

Rapid Access to Iridoids via N-Heterocyclic Carbene-Catalyzed Activation and Cascade Reaction of Unsaturated Carboxylic Esters

Zhenqian Fu[1],⁺ Xingxing Wu[1]⁺ and Yonggui Robin Chi[1, 2]*

[1] Nanyang Technological University, Division of Chemistry & Biological Chemistry, School of Physical & Mathematical Sciences, Singapore 637371, Singapore

[2] Laboratory Breeding Base of Green Pesticide and Agricultural Bioengineering, Key Laboratory of Green Pesticide and Agricultural Bioengineering, Ministry of Education, Guizhou University, Huaxi District, Guiyang 550025 (China)

E-mail: robinchi@ntu.edu.sg

I	General information	S2
II	a) Condition optimization (Table S1)	S3
	b) General procedure for the catalytic reactions of ester (1) with enone (2) to synthesize product 3	S4
	c) Stereochemistry determination 4o via X-ray crystallographic analysis	S4
	d) Synthetic transformations of catalytic reaction product 3a and 6g	S5
	e) Proposed mechanism and stereochemical modes.	S7
III	a) Preparations and characterizations of substrates	S8
	b) Characterizations of products	S14
	c) References	S38
IV	¹ H, ¹³ C NMR and HPLC data	S39

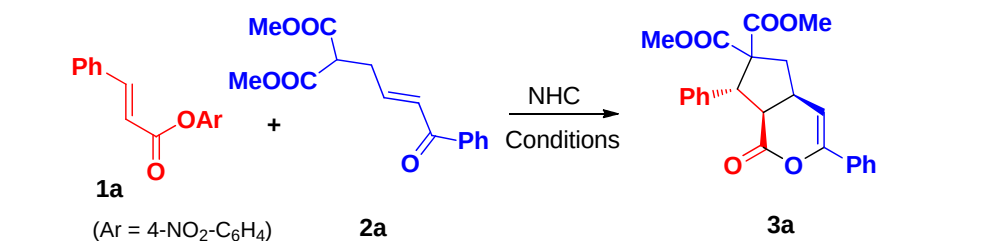
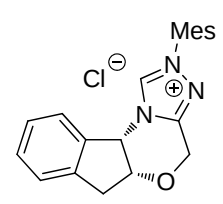
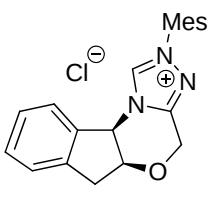
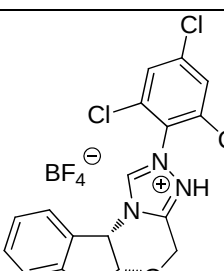
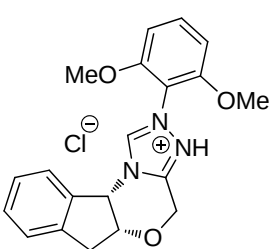
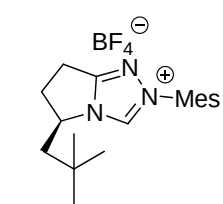
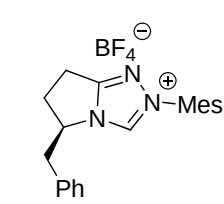
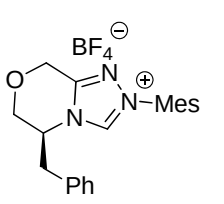
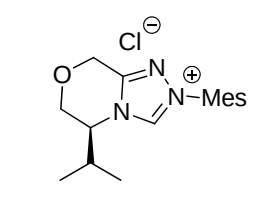
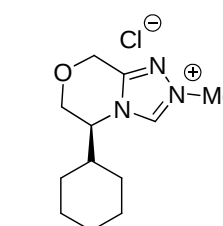
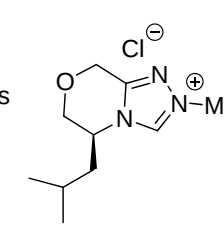
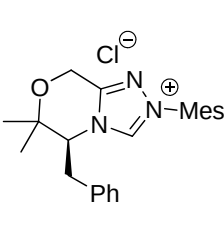
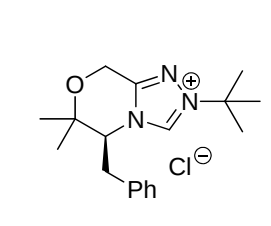
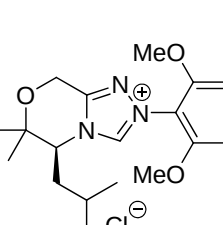
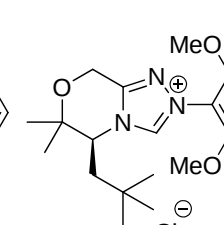
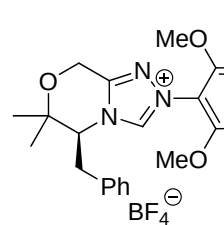
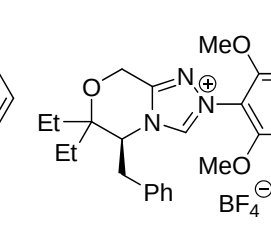
I: General Information

Commercially available materials purchased from Alfa Aesar or Sigma-Aldrich was used as received. HPLC grade CH₃CN (purchased from TEDIA) was dried over 4Å molecular sieve prior use. Toluene and DCM was dried over Pure Solv solvent purification system. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ¹H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. IR spectra were recorded on a Shimadzu IR IRAffinity-1 FT-IR Spectrometer. High resolution mass spectral analysis (HRMS) was performed on Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). The determination of enantiomeric excess was performed *via* chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractometer. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter and are reported as follows: [α]_D^t (c is in gm per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or potassium permanganate stain.

II. General procedure

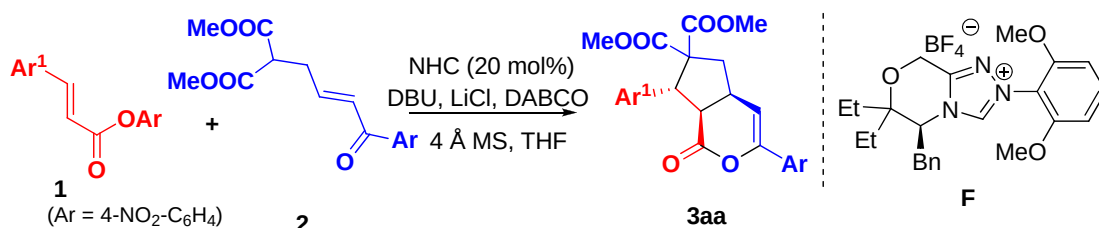
a) Condition Optimization

Table S1. Screening of NHCs for the reaction of **1a** with **2a**.^[a,b]

			
1a (Ar = 4-NO ₂ -C ₆ H ₄)	2a		3a
 24% yield 7:1 dr; 90:10 er	 18% yield 5:1 dr; 13:87 er	 nd	 34% yield 5:1 dr; 77:23 er
 31% yield 8:1 dr; 59:41 er	 55% yield 20:1 dr; 57:43 er	 43% yield 10:1 dr; 77:23 er	 19% yield 3:1 dr; 79:21 er
 43% yield 9:1 dr; 85:15 er	 63% yield 14:1 dr; 81:19 er	 25% yield 12:1 dr; 90:10 er	 <10% yield
 58% yield 7:1 dr; 91:9 er 74% yield^[c] 7:1 dr; 91:9 er	 54% yield^[c] 15:1 dr; 88:12 er	 88% yield^[c] 11:1 dr; 91:9 er	 74% yield^[c] 12:1 dr; 96:4 er

[a] Standard condition: NHC precursor (20 mol%), **1a** (0.2 mmol), **2a** (1.0 equiv), DBU (1.0 equiv), solvent (1.0 mL), 4Å MS, rt, 24 h. [b] Yields and diastereomeric ratio of **3a**, determined via ^1H NMR analysis of unpurified reaction mixtures. 1,3,5-trimethoxybenzene was used as an internal standard. [c] 0.3 eq DABCO was added, then 1.0 eq DBU was added after 20 min.

b) General procedure for the catalytic reactions of ester (1) with enone (2) to synthesize product 3:



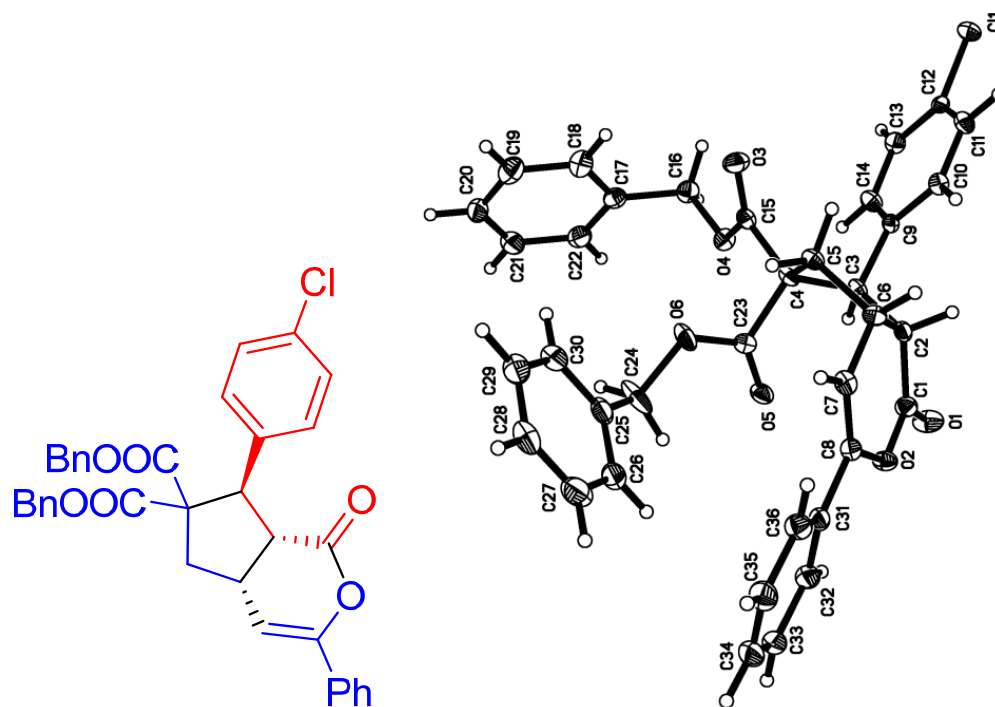
A dry Schlenk tube with stir bar was charged with ester **1** (0.10 mmol, 1.0 equiv.), NHC **F** (9.9 mg, 20 mol%), LiCl (5.0 mg, 1.0 equiv.), HOBT (2.7 mg, 20 mol%), DABCO (3.4 mg, 30 mol%) and molecular sieves (50 mg). The tube was evacuated, and refilled with nitrogen. Then the enone **2** (0.12 mmol, 1.2 equiv.) was added and the mixture was dissolved with newly distilled solvent THF (1.0 mL). After stirring at rt for 20 mins, DBU (21 μL , 1.4 equiv.) was added. Then the mixture was continued to stir at room temperature for another 3h when the substrate was consumed completely (monitored by TLC). The mixture was concentrated under vacuum and purified by column chromatography on silica gel (hexane/EtOAc) to afford desired product **3**, which was confirmed by ^1H NMR, ^{13}C NMR spectrum, and enantiomeric excess was determined by chiral HPLC.

Note: NHC **F** was prepared according to literature procedure.^[1]

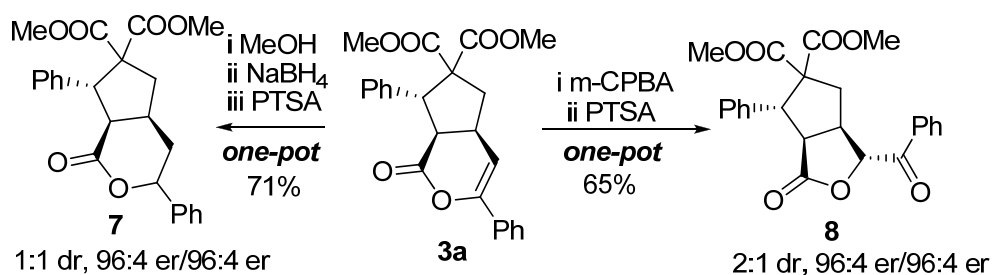
c) Stereochemistry determination 4o via X-ray crystallographic analysis:

Product **4o** was crystallized as a colorless crystal *via* vaporization of a hexane/ethyl acetate solution, and its absolute configuration was determined by x-ray structure analysis. CCDC 1404951 contains the supplementary crystallographic data

that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



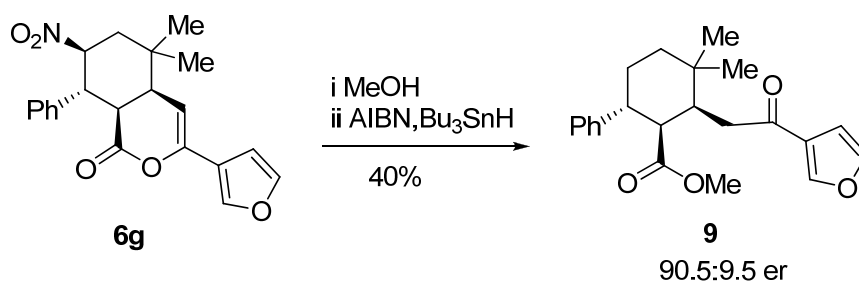
d) Synthetic transformations of catalytic reaction products 3a and 6g.



To a dry round-bottom flask was added **3a** (0.1 mmol, 40.6 mg) and anhydrous MeOH (1 mL). The resulting mixture was allowed to stir overnight at 60 °C. After the completion of reaction, NaBH₄ (0.20 mmol, 2.0 equiv.) was added and stirred 0.5h at room temperature. After the completion of reaction, the 2N HCl aq was added and the reaction mixture was extracted with DCM for three times, the combined organic layer

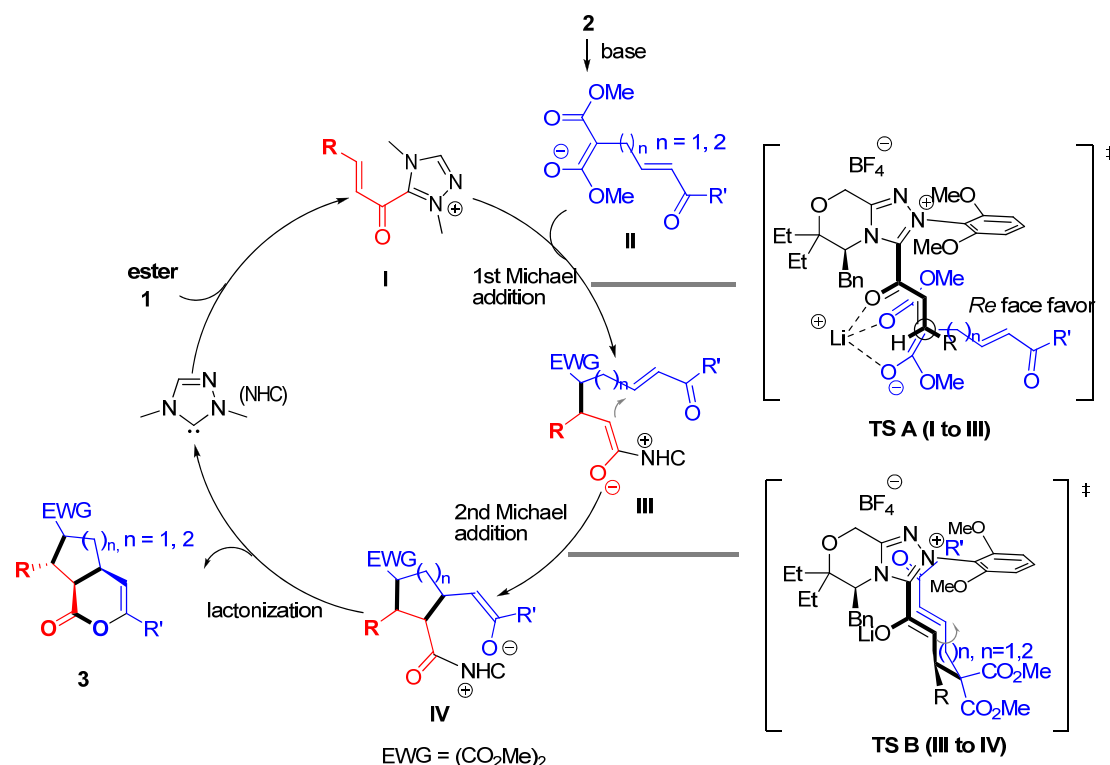
was washed with saturated brine and dried over anhydrous Na_2SO_4 . DCM was removed under reduced pressure, and then PTSA (0.09 mmol, 0.9 equiv.) and CHCl_3 (3 mL) was added, the resulting mixture was allowed to stir 4h at 60 °C. After the completion of reaction, solvent was removed under reduced pressure, the crude residue was purified by flash chromatography to afford product **7** with 29mg, 71% yield, 1:1 dr and 96:4 er/96:4 er. (The relative stereochemistry of each isomer was established through NOESY spectrum).

To a stirred solution of **3a** (40.6 mg, 0.10 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C, was added *m*CPBA (51.8 mg, 55% purity, 0.15 mmol). The mixture was stirred at 0 °C for 12 h. After the reaction finished, PTSA (1.9 mg, 0.01 mmol) was added, and the reaction was stirred for another 20 min at room temperature, quenched with aqueous NaHCO_3 solution and extracted with CH_2Cl_2 . The combined organic layers were washed with brine, dried over Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified via SiO_2 flash chromatography (n-hexane/EtOAc) to afford **8** (27.5 mg, 65% yield, 2:1 dr and 96:4 er/96:4 er). (The relative stereochemistry of each isomer was established through NOESY spectrum).



To a dry round-bottom flask was added **6g** (0.1 mmol, 36.7 mg) and anhydrous MeOH (1 mL). The resulting mixture was allowed to stir overnight at 60 °C. After the completion of reaction, solvent was removed under reduced pressure, and then AIBN (0.04 mmol, 0.4 equiv.), Bu_3SnH (0.50 mmol, 5.0 equiv.) and toluene (1 mL) was added, the resulting mixture was allowed to stir overnight at 110 °C. After the completion of reaction, solvent was removed under reduced pressure, the crude residue was purified by flash chromatography to afford product **9** with 40% yield.

e) Proposed mechanism and stereochemical modes.

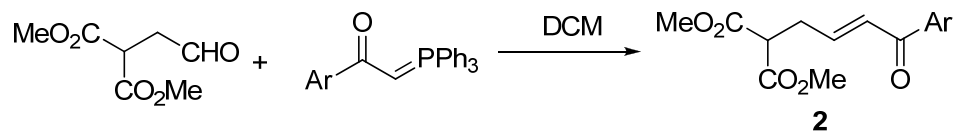


Scheme 1. Proposed mechanism and stereochemical modes. $n=1, 2$; EWG= malonate

The proposed pathway for the formation of cascade product **3** is depicted in Scheme 1. Addition of N-heterocyclic carbene (NHC) to unsaturated ester **1** could provide NHC-bounded ester intermediate **I**. Deprotonation of β -enone malonate **2** could form enolate intermediate **II** under basic conditions. Intermolecular Michael addition of intermediate **II** to intermediate **I** could give intermediate **III**, which undergoes intramolecular Michael addition to generate intermediate **IV**. Subsequent lactonization of intermediate **IV** would give the final cascade product **3** and release the NHC catalyst. In this process, the lithium ion, which is crucial to achieve the high ee, was supposed to coordinate with the enolate of malonate and the acyl azolium, helping to direct the first Michael addition of intermediate **II** to the α,β -unsaturated acylazolium in *Re* face manner (**TS A**). The relative stereochemistry of the intramolecular Michael addition was constructed through the chair-type confirmation of **TS B**, thus giving the multi-cyclic lactone products in high enantioselectivity.

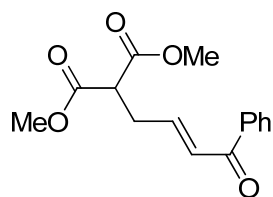
III. Characterizations of substrates and products, reference

a) Preparations and characterizations of substrates

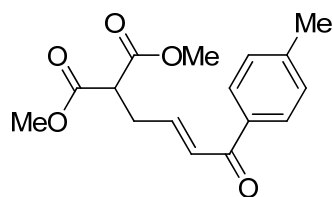


To a 100 mL round bottom flask under N_2 atmosphere, aldehyde (10 mmol, 1 equiv.) was added and then dissolved in 50 mL DCM, followed by the addition of the phosphine ylide (10 mmol, 1 equiv.). The reaction was kept stirring at rt for 12h. Then, the mixture was concentrated under vacuum to remove the DCM to give the crude product. Purification by the chromatograph on a silica gel column using hexane : ethyl acetate (3:1) as eluent can give the enone **2** as colorless oil.

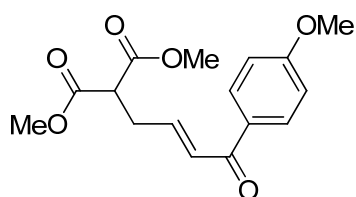
Note: The β -aldehyde malonate was prepared according to previous report^[2]



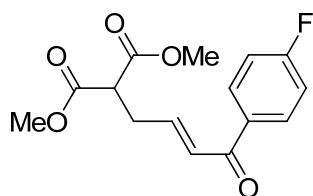
(E)-dimethyl 2-(4-oxo-4-phenylbut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.90 (d, J = 8.0 Hz, 2 H); 7.55 (t, J = 7.6 Hz, 1 H); 7.47 (t, J = 8.0 Hz, 2 H); 6.93–6.96 (m, 2 H); 3.76 (s, 6 H); 3.61 (t, J = 7.6 Hz, 1 H); 2.91 (dd, J_1 = 7.6 Hz, J_2 = 6.0 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 190.2, 168.8, 143.6, 137.5, 132.9, 128.6, 128.5, 128.1, 52.8, 50.5, 31.7 ppm. HRMS(ESI) calcd for $\text{C}_{15}\text{H}_{17}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 277.1076, Found: 277.1078.



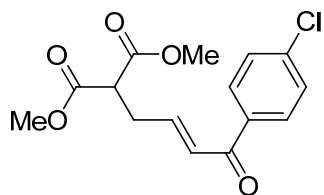
(E)-dimethyl 2-(4-oxo-4-p-tolylbut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.83 (d, J = 8.0 Hz, 2H); 7.27 (d, J = 8.0 Hz, 2H); 6.89–6.99 (m, 2H); 3.82 (s, 6H); 3.60 (t, J = 7.6 Hz, 2H); 2.91 (dd, J = 7.2, 6.0 Hz, 2H); 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 189.7, 168.8, 143.8, 143.1, 135.0, 129.3, 128.7, 128.2, 52.8, 50.6, 31.7, 21.7 ppm. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 291.1232, Found: 291.1237.



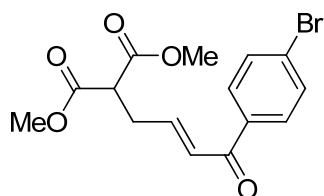
(E)-dimethyl 2-(4-(4-methoxyphenyl)-4-oxobut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.91–7.95 (m, 2H); 6.87–7.00 (m, 4H); 3.88 (s, 3H); 3.76 (s, 6H); 3.60 (t, J = 7.6 Hz, 2H); 2.91 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 188.4, 168.8, 163.5, 142.5, 130.9, 130.4, 128.0, 113.8, 55.5, 52.8, 50.6, 31.7 ppm. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_6$ ($\text{M}+\text{H}$) $^+$: 307.1182, Found: 307.1182.



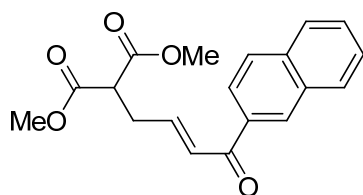
(E)-dimethyl 2-(4-(4-fluorophenyl)-4-oxobut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.93–7.97 (m, 2H); 7.12–7.17 (m, 2H); 6.93–6.95 (m, 2H); 3.77 (s, 6H); 3.61 (t, J = 7.6 Hz, 2H); 2.90–2.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 188.5, 168.7, 166.9, 164.5, 143.8, 133.9, 133.8, 131.2, 131.1, 127.8, 115.8, 115.6, 52.8, 50.5, 31.7 ppm. HRMS(ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{FO}_5$ ($\text{M}+\text{H}$) $^+$: 295.0982, Found: 295.0984.



(E)-dimethyl 2-(4-(4-chlorophenyl)-4-oxobut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.84–7.88 (m, 2H); 7.43–7.56 (m, 2H); 6.89–6.95 (m, 2H); 3.76 (s, 6H); 3.61 (t, J = 7.6 Hz, 2H); 2.92 (dd, J = 7.2, 5.6 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 188.9, 168.7, 144.2, 139.4, 135.8, 130.0, 129.0, 127.7, 52.8, 50.4, 31.7 ppm. HRMS(ESI) calcd for $\text{C}_{15}\text{H}_{16}\text{ClO}_5$ ($\text{M}+\text{H}$) $^+$: 311.0686, Found: 311.0692.

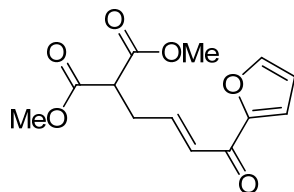


(E)-dimethyl 2-(4-(4-bromophenyl)-4-oxobut-2-enyl)malonate: white oil; ^1H NMR (500 MHz, CDCl_3): δ = 7.64–7.82 (m, 2 H); 7.58–7.65 (m, 2 H); 6.85–6.96 (m, 2 H); 3.77 (s, 6 H); 3.60 (t, J = 7.5 Hz, 1 H); 2.92 (dd, J_1 = 5.5 Hz, J_2 = 5.5 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3): δ = 189.0, 168.2, 144.3, 136.2, 131.9, 130.1, 128.1, 127.7, 52.8, 50.4, 31.7 ppm. HRMS(ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{BrO}_5\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 377.0001, Found: 376.9999.

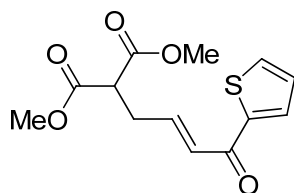


(E)-dimethyl 2-(4-(naphthalen-2-yl)-4-oxobut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 8.43 (s, 1H); 7.96–8.02 (m, 2H); 7.87–7.92 (m, 2H); 7.54–7.63 (m, 2H); 7.13 (d, J = 15.6 Hz, 1H); 6.96–7.03 (m, 1H); 3.78 (s, 6H); 3.65 (t, J = 7.6 Hz, 2H); 2.95–2.99 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 190.0, 168.8, 143.5, 135.5, 134.8, 132.5, 130.3, 129.6, 128.6, 128.5, 128.2, 127.8, 126.8, 124.4,

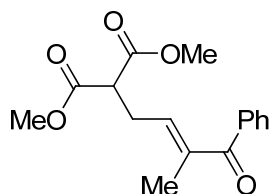
52.8, 50.6, 31.8 ppm. HRMS(ESI) calcd for $C_{19}H_{19}O_5$ (M+H)⁺: 327.1232, Found: 327.1242.



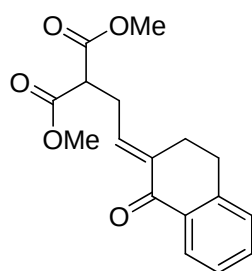
(E)-dimethyl 2-(4-(furan-2-yl)-4-oxobut-2-enyl)malonate: yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.62 (t, *J* = 0.8 Hz, 1H); 7.25 (d, *J* = 3.6 Hz, 1H); 6.99–7.06 (m, 1H); 6.87 (d, *J* = 19.6 Hz, 1H); 6.56 (dd, *J* = 3.6, 1.6 Hz, 1H); 3.76 (s, 6H); 3.60 (t, *J* = 7.2 Hz, 2H); 2.90 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 177.5, 168.8, 153.1, 146.8, 143.0, 127.3, 118.0, 112.5, 52.8, 50.5, 31.6 ppm. HRMS(ESI) calcd for $C_{13}H_{15}O_6$ (M+H)⁺: 267.0863, Found: 267.0864.



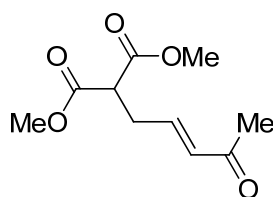
(E)-dimethyl 2-(4-oxo-4-(thiophen-2-yl)but-2-enyl)malonate: yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 3.6 Hz, 1H); 7.67 (d, *J* = 4.8 Hz, 1H); 7.15–7.17 (m, 1H); 6.95–7.03 (m, 1H); 6.87 (d, *J* = 15.2 Hz, 1H); 3.76 (s, 6H); 3.61 (t, *J* = 7.2 Hz, 2H); 2.91 (t, *J* = 7.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 181.7, 168.8, 144.8, 142.9, 134.1, 132.2, 128.3, 127.7, 52.8, 50.5, 31.6 ppm. HRMS(ESI) calcd for $C_{13}H_{15}O_5S$ (M+H)⁺: 283.0640, Found: 283.0644.



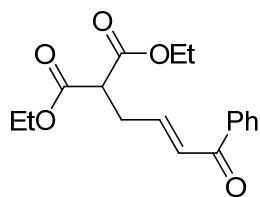
(E)-dimethyl 2-(3-methyl-4-oxo-4-phenylbut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.62–7.64 (m, 2H); 7.49–7.53 (m, 1H); 7.39–7.43 (m, 2H); 6.14–6.18 (m, 1H); 3.75 (s, 6H); 3.51 (t, J = 7.6 Hz, 2H); 2.88 (t, J = 7.6 Hz, 2H); 2.00 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 198.4, 168.9, 139.4, 138.8, 138.0, 131.8, 129.5, 128.1, 52.7, 50.7, 28.3, 12.8 ppm. HRMS(ESI) calcd for $\text{C}_{16}\text{H}_{19}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 291.1232, Found: 291.1231.



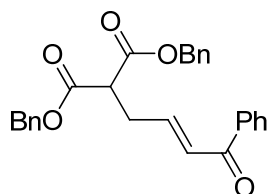
(E)-dimethyl 2-(2-(1-oxo-3,4-dihydronaphthalen-2(1H)-ylidene)ethyl)malonate: colorless oil; ^1H NMR (400 MHz, CDCl_3): δ = 8.05–8.15 (m, 1 H); 7.46–7.55 (m, 1 H); 7.30–7.40 (m, 1 H); 7.22–7.28 (m, 1 H); 6.74–6.82 (m, 1 H); 3.73 (s, 3 H); 3.58 (t, J = 7.6 Hz, 1 H); 2.92–3.02 (m, 2 H); 2.72–2.88 (m, 4 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 187.1, 169.0, 143.7, 137.6, 133.7, 133.3, 128.3, 128.2, 126.7, 52.7, 50.8, 29.0, 27.6, 25.8 ppm. HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 303.1232, Found: 303.1233.



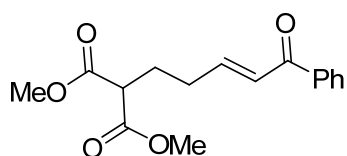
(E)-dimethyl 2-(4-oxopent-2-enyl)malonate: colorless oil; ^1H NMR (500 MHz, CDCl_3): δ = 6.73 (dt, J = 16.0, 7.0 Hz, 1 H), 6.13 (dt, J = 16.0, 1.4 Hz, 1 H), 3.76 (s, 6 H), 3.75 (d, J = 7.6 Hz, 1 H), 3.55 (t, J = 7.4 Hz, 1 H), 2.82 (td, J = 7.2, 1.5 Hz, 2H), 2.24 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ = 197.9, 168.6 (x2), 142.4, 133.1, 52.7, 50.3, 31.2, 27.0 ppm. HRMS(ESI) calcd for $\text{C}_{10}\text{H}_{15}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 215.0919, Found: 215.0911.



(E)-diethyl 2-(4-oxo-4-phenylbut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.91 (d, J = 7.2 Hz, 2 H); 7.55 (t, J = 7.2, 1 H); 7.47 (t, J = 8.0 Hz, 2 H); 6.95–6.97 (m, 2 H); 4.18–4.25 (m, 4 H); 3.57 (t, J = 7.6 Hz, 1 H); 2.89–2.93 (m, 2 H); 1.27 (t, J = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 190.2, 168.4, 143.9, 137.6, 132.9, 128.6, 128.5, 128.1, 61.7, 50.8, 31.7, 14.1 ppm. HRMS(ESI) calcd for $\text{C}_{17}\text{H}_{21}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 305.1389, Found: 305.1390.

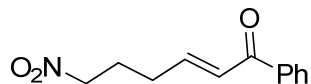


(E)-dibenzyl 2-(4-oxo-4-phenylbut-2-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.85 (d, J = 7.2 Hz, 2 H); 7.55 (t, J = 7.6, 1 H); 7.44 (t, J = 8.0 Hz, 2 H); 7.36 (t, J = 4.8 Hz, 1 H); 7.26–7.32 (m, 9 H); 6.86–6.96 (m, 2 H); 5.12–5.19 (m, 4 H); 3.69 (t, J = 7.2 Hz, 1 H); 2.93 (dd, J_1 = 7.6 Hz, J_2 = 5.6 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 190.1, 168.1, 143.5, 137.5, 135.1, 132.8, 128.6, 128.5, 128.4, 128.3, 128.1, 67.5, 50.8, 31.7 ppm. HRMS(ESI) calcd for $\text{C}_{27}\text{H}_{25}\text{O}_5$ ($\text{M}+\text{H}$) $^+$: 429.1702, Found: 429.1701.

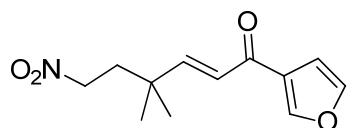


(E)-dimethyl 2-(5-oxo-5-phenylpent-3-enyl)malonate: yellow oil; ^1H NMR (400 MHz, CDCl_3): δ = 7.92 (d, J = 7.2 Hz, 2 H); 7.57 (t, J = 7.2, 1 H); 7.47 (t, J = 7.6 Hz, 2 H); 6.89–7.04 (m, 2 H); 3.75 (s, 6 H); 3.43 (t, J = 7.6 Hz, 1 H); 2.38 (dd, J_1 = 14.4 Hz, J_2 = 6.8 Hz, 2 H); 2.15 (dd, J_1 = 14.4 Hz, J_2 = 7.6 Hz, 2 H). ^{13}C NMR (100 MHz,

CDCl₃): δ = 190.5, 169.4, 146.9, 137.7, 132.8, 128.6, 128.5, 126.9, 52.6, 50.9, 30.2, 27.2 ppm. HRMS(ESI) calcd for C₁₆H₁₉O₅ (M+H)⁺: 291.1232, Found: 291.1231.

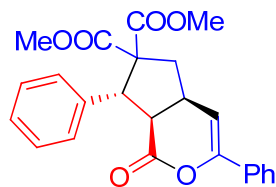


(E)-6-nitro-1-phenylhex-2-en-1-one: yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 7.93–7.96 (m, 2H); 7.56–7.60 (m, 1H); 7.47–7.50 (m, 2H); 6.94–7.03 (m, 2H); 4.45 (t, J = 6.4 Hz, 2H); 2.43–2.48 (m, 2H); 2.23–2.30 (m, 2H). ¹³C NMR (100 MHz, CDCl₃): δ = 190.1, 145.5, 137.6, 133.0, 128.7, 128.6, 127.5, 74.6, 29.2, 25.8 ppm. HRMS(ESI) calcd for C₁₂H₁₄NO₃ (M+H)⁺: 220.0974, Found: 220.0974.



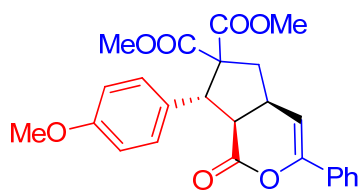
(E)-1-(furan-3-yl)-4,4-dimethyl-6-nitrohex-2-en-1-one: yellow oil; ¹H NMR (400 MHz, CDCl₃): δ = 8.09 (s, 1 H); 7.49 (t, J = 3.2 Hz, 1 H); 6.95 (d, J = 15.6 Hz, 1 H); 6.85–6.85 (m, 1H); 6.51 (d, J = 15.6 Hz, 1 H); 4.33–4.37 (m, 2 H); 2.21–2.25 (m, 2 H); 1.21 (s, 6 H). ¹³C NMR (100 MHz, CDCl₃): δ = 183.9, 153.5, 147.4, 144.4, 128.1, 124.3, 128.1, 124.3, 109.1, 72.4, 38.6, 36.0, 26.4 ppm. HRMS(ESI) calcd for C₁₂H₁₆NO₄ (M+H)⁺: 238.1079, Found: 238.1079.

b) Characterizations of products

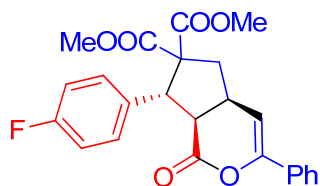


(4a*S*,7*R*,7a*R*)-dimethyl 1-oxo-3,7-diphenyl-4a,5,7,7a-tetrahydrocyclopenta[*c*]pyran-6,6(1*H*)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.70, CHCl₃) = -16.8; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz,

2 H); 7.24–7.39 (m, 8 H); 5.56 (d, $J = 3.2$ Hz, 1 H); 4.70 (d, $J = 8.8$ Hz, 1 H); 3.71 (s, 3 H); 3.52–3.61 (m, 2 H); 3.13 (m, 4 H); 2.27 (dd, $J_1 = 12.0$ Hz, $J_2 = 4.0$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.6, 170.2, 168.4, 149.2, 137.3, 132.2, 129.2, 128.7, 128.5, 128.3, 127.8, 124.8, 102.2, 65.1, 53.7, 53.1, 52.3, 47.6, 41.3, 36.7$ ppm. IR (film): ν_{max} 2952, 1731, 1515, 1425, 1272, 1211, 1008 cm^{-1} . HRMS (ESI): $\text{C}_{24}\text{H}_{23}\text{O}_6$ $[\text{M}+\text{H}]^+$ calcd: 407.1495, found: 407.1492; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 13.4 min, t_r (minor) = 16.6 min.

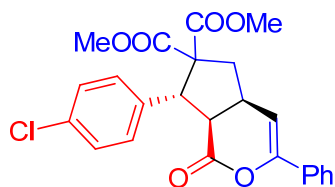


(4aS,7R,7aR)-dimethyl 7-(4-methoxyphenyl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 1.44, CHCl_3) = -40.5; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.59$ (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 2 H); 7.36–7.39 (m, 3 H); 7.25 (d, $J = 9.2$ Hz, 2 H); 6.83 (d, $J = 8.0$ Hz, 2 H); 5.53 (d, $J = 3.2$ Hz, 1 H); 4.61 (d, $J = 9.6$ Hz, 1 H); 3.77 (s, 3 H); 3.71 (s, 3 H); 3.49–3.59 (m, 2 H); 3.20 (s, 3 H); 3.11 (dd, $J_1 = 14.0$ Hz, $J_2 = 7.2$ Hz, 1 H); 2.68 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.0$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.7, 170.4, 168.4, 159.1, 149.1, 132.2, 129.9, 129.2, 129.0, 128.5, 124.8, 113.6, 102.4, 64.8, 55.2, 53.1, 53.0, 52.4, 47.6, 41.1, 36.4$ ppm. IR (film): ν_{max} 2952, 1757, 1729, 1515, 1436, 1221, 1127, 1025, 929 cm^{-1} . HRMS (ESI): $\text{C}_{25}\text{H}_{25}\text{O}_7$ $[\text{M}+\text{H}]^+$ calcd: 437.1600, found: 437.1613; 95:5 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 17.7 min, t_r (minor) = 21.5 min.

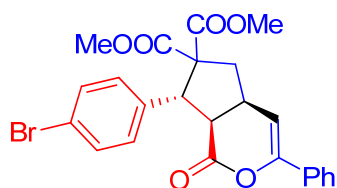


(4aS,7R,7aR)-dimethyl 7-(4-fluorophenyl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 1.90,

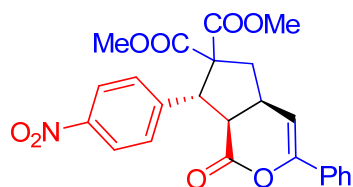
CHCl₃) = -22.9; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.4 Hz, 2 H); 7.34–7.41 (m, 3 H); 7.32 (dd, *J*₁ = 8.8 Hz, *J*₂ = 5.2 Hz, 2 H); 6.99 (t, *J* = 8.8 Hz, 2 H); 5.55 (d, *J* = 3.2 Hz, 1 H); 4.64 (d, *J* = 10.0 Hz, 1 H); 3.72 (s, 3 H); 3.56–3.62 (m, 1 H); 3.51 (t, *J* = 8.8 Hz, 1 H); 3.20 (s, 3 H); 3.11 (dd, *J*₁ = 14.0 Hz, *J*₂ = 7.2 Hz, 1 H); 2.27 (dd, *J*₁ = 14.0 Hz, *J*₂ = 4.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 170.3, 168.1, 149.2, 132.7, 132.6, 132.1, 130.5, 130.4, 129.3, 128.6, 124.8, 115.2, 115.0, 102.2, 64.8, 53.1, 52.9, 52.4, 47.5, 41.1, 36.5 ppm. IR (film): ν_{max} 2954, 1762, 1729, 1515, 1437, 1275, 1215, 1016, 929 cm⁻¹. HRMS (ESI): C₂₄H₂₂FO₆ [M+H]⁺ calcd: 425.1400, found: 425.1383; 95:5 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), *t*_r(major) = 13.0 min, *t*_r(minor) = 17.6 min.



(4a*S*,7*R*,7a*R*)-dimethyl 7-(4-chlorophenyl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[*c*]pyran-6,6(1*H*)-dicarboxylate : yellow oil; [α]_D²³ (c 1.76, CHCl₃) = -41.2; ¹H NMR (400 MHz, CDCl₃): δ = 7.58 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.4 Hz, 2 H); 7.35 – 7.39 (m, 3 H); 7.28 (s, 4 H); 5.55 (d, *J* = 3.2 Hz, 1 H); 4.62 (d, *J* = 9.6 Hz, 1 H); 3.72 (s, 3 H); 3.56–3.61 (m, 1 H); 3.50 (t, *J* = 8.8 Hz, 1 H); 3.21 (s, 3 H); 3.10 (dd, *J*₁ = 14.0 Hz, *J*₂ = 7.6 Hz, 1 H); 2.27 (dd, *J*₁ = 14.0 Hz, *J*₂ = 4.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 170.2, 168.1, 149.1, 135.5, 133.7, 132.0, 130.2, 129.3, 128.6, 128.4, 124.8, 102.2, 64.8, 53.1, 53.0, 52.1, 47.3, 41.2, 36.5 ppm. IR (film): ν_{max} 2953, 1762, 1729, 1526, 1436, 1255, 1015, 928 cm⁻¹. HRMS (ESI): C₂₄H₂₂ClO₆ [M+H]⁺ calcd: 441.1105, found: 441.1102; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), *t*_r(major) = 13.5 min, *t*_r(minor) = 18.7 min.

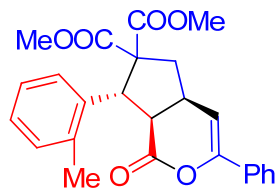


(4aS,7R,7aR)-dimethyl 7-(4-bromophenyl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 2.12, CHCl₃) = -47.3; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, J_1 = 8.0 Hz, J_2 = 2.8 Hz, 2 H); 7.36–7.44 (m, 5 H); 7.22 (d, J = 8.4 Hz, 2 H); 5.55 (d, J = 3.2 Hz, 1 H); 4.60 (d, J = 10.0 Hz, 1 H); 3.72 (s, 3 H); 3.57–3.60 (m, 1 H); 3.50 (t, J = 8.8 Hz, 1 H); 3.22 (s, 3 H); 3.10 (dd, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 1 H); 2.26 (dd, J_1 = 14.0 Hz, J_2 = 4.4 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 170.2, 168.0, 149.1, 136.1, 132.0, 131.4, 130.5, 129.3, 128.6, 128.4, 121.9, 102.2, 64.7, 53.1, 53.0, 52.5, 47.3, 41.2, 36.5 ppm. IR (film): $\nu_{\max}$ 2954, 1767, 1730, 1558, 1539, 1275, 1215, 1011, 929 cm⁻¹. HRMS (ESI): C₂₄H₂₂BrO₆ [M+H]⁺ calcd: 485.0600, found: 485.0587; 97:3 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 14.1 min, t_r (minor) = 19.6 min.



(4aS,7R,7aR)-dimethyl 7-(4-nitrophenyl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.41, CHCl₃) = -58.9; ¹H NMR (400 MHz, CDCl₃): δ = 8.17 (d, J = 8.8 Hz, 2 H); 7.59 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 2 H); 7.55 (d, J = 8.8 Hz, 2 H); 7.37–7.42 (m, 3 H); 5.59 (d, J = 3.2 Hz, 1 H); 4.72 (d, J = 10.0 Hz, 1 H); 3.75 (s, 3 H); 3.63–3.67 (m, 1 H); 3.58 (t, J = 9.6 Hz, 1 H); 3.22 (s, 3 H); 3.13 (dd, J_1 = 14.0 Hz, J_2 = 7.6 Hz, 1 H); 2.29 (dd, J_1 = 14.0 Hz, J_2 = 4.8 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 169.9, 167.7, 149.1, 147.4, 144.5, 131.9, 129.9, 129.4, 128.6, 124.8, 123.3, 101.9, 64.8, 53.3, 53.2, 52.6, 47.1, 41.4, 36.4 ppm. IR (film): $\nu_{\max}$ 2955, 1730, 1526, 1424, 1350, 1024, 925 cm⁻¹. HRMS (ESI): C₂₄H₂₂NO₈ [M+H]⁺ calcd: 452.1345, found: 452.1348; 97:3 *er* as

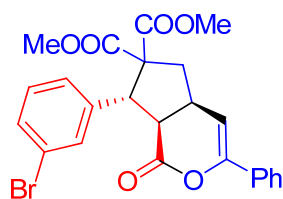
determined by HPLC (Chiralcel IB, 85:15 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 23.4 min, t_r (minor) = 42.9 min.



(4aS,7R,7aR)-dimethyl

1-oxo-3-phenyl-7-o-tolyl-4a,5,7,7a-

tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.25, CHCl₃) = +13.6; ¹H NMR (400 MHz, CDCl₃): δ = 7.60 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2 H); 7.35–7.40 (m, 3 H); 7.08–7.17 (m, 3 H); 7.04 (d, J = 8.0 Hz, 1 H); 5.58 (d, J = 4.0 Hz, 1 H); 5.18 (d, J = 6.8 Hz, 1 H); 3.67 (s, 3 H); 3.58–3.60 (m, 1 H); 3.36 (t, J = 7.6 Hz, 1 H); 3.14 (dd, J_1 = 13.6 Hz, J_2 = 6.8 Hz, 1 H) ; 3.08 (s, 3 H); 2.47 (s, 3 H); 2.67 (dd, J_1 = 14.0 Hz, J_2 = 5.6 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.6, 169.9, 168.6, 149.7, 138.0, 137.9, 132.3, 130.4, 129.2, 128.5, 127.3, 126.8, 126.0, 124.8, 101.6, 65.6, 53.1, 52.2, 50.8, 48.8, 41.8, 37.3, 20.3 ppm. IR (film): $\nu_{\max}$ 2952, 1734, 1434, 1260, 1216, 1125, 1046, 936, 884 cm⁻¹. HRMS (ESI): C₂₅H₂₅O₆ [M+H]⁺ calcd: 421.1646, found: 421.1646; 98:2 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 12.0 min, t_r (minor) = 14.5 min.

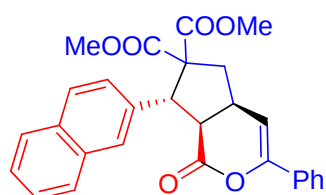


(4aS,7R,7aR)-dimethyl

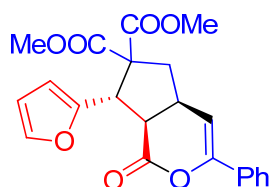
7-(3-bromophenyl)-1-oxo-3-phenyl-4a,5,7,7a-

tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.45, CHCl₃) = -21.6; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 2 H); 7.48 (s, 1 H); 7.36–7.40 (m, 3 H); 7.27 (d, J = 8.4 Hz, 2 H); 7.18 (t, J = 8.0 Hz, 1 H); 5.57 (d, J = 3.6 Hz, 1 H); 4.63 (d, J = 9.2 Hz, 1 H); 3.72 (s, 3 H); 3.59–3.62 (m, 1 H); 3.50 (t, J = 8.8 Hz, 1 H); 3.20 (s, 3 H); 3.10 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1 H) ; 2.24 (dd, J_1 = 14.0 Hz, J_2 = 4.8 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.2,

170.1, 168.0, 149.2, 139.7, 132.1, 131.9, 130.9, 129.8, 129.3, 128.6, 127.3, 124.8, 122.3, 102.0, 64.9, 53.2, 53.1, 52.4, 47.4, 41.3, 36.6 ppm. IR (film): $\nu_{\max}$ 2952, 1761, 1729, 1525, 1436, 1215, 1124, 1024, 928 cm^{-1} . HRMS (ESI): $\text{C}_{24}\text{H}_{22}\text{BrO}_6\text{Na}$ $[\text{M}+\text{Na}]^+$ calcd: 485.0600, found: 485.0603; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 13.5 min, t_r (minor) = 17.5 min.

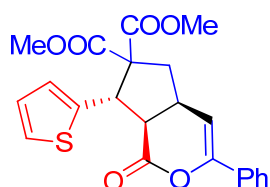


(4aS,7R,7aR)-dimethyl 7-(naphthalen-2-yl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.68, CHCl_3) = -71.8; ^1H NMR (400 MHz, CDCl_3): δ = 7.76–7.82 (m, 4 H); 7.61 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2 H); 7.36–7.47 (m, 5 H); 5.60 (d, J = 2.0 Hz, 1 H); 4.86 (d, J = 8.4 Hz, 1 H); 3.72 (s, 3 H); 3.67–3.70 (m, 2 H); 3.16–3.20 (m, 1 H); 3.02 (s, 3 H); 2.31 (dd, J_1 = 14.0 Hz, J_2 = 3.6 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.3, 168.3, 149.2, 134.7, 133.2, 132.8, 132.2, 129.3, 128.5, 128.1, 128.0, 127.8, 127.5, 126.3, 126.1, 126.0, 124.8, 102.0, 65.0, 53.9, 53.1, 52.3, 47.8, 41.4, 36.7 ppm. IR (film): $\nu_{\max}$ 2954, 1761, 1725, 1525, 1436, 1124, 1024, 928 cm^{-1} . HRMS (ESI): $\text{C}_{28}\text{H}_{25}\text{O}_6$ $[\text{M}+\text{H}]^+$ calcd: 457.1651, found: 457.1651; 96:4 *er* as determined by HPLC (Chiralcel IA, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 40.6 min, t_r (minor) = 22.5 min.

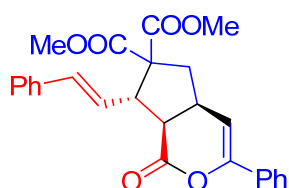


(4aS,7S,7aR)-dimethyl 7-(furan-2-yl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.60,

CHCl₃) = -11.0; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.4 Hz, 2 H); 7.33–7.40 (m, 4 H); 6.30 (s, 2 H); 5.55 (d, *J* = 2.4 Hz, 1 H); 4.73 (d, *J* = 7.6 Hz, 1 H); 3.69 (s, 3 H); 3.57–3.60 (m, 2 H); 3.44 (s, 3 H); 3.08–3.13 (m, 1 H); 2.19 (dd, *J*₁ = 14.0 Hz, *J*₂ = 4.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 170.1, 169.8, 168.0, 151.0, 148.9, 142.3, 132.1, 129.2, 128.5, 124.7, 110.6, 108.8, 101.9, 63.3, 53.1, 53.0, 48.1, 46.1, 41.0, 36.0 ppm. IR (film): ν_{max} 2954, 1734, 1554, 1527, 1424, 1215, 1013, 929 cm⁻¹. HRMS (ESI): C₂₂H₂₁O₇ [M+H]⁺ calcd: 397.1287, found: 397.1283; 96:4 *er* as determined by HPLC (Chiralcel ID, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), *t*_r (major) = 60.1 min, *t*_r (minor) = 72.5 min.



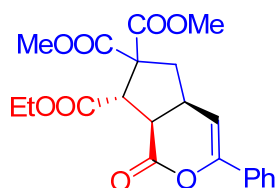
(4a*S*,7*S*,7a*R*)-dimethyl 1-oxo-3-phenyl-7-(thiophen-2-yl)-4a,5,7,7a-tetrahydrocyclopenta[*c*]pyran-6,6(1*H*)-dicarboxylate: yellow oil; [α]_D²³ (c 1.95, CHCl₃) = -21.7; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, *J*₁ = 8.0 Hz, *J*₂ = 2.4 Hz, 2 H); 7.34–7.39 (m, 3 H); 7.20 (dd, *J*₁ = 4.8 Hz, *J*₂ = 0.8 Hz, 1 H); 7.03 (d, *J* = 3.6 Hz, 1 H); 6.94 (dd, *J*₁ = 5.2 Hz, *J*₂ = 3.6 Hz, 1 H); 5.54 (d, *J* = 3.6 Hz, 1 H); 4.86 (d, *J* = 8.8 Hz, 1 H); 3.73 (s, 3 H); 3.56–3.59 (m, 2 H); 3.33 (s, 3 H); 3.10–3.15 (m, 1 H); 2.30 (dd, *J*₁ = 14.0 Hz, *J*₂ = 3.2 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 170.1, 167.8, 149.0, 139.6, 132.0, 129.3, 128.6, 126.8, 126.6, 125.1, 124.8, 102.2, 64.8, 53.1, 52.7, 49.3, 48.8, 40.8, 36.1 ppm. IR (film): ν_{max} 2952, 1762, 1730, 1558, 1517, 1434, 1024, 929 cm⁻¹. HRMS (ESI): C₂₂H₂₁O₆S [M+H]⁺ calcd: 413.1059, found: 413.1059; 95:5 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), *t*_r (major) = 15.2 min, *t*_r (minor) = 19.2 min.



(4a*S*,7*S*,7a*R*)-dimethyl

1-oxo-3-phenyl-7-styryl-4a,5,7,7a-

tetrahydrocyclopenta[*c*]pyran-6,6(1*H*)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.06, CHCl₃) = -38.7; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 2 H); 7.20–7.40 (m, 8 H); 6.64 (d, J = 15.6 Hz, 1 H); 6.09 (dd, J_1 = 16.0 Hz, J_2 = 8.8 Hz, 1 H); 5.50 (d, J = 2.8 Hz, 1 H); 3.97 (t, J = 9.2 Hz, 1 H); 3.71 (s, 3 H); 3.65 (s, 3 H); 3.42–3.47 (m, 1 H); 3.24 (t, J = 9.2 Hz, 1 H); 2.97 (dd, J_1 = 14.0 Hz, J_2 = 8.0 Hz, 1 H); 2.37 (dd, J_1 = 10.0 Hz, J_2 = 4.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.3, 170.5, 168.1, 148.6, 136.6, 134.4, 132.2, 129.2, 128.6, 128.5, 127.7, 126.6, 125.2, 124.8, 102.4, 63.5, 53.0, 52.8, 52.4, 47.6, 41.0, 36.0 ppm. IR (film): $\nu_{\max}$ 2954, 2321, 1734, 1558, 1517, 1424, 928 cm⁻¹. HRMS (ESI): C₂₆H₂₄O₆Na [M+Na]⁺ calcd: 455.1471, found: 455.1475; 94:6 *er* as determined by HPLC (Chiralcel IA, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 17.3 min, t_r (minor) = 13.6 min.

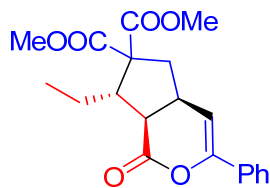


(4a*S*,7*S*,7a*R*)-7-ethyl

6,6-dimethyl

1-oxo-3-phenyl-4a,5,7,7a-

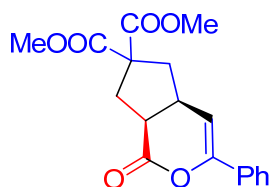
tetrahydrocyclopenta[*c*]pyran-6,6,7(1*H*)-tricarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.25, CHCl₃) = +10.2; ¹H NMR (400 MHz, CDCl₃): δ = 7.59 (dd, J_1 = 8.0 Hz, J_2 = 2.4 Hz, 2 H); 7.34–7.40 (m, 3 H); 5.62 (d, J = 4.4 Hz, 1 H); 4.16–4.25 (m, 3 H); 3.73–3.76 (m, 3 H); 3.67–3.72 (m, 3 H); 3.31 – 3.39 (m, 1 H); 2.84 (dd, J_1 = 13.2 Hz, J_2 = 7.2 Hz, 1 H); 2.18 (dd, J_1 = 13.2 Hz, J_2 = 8.4 Hz, 1 H); 1.28 (t, J = 7.2 Hz, 3 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 170.4, 169.8, 168.3, 149.1, 132.0, 129.3, 128.5, 124.7, 100.6, 62.4, 61.7, 54.3, 53.3, 53.0, 43.8, 42.2, 35.8, 14.0 ppm. IR (film): $\nu_{\max}$ 2952, 2321, 1731, 1518, 1437, 1340, 1112, 928 cm⁻¹. HRMS (ESI): C₂₁H₂₂O₈Na [M+Na]⁺ calcd: 425.1212, found: 425.1211; 94:6 *er* as determined by HPLC (Chiralcel IA, 95:5 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 37.6 min, t_r (minor) = 22.5 min.



(4aS,7S,7aR)-dimethyl

7-ethyl-1-oxo-3-phenyl-4a,5,7,7a-

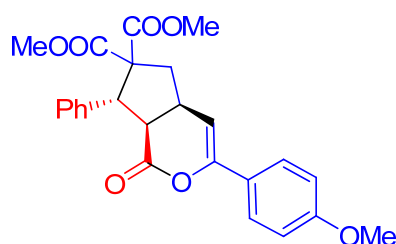
tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.06, CHCl_3) = +17.5; ^1H NMR (400 MHz, CDCl_3): δ = 7.58 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 2 H); 7.34–7.39 (m, 3 H); 5.48 (d, J = 3.2 Hz, 1 H); 3.74 (s, 3 H); 3.66 (s, 3 H); 3.34–3.39 (m, 1 H); 3.13–3.19 (m, 1 H); 2.92 (t, J = 8.4 Hz, 1 H); 2.81 (dd, J_1 = 13.6 Hz, J_2 = 7.6 Hz, 1 H); 2.23 (dd, J_1 = 10.0 Hz, J_2 = 5.2 Hz, 1 H), 1.52–1.62 (m, 2 H); 1.03 (t, J = 7.6 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.8, 171.0, 169.7, 148.6, 132.3, 129.1, 128.5, 124.7, 102.4, 62.6, 52.9, 52.6, 50.6, 47.1, 41.5, 35.7, 24.5, 12.4 ppm. IR (film): ν_{max} 2954, 1734, 1558, 1525, 1437, 1419, 1018, 928 cm^{-1} . HRMS (ESI): $\text{C}_{20}\text{H}_{23}\text{O}_6$ $[\text{M}+\text{H}]^+$ calcd: 359.1495, found: 359.1497; 75:25 *er* as determined by HPLC (Chiralcel IA, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 14.1 min, t_r (minor) = 10.2 min.



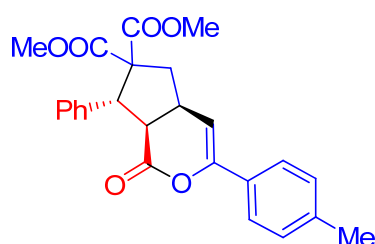
(4aS,7aS)-dimethyl

1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-

6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_D^{23}$ (c 1.34, CHCl_3) = -1.1; ^1H NMR (400 MHz, CDCl_3): δ = 7.59 (dd, J_1 = 8.0 Hz, J_2 = 4.4 Hz, 2 H); 7.34–7.40 (m, 3 H); 5.63 (d, J = 4.4 Hz, 1 H); 3.77 (s, 3 H); 3.70 (s, 3 H); 3.14–3.18 (m, 2 H); 2.78–2.90 (m, 2 H); 2.62 (dd, J_1 = 13.6 Hz, J_2 = 7.2 Hz, 1 H); 2.33 (dd, J_1 = 13.6 Hz, J_2 = 8.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 172.0, 171.2, 169.4, 149.0, 132.2, 129.2, 128.5, 124.7, 101.5, 58.8, 53.1, 53.0, 41.5, 41.0, 36.8 ppm. IR (film): ν_{max} 2952, 1734, 1549, 1525, 1437, 1023, 928 cm^{-1} . HRMS (ESI): $\text{C}_{18}\text{H}_{19}\text{O}_6$ $[\text{M}+\text{H}]^+$ calcd: 331.1182, found: 331.1174; 53:47 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 15.0 min, t_r (minor) = 16.1 min.

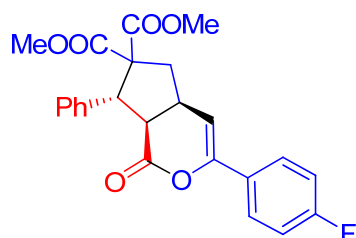


(4a*S*,7*R*,7a*R*)-dimethyl 3-(4-methoxyphenyl)-1-oxo-7-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1*H*)-dicarboxylate : yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 0.5, CHCl_3) = -80.3; ^1H NMR (400 MHz, CDCl_3): δ = 7.53 (dd, J_1 = 6.8 Hz, J_2 = 1.6 Hz, 2 H); 7.18–7.36 (m, 5 H); 6.89 (dd, 2 H, J = 6.8, 2.0 Hz, 2 H); 5.42 (d, J = 3.2 Hz, 1 H); 4.70 (d, J = 8.8 Hz, 1 H); 3.82 (s, 3 H); 3.71 (s, 3 H); 3.48–3.64 (m, 2 H); 3.13 (s, 3 H); 3.04–3.15 (m, 1 H); 2.26 (dd, J = 14.0, 4.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.2, 168.5, 160.4, 149.0, 137.4, 128.7, 128.2, 127.7, 126.2, 124.7, 113.9, 100.2, 65.1, 55.3, 53.6, 53.0, 52.2, 47.6, 41.3, 36.6 ppm. IR (film): ν_{max} 2954, 2400, 1759, 1728, 1609, 1513, 1435, 1248, 1177, 1030, 928 cm^{-1} . HRMS (ESI): $\text{C}_{25}\text{H}_{25}\text{O}_7$ $[\text{M}+\text{H}]^+$ calcd: 437.1600, found: 437.1602; 94:6 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_{r} (major) = 18.8 min, t_{r} (minor) = 21.2 min.

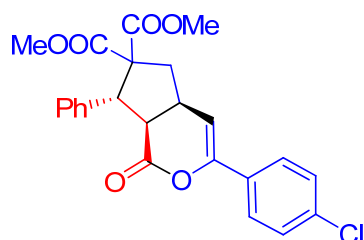


(4a*S*,7*R*,7a*R*)-dimethyl 1-oxo-7-phenyl-3-p-tolyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1*H*)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 0.5, CHCl_3) = -52.9; ^1H NMR (400 MHz, CDCl_3): δ = 7.48 (d, J = 8.0 Hz, 2 H); 7.20–7.35 (m, 5 H); 7.18 (d, J = 8.0 Hz, 2 H); 5.51 (d, J = 3.2 Hz, 1 H); 4.70 (d, J = 8.8 Hz, 1 H); 3.70 (s, 3 H); 3.49–3.64 (m, 2 H); 3.13 (s, 3 H); 3.02–3.13 (m, 3 H); 2.36 (s, 3 H); 2.26 (dd, J = 14.0, 4.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.2, 168.4, 149.2, 139.2, 137.4, 129.3, 129.2, 128.7, 128.2, 127.7, 124.7, 101.2, 65.0, 53.6, 53.0, 52.2, 47.6,

41.2, 36.6, 21.2 ppm. IR (film): ν_{max} 2952, 1730, 1570, 1533, 1272, 1126, 1042, 1017, 930 cm^{-1} . HRMS (ESI): $\text{C}_{25}\text{H}_{25}\text{O}_6$ $[\text{M}+\text{H}]^+$ calcd: 421.1651, found: 421.1652; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 13.9 min, t_r (minor) = 16.1 min.

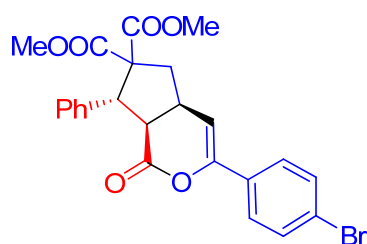


(4aS,7R,7aR)-dimethyl 3-(4-fluorophenyl)-1-oxo-7-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 1.00, CHCl_3) = -19.9; ^1H NMR (400 MHz, CDCl_3): δ = 7.54–7.62 (m, 2 H); 7.21–7.38 (m, 5 H); 7.03–7.10 (m, 2 H); 5.49 (d, J = 3.2 Hz, 1 H); 4.69 (d, J = 8.8 Hz, 1 H); 3.71 (s, 3 H); 3.52–3.65 (m, 2 H); 3.08–3.16 (m, 4 H); 2.26 (dd, J = 14.0, 4.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.1, 168.1, 163.3 (J = 248 Hz), 148.4, 137.2, 128.7, 128.39, 128.36, 128.2, 127.8, 126.8, 126.7, 115.7, 115.4, 101.9, 65.0, 53.6, 53.0, 52.3, 47.5, 41.2, 36.6 ppm. IR (film): ν_{max} 2952, 1767, 1730, 1558, 1510, 1272, 1159, 1024, 929 cm^{-1} . HRMS (ESI): $\text{C}_{24}\text{H}_{22}\text{O}_6\text{F}$ $[\text{M}+\text{H}]^+$ calcd: 425.1400, found: 425.1401; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 13.8 min, t_r (minor) = 15.7 min.

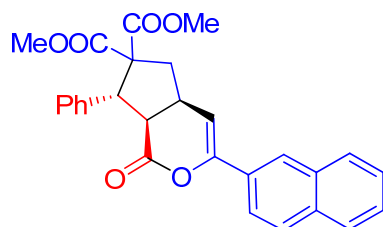


(4aS,7R,7aR)-dimethyl 3-(4-chlorophenyl)-1-oxo-7-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 0.5, CHCl_3) = -56.7; ^1H NMR (400 MHz, CDCl_3): δ = 7.53 (dd, J = 6.8, 1.6 Hz, 2 H); 7.20–7.40 (m, 7 H); 5.56 (d, J = 2.8 Hz, 1 H); 4.68 (d, J = 8.8 Hz, 1 H); 3.71 (s, 3 H); 3.52–3.68 (m,

2 H); 3.06–3.18 (m, 4 H); 2.25 (dd, $J_1 = 14.0$ Hz, $J_2 = 4.4$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.5, 170.1, 168.0, 148.2, 137.2, 135.1, 130.6, 128.7, 128.6, 128.2, 127.8, 126.0, 102.6, 65.0, 53.6, 53.0, 52.3, 47.5, 41.2, 36.6$ ppm. IR (film): ν_{max} 2954, 1728, 1523, 1435, 1012, 928 cm^{-1} . HRMS (ESI): $\text{C}_{24}\text{H}_{22}\text{O}_6\text{Cl}$ $[\text{M}+\text{H}]^+$ calcd: 441.1105, found: 441.1096; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 15.3 min, t_r (minor) = 16.9 min.

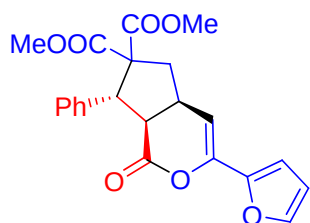


(4aS,7R,7aR)-dimethyl 3-(4-bromophenyl)-1-oxo-7-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate : yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 1.00, CHCl_3) = +29.2; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.48$ (dd, $J = 18.8, 8.8$ Hz, 4 H); 7.23–7.34 (m, 5 H); 5.57 (d, $J = 3.2$ Hz, 1 H); 4.68 (d, $J = 8.4$ Hz, 1 H); 3.71 (s, 3 H); 3.50–3.63 (m, 2 H); 3.13 (s, 3 H); 3.08–3.16 (m, 1 H); 2.25 (dd, $J = 13.6, 8.0$ Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 171.5, 170.1, 168.0, 148.3, 137.2, 131.7, 131.1, 128.7, 128.3, 127.8, 126.3, 123.4, 102.7, 65.0, 53.7, 53.0, 52.3, 47.5, 41.1, 36.7$ ppm. IR (film): ν_{max} 2954, 1762, 1729, 1515, 1437, 1275, 1215, 1016, 929 cm^{-1} . IR (film): ν_{max} 2952, 1728, 1523, 1425, 1008, 925 cm^{-1} . HRMS (ESI): $\text{C}_{24}\text{H}_{22}\text{O}_6\text{Br}$ $[\text{M}+\text{H}]^+$ calcd: 485.0600, found: 485.0602; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 20.7 min, t_r (minor) = 23.2 min.

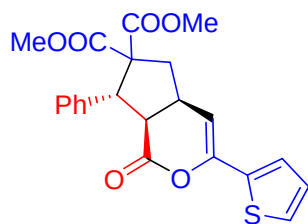


(4aS,7R,7aR)-dimethyl 3-(naphthalen-2-yl)-1-oxo-7-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 1.00, CHCl_3) = -

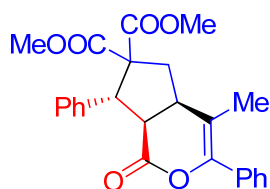
62.5; ^1H NMR (400 MHz, CDCl_3): δ = 8.14–8.20 (m, 1 H); 7.78–7.90 (m, 3 H); 7.63 (dd, J = 8.8, 2.0 Hz, 1 H); 7.50 (dd, J = 6.0, 3.2 Hz, 2 H); 7.20–7.38 (m, 5 H); 5.72 (d, J = 3.2 Hz, 1 H); 4.74 (d, J = 8.8 Hz, 1 H); 3.70 (s, 3 H); 3.56–3.68 (m, 2 H); 3.08–3.20 (m, 4 H); 2.32 (dd, J_1 = 13.6 Hz, J_2 = 4.4 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.0, 168.4, 149.1, 137.4, 133.5, 133.1, 129.1, 128.7, 128.6, 128.2, 127.7, 127.6, 126.7, 126.6, 124.3, 122.0, 102.6, 65.1, 53.7, 53.0, 52.2, 47.7, 41.3, 36.7 ppm. IR (film): ν_{max} 2952, 1756, 1729, 1515, 1436, 1192, 1130, 1045, 929 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{28}\text{H}_{25}\text{O}_6$ ($\text{M}+\text{H}$) $^+$: 457.1651, Found: 457.1649; 96:4 *er* as determined by HPLC (Chiralcel IC, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 26.8 min, t_r (minor) = 44.6 min.



