Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cobalt(III)-Catalyzed 1,4-Addition of C-H Bond of Oxime to Maleimides

Xiangxiang Chen, Jiangtao Ren, Hu Xie, Wei Sun, Meng Sun,* Biao Wu*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710127, People's Republic of China

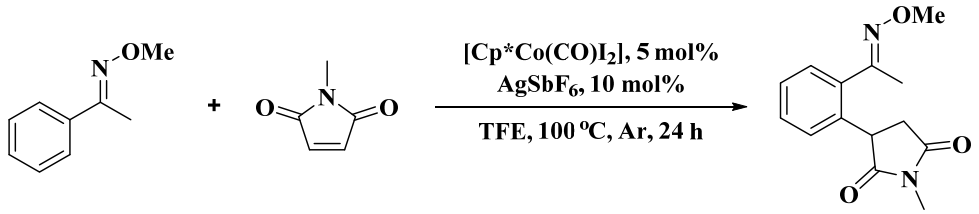
** To whom correspondence should be addressed. E-mail:* sunmeng@nwu.edu.cn

Contents:

1. General methods.

All reactions involving air- and moisture-sensitive reagents were carried out under a nitrogen atmosphere. Toluene, DMF, 1, 2-dichloroethane, DMSO, 1, 4- dioxane and CH_3CN were distilled from appropriate drying agents prior to use. All chemicals were purchased from Aldrich and used without further purification. Thin-layer chromatography (TLC) was performed using 60 mesh silica gel plates visualized with short-wavelength UV light (254 nm). Silica gel 60 (230~400 mesh) was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker INOVA-400. NMR Spectrums were recorded on a 400 instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts (δ) were measured in ppm relative to TMS δ = 0 for ^{1}H, or to chloroform δ = 77.0 for ^{13}C as internal standard. Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), Coupling constants, *J*, are reported in hertz. Mass data were measured with Thermo Scientific DSQ II mass spectrometer.

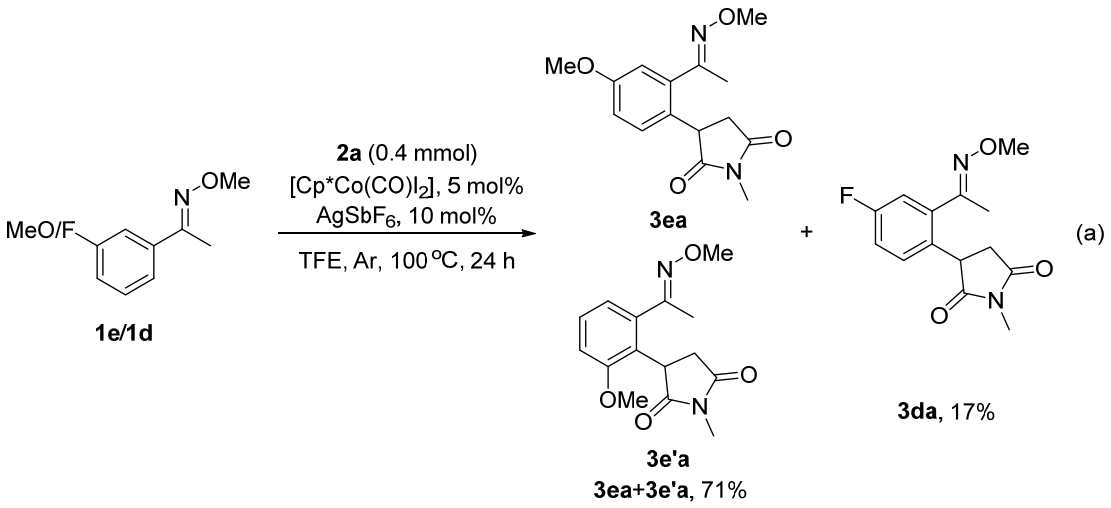
2. Experimental procedures.



A mixture of *O*-methyl ketoxime (0.2 mmol, 30.0 mg, 1.0 equiv), *N*-methylmaleimide (0.4 mmol, 44.4 mg, 2.0 equiv), [Cp*Co(CO)I_2] (0.01 mmol, 4.8 mg, 5 mol%), and $AgSbF_6$ (0.02 mmol, 6.9 mg, 10 mol%) in TFE (1.0 mL) was stirred under argon at 100 °C for 24 hours. After cooling to room temperature, the solvent was removed under reduced pressure. The contents were subjected to flash chromatography (petrol ether/EtOAc 4:1, Rf = 0.4) to give the product as a white solid (0.17 mmol, 45.2 mg, 87%).

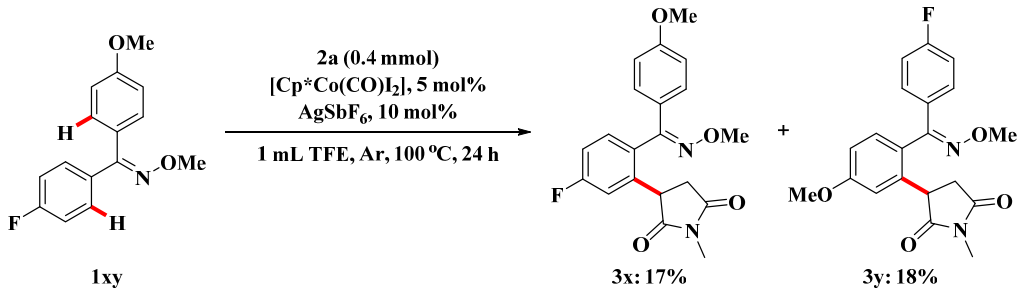
3. Mechanistic studies

Intermolecular competition experiment between 1e and 1d



To a 10 mL tube was added 1-(3-fluorophenyl)ethanone *O*-methyl oxime (33.4 mmol, 0.2 mmol, 1.0 equiv), 1-(3-methoxyphenyl)ethanone *O*-methyl oxime (35.8 mg, 0.2 mmol, 1.0 equiv), *N*-methylmaleimide (0.4 mmol, 44.4 mg, 2.0 equiv), [Cp*Co(CO)I_2] (0.01 mmol, 4.8 mg, 5 mol%), $AgSbF_6$ (0.02 mmol, 6.9 mg, 10 mol%) and TFE (1.0 mL). The mixture was stirred under argon at 100 °C for 24 hours. After cooling to room temperature, the solvent was removed under reduced pressure. Purification by flash column chromatography (petrol ether/EtOAc 4:1) gave **3ea** and **3e'a** as a mixture (colorless oil, 0.142 mmol, 41.2 mg, 71%, Rf = 0.2), and **3da** (0.034 mmol, 11.0 mg, 17%, Rf = 0.3) as pale white solid, respectively.

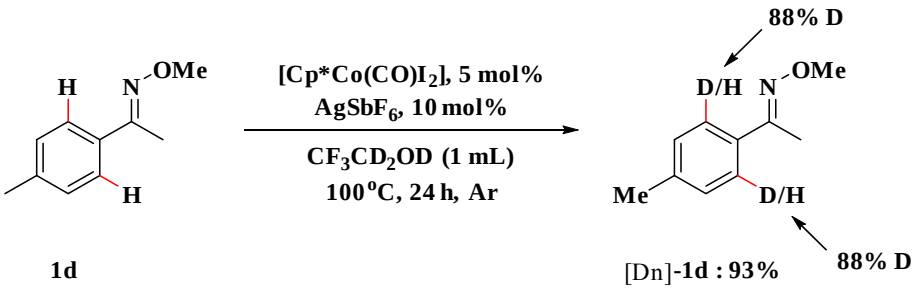
Intramolecular competition experiment of (4-fluorophenyl)(4-methoxyphenyl)methanone *O*-methyl oxime[1]



A mixture of (4-fluorophenyl)(4-methoxyphenyl)methanone *O*-methyl oxime (0.2 mmol, 51.8 mg, 1.0 equiv), *N*-methylmaleimide (0.4 mmol, 44.4 mg, 2.0 equiv), [Cp*Co(CO)I_2] (0.01 mmol, 4.8 mg, 5 mol%), and $AgSbF_6$ (0.02 mmol, 6.9 mg, 10 mol%) in TFE (1.0 mL) was stirred under argon at 100 °C for 24 hours. After cooling to room temperature, the solvent was removed under reduced pressure. Purification by flash column chromatography (petrol ether/EtOAc 4:1, Rf = 0.2)

gave **3x** (0.034 mmol, 12.6 mg, yield : 17%) and **3y** (0.036 mmol, 13.3mg, yield : 18%) as white solids, respectively.

H/D exchange experiments



1d [Dn]-**1d : 93%**

A mixture of 1-(*p*-tolyl)ethan-1-one *O*-methyl oxime (0.2 mmol, 32.6 mg, 1.0 equiv), [Cp*Co(CO)I_2] (0.01 mmol, 4.8 mg, 5 mol%), and $AgSbF_6$ (0.02 mmol, 6.9 mg, 10 mol%) in CF_3CD_2OD (1 mL) was stirred under argon at 100 °C for 24 hours. After cooling to ambient temperature, the solvent was removed in vacuo and the mixture was purified by column chromatography on silica gel (PE/EtOAc 20:1, Rf = 0.5) yielded the recovered starting material [Dn]-**1d** (0.186 mmol, 30.6 mg, 93%) as colorless oil.

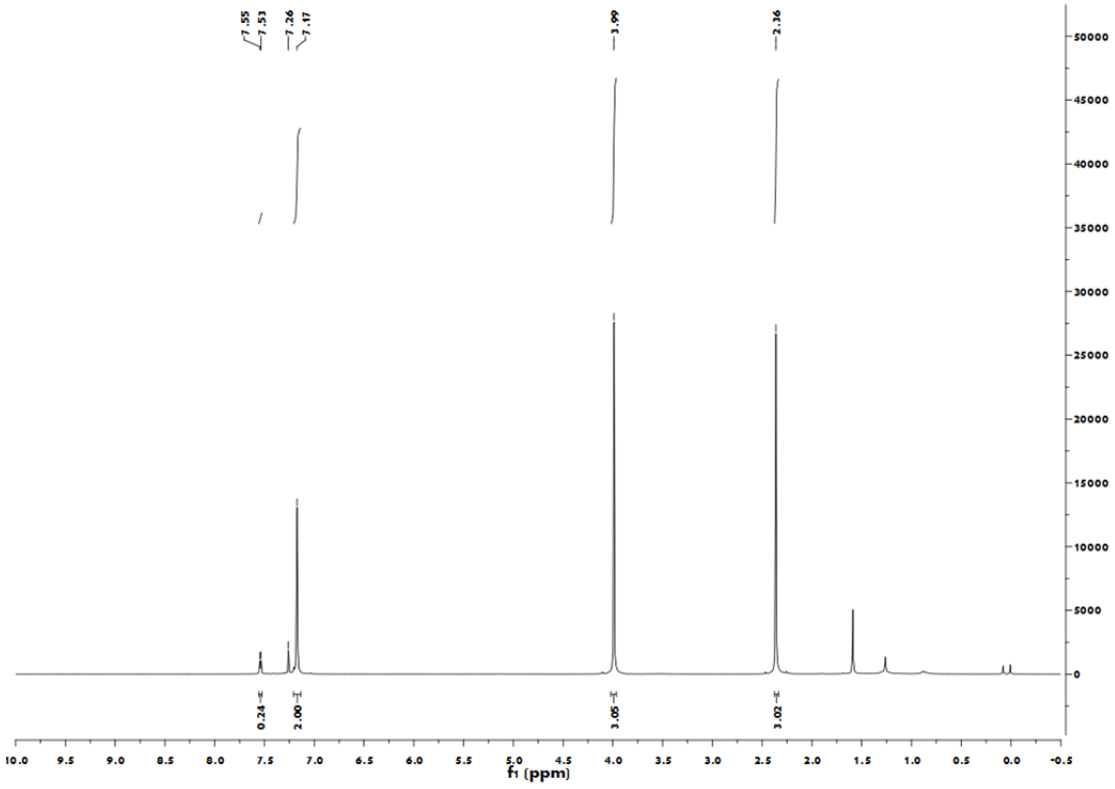
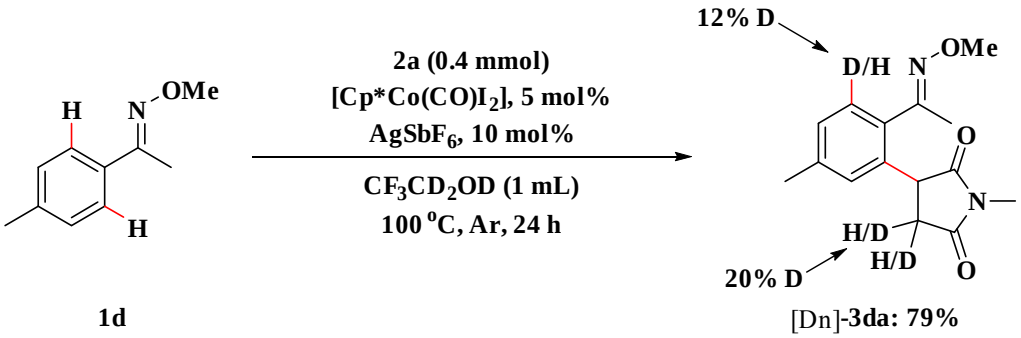


Figure 1: [Dn]-**1d** ^{1}H-NMR (400 MHz, $CDCl_3$)



1d

[Dn]-**3da: 79%**

A mixture of **1d** (0.2 mmol, 32.6 mg, 1.0 equiv), **2a** (0.4 mmol, 44.4 mg, 2.0 equiv), [Cp*Co(CO)I_2] (0.01 mmol, 4.8 mg, 5 mol%), and $AgSbF_6$ (0.02 mmol, 6.9 mg, 10 mol%) in CF_3CD_2OD was stirred under argon at 100 °C for 24 hours. After cooling to ambient temperature, the solvent was removed in vacuo and the mixture was purified by column chromatography on silica gel (PE/EtOAc = 4:1, Rf = 0.4) yielded the product [Dn]-**3da** (0.168 mmol, 44.1 mg, 79%) as a pale white solid.

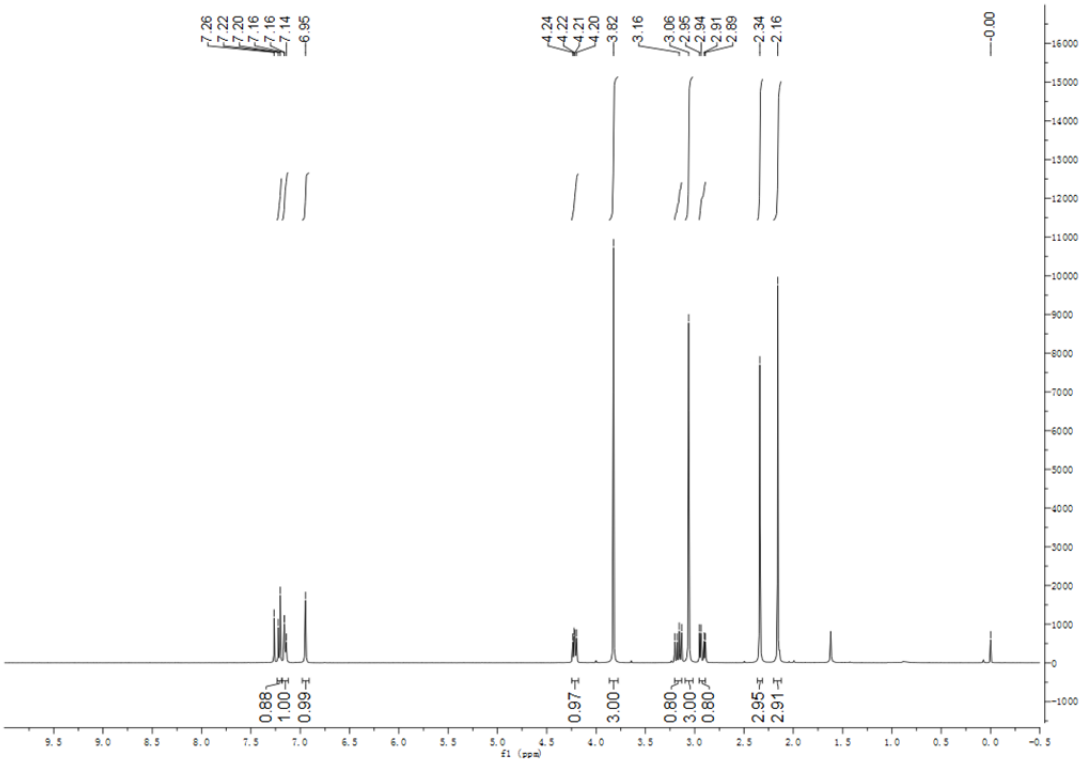
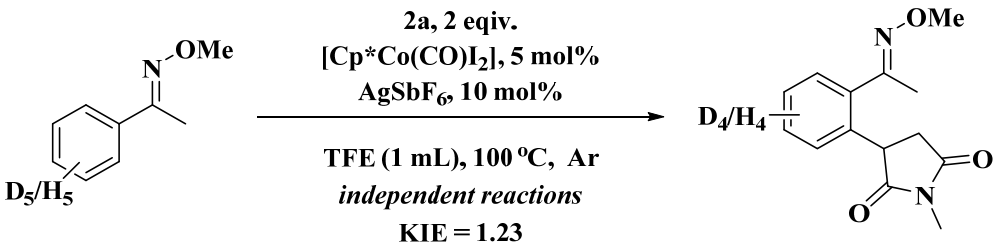


Figure 2 : [Dn]-**3ad** ^{1}H NMR (400 MHz, $CDCl_3$)



Two independent reactions with 1-phenylethan-1-one *O*-methyl oxime **1a** or deuterated substrate [D_5]-**1a** under the standard conditions were taken: To a 10-mL-tube charged with a mixture of 1-phenylethan-1-one *O*-methyl oxime (0.2 mmol, 30.0 mg, 1.0 equiv), *N*-methylmaleimide (0.4 mmol, 44.4 mg, 2.0 equiv), [Cp*Co(CO)I_2] (0.01 mmol, 4.8 mg, 5 mol%), and $AgSbF_6$ (0.02 mmol, 6.9 mg, 10 mol%) was added 1.0 mL of TFE under argon at 100 °C for 0.5 h, 1.0 h, 1.5 h, 2.0 h, 2.5 h, respectively. The consumption of substrate **1a** or [D_5]-**1a** and the appearance of the products **3aa** or [Dn]-**3aa** were monitored by ^{1}H NMR analysis. These experiments indicated that the C–H bond activation is not the turnover-limiting step.

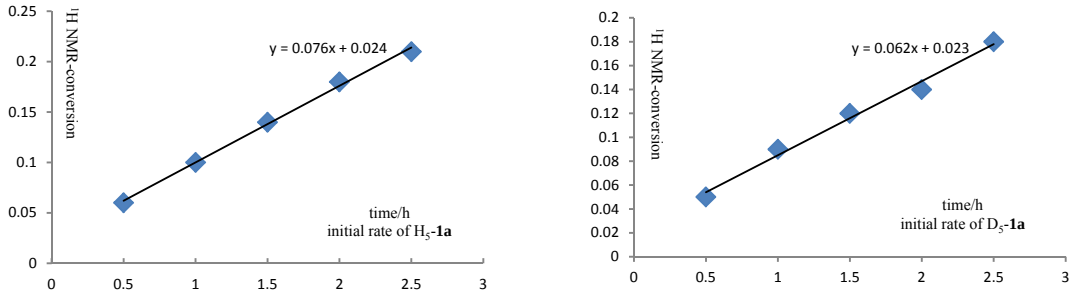
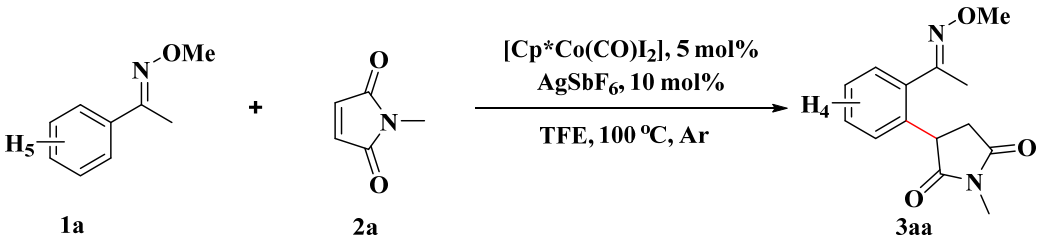
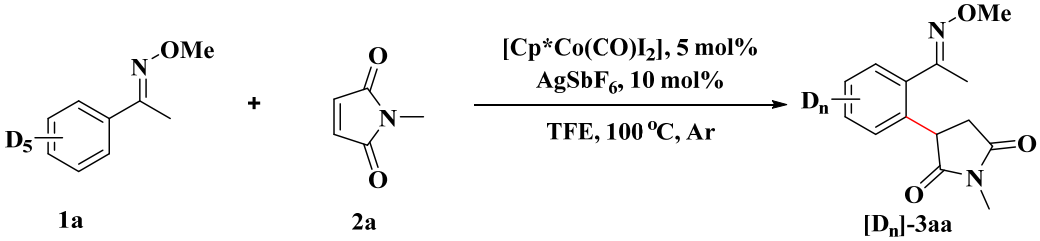


Figure 3 : initial rate of **1a** or [Dn]-**1a** (monitored by ^{1}H NMR, 400 MHz, $CDCl_3$)

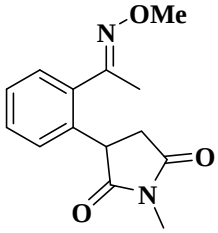


t/(h)	0.5	1.0	1.5	2.0	2.5
3aa	0.06	0.10	0.14	0.18	0.21
1a	0.94	0.90	0.86	0.82	0.79

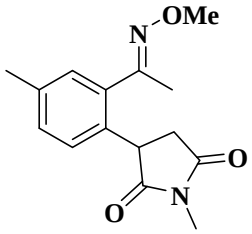


t/(h)	0.5	1.0	1.5	2.0	2.5
[D_n]-**3aa**	0.05	0.09	0.12	0.14	0.18
[D_5]-**1a**	0.95	0.91	0.88	0.86	0.82

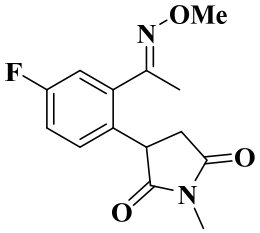
4. Characterization of the Products



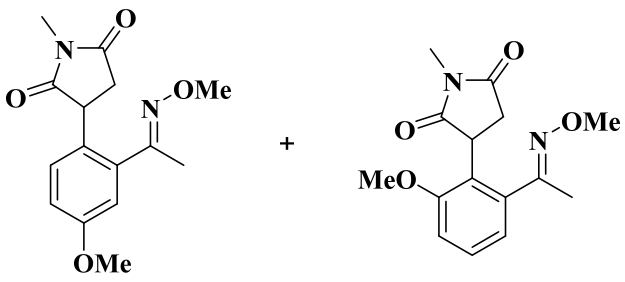
3aa: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.30 (m, 3H), 7.16-7.14 (m, 1H), 4.24 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.21-3.14 (m, 1H), 3.06 (s, 3H), 2.95-2.90 (m, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.54, 176.49, 156.77, 137.00, 135.26, 130.05, 129.08, 129.02, 127.91, 61.65, 45.48, 39.26, 25.00, 16.09. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{16}N_2O_3Na^+$: 283.1059, Found: 283.1059.



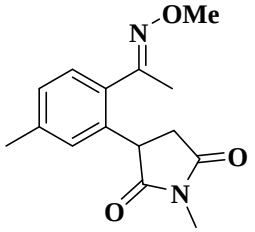
3ca: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.14-7.11 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 1H), 4.18 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.81 (s, 3H), 3.18-3.11 (m, 1H), 3.04 (s, 3H), 2.93-2.87 (m, 1H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.70, 176.58, 156.83, 137.72, 136.76, 132.23, 129.91, 129.74, 129.59, 61.59, 45.07, 39.24, 24.94, 20.96, 16.07. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{19}N_2O_3Na^+$: 297.1215, Found: 297.1211.



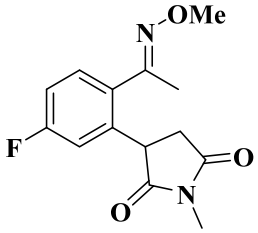
3da: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.33 (q, *J* = 4.0 Hz, 1H), 7.13-7.07 (m, 2H), 4.43 (dd, *J* = 4.0 Hz, *J* = 8.0Hz, 1H), 3.83 (s, 3H), 3.19-3.15 (m, 1H), 3.05 (s, 3H), 2.89 (br, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.97, 176.21, 161.37 (d, *J* = 245.0Hz), 139.32, 129.17 (d, *J* = 10.0 Hz), 124.49, 123.03 (d, *J* = 14.0 Hz), 115.81 (d, *J* = 30.0 Hz), 115.72 (d, *J* = 24.0 Hz), 61.83, 37.75, 29.66, 25.01, 15.98.



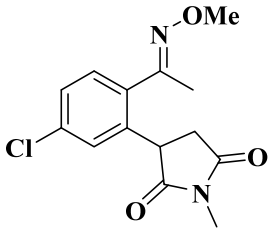
3ea and **3e'a**: Colorless oil. This compound was obtained as a 1:0.72 mixture of structural isomer. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (t, *J* = 4.0 Hz, 1H), 7.07 (d, *J* = 4.0 Hz, 1H), 6.93 (br, 1H), 6.88 (t, *J* = 4.0 Hz, 2H), 6.82 (s, 1H), 4.28-4.15 (m, 2H), 3.95-3.72 (m, 12H), 3.16-2.73 (m, 10H), 2.22-2.16 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 179.16, 178.83, 177.13, 176.62, 158.99, 156.61, 138.20, 131.19, 128.82, 128.79, 127.35, 124.06, 120.85, 114.66, 114.44, 111.48, 61.99, 61.68, 55.86, 55.41, 44.81, 40.95, 39.29, 36.99, 29.67, 24.98, 24.82, 16.49, 16.06.



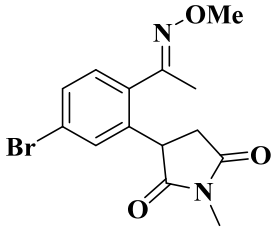
3fa: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (d, *J* = 8.0 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.94 (s, 1H), 4.24-4.20 (m, 1H), 3.82 (s, 3H), 3.20-3.13 (m, 1H), 3.06 (s, 3H), 2.95-2.89 (m, 1H), 2.34 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.66, 176.62, 156.72, 139.06, 135.12, 134.15, 130.61, 129.03, 128.68, 61.60, 45.45, 39.29, 25.00, 21.09, 16.07. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{19}N_2O_3Na^+$: 297.1215, Found: 297.1214.



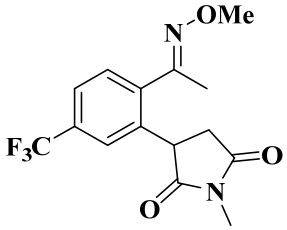
3ga: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45-7.40 (m, 1H), 7.19 (dt, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 7.01 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 4.36 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.96 (s, 3H), 3.35-3.28 (m, 1H), 3.19 (s, 3H), 3.08-3.02 (m, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.85, 176.05, 162.38 (d, *J* = 248.0 Hz), 155.95, 137.62 (d, *J* = 8.0 Hz), 133.15 (d, *J* = 3.0 Hz), 130.94 (d, *J* = 8.0 Hz), 116.93 (d, *J* = 22.0 Hz), 115.01 (d, *J* = 21.0 Hz), 61.67, 45.34, 38.98, 25.04, 16.15. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{15}FN_2O_3Na^+$: 301.0964, Found: 301.0960.



