Supporting information

Stereoselective Synthesis of Pentasubstituted 1,3-Dienes via Ni-Catalyzed Reductive Coupling of Unsymmetrical Internal Alkynes

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Contents

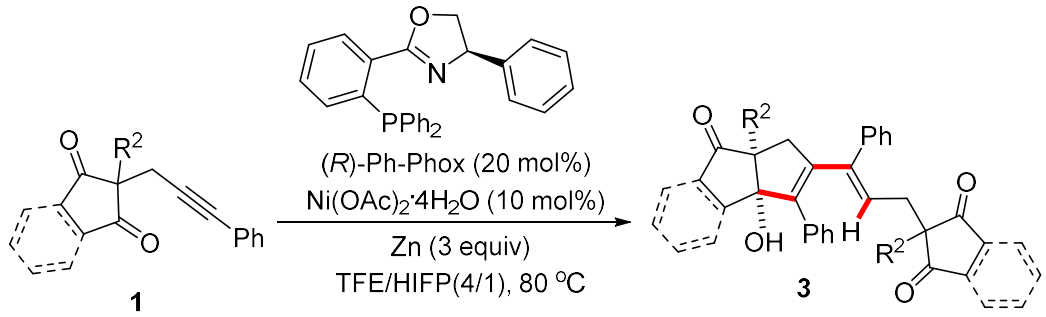
1. General Information

^{1}H and ^{13}C NMR data were recorded with Bruker ADVANCE III (400 MHz) or JNM-ECZ400S/L1 (400 MHz) spectrometers. Chemical shifts are given in ppm. The spectra are calibrated to the residual ^{1}H and ^{13}C signals of the solvents. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), septet (sept), multiplet (m), and broad (b). ^{19}F NMR spectra were recorded using $CFCl_3$ as internal standard. Gas chromatography were determined with a Varian GC 2000 gas chromatography instrument with a FID detector. High-resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer. Enantiomeric excesses were determined with a SHIMADZU LC-20ADXR system using chiral stationary phase columns (DAICEL) by comparing the samples with the corresponding racemic samples. Column and elution details were specified in each entry.

Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial suppliers (Adamas-beta®, Alfa, Aldrich and so on). All reactions dealing with air- or moisture-sensitive compounds were performed in the argon-filled glove box or by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere. Solvents were purchased in HPLC quality, degassed by purging thoroughly with nitrogen and dried over activated molecular sieves of appropriate size. More sensitive compounds were stored in a desiccator or in a glove-box if required. Reactions were monitored by thin layer chromatography (TLC) using glass 0.25 mm silica gel plates. Compounds were visualized by UV-light at 254 nm and by dipping the plates in an aqueous potassium permanganate solution followed by heating. Flash column chromatography was performed over silica gel (200-400 mesh).

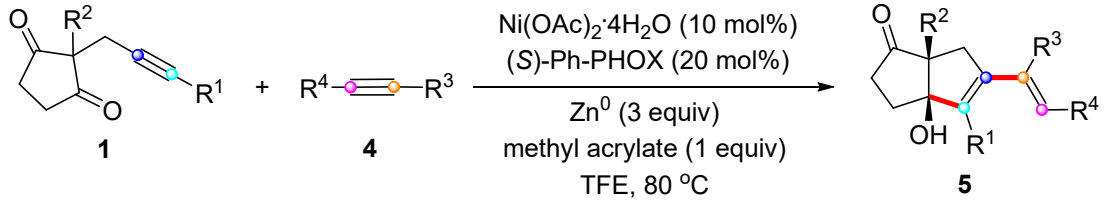
2. General Procedures

2.1 General Procedure for the Reductive Self-Coupling Reaction:



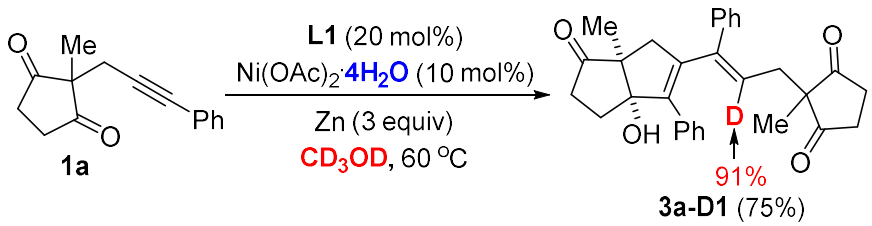
A mixture of $Ni(OAc)_2{\cdot}4H_2O$ (10 mol%), (*R*)-Ph-Phox (20 mol%), dry HFIP (0.4 mL) and dry TFE (1.6 mL) was stirred in a sealed tube at room temperature for 20 min under argon. To the resulting solution was added alkynone substrate **1** (0.2 mmol) and Zn (0.6 mmol), the reaction mixture was heated at 80 °C until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the product **3**.

2.2 General Procedure for the Reductive Cross-Coupling Reaction:

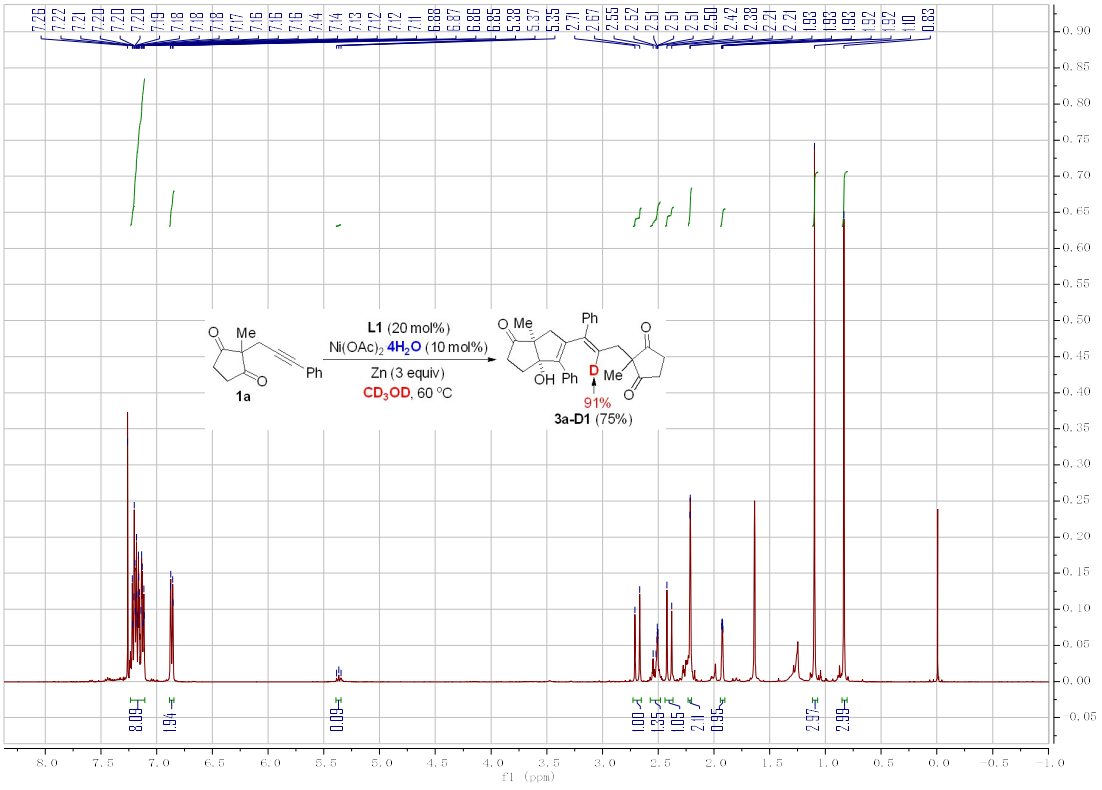


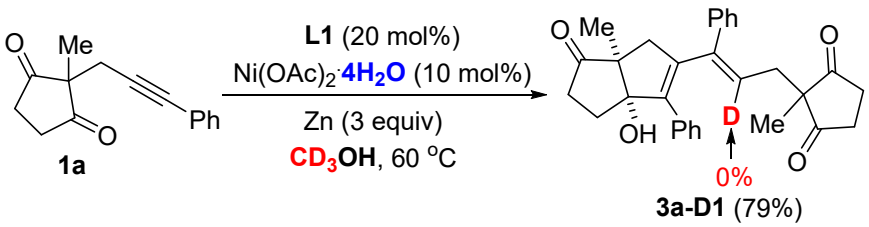
A mixture of $Ni(OAc)_2{\cdot}4H_2O$ (10 mol%), (*S*)-Ph-Phox (20 mol%), dry TFE (1 mL) was stirred in a sealed tube at room temperature for 20 min under argon. To the resulting solution was added alkynone **1** (0.2 mmol), internal alkyne **4** (0.1 mmol), methyl acrylate (0.1 mmol) and Zn (0.3 mmol), the reaction mixture was heated at 80 °C until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~4:1 (v/v) to afford the product **5**.

3. Deuterium-labelling Experiments

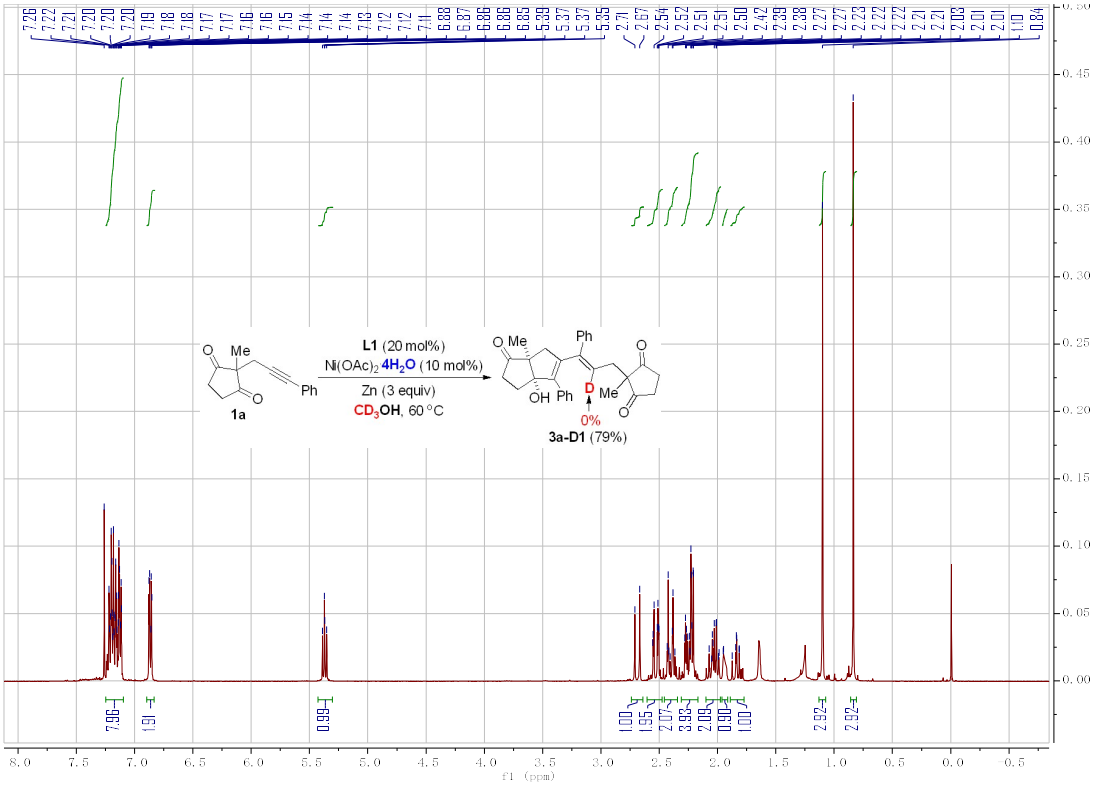


Experimental procedure: To a mixture of $Ni(OAc)_2{\cdot}4H_2O$ (0.01 mmol, 2.5 mg), **L1** (0.02 mmol, 7.2 mg), Zn (0.3 mmol, 19.6 mg) and dry CD_3OD (1 mL) in a sealed tube was added **1a** (0.1 mmol, 22.6 mg) under Argon. The reaction mixture was heated at 60 ºC for 72 hours until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **3a-D1** in 75% yield with 91% deuterium incorporation.

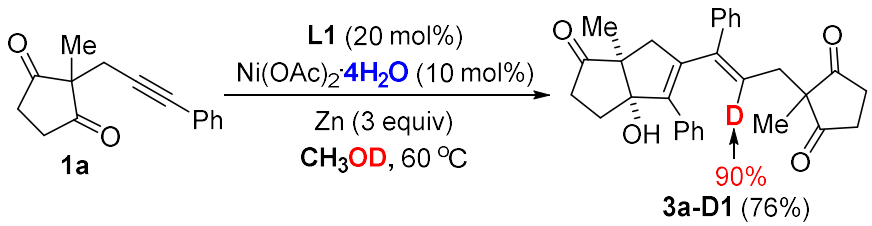




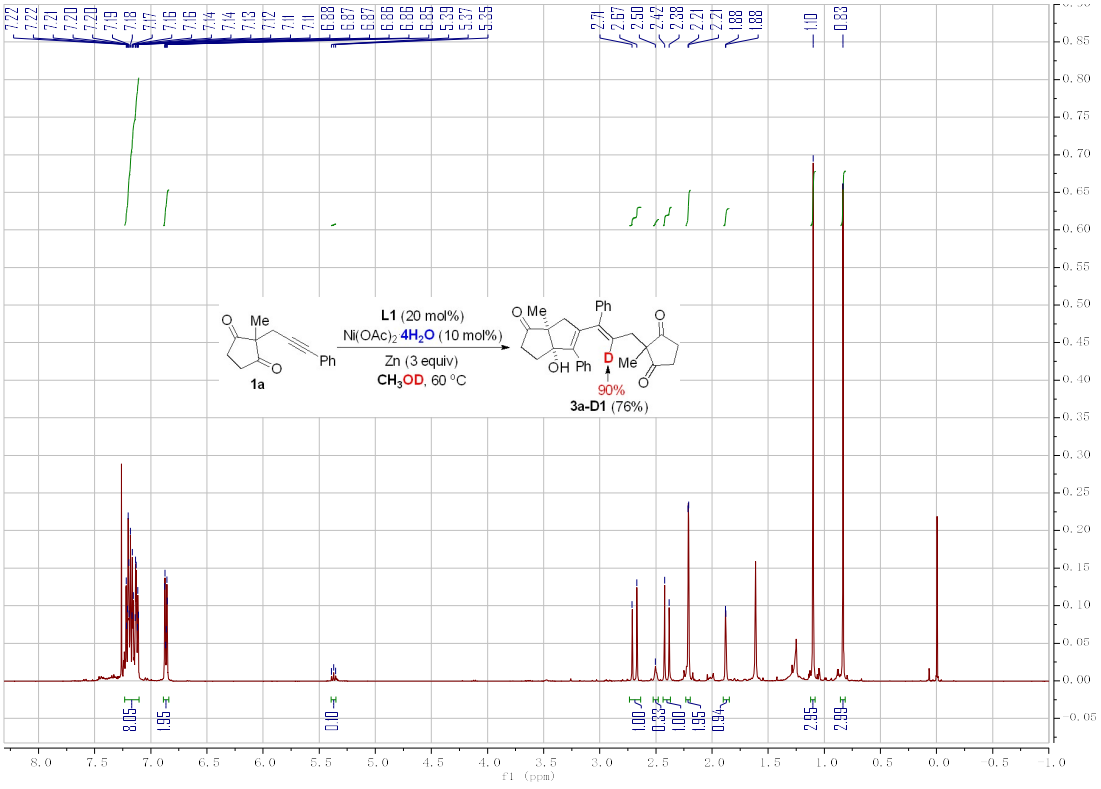
Experimental procedure: To a mixture of $Ni(OAc)_2{\cdot}4H_2O$ (0.01 mmol, 2.5 mg), **L1** (0.02 mmol, 7.2 mg), Zn (0.3 mmol, 19.6 mg) and dry CD_3OH (1 mL) in a sealed tube was added **1a** (0.1 mmol, 22.6 mg) under Argon. The reaction mixture was heated at 60 ºC for 72 hours until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **3a-D1** in 79% yield with 0% deuterium incorporation.



Conclusion: The proton was not from the methyl moiety of methanol and methanol might not act as a reducing reagent in the present reaction.

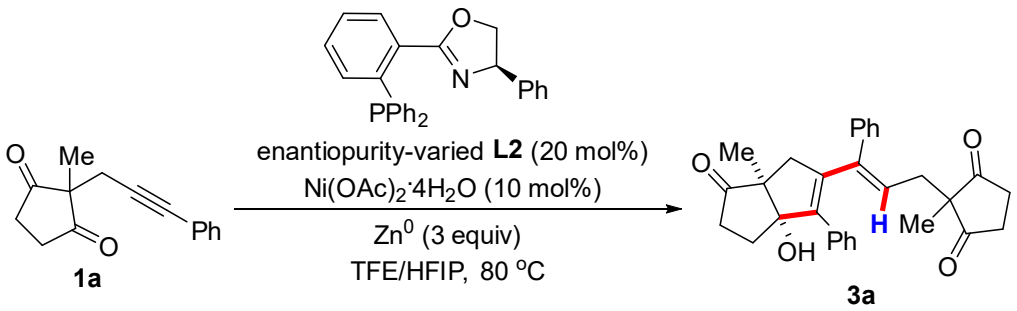


Experimental procedure: To a mixture of $Ni(OAc)_2{\cdot}4H_2O$ (0.01 mmol, 2.5 mg), **L1** (0.02 mmol, 7.2 mg), Zn (0.3 mmol, 19.6 mg) and dry CH_3OD (1 mL) in a sealed tube was added **1a** (0.1 mmol, 22.6 mg) under Argon. The reaction mixture was heated at 60 ºC for 72 hours until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **3a-D1** in 76% yield with 90% deuterium incorporation.

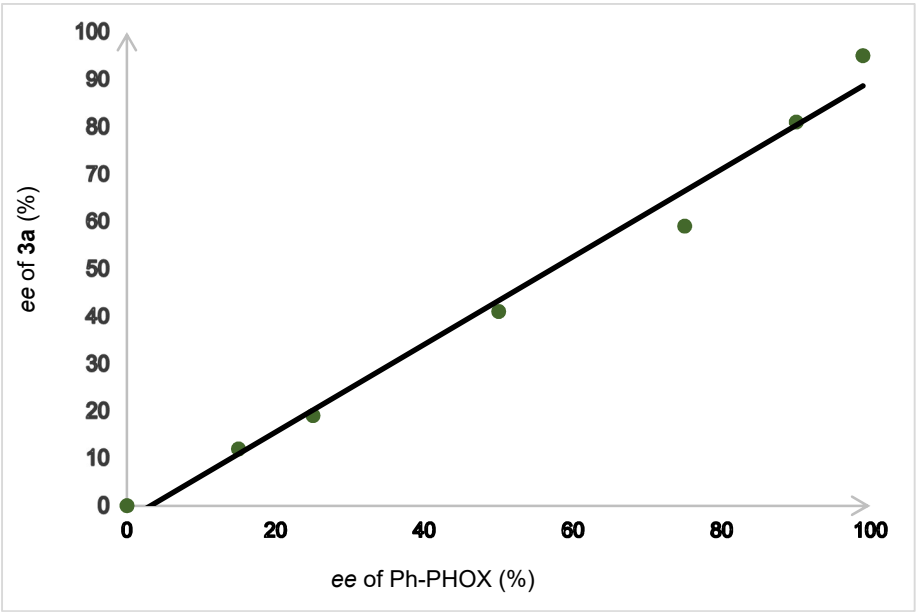


Conclusion: The proton was supplied from the hydroxyl of methanol.

4. Relationship between the ee values of the ligand and product



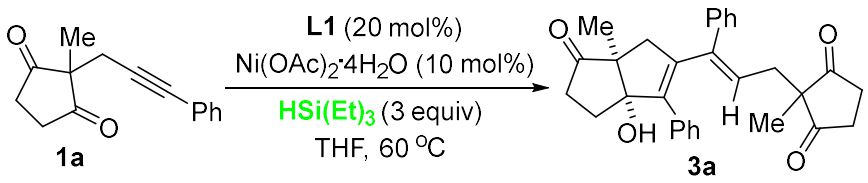
(1)	**L2** (15% ee)	**3a** (84% y, 12% ee)
(2)	**L2** (25% ee)	**3a** (85% y, 19% ee)
(3)	**L2** (50% ee)	**3a** (86% y, 41% ee)
(4)	**L2** (75% ee)	**3a** (85% y, 59% ee)
(5)	**L2** (90% ee)	**3a** (83% y, 81% ee)
(6)	**L2** (99% ee)	**3a** (85% y, 95% ee)



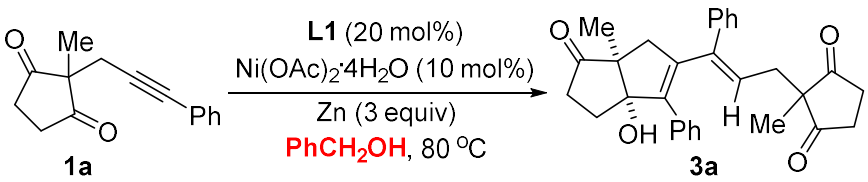
Relationship between the ee values of the ligand Ph-PHOX and product **3a**.

Conclusion: A linear relationship between the ee values of the ligand and product **3a** was observed, supporting that the reaction is catalyzed by a nickel complex bearing a single Ph-PHOX ligand.

5. Control experiments

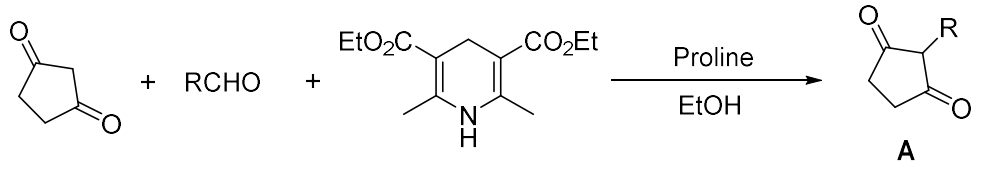


Experimental procedure: To a mixture of $Ni(OAc)_2{\cdot}4H_2O$ (0.01 mmol, 2.3 mg), **L1** (0.02 mmol, 7.8 mg) and dry THF (2 mL) in a sealed tube was added **1a** (0.1 mmol, 22.7 mg) and $HSi(Et)_3$ (0.3 mmol, 33.6 mg) under Argon. The reaction mixture was heated at 60 °C for 72 hours. After removal of the solvent under reduced pressure, redissolved in $CDCl_3$ and the crude mixture analyzed by ^1H NMR. The product **3a** was not detected, and **1a** was recovered.

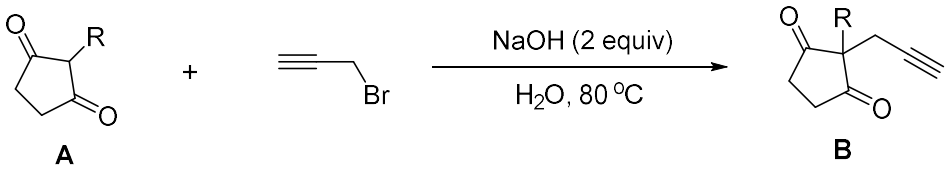


Experimental procedure: To a mixture of $Ni(OAc)_2{\cdot}4H_2O$ (0.01 mmol, 2.3 mg), **L1** (0.02 mmol, 7.8 mg), Zn (0.3 mmol, 19.8 mg) and dry BnOH (1 mL) in a sealed tube was added **1a** (0.1 mmol, 22.5 mg) under Argon. The reaction mixture was heated at 60 °C for 96 hours. Benzaldehyde was not observed by detection of the reaction mixture by GC using benzaldehyde as a reference. The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **3a** in 43% yield.

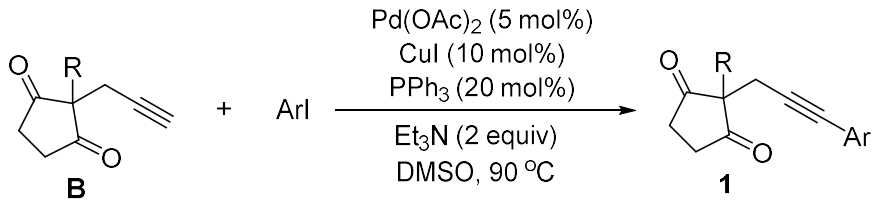
6. General procedure for the synthesis of starting materials



Proline (0.015 mmol) was added to the mixture of the aldehyde (0.9 mmol), 1,3-dione (0.3 mmol), Hantzsch ester (0.3 mmol) and EtOH (1 mL). The reaction mixture was stirred at 25 ºC for overnight. H_2O (20 mL) was added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~2:1 (v/v) to afford the products **A**.[1]



2 M aqueous NaOH (20 mmol) was added to a slurry of **A** (4 mmol) in water (10 mL). When all of the solid had dissolved, forming a bright red solution, propargyl bromide (8 mmol) was added. The mixture was stirred at 80 °C for 60 h. The mixture was cooled to room temperature, EtOAc (10 mL) was added, and the mixture was extracted with EtOAc (3 × 10 mL). The combined organic phases were dried ($MgSO_4$), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~2:1 (v/v) to afford the products **B**.[2]

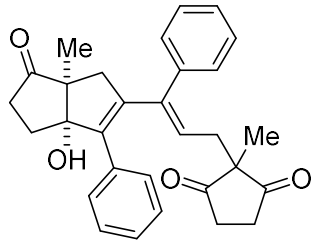


Alkyne **B** (10.0 mmol) was added to a solution of $Pd(OAc)_2$ (0.5 mmol), PPh_3 (2.00 mmol), CuI (1.0 mmol), and Et_3N (20 mmol) in anhydrous DMSO (24 mL). A solution of arylbromide (20 mmol) in anhydrous DMSO (10 mL) was added and the mixture was stirred at 90 °C. The reaction was cooled to room temperature, water (50 mL) was added,

and the mixture was extracted with Et_2O (50 mL). The organic phase was washed with 10% aqueous HCl (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:20~2:1 (v/v) to afford the alkynone products **1**.[3]

7. Characterization data of products

2-((*E*)-3-((3a*S*,6a*S*)-3a-Hydroxy-6a-methyl-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-phenylallyl)-2-methylcyclopentane-1,3-dione (**3a**)



Chemical Formula: $C_{30}H_{30}O_4$
Exact Mass: 454.2144

3a was prepared according to general procedure 2.1 using **1a** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3a** as white solid (87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.09 (m, 8H), 6.89-6.81 (m, 2H), 5.36 (dd, *J* = 7.9, 6.8 Hz, 1H), 2.68 (d, *J* = 16.9 Hz, 1H), 2.57-2.46 (m, 2H), 2.44-2.36 (m, 2H), 2.30-2.17 (m, 4H), 2.08 (s, 1H), 2.06-1.97 (m, 2H), 1.88-1.78 (m, 1H), 1.09 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 215.7, 215.3, 144.4, 141.2, 140.8, 137.5, 135.7, 129.0, 129.0, 128.3, 128.2, 127.3, 127.1, 126.2, 92.5, 56.6, 56.2, 44.6, 36.7, 35.1, 34.9, 34.4, 29.2, 18.4, 15.5; HRMS: (ESI) calcd for $C_{30}H_{31}O_4^+$[M+H]$^+$ 455.2217; found 455.2222.

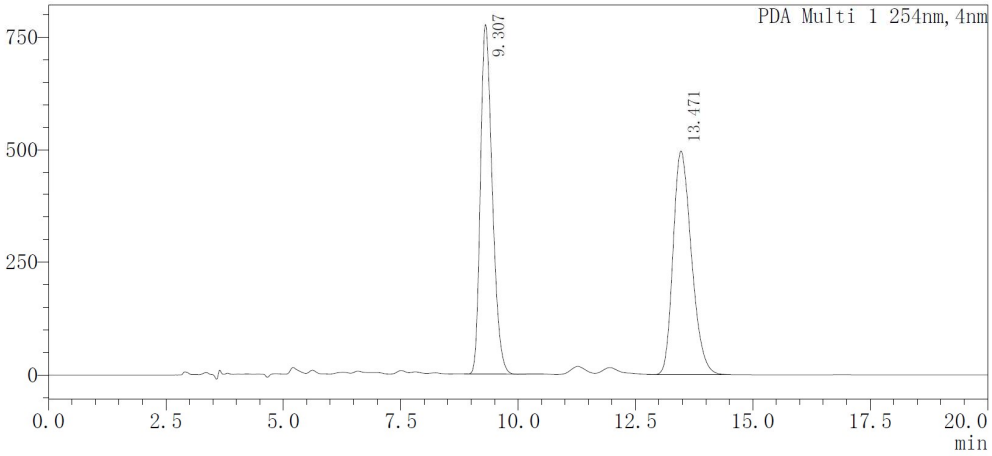
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 9 min (major), 13 min (minor).

Optical Rotation: $[\alpha]_D^{23}$ -42.6 (c 1.36, ^{i}PrOH) for 95%ee.

Absolute stereochemistry was determined through X-ray crystal diffraction study of **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

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2	13.471	13479348	496410	0.000		M	
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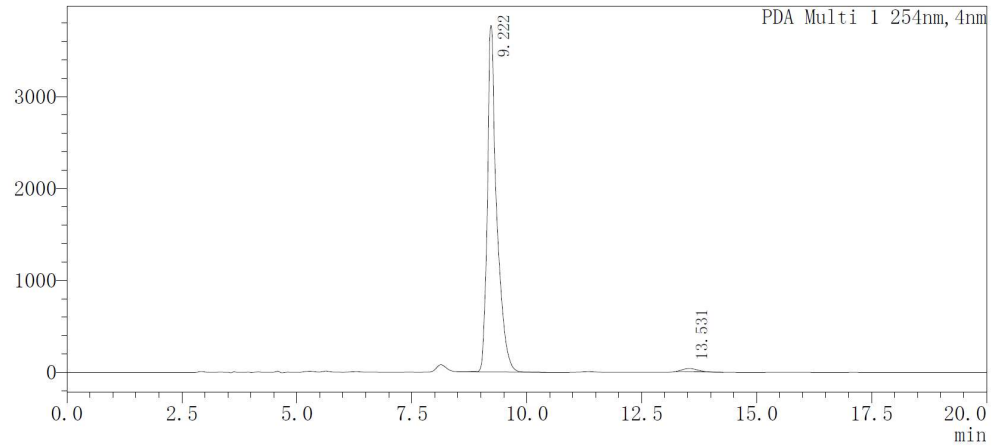
peak number ↑ retention time ↑ area ↑ height ↑

〈色谱图〉 ← HPLC chromatogram

mAU



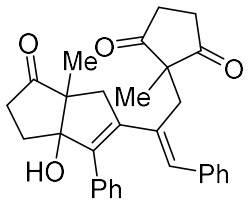
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.222	53712387	3771947	0.000		M	
2	13.531	783339	34227	0.000		M	
总计		54495726	3806174				

peak number ↑ retention time ↑ area ↑ height ↑

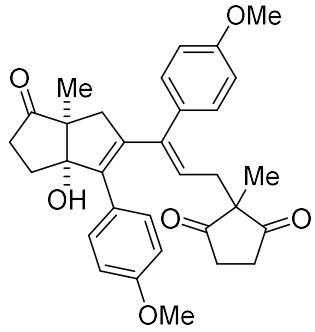
(*E*)-2-(2-(3a-Hydroxy-6a-methyl-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-phenylallyl)-2-methylcyclopentane-1,3-dione (**3a'**)



Chemical Formula: $C_{30}H_{30}O_4$
Exact Mass: 454.2144

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.50 (m, 1H), 7.48-7.29 (m, 5H), 7.26-7.20 (m, 2H), 7.14 (d, *J* = 7.4 Hz, 2H), 6.39 (s, 1H), 2.93 (d, *J* = 14.9 Hz, 1H), 2.64-2.56 (m, 2H), 2.55-2.51 (m, 1H), 2.49-2.30 (m, 7H), 2.10-2.01 (m, 1H), 1.42 (s, 1H), 1.00 (s, 3H), 0.92 (s, 3H); 219.8, 217.1, 215.6, 143.1, 137.5, 136.2, 134.3, 131.4, 130.8, 129.6, 129.4, 128.7, 128.5, 127.9, 127.4, 79.9, 55.1, 53.9, 36.2, 35.1, 34.7, 34.6, 34.2, 33.8, 22.8, 14.7; ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 215.7, 215.3, 144.4, 141.2, 140.8, 137.5, 135.7, 129.0, 129.0, 128.3, 128.2, 127.3, 127.1, 126.2, 92.5, 56.6, 56.2, 44.6, 36.7, 35.1, 34.9, 34.4, 29.2, 18.4, 15.5; HRMS: (ESI) calcd for $C_{30}H_{30}N_aO_4^+$[M+Na]$^+$ 477.2036; found 477.2046.

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(4-methoxyphenyl)allyl)-2-methylcyclopentane-1,3-dione (**3b**)



Chemical Formula: $C_{32}H_{34}O_6$
Exact Mass: 514.2355

3b was prepared according to general procedure 2.1 using **1b** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3b** as white solid (56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.04 (m, 2H), 6.80- 6.70 (m, 6H), 5.30 (dd, *J* = 8.0, 6.6 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.66 (d, *J* = 16.9 Hz, 1H), 2.59-2.50 (m, 2H), 2.40-2.33 (m, 2H), 2.32-2.20 (m, 4H), 2.07-1.93 (m, 3H), 1.89-1.78 (m, 1H), 1.09 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.6, 215.7, 215.2, 158.6, 158.5, 144.2, 140.4, 140.2, 130.0, 129.9, 129.7, 127.7, 125.3, 113.6, 113.5, 92.3, 56.5, 56.0, 55.2, 55.1, 44.5, 36.5, 35.0, 34.8, 34.5, 29.1, 18.4, 15.4; HRMS: (ESI) calcd for $C_{32}H_{34}NaO_6^+$[M+Na]$^+$ 537.2248; found 537.2243.

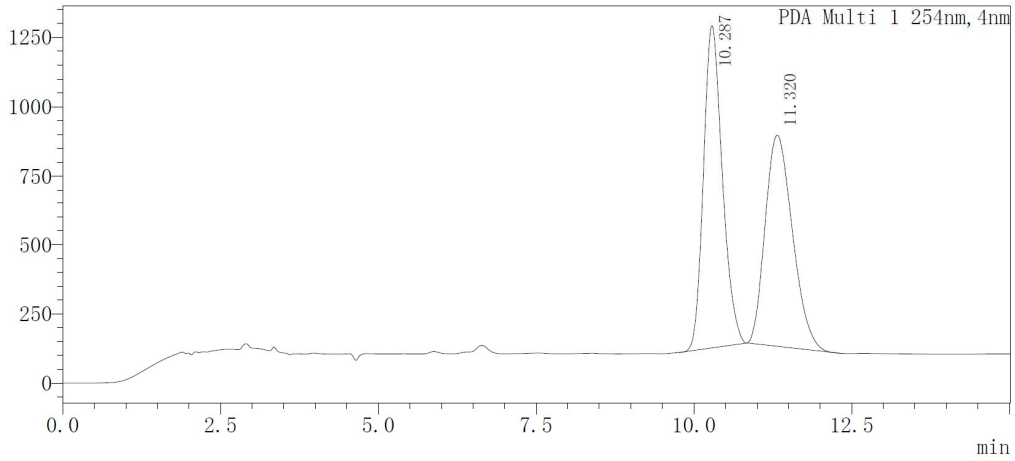
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 10 min (major), 11 min (minor).

Optical Rotation: $[\alpha]_D^{24}$ -73.0 (c 1.2, ^{i}PrOH) for 84%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

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2	11.320	22983710	765021	0.000		M	
总计		47237299	1929071				

peak number

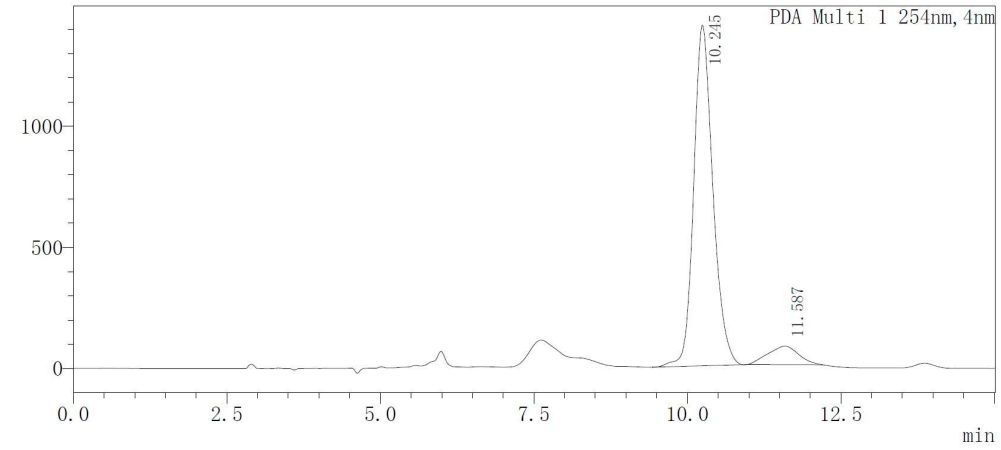
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.245	30631184	1406810	0.000		M	
2	11.587	2676344	76472	0.000		M	
总计		33307528	1483282				

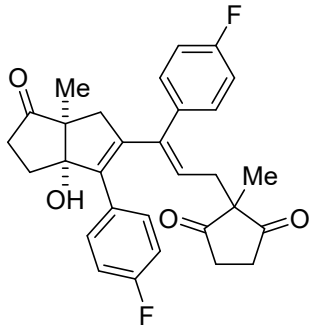
peak number

retention time

area

height

2-((*E*)-3-(4-Fluorophenyl)-3-((*3aS,6aS*)-3-(4-fluorophenyl)-3a-hydroxy-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3c**)



Chemical Formula: $C_{30}H_{28}F_2O_4$
Exact Mass: 490.1956

3c was prepared according to general procedure 2.1 using **1c** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3c** as white solid (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02-6.96 (m, 2H), 6.88-6.74 (m, 6H), 5.45 (t, *J* = 7.4 Hz, 1H), 2.77 (d, *J* = 16.9 Hz, 1H), 2.69-2.57 (m, 2H), 2.51-2.35 (m, 4H), 2.20 (d, *J* = 7.4 Hz, 2H), 2.03-1.92 (m, 3H), 1.88-1.79 (m, 1H), 1.12 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 215.2, 214.9, 163.0 (d, *J* = 17.4 Hz), 160.5 (d, *J* = 17.6 Hz), 144.1, 140.5, 139.7, 133.3 (d, *J* = 3.5 Hz), 131.3 (d, *J* = 3.6 Hz), 130.6 (d, *J* = 8.0 Hz), 130.5 (d, *J* = 7.9 Hz), 126.9, 115.1 (d, *J* = 4.9 Hz), 114.8 (d, *J* = 4.8 Hz), 92.3, 56.4, 55.9, 44.4, 36.4, 34.9, 34.8, 34.0, 29.2, 18.3, 15.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5, -114.7; HRMS: (ESI) calcd for $C_{30}H_{28}F_2NaO_4^+$[M+Na]$^+$ 513.1848; found 513.1841.

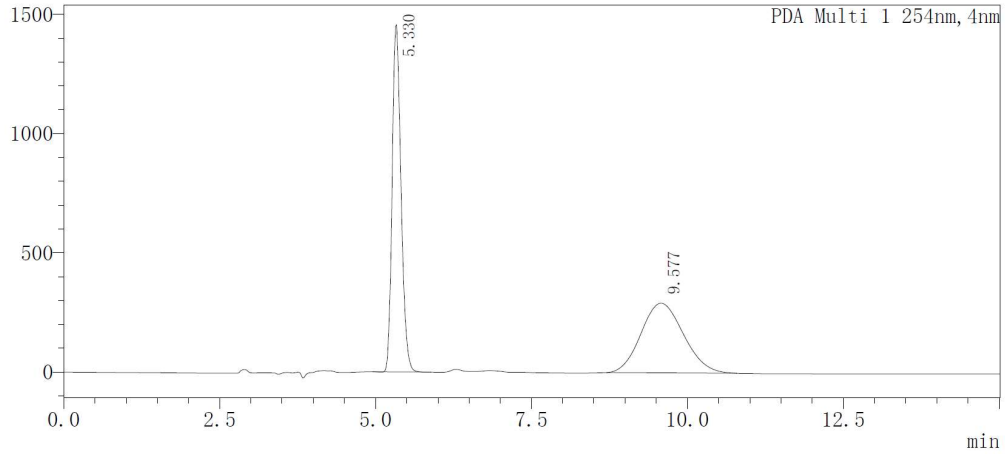
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 5 min (major), 9 min (minor).

Optical Rotation: $[\alpha]_D^{25}$ -70.5 (c 1.8, ^{i}PrOH) for 95%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.330	14349805	1456259	0.000		M	
2	9.577	13836867	292006	0.000		M	
总计		28186672	1748265				

peak number

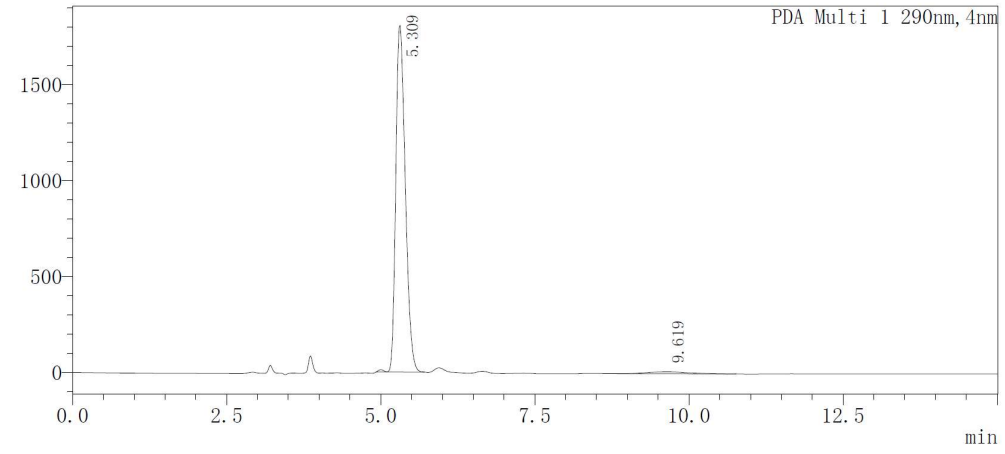
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 290nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.309	19385064	1806934	0.000		M	
2	9.619	484932	10079	0.000		M	
总计		19869996	1817012				

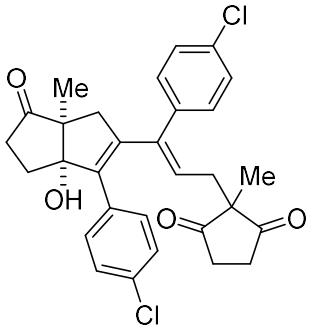
retention time

peak number

area

height

2-((*E*)-3-(4-Chlorophenyl)-3-((*3aS,6aS*)-3-(4-chlorophenyl)-3a-hydroxy-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3d**)



Chemical Formula: $C_{30}H_{28}Cl_2O_4$
Exact Mass: 522.1365

3d was prepared according to general procedure 2.1 using **1d** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3d** as white solid (79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.9 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.58 (dd, *J* = 8.2, 6.8 Hz, 1H), 2.83 (d, *J* = 17.1 Hz, 1H), 2.77-2.67 (m, 2H), 2.55-2.40 (m, 4H), 2.24-2.12 (m, 2H), 2.03-1.84 (m, 4H), 1.14 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.4, 214.9, 214.6, 144.9, 142.1, 140.5, 138.5, 131.9, 131.7, 129.9, 129.6, 129.4, 118.4, 111.2, 110.9, 92.5, 56.2, 56.1, 44.5, 36.2, 34.9, 34.8, 33.3, 29.4, 19.1, 15.1; HRMS: (ESI) calcd for $C_{30}H_{29}Cl_2O_4^+$[M+H]$^+$ 523.1437; found 523.1434.

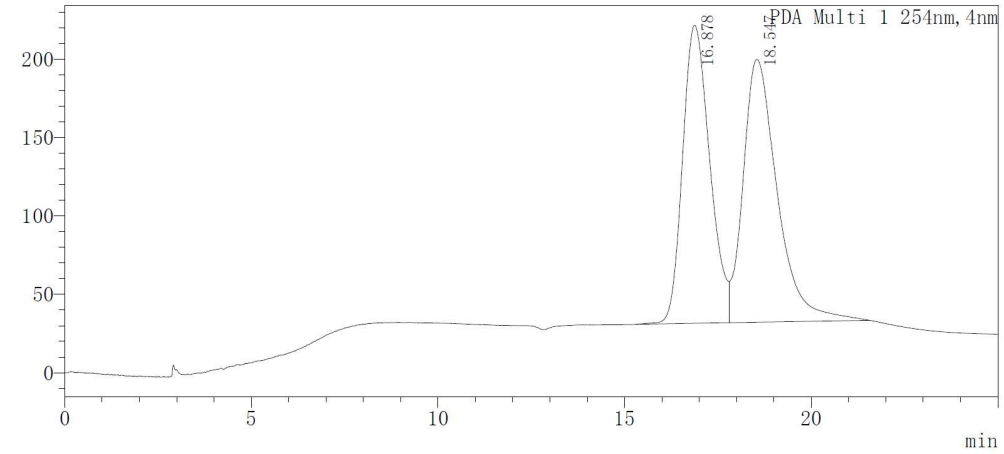
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 93/7 as eluent, 254 nm, 1 mL/min. tR = 16 min (minor), 18 min (major).

Optical Rotation: $[\alpha]_D^{26}$ -69.1 (c 1.7, ^{i}PrOH) for 97%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	16.878	9632870	189945	0.000		M	
2	18.547	10644717	167593	0.000		V M	
总计		20277587	357538				

peak number

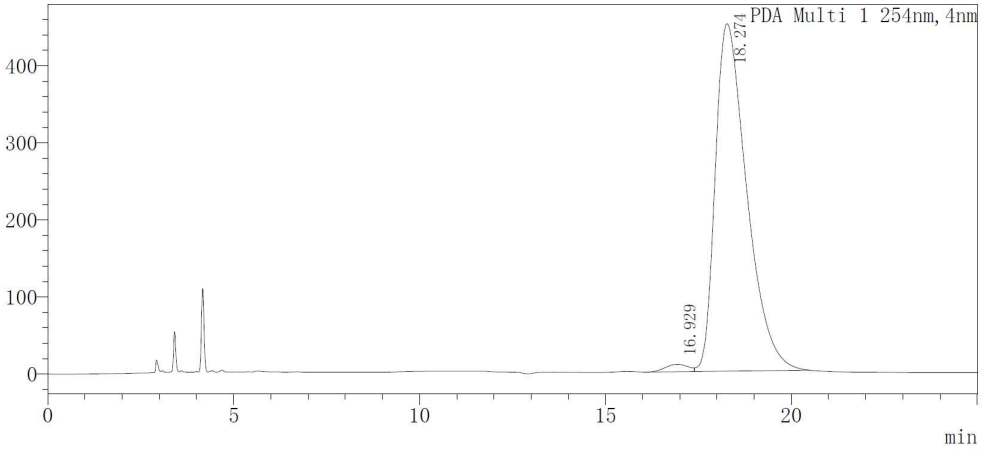
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	16.929	415793	9676	0.000		M	
2	18.274	26577318	450756	0.000		V M	
总计		26993110	460432				

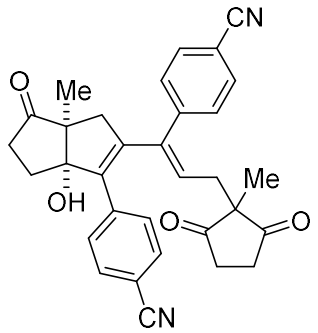
peak number

retention time

area

height

4-((*3aS,6aS*)-2-((*E*)-1-(4-Cyanophenyl)-3-(1-methyl-2,5-dioxocyclopentyl)prop-1-en-1-yl)-6a-hydroxy-3a-methyl-4-oxo-3,3a,4,5,6,6a-hexahydropentalen-1-yl)benzonitrile (**3e**)



Chemical Formula: $C_{32}H_{28}N_2O_4$
Exact Mass: 504.2049

3e was prepared according to general procedure 2.1 using **1e** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3e** as white solid (85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.9 Hz, 2H), 7.43 (d, *J* = 6.9 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 5.58 (dd, *J* = 8.2, 6.8 Hz, 1H), 2.83 (d, *J* = 17.1 Hz, 1H), 2.78-2.63 (m, 2H), 2.54-2.41 (m, 4H), 2.25-2.12 (m, 2H), 2.01-1.84 (m, 4H), 1.14 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.4, 214.8, 214.6, 144.9, 142.1, 140.5, 140.3, 138.5, 131.9, 131.7, 129.9, 129.6, 129.4, 118.4, 118.3, 111.2, 110.9, 92.5, 56.2, 56.1, 44.5, 36.2, 34.9, 34.8, 33.3, 29.4, 19.1, 15.1; HRMS: (ESI) calcd for $C_{32}H_{28}N_2NaO_4^+$[M+Na]$^+$ 527.1941; found 527.1930.

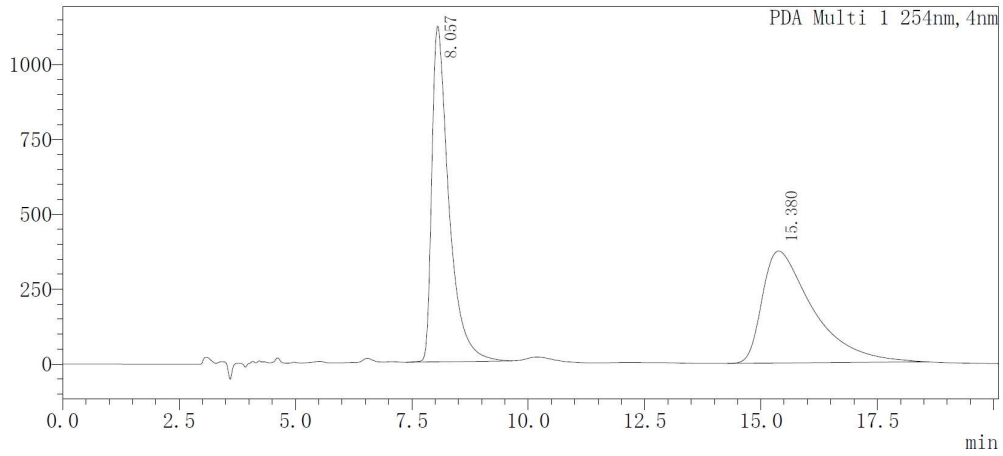
The enantiomeric purity was established by HPLC analysis using a chiral column: ID-H column, 30 °C, *n*-Hexane/*i*-Propanol = 60/40 as eluent, 254 nm, 1 mL/min. tR = 8 min (major), 15 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ -76.3 (c 1.7, ^{i}PrOH) for 93%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.057	28676491	1121665	0.000		M	
2	15.380	28359779	373879	0.000		M	
总计		57036270	1495544				

peak number

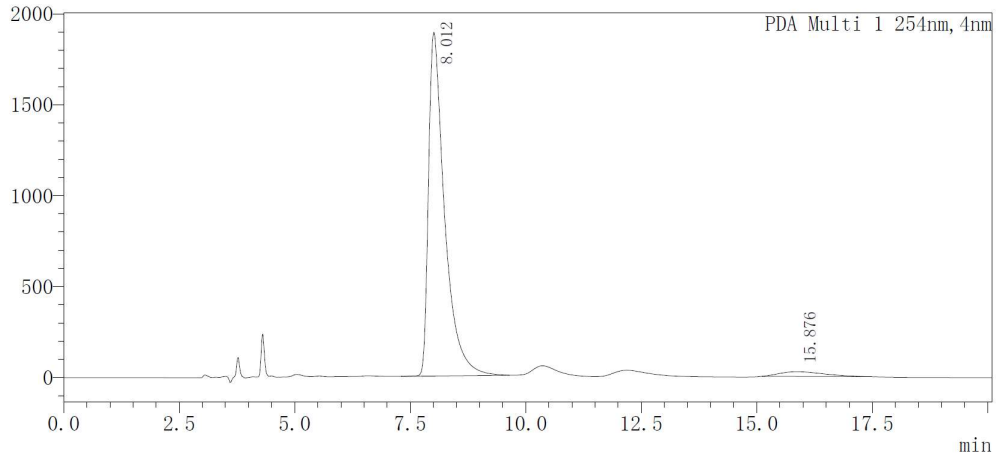
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.012	45737226	1890703	0.000		M	
2	15.876	1738345	26028	0.000		M	
总计		47475571	1916731				

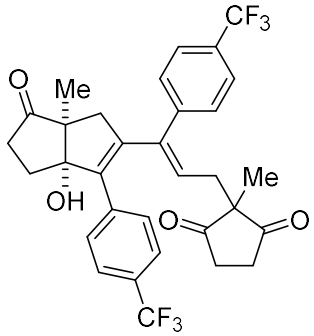
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-methyl-6-oxo-3-(4-(trifluoromethyl)phenyl)-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(4-(trifluoromethyl)phenyl)allyl)-2-methylcyclopentane-1,3-dione (**3f**)



Chemical Formula: $C_{32}H_{28}F_6O_4$
Exact Mass: 590.1892

3f was prepared according to general procedure 2.1 using **1f** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3f** as white solid (74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.04-6.99 (m, 2H), 6.89-6.84 (m, 2H), 5.61 (dd, *J* = 8.1, 6.7 Hz, 1H), 2.89 (d, *J* = 16.8 Hz, 1H), 2.75-2.63 (m, 2H), 2.58 (d, *J* = 16.8 Hz, 1H), 2.51-2.38 (m, 3H), 2.23-2.12 (m, 2H), 2.06-1.96 (m, 1H), 1.94-1.80 (m, 3H), 1.16 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 215.0, 214.8, 144.0, 141.0, 140.9, 139.4, 139.2, 129.6, 129.3, 128.4, 124.9, 124.7, 123.9 (q, *J* = 272.1 Hz), 123.8 (q, *J* = 272.0 Hz), 92.5, 56.2, 55.8, 44.2, 36.4, 34.9, 34.8, 33.7, 29.4, 18.6, 15.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8; HRMS: (ESI) calcd for $C_{32}H_{29}F_6O_4^+$[M+H]$^+$ 591.1965; found 591.1954.

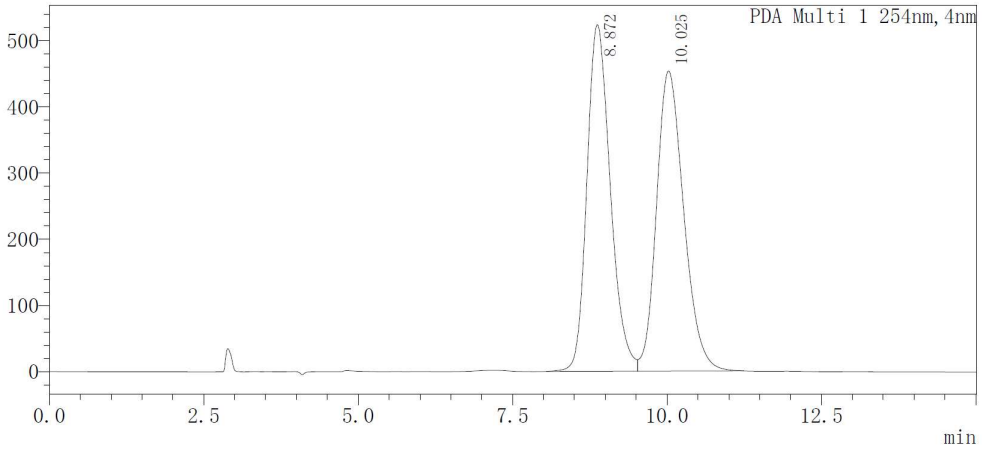
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 9 min (minor), 10 min (major).

Optical Rotation: $[\alpha]_D^{27}$ -51.4 (c 1.8, ^{i}PrOH) for 97%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.872	13826704	523928	0.000		M	
2	10.025	13912848	453619	0.000		V M	
总计		27739552	977546				

peak number

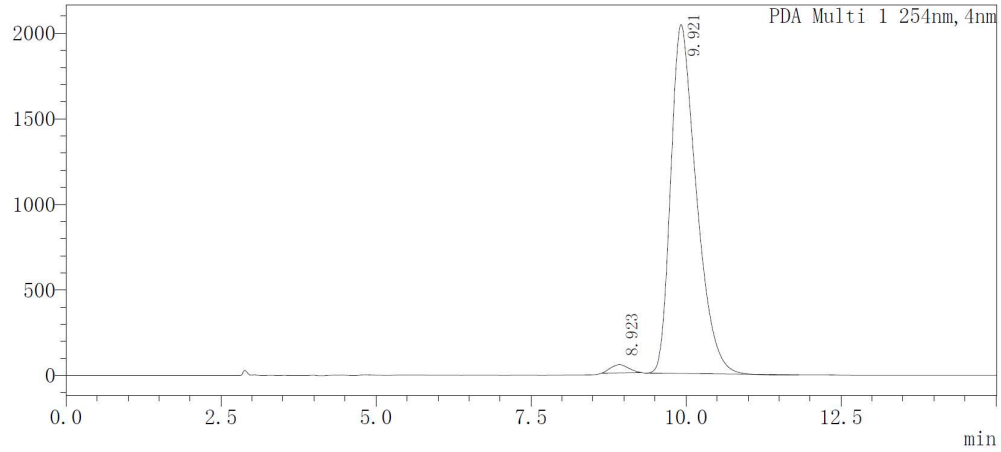
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.923	954249	47486	0.000		M	
2	9.921	58622500	2039760	0.000		M	
总计		59576749	2087246				

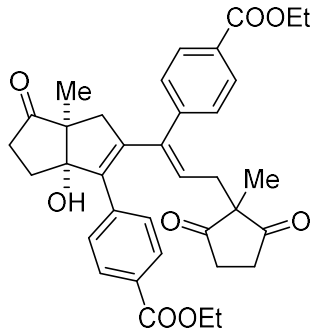
peak number

retention time

area

height

Ethyl 4-((*3aS,6aS*)-2-((*E*)-1-(4-(ethoxycarbonyl)phenyl)-3-(1-methyl-2,5-dioxocyclopentyl)prop-1-en-1-yl)-6a-hydroxy-3a-methyl-4-oxo-3,3a,4,5,6,6a-hexahydropentalen-1-yl)benzoate (**3g**)



Chemical Formula: $C_{36}H_{38}O_8$
Exact Mass: 598.2567

3g was prepared according to general procedure 2.1 using **1g** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3g** as white solid (58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.75 (m, 4H), 7.15-7.10 (m, 2H), 6.92-6.86 (m, 2H), 5.50 (t, *J* = 7.5 Hz, 1H), 4.3 (qd, *J* = 7.2, 2.7 Hz, 4H), 2.78 (d, *J* = 16.9 Hz, 1H), 2.66-2.53 (m, 2H), 2.50 (d, *J* = 17.0 Hz, 1H), 2.45-2.30 (m, 2H), 2.25 (s, 1H), 2.22-2.15 (m, 2H), 2.06-1.80 (m, 3H), 1.75 (s, 1H), 1.4 (t, *J* = 7.1 Hz, 6H), 1.12 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 215.1, 214.8, 166.2, 166.1, 144.3, 142.0, 141.0, 140.3, 139.7, 129.3, 129.2, 129.1, 129.0, 128.9, 128.8, 127.7, 92.4, 61.0, 60.9, 56.3, 56.0, 44.4, 36.4, 34.9, 34.7, 33.8, 29.1, 18.5, 15.2, 14.3; HRMS: (ESI) calcd for $C_{36}H_{39}O_8^+[M+H]^+$ 599.2639; found 599.2629.

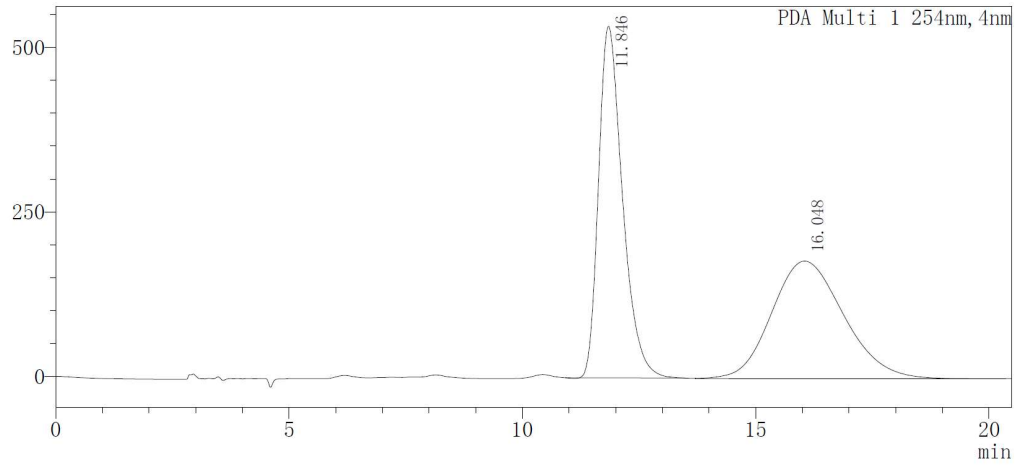
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 11 min (major), 16 min (minor).

Optical Rotation: $[\alpha]_D^{22}$ -59.8 (c 1.4, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.846	19124048	534482	0.000		M	
2	16.048	19263768	178914	0.000			
总计		38387817	713396				

peak number

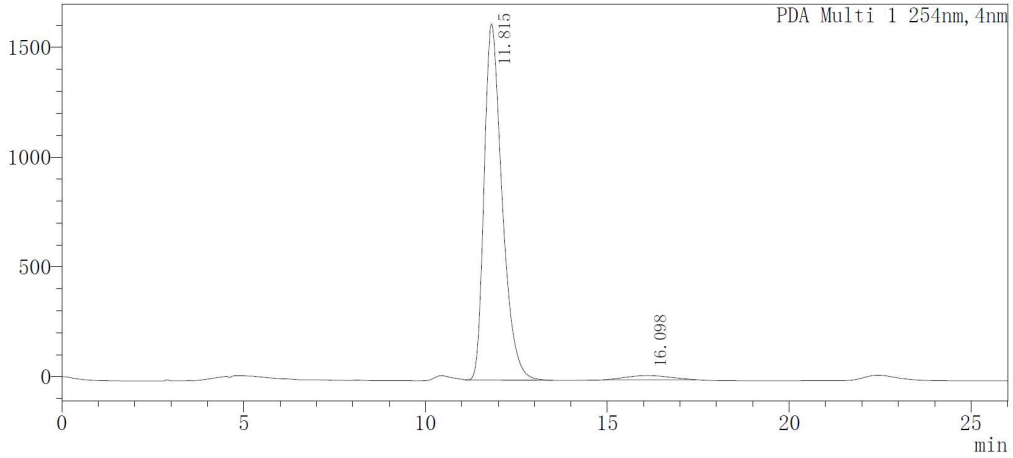
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.815	55917925	1621917	0.000		M	
2	16.098	1598488	18945	0.000		M	
总计		57516413	1640862				

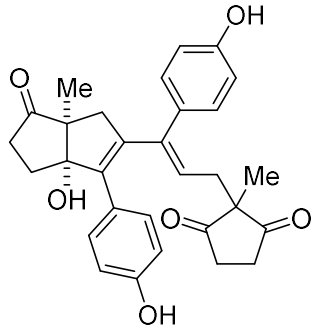
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-3-(4-hydroxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(4-hydroxyphenyl)allyl)-2-methylcyclopentane-1,3-dione (**3h**)



Chemical Formula: $C_{30}H_{30}O_6$
Exact Mass: 486.2042

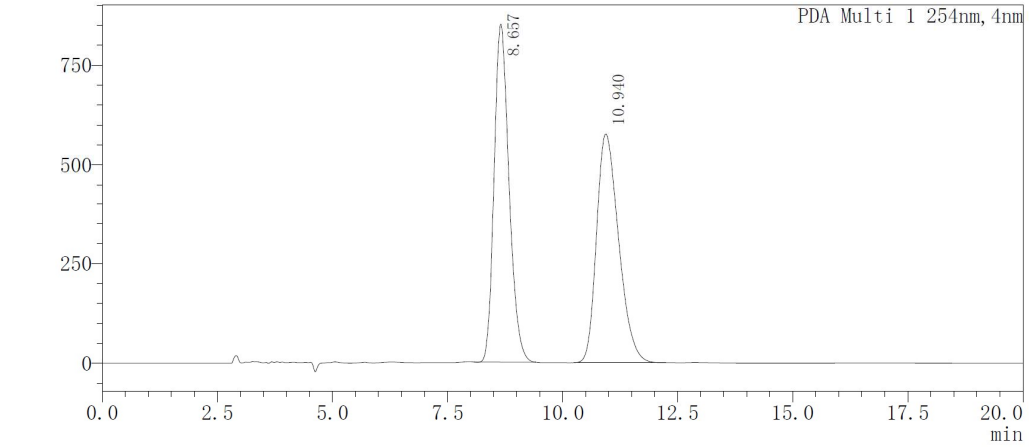
3h was prepared according to general procedure 2.1 using **1h** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3h** as white solid (45% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.41 (s, 1H), 9.26 (s, 1H), 7.06 (d, J = 8.6 Hz, 2H), 6.79 (d, J = 8.6 Hz, 2H), 6.64 (d, J = 8.6 Hz, 2H), 6.61 (d, J = 8.6 Hz, 2H), 5.23 (s, 1H), 5.17 (dd, J = 8.6, 5.6 Hz, 1H), 2.60-2.54 (m, 2H), 2.31-2.11 (m, 7H), 1.90-1.66 (m, 3H), 0.91 (s, 3H), 0.67 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 222.5, 216.8, 216.1, 156.8, 156.6, 142.8, 141.3, 139.9, 130.3, 130.1, 128.71 , 127.1, 124.4, 115.3, 115.1, 91.4, 56.1, 56.0, 55.5, 36.5, 35.5, 35.1, 34.4, 29.1, 18.4, 15.8; HRMS: (ESI) calcd for $C_{30}H_{30}NaO_6^+$[M+Na]$^+$ 509.1935; found 509.1937.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 8 min (minor), 10 min (major).

Optical Rotation: $[\alpha]_D^{20}$ -19.0 (c 0.8, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 HPLC chromatogram



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.657	19228023	850450	0.000		M	
2	10.940	19233820	576337	0.000		M	
总计		38461842	1426787				

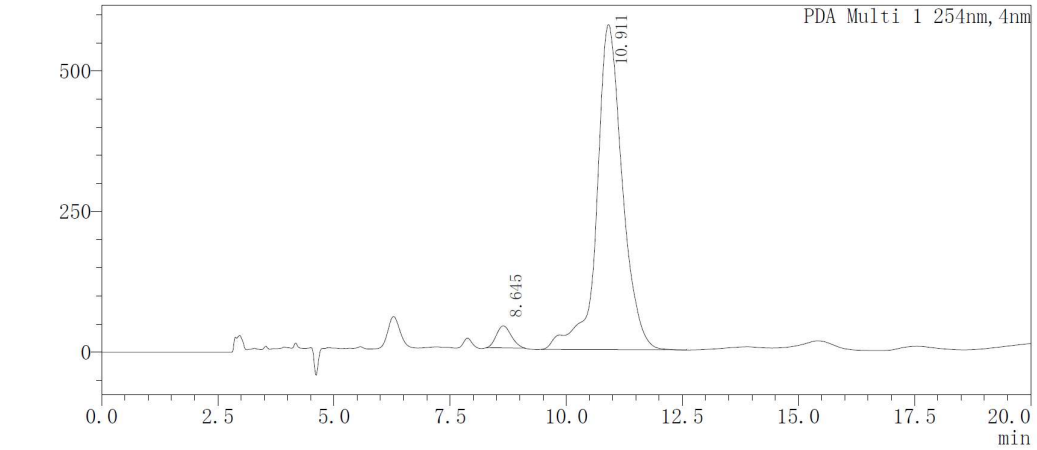
peak number

retention time

area

height

〈色谱图〉 HPLC chromatogram



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.645	877224	39189	0.000		M	
2	10.911	22299671	577867	0.000		M	
总计		23176895	617056				

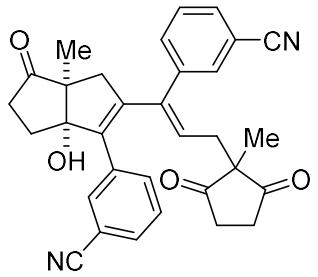
peak number

retention time

area

height

3-((*3aS,6aS*)-2-((*E*)-1-(3-Cyanophenyl)-3-(1-methyl-2,5-dioxocyclopentyl)prop-1-en-1-yl)-6a-hydroxy-3a-methyl-4-oxo-3,3a,4,5,6,6a-hexahydropentalen-1-yl)benzonitrile (**3k**)



Chemical Formula: $C_{32}H_{28}N_2O_4$
Exact Mass: 504.2049

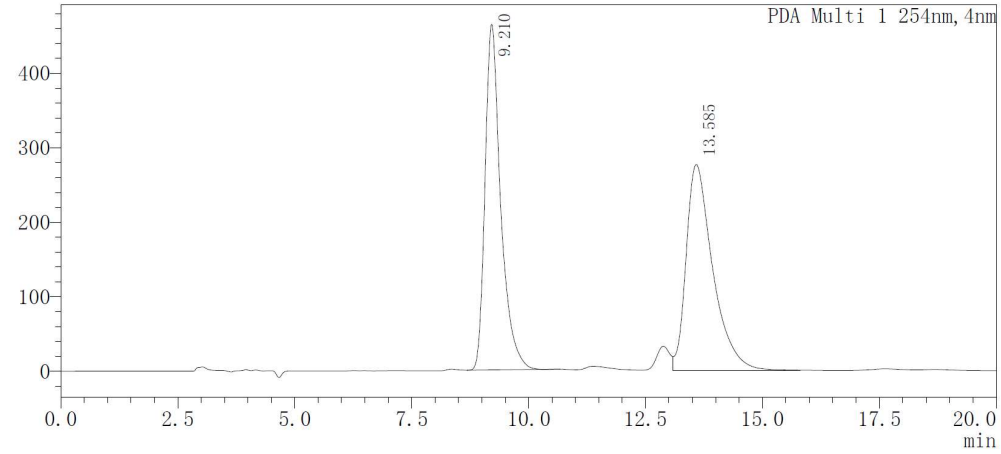
3i was prepared according to general procedure 2.1 using **1i** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3i** as white solid (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 1H), 7.34-7.31 (m, 1H), 7.25-7.18 (m, 3H), 7.15-7.12 (m, 1H), 7.08-7.01 (m, 2H), 5.72 (dd, *J* = 8.3, 6.8 Hz, 1H), 2.96 (d, *J* = 16.8 Hz, 1H), 2.78-2.69 (m, 2H), 2.66-2.53 (m, 3H), 2.48-2.38 (m, 2H), 2.24-2.10 (m, 2H), 2.03-1.92 (m, 1H), 1.87-1.80 (m, 2H), 1.17 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.7, 214.9, 214.8, 143.7, 140.2, 138.4, 138.4, 136.7, 133.8, 133.2, 132.9, 132.5, 130.8, 130.5, 129.7, 128.8, 128.7, 118.2, 118.1, 112.0, 111.9, 92.5, 56.2, 55.6, 44.3, 36.2, 34.9, 34.9, 33.6, 29.3, 18.7, 15.3; HRMS: (ESI) calcd for $C_{32}H_{29}N_2O_4^+$[M+H]$^+$ 505.2122; found 505.2136. The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 9 min (major), 13 min (minor).

Optical Rotation: $[\alpha]_D^{28}$ -29.3 (c 1.5, ^{i}PrOH) for 96%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.210	10807742	463992	0.000		M	
2	13.585	10901994	276097	0.000		M	
总计		21709736	740089				

peak number

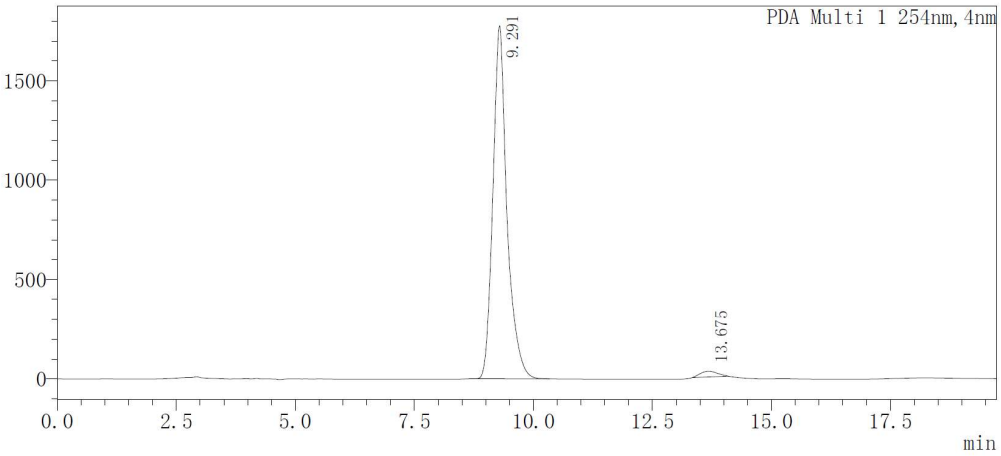
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.291	36567778	1776984	0.000		M	
2	13.675	729784	28744	0.000		M	
总计		37297561	1805727				

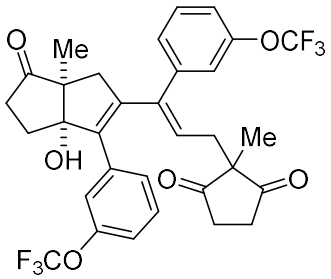
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-methyl-6-oxo-3-(3-(trifluoromethoxy)phenyl)-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(3-(trifluoromethoxy)phenyl)allyl)-2-methylcyclopentane-1,3-dione (**3j**)



Chemical Formula: $C_{32}H_{28}F_6O_6$
Exact Mass: 622.1790

3j was prepared according to general procedure 2.1 using **1j** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3j** as white solid (84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.02 (m, 2H), 6.97-6.91 (m, 1H), 6.91-6.84 (m, 2H), 6.82-6.76 (m, 1H), 6.71-6.62 (m, 2H), 5.64 (dd, *J* = 8.0, 6.9 Hz, 1H), 2.92 (d, J = 16.8 Hz, 1H), 2.72-2.38 (m, 6H), 2.25-2.14 (m, 2H), 2.06-1.89 (m, 3H), 1.87-1.77 (m, 1H), 1.16 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.9, 214.9, 214.8, 148.7, 148.6, 143.7, 140.7, 139.3, 139.2, 137.3, 129.3, 129.2, 128.2, 127.5, 121.7, 121.2, 119.5, 119.4, 92.5, 56.2, 55.8, 44.3, 36.3, 34.8, 33.9, 29.4, 17.9, 15.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.6, -57.7; HRMS: (ESI) calcd for $C_{32}H_{29}F_6O_6^+$[M+H]$^+$ 623.1863; found 623.1848.

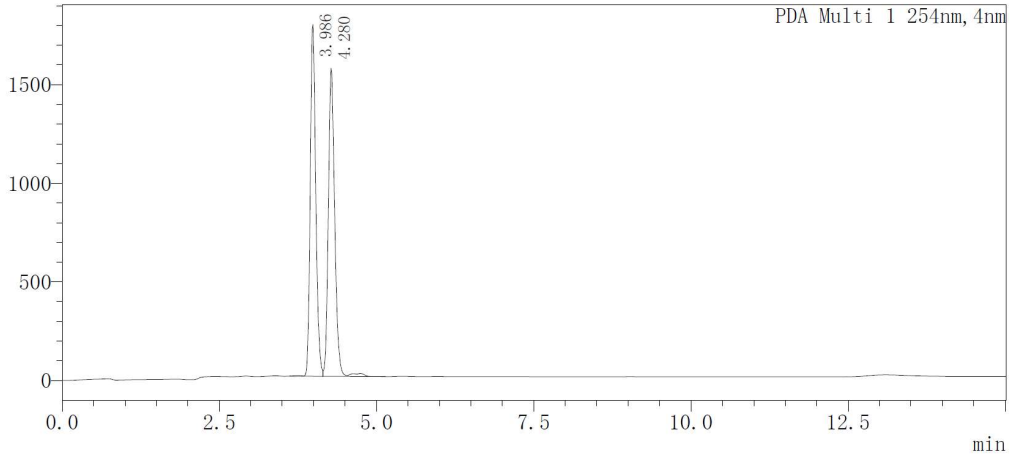
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 3 min (major), 4 min (minor).

Optical Rotation: $[\alpha]_D^{26}$ -67.8 (c 1.0, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	3.986	10887330	1783780	0.000		M	
2	4.280	11102728	1561999	0.000		V M	
总计		21990058	3345780				

peak number

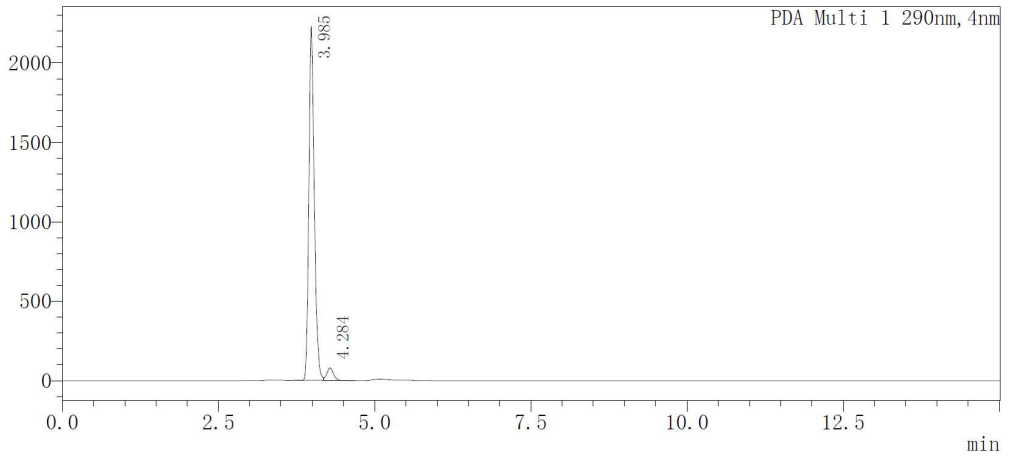
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 290nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	3.985	13454328	2229031	0.000		M	
2	4.284	583995	79223	0.000		V M	
总计		14038323	2308254				

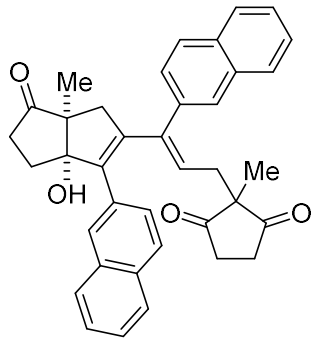
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-methyl-3-(naphthalen-2-yl)-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(naphthalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3k**)



Chemical Formula: $C_{38}H_{34}O_4$
Exact Mass: 554.2457

3k was prepared according to general procedure 2.1 using **1k** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3k** as white solid (62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.58 (m, 4H), 7.56-7.53 (m, 3H), 7.42-7.35 (m, 4H), 7.31 (s, 1H), 7.22 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.7 Hz, 1H), 5.49 (t, *J* = 7.3 Hz, 1H), 2.80 (d, *J* = 17.0 Hz, 1H), 2.51 (d, *J* = 17.0 Hz, 1H), 2.46-2.32 (m, 3H), 2.27-2.25 (m, 2H), 2.15-2.03 (m, 3H), 1.93-1.84 (m, 3H), 1.13 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 215.4, 214.9, 144.4, 141.2, 140.6, 134.9, 133.0, 132.8, 132.8, 132.2, 132.1, 128.0, 127.8, 127.8, 127.7, 127.7, 127.5, 127.4, 127.3, 126.8, 126.8, 126.6, 126.0, 125.9, 125.8, 124.9, 92.5, 56.4, 56.1, 44.5, 36.6, 34.8, 34.4, 34.1, 29.2, 18.7, 15.4; HRMS: (ESI) calcd for $C_{38}H_{34}NaO_4^+$[M+Na]$^+$ 577.2349; found 577.2343.

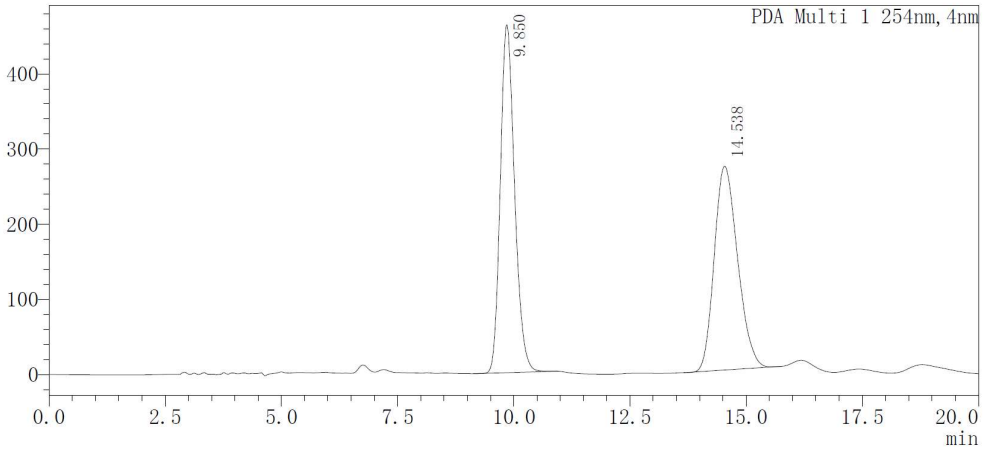
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 5 min (minor), 13 min (major).

Optical Rotation: $[\alpha]_D^{20}$ -74.9 (c 1.4, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.850	9894373	462687	0.000		M	
2	14.538	9481289	271192	0.000		M	
总计		19375662	733879				

peak number

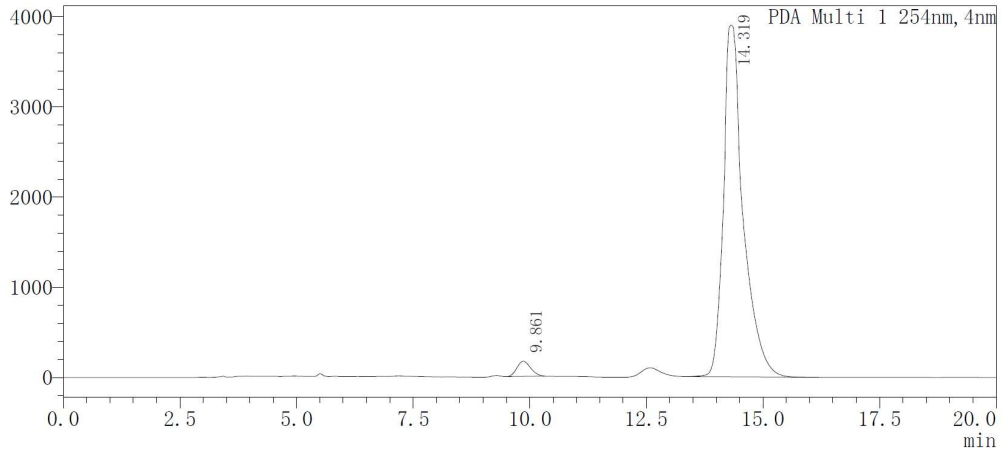
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.861	3436017	168705	0.000		M	
2	14.319	115208736	3899634	0.000		M	
总计		118644754	4068339				

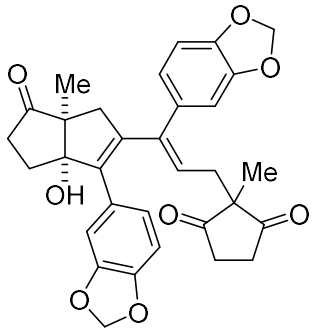
peak number

retention time

area

height

2-((*E*)-3-(Benzo[*d*][1,3]dioxol-5-yl)-3-((*3aS,6aS*)-3-(benzo[d][1,3]dioxol-5-yl)-3a-hydroxy-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3l**)



Chemical Formula: $C_{32}H_{30}O_8$
Exact Mass: 542.1941

3l was prepared according to general procedure 2.1 using **1l** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3l** as white solid (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.64 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.52 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.46 (d, *J* = 1.6 Hz, 1H), 6.29-6.25 (m, 1H), 6.24-6.23 (m, 1H), 5.91-5.85 (m, 4H), 5.41 (t, *J* = 8.0 Hz, 1H), 2.73 (d, *J* = 16.8 Hz, 1H), 2.65-2.50 (m, 2H), 2.49-2.32 (m, 4H), 2.29-2.18 (m, 2H), 2.10-1.92 (m, 3H), 1.85-1.77 (m, 1H), 1.10 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.5, 215.4, 215.1, 147.0, 146.9, 146.4, 146.3, 143.6, 140.9, 140.4, 131.1, 129.2, 126.1, 122.5, 122.2, 109.5, 109.5, 107.9, 107.8, 100.9, 100.8, 92.3, 56.5, 55.8, 44.1, 36.5, 34.9, 34.8, 34.5, 29.1, 17.8, 15.4; HRMS: (ESI) calcd for $C_{32}H_{30}NaO_8^+$[M+Na]$^+$ 565.1833; found 565.1862.

