Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Disubstituted *γ*-Butyrolactones and Spirocyclopropanes via Multicomponent Reaction of Aldehydes, Meldrum's Acid and Sulfoxonium Ylides

Shan-Shan Li,[a] Qi Qin,[a] Li-Miao Yang,[a] Zhuang Qi,[a] Yun Kang,[a] Xiang-Zhi Zhang,[a] Ai-Jun Ma,*[,a] and Jin-Bao Peng*[,a]

a. School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, Guangdong 529020, People's Republic of China. E-mail: wyuchemmaj@126.com; pengjb_05@126.com

Table of Contents

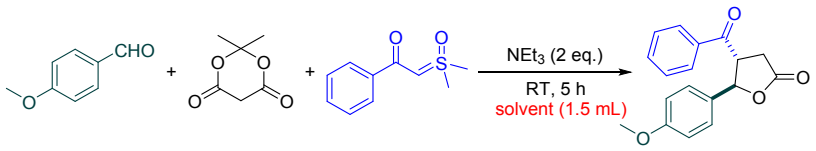
1. General Information

Reagents, solvents and analytical methods:

Unless otherwise noted, all reactions were carried out under air atmosphere. Ethyl acetate, *N,N*-diisopropylethylamine, Meldrum's acid, *p*-anisaldehyde and pentanal were from commercial sources and used as received without further purification. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.20 mm silica gel plates using UV light as the visualizing agent, and Iodine and an acidic solution of Phosphomolybdic Acid (PMA) with heat as the stains. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether and ethyl acetate as eluent. All new compounds were characterized by means of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. NMR spectra were recorded using a Bruker AVANCE NEO 500 MHz NMR spectrometer and can be found at the end of the paper. All ^{1}HNMR data are reported in δ units, parts per million (ppm), and were calibrated relative to the signals for residual chloroform (7.26 ppm) in deuterochloroform ($CDCl_3$). All ^{13}C NMR data are reported in ppm relative to $CDCl_3$ (77.16 ppm) were obtained with ^{1}H decoupling. ^{19}F NMR was recorded on a Bruker AVANCE NEO 500 MHz NMR spectrometer. The following abbreviations or combinations thereof were used to explain the multiplicities: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Single Crystal X-ray Diffraction (SCXRD). X-ray diffractions of all single crystals were carried out at 100(2) K on a Bruker D8 VENTURE diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Integration and scaling of intensity data was performed using the SAINT program. Data were corrected for the effects of absorption using SADABS. The structures were solved by direct method and refined with full-matrix least-squares technique using SHELX-2014 software. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in calculated positions and refined with a riding model.

2. Optimization of Reaction Conditions

Table S1. Optimization of solvents.[a]



Entry	Solvent	Yield (%)[b]
1	CCl_4	32
2	CH_2Cl_2	73
3	EtOAc	76
4	MeOH	0
5	EtOH	0

[a]Standard conditions: *p*-Anisaldehyde **1a** (1.5 equiv), Meldrum's acid **2** (1.5 equiv), sulfoxonium ylide **3a** (0.2 mmol), NEt_3 (2 equiv), solvent (1.5 mL), RT, 5 h. [b]Isolated yield.

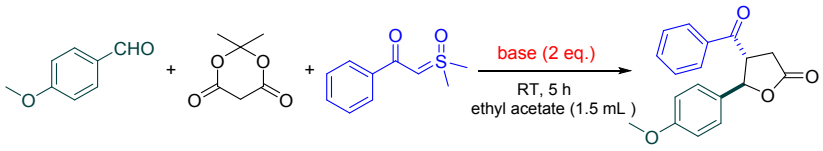
Table S2. Optimization of Ratio.[a]

Entry	SM_1:SM_2:SM_3	Yield (%)[b]
1	standard	76

2	1.2:1.5:1	56
3	1.2:2:1	51
4	1.5:2:1	86

[a]Standard conditions: *p*-Anisaldehyde **1a**, Meldrum's acid **2**, sulfoxonium ylide **3a** (0.2 mmol), NEt_3 (2 equiv), ethyl acetate (1.5 mL), RT, 5 h. [b]Isolated yield.

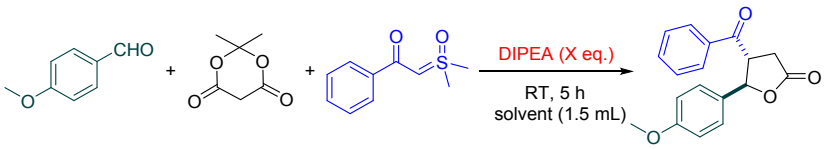
Table S3. Optimization of Bases.[a]



Entry	Base	Yield (%)[b]
1	DMAP	41
2	TNPA	94
3	DMEDA	54
4	DIPEA	98(1 h)
5	without NEt_3	trace

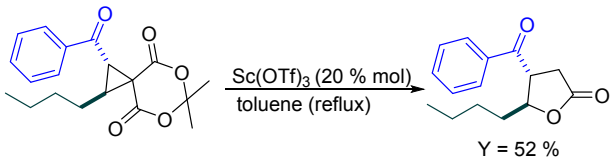
[a]Standard conditions: *p*-Anisaldehyde **1a** (1.5 equiv), Meldrum's acid **2** (2 equiv), sulfoxonium ylide **3a** (0.2 mmol), base (2 equiv), ethyl acetate (1.5 mL), RT, 5 h. [b]Isolated yield.

Table S4. Optimization of proportion of *N,N*-Diisopropylethylamine.[a]



Entry	*N,N*-Diisopropylethylamine	Yield (%)[b]	Time (h)
1	0.3 equiv	82	>5
2	0.5 equiv	98	5
3	1.0 equiv	97	3
4	2.0 equiv	98	1

[a]Standard conditions: *p*-Anisaldehyde **1a** (1.5 equiv), Meldrum's acid **2** (2 equiv), sulfoxonium ylide **3a** (0.2 mmol), *N,N*-Diisopropylethylamine (2 equiv), ethyl acetate (1.5 mL), RT, 5 h. [b]Isolated yield.



1-Benzoyl-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (0.2 mmol) and $Sc(OTf)_3$ (20 % mmol) were added in toluene (1 mL) and refluxed for 3 h. The solution was diluted with ethyl acetate (2 mL), washed with brine (1 mL, ×1) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

3. General Procedure

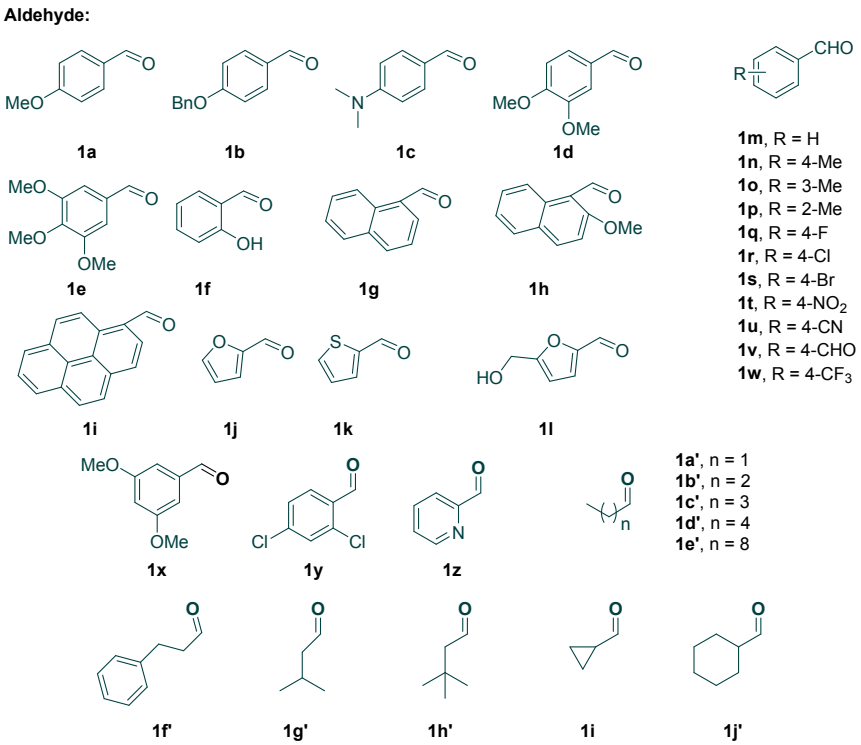


Figure S1 Substrates of Aldehydes

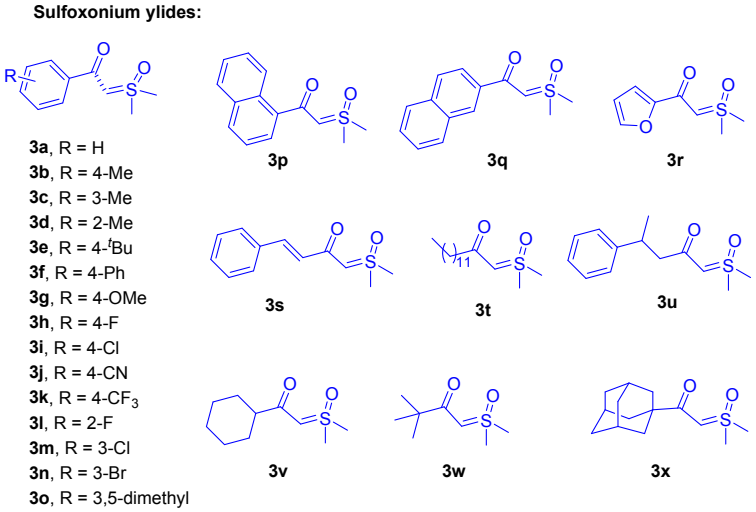
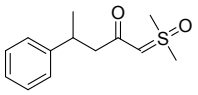


Figure S2 Substrates of Sulfoxonium Ylides

Sulfoxonium ylides were prepared according to reported procedures.[1] In a 125 mL round bottom flask attached to a reflux condenser which was carried out under air atmosphere. *t*-BuOK (4.49 g, 40 mmol, 4.0 equiv) and 50.0 mL of THF was added. Then 6.6 g of trimethylsulfoxonium iodide (30 mmol, 3.0 equiv) was added in one portion. The suspension was heated at reflux and maintained for 2 h. Then the mixture was cooled to 0 °C followed by slow addition of acid chloride (10 mmol, 1.0 equiv). The reaction mixture was allowed to warm to room temperature and stirred for 3 h. Next, the solvent was diluted with ethyl acetate (50 mL) and washed with brine

(1 mL, ×3) then dried over Na_2SO_4. The crude material was concentrated in vacuo and purified by silica gel flash column chromatography.



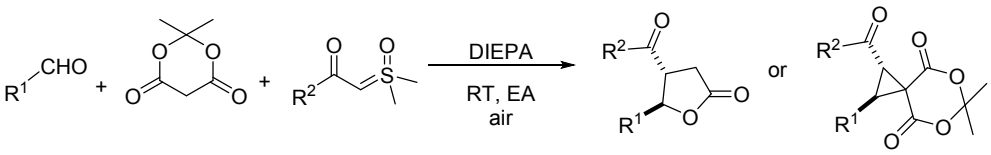
1-(dimethyl(oxo)-l6-sulfaneylidene)-4-phenylpentan-2-one (3u)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 4H), 7.23 (dq, *J* = 6.1, 2.8 Hz, 1H), 4.37 (s, 1H), 3.38 (s, 3H), 3.32 (s, 3H), 3.26 (t, *J* = 7.6 Hz, 1H), 2.11 (dt, *J* = 14.1, 7.3 Hz, 1H), 1.76 (dt, *J* = 13.7, 7.3 Hz, 1H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 141.9, 128.3, 128.0, 126.4, 69.3, 58.5, 42.3, 42.1, 26.2, 12.6.

HRMS (ESI): m/z calcd for $[C_{13}H_{18}O_2S+Na]^+$ 238.1037; found: 238.1069

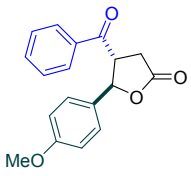
4. General Procedure



Aldhyde (0.3 mmol), Meldrum's acid (0.4 mmol) and sulfoxonium ylides (0.2 mmol) were added into an 15 mL tube which was carried out under air atmosphere. *N,N*-diisopropylethylamine (0.4 mmol) and ethyl acetate (1.5 mL) were added to the reaction tube. After a time period of 1 h, the solution was diluted with ethyl acetate (2 mL), washed with brine (1 mL, ×1) and concentrated in vacuo. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

5. Spectroscopic Data of Products

5.1. Spectroscopic Data of Products 4aa-4au

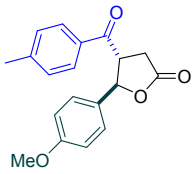


***trans*-4-Benzoyl-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4aa)** (Known compound: *Adv. Synth. Catal.* **2020**, *362*, 2385-2396)

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product as a white solid. (98%, Mp. 188-191 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.0 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.8 Hz, 2H), 7.25 (d, J = 10.0 Hz, 2H), 6.88 (d, J = 8.8 Hz, 2H), 5.73 (d, J = 7.6 Hz, 1H), 4.37 – 4.18 (m, 1H), 3.80 (s, 3H), 3.04 (qd, J = 17.6, 9.4 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 174.5, 160.3, 135.6, 134.4, 130.3, 129.2, 128.9, 127.4, 114.5, 82.8, 55.6, 51.3, 34.0.



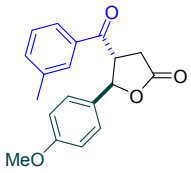
***trans*-5-(4-Methoxyphenyl)-4-(4-methylbenzoyl)dihydrofuran-2(3H)-one (4ab)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(*p*-tolyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product as a white solid. (59%, Mp. 117-121ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.29 (dd, J = 12.0, 3.4 Hz, 4H), 6.92 (d, J = 8.7 Hz, 2H), 5.76 (d, J = 7.6 Hz, 1H), 4.30 (td, J = 9.3, 7.5 Hz, 1H), 3.84 (s, 3H), 3.16 – 2.97 (m, 2H), 2.44 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 160.2, 145.6, 133.1, 130.3, 129.9, 129.0, 127.4, 114.5, 82.8, 55.6, 51.1, 34.0, 21.9.

HRMS (ESI): *m/z* calcd for $[C_{19}H_{18}O_4 + Na]^+$ 333.1097; found: 333.1097



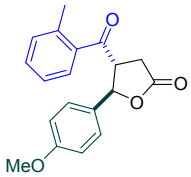
***trans*-5-(4-Methoxyphenyl)-4-(3-methylbenzoyl)dihydrofuran-2(3H)-one (4ac)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(*m*-tolyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.4 Hz, 2H), 7.38 (d, J = 7.1 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.24 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.69 (d, J = 7.7 Hz, 1H), 4.32 – 4.24 (m, 1H), 3.79 (s, 3H), 3.10 – 2.95 (m, 2H), 2.33 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 174.5, 160.2, 139.0, 135.5, 135.1, 130.3, 129.4, 129.0, 127.5, 126.0, 114.4, 82.8, 55.5, 51.4, 33.9, 21.5.

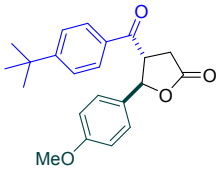
HRMS (ESI): *m/z* calcd for $[C_{22}H_{20}O_5 + Na]^+$ 333.1097; found: 333.1095



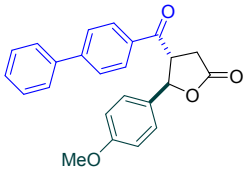
***trans*-5-(4-Methoxyphenyl)-4-(2-methylbenzoyl)dihydrofuran-2(3H)-one (4ad)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(*o*-tolyl)ethan-1-one

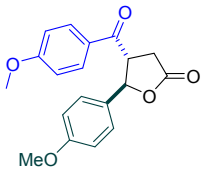
(0.2 mmol). The crude residue was purified by flash chromatography to give the product. (62%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (t, J = 6.9 Hz, 1H), 7.31 (d, J = 6.5 Hz, 1H), 7.26 (d, J = 7.6 Hz, 1H), 7.21 (d, J = 8.7 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 6.87 (d, J = 8.7 Hz, 2H), 5.67 (d, J = 7.5 Hz, 1H), 4.25 – 4.15 (m, 1H), 3.79 (s, 3H), 3.07 – 2.87 (m, 2H), 2.50 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 199.8, 174.4, 160.0, 139.5, 135.8, 132.5, 132.4, 130.1, 128.8, 127.1, 126.0, 114.3, 82.7, 55.4, 53.5, 33.6, 21.6.
HRMS (ESI): *m/z* calcd for $[C_{19}H_{18}O_4 + Na]^+$ 333.1097; found: 333.1090



***trans*-4-(4-(Tert-butyl)benzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4ae)**
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(4-(tert-butyl)phenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (90%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 5.76 (d, J = 7.5 Hz, 1H), 4.31 (q, J = 9.3 Hz, 1H), 3.80 (s, 3H), 3.03 (d, J = 9.3 Hz, 2H), 1.33 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 174.6, 160.1, 158.3, 132.9, 130.3, 128.8, 127.4, 126.1, 114.4, 82.7, 55.5, 51.0, 35.4, 34.0, 31.1.
HRMS (ESI): m/z calcd for $[C_{22}H_{24}O_4 + Na]^+$ 375.1567; found: 375.1565



***trans*-4-([1,1'-Biphenyl]-4-carbonyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4af)**
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-([1,1'-biphenyl]-4-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (72%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 7.0 Hz, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 7.26 (s, 8H), 6.90 (d, J = 8.7 Hz, 2H), 5.75 (d, J = 7.7 Hz, 1H), 4.38 – 4.25 (m, 1H), 3.80 (s, 3H), 3.17 – 2.98 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 174.3, 160.1, 146.9, 139.3, 134.0, 130.1, 129.3, 129.1, 128.6, 127.5, 127.3, 127.2, 114.3, 82.6, 55.4, 51.2, 33.8.
HRMS (ESI): m/z calcd for $[C_{24}H_{20}O_4 + Na]^+$ 395.1254; found: 395.1257



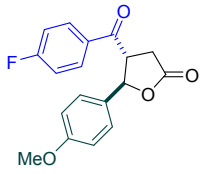
***trans*-4-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4ag)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-methoxyphenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, J = 8.9 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.87 (dd, J = 8.9, 2.7 Hz, 4H), 5.68 (d, J = 7.7 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 3.12 – 2.90 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.1, 174.7, 164.5, 160.2, 131.2, 130.3, 128.5, 127.4, 114.4, 114.3, 83.0, 55.8, 55.5, 50.9, 34.0.

HRMS (ESI): m/z calcd for $[C_{19}H_{18}O_5 + Na]^+$ 349.1046; found: 349.1046



***trans*-4-(4-Fluorobenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4ah)**

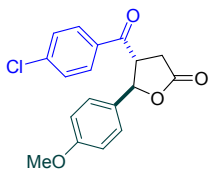
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-fluorophenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, J = 8.7, 5.4 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 7.09 (t, J = 8.5 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.67 (d, J = 7.7 Hz, 1H), 4.28 – 4.20 (m, 1H), 3.82 (s, 3H), 3.14 – 2.93 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 174.3, 166.5 (d, J = 257.4 Hz), 160.4, 131.6 (d, J = 9.6 Hz), 130.1, 127.4, 116.5, 116.3, 114.6, 82.8, 55.6, 51.4, 33.9.

^{19}F NMR (471 MHz, Chloroform-d) δ -102.65.

HRMS (ESI): m/z calcd for $[C_{18}H_{15}FO_4 + Na]^+$ 337.0847; found: 337.0849



***trans*-4-(4-Chlorobenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4ai)**

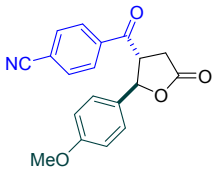
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-

dioxane-4,6-dione (0.4 mmol) and 1-(4-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan -1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (72%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.65 (d, J = 7.7 Hz, 1H), 4.29 – 4.18 (m, 1H), 3.80 (s, 3H), 3.14 – 2.93 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 174.3, 160.4, 141.1, 133.9, 130.2, 130.0, 129.5, 127.4, 114.6, 82.8, 55.6, 51.4, 33.8.

HRMS (ESI): m/z calcd for $[C_{18}H_{15}ClO_4 + Na]^+$ 353.0551; found: 353.0558



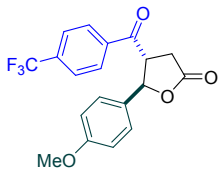
4-(*trans*-2-(4-Methoxyphenyl)-5-oxotetrahydrofuran-3-carbonyl)benzonitrile (4aj)

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 4-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)benzonitrile (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (76%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.62 (d, J = 7.7 Hz, 1H), 4.33 – 4.22 (m, 1H), 3.80 (s, 3H), 3.15 – 2.94 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.8, 173.9, 160.5, 138.4, 132.9, 129.6, 129.2, 127.5, 117.7, 117.6, 114.7, 82.6, 55.6, 51.8, 33.6.

HRMS (ESI): m/z calcd for $[C_{19}H_{15}NO_4 + Na]^+$ 344.0893; found: 344.0895



***trans*-5-(4-Methoxyphenyl)-4-(4-(trifluoromethyl)benzoyl)dihydrofuran-2(3H)-one (4ak)**

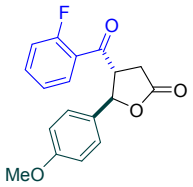
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-(trifluoromethyl) phenyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (61%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.1 Hz, 2H), 7.68 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.66 (d, J = 7.7 Hz, 1H), 4.35 – 4.24 (m, 1H), 3.80 (s, 3H), 3.13 – 2.97 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.1, 174.1, 160.4, 138.2,135.5 (q, J = 32.9 Hz), 129.8, 129.2, 127.5, 126.2, 123.5 (q, J = 273.0 Hz), 114.6, 82.6, 55.6, 51.7, 33.7.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.24.

HRMS (ESI): m/z calcd for $[C_{19}H_{15}F_3O_4 + Na]^+$ 387.0815; found: 387.0813



***trans*-4-(2-Fluorobenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4al)**

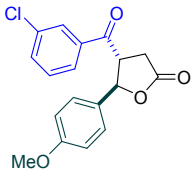
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(2-fluorophenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (83%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (td, J = 7.6, 1.9 Hz, 1H), 7.64 – 7.56 (m, 1H), 7.29 (d, J = 8.2 Hz, 3H), 7.14 (dd, J = 11.5, 8.3 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 5.89 (d, J = 7.0 Hz, 1H), 4.24 (q, J = 8.3, 7.7 Hz, 1H), 3.82 (s, 3H), 3.12 (dd, J = 17.5, 9.1 Hz, 1H), 2.93 (dd, J = 17.6, 8.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.2, 174.9 (d, *J* = 176.4 Hz),161.7 (d, *J* = 254.6 Hz), 159.9,135.9 (d, *J* = 9.6 Hz), 131.2 (d, *J* = 2.3 Hz), 130.1, 127.2, 125.0 (d, *J* = 3.3 Hz), 124.2, 116.9 (d, *J* = 23.9 Hz), 114.2, 81.8, 55.3, 55.2 (d, *J* = 7.3 Hz), 32.9.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -110.48.

HRMS (ESI): m/z calcd for $[C_{18}H_{15}FO_4 + Na]^+$ 337.0847; found: 337.0845



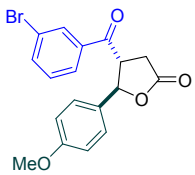
***trans*-4-(3-Chlorobenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4am)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(3-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product as a yellow solid. (56%, Mp. 135-140 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (s, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.9 Hz, 1H), 7.23 (d, J = 8.8 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.65 (d, J = 7.7 Hz, 1H), 4.23 (td, J = 9.4, 7.7 Hz, 1H), 3.79 (s, 3H), 3.14 – 2.93 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.5, 174.0, 160.2, 136.8, 135.4, 134.1, 130.3, 129.7, 128.8, 127.3, 126.7, 114.4, 82.5, 55.4, 51.5, 33.5.

HRMS (ESI): m/z calcd for $[C_{18}H_{15}ClO_4 + Na]^+$ 353.0551; found: 353.0553



***trans*-4-(3-Bromobenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4an)**

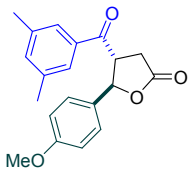
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(3-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)

ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.67 (dd, J = 13.9, 7.9 Hz, 2H), 7.29 (t, J = 7.9 Hz, 1H), 7.23 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.63 (d, J = 7.8 Hz, 1H), 4.27 – 4.17 (m, 1H), 3.80 (s, 3H), 3.15 – 2.92 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 195.4, 174.0, 160.2, 137.0, 137.0, 131.8, 130.5, 129.7, 127.3, 127.1, 123.3, 114.4, 82.5, 55.4, 51.5, 33.5.

HRMS (ESI): m/z calcd for $[C_{18}H_{15}BrO_4 + Na]^+$ 399.0025; found: 399.0026



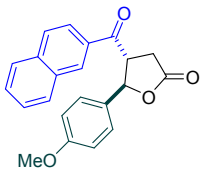
***trans*-4-(3,5-Dimethylbenzoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4ao)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(3,5-dimethylphenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (65%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.24 (d, J = 8.7 Hz, 2H), 7.20 (s, 1H), 6.87 (d, J = 8.6 Hz, 2H), 5.66 (d, J = 7.8 Hz, 1H), 4.31 – 4.21 (m, 1H), 3.79 (s, 3H), 3.12 – 2.92 (m, 2H), 2.28 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 174.6, 160.2, 138.8, 136.0, 135.6, 130.3, 127.5, 126.7, 114.4, 82.8, 55.5, 51.5, 33.8, 21.3.

HRMS (ESI): m/z calcd for $[C_{20}H_{20}O_4 + Na]^+$ 347.1254; found: 347.1256



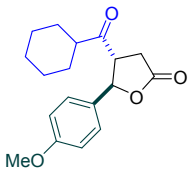
***trans*-4-(2-Naphthoyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4aq)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(naphthalen-2-yl)ethan -1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (33%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.80 (d, J = 8.2 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.56 (d, J = 6.9 Hz, 1H), 7.30 (d, J = 8.7 Hz, 2H), 6.91 (s, 2H), 5.75 (d, J = 7.8 Hz, 1H), 4.47 (q, J = 9.0 Hz, 1H), 3.80 (d, J = 10.5 Hz, 3H), 3.28 – 3.07 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.4, 174.4, 160.1, 135.9, 132.7, 132.3, 131.1, 130.1, 129.7, 129.3, 128.9, 127.8, 127.3, 127.2, 123.8, 114.4, 82.8, 55.4, 51.4, 33.7.

HRMS (ESI): m/z calcd for $[C_{22}H_{18}O_4 + Na]^+$ 369.1097; found: 369.1104



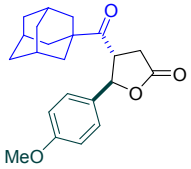
***trans*-4-(Cyclohexanecarbonyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4av)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-dyclohexyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (41%,).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.47 (d, J = 8.4 Hz, 1H), 3.80 (s, 3H), 3.69 – 3.60 (m, 1H), 2.83 (d, J = 9.6 Hz, 2H), 2.20 (tt, J = 10.9, 3.2 Hz, 1H), 1.76 – 1.56 (m, 5H), 1.14 (s, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 210.6, 174.3, 160.2, 129.9, 127.4, 114.4, 82.8, 55.4, 53.8, 51.3, 33.7, 28.0, 27.6, 25.6, 25.4, 25.3.

HRMS (ESI): m/z calcd for $[C_{18}H_{22}O_4 + Na]^+$ 325.1410; found: 325.1411



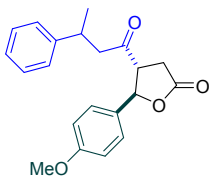
***trans*-4-(Adamantane-1-carbonyl)-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (4ax)**

The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(adamantan-1-yl)-2-(dimethyl(oxo)-λ^6- sulfaneylidene)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (46%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz, 2H), 5.56 (d, J = 8.7 Hz, 1H), 3.81 (s, 4H), 2.85 – 2.65 (m, 2H), 1.98 (s, 3H), 1.70 (d, J = 12.6 Hz, 3H), 1.58 (d, J = 9.8 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 212.8, 174.3, 160.3, 129.9, 127.4, 114.4, 83.9, 55.6, 50.1, 47.0, 37.3, 36.4, 36.1, 27.7.

HRMS (ESI): m/z calcd for $[C_{18}H_{22}O_4 + Na]^+$ 377.1723; found: 377.1726



***trans*-5-(4-Methoxyphenyl)-4-(3-phenylbutanoyl)dihydrofuran-2(3H)-one (4au)**

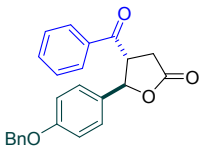
The title compound was prepared from 4-methoxybenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (76%).

4au-1

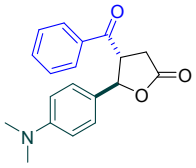
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.24 (m, 3H), 7.21 (d, J = 8.7 Hz, 2H), 7.01 – 6.91 (m, 4H), 5.35 (d, J = 8.9 Hz, 1H), 3.85 (s, 3H), 3.48 (dt, J = 10.8, 8.6 Hz, 1H), 3.18 (t, J = 7.3 Hz, 1H), 2.79 (dd, J = 17.6, 10.8 Hz, 1H), 2.25 (dd, J = 17.5, 8.4 Hz, 1H), 2.02 (dp, J = 14.4, 7.2 Hz, 1H), 1.68 – 1.59 (m, 1H), 0.74 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 206.8, 174.4, 160.5, 137.1, 129.7, 129.5, 128.7, 128.1, 127.7, 114.6, 83.2, 62.2, 55.6, 55.2, 34.0, 24.8, 12.2.
HRMS (ESI): m/z calcd for $[C_{21}H_{22}O_4 + Na]^+$ 361.1410; found: 361.1409

4au-2
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (dd, J = 4.9, 1.8 Hz, 3H), 7.03 – 6.94 (m, 2H), 6.85 (d, J = 8.8 Hz, 2H), 6.70 (d, J = 8.7 Hz, 2H), 5.48 (d, J = 7.8 Hz, 1H), 3.77 (s, 3H), 3.55 – 3.39 (m, 2H), 2.84 – 2.60 (m, 2H), 1.98 (dp, J = 14.5, 7.3 Hz, 1H), 1.72 – 1.59 (m, 1H), 0.77 (t, J = 7.4 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 207.4, 174.0, 160.0, 136.5, 129.4, 129.3, 128.6, 127.9, 127.2, 114.2, 82.4, 61.5, 55.5, 53.7, 33.9, 24.8, 12.1.
HRMS (ESI): m/z calcd for $[C_{21}H_{22}O_4 + Na]^+$ 361.1410; found: 361.1410

5.2. Spectroscopic Data of Products 4ba-4la

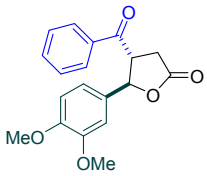


***trans*-4-Benzoyl-5-(4-(benzyloxy)phenyl)dihydrofuran-2(3H)-one (4ba)**
The title compound was prepared from 4-(benzyloxy)benzaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (93%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 7.9 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.46 – 7.33 (m, 7H), 7.25 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 5.72 (d, J = 7.5 Hz, 1H), 5.05 (s, 2H), 4.34 – 4.25 (m, 1H), 3.03 (h, J = 8.9, 8.4 Hz, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 174.4, 159.3, 136.7, 135.4, 134.4, 130.5, 129.1, 128.8, 128.3, 127.6, 127.4, 115.4, 82.6, 70.2, 51.2, 33.8.
HRMS (ESI): m/z calcd for $[C_{24}H_{20}O_4 + Na]^+$ 395.1254; found: 395.1256

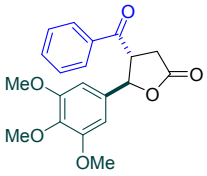


***trans*-4-Benzoyl-5-(4-(dimethylamino)phenyl)dihydrofuran-2(3H)-one (4ca)** (Known compound: *Adv. Synth. Catal.* **2020**, *362*, 2385-2396)
The title compound was prepared from 4-(benzyloxy)benzaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (52%).

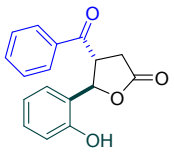
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, J = 6.8 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.43 (d, J = 7.8 Hz, 2H), 7.19 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 8.3 Hz, 2H), 5.67 (d, J = 7.3 Hz, 1H), 4.37 – 4.28 (m, 1H), 3.12 – 2.97 (m, 2H), 2.95 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 174.6, 135.4, 134.1, 128.9, 128.7, 127.1, 112.4, 83.2, 50.8, 40.5, 33.7.



***trans*-4-Benzoyl-5-(3,4-dimethoxyphenyl)dihydrofuran-2(3H)-one (4da)**
The title compound was prepared from 3,4-dimethoxybenzaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (77%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 6.87 – 6.76 (m, 3H), 5.69 (d, J = 7.8 Hz, 1H), 4.30 (q, J = 9.2 Hz, 1H), 3.81 (d, J = 23.6 Hz, 6H), 3.10 – 2.94 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 174.4, 149.5, 149.4, 135.5, 134.4, 130.5, 129.1, 128.8, 118.4, 111.3, 108.7, 82.8, 56.1, 51.3, 34.0.
HRMS (ESI): m/z calcd for $[C_{19}H_{18}O_5 + Na]^+$ 349.1046; found: 349.1050



***trans*-4-Benzoyl-5-(3,4,5-trimethoxyphenyl)dihydrofuran-2(3H)-one (4ea)**
The title compound was prepared from 3,4,5-trimethoxybenzaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (65%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 8.5 Hz, 2H), 7.65 – 7.55 (m, 1H), 7.44 (t, J = 7.7 Hz, 2H), 6.46 (s, 2H), 5.70 (d, J = 8.0 Hz, 1H), 4.27 (dd, J = 18.0, 9.3 Hz, 1H), 3.78 (d, J = 31.4 Hz, 9H), 3.15 – 2.89 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 174.1, 153.6, 138.1, 135.5, 134.4, 133.8, 129.0, 128.7, 102.2, 82.6, 60.9, 56.1, 51.3, 33.9.
HRMS (ESI): m/z calcd for $[C_{20}H_{20}O_6 + Na]^+$ 379.1152; found: 379.1150



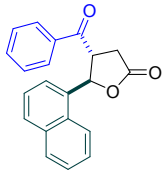
***trans*-4-Benzoyl-5-(2-hydroxyphenyl)dihydrofuran-2(3H)-one (4fa)**

The title compound was prepared from 2-hydroxybenzaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 6.9 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.38 (t, J = 7.8 Hz, 2H), 7.18 (t, J = 7.7 Hz, 1H), 7.14 (d, J = 7.6 Hz, 1H), 6.90 (d, J = 9.2 Hz, 1H), 6.84 (t, J = 7.5 Hz, 1H), 5.82 (d, J = 5.6 Hz, 1H), 4.48 (ddd, J = 10.0, 7.1, 5.7 Hz, 1H), 3.14 – 2.87 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 198.3, 177.2, 154.2, 135.1, 134.3, 130.6, 129.0, 129.0, 128.3, 124.5, 120.5, 116.7, 81.4, 48.3, 33.3.

HRMS (ESI): m/z calcd for $[C_{17}H_{14}O_4 + Na]^+$ 305.0784; found: 305.0786



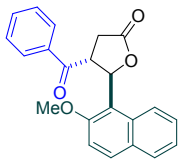
***trans*-4-Benzoyl-5-(naphthalen-1-yl)dihydrofuran-2(3H)-one(4ga)**

The title compound was prepared from 1-naphthaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane -4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 12.5, 8.5 Hz, 2H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 1H), 7.57 (t, *J* = 6.4 Hz, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.36 (m, 3H), 6.72 (d, *J* = 4.9 Hz, 1H), 4.39 (dt, *J* = 10.6, 5.6 Hz, 1H), 3.11 (dd, *J* = 17.9, 10.1 Hz, 1H), 2.93 (dd, *J* = 17.9, 6.3 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$)δ 190.6, 164.8, 162.8, 136.1, 134.3, 133.6, 133.2, 129.5, 129.3, 128.7, 128.7, 128.4, 127.9, 127.7, 127.2, 127.0, 126.7, 105.8, 46.4, 40.3, 39.8, 28.3, 27.8.

HRMS (ESI): m/z calcd for $[C_{25}H_{20}O_5 + Na]^+$ 423.1203; found: 423.1206

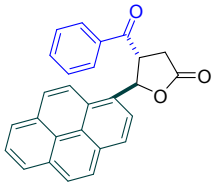


***trans*-4-Benzoyl-5-(2-methoxynaphthalen-1-yl)dihydrofuran-2(3H)-one (4ha)**

The title compound was prepared from 2-methoxy-1-naphthaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane -4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene) -4-phenylpentan- 2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (97%).

^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.70 (d, *J* = 6.9 Hz, 2H), 7.47 (dt, *J* = 15.5, 8.0 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.32 – 7.24 (m, 3H), 6.80 (d, *J* = 6.6 Hz, 1H), 4.67 (ddd, *J* = 10.2, 8.4, 6.6 Hz, 1H), 3.94 (s, 3H), 3.26 – 3.11 (m, 2H).

^{13}C NMR (126 MHz, Chloroform-*d*) δ 197.6, 176.0, 156.5, 135.4, 134.1, 132.2, 131.8, 129.2, 129.0, 128.9, 128.9, 127.8, 124.1, 122.1, 119.0, 113.8, 57.0, 48.4, 33.9.



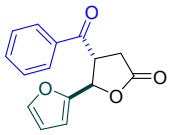
***trans*-4-Benzoyl-5-(pyren-1-yl)dihydrofuran-2(3H)-one (4ia)**

The title compound was prepared from pyrene-1-carbaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (t, J = 7.1 Hz, 2H), 8.16 (d, J = 7.7 Hz, 1H), 8.13 – 7.96 (m, 6H), 7.74 (d, J = 7.1 Hz, 2H), 7.48 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.8 Hz, 2H), 6.99 (d, J = 6.0 Hz, 1H), 4.53 (dd, J = 15.7, 7.6 Hz, 1H), 3.25 – 3.03 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 197.4, 174.9, 135.2, 134.4, 131.8, 131.6, 131.4, 130.6, 129.1, 128.9, 128.8, 128.3, 127.7, 127.5, 126.5, 126.1, 125.8, 125.3, 125.0, 124.7, 122.8, 121.8, 79.8, 50.9, 33.8.

HRMS (ESI): m/z calcd for $[C_{27}H_{18}O_3 + Na]^+$ 413.1148; found: 413.1150



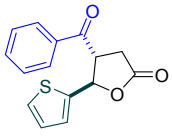
***trans*-4-Benzoyl-5-(furan-2-yl)dihydrofuran-2(3H)-one (4ja)**

The title compound was prepared from furan-2-carbaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.0 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.51 – 7.42 (m, 3H), 6.43 (d, J = 3.3 Hz, 1H), 6.36 (dd, J = 3.4, 1.8 Hz, 1H), 5.71 (d, J = 5.9 Hz, 1H), 4.62 (dd, J = 15.1, 7.5 Hz, 1H), 3.13 – 2.98 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 174.2, 149.5, 144.1, 134.9, 134.5, 129.2, 128.8, 111.0, 110.9, 75.4, 46.5, 32.4.

HRMS (ESI): m/z calcd for $[C_{15}H_{12}O_4 + Na]^+$ 279.0628; found: 279.0629



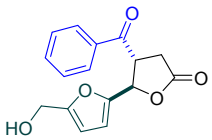
***trans*-4-Benzoyl-5-(thiophen-2-yl)dihydrofuran-2(3H)-one (4ka)**

The title compound was prepared from thiophene-2-carbaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ⁶-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (66%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.6 Hz, 2H), 7.68 – 7.55 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 5.1 Hz, 1H), 7.05 (d, J = 3.6 Hz, 1H), 7.00 – 6.89 (m, 1H), 6.01 (d, J = 6.8 Hz, 1H), 4.51 – 4.38 (m, 1H), 3.04 (h, J = 9.0 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 173.7, 140.6, 135.1, 134.5, 129.2, 128.8, 127.3, 126.8, 126.7, 78.7, 51.0, 33.4.

HRMS (ESI): m/z calcd for $[C_{15}H_{12}O_3S + Na]^+$ 295.0399; found: 295.0402



***trans*-4-Benzoyl-5-(5-(hydroxymethyl)furan-2-yl)dihydrofuran-2(3H)-one (4la)**

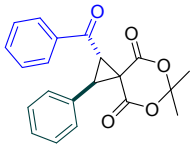
The title compound was prepared from 5-(hydroxymethyl)furan-2-carbaldehyde (0.3mmol), 2,2-dimethyl -1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-phenylethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (52%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.8 Hz, 2H), 7.61 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.8 Hz, 2H), 6.39 (d, J = 3.2 Hz, 1H), 6.27 (d, J = 3.2 Hz, 1H), 5.71 (d, J = 6.2 Hz, 1H), 4.65 (dd, J = 15.6, 7.7 Hz, 1H), 4.62 (s, 2H), 3.15 – 2.98 (m, 2H), 1.92 (b, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 174.3, 155.9, 149.3, 135.0, 134.6, 129.3, 128.9, 111.9, 109.1, 75.6, 57.6, 46.5, 32.7.

HRMS (ESI): m/z calcd for $[C_{16}H_{14}O_5 + Na]^+$ 309.0733; found: 209.0735

5.3. Spectroscopic Data of Products 5ma--5j'x



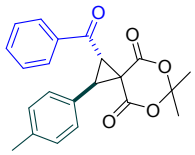
***trans*-1-Benzoyl-6,6-dimethyl-2-phenyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5ma)**

The title compound was prepared from benzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane -4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.43 – 7.36 (m, 5H), 4.44 (d, J = 9.6 Hz, 1H), 4.11 (d, J = 9.6 Hz, 1H), 1.73 (d, J = 16.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 164.8, 162.7, 136.1, 134.3, 130.3, 129.7, 129.4, 129.2, 128.9, 128.6, 105.8, 46.0, 40.0, 39.7, 28.2, 27.8.

HRMS (ESI): m/z calcd for $[C_{21}H_{18}O_5 + Na]^+$ 373.1046; found: 373.1053

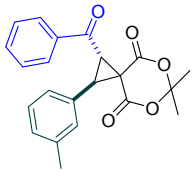


***trans*-1-Benzoyl-6,6-dimethyl-2-(p-tolyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5na)** (Known compound: *Hecheng Huaxue* **2000**, *8*, 356-360.)

The title compound was prepared from 4-methylbenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane -4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4- phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 7.9 Hz, 2H), 4.43 (d, J = 9.6 Hz, 1H), 4.08 (d, J = 9.7 Hz, 1H), 2.36 (s, 3H), 1.72 (d, J = 16.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 164.9, 162.8, 139.5, 136.1, 134.2, 129.6, 129.6, 129.2, 128.6, 127.2, 105.7, 46.3, 39.9, 39.8, 28.2, 27.8, 21.5.



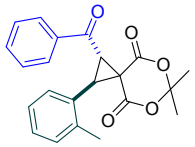
***trans*-1-Benzoyl-6,6-dimethyl-2-(m-tolyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5oa)**

The title compound was prepared from 3-methylbenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (85%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.23 – 7.16 (m, 3H), 4.42 (d, J = 9.6 Hz, 1H), 4.08 (d, J = 9.6 Hz, 1H), 2.36 (s, 3H), 1.72 (d, J = 13.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 164.8, 162.7, 138.5, 136.0, 134.1, 130.2, 130.2, 130.1, 129.1, 128.7, 128.5, 126.8, 105.7, 46.1, 39.9, 39.6, 28.1, 27.7, 21.6.

HRMS (ESI): m/z calcd for $[C_{22}H_{20}O_5 + Na]^+$ 387.1023; found: 387.1210



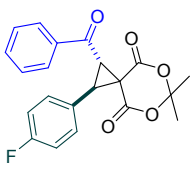
***trans*-1-Benzoyl-6,6-dimethyl-2-(*o*-tolyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5pa)**

The title compound was prepared from 2-methylbenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.0 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.47 – 7.42 (m, 1H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 4.24 (d, J = 9.9 Hz, 1H), 4.19 (d, J = 10.0 Hz, 1H), 2.31 (s, 3H), 1.88 (s, 3H), 1.76 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 165.3, 163.6, 138.3, 135.7, 134.3, 130.5, 129.6, 129.1, 128.9, 128.7, 128.3, 126.2, 105.7, 45.0, 43.3, 36.5, 28.1, 27.7, 19.8.

HRMS (ESI): m/z calcd for $[C_{22}H_{20}O_5 + Na]^+$ 387.1203; found: 387.1207



***trans*-1-Benzoyl-2-(4-fluorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5qa)**

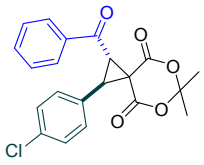
The title compound was prepared from 4-fluorobenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (78%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 6.9 Hz, 2H), 7.62 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.40 (dd, J = 8.6, 5.2 Hz, 2H), 7.09 (t, J = 8.5 Hz, 2H), 4.39 (d, J = 9.6 Hz, 1H), 4.09 (d, J = 9.6 Hz, 1H), 1.72 (d, J = 25.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.1, 164.4, 163.1 (d, J = 249.5 Hz), 162.6, 135.8, 134.1, 131.3 (d, J = 8.7 Hz), 129.1, 128.4, 125.9, 115.9 (d, J = 21.8 Hz), 105.6, 44.9, 40.1, 39.3, 38.5 (d, J = 5037.8 Hz), 28.1, 27.6.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -111.60.

HRMS (ESI): m/z calcd for $[C_{21}H_{17}FO_5 + Na]^+$ 391.0952; found: 391.0960



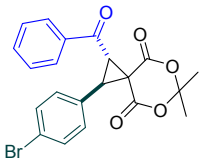
***trans*-1-Benzoyl-2-(4-chlorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5ra)**

(Known compound: *Hecheng Huaxue* **2000**, *8*, 356-360.)

The title compound was prepared from 4-chlorobenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 9.7 Hz, 2H), 7.60 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 7.8 Hz, 2H), 7.35 (s, 4H), 4.39 (d, J = 9.6 Hz, 1H), 4.08 (d, J = 9.5 Hz, 1H), 1.72 (d, J = 26.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 164.4, 162.5, 135.7, 135.3, 134.1, 130.8, 129.1, 128.9, 128.7, 128.4, 105.7, 44.7, 40.0, 39.3, 28.1, 27.6.



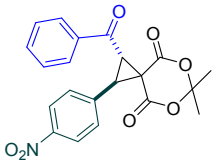
***trans*-1-Benzoyl-2-(4-bromophenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5sa)**

The title compound was prepared from 4-bromobenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (71%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 7.0 Hz, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.55 – 7.46 (m, 4H), 7.29 (d, J = 8.5 Hz, 2H), 4.38 (d, J = 9.6 Hz, 1H), 4.06 (d, J = 9.6 Hz, 1H), 1.72 (d, J = 27.3 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 164.4, 162.5, 135.7, 134.1, 131.9, 131.1, 129.2, 129.1, 128.4, 123.5, 105.7, 44.7, 39.9, 39.2, 28.1, 27.6.

HRMS (ESI): m/z calcd for $[C_{21}H_{17}BrO_5 + Na]^+$ 453.0131; found: 453.0139



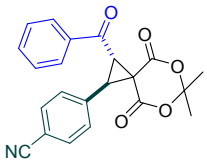
***trans*-1-Benzoyl-6,6-dimethyl-2-(4-nitrophenyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5ta)**

The title compound was prepared from 4-nitrobenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (84%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (d, J = 8.8 Hz, 2H), 7.99 (d, J = 8.1 Hz, 2H), 7.62 (dd, J = 15.9, 8.1 Hz, 3H), 7.52 (t, J = 7.7 Hz, 2H), 4.41 (d, J = 9.5 Hz, 1H), 4.18 (d, J = 9.5 Hz, 1H), 1.75 (d, J = 33.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 164.2, 162.7, 148.3, 137.9, 135.7, 134.5, 130.7, 129.3, 128.6, 124.0, 106.1, 43.5, 40.8, 39.0, 28.4, 27.8.

HRMS (ESI): m/z calcd for $[C_{21}H_{17}NO_7 + Na]^+$ 418.0897; found: 418.0902



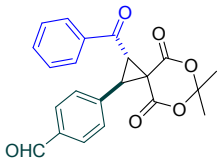
4-(*trans*-2-Benzoyl-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octan-1-yl)benzonitrile (5ua)

The title compound was prepared from 4-formylbenzonitrile (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (69%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 7.5 Hz, 2H), 7.69 (d, J = 8.3 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.57 – 7.46 (m, 4H), 4.39 (d, J = 9.5 Hz, 1H), 4.14 (d, J = 9.5 Hz, 1H), 1.74 (d, J = 34.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 164.3, 162.7, 135.9, 135.7, 134.6, 132.6, 130.5, 129.3, 128.6, 118.4, 113.2, 106.1, 44.0, 40.5, 39.0, 28.4, 27.8.

HRMS (ESI): m/z calcd for $[C_{22}H_{17}NO_5 + Na]^+$ 398.0999; found: 398.1003



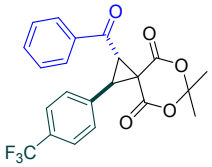
4-(*trans*-2-Benzoyl-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octan-1-yl)benzaldehyde(5va)

The title compound was prepared from terephthalaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (56%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.91 (d, J = 8.3 Hz, 2H), 7.66 – 7.56 (m, 3H), 7.50 (t, J = 7.7 Hz, 2H), 4.45 (d, J = 9.5 Hz, 1H), 4.17 (d, J = 9.5 Hz, 1H), 1.73 (d, J = 25.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.5, 189.8, 164.2, 162.5, 136.9, 136.6, 135.7, 134.2, 130.3, 129.9, 129.1, 128.4, 105.8, 44.3, 40.3, 39.0, 28.1, 27.6.

HRMS (ESI): m/z calcd for $[C_{22}H_{18}O_6 + Na]^+$ 401.0996; found: 401.1002



***trans*-1-Benzoyl-6,6-dimethyl-2-(4-(trifluoromethyl)phenyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5wa)**

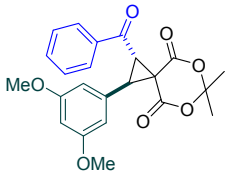
The title compound was prepared from 4-(trifluoromethyl)benzaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (73%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.0 Hz, 2H), 7.68 – 7.60 (m, 3H), 7.57 – 7.47 (m, 4H), 4.43 (d, J = 9.5 Hz, 1H), 4.14 (d, J = 9.5 Hz, 1H), 1.77 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 164.5, 162.7, 135.9, 134.5, 131.4 (d, J = 32.7 Hz), 130.1, 129.3, 128.6, 128.4 (d, J = 210.0 Hz), 125.9 (q, J = 3.7 Hz), 124.0 (d, J = 272.3 Hz), 106.0, 44.4, 40.4, 39.2, 28.4, 27.8.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.8.

HRMS (ESI): m/z calcd for $[C_{22}H_{17}F_3O_5 + Na]^+$ 441.0920; found: 441.0922



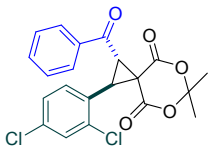
***trans*-1-Benzoyl-2-(3,5-dimethoxyphenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5xa)**

The title compound was prepared from 3,5-dimethoxybenzaldehyde (0.3mmol), 2,2-dimethy l-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan -2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 7.0 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 6.55 (d, J = 2.3 Hz, 2H), 6.44 (s, 1H), 4.39 (d, J = 9.6 Hz, 1H), 4.01 (d, J = 9.6 Hz, 1H), 3.76 (s, 6H), 1.72 (d, J = 5.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 164.7, 162.6, 160.9, 136.0, 134.1, 132.5, 129.1, 128.5, 107.7, 105.7, 101.1, 55.5, 45.9, 40.1, 39.6, 28.0, 27.7.

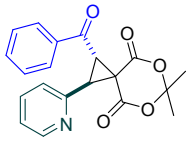
HRMS (ESI): m/z calcd for $[C_{23}H_{22}O_7 + Na]^+$ 433.1258; found: 433.1265



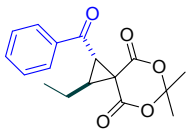
***trans*-1-Benzoyl-2-(2,4-dichlorophenyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5ya)**

The title compound was prepared from 2,4-dichlorobenzaldehyde (0.3mmol), 2,2-dimethyl-1,3-

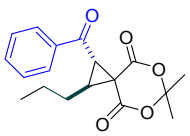
dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (91%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 6.8 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.29 (d, J = 6.3 Hz, 1H), 4.26 – 4.16 (m, 2H), 1.76 (d, J = 11.6 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 164.4, 163.3, 136.5, 135.6, 135.4, 134.3, 131.1, 129.5, 129.1, 128.5, 128.2, 127.3, 106.0, 42.5, 42.5, 36.6, 28.0, 27.7.
HRMS (ESI): m/z calcd for $[C_{21}H_{16}Cl_2O_5 + Na]^+$ 441.0267; found: 441.0271



***trans*-1-Benzoyl-6,6-dimethyl-2-(pyridin-2-yl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5za)**
The title compound was prepared from picolinaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane -4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (70%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, J = 5.7 Hz, 1H), 8.07 (d, J = 6.9 Hz, 2H), 7.72 (t, J = 7.7 Hz, 1H), 7.60 (d, J = 7.2 Hz, 1H), 7.49 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 7.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 4.45 (d, J = 9.3 Hz, 1H), 4.26 (s, 1H), 1.97 (s, 3H), 1.79 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 164.9, 163.6, 151.6, 149.7, 137.0, 135.9, 134.3, 129.2, 128.7, 124.3, 123.7, 106.4, 44.6, 41.1, 37.5, 28.0, 27.8.
HRMS (ESI): m/z calcd for $[C_{20}H_{17}NO_5 + Na]^+$ 374.0999; found: 374.0997



***trans*-1-Benzoyl-2-ethyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5a'a)**
The title compound was prepared from propionaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the productas a white solid. (95%, Mp. 143-147 ºC).
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 7.5 Hz, 1H), 7.45 – 7.38 (m, 2H), 3.60 (d, J = 9.1 Hz, 1H), 2.91 – 2.77 (m, 1H), 1.93 – 1.71 (m, 8H), 1.12 – 1.03 (m, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.7, 165.2, 164.7, 135.9, 133.8, 128.9, 128.2, 105.4, 43.6, 43.1, 35.8, 27.6, 27.5, 19.9, 12.9.
HRMS (ESI): m/z calcd for $[C_{17}H_{18}O_5 + Na]_+$ 325.1046; found: 325.1049



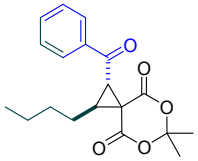
***trans*-1-Benzoyl-6,6-dimethyl-2-propyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5b'a)**

The title compound was prepared from butyraldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.0 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 3.64 (d, J = 9.1 Hz, 1H), 2.88 (td, J = 8.8, 6.0 Hz, 1H), 1.86 (dq, J = 13.7, 7.2 Hz, 1H), 1.77 (d, J = 14.0 Hz, 6H), 1.70 (dd, J = 13.7, 7.9 Hz, 1H), 1.53 (h, J = 7.4 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 165.3, 164.8, 136.0, 133.9, 129.0, 128.3, 105.5, 43.6, 41.7, 35.8, 28.3, 27.7, 27.6, 21.9, 13.7.

HRMS (ESI): m/z calcd for $[C_{18}H_{20}O_5 + Na]^+$ 339.1203; found: 339.1206



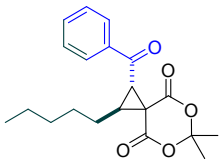
***trans*-1-Benzoyl-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'a)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane -4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 3.66 (d, J = 9.0 Hz, 1H), 2.90 (td, J = 8.7, 6.1 Hz, 1H), 1.89 (dq, J = 13.9, 7.2 Hz, 1H), 1.80 (d, J = 14.1 Hz, 6H), 1.78 – 1.71 (m, 1H), 1.54 – 1.36 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 165.4, 164.9, 136.1, 134.0, 129.1, 128.4, 105.5, 43.7, 41.9, 36.0, 30.8, 27.8, 27.7, 26.2, 22.3, 14.1.

HRMS (ESI): m/z calcd for $[C_{19}H_{22}O_5 + Na]^+$ 353.1359; found: 353.1361



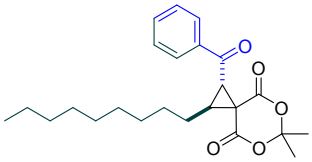
***trans*-1-Benzoyl-6,6-dimethyl-2-pentyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5d'a)**

The title compound was prepared from hexanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (82%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, J = 7.0 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.42 (t, J = 7.8 Hz, 2H), 3.63 (d, J = 9.2 Hz, 1H), 2.87 (td, J = 8.7, 6.0 Hz, 1H), 1.86 (dq, J = 14.0, 7.5 Hz, 1H), 1.76 (d, J = 15.2 Hz, 6H), 1.74 – 1.67 (m, 1H), 1.49 (p, J = 7.4 Hz, 2H), 1.43 – 1.24 (m, 4H), 0.86 (t, J = 7.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 165.2, 164.8, 136.0, 133.9, 128.9, 128.3, 105.4, 43.6, 41.8, 35.8, 31.2, 28.2, 27.6, 27.5, 26.3, 22.5, 14.0.

HRMS (ESI): m/z calcd for $[C_{20}H_{24}O_5 + Na]^+$ 367.1516; found: 367.1518

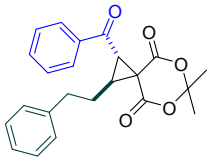


***trans*-1-Benzoyl-6,6-dimethyl-2-nonyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5e'a)**

The title compound was prepared from decanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, J = 7.1 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.39 (t, J = 7.7 Hz, 2H), 3.61 (d, J = 9.1 Hz, 1H), 2.85 (td, J = 8.8, 6.0 Hz, 1H), 1.84 (dq, J = 13.9, 7.0 Hz, 1H), 1.73 (d, J = 16.3 Hz, 6H), 1.68 (dd, J = 13.3, 5.6 Hz, 1H), 1.47 (p, J = 7.4 Hz, 2H), 1.33 (dd, J = 9.5, 5.6 Hz, 2H), 1.28 – 1.16 (m, 10H), 0.82 (t, J = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 165.1, 164.7, 135.9, 133.7, 128.8, 128.2, 105.3, 43.4, 41.7, 35.8, 31.8, 29.4, 29.4, 29.2, 29.0, 28.4, 27.5, 27.4, 26.2, 22.6, 14.1.



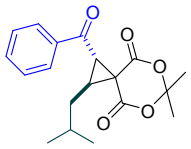
***trans*-1-Benzoyl-6,6-dimethyl-2-phenethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5f'a)**

The title compound was prepared from 3-phenylpropanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.4 Hz, 2H), 7.58 (d, J = 7.3 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.6 Hz, 2H), 7.25 – 7.17 (m, 3H), 3.62 (d, J = 9.1 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.83 (hept, J = 7.3 Hz, 2H), 2.25 (td, J = 14.3, 7.5 Hz, 1H), 2.18 – 2.08 (m, 1H), 1.77 (d, J = 5.7 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.66, 165.19, 164.99, 140.23, 135.99, 134.03, 129.04, 128.75, 128.41, 126.54, 105.48, 43.84, 41.26, 35.51, 34.81, 28.23, 27.74, 27.63.

HRMS (ESI): m/z calcd for $[C_{23}H_{22}O_5 + Na]^+$ 401.1359; found: 401.1360



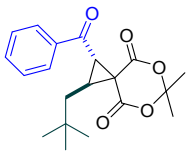
***trans*-1-Benzoyl-2-isobutyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5g'a)**

The title compound was prepared from 3-methylbutanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 7.0 Hz, 2H), 7.56 (d, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 3.69 (d, J = 9.1 Hz, 1H), 2.91 (td, J = 9.2, 4.7 Hz, 1H), 1.85 – 1.74 (m, 8H), 1.58 – 1.50 (m, 1H), 1.01 (t, J = 5.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 165.4, 165.0, 136.1, 134.1, 129.1, 128.4, 105.5, 43.6, 40.8, 35.9, 35.1, 28.3, 27.8, 27.8, 22.7, 22.3.

HRMS (ESI): m/z calcd for $[C_{19}H_{22}O_5 + Na]^+$ 353.1359; found: 353.1364



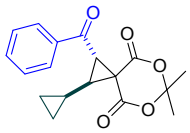
***trans*-1-Benzoyl-6,6-dimethyl-2-neopentyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5h'a)**

The title compound was prepared from 3,3-dimethylbutanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, J = 7.0 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 3.74 (d, J = 9.1 Hz, 1H), 2.90 (ddd, J = 10.6, 9.1, 3.6 Hz, 1H), 1.79 (d, J = 14.0 Hz, 6H), 1.74 (dd, J = 13.5, 3.6 Hz, 1H), 1.51 (dd, J = 13.5, 10.7 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 165.5, 164.9, 136.1, 134.1, 129.2, 128.4, 105.5, 43.7, 39.9, 39.5, 35.5, 31.8, 29.6, 27.8, 27.8.

HRMS (ESI): m/z calcd for $[C_{20}H_{24}O_5 + Na]^+$ 367.1516; found: 367.1519



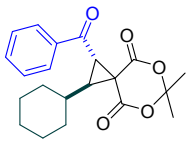
***trans*-1-Benzoyl-2-cyclopropyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5i'a)**

The title compound was prepared from cyclopropanecarbaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product as a yellow solid. (93%, Mp. 150-156 ºC).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 7.0 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 3.87 (d, J = 9.1 Hz, 1H), 2.36 (t, J = 9.1 Hz, 1H), 1.83 (d, J = 35.7 Hz, 6H), 1.20 – 1.08 (m, 1H), 0.83 – 0.76 (m, 1H), 0.74 – 0.62 (m, 2H), 0.52 – 0.40 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.6, 165.2, 164.9, 136.0, 134.0, 129.0, 128.5, 105.6, 47.2, 43.3, 36.6, 27.7, 27.5, 8.2, 5.3, 4.9.

HRMS (ESI): m/z calcd for $[C_{18}H_{18}O_5 + Na]^+$ 337.1046; found: 337.1050



***trans*-1-Benzoyl-2-cyclohexyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5j'a)**

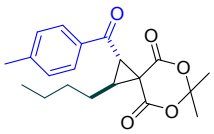
The title compound was prepared from cyclohexanecarbaldehyde (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, J = 7.0 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 3.64 (d, J = 9.2 Hz, 1H), 2.78 (t, J = 9.6 Hz, 1H), 1.93 – 1.62 (m, 12H), 1.44 – 1.25 (m, 5H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 165.5, 165.2, 136.1, 134.0, 129.1, 128.4, 105.8, 48.1, 44.9, 35.5, 32.8, 32.5, 28.3, 28.0, 26.0, 25.9, 25.6.

HRMS (ESI): m/z calcd for $[C_{21}H_{24}O_5 + Na]^+$ 397.1516; found: 397.1519

5.4. Spectroscopic Data of Products 5c'b--5c'x



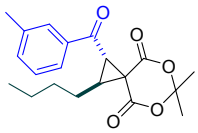
***trans*-1-Butyl-6,6-dimethyl-2-(4-methylbenzoyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'b)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(*p*-tolyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (95%)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 3.63 (d, J = 9.1 Hz, 1H), 2.88 (td, J = 8.7, 6.1 Hz, 1H), 2.39 (s, 3H), 1.88 (dq, J = 13.9, 7.2 Hz, 1H), 1.79 (d, J = 12.7 Hz, 6H), 1.77 – 1.70 (m, 1H), 1.49 (t, J = 7.7 Hz, 2H), 1.40 (dddd, J = 15.0, 12.2, 7.3, 2.8 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.4, 165.3, 165.0, 145.0, 133.7, 129.7, 128.5, 105.4, 43.9, 42.0, 35.9, 30.8, 27.7, 27.7, 26.2, 22.3, 21.9, 14.1.

HRMS (ESI): m/z calcd for $[C_{21}H_{24}O_5 + Na]^+$ 367.1516; found: 367.1520



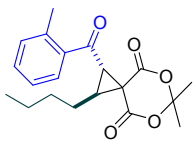
***trans*-1-Butyl-6,6-dimethyl-2-(3-methylbenzoyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'c)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(*m*-tolyl)ethan-1-one(0.2 mmol). The crude residue was purified by flash chromatography to give the product. (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.69 (d, J = 7.5 Hz, 1H), 7.40 – 7.30 (m, 2H), 3.64 (d, J = 9.1 Hz, 1H), 2.89 (td, J = 8.7, 6.1 Hz, 1H), 2.38 (s, 3H), 1.88 (dq, J = 14.0, 7.6, 7.0 Hz, 1H), 1.79 (d, J = 13.4 Hz, 6H), 1.74 (dd, J = 14.4, 7.5 Hz, 1H), 1.49 (p, J = 6.9 Hz, 2H), 1.45 – 1.35 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.0, 165.4, 165.0, 138.9, 136.1, 134.8, 128.9, 128.8, 125.7, 105.5, 43.9, 42.0, 35.9, 30.8, 27.8, 27.7, 26.2, 22.3, 21.5, 14.1.

HRMS (ESI): m/z calcd for $[C_{21}H_{24}O_5 + Na]^+$ 367.1516; found: 367.1518



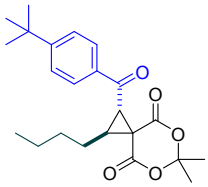
***trans*-1-Butyl-6,6-dimethyl-2-(2-methylbenzoyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'd)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(*o*-tolyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 6.7 Hz, 1H), 7.37 (t, J = 6.8 Hz, 1H), 7.23 (dt, J = 7.6, 3.6 Hz, 2H), 3.66 (d, J = 9.1 Hz, 1H), 2.80 (td, J = 8.8, 6.3 Hz, 1H), 2.55 (s, 3H), 1.85 (td, J = 14.3, 6.3 Hz, 1H), 1.80 – 1.70 (m, 7H), 1.51 – 1.33 (m, 4H), 0.89 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 165.9, 165.0, 140.8, 135.5, 132.7, 132.6, 129.6, 125.9, 105.5, 45.9, 43.1, 35.7, 30.8, 27.8, 27.7, 26.3, 22.3, 21.9, 14.1.

HRMS (ESI): m/z calcd for $[C_{21}H_{24}O_5 + Na]^+$ 367.1516; found: 367.1515



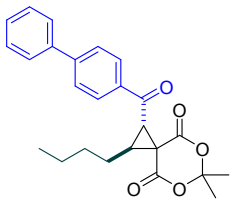
***trans*-1-Butyl-2-(4-(tert-butyl)benzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'e)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(4-(tert-butyl)phenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 3.63 (d, J = 9.1 Hz, 1H), 2.90 (td, J = 8.7, 6.1 Hz, 1H), 1.89 (dq, J = 13.9, 7.2 Hz, 1H), 1.84 – 1.72 (m, 7H), 1.49 (p, J = 7.4 Hz, 2H), 1.45 – 1.36 (m, 2H), 1.32 (s, 9H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 165.4, 165.0, 157.8, 133.6, 128.4, 126.0, 105.5, 44.0, 42.0, 35.9, 35.4, 31.2, 30.8, 27.8, 27.7, 26.2, 22.3, 14.1.

HRMS (ESI): m/z calcd for $[C_{23}H_{30}O_5 + Na]^+$ 409.1985; found: 409.1987



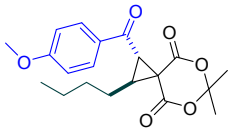
***trans*-1-([1,1'-Biphenyl]-4-carbonyl)-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'f)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-([1,1'-biphenyl]-4-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.3 Hz, 1H), 3.70 (d, J = 9.1 Hz, 1H), 2.93 (td, J = 8.7, 6.1 Hz, 1H), 1.91 (td, J = 13.7, 7.5 Hz, 1H), 1.85 – 1.73 (m, 7H), 1.56 – 1.49 (m, 2H), 1.48 – 1.39 (m, 2H), 0.93 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.5, 165.4, 165.0, 146.7, 139.9, 134.8, 129.2, 129.0, 128.6, 127.7, 127.5, 105.6, 43.8, 42.0, 36.0, 30.8, 27.8, 27.7, 26.2, 22.3, 14.1.

HRMS (ESI): m/z calcd for $[C_{25}H_{26}O_5 + Na]^+$ 429.1672; found: 429.1678



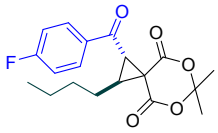
***trans*-1-Butyl-2-(4-methoxybenzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'g)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-methoxyphenyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.9 Hz, 2H), 6.88 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 3.57 (d, J = 9.2 Hz, 1H), 2.84 (td, J = 8.7, 6.2 Hz, 1H), 1.85 (dq, J = 14.0, 7.6, 7.1 Hz, 1H), 1.80 – 1.67 (m, 7H), 1.45 (tdd, J = 9.0, 7.2, 4.1 Hz, 2H), 1.37 (dddd, J = 10.9, 8.0, 6.9, 4.2 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.1, 165.2, 164.9, 164.0, 130.5, 129.1, 114.1, 105.3, 55.5, 43.9, 41.9, 35.7, 30.6, 27.6, 27.5, 26.0, 22.1, 13.9.

HRMS (ESI): m/z calcd for $[C_{20}H_{24}O_6 + Na]^+$ 383.1465; found: 383.1468



***trans*-1-Butyl-2-(4-fluorobenzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'h)**

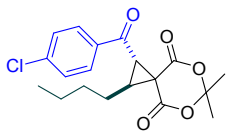
The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-fluorophenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (96%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.9, 5.3 Hz, 2H), 7.11 (t, J = 8.6 Hz, 2H), 3.60 (d, J = 9.0 Hz, 1H), 2.85 (td, J = 8.8, 5.9 Hz, 1H), 1.86 (dq, J = 13.8, 7.4 Hz, 1H), 1.78 (d, J = 15.4 Hz, 6H), 1.74 – 1.65 (m, 1H), 1.48 (p, J = 7.1 Hz, 2H), 1.39 (dtd, J = 10.0, 8.0, 7.3, 5.1 Hz, 2H), 0.89 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.3, 166.2 (d, *J* = 255.9 Hz), 165.3, 164.7, 132.6 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 9.5 Hz), 116.2 (d, *J* = 22.1 Hz), 105.5, 43.2, 41.8, 36.0, 30.7, 27.6 (d, *J* = 9.1 Hz), 26.1, 22.2, 14.0.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -103.71.

