Dimethylamino-Iodine(III)/PPh_3-Mediated Synthesis of α-Ketoamides from Glyoxylic Acids

Dan Xiao,[a] Jiaxin He,[a] Kaiyue Yang,[a] Zhijian Wang,[a] Cong Li,[a] and Yunfei Du[a*]

[a] *Tianjin Key Laboratory for Modern Drug Delivery & High-Efficiency, School of Pharmaceutical Science and Technology, Faculty of Medicine, Tianjin University, Tianjin 300072, China.*

Corresponding author' email: duyunfeier@tju.edu.cn

Supporting Information

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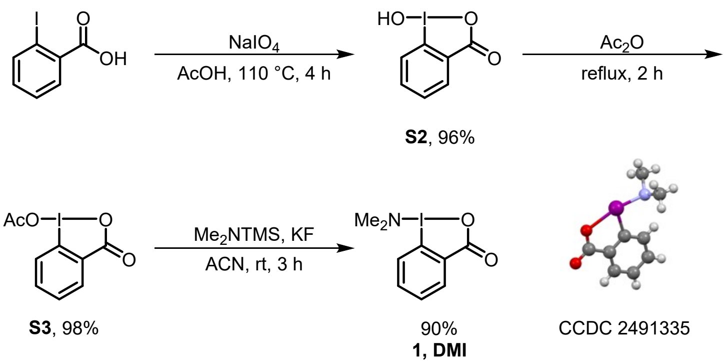
I. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer at 25 °C. Chemical shifts values are given in ppm and referred as the internal standard to TMS: 0.00 ppm. Chemical shifts were expressed in parts per million (*δ*) downfield from the internal standard tetramethylsilane, and were reported as s (singlet), d (doublet), t (triplet), q (quadruple), dd (doublet of doublet), m (multiplet), etc. The coupling constants *J*, are reported in Hertz (Hz). High resolution mass spectrometry (HRMS) data were recorded on Q Exactive HF (Q Exactive™ HF/UltiMate™ 3000 RSLCnano) using electron spray ionization (ESI) in positive (or negative) mode. Melting points were determined with a Micromelting point apparatus. TLC plates were visualized by exposure to ultraviolet light.

Reagents and solvents were purchased as reagent grade and were used without further purification. All reactions were performed in standard glassware, heated at 70 °C for 3 h before used. Flash column chromatography was performed over silica gel (200-300 m) using a mixture of ethyl acetate (EA) and petroleum ether (PE).

II. General Procedure for the Preparation of DMI and Starting Materials



S3 was prepared according to the literature procedure.[1]

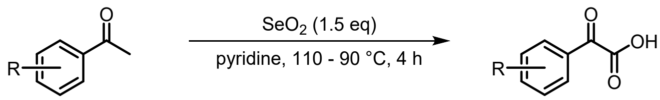
Preparation of **S2**: To a 500 mL round-bottomed flask equipped with a stirrer bar was added 2-iodo benzoic acid **S1** (8.0 g, 32.2 mmol, 1.0 equiv), 2-iodobenzamide $NaIO_4$ (7.24 g, 33.8 mmol, 1.0 equiv), and 30% (v:v) aq. AcOH (48 mL) under air. The mixture was vigorously stirred at 120 ℃ and refluxed. After stirring for 4 h, the reaction mixture was cooled to room temperature and diluted with cold water (180 mL), protecting it from light. The mixture was then filtered and further washed with ice water and cold acetone, air dried in the dark overnight to give the pure compound **S2** (8.5 g, 95%) as a white solid. It is a known compound[1] which is used directly for the next step.

Preparation of **S3**: To a 500 mL round-bottomed flask equipped with a stirrer bar was added compound **S2** (8.5 g, 32.2 mmol, 1.0 equiv) and acetic anhydride (30 mL). Then the reaction mixture was stirred and reflux at 110 ℃. Until the solution turned clear (without suspension), reaction was cool down to room temperature and white crystals started to form. The crystallization was continued at -18 °C. The crystals were then collected and dried overnight under high vacuum to give compound **S3** (8.5 g, 86%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.00 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.96 – 7.90 (m, 1H), 7.71 (m, 1H), 2.25 (s, 3H). It is a known compound; the spectra data is in agreement with the reported one.[1]

Preparation of **DMI**: To a 150 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S3** (1.00 g, 3.28 mmol, 1.00 equiv), KF (19.1 mg, 0.33 mmol, 0.1 equiv) and ACN (30 mL) under N_2 atmosphere, followed by the careful addition of $TMSNMe_2$ (4.9 mol, 0.78 mL, 1.5 equiv). The reaction mixture was stirred at room temperature for 3 h in the dark. After the completion of the reaction, the precipitate was filtered and washed with Et_2O (5 mL x 3) to give product **DMI** (0.86 g) in 90% yield as a yellow solid; mp: 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.93 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.76 (m, 1H), 7.60 (td, *J* = 7.3, 1.0 Hz, 1H), 3.44 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 133.5, 132.6, 132.6, 130.4, 125.2, 117.4, 77.2, 49.6. HRMS (ESI) calcd. for

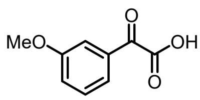
$C_9H_{11}INO_2^+$ [M + H$^+$] 291.9756, found 291.9833.

Procedure A



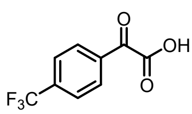
The α-keto acids were synthesized through the oxidation of corresponding methyl ketones with SeO_2 according to the literature procedure.[2]

In a dry, single-neck, 25-mL, round-bottom flask equipped with a stir bar and flushed with nitrogen, the substituted aryl-methylketone (5.0 mmol) and selenium dioxide (SeO_2, 0.835 g, 7.5 mmol, 1.5 equiv) were added followed by anhydrous pyridine (20 mL). The reaction mixture was heated in an oil bath to 110 °C for 1 h, and then the bath temperature was reduced to 90 °C. The mixture was stirred at this temperature (90 °C) for an additional 4 h, and progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the solution containing precipitated selenium was filtered using a Buckner funnel, and the residue was washed with EA (50 mL). The combined filtrate was treated with 1N HCl (20 mL), the organic layer was separated, and the aqueous layer was extracted with EA (3 × 50 mL). The organic layers were combined and treated with 1N NaOH (50 mL), and the aqueous layer was separated. The organic layer was extracted with water (25 mL) and the combined aqueous layers were acidified using 1N HCl to about pH 1.5. The mixture was extracted with EA (3 × 50 mL), and the combined organic layers were dried (anhydrous Na_2SO_4) and concentrated on a rotary evaporator. The arylglyoxylic acid product was obtained and used directly for the next step.



2h

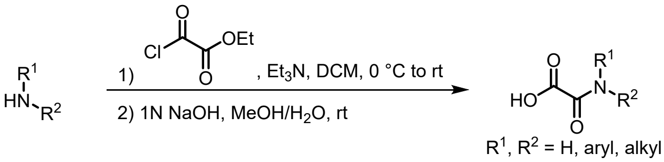
2-(3-Methoxyphenyl)-2-oxoacetic acid (**2h**) was obtained as a white solid (621 mg, 69% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.57 – 7.48 (m, 2H), 7.41 (dd, J = 2.7, 1.5 Hz, 1H), 7.36 – 7.32 (m, 1H), 3.83 (s, 3H). It is a known compound; the spectra data is in agreement with the reported one.[2]



2i

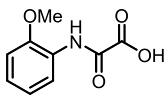
2-Oxo-2-(4-(trifluoromethyl)phenyl)acetic acid (**2i**) was obtained as a white solid (665 mg, 61% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.16 (d, J = 8.1 Hz, 2H), 7.96 (d, J = 7.7 Hz, 2H). It is a known compound; the spectra data is in agreement with the reported one.[3]

Procedure B



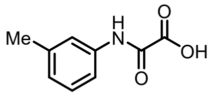
In a dry, single-neck, 25-mL, round-bottom flask equipped with a stir bar and flushed with nitrogen at 0 °C, to a solution of ethyl oxalyl chloride (1.0 g, 7.5 mmol, 1.5 equiv) in DCM (15 mL) was added a mixture of amino substrate (5.0 mmol) and Et_3N (0.76 g, 7.5 mmol, 1.5 equiv) in DCM (5 mL). The reaction mixture was stirred at room temperature for 5 h, and progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the reaction was quenched by saturated aqueous $NaHCO_3$ at 0 °C and then was extracted with DCM (3 × 50 mL). The combined organic layers were dried (anhydrous Na_2SO_4) and concentrated on a rotary evaporator. The crude product was used directly for the next step.

The crude product was dissolved in MeOH/H_2O (20 mL, v/v = 1:1), followed by addition of aqueous 1N NaOH. The resulting mixture was stirred at room temperature for an additional 6 h and progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the reaction was poured into H_2O (20 mL) and then extracted with EA (3 × 30 mL). The aqueous layer was acidified using 1N HCl to about pH 1.5. The mixture was extracted with EA (3 × 30 mL), and the combined organic layers were dried (anhydrous Na_2SO_4) and concentrated on a rotary evaporator. The arylglyoxylic acid product was obtained and used directly for the next step.