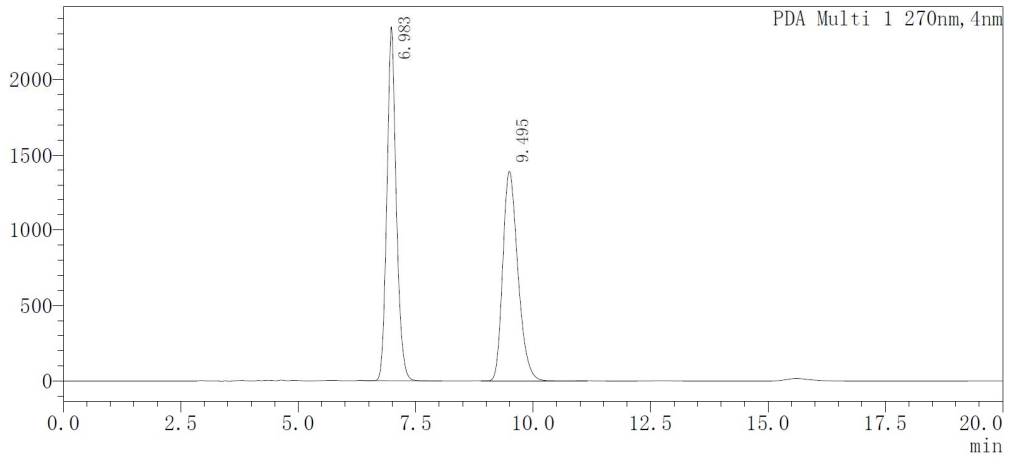
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 60/40 as eluent, 254 nm, 1 mL/min. tR = 6 min (major), 9 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ -60.9 (c 1.1, ^{i}PrOH) for 96%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 270nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.983	32540278	2345065	51.161		M	
2	9.495	31063202	1391531	48.839		M	
总计		63603480	3736596				

peak number

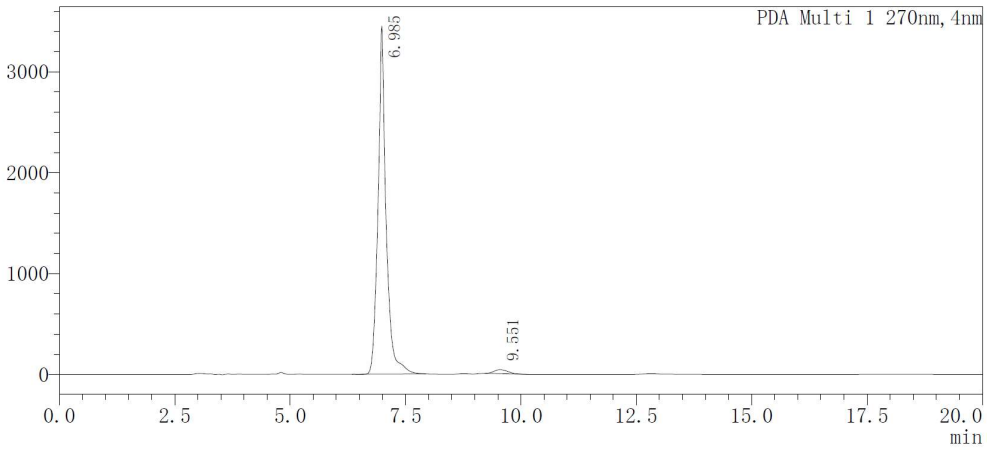
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 270nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.985	41885222	3451102	0.000		M	
2	9.551	824709	40337	0.000		M	
总计		42709931	3491438				

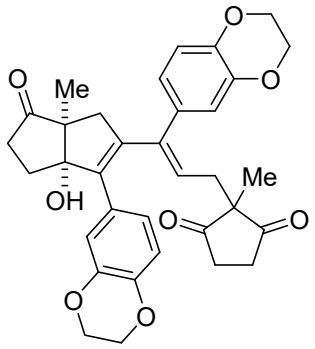
peak number

retention time

area

height

2-((*E*)-3-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-3-((*3aS,6aS*)-3-(2,3-dihydrobenzo[*b*][1,4]dioxin-6-yl)-3a-hydroxy-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3m**)



Chemical Formula: $C_{34}H_{34}O_8$
Exact Mass: 570.2254

3m was prepared according to general procedure 2.1 using **1m** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3m** as white solid (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 (d, *J* = 8.3 Hz, 1H), 6.62 (d, *J* = 8.1 Hz, 1H), 6.58-6.54 (m, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 6.30-6.26 (m, 2H), 5.38 (dd, *J* = 7.8, 6.7 Hz, 1H), 4.23-4.17 (m, 8H), 2.72 (d, *J* = 16.8 Hz, 1H), 2.62-2.51 (m, 2H), 2.48-2.33 (m, 4H), 2.31-2.21 (m, 2H), 2.09-1.96 (m, 3H), 1.86-1.75 (m, 1H), 1.10 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 215.5, 215.2, 143.5, 142.7, 142.7, 142.5, 142.4, 140.7, 140.3, 130.6, 128.7, 125.6, 122.2, 121.9, 118.0, 118.0, 116.6, 116.6, 92.3, 64.3, 64.2, 64.2, 64.2, 56.5, 55.8, 44.2, 36.6, 35.0, 34.9, 34.7, 29.2, 17.7, 15.4; HRMS: (ESI) calcd for $C_{34}H_{34}NaO_8^+$[M+Na]$^+$ 593.2154; found 593.2145.

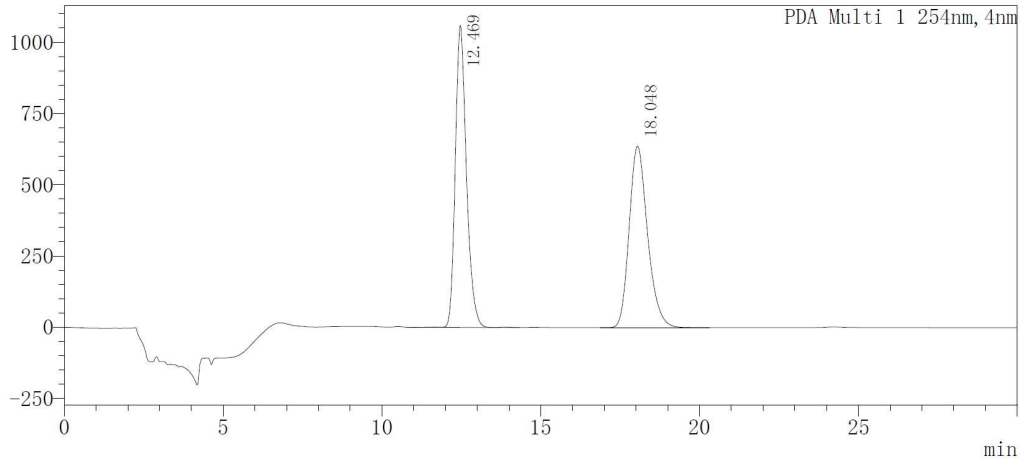
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 12 min (major), 18 min (minor).

Optical Rotation: $[\alpha]_D^{26}$ -6.3 (c 0.9, ^{i}PrOH) for 96%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.469	25835411	1059887	0.000		M	
2	18.048	25680780	637119	0.000		M	
总计		51516191	1697007				

peak number

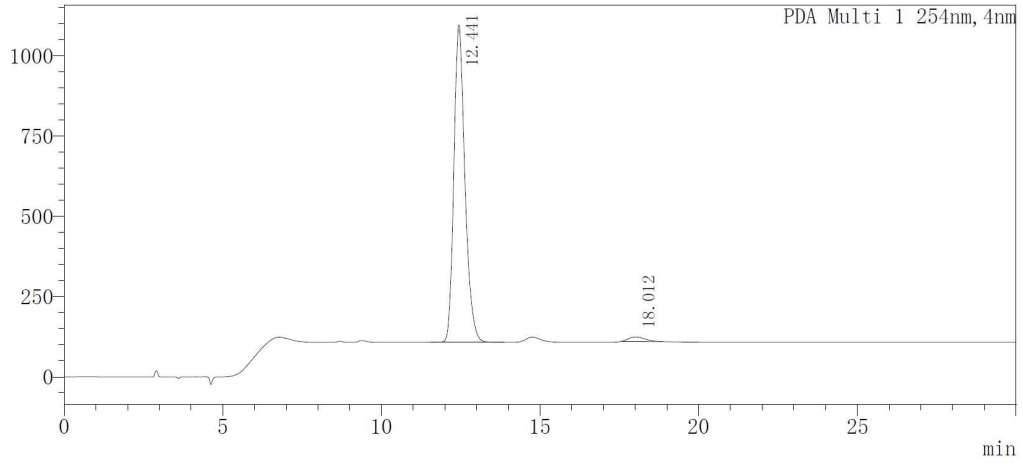
retention time

area

height

〈色谱图〉 HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.441	23958280	988063	0.000		M	
2	18.012	496595	13870	0.000		M	
总计		24454874	1001933				

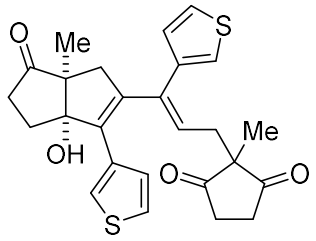
peak number

retention time

area

height

2-((*Z*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-methyl-6-oxo-3-(thiophen-3-yl)-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(thiophen-3-yl)allyl)-2-methylcyclopentane-1,3-dione (**3n**)



Chemical Formula: $C_{26}H_{26}O_4S_2$
Exact Mass: 466.1273

3n was prepared according to general procedure 2.1 using **1n** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3n** as white solid (51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.14 (m, 3H), 6.94-6.89 (m, 2H), 6.72-6.68 (m, 1H), 5.3 (dd, *J* = 8.3, 6.3 Hz, 1H), 2.8 (d, *J* = 17.2 Hz, 1H), 2.71-2.57 (m, 2H), 2.52-2.35 (m, 6H), 2.24-2.15 (m, 1H), 2.06-1.84 (m, 3H), 1.12 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.5, 215.9, 215.4, 144.3, 137.2, 136.0, 135.6, 134.7, 128.1, 127.9, 125.6, 125.5, 124.9, 123.7, 123.0, 92.3, 56.4, 56.0, 45.1, 36.6, 35.2, 35.0, 34.6, 29.4, 18.6, 15.5; HRMS: (ESI) calcd for $C_{26}H_{26}NaO_4S_2^+$[M+Na]$^+$ 489.1165; found 489.1161.

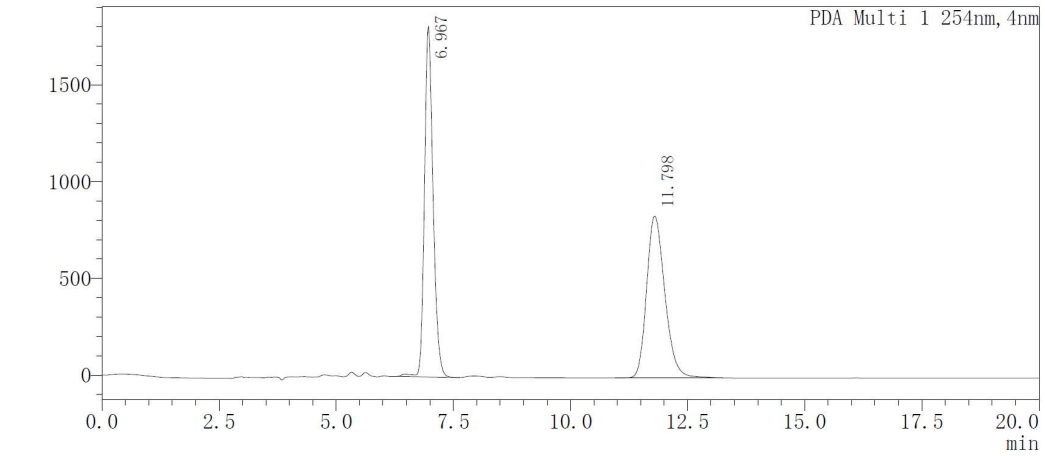
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 7 min (major), 11 min (minor).

Optical Rotation: $[\alpha]_D^{26}$ -16.2 (c 0.9, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.967	23191783	1811832	0.000		M	
2	11.798	22685066	836385	0.000		M	
总计		45876849	2648217				

peak number

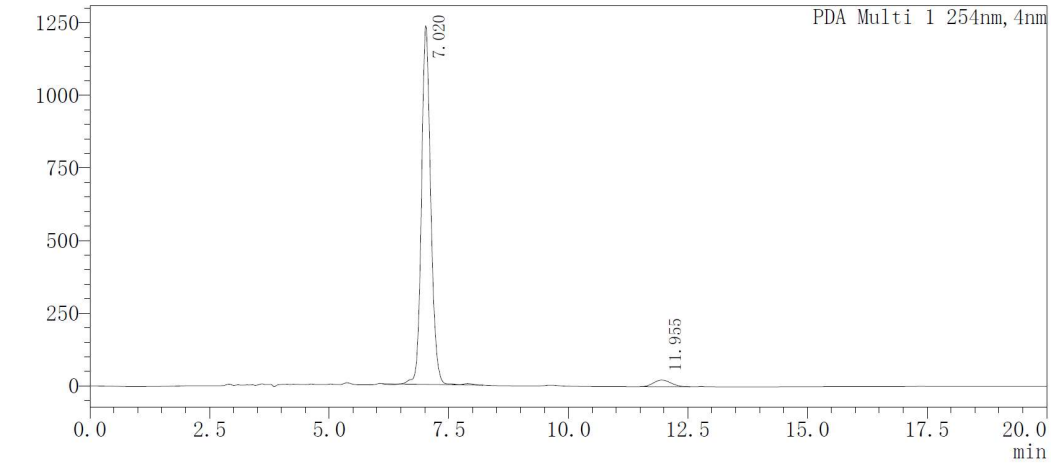
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.020	16691037	1234560	0.000		M	
2	11.955	582506	22992	0.000		M	
总计		17273543	1257552				

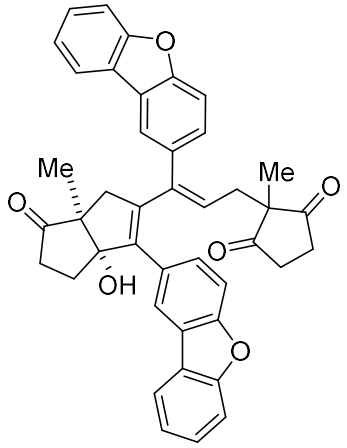
peak number

retention time

area

height

2-((*E*)-3-(Dibenzo[*b,d*]furan-2-yl)-3-((*3aS,6aS*)-3-(dibenzo[b,d]furan-2-yl)-3a-hydroxy-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3o**)



Chemical Formula: $C_{42}H_{34}O_6$
Exact Mass: 634.2355

3o was prepared according to general procedure 2.1 using **1o** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3o** as white solid (75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.64 (m, 1H), 7.63-7.59 (m, 1H), 7.39-7.30 (m, 5H), 7.24-7.13 (m, 5H), 7.08-7.02 (m, 1H), 6.86-6.80 (m, 1H), 5.66 (t, *J* = 7.5 Hz, 1H), 2.95 (d, *J* = 16.7 Hz, 1H), 2.66 (d, *J* = 16.7 Hz, 1H), 2.58-2.39 (m, 3H), 2.37-2.27 (m, 2H), 2.23 (d, *J* = 7.5 Hz, 2H), 2.18-2.08 (m, 2H), 2.08-1.97 (m, 1H), 1.89-1.79 (m, 1H), 1.20 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.5, 215.1, 215.0, 156.0, 156.0, 154.8, 154.7, 143.8, 141.6, 141.2, 132.0, 130.0, 127.9, 127.6, 127.0, 127.0, 126.6, 123.6, 123.6, 123.3, 123.3, 122.5, 122.5, 121.3, 121.1, 120.4, 120.2, 111.3, 111.3, 110.8, 110.7, 92.5, 56.5, 55.7, 44.3, 36.6, 34.8, 34.7, 34.5, 29.3, 17.7, 15.5; HRMS: (ESI) calcd for $C_{42}H_{34}NaO_6^+$[M+Na]$^+$ 657.2248; found 657.2252.

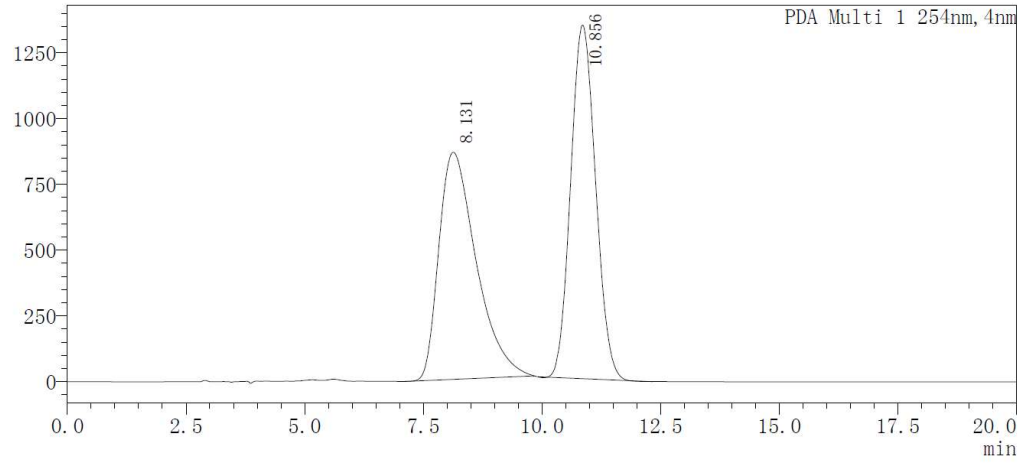
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 8 min (minor), 10 min (major).

Optical Rotation: $[\alpha]_D^{26}$ -7.9 (c 1.9, ^{i}PrOH) for 97%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图>
mAU

HPLC chromatogram



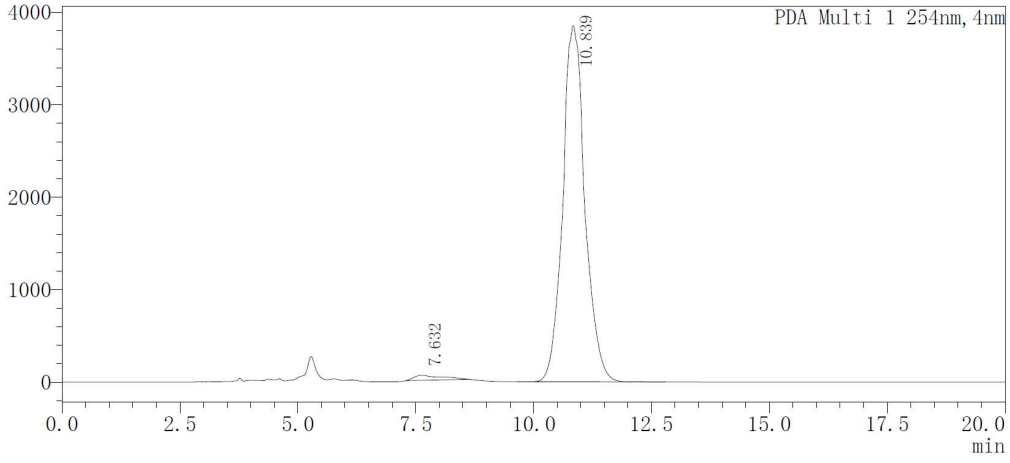
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.131	47267895	863269	0.000		M	
2	10.856	49118107	1343756	0.000		M	
总计		96386002	2207025				

peak number
retention time
area
height

<色谱图>
mAU

HPLC chromatogram

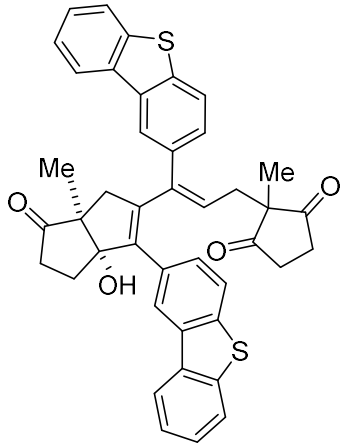


<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.632	2229381	54405	0.000		M	
2	10.839	126248076	3850333	0.000		M	
总计		128477457	3904738				

peak number
retention time
area
height

2-((*E*)-3-(Dibenzo[*b,d*]thiophen-2-yl)-3-((*3aS,6aS*)-3-(dibenzo[b,d]thiophen-2-yl)-3a-hydroxy-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3p**)



Chemical Formula: $C_{42}H_{34}O_4S_2$
Exact Mass: 666.1899

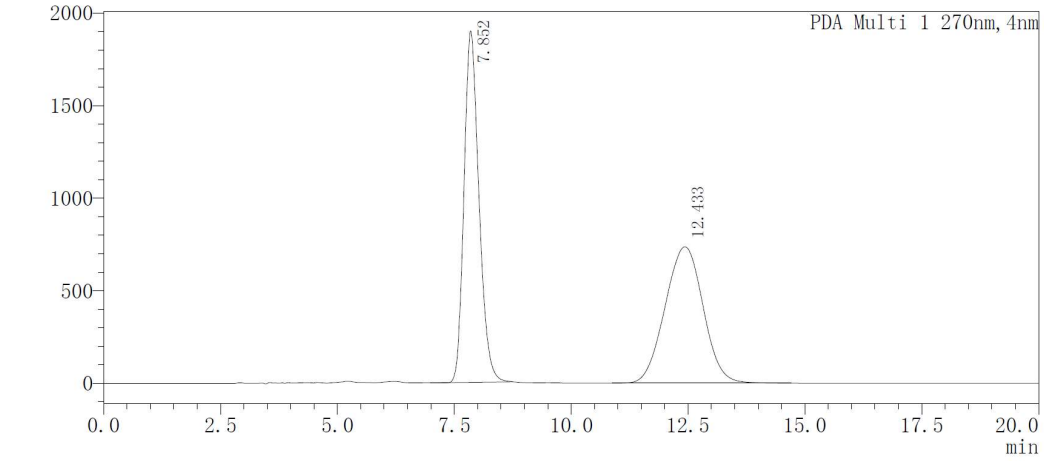
3p was prepared according to general procedure 2.1 using **1p** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3p** as white solid (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.9 Hz, 1H), 7.68-7.64 (m, 1H), 7.64-7.60 (m,1H), 7.48 (d, *J* = 1.2 Hz, 1H), 7.41 (d, *J* = 1.2 Hz, 1H), 7.38-7.28 (m, 4H), 7.26-7.17 (m, 2H), 7.01 (dd, *J* = 8.2, 1.6 Hz, 1H), 6.82 (dd, *J* = 8.2, 1.6 Hz, 1H), 5.70 (t, *J* = 7.5 Hz, 1H), 3.03 (d, *J* = 16.6 Hz, 1H), 2.72 (d, *J* = 16.6 Hz, 1H), 2.56-2.38 (m, 3H), 2.36-2.22 (m, 5H), 2.18-1.96 (m, 2H), 1.90-1.78 (m, 1H), 1.21 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.6, 215.2, 215.0, 143.4, 143.4, 141.8, 141.2, 139.4, 139.4, 137.9, 137.7, 134.7, 134.7, 134.6, 134.6, 134.5, 133.4, 131.5, 127.4, 126.8, 126.5, 126.4, 124.0, 124.0, 122.4, 122.2, 121.9, 121.9, 121.7, 121.3, 121.2, 92.5, 56.6, 55.7, 44.1, 36.5, 34.9, 34.7, 34.5, 29.3, 17.8, 15.4; HRMS: (ESI) calcd for $C_{42}H_{35}O_4S_2^+$[M+H]$^+$ 667.1971; found 667.1969.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 7 min (minor), 12 min (major).

Optical Rotation: $[\alpha]_D^{20}$ 27.8 (c 2.2, ^{i}PrOH) for 95%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram



〈峰表〉

PDA Ch1 270nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.852	42148759	1898751	0.000		M	
2	12.433	41793874	736581	0.000		M	
总计		83942633	2635332				

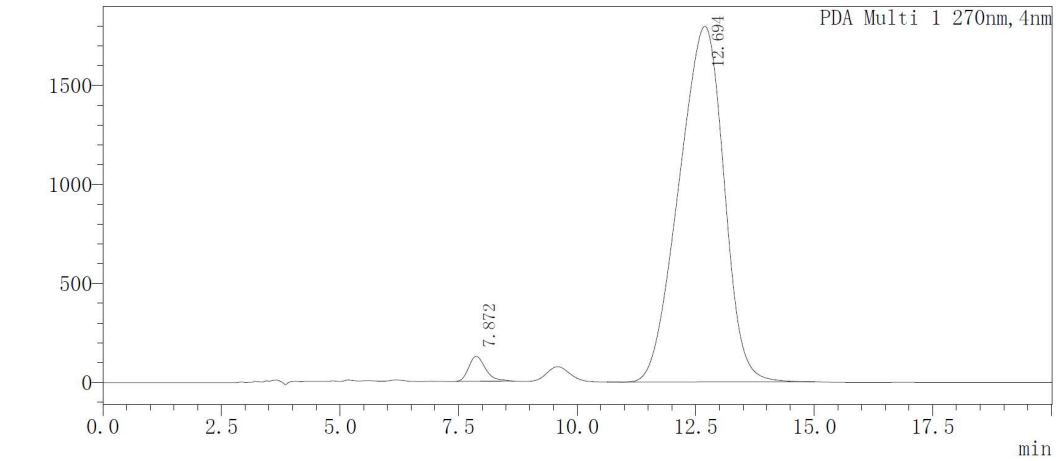
peak number

retention time

area

height

〈色谱图〉 ← HPLC chromatogram



〈峰表〉

PDA Ch1 270nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.872	3077010	126193	0.000		M	
2	12.694	118459233	1796003	0.000		M	
总计		121536243	1922197				

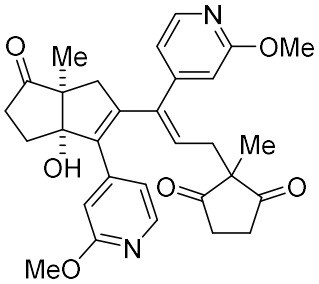
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-3-(2-methoxypyridin-4-yl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(2-methoxypyridin-4-yl)allyl)-2-methylcyclopentane-1,3-dione (**3q**)



Chemical Formula: $C_{30}H_{32}N_2O_6$
Exact Mass: 516.2260

3q was prepared according to general procedure 2.1 using **1q** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3q** as white solid (34% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.65 (m, 1H), 7.59-7.55 (m, 1H), 7.24-7.19 (m, 1H), 7.01-6.93 (m, 1H), 6.52-6.48 (m, 1H), 6.47-6.42 (m, 1H), 5.6 (t, *J* = 7.5 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.86 (d, *J* = 16.8 Hz, 1H), 2.71-2.60 (m, 2H), 2.58-2.46 (m, 3H), 2.45-2.35 (m, 1H), 2.25 (s, 1H), 2.23 (s, 1H), 2.04-1.91 (m, 2H), 1.88-1.77 (m, 2H), 1.14 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 215.1, 214.9, 162.9, 162.9, 146.8, 146.5, 144.4, 139.2, 138.8, 138.5, 137.3, 128.2, 126.0, 110.2, 110.0, 92.3, 56.4, 55.6, 53.4, 53.4, 44.3, 36.3, 34.9, 34.8, 33.9, 29.3, 18.4, 15.4; HRMS: (ESI) calcd for $C_{30}H_{33}N_2O_6^+$[M+H]$^+$ 517.2333; found 517.2333.

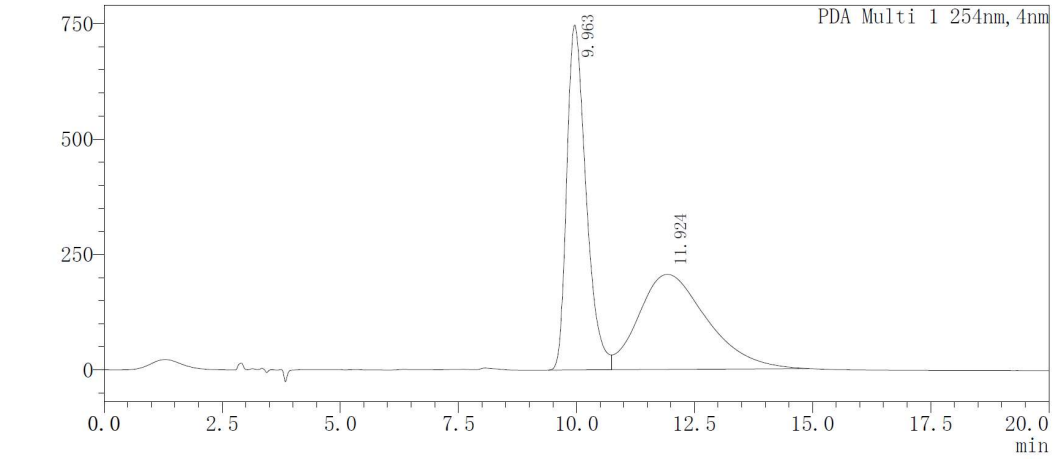
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 10 min (minor), 11 min (major).

Optical Rotation: $[\alpha]_D^{27}$ -41.9 (c 0.7, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	9.963	21272777	747500	0.000		M	
2	11.924	20757802	206217	0.000		V M	
总计		42030579	953716				

peak number

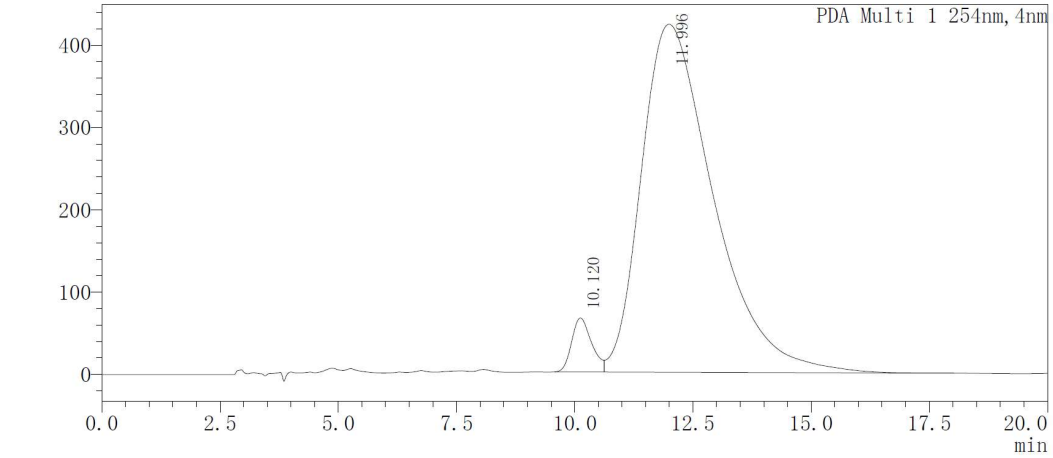
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.120	1936072	65553	0.000		M	
2	11.996	44923403	422845	0.000		V M	
总计		46859475	488398				

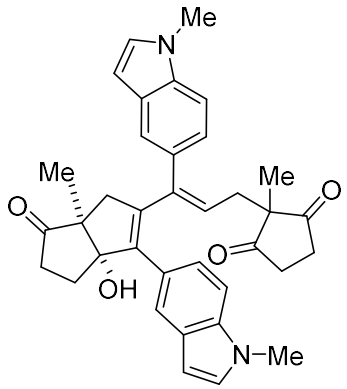
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-methyl-3-(1-methyl-1H-indol-5-yl)-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(1-methyl-1H-indol-5-yl)allyl)-2-methylcyclopentane-1,3-dione (**3r**)



Chemical Formula: $C_{36}H_{36}N_2O_4$
Exact Mass: 560.2675

3r was prepared according to general procedure 2.1 using **1r** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3r** as white solid (37% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.26-7.17 (m, 3H), 7.15-7.08 (m, 1H), 7.03 (d, *J* = 3.0 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 6.82-6.80 (m, 1H), 6.44 (d, *J* = 2.9 Hz, 1H), 6.41 (d, *J* = 2.9 Hz, 1H), 5.26 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.58 (d, *J* = 17.0 Hz, 1H), 2.42-2.21 (m, 5H), 2.21-2.05 (m, 3H), 1.89-1.62 (m, 4H), 1.06 (s, 3H), 0.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 222.0, 216.0, 215.4, 144.6, 141.5, 140.7, 135.8, 135.8, 129.0, 128.9, 128.7, 128.3, 128.1, 126.6, 124.7, 122.9, 122.3, 121.0, 121.0, 109.0, 108.9, 101.1, 101.0, 92.4, 56.4, 56.1, 44.7, 36.8, 34.8, 34.8, 34.4, 32.8, 32.8, 29.3, 18.8, 15.4; HRMS: (ESI) calcd for $C_{36}H_{36}N_2NaO_4^+$[M+Na]$^+$ 583.2567; found 583.2589.

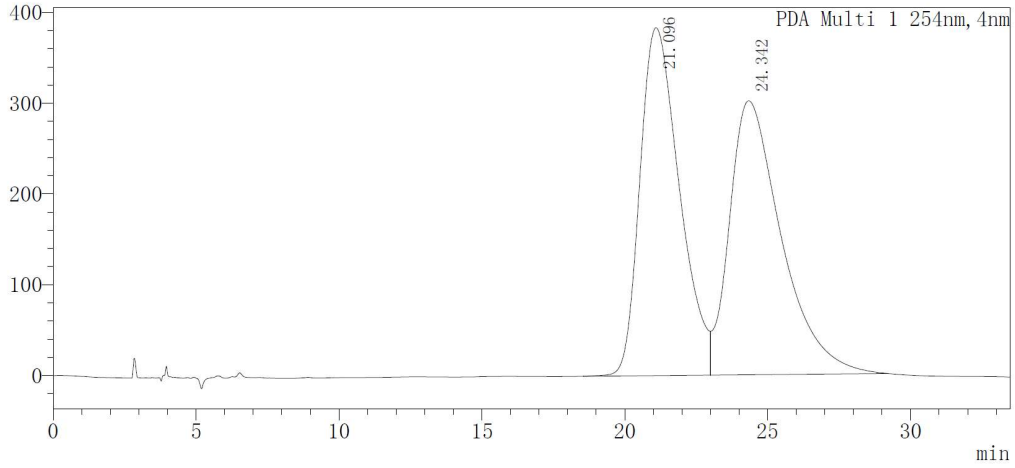
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 21 min (minor), 24 min (major).

Optical Rotation: $[\alpha]_D^{20}$ -61.0 (c 0.8, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	21.096	36875882	383599	0.000		M	
2	24.342	38169194	302033	0.000		V M	
总计		75045076	685632				

peak number

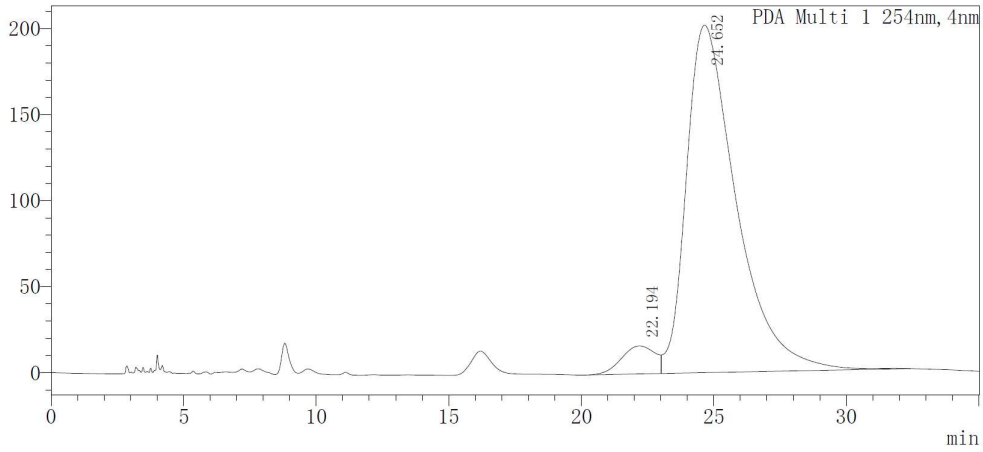
retention time

area

height

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	22.194	1433986	16274	0.000		M	
2	24.652	26511681	201924	0.000		V M	
总计		27945667	218199				

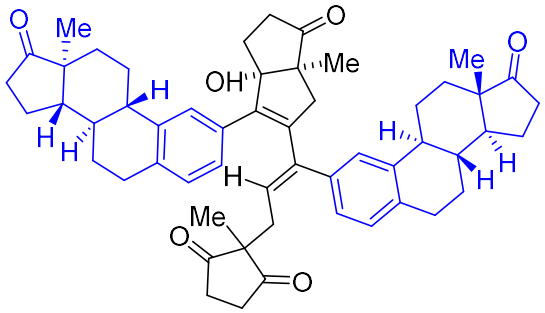
peak number

retention time

area

height

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-methyl-3-((*8R,9S,13S,14S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-2-yl)-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-((*8R,9S,13S,14S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-2-yl)allyl)-2-methylcyclopentane-1,3-dione (**3s**)



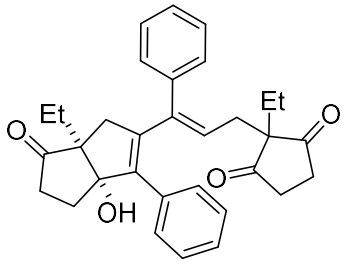
Chemical Formula: $C_{54}H_{62}O_6$
Exact Mass: 806.4546

3s was prepared according to general procedure 2.1 using **1s** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3s** as white solid (83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14-7.04 (m, 2H), 6.93-6.85 (m, 1H), 6.78 (s, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 5.27 (t, J = 7.1 Hz, 1H), 2.89-2.71 (m, 4H), 2.63 (d, J = 16.7 Hz, 1H), 2.54-2.44 (m, 4H), 2.40-2.32 (m, 4H), 2.26-2.19 (m, 5H), 2.16-2.11 (m, 1H), 2.11-1.91 (m, 10H), 1.87-1.79 (m, 1H), 1.65-1.44 (m, 11H), 1.07 (s, 3H), 0.91 (s, 3H), 0.88 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 220.9, 220.7, 215.8, 215.3, 144.3, 140.8, 140.6, 138.3, 138.1, 135.9, 135.7, 134.7, 133.0, 129.4, 129.3, 126.1, 126.1, 125.0, 124.8, 124.8, 92.1, 56.2, 56.0, 50.4, 50.4, 47.9, 47.8, 44.4, 44.4, 44.2, 38.1, 37.9, 36.6, 35.7, 35.0, 34.8, 34.7, 31.5, 29.2, 29.2, 29.1, 26.5, 26.4, 25.6, 25.5, 21.5, 18.0, 15.3, 13.8; HRMS: (ESI) calcd for $C_{54}H_{63}O_6^+$[M+H]$^+$ 807.4619; found 807.4601.

Optical Rotation: $[\alpha]_D^{20}$ 65.4 (c 2.3, ^{i}PrOH)

Absolute stereochemistry was determined through analogy with **3a**.

2-Ethyl-2-((*E*)-3-((*3aS,6aS*)-6a-ethyl-3a-hydroxy-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-phenylallyl)cyclopentane-1,3-dione (**3t**)



Chemical Formula: $C_{32}H_{34}O_4$
Exact Mass: 482.2457

3t was prepared according to general procedure 2.1 using **1t** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3t** as white solid (76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.11 (m, 8H), 6.92-6.84 (m, 2H), 5.34 (t, *J* = 7.3 Hz, 1H), 2.65 (d, *J* = 16.9 Hz, 1H), 2.51-2.33 (m, 4H), 2.29-2.18 (m, 4H), 2.06-1.86 (m, 4H), 1.78-1.68 (m, 1H), 1.61-1.52 (m, 1H), 1.33 (q, *J* = 7.4 Hz, 2H), 0.92 (t, *J* = 7.5 Hz, 3H), 0.56 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 216.2, 215.7, 144.6, 141.3, 140.5, 137.4, 135.4, 128.9, 128.8, 128.2, 128.1, 127.2, 127.0, 126.0, 92.6, 61.1, 59.8, 42.7, 36.7, 36.0, 35.8, 33.4, 29.4, 27.2, 23.6, 9.2, 8.9; HRMS: (ESI) calcd for $C_{32}H_{35}O_4^+$[M+H]$^+$ 505.2349; found 505.2345.

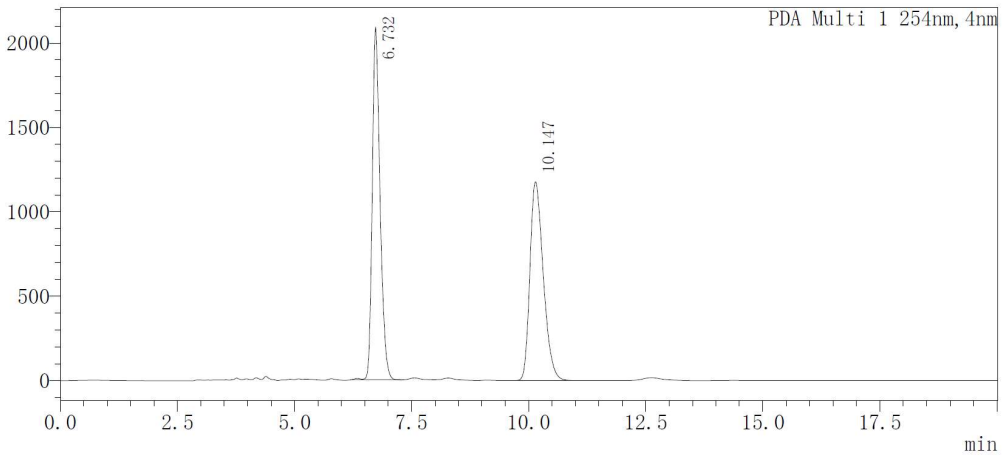
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 6 min (major), 10 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ -53.1 (c 1.5, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.732	24127421	2089649	0.000		M	
2	10.147	23283956	1176554	0.000		M	
总计		47411377	3266203				

peak number

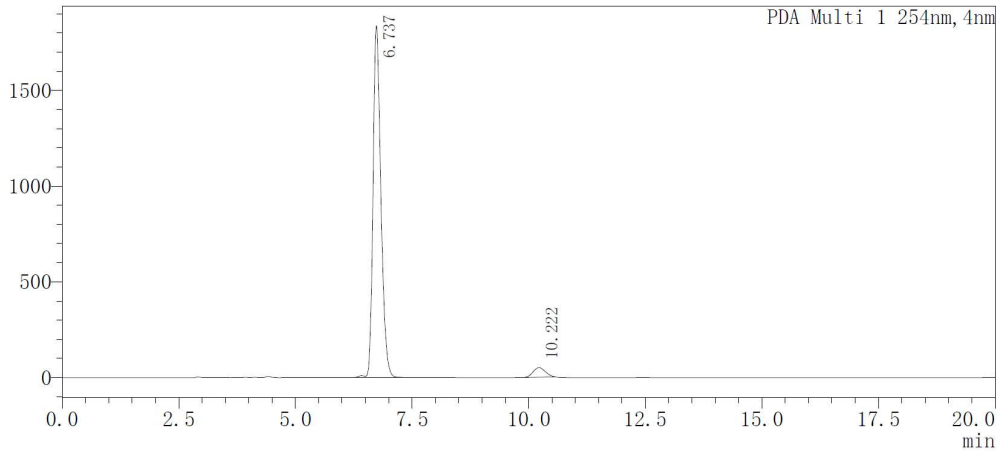
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.737	21457120	1837716	0.000		M	
2	10.222	917024	50027	0.000		M	
总计		22374144	1887743				

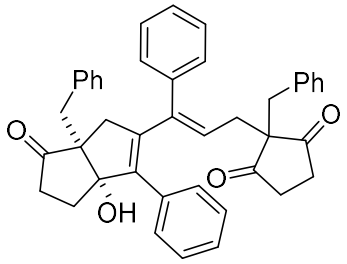
peak number

retention time

area

height

2-Benzyl-2-((*E*)-3-((*3aS,6aS*)-6a-benzyl-3a-hydroxy-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-phenylallyl)cyclopentane-1,3-dione (**3u**)



Chemical Formula: $C_{42}H_{38}O_4$
Exact Mass: 606.2770

3u was prepared according to general procedure 2.1 using **1u** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3u** as white solid (89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.09 (m, 16H), 6.91-6.87 (m, 2H), 6.86-6.82 (m, 2H), 5.35 (t, *J* = 7.3 Hz, 1H), 3.04 (d, *J* = 13.5 Hz, 1H), 2.95 (d, *J* = 13.5 Hz, 1H), 2.71-2.60 (m, 2H), 2.59-2.49 (m, 2H), 2.36 (d, *J* = 7.3 Hz, 2H), 2.10 (s, 1H), 2.02-1.83 (m, 4H), 1.81-1.62 (m, 3H), 1.36-1.14 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.6, 217.1, 216.4, 144.0, 141.4, 140.5, 137.2, 137.1, 135.3, 135.2, 130.4, 129.6, 128.9, 128.7, 128.4, 128.2, 128.2, 128.1, 127.3, 127.1, 127.1, 126.6, 125.8, 92.6, 62.2, 61.3, 44.2, 41.7, 37.4, 37.1, 36.5, 36.2, 34.8, 29.3; HRMS: (ESI) calcd for $C_{42}H_{38}NaO_4^+$[M+Na]$^+$ 629.2662; found 629.2659.

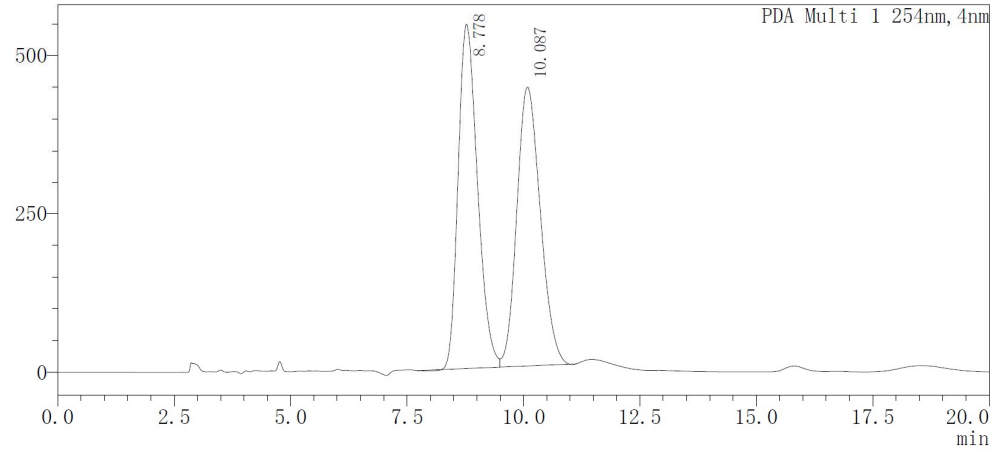
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 8 min (minor), 10 min (major).

Optical Rotation: $[\alpha]_D^{20}$ -8.5 (c 2.2, ^{i}PrOH) for 97%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.778	15691567	543264	0.000		M	
2	10.087	15430325	440167	0.000		V M	
总计		31121891	983431				

peak number

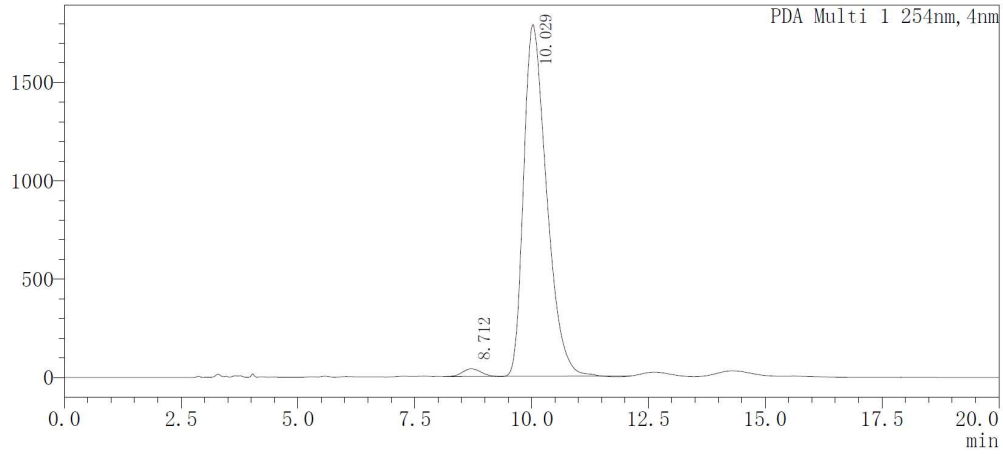
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.712	1054041	38827	0.000		M	
2	10.029	61280310	1789170	0.000		M	
总计		62334351	1827997				

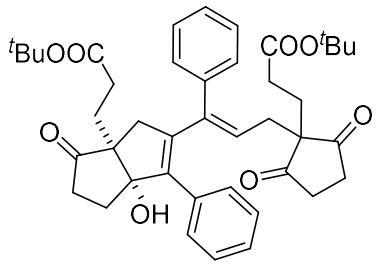
peak number

retention time

area

height

Tert-butyl 3-((*3aS,6aS*)-5-((*E*)-3-(1-(3-(*tert*-butoxy)-3-oxopropyl)-2,5-dioxocyclopentyl)-1-phenylprop-1-en-1-yl)-6a-hydroxy-3-oxo-6-phenyl-2,3,4,6a-tetrahydropentalen-3a(1*H*)-yl)propanoate (**3v**)



Chemical Formula: $C_{42}H_{50}O_8$
Exact Mass: 682.3506

3v was prepared according to general procedure 2.1 using **1v** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3v** as white solid (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.10 (m, 8H), 6.90-6.80 (m, 2H), 5.37 (t, *J* = 7.3 Hz, 1H), 2.63 (d, *J* = 16.7 Hz, 1H), 2.59-2.49 (m, 2H), 2.46-2.37 (m, 3H), 2.28-2.14 (m, 6H), 2.04-1.79 (m, 7H), 1.57-1.52 (m, 2H), 1.41 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.4, 214.7, 214.4, 173.0, 172.1, 144.0, 141.4, 140.8, 137.3, 135.3, 129.0, 128.7, 128.2, 128.1, 127.3, 127.0, 125.6, 92.5, 80.8, 80.5, 59.0, 58.5, 42.4, 36.6, 35.2, 35.1, 33.9, 30.4, 29.6, 29.3, 28.0, 27.9, 27.1, 24.9; HRMS: (ESI) calcd for $C_{42}H_{51}O_8^+$[M+H]$^+$ 683.3578; found 683.3578.

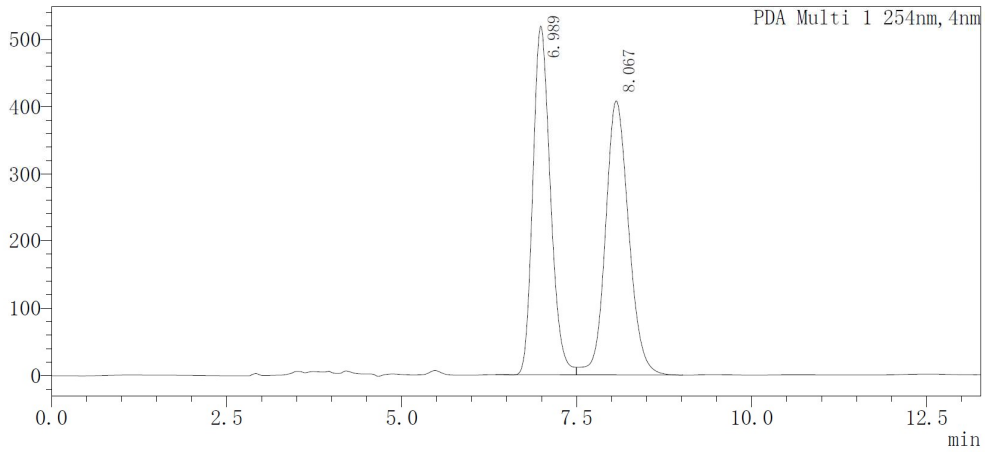
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 6 min (minor), 8 min (major).

Optical Rotation: $[\alpha]_D^{24}$ -56.4 (c 0.7, ^{i}PrOH) for 96%ee.

Absolute stereochemistry was determined through analogy with **3a**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

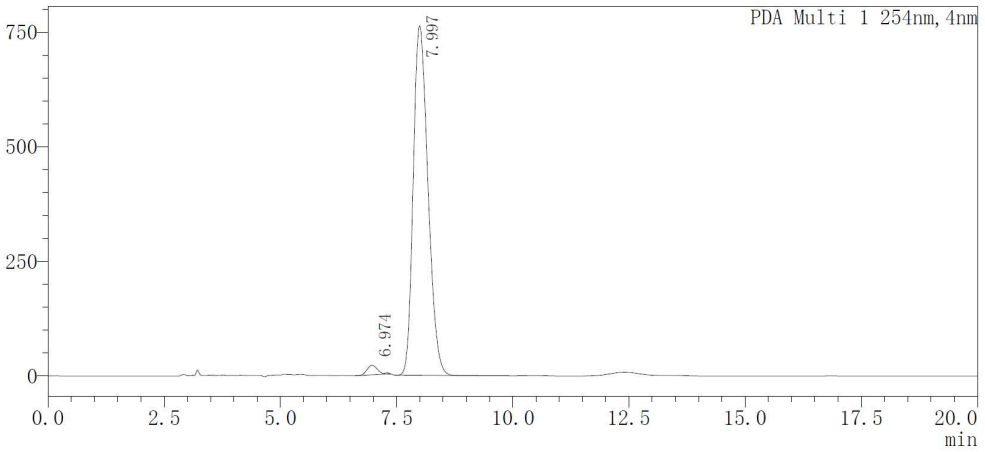
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.989	9032931	518701	0.000		M	
2	8.067	9423831	407904	0.000		V M	
总计		18456762	926604				

peak number ↑ retention time ↑ area ↑ height ↑

〈色谱图〉 ← HPLC chromatogram

mAU



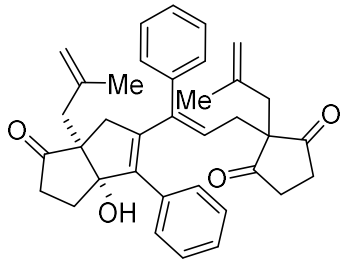
〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.974	335722	20815	0.000		M	
2	7.997	16810693	762338	0.000		M	
总计		17146416	783153				

peak number ↑ retention time ↑ area ↑ height ↑

2-((*E*)-3-((*3aS,6aS*)-3a-Hydroxy-6a-(2-methylallyl)-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-phenylallyl)-2-(2-methylallyl)cyclopentane-1,3-dione (**3w**)



Chemical Formula: $C_{36}H_{38}O_4$
Exact Mass: 534.2770

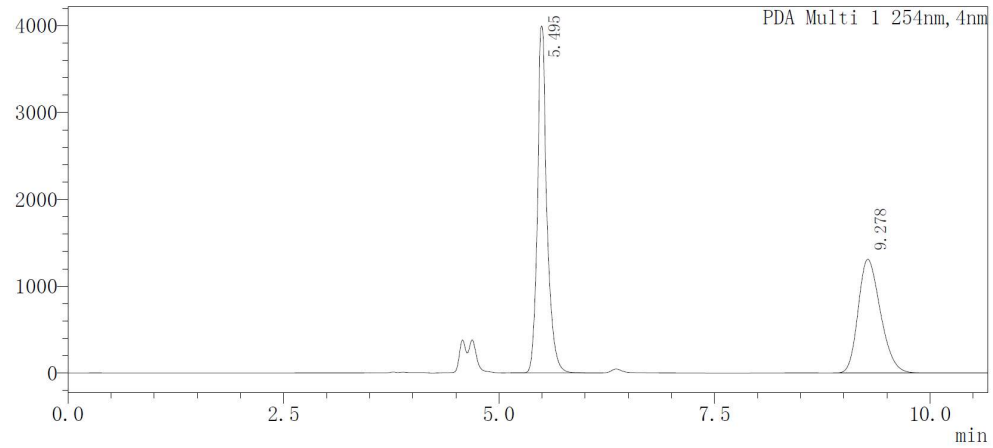
3w was prepared according to general procedure 2.1 using **1w** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **3w** as white solid (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.12 (m, 8H), 6.89-6.83 (m, 2H), 5.34 (t, *J* = 7.3 Hz, 1H), 4.85-4.81 (m, 1H), 4.79-4.76 (m, 1H), 4.70-4.64 (m, 1H), 4.41-4.35 (m, 1H), 2.69 (d, *J* = 16.8 Hz, 1H), 2.53-2.35 (m, 6H), 2.27-2.15 (m, 5H), 2.09-1.96 (m, 4H), 1.93-1.85 (m, 1H), 1.71 (s, 3H), 1.46 (dd, *J* = 1.3, 0.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.3, 216.3, 215.8, 144.5, 142.7, 141.0, 140.7, 140.3, 137.2, 135.3, 128.9, 128.7, 128.2, 128.1, 127.3, 127.1, 125.5, 115.1, 115.0, 93.0, 60.7, 59.6, 44.0, 42.4, 39.1, 36.8, 36.3, 36.1, 35.3, 29.5, 24.1, 24.0; HRMS: (ESI) calcd for $C_{36}H_{38}NaO_4^+$[M+Na]$^+$ 557.2662; found 557.2652. The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 5 min (major), 9 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ -102.0 (c 1.1, ^{i}PrOH) for 98%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.495	30470773	3994075	0.000		M	
2	9.278	23509272	1309814	0.000		M	
总计		53980045	5303889				

peak number

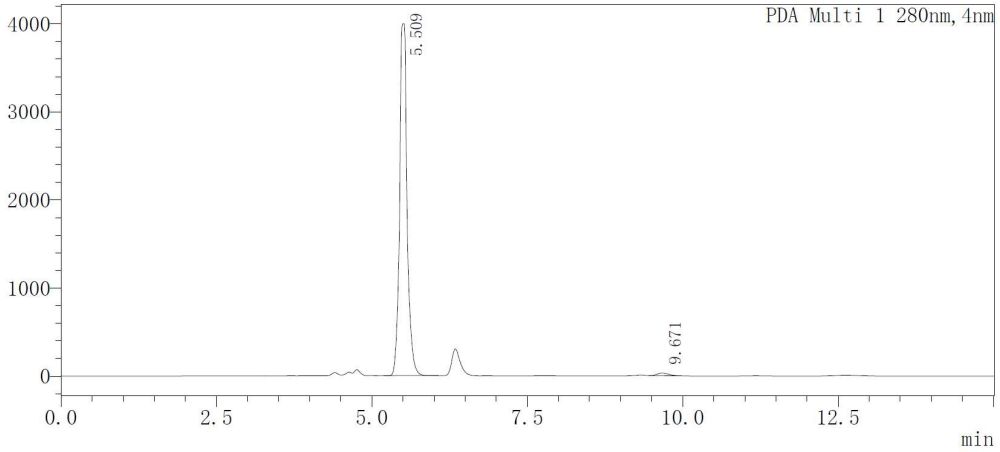
retention time

area

height

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 280nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.509	33381239	3994196	98.870		M	
2	9.671	381356	30112	1.130		M	
总计		33762594	4024307				

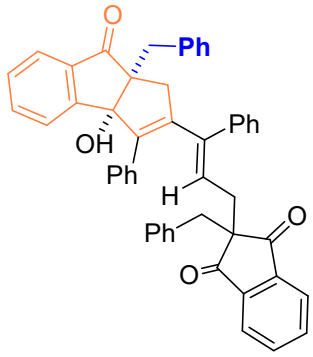
peak number

retention time

area

height

2-Benzyl-2-((*E*)-3-((3aS,8aS)-8a-benzyl-3a-hydroxy-8-oxo-3-phenyl-1,3a,8,8a-tetrahydrocyclopenta[*a*]inden-2-yl)-3-phenylallyl)-1*H*-indene-1,3(2*H*)-dione (**3x**)



Chemical Formula: $C_{50}H_{38}O_4$
Exact Mass: 702.2770

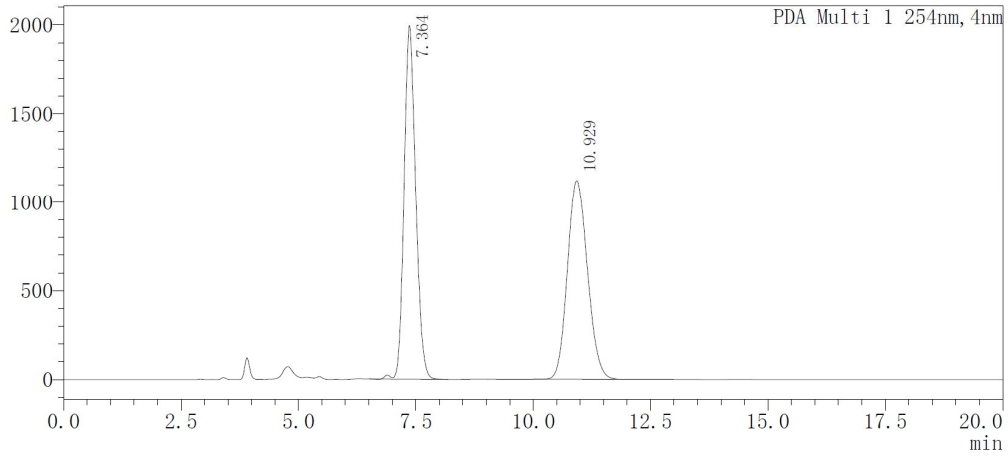
3x was prepared according to general procedure 2.1 using **1x** and was purified by silica gel column chromatography (PE/EtOAc = 12/1~10/1) to obtain **3x** as white solid (51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.69 (m, 2H), 7.67-7.61 (m, 3H), 7.31-7.27 (m, 2H), 7.15-7.10 (m, 5H), 7.09-7.05 (m, 3H), 7.02-6.98 (m, 3H), 6.95-6.89 (m, 3H), 6.80-6.76 (m, 3H), 6.74-6.69 (m, 4H), 5.50 (t, *J* = 7.3 Hz, 1H), 3.21 (d, *J* = 13.8 Hz, 1H), 3.01 (d, *J* = 13.8 Hz, 1H), 2.73-2.67 (m, 3H), 2.57 (d, *J* = 17.3 Hz, 1H), 2.44-2.38 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 202.9, 202.9, 154.3, 142.1, 141.9, 141.9, 141.8, 140.4, 137.4, 137.1, 135.5, 135.4, 135.4, 134.8, 134.2, 130.3, 129.9, 129.8, 128.9, 128.9, 127.8, 127.8, 127.8, 127.3, 126.8, 126.8, 126.4, 126.3, 126.2, 124.5, 123.3, 122.7, 92.5, 63.3, 59.6, 41.4, 39.4, 38.8, 34.5; HRMS: (ESI) calcd for $C_{50}H_{38}NaO_4^+$[M+Na]$^+$ 725.2662; found 725.2649. The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 7 min (major), 10 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ -27.4 (c 1.4, ^{i}PrOH) for 93%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.364	34263341	1994720	0.000		M	
2	10.929	33332914	1120417	0.000		M	
总计		67596255	3115137				

peak number

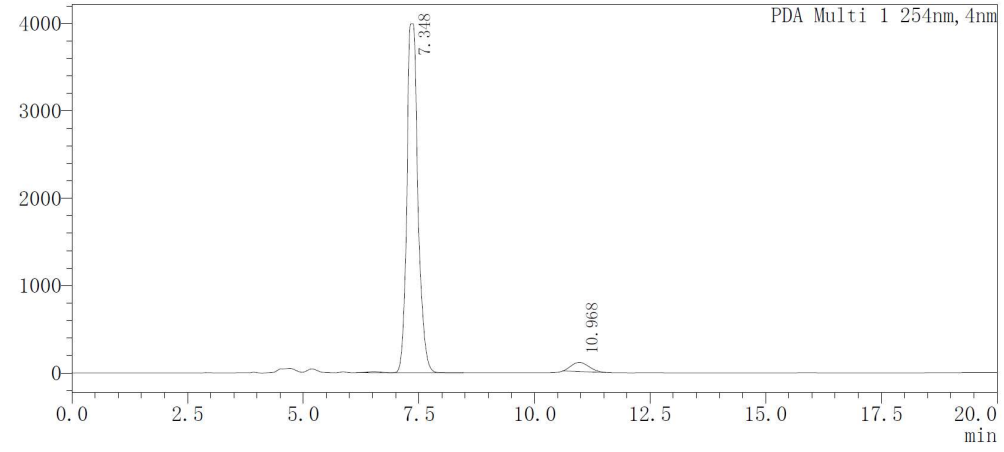
retention time

area

height

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.348	67078972	3996794	0.000		M	
2	10.968	2780663	104519	0.000		M	
总计		69859635	4101313				

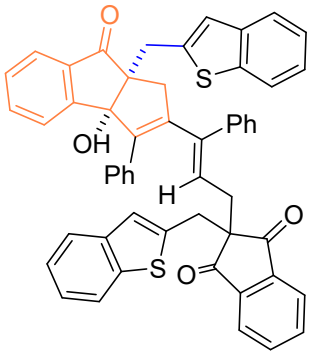
peak number

retention time

area

height

2-(Benzo[*b*]thiophen-2-ylmethyl)-2-((*E*)-3-((3aS,8aR)-8a-(benzo[*b*]thiophen-2-ylmethyl)-3a-hydroxy-8-oxo-3-phenyl-1,3a,8,8a-tetrahydrocyclopenta[*a*]inden-2-yl)-3-phenylallyl)-1*H*-indene-1,3(2*H*)-dione (**3y**)



Chemical Formula: $C_{54}H_{38}O_4S_2$
Exact Mass: 814.2212

3y was prepared according to general procedure 2.1 using **1y** and was purified by silica gel column chromatography (Toluene/EtOAc = 30/1~20/1) to obtain **3y** as white solid (57% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.73-7.69 (m, 2H), 7.65-7.58 (m, 3H), 7.54-7.48 (m, 2H), 7.37-7.32 (m, 2H), 7.30-7.26 (m, 1H), 7.25-7.21 (m, 1H), 7.19-7.15 (m, 1H), 7.14-7.07 (m, 5H), 7.02-6.94 (m, 3H), 6.89-6.85 (m, 2H), 6.82-6.78 (m, 1H), 6.73 (s, 1H), 6.63-6.58 (m, 2H), 5.56 (t, *J* = 7.3 Hz, 1H), 3.53 (d, *J* = 14.7 Hz, 1H), 3.41 (d, *J* = 14.9 Hz, 1H), 2.90 (s, 2H), 2.76 (d, *J* = 17.4 Hz, 1H), 2.68-2.61 (m, 2H), 2.36 (dd, *J* = 7.4, 1.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.6, 202.3, 202.1, 154.6, 141.70, 141.68, 141.53, 141.48, 140.8, 140.4, 139.9, 139.60, 139.58, 139.3, 138.5, 137.1, 135.68, 135.65, 134.9, 134.71, 134.67, 130.2, 129.2, 128.8, 127.8, 127.5, 127.1, 126.9, 125.6, 124.71, 124.65, 124.2, 124.0, 123.9, 123.7, 123.6, 123.1, 122.9, 121.84, 121.79, 92.3, 62.3, 59.1, 42.0, 34.8, 33.8, 32.9; HRMS: (ESI) calcd for $C_{54}H_{38}NaO_4S_2^+$ $[M+Na]^+$ 837.2104; found 837.2079.

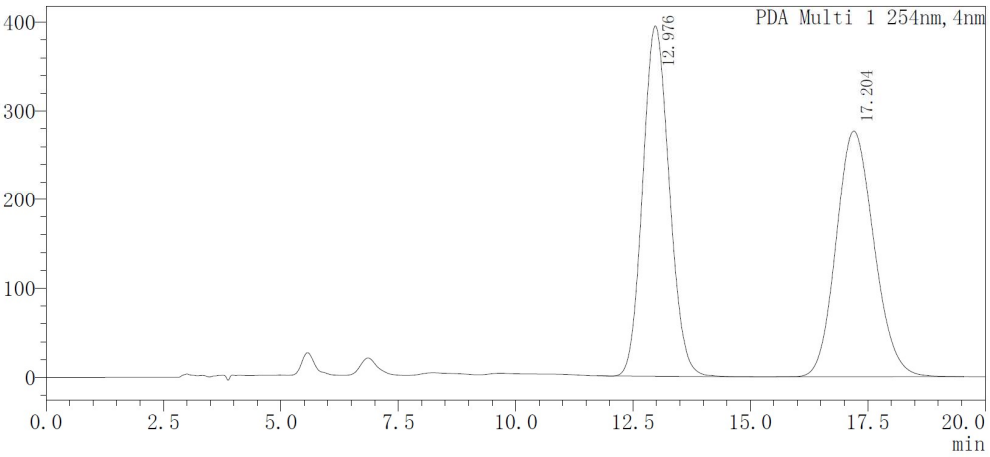
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 13 min (minor), 17 min (major).

Optical Rotation: $[\alpha]_D^{20}$ 13.7 (c 1.0, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with **3a**.

<色谱图>
mAU

HPLC chromatogram



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.976	15509019	394588	0.000		M	
2	17.204	15490950	276827	0.000		M	
总计		30999970	671415				

peak number

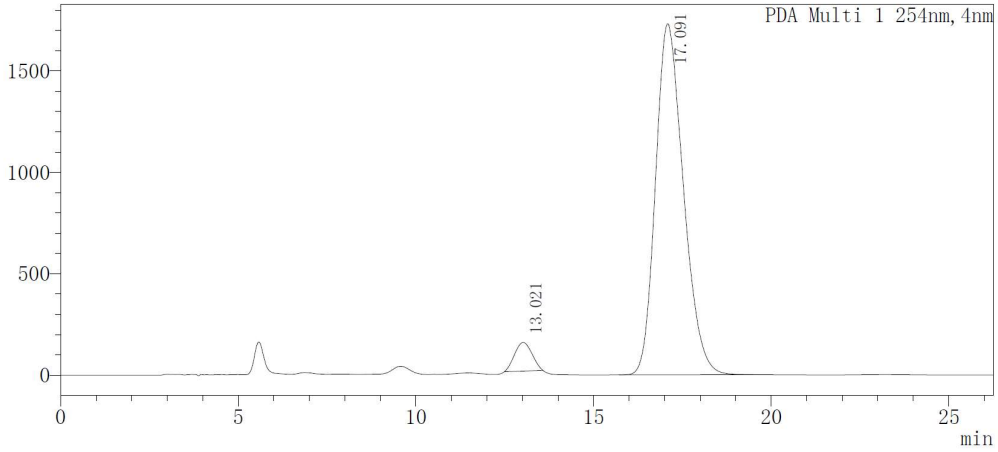
retention time

area

height

<色谱图>
mAU

HPLC chromatogram



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	13.021	4811156	141112	0.000		M	
2	17.091	94424825	1731895	0.000		M	
总计		99235981	1873007				

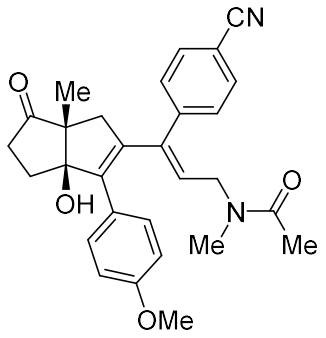
peak number

retention time

area

height

N-((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-*N*-methylacetamide (**5ba**)



Chemical Formula: $C_{29}H_{30}N_2O_4$
Exact Mass: 470.2206

5ba was prepared according to general procedure 2.2 using **1b** and **4a** and was purified by silica gel column chromatography (PE/EtOAc = 1/1~1/2.5) to obtain **5ba** as yellow oil (64% yield). ^{1}H NMR (400 MHz, $CDCl_3$, 50℃) δ 7.43-7.35 (m, 2H), 6.99-6.92 (m, 2H), 6.91-6.85 (m, 2H), 6.68-6.62 (m, 2H), 5.70-5.63 (m, 1H), 4.01-3.88 (m, 1H), 3.75 (s, 3H), 3.68 (dd, *J* = 15.0, 6.5 Hz, 1H), 2.88-2.79 (m, 1H), 2.62 (d, *J* = 11.2 Hz, 3H), 2.52 (d, J = 16.7 Hz, 1H), 2.48-2.38 (m, 1H), 2.11-2.02 (m, 2H), 1.96 (s, 3H), 1.88-1.82 (m, 1H), 1.78 (s, 1H), 1.15 (d, *J* = 4.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$, 25℃) δ 221.2, 221.1, 170.4, 170.0, 159.0, 158.8, 143.6, 142.8, 142.5, 142.2, 142.1, 141.5, 139.2, 138.7, 131.8, 131.6, 130.7, 130.1, 129.9, 129.8, 129.6, 127.2, 126.8, 118.6, 118.3, 113.6, 113.4, 111.2, 110.8, 92.2, 92.2, 56.0, 55.3, 49.0, 45.6, 44.2, 44.1, 36.5, 36.5, 35.6, 33.1, 29.5, 29.4, 21.6, 21.2, 15.3, 15.2; HRMS: (ESI) calcd for $C_{29}H_{31}N_2O_4^+$ $[M+H]^+$ 471.2278; found 471.2270.

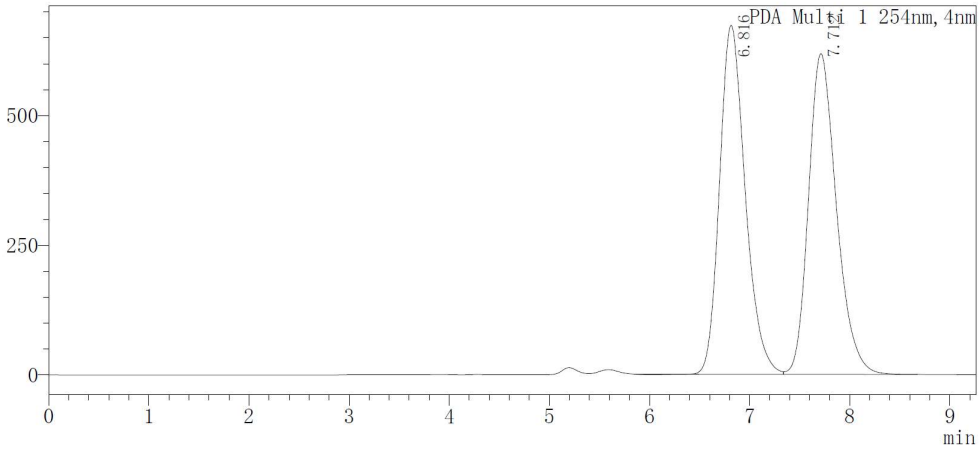
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 6.8 min (major), 7.7 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -41.0 (c 1.2, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of compound **9**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.816	11980301	673077	0.000		M	
2	7.712	11998151	618544	0.000		V M	
总计		23978452	1291621				

peak number ← 峰号

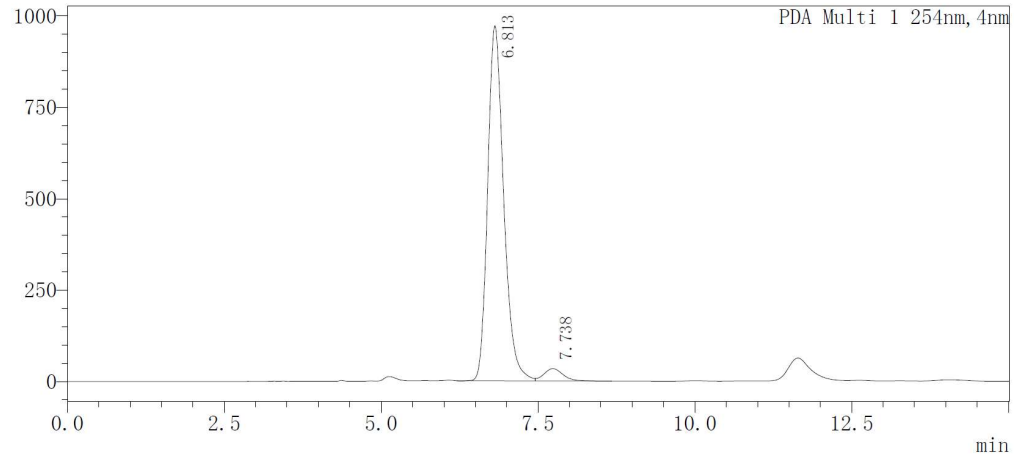
retention time ← 保留时间

area ← 面积

height ← 高度

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.813	17287186	971897	0.000		M	
2	7.738	715640	33847	0.000		V M	
总计		18002827	1005744				

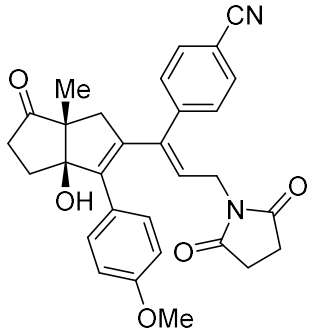
peak number ← 峰号

retention time ← 保留时间

area ← 面积

height ← 高度

4-((*E*)-3-(2,5-dioxopyrrolidin-1-yl)-1-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)prop-1-en-1-yl)benzonitrile (**5bd**)



Chemical Formula: $C_{30}H_{28}N_2O_5$
Exact Mass: 496.1998

5bd was prepared according to general procedure 2.2 using **1b** and **4d** and was purified by silica gel column chromatography (PE/EtOAc = 8/1~1/1) to obtain **5bd** as yellow oil (55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 5.54 (t, *J* = 6.8 Hz, 1H), 4.00-3.84 (m, 2H), 3.76 (s, 3H), 2.82 (d, *J* = 16.8 Hz, 1H), 2.60 (s, 4H), 2.52 (d, *J* = 16.8 Hz, 1H), 2.47-2.36 (m, 1H), 2.08-1.95 (m, 2H), 1.93-1.78 (m, 2H), 1.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.2, 176.4, 158.8, 143.4, 142.2, 141.6, 139.3, 131.6, 130.1, 129.9, 127.4, 127.0, 118.6, 113.4, 110.9, 92.2, 55.9, 55.3, 44.0, 37.2, 36.5, 29.4, 28.1, 15.2; HRMS: (ESI) calcd for $C_{30}H_{28}N_2NaO_5^+$ $[M+Na]^+$ 519.1882; found 519.1890.

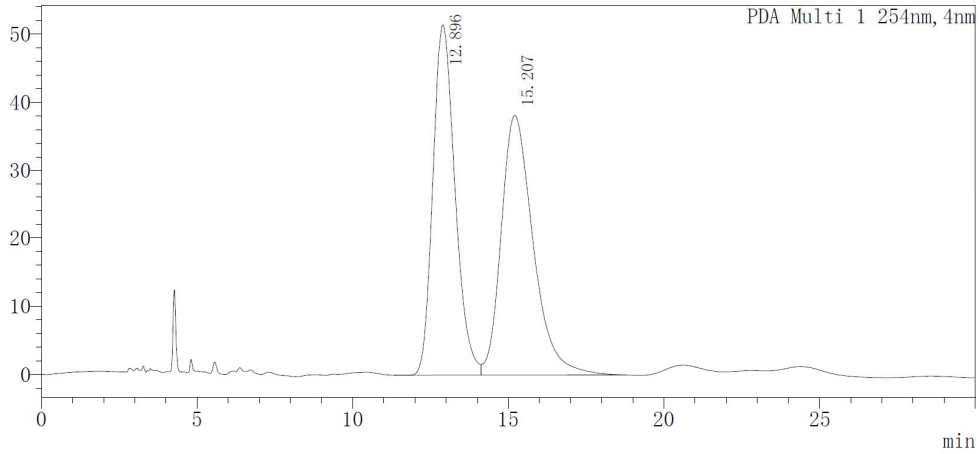
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 12 min (major), 15 min (minor).

Optical Rotation: $[\alpha]_D^{27}$ -63.0 (c 1.1, ^{i}PrOH) for 97%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of compound **9**.

〈色谱图〉 HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.896	2547295	51463	0.000		M	
2	15.207	2727490	38198	0.000		V M	
总计		5274785	89661				

peak number

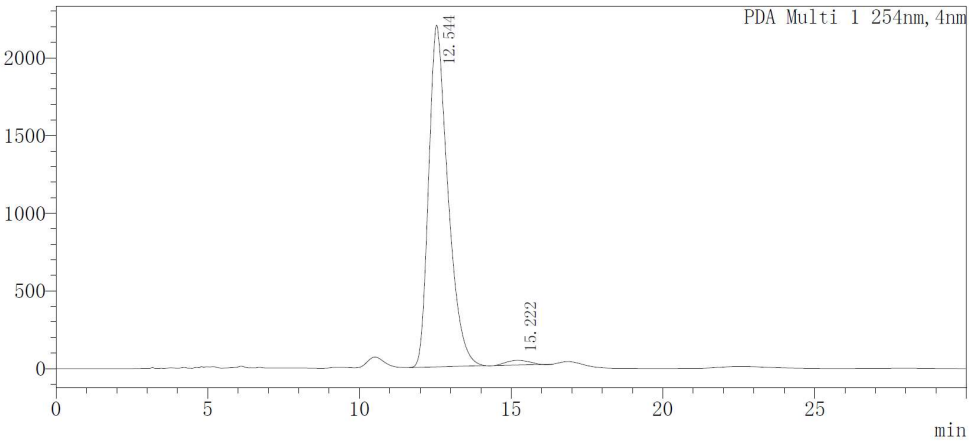
retention time

area

height

〈色谱图〉 HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.544	97012986	2199122	0.000		M	
2	15.222	1588437	29823	0.000		M	
总计		98601423	2228945				

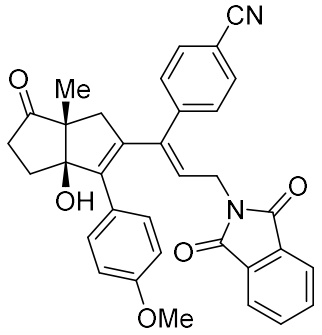
peak number

retention time

area

height

4-((*E*)-3-(1,3-dioxoisoindolin-2-yl)-1-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)prop-1-en-1-yl)benzonitrile (**5be**)



Chemical Formula: $C_{34}H_{28}N_2O_5$
Exact Mass: 544.1998

5be was prepared according to general procedure 2.2 using **1b** and **4e** and was purified by silica gel column chromatography (PE/EtOAc = 8/1~1/1) to obtain **5be** as yellow oil (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.75-7.67 (m, 2H), 7.46-7.38 (m, 2H), 7.12-7.07 (m, 2H), 6.88-6.78 (m, 2H), 6.57-6.46 (m, 2H), 5.70 (t, *J* = 6.8 Hz, 1H), 4.19-4.02 (m, 2H), 3.63 (s, 3H), 2.83 (d, *J* = 16.8 Hz, 1H), 2.53 (d, *J* = 16.7 Hz, 1H), 2.44-2.34 (m, 1H), 2.07-1.94 (m, 2H), 1.90-1.78 (m, 2H), 1.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.1, 167.6, 158.7, 143.3, 142.3, 141.5, 139.1, 134.1, 131.9, 131.6, 123.0, 129.9, 128.0, 126.8, 123.2, 118.6, 113.3, 110.9, 92.2, 55.9, 55.1, 44.0, 36.5, 36.4, 29.4, 15.3; HRMS: (ESI) calcd for $C_{34}H_{28}N_2NaO_5^+$ $[M+Na]^+$ 567.1882; found 567.1890.

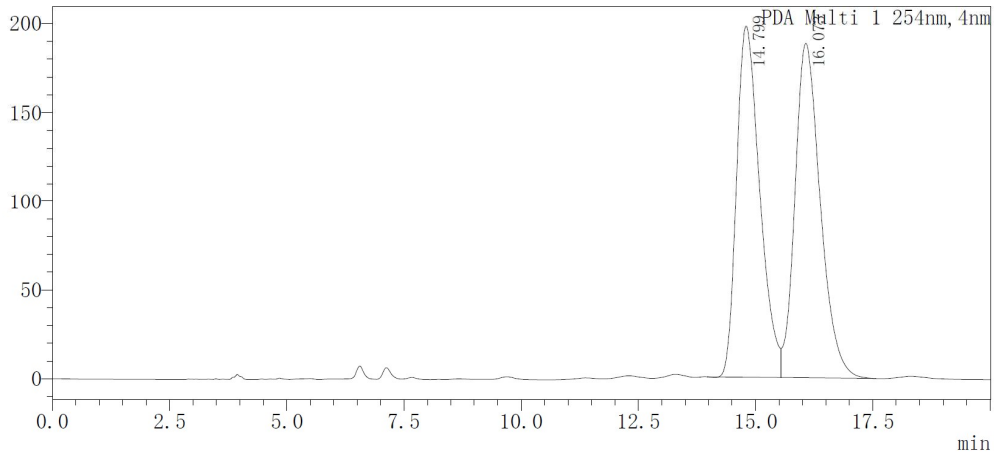
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 14 min (minor), 16 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -98.4 (c 1.4, ^{i}PrOH) for 95%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	14.799	6810548	197687	0.000		M	
2	16.073	7103191	188381	0.000		V M	
总计		13913739	386068				

peak number

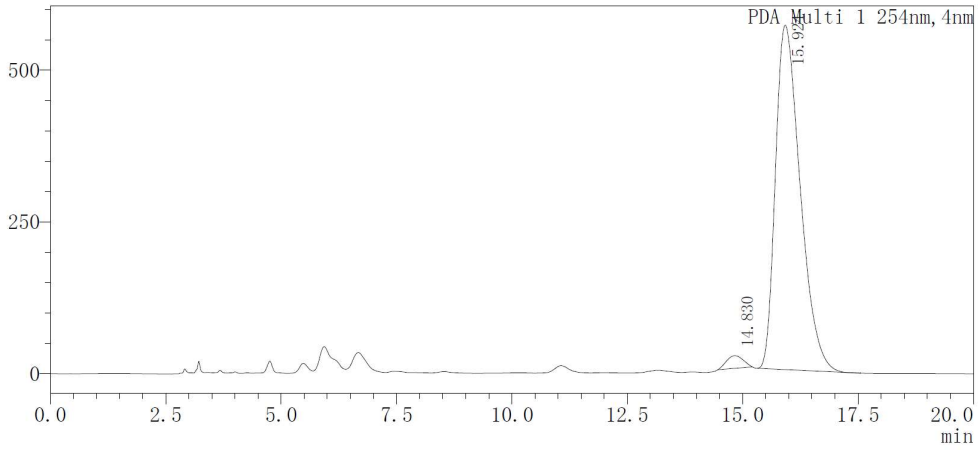
retention time

area

height

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	14.830	525104	20849	0.000		M	
2	15.924	21158863	567356	0.000		M	
总计		21683967	588205				

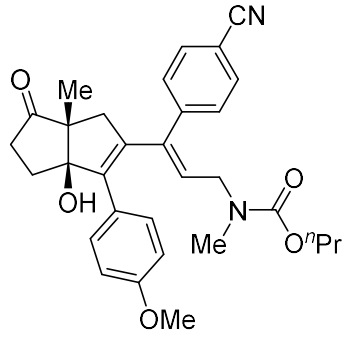
peak number

retention time

area

height

propyl ((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)(methyl)carbamate (**5bf**)



Chemical Formula: $C_{31}H_{34}N_2O_5$
Exact Mass: 514.2468

5bf was prepared according to general procedure 2.2 using **1b** and **4f** and was purified by silica gel column chromatography (PE/EtOAc = 8/1~1/1) to obtain **5bf** as yellow oil (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 6.98-6.92 (m, 2H), 6.89-6.85 (m, 2H), 6.65-6.60 (m, 2H), 5.73 (t, *J* = 6.7 Hz, 1H), 3.96 (s, 2H), 3.89-3.78 (m, 1H), 3.75 (s, 3H), 3.60 (dd, *J* = 16.0, 7.2 Hz, 1H), 2.87 (d, *J* = 16.7 Hz, 1H), 2.59-2.53 (m, 4H), 2.50-2.41 (m, 1H), 2.10-1.67 (m, 6H), 1.15 (s, 3H), 0.94-0.85 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.3, 158.8, 142.6, 142.0, 138.5, 131.5, 131.1, 130.7, 130.0, 129.9, 129.7, 127.1, 118.6, 113.4, 110.7, 92.2, 67.1, 55.9, 55.2, 47.1, 44.2, 36.5, 29.7, 29.4, 22.3, 15.3, 10.4; HRMS: (ESI) calcd for $C_{31}H_{35}N_2O_5^+$ $[M+H]^+$ 515.2540; found 515.2530.

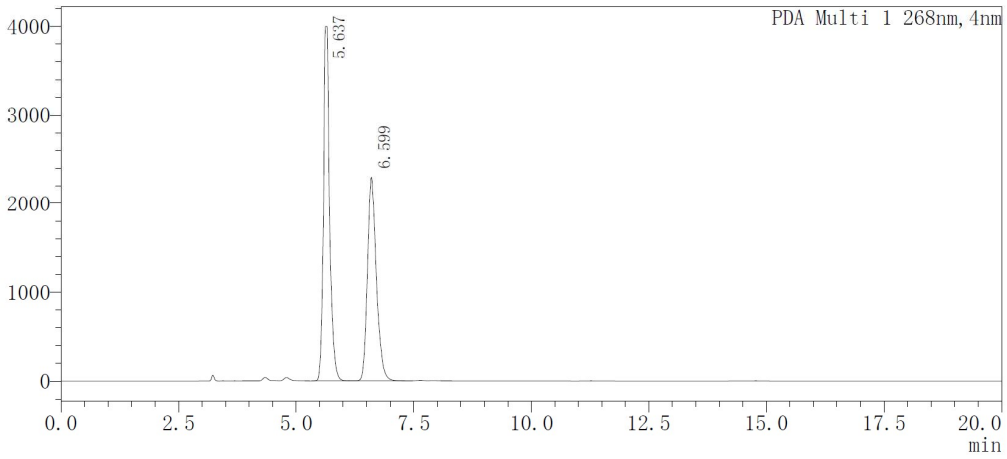
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 5.6 min (minor), 6.6 min (major).

