Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

CONTENTS:

(A) General Information

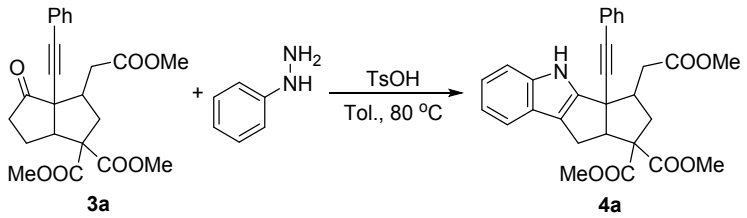
^{1}H NMR spectra were recorded on commercial instruments (400 MHz). Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. The enantiomeric excesses were determined by HPLC analysis on chiral DAICEL CHIRALPAK IA, IE, ADH or IC column at 254 nm. Optical rotations were measured on a commercial polarimeter and are reported as follows: $[\alpha]_D^{T}$ (c = g/100 mL, CH_2Cl_2). HRMS was recorded on a commercial apparatus (ESI source). Solvents were dried according to standard procedures. Racemic samples were prepared according to the methods reported in the literature.[1] All reactions were performed in sealed oven-dried glass tubes under an atmosphere of nitrogen unless otherwise noted. The diastereoisomers of the catalytic products have different Rf values and they could be isolated by flash chromatography on silica gel. Malonate **2** and Enynes were prepared according to the literature.[2,3] The *N,N'*-dioxdes were prepared according to the methods reported in the literature.[4]

(B) General experimental procedure for the preparation of polyquinanes

In a test tube, a mixture of **L-PiMe$_3$** (5.6 mg, 10 mol%) and $Y(OTf)_3$ (5.4 mg, 10 mol%) in CH_2Cl_2 (1.0 mL) was stirred at 30 ºC for 0.5 hour under N_2 atmosphere. After the sovent had been removed under vacuum, enynes (**1**) (0.1 mmol), malonate (**2**) (0.1 mmol) and CH_2Cl_2 (0.5 mL) were added. After being stirred at 30 ºC for 10 min, $^{i}Pr_2EtN$ (8.4 μL, 50 mol%) was added and the mixture was stirred at the same temperature for 48 h. The reaction mixture was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1/6-1/2) to afford the desired products.

(C) Transformations of 3a and 3o

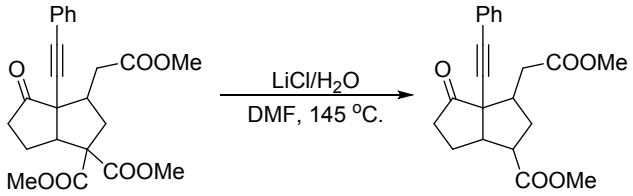
a): Synthesis of compound 4a from 3a



3a **4a**

To a solution of phenylhydrazine (0.24 mmol, 25.9 mg) in toluene (2.0 mL) was added **3a** (0.2 mmol, 82.4 mg, 97% ee), and the resulting mixture was stirred for 10 min at room temperature. TSOH (0.24 mmol, 45.6 mg) was then added and the mixture was stirred at 80 °C for another 48 h. The solution was then cooled to room temperature, diluted with water and extracted with dichloromethane. The organic layer was then washed with water, NH_4Cl (0.1 M), and saturated $NaHCO_3$. The collected organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by silica gel column chromatography (ethyl acetate/petroleum ether 1/6 – 1/3) to give compound **4a** as a white solid in 89% (86.1 mg) yield with 97% ee.

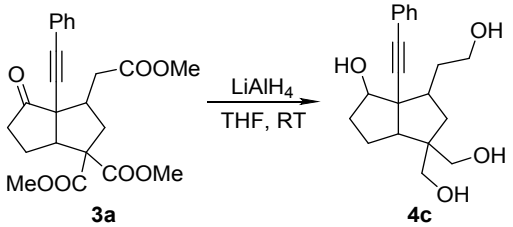
b): synthesis of compound 4b from 3a



3a **4b**

To a dry Schlenk tube was added **3a** (0.2 mmol, 82.4 mg, 97% ee), LiCl (2 mmol, 84 mg), H_2O (2 mmol, 36 mg) and DMF (2.5 mL). The reaction was stirred at 145 °C for 1 hour. The solution was then cooled to room temperature, diluted with water and extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1 - 3/1) to yield **4b** as a colourless oil in 51% yield (36.1 mg) with 97%/97% ee, 76/24 d.r.

c): Synthesis of compound 4c from 3a

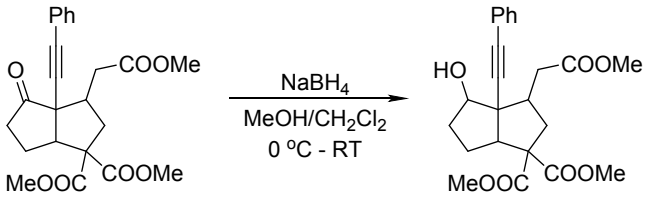


3a **4c**

To a stirred suspension of $LiAlH_4$ (3.6 mmol, 136.8 mg) in 15 mL of THF under N_2 atmosphere, was added **3a** (0.3 mmol, 123.6 mg, 97% ee) in 7.5 mL of THF via syringe at room temperature.

After 0.5 h, the reaction was quenched with H_2O, followd by aq. 10% NaOH solution, and then extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by silica gel column chromatography (MeOH/ethyl acetate = 0/1 - 1/10) to afford the product **4c** as a colourless oil in 71% yield (70.5 mg) with 97% ee.

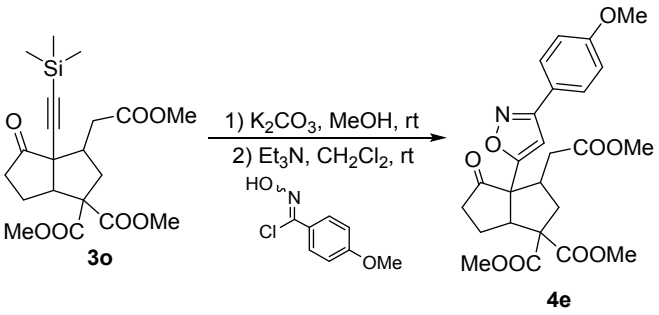
d): Synthesis of compound 4d from 3a



3a **4d**

To a stirred suspension of **3a** (0.2 mmol, 82.4 mg, 97% ee) in 3.5 mL of MeOH/CH_2Cl_2 (6/1), was added $NaBH_4$ (0.6 mmol, 22.7 mg) at 0 °C. Then the mixture was stirred at room temperature for another 3.5 h. After that the reaction was quenched with H_2O and extracted with ethyl acetate. The collected organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1 - 3/1) to afford the product **4d** as a colourless oil in 81% yield (67.5 mg) with 97% ee.

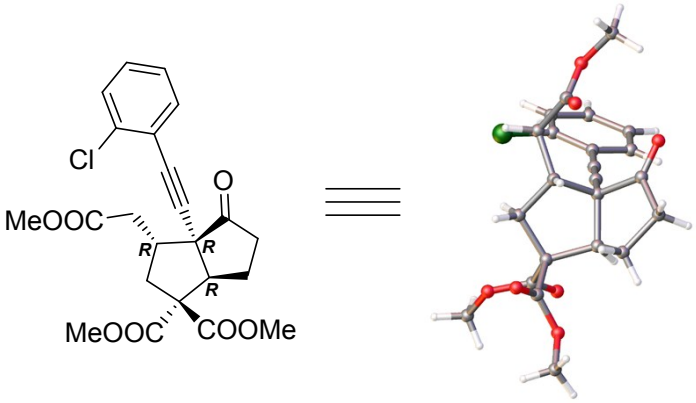
e): Synthesis of compound 4e from 3o



3o **4e**

To a stirred suspension of **3o** (0.28 mmol, 115.1 mg, 91% ee) in 2.5 mL of MeOH, was added K_2CO_3 (0.56 mmol, 77.8 mg) at room temperature. Then the mixture was stirred at the same temperature for another 1.5 h. After that, the reaction was filtered and concentrated under reduced pressure. The crude mixture was directly subjected to the next reaction without further purification. Then, N-hydroxy-4-methoxybenzimidoyl chloride (0.56 mmol, 110.6 mg), Et_3N (0.56 mmol, 56.6 mg) and CH_2Cl_2 (3 mL) was added to the mixture at room temperature. After 21 h, the reaction was concentrated and purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1 - 2/1) to afford the product **4e** as a colourless oil in 72% (98.2 mg) yield with 92% ee.

(D) The X-ray structure for 3h (CCDC 1519972)

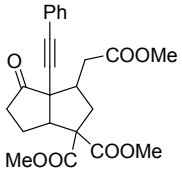


The compound **3h** was recrystallized from CH_2Cl_2 and petroleum ether.

CCDC 1519972 contains the supplementary crystallographic data of the adduct **3h** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

(E) The analytical and spectral characterization data for the compounds

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(phenylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3a)

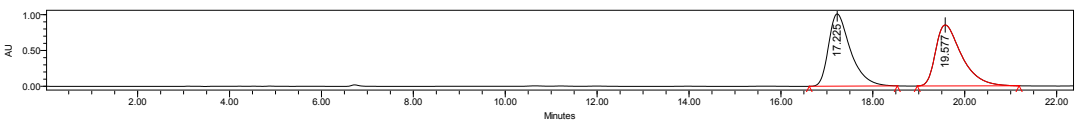


Colourless oil, 30.1 mg, 73% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.0 min, 19.4 min. $[\alpha]_D^{20}$ = - 52.31 (*c* = 0.43 in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.37 (m, 2H), 7.35 – 7.24 (m, 3H), 3.93 – 3.87 (m, 1H), 3.85 – 3.62 (m, 9H), 3.01 (dd, *J*=14.0, 7.2, 1H), 2.87 – 2.71 (m, 2H), 2.62 – 2.43 (m, 3H), 2.26 – 2.11 (m, 2H), 1.78 – 1.72 (m, 1H).

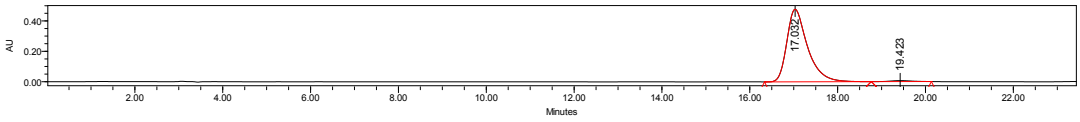
^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.5, 172.5, 171.3, 170.3, 131.9, 128.5, 128.3, 122.7, 87.4, 85.0, 62.8, 58.6, 55.0, 53.2, 52.9, 51.9, 40.8, 39.8, 37.4, 35.7, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{24}NaO_7^+$ ([M + Na]$^+$) 435.1420, found 435.1416.



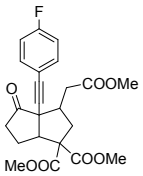
	Retention Time	Area	% Area

1	17.225	33480243	49.99
2	19.577	33488856	50.01



	Retention Time	Area	% Area
1	17.032	15546697	98.57
2	19.423	225779	1.43

Dimethyl 3a-((4-fluorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3b)

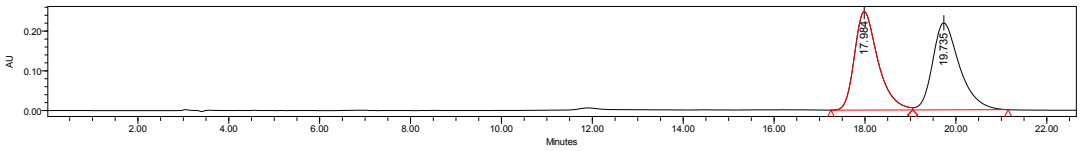


Colourless oil, 28.1 mg, 65% yield. 95% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.0 min, 19.7 min. $[\alpha]_D^{20}$ = - 42.97 (*c* = 0.38 in CH_2Cl_2).

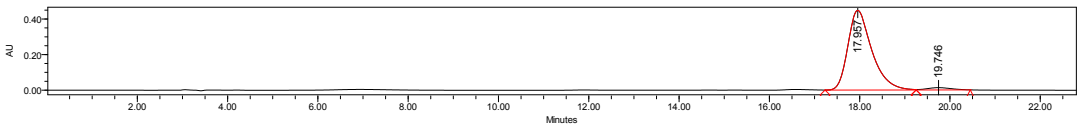
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (dd, *J*=8.0, 5.6, 2H), 6.99 (t, *J*=8.4, 2H), 3.91 – 3.86 (m, 1H), 3.79 – 3.61 (m, 9H), 3.02 (dd, *J*=14.0, 7.2, 1H), 2.86 – 2.72 (m, 2H), 2.58 – 2.45 (m, 3H), 2.23 – 2.10 (m, 2H), 1.72 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.5, 172.4, 171.3, 170.3, 162.7 (d, *J*=250), 133.9 (d, *J*=10), 118.8 (d, *J*=10), 115.6(d, *J*=20), 86.4, 84.7, 62.7, 58.7, 55.0, 53.2, 52.9, 51.9, 40.9, 39.8, 37.5, 35.7, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{23}FNaO_7^+$ ([M + Na]$^+$) 453.1326, found 453.1324.

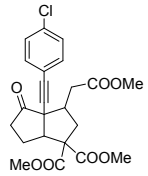


	Retention Time	Area	% Area
1	17.984	8902733	49.68
2	19.735	9017648	50.32



	Retention Time	Area	% Area
1	17.957	16467351	97.20
2	19.746	473640	2.80

Dimethyl 3a-((4-chlorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3c)

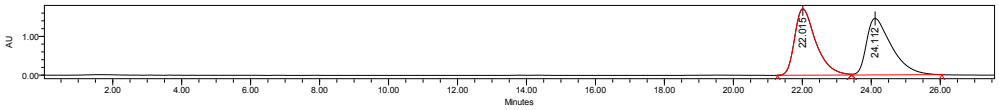


Colourless oil, 31.8 mg, 71% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 21.1 min, 24.4 min. $[\alpha]_D^{20}$ = - 49.02 (*c* = 0.51 in CH_2Cl_2).

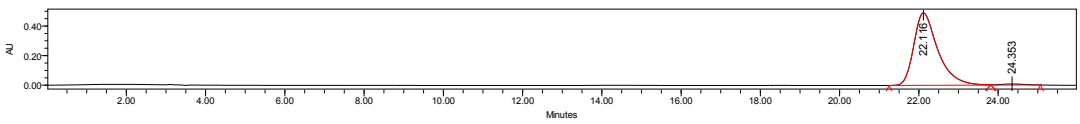
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (dd, *J*=30.8, 8.0, 4H), 3.91 – 3.86 (m, 1H), 3.85 – 3.63 (m, 9H), 3.02 (dd, *J*=14.0, 7.2, 1H), 2.86 – 2.71 (m, 2H), 2.62 – 2.43 (m, 3H), 2.25 – 2.09 (m, 2H), 1.74 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.3, 172.3, 171.3, 170.2, 134.6, 133.2, 128.7, 121.1, 86.3, 86.1, 62.7, 58.7, 55.0, 53.2, 52.9, 51.9, 40.9, 39.8, 37.4, 35.7, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{23}{}^{34.9689}ClNaO_7^+$ ([M + Na]$^+$) 469.1030, found 469.1028; calcd for $C_{23}H_{23}{}^{36.9659}ClNaO_7^+$ ([M + Na]$^+$) 471.1001, found 471.1003.



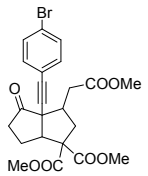
	Retention Time	Area	% Area
1	22.015	73271432	49.87
2	24.112	73660261	50.13



	Retention Time	Area	% Area
1	22.116	20671167	98.56
2	24.353	302567	1.44

Dimethyl 3a-((4-bromophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-

1,1(2H)-dicarboxylate (3d)

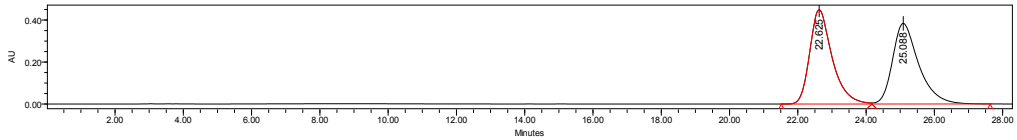


Colourless oil, 29.3 mg, 60% yield. 96% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.7 min, 25.3 min. $[\alpha]_D^{20}$ = - 44.88 (*c* = 0.51 in CH_2Cl_2).

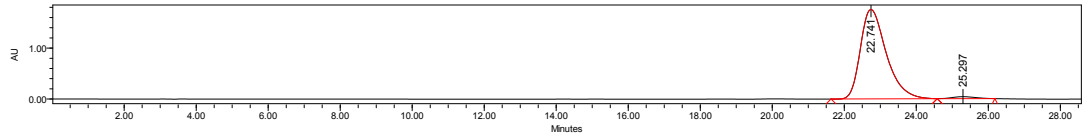
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 (d, *J*=8.4, 2H), 7.33 – 7.22 (m, 2H), 3.97 – 3.81 (m, 1H), 3.79 – 3.66 (m, 9H), 3.02 (dd, *J*=13.6, 7.2, 1H), 2.88 – 2.57 (m, 2H), 2.57 – 2.27 (m, 3H), 2.27 – 2.03 (m, 2H), 1.71 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.3, 172.3, 171.3, 170.2, 133.4, 131.6, 122.8, 121.6, 86.4, 86.3, 62.7, 58.7, 55.0, 53.2, 52.9, 51.9, 40.9, 39.8, 37.5, 35.7, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{23}{}^{78.9183}BrNaO_7^+$ ([M + Na]$^+$) 513.0525, found 513.0525; calcd for $C_{23}H_{23}{}^{80.9163}BrNaO_7^+$ ([M + Na]$^+$) 515.0504, found 515.0504.

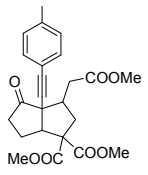


	Retention Time	Area	% Area
1	22.625	20448245	50.00
2	25.088	20447916	50.00



	Retention Time	Area	% Area
1	22.741	87637539	97.99
2	25.297	1796447	2.01

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(p-tolylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3e)

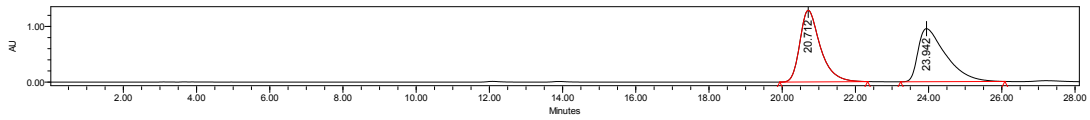


Colourless oil, 30.3 mg, 71% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 20.5 min, 24.0 min. $[\alpha]_D^{20}$ = - 48.52 (*c* = 0.47 in CH_2Cl_2).

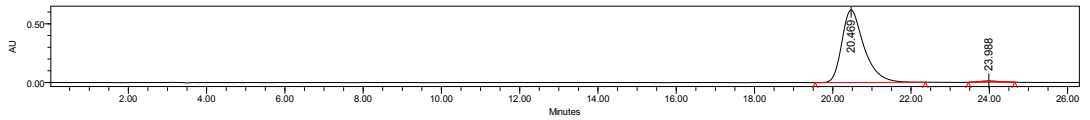
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30 (d, *J*=8.0, 2H), 7.09 (d, *J*=8.0, 2H), 3.92 – 3.63 (m, 10H), 3.00 (dd, *J*=13.2, 7.2, 1H), 2.88 – 2.71 (m, 2H), 2.61 – 2.45 (m, 3H), 2.33 (s, 3H), 2.25 – 2.11 (m, 2H), 1.75 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.7, 172.5, 171.3, 170.4, 138.6, 131.8, 129.1, 119.6, 87.6, 84.2, 62.8, 58.6, 55.1, 53.2, 52.9, 51.9, 40.8, 39.8, 37.4, 35.7, 22.6, 21.6.

HRMS (ESI-TOF): calcd for $C_{24}H_{26}NaO_7^+$ ([M + Na]$^+$) 449.1576, found 449.1572.

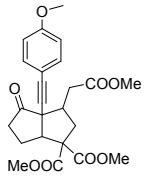


	Retention Time	Area	% Area
1	20.712	49886963	49.89
2	23.942	50103695	50.11



	Retention Time	Area	% Area
1	20.469	24270210	98.51
2	23.988	366242	1.49

Dimethyl 3-(2-methoxy-2-oxoethyl)-3a-((4-methoxyphenyl)ethynyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3f)

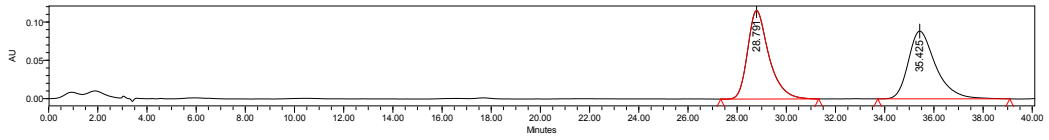


Colourless oil, 30.6 mg, 70% yield. 95% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 28.5 min, 35.1 min. $[\alpha]_D^{20}$ = - 61.6 (*c* = 0.61 in CH_2Cl_2).

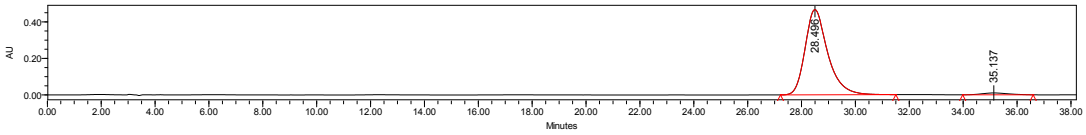
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 2H), 6.90 – 6.76 (m, 2H), 3.90 – 3.63 (m, 13H), 2.99 (dd, *J* = 13.6, 7.2 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.62 – 2.43 (m, 3H), 2.24 – 2.11 (m, 2H), 1.74 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.8, 172.5, 171.4, 170.4, 159.8, 133.4, 114.8, 113.9, 87.3, 83.5, 62.8, 58.7, 55.4, 55.1, 53.2, 52.9, 51.9, 40.8, 39.8, 37.4, 35.8, 22.6.

HRMS (ESI-TOF): calcd for $C_{24}H_{26}NaO_8^+$ ([M + Na]$^+$) 465.1525, found 465.1523.

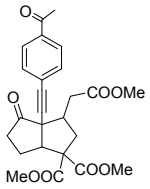


	Retention Time	Area	% Area
1	28.791	6929499	50.36
2	35.425	6830533	49.64



	Retention Time	Area	% Area
1	28.496	27117090	97.55
2	35.137	682297	2.45

Dimethyl 3a-((4-acetylphenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3g)

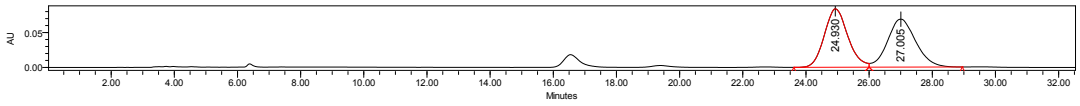


Colourless oil, 28.4 mg, 63% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 24.6 min, 26.7 min. $[\alpha]_D^{20}$ = - 48.28 (*c* = 0.52 in CH_2Cl_2).

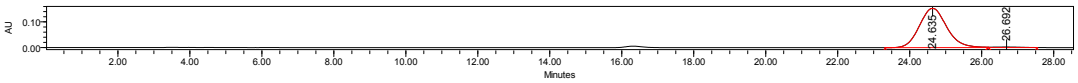
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01 – 7.79 (m, 2H), 7.64 – 7.40 (m, 2H), 3.91 (dd, *J*=9.6, 8.4, 1H), 3.81 – 3.65 (m, 9H), 3.04 (dd, *J*=14.0, 7.2, 1H), 2.89 – 2.74 (m, 2H), 2.69 – 2.44 (m, 6H), 2.27 – 2.09 (m, 2H), 1.76 – 1.70 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.1, 197.4, 172.3, 171.3, 170.2, 136.5, 132.1, 128.3, 127.5, 88.5, 86.6, 62.7, 58.8, 54.9, 53.2, 52.9, 52.0, 40.9, 39.8, 37.5, 35.6, 26.8, 22.7.

HRMS (ESI-TOF): calcd for $C_{25}H_{26}NaO_8^+$ ([M + Na]$^+$) 477.1525, found 477.1525.

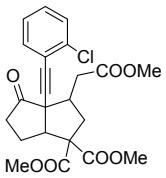


	Retention Time	Area	% Area
1	24.930	4336828	50.35
2	27.005	4275974	49.65



	Retention Time	Area	% Area
1	24.635	8078775	98.55
2	26.692	119027	1.45

Dimethyl 3a-((2-chlorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3h)

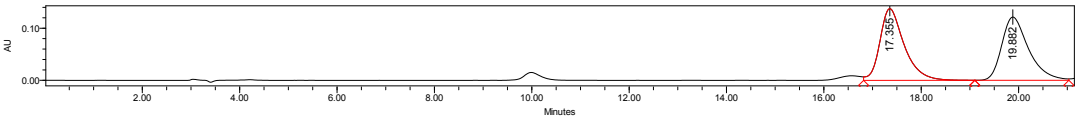


Colourless oil, 30.1 mg, 67% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.4 min, 19.9 min. $[\alpha]_D^{20}$ = - 32.27 (*c* = 0.50 in CH_2Cl_2).

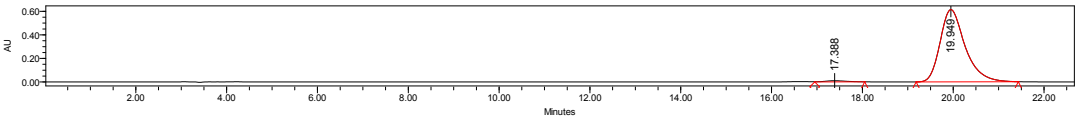
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.41 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.17 (m, 2H), 3.94 (t, *J* = 8.0 Hz, 1H), 3.88 – 3.57 (m, 9H), 3.04 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.90 – 2.74 (m, 2H), 2.67 – 2.45 (m, 3H), 2.28 – 2.14 (m, 2H), 1.74 – 1.71 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.2, 172.5, 171.2, 170.4, 136.2, 133.6, 129.5, 129.3, 126.5, 122.6, 90.5, 84.2, 62.7, 58.8, 54.8, 53.2, 52.9, 51.9, 41.1, 40.0, 37.6, 35.5, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{23}{}^{34.9689}ClNaO_7^+$ ([M + Na]$^+$) 469.1030, found 469.1031; calcd for $C_{23}H_{23}{}^{36.9659}ClNaO_7^+$ ([M + Na]$^+$) 471.1001, found 471.1024.

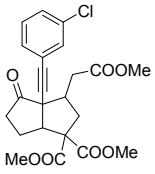


	Retention Time	Area	% Area
1	17.355	4763939	50.64
2	19.882	4643747	49.36



	Retention Time	Area	% Area
1	17.388	301982	1.27
2	19.949	23383338	98.73

Dimethyl 3a-((3-chlorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3i)

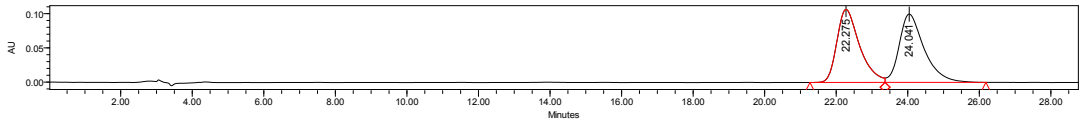


Colourless oil, 28.1 mg, 63% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.6 min, 24.3 min. $[\alpha]_D^{20}$ = - 49.40 (*c* = 0.50 in CH_2Cl_2).