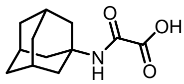
4c

2-((2-Methoxyphenyl)amino)-2-oxoacetic acid (**4c**) was obtained as a white solid (741 mg, 76% yield over two steps); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.62 (s, 1H), 8.07 (dt, J = 7.9, 1.2 Hz, 1H), 7.22 – 7.07 (m, 2H), 6.98 (td, J = 7.6, 1.6 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 161.8, 155.6, 149.1, 125.7, 125.4, 120.5, 120.1, 111.2, 55.9. It is a known compound; the spectra data is in agreement with the reported one.[4]



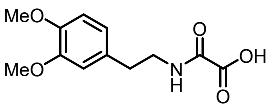
4d

2-Oxo-2-(*m*-tolylamino)acetic acid (**4d**) was obtained as a yellow solid (653 mg, 73% yield over two steps); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.58 (s, 1H), 7.59 (d, J = 2.0 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 6.95 (d, J = 7.5 Hz, 1H), 2.29 (s, 3H). It is a known compound; the spectra data is in agreement with the reported one.[4]



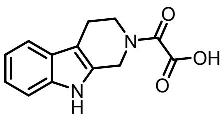
4j

2-(((3*s*,5*s*,7*s*)-Adamantan-1-yl)amino)-2-oxoacetic acid (**4j**) was obtained as a yellow solid (792 mg, 71% yield over two steps); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.86 (s, 1H), 2.05 – 1.99 (m, 3H), 1.95 (d, J = 2.9 Hz, 6H), 1.62 (t, J = 3.0 Hz, 6H). HRMS (ESI) calcd. for $C_{12}H_{18}NO_3^+$ [M + H$^+$] 224.1208, found 224.1217.



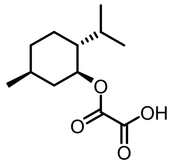
4k

2-((3,4-Dimethoxyphenethyl)amino)-2-oxoacetic acid (**4k**) was obtained as a white solid (873 mg, 69% yield over two steps); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.70 (t, J = 6.0 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.78 (d, J = 2.0 Hz, 1H), 6.69 (dd, J = 8.2, 2.0 Hz, 1H), 3.72 (d, J = 5.7 Hz, 6H), 3.40 – 3.29 (m, 2H), 2.71 (t, J = 7.3 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.8, 148.6, 147.2, 131.5, 120.4, 112.5, 111.9, 55.9, 55.3, 40.3, 34.1. HRMS (ESI) calcd. for $C_{12}H_{16}NO_5^+$ [M + H$^+$] 254.0950, found 254.0968.



4l

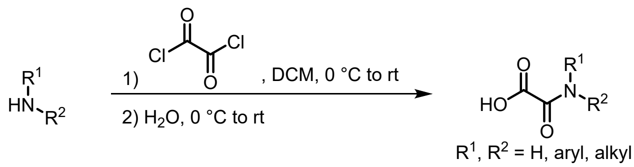
2-Oxo-2-(1,3,4,9-tetrahydro-2*H*-pyrido[3,4-b]indol-2-yl)acetic acid (**4l**) was obtained as a yellow solid (952 mg, 78% yield over two steps); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.88 (s, 1H), 7.41 (dd, J = 7.8, 4.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.15 – 7.04 (m, 1H), 6.98 (td, J = 7.5, 2.3 Hz, 1H), 4.68 (m, 2H), 3.79 (m, 2H), 2.76 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.9, 164.8, 162.4, 161.9, 136.0, 136.0, 129.69, 129.6, 126.4, 126.4, 121.2, 121.1, 118.7, 118.7, 117.7, 117.6, 111.2, 111.2, 106.9, 106.3, 44.0, 43.5, 38.9, 21.5, 20.3. HRMS (ESI) calcd. for $C_{13}H_{13}N_2O_3^+$ [M + H^+] 245.0848, found 245.0845.



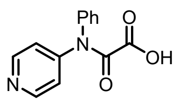
4o

2-(((1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl)oxy)-2-oxoacetic acid (**4o**) was obtained as a white solid (866 mg, 76% yield over two steps); ^{1}H NMR (600 MHz, DMSO-d_6) δ 4.71 (td, *J* = 10.9, 4.4 Hz, 1H), 1.91 (dt, *J* = 11.8, 4.2 Hz, 1H), 1.80 (m, 1H), 1.65 (dt, *J* = 13.6, 3.3 Hz, 2H), 1.55 – 1.41 (m, 2H), 1.06 (m, 2H), 0.87 (dd, *J* = 14.6, 6.7 Hz, 7H), 0.73 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 159.7, 159.0, 75.9, 46.2, 33.5, 30.8, 25.9, 23.1, 21.7, 20.3, 16.2. HRMS (ESI) calcd. for $C_{12}H_{21}O_4^+$ [M + H^+] 229.1362, found 229.1378.

Procedure C

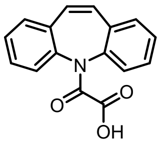


In a dry, single-neck, 25-mL, round-bottom flask equipped with a stir bar and flushed with nitrogen at 0 °C, to a solution of oxalyl chloride (0.95 g, 7.5 mmol, 1.5 equiv) in DCM (15 mL) was added a solution of amino substrate (5.0 mmol) in DCM (5 mL). The reaction mixture was stirred at room temperature for 2 h, and progress of the reaction was monitored by TLC. After completion of the reaction, as determined by TLC, the reaction was quenched by saturated H_2O (1 mL) at 0 °C. The mixture was then filtered and further washed with ice water, air dried overnight to give the desired compound.



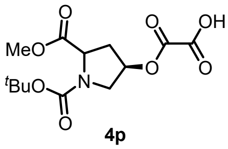
4i

2-Oxo-2-(phenyl(pyridin-4-yl)amino)acetic acid (**4i**) was obtained as a yellow solid (799 mg, 66% yield over two steps); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.83 – 8.79 (m, 2H), 7.77 – 7.72 (m, 2H), 7.62 – 7.57 (m, 3H), 7.55 (dd, *J* = 8.0, 1.9 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 163.2, 162.0, 153.7, 143.1, 136.8, 130.4, 130.3, 129.5, 118.9. HRMS (ESI) calcd. for $C_{13}H_{11}N_2O_3^+$ [M + H$^+$] 243.0691, found 243.0709.



4m

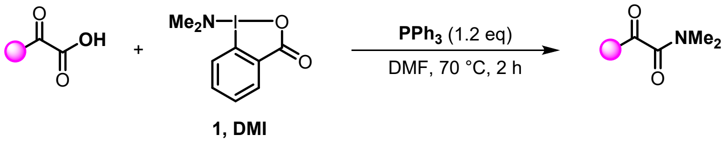
2-(5*H*-Dibenzo[*b*,*f*]azepin-5-yl)-2-oxoacetic acid (**4m**) was obtained as a white solid (1.02 g, 77% yield over two steps); ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.50 (m, 6H), 7.45 – 7.39 (m, 2H), 7.06 (s, 2H). HRMS (ESI) calcd. for $C_{16}H_{12}NO_3^+$ [M + H$^+$] 266.0739, found 266.0751.



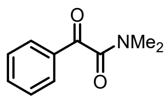
4p

2-(((3*R*)-1-(*tert*-Butoxycarbonyl)-5-(methoxycarbonyl)pyrrolidin-3-yl)oxy)-2-oxoacetic acid (**4p**) was obtained as a white solid (919 mg, 58% yield over two steps); ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 5.32 (dt, *J* = 7.0, 2.4 Hz, 1H), 4.32 – 4.21 (m, 1H), 3.67 (d, *J* = 12.4 Hz, 3H), 3.53 (dq, *J* = 12.4, 3.3, 2.5 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.22 (m, 1H), 1.37 (d, *J* = 32.7 Hz, 9H), 1.10 (dd, *J* = 13.1, 6.2 Hz, 1H). ^{13}C NMR (151 MHz, DMSO-*d*$_6$) δ 172.6, 172.1, 158.8, 158.7, 153.4, 152.7, 79.7, 79.6, 74.6, 74.0, 64.9, 57.3, 57.0, 52.0, 52.0, 51.6, 51.4, 35.4, 34.5, 27.9, 27.8, 27.8, 15.1. HRMS (ESI) calcd. for $C_{13}H_{20}NO_8^+$ [M + H$^+$] 318.1111, found 318.1156.

III. General Procedure for Dimethylamination of Glyoxylic Acids

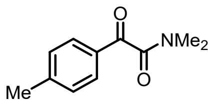


Glyoxylic acids (0.4 mmol), **DMI** (140 mg, 0.48 mmol, 1.2 equiv) and PPh_3 (126 mg, 0.48 mmol, 1.2 equiv) were placed in a 10 ml two-neck rounded bottom flask, and DMF (2.0 mL) was added. The reaction flask was placed in an oil bath and heated up to 70 °C. After substrate was fully consumed, the reaction was quenched with H_2O (10 mL) and extracted with EA (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the corresponding products.



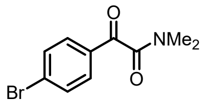
3a

N,*N*-Dimethyl-2-oxo-2-phenylacetamide (**3a**) was isolated by column chromatography (PE/EA = 4:1) as a yellow oil (58 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.86 (m, 2H), 7.63 – 7.57 (m, 1H), 7.50 – 7.44 (m, 2H), 3.07 (s, 3H), 2.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 166.9, 134.6, 132.9, 129.5, 128.9, 36.9, 33.8. It is a known compound; the spectra data is in agreement with the reported one.[5]



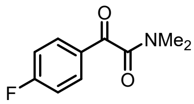
3b

N,*N*-Dimethyl-2-oxo-2-(*p*-tolyl)acetamide (**3b**) was isolated by column chromatography (PE/EA = 4:1) as a yellow oil (63 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.31 – 7.28 (m, 2H), 3.10 (s, 3H), 2.94 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.5, 167.2, 145.9, 130.7, 129.8, 37.0, 33.9, 21.9. It is a known compound; the spectra data is in agreement with the reported one.[6]



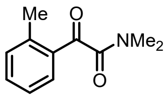
3c

2-(4-Bromophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3c**) was isolated by column chromatography (PE/EA = 3:1) as a yellow solid (72 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 3.10 (s, 3H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 166.4, 132.4, 131.9, 131.0, 130.1, 37.0, 34.1. It is a known compound; the spectra data is in agreement with the reported one.[5]



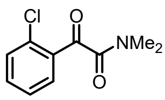
3d

2-(4-Fluorophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3d**) was isolated by column chromatography (PE/EA = 3:1) as a yellow oil (58 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.90 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H), 3.10 (s, 3H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.0, 167.5, 166.6, 165.8, 132.5, 132.4, 129.7, 116.4, 116.2, 37.0, 34.0. It is a known compound; the spectra data is in agreement with the reported one.[5]



