Supporting Information

Pd(II)-Catalyzed Asymmetric 1,6-Conjugate Addition of Arylboronic Acids to Meldrum's Acid-Derived Dienes

Song Chen, Liang Wu, Qihang Shao, Guoqiang Yang,* and Wanbin Zhang*

[a] Shanghai Key Laboratory for Molecular Engineering of Chiral Drugs, School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P. R. China. Fax: +86-21-5474-3265; Tel:+86-21-5474-3265; E-mail: gqyang@sjtu.edu.cn; wanbin@sjtu.edu.cn.

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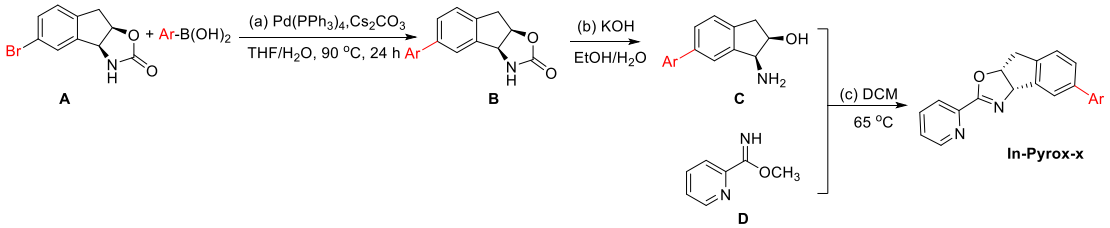
1. General Details

^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) spectra were recorded on a Varian MERCURY plus-400 spectrometer with TMS as an internal standard. HRMS was performed at the Analysis Center of Shanghai Jiao Tong University. Optical rotations were measured with a SPSI SGW-1 polarimeter. Enantioselectivity was performed on a Shimadzu LC-2010 HPLC system and using Daicel Chiralcel columns with *n*-hexane/*i*-propyl alcohol as an eluent. Chiralpak AD-H, Chiralpak OJ-H were purchased from Daicel Chiral Technologies (China) Co., Ltd., and Enantiopak AD was purchased from Guangzhou Research & Creativity Biotechnology Co. Ltd., Column chromatography was performed using 200 – 300 mesh silica gel. Melting points were measured with SGW X-4 micro melting point apparatus. Nitromethane (CH_3NO_2) was obtained from Sinopham Chemical Reagent Co. Ltd.. The other reagents were purchased from Bide Pharmatech Ltd., Adamas-Beta Ltd., Energy Chemical Inc. or J&K Scientific Inc. and used without further purification unless otherwise specified.

2. Preparation of Ligands

General Procedure for the Synthesis of Ligands In-Pyrox-2~10



A reported procedure was followed with some modifications to synthesize compound **A**.[1]

Step (a):

A reported procedure was followed with some modifications[1]. To a nitrogen-filled round-bottom flask, **A** (1 g, 4 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.230 g, 1.1 mmol, 0.05 equiv.), Cs_2CO_3 (2.58 g, 8 mmol, 2.0 equiv.) and aryl bronic acid (4.4 mmol, 1.1 equiv.) was added, followed by THF (20 mL) and H_2O (5 mL). The round-bottom flask was heated to 90 °C and stirred for 24 h before it was cooled to r.t. The reaction mixture was quenched with water (200 mL), and extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and filtered. The solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (PE/EA = 1/2) to afford crude compound **B**, which was used for the next step directly without any further purification.

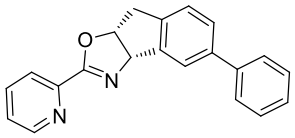
Step (b):

The **B** and KOH (0.8 g, 14.4 mmol, 3.6 equiv.) were dissolved in EtOH (10 mL), H_2O (10 mL) and then heated to 100 °C with stirring for 6 h before it was cooled to r.t.

The mixture was concentrated under vacuum to remove EtOH. The residue was extracted with EtOAc (20 mL × 3). After simple flash silica gel chromatography (PE/EA = 1/2) target crude compound **C** was obtained, which was used for the next step directly without any further purification.

Step (c):

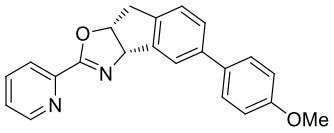
Compound **D** (1.1 equiv.) was placed in a 25 mL sealed tube. Compound **C** (1.0 equiv.) and 2.5 mL DCM (dried before used) was added. The mixture was stirred at 65 °C for 16 h before it was cooled to rt. The product was purified by flash silica gel column chromatography (PE/EA = 1/1, with 1% Et_3N) to afford target ligands.



In-Pyrox-2

(3a*S*,8a*R*)-5-Phenyl-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-2)

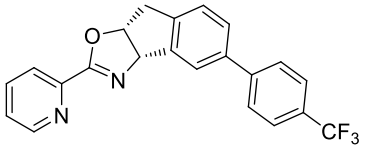
Colorless solid, 0.54 g, total yield 21%. M.p. 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 – 8.65 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.82 (s, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.38 – 7.30 (m, 3H), 5.82 (d, *J* = 7.6 Hz, 1H), 5.65 – 5.55 (m, 1H), 3.61 – 3.39 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 149.7, 146.8, 142.3, 140.9, 140.8, 138.9, 136.6, 128.7, 127.8, 127.2, 127.1, 125.6, 125.5, 124.3, 124.1, 84.2, 77.1, 39.5. HRMS (ESI) calcd for $C_{21}H_{17}N_2O$ ($[M+H]^+$): 313.1341. Found: 313.1342.



In-Pyrox-3

(3a*S*,8a*R*)-5-(4-Methoxyphenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-3)

Colorless solid, 0.23 g, total yield 27%. M.p. 138-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 4.4 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.77 (s, 1H), 7.73 (t, *J* = 7.8 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.46 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.38 – 7.28 (m, 2H), 6.99 – 6.93 (m, 2H), 5.84 (d, *J* = 8.0 Hz, 1H), 5.64 – 5.57 (m, 1H), 3.84 (s, 3H), 3.54 (dd, *J* = 14.0, 6.4 Hz, 1H), 3.47 (dd, *J* = 14.0, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 159.1, 149.7, 146.8, 142.2, 140.4, 138.2, 136.6, 133.5, 128.1, 127.4, 125.6, 125.5, 124.1, 123.8, 114.2, 84.3, 77.1, 55.3, 39.4. HRMS (ESI) calcd for $C_{22}H_{19}N_2O_2$ ($[M+H]^+$): 343.1482, Found: 343.1445.

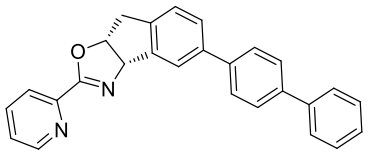


In-Pyrox-4

(3a*S*,8a*R*)-2-(Pyridin-2-yl)-5-(4-(trifluoromethyl)phenyl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-4)

Colorless solid, 0.17 g, total yield 25%. M.p. 153-155 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.70 (m, 1H), 8.07 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.80 – 7.68 (m, 5H), 7.54

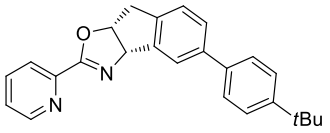
(dd, *J* = 8.0, 1.6 Hz, 1H), 7.42 – 7.37 (m, 2H), 5.89 (d, *J* = 8.0 Hz, 1H), 5.66 (ddd, *J* = 8.2, 6.4, 2.0 Hz, 1H), 3.58 (dd, *J* = 14.0, 6.4 Hz, 1H), 3.52 (dd, *J* = 14.0, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 149.8, 146.7, 144.4, 142.6, 140.0, 139.3, 136.6, 128.9 (q, *J* = 32.0 Hz), 127.8, 127.4, 125.9, 125.7 (q, *J* = 4.0 Hz), 125.6, 124.5, 124.3 (q, *J* = 270.0 Hz), 124.1, 84.2, 77.0, 39.5. HRMS (ESI) calcd for $C_{23}H_{16}F_3N_2O$ ($[M+H]^+$): 381.1215, Found: 381.1219.



In-Pyrox-5

(3a*S*,8a*R*)-5-([1,1'-Biphenyl]-4-yl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-5)

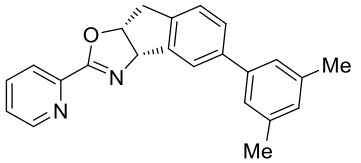
Colorless solid, 0.65 g, total yield 27%. M.p. 153-155 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 – 8.69 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.87 (s, 1H), 7.78 – 7.62 (m, 7H), 7.57 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.37-7.34 (m, 3H), 5.87 (d, *J* = 8.0 Hz, 1H), 5.64 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 3.59 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.52 (dd, *J* = 18.0, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 149.7, 146.8, 142.4, 140.7, 140.3, 140.0, 139.8, 139.1, 136.6, 128.8, 127.6, 127.5, 127.3, 127.0, 125.7, 125.6, 124.2, 124.1, 84.3, 77.1, 39.5. HRMS (ESI) calcd for $C_{27}H_{21}N_2O$ ($[M+H]^+$): 389.1654, Found: 389.1649.



In-Pyrox-6

(3a*S*,8a*R*)-5-(4-(*tert*-Butyl)phenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-6)

Colorless solid, 0.47 g, total yield 29%. M.p. 126-128 ºC.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.69 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.84 (s, 1H), 7.77 (td, *J* = 7.8, 1.8 Hz, 1H), 7.60 – 7.45 (m, 5H), 7.41 – 7.32 (m, 2H), 5.88 (d, *J* = 8.0 Hz, 1H), 5.64 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 3.58 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.51 (dd, *J* = 18.0, 1.6 Hz, 1H). 1.39 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.2, 149.7, 146.9, 142.2, 140.6, 138.6, 138.0, 136.6, 127.6, 126.8, 125.7, 125.6, 125.5, 124.2, 124.1, 84.2, 77.1, 39.5, 34.5, 31.4. HRMS (ESI) calcd for $C_{25}H_{25}N_2O$ ($[M+H]^+$): 369.1961. Found: 369.1962.

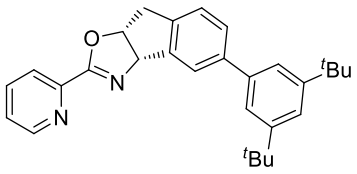


In-Pyrox-7

(3a*S*,8a*R*)-5-(3,5-Dimethylphenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-7)

Colorless solid, 0.25 g, total yield 23%. M.p. 116-118 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.67 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.80 (s, 1H), 7.74 (td, *J* = 7.8, 1.6 Hz, 1H), 7.50 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 2H), 6.98 (s, 1H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.62 (ddd, *J* = 8.2, 6.4, 2.0 Hz, 1H), 3.56 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.49 (dd, *J* = 18.0, 2.0 Hz, 1H), 2.37 (s, 6H). ^{13}C NMR (100

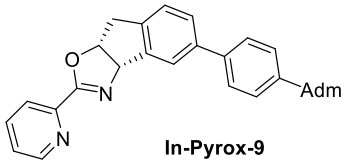
MHz, $CDCl_3$) δ 163.2, 149.7, 146.9, 142.2, 141.0, 140.9, 138.7, 138.2, 136.5, 128.8, 127.7, 125.5, 125.1, 124.3, 124.1, 100.0, 84.2, 77.1, 39.4, 21.4. HRMS (ESI) calcd for $C_{23}H_{21}N_2O$ ($[M+H]^+$): 341.1648, Found: 341.1641.



In-Pyrox-8

(3a*S*,8a*R*)-5-(3,5-Di-*tert*-butylphenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-8)

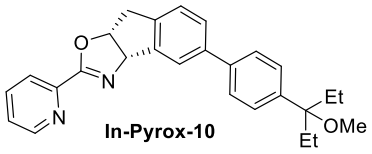
Colorless solid, 0.19 g, total yield 17%. M.p. 153-155 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.70 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.77 (td, *J* = 7.8, 1.6 Hz, 1H), 7.54 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.45 (s, 3H), 7.40 –7.35 (m, 2H), 5.90 (d, *J* = 8.0 Hz, 1H), 5.66 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 3.60 (dd, *J* = 18.0, 6.4 Hz, 1H), 3.52 (dd, *J* = 18.0, 1.2 Hz, 1H), 1.40 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 151.1, 149.7, 146.9, 142.10, 142.08, 140.4, 138.6, 136.6, 128.1, 125.53, 125.51, 124.6, 124.1, 121.7, 121.3, 84.3, 77.1, 39.5, 35.0, 31.6. HRMS (ESI) calcd for $C_{29}H_{33}N_2O$ ($[M+H]^+$): 425.2587, Found: 425.2588.



In-Pyrox-9

(3a*S*,8a*R*)-5-((1*S*,3*R*)-Adamantan-1-yl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-9)

2-(4-(Adamantan-1-yl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane[2] was used instead of the corresponding arylboronic acid. Colorless solid, 0.29 g, total yield 18%. M.p. 166-168 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.65 (m, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.74 (td, *J* = 7.8, 1.6 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.51 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.31 (m, 2H), 5.85 (d, *J* = 8.0 Hz, 1H), 5.62 (ddd, *J* = 8.0, 6.4, 2.0 Hz, 1H), 3.60 – 3.45 (m, 2H), 2.12 (s, 3H), 1.96 (d, *J* = 2.4 Hz, 6H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.5, 149.7, 146.9, 142.2, 140.7, 138.6, 138.0, 136.6, 127.6, 126.8, 125.6, 125.5, 125.3, 124.2, 124.1, 84.3, 77.1, 43.2, 39.5, 36.8, 36.1, 29.0, 24.9. HRMS (ESI) calcd for $C_{31}H_{31}N_2O$ ($[M+H]^+$): 447.2431, Found: 447.2433.



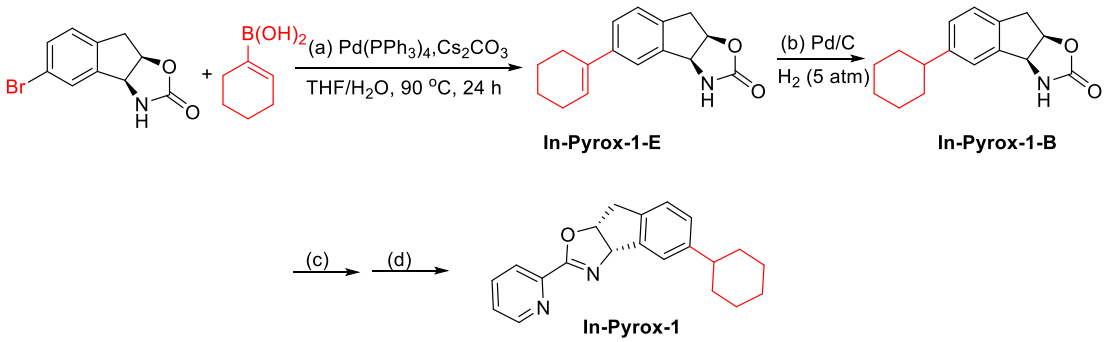
In-Pyrox-10

(3a*S*,8a*R*)-5-(4-(3-Methoxypentan-3-yl)phenyl)-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-10)

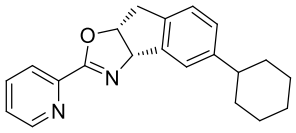
The arylboronic acid was prepared via a procedure similar to the reported methods.[3,4] Colorless oil, 0.16 g, total yield 11%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 3.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.83 (s, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m, 2H), 5.84

(d, J = 8.0 Hz, 1H), 5.61 (t, J = 6.0 Hz, 1H), 3.54 (dd, J = 18.0, 6.0 Hz, 1H), 3.48 (d, J = 18.0 Hz, 1H), 3.09 (s, 3H), 1.94 – 1.82 (m, 4H), 0.74 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 149.7, 146.8, 143.3, 142.2, 140.5, 138.9, 138.8, 136.6, 127.6, 127.0, 126.5, 125.6, 125.5, 124.2, 124.1, 84.3, 81.4, 77.1, 49.47, 39.5, 28.2, 7.5. HRMS (ESI) calcd for $C_{27}H_{29}N_2O_2$ ([M+H]$^+$): 413.2229, Found: 413.2234.

Procedure for the Synthesis of Ligand In-Pyrox-1[1]



The procedure for the synthesis of ligand **In-Pyrox-1** is almost the same as the general procedure, except the hydrogenation of **In-Pyrox-1-E** to give **In-Pyrox-1-B**. To a solution of **In-Pyrox-1-E** (0.5g, 2.0 mmol, 1.0 equiv.) in ethanol (5 mL), Pd/C (10%, 0.21 g, 0.2 mmol, 0.1 equiv.) was added and the reaction was kept under H_2 atmosphere (5 atm) for 10 h at r.t. Then the reaction mixture was filtered through a Celite pad and washed with EtOH (2 × 5 mL). The combined organic layers were added H_2O (5 mL) and KOH (0.4 g, 7.2 mmol, 3.6 equiv), heated to 100 °C with stirring for 6 h before it was cooled to rt. The mixture was concentrated under vacuum to remove EtOH. The residue was extracted with EtOAc (20 mL × 3) to give target crude compound **C**, which was used for the next step directly without any further purification.

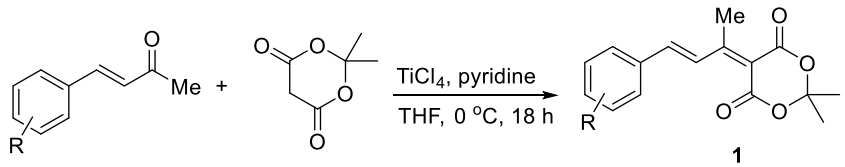


In-Pyrox-1

(3a*S*,8a*R*)-5-Cyclohexyl-2-(pyridin-2-yl)-8,8a-dihydro-3a*H*-indeno[1,2-*d*]oxazole (In-Pyrox-1)

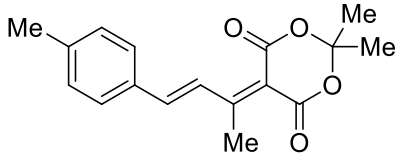
Prepared according to the general procedure. Colorless oil, 0.51 g, total yield 28%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.02 (d, J = 7.6 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.44 (s, 1H), 7.34 – 7.28 (m, 1H), 7.18 (d, J = 7.8 Hz, 1H), 7.12 (d, J = 7.8 Hz, 1H), 5.76 (d, J = 7.6 Hz, 1H), 5.54 (t, J = 7.0 Hz, 1H), 3.47 (dd, J = 18.0, 6.4 Hz, 1H), 3.39 (d, J = 18.0 Hz, 1H), 2.56 (pseudo t, J =10.0 Hz, 1H), 1.94 – 1.68 (m, 5H), 1.47 – 1.19 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 149.6, 147.4, 146.9, 141.6, 137.2, 136.4, 127.5, 125.4, 125.0, 124.0, 123.8, 84.2, 77.1, 44.4, 39.4, 34.7, 34.4, 26.9, 26.1.

3. Preparation of Substrates



1

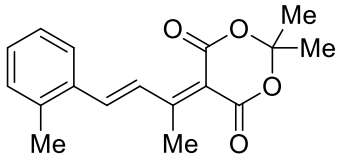
A procedure similar with reported method was used for preparation of substrate **1**.[5] In a typical reaction, a solution of $TiCl_4$ (2.1 equiv.) was added dropwise under nitrogen to dry THF at 0 ºC, which resulted in a yellow suspension. A solution containing the ketone (1.0 equiv.) and Meldrum′s acid (1.1 equiv.) in dry THF was added dropwise via a syringe to the $TiCl_4$•THF complex. The flask containing the solution of ketone and Meldrum′s acid was rinsed with THF and added to the reaction mixture. Subsequently, pyridine (5.0 equiv.) was added to the reaction mixture dropwise at 0 ºC. The reaction was allowed to warm up slowly to room temperature and stirred for 18 hours. The reaction was quenched by the addition of water and diluted with ethyl acetate. After the solid was dissolved, the layers were partitioned. The aqueous layer was extracted with ethyl acetate (2X), and the combined organic layers were washed with $NaHCO_3$ (2X), brine (1X), dried over $MgSO_4$, filtered and concentrated. Purification by either crystallization or flash chromatography (PE/EA = 5/1) provided the alkylidene Meldrum′s acids.



1a

(*E*)-2,2-Dimethyl-5-(4-(*p*-tolyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1a)

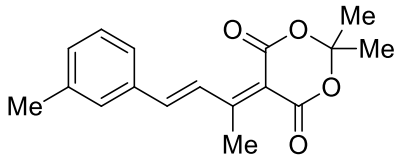
Yellow solid, 1.3 g, total yield 63%. M.p. 143-145 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.66 (s, 3H), 2.37 (s, 3H), 1.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 162.3, 161.8, 144.4, 141.5, 133.0, 130.0, 128.8, 126.7, 114.0, 103.7, 27.3, 21.8, 18.5. HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ ([M+Na]$^+$): 309.1103, Found: 309.1106.



1b

(*E*)-2,2-Dimethyl-5-(4-(*o*-tolyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1b)

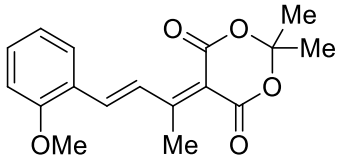
Yellow solid, 0.9 g, total yield 63%. M.p. 121-123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 16.0 Hz, 1H), 7.77 (d, *J* = 16.0 Hz, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.34 – 7.21 (m, 3H), 2.72 (s, 3H), 2.48 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.0, 161.4, 141.2, 137.7, 134.4, 130.9, 130.3, 128.6, 126.9, 126.7, 114.4, 103.6, 27.2, 19.8, 18.5. HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ ([M+Na]$^+$): 309.1103, Found: 309.1106.



1c

(*E*)-2,2-Dimethyl-5-(4-(*m*-tolyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1c)

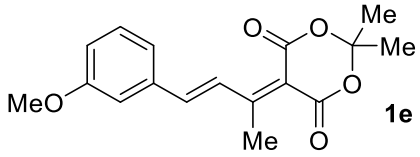
Yellow solid, 1.9 g, total yield 61%. M.p. 143-145 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.44 (s, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 2.67 (s, 3H), 2.39 (s, 3H), 1.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.0, 161.6, 144.2, 138.8, 135.4, 131.6, 129.0, 128.9, 127.2, 126.0, 114.2, 103.6, 27.1, 21.4, 18.3. HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ ([M+Na]$^+$): 309.1103, Found: 309.1106.



1d

(*E*)-5-(4-(2-Methoxyphenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1d)

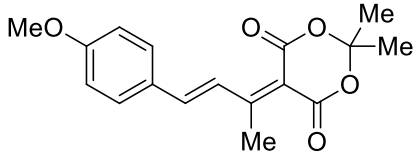
Yellow solid, 2.0 g, total yield 57%. M.p. 151-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 16.2 Hz, 1H), 7.92 (d, *J* = 16.2 Hz, 1H), 7.69 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.42 – 7.31 (m, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 2.69 (s, 3H), 1.75 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 162.2, 161.6, 158.3, 139.0, 132.0, 128.3, 127.5, 124.5, 121.0, 113.7, 111.1, 103.4, 55.6, 27.1, 18.4. HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ ([M+Na]$^+$): 309.1103, Found: 309.1106.



1e

(*E*)-5-(4-(3-Methoxyphenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1e)

Yellow solid, 0.8 g, total yield 57%. M.p. 141-143 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 16.0 Hz, 1H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.14 (s, 1H), 6.97 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.87 (s, 3H), 2.69 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 162.0, 161.5, 160.0, 143.7, 136.9, 130.0, 127.7, 121.3, 116.7, 114.5, 113.1, 103.6, 55.4, 27.2, 18.4. HRMS (ESI) calcd for $C_{17}H_{18}O_5Na$ ([M+Na]$^+$): 325.1052, Found: 325.1055.

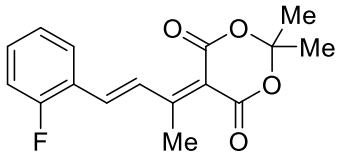


1f

(*E*)-5-(4-(4-Methoxyphenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1f)

Yellow solid, 1.3 g, total yield 67%. M.p. 151-153 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 16.0 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H), 2.69 (s, 3H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$)

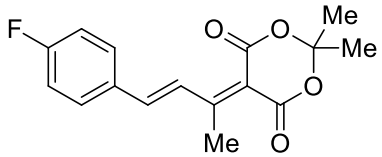
δ 166.4, 161.9, 144.1, 130.4, 128.4, 127.9, 125.3, 114.6, 114.0, 113.0, 103.4, 55.5, 27.1, 18.3. HRMS (ESI) calcd for $C_{17}H_{18}O_5Na$ ([M+Na]$^+$): 325.1052, Found: 325.1055.



1g

(*E*)-5-(4-(2-Fluorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1g)

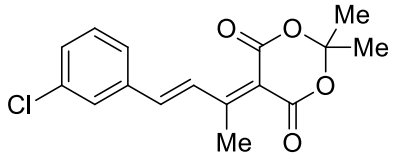
Yellow solid, 1.3 g, total yield 67%. M.p. 98-100 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 16.2 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 16.2 Hz, 1H), 7.40 (dd, *J* = 13.4, 6.0 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.15 – 7.11 (m, 1H), 2.71 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 161.8, 161.4, 161.2 (d, *J* = 251.8 Hz), 135.1 (d, *J* = 4.8 Hz), 132.0 (d, *J* = 8.8 Hz), 128.9 (d, *J* = 3.7 Hz), 127.9 (d, *J* = 2.4 Hz), 124.7 (d, *J* = 3.6 Hz), 123.6 (d, *J* = 11.3 Hz), 116.1 (d, *J* = 21.8 Hz), 115.1, 103.7, 27.2, 18.4. HRMS (ESI) calcd for $C_{16}H_{15}O_4FNa$ ([M+Na]$^+$): 314.0930, Found: 314.0931.



1h

(*E*)-5-(4-(4-Fluorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1h)

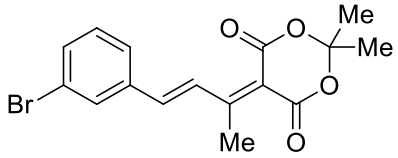
Yellow solid, 1.5 g, total yield 55%. M.p. 159-160 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 16.0 Hz, 1H), 7.67 – 7.59 (m, 2H), 7.45 (d, *J* = 16.0 Hz, 1H), 7.16 – 7.09 (m, 2H), 2.69 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.1 (d, *J* = 250.0 Hz), 162.0, 161.5, 142.4, 131.8 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 8.5 Hz), 127.2 (d, *J* = 2.4 Hz), 116.3 (d, *J* = 21.8 Hz), 114.4, 103.6, 27.2, 18.3. HRMS (ESI) calcd for $C_{16}H_{15}O_4FNa$ ([M+Na]$^+$): 314.0930, Found: 314.0931.



1i

(*E*)-5-(4-(3-Chlorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1i)

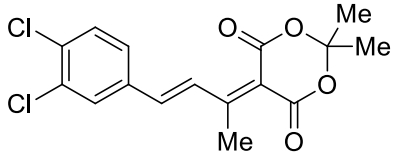
Yellow solid, 1.7 g, total yield 54%. M.p. 131-133 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 16.0 Hz, 1H), 7.60 (s, 1H), 7.53 – 7.49 (m, 1H), 7.39 (d, *J* = 16.0 Hz, 1H), 7.40 – 7.34 (m, 2H), 2.69 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 161.8, 161.4, 141.8, 137.3, 135.1, 130.3, 130.2, 128.7, 128.2, 126.5, 115.3, 103.8, 27.2, 18.4. HRMS (ESI) calcd for $C_{16}H_{15}O_4ClNa$ ([M+Na]$^+$): 329.0557, Found: 329.0557.



1j

(*E*)-5-(4-(3-Bromophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1j)

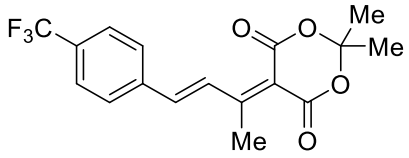
Yellow solid, 1.7 g, total yield 56%. M.p. 122-123 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 16.0 Hz, 1H), 7.75 (t, *J* = 1.6 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.38 (d, *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 2.69 (s, 3H), 1.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 161.8, 161.3, 141.7, 137.6, 133.2, 131.2, 130.5, 128.7, 126.9, 123.2, 115.3, 103.7, 27.2, 18.4. HRMS (ESI) calcd for $C_{16}H_{15}O_4BrNa$ ([M+Na]$^+$): 373.0051, Found: 373.0055.



1k

(*E*)-5-(4-(3,4-Dichlorophenyl)but-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1k)

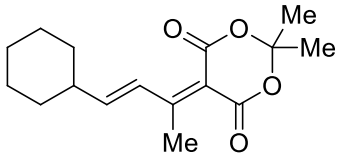
Yellow solid, 2.1 g, total yield 58%. M.p. 164-165 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 16.0 Hz, 1H), 7.69 (d, *J* = 1.6 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.34 (d, *J* = 16.0 Hz, 1H), 2.68 (s, 3H), 1.78 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 161.7, 161.3, 140.5, 135.6, 134.4, 133.4, 131.0, 130.0, 129.1, 127.2, 115.5, 103.8, 27.2, 18.4. HRMS (ESI) calcd for $C_{16}H_{14}O_4Cl_2Na$ ([M+Na]$^+$): 363.0167, Found: 363.0175.



1l

(*E*)-2,2-Mimethyl-5-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1l)

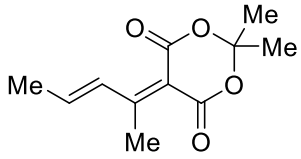
Yellow solid, 1.1 g, total yield 48%. M.p. 123-125 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 16.0 Hz, 1H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.71 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 3H), 1.77 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 161.7, 161.3, 141.2, 138.9, 131.7 (q, *J* = 32.5 Hz), 129.8, 128.5, 125.9 (q, *J* = 3.7 Hz), 123.8 (q, *J* = 270.6 Hz), 115.8, 103.8, 27.2, 18.4. HRMS (ESI) calcd for $C_{17}H_{15}O_4F_3Na$ ([M+Na]$^+$): 363.0820, Found: 363.0822.



1m

(*E*)-5-(4-Cyclohexylbut-3-en-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (1n)

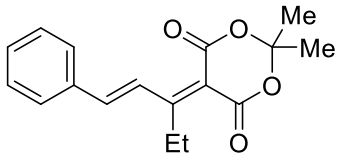
White solid, 1.7 g, total yield 58%. M.p. 87-89 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 15.8, 1.0 Hz, 1H), 6.69 (dd, *J* = 15.8, 7.2 Hz, 1H), 2.54 (s, 3H), 1.85 – 1.73 (m, 5H), 1.75 (s, 6H), 1.36 – 1.14 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.1, 161.3, 154.3, 127.8, 113.6, 103.4, 42.3, 32.1, 27.1, 25.9, 25.7, 18.6. HRMS (ESI) calcd for $C_{16}H_{22}O_4Na$ ([M+Na]$^+$): 301.1416, Found: 301.1422.



1n

(*E*)-2,2-Dimethyl-5-(pent-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1n)

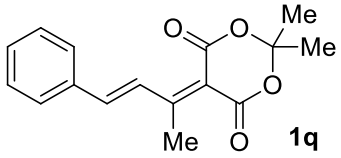
White solid, 1.1 g, total yield 45%. M.p. 76-77 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (dq, *J* = 15.6, 1.6 Hz, 1H), 6.82 (dq, *J* = 15.6, 6.8 Hz, 1H), 2.54 (s, 3H), 2.04 (dd, *J* = 6.8, 1.6 Hz, 3H), 1.74 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 162.0, 161.3, 144.2, 131.4, 113.5, 103.5, 27.1, 19.9, 18.5. HRMS (ESI) calcd for $C_{11}H_{14}O_4Na$ ([M+Na]$^+$): 233.0790, Found: 233.0793.



1o

(*E*)-2,2-Dimethyl-5-(1-phenylpent-1-en-3-ylidene)-1,3-dioxane-4,6-dione (1o)

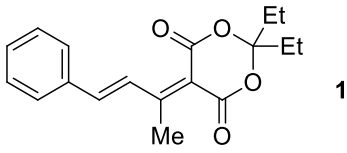
Prepared according to the general procedure. Yellow solid, 1.7 g, total yield 57%. M.p. 90-92 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 16.0 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.49 (d, *J* = 16.0 Hz, 1H), 7.45 – 7.42 (m, 3H), 3.14 (q, *J* = 7.6 Hz, 2H), 1.77 (s, 6H), 1.35 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 161.8, 161.5, 143.4, 135.6, 130.6, 129.0, 128.5, 125.9, 113.8, 103.5, 27.1, 24.4, 15.3. HRMS (ESI) calcd for $C_{17}H_{18}O_4Na$ ([M+Na]$^+$): 309.1103, Found: 309.1098.



1q

(*E*)-2,2-Dimethyl-5-(4-phenylbut-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1q)

Prepared according to the general procedure. Yellow solid, 5.4 g, yield 74%. M.p. 122-124 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 16.0 Hz, 1H), 7.62 (dd, *J* = 6.5, 2.8 Hz, 2H), 7.47 (d, *J* = 16.0 Hz, 1H), 7.43 – 7.40 (m, 3H), 2.68 (s, 3H), 1.76 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 162.0, 161.5, 143.8, 135.5, 130.6, 129.0, 128.5, 127.4, 114.4, 103.6, 27.2, 18.4. HRMS (ESI) calcd for $C_{16}H_{16}O_4Na$ ([M+Na]$^+$): 295.0946, Found: 295.0946.



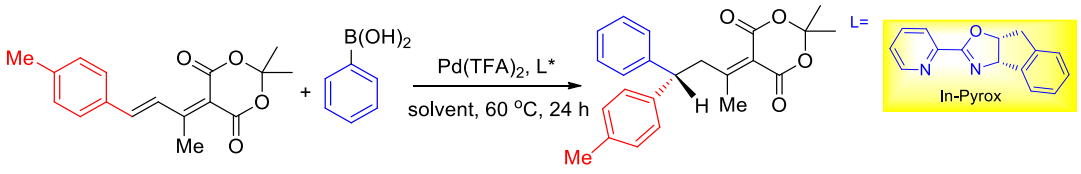
1p

(*E*)-2,2-Diethyl-5-(4-phenylbut-3-en-2-ylidene)-1,3-dioxane-4,6-dione (1p)

Yellow solid, 1.3 g, total yield 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 16.0 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.48 (d, *J* = 16.0 Hz, 1H), 7.45 – 7.41 (m, 3H), 2.70 (s, 3H), 2.01 (q, *J* = 7.6 Hz, 4H), 1.07 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 162.1, 161.6, 143.6, 135.6, 130.5, 129.0, 128.5, 127.7, 114.6, 107.5, 30.3, 18.5, 7.6. HRMS (ESI) calcd for $C_{18}H_{20}O_4Na$ ([M+Na]$^+$): 323.1259, Found: 323.1265.

4. Condition Optimization

Table S1. Effects of Solvents[a]

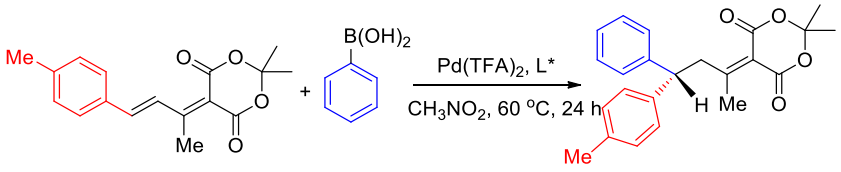


1a 2a 3aa

Entry	Solvent	Yield (%)[b]	ee (%)[c]
1	DCE	62	54
2	MeOH	NR	---
3	toluene	trace	---
4	THF	NR	---
5	1,4-dioxane	NR	---
6	TFE	85	46
7	CH_3NO_2	91	59

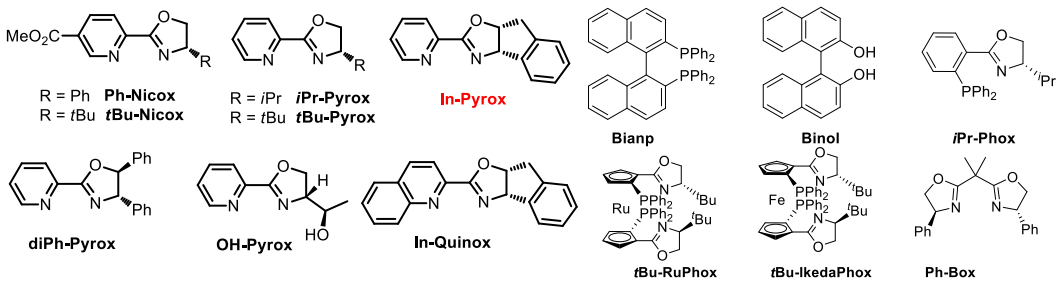
[a)] Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol % ligand and $PhB(OH)_2$ (0.30 mmol) in CH_3NO_2 (1 mL) at 60 °C for 24 h under an air atmosphere. [b)] Yield of isolated product. [c)] The *ee* values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 22.0 min (major), t_{R2} = 23.8 min (minor)]

Table S2. Effects of Ligands[a]



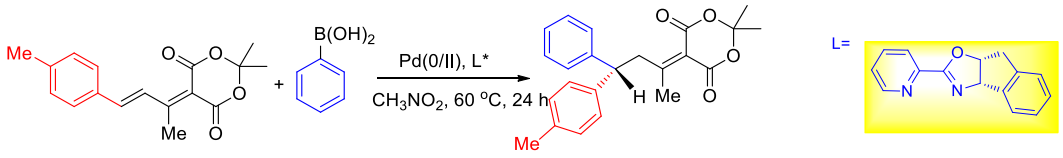
1a 2a 3aa

Entry	Ligand	Yield (%)[b]	ee (%)[c]
1	**Ph-Nicox**	40	4
2	***t*Bu-Nicox**	37	67
3	***i*Pr-Pyrox**	89	26
4	***t*Bu-Pyrox**	40	74
5	**In-Pyrox**	91	59
6	**diPh-Pyrox**	32	0
7	**OH-Pyrox**	51	2
8	**In-Quinox**	47	<5
9	**Binap**	NR	--
10	***i*Pr-Phox**	NR	--
11	**Ph-Box**	NR	--
12	**Binol**	NR	--
13	***t*Bu-RuPhox**	NR	--
14	***t*Bu-IkedaPhox**	NR	--



[a)] Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol % ligand and $PhB(OH)_2$ (0.30 mmol) in CH_3NO_2 (1 mL) at 60 °C for 24 h under an air atmosphere. [b)] Yield of isolated product. [c)] The *ee* values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 22.0 min (major), t_{R2} = 23.8 min (minor)]

Table S3. Effects of Pd Source[a]

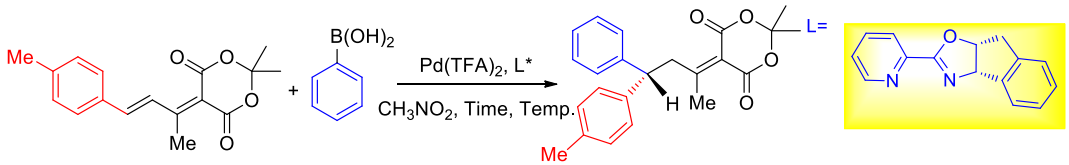


1a 2a 3aa

Entry	Pd	Yield (%)[b]	ee (%)[c]
1	$Pd(TFA)_2$	91	59
2	$Pd(OAc)_2$	47	57
3	$Pd(OH)_2$	NR	---
4	$PdCl_2$	NR	---
5	$PdBr_2$	NR	---
6	$PdCl_2(CH_3CN)_2$	NR	---
7	$Pd(PPh_3)_4$	NR	---
8	$Pd_2(dba)_3$	NR	---

[a)] Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol % ligand and $PhB(OH)_2$ (0.30 mmol) in CH_3NO_2 (1 mL) at 60 °C for 24 h under an air atmosphere. [b)] Yield of isolated product. [c)] The *ee* values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 22.0 min (major), t_{R2} = 23.8 min (minor)]

Table S4. Effects of Temperature and Time[a]



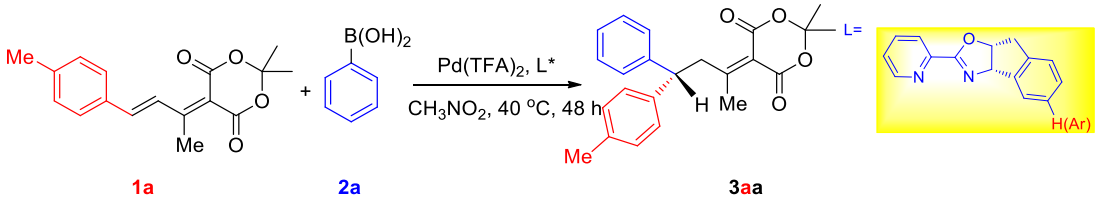
1a 2a 3aa

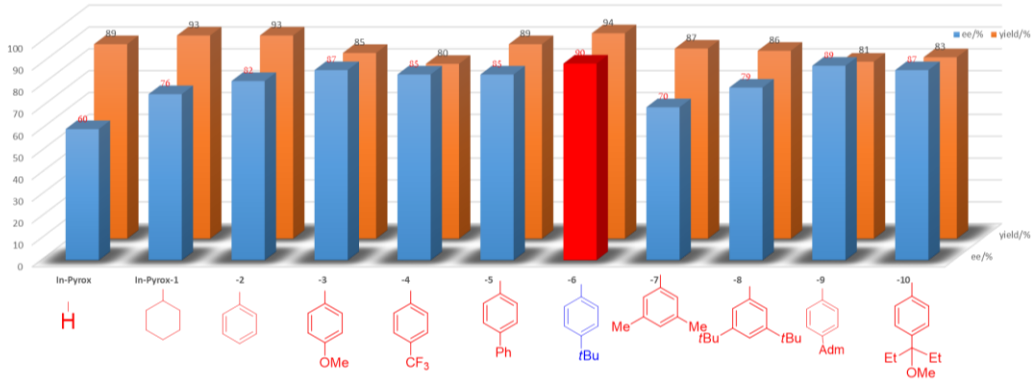
Entry	Temp. (°C)	Time (h)	Yield (%)[b]	ee (%)[c]

1	R.T.	48	24	65
2	40	24	52	59
3	40	48	89	60
4	60	24	91	59

[a)] Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol % ligand and $PhB(OH)_2$ (0.30 mmol) in CH_3NO_2 (1 mL) at 60 °C for 24 h under an air atmosphere. [b)] Yield of isolated product. [c)] The *ee* values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 22.0 min (major), t_{R2} = 23.8 min (minor)]

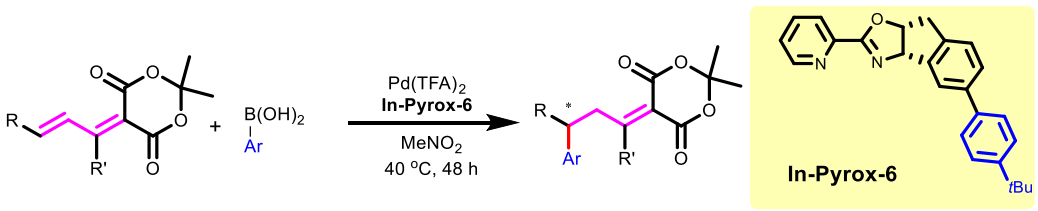
Table S5. Second Ligand Optimization[a]





[a)] Reactions were carried out on a 0.10 mmol scale using 10 mol% Pd, 12 mol% ligand and Ph-$B(OH)_2$ (0.30 mmol) in CH_3NO_2 (1 mL) at 40 °C for 48 h under an air atmosphere. [b)] Yield of isolated product. [c)] The *ee* values of the desired products were measured by HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 50.5 min (major), t_{R2} = 56.2 min (minor)]

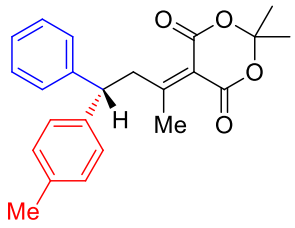
5. General Procedure for Pd-Catalyzed 1,6-Conjugate Addition



General procedure: A common test tube (20 cm x 18 mm) was charged with $Pd(TFA)_2$ (6.65 mg, 0.20 mmol, 0.1 equiv) and **In-Pyrox-6** (8.8 mg, 0.12 equiv). Unpurified CH_3NO_2 (2.0 mL) was added. The resulting mixture was stirred at room temperature for 30 min. The substrate (0.2 mmol, 1.0 equiv) and arylboronic acid (0.60

mmol, 3.0 equiv) were then added. The temperature was increased to 40 °C. After stirring for 48 h under an air atmosphere, the reaction mixture was cooled to room temperature, and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography on 200-300 mesh silica gel (dried before used) to give the corresponding products.

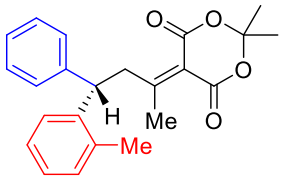
5.1 Scope of Substrates



3aa

(*S*)-2,2-Dimethyl-5-(4-phenyl-4-(*p*-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3aa)

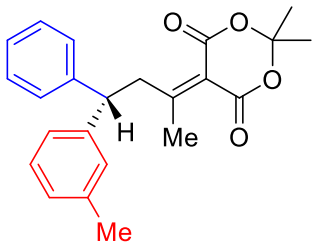
Colorless oil, 66 mg, yield 91%, ee = 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 4H), 7.22 – 7.08 (m, 5H), 4.38 (t, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.30 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 161.1, 161.0, 143.3, 140.1, 136.4, 129.4, 128.8, 127.7, 127.6, 126.8, 117.6, 103.5, 49.6, 43.1, 26.8, 26.7, 24.3, 21.0. HRMS (ESI) calcd for $C_{23}H_{24}O_4Na$ ([M+Na]$^+$): 387.1572, Found: 387.1575. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 50.5 min (major), t_{R2} = 56.2 min (minor)]; $[\alpha]^{D}_{20}$ = 1.16 (c = 1.07, $CHCl_3$).



3ba

(*S*)-2,2-Dimethyl-5-(4-phenyl-4-(*o*-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3ba)

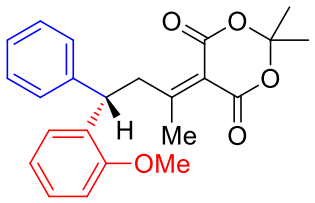
Colorless oil, 65 mg, yield 89%, ee = 90%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.29 (m, 4H), 7.23 – 7.17 (m, 3H),7.11 (d, *J* = 8.0 Hz, 2H), 4.64 (t, *J* = 8.0 Hz, 1H), 3.84 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.80 (dd, *J* = 12.8, 8.0 Hz, 1H), 2.37 (s, 3H), 2.27 (s, 3H), 1.49 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 161.4, 161.3, 143.4, 143.2, 138.6, 129.0, 128.9, 128.7, 128.0, 127.9, 127.1, 125.0, 117.9, 103.7, 50.2, 43.2, 27.0, 26.9, 24.5, 21.7. HRMS (ESI) calcd for $C_{23}H_{24}O_4Na$ ([M+Na]$^+$): 387.1572, Found:387.1571. HPLC [Daicel Chiralcel AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_{R1} = 16.0 min (minor), t_{R2} = 19.1 min (major)]; $[\alpha]^{D}_{20}$ = 4.25 (c = 1.02, $CHCl_3$).



3ca

(*S*)-2,2-Dimethyl-5-(4-phenyl-4-(*m*-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3ca)

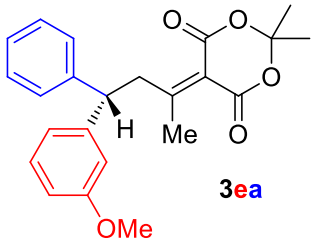
Colorless oil, 64 mg, yield 88%, ee = 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.28 (m, 4H), 7.23 – 7.16 (m, 2H), 7.10 (s, 1H), 7.09 (d, *J* = 6.4 Hz, 1H), 7.02 (d, *J* = 7.6 Hz, 1H), 4.37 (t, *J* = 8.0 Hz, 1H), 3.85 (dd, *J* = 12.4, 8.0 Hz, 1H), 3.80 (dd, *J* = 12.4, 8.0 Hz, 1H), 2.43 (s, 3H), 2.32 (s, 3H), 1.414 (s, 3H), 1.407 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 161.12, 161.07, 143.2, 143.0, 138.4, 128.8, 128.7, 128.5, 127.7, 127.6, 126.8, 124.7, 117.7, 103.5, 50.0, 43.0, 26.8, 26.7, 24.2, 21.5. HRMS (ESI) calcd for $C_{23}H_{24}O_4Na$ ([M+Na]$^+$): 387.1572, Found: 387.1575. HPLC [Enantiopak AD, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min. t_{R1} = 34.7 min (major), t_{R2} = 36.9 min (minor)]; $[\alpha]^{D}_{20}$ = 2.30 (c = 1.04, $CHCl_3$).



3da

(*S*)-5-(4-(2-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3da)

Colorless oil, 68 mg, yield 89%, ee = 96%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.23 (m, 5H), 7.18 (m, 2H), 6.92 (td, *J* = 7.6, 0.8 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 4.93 (t, *J* = 8.0 Hz, 1H), 3.97 (dd, *J* = 13.2, 8.4 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.49 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.1, 161.2, 161.1, 156.5, 142.7, 131.6, 128.6, 128.2, 128.1, 127.8, 126.6, 120.8, 117.5, 110.7, 103.4, 55.4, 42.0, 41. 9, 26.9, 26.6, 23.6. HRMS (ESI) calcd for $C_{23}H_{24}O_5Na$ ([M+Na]$^+$): 403.1521, Found: 403.1522. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 20.3 min (major), t_{R2} = 24.4 min (minor)]; $[\alpha]^{D}_{20}$ = -7.82 (c = 1.15, $CHCl_3$).

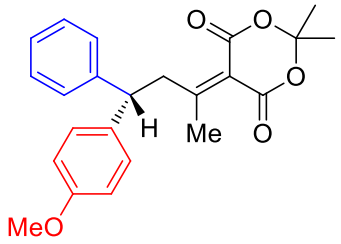


3ea

(*S*)-5-(4-(3-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ea)

Colorless oil, 68 mg, yield 89%, ee = 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.4 Hz, 4H), 7.24 – 7.11 (m, 2H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.82 (t, *J* = 2.4 Hz, 1H), 6.77 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.38 (t, *J* = 8.0 Hz, 1H), 3.88 (*J* = 12.8, 8.4 Hz, 1H), 3.77 (s,

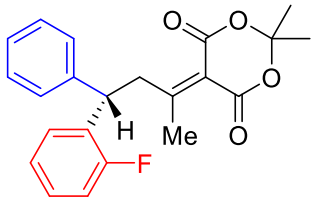
3H), 3.74 (J = 12.8, 8.4 Hz, 1H), 2.41 (s, 3H), 1.42 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 161.12, 161.07, 159.8, 144.6, 143.0, 129.8, 128.8, 127.7, 126.9, 120.1, 117.8, 113.5, 112.2, 103.5, 55.2, 49.9, 42.9, 27.1, 26.8, 26.7, 24.2. HRMS (ESI) calcd for $C_{23}H_{24}O_5Na$ ([M+Na]$^+$): 403.1521, Found: 403.1522. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 23.8 min (minor), t_{R2} = 26.2 min (major)]; $[\alpha]^D_{20}$ = -7.82 (c = 1.15, $CHCl_3$).



3fa

(*S*)-5-(4-(4-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3fa)

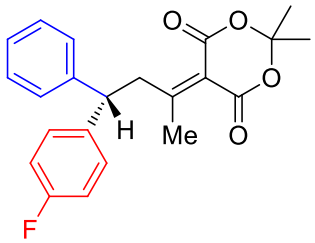
Colorless oil, 69 mg, yield 91%, ee = 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 7.21 – 7.18 (m, 3H), 6.83 (d, J = 8.4 Hz, 2H), 4.36 (t, J = 8.0 Hz, 1H), 3.82 (J = 12.4, 8.0 Hz, 1H), 3.78 (J = 12.4, 8.4 Hz, 1H), 3.77 (s, 3H), 2.41 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 161.10, 161.07, 158.4, 143.4, 135.1, 128.8, 128.7, 127.6, 126.8, 117.6, 114.1, 103.5, 55.2, 49.2, 43.3, 26.81, 26.75, 24.4. HRMS (ESI) calcd for $C_{23}H_{24}O_5Na$ ([M+Na]$^+$): 403.1521, Found: 403.1523. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 24.5 min (minor), t_{R2} = 35.9 min (major)]; $[\alpha]^D_{20}$ = -1.99 (c = 1.10, $CHCl_3$).