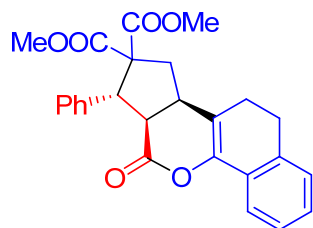
(4aS,7R,7aR)-dimethyl 3-(furan-2-yl)-1-oxo-7-phenyl-4a,5,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 0.5, CHCl_3) = -22.9; ^1H NMR (400 MHz, CDCl_3): δ = 7.38–7.44 (m, 1 H); 7.22 – 7.35 (m, 5 H); 6.59 (d, J = 3.6 Hz, 1 H); 6.44 (dd, J = 3.6, 2.0 Hz, 1 H); 5.54 (d, J = 3.2 Hz, 1 H); 4.66 (d, J = 8.8 Hz, 1 H); 3.71 (s, 3 H); 3.50–3.65 (m, 2 H); 3.05–3.18 (m, 4 H); 2.26 (dd, J = 13.6, 4.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.2, 167.6, 146.6, 143.2, 142.0, 137.1, 128.7, 128.2, 127.8, 111.5, 108.1, 100.3, 65.0, 53.7, 53.0, 52.3, 47.8, 41.1, 36.2 ppm. IR (film): ν_{max} 2954, 1728, 1524, 1425, 1012, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{O}_7$ ($\text{M}+\text{H}$) $^+$: 457.1651, Found: 457.1649; 96:4 *er* as determined by HPLC (Chiralcel IB, 97:3 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 21.0 min, t_r (minor) = 24.9 min.



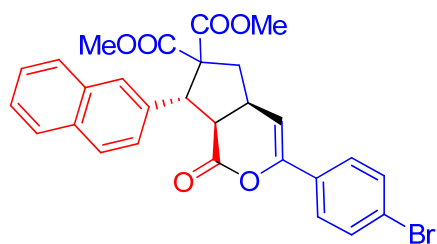
(4aS,7R,7aR)-dimethyl 1-oxo-7-phenyl-3-(thiophen-2-yl)-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 0.5, CHCl_3) = -111.5; ^1H NMR (400 MHz, CDCl_3): δ = 7.22–7.34 (m, 7 H); 7.02 (dd, J = 5.2, 4.0 Hz, 1 H); 5.44 (d, J = 3.2 Hz, 1 H); 4.69 (d, J = 8.8 Hz, 1 H); 3.73 (s, 3 H); 3.50–3.62 (m, 2 H); 3.13 (s, 3 H); 3.09 (dd, J_1 = 14.0 Hz, J_2 = 7.2 Hz, 1 H); 2.26 (dd, J = 13.6, 4.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.4, 170.1, 167.8, 145.0, 137.3, 135.6, 128.7, 128.2, 127.7, 127.6, 125.9, 124.9, 101.1, 65.0, 53.7, 53.0, 52.3, 47.7, 41.2, 36.6 ppm. IR (film): ν_{max} 2954, 1728, 1518, 1437, 1022, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{22}\text{H}_{21}\text{O}_6\text{S}$ ($\text{M}+\text{H}$) $^+$: 413.1059, Found: 413.1057; 95:5 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 14.4 min, t_r (minor) = 18.2 min.



(4aR,7R,7aR)-dimethyl 4-methyl-1-oxo-3,7-diphenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.00, CHCl_3) = +1.1; ^1H NMR (400 MHz, CDCl_3): δ = 7.34–7.45 (m, 5 H); 7.18–7.34 (m, 5 H); 4.84–4.93 (m, 1 H); 3.78 (s, 3 H); 3.42–3.55 (m, 4 H); 3.00–3.15 (m, 4 H); 2.24–2.33 (m, 1 H); 1.83 (s, 3 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.2, 168.7, 144.9, 138.2, 133.1, 128.8, 128.7, 128.6, 128.2, 128.1, 127.5, 109.8, 65.0, 53.5, 53.0, 52.1, 48.4, 42.7, 39.4, 16.6 ppm. IR (film): ν_{max} 2954, 1739, 1539, 1437, 1262, 1100, 1010, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{25}\text{H}_{25}\text{O}_6$ ($\text{M}+\text{H}$) $^+$: 421.1651, Found: 421.1641; 98:2 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 11.4 min, t_r (minor) = 12.7 min.

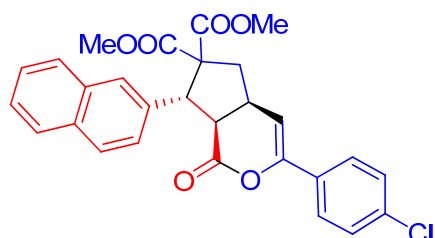


(6aR,7R,9aR)-dimethyl 6-oxo-7-phenyl-6a,7,9a,10,11-hexahydrobenzo[h]cyclopenta[c]chromene-8,8(6H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 0.5, CHCl₃) = -32.1; ¹H NMR (400 MHz, CDCl₃): δ = 7.50–7.56 (m, 1 H); 7.18–7.36 (m, 7 H); 7.08–7.18 (m, 1 H); 4.75 (d, J = 7.6 Hz, 1 H); 3.69 (s, 3 H); 3.53–3.61 (m, 2 H); 3.13 (s, 3 H); 2.98–3.12 (m, 1 H); 2.76–2.98 (m, 2 H); 2.33–2.46 (m, 2 H); 2.17–2.33 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.4, 170.2, 168.4, 142.6, 138.0, 135.3, 128.6, 128.23, 128.15, 127.6, 127.2, 126.6, 121.5, 110.7, 65.0, 54.1, 53.0, 52.2, 48.4, 40.6, 39.1, 27.5, 24.6 ppm. IR (film): $\nu_{\max}$ 2954, 1750, 1729, 1524, 1436, 1093, 1020, 928 cm⁻¹. HRMS(ESI) calcd for C₂₆H₂₅O₆ (M+H)⁺: 433.1651, Found: 433.1649; 97:3 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 21.7 min, t_r (minor) = 32.3 min.

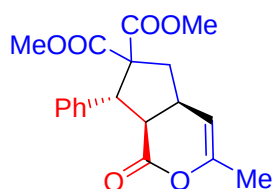


(4aS,7R,7aR)-dimethyl 3-(4-bromophenyl)-7-(naphthalen-2-yl)-1-oxo-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.00, CHCl₃) = -79.8; ¹H NMR (400 MHz, CDCl₃): δ = 7.74–7.84 (m, 4 H); 7.36–7.54 (m, 7 H); 5.60 (d, J = 2.4 Hz, 1 H); 4.84 (d, J = 8.4 Hz, 1 H); 3.72 (s, 3 H); 3.60–3.70 (m, 2 H); 3.18 (dd, J = 13.6, 7.2 Hz, 1 H); 2.29 (dd, J = 14.0, 4.0 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.5, 170.2, 168.0, 148.3, 134.6, 133.1, 132.8, 131.7, 131.1, 128.03, 127.98, 127.8, 127.5, 126.31, 126.26, 126.10, 126.06, 123.4, 102.7, 64.9, 53.9,

53.1, 52.3, 47.6, 41.3, 36.7 ppm. IR (film): $\nu_{\max}$ 2954, 1728, 1523, 1425, 1008, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{28}\text{H}_{24}\text{BrO}_6$ ($\text{M}+\text{H}$) $^{+}$: 535.0756, Found: 535.0749; 99:1 *er* as determined by HPLC (Chiralcel IC, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 18.9 min, t_r (minor) = 31.2 min.

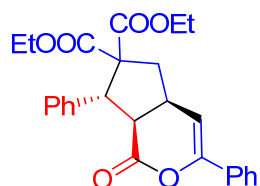


(4aS,7R,7aR)-dimethyl 3-(4-chlorophenyl)-7-(naphthalen-2-yl)-1-oxo-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.67, CHCl_3) = -64.9; ^1H NMR (400 MHz, CDCl_3): δ = 7.79–7.82 (m, 4 H); 7.53–7.77 (m, 2H); 7.34–7.47 (m, 5H); 5.58–5.59 (m, 1H); 4.84 (d, J = 8.4 Hz, 1 H); 3.72 (s, 3 H); 3.66–3.70 (m, 1 H); 3.16–3.21 (m, 1H); 3.02 (s, 3H); 2.29 (dd, J = 13.6, 4.0 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.5, 170.2, 168.0, 148.3, 135.2, 134.6, 133.2, 132.9, 130.7, 128.8, 128.1, 128.0, 127.9, 127.5, 126.3, 126.1, 126.1, 102.6, 65.0, 53.9, 53.1, 52.3, 47.7, 41.4, 36.7. IR (film): $\nu_{\max}$ 2954, 1757, 1729, 1601, 1527, 1437, 1424, 1017, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{28}\text{H}_{24}\text{ClO}_6$ ($\text{M}+\text{H}$) $^{+}$: 491.1261, Found: 491.1263; 95:5 *er* as determined by HPLC (Chiralcel IA, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 47.5 min, t_r (minor) = 24.3 min.



(4aS,7R,7aR)-dimethyl 3-methyl-1-oxo-7-phenyl-4a,5,7,7a-tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: colorless oil; $[\alpha]_D^{23}$ (c 1.61, CHCl_3) = -46.1; ^1H NMR (500 MHz, CDCl_3): δ = 7.20–7.38 (m, 5 H), 4.77 (d, J = 1.0 Hz, 1 H), 4.62 (d, J = 9.5 Hz, 1 H), 3.75 (s, 3 H), 3.34–3.52 (m, 2 H), 3.12 (s, 3 H), 3.01 (dd, J = 14.0 Hz, 7.5 Hz, 1 H), 2.13 (dd, J = 14 Hz, 4.5 Hz, 1 H), 1.88 (s, 3 H).

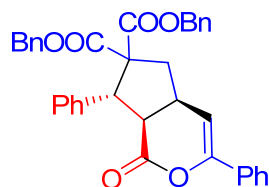
^{13}C NMR (125 MHz, CDCl_3): δ = 171.7, 170.2, 168.8, 148.5, 137.3, 128.7, 128.2, 127.6, 102.2, 65.0, 53.5, 52.9, 52.2, 47.4, 41.1, 36.1, 18.7 ppm. IR (film): ν_{max} 2986, 1723, 1422, 1264, 1112, 896 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_6$ ($\text{M}+\text{H}$) $^{+}$: 345.1338, Found: 345.1338; 95:5 *er* as determined by HPLC (Chiralcel ID, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 23.5 min, t_r (minor) = 26.9 min.



(4aS,7R,7aR)-diethyl

1-oxo-3,7-diphenyl-4a,5,7,7a-

tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 2.01, CHCl_3) = -10.0; ^1H NMR (400 MHz, CDCl_3): δ = 7.58–7.61 (m, 2H); 7.23–7.39 (m, 8H); 5.56 (d, J = 3.2 Hz, 1H); 4.70 (d, J = 4.8 Hz, 1H); 4.18 (q, J = 6.8 Hz, 2H); 3.74 (dd, J = 14.0, 7.2 Hz, 1H); 2.29 (dd, J = 14.0, 4.0 Hz, 1H); 1.20 (t, J = 7.2 Hz, 3H); 0.75 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.1, 169.9, 168.5, 149.2, 137.5, 132.2, 129.2, 128.9, 128.5, 128.2, 127.7, 124.8, 102.3, 65.0, 61.9, 61.5, 53.5, 47.9, 41.3, 36.7, 13.9, 13.3. IR (film): ν_{max} 2954, 1766, 1722, 1520, 1423, 1075, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{26}\text{H}_{27}\text{O}_6$ ($\text{M}+\text{H}$) $^{+}$: 435.1808, Found: 435.1805; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 10.0 min, t_r (minor) = 11.9 min.

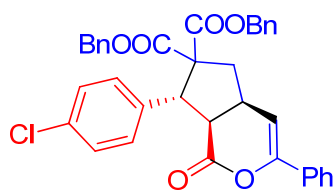


(4aS,7R,7aR)-dibenzyl

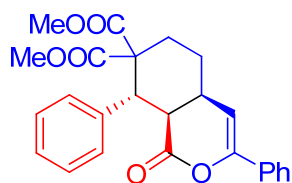
1-oxo-3,7-diphenyl-4a,5,7,7a-

tetrahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_{\text{D}}^{23}$ (c 1.39, CHCl_3) = +26.2; ^1H NMR (400 MHz, CDCl_3): δ = 7.51–7.54 (m, 2H); 7.11–7.38 (m, 16H); 6.84–6.86 (m, 2H); 5.45–5.46 (m, 1H); 5.12 (d, J = 12.4 Hz, 1H); 4.96 (d, J = 12.0 Hz, 1H); 4.71–4.75 (m, 2H); 4.18 (d, J = 12.4 Hz, 1H); 3.55–3.58 (m, 2H); 3.15

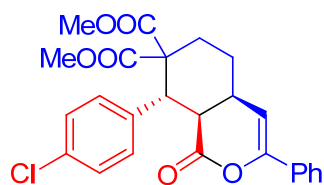
(dd, $J = 13.6, 7.2$ Hz, 1H); 2.32 (dd, $J = 13.6, 7.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.8, 169.7, 168.3, 149.3, 137.1, 135.1, 134.6, 132.2, 129.2, 128.9, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 124.9, 102.2, 67.8, 67.4, 65.2, 53.7, 47.9, 41.3, 36.7$. IR (film): ν_{max} 2954, 1767, 1721, 1419, 1025, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{36}\text{H}_{31}\text{O}_6$ ($\text{M}+\text{H}$) $^+$: 559.2121, Found: 559.2118; 96:4 *er* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 14.4 min, t_r (minor) = 16.5 min.



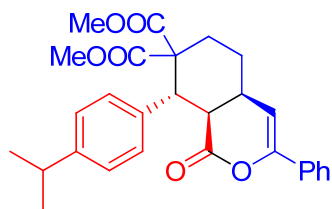
(4a*S*,7*R*,7a*R*)-dibenzyl 7-(4-chlorophenyl)-1-oxo-3-phenyl-4a,5,7,7a-tetrahydrocyclopenta[*c*]pyran-6,6(1*H*)-dicarboxylate: white solid; $[\alpha]_{\text{D}}^{23}$ (*c* 1.55, CHCl_3) = +4.7; ^1H NMR (400 MHz, CDCl_3): $\delta = 7.50\text{--}7.53$ (m, 2H); 7.34–7.37 (m, 3H); 7.22–7.32 (m, 8H); 7.15 (d, $J = 8.4$ Hz, 4H); 6.86 (d, $J = 6.8$ Hz, 2H); 5.45 (d, $J = 3.2$ Hz, 1H); 5.13 (d, $J = 12.0$ Hz, 1H); 5.01 (d, $J = 12.0$ Hz, 1H); 4.62 (d, $J = 10.0$ Hz, 1H); 4.37 (d, $J = 12.0$ Hz, 1H); 3.48–3.58 (m, 2H); 3.13 (dd, $J = 14.0, 7.6$ Hz, 1H); 2.32 (dd, $J = 14.0, 4.4$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): $\delta = 170.7, 169.6, 168.0, 149.2, 135.3, 135.0, 134.3, 133.8, 132.0, 130.3, 129.3, 128.6, 128.5, 128.5, 128.4, 128.3, 128.1, 124.8, 102.2, 67.9, 67.6, 64.9, 52.9, 47.6, 41.3, 36.5, 29.7$. IR (film): ν_{max} 2954, 1762, 1729, 1515, 1437, 1275, 1215, 1016, 929 cm^{-1} . IR (film): ν_{max} 2954, 1724, 1525, 1424, 1015, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{36}\text{H}_{30}\text{ClO}_6$ ($\text{M}+\text{H}$) $^+$: 597.1731, Found: 597.1730; 97:3 *er* as determined by HPLC (Chiralcel IA, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 16.7 min, t_r (minor) = 22.7 min.



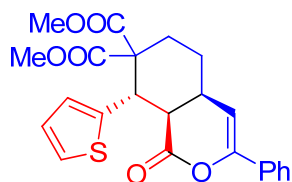
(4aS,8R,8aR)-dimethyl 1-oxo-3,8-diphenyl-5,6,8,8a-tetrahydro-1H-isochromene-7,7(4aH)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 2.10, CHCl₃) = +15.6; ¹H NMR (400 MHz, CDCl₃): δ = 7.57–7.60 (m, 2H); 7.32–7.41 (m, 4H); 7.21–7.27 (m, 4H); 5.57 (dd, J = 2.0, 1.6 Hz, 1H); 4.03 (dd, J = 12.0, 4.8 Hz, 1H); 3.70 (s, 3H); 3.45 (d, J = 12.0 Hz, 1H); 3.33 (s, 3H); 3.27 (d, J = 2.4 Hz, 1H); 2.26–2.35 (m, 1H); 1.93–1.97 (m, 1H); 1.24–1.87 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 171.0, 170.2, 168.0, 150.7, 136.5, 132.0, 130.3, 129.1, 128.6, 127.9, 127.7, 124.6, 103.2, 59.5, 52.2, 45.9, 41.7, 31.6, 30.0, 25.3. IR (film): $\nu_{\max}$ 2954, 1773, 1731, 1543, 1420, 928 cm⁻¹. HRMS(ESI) calcd for C₂₅H₂₄O₆Na (M+ Na)⁺: 443.1471, Found: 443.1471; 96:4 *er* as determined by HPLC (Chiralcel IB, 95:5 hexanes/*i*-PrOH, 0.7 mL/min), t_{r1} (major) = 21.9 min, t_{r1} (minor) = 23.7 min t_{r2} (major) = 25.4 min, t_{r2} (minor) = 33.5 min.



(4aS,8R,8aR)-dimethyl 8-(4-chlorophenyl)-1-oxo-3-phenyl-5,6,8,8a-tetrahydro-1H-isochromene-7,7(4aH)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 0.5, CHCl₃) = -24.1; ¹H NMR (400 MHz, CDCl₃): δ = 7.57–7.60 (m, 2H); 7.38–7.39 (m, 5H); 7.22 (d, J = 8.8 Hz, 2H); 5.57 (dd, J = 2.0, 1.5 Hz, 1H); 3.96–4.01 (m, 1H); 3.72 (s, 3H); 3.39 (d, J = 8.4 Hz, 1H); 3.37 (s, 3H); 3.29 (d, J = 2.8 Hz, 1H); 2.27–2.33 (m, 2H); 1.93–1.98 (m, 1H); 1.80–1.86 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 170.8, 170.0, 167.7, 150.7, 134.8, 133.8, 131.8, 131.7, 129.2, 128.6, 127.9, 124.5, 103.0, 59.5, 52.3, 45.3, 41.6, 31.6, 29.9, 25.2. IR (film): $\nu_{\max}$ 2954, 1767, 1730, 1517, 1424, 1016, 928 cm⁻¹. HRMS(ESI) calcd for C₂₅H₂₄ClO₆ (M+H)⁺: 455.1261, Found: 455.1242; 95:5 *er* as determined by HPLC (Chiralcel ID, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 18.4 min, t_r (minor) = 21.7 min.

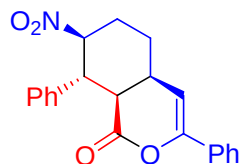


(4aS,8R,8aR)-dimethyl 8-(4-isopropylphenyl)-1-oxo-3-phenyl-5,6,8,8a-tetrahydro-1H-isochromene-7,7(4aH)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.00, CHCl_3) = -65.8; ^1H NMR (400 MHz, CDCl_3): δ = 7.58–7.60 (m, 2H); 7.33–7.41 (m, 3H); 7.28 (s, 2H); 7.09 (d, J = 4.4 Hz, 2H); 5.56 (d, J = 0.8 Hz, 1H); 4.02 (dd, J = 12.0, 4.8 Hz, 1H); 3.70 (s, 3H); 3.43 (d, J = 12.0 Hz, 1H); 3.37 (s, 3H); 2.80–2.87 (m, 1H); 2.25–2.35 (m, 2H); 1.81–1.96 (m, 2H); 1.21 (s, 3H); 1.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.0, 170.2, 168.0, 150.6, 148.2, 133.7, 132.1, 130.1, 129.1, 128.5, 125.7, 124.6, 103.2, 59.6, 52.1, 52.0, 45.6, 41.7, 33.6, 31.7, 30.0, 25.4, 23.9, 23.8. IR (film): ν_{max} 2954, 2928 1514, 1435, 1021, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{28}\text{H}_{31}\text{O}_6$ ($\text{M}+\text{H}$) $^+$: 463.2121, Found: 463.2121; 94:6 *er* as determined by HPLC (Chiralcel ODH, 98:2 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 28.9 min, t_r (minor) = 41.2 min.

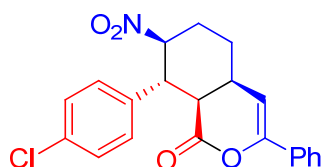


(4aS,8S,8aR)-dimethyl 1-oxo-3-phenyl-8-(thiophen-2-yl)-5,6,8,8a-tetrahydro-1H-isochromene-7,7(4aH)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.00, CHCl_3) = +231.1; ^1H NMR (400 MHz, CDCl_3): δ = 7.55–7.57 (m, 2H); 7.31–7.37 (m, 3H); 7.19 (d, J = 4.8 Hz, 1H); 7.09–7.10 (m, 1H); 6.95 (d, J = 5.2, 3.6 Hz, 1H); 5.64 (s, 1H); 4.84 (d, J = 1.6 Hz, 1H); 3.78 (s, 3H); 3.49 (s, 3H); 3.19–3.21 (m, 2H); 2.50–2.58 (m, 1H); 2.38–2.42 (m, 1H); 2.17–2.22 (m, 1H); 1.23–1.33 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 170.9, 169.2, 167.4, 149.4, 137.8, 132.1, 129.9, 129.0, 128.4, 126.1, 125.0, 124.5, 105.2, 59.4, 53.1, 52.5, 44.1, 40.0, 30.3, 28.4, 26.3. IR (film): ν_{max} 2954, 1731, 1525, 1427, 1219, 1159, 1019, 928 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{O}_6\text{S}$

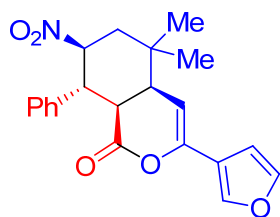
(M+H)⁺: 427.1215, Found: 427.1206; 95:5 *er* as determined by HPLC (Chiralcel ODH, 92:8 hexanes/*i*-PrOH, 0.7 mL/min), *t_r* (major) = 23.1 min, *t_r* (minor) = 27.6 min.



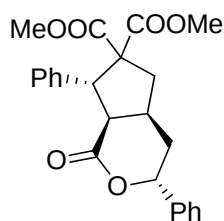
(4aS,7S,8R,8aR)-7-nitro-3,8-diphenyl-4a,5,6,7,8,8a-hexahydro-1H-isochromen-1-one: white solid; $[\alpha]_D^{23}$ (c 1.20, CHCl₃) = -43.0; ¹H NMR (400 MHz, CDCl₃): δ = 7.68 (dd, *J* = 7.2, 1.6 Hz, 2H); 7.43–7.47 (m, 3H); 7.28–7.34 (m, 3H); 7.18 (d, *J* = 7.2 Hz, 2H); 5.63 (s, 1H); 4.77–4.84 (m, 1H); 3.54 (t, *J* = 9.0 Hz, 1H); 3.28 (s, 1H); 3.01 (dd, *J* = 9.0, 0.9 Hz, 1H); 2.19–2.39 (m, 3H); 1.92–2.01 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.5, 151.2, 135.4, 131.7, 129.6, 129.1, 128.7, 128.6, 127.8, 124.7, 102.3, 88.7, 46.5, 43.8, 31.3, 27.7, 27.1. IR (film): $\nu_{\max}$ 2954, 1772, 1558, 1215, 1047, 1014, 928 cm⁻¹. HRMS(ESI) calcd for C₂₁H₂₀NO₄ (M+H)⁺: 350.1392, Found: 350.1391; 87:13 *er* as determined by HPLC (Chiralcel IA, *t_r* (major) = 37.6 min, *t_r* (minor) = 22.5 min hexanes/*i*-PrOH, 0.7 mL/min), *t_r* (major) = 19.3 min, *t_r* (minor) = 21.2 min.



(4aS,7S,8R,8aR)-8-(4-chlorophenyl)-7-nitro-3-phenyl-4a,5,6,7,8,8a-hexahydro-1H-isochromen-1-one: yellow solid; $[\alpha]_D^{23}$ (c 1.75, CHCl₃) = +0.8; ¹H NMR (400 MHz, CDCl₃): δ = 7.65 – 7.68 (m, 2 H); 7.42 – 7.47 (m, 3 H); 7.29 (d, *J* = 8.4 Hz, 2 H); 5.62 (t, *J* = 0.4 Hz, 1 H); 4.70 – 4.77 (m, 1 H); 3.82 (s, 3 H); 3.71 (s, 3 H); 3.48 – 3.64 (m, 2 H); 3.13 (s, 3 H); 3.04 – 3.15 (m, 1 H); 2.26 (dd, *J*₁ = 14.0 Hz, *J*₂ = 4.4 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 166.3, 151.2, 134.6, 134.0, 131.5, 129.7, 129.4, 129.2, 128.8, 124.6, 102.1, 88.6, 46.3, 43.2, 31.2, 27.6, 26.9 ppm. IR (film): $\nu_{\max}$ 2954, 2927, 2854, 1762, 1558, 1525, 1465, 1419, 928 cm⁻¹. HRMS(ESI) calcd for C₂₁H₁₉O₄NCl (M+ H)⁺: 384.1003, Found: 384.1004.

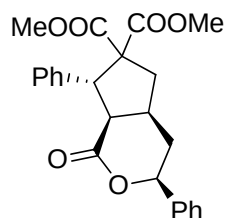


(4aS,7S,8R,8aR)-3-(furan-3-yl)-5,5-dimethyl-7-nitro-8-phenyl-4a,5,6,7,8,8a-hexahydro-1H-isochromen-1-one: yellow oil; $[\alpha]_D^{23}$ (c 1.73, CHCl_3) = +3.6; ^1H NMR (400 MHz, CDCl_3): δ = 7.71 (s, 1H); 7.47 (s, 1H); 7.31–7.35 (m, 3H); 7.26–7.30 (m, 2H); 6.59 (d, J = 1.2 Hz, 1H); 5.50 (s, 1H); 4.97–5.04 (m, 1H); 3.53 (t, J = 12.0 Hz, 1H); 3.22–3.26 (m, 1H); 2.76 (d, J = 2.0 Hz, 1H); 2.14 (t, J = 4.4 Hz, 1H); 2.04 (dd, J = 12.0, 4.0 Hz, 1H); 1.22 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ = 166.7, 145.8, 144.1, 140.4, 135.4, 129.1, 128.7, 128.6, 127.8, 119.5, 107.0, 98.0, 86.8, 44.4, 43.6, 41.4, 39.9, 33.5, 29.7, 28.2, 26.1. IR (film): ν_{max} 2927, 1768, 1558, 1517, 1419, 1018, 929 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_5$ ($\text{M}+\text{H}$) $^+$: 368.1498, Found: 368.14987; 89:11 *er* as determined by HPLC (Chiralcel IA, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 32.3 min, t_r (minor) = 19.8 min.

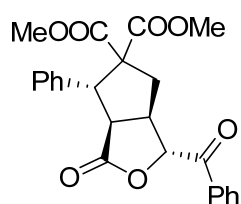


(3R,4aS,7R,7aR)-dimethyl 1-oxo-3,7-diphenylhexahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.00, CHCl_3) = -10.3; ^1H NMR (400 MHz, CDCl_3): δ = 7.29–7.41 (m, 5H); 7.22–7.28 (m, 5H); 5.59 (dd, J = 7.6, 2.8 Hz, 1H); 4.34 (d, J = 10.4 Hz, 1H); 3.74 (s, 3H); 3.47 (t, J = 10.4 Hz, 1H); 3.33 (s, 3H); 3.19 (dd, J = 8.4, 2.0 Hz, 1H); 2.89 (dd, J = 14.0, 8.4 Hz, 1H); 2.31–2.38 (m, 1H); 1.91–1.99 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ = 171.8, 171.3, 170.5, 138.9, 137.3, 128.8, 128.6, 128.2, 128.1, 127.7, 125.5, 65.2, 54.8, 52.8, 52.1, 47.8, 41.6, 35.5, 32.6. IR (film): ν_{max} 2952, 1730, 1520, 1436, 1271, 1050, 928 cm^{-1} . HRMS(ESI) calcd

for $C_{24}H_{23}O_7$ ($M+H$)⁺: 423.1444, Found: 423.1440; 96:4 *er* as determined by HPLC (Chiralcel IA, 90:10 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 32.2 min, t_r (minor) = 44.6 min.

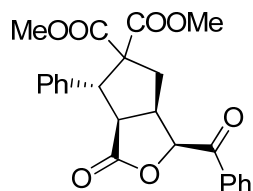


(3S,4aS,7R,7aR)-dimethyl 1-oxo-3,7-diphenylhexahydrocyclopenta[c]pyran-6,6(1H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 1.1, $CHCl_3$) = -11.0; 1H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.39 (m, 10H); 5.29 (dd, J = 11.2, 1.6 Hz, 1H); 4.73 (d, J = 7.2 Hz, 1H); 3.74 (s, 3H); 3.48–3.54 (m, 2H); 3.25 (s, 3H); 2.89 (dd, J = 13.6, 2.8 Hz, 1H); 2.37–2.41 (m, 1H); 1.77 (dd, J = 16.8, 8.8 Hz, 1H); 1.59–1.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.9, 171.3, 170.8, 139.3, 138.9, 128.7, 128.5, 128.2, 127.3, 126.0, 80.3, 65.5, 52.8, 52.6, 52.1, 48.8, 42.3, 38.1, 36.3. IR (film): ν_{max} 2952, 1730, 1520, 1436, 1271, 1050, 928 cm^{-1} . HRMS(ESI) calcd for $C_{24}H_{23}O_7$ ($M+H$)⁺: 423.1444, Found: 423.1440; 96:4 *er* as determined by HPLC (Chiralcel IA, 80:20 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 45.3 min, t_r (minor) = 25.2 min.

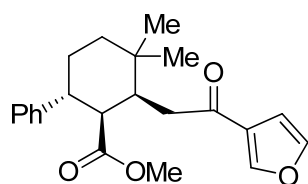


(1R,3aS,4R,6aR)-dimethyl 1-benzoyl-3-oxo-4-phenyltetrahydro-1H-cyclopenta[c]furan-5,5(3H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 0.5, $CHCl_3$) = -43.3; 1H NMR (400 MHz, $CDCl_3$): δ = 7.98–8.00 (m, 2H); 7.67 (d, J = 7.6 Hz, 1H); 7.54–7.57 (m, 2H); 7.18–7.30 (m, 5H); 5.52 (d, J = 2.4 Hz, 1H); 4.53 (d, J = 4.0 Hz, 1H); 3.76–3.80 (m, 4H); 3.43 (dd, J = 9.2, 4.0 Hz, 1H); 3.22 (s, 3H); 3.10–3.15 (m, 1H); 2.29–2.33 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.9, 177.4, 170.8, 169.4, 138.8, 134.5, 133.5, 129.2, 128.8, 128.5, 128.2, 127.7, 81.7, 67.3, 54.1, 53.2, 52.3,

50.2, 42.9, 39.9, 29.7. IR (film): $\nu_{\max}$ 2954, 1786, 1730, 1599, 1433, 1216, 1022 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{O}_7$ ($\text{M}+\text{H}$) $^{+}$: 423.1444, Found: 423.1440; 96:4 *er* as determined by HPLC (Chiralcel OJH, 70:30 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 11.3 min, t_r (minor) = 15.6 min.

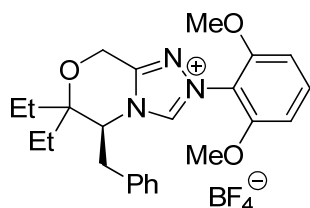


(1S,3aS,4R,6aR)-dimethyl 1-benzoyl-3-oxo-4-phenyltetrahydro-1H-cyclopenta[c]furan-5,5(3H)-dicarboxylate: yellow oil; $[\alpha]_D^{23}$ (c 0.5, CHCl_3) = -49.2; ^1H NMR (400 MHz, CDCl_3): δ = 8.02 (d, J = 7.6 Hz, 2H); 7.69 (d, J = 7.6 Hz, 1H); 7.54–7.66 (m, 2H); 7.22–7.32 (m, 5H); 5.94 (d, J = 6.8 Hz, 1H); 4.55 (d, J = 4.8 Hz, 1H); 4.23 (t, J = 11.2 Hz, 1H); 3.69 (s, 3H); 3.56 (dd, J = 8.8, 4.4 Hz, 1H); 3.11 (s, 3H); 2.41 (dd, J = 14.4, 4.0 Hz, 1H); 1.84 (dd, J = 14.4, 6.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ = 192.3, 176.6, 170.1, 170.0, 138.9, 134.5, 134.2, 129.9, 128.4, 128.2, 128.1, 127.6, 79.6, 67.7, 53.0, 52.9, 52.7, 52.1, 44.2, 35.9. IR (film): $\nu_{\max}$ 2954, 1786, 1730, 1599, 1433, 1216, 1022 cm^{-1} . HRMS(ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{O}_7$ ($\text{M}+\text{H}$) $^{+}$: 423.1444, Found: 423.1440; 96:4 *er* as determined by HPLC (Chiralcel OJH, 70:30 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 40.0 min, t_r (minor) = 62.3 min.



(1R,2S,6R)-methyl 2-(2-(furan-3-yl)-2-oxoethyl)-3,3-dimethyl-6-phenylcyclohexanecarboxylate: white solid; $[\alpha]_D^{23}$ (c 0.5, CHCl_3) = -78; ^1H NMR (400 MHz, CDCl_3): δ = 8.09 (dd, J = 1.2, 0.8 Hz, 1H); 7.43 (t, J = 1.6 Hz, 1H); 7.14–7.25 (m, 5H); 6.77 (q, J = 0.8 Hz, 1H); 3.33 (s, 3H); 3.28–3.21 (m, 1H); 3.11 (dd, J = 18.4, 4.4 Hz, 1H); 2.94 (dd, J = 18.4, 6.0 Hz, 1H); 2.80–2.84 (m, 2H); 1.52–1.72 (m, 3H); 1.31–1.35 (m, 1H); 1.25 (s, 3H); 0.88 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ =

193.4, 174.7, 146.7, 144.8, 144.0, 128.4, 127.6, 127.2, 126.3, 108.7, 51.4, 47.4, 40.9, 39.7, 36.9, 34.1, 33.2, 29.3, 26.4, 23.5. HRMS(ESI) calcd for $C_{22}H_{27}O_4NCl$ ($M+H$)⁺: 355.1904, Found: 355.1908. 90.5:9.5 *er* as determined by HPLC (Chiralcel ODH, 98:02 hexanes/*i*-PrOH, 0.7 mL/min), t_r (major) = 14.5 min, t_r (minor) = 11.9 min.



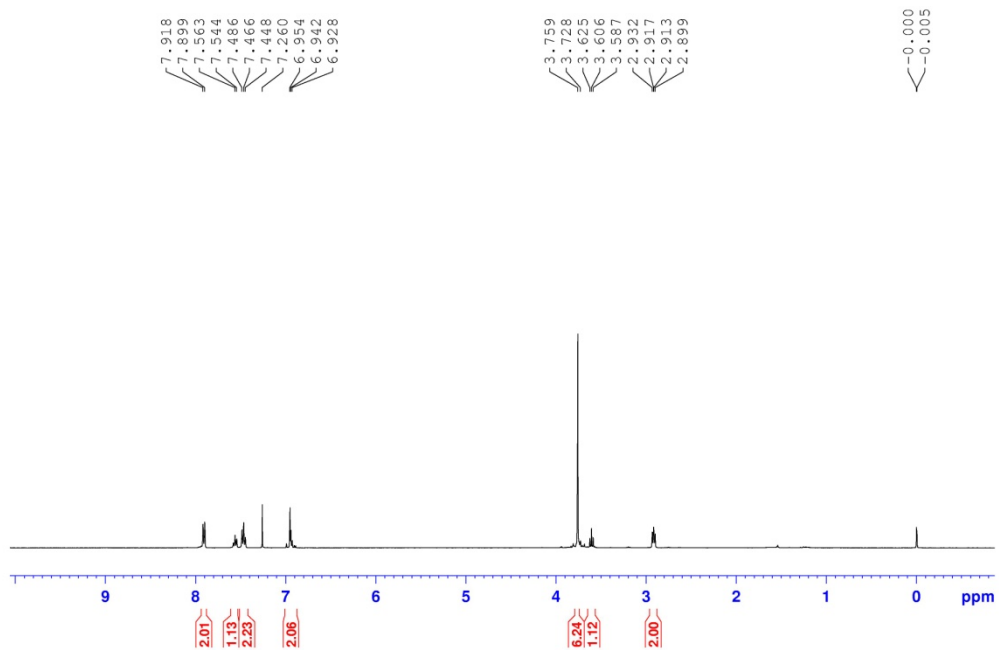
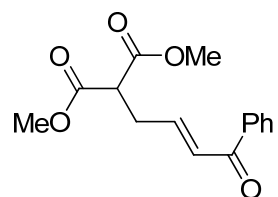
(S)-5-benzyl-2-(2,6-dimethoxyphenyl)-6,6-diethyl-6,8-dihydro-5H-

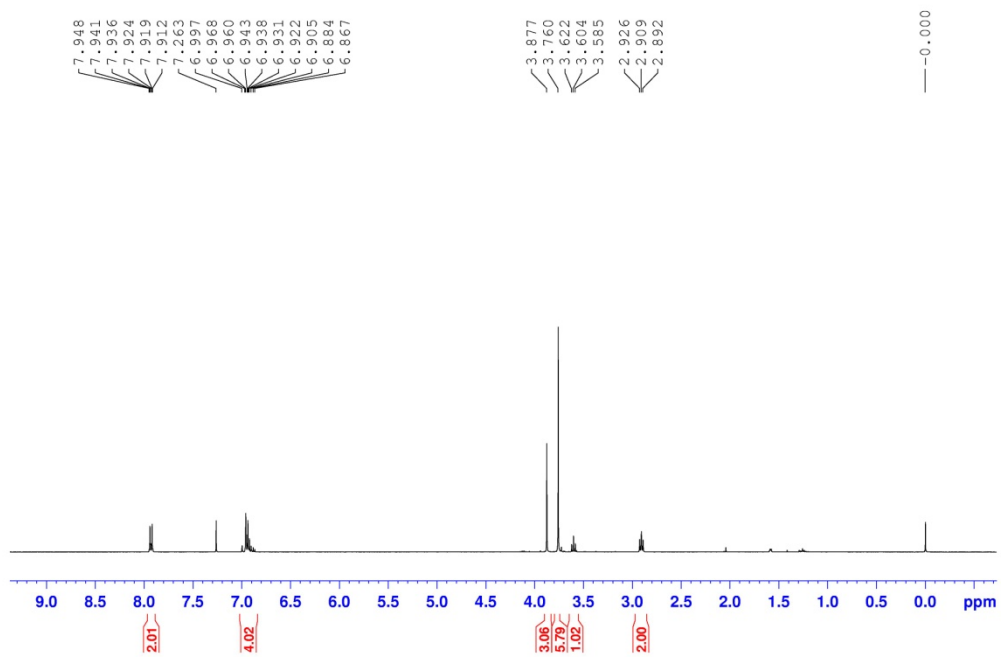
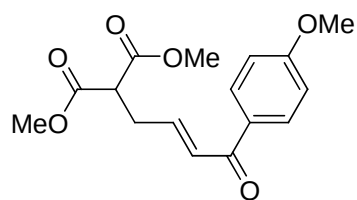
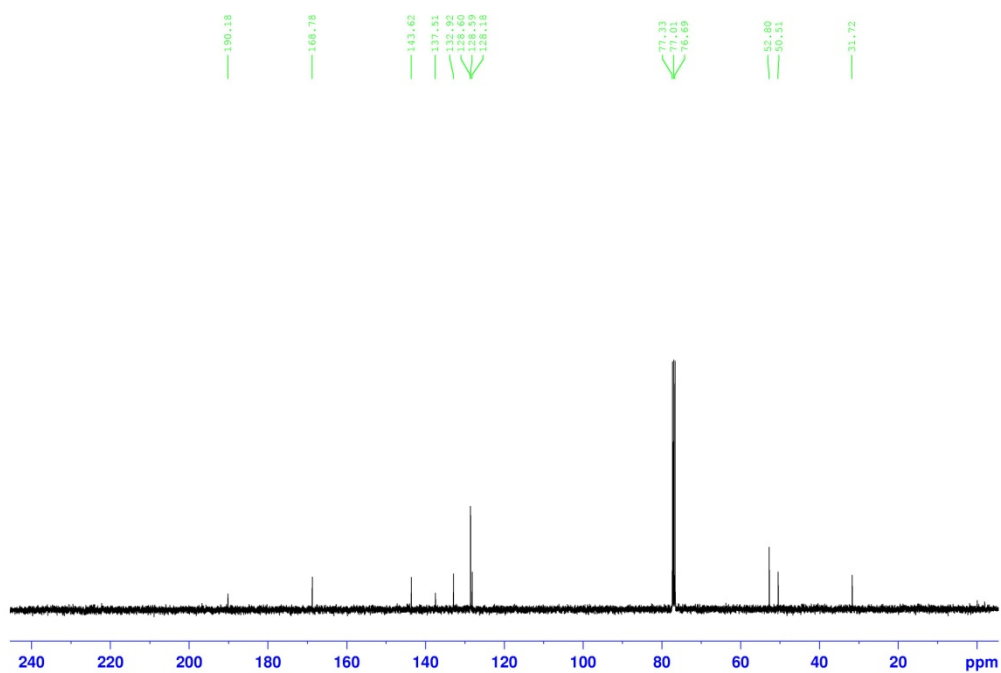
[1,2,4]triazolo[3,4-c][1,4]oxazin-2-ium tetrafluoroborate yellow solid; $[\alpha]_D^{23}$ (c 1.06, $CHCl_3$) = +3.7; 1H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1H); 7.43 (t, J = 8.8 Hz, 1H); 7.19–7.30 (m, 3H); 7.12 (d, J = 7.2 Hz, 2H); 6.62 (d, J = 8.8 Hz, 2H); 5.25 (dd, J = 10.8, 4.4 Hz, 1H); 5.11 (d, J = 17.2 Hz, 1H); 4.92 (d, J = 17.2 Hz, 1H); 3.80 (s, 6H); 3.43 (dd, J = 14.0, 4.4 Hz, 1H); 2.92 (dd, J = 14.0, 11.2 Hz, 1H); 1.78–2.04 (m, 3H); 1.58 (dd, J = 15.6, 7.2 Hz, 2H); 1.10 (t, J = 7.6 Hz, 3H); 1.00 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.4, 148.3, 144.9, 134.4, 133.5, 129.9, 129.2, 127.9, 112.0, 104.3, 78.9, 61.8, 56.5, 56.4, 36.8, 25.3, 21.9, 7.3, 6.9 ppm. IR (film): ν_{max} 1590, 1525, 1419, 1064, 1034, 928, 850 cm^{-1} . HRMS(ESI) calcd for $C_{24}H_{30}O_3N_3$ (M)⁺: 408.2287, Found: 408.2287.

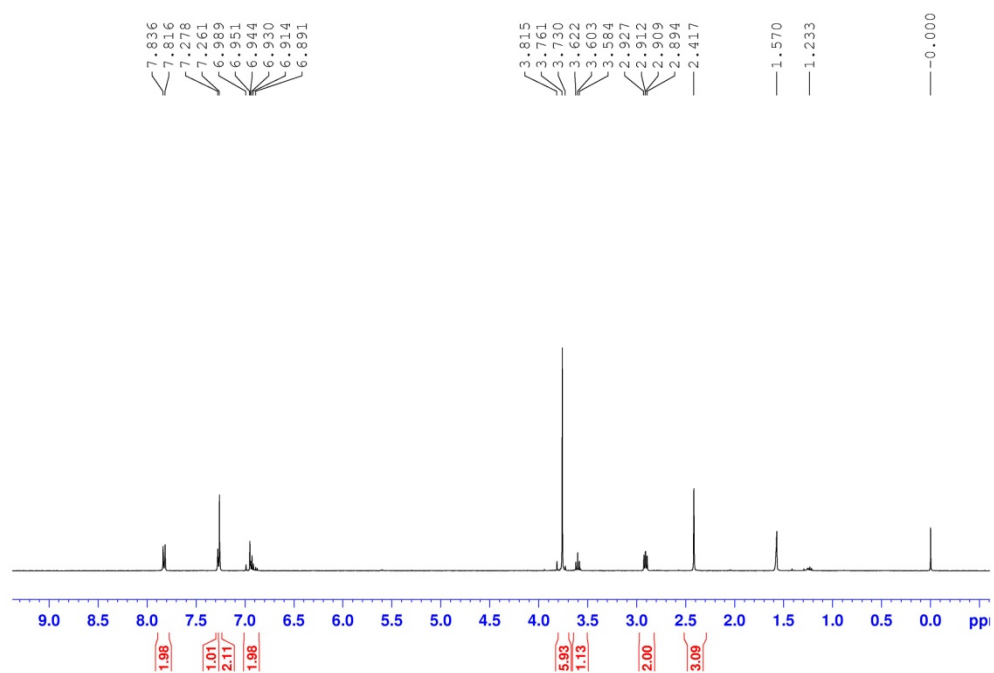
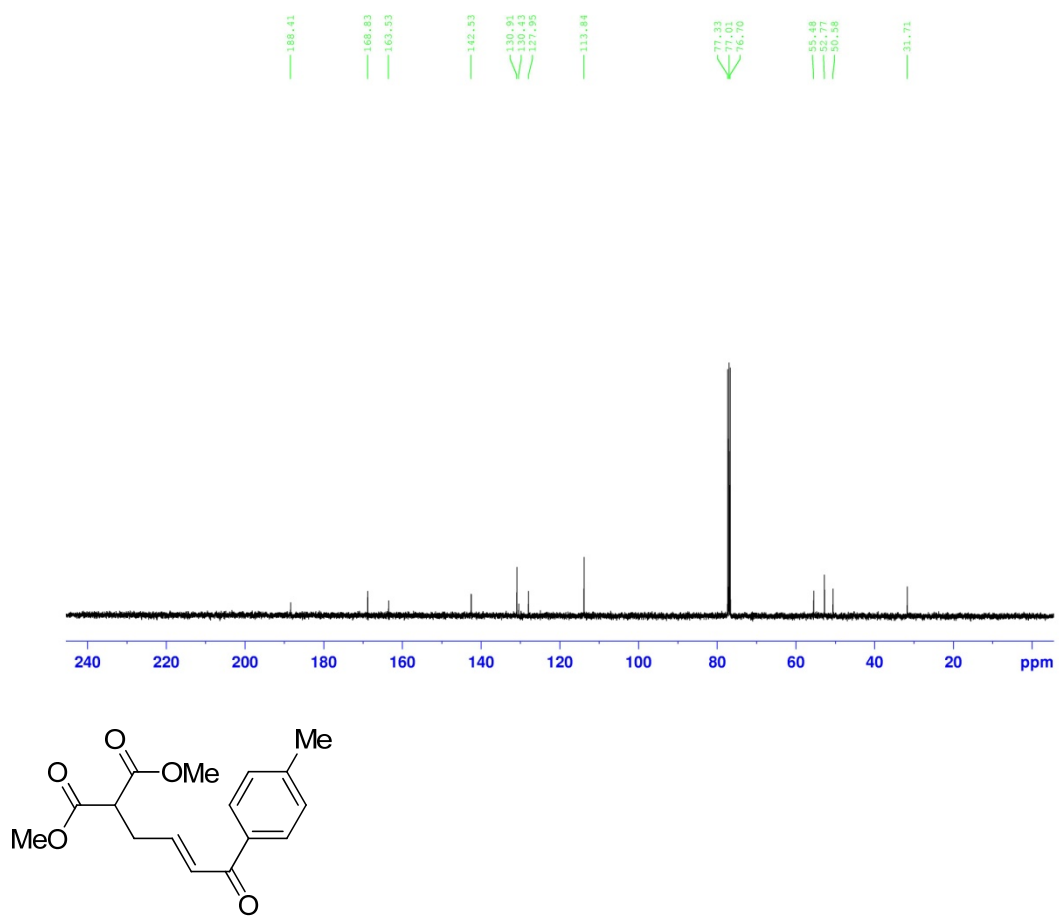
c) References

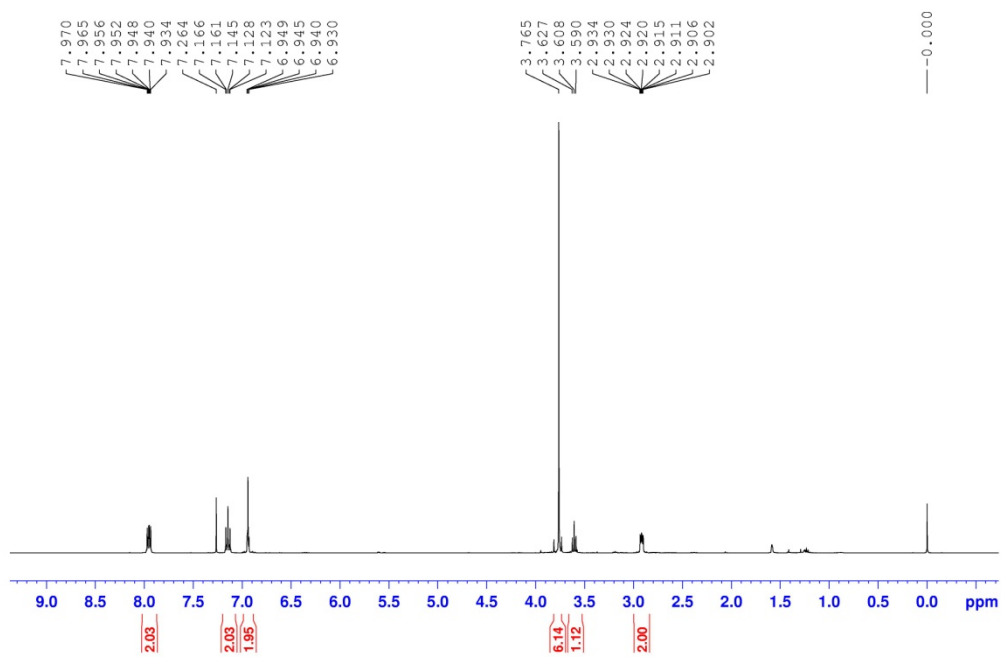
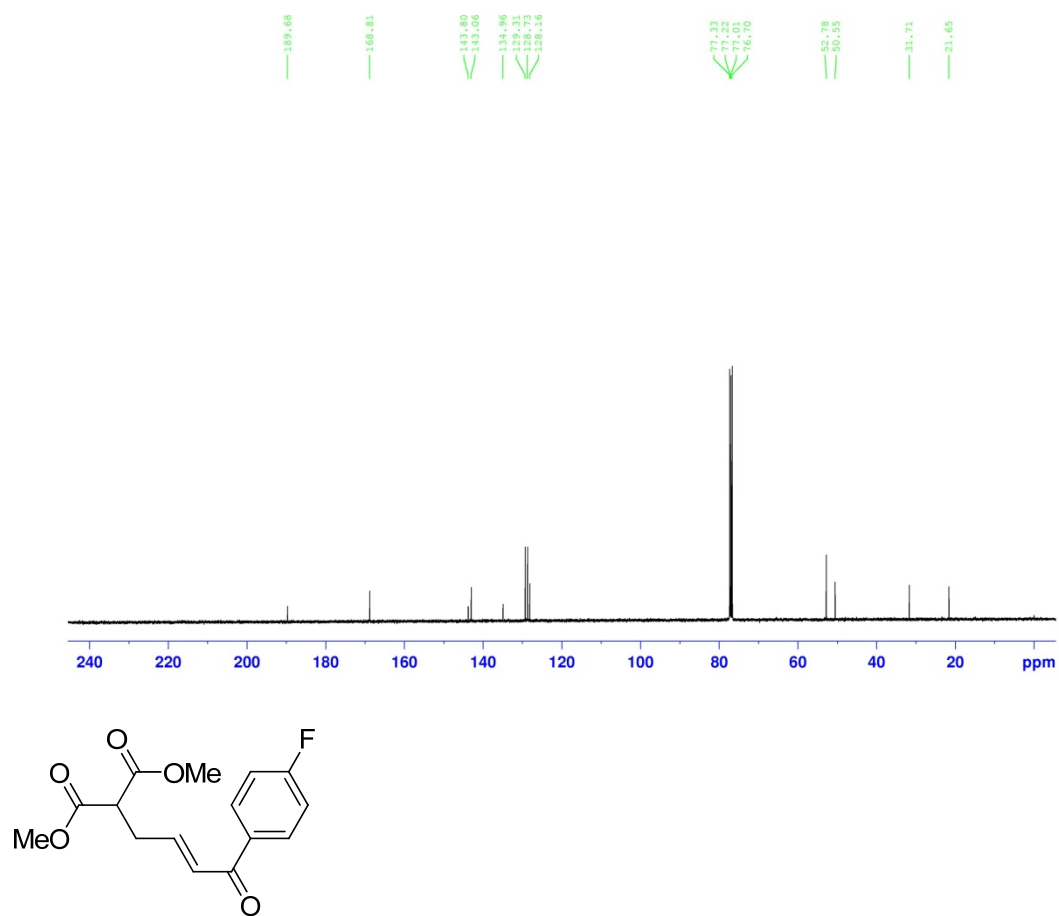
- [1] Liu, F.; Bugaut, X.; Schedler, M.; Frohlich, R.; Glorius, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 12626.
- [2] Bernard, A. M.; Piras, P. P.; Toriggia, P. *Synthesis*, **1990**, *6*, 527.

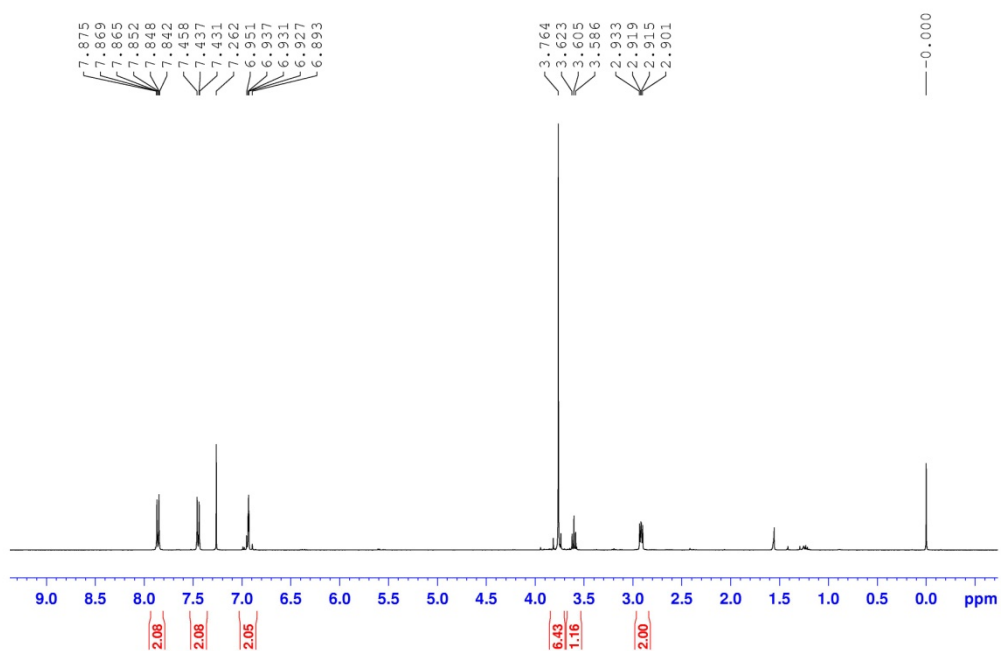
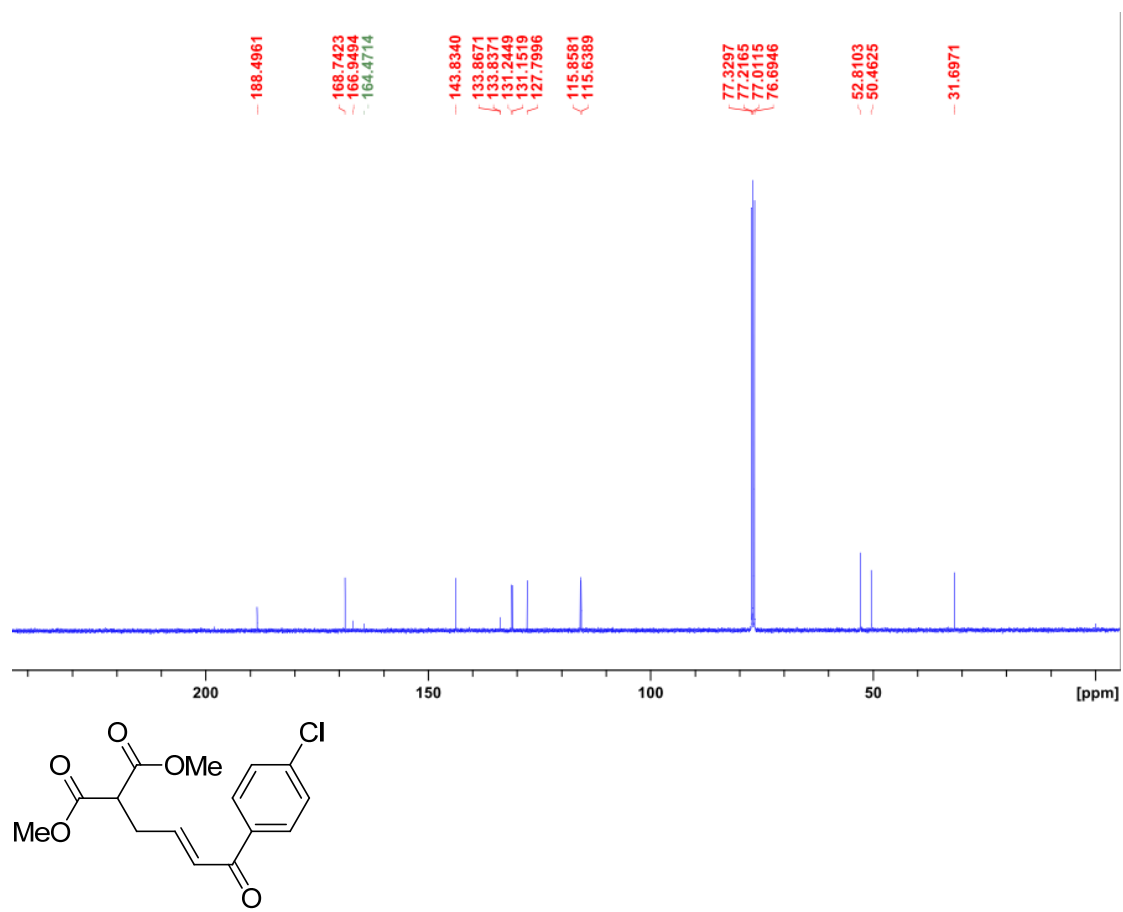
IV: ^1H and ^{13}C NMR

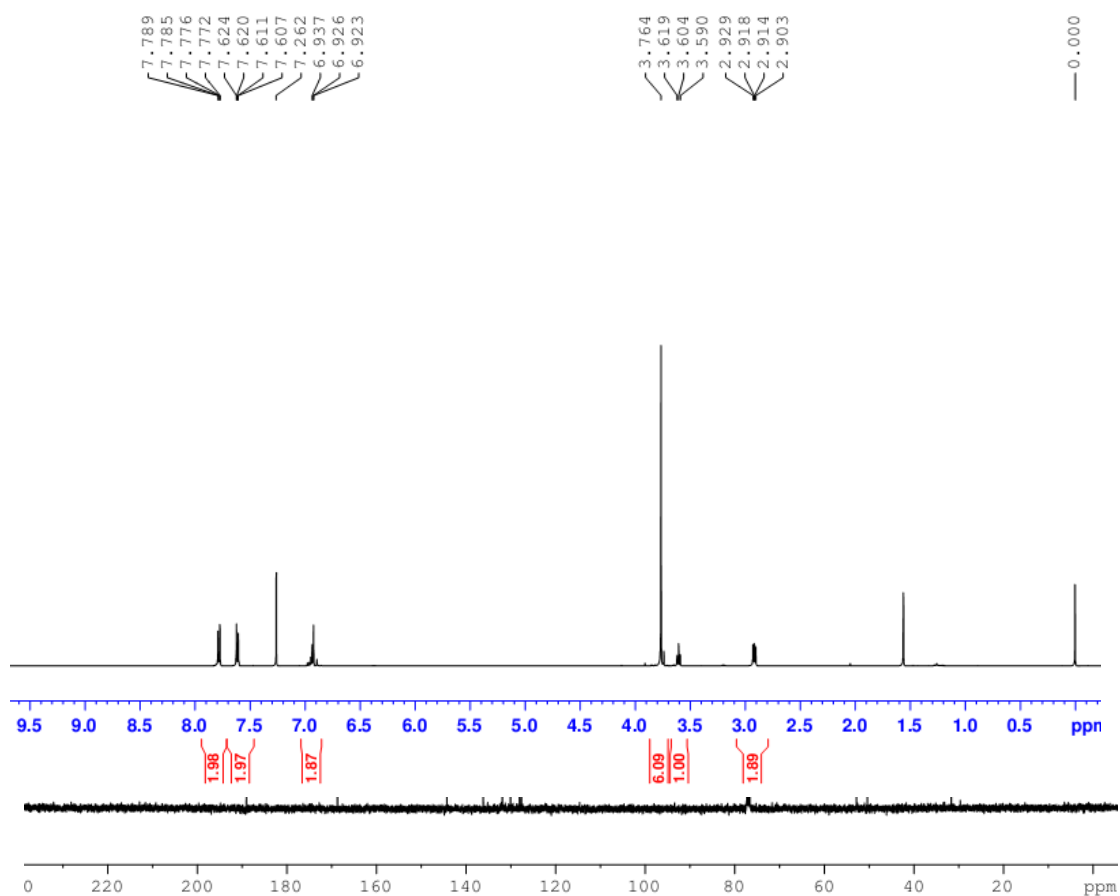
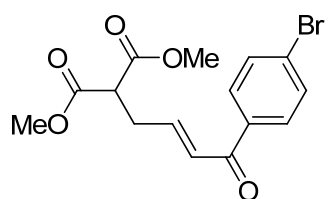
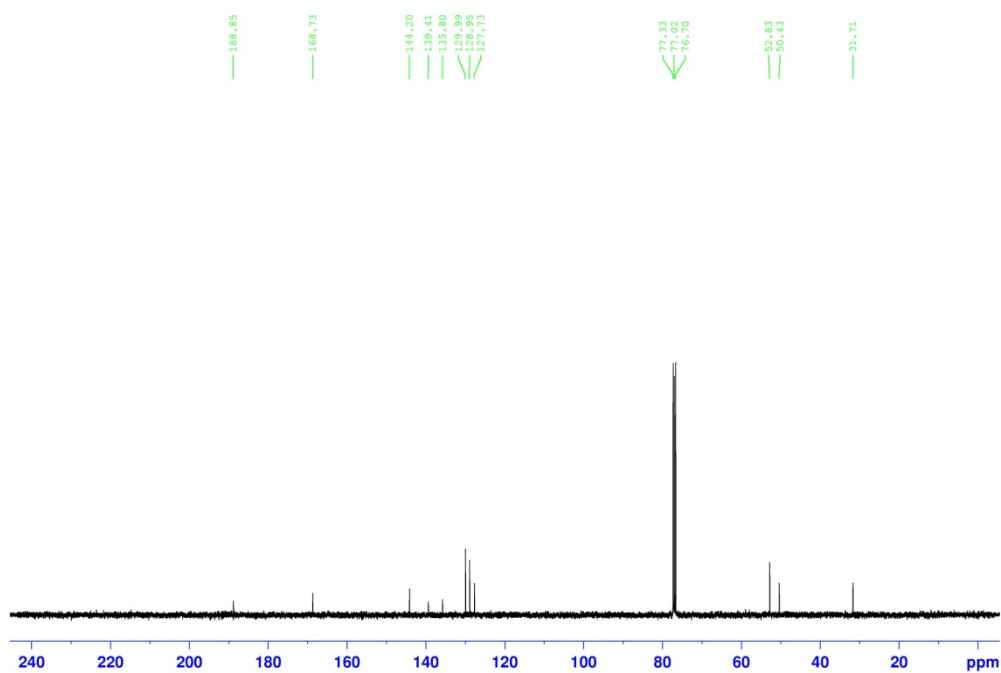


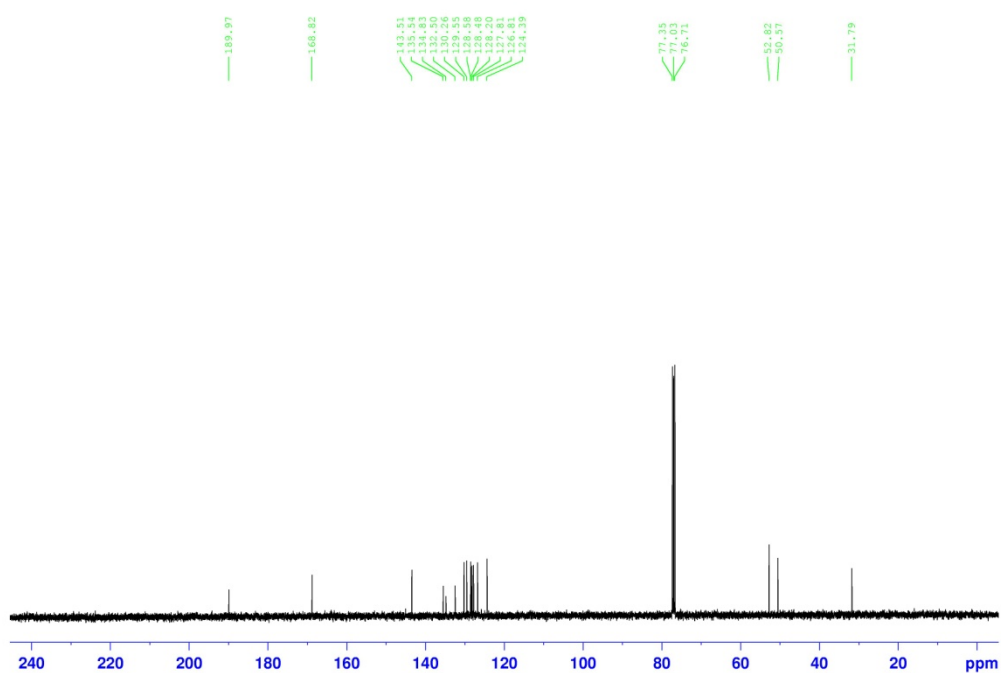
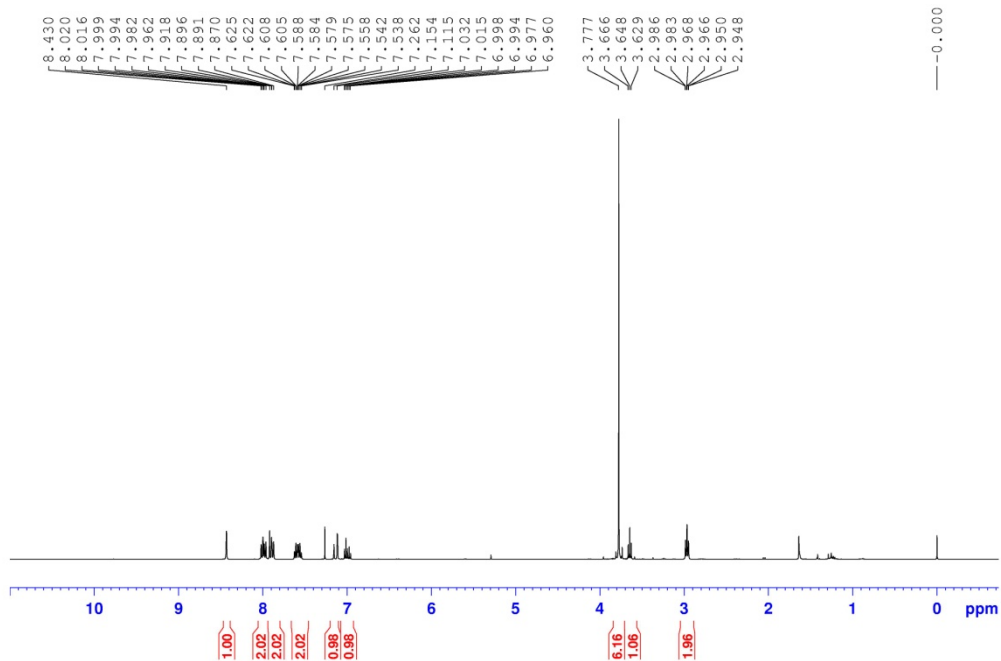
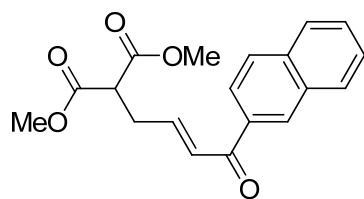


