Chiral scandium-complex-catalyzed asymmetric inverse-electron-demand oxa-Diels–Alder reaction of *o*-quinone methides with fulvenes

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1. General remarks

Reactions were carried out using commercial available reagents in over-dried apparatus. EtOAc was dried over powdered CaH_2 and distilled under nitrogen just before use. Enantiomeric excesses (*ee*) were determined by HPLC analysis using the corresponding commercial chiral column as stated in the experimental procedures at 23 ℃ with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]^{25}_{D}$ (c g/100 mL, in solvent). ^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$, δ = 7.26; DMSO, δ = 2.50). Spectra were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. ^{13}C NMR spectra were collected on commercial instruments (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, δ = 77.0; DMSO, δ = 39.5). HRMS was recorded on a commercial apparatus (ESI Source).

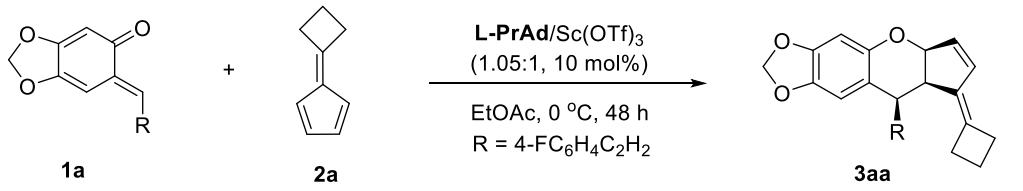
2. General procedure for catalytic asymmetric [4+2] reaction

Preparation of the chiral catalyst: *N*,*N*′-dioxide **L-PrAd** (0.105 mmol) and $Sc(OTf)_3$ (0.1 mmol) were stirred in 2 mL EtOAc at 25 ℃ for 16 h, and then dried under high vacuum.

General procedure for catalytic asymmetric reaction, Condition A: A dry reaction tube was charged with **L-PrAd**-$Sc(OTf)_3$ (1.05:1, 10 mol% catalyst loading), and *o*-QMs **1** (0.15 mmol). Then, EtOAc (0.5 mL) was added and the mixture was stirred at 25 ℃ for 0.5 h. Then, the reaction temperature was reduced to 0 ^{o}C, and fulvene **2** (0.1 mmol) was added. The reaction mixture was stirred for 48 h. The residue was purified by flash chromatography (petroleum ether/ethyl acetate 19:1) on silica gel to afford the product. The enantiomeric excess (ee) was determined by high-performance liquid chromatography (HPLC).

General procedure for catalytic asymmetric reaction, Condition B: A dry reaction tube was charged with **L-PrAd**-$Sc(OTf)_3$ (1.05:1, 10 mol% catalyst loading), and *o*-QMs **4** (0.15 mmol). Then, EtOAc (0.5 mL) was added and the mixture was stirred at 25 ℃ for 0.5 h. Then, the reaction temperature was reduced to 0 ^{o}C, and fulvene **5** (0.1 mmol) was added. After stirred at 0 ℃ for 24 h, the reaction mixture was raised to 25 ℃ for 24 h. The residue was purified by flash chromatography (petroleum ether/ethyl acetate 19:1) on silica gel to afford the product. The enantiomeric excess (ee) was determined by high-performance liquid chromatography (SFC).

3. General procedure for the scale-up reaction.



1a

4.5 mmol
1.215 g

2a

3.0 mmol
0.354 g

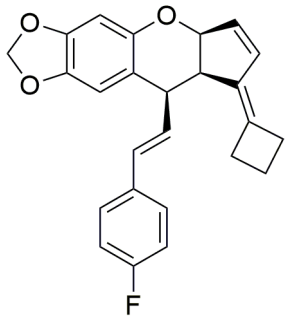
3aa

1.153 g
99% yield, > 19:1 dr, 92% ee

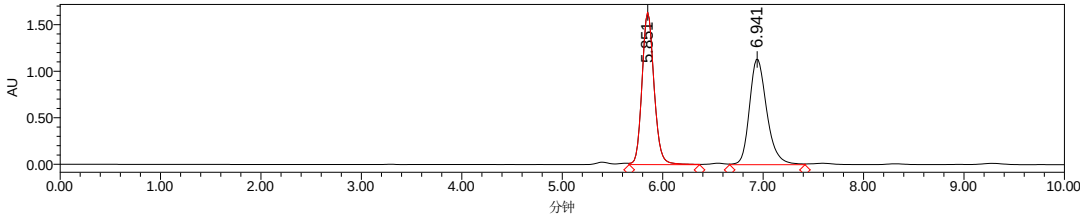
Typical procedure for the scale-up reaction: A flask (50 mL) was charged with **L-PrAd**-Sc(OTf)$_3$ (1.05:1, 10 mol% catalyst loading) and **1a** (4.5 mmol, 1.215 g) . Then, EtOAc (15 mL) was added and the mixture was stirred at 25 ℃ for 0.5 h. Then, the reaction temperature was reduced to 0 ^{o}C, and fulvene **2a** (3.0 mmol, 0.354g) was added. The reaction mixture was stirred for 48 h. The residue was purified by flash chromatography (petroleum ether/ethyl acetate 19:1) on silica gel to afford the product **3aa** as a foamed solid (1.153 g, 99% yield, 92% ee).

4. The analytical and spectral characterization data of the products

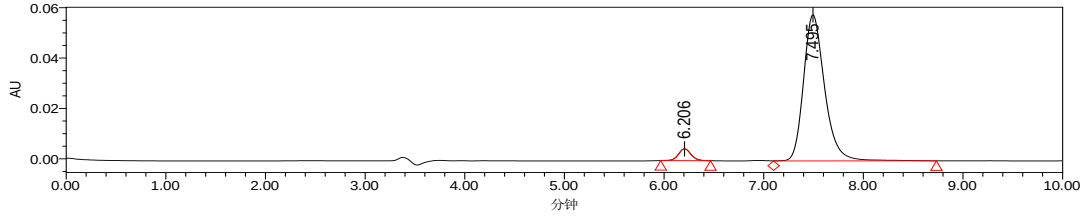
(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-4-fluorostyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3] dioxolo[4,5-*g*]chromene (3aa) :



Prepared according to the general procedure, Condition A. The title compound **3aa** was obtained as yellow oil in 38.1 mg, 98% yield, >19:1 dr, 91% ee. HPLC (Chiralcel ID, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.49 min, t_r (minor) = 6.20 min. $[\alpha]^{16.4}_D$ = +277.5 (*c* = 0.35, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.18 (m, 2H), 7.00 – 6.89 (m, 2H), 6.62 (s, 1H), 6.54 (s, 1H), 6.32 (dd, *J* = 5.6, 1.2 Hz, 1H), 6.26 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.98 (d, *J* = 5.6 Hz, 1H), 5.89 (dd, *J* = 5.6, 1.6 Hz, 2H), 5.24 (d, *J* = 7.6 Hz, 1H), 3.62 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.32 (t, *J* = 7.2 Hz, 1H), 2.95-2.63 (m, 4H), 2.13 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.1, 160.7, 149.8, 146.6, 142.4, 134.9, 134.8, 134.5, 133.8, 133.8, 131.8, 129.3, 129.2, 128.6, 127.6, 127.6, 124.0, 115.3, 115.1, 107.1, 100.9, 100.6, 85.4, 46.2, 43.1, 30.6, 30.3, 17.6. IR $\tilde{\nu}$ (film): 2951, 2906, 1508, 1477, 1446, 1257, 1224, 1147, 1039, 966, 939, 858, 823. HRMS (ESI-TOF) calcd for $C_{25}H_{21}O_3FK^+$ ([M]+K^+) = 427.1106, Found 427.1111.

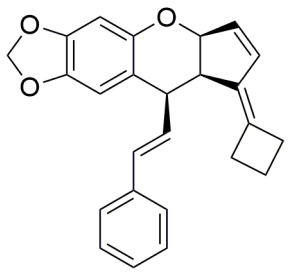


	Retention Time	Area	% Area
1	5.851	13604358	50.01
2	6.941	13599188	49.99



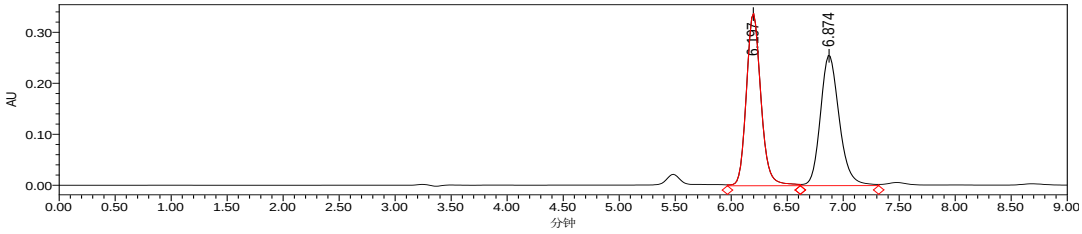
	Retention Time	Area	% Area
1	6.206	41286	4.61
2	7.495	854366	95.39

(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-styryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ba) :

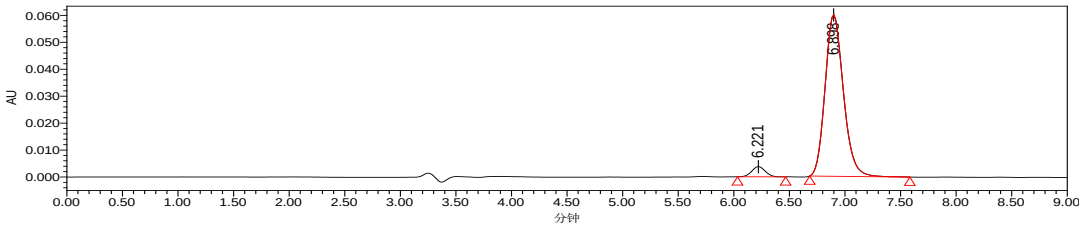


Prepared according to the general procedure, Condition A. The title compound **3ba** was obtained as yellow oil in 36.0 mg, 97% yield, >19:1 dr, 91% ee. HPLC (Chiralcel ID, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.87 min, t_r (minor) = 6.20 min. $[\alpha]^{16.3}_D$ = +266.3 (*c* = 0.65, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.10

(m, 4H), 7.11-7.05 (m, 1H), 6.55 (s, 1H), 6.46 (s, 1H), 6.28 – 6.20 (m, 2H), 6.16 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.89 (d, *J* = 5.2 Hz, 1H), 5.80 (dd, *J* = 6.0, 1.2 Hz, 2H), 5.17 (d, *J* = 7.2 Hz, 1H), 3.60 – 3.51 (m, 1H), 3.25 (t, *J* = 7.2 Hz, 1H), 2.85 – 2.54 (m, 4H), 2.02 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 146.6, 142.4, 137.7, 134.9, 134.9, 134.5, 131.8, 129.9, 129.5, 128.3, 127.1, 126.9, 126.2, 124.1, 107.2, 100.9, 100.5, 85.4, 46.2, 43.2, 30.7, 30.4, 17.6. IR $\tilde{\nu}$ (film): 2951, 2908, 1500, 1479, 1448, 1261, 1149, 1037, 964, 935, 864, 839, 754. HRMS (ESI-TOF) calcd for $C_{25}H_{22}O_3K^+$ ([M]+K^+) = 409.1201, Found 409.1200.

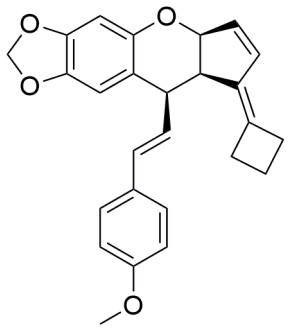


	Retention Time	Area	% Area
1	6.197	3055884	50.49
2	6.874	2997004	49.51

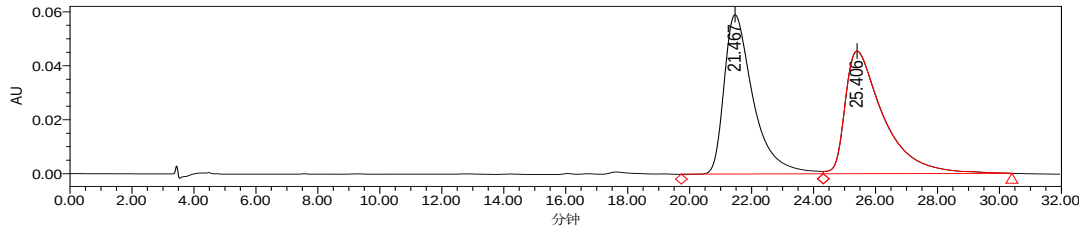


	Retention Time	Area	% Area
1	6.221	31806	4.43
2	6.898	685517	95.57

(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-4-methoxystyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ca) :



Prepared according to the general procedure, Condition A. The title compound **3ca** was obtained as yellow oil in 38.2 mg, 95% yield, >19:1 dr, 91% ee. HPLC (Chiralcel ID, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 21.47 min, t_r (minor) = 25.41 min. $[\alpha]^{17.0}_D$ = +247.5 (*c* = 0.37, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 6.84-6.76 (m, 2H), 6.63 (s, 1H), 6.53 (s, 1H), 6.31 (dd, *J* = 5.6, 1.2 Hz, 1H), 6.26 (d, *J* = 15.6 Hz, 1H), 6.10 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.96 (d, *J* = 5.2 Hz, 1H), 5.88 (dd, *J* = 5.6, 1.6 Hz, 2H), 5.26 (d, *J* = 7.6 Hz, 1H), 3.78 (s, 3H), 3.61 (dd, *J* = 8.8, 7.2 Hz, 1H), 3.33 (t, *J* = 7.6 Hz, 1H), 2.93 – 2.58 (m, 4H), 2.09 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.7, 149.7, 146.5, 142.4, 135.0, 134.9, 134.5, 134.0, 131.8, 130.5, 129.3, 127.3, 127.3, 124.3, 113.8, 107.1, 100.9, 100.5, 85.4, 55.2, 46.3, 43.1, 30.8, 30.4, 17.6. IR $\tilde{\nu}$ (film): 2953, 2908, 1606, 1508, 1479, 1450, 1247, 1151, 1035, 966, 937, 829. HRMS (ESI-TOF) calcd for $C_{26}H_{24}O_4K^+$ ([M]+K^+) = 439.1306, Found 439.1318.



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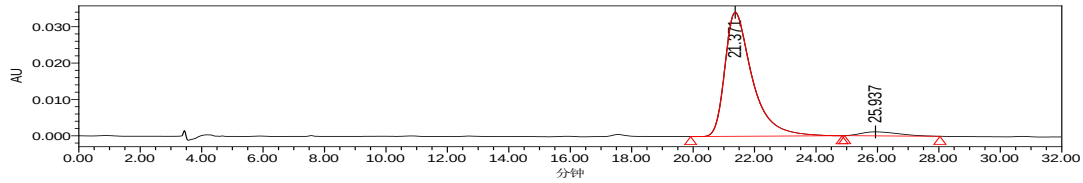
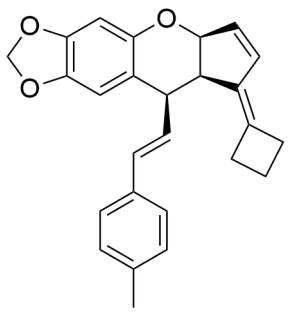
1	21.467	3851515	49.65
2	25.406	3906102	50.35

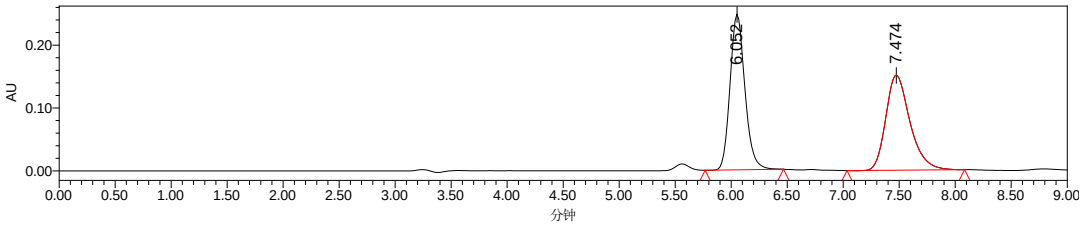


	Retention Time	Area	% Area
1	21.371	2099489	95.79
2	25.937	92320	4.21

(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-4-methylstyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3da) :

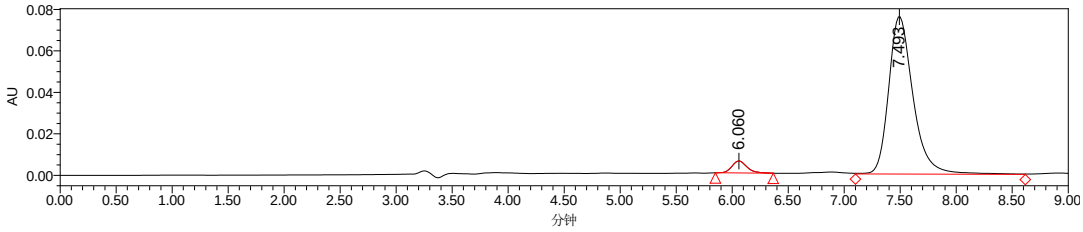


Prepared according to the general procedure, Condition A. The title compound **3da** was obtained as yellow oil in 36.4 mg, 95% yield, >19:1 dr, 91% ee. HPLC (Chiralcel ID, hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.47 min, t_r (minor) = 6.05 min. $[\alpha]^{16.6}_D$ = +242.8 (*c* = 0.59, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 6.54 (s, 1H), 6.35-6.25 (m, 2H), 6.19 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.97 (d, *J* = 5.2 Hz, 1H), 5.88 (dd, *J* = 5.2, 1.2 Hz, 2H), 5.26 (d, *J* = 7.6 Hz, 1H), 3.62 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.34 (t, *J* = 7.2 Hz, 1H), 2.98 – 2.63 (m, 4H), 2.31 (s, 3H), 2.09 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 146.5, 142.4, 136.6, 134.9, 134.9, 134.5, 131.8, 129.8, 129.0, 128.4, 126.1, 124.2, 107.1, 100.9, 100.5, 85.4, 46.3, 43.2, 30.7, 30.4, 21.1, 17.6. IR $\tilde{\nu}$ (film): 2943, 2908, 1500, 1475, 1450, 1263, 1147, 1039, 962, 935, 860, 808. HRMS (ESI-TOF) calcd for $C_{26}H_{24}O_3H^+$ ([M]+H^+) = 383.1653, Found 383.1644.



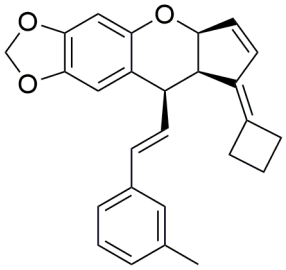
	Retention Time	Area	% Area
1	6.052	2444146	50.77

2	7.474	2369550	49.23

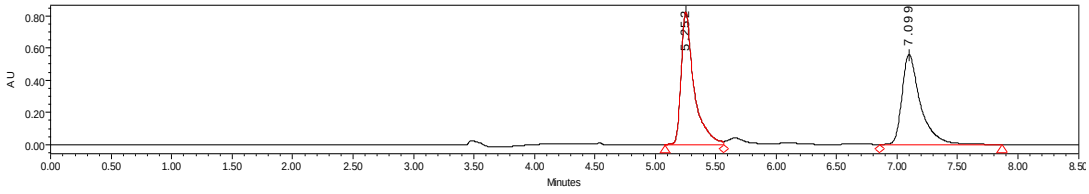


	Retention Time	Area	% Area
1	6.060	53476	4.43
2	7.493	1153191	95.57

(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-3-methylstyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ea) :



Prepared according to the general procedure, Condition A. The title compound **3ea** was obtained as yellow oil in 37.6 mg, 98% yield, >19:1 dr, 91% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.11 min, t_r (minor) = 5.30 min. $[\alpha]^{16.9}_D$ = +279.1 (*c* = 0.64, in CH_2Cl_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.98, 146.61, 142.44, 136.94, 135.29, 134.91, 134.85, 134.34, 131.90, 130.97, 129.97, 127.82, 126.87, 126.11, 125.94, 124.23, 107.22, 100.94, 100.56, 85.45, 46.31, 43.72, 30.64, 30.35, 19.80, 17.57. ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 146.6, 142.4, 137.9, 137.6, 135.0, 134.5, 131.7, 130.0, 129.2, 128.2, 127.7, 126.9, 124.2, 123.4, 107.2, 100.9, 100.5, 85.4, 46.2, 43.3, 30.7, 30.4, 21.3, 17.6. IR $\tilde{\nu}$ (film): 2951, 2910, 1502, 1475, 1450, 1259, 1151, 1085, 1039, 962, 937, 856, 773, 736. HRMS (ESI-TOF) calcd for $C_{26}H_{24}O_3H^+$ ([M]+H^+) = 383.1653, Found 383.1646.



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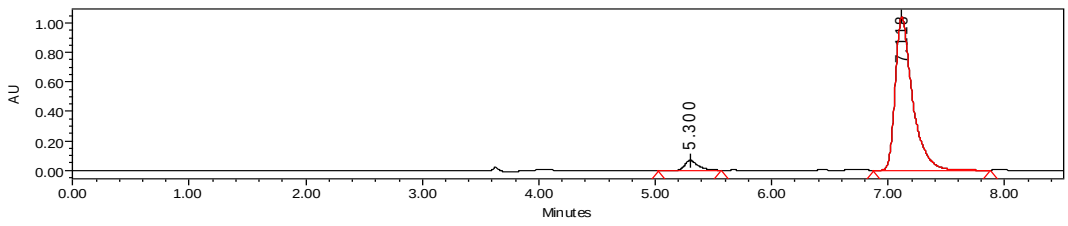
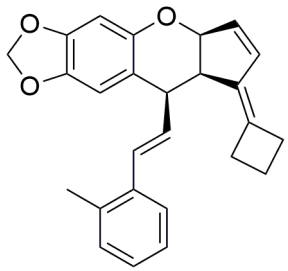
1	5.326	664092	50.96
2	7.132	638992	49.04



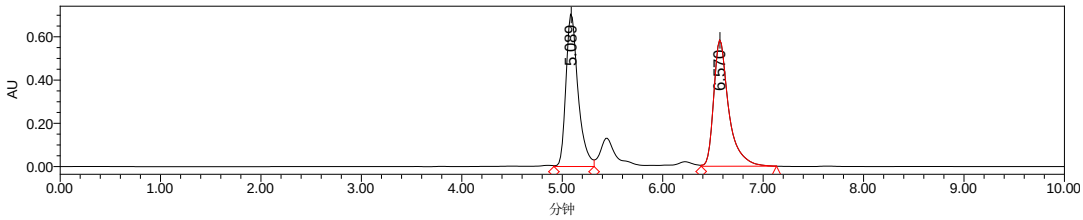
	Retention Time	Area	% Area
1	5.300	516425	4.63

2	7.118	10634293	95.37

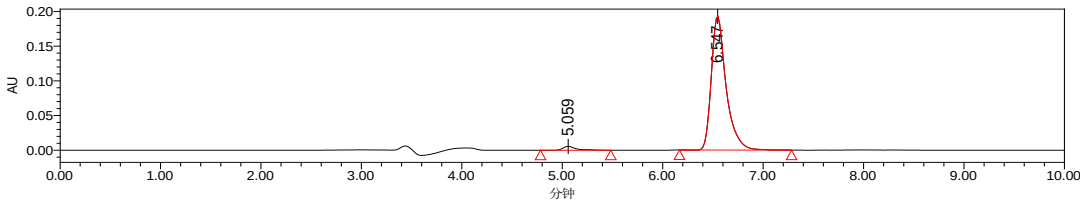
(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-2-methylstyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-g]chromene (3fa) :



Prepared according to the general procedure, Condition A. The title compound **3fa** was obtained as yellow oil in 36.8 mg, 96% yield, >19:1 dr, 95% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.57 min, t_r (minor) = 5.09 min. $[\alpha]^{16.8}_D$ = +268.7 (*c* = 0.40, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 1H), 7.09 (m, 3H), 6.65 (s, 1H), 6.55 (s, 1H), 6.51 (d, *J* = 15.6 Hz, 1H), 6.32 (dd, *J* = 5.6, 1.2 Hz, 1H), 6.07 (dd, *J* = 15.6, 9.6 Hz, 1H), 5.99 (d, *J* = 5.6 Hz, 1H), 5.89 (dd, *J* = 4.0, 1.6 Hz, 2H), 5.24 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.66 (dd, *J* = 9.2, 6.8 Hz, 1H), 3.34 (t, *J* = 7.2 Hz, 1H), 2.97 – 2.67 (m, 4H), 2.31 (s, 3H), 2.14 – 1.93 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.9, 146.6, 142.4, 136.9, 135.2, 134.9, 134.8, 134.3, 131.9, 130.9, 129.9, 127.8, 126.8, 126.1, 125.9, 124.2, 107.2, 100.9, 100.5, 85.4, 46.3, 43.7, 30.6, 30.3, 19.8, 17.5. IR $\tilde{\nu}$ (film): 2947, 2910, 1500, 1477, 1446, 1263, 1145, 1082, 1039, 966, 937, 860, 754. HRMS (ESI-TOF) calcd for $C_{26}H_{24}O_3H^+$ ([M]+H^+) = 383.1653, Found 383.1644.

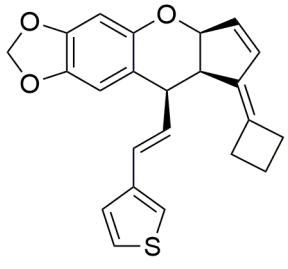


	Retention Time	Area	% Area
1	5.089	5895564	49.36
2	6.570	6048273	50.64



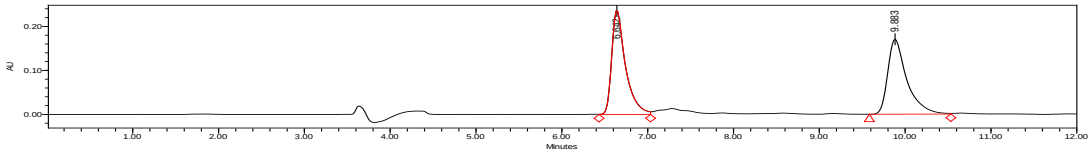
	Retention Time	Area	% Area
1	5.059	50717	2.51
2	6.547	1971682	97.49

(5a*S*,8a*R*,9*R*)-8-cyclobutylidene-9-((*E*)-2-(thiophen-3-yl)vinyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-g]chromene (3ga) :

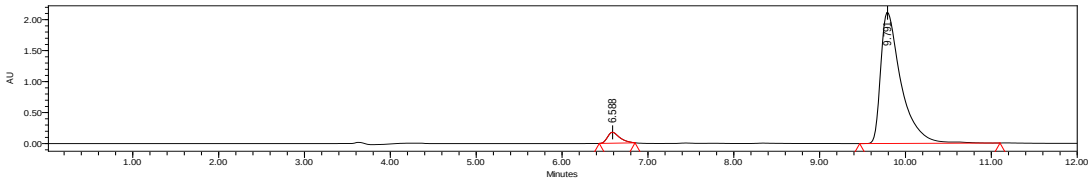


Prepared according to the general procedure, Condition A. The title compound **3ga** was obtained as yellow oil in 36.4 mg, 97% yield, >19:1 dr, 90% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 9.88 min, t_r (minor) = 6.64 min. $[\alpha]^{17.1}_D$ = +264.7 (*c* = 0.71, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.17

(m, 1H), 7.12 (dd, *J* = 5.2, 0.8 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.62 (s, 1H), 6.54 (s, 1H), 6.36 – 6.27 (m, 2H), 6.11 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.96 (d, *J* = 5.2 Hz, 1H), 5.88 (dd, *J* = 5.6, 1.6 Hz, 2H), 5.25 (d, *J* = 7.6 Hz, 1H), 3.63 – 3.54 (m, 1H), 3.33 (t, *J* = 7.6 Hz, 1H), 2.92 – 2.64 (m, 4H), 2.13 – 1.95 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 149.8, 146.6, 142.4, 140.2, 134.9, 134.5, 131.8, 129.4, 125.6, 125.3, 124.2, 124.1, 120.9, 107.1, 100.9, 100.5, 85.4, 46.2, 43.1, 30.7, 30.4, 17.6. IR $\tilde{\nu}$ (film): 2949, 2904, 1498, 1477, 1450, 1257, 1151, 1080, 1037, 962, 937, 860, 769. HRMS (ESI-TOF) calcd for $C_{23}H_{20}O_3SNa^+$ ([M]+Na^+) = 399.1025, Found 399.1032.

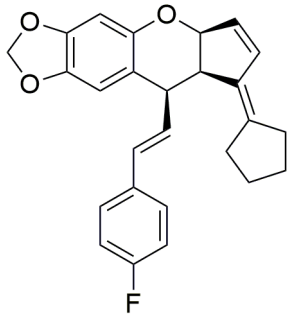


	Retention Time	Area	% Area
1	6.642	2644741	50.10
2	9.883	2634693	49.90

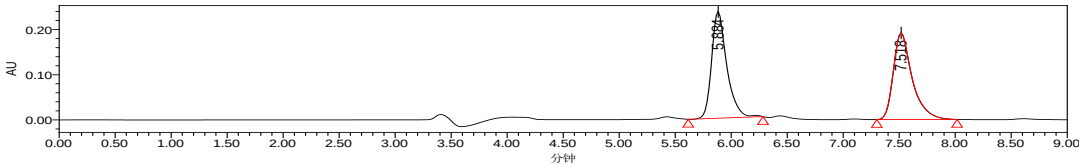


	Retention Time	Area	% Area
1	6.588	1747648	4.79
2	9.791	34720377	95.21

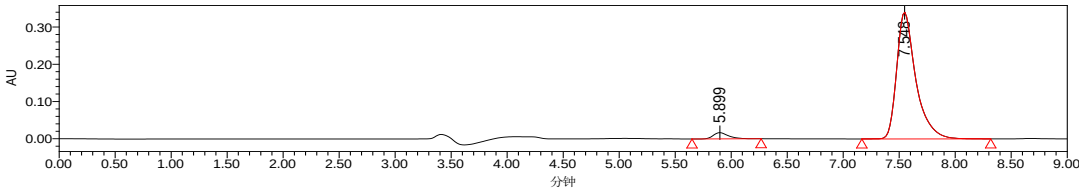
(5a*S*,8a*R*,9*R*)-8-cyclopentylidene-9-((*E*)-4-fluorostyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ab) :



Prepared according to the general procedure, Condition A. The title compound **3ab** was obtained as yellow oil in 38.6 mg, 96% yield, >19:1 dr, 92% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.52 min, t_r (minor) = 5.88 min. $[\alpha]^{17.2}_D$ = +255.8 (*c* = 0.62, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.12 (m, 2H), 6.98-6.86 (m, 2H), 6.64 (s, 1H), 6.56 (s, 1H), 6.46 (dd, *J* = 5.6, 1.2 Hz, 1H), 6.13 (d, *J* = 8.0 Hz, 2H), 6.05 (d, *J* = 5.2 Hz, 1H), 5.90 (dd, *J* = 5.6, 1.2 Hz, 2H), 5.25 (d, *J* = 7.2 Hz, 1H), 3.76 (t, *J* = 7.2 Hz, 1H), 3.31 (t, *J* = 7.2 Hz, 1H), 2.34 (dd, *J* = 21.1, 14.0 Hz, 4H), 1.82 – 1.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.1, 160.6, 149.9, 146.7, 142.4, 136.7, 136.3, 134.5, 133.8, 133.8, 132.1, 129.3, 129.3, 128.2, 127.6, 127.5, 123.8, 115.2, 115.0, 107.4, 100.9, 100.4, 85.4, 47.8, 42.6, 31.3, 31.0, 26.7, 26.4. IR $\tilde{\nu}$ (film): 2951, 2868, 1602, 1506, 1479, 1448, 1228, 1147, 1056, 1035, 966, 935, 842, 819, 740. HRMS (ESI-TOF) calcd for $C_{26}H_{23}O_3FK^+$ ([M]+K^+) = 441.1263, Found 441.1270.