3ga

(*S*)-5-(4-(2-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ga)

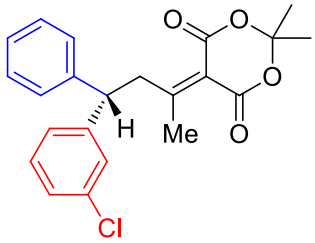
Colorless oil, 61 mg, yield 83%, ee = 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 5H), 7.24 – 7.16 (m, 2H), 7.11 (td, J = 7.6, 1.2 Hz, 1H), 7.05 – 6.97 (m, 1H), 4.80 (t, J = 8.0 Hz, 1H), 3.99 (dd, J = 12.8, 8.4 Hz, 1H), 3.68 (dd, J = 12.8, 7.6 Hz, 1H), 2.46 (s, 3H), 1.48 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 161.2(d, J = 244.0 Hz), 176.9, 161.02, 160.99, 160.2 (d, J = 243.7 Hz), 141.8, 130.2 (d, J = 14.0 Hz), 128.83 (d, J = 9.3 Hz), 128.82, 128.4 (d, J = 8.4 Hz), 127.9, 127.1, 124.5 (d, J = 3.5 Hz), 117.8, 115.6 (d, J = 22.7 Hz), 103.5, 42.0 (d, J = 2.5 Hz), 41.9, 26.9, 26.7, 24.0. HRMS (ESI) calcd for $C_{22}H_{22}FO_4$ ([M+H]$^+$): 369.1502, Found: 369.1505. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 17.9 min (minor), t_{R2} = 20.8 min (major)]; $[\alpha]^D_{20}$ = 2.37 (c = 1.08, $CHCl_3$).



3ha

(*S*)-5-(4-(4-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ha)

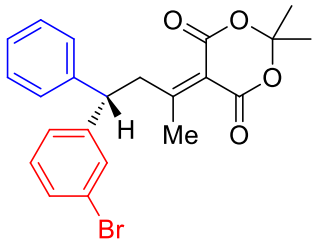
Colorless oil, 65 mg, yield 88%, ee = 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.19 (m, 8H), 6.99 (t, *J* = 8.6 Hz, 2H), 4.40 (t, *J* = 8.0 Hz, 1H), 3.79 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 161.7 (d, *J* = 245.6 Hz), 161.02, 160.99, 142.8, 138.9 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 7.9 Hz), 128.9, 127.7, 127.0, 117.7, 115.6 (d, *J* = 21.3 Hz), 103.5, 49.3, 43.2, 26.8, 26.8, 24.4. HRMS (ESI) calcd for $C_{22}H_{22}FO_4$ ($[M+H]^+$): 369.1502, Found: 369.1504. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 51.4 min (major), t_{R2} = 54.2 min (minor)]; $[\alpha]^{D}_{20}$ = 6.62 (c = 1.04, $CHCl_3$).



3ia

(*S*)-5-(4-(3-Chlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ia)

Colorless oil, 69 mg, yield 90%, ee = 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.24 (m, 6H), 7.22 – 7.17 (m, 3H), 4.39 (t, *J* = 8.0 Hz, 1H), 3.83 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.75 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.39 (s, 3H), 1.49 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 161.01, 160.99, 145.2, 142.2, 134.6, 130.1, 129.0, 127.9, 127.8, 127.2, 127.1, 126.0, 117.8, 103.6, 49.7, 42.9, 26.9, 26.8, 24.4. HRMS (ESI) calcd for $C_{22}H_{21}ClO_4Na$ ($[M+Na]^+$): 407.1026, Found: 407.1023. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 17.1 min (major), t_{R2} = 20.8 min (minor)]; $[\alpha]^{D}_{20}$ = 10.96 (c = 1.13, $CHCl_3$).

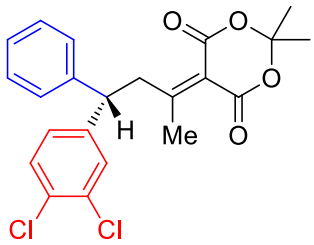


3ja

(*S*)-5-(4-(3-bromophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ja)

Colorless oil, 78 mg, yield 91%, ee = 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.21 (m, 6H), 7.20 – 7.15 (m, 3H), 4.39 (t, *J* = 8.0 Hz, 1H), 3.80 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.72 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.40 (s, 3H), 1.50 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 160.97, 160.94, 145.5, 142.2, 130.8, 130.3, 130.0, 129.0, 127.8,

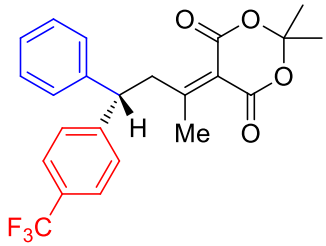
127.2, 126.4, 122.8, 117.9, 103.6, 49.7, 42.9, 26.9, 26.8, 24.4. HRMS (ESI) calcd for $C_{22}H_{21}BrO_4Na$ ([M+Na]$^+$): 451.0521, Found: 451.0528. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 18.2 min (major), t_{R2} = 22.3 min (minor)]; $[\alpha]^D_{20}$ = 8.03 (c = 1.10, $CHCl_3$).



3ka

(*S*)-5-(4-(3,4-Dichlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ka)

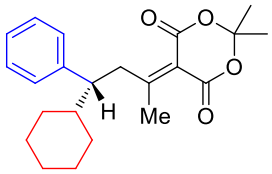
Colorless oil, 73 mg, yield 87%, ee = 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.29 (m, 4H), 7.26 – 7.21 (m, 3H), 7.15 (dd, *J* = 8.2, 2.2 Hz, 1H), 4.37 (t, *J* = 8.0 Hz, 1H), 3.78 (dd, *J* = 12.4, 8.4 Hz, 1H), 3.73 (dd, *J* = 12.4, 7.6 Hz, 1H), 2.37 (s, 3H), 1.51 (s, 3H), 1.43 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 161.0, 160.9, 143.5, 141.7, 132.7, 130.9, 130.6, 129.6, 129.1, 127.7, 127.4, 127.2, 117.9, 103.6, 49.2, 42.9, 26.9, 26.8, 24.6. HRMS (ESI) calcd for $C_{22}H_{20}ClO_4Na$ ([M+Na]$^+$): 441.0636, Found: 441.0634. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 26.3 min (major), t_{R2} = 32.2 min (minor)]; $[\alpha]^D_{20}$ = 8.35 (c = 1.10, $CHCl_3$).



3la

(*S*)-2,2-Dimethyl-5-(4-phenyl-4-(4-(trifluoromethyl)phenyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3la)

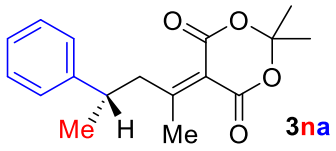
Colorless oil, 76 mg, yield 91%, ee = 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.21 (m, 5H), 4.48 (t, *J* = 8.0 Hz, 1H), 3.88 (dd, *J* = 12.6, 7.6 Hz, 1H), 3.79 (dd, *J* = 12.6, 8.4 Hz, 1H), 2.41 (s, 3H), 1.43 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 161.0, 160.9, 147.2, 142.0, 129.2 (q, *J* = 32.3 Hz), 129.0, 128.1, 127.8, 127.3, 125.7 (q, *J* = 3.0 Hz), 124.0 (q, *J* = 270.2 Hz), 117.9, 103.6, 49.8, 42.8, 26.8, 24.4. HRMS (ESI) calcd for $C_{23}H_{21}F_3O_4Na$ ([M+Na]$^+$): 441.1290, Found: 441.1293. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.5 mL/min; t_{R1} = 46.2 min (major), t_{R2} = 56.6 min (minor)]; $[\alpha]^D_{20}$ = 5.39 (c = 1.37, $CHCl_3$).



3ma

(*R*)-5-(4-Cyclohexyl-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ma)

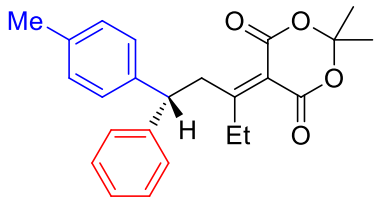
Colorless oil, 65 mg, yield 91%, ee = 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 7.4 Hz, 2H), 7.16 – 7.09 (m, 1H), 7.07 – 7.02 (m, 2H), 3.88 (t, *J* = 12.2 Hz, 1H), 3.00 (dd, *J* = 12.8, 4.0 Hz, 1H), 2.70 (ddd, *J* = 12.0, 8.4, 4.0 Hz, 1H), 2.30 (s, 3H), 2.04 (d, *J* = 12.8 Hz, 1H), 1.84 – 1.77 (m, 1H), 1.69 – 1.57 (m, 3H), 1.59 (s, 3H), 1.35 – 1.23 (m, 3H), 1.15 – 0.98 (m, 2H), 1.04 (s, 3H), 0.83 – 0.73 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.8, 161.18, 161.16, 142.3, 128.6, 128.2, 126.7, 117.2, 103.3, 51.5, 43.5, 41.0, 31.4, 31.2, 27.4, 26.4, 26.3, 26.0, 24.1. HRMS (ESI) calcd for $C_{22}H_{28}O_4Na$ ([M+Na]$^+$): 380.1964, Found: 380.1968. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 14.9 min (major), t_{R2} = 22.2 min (minor)]; $[\alpha]^{D}_{20}$ = 7.03 (c = 1.08, $CHCl_3$).



3na

(*S*)-2,2-Dimethyl-5-(5-phenylhexan-3-ylidene)-1,3-dioxane-4,6-dione (3na)

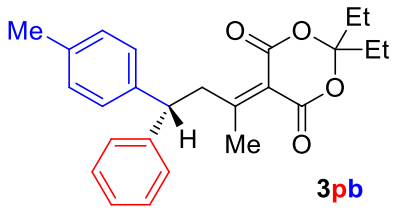
Colorless oil, 53 mg, yield 92%, ee = 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31– 7.27 (m, 2H), 7.21 – 7.17 (m, 3H), 3.49 (dd, *J* = 12.0, 9.2 Hz, 1H), 3.25 – 3.16 (m, 1H), 3.08 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.35 (s, 3H), 1.67 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 3H), 1.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.6, 161.2, 161.0, 145.1, 128.8, 126.9, 126.8, 117.1, 103.4, 46.2, 40.0, 27.4, 26.3, 24.8, 22.7. HRMS (ESI) calcd for $C_{17}H_{20}O_4Na$ ([M+Na]$^+$): 311.1259, Found: 311.1261. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 10.4 min (major), t_{R2} = 15.0 min (minor)]; $[\alpha]^{D}_{20}$ = 12.64 (c = 1.09, $CHCl_3$).



3ob

(*R*)-2,2-Dimethyl-5-(1-phenyl-1-(*p*-tolyl)pentan-3-ylidene)-1,3-dioxane-4,6-dione (3ob)

Colorless oil, 46 mg, yield 61%, ee = 90%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 4H), 7.23 – 7.14 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 4.33 (t, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 8.0 Hz, 2H), 2.73 (q, *J* = 7.4 Hz, 2H), 2.30 (s, 3H), 1.394 (s, 3H), 1.386 (s, 3H), 1.24 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.1, 161.5, 160.6, 143.4, 140.2, 136.4, 129.5, 128.8, 127.7, 127.6, 126.8, 117.4, 103.5, 50.0, 39.8, 29.2, 26.7, 26.6, 21.0, 13.3. HRMS (ESI) calcd for $C_{24}H_{26}O_4Na$ ([M+Na]$^+$): 379.1909, Found: 379.1915. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 47.4 min (minor), t_{R2} = 53.4 min (major)]; $[\alpha]^{D}_{20}$ = 12.64 (c = 1.09, $CHCl_3$).

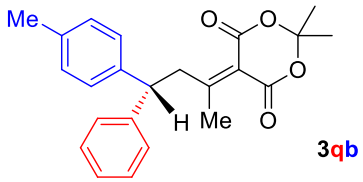


3pb

(*R*)-2,2-Diethyl-5-(4-phenyl-4-(*p*-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3pb)

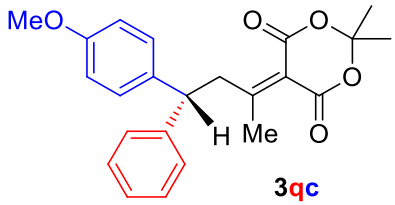
Colorless oil, 48 mg, yield 61%, ee = 91%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 4H), 7.25 – 7.17 (m, 3H), 7.13 – 7.10 (m, 2H) 4.39 (t, *J* = 8.0 Hz, 1H), 3.83 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.79 (dd, *J* = 12.8, 8.0 Hz, 1H), 2.40 (s, 3H), 2.31 (s, 3H), 1.74 – 1.54 (m, 4H), 0.94 (t, *J* = 7.6 Hz, 6H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.9, 161.2, 161.1, 143.4, 140.1, 136.4, 129.4, 128.7, 127.7, 127.6, 126.7, 117.5, 107.4, 49.6, 43.5, 30.04, 30.02, 24.7, 21.0, 7.5. HRMS (ESI) calcd for $C_{25}H_{28}O_4Na$ ([M+Na]$^+$): 415.1885, Found: 415.1885. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 28.7 min (minor), t_{R2} = 31.4 min (major)]; $[\alpha]^{D}_{20}$ = 4.86 (c = 1.11, $CHCl_3$).

5.2 Scope of Arylboronic Acids



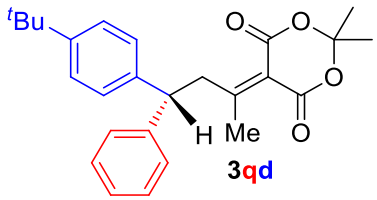
(*R*)-2,2-Dimethyl-5-(4-phenyl-4-(*p*-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3qb)

Colorless oil, 65 mg, yield 91%, ee = 90%. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 46.9 min (minor), t_{R2} = 52.3 min (major)].



(*R*)-5-(4-(4-Methoxyphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qc)

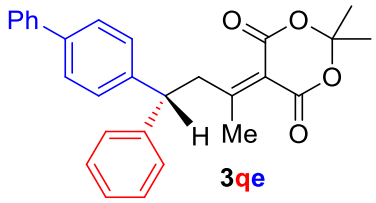
Colorless oil, 69 mg, yield 91%, ee = 89%. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} = 25.1 min (major), t_{R2} = 36.8 min (minor)].



(*R*)-5-(4-(4-(*tert*-Butyl)phenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qd)

Colorless oil, 71 mg, yield 88%, ee = 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.28 (m, 6H), 7.20 – 7.17 (m, 3H), 4.38 (t, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 8.0 Hz, 2H), 2.43 (s,

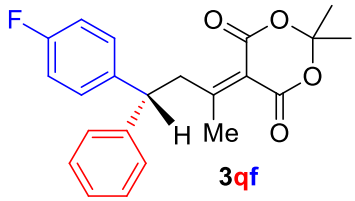
3H), 1.40 (s, 6H), 1.29 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.6, 161.11, 161.09, 149.6, 143.3, 140.0, 128.8, 127.8, 127.3, 126.8, 125.7, 117.7, 103.4, 49.6, 43.1, 34.4, 31.3, 26.8, 26.8, 24.1. HRMS (ESI) calcd for $C_{26}H_{30}O_4Na$ ($[M+Na]^+$): 429.2014, Found: 429.2013. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 16.2 min (major), t_{R2} = 23.3 min (minor)]; $[\alpha]^{D}_{20}$ = -1.19 (c = 1.17, $CHCl_3$).



3qe

(*R*)-5-(4-([1,1'-Biphenyl]-4-yl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qe)

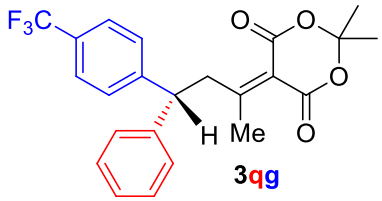
Colorless oil, 42 mg, yield 50%, ee = 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.34 – 7.29 (m, 7H), 7.23 – 7.18 (m, 1H), 4.43 (t, *J* = 8.0 Hz, 1H), 3.92 (dd, *J* = 12.6, 8.4 Hz, 1H), 3.78 (dd, *J* = 12.6, 8.0 Hz, 1H), 2.43 (s, 3H), 1.39 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 161.08, 161.08, 143.0, 142.1, 140.6, 139.8, 128.9, 128.8, 128.2, 127.8, 127.5, 127.3, 127.0, 126.9, 117.8, 103.5, 49.7, 43.0, 26.8, 26.7, 24.3. HRMS (ESI) calcd for $C_{28}H_{26}O_4Na$ ($[M+Na]^+$): 449.1729, Found: 449.172. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 23.8 min (minor), t_{R2} = 26.2 min (major)]; $[\alpha]^{D}_{20}$ = -2.75 (c = 1.09, $CHCl_3$).



3qf

(*R*)-5-(4-(4-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qf)

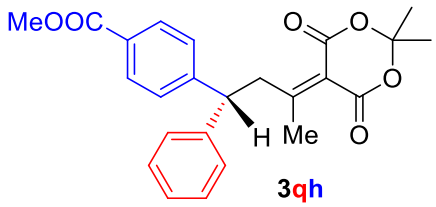
Colorless oil, 55 mg, yield 75%, ee = 87%. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min; t_{R1} = 51.5 min (minor), t_{R2} = 54.0 min (major)].



3qg

(*R*)-2,2-Dimethyl-5-(4-phenyl-4-(4-(trifluoromethyl)phenyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3qg)

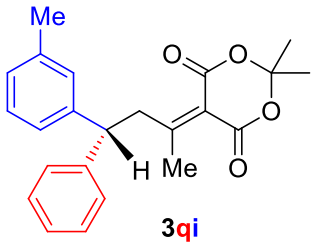
Colorless oil, 43 mg, yield 51%, ee = 90%. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.5 mL/min; t_{R1} = 52.5 min (minor), t_{R2} = 64.3 min (major)].



3qh

(*R*)-Methyl4-(3-(2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-ylidene)-1-phenylbutyl)-benzoate (3qh)

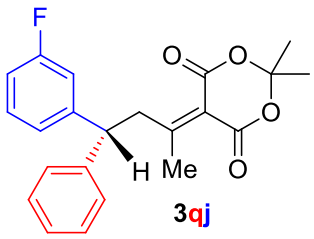
Colorless oil, 35 mg, yield 43%, ee = 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.19 (m, 7H), 4.46 (t, *J* = 7.8 Hz, 1H), 3.94 – 3.71 (m, 2H), 3.90 (s, 3H), 2.38 (s, 3H), 1.46 (s, 3H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 166.7, 161.0, 160.9, 148.4, 142.1, 130.1, 129.0, 128.8, 127.8, 127.2, 117.8, 103.5, 52.1, 50.0, 42.9, 26.9, 26.8, 24.5. HRMS (ESI) calcd for $C_{24}H_{25}O_6$ ($[M+H]^+$): 409.1651, Found: 409.1655. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.5 mL/min; t_{R1} = 47.5 min (major), t_{R2} = 53.2 min (minor)]; $[\alpha]^{D}_{20}$ = -11.95 (c = 1.07, $CHCl_3$).



3qi

(*R*)-2,2-Dimethyl-5-(4-phenyl-4-(*m*-tolyl)butan-2-ylidene)-1,3-dioxane-4,6-dione (3qi)

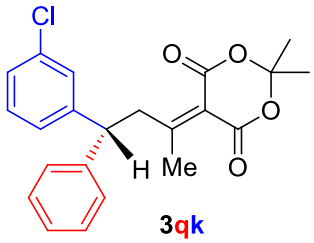
Colorless oil, 67 mg, yield 92%, ee = 91%. HPLC [Daicel Chiralcel AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.50 mL/min. t_{R1} = 34.6 min (minor), t_{R2} = 36.8 min (major)].



3qj

(*R*)-5-(4-(3-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qj)

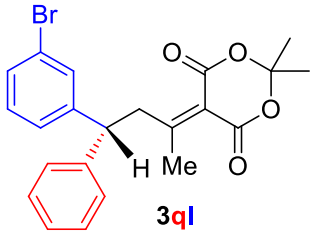
Colorless oil, 55 mg, yield 75%, ee = 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.04 – 6.97 (m, 1H), 6.94 – 6.87 (m, 1H), 4.41 (t, *J* = 8.0 Hz, 1H), 3.84 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.74 (dd, *J* = 12.8, 7.6 Hz, 1H), 2.39 (s, 3H), 1.50 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.9, 162.9 (d, *J* = 246.5 Hz), 160.99, 160.98, 145.7 (d, *J* = 6.8 Hz), 142.3, 130.2 (d, *J* = 8.3 Hz), 128.9, 127.8, 127.2, 123.4 (d, *J* = 2.8 Hz), 117.8, 114.7 (d, *J* = 21.7 Hz), 113.8 (d, *J* = 21.0 Hz), 103.6, 49.7, 43.0, 26.9, 26.8, 24.4. HRMS (ESI) calcd for $C_{22}H_{22}FO_4$ ($[M+H]^+$): 369.1502, Found: 369.1508. HPLC [Daicel Chiralcel AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min. t_{R1} = 18.4 min (minor), t_{R2} = 20.8 min (major)]; $[\alpha]^{D}_{20}$ = -6.73 (c = 1.15, $CHCl_3$).



3qk

(*S*)-5-(4-(3-Chlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qk)

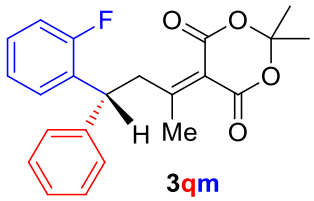
Colorless oil, 39 mg, yield 51%, ee = 92%. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 26.5 min (minor), t_{R2} = 31.3 min (major)].



3ql

(*R*)-5-(4-(3-Bromophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3ql)

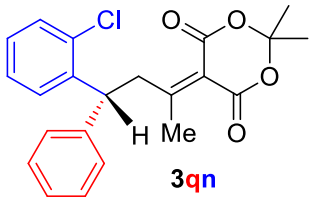
Colorless oil, 48 mg, yield 56%, ee = 91%. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 28.6 min (minor), t_{R2} = 34.7 min (major)].



3qm

(*R*)-5-(4-(2-Fluorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qm)

Colorless oil, 20 mg, yield 28%, ee = 95%. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 20.3 min (major), t_{R2} = 23.7 min (minor)].

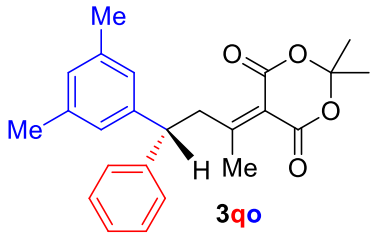


3qn

(*R*)-5-(4-(2-Chlorophenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qn)

Colorless oil, 23 mg, yield 30%, ee = 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.26 – 7.19 (m, 2H), 7.15 (td, *J* = 7.6, 1.6 Hz, 1H), 5.04 (t, *J* = 8.0 Hz, 1H), 3.94 (dd, *J* = 13.2, 8.4 Hz, 1H), 3.73 (dd, *J* = 13.2, 7.6 Hz, 1H), 2.49 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.8, 161.1, 161.0, 141.6, 140.5, 133.6, 129.9, 129.0, 128.8, 128.06, 128.05, 127.4, 127.1,

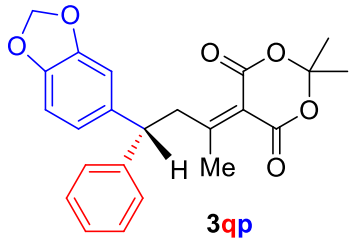
117.8, 103.5, 45.1, 42.0, 26.9, 26.8, 23.8. HRMS (ESI) calcd for $C_{22}H_{21}ClO_4Na$ ([M+Na]$^+$): 407.1026, Found: 407.1023. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 15.2 min (major), t_{R2} = 22.2 min (minor)]; $[\alpha]^D_{20}$ = 12.3 (c = 1.07, $CHCl_3$).



3qo

(*R*)-5-(4-(3,4-Dimethylphenyl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qo)

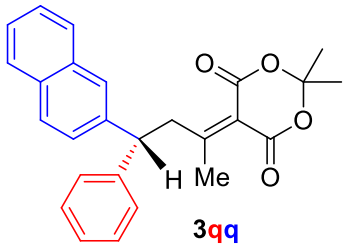
Colorless oil, 55 mg, yield 73%, ee = 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 2H), 7.24 – 7.13 (m, 2H), 6.87 (s, 2H), 6.82 (d, *J* = 9.2 Hz, 2H), 4.29 (t, *J* = 8.0 Hz, 1H), 3.82 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.73 (dd, *J* = 12.8, 8.0 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 6H), 1.39 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 161.1, 161.1, 143.3, 142.9, 138.2, 128.8, 128.7, 127.7, 126.8, 117.7, 125.5, 103.5, 49.9, 43.0, 26.6, 24.2, 21.3. HRMS (ESI) calcd for $C_{24}H_{26}O_4Na$ ([M+Na]$^+$): 401.1729, Found: 401.1730. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 12.8 min (minor), t_{R2} = 15.1 min (major)]; $[\alpha]^D_{20}$ = -0.77 (c = 0.78, $CHCl_3$).



3qp

(*R*)-5-(4-(Benzo[d][1,3]dioxol-5-yl)-4-phenylbutan-2-ylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (3qp)

Colorless oil, 66 mg, yield 84%, ee = 86%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 5H), 6.79 – 6.70 (m, 3H), 5.91 (d, *J* = 5.4 Hz, 2H), 4.34 (t, *J* = 8.0 Hz, 1H), 3.78 (dd, *J* = 12.8, 8.0 Hz, 1H), 3.74 (dd, *J* = 12.8, 8.0 Hz, 1H), 2.40 (s, 3H), 1.50 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 161.1, 161.0, 147.9, 146.4, 143.1, 137.0, 128.8, 127.6, 126.9, 120.7, 117.7, 108.33, 108.26, 103.5, 101.0, 49.6, 43.2, 26.8, 26.8, 24.4. HRMS (ESI) calcd for $C_{23}H_{22}O_6Na$ ([M+Na]$^+$): 417.1314, Found: 417.1318. HPLC [DAICEL CHIRALPAK AS-H, hexane/*i*-PrOH = 95/5, 254 nm, 1.0 mL/min; t_{R1} = 30.7 min (major), t_{R2} = 40.3 min (minor)]; $[\alpha]^D_{20}$ = -0.77 (c = 0.78, $CHCl_3$).



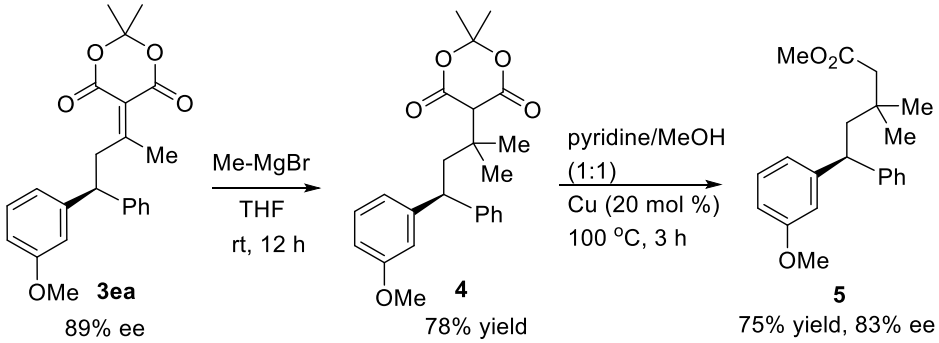
3qq

(*R*)-2,2-Dimethyl-5-(4-(naphthalen-2-yl)-4-phenylbutan-2-ylidene)-1,3-dioxane-

4,6-dione (3qq)

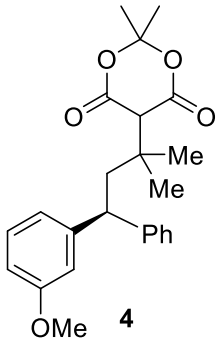
Colorless solid, 64 mg, yield 80%, ee = 93%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.72 (m, 4H), 7.58 – 7.42 (m, 2H), 7.39 – 7.24 (m, 5H), 7.22 (m, 1H), 4.58 (t, *J* = 8.0 Hz, 1H), 4.05 (dd, *J* = 12.8, 8.4 Hz, 1H), 3.86 (dd, *J* = 12.8, 7.8 Hz, 1H), 2.47 (s, 3H), 1.37 (s, 3H), 1.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 161.07, 161.05, 142.9, 140.4, 133.5, 132.4, 128.8, 128.6, 127.8, 127.8, 127.5, 127.0, 126.4, 126.3, 125.9, 125.8, 117.8, 103.5, 50.0, 42.8, 26.8, 26.4, 24.4. HRMS (ESI) calcd for $C_{26}H_{24}O_4Na$ ([M+Na]$^+$): 423.1572, Found: 423.1573. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.5 mL/min; t_{R1} = 35.4 min (major), t_{R2} = 45.3 min (minor)]; $[\alpha]^{D}_{20}$ = -12.26 (c = 1.14, $CHCl_3$).

6. Transformations



According to a reported procedure.[6] Under nitrogen atmosphere, Me-MgBr (3.0 M in Et_2O, 0.08 mL, 0.24 mmol, 1.2 equiv.) was added dropwise to a solution of **3ea** (76 mg, 0.2 mmol) in anhydrous THF (2.0 mL) was cooled to 0 °C. The resulting solution was allowed to warm to rt and stirred for 12 hours. Then 5% aq. HCl and EtOAc were added to the reaction mixture. The layers were partitioned and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with water, dried over anhydrous $MgSO_4$, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to yield the desired product **4**.

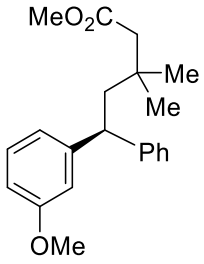
To a mixture of **4** (63 mg, 0.16 mmol) and copper powder (2.0 mg, 0.032 mmol, 0.2 equiv.), a mix solvent of pyridine/methanol (10:1, 0.1 M) was added. The resulting mixture was heated to 100 °C and stirred for 3 hours. After cooled to rt, the solvent was removed by vacuum evaporation. Purification via flash column chromatography using silica gel while eluting with hexanes : EtOAc (10:1) afforded **5** as a colorless oil in 75% yield.



4

(*S*)-5-(4-(3-Methoxyphenyl)-2-methyl-4-phenylbutan-2-yl)-2,2-dimethyl-1,3-dioxane-4,6-dion (4)

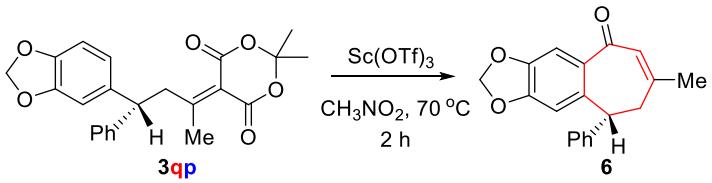
Colorless oil, 63 mg, yield 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 4H), 7.23 – 7.10 (m, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.86 (s, 1H), 6.68 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.12 (t, *J* = 7.2 Hz, 1H), 3.77 (s, 3H), 3.19 (s, 1H), 2.71 (dd, *J* = 14.6, 7.6 Hz, 1H), 2.56 (dd, *J* = 14.6, 6.8 Hz, 1H), 1.59 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 163.9, 160.1, 147.2, 145.6, 130.0, 129.0, 127.9, 126.7, 120.4, 113.6, 112.1, 104.2, 55.4, 54.4, 48.2, 45.4, 37.2, 28.8, 26.6, 26.5, 26.4. The ee of compound **4** could not be detected by HPLC using any of our chiral columns.



5

(*S*)-Methyl 5-(3-methoxyphenyl)-3,3-dimethyl-5-phenylpentanoate (5)

Colorless oil, 49 mg, yield 75%, ee = 83%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.26 (m, 4H), 7.24 – 7.12 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 2.0 Hz, 1H), 6.71 (dd, *J* = 7.8, 2.2 Hz, 1H), 4.07 (t, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 3H), 2.28 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.24 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.17 (s, 2H), 0.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 159.6, 147.8, 146.0, 129.4, 128.5, 127.7, 126.1, 120.2, 114.0, 110.8, 55.1, 51.1, 48.0, 47.2, 46.1, 34.1, 28.1. HRMS (ESI) calcd for $C_{21}H_{27}O_3Na$ ([M+Na]$^{+}$): 349.1780, Found: 349.1783. HPLC [ENANTIOPAK SCDP, Hexane/*i*-PrOH = 90/10, 254 nm, 1.0 mL/min; t_{R1} =14.4 min (minor), t_{R2} = 17.4 min (major)]; $[\alpha]^{D}_{20}$ = 8.06 (c = 1.10, $CHCl_3$).



3qp

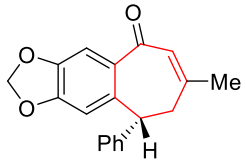
ee = 86%

6

yield = 35% ee = 81%

According to a reported procedure.[7] $Sc(OTf)_3$ (20 mg, 0.040 mmol, 20 mol%) and **3qp** (79 mg, 0.20 mmol) were added to a Schlenk tube. The Schlenk tube was charged

with 2 mL CH_3NO_2 (dried before used). The reaction mixture was then placed in a pre-heated bath at 70 ºC. After 2 hours, the crude mixture was concentrated and purified by flash column chromatography on silica gel using petroleum ether : EtOAc (5:1) to afford a light yellow oil in 35% yield.



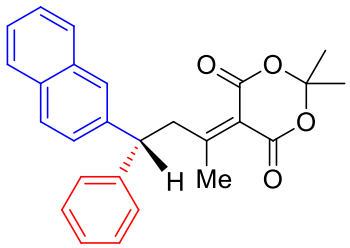
6

(*R*)-7-Methyl-9-phenyl-8,9-dihydro-5*H*-cyclohepta[4,5]benzo[1,2-*d*][1,3]dioxol-5-one (6)

Light yellow oil, 21 mg, yield 35%, ee = 81%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.26 (m, 3H), 7.25 – 7.18 (m, 3H), 6.75 – 6.69 (m, 2H), 5.94 – 5.87 (m, 2H), 4.53 (t, *J* = 7.6 Hz, 1H), 3.15 (d, *J* = 7.6 Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 147.8, 146.1, 143.9, 137.8, 128.6, 127.5, 126.5, 120.6, 108.3, 108.2, 100.9, 49.8, 45.7, 30.7. HPLC [DAICEL CHIRALPAK AD-H, hexane/*i*-PrOH = 95/5, 254 nm, 0.5 mL/min; t_{R1} = 21.1 min (major), t_{R2} = 24.9 min (minor)]; $[\alpha]^{D}_{20}$ = 3.26 (c = 1.11, $CHCl_3$). The number of observed carbons is lower due to an expected overlap of some of the carbon peaks.

7. Single Crystal of Enantioenriched 3qq

Colorless crystals of **3qq** suitable for X-ray crystallographic analysis were obtained by recrystallization from *i*-PrOH in fridge. The ORTEP drawing of **(*R*)-3qq** is shown in Figure S1. The crystal structure has been deposited at the Cambridge Crystallographic Centre (deposition number: CCDC 1813609).



(*R*)-2,2-Dimethyl-5-(4-(naphthalen-2-yl)-4-phenylbutan-2-ylidene)-1,3-dioxane-4,6-dione (3qq)

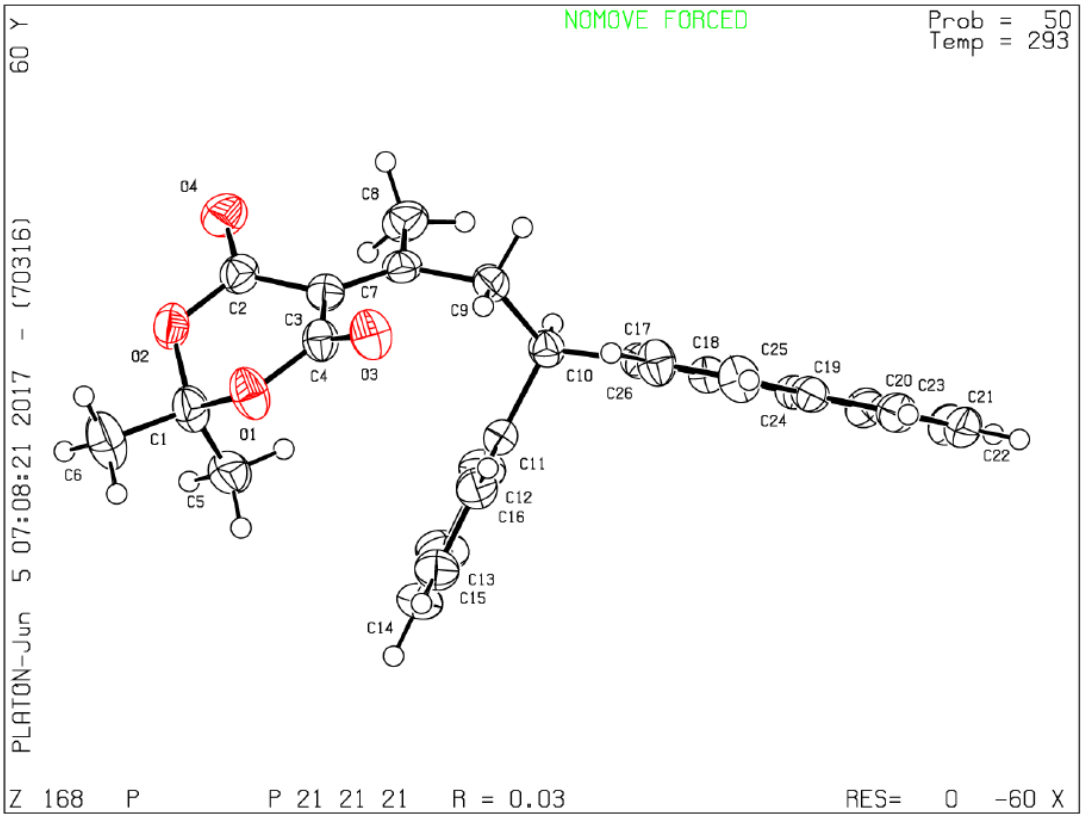


Figure S1

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) P

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: P

Bond precision: C-C = 0.0025 A Wavelength=1.54178

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alpha=90 beta=90 gamma=90
Temperature: 293 K

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Hall group	P 2ac 2ab	P 2ac 2ab
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Sum formula	C26 H24 O4	C26 H24 O4
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F000'	850.57	
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Correction method= Not given

Data completeness= 1.73/1.00 Theta(max)= 66.619

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S = 1.090 Npar= 275

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Click on the hyperlinks for more details of the test.

8. References

1. C. Liu, J. Yi, Z. Zheng, Y. Tang, L. Dai and S.-L You, *Angew. Chem. Int. Ed.*, 2016, **55**, 751.
2. A. Kopernikua, A. Foscolosa, I. Papanastasioua, G. B. Foscolosa, A. Tsotinisa and D. Schols, *Lett. Org. Chem.*, 2016, **13**, 171.
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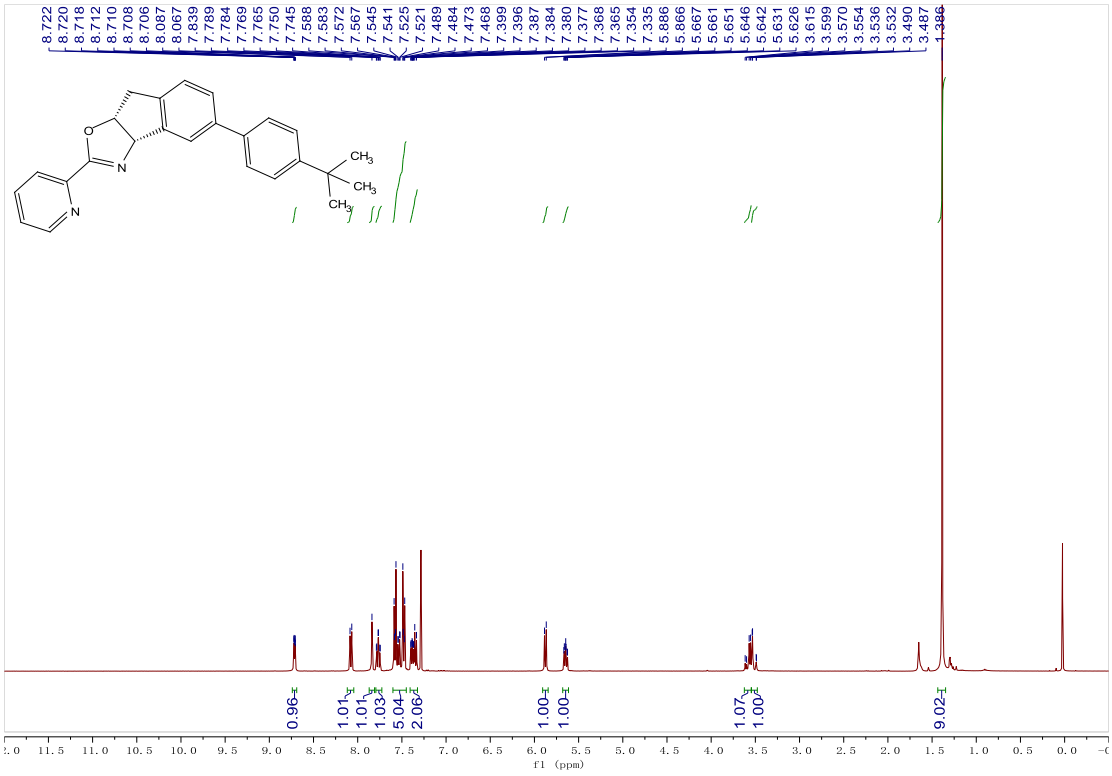
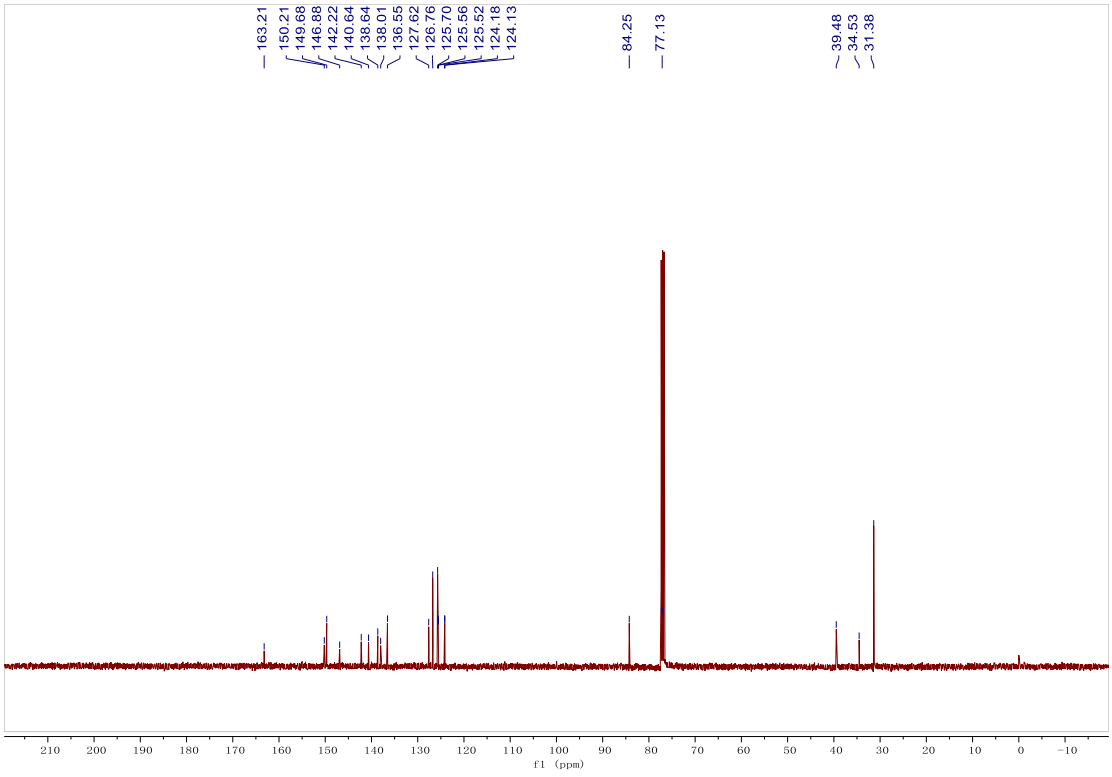
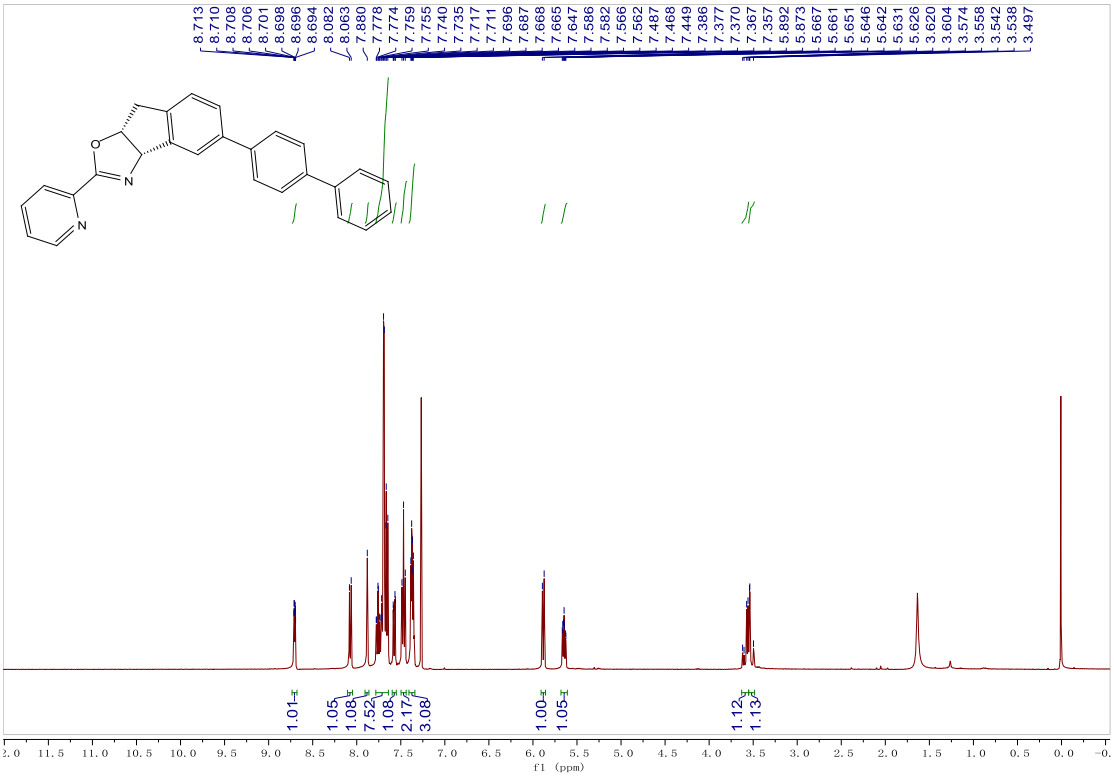
5. E. Fillion, A. Wilsiky and E. Liao, *Tetrahedron: Asymmetry*, 2006, **17**, 2957.
6. A. Wilsiky and E. Fillion, *Org. Lett.*, 2008, **13**, 2801.
7. E. Fillion and A. Wilsiky, *J. Am. Chem. Soc.*, 2006, **128**, 2774.