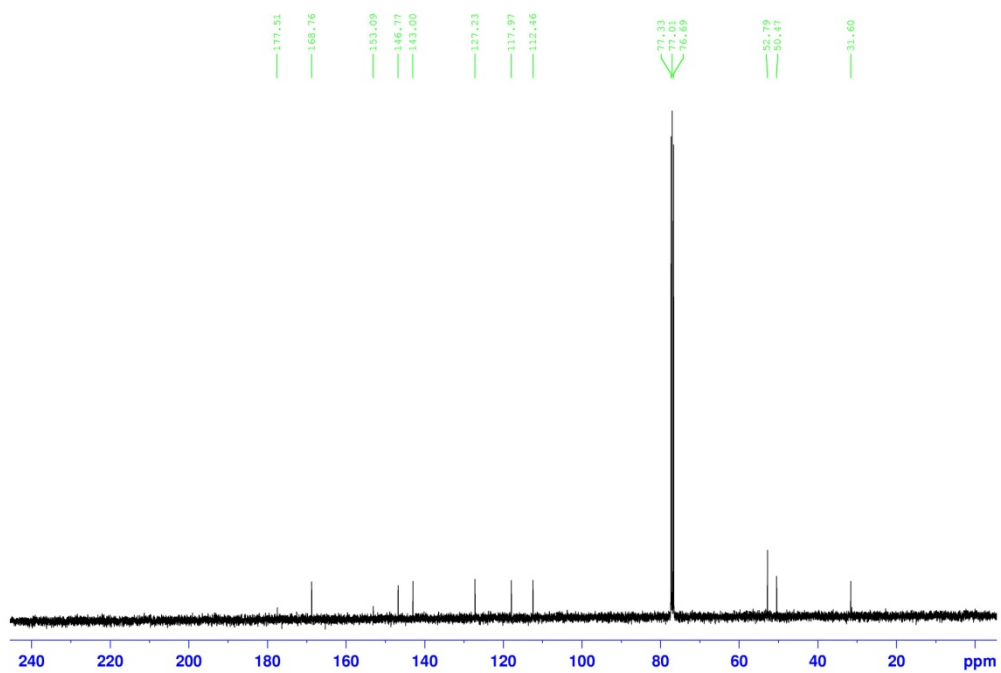
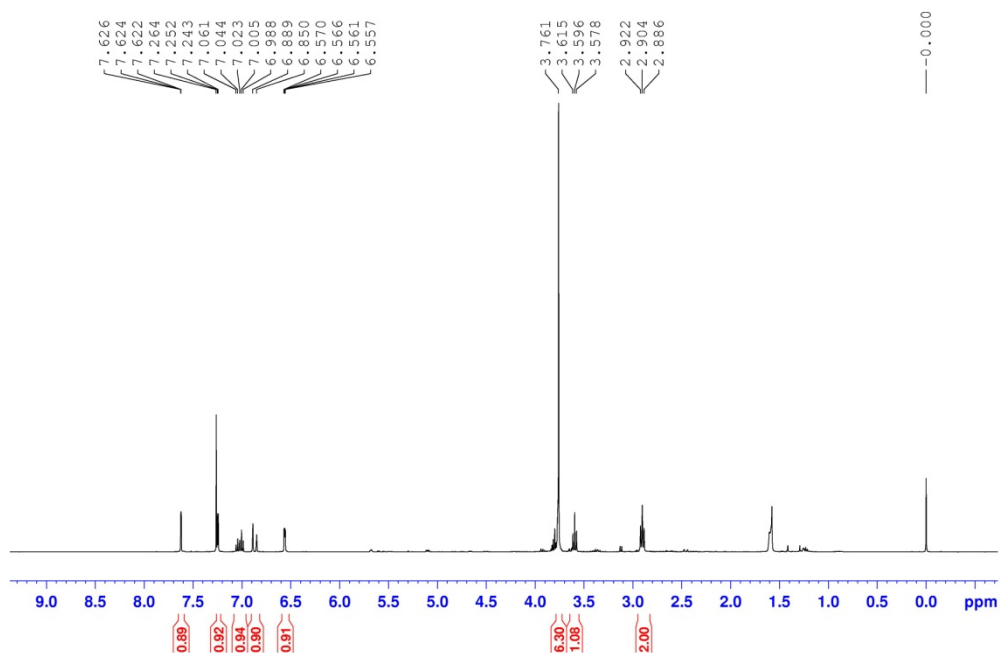
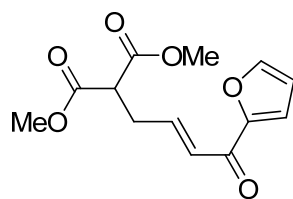


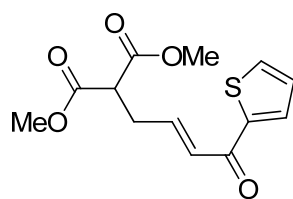




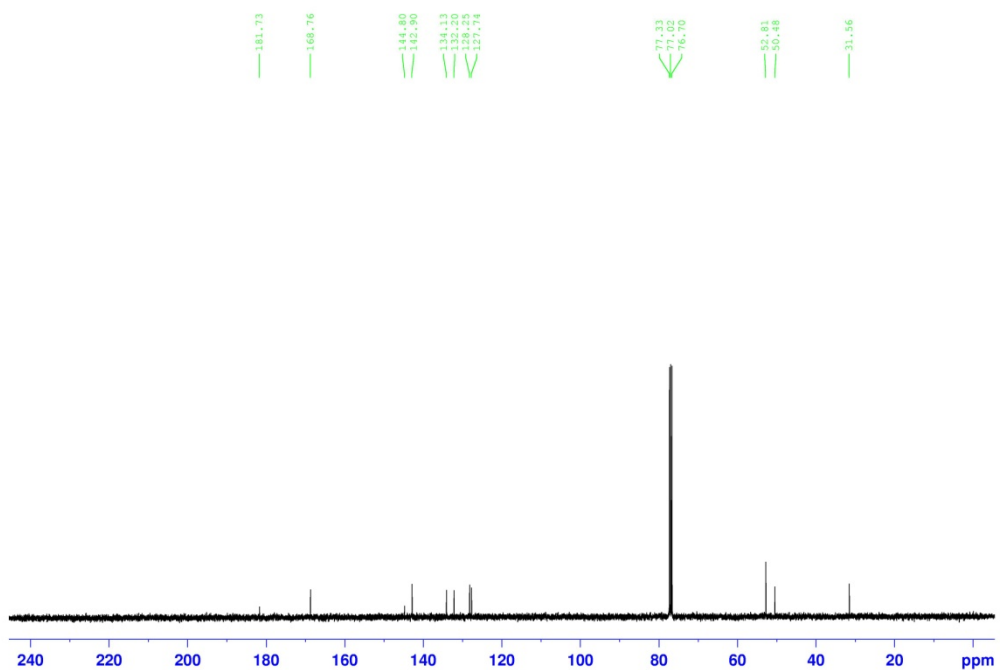
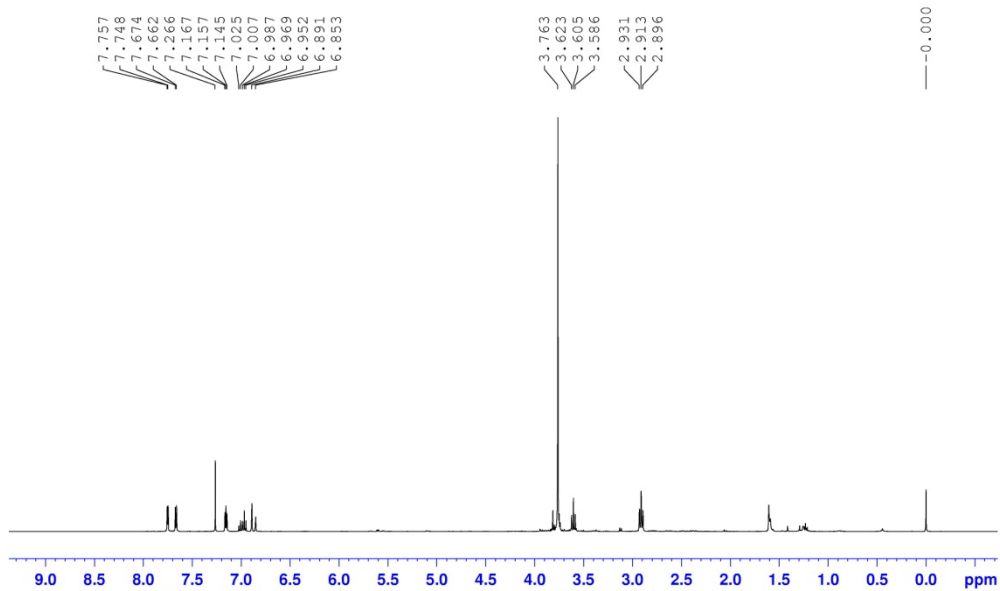


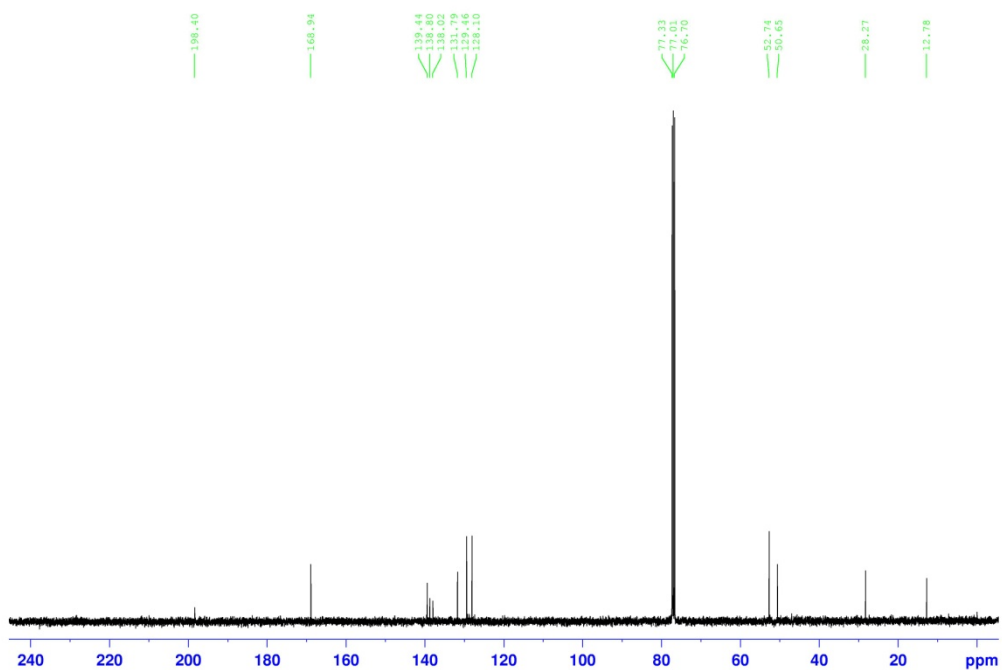
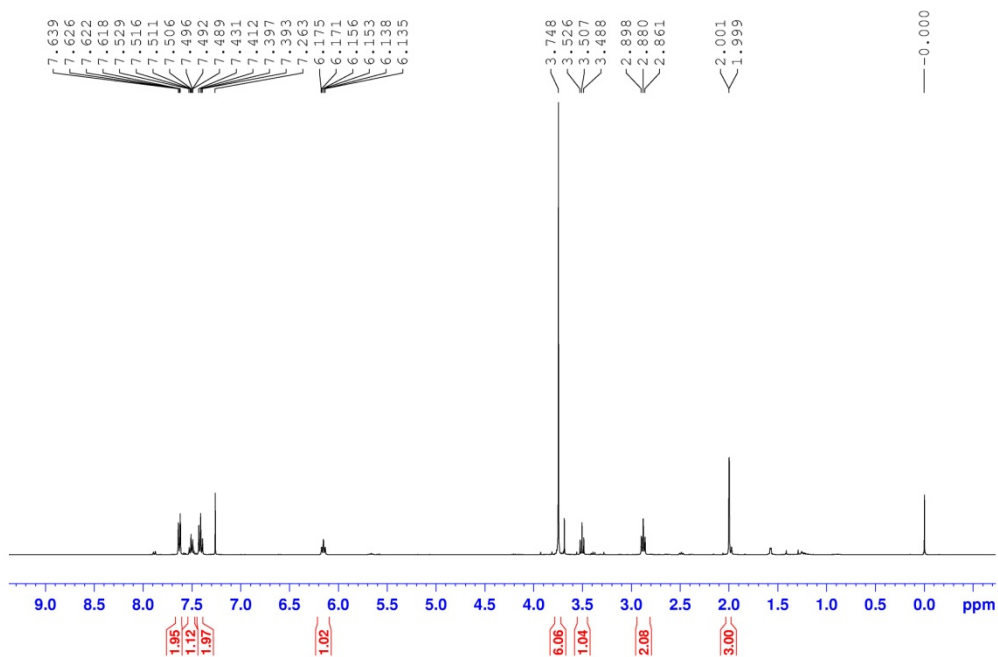
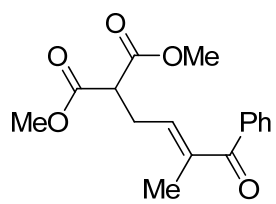


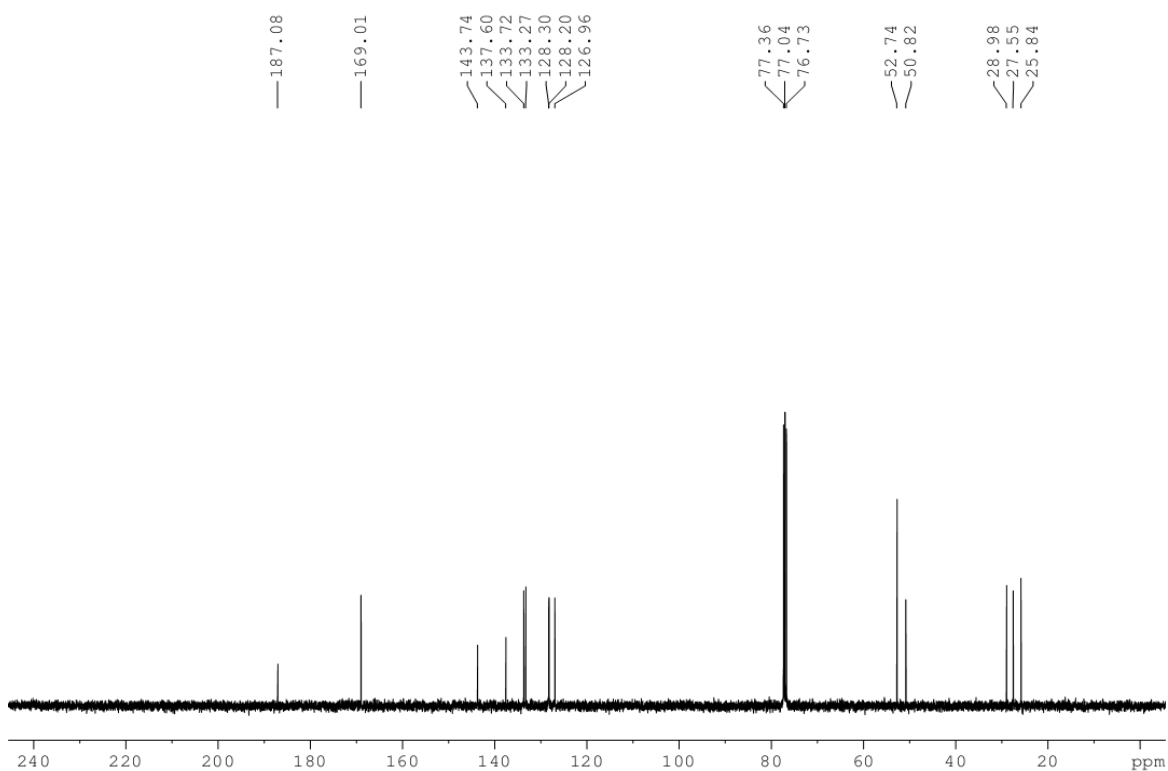
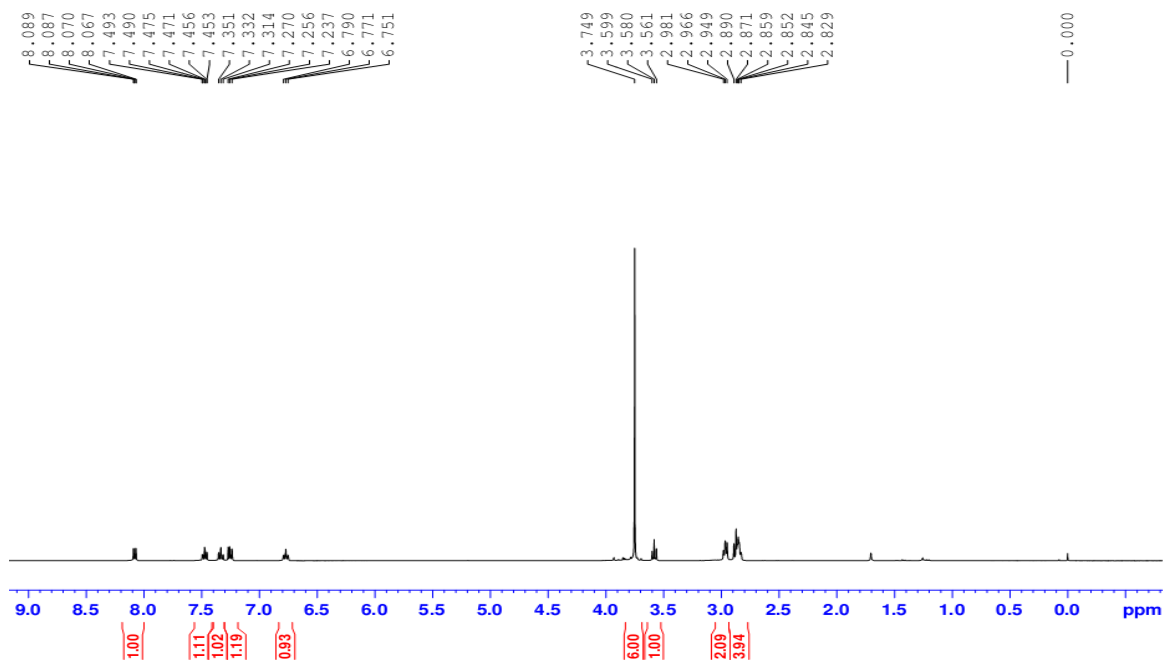
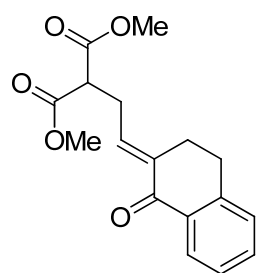


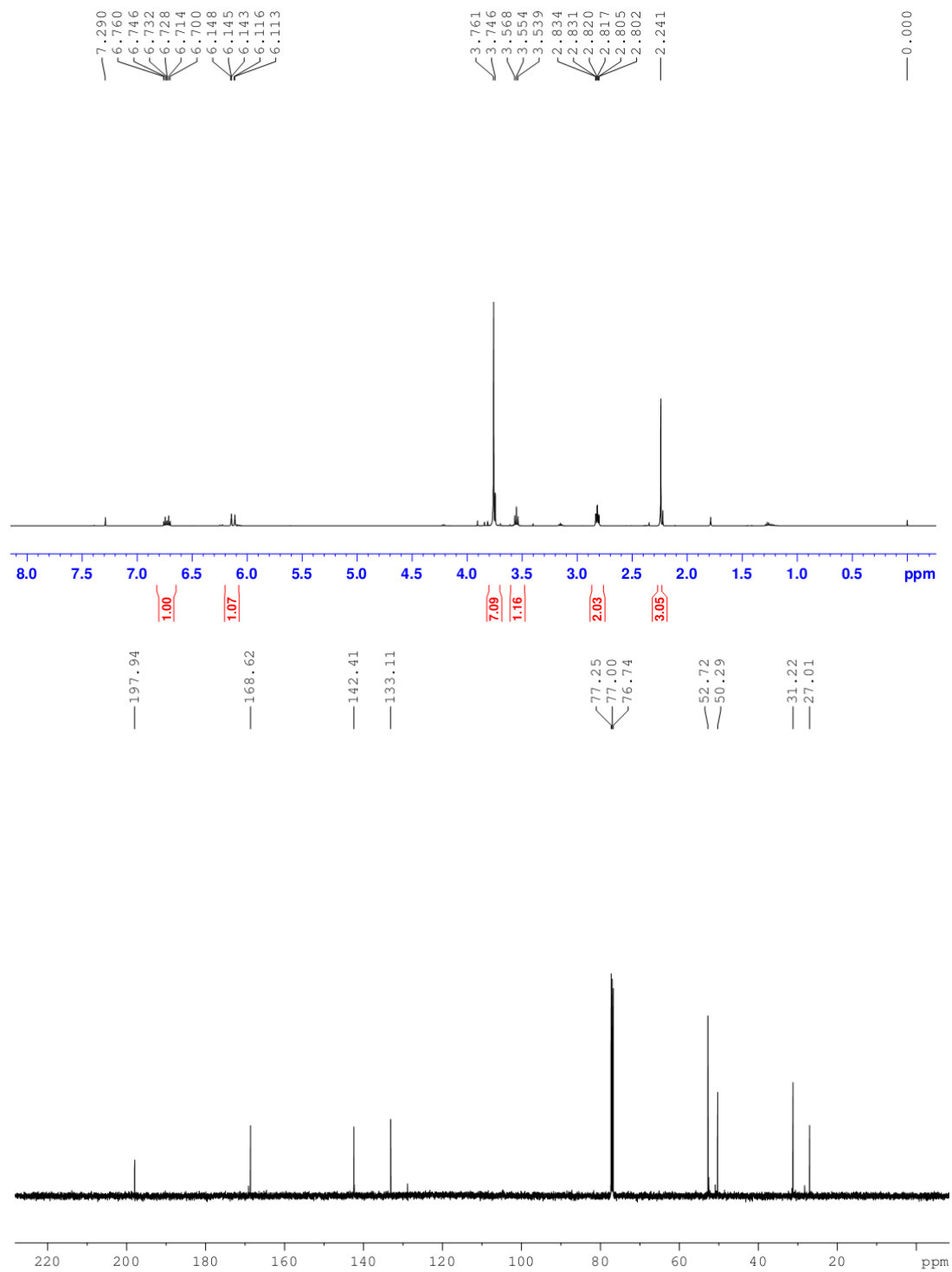
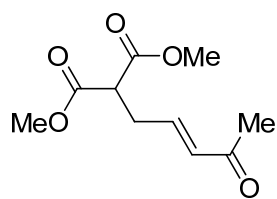


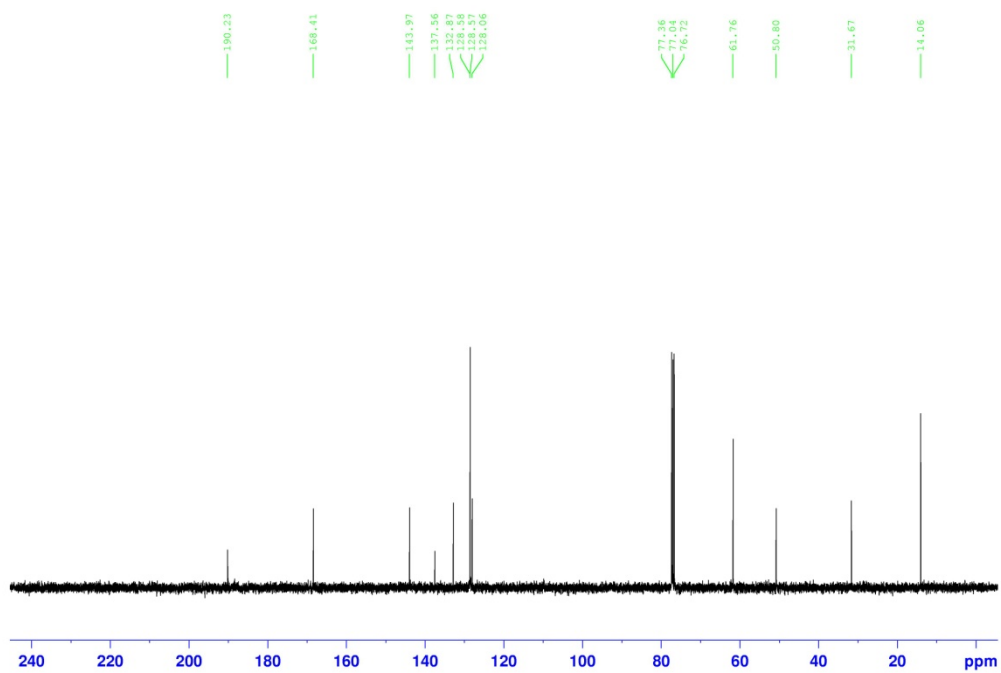
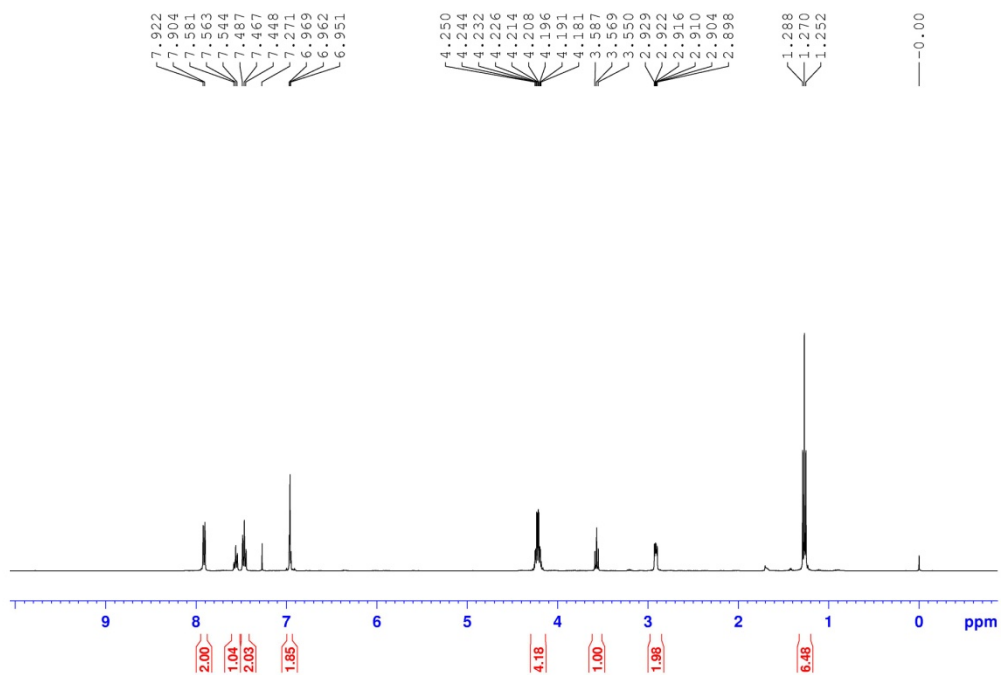
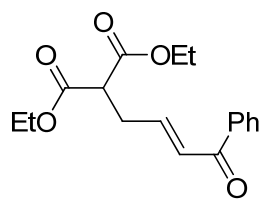
fu07-b2

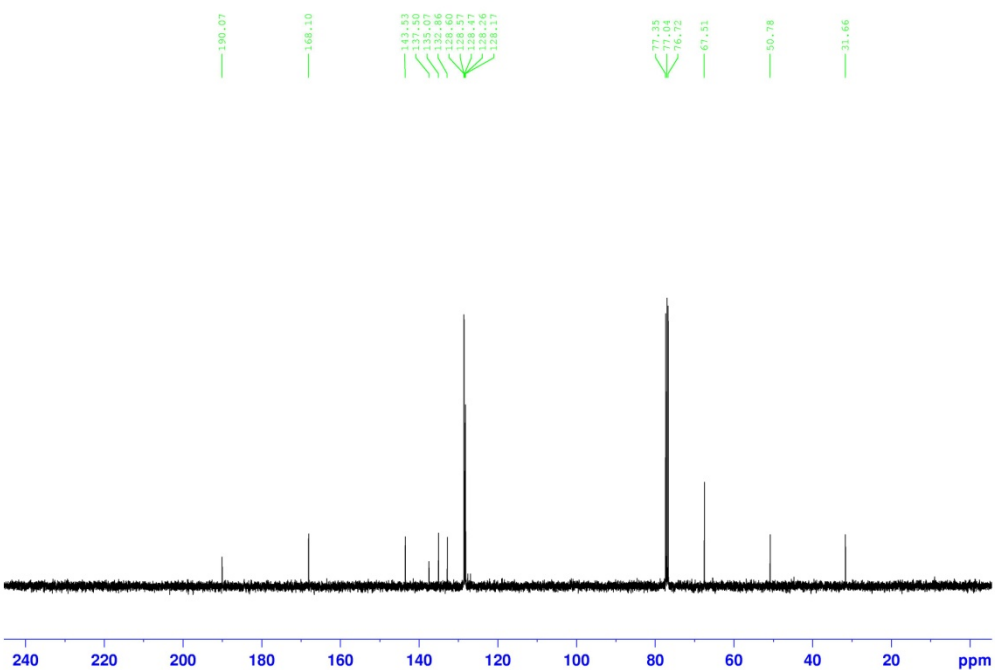
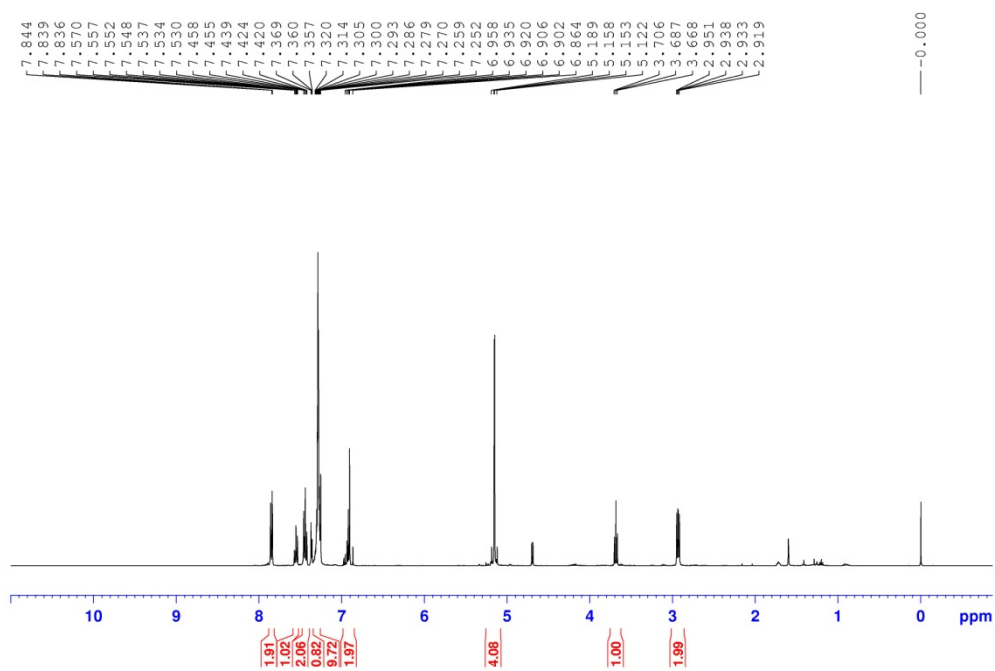
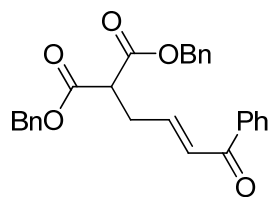


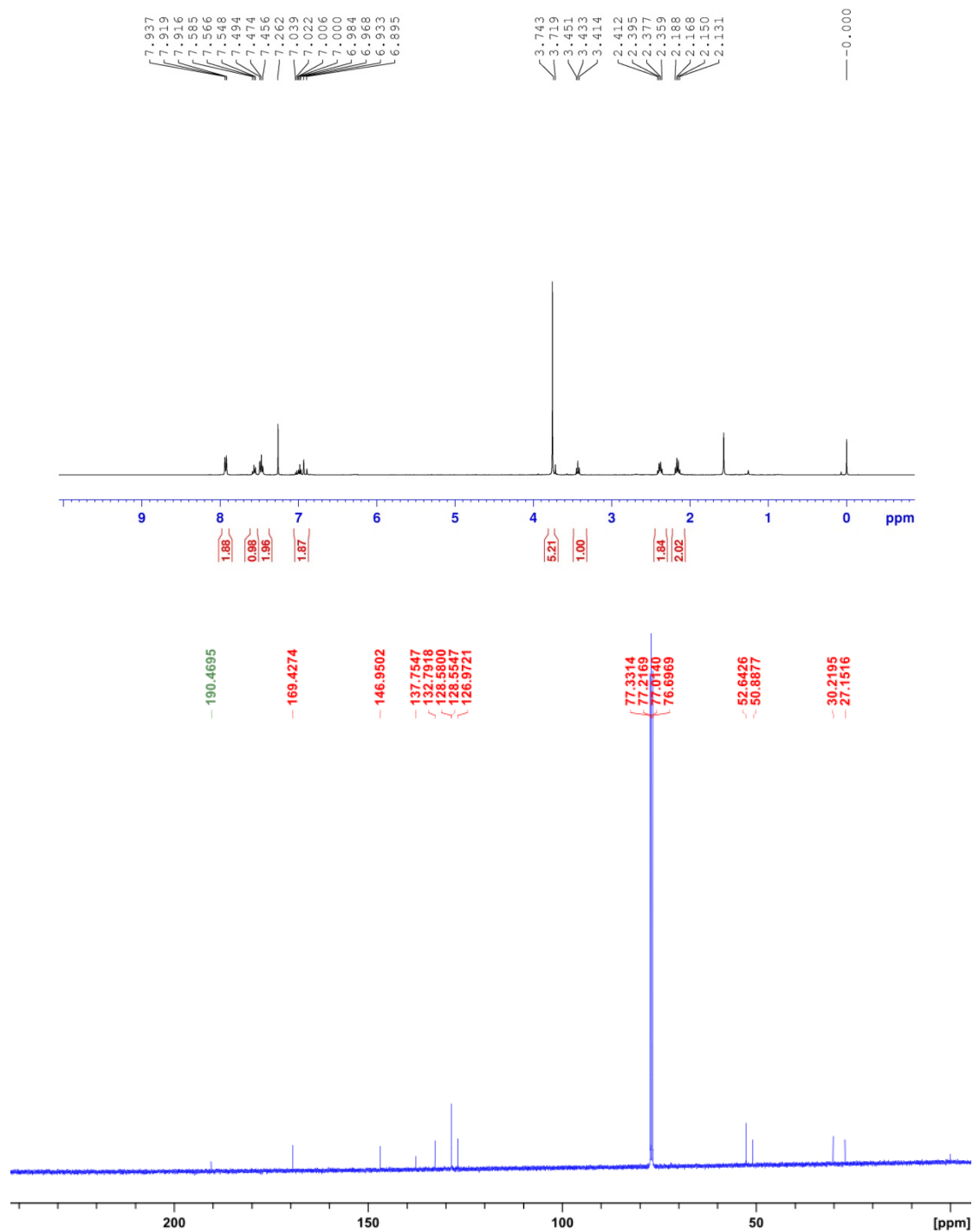
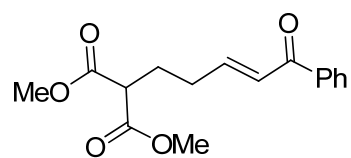


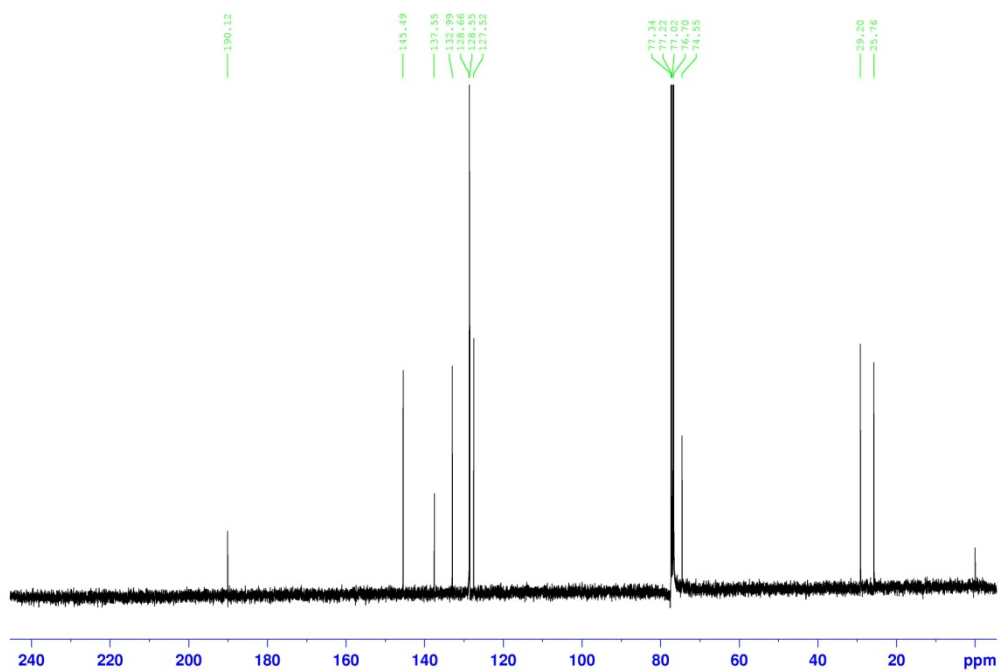
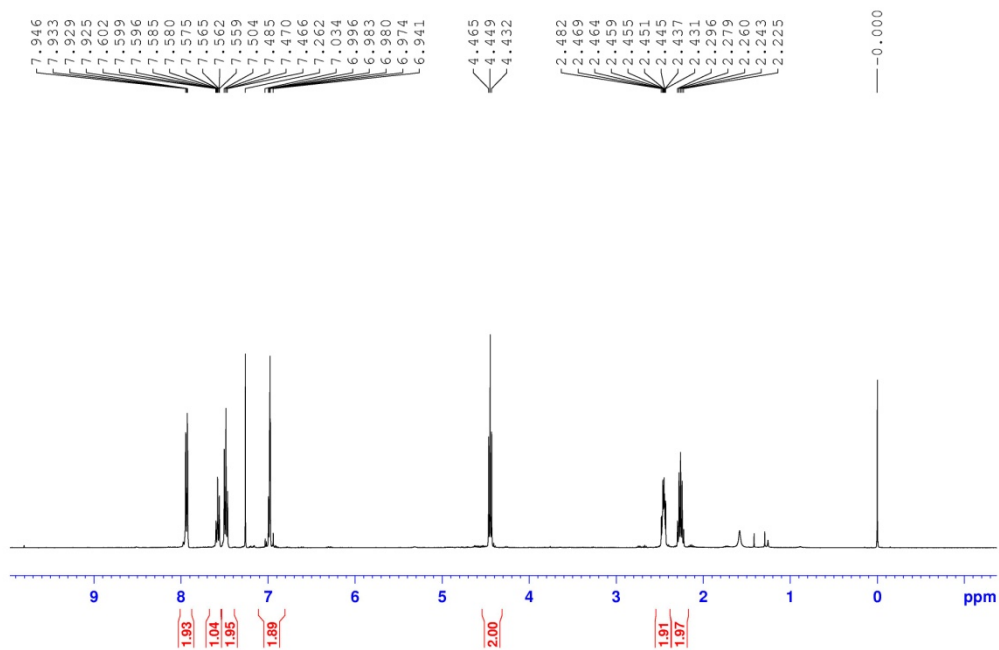
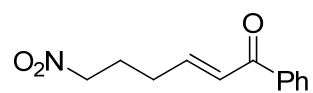


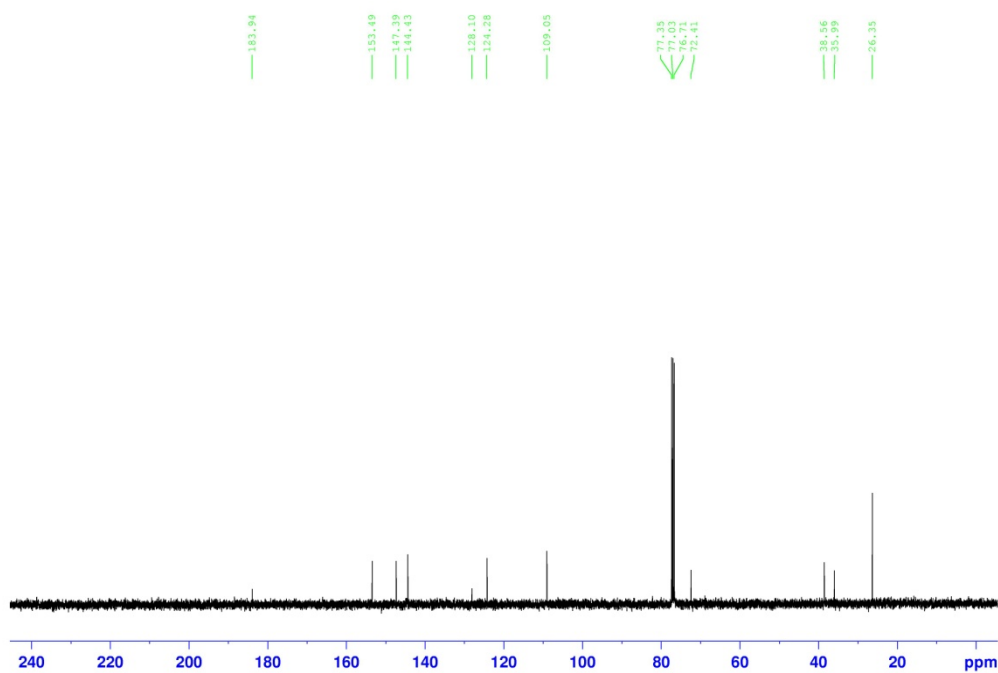
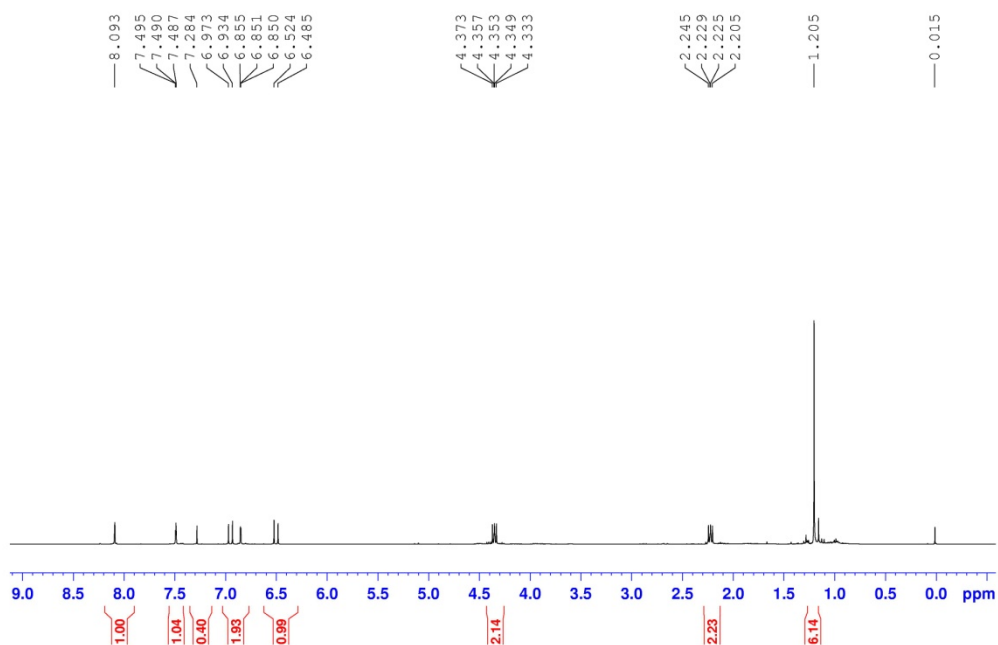
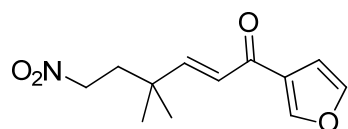


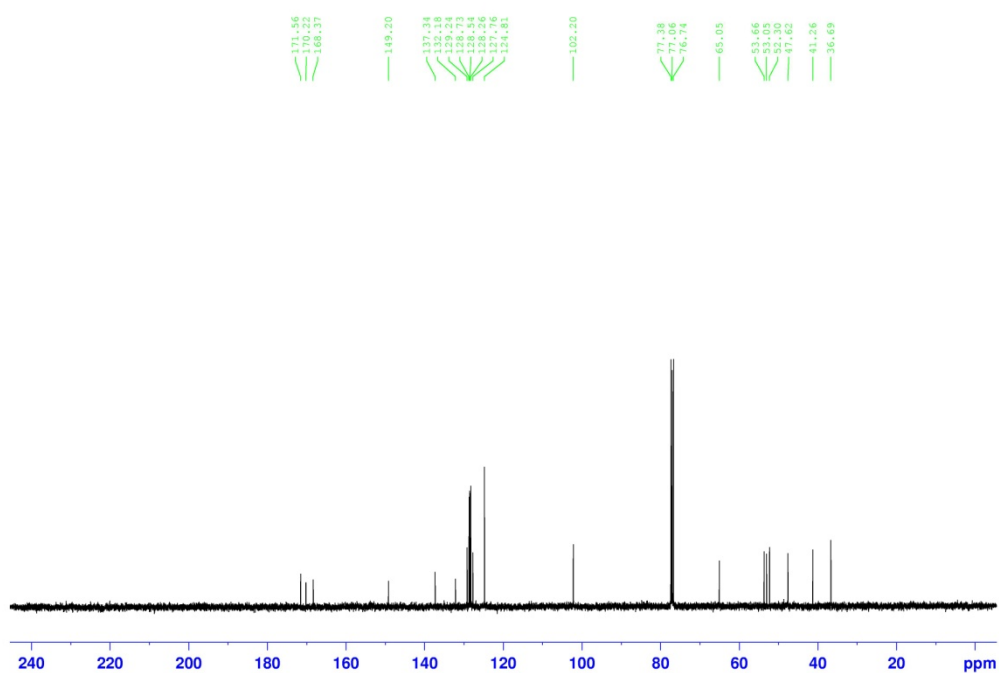
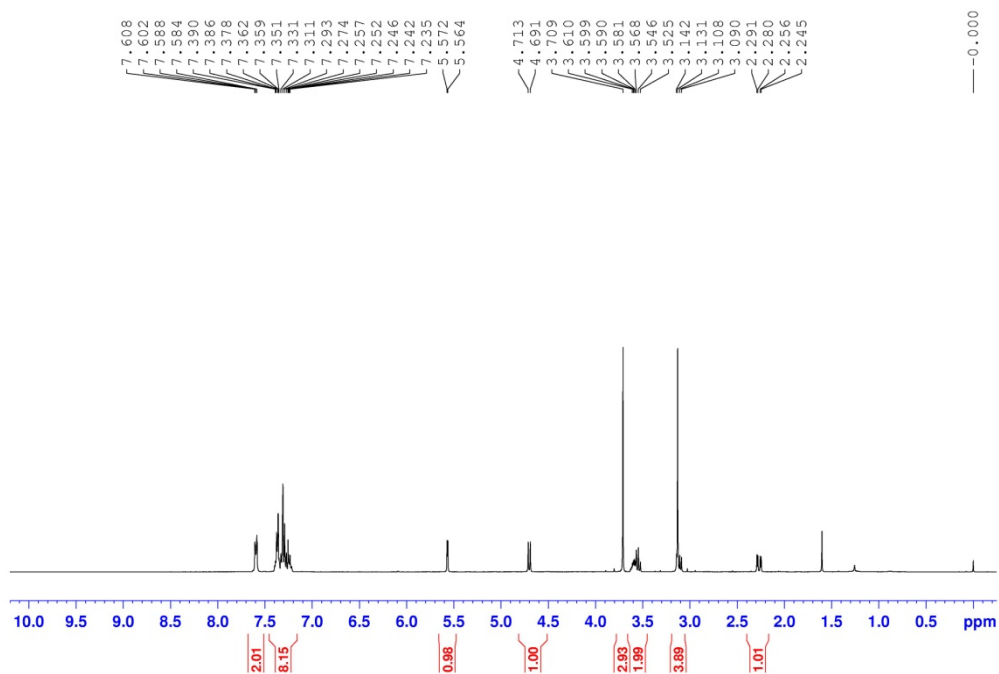
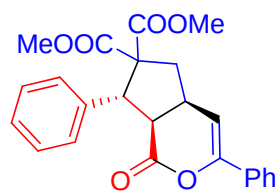


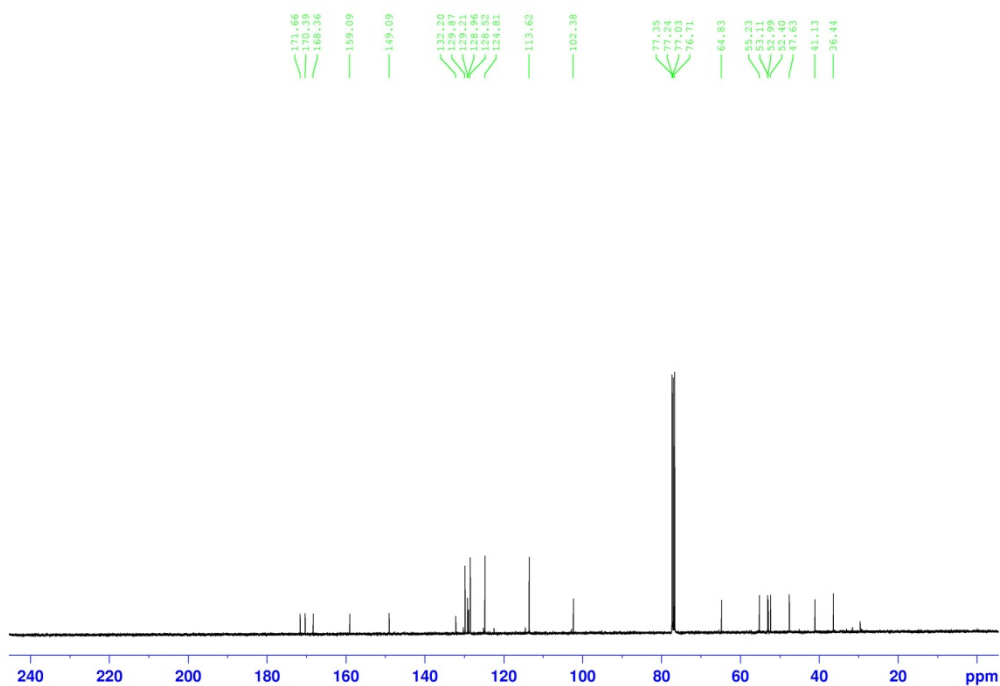
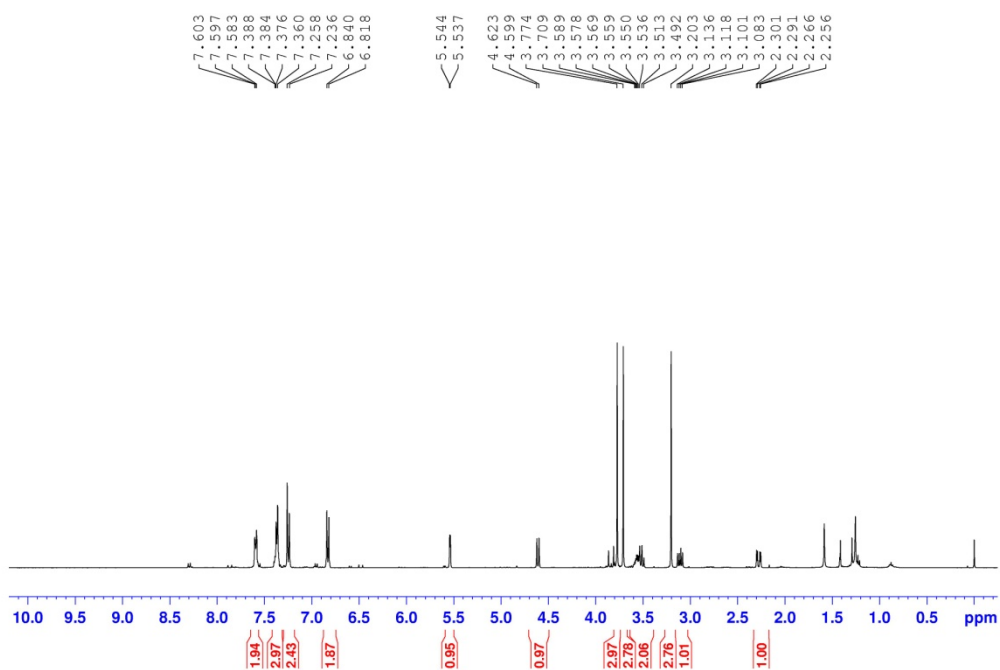
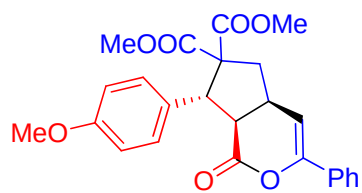


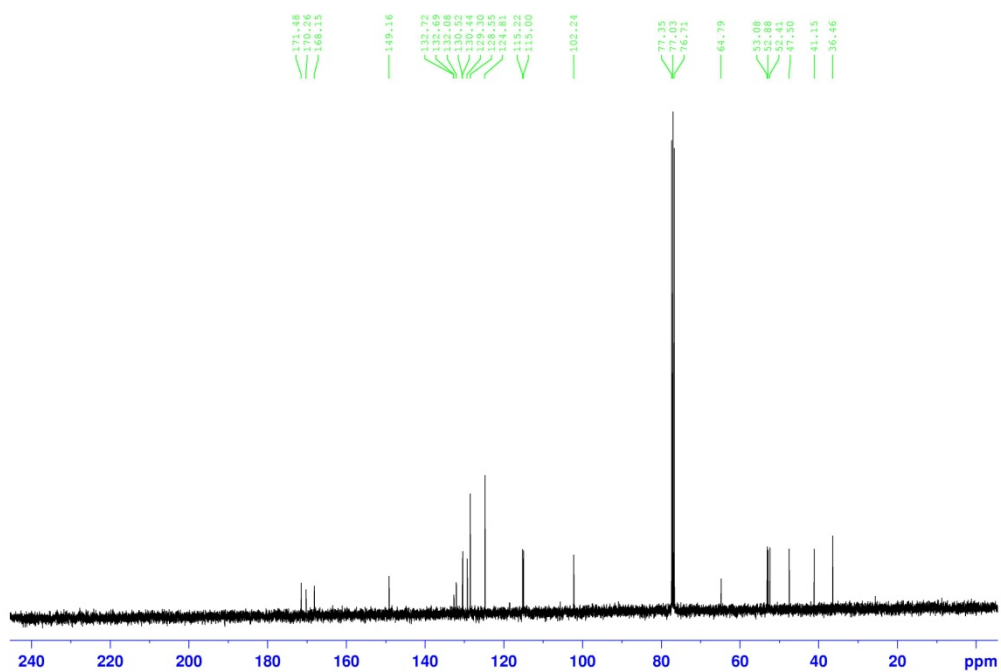
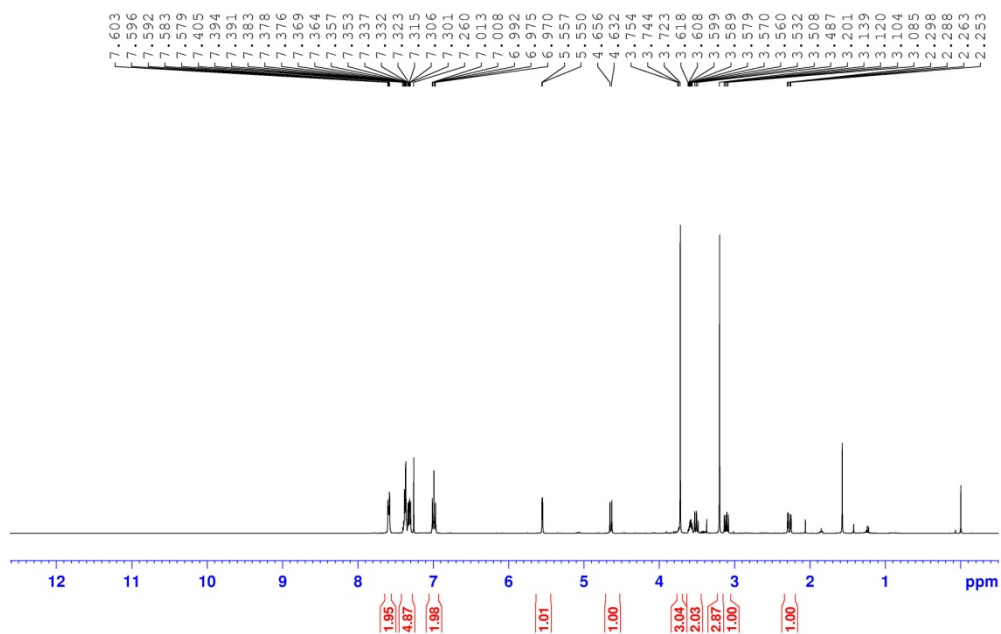
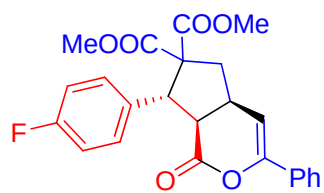


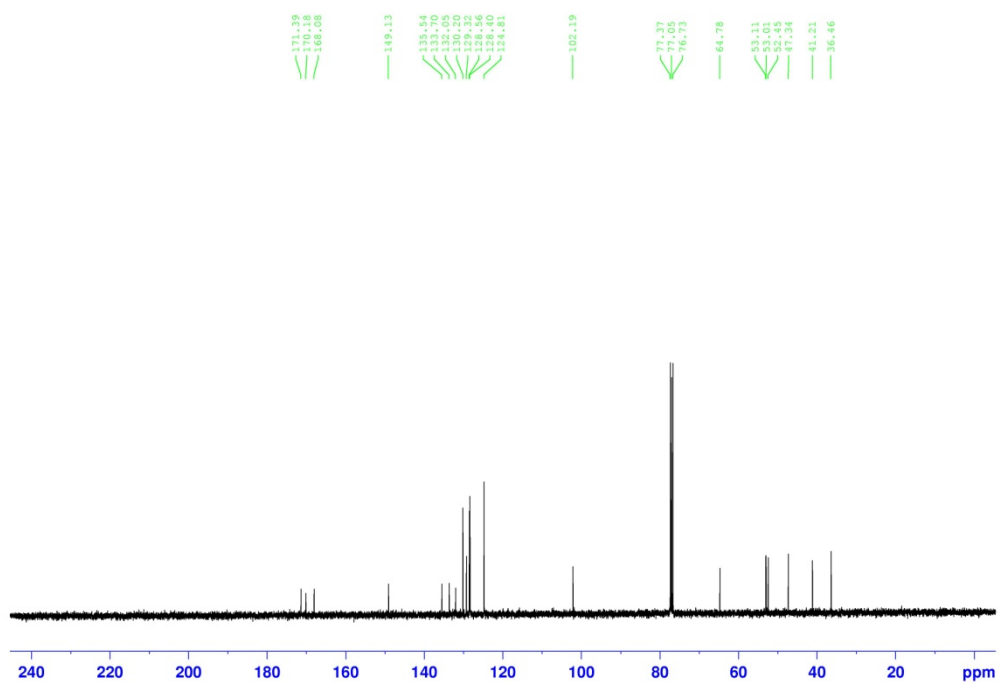
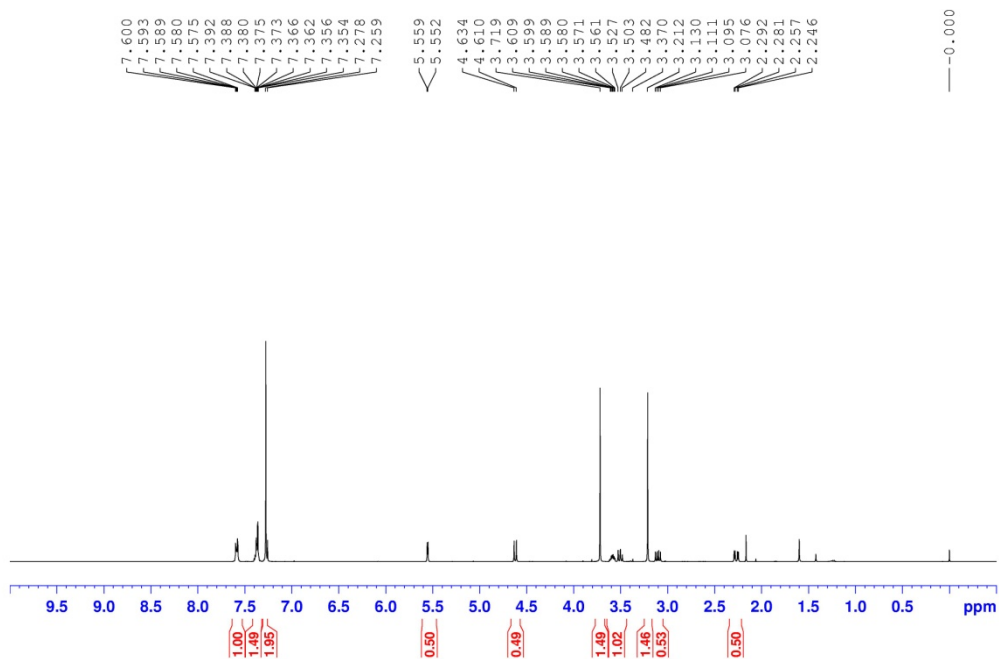
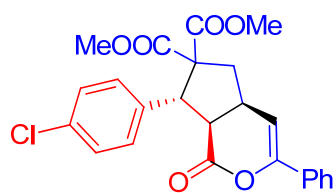


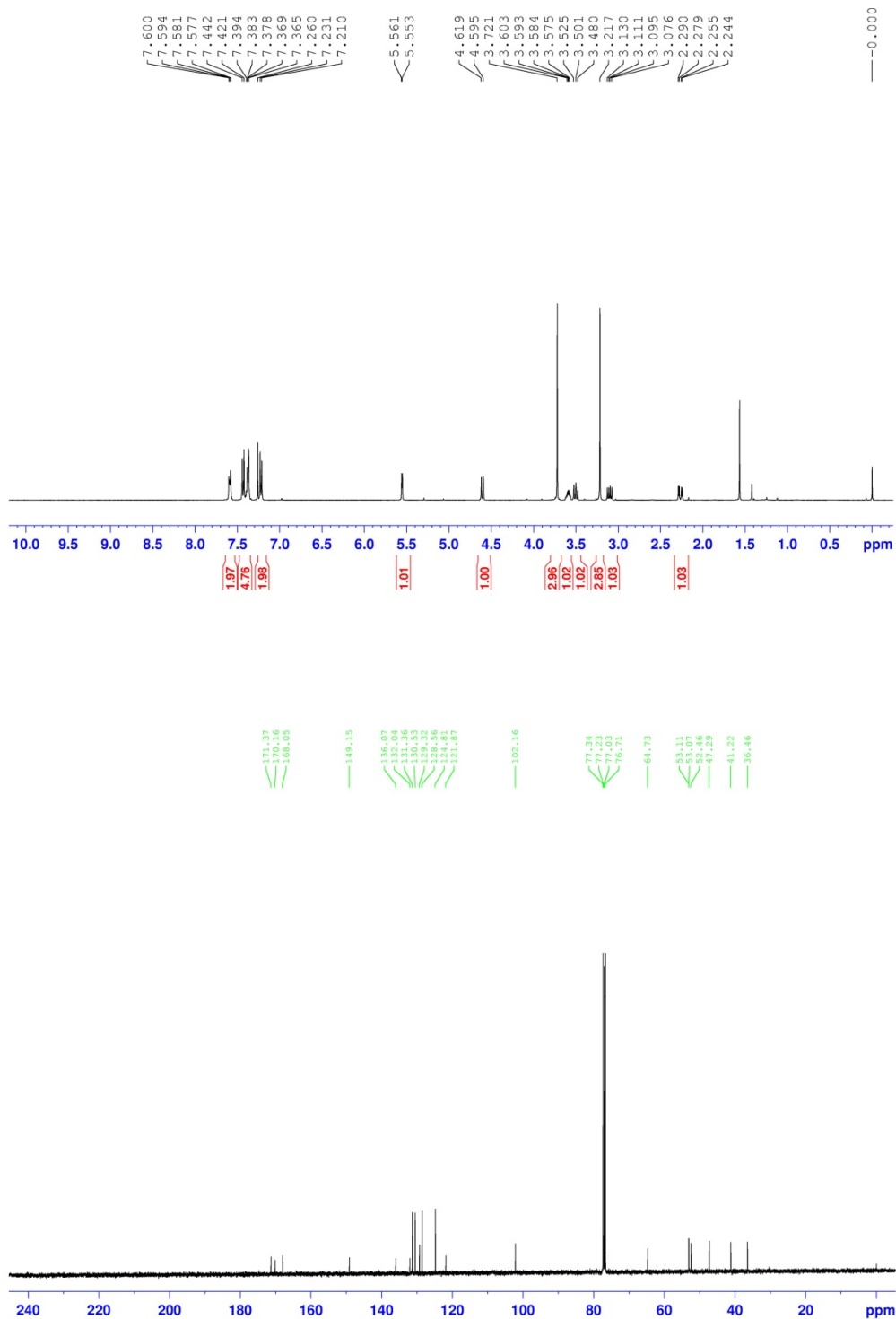
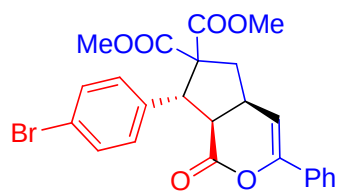


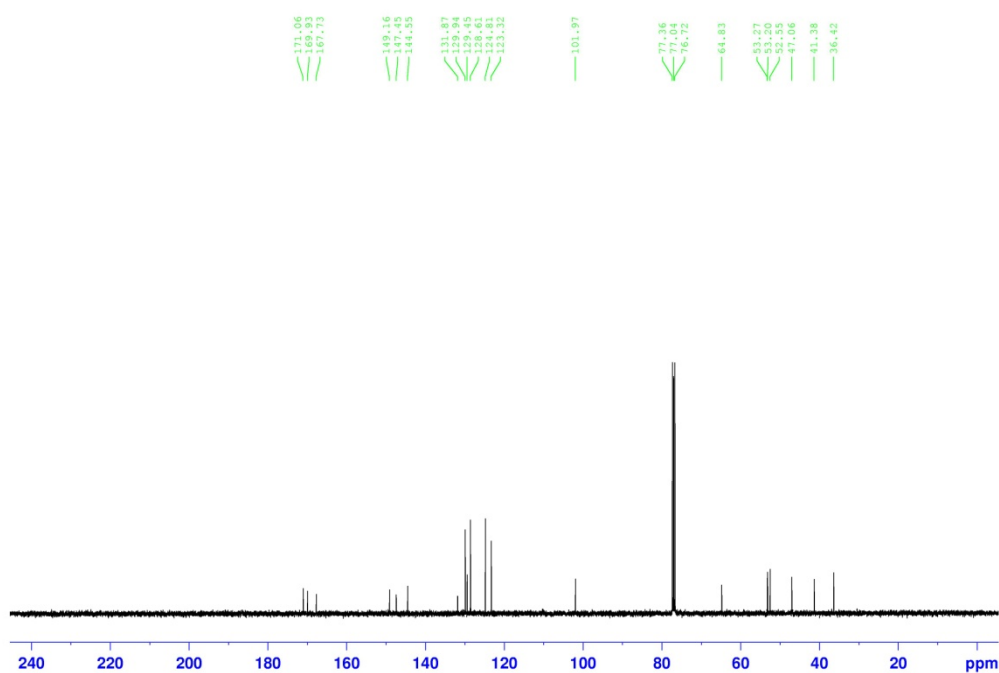
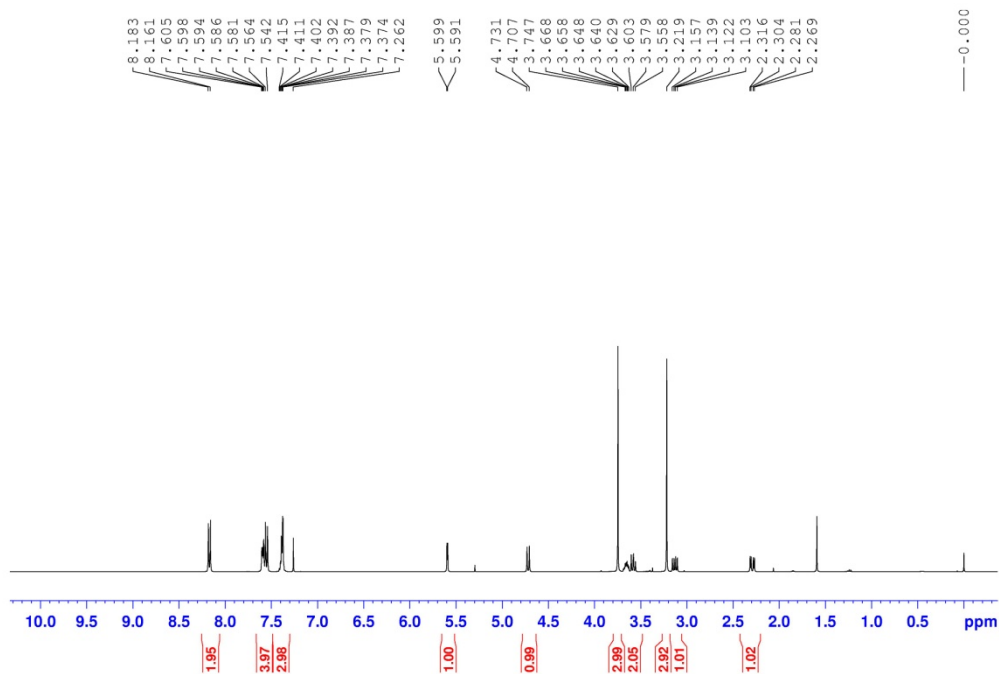
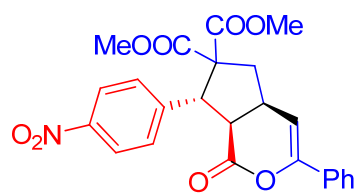