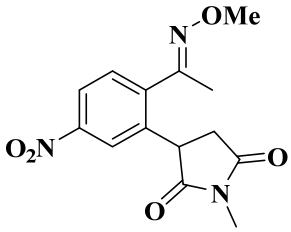
3ha: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.32 (m, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.16 (d, *J* = 2.0 Hz, 1H), 4.22-4.18 (m, 1H), 3.83 (s, 3H), 3.21-3.14 (m, 1H), 3.06 (s, 3H), 2.95-2.89 (m, 1H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.81, 176.01, 155.88, 137.07, 135.52, 134.67, 130.41, 130.18, 128.08, 61.74, 45.28, 38.99, 25.05, 15.97. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{15}ClN_2O_3Na^+$: 317.0669, Found:317.0666.



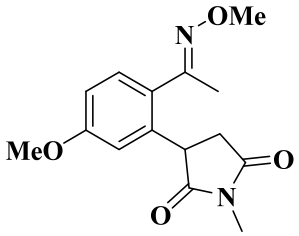
3ia: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 2.0 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 4.20-4.16 (m, 1H), 3.81 (s, 3H), 3.20-3.13 (m, 1H), 3.05 (s, 3H), 2.95-2.89 (m, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.79, 175.99, 155.94, 137.29, 136.00, 133.11, 131.03, 130.62, 122.80, 61.75, 45.23, 39.01, 25.06, 15.93. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{15}BrN_2O_3Na^+$: 361.0164, Found: 361.0164.



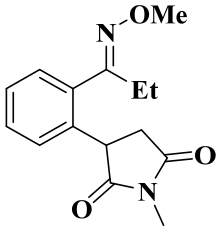
3ja: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.61 (dd, *J* = 1.2 Hz, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 4.27-4.23 (m, 1H), 3.82 (s, 3H), 3.23-3.16 (m, 1H), 3.05 (s, 3H), 2.99-2.93 (m, 1H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 175.74, 175.67, 155.90, 140.59, 136.10, 130.95 (q, *J* = 33.0 Hz), 129.75, 127.43 (q, *J* = 4.0 Hz), 124.78 (q, *J* = 4.0 Hz), 123.51 (q, *J* = 271.0 Hz), 61.83, 45.62, 38.94, 25.07, 15.90. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{15}F_3N_2O_3Na^+$: 351.0932, Found: 351.0933.



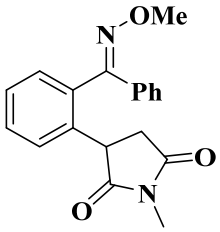
3ka: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.19 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 8.07 (d, J = 4.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 4.35-4.31 (m ,1H), 3.85 (s, 3H), 3.25-3.19 (m, 1H), 3.05 (s, 3H), 2.97-2.91 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.21, 175.42, 155.32, 147.67, 143.41, 137.23, 130.27, 125.48, 122.79, 62.05, 45.54, 38.79, 25.13, 15.82. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{14}H_{15}ClN_2O_3Na^+$: 328.0909, Found: 328.0909.



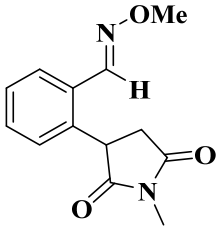
3la: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 2.0 Hz, 1H), 4.24-4.20 (m, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 3.19-3.12 (m, 1H), 3.04 (s, 3H), 2.95-2.89 (m, 1H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.22, 176.35, 159.84, 156.46, 136.87, 130.45, 129.55, 115.89, 112.96, 61.52, 55.36, 45.65, 39.14, 24.94, 16.06. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{18}N_2O_4Na^+$:313.1164, Found:313.1169.



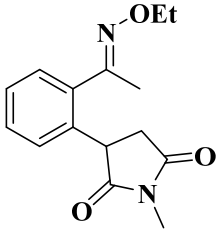
3ma: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35-7.32 (m, 3H), 7.13-7.11 (m, 1H), 4.28-4.24 (m, 1H), 3.86 (s, 3H), 3.20-3.13 (m, 1H), 3.07 (s, 3H), 2.87-2.81 (m, 1H), 2.77-2.70 (m, 1H), 2.67-2.57 (m, 1H), 1.10 (t, *J* = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.30, 176.38, 161.05, 136.24, 136.13, 129.13, 129.11, 128.92, 127.70, 61.69, 45.00, 39.33, 24.99, 23.20, 10.33. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{18}N_2O_3Na^+$: 297.1215, Found: 297.1213.



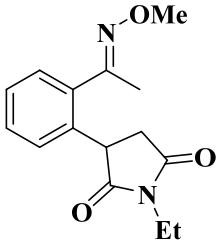
3na: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.51-7.49 (m, 2H), 7.41-7.35 (m, 4H), 7.27(dt, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 7.15 (ddd, *J* = 2.0 Hz, *J* = 4.0 Hz, *J* = 8.0 Hz, 2H), 4.33-4.29 (m, 1H), 3.91 (s, 3H), 3.05-2.98 (m, 4H), 2.88-2.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.32, 176.46, 156.38, 136.62, 136.51, 133.34, 131.54, 129.83, 129.52, 129.51, 129.21, 128.07, 127.67, 62.27, 45.07, 38.90, 25.06. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{18}N_2O_3Na^+$: 345.1215, Found: 345.1219.



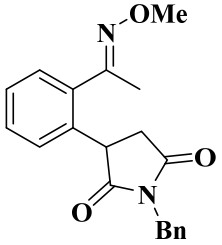
3oa: Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.18 (s, 1H), 7.45-7.43 (m, 1H), 7.37-7.35 (m, 2H), 7.17-7.15 (m, 1H), 4.62-4.58 (m, 1H), 3.90 (s, 3H), 3.26-3.19 (m, 1H), 3.10 (s, 3H), 2.78-2.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 178.07, 176.38, 148.97, 135.15, 131.42, 130.40, 130.10, 129.69, 128.18, 62.01, 45.21, 37.32, 25.07. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{13}H_{14}N_2O_3Na^+$: 269.0902, Found: 269.0900.



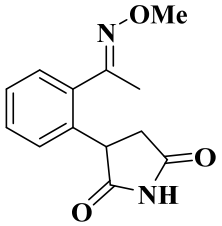
3pa: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.35-7.30 (m, 3H), 7.15-7.13 (m, 1H), 4.28-4.24 (m, 1H), 4.06 (q, *J* = 4.0 Hz, 2H), 3.20-3.13 (m, 1H), 3.05 (s, 3H), 2.93-2.87 (m, 1H), 2.19 (s, 3H), 1.24 (t, *J* = 12.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.56, 176.51, 156.26, 137.25, 135.27, 129.71, 129.05, 128.93, 127.85, 69.42, 45.29, 39.27, 24.99, 16.21, 14.61. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{18}N_2O_3Na^+$: 297.1215, Found:297.1218.



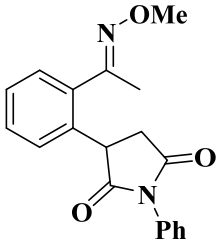
3ab: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.35-7.31 (m, 3H), 7.14-7.12 (m, 1H), 4.26-4.22 (m, 1H), 3.85 (s, 3H), 3.62 (q, *J* = 4.0 Hz, 2H), 3.20-3.13 (m, 1H), 2.95-2.89 (m, 1H), 2.18 (s, 3H), 1.23 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.29, 176.34, 156.57, 137.20, 135.39, 129.59, 129.05, 129.00, 127.86, 61.72, 45.23, 39.34, 33.93, 16.16, 13.03. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{15}H_{18}N_2O_3Na^+$: 297.1215, Found:297.1219.



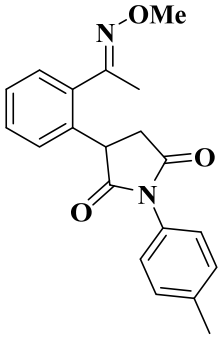
3ac: Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.44 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 2H), 7.36-7.28 (m, 6H), 7.06 (m, 1H), 4.72 (q, *J* = 8.0 Hz, 2H), 4.30-4.26 (m, 1H), 3.82 (s, 3H), 3.22-3.15 (m, 1H), 2.94-2.88 (m, 1H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.06, 176.05, 156.49, 137.15, 135.82, 135.29, 129.40, 129.07, 129.00, 128.96, 128.61, 127.94, 127.86, 61.71, 45.11, 42.57, 39.28, 16.17. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{20}H_{20}N_2O_3Na^+$: 359.1372, Found:359.1359.



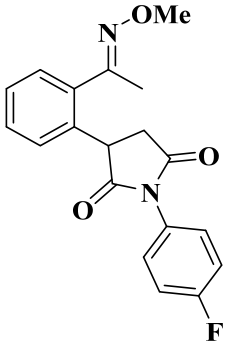
3ad: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 8.41 (s, 1H), 7.39-7.32 (m, 3H), 7.21-7.19 (m, 1H), 4.38-4.34 (m, 1H), 3.90 (s, 3H), 3.25-3.18 (m, 1H), 3.02-2.96 (m, 1H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 178.62, 176.36, 156.68, 137.02, 134.70, 129.84, 129.15, 129.11, 128.08, 61.84, 46.74, 40.37, 16.09. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{13}H_{14}N_2O_3Na^+$: 269.0902, Found: 269.0891.



3ae: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.50 (t, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 1H), 7.39-7.35 (m, 5H), 7.26-7.24 (m, 1H), 4.40-4.36 (m, 1H), 3.81 (s, 3H), 3.37-3.30 (m, 1H), 3.25-3.19 (m, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.29, 175.38, 157.21, 137.00, 134.93, 132.07, 130.62, 129.19, 129.14, 129.00, 128.57, 128.04, 126.54, 61.73, 46.03, 39.36, 16.21. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{19}H_{18}N_2O_3Na^+$: 345.1215, Found:345.1192.

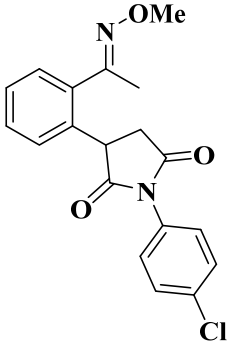


3af: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.33-7.26 (m, 3H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.18-7.15 (m, 3H), 4.32-4.28 (m, 1H), 3.75 (s, 3H), 3.29-3.22 (m, 1H), 3.16-3.10 (m, 1H), 2.32 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.44, 175.56, 157.18, 138.67, 137.09, 135.07, 130.56, 129.86, 129.45, 129.20, 129.02, 128.03, 126.37, 61.77, 46.02, 39.41, 21.22, 16.22. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{20}H_{20}N_2O_3Na^+$: 359.1372, Found:359.1359.

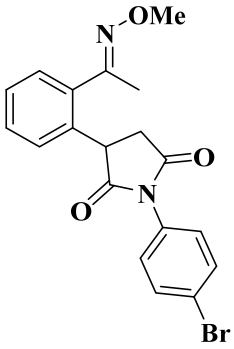


3ag: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.42-7.34 (m, 5H), 7.25 (d, *J* = 4.0 Hz, 1H), 7.22-7.16 (m, 2H), 4.39-4.35 (m, 1H), 3.80 (s, 3H), 3.37-3.30 (m, 1H), 3.26-3.20 (m, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.25, 175.27, 163.43, 160.96, 157.38, 136.93, 134.78, 130.77, 129.16 (d, *J* = 21.0 Hz), 128.41 (d, *J* = 9.0 Hz), 128.13, 127.98 (d, *J* = 3.0 Hz), 116.17 (d,

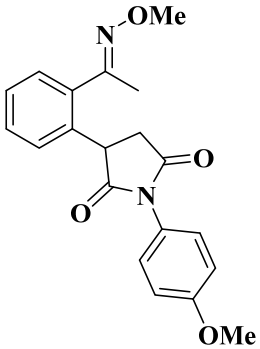
J = 13.0 Hz), 61.70, 46.11, 39.30, 16.19. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{17}FN_2O_3Na^+$: 363.1121, Found:363.1125.



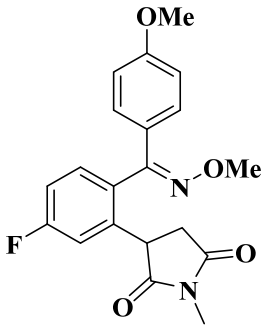
3ah: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.46 (dd, J = 2.0 Hz, J = 4.0 Hz, 2H), 7.41-7.35 (m, 3H), 7.34-7.31 (m, 2H), 7.25-7.22 (m, 1H), 4.37-4.33 (m, 1H), 3.77 (s, 3H), 3.35-3.28 (m, 1H), 3.25-3.19 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.04, 175.04, 157.39, 136.85, 134.67, 134.32, 130.82, 130.53, 129.32, 129.25, 129.04, 128.13, 127.77, 61.68, 46.13, 39.27, 16.18. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{17}ClN_2O_3Na^+$: 379.0825, Found:379.0810.



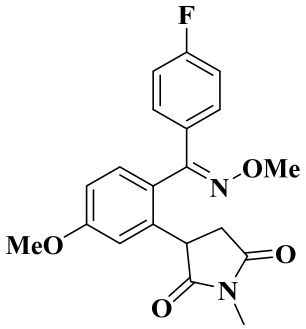
3ai: Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.62 (d, *J* = 8.0 Hz, 2H), 7.41-7.34 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.25-7.22 (m, 1H), 4.37-4.33 (m, 1H), 3.77 (s, 3H), 3.35-3.28 (m, 1H), 3.24-3.18 (m, 1H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 176.98, 174.96, 157.39, 136.83, 134.64, 132.29, 131.05, 130.84, 129.25, 129.03, 128.13, 128.06, 122.40, 61.67, 46.14, 39.27, 16.18. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{19}H_{17}BrN_2O_3Na^+$: 423.0320, Found: 423.0297.



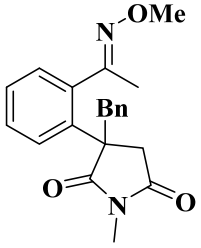
3aj: Bright yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.33-7.27 (m, 3H), 7.22-7.17 (m, 3H), 6.94 (d, *J* = 8.0 Hz, 2H), 4.31-4.27 (m, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.29-3.22 (m, 1H), 3.17-3.10 (m, 1H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.58, 175.69, 159.50, 157.23, 137.07, 135.08, 130.62, 129.21, 129.02, 128.04, 127.79, 124.73, 114.51, 61.76, 55.46, 46.02, 39.38, 16.22. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{20}N_2O_4Na^+$: 375.1321, Found:375.1299.



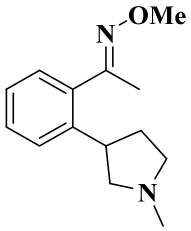
Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.49 (d, *J* = 8.0 Hz, 2H), 7.16 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 6.99 (dt, *J* = 2.4 Hz, *J* = 8.0 Hz, 1H), 6.90-6.87 (m, 3H), 4.24 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 3.06-2.99 (m, 4H), 2.85-2.79 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.58, 176.02, 162.82 (d, *J* = 247.8 Hz), 160.42, 154.92, 138.99 (d, *J* = 8.0 Hz), 133.47 (d, *J* = 8.0 Hz), 133.21 (d, *J* = 3.4 Hz), 131.93, 125.38, 115.90 (d, *J* = 23.0 Hz), 114.85 (d, *J* = 21.0 Hz), 113.43, 62.30, 55.26, 44.79, 38.64, 25.13. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{19}FN_2O_4Na^+$: 393.1227, Found: 393.1230



Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.52-7.49 (m, 2H), 7.09-7.04 (m, 2H), 6.98 (d, J = 8.0 Hz, 1H), 6.79 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 6.69 (d, J = 4.0 Hz, 1H), 4.28 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 3.14-3.07 (m, 1H), 3.02 (s, 3H), 2.96-2.90 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 196.83 (d, *J* = 207.0 Hz), 176.45, 170.78, 149.82, 144.02, 143.69, 142.91 (d, *J* = 10.0 Hz), 139.43 (d, *J* = 10.0 Hz), 123.11, 122.51 (d, *J* = 25.0 Hz), 120.99, 119.66, 59.24, 51.19, 39.20, 31.45, 14.95. HRMS (ESI) ([M+Na]$^+$) Calcd. for $C_{20}H_{19}FN_2O_4Na^+$: 393.1227, Found: 393.1230.

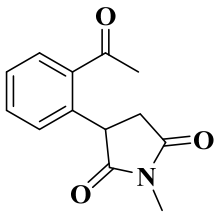


3-benzyl-3-(2-(1-(methoxyimino)ethyl)phenyl)-1-methylpyrrolidine-2,5-dione (4)[2]. To a solution of **1aa** (52 mg, 0.20 mmol, 1 equiv) and K_2CO_3 (138 mg, 1.0 mmol, 5 equiv) in DMF (1.0 mL) was added benzyl bromide (51.3 mg, 0.3 mmol, 1.5 equiv) .The reaction mixture was stirred for 12 h at 40 ^oC. After quenched with of water (10 mL), the mixture was extracted with EtOAc(3 x 10 mL). The combined organic phases was washed with brines, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (eluent : PE/EA = 2 : 1) to afford the product as a white solid (46.9 mg, 0.134 mmol, 67% yield). ^1H NMR (400 MHz, $CDCl_3$) δ : 7.67 (d, *J* = 8.0 Hz, 1H), 7.45-7.36 (m, 2H), 7.27 (d, *J* = 4.0 Hz. 4H), 7.15-7.13 (m, 2H), 3.68 (s, 3H), 3.57 (d, *J* = 12.0 Hz, 1H), 3.30 (dd, *J* = 4.0 Hz, *J* = 8.0 H, 2H), 2.97 (d, *J* = 20.0 Hz, 1H), 2.52 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 180.56, 175.24, 157.84, 139.58, 137.10, 134.69, 129.86, 129.59, 128.79, 128.47, 127.71, 127.51, 127.15, 61.47, 52.40, 44.65, 44.55, 24.01, 16.56. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{21}H_{22}N_2O_3Na^+$: 373.1528, Found: 373.1535.

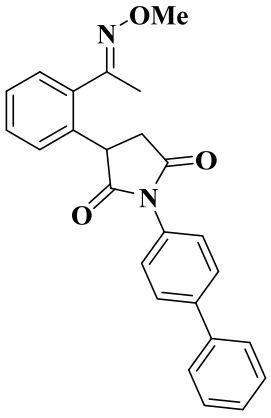


1-(2-(1-methylpyrrolidin-3-yl)phenyl)ethan-1-one O-methyl oxime (5)[3]. $LiAlH_4$ (22.8 mg, 0.6 mmol, 3 equiv) was added slowly to a solution of **1aa** (52 mg, 0.2 mmol, 1 equiv) in 2 mL of dry THF at 0 ^oC. After warmed to room temperature, the reaction was stirred till the **1aa** was completely consumed monitored by TCL. After quenched with MeOH, the reaction mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under vacuum. Then the crude reaction mixture was by column chromatography on silica gel (eluent : CH_2Cl_2/MeOH = 30 : 1) to give the product **5** (32

mg, 0.136 mmol, 68%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.47 (d, J = 8.0 Hz, 1H), 7.33 (t, J = 8.0 Hz, 1H), 7.20-7.14 (m, 2H), 3.95 (s, 3H), 3.59-3.51 (m, 1H), 2.94 (t, J = 8.0 Hz, 1H), 2.77-2.62 (m, 2H), 2.53 (t, J = 8.0 Hz, 1H), 2.40 (s, 3H), 2.33-2.28 (m, 1H), 2.16 (s, 3H), 1.91-1.82 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 156.86, 143.68, 137.25, 128.99, 127.88, 127.14, 125.91, 65.01, 61.69, 57.08, 42.25, 40.13, 35.04, 17.23. HRMS (ESI) ($[M+H]^+$) Calcd. for $C_{14}H_{21}N_2O^+$: 233.1654, Found: 233.1674.



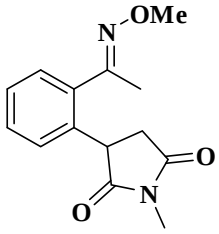
3-(2-acetylphenyl)-1-methylpyrrolidine-2,5-dione (6)[4]. To a solution of **1a** (52 mg, 0.2 mmol) in Et_2O (1 mL) was added 37% HCl (1 mL), then the mixture was stirred at room temperature for 12 h. After neutralized with saturated sodium carbonate (5 mL), the mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were dried with Na_2SO_4, evaporated under vacuum and afforded 43 mg (93%, 0.186 mmol) of **6** purified by column chromatography on silica gel (eluent: PE/EA = 2:1). Pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.88 (d, *J* = 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.27 (t, *J* = 8.0 Hz, 1H), 4.38-4.34 (m, 1H), 3.21-3.14 (m, 1H), 3.08 (s, 3H), 2.75-2.69 (m, 1H), 2.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 201.22, 178.13, 176.24, 136.47, 136.06, 132.74, 131.85, 130.86, 128.16, 46.12, 37.54, 28.68, 24.84. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{13}H_{13}NNaO_3^+$: 254.0793, Found: 254.0800.

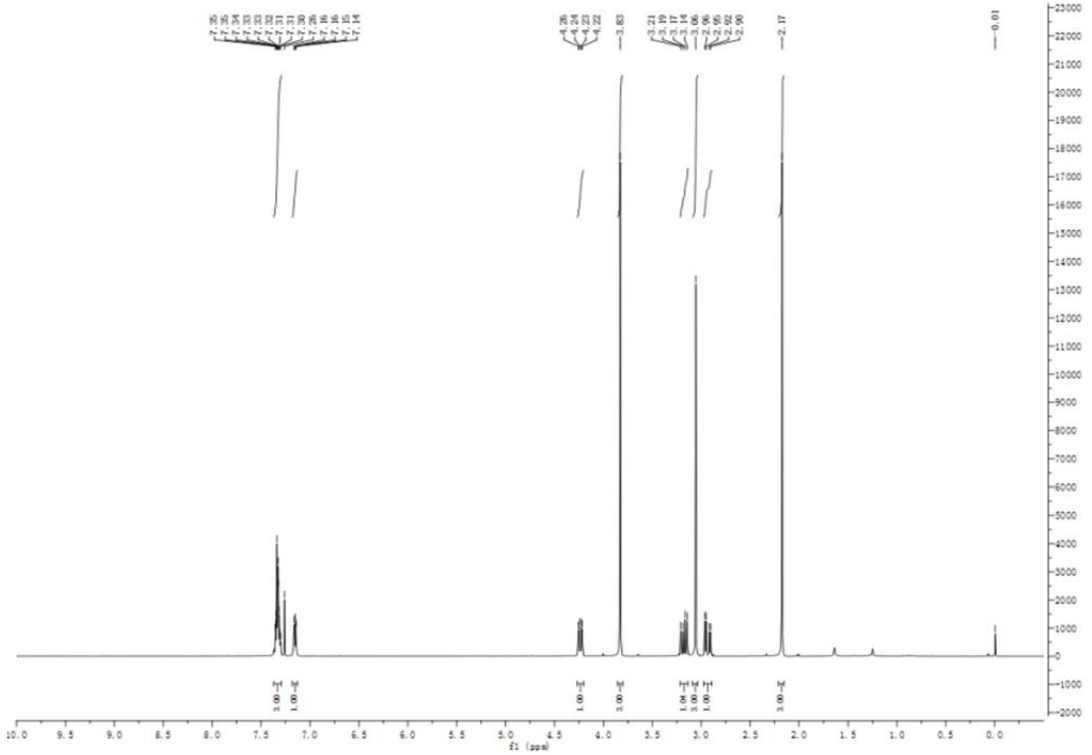


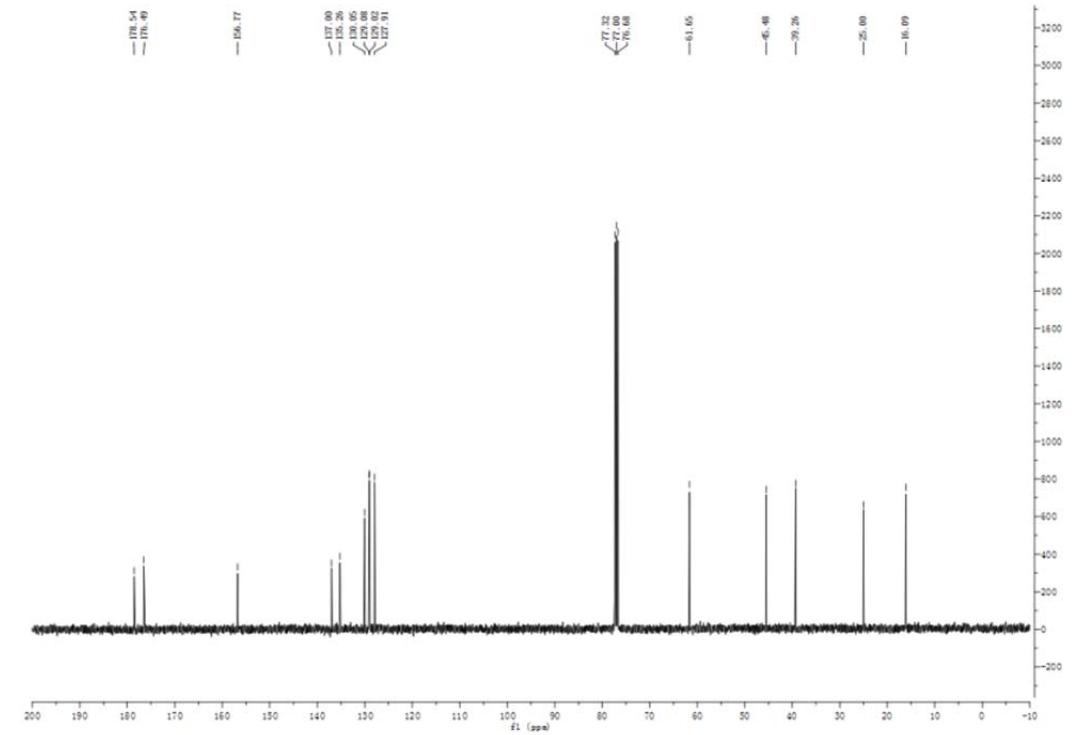
1-([1,1'-biphenyl]-4-yl)-3-(2-(1-(methoxyimino)ethyl)phenyl)pyrrolidine-2,5-dione[5] (7). To a

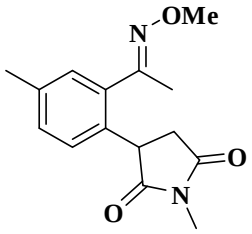
10 mL Schlenk flask purged with argon gas was added **3ai** (80.0 mg, 0.2 mmol, 1equiv), $Pd(PPh_3)_4$ (11.6 mg, 0.001 mmol, 5 mol%), sodium carbonate (43 mg, 0.4 mmol, 2 equiv) and phenylboronic acid (36.6 mg, 0.3 mmol, 1.5 equiv). Then degassed anhydrous toluene (0.8 mL) and methanol (0.2 mL) was added by syringe. The reaction mixture was stirred at 95 ˚C for 12 h. After cooling to room temperature, the solvent was removed under vacuum, and the residue was purified by column chromatography on silica gel (eluent : PE/EA = 4 : 1) to afford the product as a white solid (69.2 mg, 0.174 mmol, 87%yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.71-7.69 (m, 2H), 7.60 (d, *J* = 4.0 Hz, 2H), 7.41 (m, 8H), 7.26 (t, *J* = 4.0 Hz, 1H), 4.41 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.83 (s, 3H), 3.39-3.21 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ : 177.36, 175.44, 157.26, 141.57, 140.24, 137.01, 134.92, 131.17, 130.65, 129.22, 129.03, 128.81, 128.07, 127.93, 127.62, 127.20, 126.78, 61.77, 46.10, 39.40, 16.23. HRMS (ESI) ($[M+Na]^+$) Calcd. for $C_{25}H_{22}N_2O_3Na^+$: 421.1528, Found: 421.1524.