9. NMR and HPLC Spectra Charts



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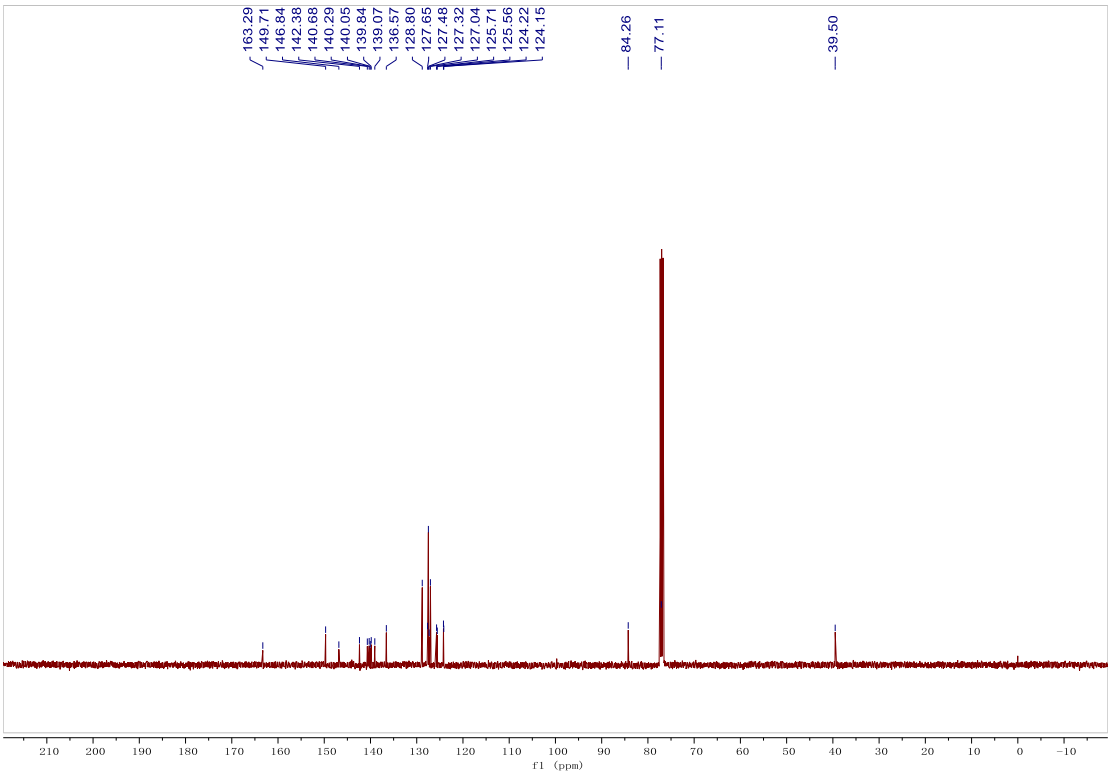
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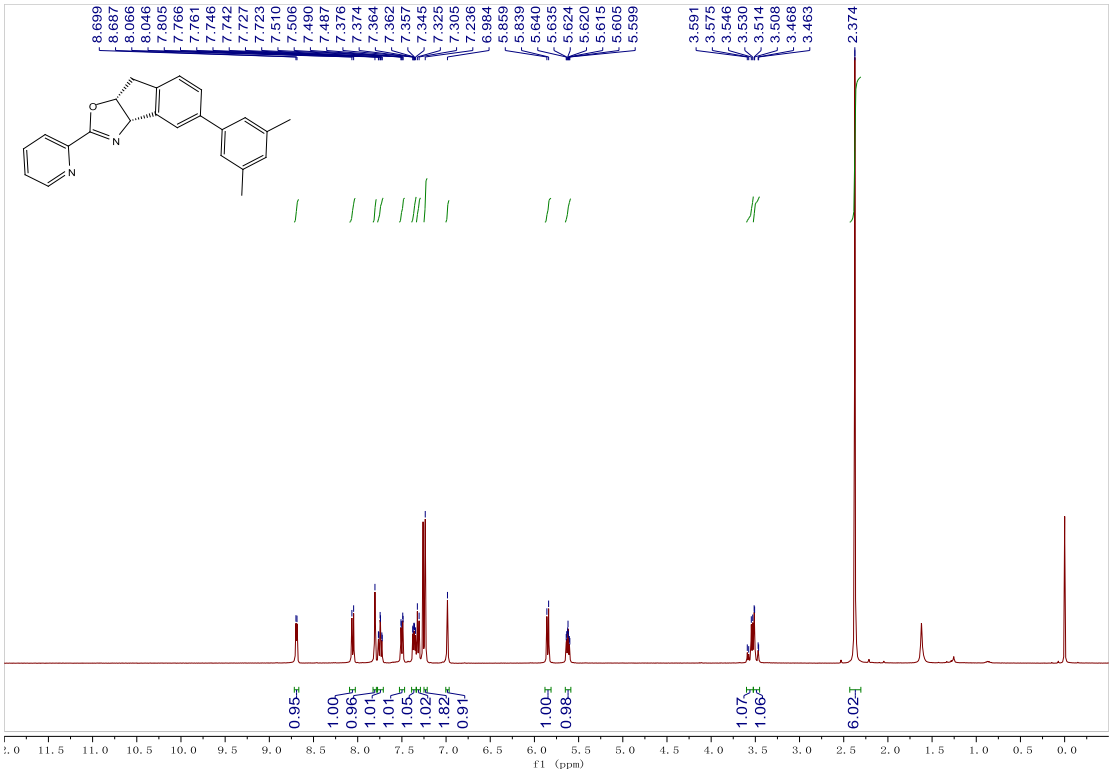
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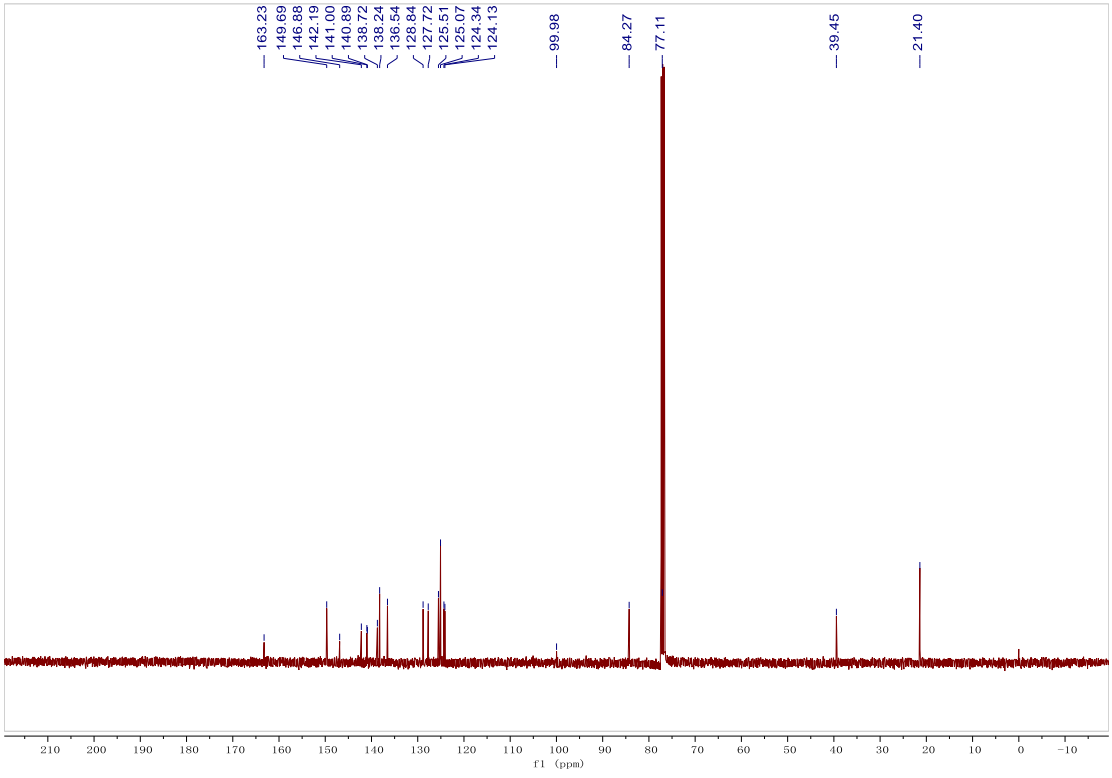
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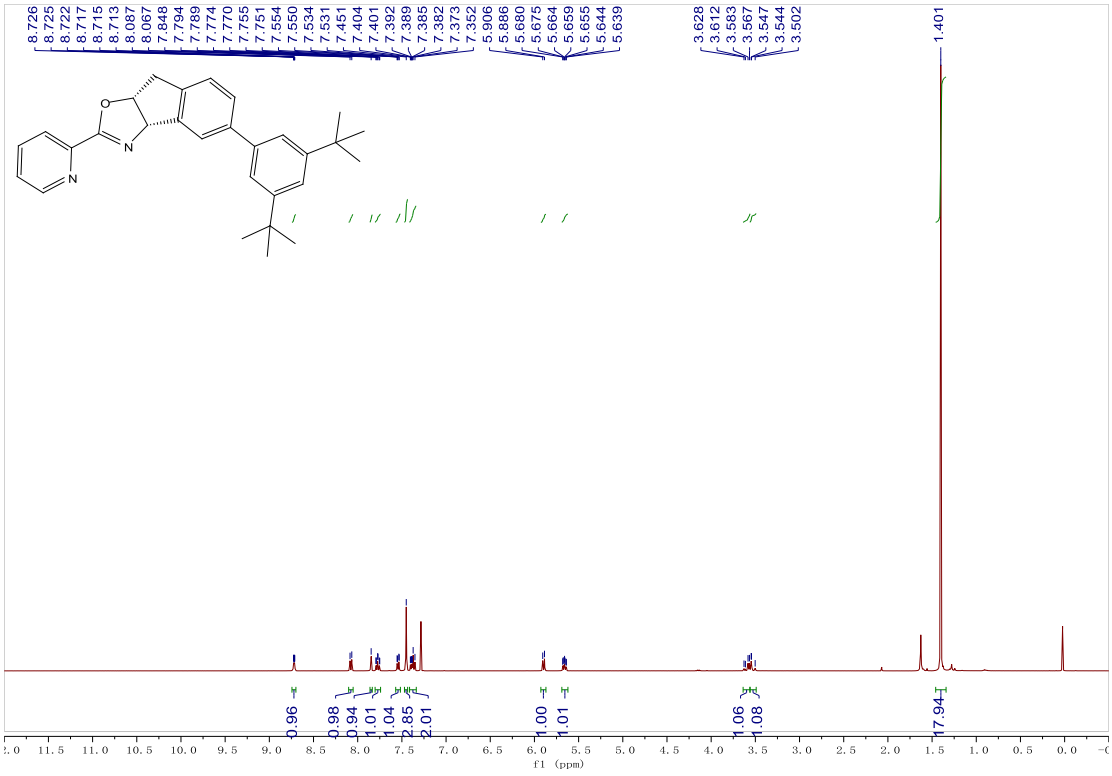
f1 (ppm)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8.067
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7.770
7.755
7.751
7.554
7.550
7.534
7.531
7.451
7.404
7.401
7.392
7.389
7.385
7.382
7.373
7.352
5.906
5.886
5.680
5.675
5.664
5.659
5.655
5.644
5.639
3.628
3.612
3.583
3.567
3.547
3.544
3.502
1.401
O
N
N
0.96
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1.04
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1.00
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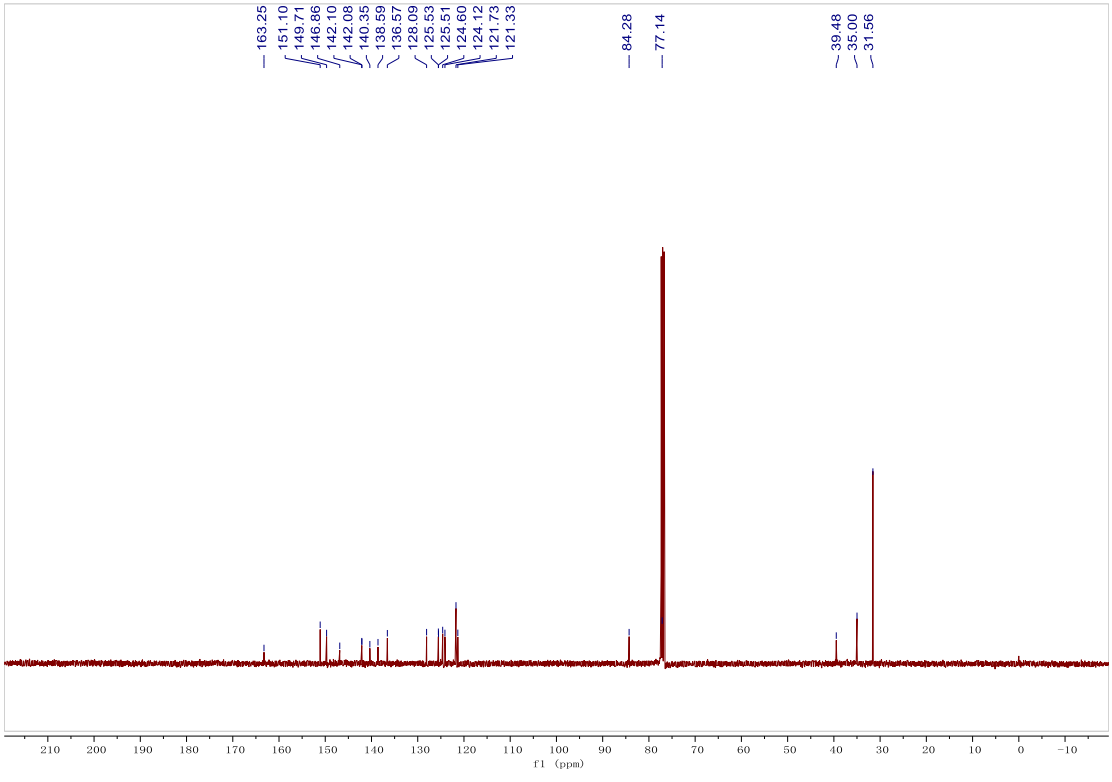
1.06
1.08
17.94
f1 (ppm)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125.51
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124.12
121.73
121.33
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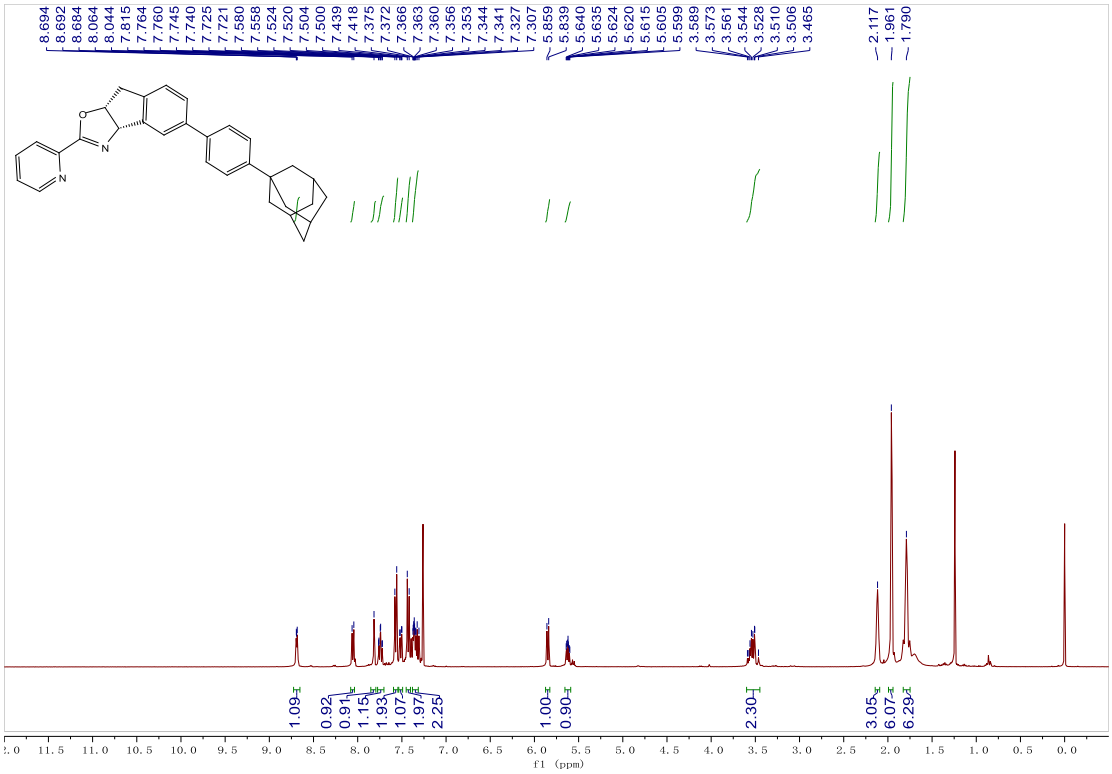
77.14
39.48
35.00
31.56
f1 (ppm)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7.725
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7.580
7.558
7.524
7.520
7.504
7.500
7.439
7.418
7.375
7.372
7.366
7.363
7.360
7.356
7.353
7.344
7.341
7.327
7.307
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5.839
5.640
5.635
5.624
5.620
5.615
5.605
5.599
3.589
3.573
3.561
3.544
3.528
3.510
3.506
3.465
2.117
1.961
1.790
1.09
0.92
0.91
1.15
1.93
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0.90
2.30
3.05
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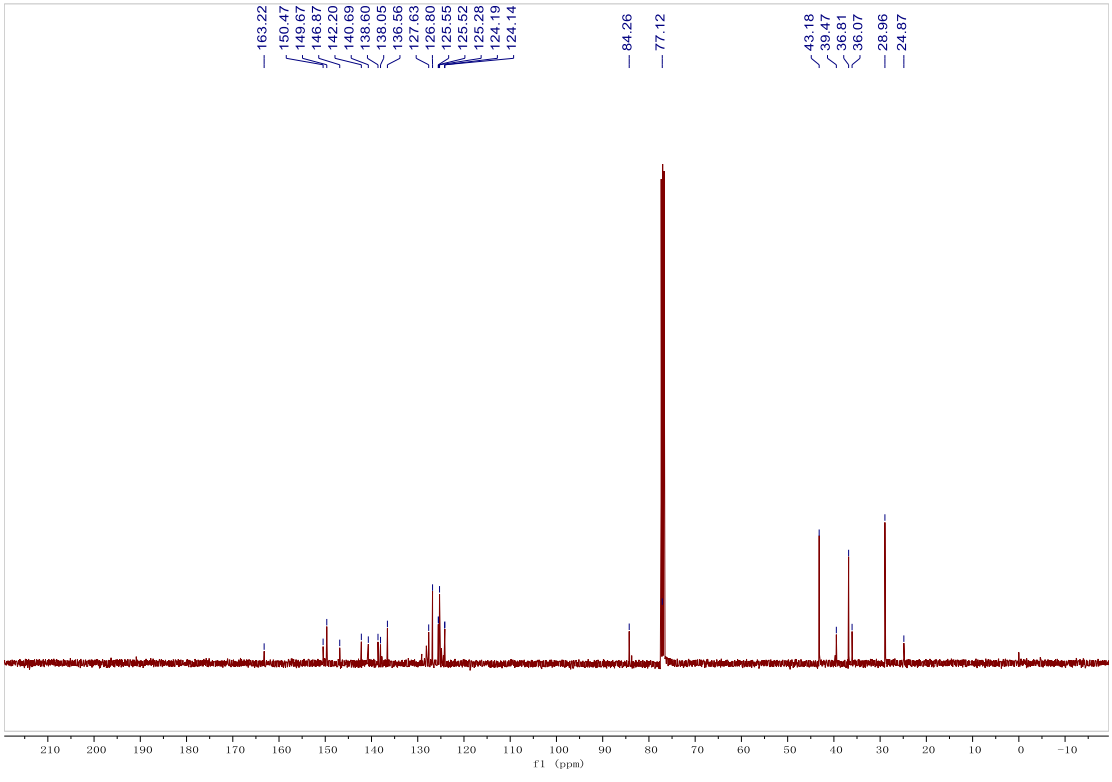
6.29
f1 (ppm)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125.52
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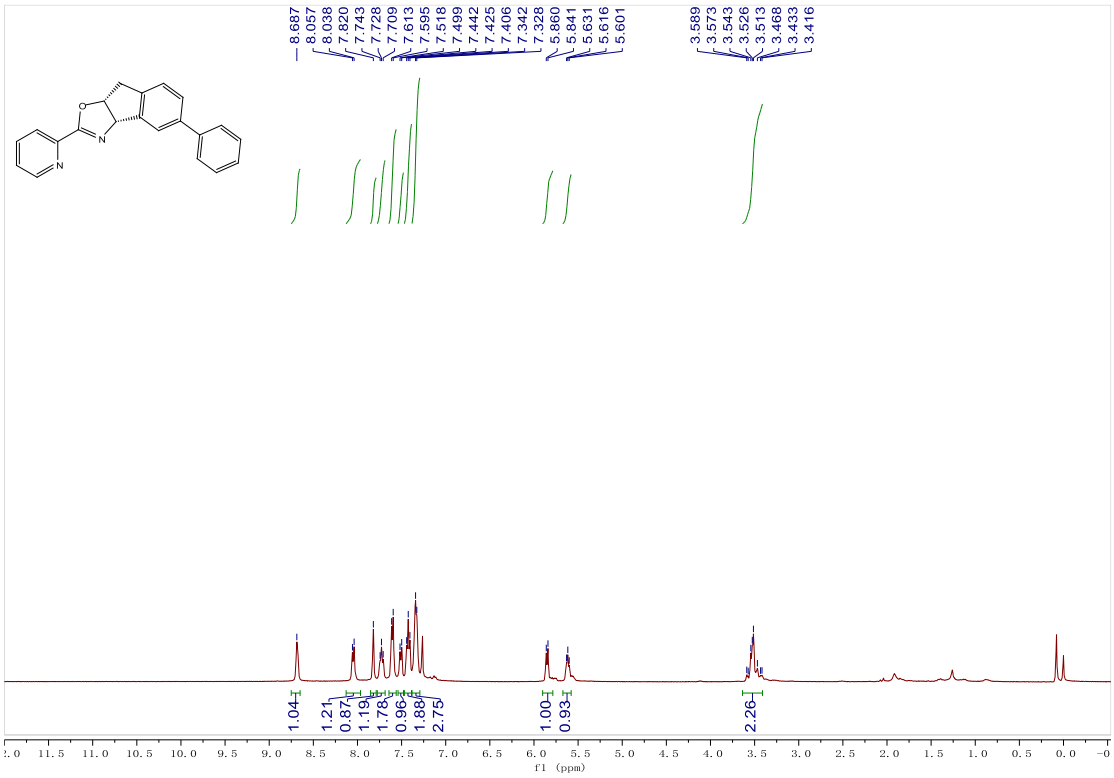
24.87
f1 (ppm)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7.613
7.595
7.518
7.499
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7.425
7.406
7.342
7.328
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5.841
5.631
5.616
5.601
3.589
3.573
3.543
3.526
3.513
3.468
3.433
3.416
O
N
N
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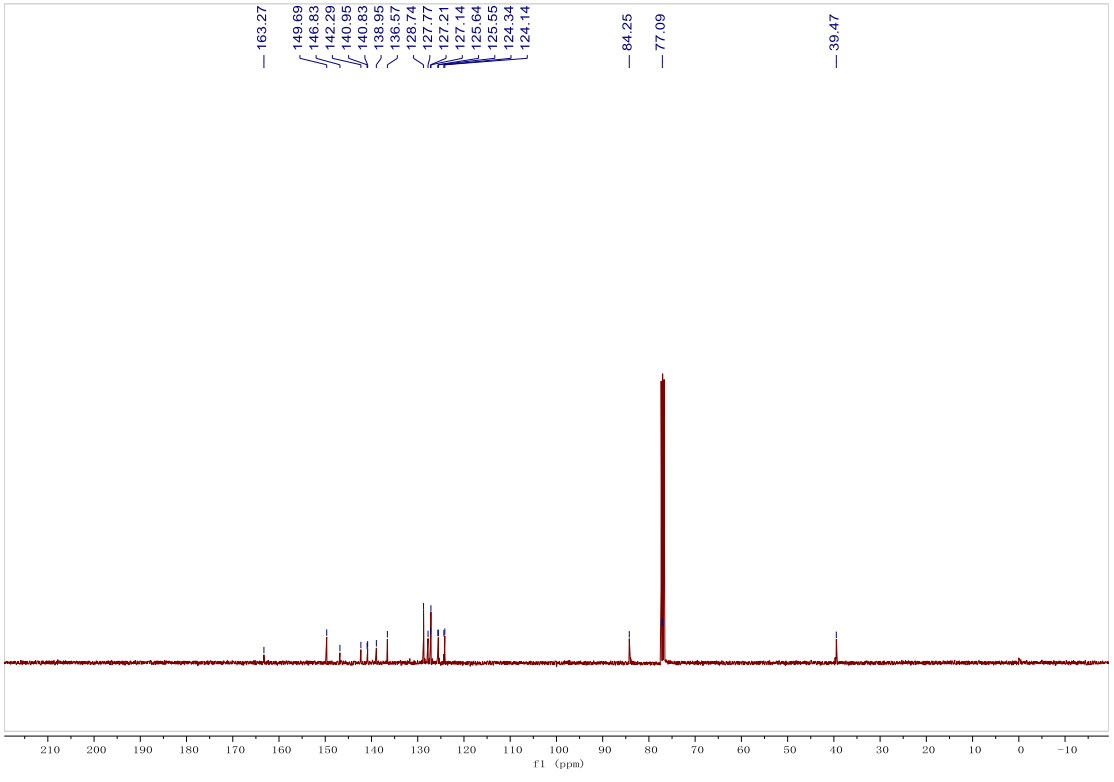
2.26
f1 (ppm)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125.55
124.34
124.14
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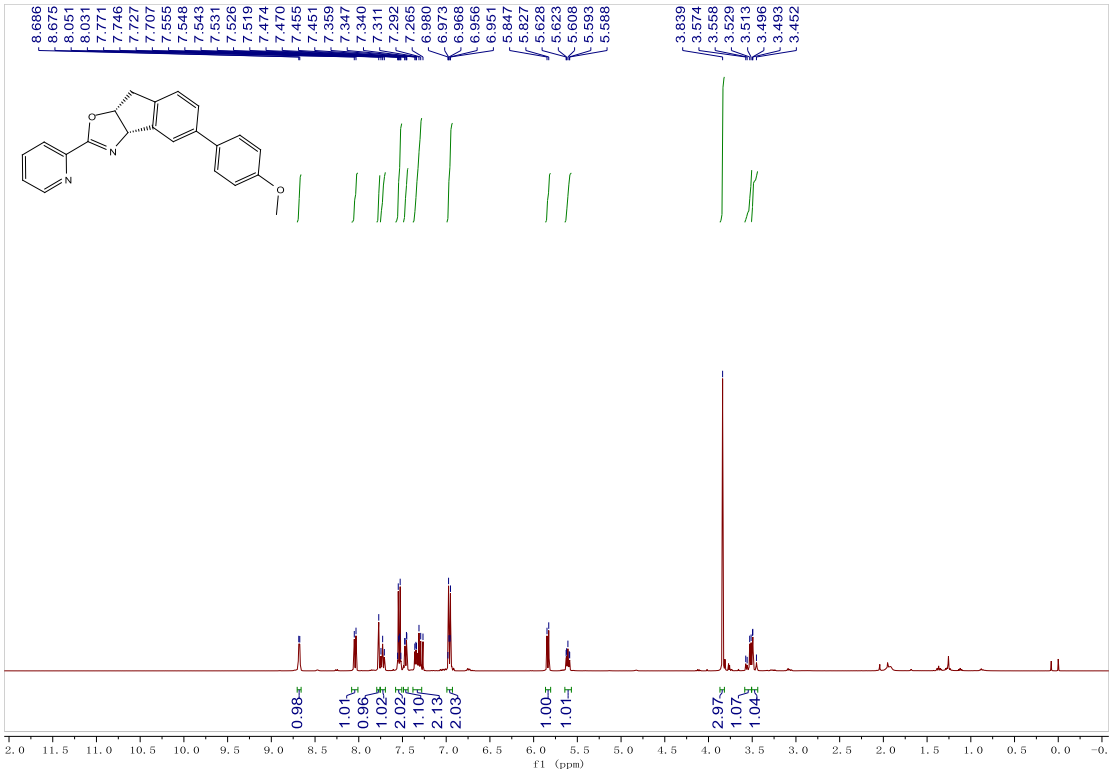
77.09
39.47
f1 (ppm)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7.543
7.531
7.526
7.519
7.474
7.470
7.455
7.451
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7.347
7.340
7.311
7.292
7.265
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6.973
6.968
6.956
6.951
5.847
5.827
5.628
5.623
5.608
5.593
5.588
3.839
3.574
3.558
3.529
3.513
3.496
3.493
3.452
O
N
N
O
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1.01
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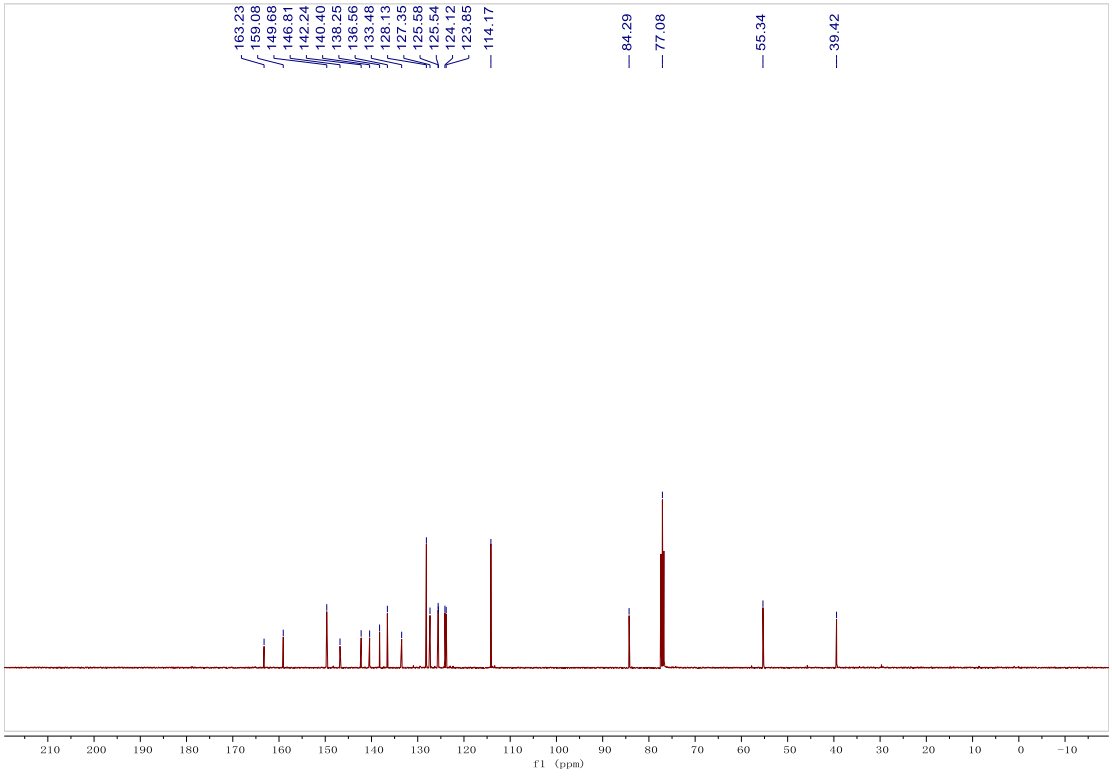
1.10
2.13
2.03
1.00
1.01
2.97
1.07
1.04
f1 (ppm)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136.56
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125.54
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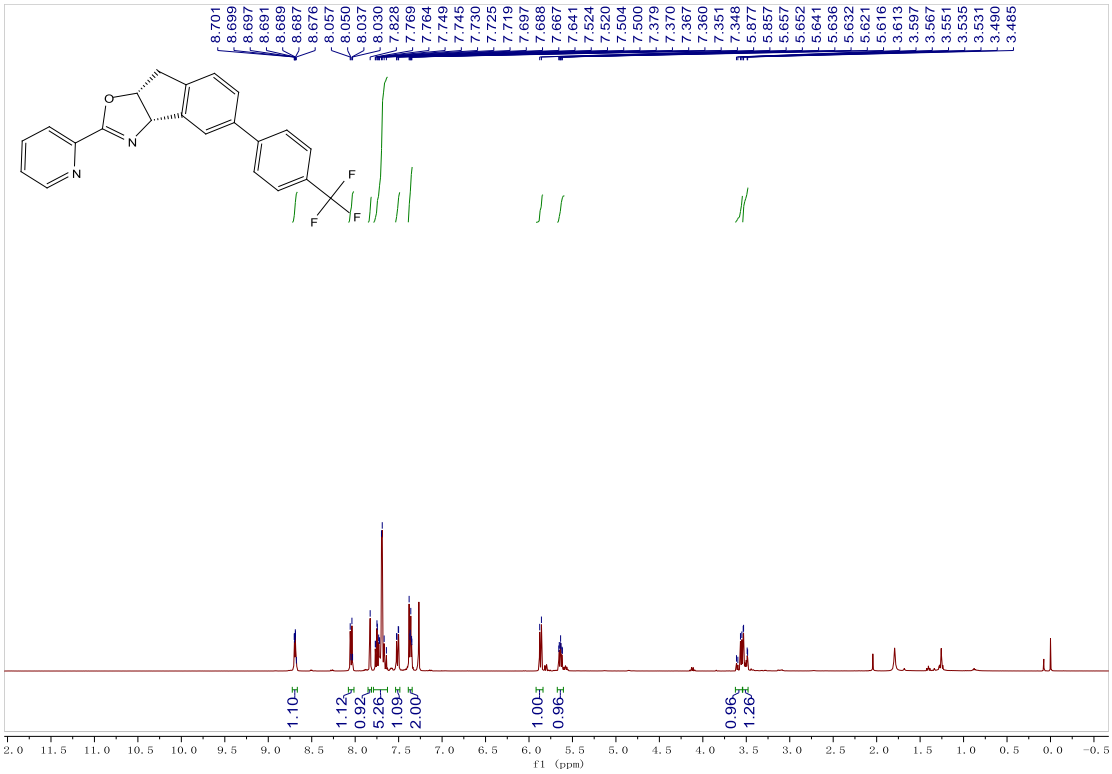
123.85
114.17
84.29
77.08
55.34
39.42
f1 (ppm)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7.745
7.730
7.725
7.719
7.697
7.688
7.667
7.641
7.524
7.520
7.504
7.500
7.379
7.370
7.367
7.360
7.351
7.348
5.877
5.857
5.657
5.652
5.641
5.636
5.632
5.621
5.616
3.613
3.597
3.567
3.551
3.535
3.531
3.490
3.485
O
N
N
F
F
F
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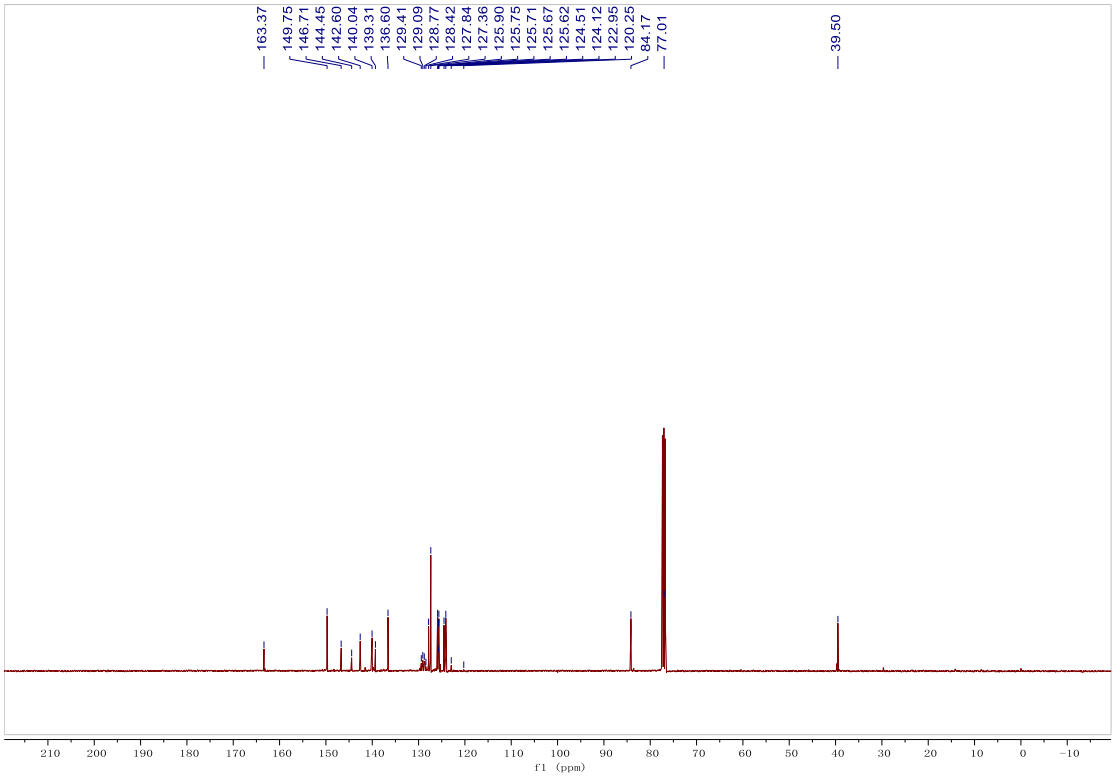
1.26
f1 (ppm)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127.36
125.90
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125.71
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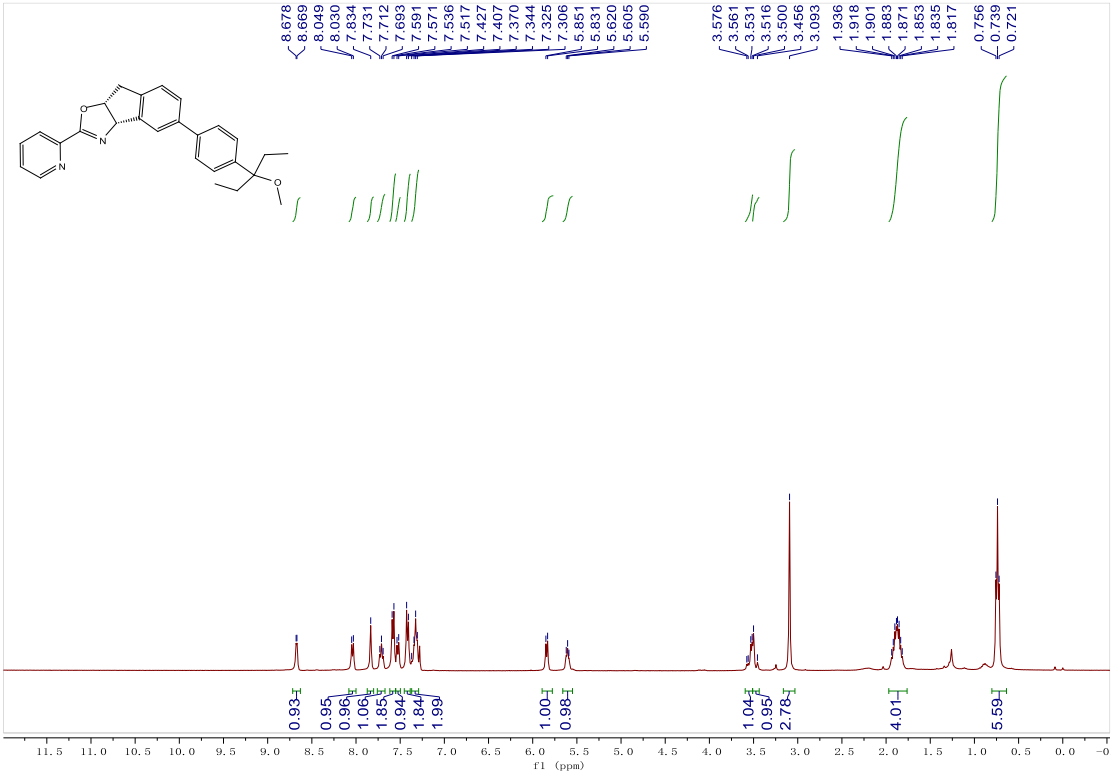
125.62
124.51
124.12
122.95
120.25
84.17
77.01
39.50
f1 (ppm)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5.590
3.576
3.561
3.531
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3.500
3.456
3.093
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1.918
1.901
1.883
1.871
1.853
1.835
1.817
0.756
0.739
0.721
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O
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0.95
0.96
1.06
1.85
0.94
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1.99
1.00
0.98
1.04
0.95
2.78
4.01
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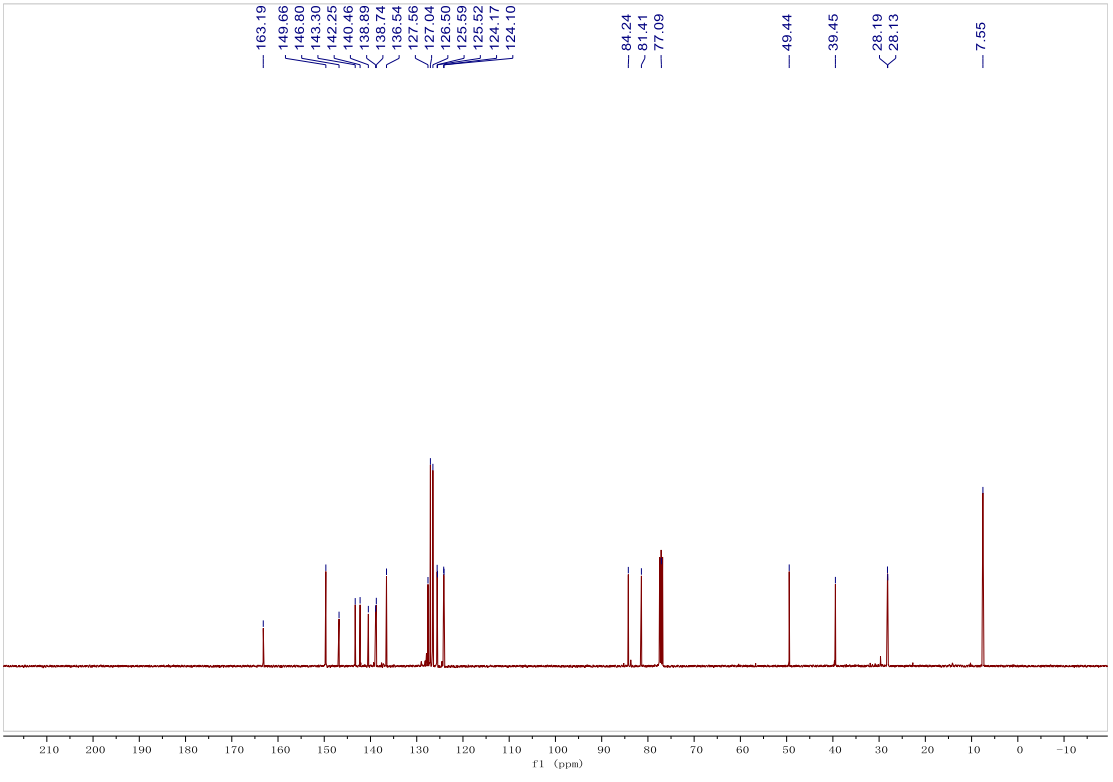
f1 (ppm)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127.04
126.50
125.59
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124.10
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77.09
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39.45
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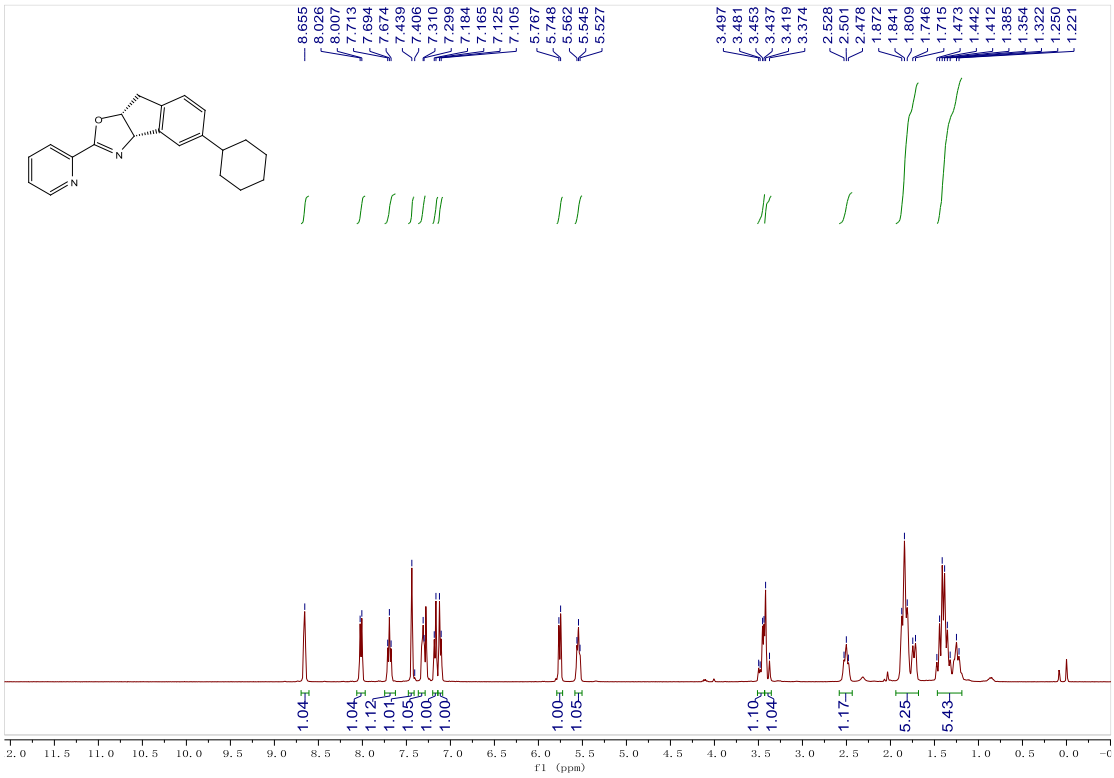
28.13
7.55
f1 (ppm)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7.165
7.125
7.105
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5.748
5.562
5.545
5.527
3.497
3.481
3.453
3.437
3.419
3.374
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2.501
2.478
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1.715
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1.385
1.354
1.322
1.250
1.221
1.04
1.04
1.12
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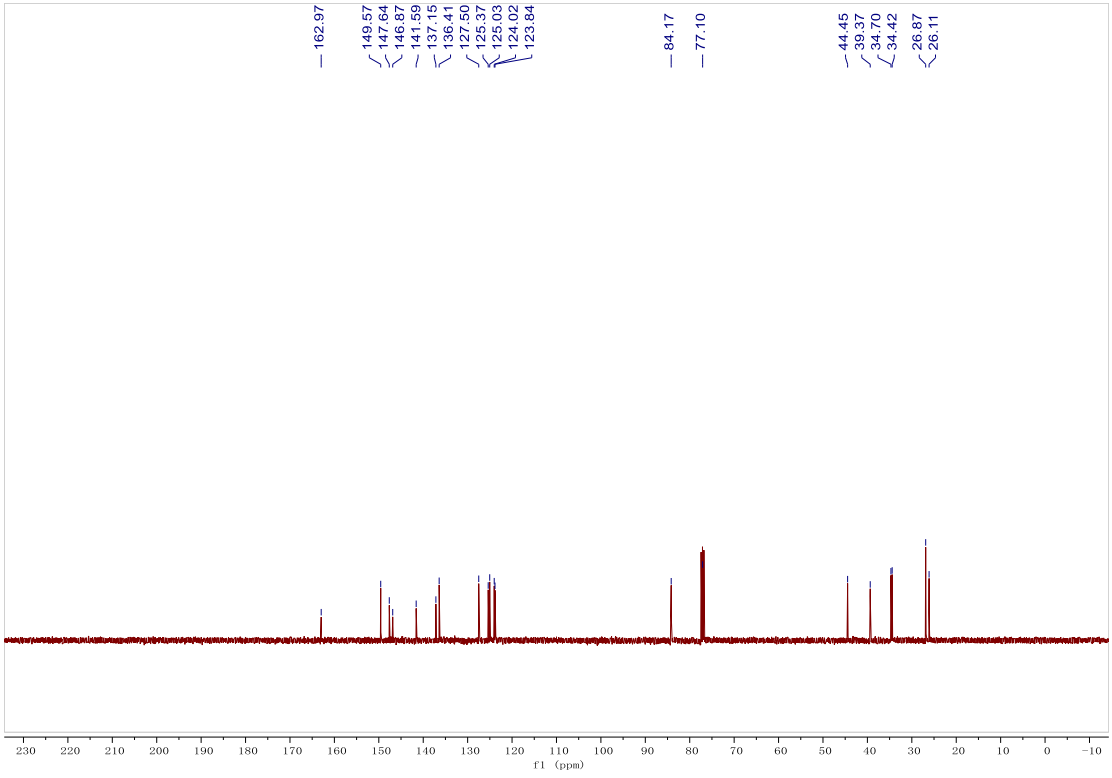
5.43
f1 (ppm)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34.42
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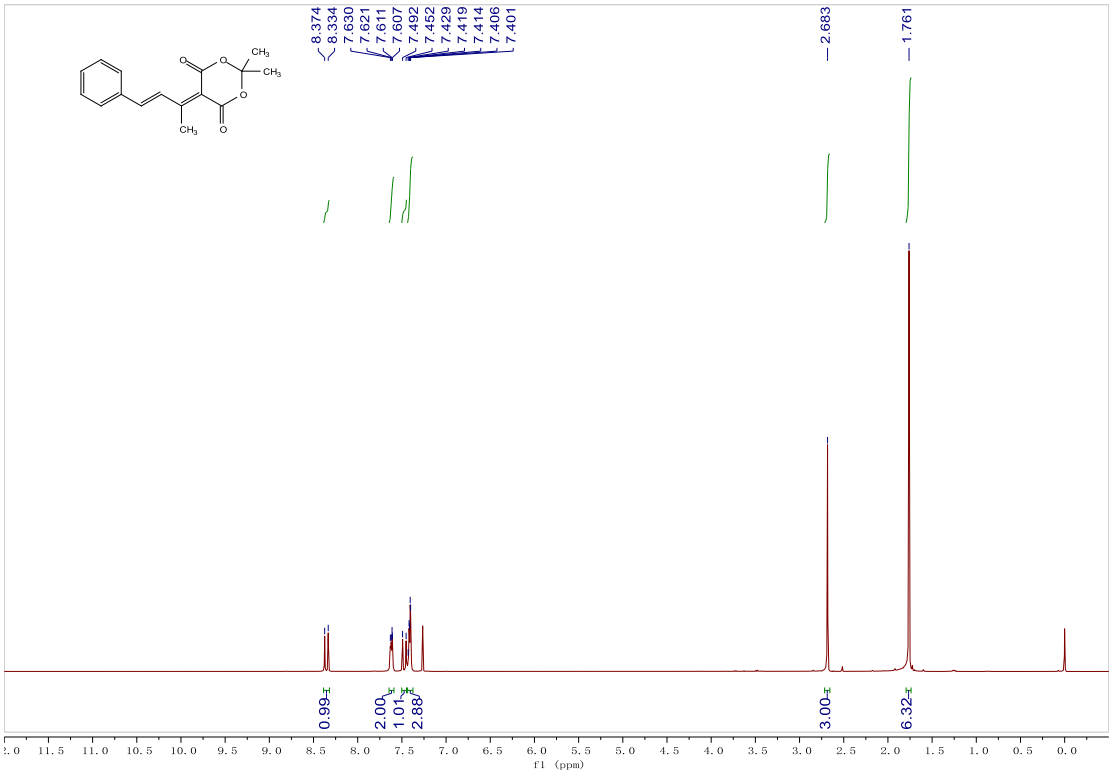
26.11
f1 (ppm)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7.452
7.429
7.419
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7.406
7.401
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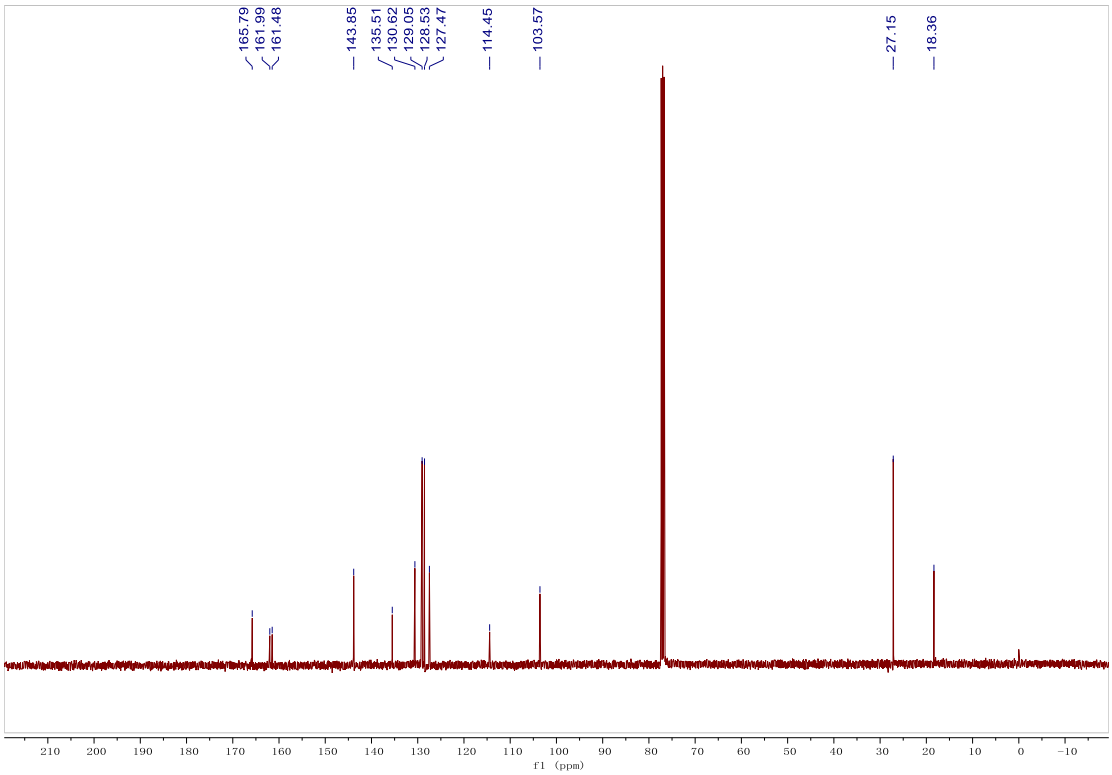
6.32
f1 (ppm)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103.57
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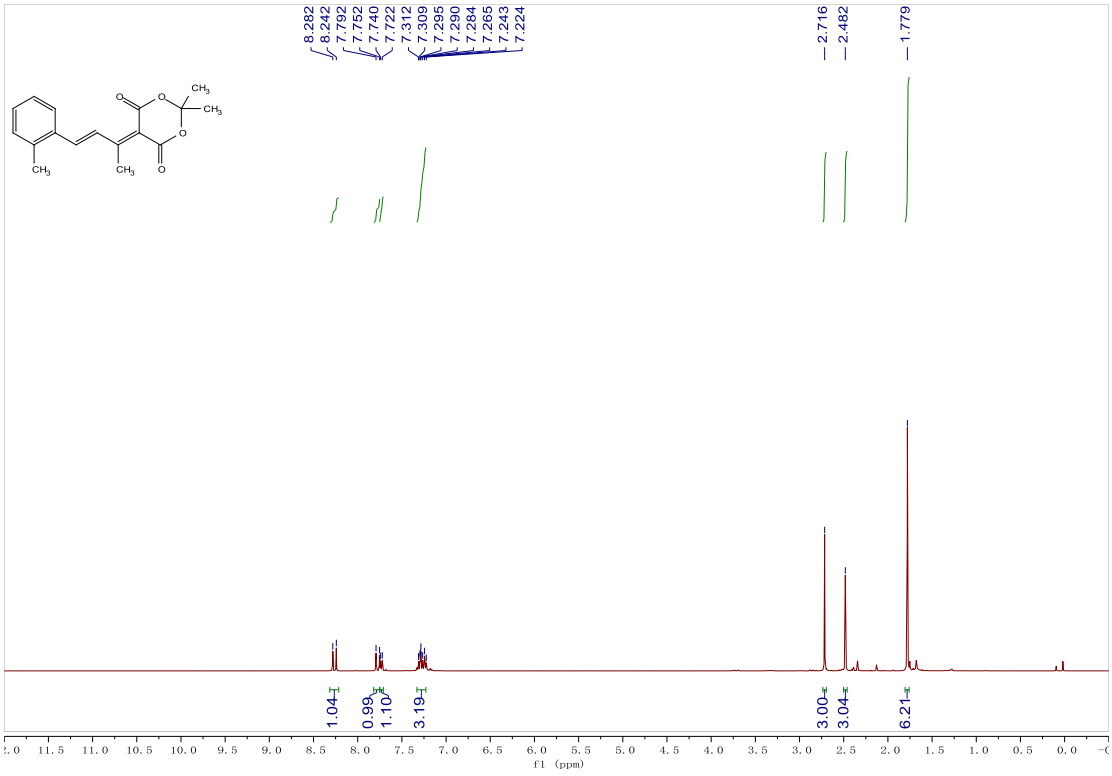
18.36
f1 (ppm)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7.290
7.284
7.265
7.243
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3.00
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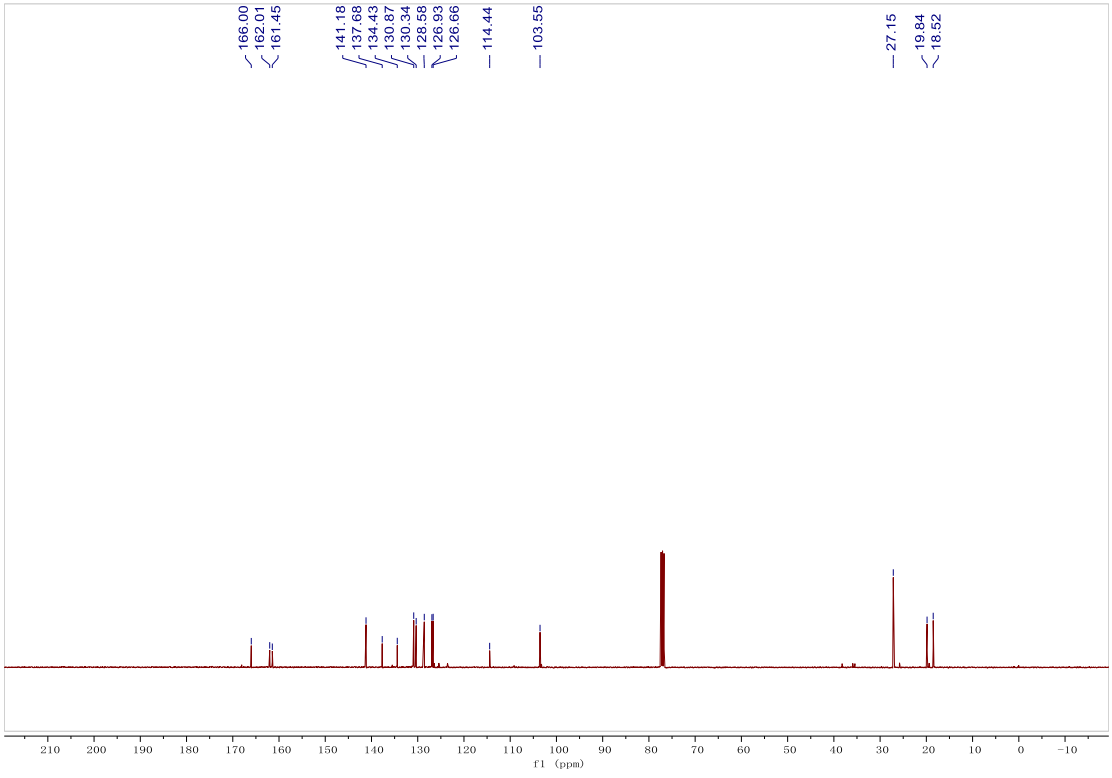
f1 (ppm)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126.66
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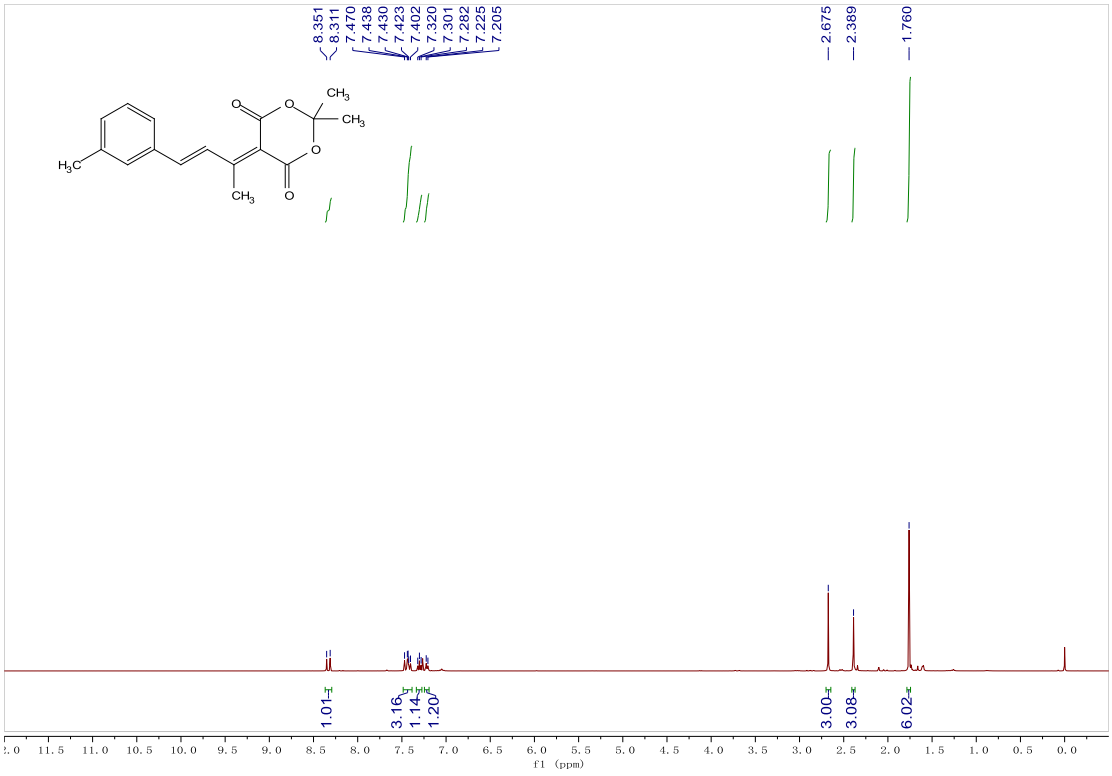
18.52
f1 (ppm)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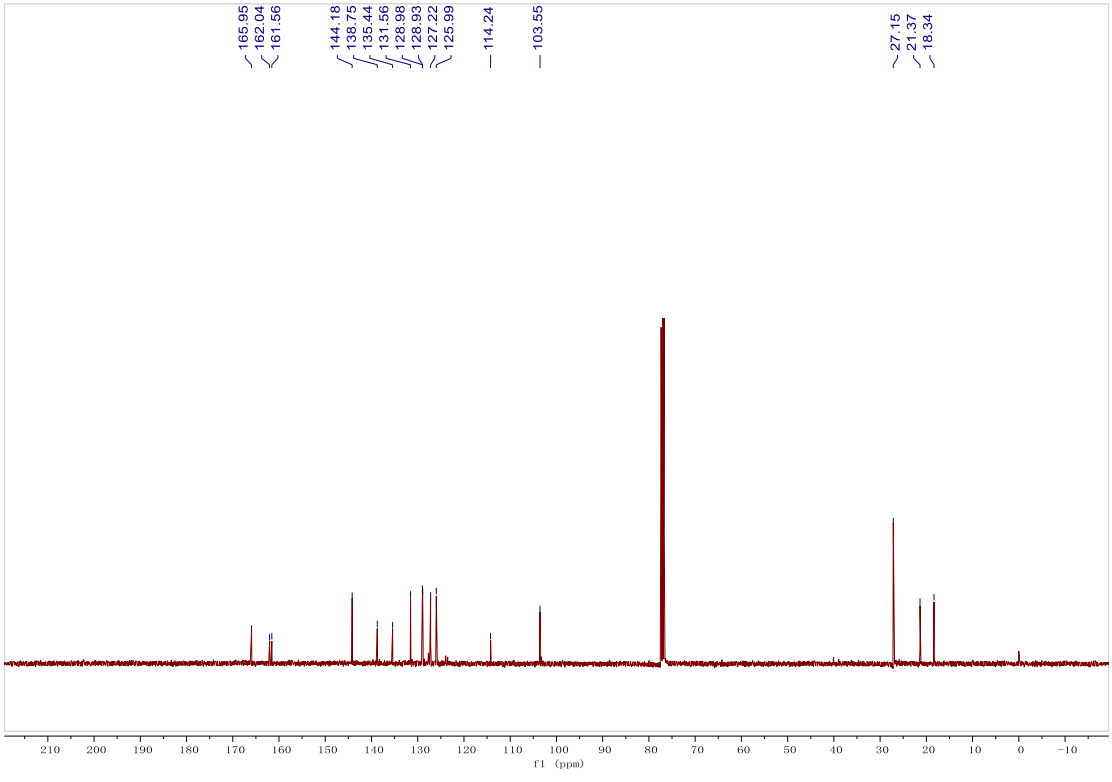
7.320
7.301
7.282
7.225
7.205
2.675
2.389
1.760
CH3
CH3
H3C
CH3
O
O
O
O
O
1.01
3.16
1.14
1.20
3.00
3.08
6.02
f1 (ppm)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125.99
114.24
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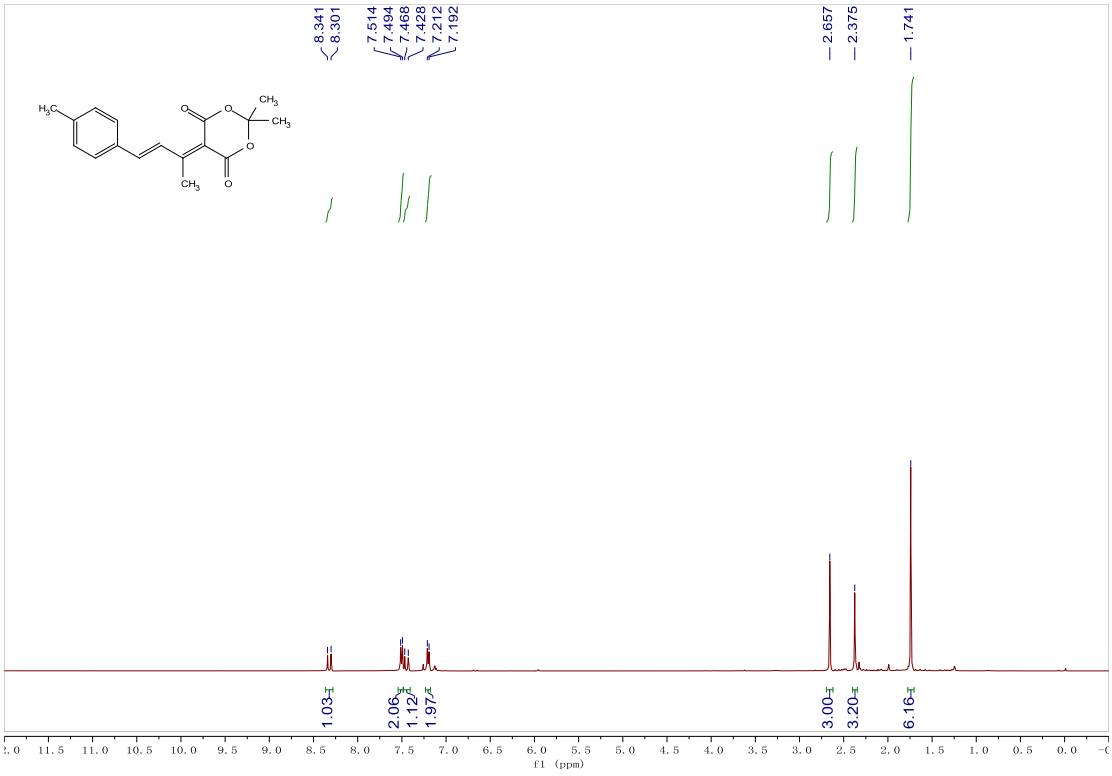
21.37
18.34
f1 (ppm)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2.06
1.12
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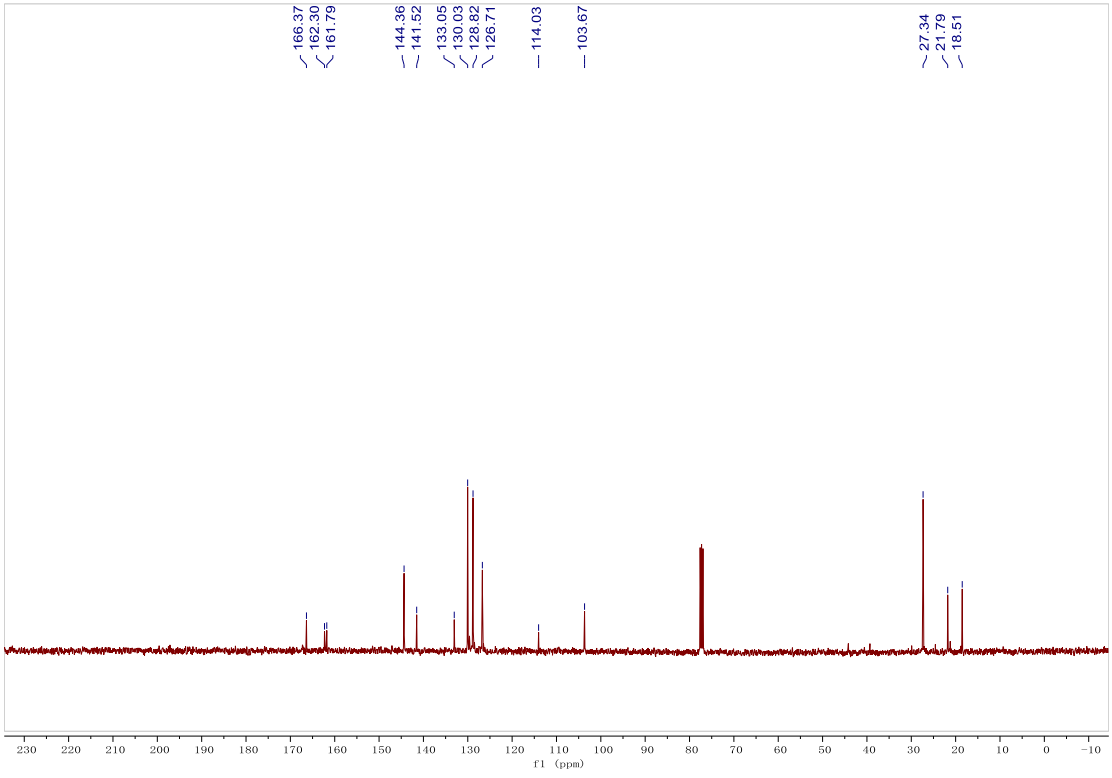
3.00
3.20
6.16
f1 (ppm)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114.03
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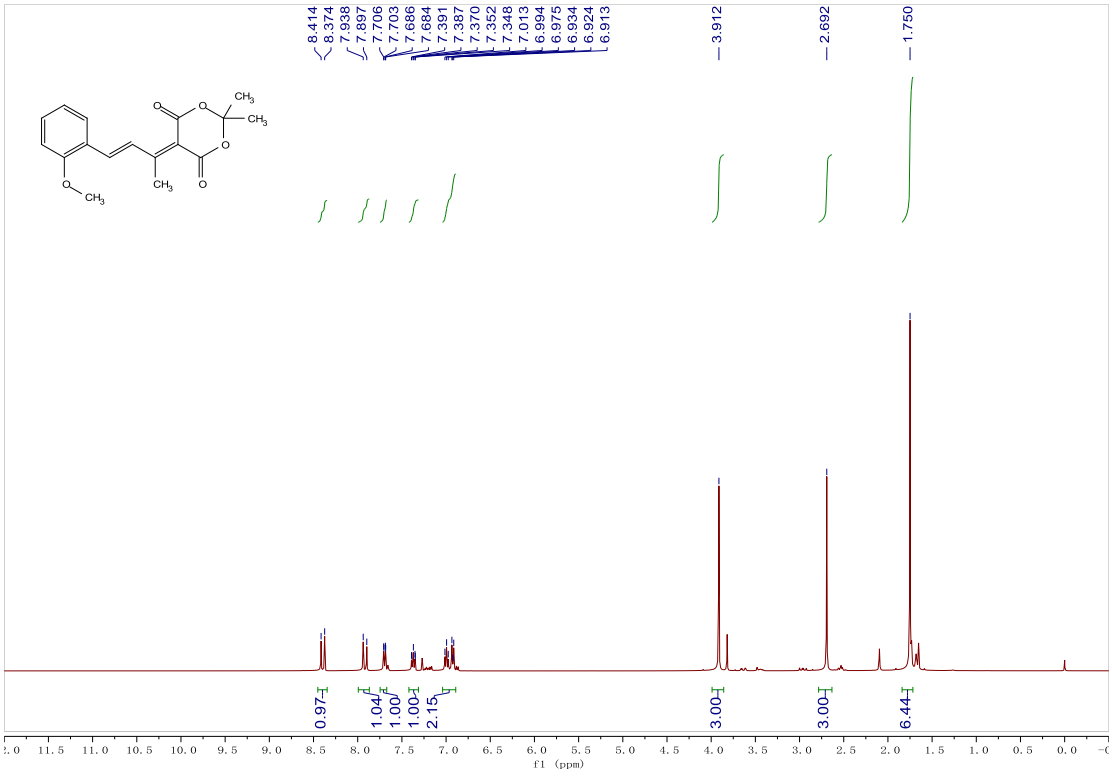
18.51
f1 (ppm)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7.348
7.013
6.994
6.975
6.934
6.924
6.913
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1.00
1.00
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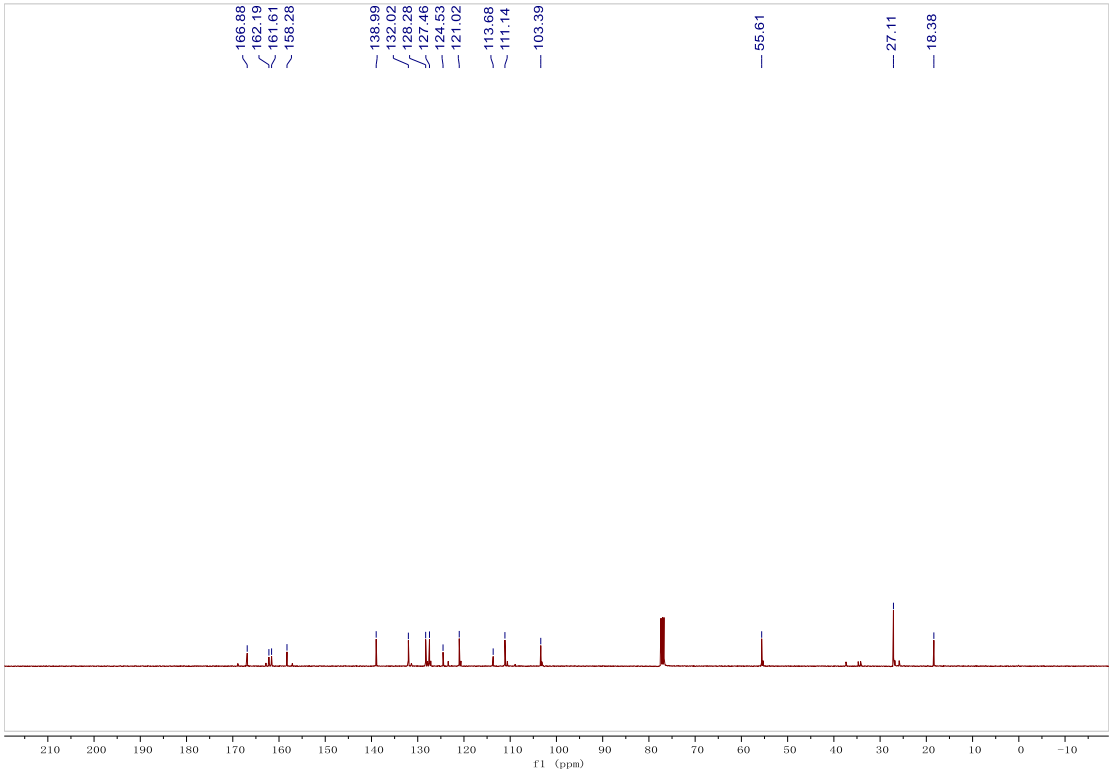
6.44
f1 (ppm)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111.14
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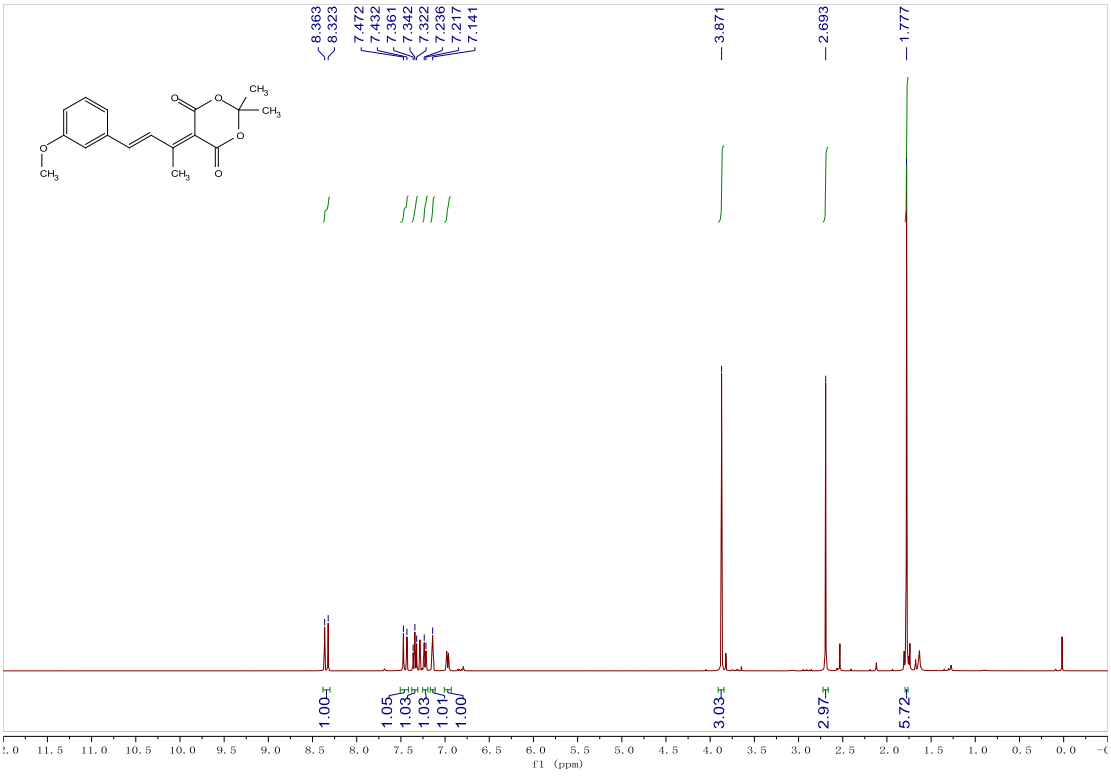
18.38
f1 (ppm)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7.217
7.141
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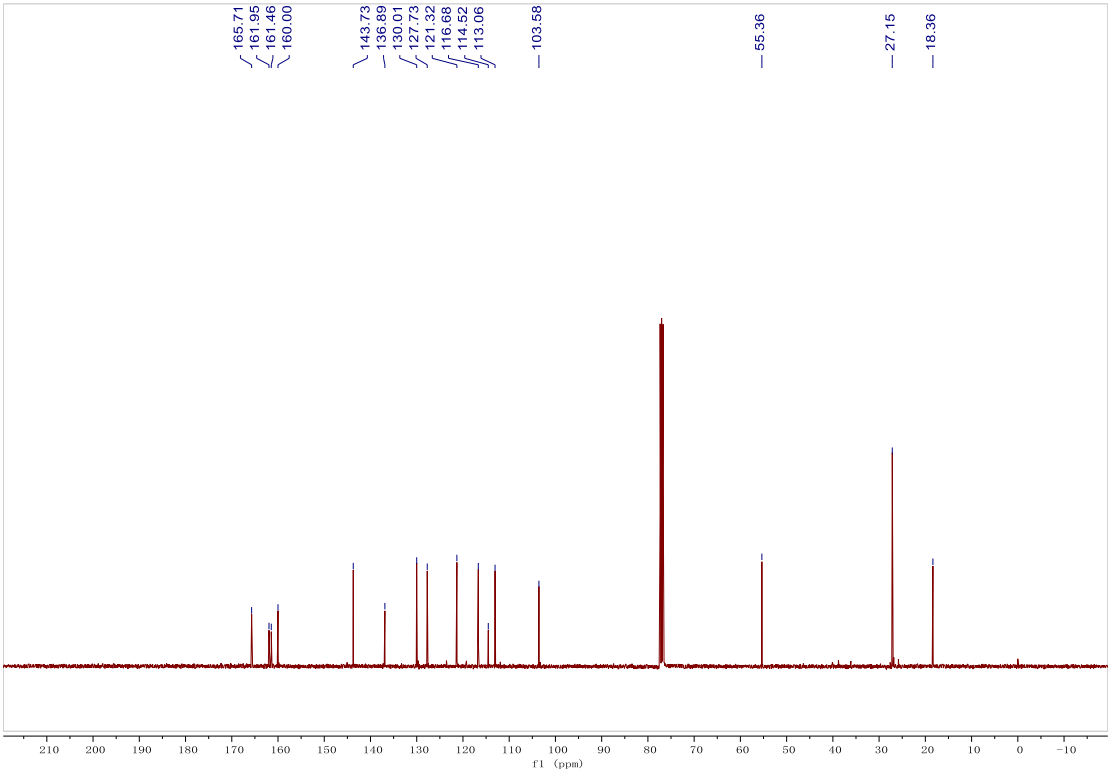
1.05
1.03
1.03
1.01
1.00
3.03
2.97
5.72
f1 (ppm)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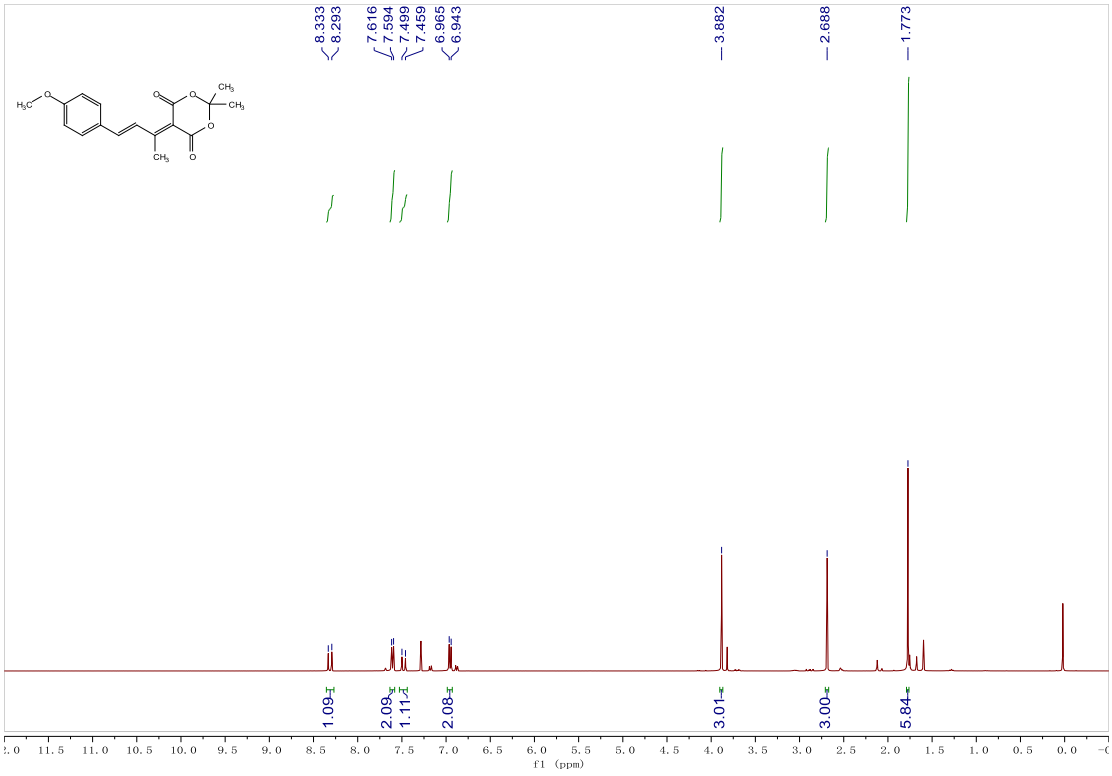
114.52
113.06
103.58
55.36
27.15
18.36
f1 (ppm)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7.459
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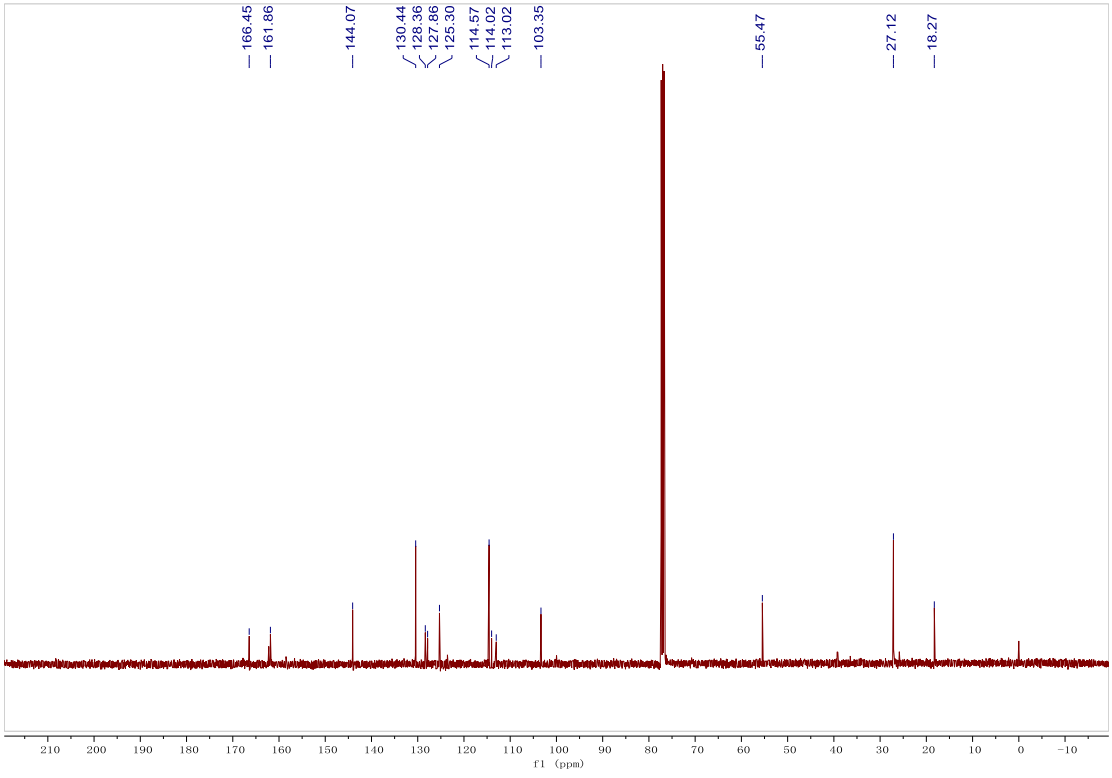
1.11
2.08
3.01
3.00
5.84
f1 (ppm)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127.86
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114.57
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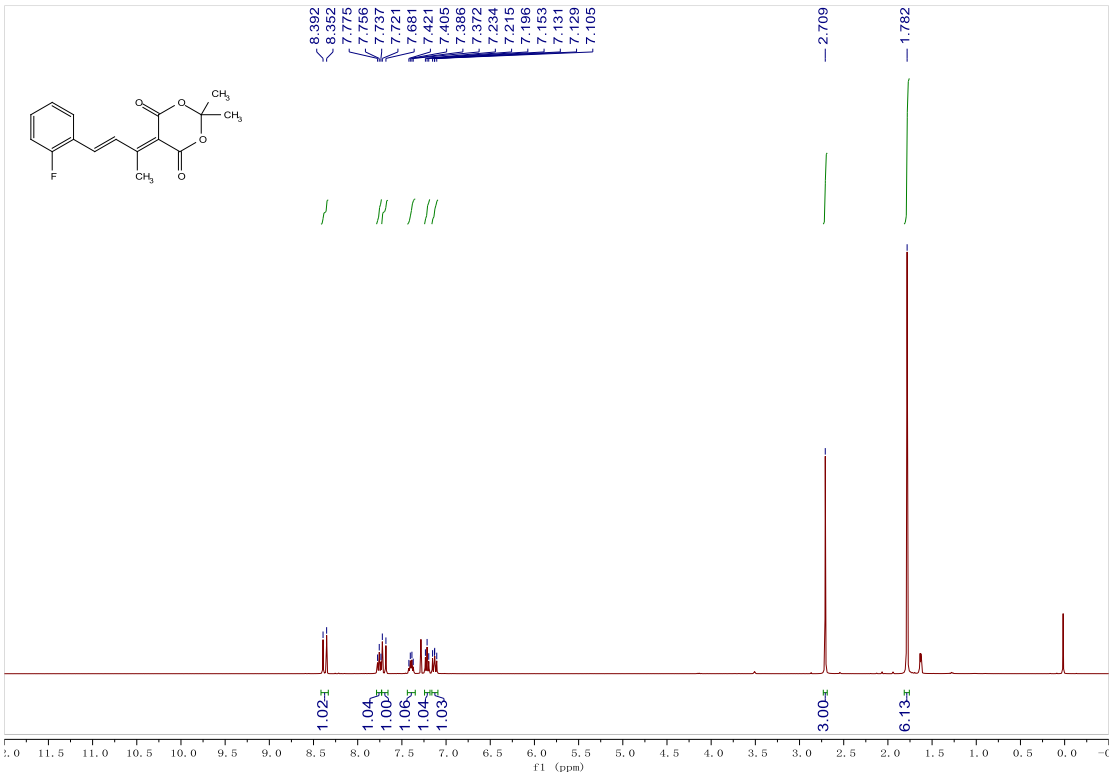
113.02
103.35
55.47
27.12
18.27
f1 (ppm)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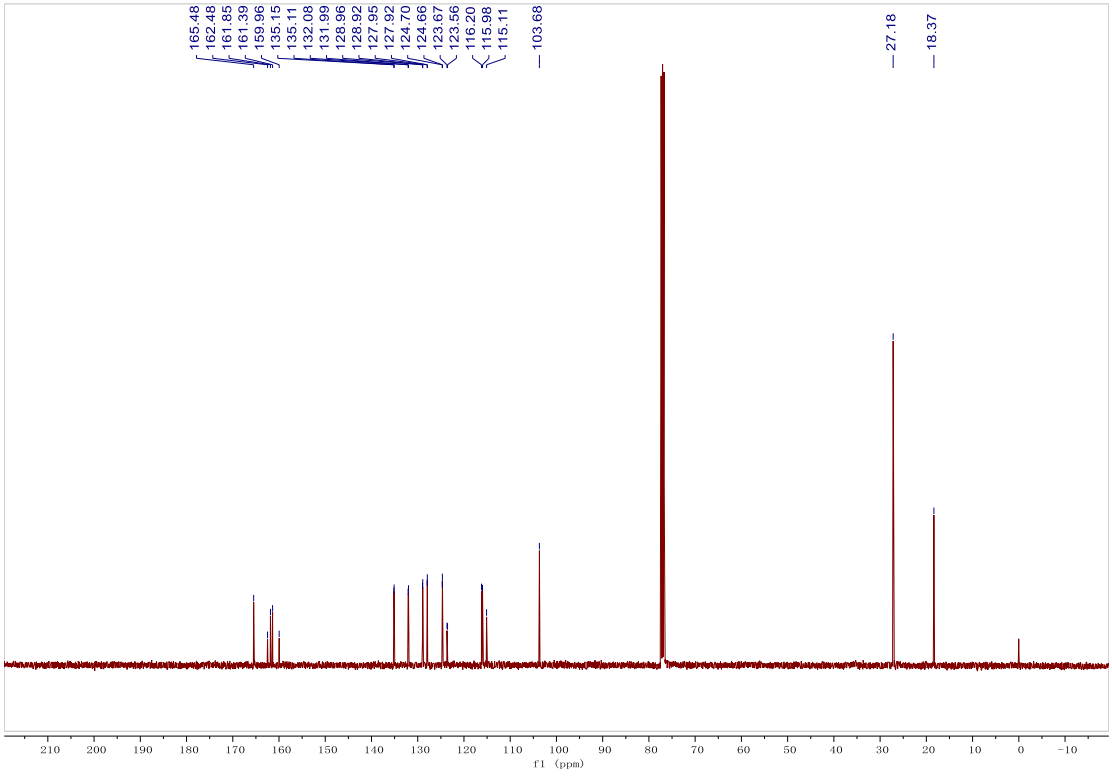
7.756
7.737
7.721
7.681
7.421
7.405
7.386
7.372
7.234
7.215
7.196
7.153
7.131
7.129
7.105
2.709
1.782
1.02
1.04
1.00
1.06
1.04
1.03
3.00
6.13
f1 (ppm)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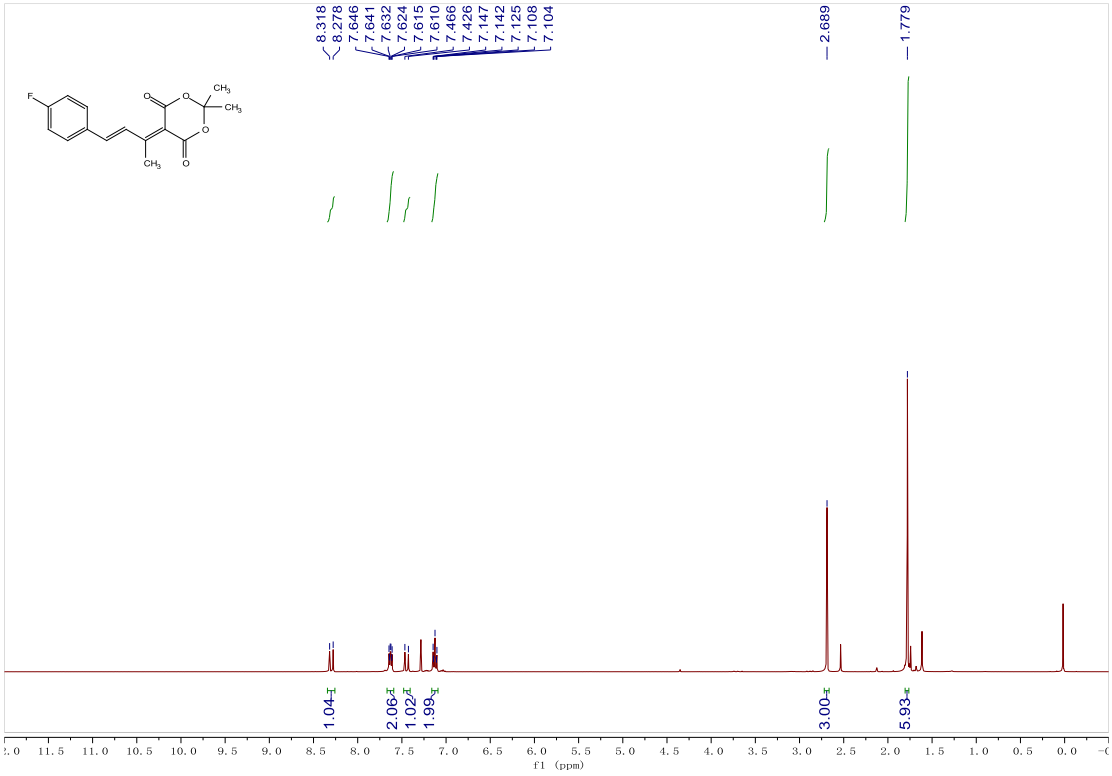
161.39
159.96
135.15
135.11
132.08
131.99
128.96
128.92
127.95
127.92
124.70
124.66
123.67
123.56
116.20
115.98
115.11
103.68
27.18
18.37
f1 (ppm)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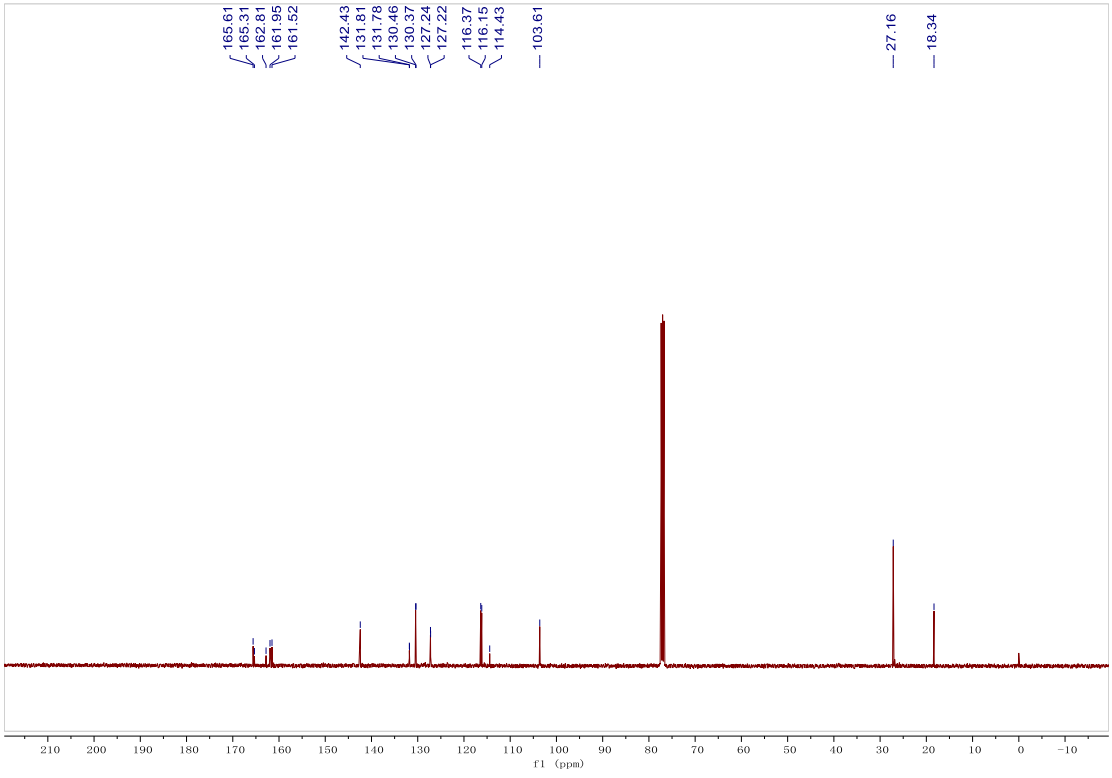
7.646
7.641
7.632
7.624
7.615
7.610
7.466
7.426
7.147
7.142
7.125
7.108
7.104
2.689
1.779
1.04
2.06
1.02
1.99
3.00
5.93
f1 (ppm)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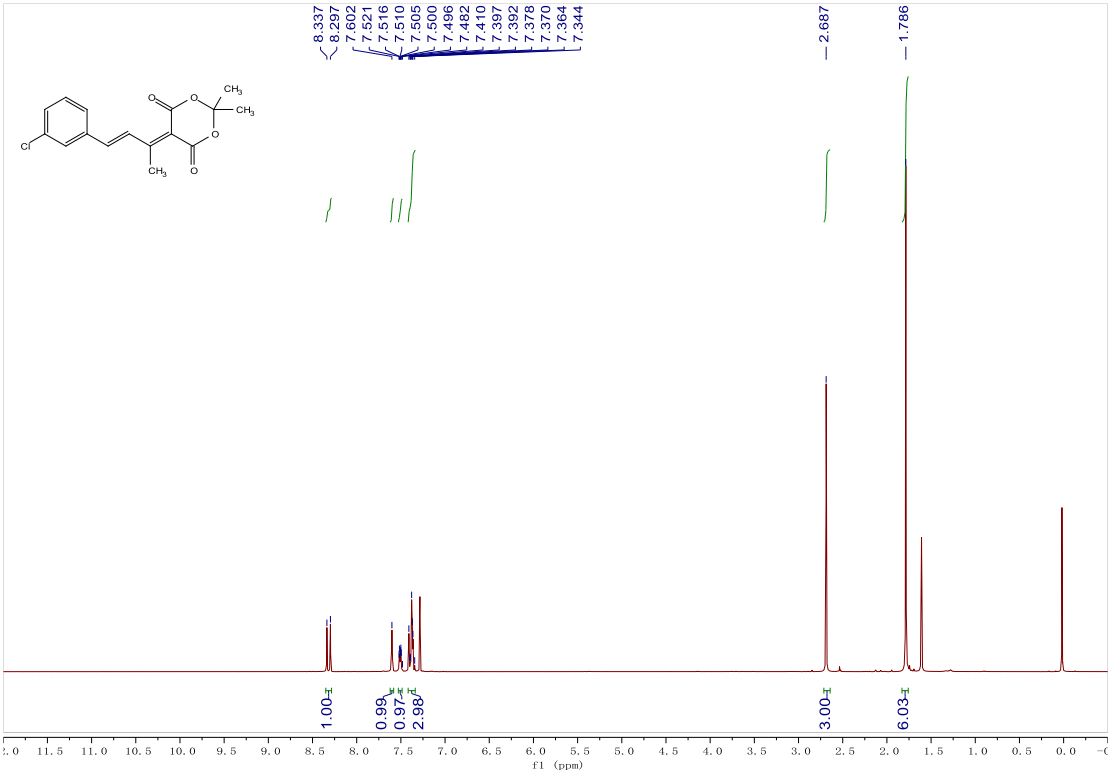
165.31
162.81
161.95
161.52
142.43
131.81
131.78
130.46
130.37
127.24
127.22
116.37
116.15
114.43
103.61
27.16
18.34
f1 (ppm)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8.297
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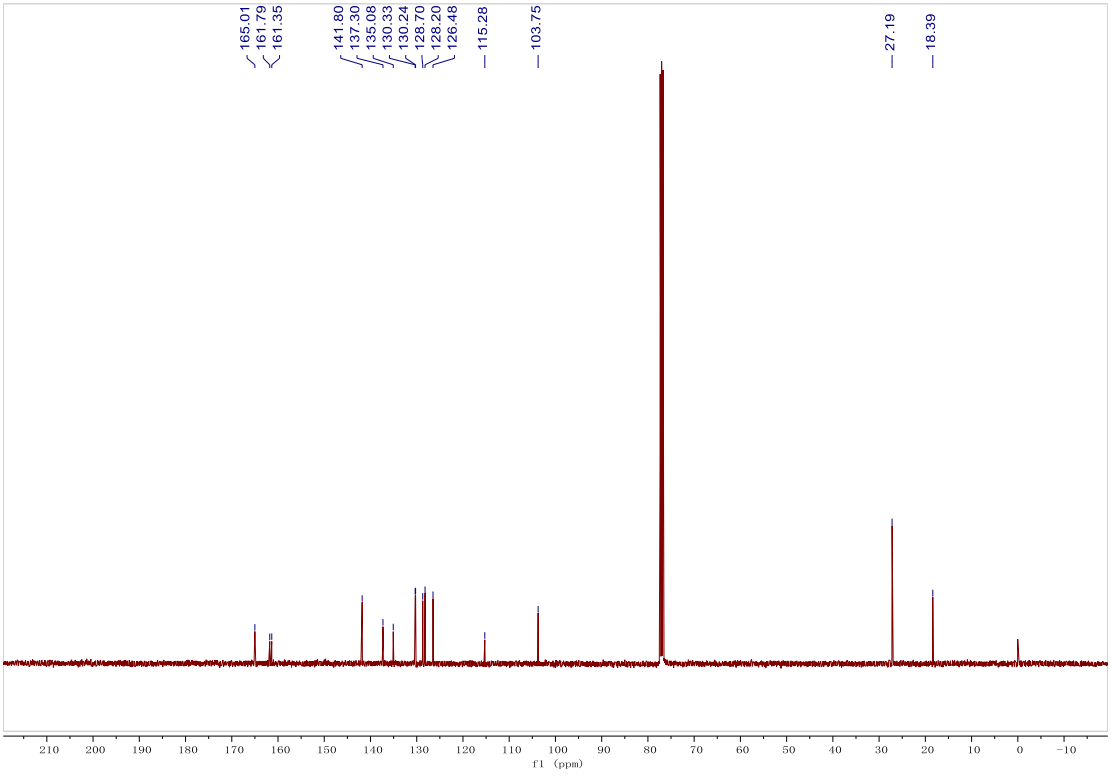
7.521
7.516
7.510
7.505
7.500
7.496
7.482
7.410
7.397
7.392
7.378
7.370
7.364
7.344
2.687
1.786
1.00
0.99
0.97
2.98
3.00
6.03
f1 (ppm)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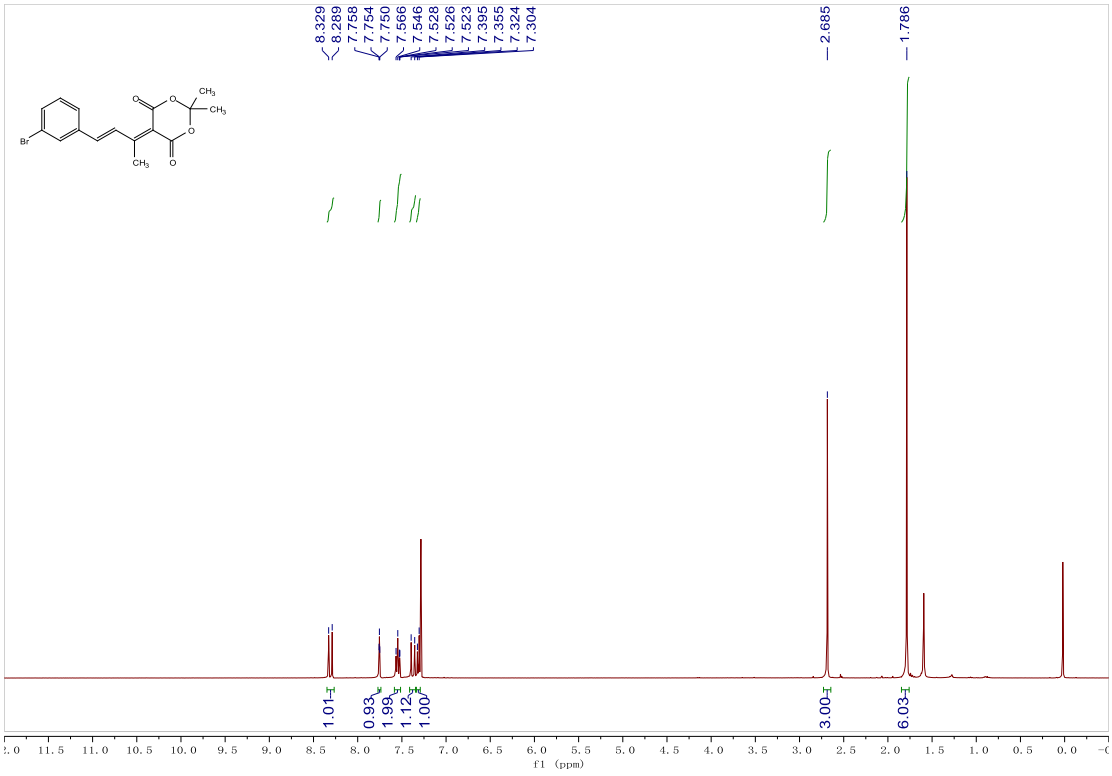
161.79
161.35
141.80
137.30
135.08
130.33
130.24
128.70
128.20
126.48
115.28
103.75
27.19
18.39
f1 (ppm)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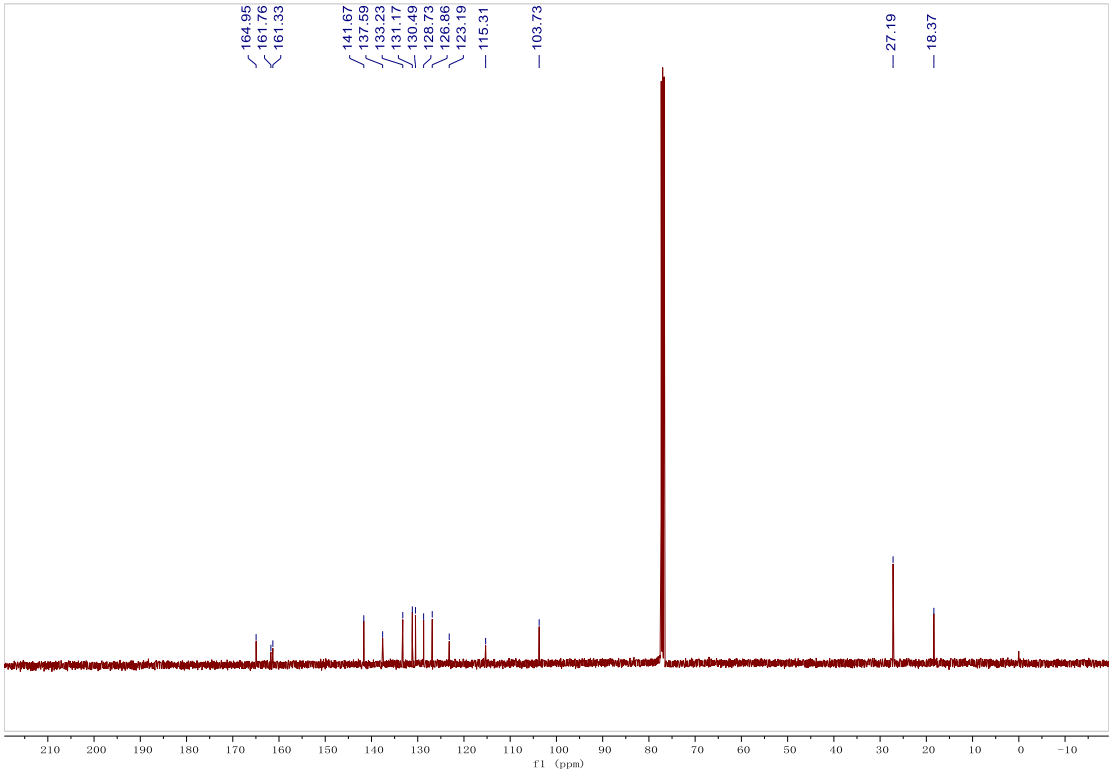
7.754
7.750
7.566
7.546
7.528
7.526
7.523
7.395
7.355
7.324
7.304
2.685
1.786
1.01
0.93
1.99
1.12
1.00
3.00
6.03
f1 (ppm)