Optical Rotation: $[\alpha]_D^{27}$ -79.7 (c 0.6, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 268nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.637	36359915	3995294	0.000		M	
2	6.599	30100481	2295507	0.000		M	
总计		66460396	6290801				

peak number

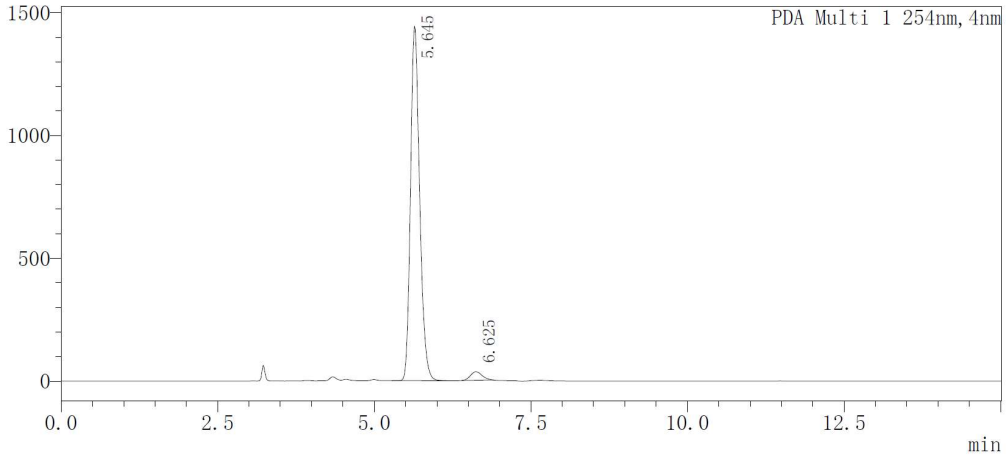
retention time

area

height

<色谱图> HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.645	14680673	1444069	0.000		M	
2	6.625	449936	34735	0.000		M	
总计		15130610	1478804				

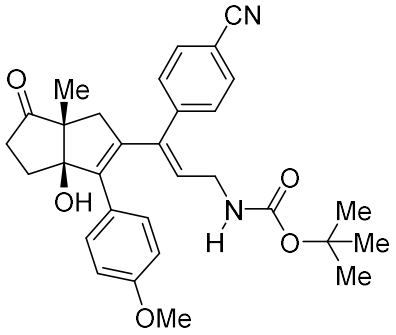
peak number

retention time

area

height

tert-butyl ((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)carbamate (**5bg**)



Chemical Formula: $C_{31}H_{34}N_2O_5$
Exact Mass: 514.2468

5bg was prepared according to general procedure 2.2 using **1b** and **4g** and was purified by silica gel column chromatography (PE/EtOAc = 8/1~2/1) to obtain **5bg** as blown oil (46% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.32 (m, 2H), 6.94-6.90 (m, 2H), 6.87-6.82 (m, 2H), 6.63-6.58 (m, 2H), 5.76 (t, *J* = 6.8 Hz, 1H), 4.38 (s, 1H), 3.74 (s, 3H), 3.67-3.59 (m, 1H), 3.53-3.46 (m, 1H), 2.89 (d, *J* = 16.7 Hz, 1H), 2.58 (d, *J* = 16.7 Hz, 1H), 2.46-2.39 (m, 1H), 2.07-1.98 (m, 2H), 1.94 (s, 1H), 1.88-1.81 (m, 1H), 1.40 (s, 9H), 1.16 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.3, 158.8, 155.5, 142.8, 142.6, 141.8, 137.9, 131.8, 131.5, 130.0, 129.7, 127.0, 118.6, 113.4, 110.6, 92.3, 79.7, 55.9, 55.2, 44.2, 39.1, 36.5, 29.4, 28.3, 15.3; HRMS: (ESI) calcd for $C_{31}H_{35}N_2O_5^+$[M+H]$^+$ 515.2540; found 515.2556.

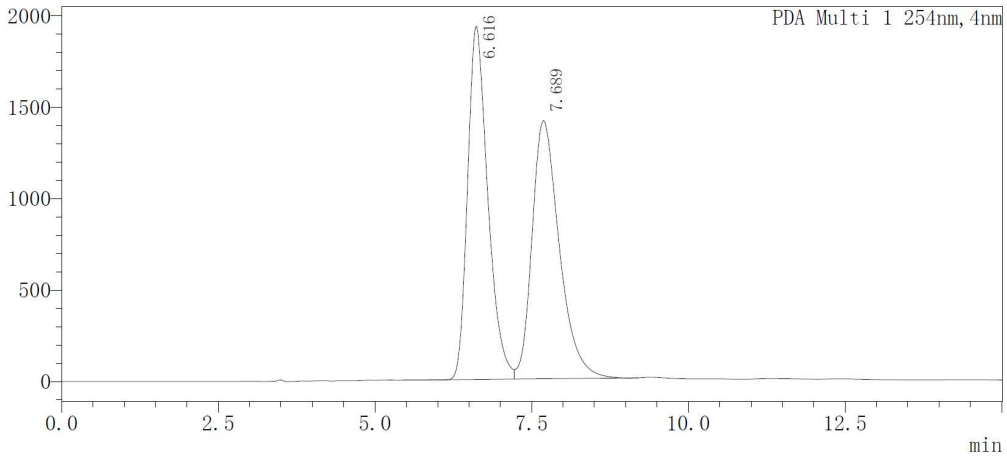
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 6.6 min (major), 7.6 min (minor).

Optical Rotation: $[\alpha]_D^{29}$ -57.1 (c 0.9, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.616	43433171	1932063	0.000		M	
2	7.689	42788689	1411683	0.000		V M	
总计		86221860	3343747				

peak number

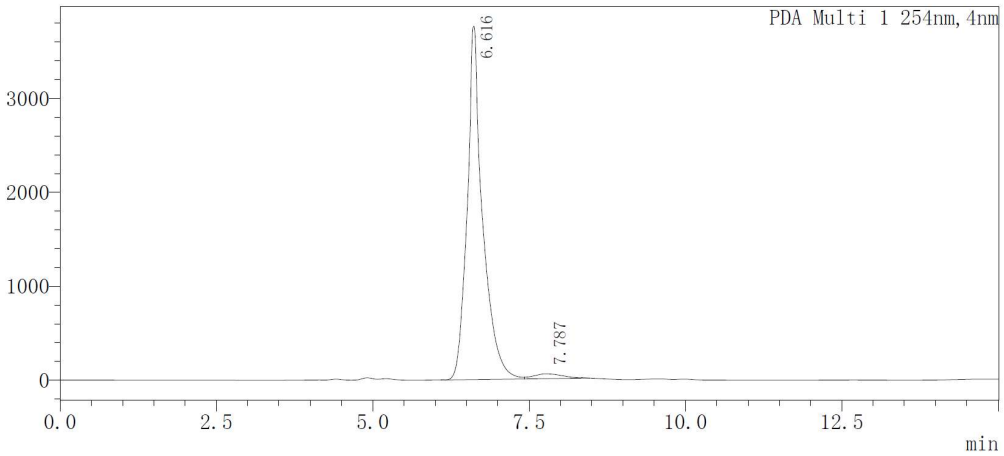
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.616	64971184	3764070	0.000		M	
2	7.787	1693462	53356	0.000		V M	
总计		66664646	3817426				

peak number

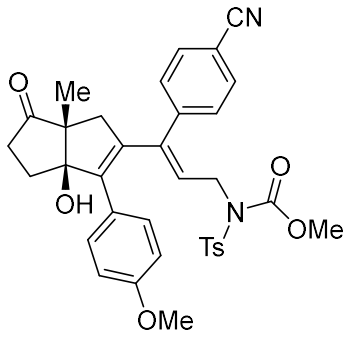
retention time

area

height

methyl ((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)(tosyl)carbamate

(**5bh**)



Chemical Formula: $C_{35}H_{34}N_2O_7S$
Exact Mass: 626.2087

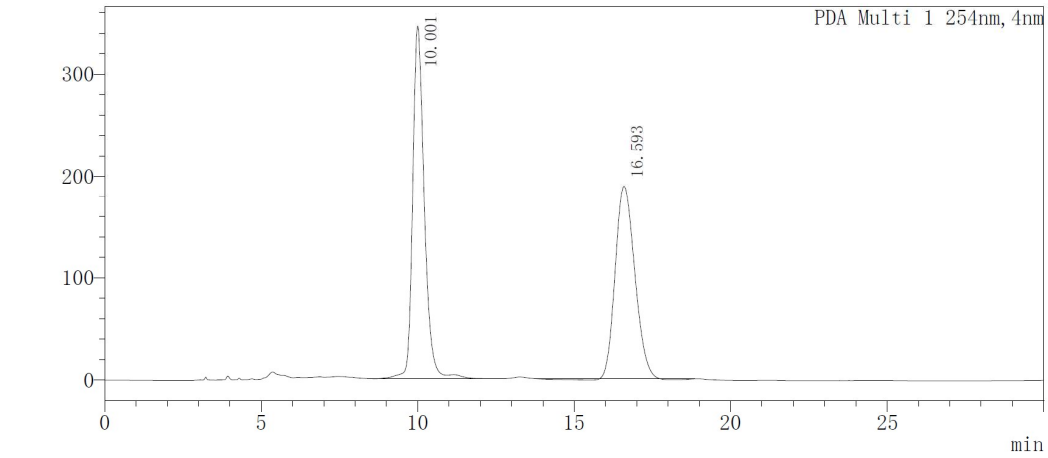
5bh was prepared according to general procedure 2.2 using **1b** and **4h** and was purified by silica gel column chromatography (PE/EtOAc = 5/1~2/1) to obtain **5bh** as yellow oil (30% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.67 (m, 2H), 7.38-7.35 (m, 2H), 7.31-7.28 (m, 2H), 7.01-6.97 (m, 2H), 6.84-6.80 (m, 2H), 6.60-6.57 (m, 2H), 5.82 (dd, *J* = 6.9, 5.9 Hz, 1H), 4.31 (dd, *J* = 16.7, 5.9 Hz, 1H), 4.21 (dd, *J* = 16.6, 6.9 Hz, 1H), 3.73 (s, 3H), 3.60 (s, 3H), 2.91 (d, *J* = 16.6 Hz, 1H), 2.60 (d, *J* = 16.6 Hz, 1H), 2.48-2.43 (m, 1H), 2.44 (s, 3H), 2.07-2.00 (m, 2H), 1.88-1.83 (m, 1H), 1.79 (s, 1H), 1.18 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.1, 158.8, 152.4, 144.9, 143.3, 142.5, 141.2, 138.6, 136.2, 131.5, 130.0, 130.0, 129.8, 129.4, 128.2, 126.8, 118.6, 113.4, 110.8, 92.4, 55.8, 55.2, 53.8, 45.6, 44.1, 36.5, 29.5, 21.7, 15.3; HRMS: (ESI) calcd for $C_{35}H_{35}N_2O_7S^+$ $[M+H]^+$ 627.2159; found 627.2151. The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 10 min (minor), 16 min (major).

Optical Rotation: $[\alpha]_D^{31}$ -19.0 (c 0.8, ^{i}PrOH) for 95%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.001	8948637	345342	0.000		M	
2	16.593	8127679	189038	0.000		M	
总计		17076315	534380				

peak number

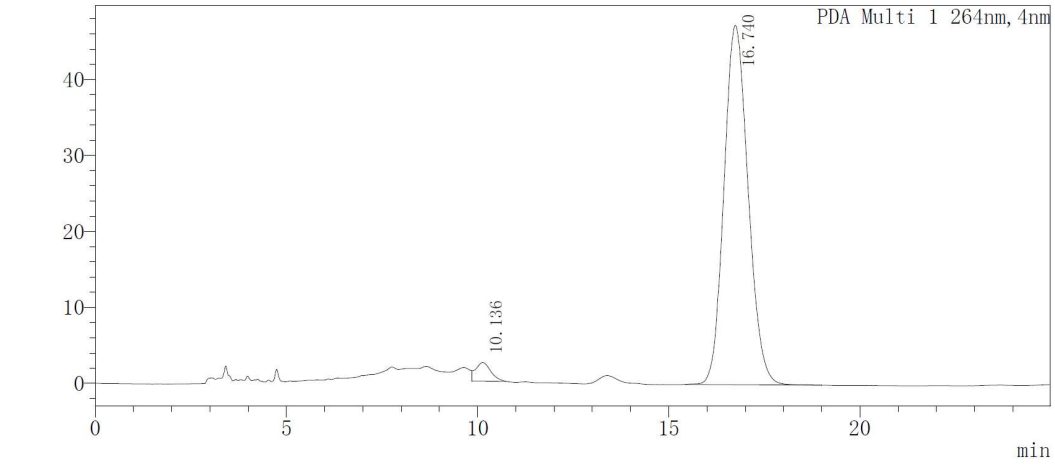
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 264nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.136	66095	2438	0.000		M	
2	16.740	2078296	47308	0.000		M	
总计		2144392	49746				

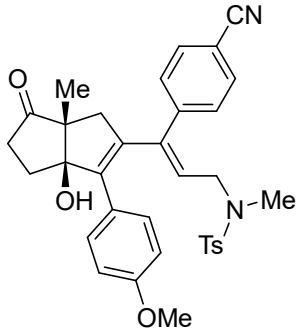
peak number

retention time

area

height

N-((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-*N*,4-dimethylbenzenesulfonamide (**5bi**)



Chemical Formula: $C_{34}H_{34}N_2O_5S$
Exact Mass: 582.2188

5bi was prepared according to general procedure 2.2 using **1b** and **4i** and was purified by silica gel column chromatography (PE/EtOAc = 5/1~2/1) to obtain **5bi** (72% yield) and **5bi'** (18% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55-7.50 (m, 2H), 7.37-7.32 (m, 2H), 7.28-.26 (m, 2H), 6.92-6.86 (m, 2H), 6.84-6.79 (m, 2H), 6.64-6.58 (m, 2H), 5.66 (dd, *J* = 7.4, 6.1 Hz, 1H), 3.74 (s, 3H), 3.63 (dd, *J* = 15.4, 6.1 Hz, 1H), 3.36 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.76 (d, *J* = 16.7 Hz, 1H), 2.47 (d, *J* = 16.6 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 2.05-1.98 (m, 2H), 1.93-1.80 (m, 2H), 1.14 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.0, 158.9, 143.6, 143.3, 142.1, 141.7, 139.6, 134.4, 131.6, 130.0, 129.7, 129.6, 129.4, 127.3, 126.9, 118.5, 113.5, 110.9, 92.2, 55.8, 55.3, 48.3, 44.1, 36.4, 34.5, 29.4, 21.5, 15.3; HRMS: (ESI) calcd for $C_{34}H_{35}N_2O_5S^+$ $[M+H]^+$ 583.2261; found 583.2257.

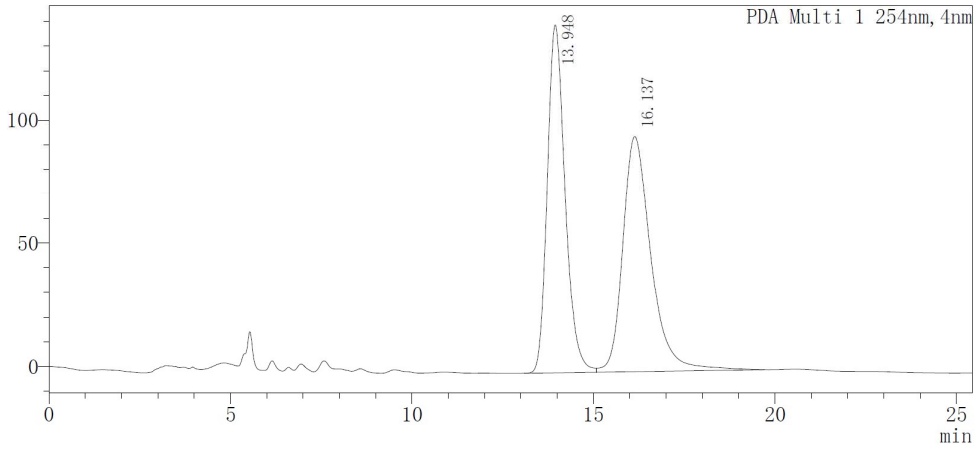
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 13 min (minor), 16 min (major).

Optical Rotation: $[\alpha]_D^{29}$ -14.1 (c 1.7, ^{i}PrOH) for 97%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	13.948	4818122	141101	0.000			
2	16.137	5162468	95501	0.000		V	
总计		9980590	236603				

peak number

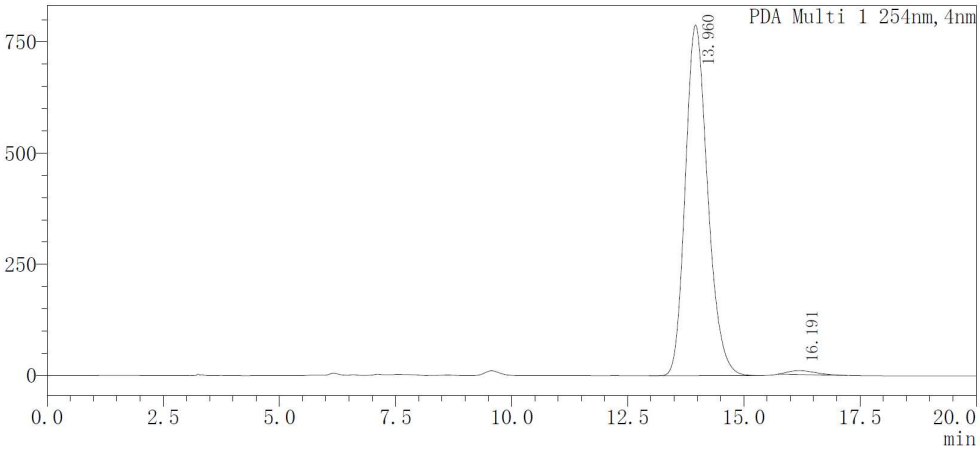
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	13.960	26479203	788574	0.000		M	
2	16.191	360556	8682	0.000		M	
总计		26839759	797256				

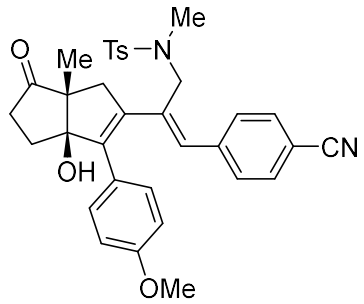
peak number

retention time

area

height

N-((*Z*)-3-(4-cyanophenyl)-2-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-*N*,4-dimethylbenzenesulfonamide (**5bi'**)

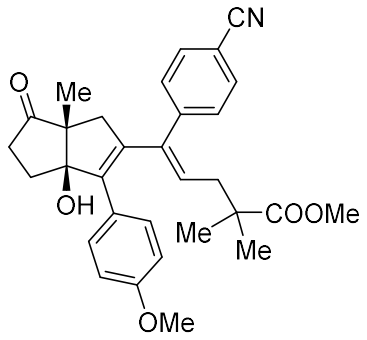


Chemical Formula: $C_{34}H_{34}N_2O_5S$
Exact Mass: 582.2188

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 6.75 (s, 1H), 3.86 (s, 3H), 3.53 (d, *J* = 14.0 Hz, 1H), 3.42 (d, *J* = 14.0 Hz, 1H), 3.02 (d, *J* = 17.0 Hz, 1H), 2.78 (d, *J* = 16.9 Hz, 1H), 2.45-2.41 (m, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 2.22-2.17 (m, 1H), 2.07-2.02 (m, 1H), 2.01-1.95 (m, 1H), 1.89-1.82 (m, 1H), 1.21 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 222.7, 159.2, 143.7, 142.0, 141.9, 140.5, 137.5, 134.2, 132.7, 132.2, 130.1, 129.7, 129.4, 127.5, 127.1, 118.5, 113.6, 111.1, 92.2, 56.9, 55.3, 48.0, 46.8, 36.3, 34.8, 28.0, 21.5, 15.2; HRMS: (ESI) calcd for $C_{34}H_{35}N_2O_5S^+[M+H]^+$ 583.2261; found 583.2274.

methyl (*E*)-5-(4-cyanophenyl)-5-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-2,2-dimethylpent-4-enoate

(**5bj**)



Chemical Formula: $C_{31}H_{33}NO_5$
Exact Mass: 499.2359

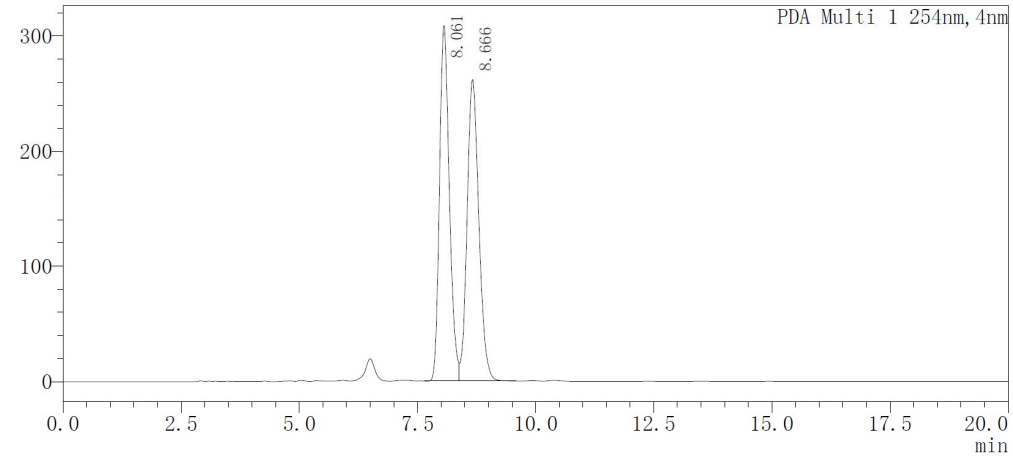
5bj was prepared according to general procedure 2.2 using **1b** and **4j** and was purified by silica gel column chromatography (PE/EtOAc = 5/1~4/1) to obtain **5bj** as yellow oil (67% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 6.94-6.89 (m, 2H), 6.87-6.80 (m, 2H), 6.67-6.61 (m, 2H), 5.74 (dd, *J* = 8.3, 6.7 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H), 2.83 (d, *J* = 16.7 Hz, 1H), 2.53 (d, *J* = 16.7 Hz, 1H), 2.46-2.40 (m, 1H), 2.15 (dd, *J* = 14.9, 6.7 Hz, 1H), 2.08-2.00 (m, 3H), 1.87-1.80 (m, 1H), 1.75 (s, 1H), 1.15 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.4, 177.4, 158.8, 143.7, 142.7, 141.5, 138.0, 131.5, 130.1, 130.0, 127.4, 118.8, 113.5, 110.3, 92.3, 55.8, 55.3, 51.8, 44.3, 42.4, 39.1, 36.5, 29.4, 25.0, 24.7, 15.3; HRMS: (ESI) calcd for $C_{31}H_{37}N_2O_5^+$[M+NH_4]$^+$ 517.2697; found 517.2684. The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 8.0 min (major), 8.6 min (minor).

Optical Rotation: $[\alpha]_D^{29}$ -100.1 (c 1.3, ^{i}PrOH) for 95%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.061	4486430	308688	0.000		M	
2	8.666	4530060	261789	0.000		V M	
总计		9016489	570477				

peak number

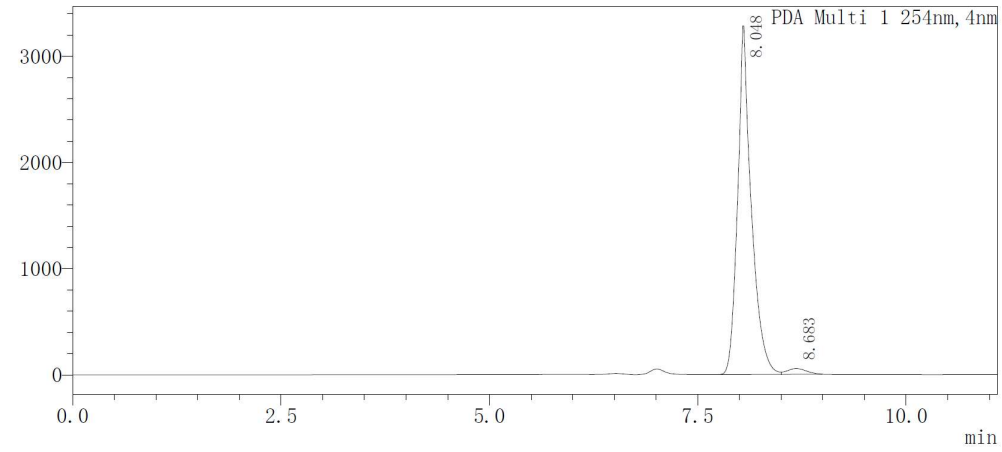
retention time

area

height

〈色谱图〉 ← HPLC chromatogram

mAU



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	8.048	37487169	3284252	0.000		M	
2	8.683	868332	54049	0.000		V M	
总计		38355501	3338301				

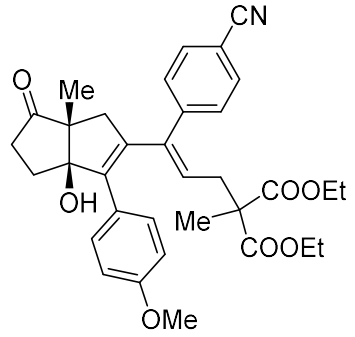
peak number

retention time

area

height

diethyl 2-((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)-2-methylmalonate (**5bk**)



Chemical Formula: $C_{34}H_{37}NO_7$
Exact Mass: 571.2570

5bk was prepared according to general procedure 2.2 using **1b** and **4k** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~2/1) to obtain **5bk** as yellow oil (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.31 (m, 2H), 6.92-6.87 (m, 2H), 6.83-6.79 (m, 2H), 6.63-6.58 (m, 2H), 5.71 (dd, *J* = 8.1, 6.8 Hz, 1H), 4.14-4.02 (m, 4H), 3.74 (s, 3H), 2.84 (d, *J* = 16.7 Hz, 1H), 2.53 (d, *J* = 16.7 Hz, 1H), 2.49-2.35 (m, 3H), 2.04-1.93 (m, 3H), 1.87-1.78 (m, 1H), 1.24 (s, 2H), 1.21-1.15 (m, 6H), 1.14 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 171.4, 171.4, 158.8, 143.3, 142.4, 142.0, 139.0, 131.5, 130.0, 129.9, 129.6, 127.2, 118.7, 113.4, 110.3, 92.2, 61.4, 61.4, 55.8, 55.2, 53.2, 44.3, 36.5, 34.7, 29.4, 19.7, 15.3, 14.0, 13.9; HRMS: (ESI) calcd for $C_{34}H_{37}NO_7Na^+$ $[M+Na]^+$ 594.2462; found 594.2452.

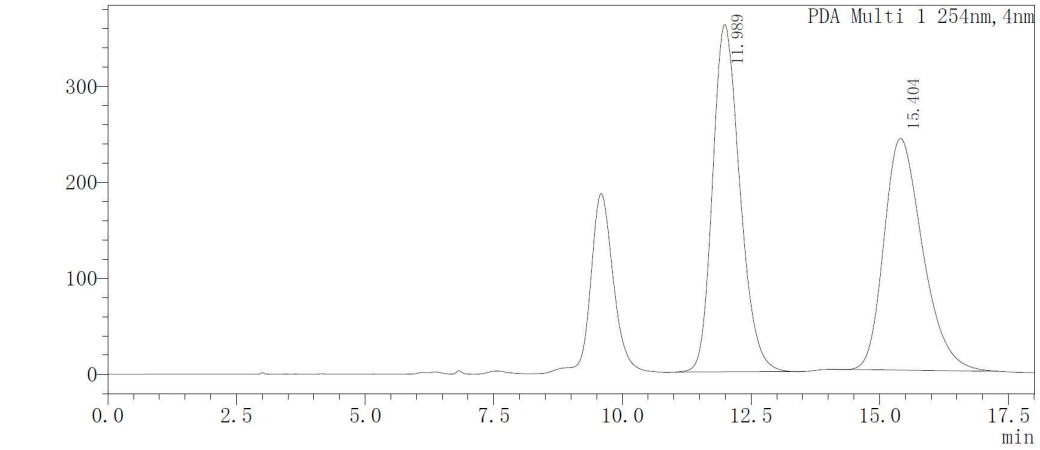
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 90/10 as eluent, 254 nm, 1 mL/min. tR = 12 min (minor), 15 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -9.4 (c 0.7, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图>
mAU

HPLC chromatogram



<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.989	13357556	361706	0.000		M	
2	15.404	12644370	241410	0.000		M	
总计		26001925	603116				

peak number

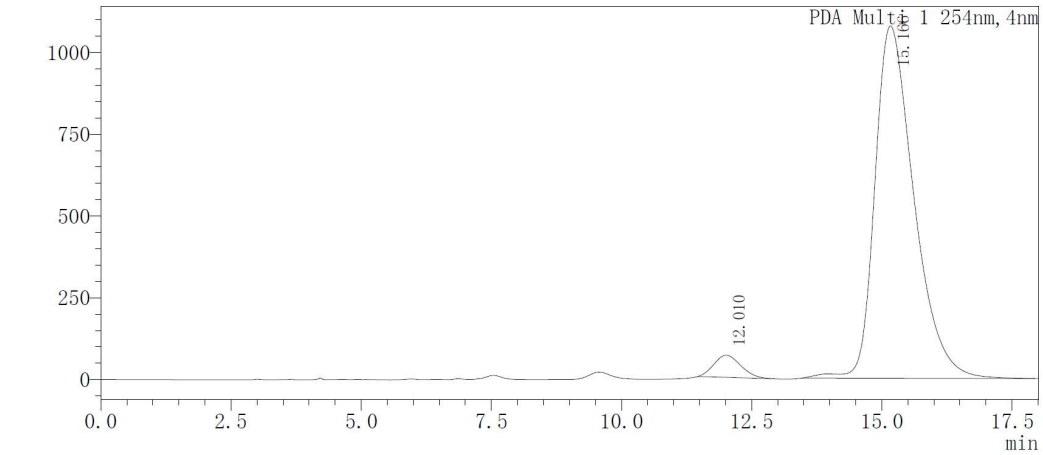
retention time

area

height

<色谱图>
mAU

HPLC chromatogram



<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	12.010	2419969	67590	0.000		M	
2	15.166	56360081	1078101	0.000		M	
总计		58780050	1145692				

peak number

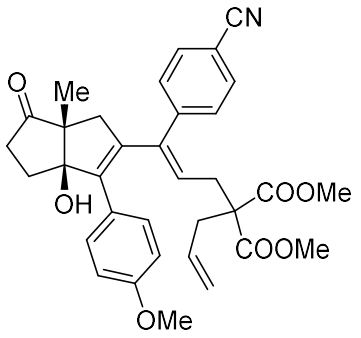
retention time

area

height

dimethyl 2-allyl-2-((*E*)-3-(4-cyanophenyl)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)allyl)malonate

(**5bl**)



Chemical Formula: $C_{34}H_{35}NO_7$
Exact Mass: 569.2414

5bl was prepared according to general procedure 2.2 using **1b** and **4l** and was purified by silica gel column chromatography (PE/EtOAc = 5/1~3/1) to obtain **5bl** as yellow oil (70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2H), 6.94-6.90 (m, 2H), 6.87-6.82 (m, 2H), 6.67-6.61 (m, 2H), 5.63 (dd, *J* = 8.3, 6.6 Hz, 1H), 5.32-5.20 (m, 1H), 4.93-4.83 (m, 2H), 3.74 (s, 3H), 3.65 (s, 3H), 3.59 (s, 3H), 2.81 (d, *J* = 16.7 Hz, 1H), 2.53-2.29 (m, 6H), 2.06-1.93 (m, 3H), 1.87-1.78 (m, 1H), 1.14 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 170.7, 170.7, 158.8, 143.1, 142.4, 142.1, 139.1, 131.7, 131.5, 130.0, 129.9, 128.9, 127.2, 119.3, 118.7, 113.6, 110.4, 92.2, 57.3, 55.8, 55.2, 52.5, 52.4, 44.3, 36.8, 36.5, 31.7, 29.4, 15.3; HRMS: (ESI) calcd for $C_{34}H_{35}NO_7Na^+$ $[M+Na]^+$ 592.2306; found 592.2317.

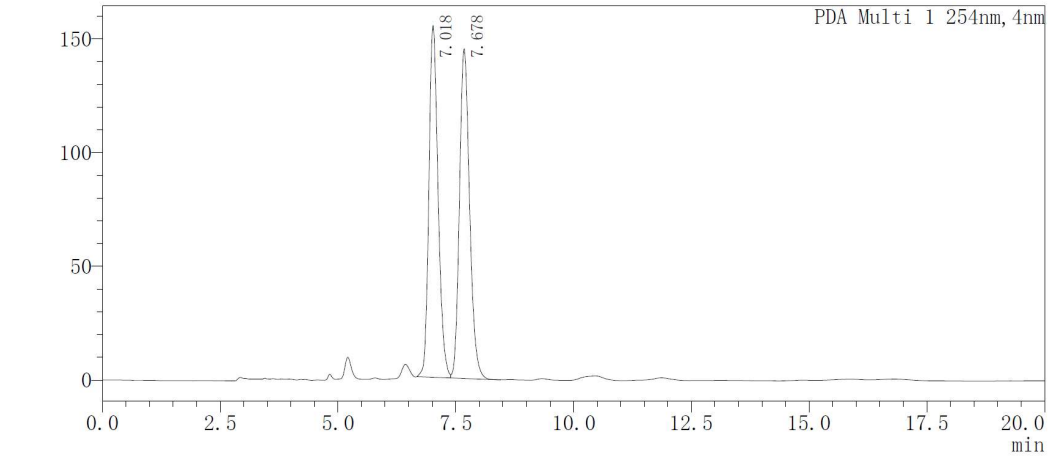
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 7.0 min (minor), 7.6 min (major).

Optical Rotation: $[\alpha]_D^{28}$ 2.8 (c 1.6, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉

HPLC chromatogram



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.018	2097462	154665	0.000		M	
2	7.678	2167208	144997	0.000		V M	
总计		4264670	299662				

peak number

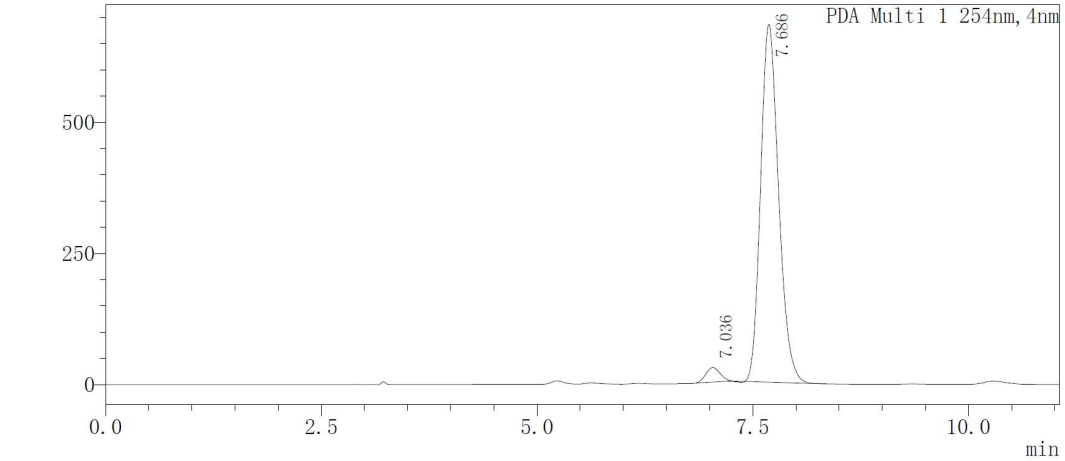
retention time

area

height

〈色谱图〉

HPLC chromatogram



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	7.036	320127	27612	0.000		M	
2	7.686	9899973	682095	0.000		M	
总计		10220100	709707				

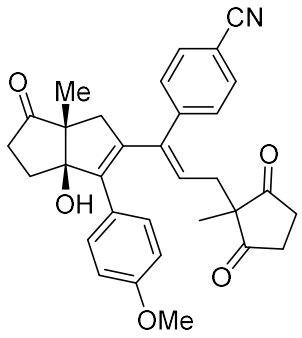
peak number

retention time

area

height

4-((*E*)-1-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(1-methyl-2,5-dioxocyclopentyl)prop-1-en-1-yl)benzonitrile (**5bm**)



Chemical Formula: $C_{32}H_{31}NO_5$
Exact Mass: 509.2202

5bm was prepared according to general procedure 2.2 using **1b** and **4m** and was purified by silica gel column chromatography (PE/EtOAc = 3/1~1.5/1) to obtain **5bm** as yellow oil (63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.34 (m, 2H), 6.94-6.88 (m, 2H), 6.87-6.80 (m, 2H), 6.68-6.60 (m, 2H), 5.51 (dd, *J* = 8.0, 6.9 Hz, 1H), 3.75 (s, 3H), 2.75 (d, *J* = 16.7 Hz, 1H), 2.71-2.61 (m, 2H), 2.50-2.36 (m, 4H), 2.17 (dd, *J* = 7.5, 4.6 Hz, 2H), 2.08-1.93 (m, 3H), 1.85-1.76 (m, 1H), 1.11 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 215.2, 214.9, 158.8, 142.8, 142.2, 142.00, 139.6, 131.6, 130.0, 129.9, 127.7, 127.2, 118.6, 113.5, 110.6, 92.2, 56.2, 55.8, 55.2, 44.2, 36.4, 35.0, 34.9, 33.8, 29.3, 19.1, 15.3; HRMS: (ESI) calcd for $C_{32}H_{32}NO_5^+$ $[M+H]^+$ 510.2275; found 510.2285.

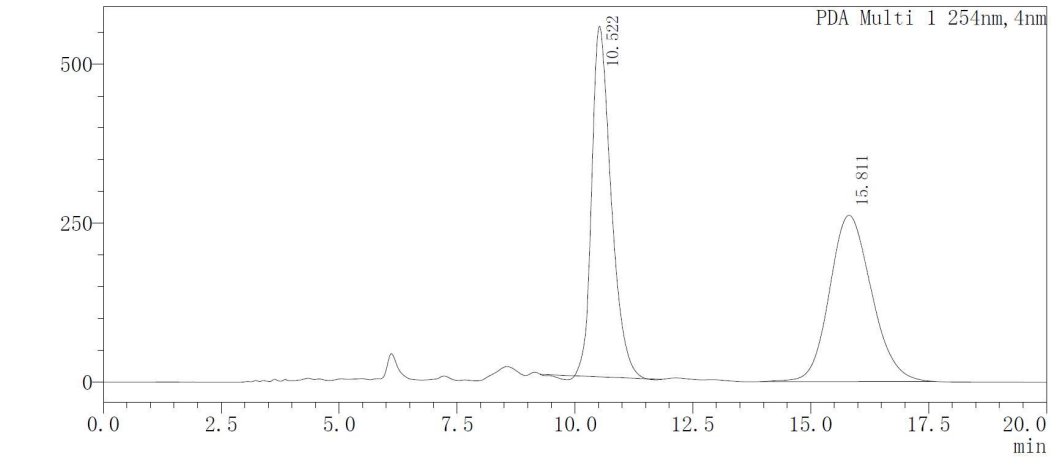
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 10 min (minor), 15 min (major).

Optical Rotation: $[\alpha]_D^{31}$ 30.9 (c 1.3, ^{i}PrOH) for 92% ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图>
mAU

HPLC chromatogram



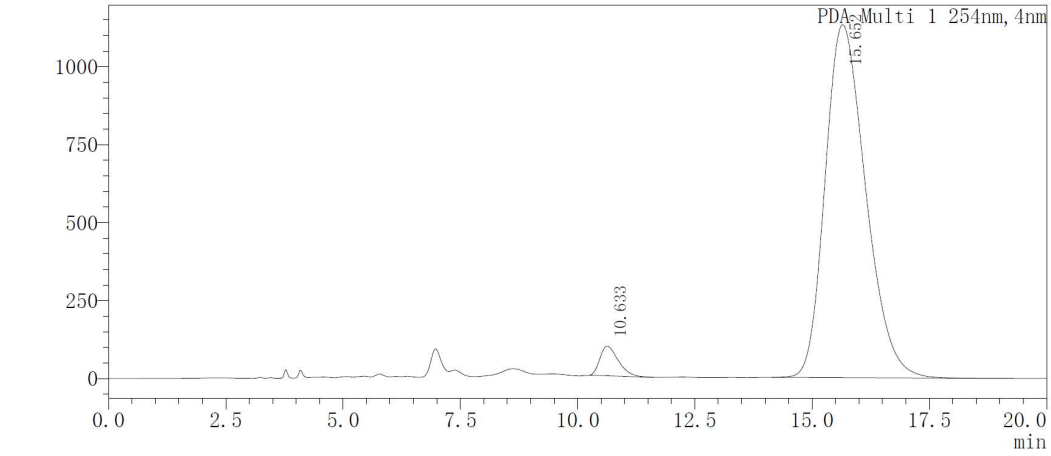
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.522	15677014	551542	0.000		M	
2	15.811	16190250	261517	0.000		M	
总计		31867265	813059				

peak number
retention time
area
height

<色谱图>
mAU

HPLC chromatogram

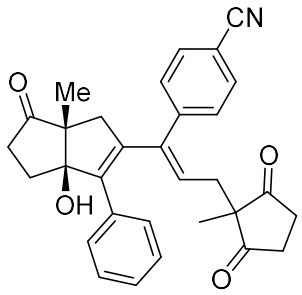


<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	10.633	2574034	94719	0.000		M	
2	15.652	68126401	1132239	0.000		M	
总计		70700435	1226958				

peak number
retention time
area
height

4-((*E*)-1-((3a*R*,6a*R*)-3a-hydroxy-6a-methyl-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-(1-methyl-2,5-dioxocyclopentyl)prop-1-en-1-yl)benzonitrile (**5an**)



Chemical Formula: $C_{31}H_{29}NO_4$
Exact Mass: 479.2097

5an was prepared according to general procedure 2.2 using **1a** and **4n** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~1.5/1) to obtain **5an** as yellow oil (60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.16-7.09 (m, 3H), 6.94-6.87 (m, 4H), 5.53 (t, *J* = 7.5 Hz, 1H), 2.77 (d, *J* = 16.7 Hz, 1H), 2.70-2.61 (m, 2H), 2.49 (d, *J* = 16.7 Hz, 1H), 2.45-2.34 (m, 3H), 2.19-2.11 (m, 2H), 2.06-1.92 (m, 3H), 1.86-1.76 (m, 1H), 1.13 (s, 4H), 0.91 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.2, 215.1, 214.9, 142.6, 142.5, 142.3, 139.4, 135.1, 131.6, 129.9, 128.9, 128.0, 127.9, 127.2, 110.7, 92.3, 56.2, 55.9, 44.2, 36.4, 35.0, 34.9, 33.7, 29.3, 19.1, 15.3; HRMS: (ESI) calcd for $C_{31}H_{30}NO_4^+$ $[M+H]^+$ 480.2169; found 480.2170.

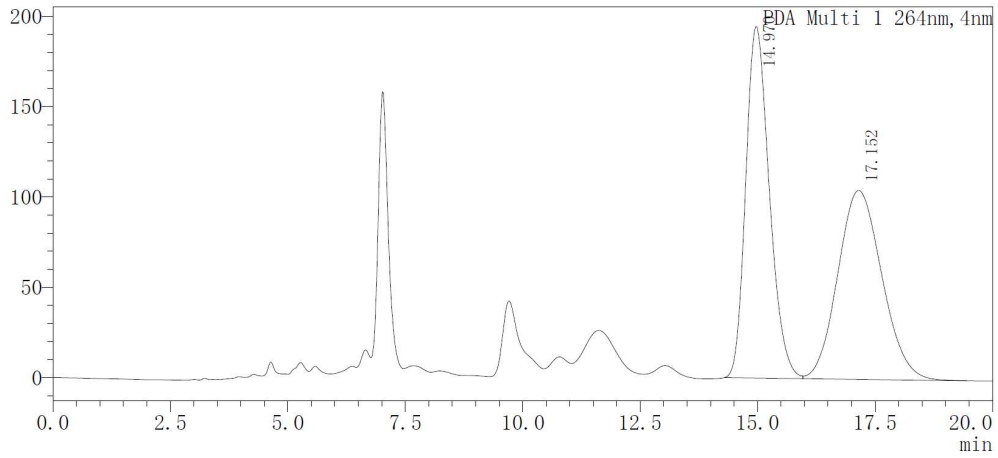
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 14 min (minor), 16 min (major).

Optical Rotation: $[\alpha]_D^{31}$ 28.9 (c 1.2, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 264nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	14.970	6808925	194664	49.905		M	
2	17.152	6834881	104653	50.095		V M	
总计		13643806	299316				

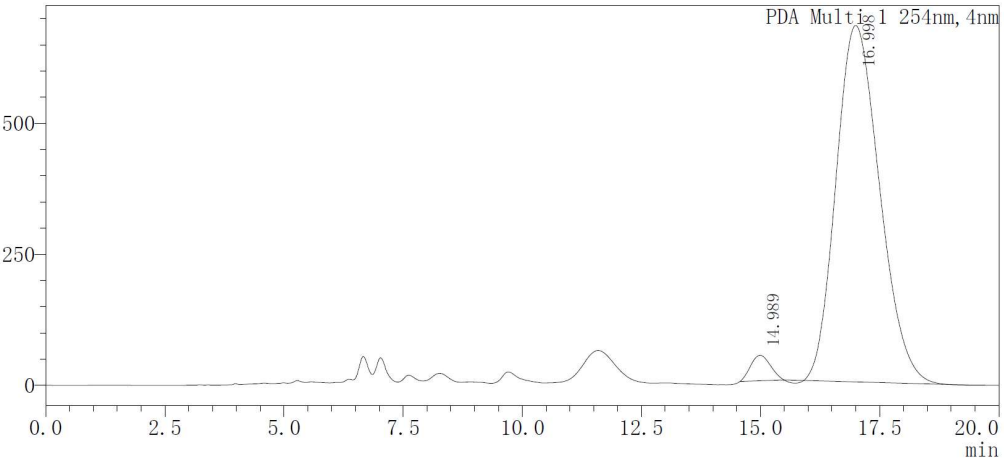
peak number ← retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

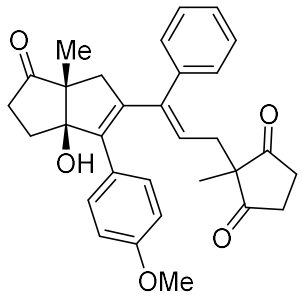
峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	14.989	1400815	48508	0.000		M	
2	16.998	43287774	680417	0.000		M	
总计		44688589	728925				

peak number ← retention time

area

height

2-((*E*)-3-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-3-phenylallyl)-2-methylcyclopentane-1,3-dione (**5bo**)



Chemical Formula: $C_{31}H_{32}O_5$
Exact Mass: 484.2250

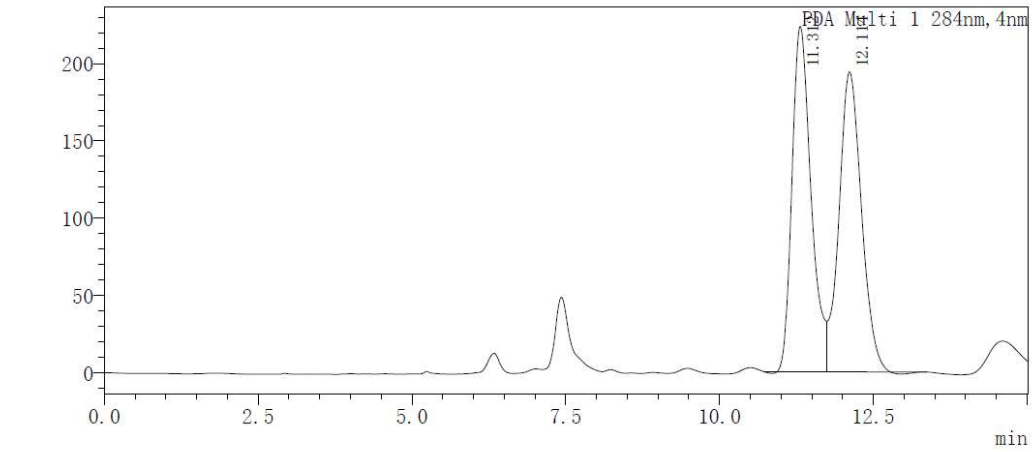
5bo was prepared according to general procedure 2.2 using **1b** and **4o** and was purified by silica gel column chromatography (PE/EtOAc = 3/1~1.5/1) to obtain **5bo** as yellow oil (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.13 (m, 3H), 7.08-7.04 (m, 2H), 6.88-6.84 (m, 2H), 6.76-6.73 (m, 2H), 5.37 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 3H), 2.68 (d, *J* = 16.9 Hz, 1H), 2.59-2.52 (m, 2H), 2.42-2.35 (m, 2H), 2.31-2.22 (m, 4H), 2.06-1.99 (m, 2H), 1.92-1.81 (m, 2H), 1.09 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.5, 215.4, 215.0, 158.7, 143.8, 140.8, 140.7, 137.5, 130.0, 128.8, 128.1, 127.7, 127.1, 125.9, 113.7, 92.4, 56.4, 56.0, 55.2, 44.6, 36.7, 35.0, 34.8, 34.4, 29.2, 18.3, 15.4; HRMS: (ESI) calcd for $C_{31}H_{32}O_5Na^+$ $[M+Na]^+$ 507.2142; found 507.2155.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 11 min (minor), 12 min (major).

Optical Rotation: $[\alpha]_D^{29}$ 37.5 (c 1.0, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉 HPLC chromatogram



〈峰表〉

PDA Ch1 284nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.312	4821440	223519	0.000		M	
2	12.114	4920245	194202	0.000		V M	
总计		9741685	417721				

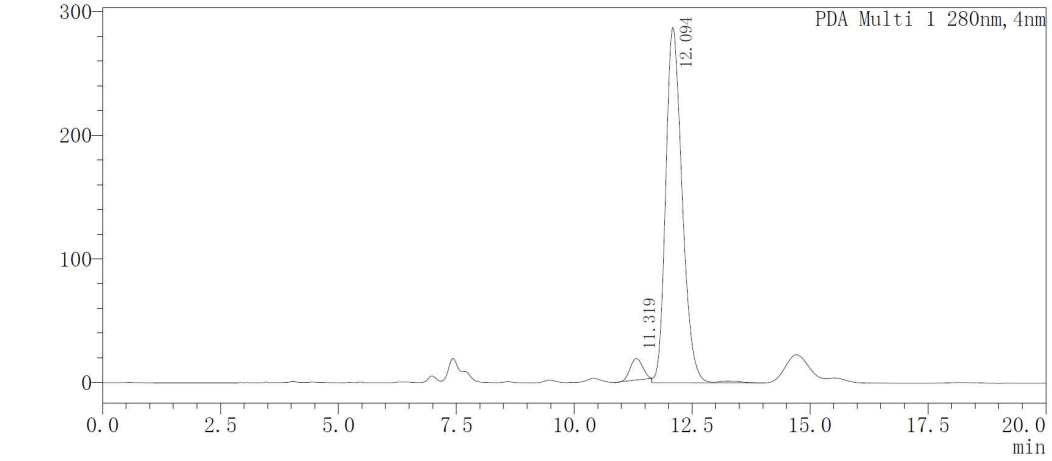
peak number

retention time

area

height

〈色谱图〉 HPLC chromatogram



〈峰表〉

PDA Ch1 280nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	11.319	318105	17453	0.000		M	
2	12.094	6995801	287198	0.000		M	
总计		7313906	304651				

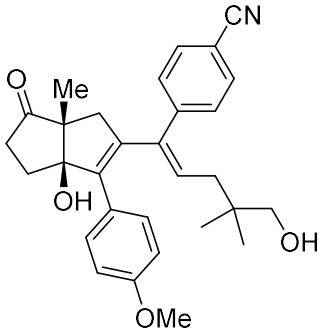
peak number

retention time

area

height

4-((*E*)-5-hydroxy-1-((3a*R*,6a*R*)-3a-hydroxy-3-(4-methoxyphenyl)-6a-methyl-6-oxo-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-4,4-dimethylpent-1-en-1-yl)benzonitrile (**5bp**)



Chemical Formula: $C_{30}H_{33}NO_4$
Exact Mass: 471.2410

5bp was prepared according to general procedure 2.2 using **1b** and **4p** and was purified by silica gel column chromatography (PE/EtOAc = 4/1~1/1) to obtain **5bp** as yellow oil (80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 6.97-6.93 (m, 2H), 6.92-6.87 (m, 2H), 6.69-6.64 (m, 2H), 5.86 (dd, *J* = 8.5, 7.0 Hz, 1H), 3.75 (s, 3H), 3.05 (dd, *J* = 2.4 Hz, 2H), 2.82 (d, *J* = 16.7 Hz, 1H), 2.52 (d, *J* = 16.7 Hz, 1H), 2.46-2.40 (m, 1H), 2.09-2.00 (m, 2H), 1.90-1.78 (m, 4H), 1.15 (s, 3H), 0.66 (s, 3H), 0.64 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.5, 158.8, 143.8, 143.2, 141.2, 137.4, 132.5, 131.5, 130.1, 130.0, 127.6, 118.8, 113.6, 110.2, 92.2, 71.2, 55.88, 55.31, 44.4, 37.4, 36.5, 36.1, 29.4, 23.7, 23.7, 15.3; HRMS: (ESI) calcd for $C_{30}H_{33}NO_4Na^+$ $[M+Na]^+$ 494.2302; found 494.2292.

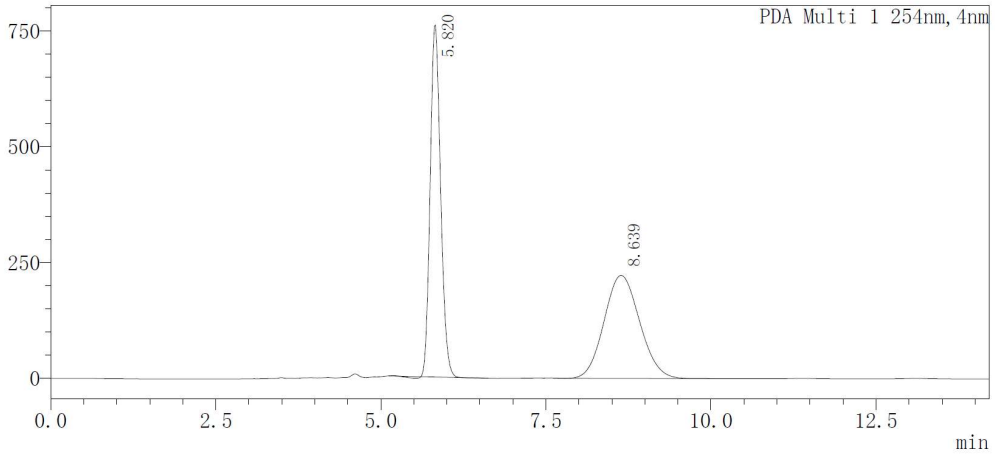
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 70/30 as eluent, 254 nm, 1 mL/min. tR = 5.8 min (major), 8.6 min (minor).

Optical Rotation: $[\alpha]_D^{30}$ -42.7 (c 1.5, ^{i}PrOH) for 94%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图>
mAU

HPLC chromatogram



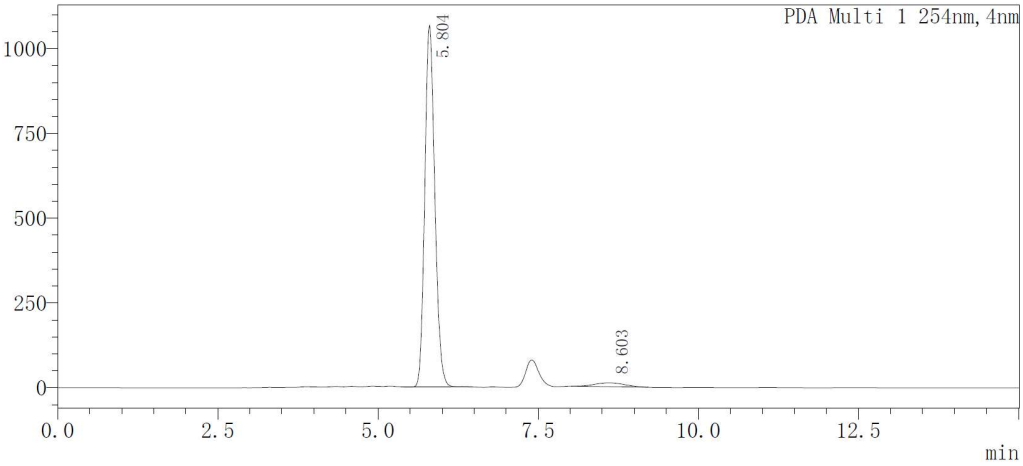
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.820	8310073	759817	0.000		M	
2	8.639	8336773	222527	0.000		M	
总计		16646846	982343				

peak number
retention time
area
height

<色谱图>
mAU

HPLC chromatogram

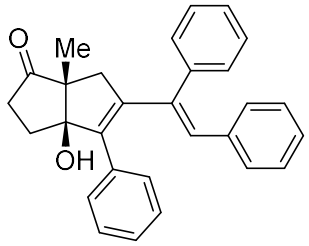


<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.804	11612080	1067326	0.000		M	
2	8.603	371318	11590	0.000		M	
总计		11983399	1078916				

peak number
retention time
area
height

(3a*R*,6a*R*)-5-((*E*)-1,2-diphenylvinyl)-3a-hydroxy-6a-methyl-4-phenyl-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**5aq**)



Chemical Formula: $C_{29}H_{26}O_2$
Exact Mass: 406.1933

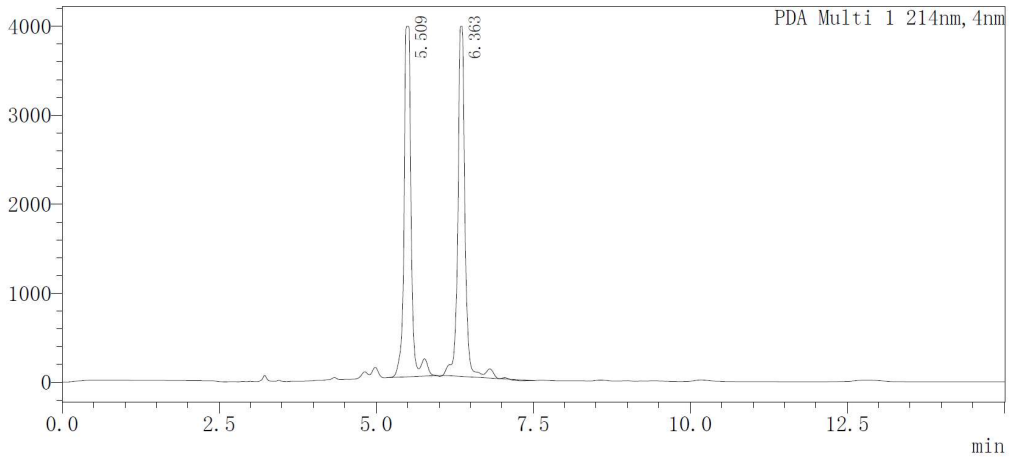
5aq was prepared according to general procedure 2.2 using **1a** and **4q** and was purified by silica gel column chromatography (PE/EtOAc = 15/1~10/1) to obtain **5aq** as faint yellow solid (71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.25 (m, 2H), 7.20-7.10 (m, 6H), 7.06-7.01 (m, 3H), 6.97-6.92 (m, 2H), 6.82-6.77 (m, 2H), 6.54 (s, 1H), 2.90 (d, *J* = 17.0 Hz, 1H), 2.57 (d, *J* = 17.0 Hz, 1H), 2.50-2.41 (m, 1H), 2.21-2.05 (m, 3H), 1.98-1.88 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.6, 145.5, 141.8, 138.5, 137.7, 136.6, 135.5, 131.9, 129.3, 129.3, 128.8, 128.3, 128.0, 127.8, 127.1, 127.0, 126.9, 92.5, 56.3, 44.5, 36.6, 29.4, 15.4; HRMS: (ESI) calcd for $C_{29}H_{26}NaO_2^+$ $[M+Na]^+$ 429.1825; found 429.1802. The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 5.5 min (minor), 6.4 min (major).

Optical Rotation: $[\alpha]_D^{31}$ 28.3 (c 0.9, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图>
mAU

HPLC chromatogram



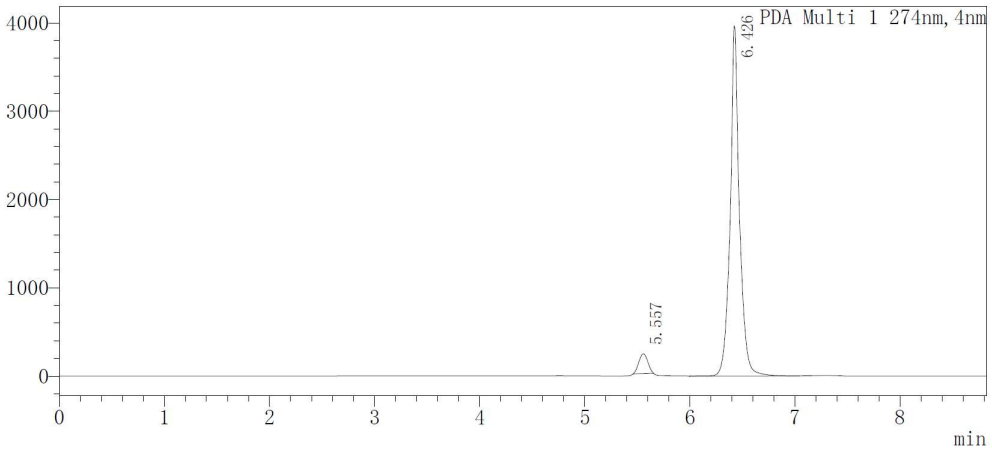
<峰表>
PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.509	31031743	3938223	49.792		M	
2	6.363	31290669	3934824	50.208		M	
总计		62322412	7873047				

peak number
retention time
area
height

<色谱图>
mAU

HPLC chromatogram

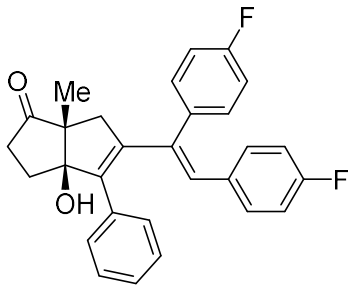


<峰表>
PDA Ch1 274nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.557	1317971	225521	0.000		M	
2	6.426	24386819	3968240	0.000		M	
总计		25704791	4193761				

peak number
retention time
area
height

(3a*R*,6a*R*)-5-((*E*)-1,2-bis(4-fluorophenyl)vinyl)-3a-hydroxy-6a-methyl-4-phenyl-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**5ar**)



Chemical Formula: $C_{29}H_{24}F_2O_2$
Exact Mass: 442.1744

5ar was prepared according to general procedure 2.2 using **1a** and **4r** and was purified by silica gel column chromatography (PE/EtOAc = 15/1~10/1) to obtain **5ar** as faint yellow solid (81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.09 (m, 5H), 6.86-6.80 (m, 2H), 6.77-6.71 (m, 6H), 6.53 (s, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 2.61 (d, *J* = 16.8 Hz, 1H), 2.51-2.41 (m, 1H), 2.15-2.05 (m, 2H), 1.95-1.83 (m, 1H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 161.9 (d, *J* = 246.7 Hz), 161.8 (d, *J* = 247.9 Hz), 144.9, 142.5, 136.8, 135.5, 134.3 (d, *J* = 3.5 Hz), 132.6 (d, *J* = 3.5 Hz), δ 131.3, 131.2 (d, *J* = 8.4 Hz), 131.1 (d, *J* = 7.8 Hz), 128.9, 128.0, 127.2, 115.4 (d, *J* = 21.3 Hz), 115.0 (d, *J* = 21.4 Hz), 92.6, 77.4, 77.1, 76.8, 56.3, 44.5, 36.7, 29.5, 15.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.97, -114.61; HRMS: (ESI) calcd for $C_{29}H_{24}F_2O_2Na^+$[M+Na]$^+$ 465.1637; found 465.1638.

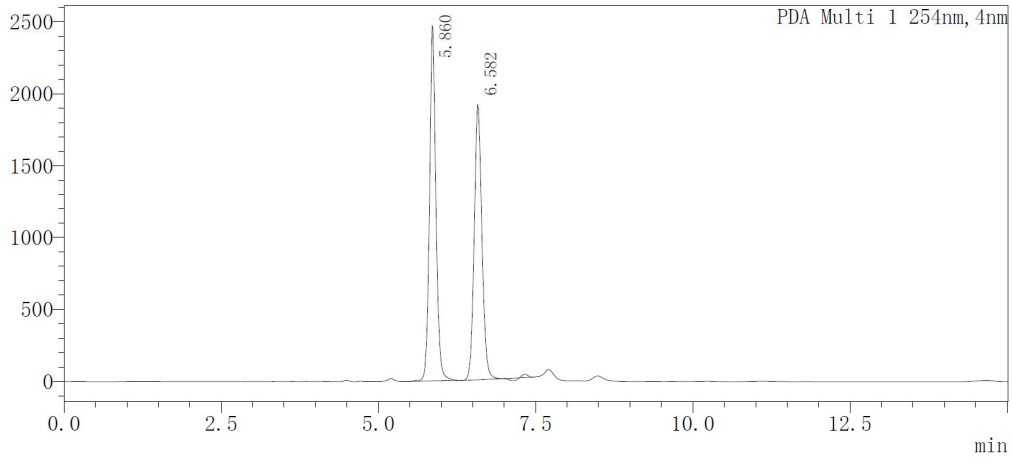
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 5 min (minor), 6 min (major).

Optical Rotation: $[\alpha]_D^{30}$ 82.4 (c 1.3, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图>
mAU

HPLC chromatogram



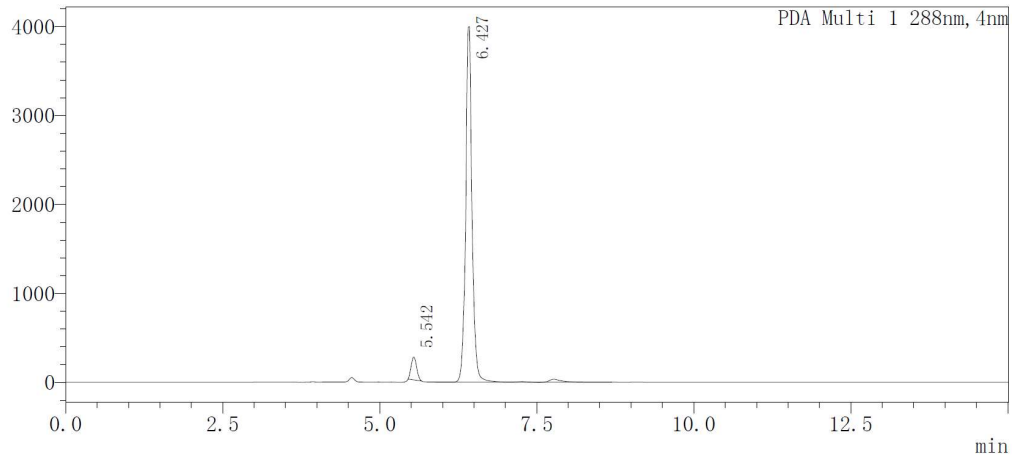
<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.860	17441630	2470999	0.000		M	
2	6.582	16249497	1915577	0.000		M	
总计		33691127	4386576				

peak number
retention time
area
height

<色谱图>
mAU

HPLC chromatogram

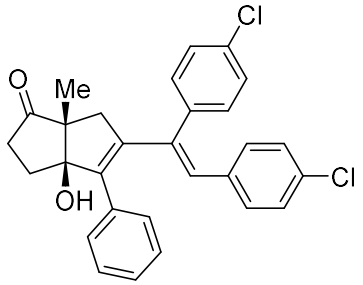


<峰表>
PDA Ch1 288nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.542	1554448	256200	0.000		M	
2	6.427	28514210	3997864	0.000		M	
总计		30068658	4254064				

peak number
retention time
area
height

(3a*R*,6a*R*)-5-((*E*)-1,2-bis(4-chlorophenyl)vinyl)-3a-hydroxy-6a-methyl-4-phenyl-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**5as**)



Chemical Formula: $C_{29}H_{24}Cl_2O_2$
Exact Mass: 474.1153

5as was prepared according to general procedure 2.2 using **1a** and **4s** and was purified by silica gel column chromatography (PE/EtOAc = 20/1~10/1) to obtain **5as** as faint yellow oil (52% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.08 (m, 5H), 7.05-7.00 (m, 4H), 6.81-6.76 (m, 2H), 6.74-6.69 (m, 2H), 6.51 (s, 1H), 2.93 (d, *J* = 16.8 Hz, 1H), 2.60 (d, J = 16.8 Hz, 1H), 2.53-2.41 (m, 1H), 2.13-2.04 (m, 2H), 1.97-1.83 (m, 2H), 1.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.4, 144.5, 142.9, 137.4, 136.6, 135.2, 134.7, 133.1, 131.2, 130.7, 130.5, 128.8, 128.6, 128.2, 128.0, 127.1, 92.4, 56.2, 44.3, 36.6, 29.5, 15.3; HRMS: (ESI) calcd for $C_{29}H_{24}Cl_2O_2Na^+$ $[M+Na]^+$ 497.1046; found 497.1035.

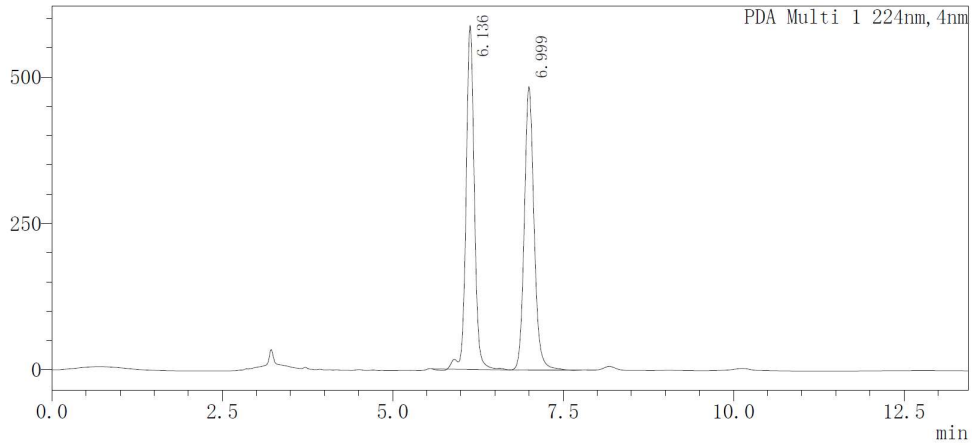
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 6 min (minor), 9 min (major).

Optical Rotation: $[\alpha]_D^{27}$ 57.1 (c 0.8, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 224nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.136	4954459	588290	0.000		M	
2	6.999	4817388	484502	0.000		M	
总计		9771848	1072792				

peak number

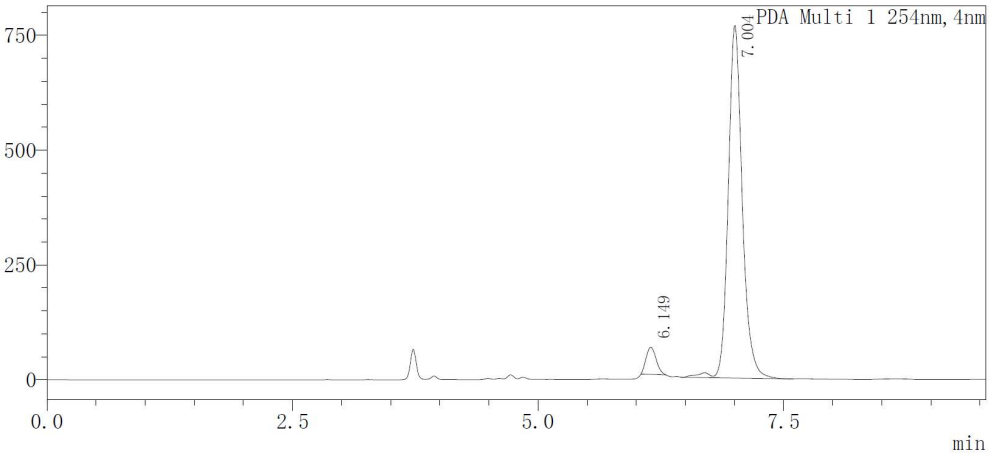
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.149	422450	59331	5.212		M	
2	7.004	7682249	767675	94.788		M	
总计		8104699	827007				

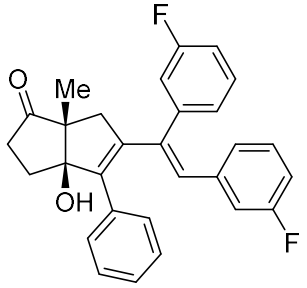
peak number

retention time

area

height

(3a*R*,6a*R*)-5-((*E*)-1,2-bis(3-fluorophenyl)vinyl)-3a-hydroxy-6a-methyl-4-phenyl-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**5at**)



Chemical Formula: $C_{29}H_{24}F_2O_2$
Exact Mass: 442.1744

5at was prepared according to general procedure 2.2 using **1a** and **4t** and was purified by silica gel column chromatography (PE/EtOAc = 20/1~10/1) to obtain **5at** as yellow oil (46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.10 (m, 5H), 7.08-6.97 (m, 2H), 6.81-6.71 (m, 2H), 6.69-6.64 (m, 1H), 6.61-6.51 (m, 3H), 6.46-6.38 (m, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 2.62 (d, *J* = 16.8 Hz, 1H), 2.51-2.33 (m, 1H), 2.18-2.04 (m, 2H), 2.00-1.86 (m, 2H), 1.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.3, 162.6 (d, *J* = 246.3 Hz), 162.3 (d, *J* = 245.2 Hz), 144.0, 143.1, 140.3 (d, *J* = 7.5 Hz), 138.3 (d, *J* = 7.8 Hz), 137.9, 135.2, 131.4, 130.0 (d, *J* = 8.3 Hz), 129.3 (d, *J* = 8.4 Hz), 128.8, 128.0, 127.2, 125.2 (d, *J* = 2.3 Hz), 125.1 (d, *J* = 2.8 Hz), 116.3 (d, *J* = 21.6 Hz), 115.7 (d, *J* = 22.2 Hz), 114.3 (d, *J* = 21.2 Hz), 114.1 (d, *J* = 21.3 Hz), 92.5, 56.1, 44.4, 36.6, 29.5, 15.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.0 (m), -113.4 (m); HRMS: (ESI) calcd for $C_{29}H_{24}F_2O_2Na^+$[M+Na]$^+$ 465.1621; found 465.1636.

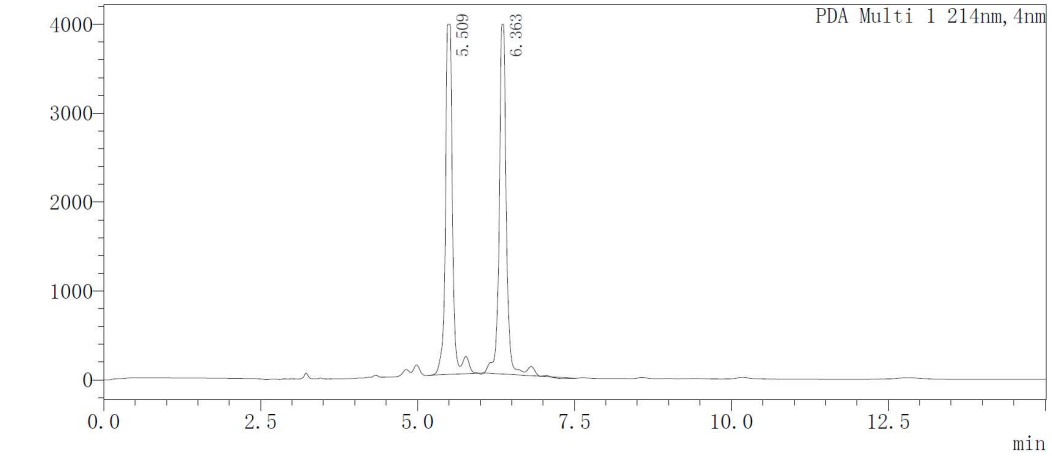
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 5.5 min (minor), 6.3 min (major).

Optical Rotation: $[\alpha]_D^{28}$ 162.6 (c 0.8, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉

HPLC chromatogram



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.509	31031743	3938223	49.792		M	
2	6.363	31290669	3934824	50.208		M	
总计		62322412	7873047				

peak number

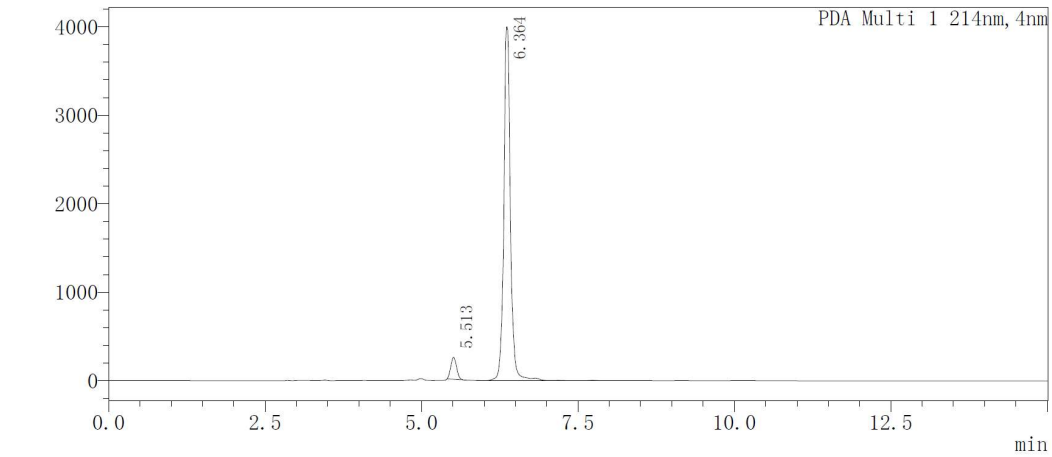
retention time

area

height

〈色谱图〉

HPLC chromatogram



〈峰表〉

PDA Ch1 214nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.513	1588878	249720	0.000		M	
2	6.364	29210781	3997797	0.000		M	
总计		30799659	4247516				

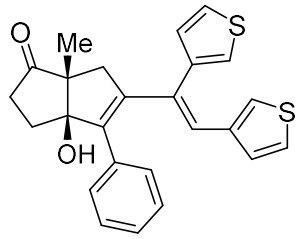
peak number

retention time

area

height

(3a*R*,6a*R*)-5-((*Z*)-1,2-di(thiophen-3-yl)vinyl)-3a-hydroxy-6a-methyl-4-phenyl-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**5au**)



Chemical Formula: $C_{25}H_{22}O_2S_2$
Exact Mass: 418.1061

5au was prepared according to general procedure 2.2 using **1a** and **4u** and was purified by silica gel column chromatography (PE/EtOAc = 15/1~10/1) to obtain **5au** as brown solid (71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.09 (m, 5H), 7.05-7.02 (m, 1H), 7.01-6.98 (m, 1H), 6.76-6.73 (m, 1H), 6.72-6.69 (m, 1H), 6.59 (s, 1H), 6.58-6.56 (m, 1H), 6.39-6.36 (m, 1H), 3.01 (d, *J* = 16.7 Hz, 1H), 2.65 (d, *J* = 16.8 Hz, 1H), 2.48-2.38 (m, 1H), 2.12-2.04 (m, 2H), 2.02-1.82 (m, 2H), 1.19 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.7, 144.2, 141.6, 139.0, 138.1, 135.6, 131.5, 128.8, 128.5, 128.0, 127.8, 127.1, 126.8, 125.2, 124.8, 124.6, 123.6, 92.5, 56.0, 44.4, 36.6, 29.3, 15.4; HRMS: (ESI) calcd for $C_{25}H_{22}O_2S_2Na^+$ $[M+Na]^+$ 441.0953; found 441.0951.

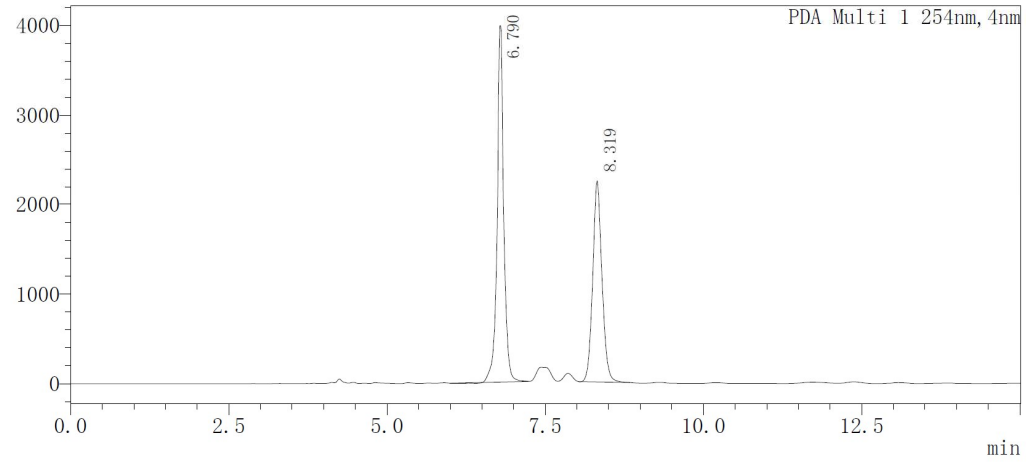
The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 6.7 min (minor), 8.3 min (major).

Optical Rotation: $[\alpha]_D^{30}$ -30.6 (c 1.2, ^{i}PrOH) for 82%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.790	28590361	3979237	0.000		M	
2	8.319	22756010	2249977	0.000		M	
总计		51346372	6229214				

peak number

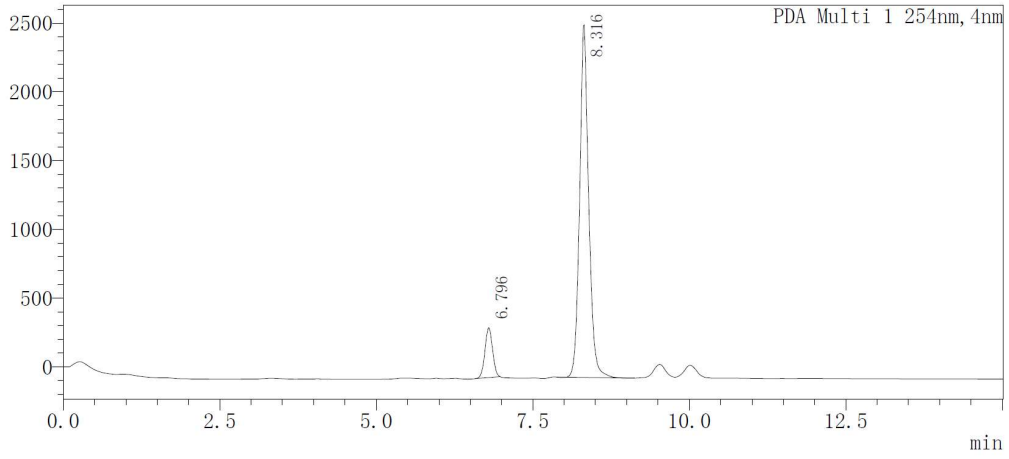
retention time

area

height

<色谱图> ← HPLC chromatogram

mAU



<峰表>

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.796	3071854	362523	0.000		M	
2	8.316	25742301	2565196	0.000		M	
总计		28814155	2927719				

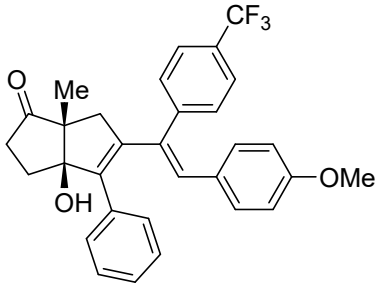
peak number

retention time

area

height

(3a*R*,6a*R*)-3a-hydroxy-5-((*E*)-2-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)vinyl)-6a-methyl-4-phenyl-3,3a,6,6a-tetrahydropentalen-1(2*H*)-one (**5av**)



Chemical Formula: $C_{31}H_{27}F_3O_3$
Exact Mass: 504.1912

5av was prepared according to general procedure 2.2 using **1a** and **4v** and was purified by silica gel column chromatography (PE/EtOAc = 15/1~10/1) to obtain **5av** as yellow oil (60% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30-7.28 (m, 2H), 7.26-7.23 (m, 2H), 7.20-7.17 (m, 2H), 7.16-7.13 (m, 1H), 6.93 - 6.89 (m, 2H), 6.84 - 6.80 (m, 2H), 6.67-6.65 (m, 2H), 6.45 (s, 1H), 3.76 (s, 3H), 2.87 (d, *J* = 17.0 Hz, 1H), 2.55 (d, *J* = 17.0 Hz, 1H), 2.50 - 2.39 (m, 1H), 2.20 - 2.08 (m, 2H), 1.97 - 1.86 (m, 2H), 1.17 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.4, 159.0, 145.5, 142.7, 140.5, 139.6, 135.3, 130.8, 130.4, 130.0, 129.7, 129.4, 128.7, 128.1, 127.2, 124.7 (q, *J* = 3.7 Hz), 114.0, 92.5, 56.4, 55.2, 44.3, 36.7, 29.4, 15.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.50; HRMS: (ESI) calcd for $C_{31}H_{28}O_3F_3^+$[M+H]$^+$ 438.2052; found 438.2064.

The enantiomeric purity was established by HPLC analysis using a chiral column: AD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 85/15 as eluent, 254 nm, 1 mL/min. tR = 5.9 min (minor), 6.7 min (major).