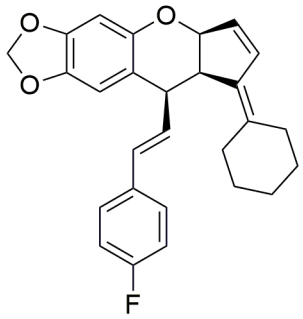


	Retention Time	Area	% Area
1	5.884	2219652	49.87
2	7.518	2231665	50.13

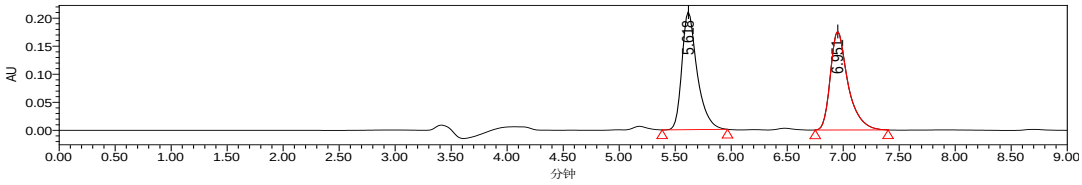


	Retention Time	Area	% Area
1	5.899	157674	3.77
2	7.548	4024883	96.23

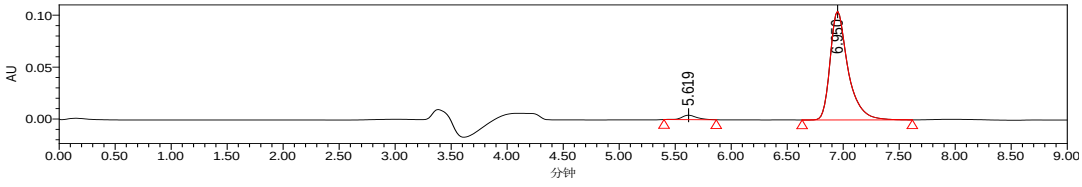
(5a*S*,8a*R*,9*R*)-8-cyclohexylidene-9-((*E*)-4-fluorostyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ac) :



Prepared according to the general procedure, Condition A. The title compound **3ac** was obtained as yellow oil in 40.3 mg, 97% yield, >19:1 dr, 93% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.95 min, t_r (minor) = 5.61 min. $[\alpha]^{17.5}_D$ = +274.4 (*c* = 0.71, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.04 (m, 2H), 6.86-6.77 (m, 2H), 6.55 (s, 1H), 6.51 (dd, *J* = 5.6, 1.6 Hz, 1H), 6.47 (s, 1H), 6.29 (s, 0.05H), 6.04 (d, *J* = 6.8 Hz, 2H), 5.99 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.81 (dd, *J* = 5.6, 1.6 Hz, 2H), 5.20 (d, *J* = 7.6 Hz, 1H), 3.53 (t, *J* = 6.4 Hz, 1H), 3.32 (t, *J* = 7.2 Hz, 1H), 2.33 – 2.04 (m, 4H), 1.63 – 1.34 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.1, 160.6, 149.9, 146.7, 142.3, 135.1, 134.3, 133.8, 133.8, 133.6, 133.0, 129.0, 128.9, 128.6, 127.6, 127.5, 123.5, 115.2, 115.0, 107.3, 100.9, 100.3, 84.7, 46.5, 44.6, 31.9, 31.5, 28.2, 28.0, 26.7. IR $\tilde{\nu}$ (film): 2927, 2854, 1602, 1506, 1477, 1444, 1224, 1147, 1072, 1039, 962, 937, 848, 823, 736. HRMS (ESI-TOF) calcd for $C_{27}H_{25}O_3FK^+$ ([M]+K^+) = 455.1419, Found 455.1428.



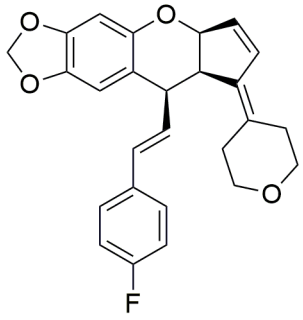
	Retention Time	Area	% Area
1	5.618	2003465	51.00
2	6.951	1924707	49.00



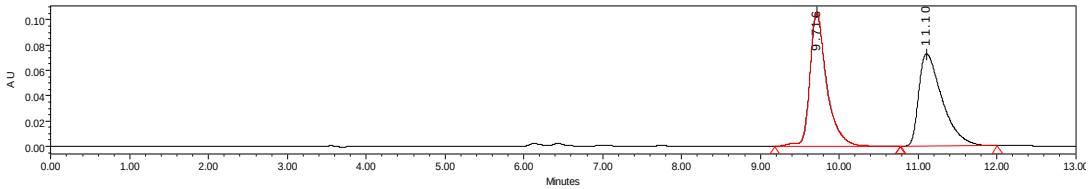
	Retention Time	Area	% Area

1	5.619	39327	3.28
2	6.950	1157868	96.72

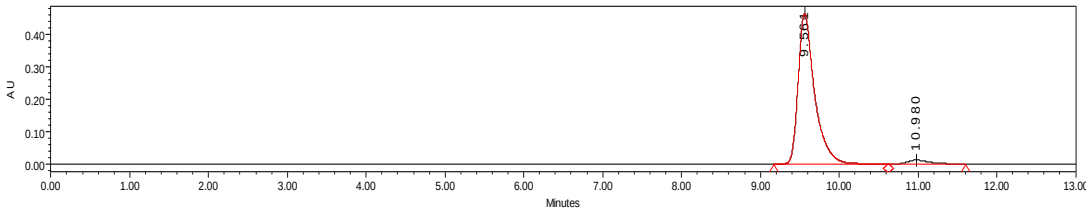
(5a*S*,8a*R*,9*R*)-9-((*E*)-4-fluorostyryl)-8-(tetrahydro-4H-pyran-4-ylidene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ad) :



Prepared according to the general procedure, Condition A. The title compound **3ad** was obtained as yellow oil in 40.1 mg, 96% yield, >19:1 dr, 94% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 9.72 min, t_r (minor) = 11.11 min. $[\alpha]^{17.3}_D$ = +278.1 (*c* = 0.86, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 2H), 6.96-6.87 (m, 2H), 6.61 (s, 1H), 6.59 – 6.53 (m, 2H), 6.23 – 6.13 (m, 2H), 6.08 (dd, *J* = 15.6, 8.8 Hz, 2H), 5.89 (dd, *J* = 7.6, 1.6 Hz, 2H), 5.28 (d, *J* = 7.6 Hz, 1H), 3.88-3.79 (m, 1H), 3.79-3.71 (m, 1H), 3.65 (t, *J* = 5.6 Hz, 2H), 3.60 (dd, *J* = 8.4, 6.8 Hz, 1H), 3.42 (t, *J* = 7.2 Hz, 1H), 2.52 – 2.40 (m, 2H), 2.37 (t, *J* = 5.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.2, 160.7, 149.8, 146.9, 142.4, 137.0, 134.2, 133.7, 133.5, 128.8, 128.5, 128.4, 127.7, 127.6, 127.5, 123.2, 115.3, 115.1, 107.2, 101.0, 100.4, 84.5, 69.0, 68.6, 46.4, 44.7, 32.3, 31.8. IR $\tilde{\nu}$ (film): 2960, 2846, 1600, 1508, 1475, 1444, 1222, 1151, 1095, 1035, 964, 927, 848, 815,734. HRMS (ESI-TOF) calcd for $C_{26}H_{23}O_4FK^+$ ([M]+K^+) = 457.1212, Found 457.1214.

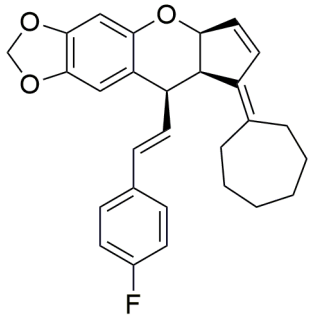


	Retention Time	Area	% Area
1	9.716	1563555	50.87
2	11.109	1510300	49.13



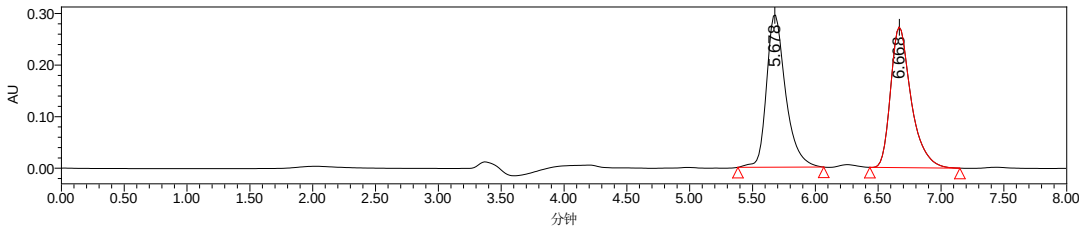
	Retention Time	Area	% Area
1	9.561	6742171	96.73
2	10.980	227972	3.27

(5a*S*,8a*R*,9*R*)-8-cycloheptylidene-9-((*E*)-4-fluorostyryl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ae) :

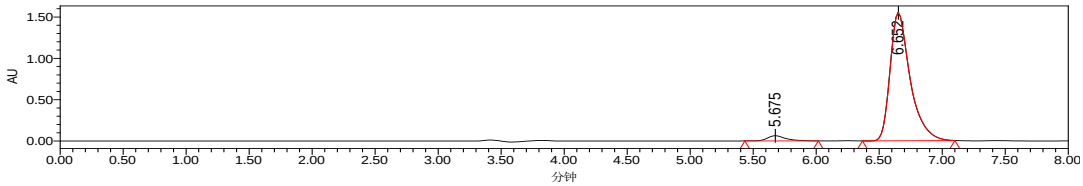


Prepared according to the general procedure, Condition A. The title compound **3ae** was obtained as yellow oil in 42.1 mg, 98% yield, >19:1 dr, 93% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.67 min, t_r (minor) = 5.68 min.

$[\alpha]^{17.6}_{D}$ = +281.6 (*c* = 0.61, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.12 (m, 2H), 6.95-6.86 (m, 2H), 6.64 (s, 1H), 6.60 (dd, *J* = 5.6, 1.6 Hz, 1H), 6.55 (s, 1H), 6.13 (d, *J* = 3.6 Hz, 2H), 6.08 (dd, *J* = 5.6, 1.6 Hz, 1H), 5.90 (dd, *J* = 5.2, 1.6 Hz, 2H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.74 – 3.67 (m, 1H), 3.37 (t, *J* = 6.8 Hz, 1H), 2.50-2.42 (m, 2H), 2.35 (d, *J* = 4.4 Hz, 2H), 1.80-1.68 (m, 2H), 1.64 – 1.47 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 160.6, 149.9, 146.7, 142.3, 137.8, 135.2, 134.8, 133.8, 133.8, 132.8, 129.1, 128.4, 127.5, 127.5, 123.5, 115.2, 115.0, 107.4, 100.9, 100.3, 85.0, 47.1, 43.8, 33.2, 31.9, 29.9, 28.9, 28.4, 27.5. IR $\tilde{\nu}$ (film): 2920, 2854, 1598, 1506, 1475, 1448, 1224, 1153, 1070, 1037, 962, 939, 846, 817, 736. HRMS (ESI-TOF) calcd for $C_{28}H_{27}O_3FK^+$ ([M]+K^+) = 469.1576, Found 469.1587.

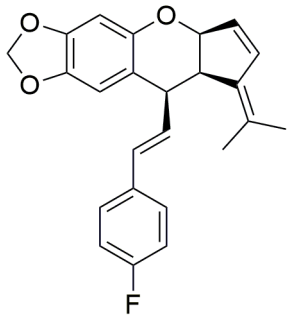


	Retention Time	Area	% Area
1	5.678	3123224	50.27
2	6.668	3089623	49.73

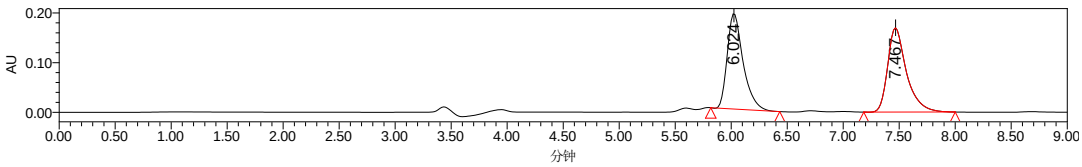


	Retention Time	Area	% Area
1	5.675	630931	3.56
2	6.652	17100282	96.44

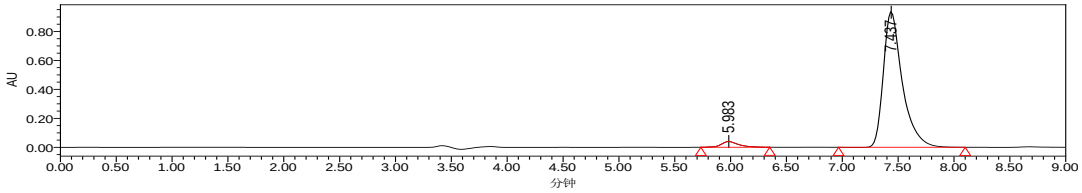
(5a*S*,8a*R*,9*R*)-9-((*E*)-4-fluorostyryl)-8-(propan-2-ylidene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3af) :



Prepared according to the general procedure, Condition A. The title compound **3af** was obtained as yellow oil in 37.2 mg, 99% yield, >19:1 dr, 93% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 7.47 min, t_r (minor) = 6.02 min. $[\alpha]^{17.7}_{D}$ = +277.5 (*c* = 0.45, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.11 (m, 2H), 6.98 – 6.87 (m, 2H), 6.64 (s, 1H), 6.60 – 6.54 (m, 2H), 6.11 (d, *J* = 7.6 Hz, 2H), 6.08-6.04 (m, 1H), 5.90 (dd, *J* = 5.6, 1.2 Hz, 2H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.71 (t, *J* = 6.8 Hz, 1H), 3.39 (t, *J* = 7.2 Hz, 1H), 1.87 (s, 3H), 1.79 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 163.1, 160.6, 149.9, 146.7, 142.3, 138.0, 135.0, 133.8, 133.8, 132.7, 129.1, 129.1, 128.3, 127.6, 127.5, 125.2, 123.6, 115.2, 115.0, 107.3, 100.9, 100.4, 85.0, 47.2, 43.9, 29.7, 21.5, 20.9. IR $\tilde{\nu}$ (film): 2906, 1598, 1508, 1481, 1448, 1373, 1257, 1222, 1147, 1041, 966, 937, 840, 817, 738. HRMS (ESI-TOF) calcd for $C_{24}H_{21}O_3FK^+$ ([M]+K^+) = 415.1106, Found 415.1113.

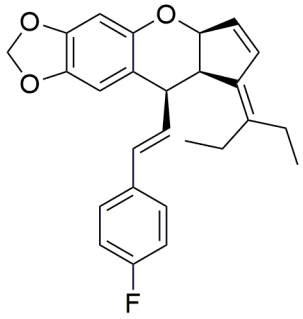


	Retention Time	Area	% Area
1	6.024	1896060	49.00
2	7.467	1973760	51.00

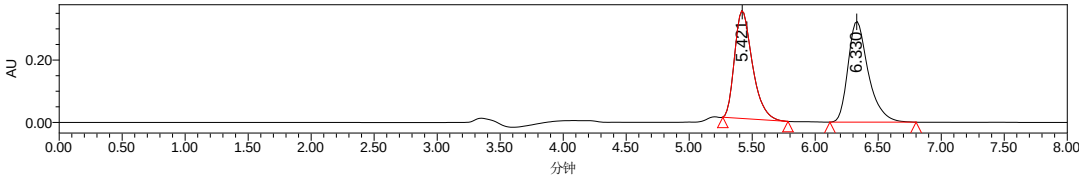


	Retention Time	Area	% Area
1	5.983	416420	3.64
2	7.437	11034338	96.36

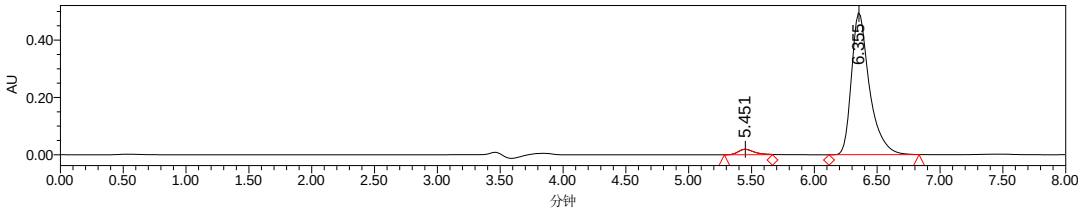
(5a*S*,8a*R*,9*R*)-9-((*E*)-4-fluorostyryl)-8-(pentan-3-ylidene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (3ag) :



Prepared according to the general procedure, Condition A. The title compound **3ag** was obtained as yellow oil in 39.2 mg, 97% yield, >19:1 dr, 93% ee. HPLC (Chiralcel IB, hexane/*i*-PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm) t_r (major) = 6.33 min, t_r (minor) = 5.42 min. $[\alpha]^{17.6}_D$ = +261.2 (*c* = 1.17, in CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.11 (m, 2H), 6.95-6.86 (m, 2H), 6.64 (s, 1H), 6.56 (m, 2H), 6.10 (m, 3H), 5.90 (dd, *J* = 5.2, 1.2 Hz, 2H), 5.27 (d, *J* = 7.6 Hz, 1H), 3.69-3.62 (m,1H), 3.39 (t, *J* = 7.2 Hz, 1H), 2.36 – 2.06 (m, 4H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 163.0, 160.6, 149.9, 146.8, 142.3, 137.2, 137.1, 134.6, 133.7, 133.7, 133.4, 128.8, 128.8, 128.5, 127.5, 127.5, 123.3, 115.2, 115.0, 107.4, 105.9, 100.9, 100.3, 98.9, 84.7, 46.5, 44.4, 25.4, 24.3, 14.1, 12.9. IR $\tilde{\nu}$ (film): 2962, 2935, 2873, 1506, 1475, 1228, 1147, 1037, 962, 941, 837, 817. HRMS (ESI-TOF) calcd for $C_{26}H_{25}O_3FK^+$ ([M]+K^+) = 443.1419, Found 443.1425.

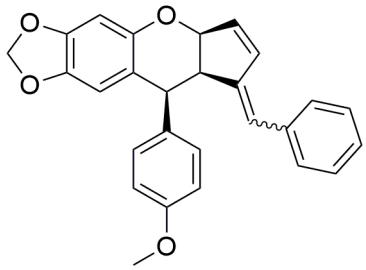


	Retention Time	Area	% Area
1	5.421	3402986	48.49
2	6.330	3615560	51.51

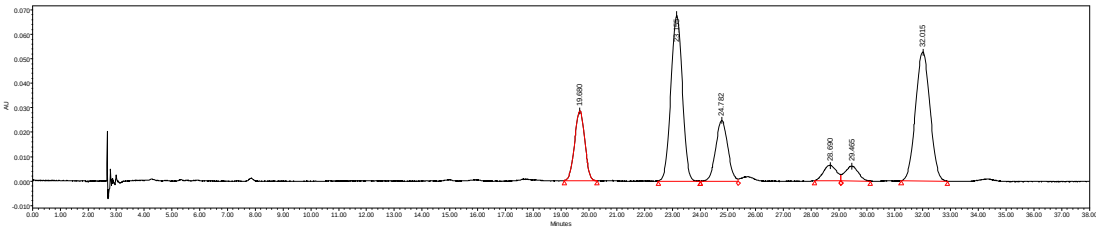


	Retention Time	Area	% Area
1	5.451	171020	3.36
2	6.355	4915994	96.64

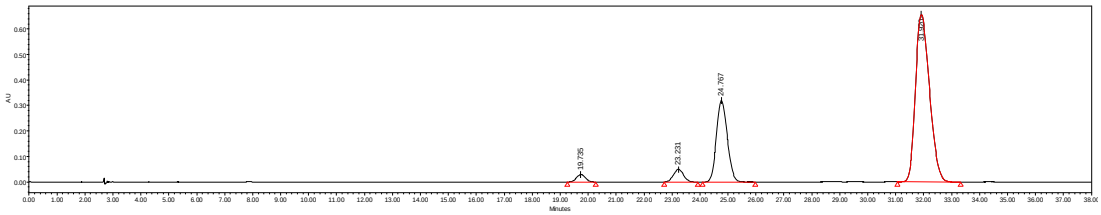
(5a*S*,8a*R*,9*S*)-8-benzylidene-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6a):



Prepared according to the general procedure, Condition B. The title compound **6a** was obtained as yellow oil in 34.9 mg, 85% yield, *E*/*Z* = 3:1, 90/86% ee. SFC (Chiralcel Lux 5μ Cellulose-1, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 19.73 min, t_2 = 23.23 min, t_3 = 24.76 min, t_4 = 31.92 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 1.34H), 7.32 – 7.27 (m, 1.30H), 7.22 – 7.13 (m, 2H), 7.12 – 7.06 (m, 1.39H), 6.78 – 6.66 (m, 2H), 6.65 – 6.58 (m, 2.29H), 6.56 – 6.49 (m, 1H), 6.29 (s, 0.34H), 6.22 – 6.16 (m, 1.31H), 6.11 (s, 0.72H), 5.93 – 5.81 (m, 2H), 5.50 – 5.40 (m, 1H), 4.25 – 4.18 (m, 1H), 4.15 (t, *J* = 7.6 Hz, 0.35H), 3.73 (s, 2H), 3.69 (s, 1H), 3.62 (t, *J* = 7.6 Hz, 0.72H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.0, 157.8, 149.7, 149.2, 146.8, 146.7, 146.6, 145.3, 142.4, 139.9, 138.7, 137.8, 137.7, 134.9, 134.2, 132.9, 132.0, 130.9, 130.0, 128.6, 128.3, 128.1, 126.8, 126.5, 123.7, 123.4, 123.4, 123.1, 112.8, 112.5, 108.1, 107.8, 101.0, 100.4, 100.3, 85.3, 83.2, 55.1, 55.0, 49.2, 46.2, 45.4, 42.6. IR $\tilde{\nu}$ (film): 2914, 1510, 1475, 1251, 1178, 1149, 1068, 1033, 935, 860. HRMS (ESI-TOF) calcd for $C_{27}H_{22}KO_4^+$ ([M]+K^+) = 449.1150, Found 449.1147.

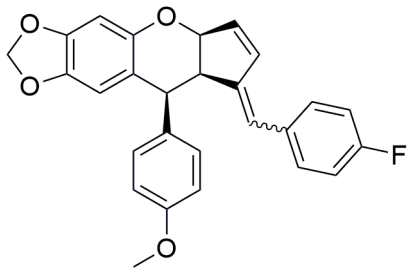


	Retention Time	Area	% Area
1	19.680	732660	12.71
2	23.155	1943306	33.70
3	24.782	752780	13.06
4	28.690	210174	3.65
5	29.465	206036	3.57
6	32.015	1920789	33.31

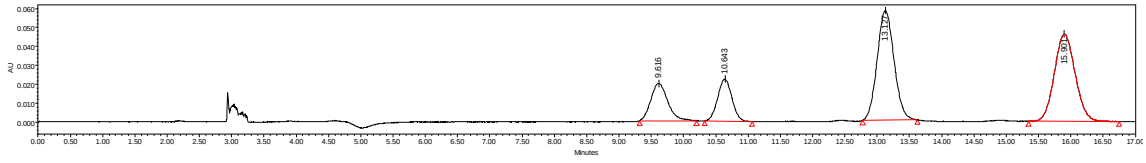


	Retention Time	Area	% Area
1	19.735	648944	1.94
2	23.231	1243365	3.71
3	24.767	8674008	25.91
4	31.920	22916747	68.44

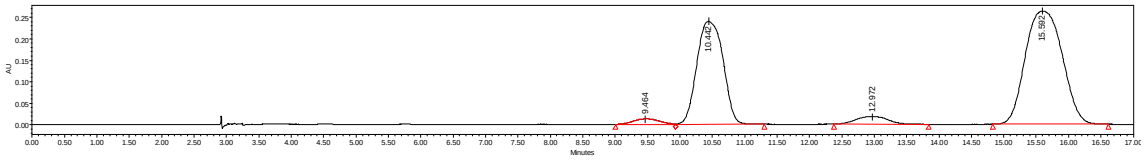
(5a*S*,8a*R*,9*S*)-8-(4-fluorobenzylidene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6b) :



Prepared according to the general procedure, Condition B. The title compound **6b** was obtained as yellow oil in 31.2 mg, 73% yield, *E*/*Z* = 1.5:1, 90/90% ee. SFC (Chiralcel Lux 5µ Cellulose-3, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 9.62 min, t_2 = 10.64 min, t_3 = 13.13 min, t_4 = 15.90 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 0.88H), 7.18 – 7.07 (m, 2H), 7.06 – 7.00 (m, 1.17H), 6.99 – 6.92 (m, 1.16H), 6.78 – 6.72 (m, 0.89H), 6.72 – 6.66 (m, 1.16H), 6.64 – 6.58 (m, 1.51H), 6.56 – 6.49 (m, 1.83H), 6.23 (s, 0.43H), 6.22 – 6.16 (m, 1.37H), 6.03 (s, 0.57H), 5.92 – 5.82 (m, 2H), 5.48 – 5.38 (m, 1H), 4.22 – 4.13 (m, 1H), 4.09 (td, *J* = 7.6, 2.0 Hz, 0.43H), 3.73 (s, 1.72H), 3.69 (s, 1.22H), 3.61 (td, *J* = 7.6, 2.0 Hz, 0.60H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.7, 160.3, 158.0, 157.9, 149.6, 149.1, 146.8, 146.8, 146.4, 145.2, 142.4, 142.4, 139.8, 138.9, 134.9, 133.9, 133.8, 133.8, 132.9, 132.0, 130.9, 129.9, 129.8, 129.7, 129.6, 129.5, 123.6, 123.3, 122.2, 122.0, 115.7, 115.5, 115.3, 115.1, 112.8, 112.6, 108.0, 107.8, 101.0, 100.4, 100.3, 85.2, 83.2, 55.1, 55.0, 49.0, 46.1, 45.1, 42.7. IR $\tilde{\nu}$ (film): 2895, 1506, 1475, 1249, 1180, 1145, 1066, 1035, 939, 858. HRMS (ESI-TOF) calcd for $C_{27}H_{21}O_4K^+$ ([M]+K^+) = 467.1055, Found 467.1065.

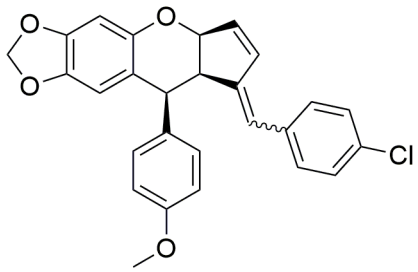


	Retention Time	Area	% Area
1	9.616	359778	12.96
2	10.643	341546	12.31
3	13.127	1048114	37.77
4	15.901	1025788	36.96

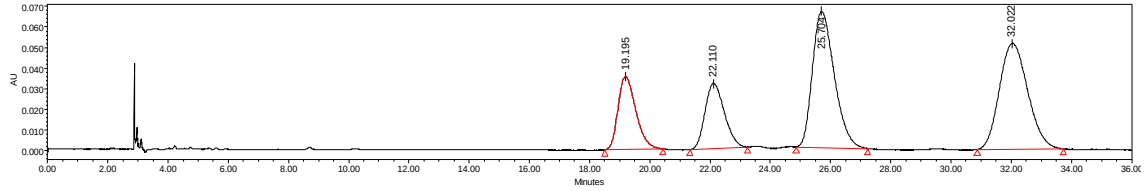


	Retention Time	Area	% Area
1	9.464	359639	1.97
2	10.442	6751508	37.00
3	12.972	625518	3.43
4	15.592	10509368	57.60

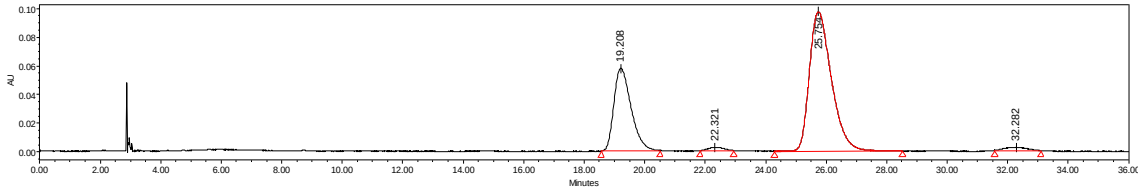
(5a*S*,8a*R*,9*S*)-8-(4-chlorobenzylidene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6c) :



Prepared according to the general procedure, Condition B. The title compound **6c** was obtained as yellow oil in 40.4 mg, 91% yield, *E*/*Z* = 1.5:1, 95/93% ee. SFC (Chiralcel Lux 5µ Amylose-2, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 19.19 min, t_2 = 22.11 min, t_3 = 25.70 min, t_4 = 32.02 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 0.78H), 7.33 – 7.28 (m, 0.78H), 7.26 – 7.20 (m, 1.22H), 7.16 – 7.10 (m, 1.22H), 7.03 – 6.98 (m, 1,22H), 6.78 – 6.73 (m, 0.80H), 6.72 – 6.66 (m, 1.25H), 6.61 (d, *J* = 6.4 Hz, 1.59H), 6.57 – 6.49 (m, 1.75H), 6.26 – 6.16 (m, 1.76H), 6.01 (s, 0.63H), 5.91-5.88 (m, 1H), 5.86 (d, *J* = 1.2 Hz, 0.61H), 5.83 (d, *J* = 1.2 Hz, 0.37H), 5.50-5.38 (m, 1H), 4.23 – 4.15 (m, 1H), 4.10 (td, *J* = 7.2, 1.6 Hz, 0.38H), 3.73 (s, 1.86H), 3.69 (s, 1.11H), 3.61 (td, *J* = 7.2, 1.6 Hz, 0.61H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 157.9, 149.6, 149.1, 147.3, 146.9, 146.8, 145.9, 142.4, 142.4, 139.8, 139.4, 136.2, 136.2, 135.5, 133.8, 132.8, 132.3, 132.1, 131.9, 130.9, 129.9, 129.5, 129.3, 128.8, 128.4, 123.5, 123.2, 122.1, 121.9, 112.8, 112.6, 108.0, 107.8, 101.0, 100.4, 100.3, 85.1, 83.1, 55.1, 55.0, 49.2, 46.1, 45.3, 42.7. IR $\tilde{\nu}$ (film): 2900, 1510, 1475, 1251, 1178, 1145, 1066, 1035, 937, 856. HRMS (ESI-TOF) calcd for $C_{27}H_{21}Cl^{34.9689}O_4K^+$ ([M]+K^+) = 483.0760, Found 483.0766; calcd for $C_{27}H_{21}Cl^{36.9659}O_4K^+$ ([M]+K^+) = 485.0730, Found 485.0732.

