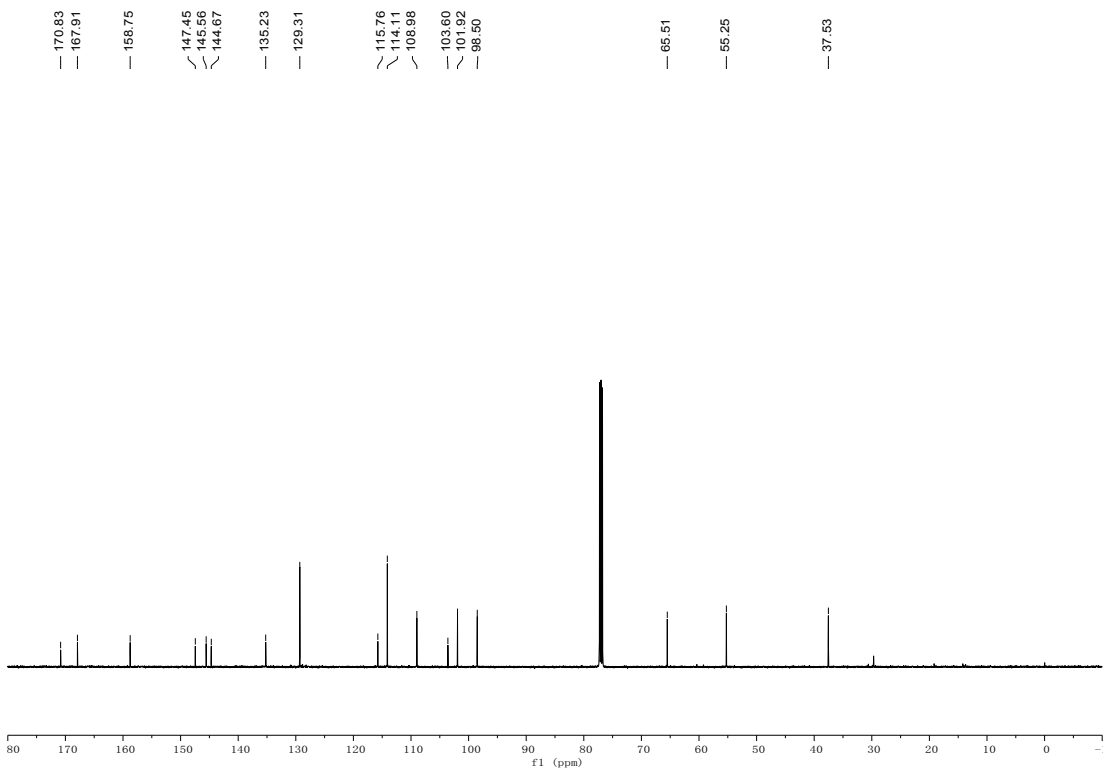
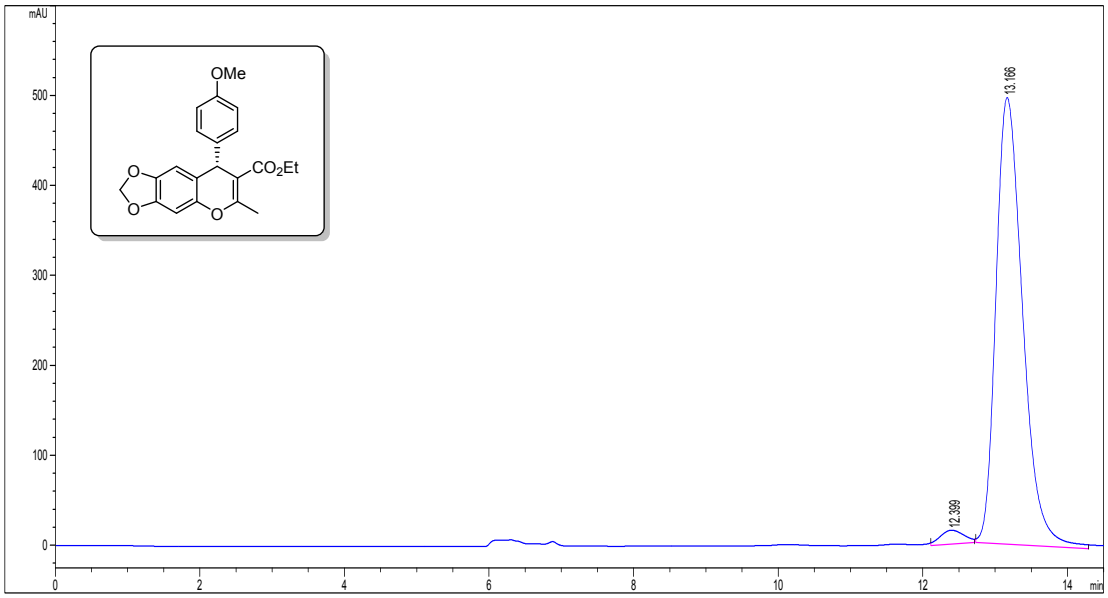
54.89
50.45
42.30
15.96
f1 (ppm)


7.26 CDCl3
7.13
7.13
7.12
7.12
6.84
6.83
6.82
6.82
6.63
6.45
5.96
5.95
5.93
5.92
4.84
4.81
4.81
4.80
4.77
4.77
3.77
0.00
OMe
O
O
O
O
O
1.97
1.98
0.94
0.96
2.00
2.98
3.00
f1 (ppm)

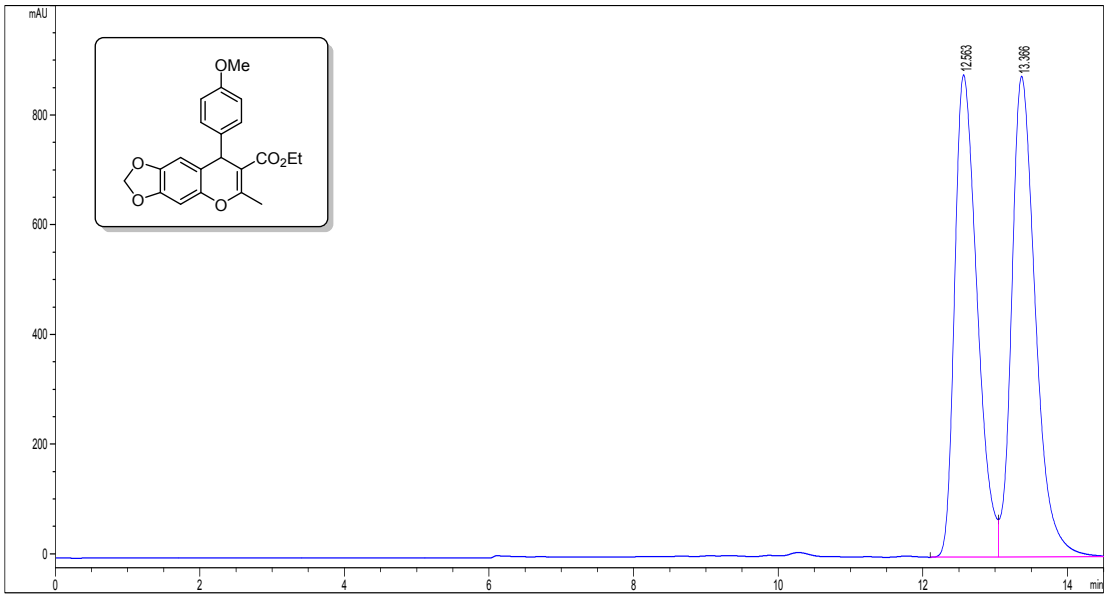

170.83
167.91
158.75
147.45
145.56
144.67
135.23
129.31
115.76
114.11
108.98
103.60
101.92
98.50
65.51
55.25
37.53
f1 (ppm)

6. HPLC Charts of the Products

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95 : 5, 0.5 mL/min, 254 nm; t (major) = 13.17 min, t (minor) = 12.40 min; 95% ee.

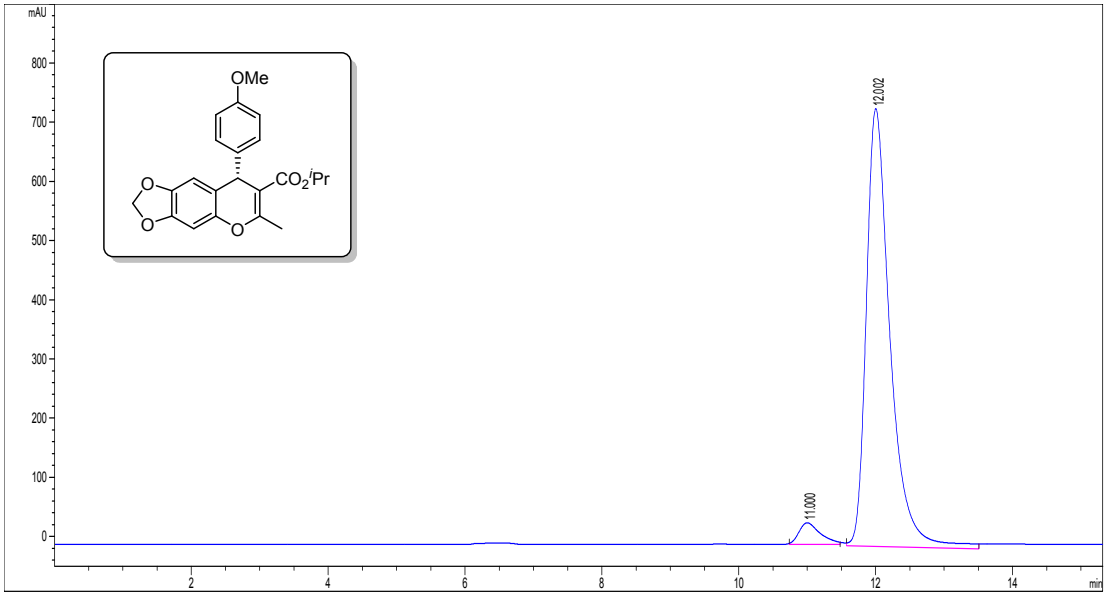


#	Time	Width	Area	Height	Area%
1	12.399	0.3820	351.1434	15.3221	2.6849
2	13.166	0.4273	1.2728e4	496.4596	97.3151

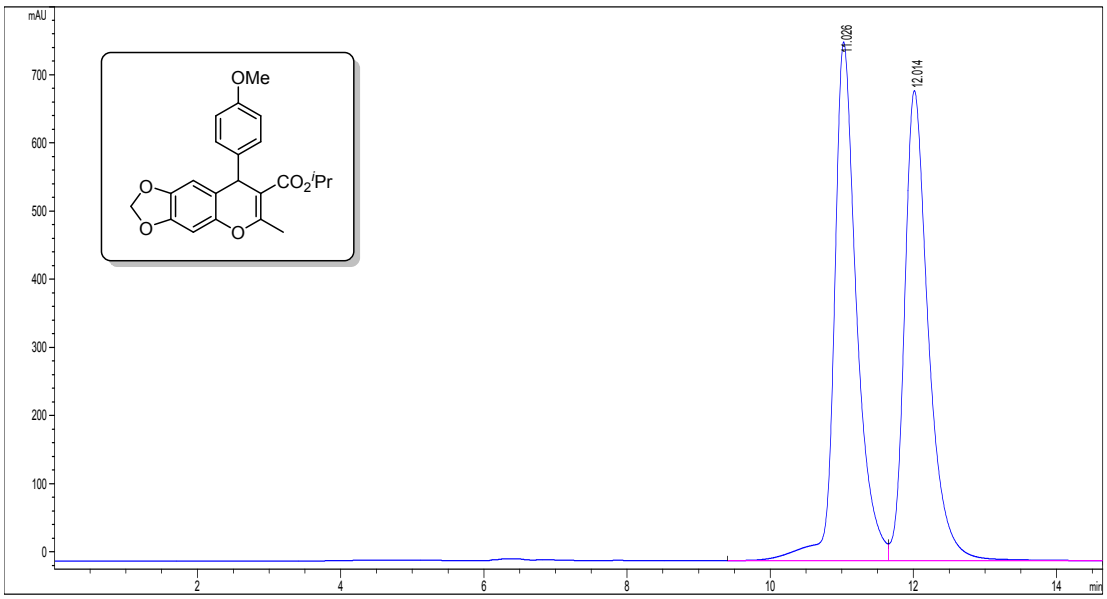


#	Time	Width	Area	Height	Area%
1	12.563	0.3361	1.8916e4	879.0369	48.6307
2	13.366	0.3511	1.9982e4	876.1941	51.3693

Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 12.00 min, t (minor) = 11.00 min; 91% ee.

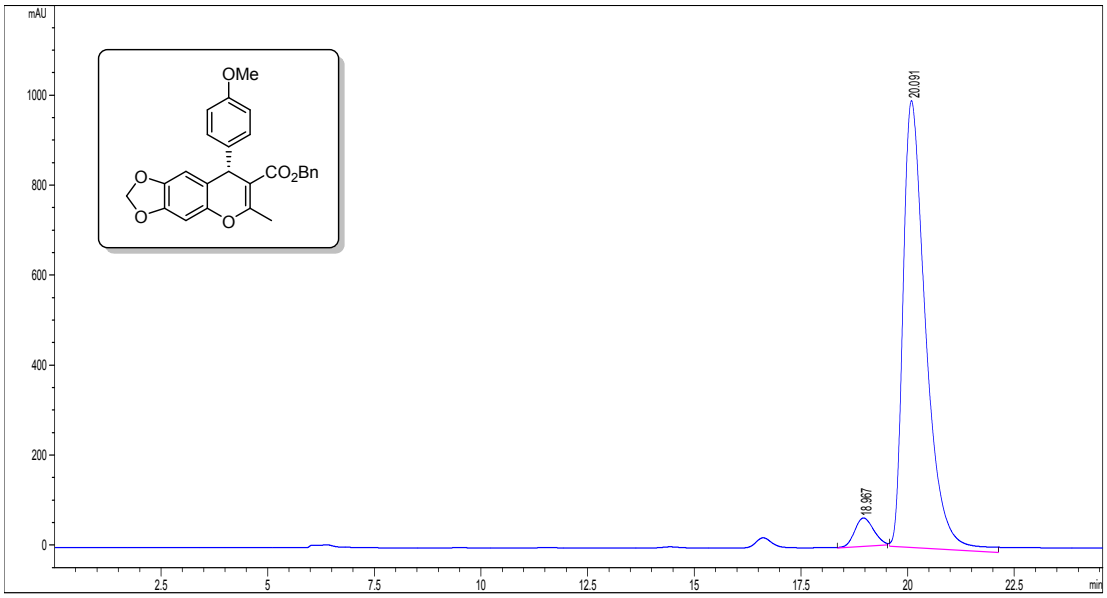


#	Time	Width	Area	Height	Area%
1	11.000	0.3628	791.7634	36.3748	4.2421
2	12.002	0.4026	1.7873e4	739.8320	95.7579

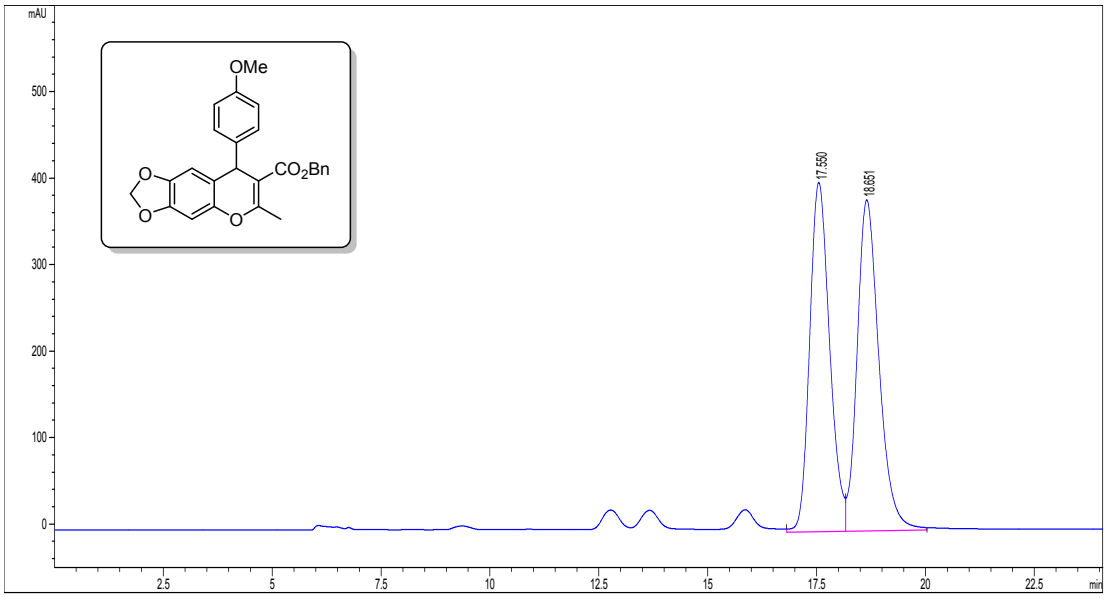


#	Time	Width	Area	Height	Area%
1	11.026	0.3214	1.6534e4	761.1704	50.8697
2	12.014	0.3471	1.5968e4	689.7336	49.1303

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 20.09 min, t (minor) = 18.97 min; 90% ee.