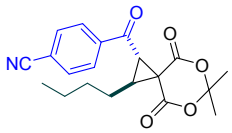
HRMS (ESI): m/z calcd for $[C_{19}H_{21}FO_5 + Na]^+$ 371.1265; found: 371.1266



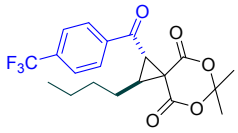
***trans*-1-Butyl-2-(4-chlorobenzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'i)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(4-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan -1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product as a white solid. (92%, Mp. 129-138 ºC).

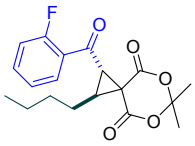
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 3.61 (d, J = 9.0 Hz, 1H), 2.86 (td, J = 8.8, 5.9 Hz, 1H), 1.87 (td, J = 13.6, 6.7 Hz, 1H), 1.80 (d, J = 14.1 Hz, 6H), 1.75 – 1.67 (m, 1H), 1.50 (dt, J = 14.5, 7.1 Hz, 2H), 1.41 (ddt, J = 14.0, 7.2, 4.9 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 165.3, 164.8, 140.5, 134.5, 129.8, 129.5, 105.7, 43.2, 41.8, 36.1, 30.8, 27.8, 27.7, 26.2, 22.3, 14.1.
HRMS (ESI): m/z calcd for $[C_{19}H_{21}ClO_5 + Na]^+$ 387.0969; found: 387.0976



4-(*trans*-2-Butyl-6,6-dimethyl-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carbonyl)benzonitrile (5c'j)
The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 4-(2-(dimethyl(oxo)-λ^6-sulfaneylidene)acetyl)benzonitrile (0.2 mmol). The crude residue was purified by flash chromatography to give the productas as a white solid. (93%, Mp. 149-153 ºC).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 3.63 (d, J = 8.9 Hz, 1H), 2.85 (td, J = 8.9, 5.6 Hz, 1H), 1.92 – 1.77 (m, 7H), 1.74 – 1.64 (m, 1H), 1.50 (q, J = 6.9 Hz, 2H), 1.42 (p, J = 6.6 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 165.4, 164.4, 139.1, 133.0, 128.7, 118.0, 117.1, 105.9, 42.4, 41.6, 36.4, 30.7, 27.8, 27.7, 26.1, 22.3, 14.1.
HRMS (ESI): m/z calcd for $[C_{20}H_{21}NO_5 + Na]^+$ 378.1311; found: 378.1316



***trans*-1-Butyl-6,6-dimethyl-2-(4-(trifluoromethyl)benzoyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'k)**
The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(4-(trifluoromethyl)phenyl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (87%).
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.1 Hz, 2H), 7.70 (d, J = 8.2 Hz, 2H), 3.64 (d, J = 8.9 Hz, 1H), 2.85 (td, J = 8.9, 5.7 Hz, 1H), 1.86 (td, J = 13.6, 7.1 Hz, 1H), 1.78 (d, J = 20.5 Hz, 6H), 1.74 – 1.64 (m, 1H), 1.49 (p, J = 7.2 Hz, 2H), 1.45 – 1.33 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 190.2, 165.4, 164.5, 138.8, 134.9 (q, *J* = 32.7 Hz), 128.6, 126.1 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.8 Hz), 105.7, 42.7, 41.6, 36.2, 30.7, 27.6, 27.6, 26.1, 22.2, 14.0.
^{19}F NMR (471 MHz, Chloroform-*d*) δ -63.19.
HRMS (ESI): m/z calcd for $[C_{20}H_{21}F_3O_5 + Na]^+$ 421.1233; found: 421.1236



***trans*-1-Butyl-2-(2-fluorobenzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'l)**

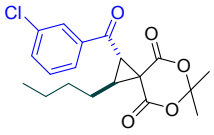
The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(2-fluorophenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (t, J = 7.7 Hz, 1H), 7.53 (q, J = 7.2 Hz, 1H), 7.29 – 7.18 (m, 1H), 7.11 (dd, J = 11.5, 7.6 Hz, 1H), 3.60 (dd, J = 9.1, 3.3 Hz, 1H), 2.89 (q, J = 7.5, 6.5 Hz, 1H), 1.88 – 1.69 (m, 8H), 1.46 (q, J = 6.9 Hz, 2H), 1.43 – 1.35 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 188.6, 188.6, 166.1, 164.7, 162.6 (d, *J* = 254.7 Hz), 135.6 (d, *J* = 9.3 Hz), 131.3 (d, *J* = 2.2 Hz), 125.0 (d, *J* = 3.2 Hz), 124.5 (d, *J* = 11.8 Hz), 116.9 (d, *J* = 23.7 Hz), 105.4, 47.3 (d, *J* = 4.9 Hz), 42.1, 42.1, 36.0 (d, *J* = 5.5 Hz), 30.8, 27.8 (d, *J* = 8.9 Hz), 26.1, 22.3, 14.1.

^{19}F NMR (471 MHz, Chloroform-*d*) δ -109.89.

HRMS (ESI): m/z calcd for $[C_{19}H_{21}FO_5 + Na]^+$ 371.1265; found: 371.1267



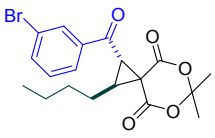
***trans*-1-Butyl-2-(3-chlorobenzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'm)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(3-chlorophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product . (97%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.76 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 8.1 Hz, 1H), 7.41 (t, J = 7.9 Hz, 1H), 3.61 (d, J = 9.0 Hz, 1H), 2.87 (td, J = 8.8, 5.9 Hz, 1H), 1.88 (td, J = 13.5, 7.4 Hz, 1H), 1.81 (d, J = 11.7 Hz, 6H), 1.77 – 1.68 (m, 1H), 1.55 – 1.46 (m, 2H), 1.41 (ddt, J = 14.3, 7.3, 4.9 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.9, 165.4, 164.7, 137.7, 135.5, 134.0, 130.4, 128.5, 126.5, 105.7, 43.1, 41.8, 36.1, 30.8, 27.8, 27.8, 26.2, 22.4, 14.1.

HRMS (ESI): m/z calcd for $[C_{19}H_{21}ClO_5 + Na]^+$ 387.0969; found: 387.0971



***trans*-1-(3-Bromobenzoyl)-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'n)**

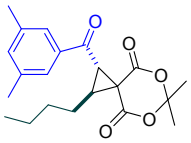
The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(3-bromophenyl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (98%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 9.6 Hz, 1H), 7.31 (t, J = 7.9 Hz, 1H), 3.58 (d, J = 9.0 Hz, 1H), 2.84 (td, J = 8.8, 5.9 Hz, 1H), 1.84 (dt, J = 13.8,

7.0 Hz, 1H), 1.77 (d, J = 12.8 Hz, 6H), 1.74 – 1.64 (m, 1H), 1.48 (p, J = 8.1, 7.3 Hz, 2H), 1.43 – 1.33 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 189.7, 165.3, 164.5, 137.7, 136.7, 131.2, 130.6, 126.8, 123.3, 105.6, 42.9, 41.7, 36.0, 30.7, 27.7, 27.6, 26.0, 22.2, 14.0.

HRMS (ESI): m/z calcd for $[C_{19}H_{21}BrO_5 + Na]^+$ 431.0464; found: 431.0468



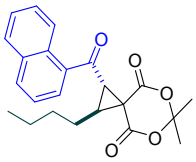
***trans*-1-Butyl-2-(3,5-dimethylbenzoyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'o)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(3,5-dimethylphenyl) ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (86%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 2H), 7.19 (s, 1H), 3.62 (d, J = 9.1 Hz, 1H), 2.88 (td, J = 8.7, 6.1 Hz, 1H), 2.33 (s, 6H), 1.88 (h, J = 7.7, 7.1 Hz, 1H), 1.79 (d, J = 11.7 Hz, 7H), 1.48 (q, J = 8.2, 7.3 Hz, 2H), 1.45 – 1.35 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 165.3, 165.0, 138.6, 136.1, 135.7, 126.2, 105.4, 44.1, 42.0, 35.7, 30.8, 27.7, 27.6, 26.1, 22.3, 21.4, 14.0.

HRMS (ESI): m/z calcd for $[C_{21}H_{26}O_5 + Na]^+$ 381.1672; found: 381.1675



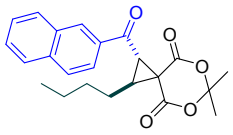
***trans*-1-(1-Naphthoyl)-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'p)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(naphthalen-1-yl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (92%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (d, J = 8.6 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.83 (d, J = 8.3 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.46 (t, J = 7.7 Hz, 1H), 3.85 (d, J = 9.1 Hz, 1H), 2.96 – 2.87 (m, 1H), 1.88 (ddt, J = 36.3, 14.5, 7.1 Hz, 2H), 1.75 (d, J = 13.8 Hz, 6H), 1.55 – 1.37 (m, 4H), 0.92 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 165.9, 165.0, 134.3, 134.2, 133.3, 130.7, 129.5, 128.7, 128.4, 126.8, 126.5, 124.2, 105.5, 46.1, 43.1, 35.8, 30.7, 27.7, 27.6, 26.2, 22.3, 14.0.

HRMS (ESI): m/z calcd for $[C_{23}H_{24}O_5 + Na]^+$ 403.1516; found: 403.1520



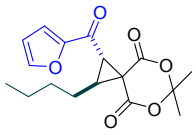
***trans*-1-(2-Naphthoyl)-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'q)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(naphthalen-2-yl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (s, 1H), 7.99 (d, J = 10.4 Hz, 1H), 7.93 (d, J = 8.2 Hz, 1H), 7.86 (dd, J = 15.5, 8.4 Hz, 2H), 7.56 (dt, J = 27.6, 7.3 Hz, 2H), 3.80 (d, J = 9.0 Hz, 1H), 3.01 – 2.92 (m, 1H), 1.93 (dq, J = 14.0, 7.0 Hz, 1H), 1.79 (d, J = 20.3 Hz, 7H), 1.53 (q, J = 7.9, 7.3 Hz, 2H), 1.43 (qd, J = 7.1, 2.3 Hz, 2H), 0.93 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 165.3, 164.9, 136.0, 133.5, 132.5, 130.2, 129.8, 129.0, 128.9, 128.0, 127.0, 123.7, 105.5, 43.8, 42.0, 36.0, 30.7, 27.7, 27.6, 26.2, 22.3, 14.0.

HRMS (ESI): m/z calcd for $[C_{23}H_{24}O_5 + Na]^+$ 403.1516; found: 403.1519



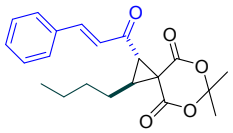
***trans*-1-Butyl-2-(furan-2-carbonyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'r)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 2-(dimethyl(oxo)-λ^6-sulfaneylidene)-1-(furan-2-yl)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (94%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.18 (d, J = 3.7 Hz, 1H), 6.51 (dd, J = 3.7, 1.7 Hz, 1H), 3.47 (d, J = 9.2 Hz, 1H), 2.84 (td, J = 8.7, 6.1 Hz, 1H), 1.85 – 1.66 (m, 8H), 1.48 – 1.40 (m, 2H), 1.36 (pd, J = 7.1, 2.5 Hz, 2H), 0.87 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 165.5, 164.7, 152.3, 147.0, 118.0, 112.7, 105.4, 43.5, 41.1, 35.2, 30.7, 27.6, 25.9, 22.2, 13.9.

HRMS (ESI): m/z calcd for $[C_{17}H_{20}O_6 + Na]^+$ 343.1152; found: 343.1152



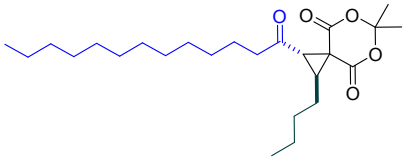
***trans*-1-Butyl-2-cinnamoyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c's)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylbut-3-en-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 3H), 7.40 (dd, J = 5.1, 2.0 Hz, 3H), 6.81 (d, J = 16.2 Hz, 1H), 3.40 (d, J = 9.2 Hz, 1H), 2.86 (td, J = 8.8, 6.1 Hz, 1H), 1.90 – 1.80 (m, 7H), 1.79 – 1.71 (m, 1H), 1.49 (p, J = 7.3 Hz, 2H), 1.45 – 1.36 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.8, 165.6, 165.1, 144.8, 134.2, 131.2, 129.2, 128.8, 125.9, 105.5, 45.1, 41.9, 35.5, 30.9, 27.8, 27.8, 26.2, 22.4, 14.1.

HRMS (ESI): m/z calcd for $[C_{21}H_{24}O_5 + Na]^+$ 379.1516; found: 379.1524

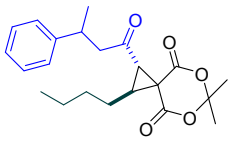


***trans*-1-Butyl-6,6-dimethyl-2-tridecanoyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c't)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and tridecanal (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (93%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 2.99 (d, J = 9.2 Hz, 1H), 2.66 (td, J = 8.9, 5.8 Hz, 1H), 2.52 (dt, J = 17.5, 7.4 Hz, 1H), 2.41 (dt, J = 17.5, 7.4 Hz, 1H), 1.78 – 1.69 (m, 7H), 1.62 (dt, J = 13.6, 7.0 Hz, 1H), 1.44 – 1.27 (m, 5H), 1.21 (d, J = 13.2 Hz, 18H), 0.84 (dt, J = 18.6, 7.2 Hz, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 201.7, 166.0, 164.8, 105.4, 46.4, 42.7, 41.9, 34.9, 32.0, 30.8, 29.7, 29.5, 29.5, 29.4, 29.1, 27.7, 27.6, 26.0, 23.4, 22.8, 22.3, 14.2, 14.0.



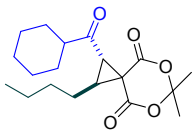
***trans*-1-Butyl-6,6-dimethyl-2-(3-phenylbutanoyl)-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'u)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-4-phenylpentan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (87%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.10 (m, 5H), 3.50 (dd, J = 9.2, 5.7 Hz, 1H), 3.00 (d, J = 9.2 Hz, 1H), 2.61 (td, J = 8.8, 5.8 Hz, 1H), 2.11 (td, J = 14.1, 13.7, 6.5 Hz, 1H), 1.92 – 1.68 (m, 7H), 1.68 – 1.56 (m, 1H), 1.45 (ddd, J = 15.6, 13.7, 7.4 Hz, 1H), 1.39 – 1.17 (m, 4H), 0.99 – 0.69 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 165.4, 165.1, 136.2, 133.6, 132.6, 130.4, 130.0, 129.1, 129.1, 128.1, 127.2, 123.9, 105.6, 43.9, 42.1, 36.1, 30.9, 27.8, 26.3, 22.4, 14.1.

HRMS (ESI): m/z calcd for $[C_{22}H_{28}O_5 + Na]^+$ 395.1829; found: 395.1827



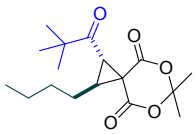
***trans*-1-Butyl-2-(cyclohexanecarbonyl)-6,6-dimethyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'v)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-cyclohexyl-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (89%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.11 (d, J = 9.3 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.41 (tt, J = 11.3, 3.5 Hz, 1H), 1.94 – 1.83 (m, 2H), 1.76 (t, J = 9.8 Hz, 9H), 1.68 – 1.57 (m, 2H), 1.43 – 1.11 (m, 9H), 0.87 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3, 166.0, 164.8, 105.3, 50.3, 45.0, 41.6, 35.0, 30.6, 28.2, 27.9, 27.6, 27.5, 25.9, 25.8, 25.6, 25.5, 22.1, 13.9.

HRMS (ESI): m/z calcd for $[C_{19}H_{28}O_5 + Na]^+$ 359.1829; found: 359.1832



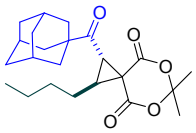
***trans*-1-Butyl-6,6-dimethyl-2-pivaloyl-5,7-dioxaspiro[2.5]octane-4,8-dione (5c'w)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-(dimethyl(oxo)-λ^6-sulfaneylidene)-3,3-dimethylbutan-2-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (95%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.21 (d, J = 9.1 Hz, 1H), 2.76 (td, J = 8.7, 6.1 Hz, 1H), 1.77 (d, J = 2.6 Hz, 7H), 1.66 – 1.54 (m, 1H), 1.43 – 1.28 (m, 4H), 1.14 (s, 9H), 0.86 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 206.2, 165.8, 164.9, 105.3, 44.8, 43.1, 41.1, 35.9, 30.7, 27.7, 27.6, 26.5, 26.0, 22.2, 14.0.

HRMS (ESI): m/z calcd for $[C_{17}H_{26}O_5 + Na]^+$ 333.1672; found: 333.1676



***trans*-1-(Adamantane-1-carbonyl)-2-butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]octan e-4,8-dione (5c'x)**

The title compound was prepared from pentanal (0.3mmol), 2,2-dimethyl-1,3-dioxane-4,6-dione (0.4 mmol) and 1-adamantan-1-yl)-2-(dimethyl(oxo)-λ^6-sulfaneylidene)ethan-1-one (0.2 mmol). The crude residue was purified by flash chromatography to give the product. (94%).

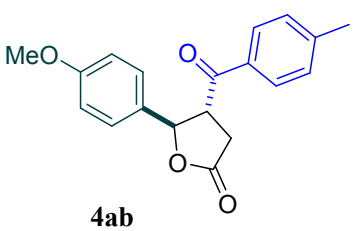
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.20 (d, J = 9.2 Hz, 1H), 2.73 (td, J = 8.8, 6.0 Hz, 1H), 1.98 (s, 3H), 1.86 – 1.54 (m, 20H), 1.43 – 1.25 (m, 4H), 0.84 (t, J = 7.2 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 205.6, 165.8, 164.9, 105.2, 46.9, 42.6, 40.8, 38.1, 36.5, 35.7, 30.6, 27.9, 27.6, 27.6, 25.9, 22.2, 13.9.

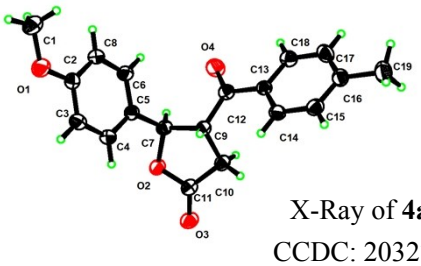
HRMS (ESI): m/z calcd for $[C_{23}H_{32}O_5 + Na]^+$ 411.2142; found: 411.2150

5. Structure Assignment of X-Ray Crystallographic Analysis

The single crystal of **4ab** and **5c'j** which were used for the determination of its relative configurations via X-ray crystallography (see below). The intensity data were collected using graphite- monochromated Mo Kα radiation.



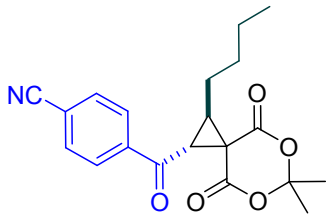
4ab



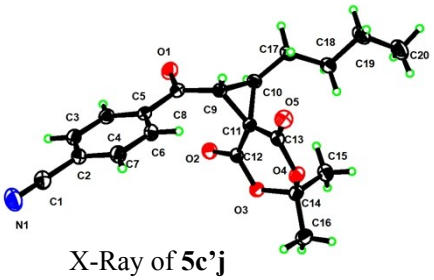
X-Ray of **4ab**

CCDC: 2032797

Identification code	**4ab**
Empirical formula	$C_{19}H_{18}O_4$
Formula weight	310.33
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	6.1019(5)
b/Å	24.438(2)
c/Å	10.8818(10)
α/°	90
β/°	103.537(3)
γ/°	90
Volume/Å^3	1577.6(2)
Z	4
ρcalcg/cm3	1.307
μ/mm-1	0.091
F(000)	656.0
Crystal size/mm^3	0.15 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.196 to 52.802
Index ranges	-7 ≤ h ≤ 7, -30 ≤ k ≤ 30, -13 ≤ l ≤ 13
Reflections collected	18064
Independent reflections	3236 [R_{int} = 0.0829, R_{sigma} = 0.0610]
Data/restraints/parameters	3236/0/210
Goodness-of-fit on F2	1.042
Final R indexes [I>=2σ (I)]	R1 = 0.0566, wR2 = 0.1175
Final R indexes [all data]	R1 = 0.1101, wR2 = 0.1514
Largest diff. peak/hole / e Å-3	0.17/-0.19



5c'j



X-Ray of **5c'j**
CCDC: 2032798

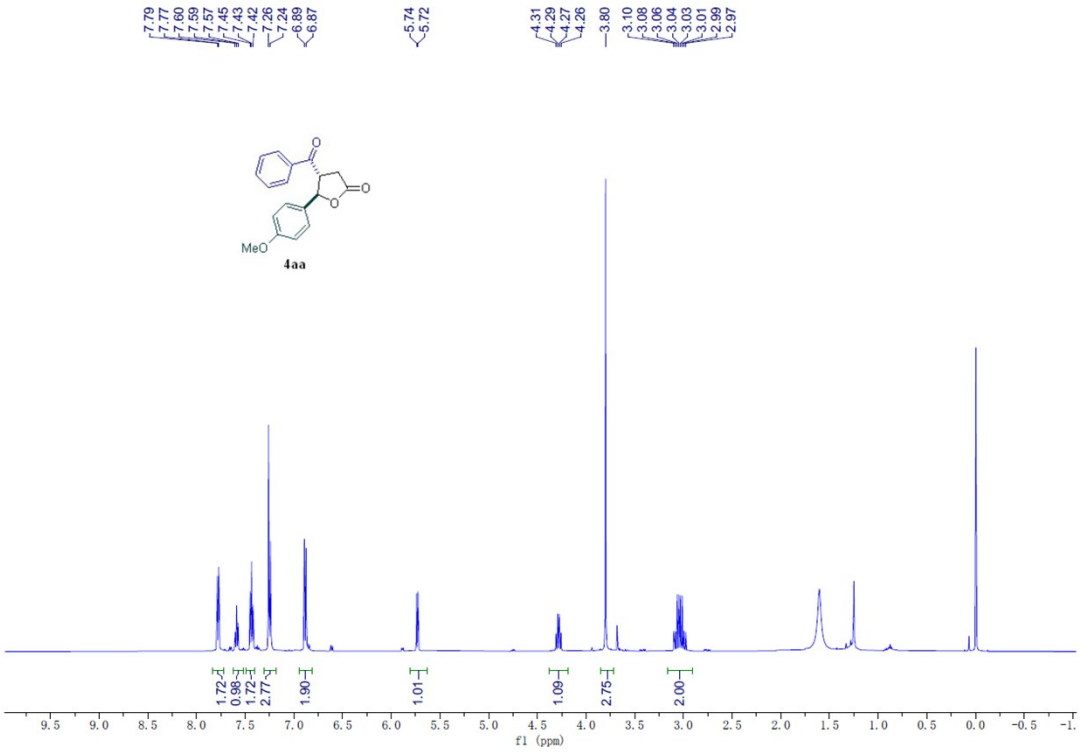
Identification code	**5c'j**
Empirical formula	$C_{20}H_{21}NO_5$
Formula weight	355.38
Temperature/K	170
Crystal system	triclinic
Space group	P-1
a/Å	10.4985(4)
b/Å	12.0839(5)
c/Å	15.4535(7)
α/°	74.6320(10)
β/°	74.3520(10)
γ/°	84.0530(10)
Volume/Å^3	1819.22(13)
Z	4
ρcalcg/cm3	1.298
μ/mm-1	0.093
F(000)	752.0
Crystal size/mm^3	0.19 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.914 to 52.994
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -19 ≤ l ≤ 19
Reflections collected	21041
Independent reflections	7441 [R_{int} = 0.0618, R_{sigma} = 0.0740]
Data/restraints/parameters	7441/0/475
Goodness-of-fit on F2	1.007
Final R indexes [I>=2σ (I)]	R_1 = 0.0500, wR_2 = 0.1103
Final R indexes [all data]	R_1 = 0.0991, wR_2 = 0.1433
Largest diff. peak/hole / e Å-3	0.21/-0.21

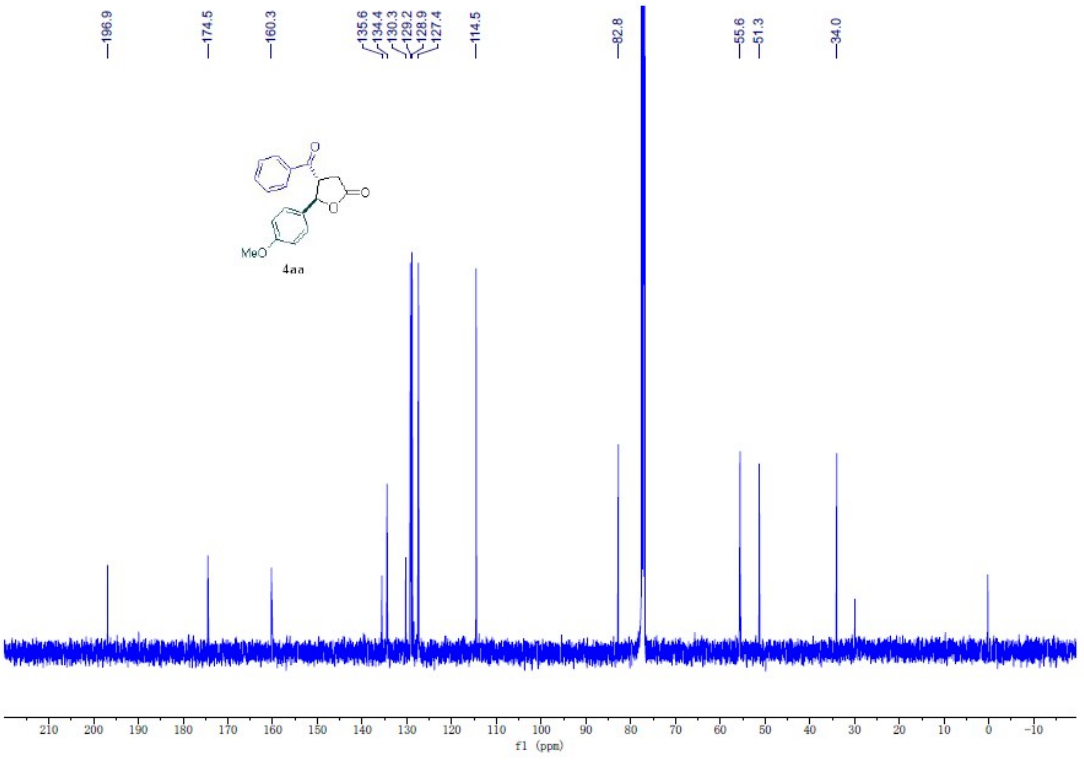
6. References

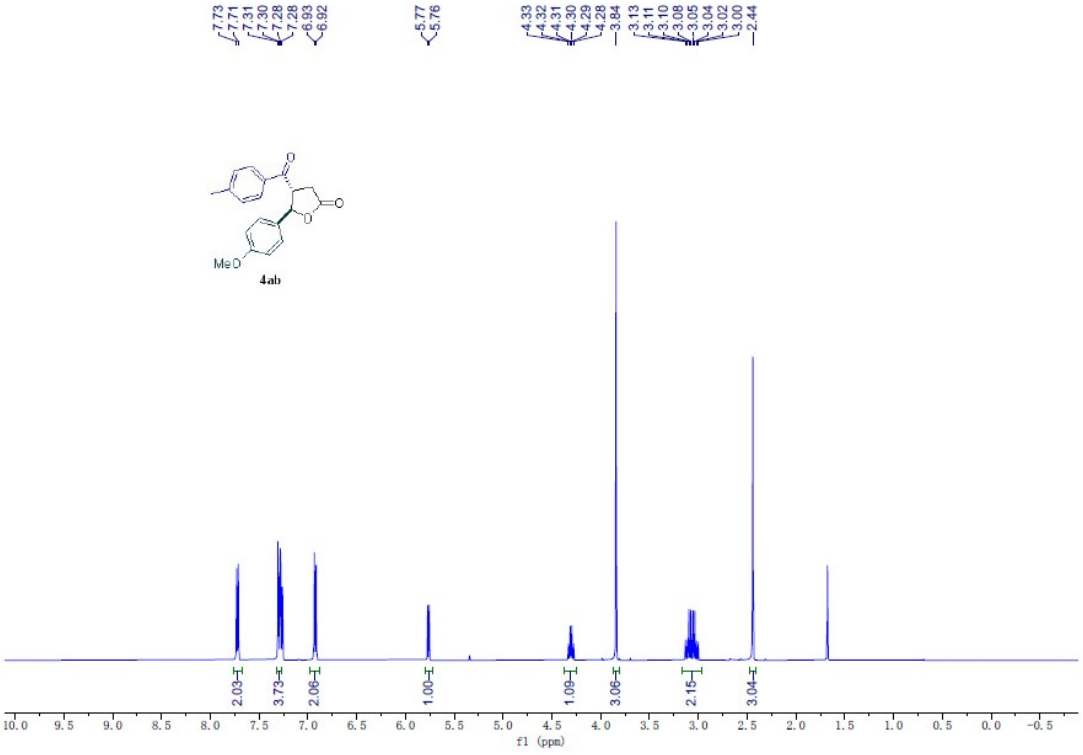
[1] D. C. G. Rafael, A. Anees, M. Gustavo, C. B. B. Antonio, α,α-Alkylation-Halogenation and Dihalogenation of Sulfoxonium Ylides. A Direct Preparation of Geminal Difunctionalized Ketones. *Chem. Eur. J.,* 2017, **23**, 16980-16984.

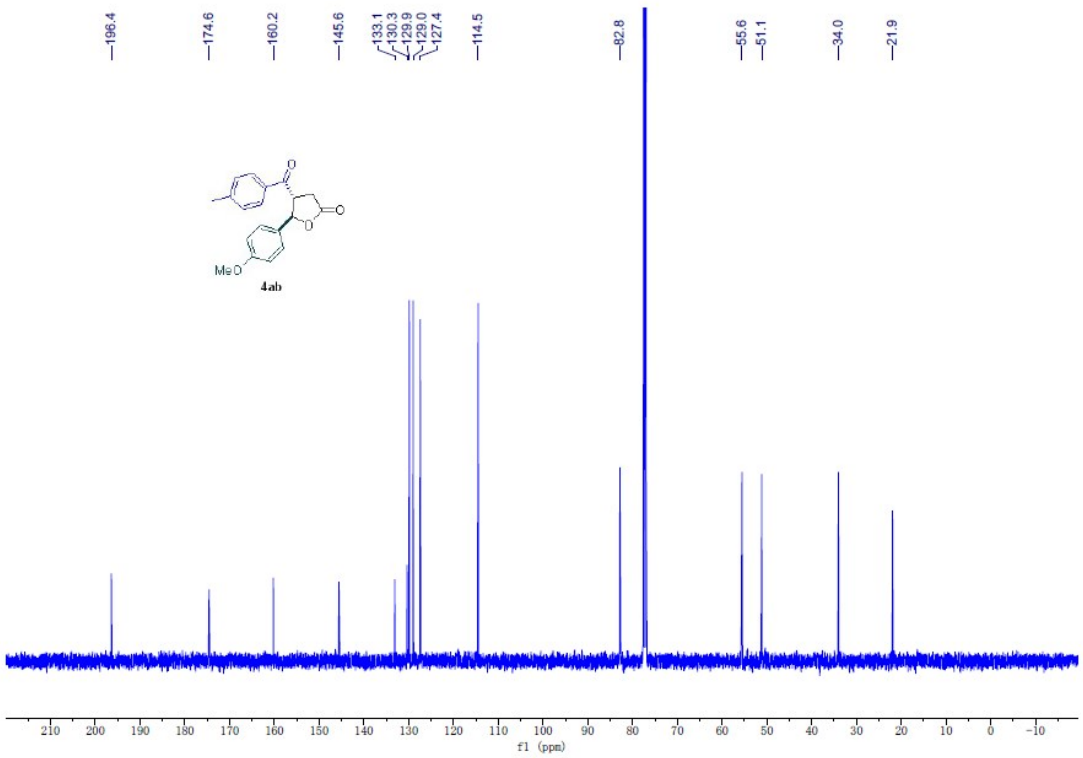
7. Copies of NMR Spectra for Compounds

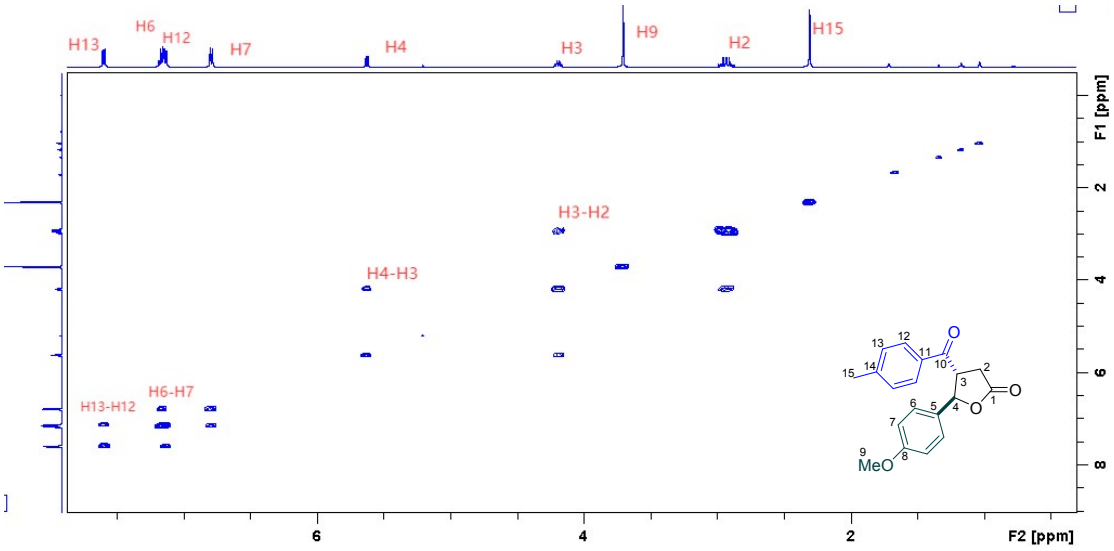
7.1. Copies of NMR Spectra for Compounds of 4aa-4au

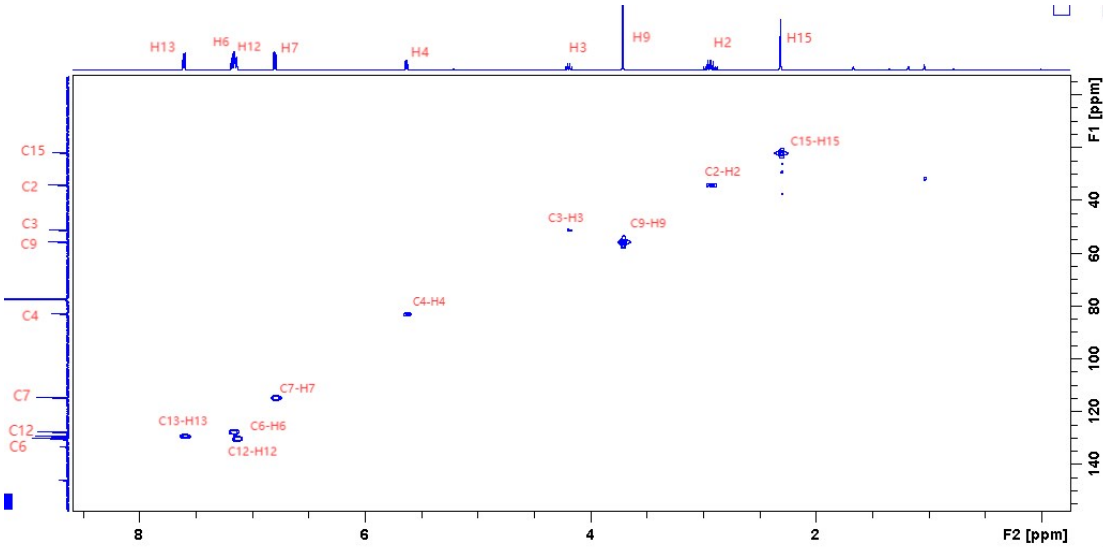


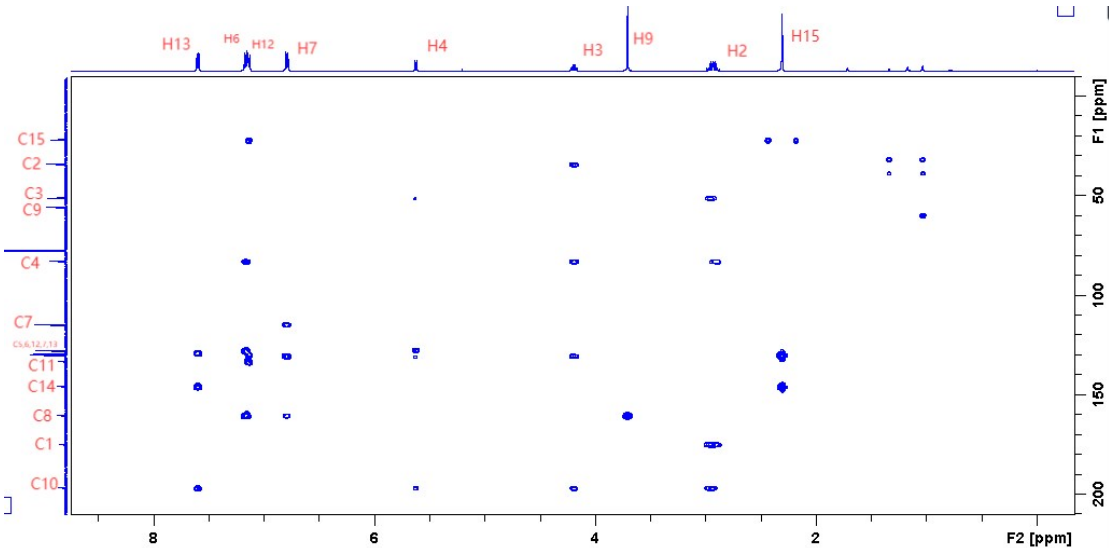


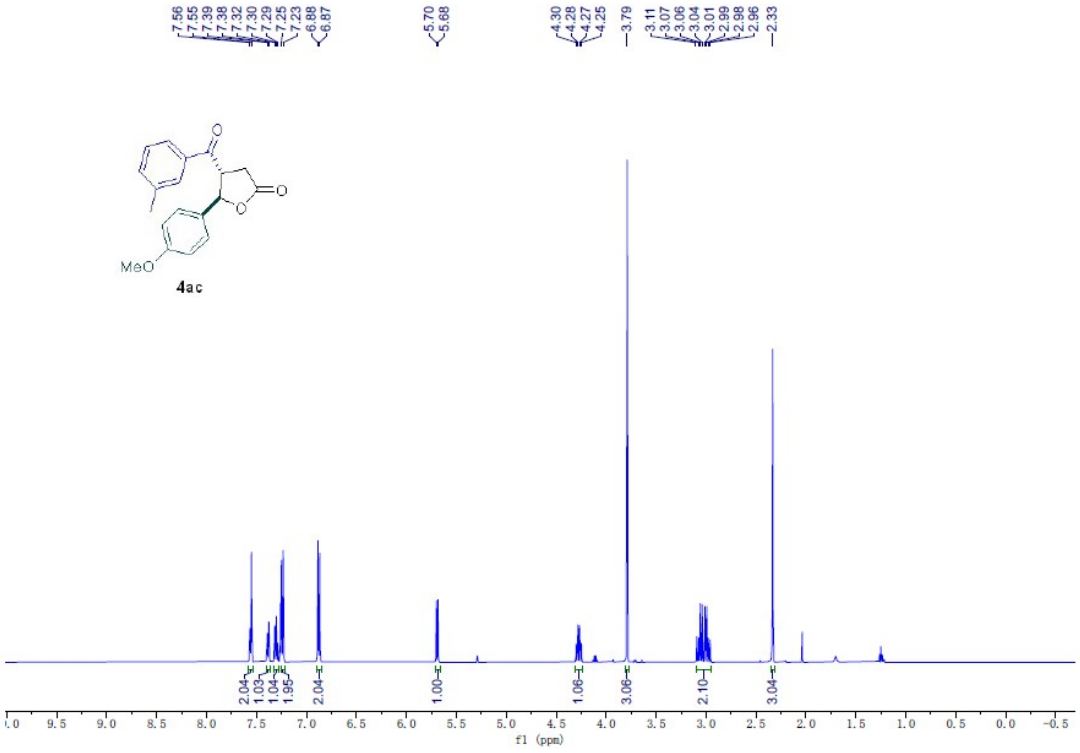

7.73
7.71
7.31
7.30
7.28
7.28
6.93
6.92
5.77
5.76
4.33
4.32
4.31
4.30
4.29
4.28
3.84
3.13
3.11
3.10
3.08
3.05
3.04
3.02
3.00
2.44
MeO
4ab
2.03
3.73
2.06
1.00
1.09
3.06
2.15
3.04
f1 (ppm)

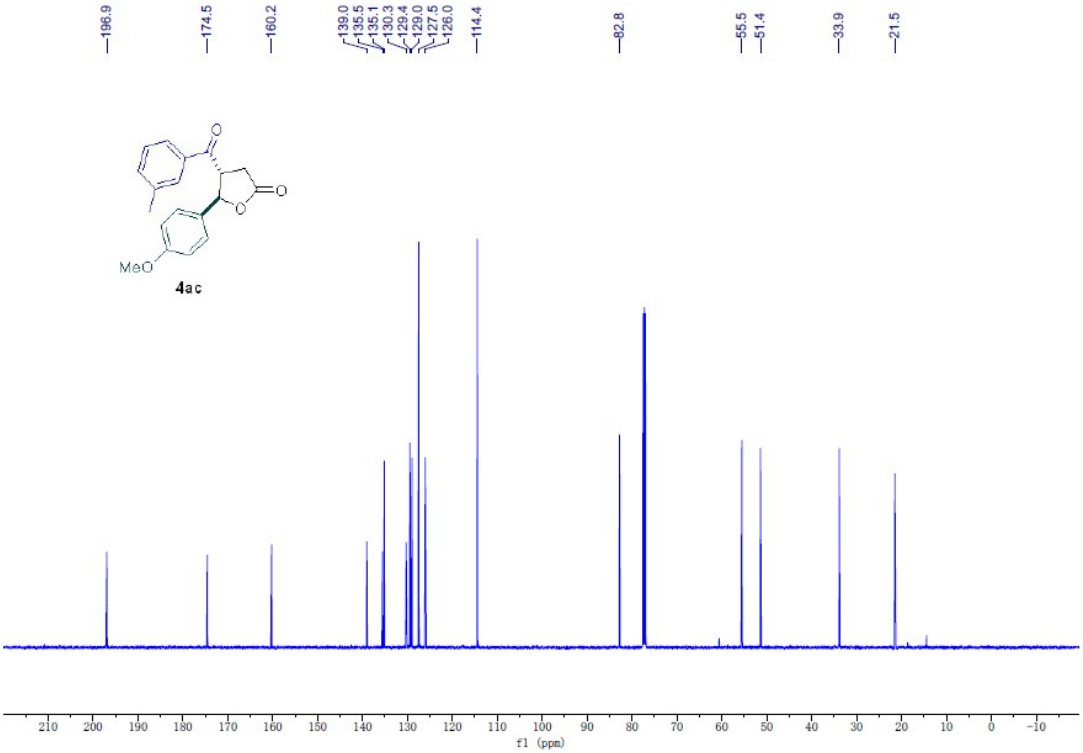

196.4
174.6
160.2
145.6
133.1
130.3
129.9
129.0
127.4
114.5
82.8
55.6
51.1
34.0
21.9
MeO
4ab
f1 (ppm)

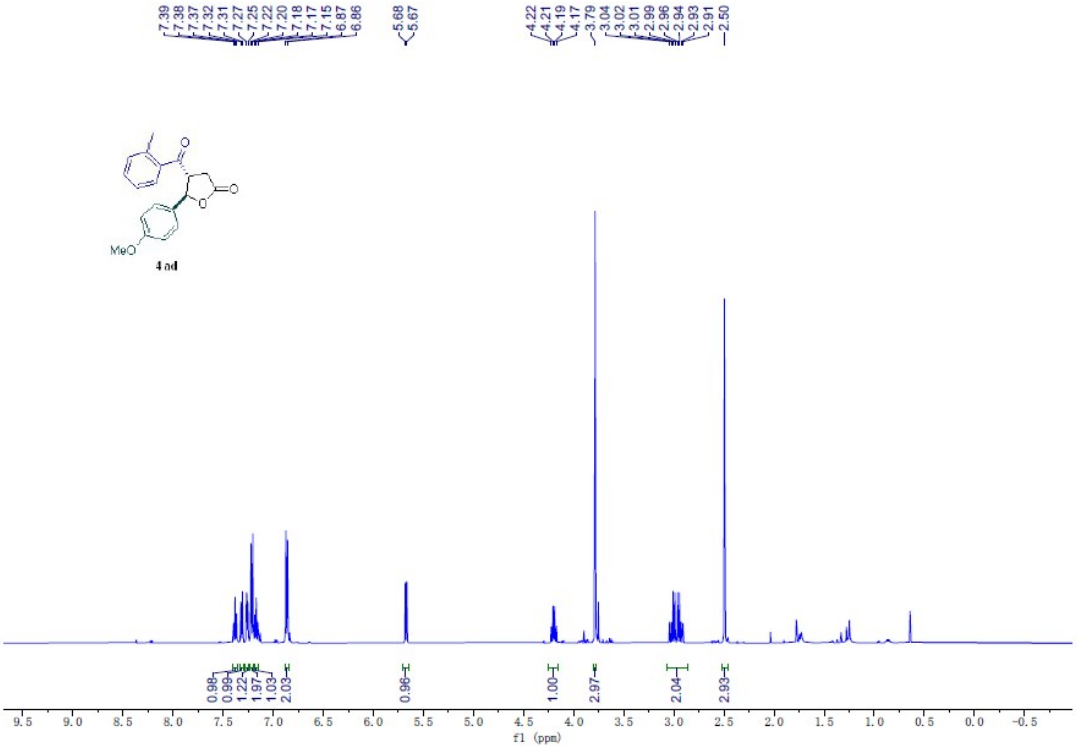

H13
H6
H12
H7
H4
H3
H9
H2
H15
H3-H2
H4-H3
H13-H12
H6-H7
F1 [ppm]
F2 [ppm]
MeO

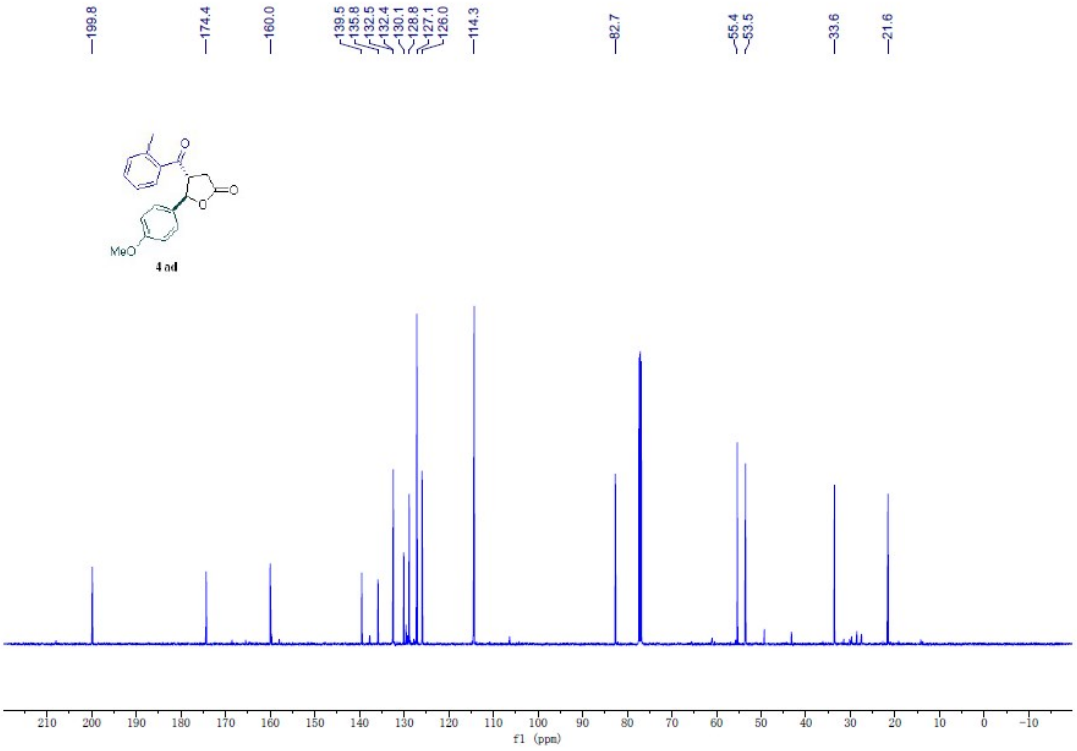

H13
H6
H12
H7
H4
H3
H9
H2
H15
C15-H15
C2-H2
C3-H3
C9-H9
C4-H4
C7-H7
C13-H13
C6-H6
C12-H12
C15
C2
C3
C9
C4
C7
C12
C6
F1 [ppm]
F2 [ppm]

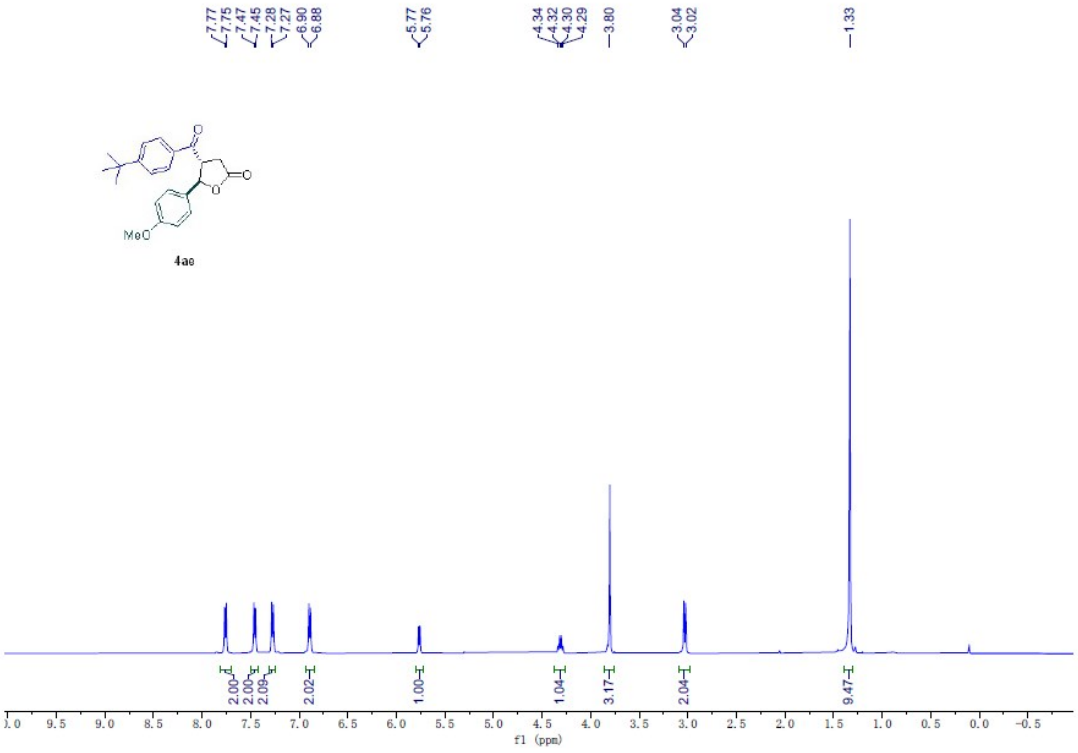

H13
H6
H12
H7
H4
H3
H9
H2
H15
C15
C2
C3
C9
C4
C7
C11
C14
C8
C1
C10
F1 [ppm]
F2 [ppm]

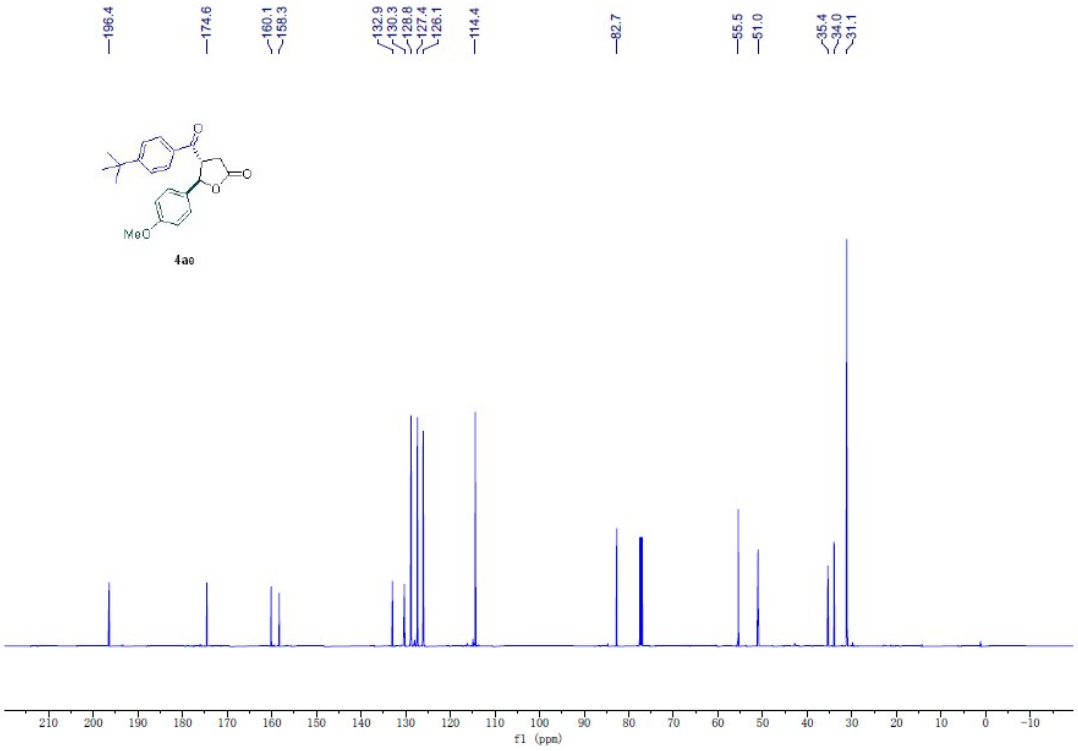

7.56
7.55
7.39
7.38
7.32
7.30
7.29
7.25
7.23
6.88
6.87
5.70
5.68
4.30
4.28
4.27
4.25
3.79
3.11
3.07
3.06
3.04
3.01
2.99
2.98
2.96
2.33
MeO
4ac
2.04
1.03
1.04
1.96
2.04
1.00
1.06
3.06
2.10
3.04
f1 (ppm)

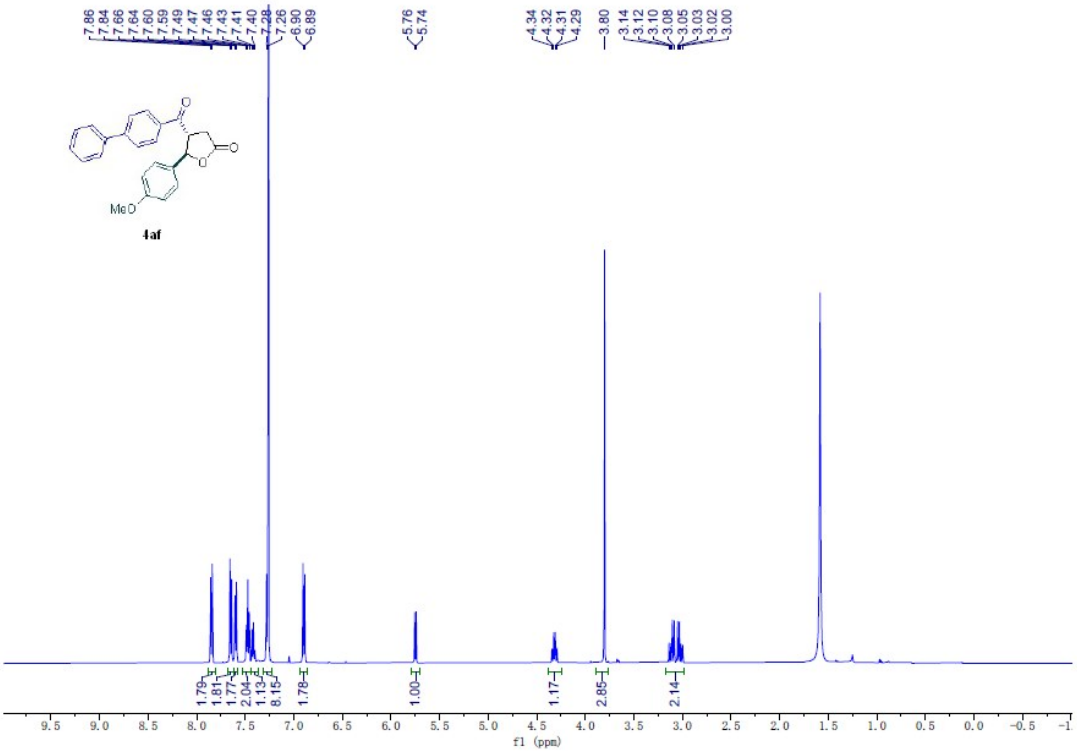

196.9
174.5
160.2
139.0
135.5
135.1
130.3
129.4
129.0
127.5
126.0
114.4
82.8
55.5
51.4
33.9
21.5
MeO
4ac
f1 (ppm)

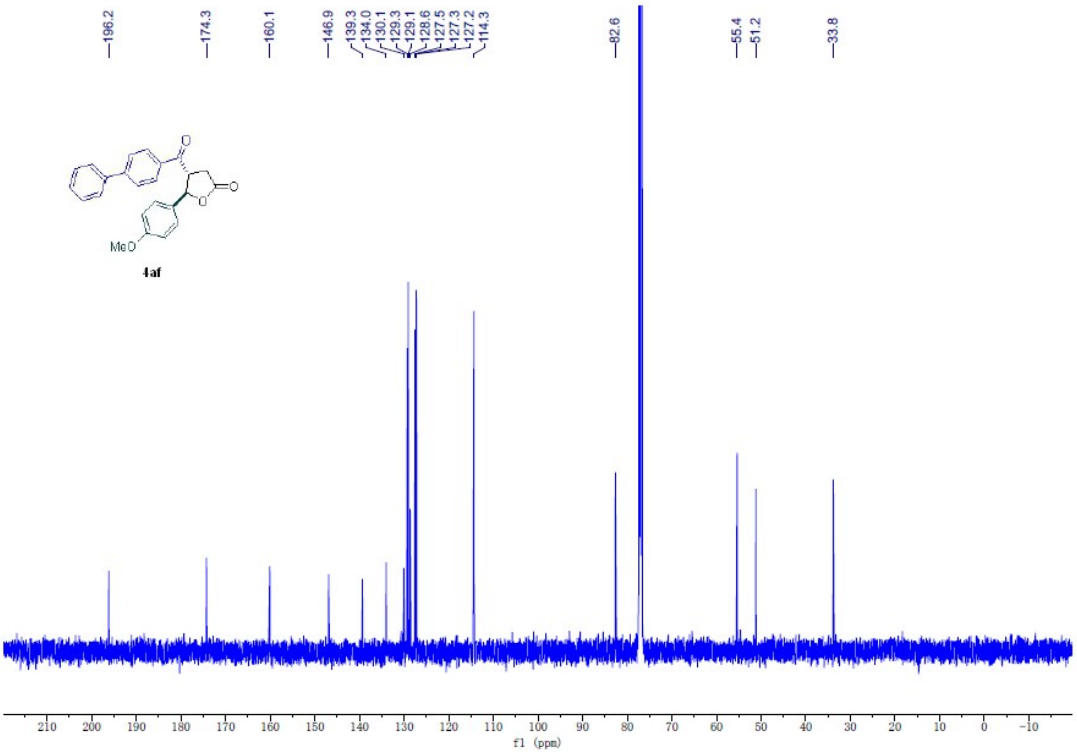

7.39
7.38
7.37
7.32
7.31
7.27
7.25
7.22
7.20
7.18
7.17
7.15
6.87
6.86
5.68
5.67
4.22
4.21
4.19
4.17
3.79
3.04
3.02
3.01
2.99
2.96
2.94
2.93
2.91
2.50
MeO
4 ad
0.98
0.99
1.22
1.97
1.03
2.03
0.96
1.00
2.97
2.04
2.93
f1 (ppm)

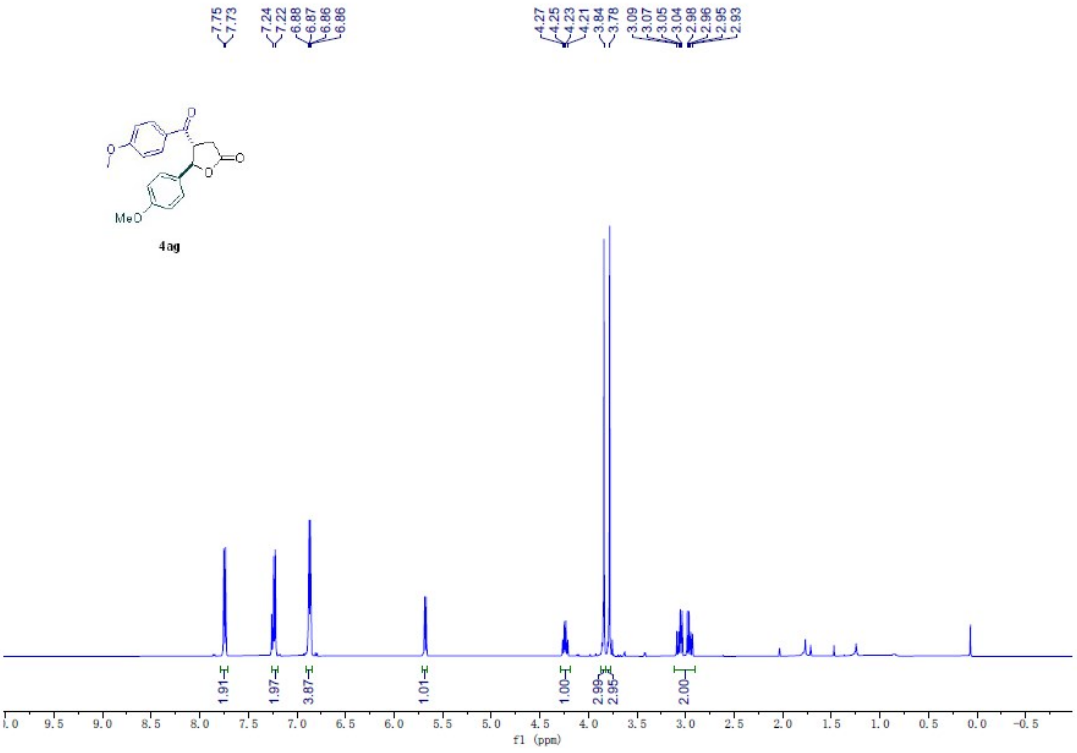

199.8
174.4
160.0
139.5
135.8
132.5
132.4
130.1
128.8
127.1
126.0
114.3
82.7
55.4
53.5
33.6
21.6
MeO
4 ad
f1 (ppm)

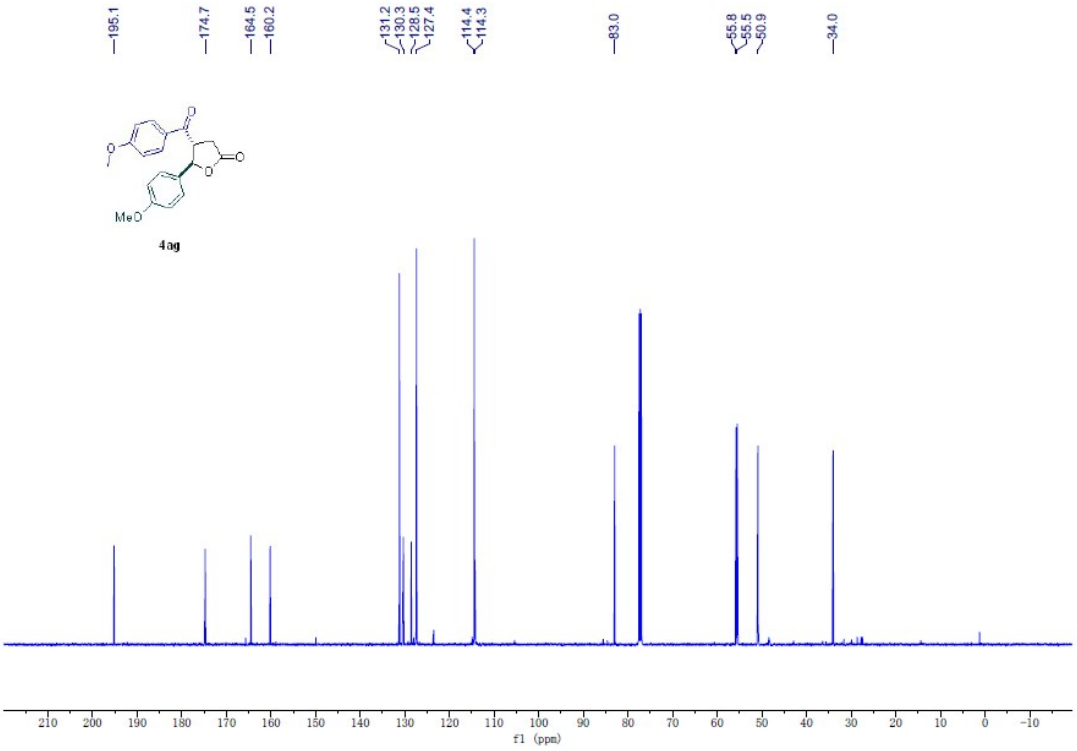

7.77
7.75
7.47
7.45
7.28
7.27
6.90
6.88
5.77
5.76
4.34
4.32
4.30
4.29
3.80
3.04
3.02
1.33
MeO
4ae
2.00
2.00
2.09
2.02
1.00
1.04
3.17
2.04
9.47
f1 (ppm)

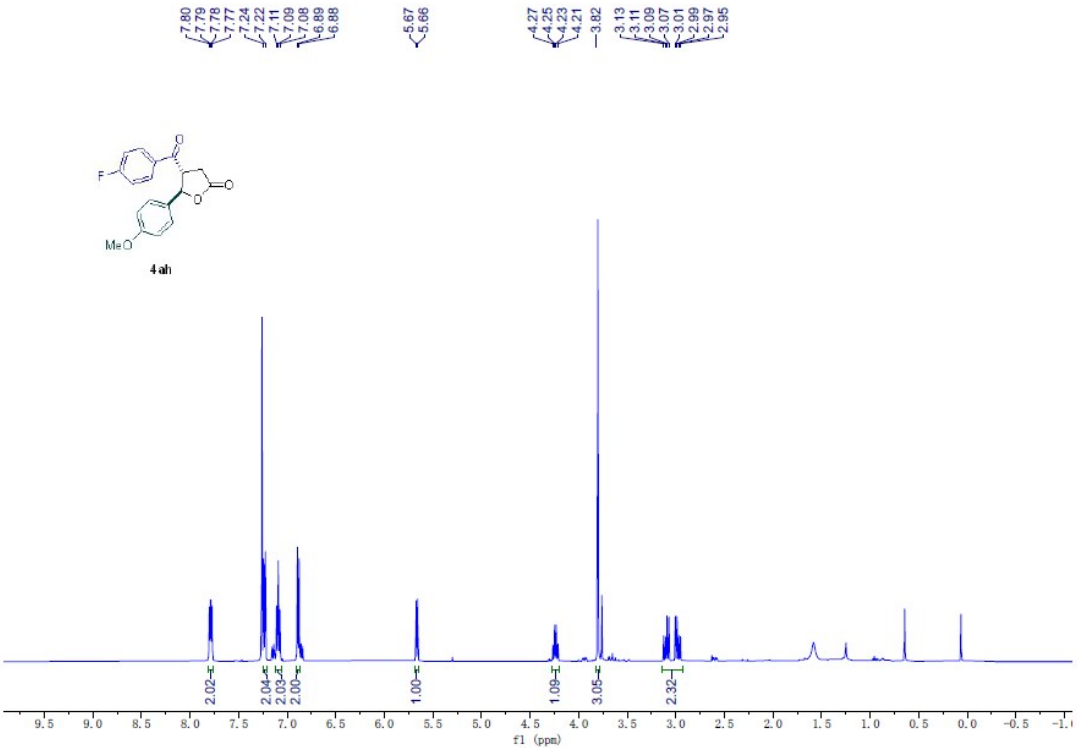

196.4
174.6
160.1
158.3
132.9
130.3
128.8
127.4
126.1
114.4
82.7
55.5
51.0
35.4
34.0
31.1
MeO
4ae
f1 (ppm)