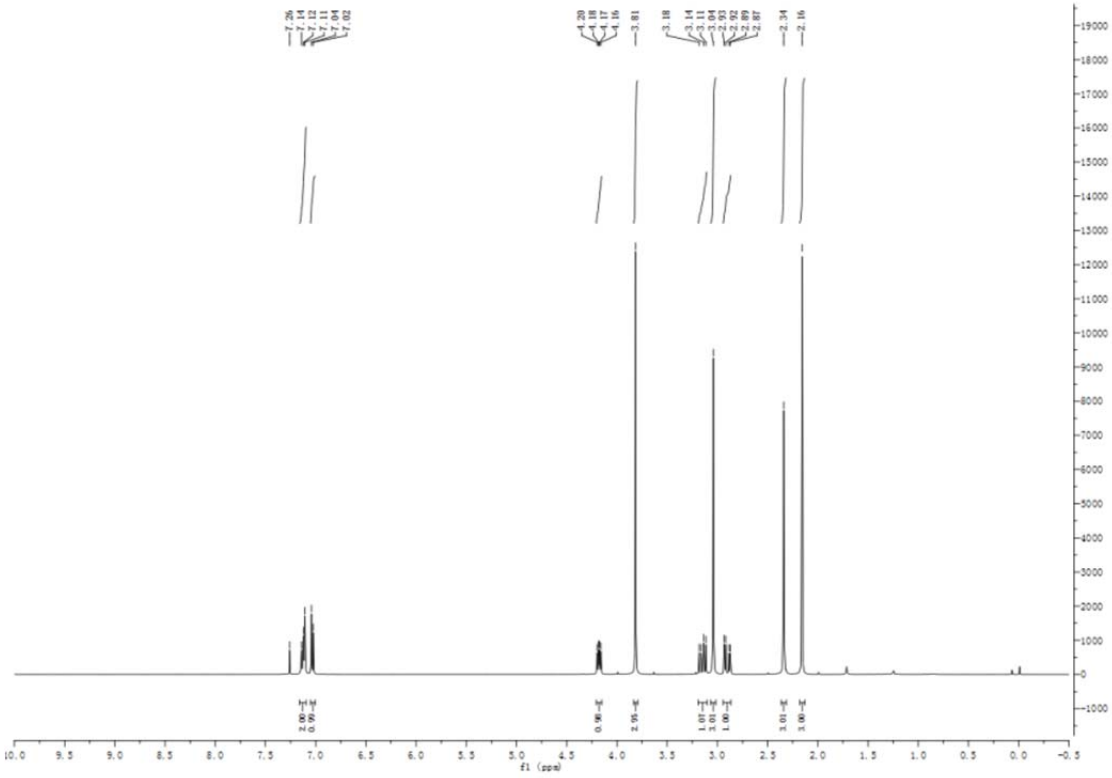
4. NMR Chart

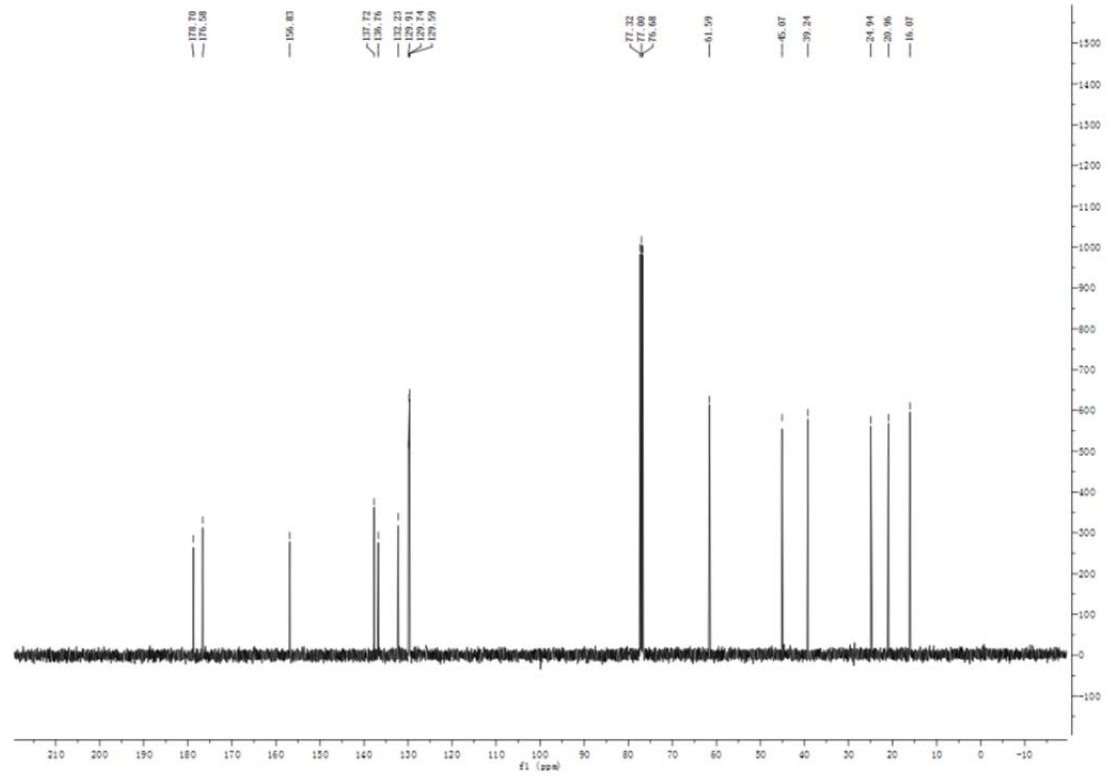


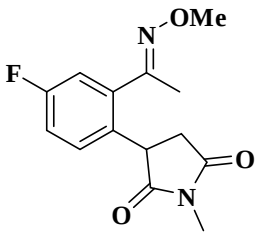


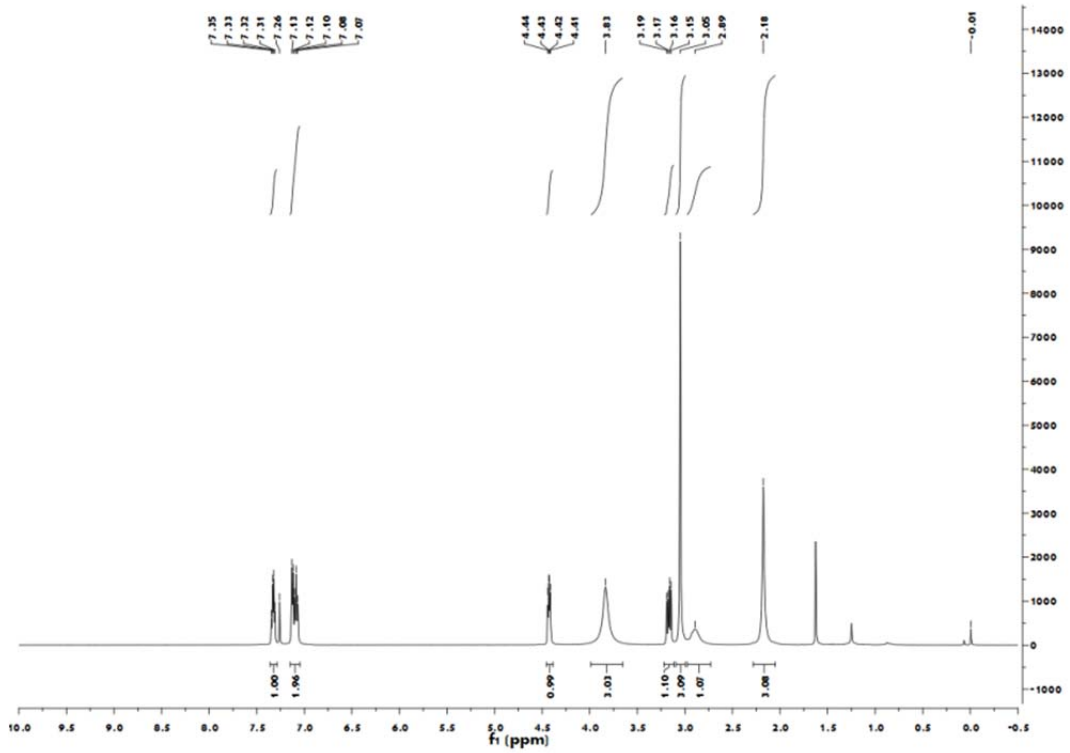


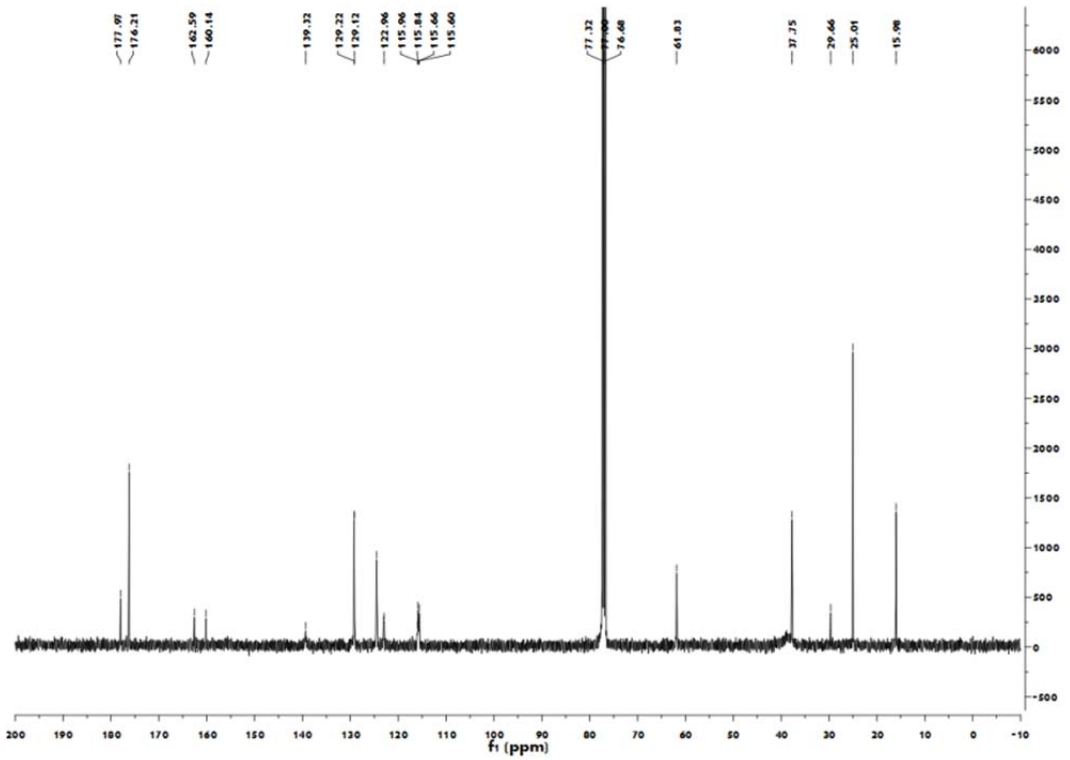

N
OMe
O
O
N

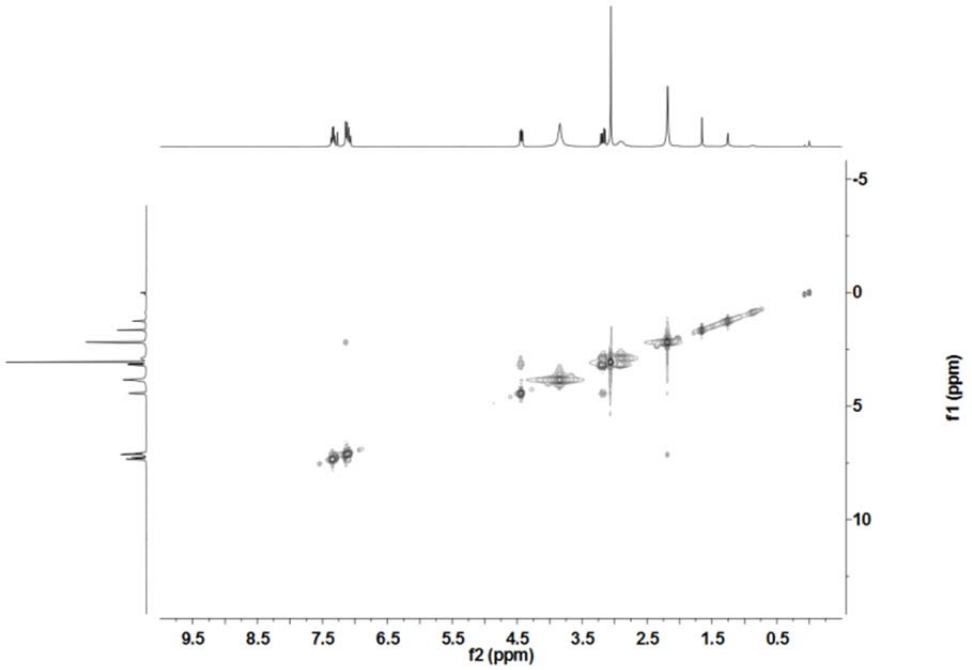




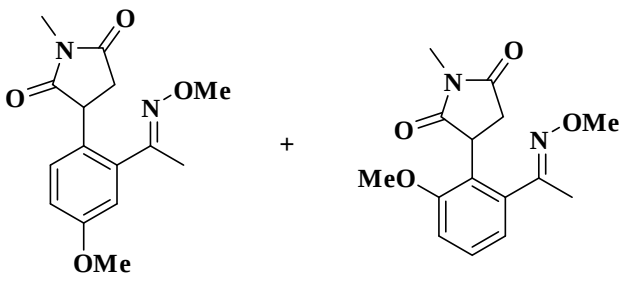

OMe
N
F
O
O
N

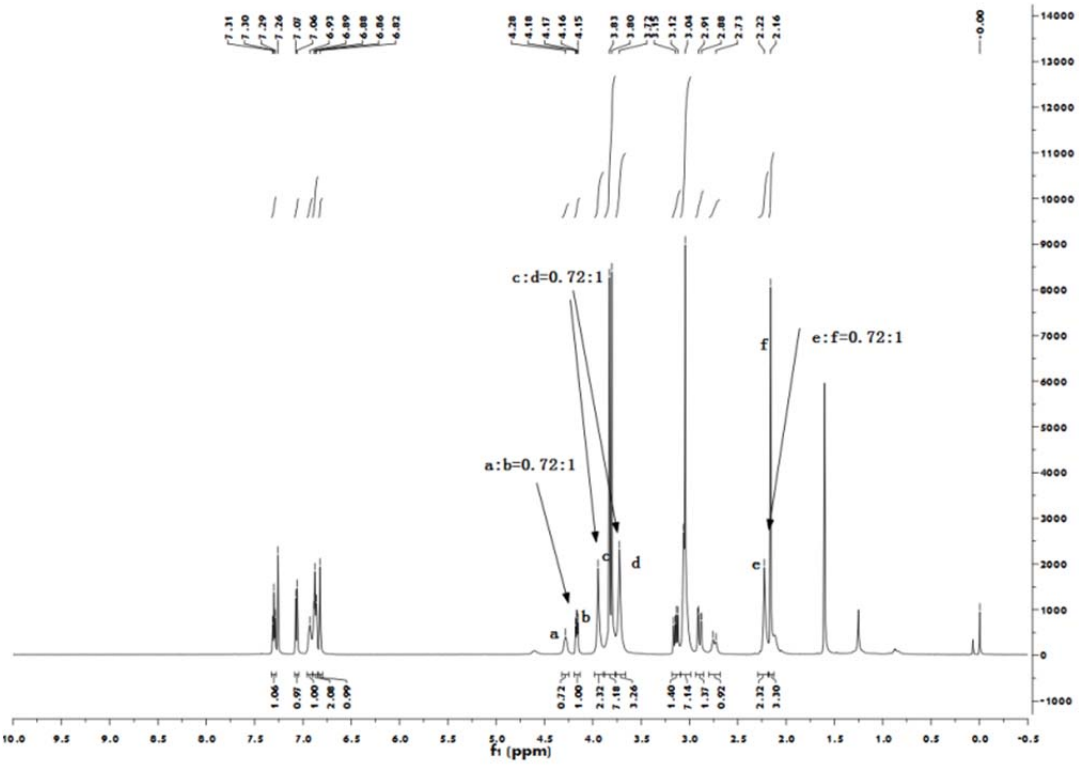

7.35
7.33
7.32
7.31
7.26
7.13
7.12
7.10
7.08
7.07
4.44
4.43
4.42
4.41
3.83
3.19
3.17
3.16
3.15
3.05
2.89
2.18
0.01
1.00
1.96
0.99
3.03
1.10
3.09
1.07
3.08
f1 (ppm)

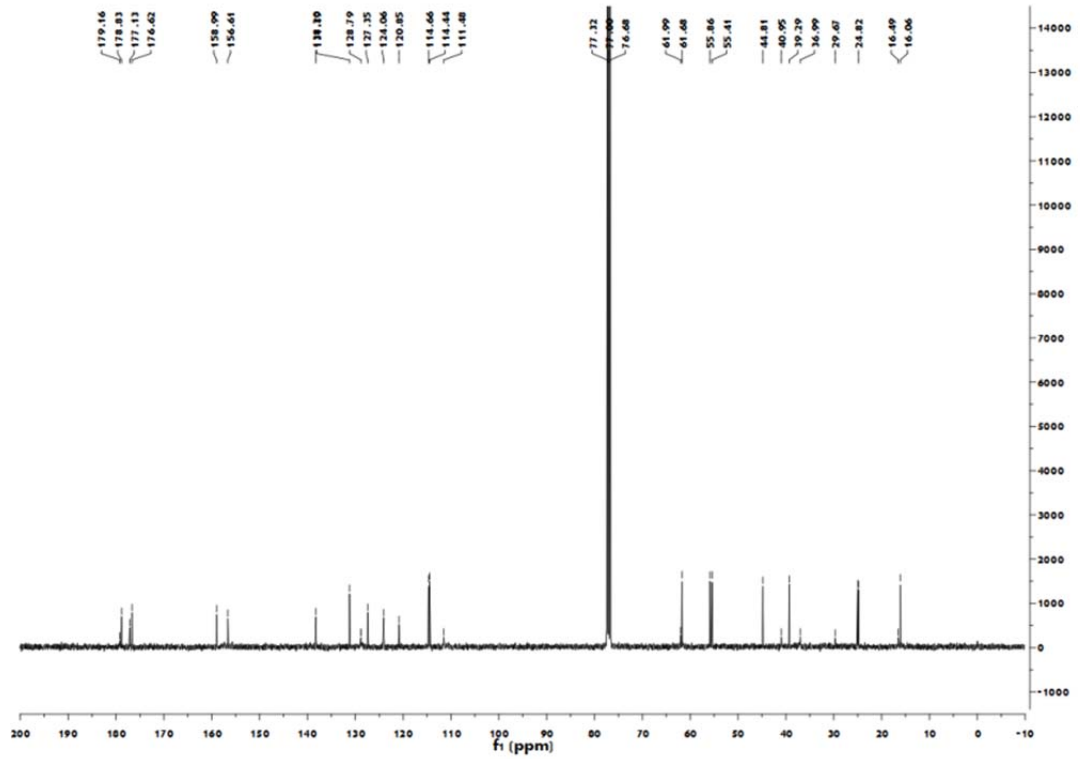

177.97
176.21
162.59
160.14
139.32
129.22
129.12
122.96
115.96
115.84
115.66
115.60
77.32
77.00
76.68
61.83
37.75
29.66
25.01
15.98
f1 (ppm)

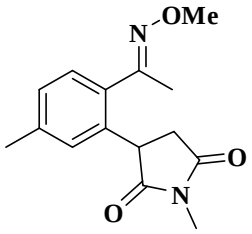


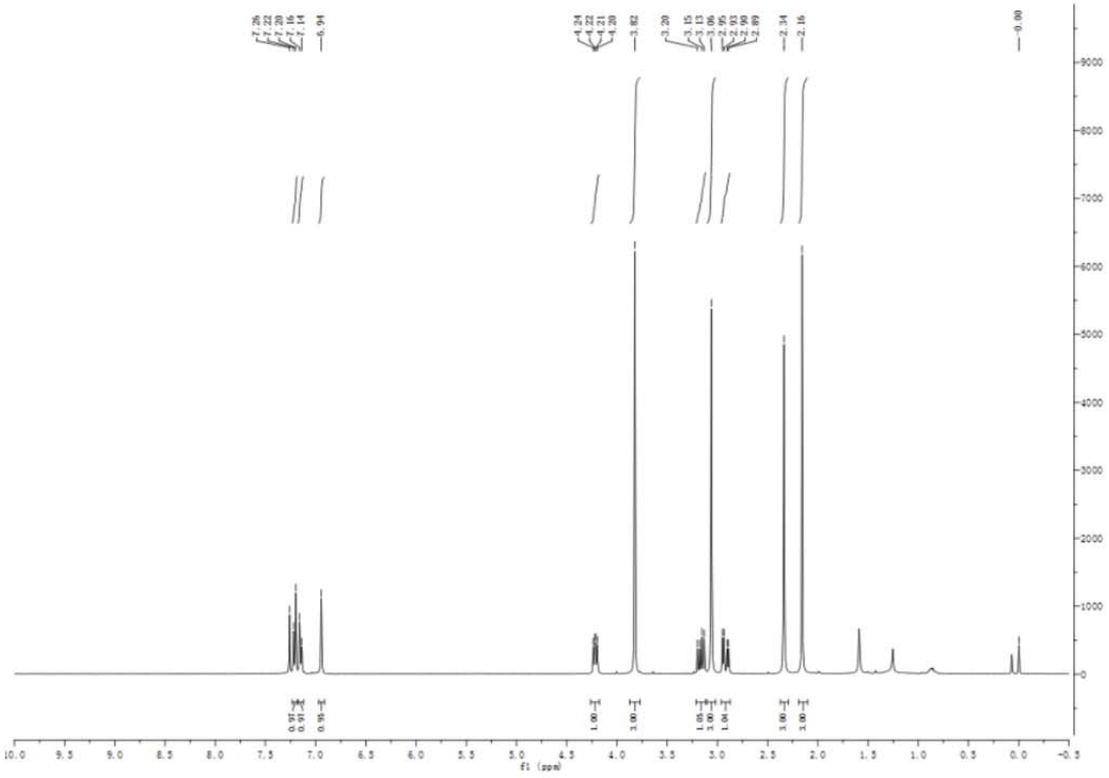
NOESY (400 MHz, $CDCl_3$)

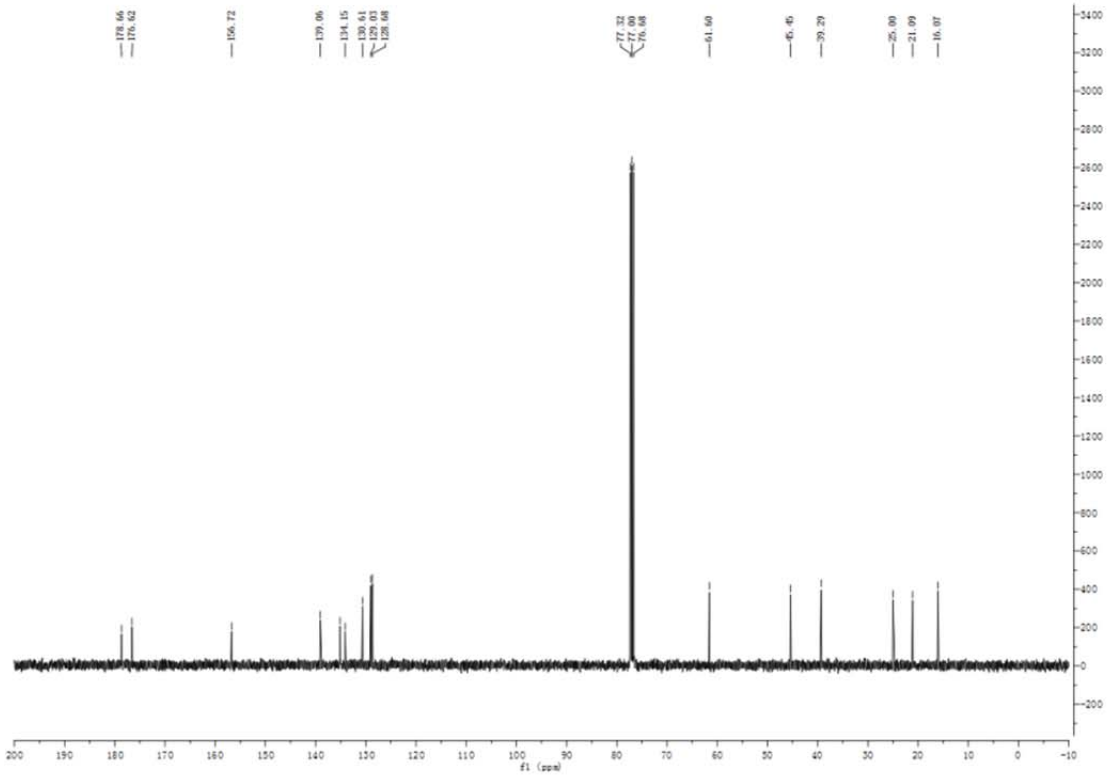

O
N
O
OMe
N
OMe
+
O
N
O
MeO
N
OMe

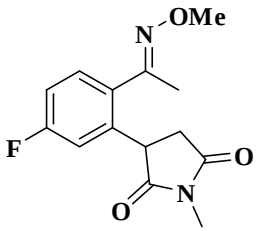

c:d=0.72:1
e:f=0.72:1
a:b=0.72:1
a
b
c
d
e
f
f1 (ppm)

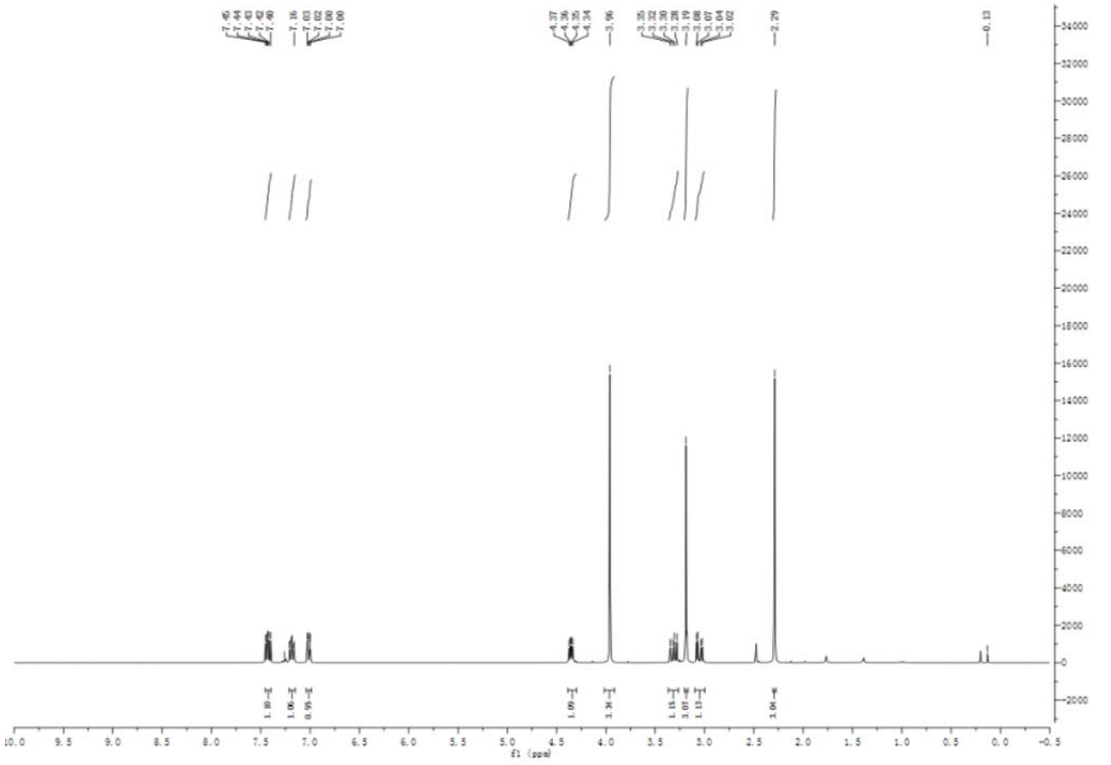

f1 (ppm)