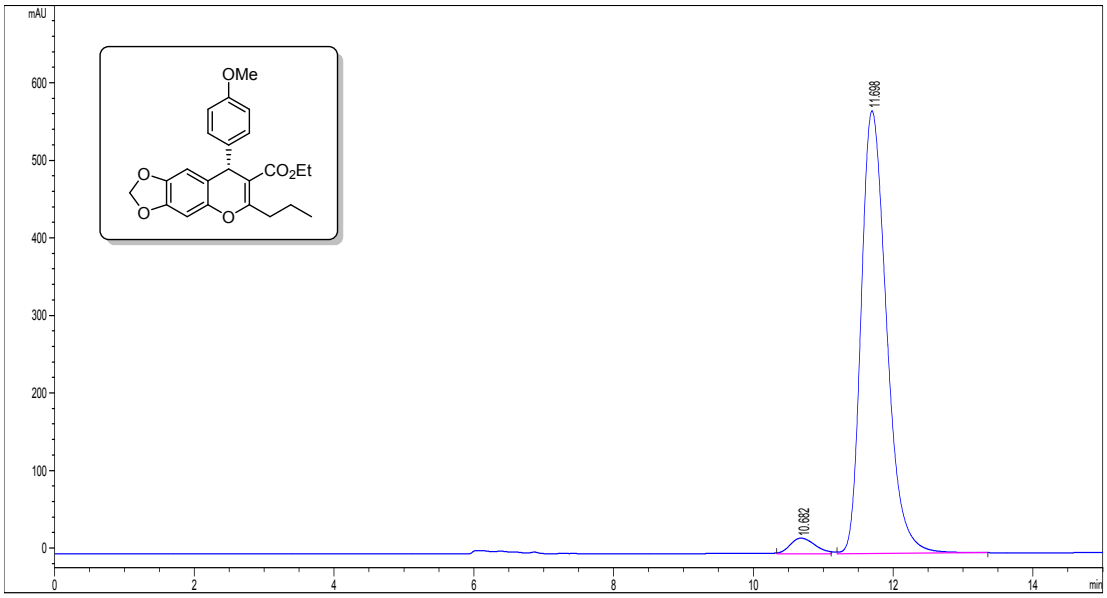


#	Time	Width	Area	Height	Area%
1	18.967	0.5128	1940.2200	63.0541	5.0432
2	20.091	0.6127	3.6532e4	993.7145	94.9568

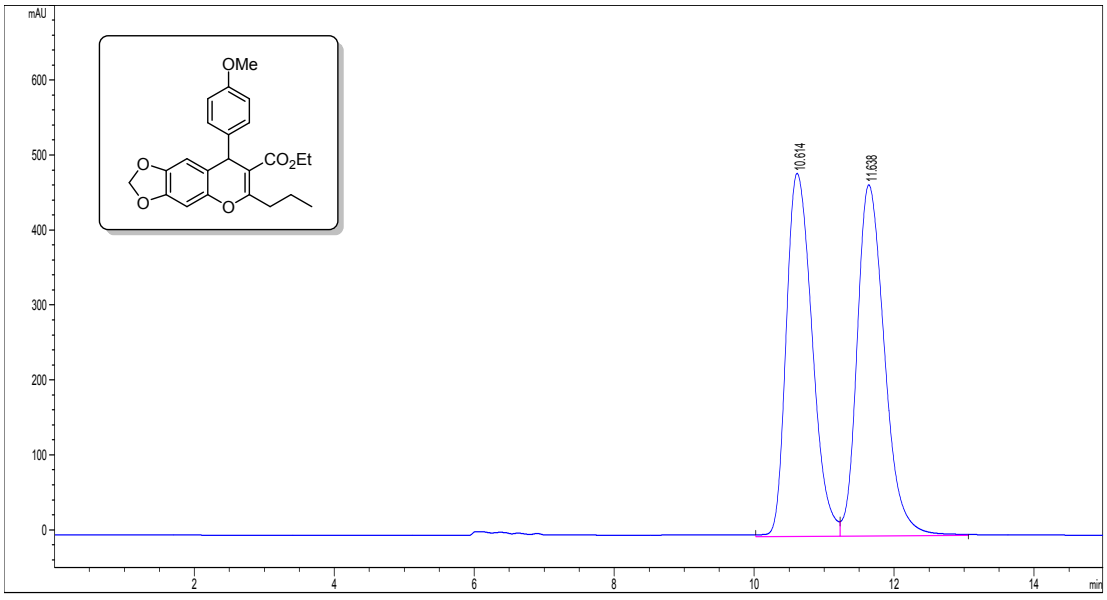


#	Time	Width	Area	Height	Area%
1	17.550	0.5309	1.2858e4	403.7023	49.0652
2	18.651	0.5814	1.3348e4	382. 6419	50.9348

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 11.70 min, t (minor) = 10.68 min; 93% ee.

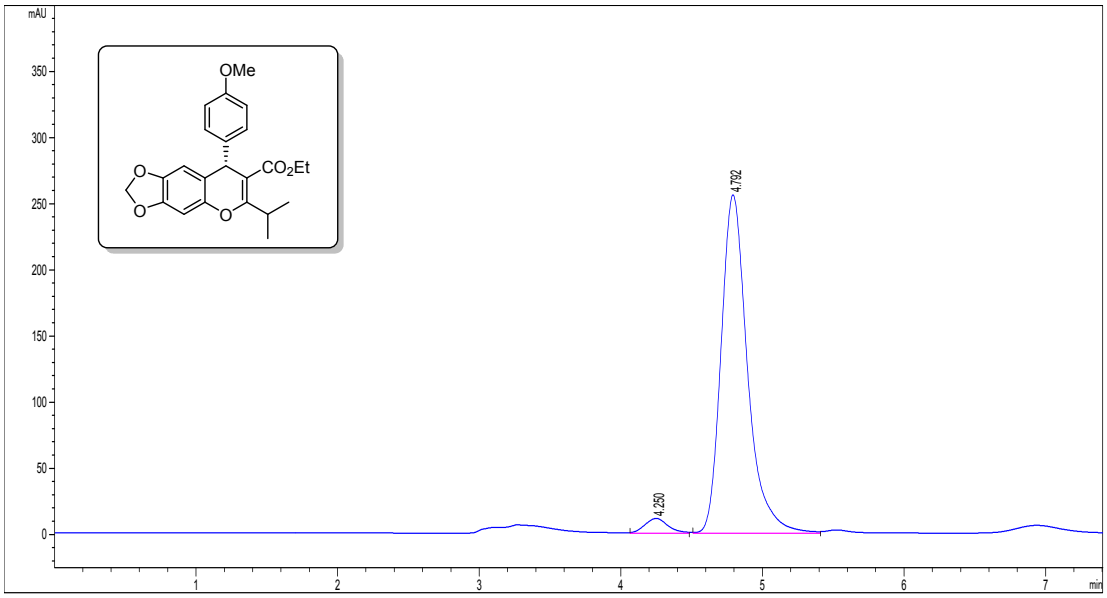


#	Time	Width	Area	Height	Area%
1	10.682	0.4153	503.3138	20.2003	3.4018
2	11.698	0.4173	1.4292e4	570.7978	96.5982

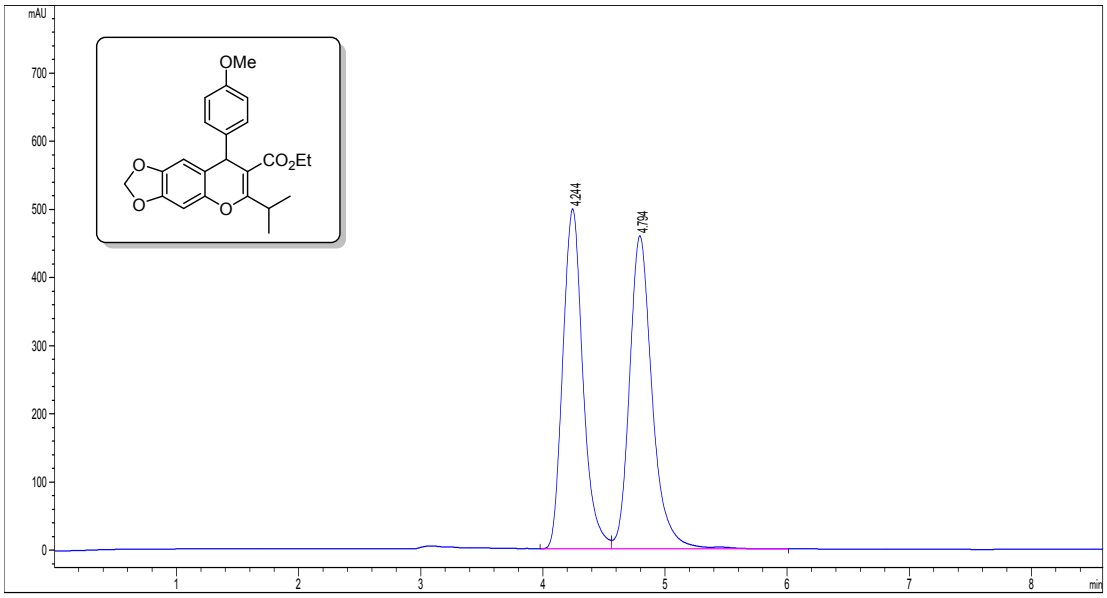


#	Time	Width	Area	Height	Area%
1	10.614	0.4281	1.2436e4	484.2076	49.4902
2	11.638	0.4516	1.2692e4	468.3732	50.5098

Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 4.79 min, t (minor) = 4.25 min; 92% ee.

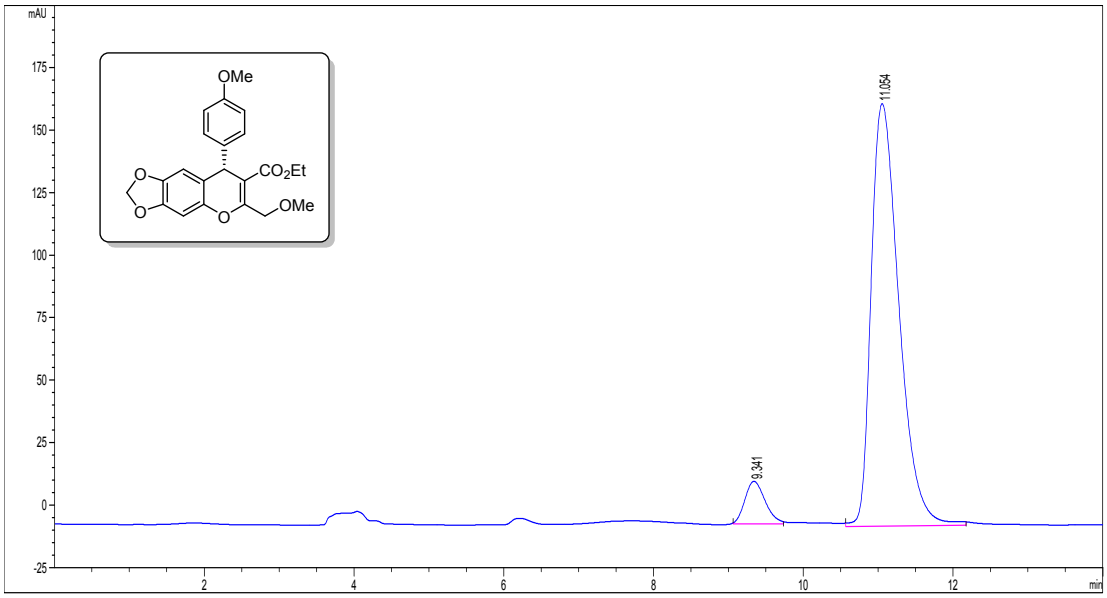


#	Time	Width	Area	Height	Area%
1	4.250	0.1928	131.6071	11.37496	3.8070
2	4.792	0.2165	3325.3440	255.95779	96.1930

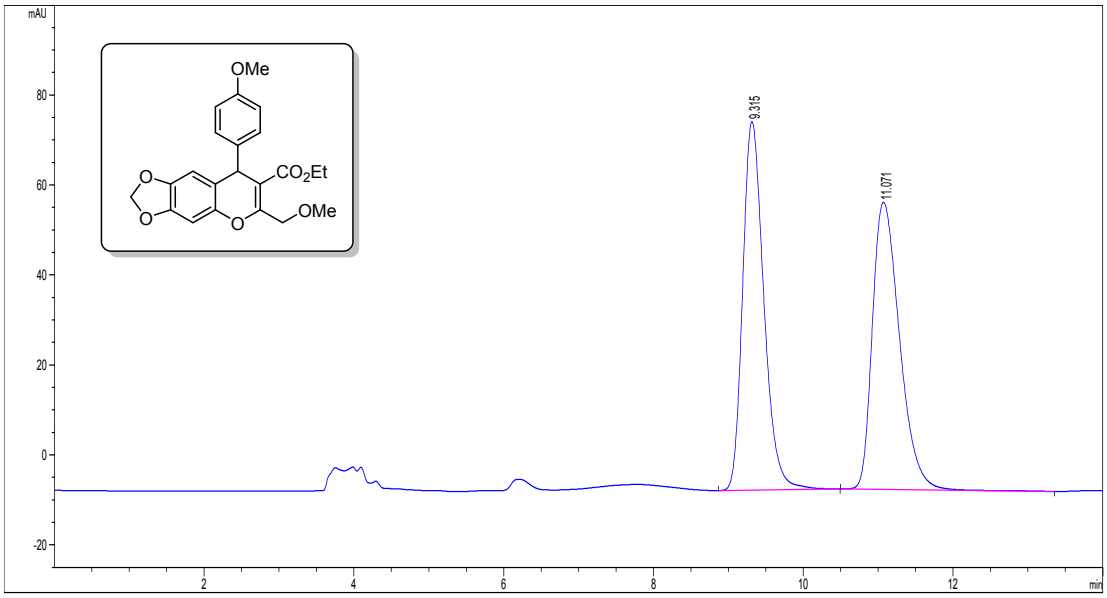


#	Time	Width	Area	Height	Area%
1	4.244	0.1775	5707.2026	498.8137	49.0016
2	4.794	0.1958	5939.7730	459.4121	50.9984

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 11.05 min, t (minor) = 9.34 min; 86% ee.

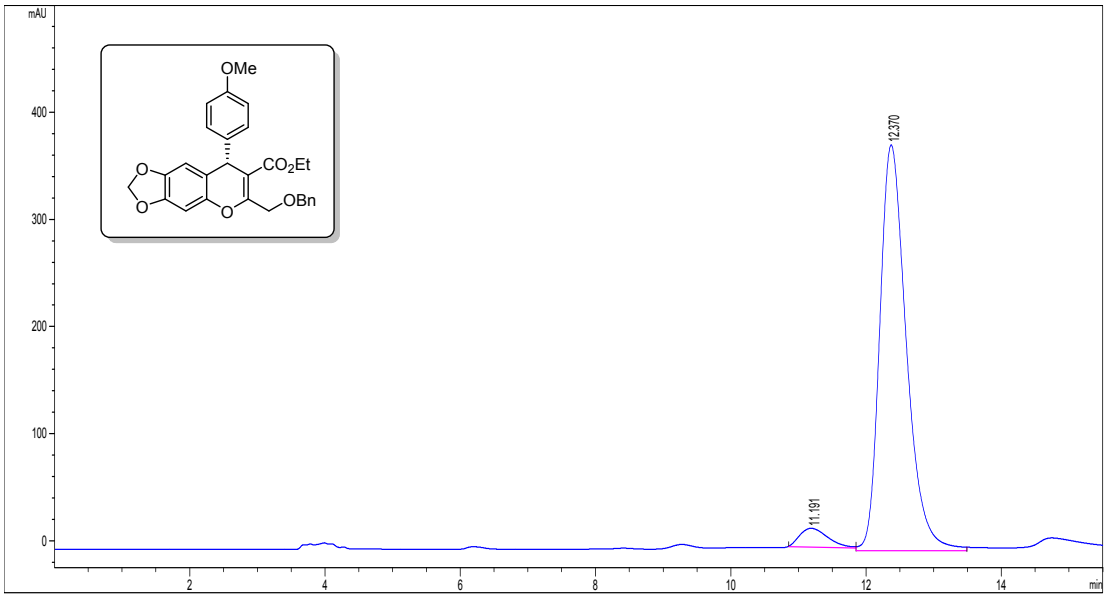


#	Time	Width	Area	Height	Area%
1	9.341	0.3127	318.9261	16.9962	6.8057
2	11.054	0.4305	4367.2114	169.0933	93.1943

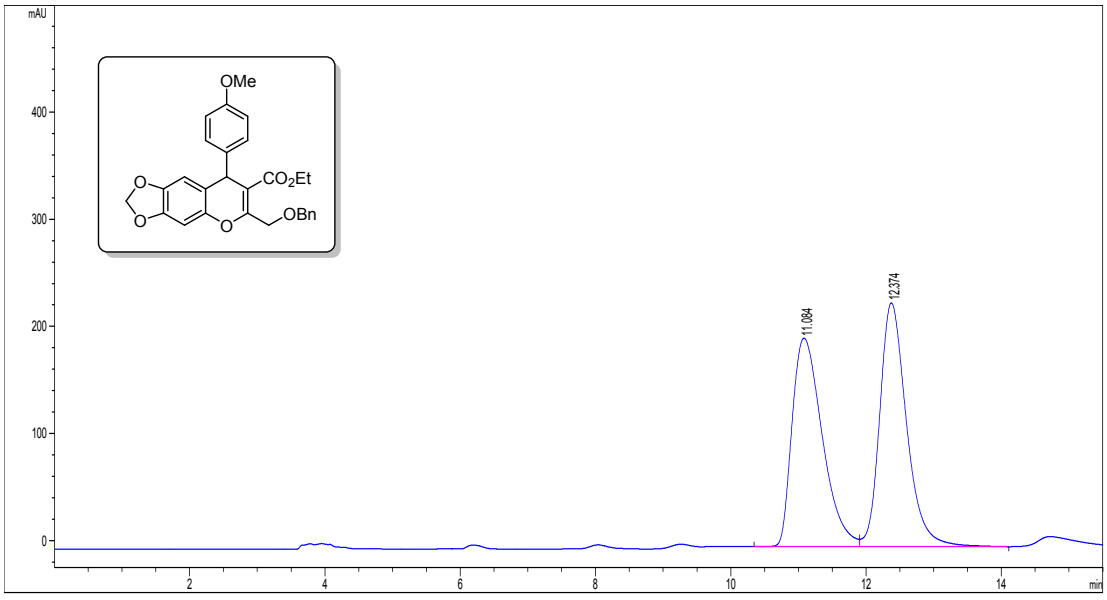


#	Time	Width	Area	Height	Area%
1	9.315	0.3022	1603.7595	81.9922	49.8734
2	11.071	0.3933	1611.9028	63.8901	50.1266

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 12.37 min, t (minor) = 11.19 min, 91% ee.