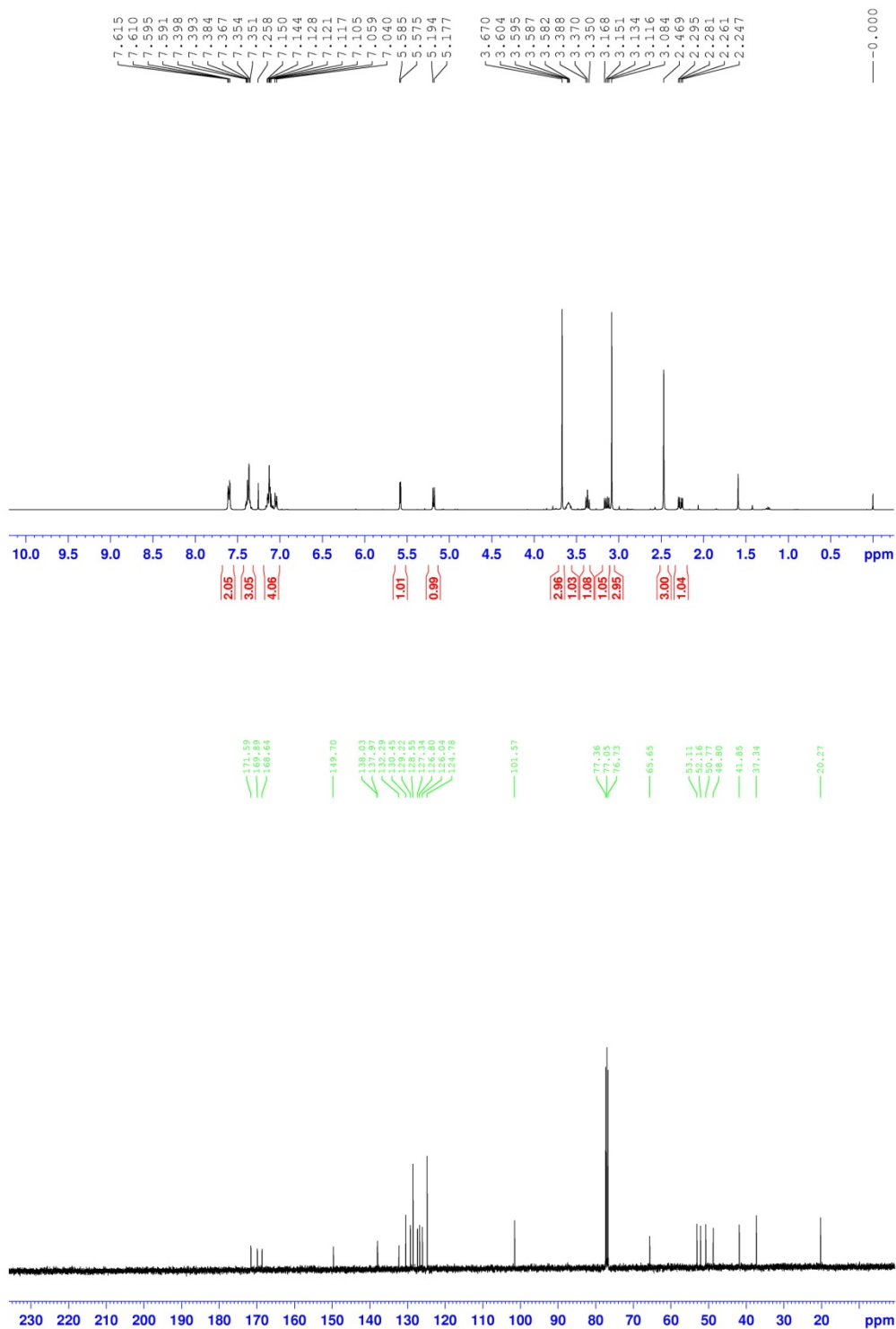
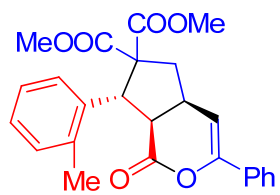


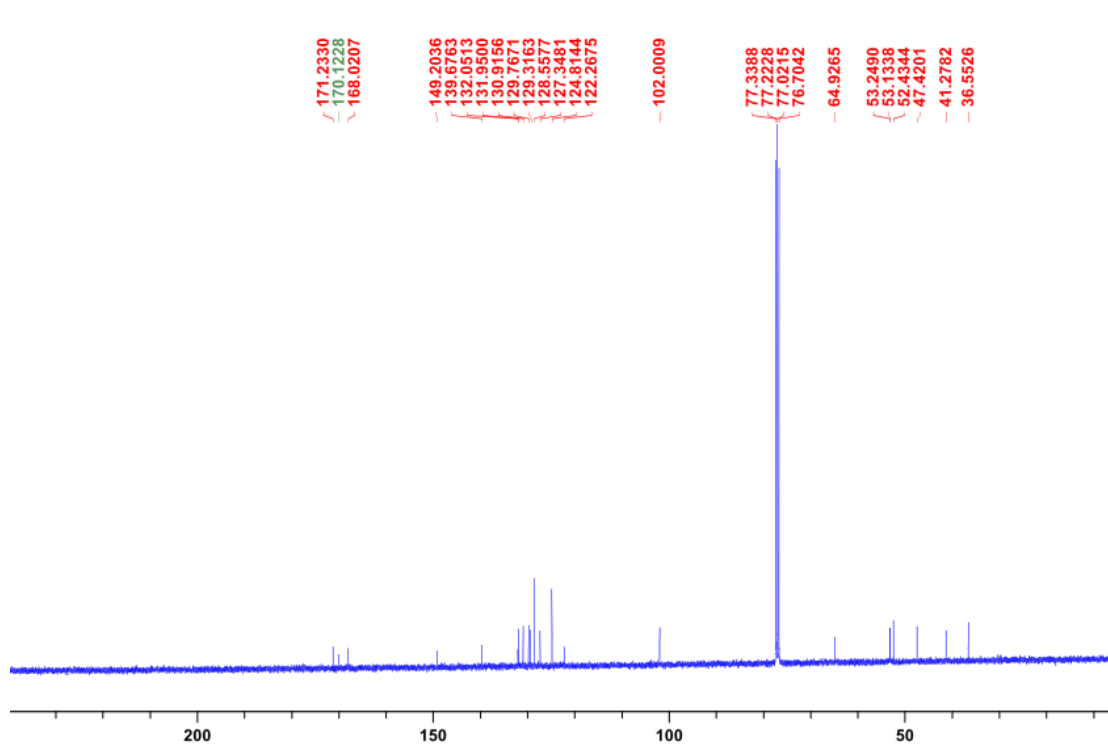
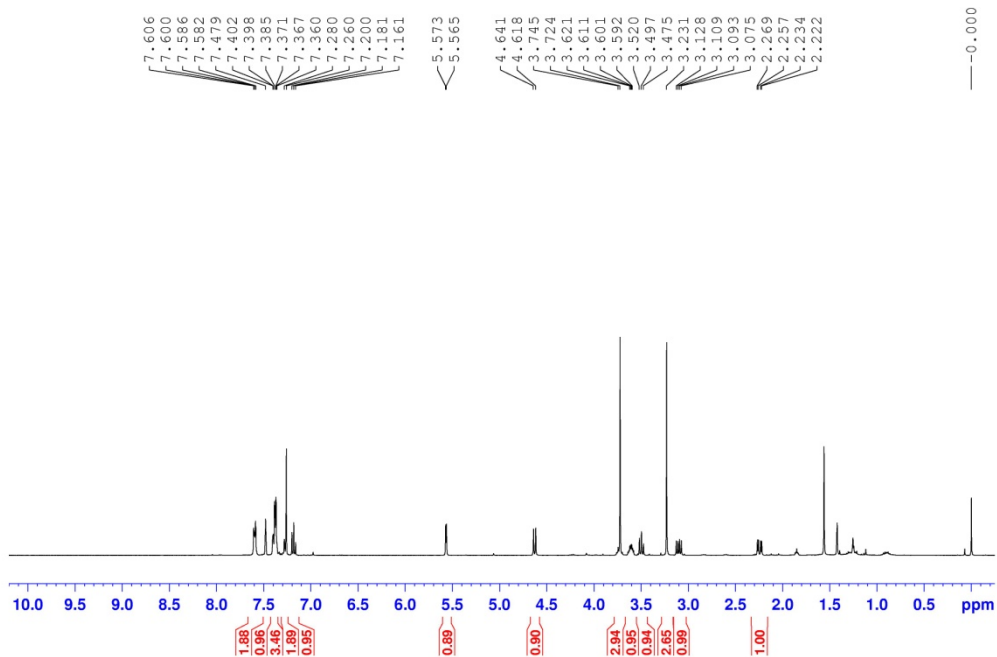
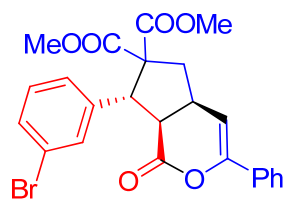


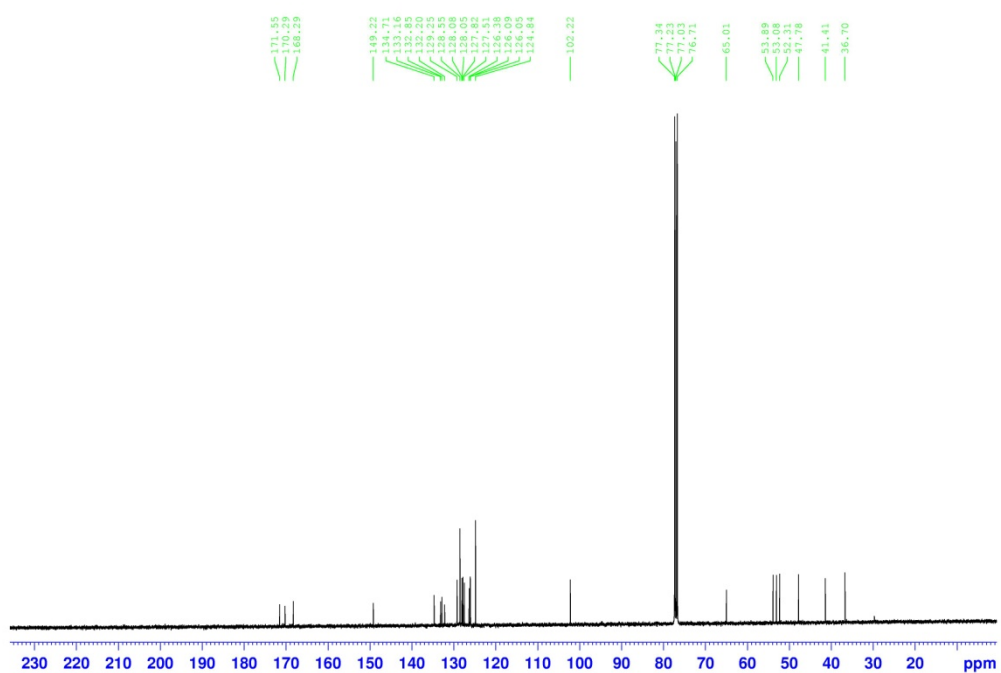
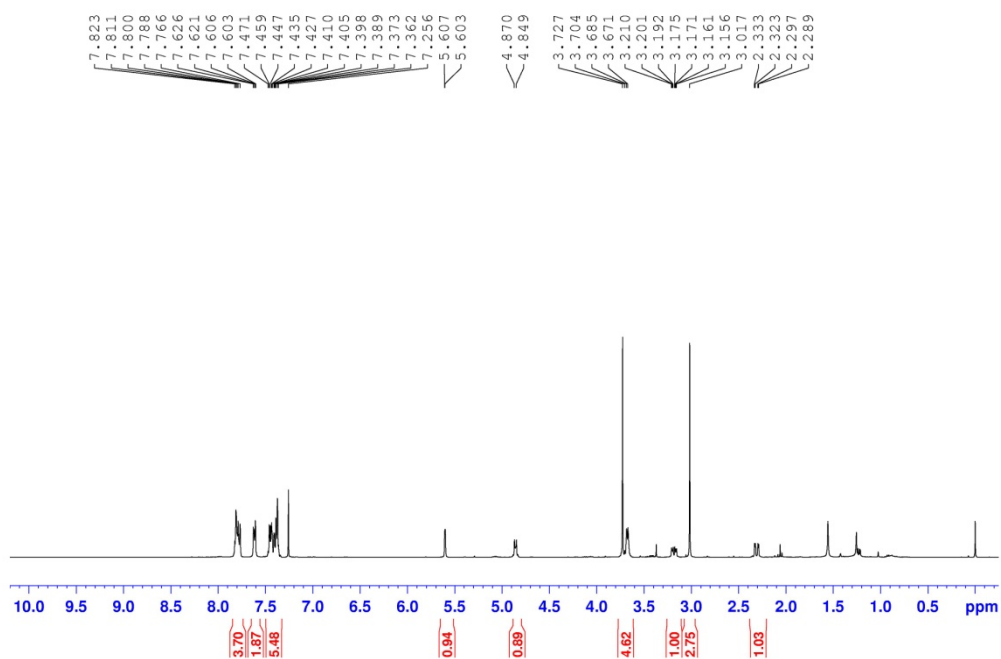
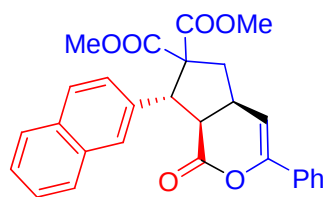


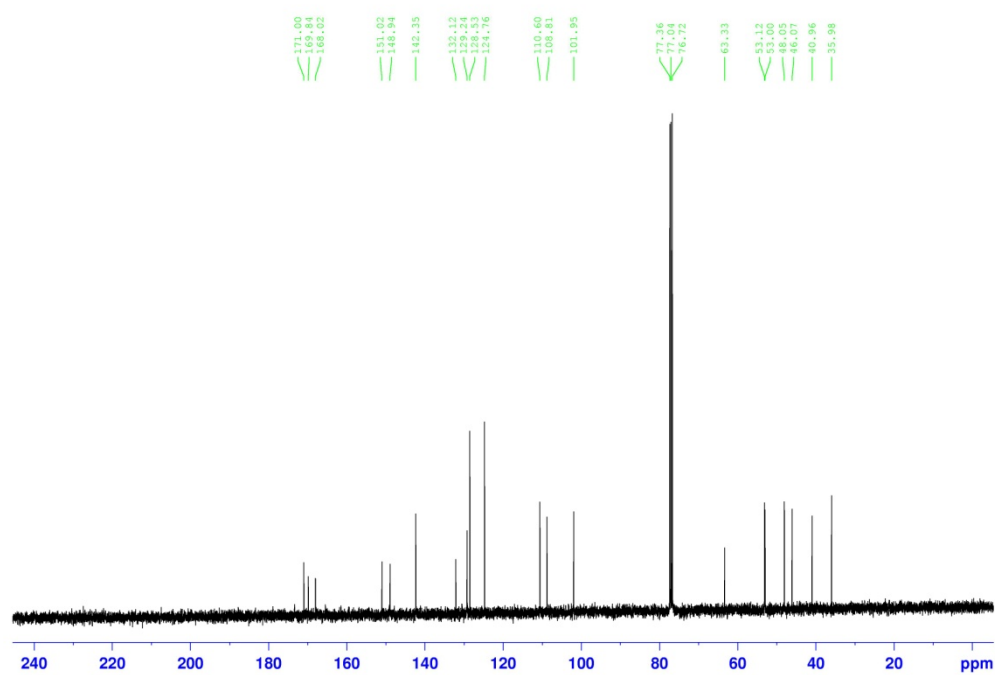
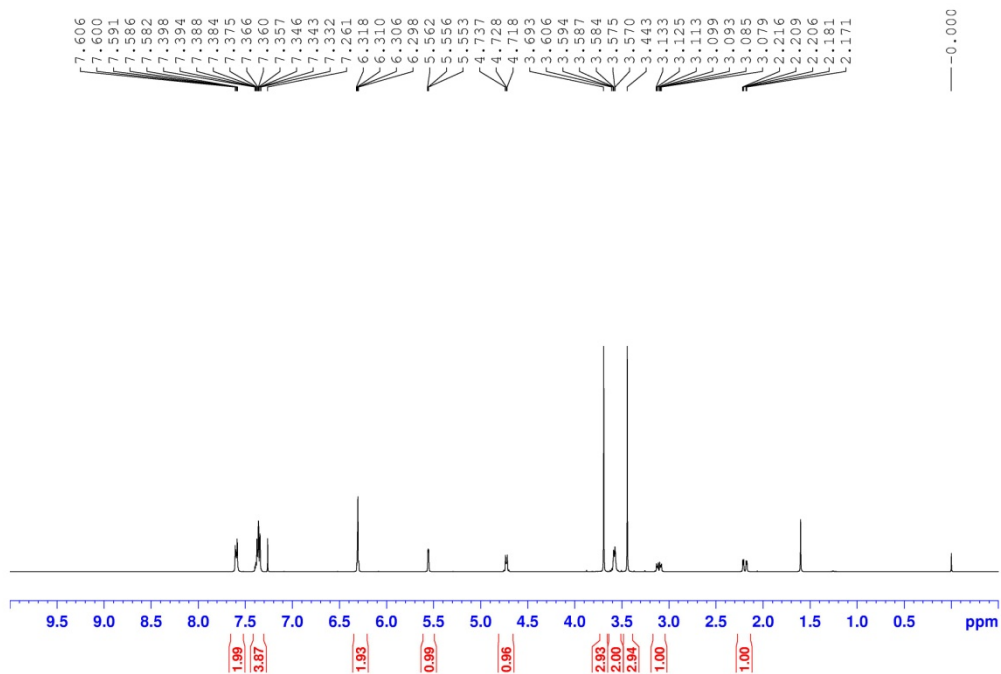
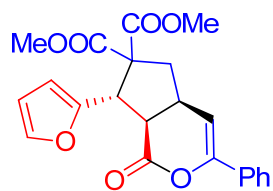


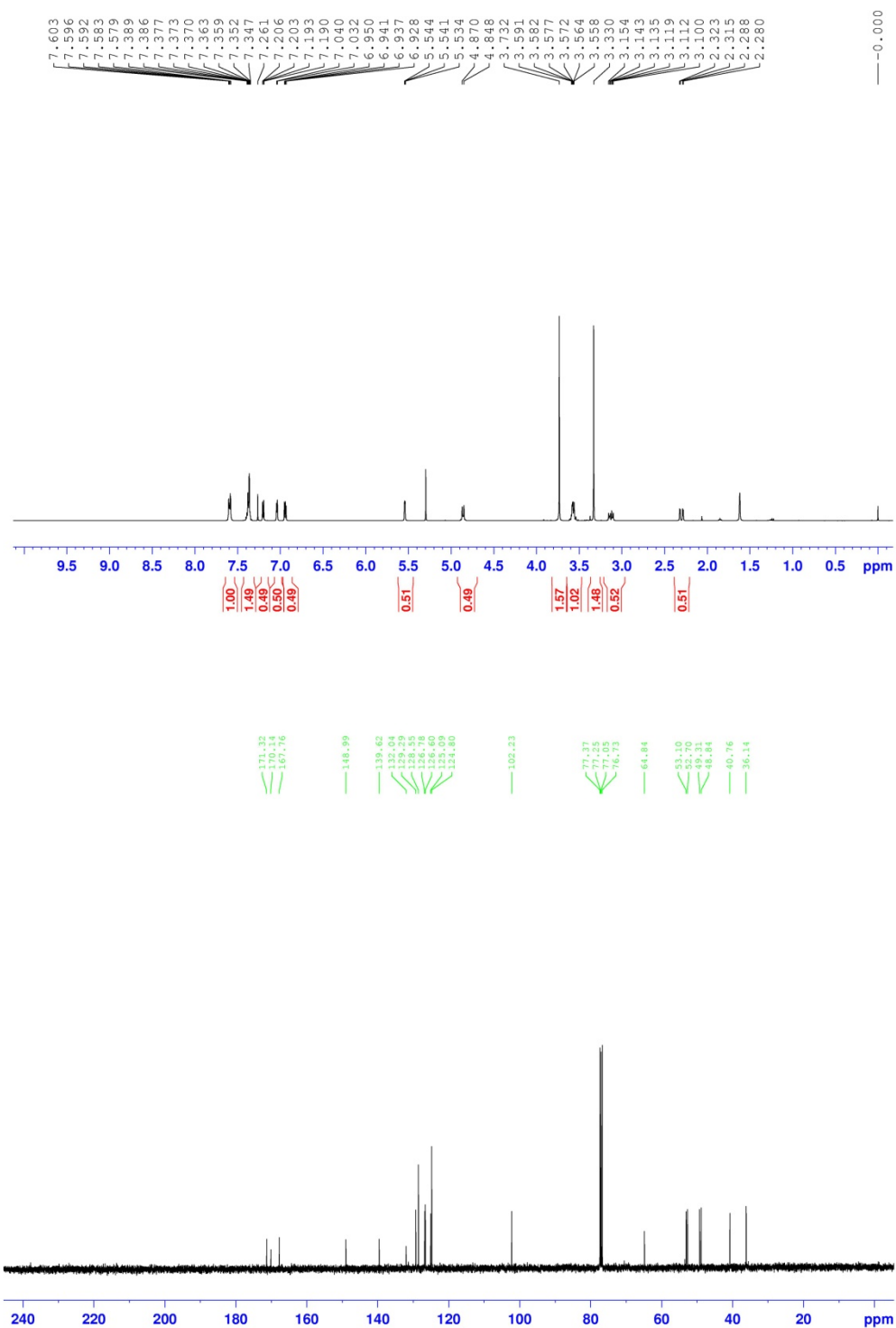
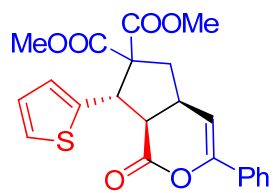


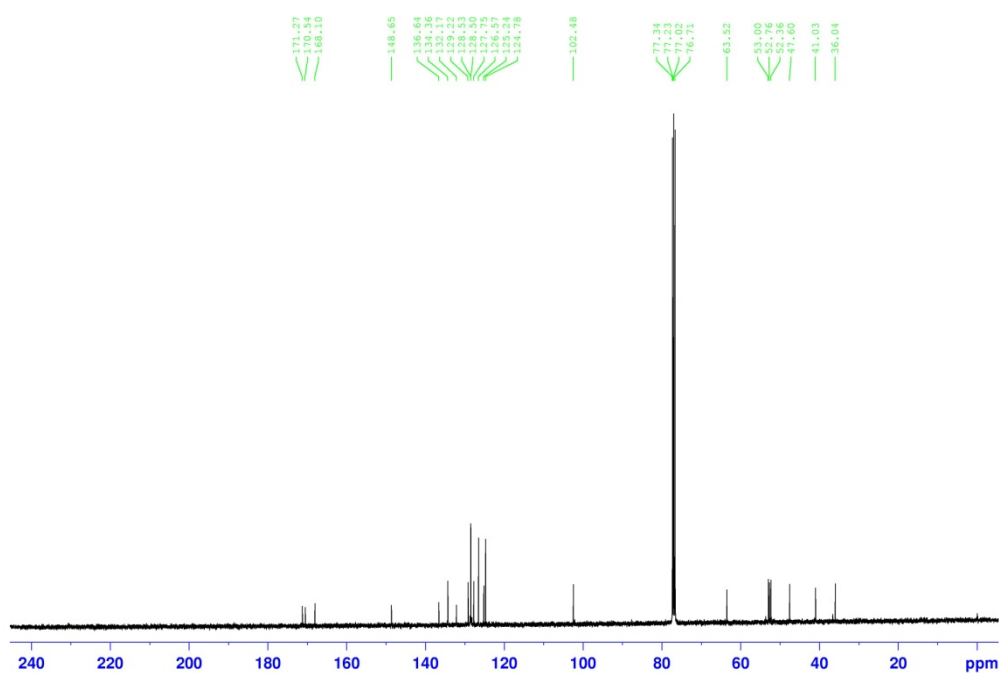
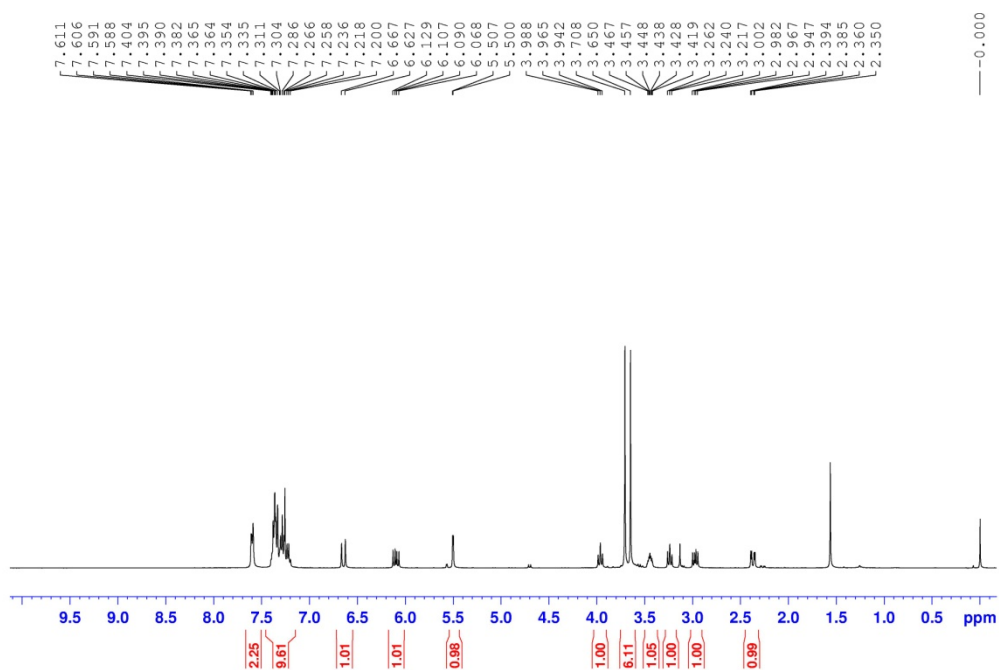
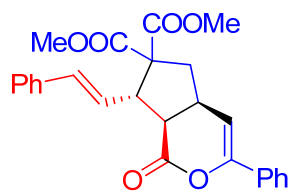


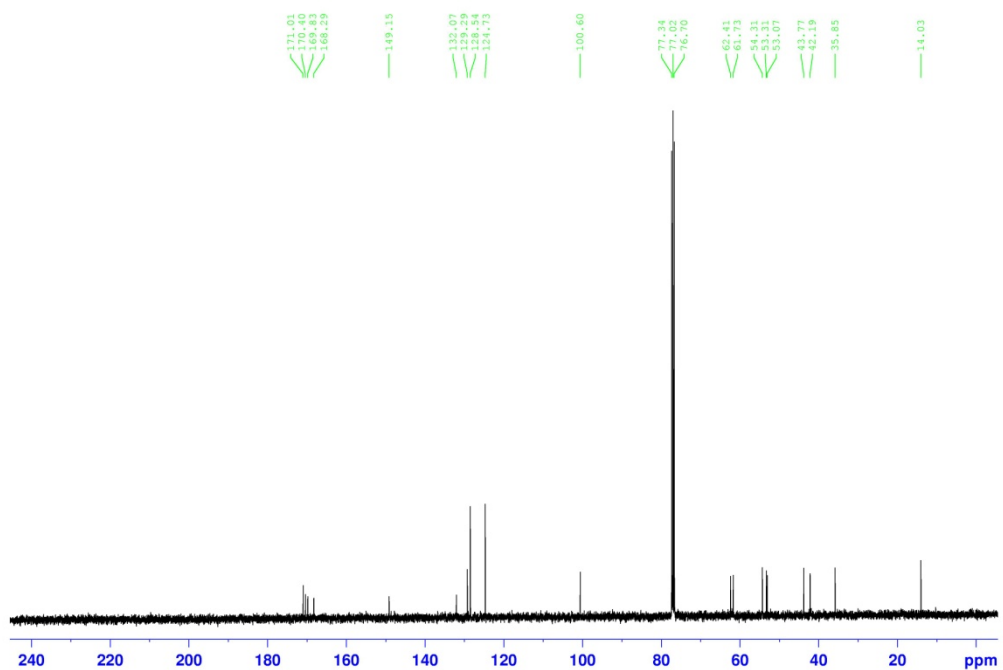
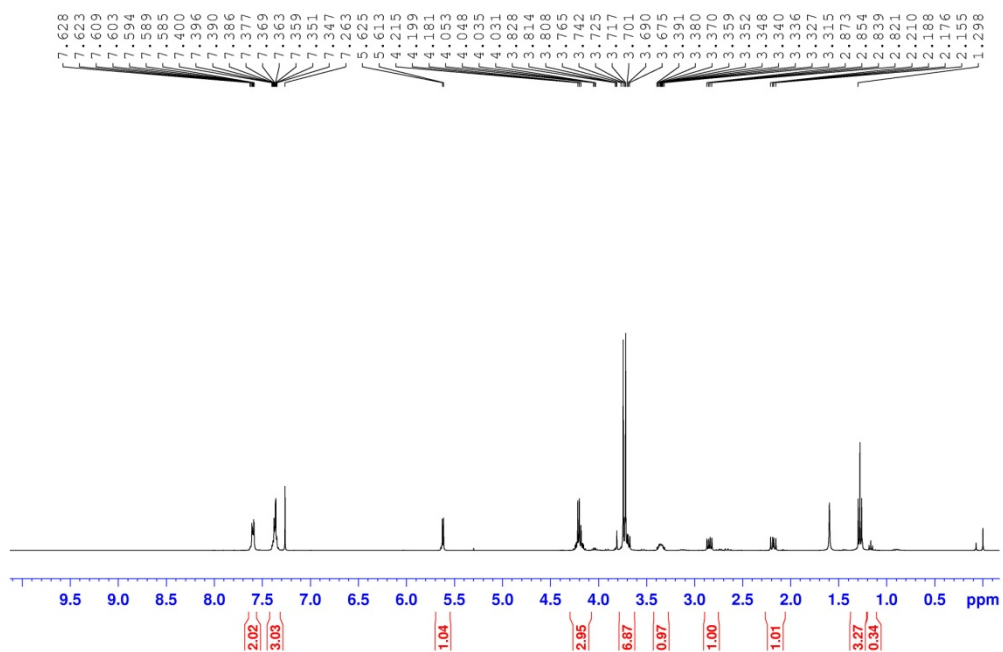
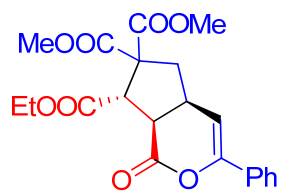


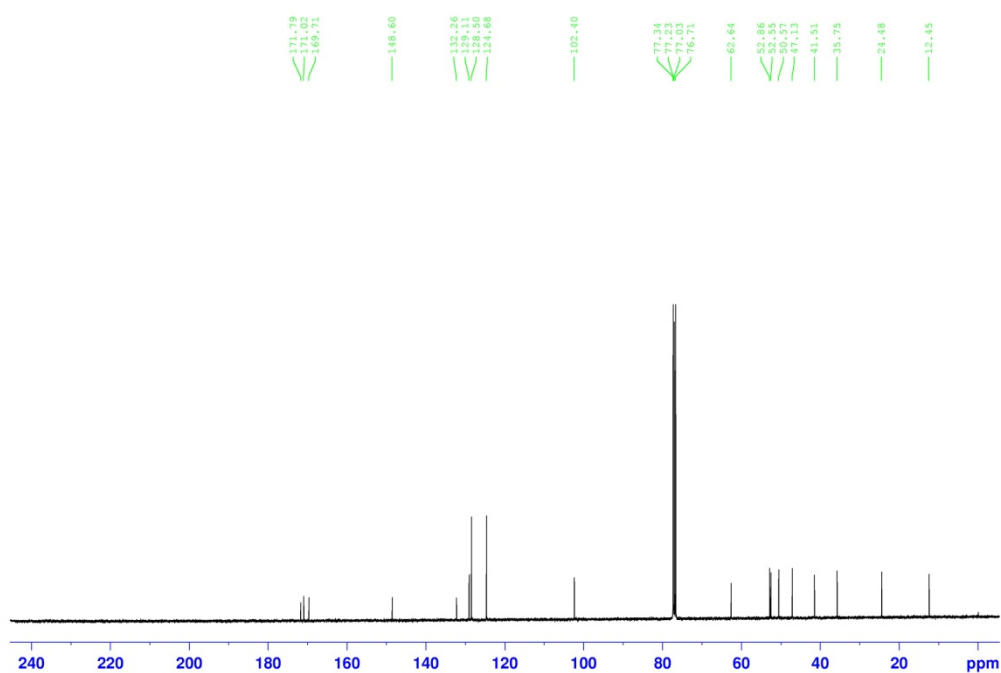
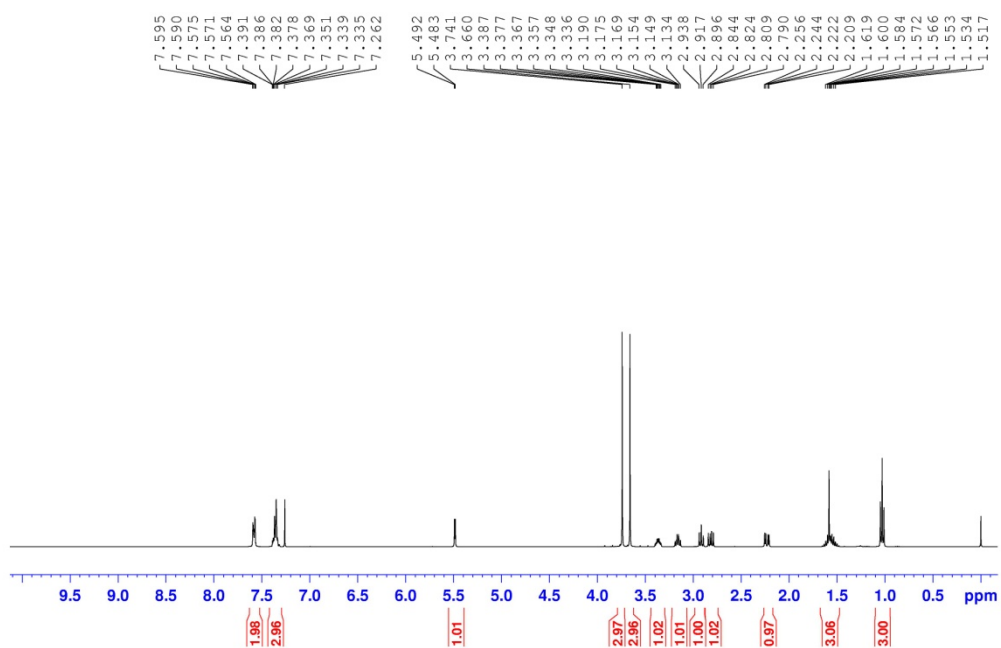
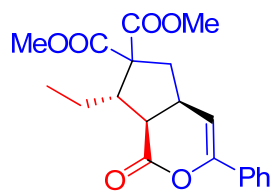


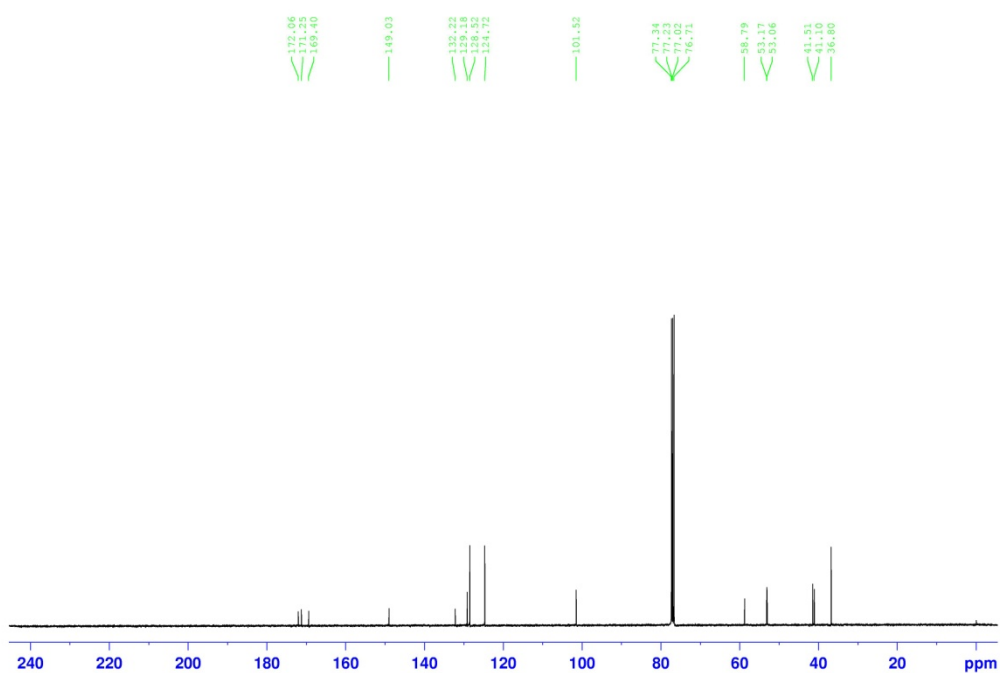
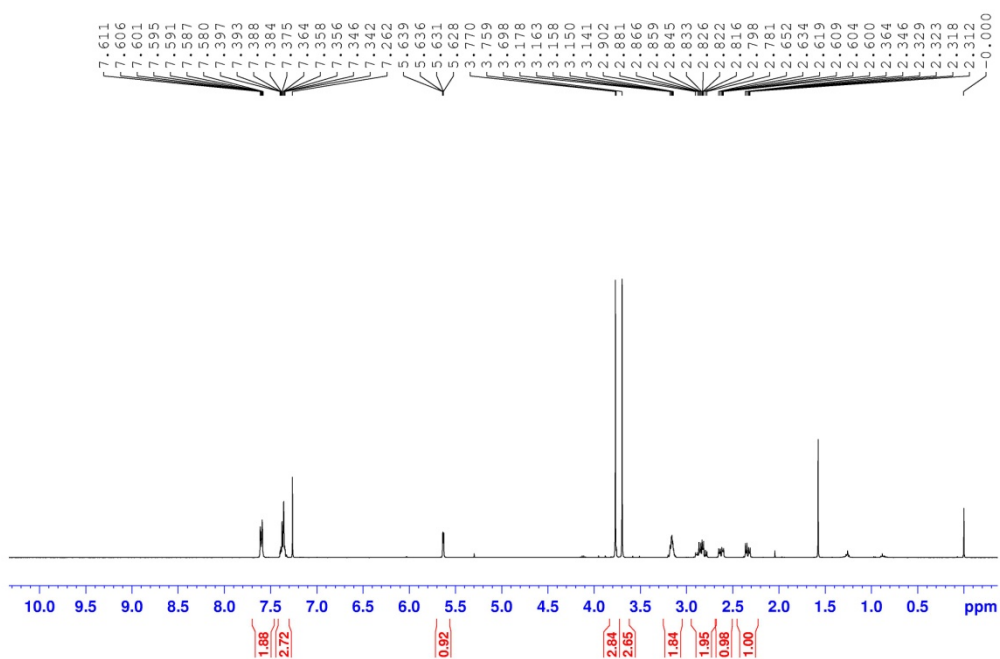
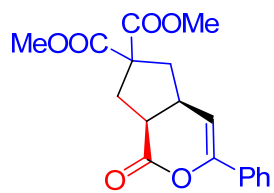


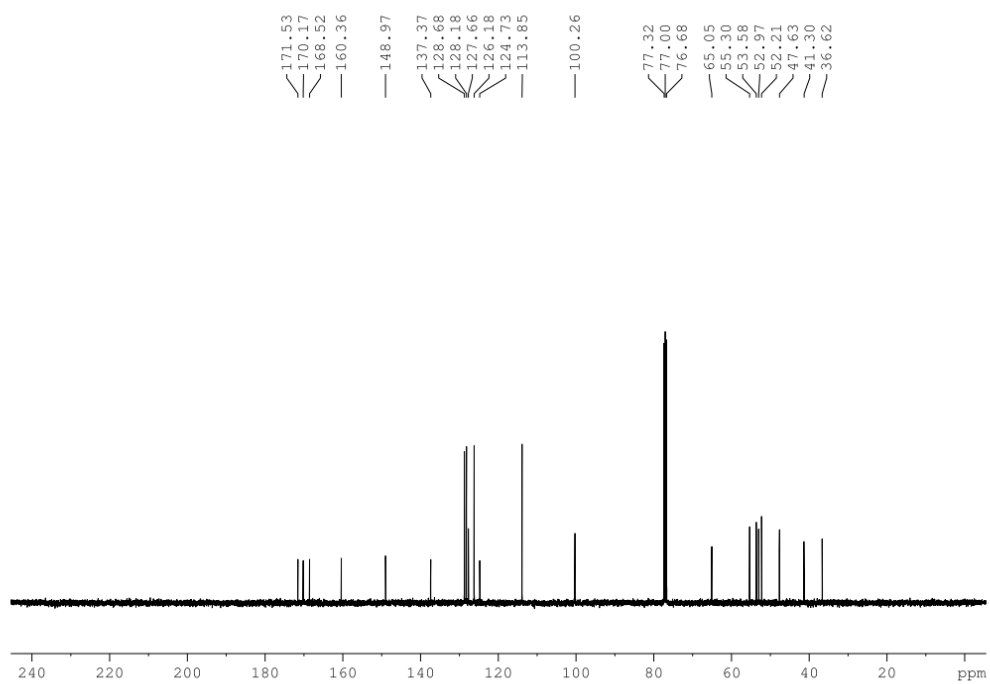
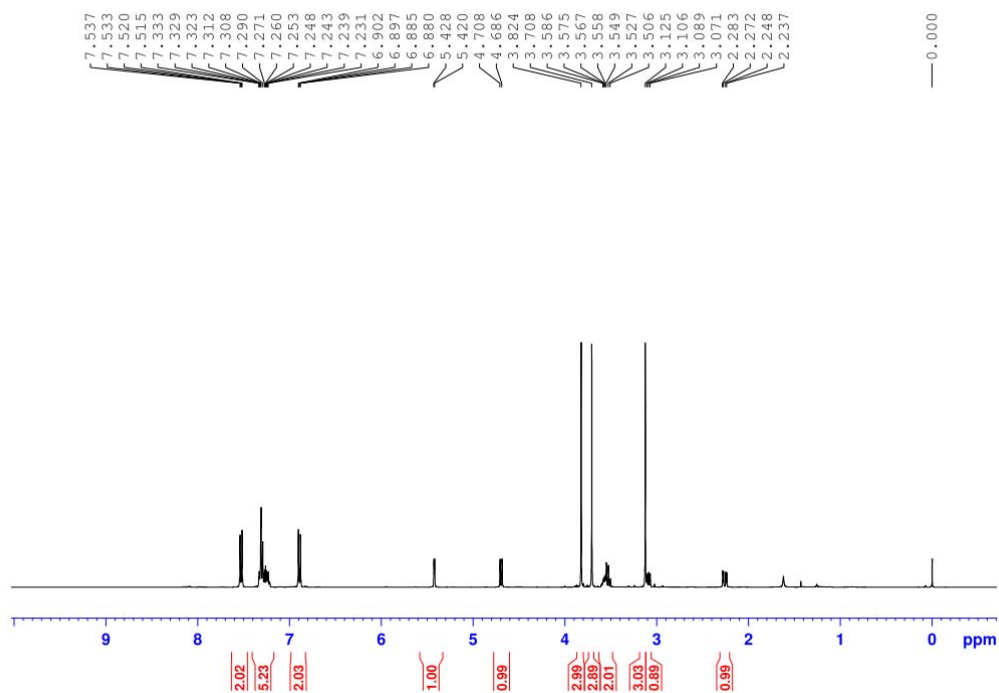
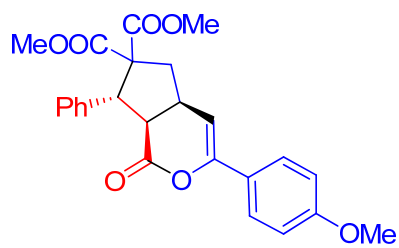


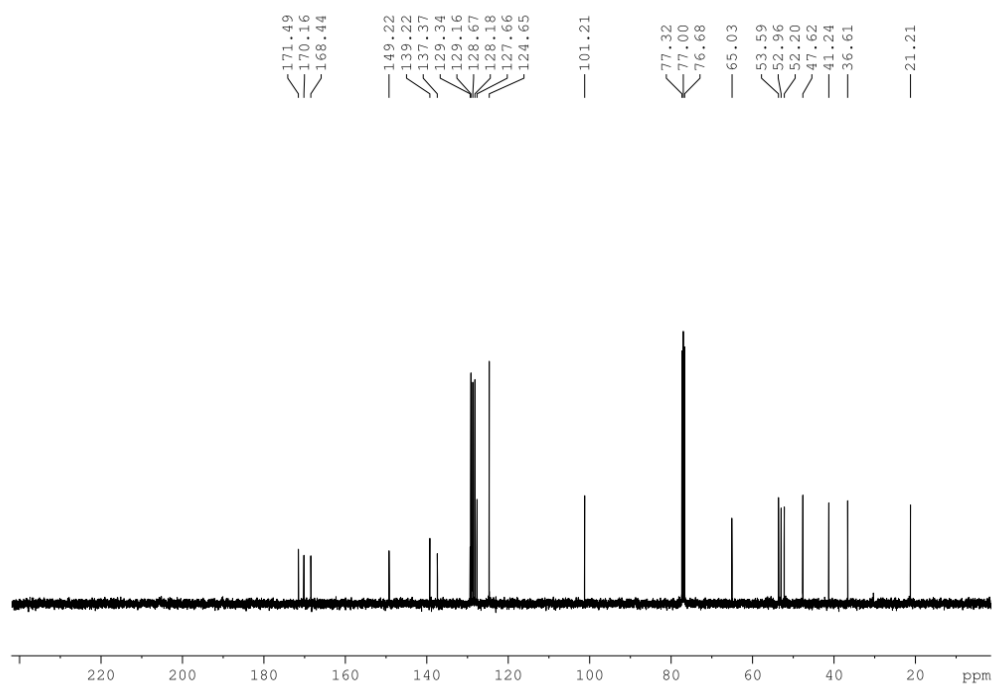
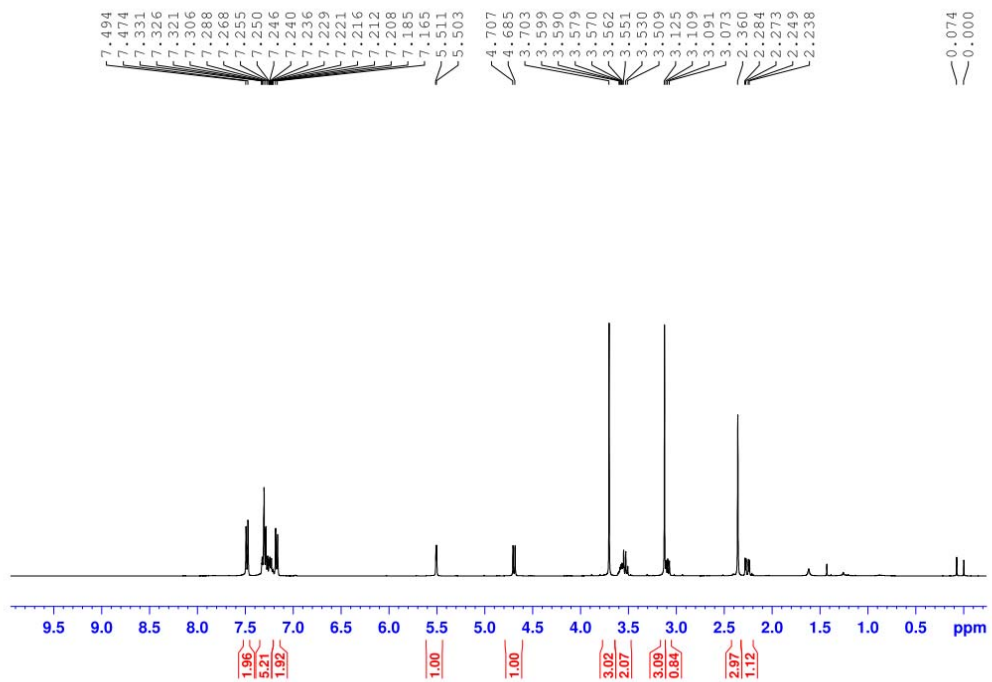
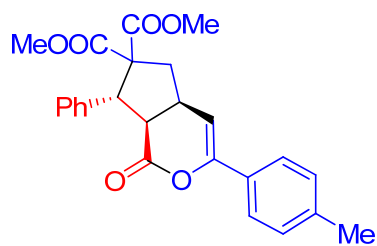


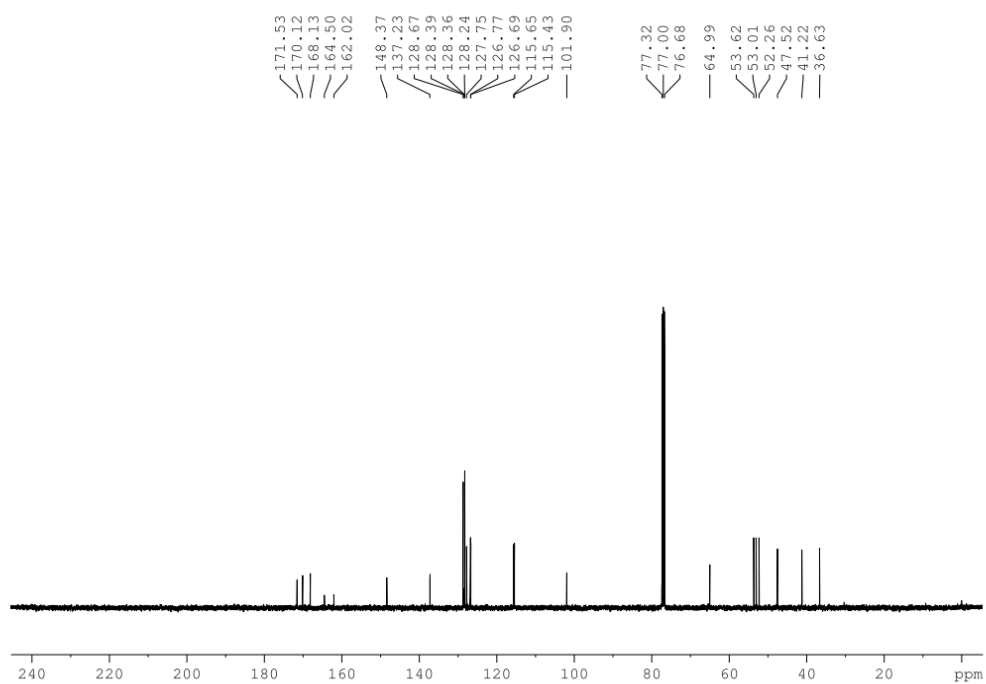
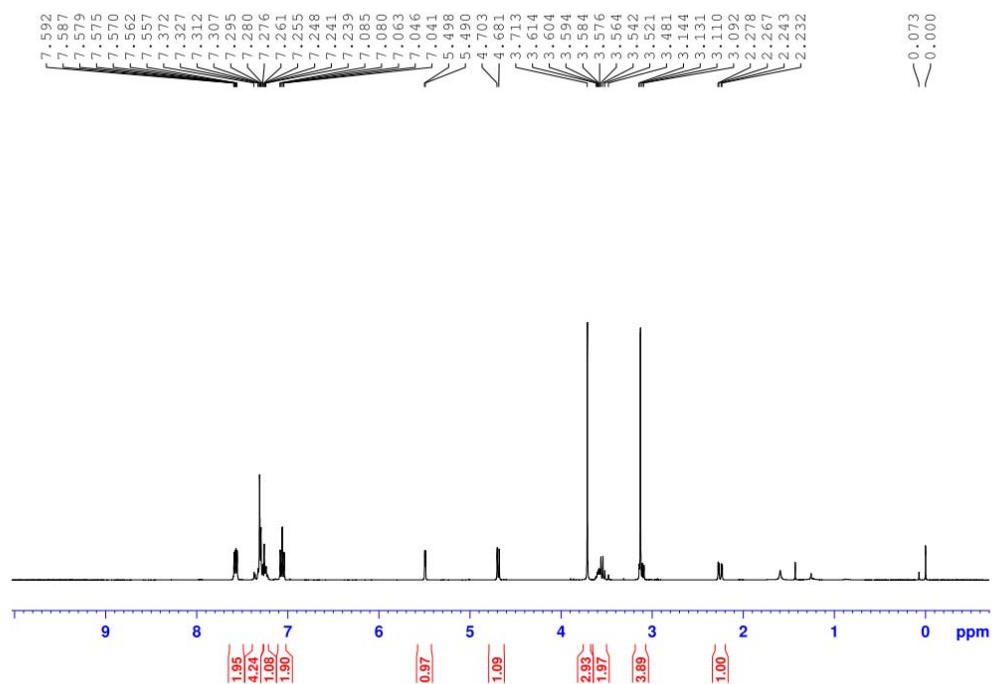
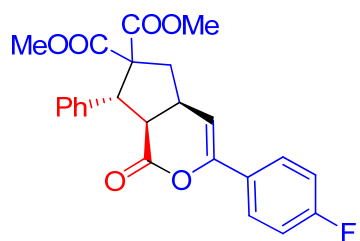


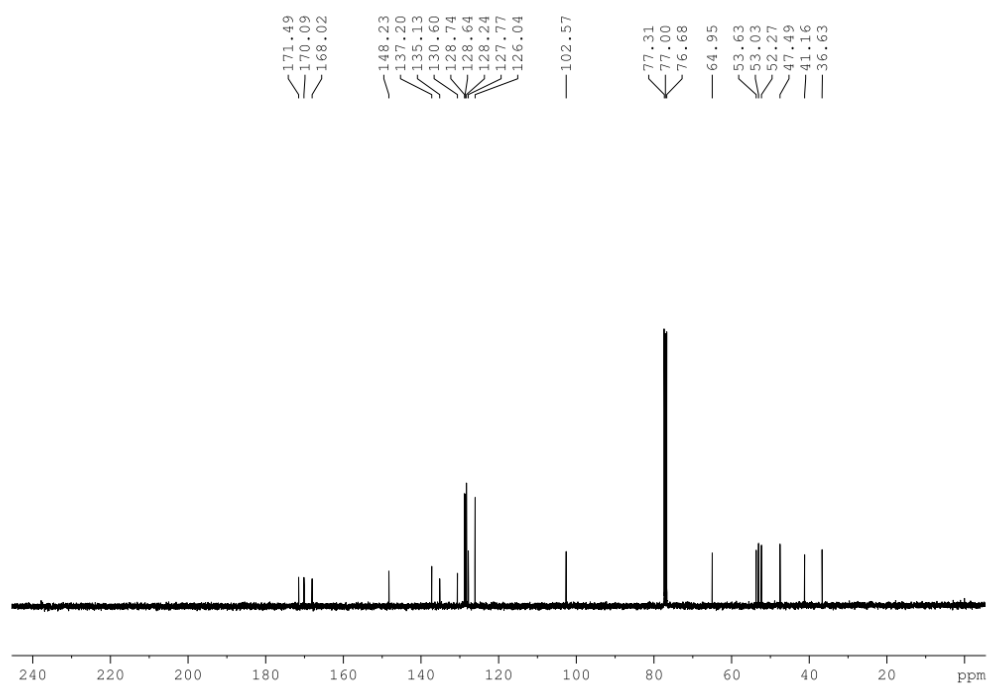
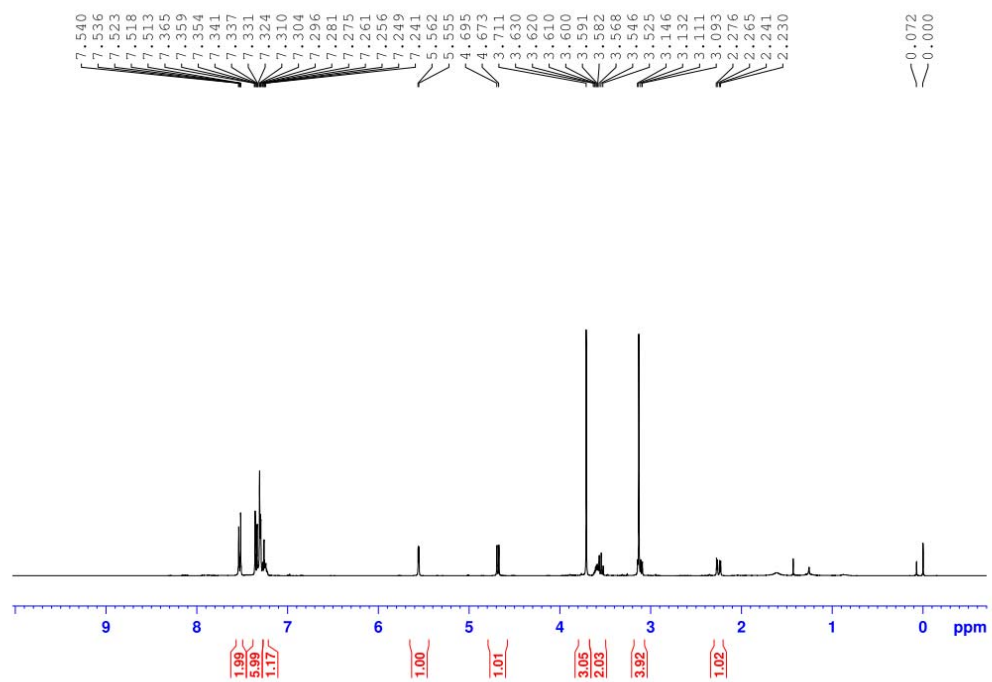
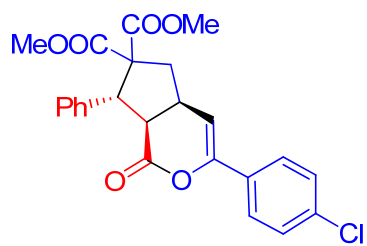


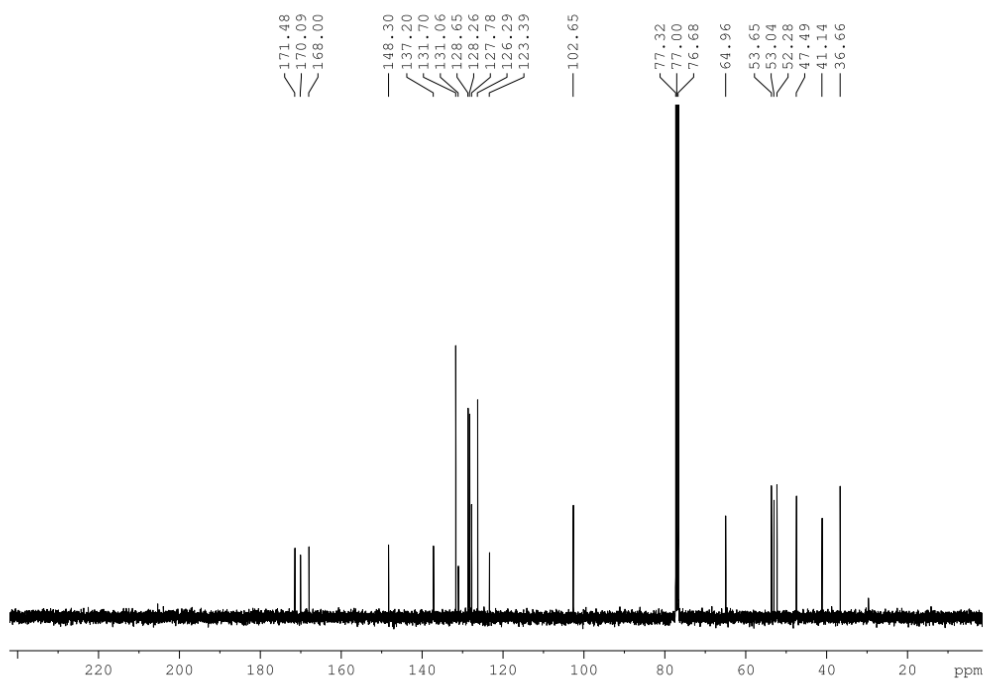
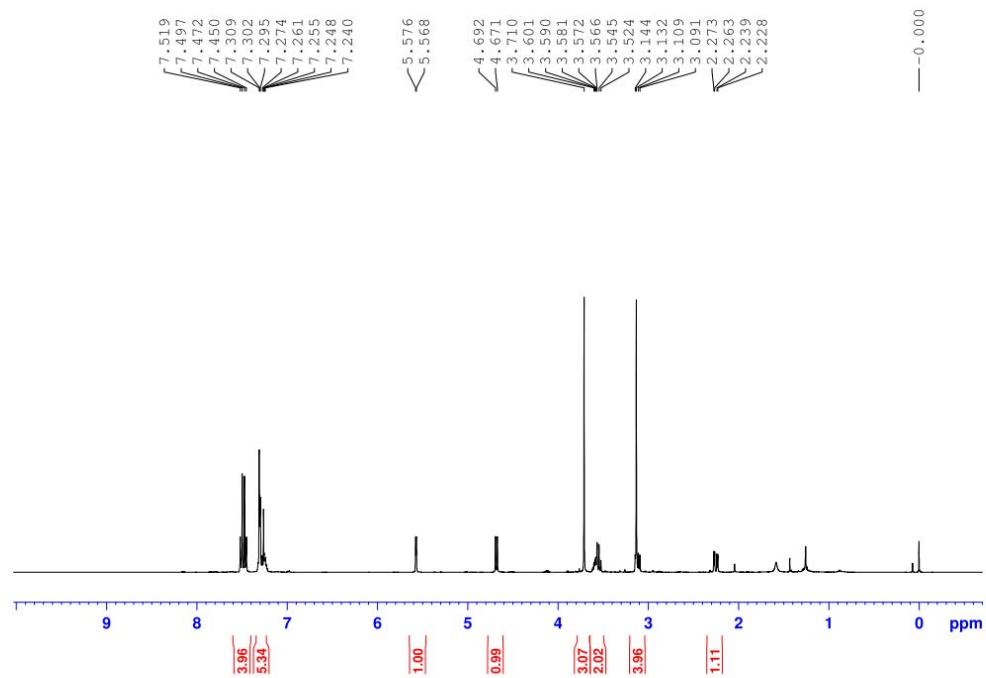
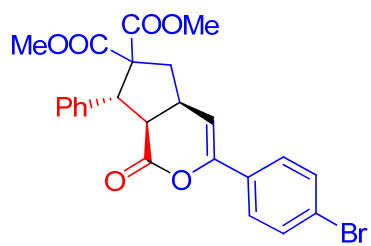


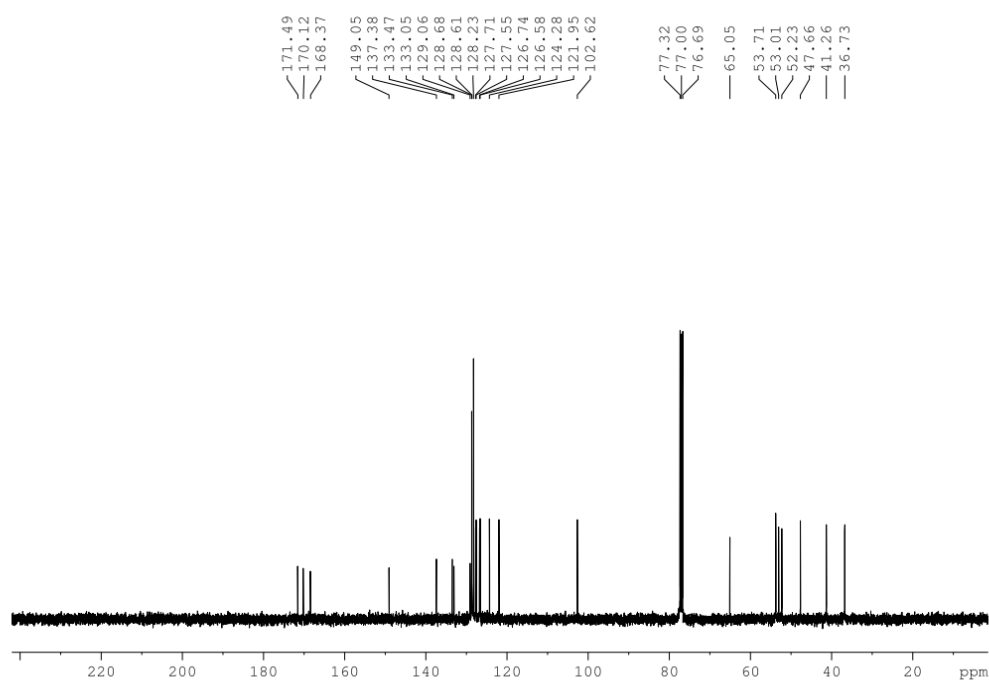
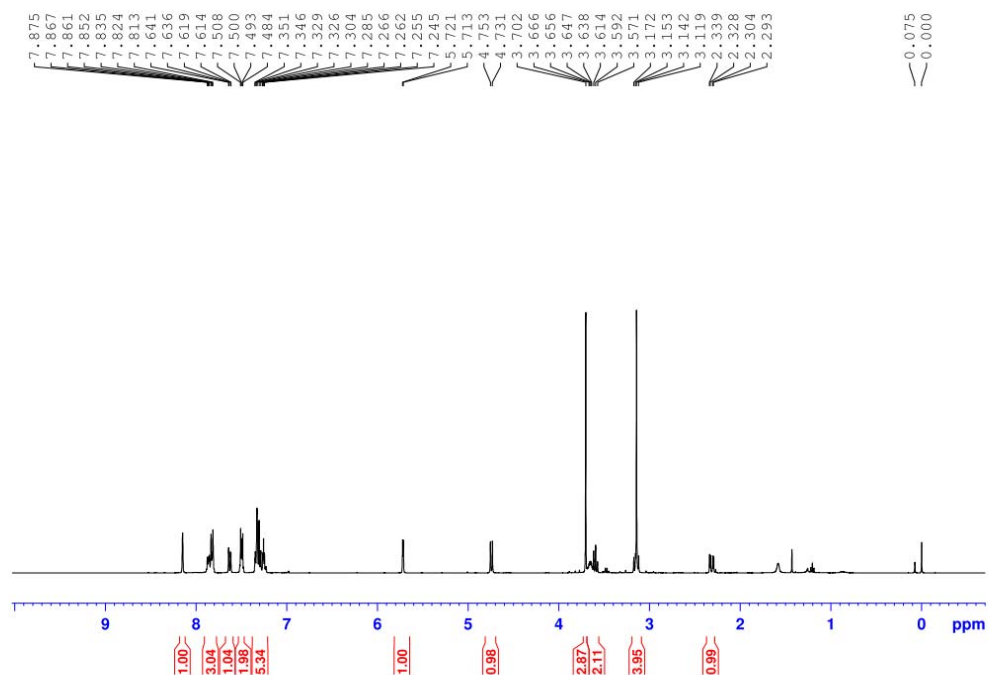
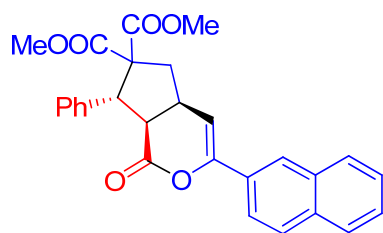


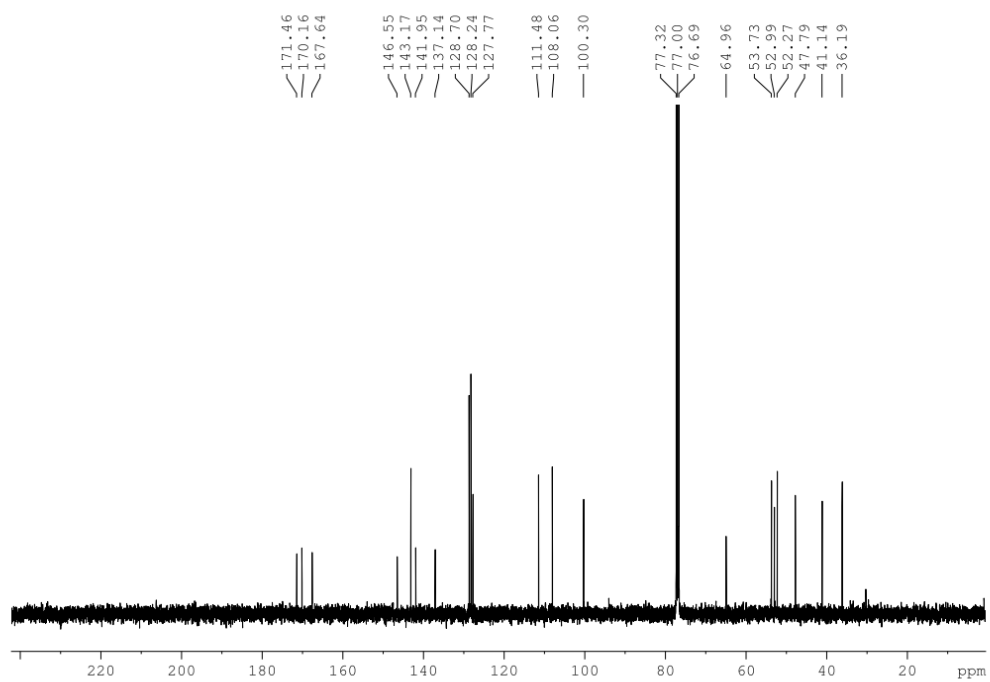
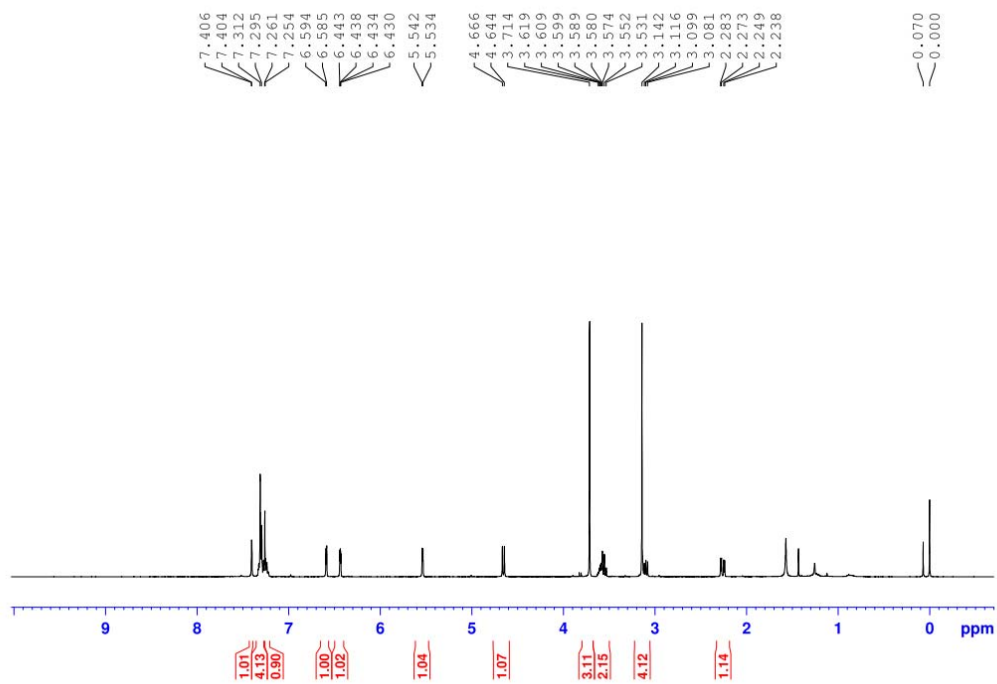
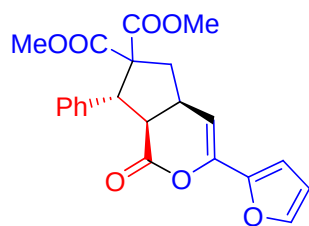