164.95
161.76
161.33
141.67
137.59
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128.73
126.86
123.19
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103.73
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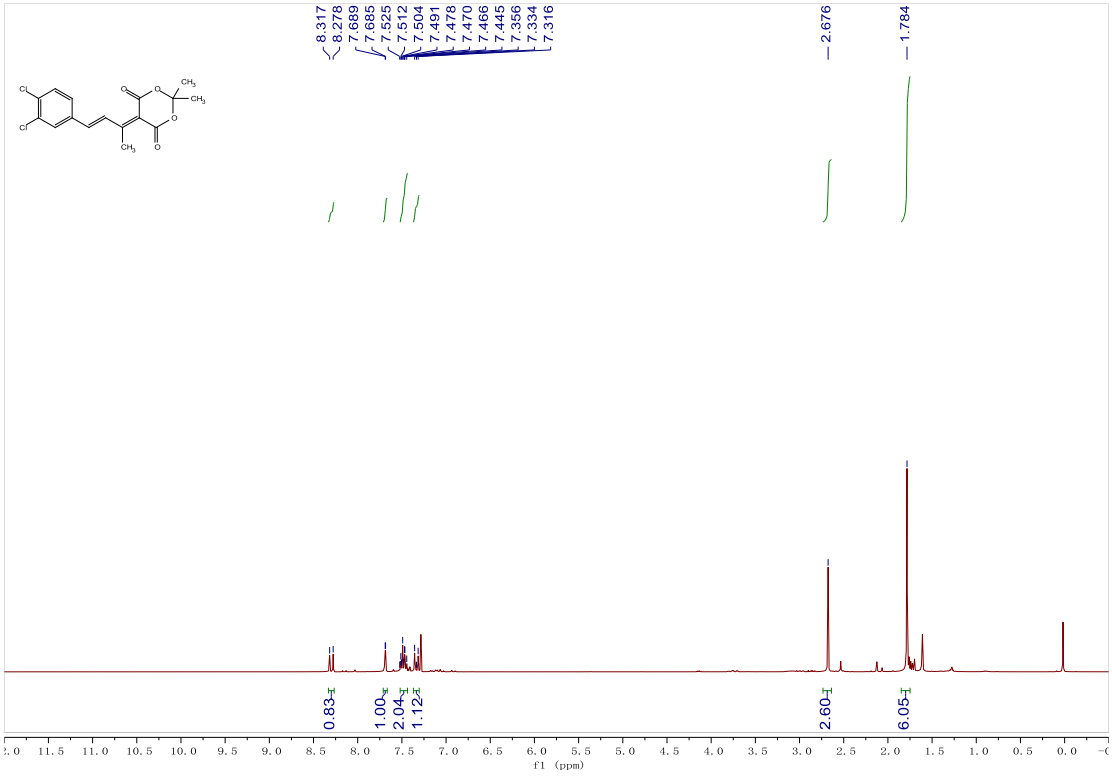
18.37
f1 (ppm)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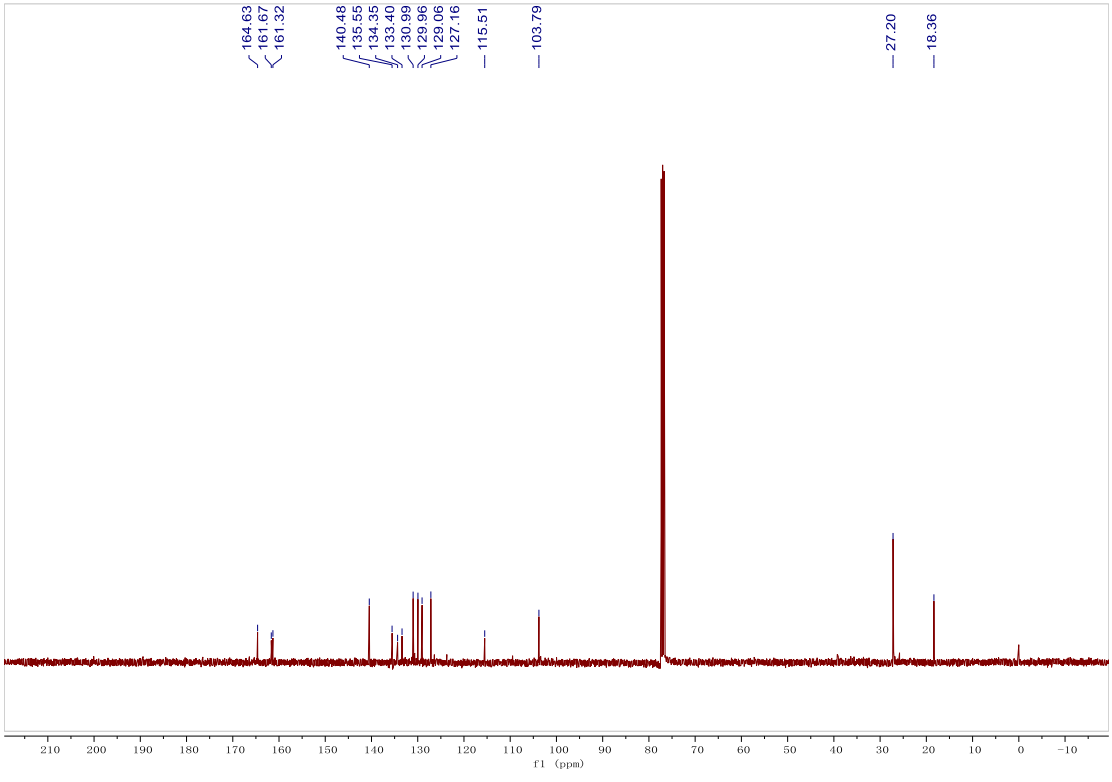
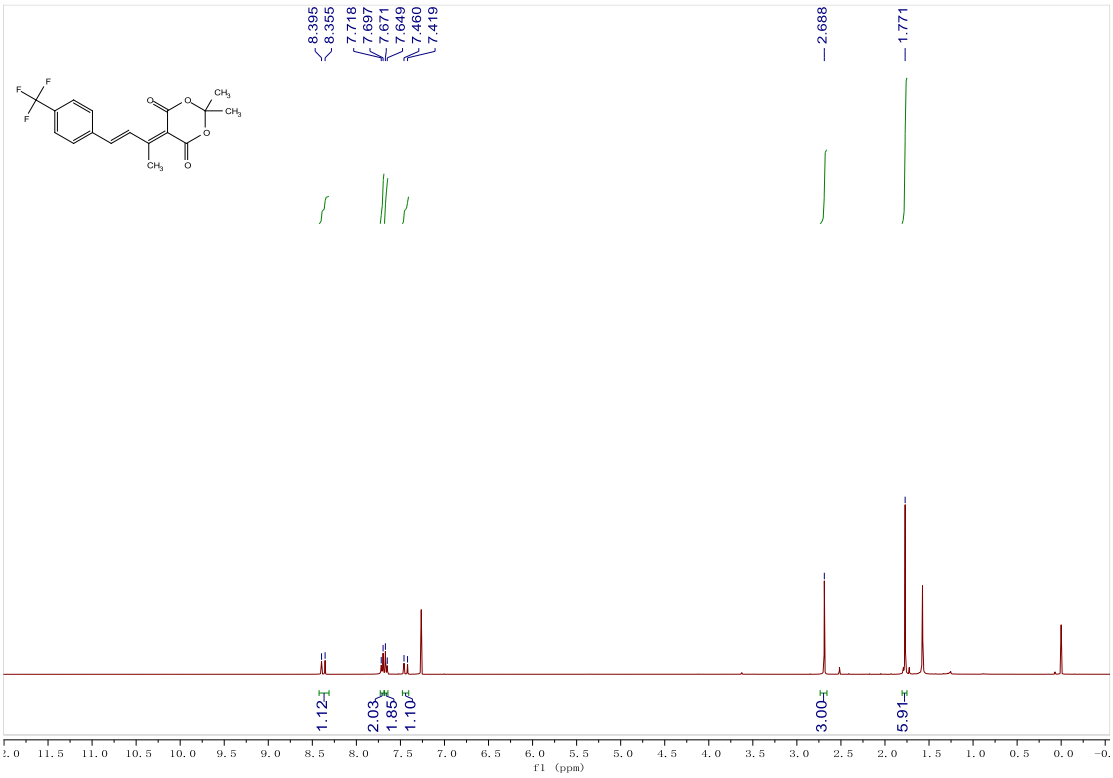
8.278
7.689
7.685
7.525
7.512
7.504
7.491
7.478
7.470
7.466
7.445
7.356
7.334
7.316
2.676
1.784
0.83
1.00
2.04
1.12
2.60
6.05
f1 (ppm)