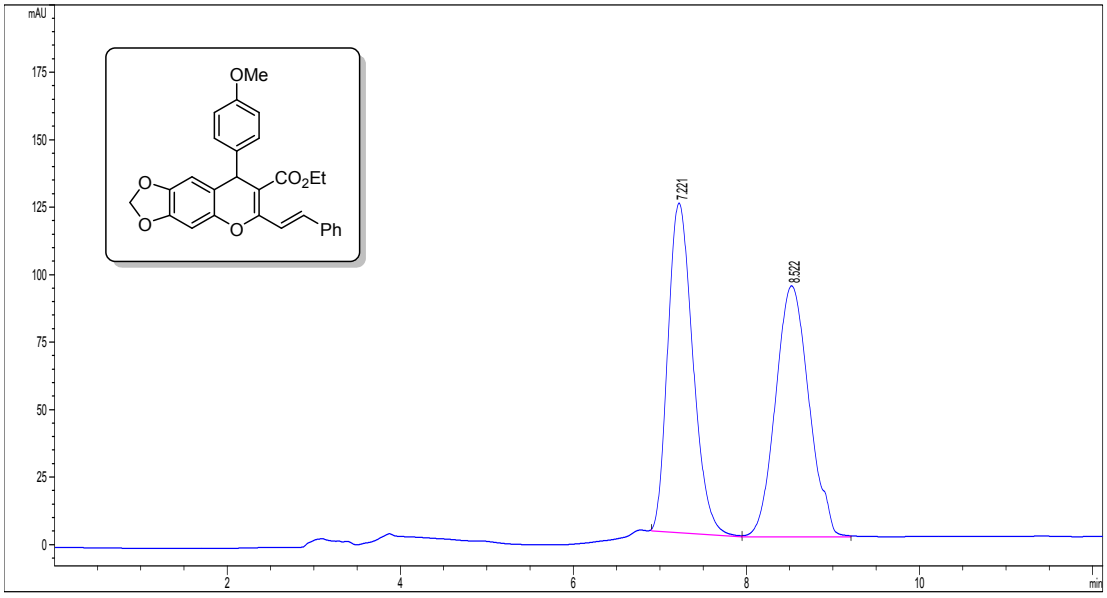


#	Time	Width	Area	Height	Area%
1	11.191	0.4818	505.4702	17.4867	4.6573
2	12.370	0.4551	1.0348e4	378.9387	95.3427

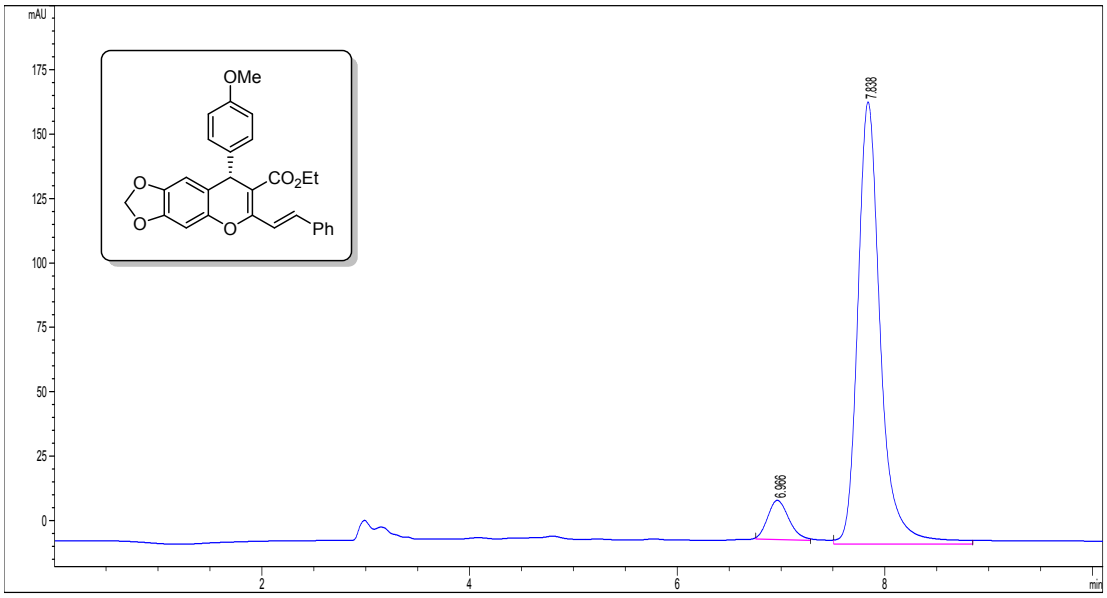


#	Time	Width	Area	Height	Area%
1	11.084	0.4876	6031.5371	194.6176	49.0454
2	12.374	0.4203	6266.3257	227.5214	50.9546

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90 : 10, 1.0 mL/min, 254 nm; t (major) = 10.69 min, t (minor) = 21.11 min, 85% ee.

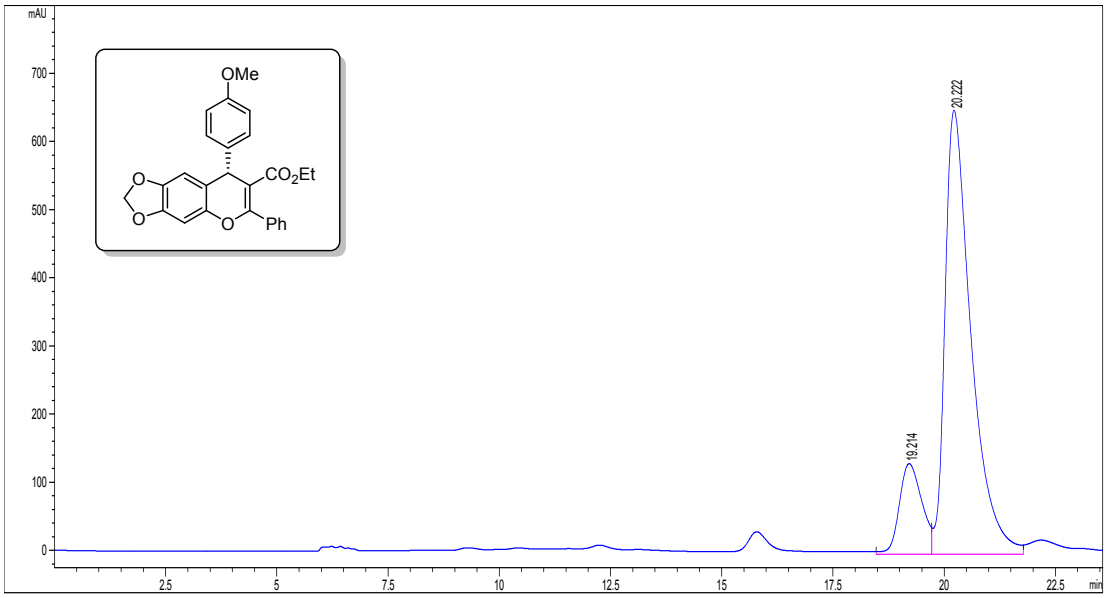


#	Time	Width	Area	Height	Area%
1	7.221	0.3346	2452.1392	122.1355	49.5900
2	8.522	0.4471	2492.6855	92.9138	50.4100

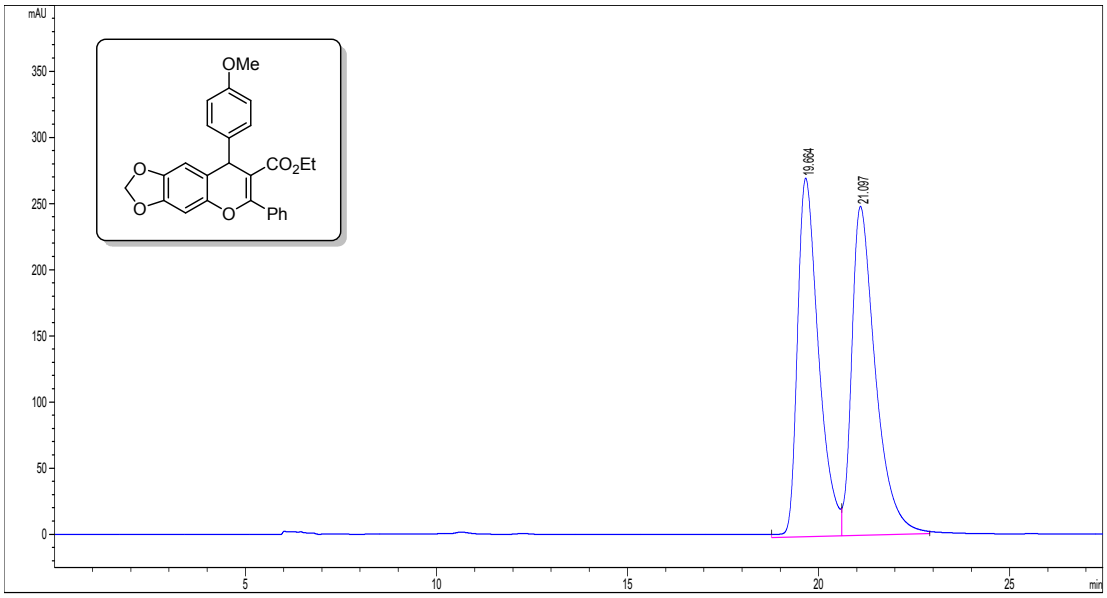


#	Time	Width	Area	Height	Area%
1	6.966	0.2370	216.0415	15.1957	7.6611
2	7.838	0.2526	2603.9341	171.7888	92.3389

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 20.22 min, t (minor) = 19.21 min; 70% ee.

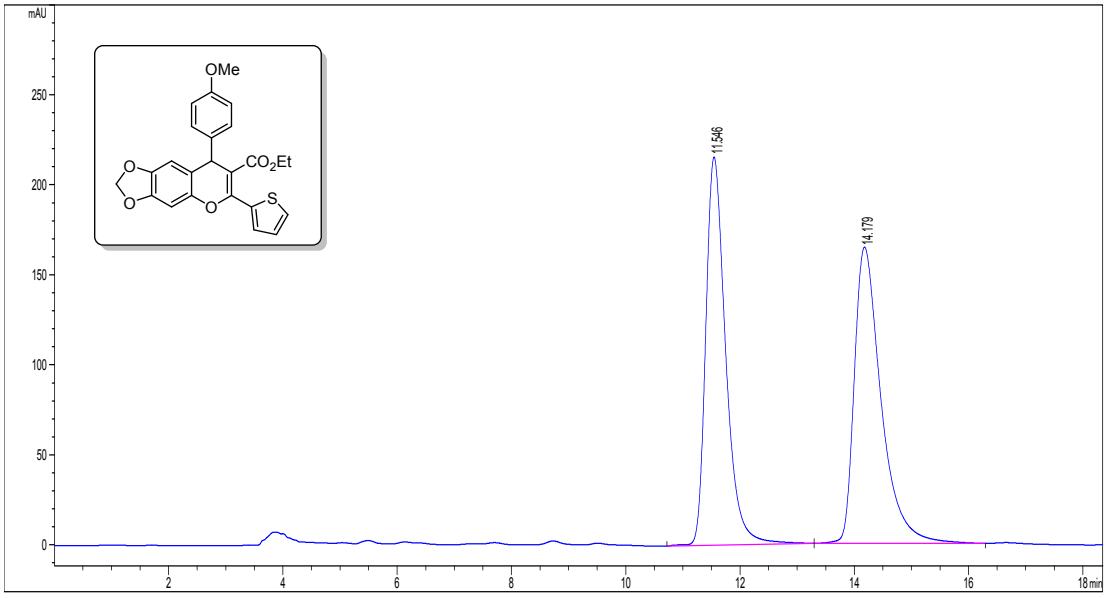


#	Time	Width	Area	Height	Area%
1	19.214	0.5875	4700.6270	133.3401	14.9905
2	20.222	0.6818	2.6657e4	651.6686	85.0095

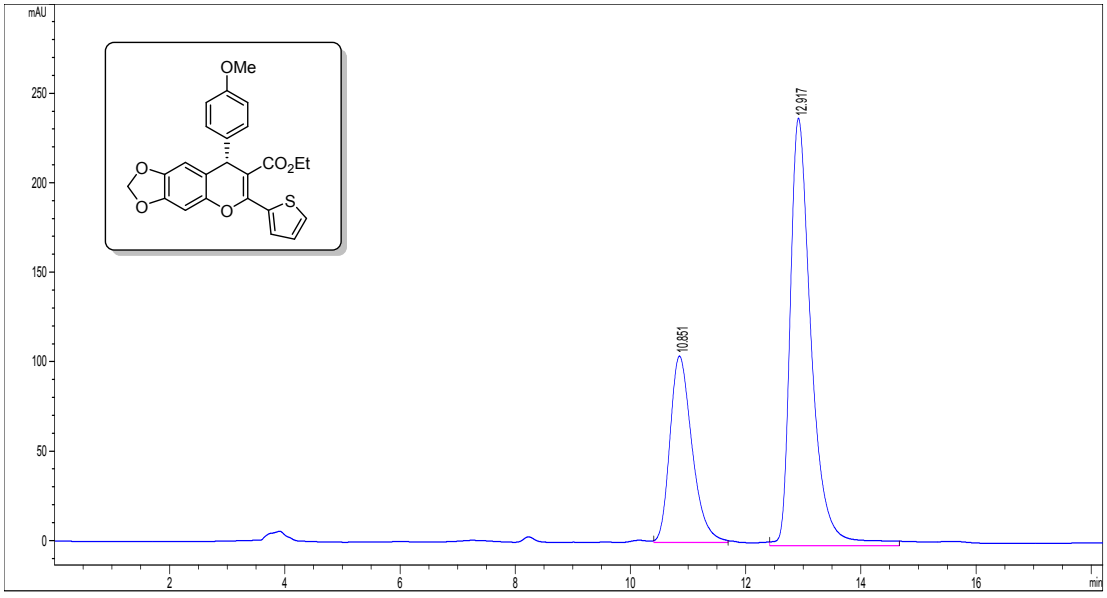


#	Time	Width	Area	Height	Area%
1	19.664	0.6422	1.0443e4	271.0310	49.3099
2	21.097	0.7195	1.0736e4	248.7006	50.6901

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90 : 10, 0.8 mL/min, 254 nm; t (major) = 12.92 min, t (minor) = 10.85 min, 37% ee.