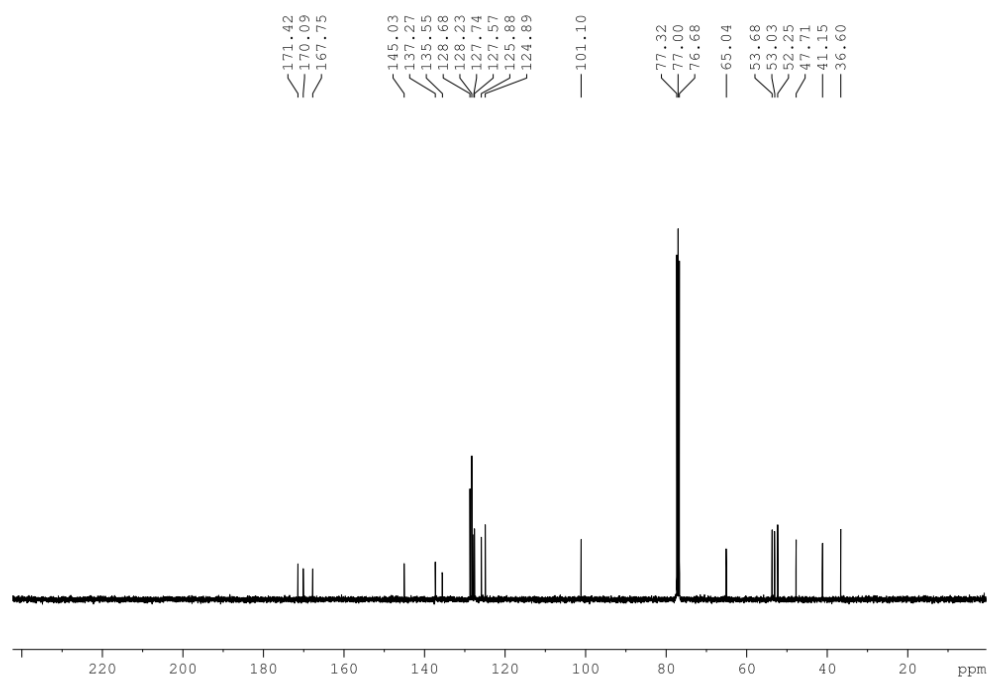
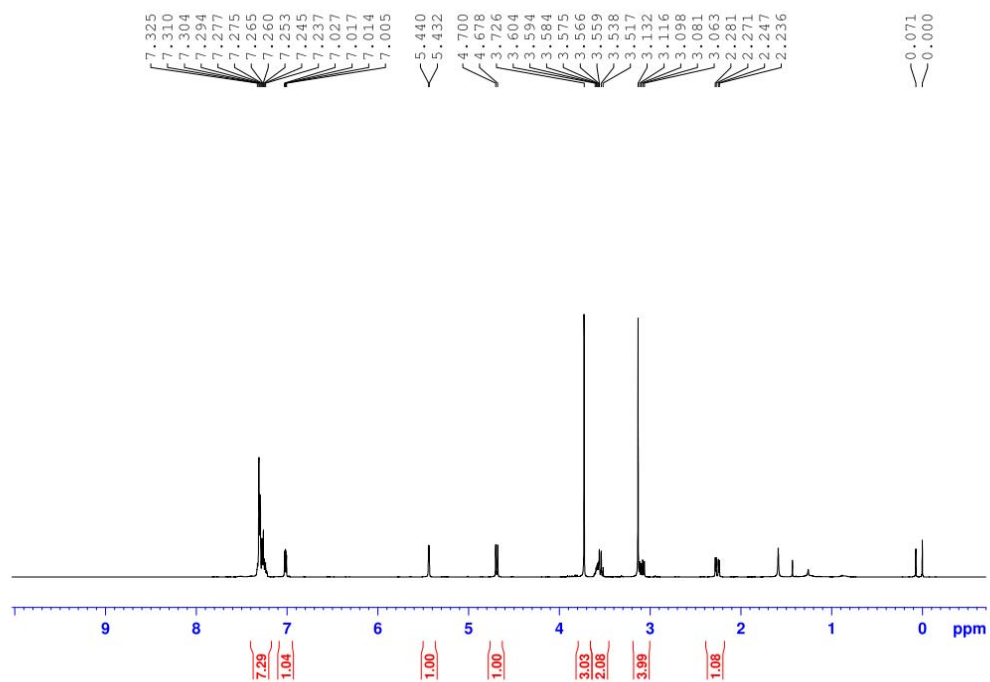
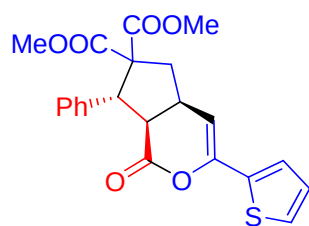


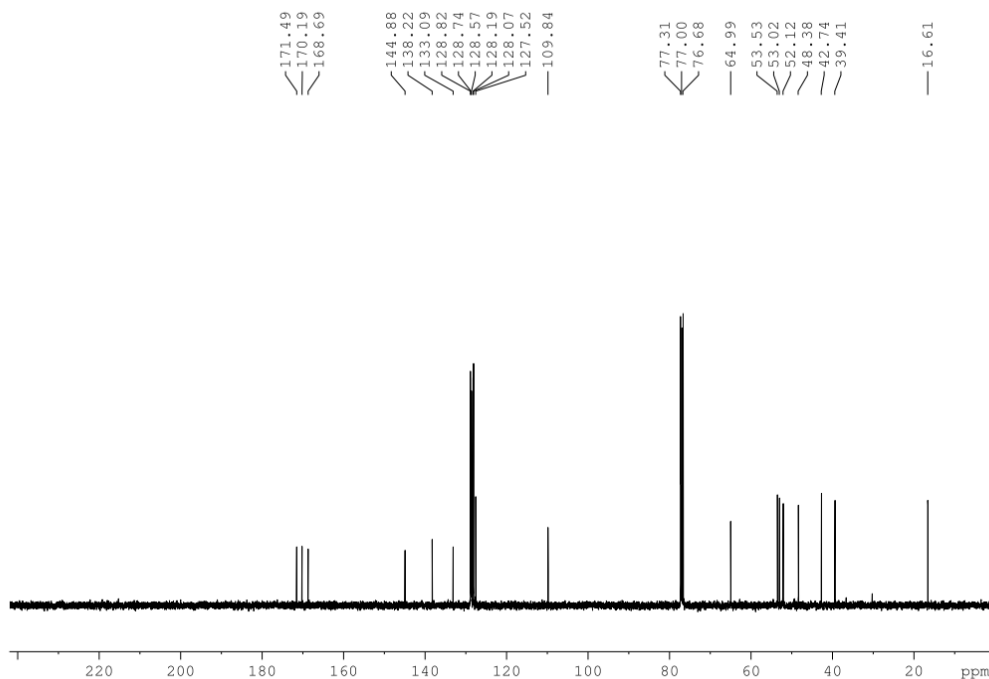
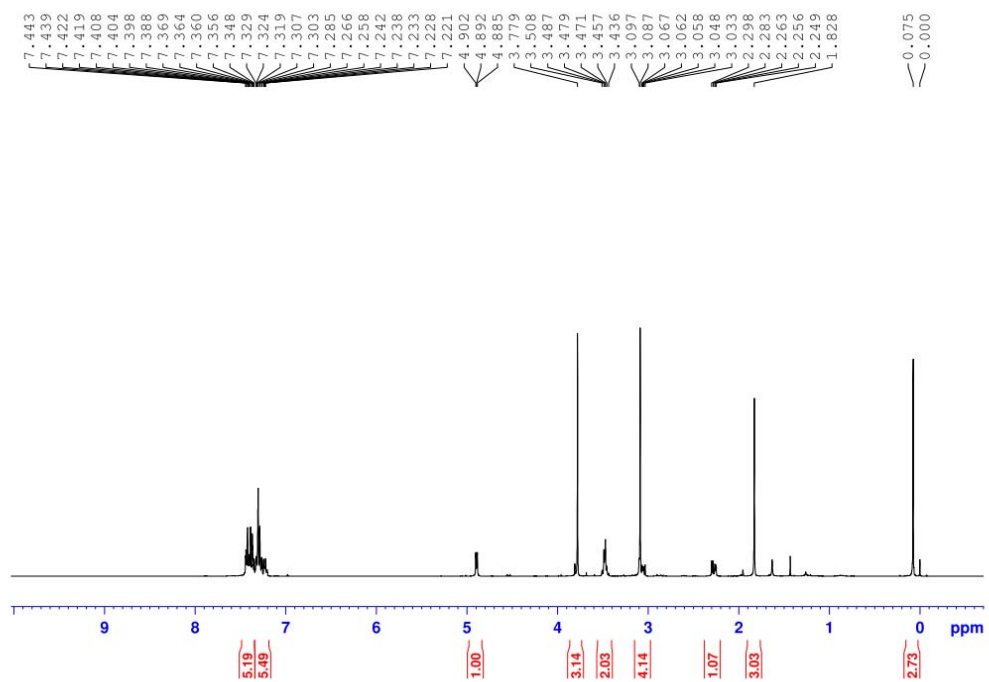
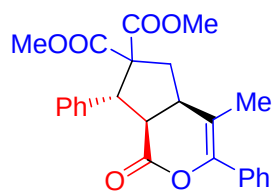


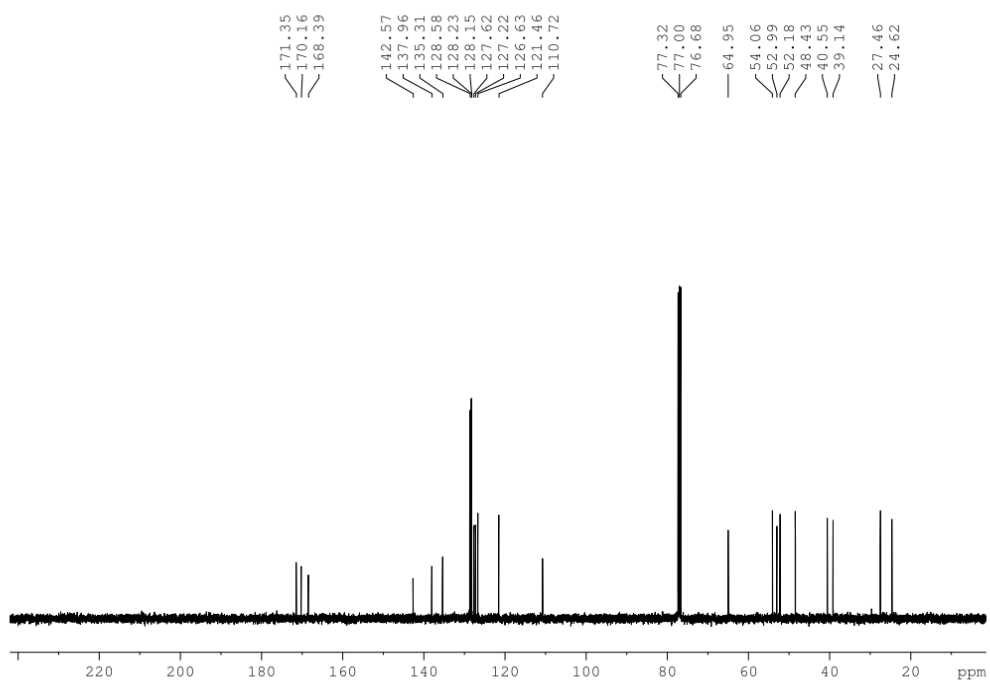
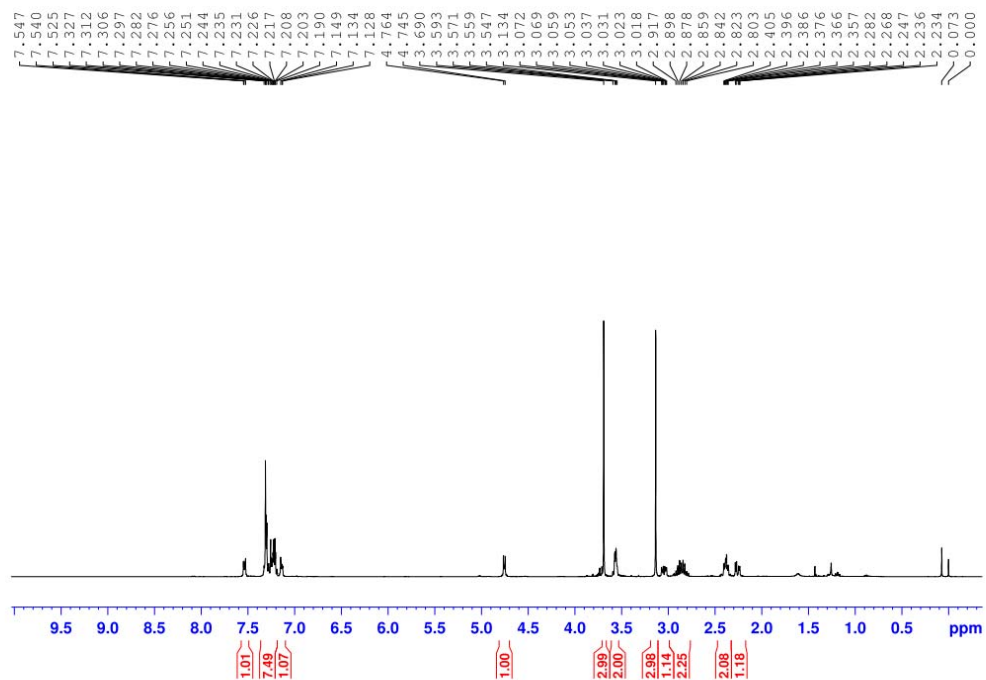
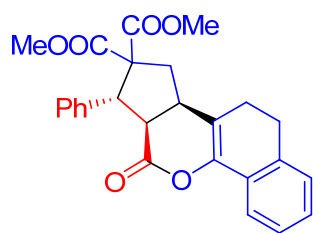


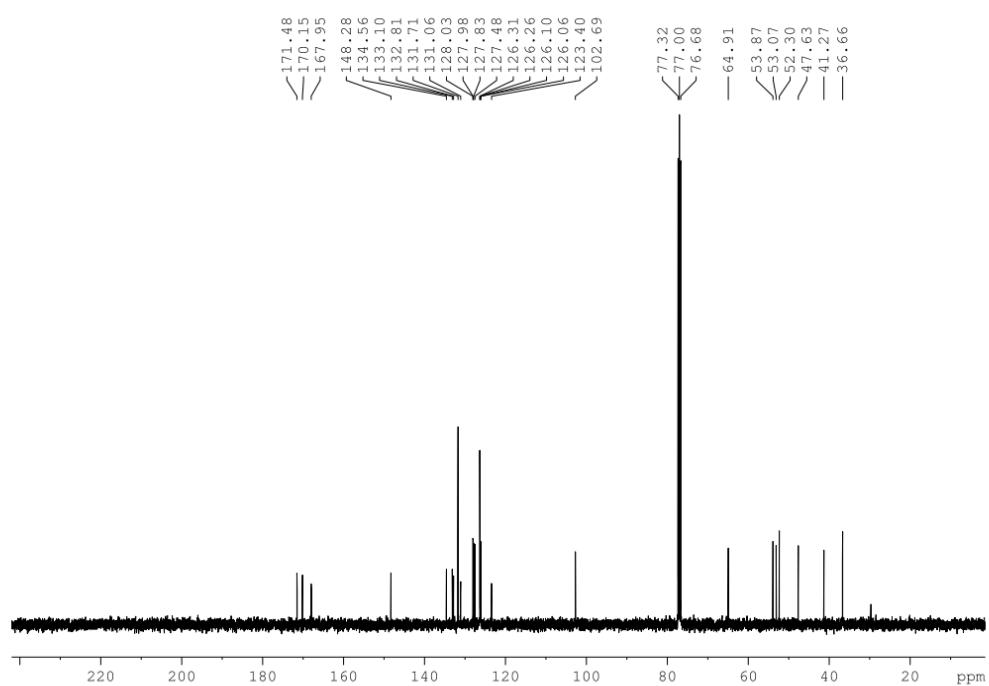
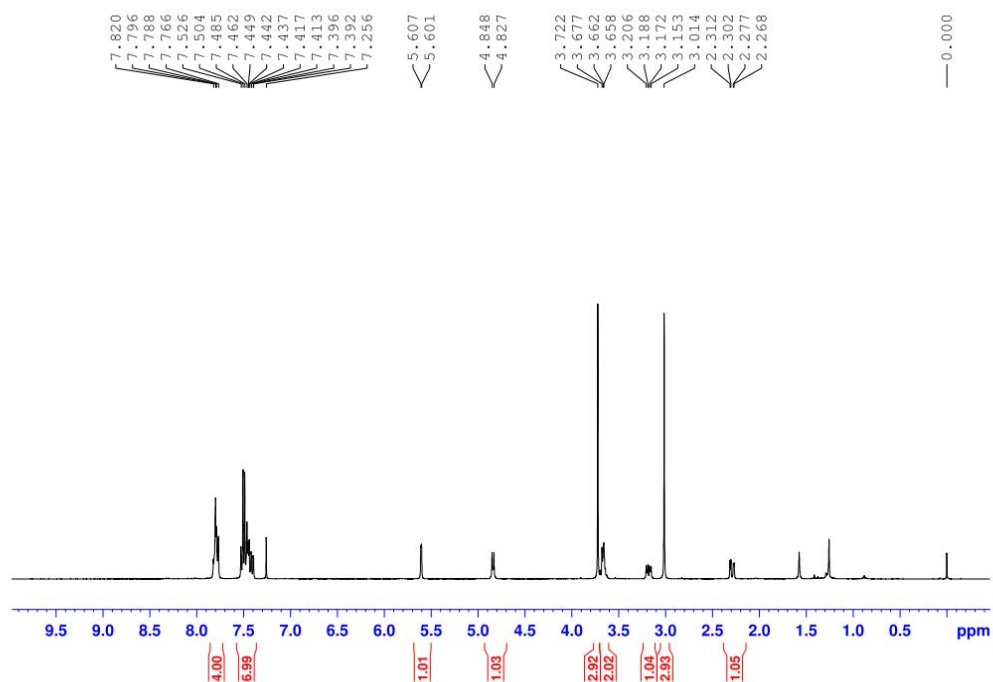
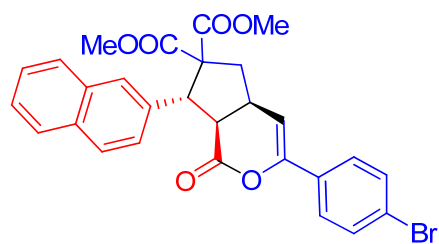


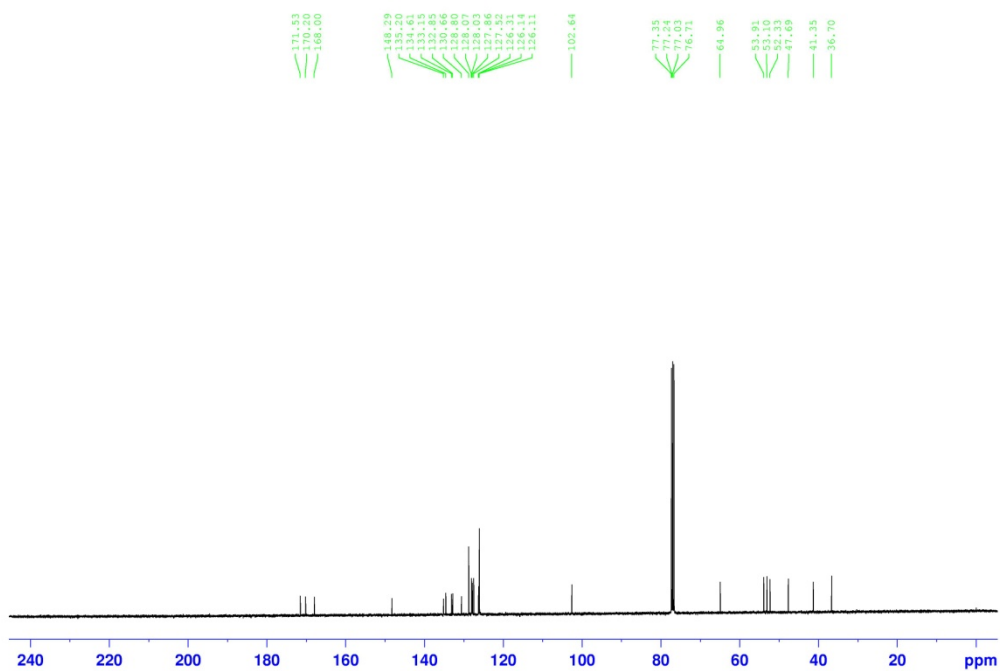
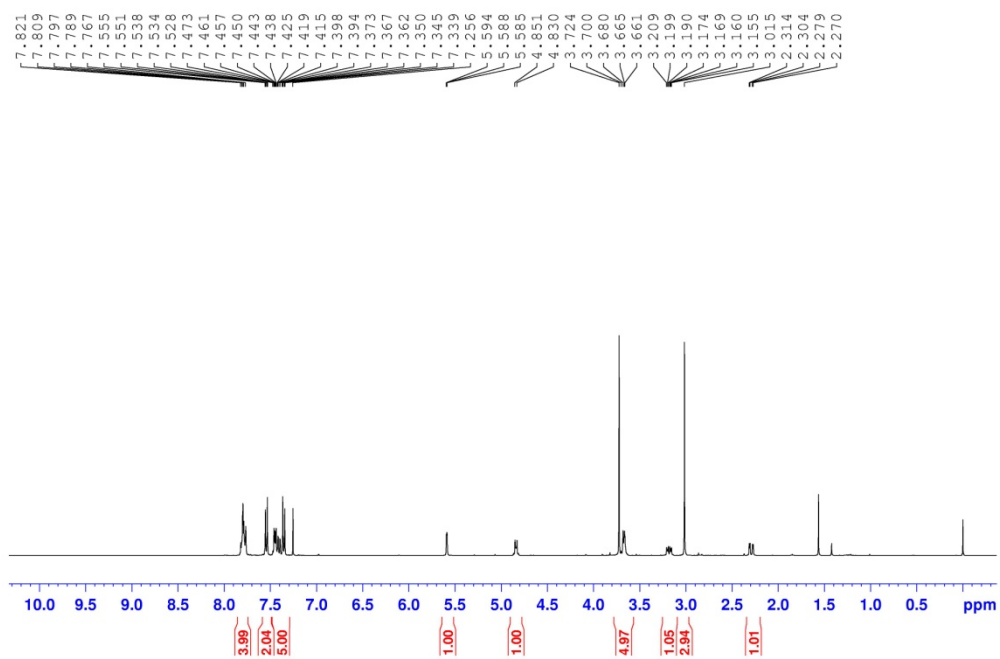
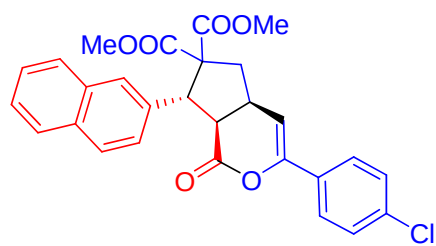


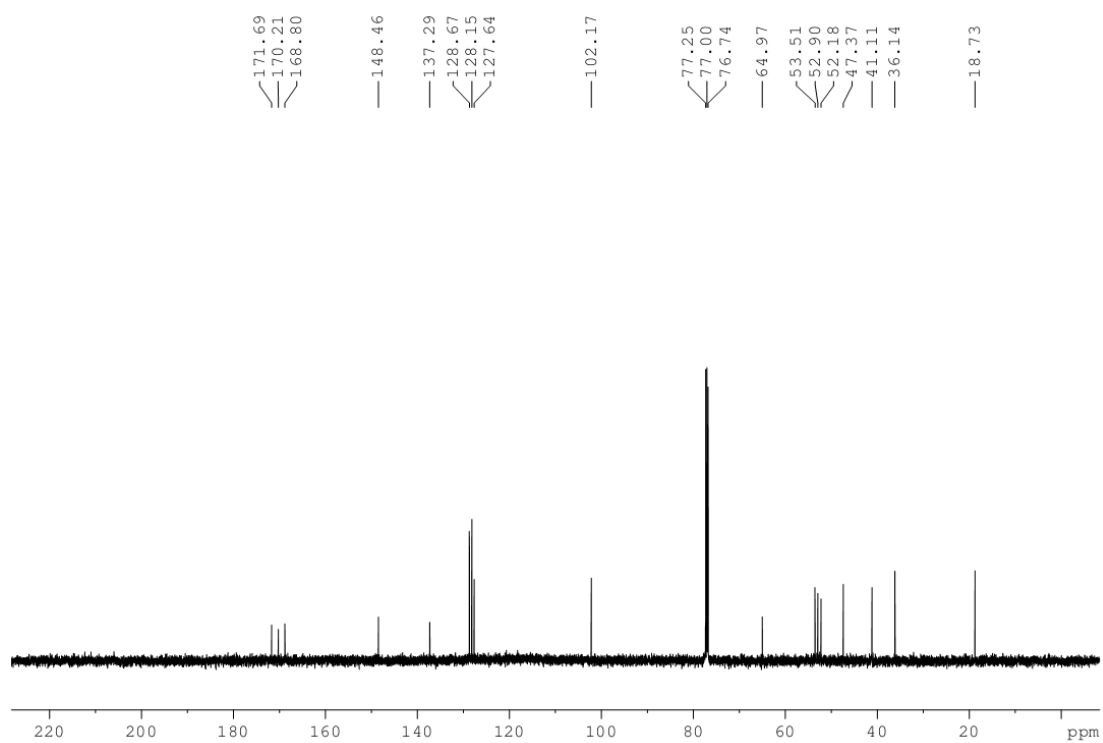
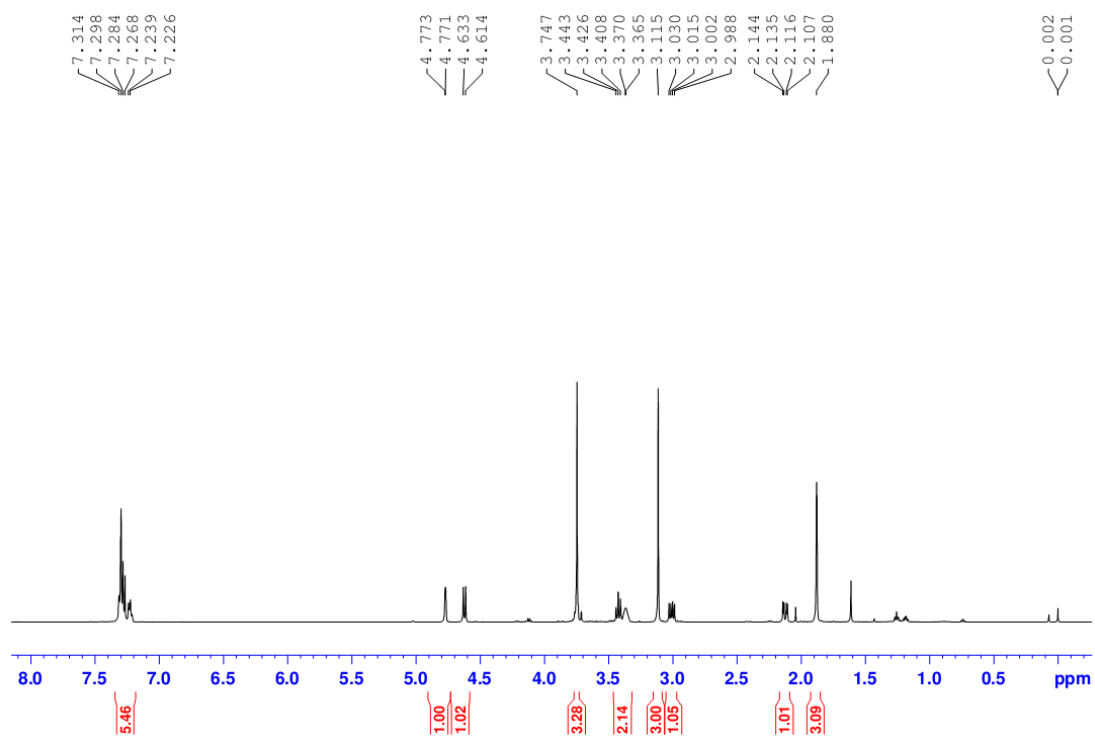
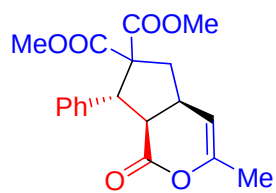


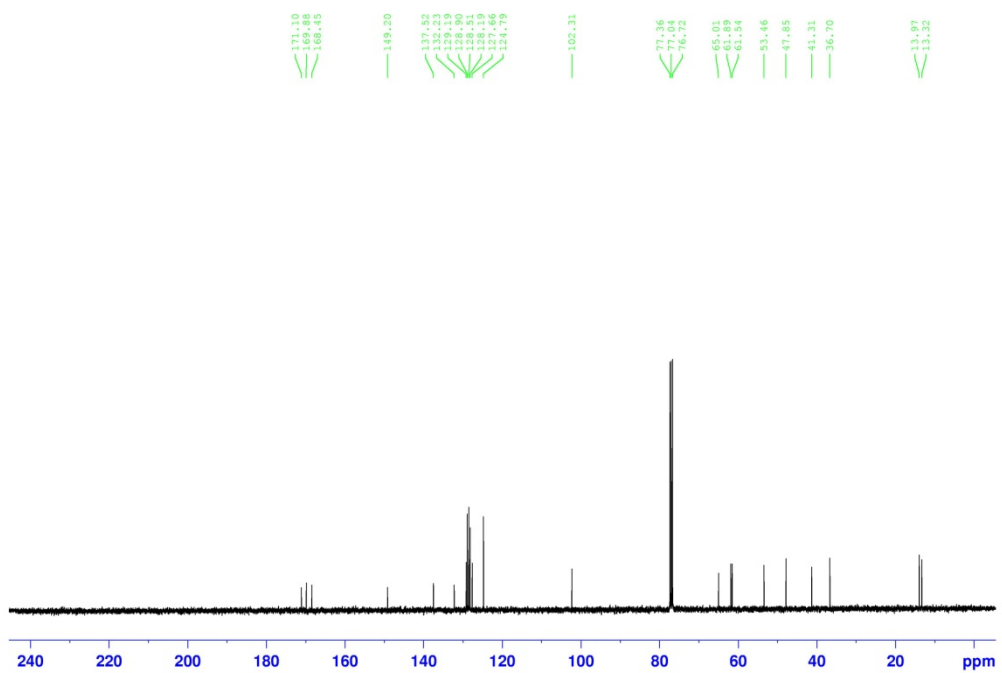


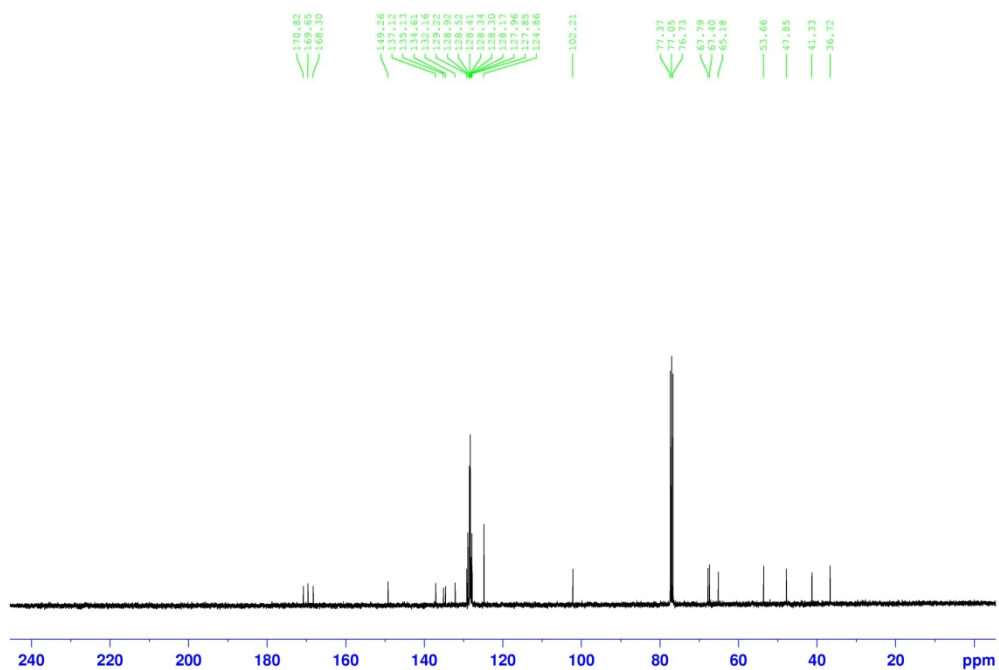
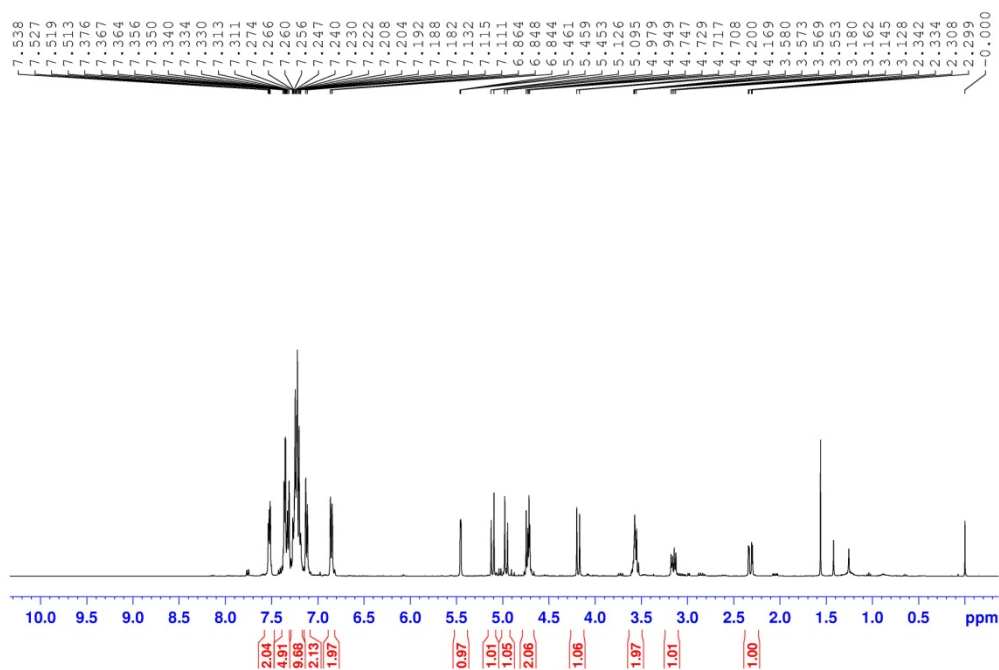
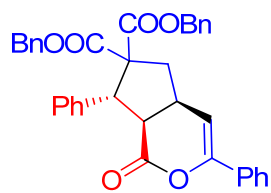


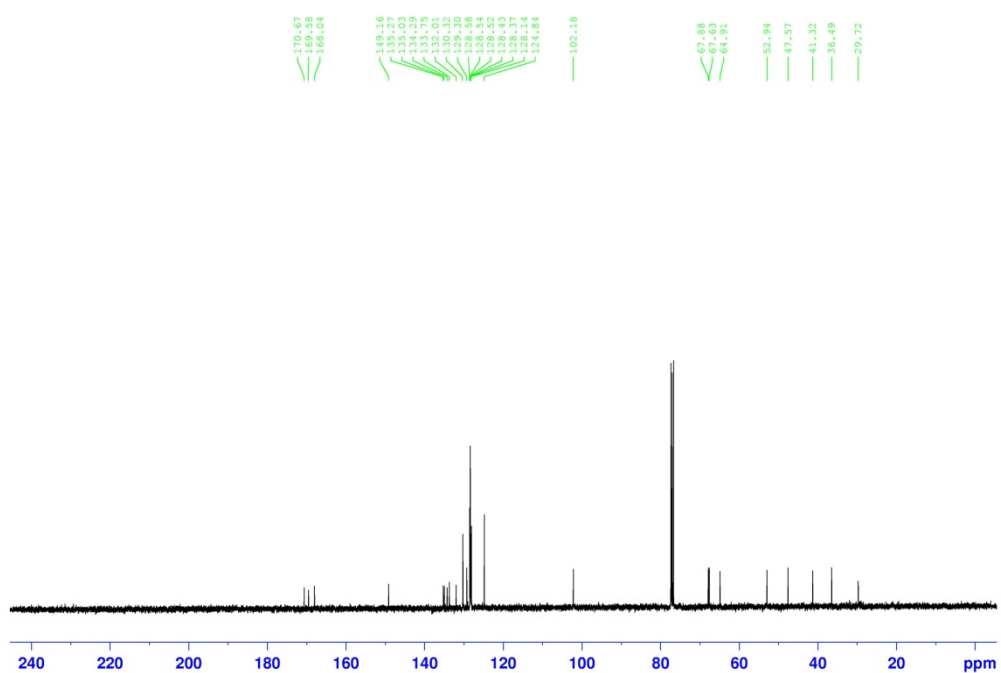
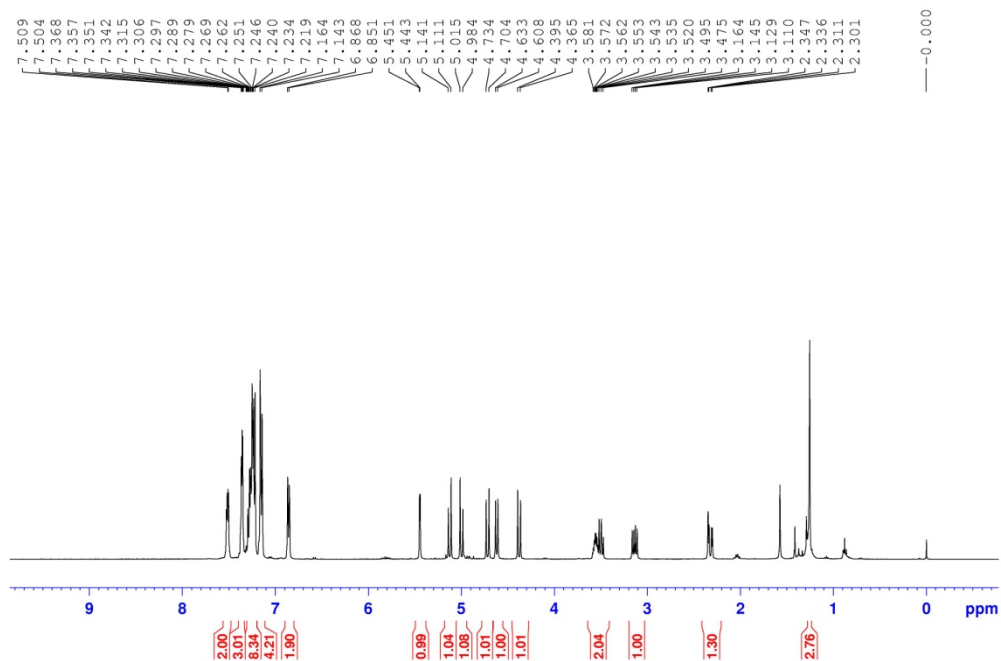
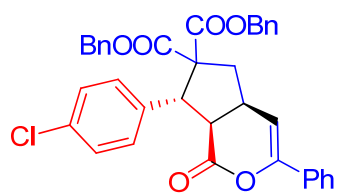


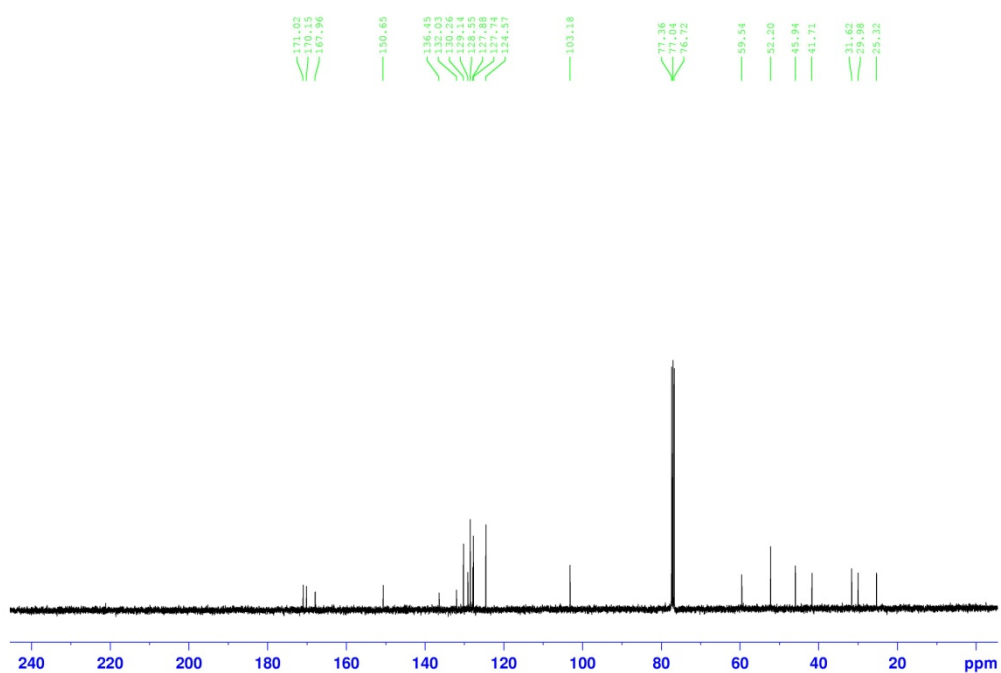
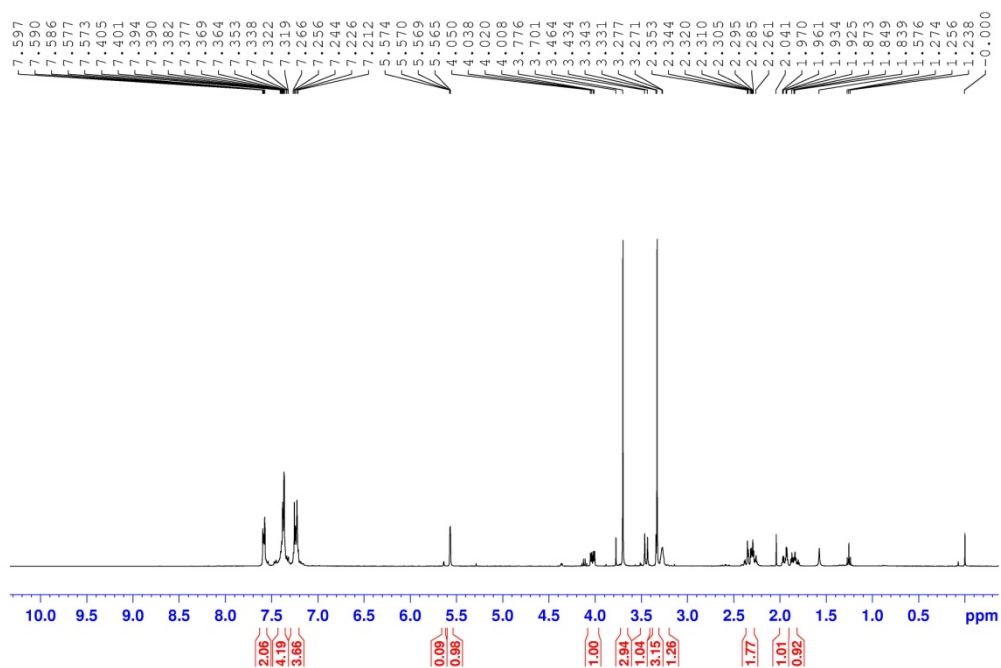
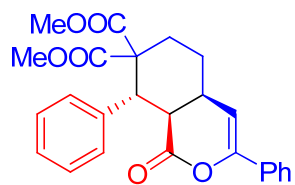


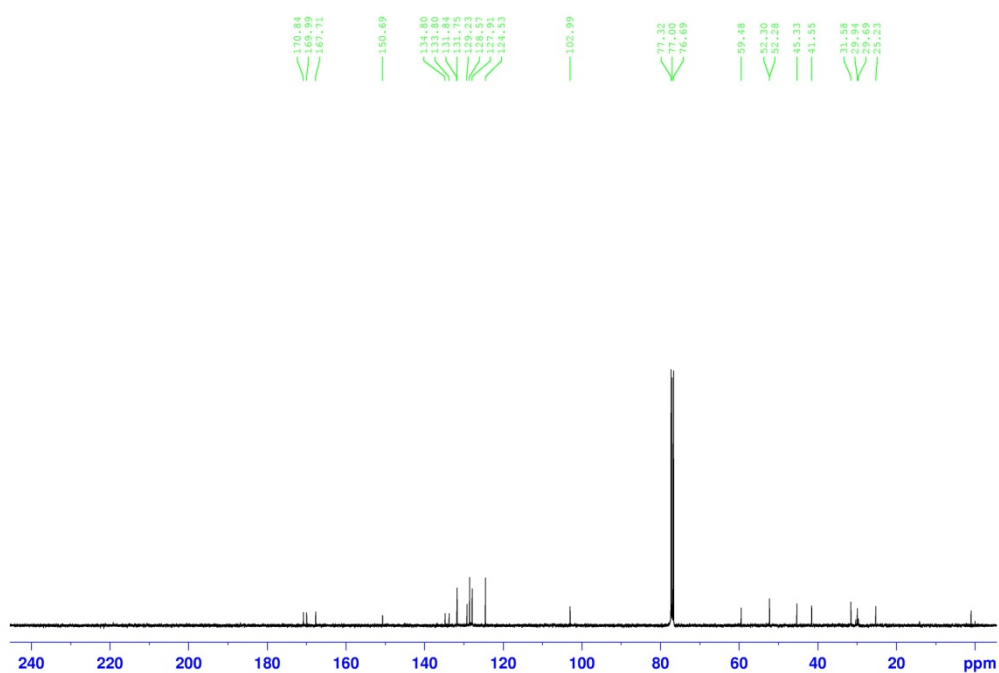
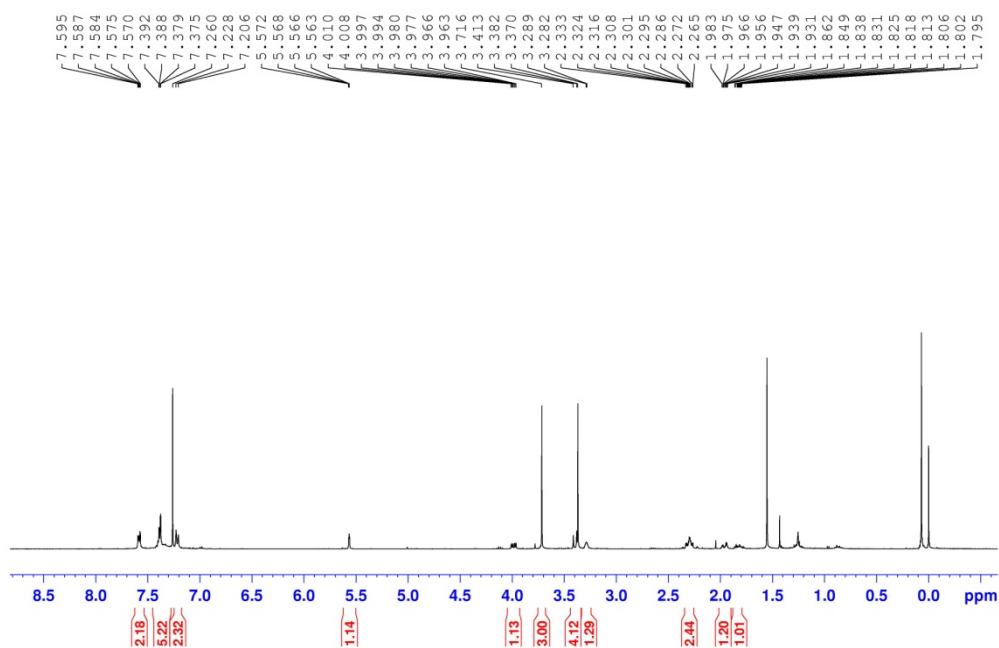
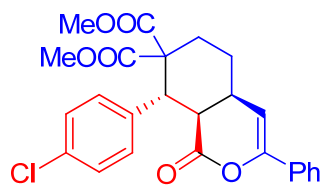


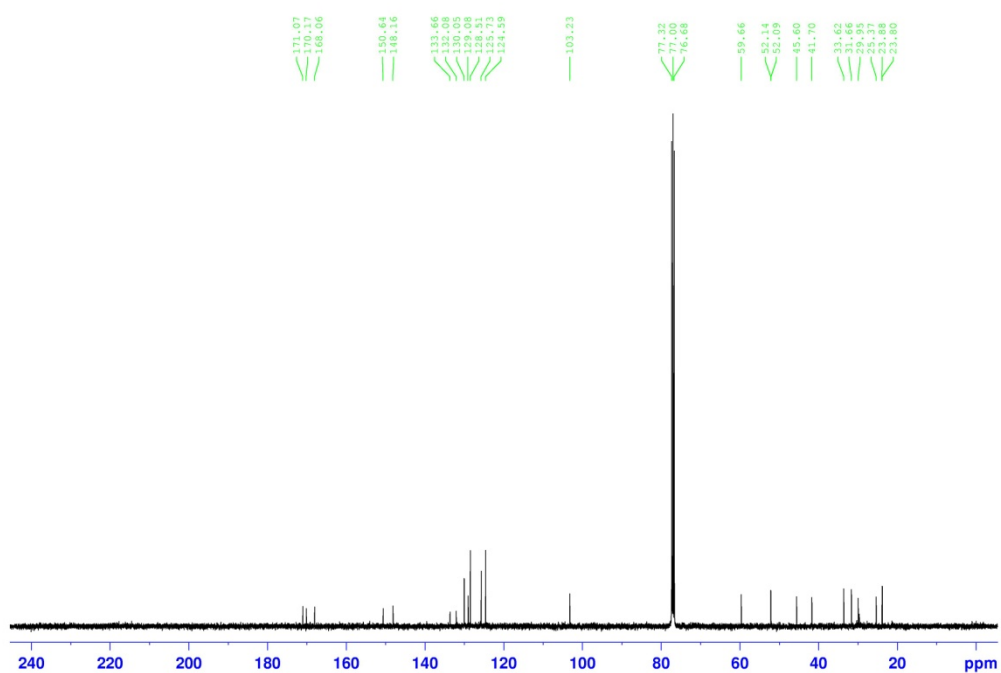
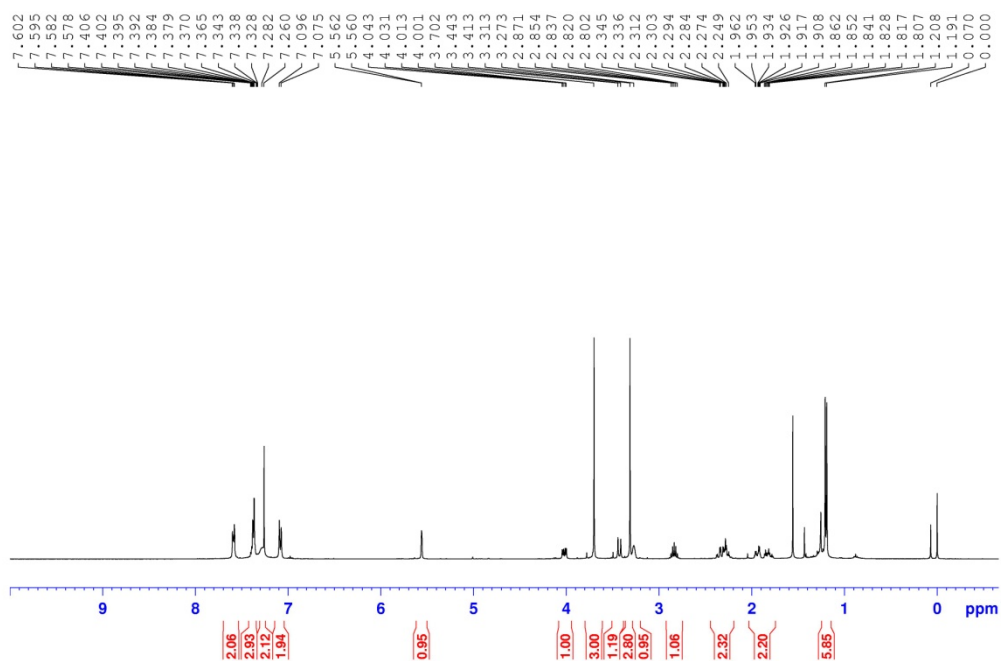
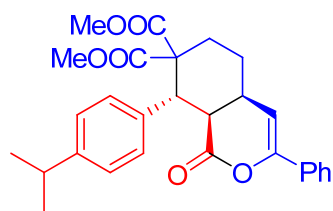


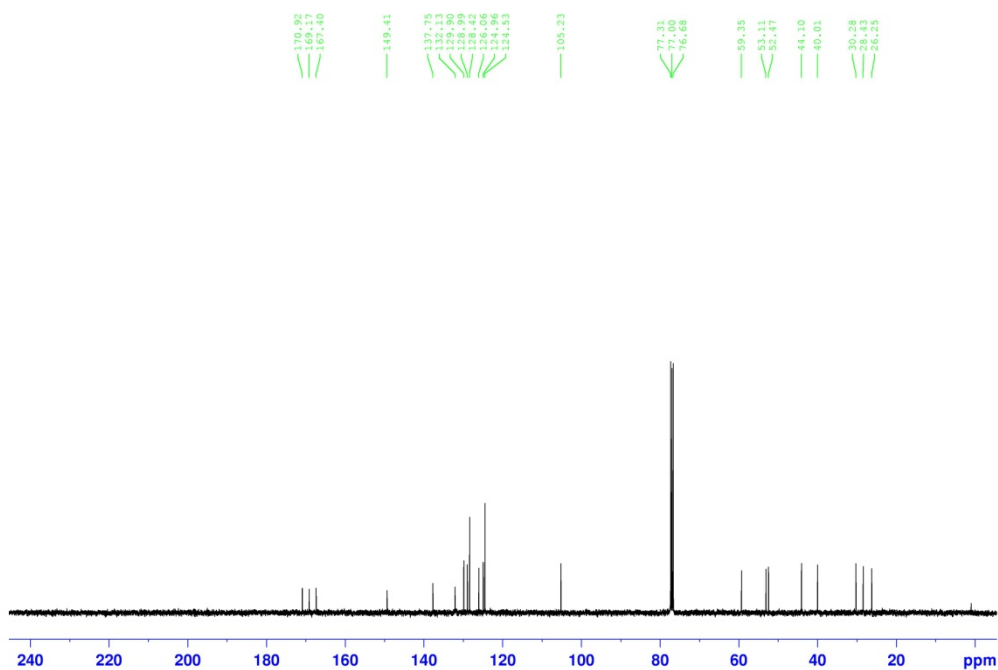
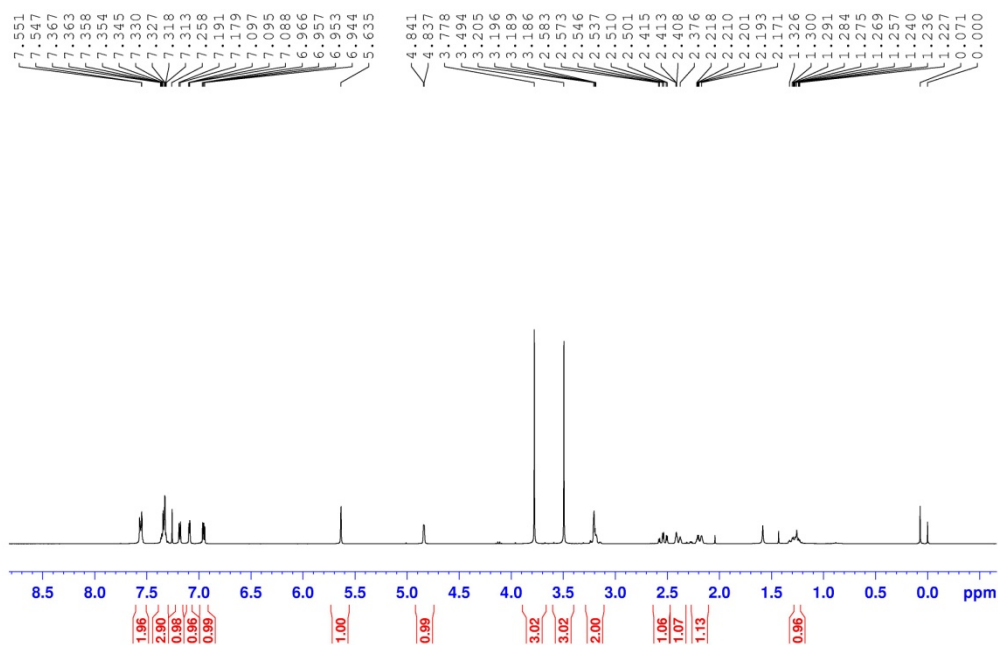
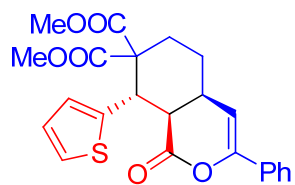


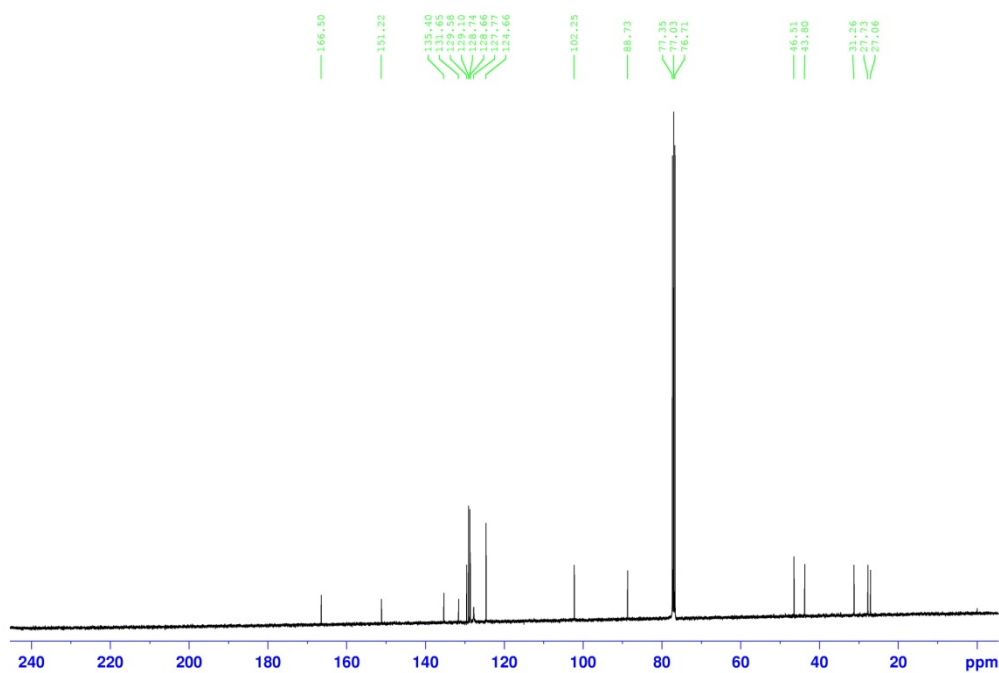
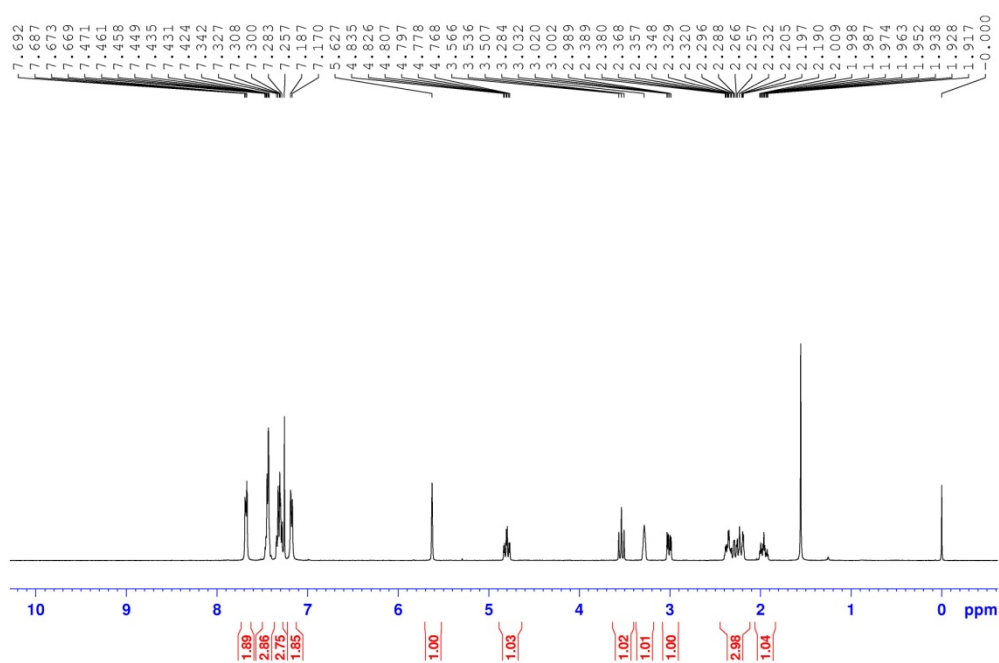
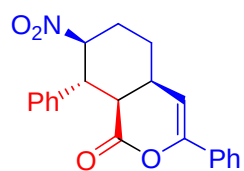


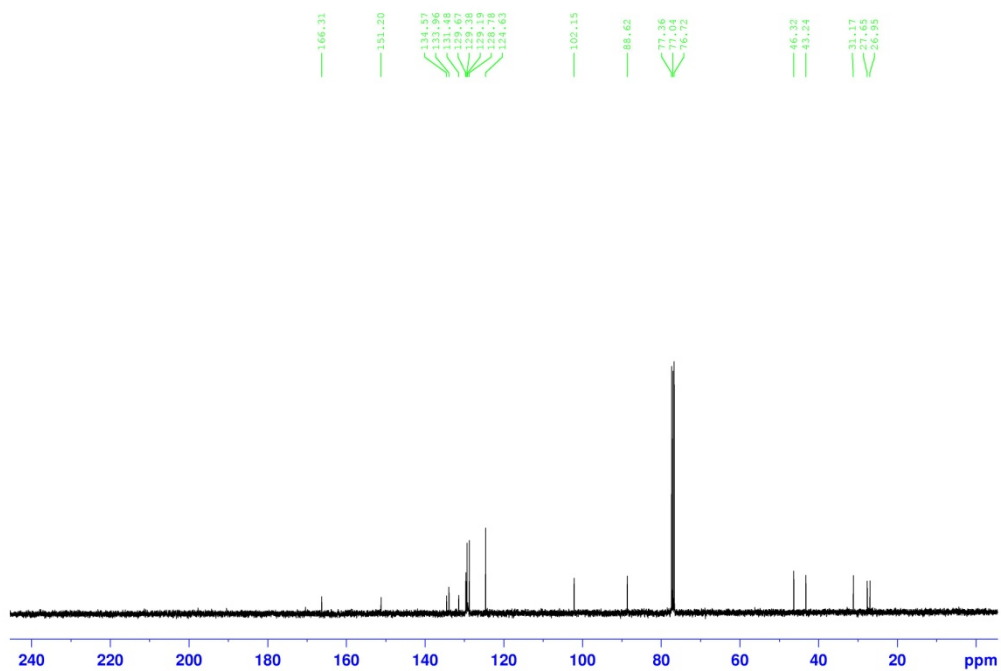
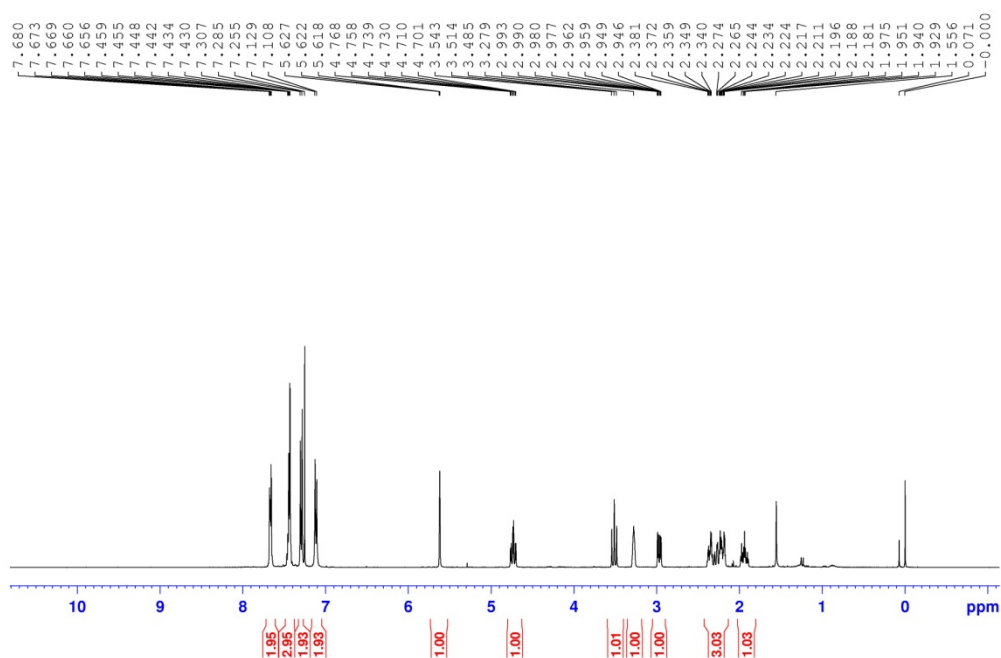
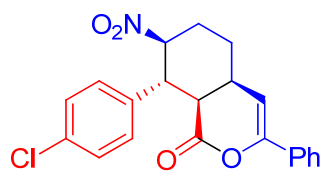