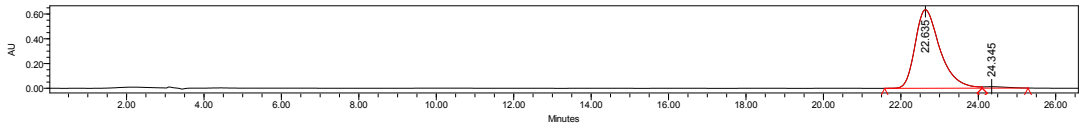
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.40 (s, 1H), 7.31 – 7.20 (m, 3H), 3.91 – 3.86 (m, 1H), 3.84 – 3.62 (m, 9H), 3.03 (dd, *J*=14.0, 7.2, 1H), 2.85 – 2.72 (m, 2H), 2.61 – 2.44 (m, 3H), 2.24 – 2.09 (m, 2H), 1.71 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.2, 172.3, 171.3, 170.2, 134.2, 131.8, 130.1, 129.6, 128.9, 124.3, 86.4, 86.0, 62.7, 58.7, 54.9, 53.3, 52.9, 51.9, 40.9, 39.8, 37.5, 35.6, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{23}{}^{34.9689}ClNaO_7^+$ ([M + Na]$^+$) 469.1030, found 469.1029; calcd for $C_{23}H_{23}{}^{36.9659}ClNaO_7^+$ ([M + Na]$^+$) 471.1001, found 471.1028.

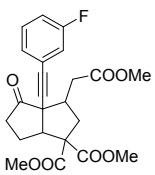


	Retention Time	Area	% Area
1	22.275	4704262	49.30
2	24.041	4838650	50.70



	Retention Time	Area	% Area
1	22.635	28253816	98.41
2	24.345	456900	1.59

Dimethyl 3a-((3-fluorophenyl)ethynyl)-3-(2-methoxy-2-oxoethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3j)



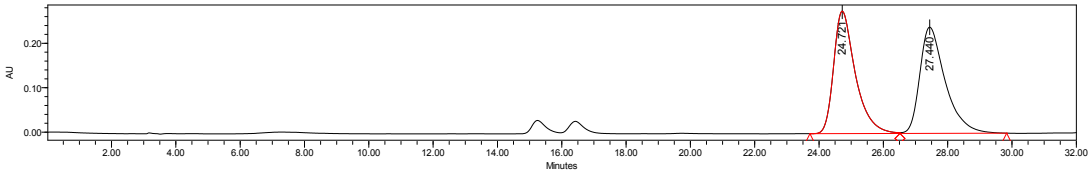
Colourless oil, 27.0 mg, 63% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm,

retention time: 24.5 min, 27.2 min. $[\alpha]_D^{20}$ = - 52.37 (*c* = 0.51 in CH_2Cl_2).

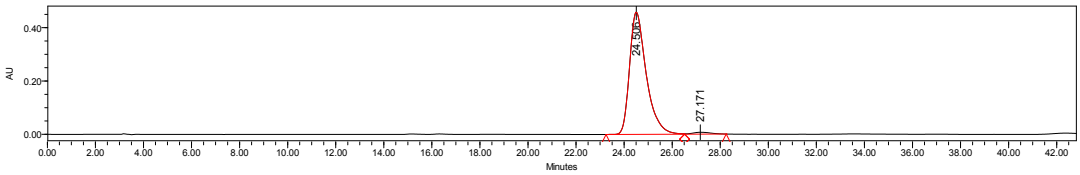
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.18 (m, 2H), 7.17 – 7.07 (m, 1H), 7.07 – 6.93 (m, 1H), 3.89 (dd, *J*=9.6, 8.4, 1H), 3.83 – 3.64 (m, 9H), 3.03 (dd, *J*=14.0, 7.2, 1H), 2.86 – 2.71 (m, 2H), 2.61 – 2.43 (m, 3H), 2.24 – 2.09 (m, 2H), 1.74 – 1.69 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.2, 172.3, 171.3, 170.2, 162.4 (d, *J*=250), 123.0 (d, *J*=10), 127.8 (d, *J*=3), 124.5 (d, *J*=10), 118.7 (d, *J*=20), 115.9 (d, *J*=20), 86.2, 86.1, 62.7, 58.6, 54.9, 53.2, 52.9, 51.9, 40.9, 39.8, 37.5, 35.6, 22.7.

HRMS (ESI-TOF): calcd for $C_{23}H_{23}FNaO_7^+$ ([M + Na]$^+$) 453.1326, found 453.1327.

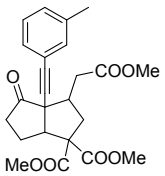


	Retention Time	Area	% Area
1	24.721	12941464	49.72
2	27.440	13085878	50.28



	Retention Time	Area	% Area
1	24.506	22031387	98.37
2	27.171	365070	1.63

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(m-tolylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3k)

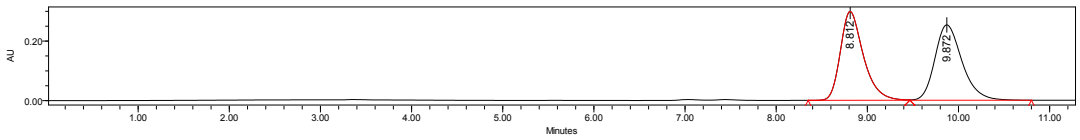


Colourless oil, 30.7 mg, 72% yield. 95% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 8.6 min, 9.6 min. $[\alpha]_D^{20}$ = - 50.98 (*c* = 0.51 in CH_2Cl_2).

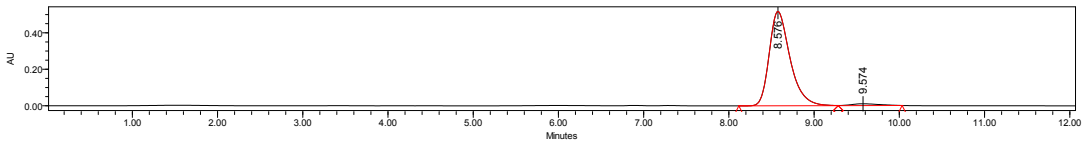
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.27 – 7.06 (m, 4H), 3.91 – 3.85 (m, 1H), 3.83 – 3.59 (m, 9H), 3.01 (dd, *J*=14.0, 7.2, 1H), 2.87 – 2.71 (m, 2H), 2.60 – 2.46 (m, 3H), 2.31 (s, 3H), 2.24 – 2.11 (m, 2H), 1.74 – 1.68 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.6, 172.5, 171.3, 170.4, 138.0, 132.5, 129.4, 129.0, 128.2, 122.4, 87.6, 84.6, 62.7, 58.6, 55.0, 53.2, 52.9, 51.9, 40.8, 39.8, 37.5, 35.7, 22.7, 21.3.

HRMS (ESI-TOF): calcd for $C_{24}H_{26}NaO_7^+$ ([M + Na]$^+$) 449.1576, found 449.1577.

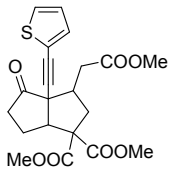


	Retention Time	Area	% Area
1	8.812	5232326	49.94
2	9.872	5244137	50.06



	Retention Time	Area	% Area
1	8.576	8756175	97.51
2	9.574	223787	2.49

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(thiophen-2-ylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3l)

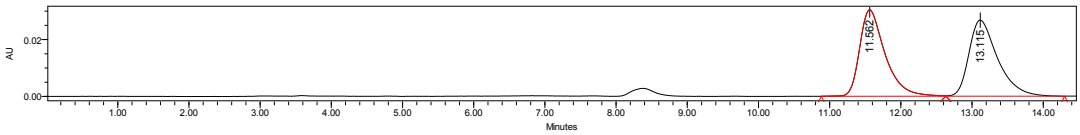


Colourless oil, 22.4 mg, 54% yield. 98% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.6 min, 13.1 min. $[\alpha]_D^{20}$ = - 47.04 (*c* = 0.37 in CH_2Cl_2).

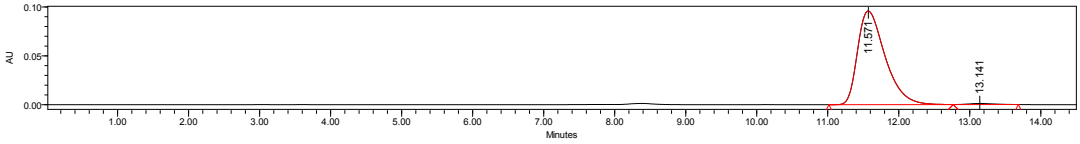
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.23 (dd, *J*=5.2, 1.2, 1H), 7.18 (dd, *J*=3.6, 1.2, 1H), 6.95 (dd, *J*=5.2, 4.0, 1H), 3.88 (dd, *J*=9.2, 8.8, 1H), 3.75 (s, 6H), 3.68 (s, 3H), 3.04 – 2.96 (m, 1H), 2.84 – 2.73 (m, 2H), 2.56 – 2.43 (m, 3H), 2.24 – 2.11 (m, 2H), 1.79 – 1.69 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.3, 172.4, 171.3, 170.3, 132.5, 127.3, 127.0, 122.5, 88.9, 80.6, 62.8, 58.9, 55.0, 53.3, 52.9, 51.9, 40.9, 39.8, 37.4, 35.7, 22.7.

HRMS (ESI-TOF): calcd for $C_{21}H_{22}NaO_7S^+$ ([M + Na]$^+$) 441.0984, found 441.0983.

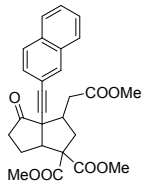


	Retention Time	Area	% Area
1	11.562	753968	50.16
2	13.115	749120	49.84



	Retention Time	Area	% Area
1	11.571	2579959	98.94
2	13.141	27634	1.06

Dimethyl 3-(2-methoxy-2-oxoethyl)-3a-(naphthalen-2-ylethynyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (3m)

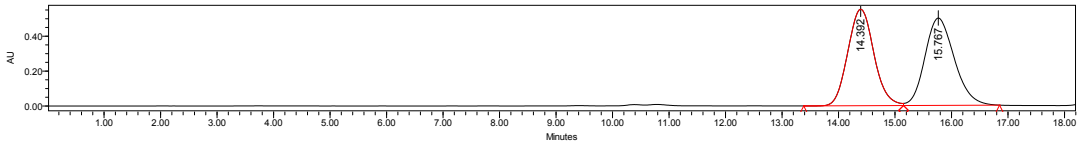


Colourless oil, 32.8 mg, 71% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.5 min, 15.8 min. $[\alpha]_D^{20}$ = - 52.18 (*c* = 0.55 in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (s, 1H), 7.85 – 7.68 (m, 3H), 7.57 – 7.36 (m, 3H), 3.97 – 3.90 (m, 1H), 3.86 – 3.51 (m, 9H), 3.04 (dd, *J*=14.0, 7.6, 1H), 2.92 – 2.75 (m, 2H), 2.67 – 2.45 (m, 3H), 2.30 – 2.15 (m, 2H), 1.80 – 1.69 (m, 1H).

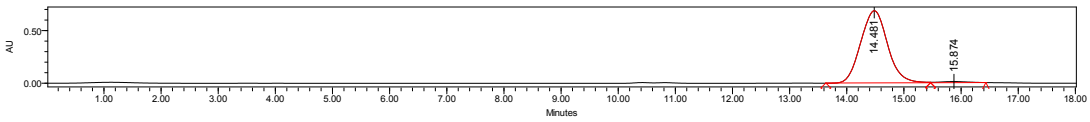
^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.6, 172.5, 171.4, 170.3, 132.9, 131.8, 128.6, 128.0, 127.8, 126.8, 126.7, 119.9, 87.8, 85.3, 62.8, 58.8, 55.1, 53.3, 52.9, 51.9, 40.9, 39.8, 37.5, 35.8, 22.70.

HRMS (ESI-TOF): calcd for $C_{27}H_{26}NaO_7^+$ ([M + Na]$^+$) 485.1576, found 485.1573.



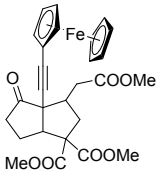
	Retention Time	Area	% Area
1	14.392	17733924	49.56

2	15.767	18051195	50.44



	Retention Time	Area	% Area
1	14.481	22293235	98.44
2	15.874	353227	1.56

((3-(2-Methoxy-2-oxoethyl)-1,1-bis(methoxycarbonyl)-4-oxohexahydropentalen-3a(1H)-yl)ethynyl)ferrocene (3n)

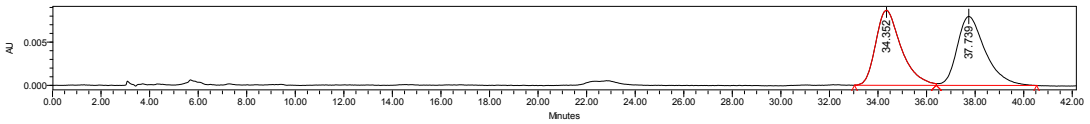


Colourless oil, 18.3 mg, 35% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm, retention time: 35.0 min, 38.2 min. $[\alpha]_D^{20}$ = - 25.80 (*c* = 0.31 in CH_2Cl_2).

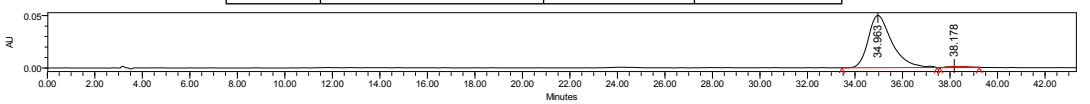
^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.45 – 4.35 (m, 2H), 4.21 (s, 4H), 4.16 (d, *J*=2.0, 2H), 3.94 – 3.64 (m, 10H), 3.00 (dd, *J*=13.6, 6.8, 1H), 2.83 (dd, *J*=16.0, 4.4, 1H), 2.76 – 2.66 (m, 1H), 2.62 – 2.41 (m, 3H), 2.22 – 2.09 (m, 2H), 1.74 – 1.66 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.9, 172.6, 171.3, 170.4, 86.1, 81.1, 71.7, 70.0, 68.7, 64.7, 62.6, 58.8, 54.9, 53.2, 52.9, 51.9, 40.6, 39.9, 37.5, 35.7, 22.6.

HRMS (ESI-TOF): calcd for $C_{27}H_{29}FeO_7^+$ ([M + H]$^+$) 521.1263, found 521.1285.

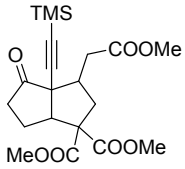


	Retention Time	Area	% Area
1	34.352	632484	49.80
2	37.739	637540	50.20



	Retention Time	Area	% Area
1	34.963	3445470	98.48
2	38.178	53285	1.52

Dimethyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-((trimethylsilyl)ethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (3o)

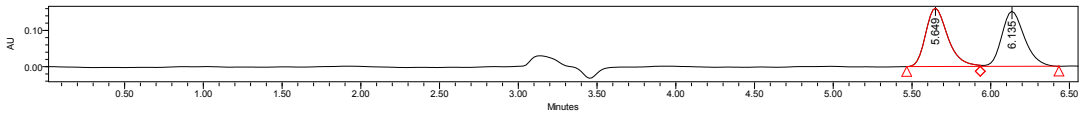


Colourless oil, 25.5 mg, 62% yield. 91% *ee* determined by HPLC (chiral IA column), *n*-hexane/*i*-PrOH = 90/10, flow rate 1.0 mL/min, λ = 210 nm, retention time: 5.7 min, 6.2 min. $[\alpha]_D^{20}$ = - 42.97 (*c* = 0.38 in CH_2Cl_2).

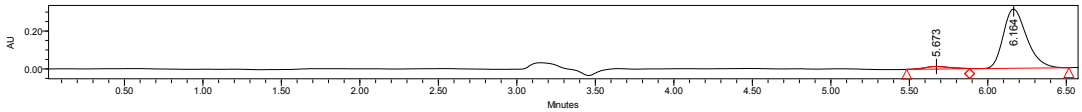
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 – 3.57 (m, 7H), 3.53 (s, 3H), 2.80 (dd, *J* = 14.0, 7.2 Hz, 1H), 2.60 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.55 – 2.47 (m, 1H), 2.36 – 2.19 (m, 3H), 2.04 – 1.88 (m, 2H), 1.55 – 1.46 (m, 1H), 0.00 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 211.4, 172.5, 171.1, 170.4, 101.2, 92.5, 62.6, 58.9, 55.0, 53.1, 52.9, 51.9, 40.5, 39.8, 37.4, 35.6, 22.5, 0.0.

HRMS (ESI-TOF): calcd for $C_{20}H_{28}NaO_7Si^+$ ([M + Na]$^+$) 431.1502, found 431.1500.

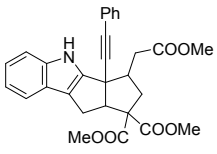


	Retention Time	Area	% Area
1	5.649	1571105	50.80
2	6.135	1521922	49.20



	Retention Time	Area	% Area
1	5.673	159620	4.69
2	6.164	3246928	95.31

Dimethyl 3-(2-methoxy-2-oxoethyl)-3a-(phenylethynyl)-2,3,3a,4,9,9a-hexahydro-1H-pentaleno[1,2-b]indole-1,1-dicarboxylate (4a)

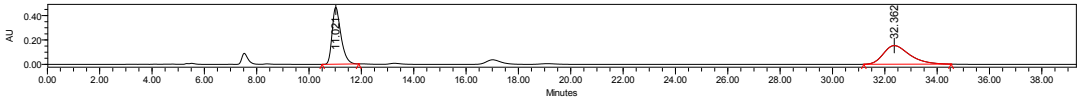


White solid, 86.1 mg, 89% yield. 97% *ee* determined by HPLC (chiral ADH column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.0 min, 32.3 min. $[\alpha]_D^{20}$ = - 46.69 (*c* = 1.72 in CH_2Cl_2).

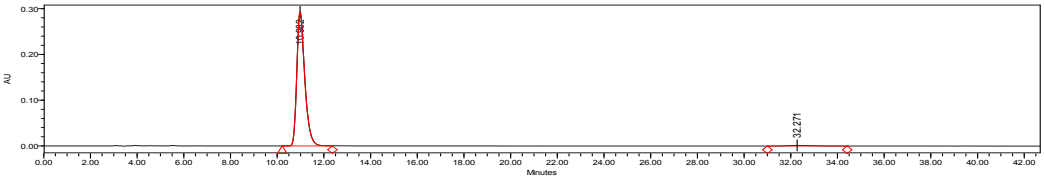
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.92 (s, 1H), 7.35 – 7.16 (m, 7H), 7.07 – 6.92 (m, 2H), 4.14 (d, *J*=6.8, 1H), 3.66 (d, *J*=17.6, 6H), 3.37 – 3.20 (m, 4H), 3.14 (dd, *J*=15.2, 7.6, 1H), 3.00 (d, *J*=15.2, 1H), 2.87 (dd, *J*=17.2, 11.6, 1H), 2.69 – 2.50 (m, 2H), 1.86 (t, *J*=12.4, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 174.5, 171.7, 170.2, 145.2, 140.9, 131.6, 128.3, 128.1, 124.3, 123.2, 121.3, 119.5, 118.9, 116.3, 112.3, 88.6, 86.2, 66.2, 62.3, 53.0, 52.4, 52.0, 51.3, 42.0, 41.6, 37.6, 26.1.

HRMS (ESI-TOF): calcd for $C_{29}H_{27}NNaO_6^+$ ([M + Na]$^+$) 508.1736, found 508.1737.

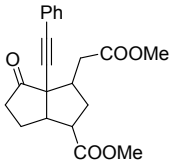


	Retention Time	Area	% Area
1	11.021	10920002	50.65
2	32.362	10640224	49.35



	Retention Time	Area	% Area
1	10.982	6939201	98.52
2	32.271	104042	1.48

Methyl 3-(2-methoxy-2-oxoethyl)-4-oxo-3a-(phenylethynyl)octahydropentalene-1-carboxylate (4b)

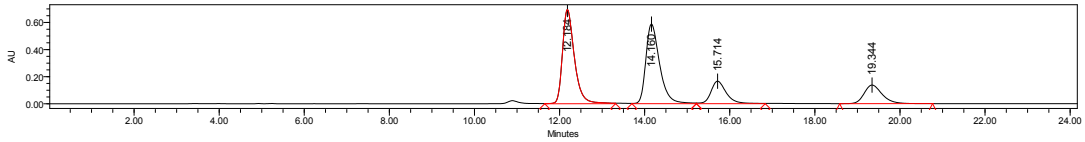


Colourless oil, 36.1 mg, 51% yield. 76/24 d.r. determined by ^{1}H NMR. 97%/97% *ee* determined by HPLC (chiral IE column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.3 min, 14.3 min, 15.8 min, 19.5 min.

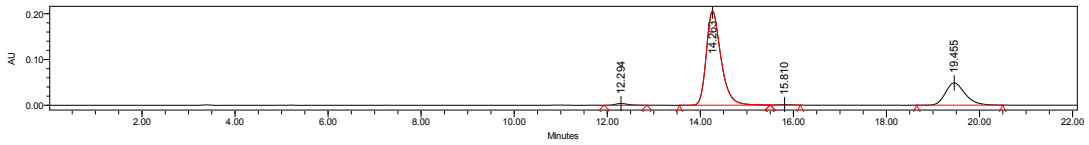
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.47 – 7.37 (m, 2H), 7.33 – 7.26 (m, 3H), 3.77 – 3.63 (m, 6H), 3.50 – 3.41 (m, 0.28H), 3.30 – 3.19 (m, 1H), 2.95 – 2.30 (m, 7.86H), 2.11 – 1.84 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 213.4, 212.3, 174.2, 173.7, 172.8, 172.6, 131.9, 131.9, 128.5, 128.5, 128.4, 128.3, 122.7, 87.0, 86.6, 85.7, 85.4, 59.4, 57.7, 53.8, 53.0, 52.2, 51.9, 51.8, 48.8, 45.4, 41.8, 40.6, 37.2, 36.6, 36.3, 35.9, 32.9, 24.9, 22.2.

HRMS (ESI-TOF): calcd for $C_{21}H_{22}NaO_5^+$ ([M + Na]$^+$) 377.1365, found 377.1369.

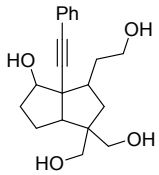


	Retention Time	Area	% Area
1	12.184	13522152	38.69
2	14.160	13238167	37.88
3	15.714	4154811	11.89
4	19.344	4030550	11.53



	Retention Time	Area	% Area
1	12.294	76286	1.27
2	14.263	4500668	74.73
3	15.810	19213	0.32
4	19.455	1426036	23.68

(4-Hydroxy-3-(2-hydroxyethyl)-3a-(phenylethynyl)octahydropentalene-1,1-diyl)dimethanol (4c)

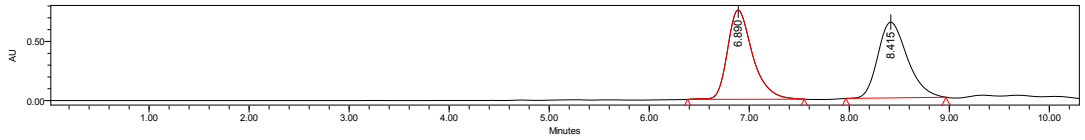


Colourless oil, 70.5 mg, 71% yield. 97% *ee* determined by HPLC (chiral IC column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 6.9 min, 8.5 min. $[\alpha]_D^{20}$ = - 33.51 (*c* = 1.14 in CH_2Cl_2).

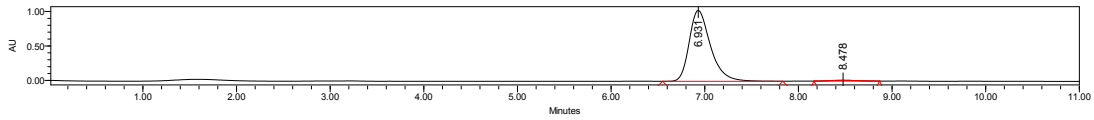
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 – 7.13 (m, 5H), 5.09 (s, 1H), 4.65 (d, *J*=32.4, 2H), 4.13 – 3.99 (m, 2H), 3.74 – 3.36 (m, 7H), 2.48 (t, *J*=8.8, 2H), 2.00 (d, *J*=7.6, 1H), 1.83 – 1.41 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 131.5, 128.3, 127.8, 123.8, 94.6, 84.6, 78.9, 71.6, 64.9, 61.2, 61.1, 58.0, 47.1, 41.3, 37.3, 35.0, 34.5, 23.7, 14.3.

HRMS (ESI-TOF): calcd for $C_{20}H_{26}NaO_4^+$ ([M + Na]$^+$) 353.1729, found 353.1730.

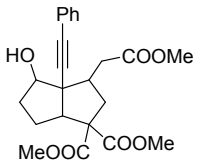


	Retention Time	Area	% Area
1	6.890	13157640	50.01
2	8.415	13154236	49.99



	Retention Time	Area	% Area
1	6.931	16284088	98.59
2	8.478	232456	1.41

Dimethyl 4-hydroxy-3-(2-methoxy-2-oxoethyl)-3a-(phenylethynyl)hexahydropentalene-1,1(2H)-dicarboxylate (4d)

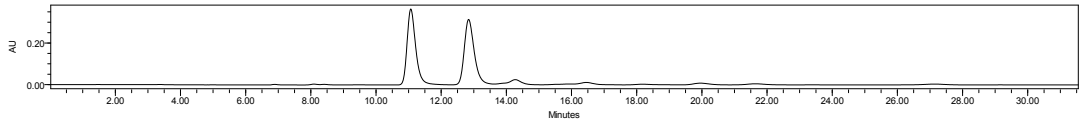


Colourless oil, 67.5 mg, 81% yield. 97% *ee* determined by HPLC (chiral IE column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.0 min, 12.8 min. $[\alpha]_D^{20}$ = - 103.07 (*c* = 1.20 in CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.41 – 7.34 (m, 2H), 7.32 – 7.25 (m, 3H), 4.15 (dd, *J*=5.6, 3.2, 1H), 4.09 – 3.98 (m, 1H), 3.77 – 3.63 (m, 10H), 3.29 – 3.11 (m, 1H), 2.86 (dd, *J*=17.6, 10.4, 1H), 2.69 (dd, *J*=12.8, 6.0, 1H), 2.58 (dd, *J*=17.6, 4.4, 1H), 2.11 – 2.06 (m, 1H), 1.99 – 1.86 (m, 2H), 1.63 – 1.47 (m, 1H).

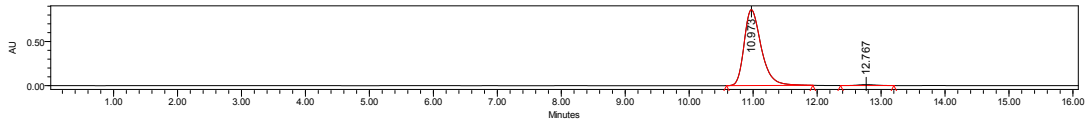
^{13}C NMR (101 MHz, $CDCl_3$) δ = 175.0, 172.1, 171.1, 131.6, 128.3, 128.0, 123.4, 92.4, 85.9, 78.7, 61.4, 59.8, 58.0, 52.9, 52.4, 52.1, 43.5, 36.4, 36.3, 36.2, 27.2.