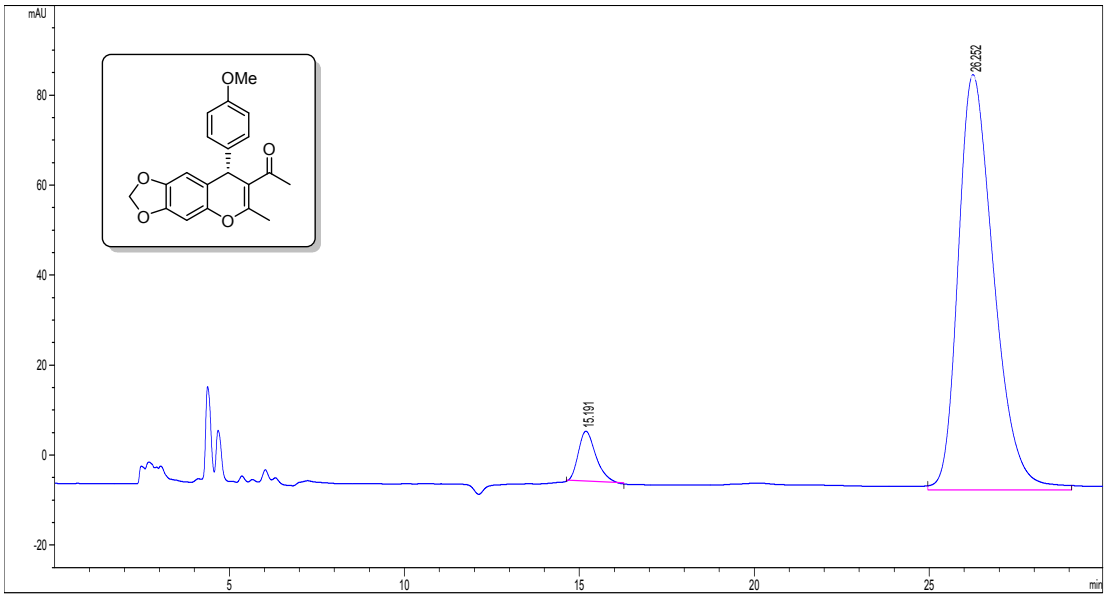


#	Time	Width	Area	Height	Area%
1	11.546	0.3693	5215.8843	215.5906	49.3761
2	14.179	0.4903	5347.7017	164.4970	50.6239

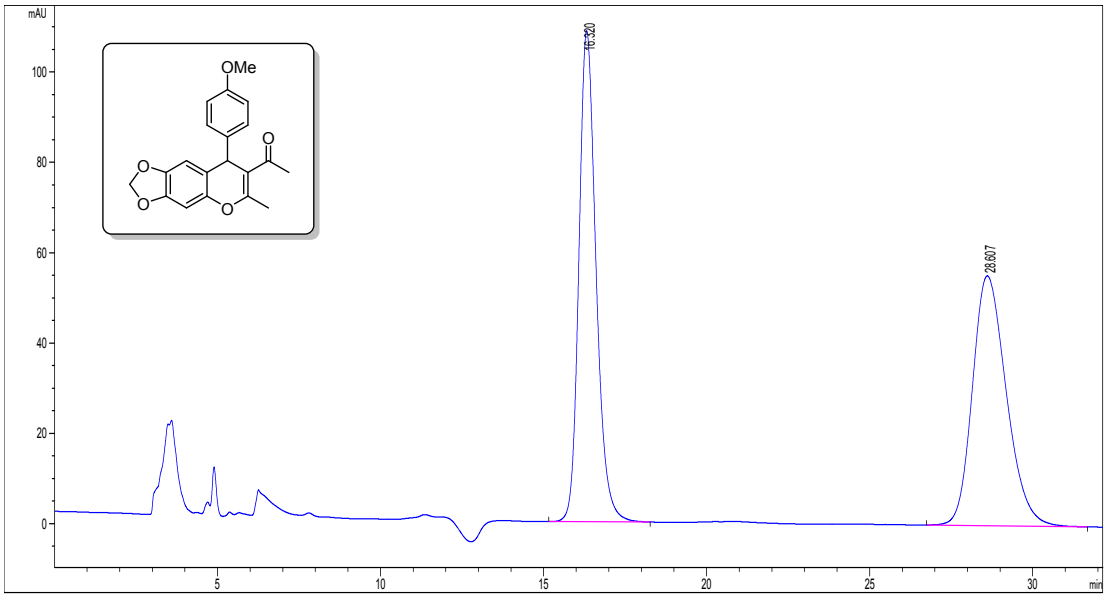


#	Time	Width	Area	Height	Area%
1	10.851	0.4452	2784.5085	104.2469	31.4544
2	12.917	0.4233	6068.0064	238.9098	68.5456

Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 26.25 min, t (minor) = 15.19 min; 89% ee.

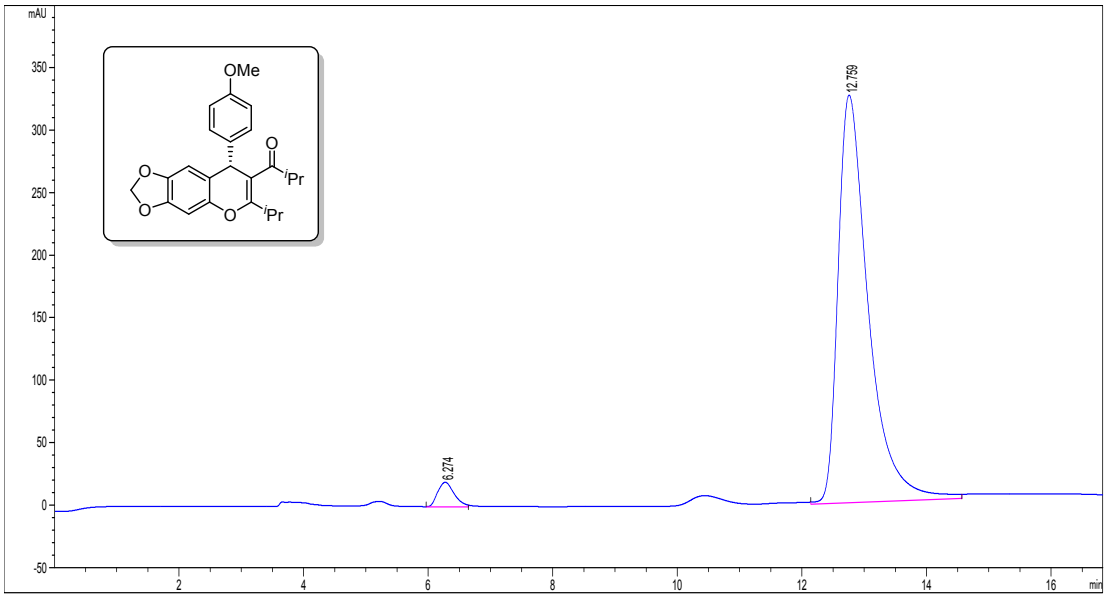


#	Time	Width	Area	Height	Area%
1	15.191	0.5764	384.1294	11.1076	5.5516
2	26.252	1.1795	6535.1567	92.3416	94.4484

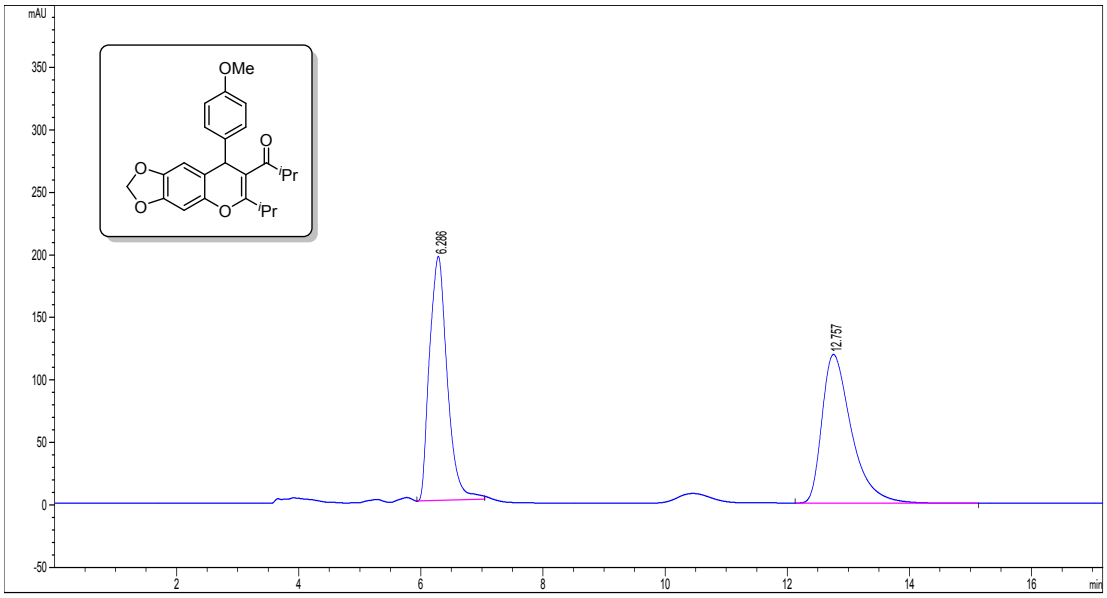


#	Time	Width	Area	Height	Area%
1	16.320	0.5592	3973.3237	108.7671	49.8262
2	28.607	1.1156	4001.0352	55.3342	50.1738

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 12.76 min, t (minor) = 6.27 min; 93% ee.

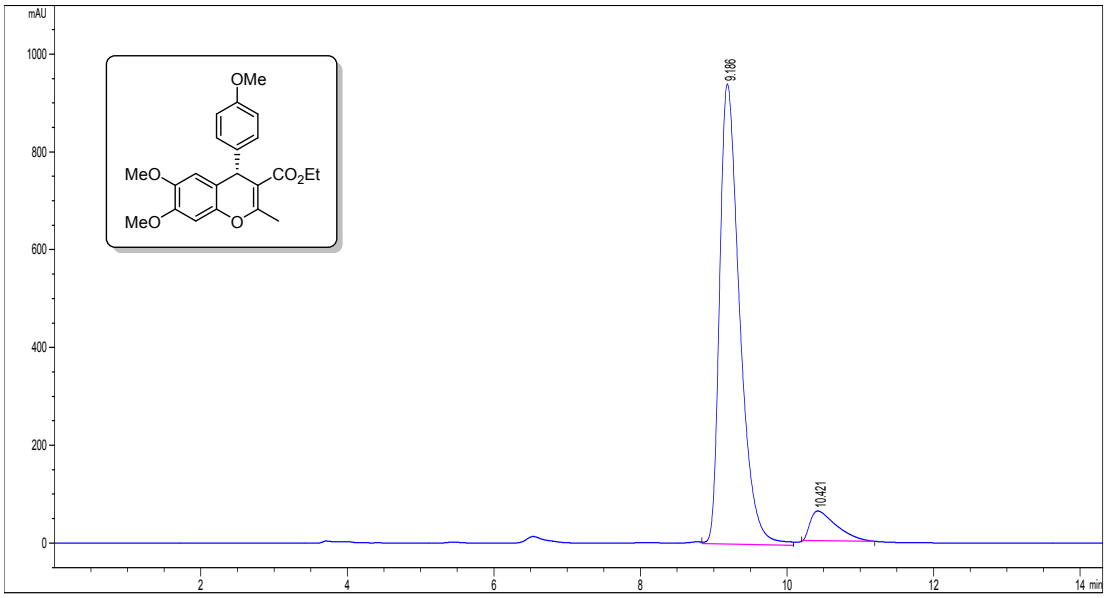


#	Time	Width	Area	Height	Area%
1	6.274	0.3106	369.8887	19.8480	3.2380
2	12.759	0.5645	1.1054e4	326.3401	96.7620

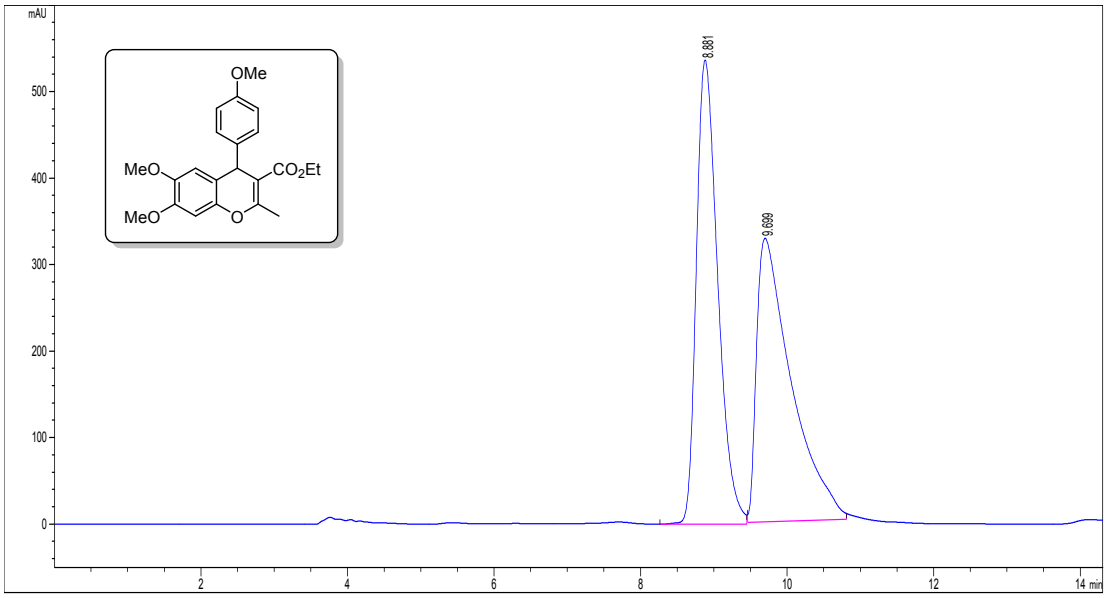


#	Time	Width	Area	Height	Area%
1	6.286	0.3353	3929.0396	195.2711	49.6895
2	12.757	0.5081	3978.1399	118.9805	50.3105

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 9.19 min, t (minor) = 10.42 min; 84% ee.

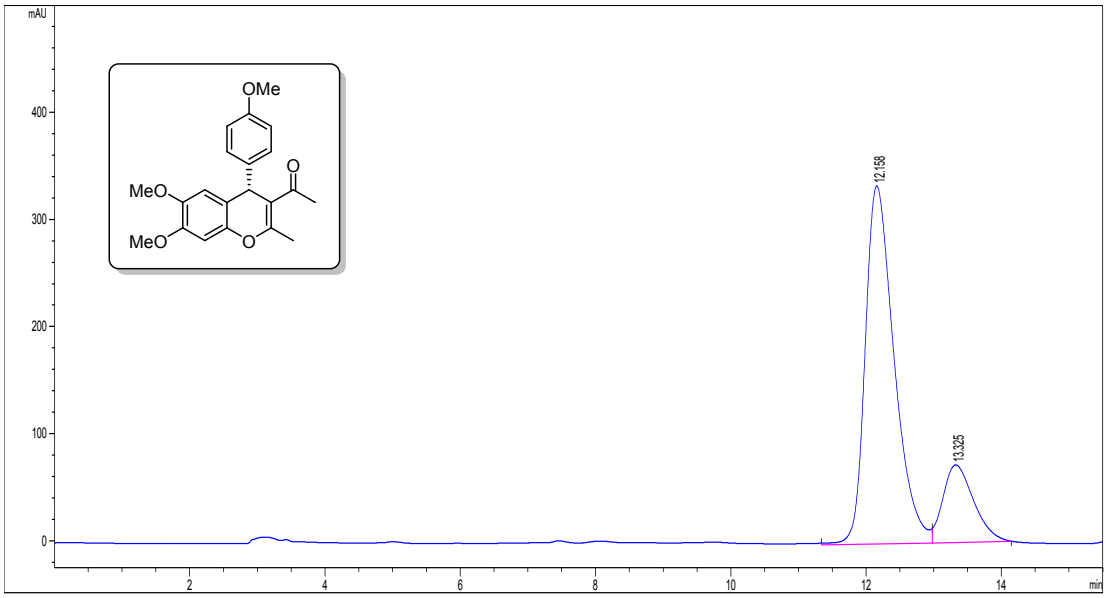


#	Time	Width	Area	Height	Area%
1	9.186	0.3148	1.7784e4	941.4763	92.2574
2	10.421	0.4114	1492.4746	60.4568	7.7426

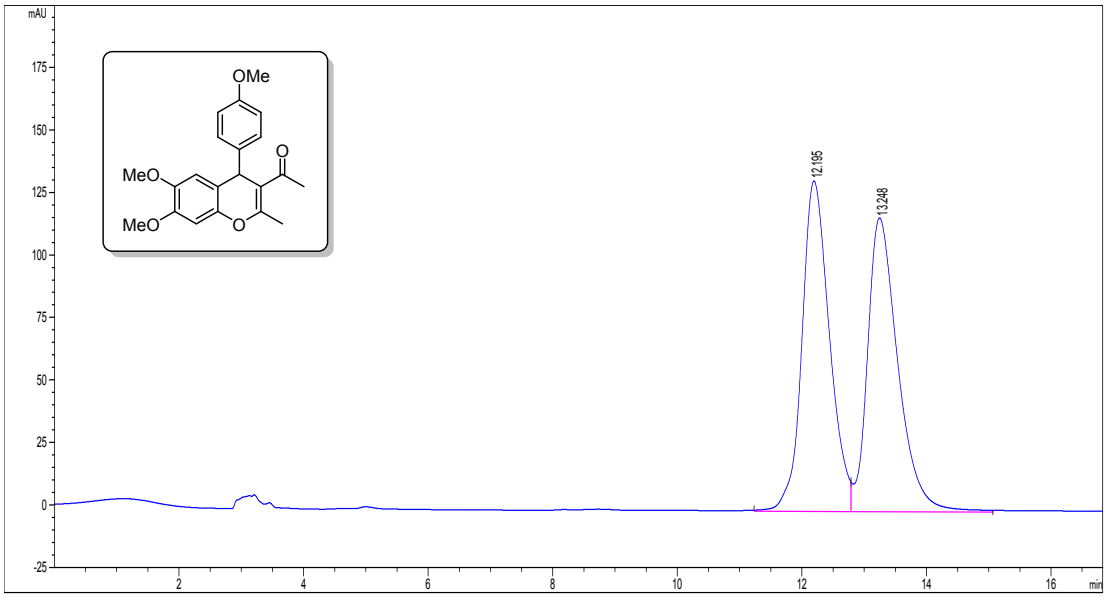


#	Time	Width	Area	Height	Area%
1	8.881	0.3125	1.0870e4	536.3215	50.2208
2	9.699	0.5474	1.0774e4	328.0470	49.7792

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90: 10, 1.0 mL/min, 254 nm; t (major) = 12.16 min, t (minor) = 12.32 min; 63% ee.