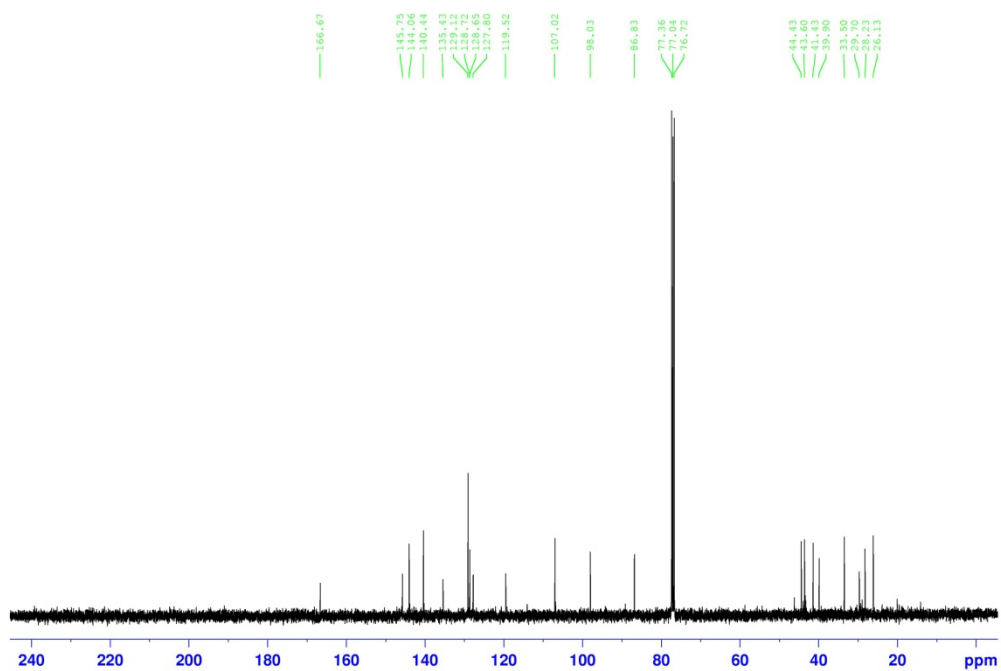
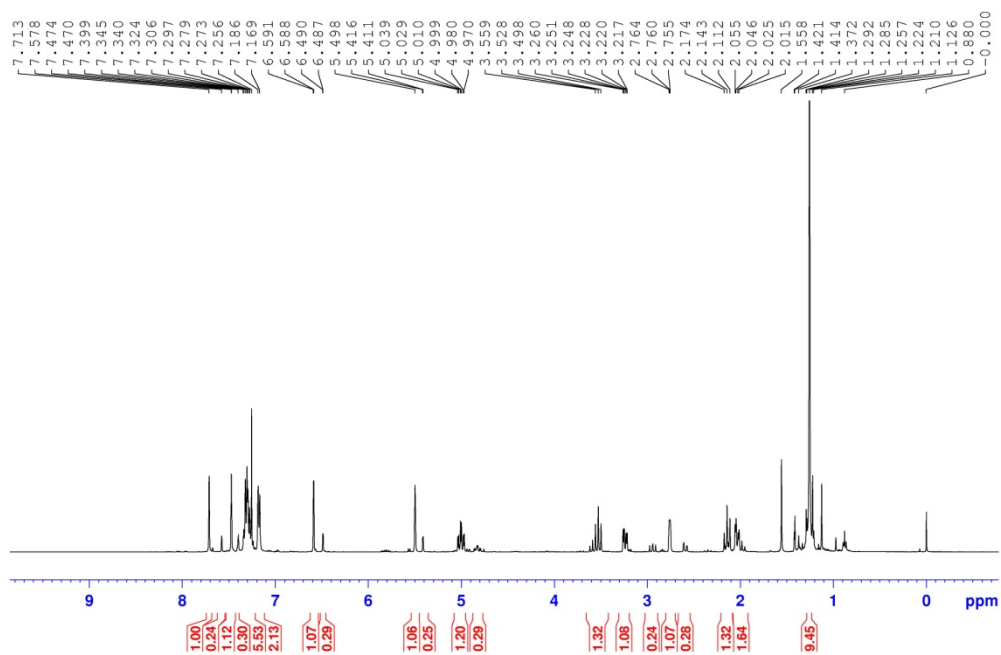
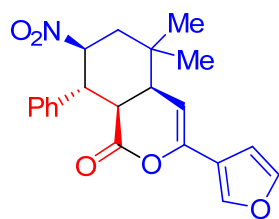


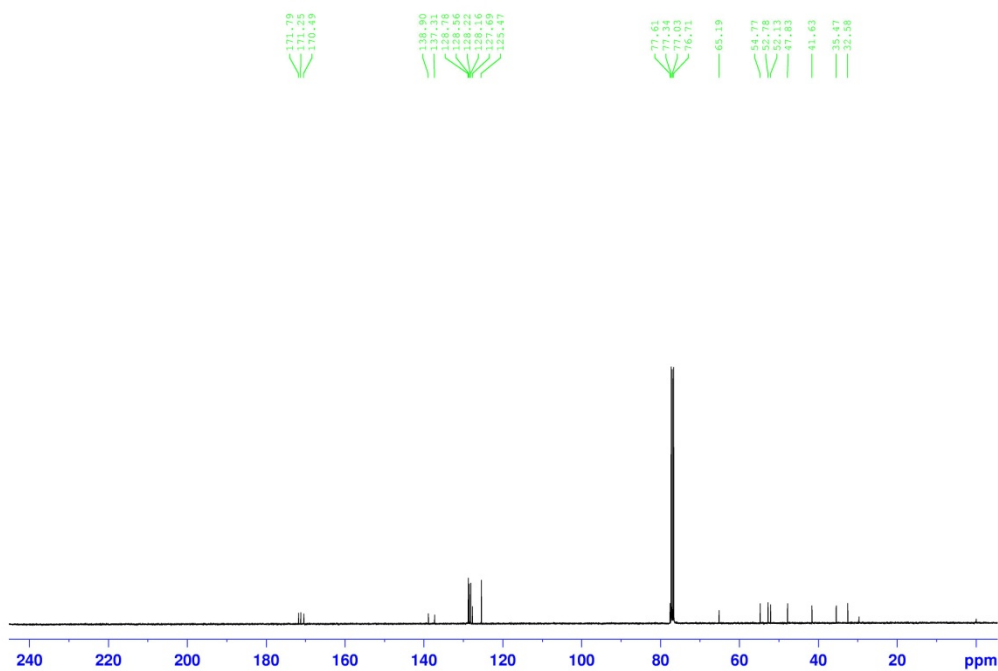
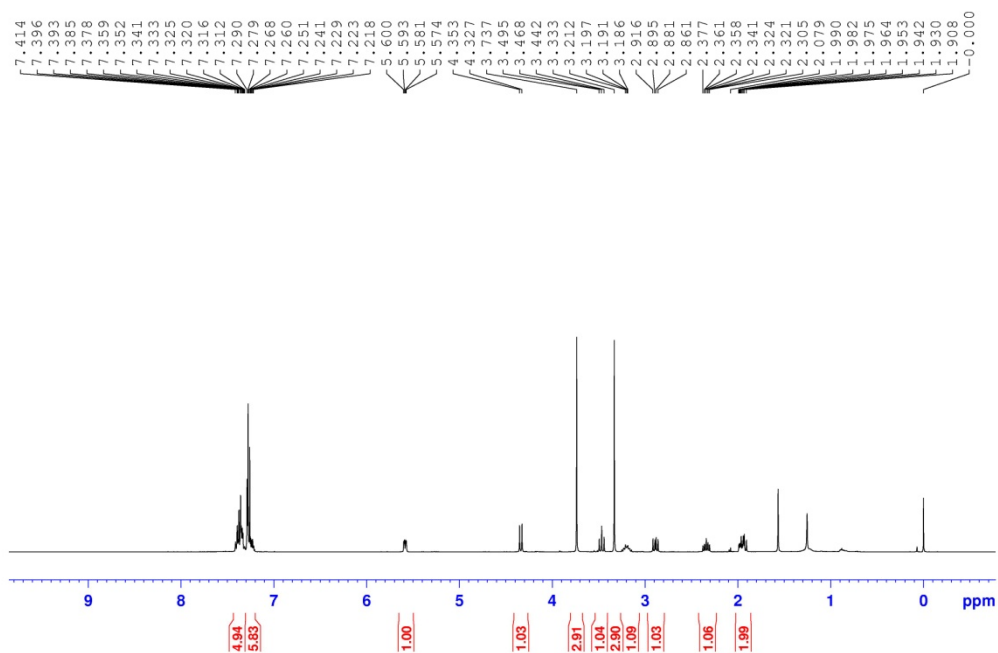
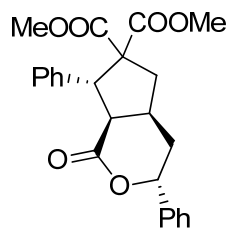


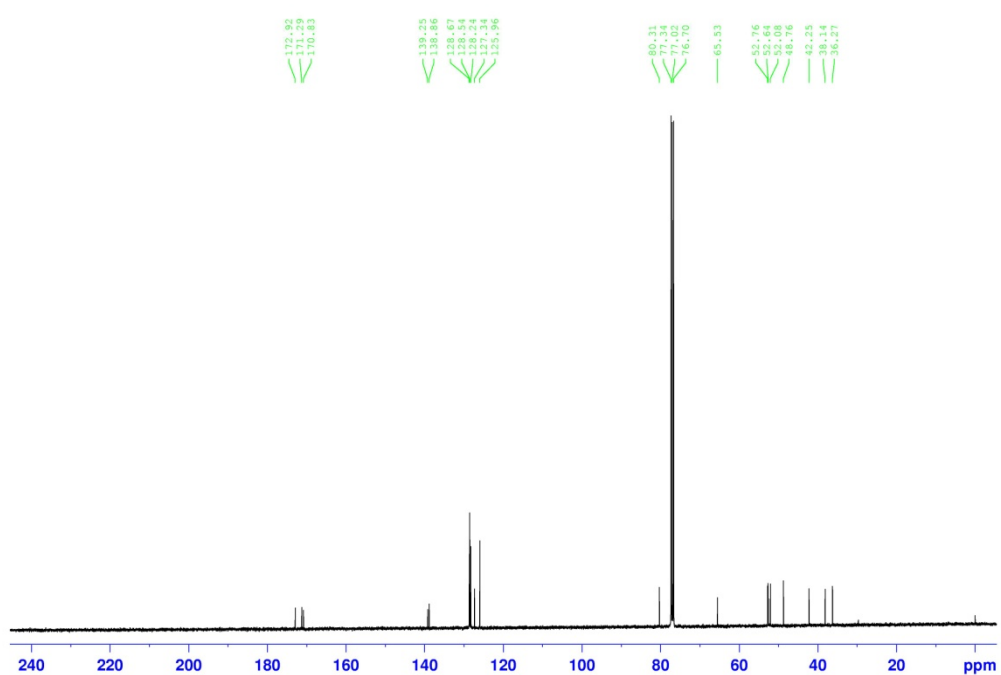
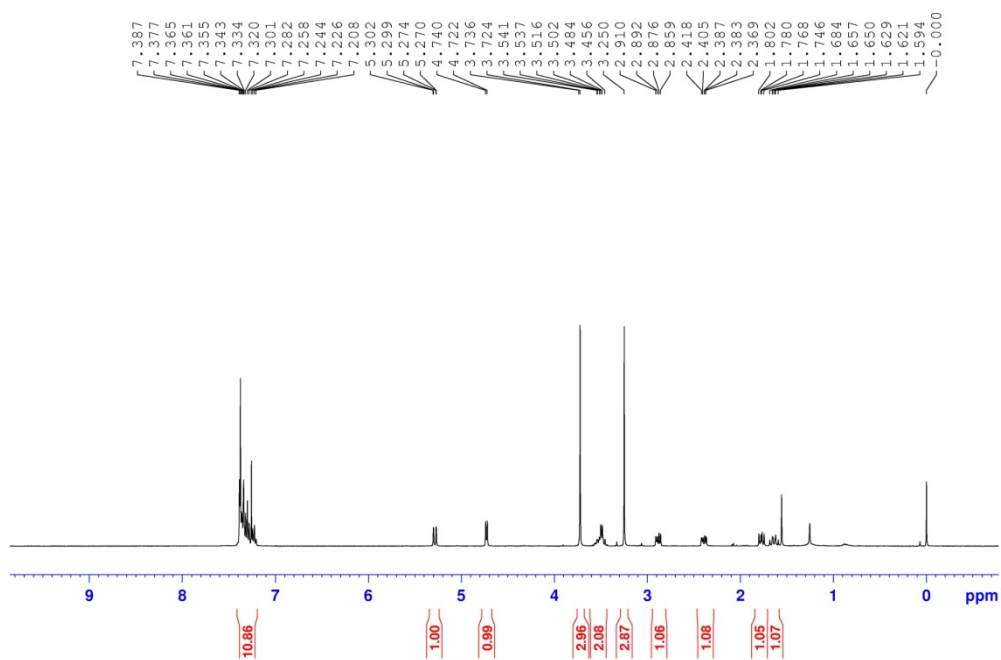
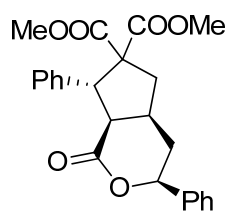


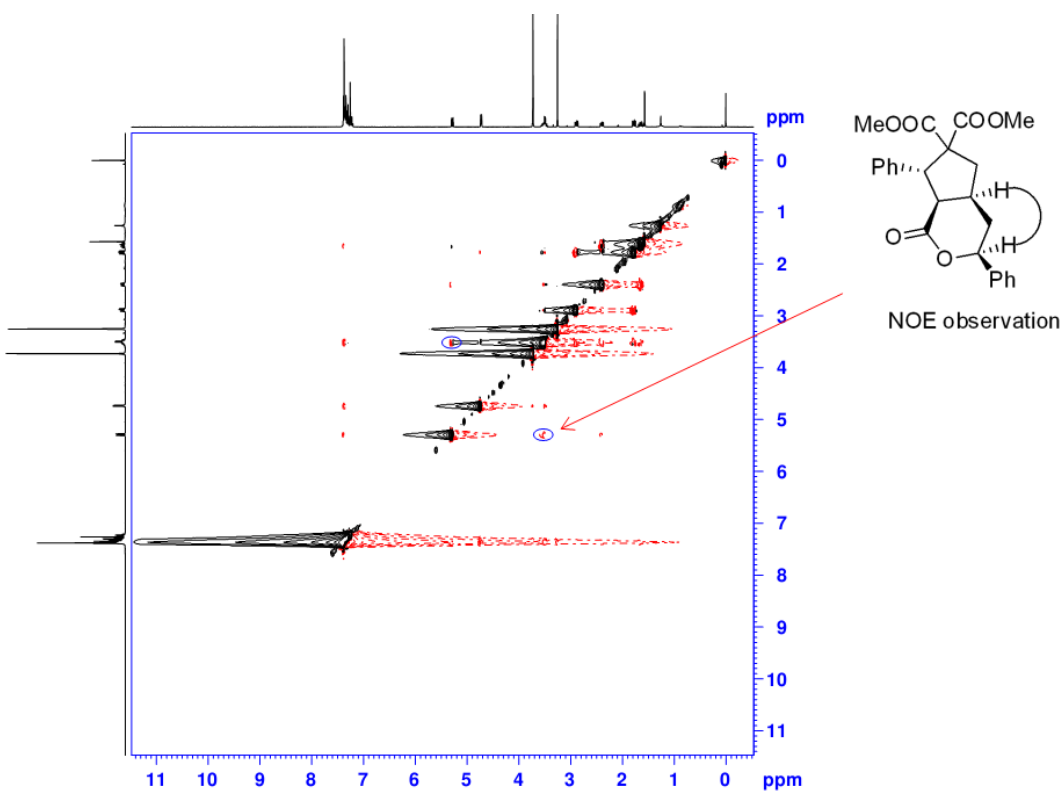
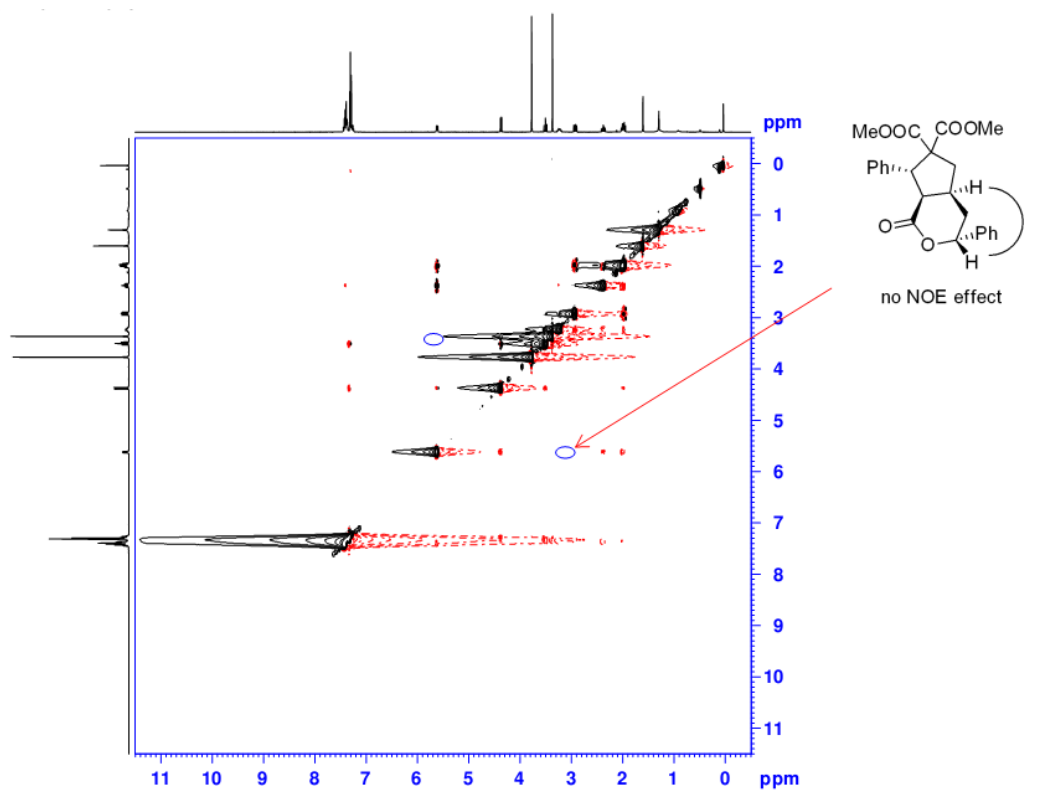


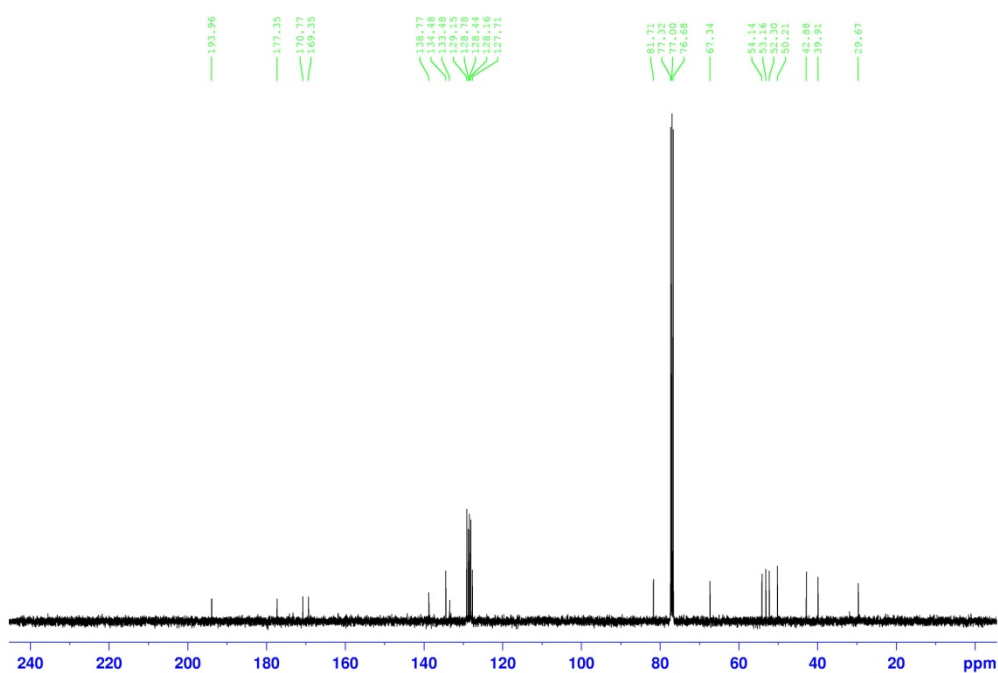
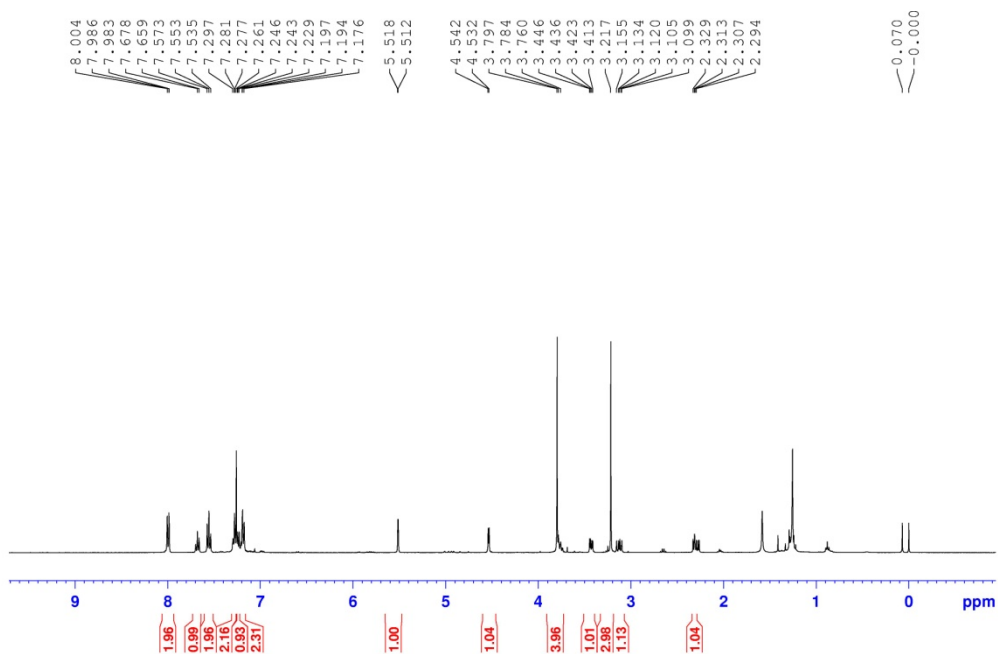
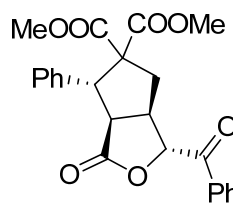


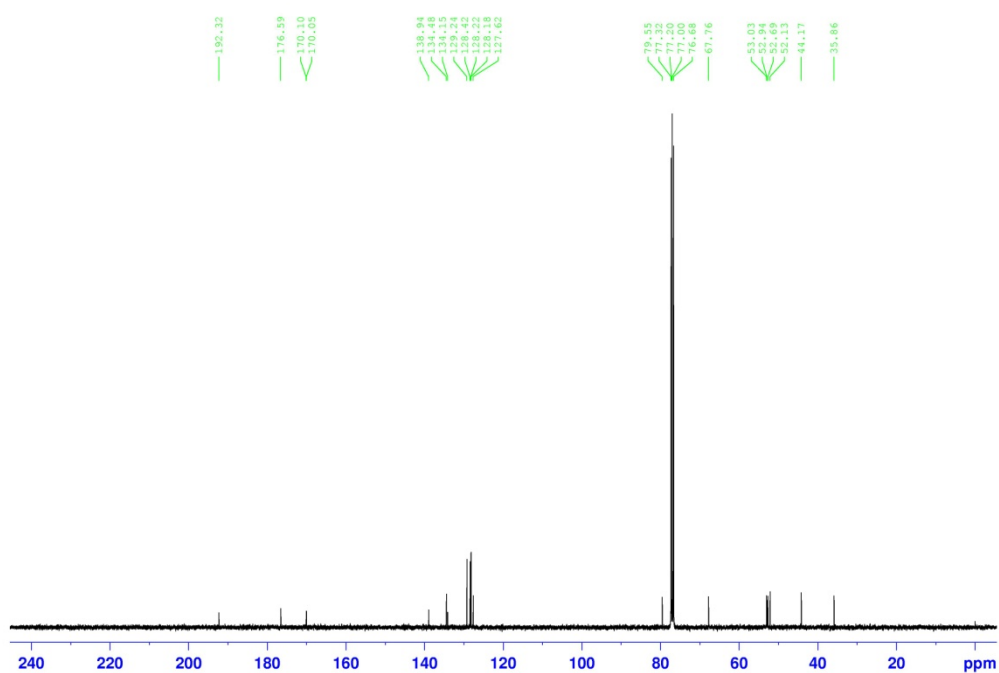
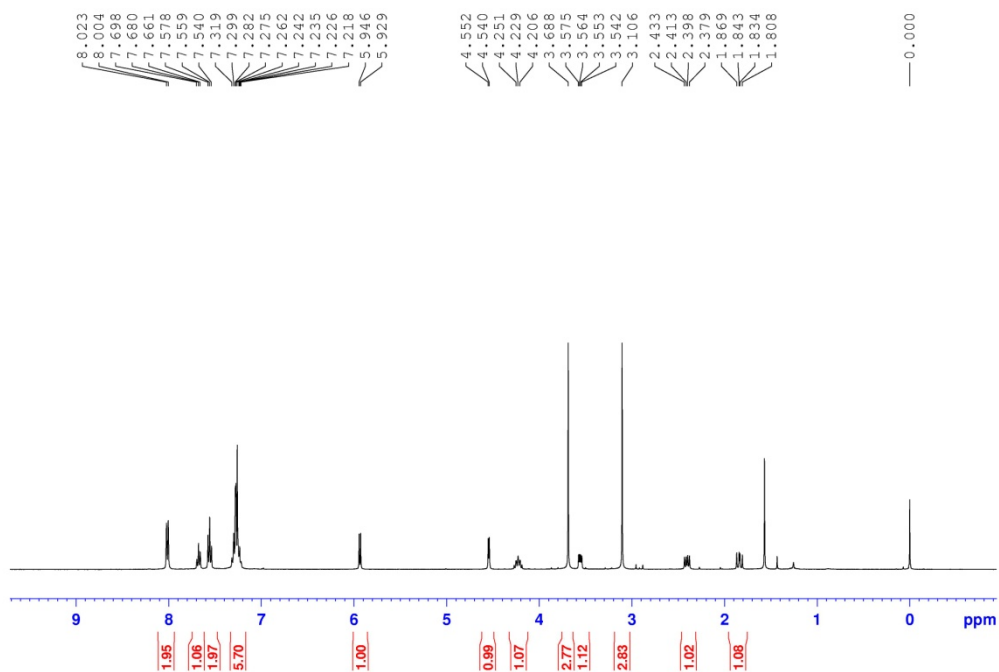
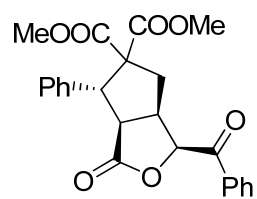


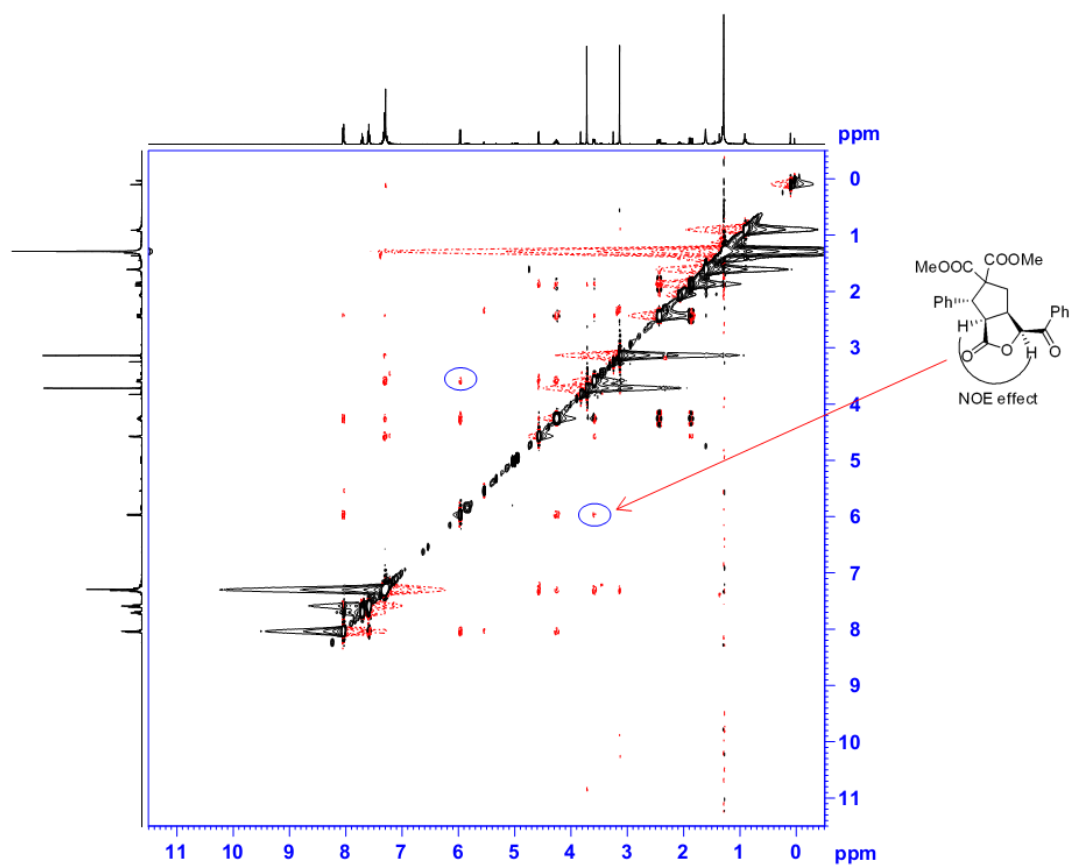
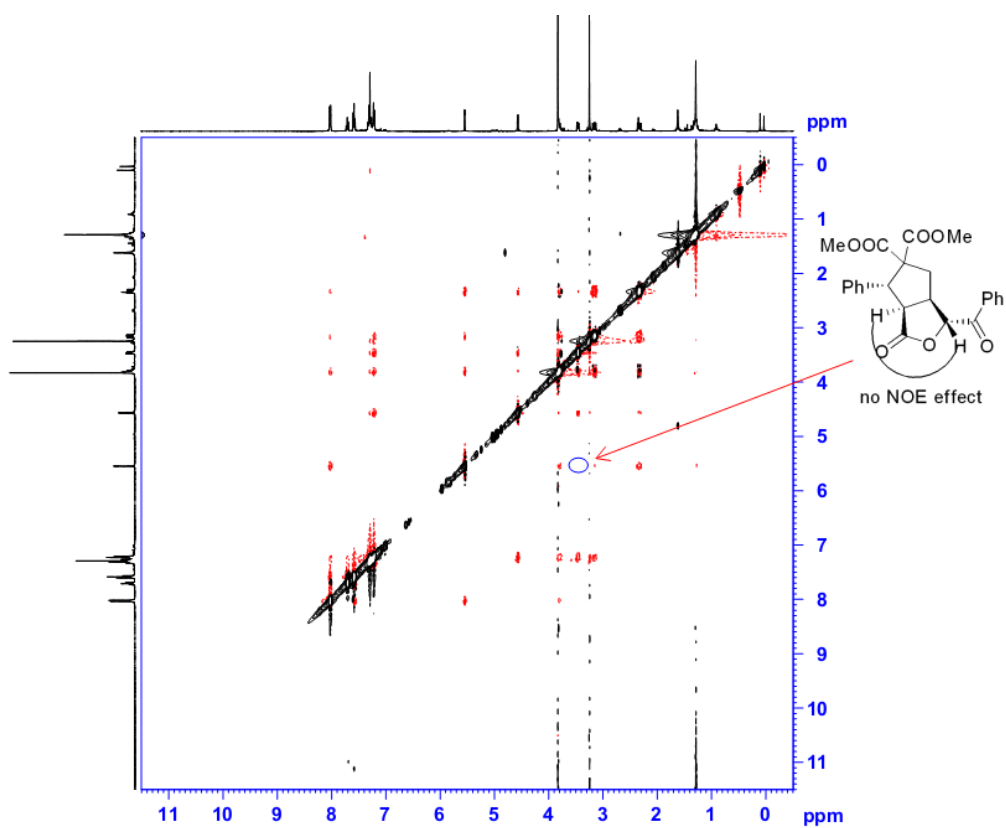


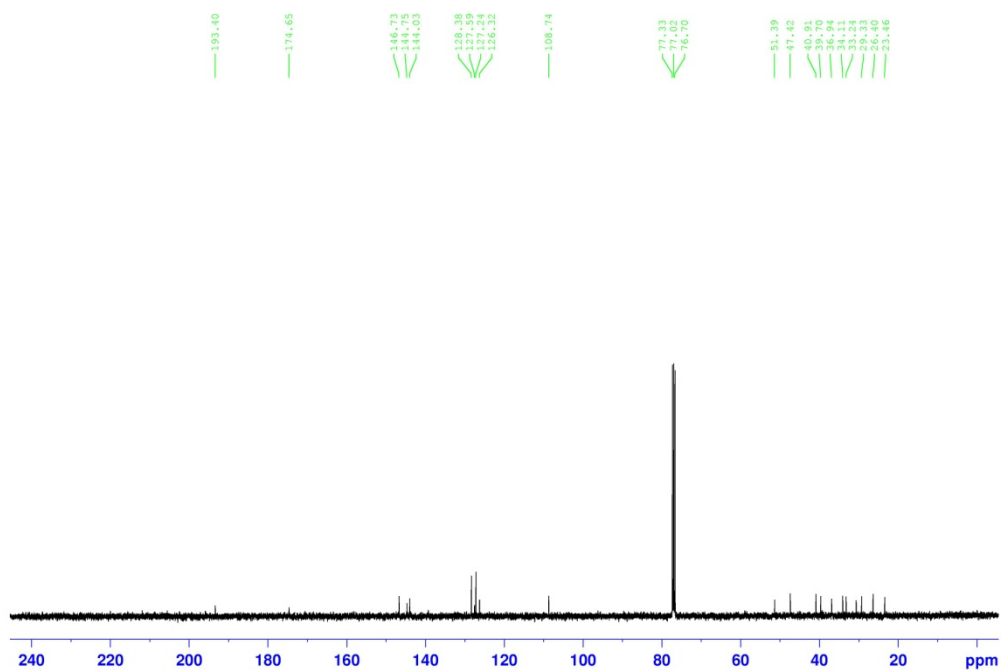
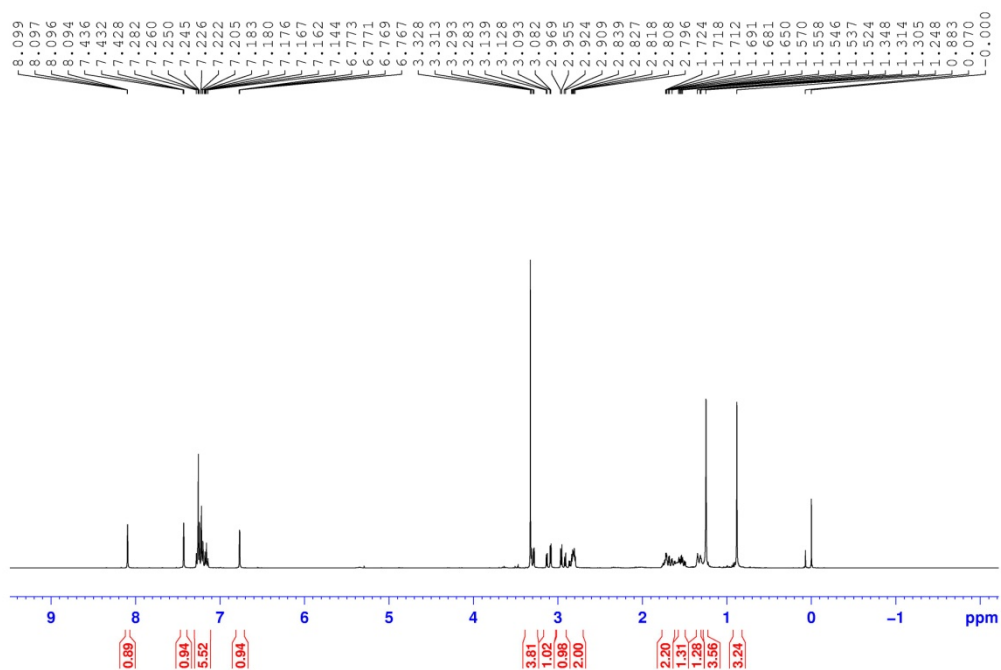
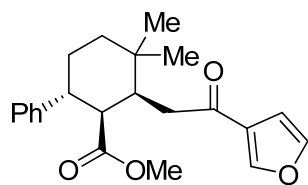


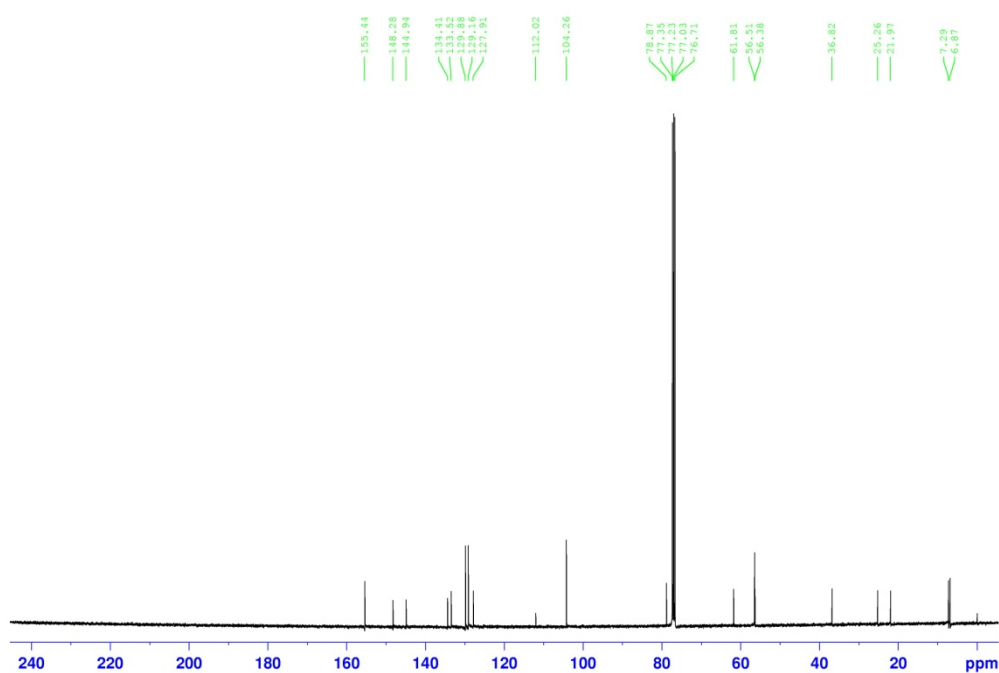
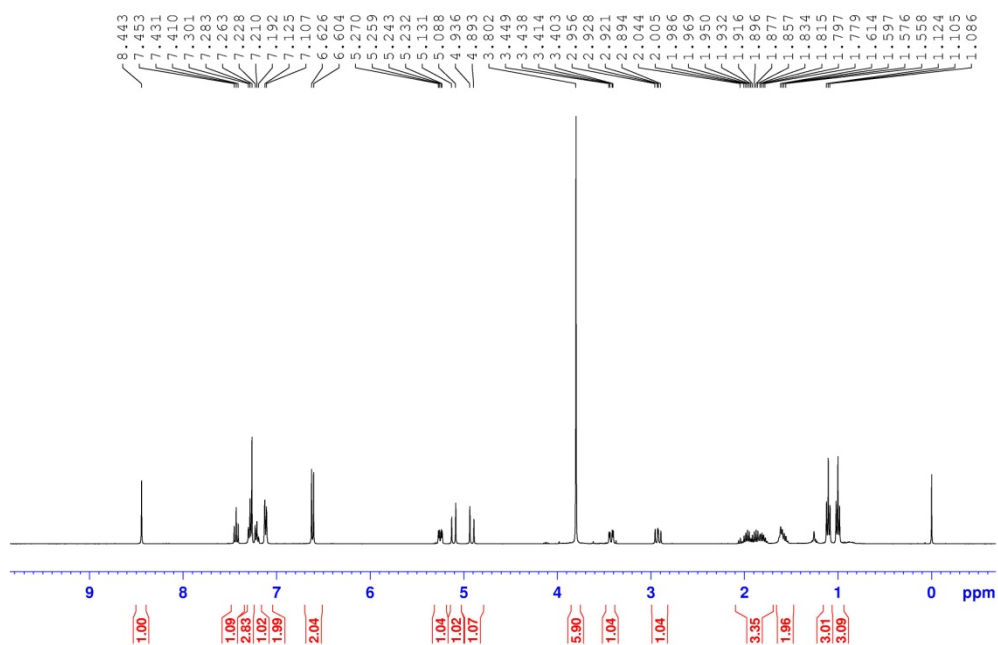
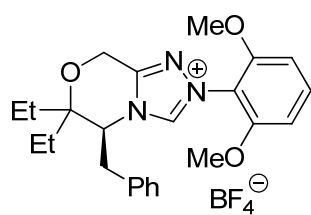




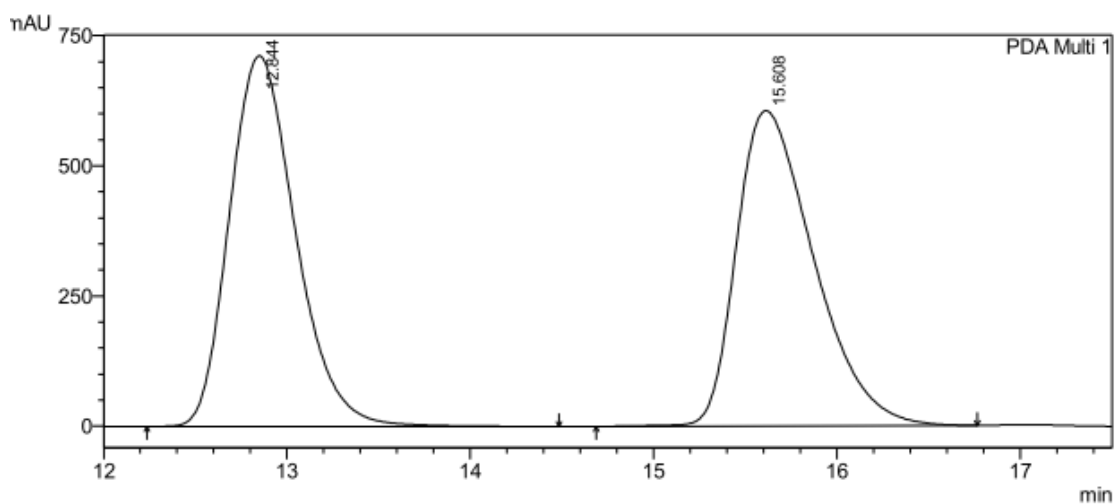
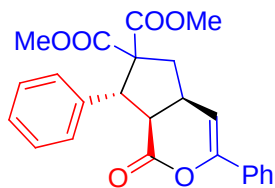






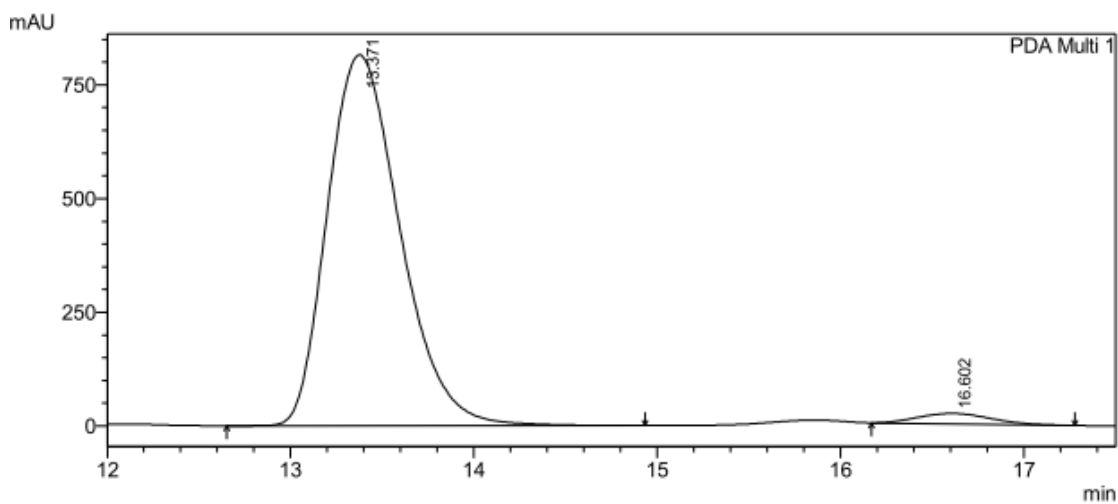


HPLC spectra of the products.



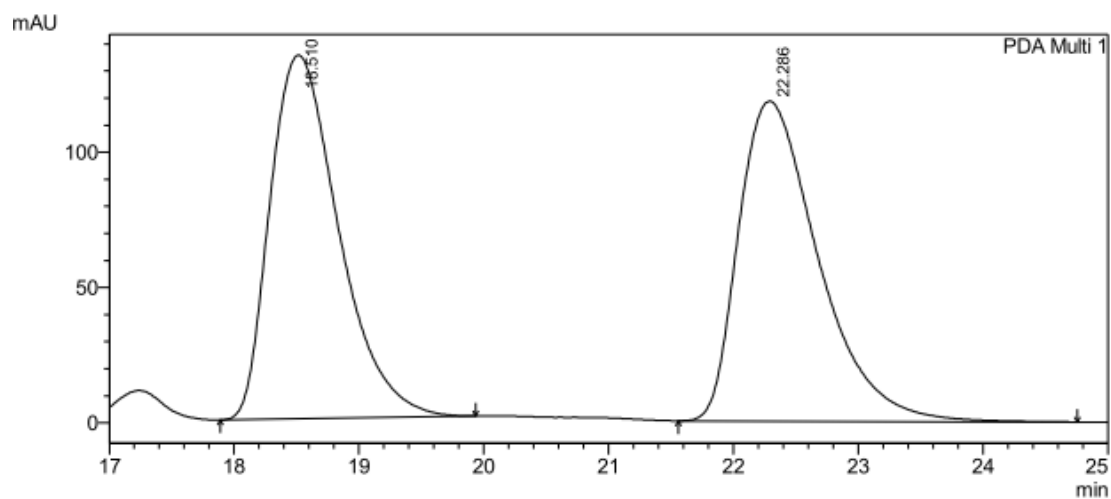
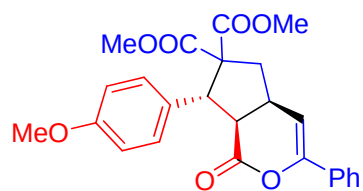
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.844	17875148	711692	50.151	54.040
2	15.608	17767467	605292	49.849	45.960
Total		35642615	1316984	100.000	100.000



PDA Ch1 254nm 4nm

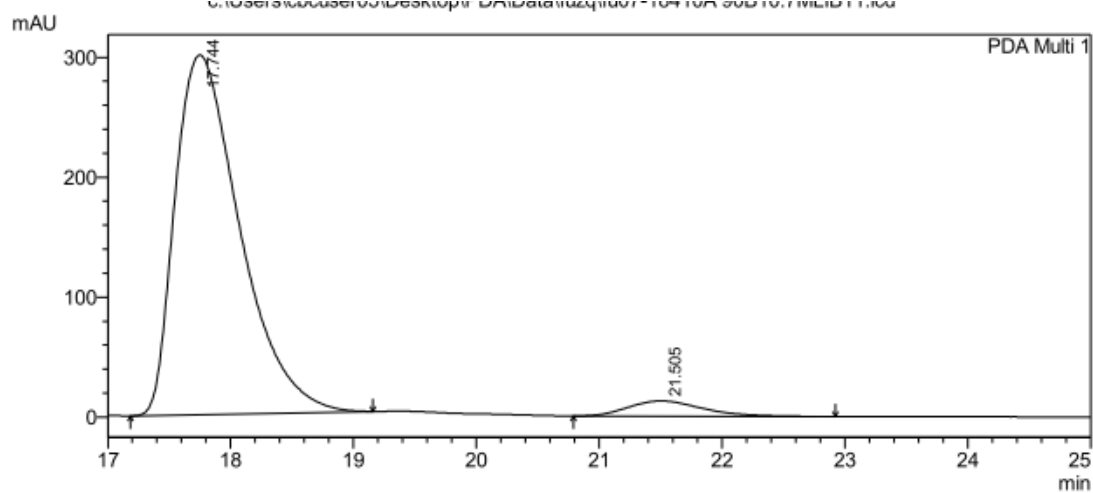
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.371	22492794	815524	97.247	97.260
2	16.602	636865	22974	2.753	2.740
Total		23129659	838498	100.000	100.000



PDA Ch1 254nm 4nm

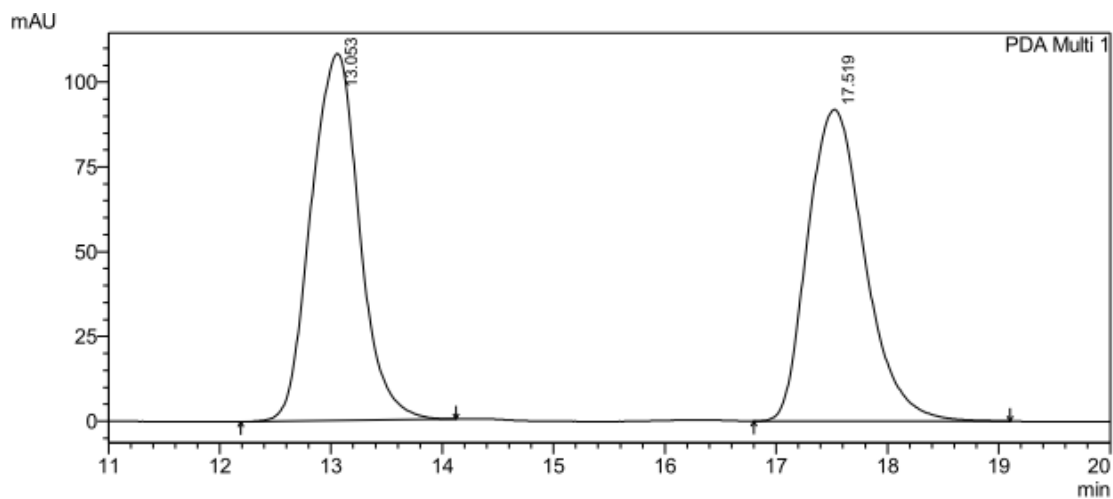
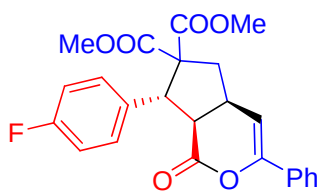
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.510	5145229	134328	49.446	53.198
2	22.286	5260521	118177	50.554	46.802
Total		10405750	252505	100.000	100.000

C:\Users\user\Desktop\1-Data\12241001-10410575010.7.MW.D11.D



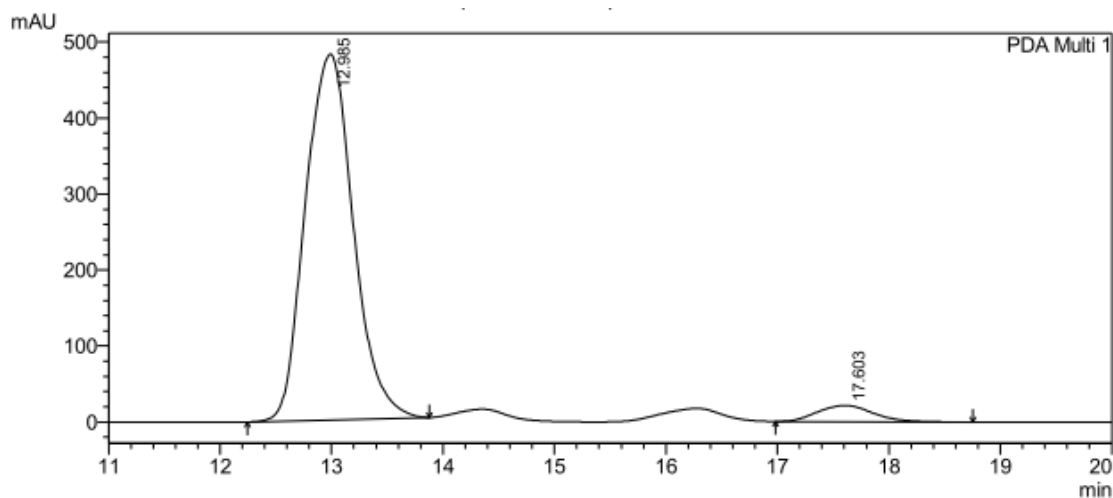
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.744	11013551	299906	95.374	95.932
2	21.505	534145	12717	4.626	4.068
Total		11547696	312624	100.000	100.000



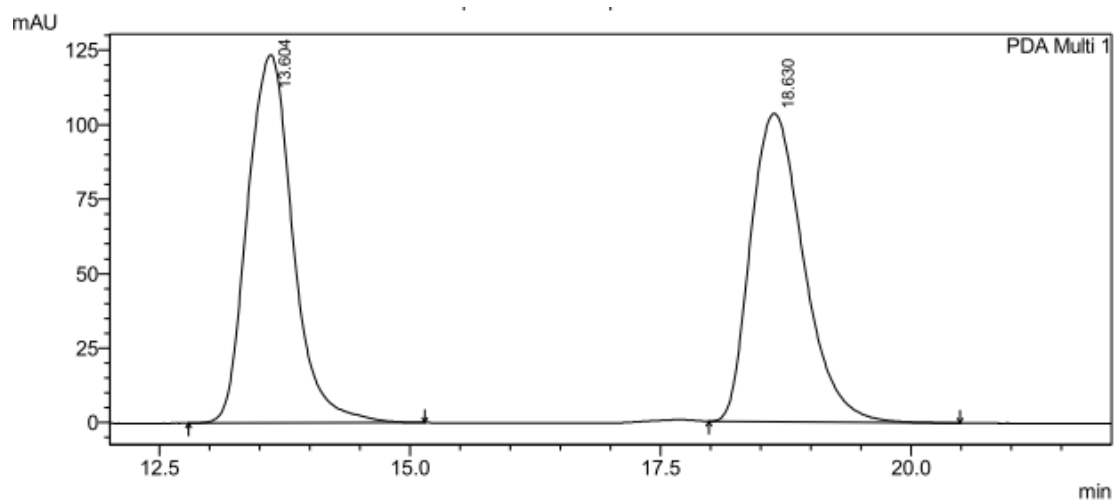
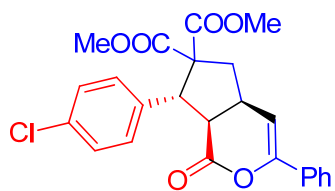
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.053	3267959	108180	49.845	54.062
2	17.519	3288313	91925	50.155	45.938
Total		6556272	200105	100.000	100.000



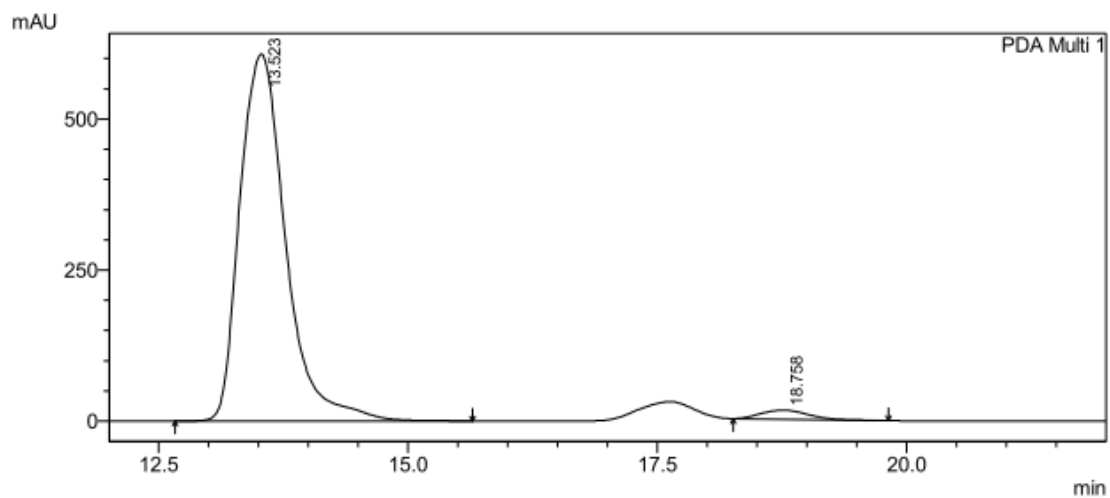
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.985	14385775	481570	95.081	95.767
2	17.603	744256	21283	4.919	4.233
Total		15130031	502853	100.000	100.000



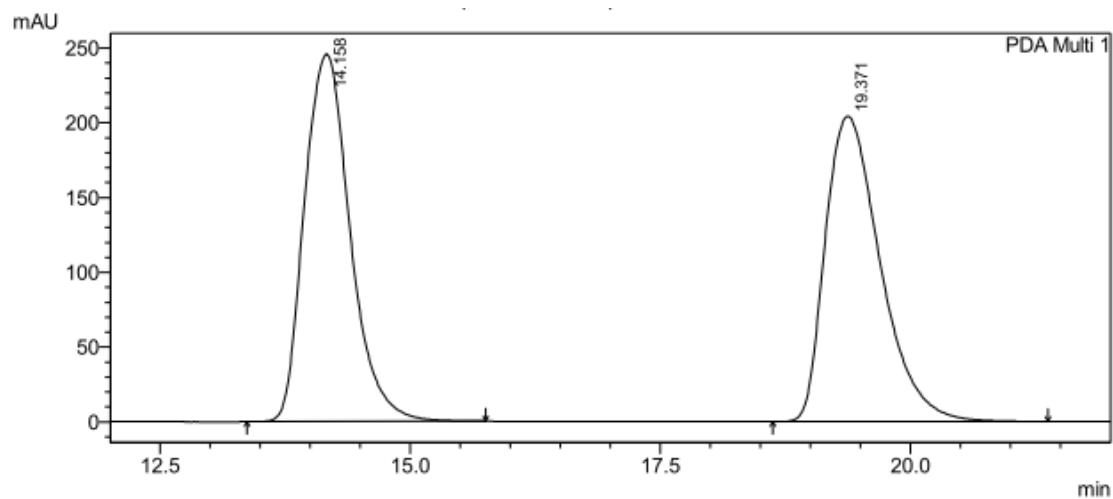
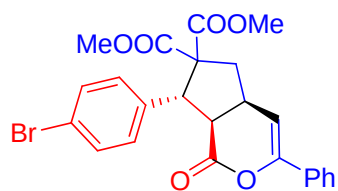
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.604	3905208	123590	50.585	54.417
2	18.630	3814888	103525	49.415	45.583
Total		7720097	227116	100.000	100.000



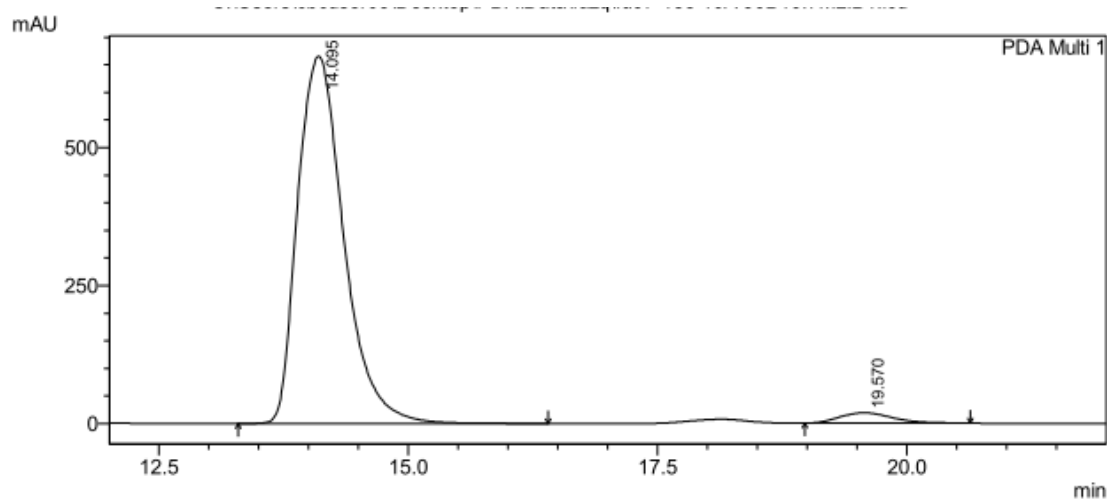
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.523	19413203	607200	97.495	97.589
2	18.758	498775	15001	2.505	2.411
Total		19911978	622201	100.000	100.000



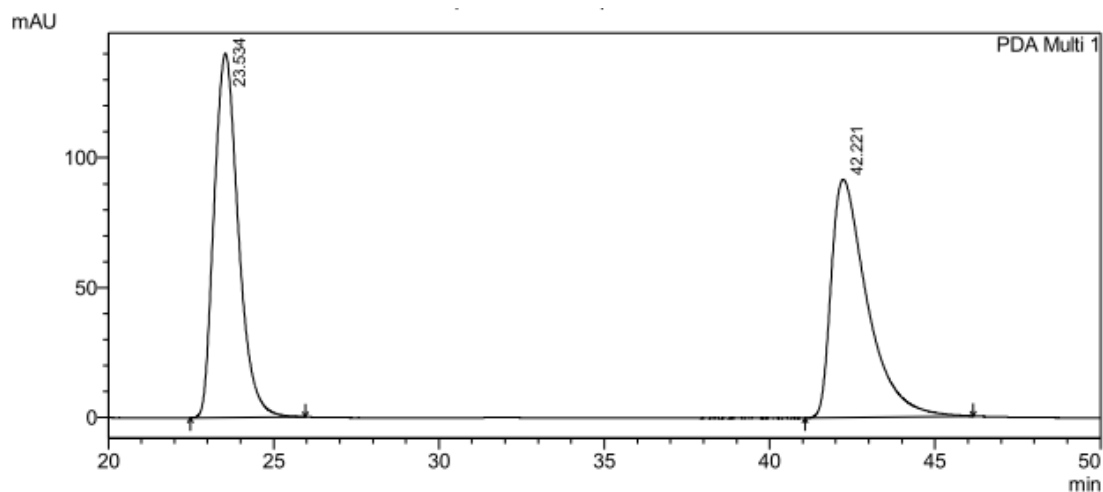
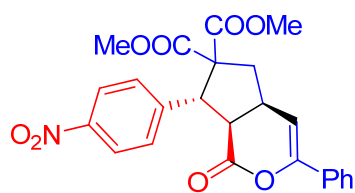
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.158	7821927	245815	49.989	54.622
2	19.371	7825401	204213	50.011	45.378
Total		15647327	450028	100.000	100.000



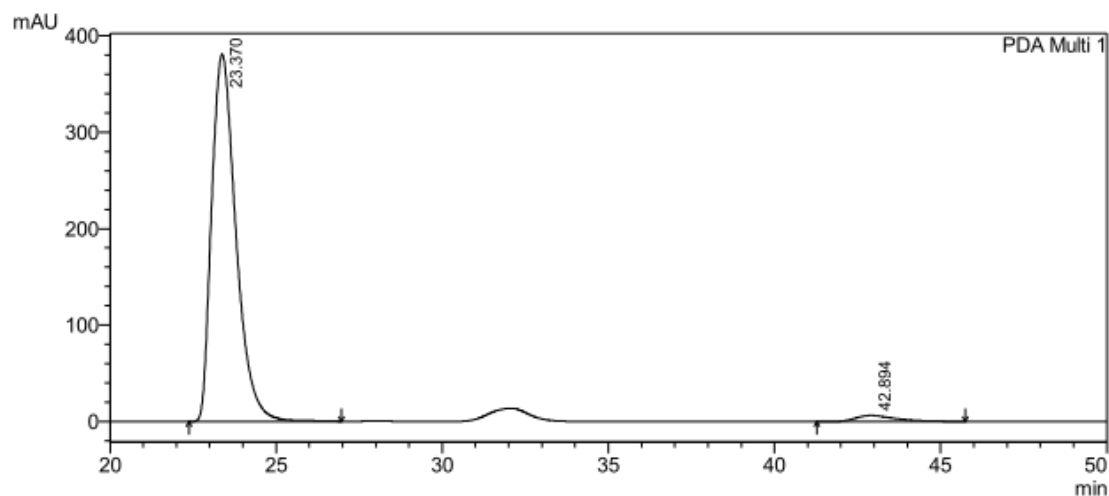
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.095	21407129	665034	96.837	97.250
2	19.570	699259	18808	3.163	2.750
Total		22106388	683842	100.000	100.000



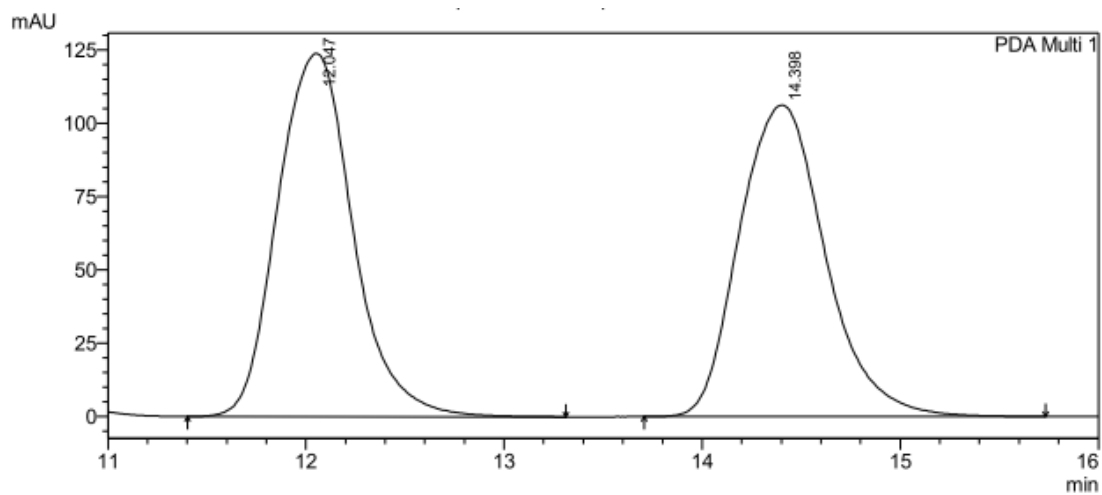
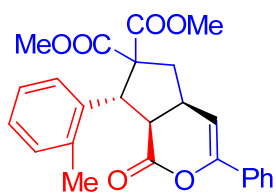
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.534	7135008	140150	50.670	60.432
2	42.221	6946211	91764	49.330	39.568
Total		14081219	231913	100.000	100.000



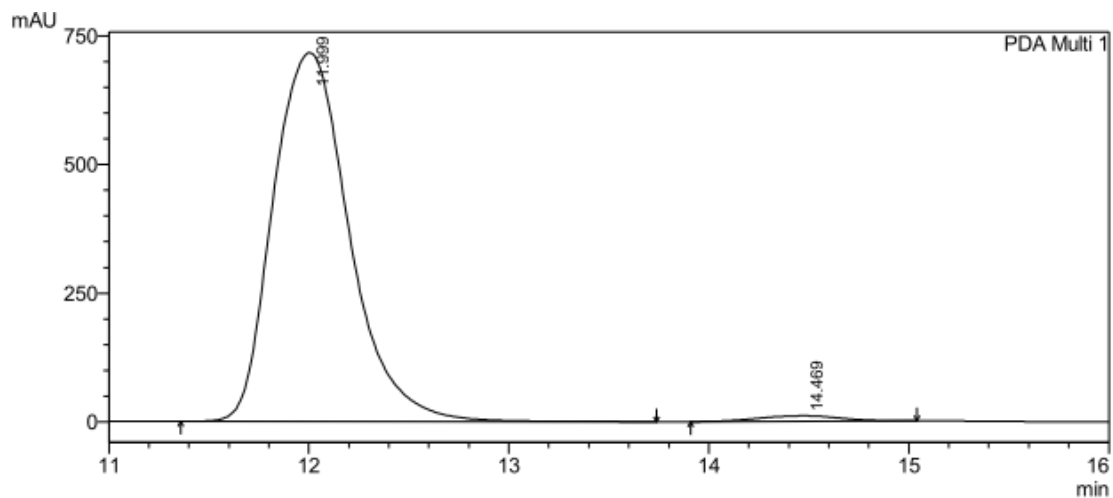
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.370	19356006	380762	97.270	98.346
2	42.894	543272	6406	2.730	1.654
Total		19899278	387167	100.000	100.000



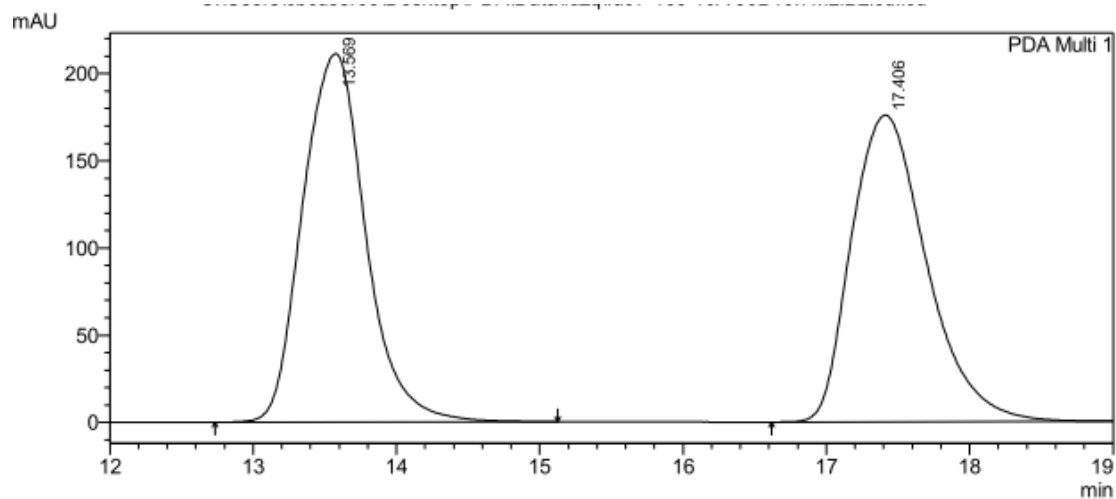
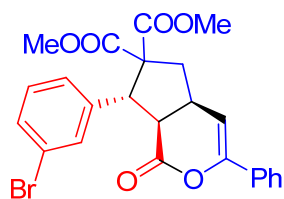
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.047	3281459	123820	50.510	53.810
2	14.398	3215248	106287	49.490	46.190
Total		6496708	230106	100.000	100.000