164.63
161.67
161.32
140.48
135.55
134.35
133.40
130.99
129.96
129.06
127.16
115.51
103.79
27.20
18.36
f1 (ppm)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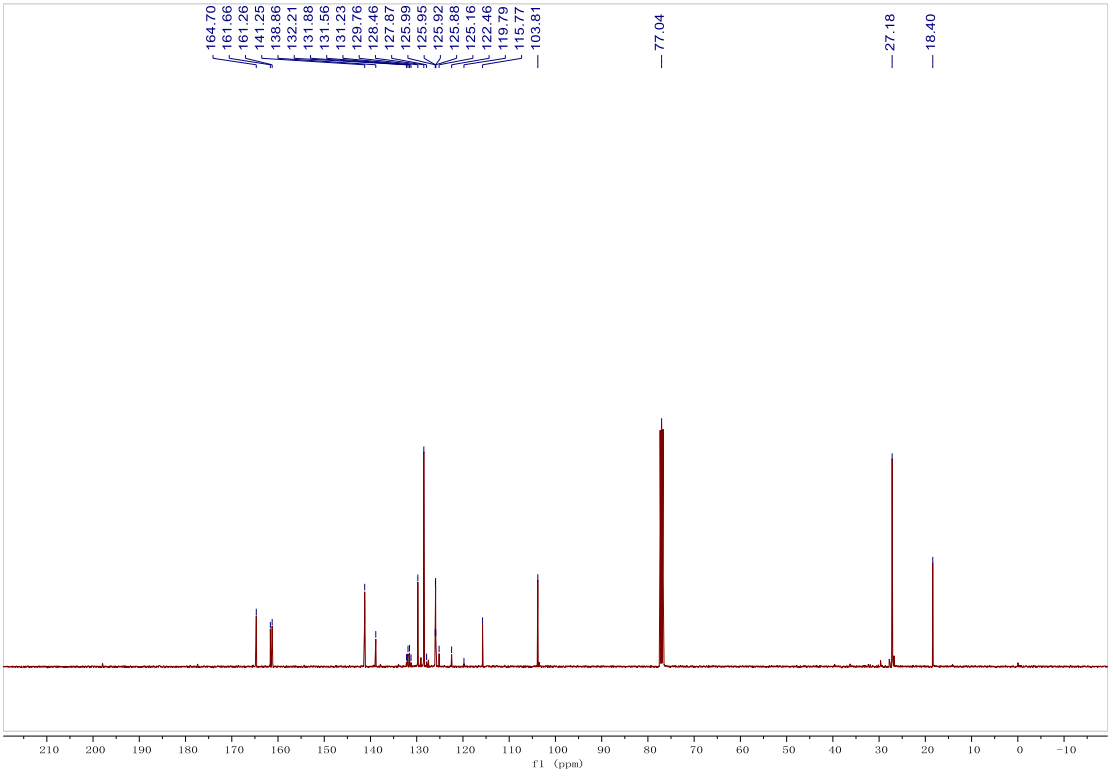
8.355
7.718
7.697
7.671
7.649
7.460
7.419
2.688
1.771
1.12
2.03
1.85
1.10
3.00
5.91
f1 (ppm)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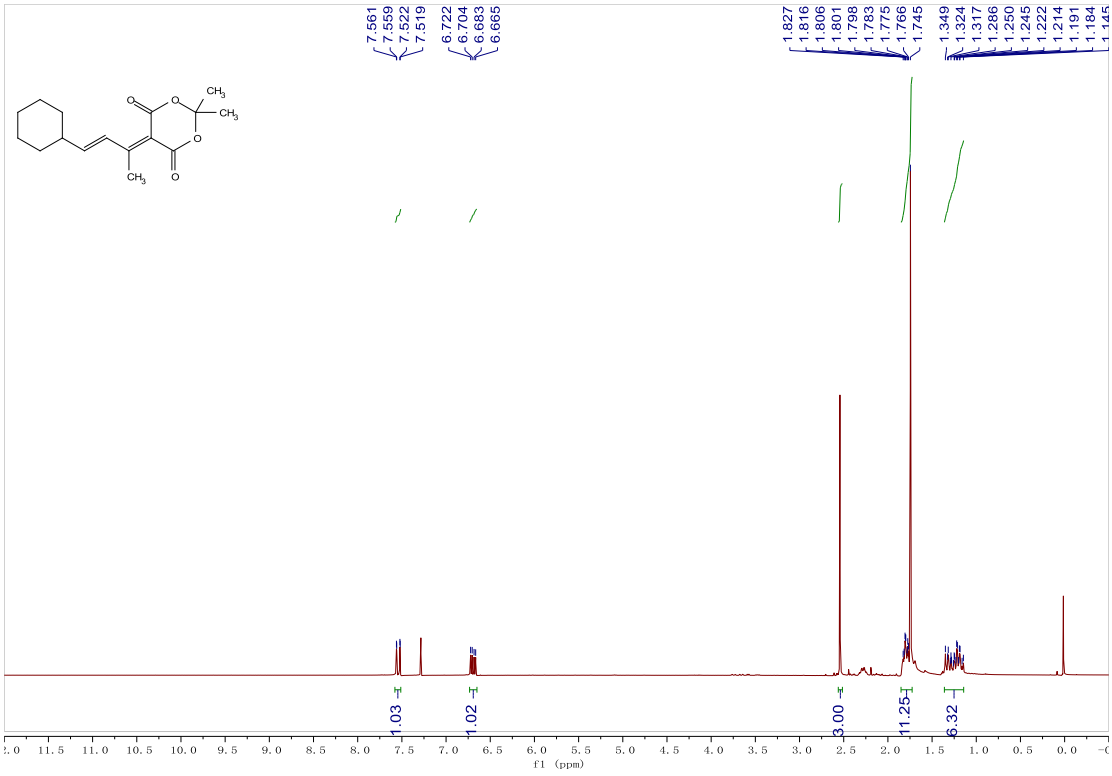
161.66
161.26
141.25
138.86
132.21
131.88
131.56
131.23
129.76
128.46
127.87
125.99
125.95
125.92
125.88
125.16
122.46
119.79
115.77
103.81
77.04
27.18
18.40
f1 (ppm)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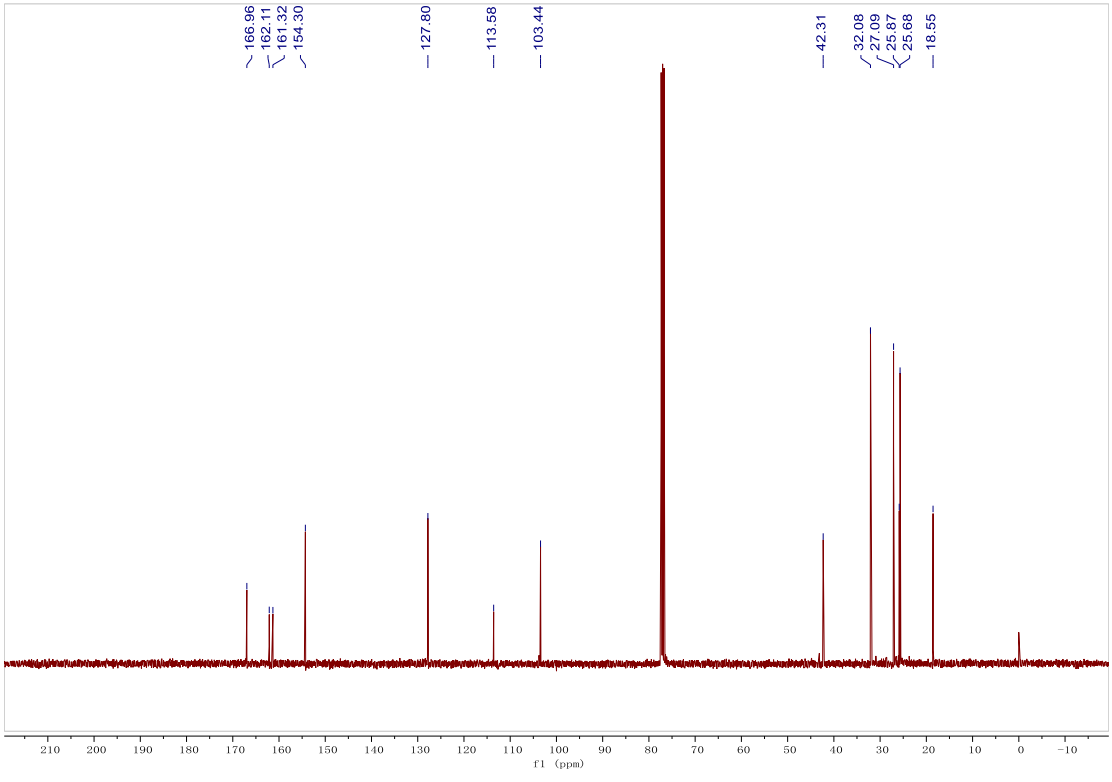
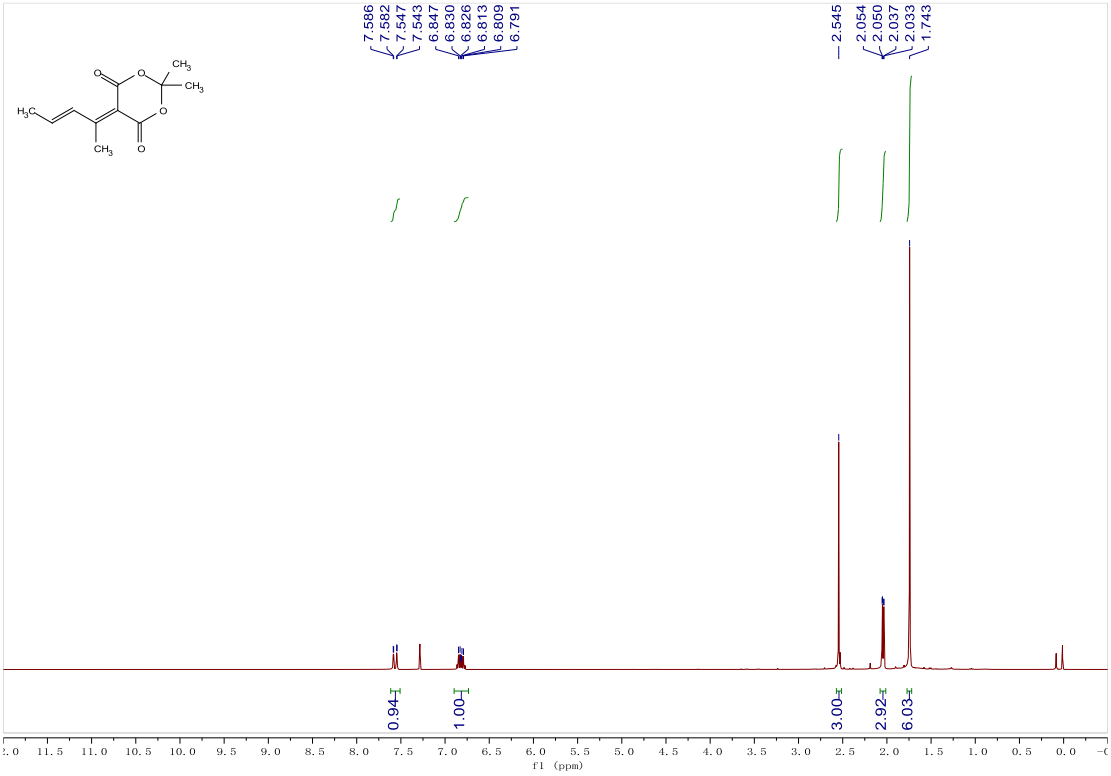
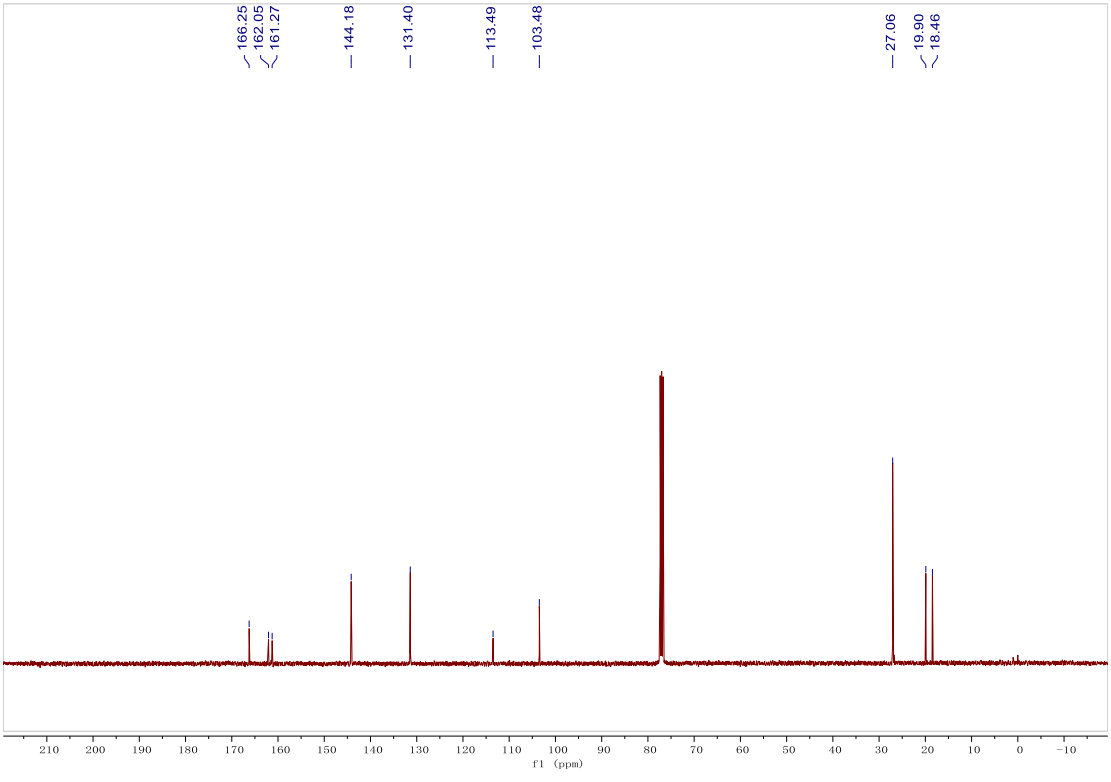
7.522
7.519
6.722
6.704
6.683
6.665
1.827
1.816
1.806
1.801
1.798
1.783
1.775
1.766
1.745
1.349
1.324
1.317
1.286
1.250
1.245
1.222
1.214
1.191
1.184
1.03
1.02
3.00
11.25
6.32
f1 (ppm)


166.96
162.11
161.32
154.30
127.80
113.58
103.44
42.31
32.08
27.09
25.87
25.68
18.55
f1 (ppm)


7.586
7.582
7.547
7.543
6.847
6.830
6.826
6.813
6.809
6.791
2.545
2.054
2.050
2.037
2.033
1.743
0.94
1.00
3.00
2.92
6.03
f1 (ppm)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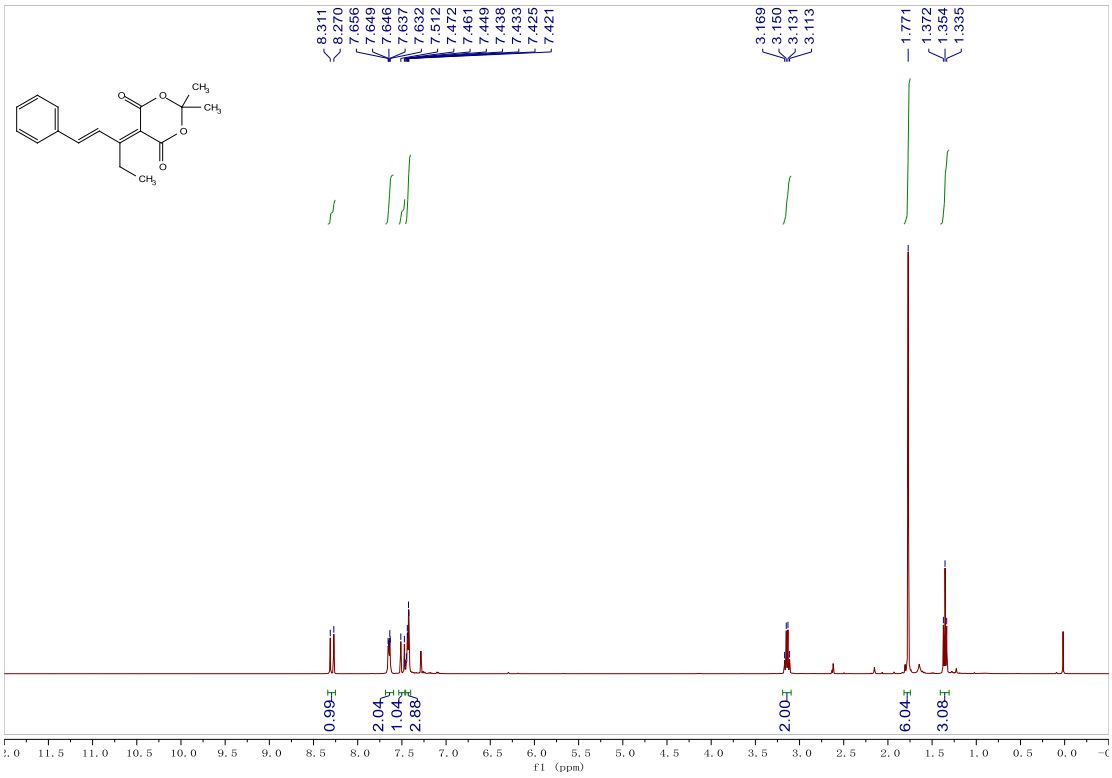
162.05
161.27
144.18
131.40
113.49
103.48
27.06
19.90
18.46
f1 (ppm)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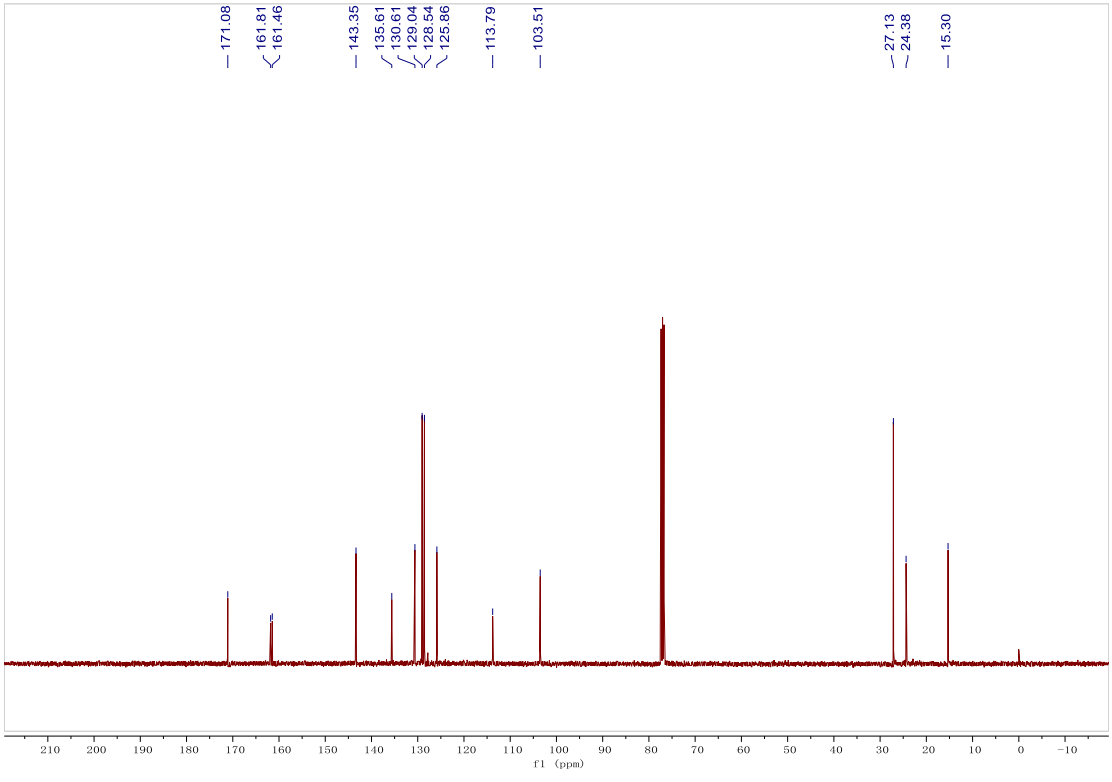
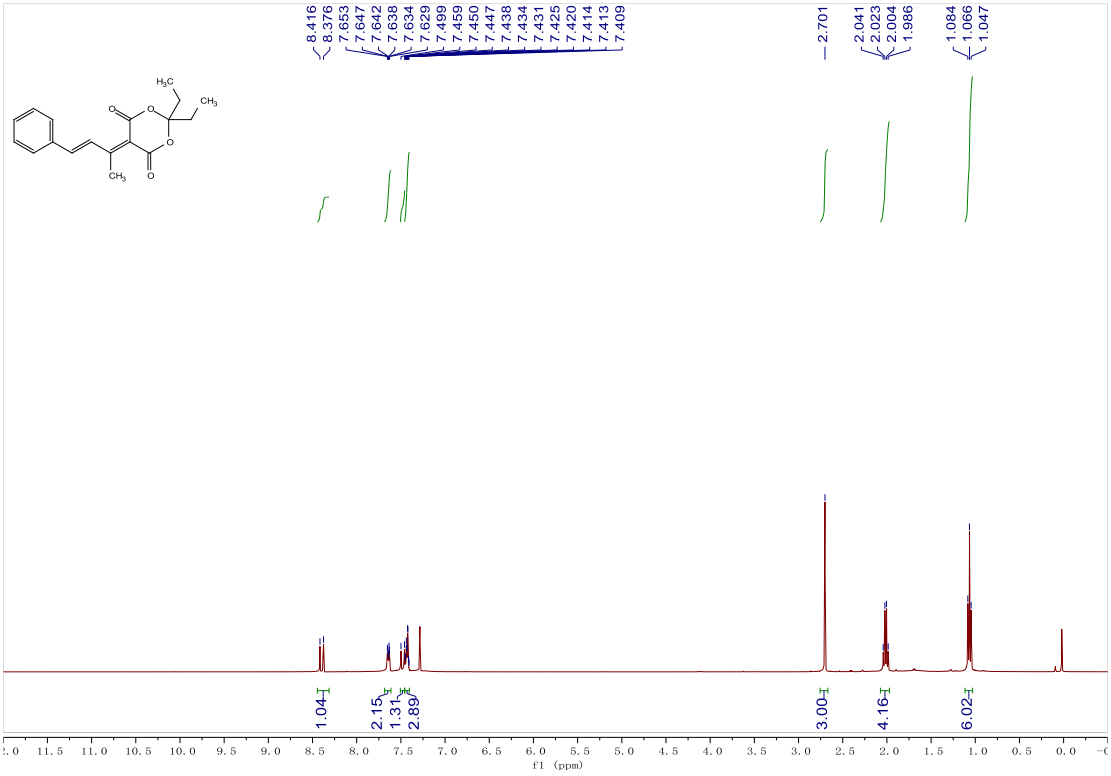
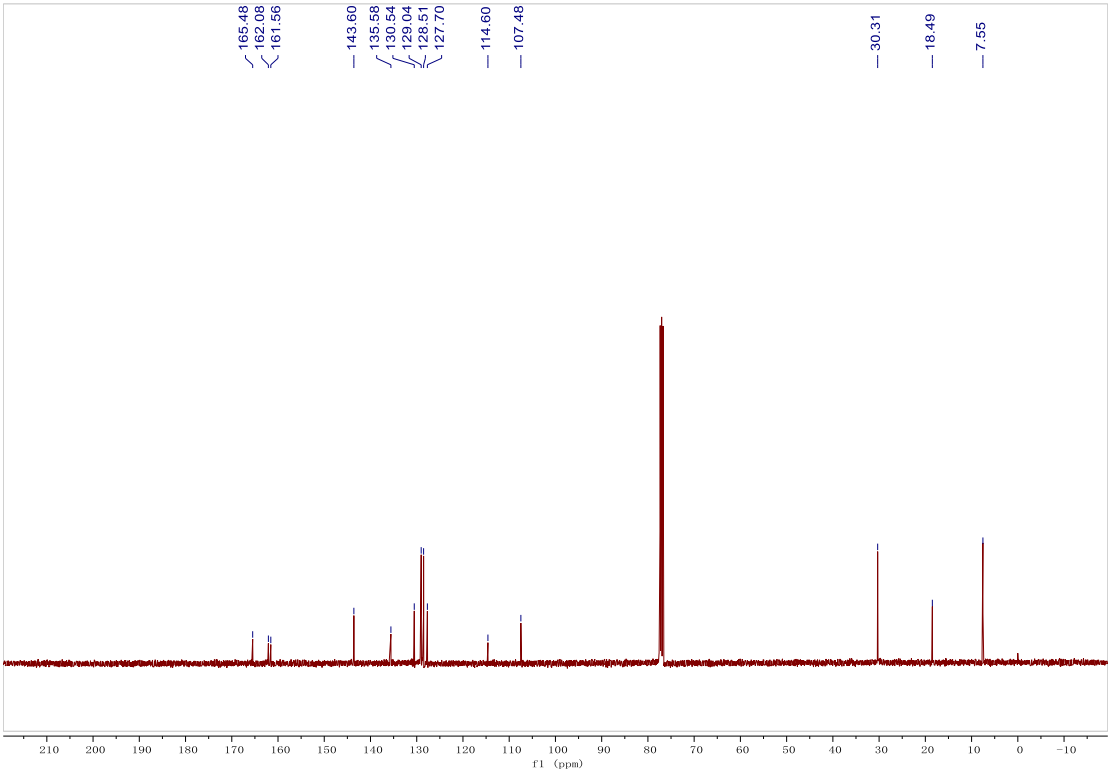
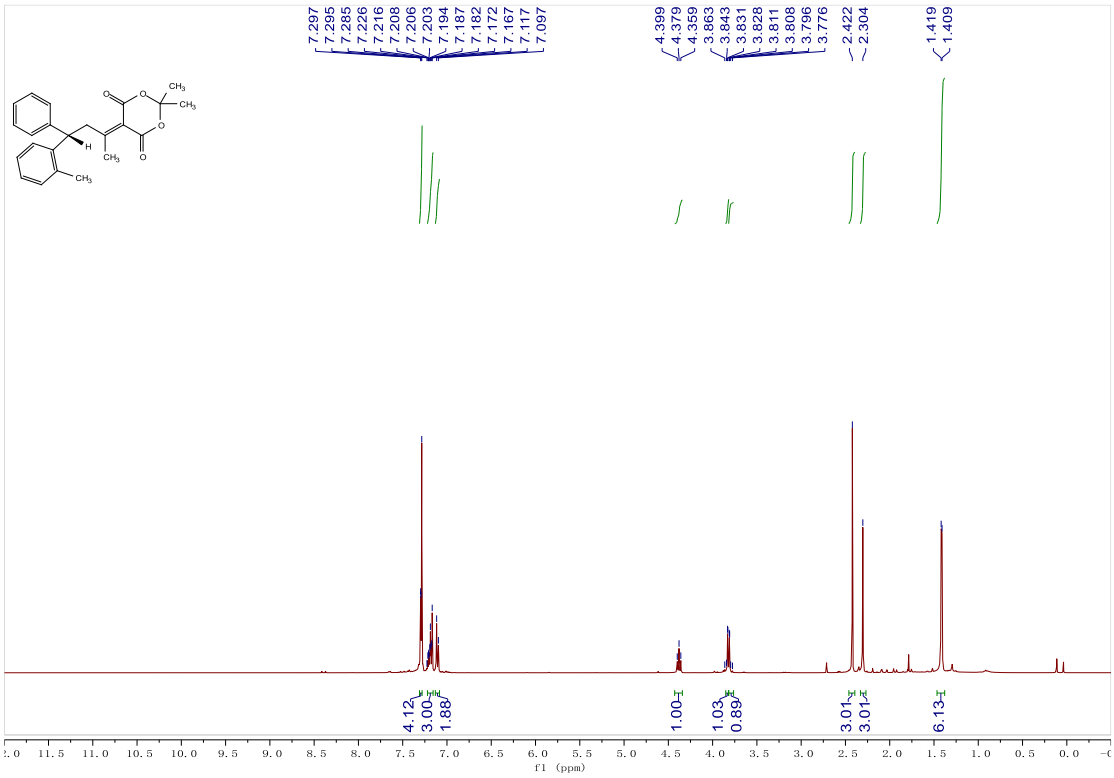
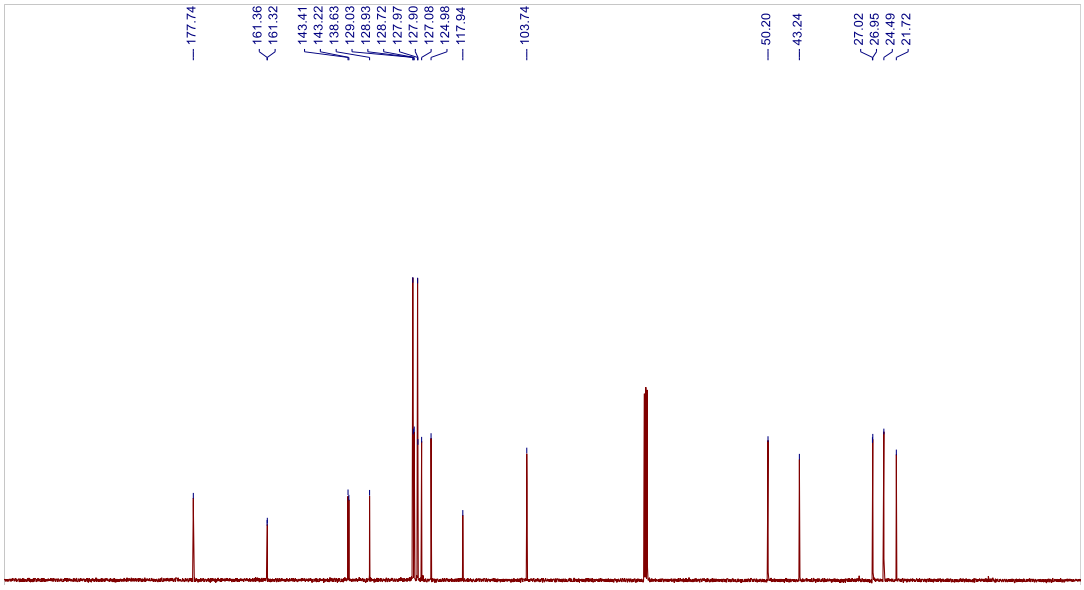
7.649
7.646
7.637
7.632
7.512
7.472
7.461
7.449
7.438
7.433
7.425
7.421
3.169
3.150
3.131
3.113
1.771
1.372
1.354
1.335
0.99
2.04
1.04
2.88
2.00
6.04
3.08
f1 (ppm)

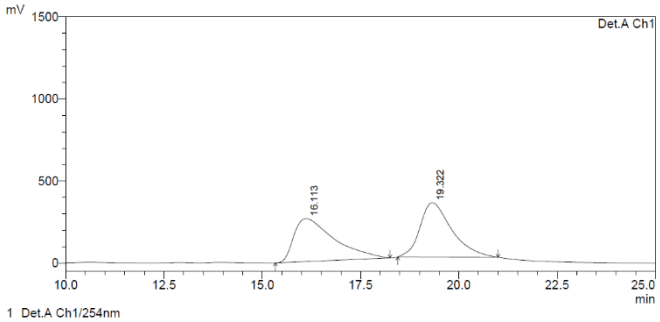

171.08
161.81
161.46
143.35
135.61
130.61
129.04
128.54
125.86
113.79
103.51
27.13
24.38
15.30
f1 (ppm)


8.416
8.376
7.653
7.647
7.642
7.638
7.634
7.629
7.499
7.459
7.450
7.447
7.438
7.434
7.431
7.425
7.420
7.414
7.413
7.409
2.701
2.041
2.023
2.004
1.986
1.084
1.066
1.047
1.04
2.15
1.31
2.89
3.00
4.16
6.02
f1 (ppm)


165.48
162.08
161.56
143.60
135.58
130.54
129.04
128.51
127.70
114.60
107.48
30.31
18.49
7.55
f1 (ppm)



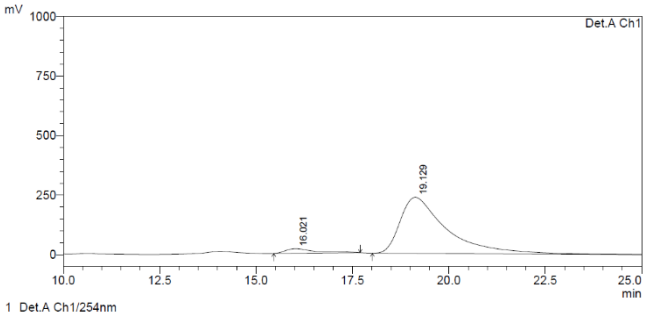




PeakTable

Detector A Ch1 254nm

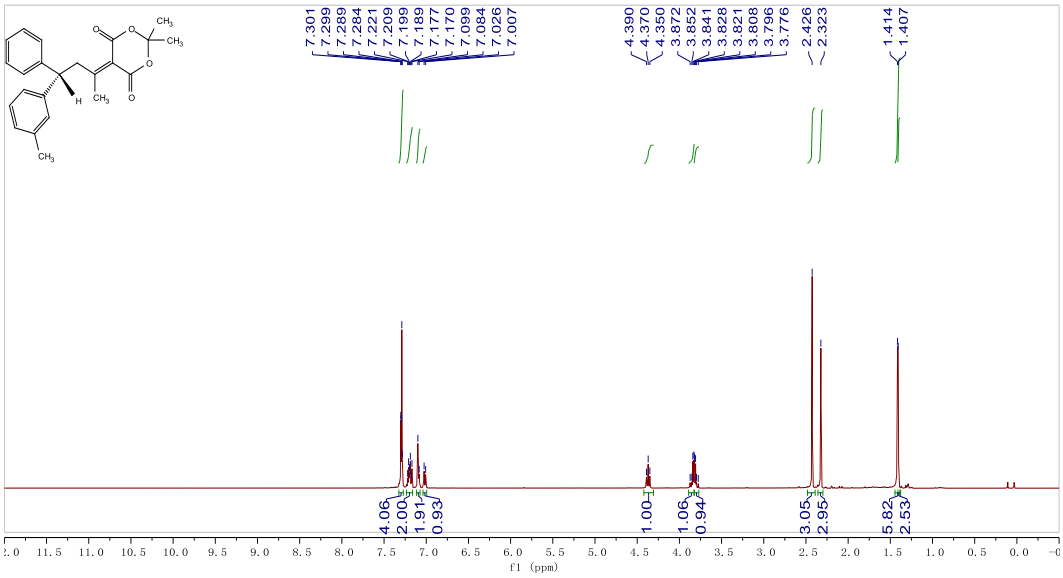
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.113	18629614	262243	49.938	44.189
2	19.322	18675522	331208	50.062	55.811
Total		37305135	593450	100.000	100.000

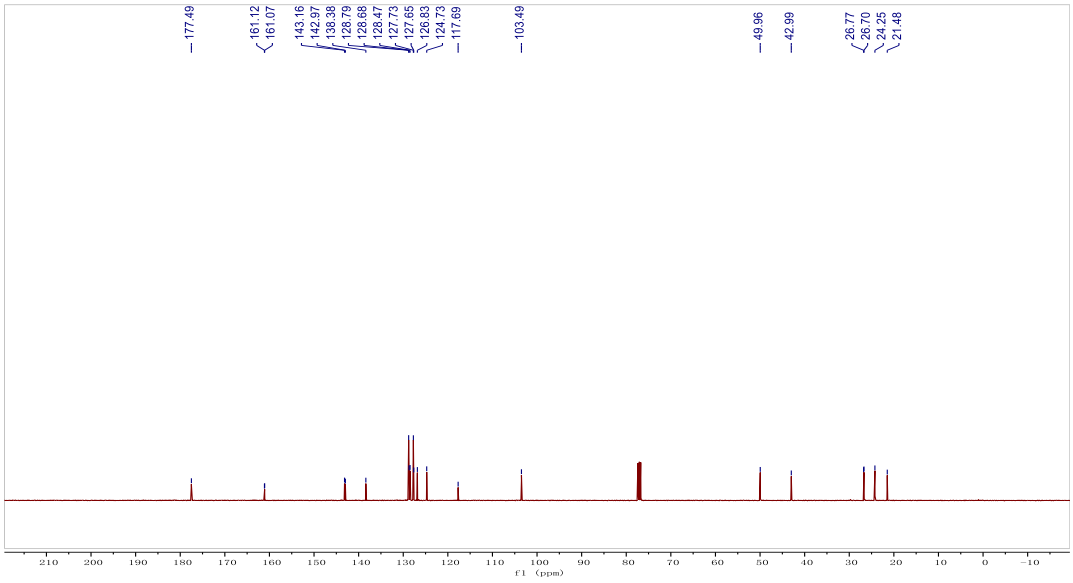


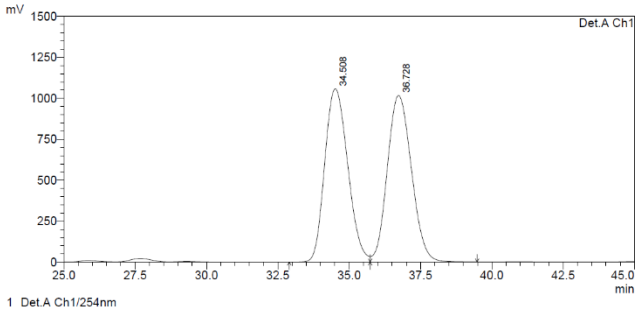
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.021	1065906	19237	5.105	7.550
2	19.129	19815508	235559	94.895	92.450
Total		20881414	254796	100.000	100.000





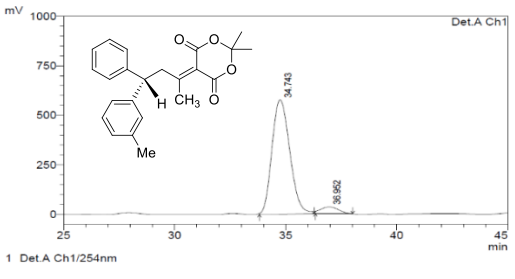


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.508	59316688	1057804	49.805	50.994
2	36.728	59780995	1016548	50.195	49.006
Total		119097683	2074352	100.000	100.000

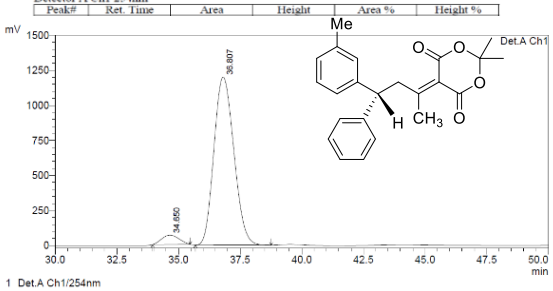


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %

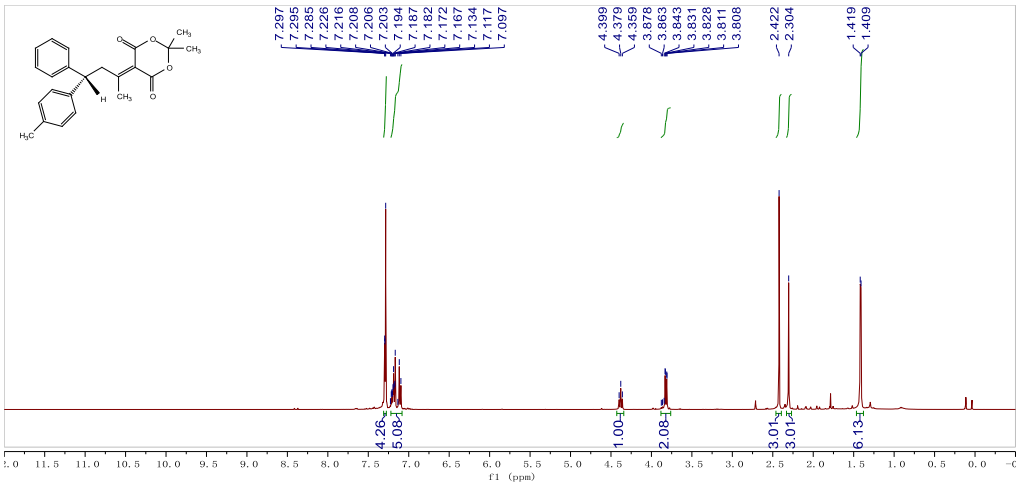


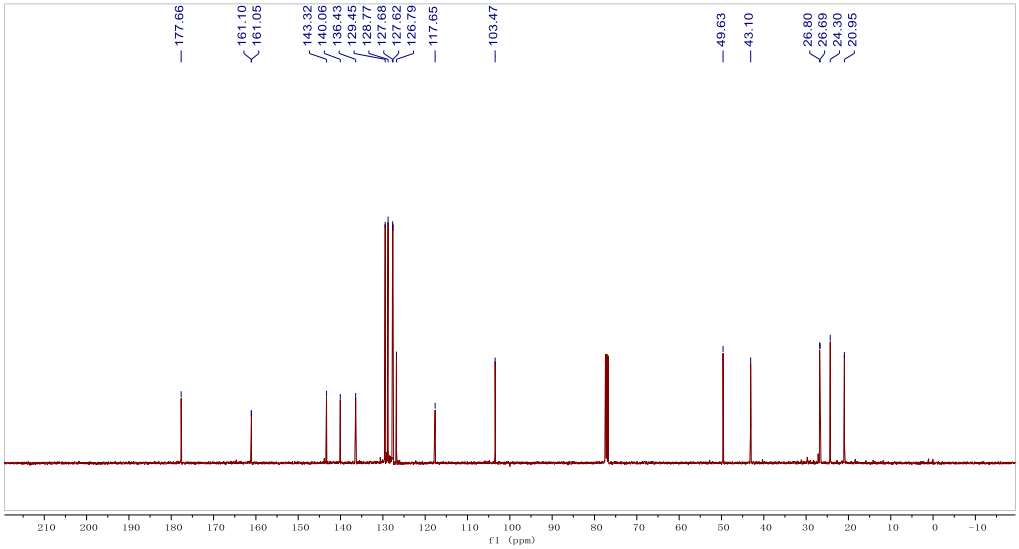
1 Det.A Ch1/254nm

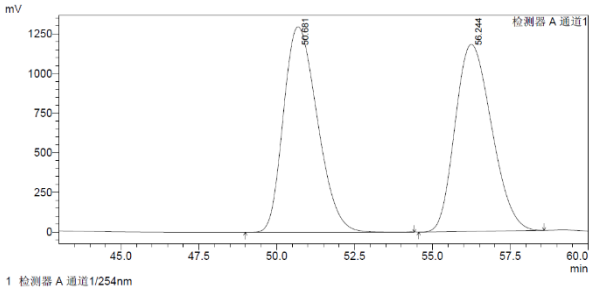
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.650	3223134	66125	4.562	5.226
2	36.807	67432441	1199191	95.438	94.774
Total		70655574	1265316	100.000	100.000





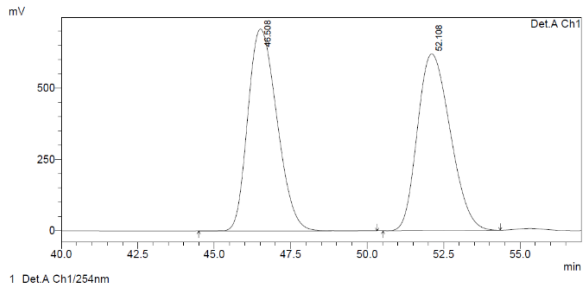


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	50.681	98173810	1295367	50.466	52.339
2	56.244	96360384	1179682	49.534	47.661
总计		194534195	2474949	100.000	100.000