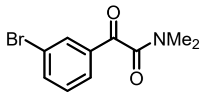
3e

N,*N*-Dimethyl-2-oxo-2-(*o*-tolyl)acetamide (**3e**) was isolated by column chromatography (PE/EA = 4:1) as a yellow oil (60 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 1H), 7.46 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 2H), 3.10 (s, 3H), 2.97 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 167.8, 141.4, 133.6, 132.6, 132.5, 131.6, 126.1, 37.0, 34.0, 21.6. It is a known compound; the spectra data is in agreement with the reported one.[6]



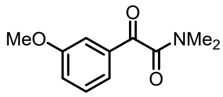
3f

2-(2-Chlorophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3f**) was isolated by column chromatography (PE/EA = 3:1) as a yellow oil (63 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.36 (dd, *J* = 3.7, 0.8 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.07 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 166.9, 134.3, 133.7, 133.4, 132.2, 130.7, 127.2, 37.0, 34.5. It is a known compound; the spectra data is in agreement with the reported one.[5]



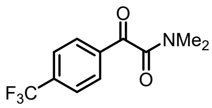
3g

2-(3-Bromophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3g**) was isolated by column chromatography (PE/EA = 3:1) as a yellow solid (76 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 1.8 Hz, 1H), 7.87 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.75 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 3.11 (s, 3H), 2.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 166.2, 137.5, 134.9, 132.4, 130.5, 128.3, 123.2, 37.0, 34.1. It is a known compound; the spectra data is in agreement with the reported one.[5]



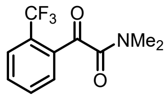
3h

2-(3-Methoxyphenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3h**) was isolated by column chromatography (PE/EA = 2:1) as a white solid (58 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.39 (t, *J* = 8.1 Hz, 1H), 7.16 (m, 1H), 3.84 (s, 3H), 3.09 (s, 3H), 2.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.6, 167.0, 160.1, 134.4, 130.0, 122.7, 121.5, 112.8, 55.5, 37.0, 33.9. It is a known compound; the spectra data is in agreement with the reported one.[7]



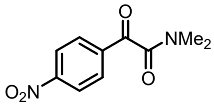
3i

N,*N*-Dimethyl-2-oxo-2-(4-(trifluoromethyl)phenyl)acetamide (**3i**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (89 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.79 – 7.71 (m, 2H), 3.13 (d, *J* = 2.2 Hz, 3H), 2.97 (d, *J* = 2.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 166.2, 136.1, 136.0, 135.9, 135.7, 130.1, 126.1, 126.1, 126.1, 126.1, 124.4, 37.1, 34.3. It is a known compound; the spectra data is in agreement with the reported one.[6]



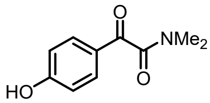
3j

N,*N*-Dimethyl-2-oxo-2-(4-(trifluoromethyl)phenyl)acetamide (**3j**) was isolated by column chromatography (PE/EA = 3:1) as a yellow oil (82 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.70 – 7.60 (m, 2H), 3.08 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 165.6, 134.4, 132.4, 131.9, 131.5, 127.3, 127.2, 127.1, 127.1, 124.7, 121.9, 37.0, 34.7. It is a known compound; the spectra data is in agreement with the reported one.[6]



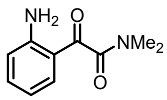
3k

N,*N*-Dimethyl-2-(4-nitrophenyl)-2-oxoacetamide (**3k**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (80 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.8 Hz, 2H), 3.15 (s, 3H), 3.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 165.6, 151.1, 137.6, 130.8, 124.1, 77.2, 37.1, 34.3. It is a known compound; the spectra data is in agreement with the reported one.[5]



3l

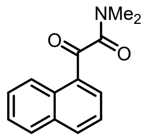
2-(4-Hydroxyphenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3l**) was isolated by column chromatography (PE/EA = 1:2) as a yellow oil (39 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 8.6 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.3, 161.8, 132.6, 130.1, 116.2, 29.8, 1.2. HRMS (ESI) calcd. for $C_{10}H_{12}NO_3^+$ [M + H$^+$] 194.0739, found 194.0744.



3m

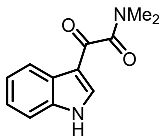
2-(2-Aminophenyl)-*N*,*N*-dimethyl-2-oxoacetamide (**3m**) was isolated by column chromatography (PE/EA

= 1:3) as a brown oil (53 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.30 (m, 1H), 6.71 – 6.61 (m, 2H), 3.10 (s, 3H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 167.4, 151.7, 136.0, 133.3, 117.2, 116.4, 114.3, 37.2, 34.0, 1.1. It is a known compound; the spectra data is in agreement with the reported one.[8]



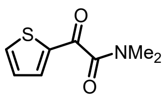
3n

N,*N*-Dimethyl-2-(naphthalen-1-yl)-2-oxoacetamide (**3n**) was isolated by column chromatography (PE/EA = 3:1) as a yellow oil (74 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 – 9.22 (m, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.99 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.76 – 7.68 (m, 1H), 7.62 – 7.58 (m, 1H), 7.54 (dd, *J* = 8.1, 7.2 Hz, 1H), 3.16 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 167.6, 135.9, 134.3, 134.1, 131.0, 129.3, 128.7, 128.5, 127.0, 125.8, 124.5, 37.2, 34.1. It is a known compound; the spectra data is in agreement with the reported one.[5]



3o

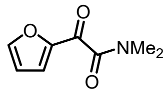
2-(1*H*-Indol-3-yl)-*N*,*N*-dimethyl-2-oxoacetamide (**3o**) was isolated by column chromatography (PE/EA = 1:1) as a yellow oil (66 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 – 10.12 (m, 1H), 8.30 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 3.1 Hz, 1H), 7.33 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.29 (td, *J* = 7.6, 1.1 Hz, 1H), 7.25 – 7.22 (m, 1H), 3.07 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.2, 168.2, 136.9, 135.9, 125.4, 124.3, 123.3, 122.0, 114.4, 112.3, 37.7, 34.6. It is a known compound; the spectra data is in agreement with the reported one.[9]



3p

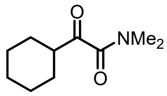
N,*N*-Dimethyl-2-oxo-2-(thiophen-2-yl)acetamide (**3p**) was isolated by column chromatography (PE/EA = 2:1) as a brown oil (66 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.78

(dd, *J* = 4.9, 1.2 Hz, 1H), 7.17 (dd, *J* = 4.9, 3.9 Hz, 1H), 3.09 (s, 3H), 3.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 165.8, 140.3, 136.4, 136.1, 128.6, 77.2, 37.3, 34.5. It is a known compound; the spectra data is in agreement with the reported one.[6]



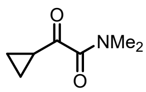
3q

2-(Furan-2-yl)-*N*,*N*-dimethyl-2-oxoacetamide (**3q**) was isolated by column chromatography (PE/EA = 1:1) as a yellow oil (52 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.36 (dd, *J* = 3.7, 0.8 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H), 3.07 (s, 3H), 3.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.5, 165.4, 150.2, 148.6, 122.2, 112.8, 37.2, 34.5. It is a known compound; the spectra data is in agreement with the reported one.[5]



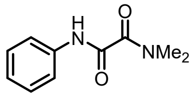
3r

2-Cyclohexyl-*N*,*N*-dimethyl-2-oxoacetamide (**3r**) was isolated by column chromatography (PE/EA = 6:1) as a yellow oil (49 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (d, *J* = 12.7 Hz, 7H), 1.93 – 1.84 (m, 2H), 1.80 – 1.70 (m, 2H), 1.68 – 1.60 (m, 1H), 1.32 – 1.12 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.8, 167.4, 46.7, 36.8, 34.2, 27.0, 25.7, 25.2. HRMS (ESI) calcd. for $C_{10}H_{18}NO_2^+$ [M + H$^+$] 184.1259, found 184.1257.



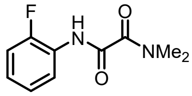
3s

2-Cyclopropyl-*N*,*N*-dimethyl-2-oxoacetamide (**3s**) was isolated by column chromatography (PE/EA = 6:1) as a yellow oil (49 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00 (d, *J* = 1.8 Hz, 6H), 2.35 (tt, *J* = 7.9, 4.6 Hz, 1H), 1.25 – 1.21 (m, 2H), 1.13 – 1.08 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 167.0, 37.1, 34.5, 19.5, 12.6. It is a known compound; the spectra data is in agreement with the reported one.[10]



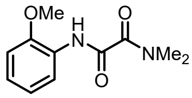
5a

N,*N*-Dimethyl-*N*'-phenyloxalamide (**5a**) was isolated by column chromatography (PE/EA = 1:1) as a yellow oil (48 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 3.52 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 158.4, 136.9, 129.1, 125.0, 119.8, 38.8, 37.9. It is a known compound; the spectra data is in agreement with the reported one.[11]



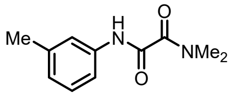
5b

N-(2-Fluorophenyl)-*N'*,*N'*-dimethyloxalamide (**5b**) was isolated by column chromatography (PE/EA = 1:1) as a yellow oil (51 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.29 (td, *J* = 7.5, 1.4 Hz, 1H), 7.12 (m, 3H), 3.49 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 158.5, 154.0, 151.6, 125.4, 125.3, 125.2, 124.5, 124.4, 121.3, 115.2, 115.0, 77.2, 38.7, 37.7. HRMS (ESI) calcd. for $C_{10}H_{12}FN_2O_2^+$ [M + H$^+$] 211.0805, found 211.0809.