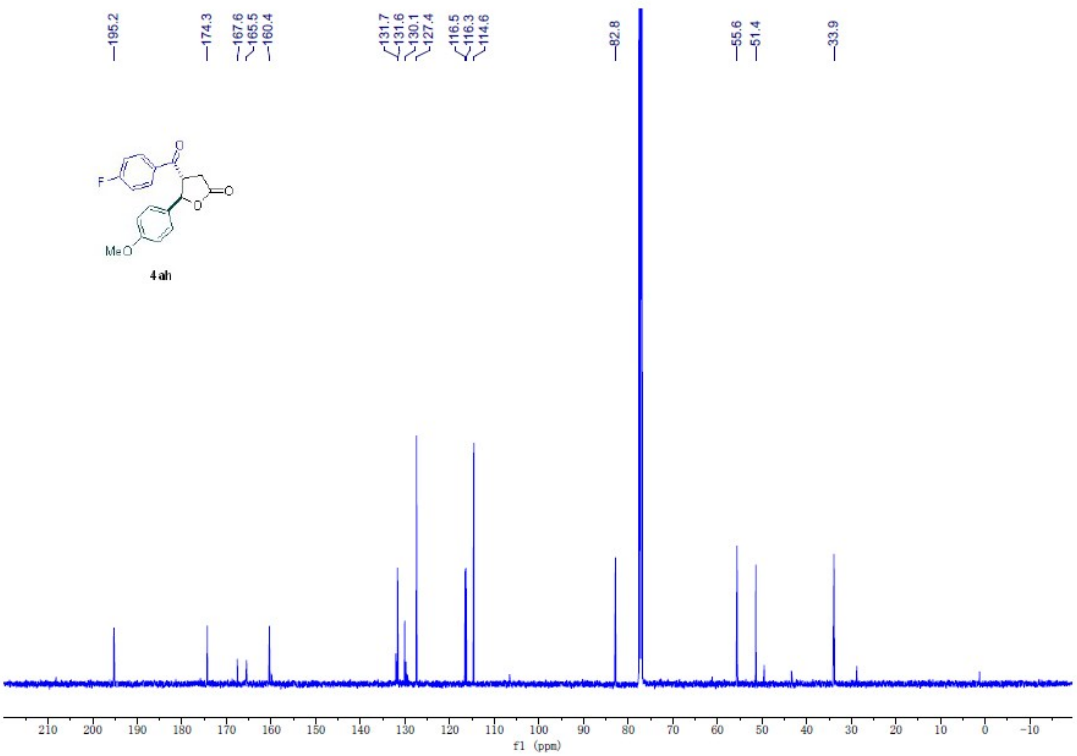

7.86
7.84
7.66
7.64
7.60
7.59
7.49
7.47
7.46
7.43
7.41
7.40
7.28
6.90
6.89
5.76
5.74
4.34
4.32
4.31
4.29
3.80
3.14
3.12
3.10
3.08
3.05
3.03
3.02
3.00
MeO
4af
1.79
1.81
1.77
2.04
1.13
8.15
1.78
1.00
1.17
2.85
2.14
f1 (ppm)

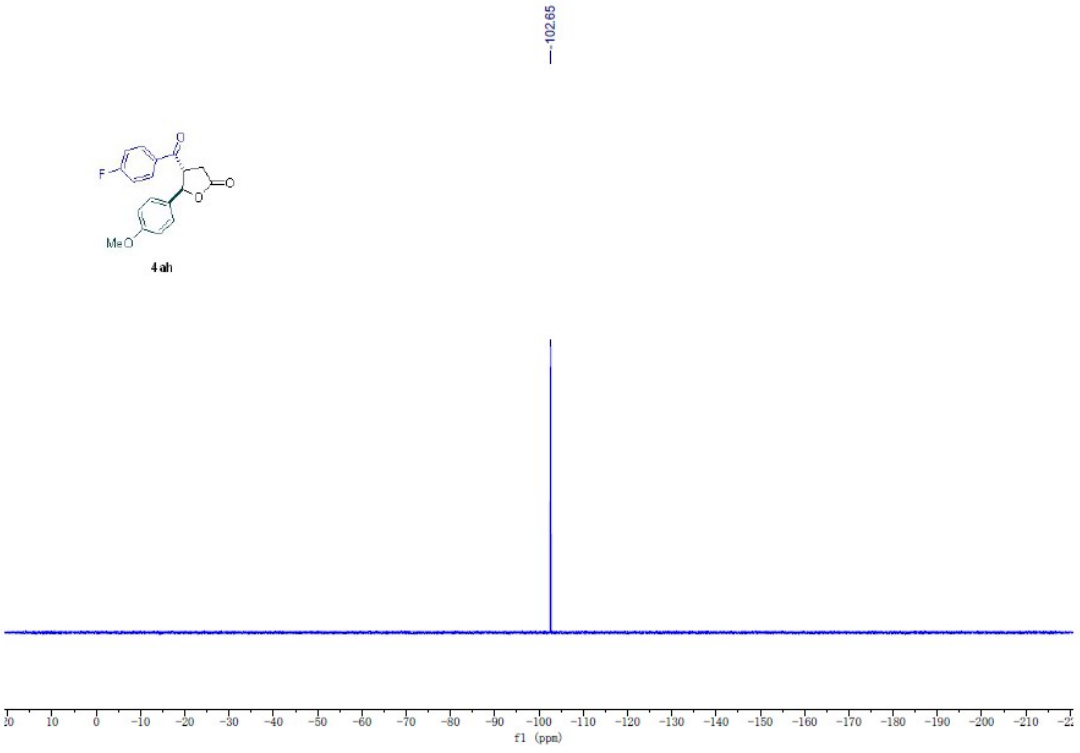

196.2
174.3
160.1
146.9
139.3
134.0
130.1
129.3
129.1
128.6
127.5
127.3
127.2
114.3
82.6
55.4
51.2
33.8
MeO
4af
f1 (ppm)

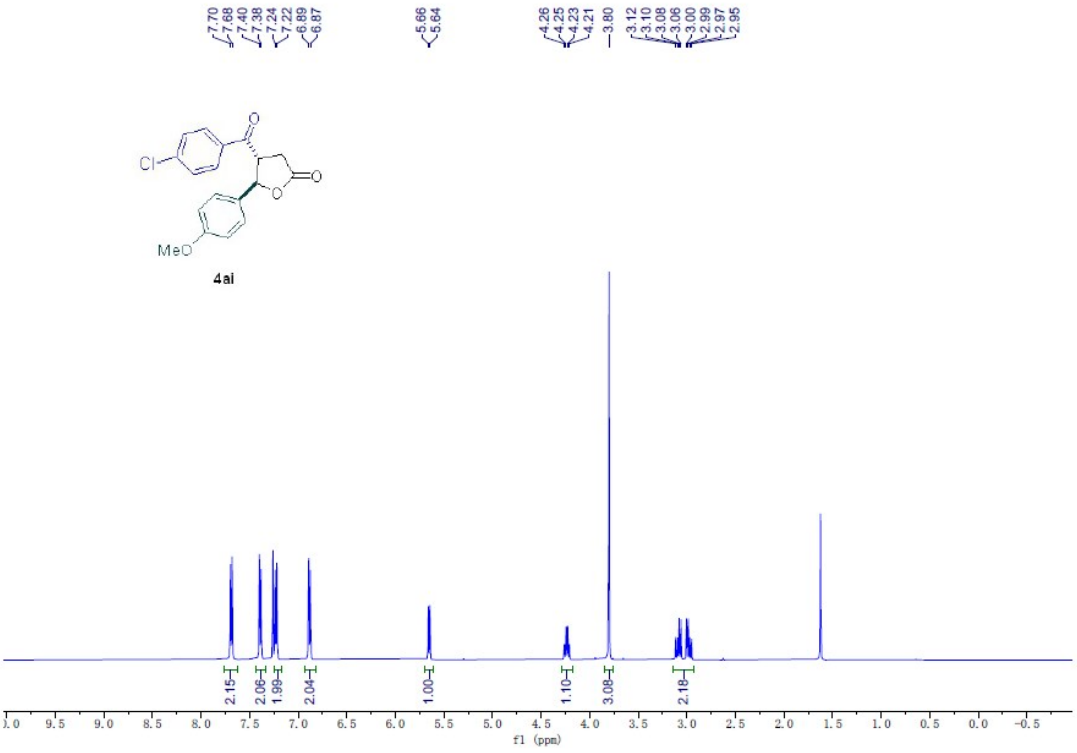

7.75
7.73
7.24
7.22
6.88
6.87
6.86
6.86
4.27
4.25
4.23
4.21
3.84
3.78
3.09
3.07
3.05
3.04
2.98
2.96
2.95
2.93
MeO
4ag
1.91
1.97
3.87
1.01
1.00
2.99
2.95
2.00
f1 (ppm)


195.1
174.7
164.5
160.2
131.2
130.3
128.5
127.4
114.4
114.3
83.0
55.8
55.5
50.9
34.0
MeO
4ag
f1 (ppm)

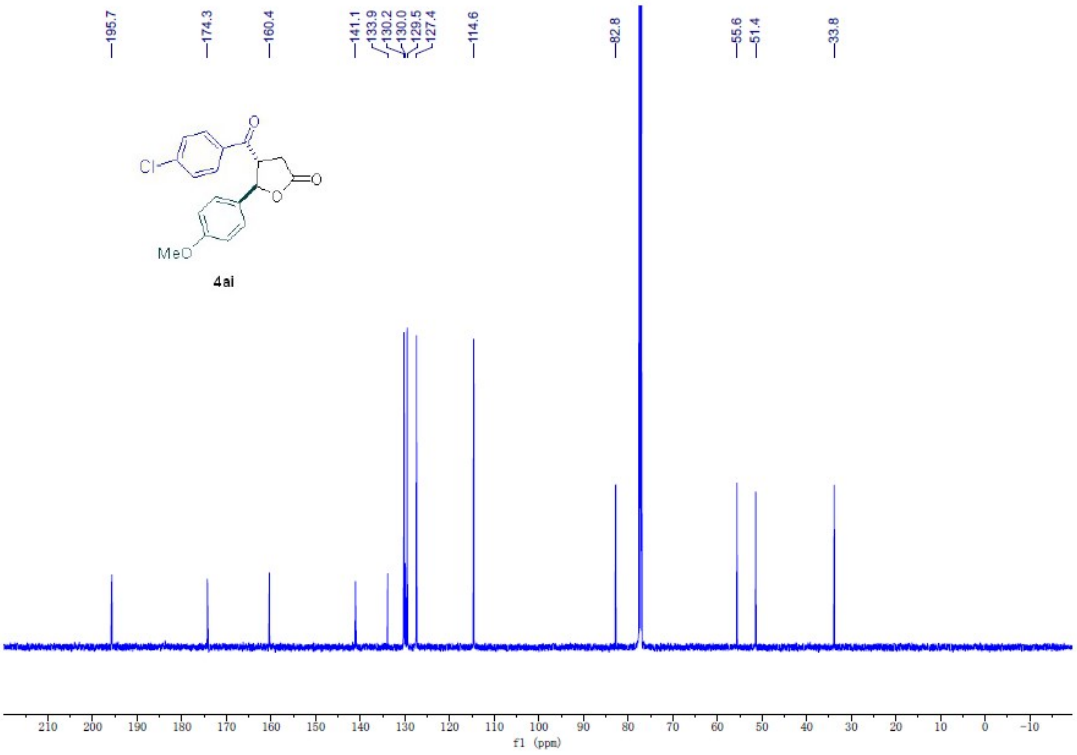

7.80
7.79
7.78
7.77
7.24
7.22
7.11
7.09
7.08
6.89
6.88
5.67
5.66
4.27
4.25
4.23
4.21
3.82
3.13
3.11
3.09
3.07
3.01
2.99
2.97
2.95
F
O
O
MeO
4ah
2.02
2.04
2.03
2.00
1.00
1.09
3.05
2.32
f1 (ppm)


195.2
174.3
167.6
165.5
160.4
131.7
131.6
130.1
127.4
116.5
116.3
114.6
82.8
55.6
51.4
33.9
F
O
O
MeO
4ah
f1 (ppm)

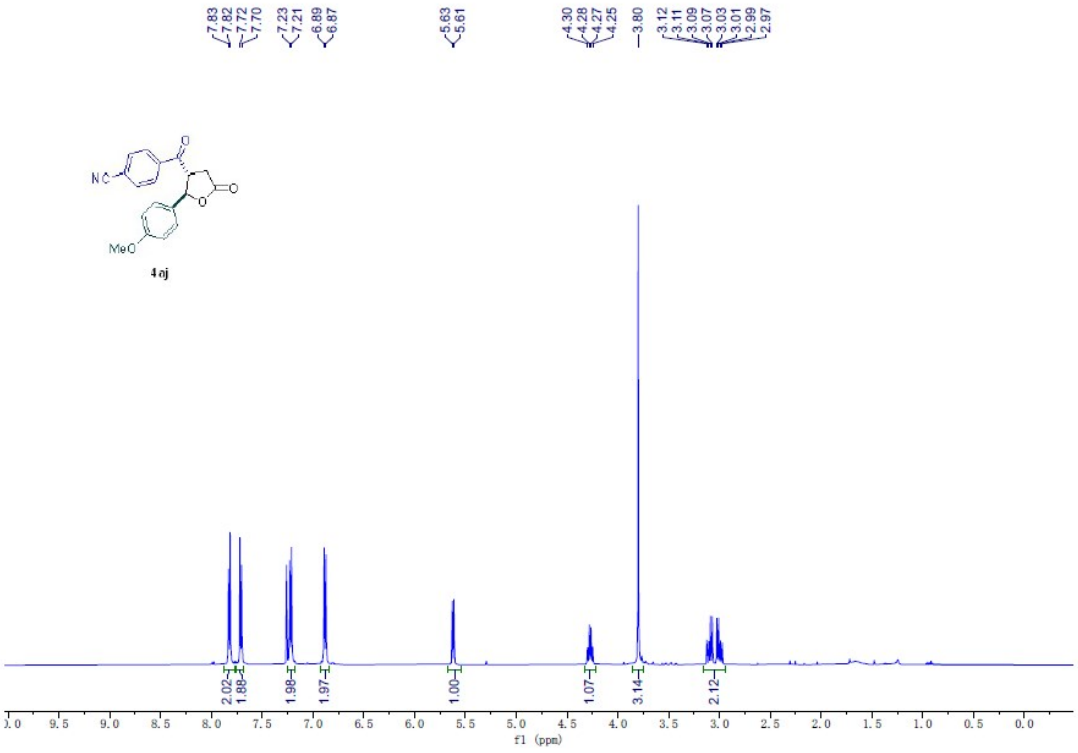

-102.65
F
O
O
O
MeO
4ah
f1 (ppm)

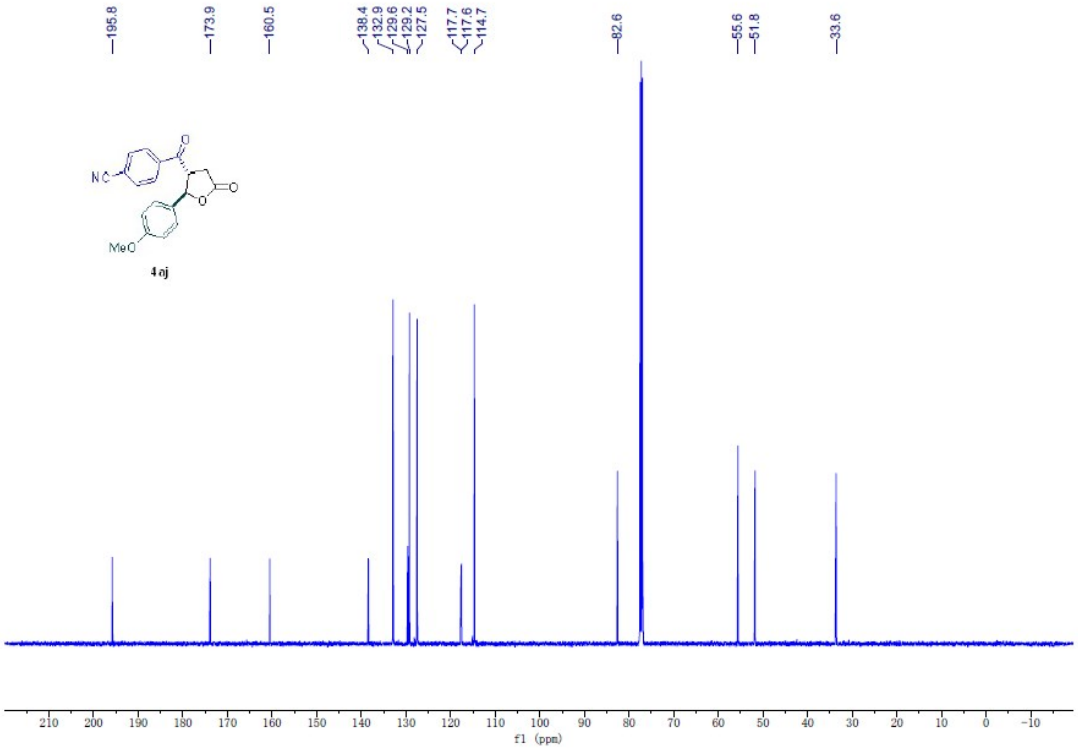

7.70
7.68
7.40
7.38
7.24
7.22
6.89
6.87
5.66
5.64
4.26
4.25
4.23
4.21
3.80
3.12
3.10
3.08
3.06
3.00
2.99
2.97
2.95
Cl
O
O
O
MeO
2.15
2.06
1.99
2.04
1.00
1.10
3.08
2.18
f1 (ppm)

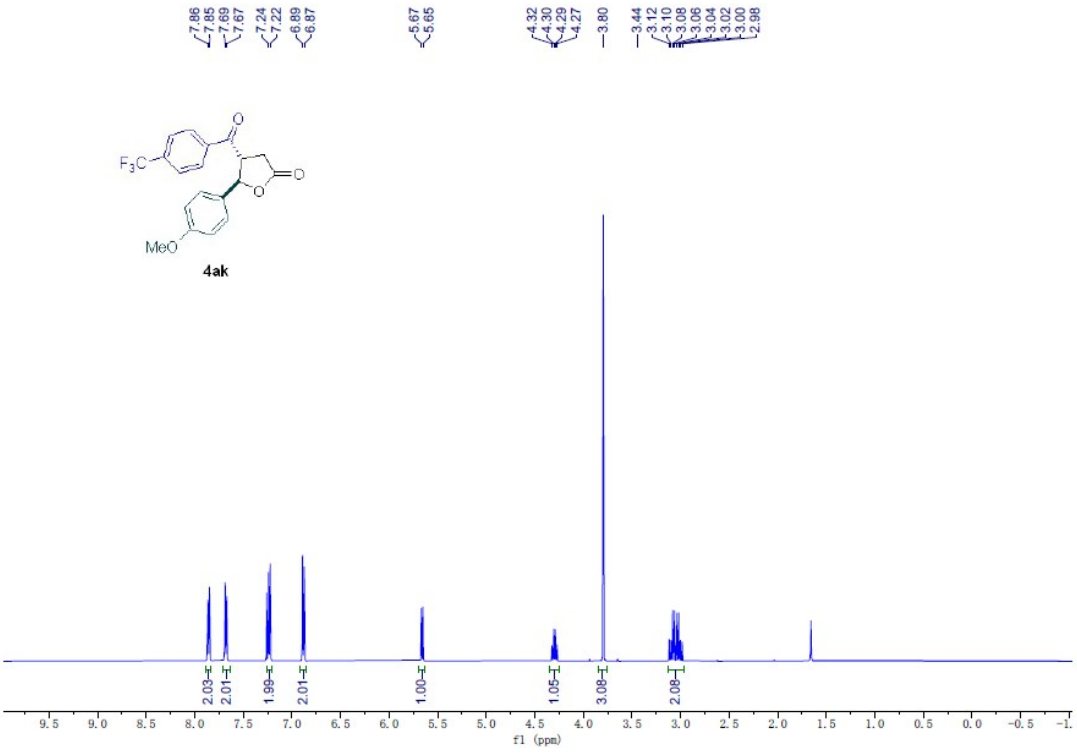
4ai

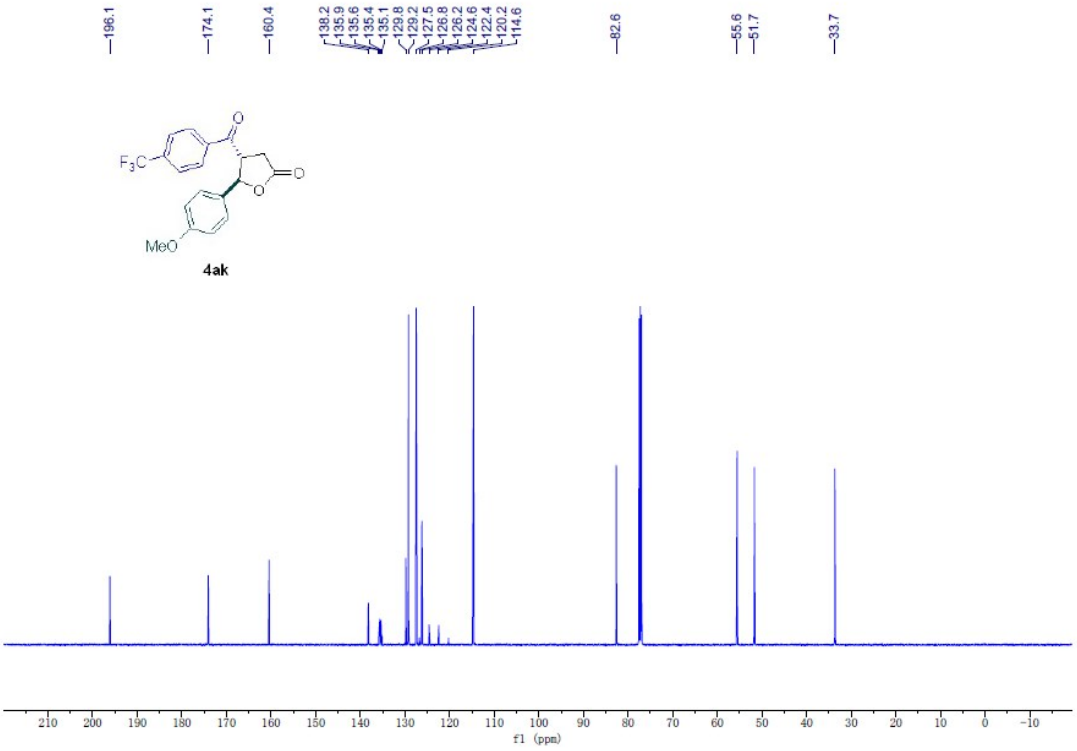

195.7
174.3
160.4
141.1
133.9
130.2
130.0
129.5
127.4
114.6
82.8
55.6
51.4
33.8
Cl
O
O
O
MeO
f1 (ppm)

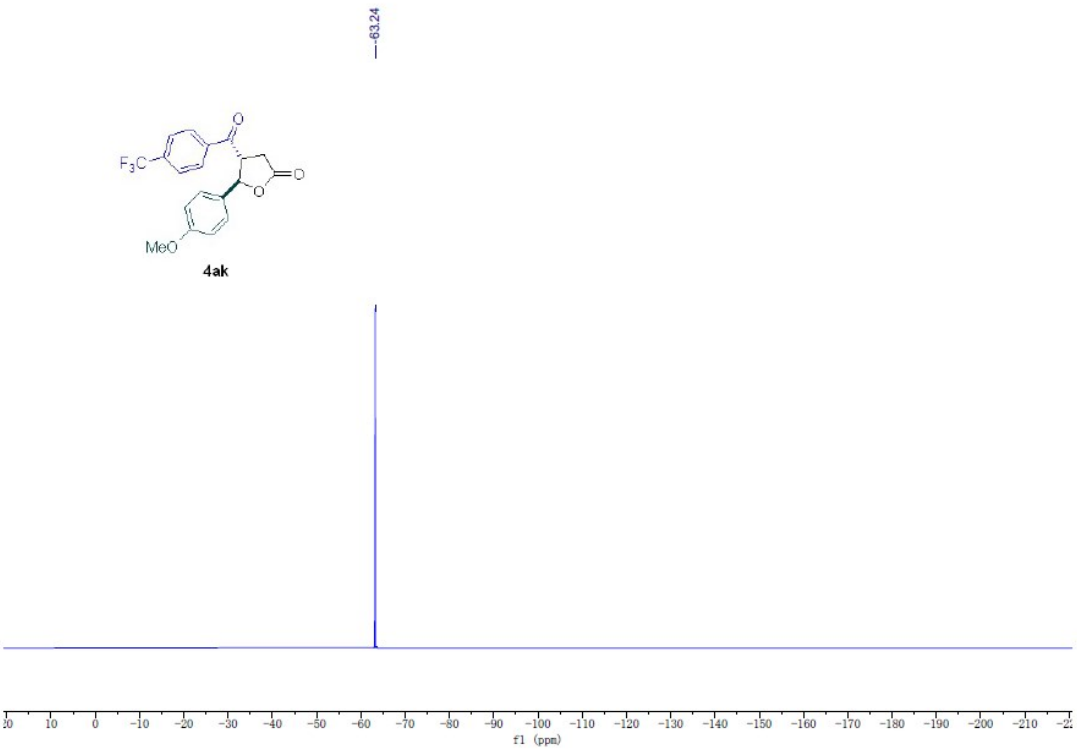
4ai

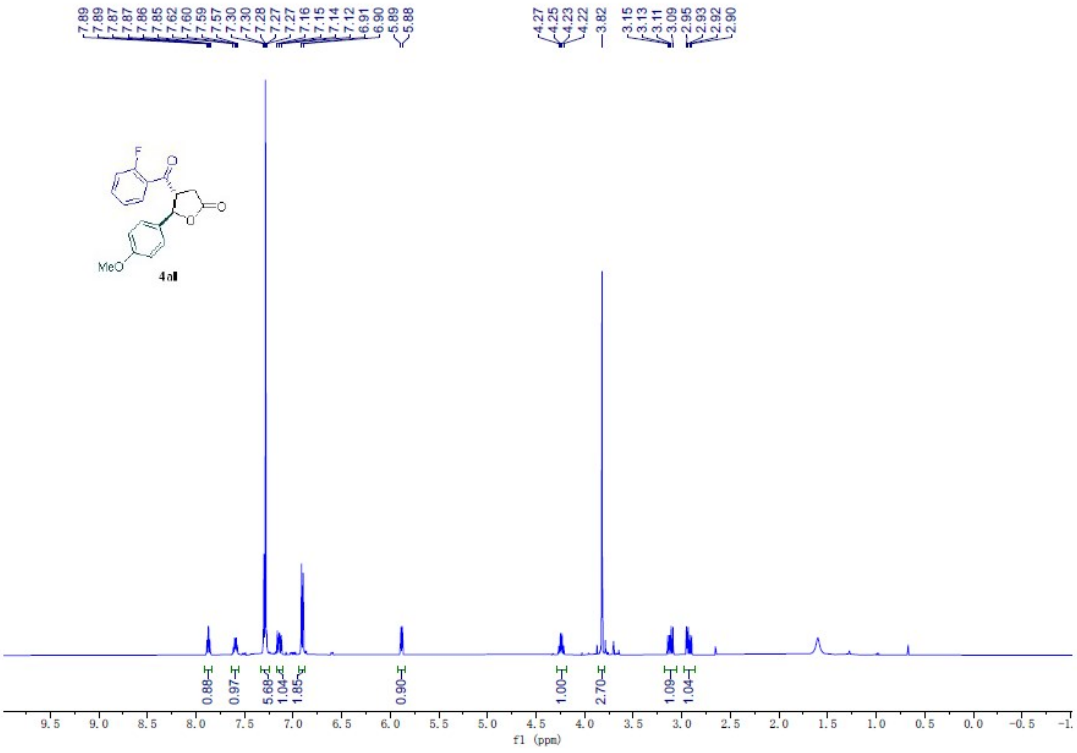

7.83
7.82
7.72
7.70
7.23
7.21
6.89
6.87
5.63
5.61
4.30
4.28
4.27
4.25
3.80
3.12
3.11
3.09
3.07
3.03
3.01
2.99
2.97
NC
O
O
O
MeO
4aj
2.02
1.88
1.98
1.97
1.00
1.07
3.14
2.12
f1 (ppm)

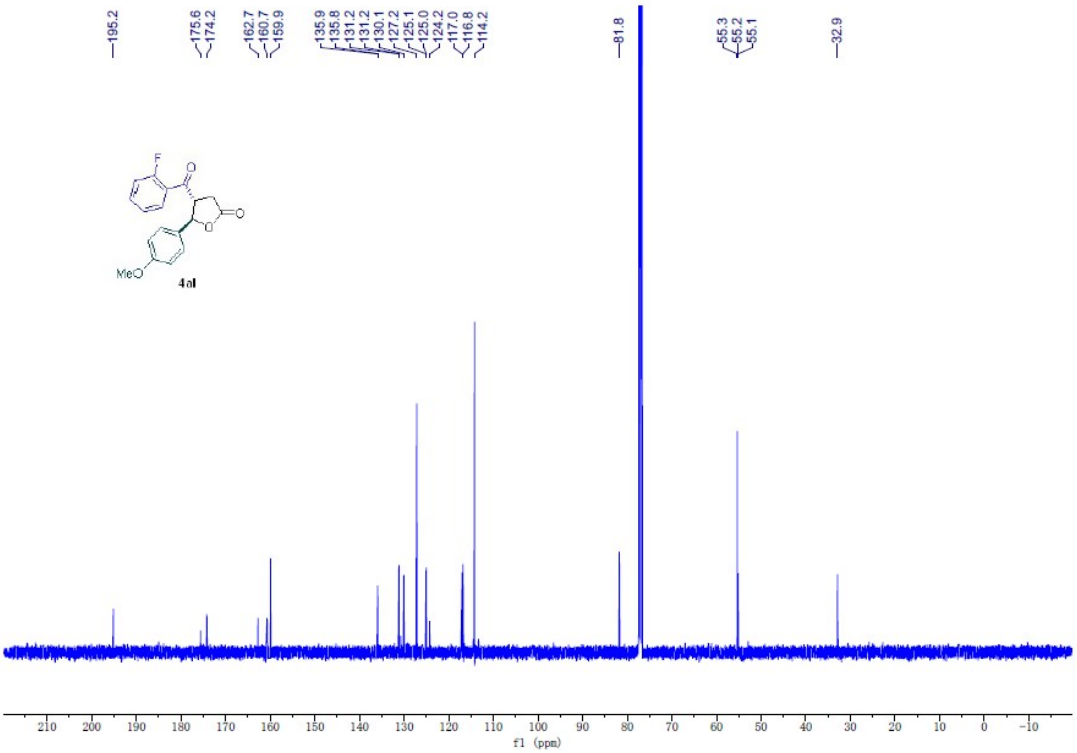

195.8
173.9
160.5
138.4
132.9
129.6
129.2
127.5
117.7
117.6
114.7
82.6
55.6
51.8
33.6
NC
O
O
O
MeO
4aj
f1 (ppm)

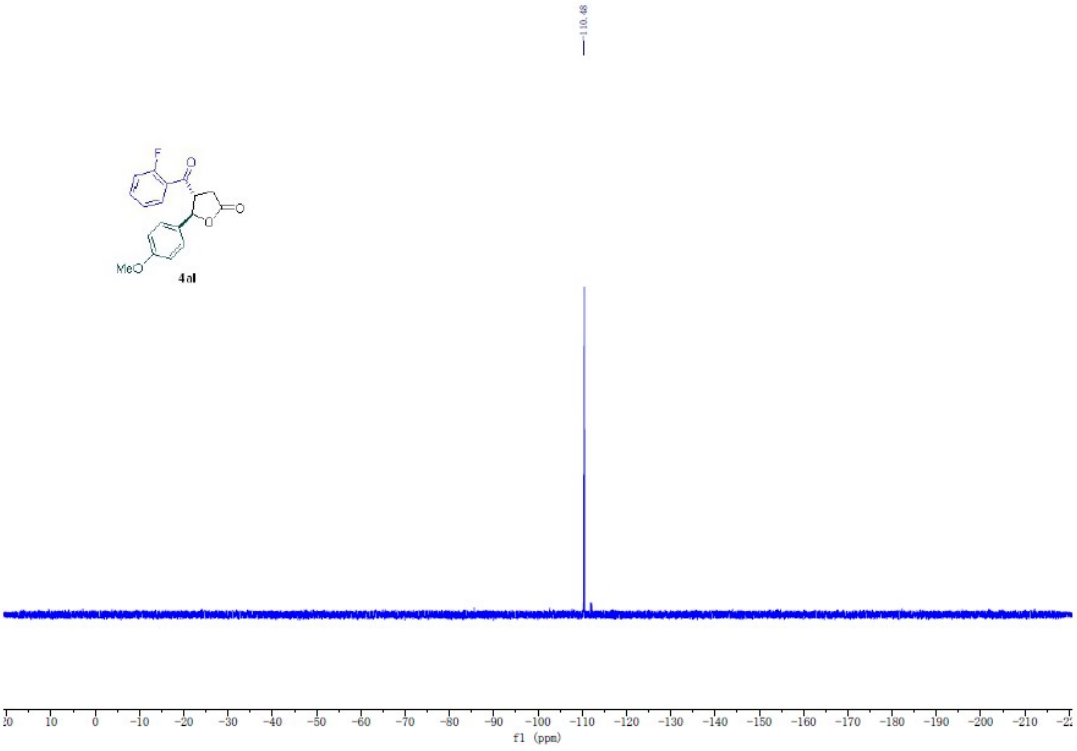

7.86
7.85
7.69
7.67
7.24
7.22
6.89
6.87
5.67
5.65
4.32
4.30
4.29
4.27
3.80
3.44
3.12
3.10
3.08
3.06
3.04
3.02
3.00
2.98
F3C
O
O
O
MeO
4ak
2.03
2.01
1.99
2.01
1.00
1.05
3.08
2.08
f1 (ppm)

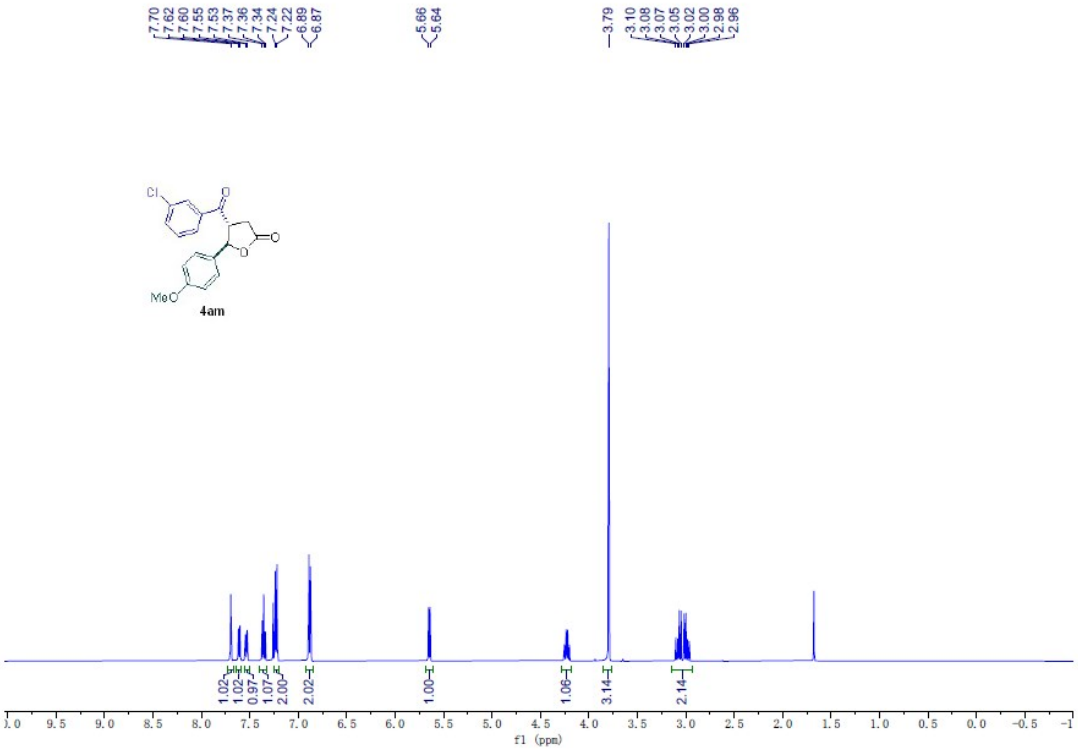

196.1
174.1
160.4
138.2
135.9
135.6
135.4
135.1
129.8
129.2
127.5
126.8
126.2
124.6
122.4
120.2
114.6
82.6
55.6
51.7
33.7
F3C
O
O
O
MeO
4ak
f1 (ppm)

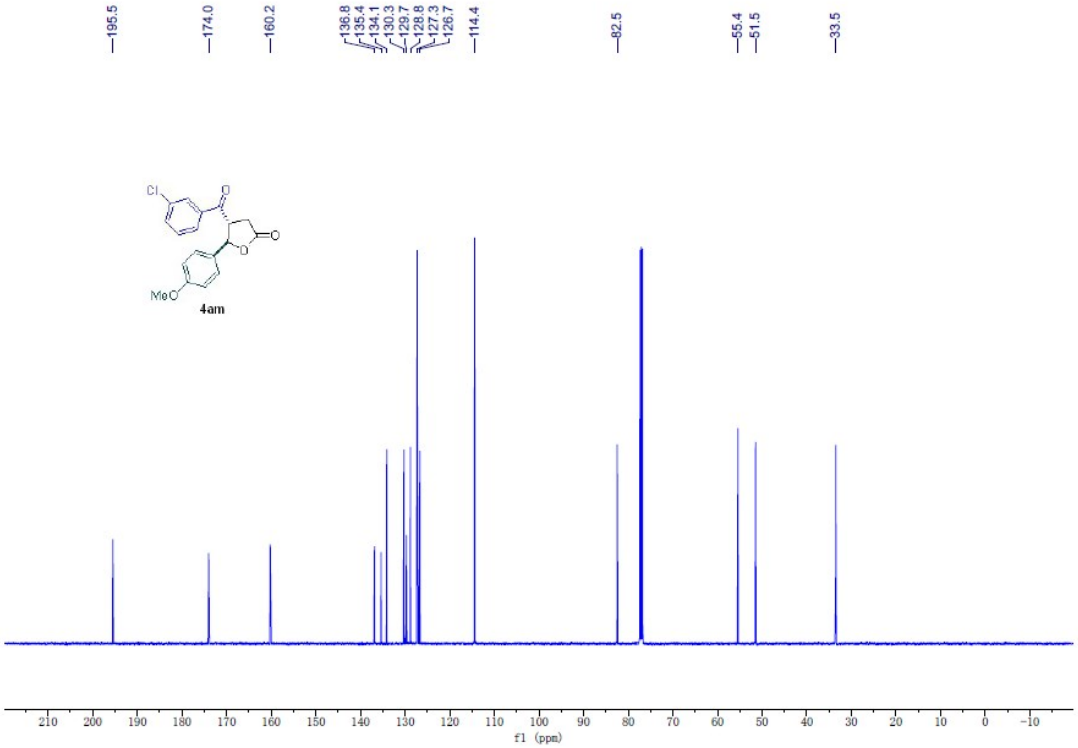

-63.24
F3C
O
O
O
MeO
4ak
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

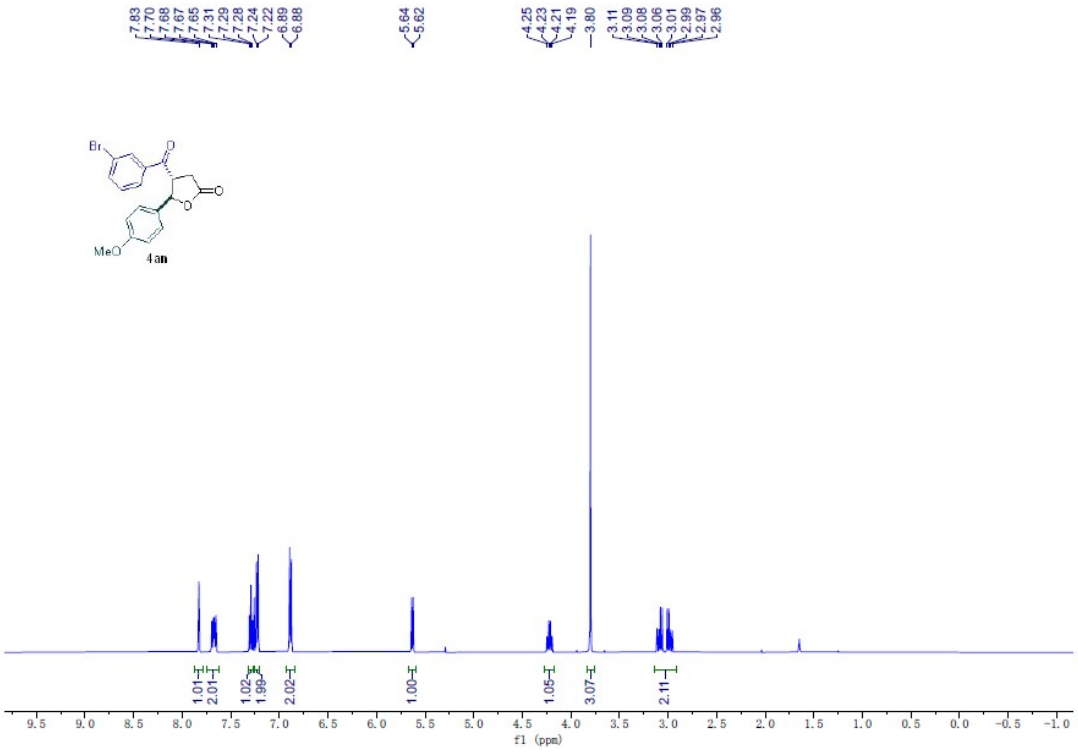

7.89
7.89
7.87
7.87
7.86
7.85
7.62
7.60
7.59
7.57
7.30
7.30
7.28
7.27
7.27
7.16
7.15
7.14
7.12
6.91
6.90
5.89
5.88
4.27
4.25
4.23
4.22
3.82
3.15
3.13
3.11
3.09
2.95
2.93
2.92
2.90
F
O
O
O
MeO
4al
0.88
0.97
5.68
1.04
1.85
0.90
1.00
2.70
1.09
1.04
f1 (ppm)

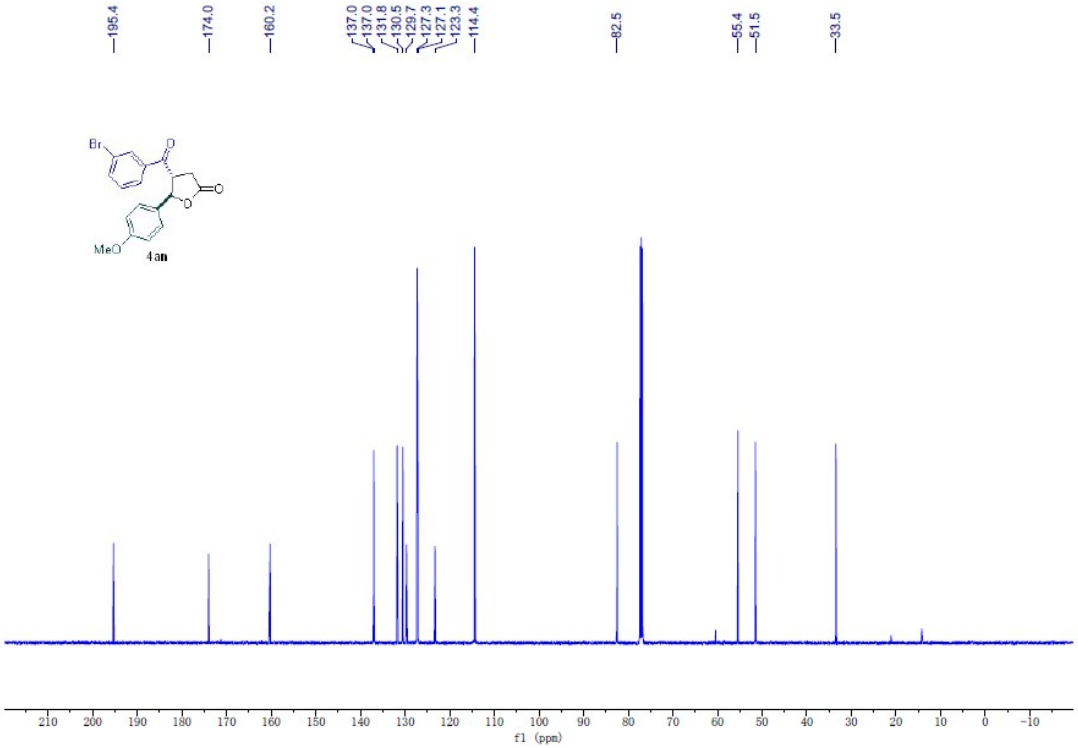

195.2
175.6
174.2
162.7
160.7
159.9
135.9
135.8
131.2
131.2
130.1
127.2
125.1
125.0
124.2
117.0
116.8
114.2
81.8
55.3
55.2
55.1
32.9
F
O
O
O
MeO
4al
f1 (ppm)

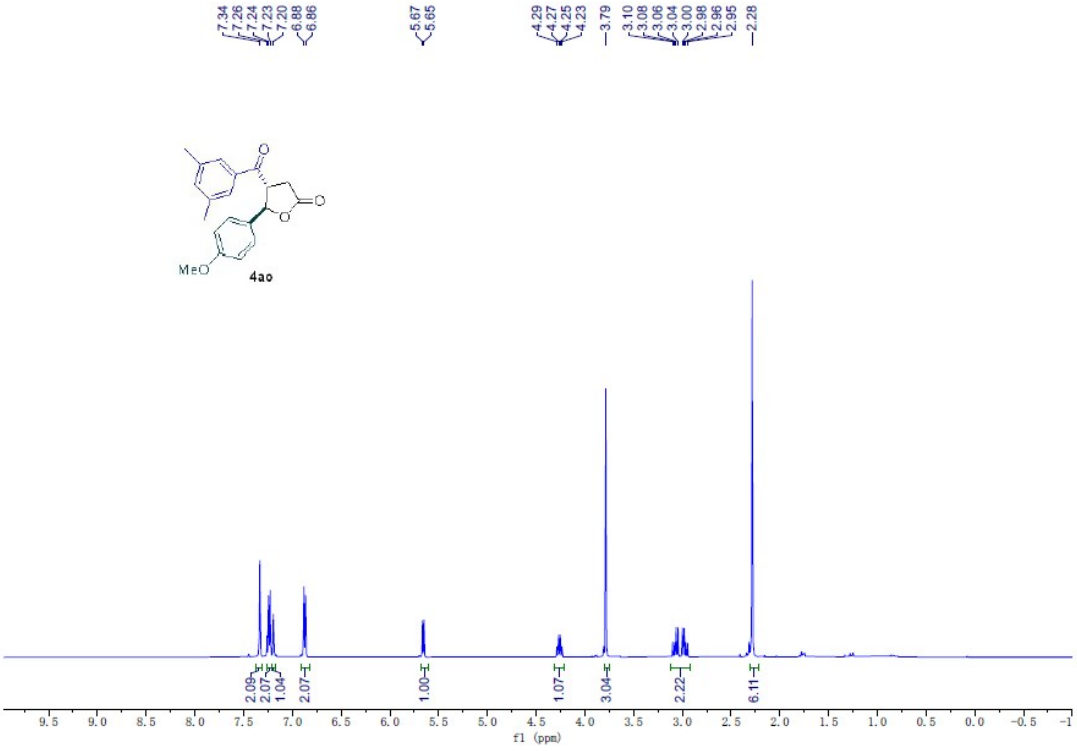

-110.68
F
O
O
O
MeO
4al
10
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

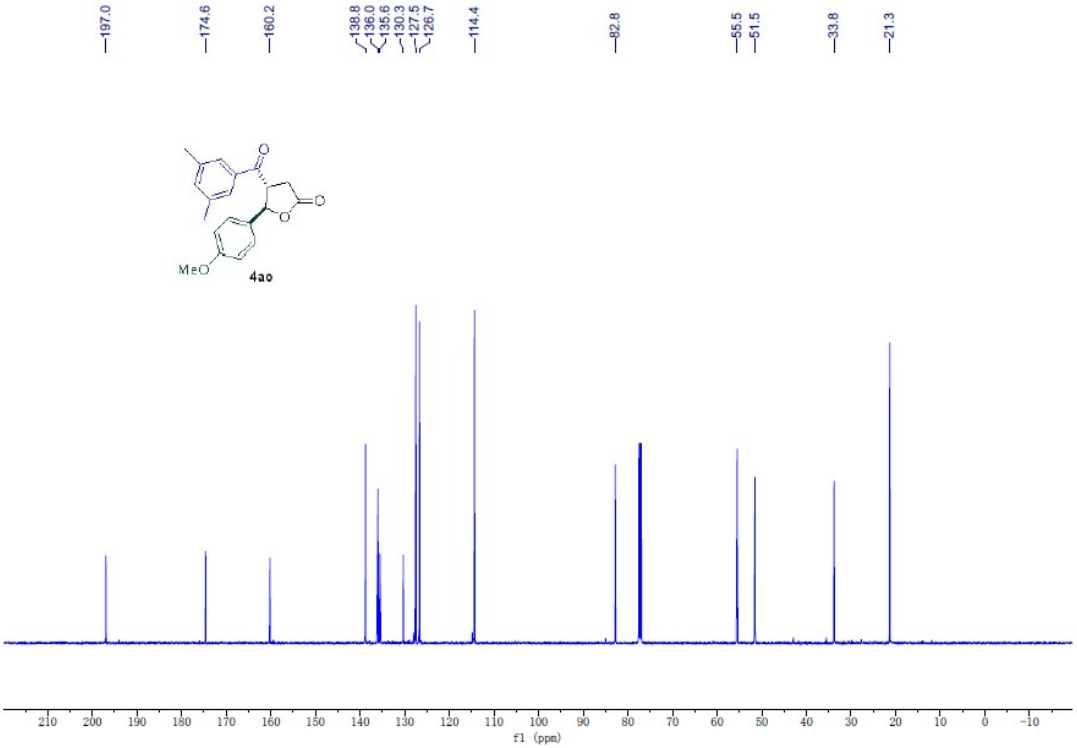

7.70
7.62
7.60
7.55
7.53
7.37
7.36
7.34
7.24
7.22
6.89
6.87
5.66
5.64
3.79
3.10
3.08
3.07
3.05
3.02
3.00
2.98
2.96
Cl
O
O
O
MeO
4am
1.02
1.02
0.97
1.07
2.00
2.02
1.00
1.06
3.14
2.14
f1 (ppm)

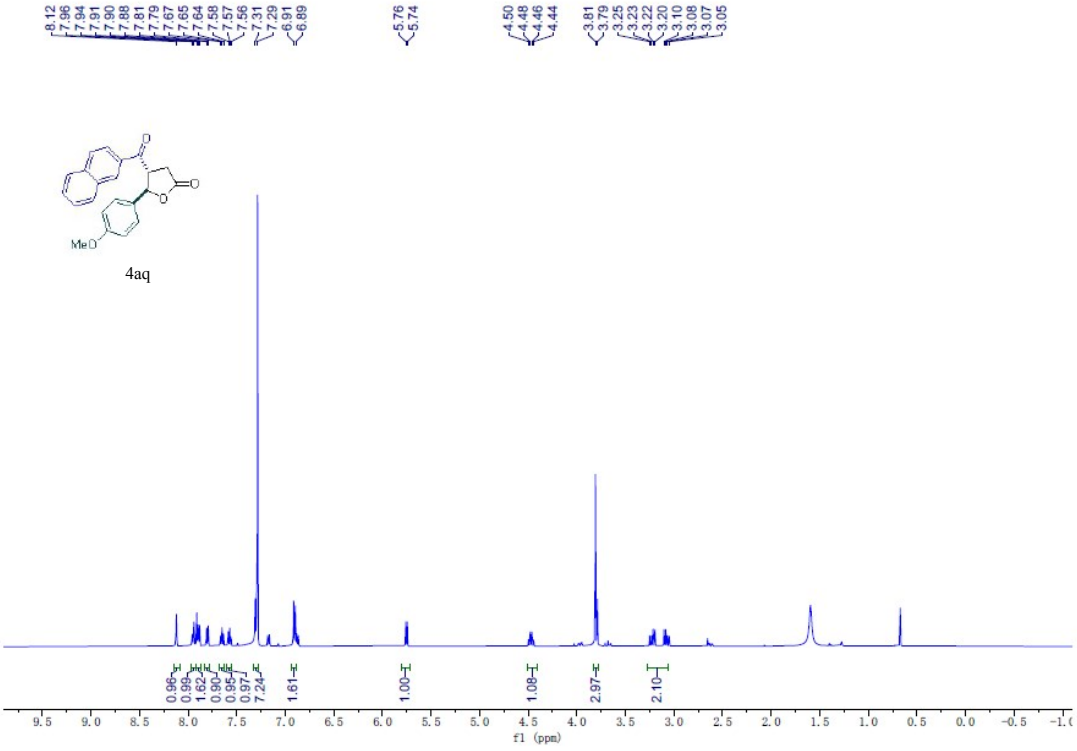

195.5
174.0
160.2
136.8
135.4
134.1
130.3
129.7
128.8
127.3
126.7
114.4
82.5
55.4
51.5
33.5
Cl
O
O
O
MeO
4am
f1 (ppm)


7.83
7.70
7.68
7.67
7.65
7.31
7.29
7.28
7.24
7.22
6.89
6.88
5.64
5.62
4.25
4.23
4.21
4.19
3.80
3.11
3.09
3.08
3.06
3.01
2.99
2.97
2.96
Br
O
O
O
MeO
4an
1.01
2.01
1.02
1.99
2.02
1.00
1.05
3.07
2.11
f1 (ppm)

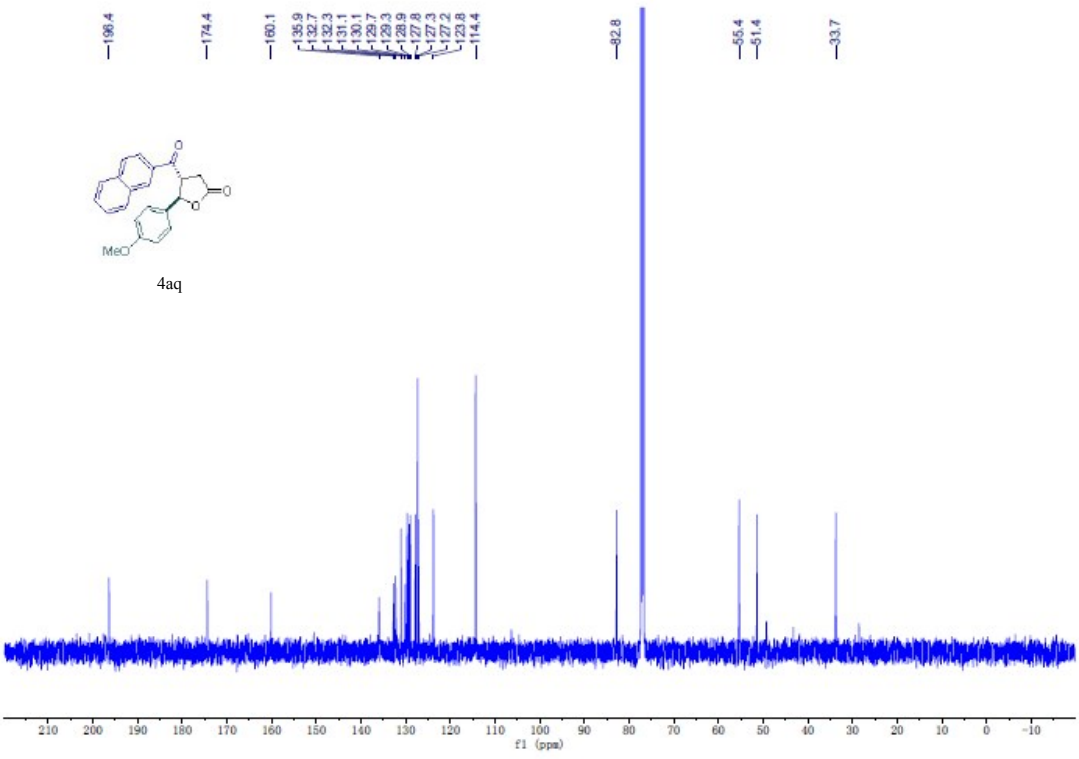

195.4
174.0
160.2
137.0
137.0
131.8
130.5
129.7
127.3
127.1
123.3
114.4
82.5
55.4
51.5
33.5
Br
O
O
O
MeO
4an
f1 (ppm)


7.34
7.26
7.24
7.23
7.20
6.88
6.86
5.67
5.65
4.29
4.27
4.25
4.23
3.79
3.10
3.08
3.06
3.04
3.00
2.98
2.96
2.95
2.28
MeO
4ao
2.09
2.07
1.04
2.07
1.00
1.07
3.04
2.22
6.11
f1 (ppm)

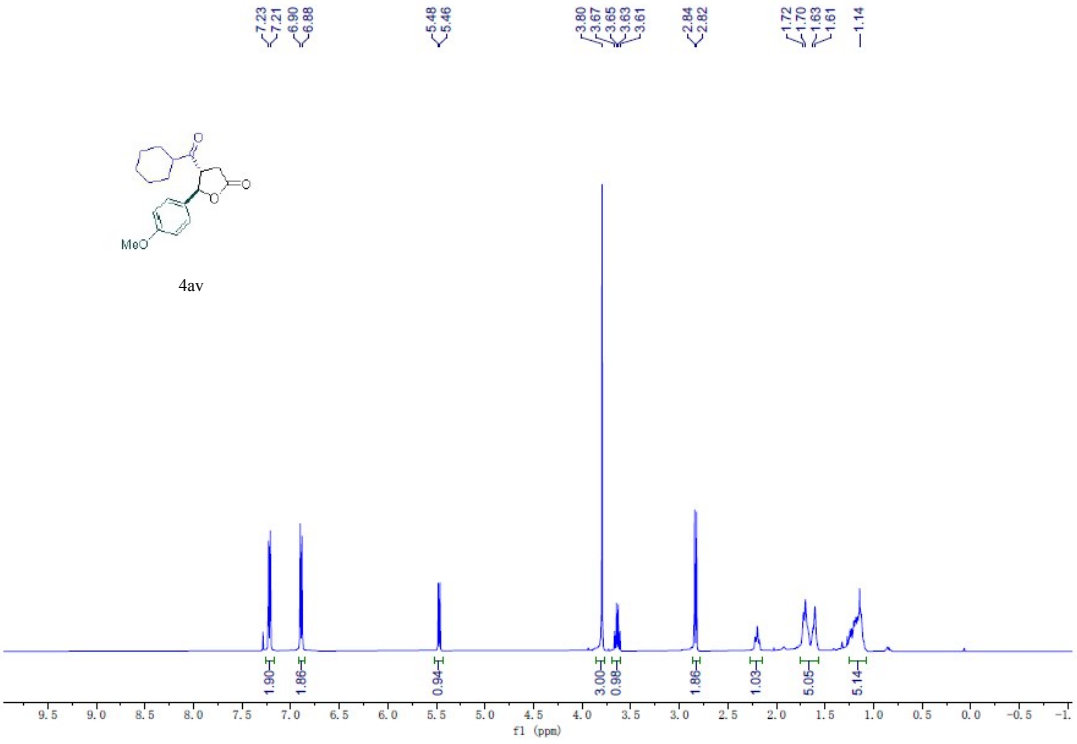

197.0
174.6
160.2
138.8
136.0
135.6
130.3
127.5
126.7
114.4
82.8
55.5
51.5
33.8
21.3
MeO
4ao
f1 (ppm)


8.12
7.96
7.94
7.91
7.90
7.88
7.81
7.79
7.67
7.65
7.64
7.58
7.57
7.56
7.31
7.29
6.91
6.89
5.76
5.74
4.50
4.48
4.46
4.44
3.81
3.79
3.25
3.23
3.22
3.20
3.10
3.08
3.07
3.05
MeO
0.96
0.99
1.62
0.90
0.95
0.97
7.24
1.61
1.00
1.08
2.97
2.10
f1 (ppm)

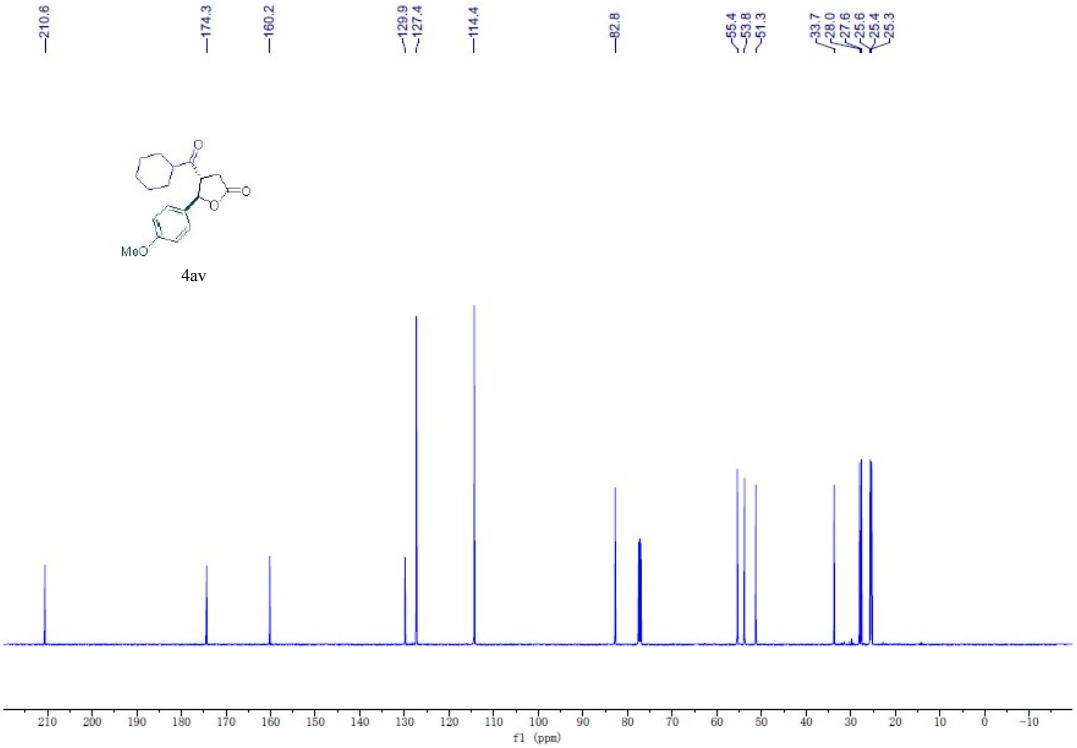
4aq


196.4
174.4
160.1
135.9
132.7
132.3
131.1
130.1
129.7
129.3
128.9
127.8
127.3
127.2
123.8
114.4
82.8
55.4
51.4
33.7
MeO
f1 (ppm)

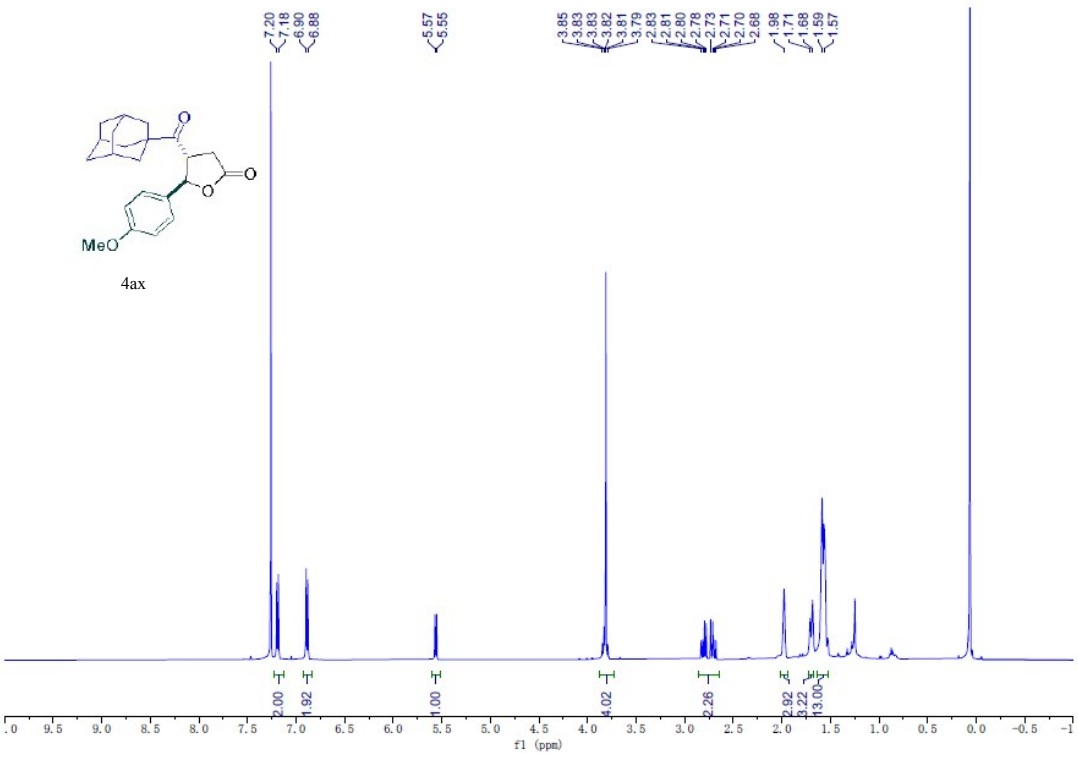
4aq


7.23
7.21
6.90
6.88
5.48
5.46
3.80
3.67
3.65
3.63
3.61
2.84
2.82
1.72
1.70
1.63
1.61
1.14
MeO
1.90
1.86
0.94
3.00
0.98
1.86
1.03
5.06
5.14
f1 (ppm)

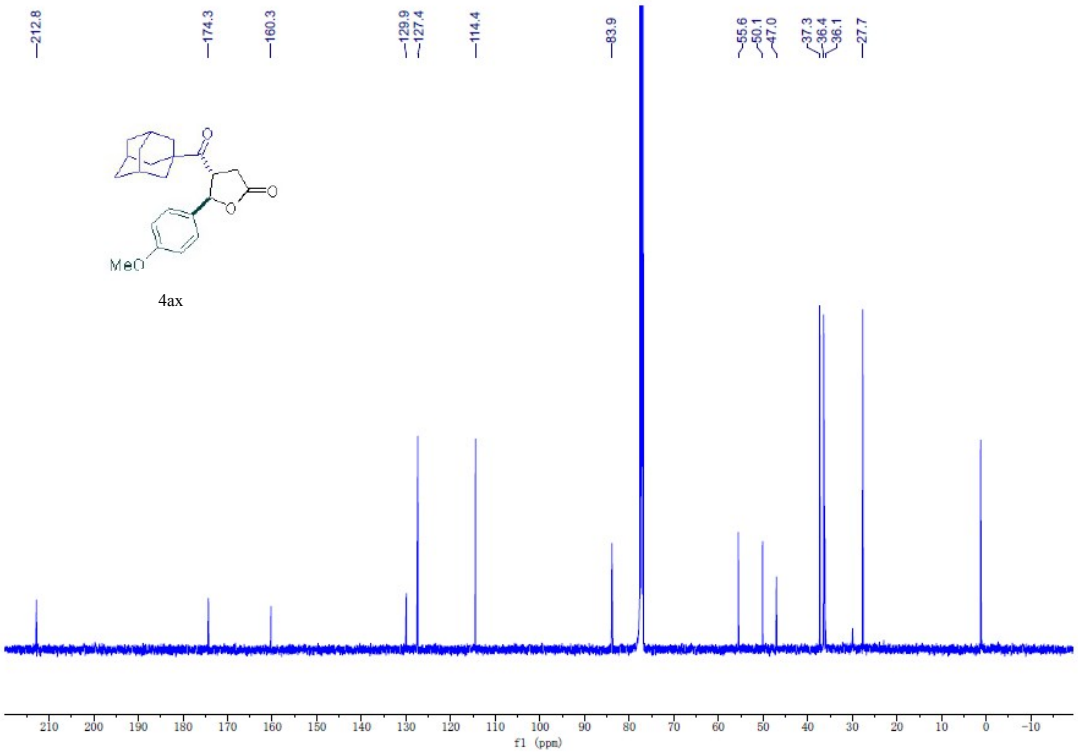
4av


210.6
174.3
160.2
129.9
127.4
114.4
82.8
55.4
53.8
51.3
33.7
28.0
27.6
25.6
25.4
25.3
MeO
f1 (ppm)