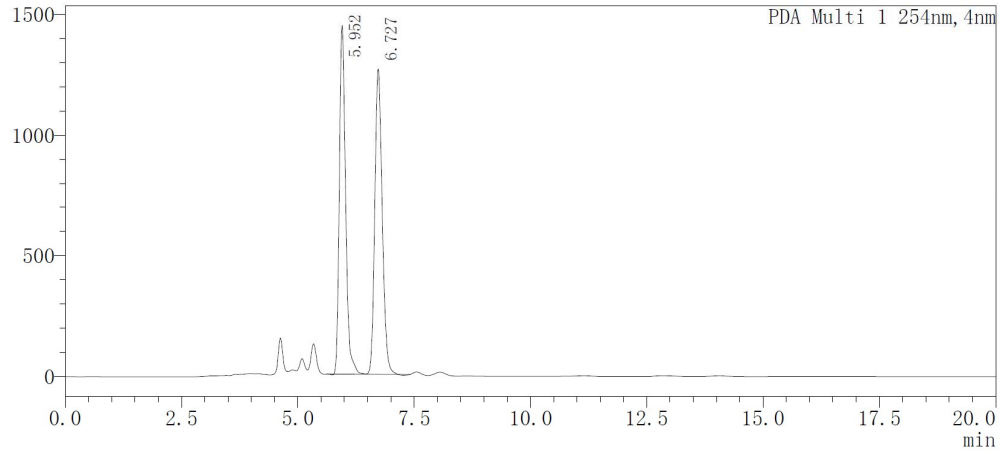
Optical Rotation: $[\alpha]_D^{28}$ 149.5 (c 1.2, ^{i}PrOH) for 90%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

〈色谱图〉

mAU

HPLC chromatogram



〈峰表〉

PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.952	13460205	1444343	0.000		M	
2	6.727	14035702	1264552	0.000		V M	
总计		27495907	2708895				

peak number

retention time

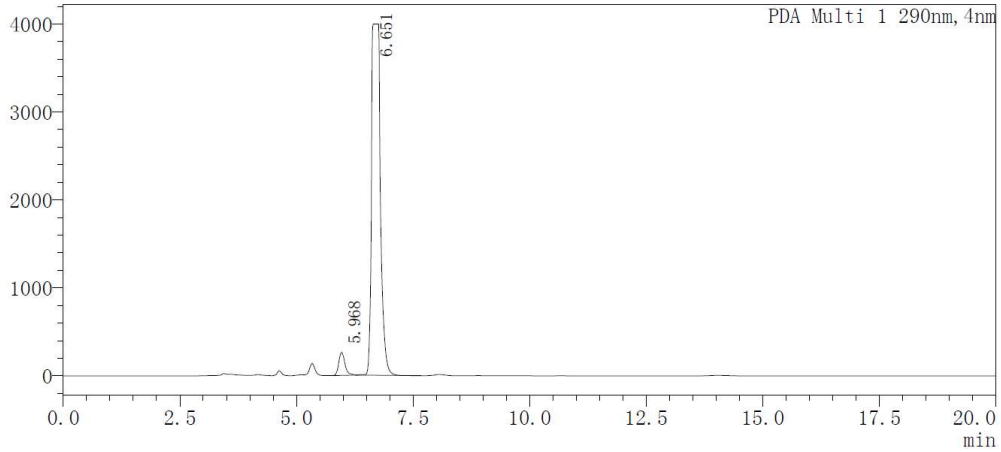
area

height

〈色谱图〉

mAU

HPLC chromatogram



〈峰表〉

PDA Ch1 290nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	5.968	2446083	261866	4.404		M	
2	6.651	53098759	3992673	95.596		M	
总计		55544842	4254539				

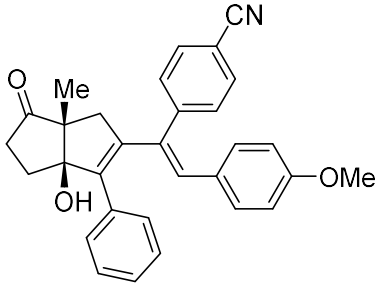
peak number

retention time

area

height

4-((*E*)-1-((3a*R*,6a*R*)-3a-hydroxy-6a-methyl-6-oxo-3-phenyl-1,3a,4,5,6,6a-hexahydropentalen-2-yl)-2-(4-methoxyphenyl)vinyl)benzonitrile (**5aw**)



Chemical Formula: $C_{31}H_{27}NO_3$
Exact Mass: 461.1991

5aw was prepared according to general procedure 2.2 using **1a** and **4w** and was purified by silica gel column chromatography (PE/EtOAc = 15/1~10/1) to obtain **5aw** as yellow oil (50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.28 (m, 2H), 7.23-7.12 (m, 5H), 6.90-6.86 (m, 2H), 6.83-6.75 (m, 2H), 6.68-6.63 (m, 2H), 6.41 (s, 1H), 3.75 (s, 3H), 2.87 (d, *J* = 17.0 Hz, 1H), 2.54 (d, *J* = 17.0 Hz, 1H), 2.51-2.42 (m, 1H), 2.19-2.05 (m, 2H), 2.02-1.97 (m, 1H), 1.97-1.87 (m, 1H), 1.16 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 221.3, 159.2, 145.2, 143.3, 141.7, 140.8, 135.2, 131.6, 130.3, 129.7, 129.7, 129.3, 128.7, 128.1, 127.2, 118.9, 114.1, 109.8, 92.5, 56.4, 55.2, 44.3, 36.7, 29.4, 15.3; HRMS: (ESI) calcd for $C_{31}H_{28}NO_3^+$ $[M+H]^+$ 462.2064; found 462.2054.

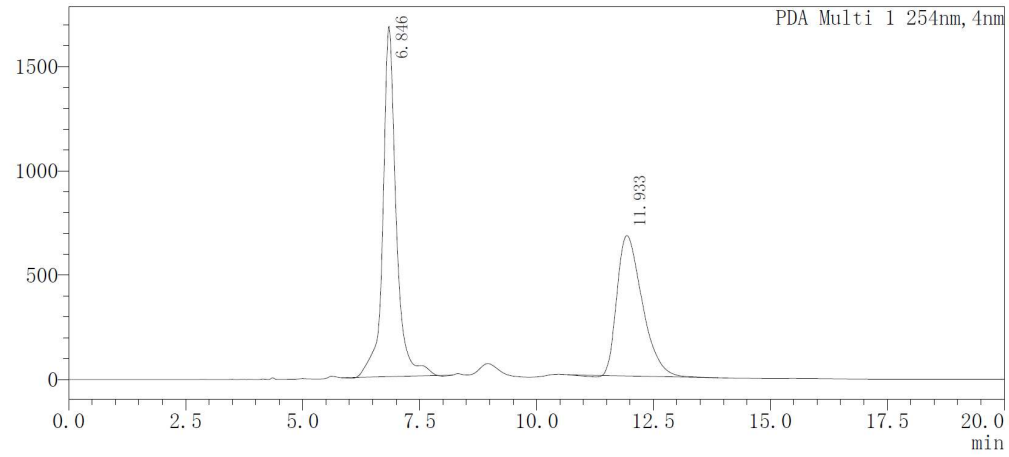
The enantiomeric purity was established by HPLC analysis using a chiral column: OD-H column, 30 °C, *n*-Hexane/*i*-Propanol = 80/20 as eluent, 254 nm, 1 mL/min. tR = 6 min (major), 12 min (minor).

Optical Rotation: $[\alpha]_D^{27}$ 189.3 (c 0.4, ^{i}PrOH) for 92%ee.

Absolute stereochemistry was determined through analogy with X-ray crystal diffraction study of **9**.

<色谱图>
mAU

HPLC chromatogram



<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.846	33268582	1680158	0.000		M	
2	11.933	25248975	673424	0.000		M	
总计		58517557	2353582				

peak number

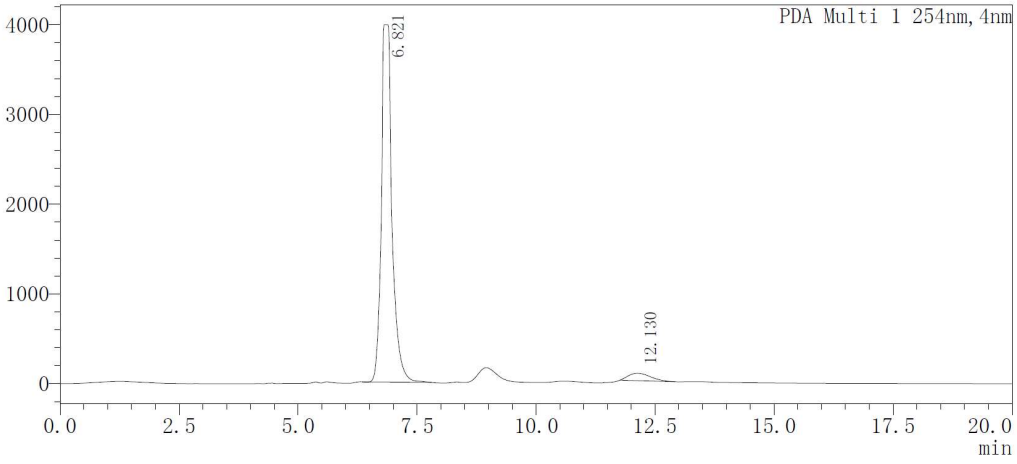
retention time

area

height

<色谱图>
mAU

HPLC chromatogram



<峰表>
PDA Ch1 254nm

峰号	保留时间	面积	高度	浓度	浓度单位	标记	化合物名
1	6.821	62565039	3982805	0.000		M	
2	12.130	2657071	82494	0.000		M	
总计		65222110	4065299				

peak number

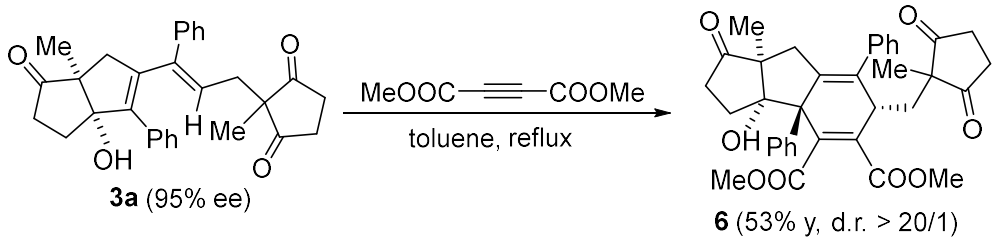
retention time

area

height

8. Synthetic Applications

dimethyl (3a*S*, 3b*R*, 6*S*, 8a*S*)-3a-hydroxy-8a-methyl-6-((1-methyl-2,5-dioxocyclopentyl) methyl)-1-oxo-3b,7-diphenyl-1,2,3,3a,3b,6,8,8a-octahydrocyclopenta[*a*]indene-4,5-dicarboxylate (**6**)

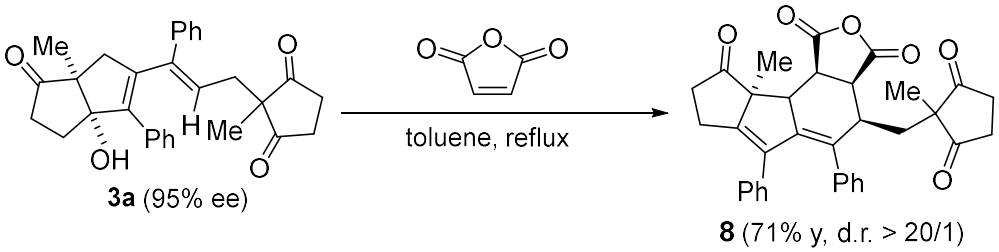


3a (95% ee)

6 (53% y, d.r. > 20/1)

Experimental procedure: To a mixture of **3a** (0.05 mmol, 22.5 mg, 95% ee) and dry toluene (1.5 mL) in a sealed tube was added DMAD (0.15 mmol, 21.3 mg) under Argon. The reaction mixture was heated at 130 ºC for 96 hours (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **6** in 53% yield (> 20/1 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$-*d*) δ 7.21-7.10 (m, 8H), 6.96-6.91 (m, 2H), 5.51 (dd, *J* = 8.4, 6.6 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H), 2.62-2.47 (m, 4H), 2.45-2.21 (m, 6H), 2.01-1.92 (m, 1H), 1.14 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4, 215.3, 212.8, 165.8, 163.2, 154.0, 152.2, 149.7, 142.4, 140.9, 136.6, 134.4, 129.3, 128.1, 128.0, 127.6, 127.1, 124.6, 87.2, 57.2, 56.7, 52.3, 52.2, 40.2, 35.0, 34.9, 34.6, 20.1, 18.1, 14.6. HRMS: (ESI) calcd for $C_{36}H_{37}O_8^+[M+H]^+$ 597.2483; found 597.2389.

(3a*S*, 4*R*, 9a*S*, 9c*R*)-9a-methyl-4-((1-methyl-2,5-dioxocyclopentyl)methyl)-5,6-diphenyl-4,7,8,9a,9b,9c-hexahydrocyclopenta[2,3]indeno[4,5-*c*]furan-1,3,9(3a*H*)-trione (**8**)

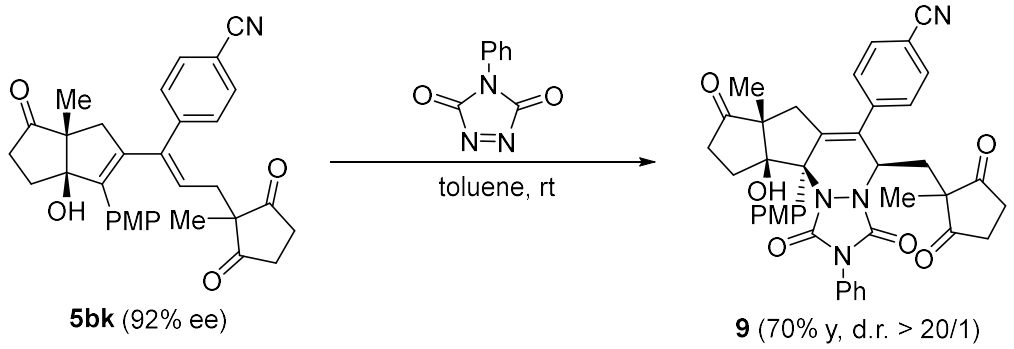


3a (95% ee)

8 (71% y, d.r. > 20/1)

Experimental procedure: To a mixture of **3a** (0.05 mmol, 22.5 mg, 95% ee) and dry toluene (1.5 mL) in a sealed tube was added maleic anhydride (0.15 mmol, 14.7 mg) under Argon. The reaction mixture was heated at 130 ºC for 96 hours (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **8** in 71% yield (> 20/1 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03-6.97 (m, 1H), 6.90-6.85 (m, 2H), 6.84-6.74 (m, 2H), 6.67-6.61 (m, 1H), 6.59-6.27 (m, 4H), 4.30 (dd, *J* = 9.1, 4.5 Hz, 1H), 3.58 (dd, *J* = 9.1, 6.3 Hz, 1H), 3.11-3.03 (m, 1H), 2.92-2.78 (m, 2H), 2.76-2.68 (m, 3H), 2.62-2.53 (m, 1H), 2.48-2.41 (m, 3H), 2.30 (dd, *J* = 15.3, 7.7 Hz, 1H), 1.81 (dd, *J* = 15.3, 4.5 Hz, 1H), 1.50 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.4, 215.3, 215.0, 172.5, 170.8, 160.8, 147.0, 136.7, 134.3, 133.6, 131.6, 130.8, 128.3, 128.2, 127.5, 127.2, 127.1, 126.9, 126.2, 59.0, 55.8, 47.6, 43.2, 42.0, 40.0, 36.8, 34.8, 34.6, 32.6, 25.6, 22.5, 15.7; HRMS: (ESI) calcd for $C_{34}H_{30}O_6^+$[M+H]$^+$535.2103; found 535.2115.

4-((5*R*, 7a*R*, 10a*S*, 10b*R*)-10a-hydroxy-10b-(4-methoxyphenyl)-7a-methyl-5-((1-methyl-2,5-dioxocyclopentyl)methyl)-1,3,8-trioxo-2-phenyl-2,3,5,7,7a,8,9,10,10a,10b-decahydro-1*H*-pentaleno[1,2-*c*][1,2,4]triazolo[1,2-a]pyridazin-6-yl)benzonitrile (**9**)



5bk (92% ee) **9** (70% y, d.r. > 20/1)

Experimental procedure: To a mixture of **5bk** (0.05 mmol, 25.0 mg, 92% ee) and dry toluene (2 mL) in a sealed tube was added 4-phenyl-3*H*-1,2,4-triazole-3,5(4*H*)-dione (0.15 mmol, 26.5 mg). The reaction mixture was stirred at room temperature for 72 hours until the reaction was complete (monitored by TLC). The solvent was then removed under vacuum and the residue was purified by chromatography on silica gel, eluting with ethyl acetate/petroleum ether 1:4~1:1 (v/v) to afford the desired product **9** in 70% yield (> 20/1 d.r.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.77 (m, 2H), 7.57-7.47 (m, 4H), 7.47-7.42 (m, 1H), 7.42-7.36 (m, 2H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.75 (d, *J* = 9.0 Hz, 2H), 4.88 (d, *J* = 10.2 Hz, 1H), 3.91 (s, 1H), 3.77 (s, 3H), 3.18-3.07 (m, 1H), 2.73 (dd, *J* = 18.2, 2.9 Hz, 1H), 2.67-2.52 (m, 4H), 2.38-2.21 (m, 4H), 1.54 (d, *J* = 14.0 Hz, 1H), 1.21 (s, 3H), 1.09-1.01 (m, 1H), 0.96 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 218.1, 214.2, 213.7, 160.2, 152.4, 141. 9, 140. 8, 133.0, 130.9, 129.5, 129.4, 129.1, 128.7, 126.7, 114.3, 89.6, 76.3, 58.4, 56.4, 55.2, 52.0, 36.6, 35.9, 33.9, 33.9, 32.0, 30.9, 26.1, 18.7; HRMS: (ESI) calcd for $C_{40}H_{36}N_4O_7^+$[M+H]$^+$ 685.2639; found 685.2657.

9. Crystallographic data

7.1 Compound 3a

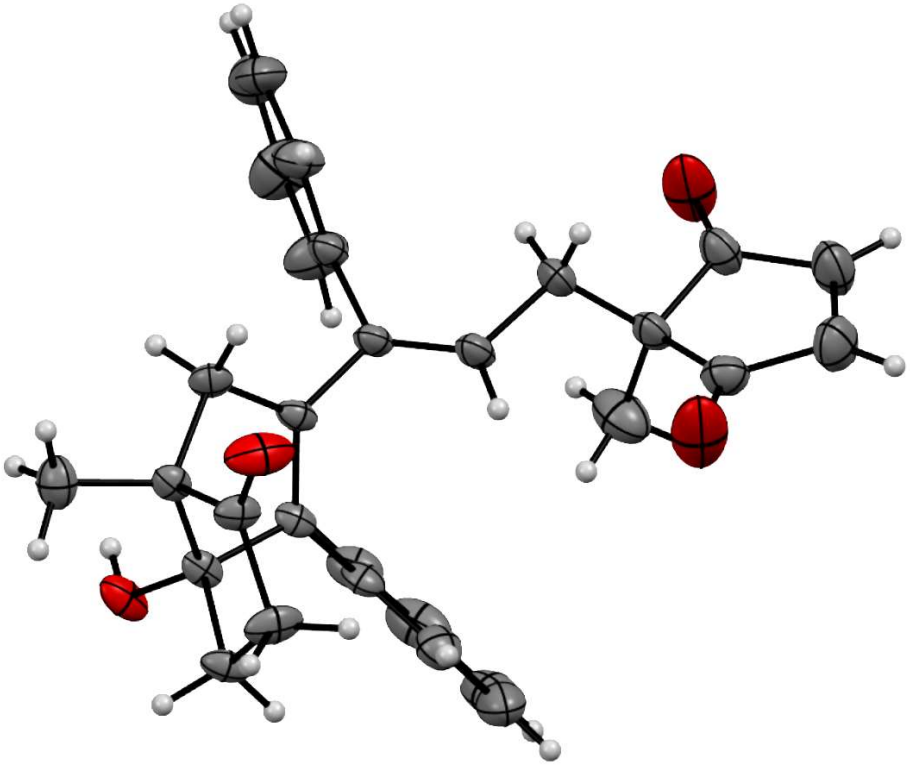


Table 1. Crystal data and structure refinement for **3a**.

Identification code	cu_190113a_0m	
Empirical formula	C30 H30 O5	
Formula weight	470.54	
Temperature	273.15 K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 6.6633(2) Å	□= 90°.
	b = 19.2862(4) Å	□= 90°.
	c = 19.4190(4) Å	□ = 90°.
Volume	2495.53(10) $Å^3$	
Z	4	
Density (calculated)	1.252 Mg/m^3	
Absorption coefficient	0.679 mm^{-1}	
F(000)	1000	
Crystal size	0.12 x 0.1 x 0.1 mm^3	
Theta range for data collection	5.121 to 64.970°.	
Index ranges	-7<=h<=7, -21<=k<=22, -22<=l<=19	
Reflections collected	9459	
Independent reflections	4089 [R(int) = 0.0962]	
Completeness to theta = 64.970°	98.1 %	
Absorption correction	None	
Max. and min. transmission	0.7530 and 0.3549	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4089 / 0 / 319	
Goodness-of-fit on F^2	1.061	
Final R indices [I>2sigma(I)]	R1 = 0.0926, wR2 = 0.2421	
R indices (all data)	R1 = 0.0966, wR2 = 0.2483	
Absolute structure parameter	-0.1(2)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.409 and -0.573 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-4707(8)	-4742(2)	-4417(3)	31(1)
C(2)	-4316(9)	-5401(3)	-4838(3)	38(1)
C(3)	-5662(12)	-5430(3)	-5455(3)	52(2)
C(4)	-7228(11)	-4867(3)	-5357(3)	49(2)
C(5)	-6678(9)	-4487(3)	-4710(3)	38(1)
C(6)	-3042(12)	-4219(4)	-4582(4)	56(2)
C(7)	-4825(9)	-4911(2)	-3650(3)	35(1)
C(8)	-4830(8)	-4285(2)	-3191(3)	29(1)
C(9)	-3783(7)	-4222(2)	-2612(3)	26(1)
C(10)	-2464(8)	-4792(2)	-2351(3)	27(1)
C(11)	-3157(9)	-5293(3)	-1899(3)	39(1)
C(12)	-1930(12)	-5830(3)	-1692(3)	49(2)
C(13)	-19(11)	-5882(3)	-1929(4)	55(2)
C(14)	717(11)	-5390(4)	-2370(4)	61(2)
C(15)	-483(10)	-4834(3)	-2568(4)	50(2)
C(16)	-3915(7)	-3592(2)	-2169(3)	23(1)
C(17)	-4508(7)	-3632(2)	-1423(2)	26(1)
C(18)	-4947(7)	-2877(2)	-1240(2)	24(1)
C(19)	-3763(6)	-2435(2)	-1765(2)	23(1)
C(20)	-3549(6)	-2932(2)	-2373(3)	22(1)
C(21)	-7102(7)	-2696(2)	-1428(3)	28(1)
C(22)	-7181(7)	-2030(3)	-1845(3)	38(1)
C(23)	-5026(7)	-1786(2)	-1893(3)	28(1)
C(24)	-4584(9)	-2691(3)	-488(3)	39(1)
C(25)	-2798(8)	-2707(2)	-3056(3)	28(1)
C(26)	-4017(9)	-2340(3)	-3509(3)	39(1)
C(27)	-3306(11)	-2123(3)	-4140(3)	50(2)
C(28)	-1371(13)	-2277(3)	-4338(4)	54(2)
C(29)	-165(11)	-2648(3)	-3903(4)	51(2)

C(30)	-843(9)	-2864(3)	-3268(3)	38(1)
O(1)	-3047(9)	-5819(3)	-4708(3)	72(2)
O(2)	-7682(10)	-4027(3)	-4467(3)	78(2)
O(3)	-1842(5)	-2201(2)	-1543(2)	35(1)
O(4)	-8553(6)	-3040(2)	-1276(3)	51(1)
O(5)	-8754(9)	-5918(3)	-4195(4)	80(2)

Table 3. Bond lengths [Å] and angles [°] for **3a**.

C(1)-C(2)	1.534(6)
C(1)-C(5)	1.513(8)
C(1)-C(6)	1.533(9)
C(1)-C(7)	1.527(7)
C(2)-C(3)	1.498(8)
C(2)-O(1)	1.194(7)
C(3)-H(3)	0.9300
C(3)-C(4)	1.519(9)
C(4)-H(4)	0.9300
C(4)-C(5)	1.501(8)
C(5)-O(2)	1.207(8)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-C(8)	1.501(6)
C(8)-H(8)	0.9300
C(8)-C(9)	1.329(7)
C(9)-C(10)	1.495(6)
C(9)-C(16)	1.490(6)
C(10)-C(11)	1.385(7)
C(10)-C(15)	1.389(8)
C(11)-H(11)	0.9300
C(11)-C(12)	1.380(9)
C(12)-H(12)	0.9300
C(12)-C(13)	1.358(11)
C(13)-H(13)	0.9300
C(13)-C(14)	1.368(11)
C(14)-H(14)	0.9300
C(14)-C(15)	1.391(9)
C(15)-H(15)	0.9300
C(16)-C(17)	1.504(7)

C(16)-C(20)	1.355(6)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(17)-C(18)	1.527(6)
C(18)-C(19)	1.544(7)
C(18)-C(21)	1.522(6)
C(18)-C(24)	1.523(7)
C(19)-C(20)	1.528(6)
C(19)-C(23)	1.529(6)
C(19)-O(3)	1.424(6)
C(20)-C(25)	1.482(7)
C(21)-C(22)	1.518(7)
C(21)-O(4)	1.209(6)
C(22)-H(22A)	0.9700
C(22)-H(22B)	0.9700
C(22)-C(23)	1.514(7)
C(23)-H(23A)	0.9700
C(23)-H(23B)	0.9700
C(24)-H(24A)	0.9600
C(24)-H(24B)	0.9600
C(24)-H(24C)	0.9600
C(25)-C(26)	1.392(8)
C(25)-C(30)	1.399(7)
C(26)-H(26)	0.9300
C(26)-C(27)	1.378(9)
C(27)-H(27)	0.9300
C(27)-C(28)	1.378(11)
C(28)-H(28)	0.9300
C(28)-C(29)	1.370(11)
C(29)-H(29)	0.9300
C(29)-C(30)	1.377(9)
C(30)-H(30)	0.9300
O(3)-H(3A)	0.8200
O(5)-H(5A)	0.8498
O(5)-H(5B)	0.8331

C(5)-C(1)-C(2)	102.5(4)
C(5)-C(1)-C(6)	109.6(5)
C(5)-C(1)-C(7)	113.0(5)
C(6)-C(1)-C(2)	108.2(5)
C(7)-C(1)-C(2)	110.6(4)
C(7)-C(1)-C(6)	112.4(5)
C(3)-C(2)-C(1)	110.8(5)
O(1)-C(2)-C(1)	124.5(5)
O(1)-C(2)-C(3)	124.6(5)
C(2)-C(3)-H(3)	126.7
C(2)-C(3)-C(4)	106.5(5)
C(4)-C(3)-H(3)	126.7
C(3)-C(4)-H(4)	126.7
C(5)-C(4)-C(3)	106.7(5)
C(5)-C(4)-H(4)	126.7
C(4)-C(5)-C(1)	111.6(5)
O(2)-C(5)-C(1)	125.0(6)
O(2)-C(5)-C(4)	123.4(6)
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(1)-C(7)-H(7A)	108.7
C(1)-C(7)-H(7B)	108.7
H(7A)-C(7)-H(7B)	107.6
C(8)-C(7)-C(1)	114.1(4)
C(8)-C(7)-H(7A)	108.7
C(8)-C(7)-H(7B)	108.7
C(7)-C(8)-H(8)	117.4
C(9)-C(8)-C(7)	125.1(4)
C(9)-C(8)-H(8)	117.4
C(8)-C(9)-C(10)	121.9(4)
C(8)-C(9)-C(16)	122.1(4)
C(16)-C(9)-C(10)	116.0(4)

C(11)-C(10)-C(9)	122.1(5)
C(11)-C(10)-C(15)	117.9(5)
C(15)-C(10)-C(9)	120.0(5)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-C(10)	120.8(6)
C(12)-C(11)-H(11)	119.6
C(11)-C(12)-H(12)	119.6
C(13)-C(12)-C(11)	120.8(6)
C(13)-C(12)-H(12)	119.6
C(12)-C(13)-H(13)	120.1
C(12)-C(13)-C(14)	119.8(6)
C(14)-C(13)-H(13)	120.1
C(13)-C(14)-H(14)	120.0
C(13)-C(14)-C(15)	120.1(7)
C(15)-C(14)-H(14)	120.0
C(10)-C(15)-C(14)	120.6(6)
C(10)-C(15)-H(15)	119.7
C(14)-C(15)-H(15)	119.7
C(9)-C(16)-C(17)	122.0(4)
C(20)-C(16)-C(9)	125.9(4)
C(20)-C(16)-C(17)	112.1(4)
C(16)-C(17)-H(17A)	111.2
C(16)-C(17)-H(17B)	111.2
C(16)-C(17)-C(18)	103.1(4)
H(17A)-C(17)-H(17B)	109.1
C(18)-C(17)-H(17A)	111.2
C(18)-C(17)-H(17B)	111.2
C(17)-C(18)-C(19)	105.9(4)
C(21)-C(18)-C(17)	110.1(4)
C(21)-C(18)-C(19)	101.4(4)
C(21)-C(18)-C(24)	109.0(4)
C(24)-C(18)-C(17)	114.6(4)
C(24)-C(18)-C(19)	114.9(4)
C(20)-C(19)-C(18)	102.2(3)
C(20)-C(19)-C(23)	116.1(4)
C(23)-C(19)-C(18)	106.1(4)

O(3)-C(19)-C(18)	115.7(4)
O(3)-C(19)-C(20)	110.5(4)
O(3)-C(19)-C(23)	106.5(4)
C(16)-C(20)-C(19)	110.3(4)
C(16)-C(20)-C(25)	126.6(4)
C(25)-C(20)-C(19)	122.6(4)
C(22)-C(21)-C(18)	110.7(4)
O(4)-C(21)-C(18)	124.7(4)
O(4)-C(21)-C(22)	124.5(4)
C(21)-C(22)-H(22A)	110.7
C(21)-C(22)-H(22B)	110.7
H(22A)-C(22)-H(22B)	108.8
C(23)-C(22)-C(21)	105.2(4)
C(23)-C(22)-H(22A)	110.7
C(23)-C(22)-H(22B)	110.7
C(19)-C(23)-H(23A)	110.8
C(19)-C(23)-H(23B)	110.8
C(22)-C(23)-C(19)	104.9(4)
C(22)-C(23)-H(23A)	110.8
C(22)-C(23)-H(23B)	110.8
H(23A)-C(23)-H(23B)	108.8
C(18)-C(24)-H(24A)	109.5
C(18)-C(24)-H(24B)	109.5
C(18)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(26)-C(25)-C(20)	121.2(5)
C(26)-C(25)-C(30)	117.9(5)
C(30)-C(25)-C(20)	121.0(5)
C(25)-C(26)-H(26)	119.5
C(27)-C(26)-C(25)	121.0(6)
C(27)-C(26)-H(26)	119.5
C(26)-C(27)-H(27)	119.8
C(28)-C(27)-C(26)	120.4(7)
C(28)-C(27)-H(27)	119.8

C(27)-C(28)-H(28)	120.4
C(29)-C(28)-C(27)	119.3(6)
C(29)-C(28)-H(28)	120.4
C(28)-C(29)-H(29)	119.4
C(28)-C(29)-C(30)	121.2(6)
C(30)-C(29)-H(29)	119.4
C(25)-C(30)-H(30)	119.9
C(29)-C(30)-C(25)	120.2(6)
C(29)-C(30)-H(30)	119.9
C(19)-O(3)-H(3A)	109.5
H(5A)-O(5)-H(5B)	117.3

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	37(3)	22(2)	35(2)	-9(2)	-5(2)	3(2)
C(2)	39(3)	32(3)	43(3)	-14(2)	-4(3)	4(2)
C(3)	61(4)	46(3)	49(3)	-17(3)	-17(3)	10(3)
C(4)	43(4)	53(3)	51(3)	-4(3)	-17(3)	6(3)
C(5)	40(3)	29(3)	44(3)	1(2)	-2(3)	5(2)
C(6)	58(5)	49(4)	62(4)	-9(3)	11(3)	-16(3)
C(7)	48(3)	23(2)	33(2)	-6(2)	-9(2)	-1(2)
C(8)	31(3)	19(2)	38(2)	-4(2)	-7(2)	2(2)
C(9)	27(3)	16(2)	34(2)	-2(2)	-3(2)	2(2)
C(10)	28(3)	18(2)	34(2)	-2(2)	-3(2)	2(2)
C(11)	37(3)	27(2)	54(3)	5(2)	-2(3)	-4(2)
C(12)	66(4)	27(3)	55(3)	10(2)	-17(3)	-3(3)
C(13)	67(5)	39(3)	60(4)	-9(3)	-22(4)	26(3)
C(14)	45(4)	71(4)	67(4)	7(4)	4(4)	30(4)
C(15)	37(4)	49(3)	62(4)	14(3)	11(3)	17(3)
C(16)	18(2)	16(2)	36(2)	-1(2)	-2(2)	1(2)
C(17)	26(2)	21(2)	33(2)	1(2)	2(2)	7(2)
C(18)	17(2)	22(2)	33(2)	-3(2)	-2(2)	4(2)
C(19)	10(2)	22(2)	37(2)	-5(2)	-1(2)	3(2)
C(20)	11(2)	20(2)	34(2)	-2(2)	2(2)	-2(2)
C(21)	17(2)	24(2)	42(3)	5(2)	0(2)	4(2)
C(22)	16(3)	34(3)	63(4)	18(3)	-1(2)	6(2)
C(23)	19(2)	18(2)	48(3)	0(2)	5(2)	1(2)
C(24)	36(3)	48(3)	33(3)	-8(2)	-1(2)	4(2)
C(25)	27(3)	22(2)	36(2)	-2(2)	4(2)	-8(2)
C(26)	35(3)	35(3)	46(3)	0(2)	-3(2)	-7(2)
C(27)	68(5)	39(3)	42(3)	5(3)	-3(3)	-10(3)
C(28)	78(5)	38(3)	46(3)	-1(3)	22(3)	-18(3)
C(29)	48(4)	42(3)	64(4)	-12(3)	30(3)	-10(3)
C(30)	31(3)	32(2)	52(3)	-3(2)	14(2)	-3(2)

O(1)	70(4)	62(3)	83(3)	-33(3)	-33(3)	43(3)
O(2)	81(4)	77(4)	77(4)	-27(3)	-28(3)	50(3)
O(3)	15(2)	30(2)	61(2)	-11(2)	-7(2)	-2(1)
O(4)	20(2)	44(2)	90(3)	26(2)	3(2)	-4(2)
O(5)	73(4)	63(3)	103(4)	22(3)	-29(4)	-11(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3a**.

	x	y	z	U(eq)
H(3)	-5560	-5734	-5826	62
H(4)	-8316	-4775	-5643	59
H(6A)	-1789	-4386	-4403	85
H(6B)	-3357	-3781	-4374	85
H(6C)	-2938	-4163	-5072	85
H(7A)	-6037	-5176	-3565	42
H(7B)	-3691	-5201	-3528	42
H(8)	-5628	-3912	-3322	35
H(11)	-4464	-5267	-1733	47
H(12)	-2417	-6161	-1386	59
H(13)	787	-6251	-1793	66
H(14)	2021	-5428	-2537	73
H(15)	47	-4489	-2848	59
H(17A)	-3423	-3815	-1144	32
H(17B)	-5689	-3919	-1362	32
H(22A)	-7727	-2116	-2300	45
H(22B)	-8007	-1686	-1616	45
H(23A)	-4750	-1435	-1547	34
H(23B)	-4749	-1594	-2344	34
H(24A)	-4855	-2207	-419	58
H(24B)	-3212	-2787	-371	58
H(24C)	-5456	-2962	-201	58
H(26)	-5333	-2239	-3384	47
H(27)	-4137	-1873	-4433	60
H(28)	-890	-2129	-4763	65
H(29)	1137	-2757	-4038	62
H(30)	1	-3116	-2979	46
H(3A)	-1105	-2536	-1481	53
H(5A)	-8586	-6249	-3913	120
H(5B)	-9869	-5887	-4387	120

Table 6. Torsion angles [°] for **3a**.

C(1)-C(2)-C(3)-C(4)	-11.5(8)
C(1)-C(7)-C(8)-C(9)	-136.8(6)
C(2)-C(1)-C(5)-C(4)	-11.5(6)
C(2)-C(1)-C(5)-O(2)	169.8(7)
C(2)-C(1)-C(7)-C(8)	169.5(5)
C(2)-C(3)-C(4)-C(5)	3.9(7)
C(3)-C(4)-C(5)-C(1)	5.1(7)
C(3)-C(4)-C(5)-O(2)	-176.2(7)
C(5)-C(1)-C(2)-C(3)	14.1(6)
C(5)-C(1)-C(2)-O(1)	-169.1(7)
C(5)-C(1)-C(7)-C(8)	-76.3(6)
C(6)-C(1)-C(2)-C(3)	-101.7(6)
C(6)-C(1)-C(2)-O(1)	75.1(8)
C(6)-C(1)-C(5)-C(4)	103.2(6)
C(6)-C(1)-C(5)-O(2)	-75.5(8)
C(6)-C(1)-C(7)-C(8)	48.5(7)
C(7)-C(1)-C(2)-C(3)	134.8(6)
C(7)-C(1)-C(2)-O(1)	-48.4(9)
C(7)-C(1)-C(5)-C(4)	-130.6(5)
C(7)-C(1)-C(5)-O(2)	50.7(8)
C(7)-C(8)-C(9)-C(10)	-0.4(8)
C(7)-C(8)-C(9)-C(16)	-178.0(5)
C(8)-C(9)-C(10)-C(11)	-91.4(7)
C(8)-C(9)-C(10)-C(15)	87.9(7)
C(8)-C(9)-C(16)-C(17)	123.0(5)
C(8)-C(9)-C(16)-C(20)	-56.5(7)
C(9)-C(10)-C(11)-C(12)	177.0(5)
C(9)-C(10)-C(15)-C(14)	-175.2(6)
C(9)-C(16)-C(17)-C(18)	-166.3(4)
C(9)-C(16)-C(20)-C(19)	-177.8(4)
C(9)-C(16)-C(20)-C(25)	-5.0(8)
C(10)-C(9)-C(16)-C(17)	-54.6(6)
C(10)-C(9)-C(16)-C(20)	125.8(5)
C(10)-C(11)-C(12)-C(13)	-0.4(9)

C(11)-C(10)-C(15)-C(14)	4.1(10)
C(11)-C(12)-C(13)-C(14)	1.2(10)
C(12)-C(13)-C(14)-C(15)	0.7(11)
C(13)-C(14)-C(15)-C(10)	-3.4(11)
C(15)-C(10)-C(11)-C(12)	-2.2(9)
C(16)-C(9)-C(10)-C(11)	86.3(6)
C(16)-C(9)-C(10)-C(15)	-94.5(6)
C(16)-C(17)-C(18)-C(19)	-23.4(5)
C(16)-C(17)-C(18)-C(21)	85.5(5)
C(16)-C(17)-C(18)-C(24)	-151.2(4)
C(16)-C(20)-C(25)-C(26)	111.3(6)
C(16)-C(20)-C(25)-C(30)	-68.1(7)
C(17)-C(16)-C(20)-C(19)	2.6(5)
C(17)-C(16)-C(20)-C(25)	175.4(5)
C(17)-C(18)-C(19)-C(20)	24.7(5)
C(17)-C(18)-C(19)-C(23)	146.7(4)
C(17)-C(18)-C(19)-O(3)	-95.4(4)
C(17)-C(18)-C(21)-C(22)	-130.2(5)
C(17)-C(18)-C(21)-O(4)	48.7(7)
C(18)-C(19)-C(20)-C(16)	-17.2(5)
C(18)-C(19)-C(20)-C(25)	169.7(4)
C(18)-C(19)-C(23)-C(22)	-34.2(5)
C(18)-C(21)-C(22)-C(23)	-1.9(6)
C(19)-C(18)-C(21)-C(22)	-18.4(5)
C(19)-C(18)-C(21)-O(4)	160.6(6)
C(19)-C(20)-C(25)-C(26)	-76.8(6)
C(19)-C(20)-C(25)-C(30)	103.8(5)
C(20)-C(16)-C(17)-C(18)	13.3(5)
C(20)-C(19)-C(23)-C(22)	78.5(5)
C(20)-C(25)-C(26)-C(27)	179.1(5)
C(20)-C(25)-C(30)-C(29)	-179.7(5)
C(21)-C(18)-C(19)-C(20)	-90.3(4)
C(21)-C(18)-C(19)-C(23)	31.8(5)
C(21)-C(18)-C(19)-O(3)	149.6(4)
C(21)-C(22)-C(23)-C(19)	21.8(6)
C(23)-C(19)-C(20)-C(16)	-132.1(4)

C(23)-C(19)-C(20)-C(25)	54.8(6)
C(24)-C(18)-C(19)-C(20)	152.3(4)
C(24)-C(18)-C(19)-C(23)	-85.6(5)
C(24)-C(18)-C(19)-O(3)	32.3(5)
C(24)-C(18)-C(21)-C(22)	103.2(5)
C(24)-C(18)-C(21)-O(4)	-77.8(7)
C(25)-C(26)-C(27)-C(28)	0.9(9)
C(26)-C(25)-C(30)-C(29)	1.0(7)
C(26)-C(27)-C(28)-C(29)	0.2(9)
C(27)-C(28)-C(29)-C(30)	-0.7(9)
C(28)-C(29)-C(30)-C(25)	0.1(9)
C(30)-C(25)-C(26)-C(27)	-1.5(7)
O(1)-C(2)-C(3)-C(4)	171.6(7)
O(3)-C(19)-C(20)-C(16)	106.5(4)
O(3)-C(19)-C(20)-C(25)	-66.6(6)
O(3)-C(19)-C(23)-C(22)	-158.1(4)
O(4)-C(21)-C(22)-C(23)	179.2(6)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for **3a** 0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)

7.2 Compound 8

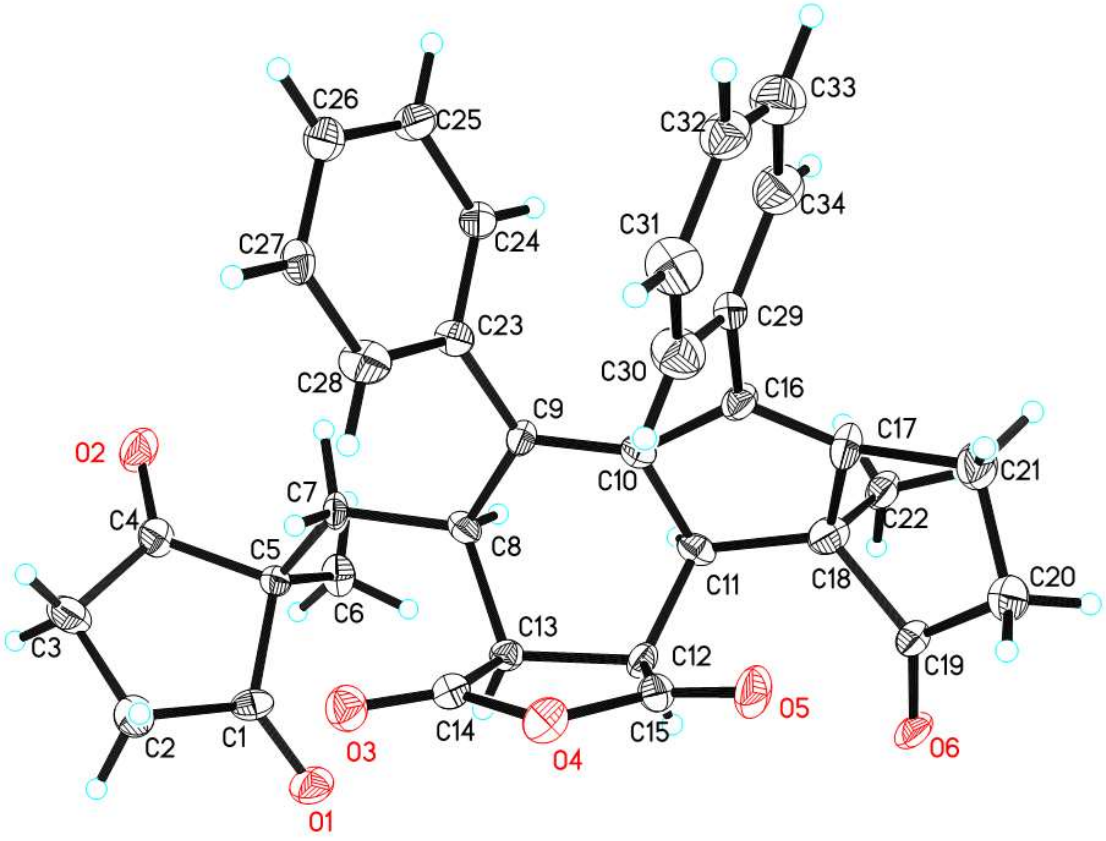


Table 8. Crystal data and structure refinement for **8**.

Identification code	cu_190514b_0m	
Empirical formula	C34 H30 O6	
Formula weight	534.58	
Temperature	293(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 6.6786(13) Å	a= 90°.
	b = 19.494(4) Å	b= 92.008(9)°.
	c = 21.437(4) Å	g = 90°.
Volume	2789.2(9) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	0.703 mm^{-1}	
F(000)	1128	
Crystal size	0.06 x 0.04 x 0.02 mm^3	
Theta range for data collection	2.06 to 50.40°.	
Index ranges	-5<=h<=6, -19<=k<=18, -21<=l<=21	
Reflections collected	7810	
Independent reflections	4964 [R(int) = 0.2470]	
Completeness to theta = 50.40°	97.2 %	
Absorption correction	None	
Max. and min. transmission	0.7500 and 0.4201	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4964 / 166 / 678	
Goodness-of-fit on F^2	0.944	
Final R indices [I>2sigma(I)]	R1 = 0.0967, wR2 = 0.2063	
R indices (all data)	R1 = 0.2052, wR2 = 0.2695	
Absolute structure parameter	0.3(8)	
Extinction coefficient	0.0075(8)	
Largest diff. peak and hole	0.215 and -0.215 e.$Å^{-3}$	

Table 9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	-4970(20)	8358(9)	396(8)	78(5)
C(2)	-5890(30)	7888(10)	872(8)	103(6)
C(3)	-4130(30)	7521(10)	1170(9)	115(7)
C(4)	-2370(30)	7644(9)	765(7)	81(6)
C(5)	-3040(20)	8042(9)	184(6)	71(5)
C(6)	-1530(20)	8614(9)	53(7)	86(6)
C(7)	-3300(20)	7537(7)	-371(6)	64(5)
C(8)	-3710(20)	7814(8)	-1022(6)	66(5)
C(9)	-3630(20)	7278(8)	-1526(7)	58(4)
C(10)	-3870(20)	7544(8)	-2089(8)	64(4)
C(11)	-4180(20)	8320(8)	-2178(7)	64(4)
C(12)	-5960(20)	8480(8)	-1818(7)	67(5)
C(13)	-5690(20)	8251(8)	-1131(6)	60(4)
C(14)	-7410(30)	7821(10)	-986(10)	83(6)
C(15)	-7830(30)	8093(9)	-2005(10)	74(5)
C(16)	-4310(30)	7248(9)	-2723(8)	75(5)
C(17)	-4530(30)	7724(8)	-3159(6)	83(6)
C(18)	-4350(30)	8431(8)	-2879(9)	90(6)
C(19)	-6020(20)	8845(8)	-3202(7)	74(5)
C(20)	-6740(30)	8453(8)	-3782(7)	106(6)
C(21)	-5500(30)	7811(9)	-3802(7)	104(6)
C(22)	-2480(30)	8807(8)	-3121(7)	88(6)
C(23)	-3237(19)	6538(4)	-1403(5)	68(5)
C(28)	-4596(16)	6147(6)	-1080(5)	98(6)
C(27)	-4225(19)	5454(6)	-973(5)	78(5)
C(26)	-2500(20)	5153(5)	-1190(5)	93(6)
C(25)	-1136(16)	5545(6)	-1514(5)	92(6)
C(24)	-1507(16)	6238(6)	-1620(5)	70(5)
C(29)	-4610(20)	6503(5)	-2884(6)	75(5)
C(30)	-6350(20)	6179(8)	-2701(6)	123(8)
C(31)	-6734(19)	5505(8)	-2880(6)	125(7)

C(32)	-5380(20)	5155(5)	-3242(6)	105(6)
C(33)	-3650(20)	5480(7)	-3425(6)	130(8)
C(34)	-3261(18)	6154(8)	-3246(6)	122(7)
O(1)	-5750(20)	8888(6)	228(5)	106(5)
O(2)	-760(20)	7394(7)	824(6)	114(5)
O(3)	-7930(20)	7560(6)	-519(6)	99(4)
O(4)	-8689(18)	7776(6)	-1518(6)	92(4)
O(5)	-8540(20)	8017(7)	-2530(5)	109(5)
O(6)	-6610(20)	9388(6)	-3056(5)	110(5)
C(1A)	130(30)	156(11)	-1119(9)	89(6)
C(2A)	1210(30)	487(10)	-587(9)	112(7)
C(3A)	-330(30)	886(10)	-219(9)	102(6)
C(4A)	-2150(30)	900(10)	-640(9)	80(6)
C(5A)	-1830(20)	543(8)	-1246(7)	67(5)
C(6A)	-3570(30)	35(9)	-1396(7)	87(6)
C(7A)	-1700(20)	1136(8)	-1738(8)	73(5)
C(8A)	-1820(20)	957(8)	-2430(7)	62(4)
C(9A)	-2230(20)	1537(9)	-2903(8)	65(5)
C(10A)	-2460(20)	1326(8)	-3479(8)	62(5)
C(11A)	-2110(20)	601(7)	-3664(6)	51(4)
C(12A)	-20(30)	430(8)	-3341(8)	73(5)
C(13A)	50(30)	556(8)	-2649(7)	67(5)
C(14A)	1960(30)	936(10)	-2498(10)	75(5)
C(15A)	1550(30)	946(11)	-3550(10)	86(6)
C(16A)	-2350(30)	576(9)	-4381(7)	73(5)
C(17A)	-2650(30)	1293(9)	-4558(7)	78(5)
C(18A)	-2680(20)	1721(8)	-4071(8)	65(5)
C(19A)	-2160(30)	1349(9)	-5239(7)	93(6)
C(20A)	-620(30)	785(9)	-5318(8)	129(9)
C(21A)	-730(30)	304(11)	-4764(8)	99(6)
C(22A)	-2420(20)	2266(5)	-2677(5)	73(5)
C(23A)	-755(16)	2609(7)	-2426(5)	93(6)
C(24A)	-880(20)	3305(7)	-2288(5)	103(7)
C(25A)	-2660(30)	3656(5)	-2401(5)	128(9)
C(26A)	-4328(19)	3313(7)	-2652(5)	103(7)
C(27A)	-4206(16)	2617(7)	-2790(5)	81(5)

C(28A)	-2830(20)	2482(5)	-4178(5)	84(6)
C(29A)	-1173(16)	2905(9)	-4078(5)	93(6)
C(30A)	-1330(20)	3605(8)	-4192(6)	112(8)
C(31A)	-3150(30)	3882(5)	-4406(6)	123(8)
C(32A)	-4800(20)	3459(7)	-4505(5)	98(6)
C(33A)	-4644(18)	2759(7)	-4391(5)	89(6)
C(34A)	-4160(30)	132(8)	-4551(8)	107(7)
O(1A)	620(20)	-336(7)	-1406(6)	106(5)
O(2A)	-3690(20)	1137(7)	-473(6)	103(5)
O(3A)	2790(20)	1064(7)	-2038(7)	104(5)
O(4A)	2698(18)	1153(6)	-3064(6)	85(4)
O(5A)	1859(18)	1115(6)	-4074(6)	89(4)
O(6A)	250(20)	-212(6)	-4710(5)	114(5)

Table 10. Bond lengths [Å] and angles [°] for **8**.

C(1)-C(2)	1.515(10)
C(1)-C(5)	1.516(10)
C(1)-O(1)	1.206(16)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(2)-C(3)	1.498(10)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(3)-C(4)	1.506(10)
C(4)-C(5)	1.519(10)
C(4)-O(2)	1.181(18)
C(5)-C(6)	1.53(2)
C(5)-C(7)	1.550(19)
C(6)-H(6A)	0.9600
C(6)-H(6B)	0.9600
C(6)-H(6C)	0.9600
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(7)-C(8)	1.511(17)
C(8)-H(8)	0.9800
C(8)-C(9)	1.507(18)
C(8)-C(13)	1.584(19)
C(9)-C(10)	1.317(18)
C(9)-C(23)	1.488(16)
C(10)-C(11)	1.54(2)
C(10)-C(16)	1.50(2)
C(11)-H(11)	0.9800
C(11)-C(12)	1.474(19)
C(11)-C(18)	1.52(2)
C(12)-H(12)	0.9800
C(12)-C(13)	1.542(17)
C(12)-C(15)	1.50(2)
C(13)-H(13)	0.9800
C(13)-C(14)	1.47(2)

C(14)-O(3)	1.185(18)
C(14)-O(4)	1.40(2)
C(15)-O(4)	1.356(18)
C(15)-O(5)	1.215(19)
C(16)-C(17)	1.323(19)
C(16)-C(29)	1.504(18)
C(17)-C(18)	1.507(10)
C(17)-C(21)	1.511(10)
C(18)-C(19)	1.523(10)
C(18)-C(22)	1.55(2)
C(19)-C(20)	1.524(10)
C(19)-O(6)	1.177(16)
C(20)-H(20A)	0.9700
C(20)-H(20B)	0.9700
C(20)-C(21)	1.506(10)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600
C(22)-H(22C)	0.9600
C(23)-C(28)	1.3900
C(23)-C(24)	1.3900
C(28)-H(28)	0.9300
C(28)-C(27)	1.3900
C(27)-H(27)	0.9300
C(27)-C(26)	1.3900
C(26)-H(26)	0.9300
C(26)-C(25)	1.3900
C(25)-H(25)	0.9300
C(25)-C(24)	1.3900
C(24)-H(24)	0.9300
C(29)-C(30)	1.3900
C(29)-C(34)	1.3900
C(30)-H(30)	0.9300
C(30)-C(31)	1.3900
C(31)-H(31)	0.9300

C(31)-C(32)	1.3900
C(32)-H(32)	0.9300
C(32)-C(33)	1.3900
C(33)-H(33)	0.9300
C(33)-C(34)	1.3900
C(34)-H(34)	0.9300
C(1A)-C(2A)	1.48(2)
C(1A)-C(5A)	1.52(2)
C(1A)-O(1A)	1.19(2)
C(2A)-H(2AA)	0.9700
C(2A)-H(2AB)	0.9700
C(2A)-C(3A)	1.53(2)
C(3A)-H(3AA)	0.9700
C(3A)-H(3AB)	0.9700
C(3A)-C(4A)	1.49(2)
C(4A)-C(5A)	1.50(2)
C(4A)-O(2A)	1.194(19)
C(5A)-C(6A)	1.56(2)
C(5A)-C(7A)	1.57(2)
C(6A)-H(6AA)	0.9600
C(6A)-H(6AB)	0.9600
C(6A)-H(6AC)	0.9600
C(7A)-H(7AA)	0.9700
C(7A)-H(7AB)	0.9700
C(7A)-C(8A)	1.523(19)
C(8A)-H(8A)	0.9800
C(8A)-C(9A)	1.54(2)
C(8A)-C(13A)	1.56(2)
C(9A)-C(10A)	1.304(19)
C(9A)-C(22A)	1.509(19)
C(10A)-C(11A)	1.487(18)
C(10A)-C(18A)	1.49(2)
C(11A)-H(11A)	0.9800
C(11A)-C(12A)	1.570(19)
C(11A)-C(16A)	1.541(18)
C(12A)-H(12A)	0.9800

C(12A)-C(13A)	1.50(2)
C(12A)-C(15A)	1.53(2)
C(13A)-H(13A)	0.9800
C(13A)-C(14A)	1.50(2)
C(14A)-O(3A)	1.14(2)
C(14A)-O(4A)	1.390(19)
C(15A)-O(4A)	1.34(2)
C(15A)-O(5A)	1.196(19)
C(16A)-C(17A)	1.46(2)
C(16A)-C(21A)	1.482(16)
C(16A)-C(34A)	1.52(2)
C(17A)-C(18A)	1.337(18)
C(17A)-C(19A)	1.511(10)
C(18A)-C(28A)	1.504(17)
C(19A)-H(19A)	0.9700
C(19A)-H(19B)	0.9700
C(19A)-C(20A)	1.523(10)
C(20A)-H(20C)	0.9700
C(20A)-H(20D)	0.9700
C(20A)-C(21A)	1.516(9)
C(21A)-O(6A)	1.20(2)
C(22A)-C(23A)	1.3900
C(22A)-C(27A)	1.3900
C(23A)-H(23A)	0.9300
C(23A)-C(24A)	1.3900
C(24A)-H(24A)	0.9300
C(24A)-C(25A)	1.3900
C(25A)-H(25A)	0.9300
C(25A)-C(26A)	1.3900
C(26A)-H(26A)	0.9300
C(26A)-C(27A)	1.3900
C(27A)-H(27A)	0.9300
C(28A)-C(29A)	1.3900
C(28A)-C(33A)	1.3900
C(29A)-H(29A)	0.9300
C(29A)-C(30A)	1.3900

C(30A)-H(30A)	0.9300
C(30A)-C(31A)	1.3900
C(31A)-H(31A)	0.9300
C(31A)-C(32A)	1.3900
C(32A)-H(32A)	0.9300
C(32A)-C(33A)	1.3900
C(33A)-H(33A)	0.9300
C(34A)-H(34A)	0.9600
C(34A)-H(34B)	0.9600
C(34A)-H(34C)	0.9600

C(2)-C(1)-C(5)	109.0(15)
O(1)-C(1)-C(2)	122.7(16)
O(1)-C(1)-C(5)	128.4(16)
C(1)-C(2)-H(2A)	110.9
C(1)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	108.9
C(3)-C(2)-C(1)	104.3(15)
C(3)-C(2)-H(2A)	110.9
C(3)-C(2)-H(2B)	110.9
C(2)-C(3)-H(3A)	110.3
C(2)-C(3)-H(3B)	110.3
C(2)-C(3)-C(4)	107.1(16)
H(3A)-C(3)-H(3B)	108.5
C(4)-C(3)-H(3A)	110.3
C(4)-C(3)-H(3B)	110.3
C(3)-C(4)-C(5)	109.9(15)
O(2)-C(4)-C(3)	126.6(15)
O(2)-C(4)-C(5)	122.6(16)
C(1)-C(5)-C(4)	101.0(14)
C(1)-C(5)-C(6)	109.3(14)
C(1)-C(5)-C(7)	114.4(13)
C(4)-C(5)-C(6)	110.2(14)
C(4)-C(5)-C(7)	109.1(13)
C(6)-C(5)-C(7)	112.2(12)
C(5)-C(6)-H(6A)	109.5

C(5)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	107.4
C(5)-C(7)-H(7B)	107.4
H(7A)-C(7)-H(7B)	107.0
C(8)-C(7)-C(5)	119.6(12)
C(8)-C(7)-H(7A)	107.4
C(8)-C(7)-H(7B)	107.4
C(7)-C(8)-H(8)	105.6
C(7)-C(8)-C(13)	116.7(12)
C(9)-C(8)-C(7)	113.9(12)
C(9)-C(8)-H(8)	105.6
C(9)-C(8)-C(13)	108.4(12)
C(13)-C(8)-H(8)	105.6
C(10)-C(9)-C(8)	112.2(13)
C(10)-C(9)-C(23)	124.0(14)
C(23)-C(9)-C(8)	123.7(12)
C(9)-C(10)-C(11)	120.9(14)
C(9)-C(10)-C(16)	133.8(16)
C(16)-C(10)-C(11)	104.2(14)
C(10)-C(11)-H(11)	109.8
C(12)-C(11)-C(10)	104.4(13)
C(12)-C(11)-H(11)	109.8
C(12)-C(11)-C(18)	117.1(13)
C(18)-C(11)-C(10)	105.6(13)
C(18)-C(11)-H(11)	109.8
C(11)-C(12)-H(12)	109.6
C(11)-C(12)-C(13)	111.8(12)
C(11)-C(12)-C(15)	115.7(14)
C(13)-C(12)-H(12)	109.6
C(15)-C(12)-H(12)	109.6
C(15)-C(12)-C(13)	100.3(13)
C(8)-C(13)-H(13)	109.8

C(12)-C(13)-C(8)	111.4(12)
C(12)-C(13)-H(13)	109.8
C(14)-C(13)-C(8)	108.6(13)
C(14)-C(13)-C(12)	107.5(14)
C(14)-C(13)-H(13)	109.8
O(3)-C(14)-C(13)	132.9(19)
O(3)-C(14)-O(4)	118(2)
O(4)-C(14)-C(13)	108.8(16)
O(4)-C(15)-C(12)	113.1(15)
O(5)-C(15)-C(12)	127.2(18)
O(5)-C(15)-O(4)	119.6(17)
C(10)-C(16)-C(29)	127.1(14)
C(17)-C(16)-C(10)	112.7(15)
C(17)-C(16)-C(29)	120.2(14)
C(16)-C(17)-C(18)	110.7(13)
C(16)-C(17)-C(21)	139.3(15)
C(18)-C(17)-C(21)	106.7(13)
C(11)-C(18)-C(19)	123.6(15)
C(11)-C(18)-C(22)	111.5(13)
C(17)-C(18)-C(11)	105.5(13)
C(17)-C(18)-C(19)	104.7(13)
C(17)-C(18)-C(22)	110.8(15)
C(19)-C(18)-C(22)	100.4(14)
C(18)-C(19)-C(20)	108.3(14)
O(6)-C(19)-C(18)	127.0(13)
O(6)-C(19)-C(20)	124.6(14)
C(19)-C(20)-H(20A)	110.5
C(19)-C(20)-H(20B)	110.5
H(20A)-C(20)-H(20B)	108.7
C(21)-C(20)-C(19)	106.2(14)
C(21)-C(20)-H(20A)	110.5
C(21)-C(20)-H(20B)	110.5
C(17)-C(21)-H(21A)	110.4
C(17)-C(21)-H(21B)	110.4
C(20)-C(21)-C(17)	106.6(13)
C(20)-C(21)-H(21A)	110.4

C(20)-C(21)-H(21B)	110.4
H(21A)-C(21)-H(21B)	108.6
C(18)-C(22)-H(22A)	109.5
C(18)-C(22)-H(22B)	109.5
C(18)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(28)-C(23)-C(9)	120.5(11)
C(28)-C(23)-C(24)	120.0
C(24)-C(23)-C(9)	119.5(11)
C(23)-C(28)-H(28)	120.0
C(27)-C(28)-C(23)	120.0
C(27)-C(28)-H(28)	120.0
C(28)-C(27)-H(27)	120.0
C(28)-C(27)-C(26)	120.0
C(26)-C(27)-H(27)	120.0
C(27)-C(26)-H(26)	120.0
C(27)-C(26)-C(25)	120.0
C(25)-C(26)-H(26)	120.0
C(26)-C(25)-H(25)	120.0
C(26)-C(25)-C(24)	120.0
C(24)-C(25)-H(25)	120.0
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-C(23)	120.0
C(25)-C(24)-H(24)	120.0
C(30)-C(29)-C(16)	118.8(13)
C(30)-C(29)-C(34)	120.0
C(34)-C(29)-C(16)	121.0(13)
C(29)-C(30)-H(30)	120.0
C(31)-C(30)-C(29)	120.0
C(31)-C(30)-H(30)	120.0
C(30)-C(31)-H(31)	120.0
C(32)-C(31)-C(30)	120.0
C(32)-C(31)-H(31)	120.0
C(31)-C(32)-H(32)	120.0

C(31)-C(32)-C(33)	120.0
C(33)-C(32)-H(32)	120.0
C(32)-C(33)-H(33)	120.0
C(34)-C(33)-C(32)	120.0
C(34)-C(33)-H(33)	120.0
C(29)-C(34)-H(34)	120.0
C(33)-C(34)-C(29)	120.0
C(33)-C(34)-H(34)	120.0
C(15)-O(4)-C(14)	109.6(15)
C(2A)-C(1A)-C(5A)	108.4(19)
O(1A)-C(1A)-C(2A)	128(2)
O(1A)-C(1A)-C(5A)	123.7(17)
C(1A)-C(2A)-H(2AA)	110.2
C(1A)-C(2A)-H(2AB)	110.2
C(1A)-C(2A)-C(3A)	107.5(18)
H(2AA)-C(2A)-H(2AB)	108.5
C(3A)-C(2A)-H(2AA)	110.2
C(3A)-C(2A)-H(2AB)	110.2
C(2A)-C(3A)-H(3AA)	110.9
C(2A)-C(3A)-H(3AB)	110.9
H(3AA)-C(3A)-H(3AB)	108.9
C(4A)-C(3A)-C(2A)	104.2(16)
C(4A)-C(3A)-H(3AA)	110.9
C(4A)-C(3A)-H(3AB)	110.9
C(3A)-C(4A)-C(5A)	112.2(17)
O(2A)-C(4A)-C(3A)	121.2(19)
O(2A)-C(4A)-C(5A)	126.4(19)
C(1A)-C(5A)-C(6A)	110.7(14)
C(1A)-C(5A)-C(7A)	114.8(14)
C(4A)-C(5A)-C(1A)	103.0(15)
C(4A)-C(5A)-C(6A)	110.2(14)
C(4A)-C(5A)-C(7A)	104.6(14)
C(6A)-C(5A)-C(7A)	112.8(12)
C(5A)-C(6A)-H(6AA)	109.5
C(5A)-C(6A)-H(6AB)	109.5
C(5A)-C(6A)-H(6AC)	109.5

H(6AA)-C(6A)-H(6AB)	109.5
H(6AA)-C(6A)-H(6AC)	109.5
H(6AB)-C(6A)-H(6AC)	109.5
C(5A)-C(7A)-H(7AA)	107.6
C(5A)-C(7A)-H(7AB)	107.6
H(7AA)-C(7A)-H(7AB)	107.0
C(8A)-C(7A)-C(5A)	118.9(13)
C(8A)-C(7A)-H(7AA)	107.6
C(8A)-C(7A)-H(7AB)	107.6
C(7A)-C(8A)-H(8A)	105.7
C(7A)-C(8A)-C(9A)	118.4(14)
C(7A)-C(8A)-C(13A)	113.2(12)
C(9A)-C(8A)-H(8A)	105.7
C(9A)-C(8A)-C(13A)	107.1(13)
C(13A)-C(8A)-H(8A)	105.7
C(10A)-C(9A)-C(8A)	113.9(15)
C(10A)-C(9A)-C(22A)	126.3(14)
C(22A)-C(9A)-C(8A)	119.7(14)
C(9A)-C(10A)-C(11A)	122.5(14)
C(9A)-C(10A)-C(18A)	130.4(15)
C(11A)-C(10A)-C(18A)	106.0(13)
C(10A)-C(11A)-H(11A)	109.0
C(10A)-C(11A)-C(12A)	103.3(11)
C(10A)-C(11A)-C(16A)	106.5(12)
C(12A)-C(11A)-H(11A)	109.0
C(16A)-C(11A)-H(11A)	109.0
C(16A)-C(11A)-C(12A)	119.6(13)
C(11A)-C(12A)-H(12A)	110.9
C(13A)-C(12A)-C(11A)	113.5(14)
C(13A)-C(12A)-H(12A)	110.9
C(13A)-C(12A)-C(15A)	100.5(14)
C(15A)-C(12A)-C(11A)	109.7(13)
C(15A)-C(12A)-H(12A)	110.9
C(8A)-C(13A)-H(13A)	108.6
C(12A)-C(13A)-C(8A)	112.3(14)
C(12A)-C(13A)-H(13A)	108.6

C(14A)-C(13A)-C(8A)	111.8(14)
C(14A)-C(13A)-C(12A)	106.9(14)
C(14A)-C(13A)-H(13A)	108.6
O(3A)-C(14A)-C(13A)	132.5(19)
O(3A)-C(14A)-O(4A)	121(2)
O(4A)-C(14A)-C(13A)	106.6(16)
O(4A)-C(15A)-C(12A)	110.6(17)
O(5A)-C(15A)-C(12A)	126.8(19)
O(5A)-C(15A)-O(4A)	122(2)
C(17A)-C(16A)-C(11A)	103.7(12)
C(17A)-C(16A)-C(21A)	107.1(16)
C(17A)-C(16A)-C(34A)	112.5(15)
C(21A)-C(16A)-C(11A)	120.7(14)
C(21A)-C(16A)-C(34A)	104.7(15)
C(34A)-C(16A)-C(11A)	108.3(14)
C(16A)-C(17A)-C(19A)	106.8(14)
C(18A)-C(17A)-C(16A)	113.6(13)
C(18A)-C(17A)-C(19A)	136.0(17)
C(10A)-C(18A)-C(28A)	130.2(14)
C(17A)-C(18A)-C(10A)	109.8(14)
C(17A)-C(18A)-C(28A)	120.0(15)
C(17A)-C(19A)-H(19A)	111.2
C(17A)-C(19A)-H(19B)	111.2
C(17A)-C(19A)-C(20A)	103.0(14)
H(19A)-C(19A)-H(19B)	109.1
C(20A)-C(19A)-H(19A)	111.2
C(20A)-C(19A)-H(19B)	111.2
C(19A)-C(20A)-H(20C)	110.1
C(19A)-C(20A)-H(20D)	110.1
H(20C)-C(20A)-H(20D)	108.4
C(21A)-C(20A)-C(19A)	108.0(16)
C(21A)-C(20A)-H(20C)	110.1
C(21A)-C(20A)-H(20D)	110.1
C(16A)-C(21A)-C(20A)	105.6(17)
O(6A)-C(21A)-C(16A)	130.7(18)
O(6A)-C(21A)-C(20A)	123.5(18)

C(23A)-C(22A)-C(9A)	120.2(11)
C(23A)-C(22A)-C(27A)	120.0
C(27A)-C(22A)-C(9A)	119.4(11)
C(22A)-C(23A)-H(23A)	120.0
C(24A)-C(23A)-C(22A)	120.0
C(24A)-C(23A)-H(23A)	120.0
C(23A)-C(24A)-H(24A)	120.0
C(23A)-C(24A)-C(25A)	120.0
C(25A)-C(24A)-H(24A)	120.0
C(24A)-C(25A)-H(25A)	120.0
C(24A)-C(25A)-C(26A)	120.0
C(26A)-C(25A)-H(25A)	120.0
C(25A)-C(26A)-H(26A)	120.0
C(27A)-C(26A)-C(25A)	120.0
C(27A)-C(26A)-H(26A)	120.0
C(22A)-C(27A)-H(27A)	120.0
C(26A)-C(27A)-C(22A)	120.0
C(26A)-C(27A)-H(27A)	120.0
C(29A)-C(28A)-C(18A)	121.0(12)
C(29A)-C(28A)-C(33A)	120.0
C(33A)-C(28A)-C(18A)	119.0(12)
C(28A)-C(29A)-H(29A)	120.0
C(28A)-C(29A)-C(30A)	120.0
C(30A)-C(29A)-H(29A)	120.0
C(29A)-C(30A)-H(30A)	120.0
C(29A)-C(30A)-C(31A)	120.0
C(31A)-C(30A)-H(30A)	120.0
C(30A)-C(31A)-H(31A)	120.0
C(32A)-C(31A)-C(30A)	120.0
C(32A)-C(31A)-H(31A)	120.0
C(31A)-C(32A)-H(32A)	120.0
C(33A)-C(32A)-C(31A)	120.0
C(33A)-C(32A)-H(32A)	120.0
C(28A)-C(33A)-H(33A)	120.0
C(32A)-C(33A)-C(28A)	120.0
C(32A)-C(33A)-H(33A)	120.0

C(16A)-C(34A)-H(34A)	109.5
C(16A)-C(34A)-H(34B)	109.5
C(16A)-C(34A)-H(34C)	109.5
H(34A)-C(34A)-H(34B)	109.5
H(34A)-C(34A)-H(34C)	109.5
H(34B)-C(34A)-H(34C)	109.5
C(15A)-O(4A)-C(14A)	112.2(17)

Symmetry transformations used to generate equivalent atoms:

Table 11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	77(15)	56(12)	101(15)	-19(11)	-5(11)	10(11)
C(2)	96(10)	114(10)	100(10)	11(8)	13(8)	3(9)
C(3)	105(19)	122(18)	123(16)	-3(14)	51(16)	14(15)
C(4)	73(16)	111(16)	56(12)	-11(11)	-20(12)	0(12)
C(5)	63(13)	93(14)	57(12)	8(10)	7(9)	21(11)
C(6)	74(15)	109(15)	75(12)	10(11)	-4(10)	-23(12)
C(7)	86(14)	70(11)	37(10)	12(9)	-1(9)	0(10)
C(8)	74(13)	66(11)	58(11)	-10(9)	15(9)	1(9)
C(9)	77(13)	47(11)	50(11)	2(9)	-10(9)	-2(8)
C(10)	64(13)	63(12)	64(12)	-9(10)	5(9)	0(9)
C(11)	39(11)	83(13)	70(11)	-21(9)	5(9)	-8(9)
C(12)	49(12)	85(13)	68(11)	28(9)	-3(9)	7(10)
C(13)	54(8)	67(8)	60(8)	-6(7)	-4(7)	6(7)
C(14)	83(10)	87(9)	79(9)	8(8)	5(8)	23(8)
C(15)	76(10)	75(9)	73(9)	10(8)	14(8)	2(7)
C(16)	99(16)	52(12)	74(13)	5(10)	-11(10)	12(9)
C(17)	114(16)	68(13)	63(11)	14(10)	-25(10)	-13(10)
C(18)	88(10)	82(9)	99(10)	-3(8)	-11(8)	12(8)
C(19)	79(9)	68(9)	74(9)	13(7)	-2(7)	11(8)
C(20)	107(10)	123(10)	86(9)	-2(8)	-10(8)	8(8)
C(21)	130(11)	101(10)	81(9)	-7(8)	-15(8)	2(8)
C(22)	124(19)	63(12)	75(12)	-1(9)	-25(11)	16(12)
C(23)	67(14)	53(12)	86(13)	-2(9)	18(10)	-14(10)
C(28)	110(18)	51(13)	133(17)	-26(11)	13(13)	-25(11)
C(27)	89(9)	76(9)	68(8)	15(7)	14(7)	-17(8)
C(26)	104(17)	81(14)	96(14)	12(11)	18(12)	-4(12)
C(25)	94(10)	76(9)	107(9)	3(8)	4(8)	16(8)
C(24)	80(9)	61(8)	70(8)	-5(7)	0(7)	-6(7)
C(29)	83(15)	90(15)	54(11)	7(10)	4(10)	18(11)
C(30)	133(11)	111(11)	125(11)	-12(9)	15(9)	-8(9)
C(31)	135(11)	108(10)	132(10)	-11(8)	8(9)	-29(9)

C(32)	119(10)	80(9)	117(10)	4(8)	2(8)	0(8)
C(33)	138(12)	118(11)	135(11)	-11(9)	11(9)	9(9)
C(34)	126(11)	109(11)	130(11)	4(8)	-2(9)	0(9)
O(1)	138(13)	78(10)	102(10)	-19(7)	-7(8)	33(9)
O(2)	102(12)	136(12)	102(9)	32(8)	-18(9)	19(10)
O(3)	111(11)	103(10)	82(9)	-4(8)	-3(8)	1(8)
O(4)	79(9)	93(9)	103(9)	0(7)	-16(8)	-9(7)
O(5)	120(12)	137(11)	67(8)	7(8)	-36(8)	6(8)
O(6)	162(13)	82(9)	84(8)	-4(7)	-28(8)	70(9)
C(1A)	88(10)	98(10)	79(9)	11(8)	-6(8)	-3(8)
C(2A)	112(11)	122(10)	100(10)	0(8)	-9(8)	-2(9)
C(3A)	99(10)	104(10)	104(9)	-16(8)	-8(8)	0(8)
C(4A)	82(18)	66(13)	92(16)	-2(12)	-1(13)	-6(11)
C(5A)	67(14)	73(13)	62(11)	-4(10)	-15(9)	10(10)
C(6A)	85(12)	93(12)	83(11)	-8(9)	-22(9)	-13(10)
C(7A)	42(11)	66(12)	111(16)	-18(11)	-11(10)	20(8)
C(8A)	32(11)	79(12)	74(13)	20(10)	-3(8)	-5(9)
C(9A)	36(11)	92(14)	67(13)	23(11)	7(9)	-13(9)
C(10A)	60(13)	64(12)	59(12)	16(10)	-26(9)	-4(8)
C(11A)	58(8)	45(7)	49(7)	-6(6)	-14(6)	10(6)
C(12A)	90(15)	41(11)	88(14)	5(9)	-8(11)	-5(10)
C(13A)	58(14)	65(12)	75(13)	13(9)	-17(10)	-29(10)
C(14A)	68(16)	88(15)	70(15)	5(13)	22(12)	26(12)
C(15A)	106(18)	95(16)	56(13)	-19(13)	-13(14)	37(13)
C(16A)	87(15)	82(14)	50(11)	-27(10)	-15(10)	14(11)
C(17A)	119(17)	60(13)	54(12)	13(11)	-15(10)	16(10)
C(18A)	64(13)	48(11)	85(14)	-16(11)	17(10)	1(9)
C(19A)	129(19)	78(14)	69(14)	5(10)	-19(12)	2(12)
C(20A)	200(30)	92(16)	93(16)	-15(13)	-23(15)	35(16)
C(21A)	103(10)	96(10)	98(10)	-3(9)	-7(8)	16(8)
C(22A)	95(16)	61(13)	61(11)	-1(10)	-23(10)	2(11)
C(23A)	150(20)	48(12)	80(13)	-29(10)	-39(12)	16(11)
C(24A)	120(20)	105(19)	84(14)	-28(13)	-16(13)	-37(14)
C(25A)	200(30)	79(15)	109(17)	-15(13)	7(17)	32(18)
C(26A)	115(11)	103(10)	91(9)	5(8)	2(8)	15(9)
C(27A)	106(18)	60(12)	76(12)	0(10)	1(11)	8(11)

C(28A)	96(17)	73(14)	81(13)	16(10)	-6(11)	25(12)
C(29A)	97(18)	105(18)	78(13)	19(12)	13(11)	1(14)
C(30A)	180(30)	53(14)	105(16)	1(12)	17(15)	-14(14)
C(31A)	180(30)	71(15)	120(18)	11(12)	-12(17)	19(17)
C(32A)	99(10)	94(10)	102(10)	0(8)	-3(8)	24(8)
C(33A)	95(10)	86(9)	87(9)	16(7)	-4(8)	4(8)
C(34A)	170(20)	47(12)	99(14)	-3(10)	-48(14)	-4(12)
O(1A)	114(12)	112(11)	90(9)	8(8)	-6(8)	48(9)
O(2A)	100(12)	130(12)	79(9)	-14(8)	-16(8)	16(9)
O(3A)	98(11)	111(10)	100(10)	9(8)	-38(9)	-11(8)
O(4A)	84(10)	107(10)	64(9)	-10(7)	-7(8)	-10(7)
O(5A)	72(9)	116(10)	78(9)	-9(8)	8(7)	1(7)
O(6A)	160(14)	108(11)	74(8)	-3(7)	-1(8)	51(9)

Table 12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **8**.

	x	y	z	U(eq)
H(2A)	-6600	8150	1179	124
H(2B)	-6812	7566	670	124
H(3A)	-4408	7034	1199	138
H(3B)	-3852	7697	1587	138
H(6A)	-2041	8891	-287	129
H(6B)	-278	8414	-55	129
H(6C)	-1342	8894	419	129
H(7A)	-2098	7259	-381	77
H(7B)	-4395	7230	-278	77
H(8)	-2598	8130	-1099	79
H(11)	-3011	8569	-2003	76
H(12)	-6221	8974	-1835	81
H(13)	-5646	8655	-858	73
H(20A)	-8153	8340	-3756	127
H(20B)	-6566	8727	-4154	127
H(21A)	-4482	7854	-4113	125
H(21B)	-6335	7418	-3908	125
H(22A)	-2461	9270	-2968	132
H(22B)	-2547	8812	-3570	132
H(22C)	-1292	8573	-2977	132
H(28)	-5753	6348	-935	117
H(27)	-5134	5192	-757	93
H(26)	-2247	4690	-1119	112
H(25)	21	5344	-1659	111
H(24)	-597	6500	-1837	85
H(30)	-7256	6413	-2458	147
H(31)	-7896	5288	-2757	150
H(32)	-5639	4704	-3361	126
H(33)	-2740	5246	-3667	156
H(34)	-2099	6371	-3369	146
H(2AA)	2225	797	-737	134

H(2AB)	1861	144	-323	134
H(3AA)	-603	655	170	123
H(3AB)	138	1347	-127	123
H(6AA)	-3308	-212	-1772	131
H(6AB)	-4803	286	-1453	131
H(6AC)	-3690	-282	-1057	131
H(7AA)	-2777	1456	-1660	88
H(7AB)	-452	1378	-1656	88
H(8A)	-2950	639	-2482	74
H(11A)	-3133	310	-3483	61
H(12A)	388	-40	-3436	88
H(13A)	109	111	-2435	80
H(19A)	-1610	1796	-5333	111
H(19B)	-3344	1271	-5506	111
H(20C)	-897	536	-5703	154
H(20D)	713	982	-5334	154
H(23A)	441	2374	-2351	111
H(24A)	237	3534	-2120	124
H(25A)	-2745	4121	-2309	153
H(26A)	-5523	3548	-2728	123
H(27A)	-5320	2388	-2958	97
H(29A)	42	2720	-3936	112
H(30A)	-226	3889	-4126	134
H(31A)	-3256	4351	-4482	148
H(32A)	-6019	3644	-4648	118
H(33A)	-5752	2476	-4458	107
H(34A)	-3814	-343	-4494	161
H(34B)	-4564	210	-4979	161
H(34C)	-5242	247	-4287	161

Table 13. Torsion angles [°] for **8**.