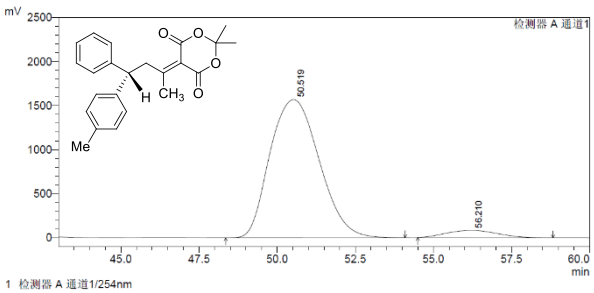


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.508	46948618	708058	50.352	53.331
2	52.108	46291954	619616	49.648	46.669
Total		93240572	1327674	100.000	100.000

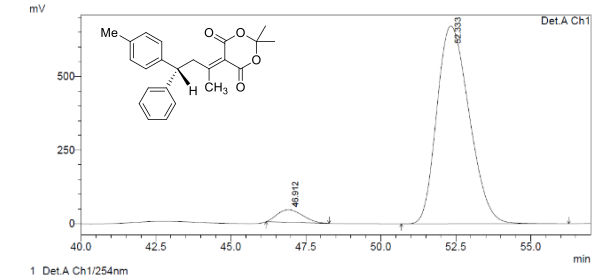


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	50.519	172361224	1569089	94.896	95.074
2	56.210	9270630	81293	5.104	4.926
总计		181631853	1650382	100.000	100.000

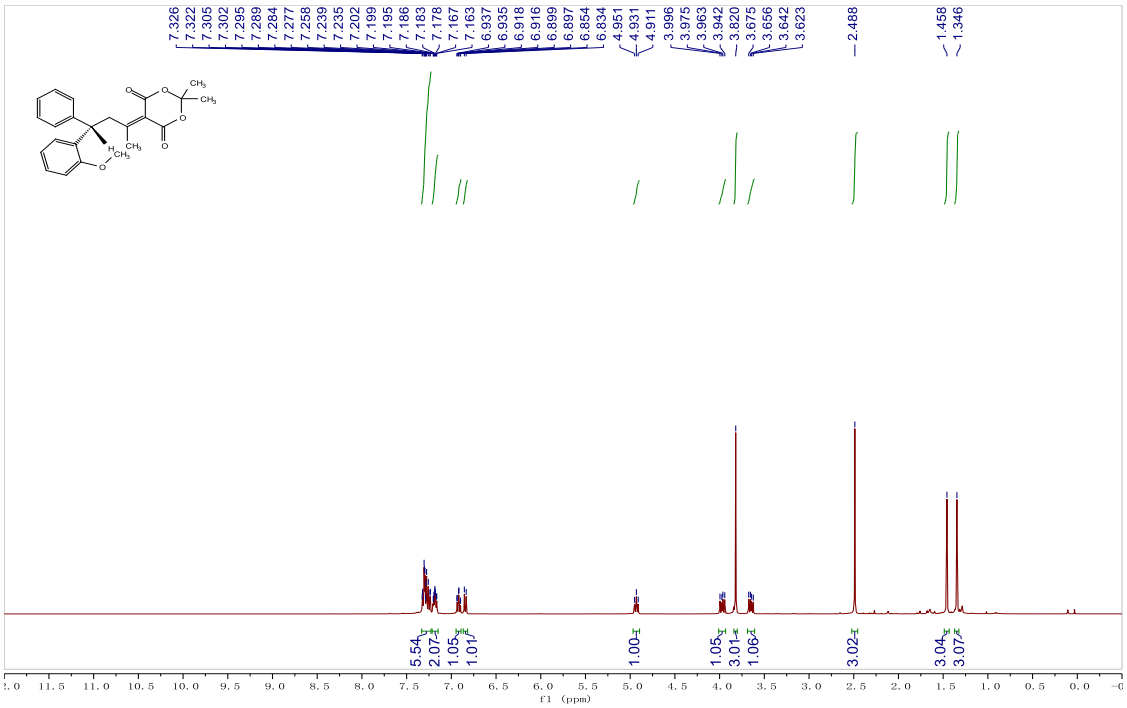


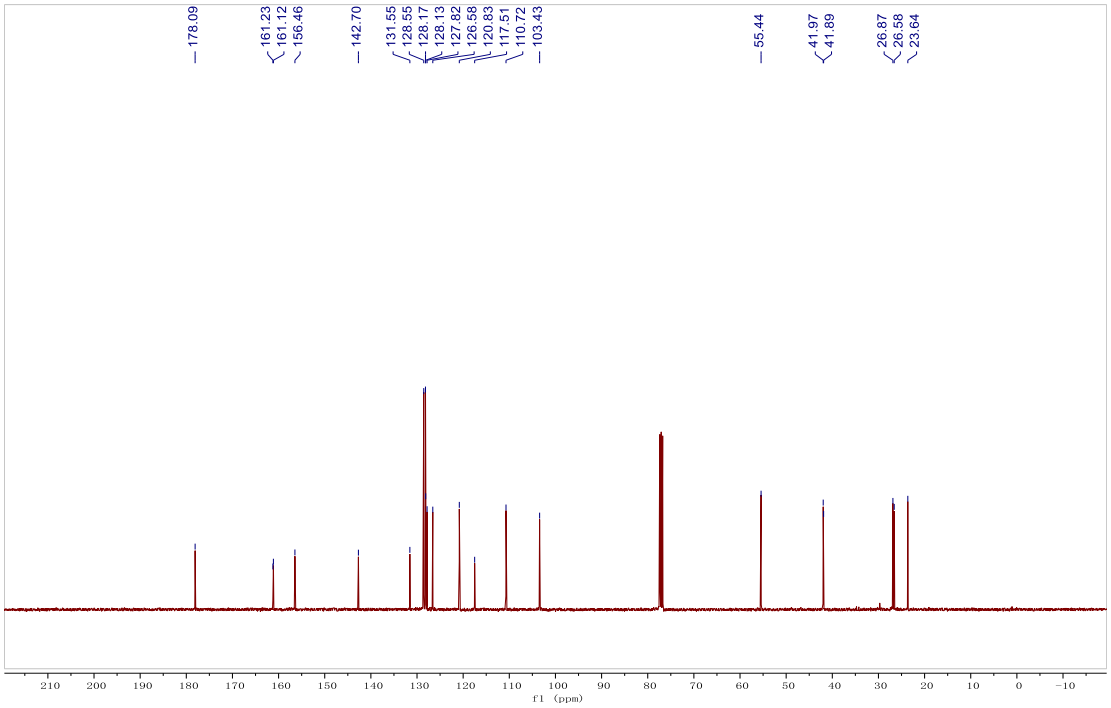
1 Det.A Ch1/254nm

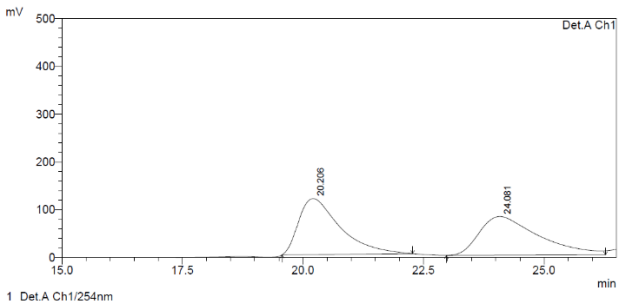
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	46.912	2508052	42642	4.728	5.969
2	52.333	50540186	671745	95.272	94.031
Total		53048238	714388	100.000	100.000



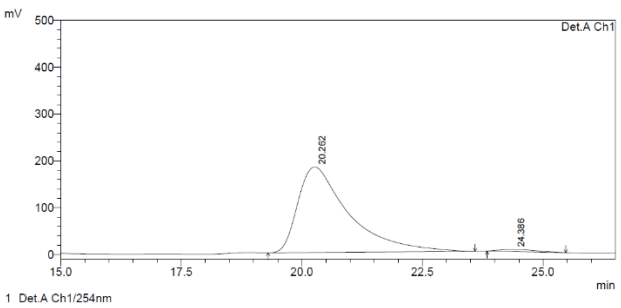




PeakTable

Detector A Ch1 254nm

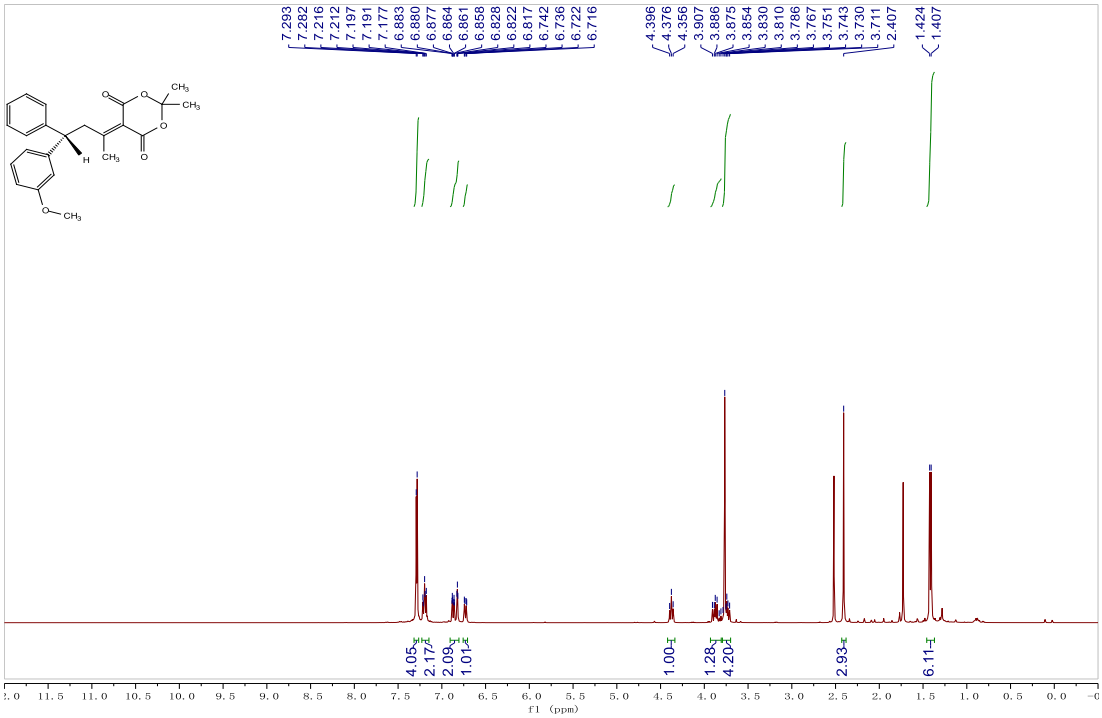
Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.206	7018860	117291	50.173	59.096
2	24.081	6970484	81186	49.827	40.904
Total		13989343	198477	100.000	100.000

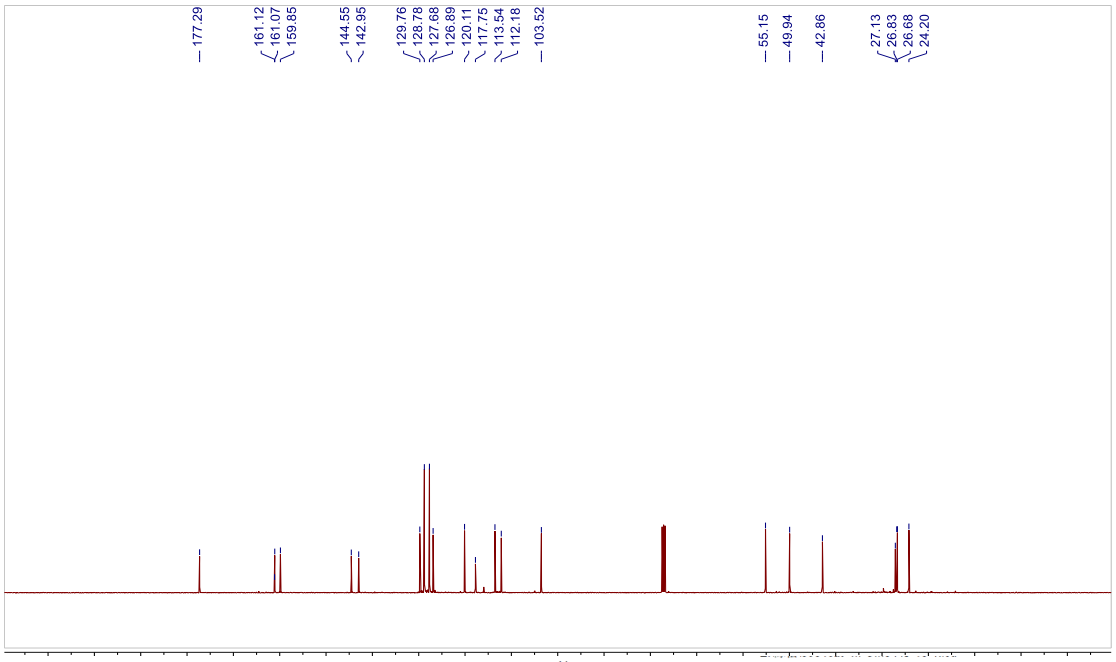


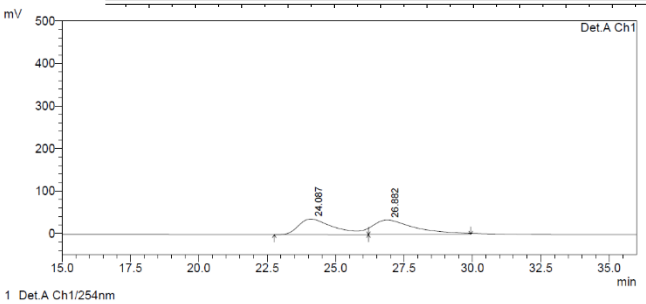
PeakTable

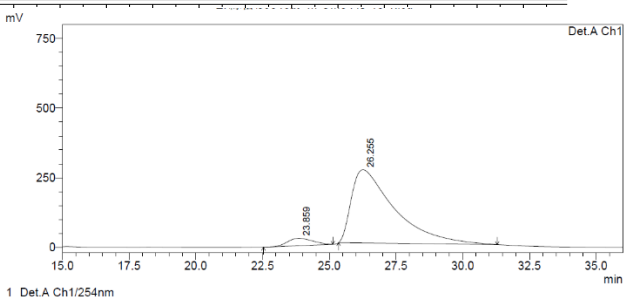
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.262	13387471	182683	98.254	97.696
2	24.386	237956	4308	1.746	2.304
Total		13625428	186991	100.000	100.000









PeakTable

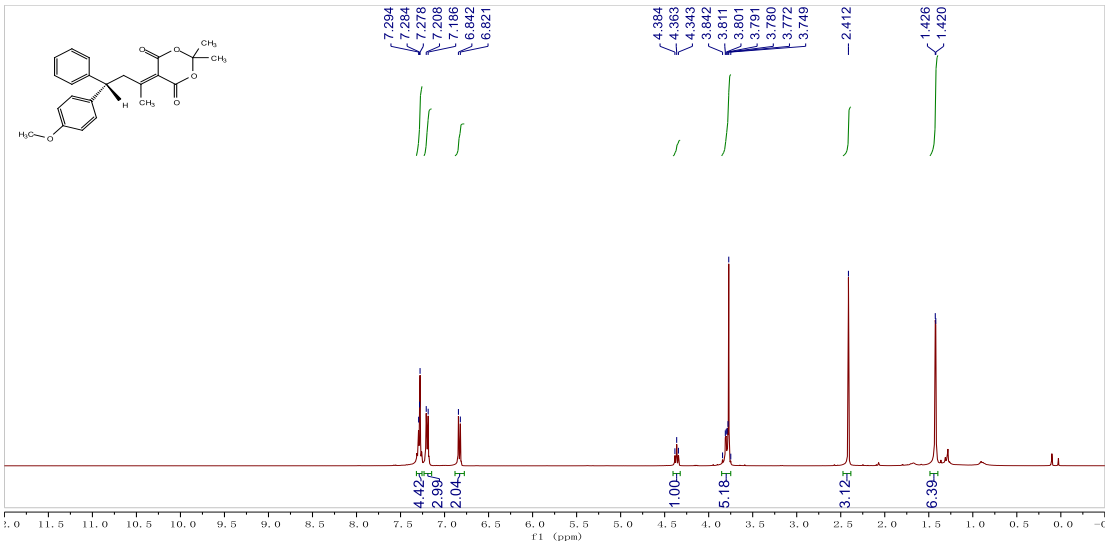
Detector A Ch1 254nm

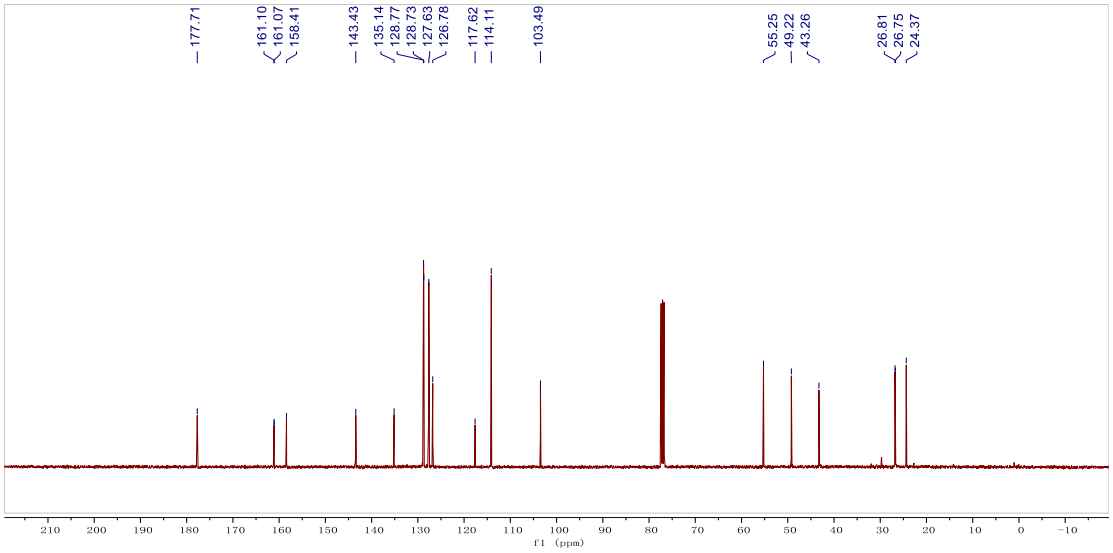
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.087	3426688	36743	49.073	52.127
2	26.882	3556205	33744	50.927	47.873
Total		6982893	70487	100.000	100.000

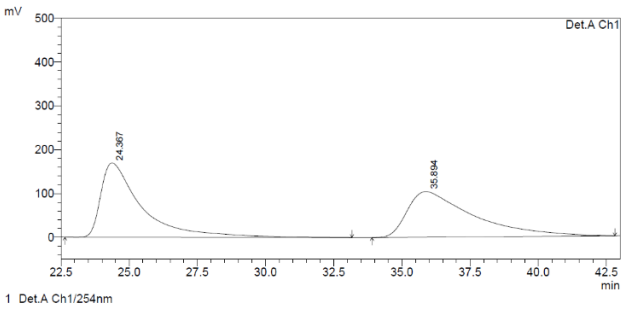
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.859	1734511	26746	5.538	9.239
2	26.255	29583355	262733	94.462	90.761
Total		31317866	289479	100.000	100.000





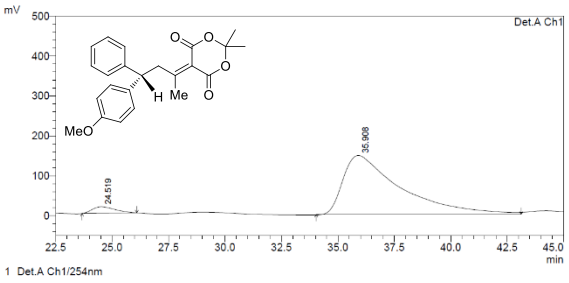


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.367	17643573	169707	50.226	61.973
2	35.894	17484739	104131	49.774	38.027
Total		35128312	273838	100.000	100.000

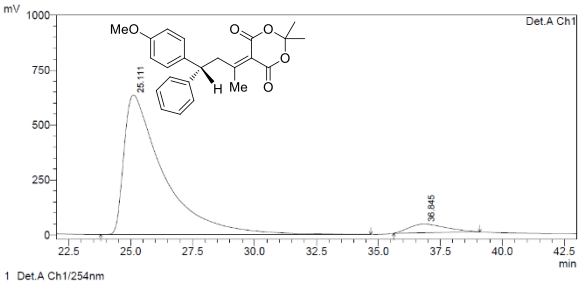


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.519	1148219	16367	4.203	9.967
2	35.908	26173593	147845	95.797	90.033
Total		27321812	164211	100.000	100.000

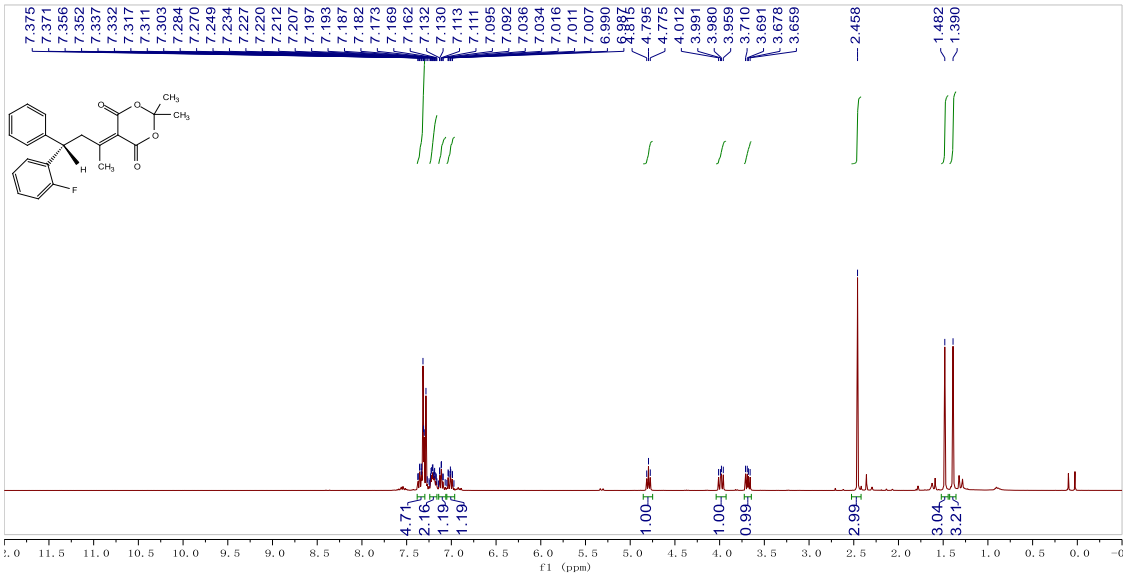


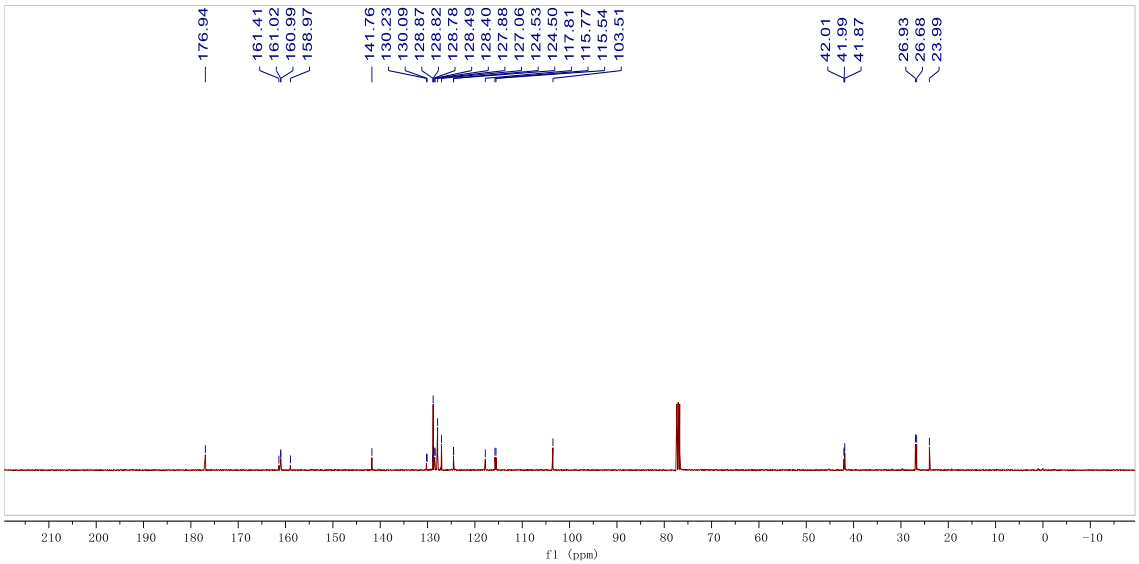
1 Det.A Ch1/254nm

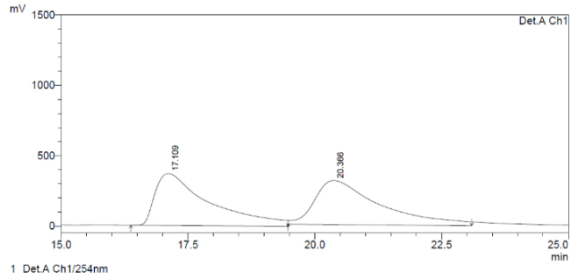
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.111	70091783	634445	94.515	94.137
2	36.845	4067863	39512	5.485	5.863
Total		74159646	673956	100.000	100.000



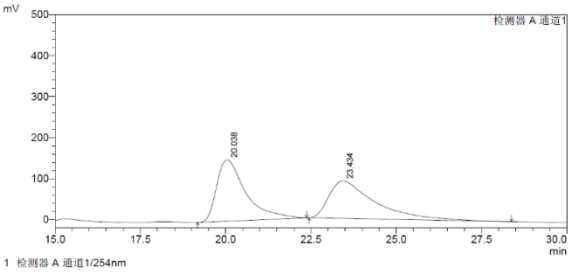




PeakTable

Detector A Ch1 254nm

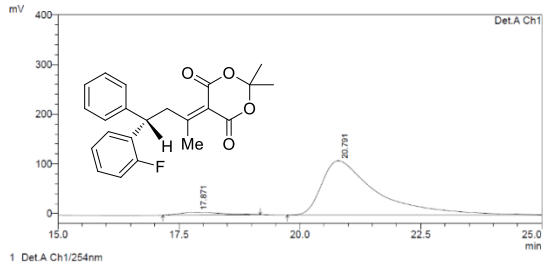
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.109	27484612	368763	49.413	54.121
2	20.366	28137540	312603	50.587	45.879
Total		55622152	681367	100.000	100.000



峰表

检测器 A Ch1 254nm

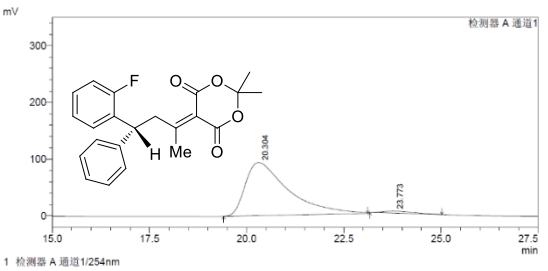
峰#	保留时间	面积	高度	面积 %	高度 %
1	20.038	8853396	149434	50.871	62.004
2	23.434	8550381	91572	49.129	37.996
总计		17403777	241006	100.000	100.000



PeakTable

Detector A Ch1 254nm

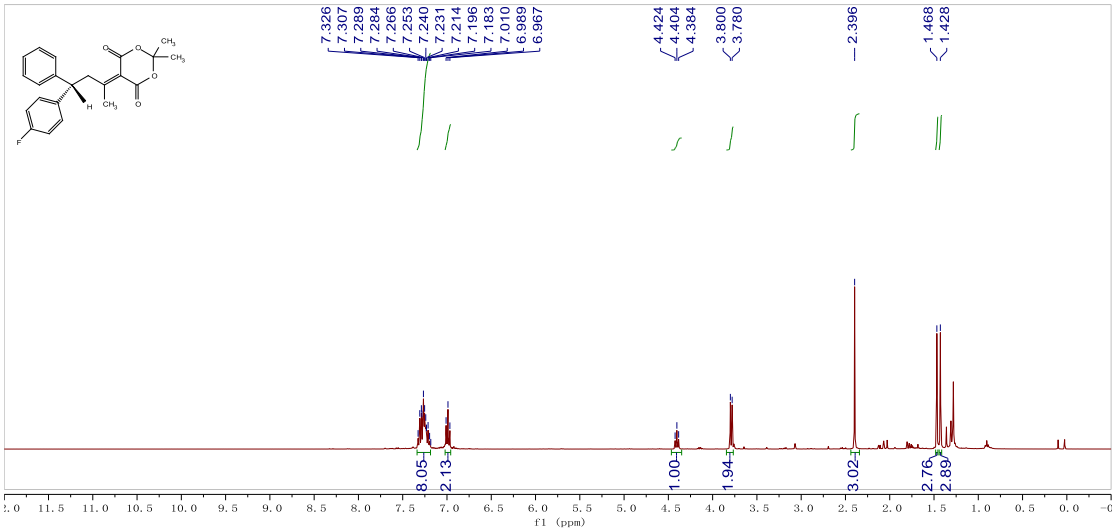
Peak#	Ret. Time	Area	Height	Area %	Height %
1	17.871	317964	5468	3.527	4.760
2	20.791	8696942	109406	96.473	95.240
Total		9014905	114873	100.000	100.000

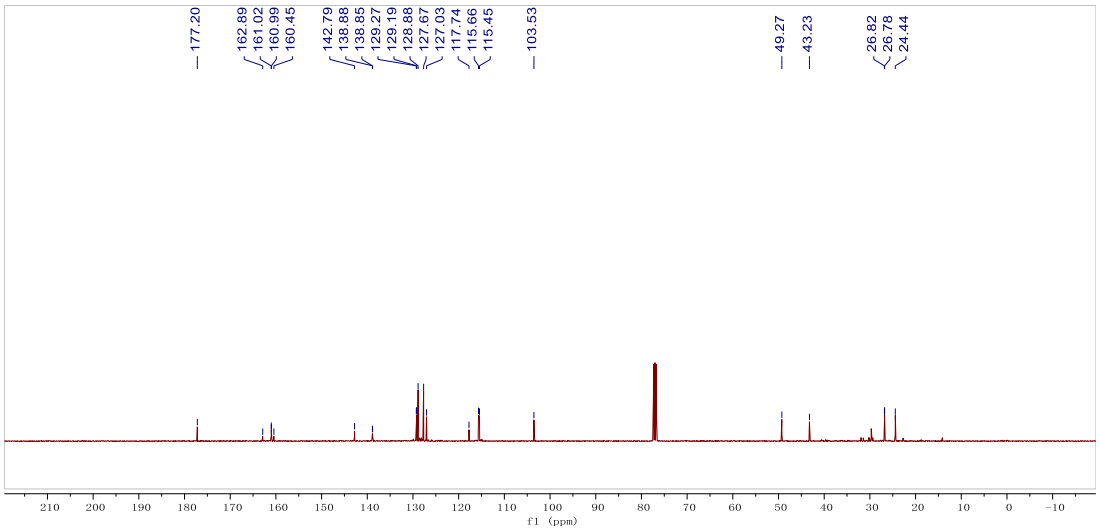


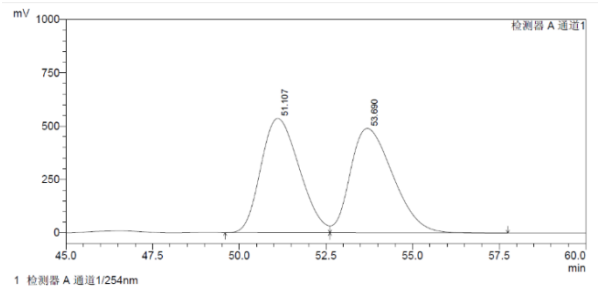
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	20.304	7249012	93757	97.445	96.657
2	23.773	190097	3242	2.555	3.343
总计		7439109	96999	100.000	100.000





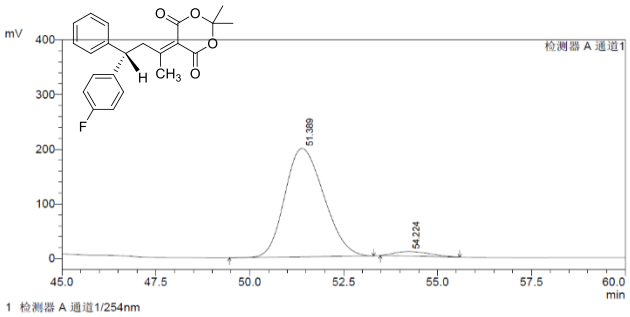


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	51.107	41336574	535532	49.651	52.258
2	53.690	41917723	489251	50.349	47.742
总计		83254297	1024784	100.000	100.000

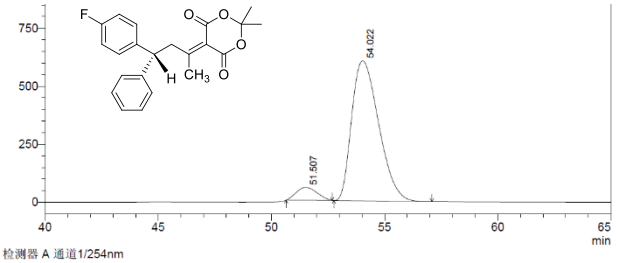


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	51.389	14346111	198357	96.336	95.992
2	54.224	545691	8282	3.664	4.008
总计		14891802	206639	100.000	100.000

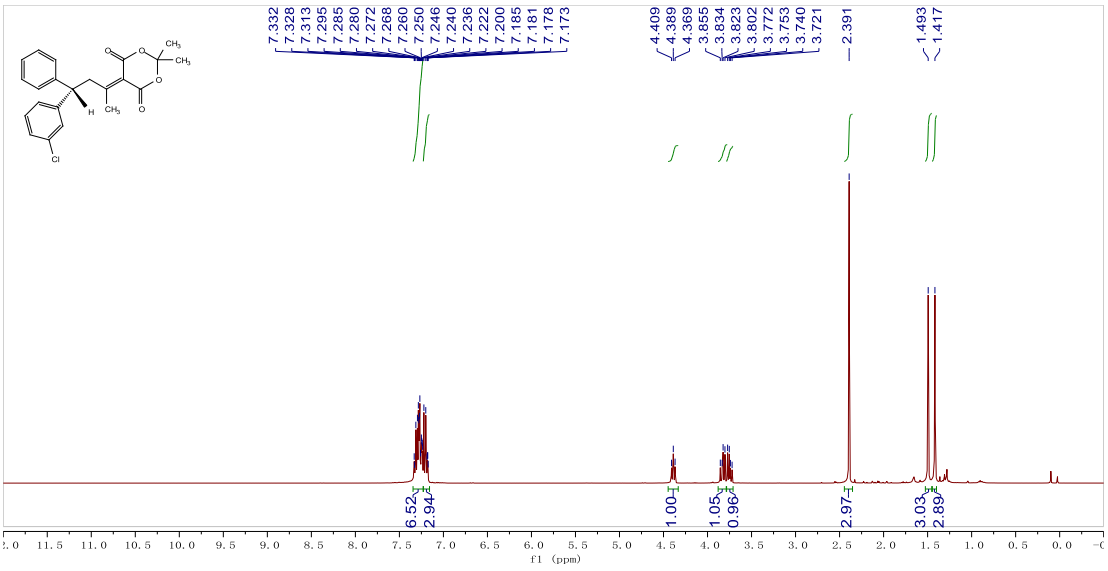


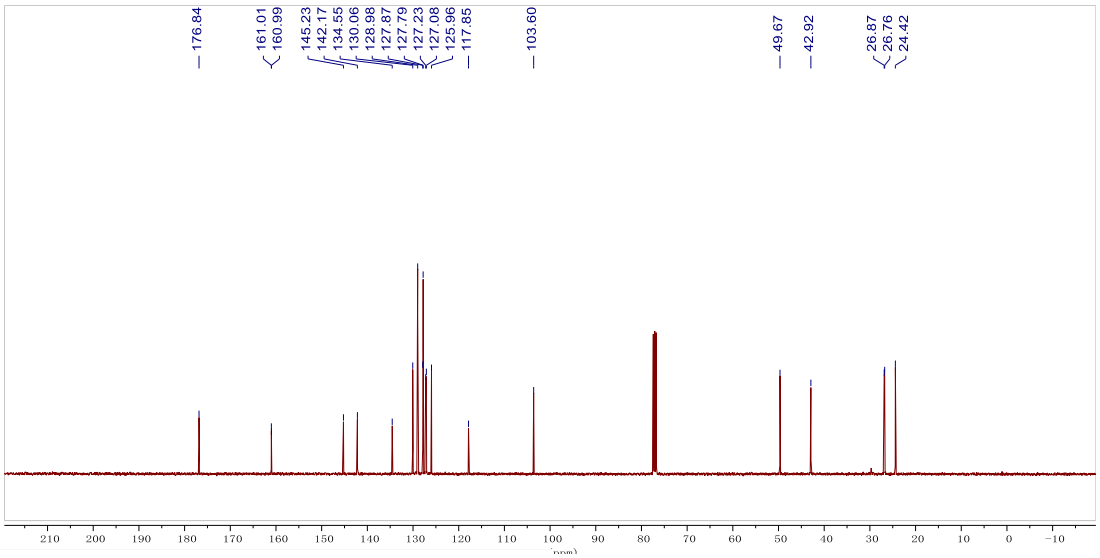
1 检测器 A 通道1/254nm

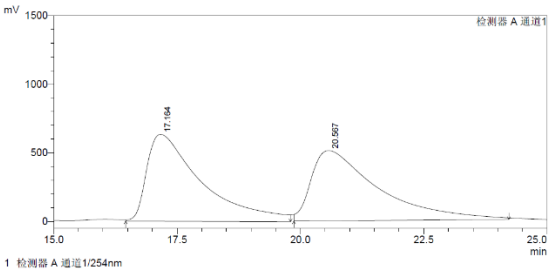
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	51.507	3511280	55087	6.536	8.369
2	54.022	50209638	603158	93.464	91.631
总计		53720917	658246	100.000	100.000





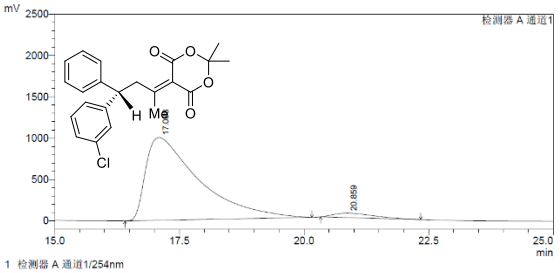


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	17.164	48894203	633914	50.257	55.266
2	20.567	48394011	513120	49.743	44.734
总计		97288214	1147034	100.000	100.000

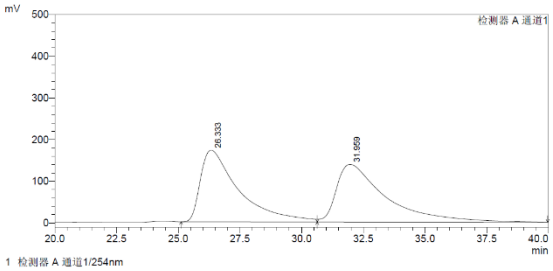


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	17.088	74476237	1001525	96.090	94.949
2	20.859	3030300	53280	3.910	5.051
总计		77506536	1054805	100.000	100.000

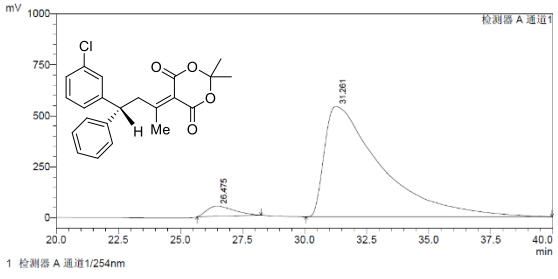


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.333	18621180	171874	49.182	53.436
2	31.959	19240819	138169	50.818	44.564
总计		37861999	310042	100.000	100.000

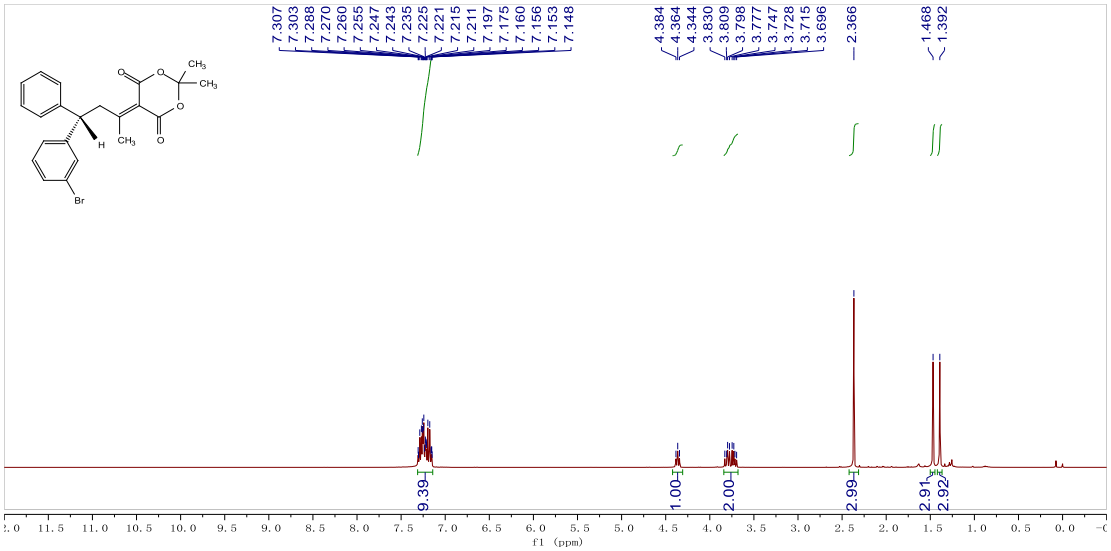


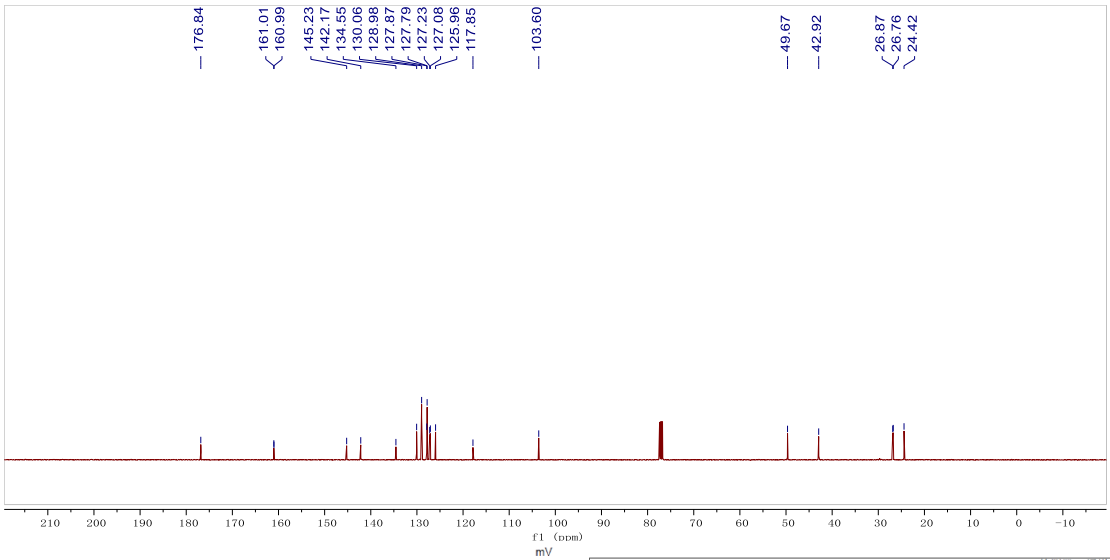
1 检测器 A 通道1/254nm

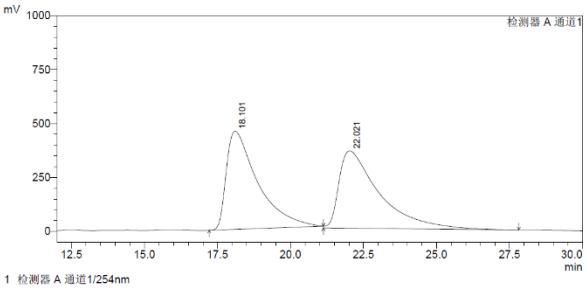
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.475	3769336	49341	4.192	8.369
2	31.261	86146373	540196	95.808	91.631
总计		89915709	589537	100.000	100.000





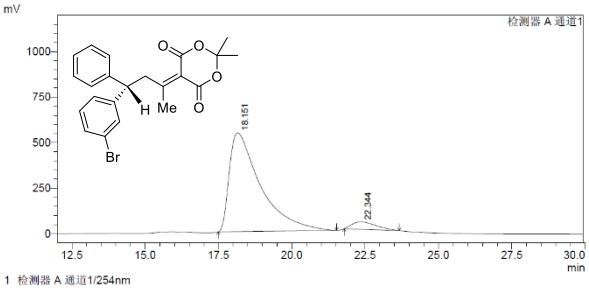


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	18.101	34043119	454734	49.668	55.903
2	22.021	34498148	358697	50.332	44.097
总计		68541267	813431	100.000	100.000

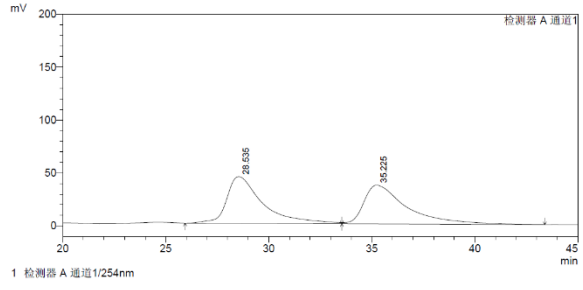


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	18.151	40077452	542406	94.467	92.986
2	22.344	2347533	40911	5.533	7.014
总计		42424985	583318	100.000	100.000

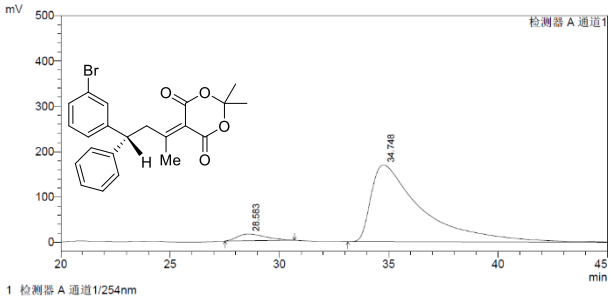


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	28.535	5378096	44190	50.344	54.653
2	35.225	5304647	36666	49.656	45.347
总计		10682743	80856	100.000	100.000

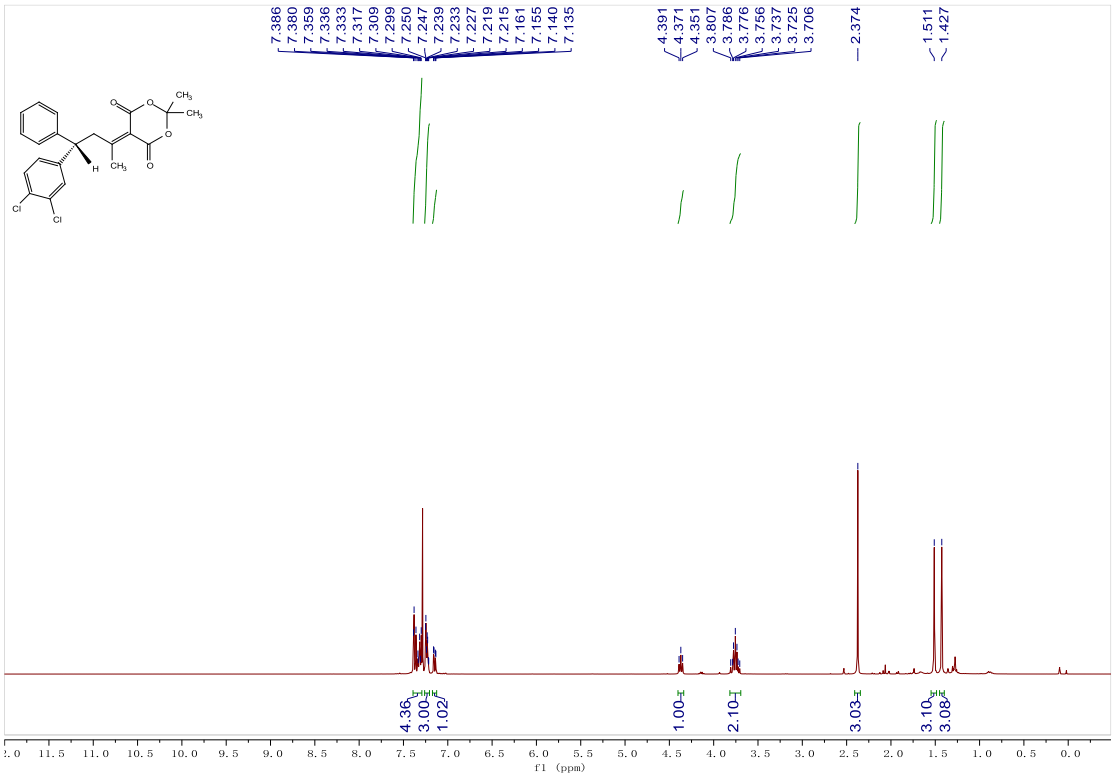


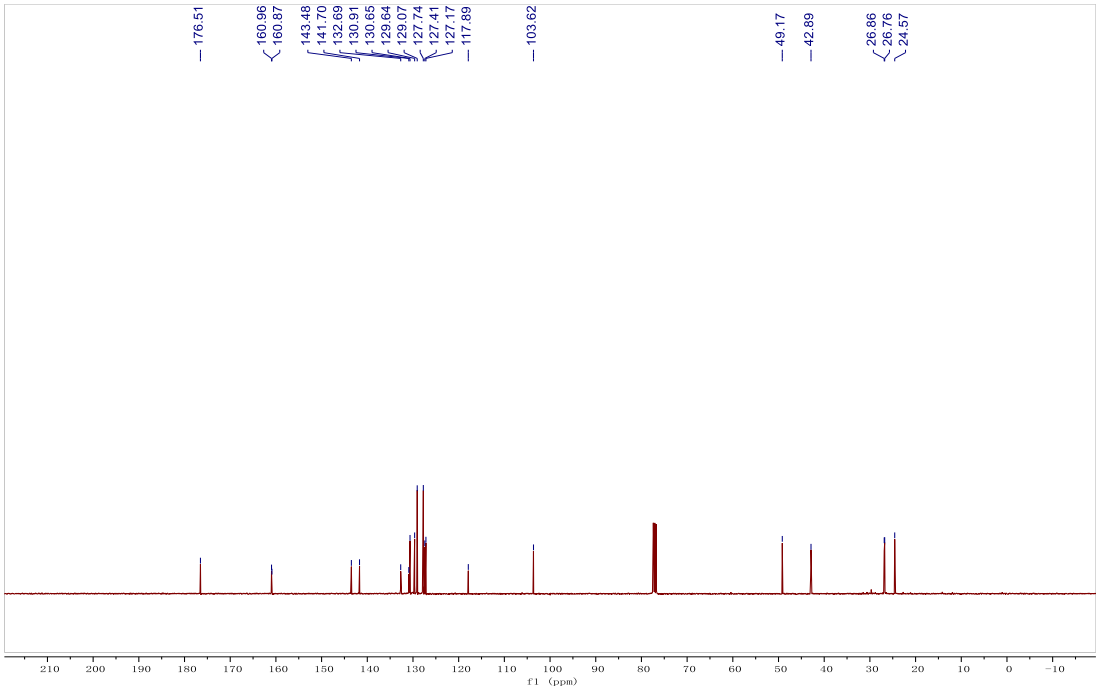
1 检测器 A 通道1/254nm

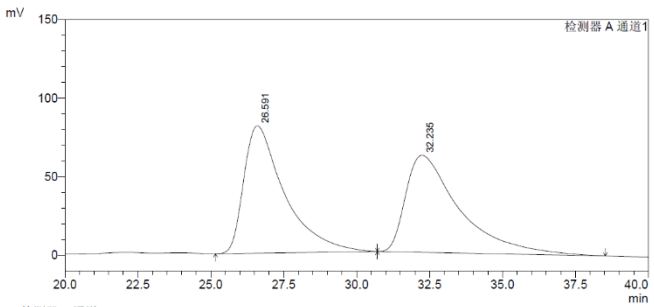
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	28.583	1351765	14785	4.677	8.018
2	34.748	27549550	169613	95.323	91.982
总计		28901315	184398	100.000	100.000