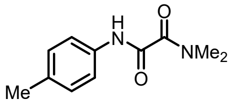
5c

N-(2-Methoxyphenyl)-*N'*,*N'*-dimethyloxalamide (**5c**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (56 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.33 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.07 (td, *J* = 7.8, 1.6 Hz, 1H), 6.94 (td, *J* = 7.8, 1.3 Hz, 1H), 6.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 3.85 (s, 3H), 3.45 (s, 3H), 3.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 1161.9, 158.5, 148.7, 126.6, 124.8, 120.9, 119.6, 110.2, 55.7, 38.7, 37.5. HRMS (ESI) calcd. for $C_{11}H_{15}N_2O_3^+$ [M + H$^+$] 223.1004, found 223.1009.



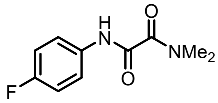
5d

N,*N*-Dimethyl-*N'*-(m-tolyl)oxalamide (**5d**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (58 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 7.48 – 7.44 (m, 1H), 7.41 – 7.34 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.96 (m, 1H), 3.48 (s, 3H), 3.07 (s, 3H), 2.34 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 158.6, 139.1, 136.9, 129.0, 125.9, 120.6, 117.1, 77.4, 38.9, 37.8, 21.6. HRMS (ESI) calcd. for $C_{11}H_{15}N_2O_2^+$ [M + H$^+$] 207.1055, found 207.1061.



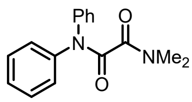
5e

N,*N*-Dimethyl-*N'*-(*p*-tolyl)oxalamide (**5e**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (49 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 7.52 – 7.45 (m, 2H), 7.14 (d, *J* = 8.1 Hz, 2H), 3.48 (s, 3H), 3.06 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 158.4, 134.6, 134.3, 129.5, 119.8, 38.7, 37.6, 20.9. It is a known compound; the spectra data is in agreement with the reported one.[11]



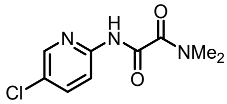
5f

N-(4-Fluorophenyl)-*N'*,*N'*-dimethyloxalamide (**5f**) was isolated by column chromatography (PE/EA = 1:1) as a brown oil (49 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s, 1H), 7.60 – 7.53 (m, 2H), 7.09 – 7.00 (m, 2H), 3.51 (s, 3H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 160.9, 158.3, 132.9, 132.9, 121.6, 121.5, 115.9, 115.7, 77.2, 38.8, 37.9. HRMS (ESI) calcd. for $C_{10}H_{12}FN_2O_2^+$ [M + H$^+$] 211.0805, found 211.0810.



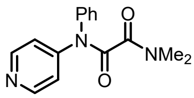
5g

N,*N*-Dimethyl-*N'*,*N'*-diphenyloxalamide (**5g**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (81 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (m, 6H), 7.32 – 7.22 (m, 4H), 3.09 (s, 3H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.5, 129.1, 128.4, 127.8, 126.8, 125.9, 37.2, 33.5. HRMS (ESI) calcd. for $C_{16}H_{17}N_2O_2^+$ [M + H$^+$] 269.1212, found 269.1213.



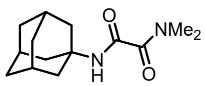
5h

N-(5-Chloropyridin-2-yl)-*N'*,*N'*-dimethyloxalamide (**5h**) was isolated by column chromatography (PE/EA = 1:1) as a yellow oil (75 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.79 (s, 1H), 8.29 (d, *J* = 2.6 Hz, 1H), 8.17 (d, *J* = 8.9 Hz, 1H), 7.68 (dd, *J* = 8.8, 2.6 Hz, 1H), 3.44 (s, 3H), 3.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 159.1, 148.8, 147.1, 138.0, 127.6, 114.6, 38.7, 37.7. HRMS (ESI) calcd. for $C_9H_{11}ClN_3O_2^+$ [M + H$^+$] 228.0462, found 228.0465.



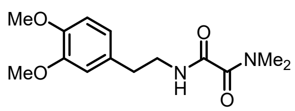
5i

N,*N*-Dimethyl-*N'*-phenyl-*N'*-(pyridin-4-yl)oxalamide (**5i**) was isolated by column chromatography (PE/EA = 1:2) as a yellow oil (77 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 2H), 7.51 – 7.42 (m, 3H), 7.30 (dt, *J* = 8.4, 2.8 Hz, 4H), 3.10 – 3.02 (m, 3H), 2.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 163.1, 150.5, 148.3, 129.9, 37.2, 33.6. HRMS (ESI) calcd. for $C_{15}H_{16}N_3O_2^+$ [M + H$^+$] 270.1164, found 270.1168.



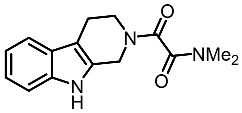
5j

N-((3*s*,5*s*,7*s*)-Adamantan-1-yl)-*N'*,*N'*-dimethyloxalamide (**5j**) was isolated by column chromatography (PE/EA = 4:1) as a yellow oil (80 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (s, 1H), 3.35 (d, *J* = 1.7 Hz, 3H), 2.96 (s, 3H), 2.10 – 2.04 (m, 3H), 2.00 (d, *J* = 3.1 Hz, 6H), 1.66 (t, *J* = 3.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 160.2, 52.0, 41.0, 38.5, 37.1, 36.2, 29.2. HRMS (ESI) calcd. for $C_{14}H_{23}N_2O_2^+$ [M + H$^+$] 251.1681, found 251.1683.



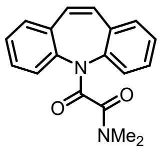
5k

N-(3,4-Dimethoxyphenethyl)-*N'*,*N'*-dimethyloxalamide (**5k**) was isolated by column chromatography (PE/EA = 1:2) as a white oil (90 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.70 (m, 2H), 3.86 (d, *J* = 11.3 Hz, 6H), 3.52 (q, *J* = 6.9 Hz, 2H), 3.37 (s, 3H), 2.99 (s, 3H), 2.79 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.0, 161.1, 149.0, 147.7, 130.9, 120.6, 111.8, 111.4, 55.9, 55.8, 40.6, 38.3, 37.0, 35.0, 29.7. HRMS (ESI) calcd. for $C_{14}H_{21}N_2O_4^+$ [M + H$^+$] 281.1423, found 281.1413.



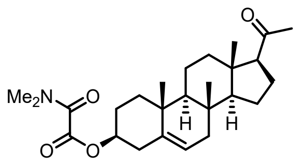
5l

N,*N*-Dimethyl-2-oxo-2-(1,3,4,9-tetrahydro-2*H*-pyrido[3,4-b]indol-2-yl)acetamide (**5l**) was isolated by column chromatography (PE/EA = 1:1) as a brown oil (93 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.68 (m, 1H), 7.50 – 7.42 (m, 2H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.11 (m, 1H), 4.85 (t, *J* = 1.5 Hz, 2H), 4.60 (q, *J* = 1.5 Hz, 1H), 3.99 – 3.95 (m, 1H), 3.79 – 3.73 (m, 2H), 3.06 (s, 3H), 3.03 (s, 3H), 3.02 (s, 1H), 2.96 (d, *J* = 1.0 Hz, 2H), 2.89 – 2.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 1164.8, 164.6, 162.6, 136.3, 132.1, 132.1, 132.0, 128.6, 128.5, 126.7, 122.2, 122.1, 119.8, 118.1, 118.0, 111.1, 107.9, 44.5, 44.1, 39.6, 39.5, 37.3, 36.5, 33.9, 33.8, 29.7, 22.0, 20.8. HRMS (ESI) calcd. for $C_{15}H_{18}N_3O_2^+$ [M + H$^+$] 272.1321, found 272.1333.



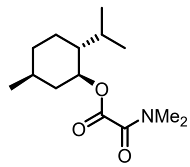
5m

N,*N*-Dimethyl-2-oxo-2-(1,3,4,9-tetrahydro-2*H*-pyrido[3,4-b]indol-2-yl)acetamide (**5m**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (85 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.56 (m, 1H), 7.53 – 7.47 (m, 2H), 7.43 – 7.32 (m, 5H), 7.01 – 6.91 (m, 2H), 2.81 (s, 3H), 2.65 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.4, 163.9, 137.9, 137.6, 134.8, 133.5, 131.2, 129.7, 129.7, 129.6, 129.4, 129.0, 128.5, 128.2, 128.1, 37.2, 33.3. HRMS (ESI) calcd. for $C_{18}H_{17}N_2O_2^+$ [M + H$^+$] 293.1212, found 293.1243.



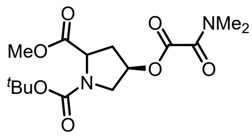
5n

(3*S*,8*S*,9*S*,10*R*,13*S*,14*S*,17*S*)-17-Acetyl-8,10,13-trimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-(dimethylamino)-2-oxoacetate (**5n**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (111 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.44 – 5.40 (m, 1H), 4.86 – 4.76 (m, 1H), 3.02 (s, 3H), 2.98 (d, *J* = 1.6 Hz, 3H), 2.54 (t, *J* = 9.0 Hz, 1H), 2.47 – 2.41 (m, 2H), 2.22 – 2.15 (m, 1H), 2.13 (d, *J* = 1.6 Hz, 3H), 2.08 – 1.96 (m, 3H), 1.92 (dd, *J* = 13.5, 3.6 Hz, 1H), 1.76 – 1.65 (m, 3H), 1.62 (td, *J* = 11.5, 10.4, 5.5 Hz, 2H), 1.53 – 1.44 (m, 3H), 1.28 – 1.20 (m, 2H), 1.20 – 1.13 (m, 2H), 1.03 (s, 3H), 0.64 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 139.0, 123.0, 75.9, 63.6, 56.8, 49.8, 43.9, 38.7, 37.7, 37.0, 36.9, 36.6, 34.0, 31.8, 31.7, 31.5, 27.4, 24.4, 22.8, 21.0, 19.2, 13.2. HRMS (ESI) calcd. for $C_{26}H_{40}NO_4^+$ [M + H$^+$] 430.2879, found 430.2885.