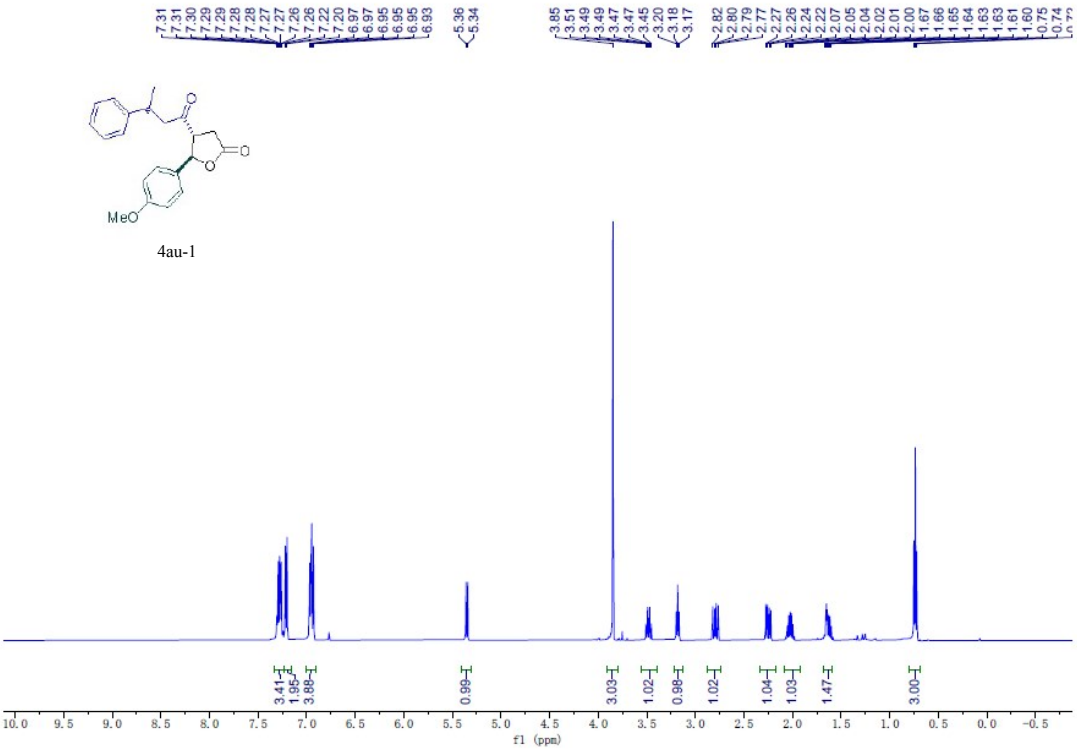
4av

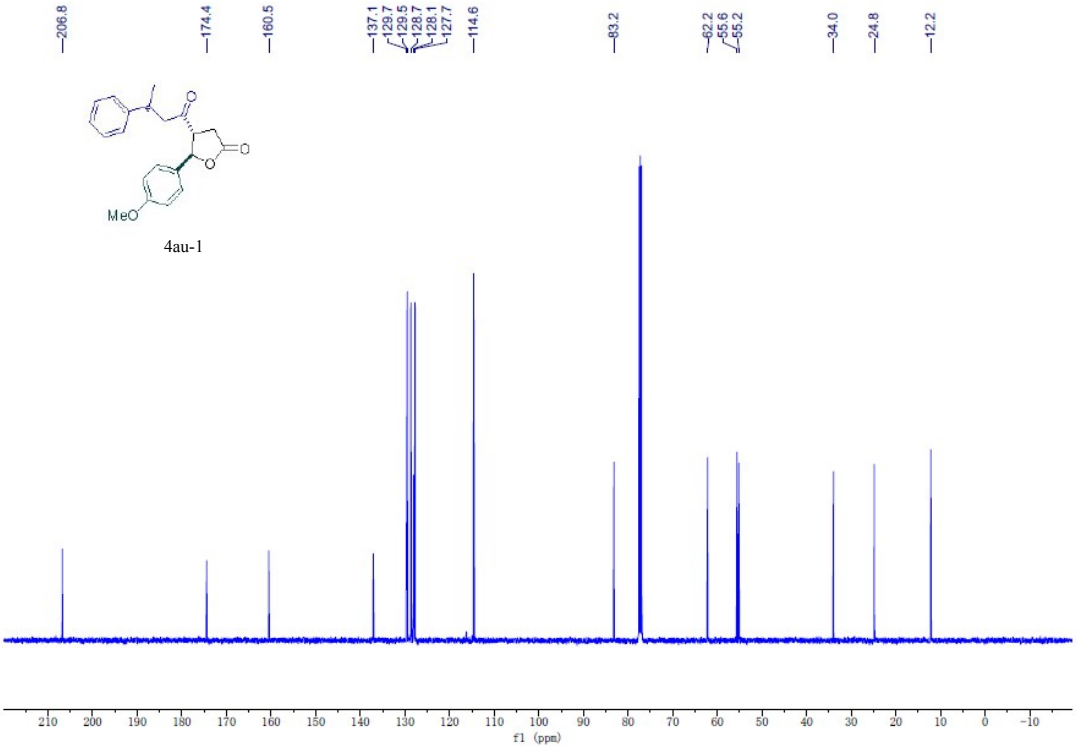

7.20
7.18
6.90
6.88
5.57
5.55
3.85
3.83
3.83
3.82
3.81
3.79
2.83
2.81
2.80
2.78
2.73
2.71
2.70
2.68
1.98
1.71
1.68
1.59
1.57
MeO
2.00
1.92
1.00
4.02
2.26
2.92
3.22
13.00
f1 (ppm)

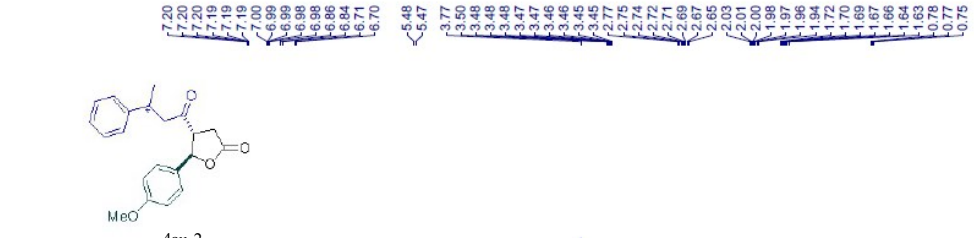
4ax


212.8
174.3
160.3
129.9
127.4
114.4
83.9
55.6
50.1
47.0
37.3
36.4
36.1
27.7
MeO
f1 (ppm)

4ax

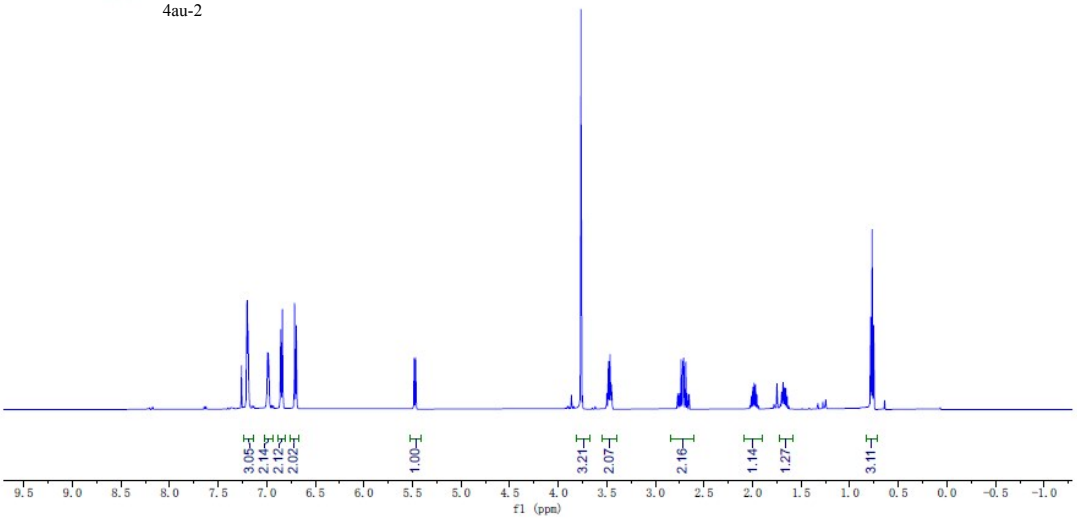

MeO
4au-1
f1 (ppm)

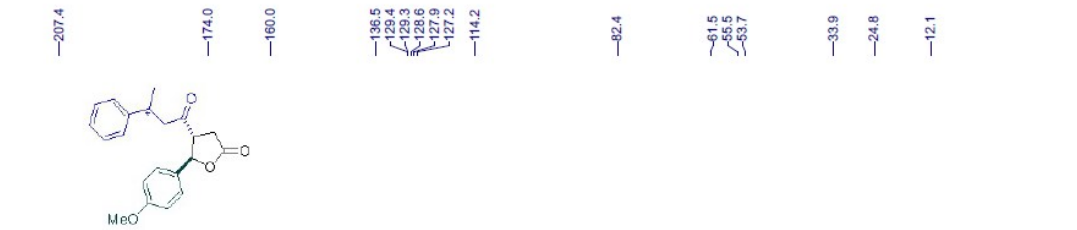

MeO
4au-1
f1 (ppm)


7.20
7.20
7.20
7.19
7.19
7.19
7.00
6.99
6.99
6.98
6.98
6.86
6.84
6.71
6.70
5.48
5.47
3.77
3.50
3.48
3.48
3.48
3.47
3.47
3.46
3.46
3.45
3.45
2.77
2.75
2.74
2.72
2.71
2.69
2.67
2.65
2.03
2.01
2.00
1.98
1.97
1.96
1.94
1.72
1.70
1.69
1.67
1.66
1.64
1.63
0.78
0.77
0.75

O
O
O
MeO

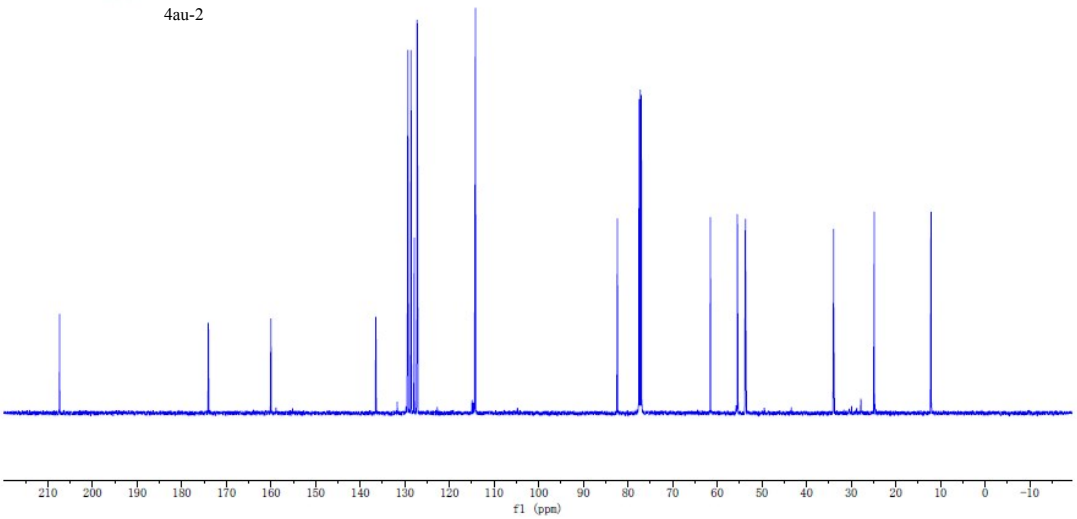
4au-2


3.06
2.14
2.12
2.02
1.00
3.21
2.07
2.16
1.14
1.27
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

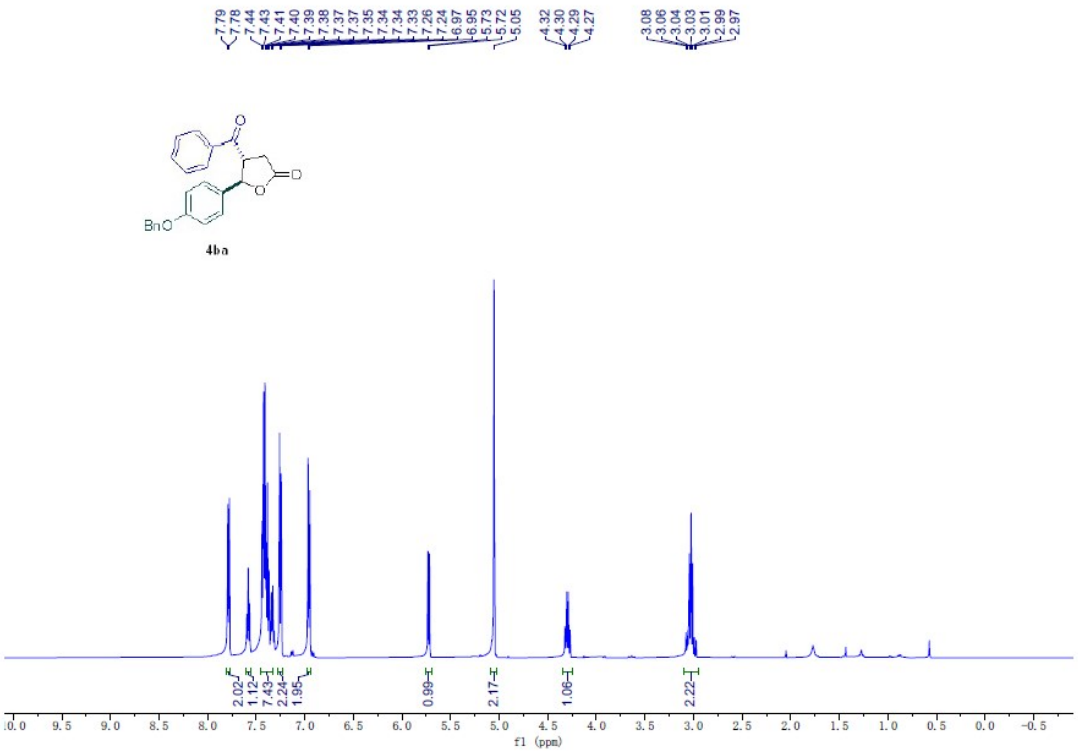

207.4
174.0
160.0
136.5
129.4
129.3
128.6
127.9
127.2
114.2
82.4
61.5
55.5
53.7
33.9
24.8
12.1

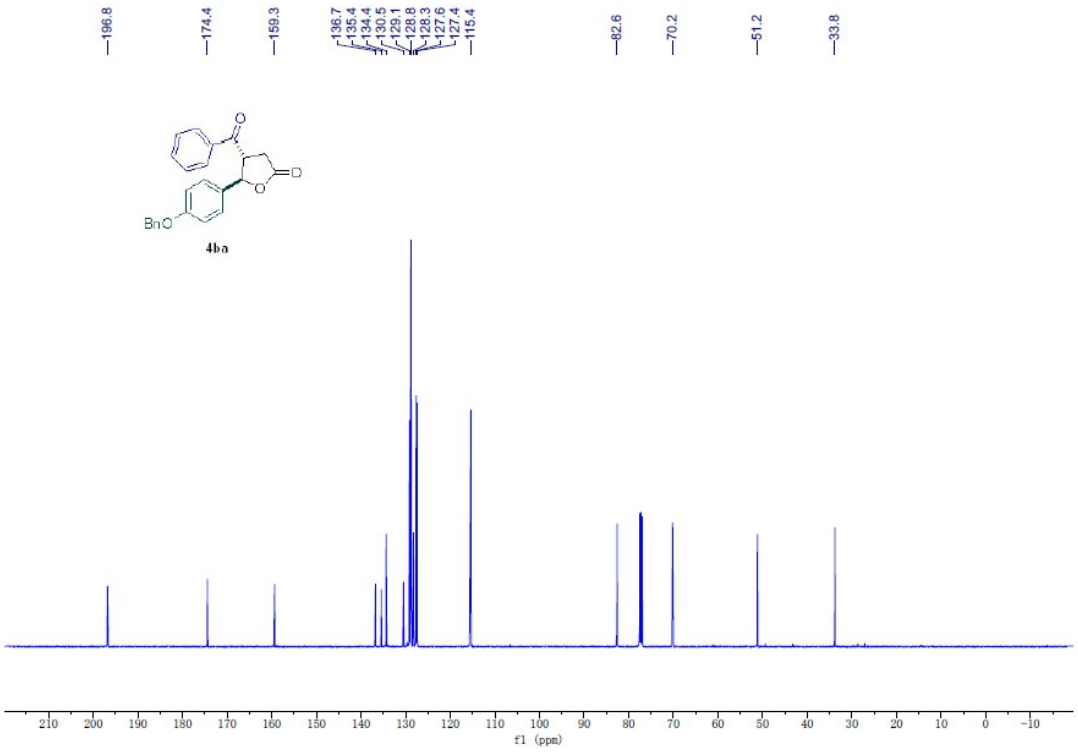
O
O
O
MeO

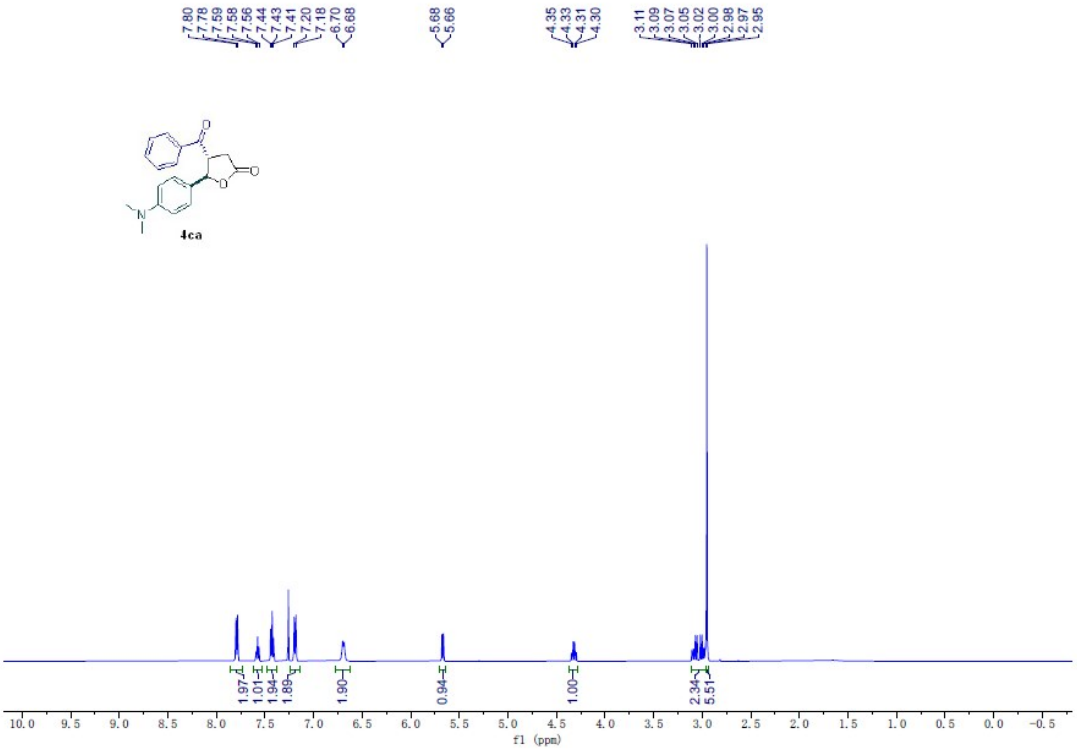
4au-2

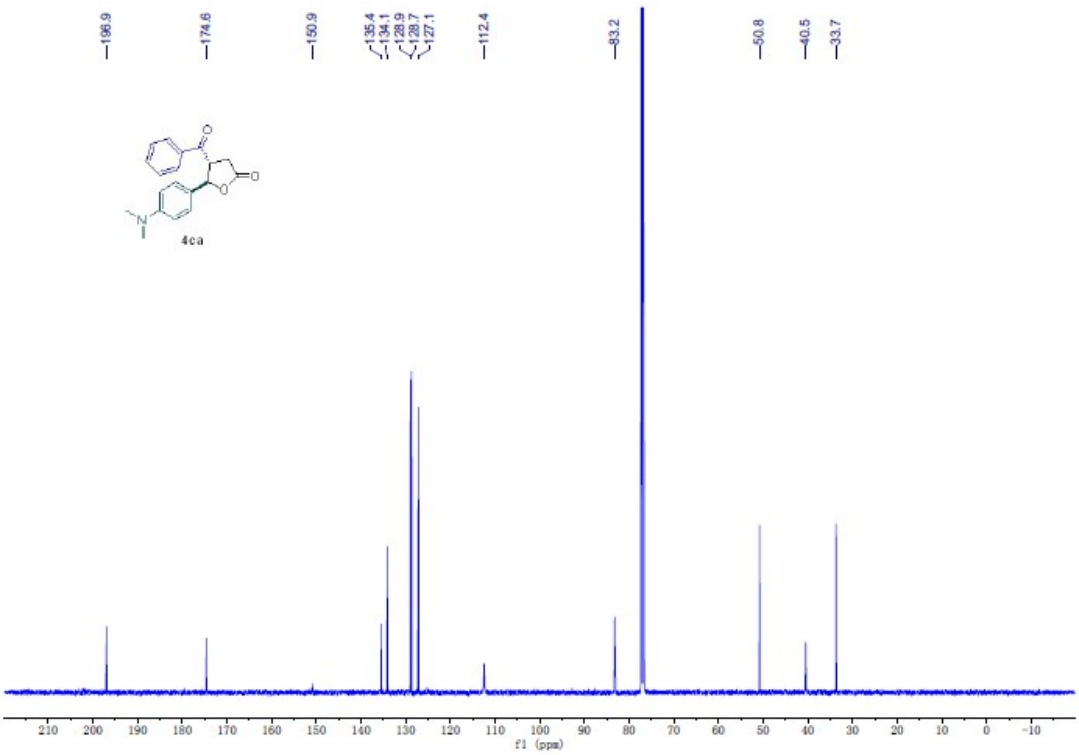

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

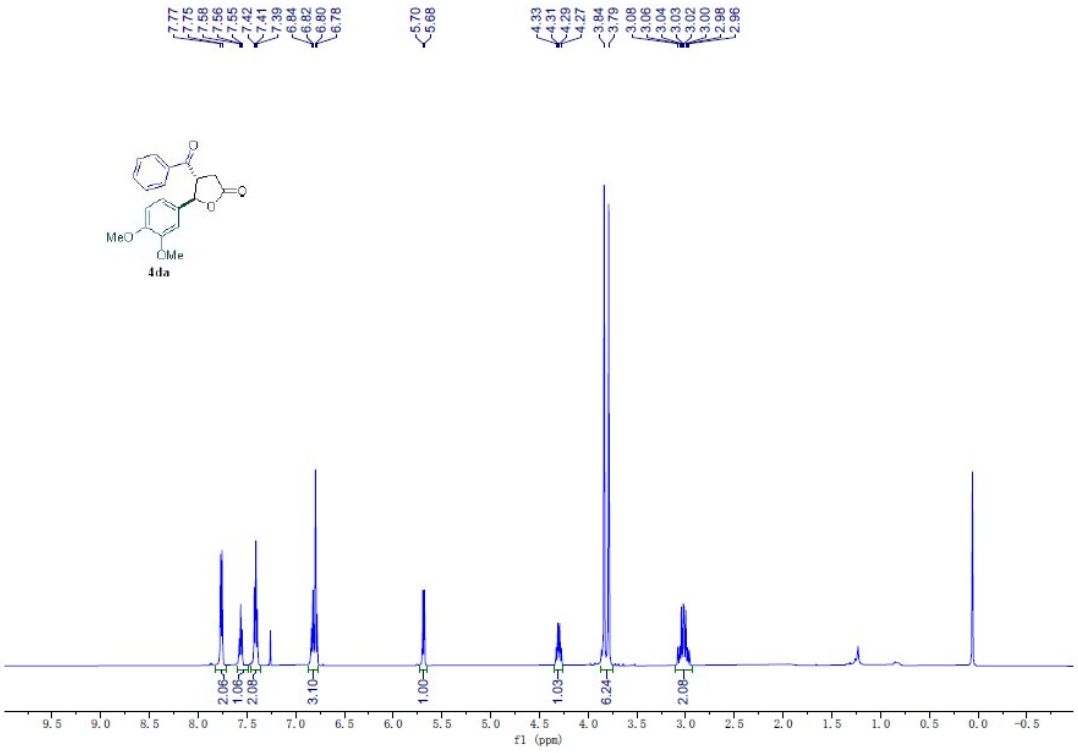
7.2. Copies of NMR Spectra for Compounds of 4ba-4la

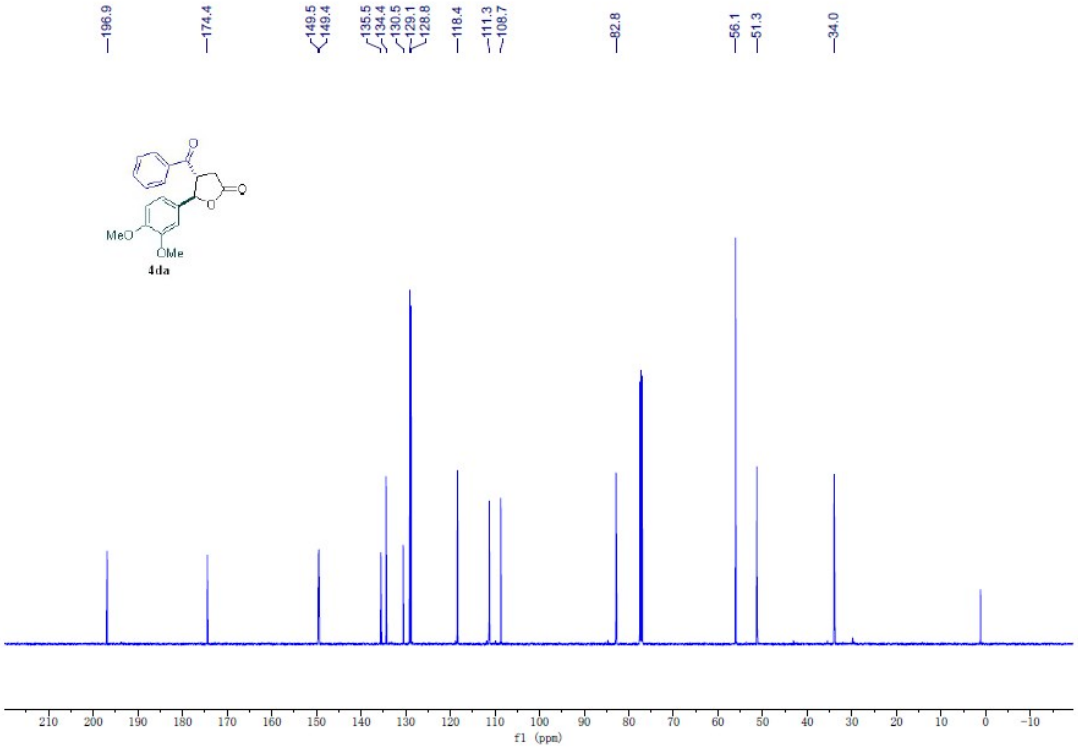


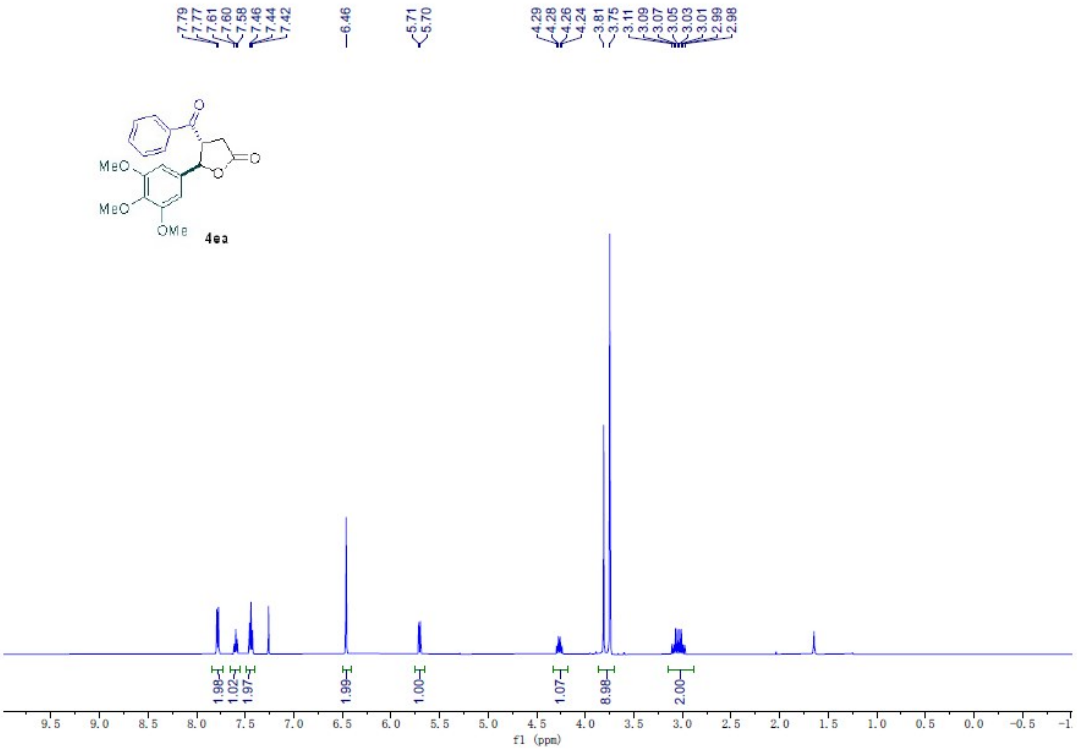


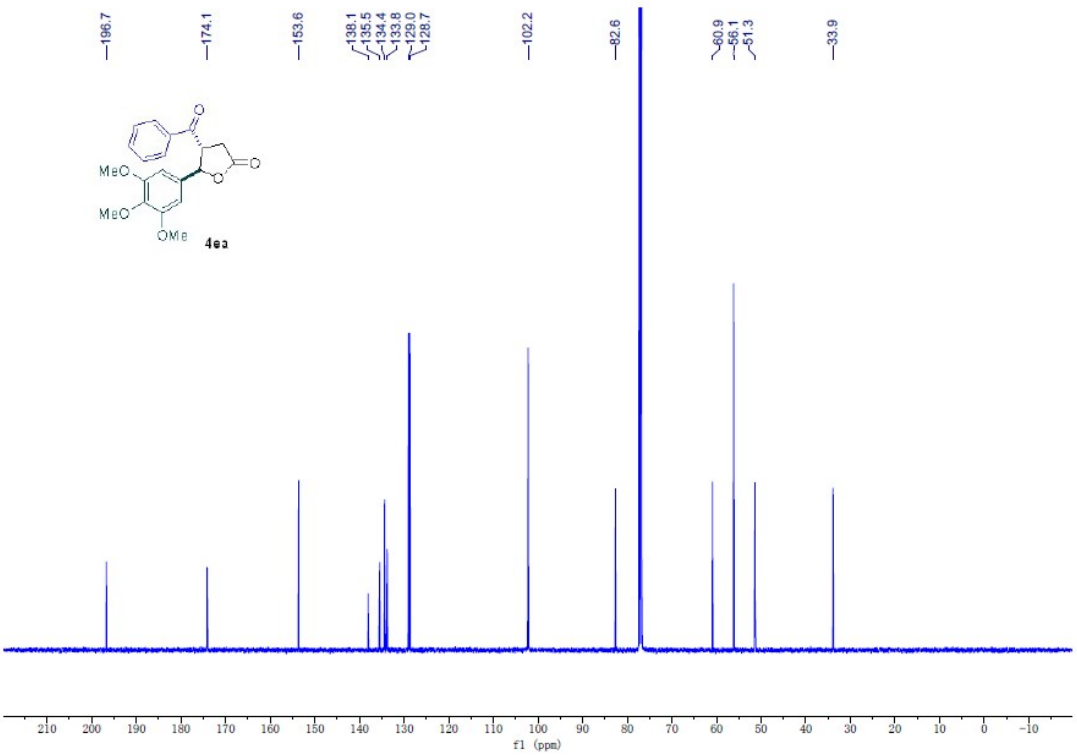

7.80
7.78
7.59
7.58
7.56
7.44
7.43
7.41
7.20
7.18
6.70
6.68
5.68
5.66
4.35
4.33
4.31
4.30
3.11
3.09
3.07
3.05
3.02
3.00
2.98
2.97
2.95
4ca
1.97
1.01
1.94
1.89
1.90
0.94
1.00
2.34
5.51
f1 (ppm)

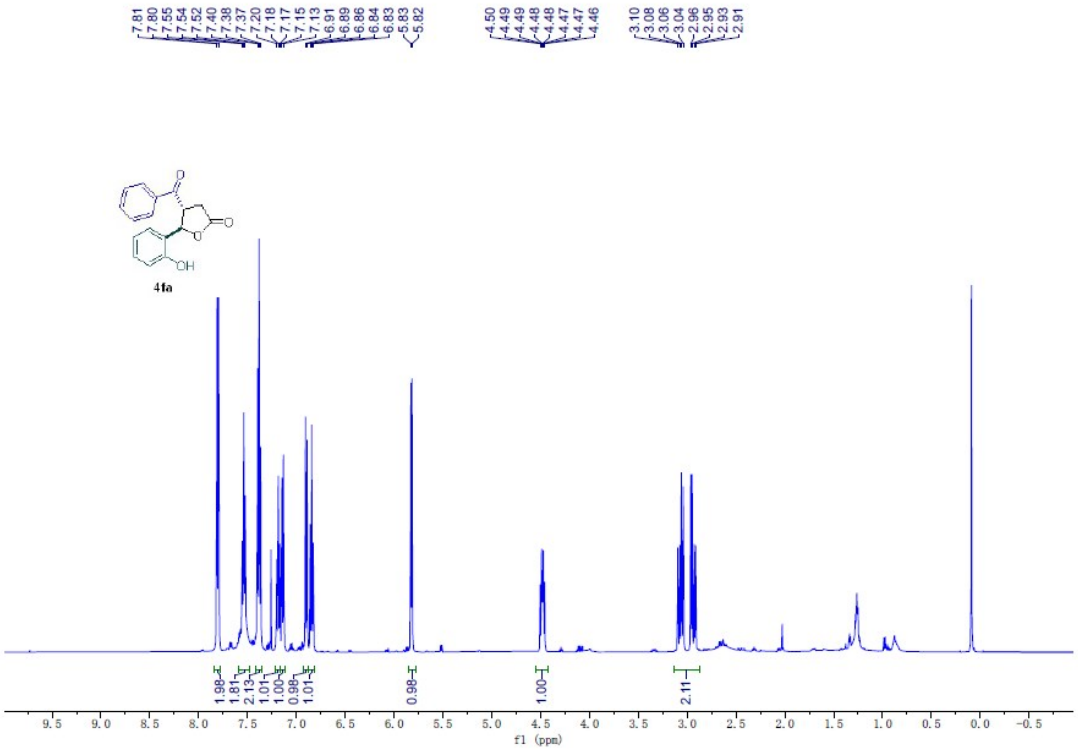

196.9
174.6
150.9
135.4
134.1
128.9
128.7
127.1
112.4
83.2
50.8
40.5
33.7
4ca
f1 (ppm)

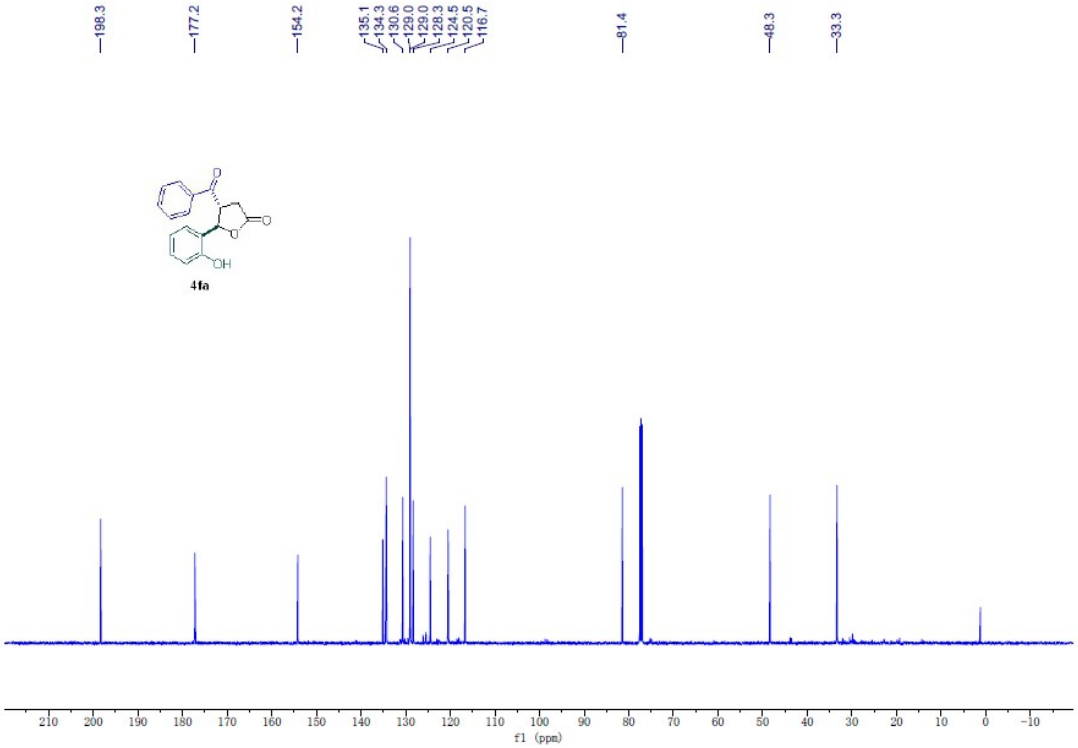

7.77
7.75
7.58
7.56
7.55
7.42
7.41
7.39
6.84
6.82
6.80
6.78
5.70
5.68
4.33
4.31
4.29
4.27
3.84
3.79
3.08
3.06
3.04
3.03
3.02
3.00
2.98
2.96
MeO
OMe
4da
2.06
1.06
2.08
3.10
1.00
1.03
6.24
2.08
f1 (ppm)

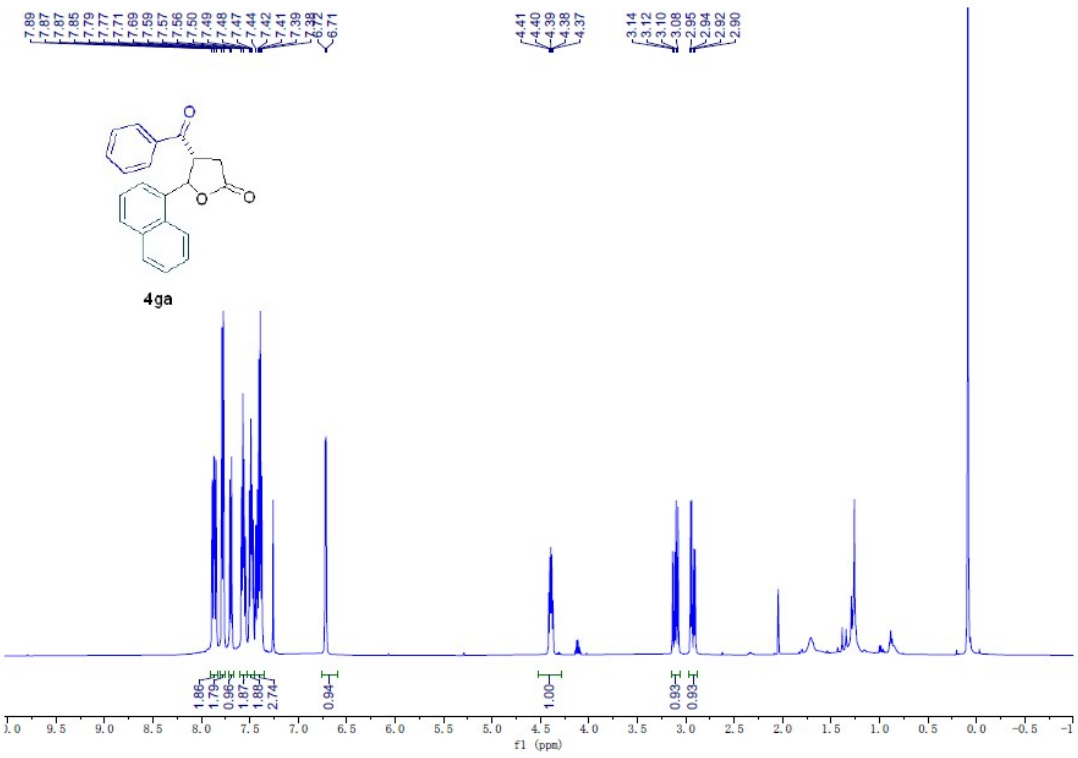

196.9
174.4
149.5
149.4
135.5
134.4
130.5
129.1
128.8
118.4
111.3
108.7
82.8
56.1
51.3
34.0
MeO
OMe
4da
f1 (ppm)

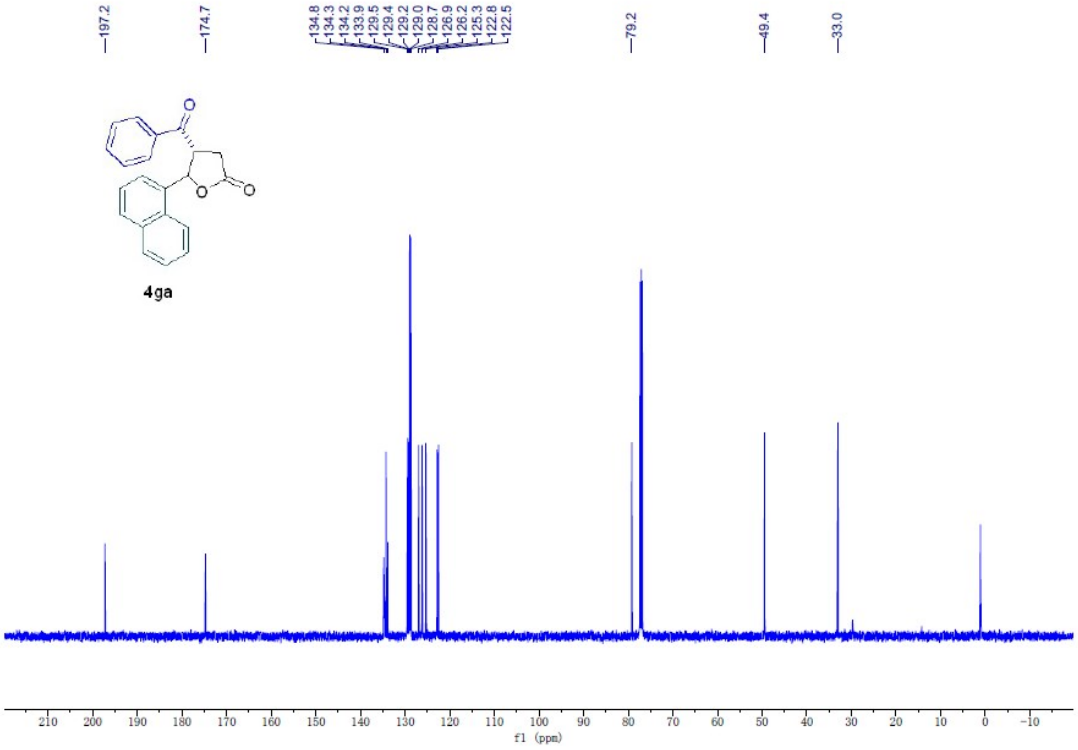

7.79
7.77
7.61
7.60
7.58
7.46
7.44
7.42
6.46
5.71
5.70
4.29
4.28
4.26
4.24
3.81
3.75
3.11
3.09
3.07
3.05
3.03
3.01
2.99
2.98
MeO
MeO
OMe
4ea
1.98
1.02
1.97
1.99
1.00
1.07
8.98
2.00
f1 (ppm)

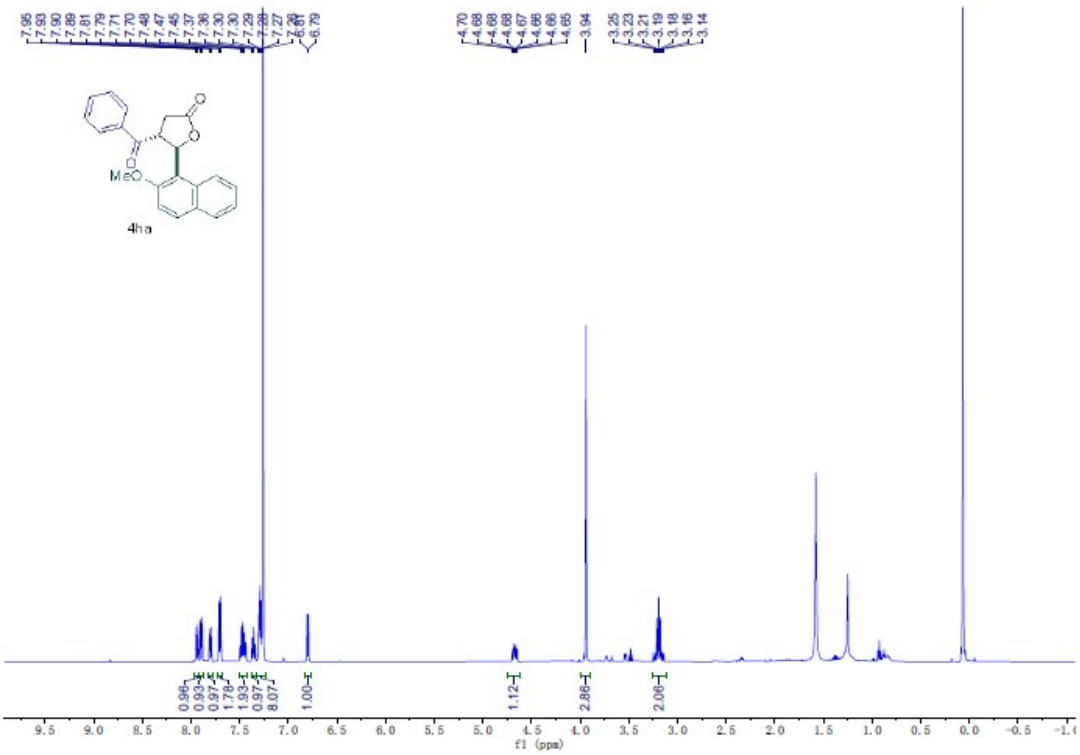

196.7
174.1
153.6
138.1
135.5
134.4
133.8
129.0
128.7
102.2
82.6
60.9
56.1
51.3
33.9
MeO
MeO
OMe
4ea
f1 (ppm)

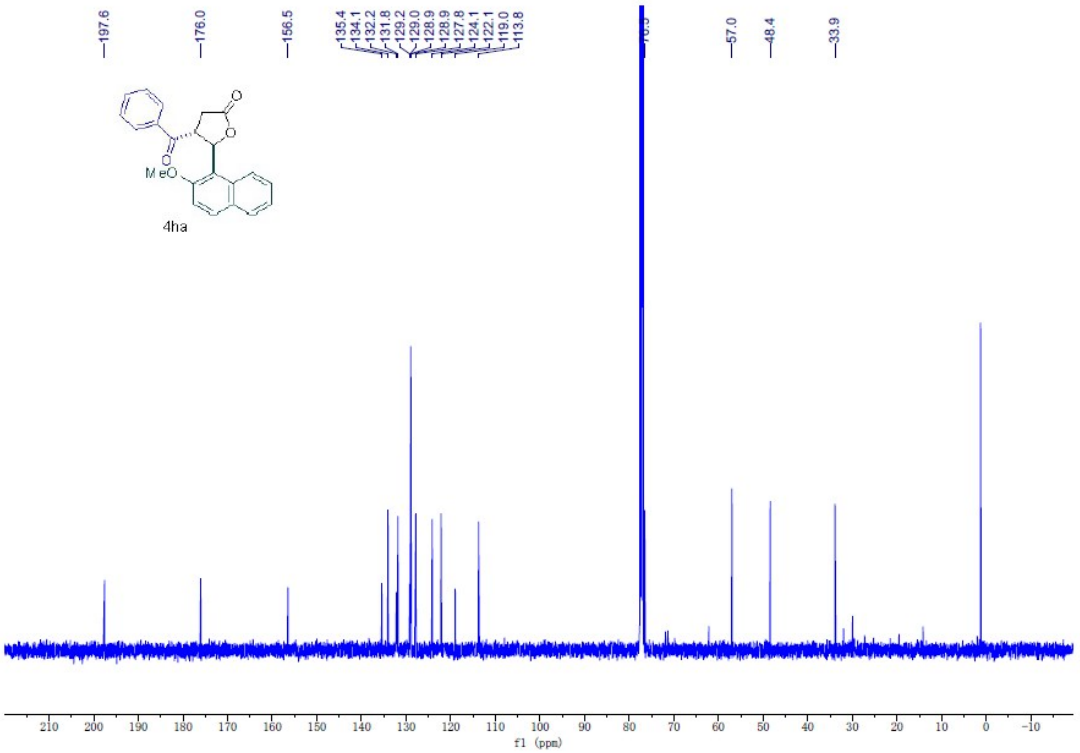

7.81
7.80
7.55
7.54
7.52
7.40
7.38
7.37
7.20
7.18
7.17
7.15
7.13
6.91
6.89
6.86
6.84
6.83
5.83
5.82
4.50
4.49
4.49
4.48
4.48
4.47
4.47
4.46
3.10
3.08
3.06
3.04
2.96
2.95
2.93
2.91
4fa
1.98
1.81
2.13
1.01
1.00
0.98
1.01
0.98
1.00
2.11
f1 (ppm)

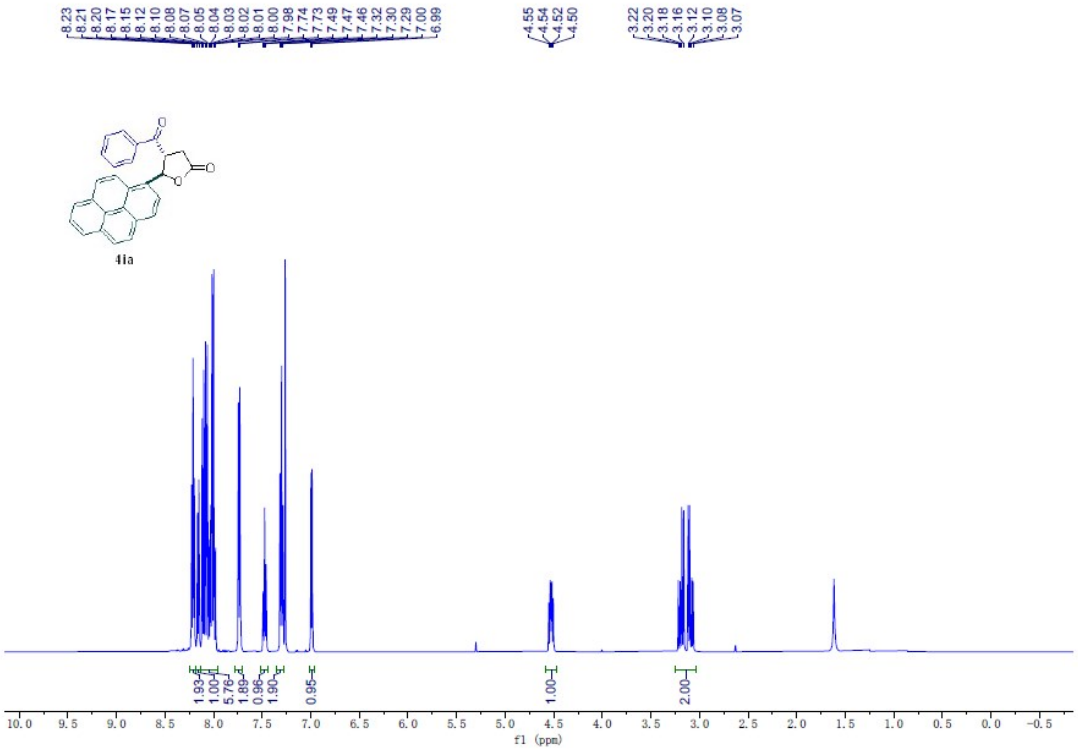

198.3
177.2
154.2
135.1
134.3
130.6
129.0
129.0
128.3
124.5
120.5
116.7
81.4
48.3
33.3
4fa
f1 (ppm)

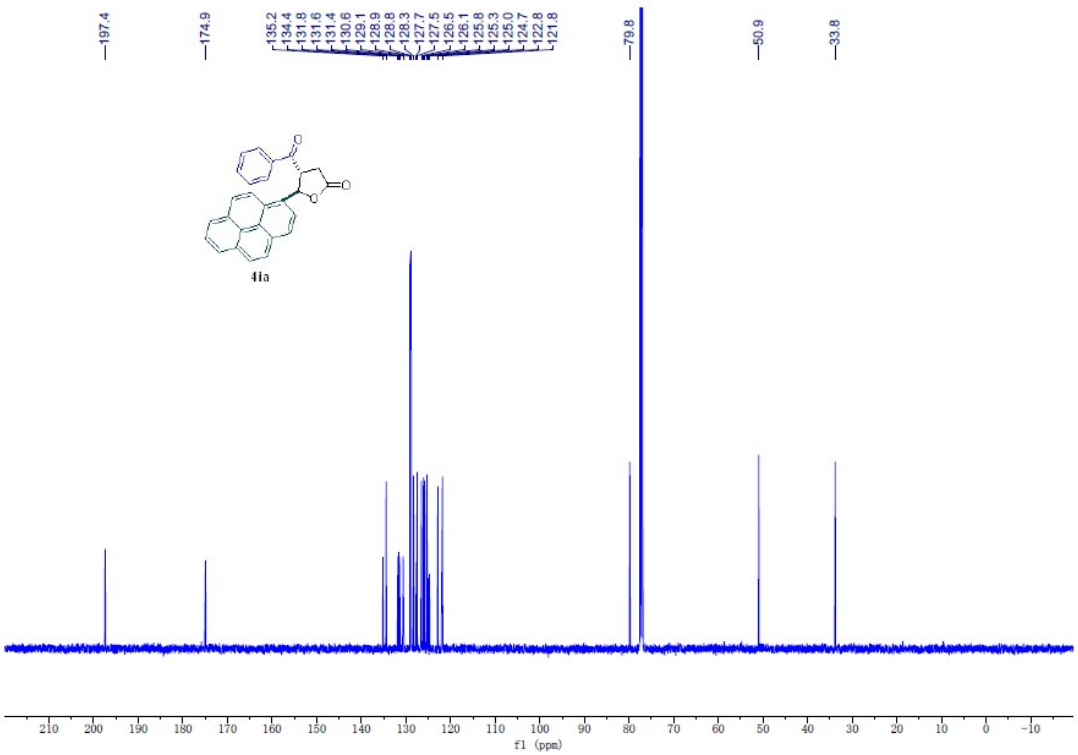

4ga
f1 (ppm)

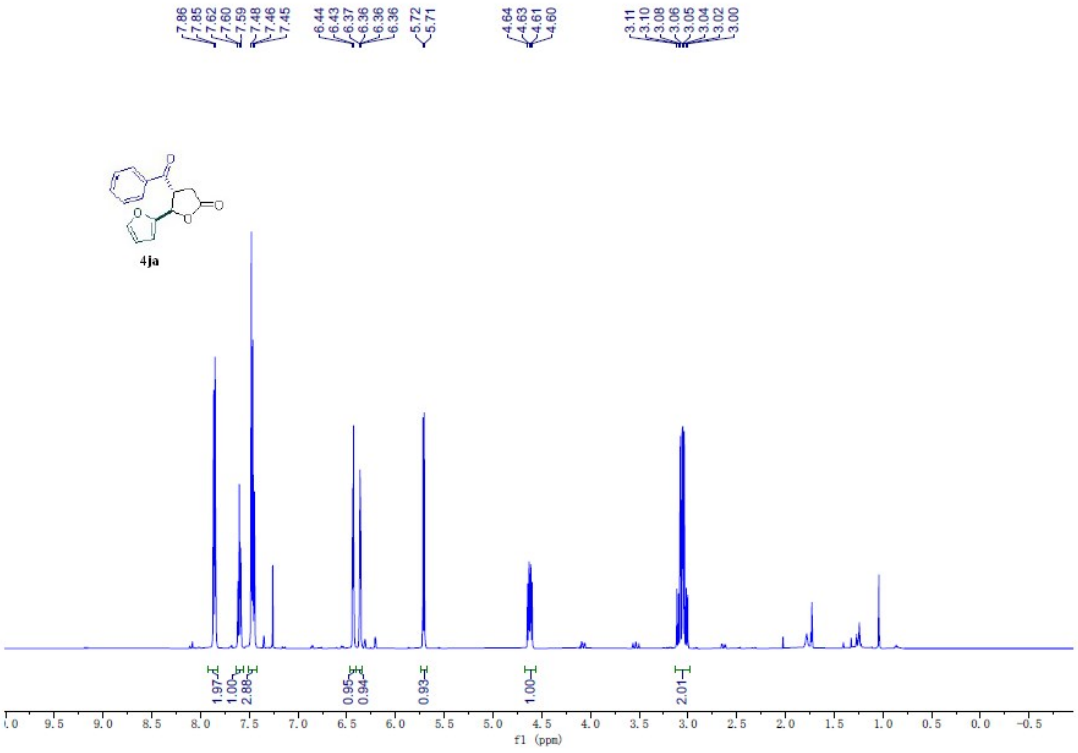

4ga
f1 (ppm)

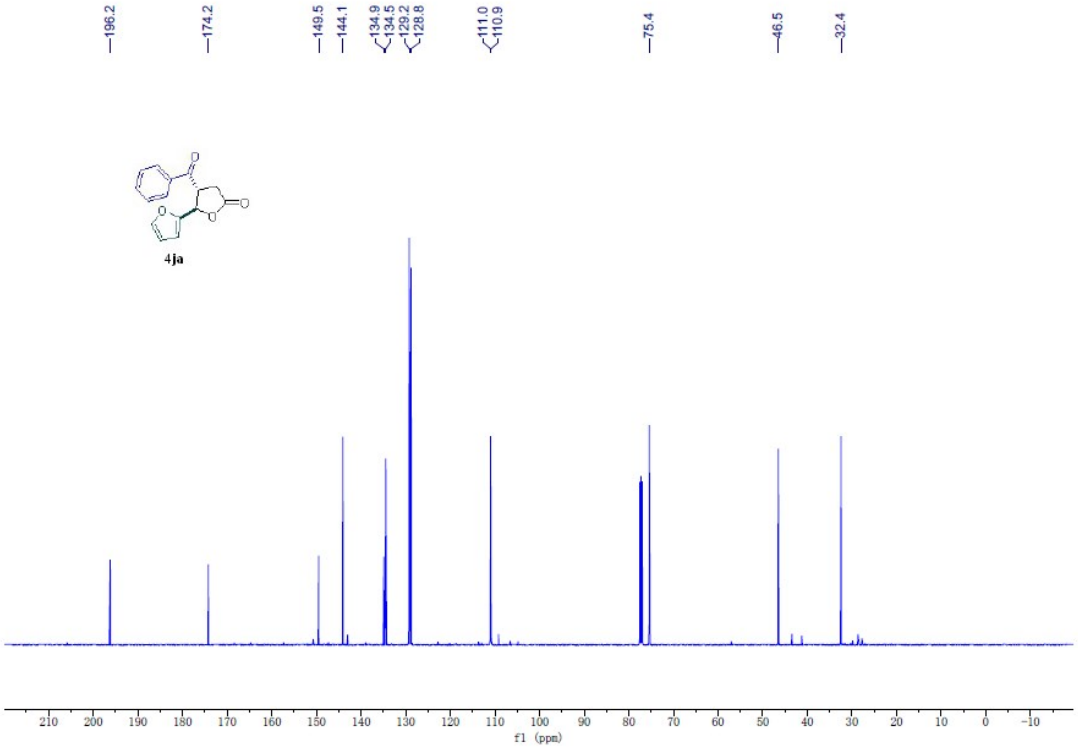

4ha
f1 (ppm)

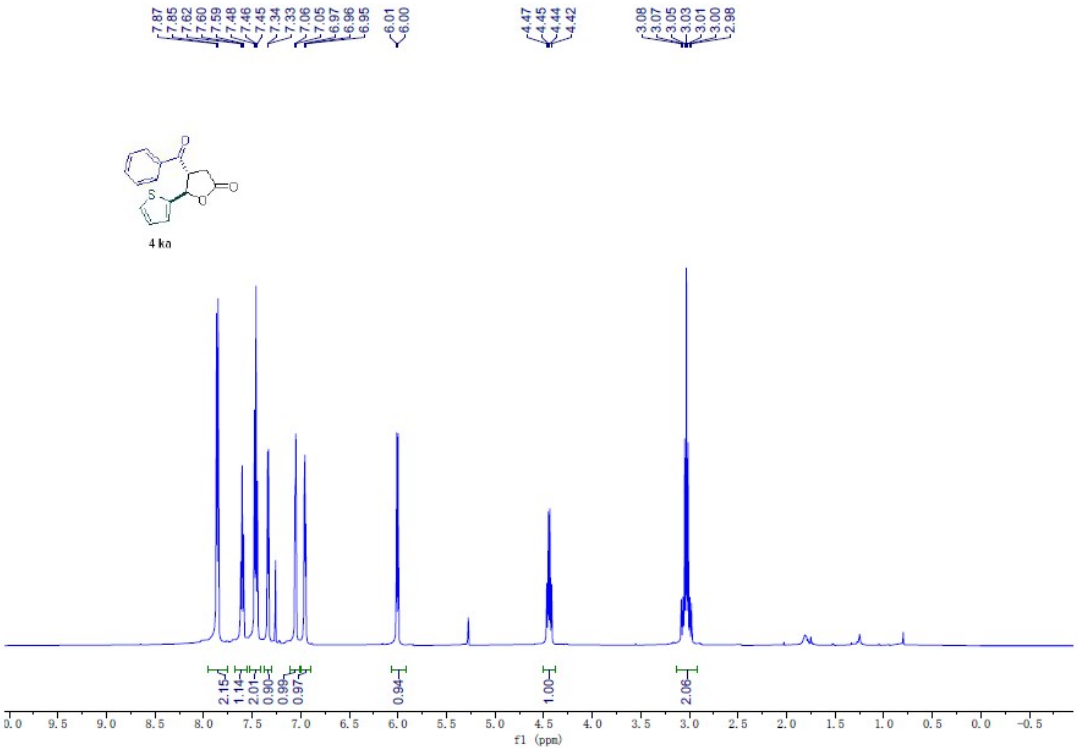

4ha
f1 (ppm)

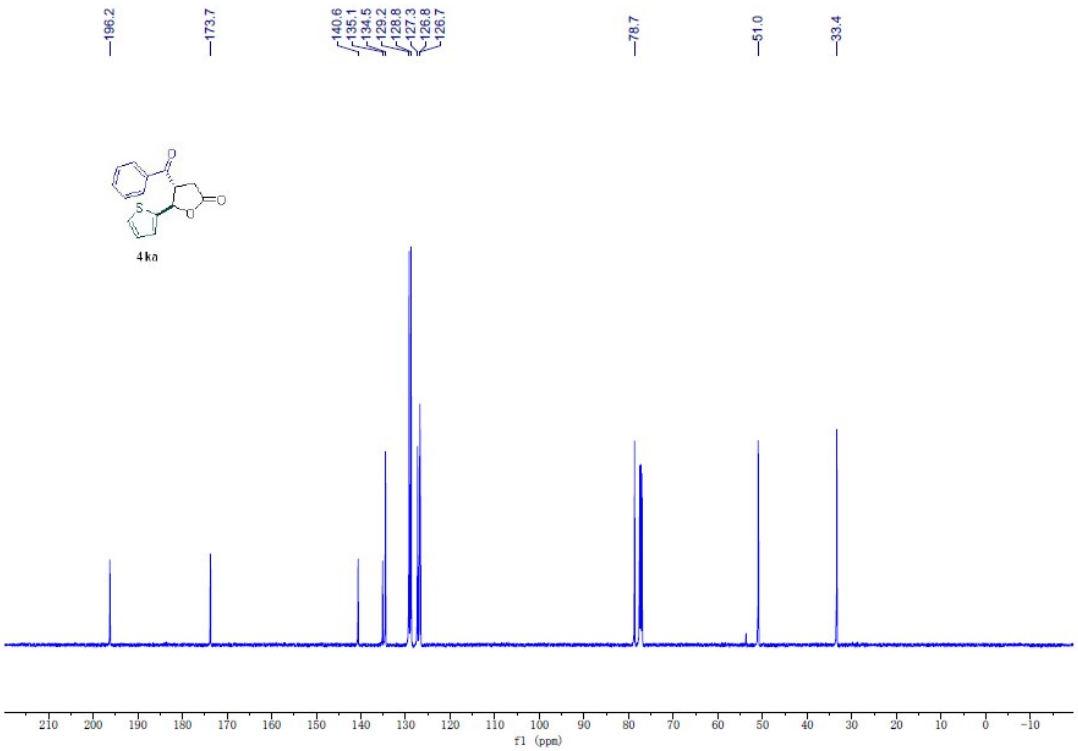

8.23
8.21
8.20
8.17
8.15
8.12
8.10
8.08
8.07
8.05
8.04
8.03
8.02
8.01
8.00
7.98
7.74
7.73
7.49
7.47
7.46
7.32
7.30
7.29
7.00
6.99
4.55
4.54
4.52
4.50
3.22
3.20
3.18
3.16
3.12
3.10
3.08
3.07
4la
1.93
1.00
5.76
1.89
0.96
1.90
0.95
1.00
2.00
f1 (ppm)

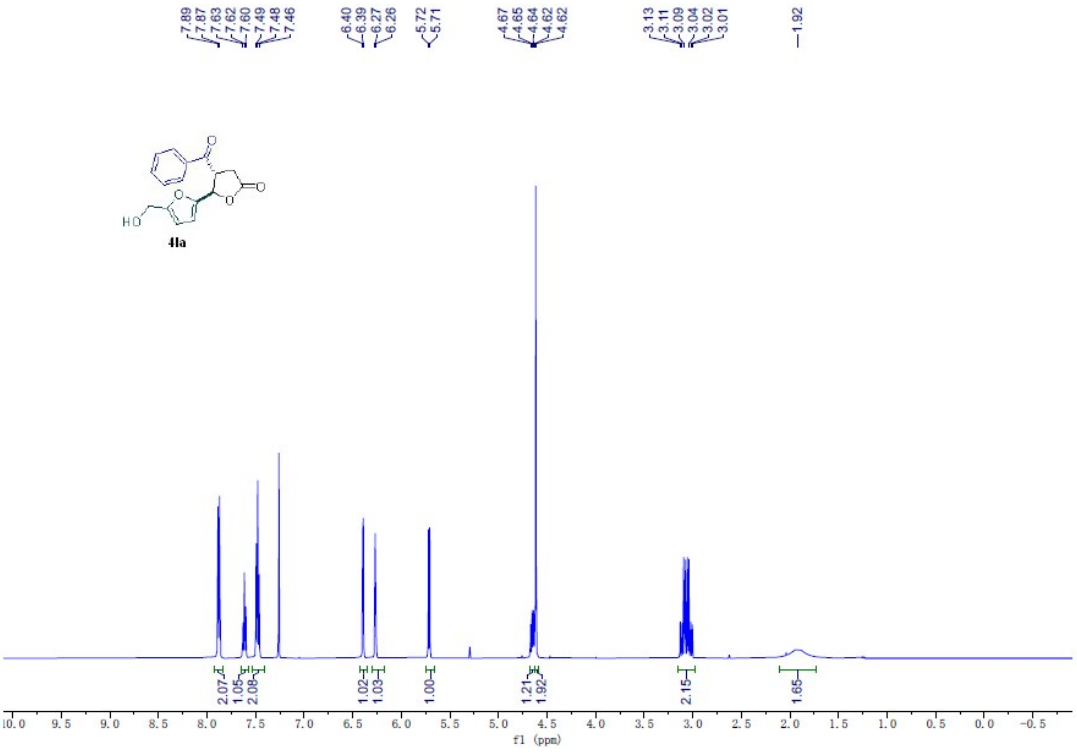

197.4
174.9
135.2
134.4
131.8
131.6
131.4
130.6
129.1
128.9
128.8
128.3
127.7
127.5
126.5
126.1
125.8
125.3
125.0
124.7
122.8
121.8
79.8
50.9
33.8
4la
f1 (ppm)

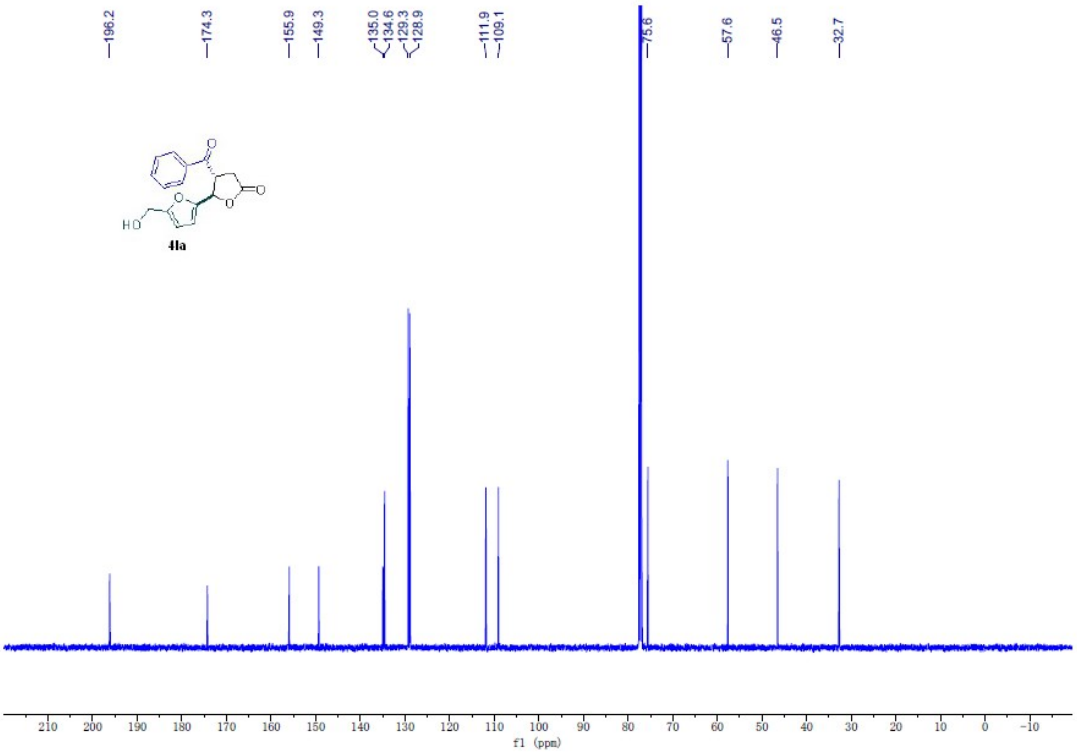

7.86
7.85
7.62
7.60
7.59
7.48
7.46
7.45
6.44
6.43
6.37
6.36
6.36
6.36
5.72
5.71
4.64
4.63
4.61
4.60
3.11
3.10
3.08
3.06
3.05
3.04
3.02
3.00
4ja
1.97
1.00
2.88
0.95
0.94
0.93
1.00
2.01
f1 (ppm)


