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Supporting Information

Asymmetric Synthesis of Chromans via Friedel-Crafts Alkylation-Hemiketalization Catalysed by *N,N′*-dioxide Scandium (III) Complex

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Contents:

1. General information

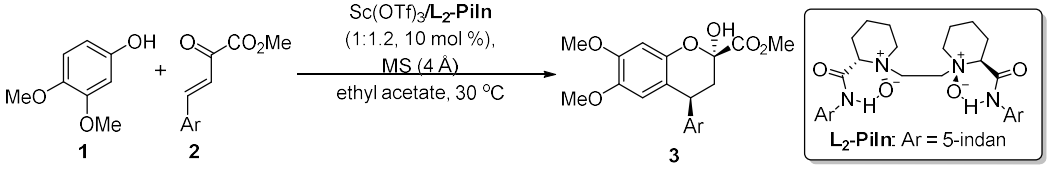
^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (100 MHz and 150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Melting points (m.p.) were measured on electrothermal digital melting point apparatus and were uncorrected. Enantiomer excesses were determined by SFC on Lux 5u cellulose-3 or chiral HPLC analysis on Daicel Chiralcel AD-H/IA/IC in comparison with the authentic racemates. Optical rotations were reported as follows: $[\alpha]^T_D$ (c: g/100 mL, in solvent). HRMS was recorded on a commercial apparatus (ESI Source). All the solvents were purified by usual methods before use. α,β-Unsaturated ketoesters[1a] were synthesized according to the previously reported method.

The corresponding racemic products **3** were obtained by using racemic *N,N′*–dioxide-Sc(OTf)$_3$ as the catalyst.

2. General procedure for chiral *N,N′*-dioxide preparation

The *N,N′*–dioxide ligands were synthesized by the same procedure in the literature.[1b]

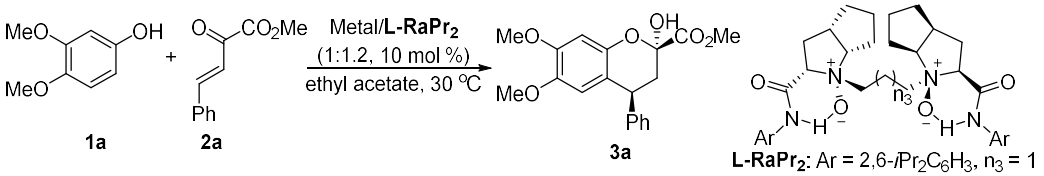
3. General procedure for enantioselective cascade cyclization reaction



1 2 3

To a 1.0 mL volumetric flask, **L$_2$-PiIn** (0.012 mmol, 6.4 mg), Sc(OTf)$_3$ (0.01 mmol, 5.0 mg), 4 Å MS, ester **2** and ethylacetate (0.5 mL) were added. The reaction mixsture stirred at 30 °C under N_2 for 0.5 h. Then, phenol **1** was added to the mixture. After stirring for the 12 h, the crude mixture was purified by flash chromatography on silica gel (ethylacetate : petroleum ether = 4:1) to afford the procut **3**.

4. Screening of metal salts



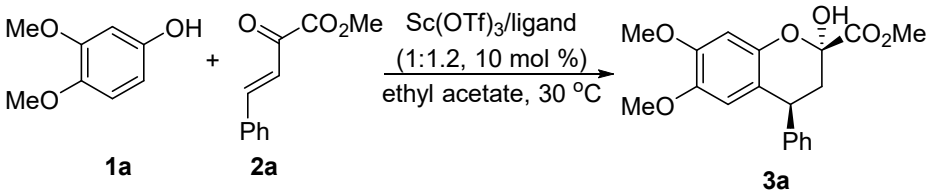
1a 2a 3a

Entry[a]	Metal	ee (%)[c]	yield (%)[b,d]
1	$Cu(OTf)_2$	-	n.r.
2	**$Sc(OTf)_3$**	**0**	**90**
3	$Y(OTf)_3$	-	n.r.
4	$Ni(OTf)_2$	-	n.r.

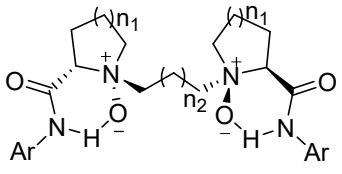
5	$Zn(OTf)_2$	-	n.r.
6	La $(OTf)_3$	-	n.r.
7	$Fe(acac)_3$	-	n.r.
8	$Co(acac)_2$	-	n.r.
9	$ScCl_3$	-	n.r.
10	$Sc(acac)_3$	-	n.r.

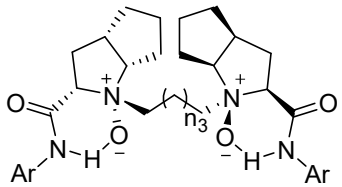
[a] Unless otherwise noted, all reactions were performed with **L-RaPr$_2$** (12 mol %), metal (10 mol %), **1a** (0.1 mmol) and **2a** (0.1 mmol) in ethylacetate (0.5 mL) at 30 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis,

5. Screening of the *N,N'*–dioxide ligands



1a **2a** **3a**





L$_2$-PrPh: Ar = Phenyl, n_1 = 1, n_2 = 0
L$_2$-PiPh: Ar = Phenyl, n_1 = 2, n_2 = 0
L$_2$-PiMe$_2$: Ar = 2,6-$Me_2C_6H_3$, n_1 = 2, n_2 = 0
L$_2$-PiEt$_2$: Ar = 2,6-$Et_2C_6H_3$, n_1 = 2, n_2 = 0
L$_2$-Pi*p*Me: Ar = 4-MeC_6H_4, n_1 = 2, n_2 = 0
L$_2$-Pi*p,m*Me$_2$: Ar = 3,4-$Me_2C_6H_3$, n_1 = 2, n_2 = 0
L$_2$-PiIn: Ar = 5-Indanyl, n_1 = 2, n_2 = 0
L-PrPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$, n_1 = 1, n_2 = 1
L-PiPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$, n_1 = 2, n_2 = 1
L$_2$-PiBn: Ar = benzyl, n_1 = 2, n_2 = 0
L$_2$-PiAd: Ar = adamantyl, n_1 = 2, n_2 = 0
L$_2$-Pi*m*Cl: Ar = 3-ClC_6H_4, n_1 = 2, n_2 = 0
L$_2$-Pi*m*Pr: Ar = 3-*i*PrC_6H_4, n_1 = 2, n_2 = 0
L$_2$-Pi*p*F: Ar = 4-FC_6H_4, n_1 = 2, n_2 = 0
L$_2$-Pi*p*MeO: Ar = 4-$MeOC_6H_4$, n_1 = 2, n_2 = 0
L$_2$-Pi*p*OCF$_3$: Ar = 4-$CF_3OC_6H_4$, n_1 = 2, n_2 = 0
L$_2$-Pi*o,p*Me$_2$: Ar = 2,4-$Me_2C_6H_3$, n_1 = 2, n_2 = 0
L$_2$-Pi*m,m*^{t}Bu$_2$: Ar = 3,5-$tBu_2C_6H_3$, n_1 = 2, n_2 = 0

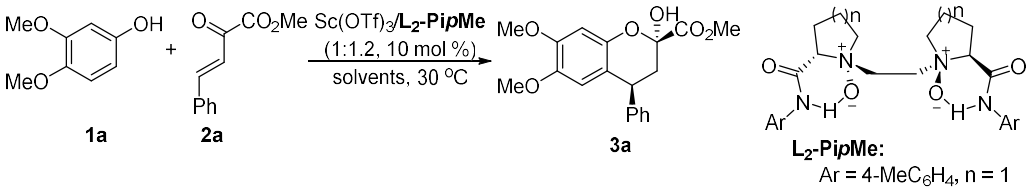
L-RaPr$_2$: Ar = 2,6-*i*$Pr_2C_6H_3$, n_3 = 1
L$_2$-RaPh: Ar = Phenyl, n_3 = 0

Entry[a]	Ligand	yield (%)[b]	ee (%)[c]
1	**L-RaPr$_2$**	90	0
2	**L$_2$-RaPh**	82	20
3	**L$_2$-PrPh**	64	36
4	**L$_2$-PiPh**	95	62
5	**L$_2$-PiMe$_2$**	80	24

6	**L_2-PiEt$_2$**	60	30
7	**L_2-Pi*p*Me**	96	72
8	**L_2-Pi*p*,*m*Me$_2$**	96	82
9[d]	**L_2-Pi*p*,*m*Me$_2$**	96	88
10[d]	**L_2-PiIn**	95	90
11	**L-PiPr$_2$**	30	17
12	**L-PrPr$_2$**	65	20
13	**L_2-PiBn**	33	25
14	**L_2-PiAd**	38	30
15	**L_2-Pi*m*Pr**	97	70
16	**L_2-Pi*m*Cl**	96	57
17	**L_2-Pi*p*OCF$_3$**	95	62
18	**L_2-Pi*p*OMe**	94	67
19	**L_2-Pi*p*F**	94	67
20	**L_2-Pi*o*,*p*Me$_2$**	50	50
21	**L_2-Pi*m*,*m*^{t}Bu$_2$**	88	62
22	**L_2-Pi*m*,*m*Me$_2$**	88	42

[a] Unless otherwise noted, all reactions were performed with ligand (12 mol %), $Sc(OTf)_3$ (10 mol %), **1a** (0.1 mmol) and **2a** (0.1 mmol) in ethylacetate (0.5 mL) at 30 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis, dr = 10:1. [d] 4 Å molecular sieve (10 mg) was used as additive

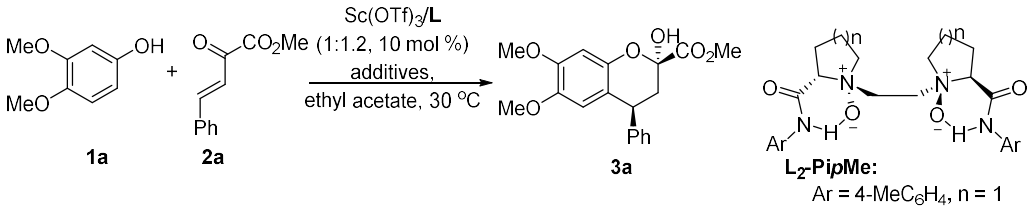
6. Screening of the solvents



Entry[a]	Solvent	ee (%)[c]	yield (%)[b]
1	CH_2Cl_2	42	88
2	THF	37	33
3	toluene	45	80
4	*n*-hexane	-	n.r.
5	Et_2O	33	85
6	methol	0	90

[a] Unless otherwise noted, all reactions were performed with **L** (12 mol %), $Sc(OTf)_3$ (10 mol %), **1a** (0.1 mmol) and **2a** (0.1 mmol) in solvents (0.5 mL) at 30 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis.

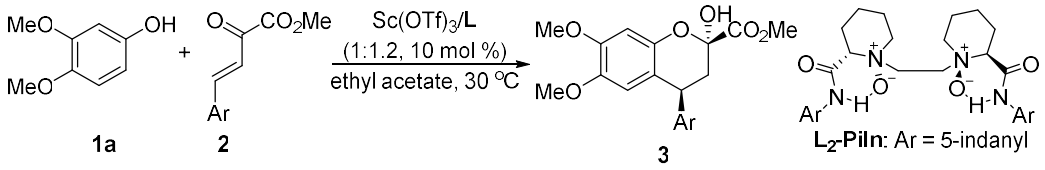
7. Screening of the additives



Entry[a]	Additive (mg)	ee (%)[c]	yield (%)[b]
1	3 Å (10)	84	95
2	4 Å (10)	88	96
3	5 Å (10)	79	95

[a] Unless otherwise noted, all reactions were performed with **L** (12 mol %), $Sc(OTf)_3$ (10 mol %), **1a** (0.1 mmol) and **2a** (0.1 mmol) in solvents (0.5 mL) at 30 °C. [b] Yield of isolated product. [c] Determined by HPLC analysis.

8. Full list of the products 3

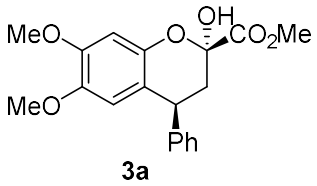


Entry	Ar	3	Yield (%)[b]	ee (%)[c]
1	Ph	**3a**	96	90
2	2-FC_6H_4	**3b**	95	90
3	3-ClC_6H_4	**3c**	95	89
4	3-MeC_6H_4	**3d**	95	90
5	3-$MeOC_6H_4$	**3e**	92	90
6	3-PhenoxylC_6H_4	**3f**	75	93
7	4-FC_6H_4	**3g**	97	91
8	4-ClC_6H_4	**3h**	95	84
9	4-$BrOC_6H_4$	**3i**	96	88
10	4-PhenylC_6H_4	**3j**	95	95
11	3,4-$Cl_2C_6H_4$	**3k**	97	87
12	5-piperonyl	**3l**	92	93
13	2-naphthyl	**3m**	90	88
14	2-thiophenyl	**3n**	89	87
15	3-thiophenyl	**3o**	96	88
16		**3p**	95	80
17	2,6-$Cl_2C_6H_3$		Trace	-

18	2-MeC_6H_4	30	33
19	cyclohexyl	73	20

9. The ananlytical and spectral datas of the products 3

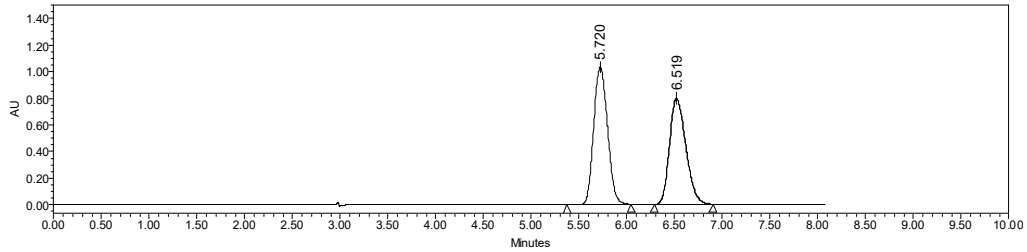
Methyl 2-hydroxy-5,6-dimethoxy-4-phenylchromane-2-carboxylate

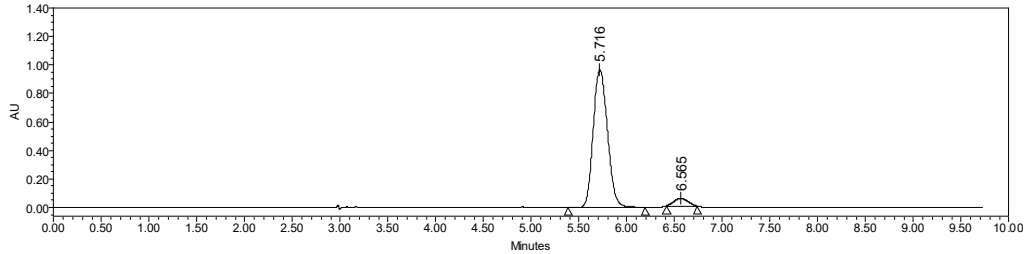


3a

White foam; 95% yield, 14:1 dr, 90% ee. $[\alpha]^{365}_{18}$ = -19 (c = 0.66 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20, flow rate = 1.0 mL/min, retention time: 5.72 min (major) and 6.57 min (minor); HRMS (ESI-TOF) calcd for $C_{19}H_{20}O_6$ ([M+K^+]) = 383.0891, Found 383.0898.

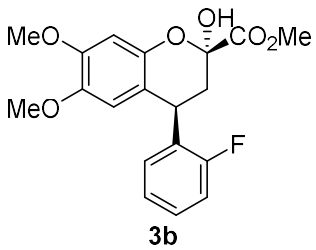
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.32 (m, 2H), 7.29 – 7.24 (m, 3H), 6.52 (s, 0.08H), 6.47 (s, 1H), 6.30 (s, 0.07H), 6.23 (s, 1H), 4.40 (d, *J* = 1.6 Hz, 1H), 4.28 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.58 (s, 3H), 2.41 (td, *J* = 13.2, 1.6 Hz, 1H), 2.28 (dd, *J* = 13.6, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.32, 148.87, 145.33, 143.83, 143.47, 128.82, 128.75, 127.03, 115.96, 112.00, 100.94, 94.31, 56.36, 55.91, 53.57, 37.41, 37.16.





	Retention Time	% Area
1	5.716	94.8
2	6.565	5.2

methyl 4-(2-fluorophenyl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate

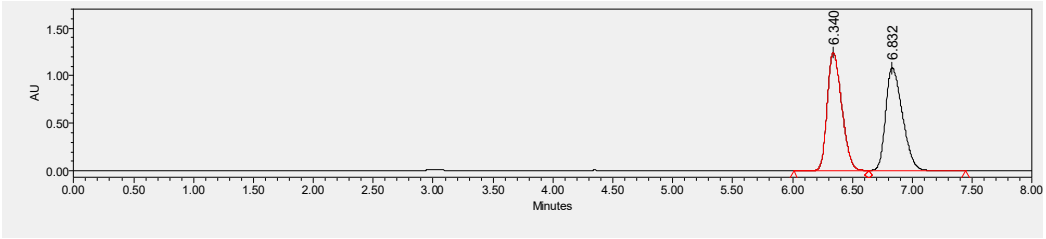


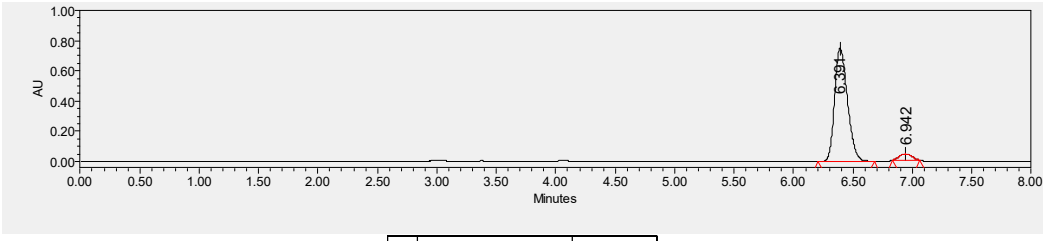
3b

white foam; 95% yield, 10:1 dr, 90% ee. $[\alpha]^{365}_{15}$ = -23.0 (c = 0.82 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20 flow rate = 1.0 mL/min, retention time: 6.35 min (major) and 6.83 min (minor); HRMS (ESI-TOF) calcd for $C_{19}H_{19}O_6F$ ([M+Na^+]) = 385.1058, Found 385.1055;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 1H), 7.21 (m, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 7.07 (m, 1H), 6.53 (s, 0.11H), 6.48 (s, 1H), 6.36 (s, 0.11H), 6.24 (s, 1H), 4.66 (dd, *J* = 12.8, 5.6 Hz, 1H), 4.41 (s, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.69 (s,

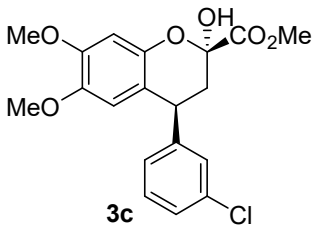
0.35H), 3.61 (s, 3H), 2.46 (t, J = 12.8 Hz, 1H), 2.29 (dd, J = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.20, 162.64 (J = 250 Hz, 1C), 148.91, 145.40, 143.95, 130.31 (J = 2 Hz, 1C), 129.95, 128.69 (J = 8 Hz, 2C), 124.49, 124.46, 115.86 (J = 22 Hz, 2C), 114.81, 111.43, 101.19, 94.26, 56.42, 55.91, 53.56, 35.17.





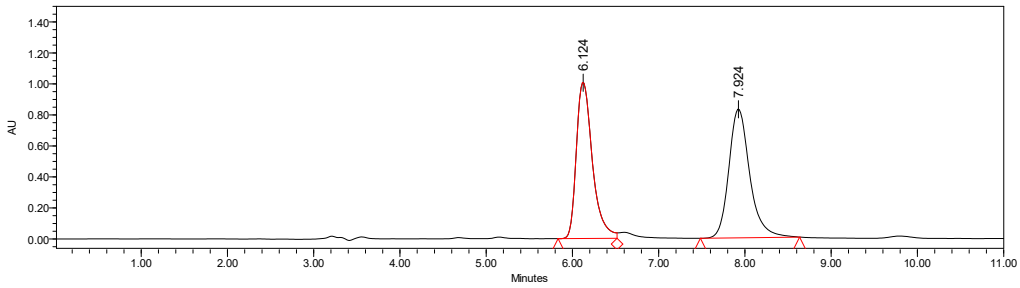
	Retention Time	% Area
1	6.391	94.6
2	6.942	5.4

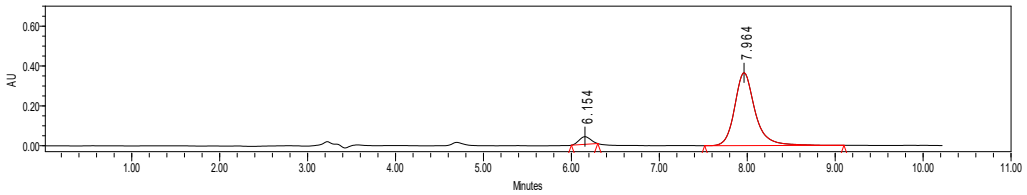
methyl 4-(3-chlorophenyl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate



white foam; 95% yield, 12:1 dr 89% ee. $[\alpha]^{365}_{26}$ = -20 (c = 0.70 in CH_2Cl_2). HPLC IA n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 6.12 min (minor) and 7.92 min (major); HRMS (ESI-TOF) calcd for $C_{19}H_{19}O_6Cl$ ([M+Na$^+$]) = 401.0762, Found 401.0760;

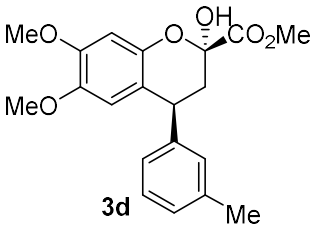
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 3H), 7.18 – 7.12 (m, 1H), 6.51 (s, 0.09H), 6.47 (s, 1H), 6.30 (s, 0.08H), 6.20 (s, 1H), 4.44 (s, 1H), 4.27 (dd, J = 12.8, 6.0 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 4H), 3.67 (s, 0.28H), 3.61 (s, 3H), 2.36 (t, J = 13.2 Hz, 1H), 2.27 (dd, J = 13.2, 6.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.15, 149.10, 145.72, 145.37, 143.95, 134.54, 130.04, 128.89, 127.30, 127.07, 115.08, 111.82, 101.08, 94.16, 56.45, 55.93, 53.61, 37.30, 37.08.