5o

(1*S*,2*R*,5*S*)-2-Isopropyl-5-methylcyclohexyl 2-(dimethylamino)-2-oxoacetate (**5o**) was isolated by column chromatography (PE/EA = 4:1) as a yellow oil (93 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (td, *J* = 10.9, 4.4 Hz, 1H), 2.96 (d, *J* = 11.1 Hz, 6H), 2.06 (dd, *J* = 11.5, 4.2 Hz, 1H), 1.93 (m, 1H), 1.74 – 1.64 (m, 2H), 1.55 – 1.41 (m, 2H), 1.15 – 1.00 (m, 2H), 0.89 (dd, *J* = 10.1, 6.8 Hz, 7H), 0.76 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.9, 162.0, 76.3, 46.7, 40.3, 36.9, 33.9, 33.8, 31.4, 25.9, 23.1, 21.8, 20.6, 15.9. HRMS (ESI) calcd. for $C_{14}H_{26}NO_3^+$ [M + H$^+$] 256.1834, found 256.1701.

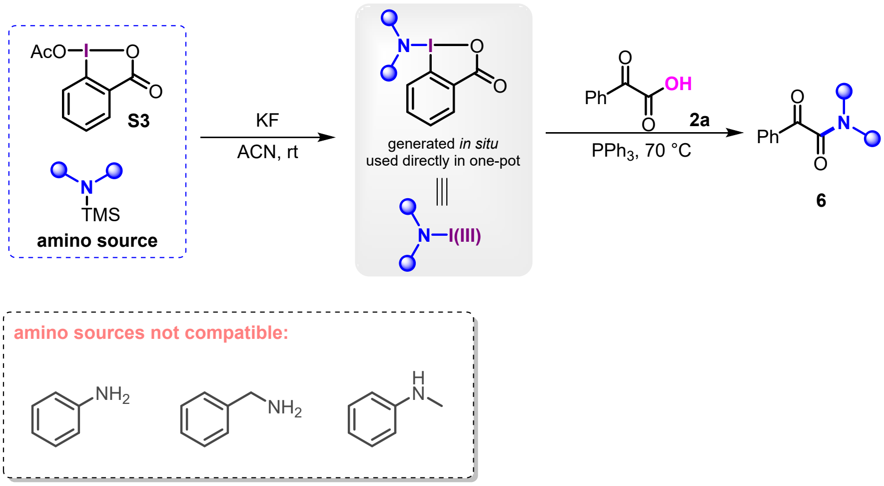


5p

1-(*tert*-Butyl) 2-methyl (4*R*)-4-(2-(dimethylamino)-2-oxoacetoxy)pyrrolidine-1,2-dicarboxylate (**5p**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (116 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.41 (dt, *J* = 34.2, 7.9 Hz, 1H), 3.78 – 3.65 (m, 5H), 2.97 (d, *J* = 5.6 Hz, 6H), 2.55 – 2.40 (m, 1H), 2.26 (m, 1H), 1.41 (d, *J* = 23.6 Hz, 9H). ^{13}C NMR (101 MHz,

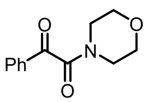
$CDCl_3$) δ 172.8, 172.6, 162.3, 162.2, 160.9, 80.7, 74.5, 73.7, 57.6, 57.3, 52.4, 52.2, 51.8, 51.7, 37.0, 36.9, 36.3, 35.3, 34.1, 29.6, 28.3, 28.2, 28.1. HRMS (ESI) calcd. for $C_{15}H_{25}N_2O_7^+$ [M + H^+] 345.1584, found 345.1576.

IV. General Procedure for Amination in One Pot



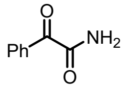
Scheme S1. Introduction of diverse amino functional groups in one-pot protocol.

To a 50 mL two-necked round-bottomed flask equipped with a stirrer bar were added compound **S3** (100 mg, 0.33 mmol, 1.00 equiv), KF (1.9 mg, 0.033 mmol, 0.1 equiv) and ACN (5 mL) under N_2 atmosphere, followed by the careful addition of amino source (0.49 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature for 3 h in the dark. Then benzoylformic acid (0.3 mmol) and PPh_3 (94 mg, 0.36 mmol, 1.2 equiv) were added to the reaction mixture. The reaction flask was placed in an oil bath and heated up to 70 °C. After substrate was fully consumed, the reaction was quenched with H_2O (10 mL) and extracted with EA (15 mL x 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give the corresponding products.



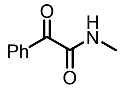
6a

1-Morpholino-2-phenylethane-1,2-dione (**6a**) was isolated by column chromatography (PE/EA = 4:1) as a colorless oil (56 mg, 85% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 2H), 7.64 (td, J = 7.5, 1.4 Hz, 1H), 7.54 – 7.48 (m, 2H), 3.82 – 3.74 (m, 4H), 3.67 – 3.58 (m, 2H), 3.40 – 3.33 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 165.5, 135.0, 133.1, 129.7, 129.2, 66.8, 66.8, 46.3, 41.7. It is a known compound; the spectra data is in agreement with the reported one.[12]



6b

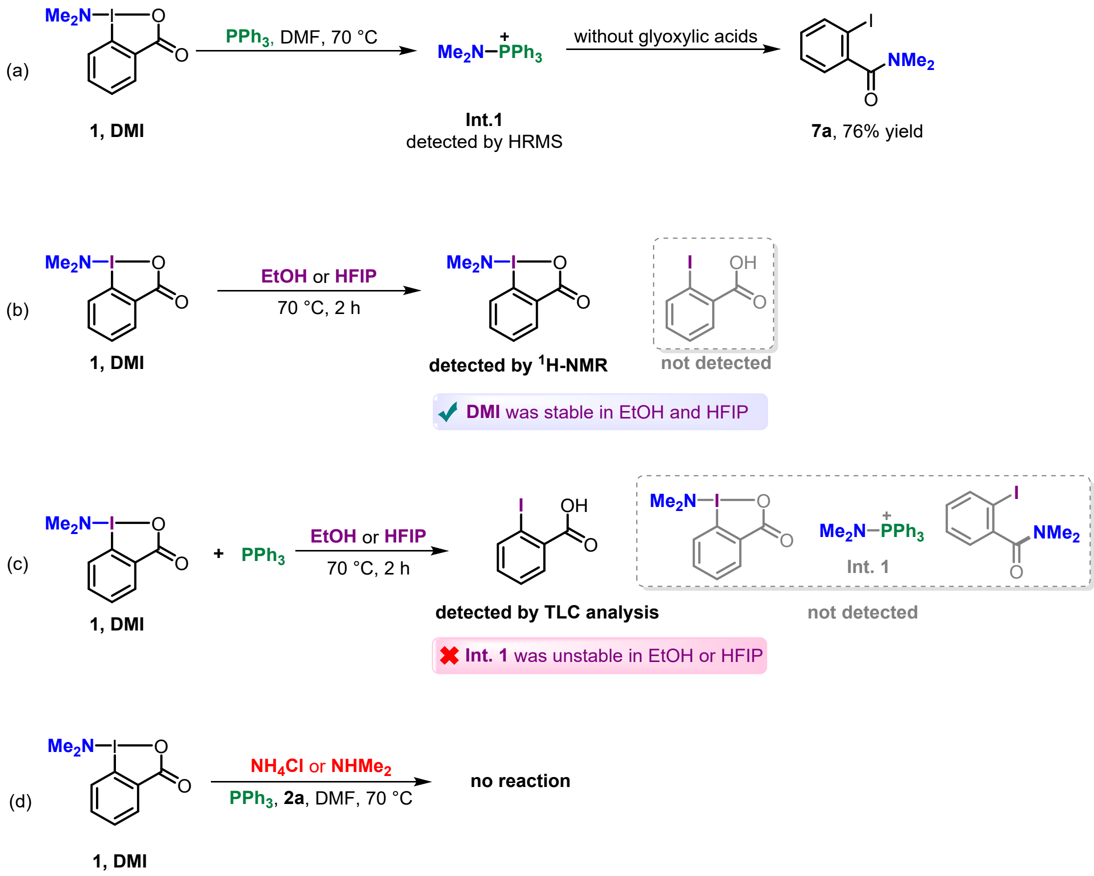
2-Oxo-2-phenylacetamide (**6b**) was isolated by column chromatography (PE/EA = 2:1) as a yellow oil (27 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.67 – 7.61 (m, 1H), 7.49 (dd, *J* = 8.5, 7.2 Hz, 2H), 6.96 (s, 1H), 5.82 (s, 1H). It is a known compound; the spectra data is in agreement with the reported one.[13]



6c

N-Methyl-2-oxo-2-phenylacetamide (**6c**) was isolated by column chromatography (PE/EA = 3:1) as a yellow oil (32 mg, 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.8 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.12 (s, 1H), 2.97 (d, *J* = 5.1 Hz, 3H). It is a known compound; the spectra data is in agreement with the reported one.[14]

V. Mechanistic Studies



Scheme S2. Control experiments

DMI (140 mg, 0.48 mmol, 1.2 equiv) and PPh_3 (126 mg, 0.48 mmol, 1.2 equiv) were placed in a 10 ml two-neck rounded bottom flask, and DMF (2.0 mL) was added. The reaction flask was placed in an oil bath and heated up to 70 °C. After 10 mins, Int.1 was detected by LC-MS analysis and when substrate was fully consumed, the reaction was quenched with H_2O (10 mL) and extracted with EA (20 mL x 3). The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated in vacuo to afford the crude product, which was then purified by silica gel flash chromatography to give product **7a** with 76% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.38 (td, *J* = 7.6, 1.2 Hz, 1H), 7.21 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.06 (td, *J* = 7.7, 1.7 Hz, 1H), 3.13 (s, 3H), 2.84 (s, 3H). It is a known compound; the spectra data is in agreement with the reported one.[15]

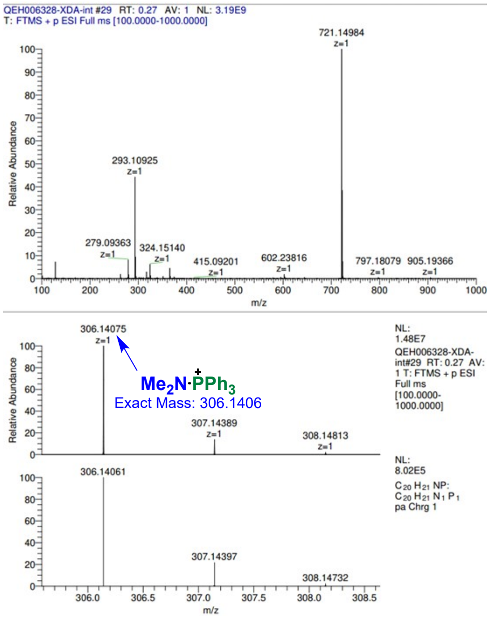


Figure S1 Analysis of reaction by HRMS.