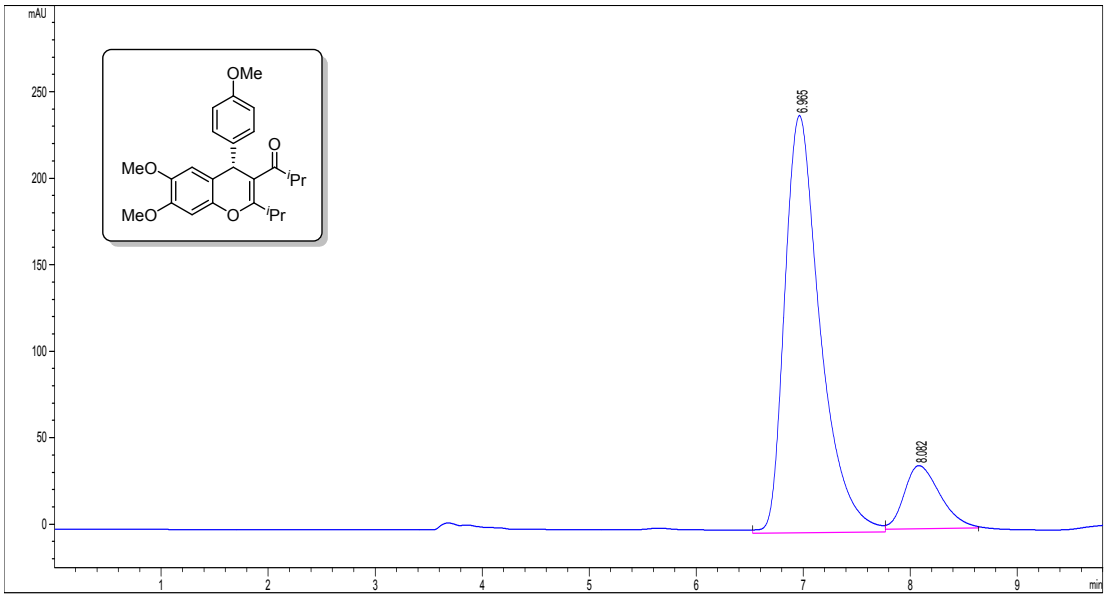


#	Time	Width	Area	Height	Area%
1	12.158	0.4957	9942.6260	334.3191	81.3203
2	13.325	0.5260	2283.8740	72.3669	18.6797

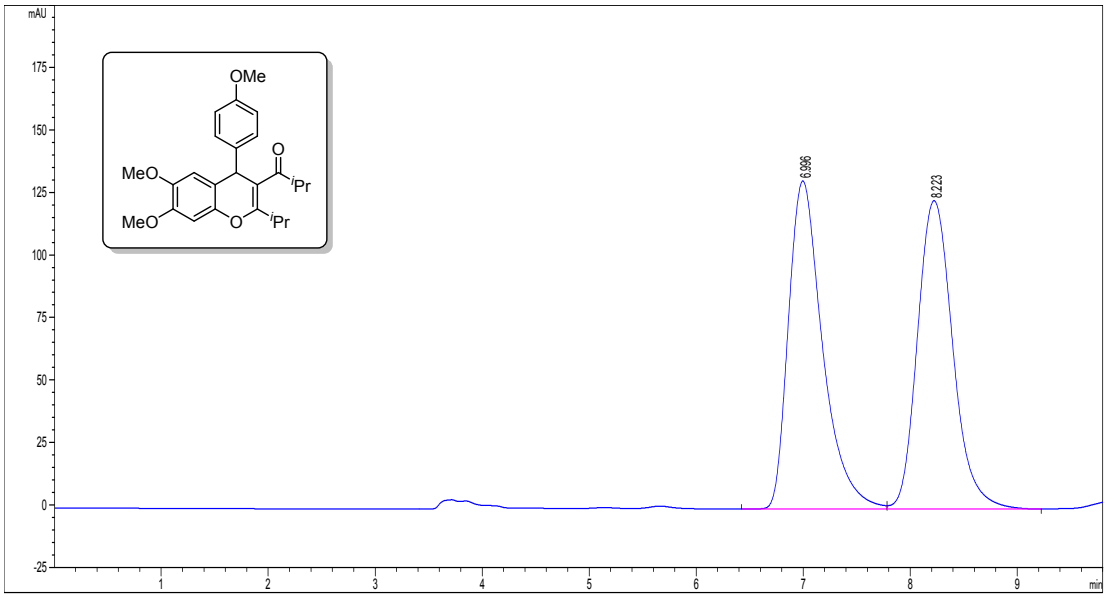


#	Time	Width	Area	Height	Area%
1	12.195	0.5111	4054.5391	132.2274	50.4249
2	13.248	0.5653	3986.2014	117.5336	49.5751

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 6.96 min, t (minor) = 8.08 min; 74% ee.

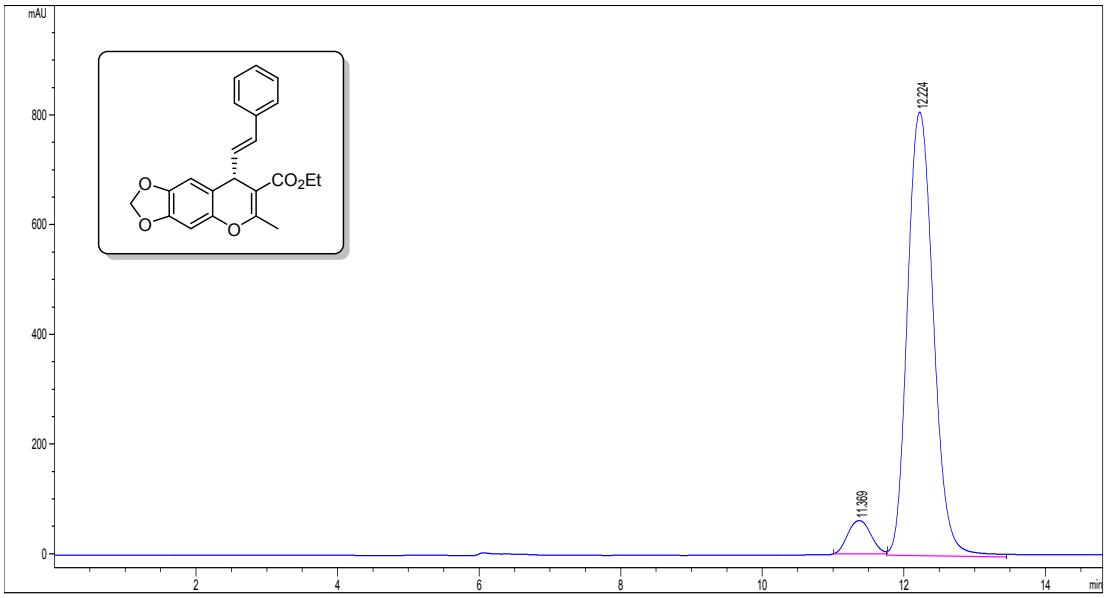


#	Time	Width	Area	Height	Area%
1	6.965	0.3847	5568.5952	241.2363	86.8118
2	8.082	0.3867	845.9674	36.4625	13.1882

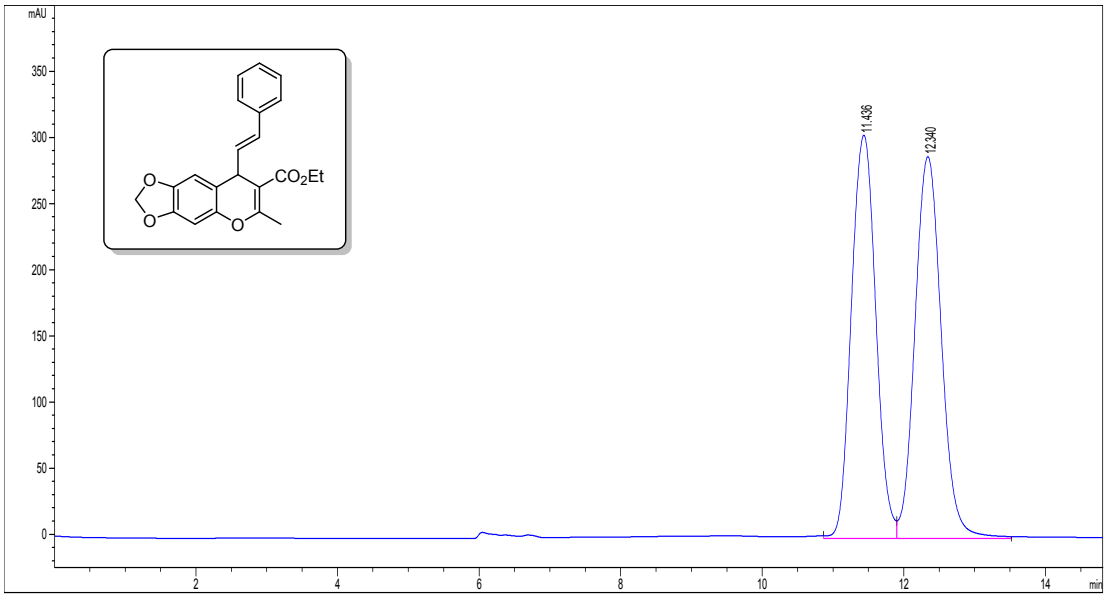


#	Time	Width	Area	Height	Area%
1	6.996	0.3373	2905.6611	131.2627	50.6071
2	8.223	0.3600	2835.9458	123.4408	49.3929

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 12.22 min, t (minor) = 11.37 min; 88% ee.

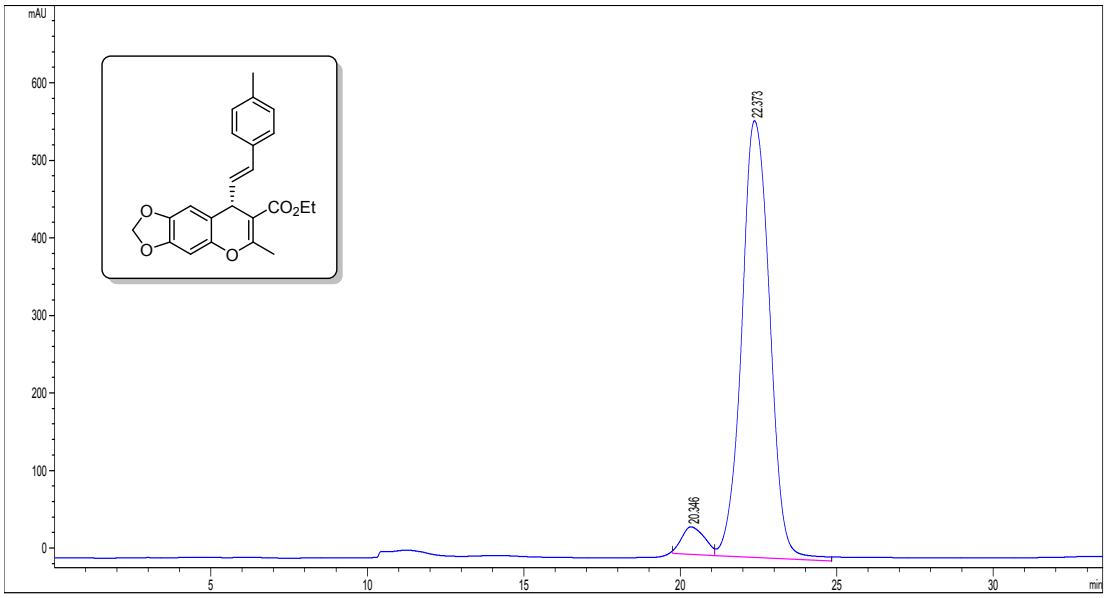


#	Time	Width	Area	Height	Area%
1	11.369	0.3758	1364.9693	60.5412	6.2176
2	12.224	0.4243	2.0588e4	808.7687	93.7824

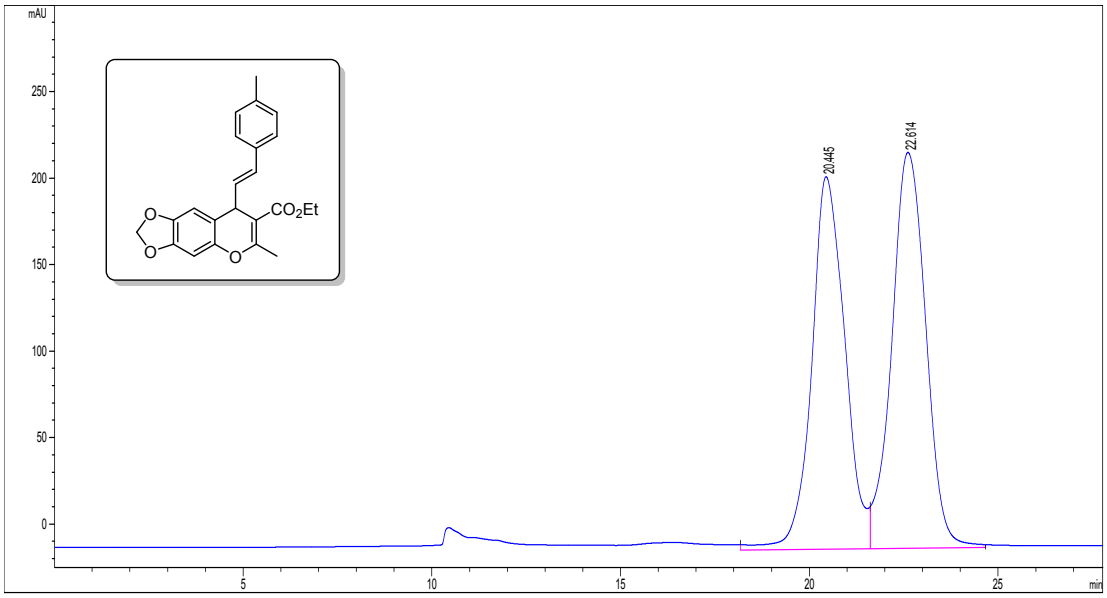


#	Time	Width	Area	Height	Area%
1	11.436	0.3998	7310.7627	304.8051	49.4238
2	12.340	0.4320	7481.2349	288.6233	50.5762

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 22.37 min, t (minor) = 20.35 min; 90% ee.