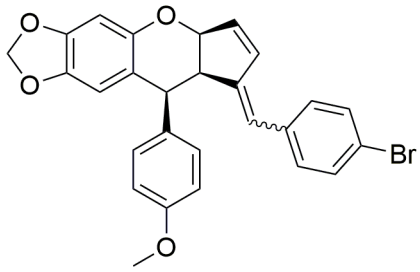


	Retention Time	Area	% Area
1	19.195	1467129	15.28
2	22.110	1415335	14.74
3	25.704	3345324	34.84
4	32.022	3373864	35.14

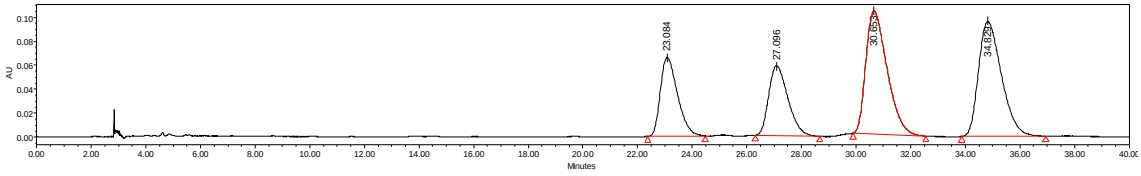


	Retention Time	Area	% Area
1	19.208	2279860	30.96
2	22.321	85008	1.15
3	25.754	4874218	66.20
4	32.282	124124	1.69

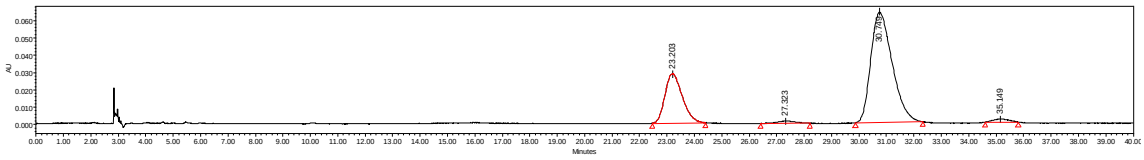
(5a*S*,8a*R*,9*S*)-8-(4-bromobenzylidene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6d) :



Prepared according to the general procedure, Condition B. The title compound **6d** was obtained as yellow oil in 45.8 mg, 94% yield, *E*/*Z* = 2.3:1, 96/90% ee. SFC (Chiralcel Lux 5μ Amylose-2, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 23.08 min, t_2 = 27.09 min, t_3 = 30.65 min, t_4 = 34.83 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 0.7H), 7.38 (d, *J* = 8.4 Hz, 1.3H), 7.24 (d, *J* = 8.4 Hz, 0.7H), 7.12 (d, *J* = 8.4 Hz, 1.3H), 6.94 (d, *J* = 8.4 Hz, 1.3H), 6.74 (d, *J* = 8.7 Hz, 0.7H), 6.71 – 6.65 (m, 1.3H), 6.60 (d, *J* = 7.2 Hz, 1.6H), 6.53 (m, 1.6H), 6.24 – 6.16 (m, 1.6H), 5.99 (s, 0.7H), 5.87 (m, 2H), 5.43 (d, *J* = 7.2 Hz, 1H), 4.17 (dd, *J* = 7.6, 3.6 Hz, 1H), 4.09 (m, 0.3H), 3.73 (s, 2H), 3.69 (s, 1H), 3.64 – 3.57 (m, 0.7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.1, 157.9, 149.6, 149.0, 147.4, 146.8, 146.0, 142.4, 139.8, 139.5, 136.6, 135.6, 133.8, 132.7, 131.9, 131.7, 131.4, 130.9, 129.9, 129.8, 129.6, 123.2, 122.1, 121.9, 120.4, 120.3, 112.8, 112.6, 108.0, 107.8, 101.0, 100.4, 100.3, 85.1, 83.1, 55.1, 49.2, 46.1, 45.3, 42.6. IR $\tilde{\nu}$ (film): 2893, 1508, 1475, 1251, 1182, 1149, 1068, 1033, 939, 856. HRMS (ESI-TOF) calcd for $C_{27}H_{21}Br^{78.9183}O_3K^+$ ([M]+K^+) = 527.0255, Found 527.0260; calcd for $C_{27}H_{21}Br^{80.9163}O_3K^+$ ([M]+K^+) = 529.0234, Found 527.0240

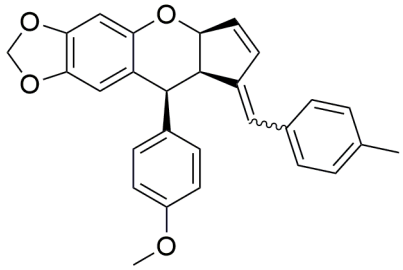


	Retention Time	Area	% Area
1	23.084	2873768	17.04
2	27.096	2858535	16.95
3	30.653	5563804	32.99
4	34.829	5569355	33.02

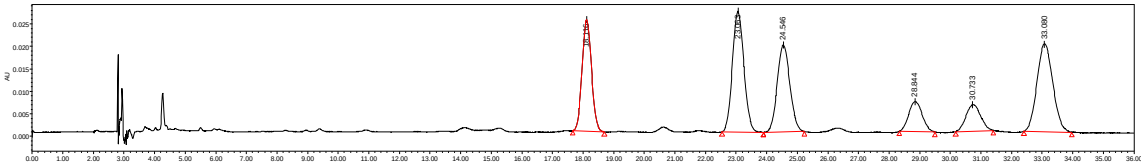


	Retention Time	Area	% Area
1	23.203	1248624	25.80
2	27.271	62418	1.29
3	30.749	3454892	71.39
4	35.149	73470	1.52

(5a*S*,8a*R*,9*S*)-9-(4-methoxyphenyl)-8-(4-methylbenzylidene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6e) :

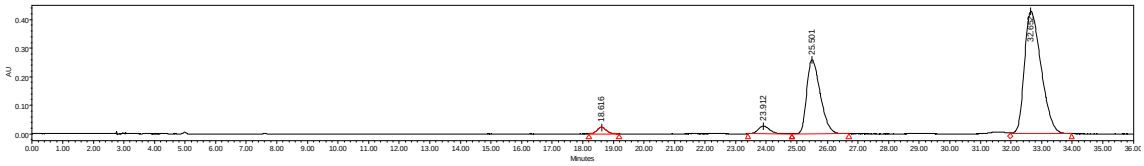


Prepared according to the general procedure, Condition B. The title compound **6e** was obtained as yellow oil in 31.4 mg, 94% yield, *E*/*Z* = 2.3:1, 92/89% ee. SFC (Chiralcel Lux 5μ Cellulose-1, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 18.11 min, t_2 = 23.06 min, t_3 = 24.54 min, t_4 = 28.84 min, t_5 = 30.73 min, t_6 = 33.08 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz, 0.80H), 7.22 (d, *J* = 8.0 Hz, 0.80H), 7.17 – 7.12 (m, 1.27H), 7.09 (d, *J* = 8.0 Hz, 1.23H), 7.04 – 6.98 (m 1H), 6.79 – 6.74 (m, 0.78H), 6.72 – 6.66 (m, 1.23H), 6.65 – 6.58 (m, 2.19H), 6.57 – 6.50 (m, 1.16H), 6.26 (s, 0.41H), 6.20 – 6.12 (m, 1.40H), 6.08 (s, 0.60H), 5.94 – 5.82 (m, 2H), 5.51 – 5.40 (m, 1H), 4.25 (d, *J* = 7.6 Hz, 0.39H), 4.18 (d, *J* = 7.6 Hz, 0.61H), 4.12 (td, *J* = 7.6, 2.0 Hz, 0.38H), 3.73 (s, 1.85H), 3.69 (s, 1.15H), 3.61 (td, *J* = 7.6, 1.2 Hz, 0.61H), 2.43 (s, 1.14H), 2.33 (s, 1,85H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.0, 157.8, 149.7, 149.2, 146.8, 146.7, 145.7, 144.5, 142.3, 139.9, 138.3, 136.6, 136.2, 134.9, 134.8, 134.5, 134.3, 132.8, 132.0, 130.9, 130.1, 129.4, 129.0, 128.2, 128.0, 123.7, 123.4, 123.3, 123.1, 112.8, 112.5, 108.1, 107.8, 100.9, 100.4, 100.2, 85.3, 83.3, 55.1, 55.0, 49.2, 46.2, 45.4, 42.5, 21.3, 21.1. IR $\tilde{\nu}$ (film): 2920, 1508, 1477, 1249, 1182, 1145, 1068, 1039, 941, 867. HRMS (ESI-TOF) calcd for $C_{28}H_{24}O_4K^+$ ([M]+K^+) = 463.1306, Found 463.1305.



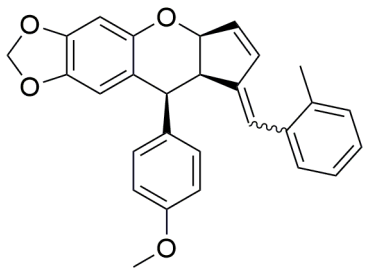
	Retention Time	Area	% Area
1	18.116	533078	18.30
2	23.063	705648	24.22
3	24.546	557818	19.15
4	28.844	207823	7.13
5	30.733	204823	7.03

6	33.080	704316	24.17

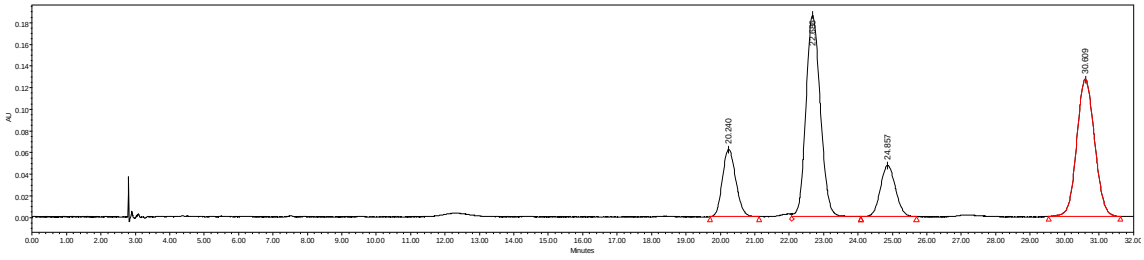


	Retention Time	Area	% Area
1	18.616	476198	1.87
2	23.912	722112	2.84
3	25.501	7960364	31.31
4	32.652	16265390	63.98

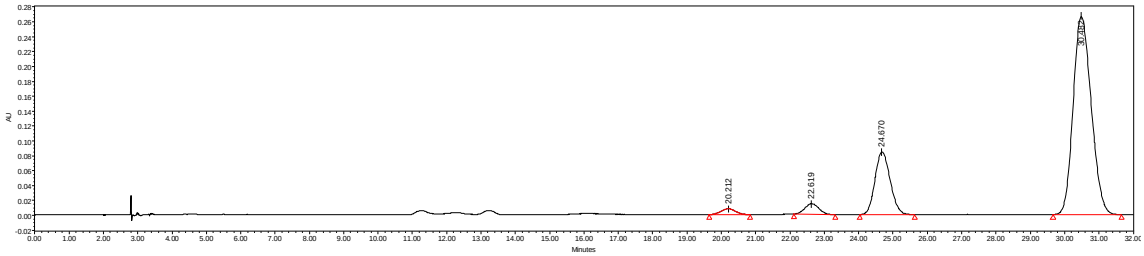
(5a*S*,8a*R*,9*S*)-9-(4-methoxyphenyl)-8-(2-methylbenzylidene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6f) :



Prepared according to the general procedure, Condition B. The title compound **6f** was obtained as yellow oil in 35.2 mg, 83% yield, *E*/*Z* = 4:1, 92/83% ee. SFC (Chiralcel Lux 5μ Cellulose-1, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 20.24 min, t_2 = 22.69 min, t_3 = 24.86 min, t_4 = 30.61 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 0.3H), 7.25 – 7.16 (m, 2H), 7.14 – 7.05 (m, 2H), 6.96-6.91 (m, 0.8H), 6.74-6.66 (m, 2H), 6.65 (s, 0.76H), 6.61 (s, 0.74H), 6.56 (s, 0.26H), 6.54-6.52 (m, 0.28H), 6.52-6.50 (m, 0.23H), 6.49-6.45 (m, 0.78H), 6.43 (s, 0.24H), 6.41-6.37 (m, 0.26H), 6.31 – 6.19 (m, 2H), 5.90 (d, *J* = 1.2 Hz, 0.79H), 5.88-5.84 (m, 1H), 5.79 (d, *J* = 1.2 Hz, 0.23H), 5.45 – 5.37 (m, 1H), 4.28 – 4.18 (m, 1H), 3.95 – 3.90 (m, 0.27H), 3.77 – 3.66 (m, 3.85H), 2.13 (s, 2.34H), 1.92 (s, 0.72H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.0, 157.8, 149.7, 149.1, 146.8, 146.7, 146.6, 145.7, 142.4, 140.7, 137.8, 137.2, 136.9, 136.7, 136.1, 135.0, 134.5, 134.2, 133.2, 130.5, 130.1, 129.8, 129.4, 129.0, 127.1, 127.1, 126.8, 125.8, 125.5, 124.7, 123.9, 122.0, 113.0, 112.7, 108.0, 107.9, 101.0, 100.9, 100.5, 100.45, 85.2, 83.7, 55.1, 48.1, 46.3, 44.1, 43.4, 19.9. IR $\tilde{\nu}$ (film): 3064, 2916, 1508, 1475, 1251, 1182, 1147, 1035, 937, 752. HRMS (ESI-TOF) calcd for $C_{28}H_{24}O_4K^+$ ([M]+K^+) = 463.1306, Found 463.1313.

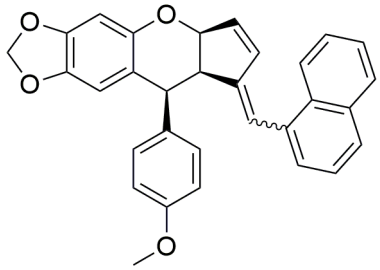


	Retention Time	Area	% Area
1	20.240	1682133	12.82
2	22.686	5417117	41.28
3	24.857	1451290	11.06
4	30.609	4571102	34.84

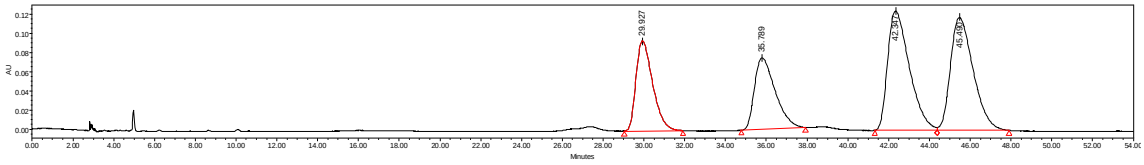


	Retention Time	Area	% Area
1	20.212	236732	1.82
2	22.619	407622	3.14
3	24.670	2596508	19.98
4	30.482	9754739	75.06

(5a*S*,8a*R*,9*S*)-9-(4-methoxyphenyl)-8-(naphthalen-1-ylmethylene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6g) :

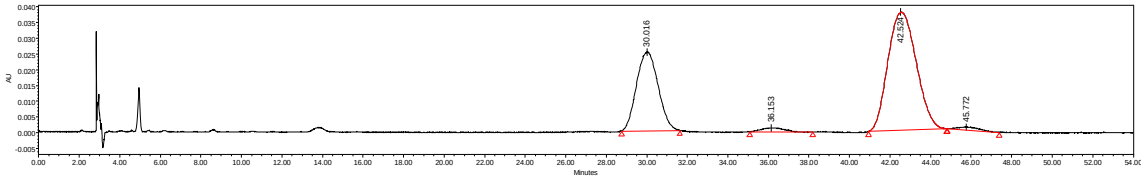


Prepared according to the general procedure, Condition B. The title compound **6g** was obtained as yellow oil in 32.7 mg, 71% yield, *E*/*Z* = 2.3:1, 96/90% ee. SFC (Chiralcel Lux 5μ Amylose-2, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 29.92 min, t_2 = 35.79 min, t_3 = 42.34 min, t_4 = 45.49 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.4 Hz, 0.33H), 7.84 (d, *J* = 8.4 Hz, 0.33H), 7.80 (d, *J* = 8.4 Hz, 0.70H), 7.71 (d, *J* = 8.4 Hz, 0.70H), 7.65 – 7.59 (m, 0.66H), 7.55 – 7.49 (m, 0.67H), 7.48 – 7.41 (m, 1.67H), 7.40 – 7.33 (m, 1.51H), 7.33 – 7.27 (m, 1.40H), 7.10 (d, *J* = 6.8 Hz, 0.71H), 6.82 (s, 0.32H), 6.78 – 6.72 (m, 1.41H), 6.69 (s, 0.71H), 6.64 – 6.58 (m, 1.37H), 6.55 (s, 0.29H), 6.51 – 6.46 (m, 0.92H), 6.43 (d, *J* = 6.0 Hz, 1H), 6.35 – 6.30 (m, 0.61H), 6.29 – 6.19 (m, 1.32H), 5.91 (d, *J* = 1.6 Hz, 0.7H), 5.87 (d, *J* = 1.2 Hz, 0.7H), 5.83 (d, *J* = 1.6 Hz, 0.3H), 5.76 (d, *J* = 1.2 Hz, 0.3H), 5.43 (d, *J* = 7.6 Hz, 1H), 4.35 (d, *J* = 8.4 Hz, 0.7H), 4.25 (td, *J* = 8.0, 2.0 Hz, 0H), 3.86 – 3.80 (m, 0.72H), 3.78 – 3.69 (m, 2.41H), 3.62 (s, 0.90H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 157.6, 149.7, 149.1, 148.2, 147.3, 146.7, 146.5, 142.5, 142.3, 140.2, 137.7, 135.5, 135.1, 135.0, 134.9, 133.8, 133.7, 133.6, 133.4, 132.0, 131.7, 130.5, 129.6, 128.3, 128.1, 127.6, 127.2, 126.4, 125.8, 125.6, 125.4, 125.3, 125.2, 125.0, 124.4, 124.1, 121.2, 121.0, 113.3, 112.5, 107.9, 101.0, 100.9, 100.5, 100.3, 99.9, 84.9, 83.8, 55.1, 54.9, 47.9, 46.3, 44.4, 43.3. IR $\tilde{\nu}$ (film): 3059, 2918, 1508, 1475, 1249, 1182, 1145, 1035, 794, 781. HRMS (ESI-TOF) calcd for $C_{31}H_{24}O_4K^+$ ([M]+K^+) = 499.1306, Found 499.1313.



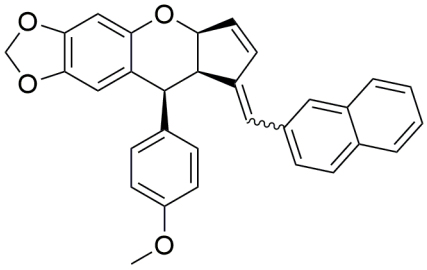
	Retention Time	Area	% Area
1	29.927	5348800	18.49
2	35.789	5272462	18.22
3	42.347	9213630	31.84

4	45.490	9100888	31.45

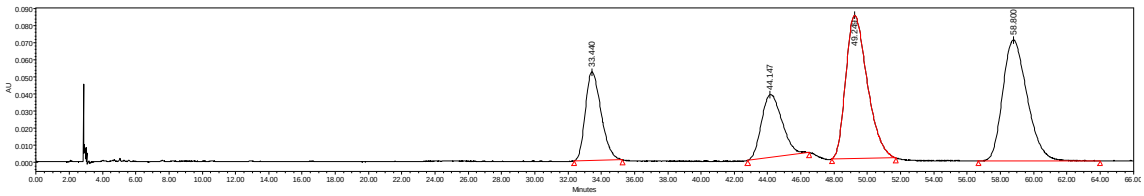


	Retention Time	Area	% Area
1	30.016	1861691	33.14
2	36.153	95385	1.70
3	42.524	3597882	64.04
4	45.772	63477	1.13

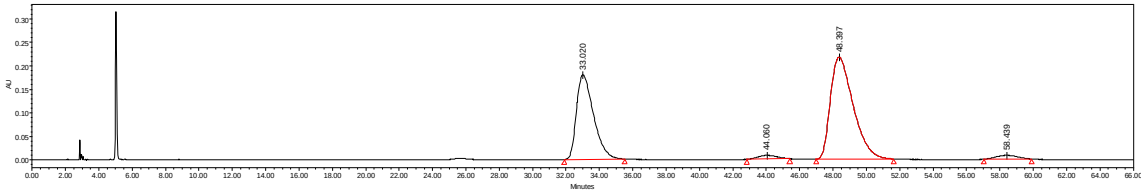
(5a*S*,8a*R*,9*S*)-9-(4-methoxyphenyl)-8-(naphthalen-2-ylmethylene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6h) :



Prepared according to the general procedure, Condition B. The title compound **6h** was obtained as yellow oil in 42.1 mg, 92% yield, *E*/*Z* = 1.5:1, 93/91% ee. SFC (Chiralcel Lux 5μ Amylose-2, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 33.44 min, t_2 = 44.14 min, t_3 = 49.25 min, t_4 = 58.80 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.79 (m, 2H), 7.79 – 7.72 (m, 1.44H), 7.59 – 7.40 (m, 3H), 7.27 -7.25(m, 0.81H), 7.22 – 7.15 (m, 1.16H), 6.77 – 6.68 (m, 2.57H), 6.67 – 6.61 (m, 1.50H), 6.55 – 6.47 (m, 1.24H), 6.45 (s, 0.46H), 6.30 – 6.18 (m, 2H), 5.94 – 5.82 (m, 2H), 5.56 – 5.44 (m, 1H), 4.32 – 4.20 (m, 1.41H), 3.76-3.64 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.1, 157.8, 149.7, 149.2, 147.1, 146.9, 146.8, 145.7, 142.4, 140.0, 139.1, 135.3, 135.2, 134.3, 133.7, 133.4, 132.8, 132.3, 132.1, 131.9, 131.0, 130.1, 128.2, 127.9, 127.8, 127.7, 127.6, 127.2, 126.7, 126.5, 126.4, 126.3, 126.2, 126.0, 125.7, 123.7, 123.5, 123.3, 123.2, 112.8, 112.5, 108.1, 107.8, 101.0, 100.4, 100.3, 85.3, 83.2, 55.1, 55.0, 49.4, 46.2, 45.6, 42.9. IR $\tilde{\nu}$ (film): 3055, 2902, 1510, 1475, 1251, 1180, 1147, 1043, 1037, 939, 746. HRMS (ESI-TOF) calcd for $C_{31}H_{24}O_4K^+$ ([M]+K^+) = 499.1306, Found 499.1313.

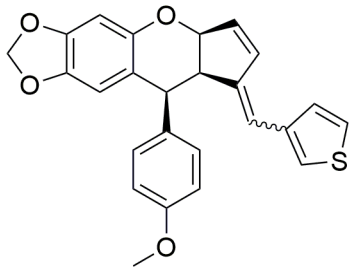


	Retention Time	Area	% Area
1	33.440	3415790	16.14
2	44.147	3167608	14.97
3	49.249	7355674	34.76
4	58.800	7220056	34.12

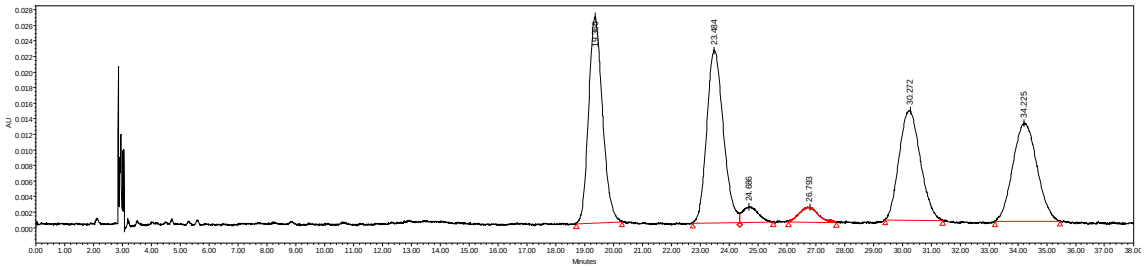


	Retention Time	Area	% Area
1	33.020	12833337	36.91
2	44.060	629182	1.81
3	48.397	20566503	59.15
4	58.439	738984	2.13

(5a*S*,8a*R*,9*S*)-9-(4-methoxyphenyl)-8-(thiophen-3-ylmethylene)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6i) :

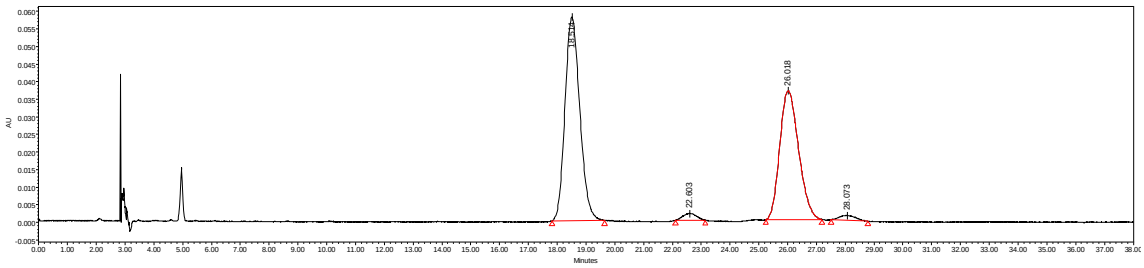


Prepared according to the general procedure, Condition B. The title compound **6i** was obtained as yellow oil in 27.1 mg, 55% yield, *E*/*Z* = 1:1, 93/93% ee. SFC (Chiralcel Lux 5μ Amylose-2, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 19.36 min, t_2 = 23.48 min, t_3 = 24.69 min, t_4 = 26.79 min, t_5 = 30.27 min, t_6 = 34.22 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 - 7.37 (m, 0.5H), 7.26 – 7.21 (m, 1.5H), 7.17 – 7.10 (m, 1H), 6.99 – 6.91 (m, 1H), 6.85 – 6.77 (m, 1H), 6.73 – 6.67 (m, 1H), 6.65 – 6.60 (m, 2H), 6.59 – 6.53 (m, 1H), 6.32 (s, 0.5H), 6.17 (dt, *J* = 5.6, 1.6 Hz, 0H), 6.14 – 6.09 (m, 1H), 6.00 (s, 0.5H), 5.92 – 5.83 (m, 2H), 5.50 – 5.40 (m, 1H), 4.33 (d, *J* = 7.6 Hz, 0.5H), 4.17 (d, *J* = 7.6 Hz, 0.5H), 3.97 (td, *J* = 7.6, 1.6 Hz, 0.5H), 3.73 (s, 1.5H), 3.69 (s, 1.5H), 3.59 (td, *J* = 7.6, 1.6 Hz, 0.5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 158.0, 157.8, 149.6, 149.3, 146.9, 146.7, 145.4, 144.4, 142.4, 142.3, 139.2, 139.0, 138.8, 138.3, 135.0, 134.4, 132.5, 131.8, 131.0, 130.2, 127.7, 127.7, 125.9, 125.3, 123.4, 123.3, 122.7, 121.8, 117.3, 112.8, 112.5, 108.1, 107.8, 101.0, 101.0, 100.4, 100.2, 85.2, 83.3, 55.1, 55.0, 49.2, 46.2, 46.0, 42.7. IR $\tilde{\nu}$ (film): 3049, 2916, 1508, 1477, 1249, 1182, 1149, 1064, 1033, 935, 837, 736. HRMS (ESI-TOF) calcd for $C_{25}H_{20}O_4SK^+$ ([M]+K^+) = 455.0714, Found 455.0717.