C(1)-C(2)-C(3)-C(4)	-14(2)
C(1)-C(5)-C(7)-C(8)	75.5(19)
C(2)-C(1)-C(5)-C(4)	-29.6(18)
C(2)-C(1)-C(5)-C(6)	-145.8(14)
C(2)-C(1)-C(5)-C(7)	87.4(16)
C(2)-C(3)-C(4)-C(5)	-4(2)
C(2)-C(3)-C(4)-O(2)	-173.9(19)
C(3)-C(4)-C(5)-C(1)	20.4(18)
C(3)-C(4)-C(5)-C(6)	135.9(15)
C(3)-C(4)-C(5)-C(7)	-100.4(16)
C(4)-C(5)-C(7)-C(8)	-172.3(14)
C(5)-C(1)-C(2)-C(3)	28(2)
C(5)-C(7)-C(8)-C(9)	171.5(13)
C(5)-C(7)-C(8)-C(13)	-61(2)
C(6)-C(5)-C(7)-C(8)	-49.8(19)
C(7)-C(8)-C(9)-C(10)	-176.3(14)
C(7)-C(8)-C(9)-C(23)	1(2)
C(7)-C(8)-C(13)-C(12)	-177.9(13)
C(7)-C(8)-C(13)-C(14)	-59.6(18)
C(8)-C(9)-C(10)-C(11)	0(2)
C(8)-C(9)-C(10)-C(16)	-166.1(17)
C(8)-C(9)-C(23)-C(28)	65.4(16)
C(8)-C(9)-C(23)-C(24)	-115.3(14)
C(8)-C(13)-C(14)-O(3)	64(3)
C(8)-C(13)-C(14)-O(4)	-121.3(13)
C(9)-C(8)-C(13)-C(12)	-47.6(17)
C(9)-C(8)-C(13)-C(14)	70.6(16)
C(9)-C(10)-C(11)-C(12)	-57.3(19)
C(9)-C(10)-C(11)-C(18)	178.7(15)
C(9)-C(10)-C(16)-C(17)	176.6(19)
C(9)-C(10)-C(16)-C(29)	0(3)
C(9)-C(23)-C(28)-C(27)	179.3(11)
C(9)-C(23)-C(24)-C(25)	-179.3(11)
C(10)-C(9)-C(23)-C(28)	-117.3(15)

C(10)-C(9)-C(23)-C(24)	62.0(17)
C(10)-C(11)-C(12)-C(13)	55.8(16)
C(10)-C(11)-C(12)-C(15)	-58.1(16)
C(10)-C(11)-C(18)-C(17)	10.5(17)
C(10)-C(11)-C(18)-C(19)	130.4(16)
C(10)-C(11)-C(18)-C(22)	-109.9(14)
C(10)-C(16)-C(17)-C(18)	-2(2)
C(10)-C(16)-C(17)-C(21)	-158(2)
C(10)-C(16)-C(29)-C(30)	70.5(18)
C(10)-C(16)-C(29)-C(34)	-113.8(16)
C(11)-C(10)-C(16)-C(17)	8.6(19)
C(11)-C(10)-C(16)-C(29)	-167.7(15)
C(11)-C(12)-C(13)-C(8)	-8.1(19)
C(11)-C(12)-C(13)-C(14)	-126.9(15)
C(11)-C(12)-C(15)-O(4)	127.8(15)
C(11)-C(12)-C(15)-O(5)	-49(2)
C(11)-C(18)-C(19)-C(20)	-136.4(17)
C(11)-C(18)-C(19)-O(6)	47(3)
C(12)-C(11)-C(18)-C(17)	-105.1(16)
C(12)-C(11)-C(18)-C(19)	15(2)
C(12)-C(11)-C(18)-C(22)	134.5(15)
C(12)-C(13)-C(14)-O(3)	-175.2(19)
C(12)-C(13)-C(14)-O(4)	-0.6(18)
C(12)-C(15)-O(4)-C(14)	-8.4(19)
C(13)-C(8)-C(9)-C(10)	51.9(17)
C(13)-C(8)-C(9)-C(23)	-130.6(14)
C(13)-C(12)-C(15)-O(4)	7.5(18)
C(13)-C(12)-C(15)-O(5)	-168.9(17)
C(13)-C(14)-O(4)-C(15)	5.4(18)
C(15)-C(12)-C(13)-C(8)	115.0(14)
C(15)-C(12)-C(13)-C(14)	-3.8(17)
C(16)-C(10)-C(11)-C(12)	112.7(14)
C(16)-C(10)-C(11)-C(18)	-11.4(16)
C(16)-C(17)-C(18)-C(11)	-6(2)
C(16)-C(17)-C(18)-C(19)	-137.4(17)
C(16)-C(17)-C(18)-C(22)	115.2(17)

C(16)-C(17)-C(21)-C(20)	129(2)
C(16)-C(29)-C(30)-C(31)	175.7(11)
C(16)-C(29)-C(34)-C(33)	-175.6(11)
C(17)-C(16)-C(29)-C(30)	-105.5(17)
C(17)-C(16)-C(29)-C(34)	70.2(19)
C(17)-C(18)-C(19)-C(20)	-16(2)
C(17)-C(18)-C(19)-O(6)	167.3(19)
C(18)-C(11)-C(12)-C(13)	172.1(13)
C(18)-C(11)-C(12)-C(15)	58(2)
C(18)-C(17)-C(21)-C(20)	-27(2)
C(18)-C(19)-C(20)-C(21)	0(2)
C(19)-C(20)-C(21)-C(17)	17(2)
C(21)-C(17)-C(18)-C(11)	158.1(14)
C(21)-C(17)-C(18)-C(19)	26(2)
C(21)-C(17)-C(18)-C(22)	-81.1(17)
C(22)-C(18)-C(19)-C(20)	98.8(15)
C(22)-C(18)-C(19)-O(6)	-78(2)
C(23)-C(9)-C(10)-C(11)	-177.2(13)
C(23)-C(9)-C(10)-C(16)	16(3)
C(23)-C(28)-C(27)-C(26)	0.0
C(28)-C(23)-C(24)-C(25)	0.0
C(28)-C(27)-C(26)-C(25)	0.0
C(27)-C(26)-C(25)-C(24)	0.0
C(26)-C(25)-C(24)-C(23)	0.0
C(24)-C(23)-C(28)-C(27)	0.0
C(29)-C(16)-C(17)-C(18)	174.6(15)
C(29)-C(16)-C(17)-C(21)	19(3)
C(29)-C(30)-C(31)-C(32)	0.0
C(30)-C(29)-C(34)-C(33)	0.0
C(30)-C(31)-C(32)-C(33)	0.0
C(31)-C(32)-C(33)-C(34)	0.0
C(32)-C(33)-C(34)-C(29)	0.0
C(34)-C(29)-C(30)-C(31)	0.0
O(1)-C(1)-C(2)-C(3)	-152.8(18)
O(1)-C(1)-C(5)-C(4)	151.2(18)
O(1)-C(1)-C(5)-C(6)	35(2)

O(1)-C(1)-C(5)-C(7)	-92(2)
O(2)-C(4)-C(5)-C(1)	-169.5(18)
O(2)-C(4)-C(5)-C(6)	-54(2)
O(2)-C(4)-C(5)-C(7)	70(2)
O(3)-C(14)-O(4)-C(15)	-179.0(16)
O(5)-C(15)-O(4)-C(14)	168.2(16)
O(6)-C(19)-C(20)-C(21)	176.4(19)
C(1A)-C(2A)-C(3A)-C(4A)	-13(2)
C(1A)-C(5A)-C(7A)-C(8A)	80.7(19)
C(2A)-C(1A)-C(5A)-C(4A)	-21.2(19)
C(2A)-C(1A)-C(5A)-C(6A)	-139.0(16)
C(2A)-C(1A)-C(5A)-C(7A)	91.9(18)
C(2A)-C(3A)-C(4A)-C(5A)	-1(2)
C(2A)-C(3A)-C(4A)-O(2A)	174.9(19)
C(3A)-C(4A)-C(5A)-C(1A)	13(2)
C(3A)-C(4A)-C(5A)-C(6A)	131.3(16)
C(3A)-C(4A)-C(5A)-C(7A)	-107.2(16)
C(4A)-C(5A)-C(7A)-C(8A)	-167.2(14)
C(5A)-C(1A)-C(2A)-C(3A)	22(2)
C(5A)-C(7A)-C(8A)-C(9A)	164.9(13)
C(5A)-C(7A)-C(8A)-C(13A)	-68.5(17)
C(6A)-C(5A)-C(7A)-C(8A)	-47.4(19)
C(7A)-C(8A)-C(9A)-C(10A)	-174.8(14)
C(7A)-C(8A)-C(9A)-C(22A)	2(2)
C(7A)-C(8A)-C(13A)-C(12A)	-175.7(13)
C(7A)-C(8A)-C(13A)-C(14A)	-55.5(18)
C(8A)-C(9A)-C(10A)-C(11A)	-7(2)
C(8A)-C(9A)-C(10A)-C(18A)	-173.6(15)
C(8A)-C(9A)-C(22A)-C(23A)	68.9(14)
C(8A)-C(9A)-C(22A)-C(27A)	-118.9(12)
C(8A)-C(13A)-C(14A)-O(3A)	68(3)
C(8A)-C(13A)-C(14A)-O(4A)	-110.8(14)
C(9A)-C(8A)-C(13A)-C(12A)	-43.3(17)
C(9A)-C(8A)-C(13A)-C(14A)	76.9(18)
C(9A)-C(10A)-C(11A)-C(12A)	-48(2)
C(9A)-C(10A)-C(11A)-C(16A)	-175.1(15)

C(9A)-C(10A)-C(18A)-C(17A)	172.9(17)
C(9A)-C(10A)-C(18A)-C(28A)	-4(3)
C(9A)-C(22A)-C(23A)-C(24A)	172.2(11)
C(9A)-C(22A)-C(27A)-C(26A)	-172.3(11)
C(10A)-C(9A)-C(22A)-C(23A)	-114.3(16)
C(10A)-C(9A)-C(22A)-C(27A)	57.9(19)
C(10A)-C(11A)-C(12A)-C(13A)	55.3(17)
C(10A)-C(11A)-C(12A)-C(15A)	-56.3(17)
C(10A)-C(11A)-C(16A)-C(17A)	4.8(18)
C(10A)-C(11A)-C(16A)-C(21A)	124.6(18)
C(10A)-C(11A)-C(16A)-C(34A)	-115.0(15)
C(10A)-C(18A)-C(28A)-C(29A)	71.3(19)
C(10A)-C(18A)-C(28A)-C(33A)	-110.0(16)
C(11A)-C(10A)-C(18A)-C(17A)	4.9(18)
C(11A)-C(10A)-C(18A)-C(28A)	-172.3(15)
C(11A)-C(12A)-C(13A)-C(8A)	-10.9(18)
C(11A)-C(12A)-C(13A)-C(14A)	-133.9(14)
C(11A)-C(12A)-C(15A)-O(4A)	136.5(14)
C(11A)-C(12A)-C(15A)-O(5A)	-49(2)
C(11A)-C(16A)-C(17A)-C(18A)	-2(2)
C(11A)-C(16A)-C(17A)-C(19A)	160.0(14)
C(11A)-C(16A)-C(21A)-C(20A)	-138.1(17)
C(11A)-C(16A)-C(21A)-O(6A)	47(3)
C(12A)-C(11A)-C(16A)-C(17A)	-111.6(15)
C(12A)-C(11A)-C(16A)-C(21A)	8(2)
C(12A)-C(11A)-C(16A)-C(34A)	128.6(15)
C(12A)-C(13A)-C(14A)-O(3A)	-168(2)
C(12A)-C(13A)-C(14A)-O(4A)	12.5(18)
C(12A)-C(15A)-O(4A)-C(14A)	-10.0(18)
C(13A)-C(8A)-C(9A)-C(10A)	55.7(17)
C(13A)-C(8A)-C(9A)-C(22A)	-127.1(14)
C(13A)-C(12A)-C(15A)-O(4A)	16.7(18)
C(13A)-C(12A)-C(15A)-O(5A)	-169.0(18)
C(13A)-C(14A)-O(4A)-C(15A)	-1.6(18)
C(15A)-C(12A)-C(13A)-C(8A)	106.1(14)
C(15A)-C(12A)-C(13A)-C(14A)	-16.8(17)

C(16A)-C(11A)-C(12A)-C(13A)	173.3(13)
C(16A)-C(11A)-C(12A)-C(15A)	61.7(19)
C(16A)-C(17A)-C(18A)-C(10A)	-2(2)
C(16A)-C(17A)-C(18A)-C(28A)	175.7(14)
C(16A)-C(17A)-C(19A)-C(20A)	-29.2(19)
C(17A)-C(16A)-C(21A)-C(20A)	-20.0(19)
C(17A)-C(16A)-C(21A)-O(6A)	166(2)
C(17A)-C(18A)-C(28A)-C(29A)	-105.6(15)
C(17A)-C(18A)-C(28A)-C(33A)	73.1(17)
C(17A)-C(19A)-C(20A)-C(21A)	17(2)
C(18A)-C(10A)-C(11A)-C(12A)	121.0(13)
C(18A)-C(10A)-C(11A)-C(16A)	-5.8(17)
C(18A)-C(17A)-C(19A)-C(20A)	127(2)
C(18A)-C(28A)-C(29A)-C(30A)	178.7(12)
C(18A)-C(28A)-C(33A)-C(32A)	-178.7(12)
C(19A)-C(17A)-C(18A)-C(10A)	-156.5(19)
C(19A)-C(17A)-C(18A)-C(28A)	21(3)
C(19A)-C(20A)-C(21A)-C(16A)	1(2)
C(19A)-C(20A)-C(21A)-O(6A)	176(2)
C(21A)-C(16A)-C(17A)-C(18A)	-130.6(16)
C(21A)-C(16A)-C(17A)-C(19A)	31.3(18)
C(22A)-C(9A)-C(10A)-C(11A)	175.9(14)
C(22A)-C(9A)-C(10A)-C(18A)	9(3)
C(22A)-C(23A)-C(24A)-C(25A)	0.0
C(23A)-C(22A)-C(27A)-C(26A)	0.0
C(23A)-C(24A)-C(25A)-C(26A)	0.0
C(24A)-C(25A)-C(26A)-C(27A)	0.0
C(25A)-C(26A)-C(27A)-C(22A)	0.0
C(27A)-C(22A)-C(23A)-C(24A)	0.0
C(28A)-C(29A)-C(30A)-C(31A)	0.0
C(29A)-C(28A)-C(33A)-C(32A)	0.0
C(29A)-C(30A)-C(31A)-C(32A)	0.0
C(30A)-C(31A)-C(32A)-C(33A)	0.0
C(31A)-C(32A)-C(33A)-C(28A)	0.0
C(33A)-C(28A)-C(29A)-C(30A)	0.0
C(34A)-C(16A)-C(17A)-C(18A)	114.9(17)

C(34A)-C(16A)-C(17A)-C(19A)	-83.2(18)
C(34A)-C(16A)-C(21A)-C(20A)	99.7(17)
C(34A)-C(16A)-C(21A)-O(6A)	-75(3)
O(1A)-C(1A)-C(2A)-C(3A)	-157(2)
O(1A)-C(1A)-C(5A)-C(4A)	157.6(19)
O(1A)-C(1A)-C(5A)-C(6A)	40(2)
O(1A)-C(1A)-C(5A)-C(7A)	-89(2)
O(2A)-C(4A)-C(5A)-C(1A)	-162(2)
O(2A)-C(4A)-C(5A)-C(6A)	-44(3)
O(2A)-C(4A)-C(5A)-C(7A)	78(2)
O(3A)-C(14A)-O(4A)-C(15A)	179.2(18)
O(5A)-C(15A)-O(4A)-C(14A)	175.4(17)

7.3 Compound 9

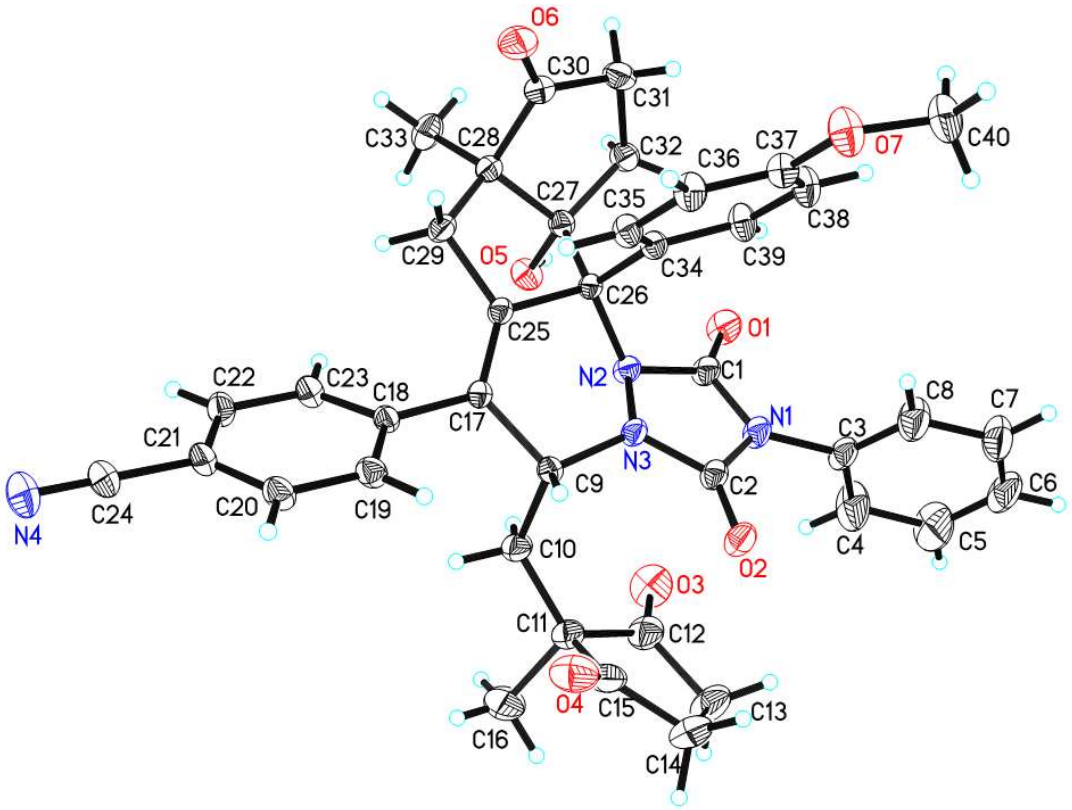


Table 14. Crystal data and structure refinement for **9**.

Identification code	mo_191205a_0m	
Empirical formula	C41 H37 Cl3 N4 O7	
Formula weight	804.09	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 13.3144(9) Å	a= 90°.
	b = 9.8595(7) Å	b= 95.339(2)°.
	c = 14.5355(10) Å	g = 90°.
Volume	1899.8(2) $Å^3$	
Z	2	
Density (calculated)	1.406 Mg/m^3	
Absorption coefficient	0.298 mm^{-1}	
F(000)	836	
Crystal size	0.15 x 0.12 x 0.1 mm^3	
Theta range for data collection	1.536 to 30.692°.	
Index ranges	-18<=h<=18, -14<=k<=14, -17<=l<=20	
Reflections collected	33634	
Independent reflections	10874 [R(int) = 0.0362]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7461 and 0.5746	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10874 / 31 / 525	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0644, wR2 = 0.1816	
R indices (all data)	R1 = 0.0776, wR2 = 0.2025	
Absolute structure parameter	-0.03(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.361 and -0.708 $e.Å^{-3}$	

Table 15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **9**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7918(2)	8341(4)	7596(2)	36(1)
C(2)	8088(2)	7011(3)	6331(2)	34(1)
C(3)	9633(2)	7450(4)	7385(3)	43(1)
C(4)	10288(4)	8434(7)	7167(5)	81(2)
C(5)	11319(4)	8263(9)	7412(5)	92(2)
C(6)	11647(3)	7129(7)	7899(4)	69(1)
C(7)	10990(4)	6174(7)	8119(4)	73(1)
C(8)	9961(3)	6312(6)	7841(4)	63(1)
C(9)	6349(2)	7419(3)	5557(2)	28(1)
C(10)	6563(3)	8554(4)	4879(2)	40(1)
C(11)	7487(3)	8472(4)	4327(3)	44(1)
C(12)	8489(3)	8916(5)	4839(3)	51(1)
C(13)	9343(4)	8224(6)	4399(4)	70(1)
C(14)	8880(4)	7053(7)	3846(4)	69(1)
C(15)	7745(3)	7119(5)	3911(3)	51(1)
C(16)	7308(5)	9473(6)	3499(4)	72(2)
C(17)	5312(2)	7616(3)	5911(2)	27(1)
C(18)	4436(2)	7653(3)	5192(2)	28(1)
C(19)	4339(3)	6722(3)	4472(2)	35(1)
C(20)	3498(3)	6707(4)	3830(2)	39(1)
C(21)	2740(2)	7655(4)	3900(2)	38(1)
C(22)	2835(3)	8637(4)	4594(2)	40(1)
C(23)	3678(2)	8633(3)	5221(2)	34(1)
C(24)	1853(3)	7656(6)	3248(3)	54(1)
C(25)	5204(2)	7721(3)	6820(2)	28(1)
C(26)	6084(2)	7713(3)	7569(2)	27(1)
C(27)	5708(2)	8758(3)	8277(2)	30(1)
C(28)	4579(2)	8361(3)	8265(2)	32(1)
C(29)	4241(2)	7847(4)	7292(2)	37(1)
C(30)	4597(3)	7302(4)	9031(2)	39(1)
C(31)	5472(3)	7599(5)	9745(2)	48(1)

C(32)	6114(3)	8678(4)	9307(2)	38(1)
C(33)	3927(3)	9537(4)	8569(3)	48(1)
C(34)	6283(2)	6268(3)	7945(2)	29(1)
C(35)	5691(2)	5168(3)	7621(2)	35(1)
C(36)	5882(3)	3855(3)	7945(3)	39(1)
C(37)	6698(3)	3607(3)	8579(2)	37(1)
C(38)	7302(3)	4681(4)	8909(3)	42(1)
C(39)	7094(3)	5986(3)	8600(2)	39(1)
C(40)	7738(4)	1972(5)	9428(4)	57(1)
N(1)	8574(2)	7611(3)	7120(2)	38(1)
N(2)	6968(2)	8210(3)	7109(2)	32(1)
N(3)	7097(2)	7332(3)	6351(2)	31(1)
N(4)	1151(3)	7677(7)	2736(3)	79(2)
O(1)	8109(2)	8968(3)	8303(2)	49(1)
O(2)	8463(2)	6381(3)	5738(2)	43(1)
O(3)	8571(3)	9713(4)	5465(3)	69(1)
O(4)	7150(3)	6261(4)	3651(2)	65(1)
O(5)	5799(2)	10066(2)	7897(2)	41(1)
O(6)	4002(2)	6390(4)	9067(2)	56(1)
O(7)	6849(2)	2284(3)	8847(2)	53(1)
C(41)	9263(8)	6981(13)	1020(8)	148(5)
Cl(1)	9447(5)	7968(11)	115(4)	222(4)
Cl(2)	8050(5)	7046(11)	1280(5)	168(4)
Cl(3)	9630(5)	5461(9)	650(7)	243(4)
C(41A)	9390(20)	7080(40)	1120(12)	148(5)
Cl(1A)	8146(15)	7550(30)	1054(17)	136(8)
Cl(2A)	9718(19)	5800(30)	1890(20)	243(4)
Cl(3A)	9601(9)	6580(20)	30(8)	116(5)

—

Table 16. Bond lengths [Å] and angles [°] for **9**.

C(1)-N(1)	1.369(4)
C(1)-N(2)	1.398(4)
C(1)-O(1)	1.205(4)
C(2)-N(1)	1.395(4)
C(2)-N(3)	1.360(4)
C(2)-O(2)	1.208(4)
C(3)-C(4)	1.362(6)
C(3)-C(8)	1.355(7)
C(3)-N(1)	1.435(4)
C(4)-C(5)	1.395(7)
C(5)-C(6)	1.373(10)
C(6)-C(7)	1.344(9)
C(7)-C(8)	1.399(6)
C(9)-C(10)	1.536(4)
C(9)-C(17)	1.531(4)
C(9)-N(3)	1.455(3)
C(10)-C(11)	1.532(5)
C(11)-C(12)	1.530(6)
C(11)-C(15)	1.517(6)
C(11)-C(16)	1.557(6)
C(12)-C(13)	1.518(6)
C(12)-O(3)	1.200(6)
C(13)-C(14)	1.505(9)
C(14)-C(15)	1.523(6)
C(15)-O(4)	1.196(6)
C(17)-C(18)	1.492(3)
C(17)-C(25)	1.346(4)
C(18)-C(19)	1.389(4)
C(18)-C(23)	1.400(4)
C(19)-C(20)	1.389(5)
C(20)-C(21)	1.387(5)
C(21)-C(22)	1.395(5)
C(21)-C(24)	1.443(4)
C(22)-C(23)	1.378(4)

C(24)-N(4)	1.140(5)
C(25)-C(26)	1.523(3)
C(25)-C(29)	1.515(4)
C(26)-C(27)	1.572(4)
C(26)-C(34)	1.540(4)
C(26)-N(2)	1.490(3)
C(27)-C(28)	1.551(4)
C(27)-C(32)	1.545(4)
C(27)-O(5)	1.413(4)
C(28)-C(29)	1.530(4)
C(28)-C(30)	1.525(4)
C(28)-C(33)	1.538(5)
C(30)-C(31)	1.515(5)
C(30)-O(6)	1.203(5)
C(31)-C(32)	1.539(5)
C(34)-C(35)	1.397(4)
C(34)-C(39)	1.399(4)
C(35)-C(36)	1.393(5)
C(36)-C(37)	1.380(5)
C(37)-C(38)	1.388(5)
C(37)-O(7)	1.371(4)
C(38)-C(39)	1.382(5)
C(40)-O(7)	1.422(5)
N(2)-N(3)	1.424(3)
C(41)-Cl(1)	1.673(10)
C(41)-Cl(2)	1.694(10)
C(41)-Cl(3)	1.680(10)
C(41A)-Cl(1A)	1.713(13)
C(41A)-Cl(2A)	1.723(13)
C(41A)-Cl(3A)	1.709(13)

N(1)-C(1)-N(2)	106.6(3)
O(1)-C(1)-N(1)	127.4(3)
O(1)-C(1)-N(2)	126.0(3)
N(3)-C(2)-N(1)	105.1(3)
O(2)-C(2)-N(1)	127.9(3)

O(2)-C(2)-N(3)	127.0(3)
C(4)-C(3)-N(1)	119.6(4)
C(8)-C(3)-C(4)	121.3(4)
C(8)-C(3)-N(1)	119.1(3)
C(3)-C(4)-C(5)	119.4(6)
C(6)-C(5)-C(4)	119.3(6)
C(7)-C(6)-C(5)	120.7(4)
C(6)-C(7)-C(8)	120.3(6)
C(3)-C(8)-C(7)	119.0(5)
C(17)-C(9)-C(10)	110.5(2)
N(3)-C(9)-C(10)	113.5(2)
N(3)-C(9)-C(17)	108.3(2)
C(11)-C(10)-C(9)	120.2(3)
C(10)-C(11)-C(16)	107.3(3)
C(12)-C(11)-C(10)	115.9(3)
C(12)-C(11)-C(16)	105.0(4)
C(15)-C(11)-C(10)	118.6(3)
C(15)-C(11)-C(12)	103.1(3)
C(15)-C(11)-C(16)	105.9(4)
C(13)-C(12)-C(11)	108.6(4)
O(3)-C(12)-C(11)	124.8(4)
O(3)-C(12)-C(13)	126.5(4)
C(14)-C(13)-C(12)	106.5(4)
C(13)-C(14)-C(15)	107.1(4)
C(11)-C(15)-C(14)	108.9(4)
O(4)-C(15)-C(11)	125.4(4)
O(4)-C(15)-C(14)	125.6(5)
C(18)-C(17)-C(9)	116.0(2)
C(25)-C(17)-C(9)	121.4(2)
C(25)-C(17)-C(18)	122.6(2)
C(19)-C(18)-C(17)	121.6(3)
C(19)-C(18)-C(23)	117.5(3)
C(23)-C(18)-C(17)	120.9(2)
C(18)-C(19)-C(20)	121.7(3)
C(21)-C(20)-C(19)	119.4(3)
C(20)-C(21)-C(22)	120.2(3)

C(20)-C(21)-C(24)	120.6(3)
C(22)-C(21)-C(24)	119.2(3)
C(23)-C(22)-C(21)	119.3(3)
C(22)-C(23)-C(18)	121.8(3)
N(4)-C(24)-C(21)	178.9(6)
C(17)-C(25)-C(26)	123.8(2)
C(17)-C(25)-C(29)	128.6(2)
C(29)-C(25)-C(26)	107.7(2)
C(25)-C(26)-C(27)	101.2(2)
C(25)-C(26)-C(34)	110.8(2)
C(34)-C(26)-C(27)	115.4(2)
N(2)-C(26)-C(25)	105.4(2)
N(2)-C(26)-C(27)	113.0(2)
N(2)-C(26)-C(34)	110.3(2)
C(28)-C(27)-C(26)	101.2(2)
C(32)-C(27)-C(26)	119.8(2)
C(32)-C(27)-C(28)	104.5(2)
O(5)-C(27)-C(26)	107.3(2)
O(5)-C(27)-C(28)	110.2(2)
O(5)-C(27)-C(32)	113.0(3)
C(29)-C(28)-C(27)	107.2(2)
C(29)-C(28)-C(33)	112.9(3)
C(30)-C(28)-C(27)	102.4(2)
C(30)-C(28)-C(29)	115.6(3)
C(30)-C(28)-C(33)	106.1(3)
C(33)-C(28)-C(27)	112.3(3)
C(25)-C(29)-C(28)	104.9(2)
C(31)-C(30)-C(28)	109.0(3)
O(6)-C(30)-C(28)	125.3(3)
O(6)-C(30)-C(31)	125.7(3)
C(30)-C(31)-C(32)	105.8(3)
C(31)-C(32)-C(27)	106.1(3)
C(35)-C(34)-C(26)	121.7(3)
C(35)-C(34)-C(39)	116.8(3)
C(39)-C(34)-C(26)	121.5(3)
C(36)-C(35)-C(34)	121.9(3)

C(37)-C(36)-C(35)	119.9(3)
C(36)-C(37)-C(38)	119.4(3)
O(7)-C(37)-C(36)	116.4(3)
O(7)-C(37)-C(38)	124.2(3)
C(39)-C(38)-C(37)	120.4(3)
C(38)-C(39)-C(34)	121.7(3)
C(1)-N(1)-C(2)	111.7(2)
C(1)-N(1)-C(3)	125.4(3)
C(2)-N(1)-C(3)	122.9(3)
C(1)-N(2)-C(26)	121.2(2)
C(1)-N(2)-N(3)	106.2(2)
N(3)-N(2)-C(26)	107.7(2)
C(2)-N(3)-C(9)	126.2(2)
C(2)-N(3)-N(2)	110.2(2)
N(2)-N(3)-C(9)	117.0(2)
C(37)-O(7)-C(40)	117.8(3)
Cl(1)-C(41)-Cl(2)	111.5(7)
Cl(1)-C(41)-Cl(3)	101.4(8)
Cl(3)-C(41)-Cl(2)	114.7(9)
Cl(1A)-C(41A)-Cl(2A)	114.7(19)
Cl(3A)-C(41A)-Cl(1A)	105.5(17)
Cl(3A)-C(41A)-Cl(2A)	109.5(19)

Symmetry transformations used to generate equivalent atoms:

Table 17. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **9**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	25(1)	45(2)	38(1)	-4(1)	1(1)	-8(1)
C(2)	24(1)	38(1)	38(1)	-1(1)	2(1)	-4(1)
C(3)	23(1)	60(2)	45(2)	-10(2)	0(1)	-2(1)
C(4)	35(2)	86(4)	118(5)	28(4)	-13(2)	-17(2)
C(5)	33(2)	125(6)	116(5)	16(4)	-9(2)	-26(3)
C(6)	28(2)	107(4)	71(3)	-19(3)	-2(2)	4(2)
C(7)	45(2)	87(4)	83(3)	5(3)	-8(2)	17(2)
C(8)	37(2)	65(3)	86(3)	9(2)	-1(2)	1(2)
C(9)	26(1)	33(1)	25(1)	0(1)	0(1)	-1(1)
C(10)	37(2)	43(2)	43(2)	12(1)	12(1)	4(1)
C(11)	39(2)	51(2)	43(2)	8(2)	12(1)	1(1)
C(12)	44(2)	52(2)	59(2)	8(2)	13(2)	-7(2)
C(13)	42(2)	88(4)	83(3)	4(3)	25(2)	-5(2)
C(14)	63(3)	86(3)	61(3)	-4(2)	29(2)	12(3)
C(15)	58(2)	61(2)	37(2)	4(2)	17(2)	1(2)
C(16)	77(3)	82(4)	61(3)	38(3)	22(2)	9(3)
C(17)	23(1)	31(1)	28(1)	0(1)	0(1)	-1(1)
C(18)	26(1)	31(1)	25(1)	2(1)	-1(1)	-2(1)
C(19)	41(2)	36(1)	29(1)	-3(1)	2(1)	6(1)
C(20)	44(2)	43(2)	28(1)	-5(1)	-3(1)	0(1)
C(21)	34(1)	49(2)	29(1)	3(1)	-6(1)	0(1)
C(22)	37(2)	43(2)	38(2)	0(1)	-3(1)	9(1)
C(23)	39(2)	32(1)	31(1)	-2(1)	-3(1)	4(1)
C(24)	43(2)	82(3)	34(2)	-1(2)	-7(1)	2(2)
C(25)	22(1)	34(1)	28(1)	-2(1)	1(1)	-2(1)
C(26)	21(1)	34(1)	25(1)	0(1)	0(1)	-3(1)
C(27)	30(1)	32(1)	29(1)	-1(1)	1(1)	-1(1)
C(28)	28(1)	38(1)	31(1)	-1(1)	5(1)	2(1)
C(29)	24(1)	56(2)	31(1)	-5(1)	4(1)	-2(1)
C(30)	36(1)	48(2)	35(1)	3(1)	8(1)	0(1)
C(31)	44(2)	69(2)	31(1)	8(2)	2(1)	-7(2)

C(32)	37(2)	48(2)	29(1)	-5(1)	-2(1)	-4(1)
C(33)	38(2)	48(2)	58(2)	-12(2)	8(2)	8(1)
C(34)	26(1)	33(1)	28(1)	-3(1)	-1(1)	-2(1)
C(35)	32(1)	37(2)	35(1)	-3(1)	-4(1)	-5(1)
C(36)	36(2)	35(2)	45(2)	-6(1)	-6(1)	-6(1)
C(37)	37(1)	34(1)	39(2)	-1(1)	1(1)	-1(1)
C(38)	38(2)	36(2)	50(2)	-1(1)	-12(1)	1(1)
C(39)	35(2)	34(2)	45(2)	-2(1)	-12(1)	-4(1)
C(40)	57(2)	43(2)	69(3)	8(2)	-12(2)	6(2)
N(1)	24(1)	49(2)	40(1)	-6(1)	-1(1)	-4(1)
N(2)	25(1)	40(1)	30(1)	-6(1)	1(1)	-5(1)
N(3)	22(1)	42(1)	30(1)	-5(1)	1(1)	0(1)
N(4)	49(2)	133(5)	50(2)	-5(3)	-17(2)	-1(3)
O(1)	39(1)	61(2)	46(1)	-16(1)	-2(1)	-12(1)
O(2)	30(1)	53(1)	46(1)	-9(1)	5(1)	1(1)
O(3)	66(2)	58(2)	82(2)	-10(2)	5(2)	-15(2)
O(4)	78(2)	69(2)	50(2)	-9(2)	13(2)	-14(2)
O(5)	47(1)	33(1)	42(1)	3(1)	0(1)	-5(1)
O(6)	50(2)	59(2)	57(2)	13(1)	9(1)	-14(1)
O(7)	54(2)	36(1)	66(2)	2(1)	-15(1)	-2(1)
C(41)	119(8)	219(16)	100(7)	-42(8)	-16(6)	-27(9)
Cl(1)	175(5)	342(12)	149(4)	86(6)	20(3)	8(6)
Cl(2)	106(3)	296(10)	99(3)	-1(4)	0(2)	-79(4)
Cl(3)	154(4)	250(7)	307(9)	10(8)	-67(5)	-5(5)
C(41A)	119(8)	219(16)	100(7)	-42(8)	-16(6)	-27(9)
Cl(1A)	89(11)	210(20)	98(13)	17(13)	-39(9)	-7(14)
Cl(2A)	154(4)	250(7)	307(9)	10(8)	-67(5)	-5(5)
Cl(3A)	78(6)	191(14)	74(5)	-13(7)	-21(4)	-25(7)

Table 18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **9**.

	x	y	z	U(eq)
H(4)	10052	9212	6857	97
H(5)	11778	8910	7248	111
H(6)	12331	7020	8078	83
H(7)	11221	5418	8458	87
H(8)	9509	5633	7968	76
H(9)	6344	6553	5225	34
H(10A)	5974	8633	4436	49
H(10B)	6615	9395	5226	49
H(13A)	9659	8851	4000	83
H(13B)	9850	7901	4870	83
H(14A)	9148	6201	4095	82
H(14B)	9028	7123	3207	82
H(16A)	6763	9148	3078	109
H(16B)	7910	9535	3185	109
H(16C)	7142	10352	3724	109
H(19)	4851	6093	4418	42
H(20)	3444	6067	3358	47
H(22)	2335	9287	4634	47
H(23)	3746	9299	5675	41
H(29A)	3907	6975	7318	44
H(29B)	3781	8485	6967	44
H(31A)	5865	6785	9888	58
H(31B)	5230	7941	10310	58
H(32A)	6820	8417	9367	46
H(32B)	6050	9549	9606	46
H(33A)	4147	9787	9193	72
H(33B)	3233	9257	8533	72
H(33C)	3992	10302	8169	72
H(35)	5153	5317	7177	42
H(36)	5461	3147	7733	47

H(38)	7850	4522	9339	51
H(39)	7503	6694	8833	47
H(40A)	8320	2235	9127	86
H(40B)	7763	1014	9548	86
H(40C)	7732	2455	10001	86
H(5A)	6043	10585	8299	61
H(41)	9713	7266	1558	177
H(41A)	9809	7881	1287	177

Table 19. Torsion angles [°] for **9**.

C(1)-N(2)-N(3)-C(2)	-4.1(3)
C(1)-N(2)-N(3)-C(9)	-157.5(3)
C(3)-C(4)-C(5)-C(6)	-2.4(12)
C(4)-C(3)-C(8)-C(7)	2.2(9)
C(4)-C(3)-N(1)-C(1)	-82.7(6)
C(4)-C(3)-N(1)-C(2)	98.0(6)
C(4)-C(5)-C(6)-C(7)	1.6(11)
C(5)-C(6)-C(7)-C(8)	1.1(10)
C(6)-C(7)-C(8)-C(3)	-3.0(9)
C(8)-C(3)-C(4)-C(5)	0.5(10)
C(8)-C(3)-N(1)-C(1)	97.9(5)
C(8)-C(3)-N(1)-C(2)	-81.4(5)
C(9)-C(10)-C(11)-C(12)	-81.3(4)
C(9)-C(10)-C(11)-C(15)	42.1(5)
C(9)-C(10)-C(11)-C(16)	161.9(4)
C(9)-C(17)-C(18)-C(19)	44.8(4)
C(9)-C(17)-C(18)-C(23)	-135.3(3)
C(9)-C(17)-C(25)-C(26)	2.6(4)
C(9)-C(17)-C(25)-C(29)	-176.7(3)
C(10)-C(9)-C(17)-C(18)	58.3(3)
C(10)-C(9)-C(17)-C(25)	-123.0(3)
C(10)-C(9)-N(3)-C(2)	-64.6(4)
C(10)-C(9)-N(3)-N(2)	84.0(3)
C(10)-C(11)-C(12)-C(13)	155.3(4)
C(10)-C(11)-C(12)-O(3)	-26.8(6)
C(10)-C(11)-C(15)-C(14)	-151.3(4)
C(10)-C(11)-C(15)-O(4)	30.7(6)
C(11)-C(12)-C(13)-C(14)	-17.7(6)
C(12)-C(11)-C(15)-C(14)	-21.7(4)
C(12)-C(11)-C(15)-O(4)	160.3(4)
C(12)-C(13)-C(14)-C(15)	3.7(6)
C(13)-C(14)-C(15)-C(11)	11.6(5)
C(13)-C(14)-C(15)-O(4)	-170.4(5)
C(15)-C(11)-C(12)-C(13)	24.2(4)

C(15)-C(11)-C(12)-O(3)	-157.9(4)
C(16)-C(11)-C(12)-C(13)	-86.5(5)
C(16)-C(11)-C(12)-O(3)	91.4(5)
C(16)-C(11)-C(15)-C(14)	88.2(4)
C(16)-C(11)-C(15)-O(4)	-89.7(5)
C(17)-C(9)-C(10)-C(11)	-171.4(3)
C(17)-C(9)-N(3)-C(2)	172.4(3)
C(17)-C(9)-N(3)-N(2)	-39.0(3)
C(17)-C(18)-C(19)-C(20)	176.4(3)
C(17)-C(18)-C(23)-C(22)	-176.2(3)
C(17)-C(25)-C(26)-C(27)	143.4(3)
C(17)-C(25)-C(26)-C(34)	-93.7(3)
C(17)-C(25)-C(26)-N(2)	25.5(4)
C(17)-C(25)-C(29)-C(28)	-163.1(3)
C(18)-C(17)-C(25)-C(26)	-178.8(3)
C(18)-C(17)-C(25)-C(29)	1.9(5)
C(18)-C(19)-C(20)-C(21)	0.9(5)
C(19)-C(18)-C(23)-C(22)	3.7(5)
C(19)-C(20)-C(21)-C(22)	1.7(5)
C(19)-C(20)-C(21)-C(24)	-179.5(3)
C(20)-C(21)-C(22)-C(23)	-1.5(5)
C(21)-C(22)-C(23)-C(18)	-1.2(5)
C(23)-C(18)-C(19)-C(20)	-3.5(5)
C(24)-C(21)-C(22)-C(23)	179.6(3)
C(25)-C(17)-C(18)-C(19)	-133.8(3)
C(25)-C(17)-C(18)-C(23)	46.0(4)
C(25)-C(26)-C(27)-C(28)	41.2(3)
C(25)-C(26)-C(27)-C(32)	155.2(3)
C(25)-C(26)-C(27)-O(5)	-74.3(3)
C(25)-C(26)-C(34)-C(35)	-1.2(4)
C(25)-C(26)-C(34)-C(39)	176.1(3)
C(25)-C(26)-N(2)-C(1)	179.8(3)
C(25)-C(26)-N(2)-N(3)	-57.8(3)
C(26)-C(25)-C(29)-C(28)	17.6(3)
C(26)-C(27)-C(28)-C(29)	-31.9(3)
C(26)-C(27)-C(28)-C(30)	90.2(3)

C(26)-C(27)-C(28)-C(33)	-156.4(3)
C(26)-C(27)-C(32)-C(31)	-83.3(3)
C(26)-C(34)-C(35)-C(36)	178.6(3)
C(26)-C(34)-C(39)-C(38)	-177.1(3)
C(26)-N(2)-N(3)-C(2)	-135.4(3)
C(26)-N(2)-N(3)-C(9)	71.2(3)
C(27)-C(26)-C(34)-C(35)	113.0(3)
C(27)-C(26)-C(34)-C(39)	-69.7(4)
C(27)-C(26)-N(2)-C(1)	70.1(4)
C(27)-C(26)-N(2)-N(3)	-167.4(2)
C(27)-C(28)-C(29)-C(25)	9.7(3)
C(27)-C(28)-C(30)-C(31)	28.7(3)
C(27)-C(28)-C(30)-O(6)	-152.2(4)
C(28)-C(27)-C(32)-C(31)	28.9(3)
C(28)-C(30)-C(31)-C(32)	-11.2(4)
C(29)-C(25)-C(26)-C(27)	-37.2(3)
C(29)-C(25)-C(26)-C(34)	85.7(3)
C(29)-C(25)-C(26)-N(2)	-155.1(3)
C(29)-C(28)-C(30)-C(31)	144.9(3)
C(29)-C(28)-C(30)-O(6)	-36.0(5)
C(30)-C(28)-C(29)-C(25)	-103.8(3)
C(30)-C(31)-C(32)-C(27)	-11.2(4)
C(32)-C(27)-C(28)-C(29)	-156.9(3)
C(32)-C(27)-C(28)-C(30)	-34.8(3)
C(32)-C(27)-C(28)-C(33)	78.6(3)
C(33)-C(28)-C(29)-C(25)	133.8(3)
C(33)-C(28)-C(30)-C(31)	-89.1(3)
C(33)-C(28)-C(30)-O(6)	89.9(4)
C(34)-C(26)-C(27)-C(28)	-78.4(3)
C(34)-C(26)-C(27)-C(32)	35.6(3)
C(34)-C(26)-C(27)-O(5)	166.1(2)
C(34)-C(26)-N(2)-C(1)	-60.7(3)
C(34)-C(26)-N(2)-N(3)	61.8(3)
C(34)-C(35)-C(36)-C(37)	-2.3(5)
C(35)-C(34)-C(39)-C(38)	0.3(5)
C(35)-C(36)-C(37)-C(38)	1.9(5)

C(35)-C(36)-C(37)-O(7)	-178.5(3)
C(36)-C(37)-C(38)-C(39)	-0.4(6)
C(36)-C(37)-O(7)-C(40)	173.8(4)
C(37)-C(38)-C(39)-C(34)	-0.7(6)
C(38)-C(37)-O(7)-C(40)	-6.6(6)
C(39)-C(34)-C(35)-C(36)	1.2(5)
N(1)-C(1)-N(2)-C(26)	125.3(3)
N(1)-C(1)-N(2)-N(3)	2.2(3)
N(1)-C(2)-N(3)-C(9)	154.6(3)
N(1)-C(2)-N(3)-N(2)	4.3(3)
N(1)-C(3)-C(4)-C(5)	-179.0(6)
N(1)-C(3)-C(8)-C(7)	-178.4(5)
N(2)-C(1)-N(1)-C(2)	0.4(4)
N(2)-C(1)-N(1)-C(3)	-179.0(3)
N(2)-C(26)-C(27)-C(28)	153.4(2)
N(2)-C(26)-C(27)-C(32)	-92.6(3)
N(2)-C(26)-C(27)-O(5)	37.9(3)
N(2)-C(26)-C(34)-C(35)	-117.4(3)
N(2)-C(26)-C(34)-C(39)	59.8(3)
N(3)-C(2)-N(1)-C(1)	-2.9(4)
N(3)-C(2)-N(1)-C(3)	176.5(3)
N(3)-C(9)-C(10)-C(11)	66.8(4)
N(3)-C(9)-C(17)-C(18)	-176.8(2)
N(3)-C(9)-C(17)-C(25)	1.9(4)
O(1)-C(1)-N(1)-C(2)	179.7(4)
O(1)-C(1)-N(1)-C(3)	0.3(6)
O(1)-C(1)-N(2)-C(26)	-54.0(5)
O(1)-C(1)-N(2)-N(3)	-177.1(4)
O(2)-C(2)-N(1)-C(1)	174.7(4)
O(2)-C(2)-N(1)-C(3)	-5.9(6)
O(2)-C(2)-N(3)-C(9)	-23.0(5)
O(2)-C(2)-N(3)-N(2)	-173.4(3)
O(3)-C(12)-C(13)-C(14)	164.4(5)
O(5)-C(27)-C(28)-C(29)	81.5(3)
O(5)-C(27)-C(28)-C(30)	-156.5(2)
O(5)-C(27)-C(28)-C(33)	-43.0(4)

O(5)-C(27)-C(32)-C(31)	148.7(3)
O(6)-C(30)-C(31)-C(32)	169.7(4)
O(7)-C(37)-C(38)-C(39)	180.0(4)

Symmetry transformations used to generate equivalent atoms:

Table 20. Hydrogen bonds for **9** [Å and °].

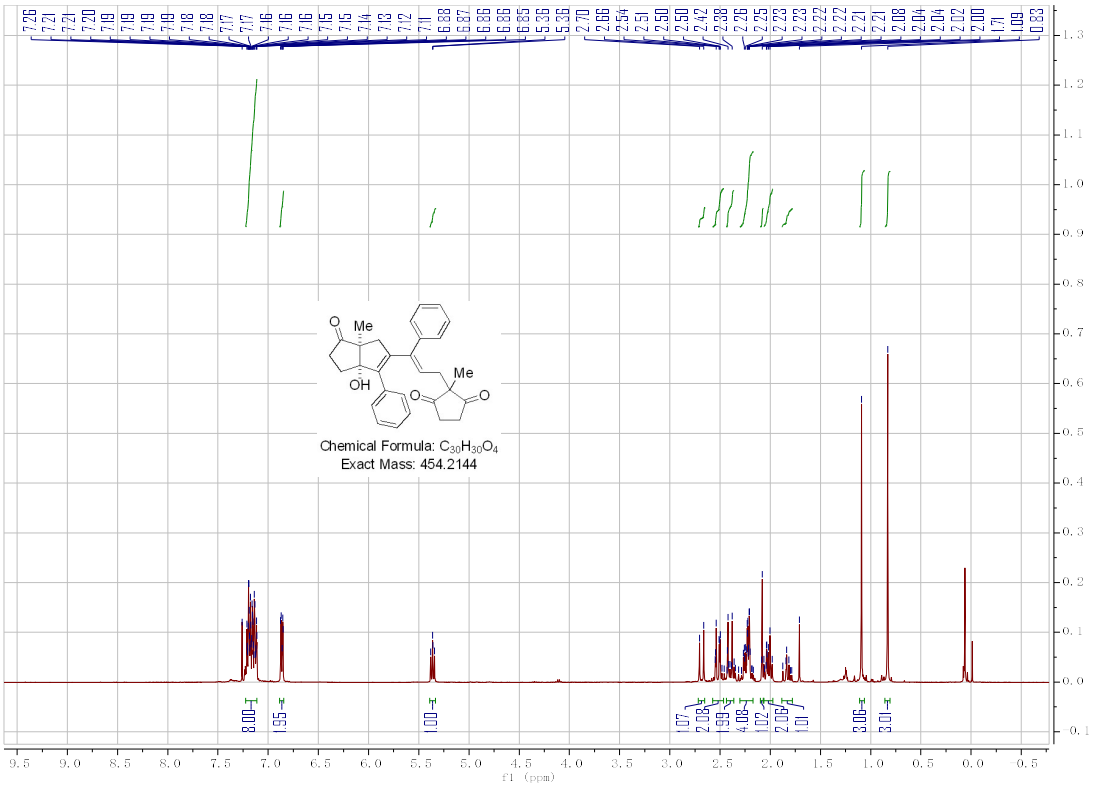
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(5)-H(5A)...O(7)#1	0.82	2.11	2.878(4)	156.9

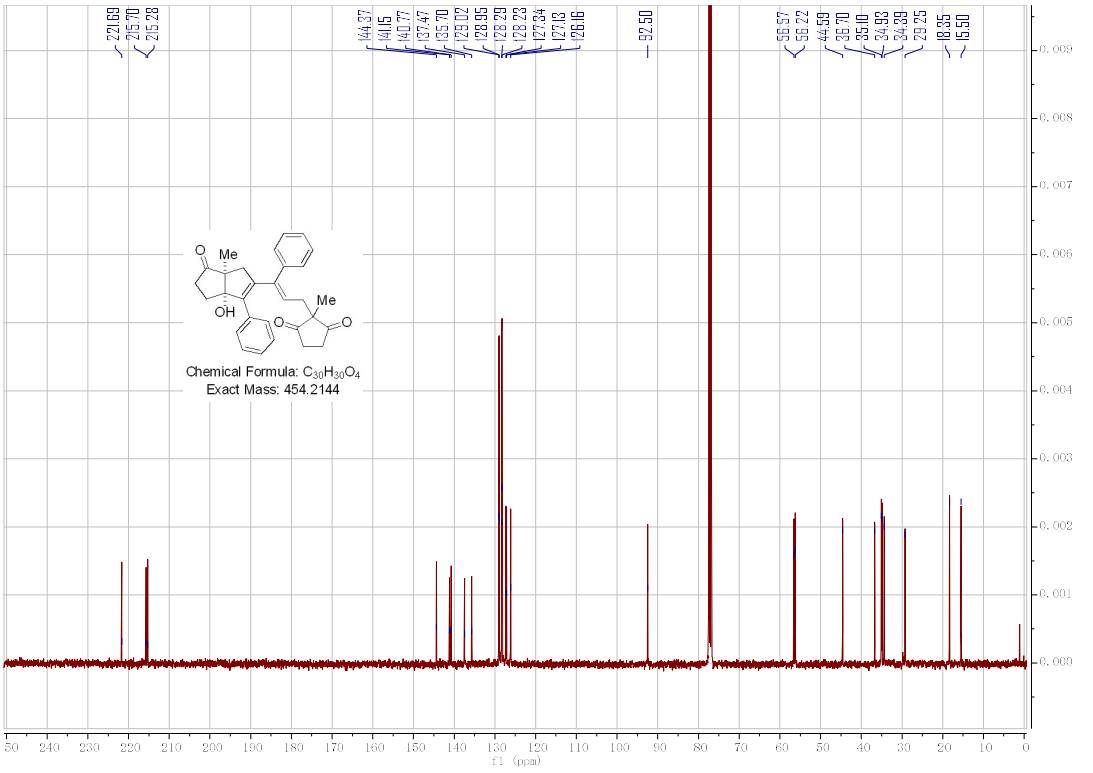
Symmetry transformations used to generate equivalent atoms:

#1 x,y+1,z

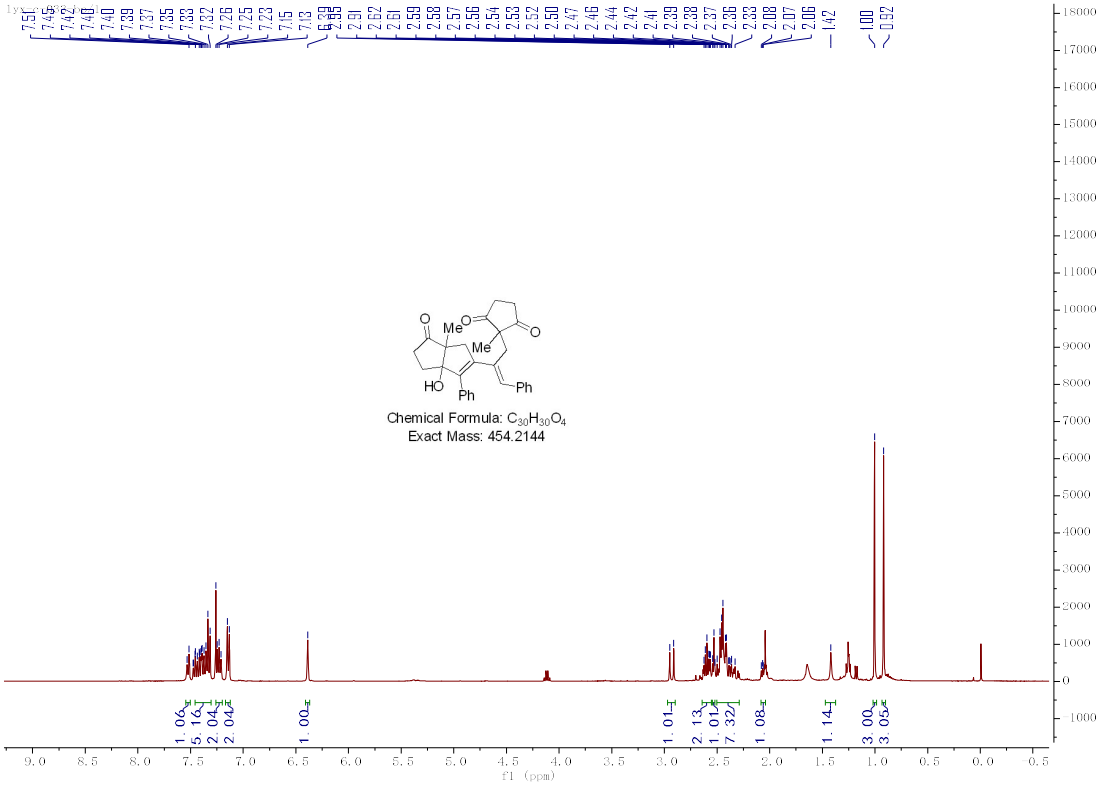
10. Copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra

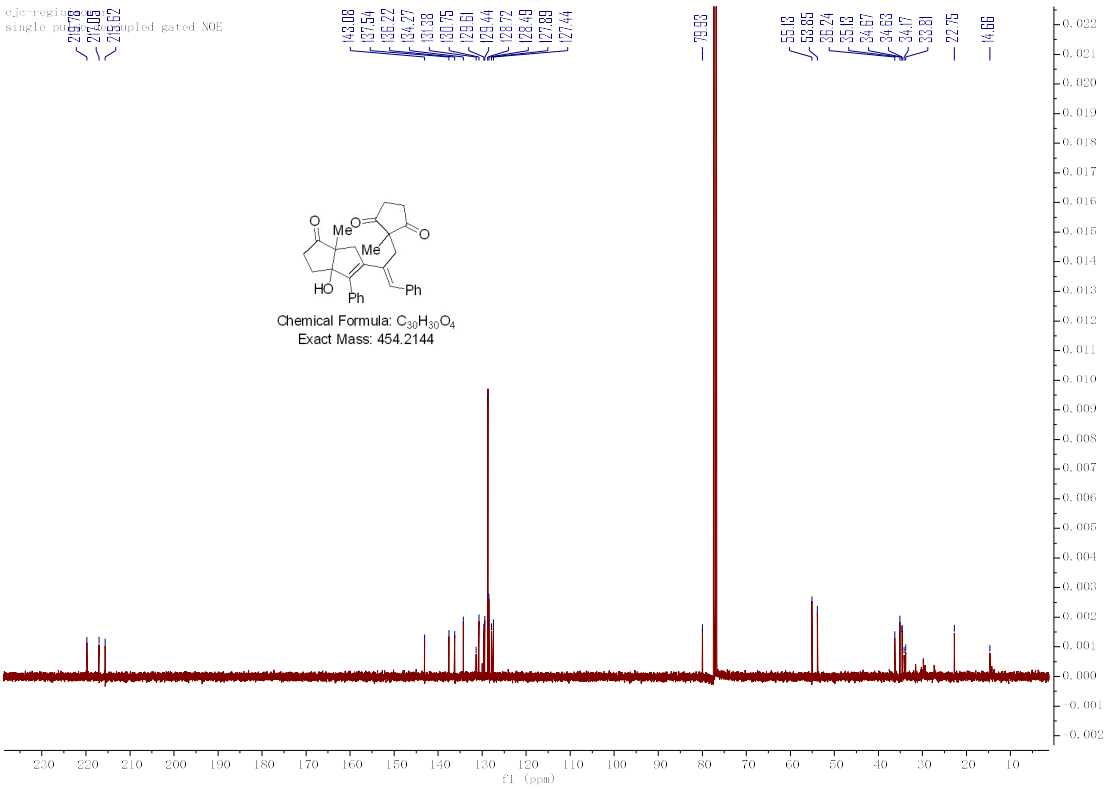
3a



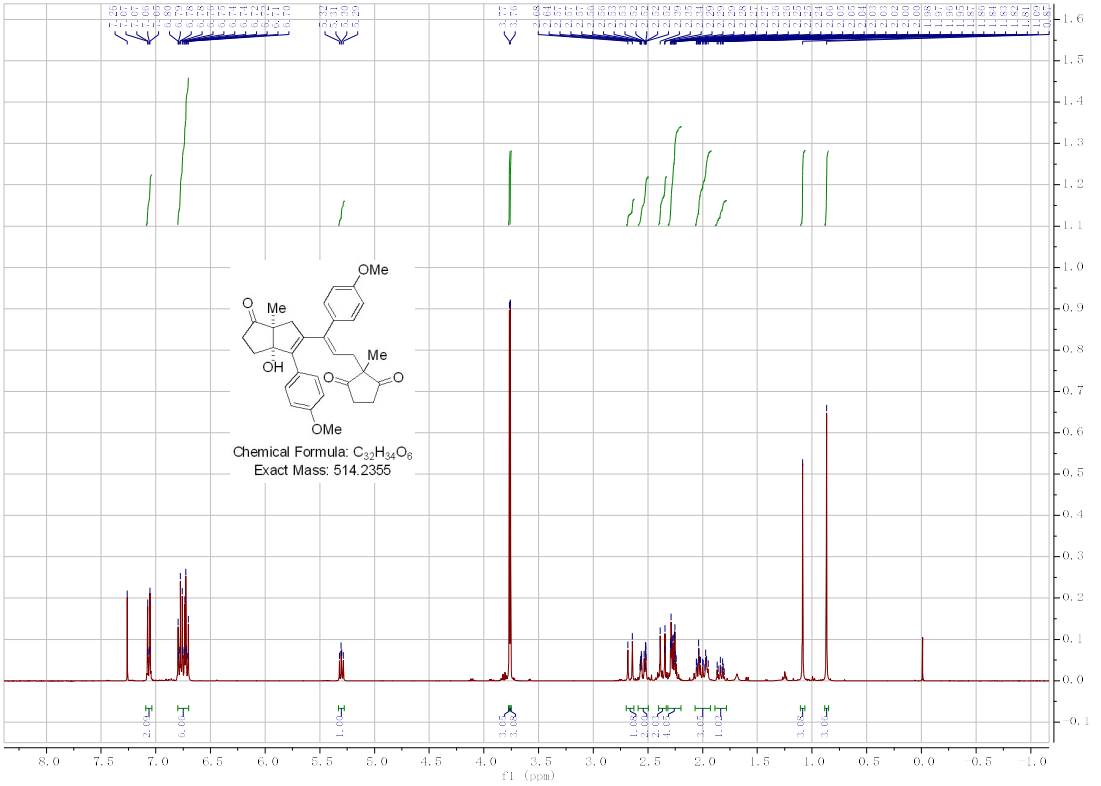


3a’


Chemical Formula: C30H30O4
Exact Mass: 454.2144


Chemical Formula: C30H30O4
Exact Mass: 454.2144

3b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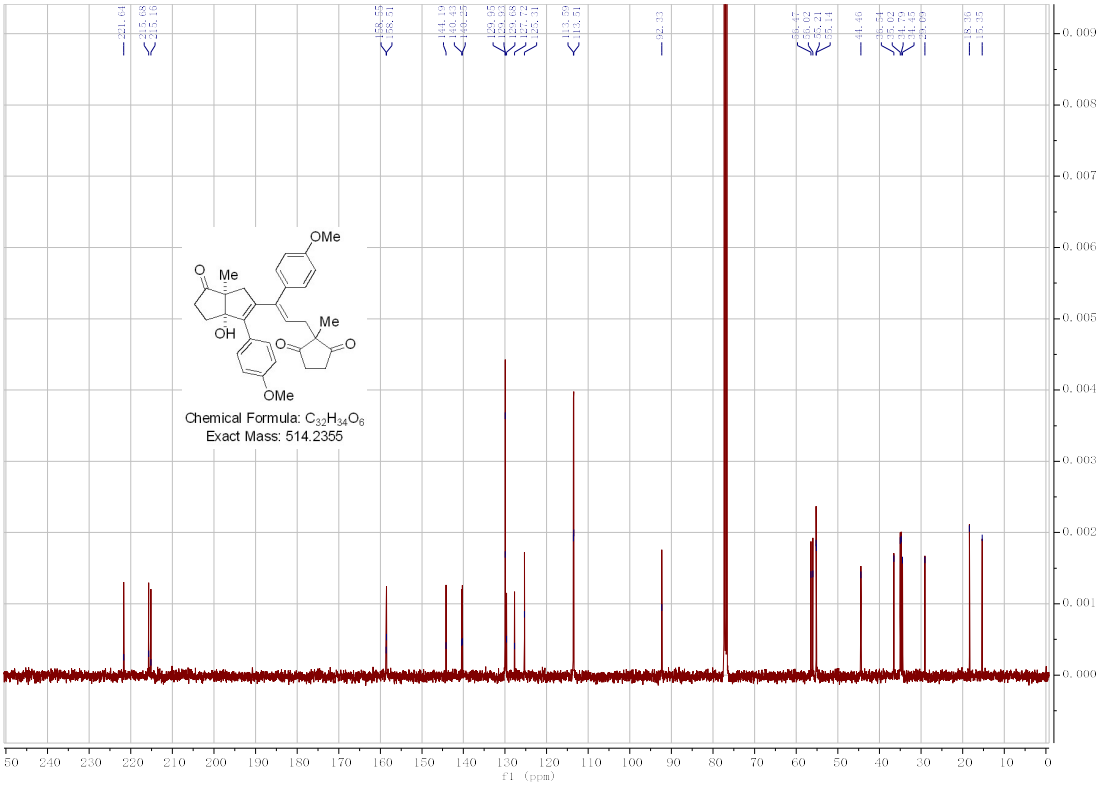
Me
O
OH
Me
O
O
OMe
Chemical Formula: C32H34O6
Exact Mass: 514.2355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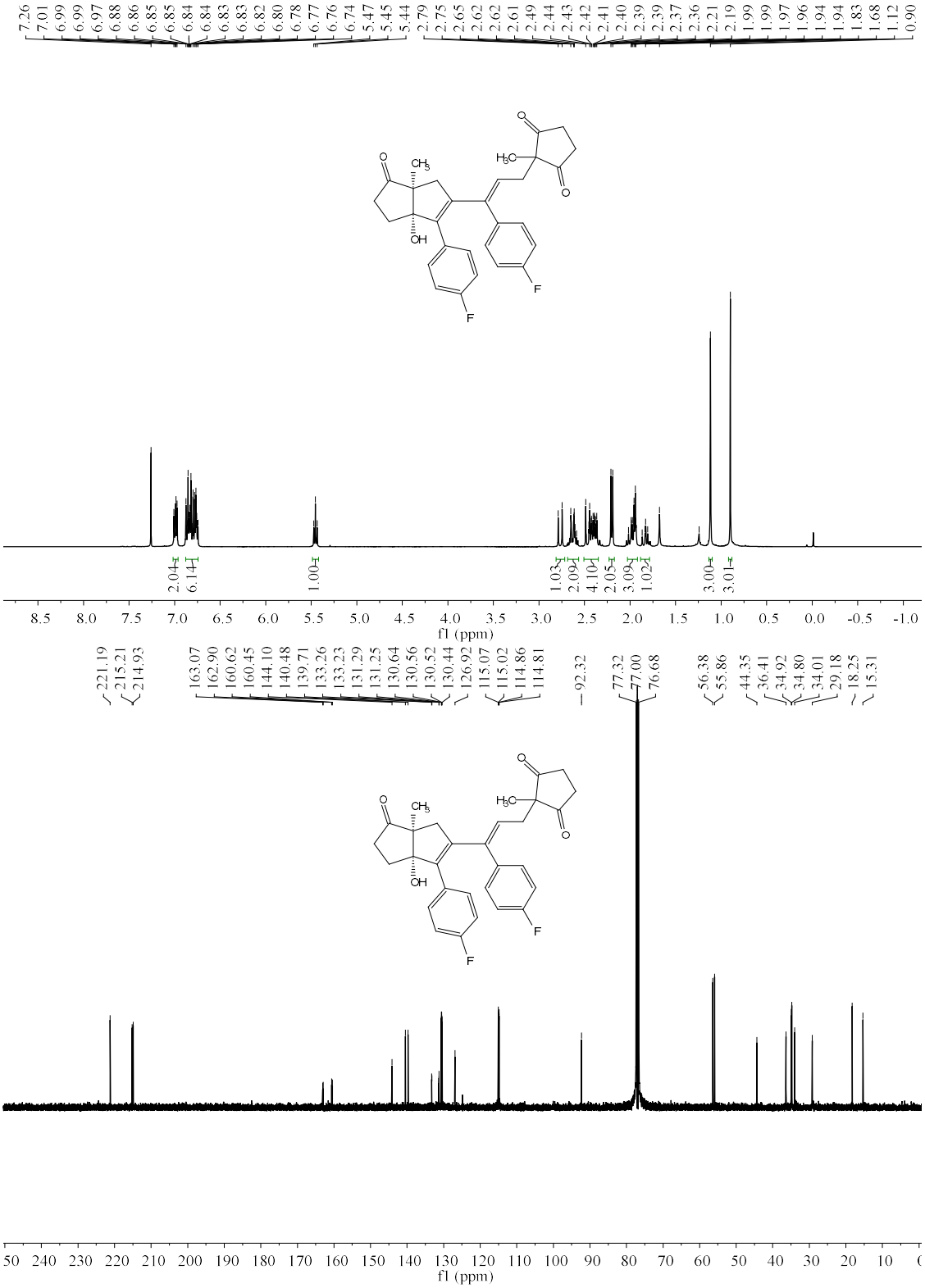
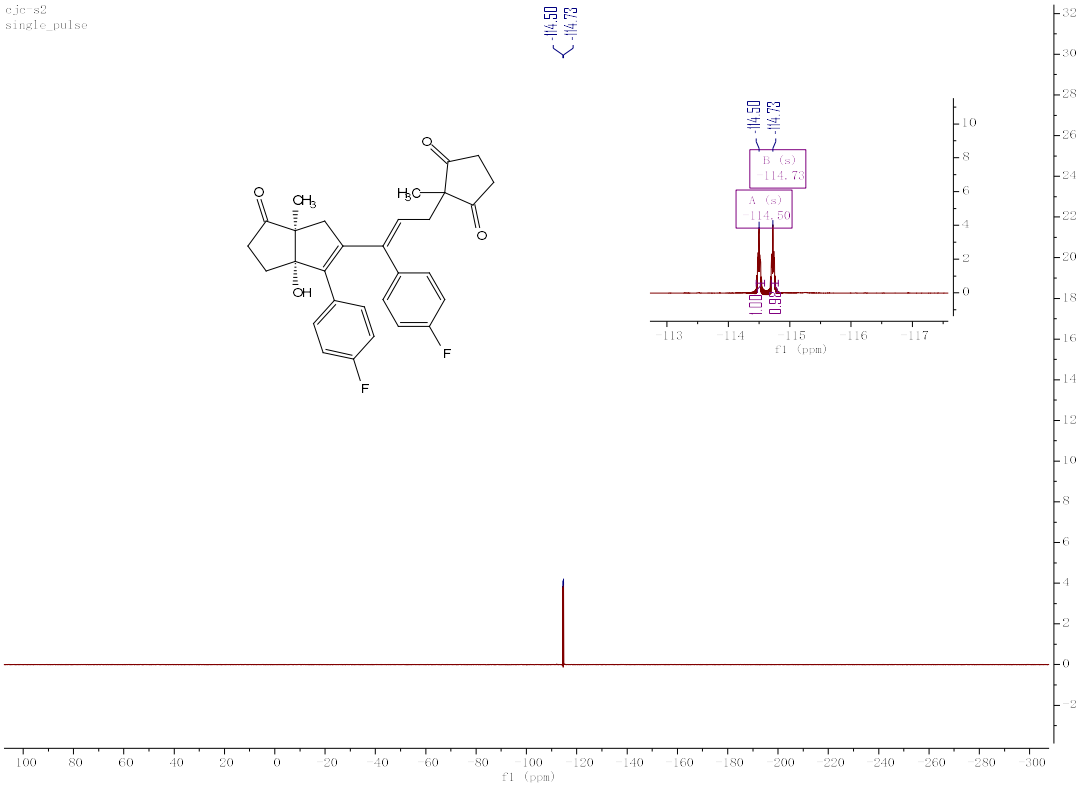
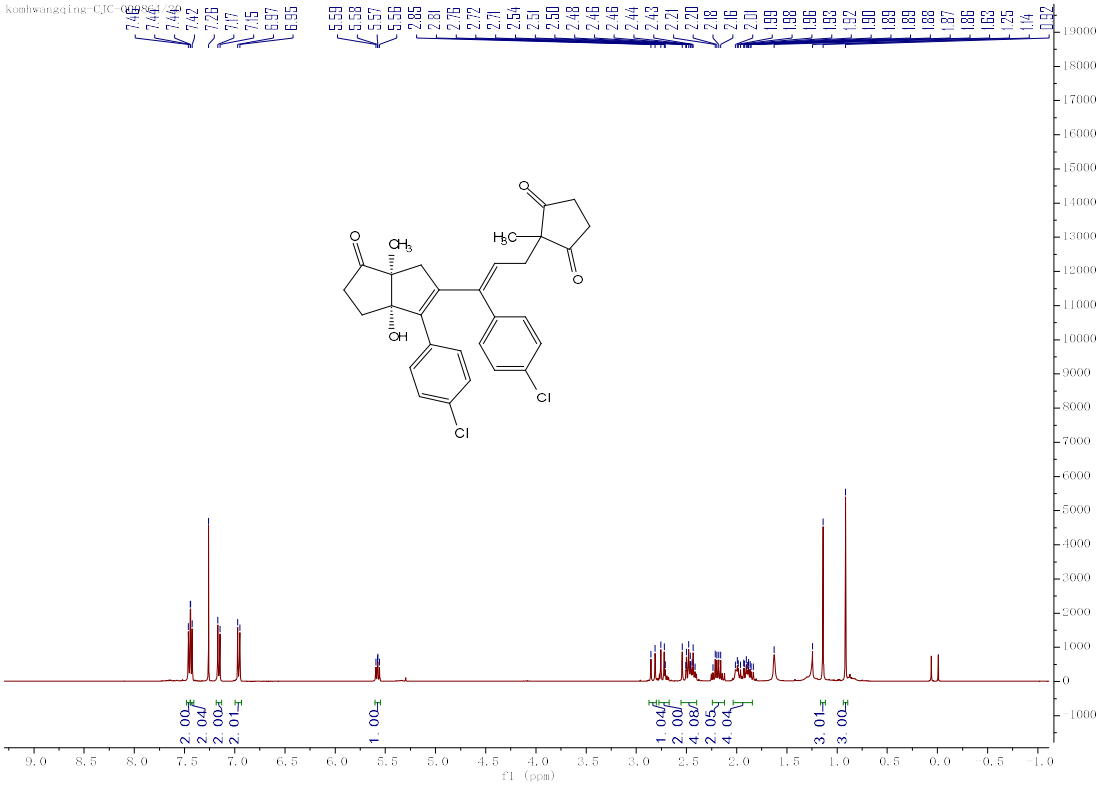
Me
O
OH
Me
O
O
OMe
Chemical Formula: C32H34O6
Exact Mass: 514.2355

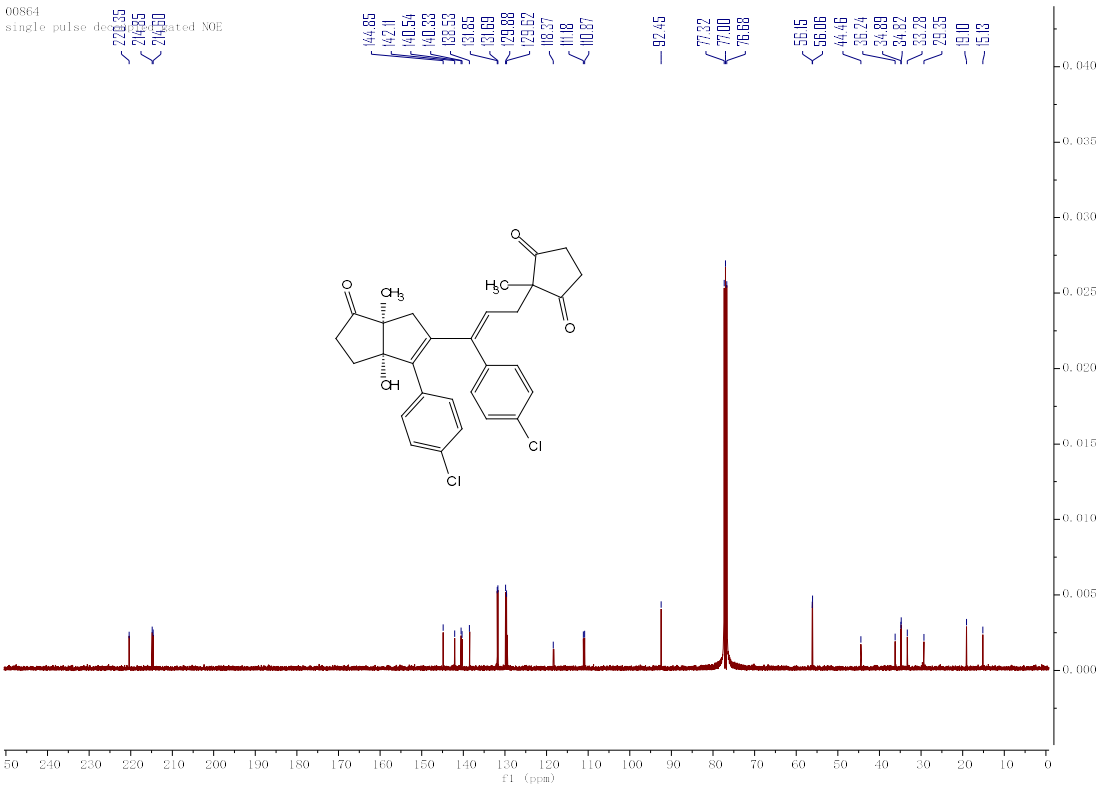
3c


7.26 7.01 6.99 6.99 6.97 6.88 6.86 6.85 6.85 6.84 6.84 6.83 6.83 6.82 6.80 6.78 6.77 6.76 6.74 5.47 5.45 5.44
2.79 2.75 2.65 2.62 2.62 2.61 2.49 2.44 2.43 2.42 2.41 2.40 2.39 2.39 2.37 2.36 2.21 2.19 1.99 1.99 1.97 1.96 1.94 1.94 1.83 1.68 1.12 0.90
O
CH3
H3C
O
O
OH
F
F
2.04 6.14 1.00 1.03 2.09 4.10 2.05 3.09 1.02 3.00 3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
221.19 215.21 214.93
163.07 162.90 160.62 160.45 144.10 140.48 139.71 133.26 133.23 131.29 131.25 130.64 130.56 130.52 130.44 126.92 115.07 115.02 114.86 114.81
92.32
77.32 77.00 76.68
56.38 55.86 44.35 36.41 34.92 34.80 34.01 29.18 18.25 15.31
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

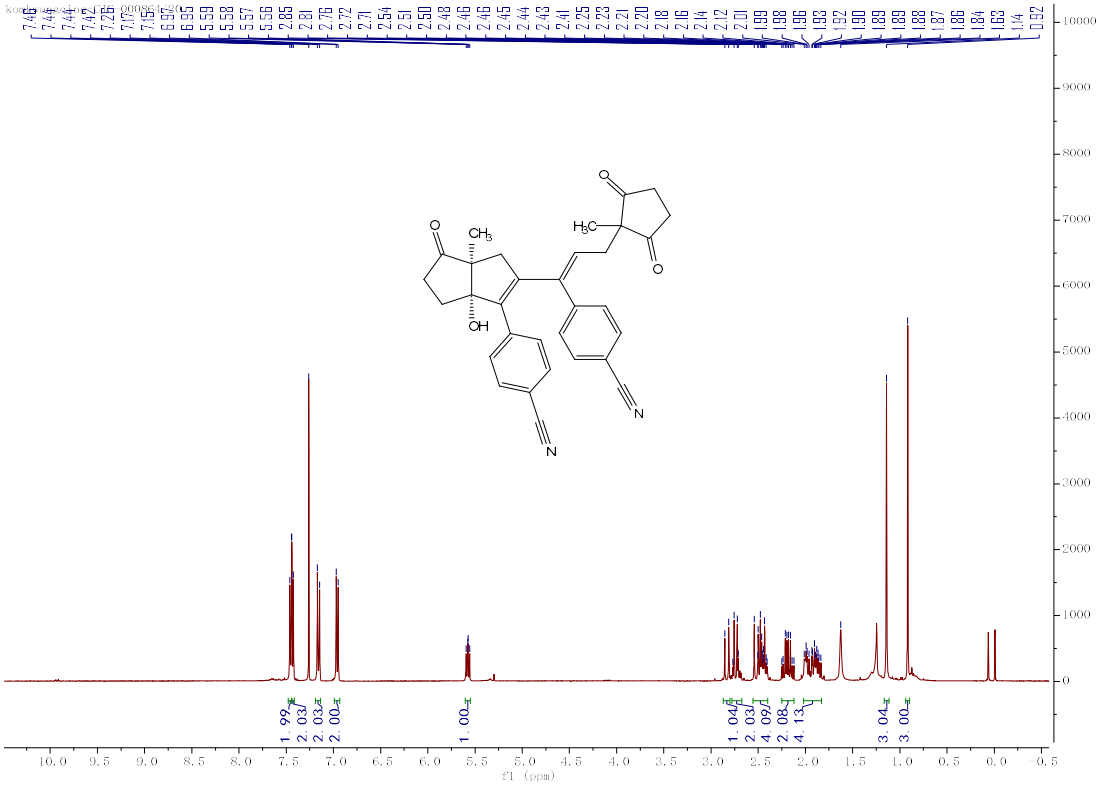

cjc-s2
single_pulse
-114.50
-114.73
B (s)
-114.73
A (s)
-114.50
1.00
0.96
f1 (ppm)
f1 (ppm)

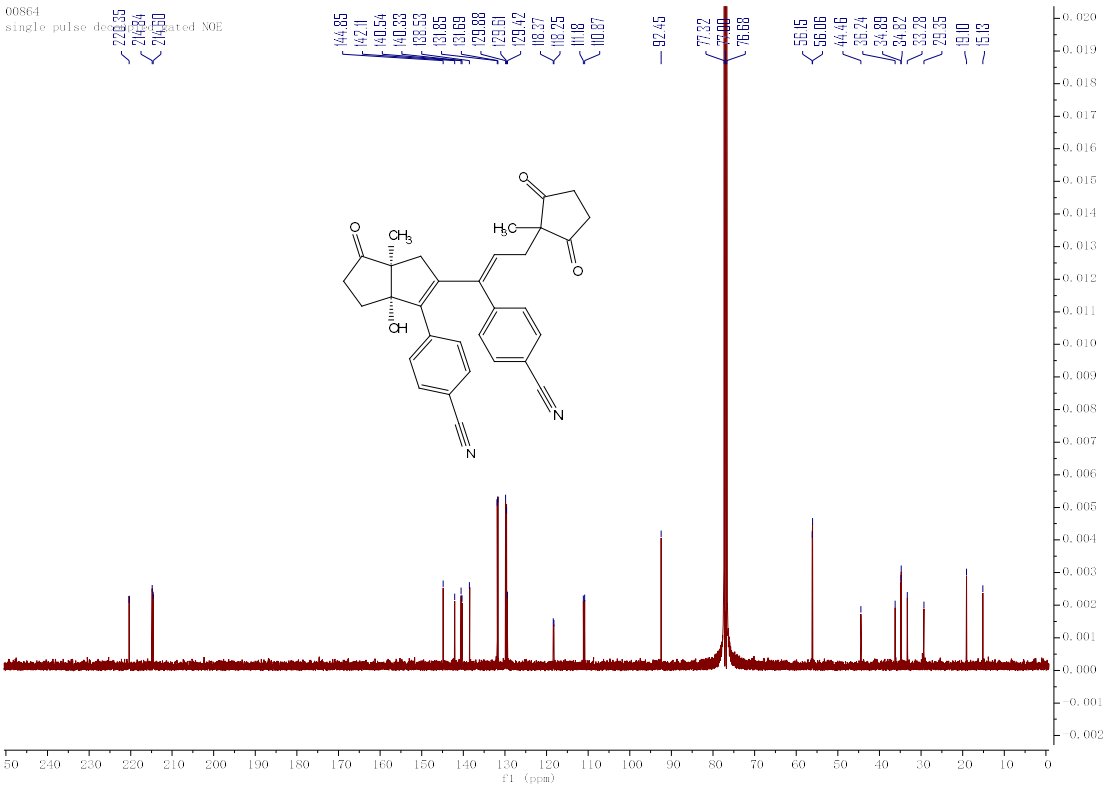
3d



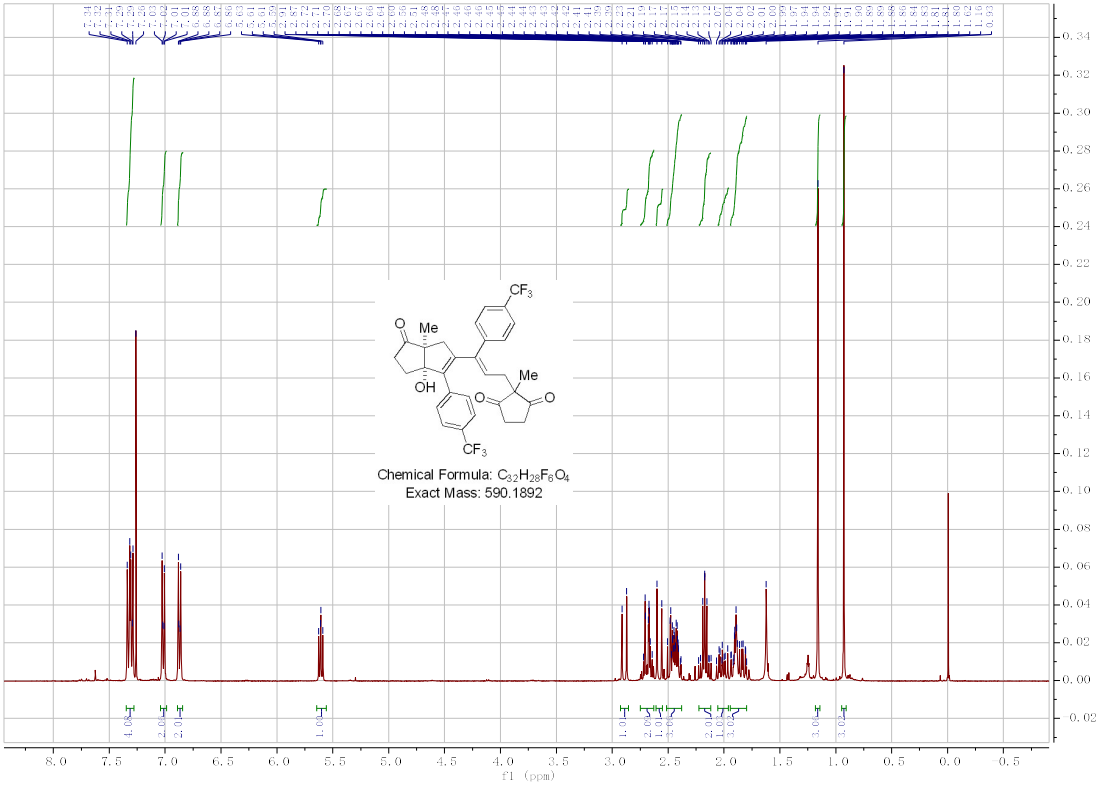


3e





3f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OH
Me
O
O
CF3
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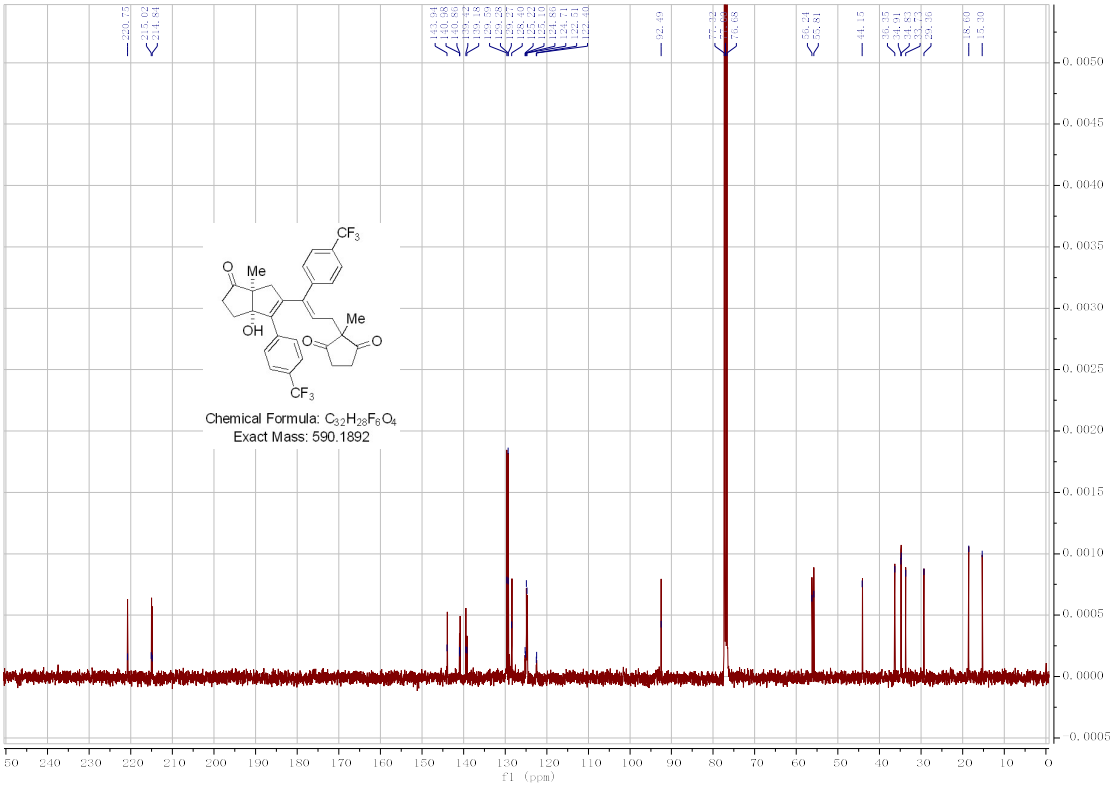
Exact Mass: 590.1892
f1 (ppm)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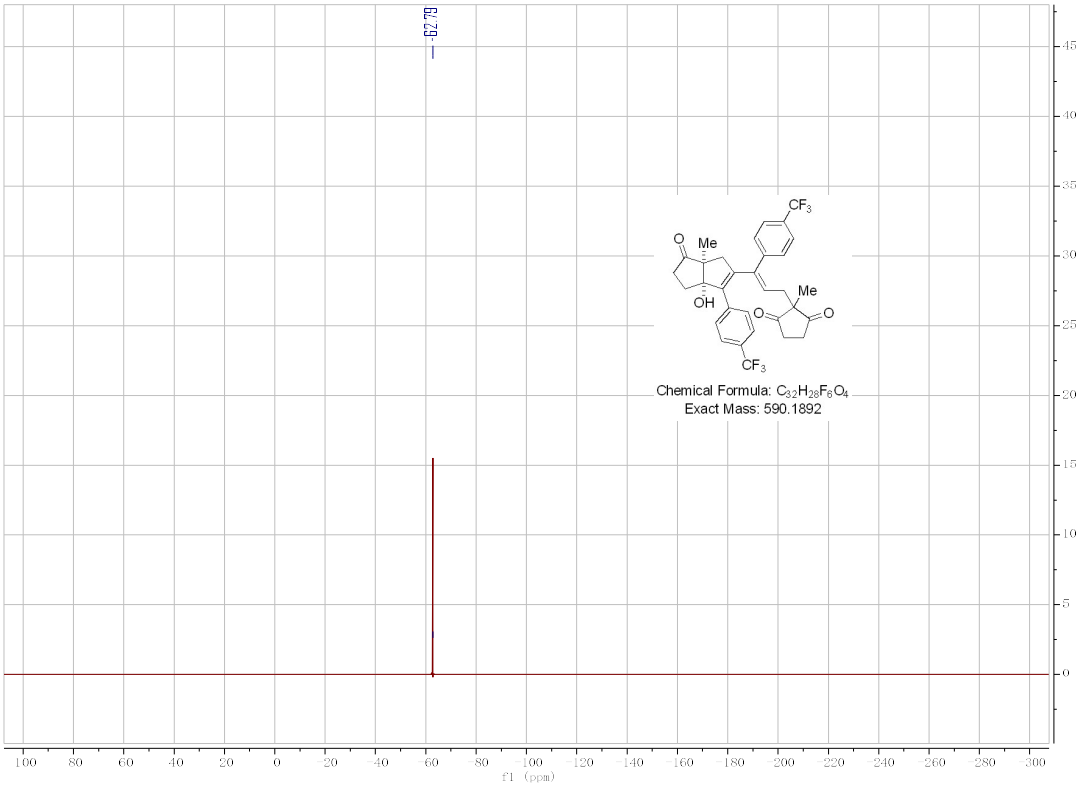
OH
Me
O
O
CF3
Chemical Formula: C32H28F6O4
Exact Mass: 590.1892
f1 (ppm)