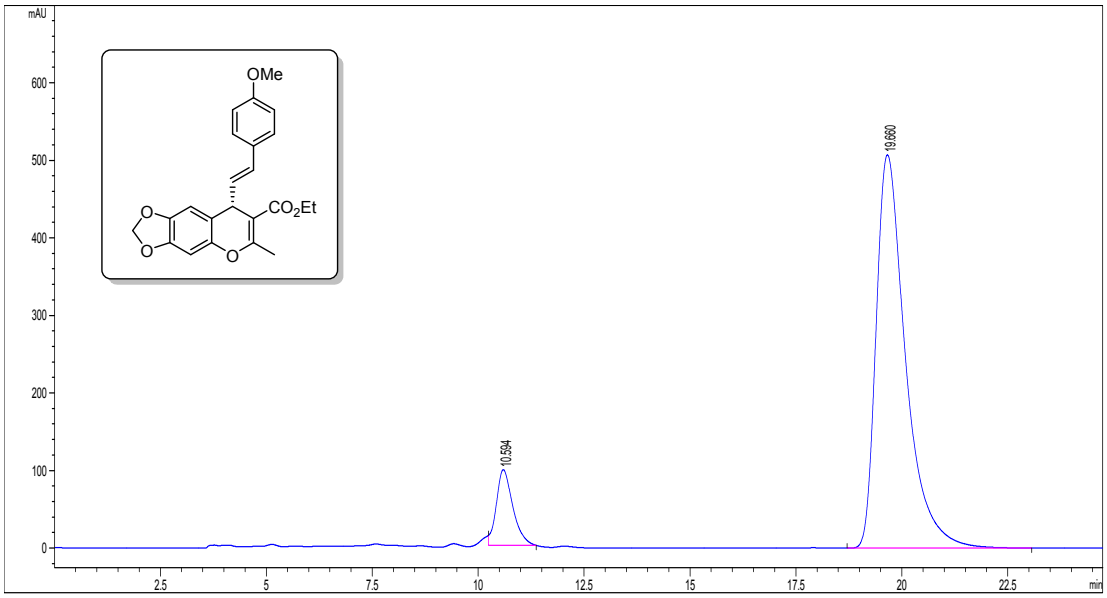


#	Time	Width	Area	Height	Area%
1	20.346	0.8506	1816.9775	35.6002	4.9275
2	22.373	1.0376	3.5057e4	563.1126	95.0725

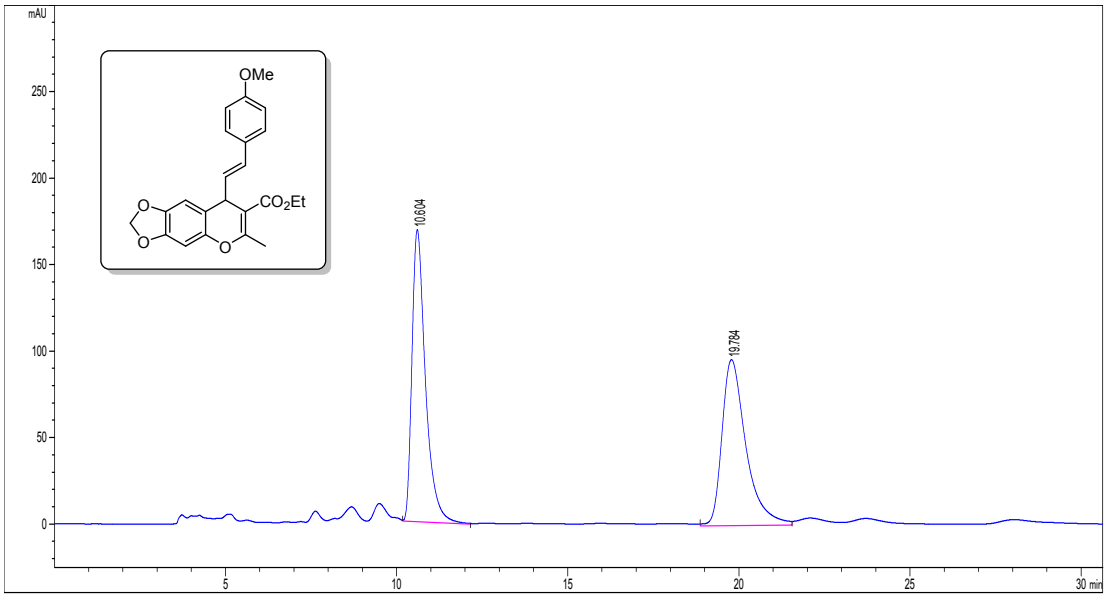


#	Time	Width	Area	Height	Area%
1	20.445	1.0227	1.3208e4	215.2437	47.9346
2	22.614	1.0450	1.4347e4	228.8174	52.0654

Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 19.66 min, t (minor) = 10.59 min; 80% ee.

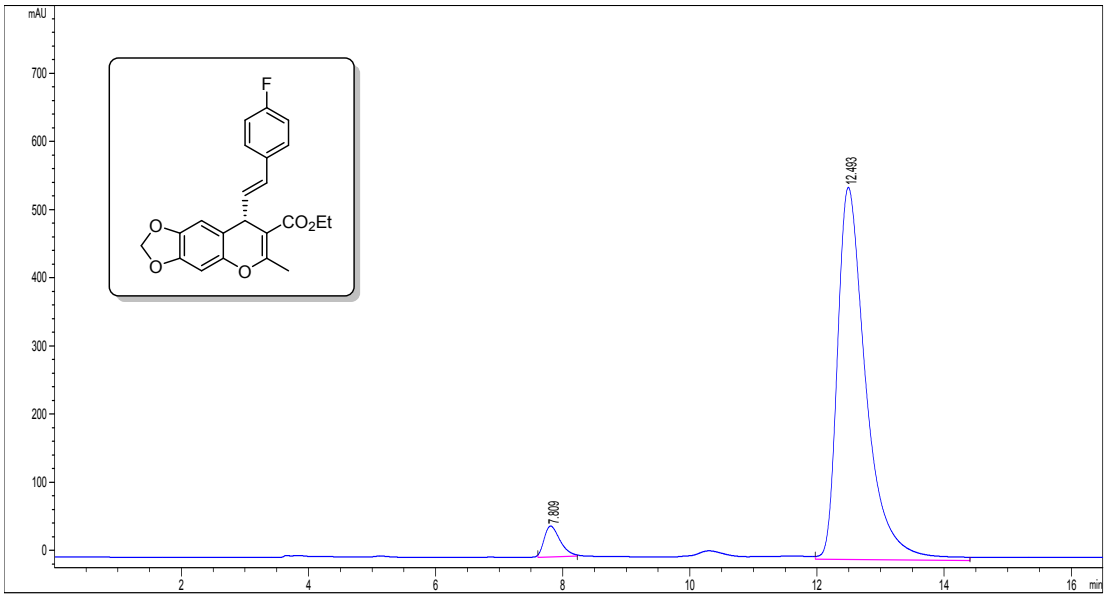


#	Time	Width	Area	Height	Area%
1	10.594	0.4509	2644.2656	97.7504	9.7663
2	19.660	0.7281	2.4431e4	507.0810	90.2337

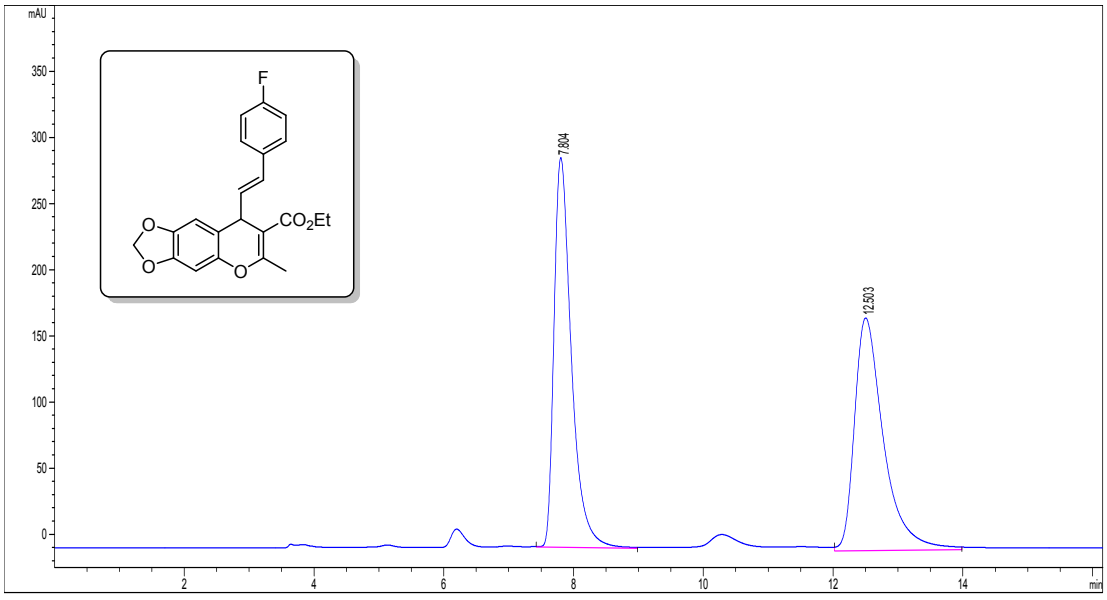


#	Time	Width	Area	Height	Area%
1	10.604	0.4571	4631.5220	168.8865	49.6934
2	19.784	0.8138	4688.6709	96.0213	50.3066

Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 12.49 min, t (minor) = 7.81 min; 92% ee.

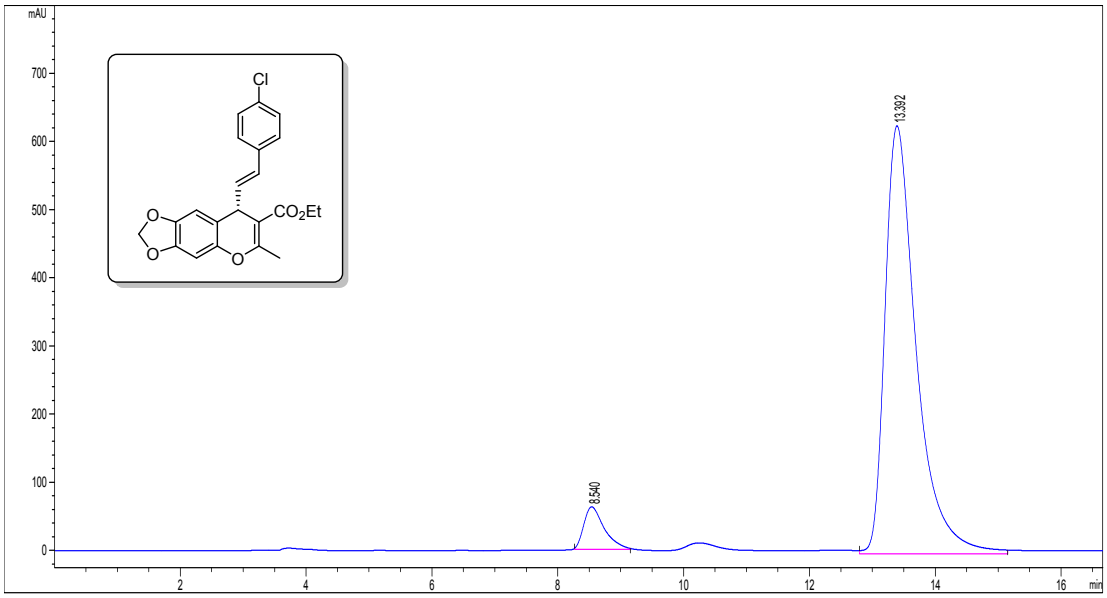


#	Time	Width	Area	Height	Area%
1	7.809	0.2909	791.7720	45.3590	4.4584
2	12.493	0.5180	1.6967e4	545.9666	95.5416

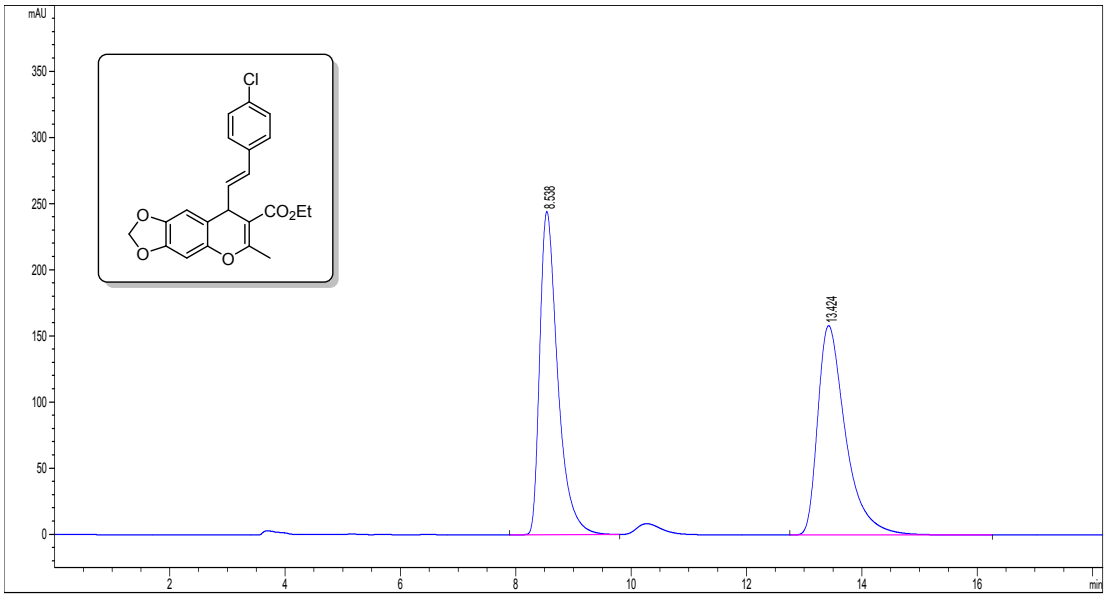


#	Time	Width	Area	Height	Area%
1	7.804	0.3097	5472.3662	294.5315	49.9467
2	12.503	0.5195	5484.0386	175.9236	50.0533

Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 13.39 min, t (minor) = 8.54 min; 88% ee.

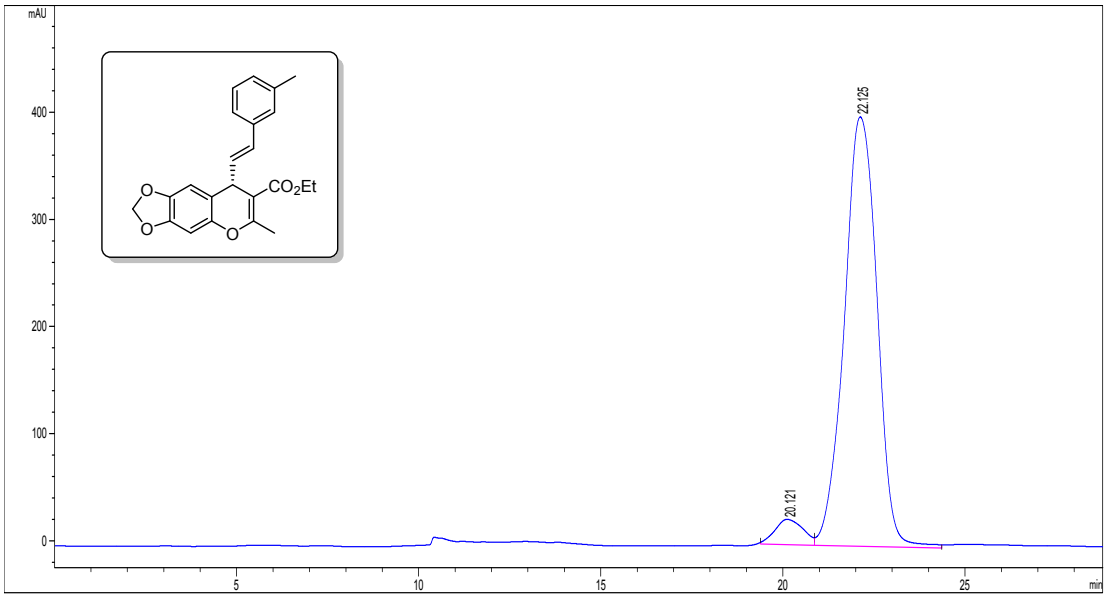


#	Time	Width	Area	Height	Area%
1	8.540	0.3758	1405.0531	62.3221	6.0889
2	13.392	0.5754	2.1670e4	627.6981	93.9111

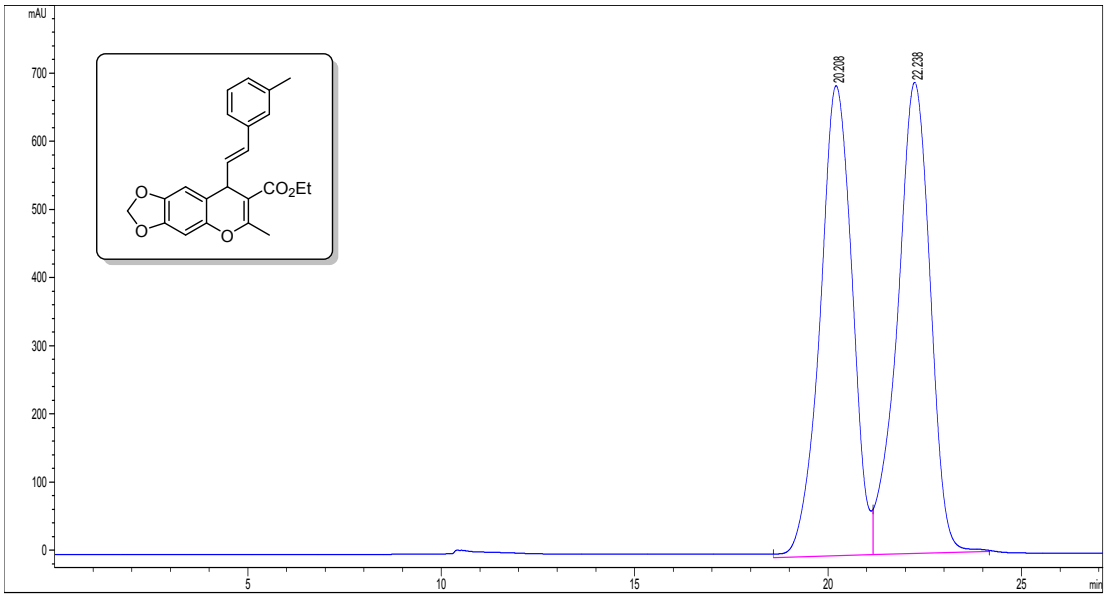


#	Time	Width	Area	Height	Area%
1	8.538	0.3299	5296.0298	244.3203	49.9741
2	13.424	0.5068	5301.5112	158.2773	50.0259

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 98: 2, 0.3 mL/min, 254 nm; t (major) = 22.12 min, t (minor) = 20.12 min; 91% ee.