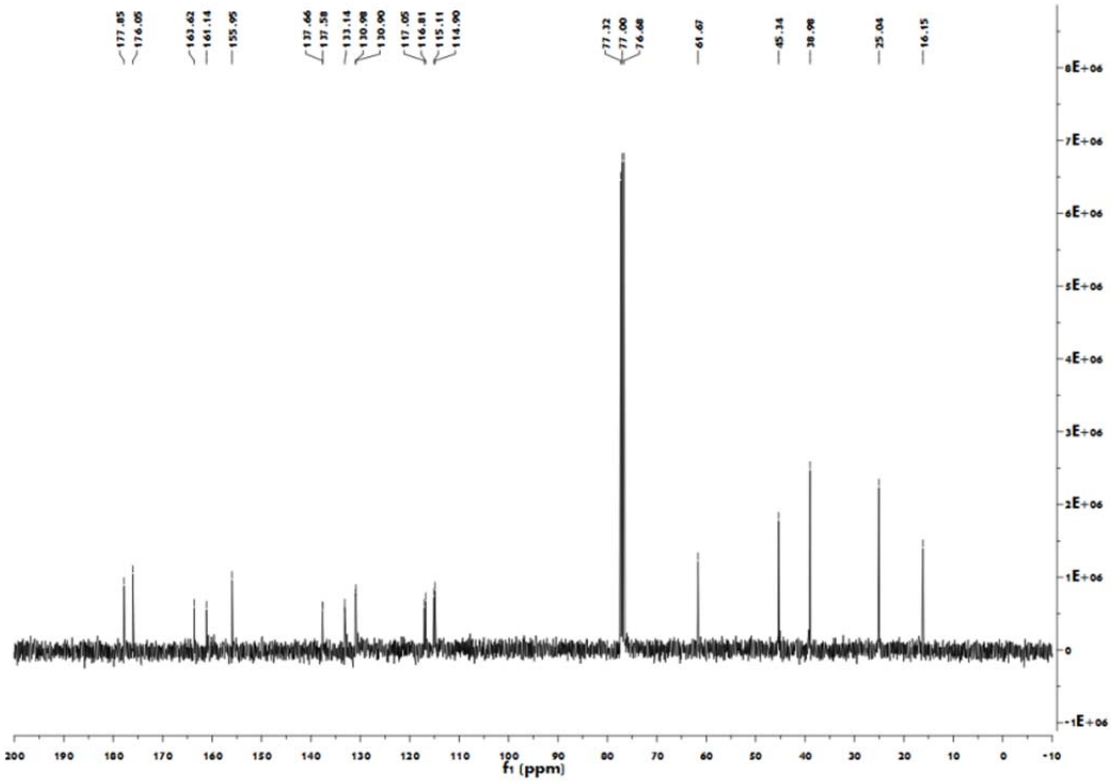

N
OMe
O
O
N

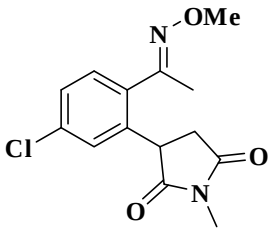

7.26
7.22
7.20
7.16
7.14
6.94
4.24
4.22
4.21
4.20
3.82
3.20
3.15
3.11
3.06
2.95
2.93
2.90
2.89
2.34
2.16
0.00
f1 (ppm)

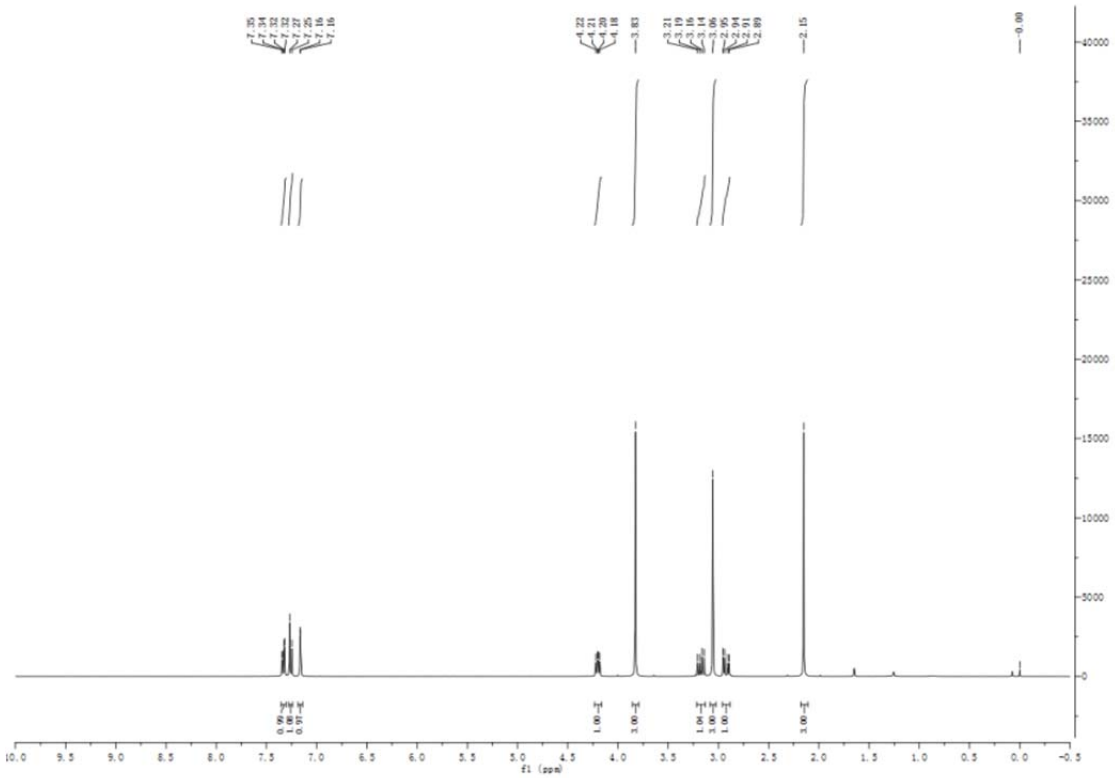

178.66
176.62
156.72
139.06
134.15
130.61
129.03
128.68
77.32
77.00
76.68
61.60
45.45
39.29
25.00
21.09
16.07
f1 (ppm)

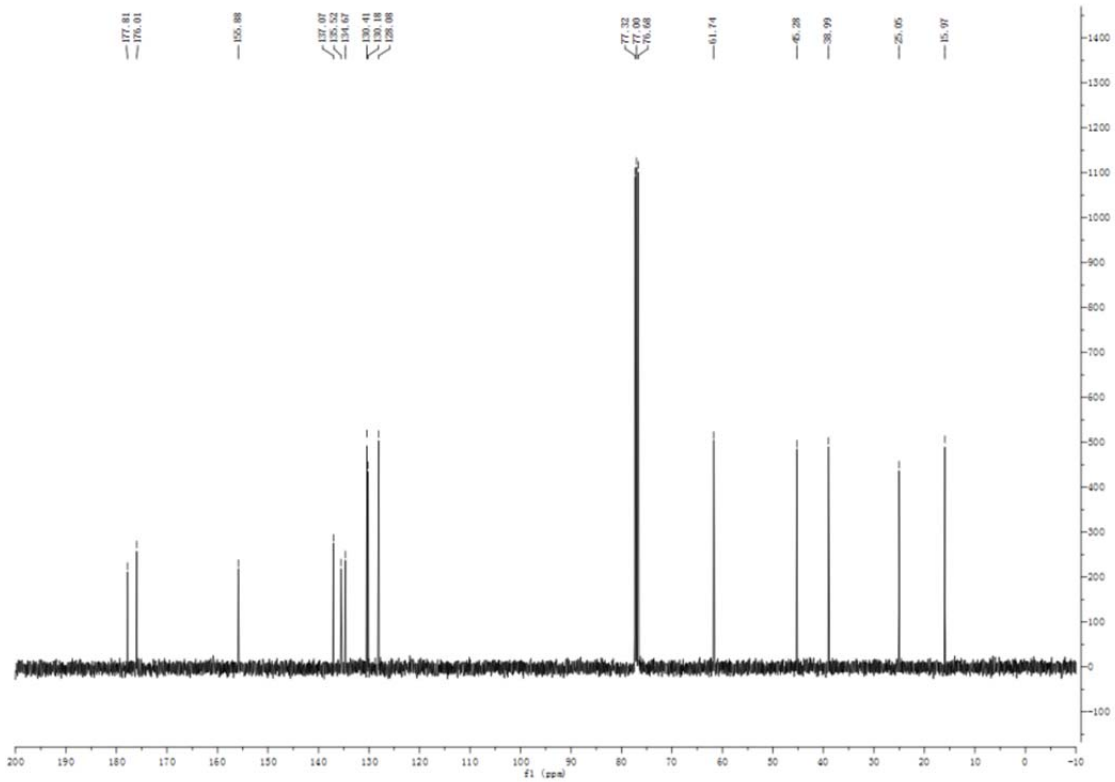

N
OMe
F
O
O
N

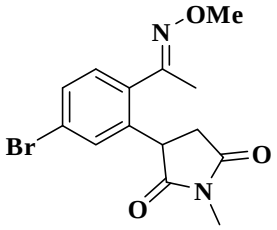

7.45
7.44
7.43
7.42
7.40
7.16
7.01
7.02
7.00
7.00
4.37
4.36
4.35
4.34
3.96
3.35
3.32
3.30
3.28
3.19
3.18
3.07
3.04
3.02
2.29
0.13
f1 (ppm)

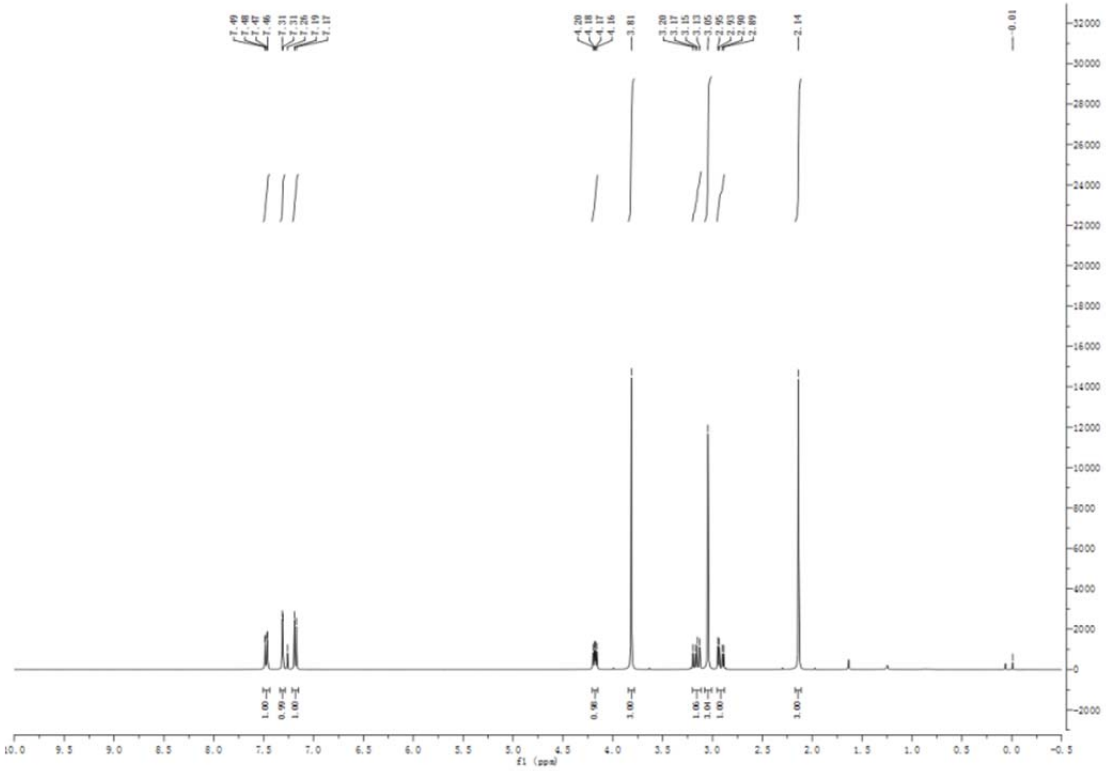

177.85
176.05
163.62
161.14
155.95
137.66
137.58
133.14
130.98
130.90
117.05
116.81
115.11
114.90
77.32
77.00
76.68
61.67
45.34
30.98
25.04
16.15
f1 (ppm)

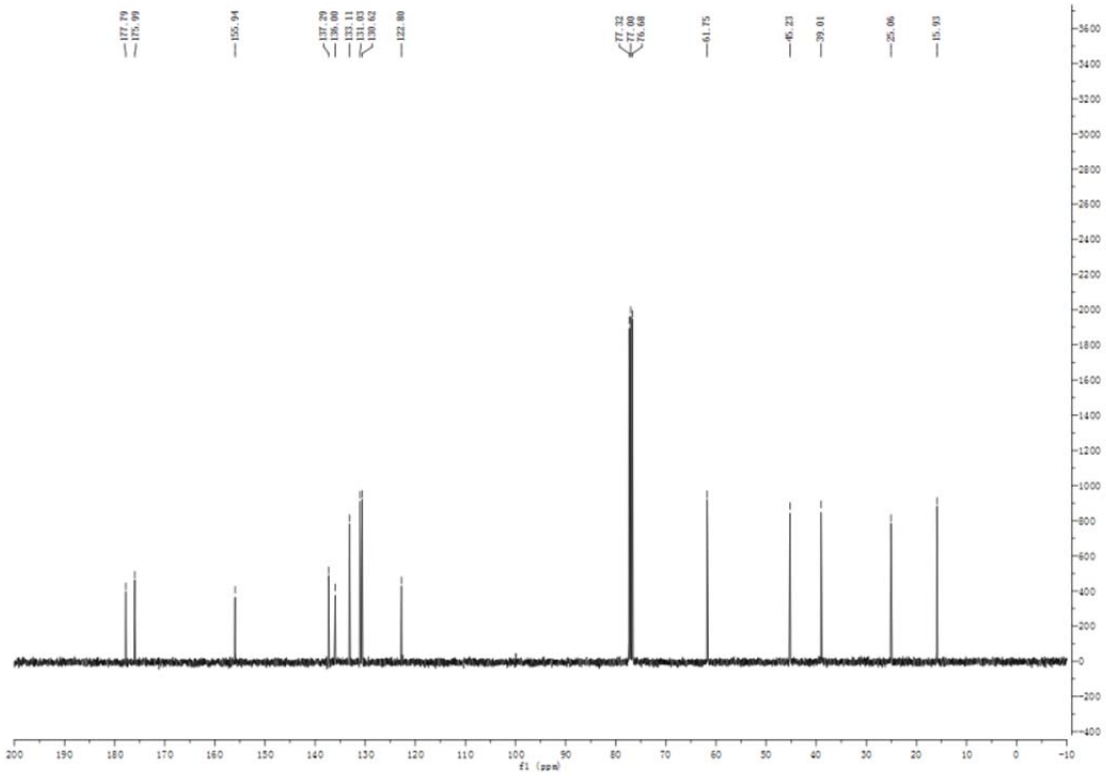

N
OMe
Cl
O
O
N

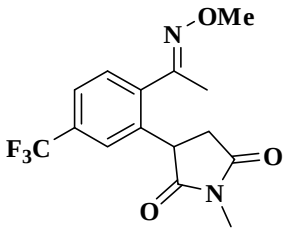

7.35
7.34
7.32
7.32
7.27
7.25
7.16
7.16
4.22
4.21
4.20
4.18
3.83
3.21
3.19
3.16
3.14
3.06
2.95
2.94
2.91
2.89
2.15
0.00
f1 (ppm)

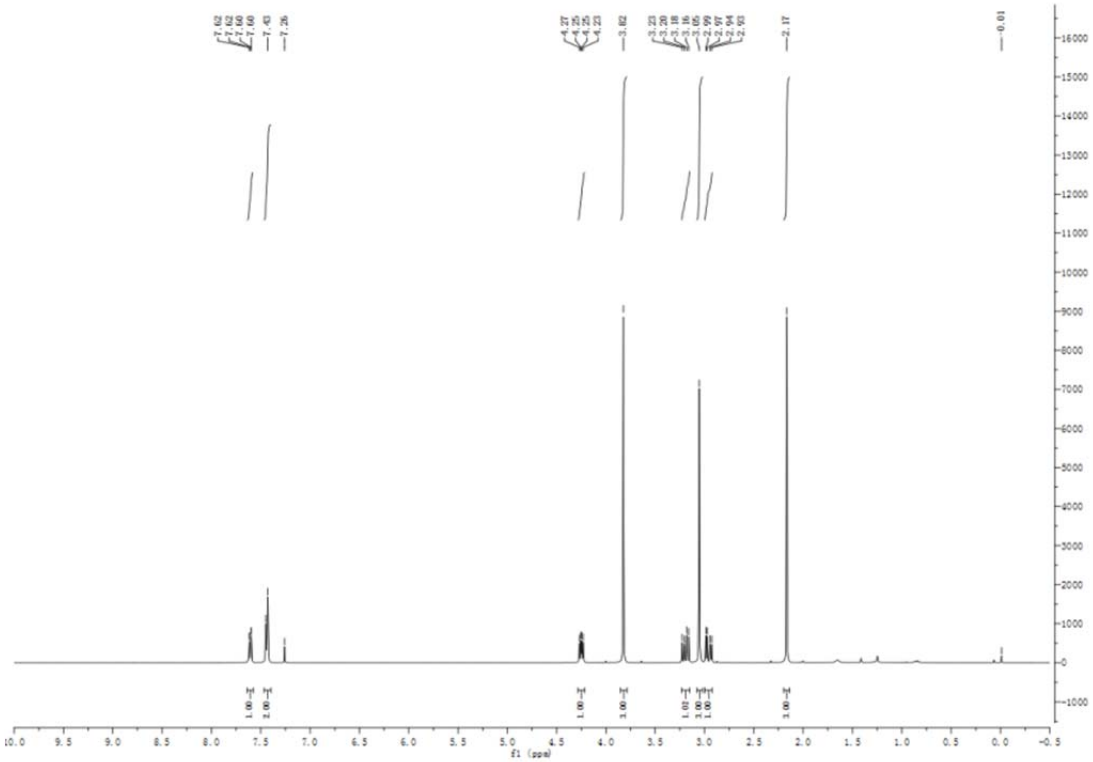

177.81
176.01
155.88
137.07
135.52
134.67
130.41
130.18
128.08
77.32
77.00
76.68
61.74
45.28
38.99
25.05
15.97
f1 (ppm)

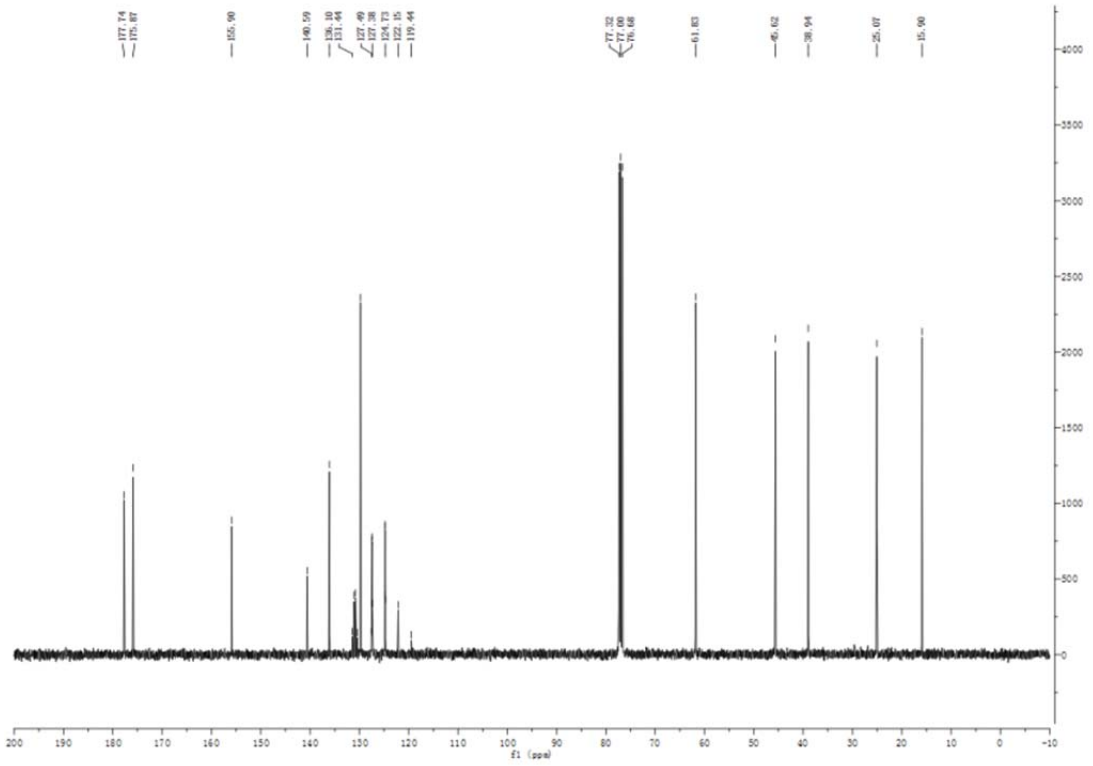

N
OMe
Br
O
O
N

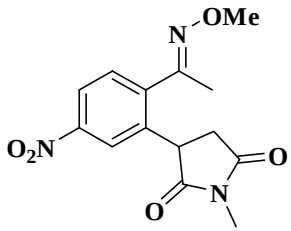

7.49
7.48
7.47
7.46
7.31
7.31
7.26
7.19
7.17
4.20
4.18
4.17
4.16
3.81
3.20
3.17
3.15
3.13
3.05
2.95
2.93
2.89
2.89
2.14
0.01
1.00
0.99
1.00
0.96
1.00
1.06
1.04
1.00
1.00
f1 (ppm)

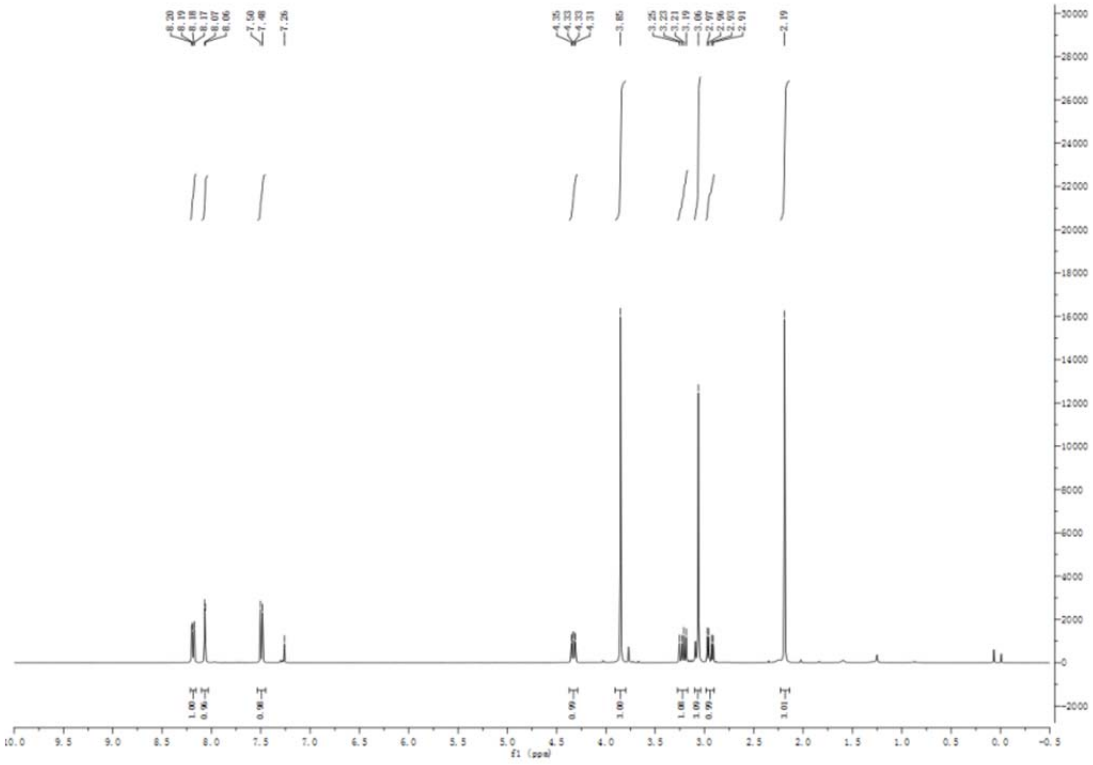

177.79
175.99
155.94
137.29
136.89
133.11
131.03
130.62
122.80
77.32
77.00
76.68
61.75
45.23
39.01
25.06
15.93
f1 (ppm)

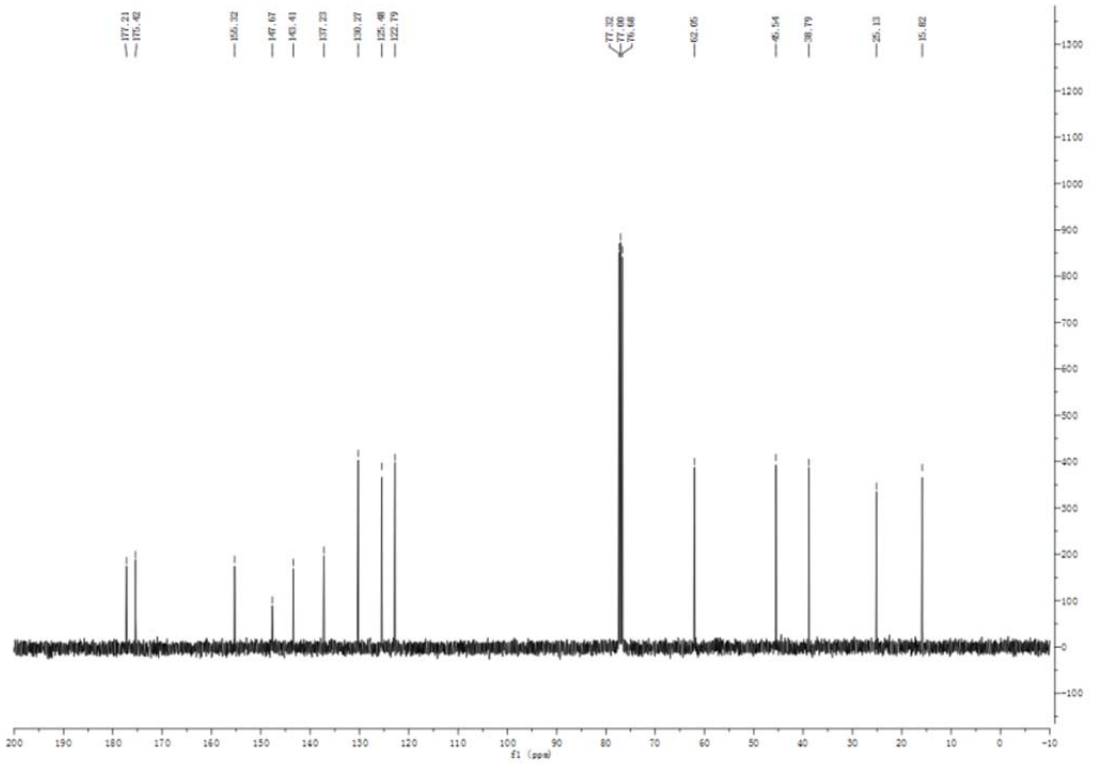

N
OMe
F3C
O
O
N

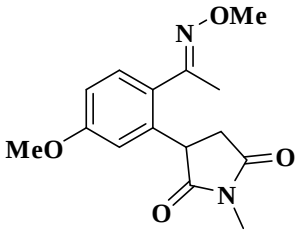

7.62
7.62
7.60
7.60
7.43
7.26
4.27
4.25
4.25
4.23
3.82
3.23
3.20
3.18
3.16
3.00
2.99
2.97
2.94
2.93
2.17
0.01
f1 (ppm)