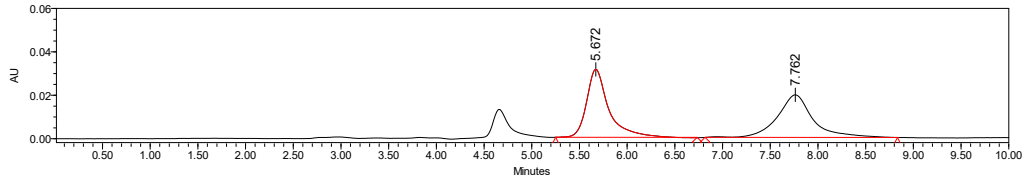
	Retention Time	% Area
1	6.154	5.56
2	7.964	94.44

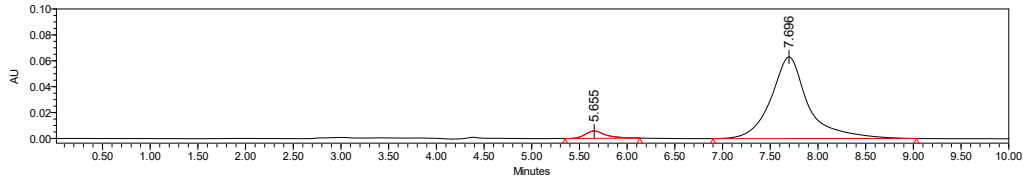
methyl 2-hydroxy-5,6-dimethoxy-4-(m-tolyl)chromane-2-carboxylate



white foam; 95% yield, 13:1 dr, 90% ee. $[\alpha]^{436}_{33}$ = -2.08 (c = 0.72 in CH_2Cl_2). HPLC IA n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 5.67 min (minor) and 7.76 min (major); HRMS (ESI-TOF) calcd for $C_{20}H_{22}O_6$ ([M+Na^+]) = 381.1309, Found 381.1306;

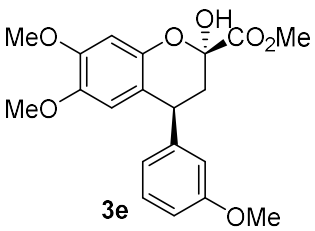
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 13.6, 6.2 Hz, 1H), 7.07 (m, 3H), 6.52 (s, 0.08H), 6.47 (s, 1H), 6.31 (s, 0.08H), 6.25 (s, 1H), 4.39 (s, 1H), 4.24 (dd, *J* = 13.2, 6.0 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.59 (s, 3H), 2.39 (t, *J* = 13.2 Hz, 1H), 2.33 (s, 3H), 2.26 (dd, *J* = 13.6, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 148.91, 145.39, 143.85, 143.40, 138.34, 129.45, 128.58, 127.75, 125.89, 116.13, 112.29, 101.00, 94.36, 56.48, 55.91, 53.50, 37.32, 37.20, 21.43.





	Retention Time	% Area
1	5.655	4.75
2	7.696	95.25

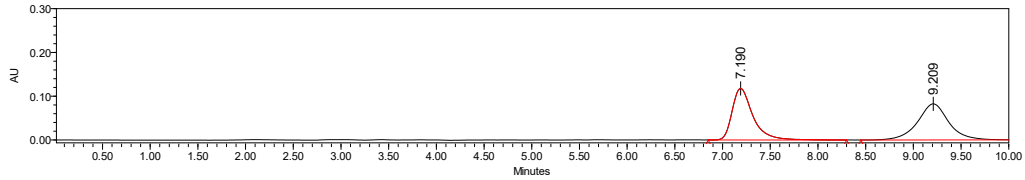
methyl 2-hydroxy-5,6-dimethoxy-4-(3-methoxyphenyl)chromane-2-carboxylate

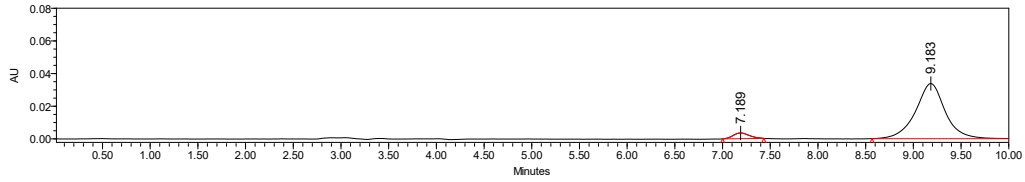


white foam; 92% yield, 13:1 dr, 90% ee. $[\alpha]^{365}_{18}$ = -8.3 (c = 0..80 in CH_2Cl_2). HPLC IA n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 7.19 min (minor) and 9.21 min (major); HRMS (ESI-TOF) calcd for $C_{20}H_{22}O_7$ ([M+K^+]) = 413.0997, Found 413.0998;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.80 – 6.75 (m, 2H), 6.51 (s, 0.08H), 6.46 (s, 1H), 6.32 (s,

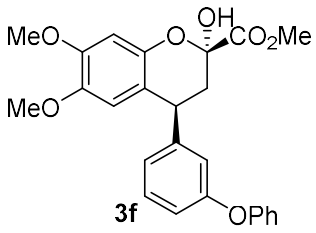
0.08H), 6.27 (s, 1H), 4.42 (d, J = 3.2 Hz, 1H), 4.26 (dd, J = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 3.65 (s, 0.25H), 3.60 (s, 3H), 2.40 (dt, J = 13.2, 1.6 Hz, 1H), 2.27 (dd, J = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 159.90, 148.93, 145.31, 145.11, 143.87, 129.72, 121.21, 115.79, 114.41, 112.43, 112.09, 100.98, 94.32, 56.44, 55.91, 55.23, 53.54, 37.50, 37.09.





	Retention Time	% Area
1	7.189	5.28
2	9.183	94.72

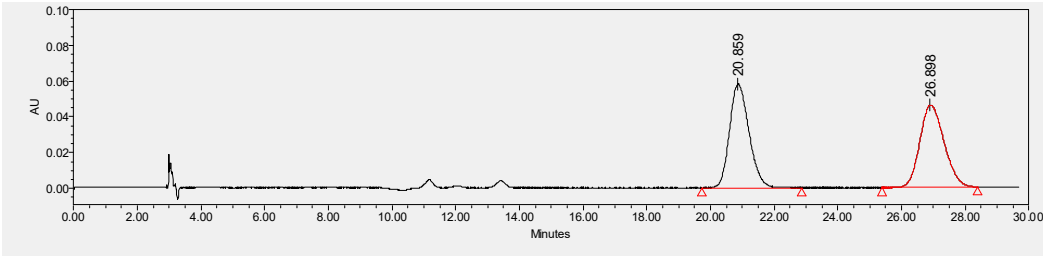
methyl 2-hydroxy-5,6-dimethoxy-4-(3-phenoxyphenyl)chromane-2-carboxylate

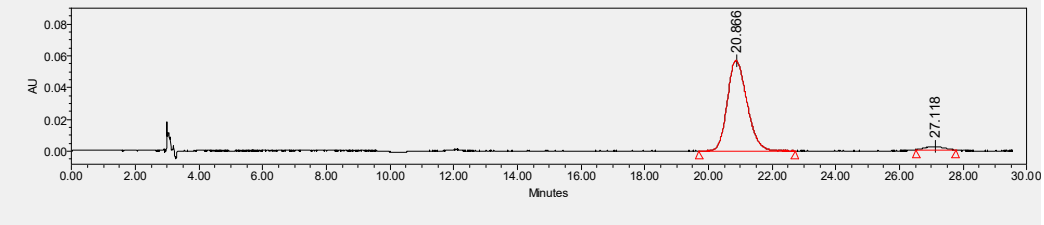


3f

white foam; 75% yield, 14:1 dr, 93% ee. $[\alpha]^{365}_{25}$ = +70 (c = 0.66 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20 flow rate = 1.0 mL/min, retention time: 20.86 min (major) and 26.70 min (minor); HRMS (ESI-TOF) calcd for $C_{25}H_{24}O_7$ ([M+K^+]) = 475.1154, Found 475.1168.

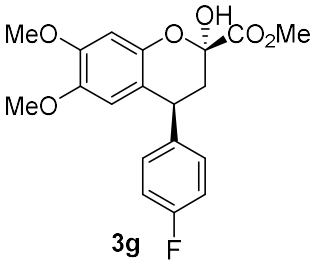
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 1H), 7.30 (m, 2H), 7.09 (m, 1H), 7.03 (s, 1H), 7.00 – 6.96 (m, 2H), 6.93 (m, 2H), 6.49 (s, 0.09H), 6.45 (s, 1H), 6.33 (s, 0.08H), 6.26 (s, 1H), 4.37 (s, 1H), 4.26 (dd, J = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.68 (s, 0.26H), 3.63 (s, 3H), 2.38 (td, J = 13.2, 2.0 Hz, 1H), 2.28 (dd, J = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.24, 157.45, 157.22, 148.99, 145.64, 145.31, 143.88, 130.04, 129.76, 123.82, 123.26, 119.49, 118.63, 117.59, 115.51, 111.93, 101.02, 94.24, 56.43, 55.92, 53.57, 37.35, 36.97.





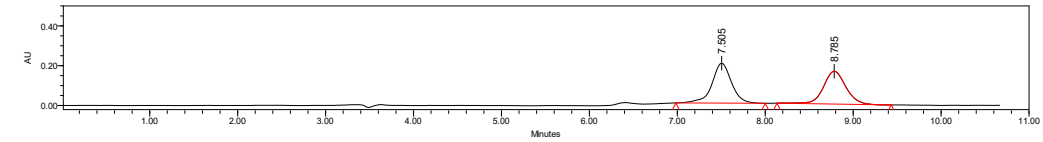
	Retention Time	% Area
1	20.866	96.5
2	27.118	3.5

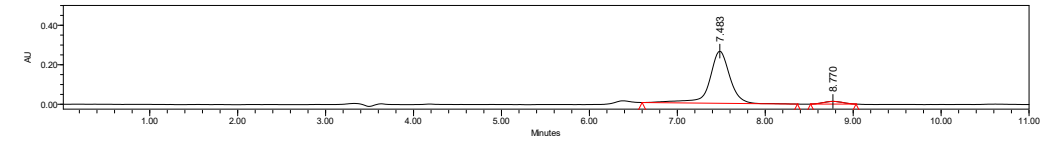
methyl 4-(4-fluorophenyl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate



white foam; 97% yield, 11:1 dr, 91% ee. $[\alpha]^{365}_{33}$ = -9.8 (c = 0.80 in CH_2Cl_2). HPLC IC n-hexane/2-propanol = 70/30, 210 nm flow rate = 1.0 mL/min, retention time: 7.50 min (major) and 8.79 min (minor); HRMS (ESI-TOF) calcd for $C_{19}H_{19}O_6F$ ([M+Na^+]) = 385.1058, Found 385.1057;

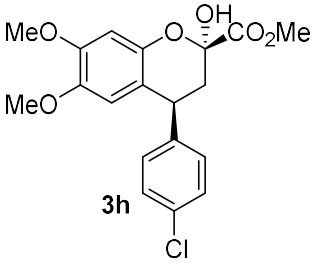
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 2H), 7.03 (t, *J* = 8.4 Hz, 2H), 6.51 (s, 0.09H), 6.46 (s, 1H), 6.27 (s, 0.09H), 6.19 (s, 1H), 4.40 (s, 1H), 4.28 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.65 (s, 0.29H), 3.60 (s, 3H), 2.36 (t, *J* = 13.2 Hz, 1H), 2.25 (dd, *J* = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.20, 163.08 (*J* = 240 Hz, 1C), 149.05, 145.37, 143.94, 139.18 (*J* = 3 Hz, 1C), 130.29 (*J* = 8 Hz, 2C), 115.80, 115.70, 115.49, 111.94, 101.09, 94.28, 56.40, 55.93, 53.54, 37.24, 36.74.





	Retention Time	% Area
1	7.483	95.33
2	8.770	4.67

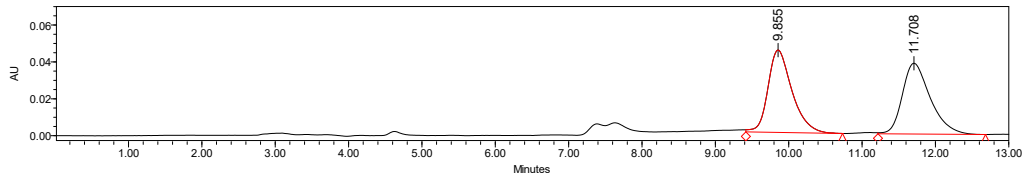
methyl 4-(4-chlorophenyl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate

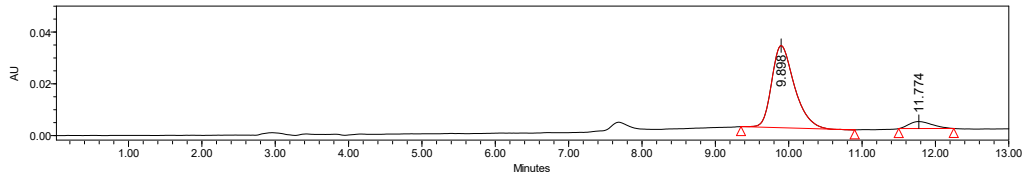


white foam; 95% yield, 12.5:1 dr 84% ee. $[\alpha]^{436}_{33}$ = +7.8 (c = 0.70 in CH_2Cl_2). HPLC ADH n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 9.86 min (major) and 11.71 min (minor); HRMS (ESI-TOF) calcd for $C_{19}H_{19}O_6Cl$ ([M+Na^+]) = 401.0762, Found 401.0766;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 0.08H), 6.46 (s, 1H), 6.28 (s, 0.08H), 6.18 (s, 1H), 4.40 (s, 1H), 4.27 (dd, *J* = 12.8, 6.0 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.66 (s, 0.27H), 3.60 (s, 3H), 2.35 (dt, *J* = 13.2, 2.0 Hz, 1H), 2.25 (dd, *J* = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

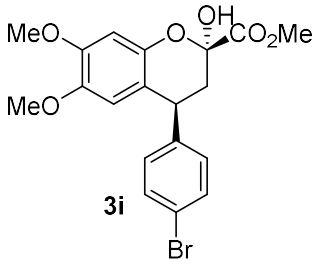
170.15, 149.08, 145.37, 143.95, 142.07, 132.75, 130.15, 128.93, 115.36, 111.79, 101.08, 94.19, 56.42, 55.93, 53.58, 37.15, 36.94.





	Retention Time	% Area
1	9.898	92.06
2	11.774	7.94

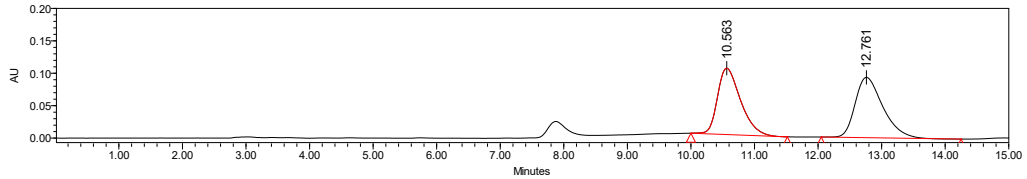
methyl 4-(4-bromophenyl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate

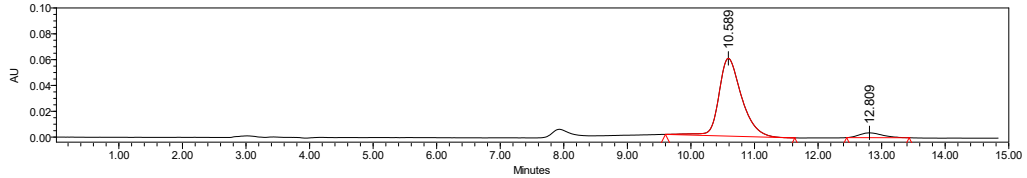


3i

white foam; 96% yield, 11:1 dr, 88% ee. $[\alpha]^{436}_{33}$ = +14 (c = 0.82 in CH_2Cl_2). HPLC ADH n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 10.56 min (major) and 12.76 min (minor); HRMS (ESI-TOF) calcd for $C_{19}H_{19}O_6Br^{78.9}$ ([M+Na$^+$]) = 445.0257, Found 445.0258; $C_{19}H_{19}O_6Br^{80.9}$ ([M+Na$^+$]) = 445.0257, Found 447.0242;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.51 (s, 0.09H), 6.46 (s, 1H), 6.28 (s, 0.08H), 6.18 (s, 1H), 4.41 (d, *J* = 2.0 Hz, 1H), 4.26 (dd, *J* = 12.8, 6.0 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.66 (s, 0.27H), 3.61 (s, 3H), 2.34 (dt, *J* = 13.2, 2.0 Hz, 1H), 2.25 (dd, *J* = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.13, 149.09, 145.38, 143.96, 142.62, 131.89, 130.54, 120.83, 115.25, 111.78, 101.09, 94.17, 56.44, 55.92, 53.59, 37.12, 37.03.

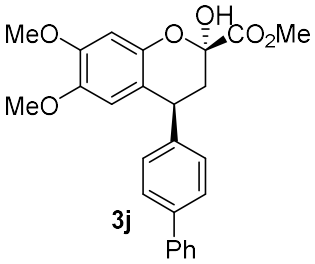




	Retention Time	% Area
1	10.589	94.11

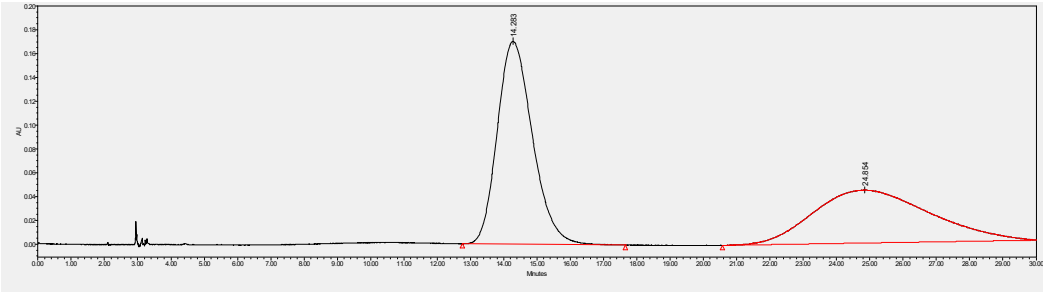
2	12.809	5.89

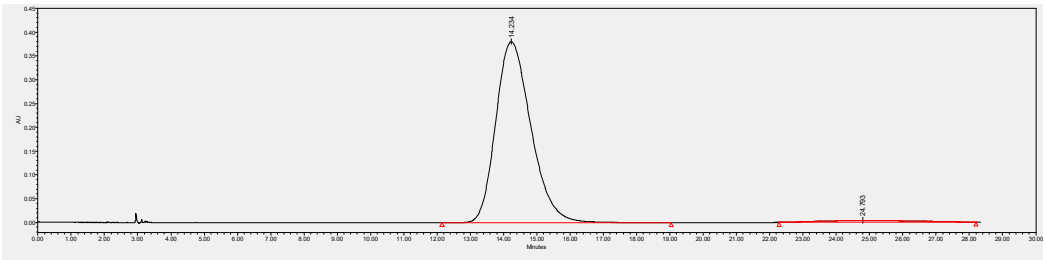
methyl 4-([1,1'-biphenyl]-4-yl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate



white foam; 95% yield, 14:1 dr, 95% ee. $[\alpha]^{365}_{18}$ = -69 (c = 0.80 in CH_2Cl_2). SFC Lux 5u cellulose-3 CO_2/2-propanol = 70/30, flow rate = 1.0 mL/min, retention time: 14.28 min (major) and 24.85 min (minor); HRMS (ESI-TOF) calcd for $C_{25}H_{24}O_6$ ([M+Na^+]) = 443.1465, Found 443.1463;

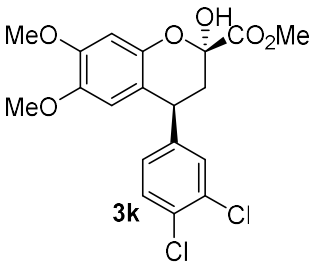
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 3H), 6.54 (s, 0.07H), 6.49 (s, 1H), 6.36 (s, 0.07H), 6.30 (s, 1H), 4.49 (d, *J* = 1.6 Hz, 1H), 4.34 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.66 (s, 0.24H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.34, 148.97, 145.43, 143.90, 142.61, 140.72, 139.87, 129.24, 128.83, 127.44, 127.31, 127.01, 115.84, 112.10, 101.04, 94.34, 56.47, 55.93, 53.57, 37.27, 37.12.