HRMS (ESI-TOF): calcd for $C_{23}H_{26}NaO_7^+$ ([M + Na]$^+$) 437.1576, found 437.1570.



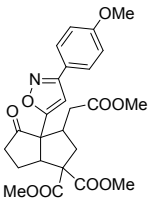
	Retention Time	Area	% Area

1	11.068	6777778	50.04
2	12.842	6767473	49.96



	Retention Time	Area	% Area
1	10.973	15978289	98.71
2	12.767	208833	1.29

Dimethyl 3a-(3-(4-methoxyphenyl)isoxazol-5-yl)-3-(2-(methylperoxy)-2l2-ethyl)-4-oxohexahydropentalene-1,1(2H)-dicarboxylate (4e)

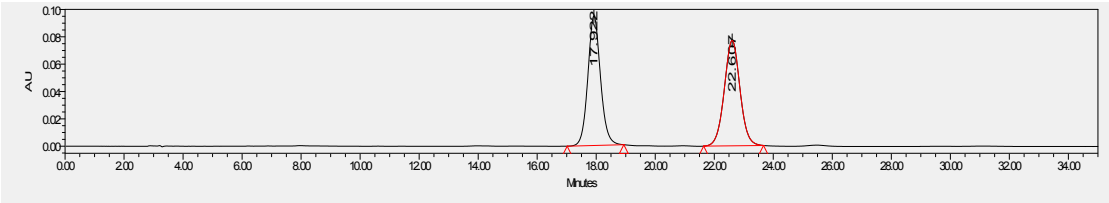


Colourless oil, 98.2 mg, 72% yield. 92% *ee* determined by HPLC (chiral IA column), *n*-hexane/*i*-PrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 17.9 min, 23.2 min. $[\alpha]_\lambda^{20}$ = - 188.55 (*c* = 1.75 in CH_2Cl_2, λ = 365 nm).

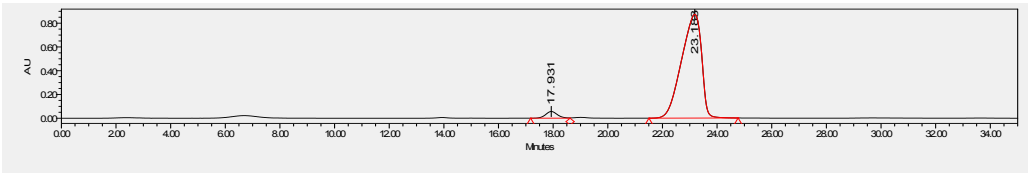
^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.77 – 7.67 (m, 2H), 6.99 – 6.92 (m, 2H), 6.51 (s, 1H), 4.13 – 4.10 (m, 1H), 3.86 – 3.75 (m, 9H), 3.63 (s, 3H), 3.08 – 2.95 (m, 2H), 2.64 – 2.44 (m, 3H), 2.30 – 2.19 (m, 2H), 2.03 – 1.97 (m, 1H), 1.90 – 1.81 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ = 213.4, 171.9, 171.1, 170.7, 168.54, 161.9, 161.1, 128.2, 121.1, 114.3, 101.3, 63.1, 62.0, 60.4, 55.4, 55.3, 53.2, 53.2, 52.9, 52.9, 52.2, 51.8, 41.9, 40.6, 38.0, 34.9, 22.7, 21.1, 14.2.

HRMS (ESI-TOF): calcd for $C_{25}H_{27}NNaO_9^+$ ([M + Na]$^+$) 508.1584, found 508.1584.



	Retention Time	Area	% Area
1	17.922	2827910	49.81
2	22.607	2849045	50.19



	Retention Time	Area	% Area
1	17.931	1693215	3.68
2	23.183	44279309	96.32

(F) Reference

[1] W. Li, Y. Xiao, J. Zhang, *Adv. Synth. Catal*. **2009**, *351*, 3083.

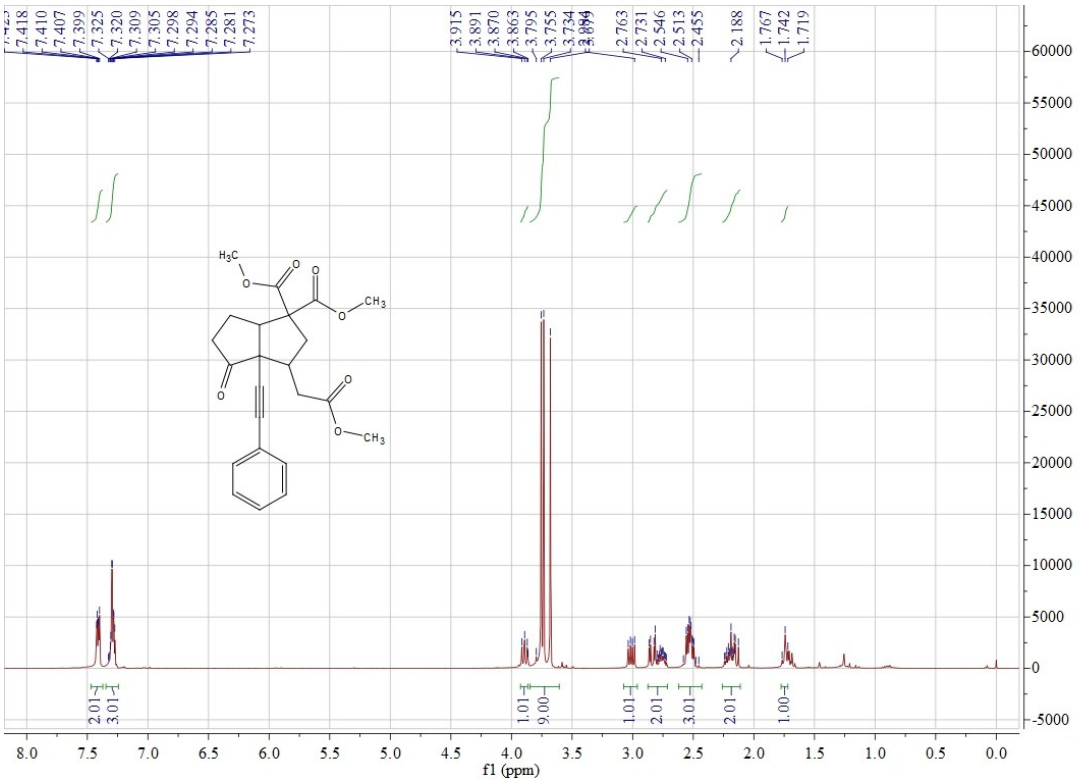
[2] D. Enders, D. P. Göddertz, C. Beceño, G. Raabe, *Adv. Synth. Catal*. **2010**, *352*, 2863.

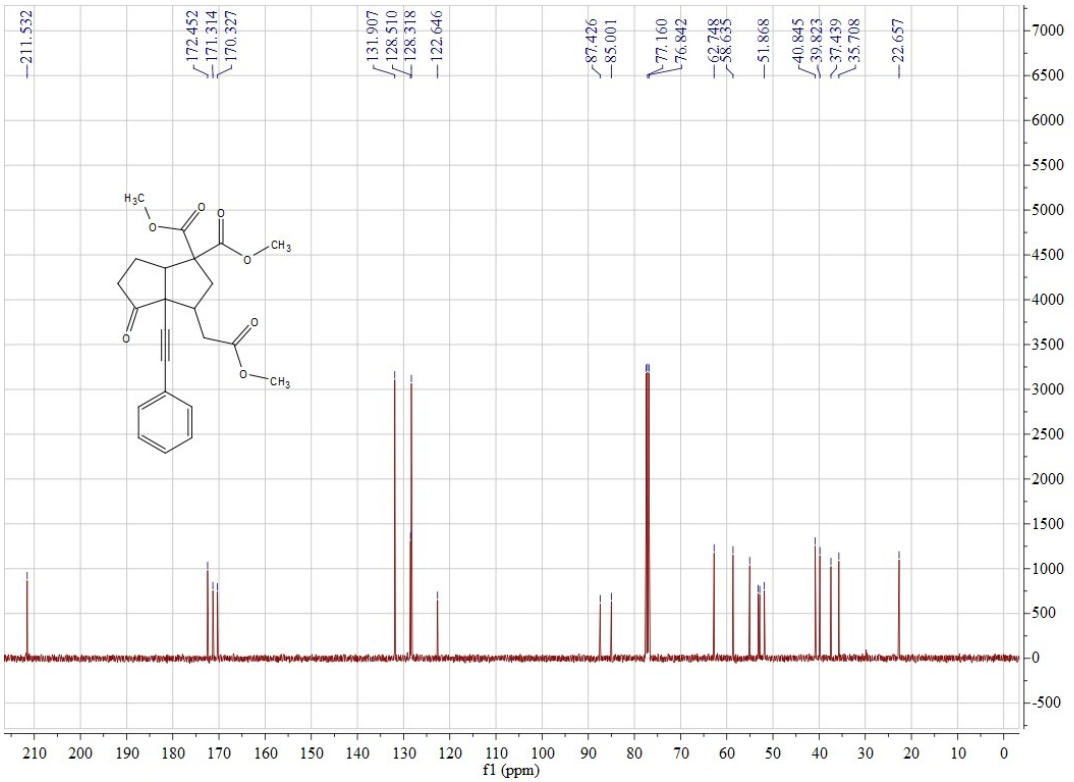
[3] T. Yao, X. Zhang, R. C. Larock, *J. Org. Chem.* **2005**, *70*, 7679.

[4] a) Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin, X. M. Feng, *Synlett* **2005**, 2445; b) J. L. Huang, X. H. Liu, Y. H. Wen, B. Qin, X. M. Feng, *J. Org. Chem.* **2007**, *72*, 204; c) D. J. Shang, J. G. Xin, Y. L. Liu, X. Zhou, X. H. Liu, X. M. Feng, *J. Org. Chem.* **2008**, *73*, 630; d) X. Li, X. H. Liu, Y. Z. Fu, L. J. Wang, L. Zhou, X. M. Feng, *Chem. Eur. J.* **2008**, *14*, 4796; e) J. L. Huang, J. Wang, X. H. Chen, Y. H. Wen, X. H. Liu, X. M. Feng, *Adv. Synth. Catal.* **2008**, *350*, 287; f) X. Yang, X. Zhou, L. L. Lin, L. Chang, X. H. Liu, X. M. Feng, *Angew. Chem.* **2008**, *120,* 7187; *Angew. Chem. Int. Ed.* **2008**, *47*, 7079; g) Y. L. Liu, D. J. Shang, X. Zhou, X. H. Liu, X. M. Feng, *Chem. Eur. J.* **2009**, *15*, 2055; h) D. J. Shang, Y. L. Liu, X. Zhou, X. H. Liu, X. M. Feng, *Chem. Eur. J.* **2009**, *15*, 3678.

(G) Copies of the NMR spectra

3a

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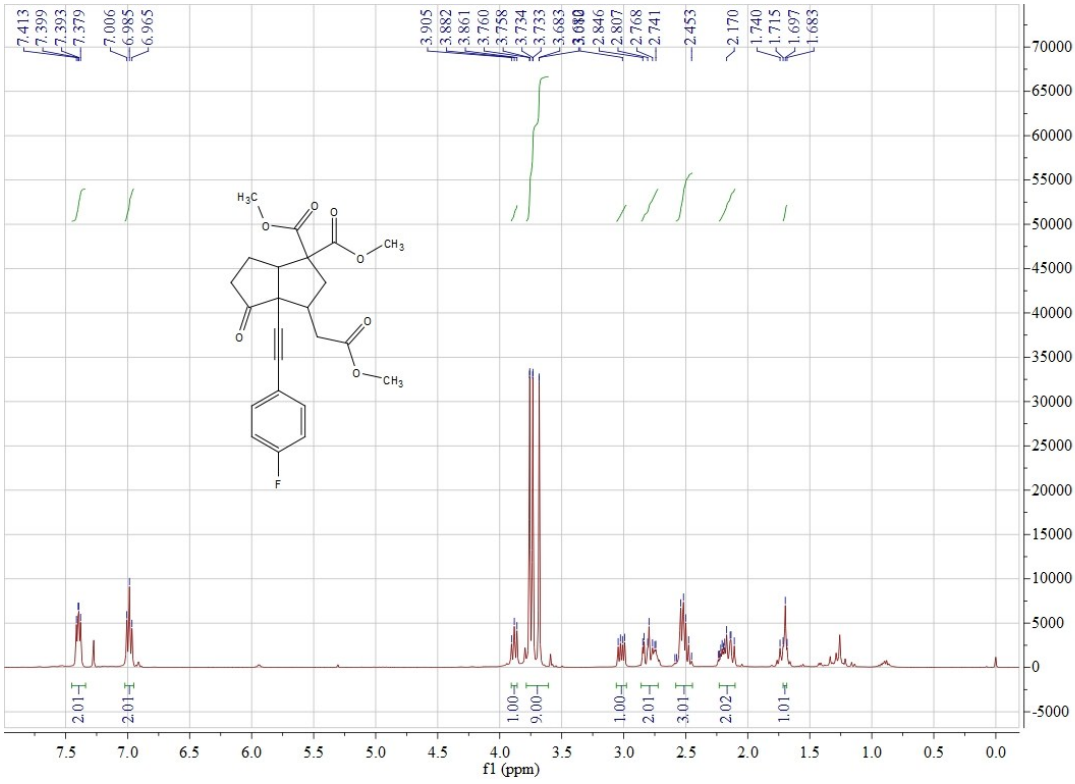
22.657
f1 (ppm)

3b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3.734
3.733
3.683
2.846
2.807
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2.453
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9.00
1.00
2.01
3.01
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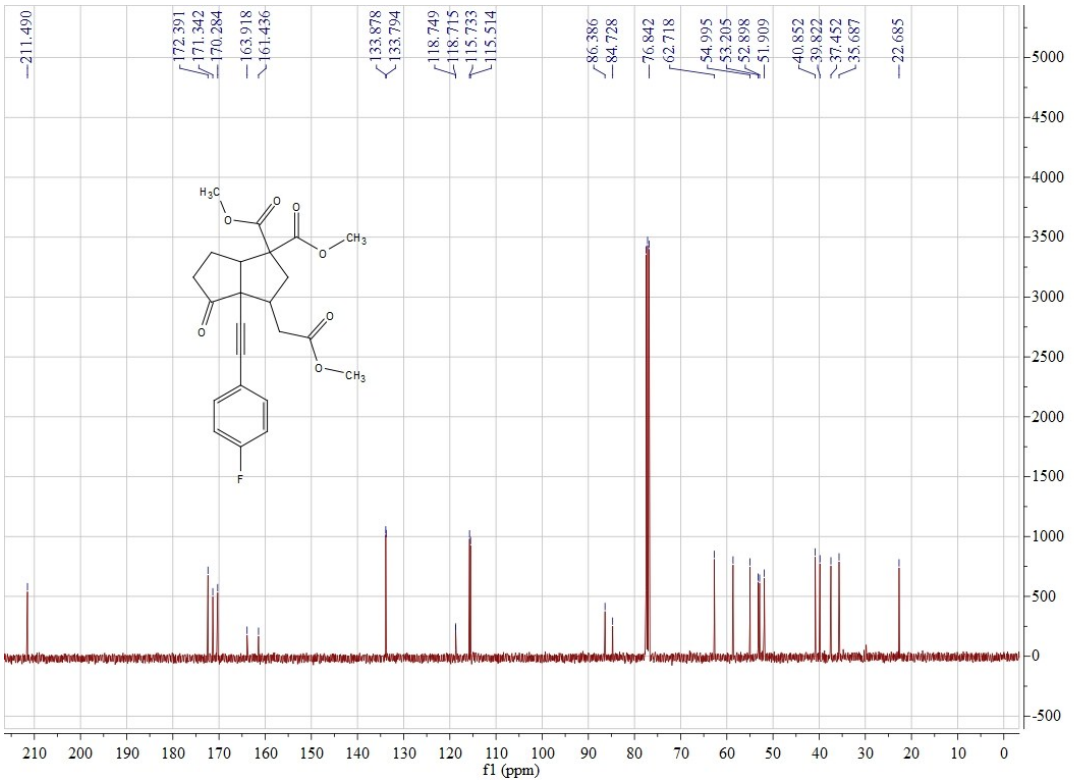
1.01
f1 (ppm)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86.386
84.728
76.842
62.718
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52.898
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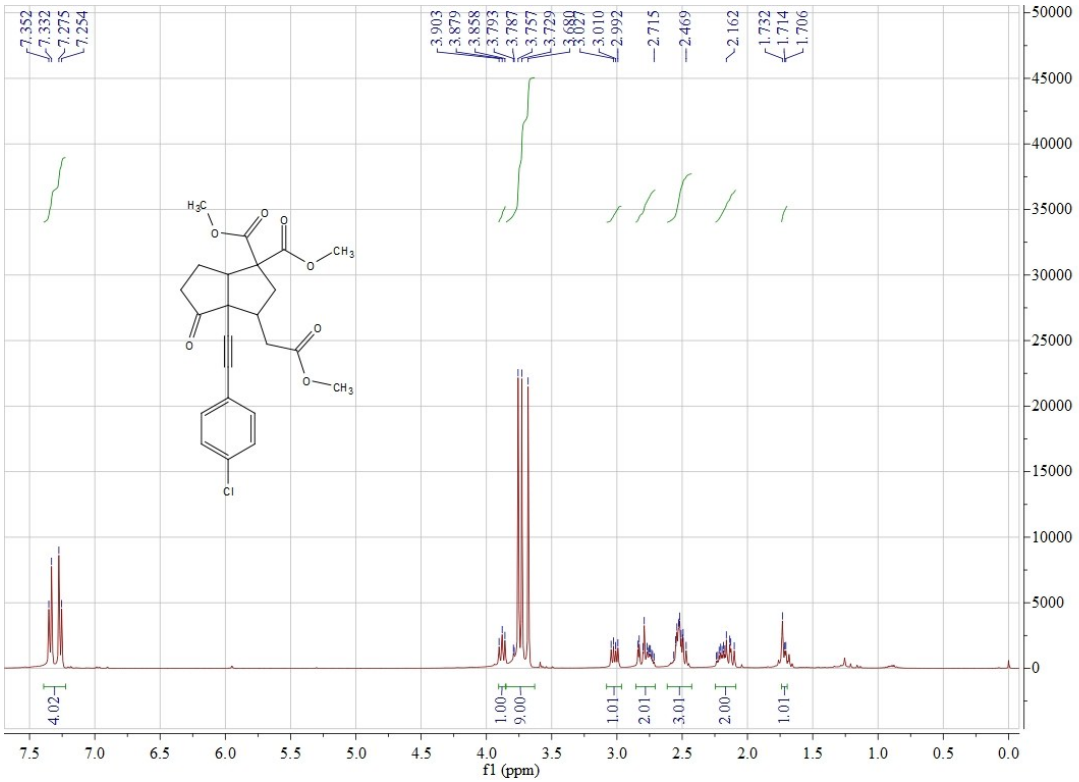
22.685
f1 (ppm)

3c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2.992
2.715
2.469
2.162
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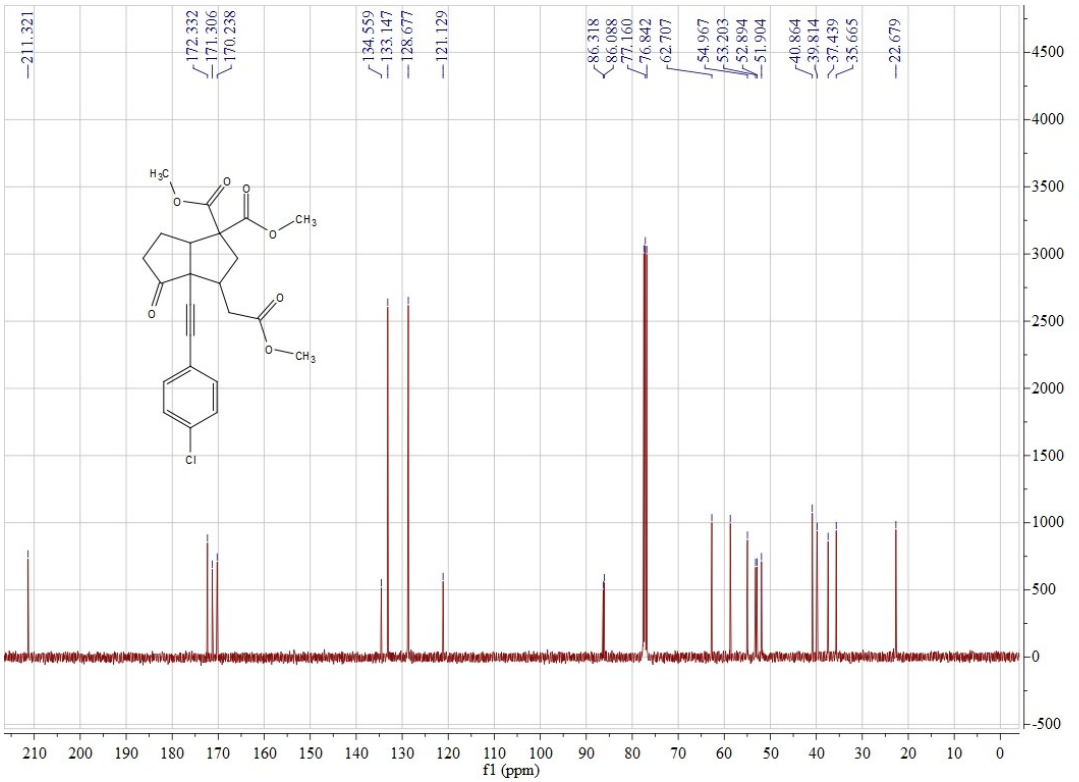
9.00
1.01
2.01
3.01
2.00
1.01
f1 (ppm)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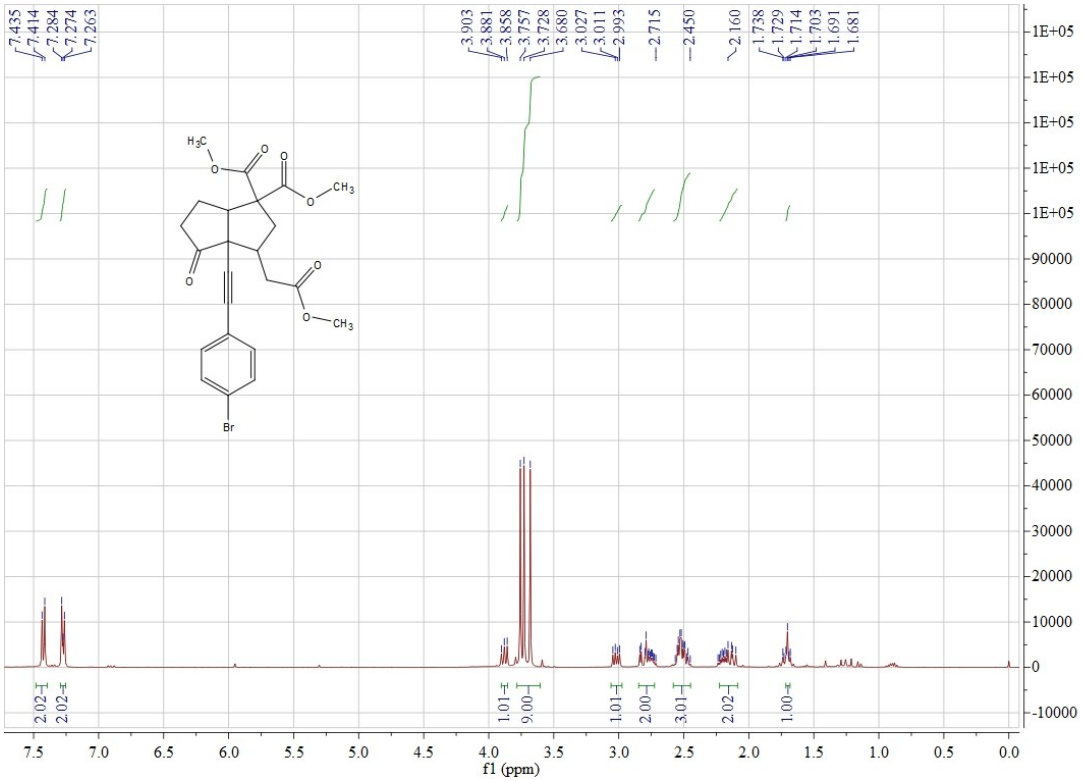
22.679
f1 (ppm)