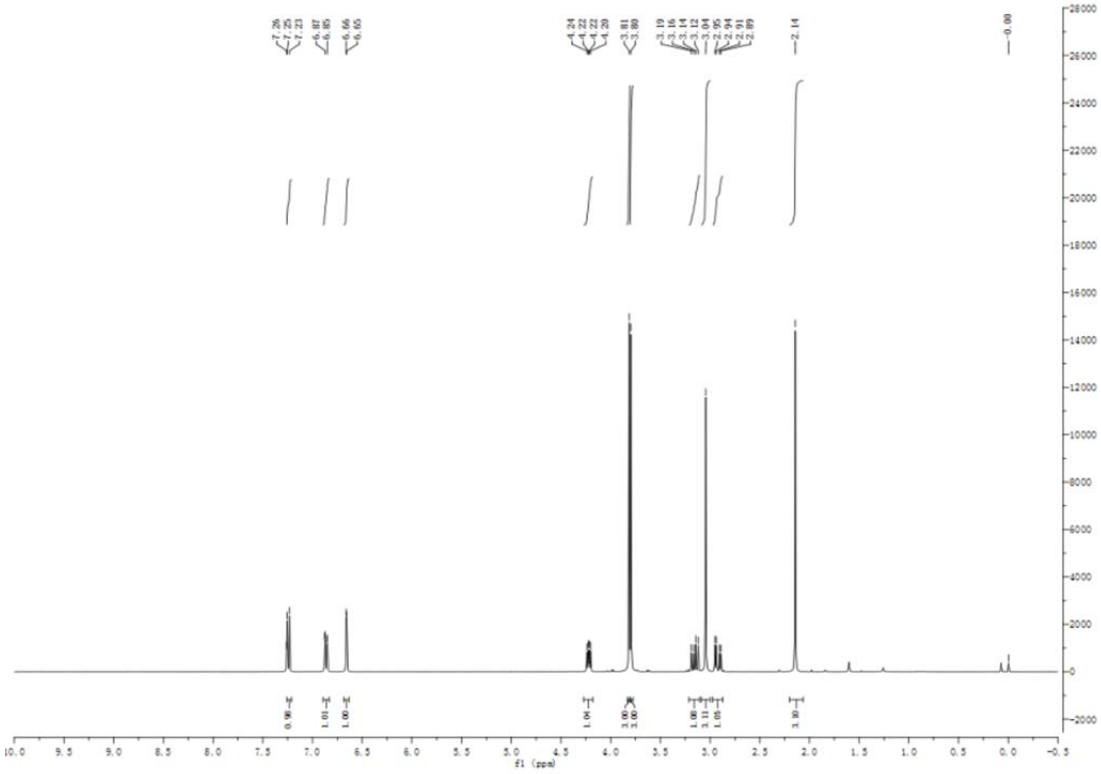

177.74
175.87
155.90
140.59
136.10
131.44
127.49
127.38
124.73
122.15
119.44
77.32
77.00
76.68
61.83
45.62
38.94
25.07
15.90
f1 (ppm)

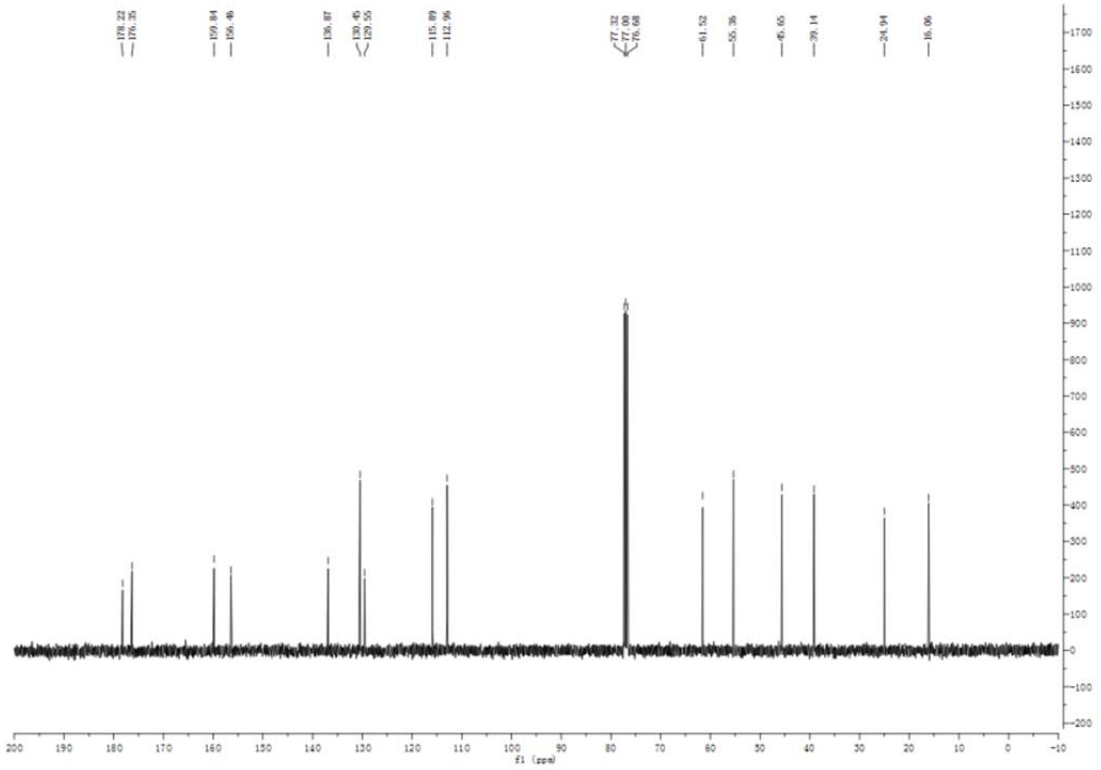

N
OMe
O2N
O
O
N

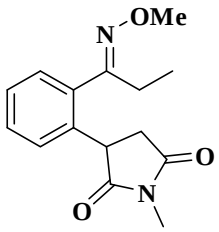

8.20
8.19
8.18
8.17
8.07
8.06
7.50
7.48
7.26
4.35
4.33
4.33
4.31
3.85
3.25
3.23
3.21
3.19
3.16
2.97
2.96
2.93
2.91
2.19
1.00
0.96
0.98
0.99
3.00
1.08
3.09
0.99
3.01
f1 (ppm)

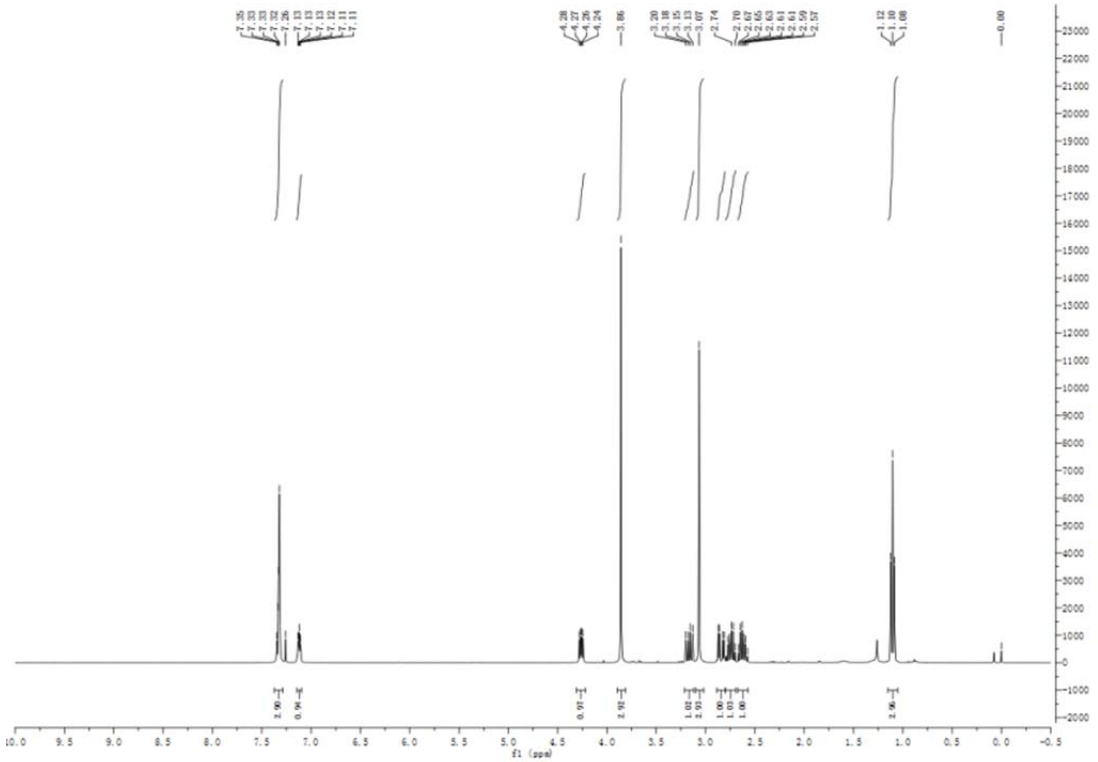

177.21
175.42
155.32
147.67
143.41
137.23
130.27
125.48
122.79
77.32
77.00
76.68
62.05
45.54
38.79
25.13
15.82
f1 (ppm)

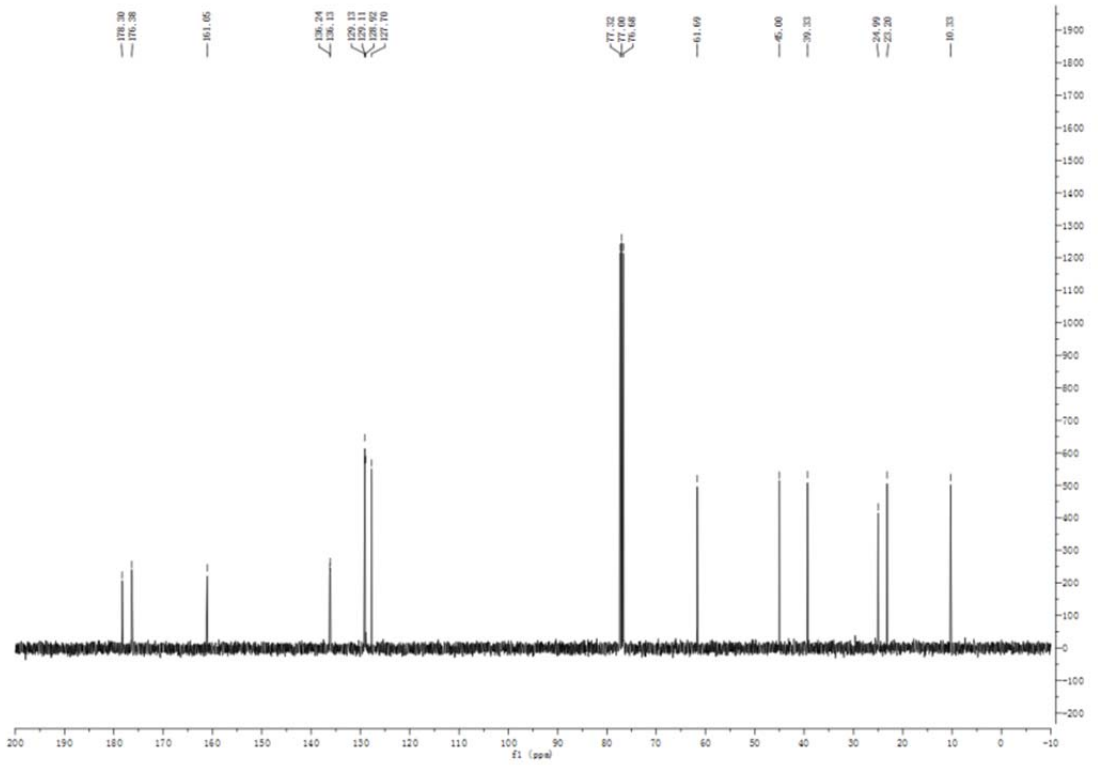

N
OMe
MeO
O
O
N

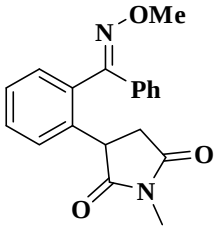

7.26
7.25
7.23
6.87
6.85
6.66
6.65
4.24
4.22
4.22
4.20
3.81
3.80
3.19
3.16
3.14
3.12
3.04
2.95
2.94
2.91
2.89
2.14
0.00
f1 (ppm)

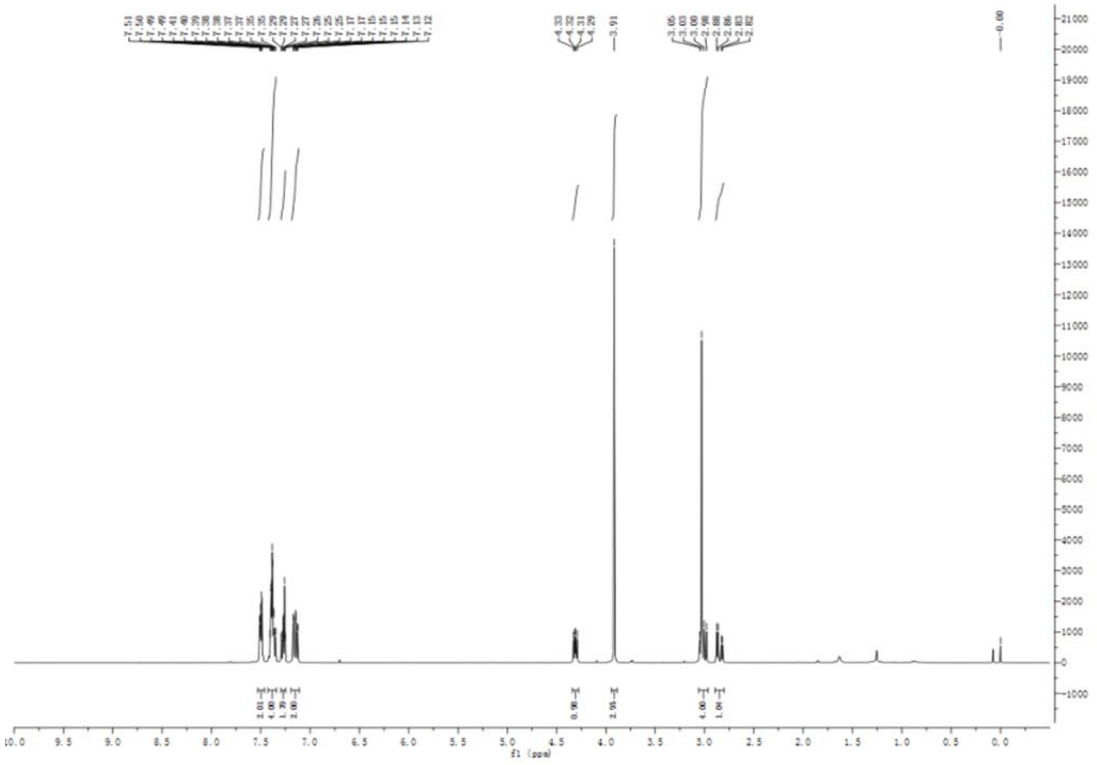

178.22
176.35
159.84
156.46
136.87
130.45
129.55
115.89
112.96
77.32
77.00
76.68
61.52
55.36
45.65
39.14
24.94
16.06
f1 (ppm)

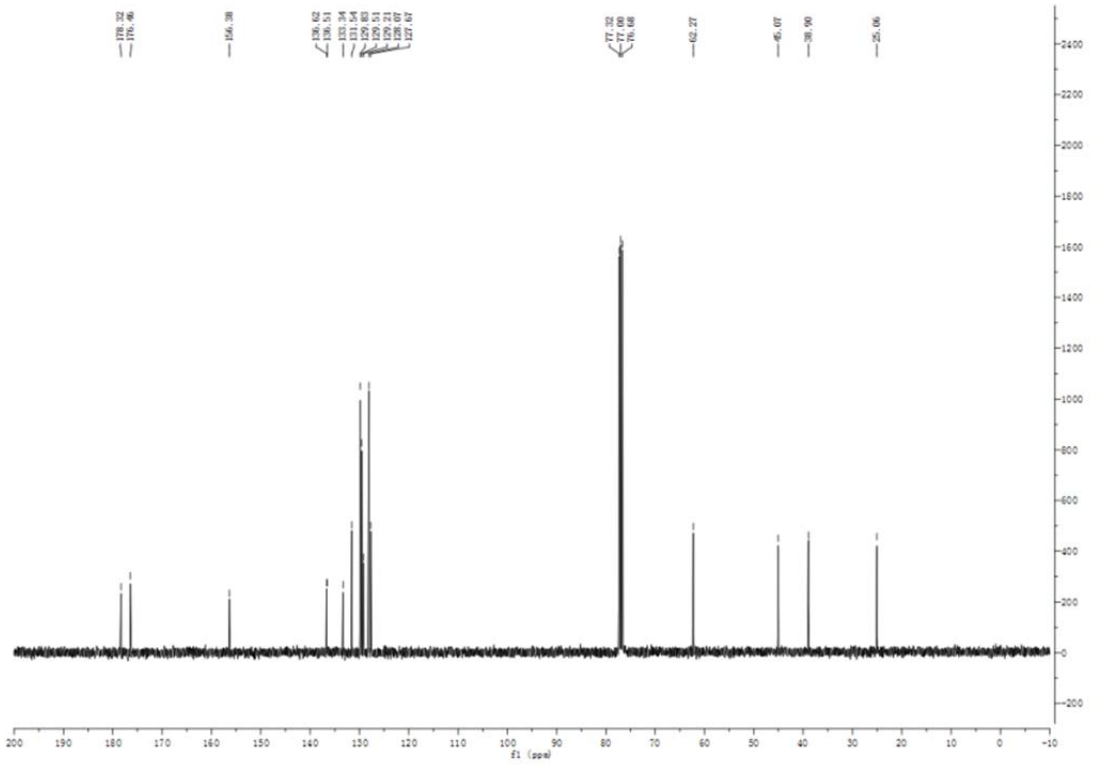

N
OMe
O
O
N

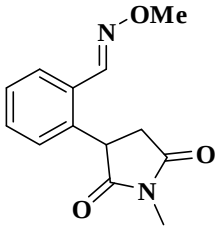

7.35
7.33
7.33
7.32
7.26
7.13
7.13
7.13
7.12
7.11
7.11
4.28
4.27
4.26
4.24
3.86
3.20
3.18
3.15
3.13
3.07
2.74
2.70
2.67
2.65
2.63
2.61
2.59
2.57
1.12
1.10
1.08
0.00
2.99
0.94
0.97
2.91
1.01
1.00
1.03
1.08
2.96
f1 (ppm)

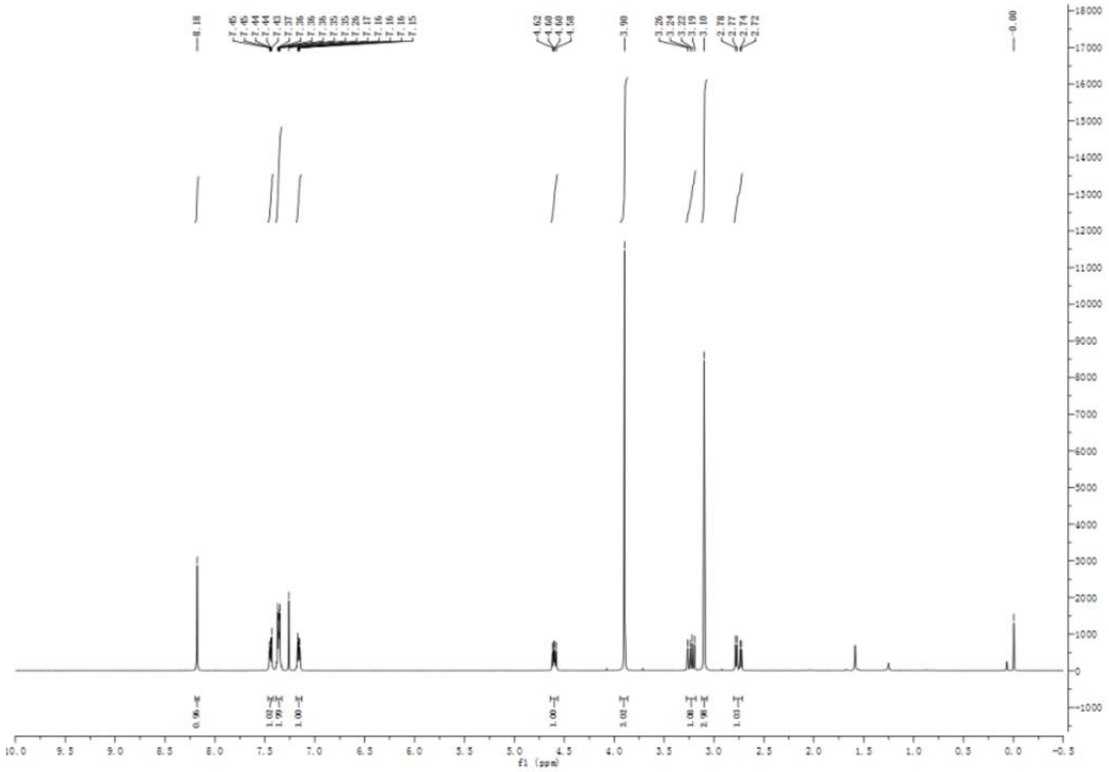

178.30
176.38
161.65
136.24
136.13
129.13
129.11
128.92
127.70
77.32
77.00
76.68
61.69
45.00
39.33
24.99
23.20
10.33
f1 (ppm)