VI. X-Ray Diffraction Data of DMI

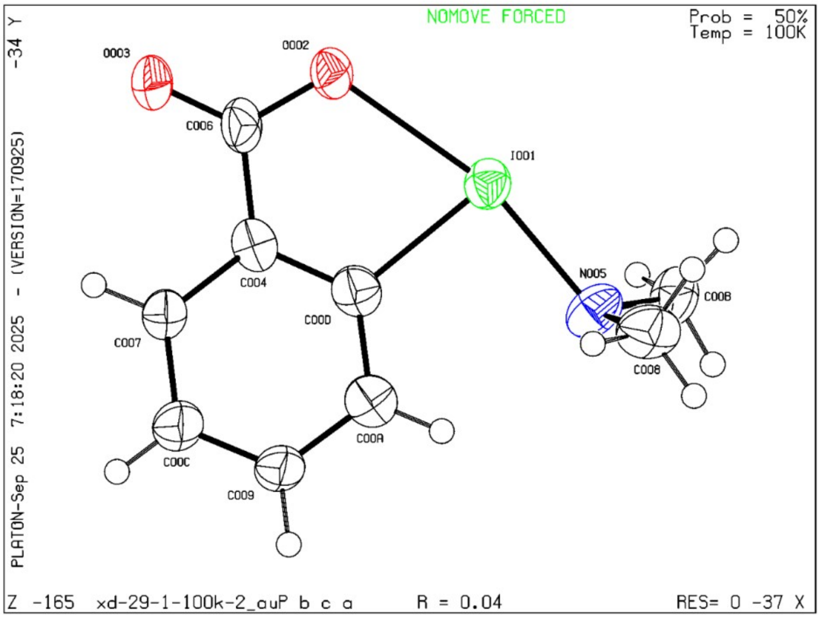


Figure 2 X-ray crystal structure of DMI with 40% ellipsoid probability

Table 1 Crystal data and structure refinement for DMI.

Identification code	**DMI**
Empirical formula	$C_{11}H_{10}NOI$
Formula weight	172.20
Temperature/K	99.98(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	7.9000(8)
b/Å	15.6486(13)
c/Å	15.661(2)
α/°	90
β/°	90
γ/°	90
Volume/Å3	1936.0(4)
Z	8
ρcalcg/cm3	1.182
μ/mm-1	0.608
F(000)	728.0

Crystal size/mm^3	0.1 × 0.04 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	11.3 to 88.512
Index ranges	-3 ≤ h ≤ 7, -14 ≤ k ≤ 14, -13 ≤ l ≤ 9
Reflections collected	1697
Independent reflections	666 [R_{int} = 0.0552, R_{sigma} = 0.0705]
Data/restraints/parameters	666/194/121
Goodness-of-fit on F2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.0713
Final R indexes [all data]	R_1 = 0.0636, wR_2 = 0.0789
Largest diff. peak/hole / e Å-3	0.55/-0.44

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 2491335. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I001	4077.3(12)	3101.3(5)	4308.0(6)	37.7(4)
O002	6396(10)	3168(6)	5262(6)	37(2)
O003	8526(12)	4018(5)	5653(7)	45(3)
C004	6792(18)	4415(8)	4471(10)	29(3)
N005	2386(15)	3302(7)	3328(8)	45(4)
C006	7310(20)	3849(10)	5193(11)	40(4)
C007	7731(18)	5150(8)	4254(10)	33(3)
C008	710(20)	3611(9)	3652(10)	54(5)
C009	5840(20)	5461(8)	3108(10)	41(4)
C00A	4880(19)	4731(9)	3310(10)	39(4)
C00B	2185(19)	2542(9)	2786(9)	46(4)
C00C	7270(20)	5656(9)	3557(10)	43(4)
C00D	5397(19)	4217(9)	3974(11)	40(4)

Table 3 Anisotropic Displacement Parameters ($Å^2$×10^3) for 2491335. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I001	38.9(7)	41.8(6)	32.4(7)	-3.9(6)	-0.6(8)	-4.0(6)
O002	25(6)	45(5)	41(6)	3(5)	5(5)	-7(4)
O003	31(7)	53(6)	52(7)	6(6)	-4(6)	-14(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 2491335. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C004	33(8)	24(6)	32(8)	-16(6)	11(6)	4(5)
N005	46(7)	50(9)	38(9)	-9(6)	-7(6)	12(5)
C006	23(9)	45(8)	52(9)	1(7)	2(7)	-7(6)
C007	26(8)	28(7)	45(9)	-7(6)	0(8)	7(5)
C008	45(9)	52(9)	64(14)	8(9)	5(8)	17(9)
C009	42(9)	29(7)	53(11)	2(7)	-11(8)	7(7)
C00A	35(9)	35(8)	47(10)	-4(6)	7(7)	8(6)
C00B	45(11)	57(9)	35(10)	-10(8)	-2(8)	-7(8)
C00C	38(10)	34(8)	57(10)	0(7)	-8(8)	8(7)
C00D	36(9)	31(8)	52(10)	-2(6)	2(6)	5(6)

Table 4 Bond Lengths for DMI.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I001	O002	2.366(9)	C004	C00D	1.385(18)
I001	N005	2.059(12)	N005	C008	1.495(18)
I001	C00D	2.100(14)	N005	C00B	1.470(15)
O002	C006	1.294(16)	C007	C00C	1.397(17)
O003	C006	1.227(16)	C009	C00A	1.408(18)
C004	C006	1.50(2)	C009	C00C	1.362(19)
C004	C007	1.410(18)	C00A	C00D	1.376(18)

Table 5 Bond Angles for DMI.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N005	I001	O002	165.1(4)	O002	C006	C004	113.3(15)
N005	I001	C00D	90.5(6)	O003	C006	O002	124.5(15)
C00D	I001	O002	74.7(5)	O003	C006	C004	122.1(15)
C006	O002	I001	114.7(10)	C00C	C007	C004	120.8(15)
C007	C004	C006	121.3(15)	C00C	C009	C00A	120.8(15)
C00D	C004	C006	120.8(14)	C00D	C00A	C009	118.9(15)
C00D	C004	C007	117.8(15)	C009	C00C	C007	119.5(15)
C008	N005	I001	111.7(9)	C004	C00D	I001	116.2(12)
C00B	N005	I001	112.2(8)	C00A	C00D	I001	121.8(12)

C00B	N005	C008	111.2(12)	C00A	C00D	C004	122.0(14)

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for 2491335.

Atom	x	y	z	U(eq)
H007	8691.8	5302.25	4585.34	40
H00A	194.72	3167.18	4007.23	81
H00B	-28.79	3740.02	3168.25	81
H00C	882.69	4128.97	3993.95	81
H009	5491.97	5822.45	2653.52	50
H00D	3890.31	4595.17	2992.44	47
H00E	3302.57	2315.55	2636.35	68
H00F	1576.28	2698.96	2263.36	68
H00G	1541.31	2105.96	3095.72	68
H00H	7941.51	6132.71	3397.51	51

Table 7 Atomic Occupancy for 2491335.

Atom	Occupancy
N005	1.01(3)