3d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1.729
1.714
1.703
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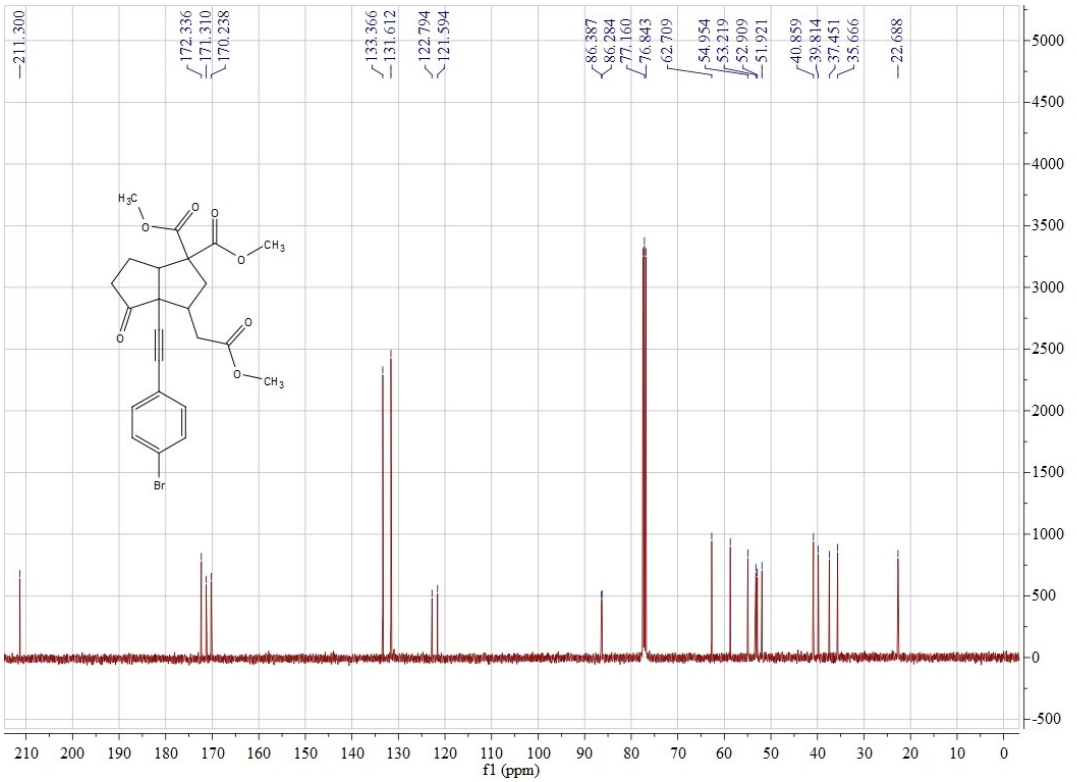
2.00
3.01
2.02
1.00
f1 (ppm)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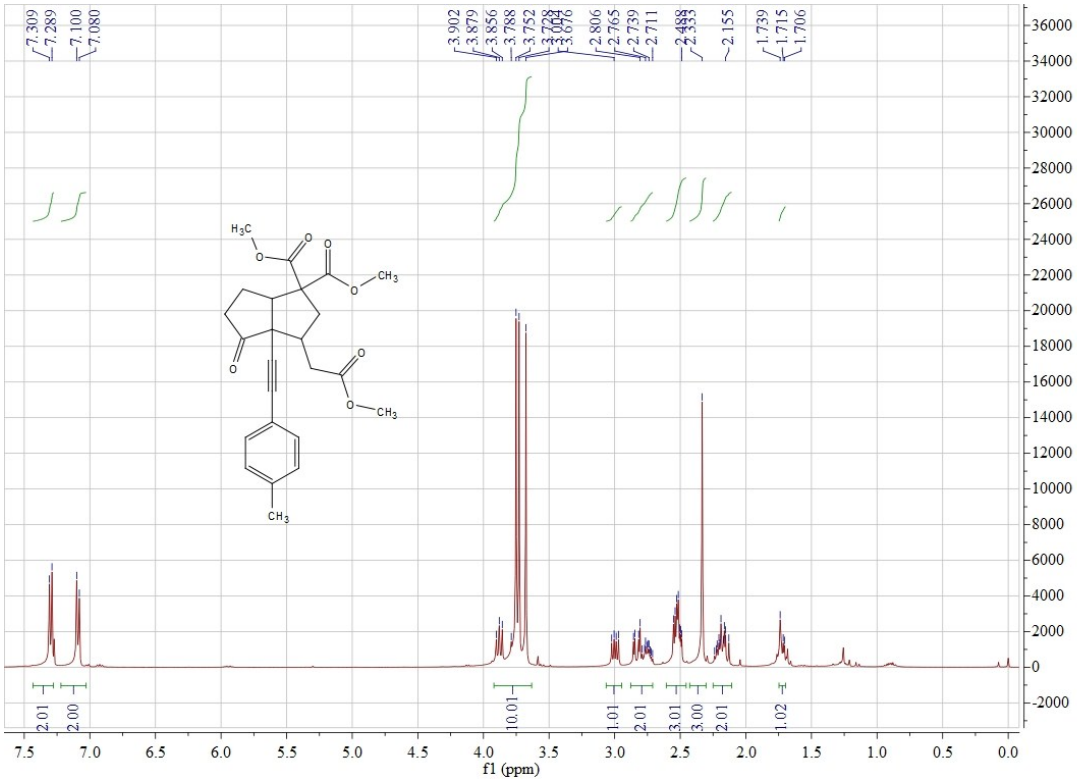
f1 (ppm)

3e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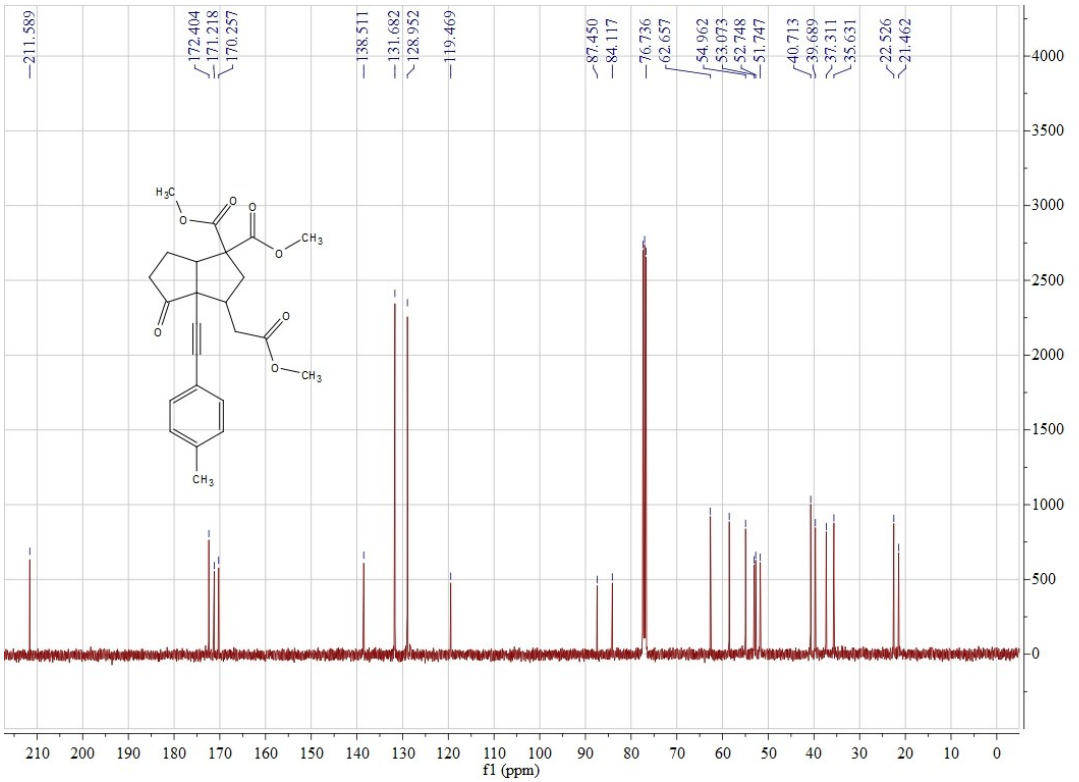
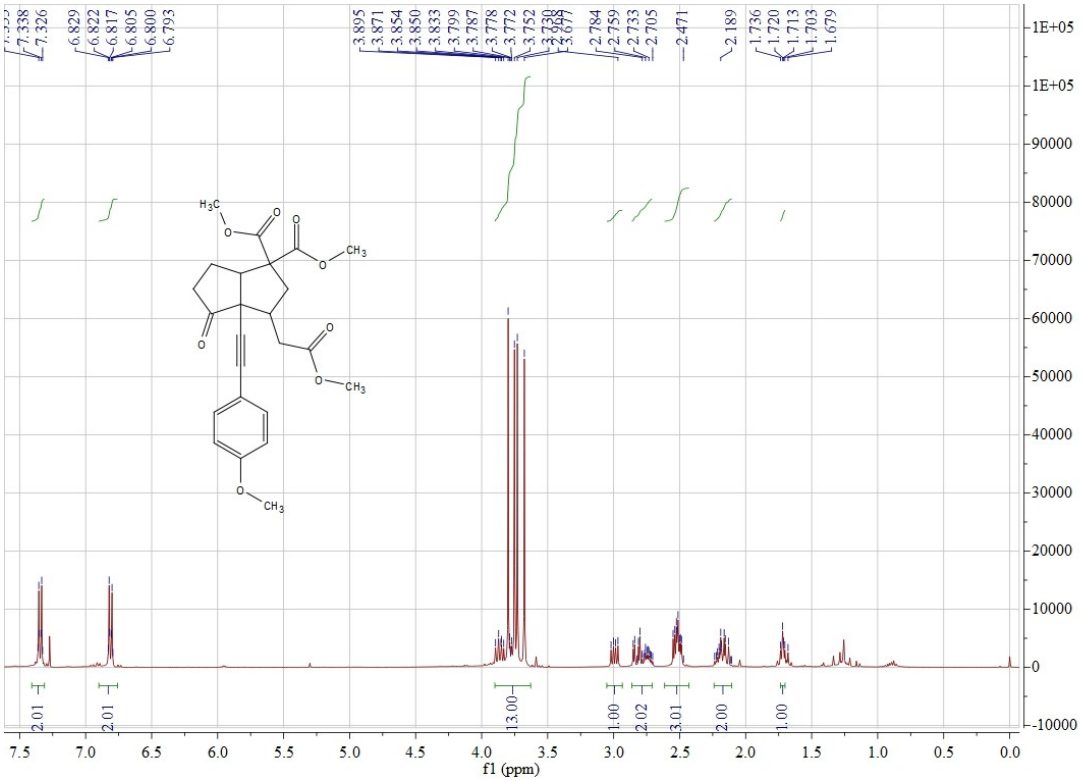
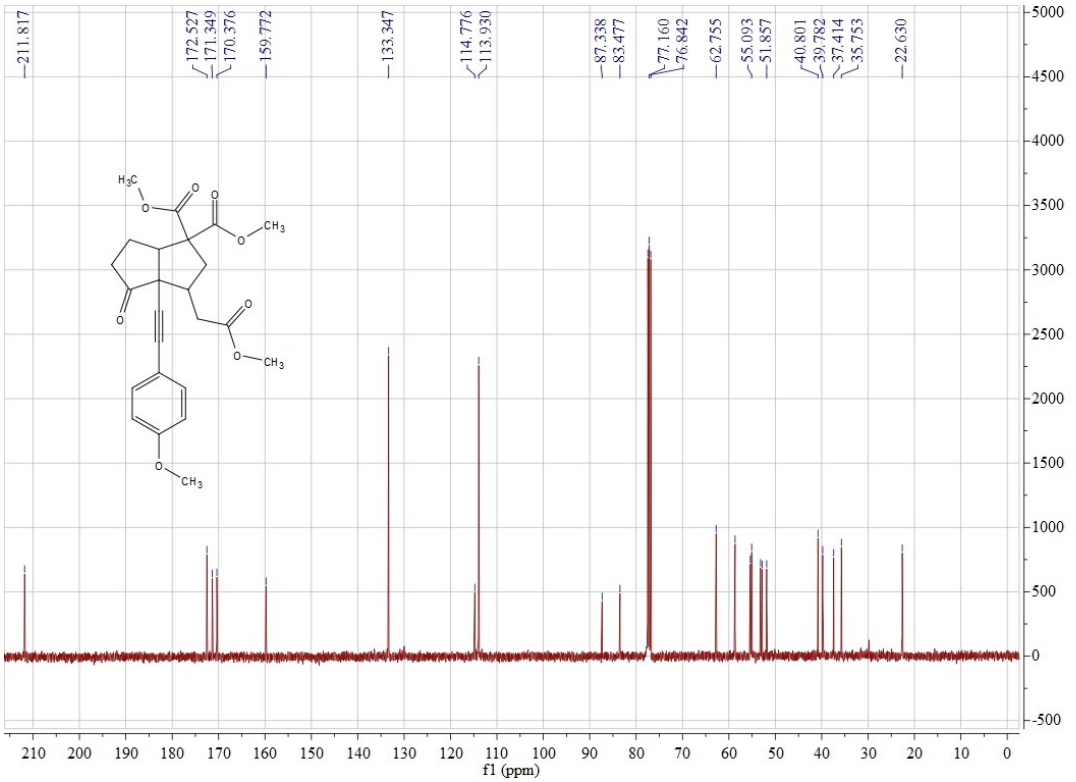
2.739
2.711
2.488
2.333
2.155
1.739
1.715
1.706
2.01
2.00
10.01
1.01
2.01
3.01
3.00
2.01
1.02
f1 (ppm)

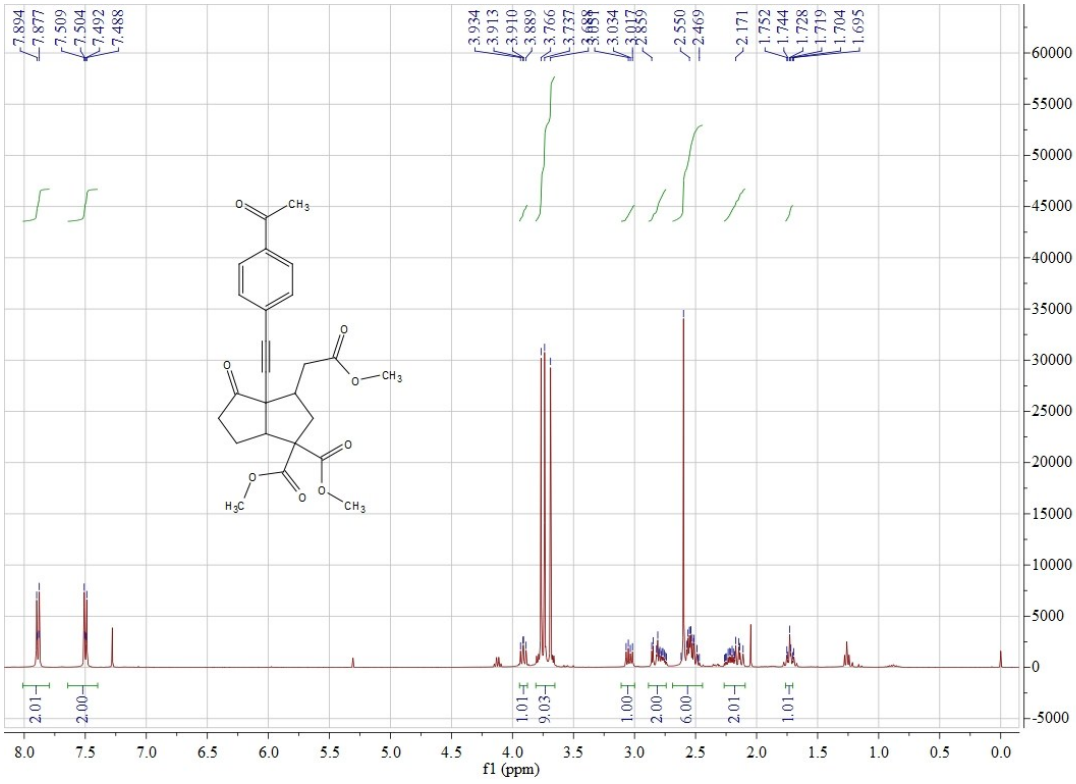

211.589
172.404
171.218
170.257
138.511
131.682
128.952
119.469
87.450
84.117
76.736
62.657
54.962
53.073
52.748
51.747
40.713
39.689
37.311
35.631
22.526
21.462
f1 (ppm)

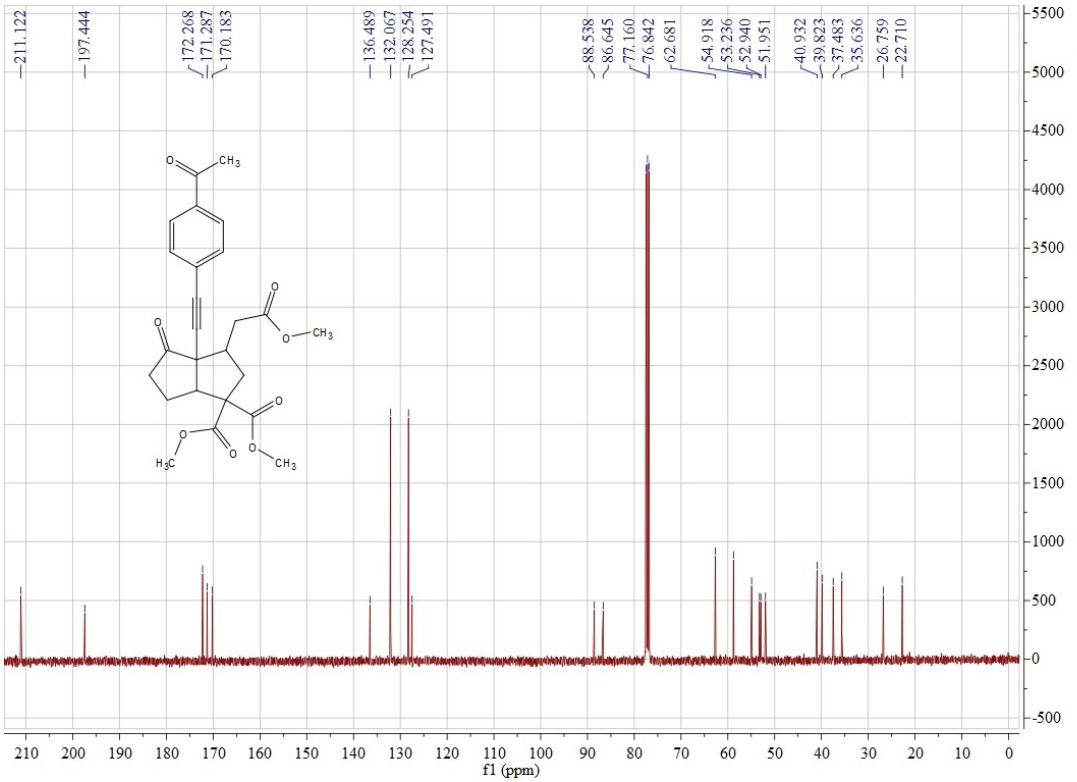
3f


7.338
7.326
6.829
6.822
6.817
6.805
6.800
6.793
3.895
3.871
3.854
3.850
3.833
3.799
3.787
3.778
3.772
3.752
2.784
2.759
2.733
2.705
2.471
2.189
1.736
1.720
1.713
1.703
1.679
2.01
2.01
13.00
1.00
2.02
3.01
2.00
1.00
f1 (ppm)

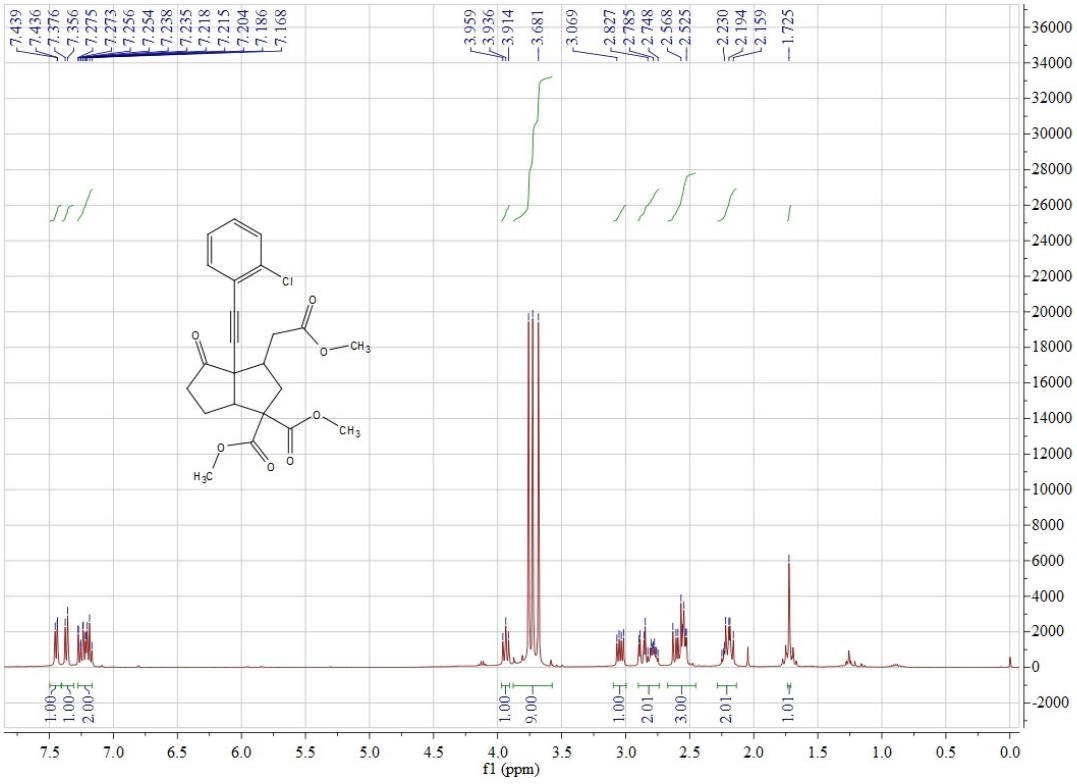

211.817
172.527
171.349
170.376
159.772
133.347
114.776
113.930
87.338
83.477
77.160
76.842
62.755
55.093
51.857
40.801
39.782
37.414
35.753
22.630
f1 (ppm)

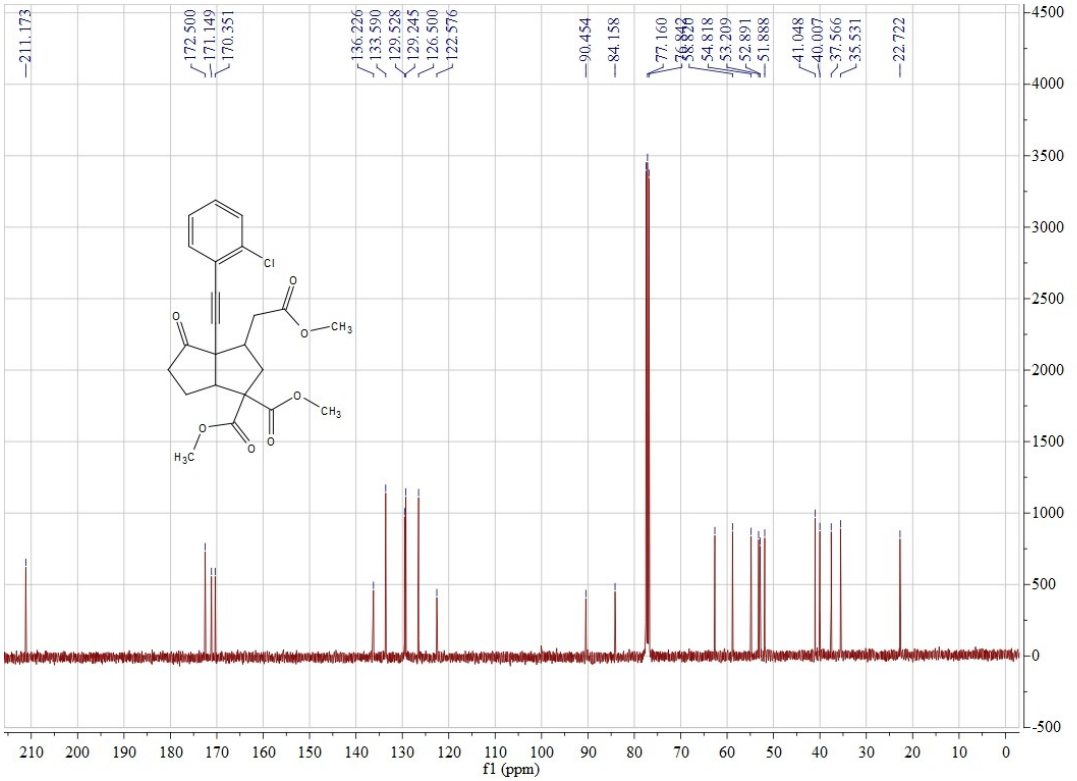
3g


7.894
7.877
7.509
7.504
7.492
7.488
3.934
3.913
3.910
3.889
3.766
3.737
3.034
3.017
2.855
2.550
2.469
2.171
1.752
1.744
1.728
1.719
1.704
1.695
2.01
2.00
1.01
9.03
1.00
2.00
6.00
2.01
1.01
f1 (ppm)

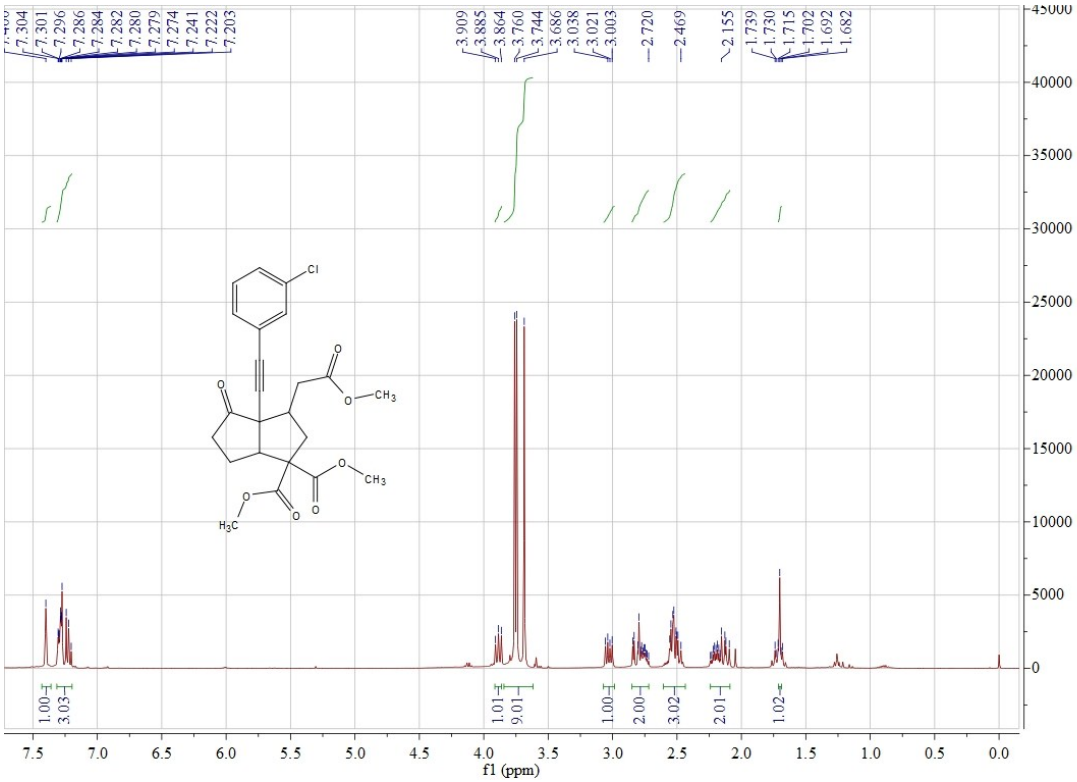

211.122
197.444
172.268
171.287
170.183
136.489
132.067
128.254
127.491
88.538
86.645
77.160
76.842
62.681
54.918
53.236
52.940
51.951
40.932
39.823
37.483
35.636
26.759
22.710
f1 (ppm)

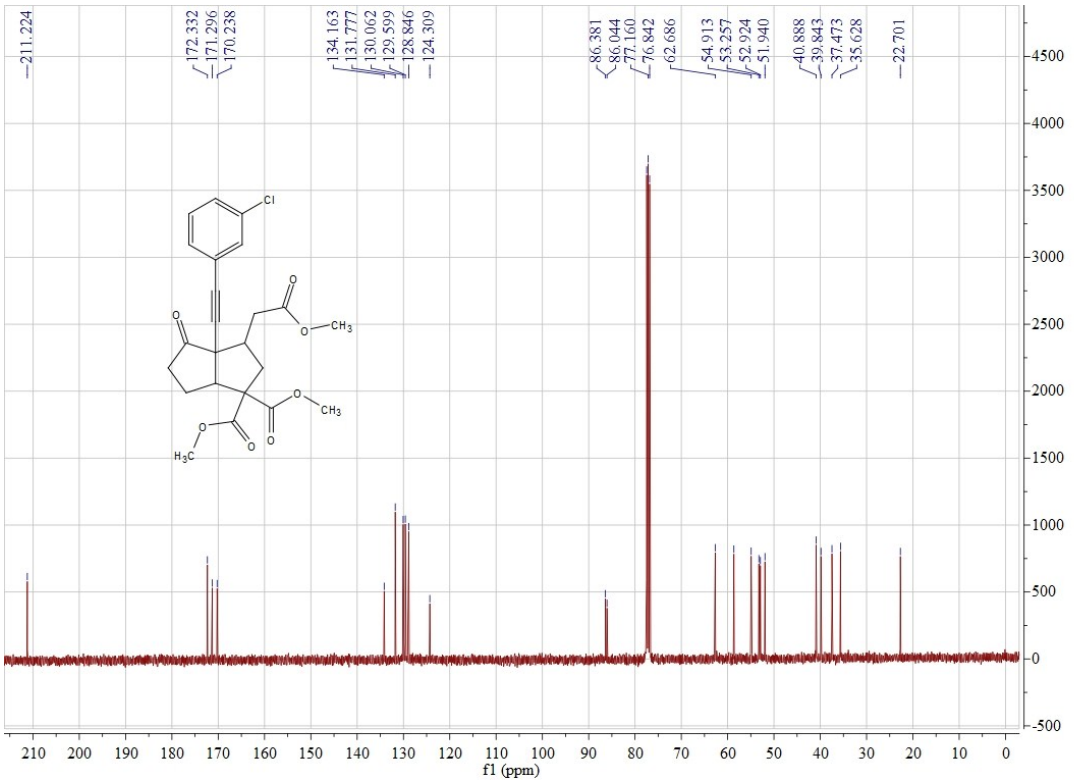
3h


7.439
7.436
7.376
7.356
7.275
7.273
7.256
7.254
7.238
7.235
7.218
7.215
7.204
7.186
7.168
3.959
3.936
3.914
3.681
3.069
2.827
2.785
2.748
2.568
2.525
2.230
2.194
2.159
1.725
f1 (ppm)