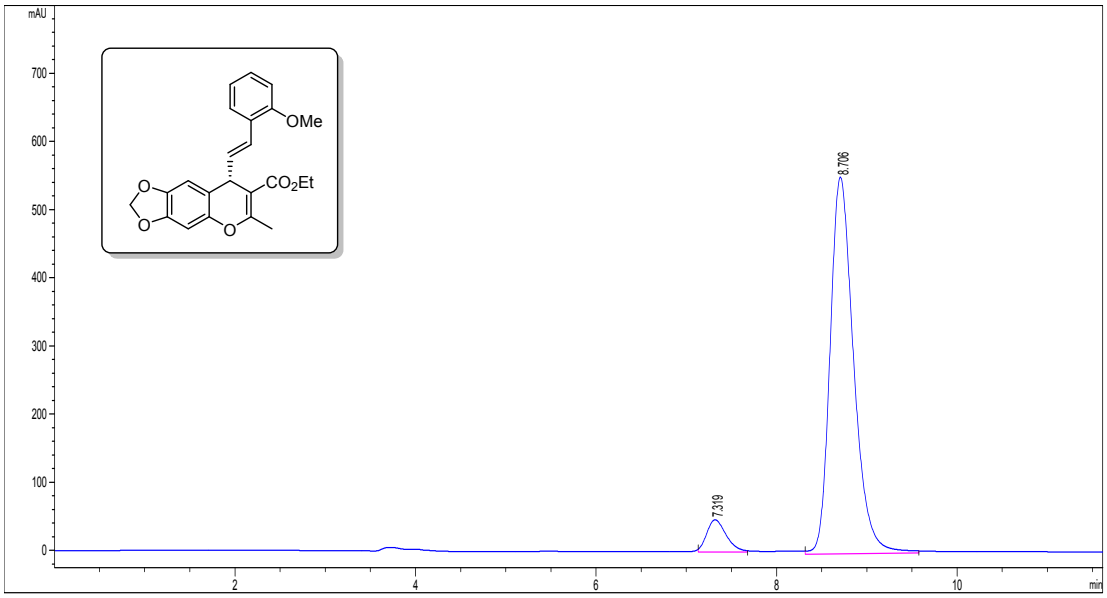


#	Time	Width	Area	Height	Area%
1	20.121	0.8996	1266.8779	23.4710	4.8093
2	22.125	1.0425	2.5075e4	400.8650	95.1907

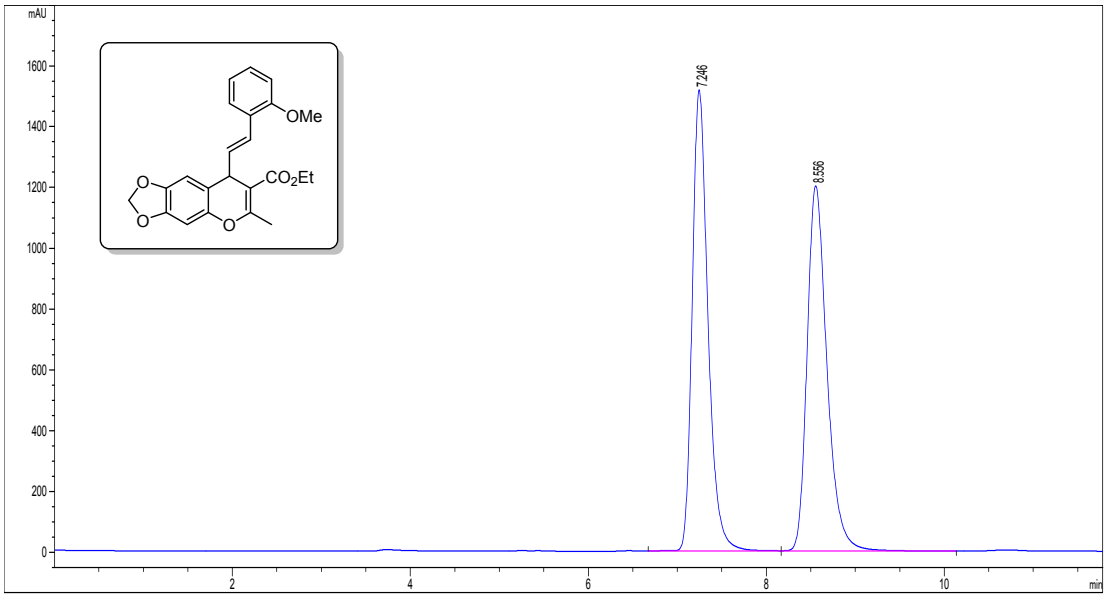


#	Time	Width	Area	Height	Area%
1	20.208	0.9661	3.9984e4	689.7943	49.4575
2	22.238	0.9854	4.0861e4	691.1212	50.5425

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 8.71 min, t (minor) = 7.32 min; 87% ee.

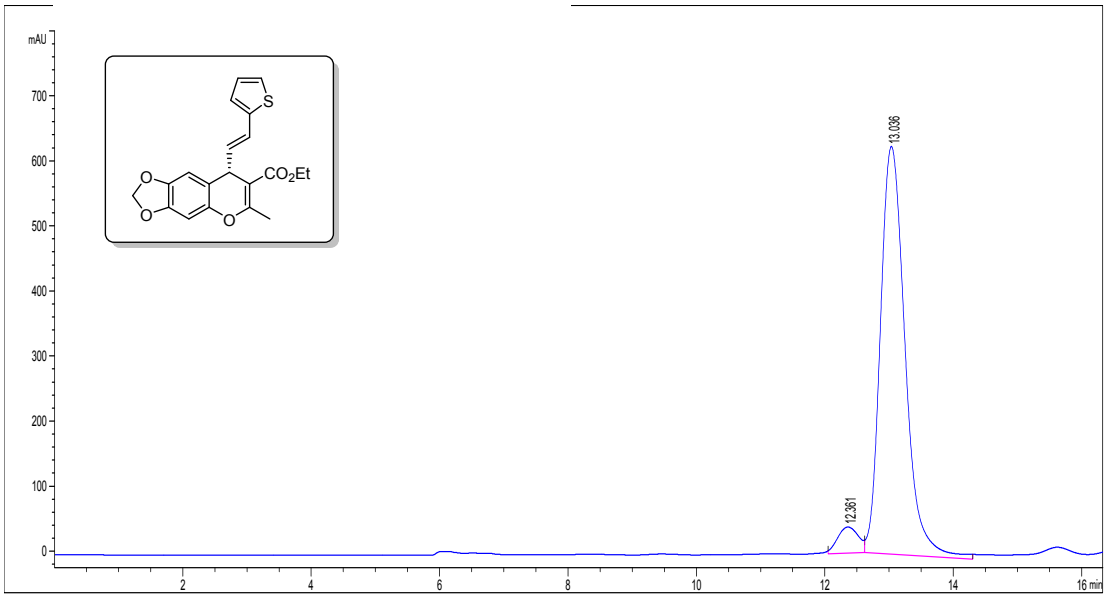


#	Time	Width	Area	Height	Area%
1	7.319	0.2495	705.9175	47.1537	6.5643
2	8.706	0.3028	1.0048e4	553.0427	93.4357

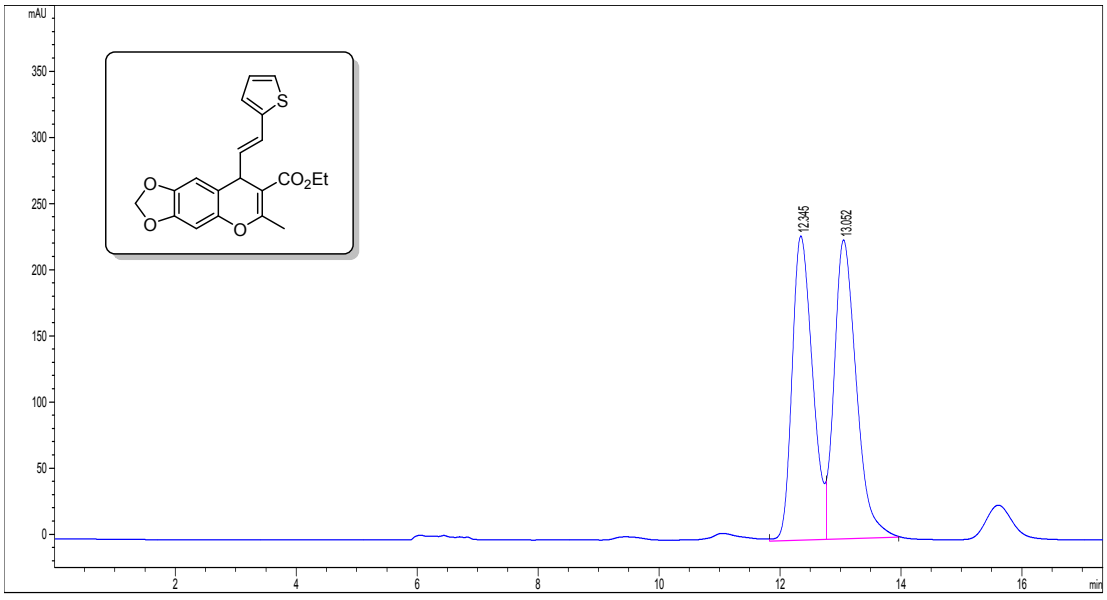


#	Time	Width	Area	Height	Area%
1	7.246	0.1863	1.8642e4	1517.2754	50.0759
2	8.556	0.2356	1.8586e4	1200.6909	49.9241

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 95: 5, 0.5 mL/min, 254 nm; t (major) = 13.04 min, t (minor) = 12.36 min; 90% ee.

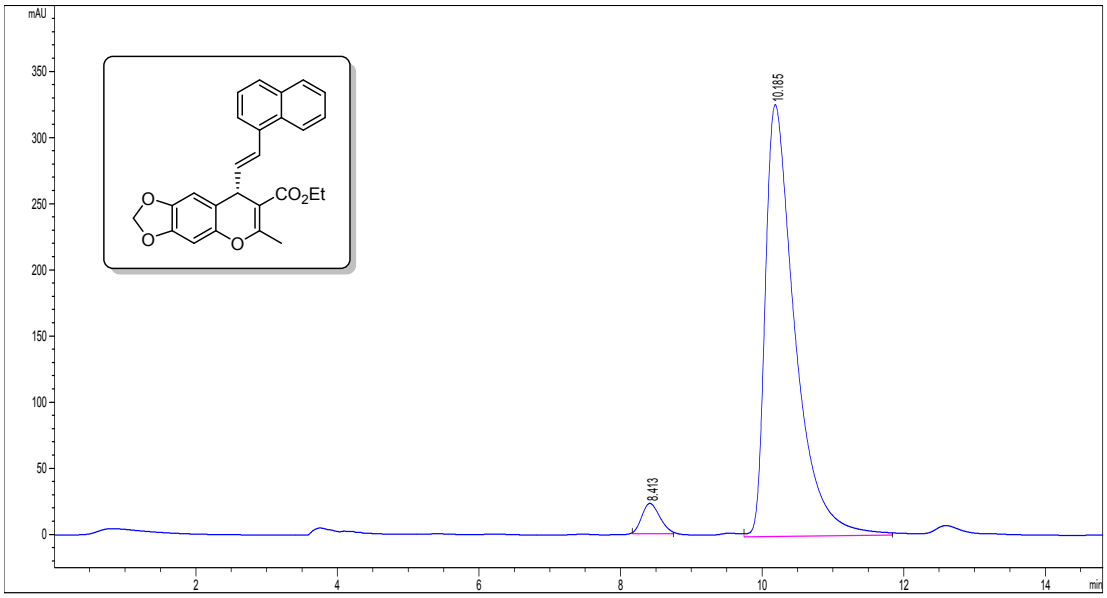


#	Time	Width	Area	Height	Area%
1	12.361	0.3784	904.7680	39.8485	5.1529
2	13.036	0.4430	1.6654e4	626.5772	94.8471

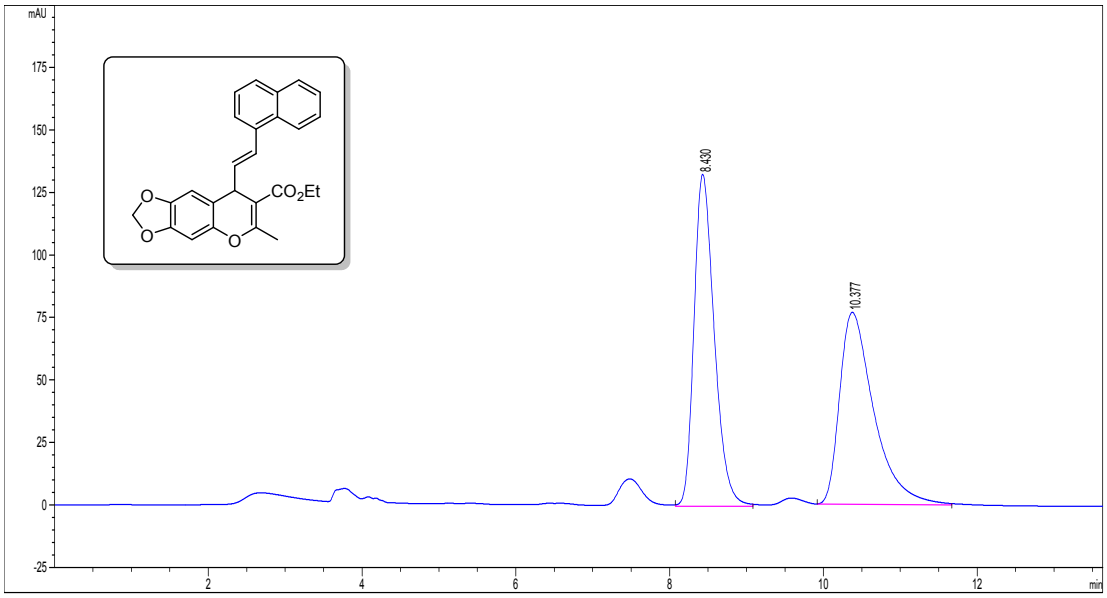


#	Time	Width	Area	Height	Area%
1	12.345	0.3928	5415.6929	229.8174	48.6725
2	13.052	0.4213	5711.1177	225.9395	51.3275

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 10.18 min, t (minor) = 8.41 min; 92% ee.

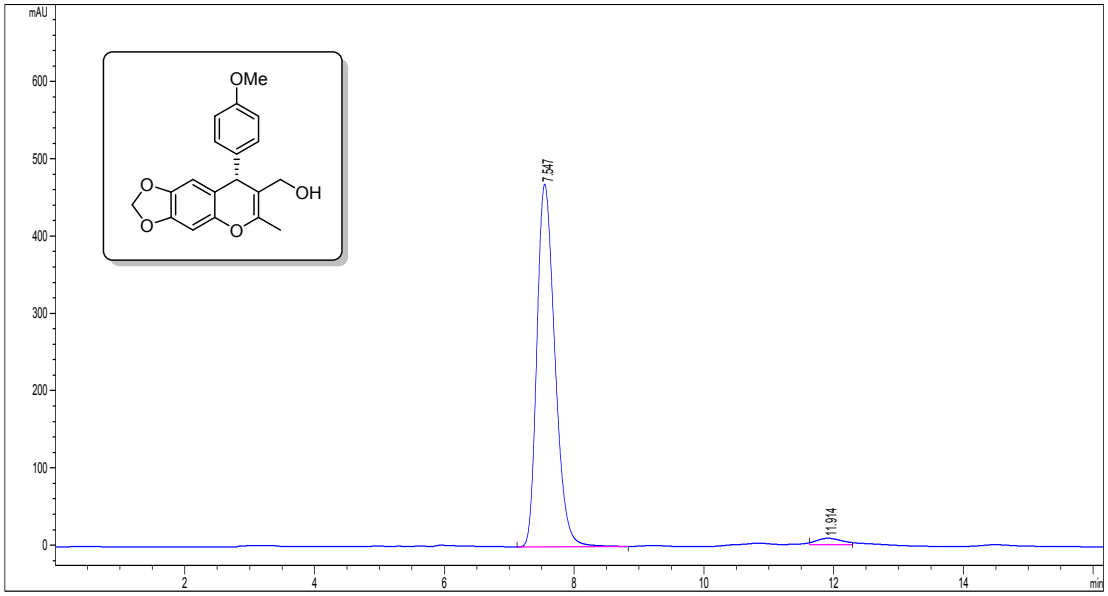


#	Time	Width	Area	Height	Area%
1	8.413	0.2937	404.2397	22.9384	4.0924
2	10.185	0.4839	9473.6172	326.3145	95.9076

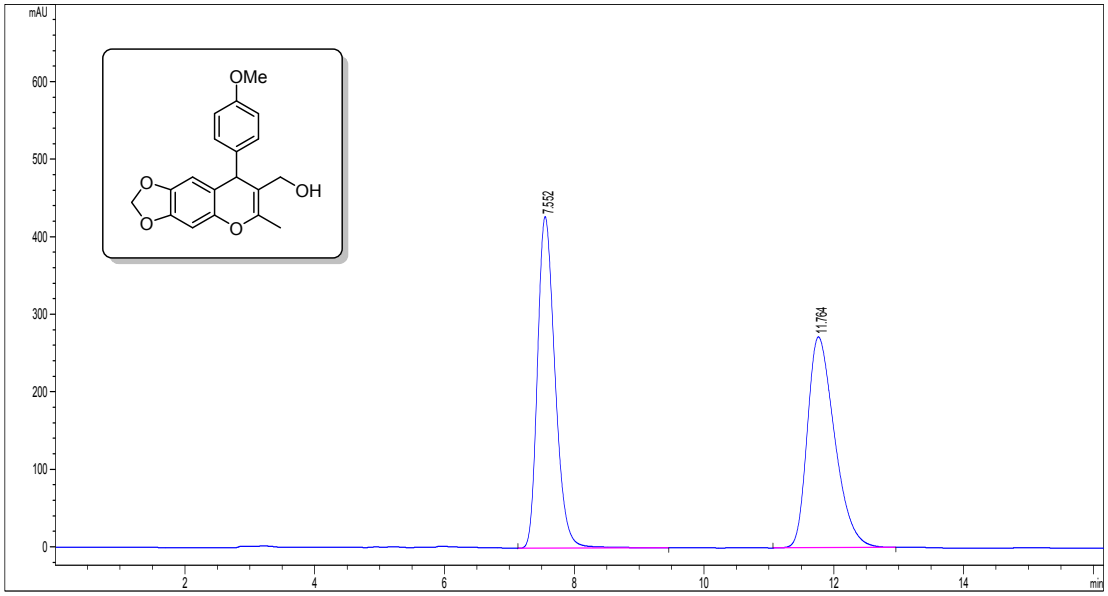


#	Time	Width	Area	Height	Area%
1	8.430	0.3051	2431.8967	132.8485	50.5553
2	10.377	0.5160	2378.4734	76.8238	49.4447

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 80: 20, 1.0 mL/min, 254 nm; t (major) = 7.55 min, t (minor) = 11.91 min; 95% ee.