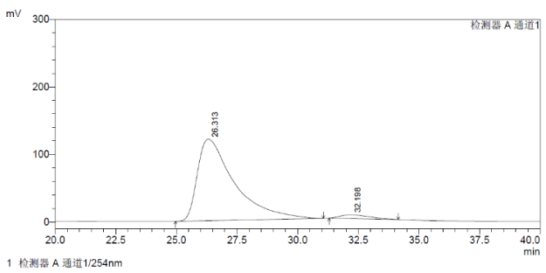


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.591	7874043	81079	49.862	56.754
2	32.235	7917612	61781	50.138	43.246
总计		15791655	142860	100.000	100.000

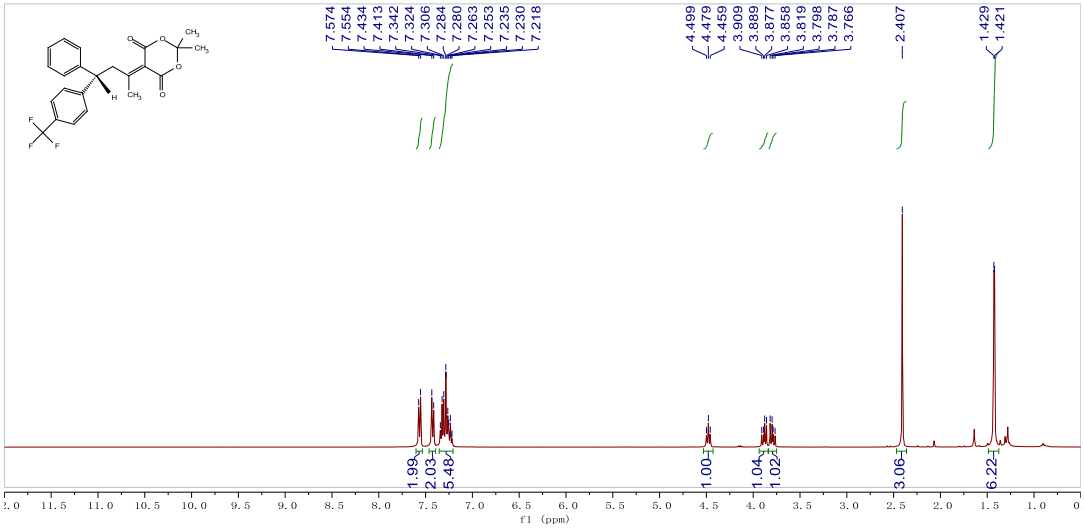


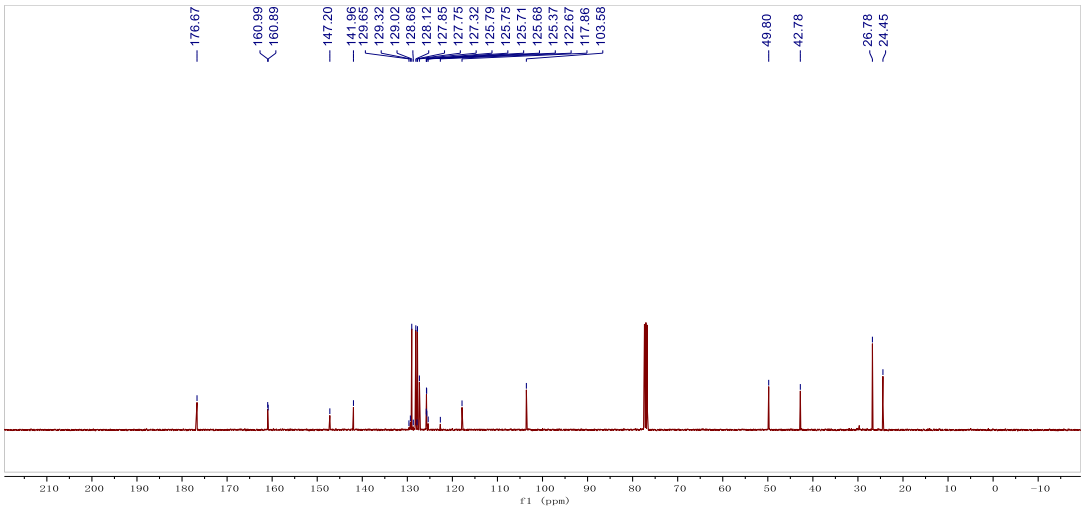
1 检测器 A 通道1/254nm

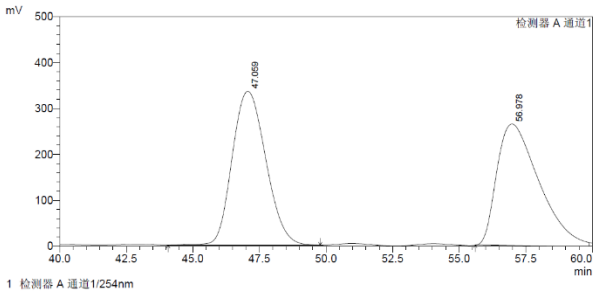
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	26.313	12841745	120655	96.421	95.600
2	32.198	476702	5553	3.579	4.400
总计		13318447	126207	100.000	100.000



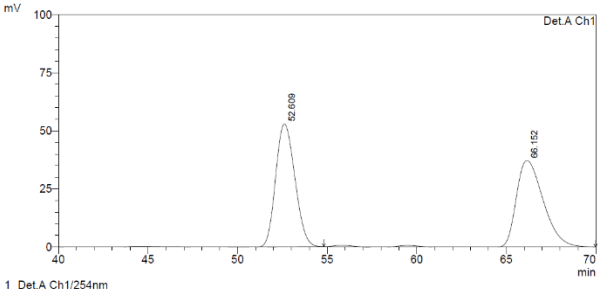




峰表

检测器 A Ch1 254nm

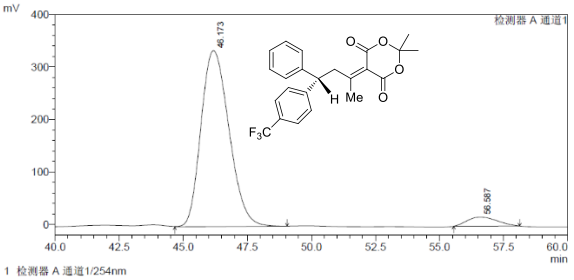
峰#	保留时间	面积	高度	面积 %	高度 %
1	47.059	29486185	335035	50.257	55.875



PeakTable

Detector A Ch1 254nm

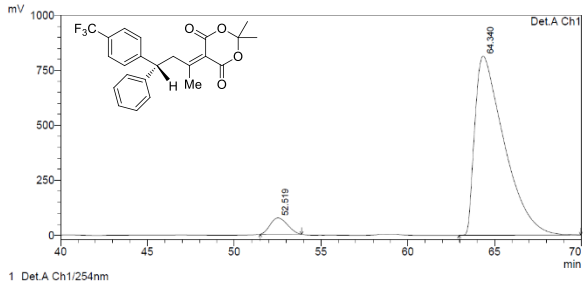
Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.609	3954947	52968	50.373	58.639
2	66.152	3896399	37360	49.627	41.361
Total		7851346	90328	100.000	100.000



峰表

检测器 A Ch1 254nm

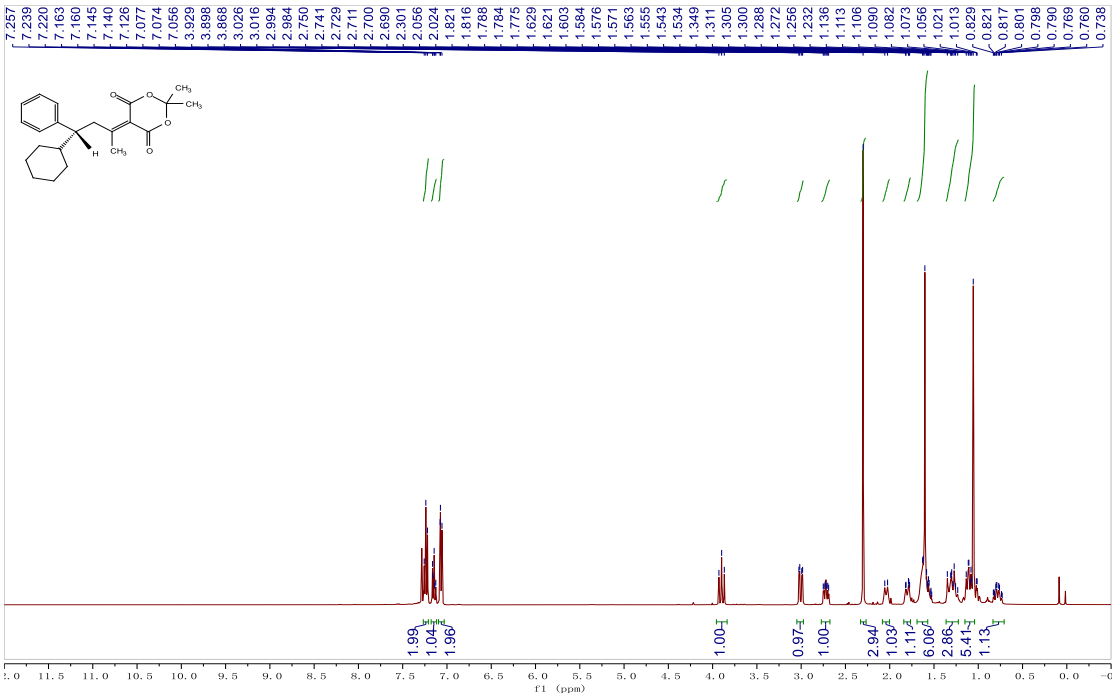
峰#	保留时间	面积	高度	面积 %	高度 %
1	46.173	25523260	335206	94.819	95.103
2	56.587	1394675	17262	5.181	4.897
总计		26917934	352468	100.000	100.000

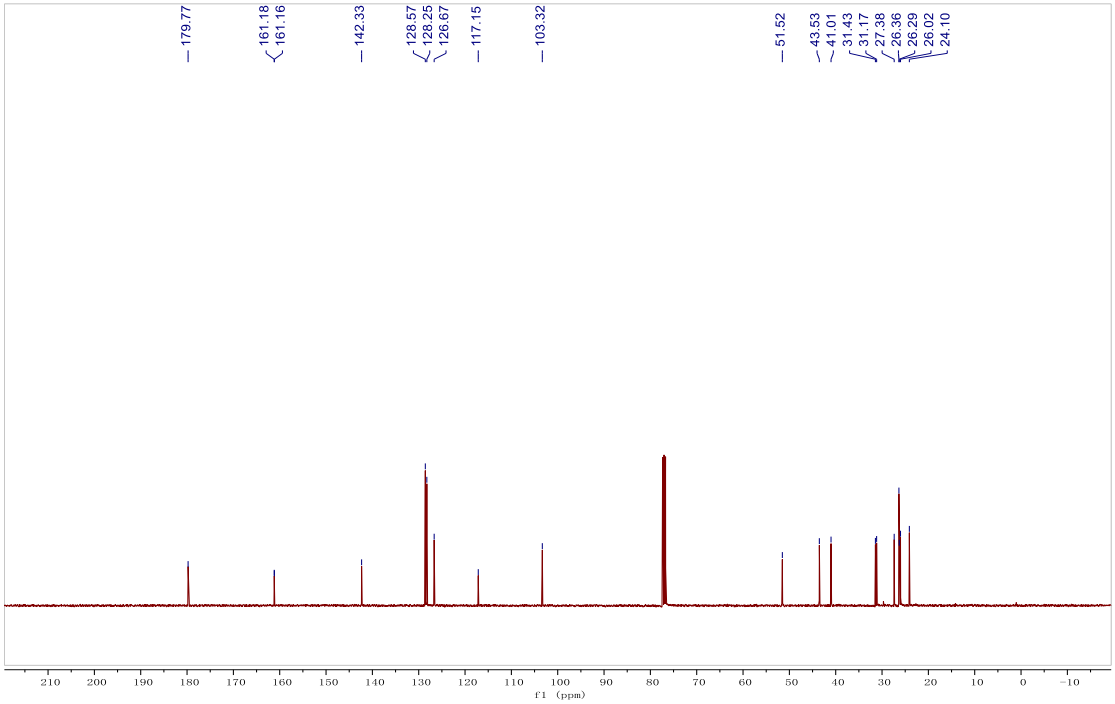


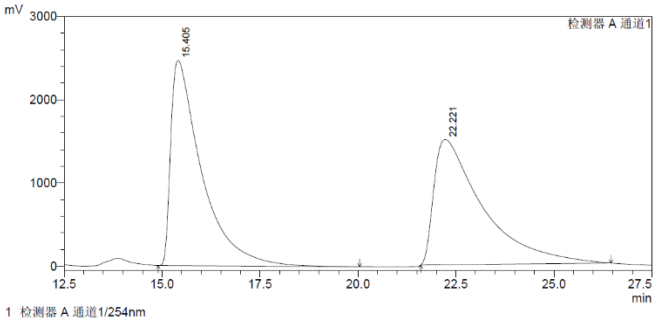
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.519	5130808	74176	5.075	8.341
2	64.340	95968360	815103	94.925	91.659
Total		101099168	889279	100.000	100.000





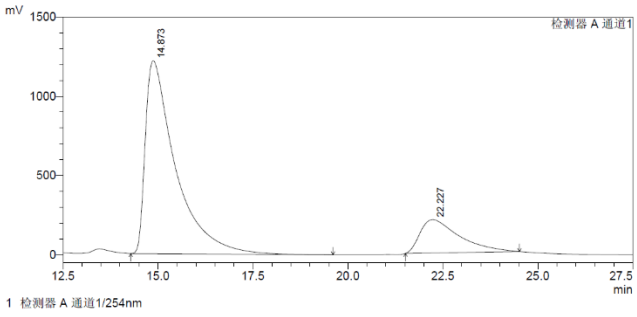


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	15.405	135083341	2465845	50.753	62.074
2	22.221	131075141	1506575	49.247	37.926
总计		266158483	3972420	100.000	100.000

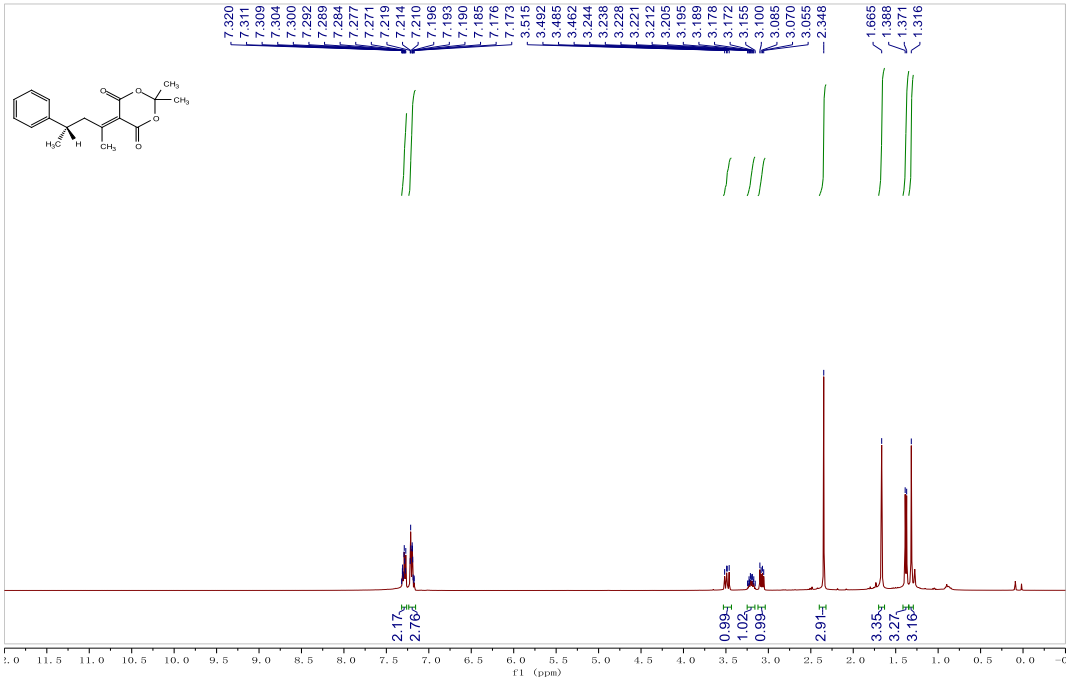


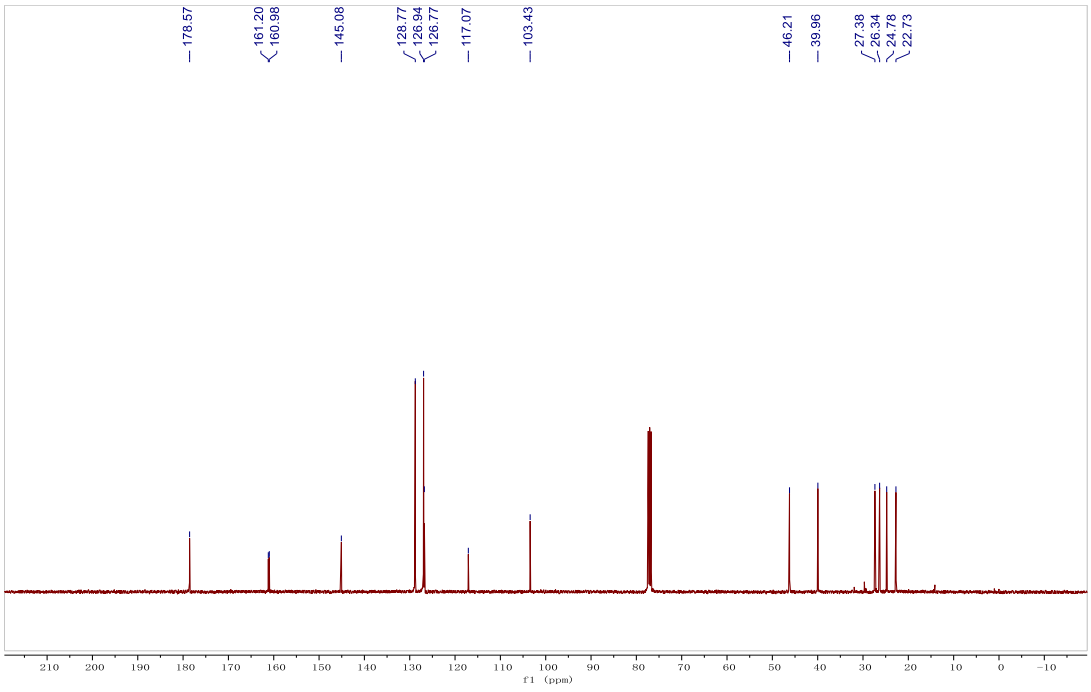
1 检测器 A 通道1/254nm

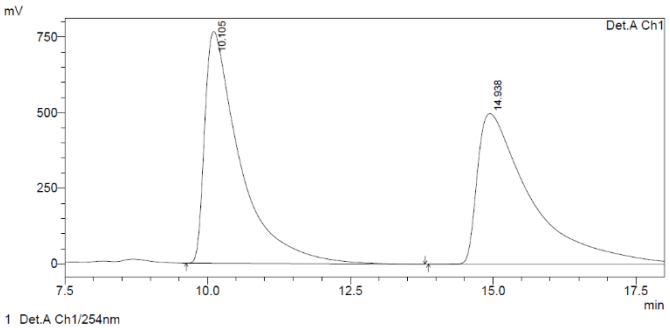
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	14.873	67359959	1218159	81.626	85.247
2	22.227	15163030	210810	18.374	14.753
总计		82522989	1428970	100.000	100.000





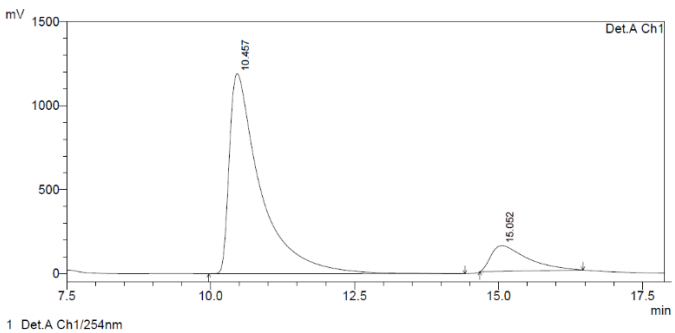


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.105	32989081	766313	50.230	60.650
2	14.938	32686330	497197	49.770	39.350
Total		65675411	1263510	100.000	100.000

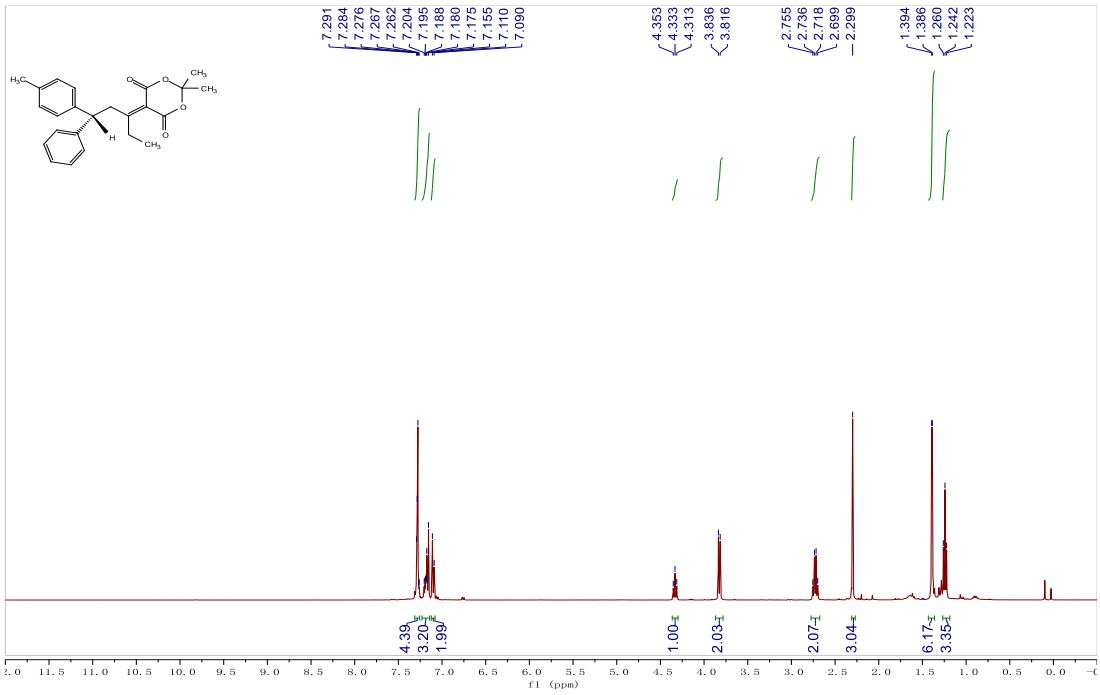


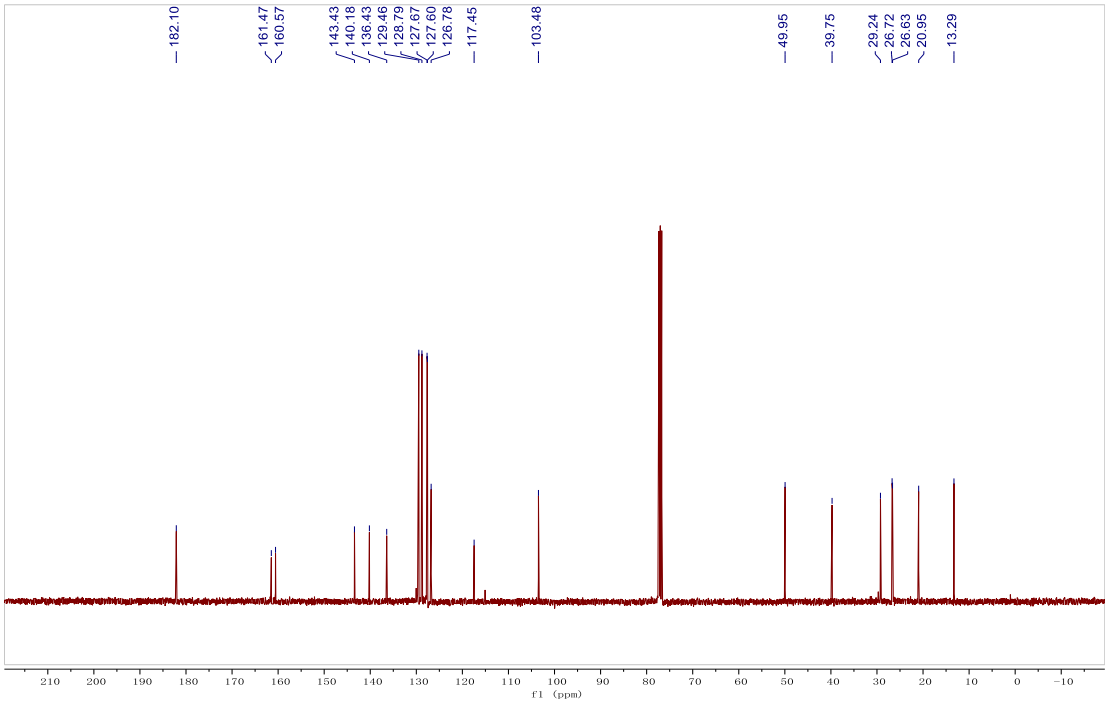
1 Det.A Ch1/254nm

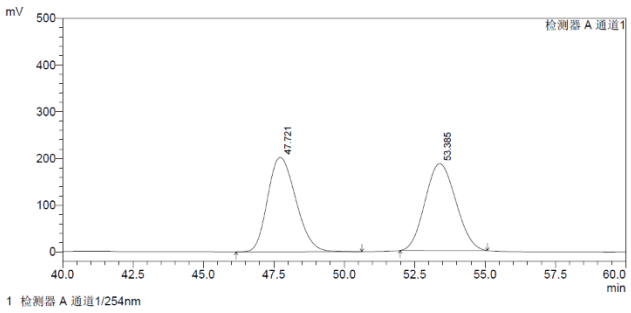
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.457	44856753	1190844	86.942	88.576
2	15.052	6737423	153581	13.058	11.424
Total		51594176	1344425	100.000	100.000





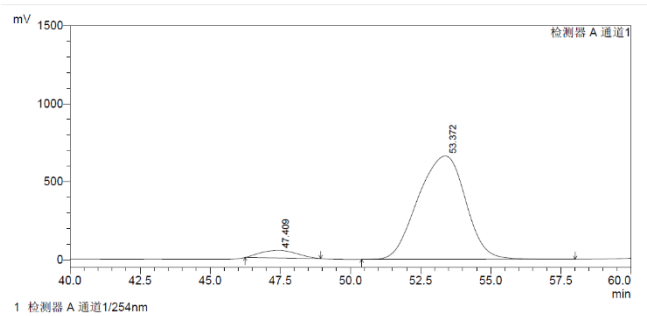


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	47.721	14115081	202395	49.948	52.120
2	53.385	14144388	185928	50.052	47.880
总计		28259469	388324	100.000	100.000

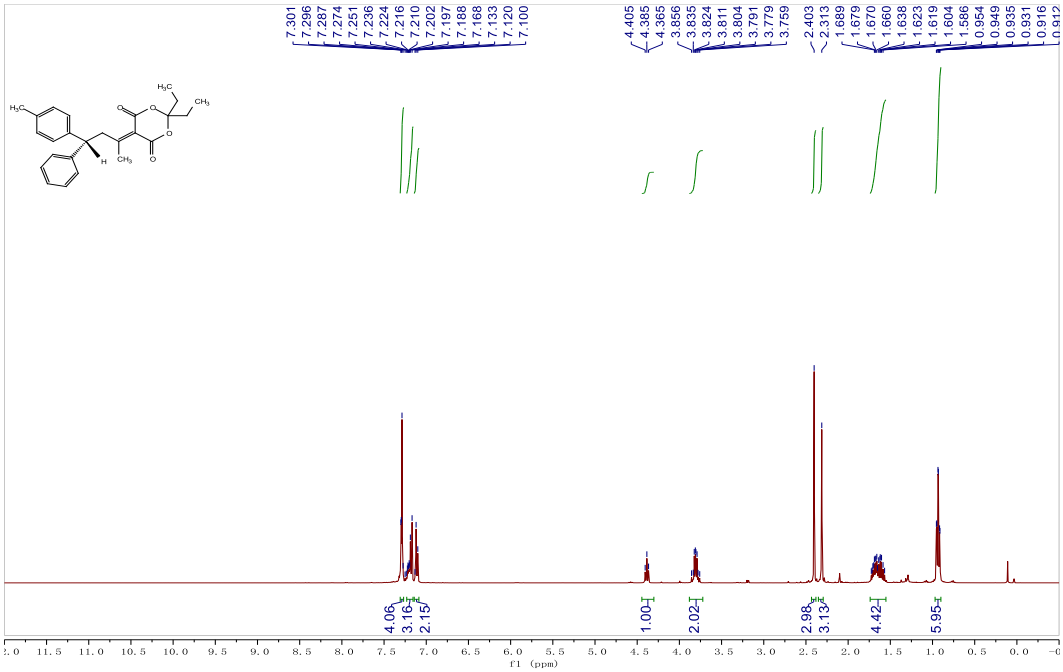


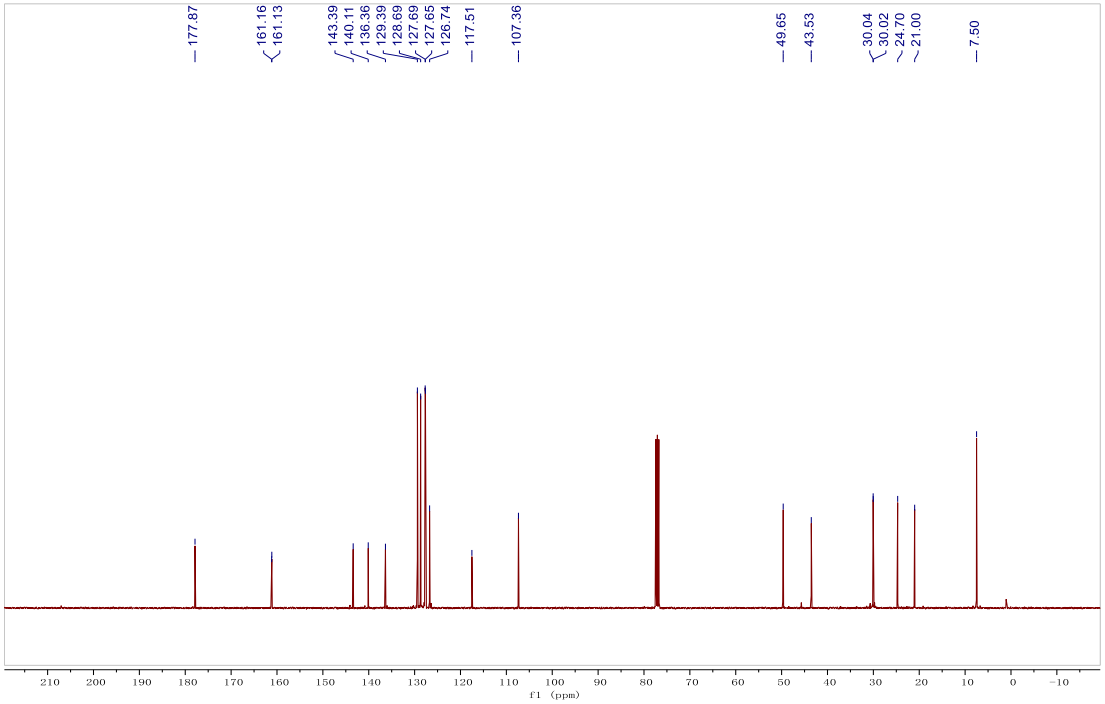
1 检测器 A 通道1/254nm

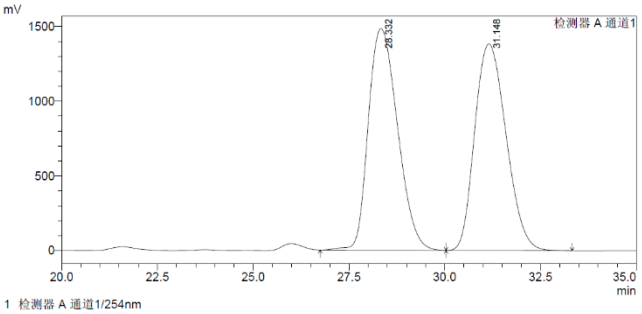
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	47.409	4380397	48089	5.300	6.766
2	53.372	78269076	662680	94.700	93.234
总计		82649473	710769	100.000	100.000





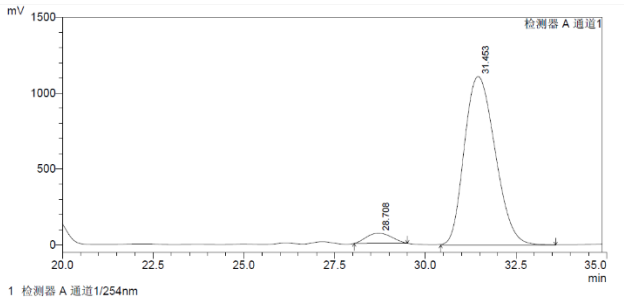


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	28.332	78865685	1482985	50.027	51.765
2	31.148	78779420	1381853	49.973	48.235
总计		157645105	2864839	100.000	100.000

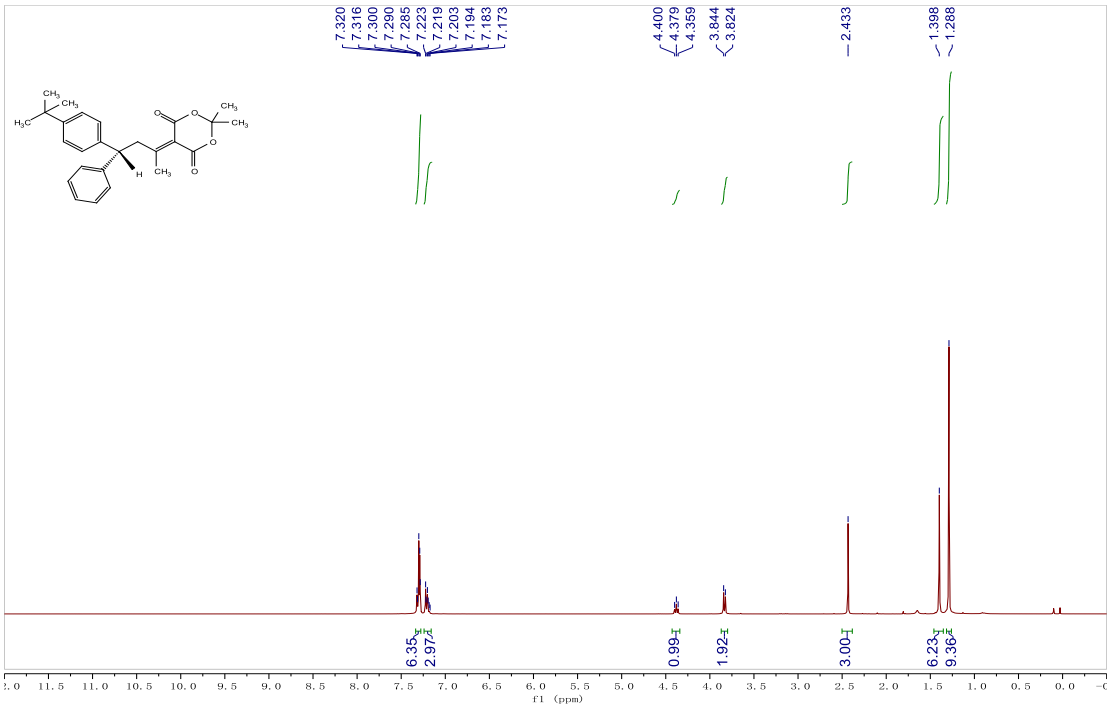


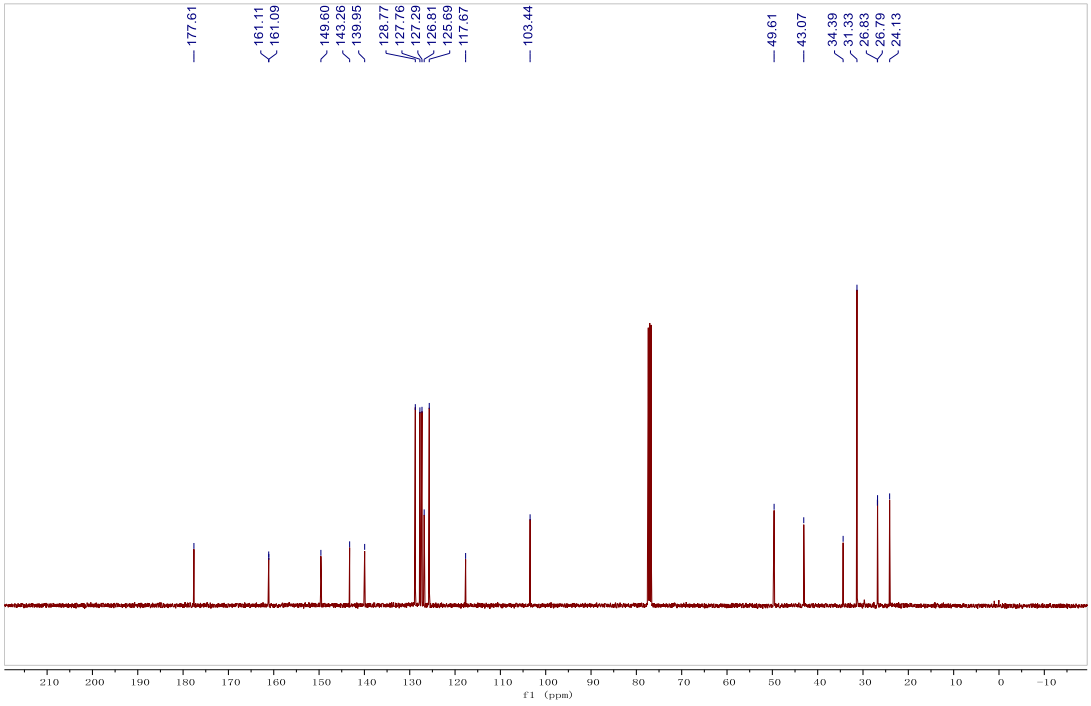
1 检测器 A 通道1/254nm

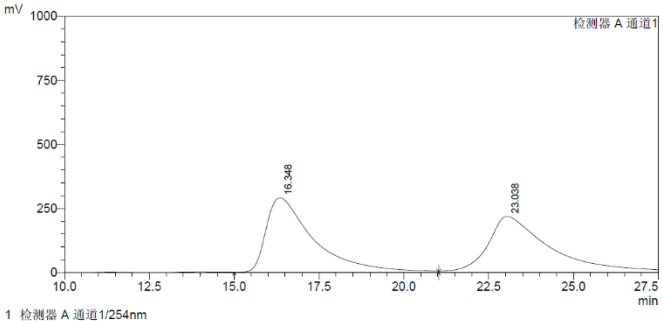
峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	28.708	3240382	67244	4.683	5.703
2	31.453	65955033	1111759	95.317	94.297
总计		69195416	1179003	100.000	100.000





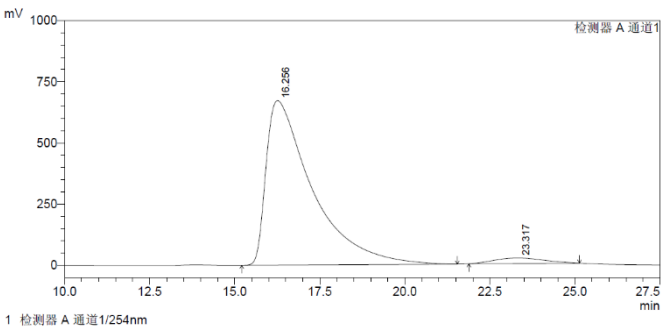


1 检测器 A 通道1/254nm

峰表

检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.348	28142816	290154	50.089	57.141
2	23.038	28043256	217633	49.911	42.859
总计		56186072	507787	100.000	100.000

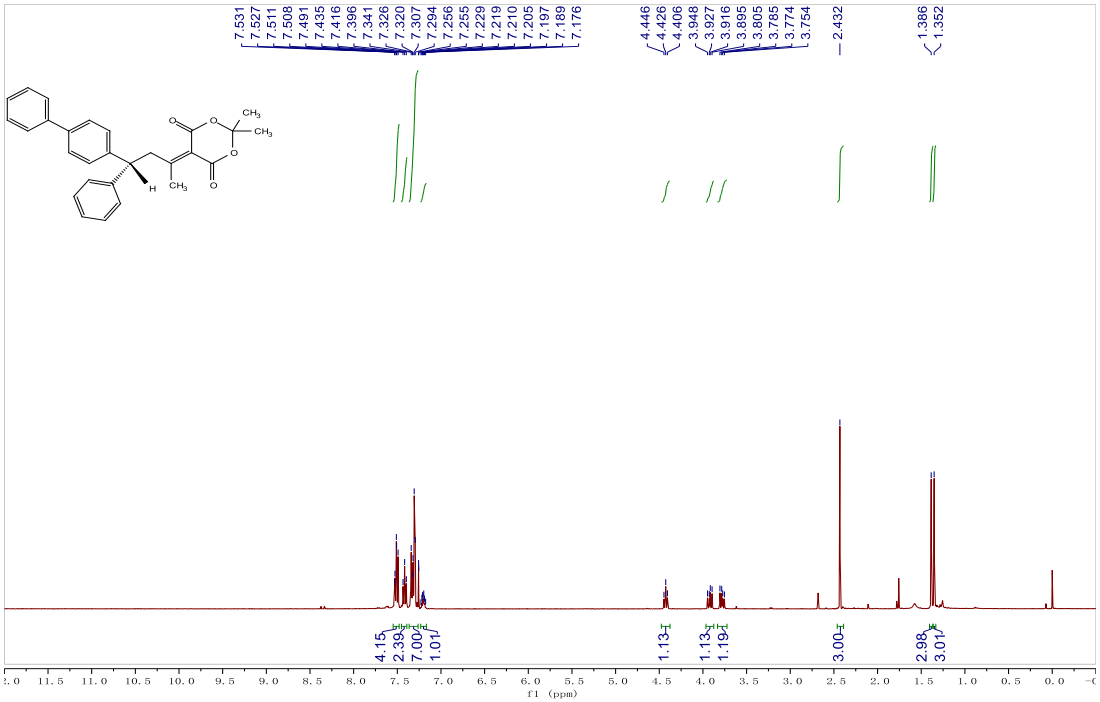


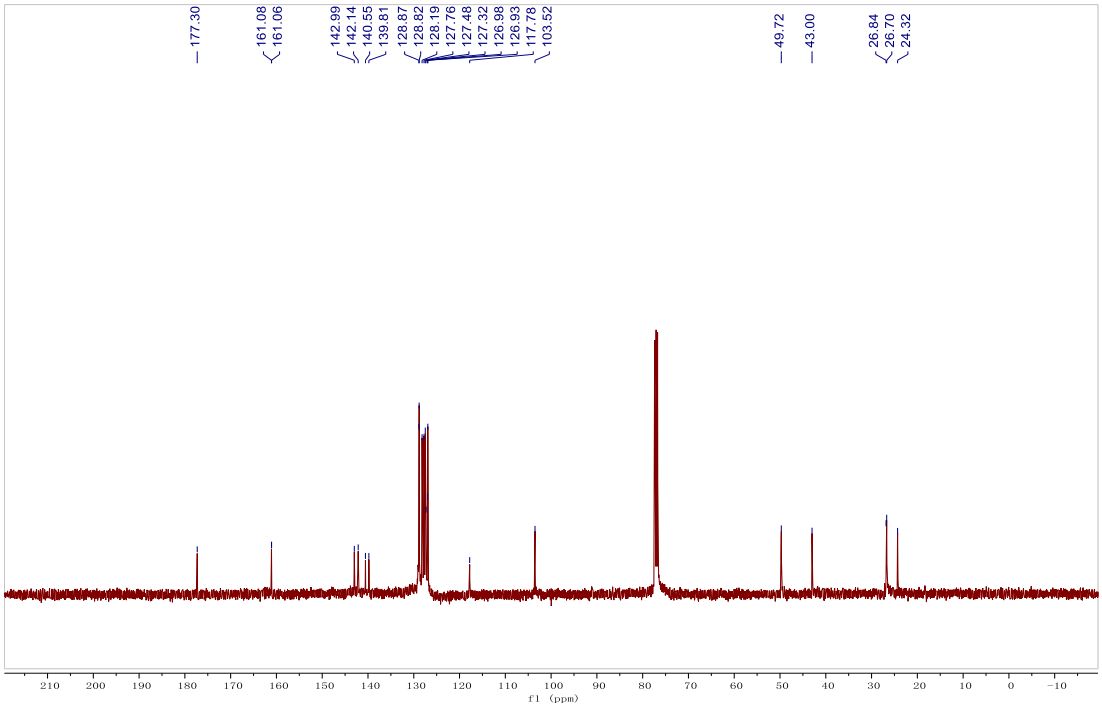
1 检测器 A 通道1/254nm

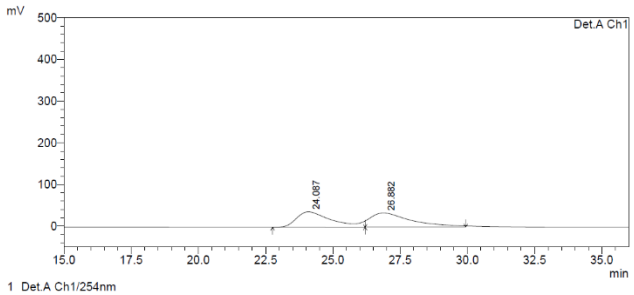
峰表

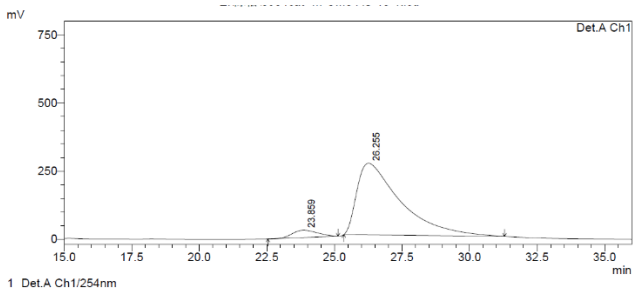
检测器 A Ch1 254nm

峰#	保留时间	面积	高度	面积 %	高度 %
1	16.256	63442896	672150	96.491	96.763
2	23.317	2307174	22486	3.509	3.237
总计		65750071	694636	100.000	100.000









PeakTable

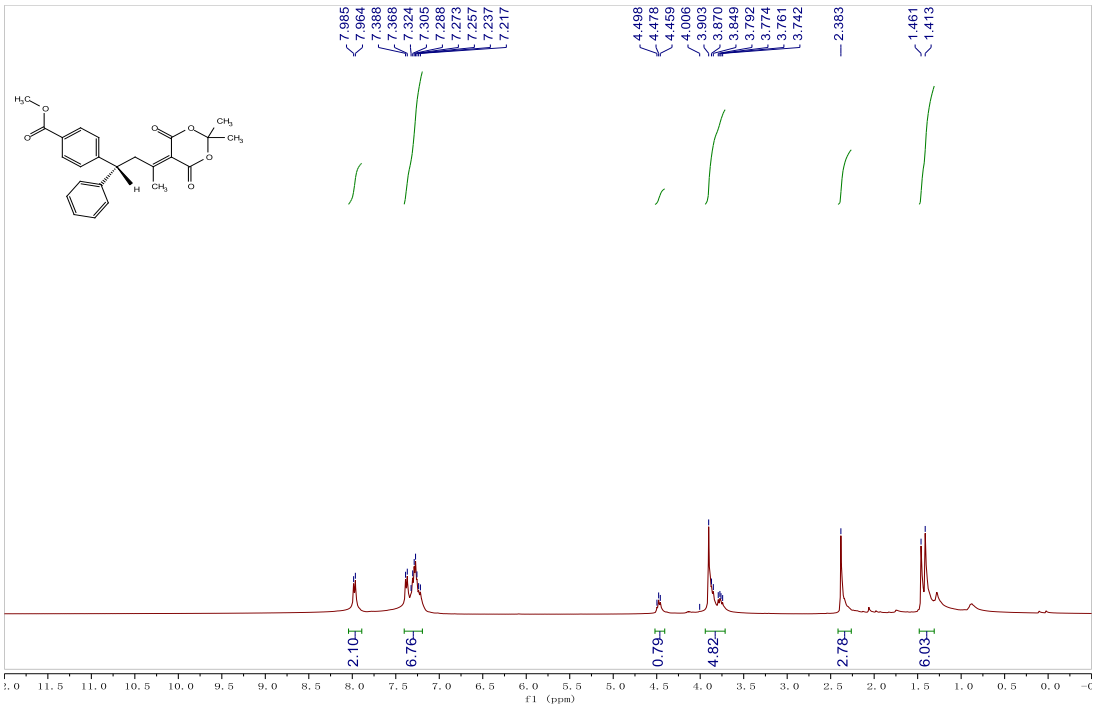
Detector A Ch1 254nm

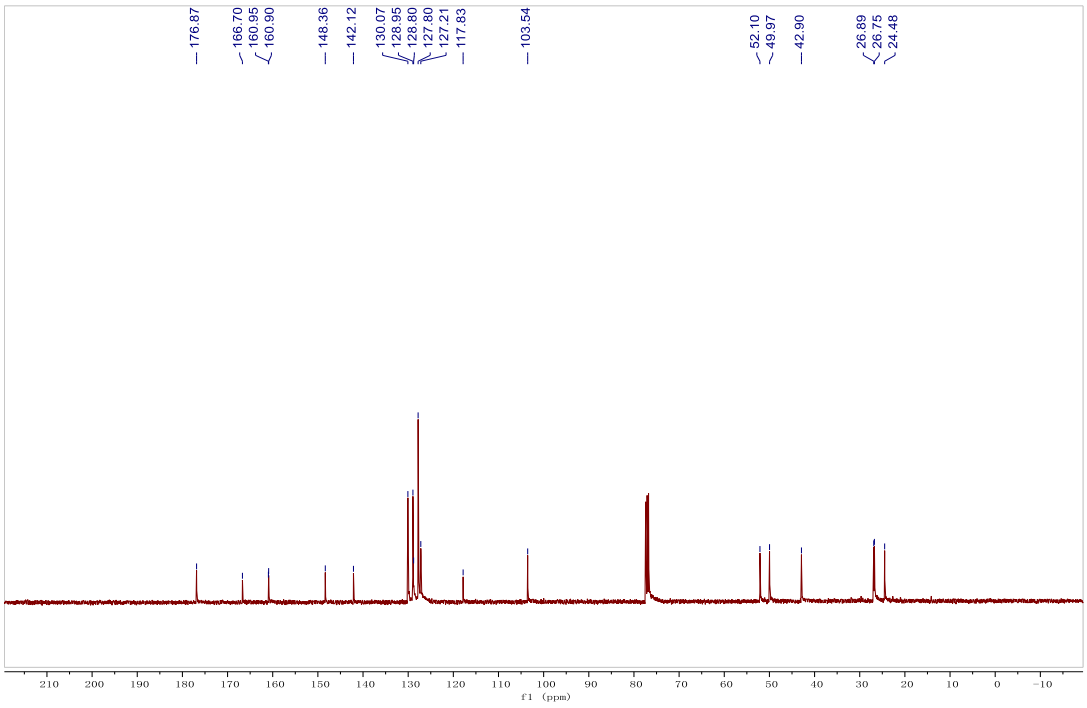
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.087	3426688	36743	49.073	52.127
2	26.882	3556205	33744	50.927	47.873
Total		6982893	70487	100.000	100.000

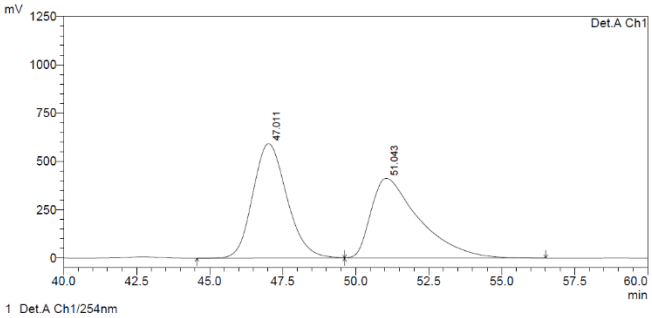
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.859	1734511	26746	5.538	9.239
2	26.255	29583355	262733	94.462	90.761
Total		31317866	289479	100.000	100.000





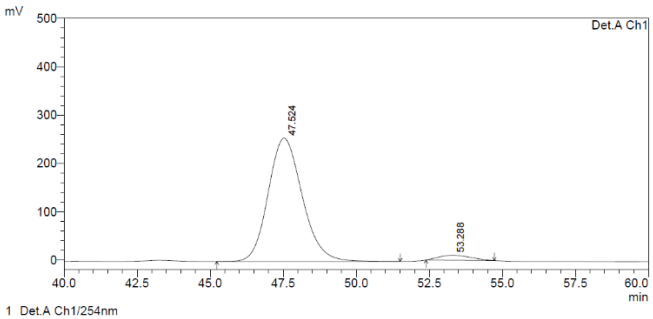


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.011	48208999	592412	50.440	58.904
2	51.043	47367698	413308	49.560	41.096
Total		95576697	1005720	100.000	100.000