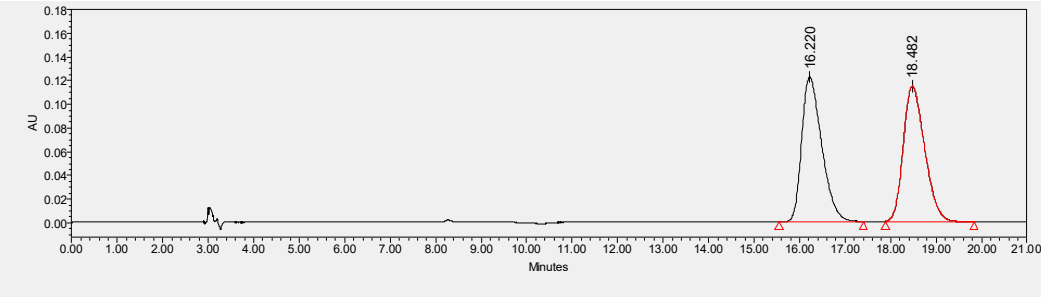
	Retention Time	% Area
1	14.234	97.31
2	24.793	2.69

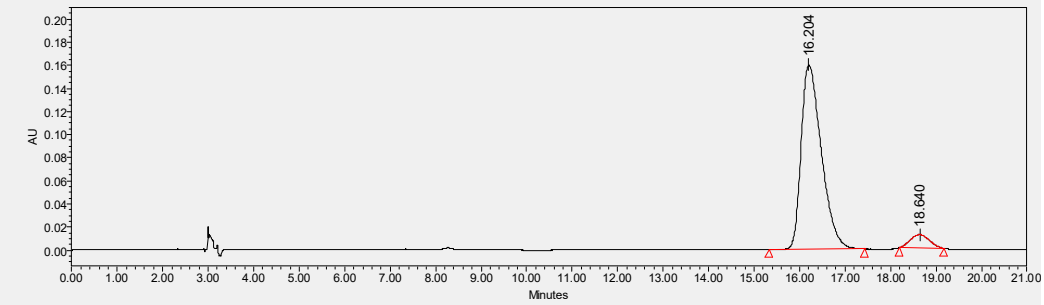
methyl 4-(3,4-dichlorophenyl)-2-hydroxy-5,6-dimethoxychromane-2-carboxylate



white foam; 97% yield, 11:1 dr, 87% ee. $[\alpha]^{365}_{25}$ = +7.3 (c = 0.82 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20 flow rate = 1.0 mL/min, retention time: 16.22 min (major) and 18.48 min (minor); HRMS (ESI-TOF) calcd for $C_{19}H_{18}O_6Cl^{35}{}_2$ ([M+K^+]) = 451.0112, Found 451.0117, $C_{19}H_{18}O_6Cl^{37}{}_2$ ([M+K^+]) = 453.0083, Found 453.0092;

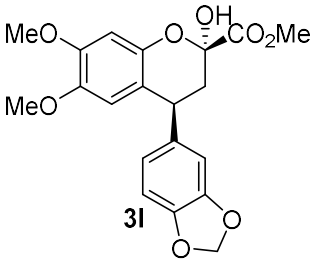
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 2.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 0.08H), 7.10 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.03 (dd, *J* = 8.4, 2.0 Hz, 0.08H), 6.51 (s, 0.09H), 6.47 (s, 1H), 6.30 (s, 0.09H), 6.18 (s, 1H), 4.43 (d, *J* = 1.2 Hz, 1H), 4.26 (dd, *J* = 12.4, 6.0 Hz, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 3.69 (s, 0H), 3.63 (s, 3H), 2.37 – 2.29 (m, 1H), 2.28 – 2.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.00, 149.26, 145.40, 144.05, 144.01, 132.77, 131.05, 130.75, 130.73, 128.20, 114.58, 111.61, 101.18, 94.06, 56.50, 55.94, 53.63, 37.09, 36.92.





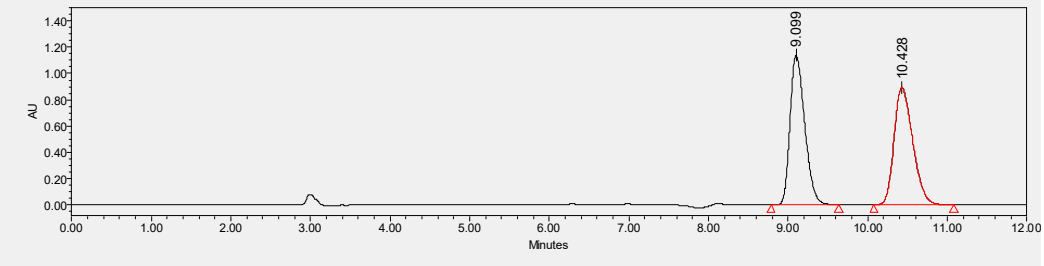
	Retention Time	% Area
1	16.204	93.6
2	18.640	6.5

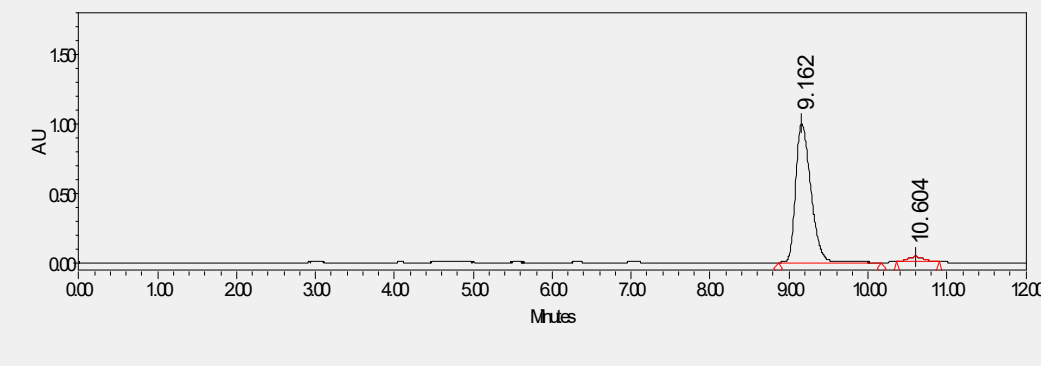
methyl 7-hydroxy-9-phenyl-8,9-dihydro-7H-[1,3]dioxolo[4,5-f]chromene-7-carboxylate



white foam; 92% yield, 11:1 dr, 93% ee. $[\alpha]^{365}_{26}$ = -37.2 (c = 0.7 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20 flow rate = 1.0 mL/min, retention time: 9.10 min (major) and 10.43 min (minor); HRMS (ESI-TOF) calcd for $C_{20}H_{20}O_8$ ([M+Na^+]) = 411.1050, Found 411.1052;

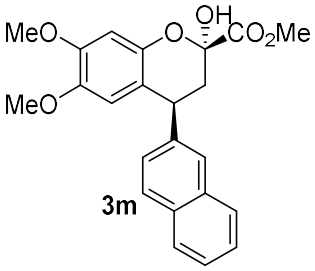
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.81 – 6.73 (m, 2H), 6.68 (m, 1H), 6.50 (s, 0.09H), 6.45 (s, 1H), 6.33 (s, 0.09H), 6.28 (s, 1H), 5.95 (d, *J* = 4.0 Hz, 2H), 4.44 (d, *J* = 2.0 Hz, 1H), 4.28 (s, 0.09H), 4.20 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.82 (s, 3H), 3.67 (s, 0.25H), 3.63 (s, 3H), 2.35 (td, *J* = 13.2, 1.6 Hz, 1H), 2.24 (dd, *J* = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.28, 148.91, 147.95, 146.53, 145.28, 143.86, 137.23, 122.13, 116.01, 111.99, 108.76, 108.31, 101.02, 100.95, 94.34, 56.46, 55.91, 53.55, 37.23, 37.15.





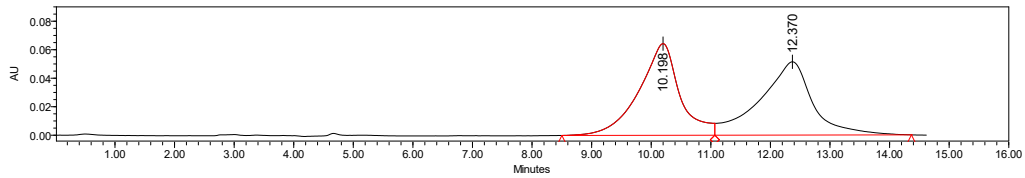
	Retention Time	% Area
1	9.162	96.6
2	10.598	3.3

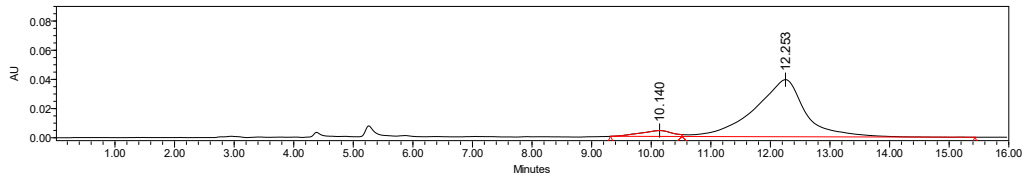
methyl 2-hydroxy-5,6-dimethoxy-4-(naphthalen-2-yl)chromane-2-carboxylate



white foam; 90% yield, 11:1 dr, 88% ee. $[\alpha]^{365}_{33}$ = +197 (c = 0.70 in CH_2Cl_2). HPLC IA n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 10.20 min (minor) and 12.37 min (major); HRMS (ESI-TOF) calcd for $C_{23}H_{22}O_6$ ([M+Na^+]) = 417.1309, Found 417.1307;

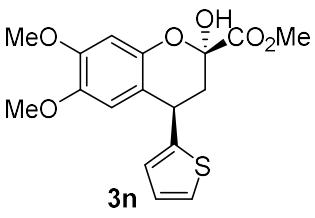
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (m, 4H), 7.54 – 7.42 (m, 2H), 7.30 (d, *J* = 8.8 Hz, 1H), 6.56 (s, 0.09H), 6.50 (s, 1H), 6.32 (s, 0.09H), 6.25 (s, 1H), 4.47 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 3.51 (s, 3H), 2.50 (t, *J* = 13.2 Hz, 1H), 2.32 (dd, *J* = 13.6, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 149.04, 145.47, 144.00, 140.82, 133.60, 132.68, 128.59, 127.84, 127.72, 127.67, 126.51, 126.21, 125.79, 115.85, 112.18, 101.12, 94.37, 56.41, 55.94, 53.54, 37.65, 37.14.





	Retention Time	% Area
1	10.140	6.08
2	12.253	93.92

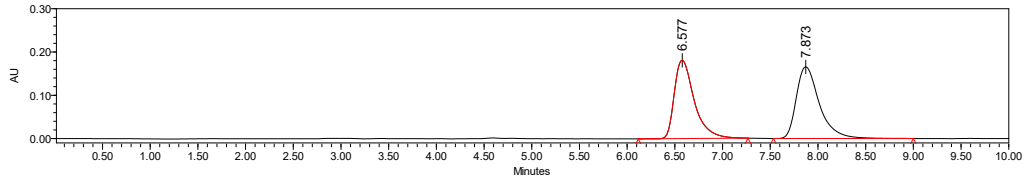
methyl 2-hydroxy-5,6-dimethoxy-4-(thiophen-2-yl)chromane-2-carboxylate

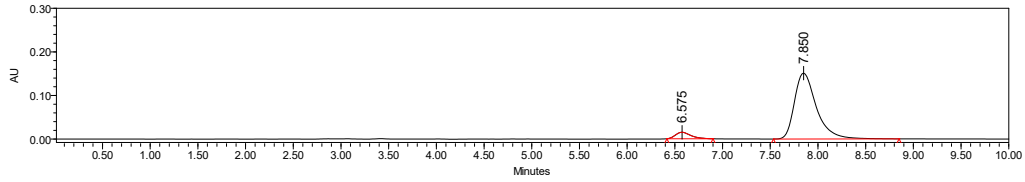


white foam; 89% yield, 10:1 dr, 87% ee. $[\alpha]^{436}_{33}$ = -25 (c = 0.64 in CH_2Cl_2). HPLC IA n-hexane/2-propanol = 70/30, 210 nm, flow rate = 1.0 mL/min, retention time: 6.58 min (minor) and 7.87 min (major);

HRMS (ESI-TOF) calcd for $C_{17}H_{18}O_6S$ ([M+Na^+]) = 373.0716, Found 373.0716;

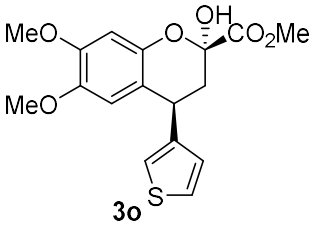
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 4.8 Hz, 1H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.99 (dd, *J* = 4.8, 3.2 Hz, 1H), 6.44 (s, 2H), 4.64 (dd, *J* = 12.8, 5.6 Hz, 1H), 4.43 (s, 1H), 3.90 (s, 3H), 3.86 (s, 0H), 3.81 (s, 3H), 3.65 (s, 3H), 2.48 (t, *J* = 12.8 Hz, 1H), 2.38 (dd, *J* = 13.2, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.11, 149.17, 146.51, 144.74, 143.91, 126.65, 126.15, 124.47, 115.66, 111.62, 100.92, 94.25, 56.41, 55.92, 53.59, 37.70, 32.71.





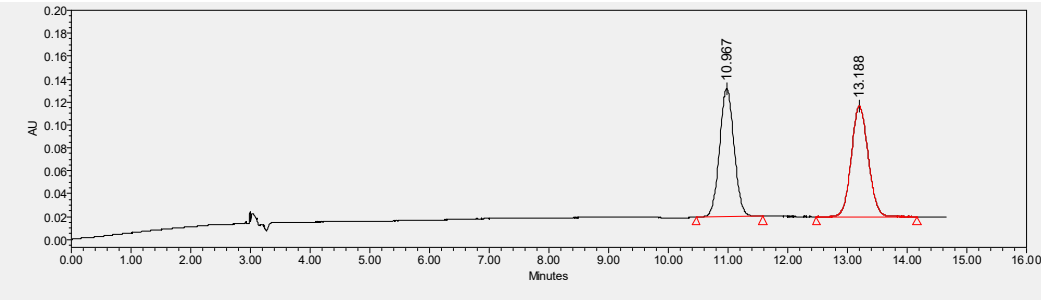
	Retention Time	% Area
1	6.575	6.40
2	7.850	93.60

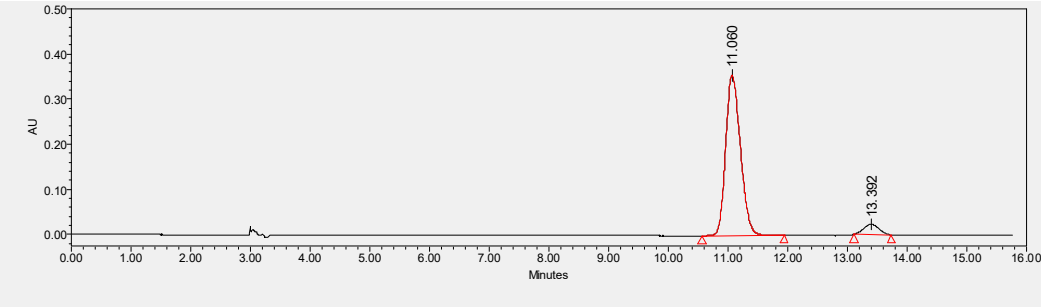
methyl 2-hydroxy-5,6-dimethoxy-4-(thiophen-2-yl)chromane-2-carboxylate



white foam; 96% yield, 11:1 dr, 88% ee. $[\alpha]^{365}_{25}$ = +67.5 (c = 0.74 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20 flow rate = 1.0 mL/min, retention time: 11.06 min (major) and 13.39 min (minor); HRMS (ESI-TOF) calcd for $C_{17}H_{18}O_6S$ ([M+K^+]) = 389.0456, Found 389.0464;

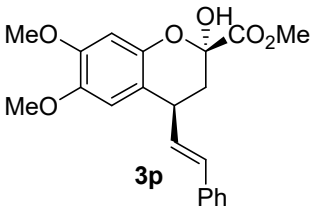
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m, 1H), 7.20 – 7.16 (m, 1H), 6.91 (d, *J* = 4.8 Hz, 1H), 6.51 (s, 0.09H), 6.46 (s, 1H), 6.41 (s, 0.09H), 6.31 (s, 1H), 4.44 (dd, *J* = 12.8, 5.2 Hz, 1H), 4.39 (d, *J* = 2.0 Hz, 1H), 3.89 (d, *J* = 0.8 Hz, 3H), 3.86 (d, *J* = 0.8 Hz, 0.27H), 3.82 (s, 3H), 3.69 (d, *J* = 0.7 Hz, 0.26H), 3.63 (d, *J* = 0.8 Hz, 3H), 2.41 (t, *J* = 13.2 Hz, 1H), 2.27 (dd, *J* = 13.2, 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.26, 148.95, 144.93, 143.85, 143.56, 127.23, 126.27, 122.44, 115.64, 111.64, 100.97, 94.31, 56.40, 55.92, 53.56, 36.33, 32.49.





	Retention Time	% Area
1	11.060	94
2	13.392	6

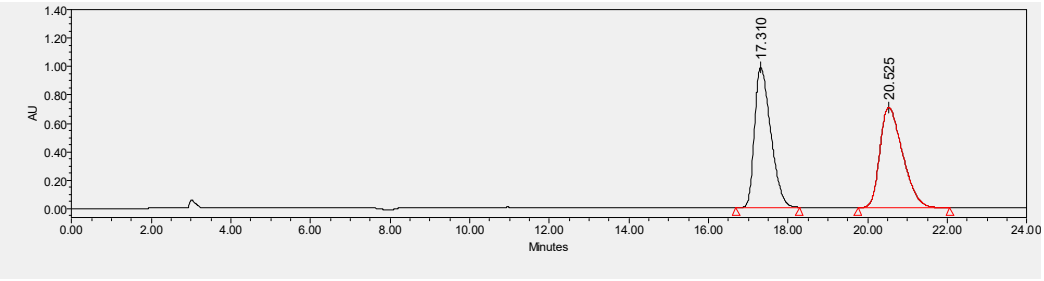
methyl (E)-2-hydroxy-5,6-dimethoxy-4-styrylchromane-2-carboxylate

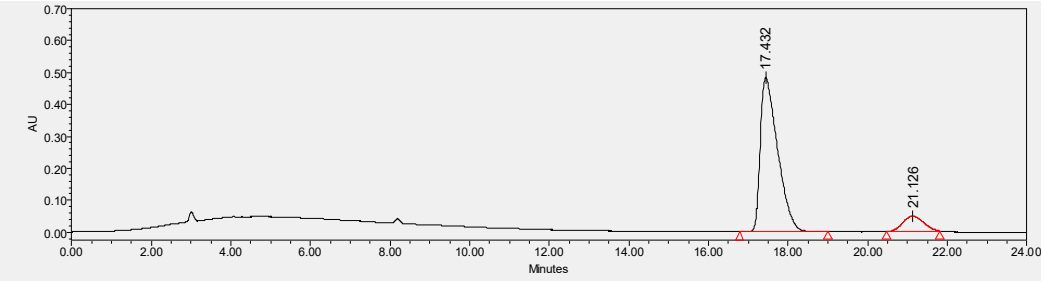


3p

white foam; 95% yield, 10:1 dr, 80% ee. $[\alpha]^{D}_{15}$ = -54 (c = 0.94 in CH_2Cl_2). SFC Lux 5u cellulose-3 CO_2/2-propanol = 80/20, flow rate = 1.0 mL/min, retention time: 17.31 min (major) and 20.53 min (minor); HRMS (ESI-TOF) calcd for $C_{21}H_{22}O_6$ ([M+Na^+]) = 393.1309, Found 393.1310;

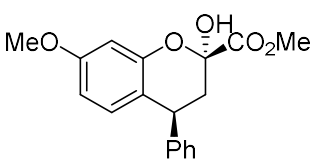
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.20 (m, 1H), 6.69 (m, 2H), 6.46 (s, 1H), 6.13 (dd, *J* = 15.6, 9.2 Hz, 1H), 4.40 (d, *J* = 0.8 Hz, 1H), 4.37 (s, 0.16H), 3.90 (s, 3H), 3.81 (s, 3H), 3.75 (s, 3H), 2.21 (t, *J* = 9.2 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.31, 149.06, 144.73, 143.96, 136.94, 132.95, 130.89, 128.68, 128.58, 127.62, 126.38, 126.34, 114.66, 111.38, 101.22, 94.15, 56.55, 55.95, 53.58, 34.98, 34.60.