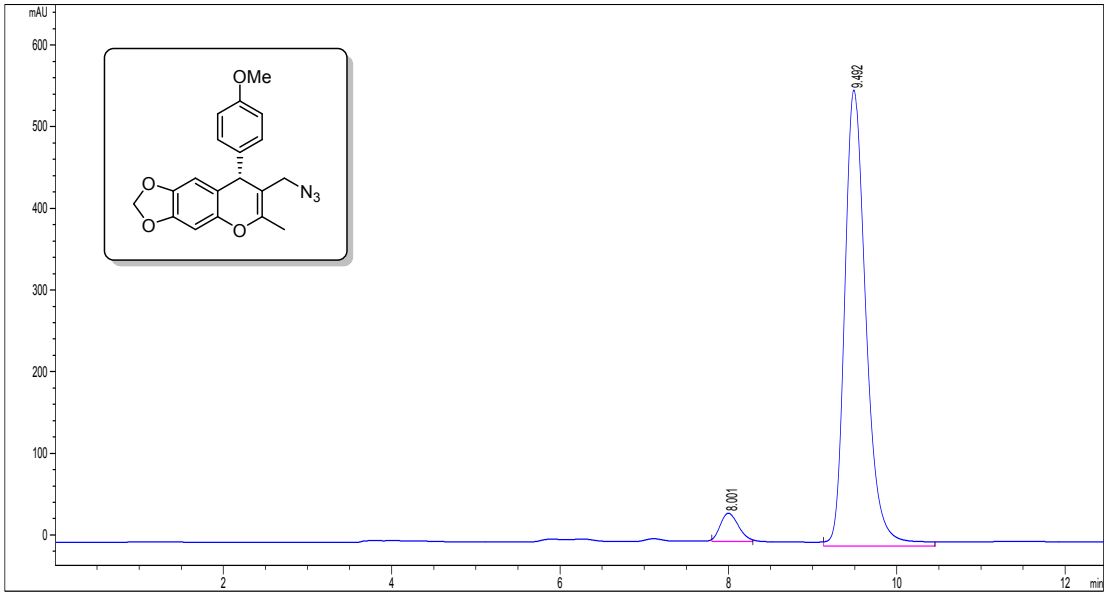


#	Time	Width	Area	Height	Area%
1	7.547	0.2993	9021.9658	469.2894	97.4273
2	11.914	0.4650	238.2393	8.5397	2.5727

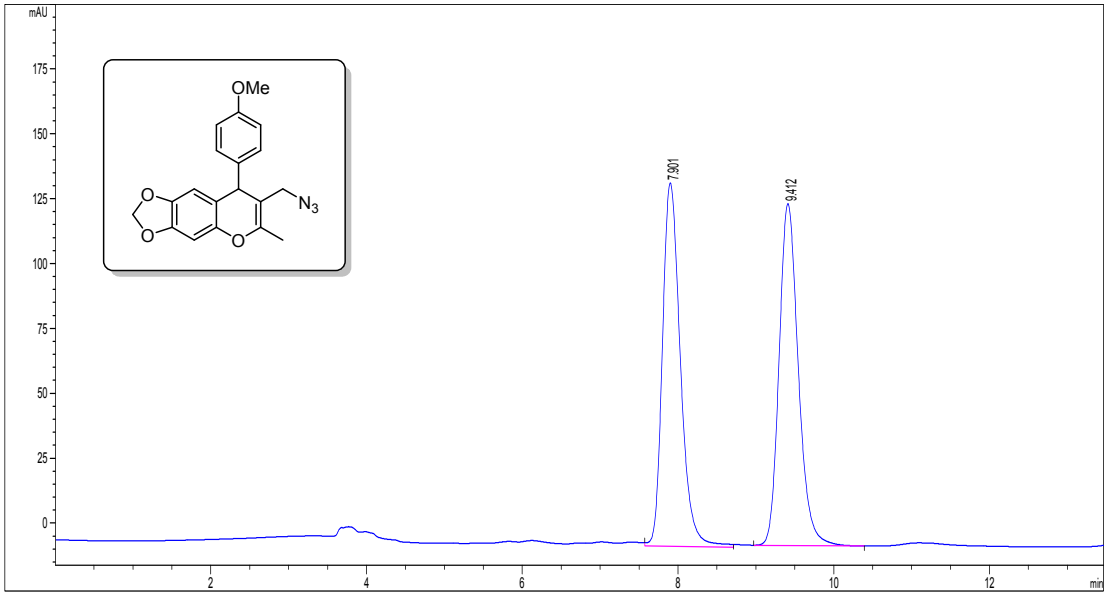


#	Time	Width	Area	Height	Area%
1	7.552	0.2900	8029.5938	427.7153	50.3474
2	11.764	0.4488	7918.7866	271.9067	49.6526

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 90: 10, 0.8 mL/min, 254 nm; t (major) = 9.50 min, t (minor) = 8.00 min; 90% ee.

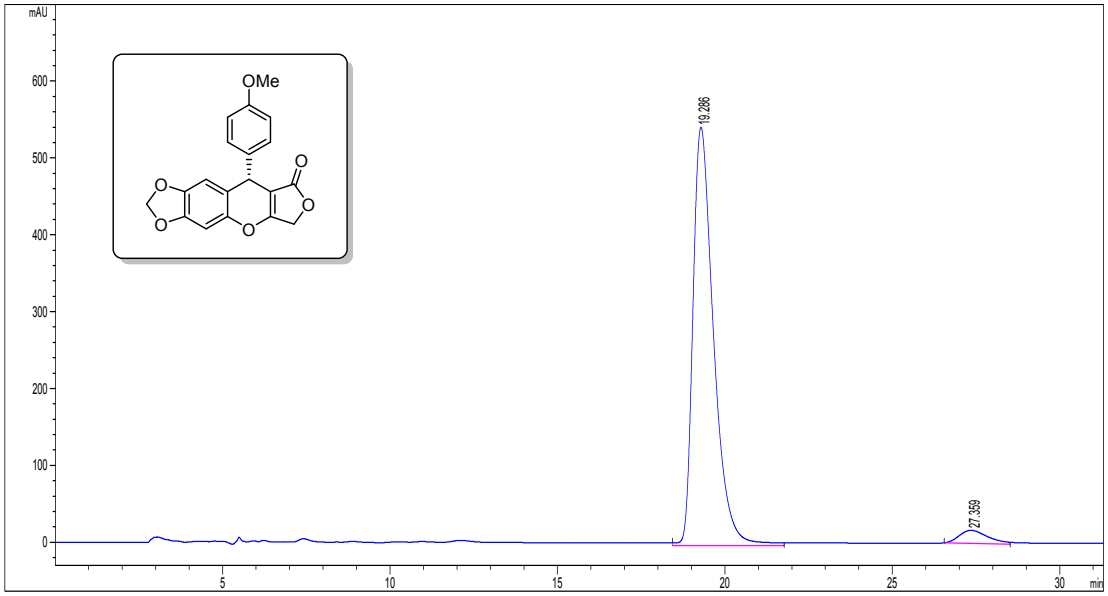


#	Time	Width	Area	Height	Area%
1	8.001	0.2487	515.8508	34.5670	5.0100
2	9.492	0.2918	9780.4961	558.6799	94.9900

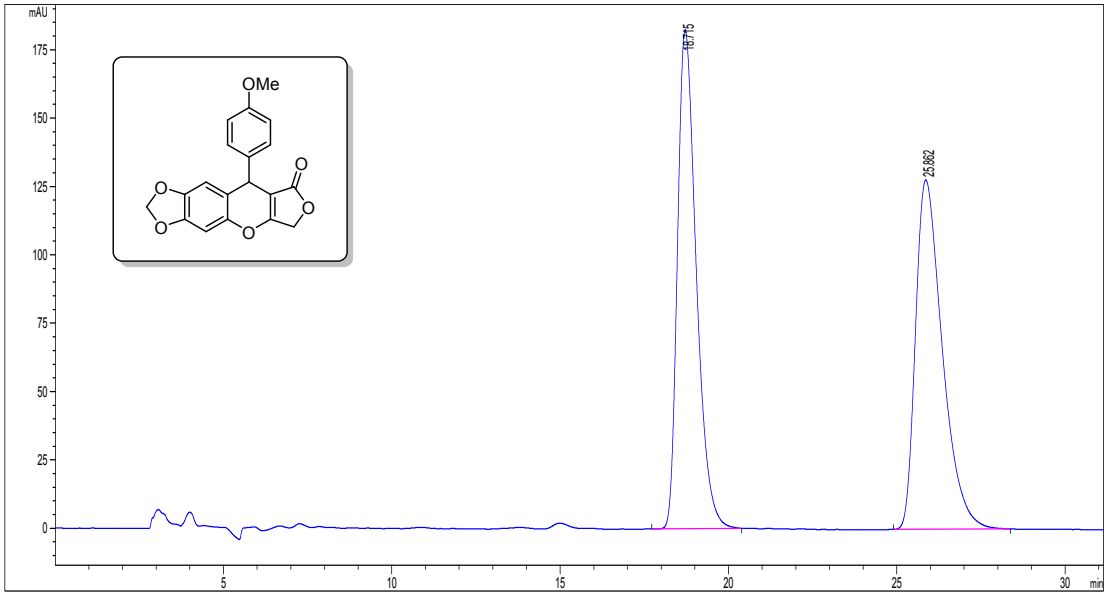


#	Time	Width	Area	Height	Area%
1	7.901	0.2670	2243.2156	140.0278	49.8628
2	9.412	0.2637	2255.5630	131.7546	50.1372

Daicel Chiralcel OD-H column, n-hexane/i-PrOH = 80: 20, 1.0 mL/min, 254 nm; t (major) = 19.29 min, t (minor) = 27.36 min; 92% ee.



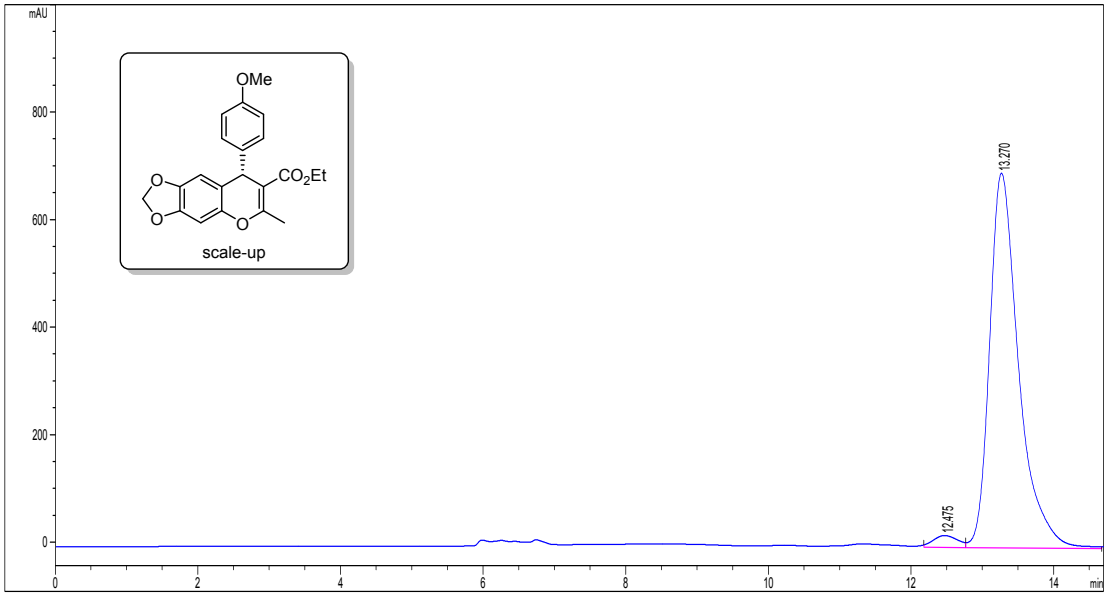
#	Time	Width	Area	Height	Area%
1	19.286	0.7133	2.3299e4	544.3796	95.8441
2	27.359	0.9958	1010.2696	16.9093	4.1559



#	Time	Width	Area	Height	Area%
1	18.715	0.5951	7058.4585	182.5420	49.9433
2	25.862	0.8389	7074.4883	127.7914	50.0567

The HPLC chart for the scale-up synthesis of 3aa

Daicel Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 95 : 5, 0.5 mL/min, 254 nm; t (major) = 13.27 min, t (minor) = 12.48 min; 95% ee.



#	Time	Width	Area	Height	Area%
1	12.475	0.4010	534.8718	22.2313	2.6387
2	13.270	0.4719	1.9735e4	697.0076	97.3613

7. The structure of 3ab by X-ray diffraction analysis

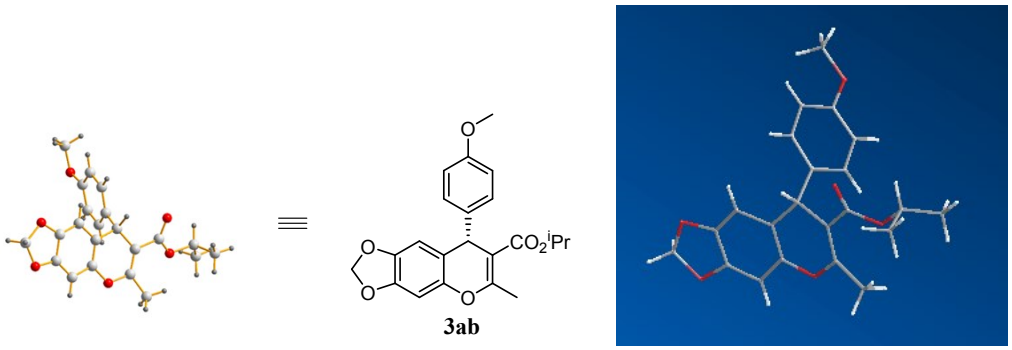


Table 1: Crystal data and structure refinement for (***S***)**-3ae (CCDC 1941671)**

Identification code	exp_6007
Empirical formula	$C_{22}H_{22}O_6$
Formula weight	382.39
Temperature / K	110.1(3)
Crystal system	monoclinic
Space group	$P2_1$
a / Å, b / Å, c / Å	21.7453(6), 10.7363(2), 25.2540(7)
α/°, β/°, γ/°	90, 106.562(3), 90
Volume / Å^3	5651.3(3)
Z	12
ρ_{calc} / mg mm^{-3}	1.348
μ / mm^{-1}	0.810
F(000)	2424
Crystal size / mm^3	0.350 × 0.280 × 0.080
2Θ range for data collection	7.326 to 142.55°
Index ranges	-26 ≤ h ≤ 25, -12 ≤ k ≤ 13, -27 ≤ l ≤ 30
Reflections collected	62103
Independent reflections	19967[R(int) = 0.0347 (inf-0.9Å)]
Data/restraints/parameters	19967/1/1537
Goodness-of-fit on F^2	1.060
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0615, wR_2 = 0.1652
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.1688
Largest diff. peak/hole / e Å^{-3}	0.588/-0.321
Flack Parameters	0.06(5)
Completeness	0.9993

8. References:

1. Jurd, L. *Teterhedron.*, 1977, 33, 163-168.

2. (a) Luan, Y; Schaus, S. E. *J. Am. Chem. Soc.*, 2012, 134, 19965-19968. (b) Lian, X.-L; Adili, A; Liu, B; Tao, Z.-L; Han, Z.-Y. *Org. Biomol. Chem.*, 2017, 15, 3670-3673.