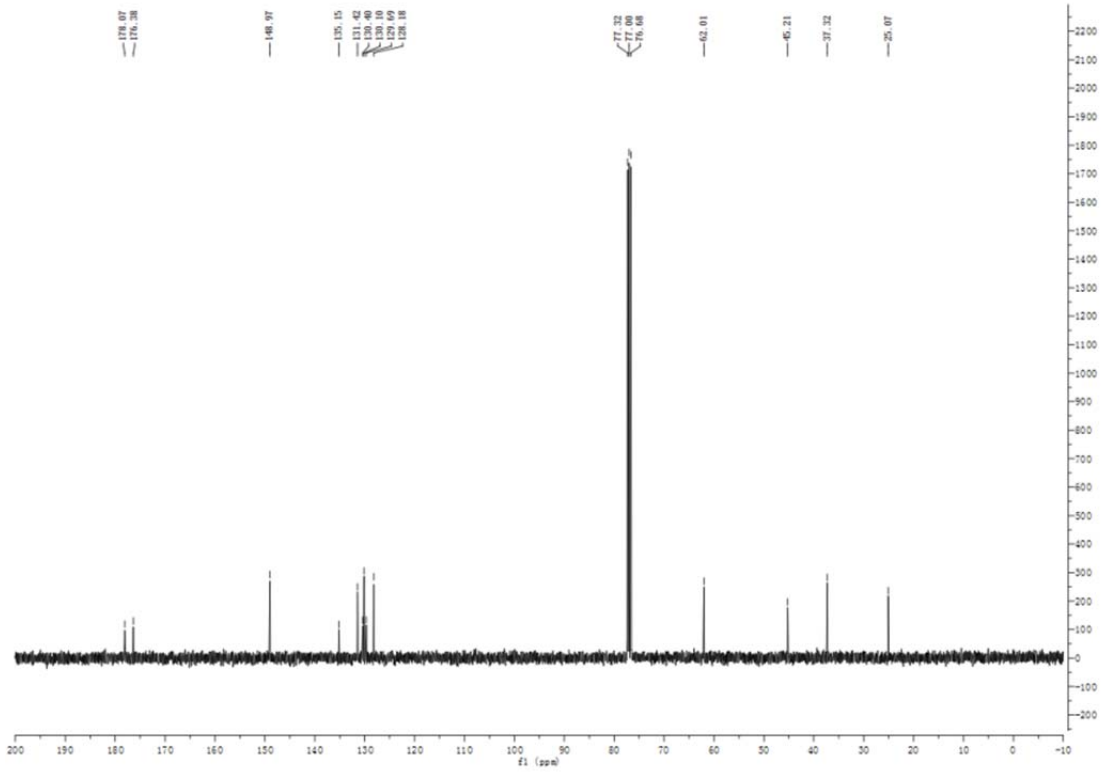

OMe
N
Ph
O
O
N

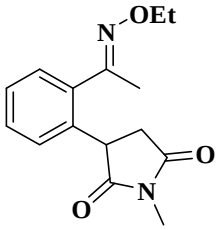


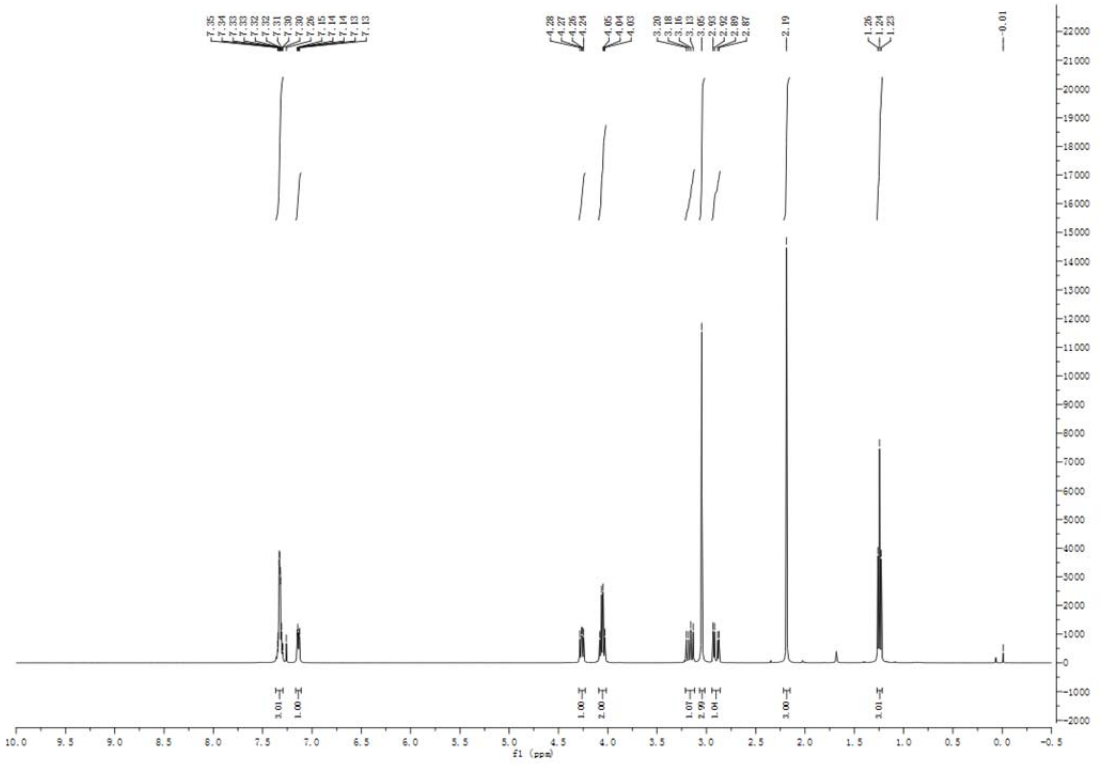


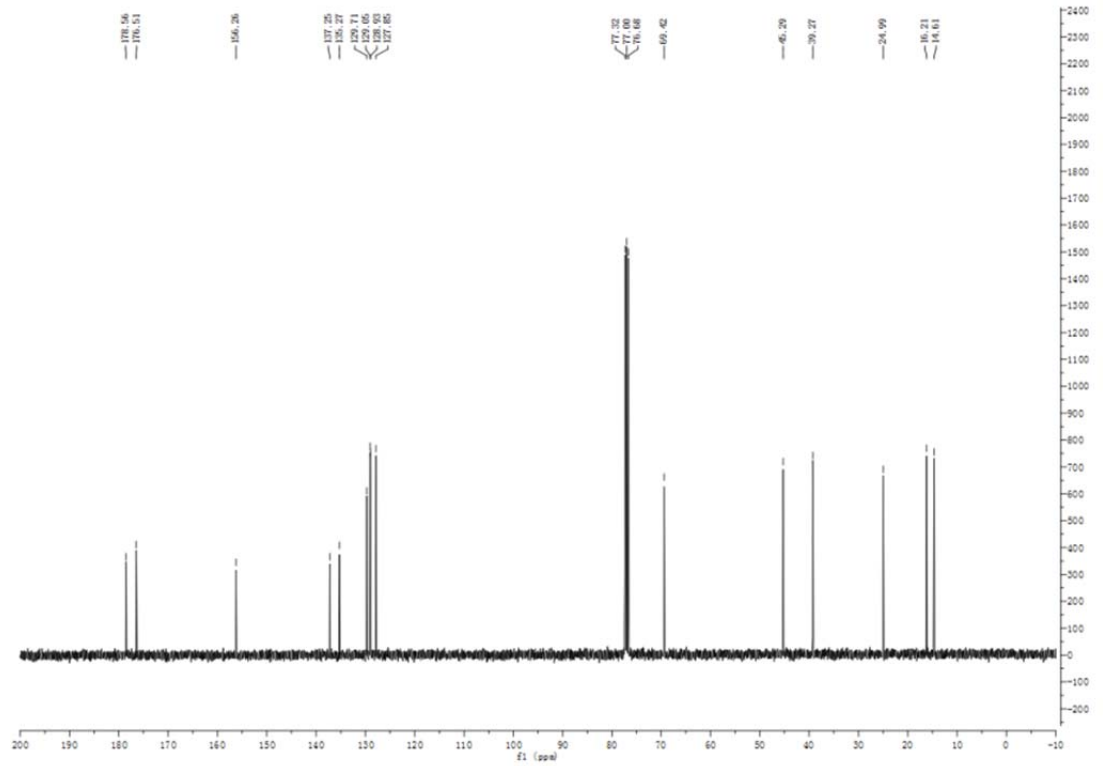

N
OMe
O
O
N

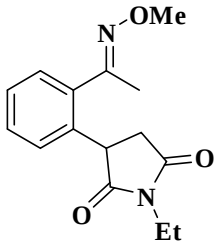


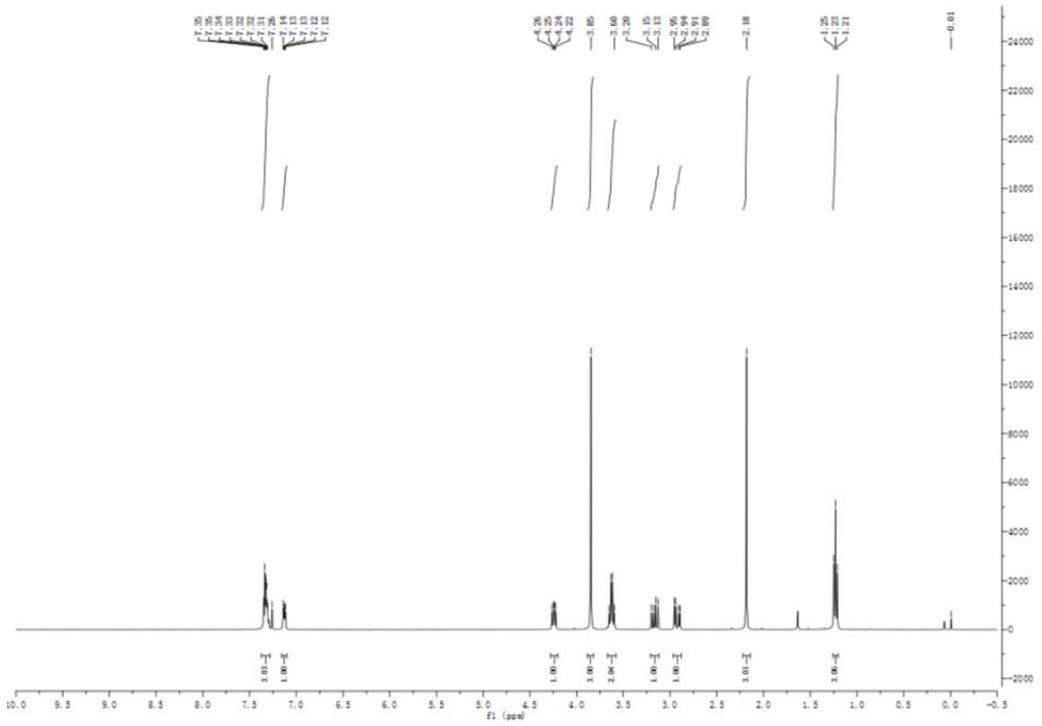


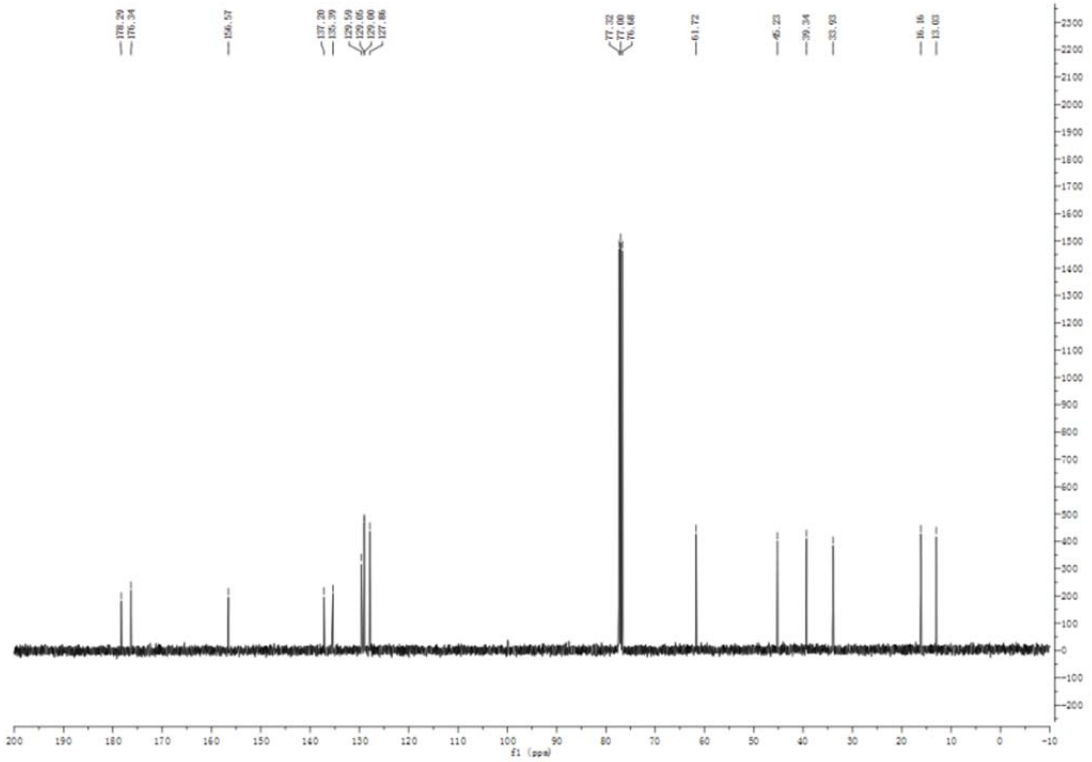

N
OEt
O
O
N

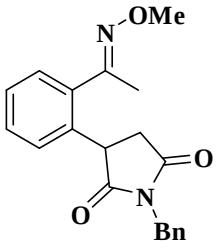

7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.26
7.15
7.14
7.14
7.13
7.13
4.28
4.27
4.26
4.24
4.05
4.04
4.03
3.20
3.18
3.16
3.13
3.05
2.93
2.92
2.89
2.87
2.19
1.26
1.24
1.23
0.01
3.01
1.00
1.00
2.00
1.07
2.99
1.04
3.00
3.01
f1 (ppm)

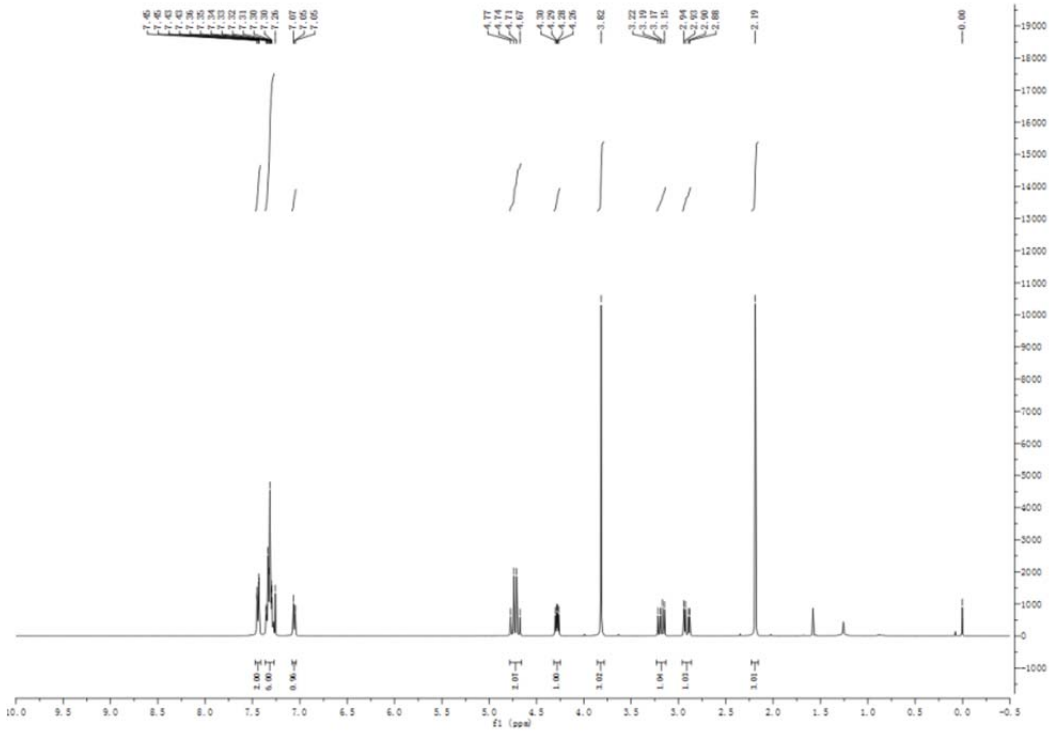

178.56
176.51
156.26
137.25
135.27
129.71
129.05
128.93
127.85
77.32
77.00
76.68
69.42
45.29
39.27
24.99
16.21
14.61
f1 (ppm)