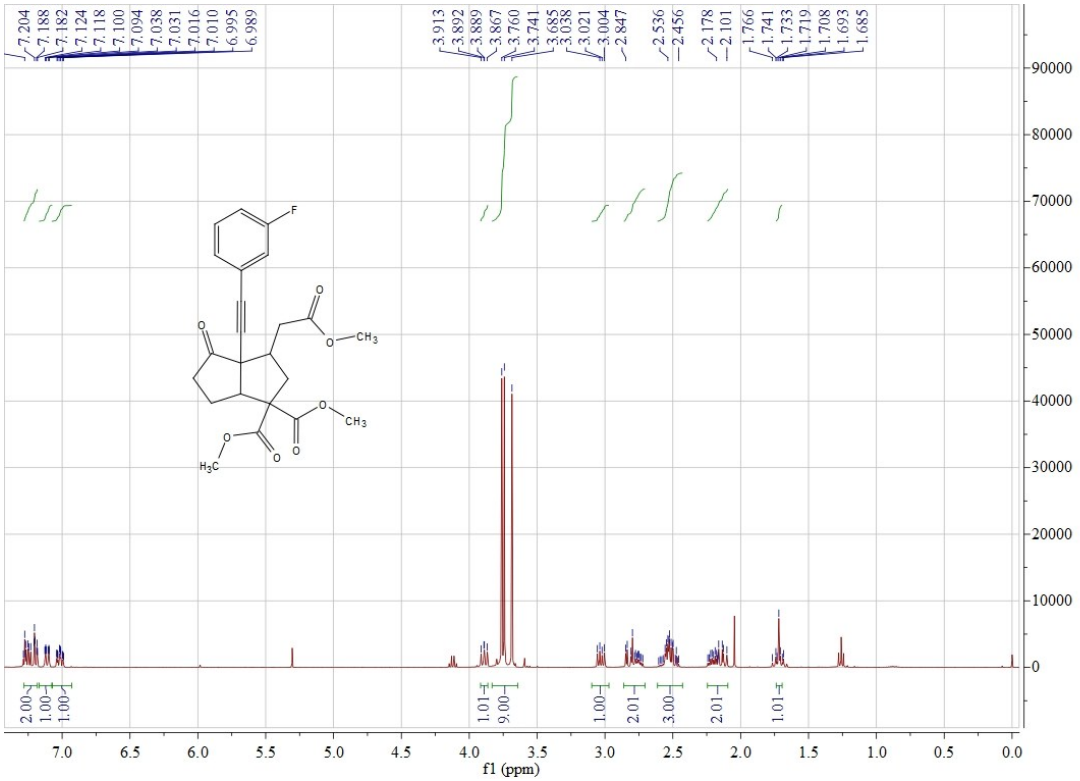

211.173
172.500
171.149
170.351
136.226
133.590
129.528
129.245
126.500
122.576
90.454
84.158
77.160
54.818
53.209
52.891
51.888
41.048
40.007
37.566
35.531
22.722
Cl
CH3
H3C
f1 (ppm)

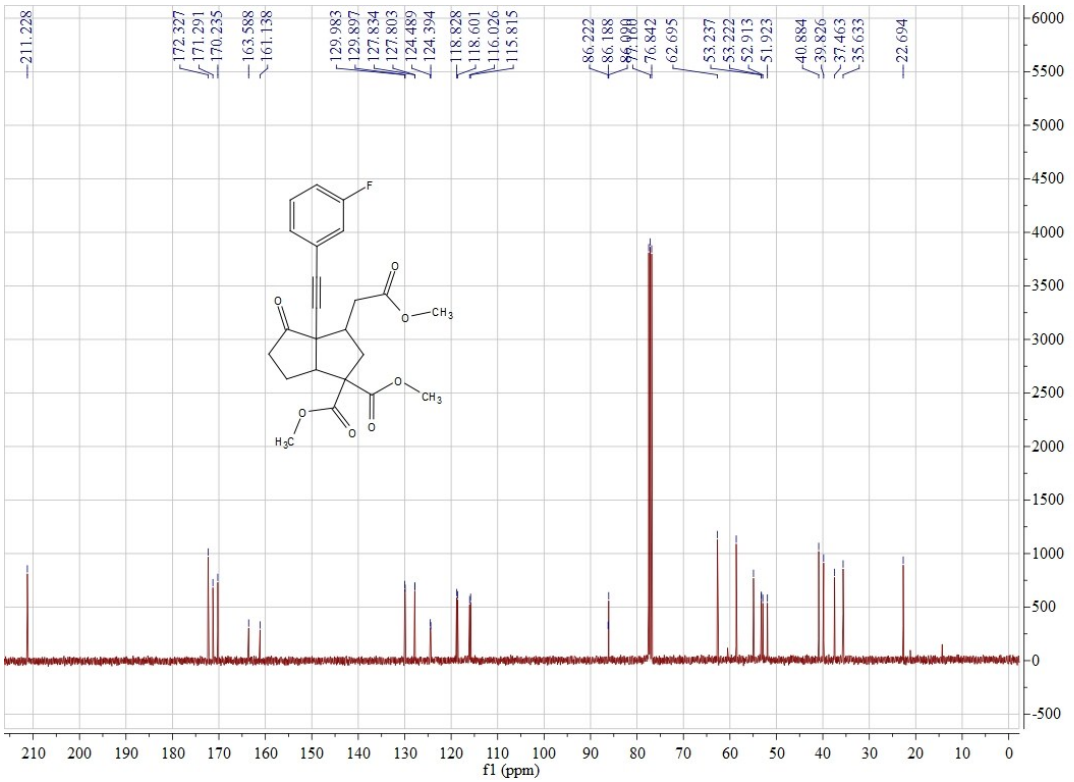
3i


7.304
7.301
7.296
7.286
7.284
7.282
7.280
7.279
7.274
7.241
7.222
7.203
3.909
3.885
3.864
3.760
3.744
3.686
3.038
3.021
3.003
2.720
2.469
2.155
1.739
1.730
1.715
1.702
1.692
1.682
1.00
3.03
1.01
9.01
1.00
2.00
3.02
2.01
1.02
Cl
CH3
H3C
f1 (ppm)

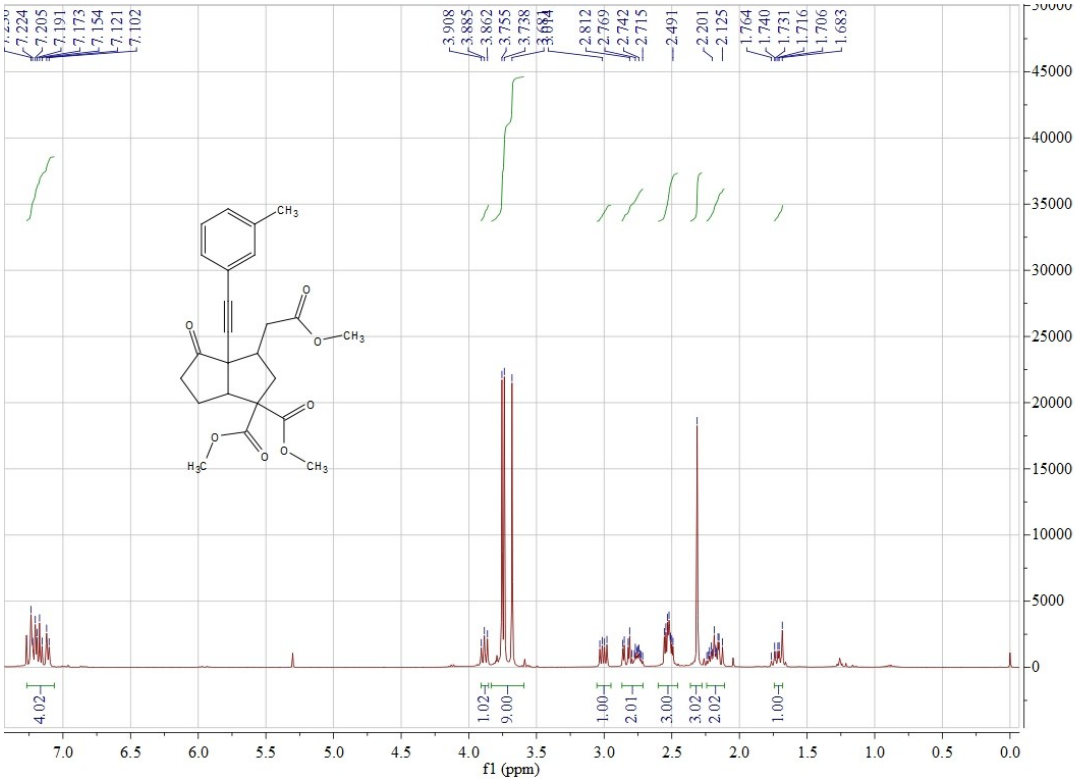

211.224
172.332
171.296
170.238
134.163
131.777
130.062
129.599
128.846
124.309
86.381
86.044
77.160
76.842
62.686
54.913
53.257
52.924
51.940
40.888
39.843
37.473
35.628
22.701
Cl
O
CH3
H3C
f1 (ppm)

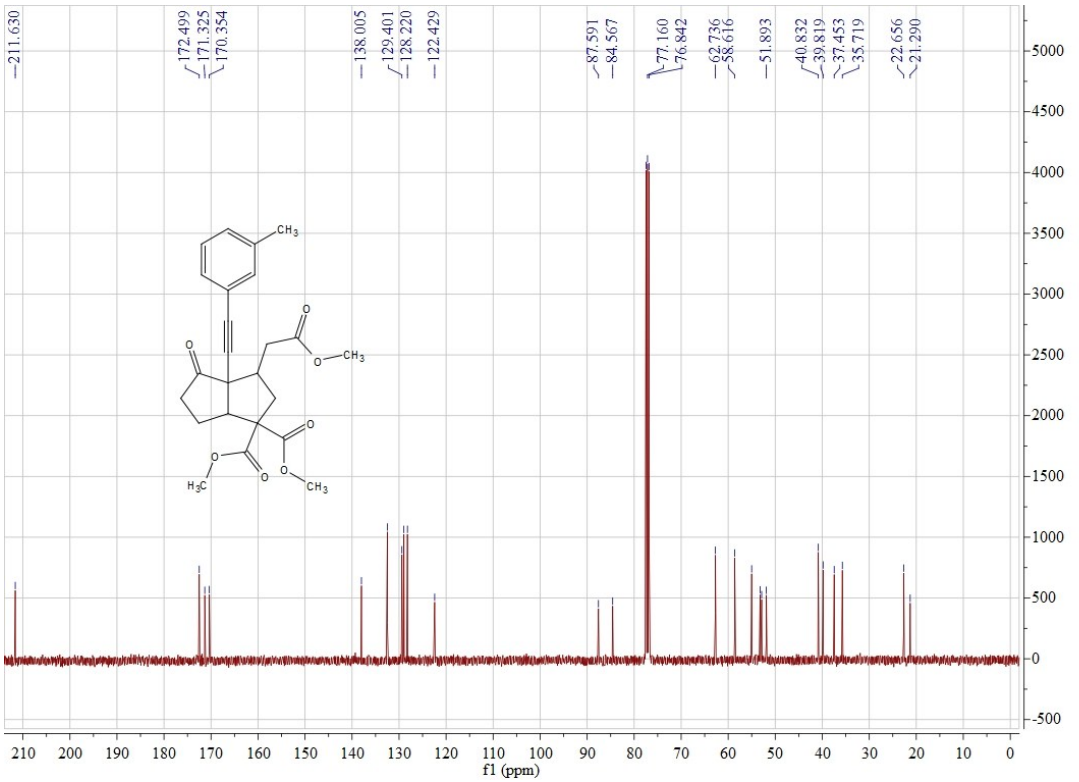
3j


7.204
7.188
7.182
7.124
7.118
7.100
7.094
7.038
7.031
7.016
7.010
6.995
6.989
3.913
3.892
3.889
3.867
3.760
3.741
3.685
3.038
3.021
3.004
2.847
2.536
2.456
2.178
2.101
1.766
1.741
1.733
1.719
1.708
1.693
1.685
F
O
CH3
H3C
2.00
1.00
1.00
1.01
9.00
1.00
2.01
3.00
2.01
1.01
f1 (ppm)

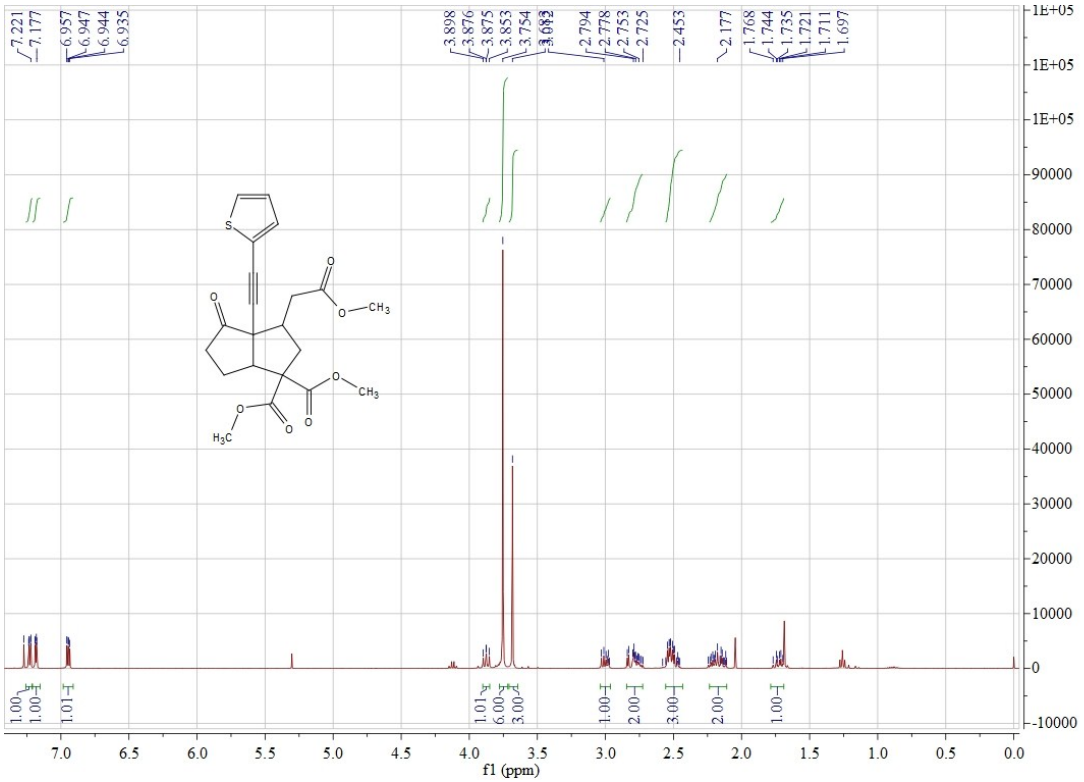

211.228
172.327
171.291
170.235
163.588
161.138
129.983
129.897
127.834
127.803
124.489
124.394
118.828
118.601
116.026
115.815
86.222
86.188
76.842
62.695
53.237
53.222
52.913
51.923
40.884
39.826
37.463
35.633
22.694
F
O
O
O
CH3
O
CH3
O
O
H3C
O
f1 (ppm)

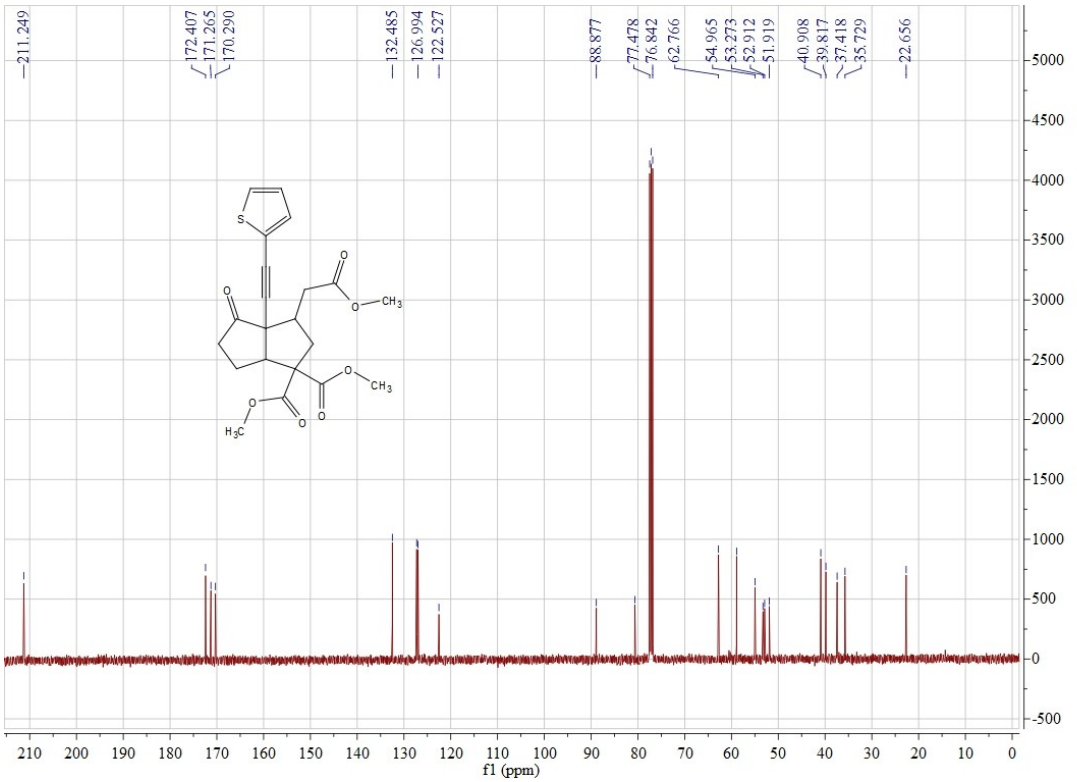
3k


7.224
7.205
7.191
7.173
7.154
7.121
7.102
3.908
3.885
3.862
3.755
3.738
2.812
2.769
2.742
2.715
2.491
2.201
2.125
1.764
1.740
1.731
1.716
1.706
1.683
CH3
O
O
CH3
O
O
H3C
O
CH3
4.02
1.02
9.00
1.00
2.01
3.00
3.02
2.02
1.00
f1 (ppm)

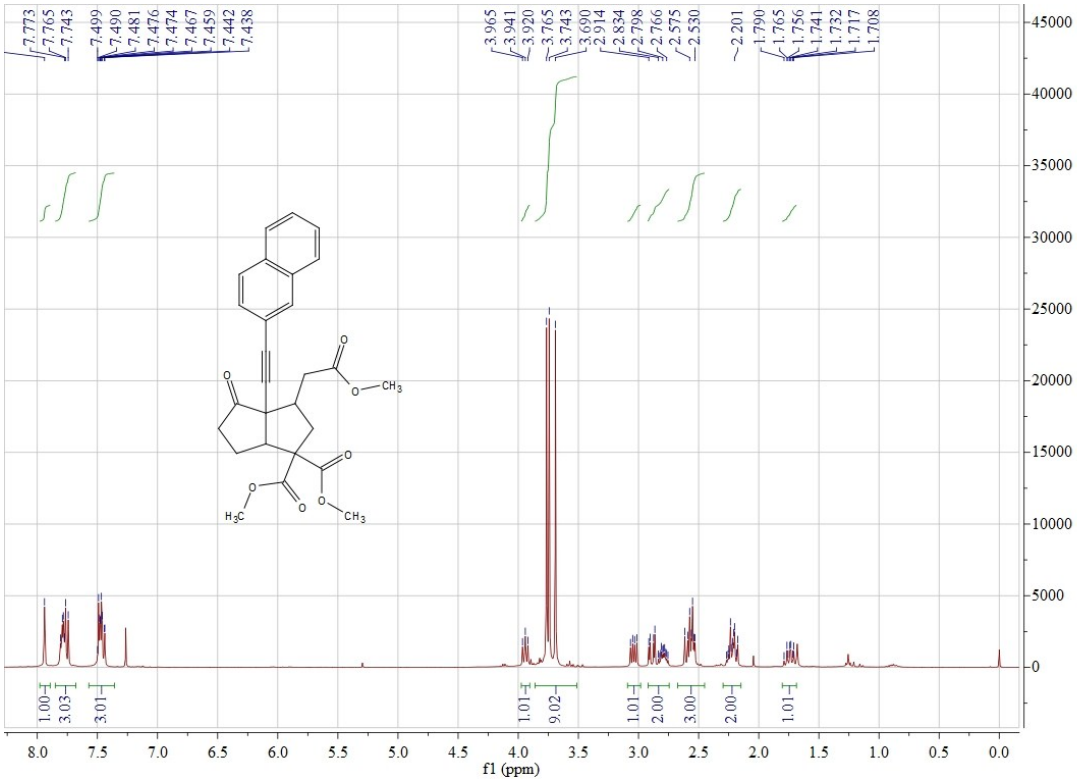

211.630
172.499
171.325
170.354
138.005
129.401
128.220
122.429
87.591
84.567
77.160
76.842
62.736
58.616
51.893
40.832
39.819
37.453
35.719
22.656
21.290
f1 (ppm)

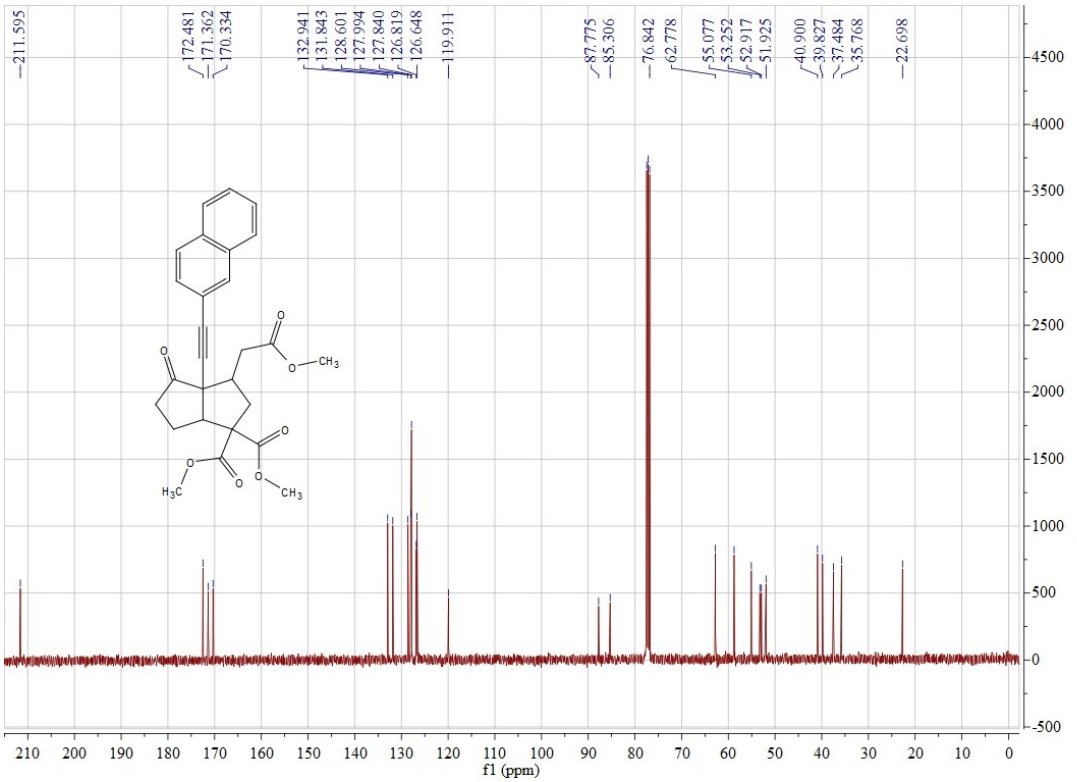
3l


7.221
7.177
6.957
6.947
6.944
6.935
3.898
3.876
3.875
3.853
3.754
2.794
2.778
2.753
2.725
2.453
2.177
1.768
1.744
1.735
1.721
1.711
1.697
1.00
1.00
1.01
1.01
6.00
3.00
1.00
2.00
3.00
2.00
1.00
f1 (ppm)

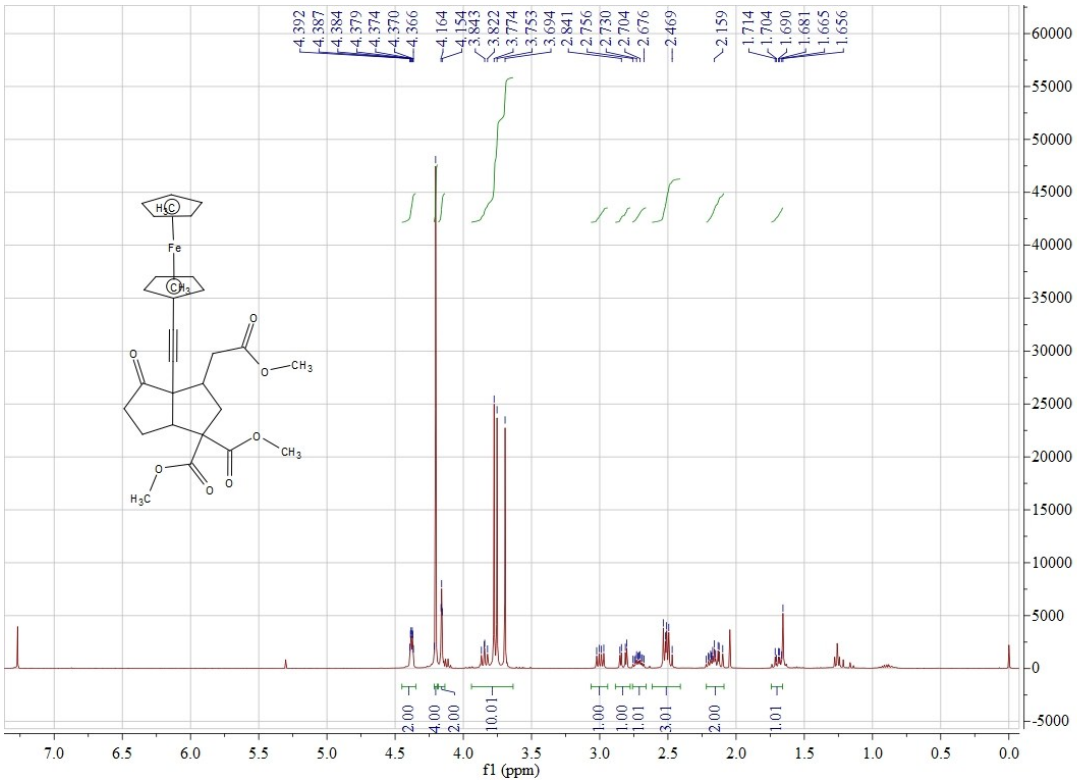

211.249
172.407
171.265
170.290
132.485
126.994
122.527
88.877
77.478
76.842
62.766
54.965
53.273
52.912
51.919
40.908
39.817
37.418
35.729
22.656
f1 (ppm)