62.79
CF3
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Me
OH
Me
O
O
CF3
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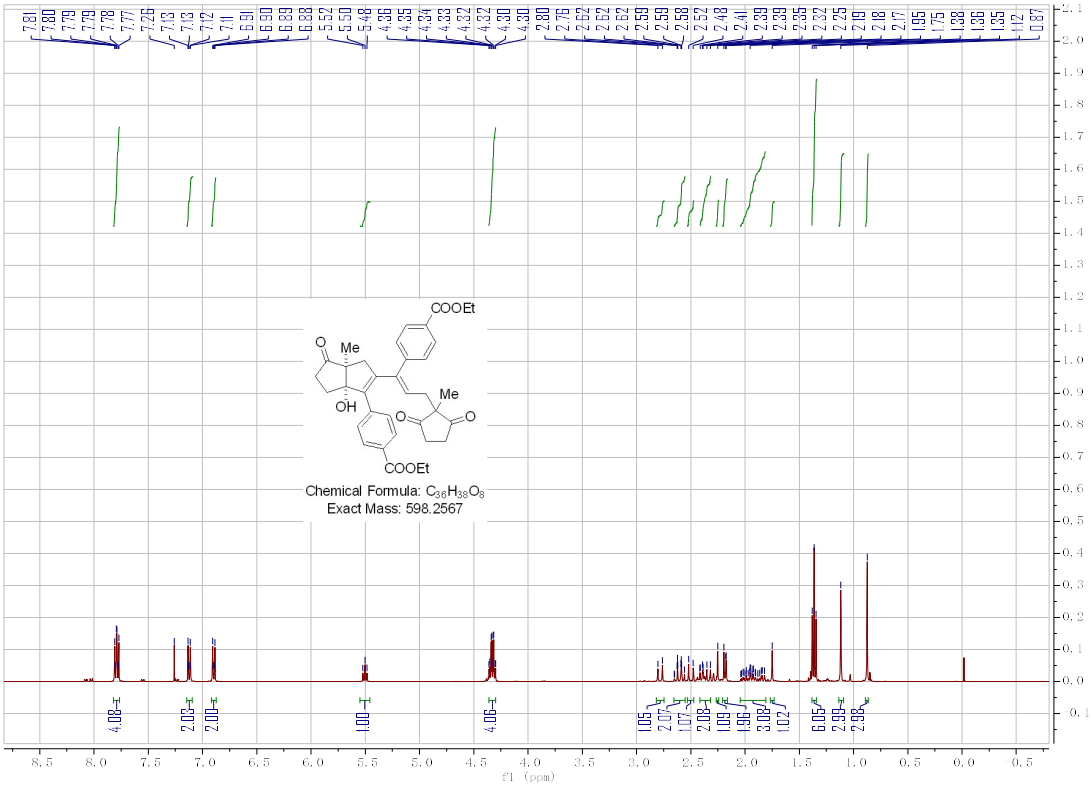
Exact Mass: 590.1892
45
40
35
30
25
20
15
10
5
0
100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300
f1 (ppm)

3g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OH
Me
COOEt
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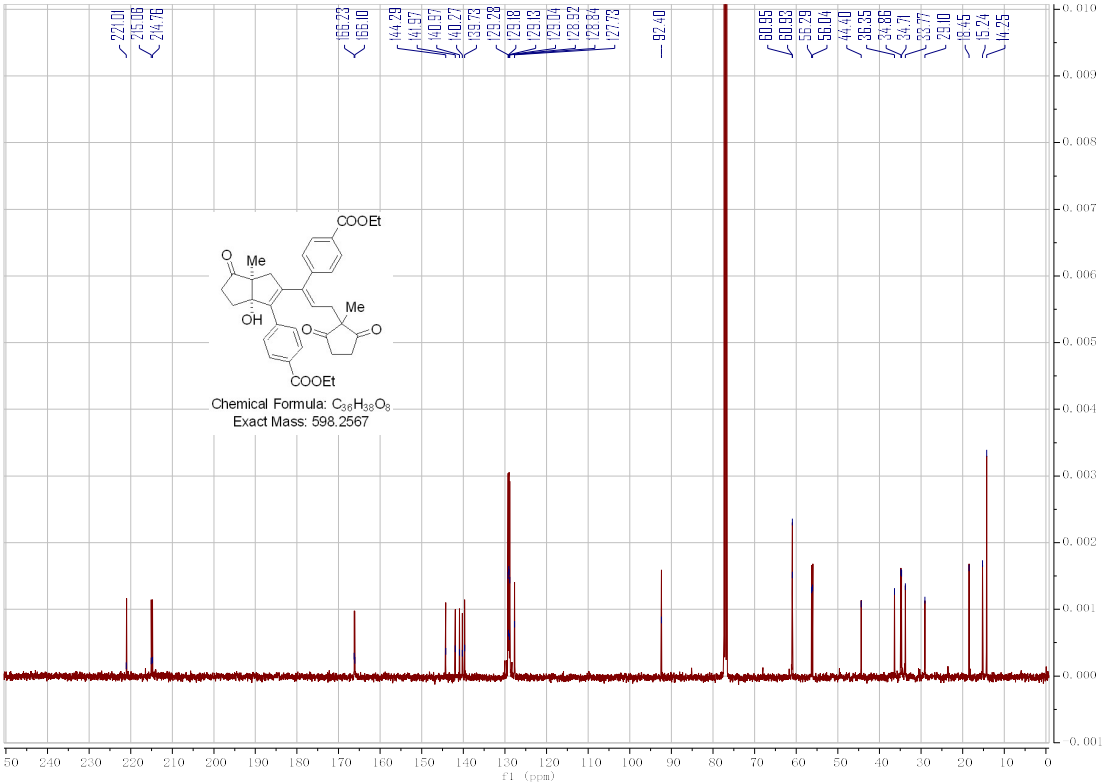
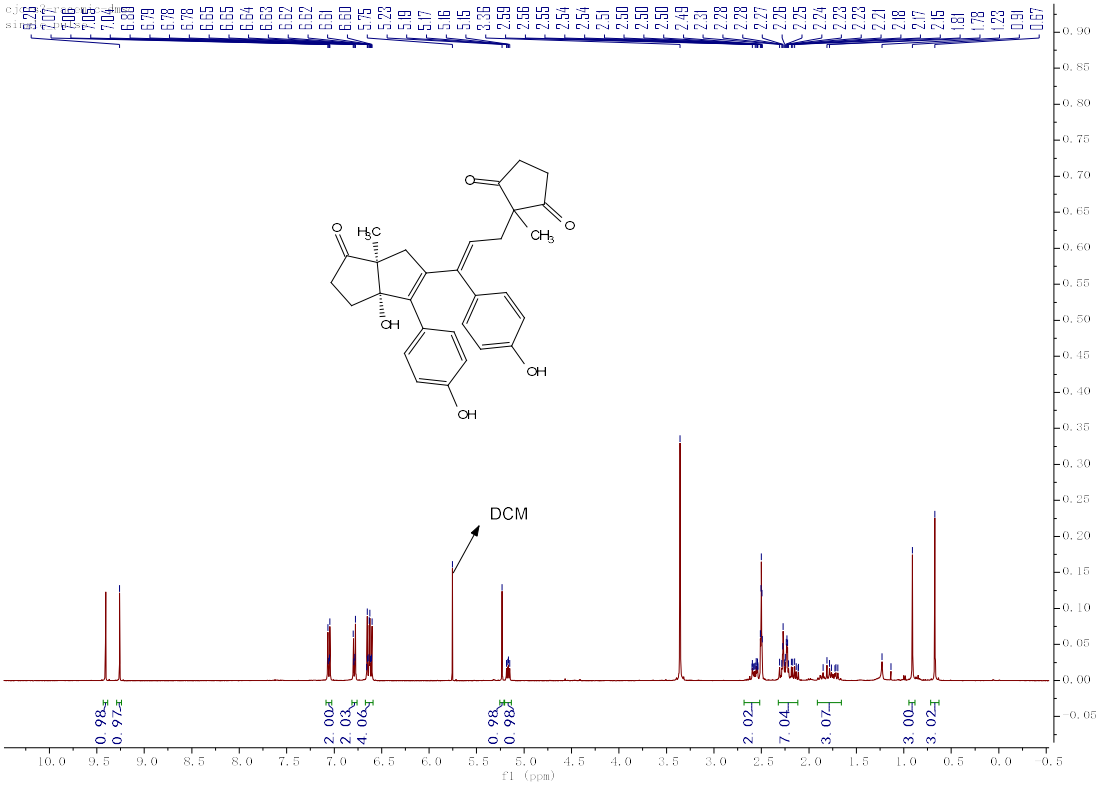
Exact Mass: 598.2567


COOEt
Me
OH
Me
COOEt
Chemical Formula: C36H38O8
Exact Mass: 598.2567

3h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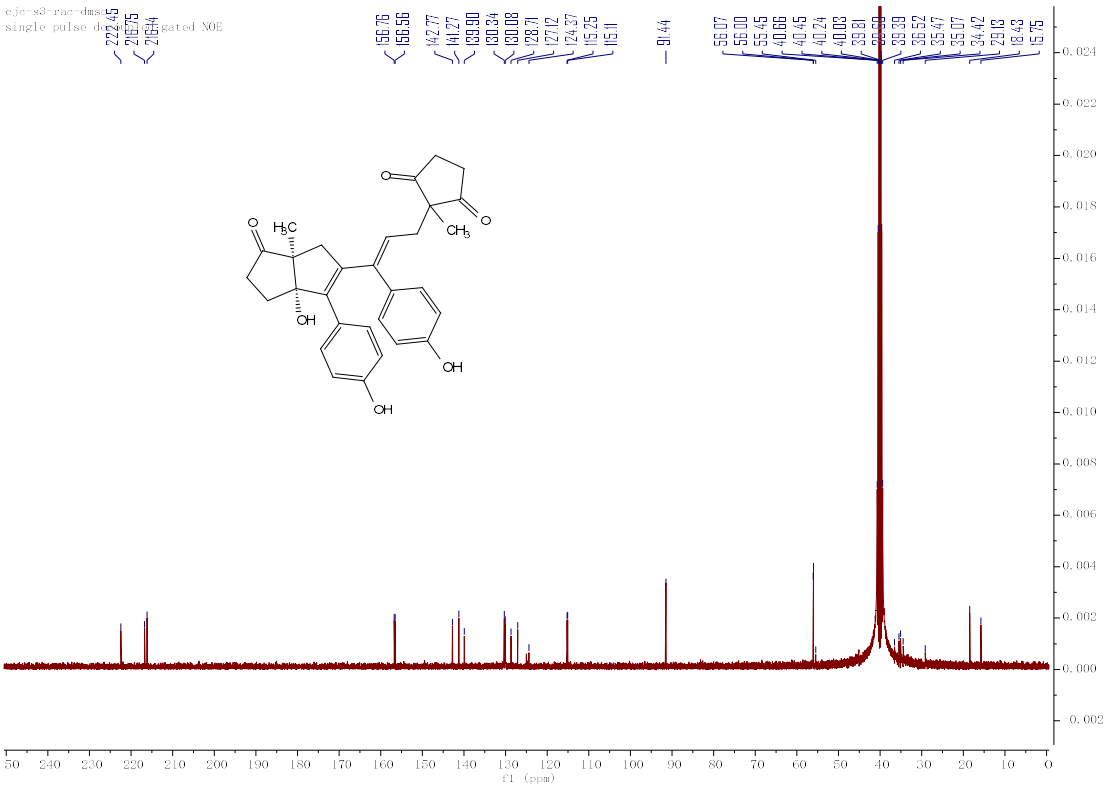
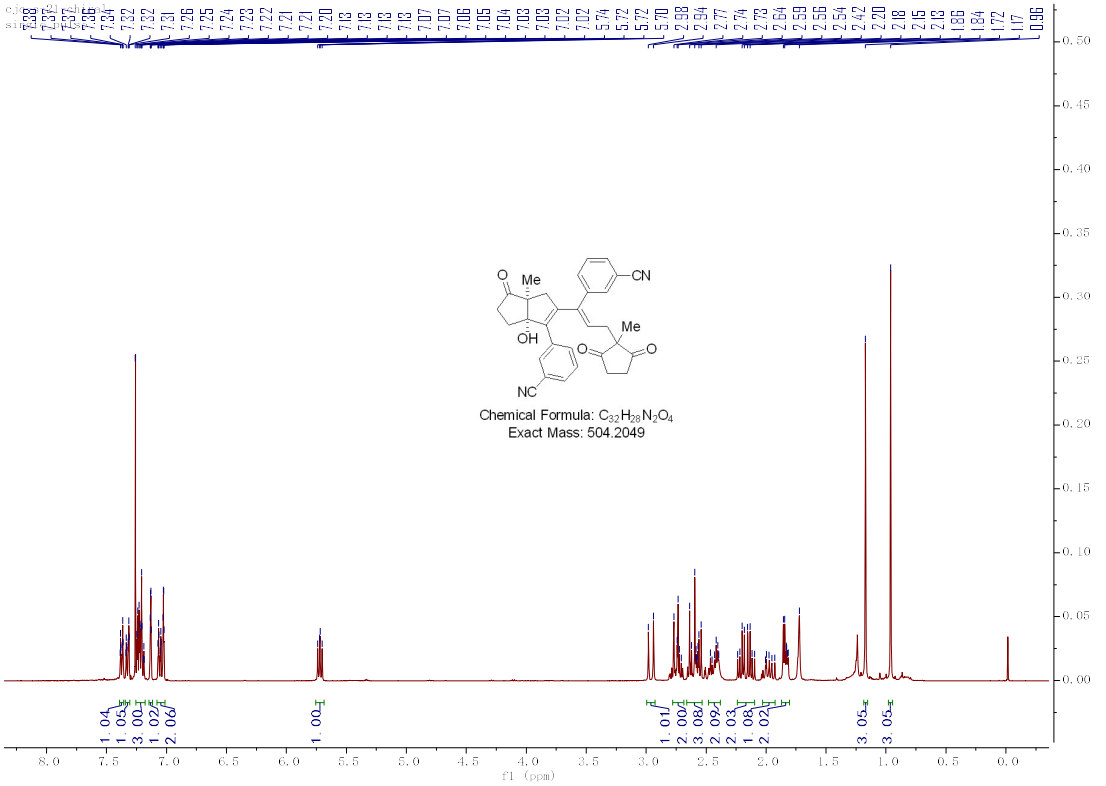
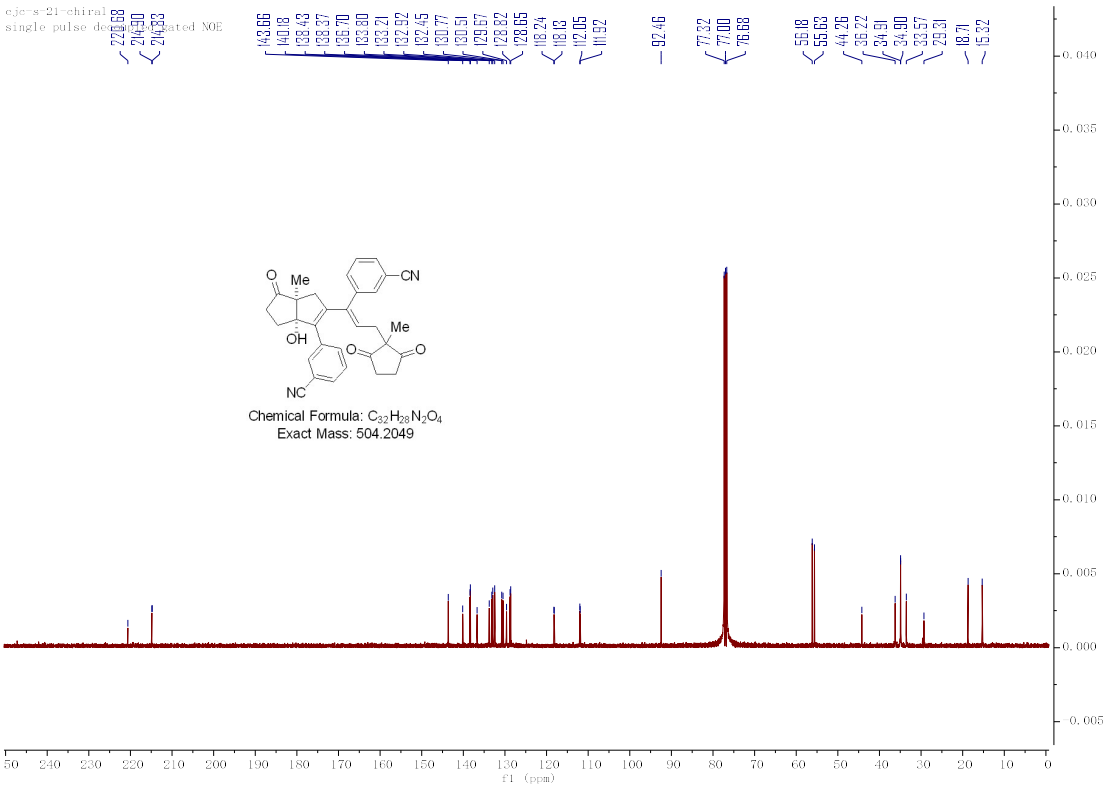
H3C
CH3
OH
OH
OH
f1 (ppm)

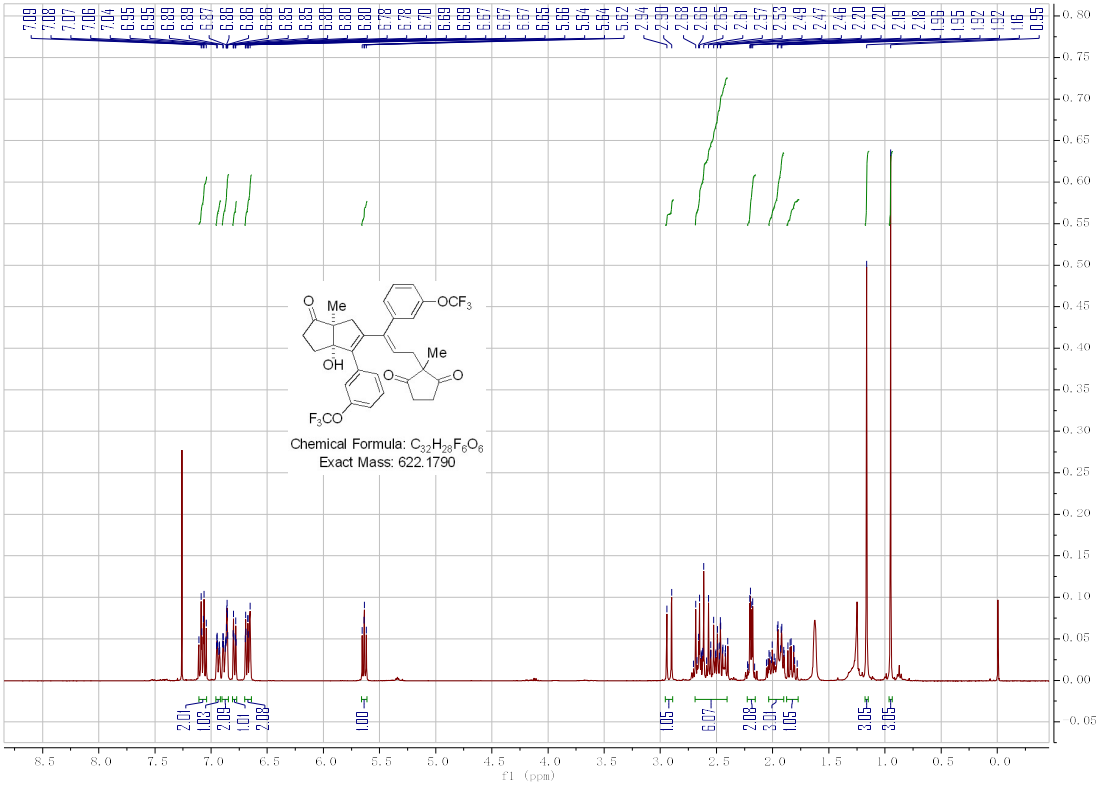

cjc-s3-rac-dmso
single pulse decoupled NOE
H3C
CH3
OH
OH
OH
f1 (ppm)

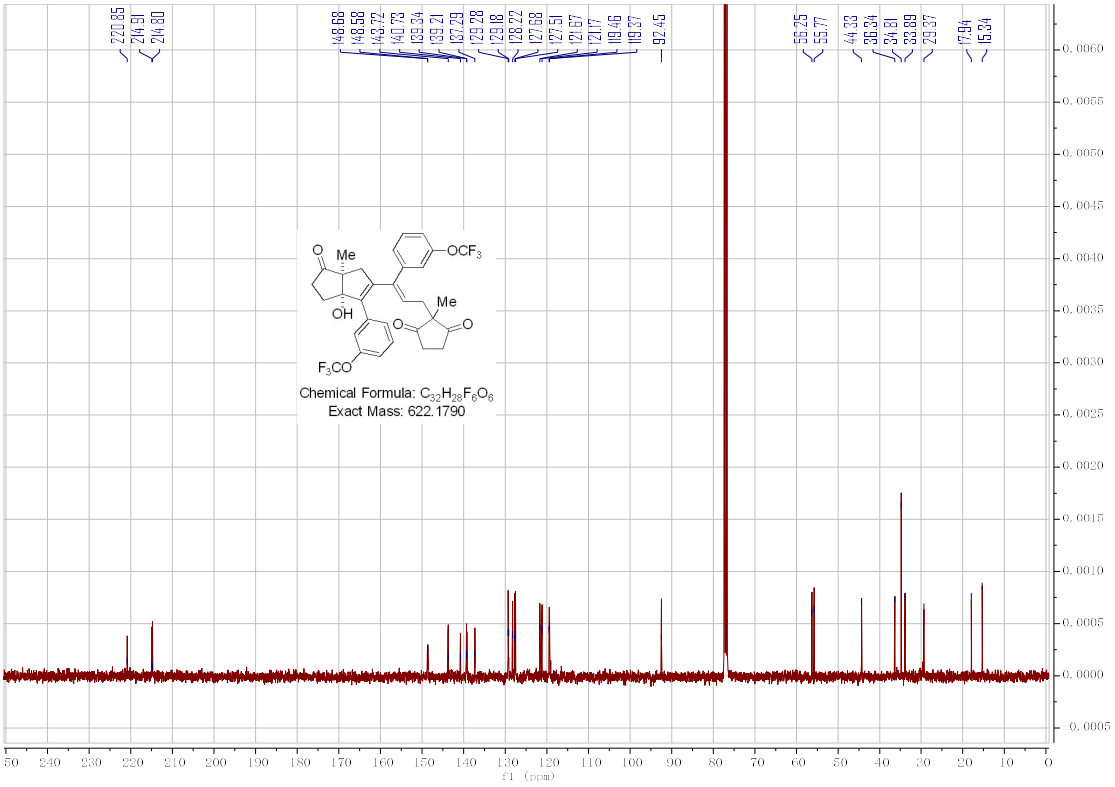
3i

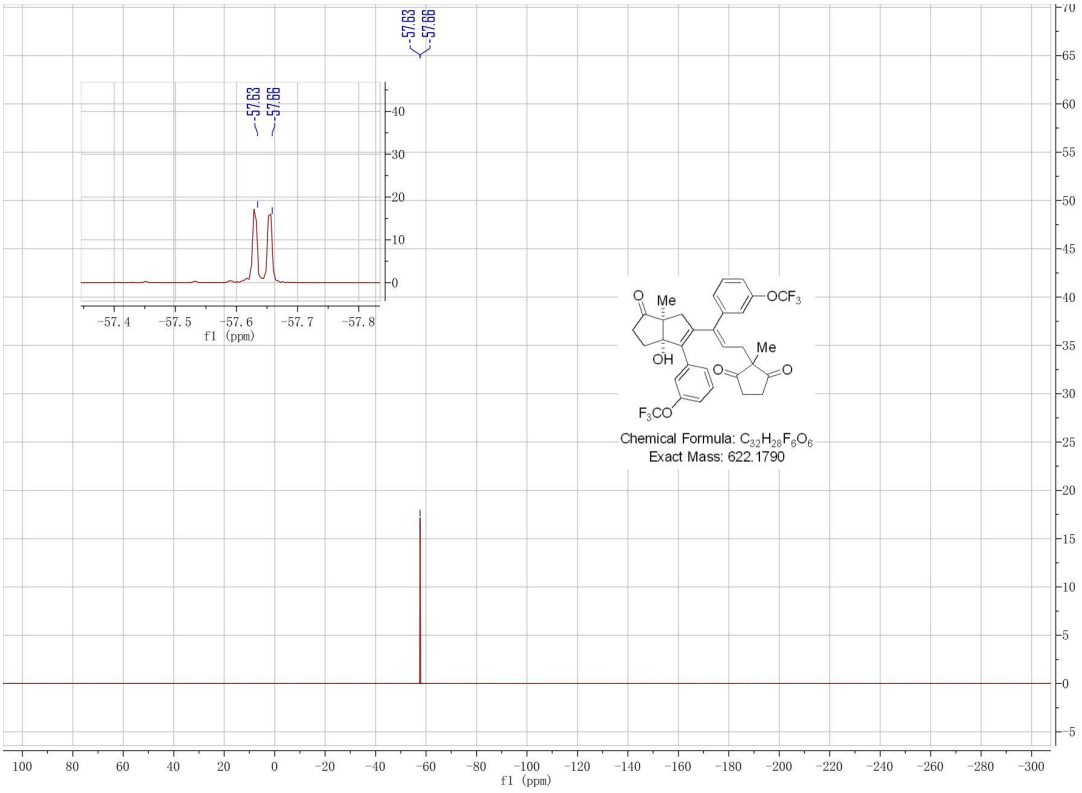

Chemical Formula: C32H28N2O4
Exact Mass: 504.2049


Chemical Formula: C32H28N2O4
Exact Mass: 504.2049

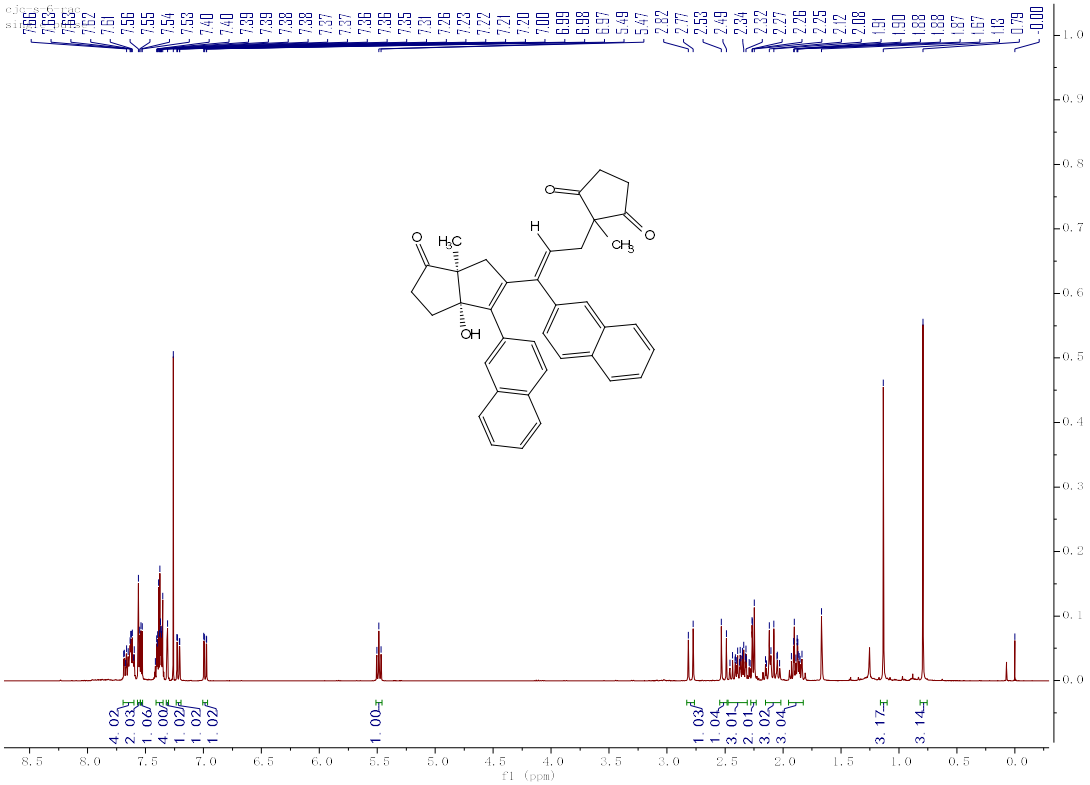
3j

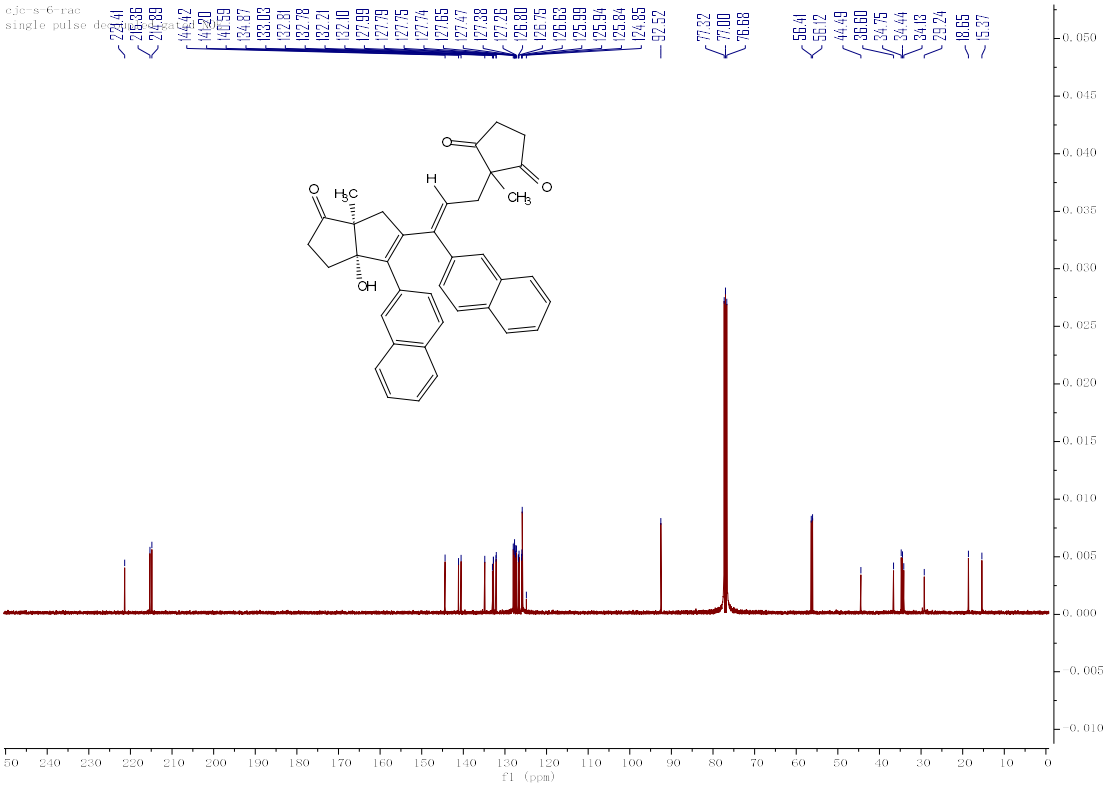

Me
OCF3
OH
Me
O
O
F3CO
Chemical Formula: C32H28F6O6
Exact Mass: 622.1790


Me
OCF3
OH
Me
O
O
F3CO
Chemical Formula: C32H28F6O6
Exact Mass: 622.1790

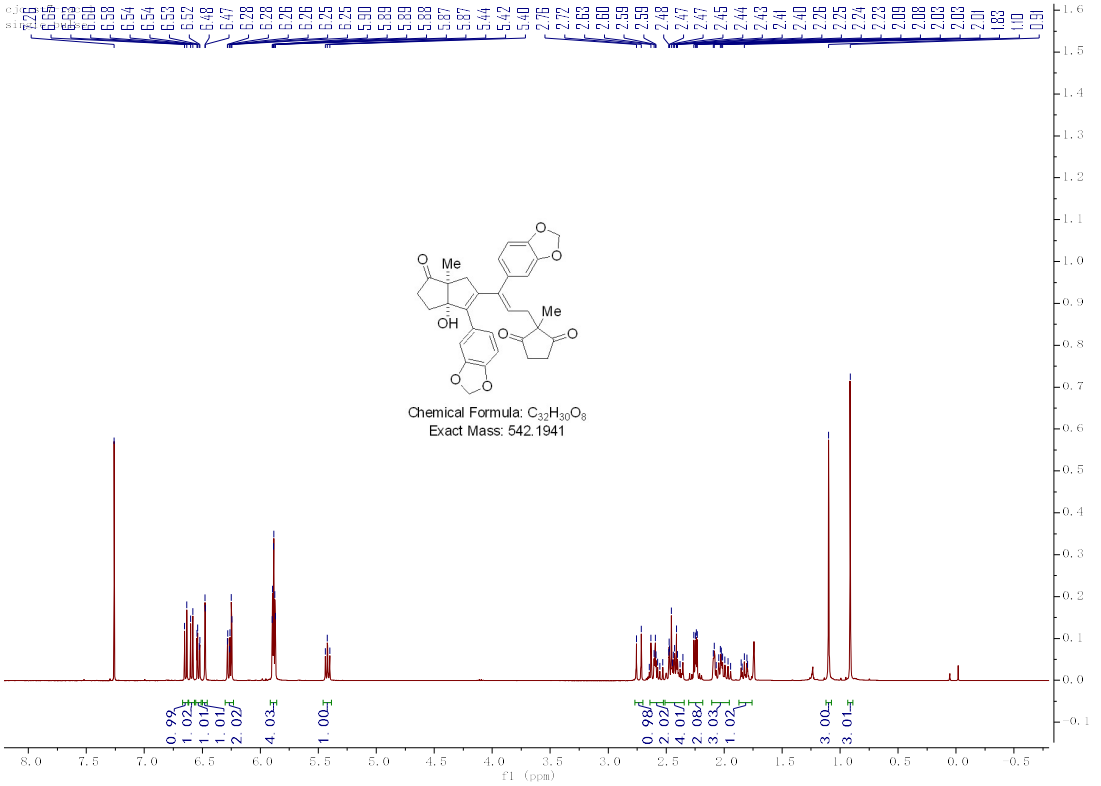

-57.63
-57.66
-57.63
-57.66
f1 (ppm)
Me
OCF3
OH
Me
F3CO
Chemical Formula: C32H28F6O6
Exact Mass: 622.1790
f1 (ppm)

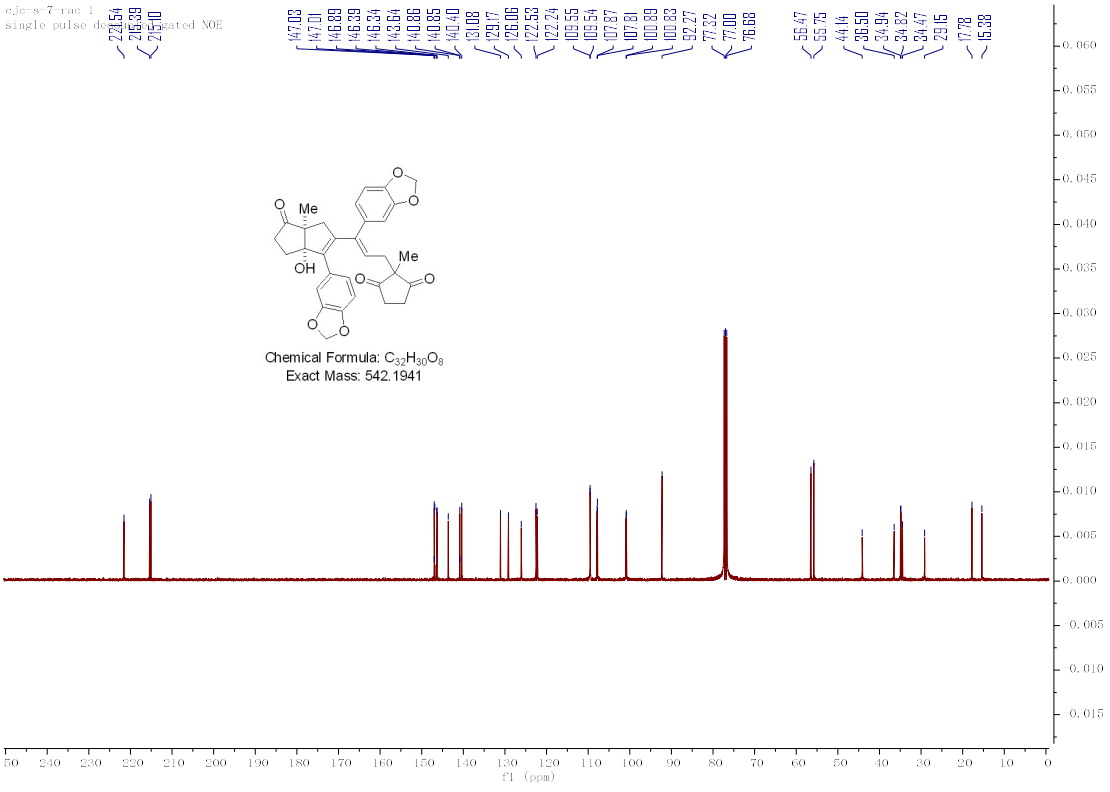
3k



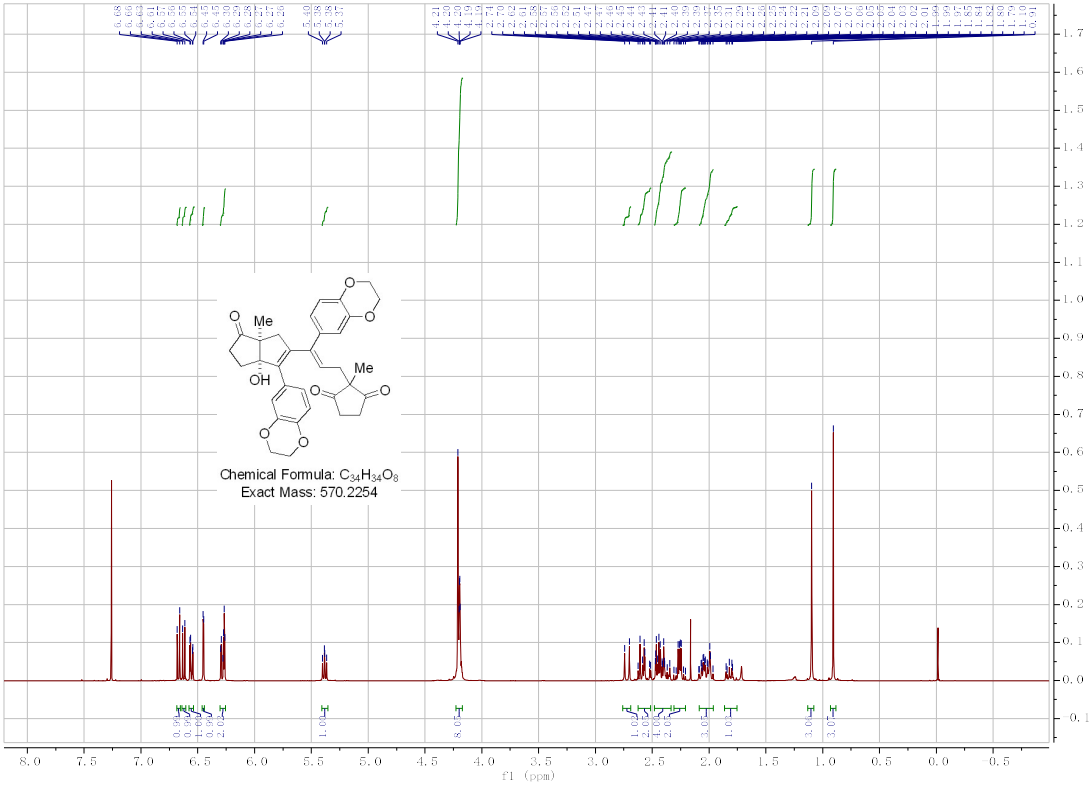


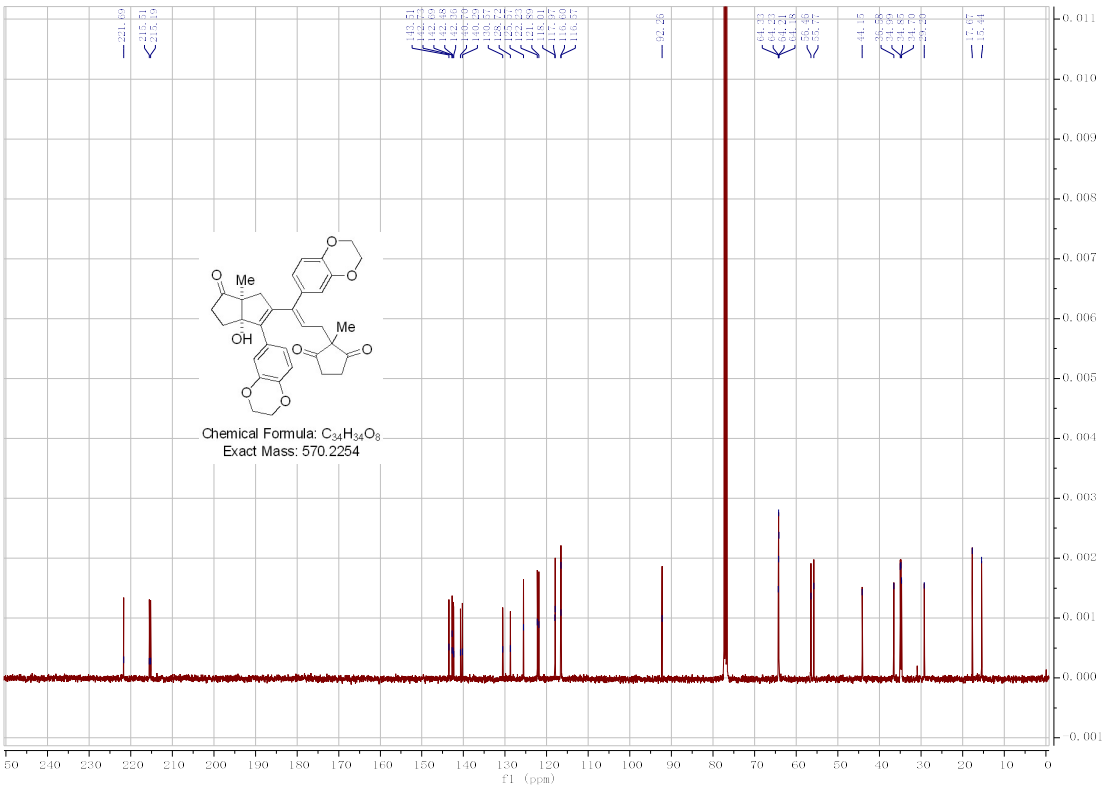
3l


Me
OH
Me
Chemical Formula: C32H30O8
Exact Mass: 542.1941
f1 (ppm)

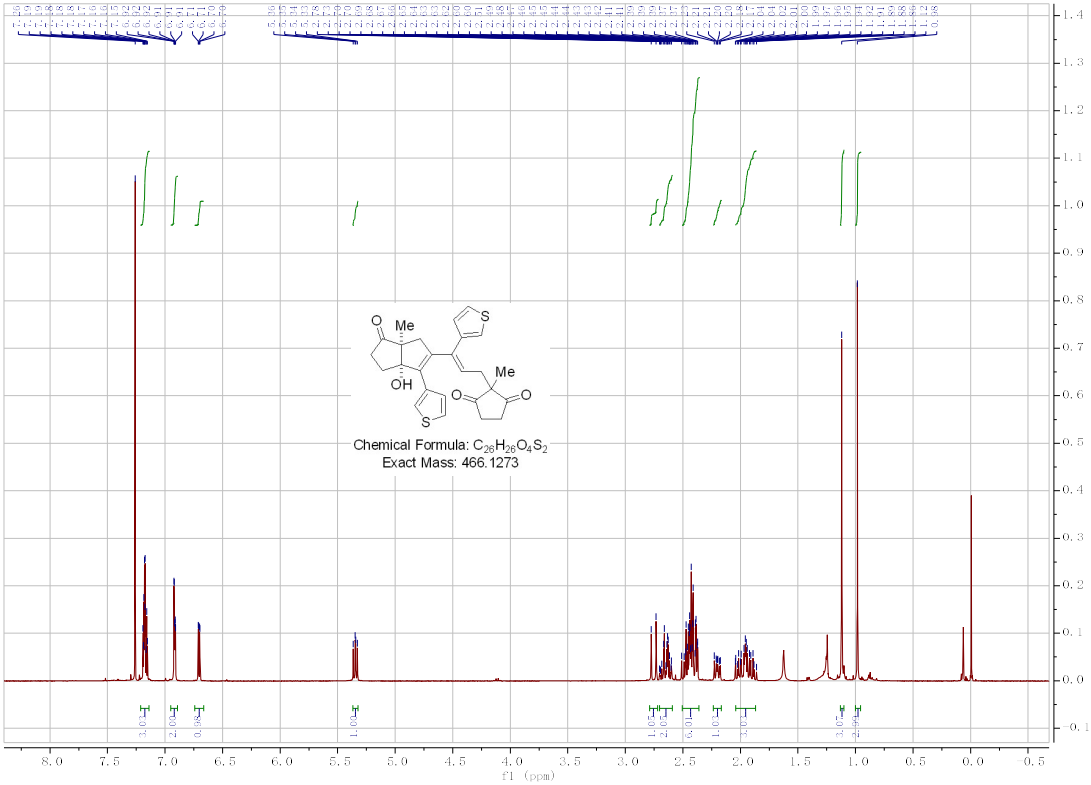

Me
OH
Me
Chemical Formula: C32H30O8
Exact Mass: 542.1941
f1 (ppm)

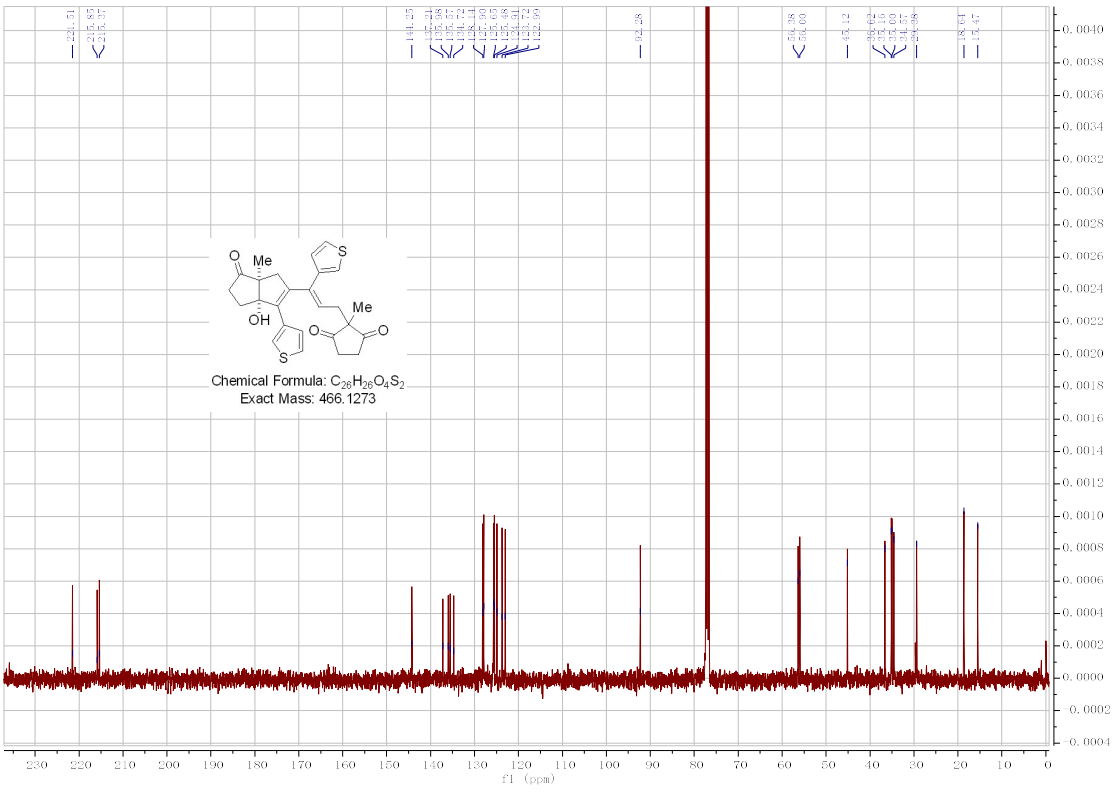
3m


Me
OH
Me
Chemical Formula: C34H34O8
Exact Mass: 570.2254
f1 (ppm)

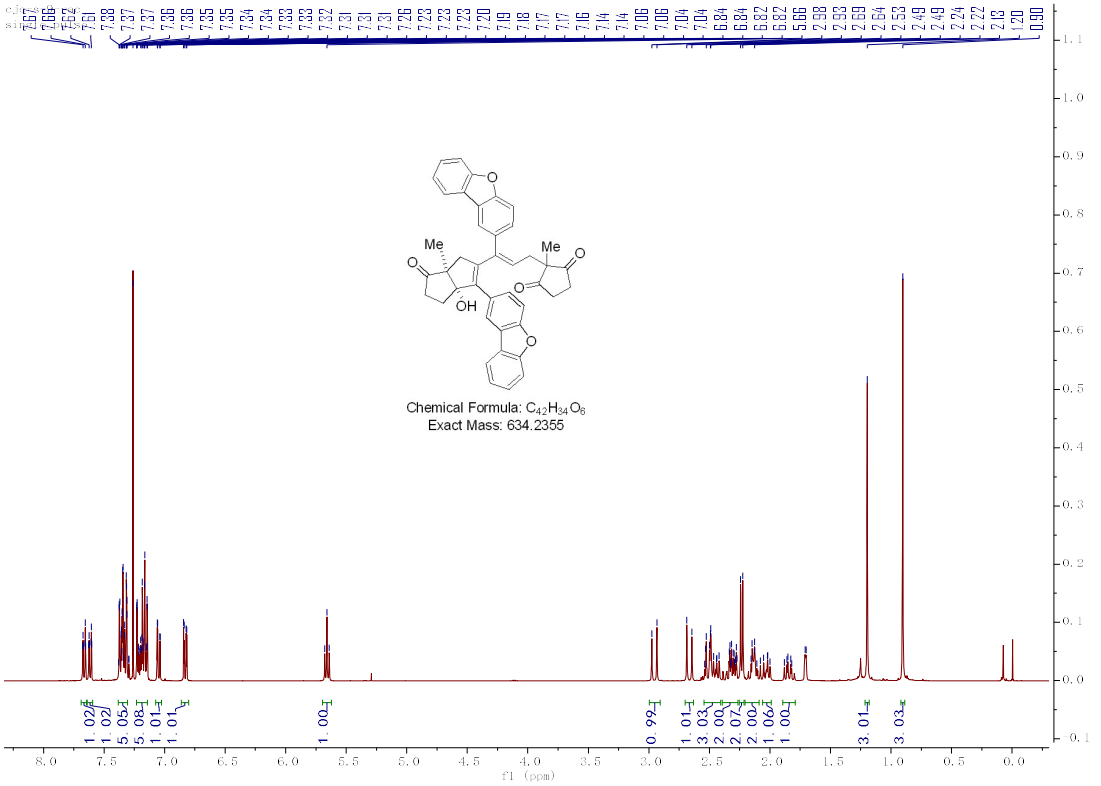

Me
OH
Me
Chemical Formula: C34H34O8
Exact Mass: 570.2254
f1 (ppm)

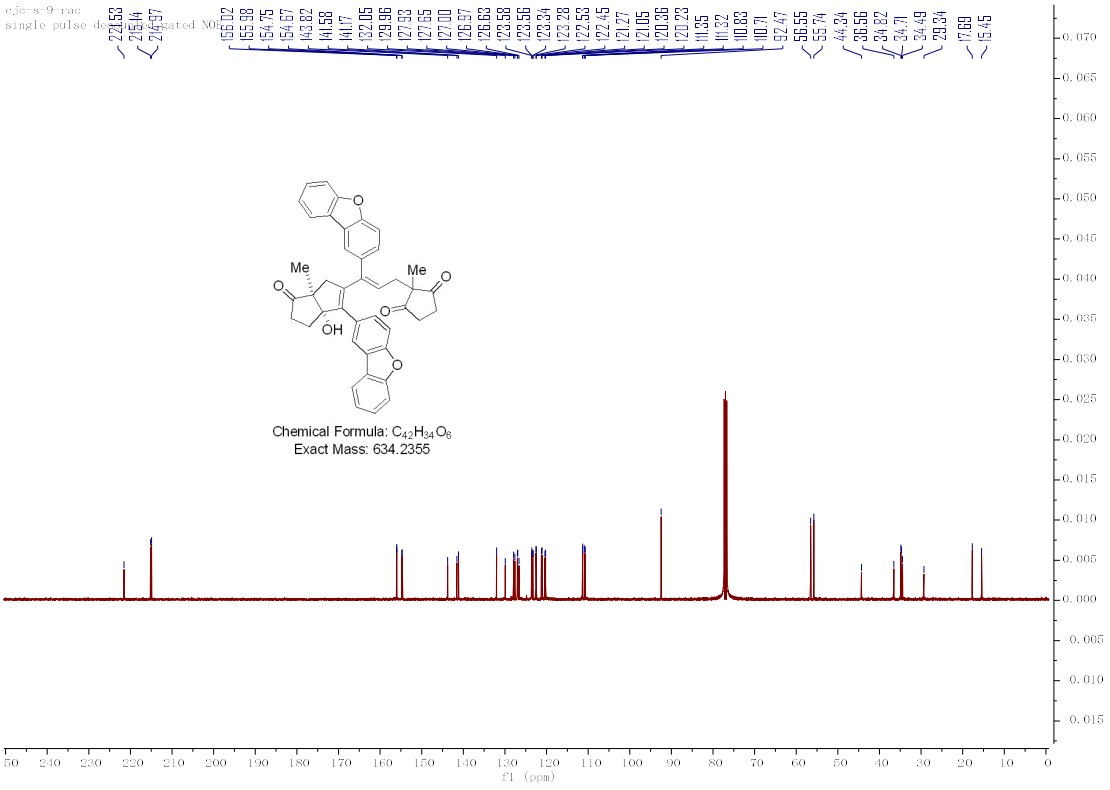
3n


Me
O
S
OH
Me
O
O
S
Chemical Formula: $C_{26}H_{26}O_4S_2$
Exact Mass: 466.1273
f1 (ppm)

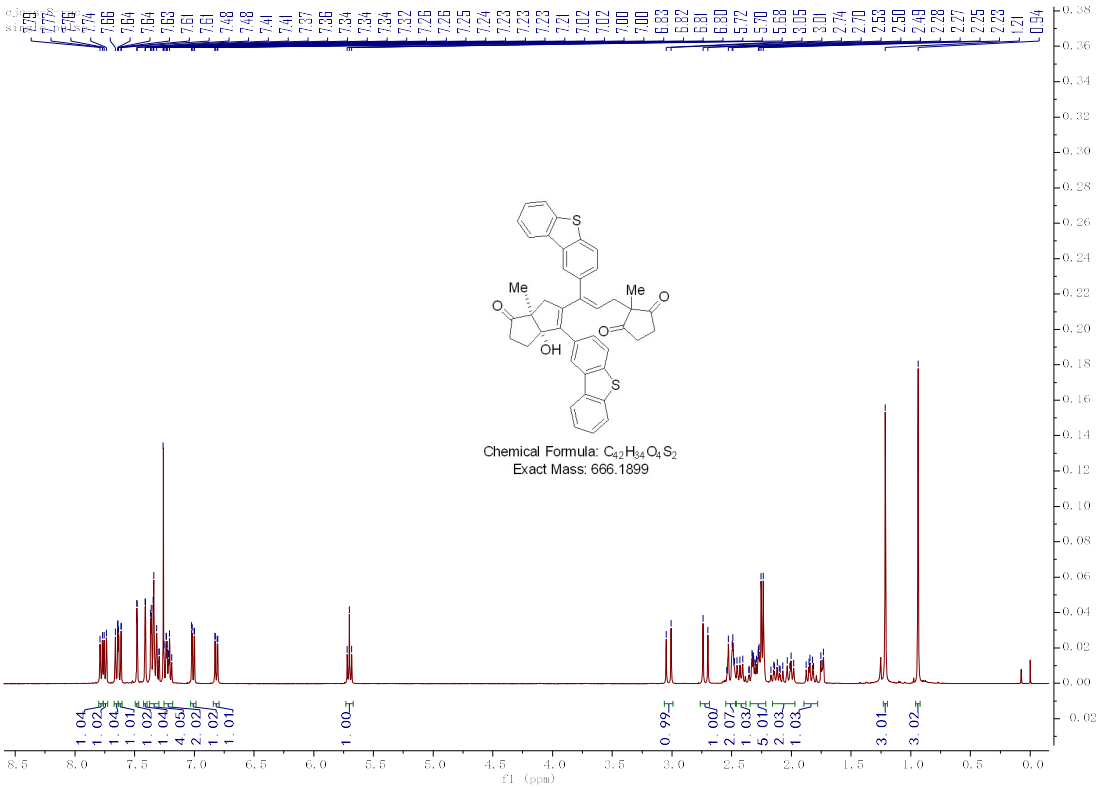

Me
O
S
OH
Me
O
O
S
Chemical Formula: $C_{26}H_{26}O_4S_2$
Exact Mass: 466.1273
f1 (ppm)

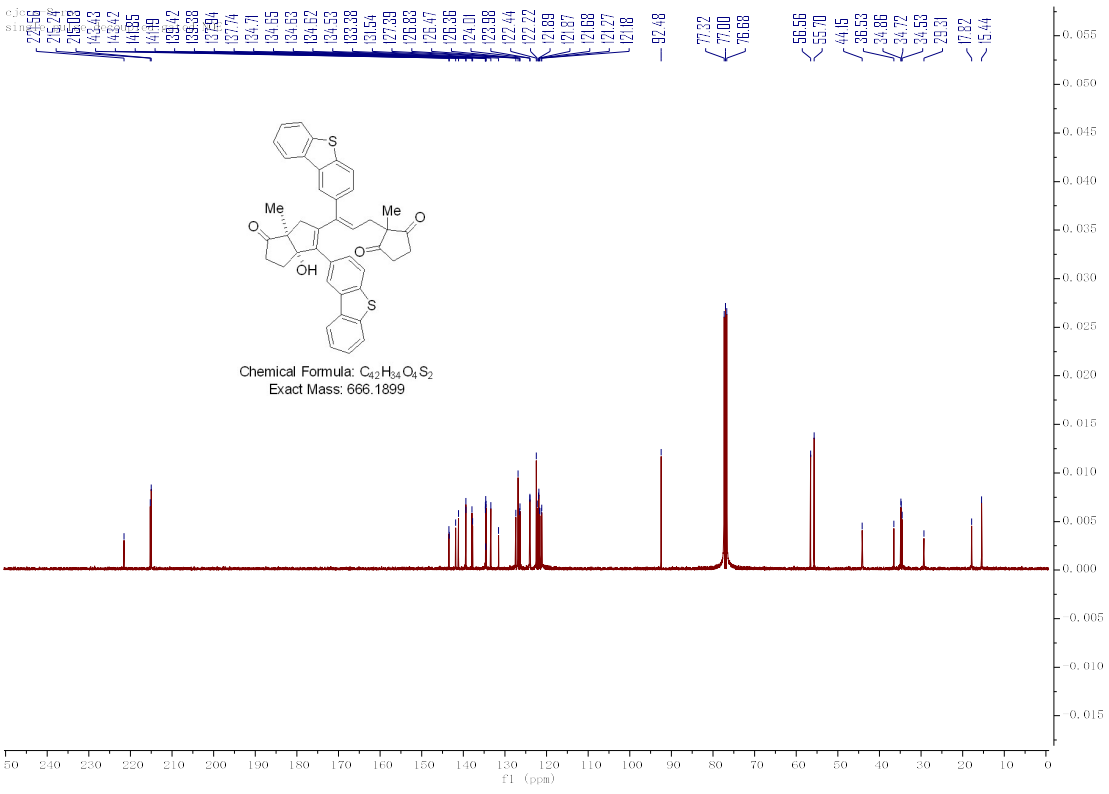
3o


Me
Me
O
O
OH
O
Chemical Formula: C42H34O6
Exact Mass: 634.2355

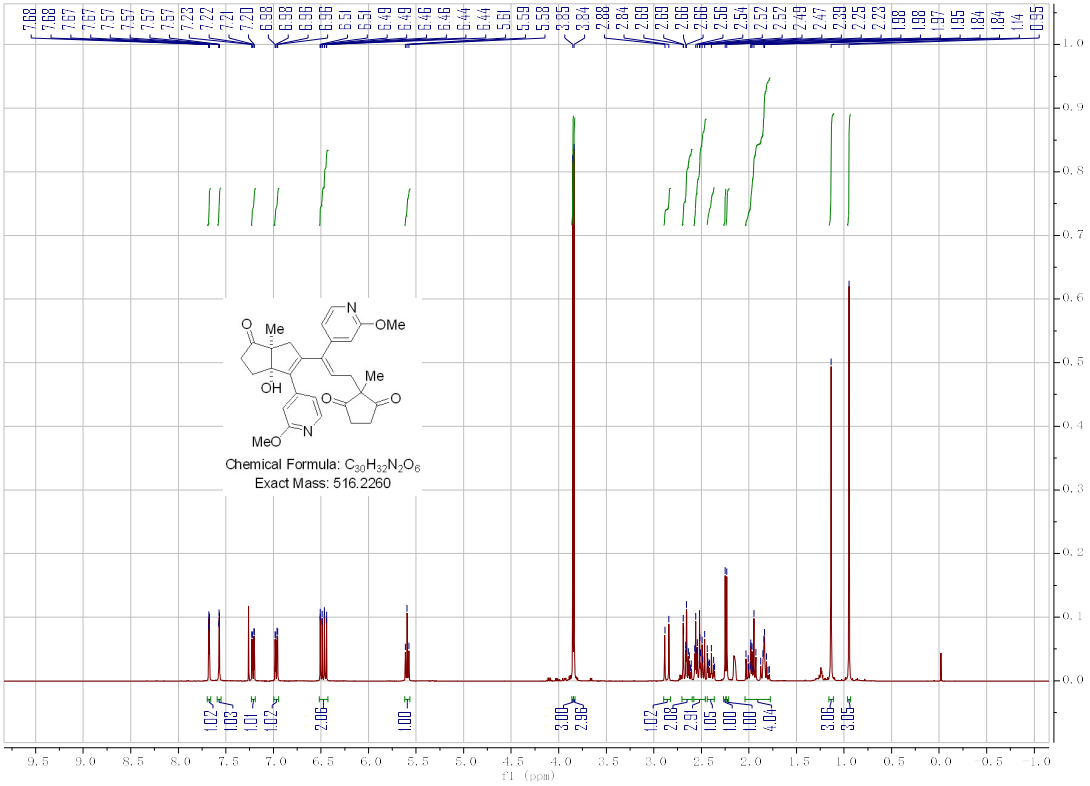

Me
Me
O
O
OH
O
Chemical Formula: C42H34O6
Exact Mass: 634.2355

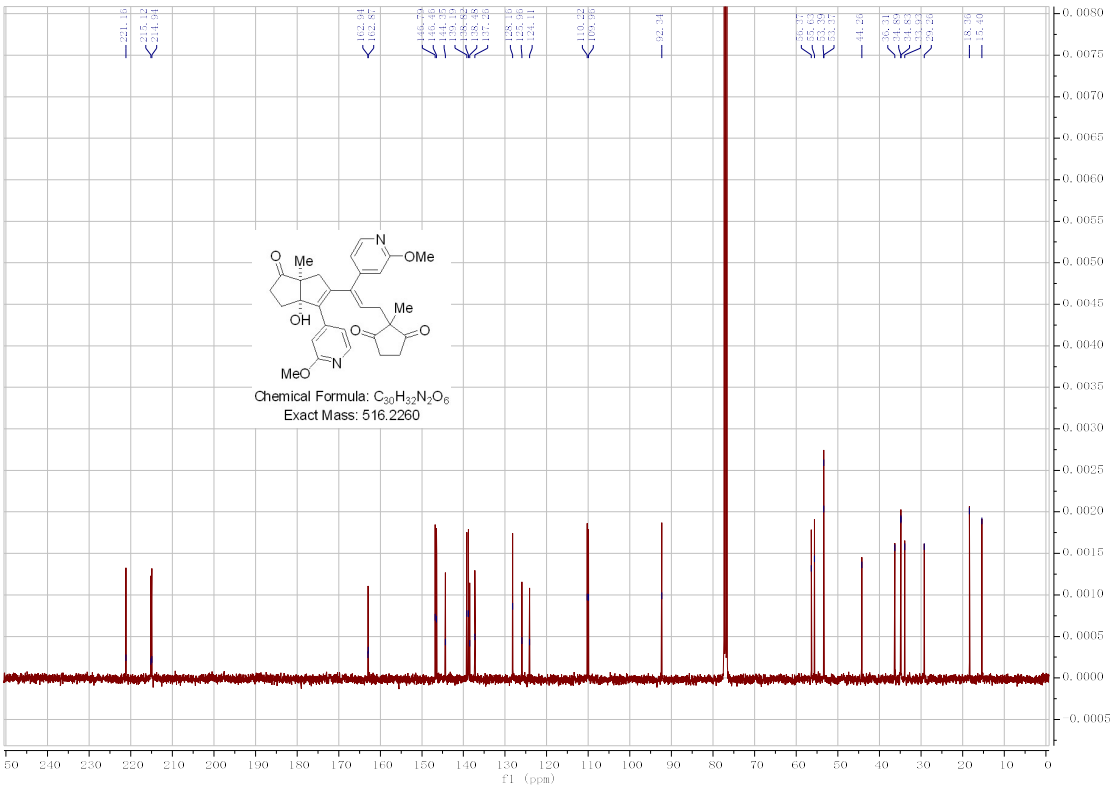
3p


Chemical Formula: C42H34O4S2
Exact Mass: 666.1899

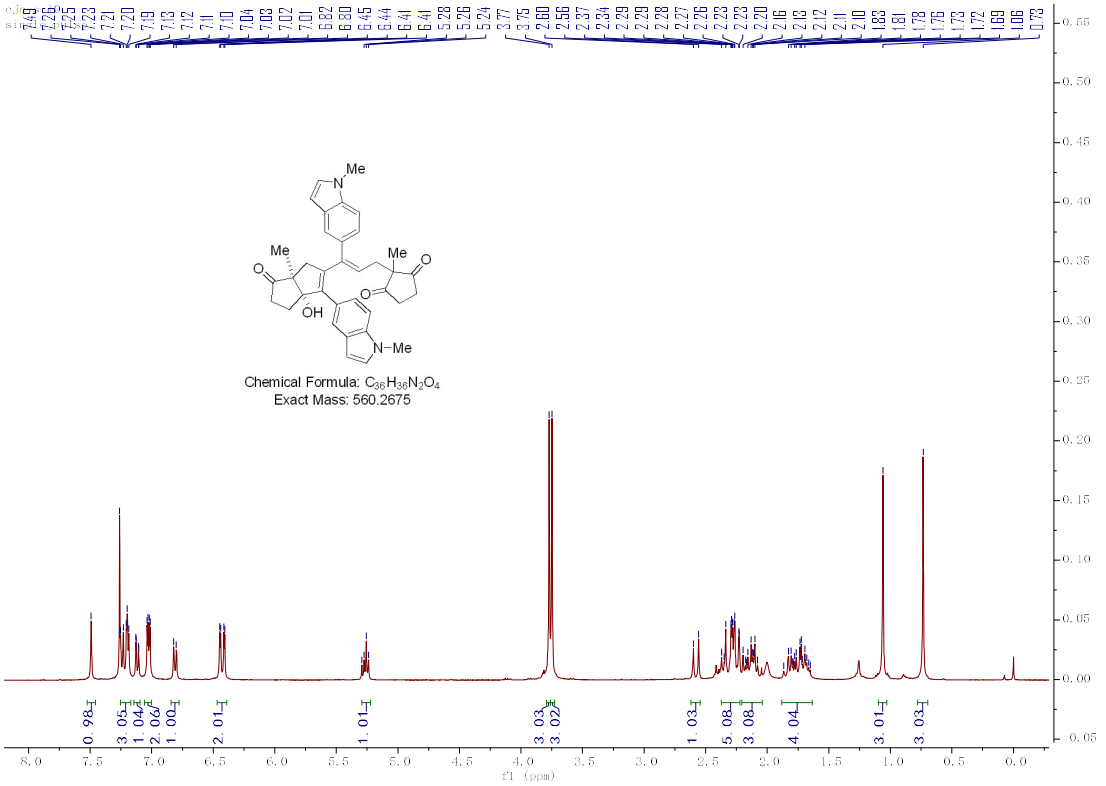

Chemical Formula: C42H34O4S2
Exact Mass: 666.1899

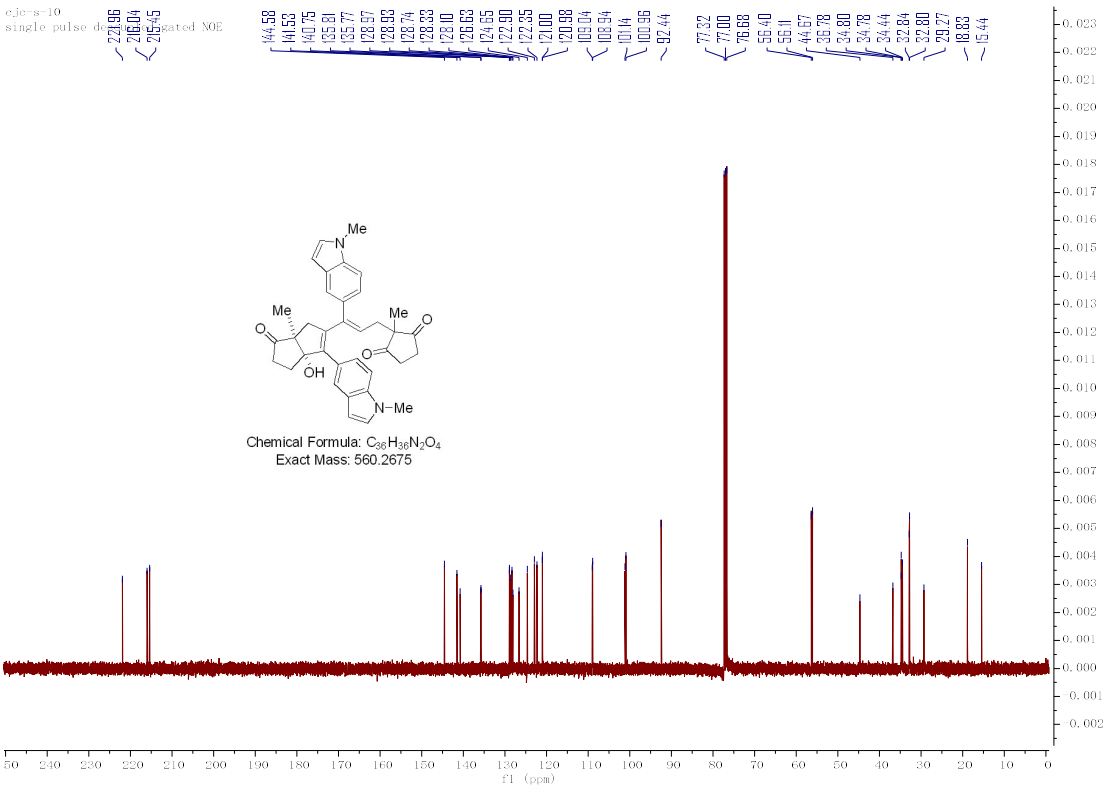
3q


Me
OMe
OH
Me
O
O
MeO
N
Chemical Formula: $C_{30}H_{32}N_2O_6$
Exact Mass: 516.2260
f1 (ppm)

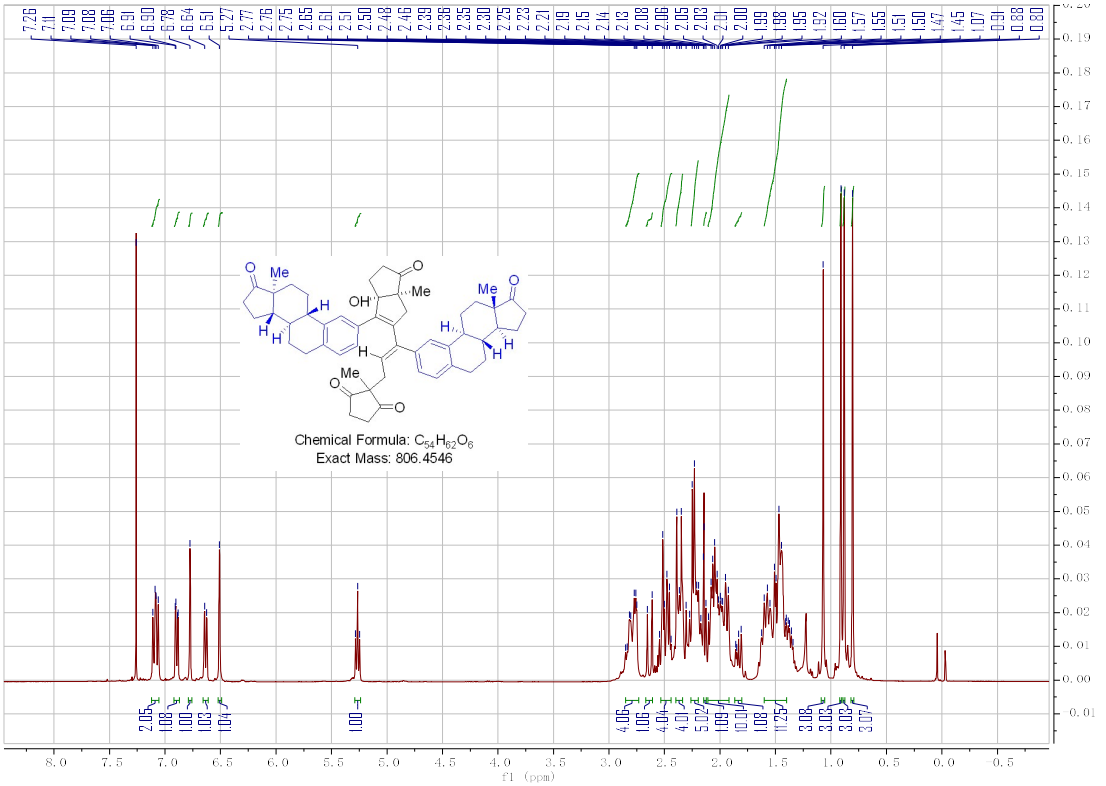

Me
OMe
OH
Me
O
O
MeO
N
Chemical Formula: $C_{30}H_{32}N_2O_6$
Exact Mass: 516.2260
f1 (ppm)

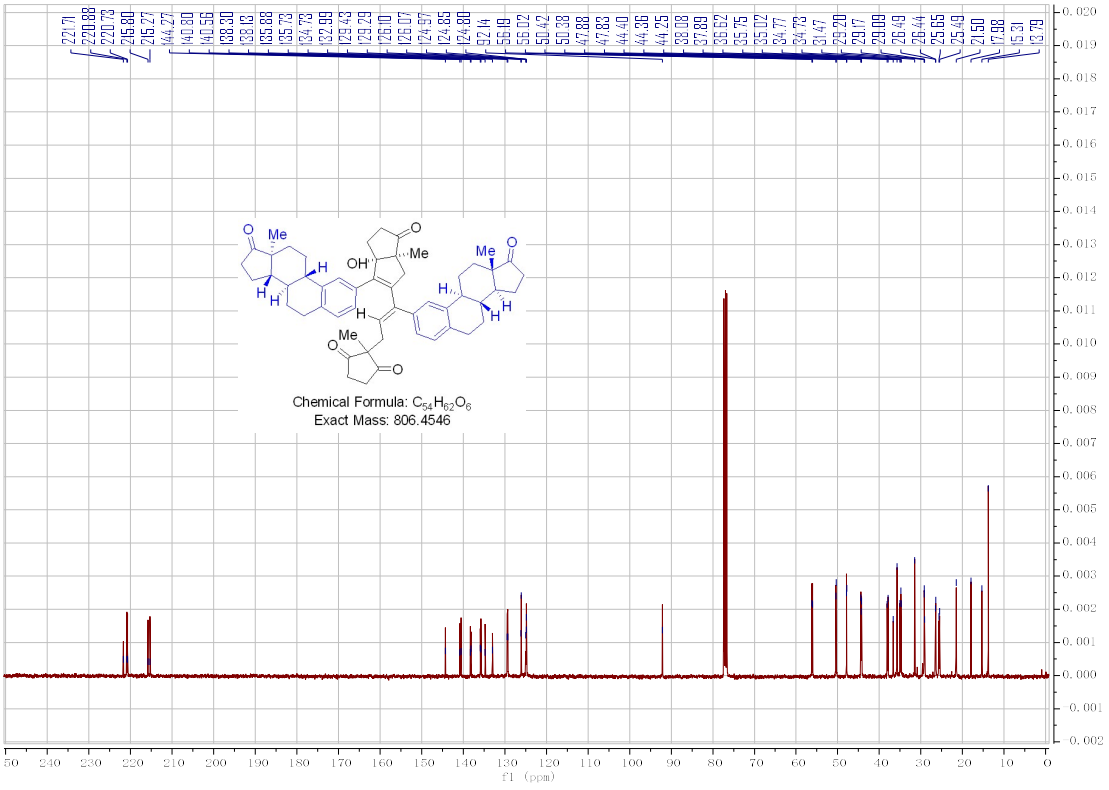
3r


Me
N
Me
Me
O
O
O
OH
N–Me
Chemical Formula: C36H36N2O4
Exact Mass: 560.2675

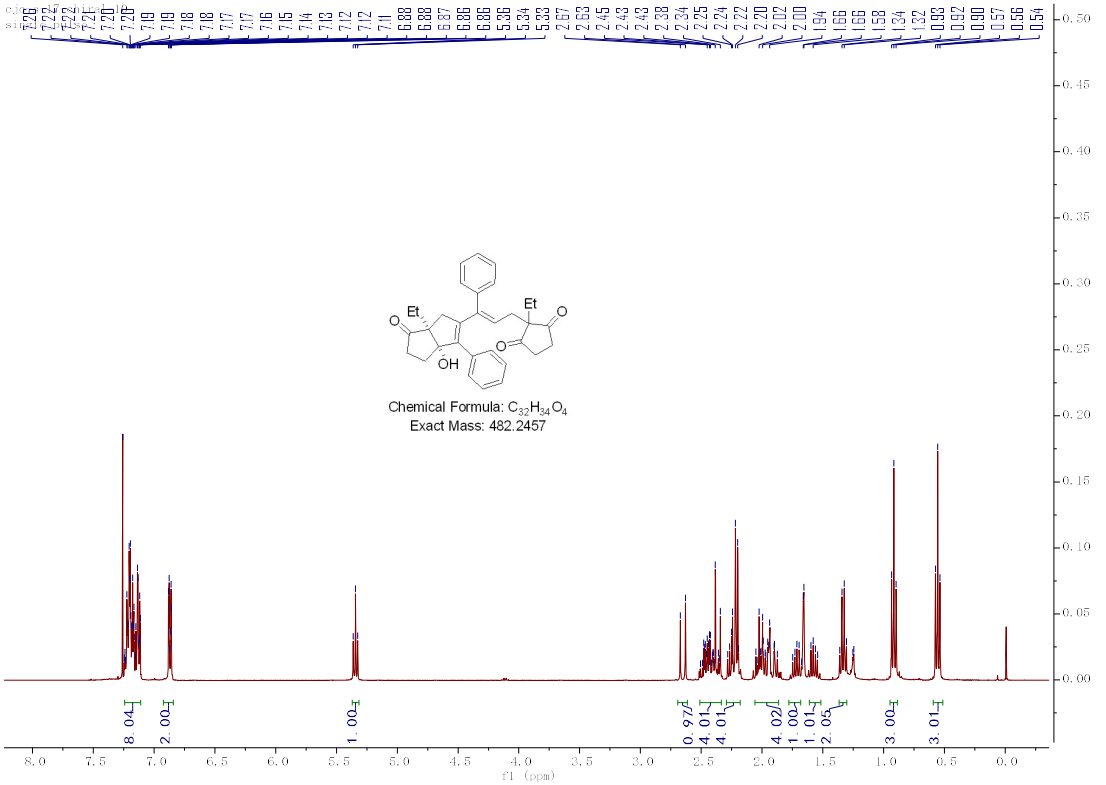

Me
N
Me
Me
O
O
O
OH
N–Me
Chemical Formula: C36H36N2O4
Exact Mass: 560.2675

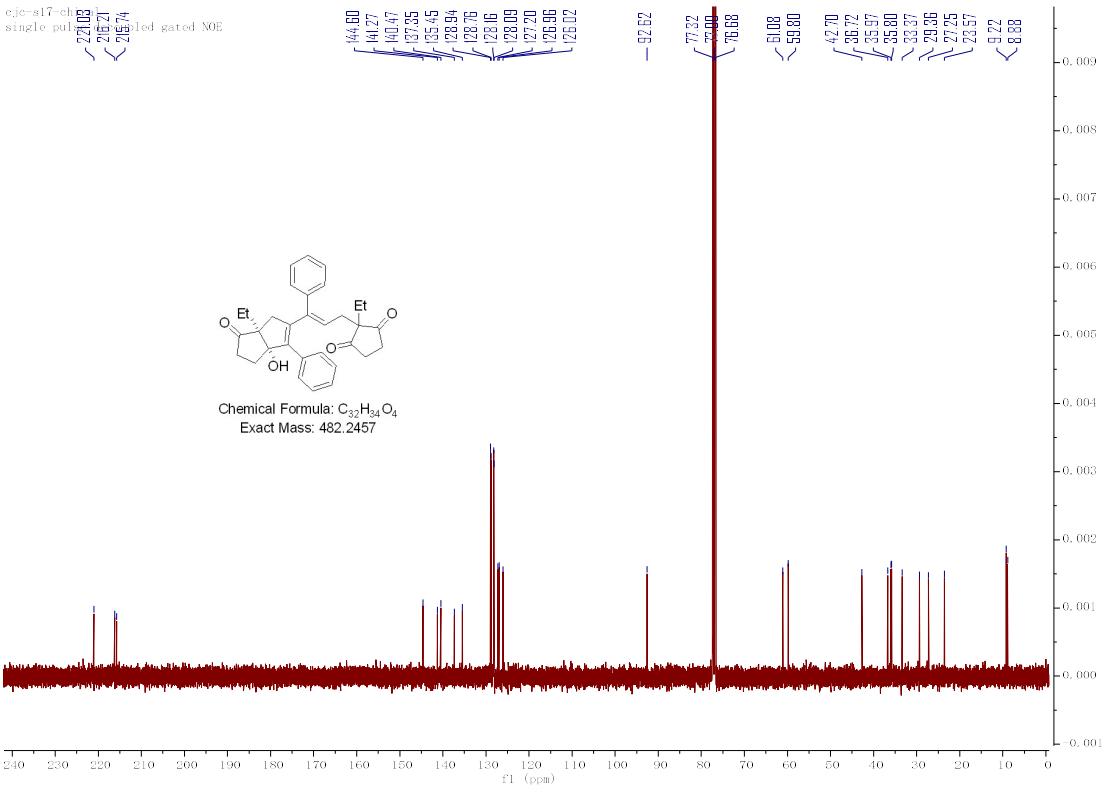
3s


Chemical Formula: C54H62O6
Exact Mass: 806.4546
f1 (ppm)

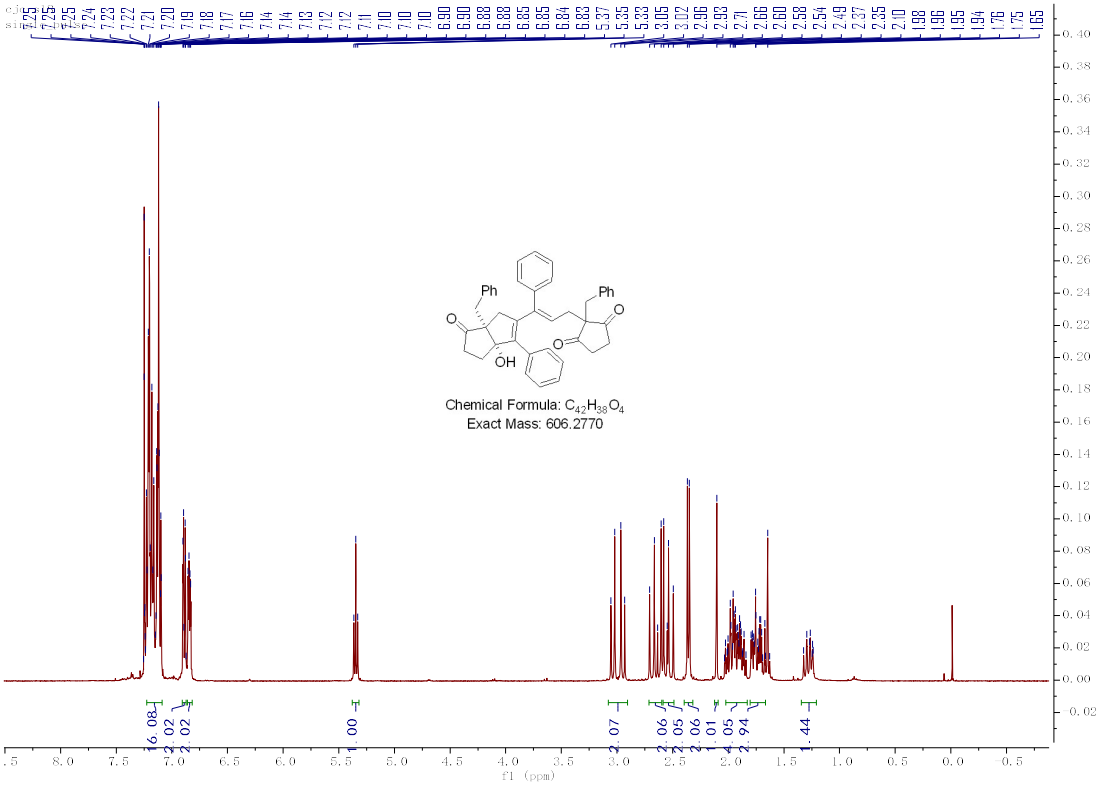

Chemical Formula: C54H62O6
Exact Mass: 806.4546
f1 (ppm)