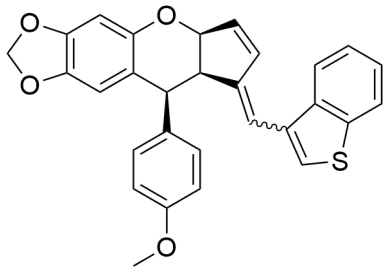
	Retention Time	Area	% Area
1	19.366	885877	26.03
2	23.484	891957	26.20
3	24.686	75362	2.21
4	26.793	87108	2.56

5	30.272	724191	21.28
6	34.225	739383	21.72

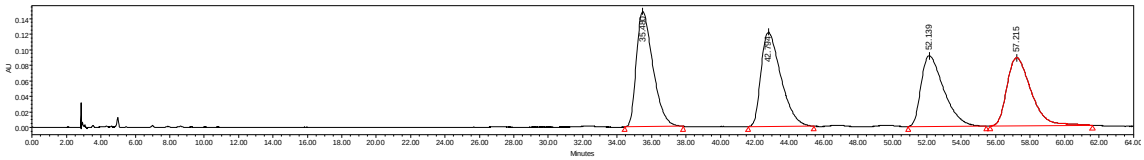


	Retention Time	Area	% Area
1	18.514	2077117	53.78
2	22.603	63384	1.64
3	26.018	1667598	43.18
4	28.073	54116	1.40

(5a*S*,8a*R*,9*S*)-8-(benzo[*b*]thiophen-3-ylmethylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydro cyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6j) :

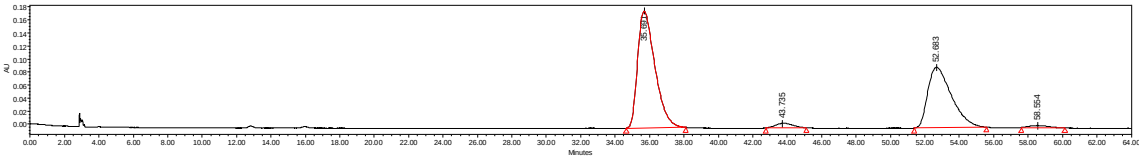


Prepared according to the general procedure, Condition B. The title compound **6j** was obtained as yellow oil in 41.9 mg, 90% yield, *E*/*Z* = 1.2:1, 94/92% ee. SFC (Chiralcel Lux 5µ Amylose-2, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 35.48 min, t_2 = 42.79 min, t_3 = 52.14 min, t_4 = 57.22 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 0.54H), 7.86 – 7.80 (m, 0.46H), 7.63 – 7.57 (m, 0.56H), 7.51 (s, 0.58H), 7.46 – 7.39 (m, 1H), 7.39 – 7.30 (m, 1.46H), 7.26 – 7.20 (m, 1H), 7.05 (d, *J* = 0.4 Hz, 0.46H), 6.75 – 6.69 (m, 1H), 6.68 – 6.63 (m, 1.55H), 6.61 (d, *J* = 6.0 Hz, 1H), 6.57 – 6.53 (m, 0.50H), 6.51 – 6.47 (m, 1H), 6.40 – 6.35 (m, 1H), 6.34 – 6.30 (m, 0.56H), 6.28 – 6.18 (m, 1.47H), 5.92 – 5.80 (m, 2H), 5.50 – 5.42 (m, 1H), 4.30 – 4.21 (m, 1H), 4.11 (td, *J* = 7.6, 1.6 Hz, 1H), 3.77 – 3.70 (m, 1.85H), 3.63 (s, 1.62H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2, 157.7, 149.6, 149.1, 148.2, 147.4, 146.8, 142.4, 142.4, 139.7, 139.4, 139.0, 138.5, 138.3, 135.6, 135.2, 133.3, 133.2, 132.9, 132.7, 130.8, 129.9, 124.4, 123.9, 123.6, 123.6, 122.7, 122.6, 122.4, 122.1, 122.0, 115.3, 114.8, 113.1, 112.5, 108.1, 107.8, 101.0, 100.5, 100.3, 84.9, 83.6, 55.1, 54.9, 48.5, 46.2, 45.7, 42.3. IR $\tilde{\nu}$ (film): 3066, 2897, 1510, 1477, 1249, 1182, 1147, 1064, 1039, 937, 869, 759, 731. HRMS (ESI-TOF) calcd for $C_{29}H_{22}O_4SK^+$ ([M]+K^+) = 505.0870, Found 505.0880.



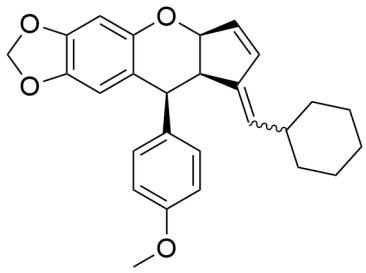
	Retention Time	Area	% Area
1	35.480	9887298	27.09

2	42.794	9758360	26.74
3	52.139	8344175	22.86
4	57.215	8510040	23.32

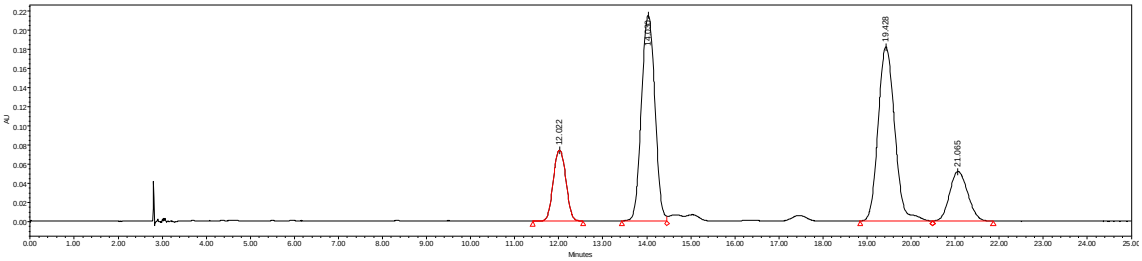


	Retention Time	Area	% Area
1	35.691	12530525	56.55
2	43.735	502172	2.27
3	52.683	8861894	39.99
4	58.554	265032	1.20

(5a*S*,8a*R*,9*S*)-8-(cyclohexylmethylene)-9-(4-methoxyphenyl)-5a,8,8a,9-tetrahydrocyclopenta[*b*][1,3]dioxolo[4,5-*g*]chromene (6k) :

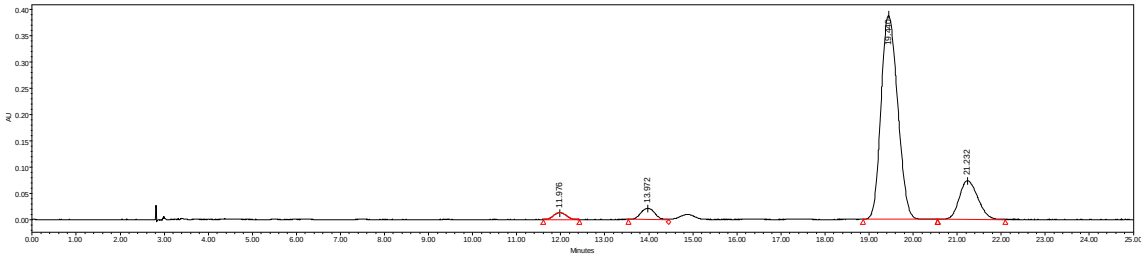


Prepared according to the general procedure, Condition B. The title compound **6k** was obtained as yellow oil in 30.7 mg, 74% yield, *E*/*Z* = 4:1, 92/79% ee. SFC (Chiralcel Lux 5μ Cellulose-1, CO_2/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm) t_1 = 12.02 min, t_2 = 14.03 min, t_3 = 19.43 min, t_4 = 21.07 min. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.07 (m, 2H), 6.71 – 6.64 (m, 2H), 6.63 – 6.54 (m, 2H), 6.35 (d, *J* = 5.6 Hz, 0.78H), 6.05 (dd, *J* = 5.6, 0.8 Hz, 0.28H), 6.00 (dt, *J* = 5.6, 2.0 Hz, 1H), 5.96 (dd, *J* = 5.6, 2.0 Hz, 0.24H), 5.90 – 5.86 (m, 1H), 5.84 (d, *J* = 1.2 Hz, 1H), 5.38-5.30 (m, 1H), 5.16 (d, *J* = 9.6 Hz, 0.23H), 4.88 (d, *J* = 9.6 Hz, 0.77H), 4.18 (d, *J* = 8.0 Hz, 0.24H), 4.04 (d, *J* = 8.0 Hz, 0.77H), 3.74 (s, 2.23H), 3.72 (s, 0.67H), 3.61 (td, *J* = 7.6, 1.6 Hz, 0.24H), 3.42 (td, *J* = 7.6, 1.6 Hz, 0.77H), 2.23-2.04 (m, 1H), 1.81 – 1.60 (m, 3H), 1.54 (m, 1H), 1.40 – 1.33 (m 1H), 1.31 – 1.10 (m, 3H), 1.06 – 0.86 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.9, 149.7, 149.5, 146.7, 146.6, 142.3, 142.2, 141.0, 138.9, 134.7, 134.1, 133.5, 132.9, 132.7, 130.9, 130.4, 130.0, 129.9, 124.1, 123.9, 112.8, 112.7, 107.8, 100.9, 100.4, 100.3, 85.0, 83.9, 55.1, 55.0, 47.3, 45.9, 45.3, 45.2, 38.7, 38.3, 33.4, 33.2, 32.8, 26.0, 25.9, 25.8, 25.8. IR $\tilde{\nu}$ (film): 2922, 2850, 1510, 1477, 1249, 1182, 1145, 1037, 939, 854. HRMS (ESI-TOF) calcd for $C_{27}H_{28}O_4K^+$ ([M]+K^+) = 455.1619, Found 455.1626.



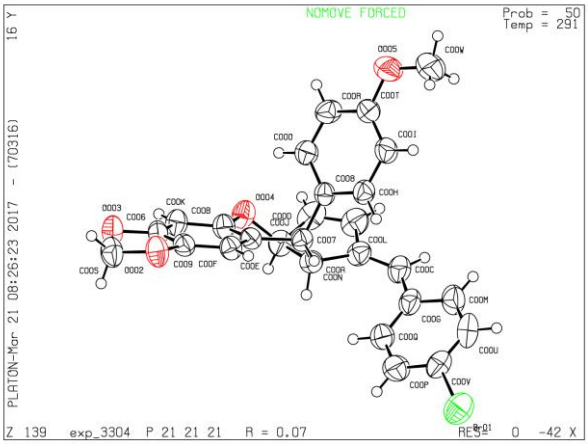
	Retention Time	Area	% Area

1	12.022	1478126	12.00
2	14.030	4573911	37.14
3	19.428	4780068	38.82
4	21.065	1481836	12.03

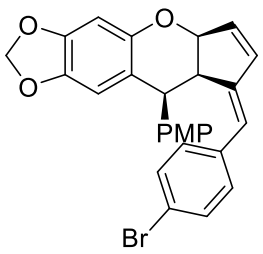


	Retention Time	Area	% Area
1	11.976	255979	1.96
2	13.972	458314	3.51
3	19.440	10195369	77.99
4	21.232	2162934	16.55

5. The X-ray data for 6d.



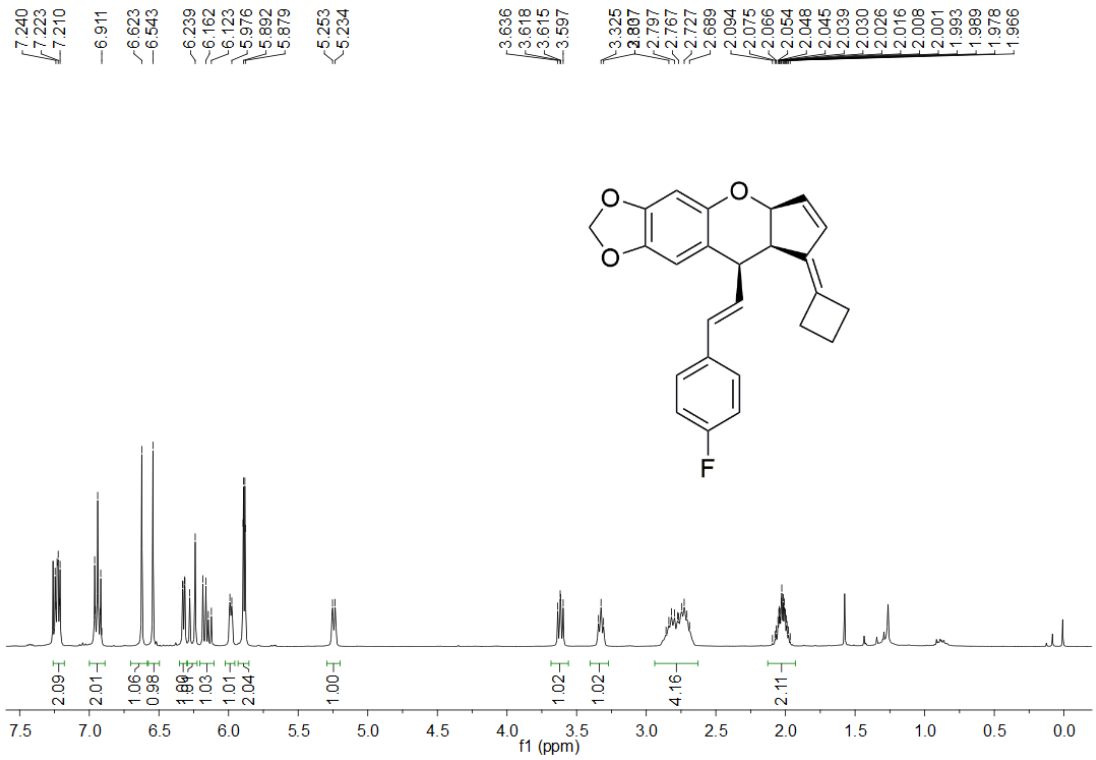
≡

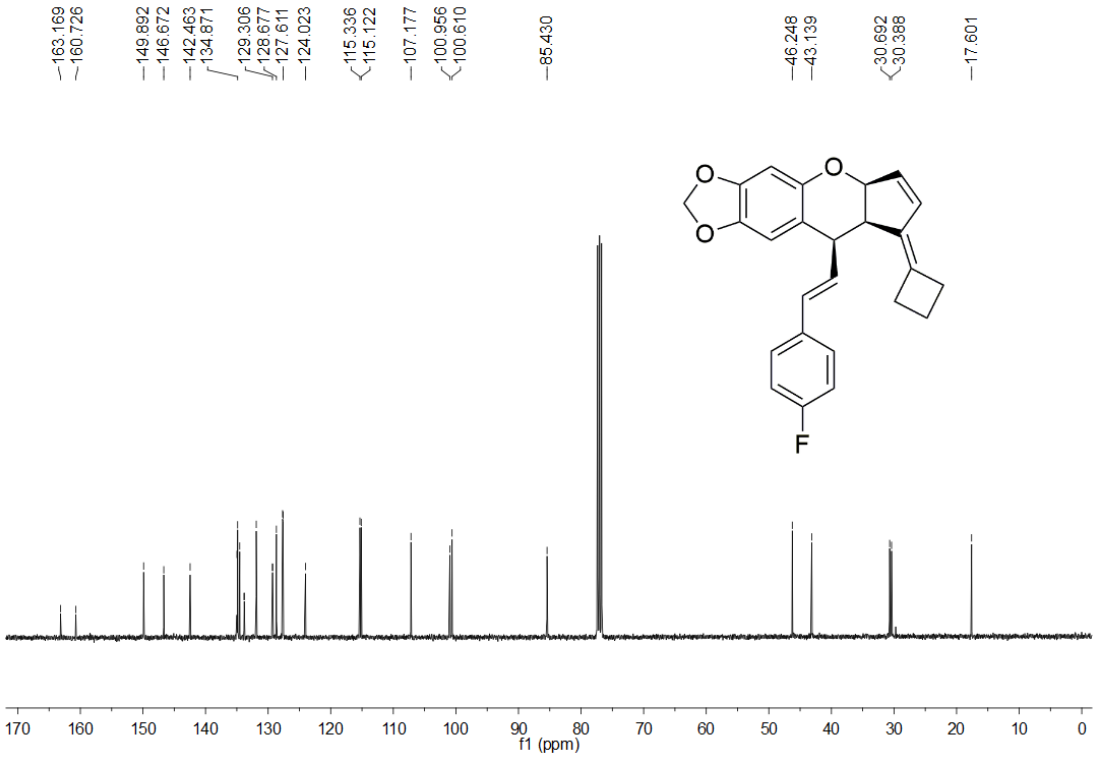


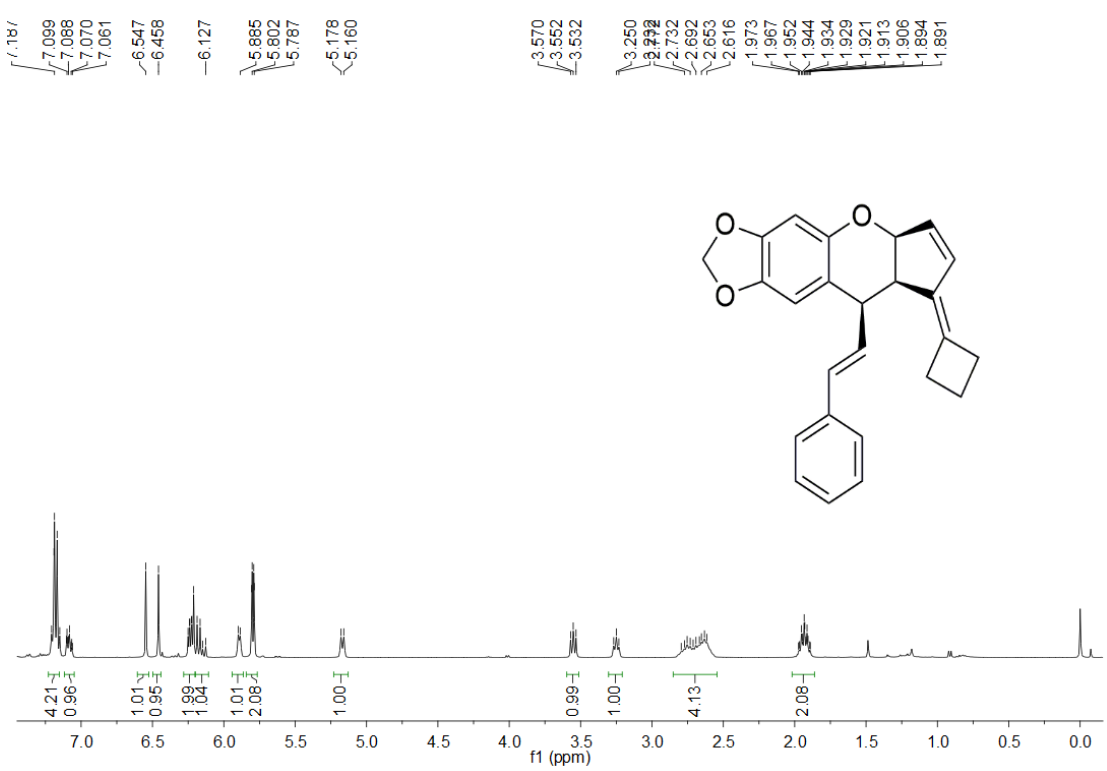
The product **6d** was recrystallized from DCM, *i*PrOH and Petroleum ether.

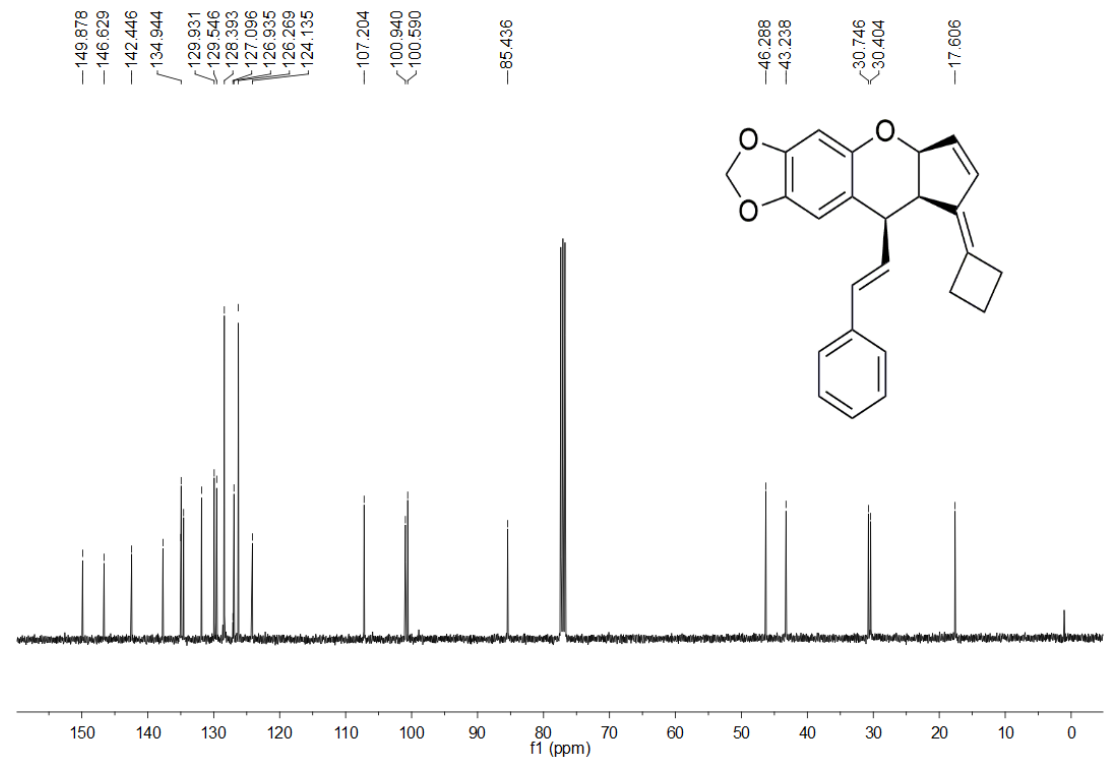
CCDC-1569433 (**6d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk./ data_request/cif.

6. Copy of NMR spectra






7.099
7.088
7.070
7.061
6.547
6.458
6.127
5.885
5.802
5.787
5.178
5.160
3.570
3.552
3.532
3.250
2.732
2.692
2.653
2.616
1.973
1.967
1.952
1.944
1.934
1.929
1.921
1.913
1.906
1.894
1.891
4.21
0.96
1.01
0.95
1.99
1.04
1.01
2.08
1.00
0.99
1.00
4.13
2.08
f1 (ppm)