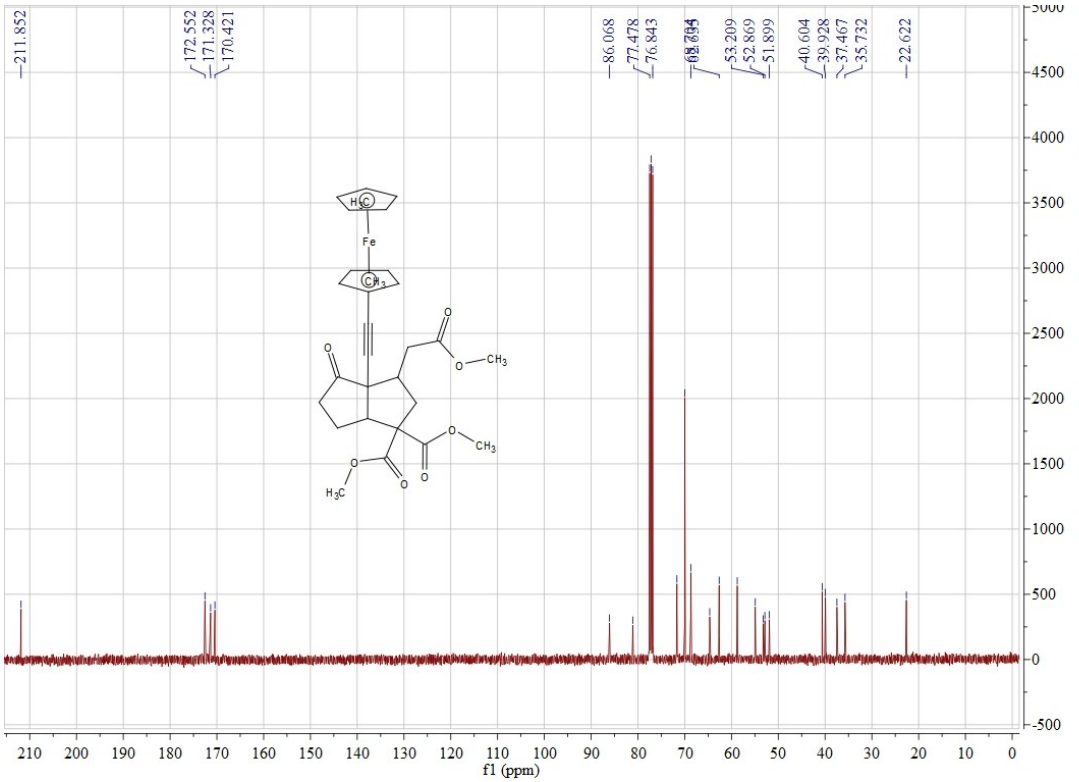
3m


7.773
7.765
7.743
7.499
7.490
7.481
7.476
7.474
7.467
7.459
7.442
7.438
3.965
3.941
3.920
3.765
3.743
3.690
2.914
2.834
2.798
2.766
2.575
2.530
2.201
1.790
1.765
1.756
1.741
1.732
1.717
1.708
1.00
3.03
3.01
1.01
9.02
1.01
2.00
3.00
2.00
1.01
f1 (ppm)

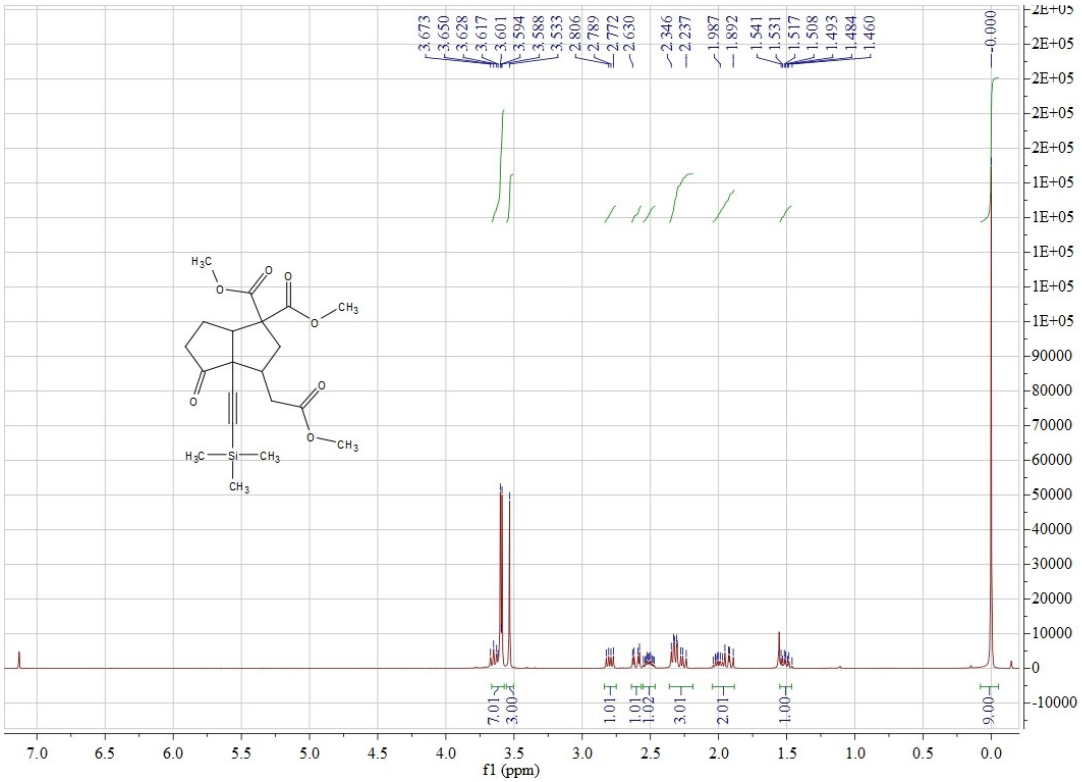

211.595
172.481
171.362
170.334
132.941
131.843
128.601
127.994
127.840
126.819
126.648
119.911
87.775
85.306
76.842
62.778
55.077
53.252
52.917
51.925
40.900
39.827
37.484
35.768
22.698
f1 (ppm)

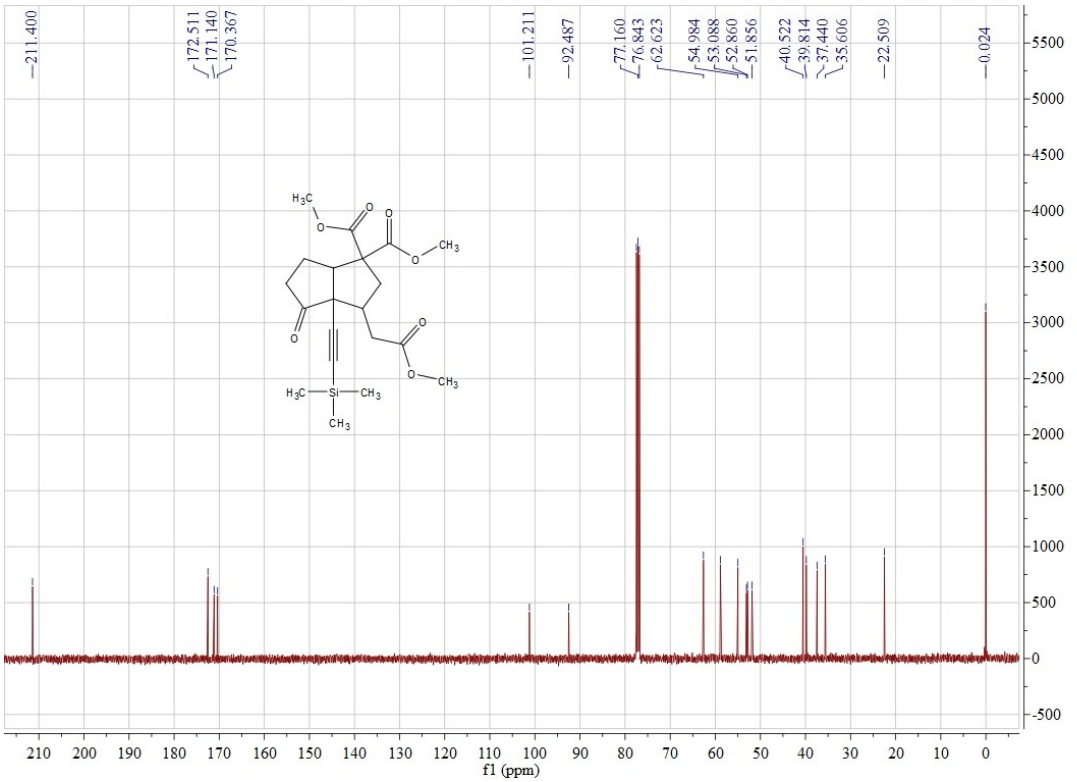
3n


4.392
4.387
4.384
4.379
4.374
4.370
4.366
4.164
4.154
3.843
3.822
3.774
3.753
3.694
2.841
2.756
2.730
2.704
2.676
2.469
2.159
1.714
1.704
1.690
1.681
1.665
1.656
2.00
4.00
2.00
10.01
1.00
1.00
1.01
3.01
2.00
1.01
f1 (ppm)

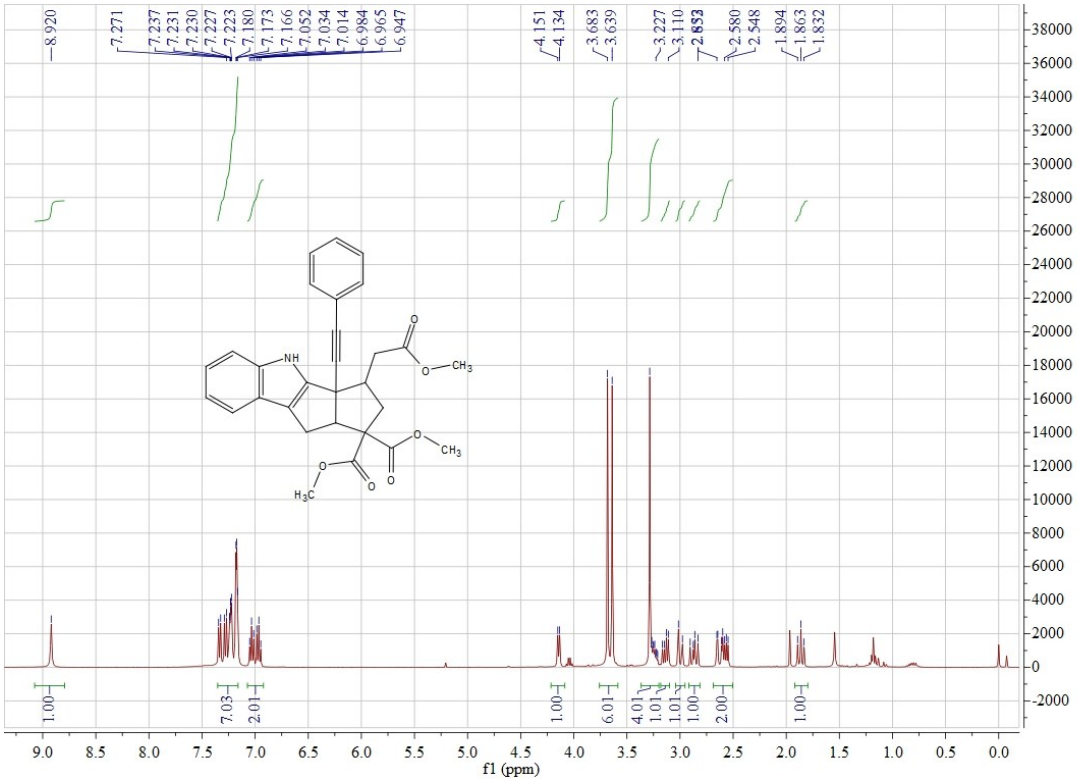

211.852
172.552
171.328
170.421
86.068
77.478
76.843
53.209
52.869
51.899
40.604
39.928
37.467
35.732
22.622
f1 (ppm)

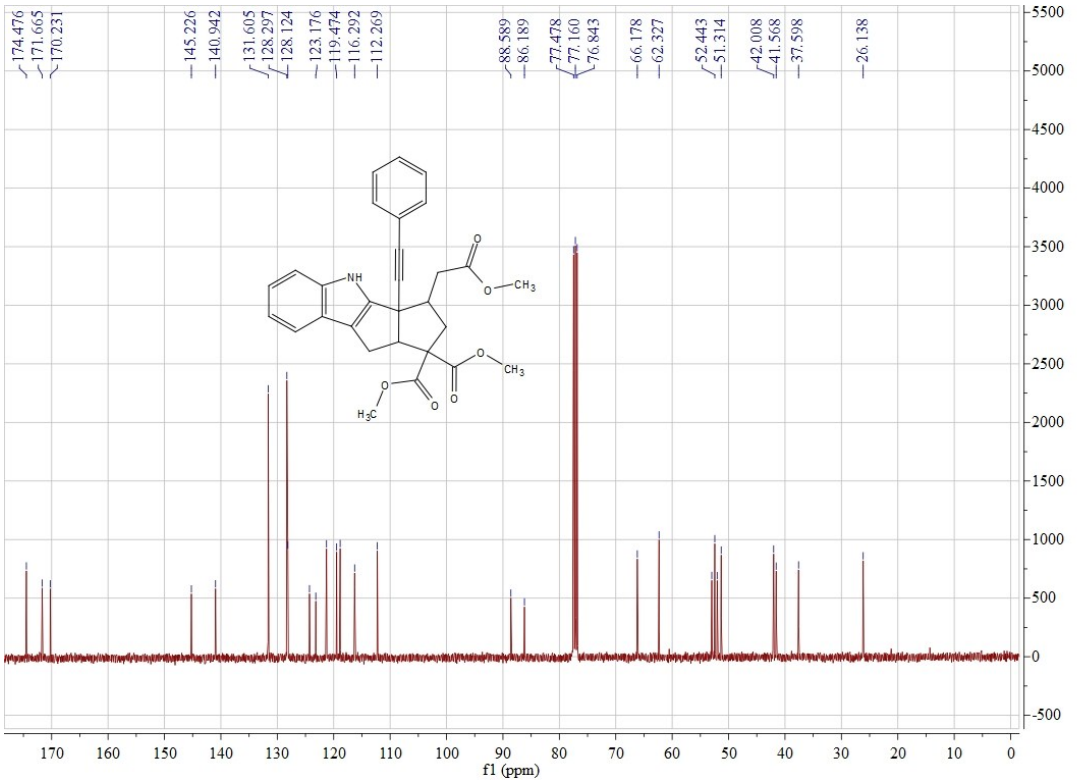
3o


3.673
3.650
3.628
3.617
3.601
3.594
3.588
3.533
2.806
2.789
2.772
2.630
2.346
2.237
1.987
1.892
1.541
1.531
1.517
1.508
1.493
1.484
1.460
0.000
7.01
3.00
1.01
1.01
1.02
3.01
2.01
1.00
9.00
f1 (ppm)

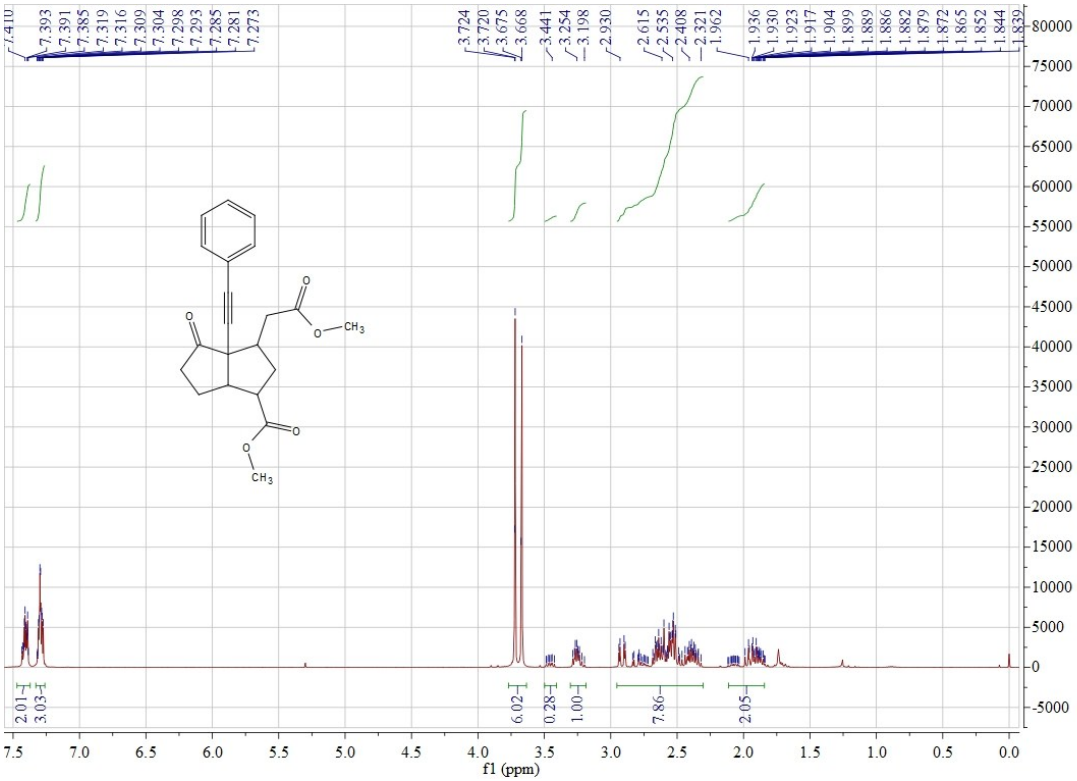

211.400
172.511
171.140
170.367
101.211
92.487
77.160
76.843
62.623
54.984
53.088
52.860
51.856
40.522
39.814
37.440
35.606
22.509
0.024
f1 (ppm)

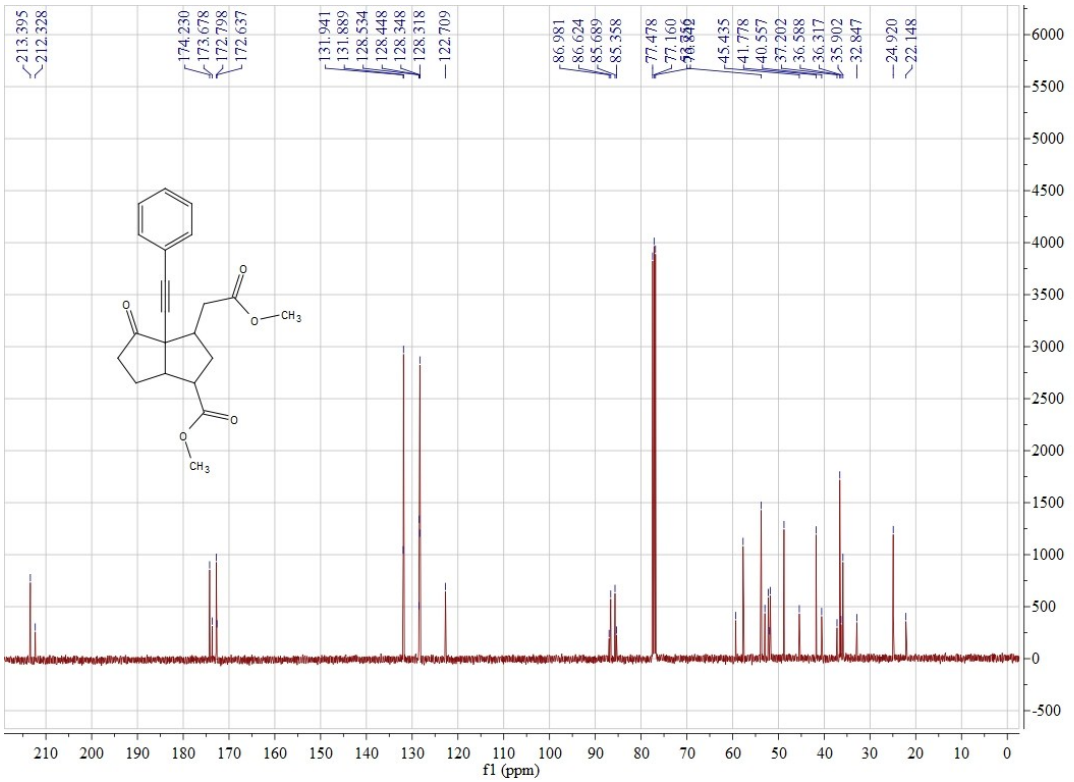
4a


8.920
7.271
7.237
7.231
7.230
7.227
7.223
7.180
7.173
7.166
7.052
7.034
7.014
6.984
6.965
6.947
4.151
4.134
3.683
3.639
3.227
3.110
2.853
2.580
2.548
1.894
1.863
1.832
1.00
7.03
2.01
1.00
6.01
4.01
1.01
1.01
1.00
2.00
1.00
f1 (ppm)

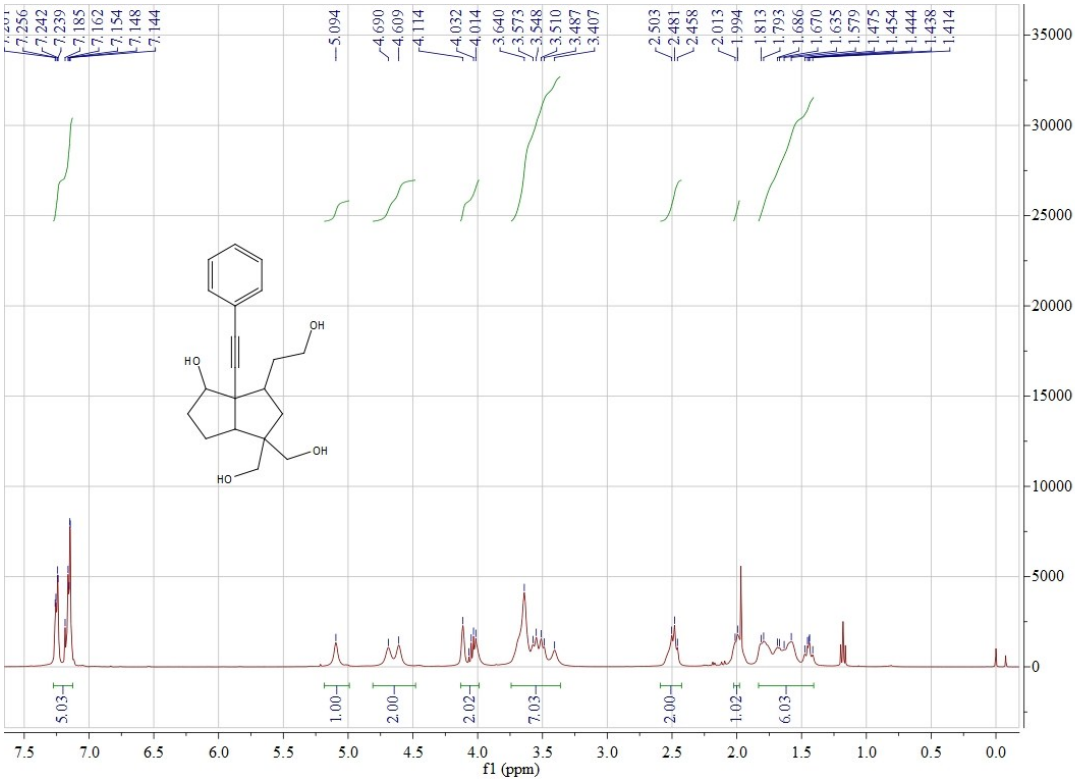

174.476
171.665
170.231
145.226
140.942
131.605
128.297
128.124
123.176
119.474
116.292
112.269
88.589
86.189
77.478
77.160
76.843
66.178
62.327
52.443
51.314
42.008
41.568
37.598
26.138
NH
O
CH3
H3C
f1 (ppm)

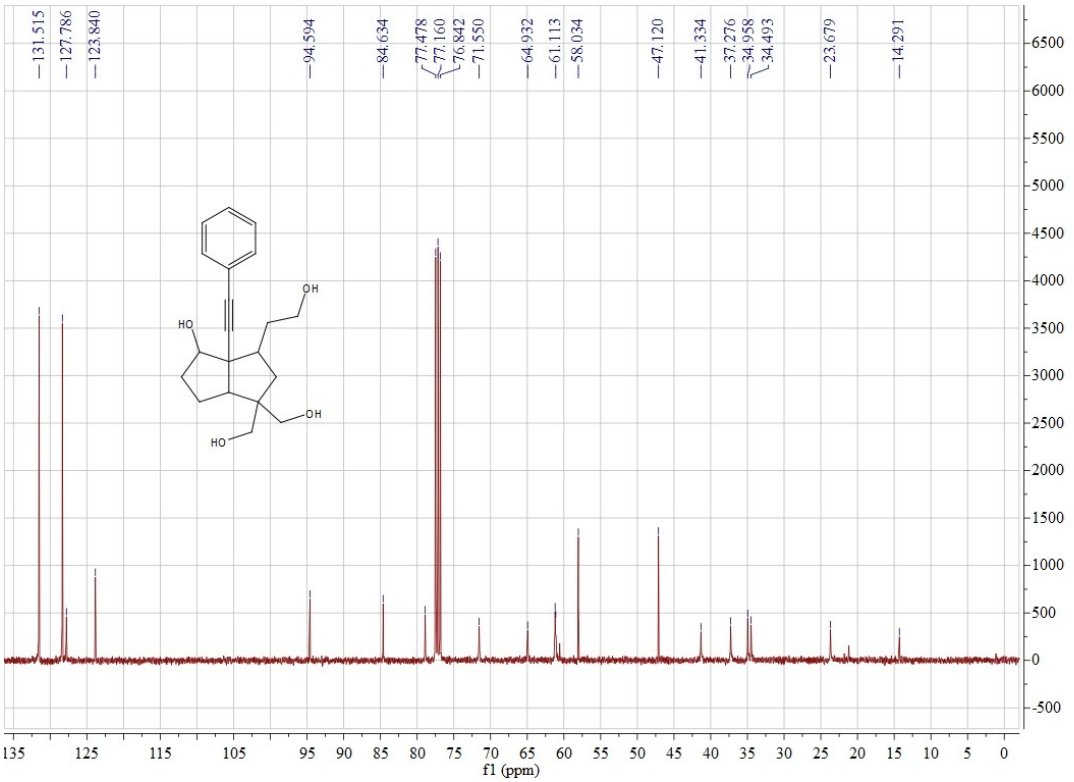
4b


7.410
7.393
7.391
7.385
7.319
7.316
7.309
7.304
7.298
7.293
7.285
7.281
7.273
3.724
3.720
3.675
3.668
3.441
3.254
3.198
2.930
2.615
2.535
2.408
2.321
1.962
1.936
1.930
1.923
1.917
1.904
1.899
1.889
1.886
1.882
1.879
1.872
1.865
1.852
1.844
1.839
2.01
3.03
6.02
0.28
1.00
7.86
2.05
O
CH3
f1 (ppm)