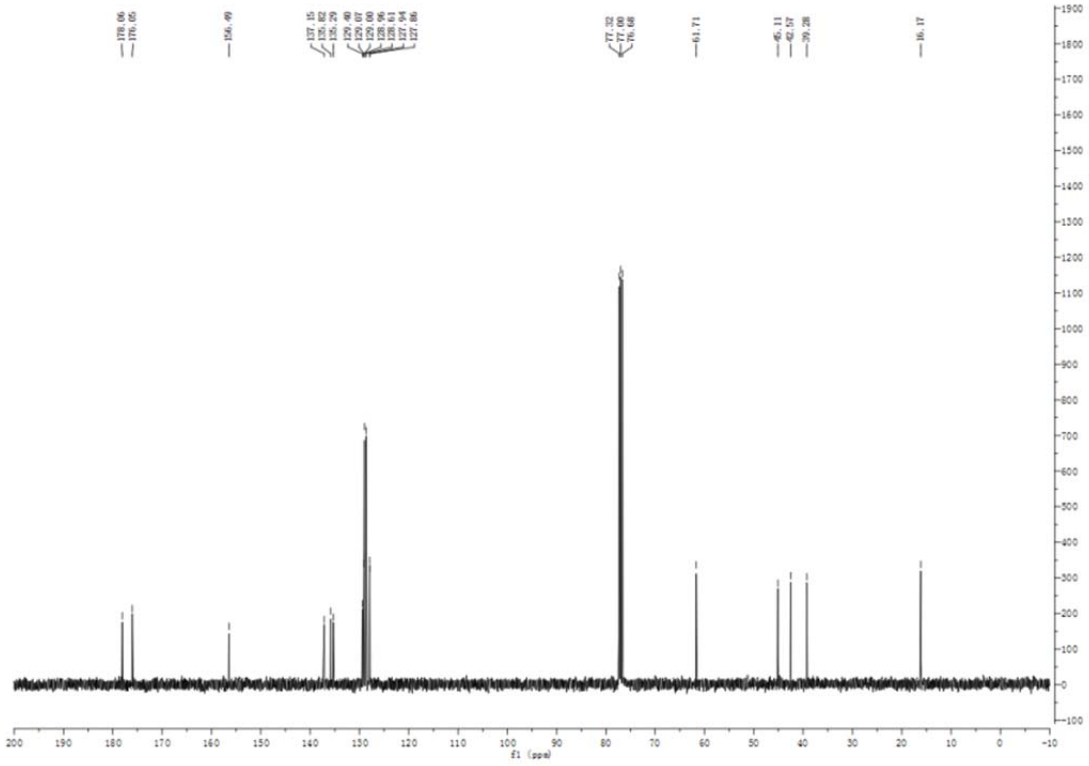

N
OMe
O
O
N
Et

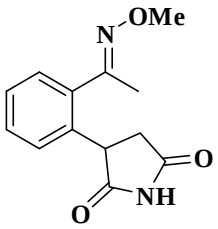


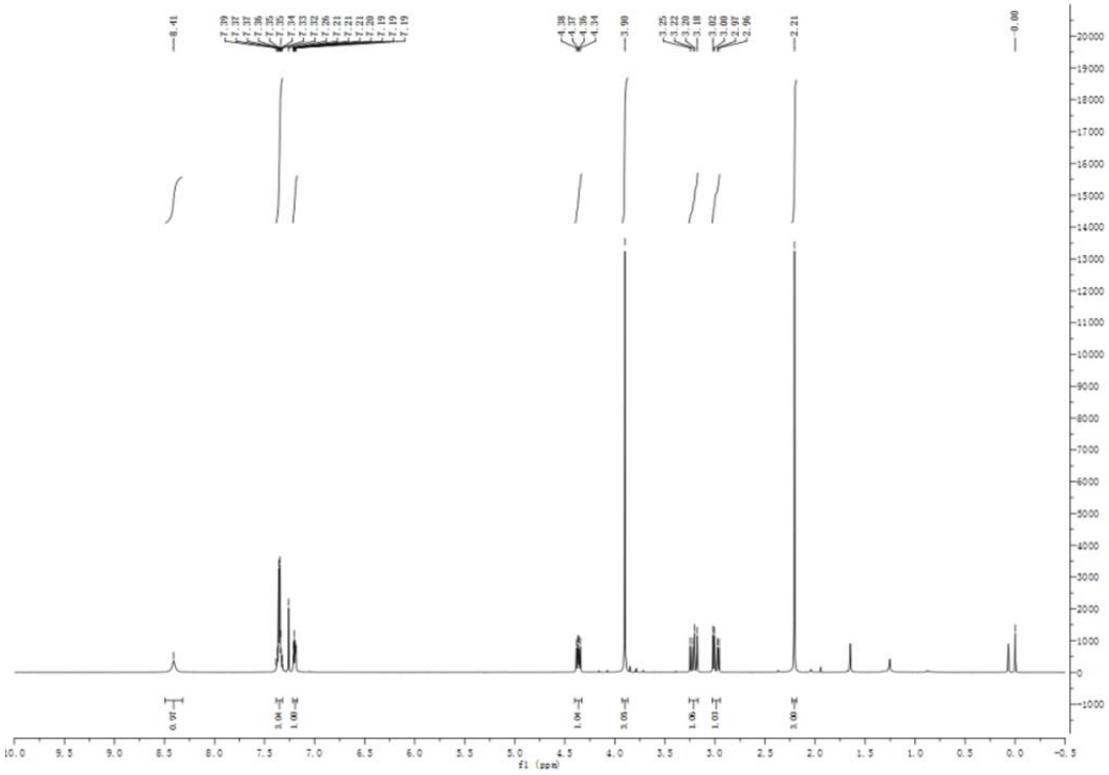


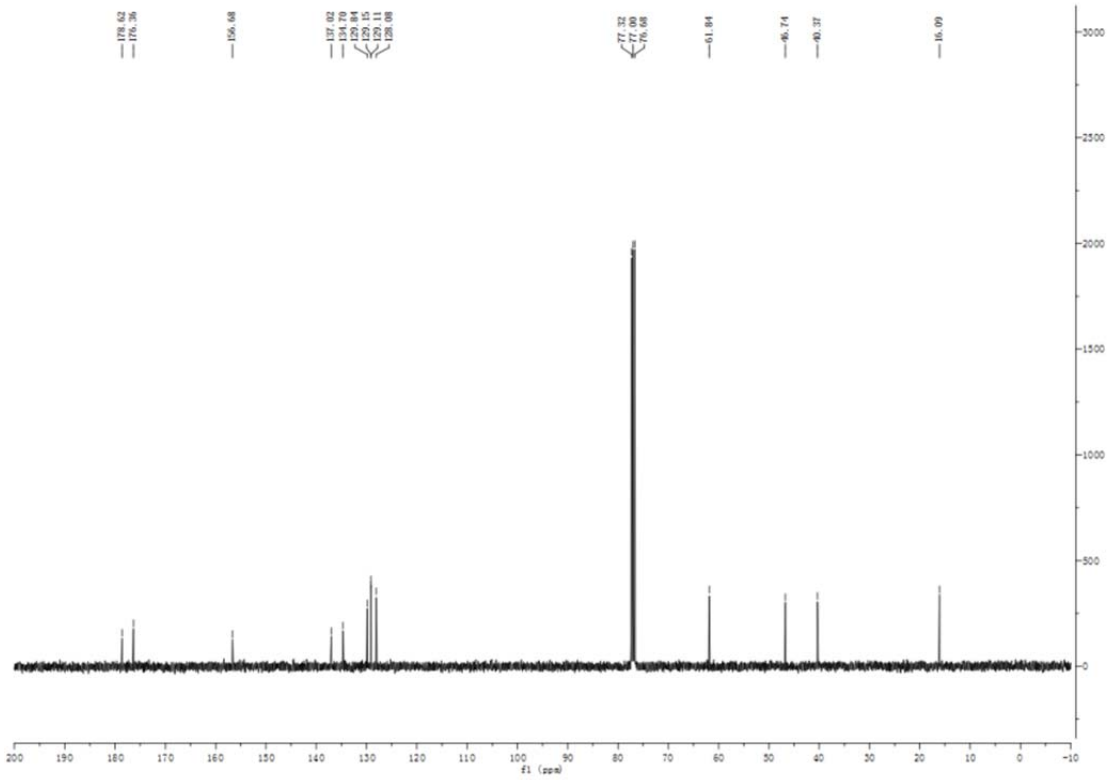

N
OMe
O
O
N
Bn

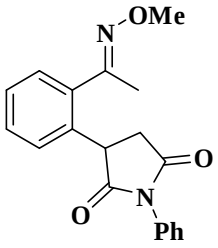


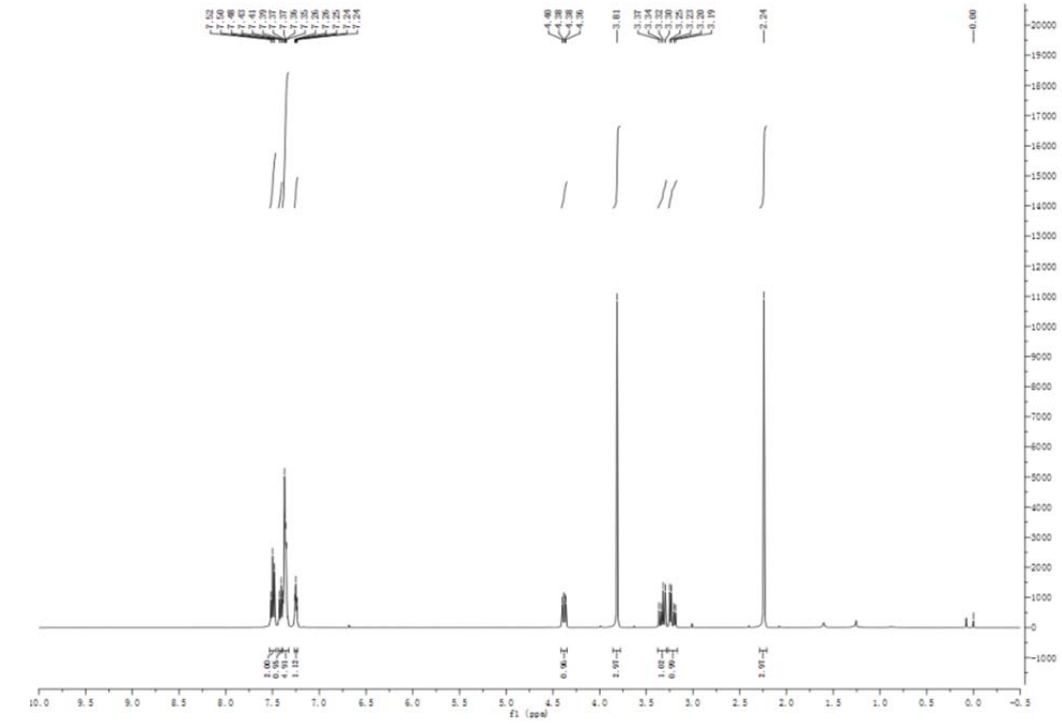


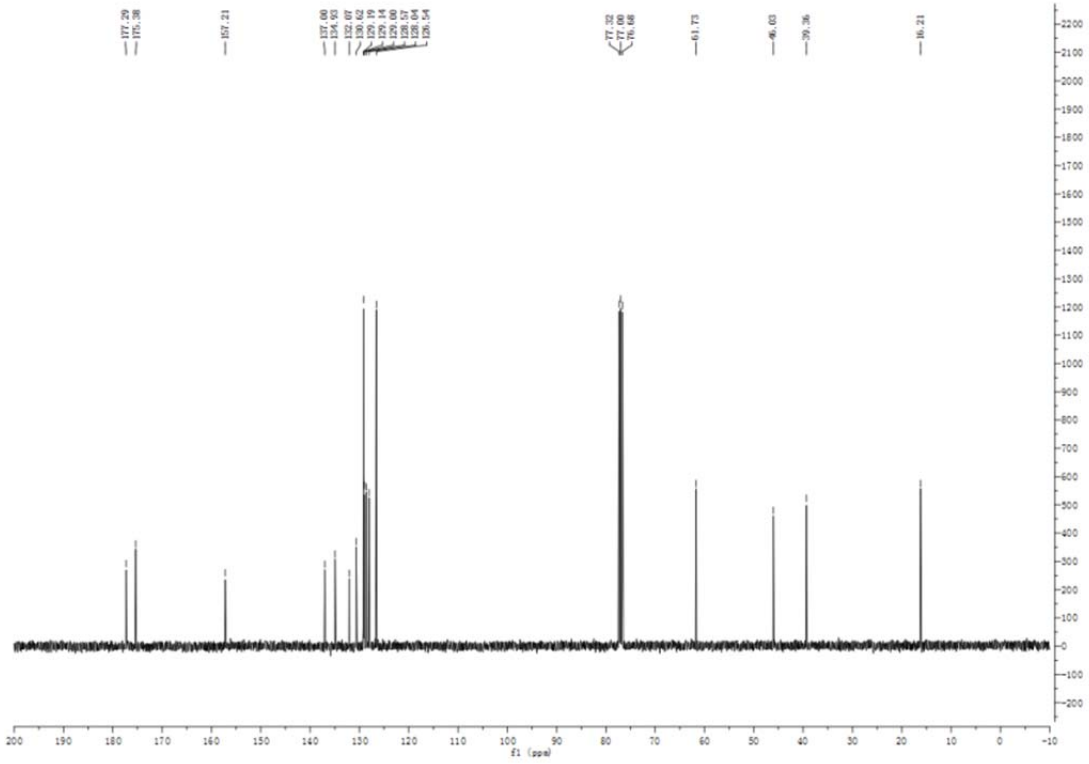

N
OMe
O
NH
O

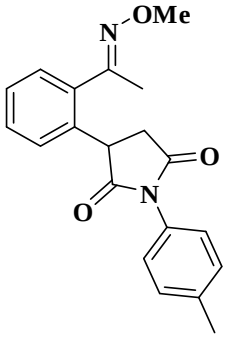


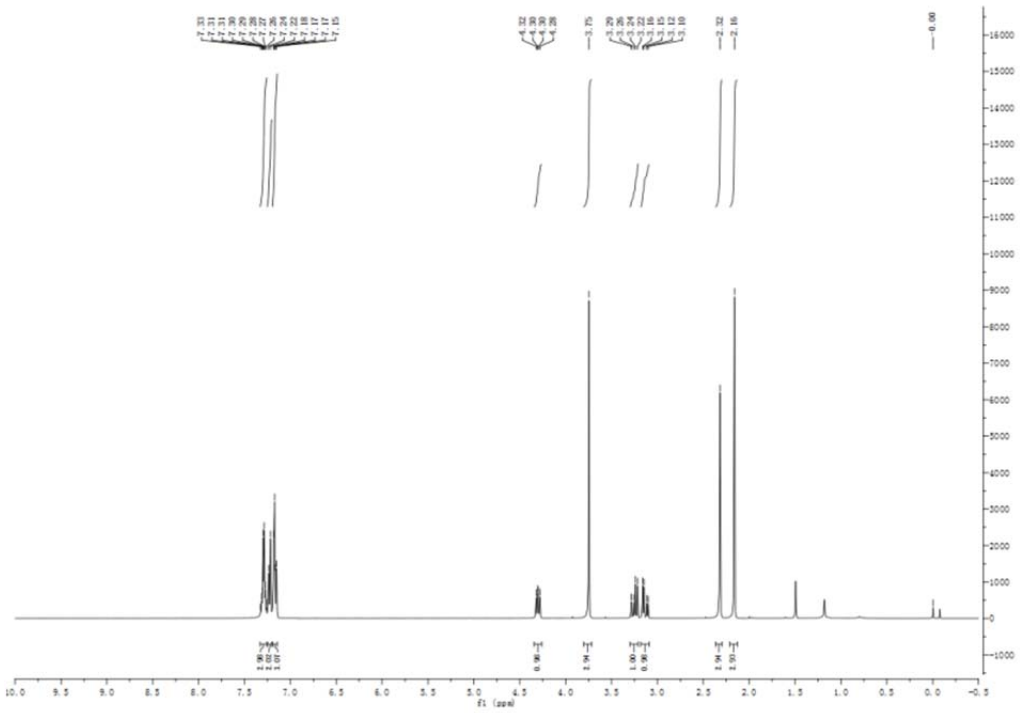


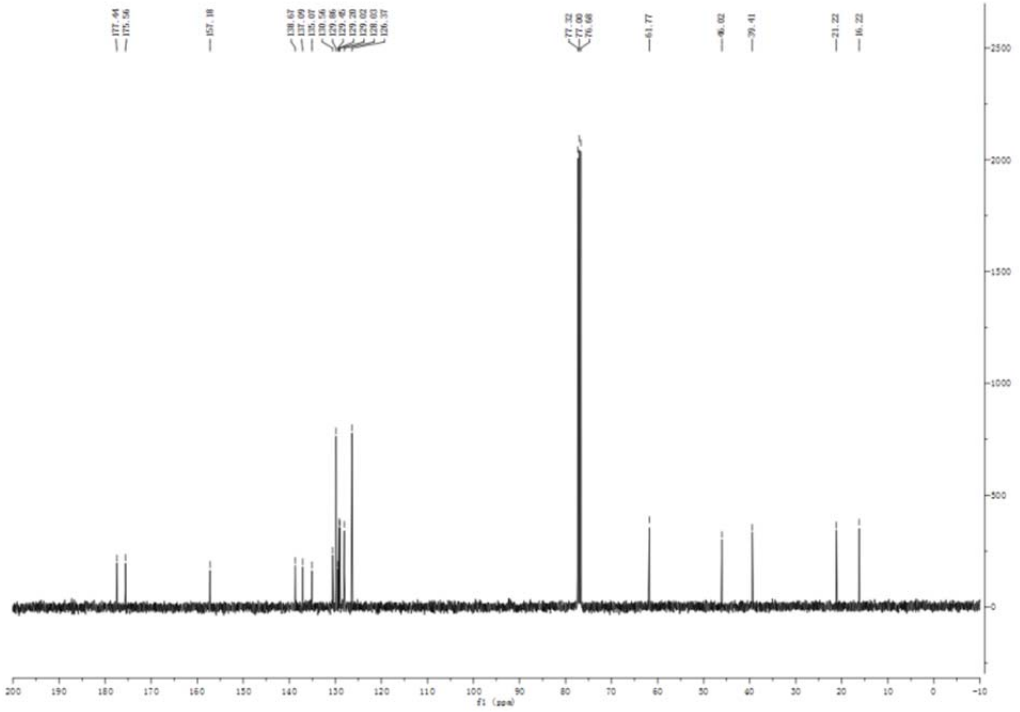

N
OMe
O
O
N
Ph

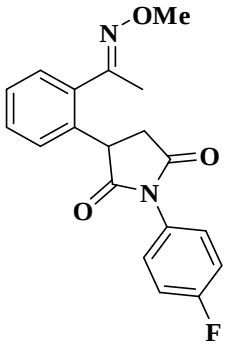


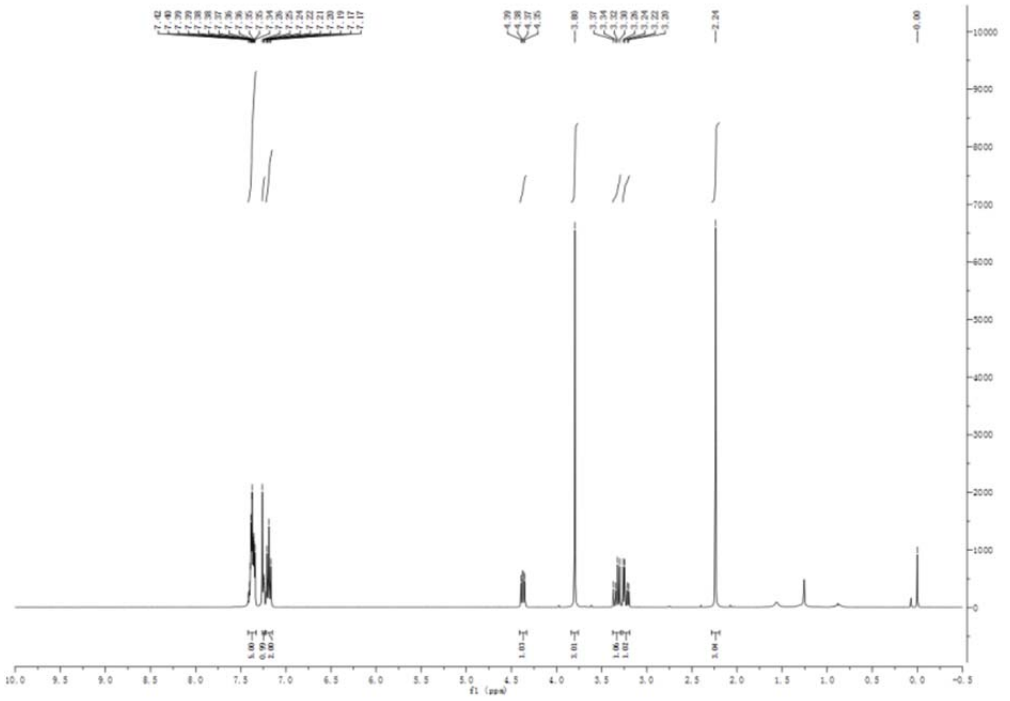


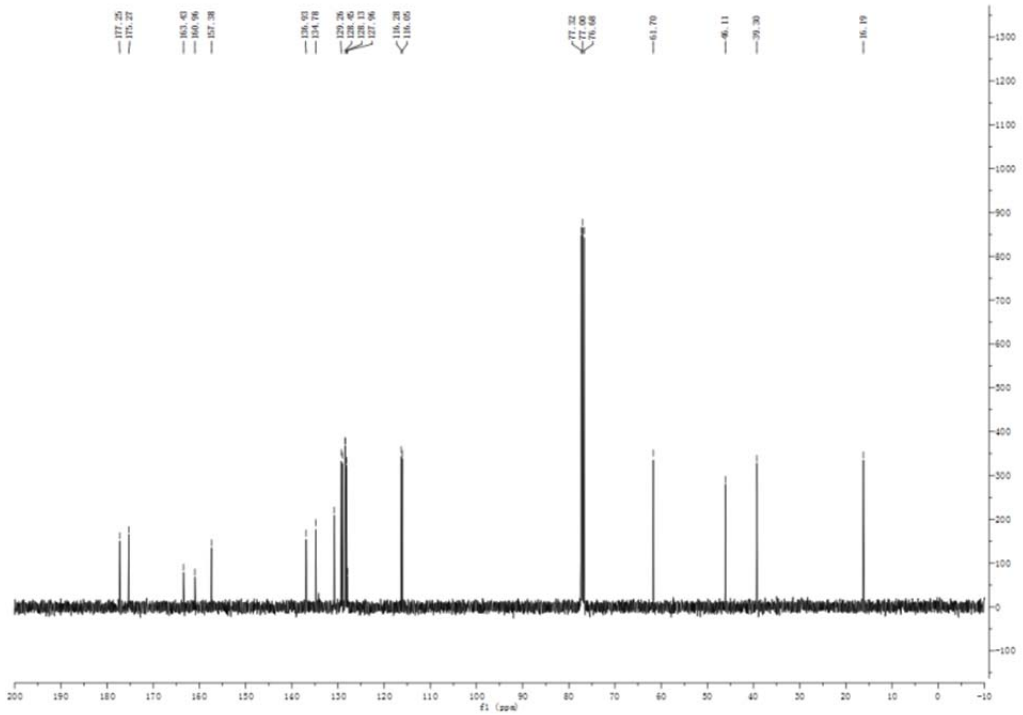

N
OMe
O
O
N

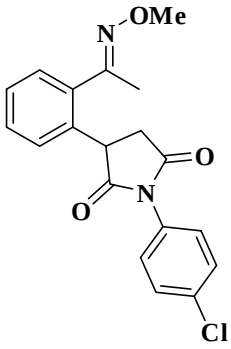


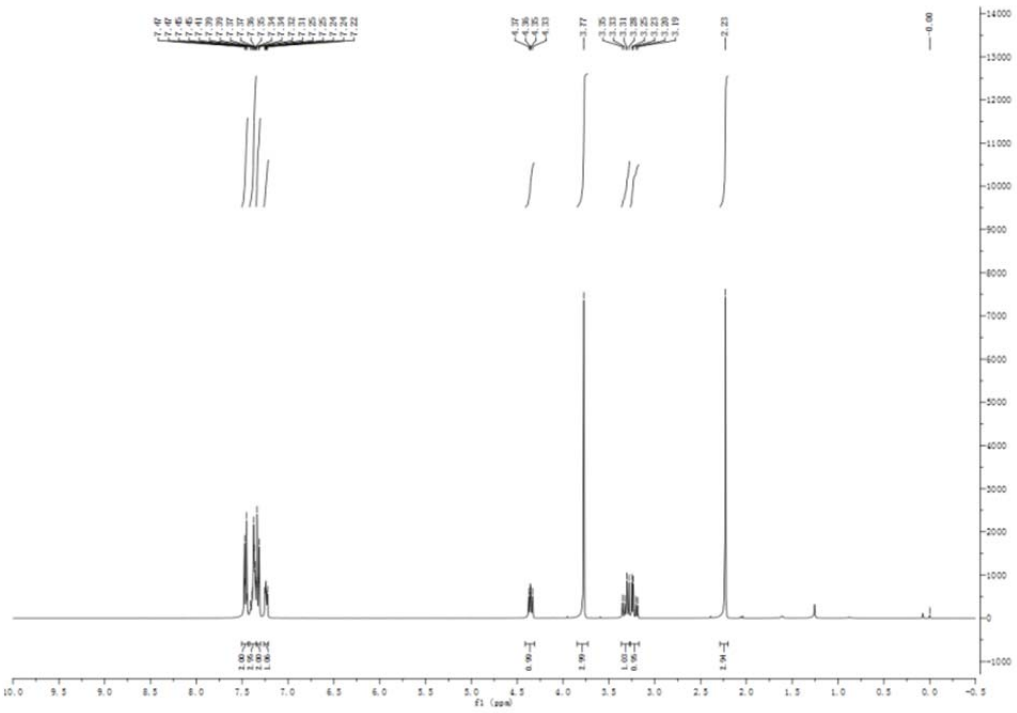


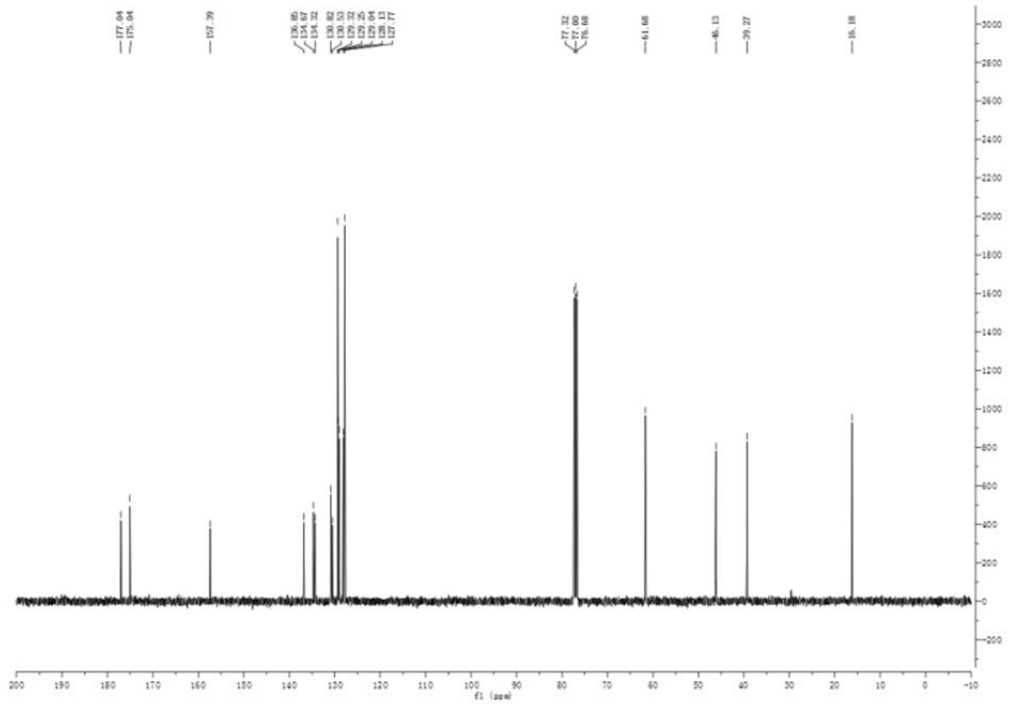

N
OMe
O
O
N
F

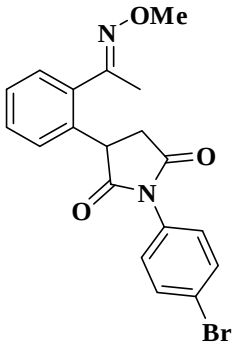


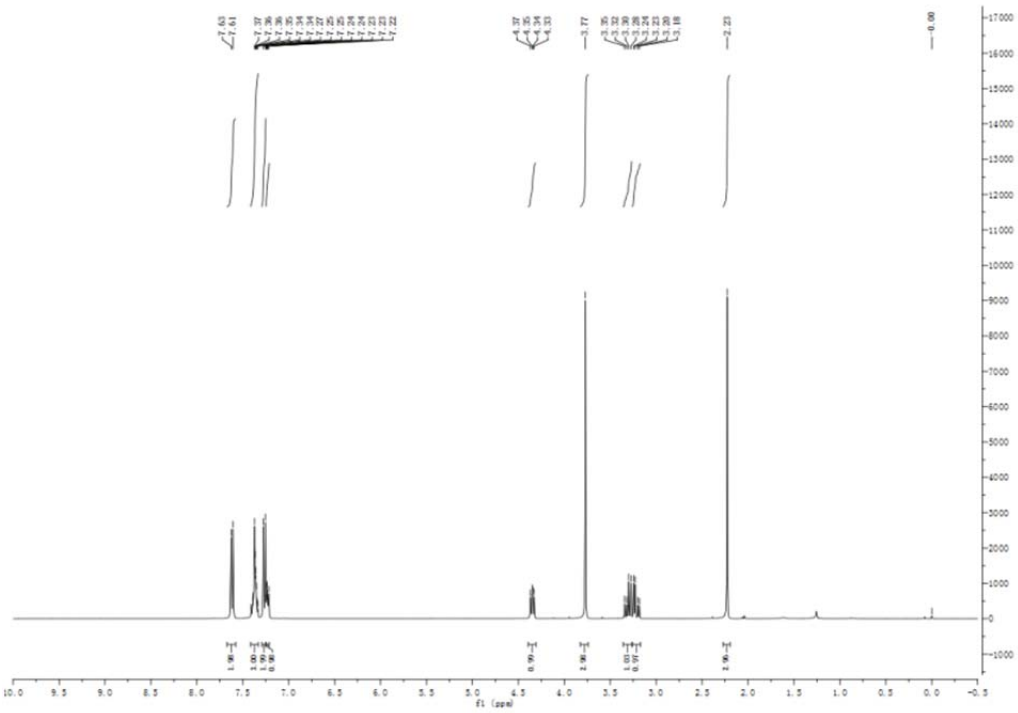


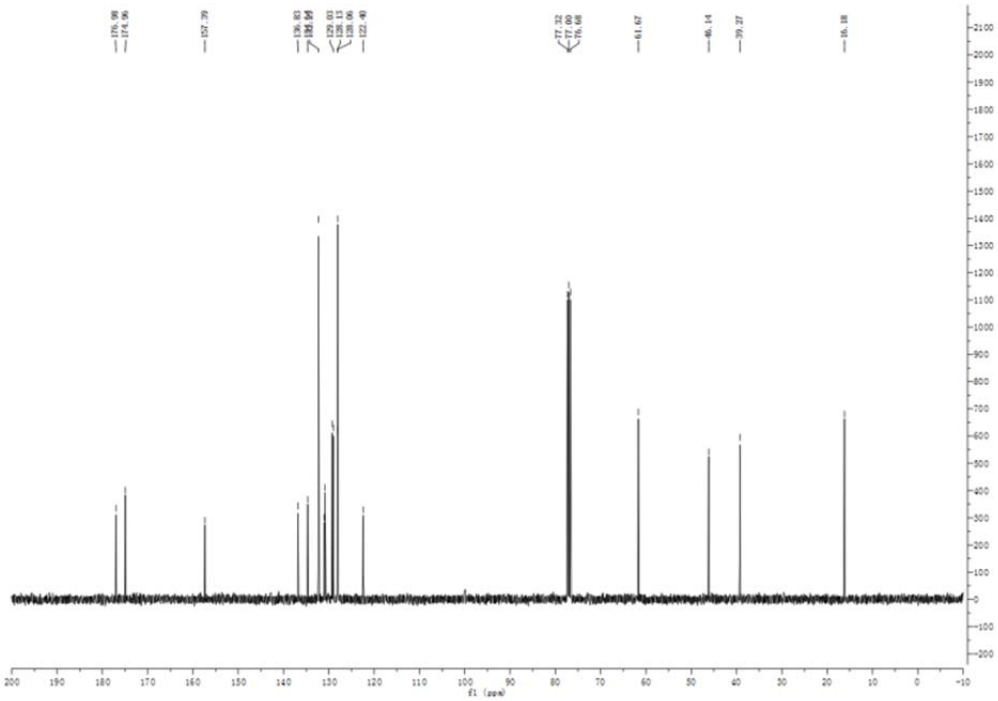

N
OMe
O
O
N
Cl

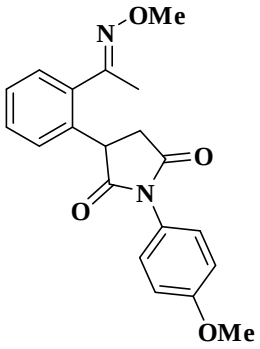


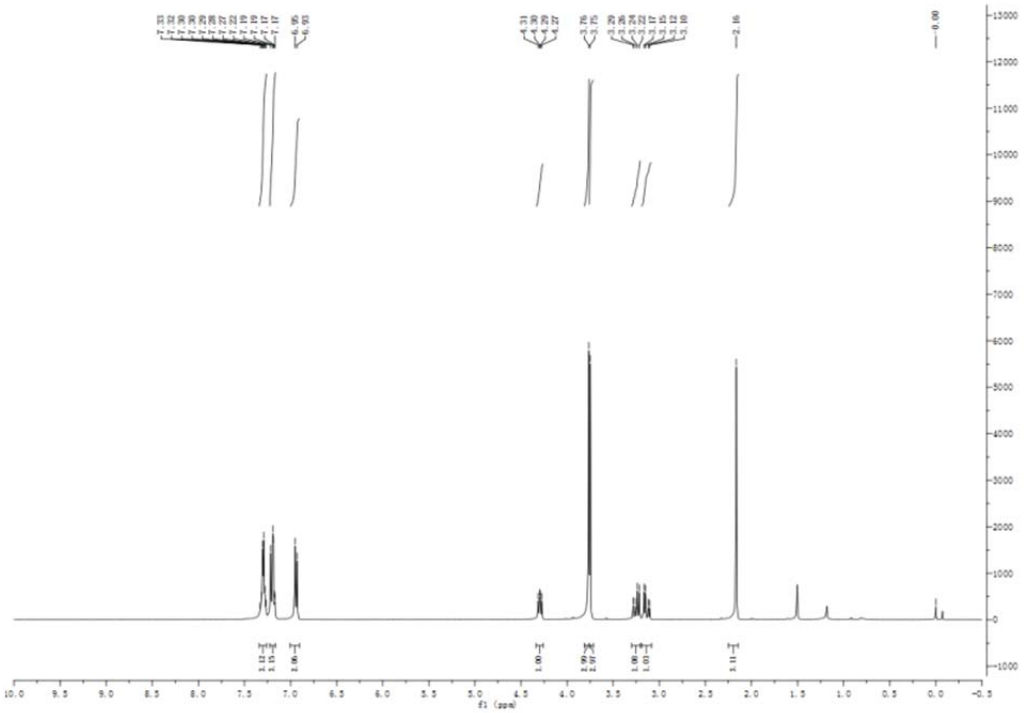


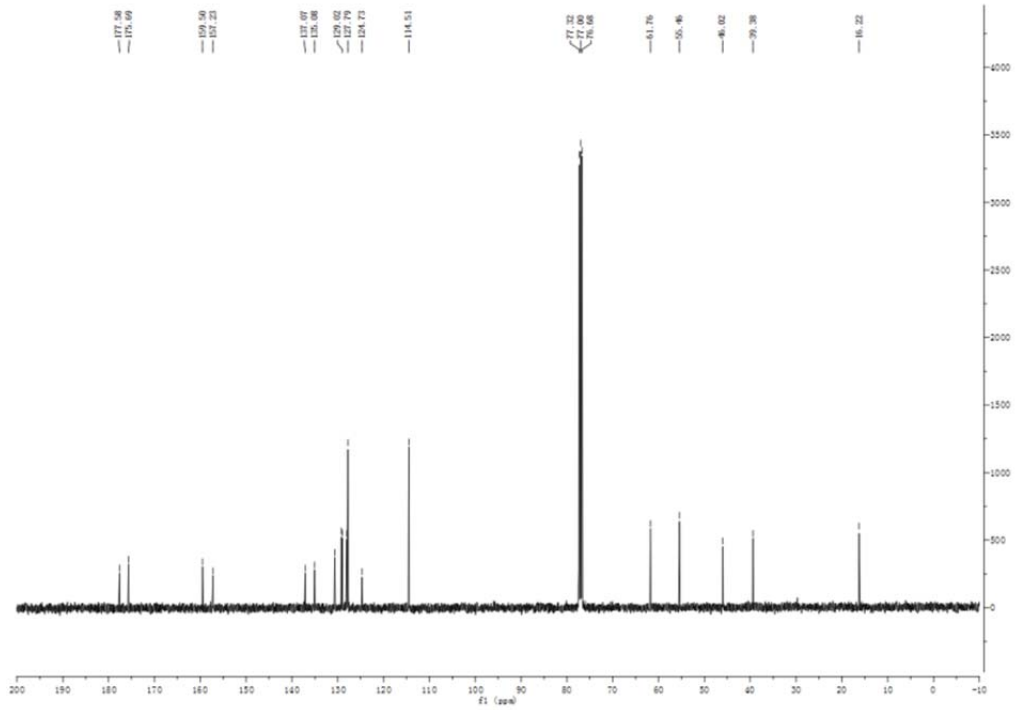

N
OMe
O
O
N
Br

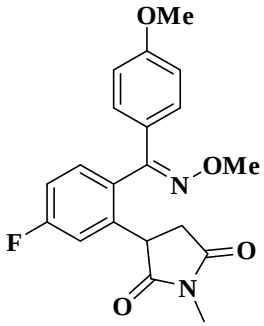


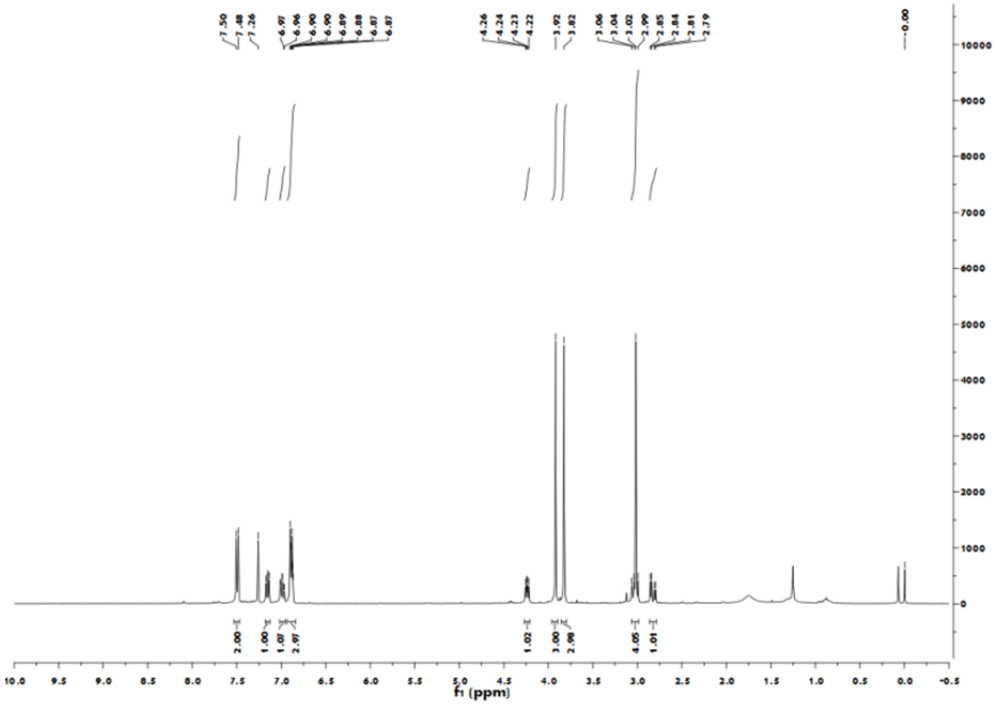


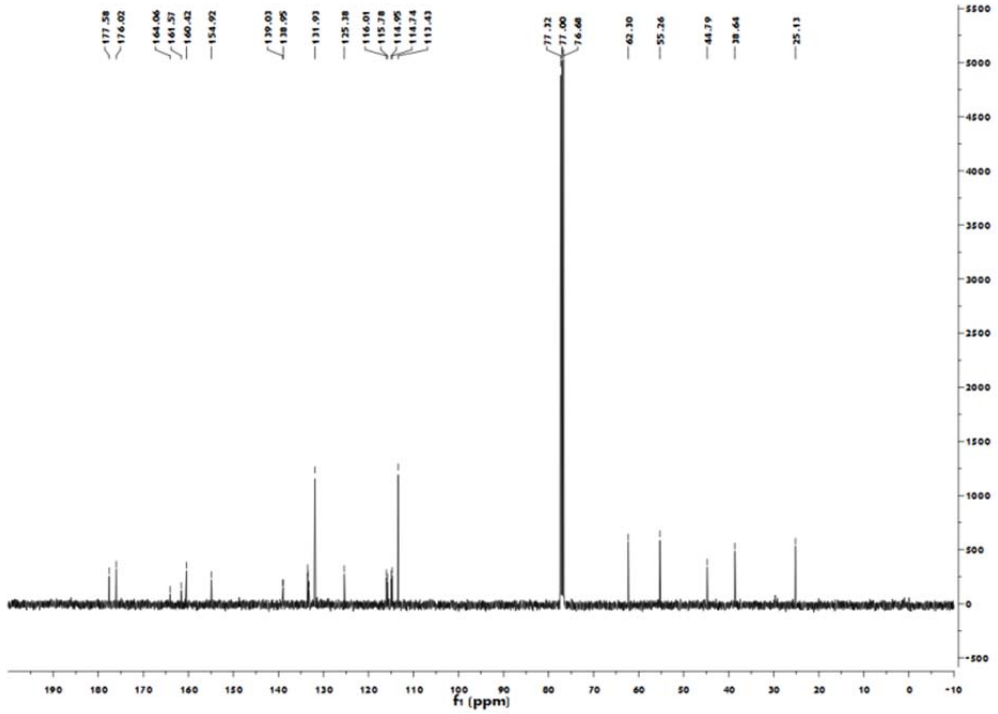

N
OMe
O
O
N
OMe

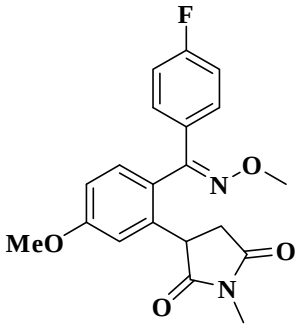


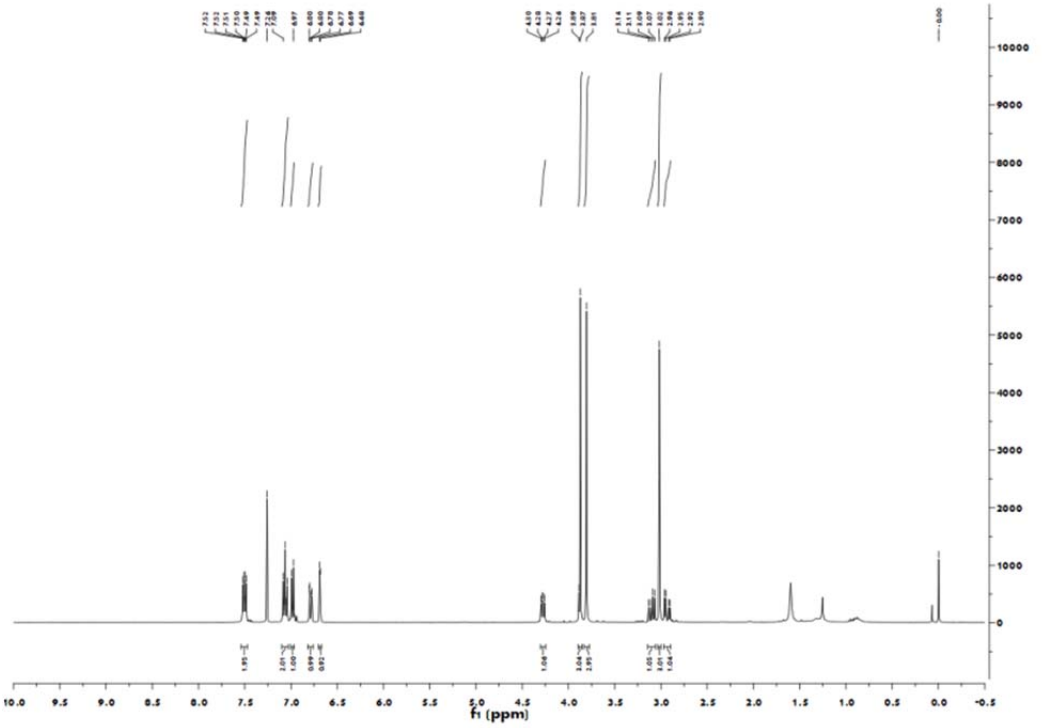


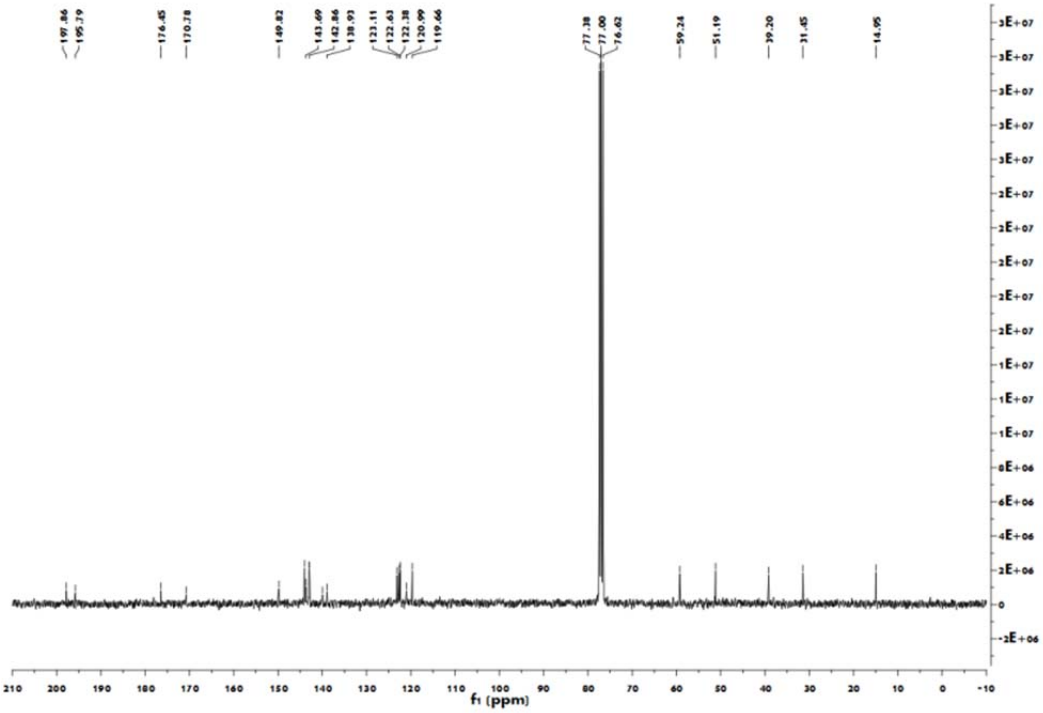

OMe
N
OMe
F
O
O
N

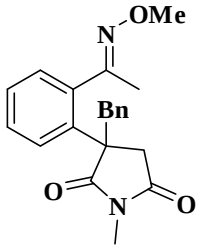

f1 (ppm)