149.878
146.629
142.446
134.944
129.931
129.546
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126.935
126.269
124.135
107.204
100.940
100.590
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46.288
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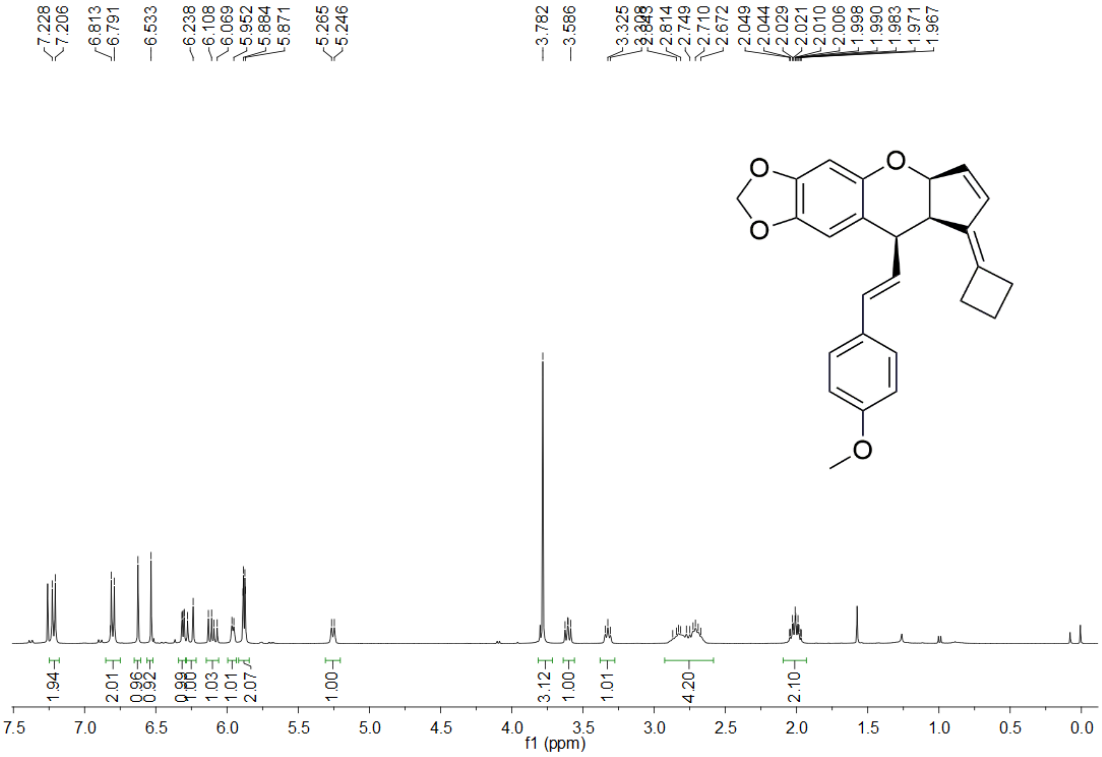
f1 (ppm)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3.782
3.586
3.325
2.814
2.749
2.710
2.672
2.049
2.044
2.029
2.021
2.010
2.006
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1.990
1.983
1.971
1.967
1.94
2.01
0.96
0.92
1.03
1.01
2.07
1.00
3.12
1.00
1.01
4.20
2.10
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6.0
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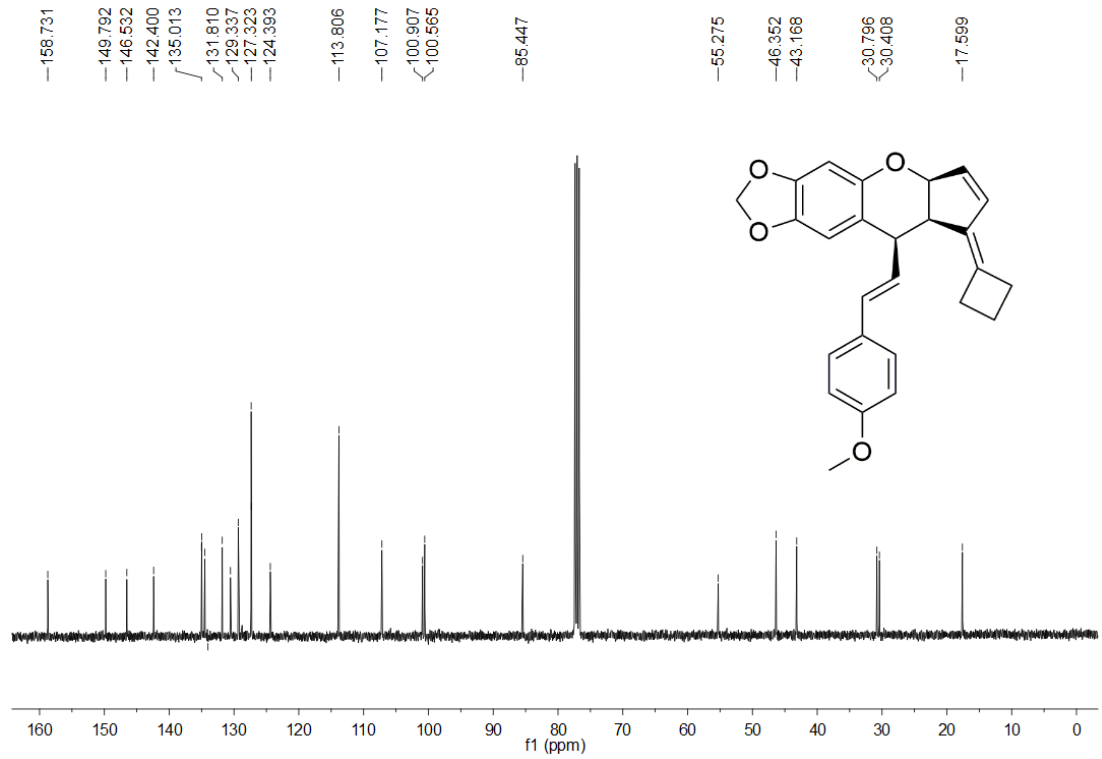
f1 (ppm)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127.323
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113.806
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100.907
100.565
85.447
55.275
46.352
43.168
30.796
30.408
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130
120
110
100
90
80
70
60
50
40
30
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10
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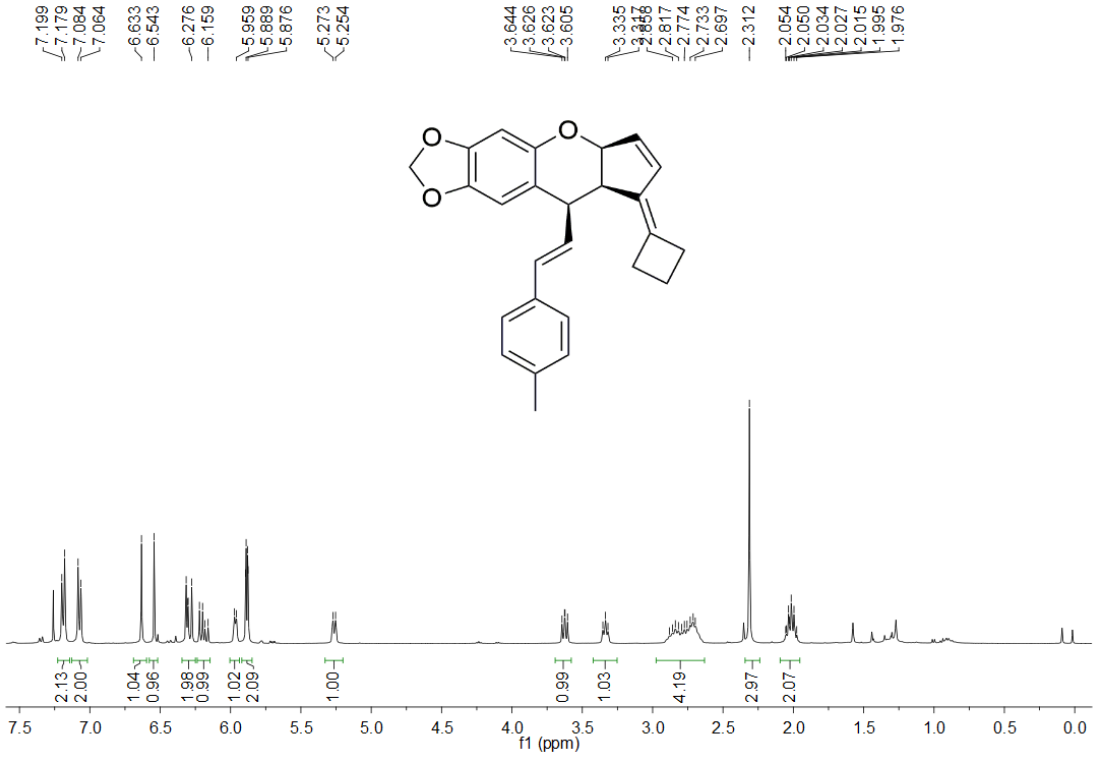
f1 (ppm)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6.543
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6.159
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5.889
5.876
5.273
5.254
3.644
3.626
3.623
3.605
3.335
2.817
2.774
2.733
2.697
2.312
2.054
2.050
2.034
2.027
2.015
1.995
1.976
2.13
2.00
1.04
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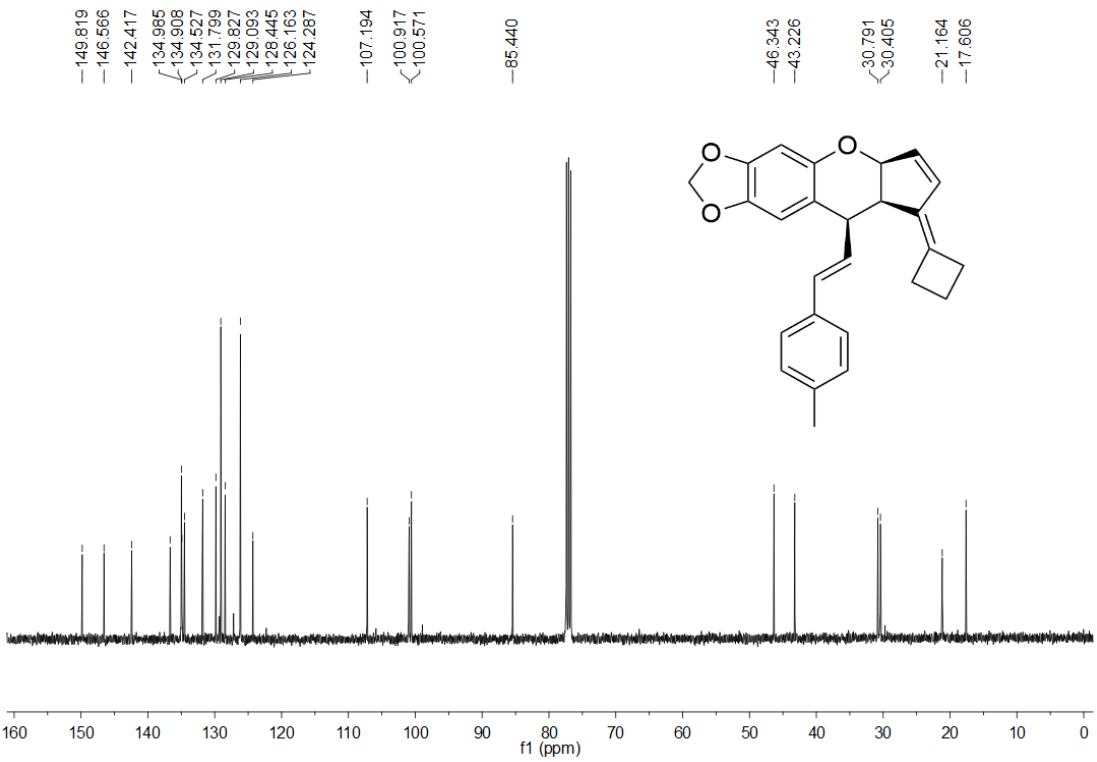
0.99
1.02
2.09
1.00
0.99
1.03
4.19
2.97
2.07
f1 (ppm)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129.093
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100.571
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46.343
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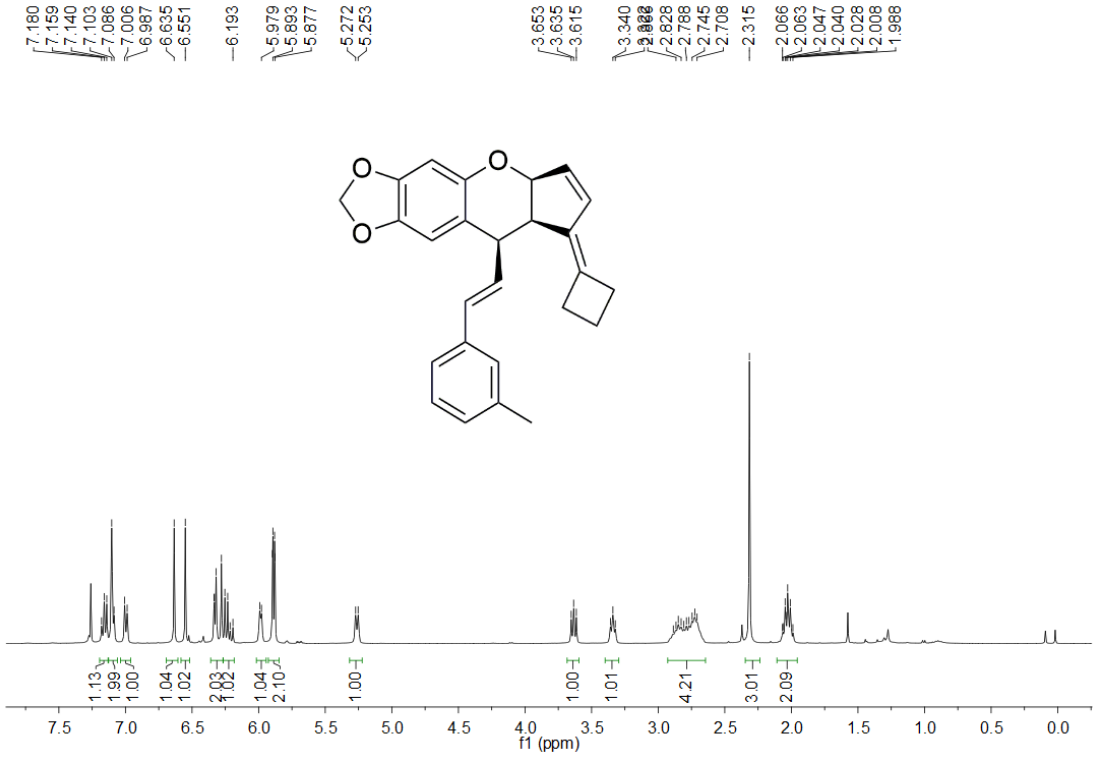
30.405
21.164
17.606
f1 (ppm)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7.006
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6.635
6.551
6.193
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5.877
5.272
5.253
3.653
3.635
3.615
3.340
2.828
2.788
2.745
2.708
2.315
2.066
2.063
2.047
2.040
2.028
2.008
1.988
1.13
1.99
1.00
1.04
1.02
2.03
1.02
1.04
2.10
1.00
1.00
1.01
4.21
3.01
2.09
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6.5
6.0
5.5
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3.0
2.5
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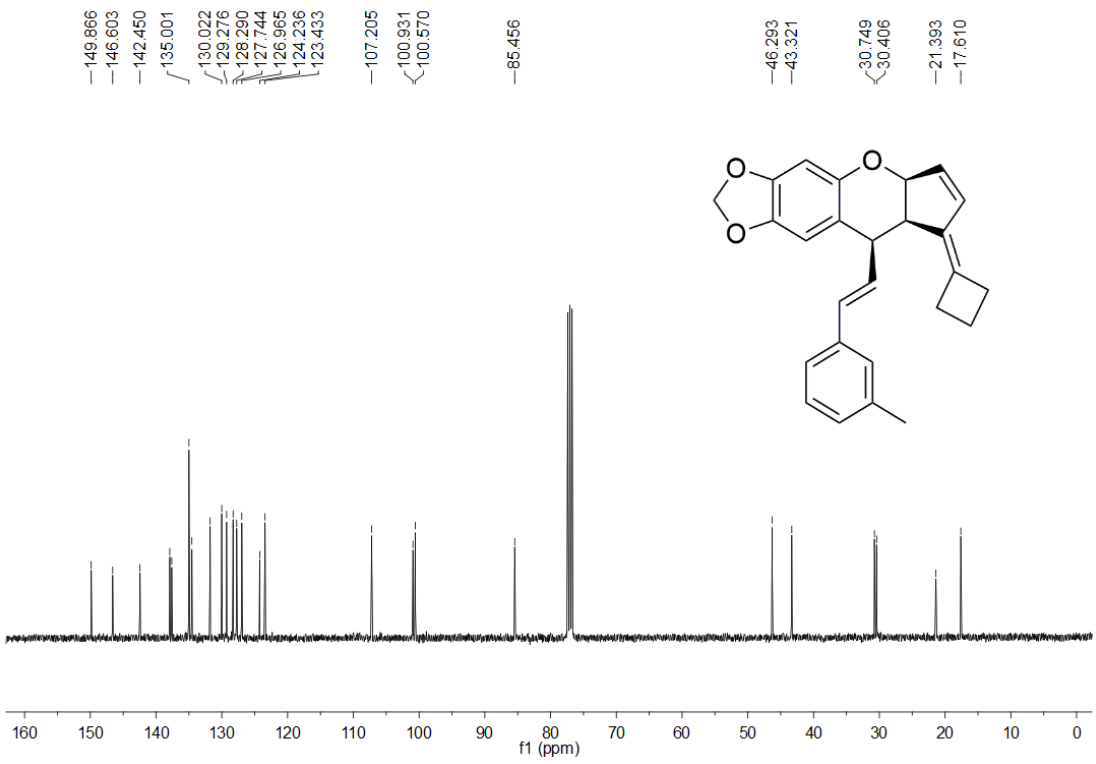
0.0
f1 (ppm)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124.236
123.433
107.205
100.931
100.570
85.456
46.293
43.321
30.749
30.406
21.393
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150
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130
120
110
100
90
80
70
60
50
40
30
20
10
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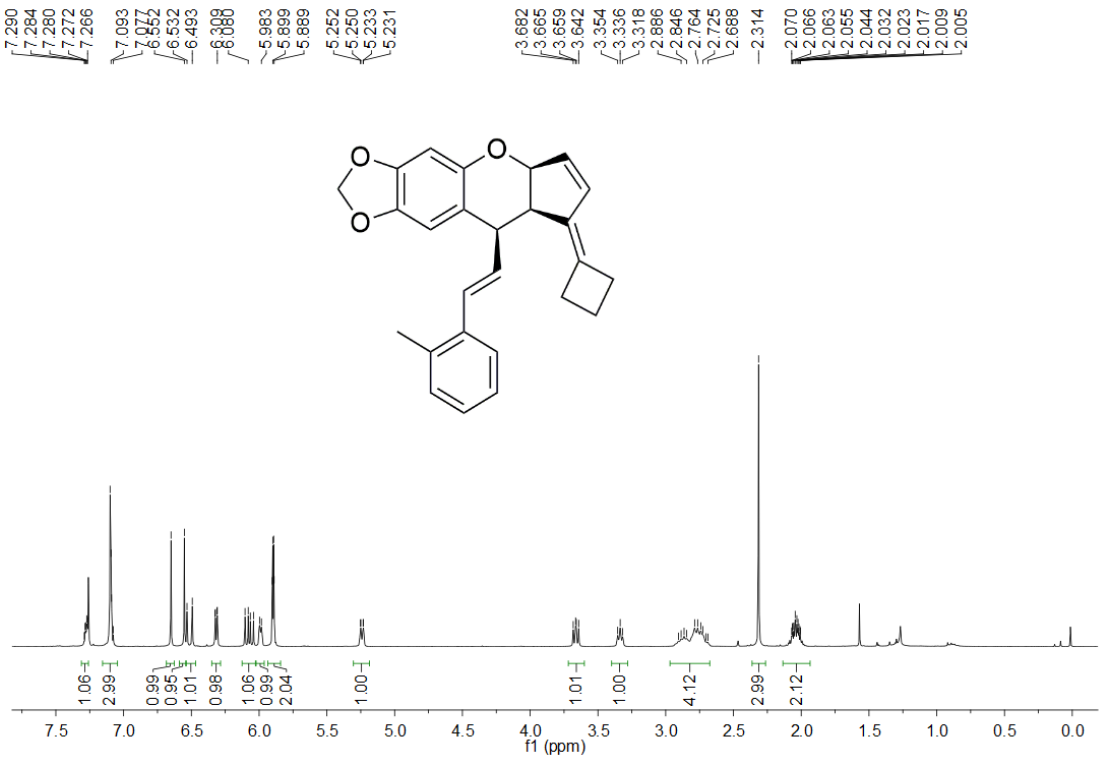
f1 (ppm)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7.077
6.552
6.532
6.493
6.309
6.080
5.983
5.899
5.889
5.252
5.250
5.233
5.231
3.682
3.665
3.659
3.642
3.354
3.336
3.318
2.886
2.846
2.764
2.725
2.688
2.314
2.070
2.066
2.063
2.055
2.044
2.032
2.023
2.017
2.009
2.005
1.06
2.99
0.99
0.95
1.01
0.98
1.06
0.99
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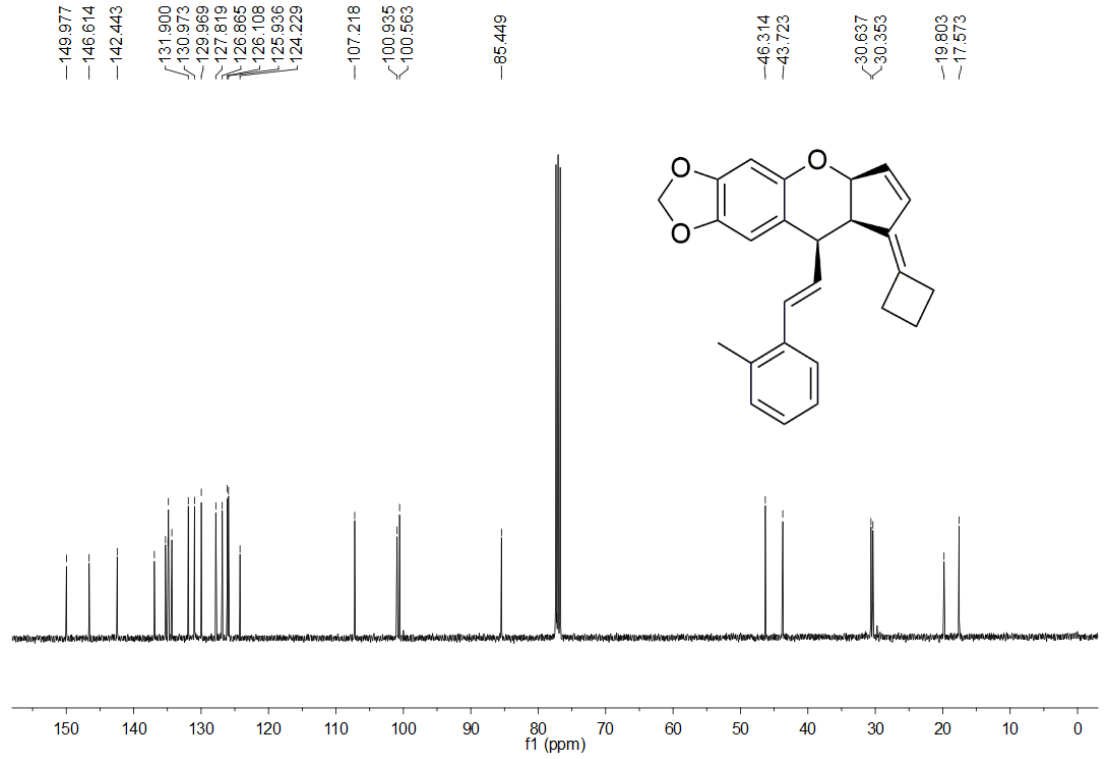
1.00
1.01
1.00
4.12
2.99
2.12
f1 (ppm)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126.865
126.108
125.936
124.229
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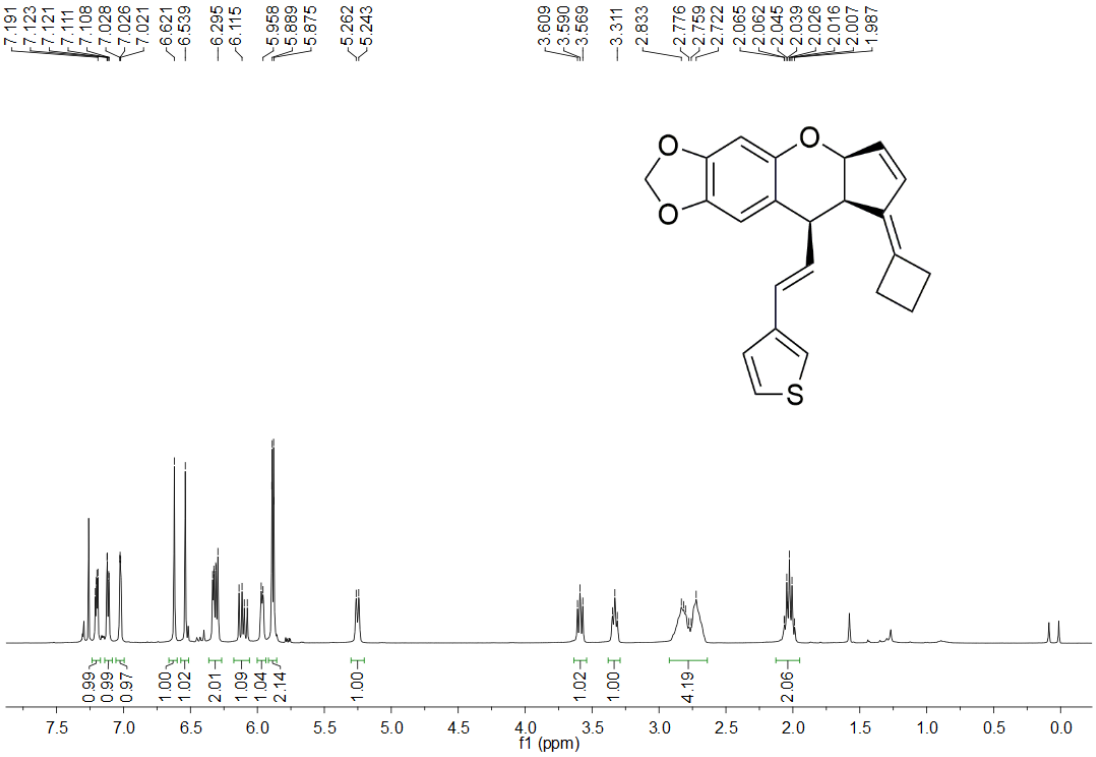
100.563
85.449
46.314
43.723
30.637
30.353
19.803
17.573
f1 (ppm)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7.121
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7.026
7.021
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6.295
6.115
5.958
5.889
5.875
5.262
5.243
3.609
3.590
3.569
3.311
2.833
2.776
2.759
2.722
2.065
2.062
2.045
2.039
2.026
2.016
2.007
1.987
O
O
O
S
0.99
0.99
0.97
1.00
1.02
2.01
1.09
1.04
2.14
1.00
1.02
1.00
4.19
2.06
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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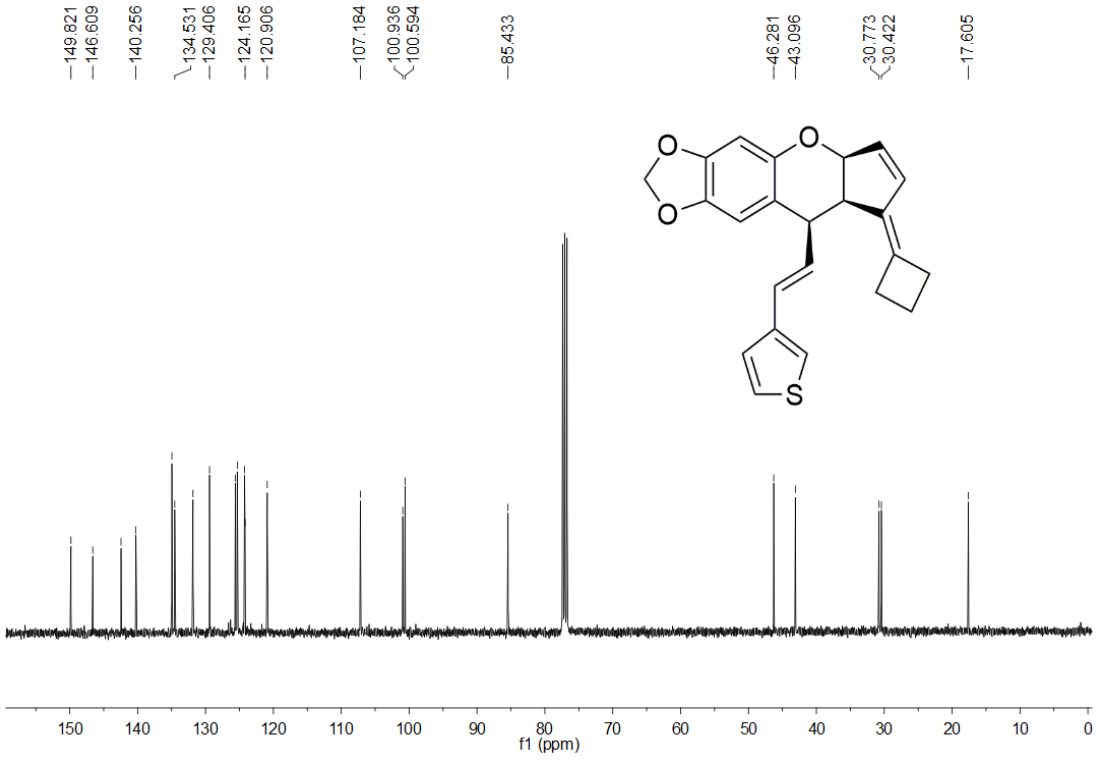
0.0
f1 (ppm)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43.096
30.773
30.422
17.605
O
O
O
S
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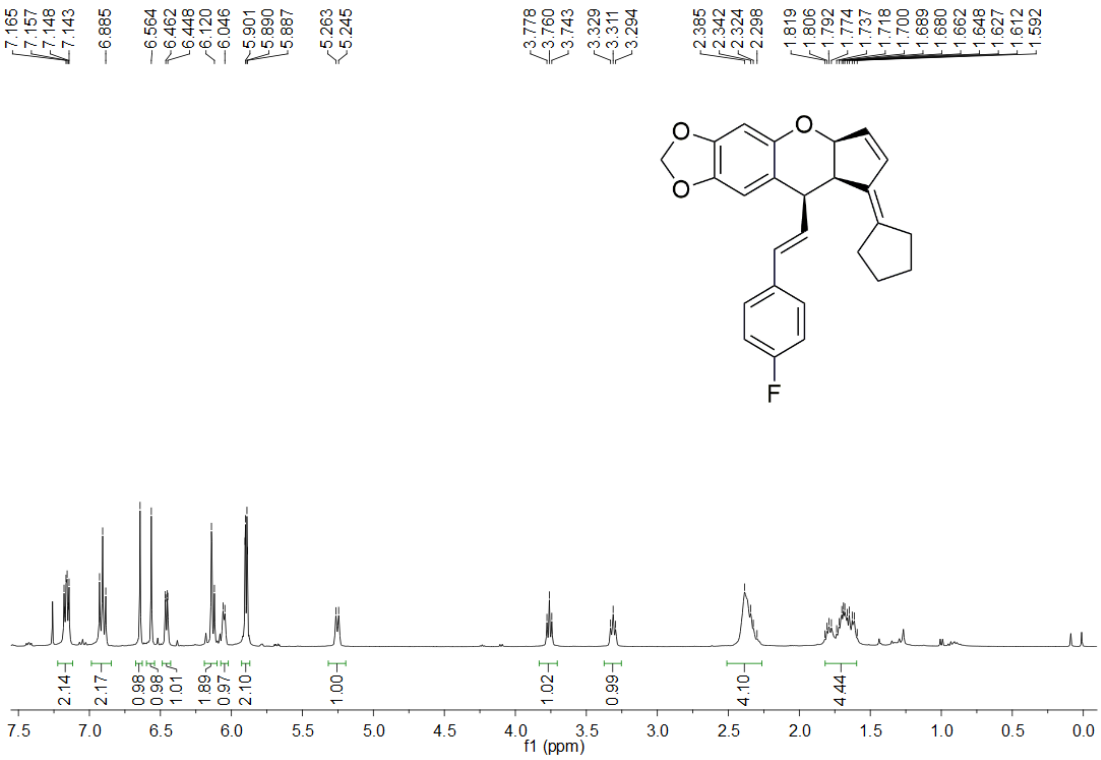
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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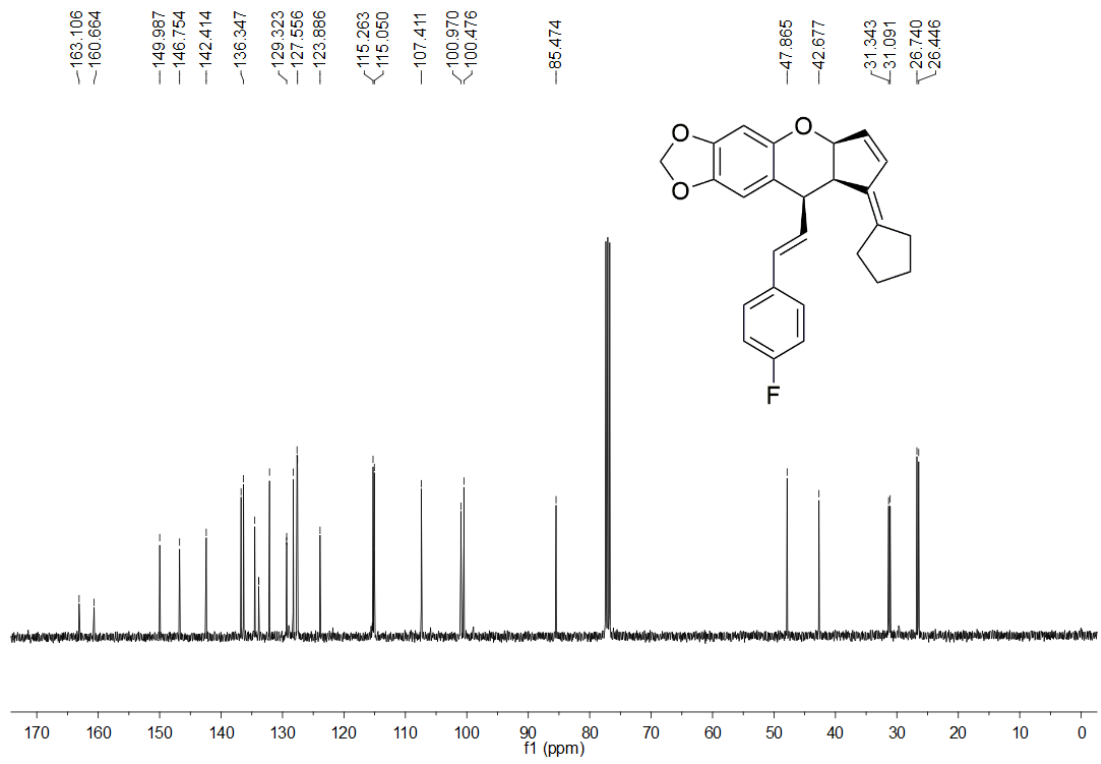
6.448
6.120
6.046
5.901
5.890
5.887
5.263
5.245
3.778
3.760
3.743
3.329
3.311
3.294
2.385
2.342
2.324
2.298
1.819
1.806
1.792
1.774
1.737
1.718
1.700
1.689
1.680
1.662
1.648
1.627
1.612
1.592
O
O
O
F
2.14
2.17
0.98
0.98
1.01
1.89
0.97
2.10
1.00
1.02
0.99
4.10
4.44
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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115.050
107.411
100.970
100.476
85.474
47.865
42.677
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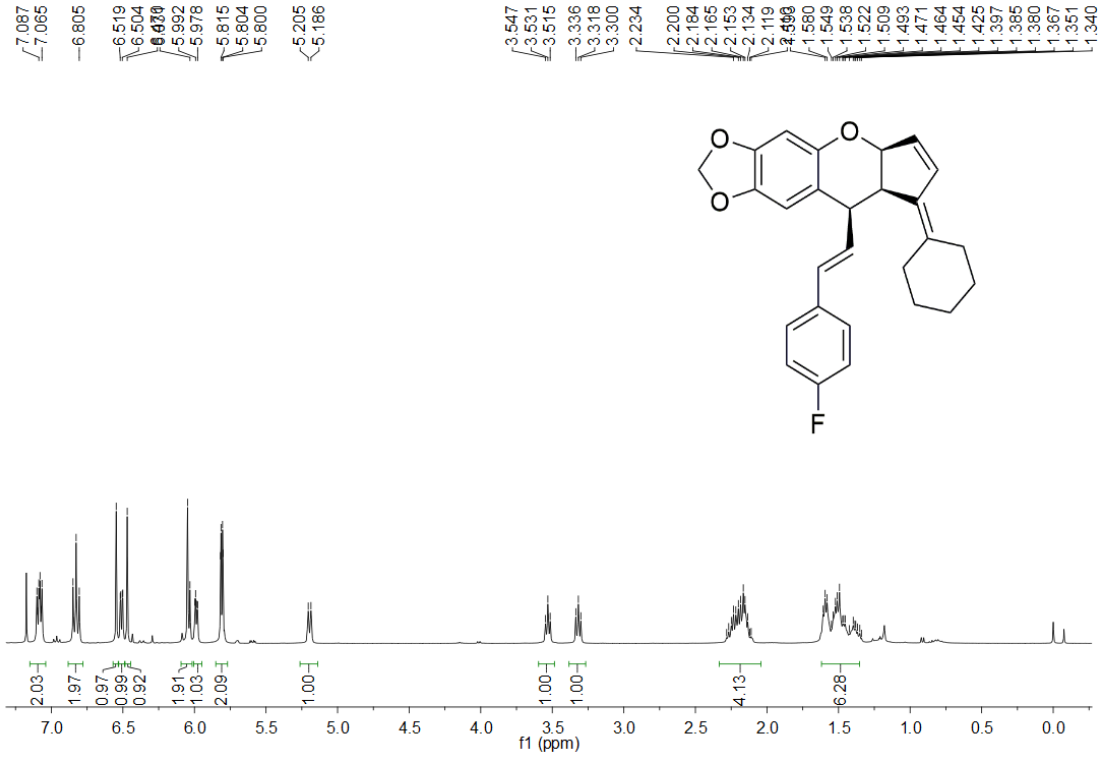
26.740
26.446
O
O
O
F
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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3.547
3.531
3.515
3.336
3.318
3.300
2.234
2.200
2.184
2.165
2.153
2.134
2.119
1.580
1.549
1.538
1.522
1.509
1.493
1.471
1.464
1.454
1.425
1.397
1.385
1.380
1.367
1.351
1.340
O
O
O
F
2.03
1.97
0.97
0.99
0.92
1.91
1.03
2.09
1.00
1.00
1.00
4.13
6.28
7.0
6.5
6.0
5.5
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3.0
2.5
2.0
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1.0
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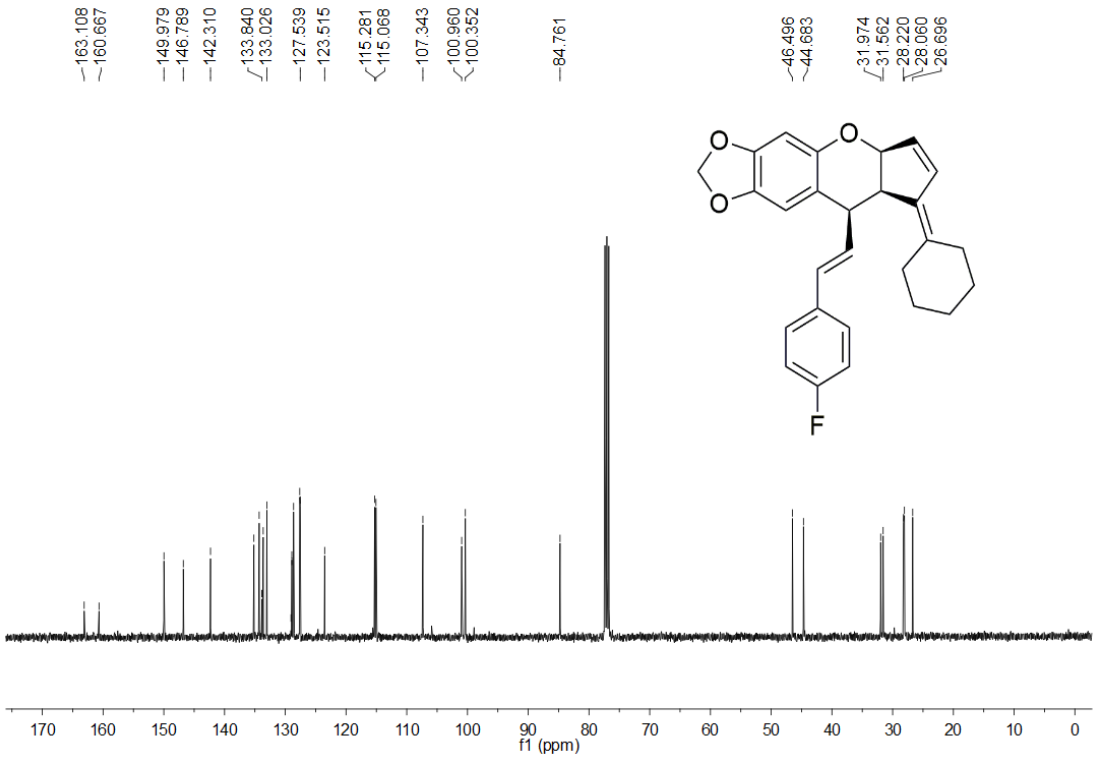
0.0
f1 (ppm)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127.539
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115.068
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100.352
84.761
46.496
44.683
31.974
31.562
28.220
28.060
26.696
O
O
O
F
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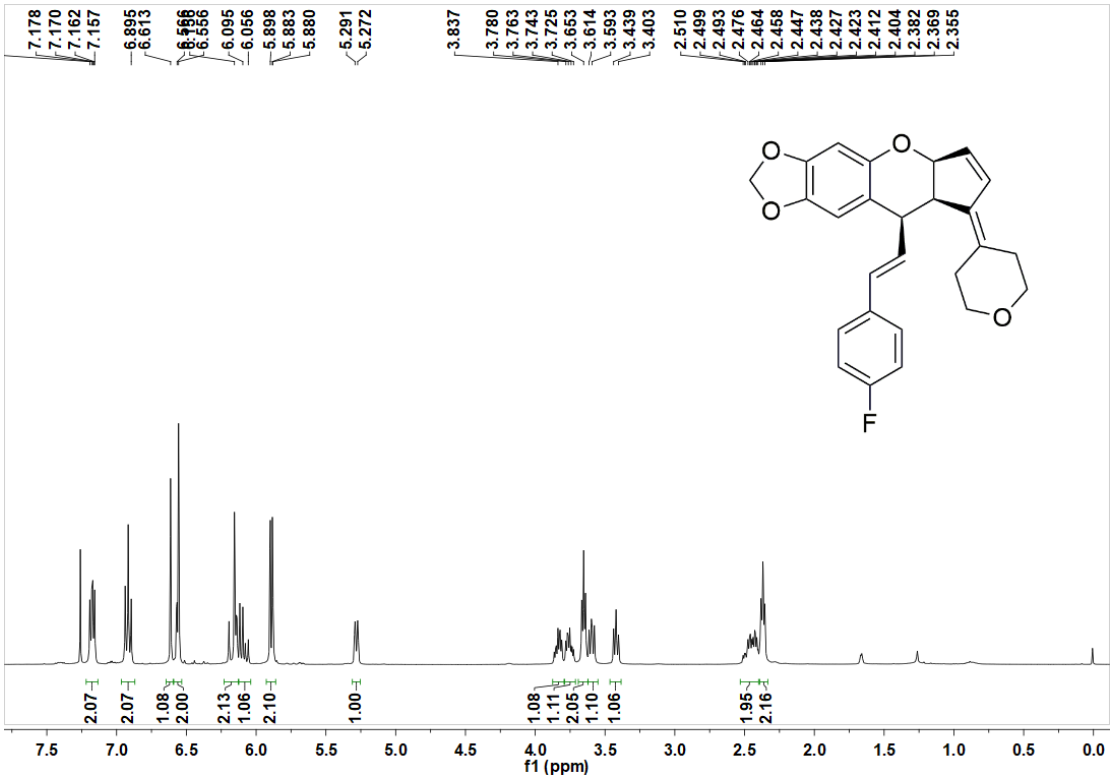
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.056
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5.291
5.272
3.837
3.780
3.763
3.743
3.725
3.653
3.614
3.593
3.439
3.403
2.510
2.499
2.493
2.476
2.464
2.458
2.447
2.438
2.427
2.423
2.412
2.404
2.382
2.369
2.355
O
O
O
O
F
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2.07
1.08
2.00
2.13
1.06
2.10
1.00
1.08
1.11
2.05
1.10
1.06
1.95
2.16
7.5
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6.5
6.0
5.5
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4.5