196.2
174.2
149.5
144.1
134.9
134.5
129.2
128.8
111.0
110.9
75.4
46.5
32.4
4ja
f1 (ppm)

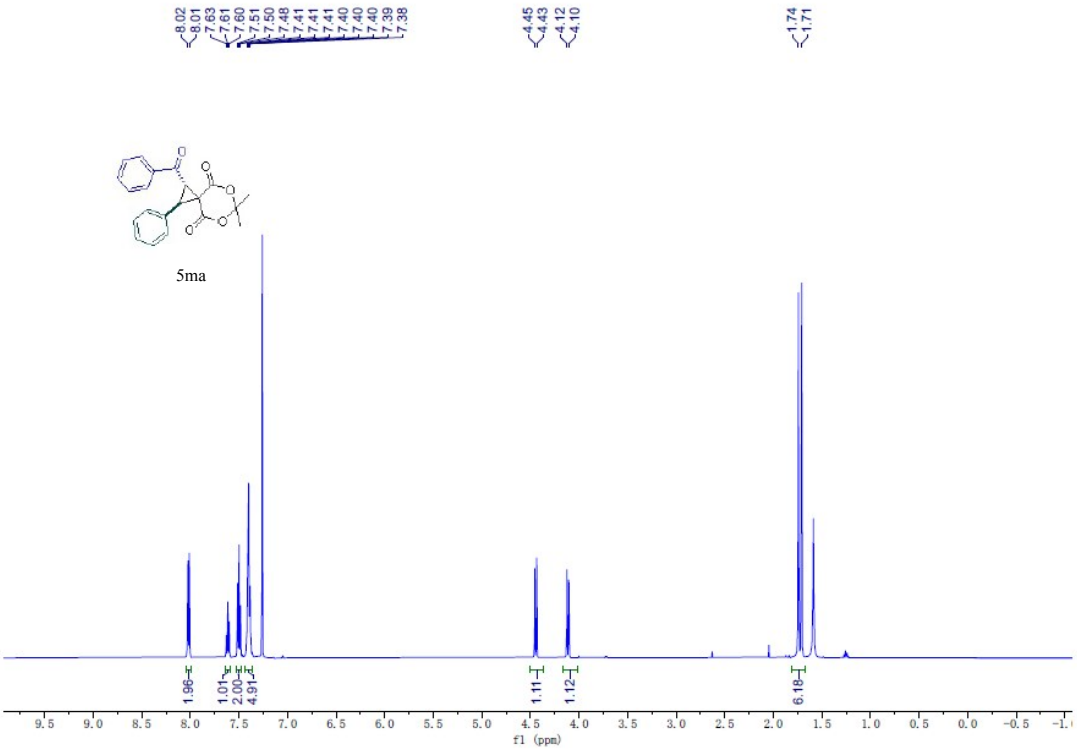

7.87
7.85
7.62
7.60
7.59
7.48
7.46
7.45
7.34
7.33
7.06
7.05
6.97
6.96
6.95
6.01
6.00
4.47
4.45
4.44
4.42
3.08
3.07
3.05
3.03
3.01
3.00
2.98
4ka
2.15
1.14
2.01
0.90
0.98
0.97
0.94
1.00
2.06
f1 (ppm)

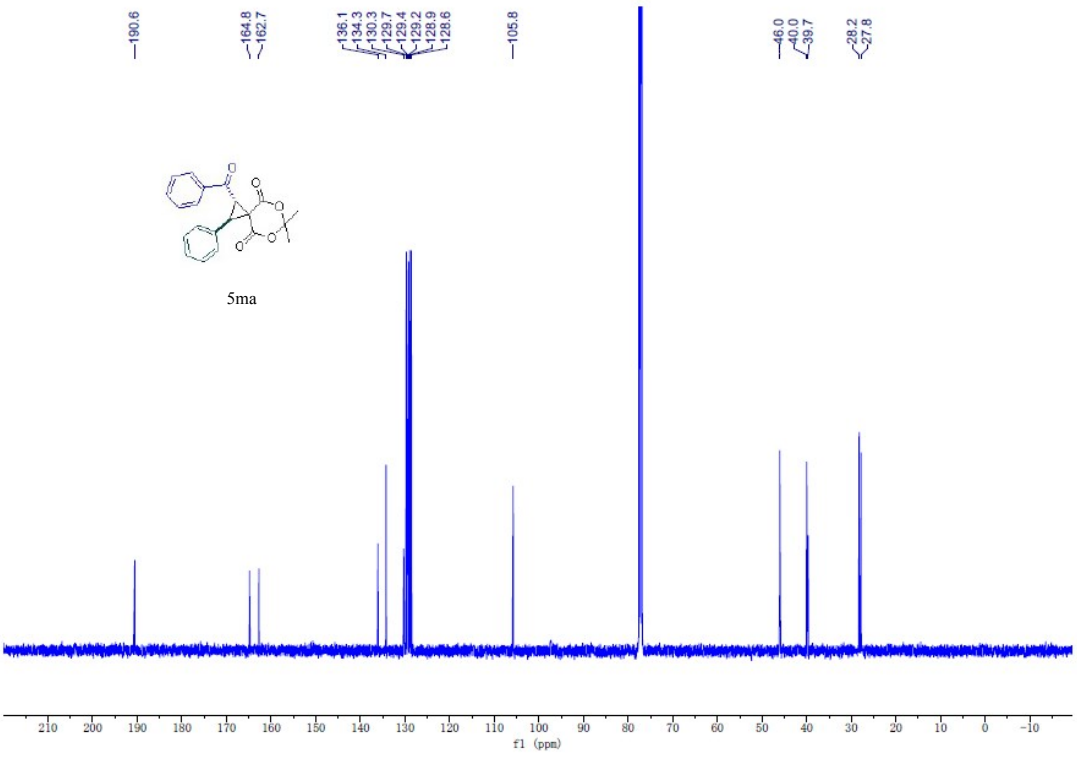

196.2
173.7
140.6
135.1
134.5
129.2
128.8
127.3
126.8
126.7
78.7
51.0
33.4
4ka
f1 (ppm)

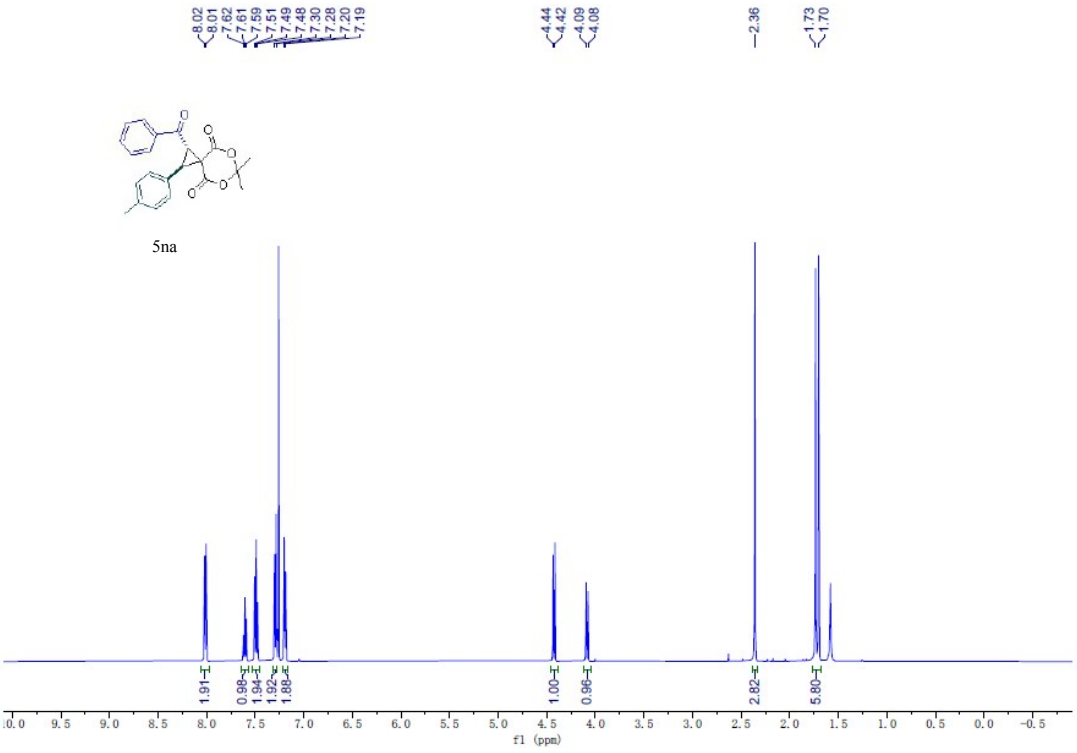

7.89
7.87
7.63
7.62
7.60
7.49
7.48
7.46
6.40
6.39
6.27
6.26
5.72
5.71
4.67
4.65
4.64
4.62
4.62
3.13
3.11
3.09
3.04
3.02
3.01
1.92
HO
4la
2.07
1.05
2.08
1.02
1.03
1.00
1.21
1.92
2.15
1.65
f1 (ppm)

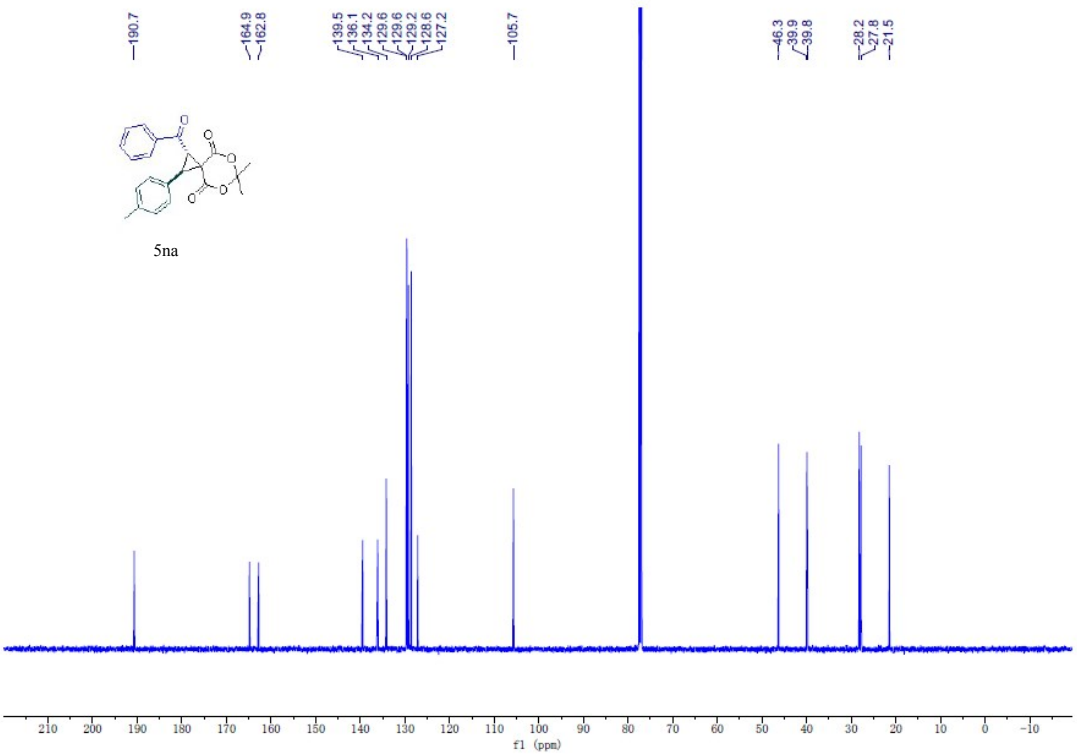

196.2
174.3
155.9
149.3
135.0
134.6
129.3
128.9
111.9
109.1
75.8
57.6
46.5
32.7
HO
4la
f1 (ppm)

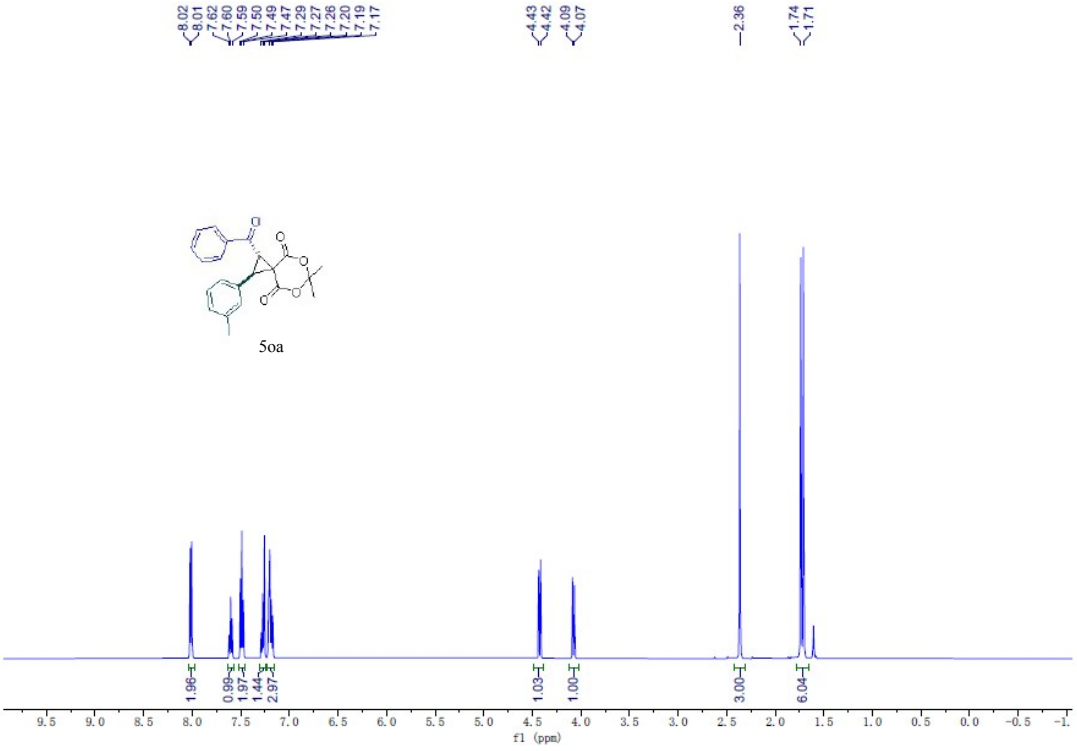
7.3. Copies of NMR Spectra for Compounds of 5ma-5j'a



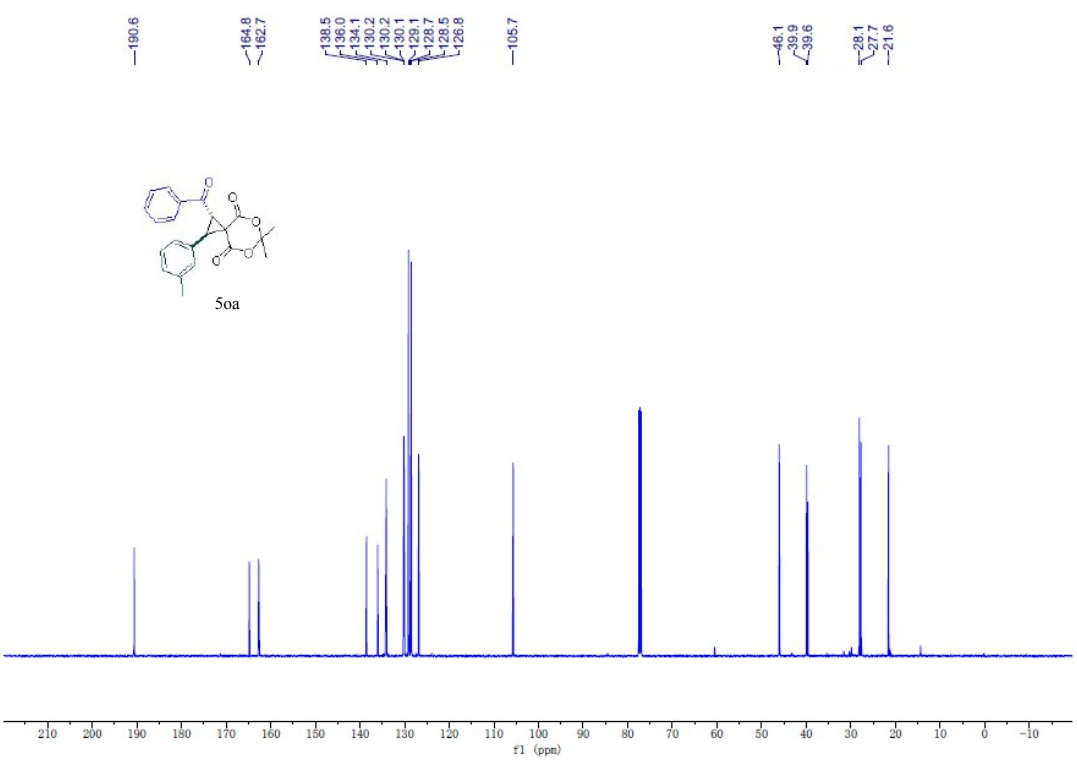



8.02
8.01
7.62
7.61
7.59
7.51
7.49
7.48
7.30
7.28
7.20
7.19
4.44
4.42
4.09
4.08
2.36
1.73
1.70
5na
1.91
0.98
1.94
1.92
1.88
1.00
0.96
2.82
5.80
f1 (ppm)

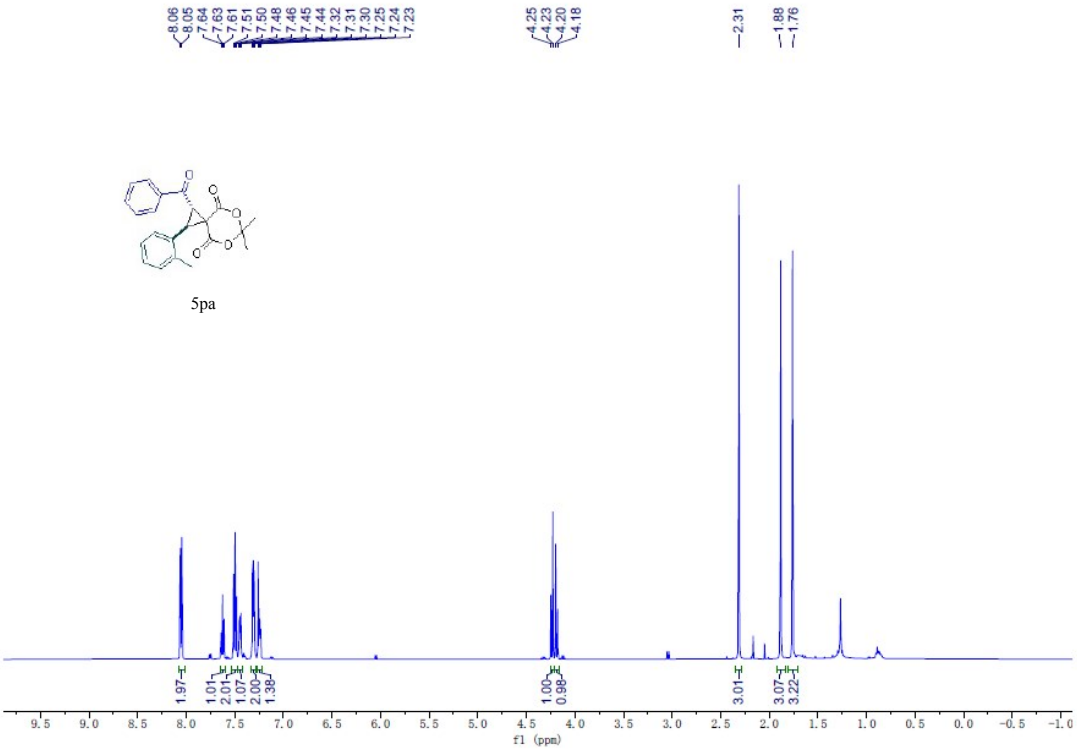

190.7
164.9
162.8
139.5
136.1
134.2
129.6
129.6
129.2
128.6
127.2
105.7
46.3
39.9
39.8
28.2
27.8
21.5
5na
f1 (ppm)


8.02
8.01
7.62
7.60
7.59
7.50
7.49
7.47
7.29
7.27
7.26
7.20
7.19
7.17
4.43
4.42
4.09
4.07
2.36
1.74
1.71
1.96
0.99
1.97
1.44
2.97
1.03
1.00
3.00
6.04
f1 (ppm)

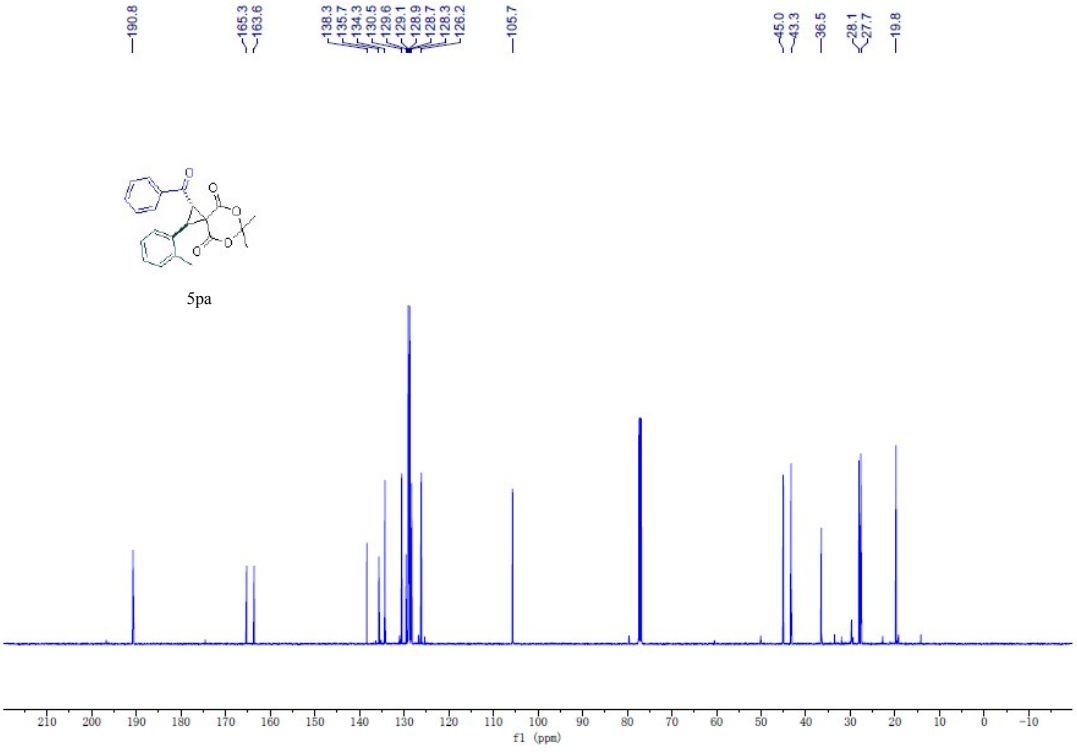
5oa


190.6
164.8
162.7
138.5
136.0
134.1
130.2
130.2
130.1
129.1
128.7
128.5
126.8
105.7
46.1
39.9
39.6
28.1
27.7
21.6
f1 (ppm)

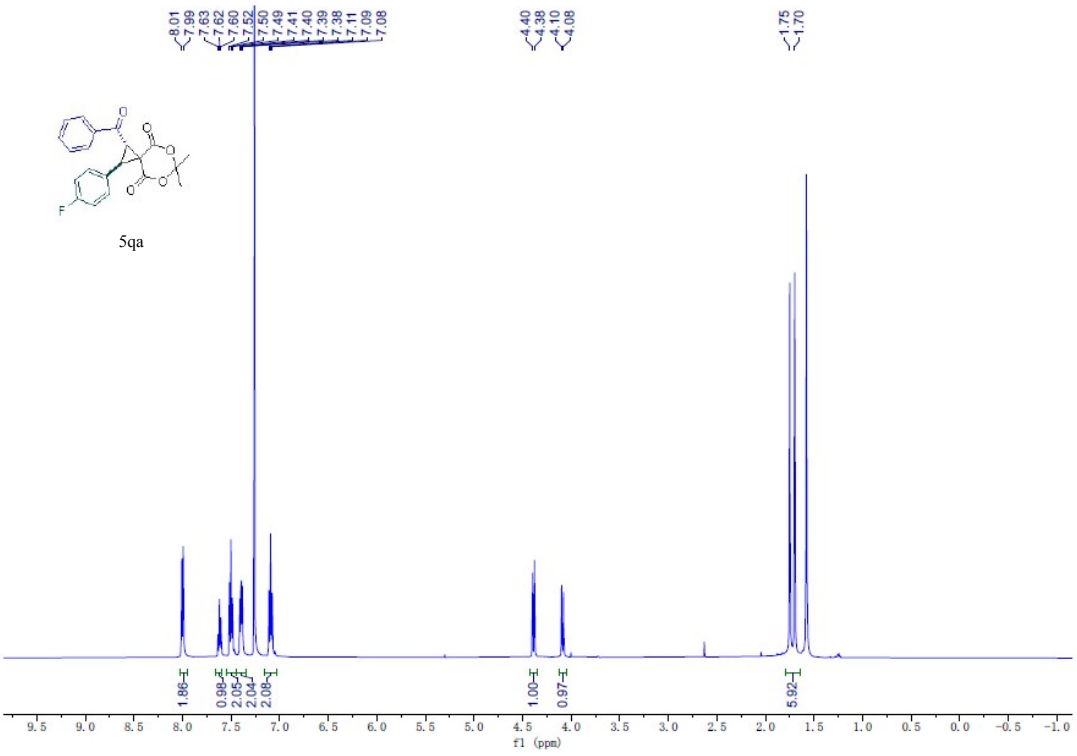
5oa


8.06
8.05
7.64
7.63
7.61
7.51
7.50
7.48
7.46
7.45
7.44
7.32
7.31
7.30
7.25
7.24
7.23
4.25
4.23
4.20
4.18
2.31
1.88
1.76
1.97
1.01
2.01
1.07
2.00
1.38
1.00
0.98
3.01
3.07
3.22
f1 (ppm)

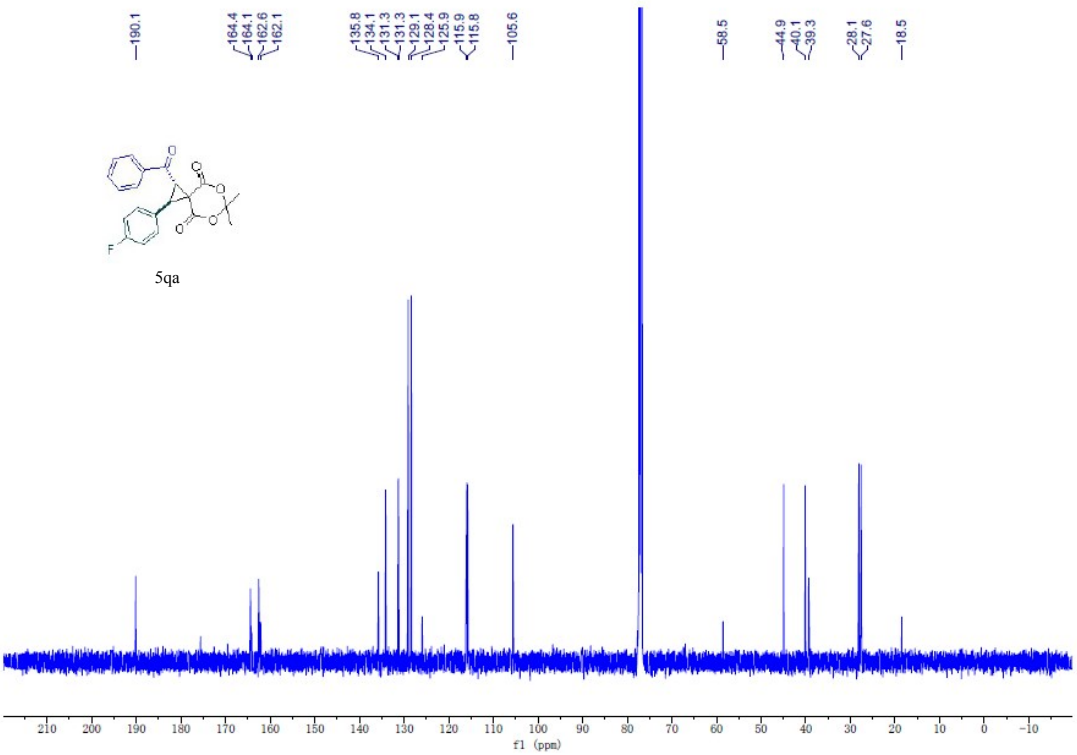
5pa


190.8
165.3
163.6
138.3
135.7
134.3
130.5
129.6
129.1
128.9
128.7
128.3
126.2
105.7
45.0
43.3
36.5
28.1
27.7
19.8
f1 (ppm)

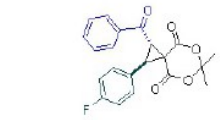
5pa


8.01
7.99
7.63
7.62
7.60
7.52
7.50
7.49
7.41
7.40
7.39
7.38
7.11
7.09
7.08
4.40
4.38
4.10
4.08
1.75
1.70
1.86
0.98
2.05
2.04
2.08
1.00
0.97
5.92
f1 (ppm)

5qa

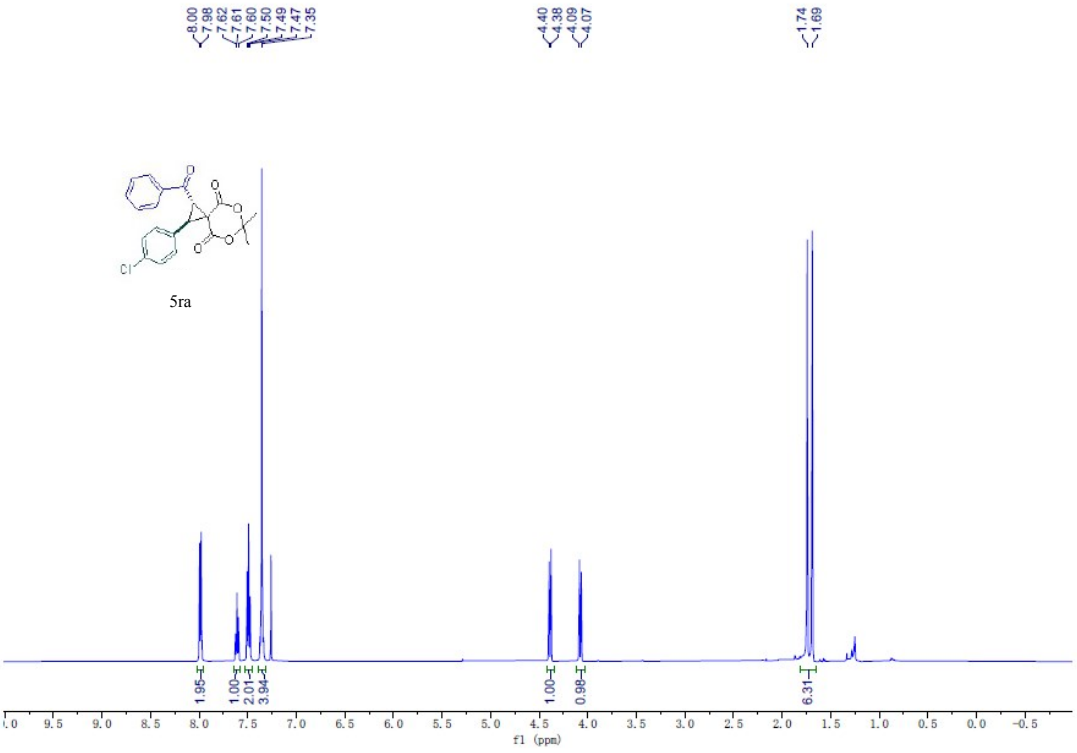

190.1
164.4
164.1
162.6
162.1
135.8
134.1
131.3
131.3
129.1
128.4
125.9
115.9
115.8
105.6
58.5
44.9
40.1
39.3
28.1
27.6
18.5
f1 (ppm)

5qa

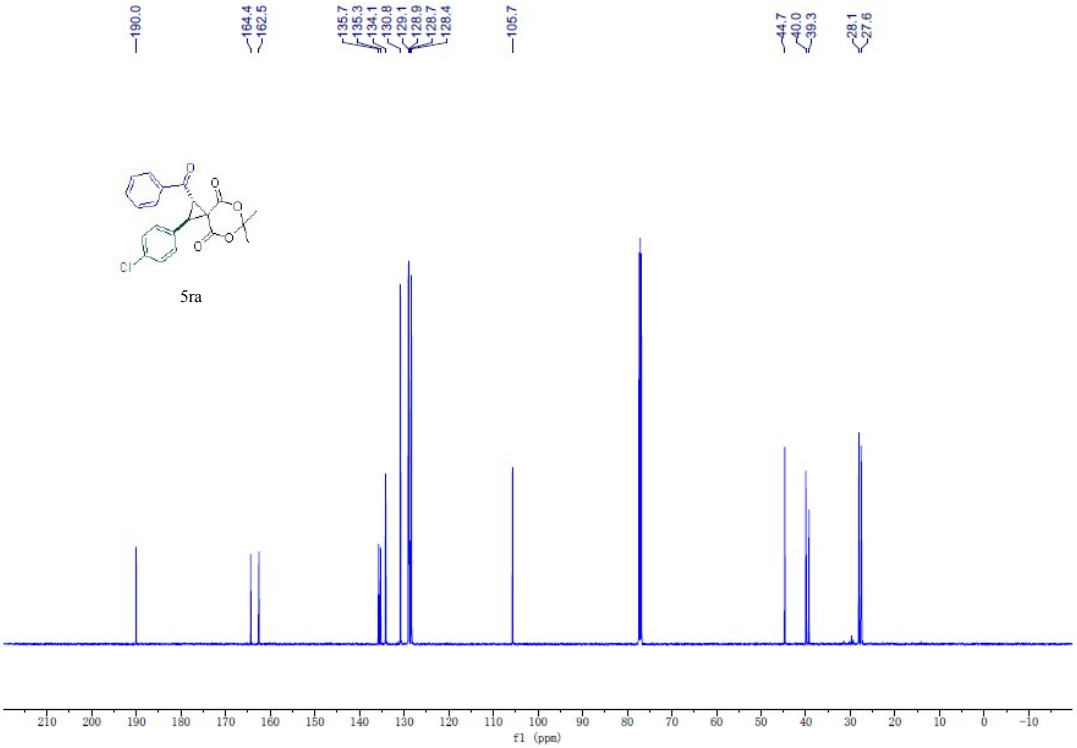


5qa

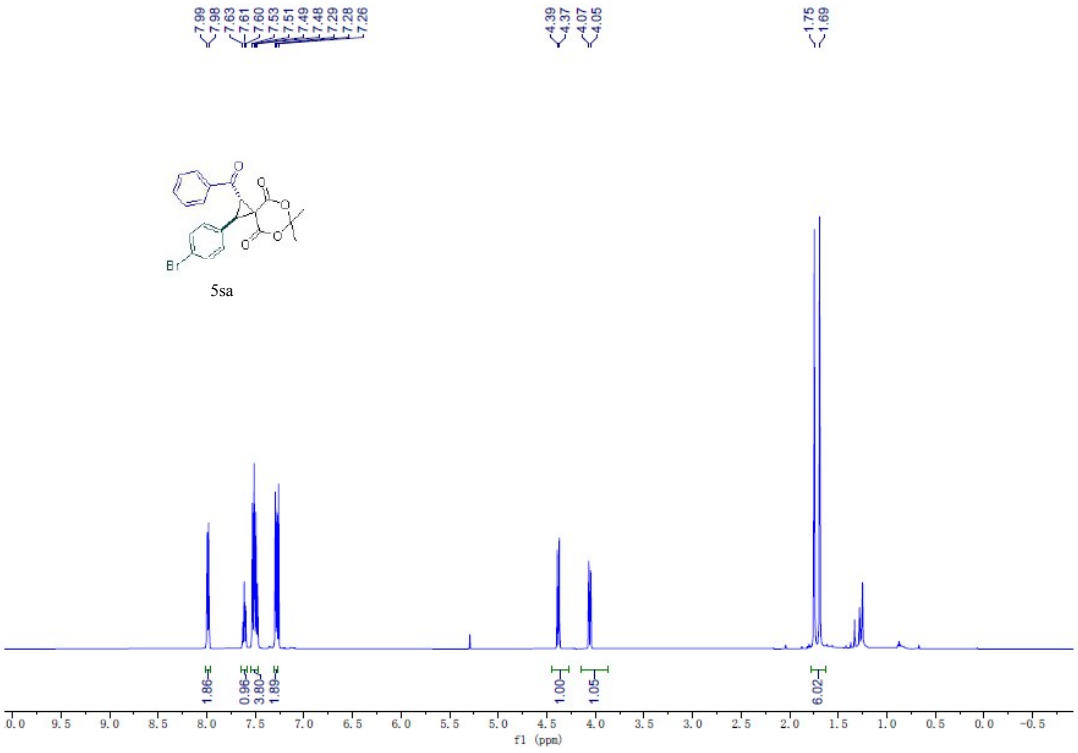
-111.60
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


8.00
7.98
7.62
7.61
7.60
7.50
7.49
7.47
7.35
4.40
4.38
4.09
4.07
1.74
1.69
1.95
1.00
2.01
3.94
1.00
0.98
6.31
f1 (ppm)

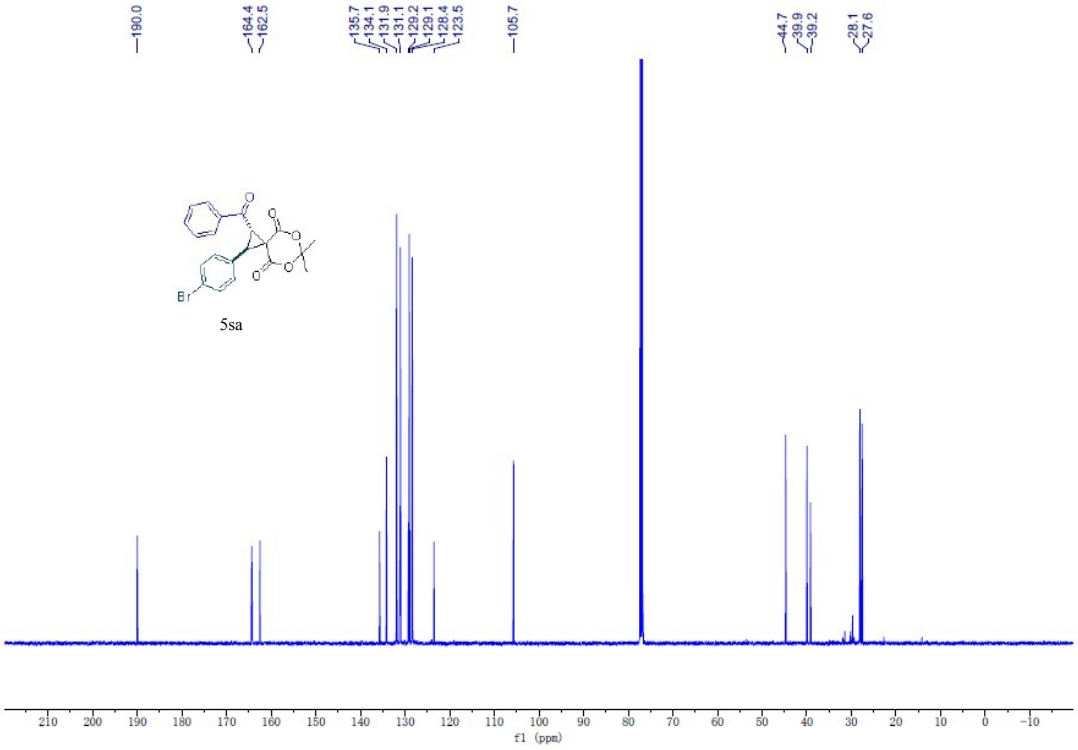
5ra


190.0
164.4
162.5
135.7
135.3
134.1
130.8
129.1
128.9
128.7
128.4
105.7
44.7
40.0
39.3
28.1
27.6
f1 (ppm)

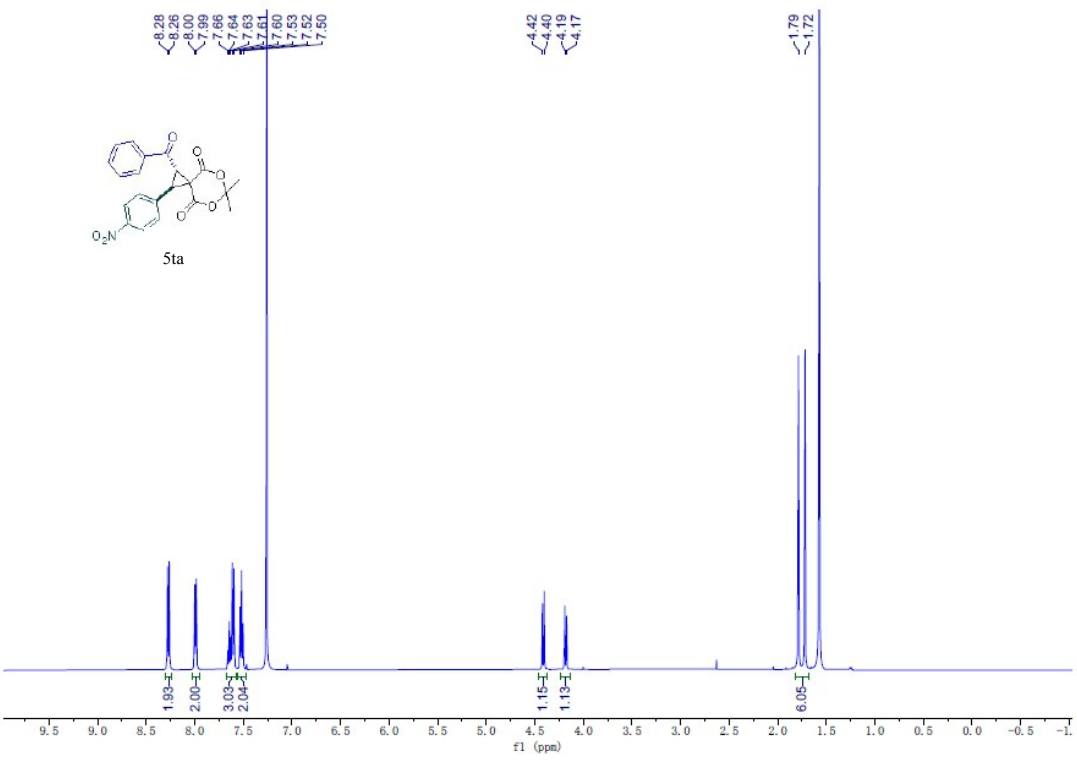
5ra


7.99
7.98
7.63
7.61
7.60
7.53
7.51
7.49
7.48
7.29
7.28
7.26
4.39
4.37
4.07
4.05
1.75
1.69
Br
1.86
0.96
3.80
1.89
1.00
1.05
6.02
f1 (ppm)

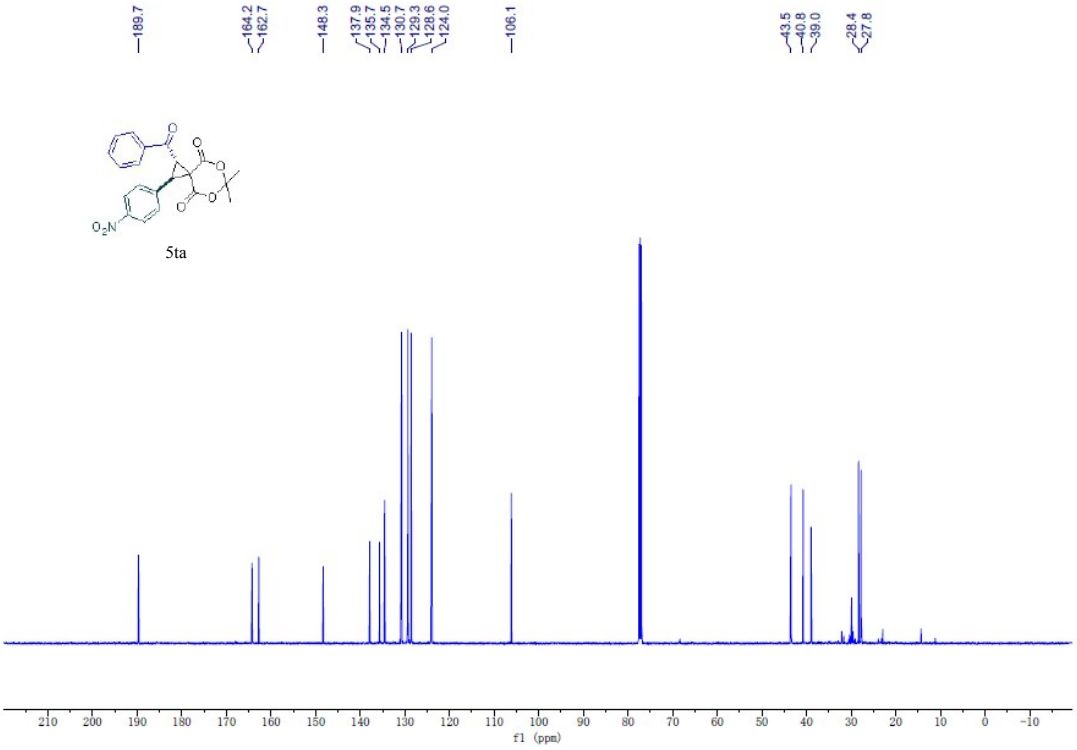
5sa


190.0
164.4
162.5
135.7
134.1
131.9
131.1
129.2
129.1
128.4
123.5
105.7
44.7
39.9
39.2
28.1
27.6
Br
f1 (ppm)

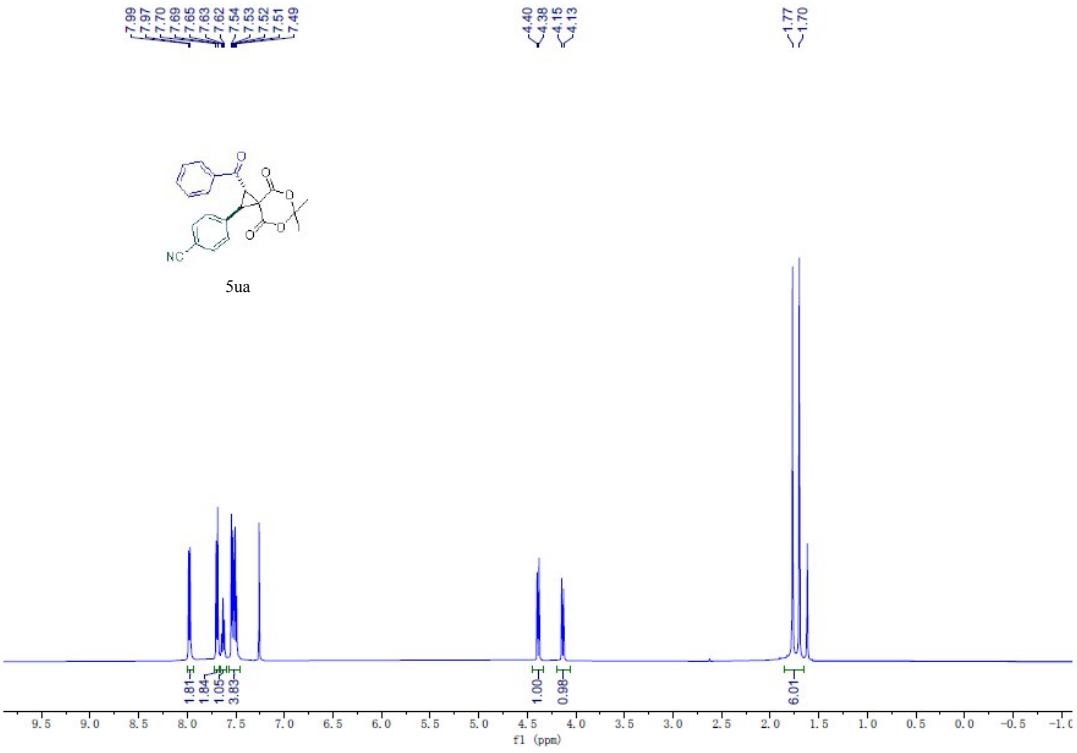
5sa


8.28
8.26
8.00
7.99
7.66
7.64
7.63
7.61
7.60
7.53
7.52
7.50
4.42
4.40
4.19
4.17
1.79
1.72
1.93
2.00
3.03
2.04
1.15
1.13
6.05
f1 (ppm)

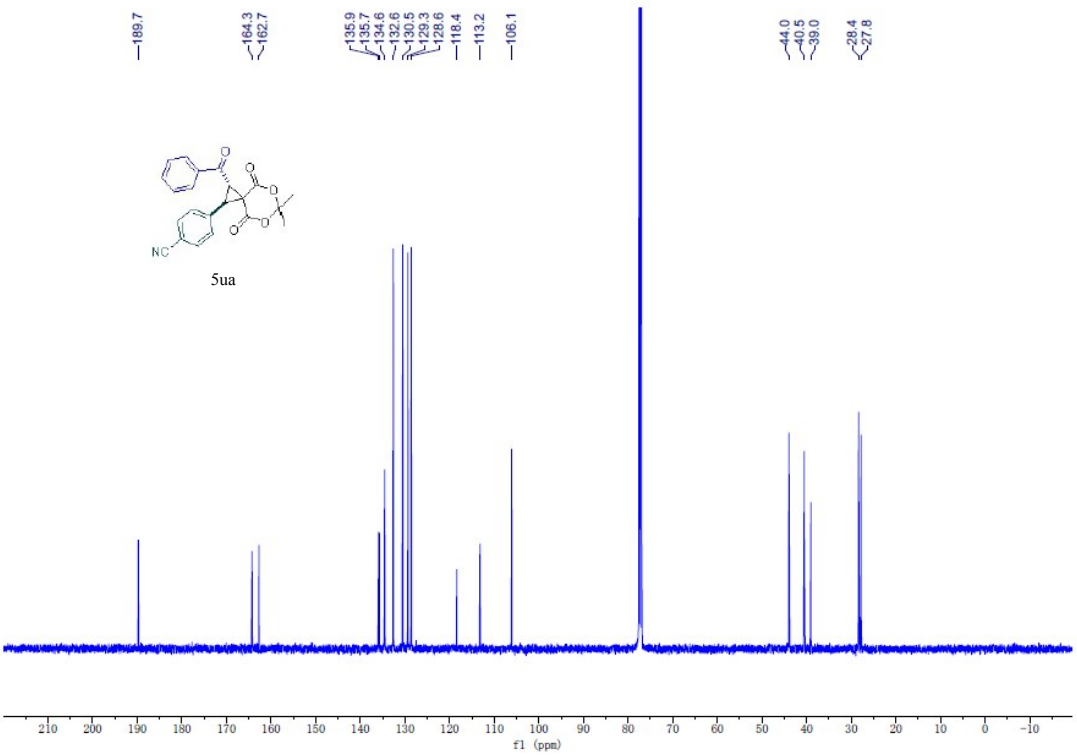
5ta


189.7
164.2
162.7
148.3
137.9
135.7
134.5
130.7
129.3
128.6
124.0
106.1
43.5
40.8
39.0
28.4
27.8
f1 (ppm)

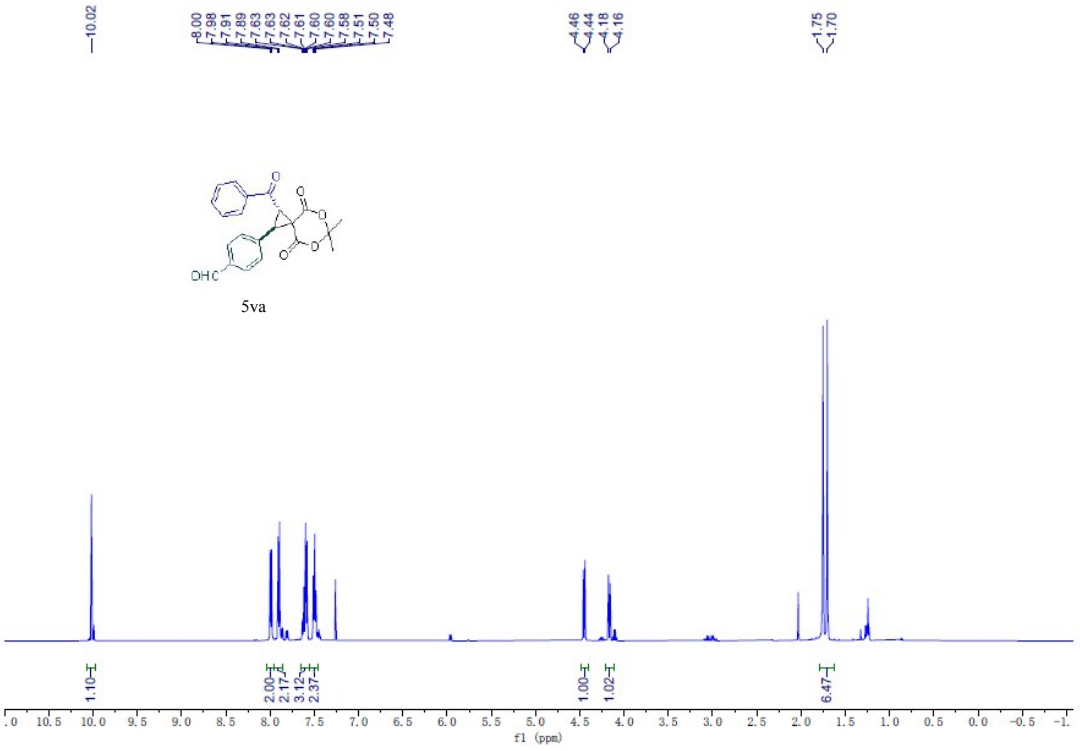
5ta


7.99
7.97
7.70
7.69
7.65
7.63
7.62
7.54
7.53
7.52
7.51
7.49
4.40
4.38
4.15
4.13
1.77
1.70
NC
1.81
1.84
1.05
3.83
1.00
0.98
6.01
f1 (ppm)

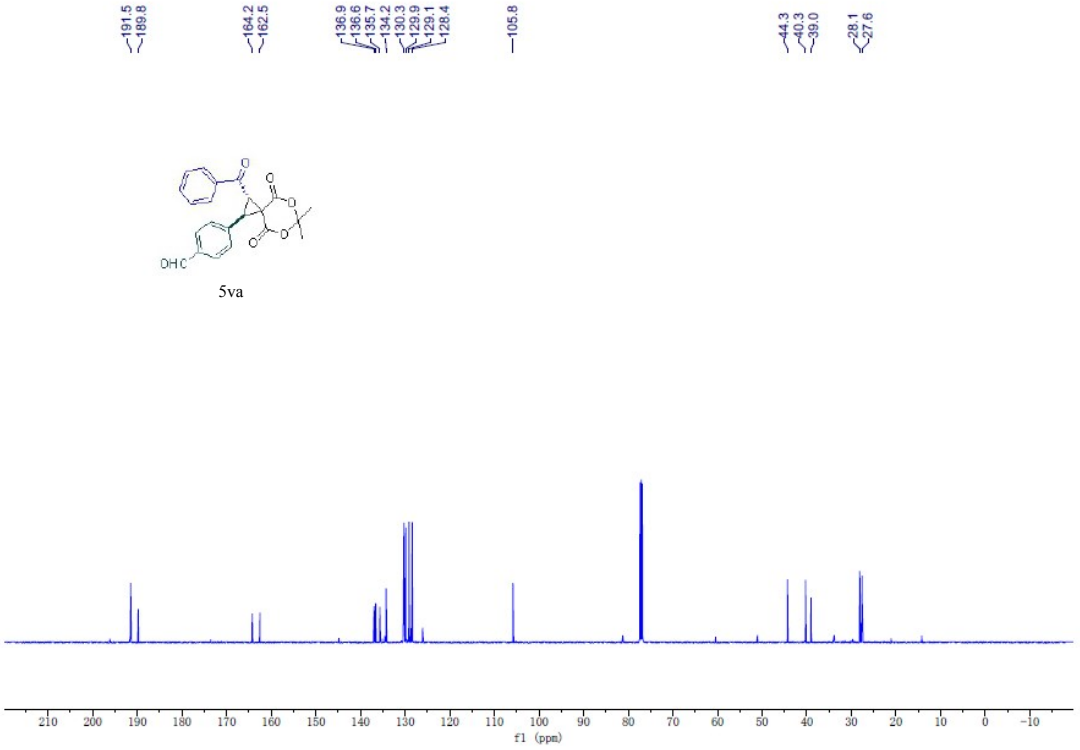
5ua


189.7
164.3
162.7
135.9
135.7
134.6
132.6
130.5
129.3
128.6
118.4
113.2
106.1
44.0
40.5
39.0
28.4
27.8
NC
f1 (ppm)

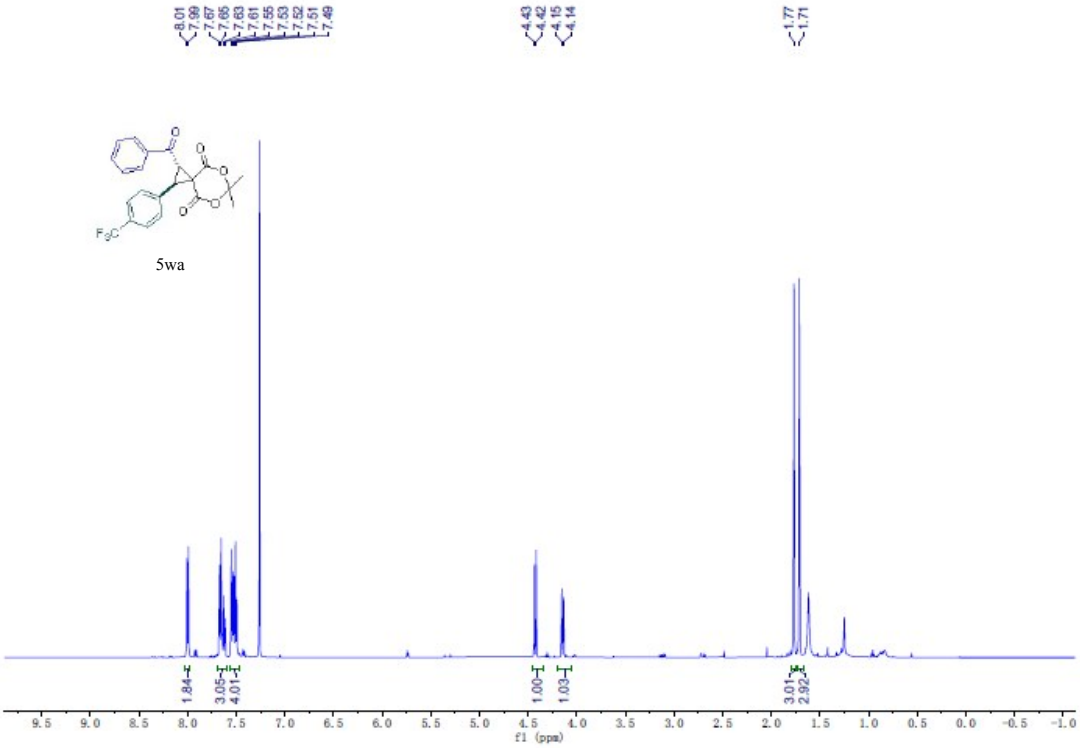
5ua


10.02
8.00
7.98
7.91
7.89
7.63
7.63
7.62
7.61
7.60
7.60
7.58
7.51
7.50
7.48
4.46
4.44
4.18
4.16
1.75
1.70
OHC
1.10
2.00
2.17
3.12
2.37
1.00
1.02
6.47
f1 (ppm)

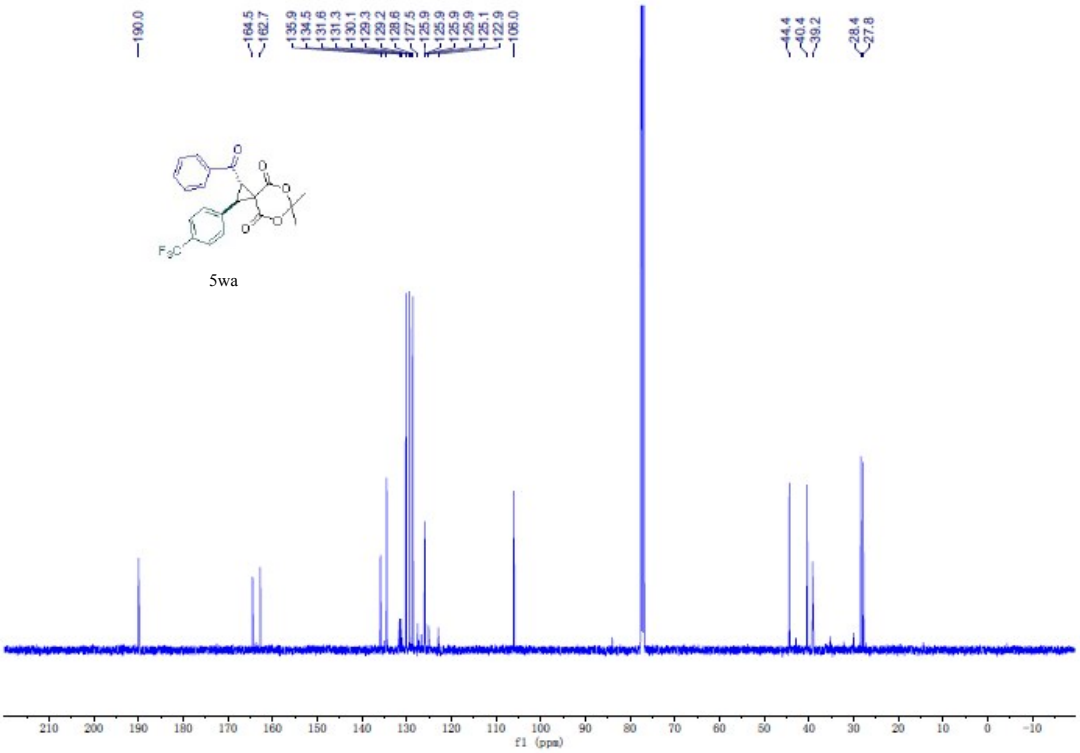
5va


191.5
189.8
164.2
162.5
136.9
136.6
135.7
134.2
130.3
129.9
129.1
128.4
105.8
44.3
40.3
39.0
28.1
27.6
OHC
f1 (ppm)

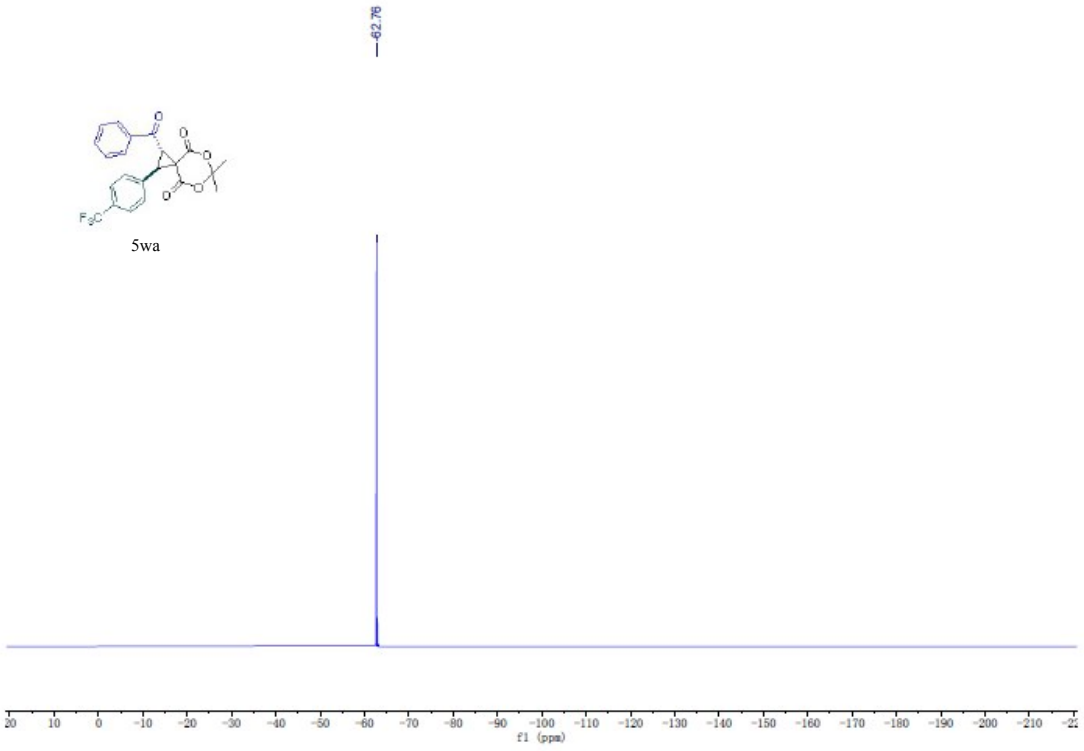
5va


8.01
7.99
7.67
7.65
7.63
7.61
7.55
7.53
7.52
7.51
7.49
4.43
4.42
4.15
4.14
1.77
1.71
1.84
3.05
4.01
1.00
1.03
3.01
2.92
f1 (ppm)

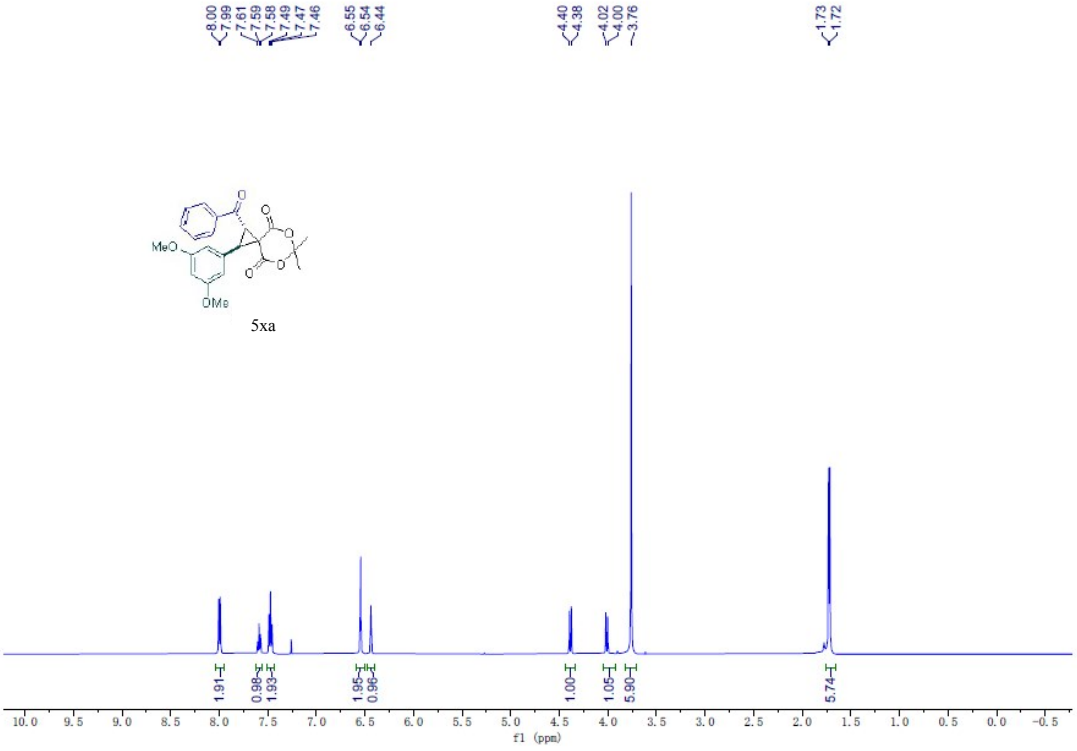
5wa


190.0
164.5
162.7
135.9
134.5
131.6
131.3
130.1
129.3
129.2
128.6
127.5
125.9
125.9
125.9
125.9
125.1
122.9
106.0
44.4
40.4
39.2
28.4
27.8
f1 (ppm)