	Retention Time	% Area
1	17.432	90.07
2	21.126	9.93

methyl 2-hydroxy-5-methoxy-4-phenylchromane-2-carboxylate

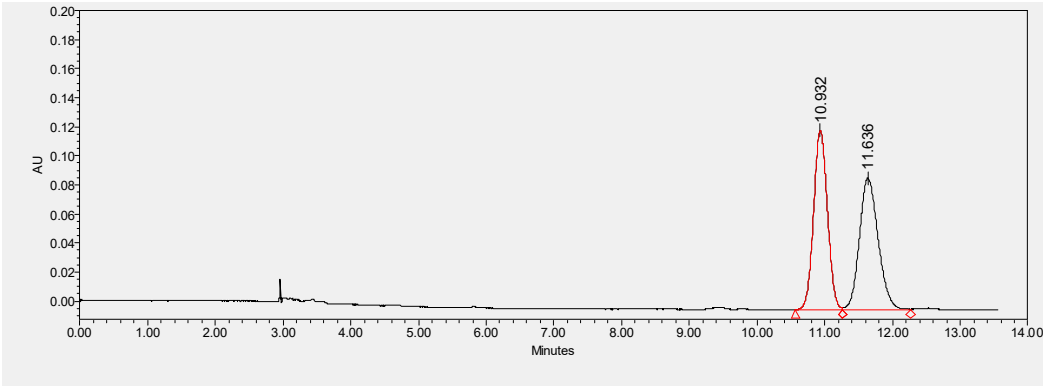


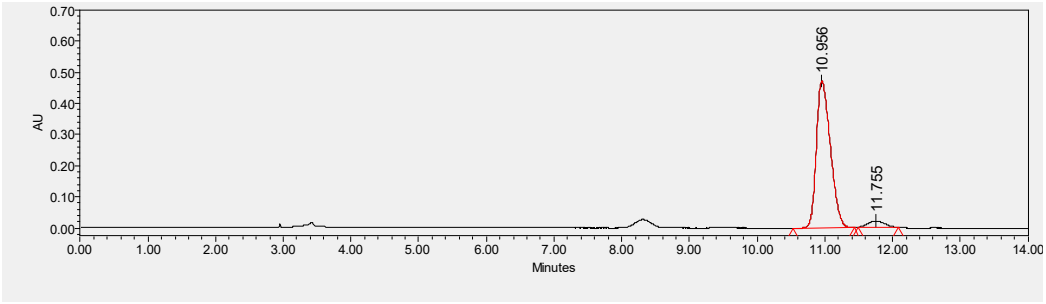
3q

white foam; 71% yield, 10:1 dr, 90% ee. $[\alpha]^{365}_{18}$ = +30 (c = 0.52 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/methol = 90/10 flow rate =

1.0 mL/min, retention time: 10.93 min (major) and 11.64min (minor); HRMS (ESI-TOF) calcd for $C_{18}H_{18}O_5$ ([M+K$^+$]) = 353.0786, Found 353.0791;

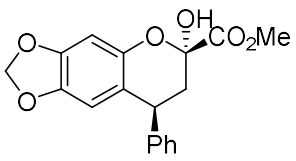
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (m, 2H), 7.29 – 7.25 (m, 3H), 6.63 (d, *J* = 8.4 Hz, 1H), 6.46 – 6.41 (m, 2H), 4.43 (d, *J* = 2.0 Hz, 1H), 4.28 (dd, *J* = 13.2, 5.6 Hz, 2H), 3.90 (s, 4H), 3.74 (s, 3H), 3.35 (s, 0.29H), 2.44 (td, *J* = 13.2, 2.0 Hz, 1H), 2.27 (dd, *J* = 13.6, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.27, 159.41, 152.15, 143.52, 129.96, 128.86, 128.73, 126.97, 117.78, 108.49, 101.74, 94.49, 55.34, 53.58, 37.08, 36.80.





	Retention Time	% Area
1	10.956	95.13
2	11.755	4.87

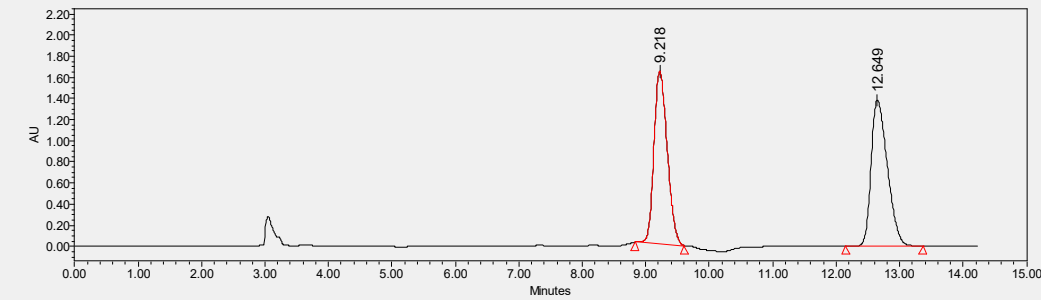
methyl 7-hydroxy-9-phenyl-8,9-dihydro-7H-[1,3]dioxolo[4,5-f]chromene-7-carboxylate

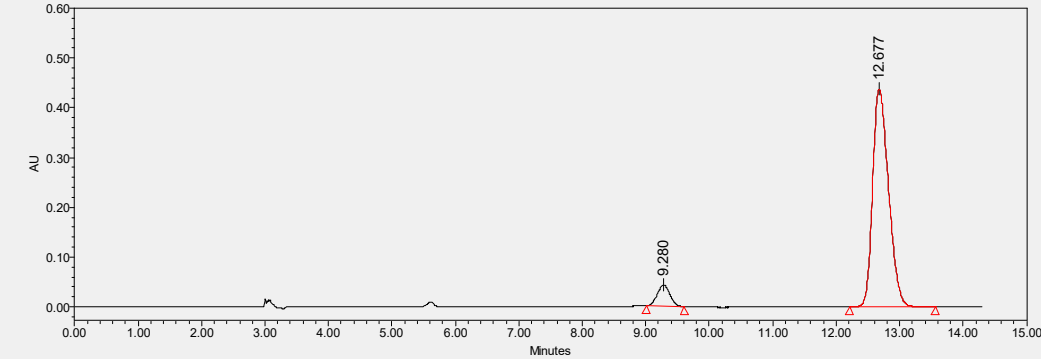


3r

white foam; 84% yield, 12.5:1 dr, 86% ee. $[\alpha]^{365}_{18}$ = -100 (c = 0.60 in CH_2Cl_2). SFC Lux 5u cellulose-3, CO_2/2-propanol = 80/20 flow rate = 1.0 mL/min, retention time: 9.22 min (minor) and 12.65 min (major); HRMS (ESI-TOF) calcd for $C_{18}H_{16}O_6$ ([M+K$^+$]) = 367.0578, Found 367.0585;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 2H), 7.29 (m, 1H), 7.26 – 7.22 (m, 2H), 6.47 (s, 0.06H), 6.42 (s, 1H), 6.22 (s, 0.06H), 6.18 (d, *J* = 0.8 Hz, 1H), 5.85 (d, *J* = 1.2 Hz, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 4.42 (d, *J* = 2.0 Hz, 1H), 4.23 (dd, *J* = 12.8, 5.6 Hz, 1H), 3.88 (s, 3H), 3.85 (s, 0.24H), 2.41 (td, *J* = 13.2, 2.0 Hz, 1H), 2.25 (dd, *J* = 13.6, 5.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.26, 146.89, 145.96, 143.42, 142.27, 128.82, 128.80, 127.07, 117.36, 108.11, 101.02, 98.73, 94.28, 53.54, 37.77, 36.71.





	Retention Time	% Area
1	9.280	7
2	12.677	93

10. X-ray structure of the product 3i and spectra for control experiments

Bond precision: C-C = 0.0060 A Wavelength=1.54184

Cell: a=22.0623(4) b=14.5144(3) c=5.67392(10) alpha=90 beta=90 gamma=90 Temperature: 294 K

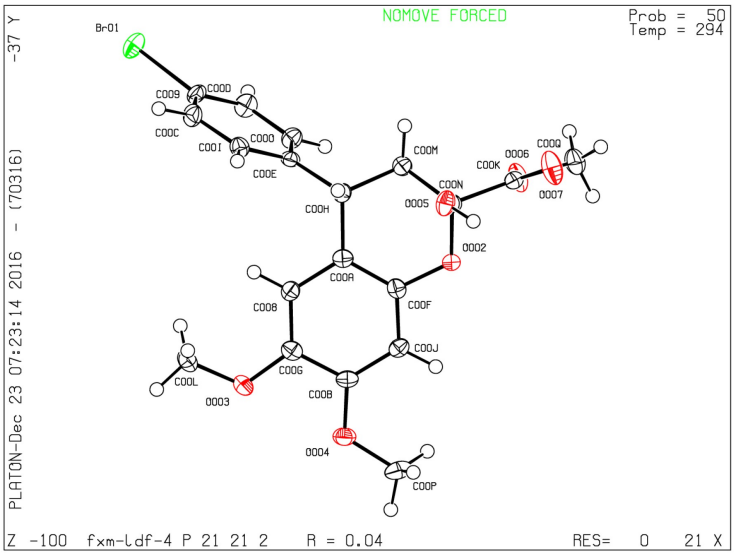
Calculated Reported Volume 1816.91(6) 1816.91(6) Space group P 21 21 2 P 21 21 2 Hall group P 2 2ab P 2 2ab Moiety formula C19 H19 Br O6 C19 H19 Br O6 Sum formula C19 H19 Br O6 C19 H19 Br O6 Mr 423.24 423.25 Dx,g cm-3 1.547 1.547 Z 4 4 Mu (mm-1) 3.378 3.378 F000 864.0 864.0 F000' 863.77 h,k,lmax 26,17,6 26,17,6 Nref 3261[1916] 3260 Tmin,Tmax 0.278,0.430 0.293,1.000 Tmin' 0.161

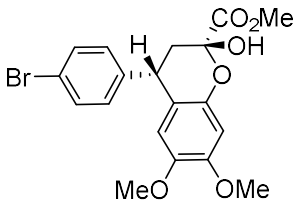
Correction method= # Reported T Limits: Tmin=0.293 Tmax=1.000 AbsCorr = MULTI-SCAN

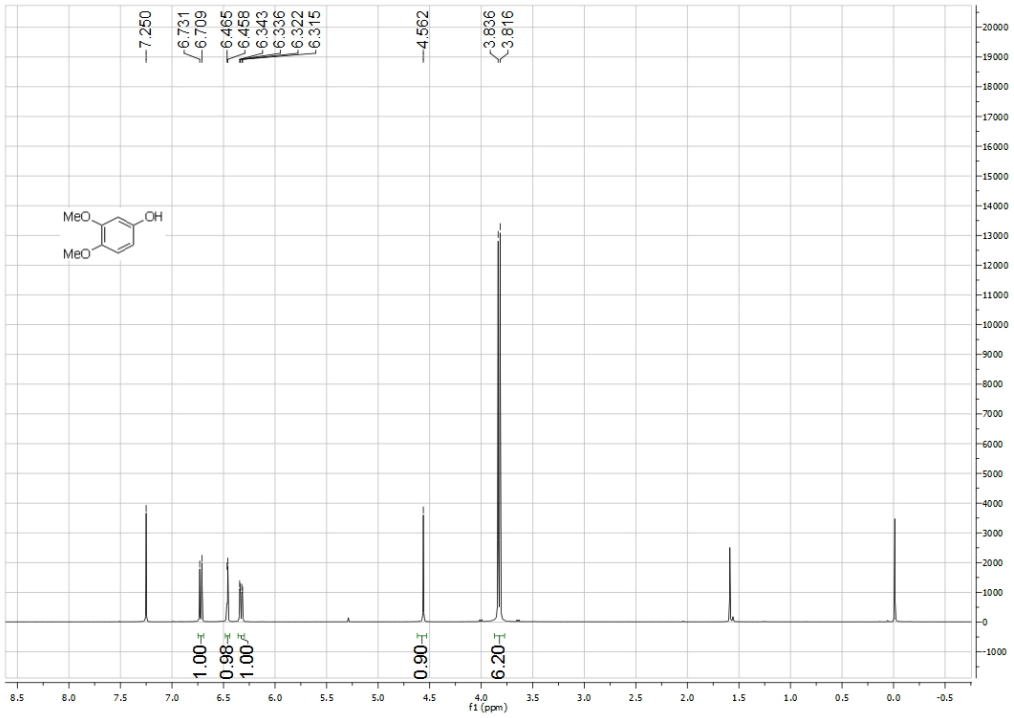
Data completeness= 1.70/1.00 Theta(max)= 67.078

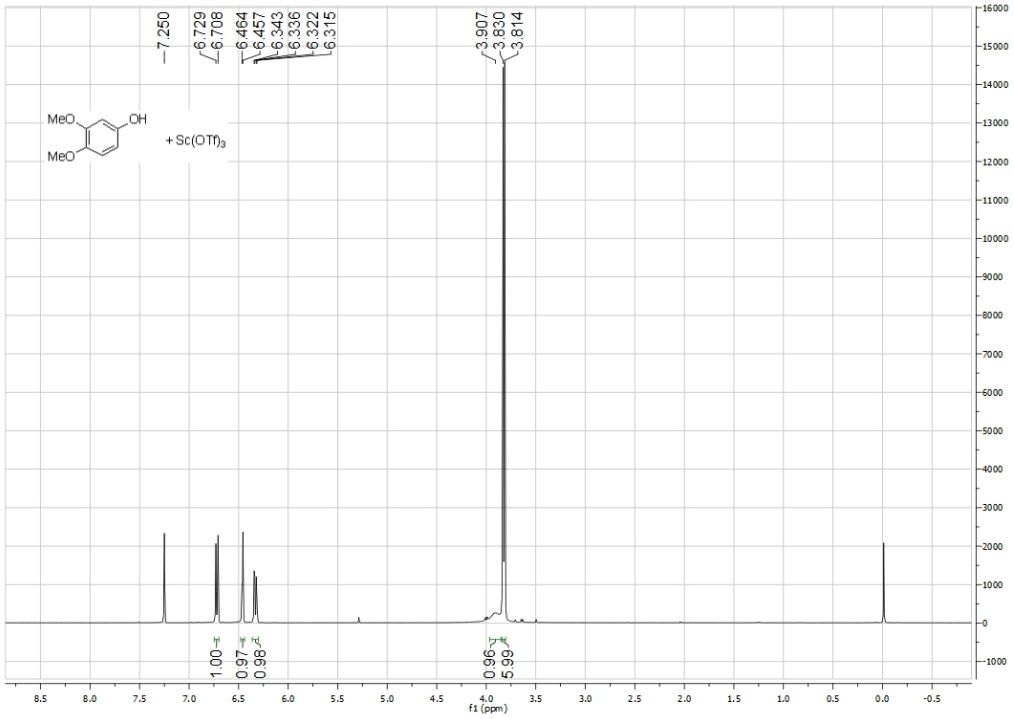
R(reflections)= 0.0420(3171) wR2(reflections)= 0.1042(3260)

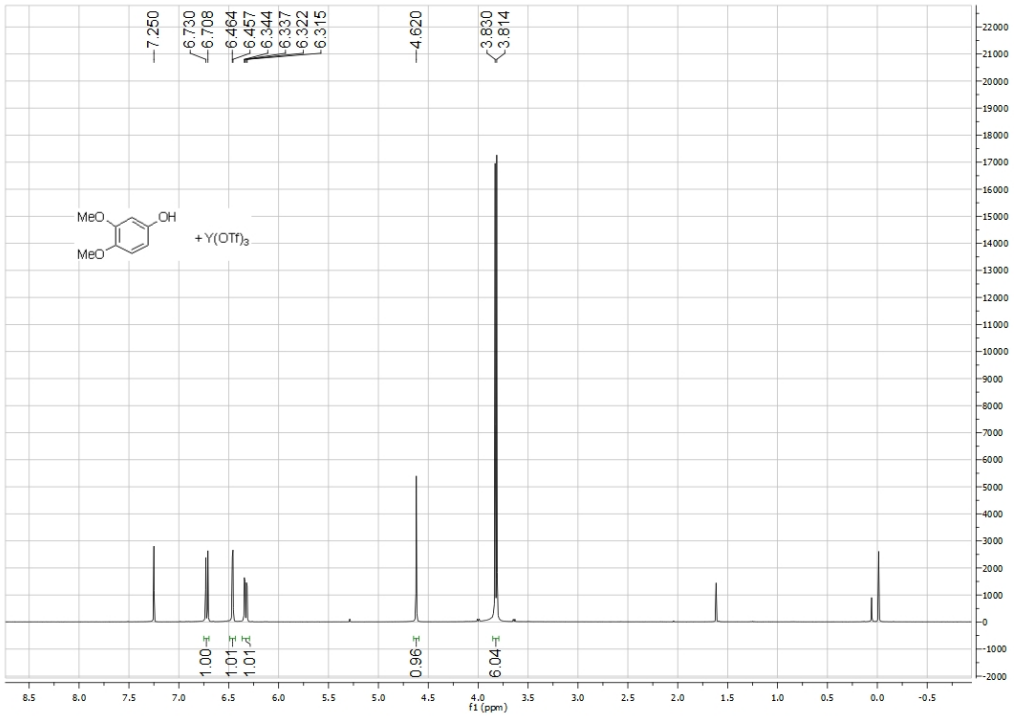
S = 1.071 Npar= 239


NOMOVE FORCED
Prob = 50
Temp = 294
PLATON-Dec 23 07:23:14 2016 - (70316)
Z -100 fxm-Ldf-4 P 21 21 2 R = 0.04
RES= 0 21 X


CO2Me
H
OH
Br
O
MeO
OMe


7.250
6.731
6.709
6.465
6.458
6.343
6.336
6.322
6.315
4.562
3.836
3.816
MeO
OH
MeO
1.00
0.98
1.00
0.90
6.20
f1 (ppm)

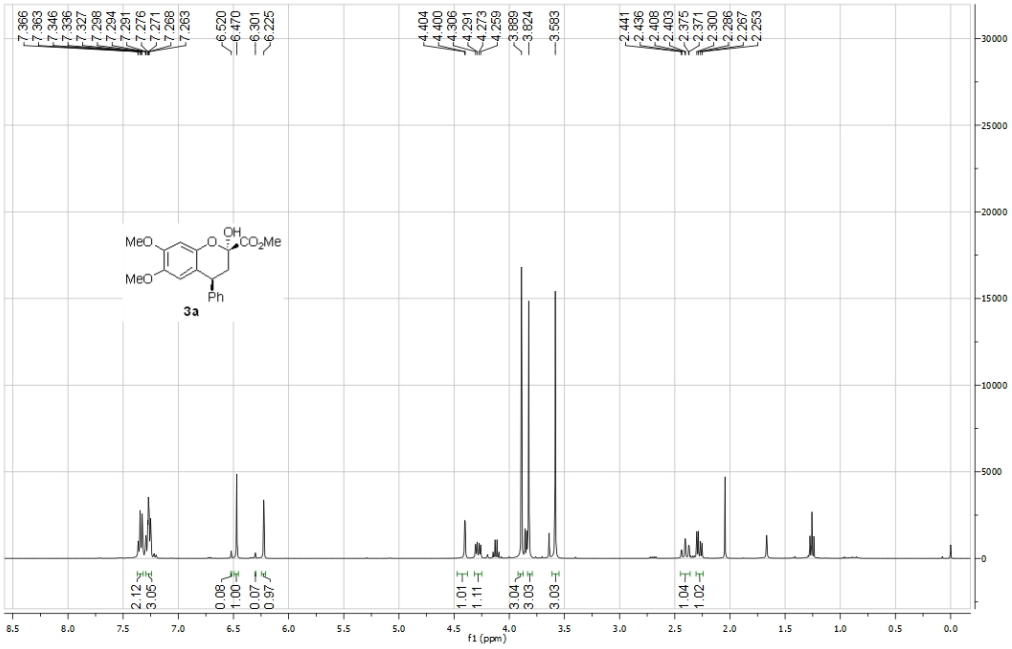


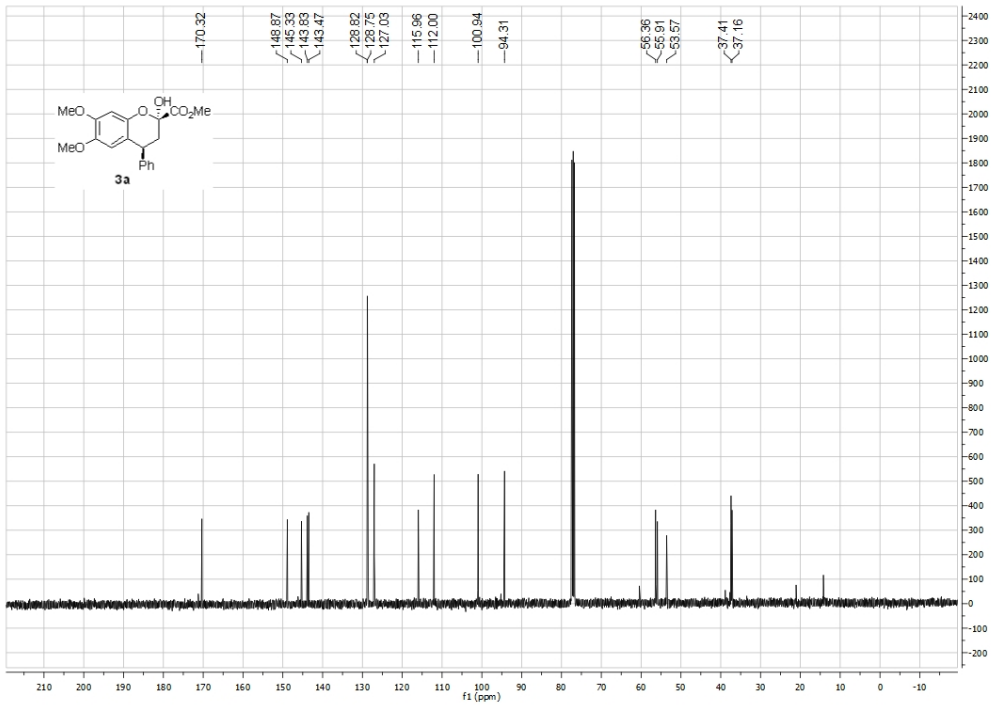


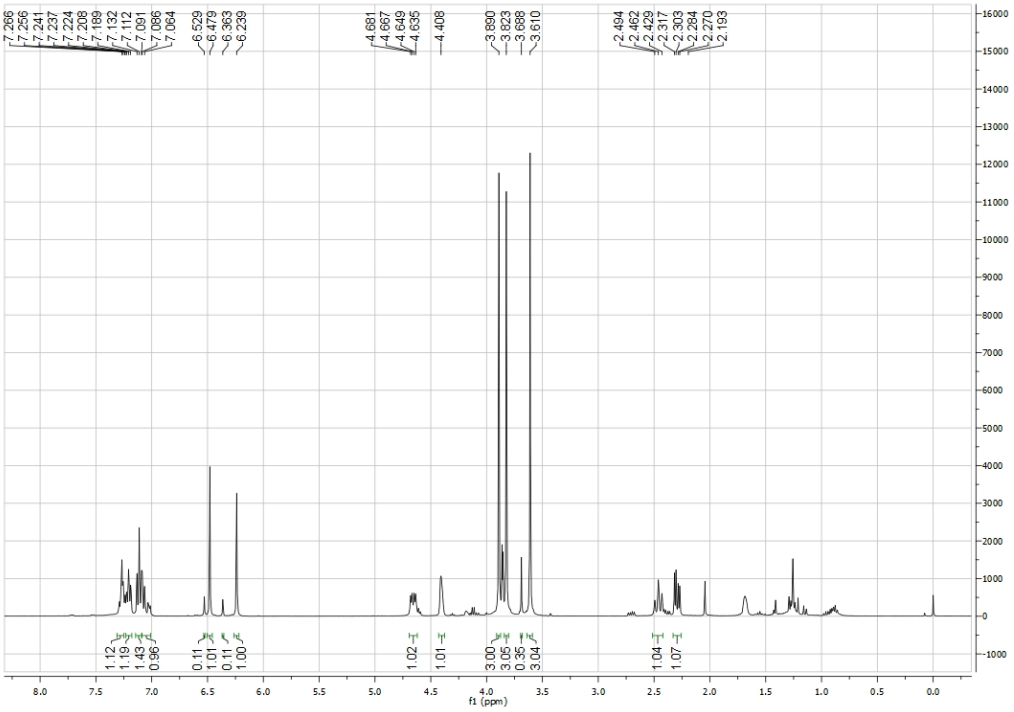
11. References

[1] a) Wen Y. H., Huang X., Huang J. L., Xiong Y., Qin B., Feng X. M., Asymmetric cyanosilylation of aldehydes catalyzed by novel organocatalysts. *Synlett.* **2005,** 2445; b) Liu X. H., Lin L. L., Feng X. M., *Acc*. *Chem*. *Res*. **2011**, *44*, 574-587.