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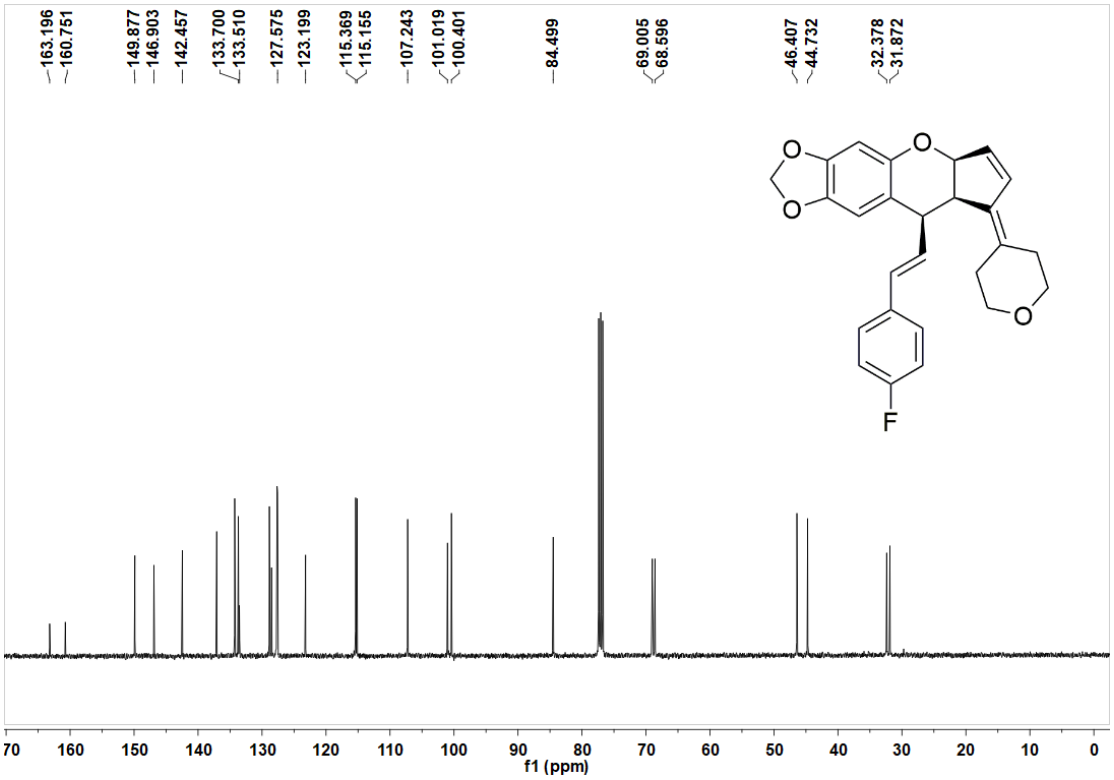
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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101.019
100.401
84.499
69.005
68.596
46.407
44.732
32.378
31.872
O
O
O
O
F
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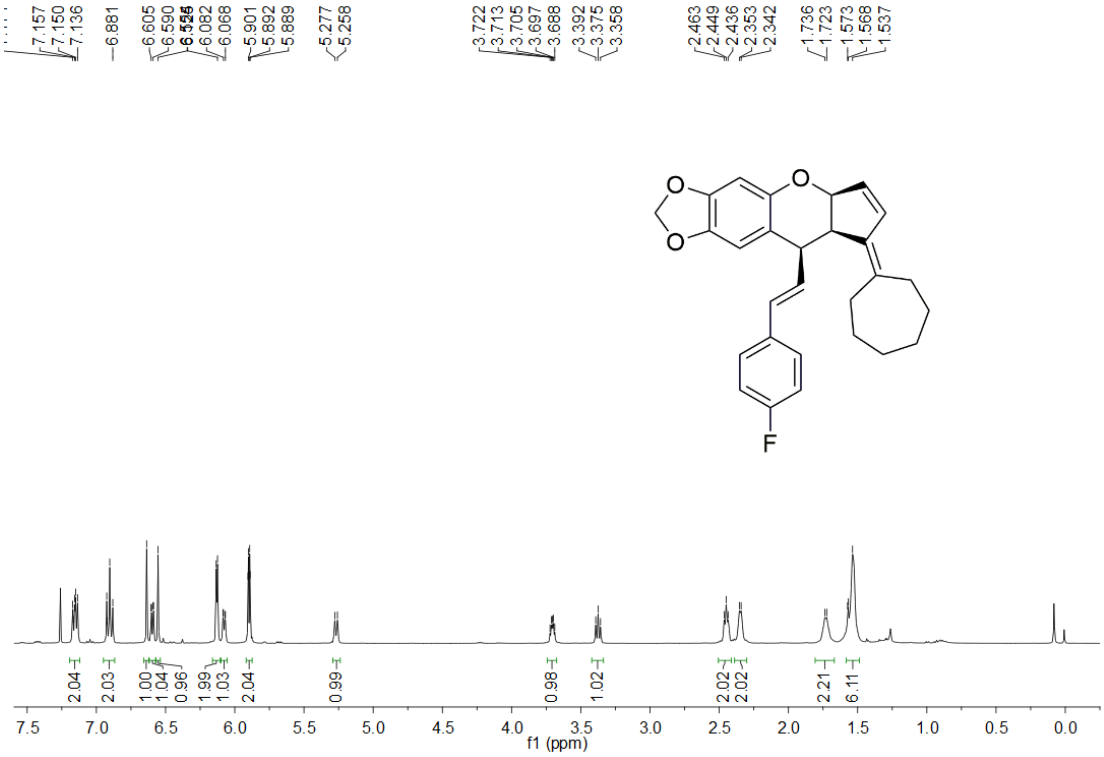
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.068
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5.258
3.722
3.713
3.705
3.697
3.688
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2.342
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1.723
1.573
1.568
1.537
O
O
O
F
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2.03
1.00
1.04
0.96
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1.03
2.04
0.99
0.98
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2.02
2.02
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6.0
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1.0
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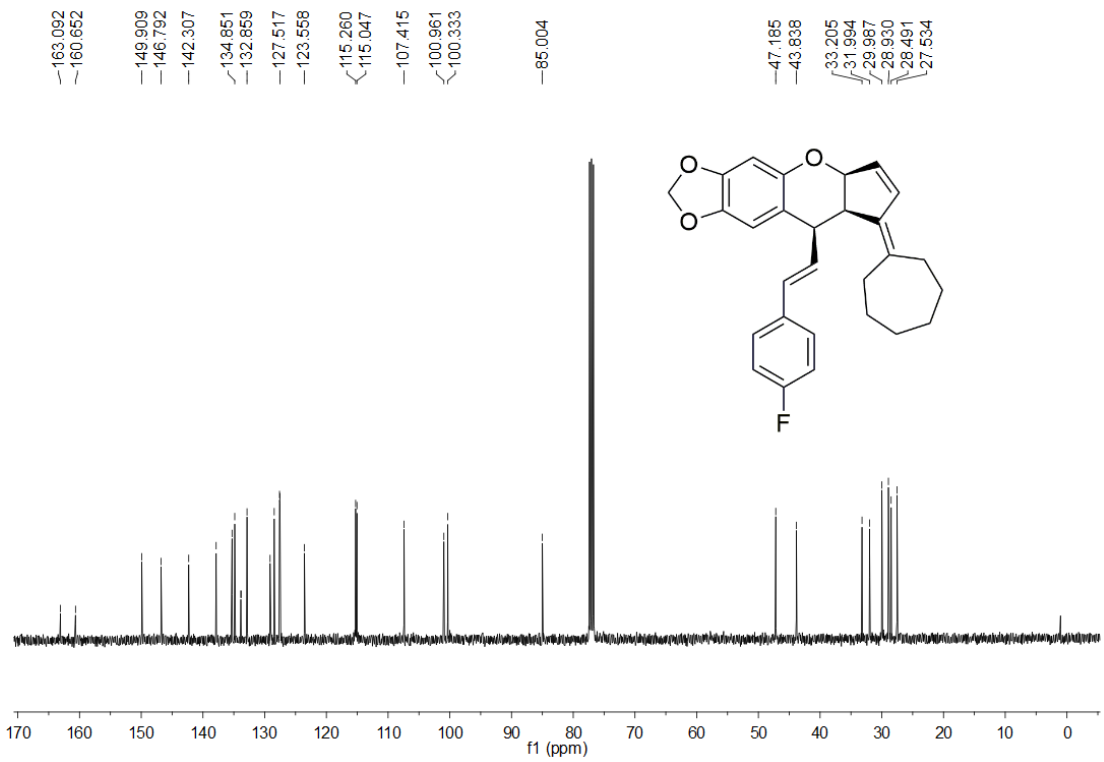
f1 (ppm)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85.004
47.185
43.838
33.205
31.994
29.987
28.930
28.491
27.534
O
O
O
F
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150
140
130
120
110
100
90
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70
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50
40
30
20
10
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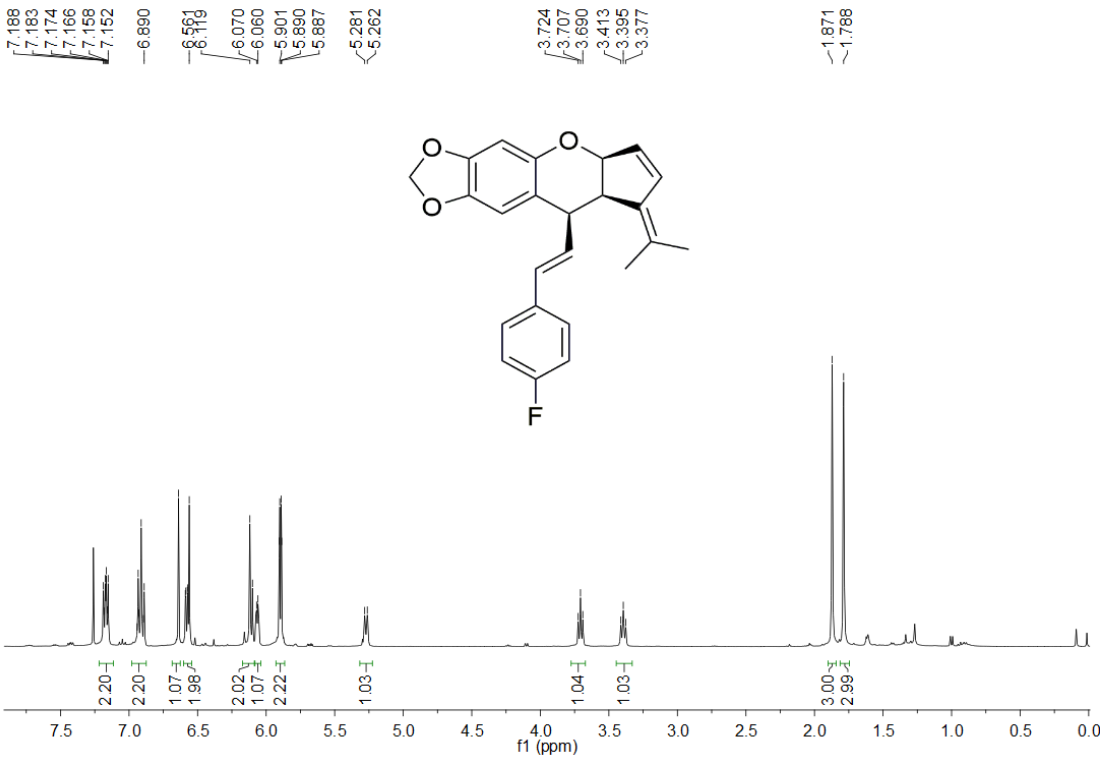
f1 (ppm)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6.060
5.901
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5.887
5.281
5.262
3.724
3.707
3.690
3.413
3.395
3.377
1.871
1.788
O
O
O
F
2.20
2.20
1.07
1.98
2.02
1.07
2.22
1.03
1.04
1.03
3.00
2.99
7.5
7.0
6.5
6.0
5.5
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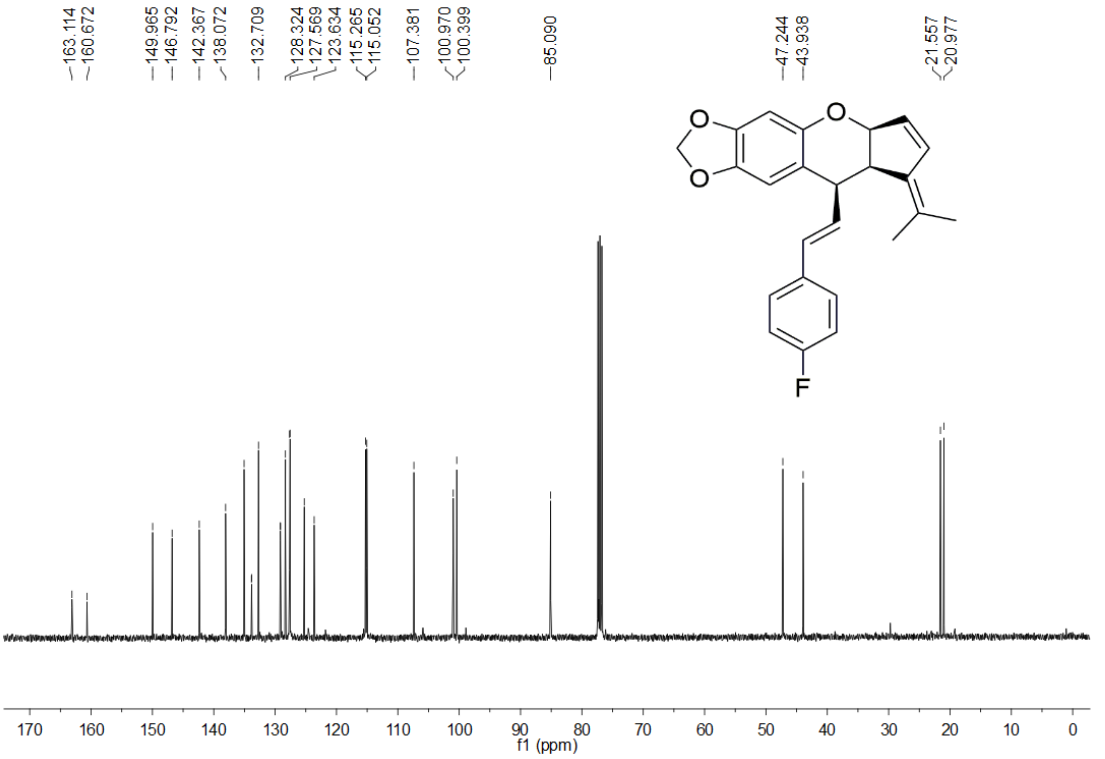
0.0
f1 (ppm)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100.970
100.399
85.090
47.244
43.938
21.557
20.977
O
O
O
F
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120
110
100
90
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40
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20
10
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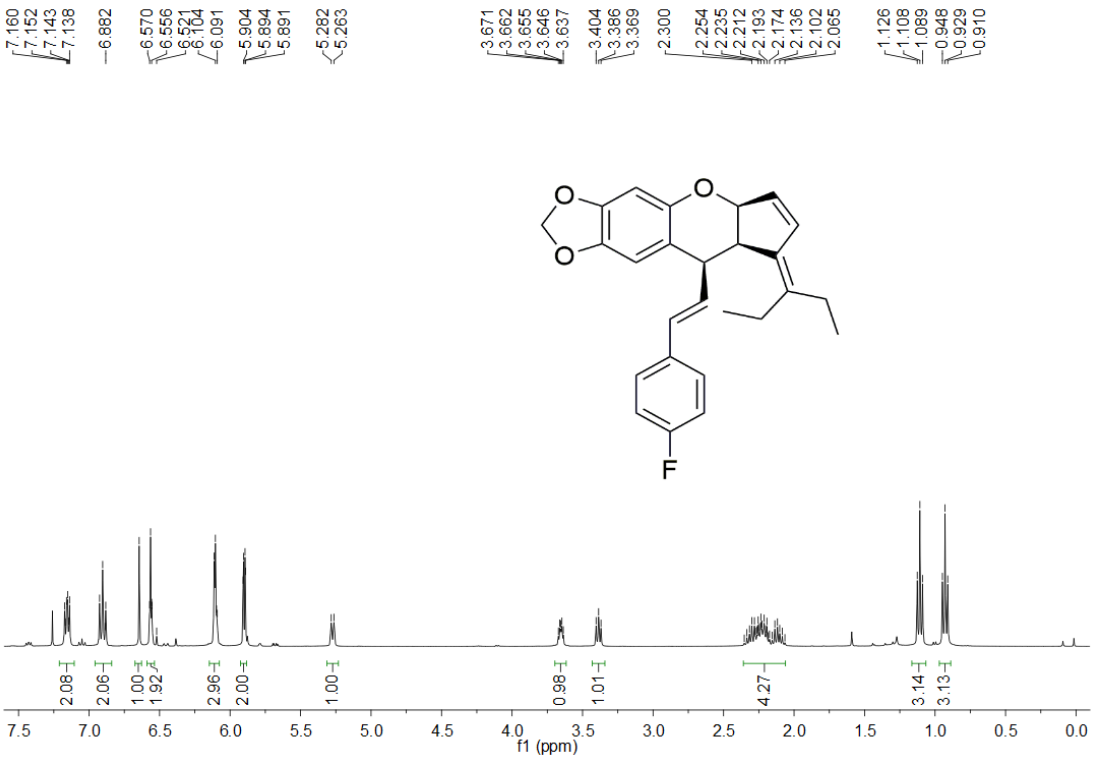
f1 (ppm)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1.108
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0.929
0.910
O
O
O
F
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1.92
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2.00
1.00
0.98
1.01
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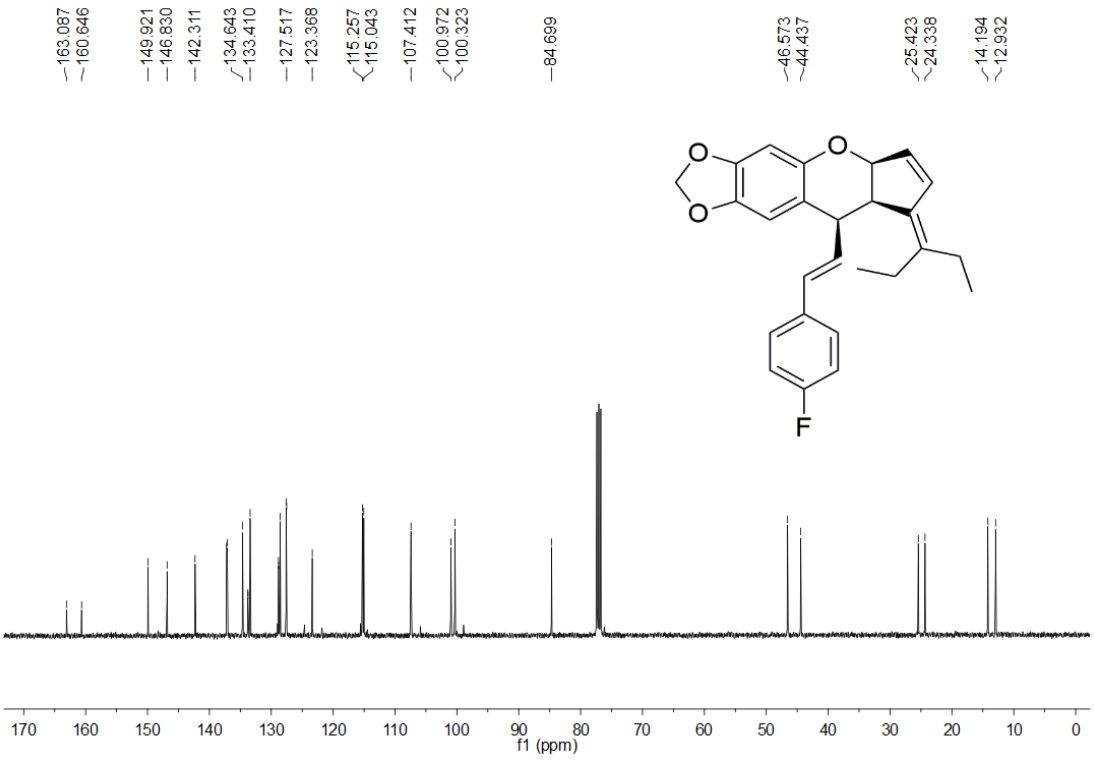
f1 (ppm)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100.323
84.699
46.573
44.437
25.423
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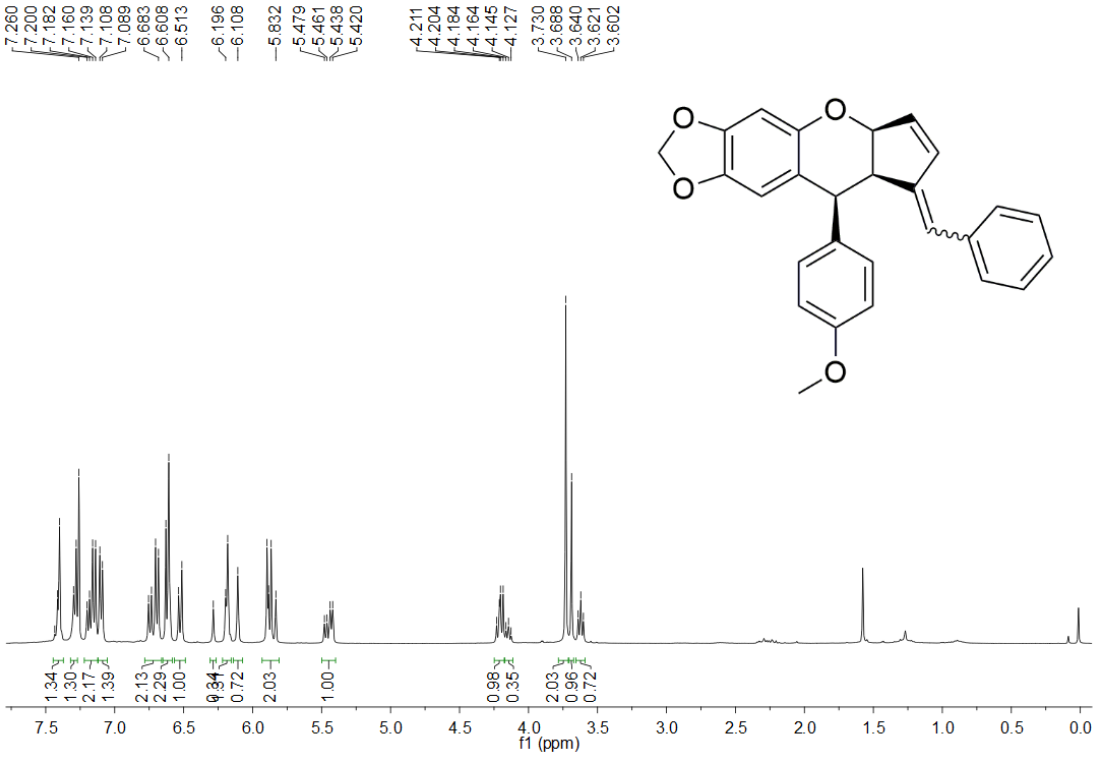
14.194
12.932
O
O
O
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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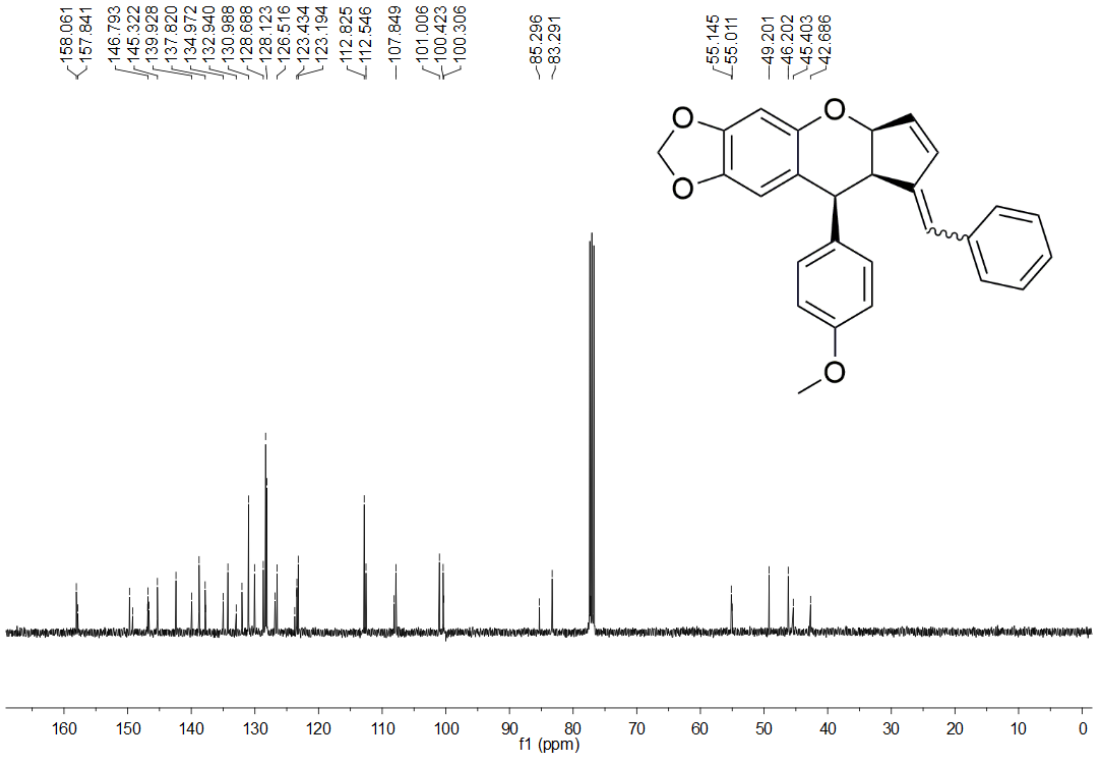
7.160
7.139
7.108
7.089
6.683
6.608
6.513
6.196
6.108
5.832
5.479
5.461
5.438
5.420
4.211
4.204
4.184
4.164
4.145
4.127
3.730
3.688
3.640
3.621
3.602
1.34
1.30
2.17
1.39
2.13
2.29
1.00
0.72
2.03
1.00
0.98
0.35
2.03
0.96
0.72
f1 (ppm)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132.940
130.988
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126.516
123.434
123.194
112.825
112.546
107.849
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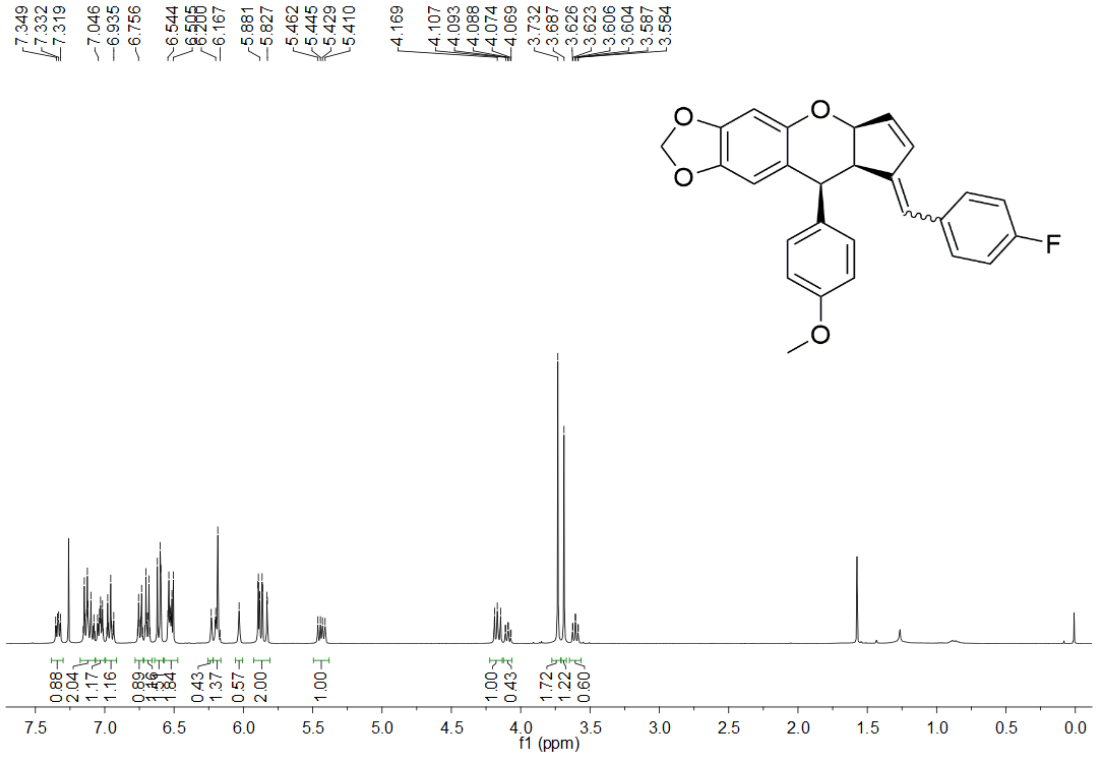
83.291
55.145
55.011
49.201
46.202
45.403
42.686
f1 (ppm)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7.332
7.319
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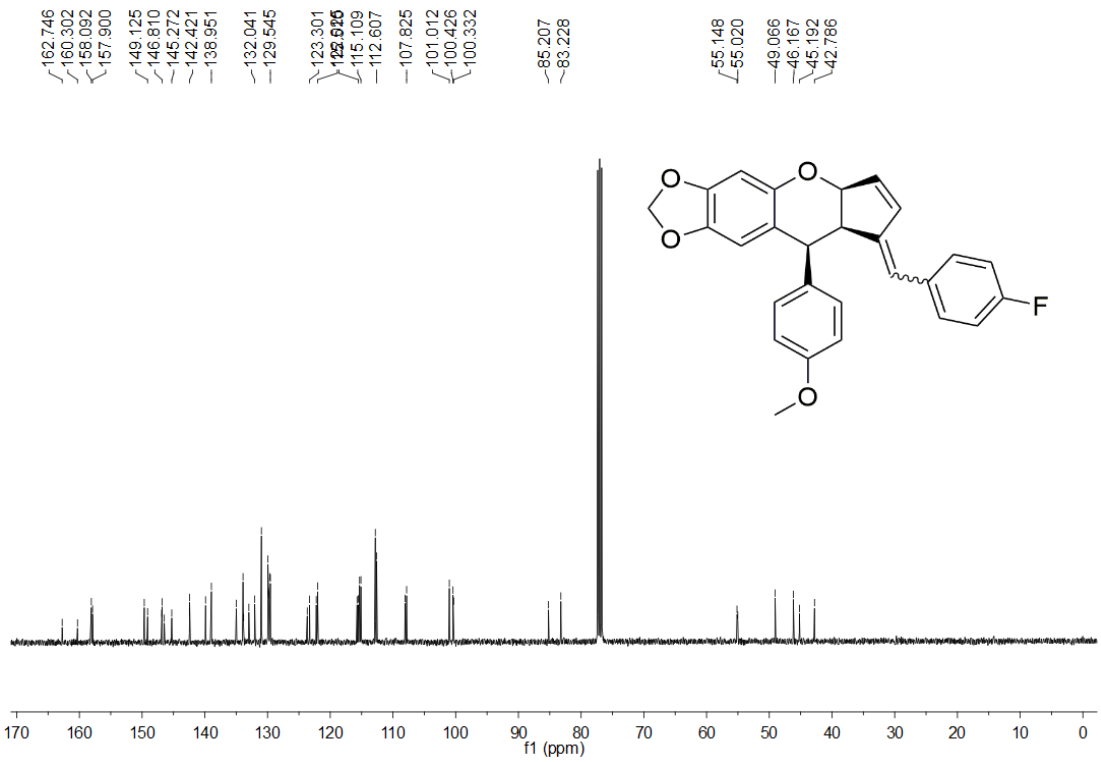
6.544
6.167
5.881
5.827
5.462
5.445
5.429
5.410
4.169
4.107
4.093
4.088
4.074
4.069
3.732
3.687
3.626
3.623
3.606
3.604
3.587
3.584
O
O
O
O
F
0.88
2.04
1.17
1.16
0.89
1.84
0.43
1.37
0.57
2.00
1.00
1.00
0.43
1.72
1.22
0.60
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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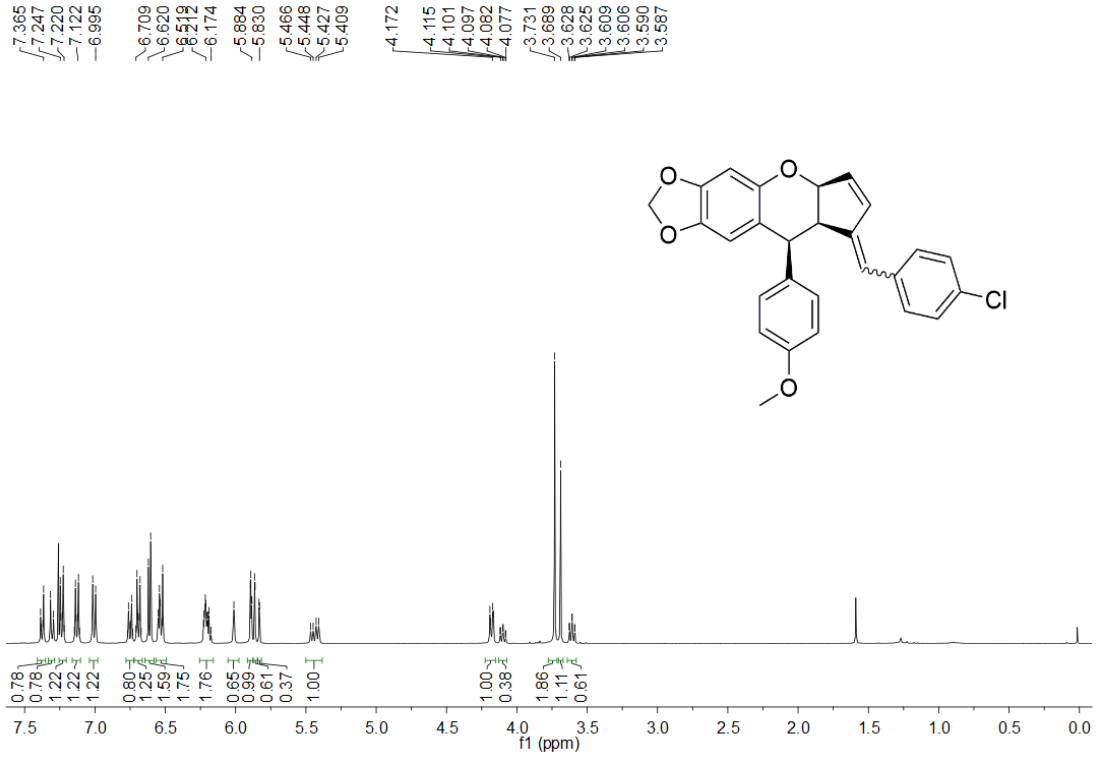
158.092
157.900
149.125
146.810
145.272
142.421
138.951
132.041
129.545
123.301
115.109
112.607
107.825
101.012
100.426
100.332
85.207
83.228
55.148
55.020
49.066
46.167
45.192
42.786
O
O
O
O
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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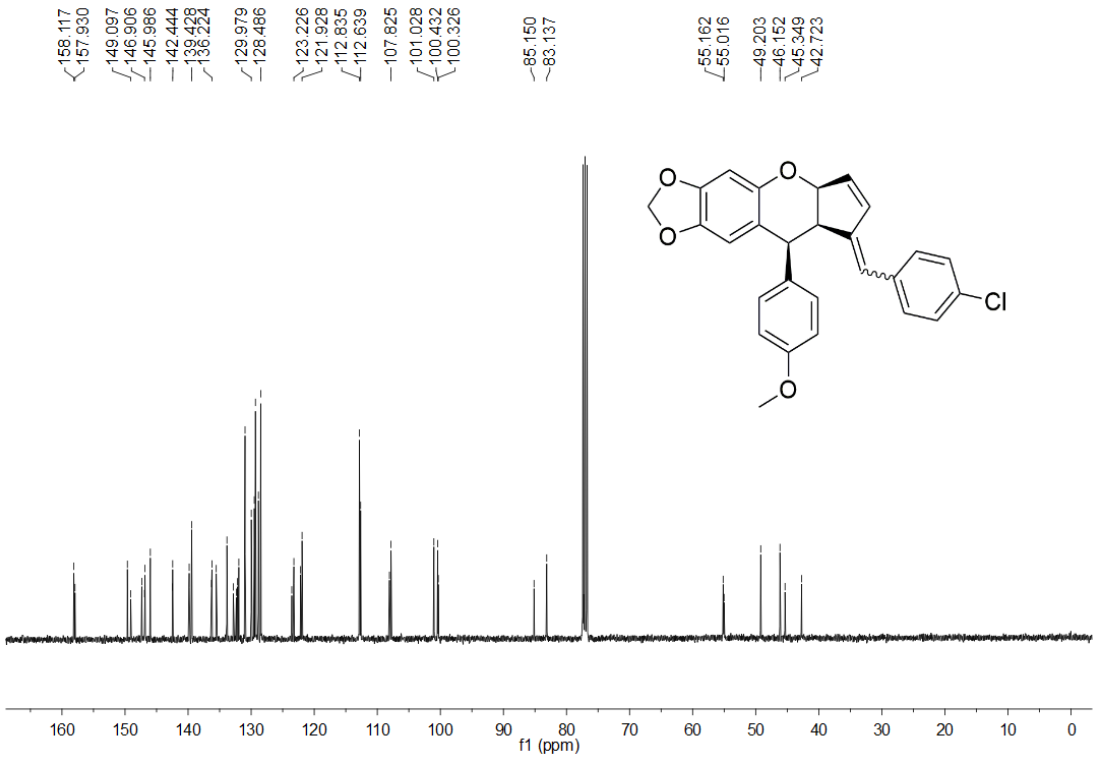
6.620
6.519
6.212
6.174
5.884
5.830
5.466
5.448
5.427
5.409
4.172
4.115
4.101
4.097
4.082
4.077
3.731
3.689
3.628
3.625
3.609
3.606
3.590
3.587
O
O
O
O
Cl
0.78
0.78
1.22
1.22
1.22
0.80
1.25
1.59
1.75
1.76
0.65
0.99
0.61
0.37
1.00
1.00
0.38
1.86
1.11
0.61
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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149.097
146.906
145.986
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136.224
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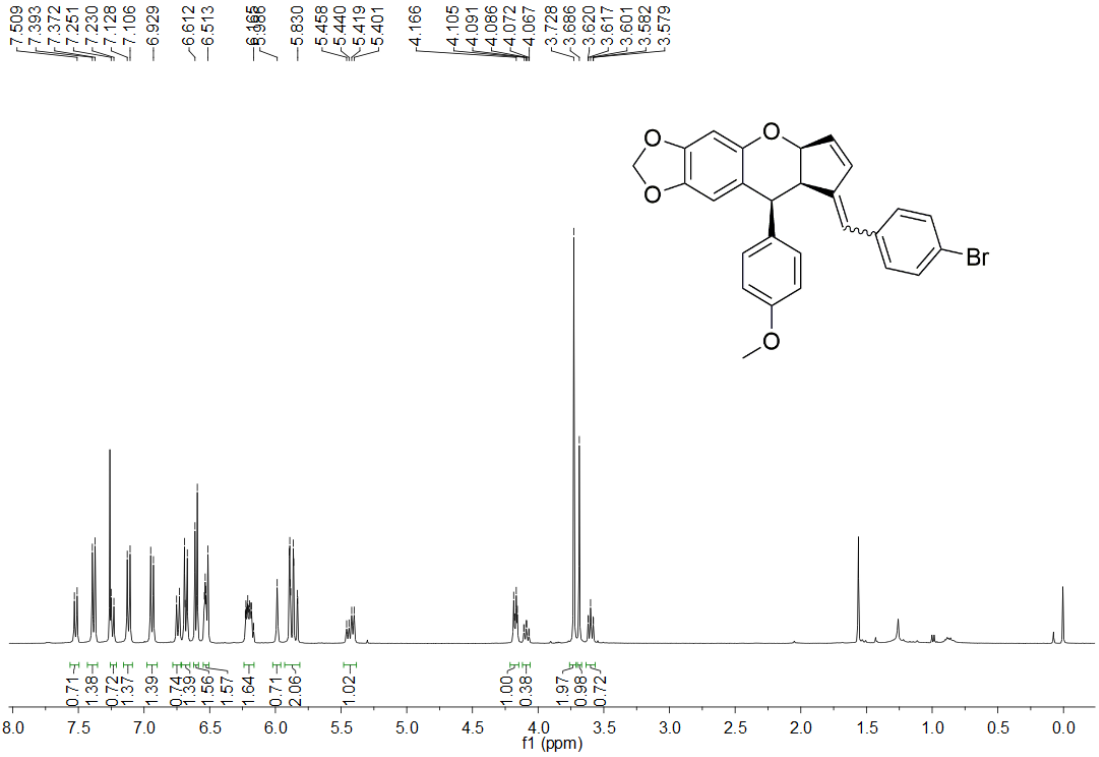
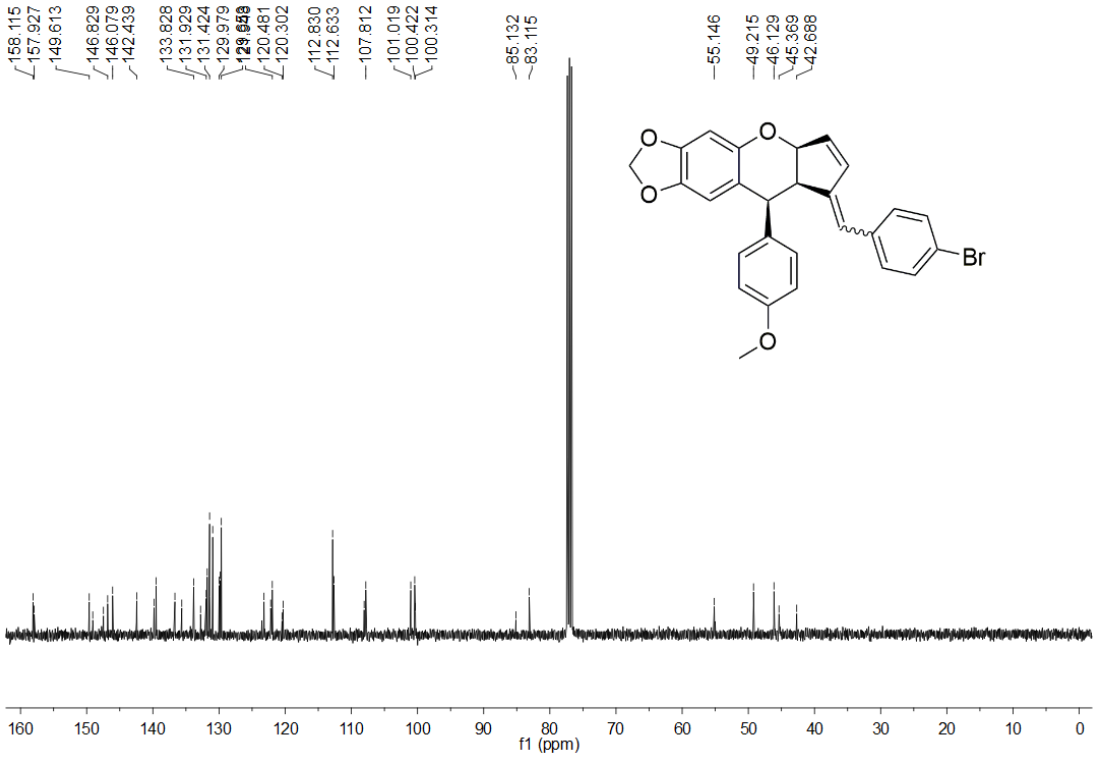
128.486
123.226
121.928
112.835
112.639
107.825
101.028
100.432
100.326
85.150
83.137
55.162
55.016
49.203
46.152
45.349
42.723
O
O
O
O
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.509
7.393
7.372
7.251
7.230
7.128
7.106
6.929
6.612
6.513
5.830
5.458
5.440
5.419
5.401
4.166
4.105
4.091
4.086
4.072
4.067
3.728
3.686
3.620
3.617
3.601
3.582
3.579
Br
O
O
O
O
0.71
1.38
0.72
1.37
1.39
0.74
1.39
1.56
1.57
1.64
0.71
2.06
1.02
1.00
0.38
1.97
0.98
0.72
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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157.927
149.613
146.829
146.079
142.439
133.828
131.929
131.424
129.979
120.481
120.302
112.830
112.633
107.812
101.019
100.422
100.314
85.132
83.115
55.146
49.215
46.129
45.369
42.688
Br
O
O
O
O
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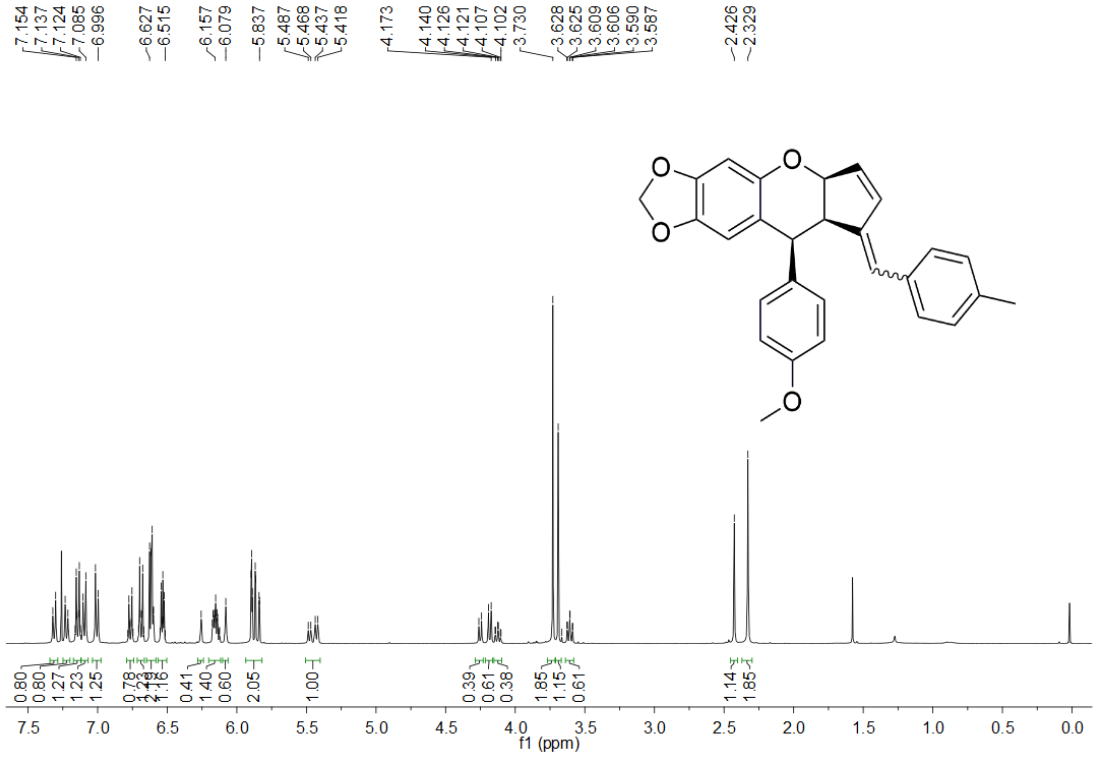
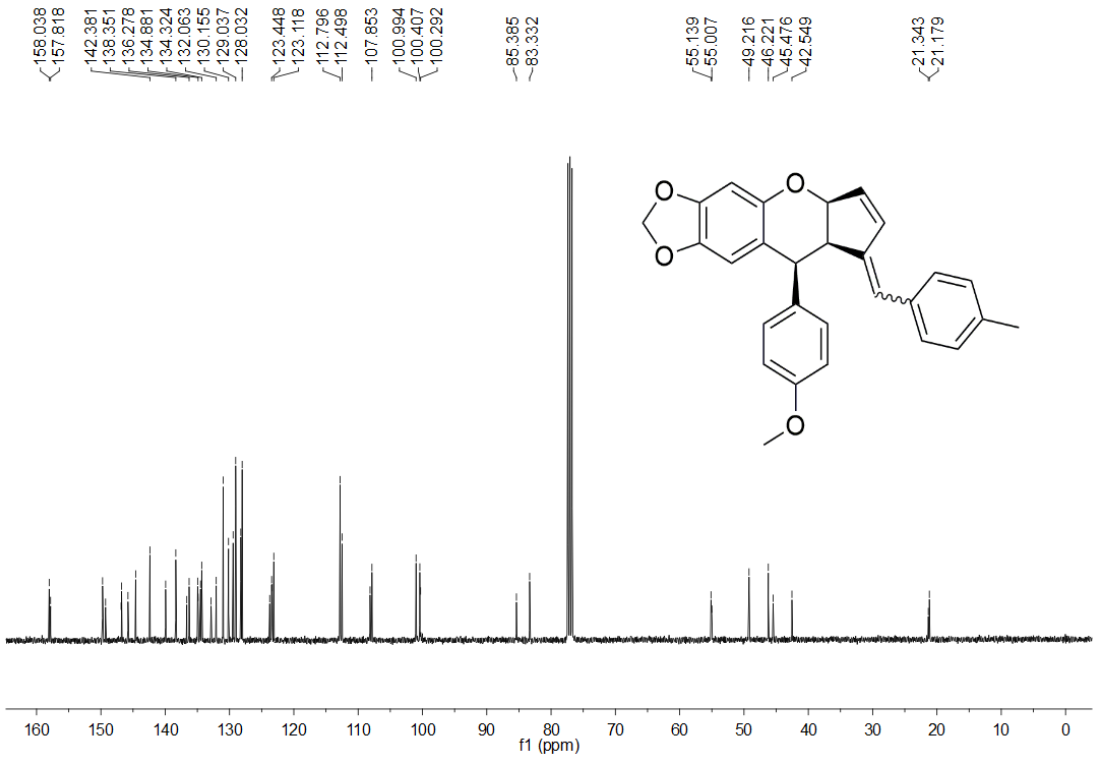
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.154
7.137
7.124
7.085
6.996
6.627
6.515
6.157
6.079
5.837
5.487
5.468
5.437
5.418
4.173
4.140
4.126
4.121
4.107
4.102
3.730
3.628
3.625
3.609
3.606
3.590
3.587
2.426
2.329
0.80
0.80
1.27
1.23
1.25
0.78
1.23
1.18
1.16
0.41
1.40
0.60
2.05
1.00
0.39
0.61
0.38
1.85
1.15
0.61
1.14
1.85
f1 (ppm)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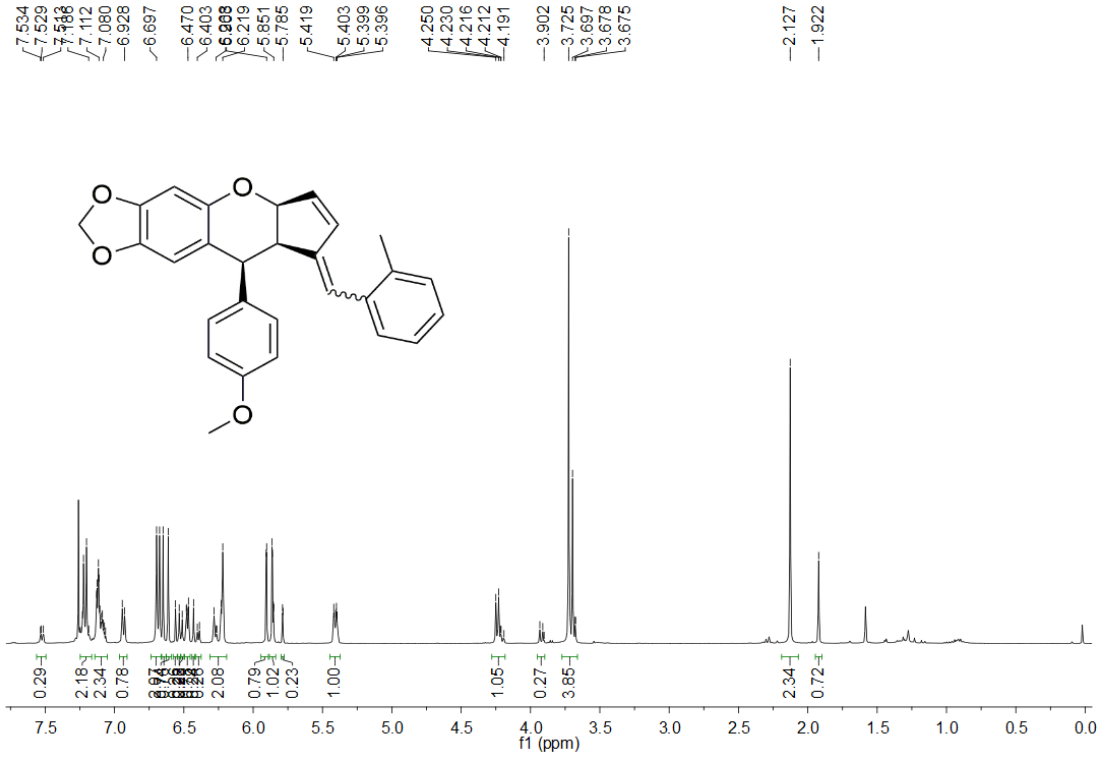
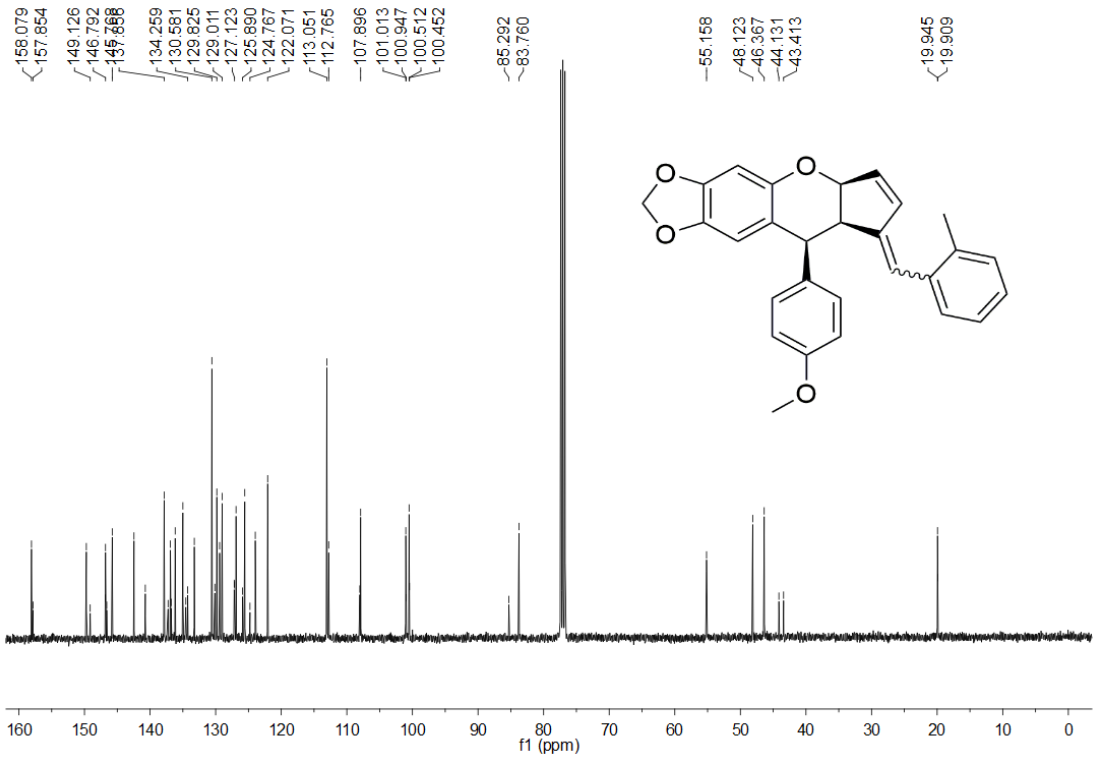
142.381
138.351
136.278
134.881
134.324
132.063
130.155
129.037
128.032
123.448
123.118
112.796
112.498
107.853
100.994
100.407
100.292
85.385
83.332
55.139
55.007
49.216
46.221
45.476
42.549
21.343
21.179
f1 (ppm)