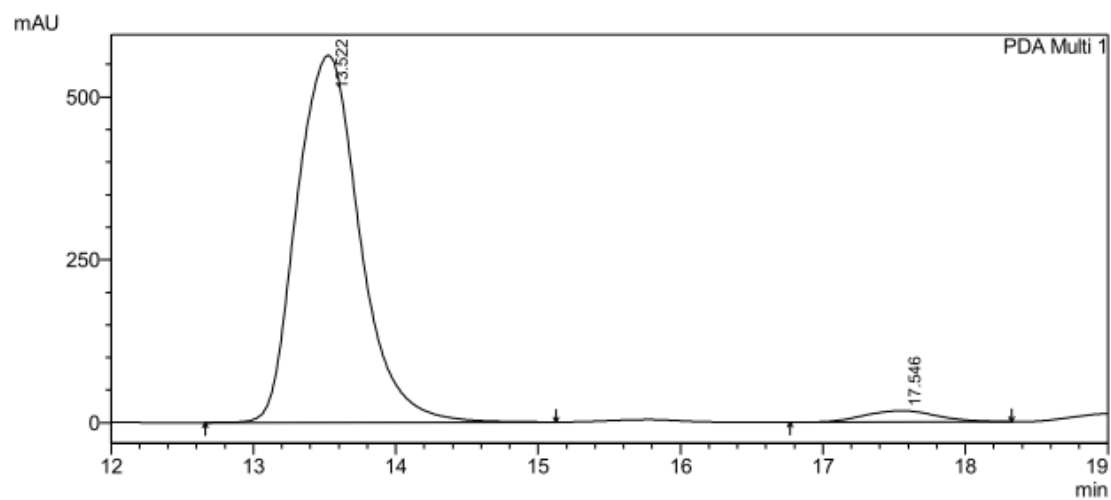
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.999	18992951	716799	98.442	98.537
2	14.469	300651	10640	1.558	1.463
Total		19293602	727439	100.000	100.000



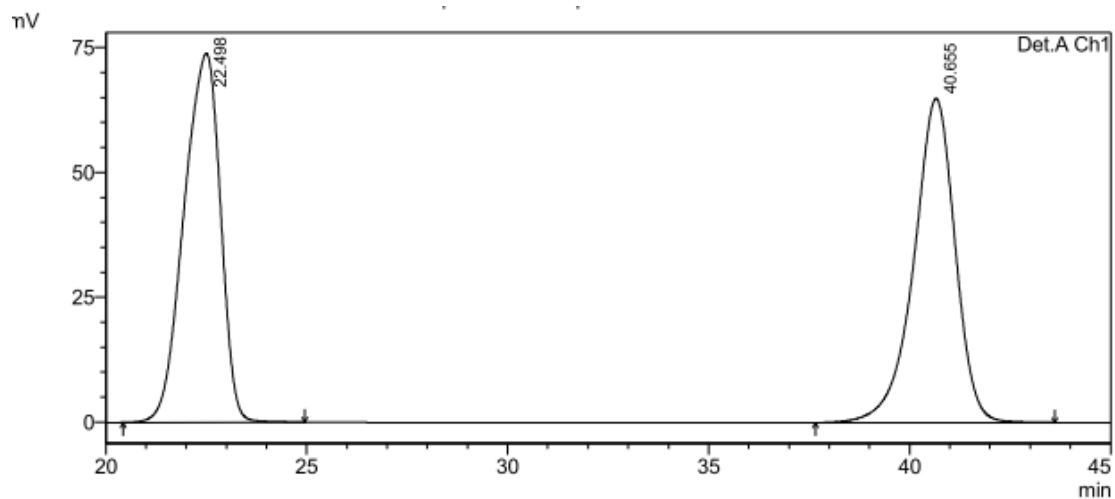
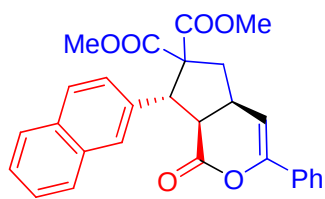
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.569	6479986	211205	50.204	54.560
2	17.406	6427412	175904	49.796	45.440
Total		12907398	387109	100.000	100.000



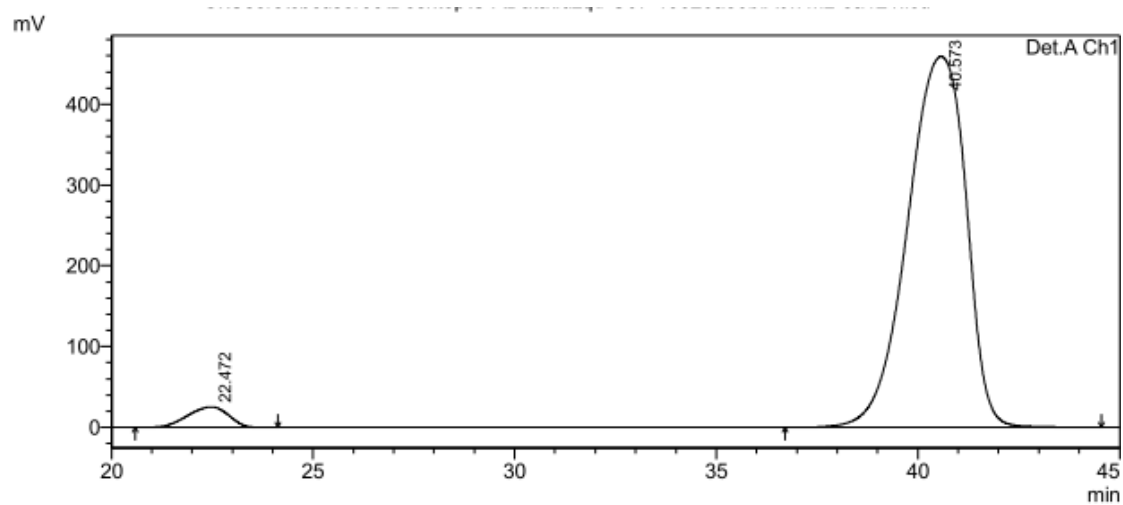
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.522	17317905	563463	96.541	97.009
2	17.546	620507	17372	3.459	2.991
Total		17938412	580836	100.000	100.000



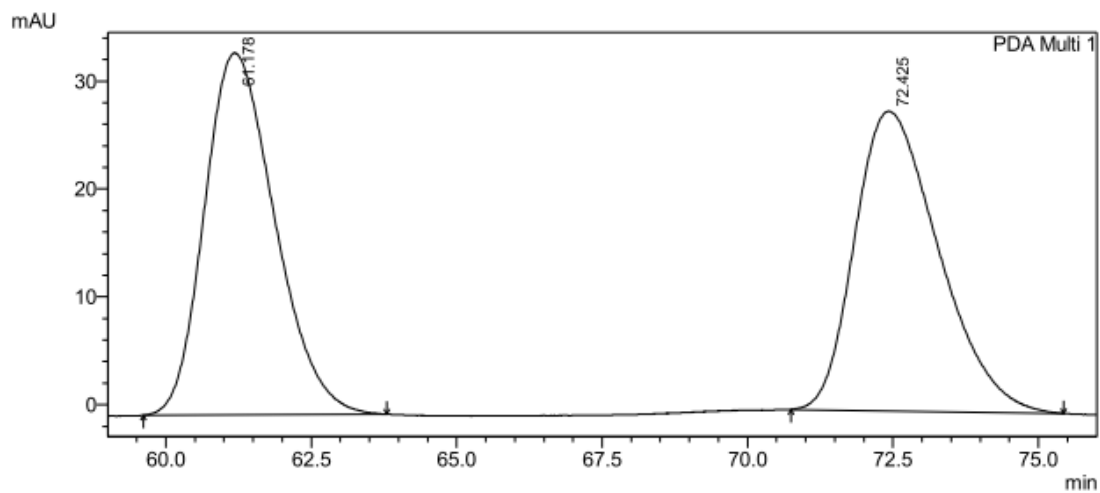
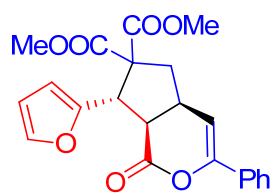
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.498	4668134	73902	50.041	53.237
2	40.655	4660531	64915	49.959	46.763
Total		9328666	138817	100.000	100.000



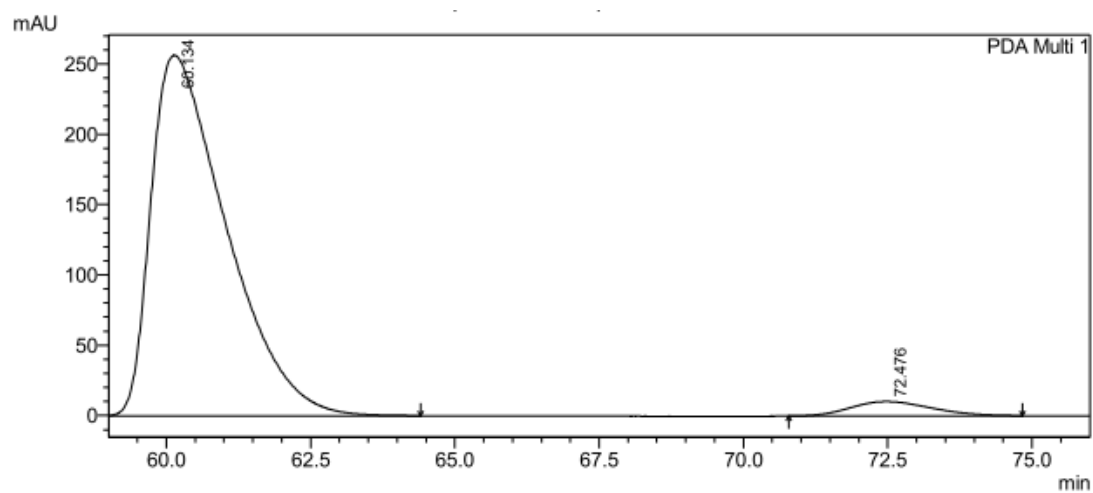
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.472	1792429	25396	3.721	5.240
2	40.573	46382699	459268	96.279	94.760
Total		48175129	484664	100.000	100.000



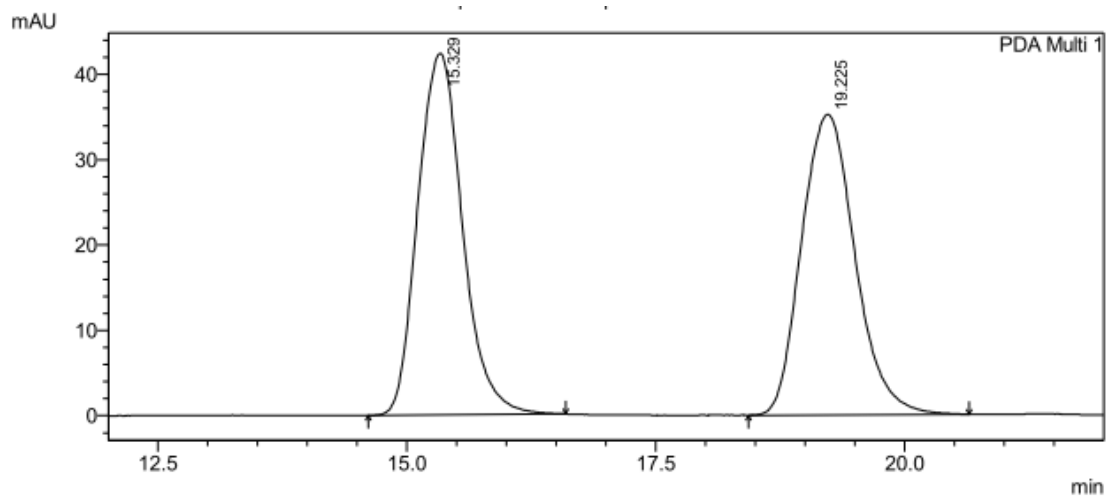
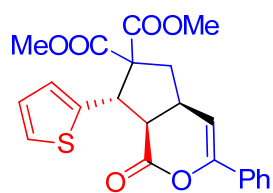
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	61.178	2827245	33546	50.344	54.720
2	72.425	2788587	27759	49.656	45.280
Total		5615831	61305	100.000	100.000



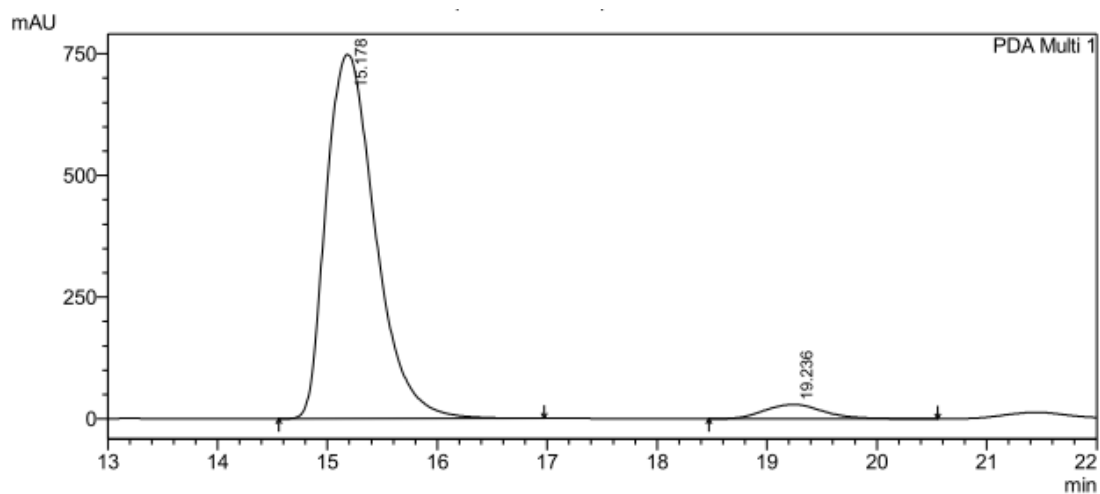
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	60.134	23300275	256380	95.898	96.165
2	72.476	996566	10225	4.102	3.835
Total		24296841	266605	100.000	100.000



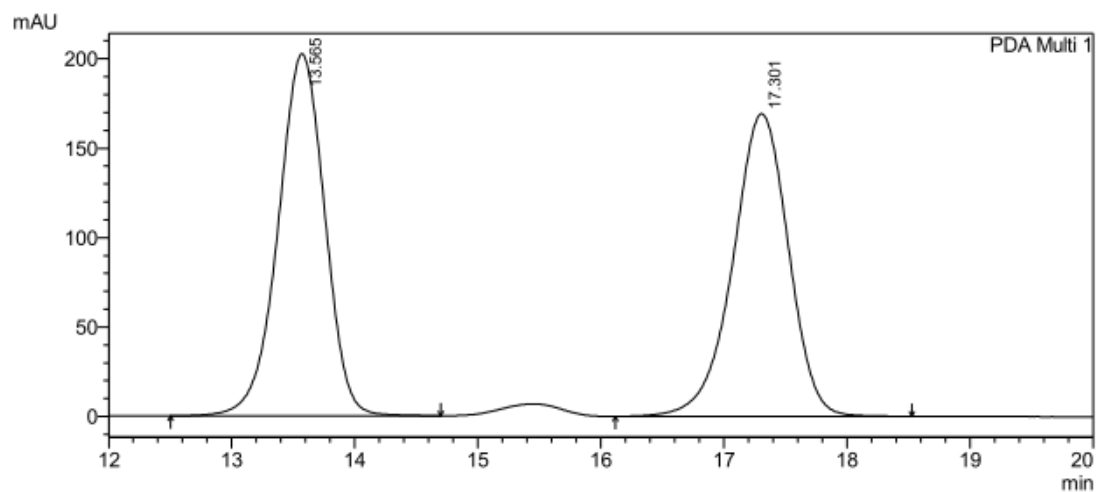
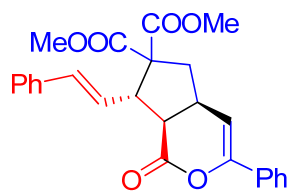
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.329	1323677	42364	50.073	54.597
2	19.225	1319833	35231	49.927	45.403
Total		2643510	77595	100.000	100.000



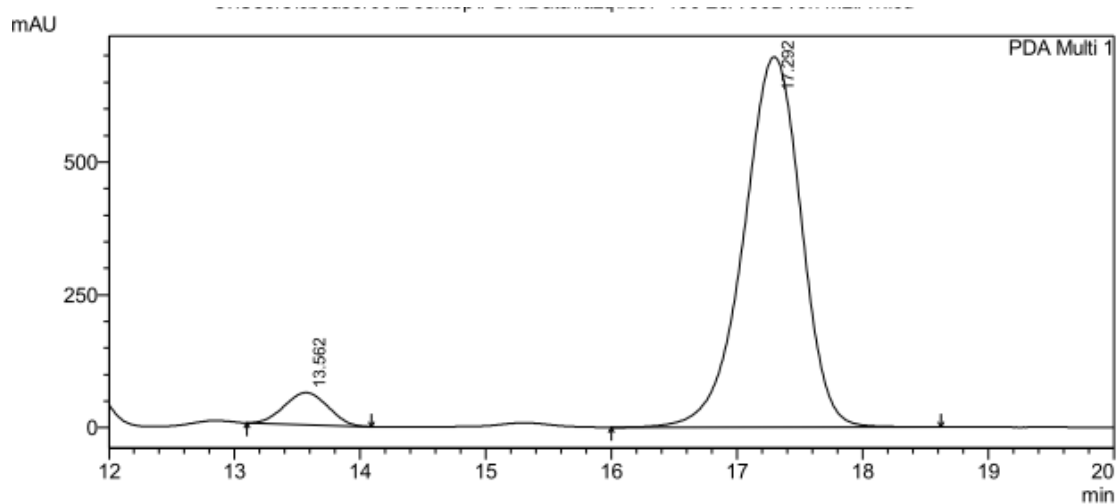
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.178	23268448	748361	95.544	96.257
2	19.236	1085275	29100	4.456	3.743
Total		24353723	777462	100.000	100.000



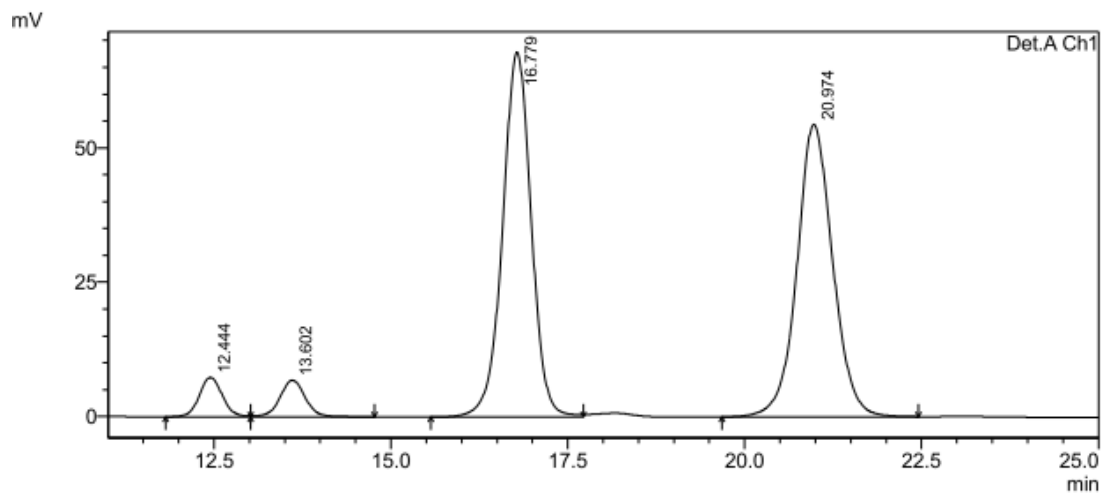
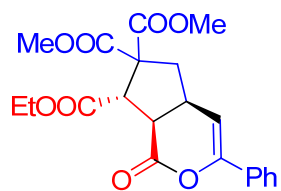
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.565	5346977	202415	50.131	54.476
2	17.301	5319115	169152	49.869	45.524
Total		10666092	371568	100.000	100.000



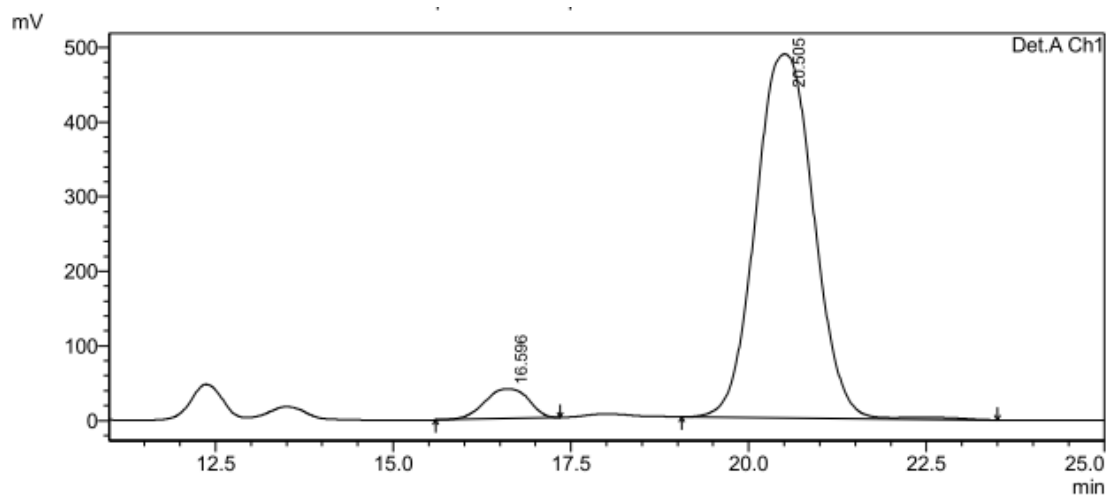
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.562	1461591	60470	6.181	7.986
2	17.292	22184420	696721	93.819	92.014
Total		23646011	757191	100.000	100.000



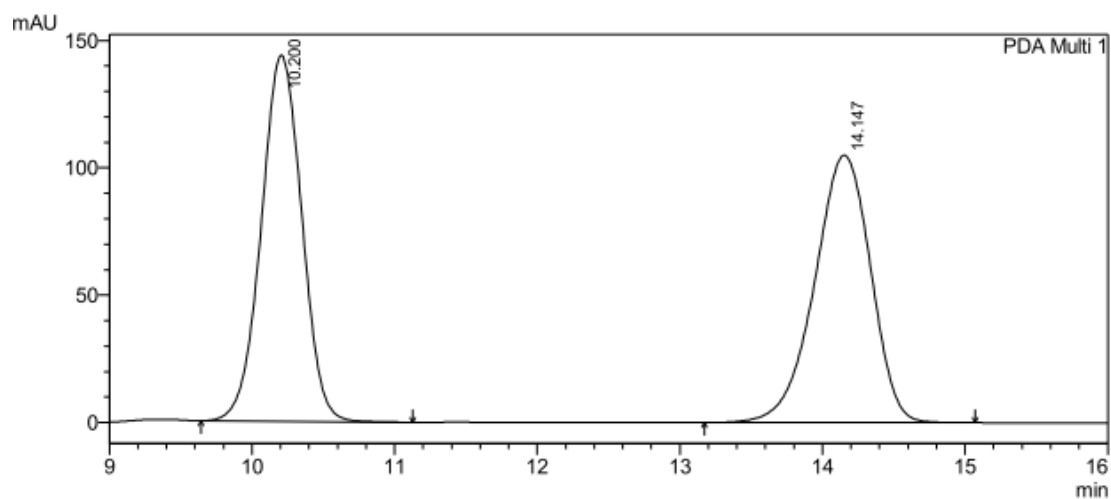
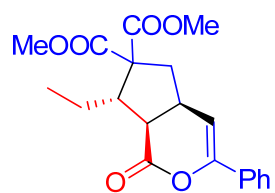
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.444	166797	7312	3.990	5.356
2	13.602	171479	6830	4.102	5.003
3	16.779	1920143	67915	45.931	49.748
4	20.974	1922119	54461	45.978	39.893
Total		4180538	136518	100.000	100.000



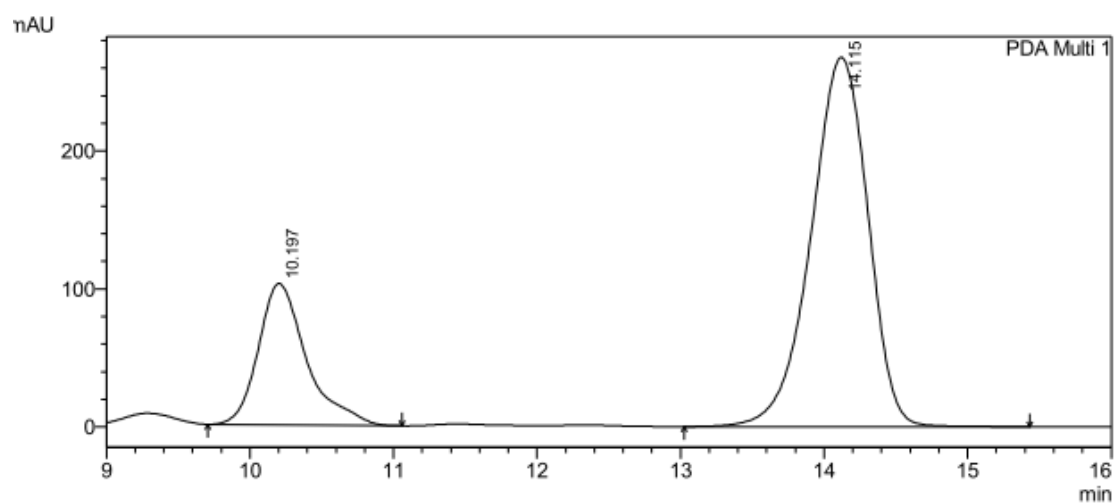
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.596	1703336	39662	5.800	7.518
2	20.505	27664171	487910	94.200	92.482
Total		29367507	527572	100.000	100.000



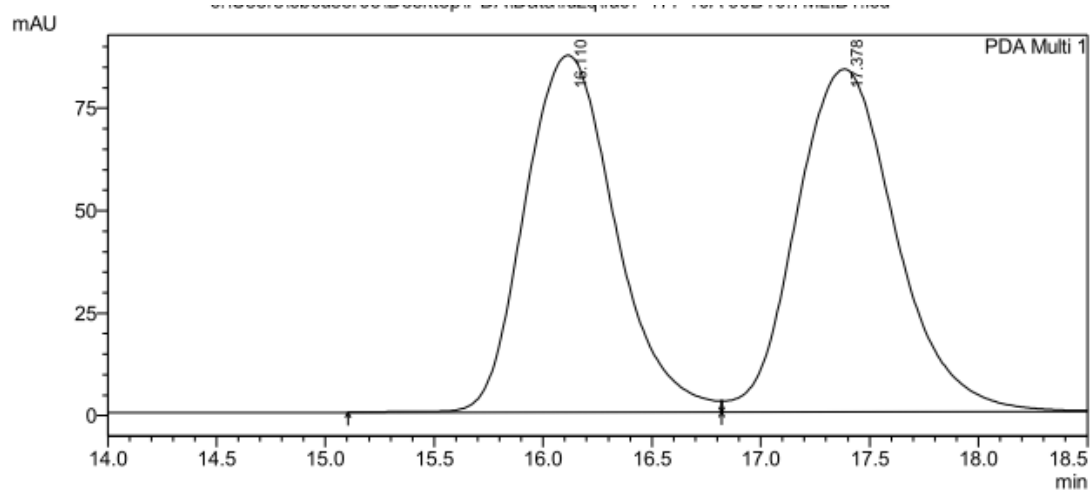
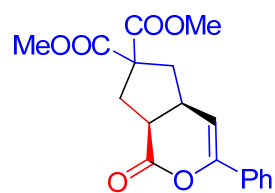
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.200	2848965	143822	49.732	57.792
2	14.147	2879657	105039	50.268	42.208
Total		5728622	248861	100.000	100.000



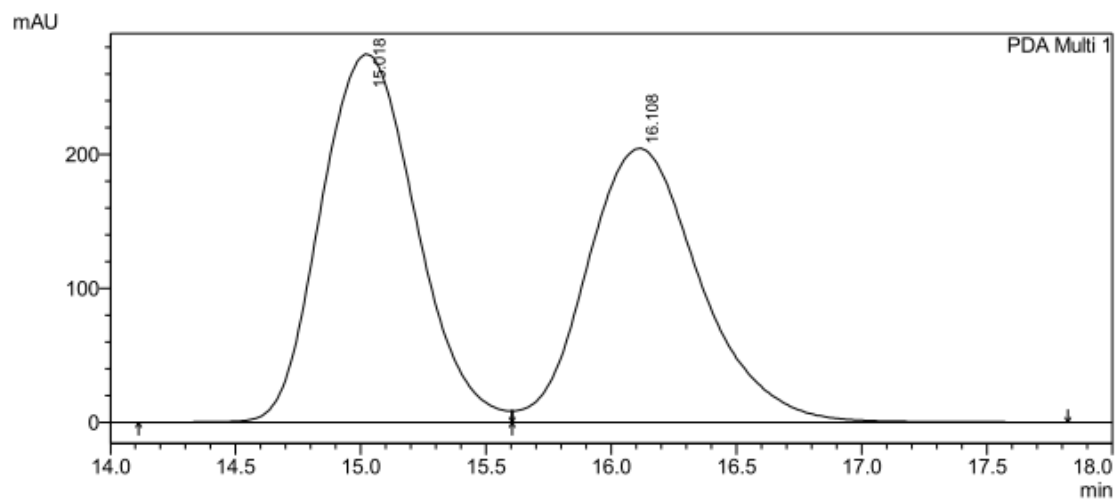
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.197	2399850	102428	24.519	27.676
2	14.115	7387832	267671	75.481	72.324
Total		9787682	370099	100.000	100.000



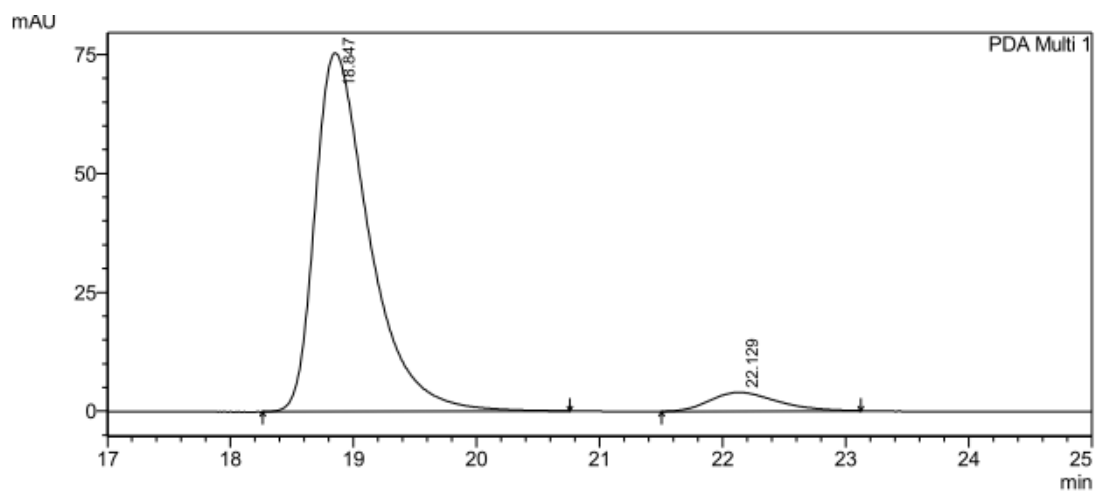
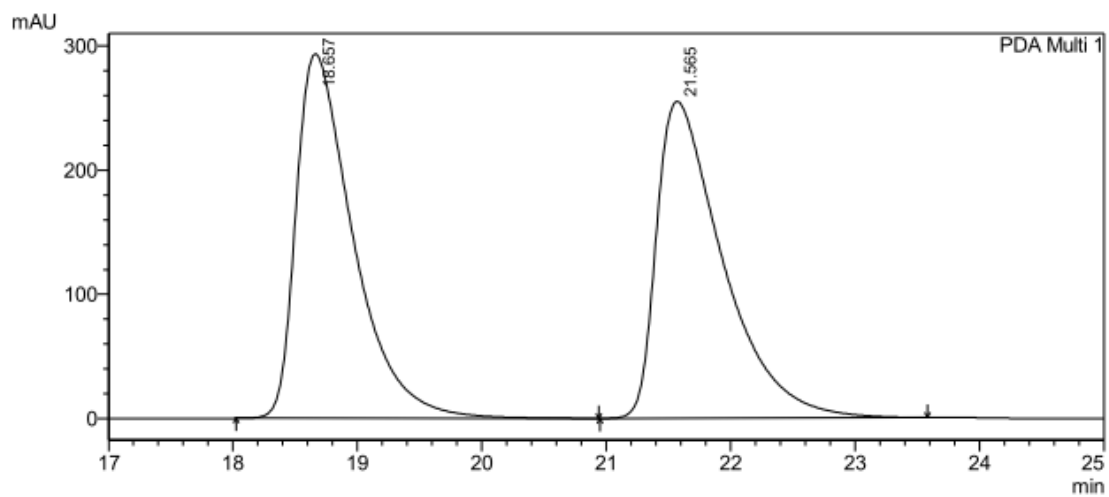
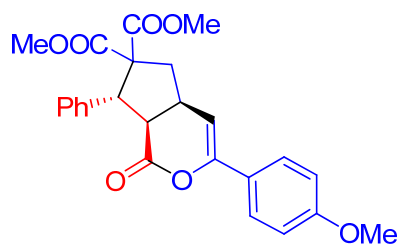
PDA Ch1 254nm 4nm

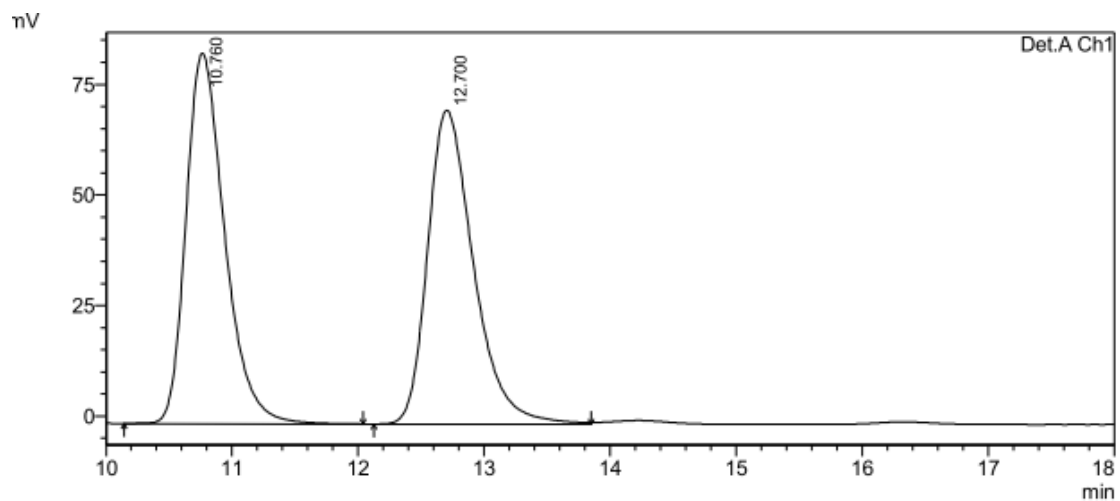
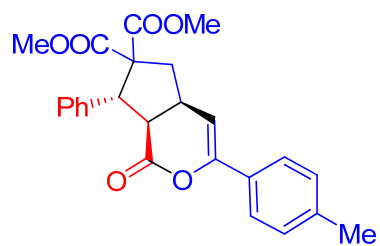
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.110	2514042	87055	48.620	51.010
2	17.378	2656794	83607	51.380	48.990
Total		5170836	170661	100.000	100.000



PDA Ch1 254nm 4nm

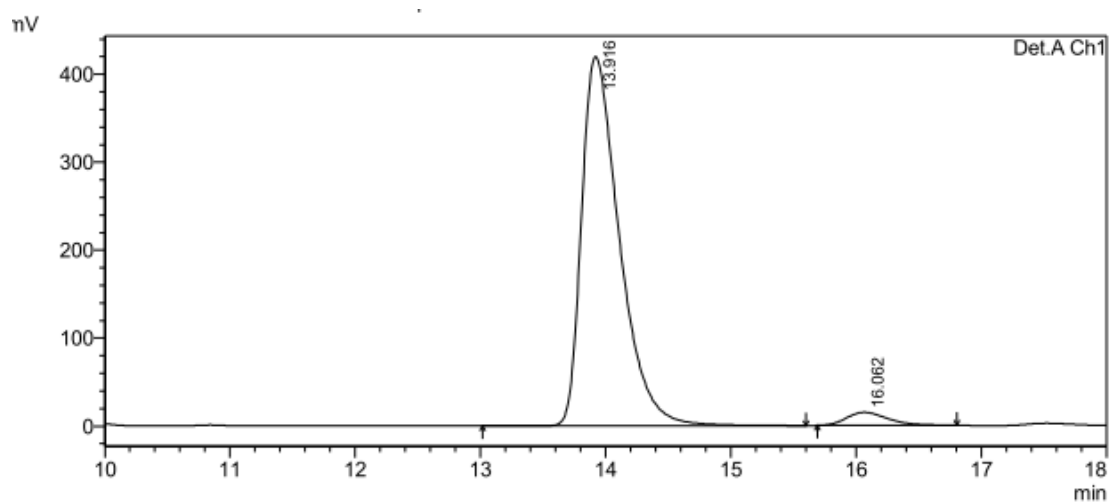
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.018	7269863	274766	53.118	57.329
2	16.108	6416357	204510	46.882	42.671
Total		13686220	479275	100.000	100.000



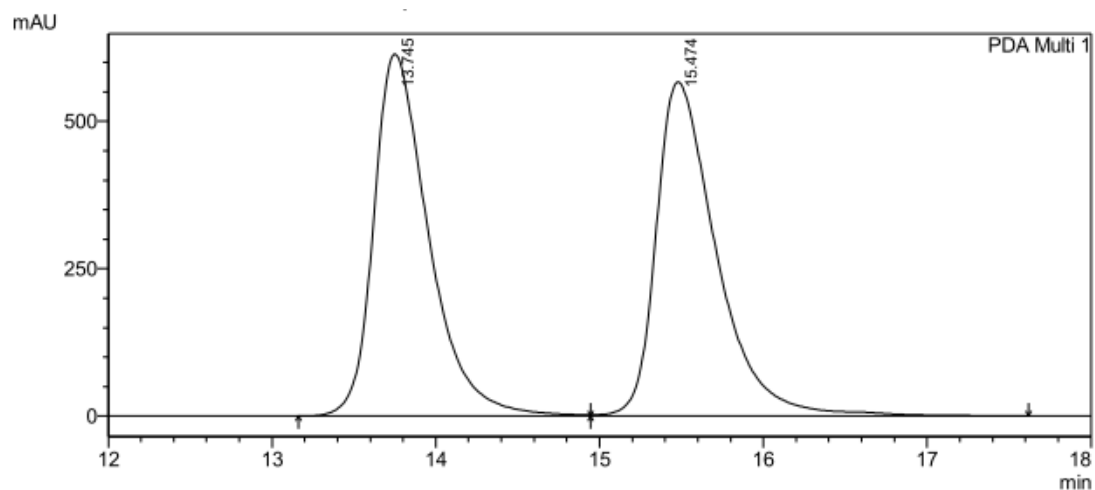
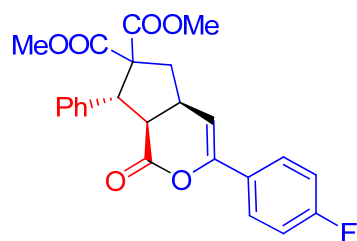


UV Detector Ch1 254nm

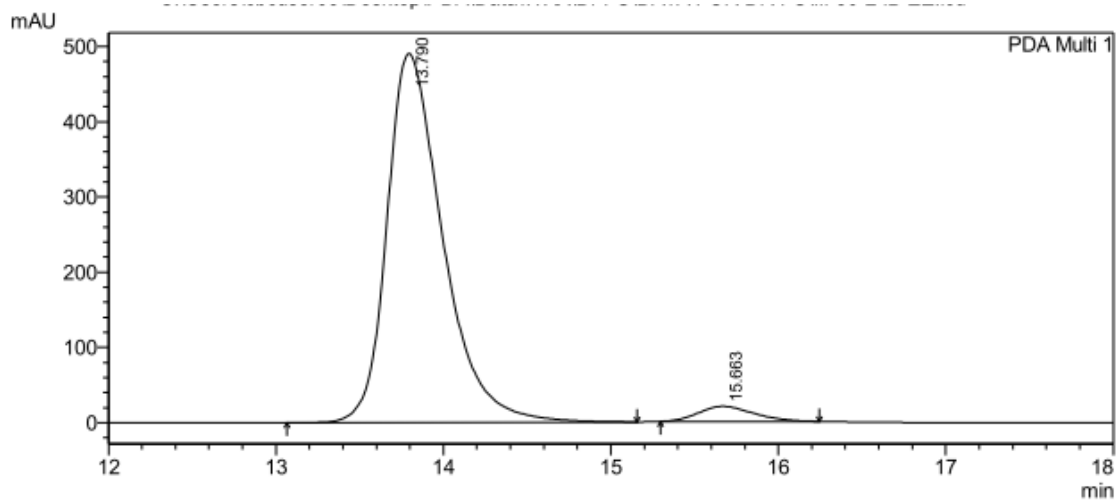
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.760	1787654	83720	49.821	54.139
2	12.700	1800534	70920	50.179	45.861
Total		3588188	154640	100.000	100.000



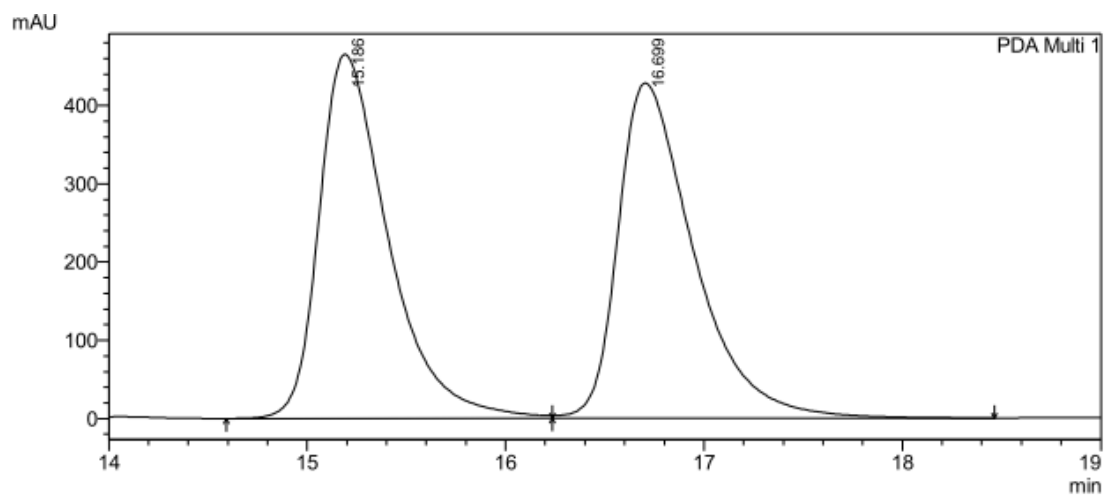
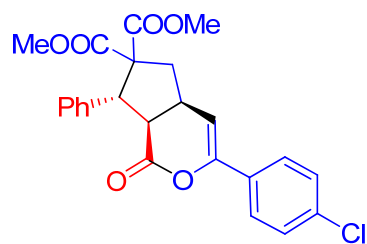
Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.916	8834138	419714	96.261	96.574
2	16.062	343113	14892	3.739	3.426
Total		9177251	434606	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.745	14360503	613903	49.753	51.987
2	15.474	14503330	566971	50.247	48.013
Total		28863834	1180874	100.000	100.000

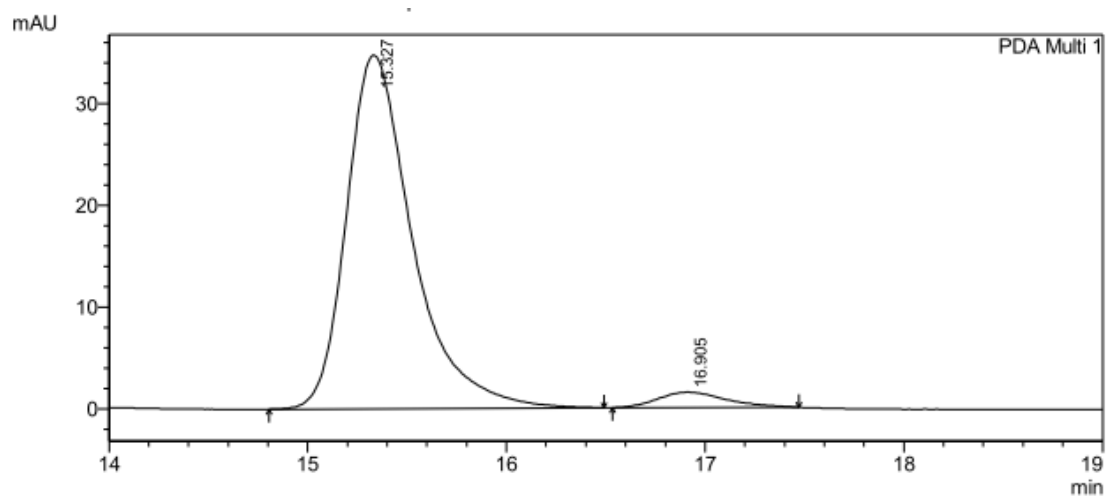


Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.790	11340985	490057	96.080	96.068
2	15.663	462717	20059	3.920	3.932
Total		11803701	510116	100.000	100.000

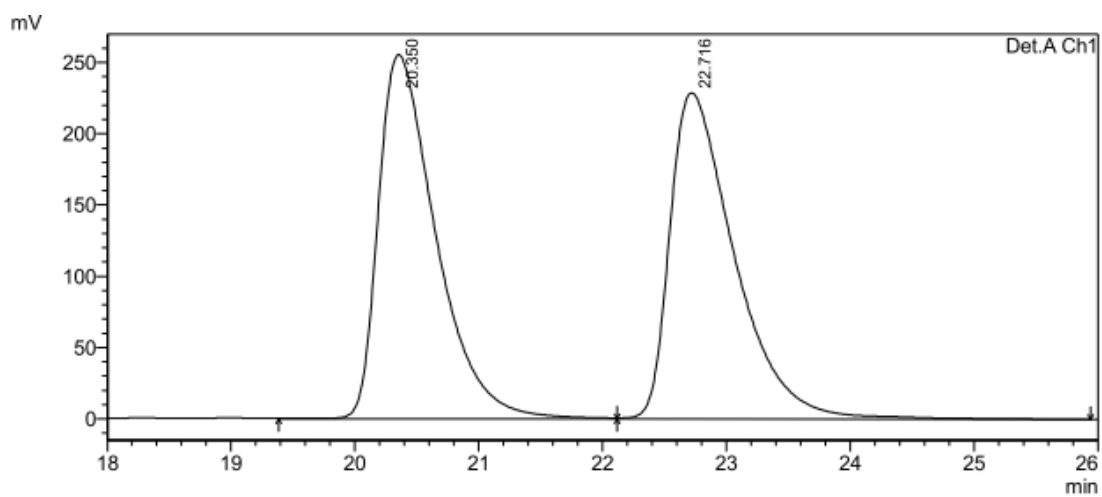
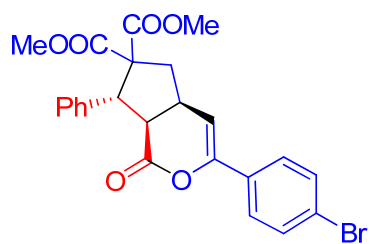


PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.186	11299630	465251	49.835	52.069
2	16.699	11374248	428282	50.165	47.931
Total		22673877	893533	100.000	100.000

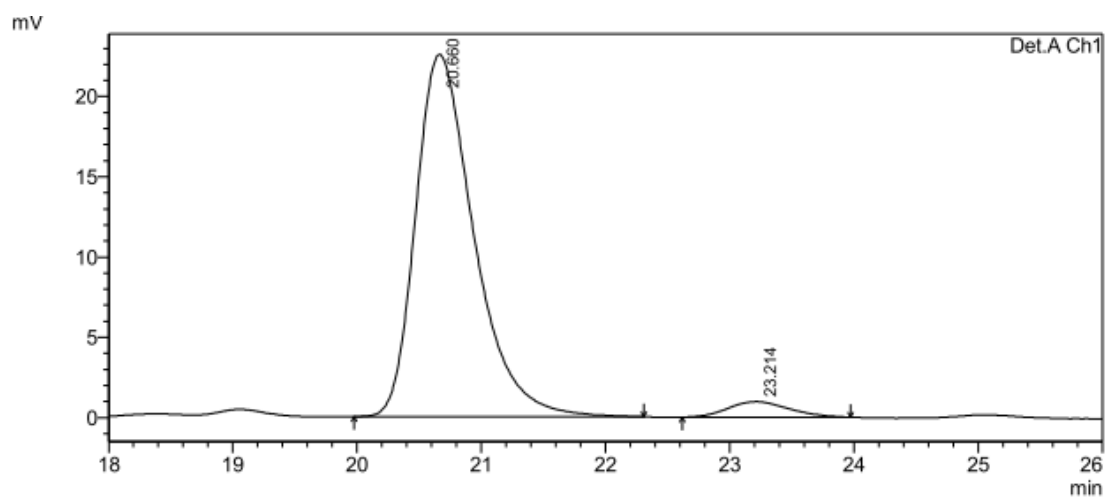


Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.327	802000	34750	95.736	95.862
2	16.905	35724	1500	4.264	4.138
Total		837724	36250	100.000	100.000

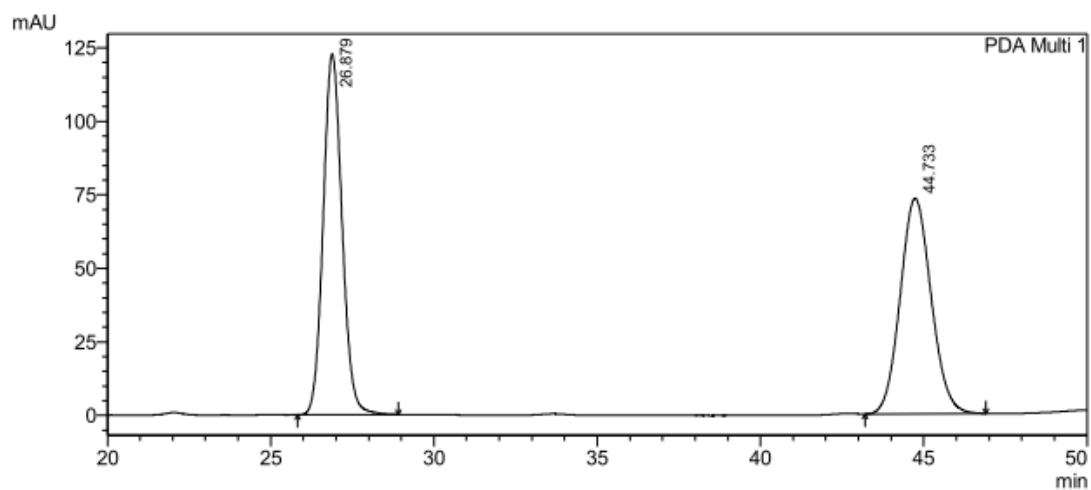
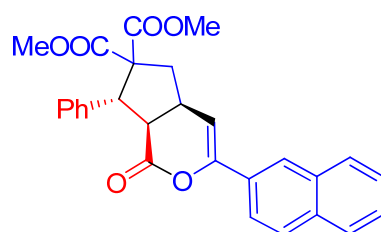


UV Detector Ch1 254nm

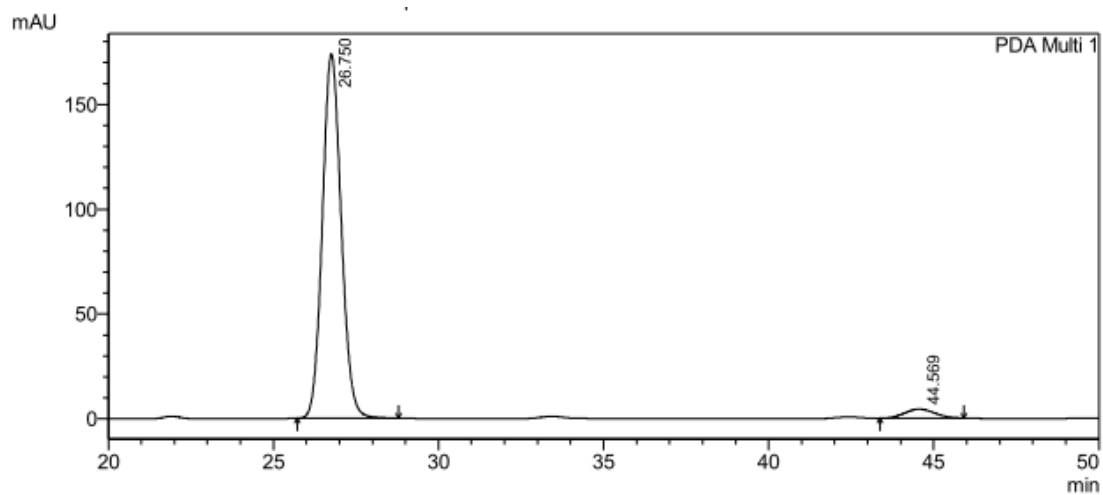
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.350	8277496	255492	49.866	52.740
2	22.716	8322125	228945	50.134	47.260
Total		16599622	484437	100.000	100.000



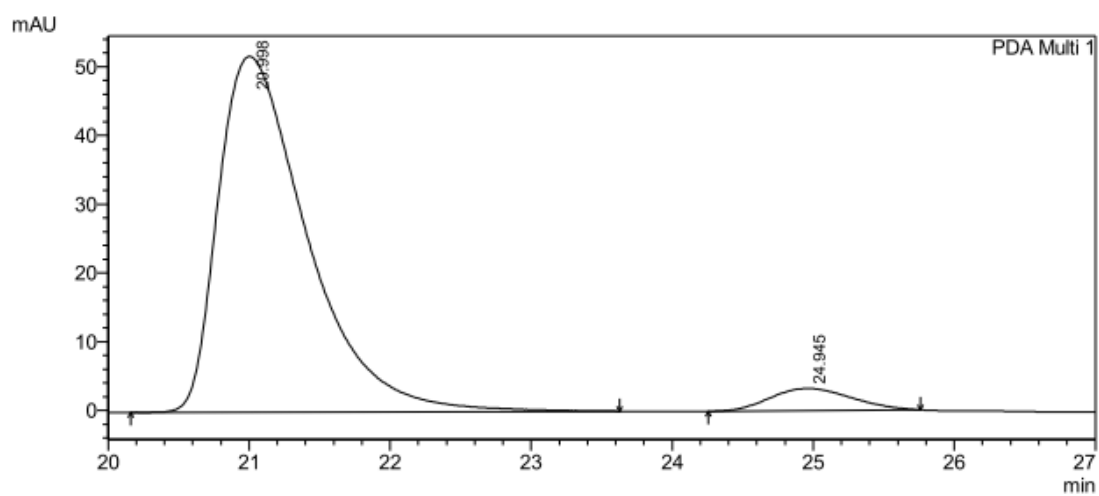
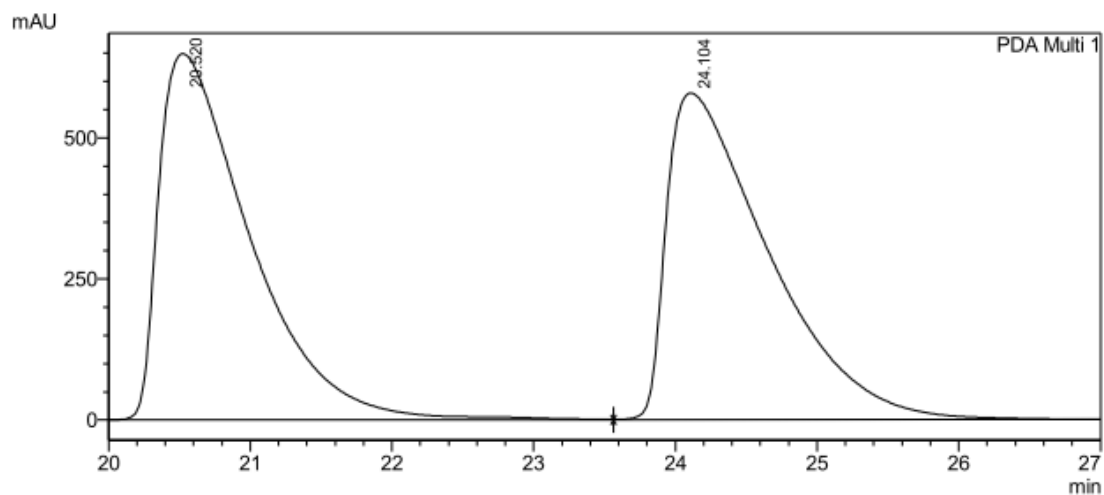
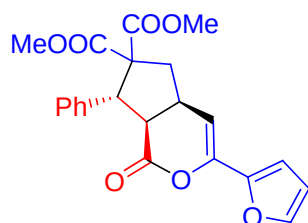
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.660	735957	22560	95.763	95.889
2	23.214	32565	967	4.237	4.111
Total		768522	23527	100.000	100.000

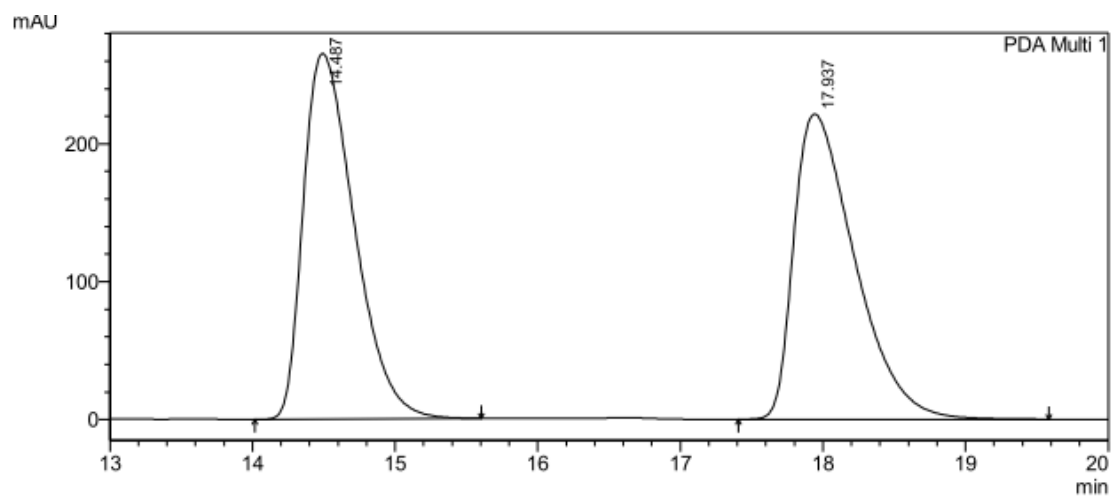
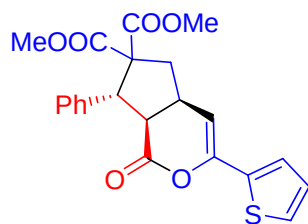


Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.879	4930477	122616	50.467	62.584
2	44.733	4839196	73307	49.533	37.416
Total		9769673	195923	100.000	100.000

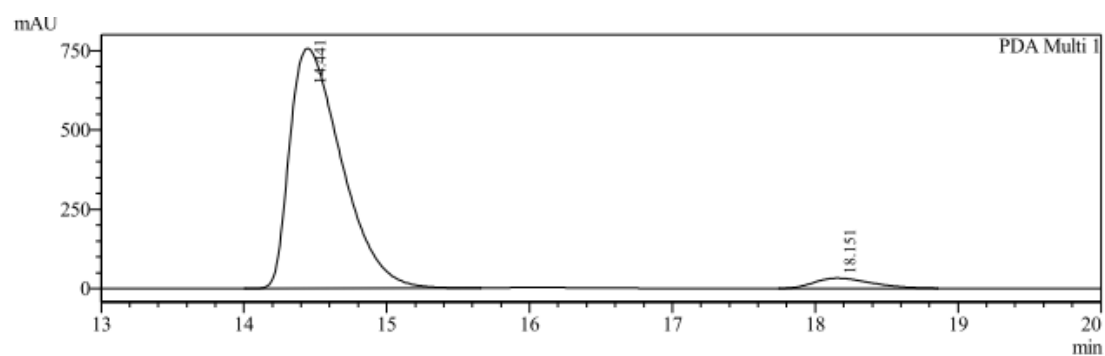


Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.750	6889050	173753	96.107	97.551
2	44.569	279046	4362	3.893	2.449
Total		7168097	178116	100.000	100.000



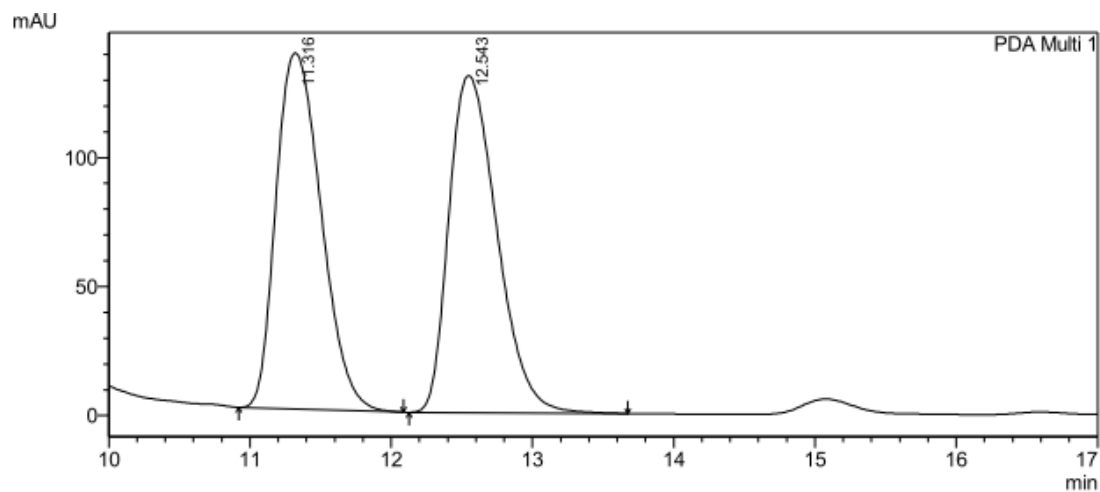
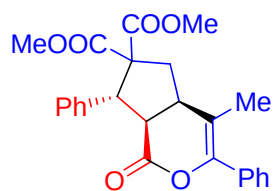


Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.487	6602535	265158	50.061	54.501
2	17.937	6586459	221359	49.939	45.499
Total		13188994	486516	100.000	100.000

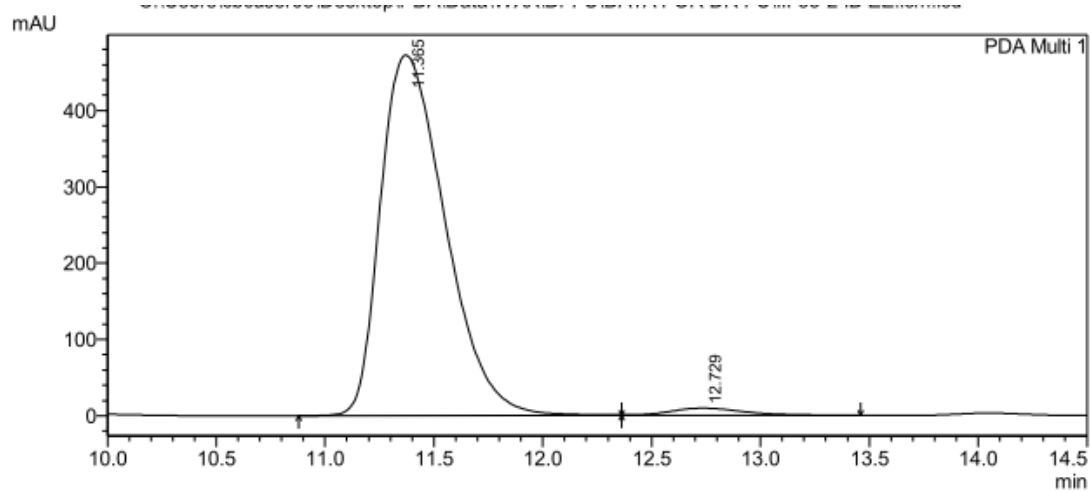


PDA Ch1 254nm 4nm

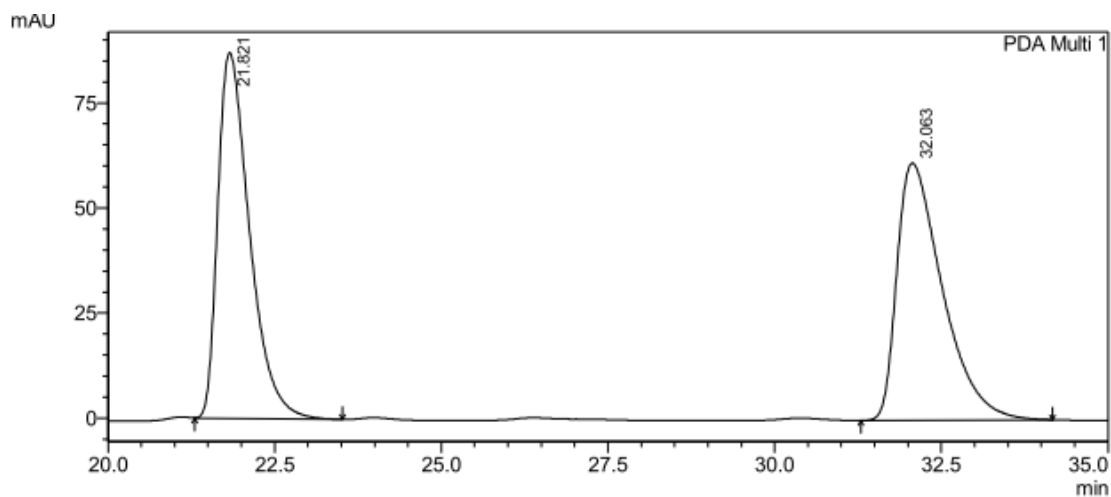
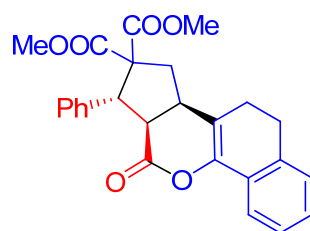
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.441	19143579	757139	95.521	95.908
2	18.151	897584	32304	4.479	4.092
Total		20041163	789443	100.000	100.000



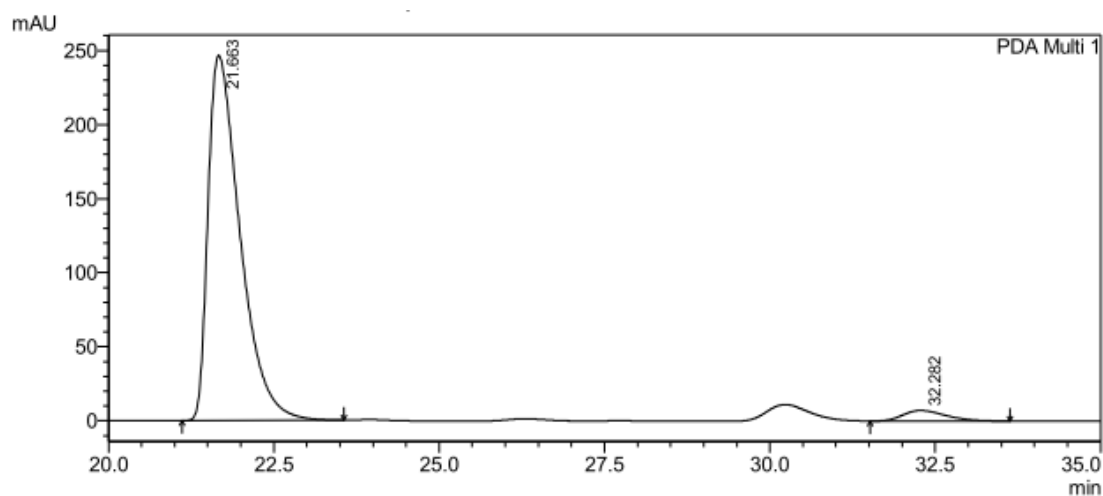
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.316	3071597	138008	49.773	51.371
2	12.543	3099672	130643	50.227	48.629
Total		6171269	268651	100.000	100.000



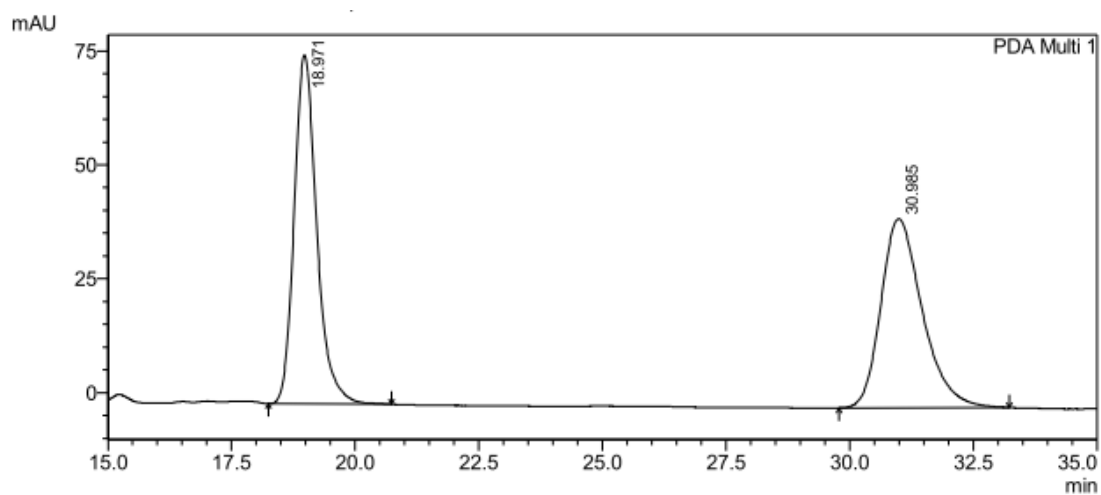
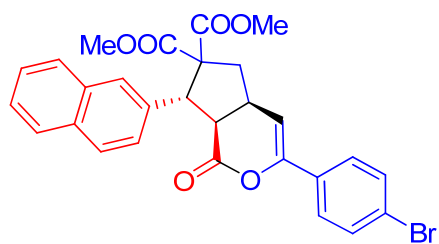
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.365	9799486	472500	97.769	98.033
2	12.729	223579	9480	2.231	1.967
Total		10023064	481980	100.000	100.000