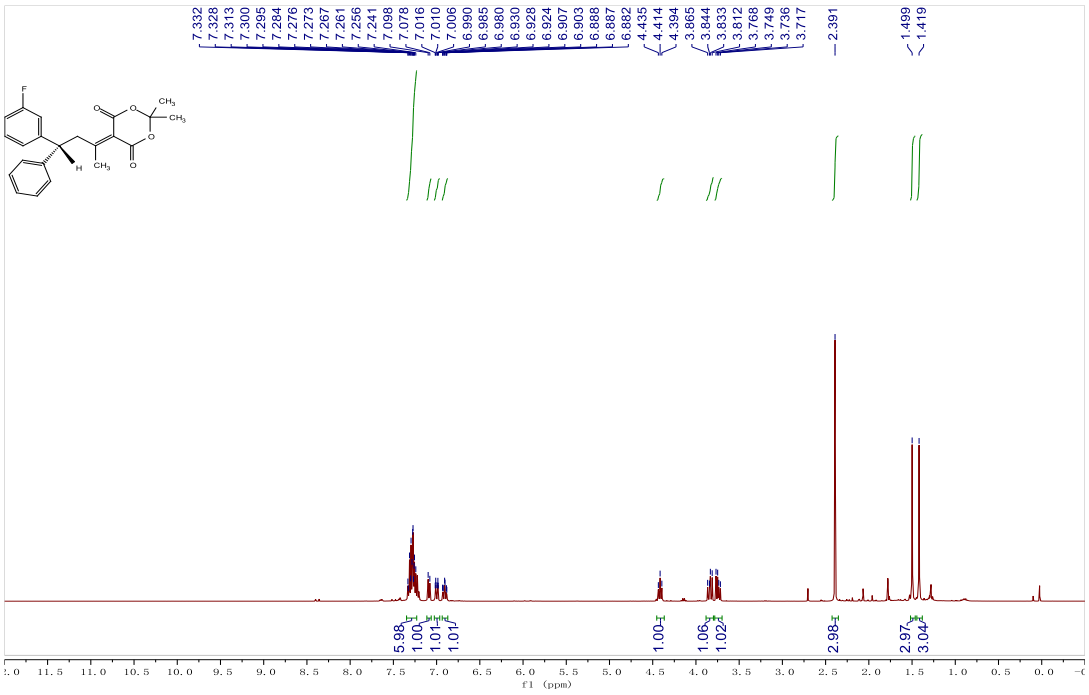


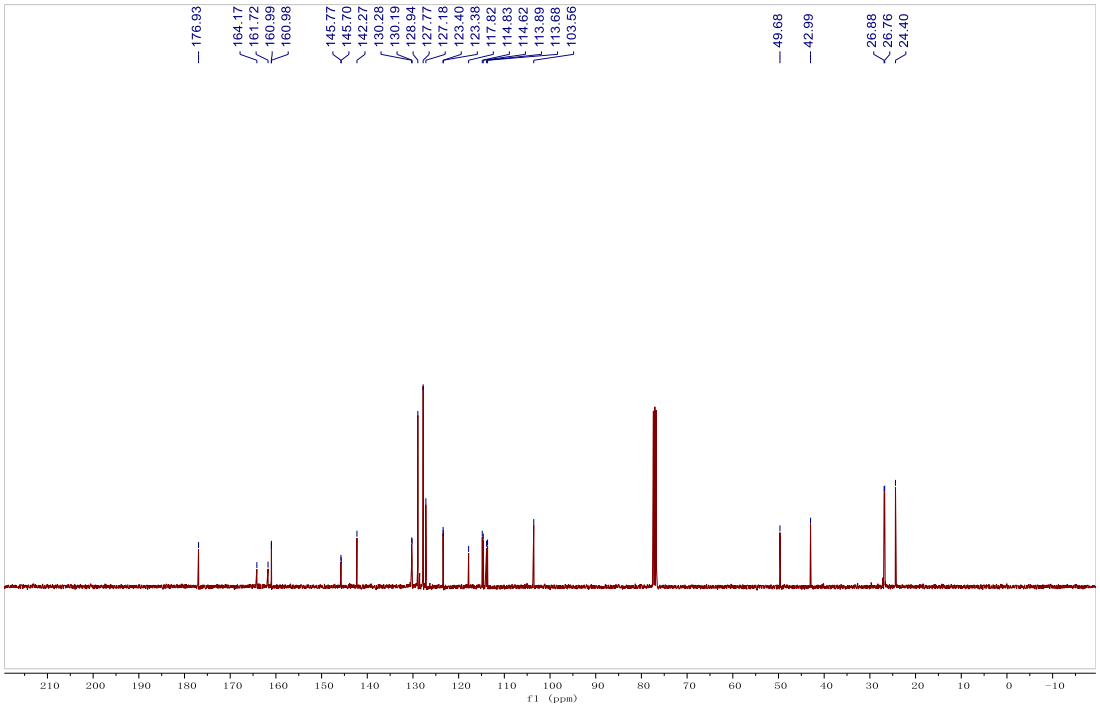
1 Det.A Ch1/254nm

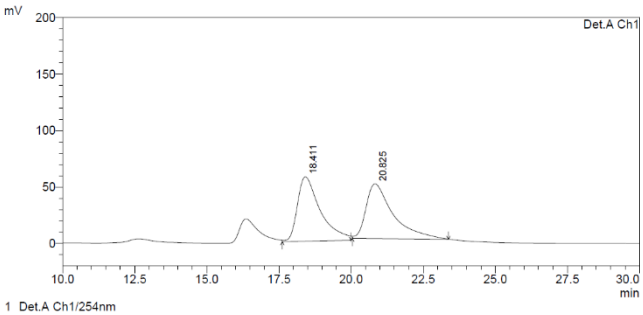
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	47.524	20690855	255112	96.406	96.146
2	53.288	771325	10225	3.594	3.854
Total		21462180	265338	100.000	100.000





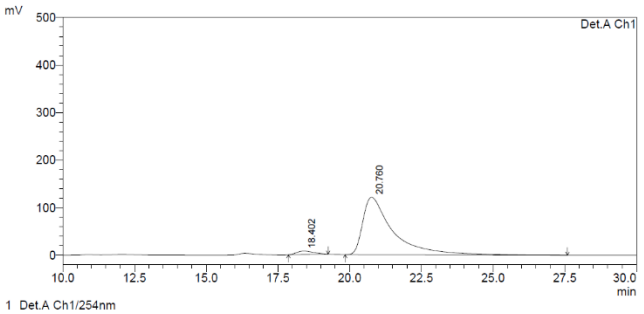


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.411	3153251	57108	49.715	54.051
2	20.825	3189409	48547	50.285	45.949
Total		6342660	105654	100.000	100.000

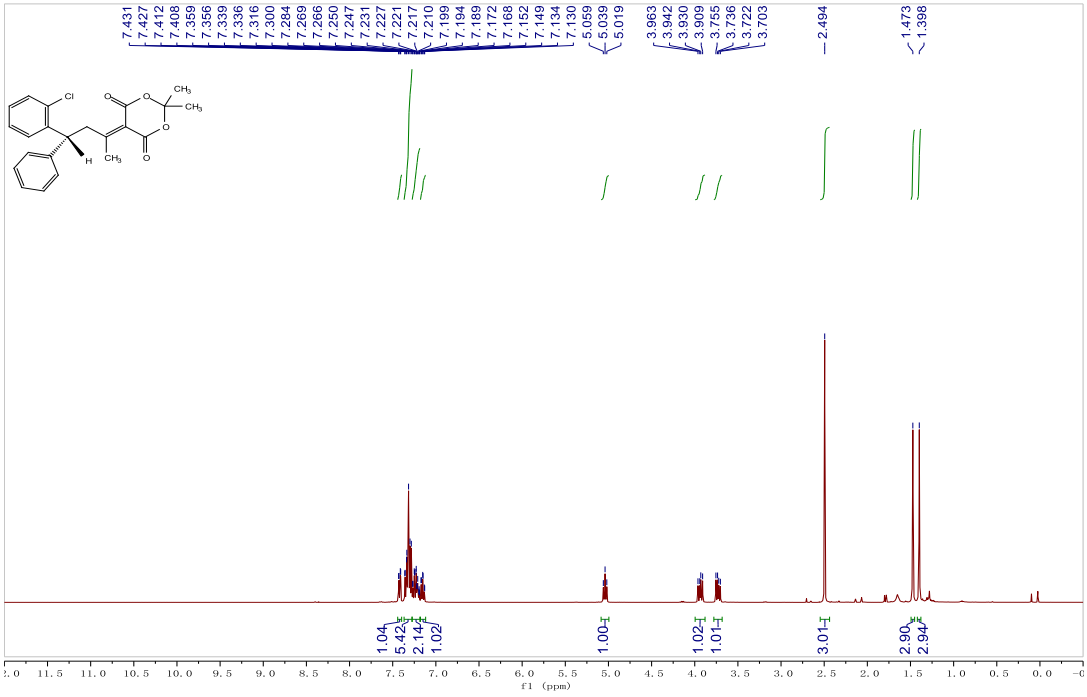


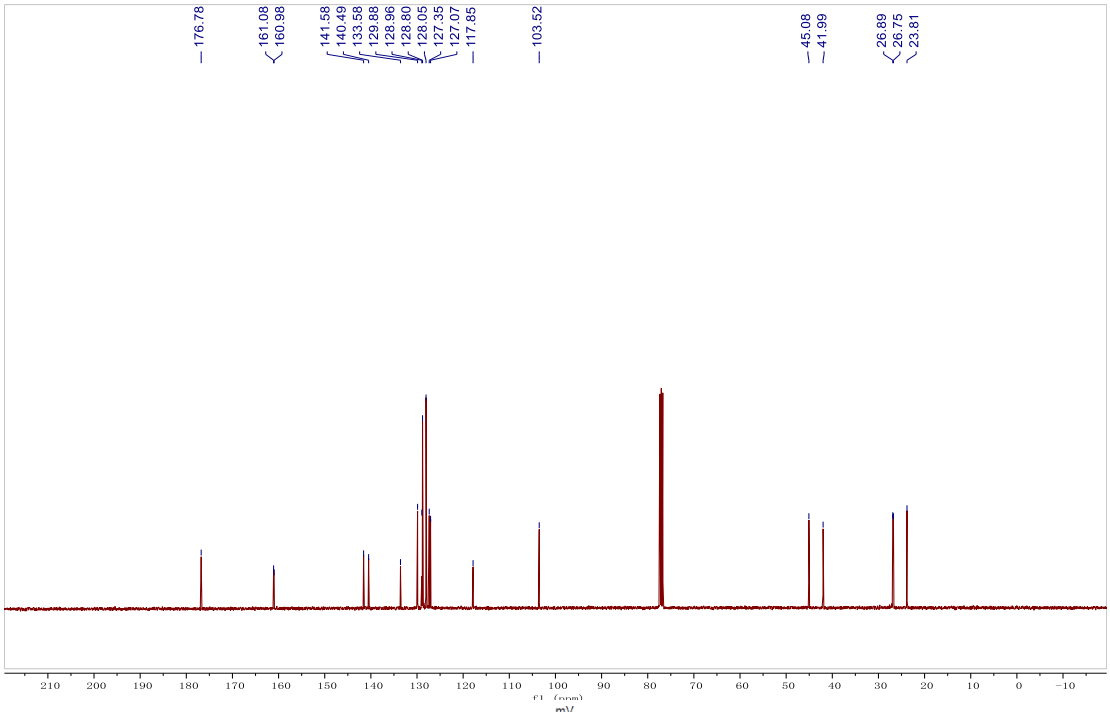
1 Det.A Ch1/254nm

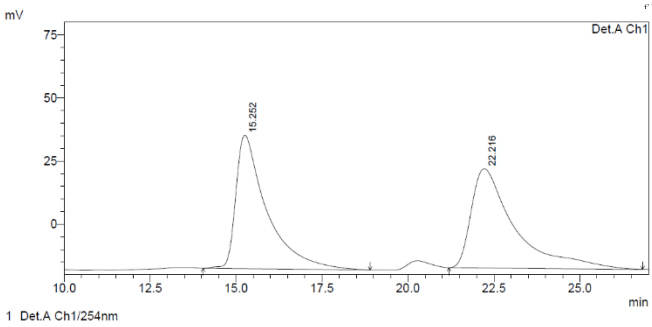
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.402	300632	7311	3.274	5.703
2	20.760	8881797	120894	96.726	94.297
Total		9182429	128205	100.000	100.000



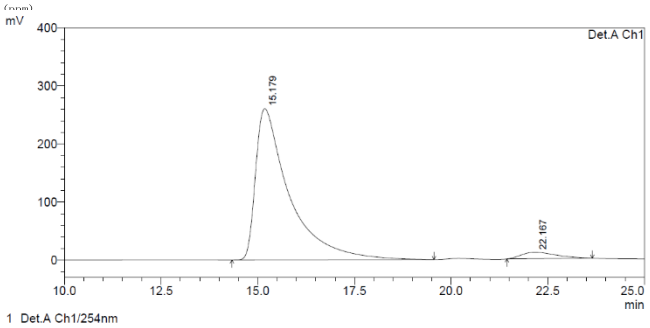




PeakTable

Detector A Ch1 254nm

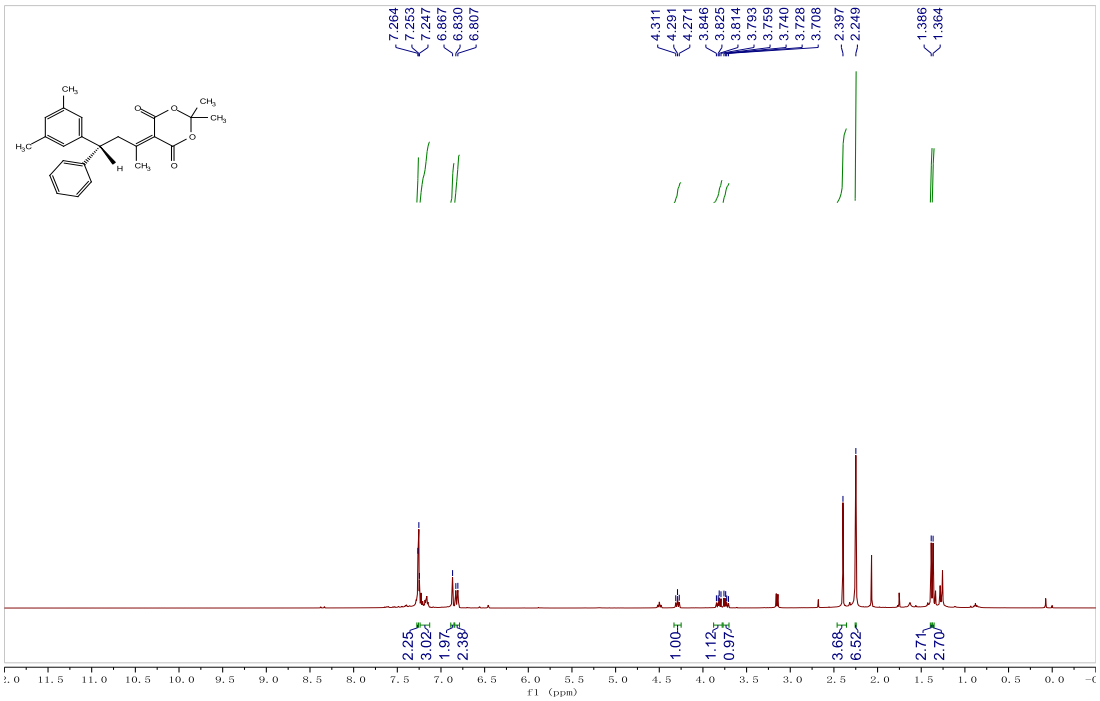
Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.252	3308586	52898	49.005	57.355
2	22.216	3442989	39332	50.995	42.645
Total		6751575	92230	100.000	100.000

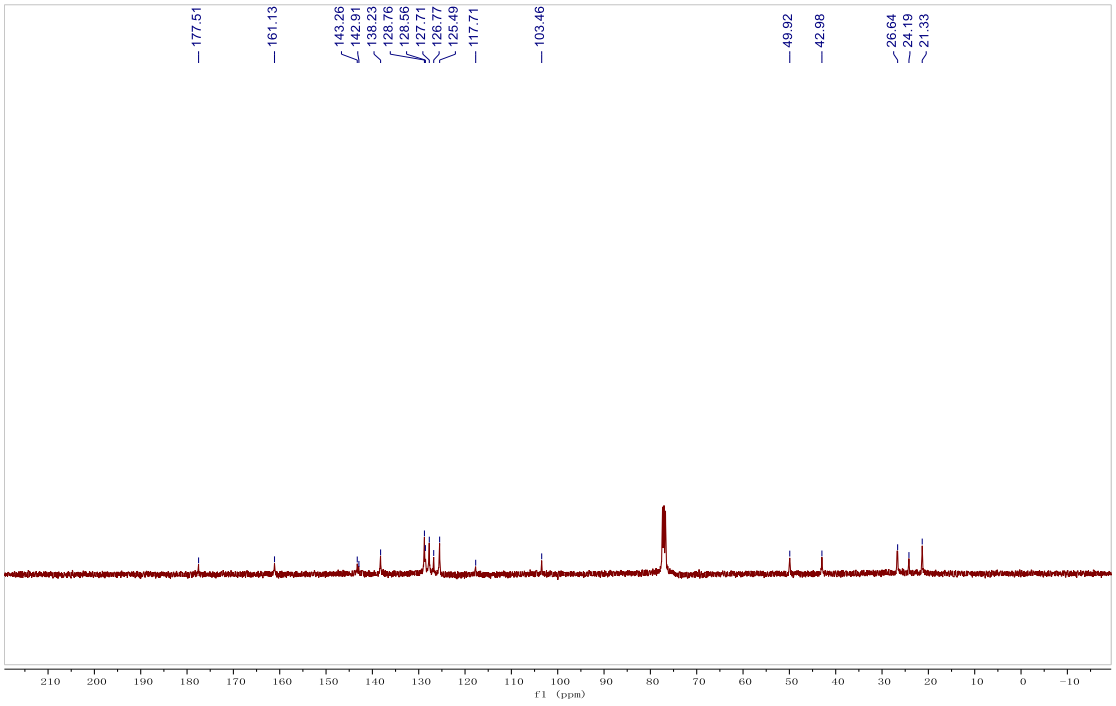


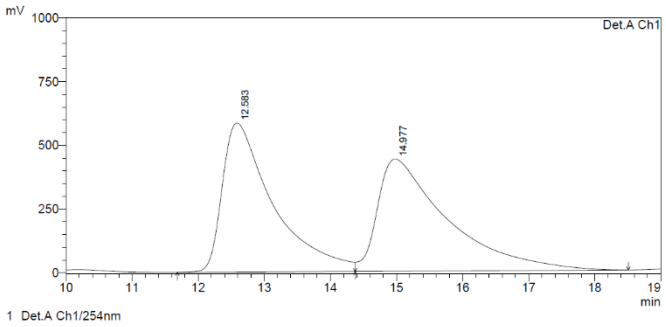
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.179	15824963	260499	95.775	95.875
2	22.167	698062	11207	4.225	4.125
Total		16523026	271706	100.000	100.000



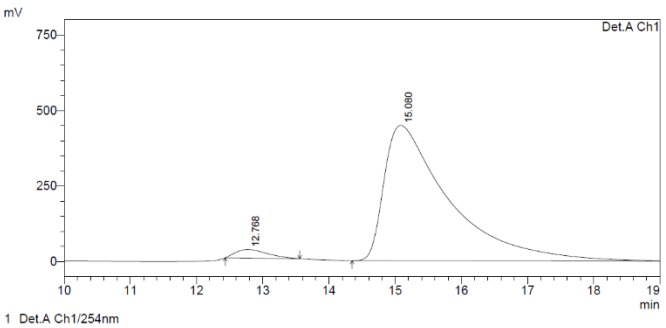




PeakTable

Detector A Ch1 254nm

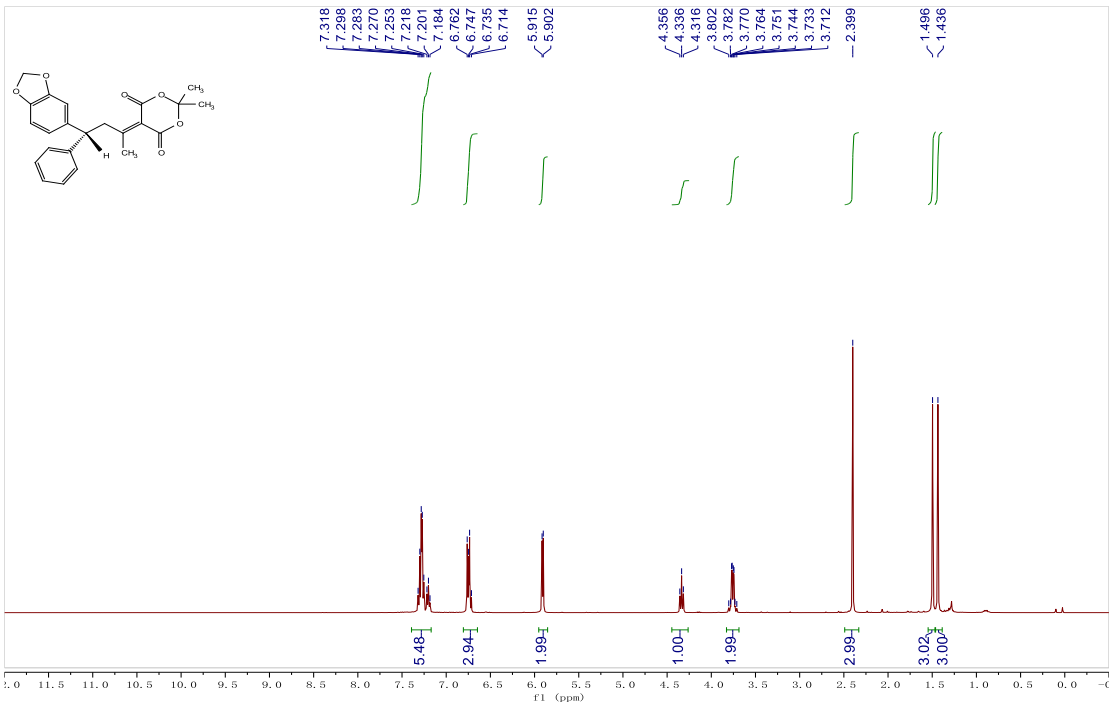
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.583	31181789	584794	49.227	57.063
2	14.977	32160539	440021	50.773	42.937
Total		63342328	1024815	100.000	100.000

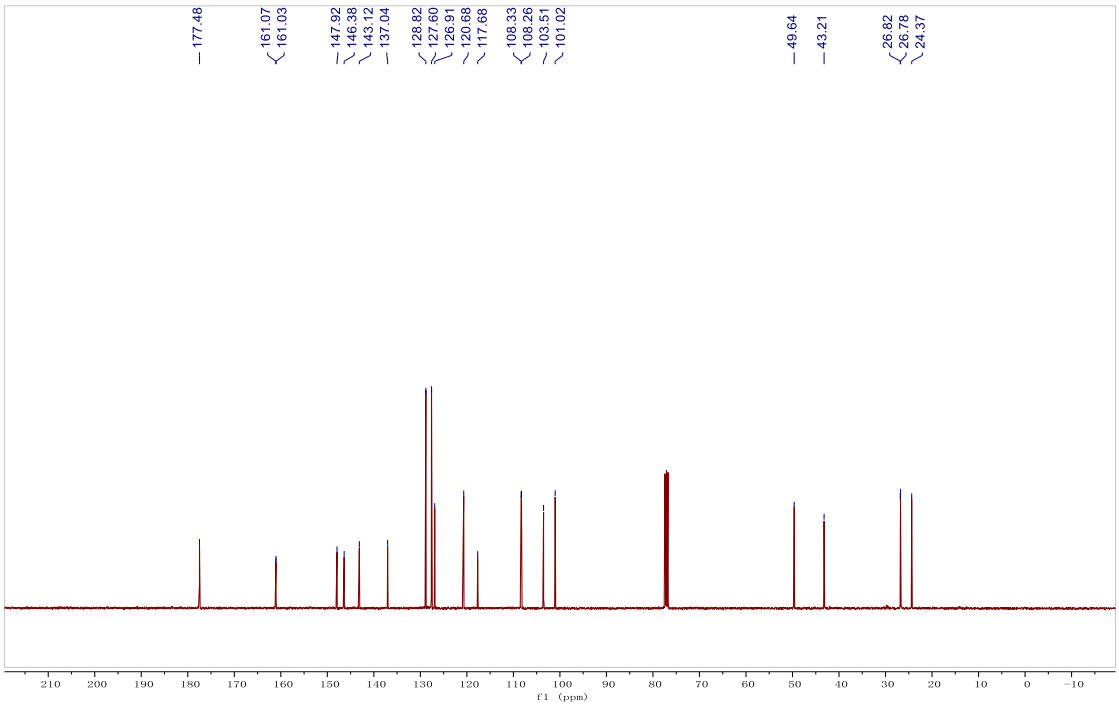


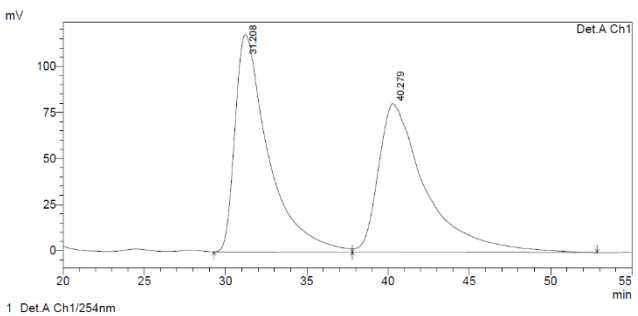
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.768	946984	28413	2.990	5.966
2	15.080	30721700	447841	97.010	94.034
Total		31668684	476255	100.000	100.000



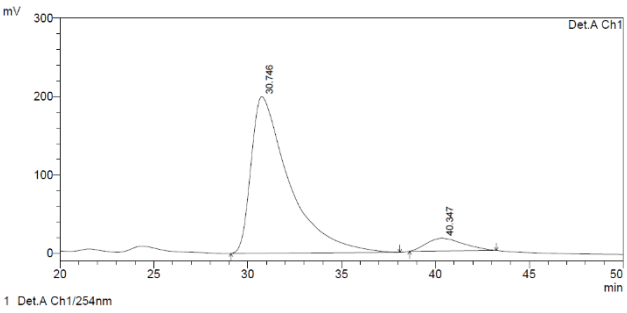




PeakTable

Detector A Ch1 254nm

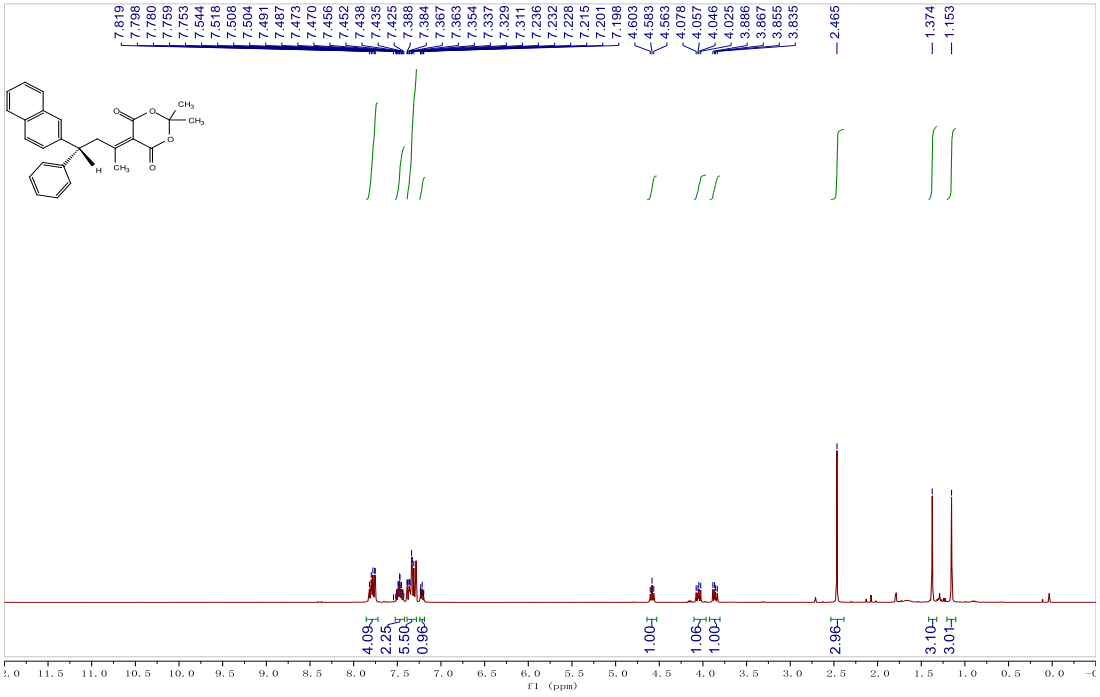
Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.208	16822119	117786	50.856	59.371
2	40.279	16255964	80604	49.144	40.629
Total		33078083	198390	100.000	100.000

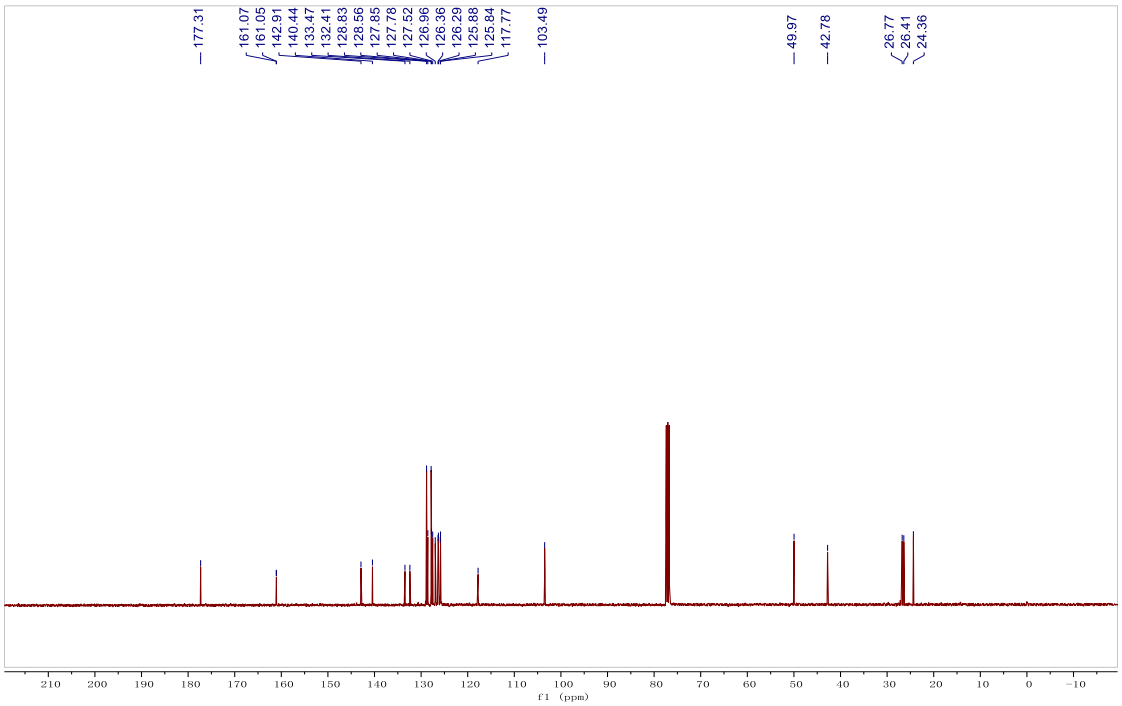


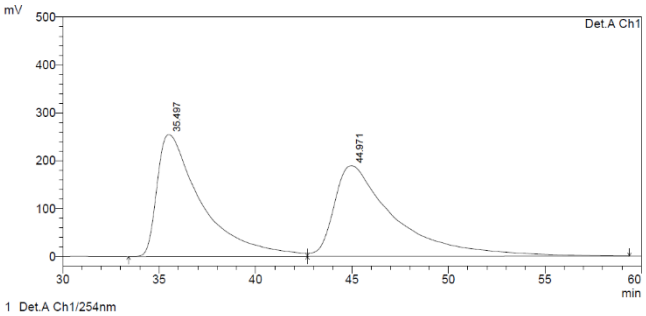
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.746	28159930	199921	92.742	92.535
2	40.347	2203655	16128	7.258	7.465
Total		30363585	216049	100.000	100.000



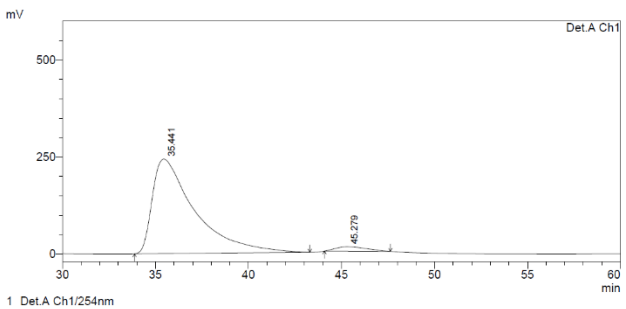




PeakTable

Detector A Ch1 254nm

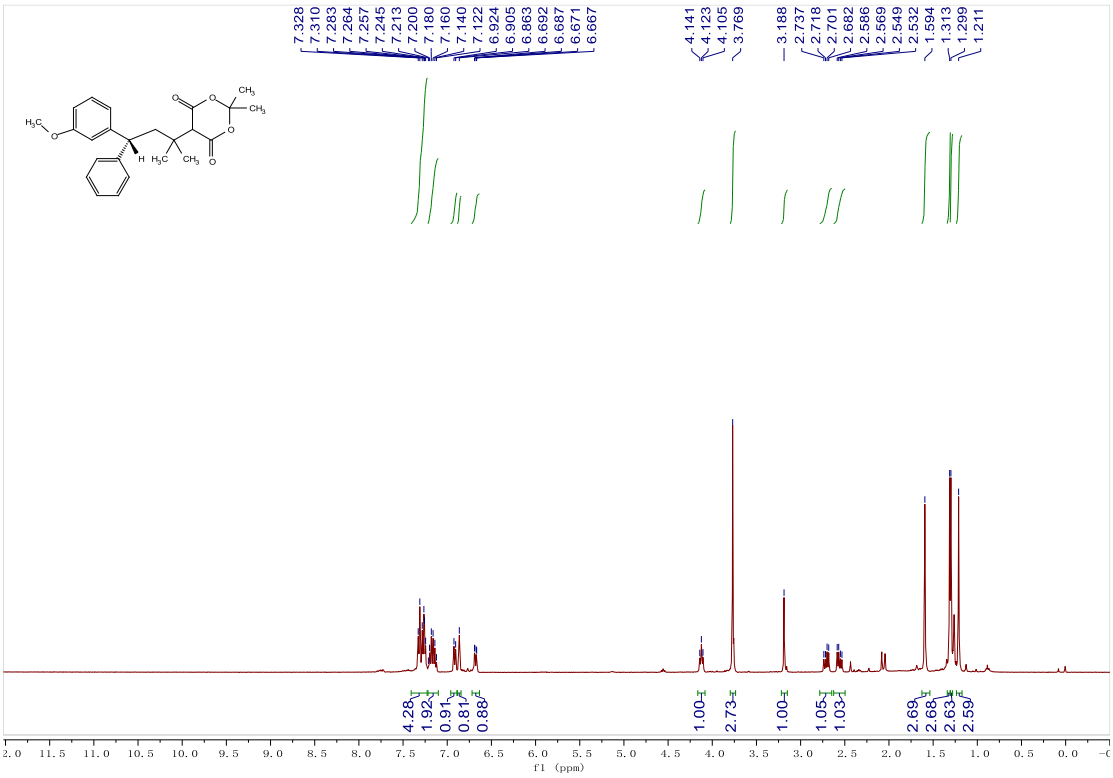
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.497	40703208	254193	49.619	57.359
2	44.971	41327658	188972	50.381	42.641
Total		82030866	443166	100.000	100.000

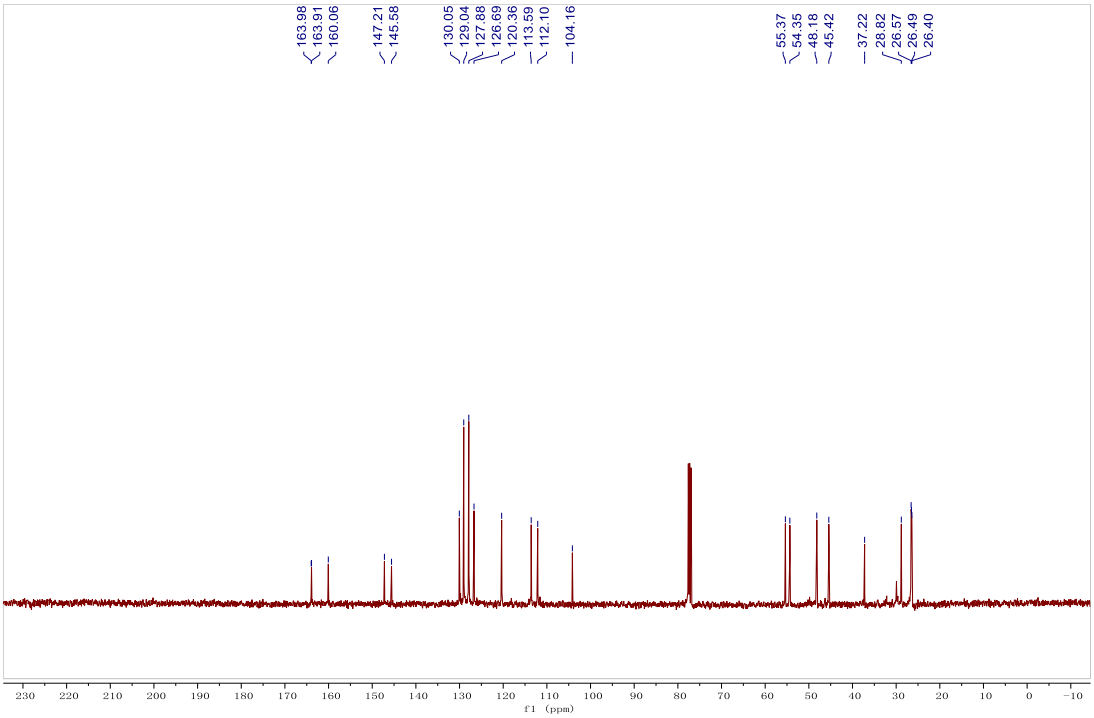


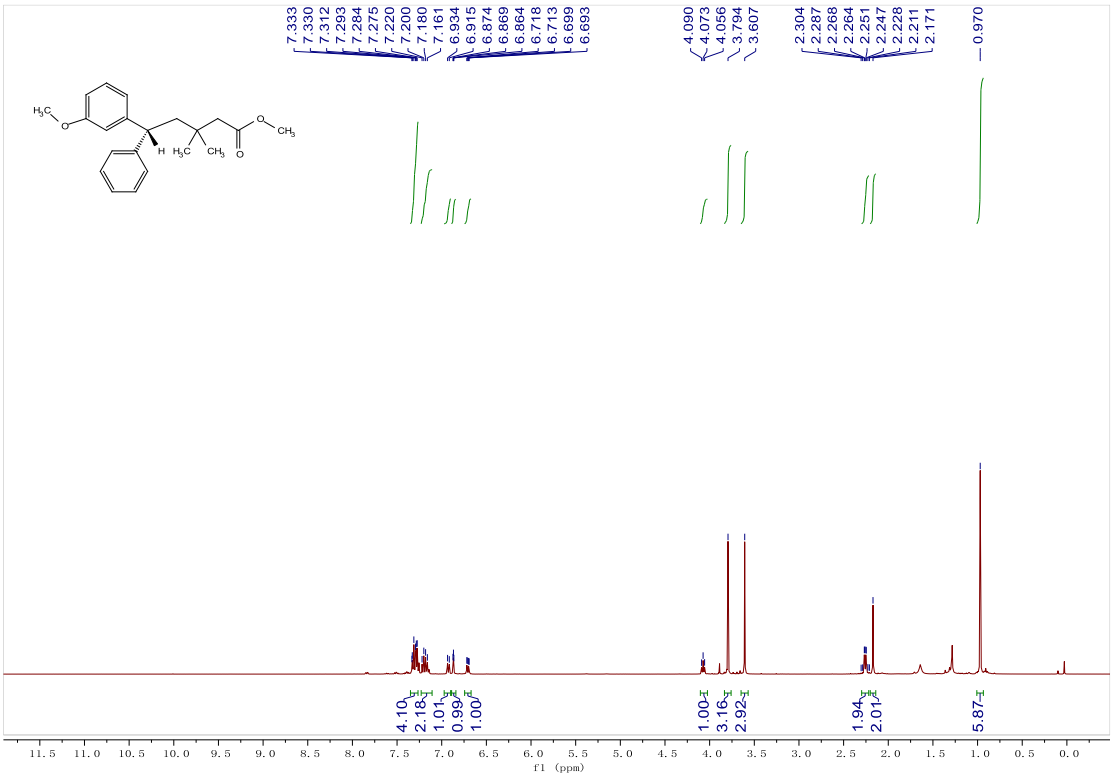
PeakTable

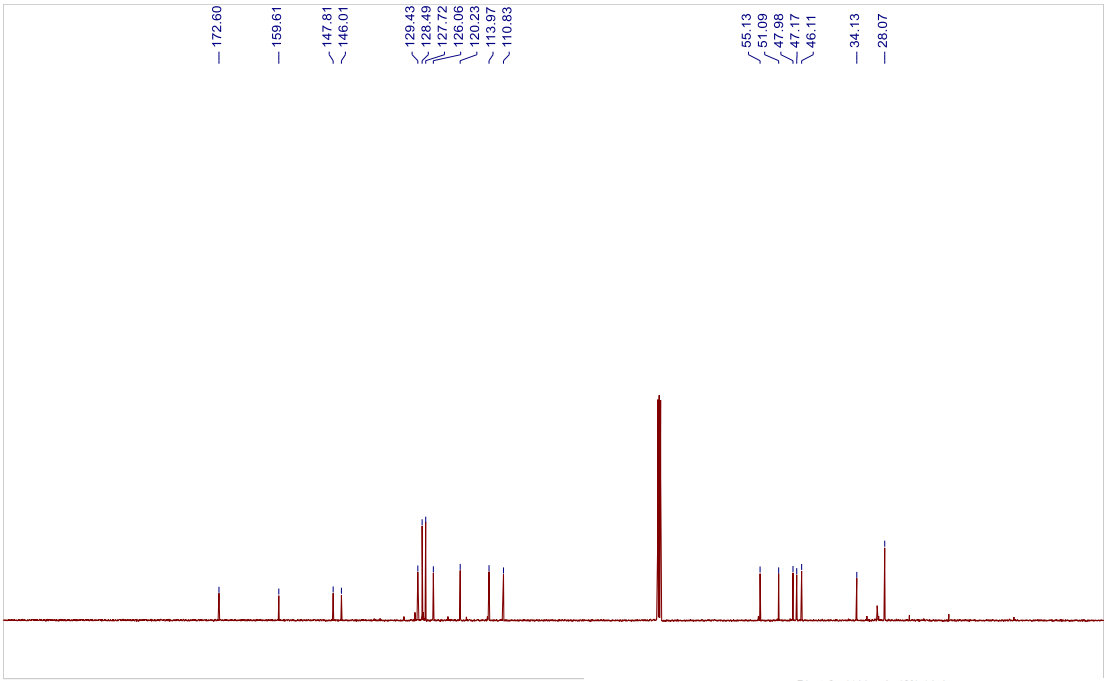
Detector A Ch1 254nm

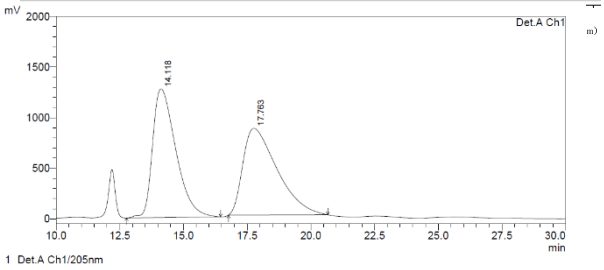
Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.441	38614479	243638	96.698	95.481
2	45.279	1318465	11530	3.302	4.519
Total		39932944	255168	100.000	100.000


7.328
7.310
7.283
7.264
7.257
7.245
7.213
7.200
7.180
7.160
7.140
7.122
6.924
6.905
6.863
6.692
6.687
6.671
6.667
4.141
4.123
4.105
3.769
3.188
2.737
2.718
2.701
2.682
2.586
2.569
2.549
2.532
1.594
1.313
1.299
1.211
4.28
1.92
0.91
0.81
0.88
1.00
2.73
1.00
1.05
1.03
2.69
2.68
2.63
2.59
f1 (ppm)


163.98
163.91
160.06
147.21
145.58
130.05
129.04
127.88
126.69
120.36
113.59
112.10
104.16
55.37
54.35
48.18
45.42
37.22
28.82
26.57
26.49
26.40
f1 (ppm)



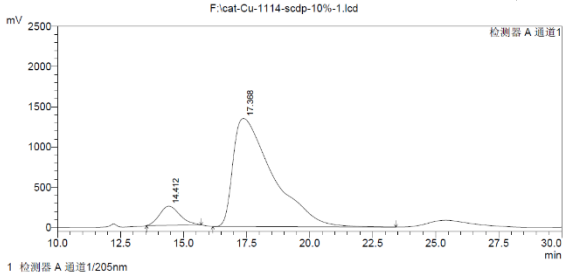




PeakTable

Detector A Ch1 205nm

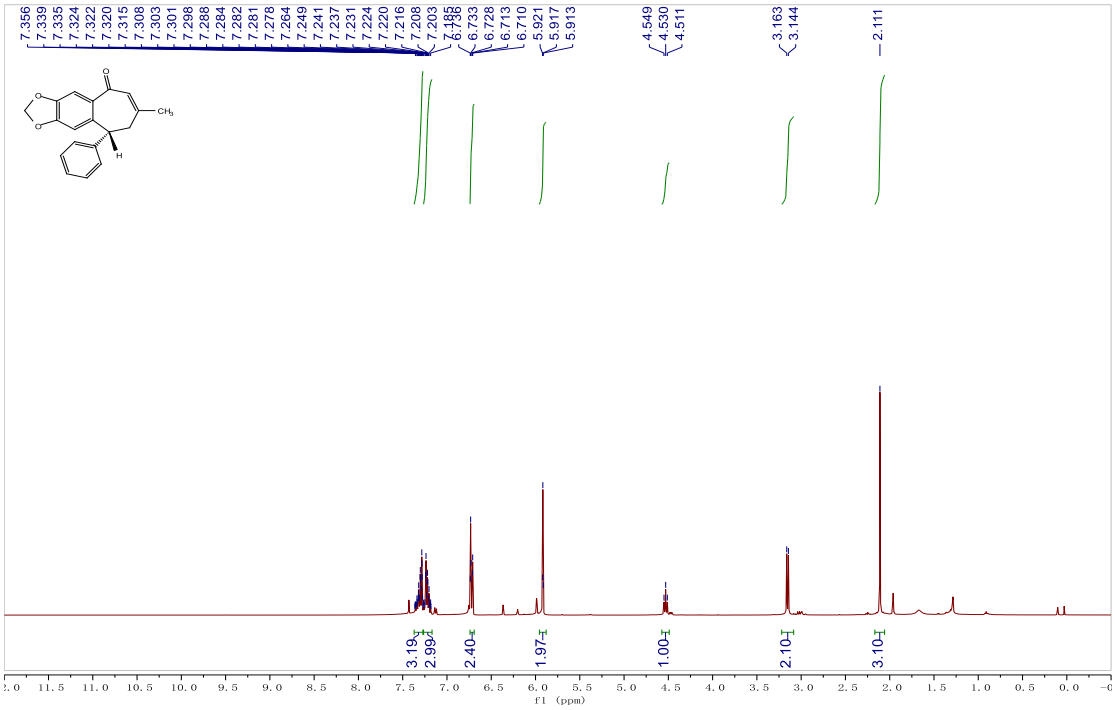
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.118	80817924	1271820	50.224	59.728
2	17.763	80097787	857520	49.776	40.272
Total		160915711	2129340	100.000	100.000

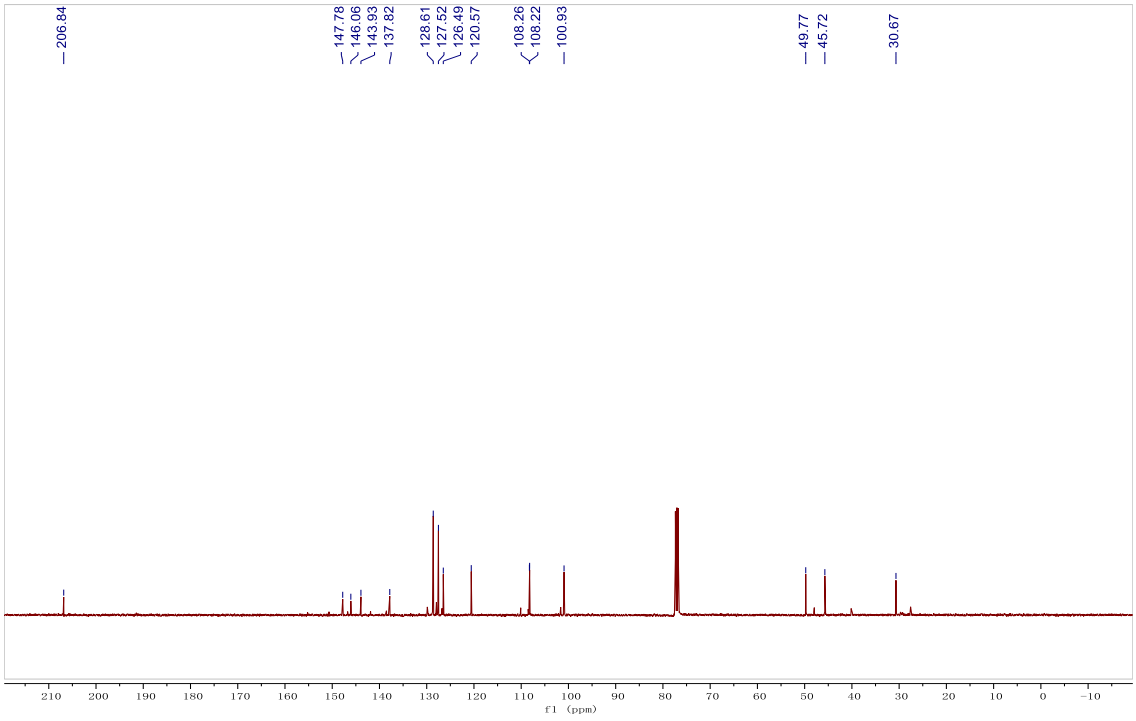


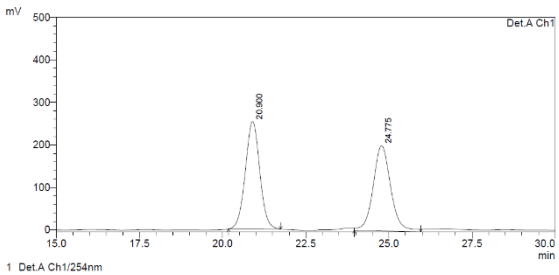
PeakTable

Detector A Ch1 205nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.412	13432143	238464	8.317	15.062
2	17.368	148077259	1344742	91.683	84.938
总计		161509402	1583206	100.000	100.000



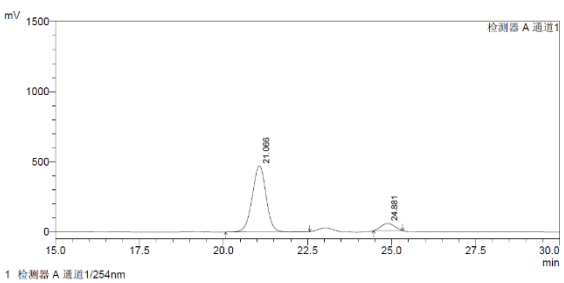




PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.800	7623917	252878	50.684	55.760
2	24.775	7418090	200636	49.316	44.240
Total		15042007	453514	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.066	13346943	471991	90.421	90.154
2	24.881	1413951	51547	9.579	9.846
总计		14760895	523538	100.000	100.000