12. Copy of ^{1}H NMR and ^{13}C NMR spectra for the products



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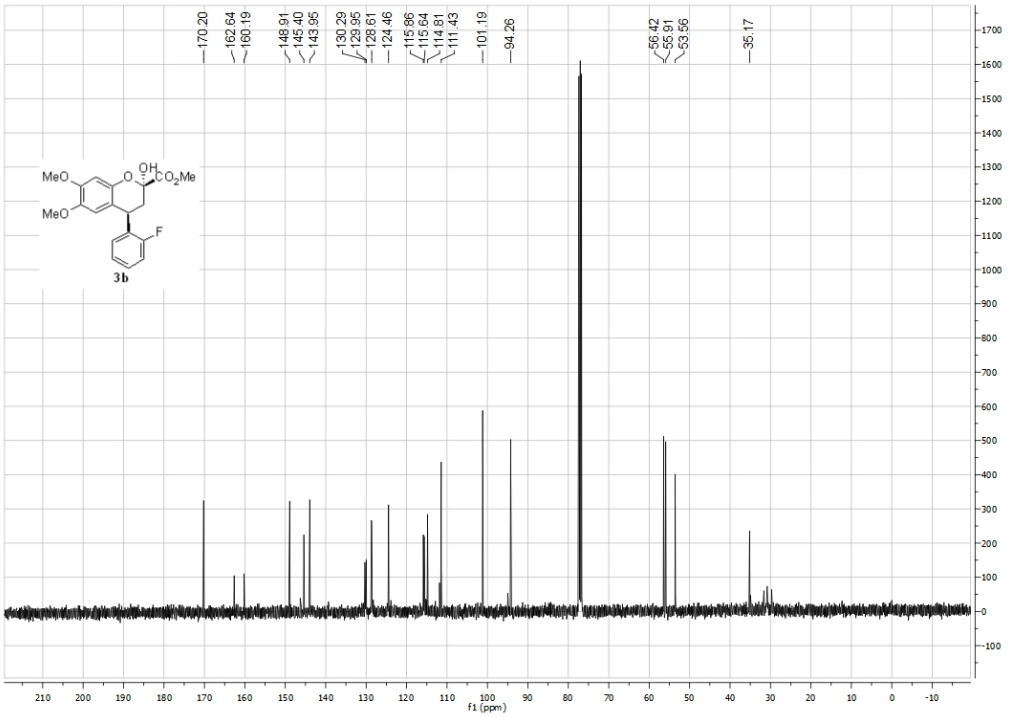
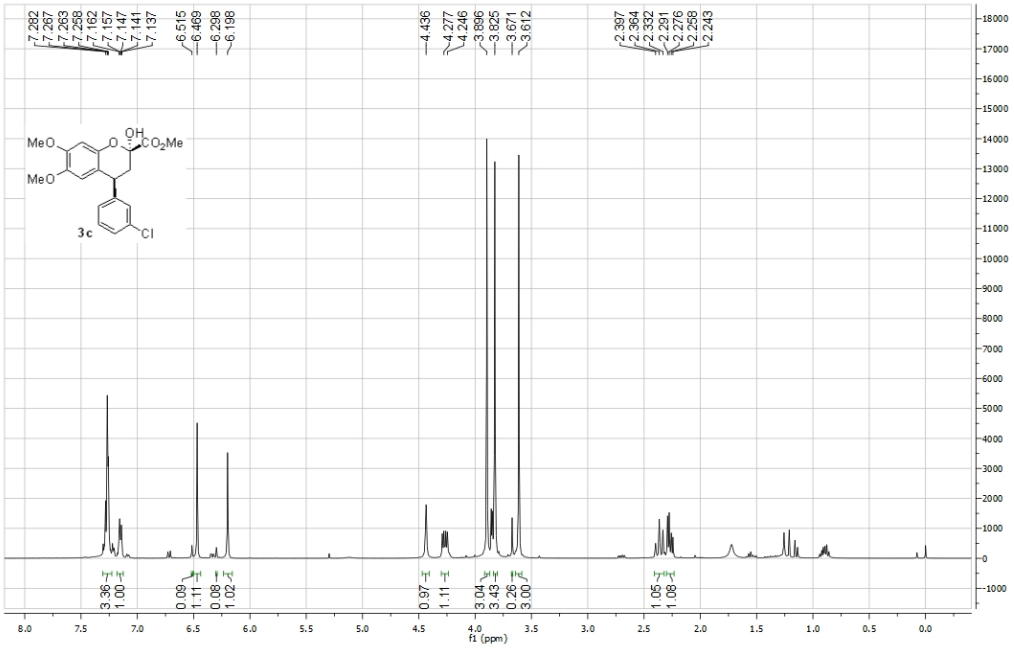
7.241
7.237
7.224
7.208
7.189
7.132
7.112
7.091
7.086
7.064
6.529
6.479
6.363
6.239
4.681
4.667
4.649
4.635
4.408
3.890
3.823
3.688
3.610
2.494
2.462
2.429
2.317
2.303
2.284
2.270
2.193
1.12
1.19
1.43
0.96
0.11
1.01
0.11
1.00
1.02
1.01
3.00
3.05
0.35
3.04
1.04
1.07
f1 (ppm)


170.20
162.64
160.19
148.91
145.40
143.95
130.29
129.95
128.61
124.46
115.86
115.64
114.81
111.43
101.19
94.26
56.42
55.91
53.56
35.17
MeO
MeO
OH
CO2Me
F
3b
f1 (ppm)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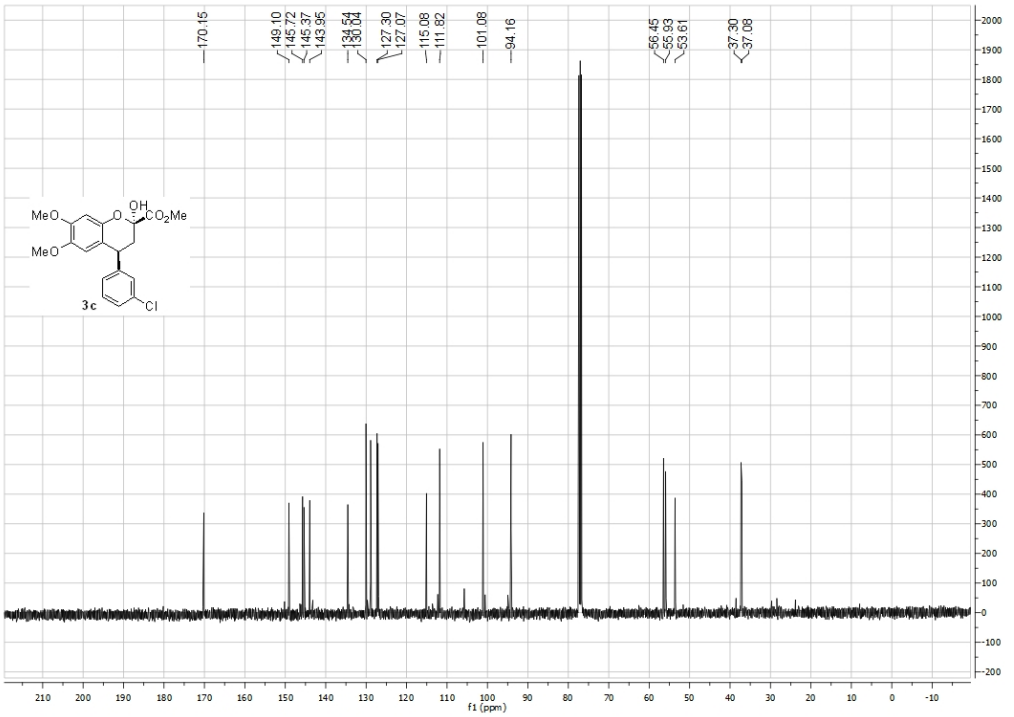
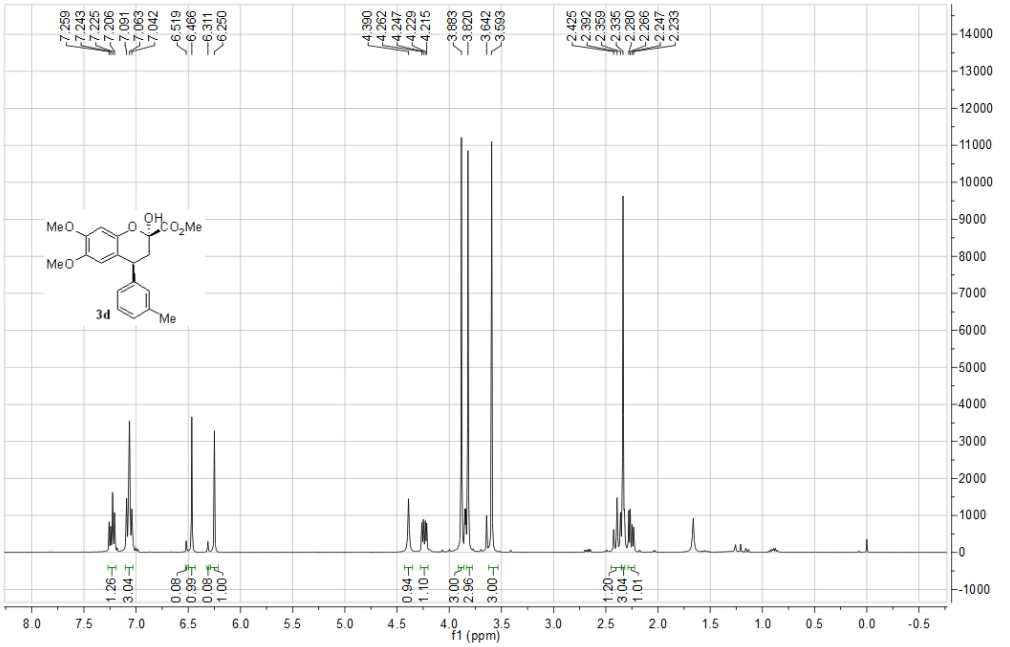
7.267
7.263
7.258
7.162
7.157
7.147
7.141
7.137
6.515
6.469
6.298
6.198
4.436
4.277
4.246
3.896
3.825
3.671
3.612
2.397
2.364
2.332
2.291
2.276
2.258
2.243
MeO
MeO
OH
CO2Me
Cl
3c
3.36
1.00
0.09
1.11
0.08
1.02
0.97
1.11
3.04
3.43
0.26
3.00
1.05
1.08
f1 (ppm)