VII. Reference

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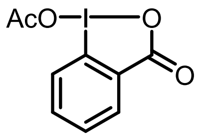
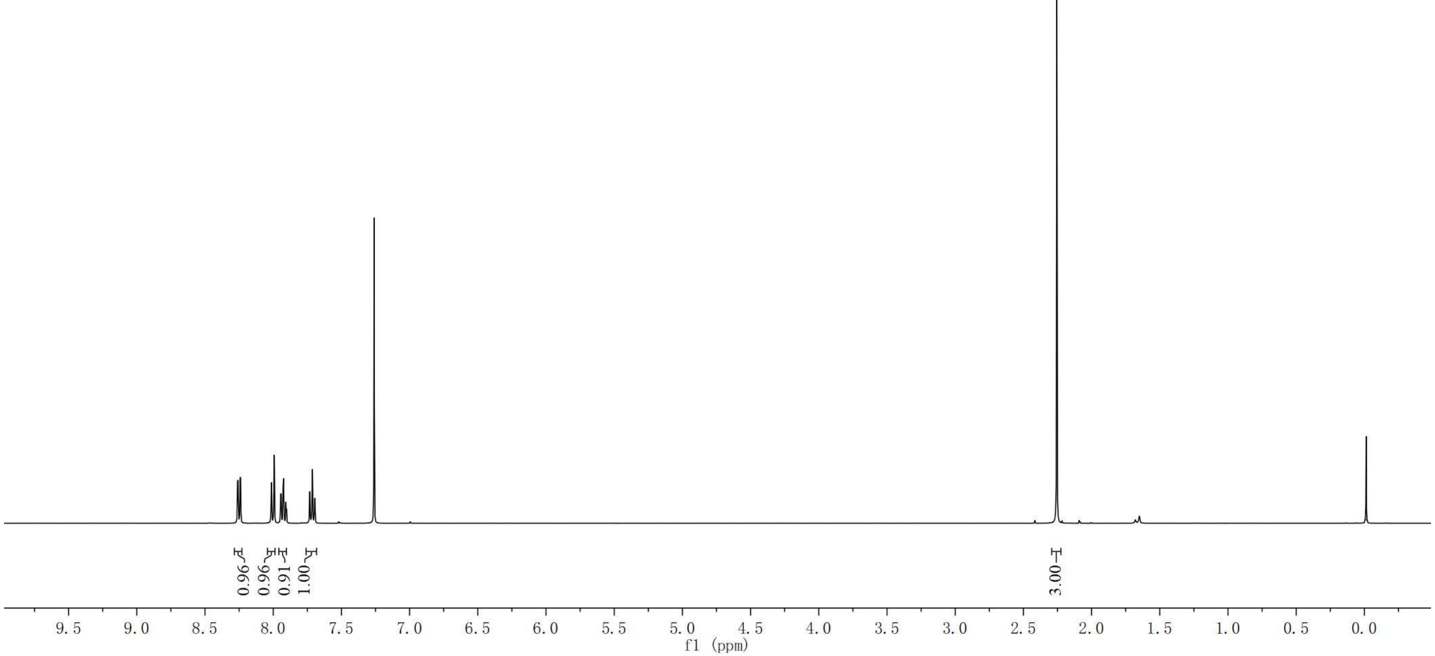
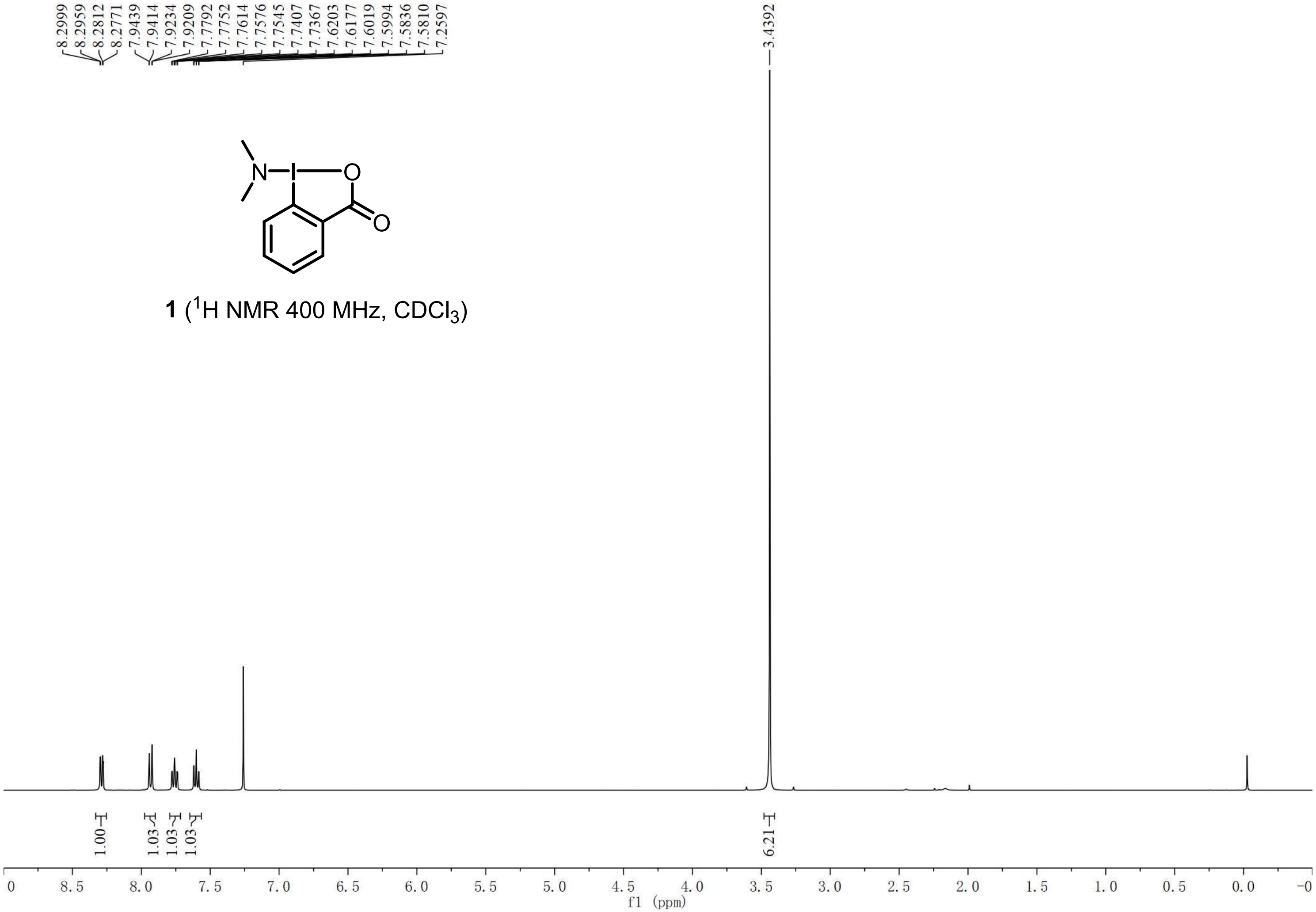
Mechanochemical Conditions. *Org. Lett.* **2023**, *26*, 2800-2805.

V. NMR Spectra of Starting Materials and Products



S3 ([1]H NMR 400 MHz, $CDCl_3$)





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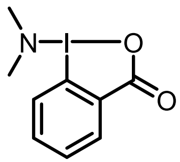

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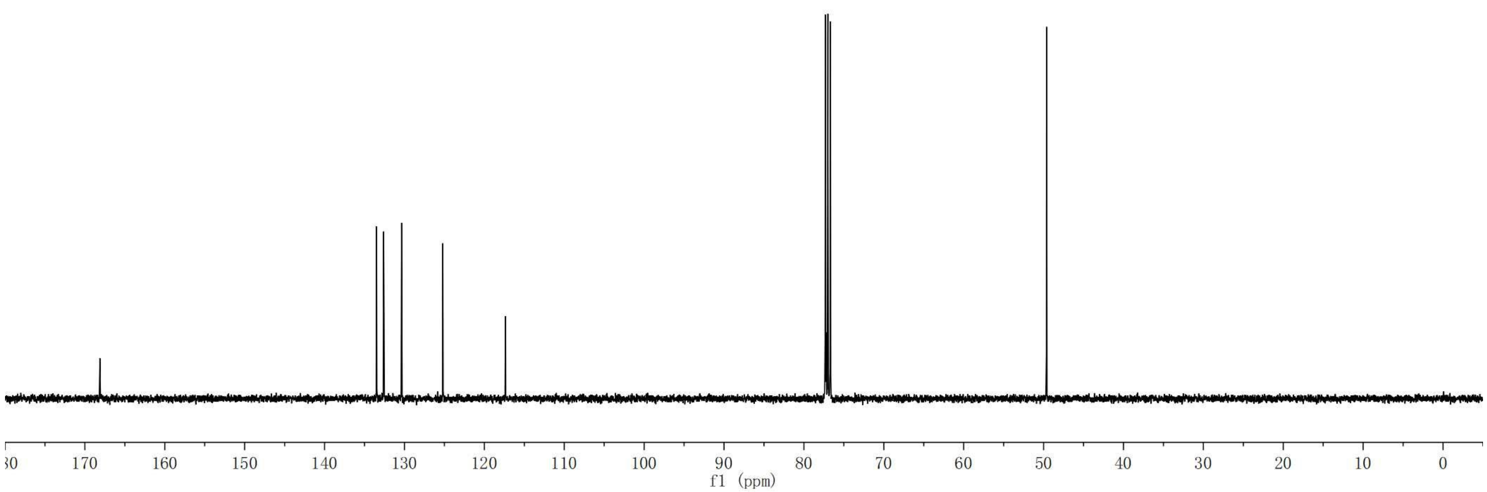