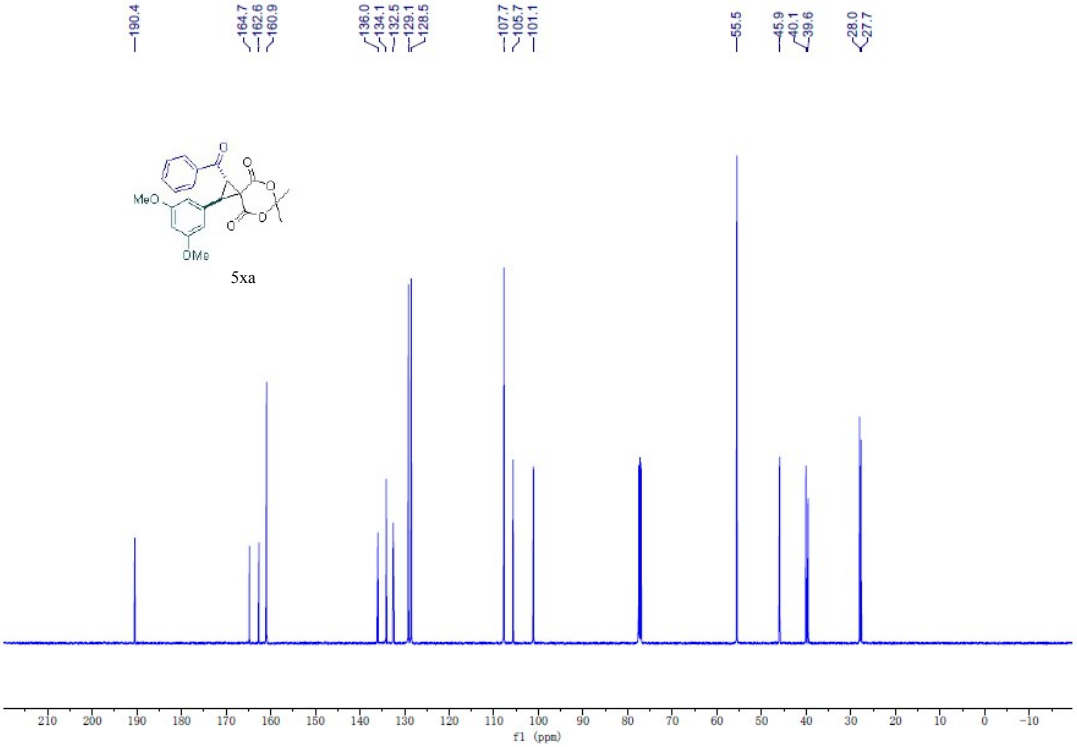
5wa


-62.76
F3C
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

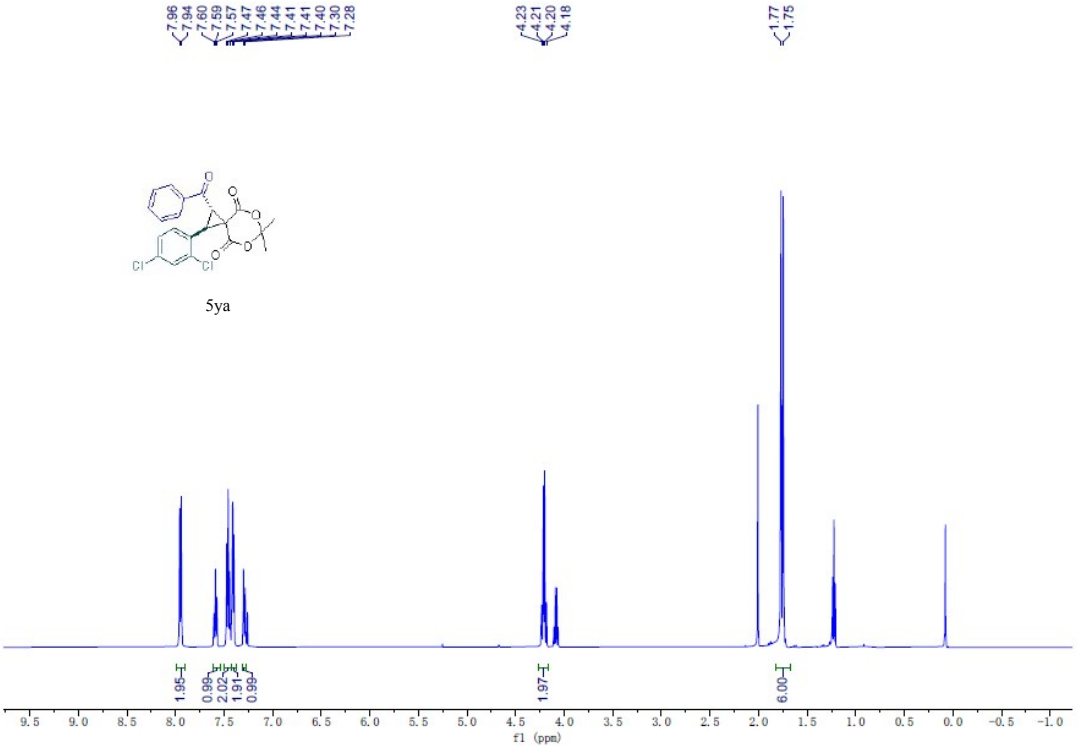
5wa


8.00
7.99
7.61
7.59
7.58
7.49
7.47
7.46
6.55
6.54
6.44
4.40
4.38
4.02
4.00
3.76
1.73
1.72
MeO
OMe
O
O
O
O
O
1.91
0.98
1.93
1.95
0.96
1.00
1.05
5.90
5.74
f1 (ppm)

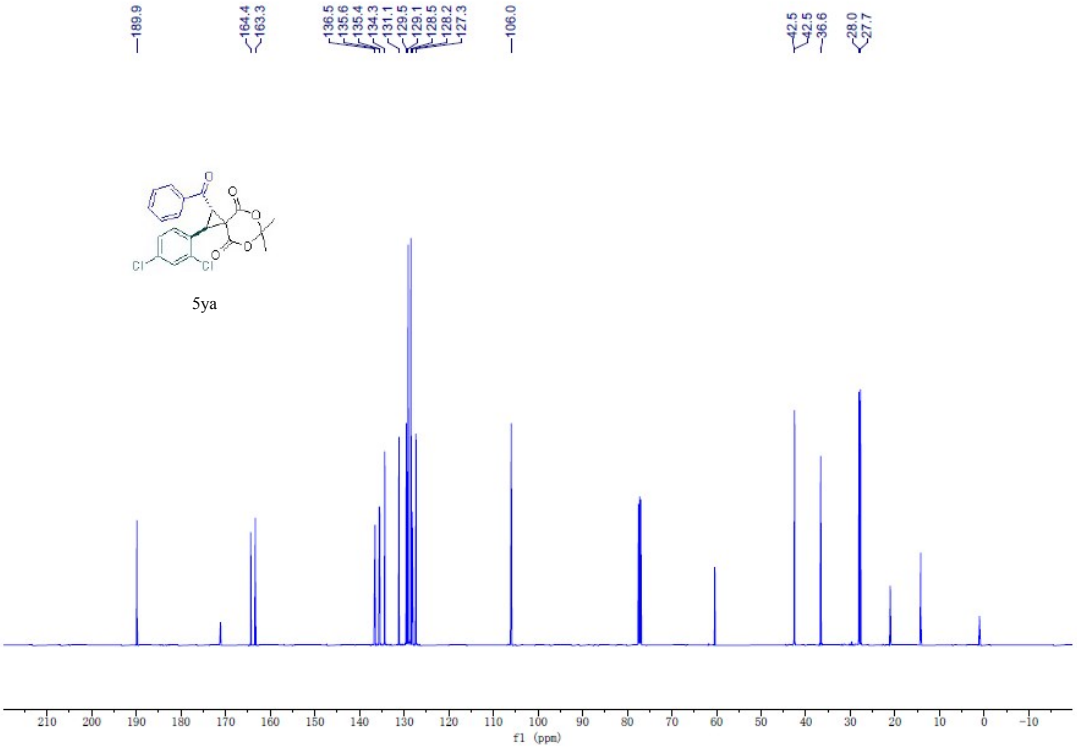
5xa


190.4
164.7
162.6
160.9
136.0
134.1
132.5
129.1
128.5
107.7
105.7
101.1
55.5
45.9
40.1
39.6
28.0
27.7
MeO
OMe
O
O
O
O
O
f1 (ppm)

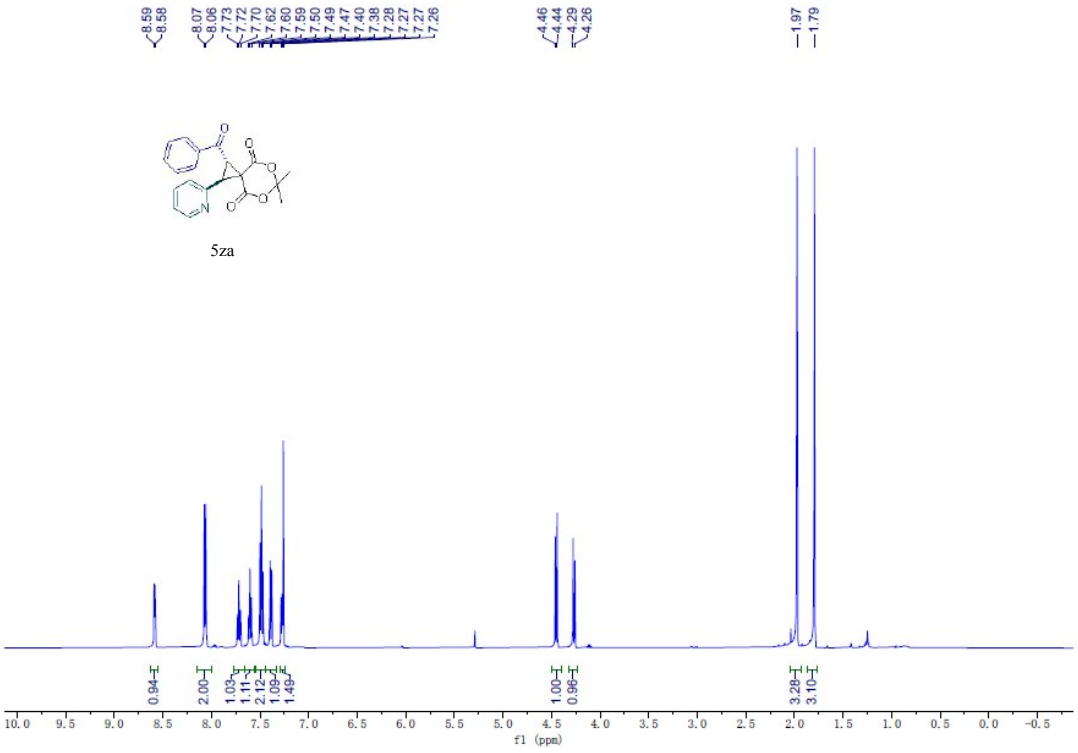
5xa


7.96
7.94
7.60
7.59
7.57
7.47
7.46
7.44
7.41
7.40
7.30
7.28
4.23
4.21
4.20
4.18
1.77
1.75
1.95
0.99
2.02
1.91
0.99
1.97
6.00
f1 (ppm)

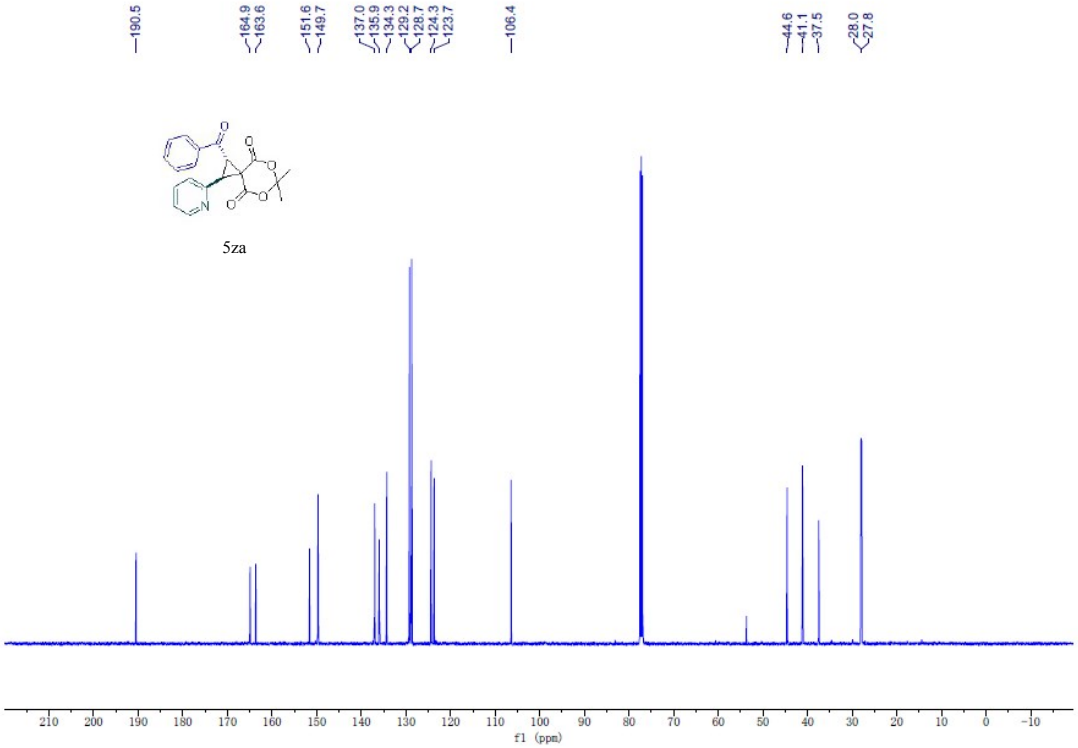
5ya


189.9
164.4
163.3
136.5
135.6
135.4
134.3
131.1
129.5
129.1
128.5
128.2
127.3
106.0
42.5
42.5
36.6
28.0
27.7
f1 (ppm)

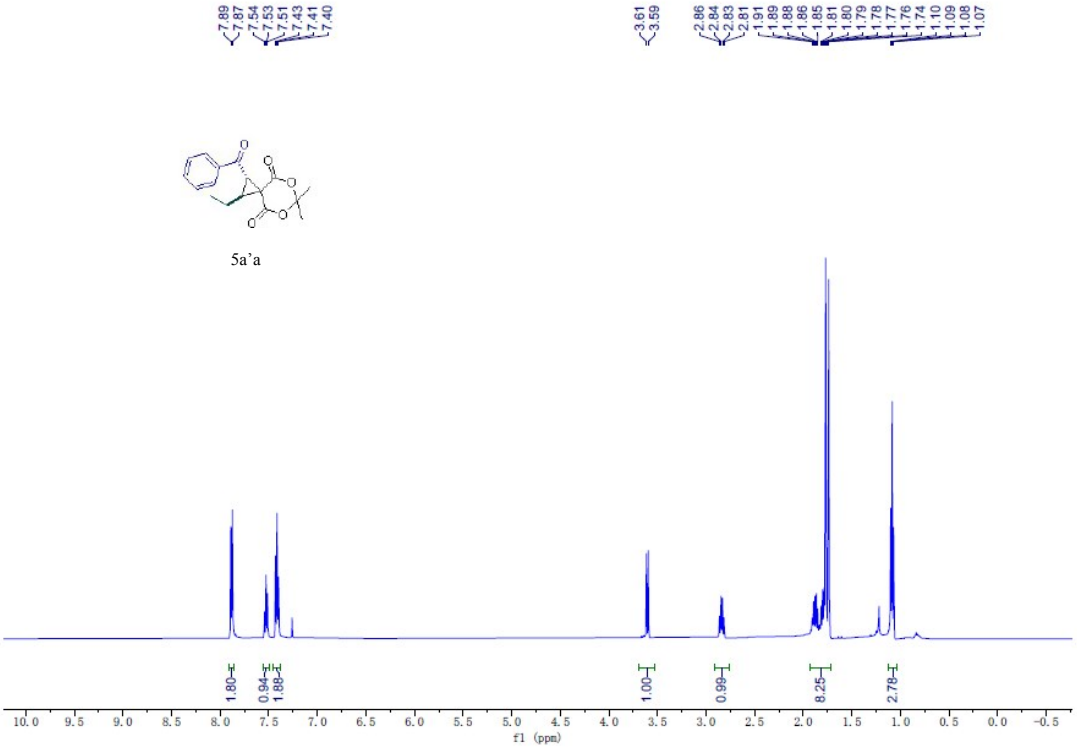
5ya

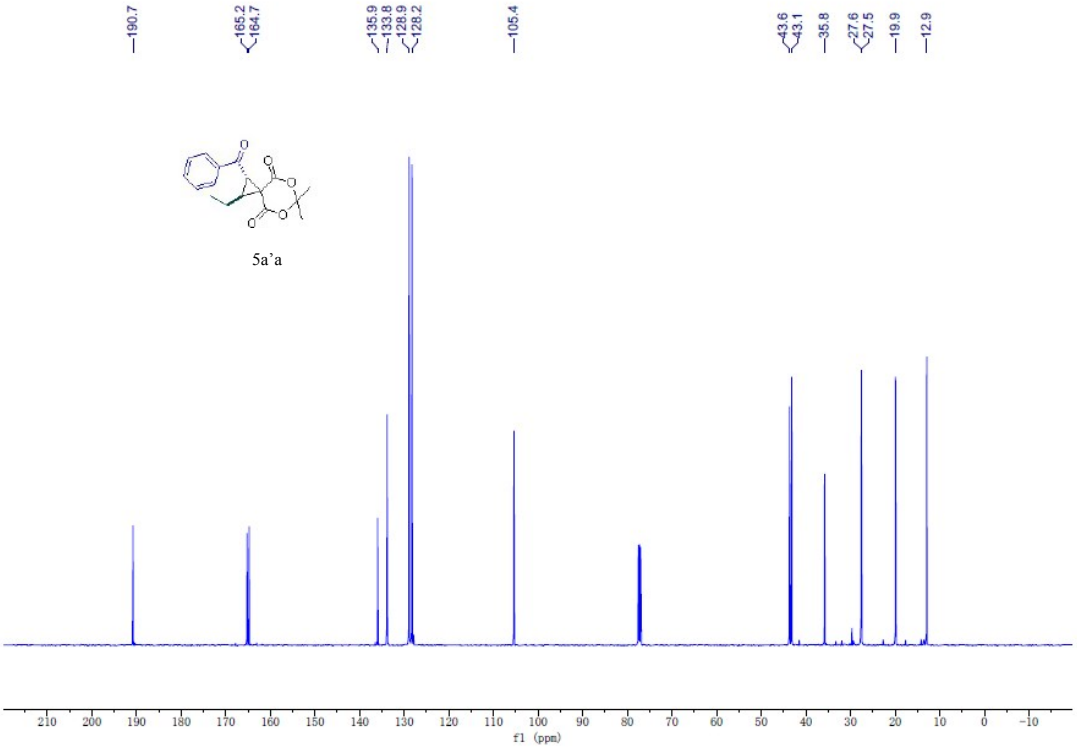

8.59
8.58
8.07
8.06
7.73
7.72
7.70
7.62
7.60
7.59
7.50
7.49
7.47
7.40
7.38
7.28
7.27
7.27
7.26
4.46
4.44
4.29
4.26
1.97
1.79
0.94
2.00
1.03
1.11
2.12
1.09
1.49
1.00
0.96
3.28
3.10
f1 (ppm)

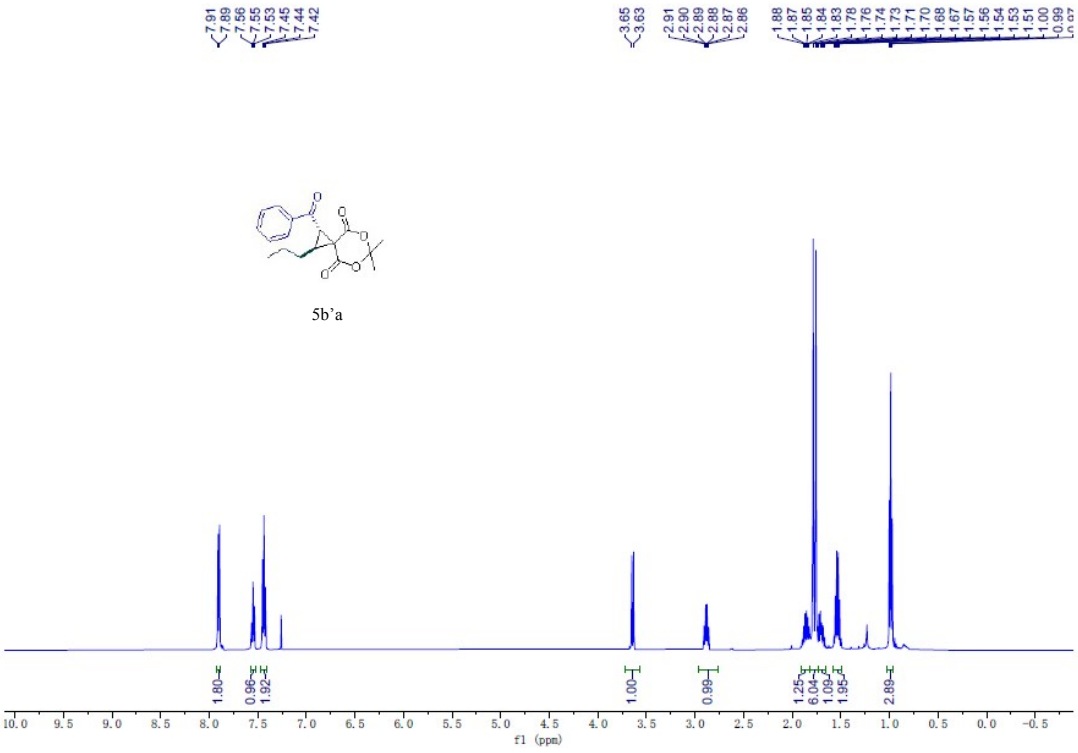
5za


190.5
164.9
163.6
151.6
149.7
137.0
135.9
134.3
129.2
128.7
124.3
123.7
106.4
44.6
41.1
37.5
28.0
27.8
f1 (ppm)

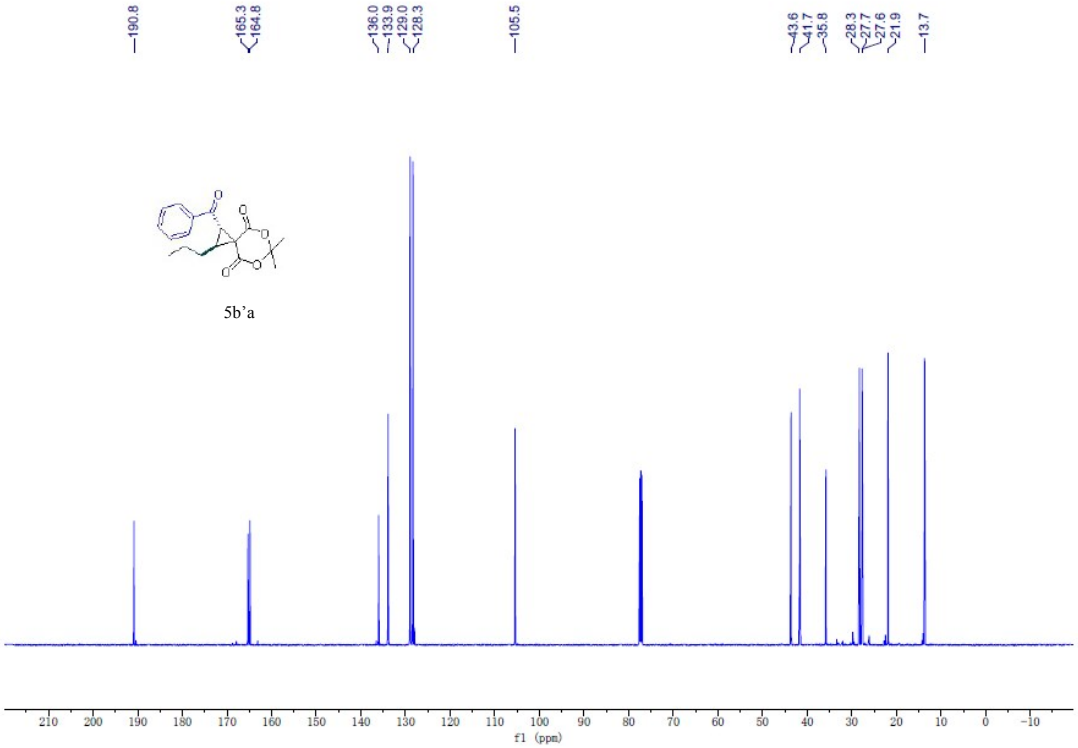
5za


7.89
7.87
7.54
7.53
7.51
7.43
7.41
7.40
3.61
3.59
2.86
2.84
2.83
2.81
1.91
1.89
1.88
1.86
1.85
1.81
1.80
1.79
1.78
1.77
1.76
1.74
1.10
1.09
1.08
1.07
5a'a
1.80
0.94
1.88
1.00
0.99
8.25
2.78
f1 (ppm)

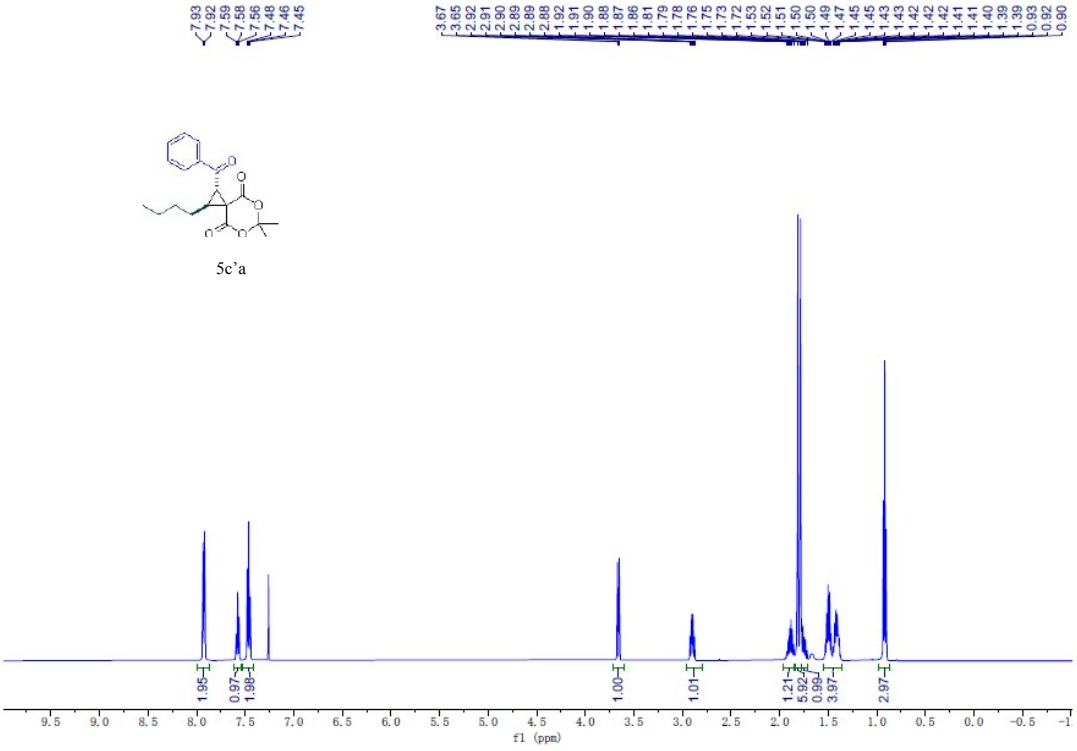

190.7
165.2
164.7
135.9
133.8
128.9
128.2
105.4
43.6
43.1
35.8
27.6
27.5
19.9
12.9
5a'a
f1 (ppm)


7.91
7.89
7.56
7.55
7.53
7.45
7.44
7.42
3.65
3.63
2.91
2.90
2.89
2.88
2.87
2.86
1.88
1.87
1.85
1.84
1.83
1.78
1.76
1.74
1.73
1.71
1.70
1.68
1.67
1.57
1.56
1.54
1.53
1.51
1.00
0.99
1.80
0.96
1.92
1.00
0.99
1.25
6.04
1.09
1.95
2.89
f1 (ppm)

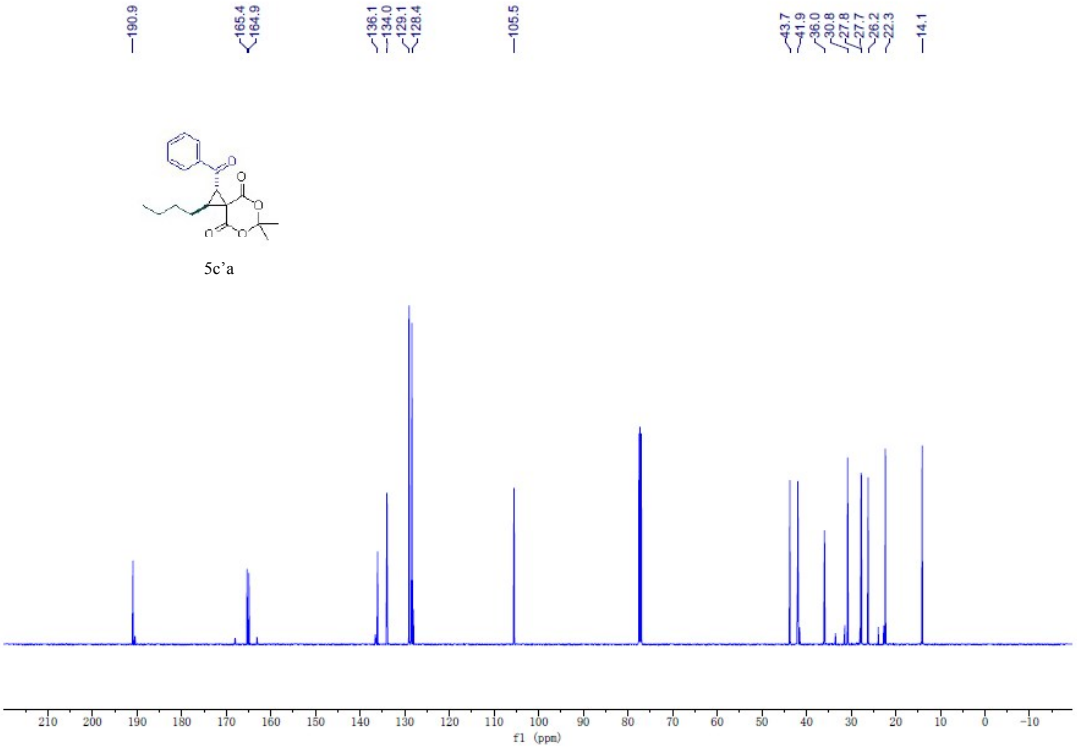
5b'a


190.8
165.3
164.8
136.0
133.9
129.0
128.3
105.5
43.6
41.7
35.8
28.3
27.7
27.6
21.9
13.7
f1 (ppm)

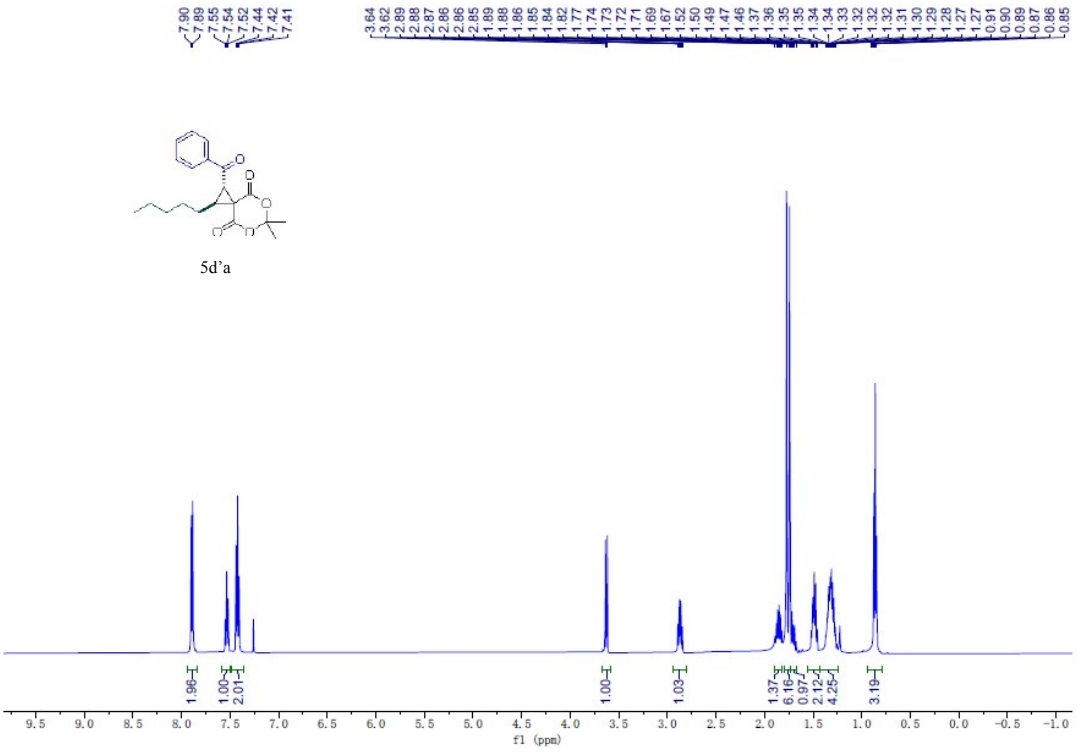
5b'a


7.93
7.92
7.59
7.58
7.56
7.48
7.46
7.45
3.67
3.65
2.92
2.91
2.90
2.89
2.89
2.88
1.92
1.91
1.90
1.88
1.87
1.86
1.81
1.79
1.78
1.76
1.75
1.73
1.72
1.53
1.52
1.51
1.50
1.50
1.49
1.47
1.45
1.45
1.43
1.43
1.42
1.42
1.42
1.41
1.41
1.40
1.39
0.93
0.92
0.90
1.96
0.97
1.98
1.00
1.01
1.21
5.92
0.99
3.97
2.97
f1 (ppm)

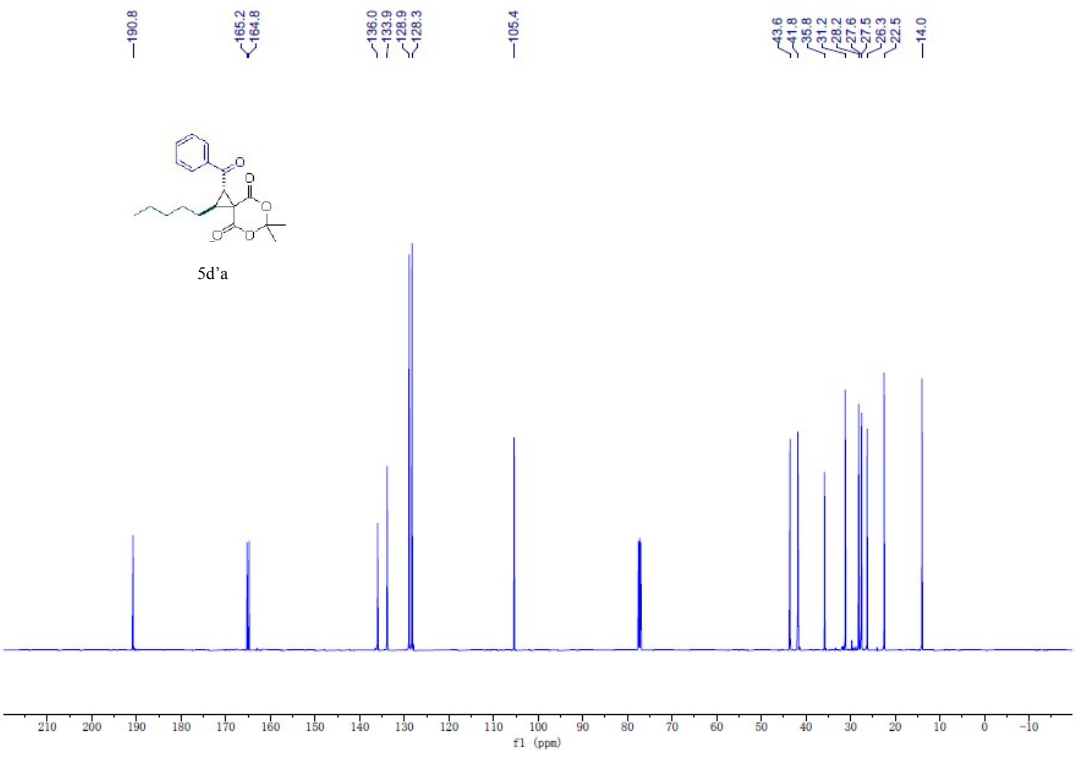
5c'a


190.9
165.4
164.9
136.1
134.0
129.1
128.4
105.5
43.7
41.9
36.0
30.8
27.8
27.7
26.2
22.3
14.1
f1 (ppm)

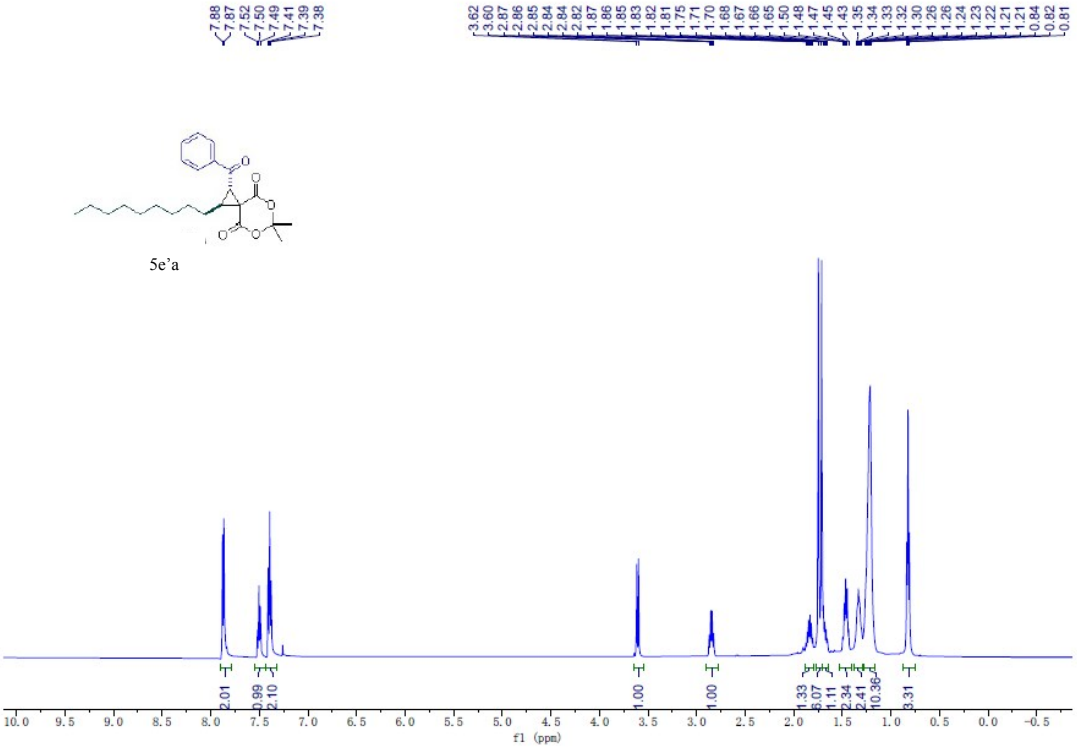
5c'a

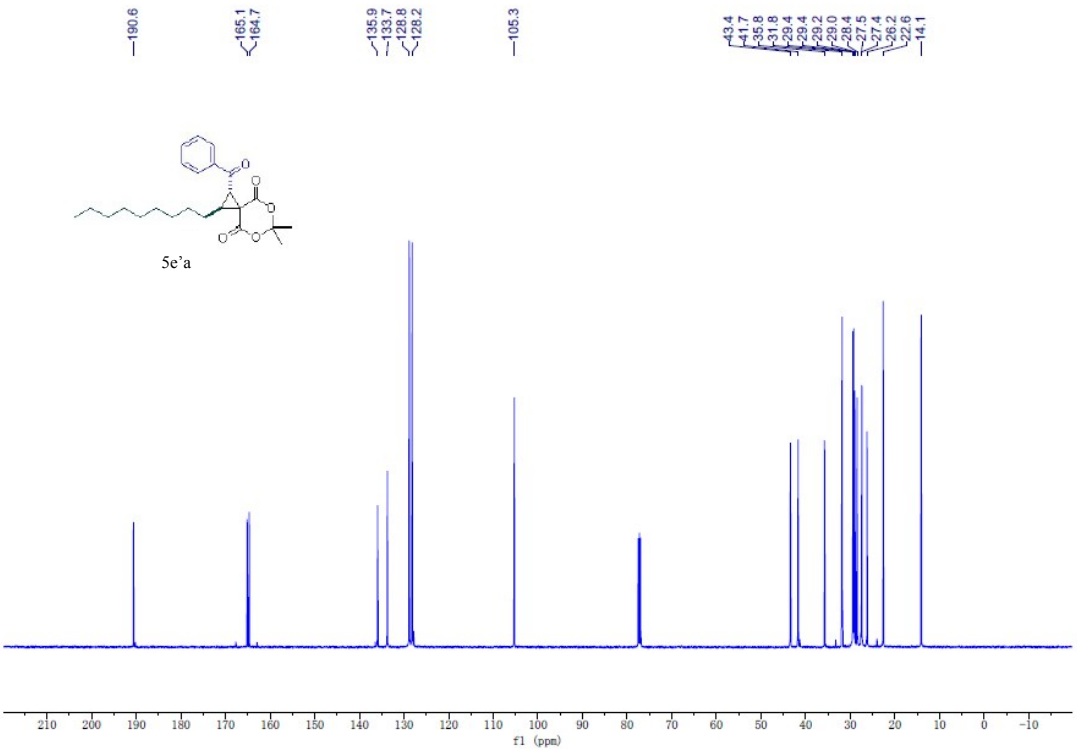

7.90
7.89
7.55
7.54
7.52
7.44
7.42
7.41
3.64
3.62
2.89
2.88
2.87
2.86
2.86
2.85
1.89
1.88
1.86
1.85
1.84
1.82
1.77
1.74
1.73
1.72
1.71
1.69
1.67
1.52
1.50
1.50
1.49
1.47
1.46
1.37
1.36
1.35
1.35
1.34
1.34
1.33
1.32
1.32
1.32
1.31
1.30
1.29
1.28
1.27
1.27
0.91
0.90
0.89
0.87
0.86
0.85
1.96
1.00
2.01
1.00
1.03
1.37
6.16
0.97
2.12
4.25
3.19
f1 (ppm)

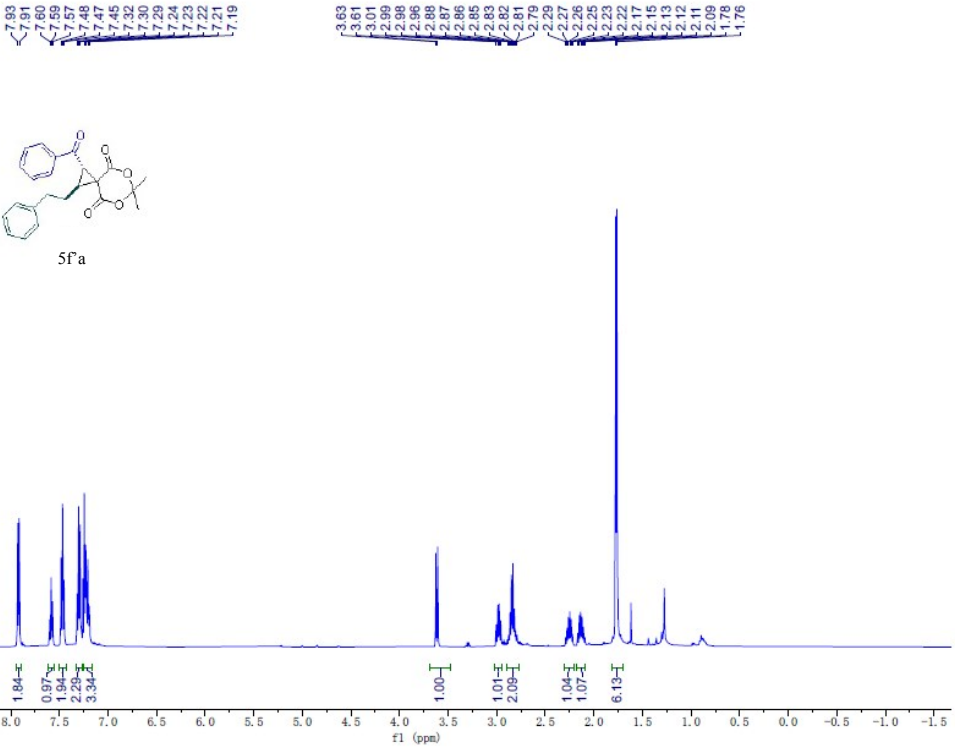
5d'a

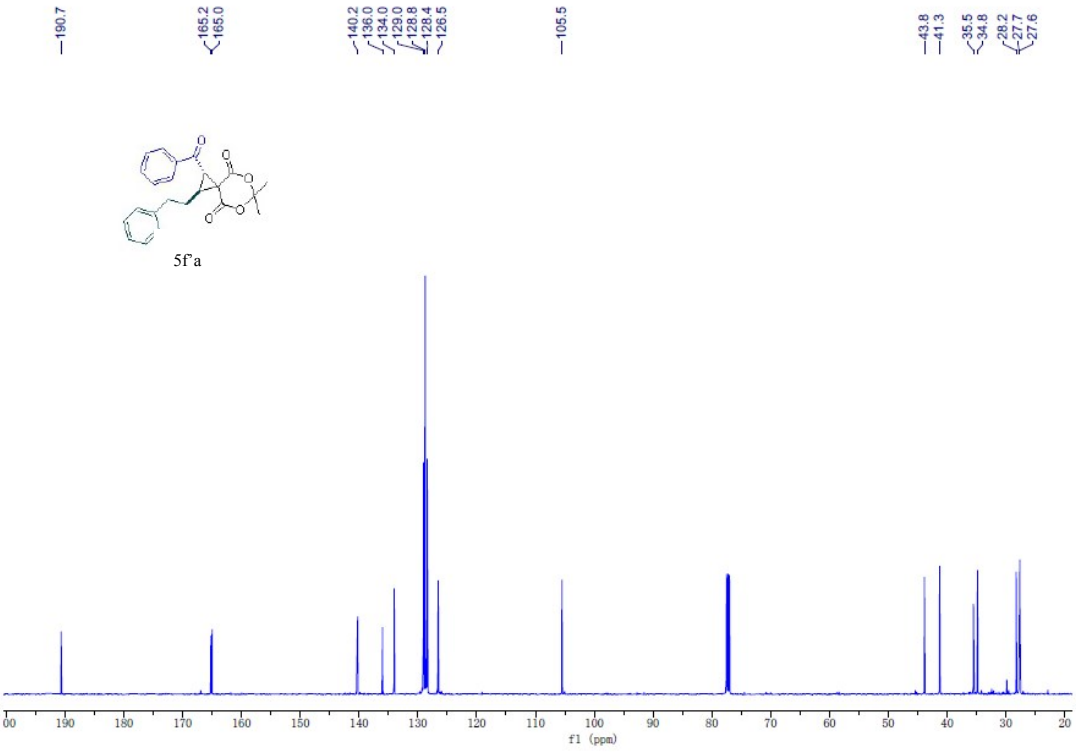

190.8
165.2
164.8
136.0
133.9
128.9
128.3
105.4
43.6
41.8
35.8
31.2
28.2
27.6
27.5
26.3
22.5
14.0
f1 (ppm)

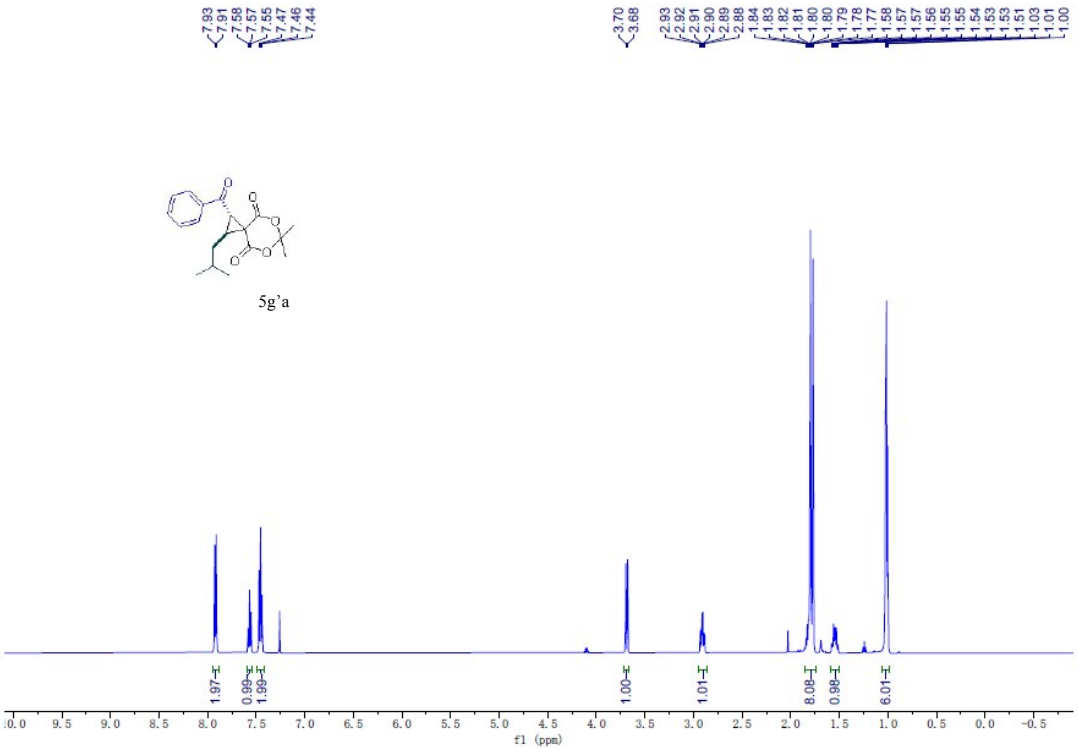
5d'a

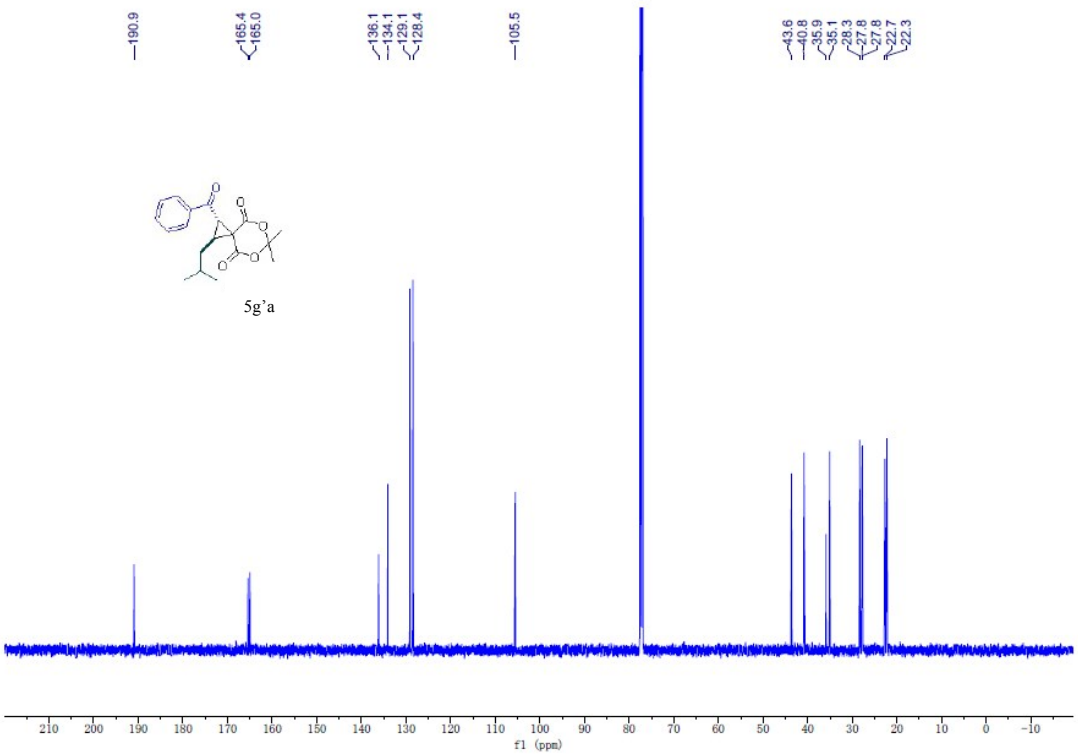

7.88
7.87
7.52
7.50
7.49
7.41
7.39
7.38
3.62
3.60
2.87
2.86
2.85
2.84
2.84
2.82
1.87
1.86
1.85
1.83
1.82
1.81
1.75
1.71
1.70
1.68
1.67
1.66
1.65
1.50
1.48
1.47
1.45
1.43
1.35
1.34
1.33
1.32
1.30
1.26
1.26
1.24
1.23
1.22
1.21
1.21
0.84
0.82
0.81
5e'a
2.01
0.99
2.10
1.00
1.00
1.33
6.07
1.11
2.34
2.41
10.36
3.31
f1 (ppm)

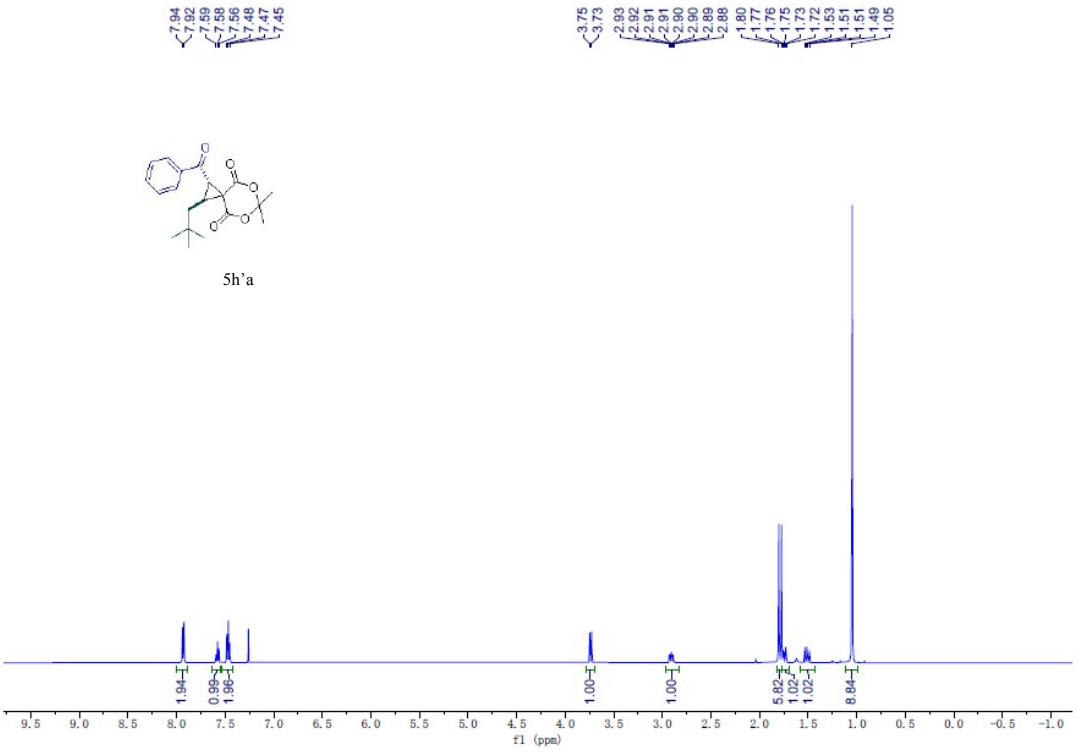

190.6
165.1
164.7
135.9
133.7
128.8
128.2
105.3
43.4
41.7
35.8
31.8
29.4
29.4
29.2
29.0
28.4
27.5
27.4
26.2
22.6
14.1
5e'a
f1 (ppm)


7.93
7.91
7.60
7.59
7.57
7.48
7.47
7.45
7.32
7.30
7.29
7.24
7.23
7.22
7.21
7.19
3.63
3.61
3.01
2.99
2.98
2.96
2.88
2.87
2.86
2.85
2.83
2.82
2.81
2.79
2.29
2.27
2.26
2.25
2.23
2.22
2.17
2.15
2.13
2.12
2.11
2.09
1.78
1.76
5f'a
1.84
0.97
1.94
2.29
3.34
1.00
1.01
2.09
1.04
1.07
6.13
f1 (ppm)

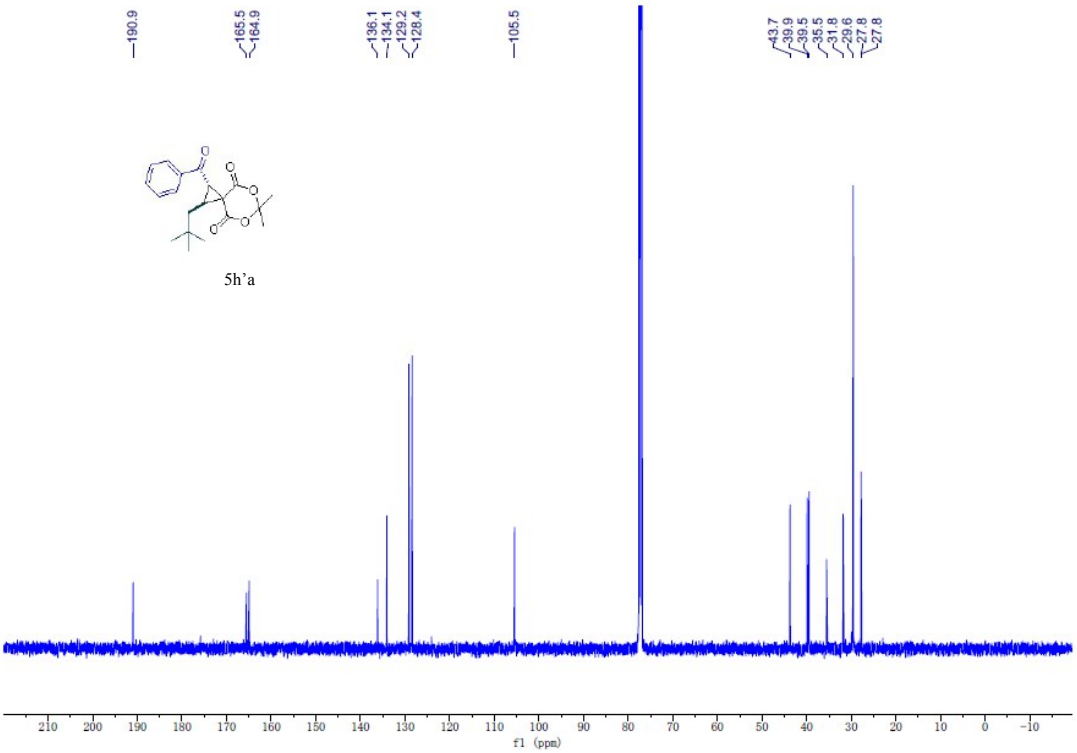

190.7
165.2
165.0
140.2
136.0
134.0
129.0
128.8
128.4
126.5
105.5
43.8
41.3
35.5
34.8
28.2
27.7
27.6
5f'a
f1 (ppm)


7.93
7.91
7.58
7.57
7.55
7.47
7.46
7.44
3.70
3.68
2.93
2.92
2.91
2.90
2.89
2.88
1.84
1.83
1.82
1.81
1.80
1.80
1.79
1.78
1.77
1.58
1.57
1.57
1.56
1.55
1.55
1.54
1.53
1.53
1.51
1.03
1.01
1.00
5g'a
1.97
0.99
1.99
1.00
1.01
8.08
0.98
6.01
f1 (ppm)

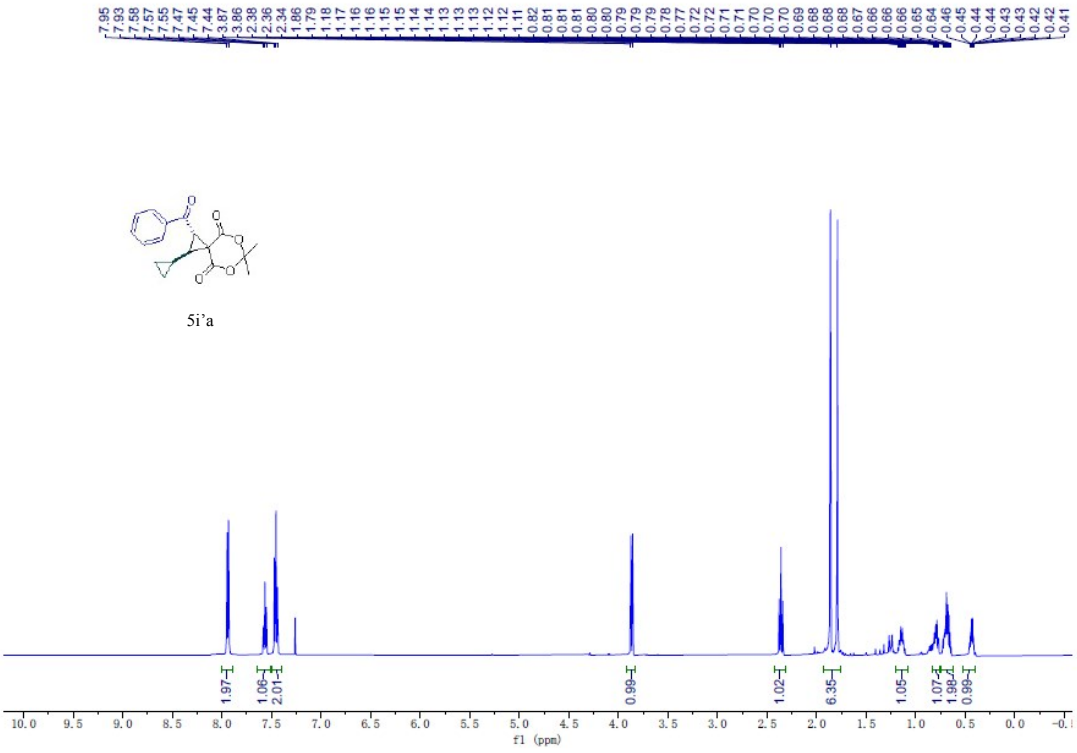

190.9
165.4
165.0
136.1
134.1
129.1
128.4
105.5
43.6
40.8
35.9
35.1
28.3
27.8
27.8
22.7
22.3
5g'a
f1 (ppm)

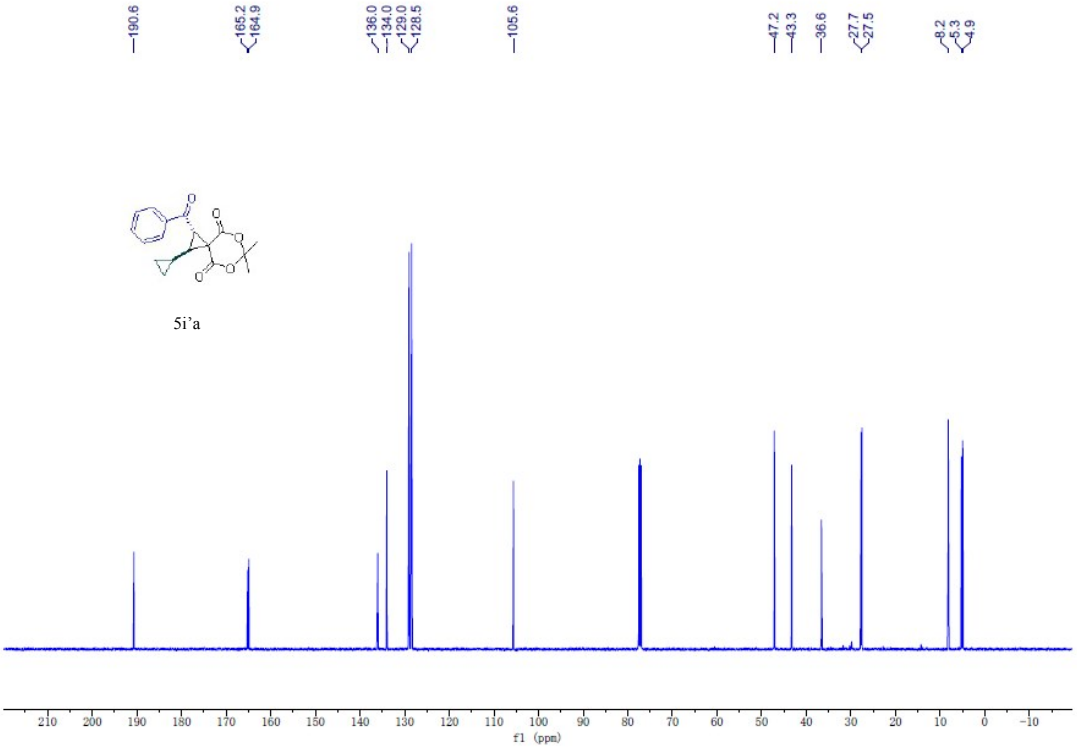

7.94
7.92
7.59
7.58
7.56
7.48
7.47
7.45
3.75
3.73
2.93
2.92
2.91
2.91
2.90
2.90
2.89
2.88
1.80
1.77
1.76
1.75
1.73
1.72
1.53
1.51
1.51
1.49
1.05
1.94
0.98
1.96
1.00
1.00
5.82
1.02
1.02
8.84
f1 (ppm)

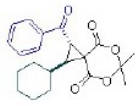
5h'a


190.9
165.5
164.9
136.1
134.1
129.2
128.4
105.5
43.7
39.9
39.5
35.5
31.8
29.6
27.8
27.8
f1 (ppm)

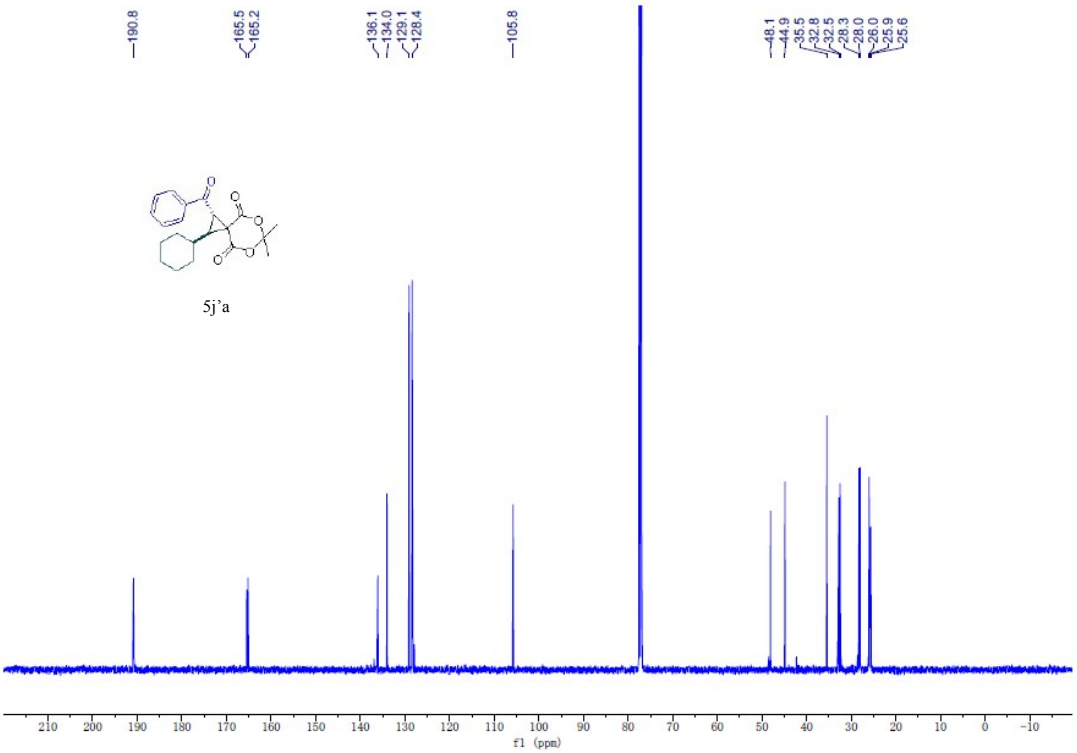
5h'a


7.95 7.93 7.58 7.57 7.55 7.47 7.45 7.44 3.87 3.86 2.38 2.36 2.34 1.86 1.79 1.18 1.17 1.16 1.16 1.15 1.15 1.14 1.14 1.13 1.13 1.13 1.12 1.12 1.11 0.82 0.81 0.81 0.81 0.80 0.80 0.80 0.79 0.79 0.79 0.78 0.77 0.72 0.72 0.71 0.71 0.70 0.70 0.70 0.69 0.68 0.68 0.68 0.67 0.66 0.66 0.66 0.65 0.64 0.46 0.45 0.44 0.44 0.43 0.43 0.42 0.42 0.41
5i'a
1.97 1.06 2.01 0.99 1.02 6.35 1.05 1.07 1.98 0.99
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


190.6 165.2 164.9 136.0 134.0 129.0 128.5 105.6 47.2 43.3 36.6 27.7 27.5 8.2 5.3 4.9
5i'a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