170.15
149.10
145.72
145.37
143.95
130.54
130.04
127.30
127.07
115.08
111.82
101.08
94.16
56.45
55.93
53.61
37.30
37.08
MeO
MeO
OH
CO2Me
Cl
3c
f1 (ppm)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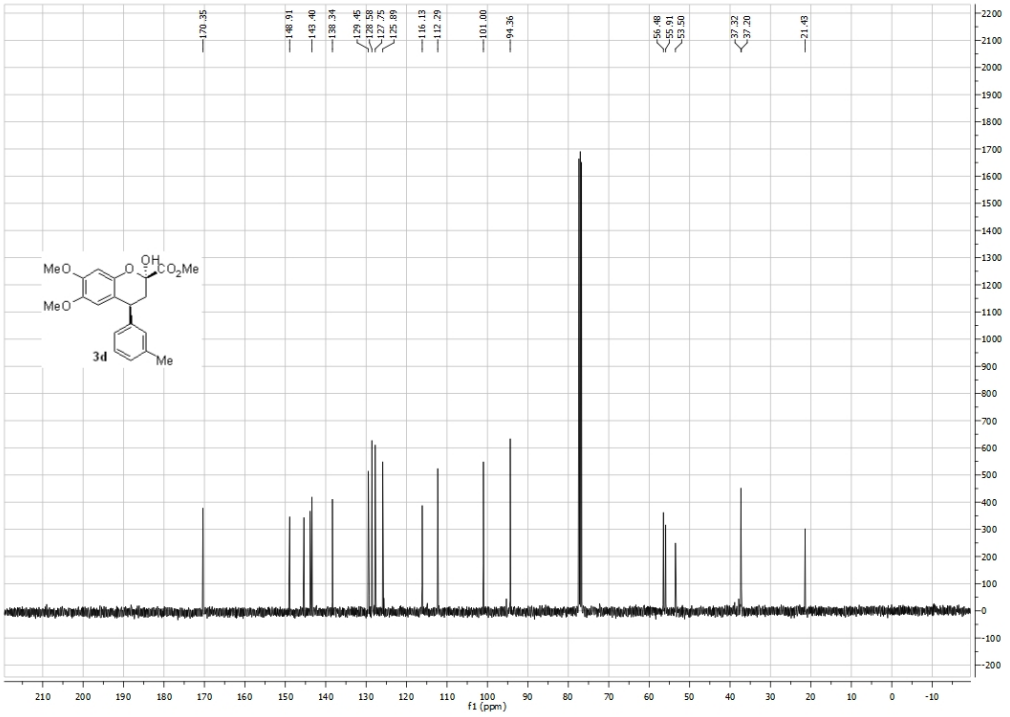
7.225
7.206
7.091
7.063
7.042
6.519
6.496
6.311
6.250
4.390
4.262
4.247
4.229
4.215
3.883
3.820
3.642
3.593
2.425
2.392
2.359
2.335
2.280
2.266
2.247
2.233
MeO
MeO
OH
CO2Me
3d
Me
1.26
3.04
0.08
0.99
0.08
1.00
0.94
1.10
3.00
2.96
3.00
1.20
3.04
1.01
f1 (ppm)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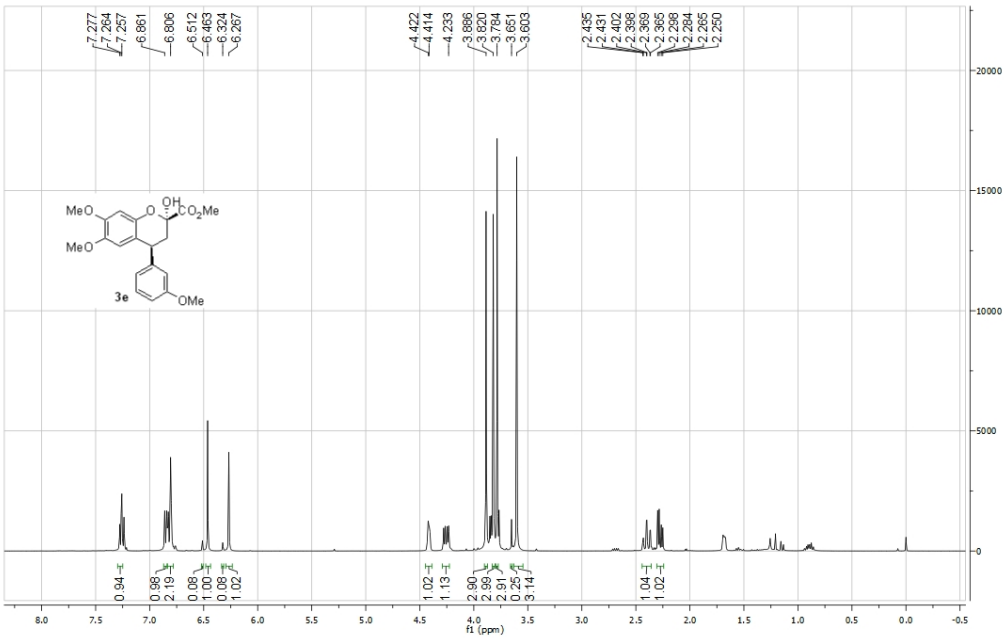
148.91
143.40
138.34
129.45
128.58
127.75
125.89
116.13
112.29
101.00
94.36
56.48
55.91
53.50
37.32
37.20
21.43
MeO
MeO
OH
CO2Me
3d
Me
f1 (ppm)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7.264
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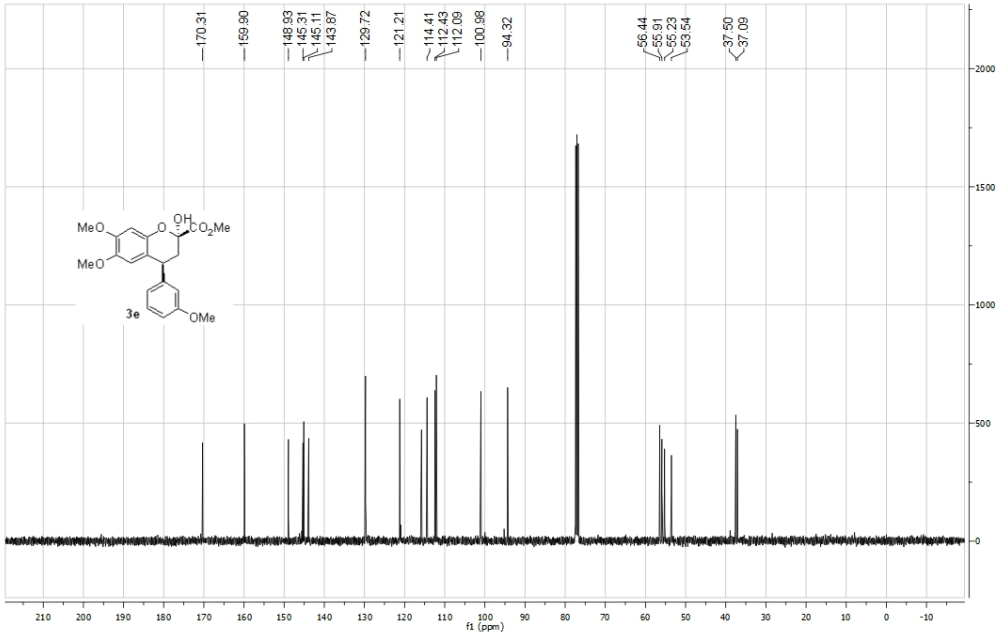
3.820
3.784
3.651
3.603
2.435
2.431
2.402
2.398
2.369
2.365
2.298
2.284
2.265
2.250
MeO
MeO
OH
CO2Me
3e
OMe
0.94
0.98
2.19
0.08
1.00
0.08
1.02
1.02
1.13
2.90
2.99
2.91
0.25
3.14
1.04
1.02
f1 (ppm)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148.93
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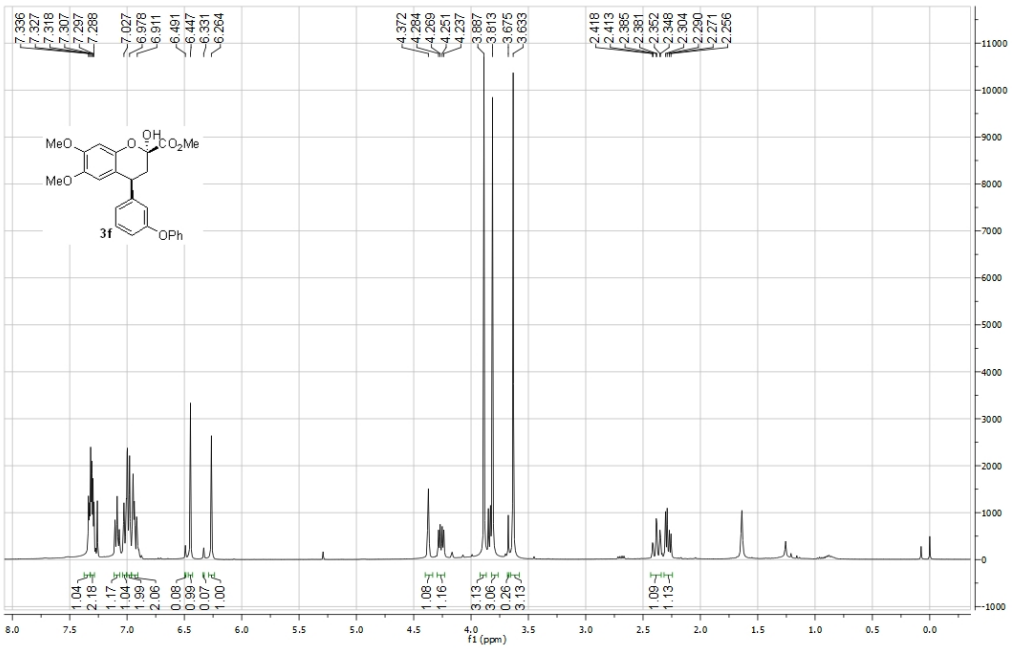
145.11
143.87
129.72
121.21
114.41
112.43
112.09
100.98
94.32
56.44
55.91
55.23
53.54
37.50
37.09
MeO
MeO
OH
CO2Me
3e
OMe
f1 (ppm)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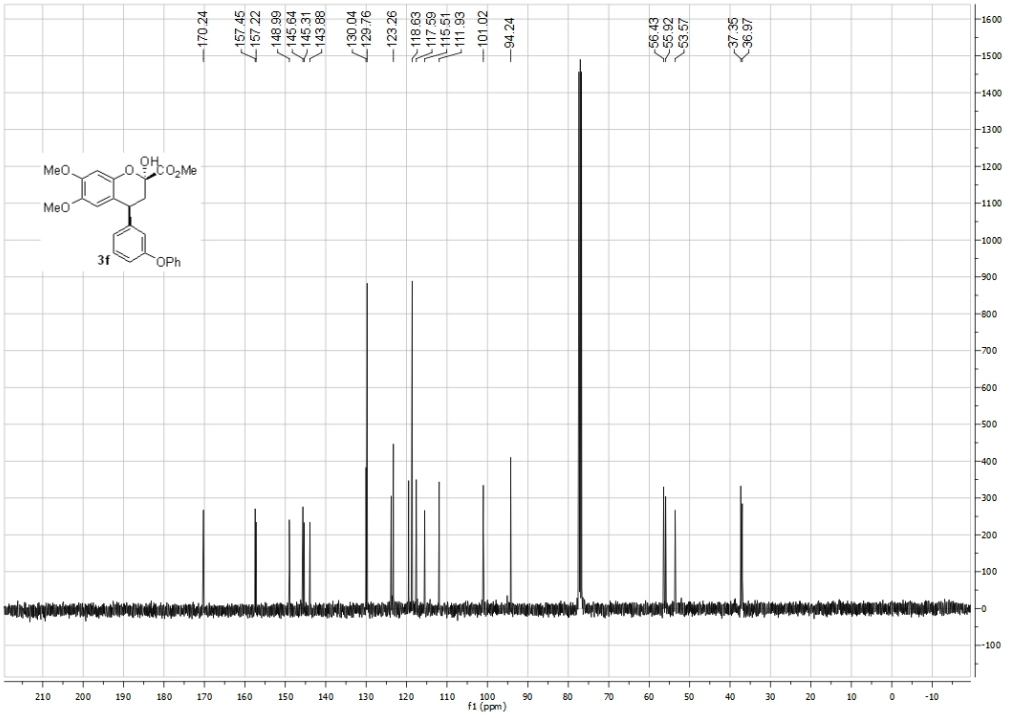
7.288
7.027
6.978
6.911
6.491
6.447
6.331
6.264
4.372
4.284
4.269
4.251
4.237
3.887
3.813
3.675
3.633
2.418
2.413
2.385
2.361
2.352
2.348
2.304
2.290
2.271
2.256
MeO
MeO
OH
CO2Me
OPh
3f
1.04
2.18
1.17
1.04
1.99
2.06
0.09
0.99
0.07
1.00
1.08
1.16
3.13
3.06
0.26
3.13
1.09
1.13
f1 (ppm)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157.22
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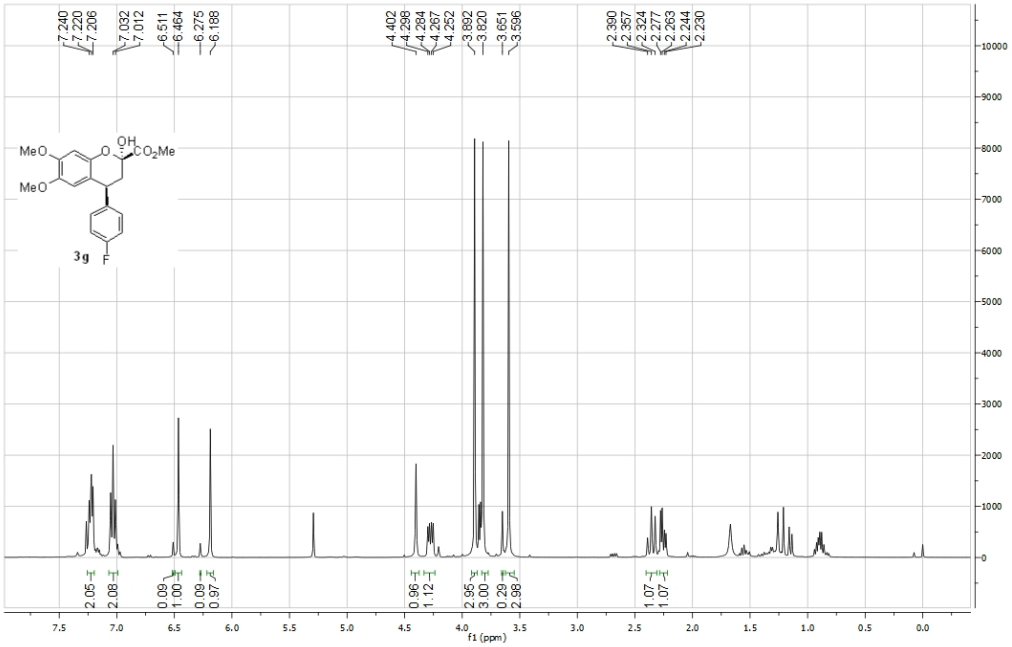
143.88
130.04
129.76
123.26
118.63
117.59
115.51
111.93
101.02
94.24
56.43
55.92
53.57
37.35
36.97
MeO
MeO
OH
CO2Me
OPh
3f
f1 (ppm)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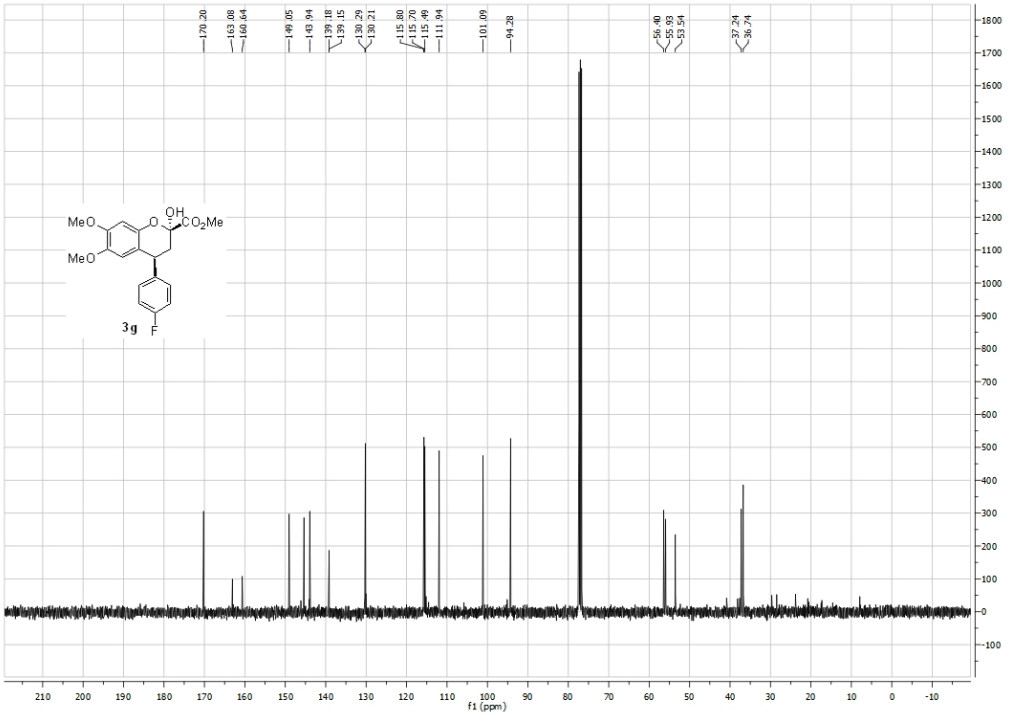
7.206
7.032
7.012
6.511
6.464
6.275
6.188
4.402
4.298
4.284
4.267
4.252
3.892
3.820
3.651
3.596
2.390
2.357
2.324
2.277
2.263
2.244
2.230
MeO
MeO
OH
CO2Me
3g
F
2.05
2.08
0.09
1.00
0.09
0.97
0.96
1.12
2.95
3.00
0.29
2.98
1.07
1.07
f1 (ppm)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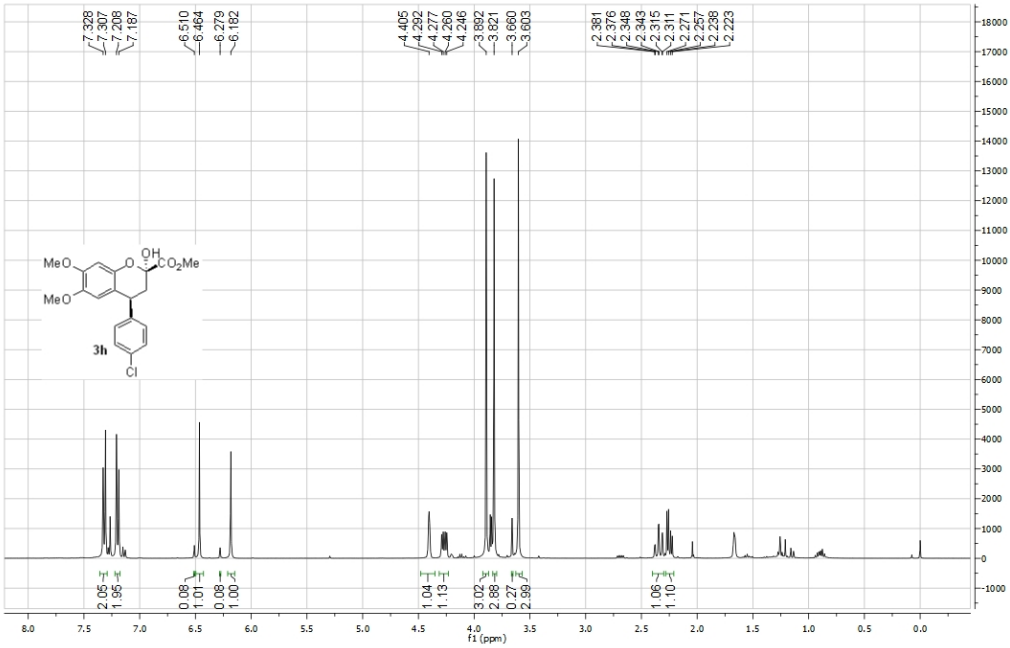
163.08
160.64
149.05
149.94
139.18
139.15
130.29
130.21
115.80
115.70
115.49
111.94
101.09
94.28
56.40
55.93
53.54
37.24
36.74
MeO
MeO
OH
CO2Me
3g
F
f1 (ppm)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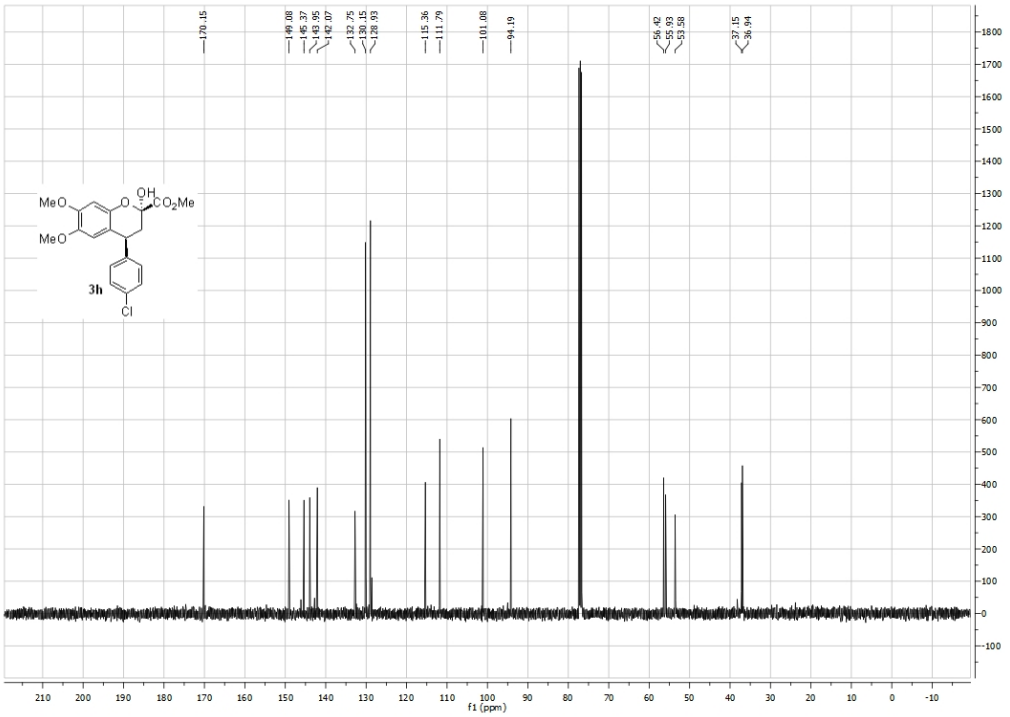
7.307
7.208
7.187
6.510
6.464
6.279
6.182
4.405
4.292
4.277
4.260
4.246
3.892
3.821
3.660
3.603
2.381
2.376
2.348
2.343
2.315
2.311
2.271
2.257
2.238
2.223
MeO
MeO
OH
CO2Me
3h
Cl
2.05
1.95
0.08
1.01
0.08
1.00
1.04
1.13
3.02
2.88
0.27
2.99
1.06
1.10
f1 (ppm)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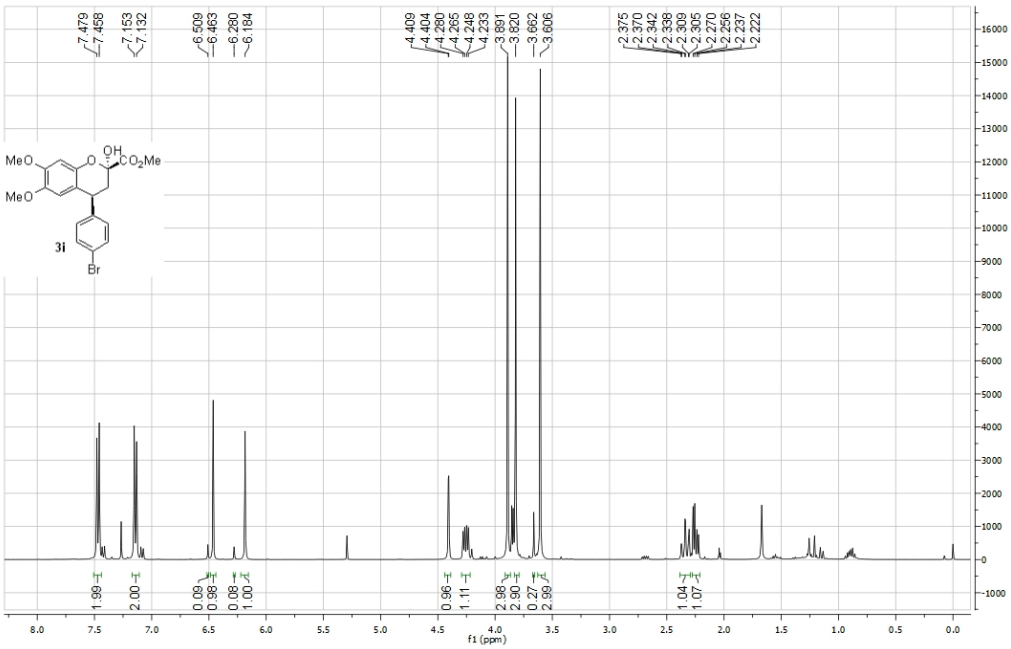
145.85
142.07
132.75
130.15
128.93
115.36
111.79
101.08
94.19
56.42
55.93
53.58
37.15
36.94
MeO
MeO
OH
CO2Me
3h
Cl
f1 (ppm)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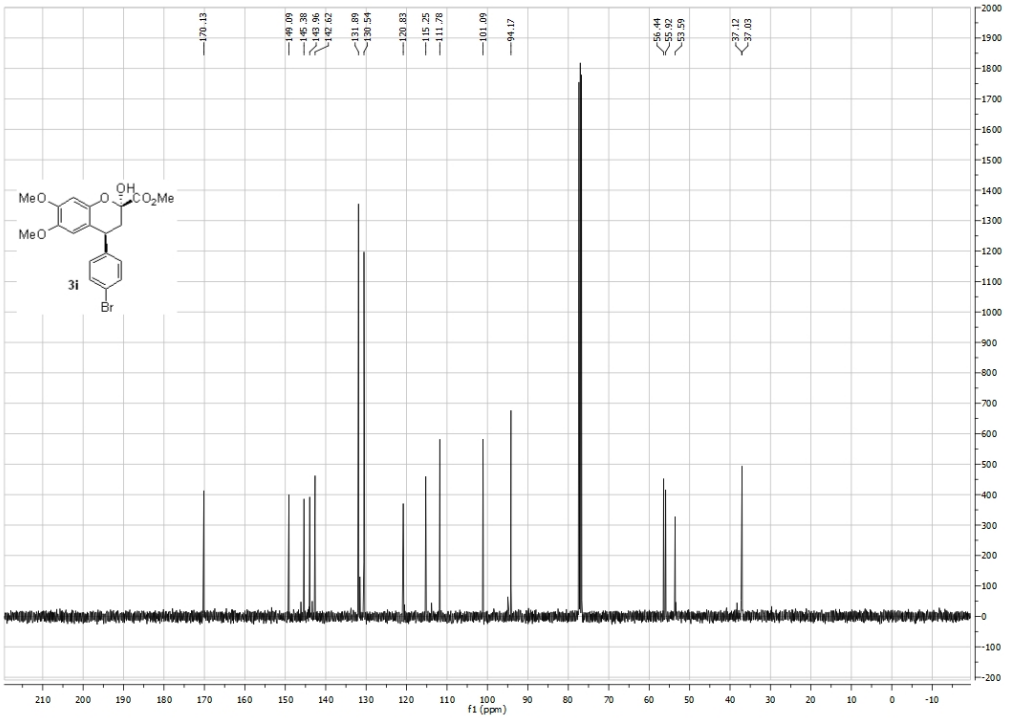
7.458
7.153
7.132
6.509
6.463
6.280
6.184
4.409
4.404
4.290
4.265
4.248
4.233
3.891
3.820
3.662
3.606
2.375
2.370
2.342
2.338
2.309
2.305
2.270
2.256
2.237
2.222
MeO
MeO
OH
CO2Me
3i
Br
1.99
2.00
0.09
0.98
0.08
1.00
0.96
1.11
2.98
2.90
0.27
2.99
1.04
1.07
f1 (ppm)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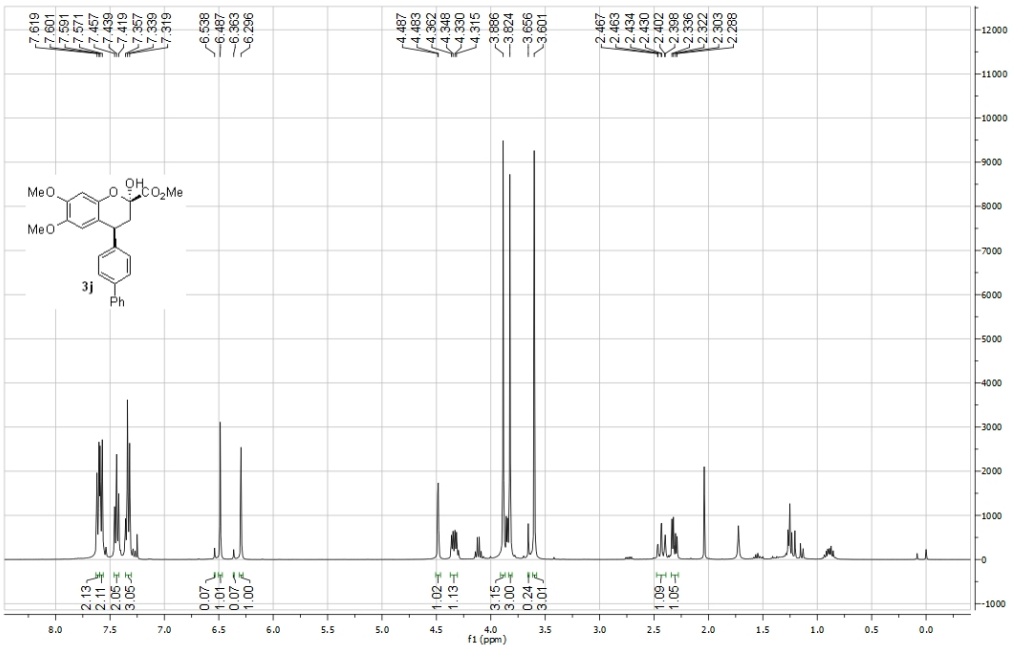
149.09
146.38
145.96
142.62
131.89
130.54
120.83
115.25
111.78
101.09
94.17
56.44
55.92
53.59
37.12
37.03
MeO
MeO
OH
CO2Me
3i
Br
f1 (ppm)