7.534
7.529
7.112
7.080
6.928
6.697
6.470
6.403
6.219
5.851
5.785
5.419
5.403
5.399
5.396
4.250
4.230
4.216
4.212
4.191
3.902
3.725
3.697
3.678
3.675
2.127
1.922
0.29
2.18
2.34
0.78
2.08
0.79
1.02
0.23
1.00
1.05
0.27
3.85
2.34
0.72
f1 (ppm)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146.792
134.259
130.581
129.825
129.011
127.123
125.890
124.767
122.071
113.051
112.765
107.896
101.013
100.947
100.512
100.452
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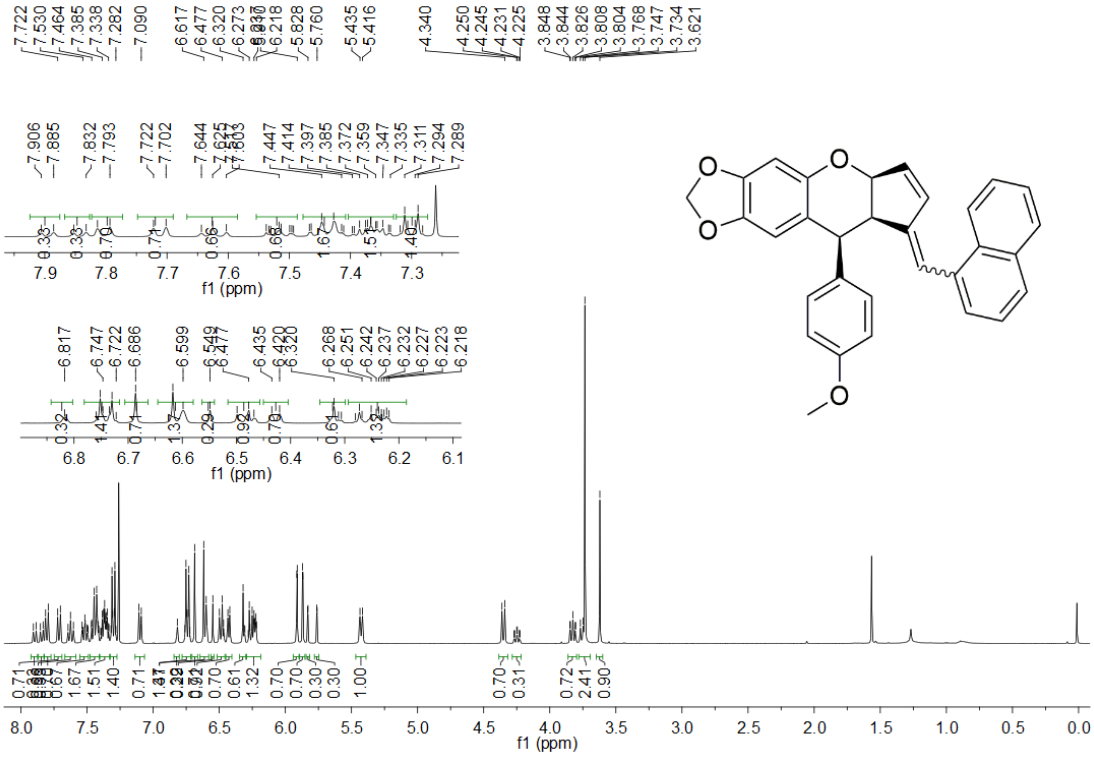
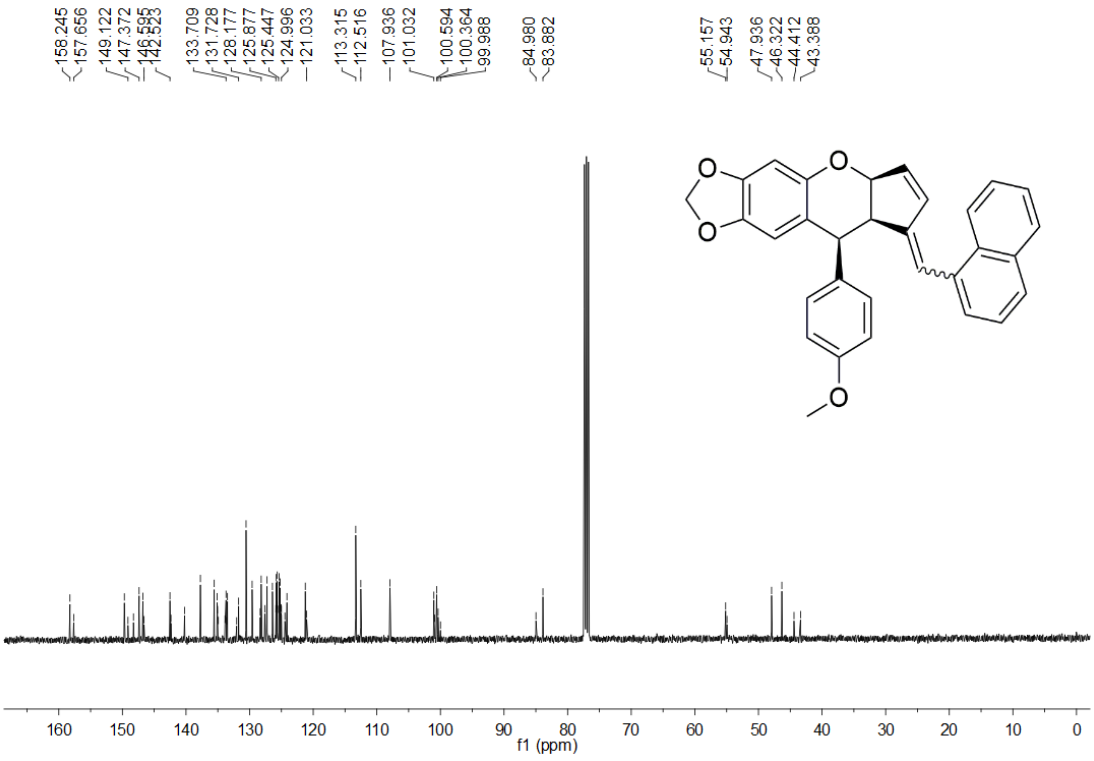
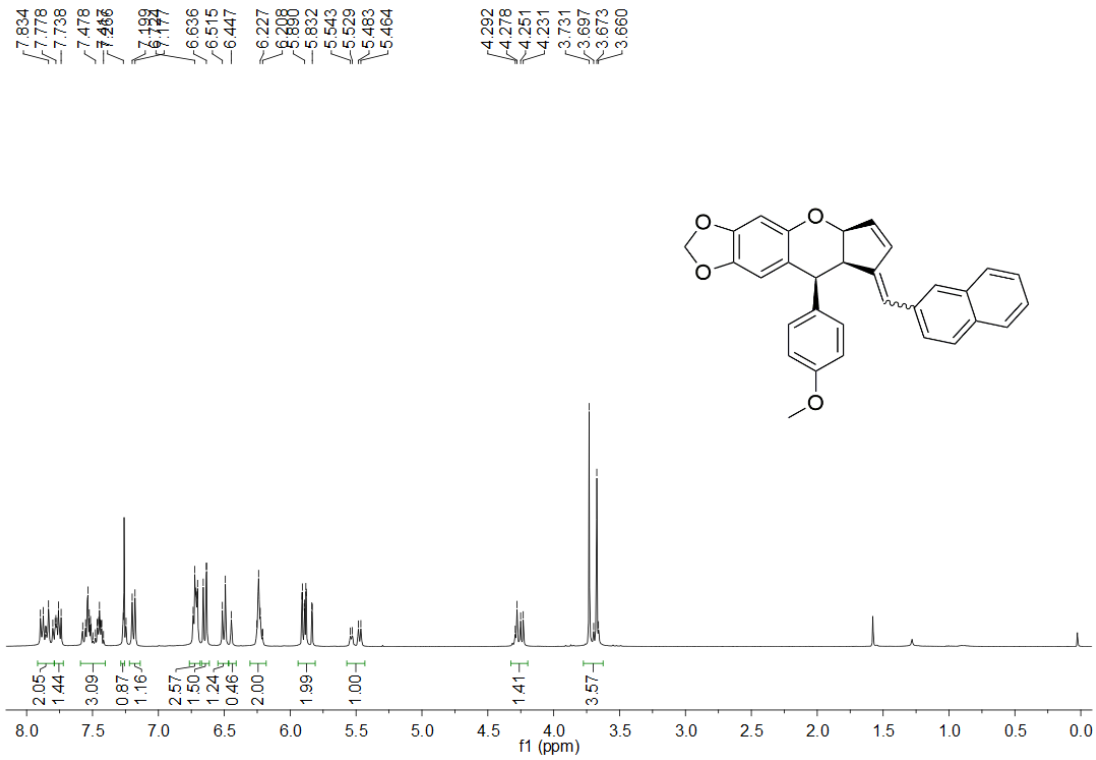
83.760
55.158
48.123
46.367
44.131
43.413
19.945
19.909
f1 (ppm)