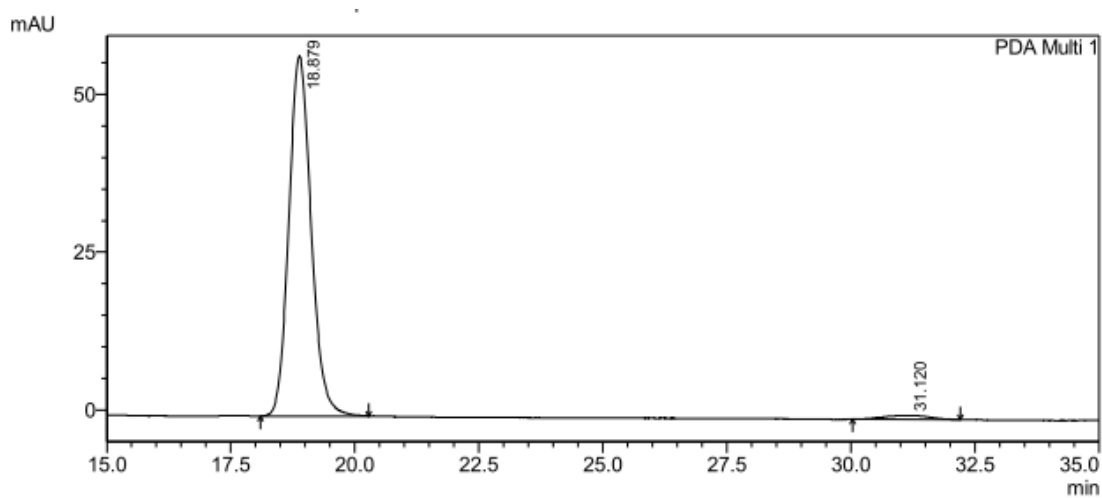
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.821	2883286	86977	49.820	58.689
2	32.063	2904075	61223	50.180	41.311
Total		5787361	148200	100.000	100.000



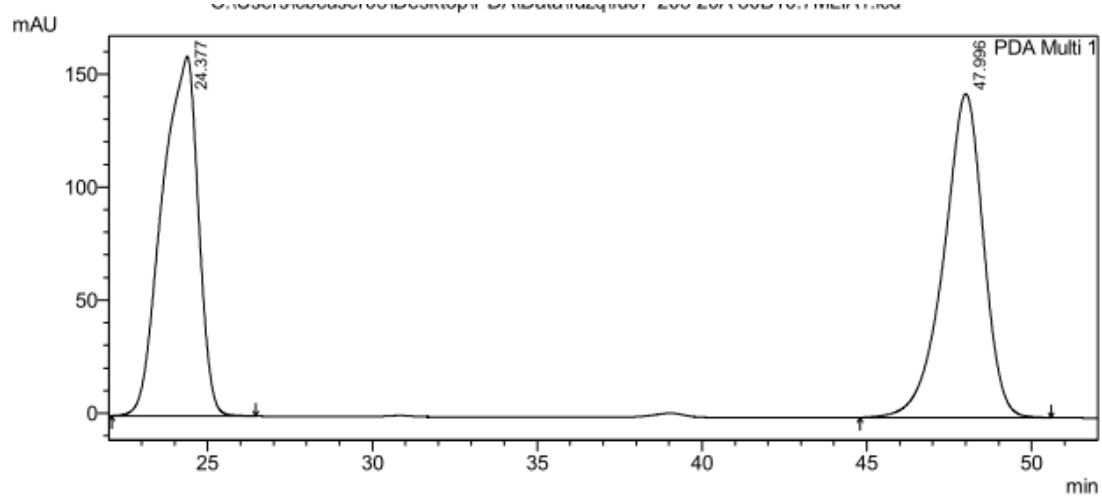
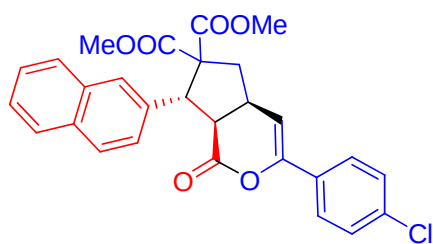
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.663	8317490	246543	96.229	97.168
2	32.282	325987	7185	3.771	2.832
Total		8643477	253728	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.971	2433080	76512	50.183	64.838
2	30.985	2415296	41492	49.817	35.162
Total		4848376	118004	100.000	100.000

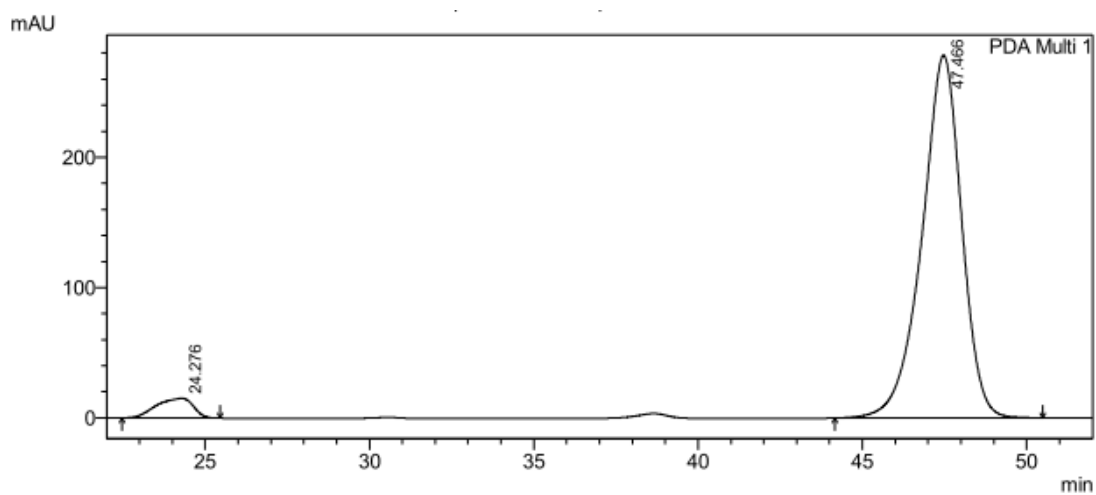


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.879	1784183	57016	97.772	98.911
2	31.120	40657	628	2.228	1.089
Total		1824840	57644	100.000	100.000



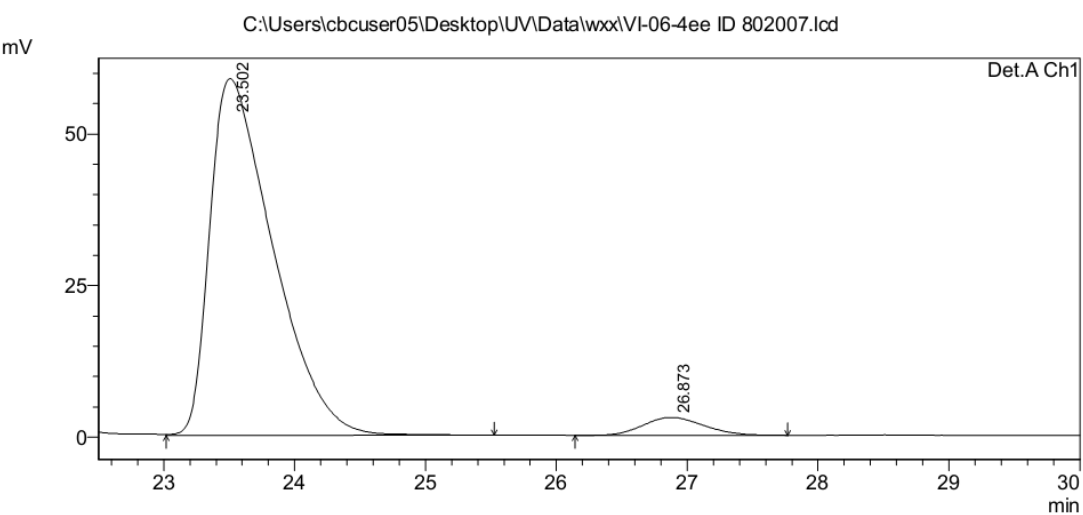
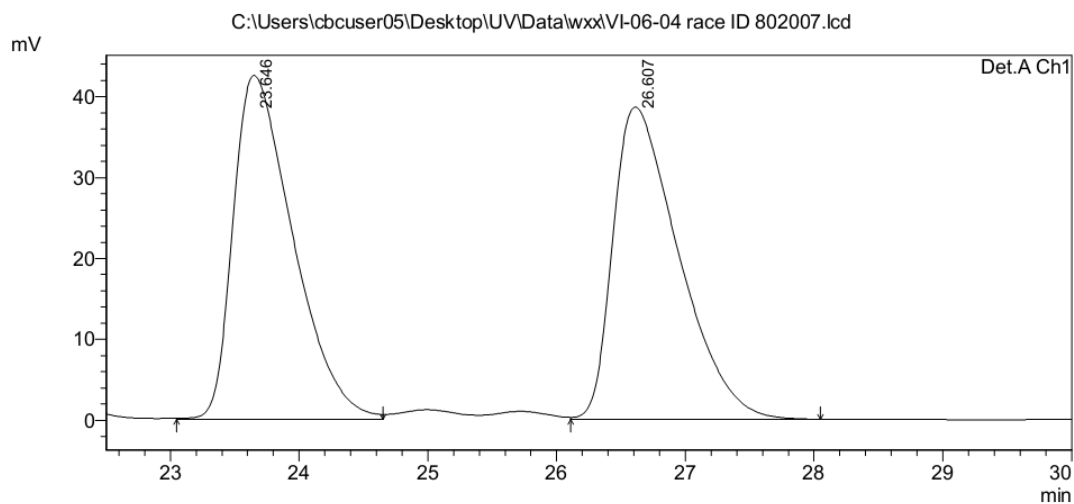
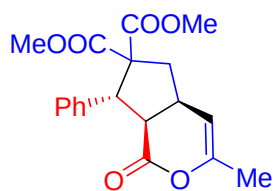
PDA Ch1 254nm 4nm

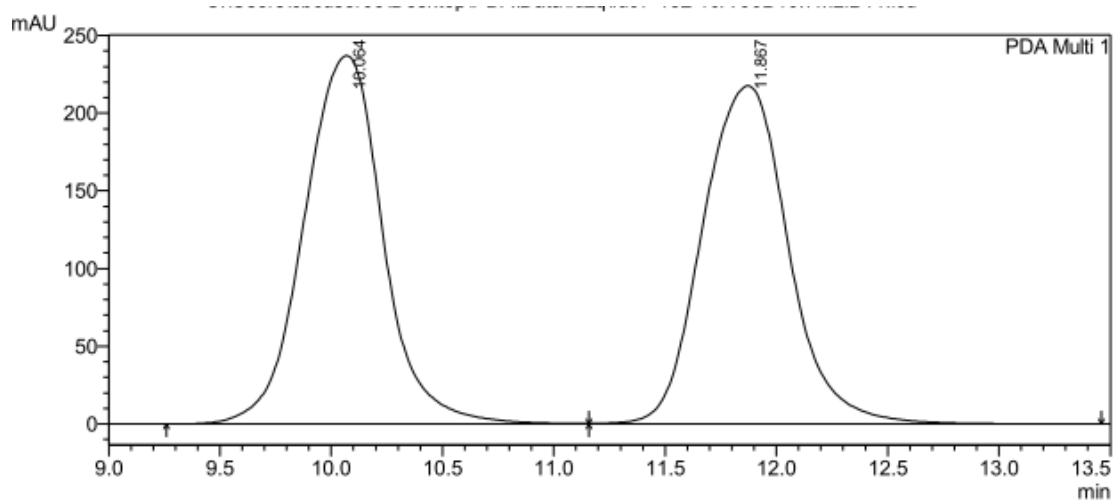
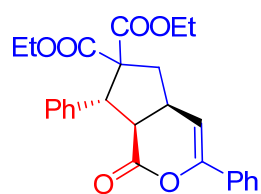
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.377	12093963	159049	50.193	52.611
2	47.996	12000835	143261	49.807	47.389
Total		24094799	302310	100.000	100.000



PDA Ch1 254nm 4nm

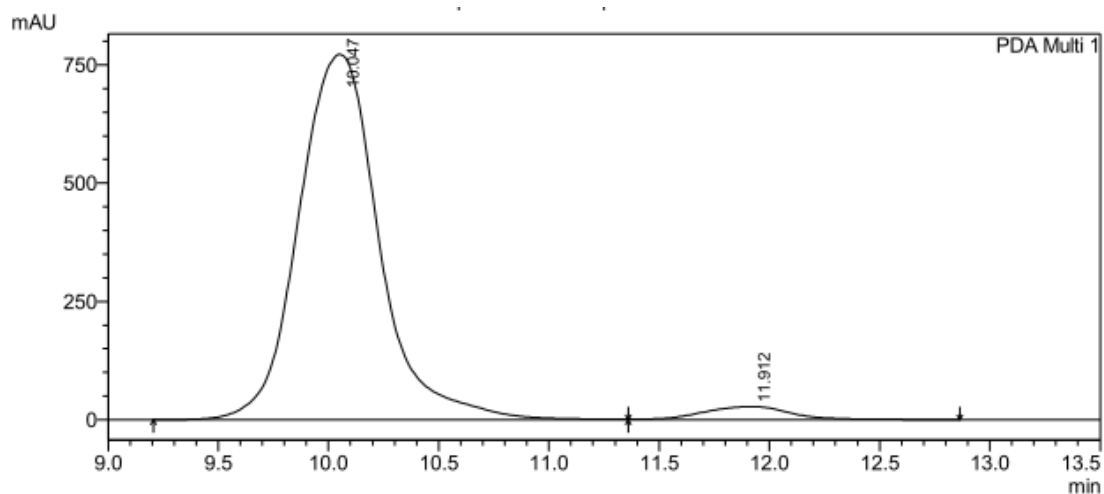
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.276	1185922	15141	4.813	5.159
2	47.466	23453768	278366	95.187	94.841
Total		24639690	293506	100.000	100.000





PDA Ch1 254nm 4nm

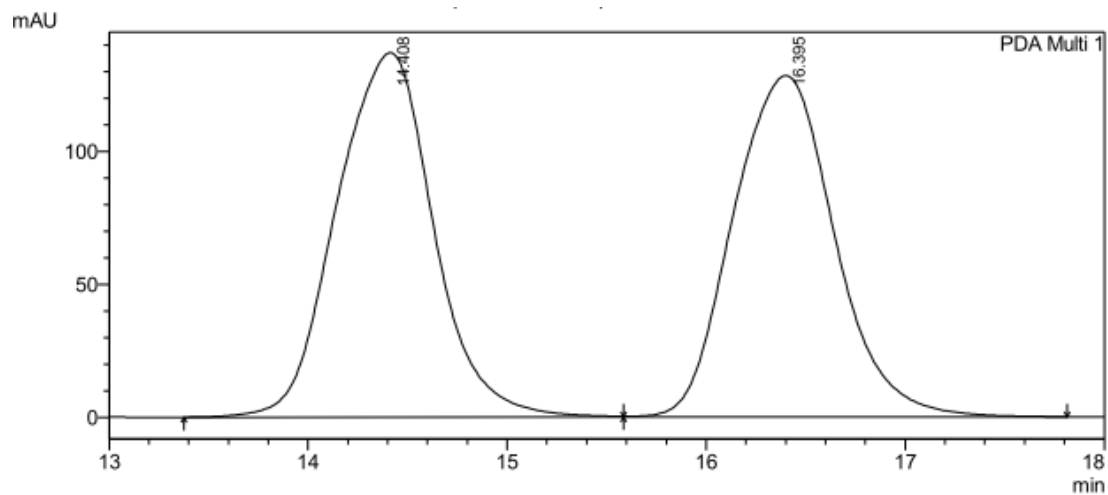
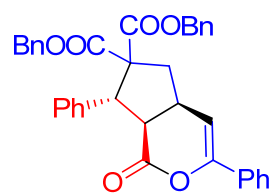
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.064	5845239	237080	50.000	52.140
2	11.867	5845207	217615	50.000	47.860
Total		11690447	454694	100.000	100.000



Peak Table

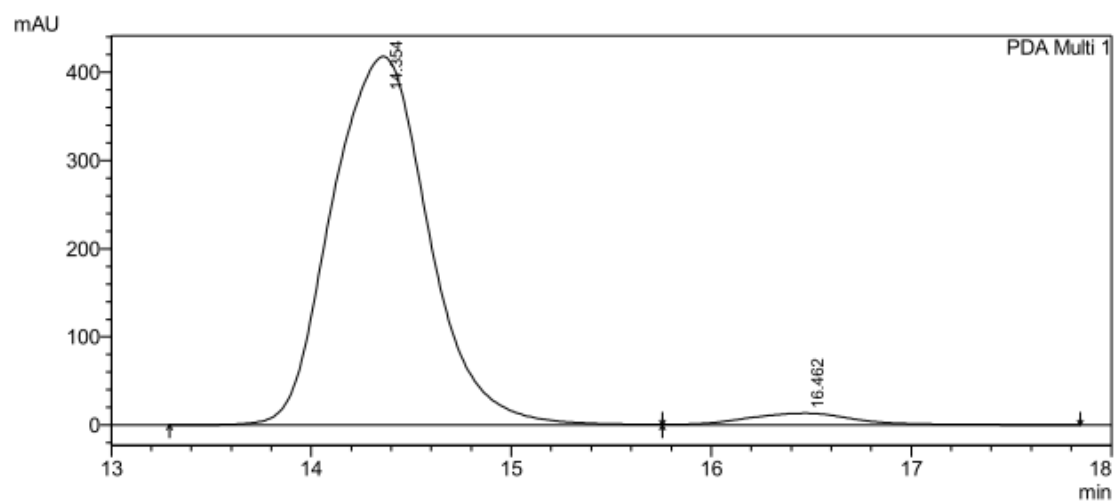
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.047	19549663	771658	96.315	96.573
2	11.912	747890	27386	3.685	3.427
Total		20297553	799044	100.000	100.000



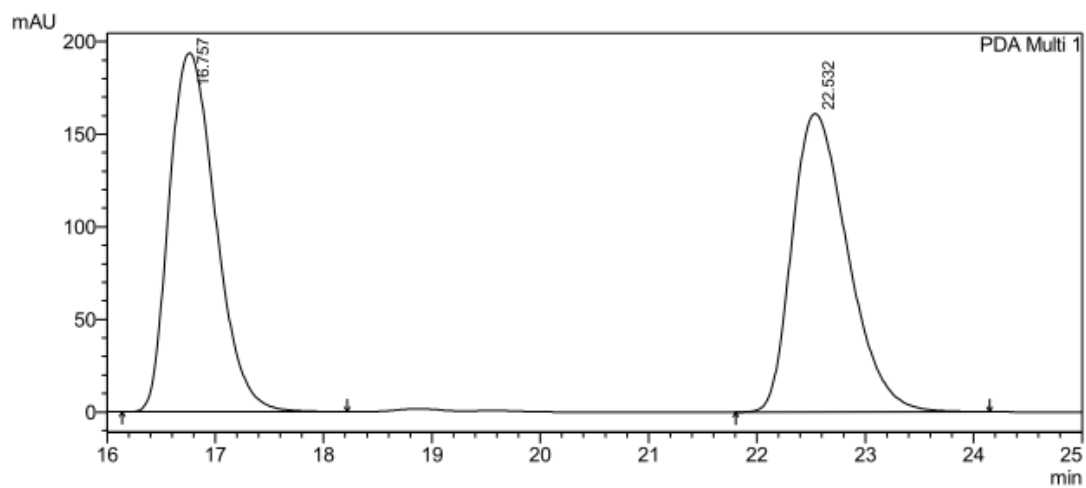
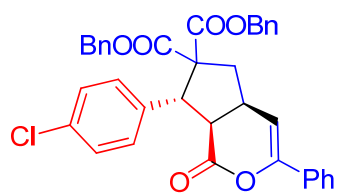
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.408	4636059	137022	50.474	51.642
2	16.395	4549000	128310	49.526	48.358
Total		9185059	265332	100.000	100.000



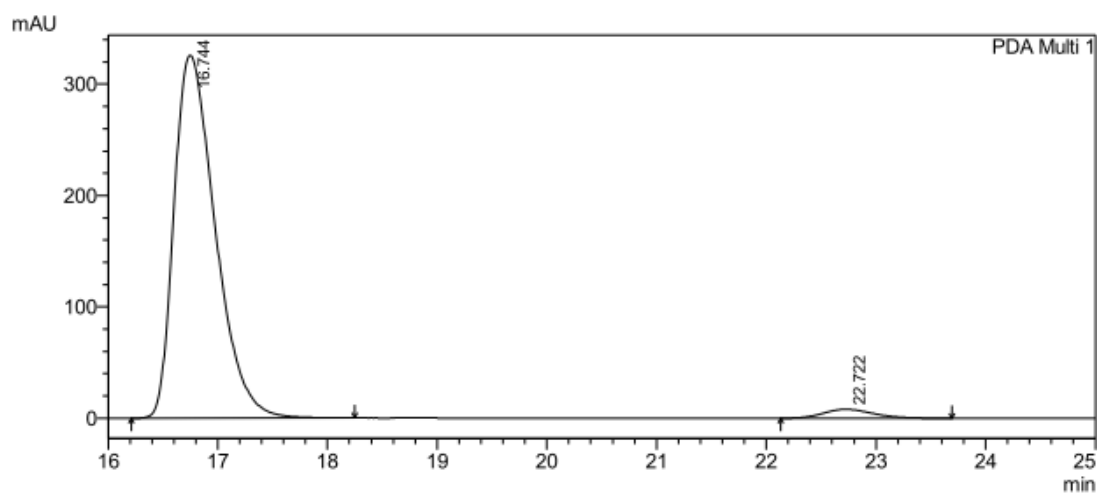
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.354	14030015	417576	96.578	96.932
2	16.462	497076	13217	3.422	3.068
Total		14527091	430793	100.000	100.000



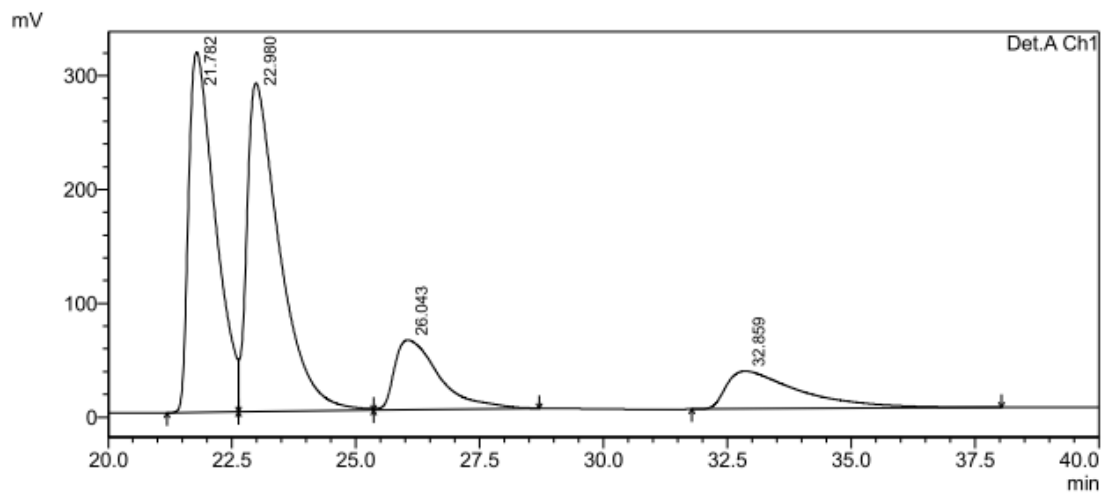
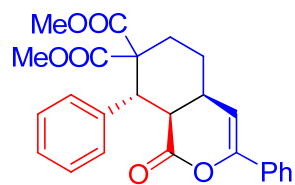
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.757	5769409	193548	49.995	54.584
2	22.532	5770662	161039	50.005	45.416
Total		11540071	354587	100.000	100.000



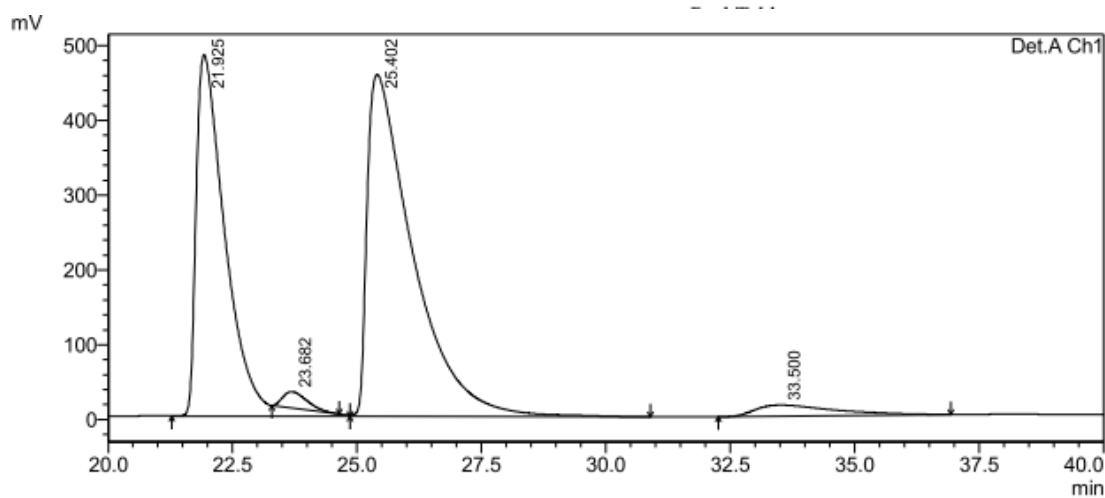
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.744	8499046	325590	97.125	97.598
2	22.722	251575	8014	2.875	2.402
Total		8750621	333604	100.000	100.000



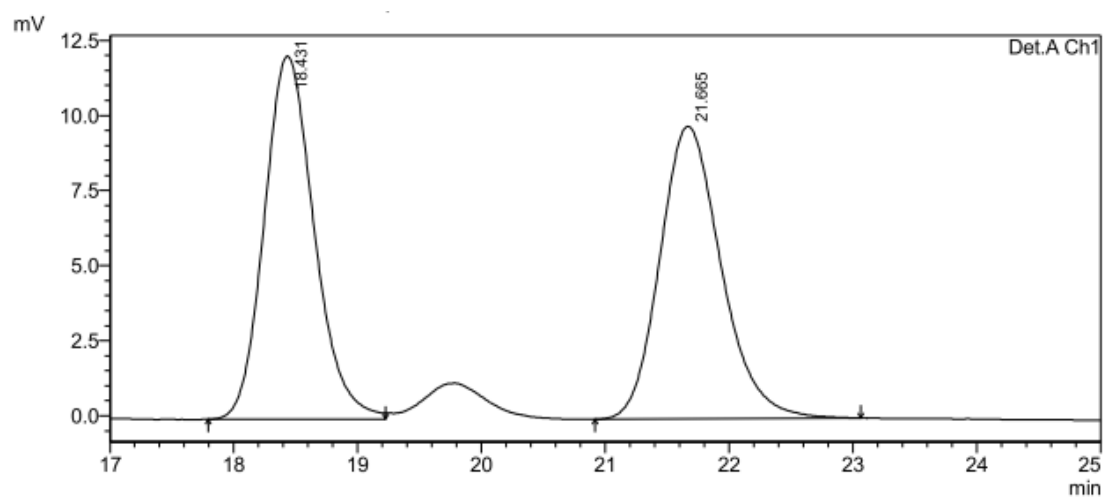
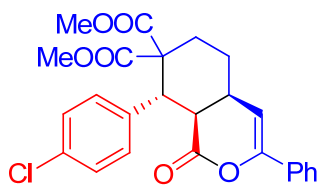
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.782	11873025	316497	36.617	45.227
2	22.980	13285220	288720	40.972	41.258
3	26.043	3827985	61408	11.806	8.775
4	32.859	3438515	33174	10.605	4.741
Total		32424744	699800	100.000	100.000



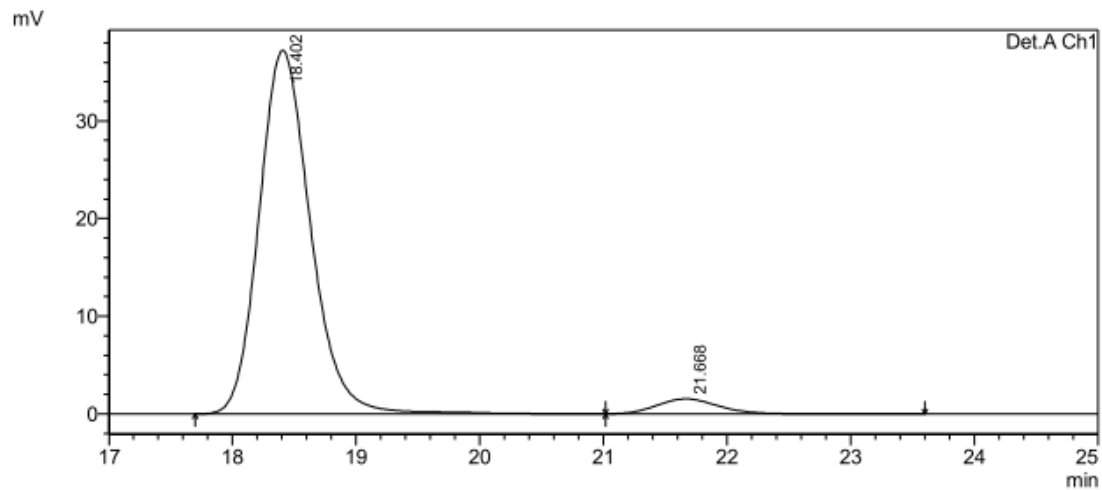
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.925	20029775	483086	38.790	49.449
2	23.682	736895	21725	1.427	2.224
3	25.402	29195460	457204	56.540	46.799
4	33.500	1674331	14929	3.243	1.528
Total		51636461	976945	100.000	100.000

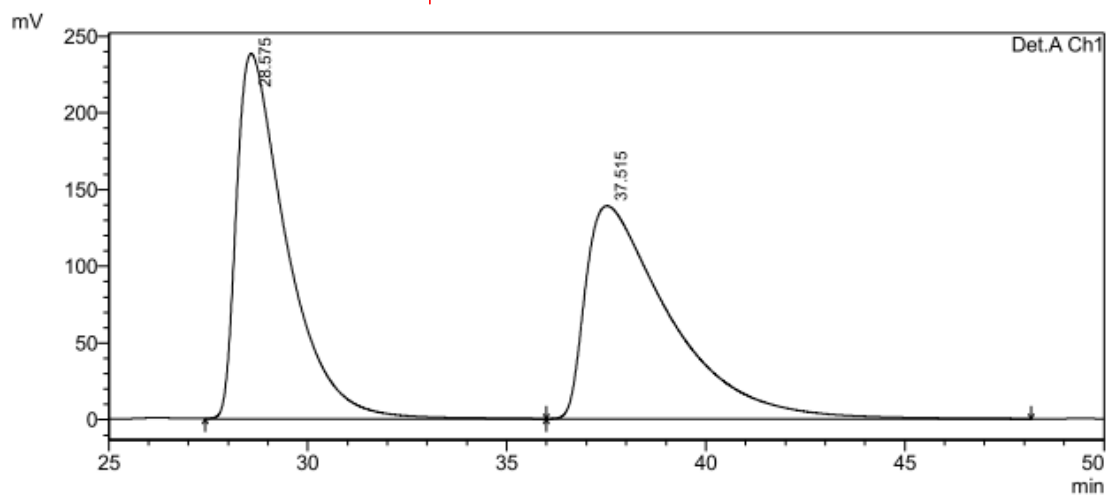
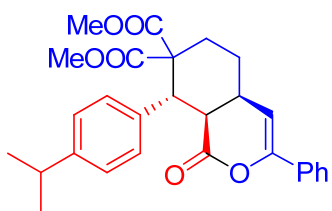


UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.431	339511	12095	50.245	55.367
2	21.665	336197	9750	49.755	44.633
Total		675708	21846	100.000	100.000

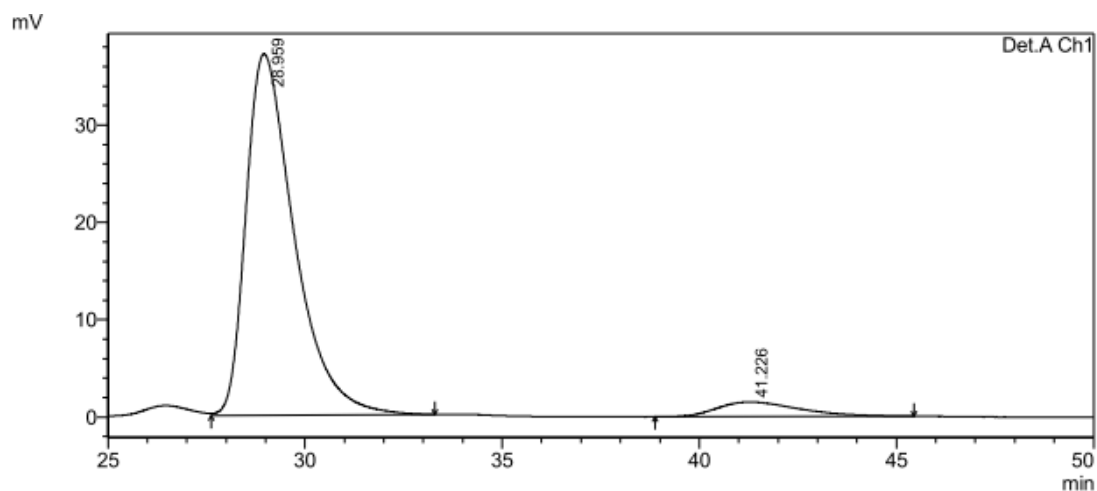


Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.402	1080401	37246	95.302	96.010
2	21.668	53265	1548	4.698	3.990
Total		1133666	38794	100.000	100.000

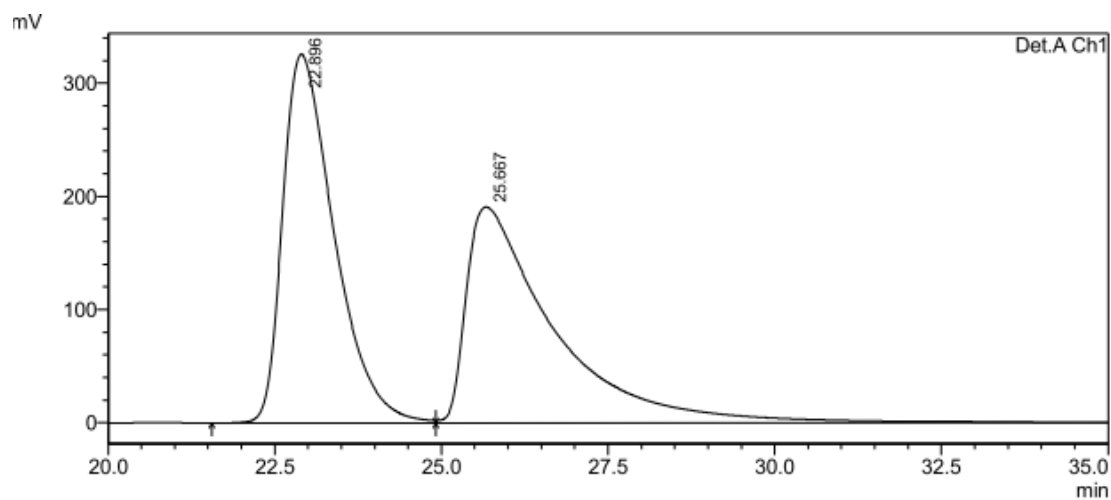
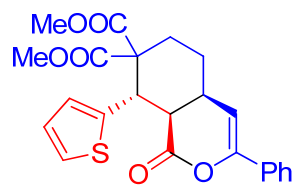


UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.575	20877875	238145	50.441	63.169
2	37.515	20512625	138851	49.559	36.831
Total		41390501	376996	100.000	100.000

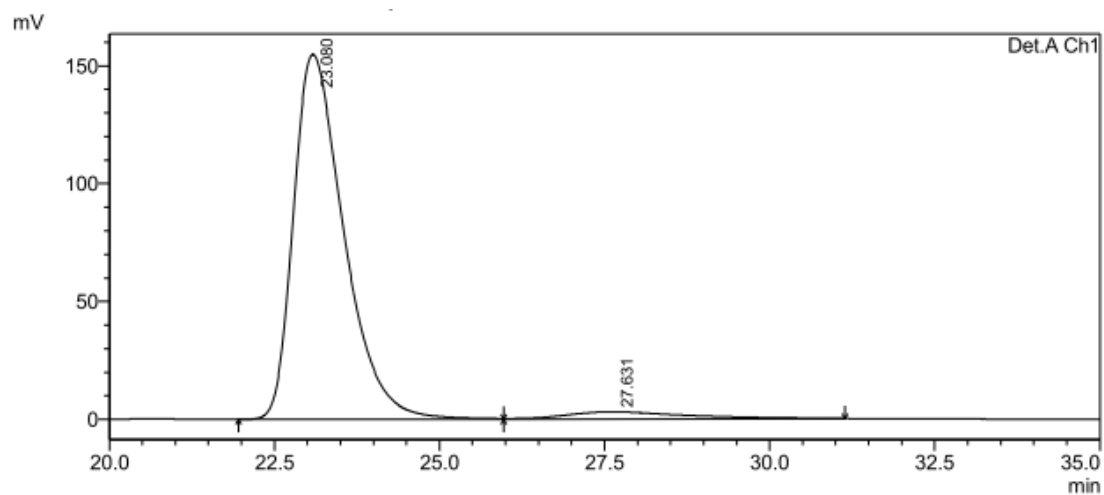


Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.959	3172143	37147	93.639	96.116
2	41.226	215486	1501	6.361	3.884
Total		3387629	38648	100.000	100.000

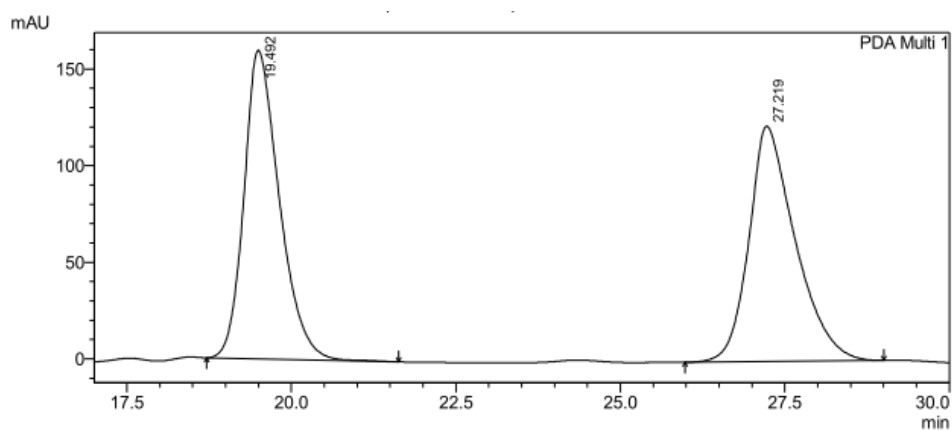
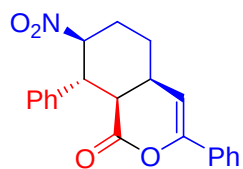


UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.896	17537841	326133	49.999	63.066
2	25.667	17538708	190997	50.001	36.934
Total		35076549	517131	100.000	100.000

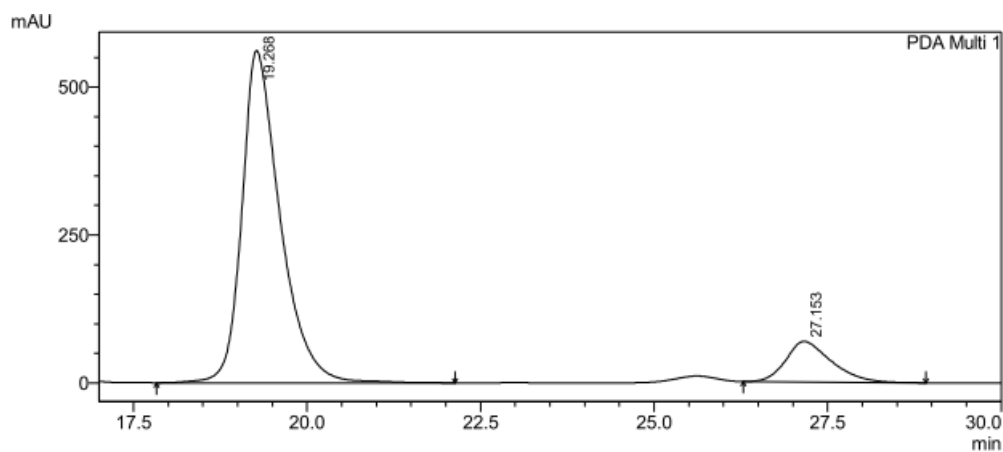


Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.080	8222935	154782	95.174	98.033
2	27.631	416934	3106	4.826	1.967
Total		8639869	157889	100.000	100.000



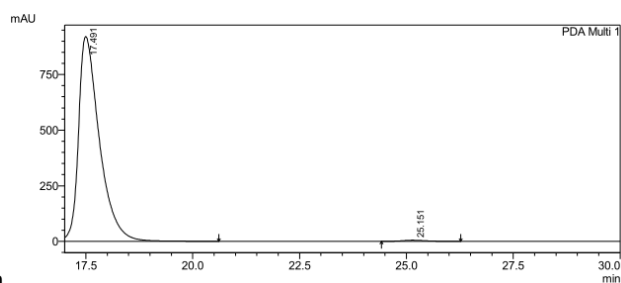
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.492	5984375	159658	50.032	56.718
2	27.219	5976754	121838	49.968	43.282
Total		11961130	281496	100.000	100.000



PDA Ch1 254nm 4nm

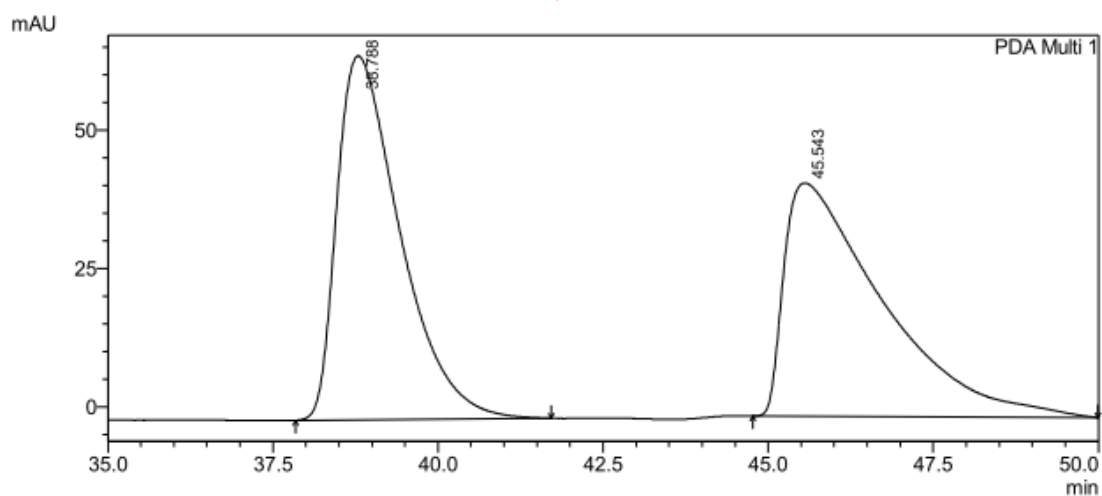
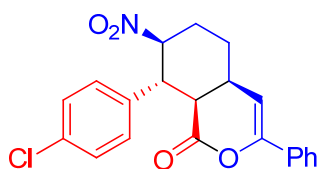
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.268	21613810	561306	87.292	89.088
2	27.153	3146622	68752	12.708	10.912
Total		24760432	630059	100.000	100.000



After recrystallization

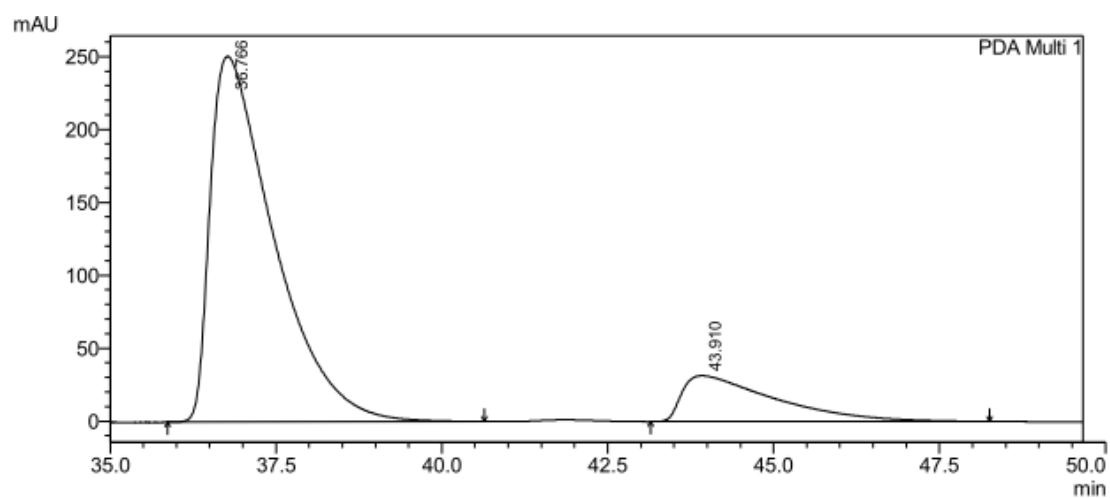
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.491	31276082	920289	99.374	99.441
2	25.151	197101	5170	0.626	0.559
Total		31473183	925459	100.000	100.000



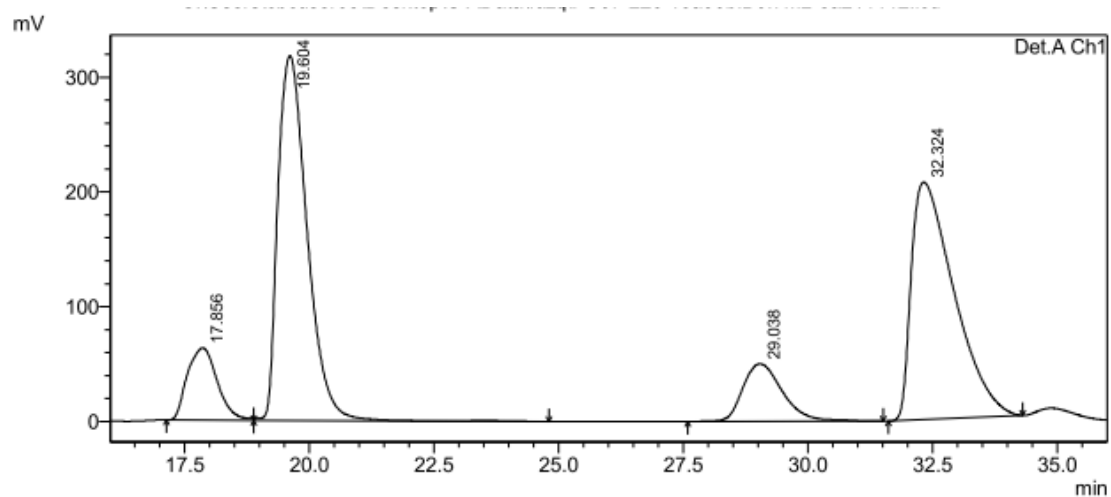
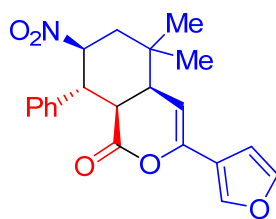
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.788	4382396	65762	50.148	60.939
2	45.543	4356453	42153	49.852	39.061
Total		8738849	107915	100.000	100.000



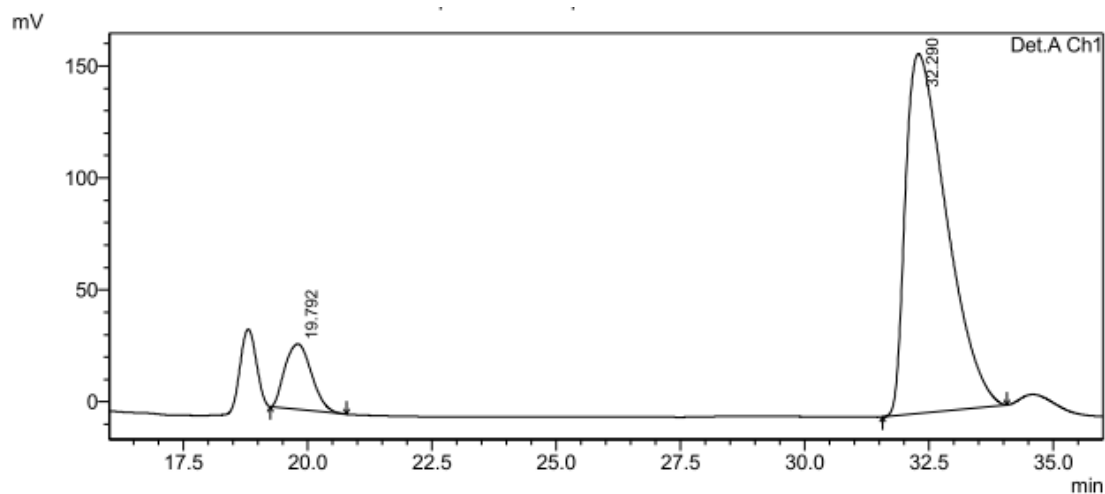
PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	36.766	16797919	250765	84.640	88.850
2	43.910	3048337	31469	15.360	11.150
Total		19846256	282234	100.000	100.000



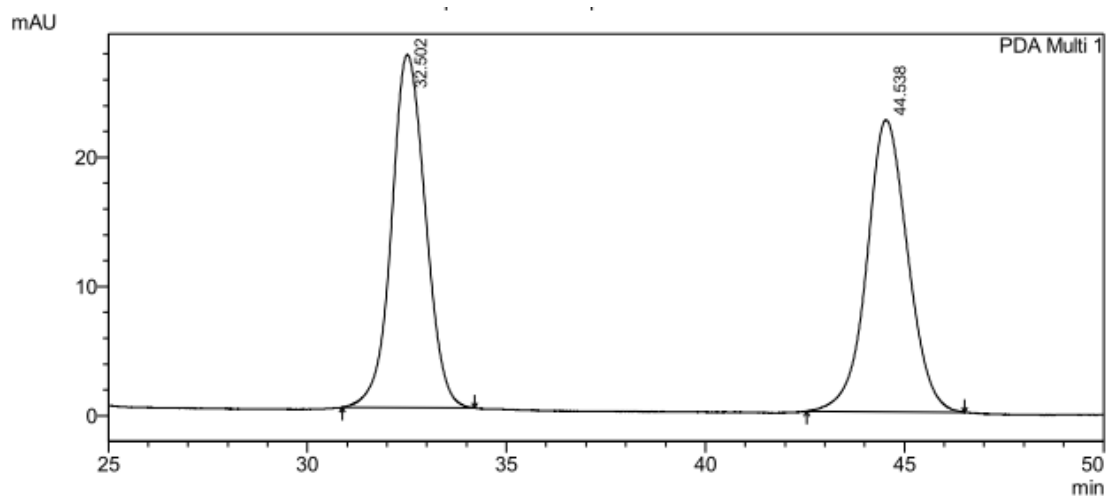
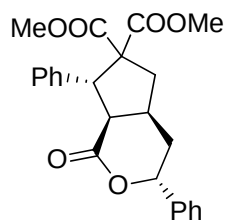
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.856	2635401	63133	8.572	9.886
2	19.604	12940388	318088	42.092	49.812
3	29.038	2792918	50221	9.085	7.865
4	32.324	12374254	207135	40.251	32.437
Total		30742960	638576	100.000	100.000



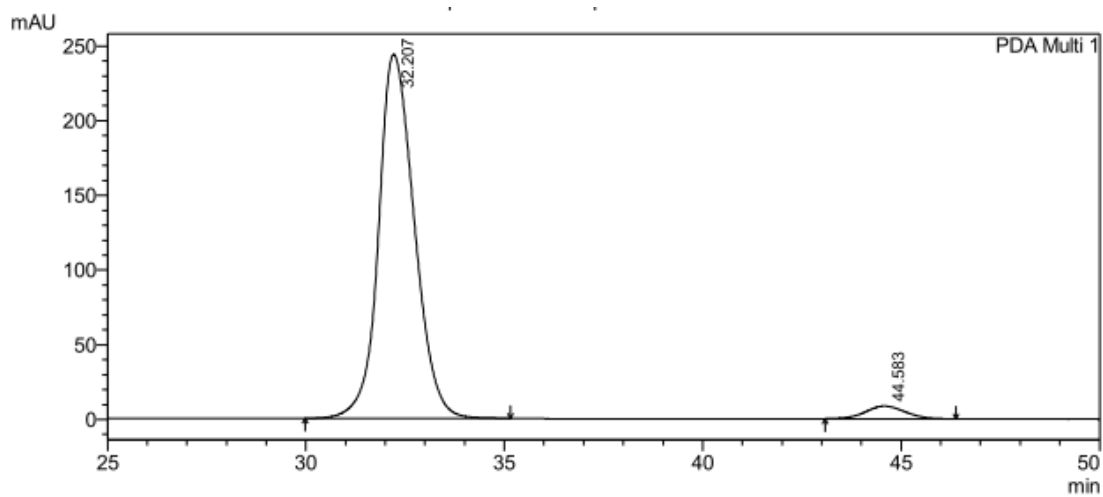
UV Detector Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.792	1091946	29196	10.543	15.380
2	32.290	9264700	160635	89.457	84.620
Total		10356646	189831	100.000	100.000



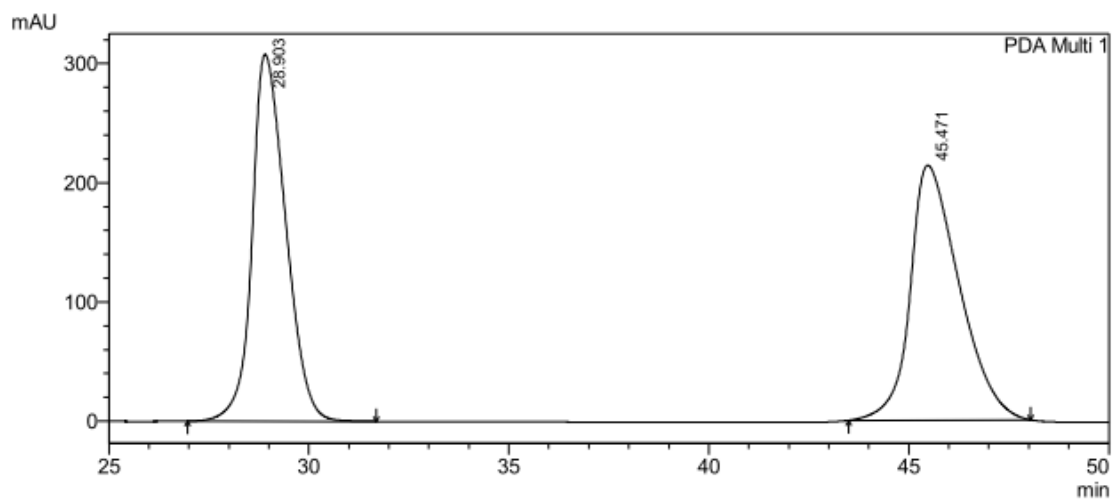
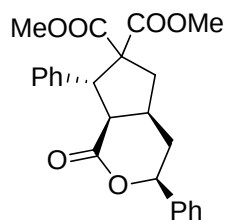
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.502	1622417	27321	50.097	54.744
2	44.538	1616117	22586	49.903	45.256
Total		3238534	49906	100.000	100.000



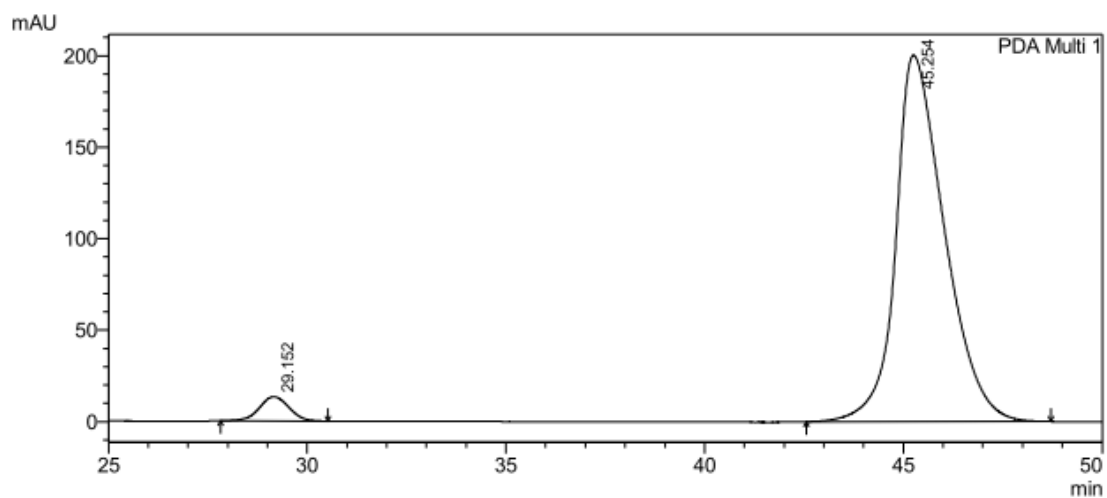
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.207	15307028	243699	96.261	96.623
2	44.583	594581	8517	3.739	3.377
Total		15901610	252216	100.000	100.000



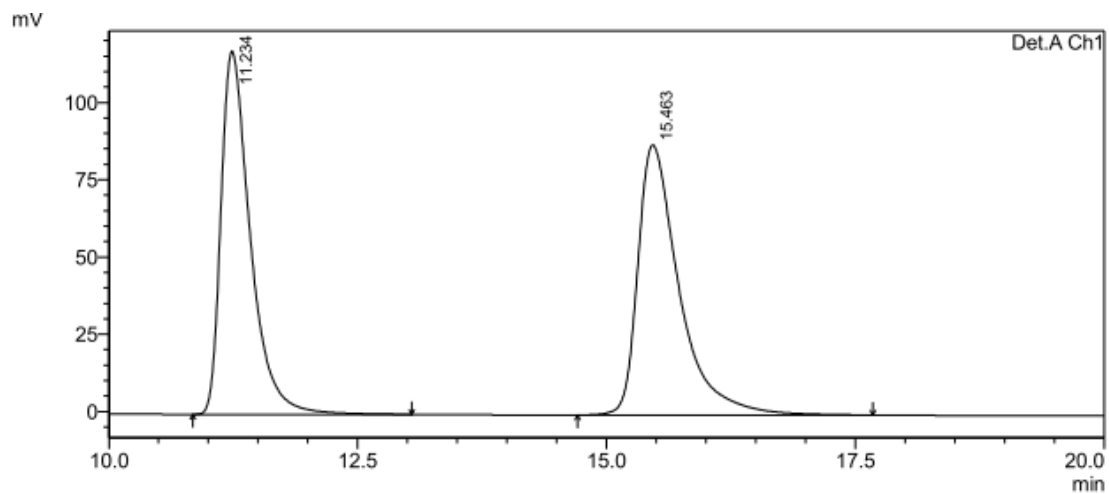
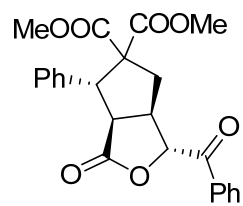
PDA Ch1 220nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.903	18054420	307724	49.685	59.017
2	45.471	18283221	213694	50.315	40.983
Total		36337641	521418	100.000	100.000

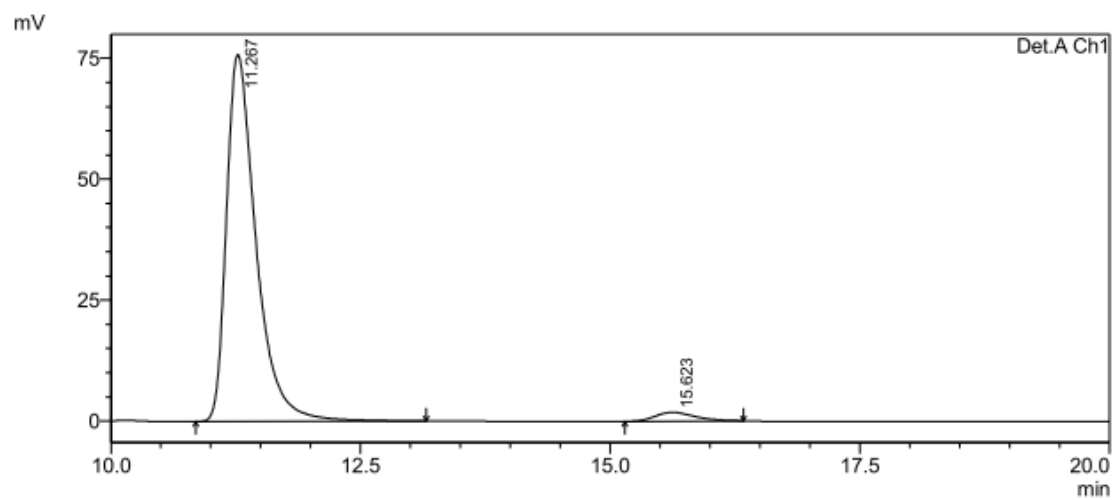


PDA Ch1 220nm 4nm

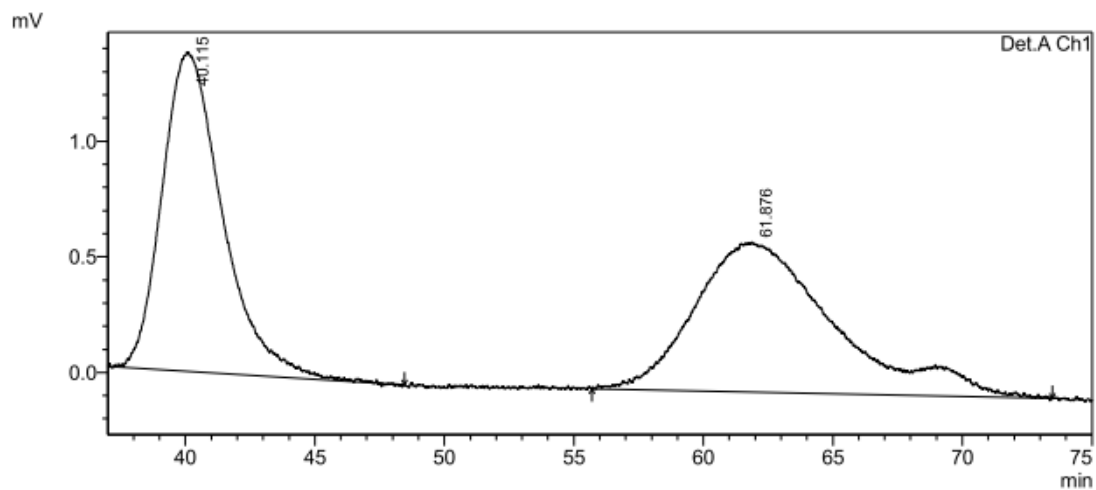
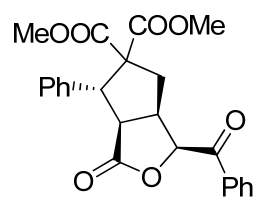
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.152	692534	13265	3.883	6.209
2	45.254	17143369	200370	96.117	93.791
Total		17835903	213636	100.000	100.000



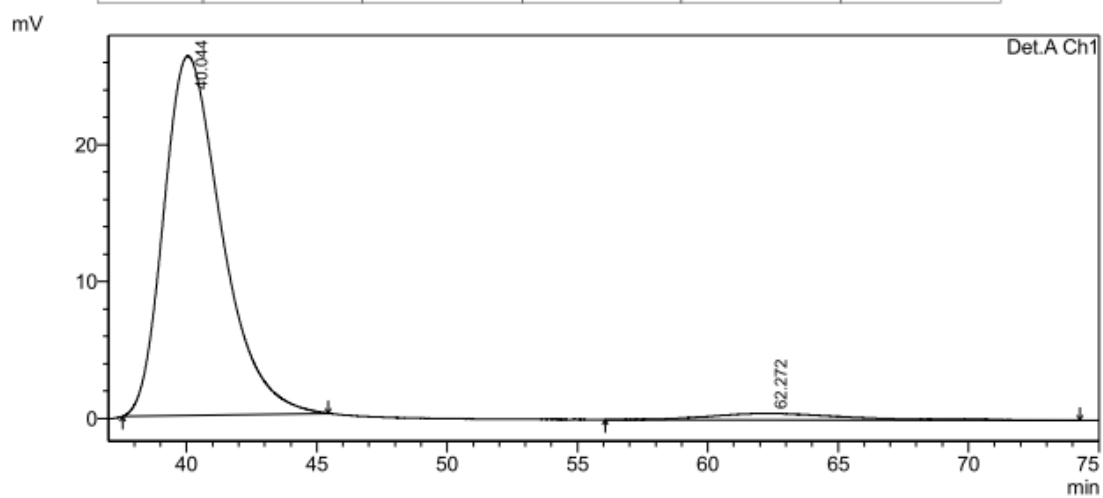
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.234	2410241	117411	48.847	57.328
2	15.463	2523979	87396	51.153	42.672
Total		4934220	204806	100.000	100.000



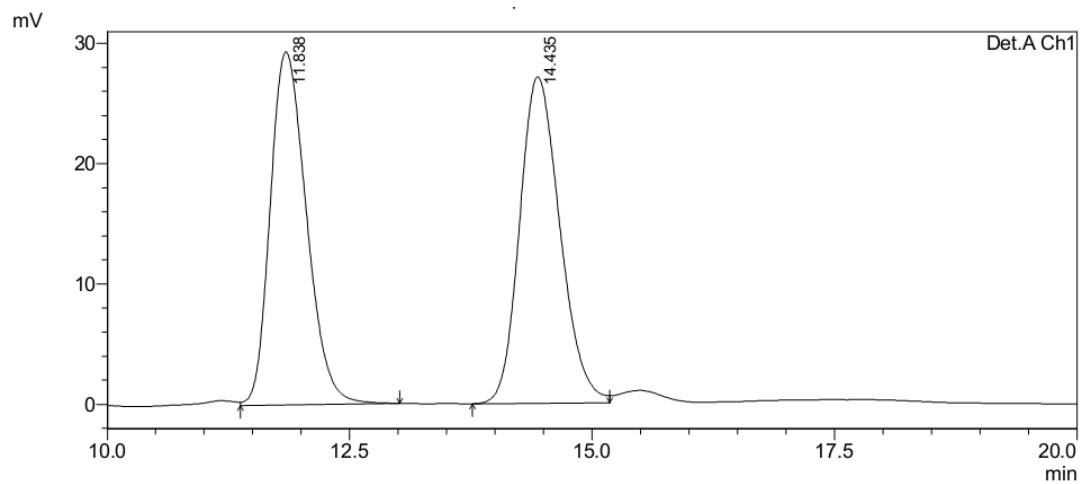
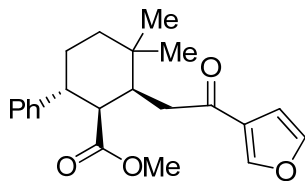
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.267	1527769	75386	96.337	97.558
2	15.623	58096	1887	3.663	2.442
Total		1585865	77273	100.000	100.000



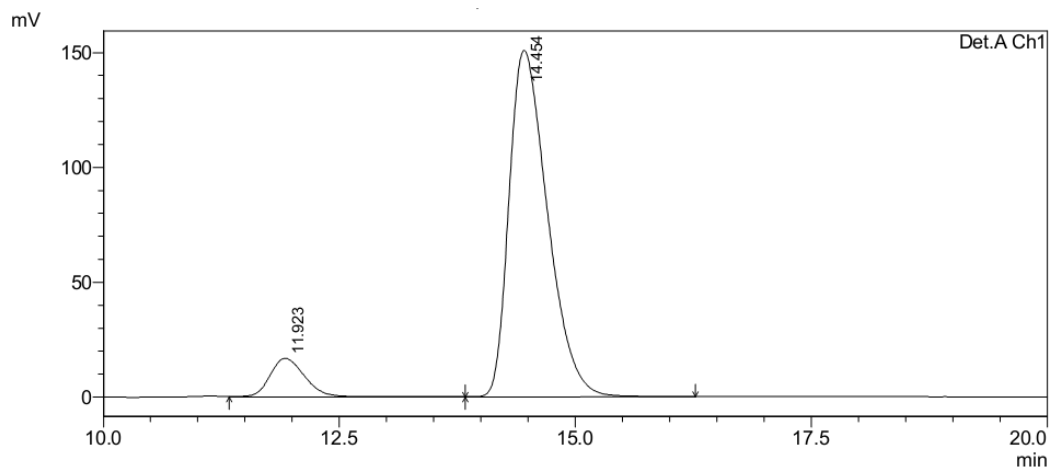
Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.115	224283	1379	48.170	68.082
2	61.876	241321	647	51.830	31.918
Total		465605	2026	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	40.044	4061601	26260	95.934	98.230
2	62.272	172134	473	4.066	1.770
Total		4233735	26733	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.838	762613	29348	49.269	51.952
2	14.435	785244	27143	50.731	48.048
Total		1547857	56491	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.923	449567	16884	9.498	10.066
2	14.454	4283512	150845	90.502	89.934
Total		4733079	167729	100.000	100.000