7.619
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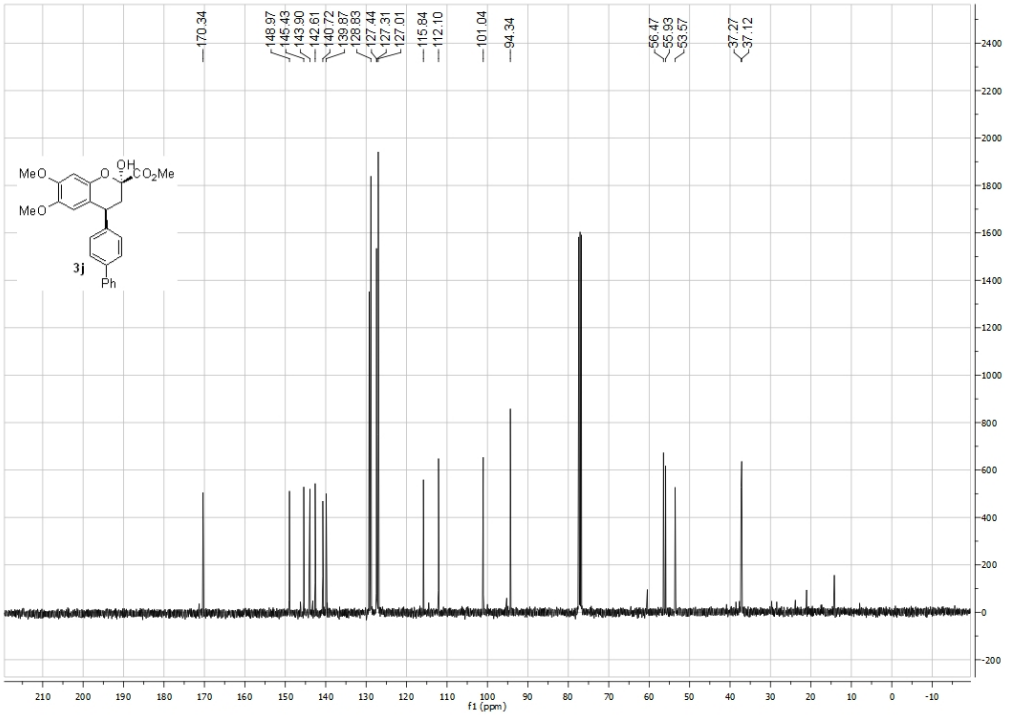
7.571
7.457
7.439
7.419
7.357
7.339
7.319
6.538
6.487
6.363
6.296
4.487
4.483
4.362
4.348
4.330
4.315
3.886
3.824
3.656
3.601
2.467
2.463
2.434
2.430
2.402
2.398
2.336
2.322
2.303
2.288
MeO
MeO
OH
CO2Me
3j
Ph
2.13
2.11
2.05
3.05
0.07
1.01
0.07
1.00
1.02
1.13
3.15
3.00
0.24
3.01
1.09
1.05
f1 (ppm)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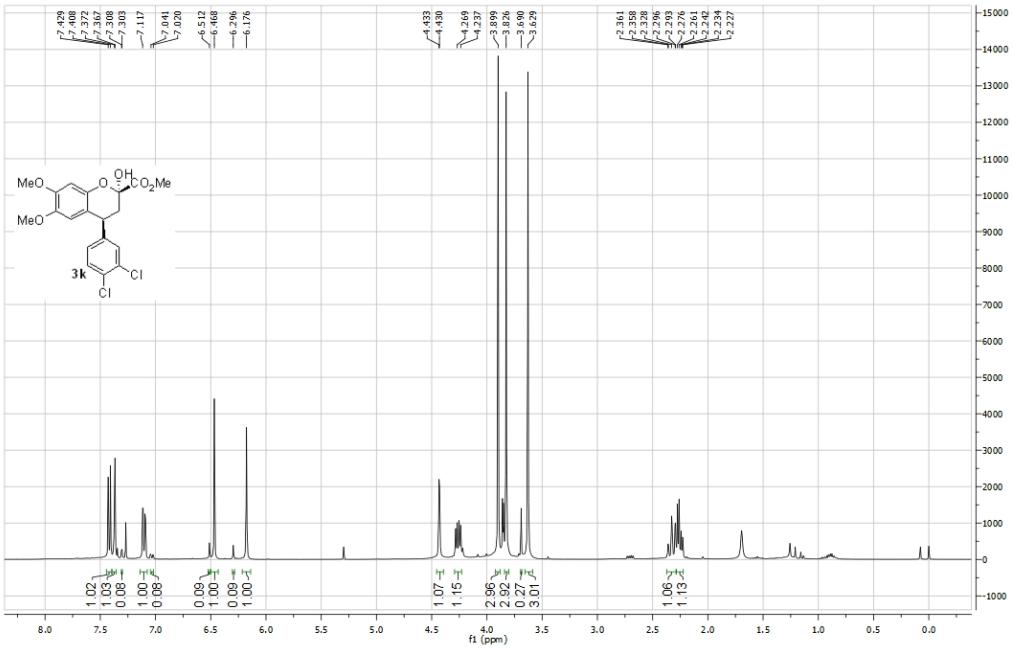
145.43
143.90
142.61
140.72
139.87
128.83
127.44
127.31
127.01
115.84
112.10
101.04
94.34
56.47
55.93
53.57
37.27
37.12
MeO
MeO
OH
CO2Me
3j
Ph
f1 (ppm)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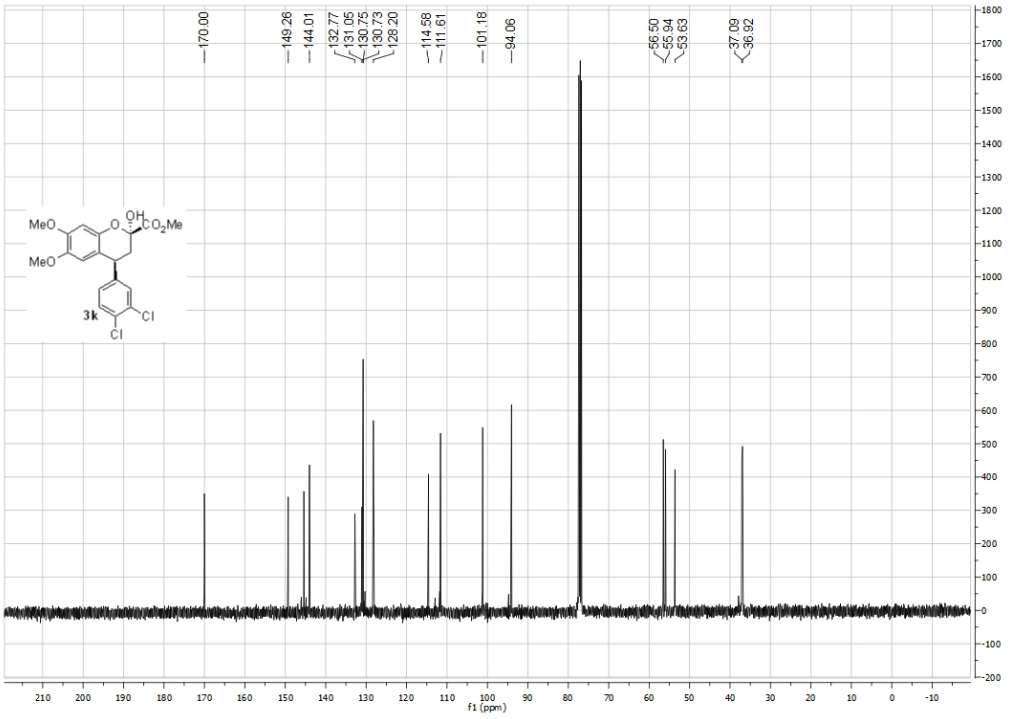
7.408
7.372
7.367
7.308
7.303
7.117
7.041
7.020
6.512
6.468
6.296
6.176
4.433
4.430
4.269
4.237
3.899
3.826
3.690
3.629
2.361
2.358
2.328
2.296
2.293
2.276
2.261
2.242
2.234
2.227
MeO
MeO
OH
CO2Me
3k
Cl
Cl
1.02
1.03
0.08
1.00
0.08
0.09
1.00
0.09
1.00
1.07
1.15
2.96
2.92
0.27
3.01
1.06
1.13
f1 (ppm)


170.00
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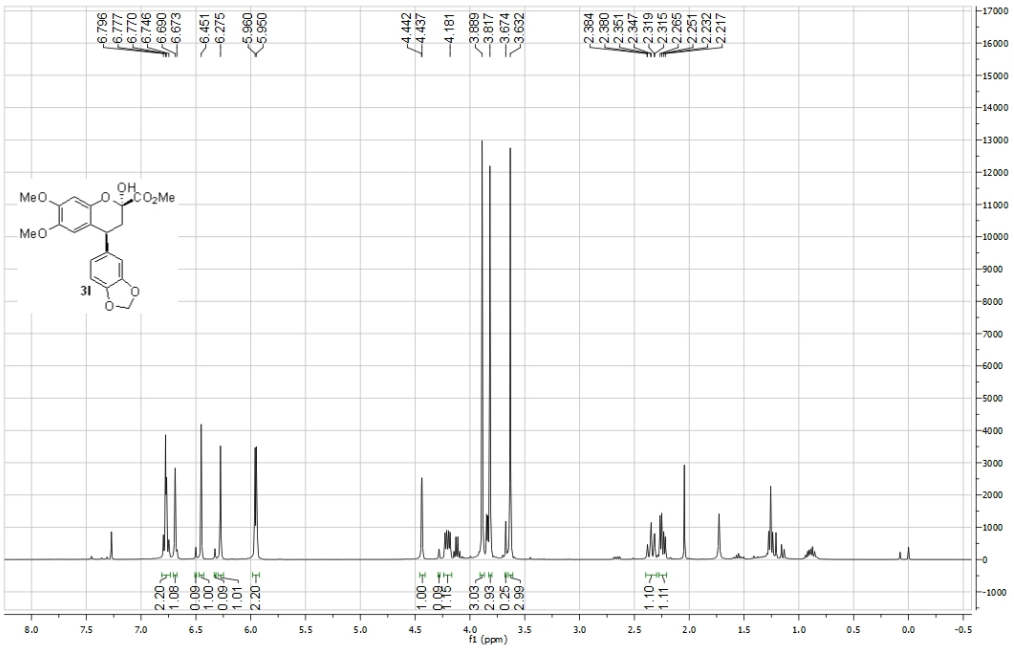
132.77
131.05
130.75
130.73
128.20
114.58
111.61
101.18
94.06
56.50
55.94
53.63
37.09
36.92
MeO
MeO
OH
CO2Me
3k
Cl
Cl
f1 (ppm)