f1 (ppm)


f1 (ppm)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6.227
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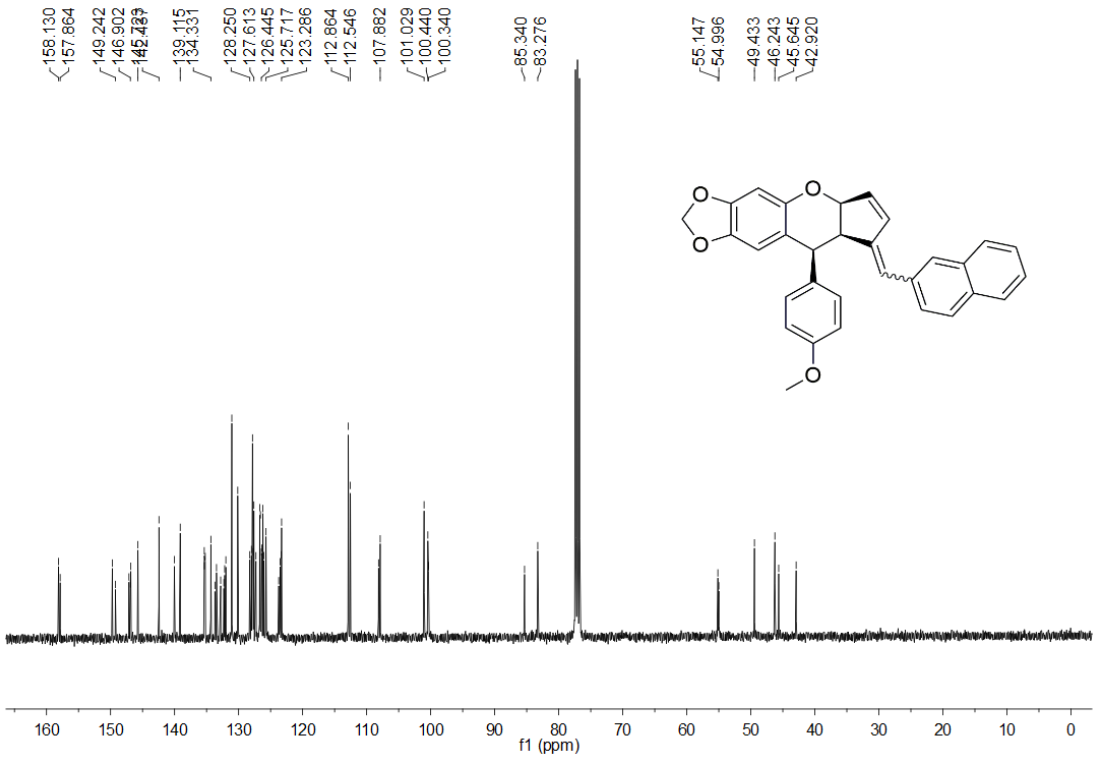
5.529
5.483
5.464
4.292
4.278
4.251
4.231
3.731
3.697
3.673
3.660
2.05
1.44
3.09
0.87
1.16
2.57
1.50
1.24
0.46
2.00
1.99
1.00
1.41
3.57
f1 (ppm)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134.331
128.250
127.613
126.445
125.717
123.286
112.864
112.546
107.882
101.029
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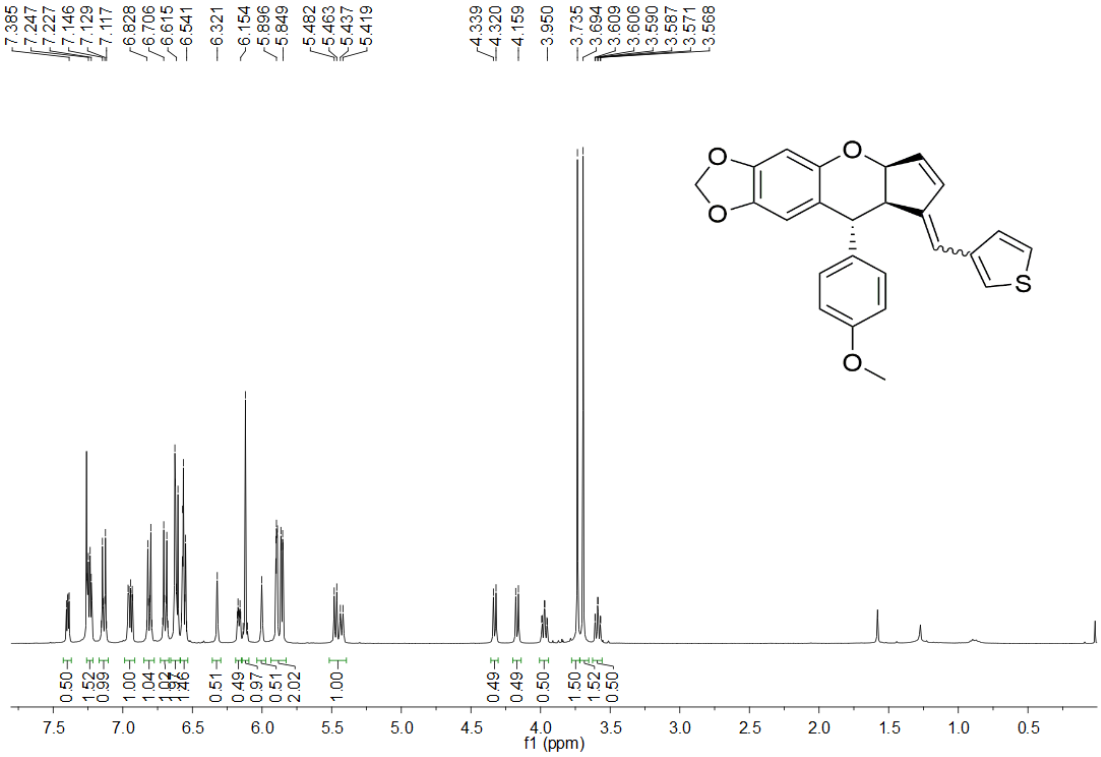
85.340
83.276
55.147
54.996
49.433
46.243
45.645
42.920
f1 (ppm)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7.117
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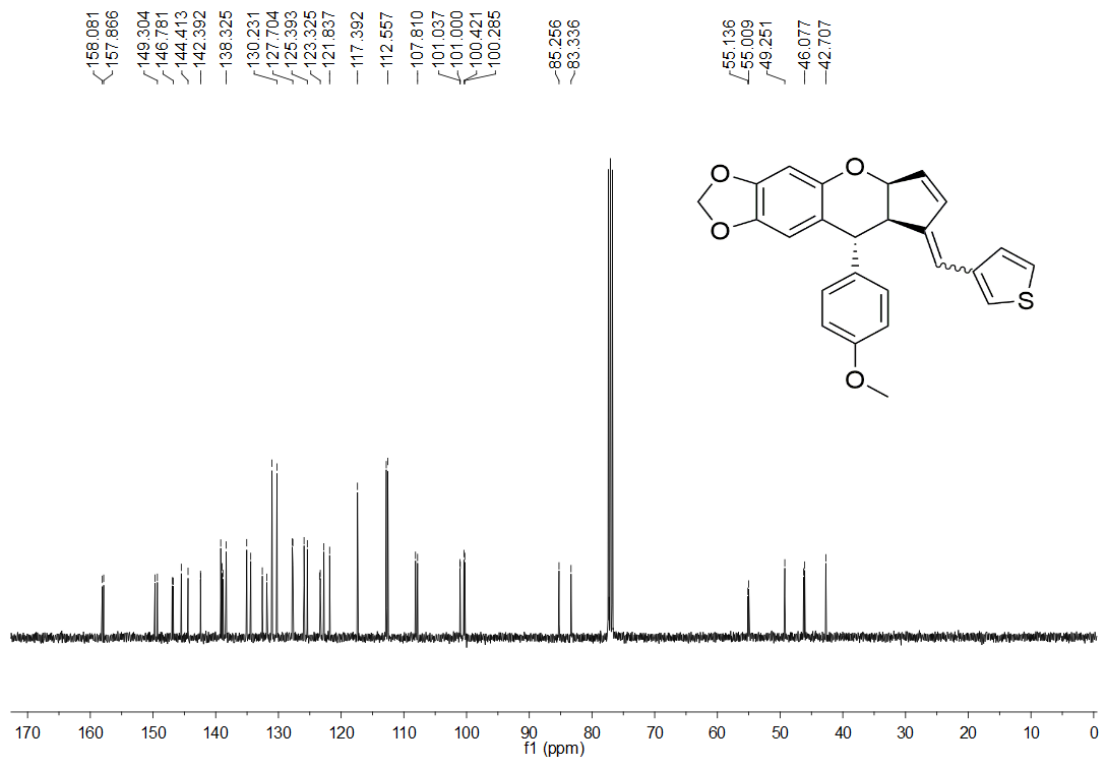
6.706
6.615
6.541
6.321
6.154
5.896
5.849
5.482
5.463
5.437
5.419
4.339
4.320
4.159
3.950
3.735
3.694
3.609
3.606
3.590
3.587
3.571
3.568
0.50
1.52
0.99
1.00
1.04
1.97
1.46
0.51
0.49
0.97
0.51
2.02
1.00
0.49
0.49
0.50
1.50
1.52
0.50
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
O
O
O
O
S
O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142.392
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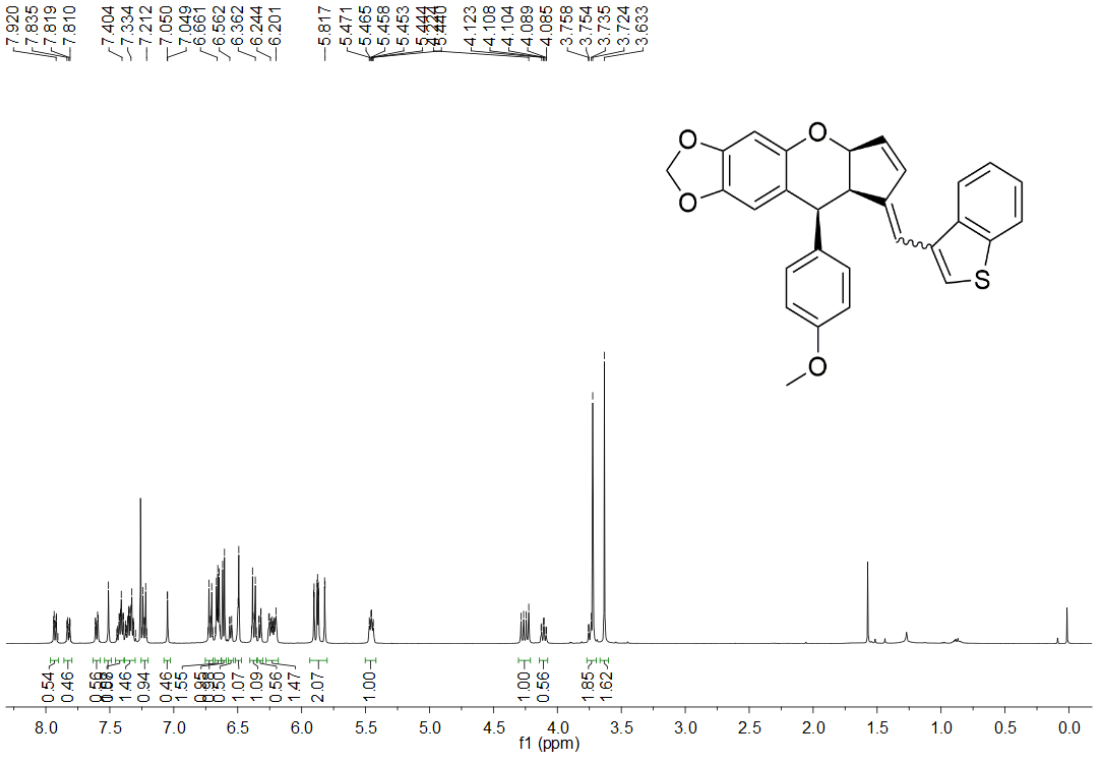
130.231
127.704
125.393
123.325
121.837
117.392
112.557
107.810
101.037
101.000
100.421
100.285
85.256
83.336
55.136
55.009
49.251
46.077
42.707
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
O
O
O
O
S
O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7.404
7.334
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7.050
7.049
6.661
6.562
6.362
6.244
6.201
5.817
5.471
5.465
5.458
5.453
4.123
4.108
4.104
4.089
4.085
3.758
3.754
3.735
3.724
3.633
O
O
O
S
O
0.54
0.46
1.46
0.94
0.46
1.55
1.07
1.09
0.56
1.47
2.07
1.00
1.00
0.56
1.85
1.62
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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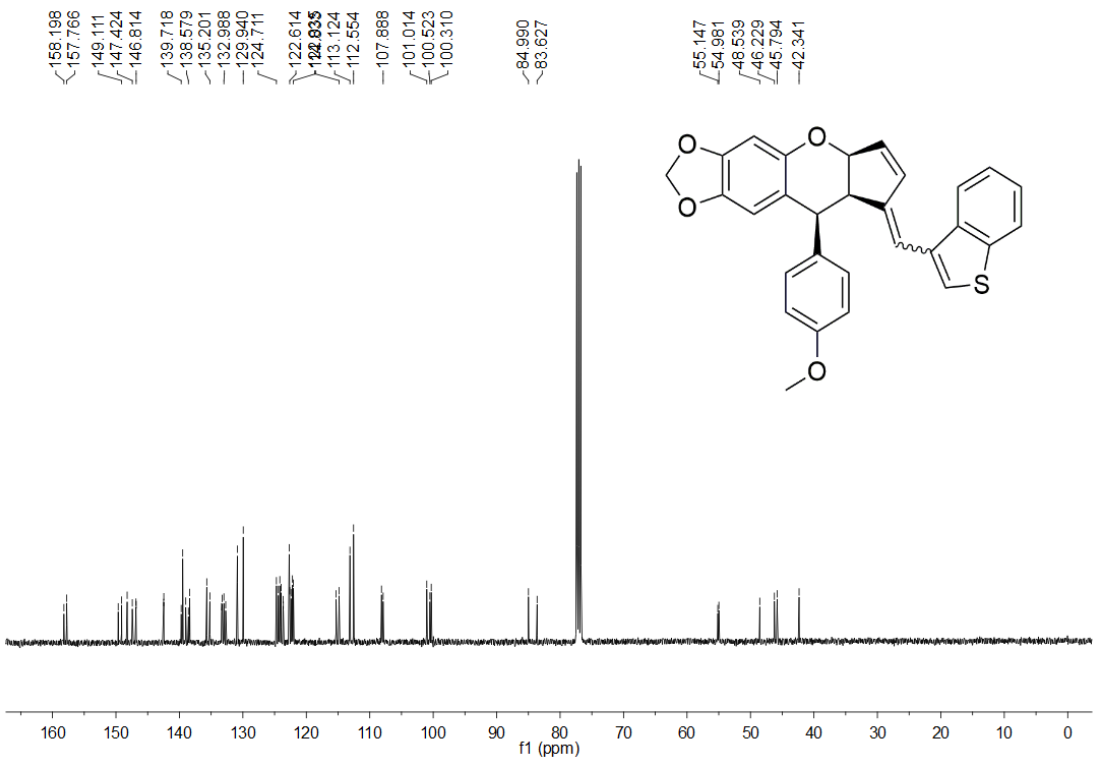
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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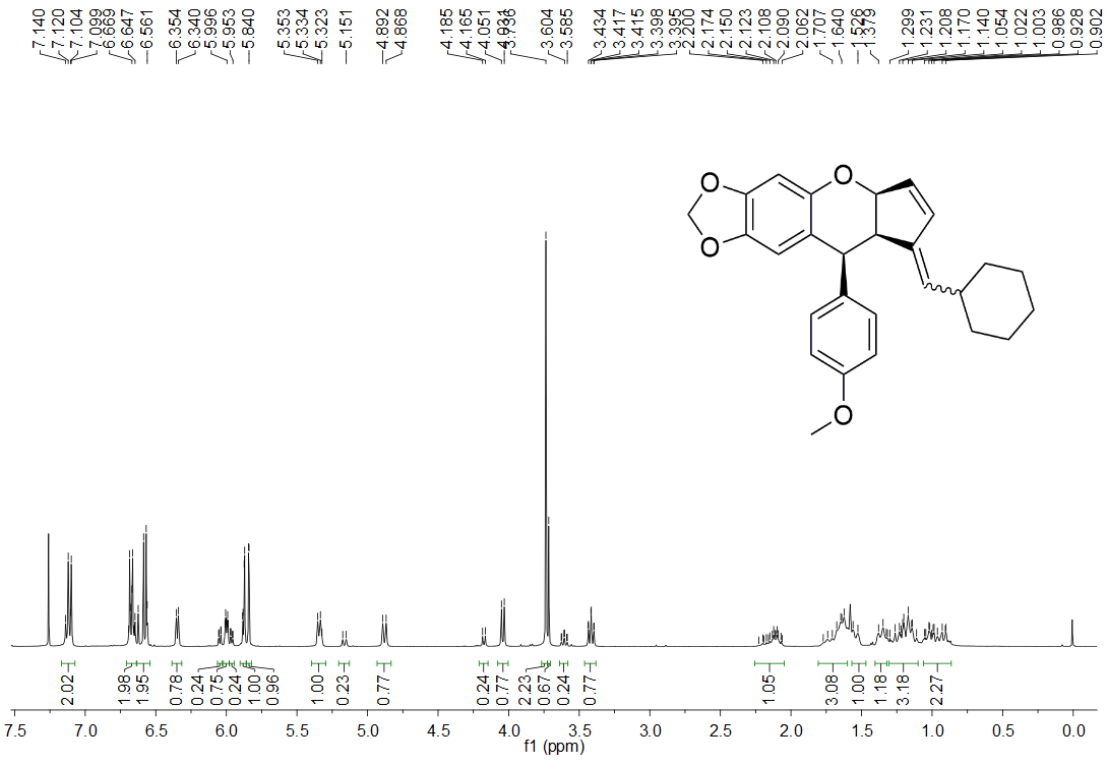
139.718
138.579
135.201
132.988
129.940
124.711
122.614
113.124
112.554
107.888
101.014
100.523
100.310
84.990
83.627
55.147
54.981
48.539
46.229
45.794
42.341
O
O
O
S
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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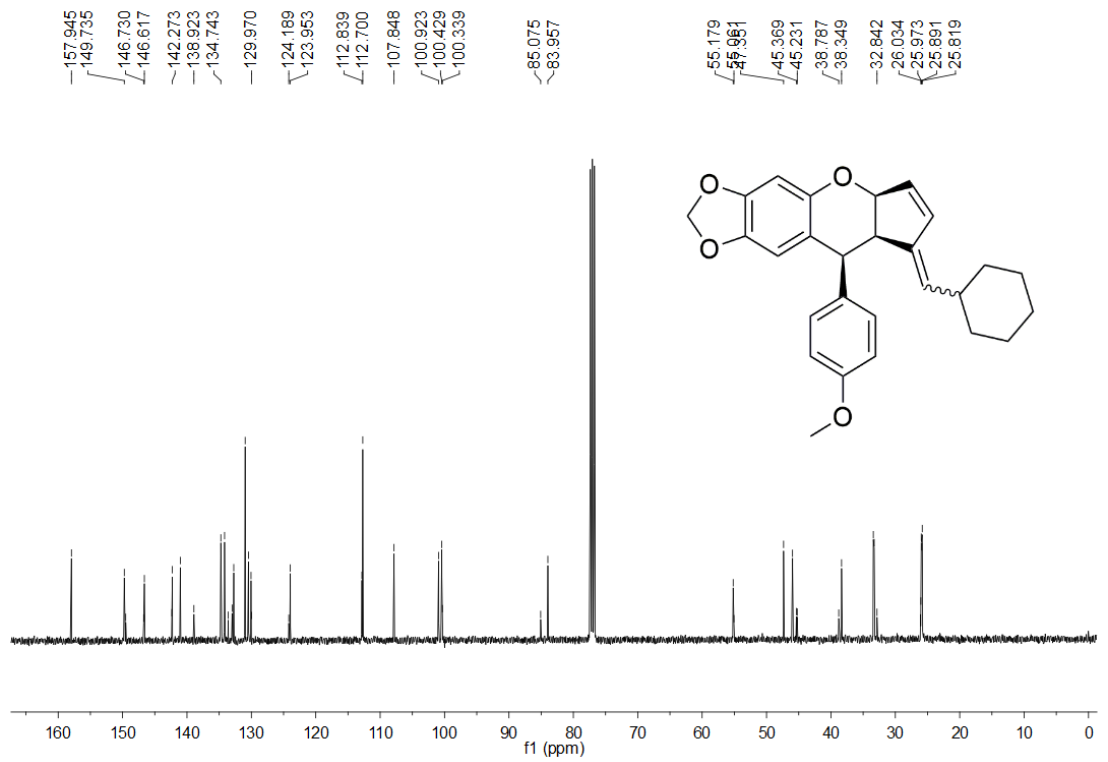
5.953
5.840
5.353
5.334
5.323
5.151
4.892
4.868
4.185
4.165
4.051
3.604
3.585
3.434
3.417
3.415
3.398
3.395
2.200
2.174
2.150
2.123
2.108
2.090
2.062
1.707
1.640
1.299
1.231
1.208
1.170
1.140
1.054
1.022
1.003
0.986
0.928
0.902
2.02
1.98
1.95
0.78
0.24
0.75
0.24
1.00
0.96
1.00
0.23
0.77
0.24
0.77
2.23
0.67
0.24
0.77
1.05
3.08
1.00
1.18
3.18
2.27
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.743
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124.189
123.953
112.839
112.700
107.848
100.923
100.429
100.339
85.075
83.957
55.179
47.351
45.369
45.231
38.787
38.349
32.842
26.034
25.973
25.891
25.819
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)