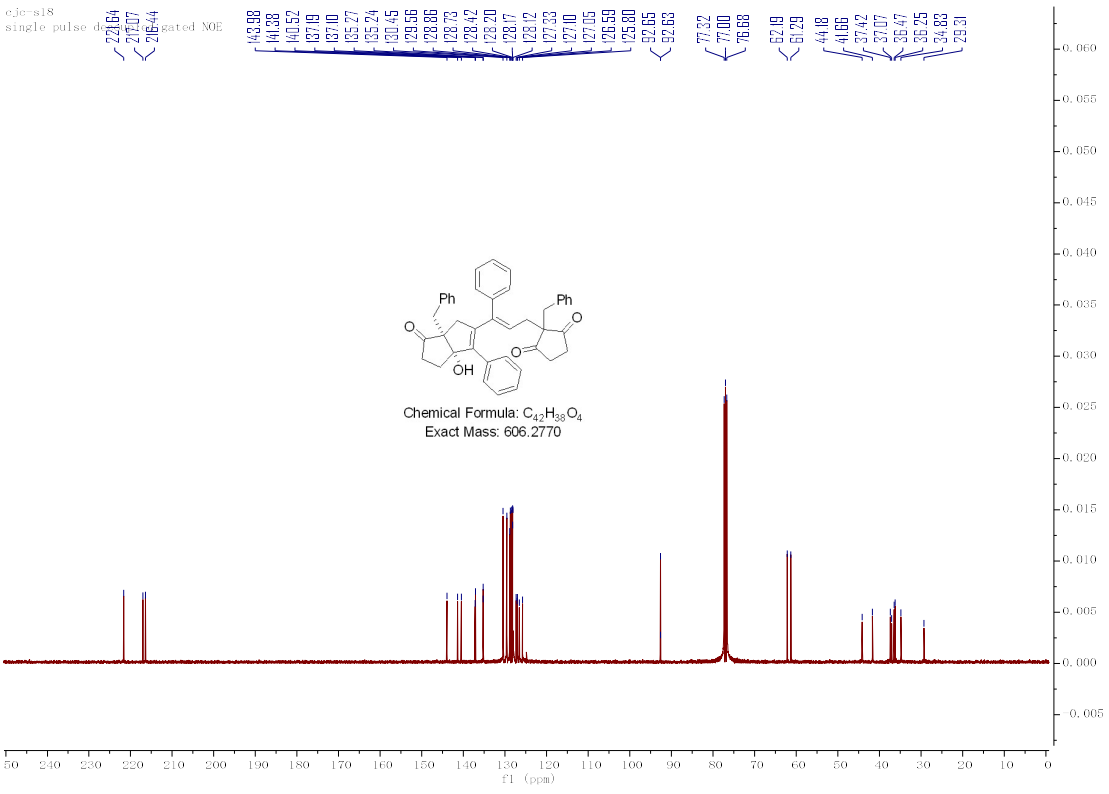
3t


Et
Et
O
O
O
OH
Chemical Formula: C32H34O4
Exact Mass: 482.2457

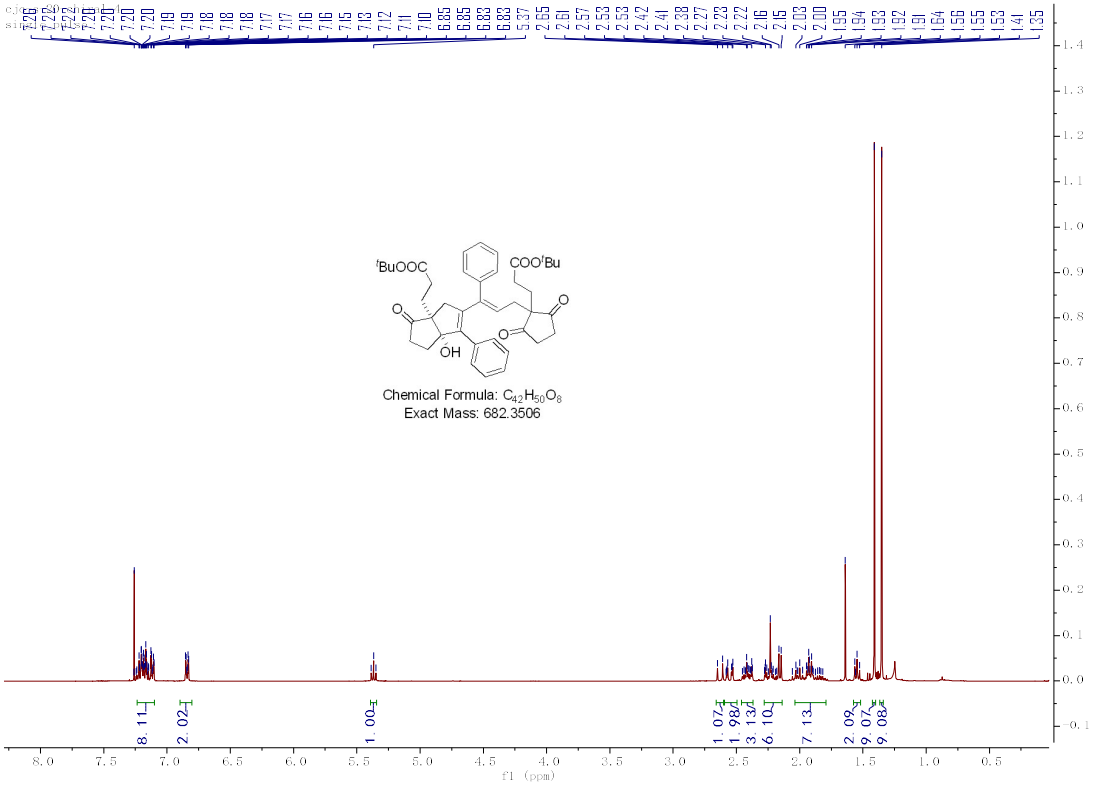

Et
Et
O
O
O
OH
Chemical Formula: C32H34O4
Exact Mass: 482.2457

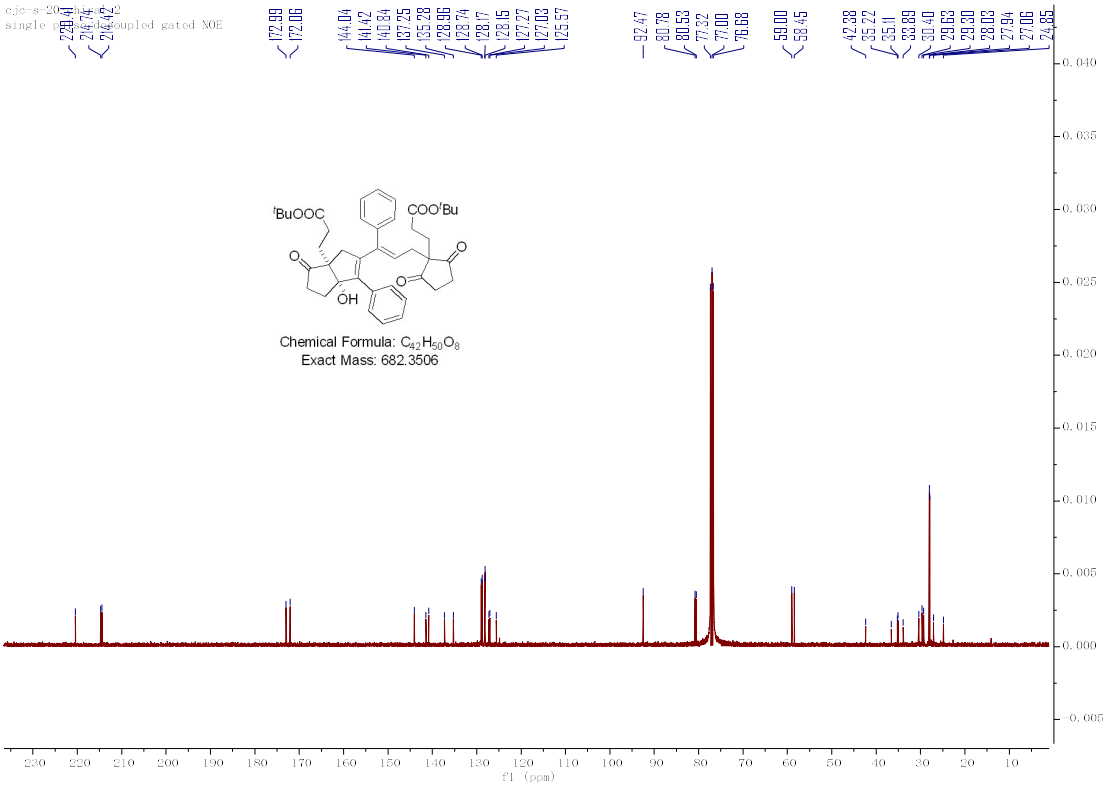
3u


Ph
Ph
O
O
O
OH
Chemical Formula: C42H38O4
Exact Mass: 606.2770

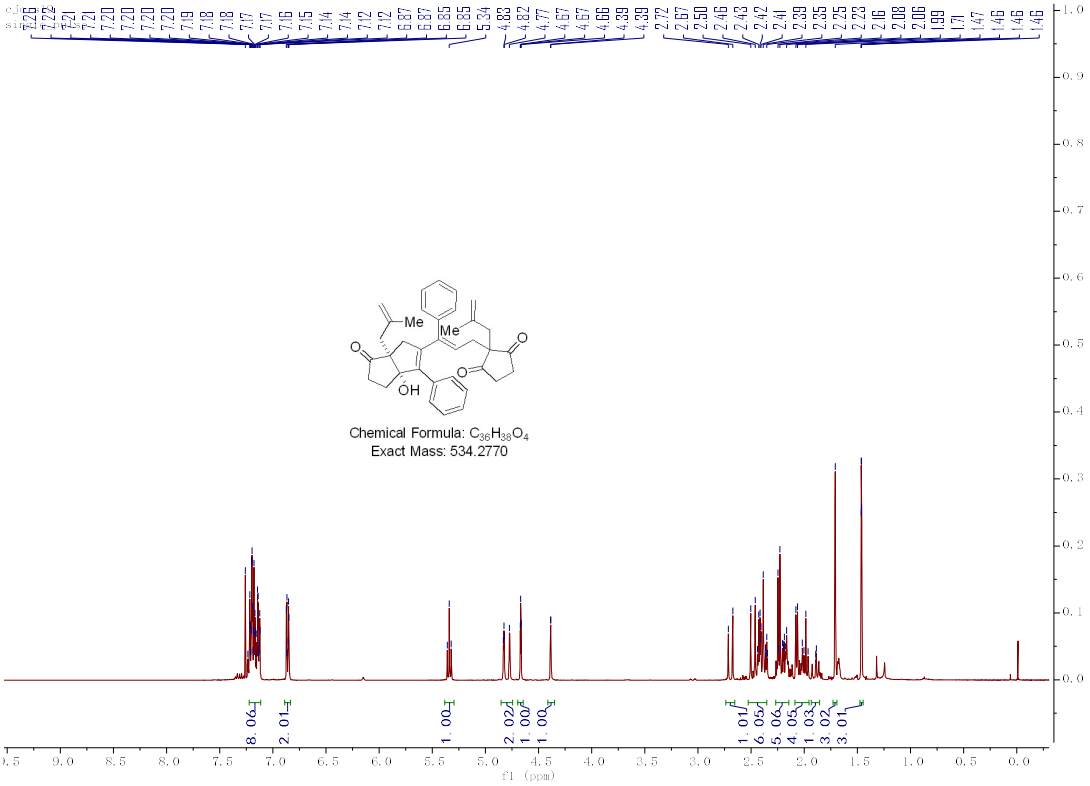

Ph
Ph
O
O
O
OH
Chemical Formula: C42H38O4
Exact Mass: 606.2770

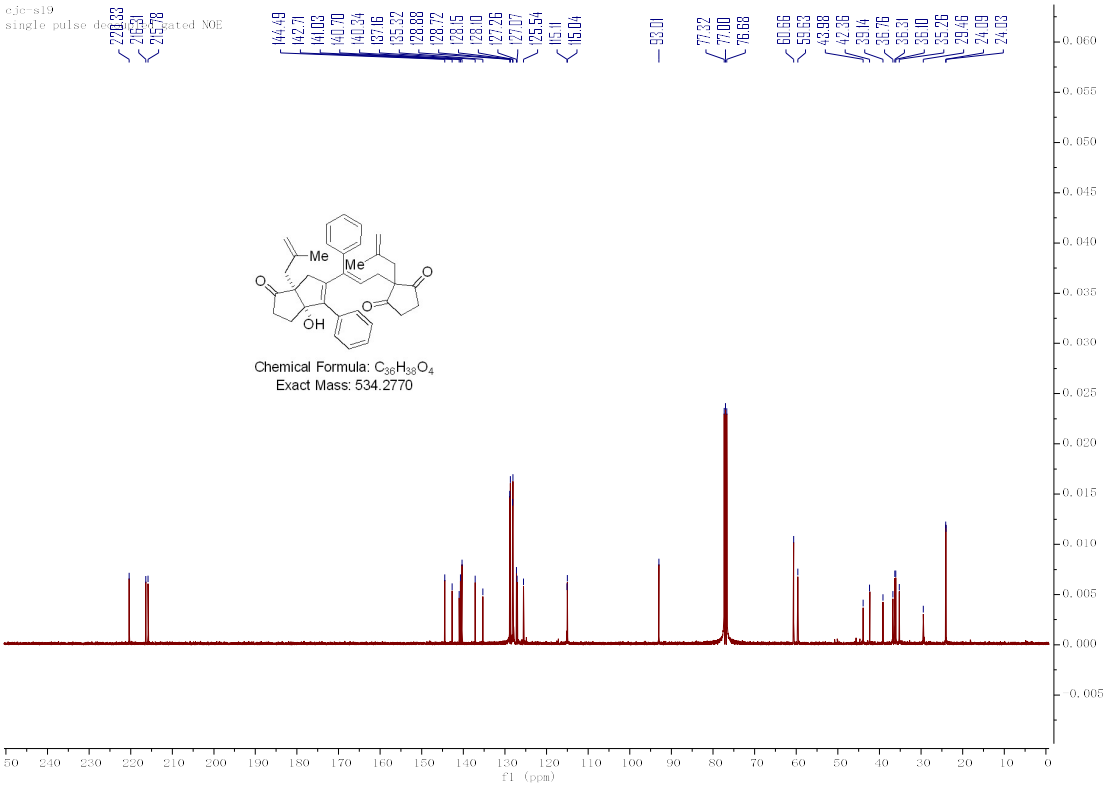
3v


tBuOOC
COOtBu
O
O
O
OH
Chemical Formula: C42H50O8
Exact Mass: 682.3506
f1 (ppm)

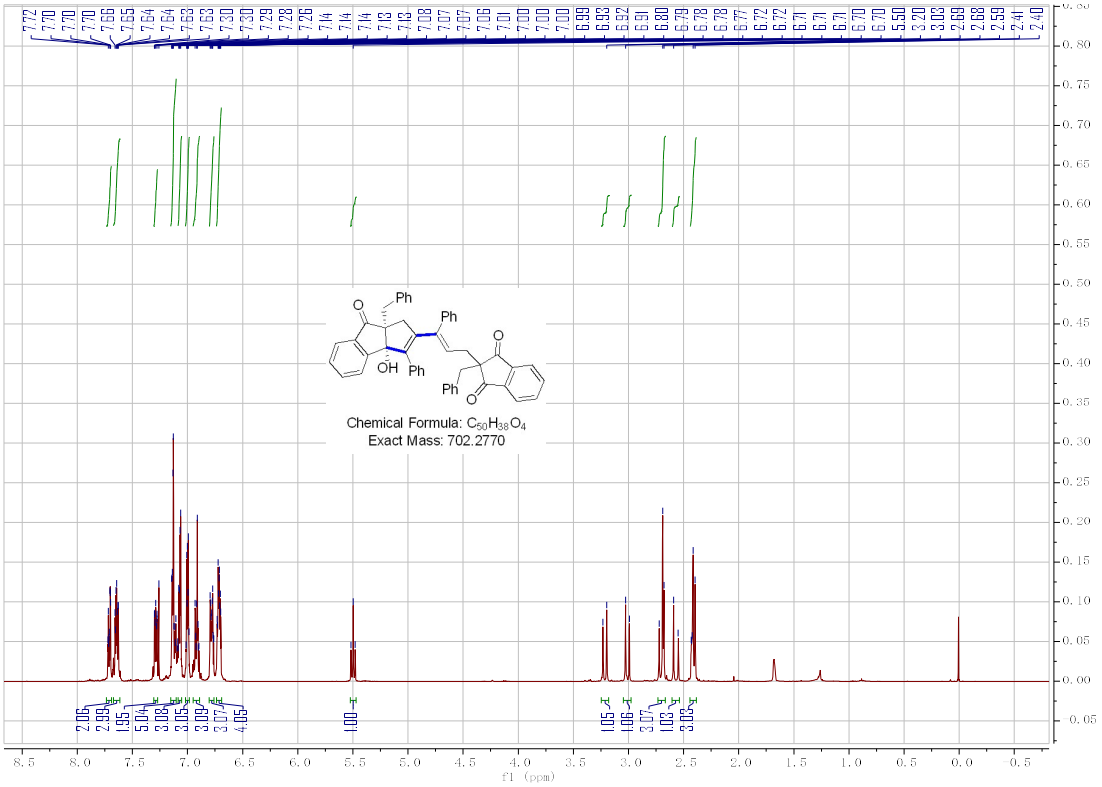

tBuOOC
COOtBu
O
O
O
OH
Chemical Formula: C42H50O8
Exact Mass: 682.3506
f1 (ppm)

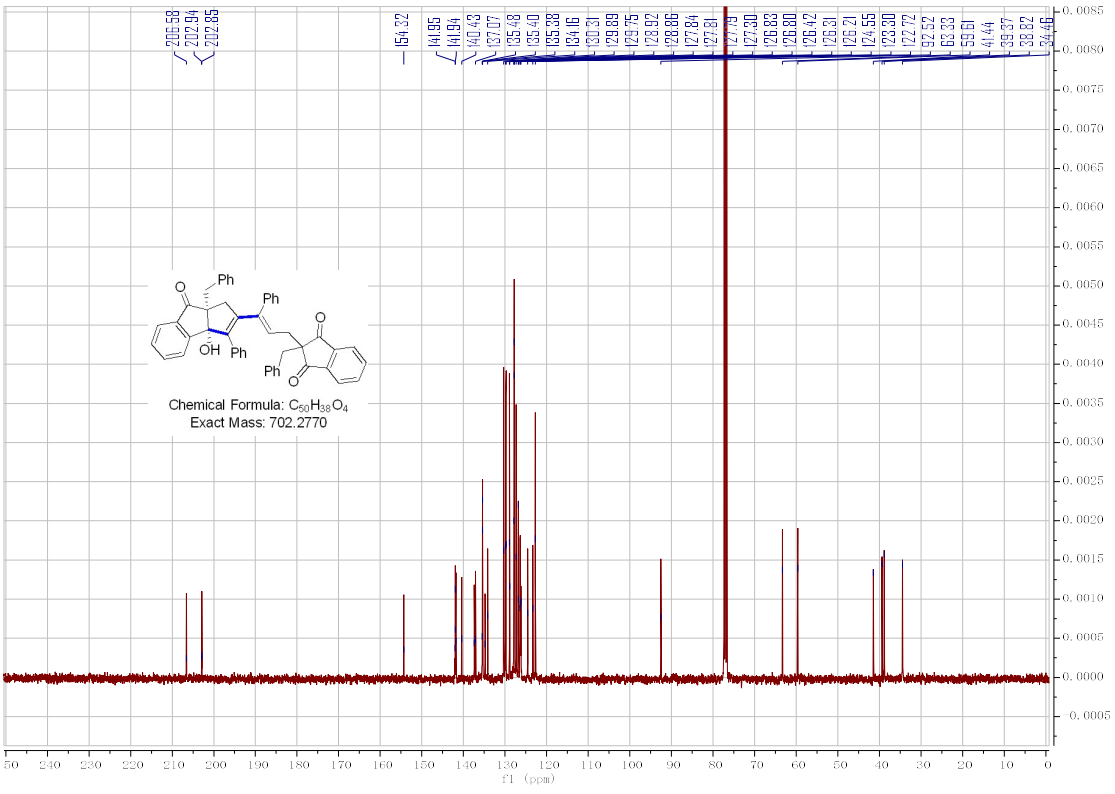
3w


Me
Me
O
O
O
OH
Chemical Formula: C36H38O4
Exact Mass: 534.2770

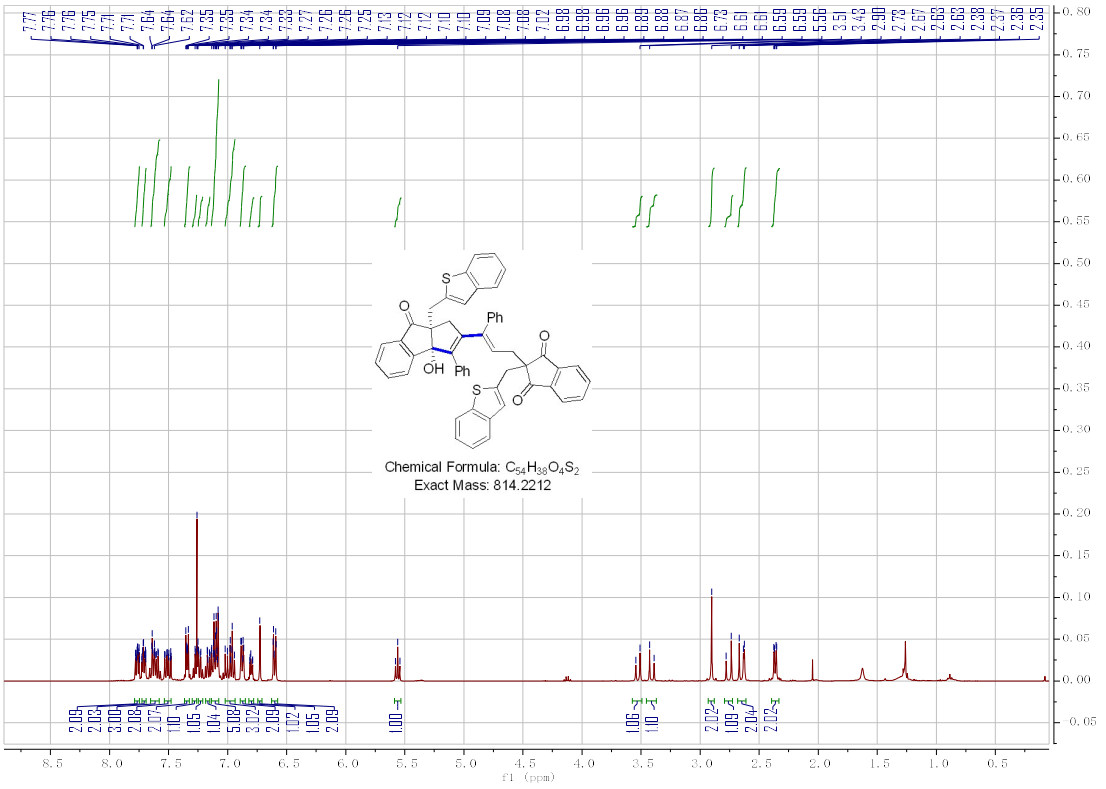

Me
Me
O
O
O
OH
Chemical Formula: C36H38O4
Exact Mass: 534.2770

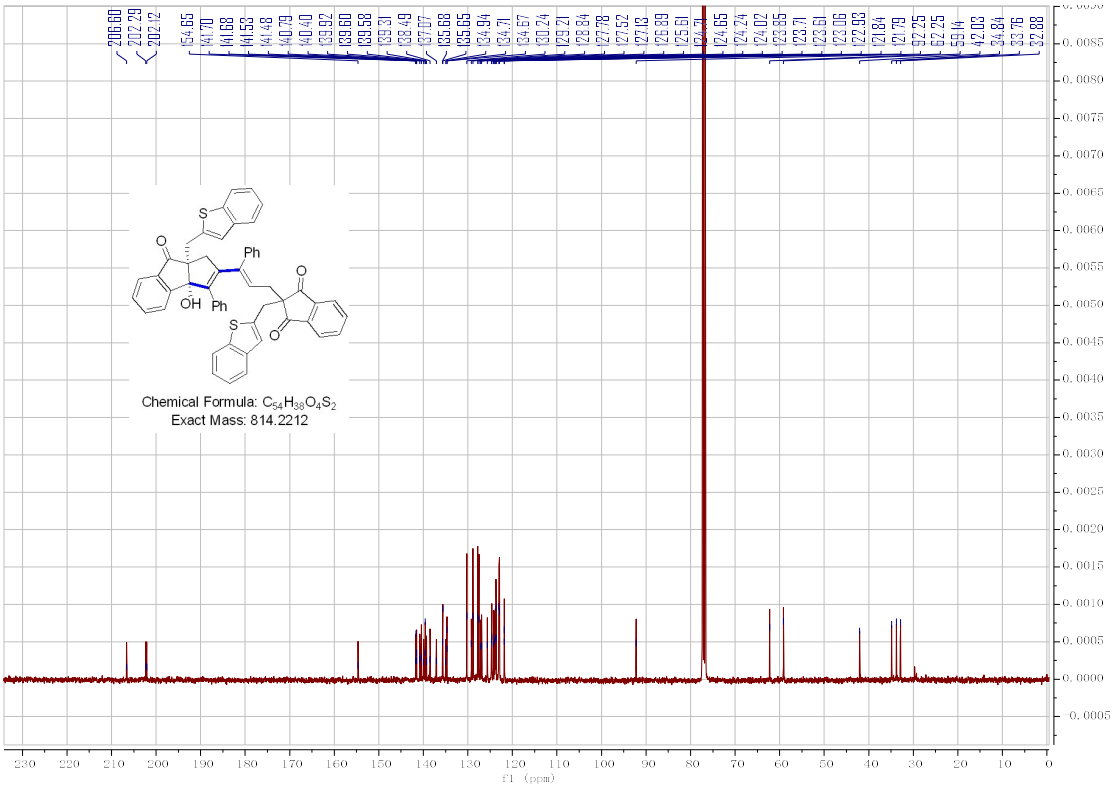
3x


Ph
Ph
O
OH
Ph
Ph
O
Chemical Formula: $C_{50}H_{38}O_4$
Exact Mass: 702.2770

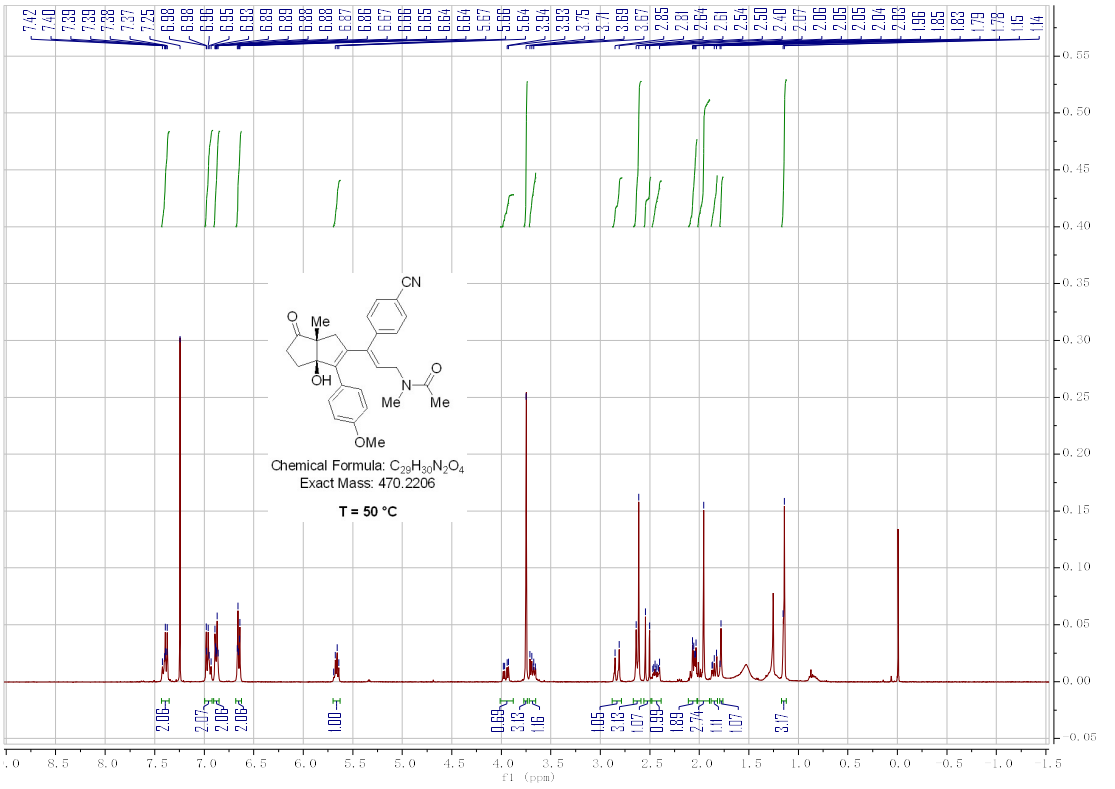

Ph
Ph
O
OH
Ph
Ph
O
Chemical Formula: $C_{50}H_{38}O_4$
Exact Mass: 702.2770

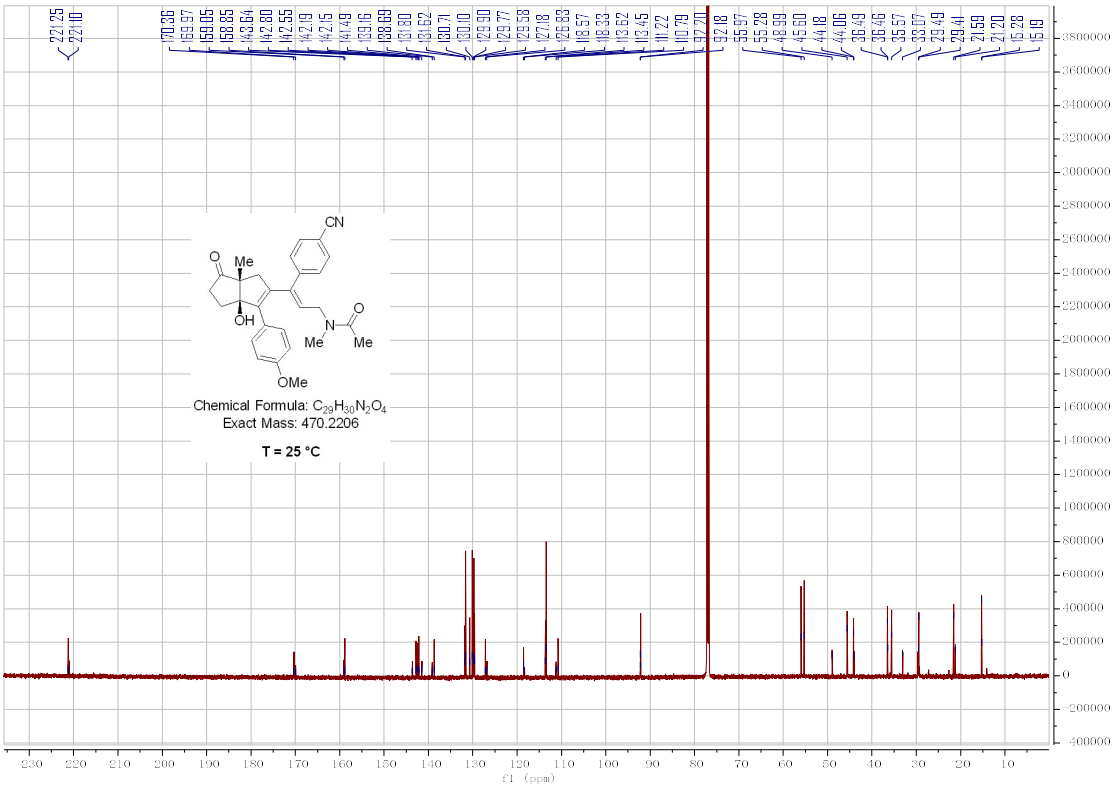
3y


Chemical Formula: C54H38O4S2
Exact Mass: 814.2212

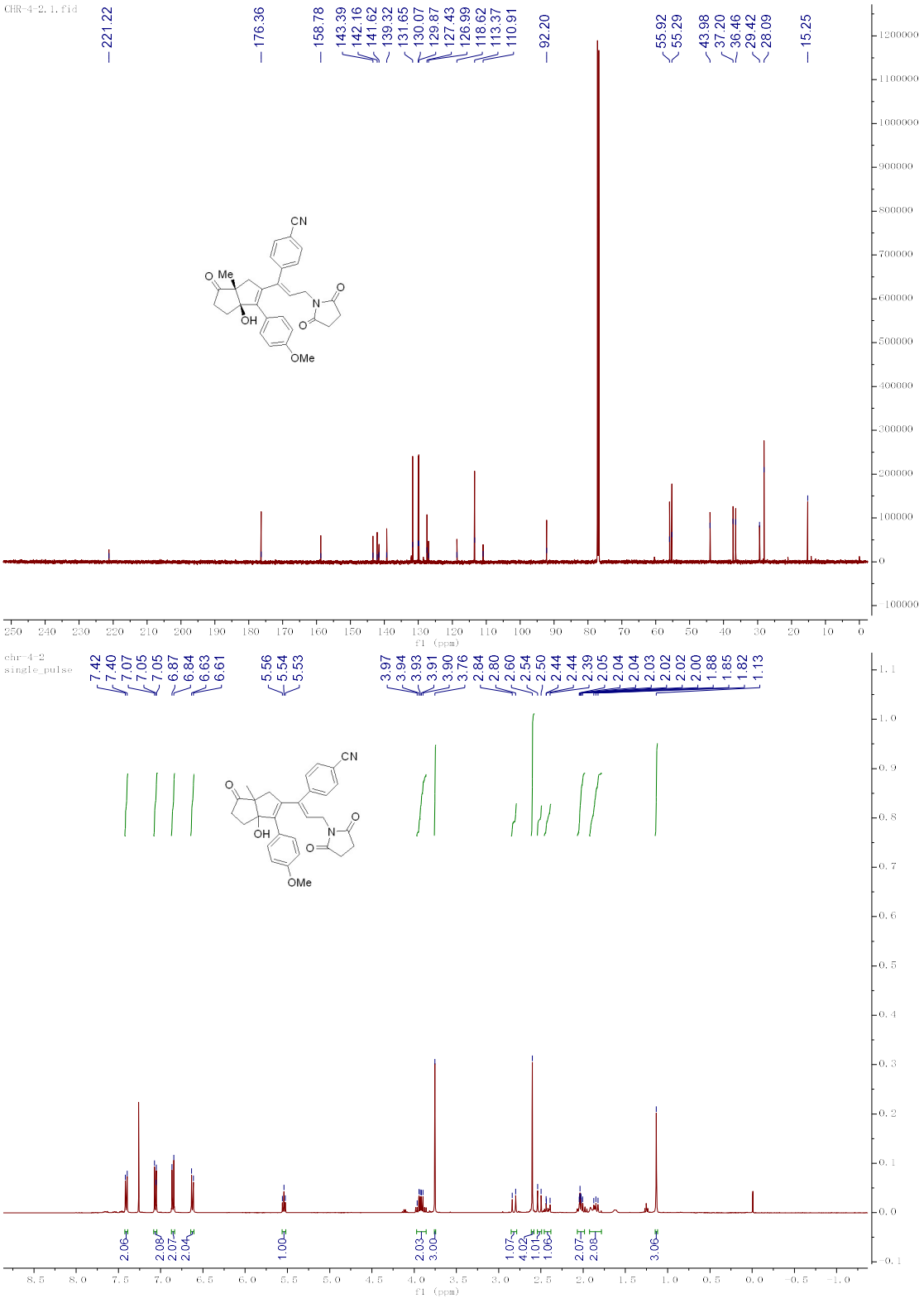

Chemical Formula: C54H38O4S2
Exact Mass: 814.2212

5ba

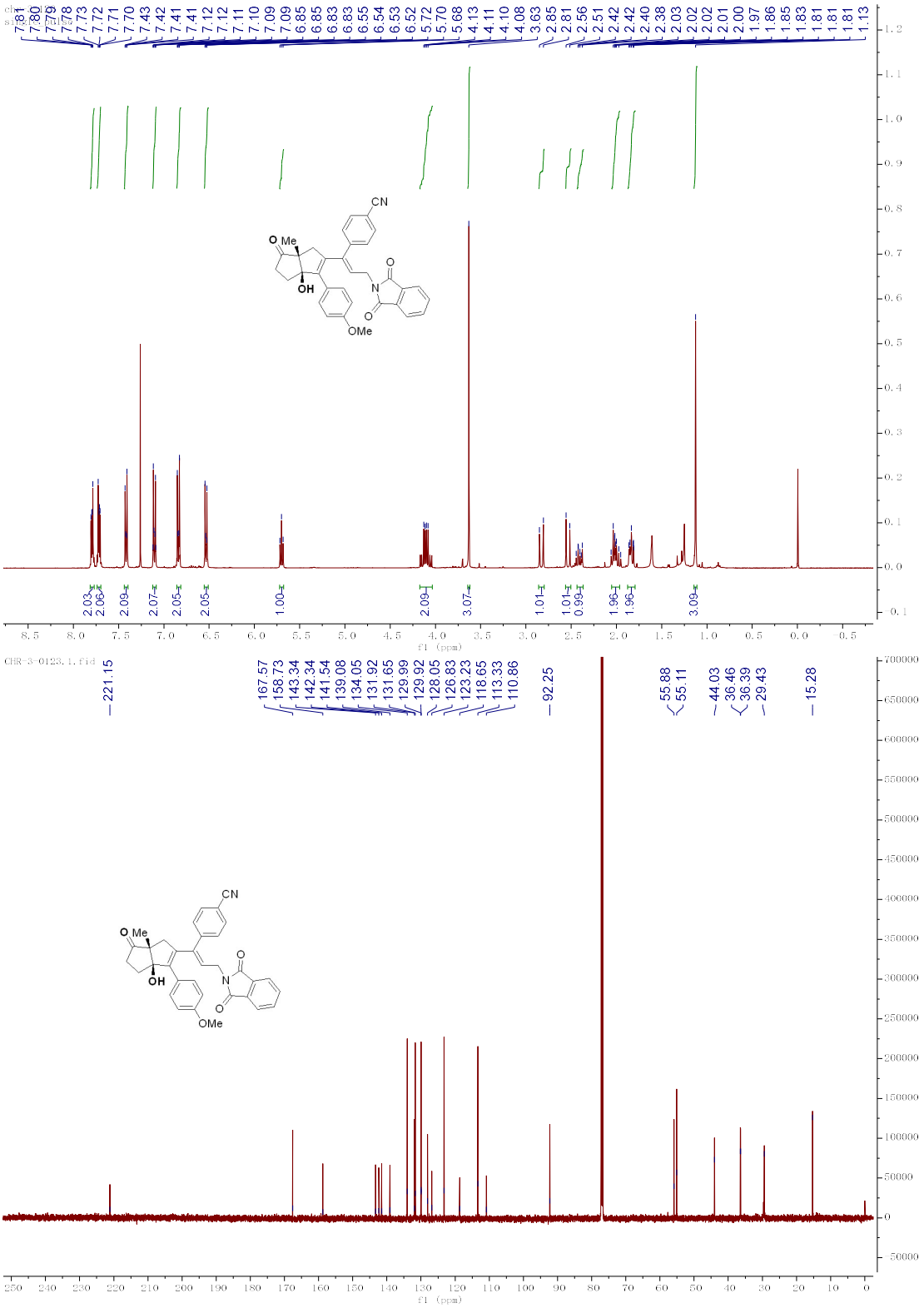

CN
Me
O
OH
N
O
Me
Me
OMe
Chemical Formula: C29H30N2O4
Exact Mass: 470.2206
T = 50 °C


CN
Me
O
OH
N
O
Me
Me
OMe
Chemical Formula: C29H30N2O4
Exact Mass: 470.2206
T = 25 °C

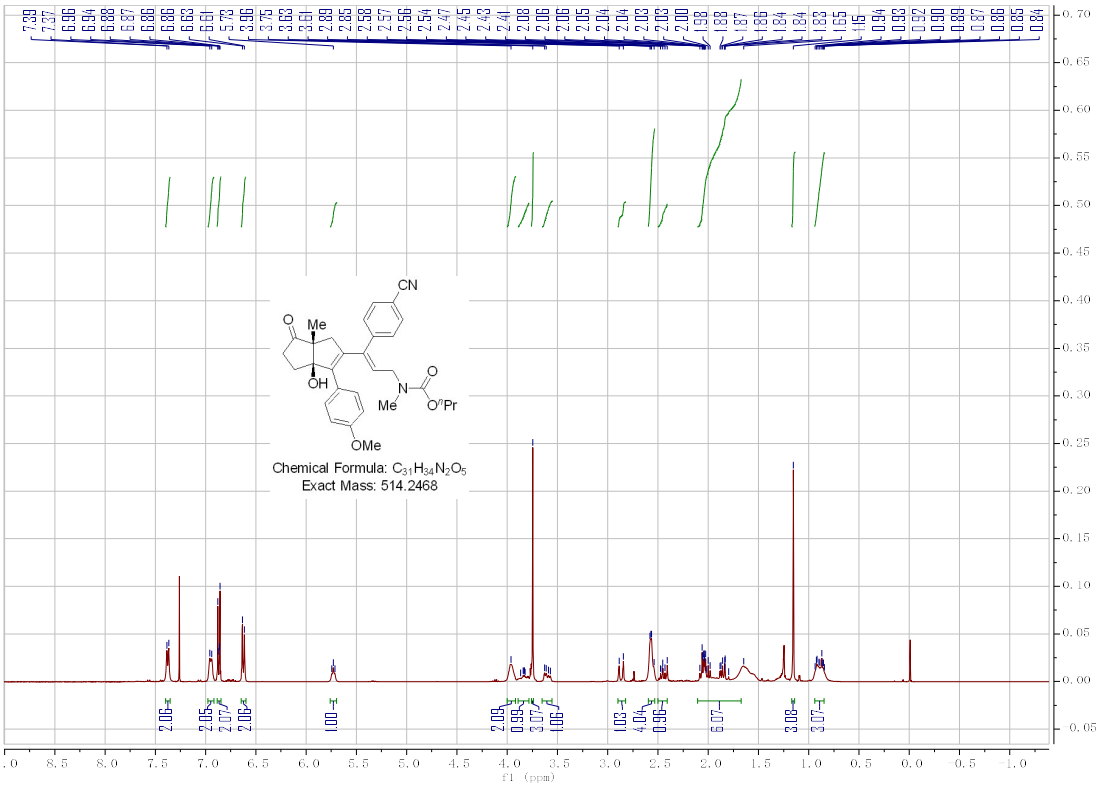
5bd

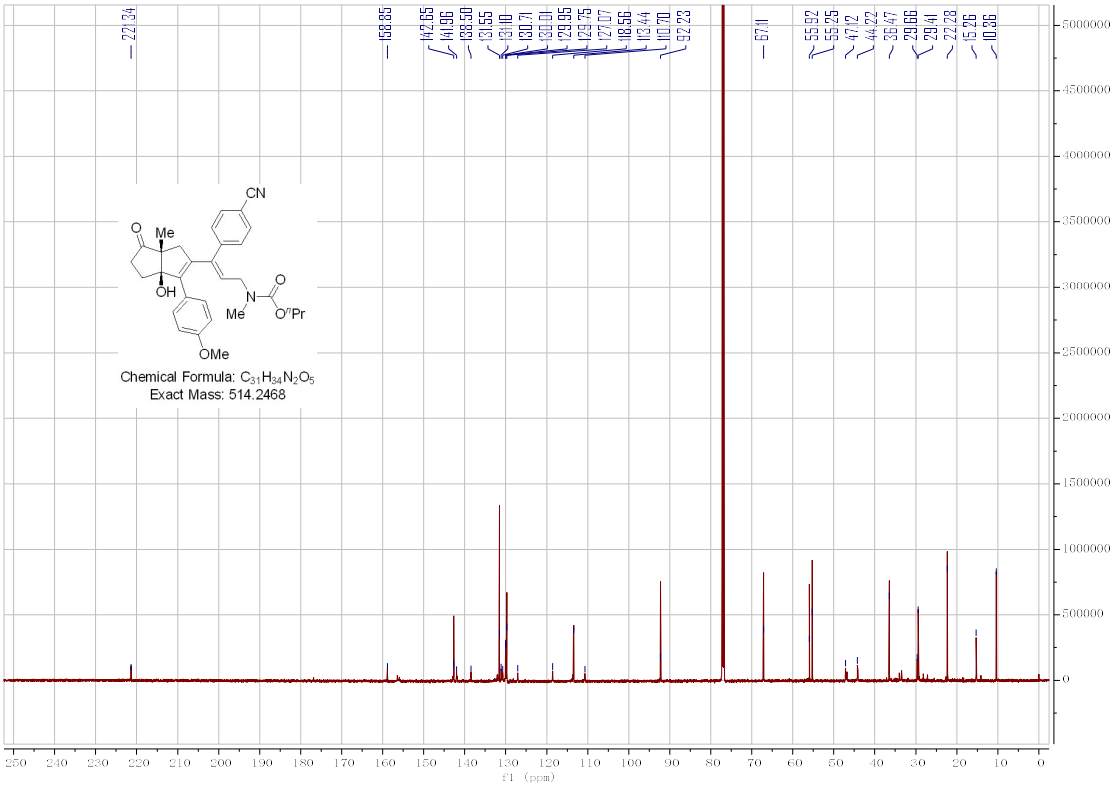

CHR-4-2.1.fid
221.22
176.36
158.78
143.39
142.16
141.62
139.32
131.65
130.07
129.87
127.43
126.99
118.62
113.37
110.91
92.20
55.92
55.29
43.98
37.20
36.46
29.42
28.09
15.25
CN
O
Me
OH
N
O
O
OMe
f1 (ppm)
chr-4-2
single_pulse
7.42
7.40
7.07
7.05
7.05
6.87
6.84
6.63
6.61
5.56
5.54
5.53
3.97
3.94
3.93
3.91
3.90
3.76
2.84
2.80
2.60
2.54
2.50
2.44
2.44
2.39
2.05
2.04
2.04
2.03
2.02
2.02
2.00
1.88
1.85
1.82
1.13
2.06
2.08
2.07
2.04
1.00
2.03
3.00
1.07
4.02
1.01
1.06
2.07
2.08
3.06
f1 (ppm)

5be

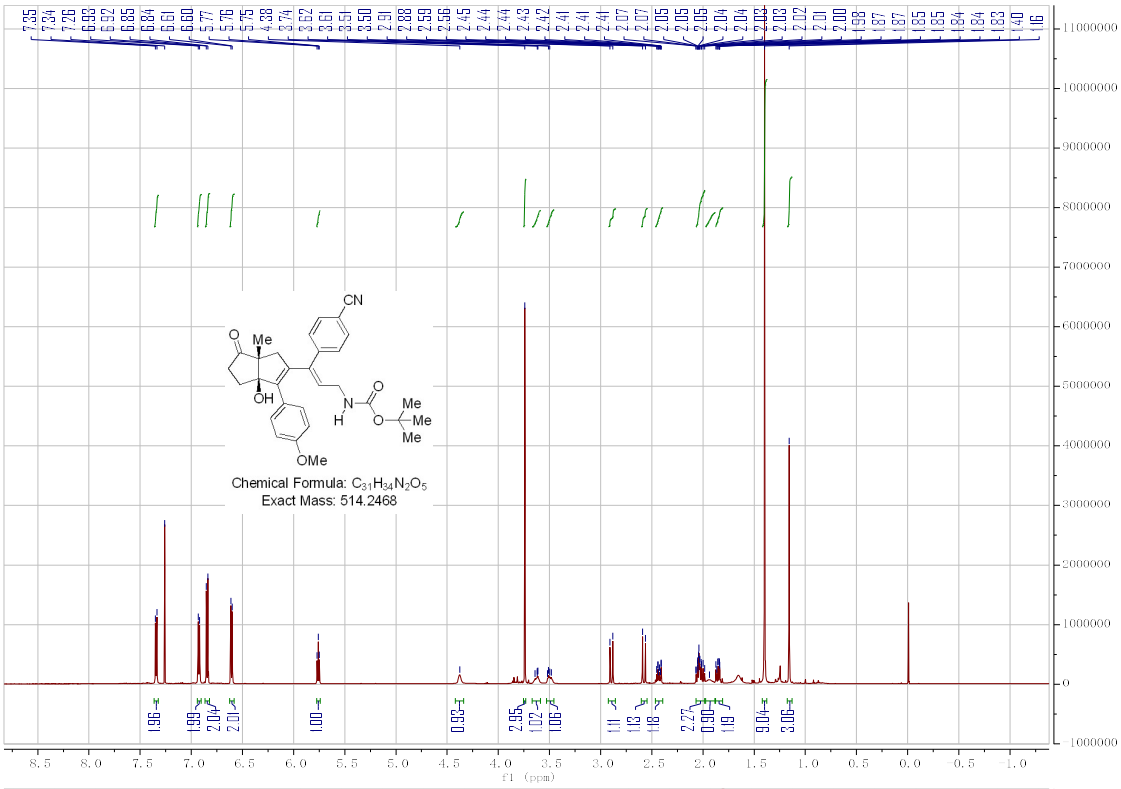

7.81 7.80 7.79 7.78 7.73 7.72 7.71 7.70 7.43 7.42 7.41 7.41 7.12 7.11 7.10 7.09 7.09 6.85 6.85 6.83 6.55 6.54 6.53 6.52 5.72 5.70 5.68 4.13 4.11 4.10 4.08 3.63 2.85 2.81 2.56 2.51 2.42 2.42 2.40 2.38 2.03 2.02 2.02 2.01 2.00 1.97 1.86 1.85 1.83 1.81 1.81 1.81 1.13
CN
O Me
OH
O
N
O
OMe
2.03 2.06 2.09 2.07 2.05 2.05 1.00 2.09 3.07 1.01 1.01 0.99 1.96 1.96 3.09
f1 (ppm)
CHR-3-0123.1.fid
221.15
167.57 158.73 143.34 142.34 141.54 139.08 134.05 131.92 131.65 129.99 129.92 128.05 126.83 123.23 118.65 113.33 110.86
92.25
55.88 55.11
44.03 36.46 36.39 29.43
15.28
CN
O Me
OH
O
N
O
OMe
f1 (ppm)

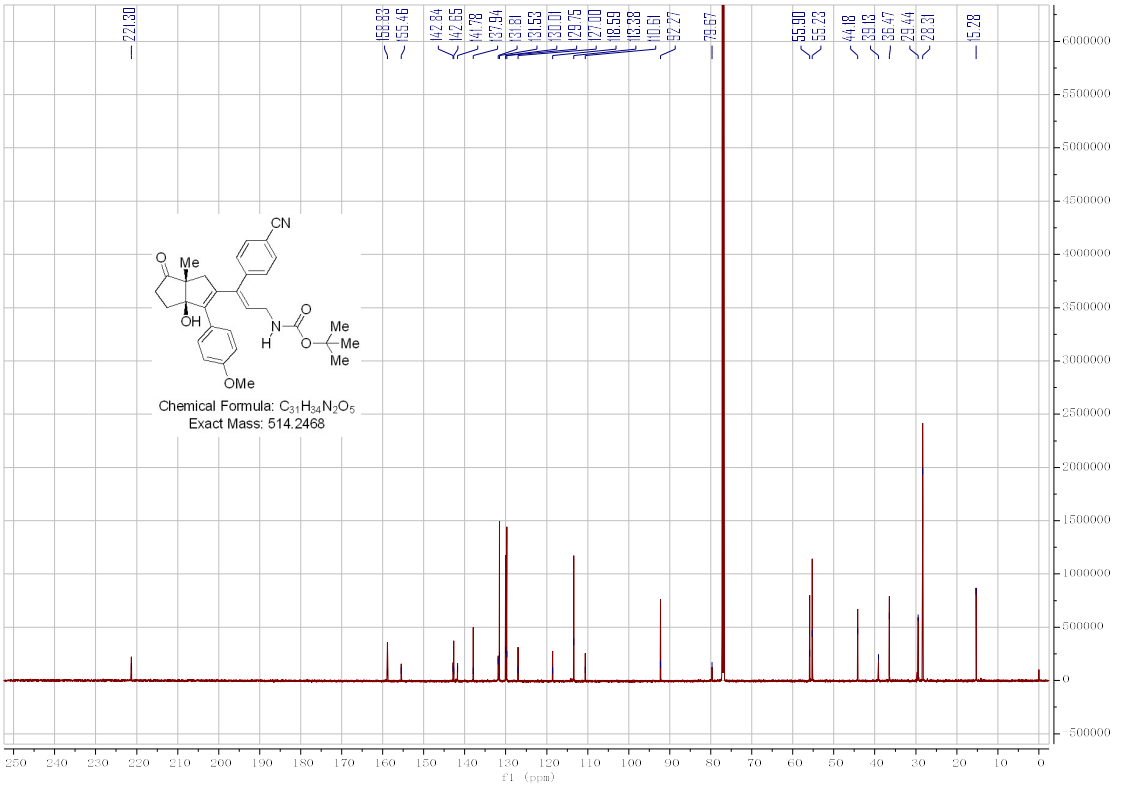
5bf


CN
Me
O
OH
N
Me
O
O^{i}Pr
OMe
Chemical Formula: $C_{31}H_{34}N_2O_5$
Exact Mass: 514.2468

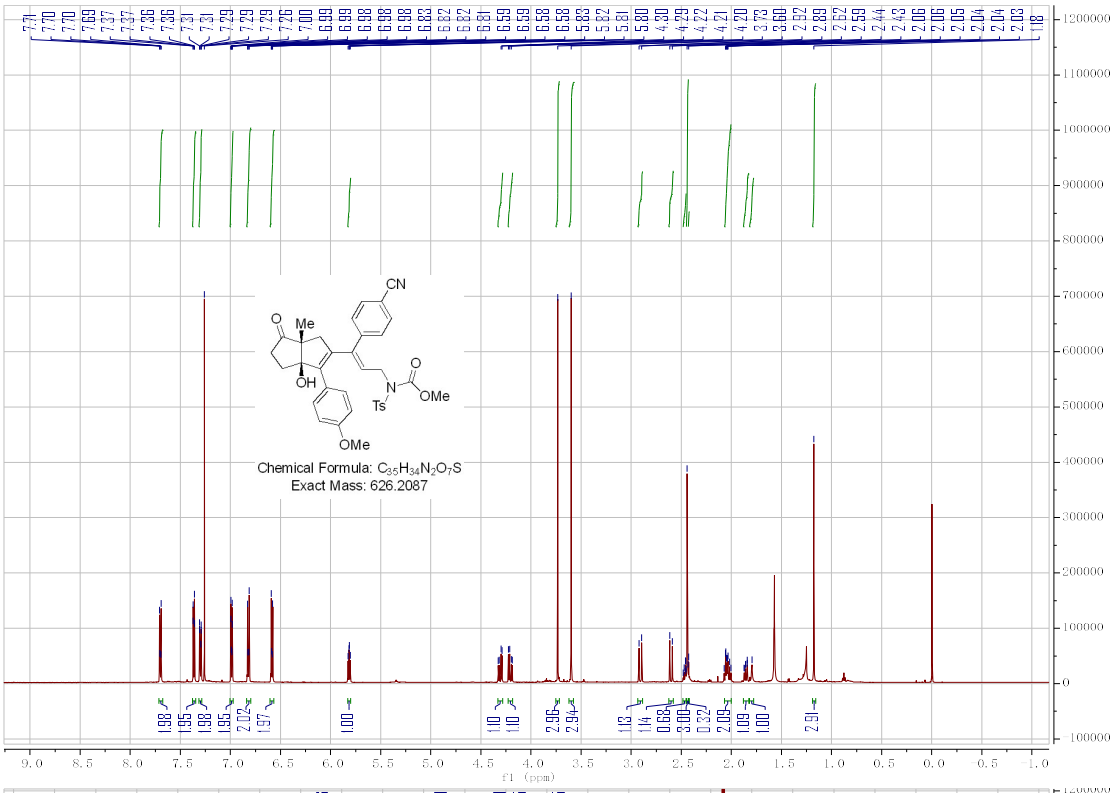

CN
Me
O
OH
N
Me
O
O^{i}Pr
OMe
Chemical Formula: $C_{31}H_{34}N_2O_5$
Exact Mass: 514.2468

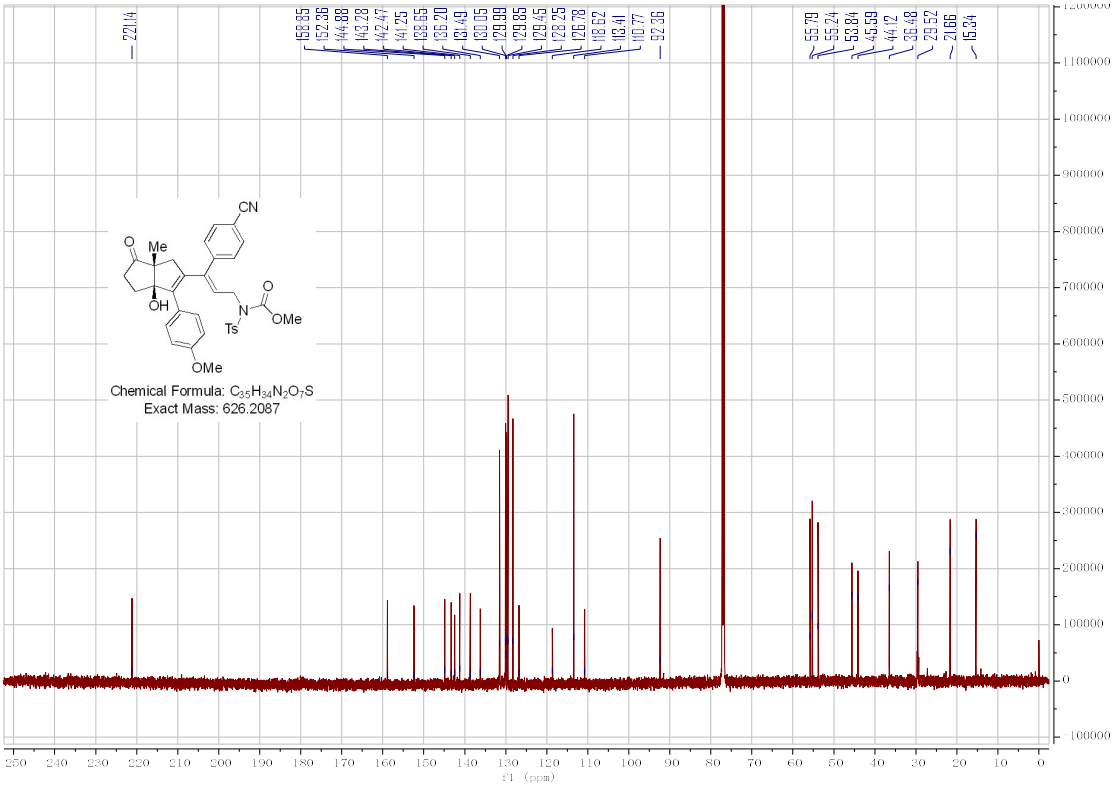
5bg


CN
Me
O
OH
N
H
O
O
Me
Me
Me
OMe
Chemical Formula: $C_{31}H_{34}N_2O_5$
Exact Mass: 514.2468

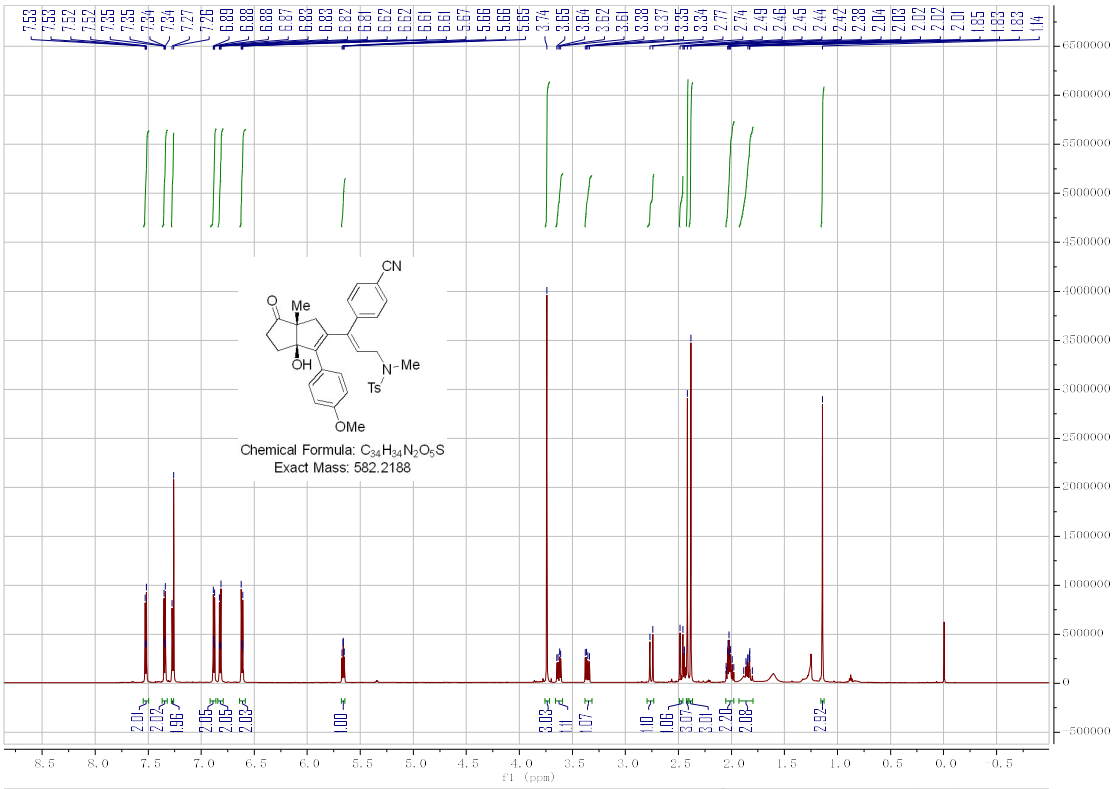

CN
Me
O
OH
N
H
O
O
Me
Me
Me
OMe
Chemical Formula: $C_{31}H_{34}N_2O_5$
Exact Mass: 514.2468

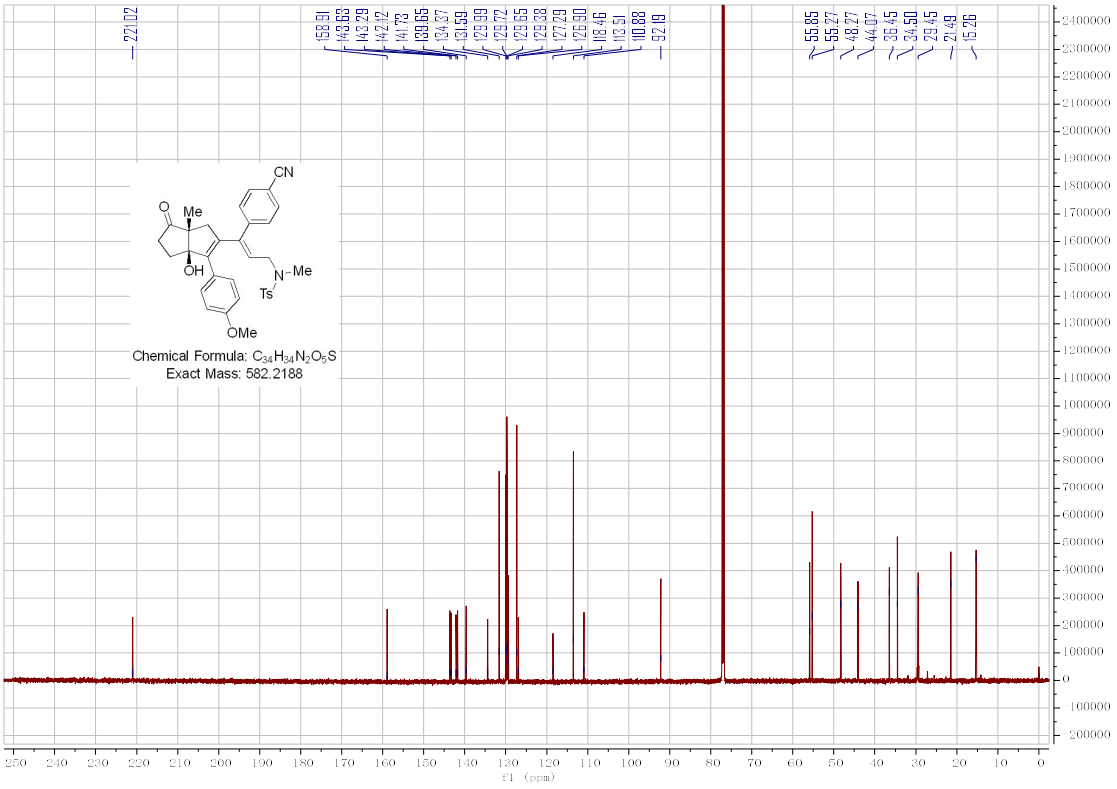
5bh


CN
Me
O
OH
N
Ts
O
OMe
OMe
Chemical Formula: C35H34N2O7S
Exact Mass: 626.2087

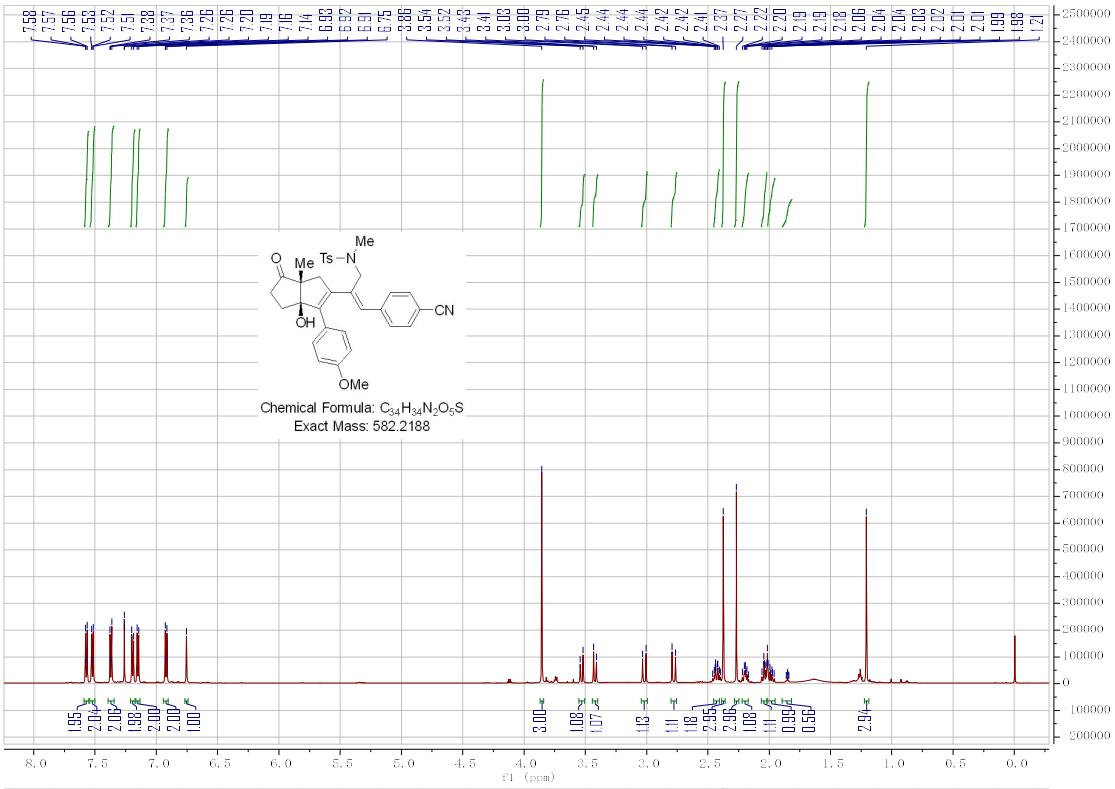

CN
Me
O
OH
N
Ts
O
OMe
OMe
Chemical Formula: C35H34N2O7S
Exact Mass: 626.2087

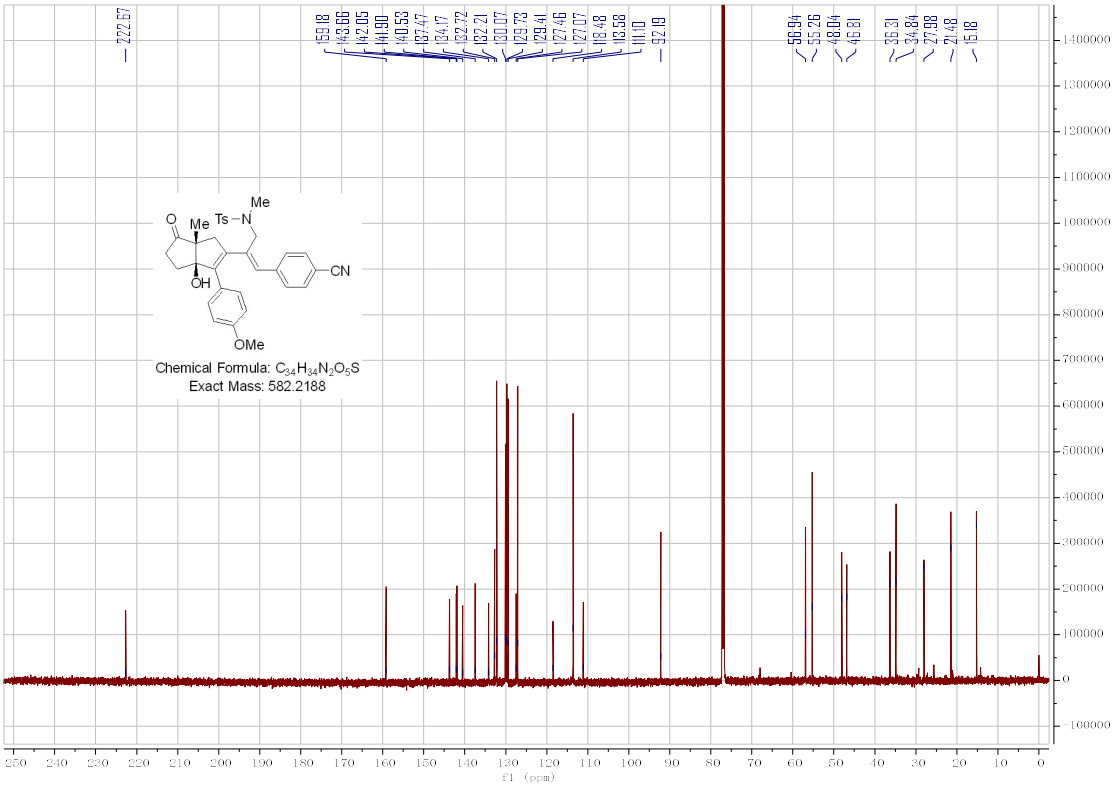
5bi


CN
Me
O
OH
N-Me
Ts
OMe
Chemical Formula: C34H34N2O5S
Exact Mass: 582.2188

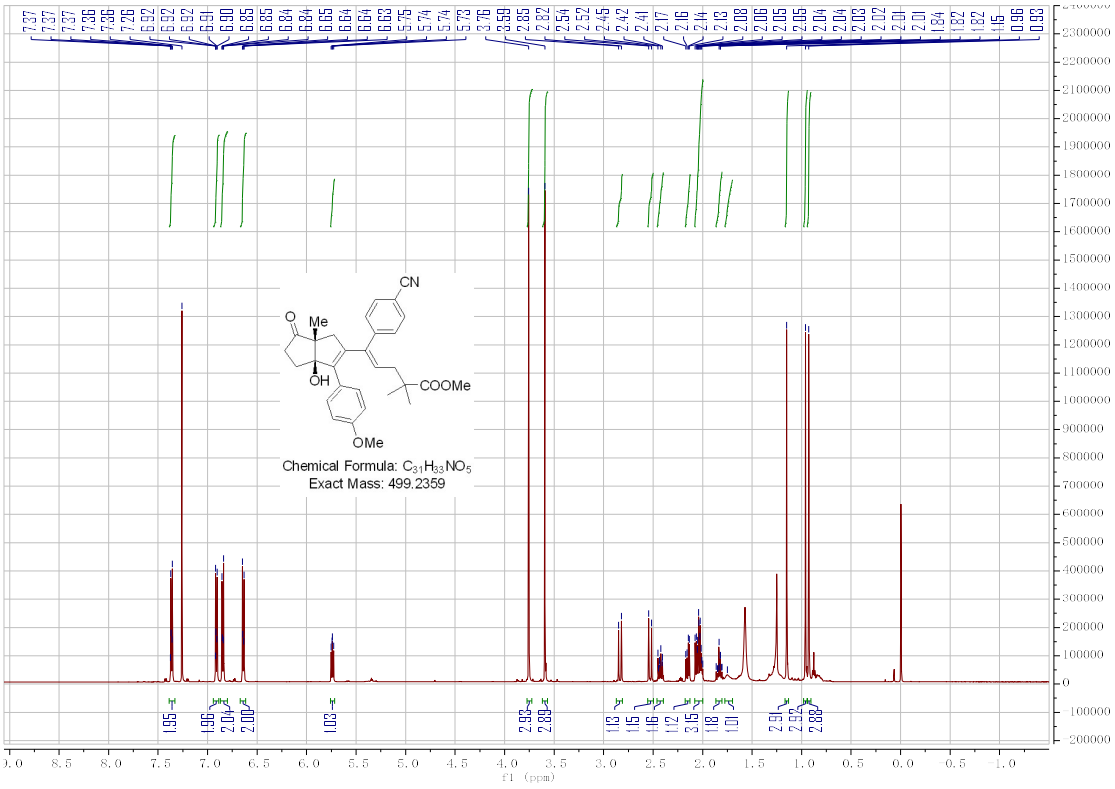

CN
Me
O
OH
N-Me
Ts
OMe
Chemical Formula: C34H34N2O5S
Exact Mass: 582.2188

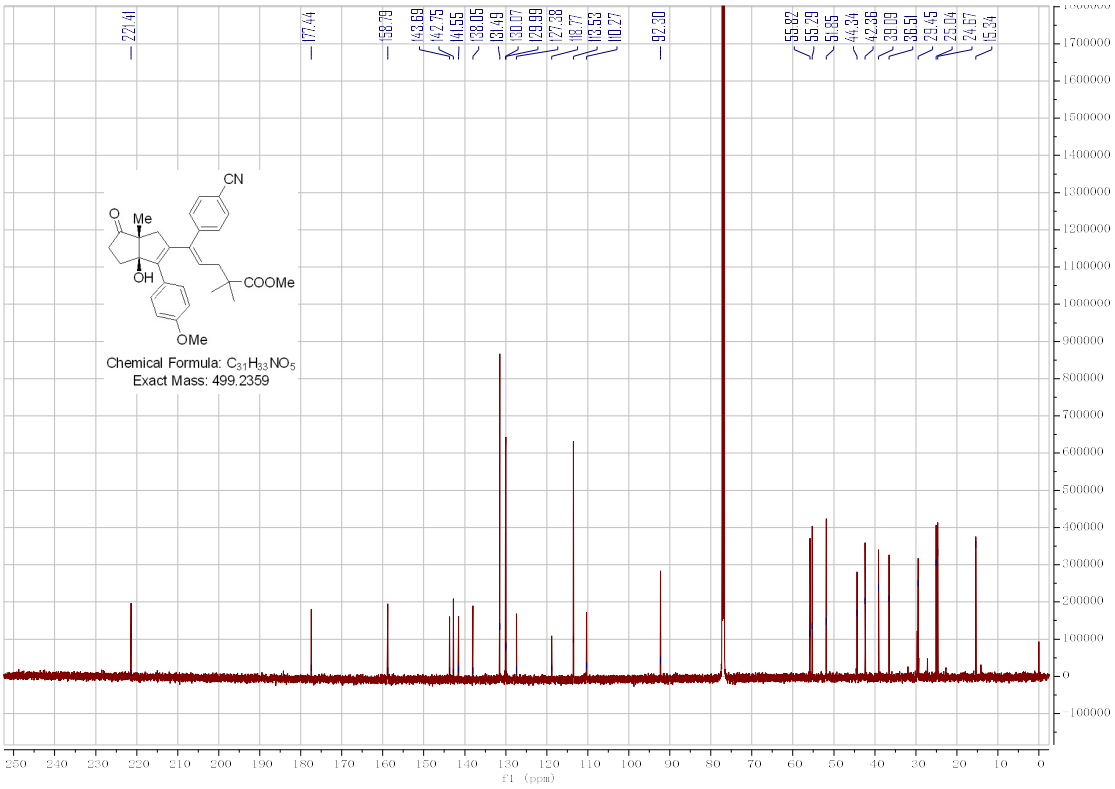
5bi’


Me
Ts–N
O
Me
OH
CN
OMe
Chemical Formula: C34H34N2O5S
Exact Mass: 582.2188

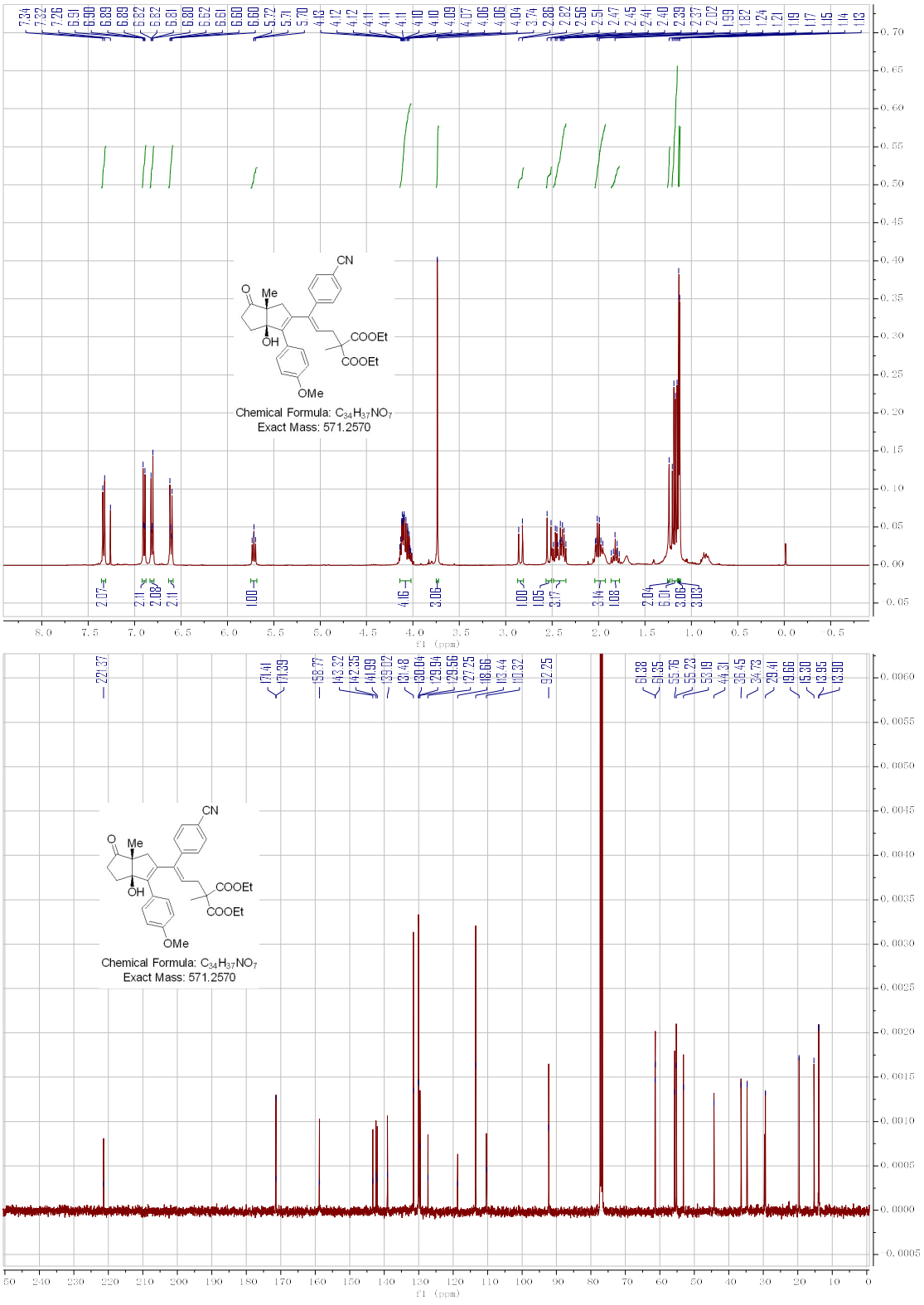

Me
Ts–N
O
Me
OH
CN
OMe
Chemical Formula: C34H34N2O5S
Exact Mass: 582.2188

5bj

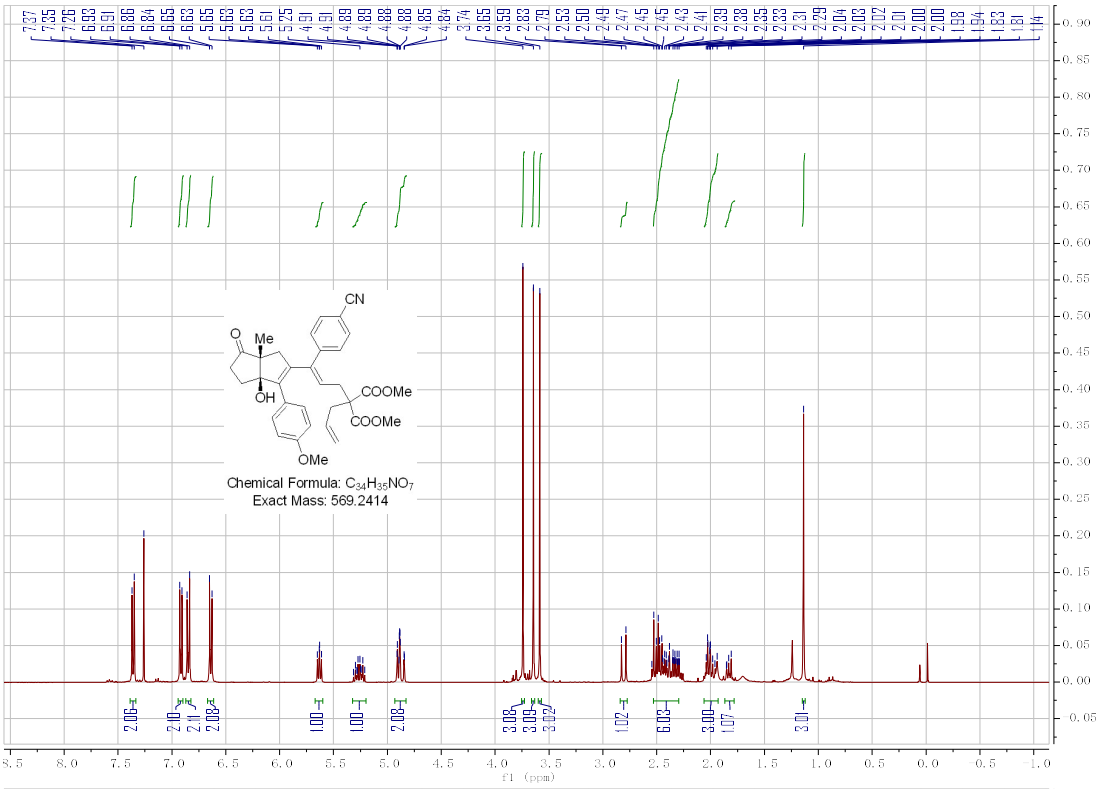

CN
Me
O
OH
COOMe
OMe
Chemical Formula: C31H33NO5
Exact Mass: 499.2359

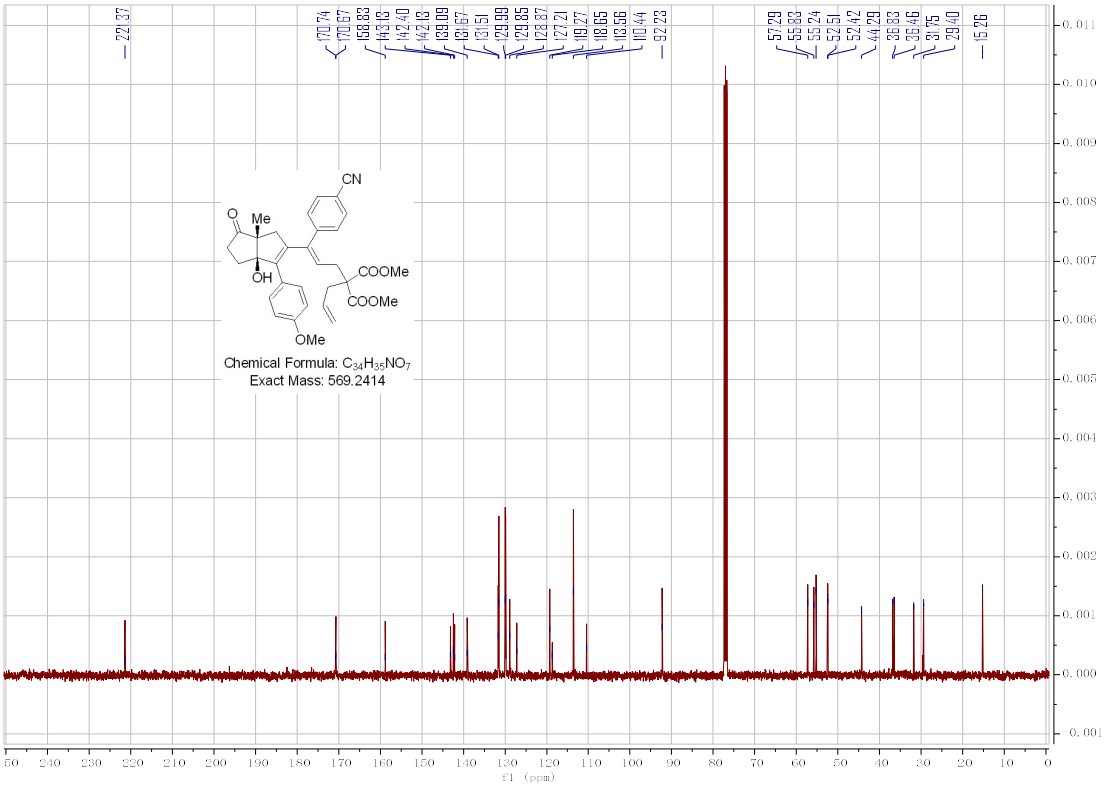

CN
Me
O
OH
COOMe
OMe
Chemical Formula: C31H33NO5
Exact Mass: 499.2359

5bk

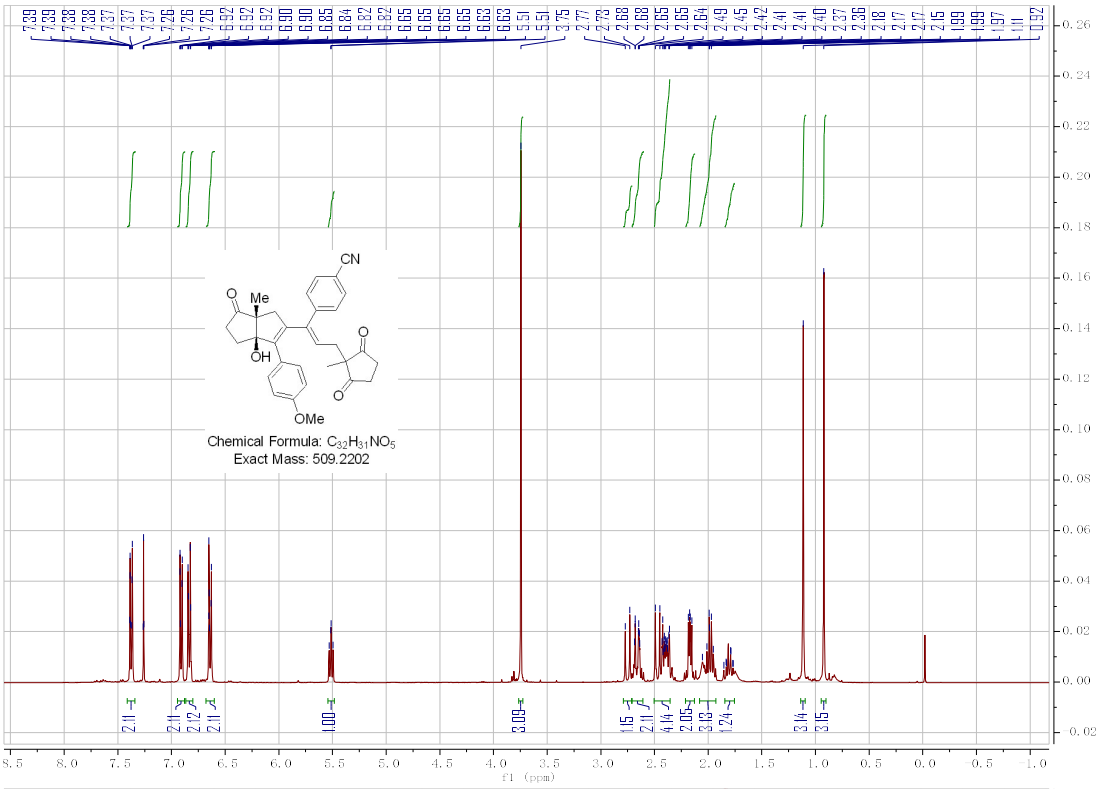

CN
Me
O
OH
COOEt
COOEt
OMe
Chemical Formula: C34H37NO7
Exact Mass: 571.2570
f1 (ppm)