6.796
6.777
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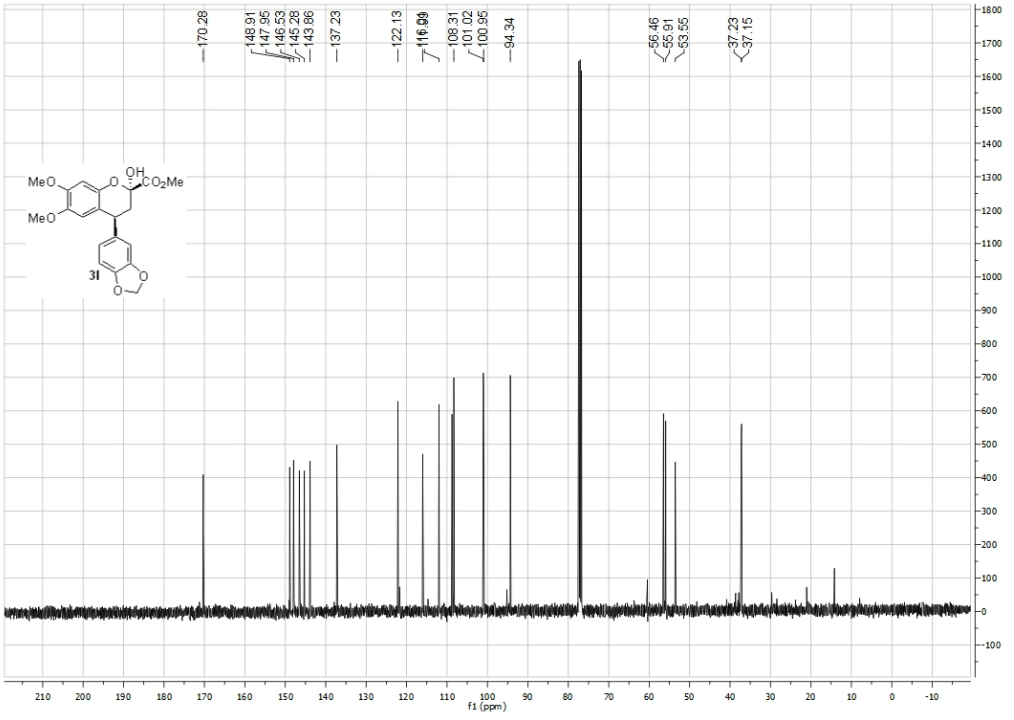
6.690
6.673
6.451
6.275
5.960
5.950
4.442
4.437
4.181
3.889
3.817
3.674
3.632
2.384
2.380
2.351
2.347
2.319
2.315
2.265
2.251
2.232
2.217
MeO
MeO
OH
CO2Me
3l
f1 (ppm)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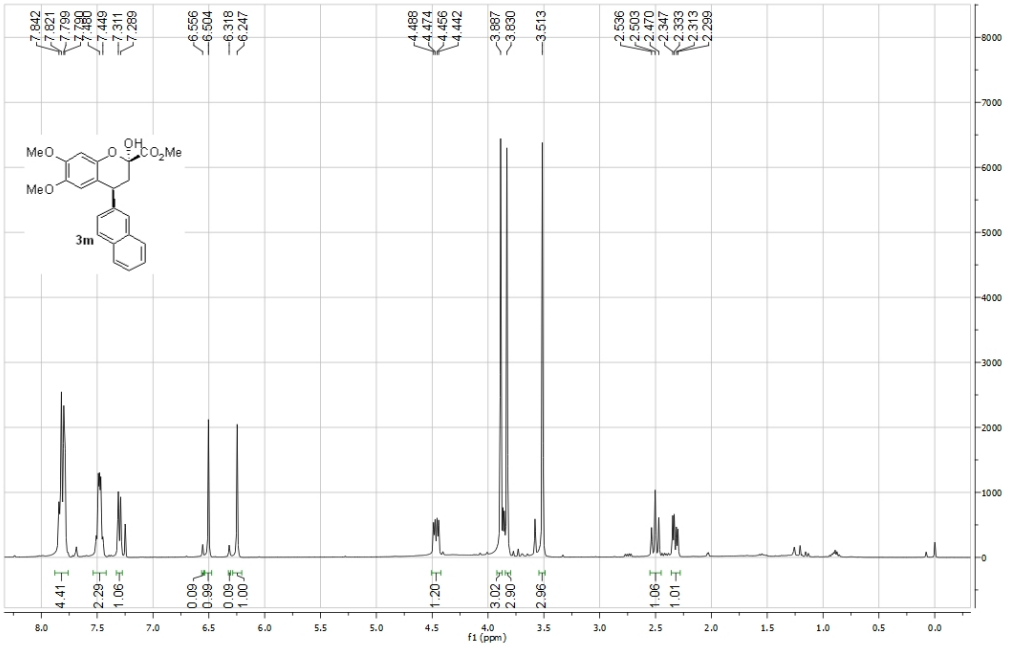
147.95
146.53
145.28
143.86
137.23
122.13
108.31
101.02
100.95
94.34
56.46
55.91
53.55
37.23
37.15
MeO
MeO
OH
CO2Me
3l
f1 (ppm)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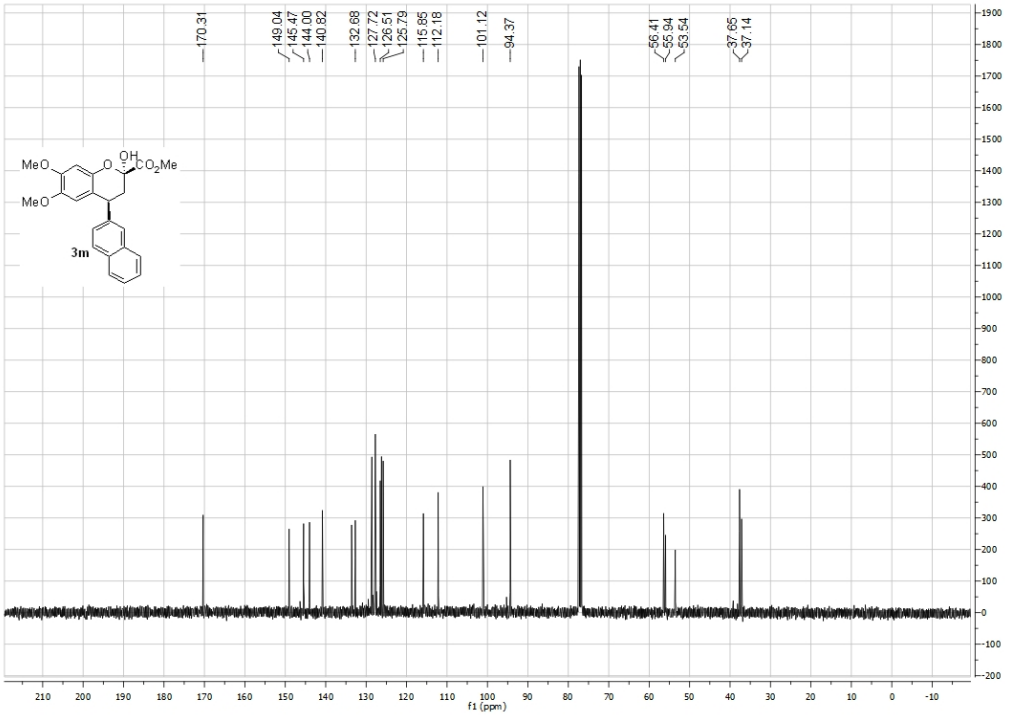
7.289
6.556
6.504
6.318
6.247
4.488
4.474
4.456
4.442
3.887
3.830
3.513
2.536
2.503
2.470
2.347
2.333
2.313
2.299
MeO
MeO
OH
CO2Me
3m
4.41
2.29
1.06
0.09
0.99
0.09
1.00
1.20
3.02
2.90
2.96
1.06
1.01
f1 (ppm)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145.47
144.00
140.82
132.68
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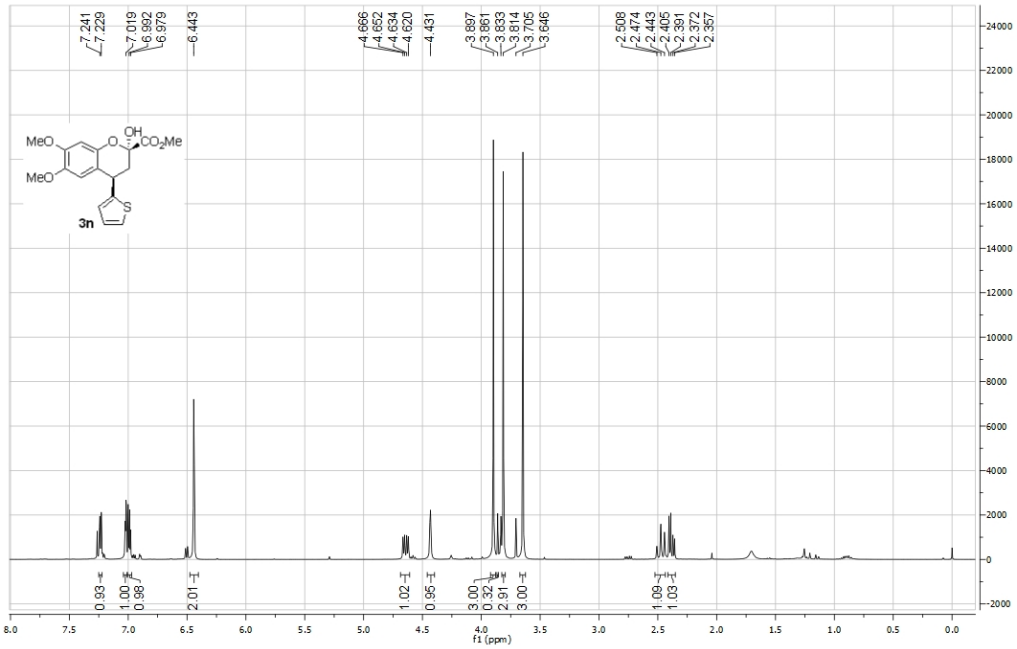
126.51
125.79
115.85
112.18
101.12
94.37
56.41
55.94
53.54
37.65
37.14
MeO
MeO
OH
CO2Me
3m
f1 (ppm)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4.652
4.634
4.620
4.431
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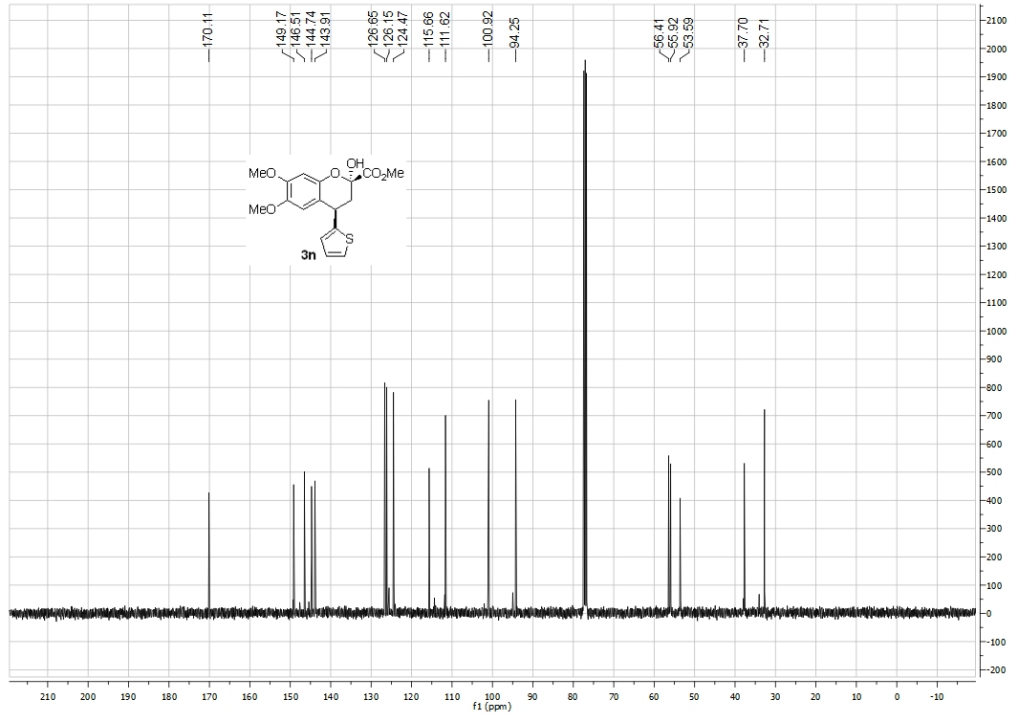
3.861
3.833
3.814
3.705
3.646
2.508
2.474
2.443
2.405
2.391
2.372
2.357
MeO
MeO
OH
CO2Me
S
3n
0.93
1.00
0.98
2.01
1.02
0.95
3.00
0.32
2.91
3.00
1.09
1.03
f1 (ppm)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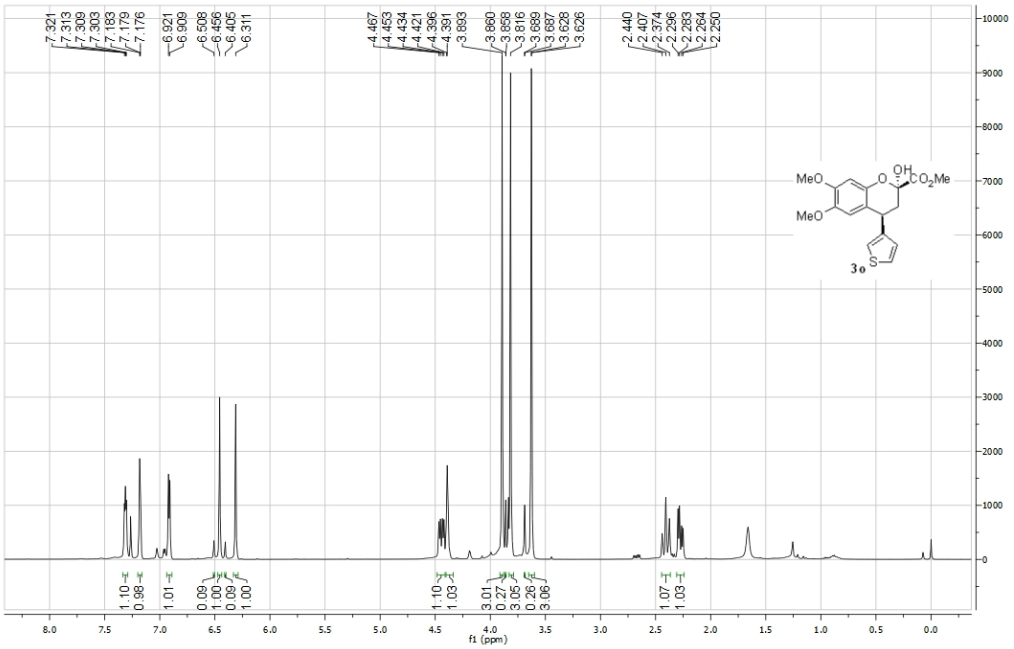
143.91
126.85
126.15
124.47
115.66
111.62
100.92
94.25
56.41
55.92
53.59
37.70
32.71
MeO
MeO
OH
CO2Me
S
3n
f1 (ppm)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7.303
7.183
7.179
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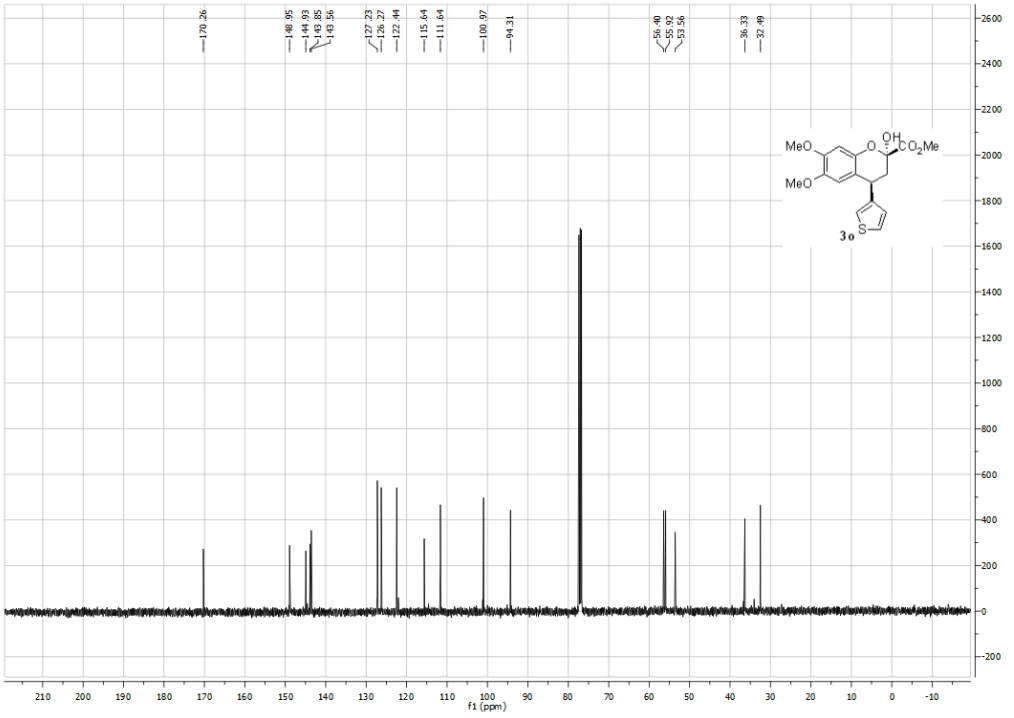
6.909
6.508
6.456
6.405
6.311
4.467
4.453
4.434
4.421
4.396
4.391
3.893
3.860
3.858
3.816
3.689
3.687
3.628
3.626
2.440
2.407
2.374
2.296
2.293
2.264
2.250
1.10
0.98
1.01
0.09
1.00
0.09
1.00
1.10
1.03
3.01
0.27
3.05
0.26
3.06
1.07
1.03
f1 (ppm)
MeO
MeO
OH
CO2Me
3o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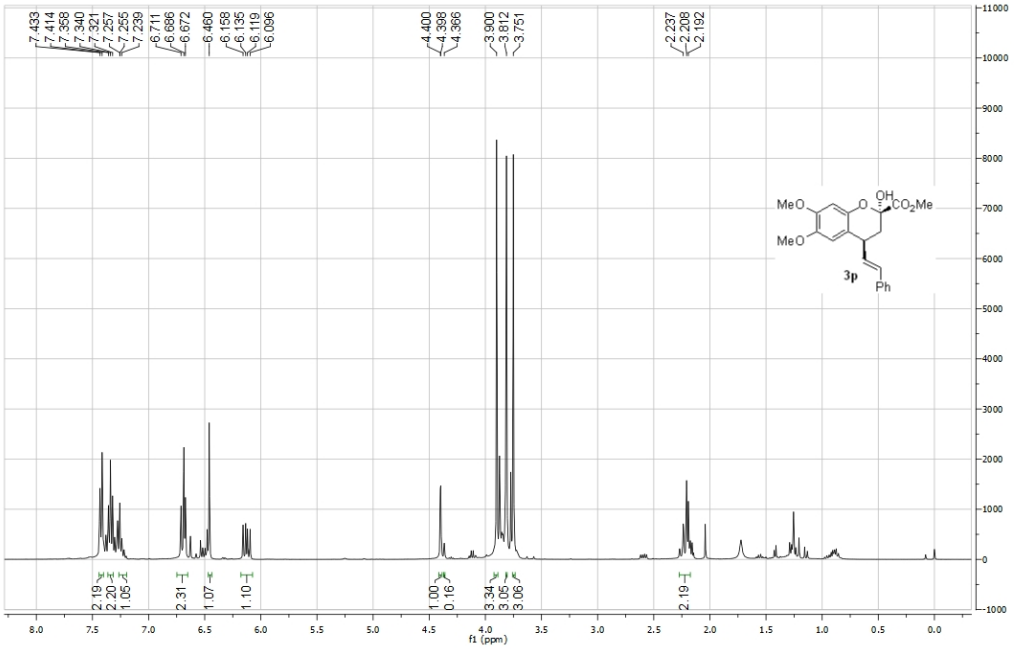
127.23
126.27
122.44
115.64
111.64
100.97
94.31
56.40
55.92
53.56
36.33
32.49
f1 (ppm)
MeO
MeO
OH
CO2Me
3o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7.239
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6.686
6.672
6.460
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6.135
6.119
6.096
4.400
4.398
4.366
3.900
3.812
3.751
2.237
2.208
2.192
MeO
MeO
OH
CO2Me
3p
Ph
2.19
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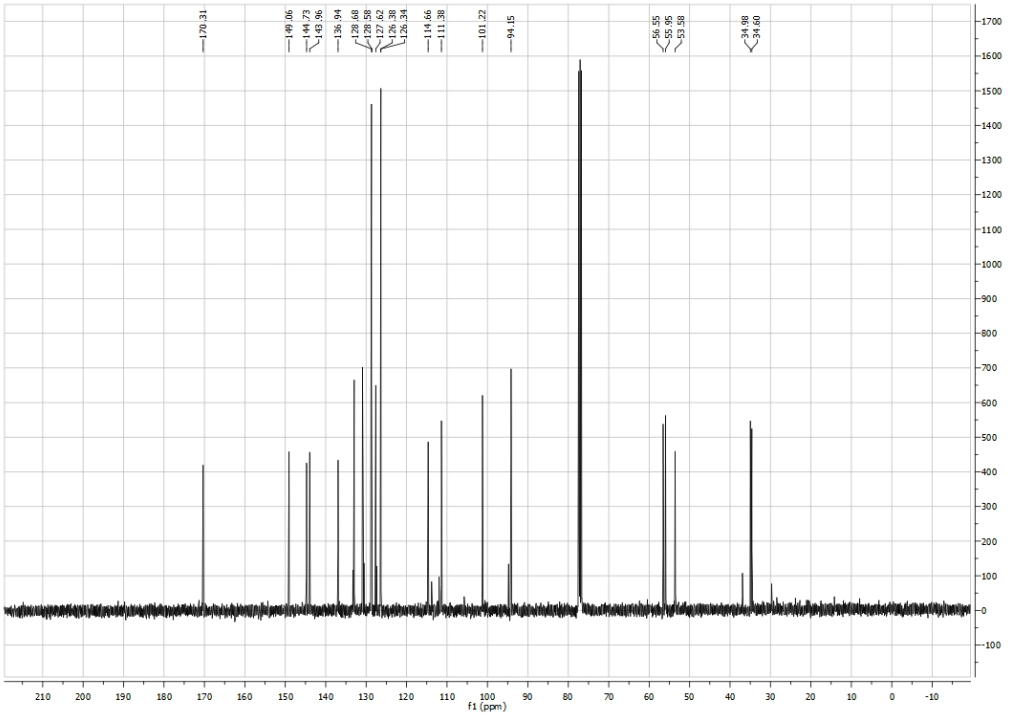
1.07
1.10
1.00
0.16
3.34
3.05
3.06
2.19
f1 (ppm)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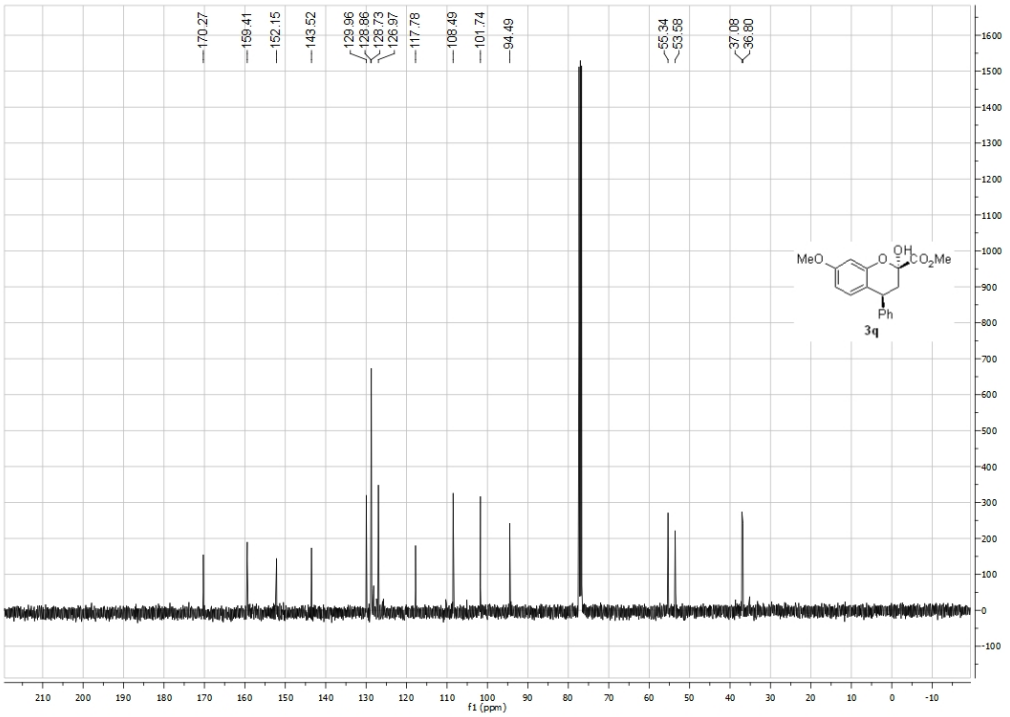
144.73
143.96
136.94
128.68
128.58
127.62
126.38
126.34
114.66
111.30
101.22
94.15
56.55
55.95
53.38
34.88
34.60
f1 (ppm)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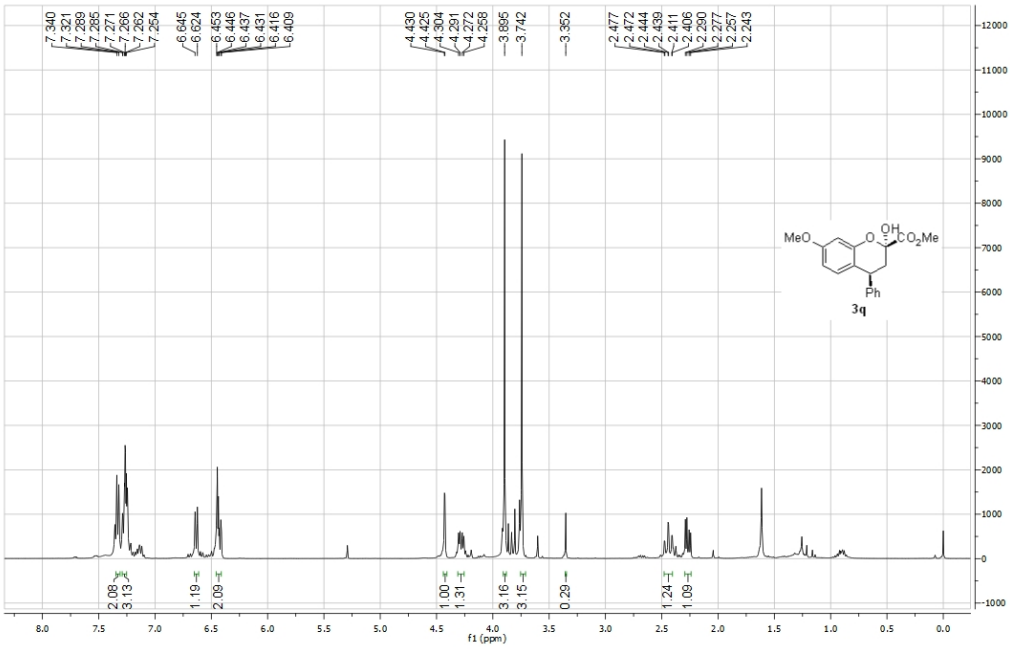
143.52
129.96
128.86
128.73
126.97
117.78
108.49
101.74
94.49
55.34
53.58
37.08
36.80
MeO
OH
CO2Me
Ph
3q
f1 (ppm)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7.271
7.266
7.262
7.254
6.645
6.624
6.453
6.446
6.437
6.431
6.416
6.409
4.430
4.425
4.304
4.291
4.272
4.258
3.895
3.742
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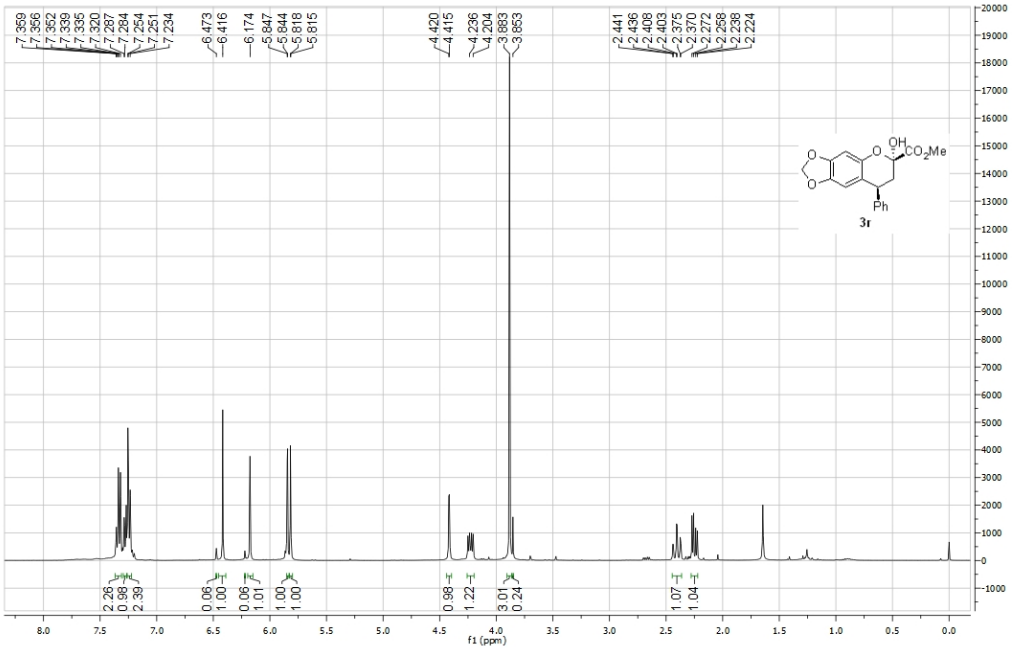
2.472
2.444
2.439
2.411
2.406
2.290
2.277
2.257
2.243
2.08
3.13
1.19
2.09
1.00
1.31
3.16
3.15
0.29
1.24
1.09
MeO
OH
CO2Me
Ph
3q
f1 (ppm)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7.284
7.254
7.251
7.234
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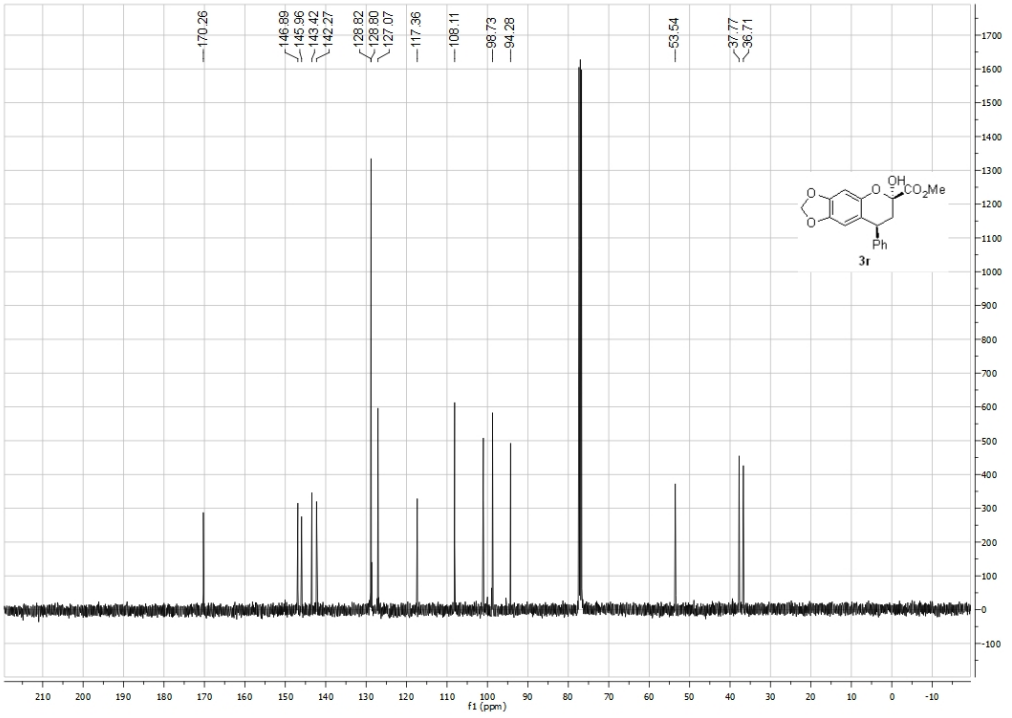
6.416
6.174
5.847
5.844
5.818
5.815
4.420
4.415
4.236
4.204
3.883
3.853
2.441
2.436
2.408
2.403
2.375
2.370
2.272
2.258
2.238
2.224
OH
CO2Me
O
O
O
Ph
3r
2.26
0.98
2.39
0.06
1.00
0.06
1.01
1.00
1.00
0.98
1.22
3.01
0.24
1.07
1.04
f1 (ppm)


170.26
146.89
145.96
143.42
142.27
128.82
128.80
127.07
117.36
108.11
98.73
94.28
53.54
37.77
36.71
OH
CO2Me
O
O
O
Ph
3r
f1 (ppm)