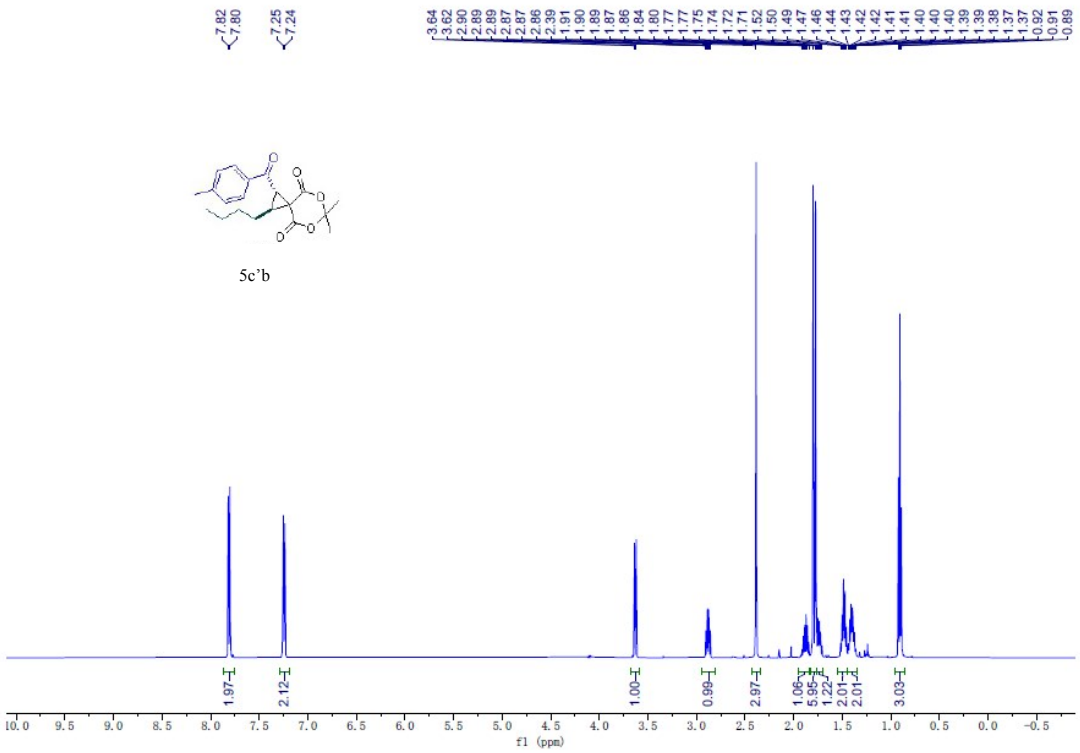
5j’a

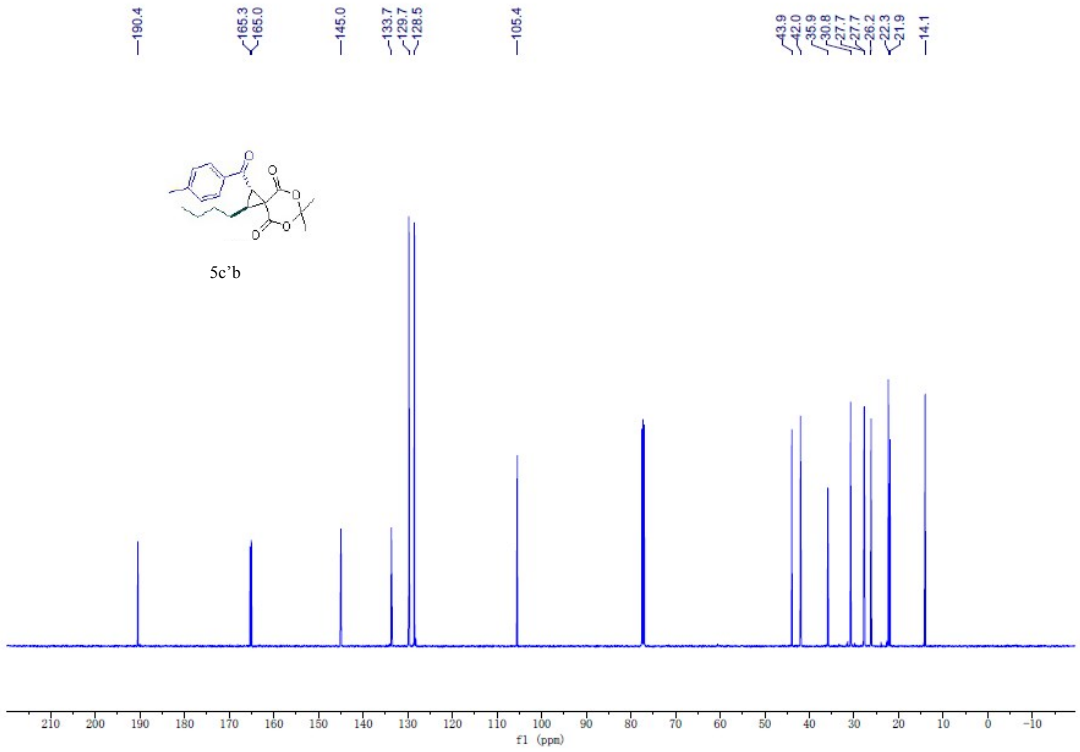

1.95
1.06
2.13
1.00
1.01
13.57
5.33
f1 (ppm)

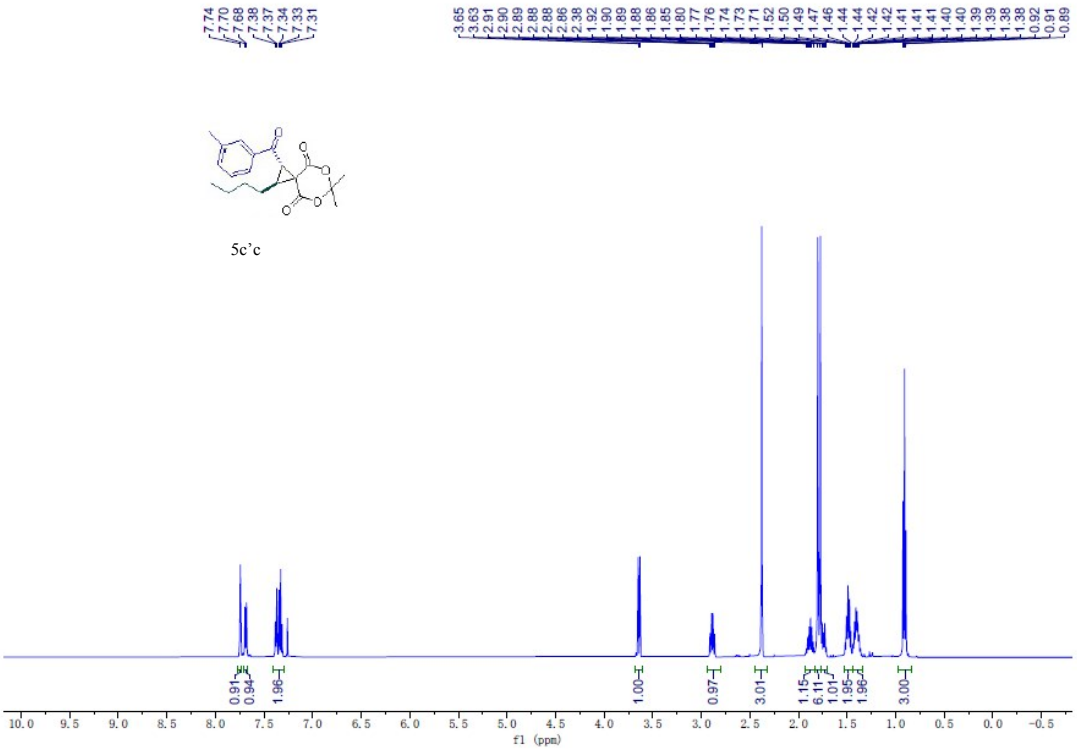
190.8
165.5
165.2
136.1
134.0
129.1
128.4
105.8
48.1
44.9
35.5
32.8
32.5
28.3
28.0
26.0
25.9
25.6
f1 (ppm)

5j’a

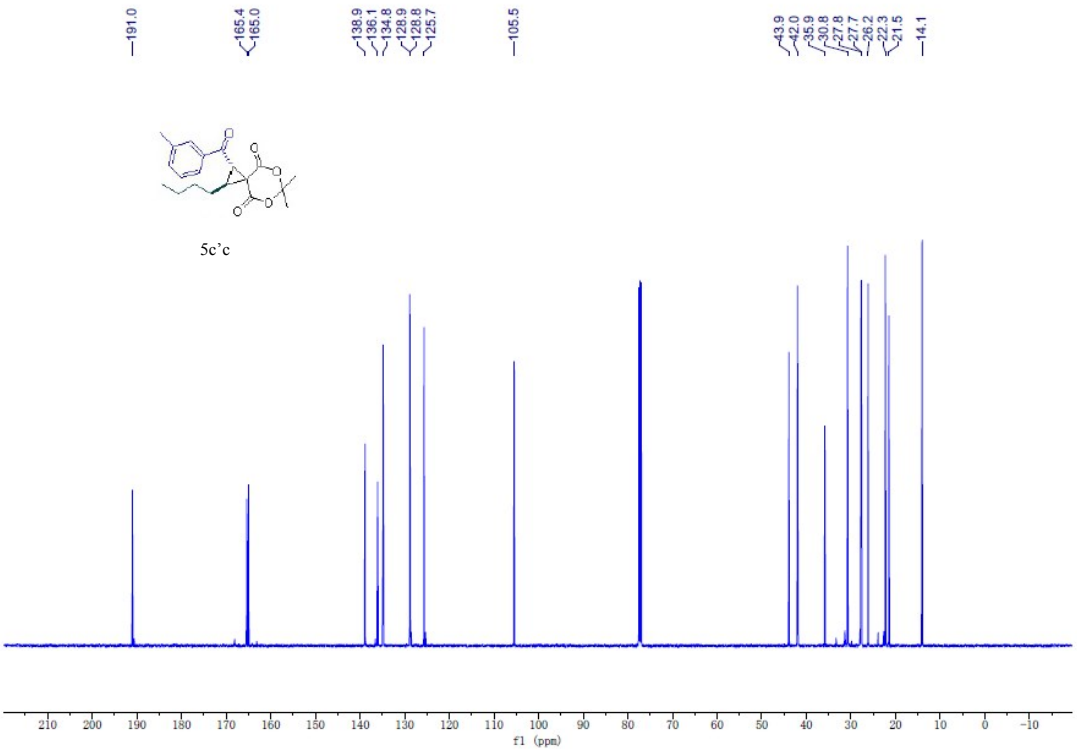
7.4. Copies of NMR Spectra for Compounds of 5c'b--5c'x



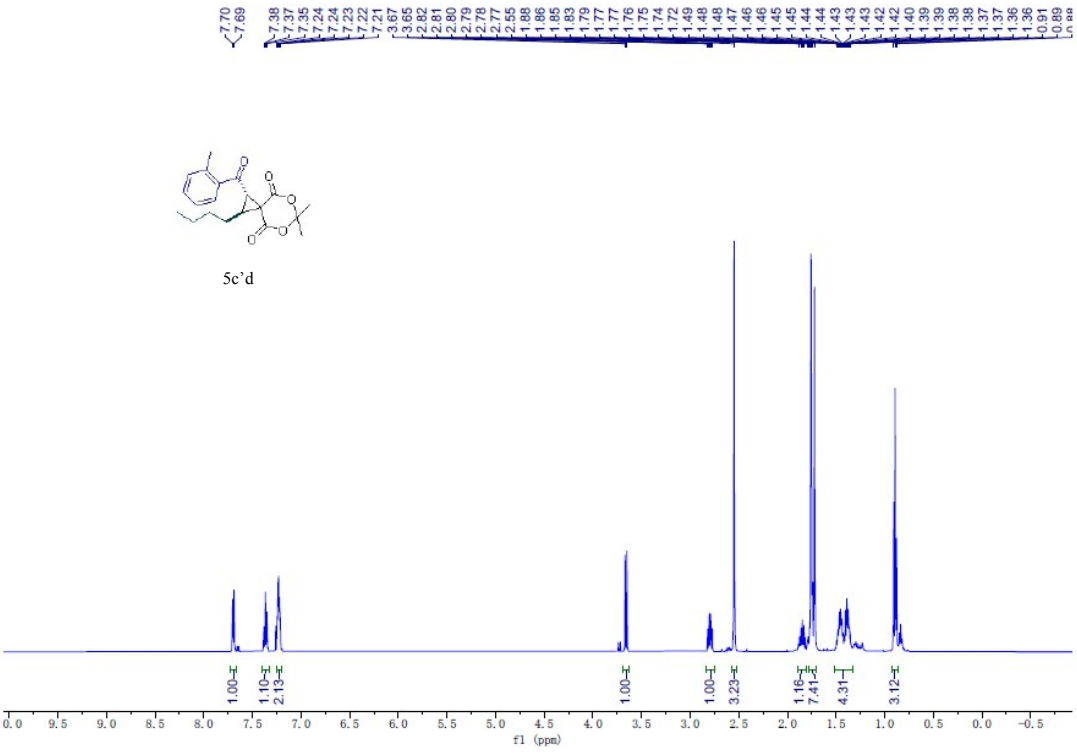




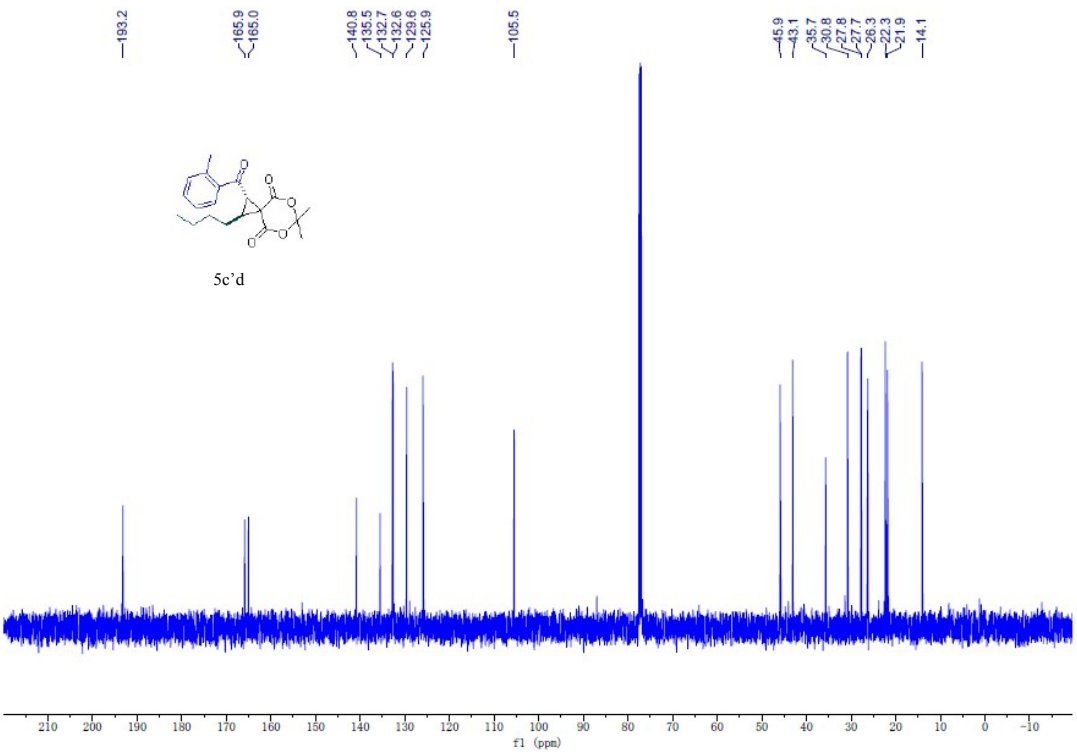
5c’c



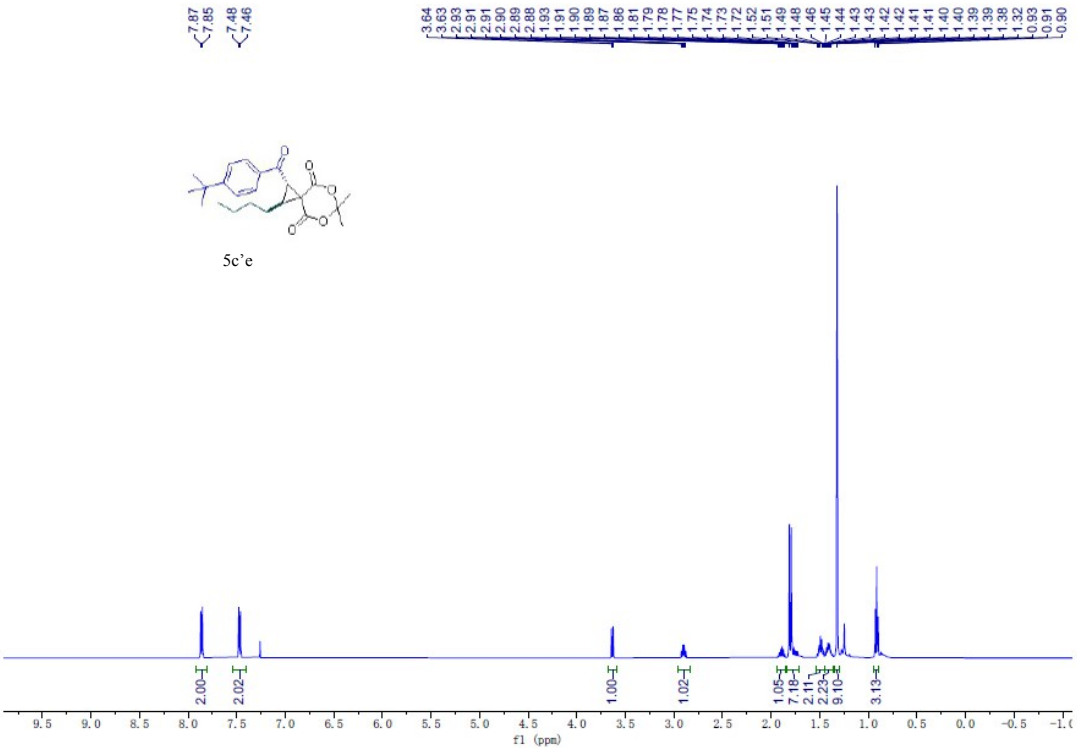
5c’c

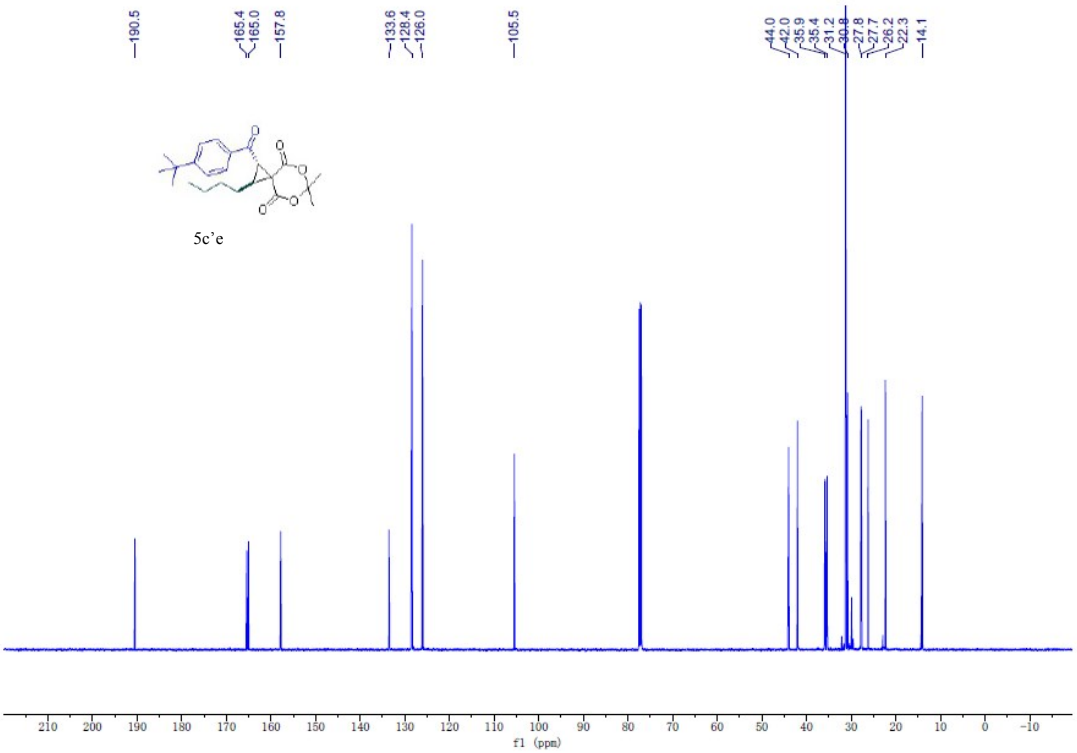

7.70
7.69
7.38
7.37
7.35
7.24
7.24
7.23
7.22
7.21
3.67
3.65
2.82
2.81
2.80
2.79
2.78
2.77
2.55
1.88
1.86
1.85
1.83
1.79
1.77
1.77
1.76
1.75
1.74
1.72
1.49
1.48
1.48
1.47
1.46
1.46
1.45
1.45
1.44
1.44
1.43
1.43
1.43
1.42
1.42
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.36
1.36
0.91
0.89
1.00
1.10
2.13
1.00
1.00
3.23
1.16
7.41
4.31
3.12
f1 (ppm)

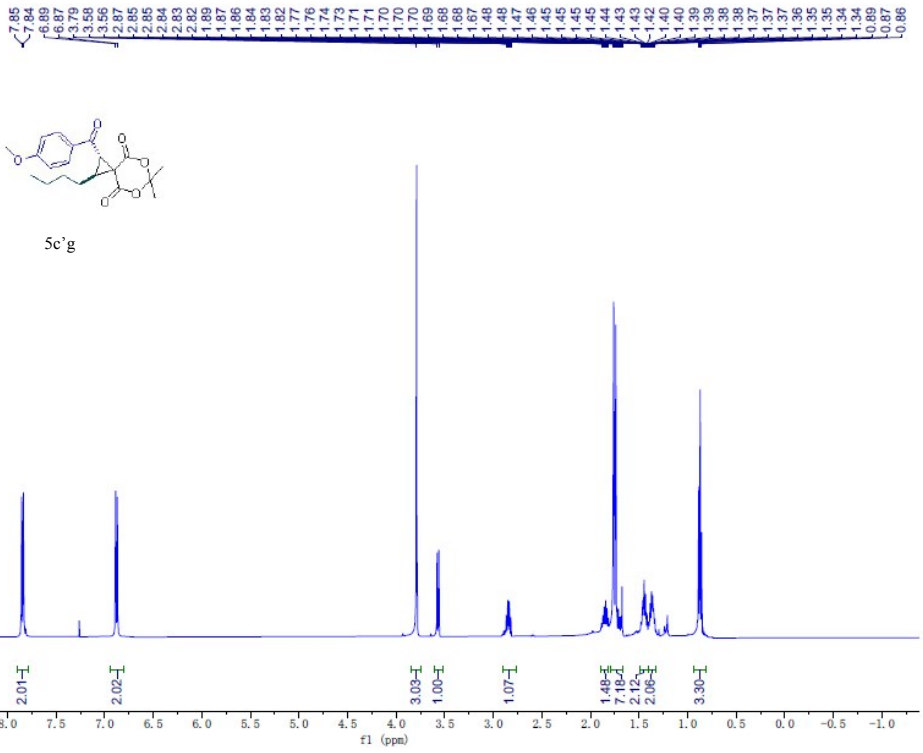
5c'd


193.2
165.9
165.0
140.8
135.5
132.7
132.6
129.6
125.9
105.5
45.9
43.1
35.7
30.8
27.8
27.7
26.3
22.3
21.9
14.1
f1 (ppm)

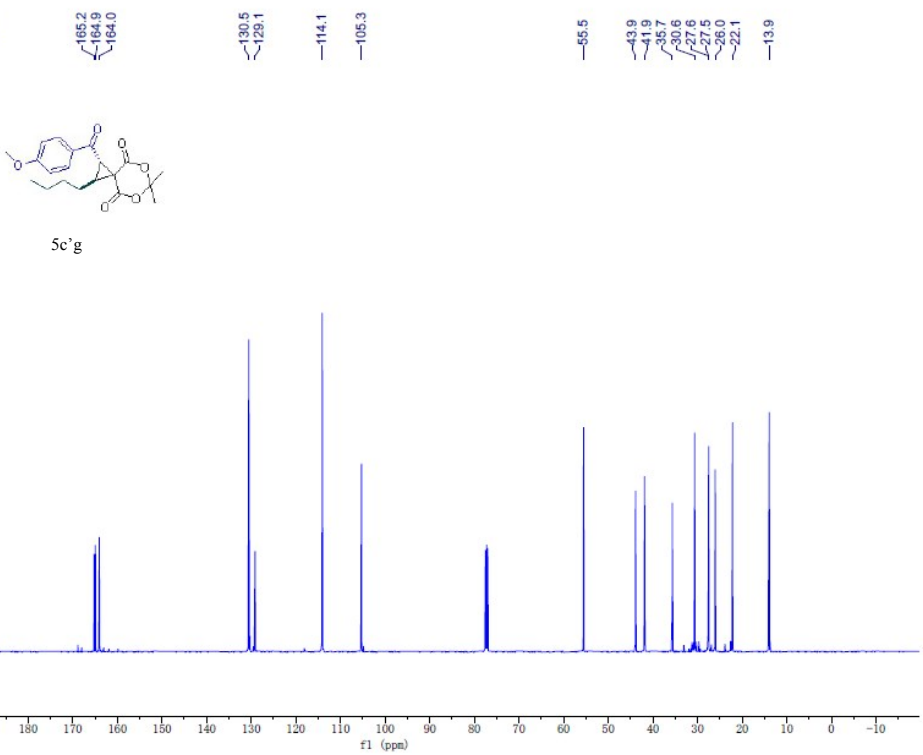
5c'd


7.87
7.85
7.48
7.46
3.64
3.63
2.93
2.91
2.91
2.90
2.89
2.88
1.93
1.91
1.90
1.89
1.87
1.86
1.81
1.79
1.78
1.77
1.75
1.74
1.73
1.72
1.52
1.51
1.49
1.48
1.46
1.45
1.44
1.43
1.43
1.42
1.42
1.41
1.41
1.40
1.40
1.39
1.38
1.32
0.93
0.91
0.90
5c'e
2.00
2.02
1.00
1.02
1.05
7.18
2.11
2.23
9.10
3.13
f1 (ppm)

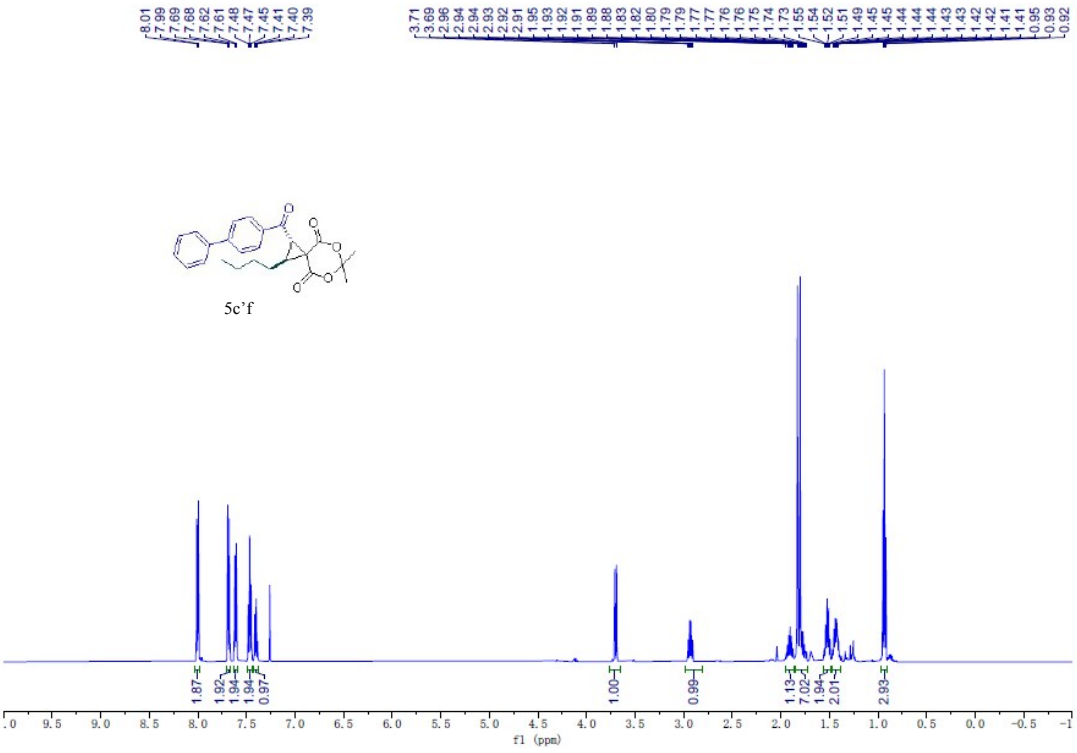

190.5
165.4
165.0
157.8
133.6
128.4
126.0
105.5
44.0
42.0
35.9
35.4
31.2
30.8
27.8
27.7
26.2
22.3
14.1
5c'e
f1 (ppm)

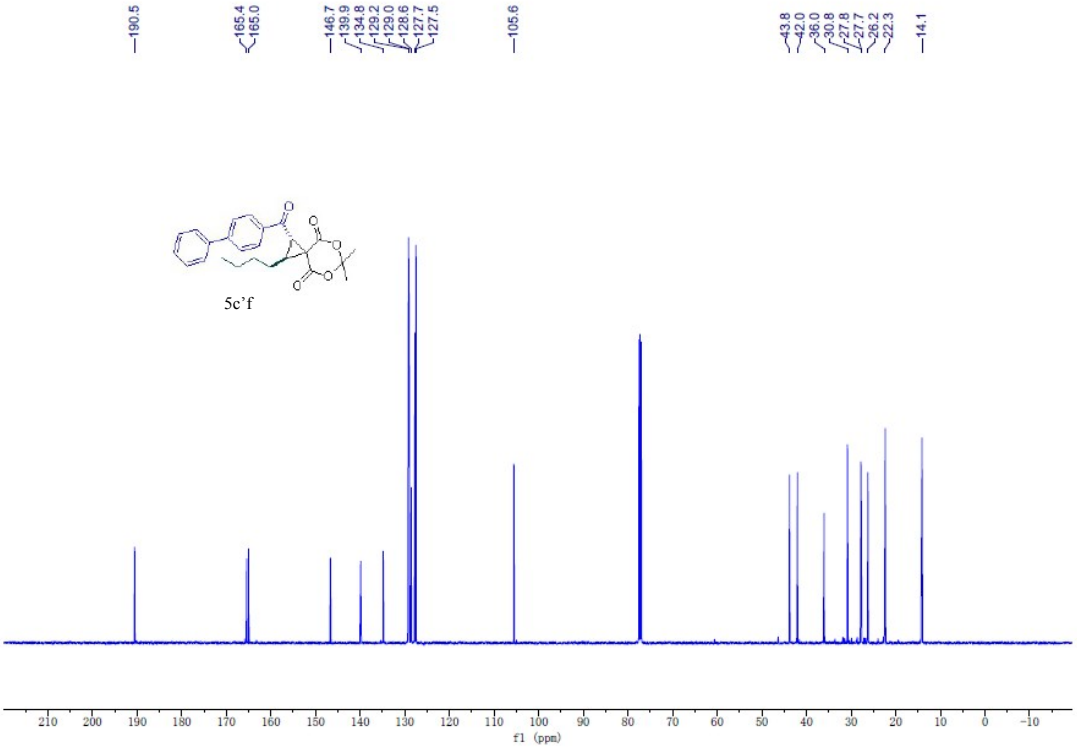

7.85
7.84
6.89
6.87
3.79
3.58
3.56
2.87
2.85
2.85
2.84
2.83
2.82
1.89
1.87
1.86
1.84
1.83
1.82
1.77
1.76
1.74
1.73
1.71
1.71
1.70
1.70
1.70
1.69
1.68
1.68
1.67
1.48
1.48
1.47
1.46
1.45
1.45
1.45
1.45
1.44
1.43
1.43
1.42
1.40
1.40
1.39
1.39
1.38
1.38
1.37
1.37
1.37
1.36
1.35
1.35
1.34
1.34
0.89
0.87
0.86
2.01
2.02
3.03
1.00
1.07
1.48
7.18
2.12
2.06
3.30
f1 (ppm)

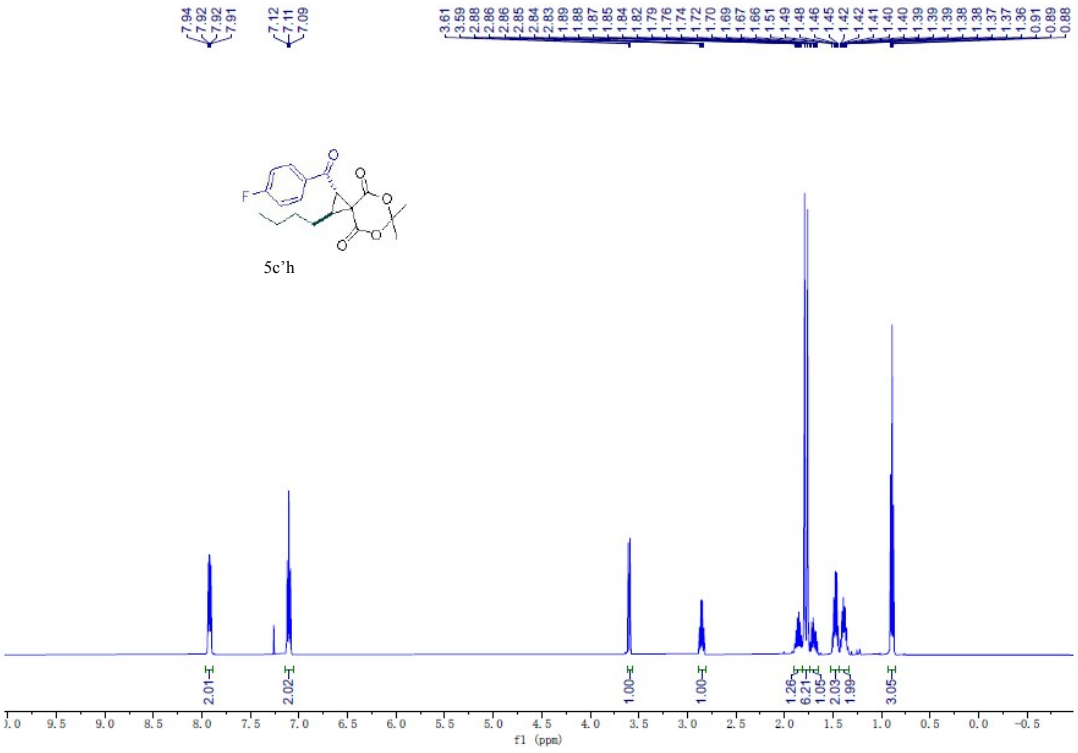
5c'g

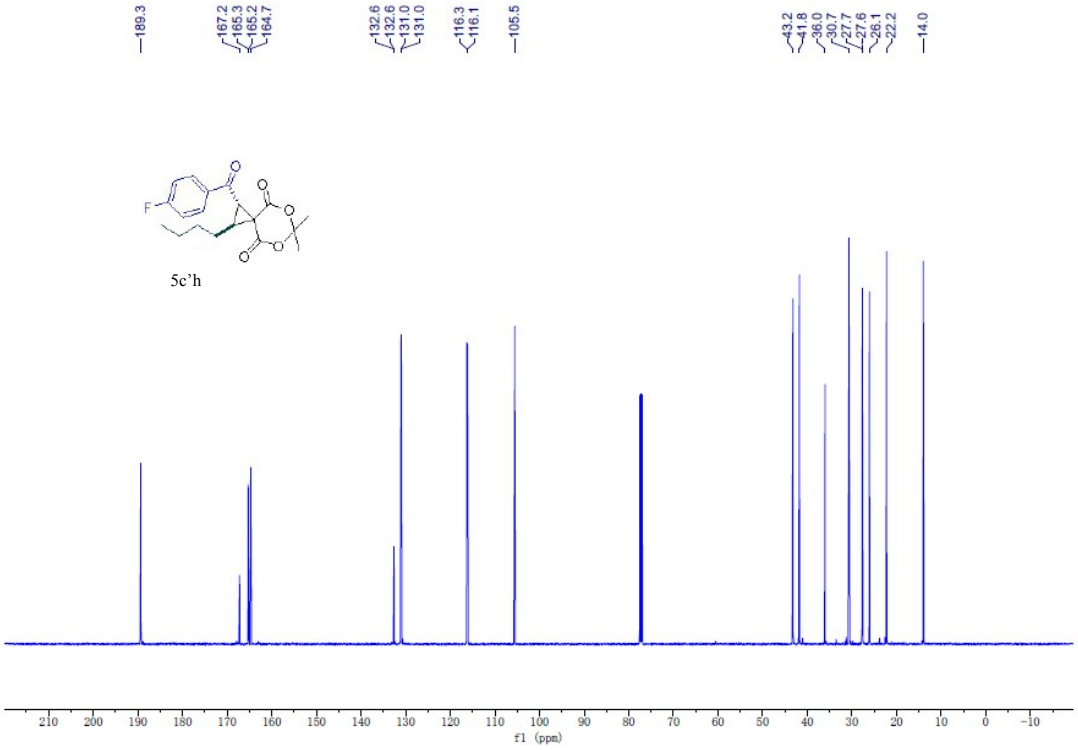

189.1
165.2
164.9
164.0
130.5
129.1
114.1
105.3
55.5
43.9
41.9
35.7
30.6
27.6
27.5
26.0
22.1
13.9
f1 (ppm)

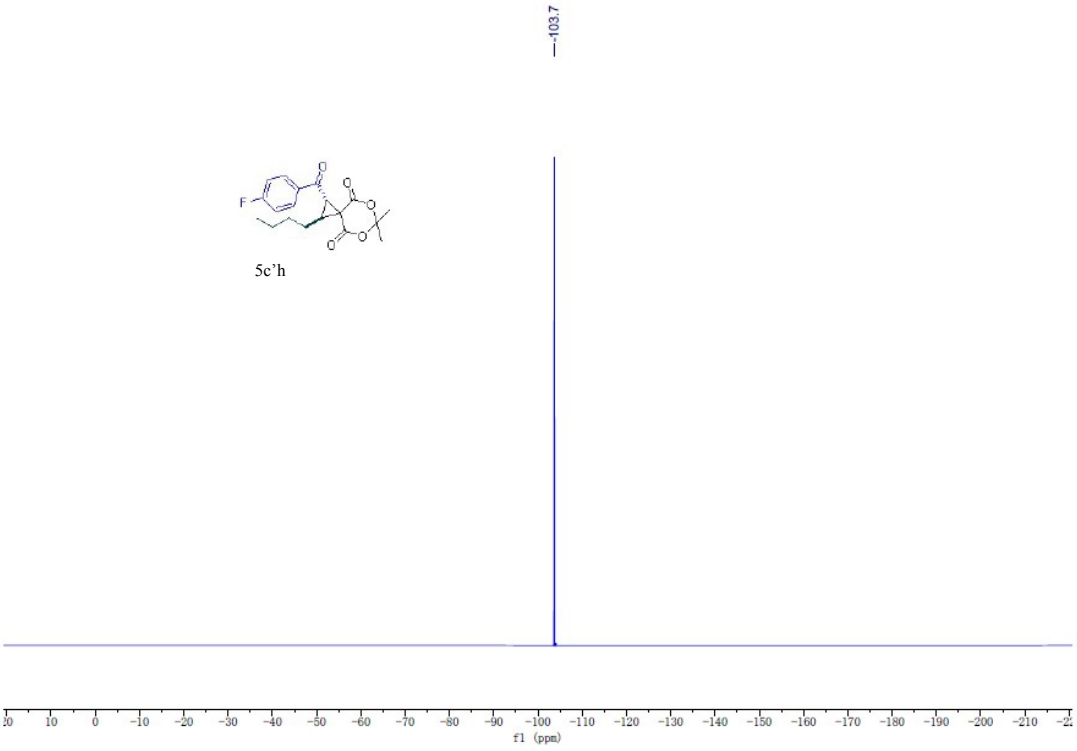
5c'g


8.01
7.99
7.69
7.68
7.62
7.61
7.48
7.47
7.45
7.41
7.40
7.39
3.71
3.69
2.96
2.94
2.94
2.93
2.92
2.91
1.95
1.93
1.92
1.91
1.89
1.88
1.83
1.82
1.80
1.79
1.79
1.77
1.77
1.76
1.76
1.75
1.74
1.73
1.55
1.54
1.52
1.51
1.49
1.45
1.45
1.44
1.44
1.43
1.42
1.42
1.41
1.41
0.95
0.93
0.92
5c'f
1.87
1.92
1.94
1.94
0.97
1.00
0.99
1.13
7.02
1.94
2.01
2.93
f1 (ppm)

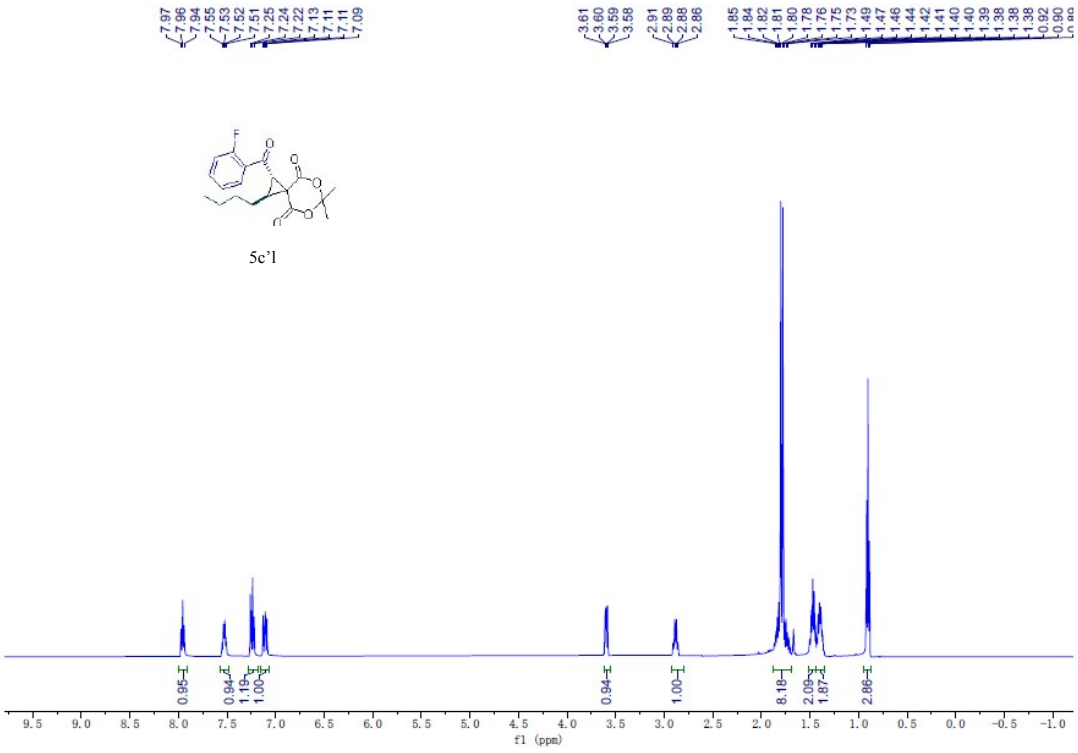

190.5
165.4
165.0
146.7
139.9
134.8
129.2
129.0
128.6
127.7
127.5
105.6
43.8
42.0
36.0
30.8
27.8
27.7
26.2
22.3
14.1
5c'f
f1 (ppm)


7.94
7.92
7.92
7.91
7.12
7.11
7.09
3.61
3.59
2.88
2.86
2.86
2.85
2.84
2.83
1.89
1.88
1.87
1.85
1.84
1.82
1.79
1.76
1.74
1.72
1.70
1.69
1.67
1.66
1.51
1.49
1.48
1.46
1.45
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.39
1.38
1.38
1.37
1.37
1.36
0.91
0.89
0.88
F
5c'h
2.01
2.02
1.00
1.00
1.26
6.21
1.05
2.03
1.99
3.06
f1 (ppm)

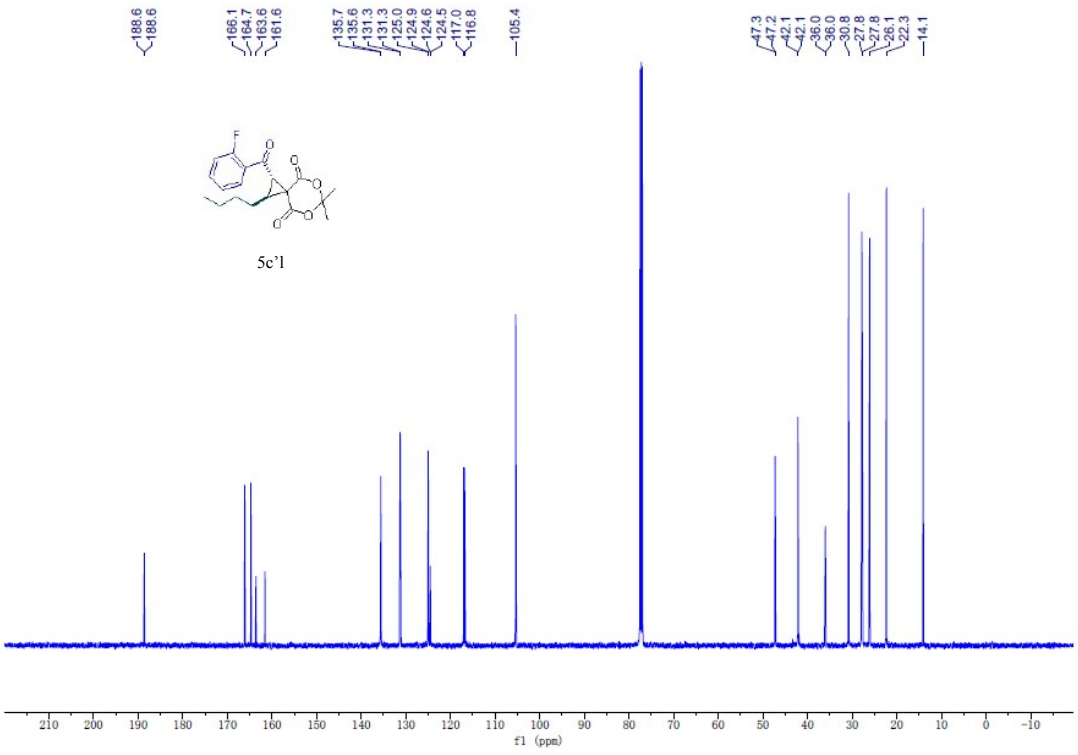

189.3
167.2
165.3
165.2
164.7
132.6
132.6
131.0
131.0
116.3
116.1
105.5
43.2
41.8
36.0
30.7
27.7
27.6
26.1
22.2
14.0
F
5c'h
f1 (ppm)



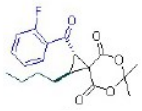
5c'h


7.97
7.96
7.94
7.55
7.53
7.52
7.51
7.25
7.24
7.22
7.13
7.11
7.11
7.09
3.61
3.60
3.59
3.58
2.91
2.89
2.88
2.86
1.85
1.84
1.82
1.81
1.80
1.78
1.76
1.75
1.73
1.49
1.47
1.46
1.44
1.42
1.41
1.40
1.40
1.39
1.38
1.38
0.92
0.90
F
O
O
O
O
O
0.95
0.94
1.19
1.00
0.94
1.00
8.18
2.09
1.87
2.86
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

5c'l

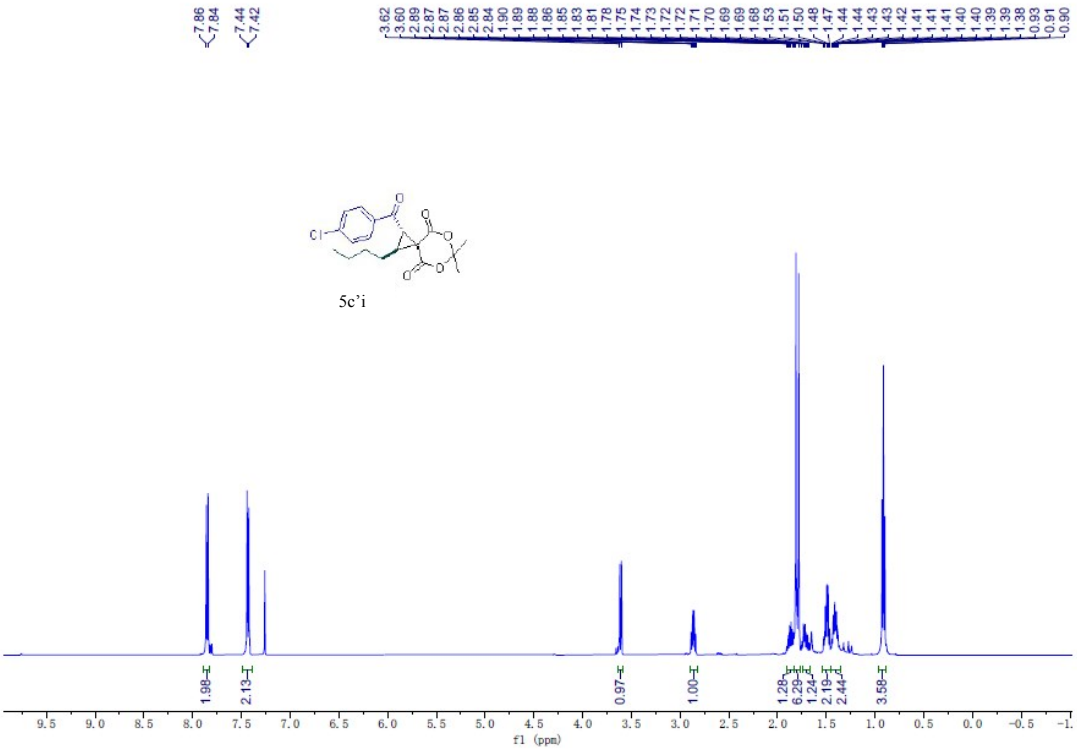

188.6
188.6
166.1
164.7
163.6
161.6
135.7
135.6
131.3
131.3
125.0
124.9
124.6
124.5
117.0
116.8
105.4
47.3
47.2
42.1
42.1
36.0
36.0
30.8
27.8
27.8
26.1
22.3
14.1
F
O
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

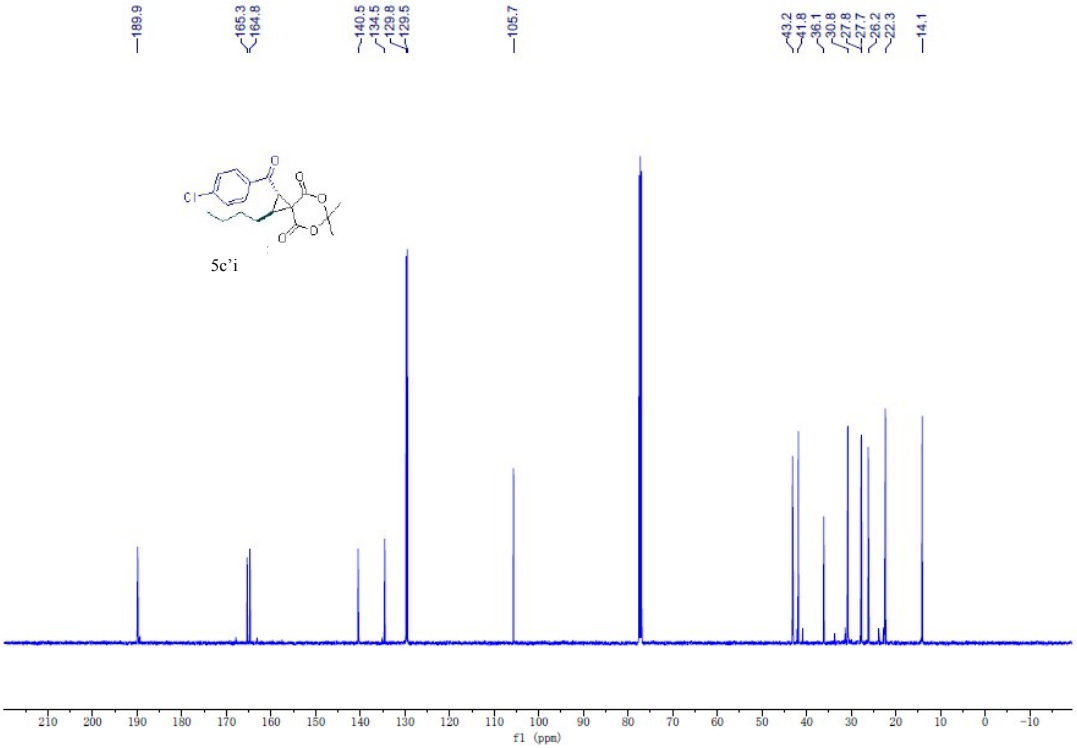
5c'l

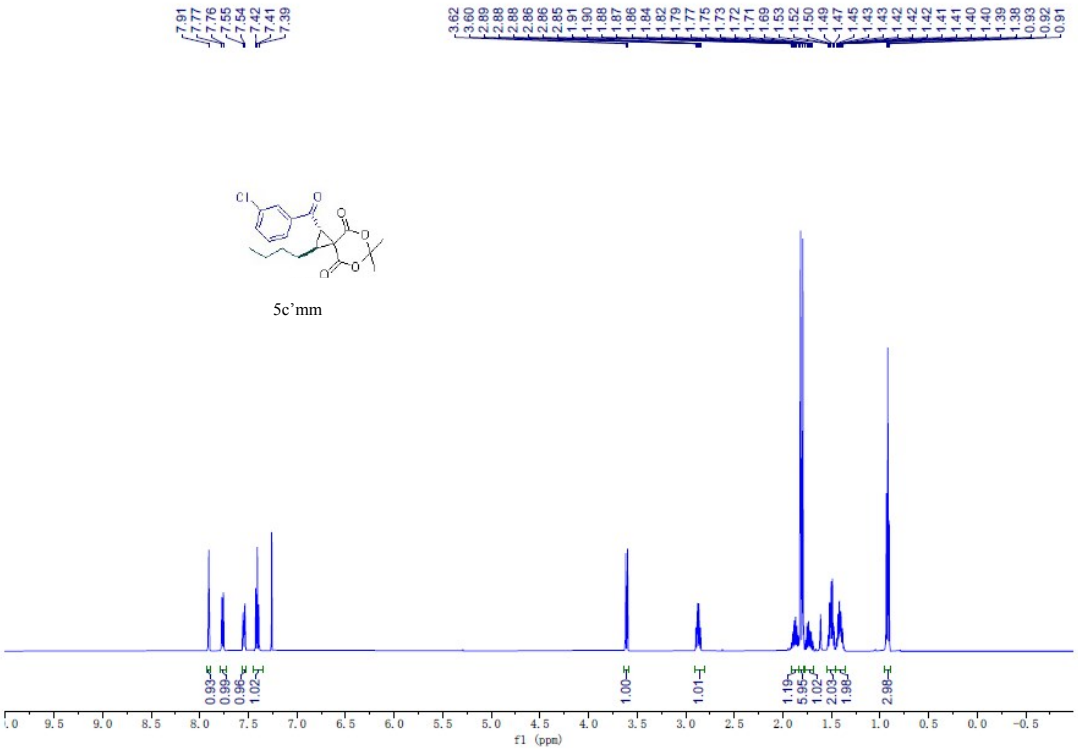


5c'l

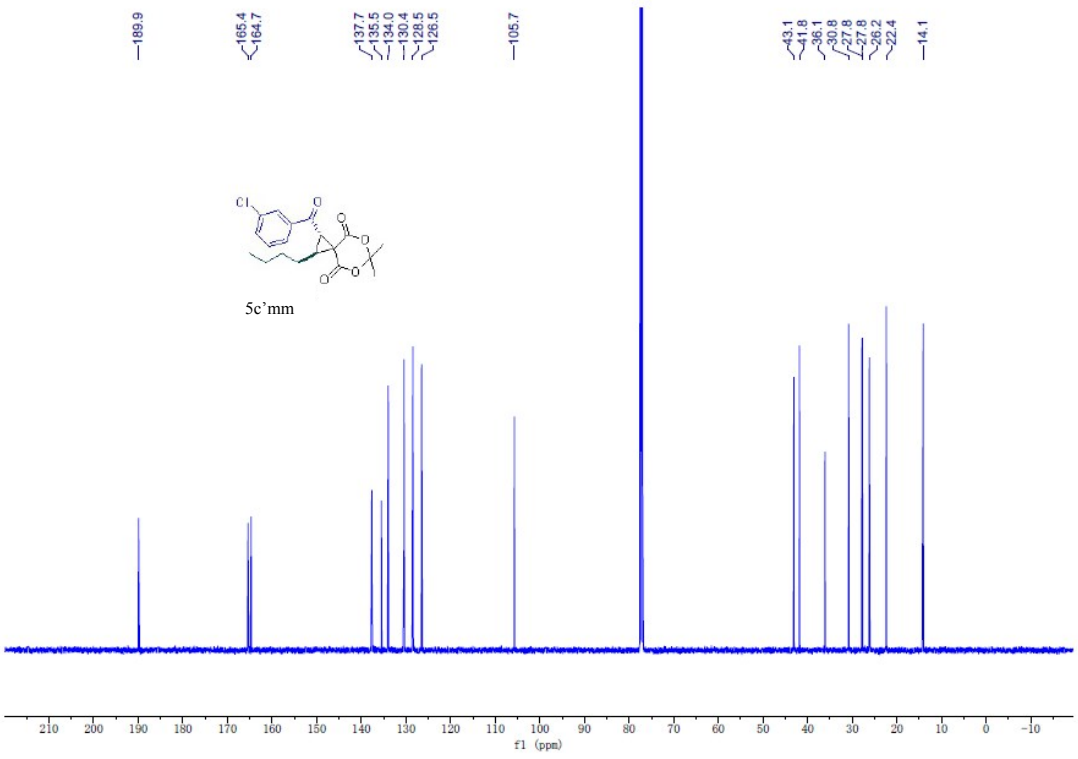
-109.89
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.86
7.84
7.44
7.42
3.62
3.60
2.89
2.87
2.87
2.86
2.85
2.84
1.90
1.89
1.88
1.86
1.85
1.83
1.81
1.78
1.75
1.74
1.73
1.72
1.72
1.71
1.70
1.69
1.69
1.68
1.53
1.51
1.50
1.48
1.47
1.44
1.44
1.43
1.43
1.42
1.41
1.41
1.41
1.40
1.40
1.39
1.39
1.38
0.93
0.91
0.90
5c'i
1.98
2.13
0.97
1.00
1.28
6.29
1.24
2.19
2.44
3.58
f1 (ppm)

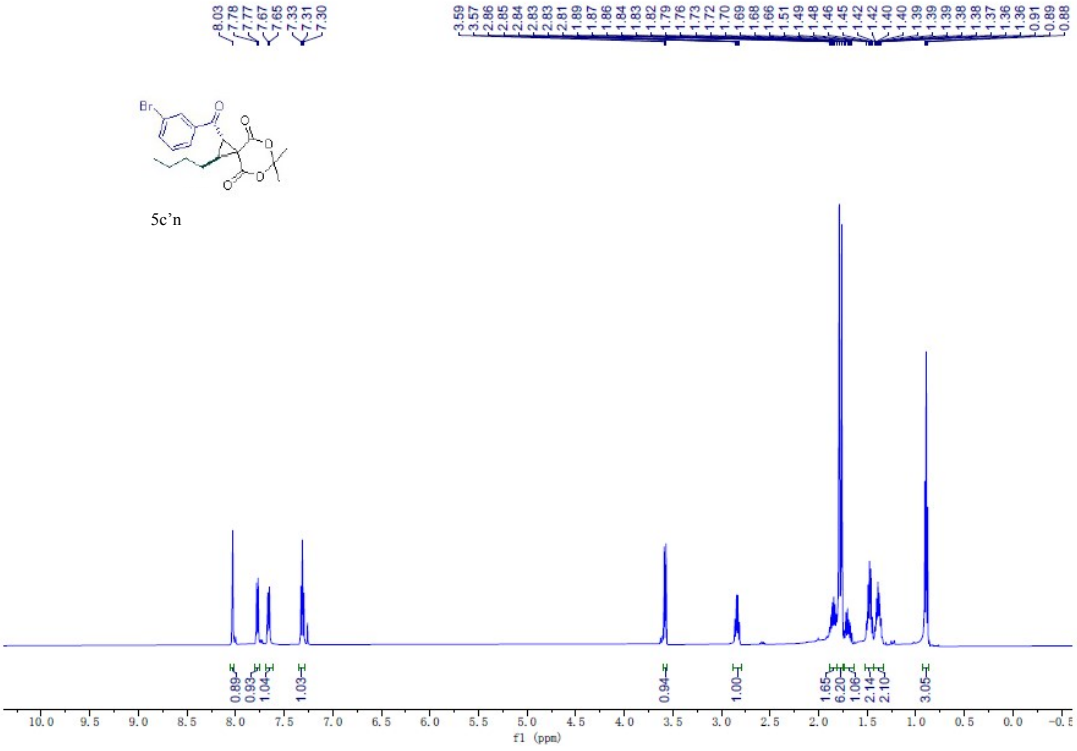

189.9
165.3
164.8
140.5
134.5
129.8
129.5
105.7
43.2
41.8
36.1
30.8
27.8
27.7
26.2
22.3
14.1
5c'i
f1 (ppm)


7.91
7.77
7.76
7.55
7.54
7.42
7.41
7.39
3.62
3.60
2.89
2.88
2.88
2.86
2.86
2.85
1.91
1.90
1.88
1.87
1.86
1.84
1.82
1.79
1.77
1.75
1.73
1.72
1.71
1.69
1.53
1.52
1.50
1.50
1.49
1.47
1.45
1.43
1.43
1.42
1.42
1.42
1.41
1.41
1.40
1.40
1.39
1.38
0.93
0.92
0.91
Cl
O
O
O
O
O
O
0.93
0.98
0.96
1.02
1.00
1.01
1.19
5.95
1.02
2.03
1.98
2.98
f1 (ppm)

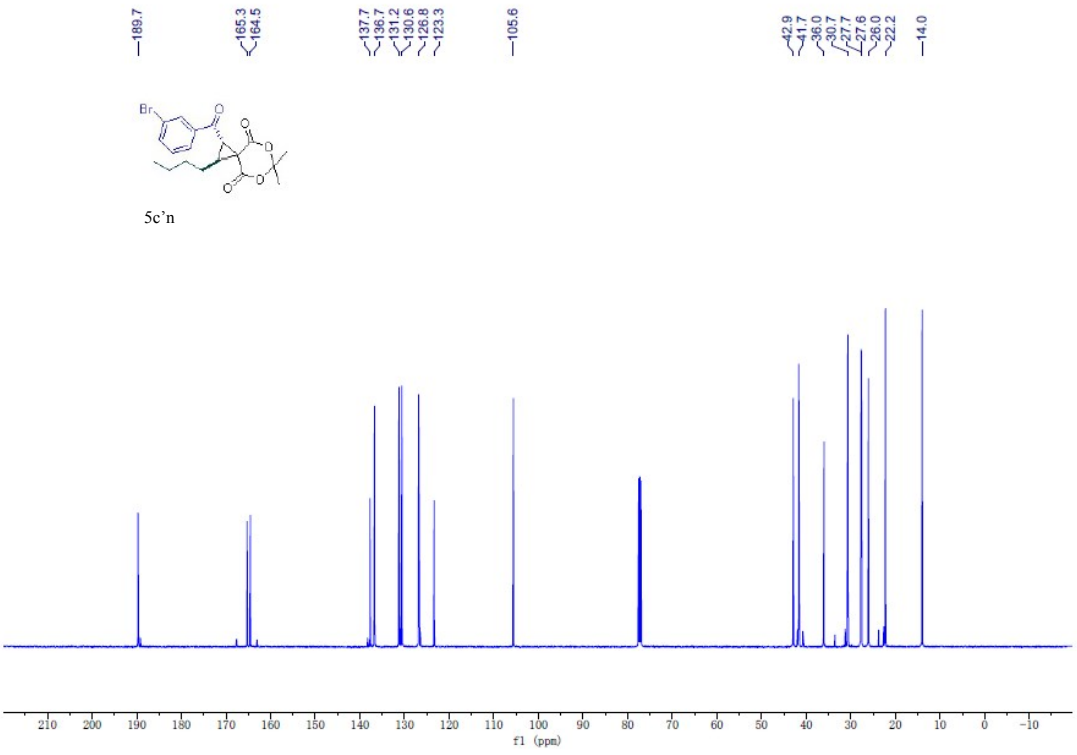
5c'mm


189.9
165.4
164.7
137.7
135.5
134.0
130.4
128.5
126.5
105.7
43.1
41.8
36.1
30.8
27.8
27.8
26.2
22.4
14.1
Cl
O
O
O
O
O
O
f1 (ppm)

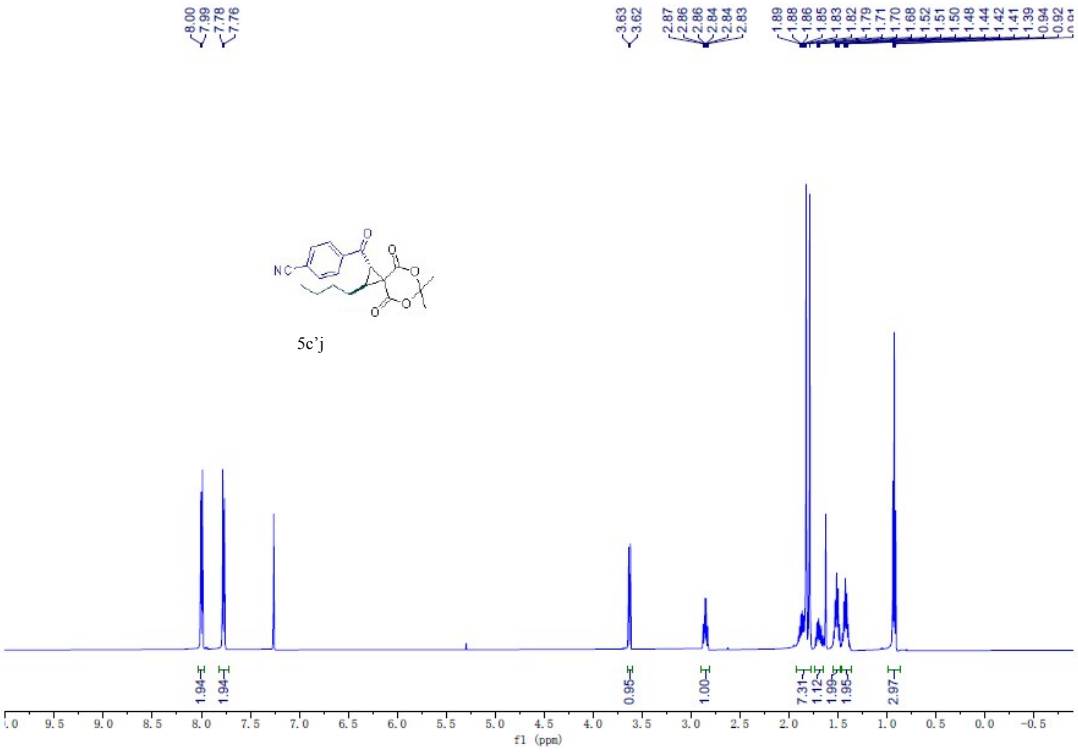
5c'mm


8.03
7.78
7.77
7.67
7.65
7.33
7.31
7.30
3.59
3.57
2.86
2.85
2.84
2.83
2.83
2.81
1.89
1.87
1.86
1.84
1.83
1.82
1.79
1.76
1.73
1.72
1.70
1.69
1.68
1.66
1.51
1.49
1.48
1.46
1.45
1.42
1.42
1.40
1.40
1.39
1.39
1.39
1.38
1.38
1.37
1.36
1.36
0.91
0.89
0.88
Br
O
O
O
O
O
0.89
0.93
1.04
1.03
0.94
1.00
1.65
6.20
1.06
2.14
2.10
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

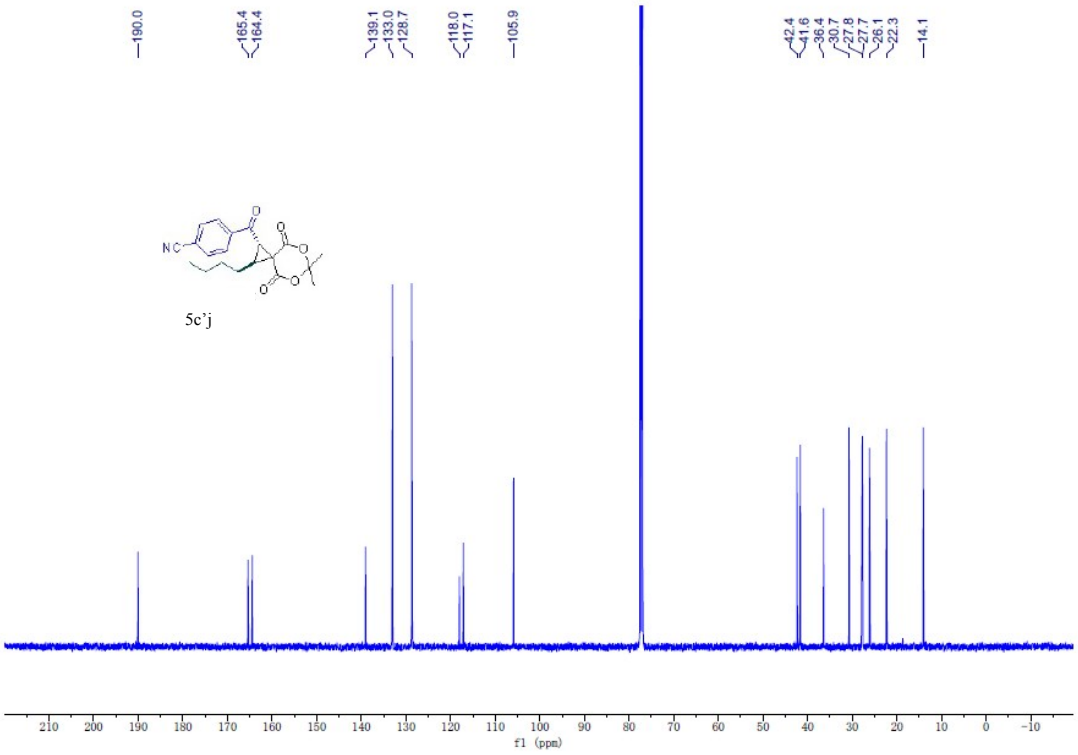
5c'n


189.7
165.3
164.5
137.7
136.7
131.2
130.6
126.8
123.3
105.6
42.9
41.7
36.0
30.7
27.7
27.6
26.0
22.2
14.0
Br
O
O
O
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