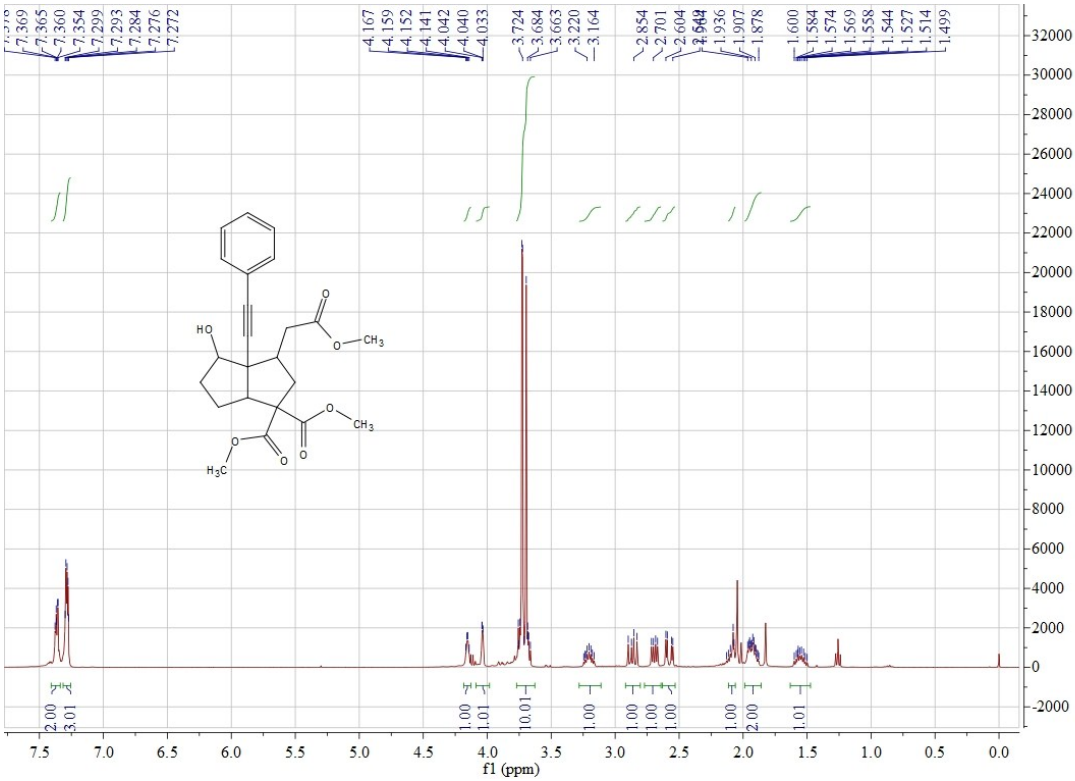

213.395
212.328
174.230
173.678
172.798
172.637
131.941
131.889
128.534
128.448
128.348
128.318
122.709
86.981
86.624
85.689
85.358
77.478
77.160
45.435
41.778
40.557
37.202
36.588
36.317
35.902
32.847
24.920
22.148
O
O
O
CH3
O
O
CH3
f1 (ppm)

4c


7.256
7.242
7.239
7.185
7.162
7.154
7.148
7.144
5.094
4.690
4.609
4.114
4.032
4.014
3.640
3.573
3.548
3.510
3.487
3.407
2.503
2.481
2.458
2.013
1.994
1.813
1.793
1.686
1.670
1.635
1.579
1.475
1.454
1.444
1.438
1.414
OH
HO
OH
HO
5.03
1.00
2.00
2.02
7.03
2.00
1.02
6.03
f1 (ppm)


131.515
127.786
123.840
94.594
84.634
77.478
77.160
76.842
71.550
64.932
61.113
58.034
47.120
41.334
37.276
34.958
34.493
23.679
14.291
HO
OH
OH
HO
f1 (ppm)

4d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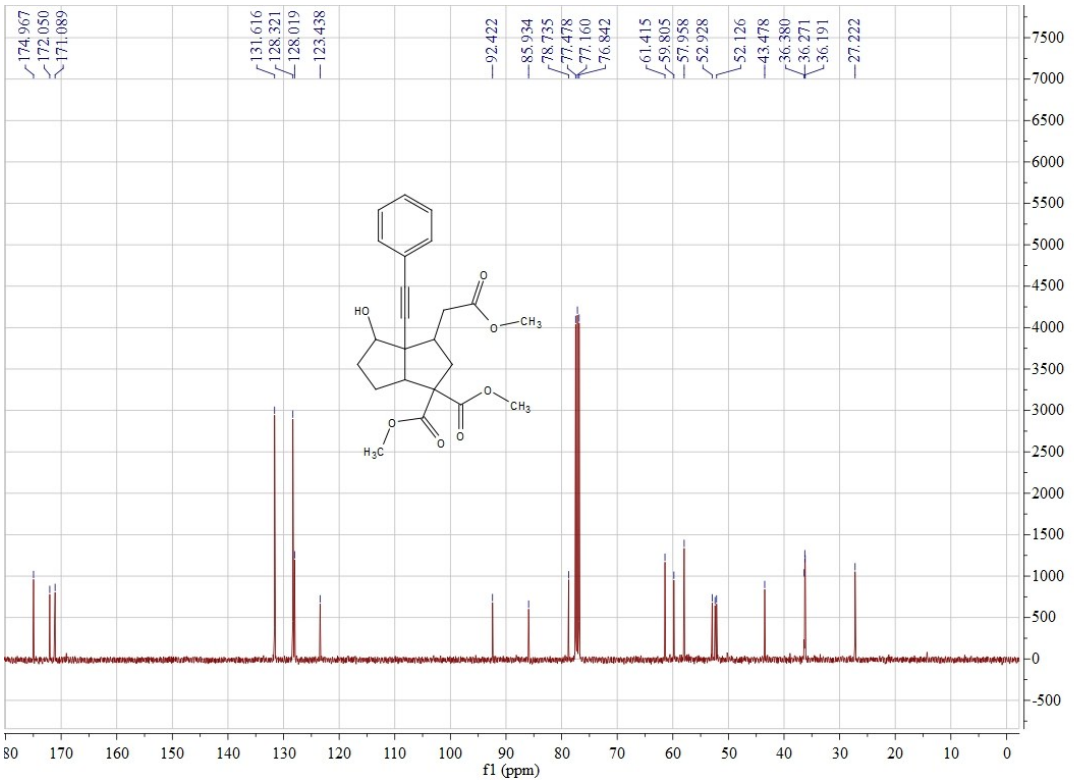
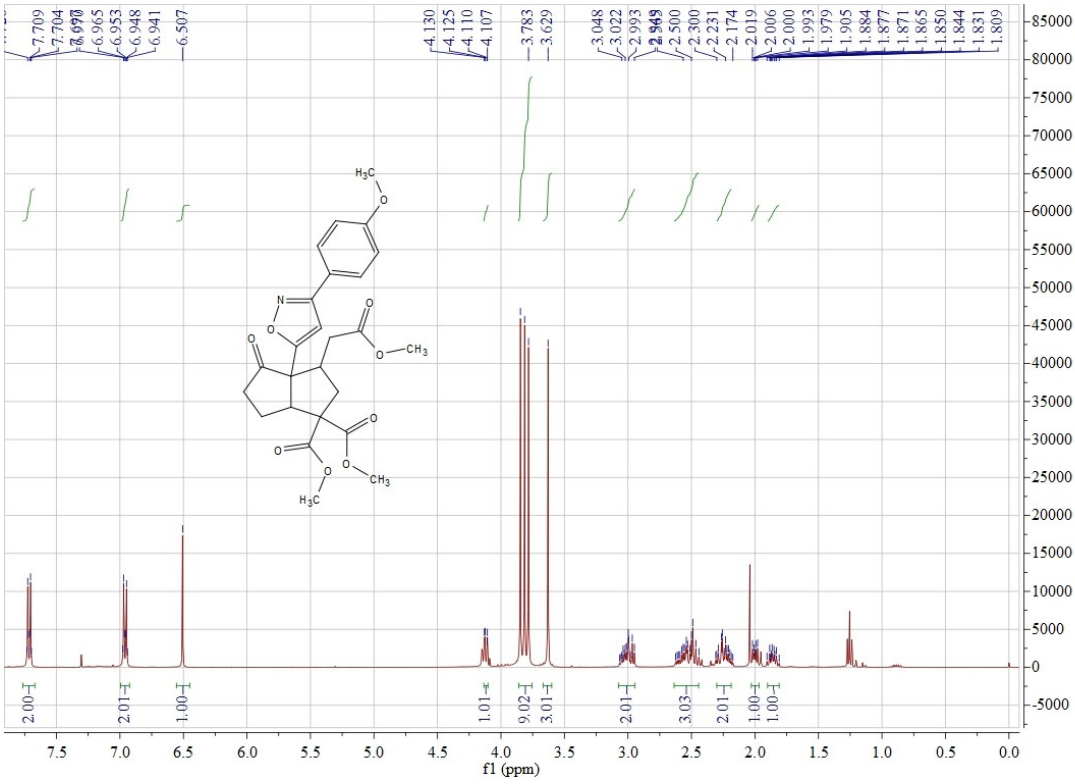
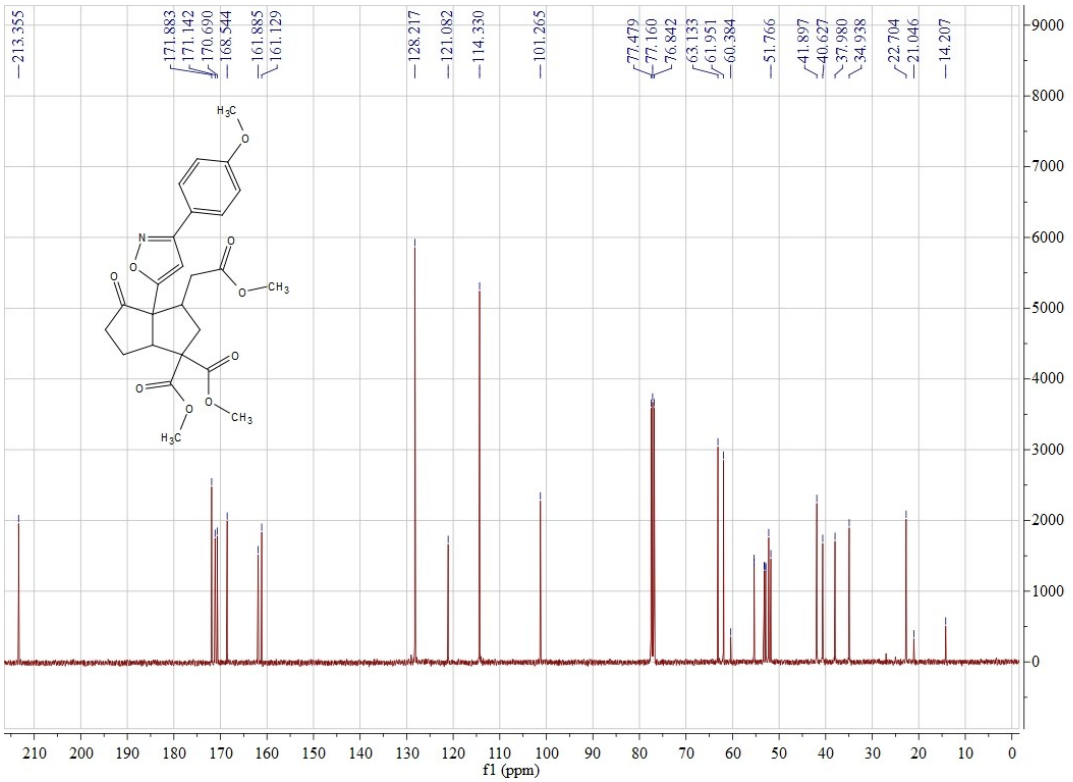
7.365
7.360
7.354
7.299
7.293
7.284
7.276
7.272
4.167
4.159
4.152
4.141
4.042
4.040
4.033
3.724
3.684
3.663
3.220
3.164
2.854
2.701
2.604
1.936
1.907
1.878
1.600
1.584
1.574
1.569
1.558
1.544
1.527
1.514
1.499
HO
CH3
CH3
H3C
2.00
3.01
1.00
1.01
10.01
1.00
1.00
1.00
1.00
1.00
2.00
1.01
f1 (ppm)

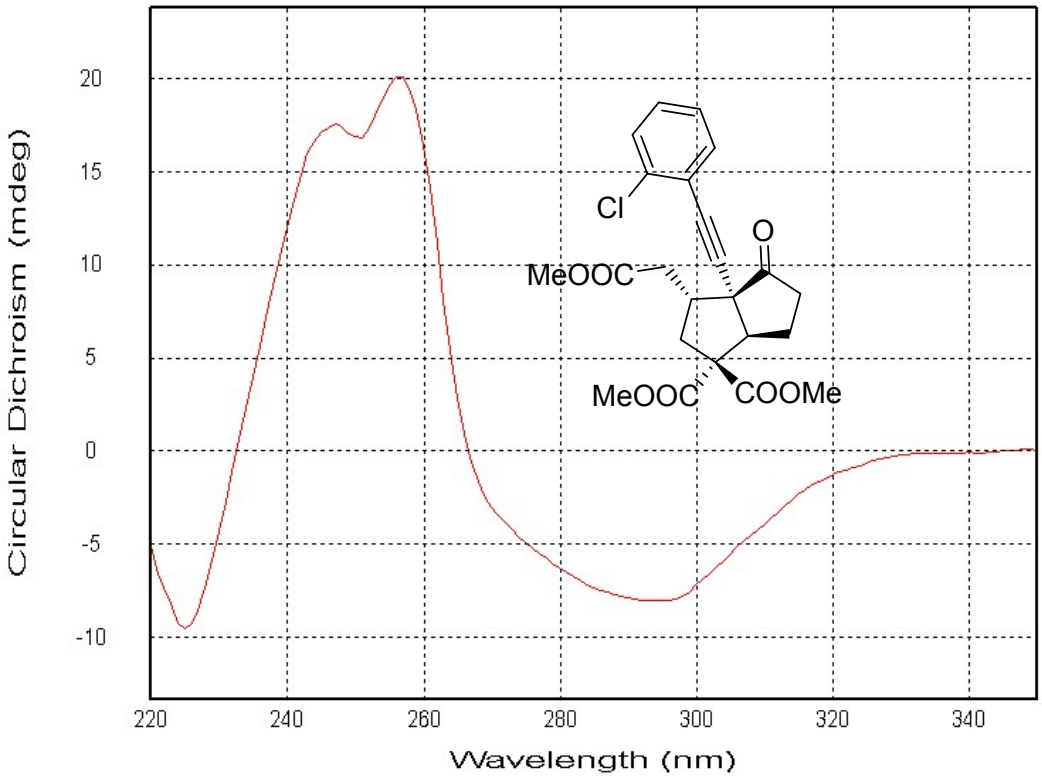

174.967
172.050
171.089
131.616
128.321
128.019
123.438
92.422
85.934
78.735
77.478
77.160
76.842
61.415
59.805
57.958
52.928
52.126
43.478
36.380
36.271
36.191
27.222
HO
O
O
CH3
O
O
CH3
O
O
H3C
f1 (ppm)

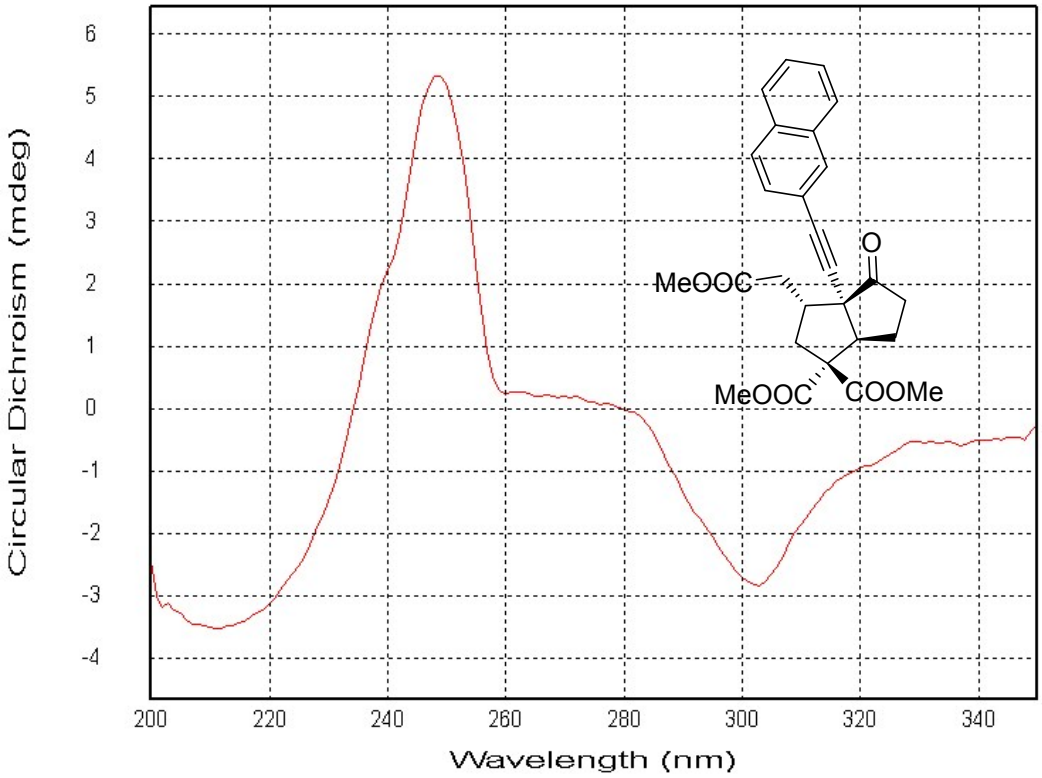
4e

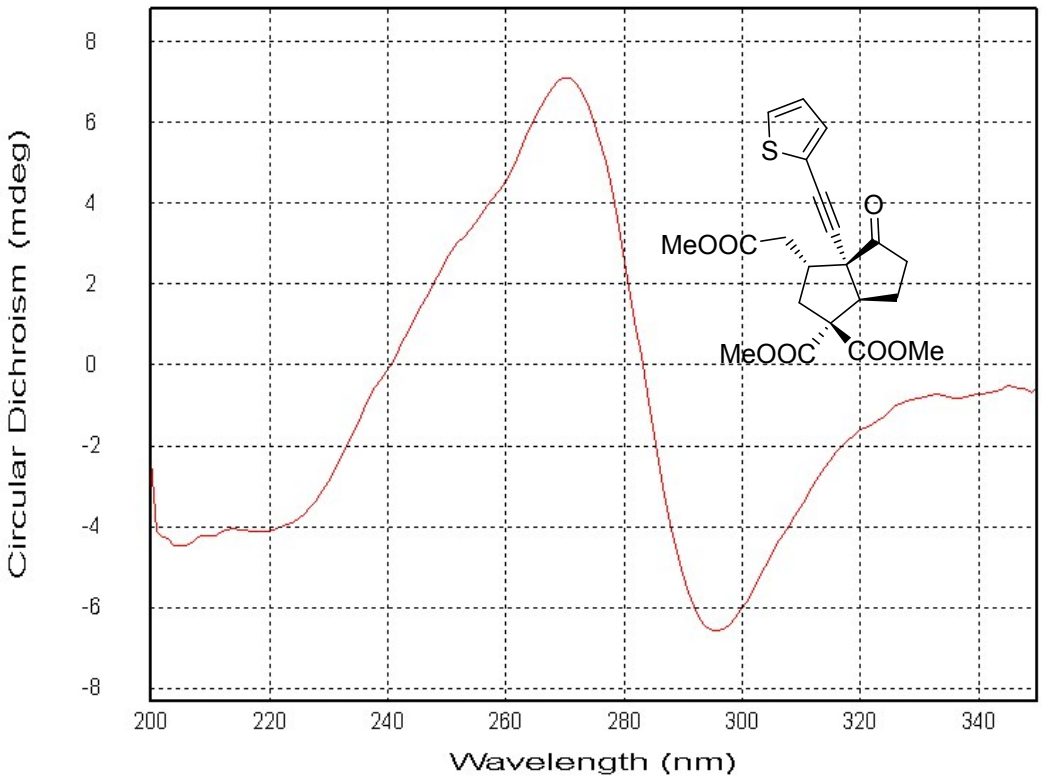

7.709
7.704
6.965
6.953
6.948
6.941
6.507
4.130
4.125
4.110
4.107
3.783
3.629
3.048
3.022
2.993
2.500
2.300
2.231
2.174
2.019
2.006
2.000
1.993
1.979
1.905
1.884
1.877
1.871
1.865
1.850
1.844
1.831
1.809
H3C
O
N
O
O
O
O
CH3
O
O
O
CH3
H3C
2.00
2.01
1.00
1.01
9.02
3.01
2.01
3.03
2.01
1.00
1.00
f1 (ppm)