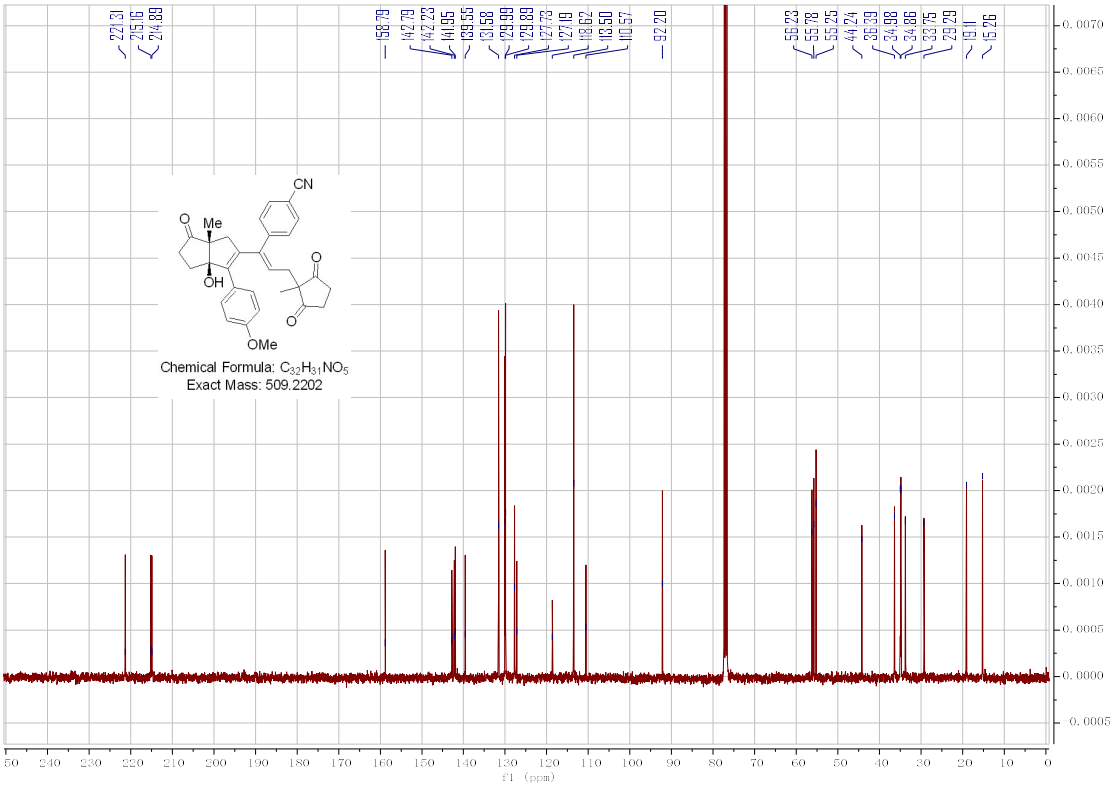
5bl


CN
Me
O
OH
COOMe
COOMe
OMe
Chemical Formula: C34H35NO7
Exact Mass: 569.2414
f1 (ppm)

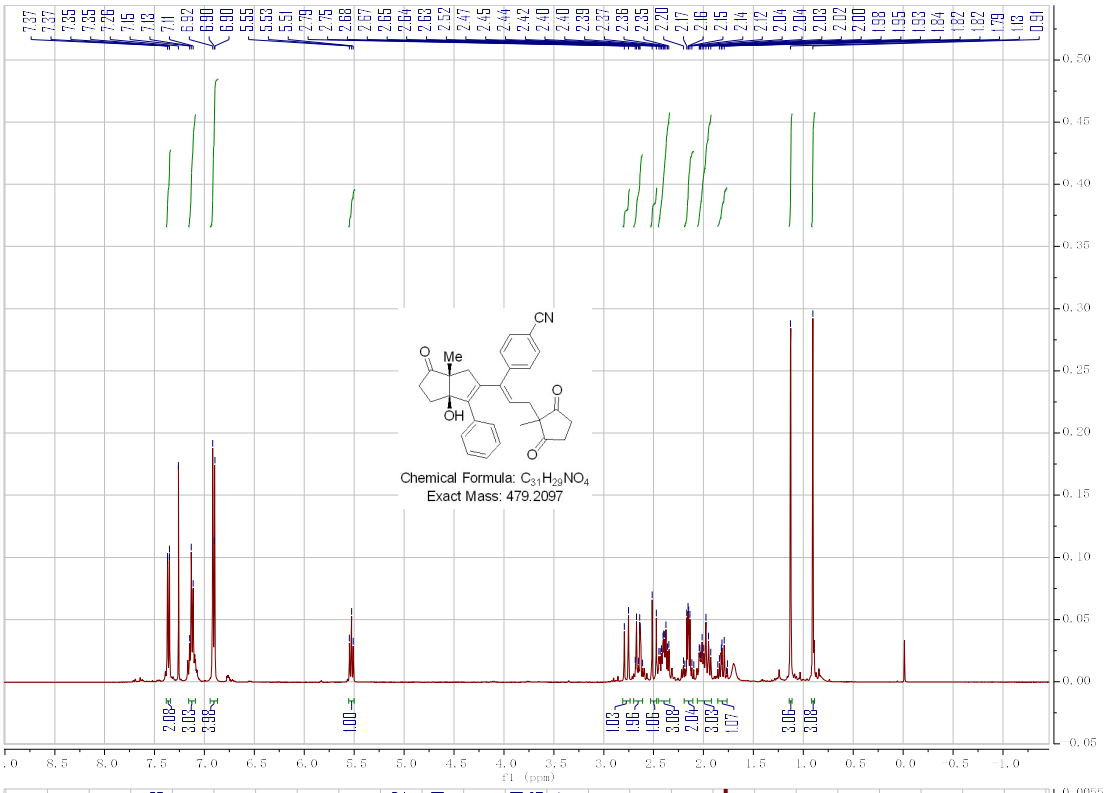

CN
Me
O
OH
COOMe
COOMe
OMe
Chemical Formula: C34H35NO7
Exact Mass: 569.2414
f1 (ppm)

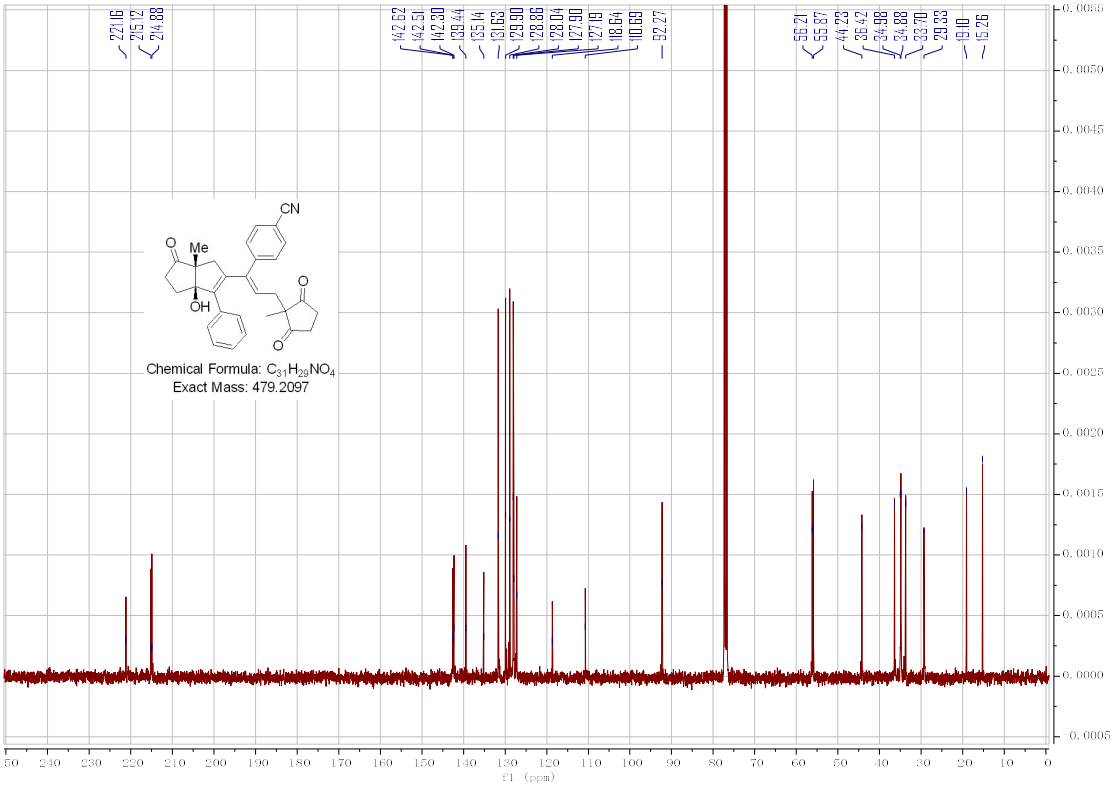
5bm


CN
Me
O
OH
O
O
OMe
Chemical Formula: C32H31NO5
Exact Mass: 509.2202

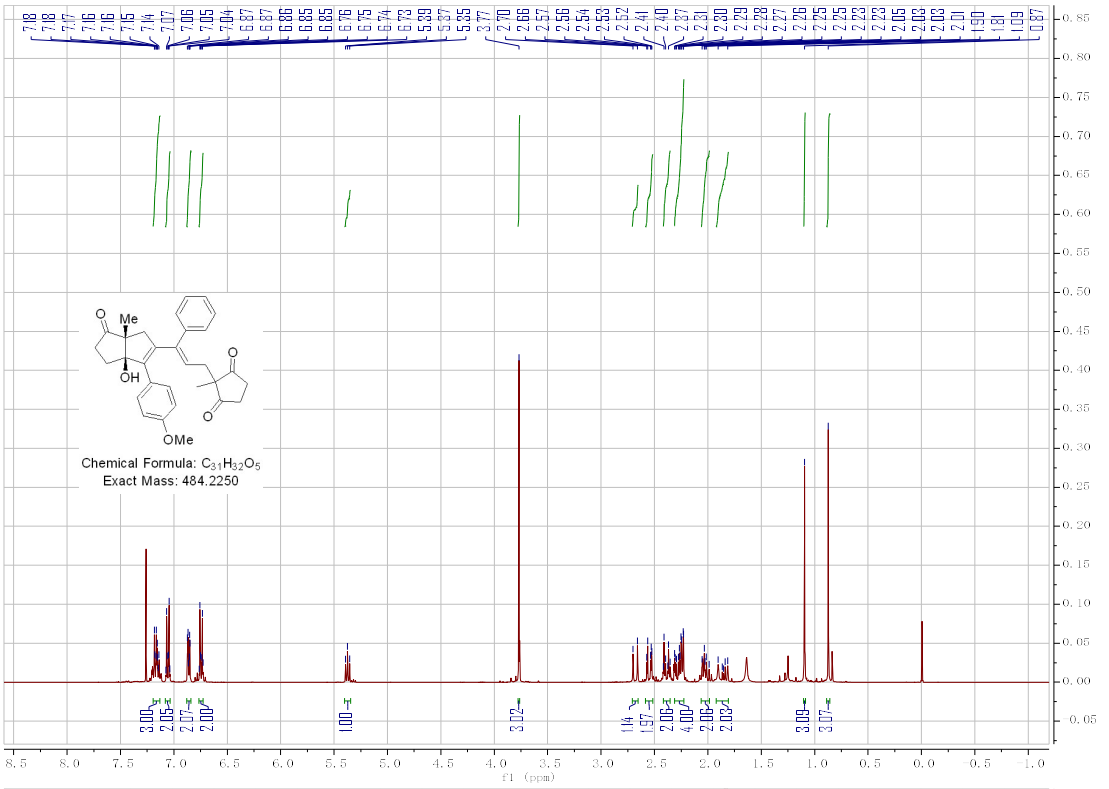

CN
Me
O
OH
O
O
OMe
Chemical Formula: C32H31NO5
Exact Mass: 509.2202

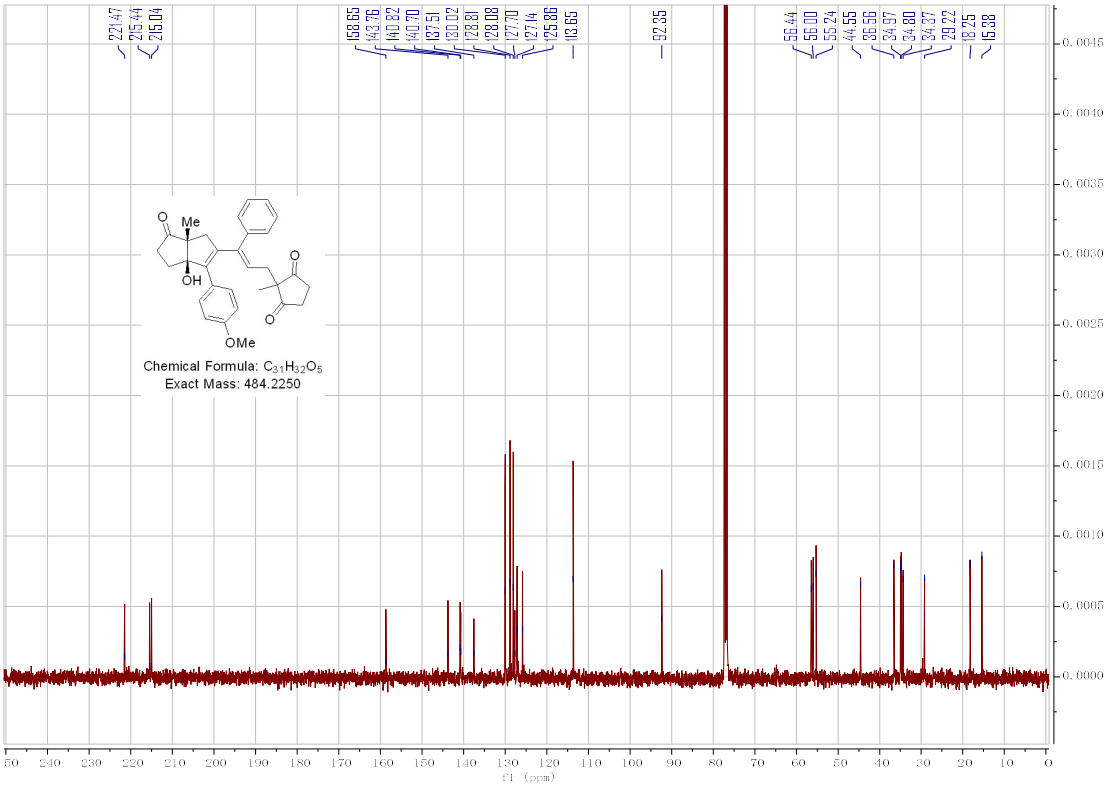
5an


CN
Me
O
OH
O
O
Chemical Formula: C31H29NO4
Exact Mass: 479.2097

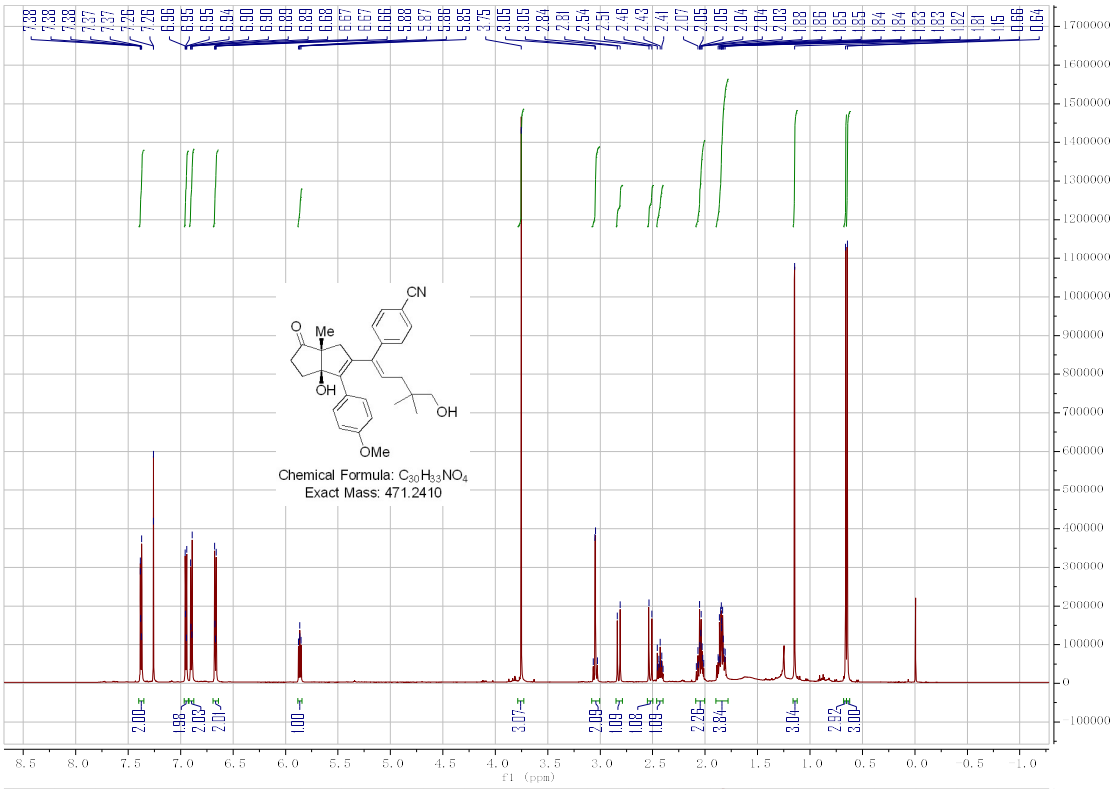

CN
Me
O
OH
O
O
Chemical Formula: C31H29NO4
Exact Mass: 479.2097

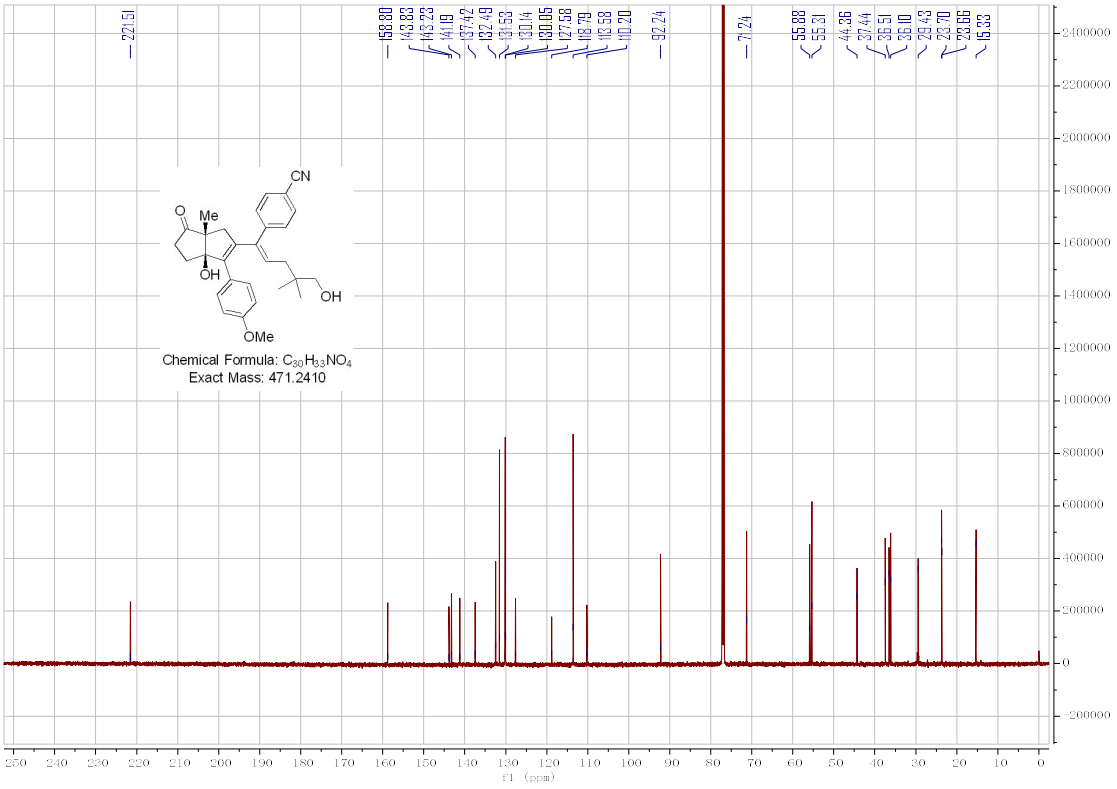
5bo


Me
OH
O
O
O
OMe
Chemical Formula: C31H32O5
Exact Mass: 484.2250

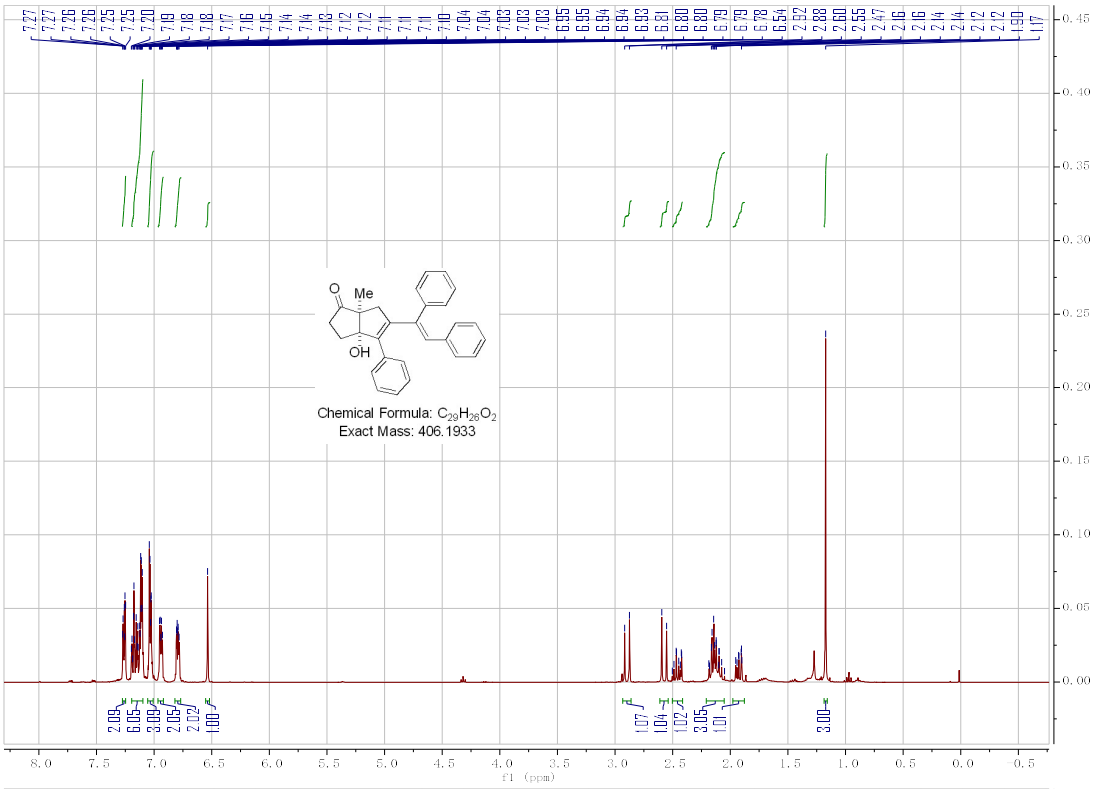

Me
OH
O
O
O
OMe
Chemical Formula: C31H32O5
Exact Mass: 484.2250

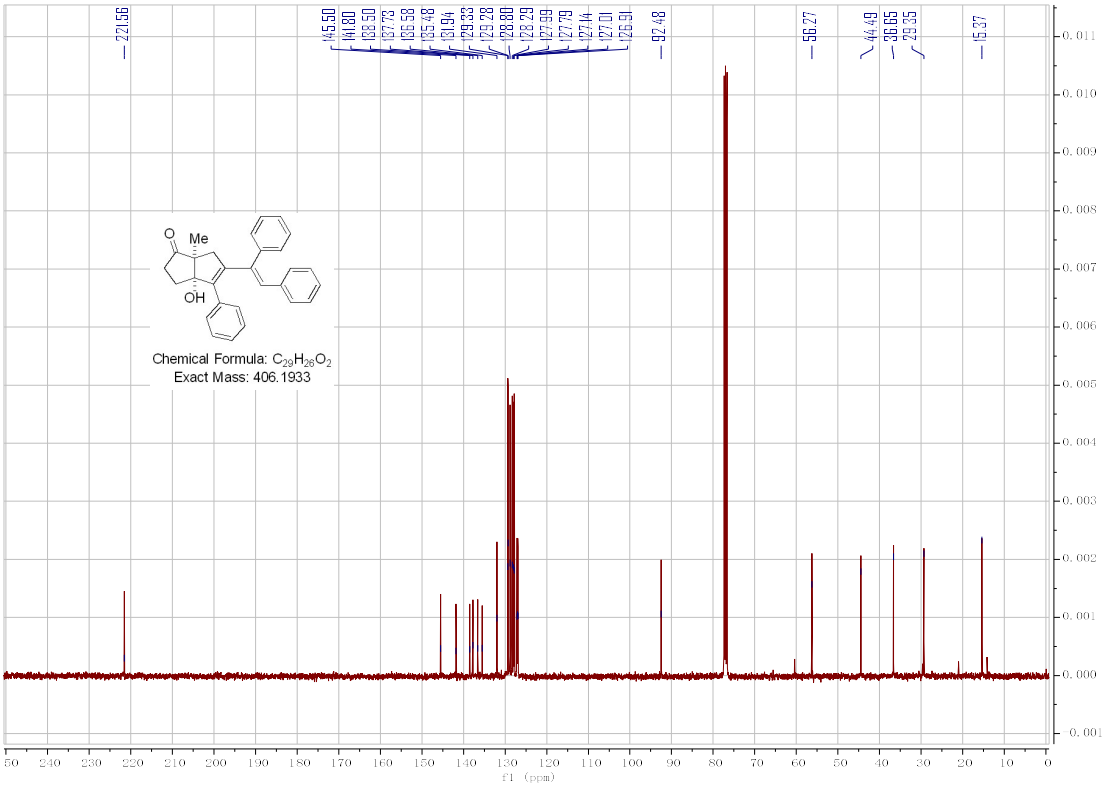
5bp


CN
O
Me
OH
OH
OMe
Chemical Formula: C30H33NO4
Exact Mass: 471.2410

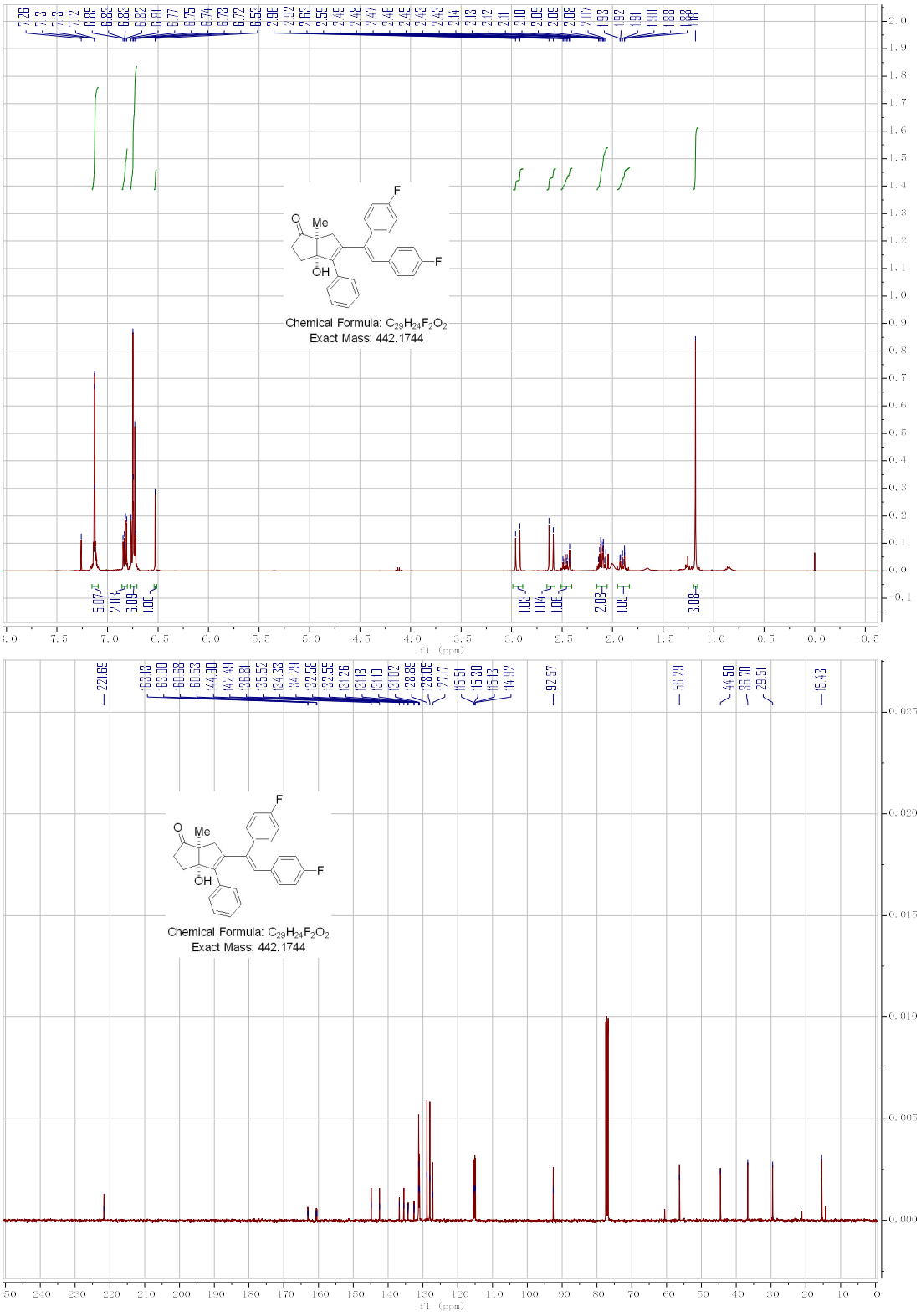

CN
O
Me
OH
OH
OMe
Chemical Formula: C30H33NO4
Exact Mass: 471.2410

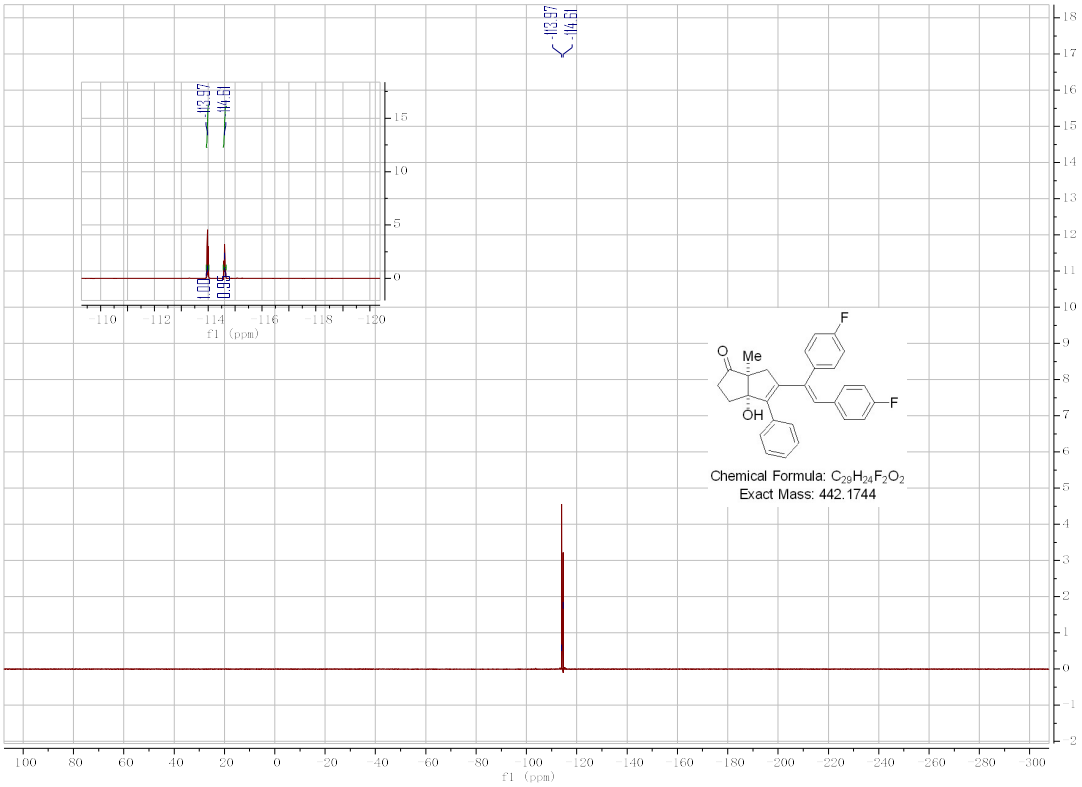
5aq


Me
OH
Chemical Formula: C29H26O2
Exact Mass: 406.1933

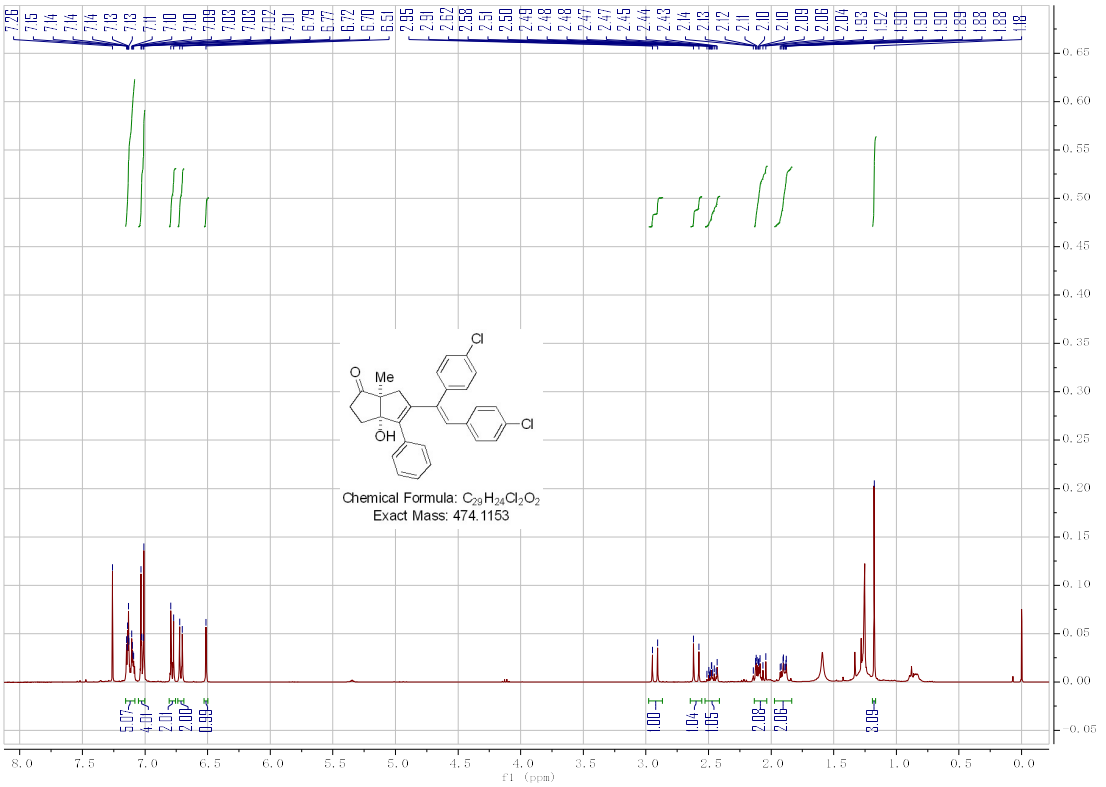

Me
OH
Chemical Formula: C29H26O2
Exact Mass: 406.1933

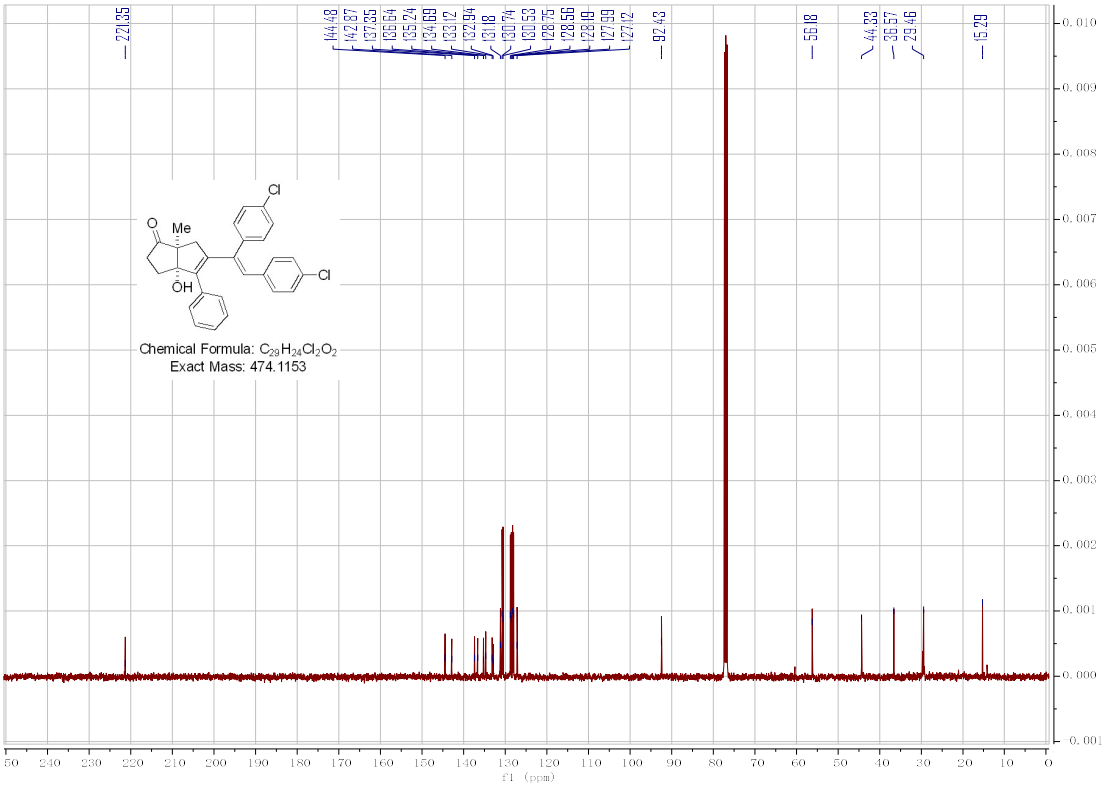
5ar



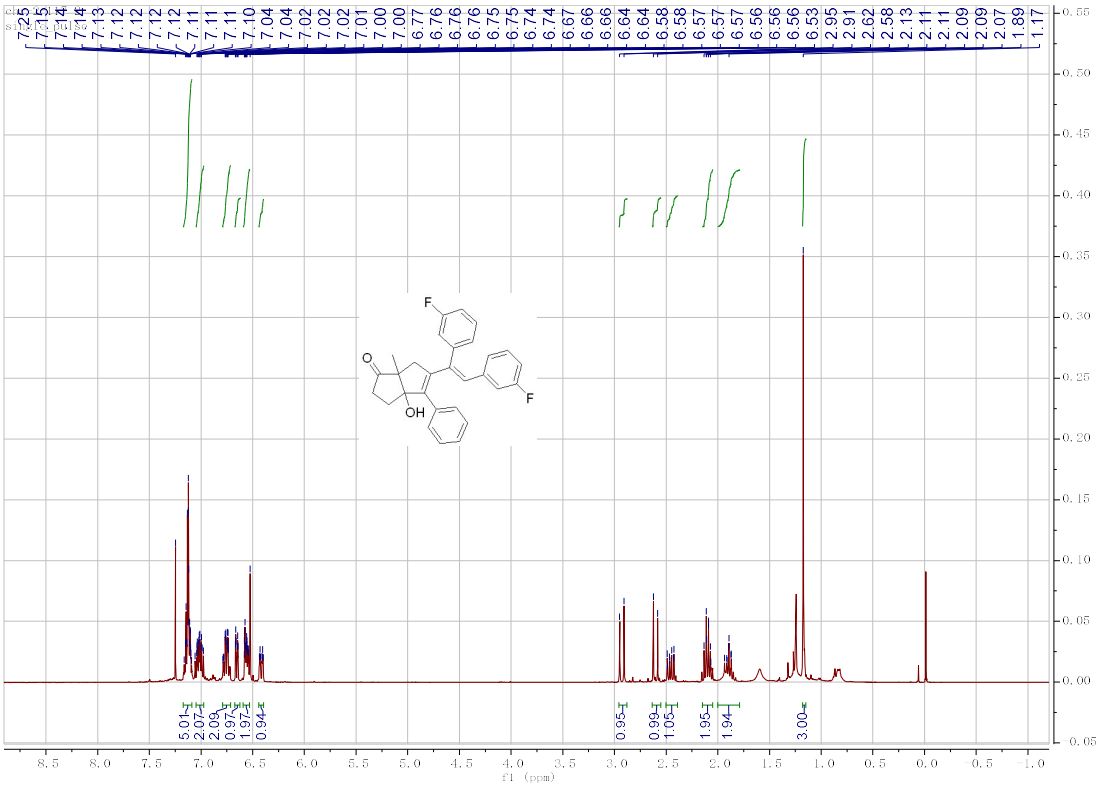

-113.957
-114.161
-113.957
-114.161
1.00
0.89
-110
-112
-114
-116
-118
-120
f1 (ppm)
O
Me
OH
F
F
Chemical Formula: C29H24F2O2
Exact Mass: 442.1744
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
f1 (ppm)

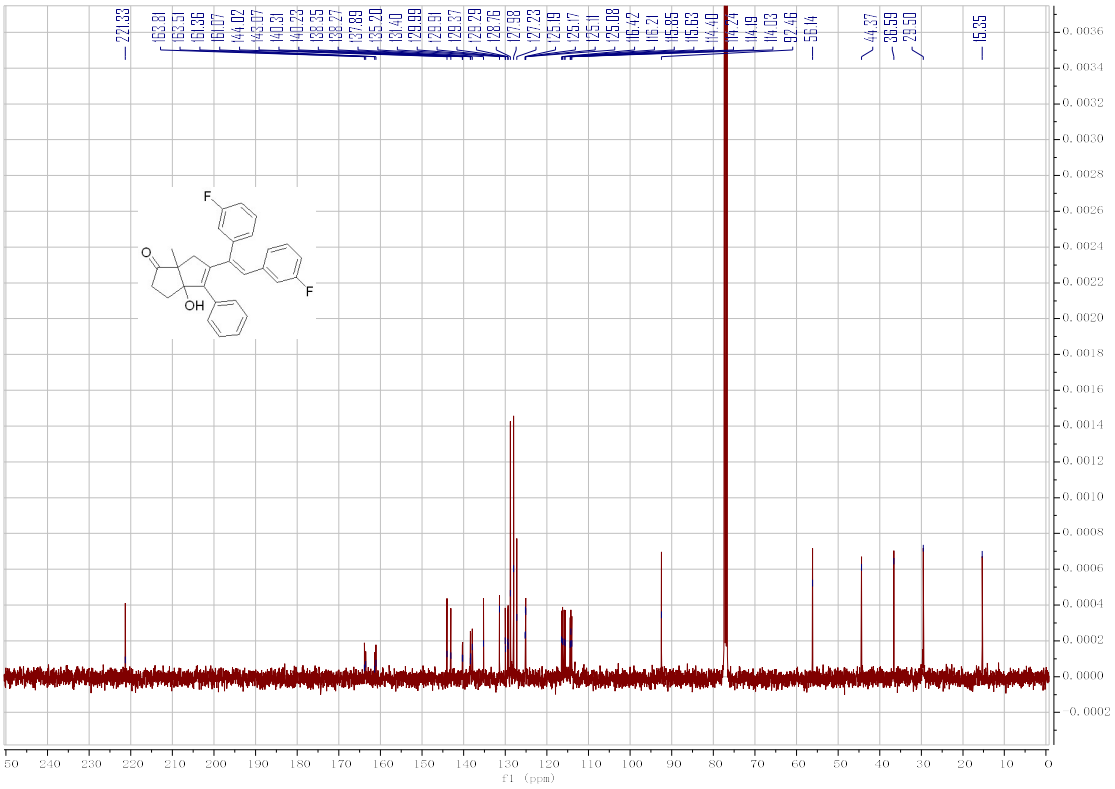
5as

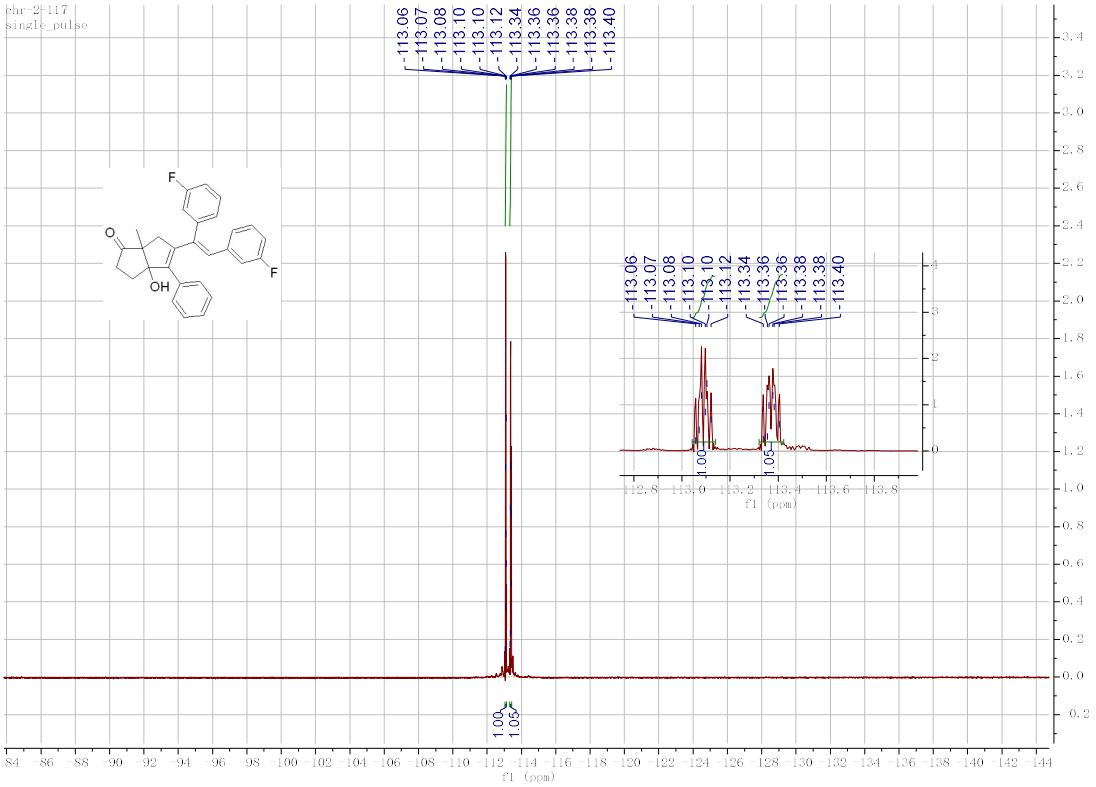

Cl
O
Me
OH
Cl
Chemical Formula: C29H24Cl2O2
Exact Mass: 474.1153
f1 (ppm)


Cl
O
Me
OH
Cl
Chemical Formula: C29H24Cl2O2
Exact Mass: 474.1153
f1 (ppm)

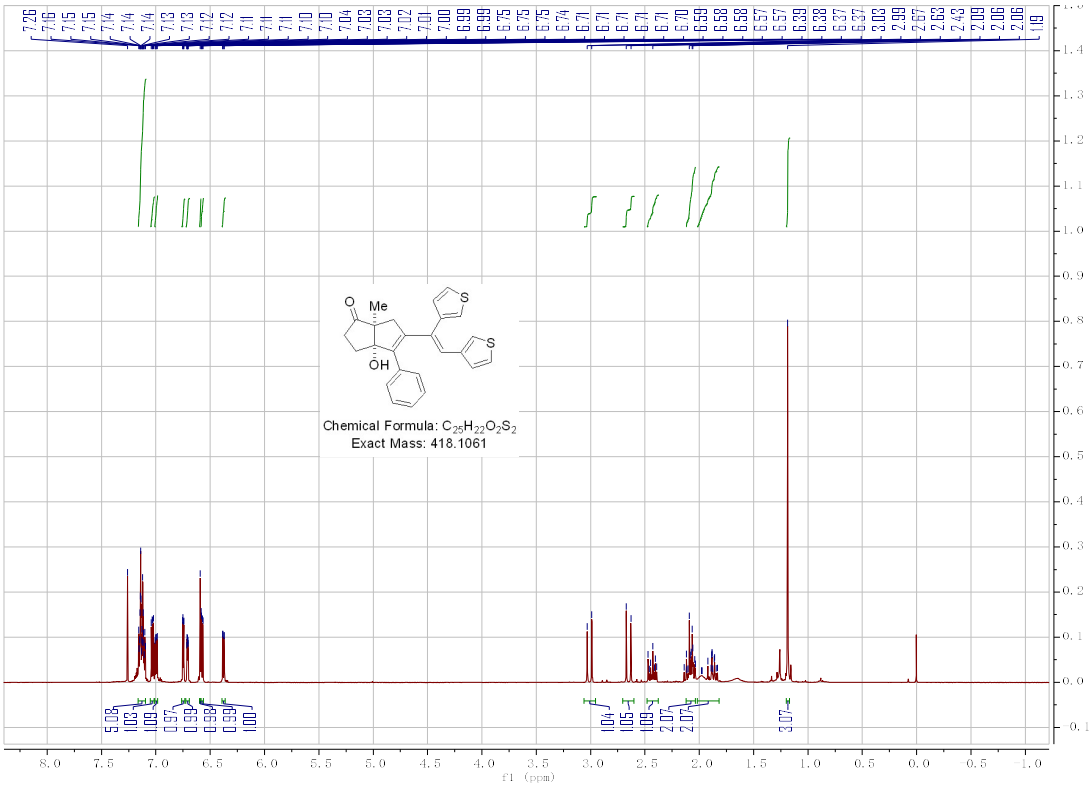
5at

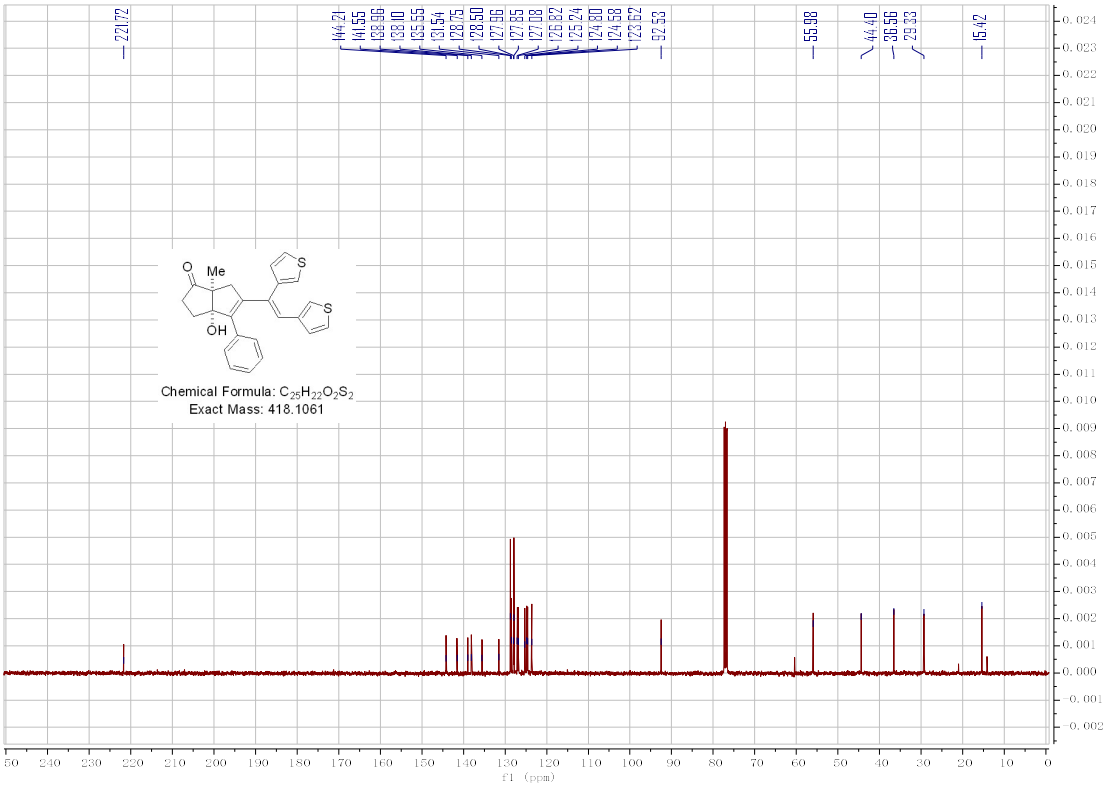

F
O
OH
F
5.01
2.07
2.09
0.97
1.97
0.94
0.95
0.99
1.05
1.95
1.94
3.00
f1 (ppm)


221.33
163.81
160.51
161.36
161.07
144.02
140.07
140.31
140.23
138.35
138.27
137.89
135.20
131.40
129.99
129.91
129.37
129.29
128.76
127.98
127.23
125.19
125.17
125.11
125.08
116.42
116.21
115.85
115.63
114.40
114.24
114.19
114.03
92.46
56.14
44.37
38.59
29.50
15.95
F
O
OH
F
f1 (ppm)

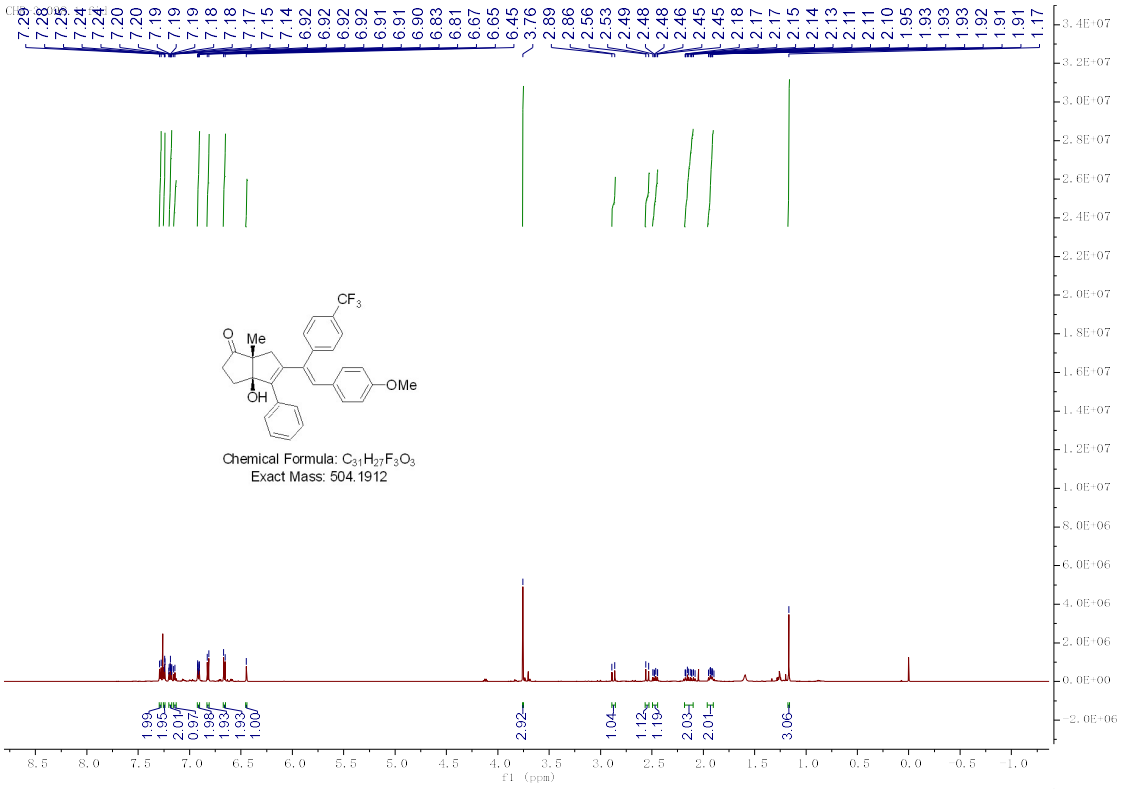

chr-2-117
single_pulse
-113.06
-113.07
-113.08
-113.10
-113.10
-113.12
-113.34
-113.36
-113.38
-113.38
-113.40
F
O
OH
F
1.00
1.05
f1 (ppm)

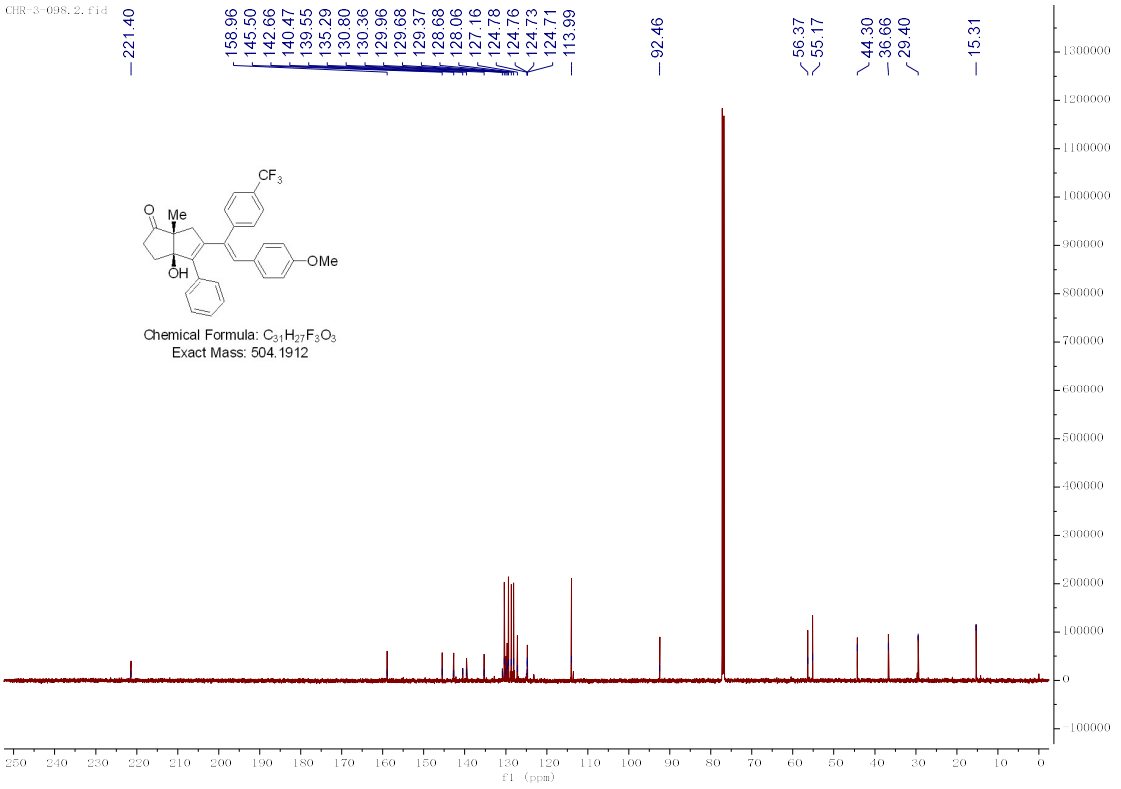
5au

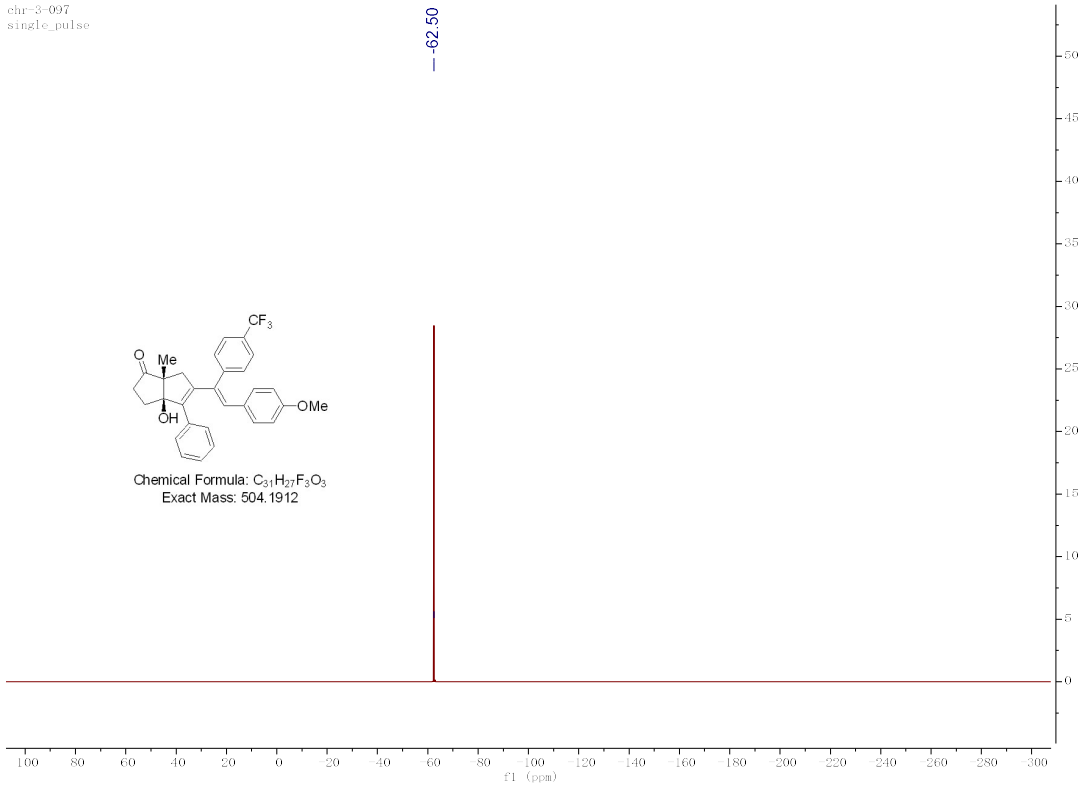

Me
O
OH
S
S
Chemical Formula: C25H22O2S2
Exact Mass: 418.1061


Me
O
OH
S
S
Chemical Formula: C25H22O2S2
Exact Mass: 418.1061

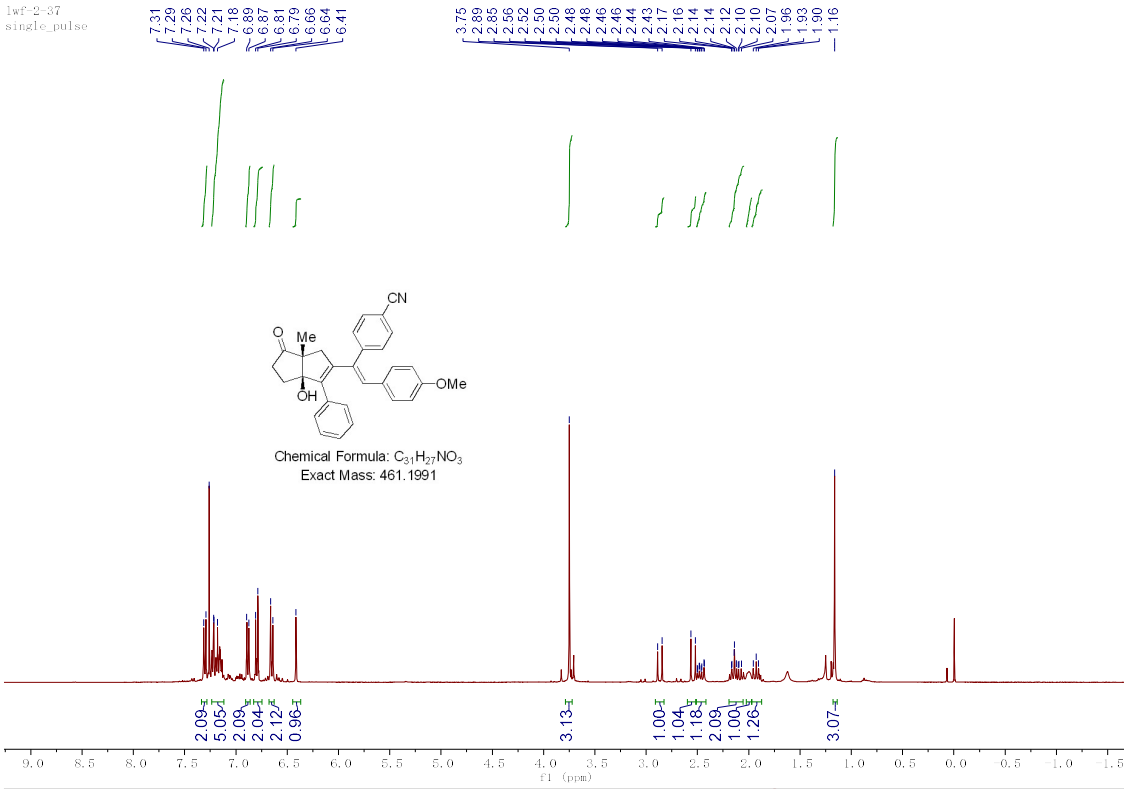
5av

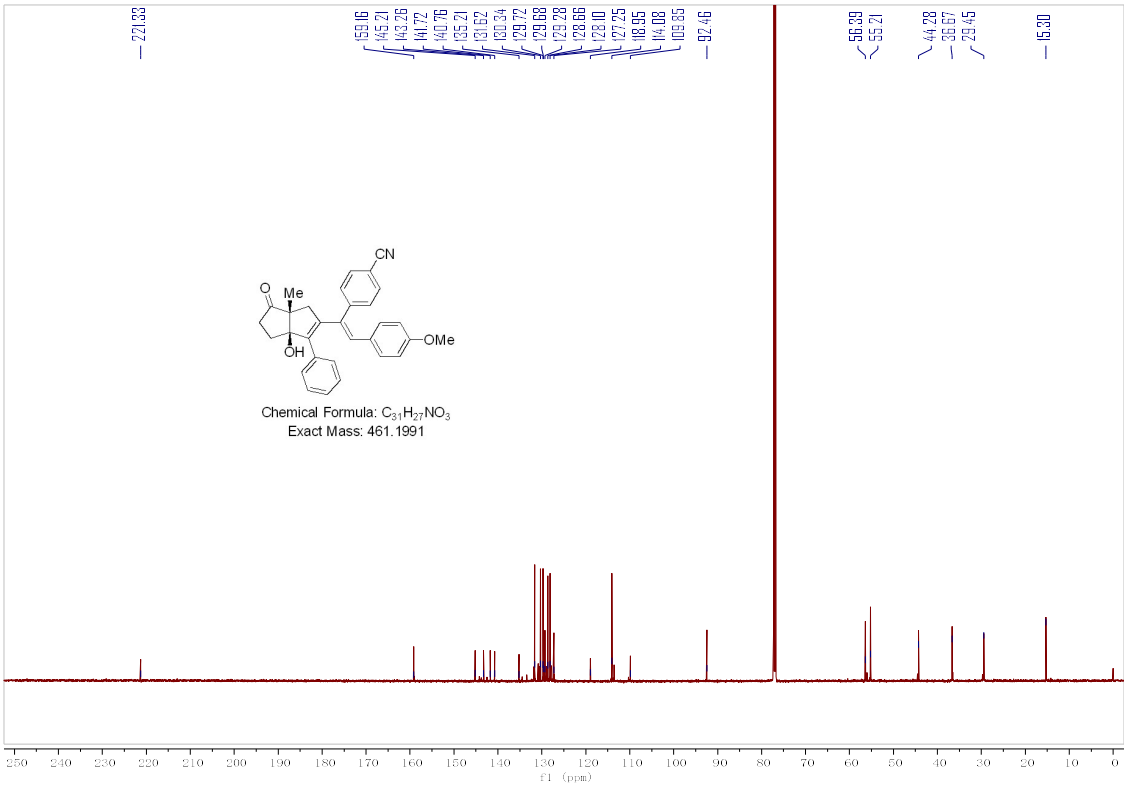

CF3
O
Me
OH
OMe
Chemical Formula: C31H27F3O3
Exact Mass: 504.1912


CF3
O
Me
OH
OMe
Chemical Formula: C31H27F3O3
Exact Mass: 504.1912

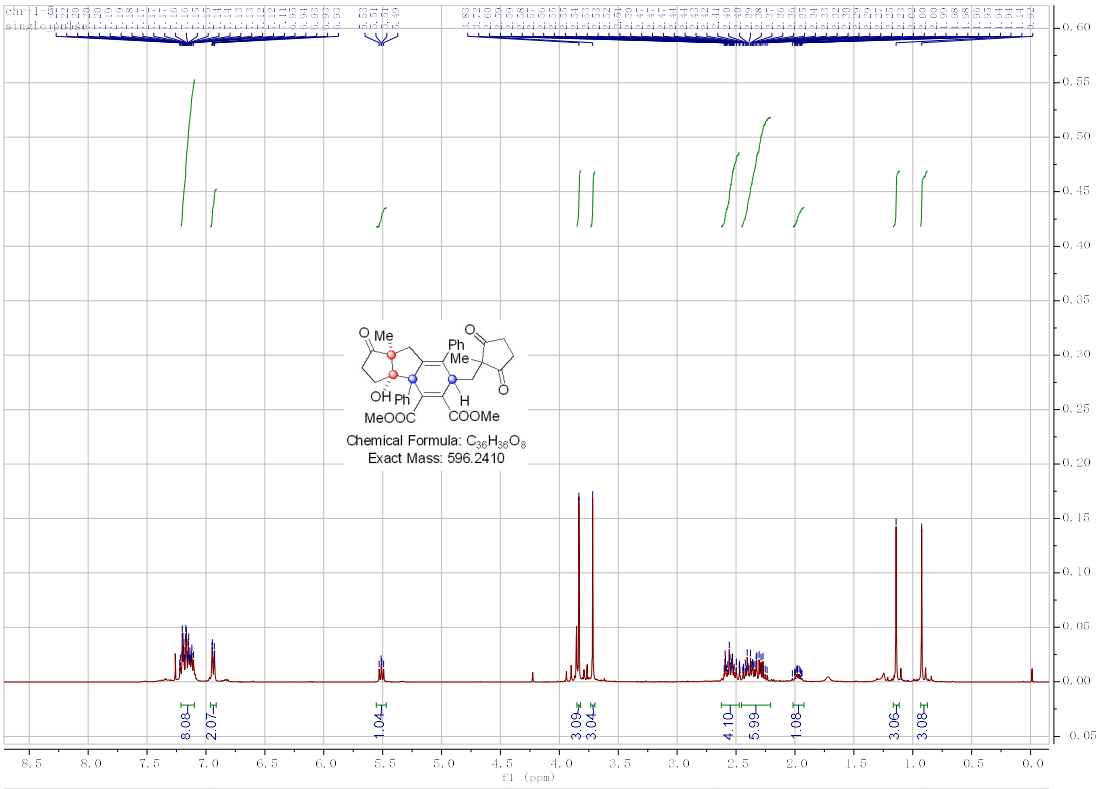

chr-3-097
single_pulse
-62.50
CF3
O
Me
OH
OMe
Chemical Formula: C31H27F3O3
Exact Mass: 504.1912
f1 (ppm)

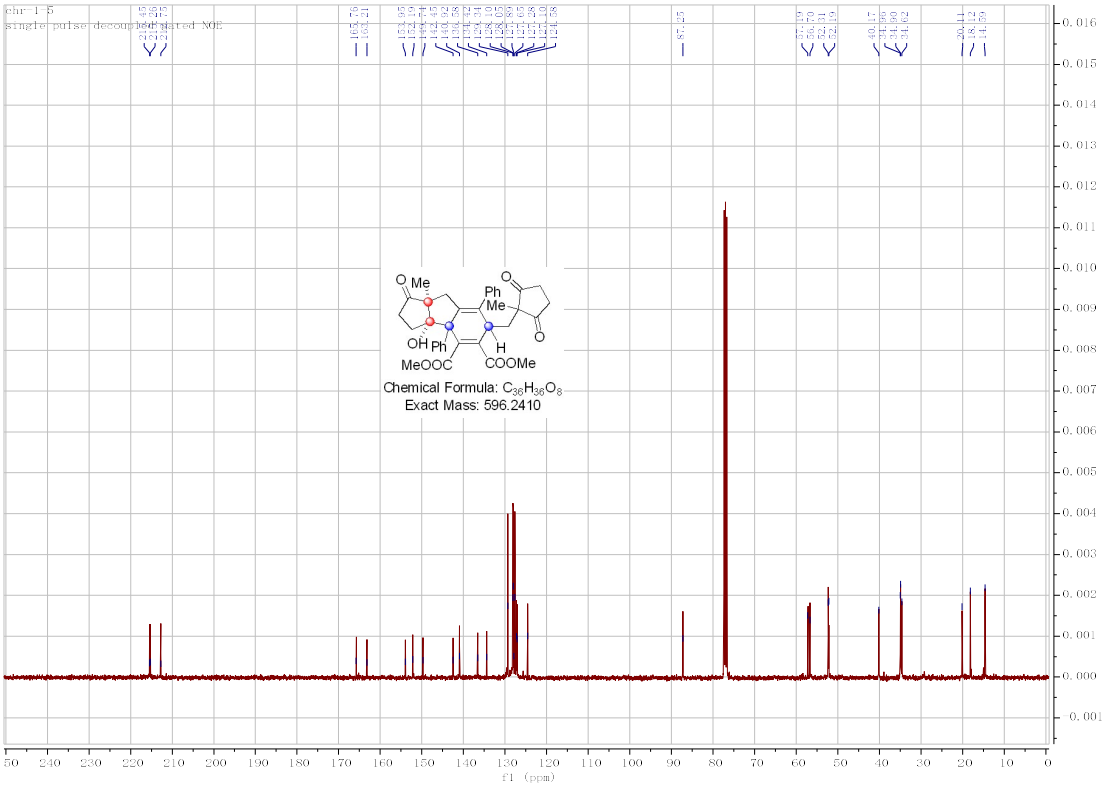
5aw


lwf-2-37
single_pulse
7.31
7.29
7.26
7.22
7.21
7.18
6.89
6.87
6.81
6.79
6.66
6.64
6.41
3.75
2.89
2.85
2.56
2.52
2.50
2.48
2.46
2.44
2.43
2.17
2.16
2.14
2.12
2.10
2.07
1.96
1.93
1.90
1.16
CN
O
Me
OH
OMe
Chemical Formula: C31H27NO3
Exact Mass: 461.1991
2.09
5.05
2.09
2.04
2.12
0.96
3.13
1.00
1.04
1.18
2.09
1.00
1.26
3.07
f1 (ppm)

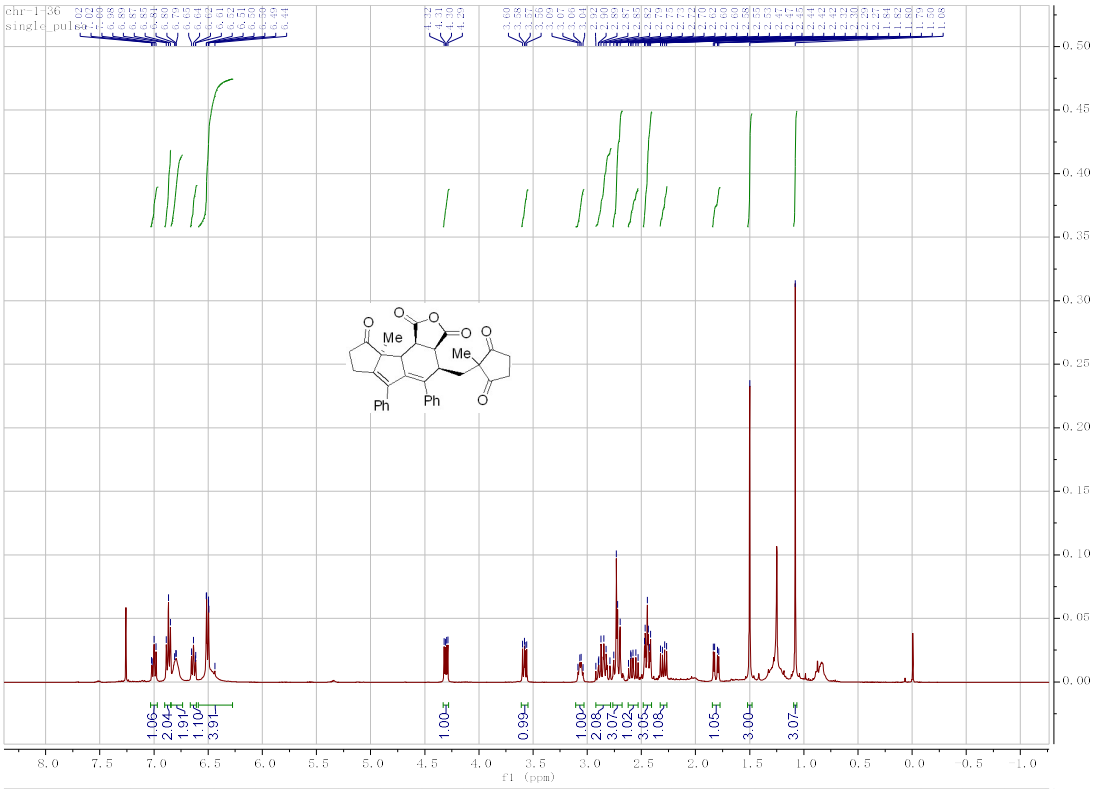

221.33
159.16
145.21
143.26
141.72
140.76
135.21
131.52
130.34
129.72
129.68
129.28
128.66
128.10
127.25
118.95
114.08
109.85
92.46
58.39
55.21
44.28
36.67
29.45
15.30
CN
O
Me
OH
OMe
Chemical Formula: C31H27NO3
Exact Mass: 461.1991
f1 (ppm)

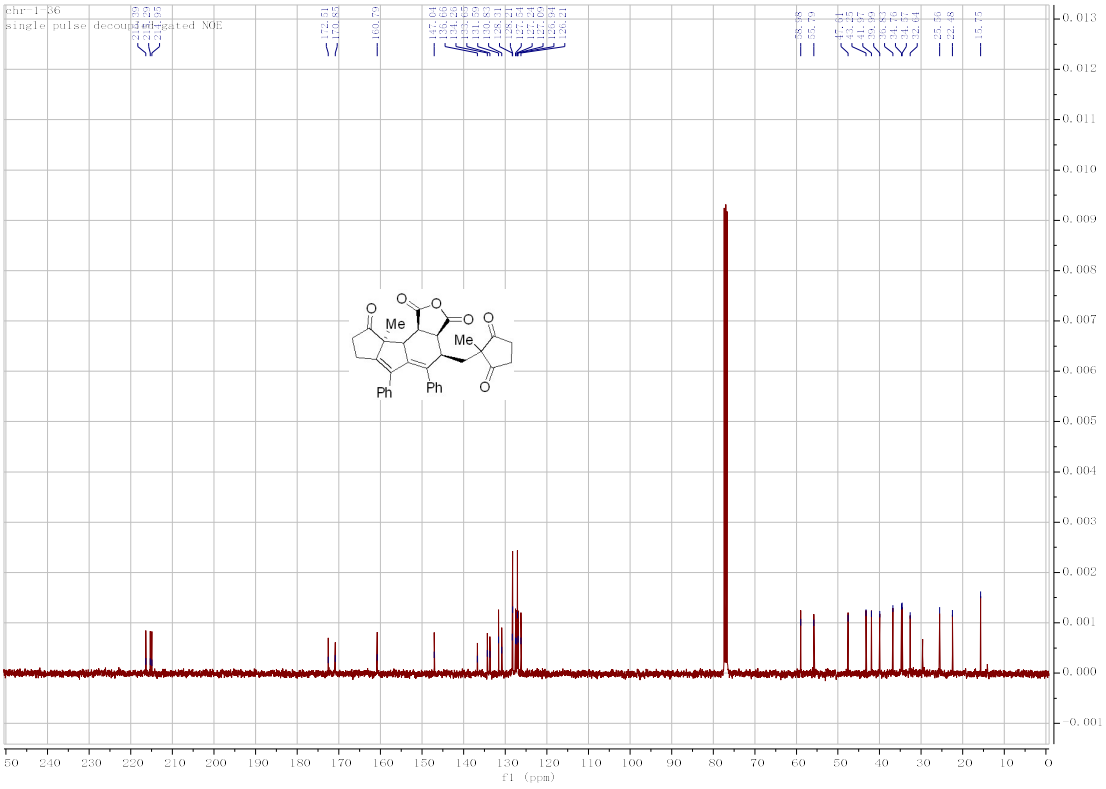
6


Me
Ph
Me
OH Ph
MeOOC
H
COOMe
Chemical Formula: C36H36O8
Exact Mass: 596.2410
8.08
2.07
1.04
3.09
3.04
4.10
5.99
1.08
3.06
3.08
f1 (ppm)

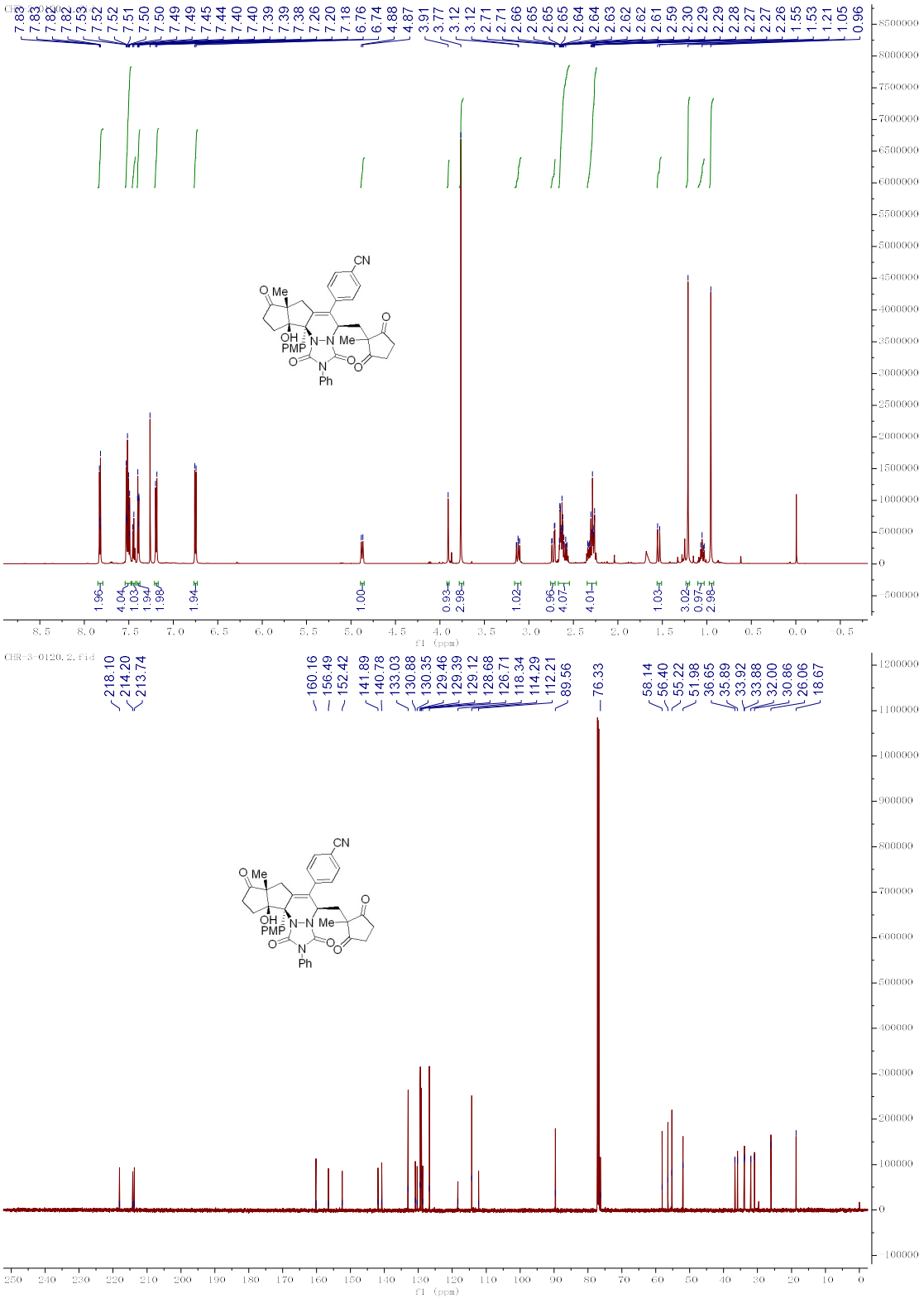

Me
Ph
Me
OH Ph
MeOOC
H
COOMe
Chemical Formula: C36H36O8
Exact Mass: 596.2410
f1 (ppm)

8





9


7.83
7.82
7.53
7.52
7.51
7.50
7.49
7.45
7.44
7.40
7.39
7.38
7.26
7.20
7.18
6.76
6.74
4.88
4.87
3.91
3.77
3.12
2.71
2.66
2.65
2.64
2.63
2.62
2.61
2.59
2.30
2.29
2.28
2.27
2.26
1.55
1.53
1.21
1.05
0.96
CN
Me
OH
PMP
N–N
Me
Ph
1.96
4.04
1.03
1.94
1.98
1.94
1.00
0.93
2.98
1.02
0.96
4.07
4.01
1.03
3.02
0.97
2.98
f1 (ppm)
CHR-3-0120.2.fid
218.10
214.20
213.74
160.16
156.49
152.42
141.89
140.78
133.03
130.88
130.35
129.46
129.39
129.12
128.68
126.71
118.34
114.29
112.21
89.56
76.33
58.14
56.40
55.22
51.98
36.65
35.89
33.92
33.88
32.00
30.86
26.06
18.67
f1 (ppm)

11. References

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