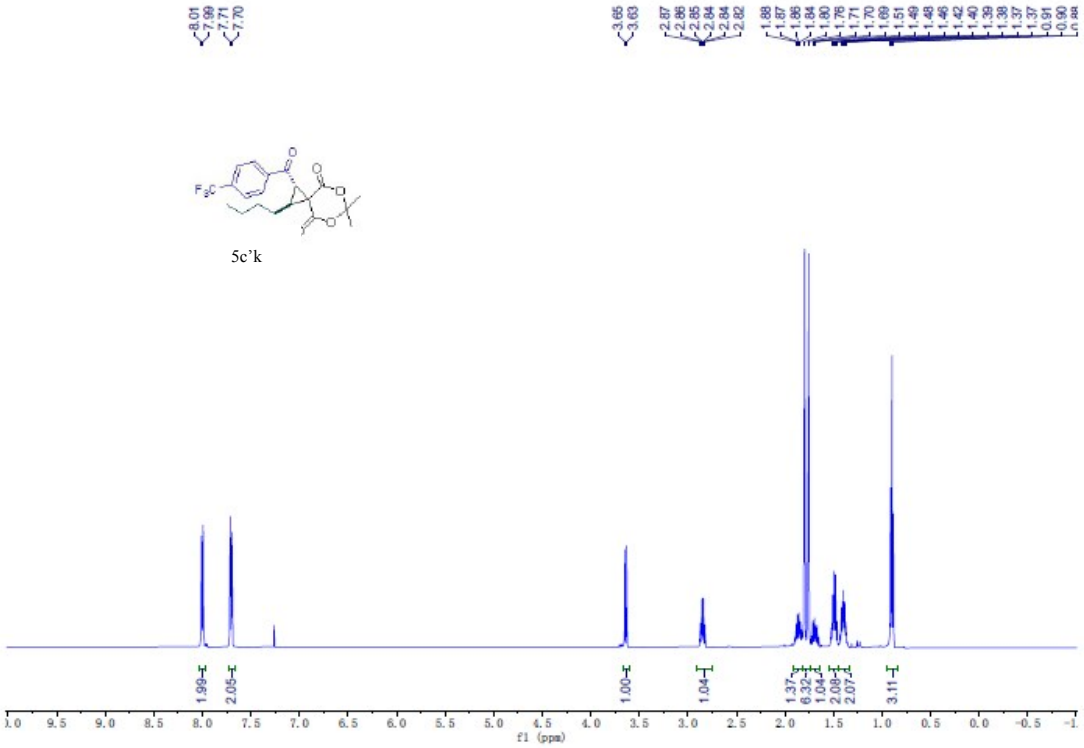
5c'n


8.00
7.99
7.78
7.76
3.63
3.62
2.87
2.86
2.86
2.84
2.84
2.83
1.89
1.88
1.86
1.85
1.83
1.82
1.79
1.71
1.70
1.68
1.52
1.51
1.50
1.48
1.44
1.42
1.41
1.39
0.94
0.92
NC
1.94
1.94
0.95
1.00
7.31
1.12
1.99
1.95
2.97
f1 (ppm)

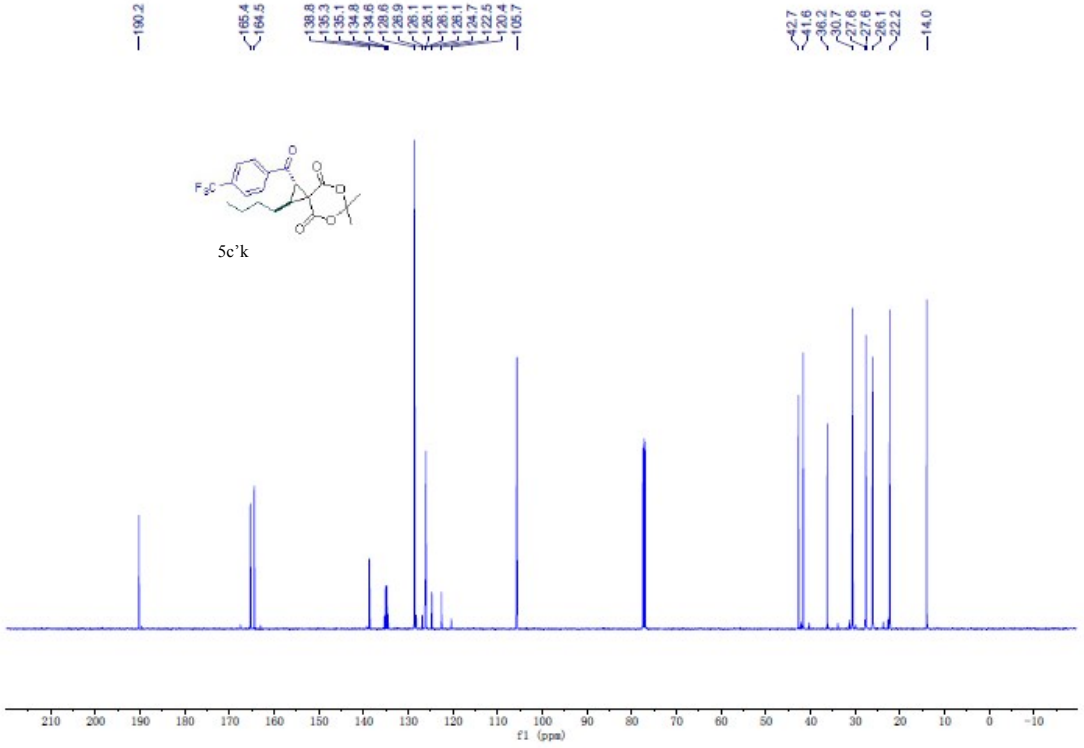
5c'j


190.0
165.4
164.4
139.1
133.0
128.7
118.0
117.1
105.9
42.4
41.6
36.4
30.7
27.8
27.7
26.1
22.3
14.1
NC
f1 (ppm)

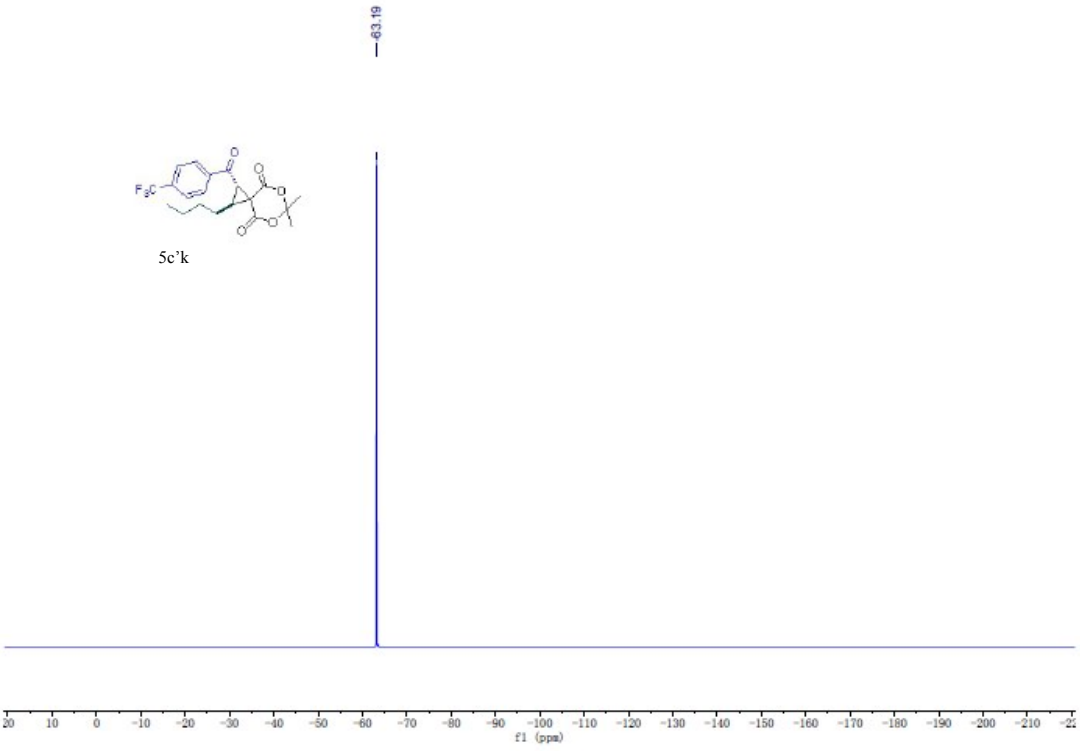
5c'j


8.01
7.99
7.71
7.70
3.65
3.63
2.87
2.86
2.85
2.84
2.84
2.82
1.88
1.87
1.86
1.84
1.80
1.76
1.71
1.70
1.69
1.51
1.49
1.48
1.46
1.42
1.40
1.39
1.38
1.37
1.37
0.91
0.90
F3C
O
O
O
O
1.99
2.05
1.00
1.04
1.37
6.32
1.04
2.08
2.07
3.11
f1 (ppm)

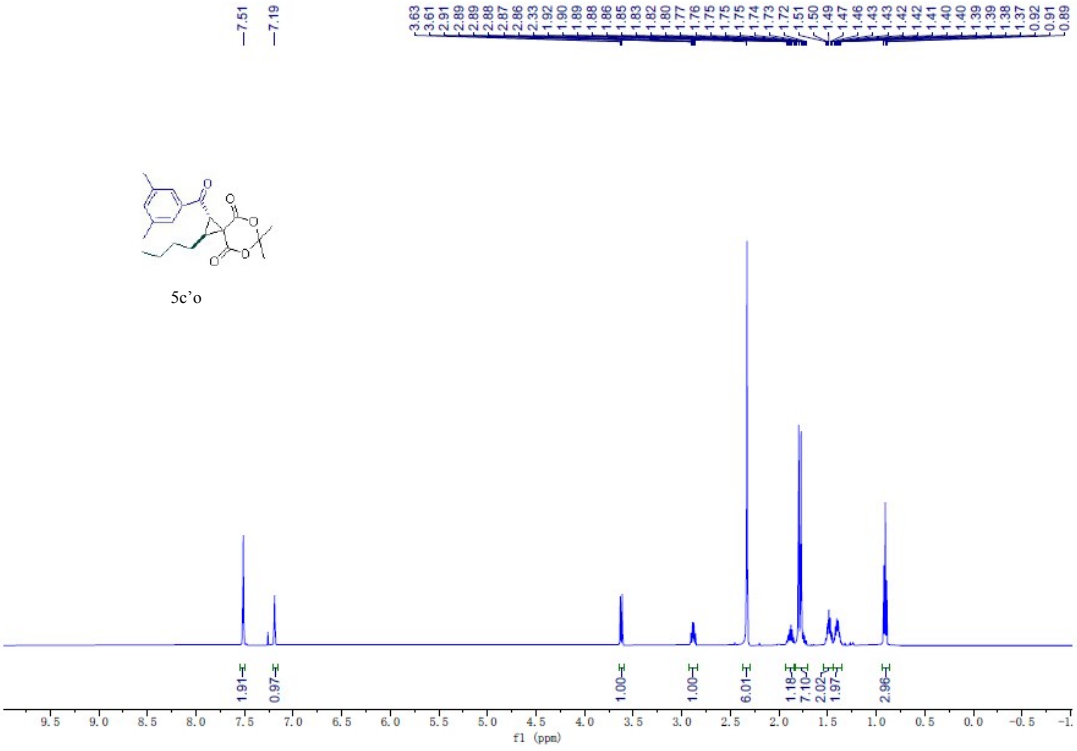
5c'k

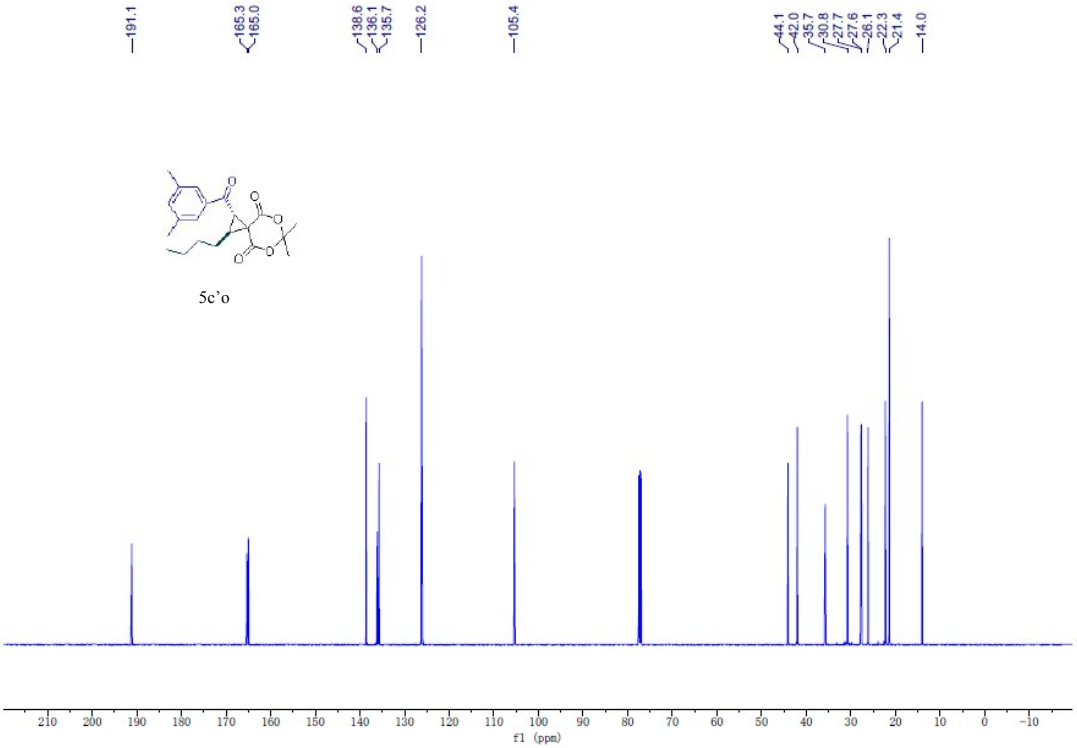

190.2
165.4
164.5
138.8
135.3
135.1
134.8
134.6
128.6
126.9
126.1
126.1
126.1
126.1
124.7
122.5
120.4
105.7
42.7
41.6
36.2
30.7
27.6
27.6
27.6
26.1
22.2
14.0
F3C
O
O
O
O
f1 (ppm)

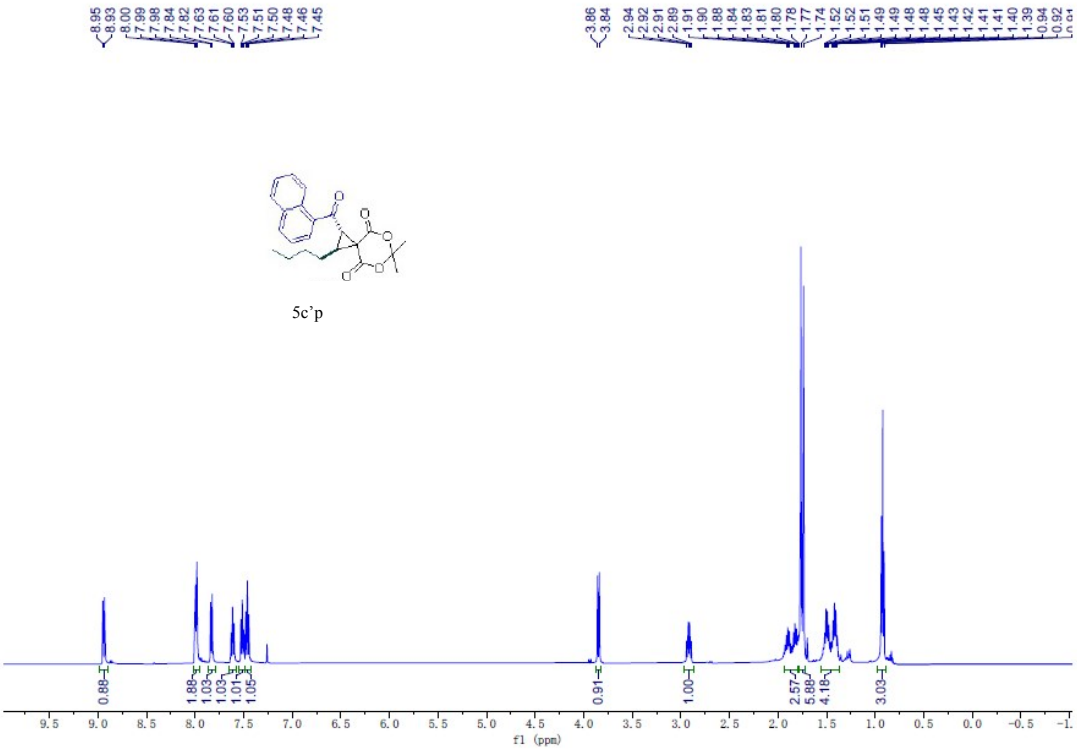
5c'k


-63.19
F3C
O
O
O
O
O
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

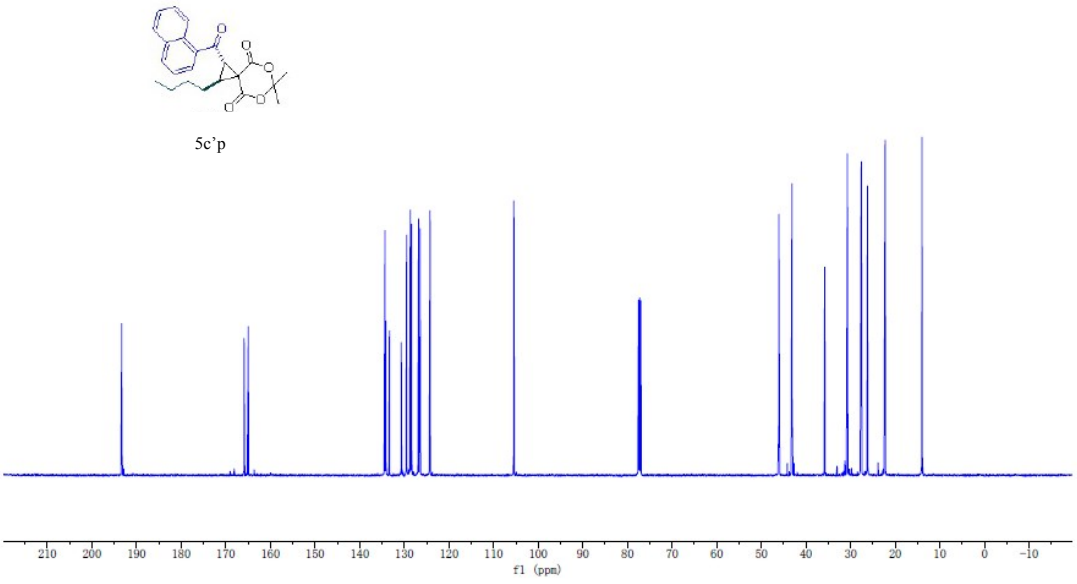
5c'k


7.51
7.19
3.63
3.61
2.91
2.89
2.89
2.88
2.87
2.86
2.33
1.92
1.90
1.89
1.88
1.86
1.85
1.83
1.82
1.80
1.77
1.76
1.75
1.75
1.74
1.73
1.72
1.51
1.50
1.49
1.47
1.46
1.43
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.39
1.38
1.37
0.92
0.91
0.89
5c'o
1.91
0.97
1.00
1.00
6.01
1.18
7.10
2.02
1.97
2.96
f1 (ppm)

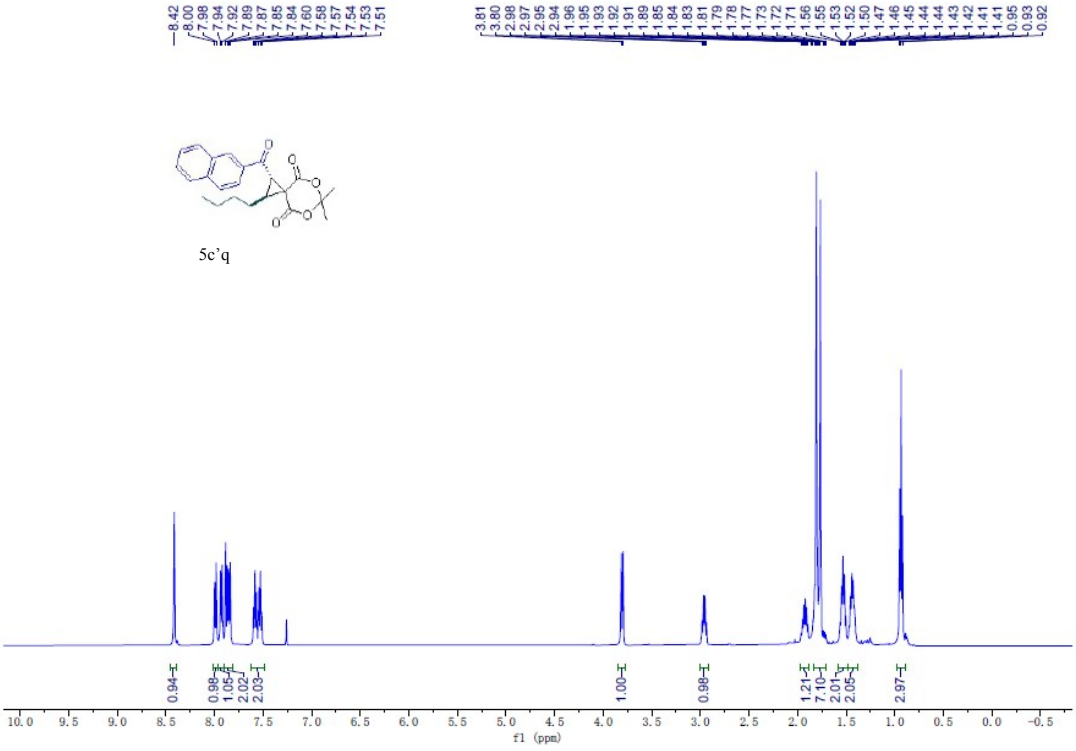

191.1
165.3
165.0
138.6
136.1
135.7
126.2
105.4
44.1
42.0
35.7
30.8
27.7
27.6
26.1
22.3
21.4
14.0
5c'o
f1 (ppm)


8.95
8.93
8.00
7.99
7.98
7.84
7.82
7.63
7.61
7.60
7.53
7.51
7.50
7.48
7.46
7.45
3.86
3.84
2.94
2.92
2.91
2.89
1.91
1.90
1.88
1.84
1.83
1.81
1.80
1.78
1.77
1.74
1.52
1.51
1.49
1.48
1.45
1.43
1.42
1.41
1.40
1.39
0.94
0.92
0.88
1.88
1.03
1.03
1.01
1.05
0.91
1.00
2.57
5.88
4.18
3.03
f1 (ppm)

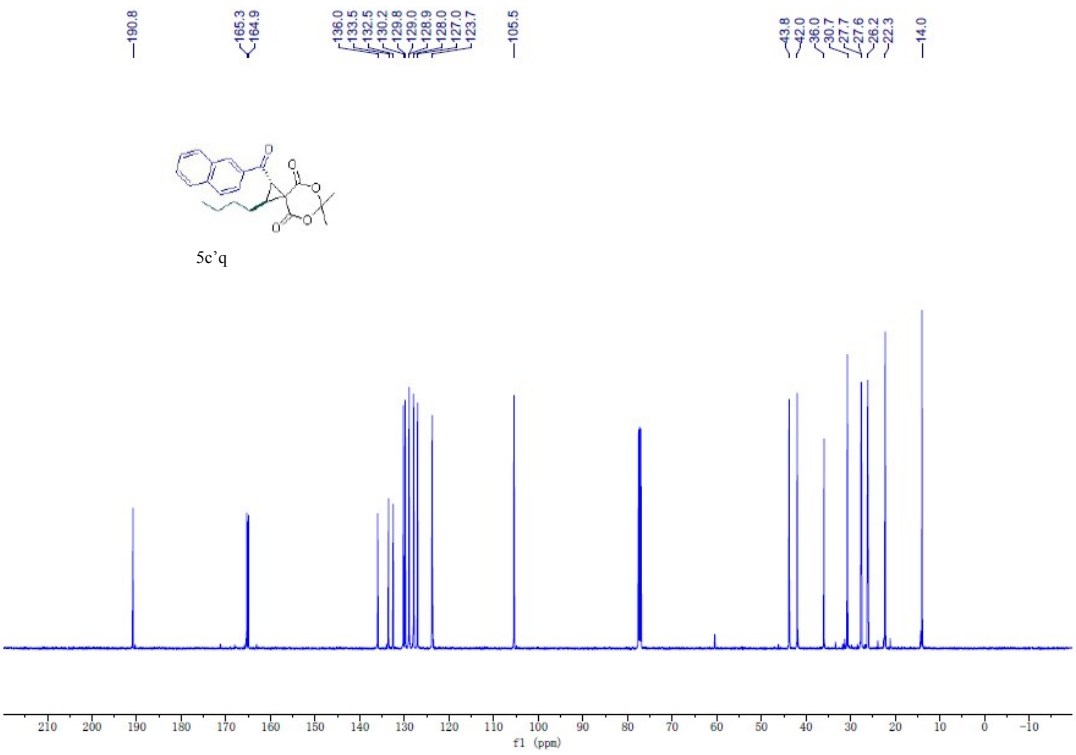
5c'p


193.3
165.9
165.0
134.3
134.2
133.3
130.7
129.5
128.7
128.4
126.8
126.5
124.2
105.5
46.1
43.1
35.8
30.7
27.7
27.6
26.2
22.3
14.0
f1 (ppm)

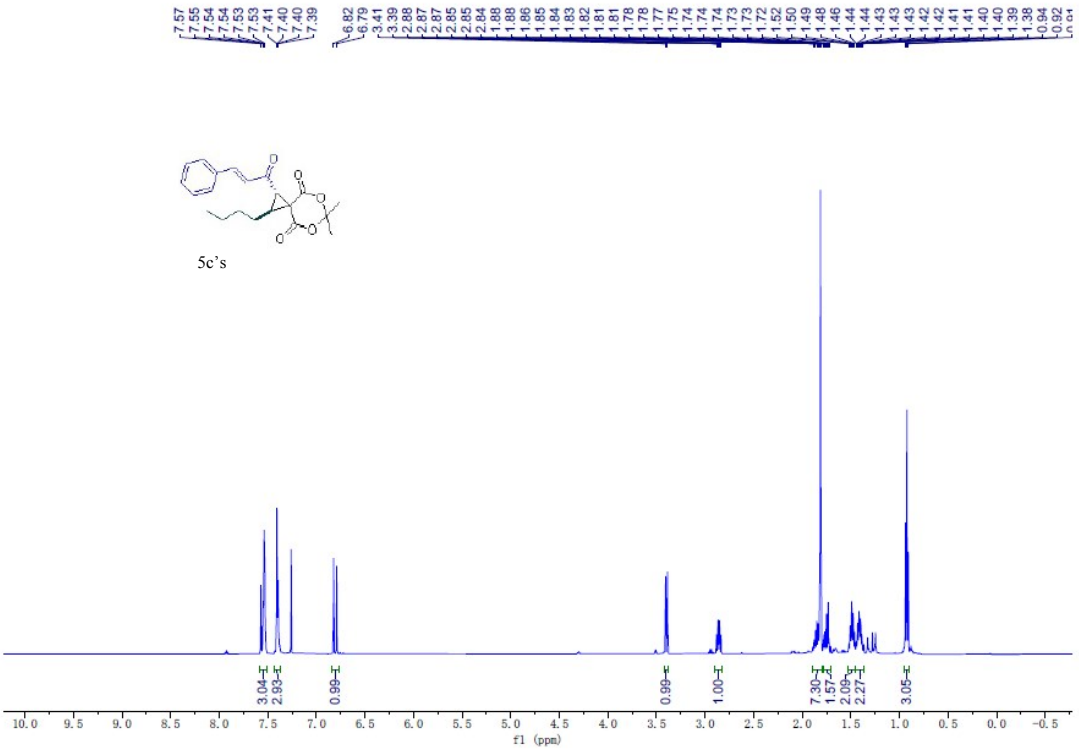
5c'p

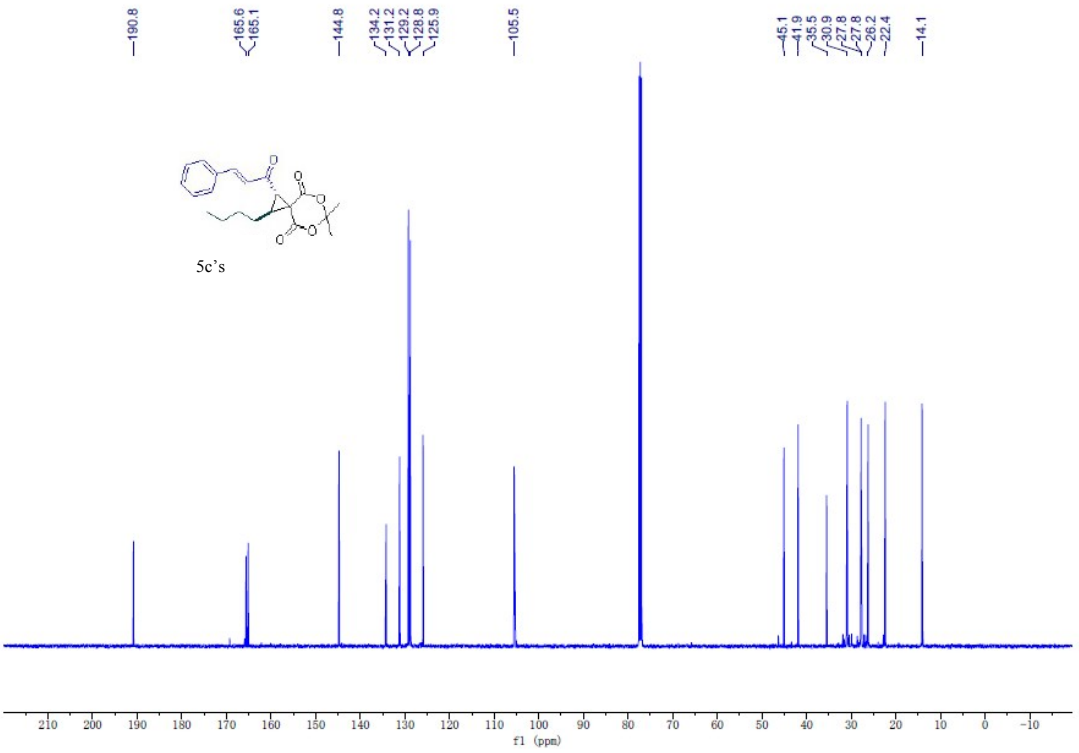

8.42
8.00
7.98
7.94
7.92
7.89
7.87
7.85
7.84
7.60
7.58
7.57
7.54
7.53
7.51
3.81
3.80
2.98
2.97
2.95
2.94
1.96
1.95
1.93
1.92
1.91
1.89
1.85
1.84
1.83
1.81
1.79
1.78
1.77
1.73
1.72
1.71
1.56
1.55
1.53
1.52
1.50
1.47
1.46
1.45
1.44
1.44
1.43
1.42
1.41
1.41
0.95
0.93
0.92
0.94
0.98
1.05
2.02
2.03
1.00
0.98
1.21
7.10
2.01
2.05
2.97
f1 (ppm)

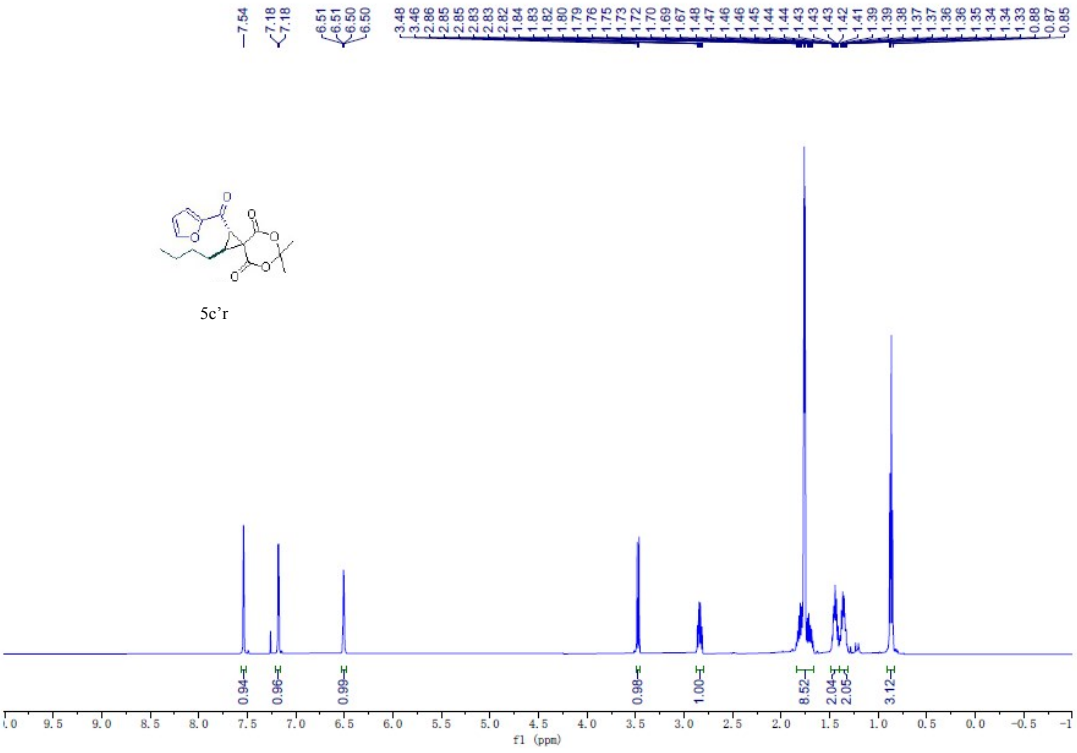
5c'q


190.8
165.3
164.9
136.0
133.5
132.5
130.2
129.8
129.0
128.9
128.0
127.0
123.7
105.5
43.8
42.0
36.0
30.7
27.7
27.6
26.2
22.3
14.0
f1 (ppm)

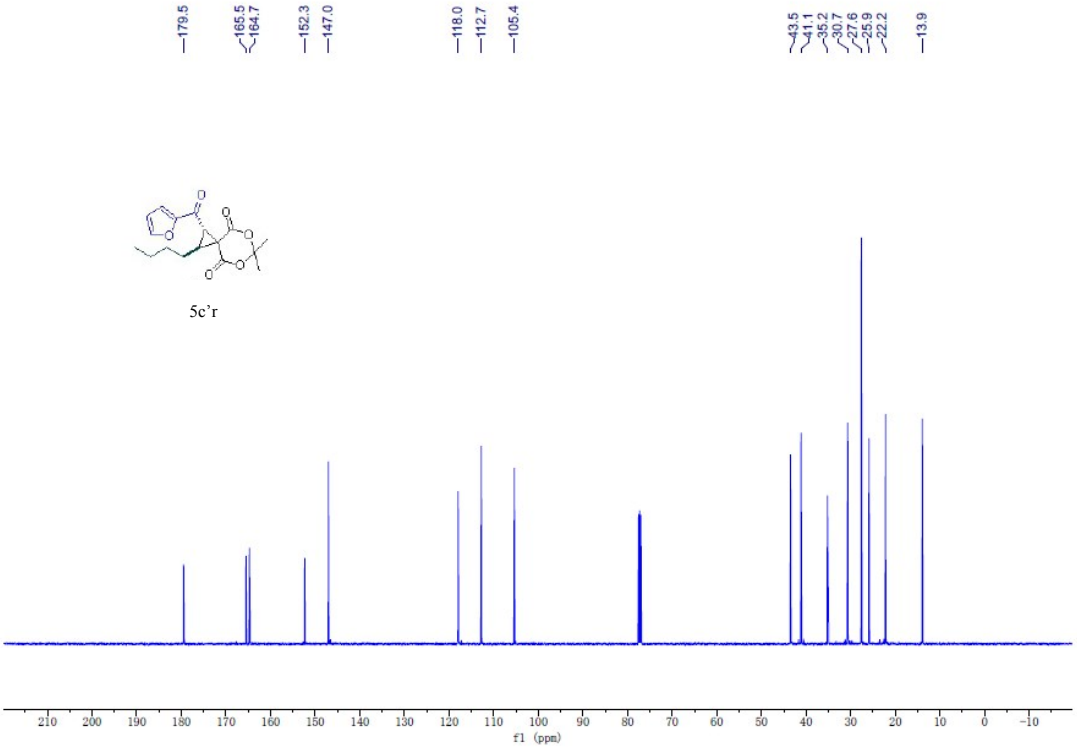
5c'q


7.57
7.55
7.54
7.54
7.53
7.53
7.41
7.40
7.40
7.39
6.82
6.79
3.41
3.39
2.88
2.87
2.87
2.85
2.85
2.84
1.88
1.88
1.86
1.85
1.84
1.83
1.82
1.81
1.81
1.78
1.78
1.77
1.75
1.74
1.74
1.74
1.73
1.73
1.72
1.52
1.50
1.49
1.48
1.46
1.44
1.44
1.43
1.43
1.42
1.42
1.41
1.41
1.40
1.40
1.39
1.38
0.94
0.92
5c's
3.04
2.93
0.99
0.99
1.00
7.30
1.57
2.09
2.27
3.05
f1 (ppm)

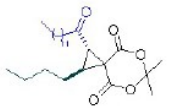

190.8
165.6
165.1
144.8
134.2
131.2
129.2
128.8
125.9
105.5
45.1
41.9
35.5
30.9
27.8
27.8
26.2
22.4
14.1
5c's
f1 (ppm)


7.54
7.18
7.18
6.51
6.51
6.50
6.50
3.48
3.46
3.46
2.86
2.85
2.85
2.83
2.83
2.82
1.84
1.83
1.82
1.80
1.79
1.76
1.75
1.73
1.72
1.70
1.69
1.67
1.48
1.47
1.46
1.46
1.45
1.44
1.44
1.43
1.43
1.43
1.42
1.41
1.39
1.39
1.38
1.37
1.37
1.36
1.36
1.35
1.34
1.34
1.33
0.88
0.87
0.85
0.94
0.96
0.99
0.98
1.00
8.52
2.04
2.05
3.12
f1 (ppm)

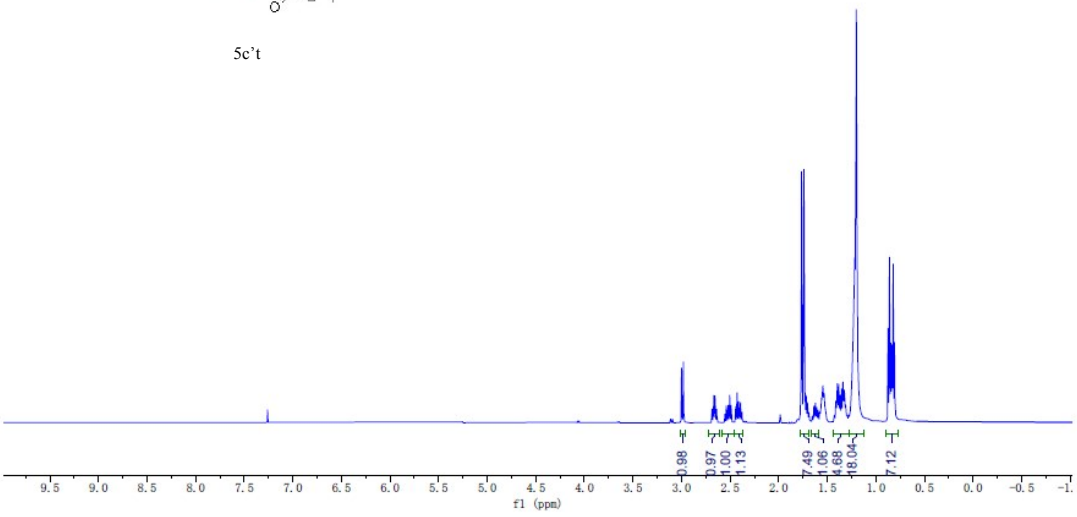
5c'r

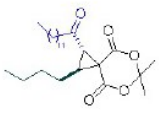

179.5
165.5
164.7
152.3
147.0
118.0
112.7
105.4
43.5
41.1
35.2
30.7
27.6
25.9
22.2
13.9
f1 (ppm)

5c'r

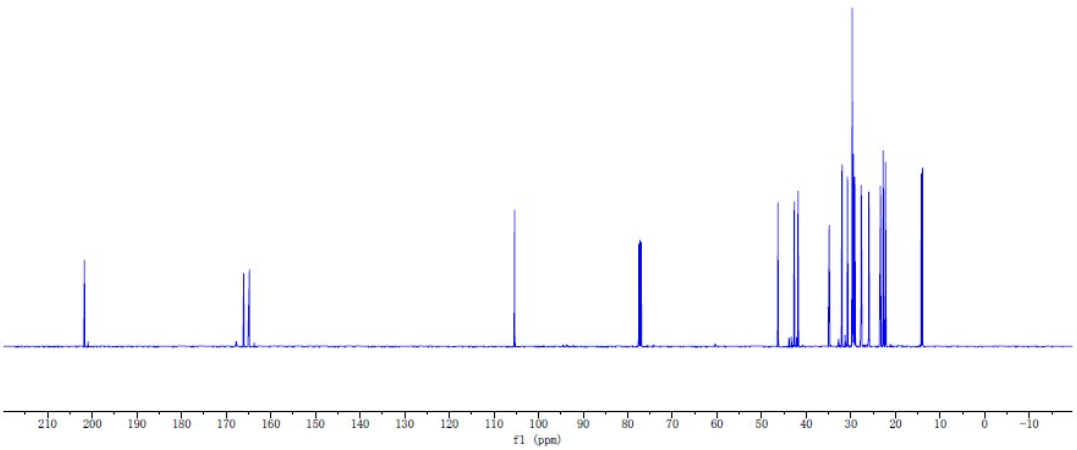


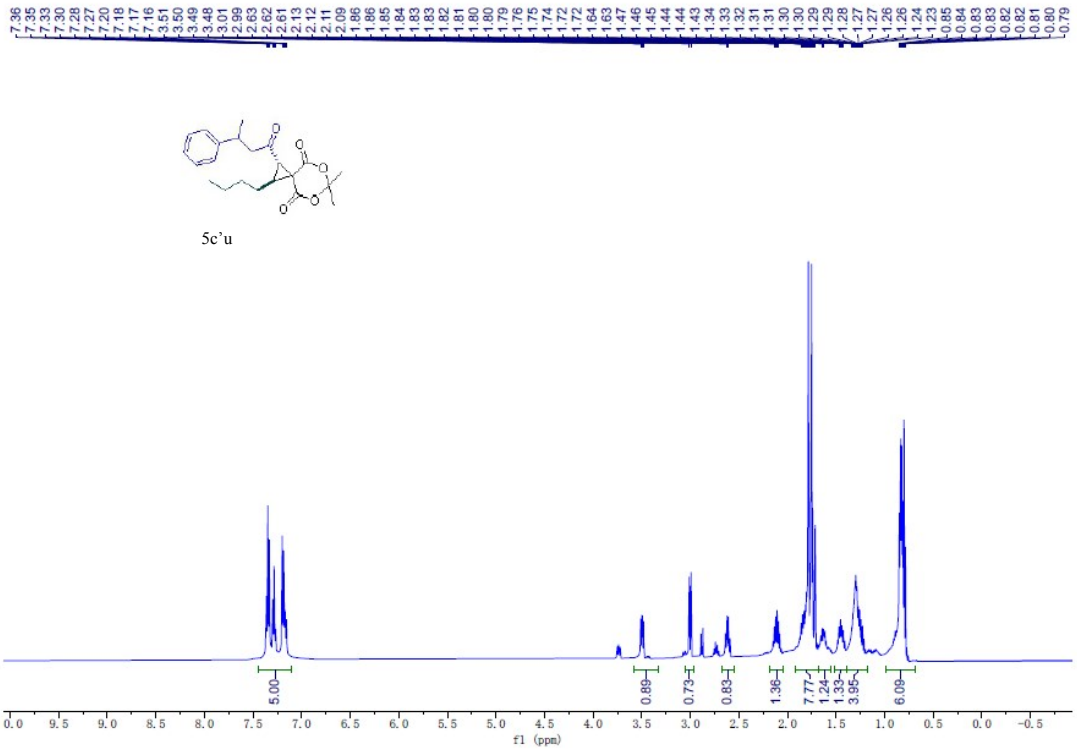
5c't

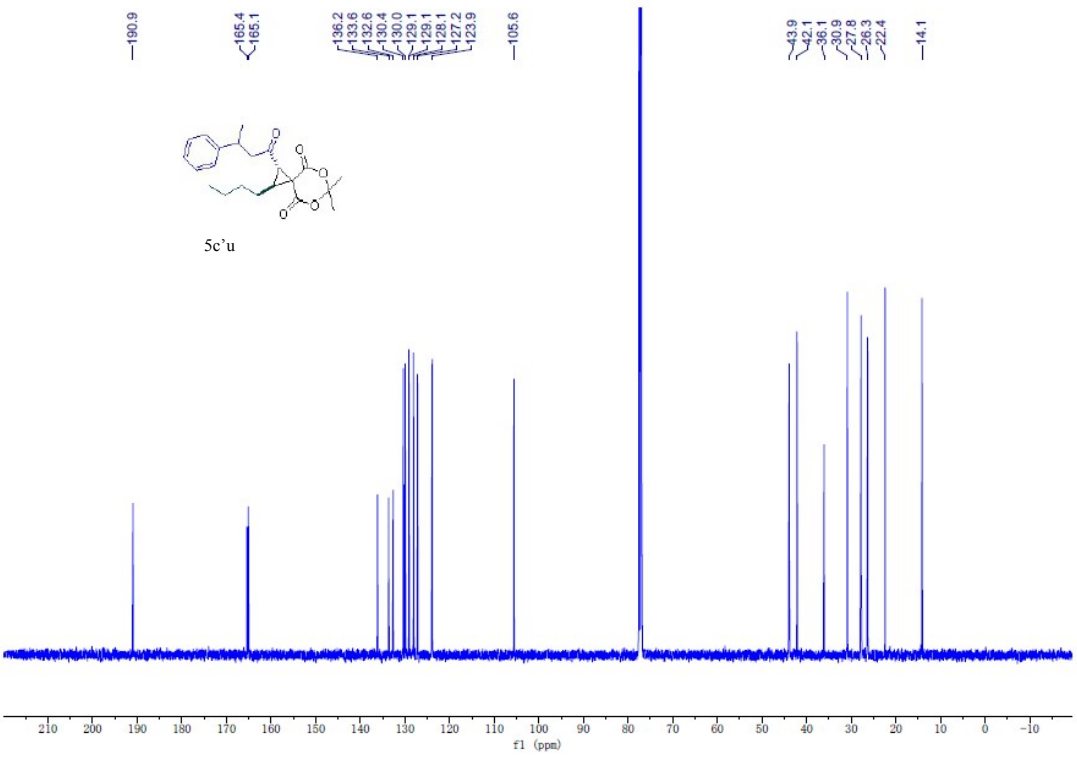


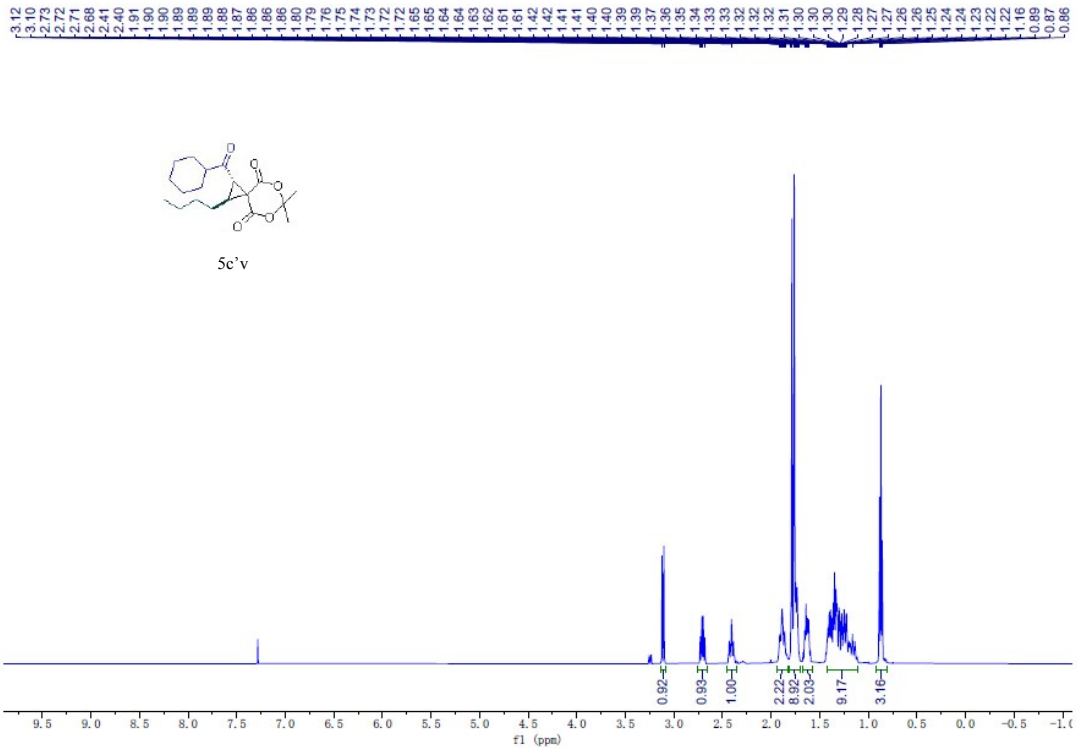


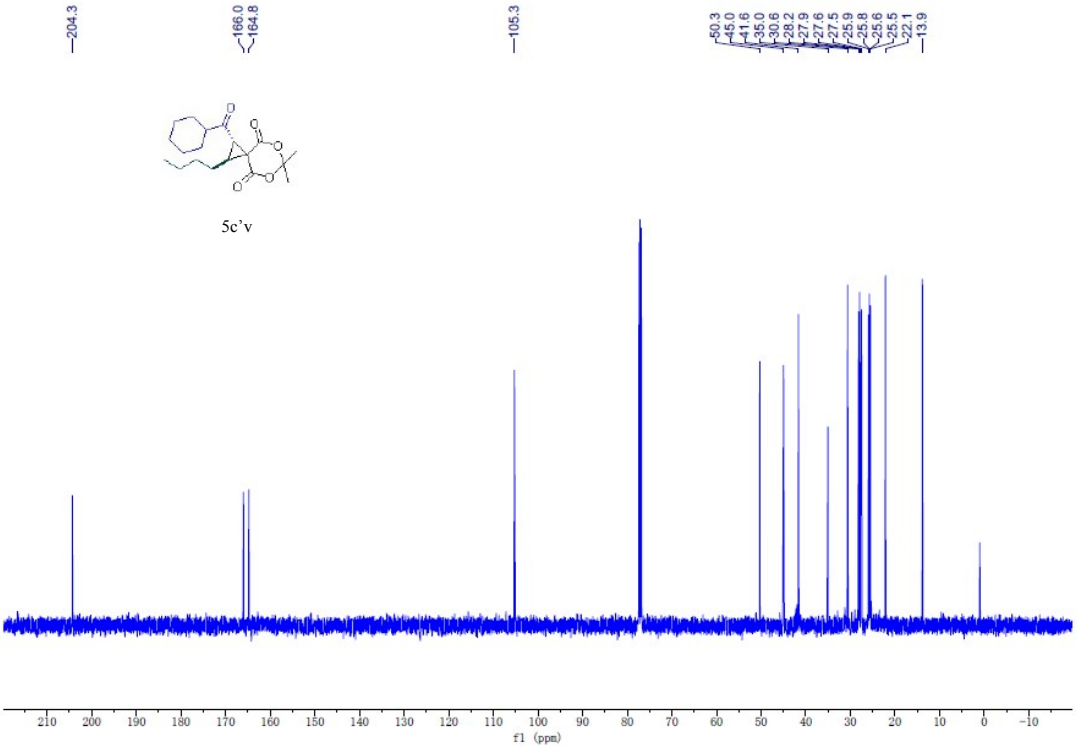
5c't

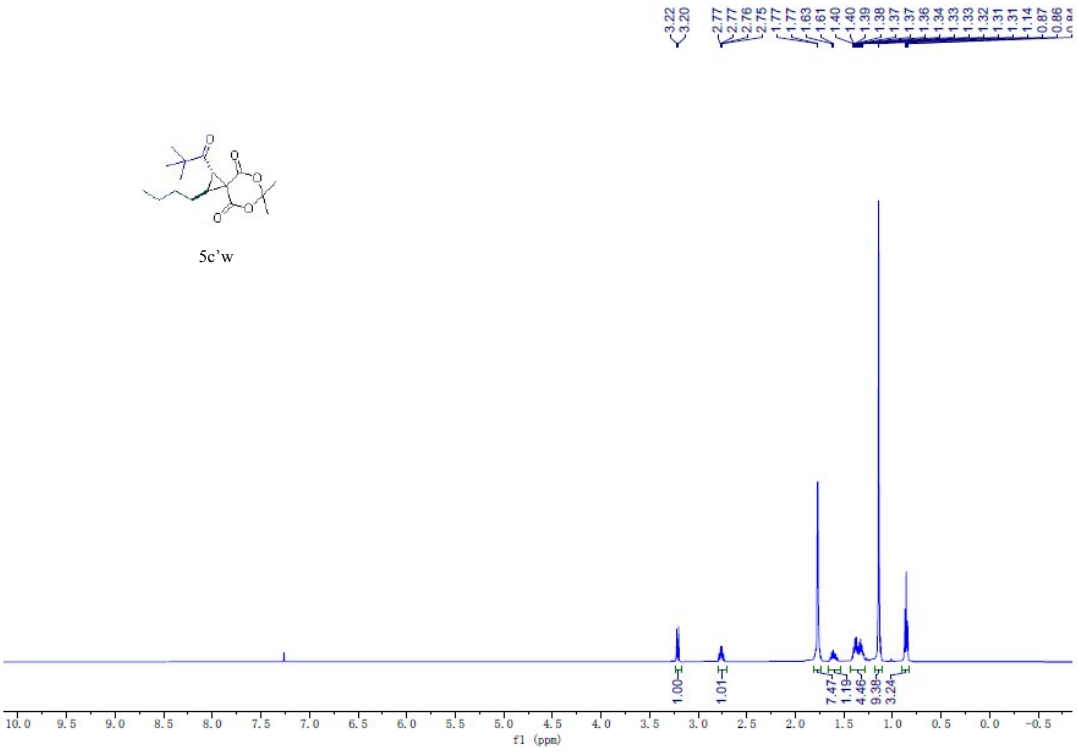



7.36
7.35
7.33
7.30
7.28
7.27
7.20
7.18
7.17
7.16
3.51
3.50
3.49
3.48
3.01
2.99
2.63
2.62
2.61
2.13
2.12
2.11
2.09
1.86
1.86
1.85
1.84
1.83
1.83
1.82
1.81
1.80
1.80
1.79
1.76
1.75
1.74
1.72
1.72
1.64
1.63
1.47
1.46
1.45
1.44
1.44
1.43
1.34
1.33
1.32
1.31
1.31
1.30
1.30
1.29
1.29
1.28
1.27
1.27
1.26
1.26
1.24
1.23
0.85
0.84
0.83
0.83
0.82
0.82
0.81
0.80
0.79
5c'u
5.00
0.89
0.73
0.83
1.36
7.77
1.24
1.33
3.95
6.09
f1 (ppm)

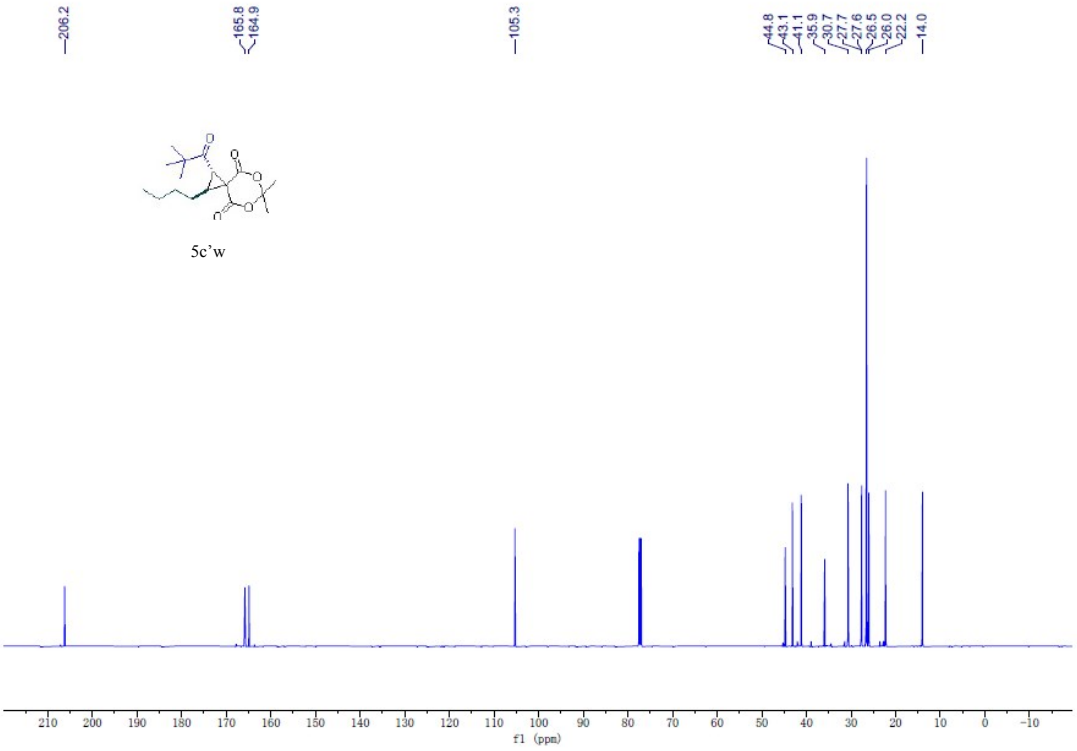

190.9
165.4
165.1
136.2
133.6
132.6
130.4
130.0
129.1
129.1
128.1
127.2
123.9
105.6
43.9
42.1
36.1
30.9
27.8
26.3
22.4
14.1
5c'u
f1 (ppm)


5c'v
f1 (ppm)

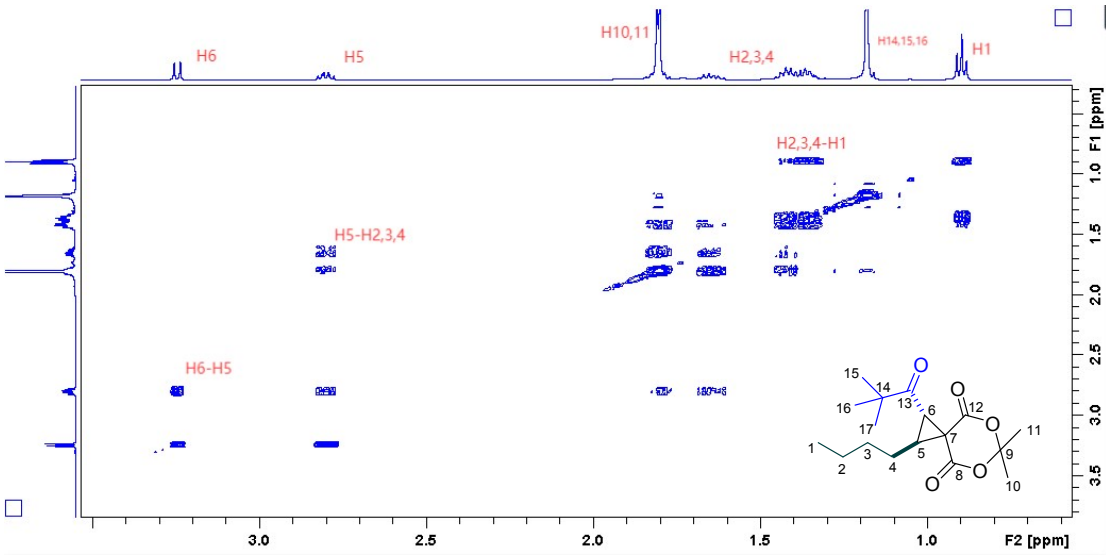

5c'v
f1 (ppm)

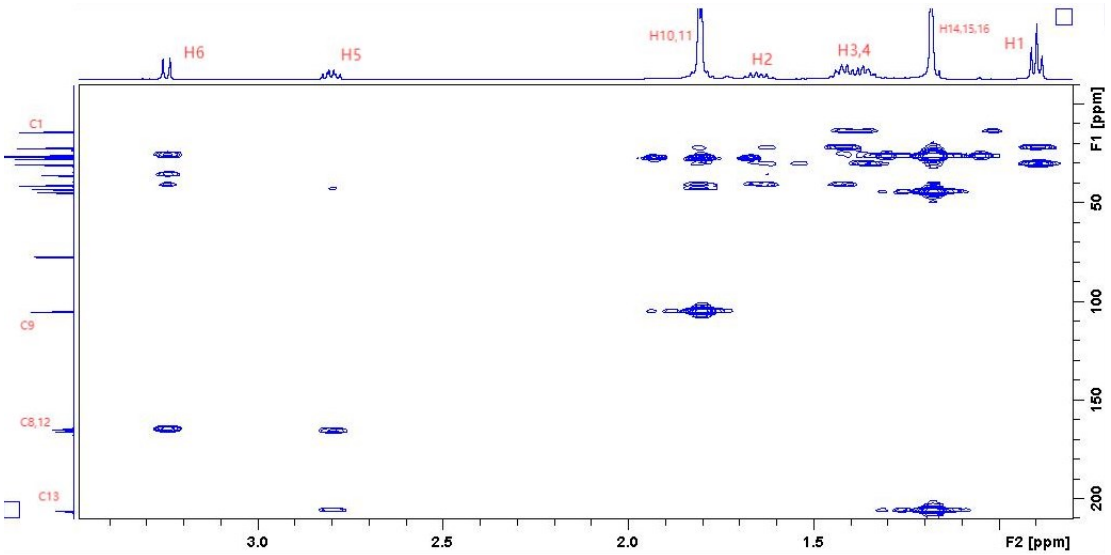


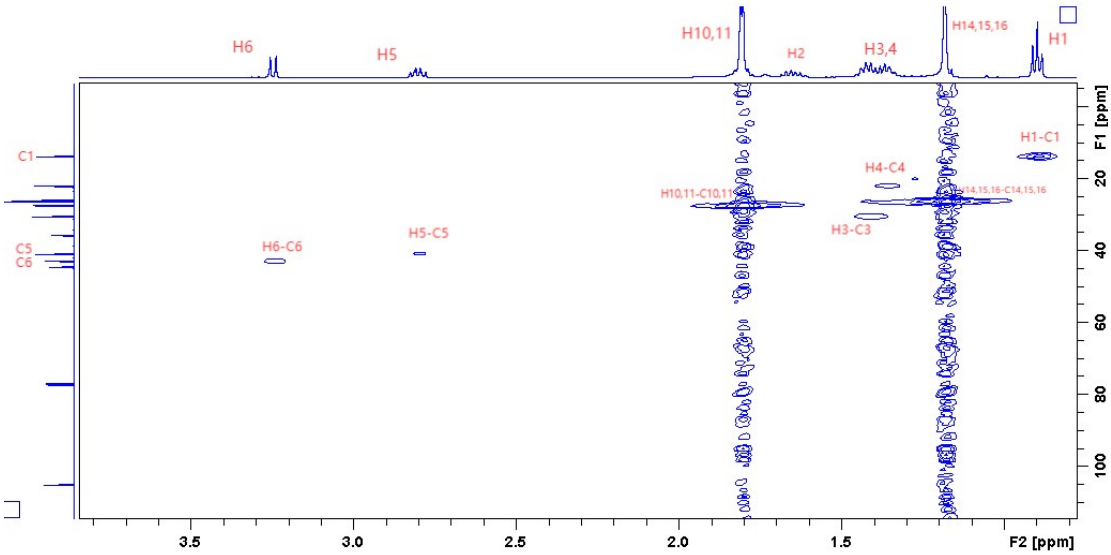
5c’w



5c’w


H6
H5
H10,11
H2,3,4
H14,15,16
H1
H2,3,4-H1
H5-H2,3,4
H6-H5
F1 [ppm]
F2 [ppm]


H6
H5
H10,11
H2
H3,4
H14,15,16
H1
C1
C9
C8,12
C13
F1 [ppm]
F2 [ppm]

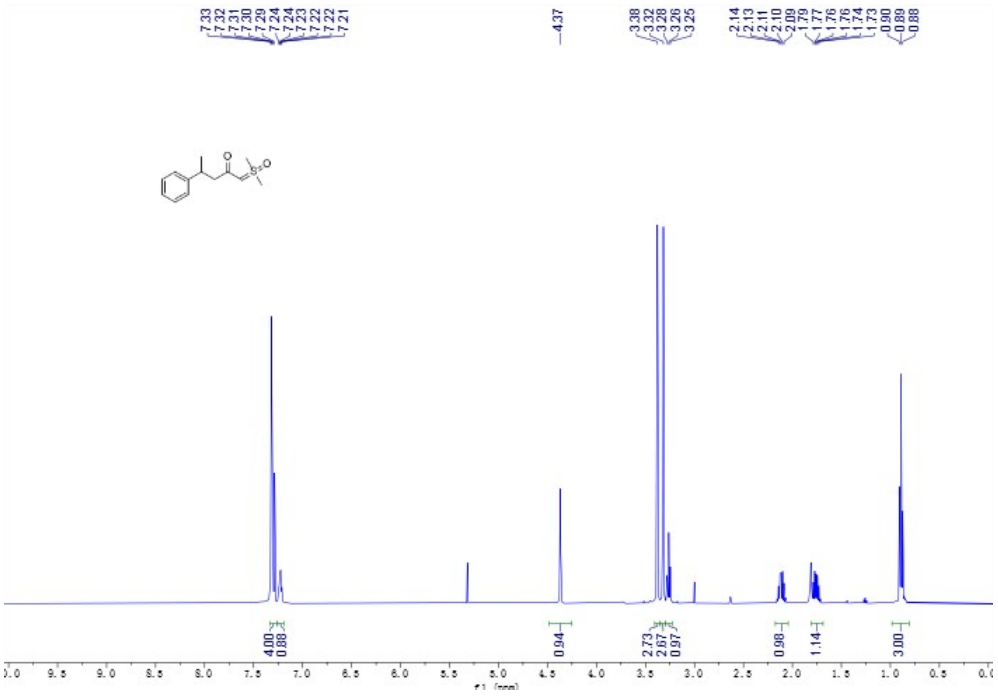

H6
H5
H10,11
H2
H3,4
H14,15,16
H1
C1
C5
C6
H6-C6
H5-C5
H10,11-C10,11
H4-C4
H3-C3
H14,15,16-C14,15,16
H1-C1
F1 [ppm]
F2 [ppm]

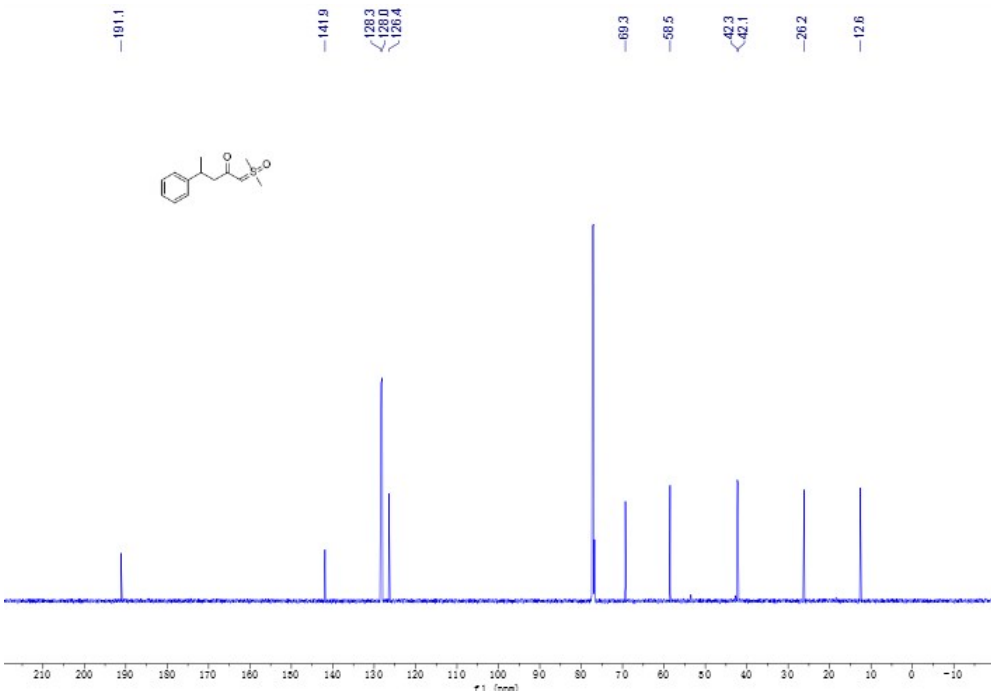
5c’x

3.21
3.19
2.76
2.74
2.74
2.73
2.72
2.71
1.98
1.40
1.38
1.38
1.37
1.35
1.35
1.34
1.32
1.31
1.31
1.30
1.29
1.29
1.28
1.28
0.85
0.84
0.82
0.99
1.00
3.18
21.27
4.34
3.38
f1 (ppm)

5c’x

205.6
165.8
164.9
105.2
46.9
42.6
40.8
38.1
36.5
35.7
30.6
27.9
27.6
27.6
25.9
22.2
13.9
f1 (ppm)


7.33
7.32
7.31
7.30
7.29
7.24
7.24
7.23
7.22
7.22
7.21
4.37
3.38
3.32
3.28
3.26
3.25
2.14
2.13
2.11
2.10
2.09
1.79
1.77
1.76
1.76
1.74
1.73
0.90
0.89
0.88
4.00
0.88
0.94
2.73
2.67
0.97
0.98
1.14
3.00


191.1
141.9
128.3
128.0
126.4
69.3
58.5
42.3
42.1
26.2
12.6