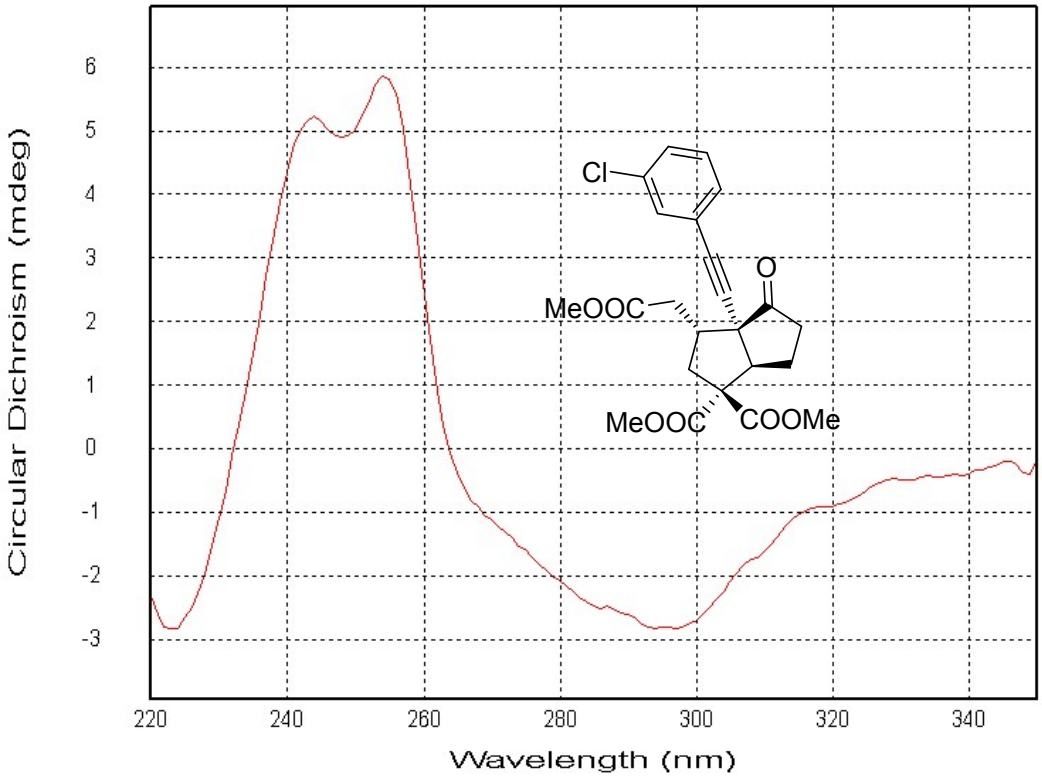


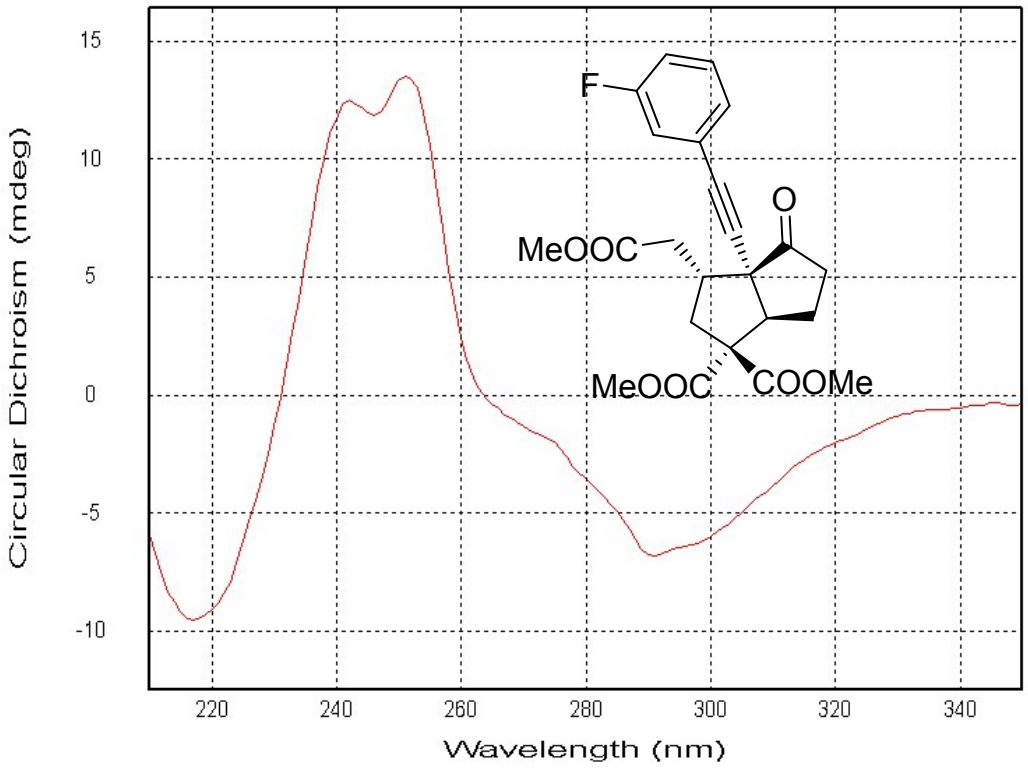
(H) Copies of the CD spectra

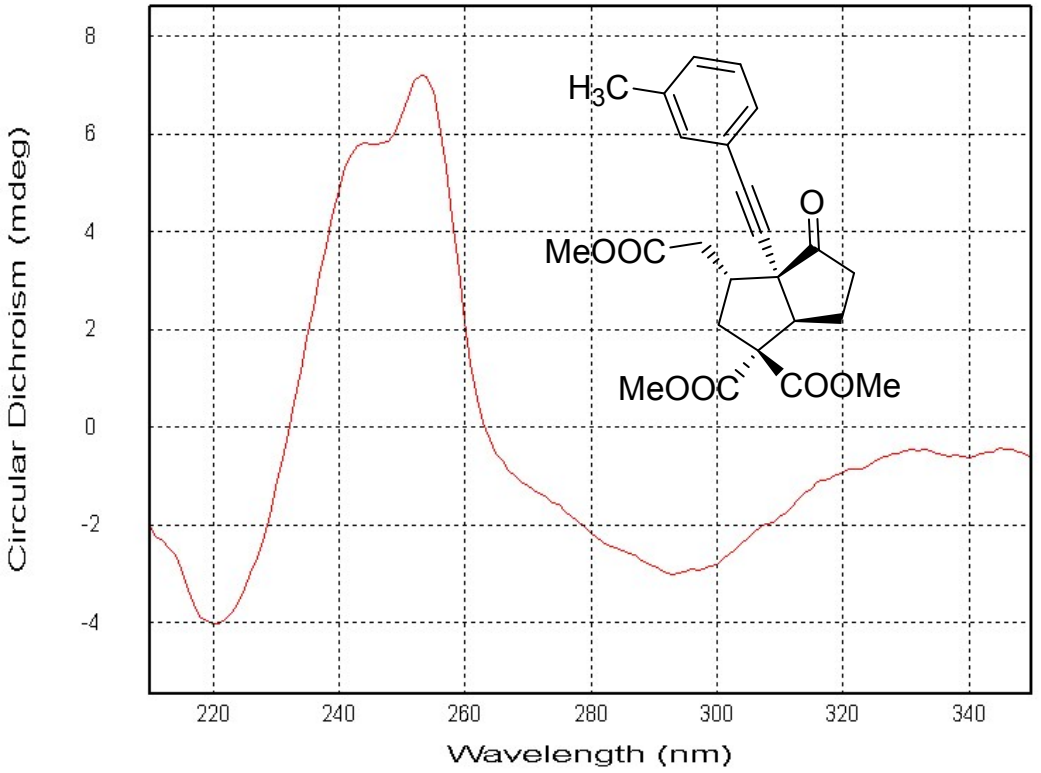


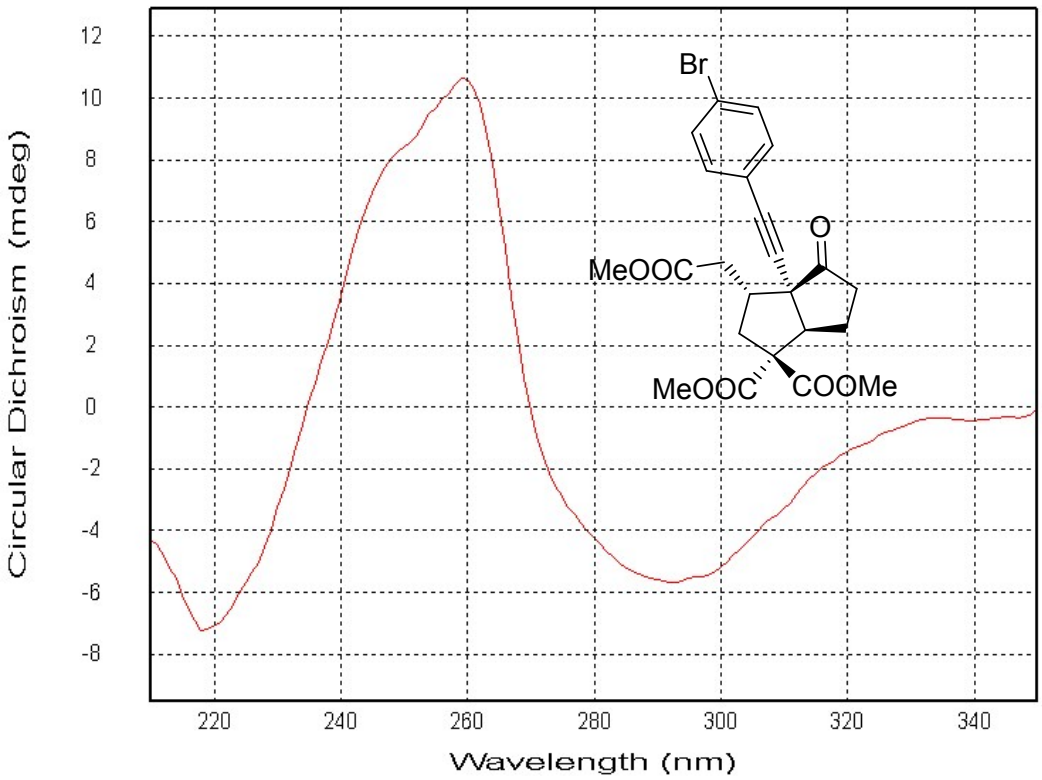

Circular Dichroism (mdeg)
6
5
4
3
2
1
0
-1
-2
-3
-4
200
220
240
260
280
300
320
340
Wavelength (nm)
O
MeOOC
MeOOC
COOMe

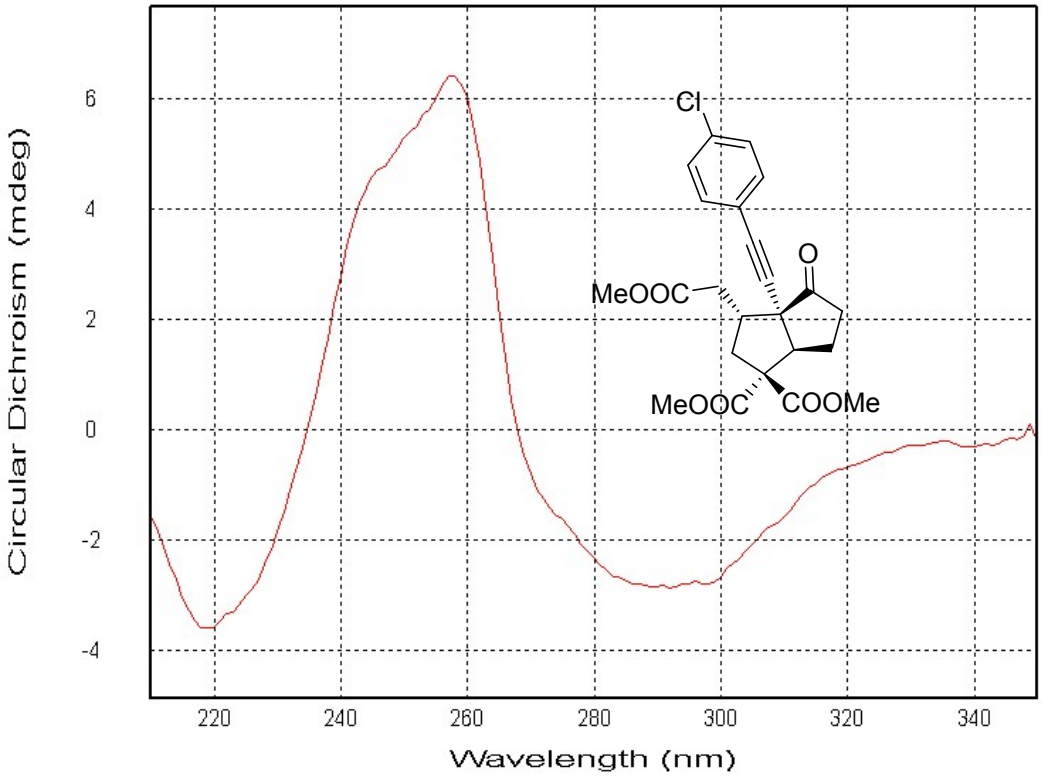

Circular Dichroism (mdeg)
8
6
4
2
0
-2
-4
-6
-8
200
220
240
260
280
300
320
340
Wavelength (nm)
S
O
MeOOC
MeOOC
COOMe

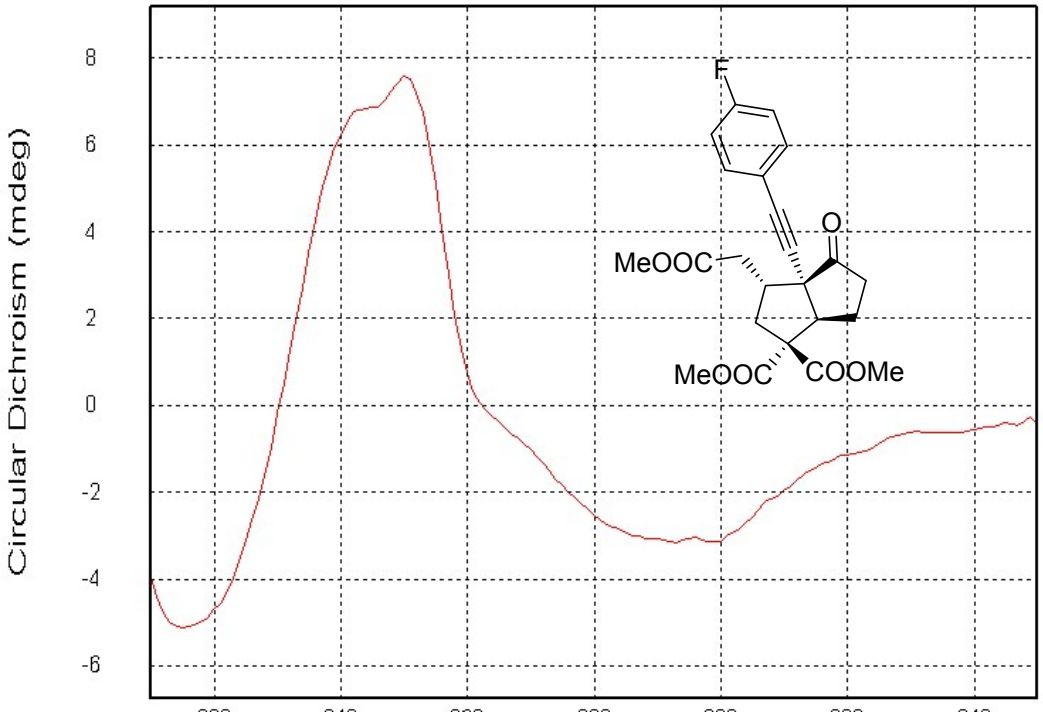

Circular Dichroism (mdeg)
6
5
4
3
2
1
0
-1
-2
-3
220
240
260
280
300
320
340
Wavelength (nm)
Cl
O
MeOOC
MeOOC
COOMe

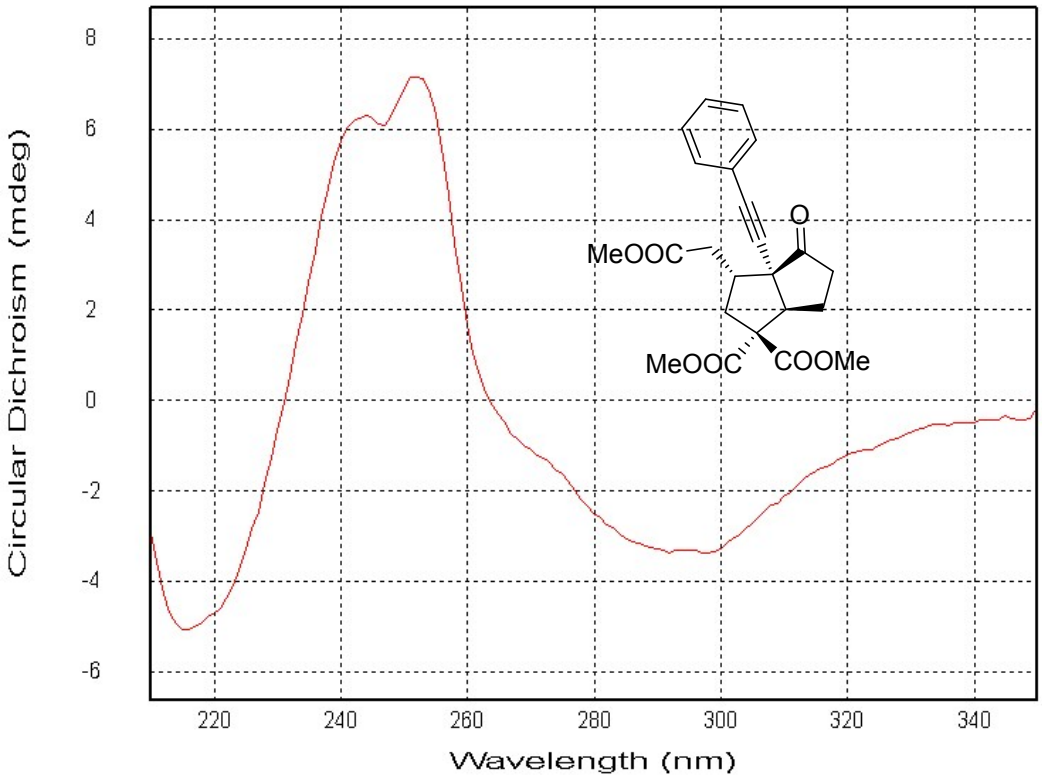

Circular Dichroism (mdeg)
15
10
5
0
-5
-10
220
240
260
280
300
320
340
Wavelength (nm)
F
O
MeOOC
MeOOC
COOMe

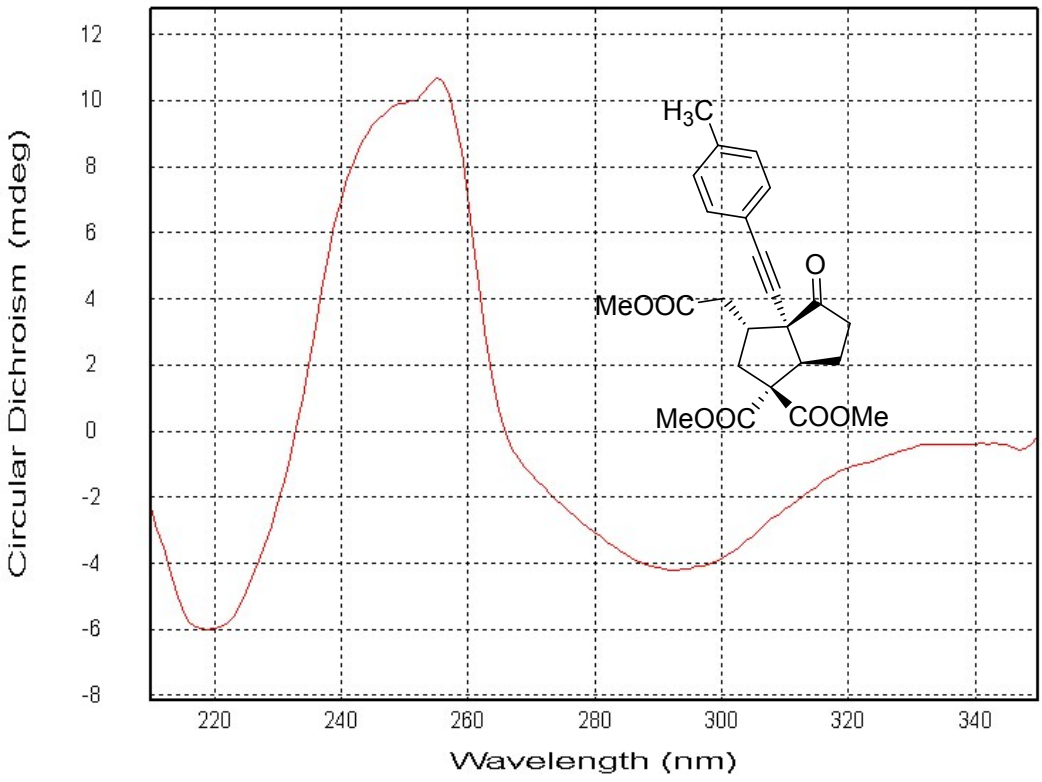

Circular Dichroism (mdeg)
8
6
4
2
0
-2
-4
220
240
260
280
300
320
340
Wavelength (nm)
H3C
O
MeOOC
MeOOC
COOMe

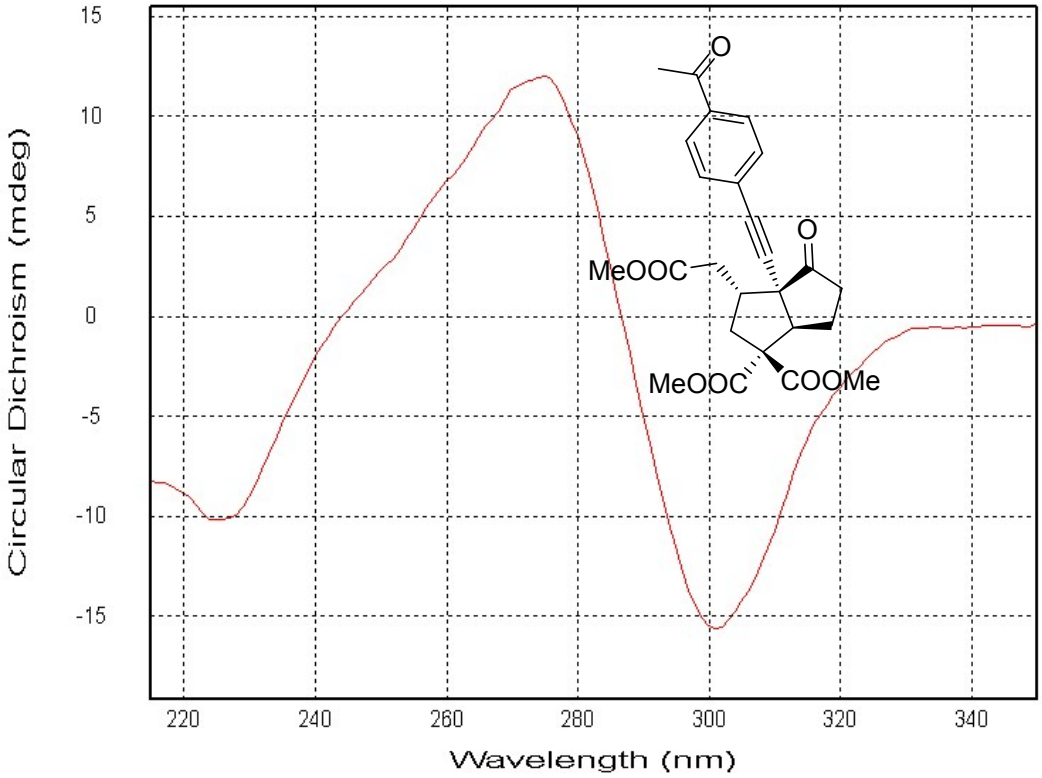

Circular Dichroism (mdeg)
12
10
8
6
4
2
0
-2
-4
-6
-8
220
240
260
280
300
320
340
Wavelength (nm)
Br
O
MeOOC
MeOOC
COOMe

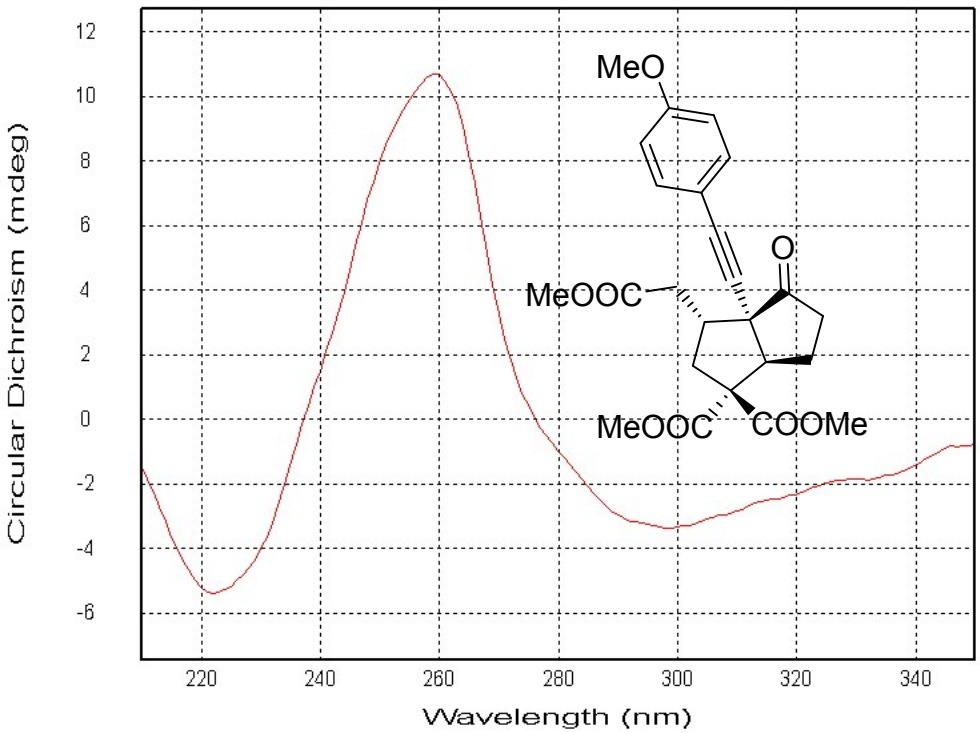

Circular Dichroism (mdeg)
6
4
2
0
-2
-4
220
240
260
280
300
320
340
Wavelength (nm)
Cl
O
MeOOC
MeOOC
COOMe

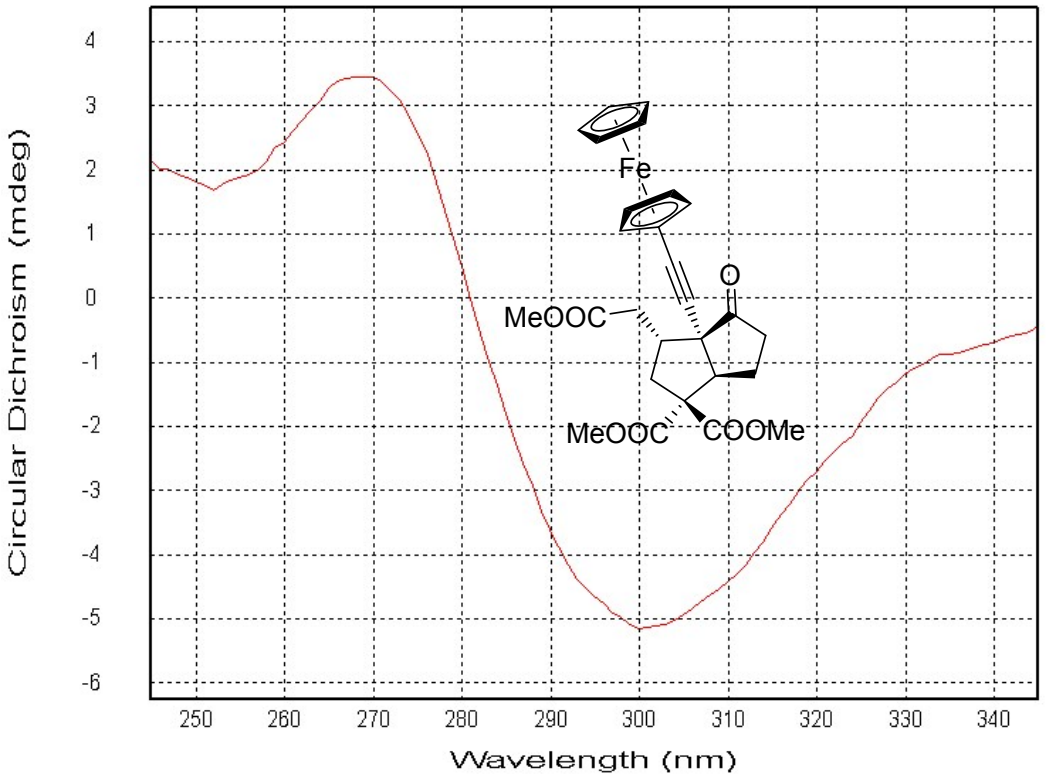

Circular Dichroism (mdeg)
8
6
4
2
0
-2
-4
-6
F
O
MeOOC
MeOOC
COOMe

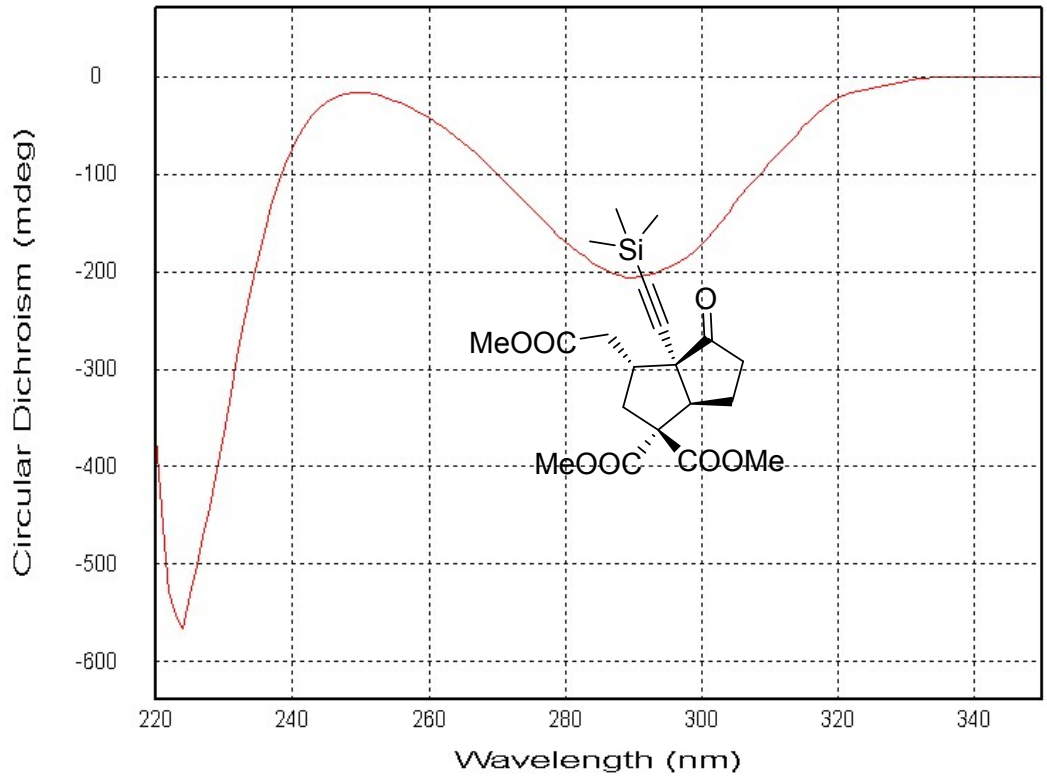

Circular Dichroism (mdeg)
8
6
4
2
0
-2
-4
-6
220
240
260
280
300
320
340
Wavelength (nm)
O
MeOOC
MeOOC
COOMe


Circular Dichroism (mdeg)
12
10
8
6
4
2
0
-2
-4
-6
-8
220
240
260
280
300
320
340
Wavelength (nm)
H3C
O
MeOOC
MeOOC
COOMe


Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
220
240
260
280
300
320
340
Wavelength (nm)
O
O
MeOOC
MeOOC
COOMe


Circular Dichroism (mdeg)
12
10
8
6
4
2
0
-2
-4
-6
220
240
260
280
300
320
340
Wavelength (nm)
MeO
O
MeOOC
MeOOC
COOMe


Circular Dichroism (mdeg)
4
3
2
1
0
-1
-2
-3
-4
-5
-6
250
260
270
280
290
300
310
320
330
340
Wavelength (nm)
Fe
O
MeOOC
MeOOC
COOMe


Circular Dichroism (mdeg)
0
-100
-200
-300
-400
-500
-600
220
240
260
280
300
320
340
Wavelength (nm)
Si
O
MeOOC
MeOOC
COOMe