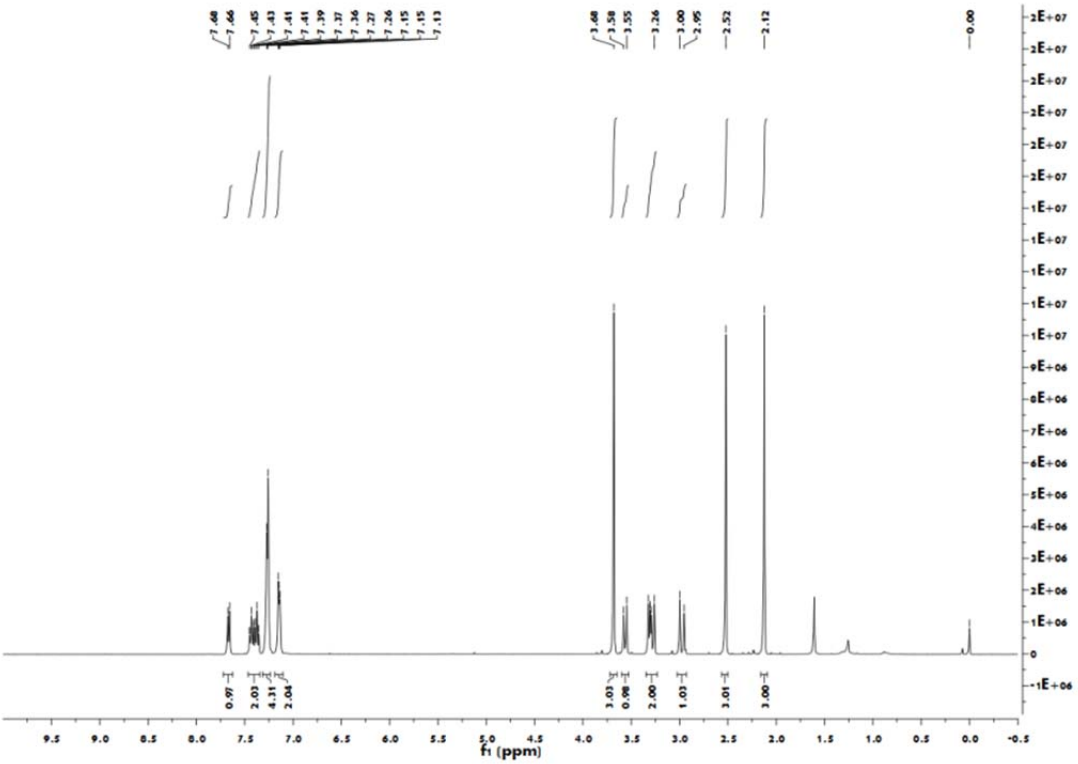

f1 (ppm)

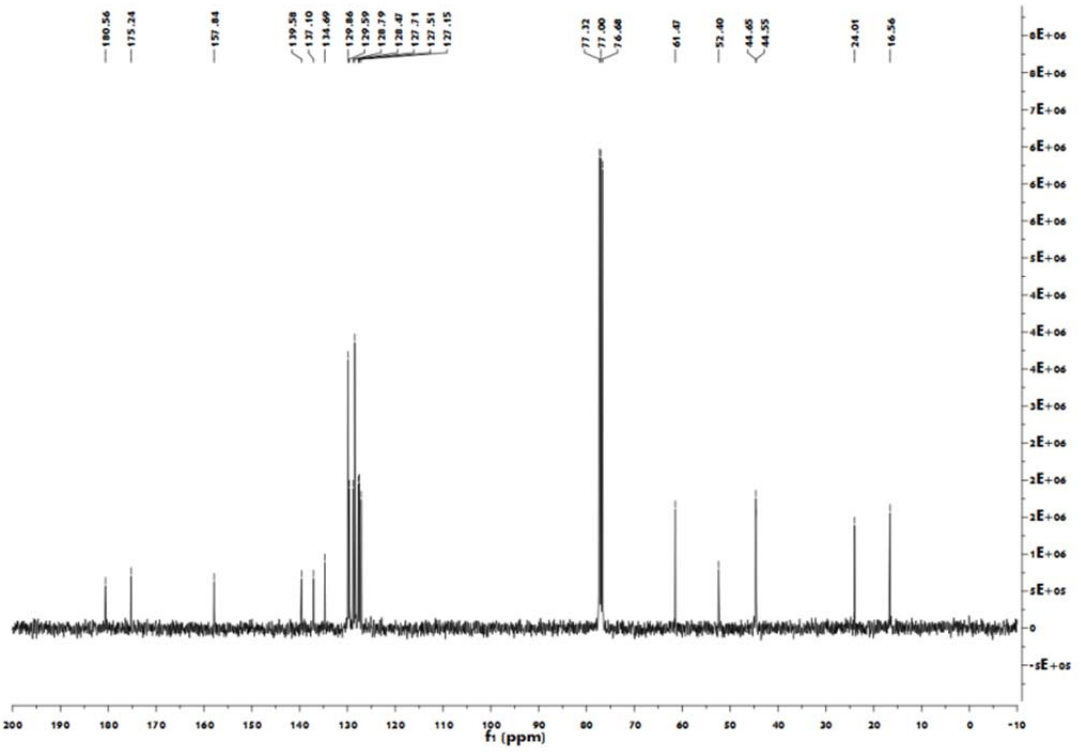

F
N
O
MeO
O
O
N

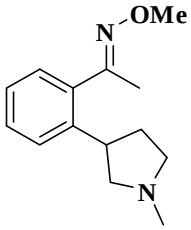

f1 (ppm)

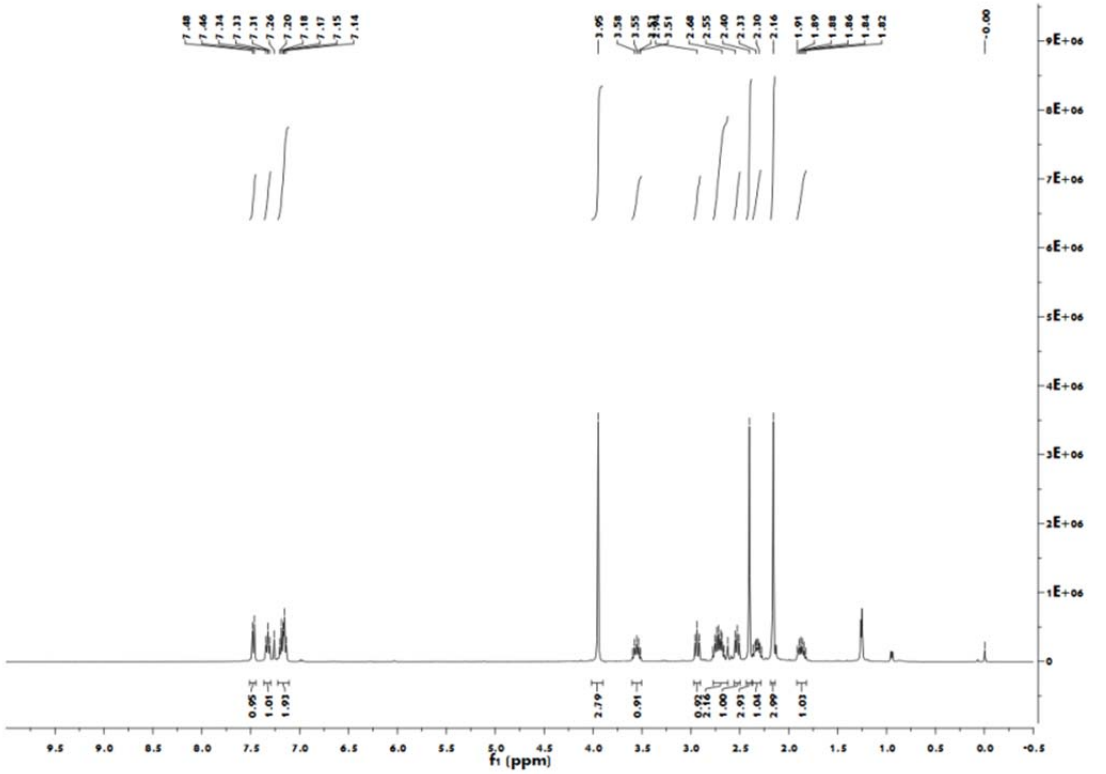

197.86
195.79
176.45
170.78
149.82
143.69
142.86
138.93
123.11
122.63
122.38
120.99
119.66
77.38
77.00
76.62
59.24
51.19
39.20
31.45
14.95
f1 (ppm)

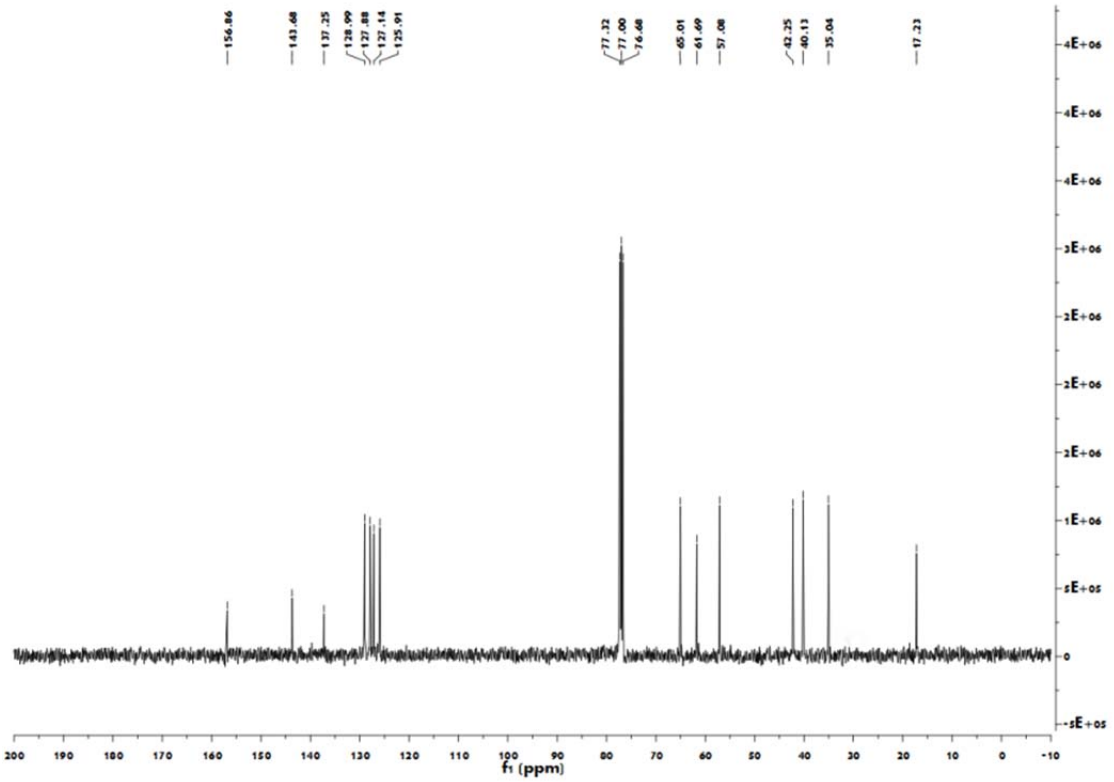

OMe
N
Bn
O
N
O

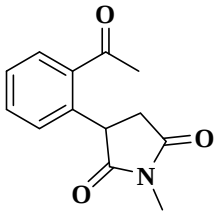

7.48
7.46
7.45
7.43
7.41
7.41
7.39
7.37
7.36
7.27
7.26
7.15
7.15
7.13
3.68
3.58
3.55
3.26
3.00
2.95
2.52
2.12
0.00
0.97
2.03
4.31
2.04
3.03
0.98
2.00
1.03
3.01
3.00
f1 (ppm)

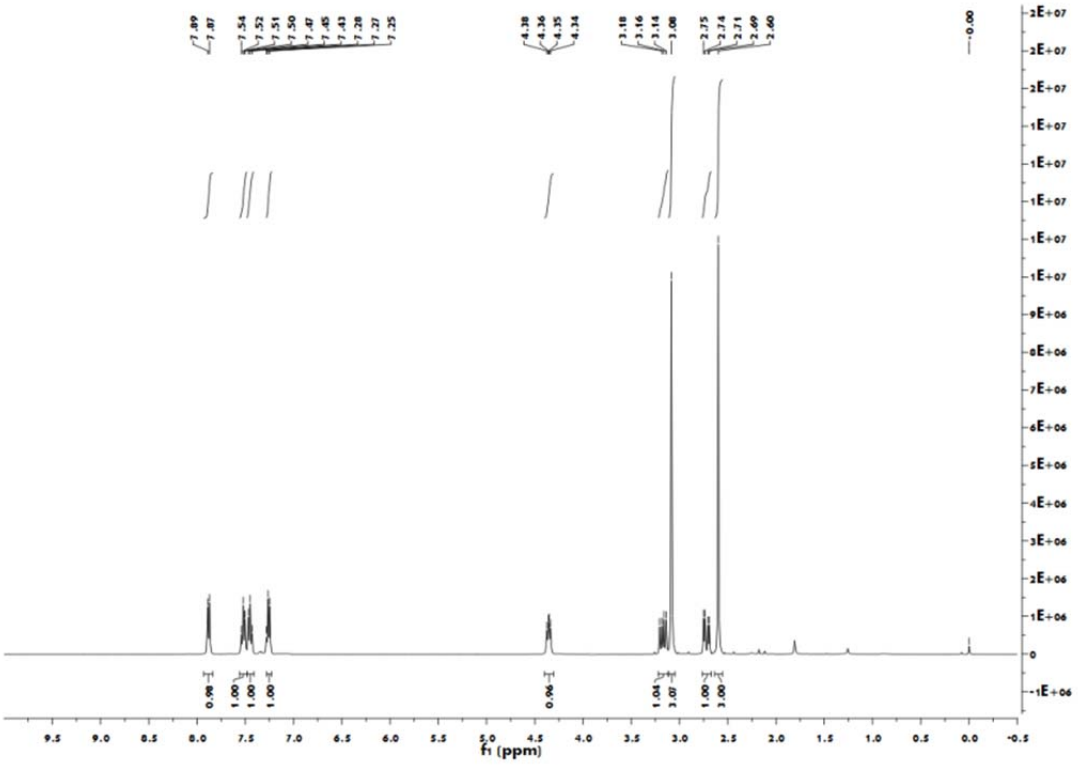

180.56
175.24
157.84
139.58
137.10
134.69
129.86
129.59
128.79
128.42
127.71
127.51
127.15
77.32
77.00
76.68
61.47
52.40
44.65
44.55
24.01
16.56
f1 (ppm)

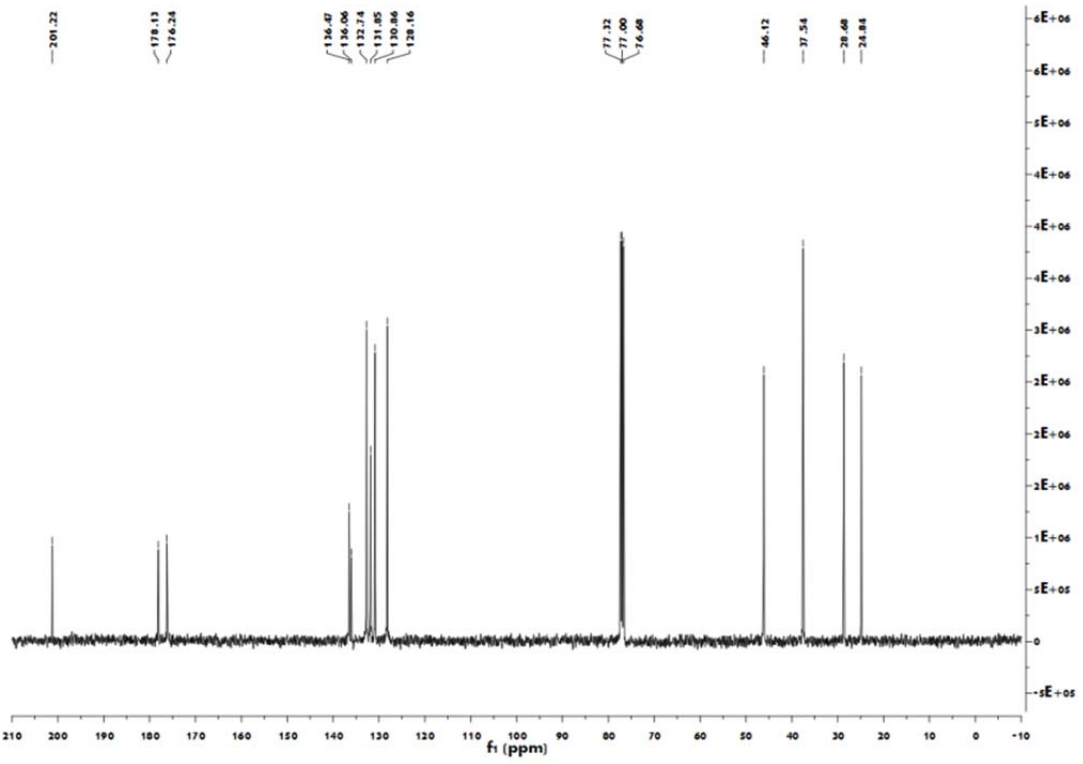

N
OMe
N

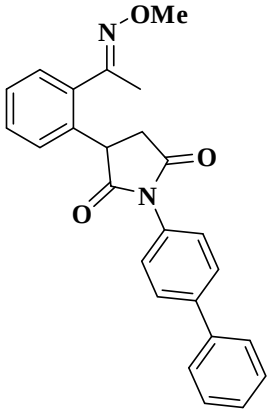

f1 (ppm)

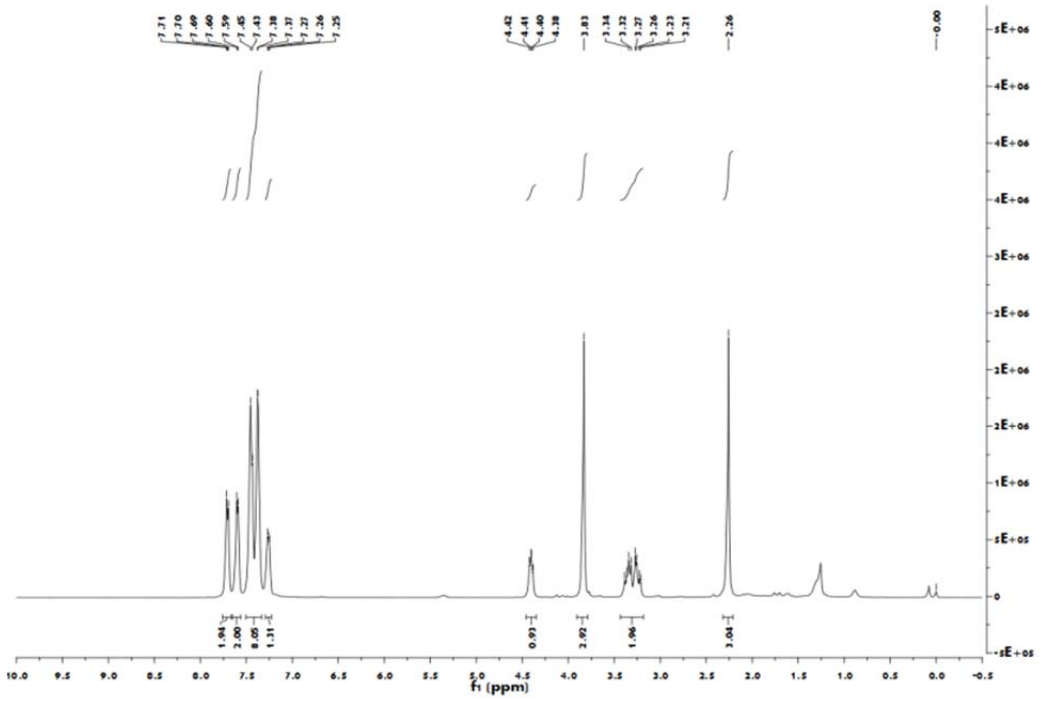

f1 (ppm)

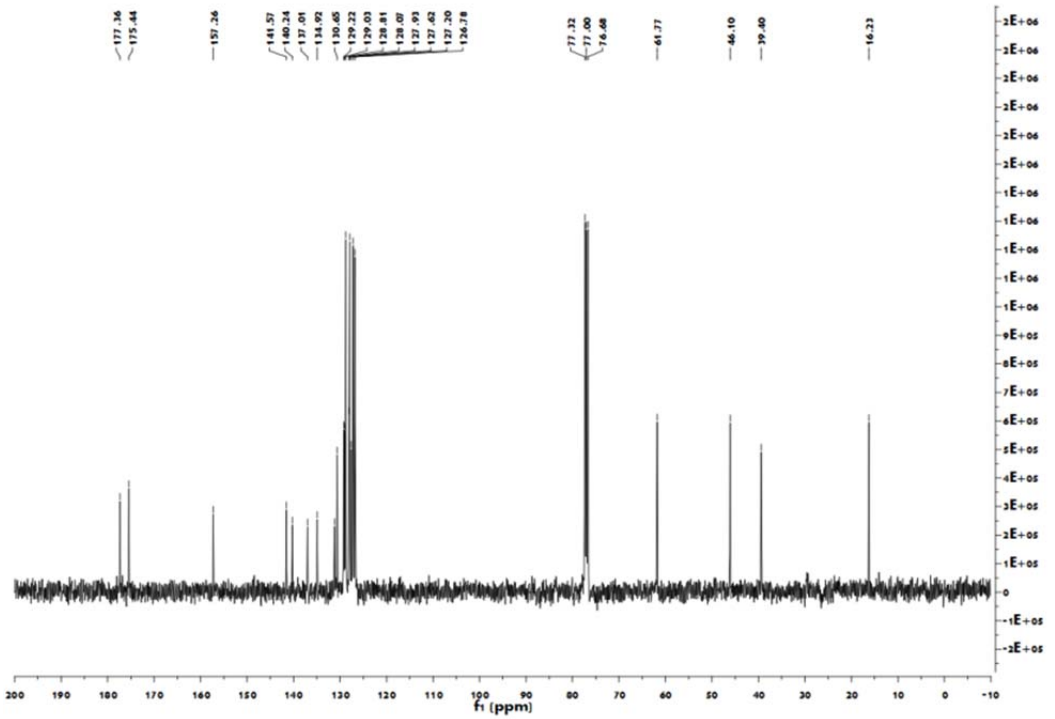

O
O
O
N


7.89
7.87
7.54
7.52
7.51
7.50
7.47
7.45
7.43
7.28
7.27
7.25
4.38
4.36
4.35
4.34
3.18
3.16
3.14
3.08
2.75
2.74
2.71
2.69
2.60
0.00
0.98
1.00
1.00
1.00
0.96
1.04
3.07
1.00
3.00
f1 (ppm)


201.22
178.13
176.24
136.47
136.06
132.74
131.85
130.86
128.16
77.32
77.00
76.68
46.12
37.54
29.68
24.84
f1 (ppm)


N
OMe
O
O
N


7.71
7.70
7.69
7.60
7.59
7.45
7.43
7.38
7.37
7.27
7.26
7.25
4.42
4.41
4.40
4.38
3.83
3.34
3.32
3.27
3.26
3.23
3.21
2.26
0.00
1.94
2.00
8.05
1.31
0.93
2.92
1.96
3.04
f1 (ppm)



5. References

(1) For the substrate bearing *meta*-fluoro and *meta*-methoxy substituents, the isolated products in intramolecular competition experiment could not be purified.

(2) Duan, W.; Yusuke, I.; Ryo, S.; Tamio, H. *Tetrahedron* **2007**, *63*, 8529-8536.

(3) Lanke, V.; Bettadapur, K. R.; Prabhu, K. R. *Org. Lett.* **2015**, *17*, 4662−4665.

(4) Liang, Y.-F.; Wang, X.; Yuan, Y.; Liang, Y.; Li, X.; Jiao, N. *ACS Catal.* **2015**, *5*, 6148.

(5) Kim, K. O.; Choi, T.-L. *Macromolecules* **2013**, *46*, 5905.