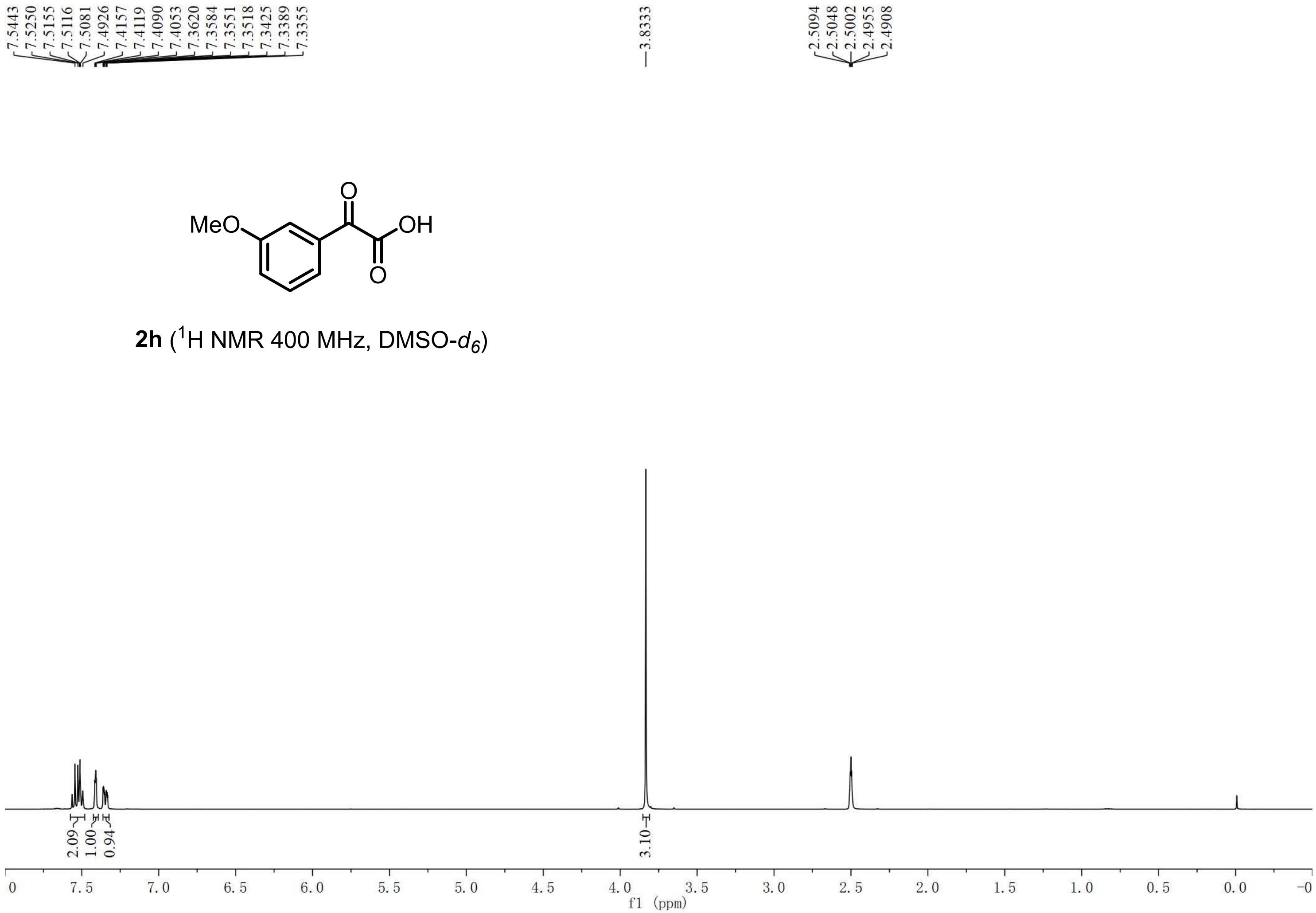

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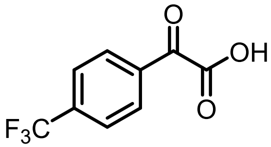

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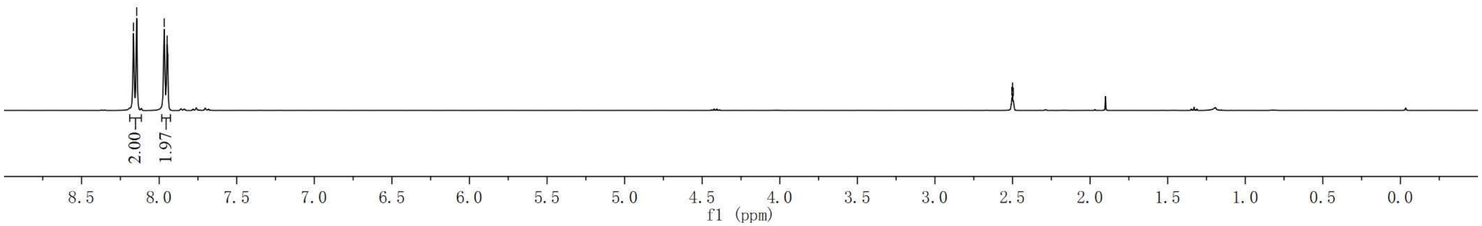

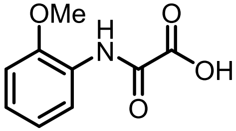

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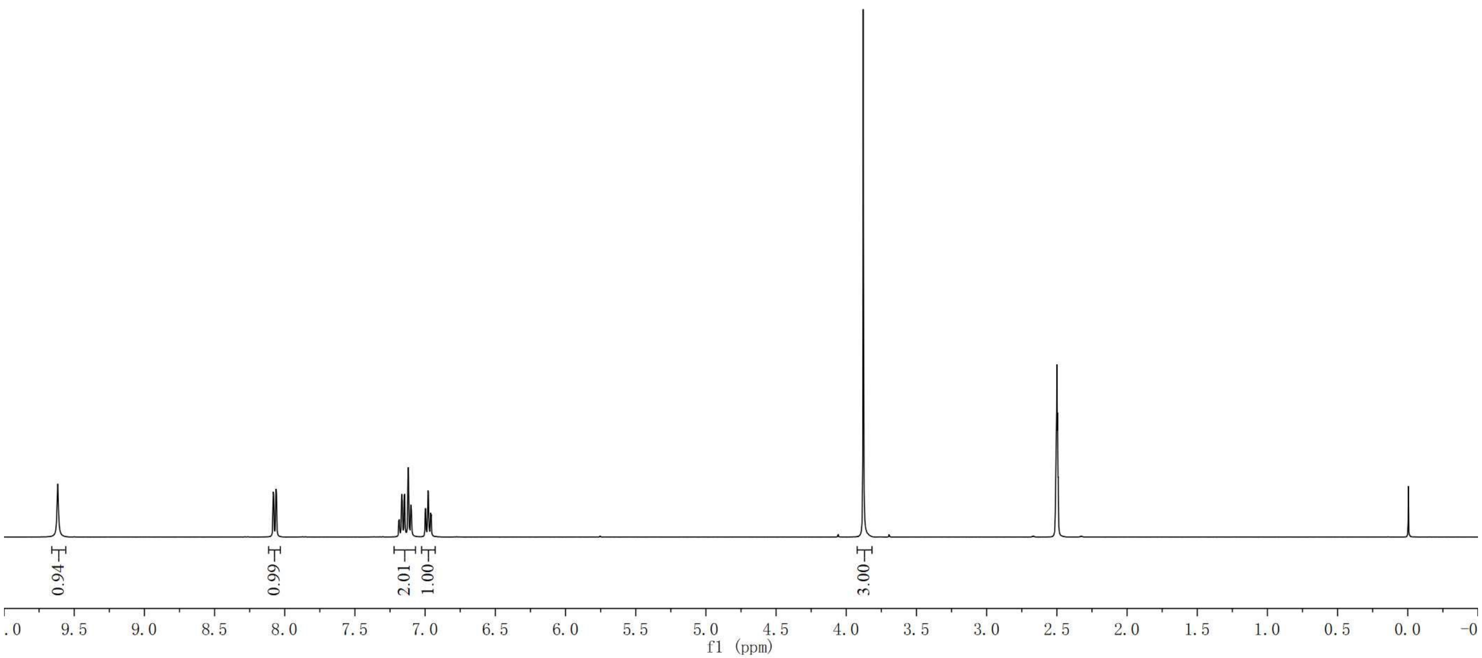

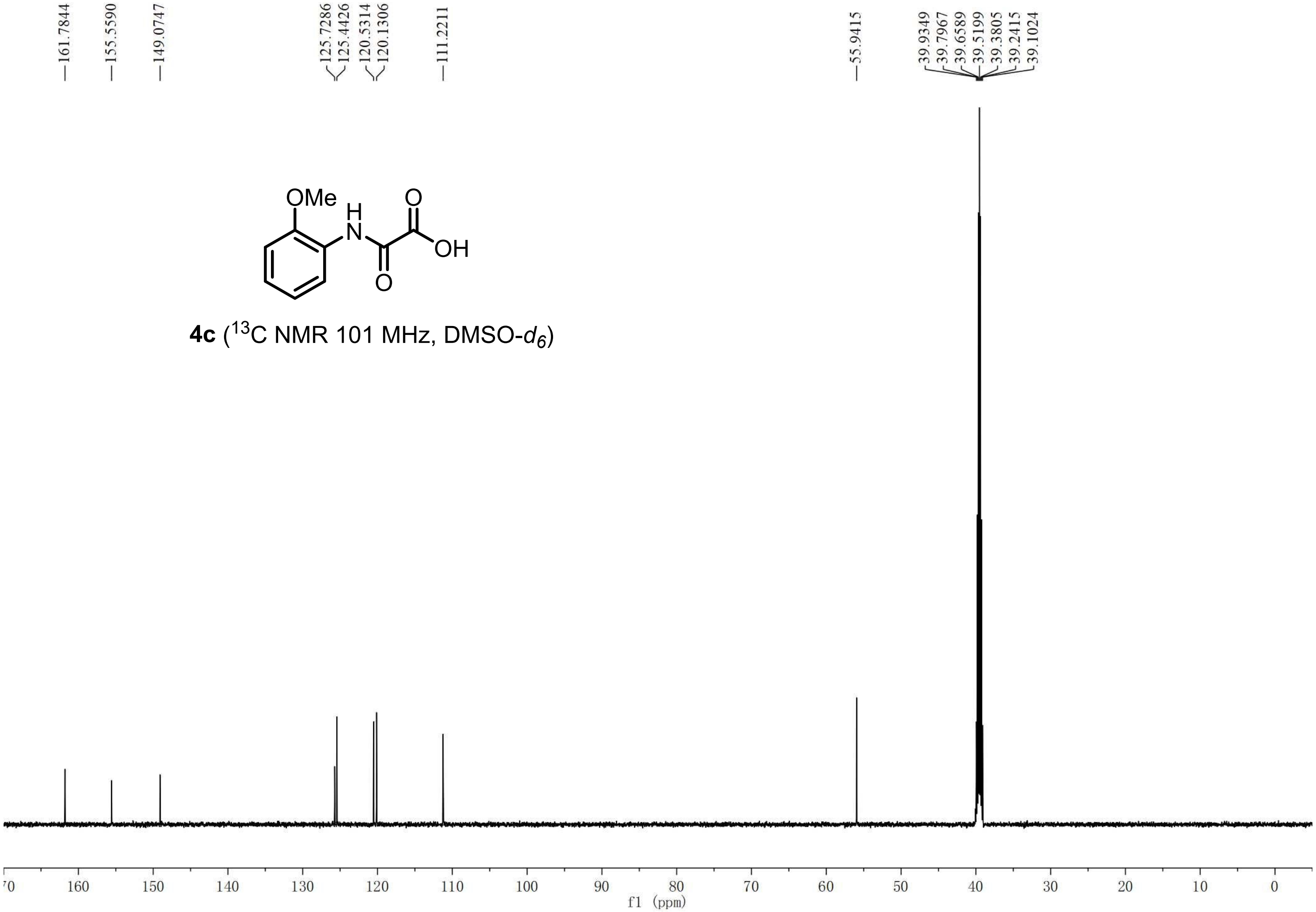

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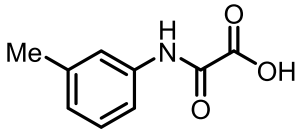

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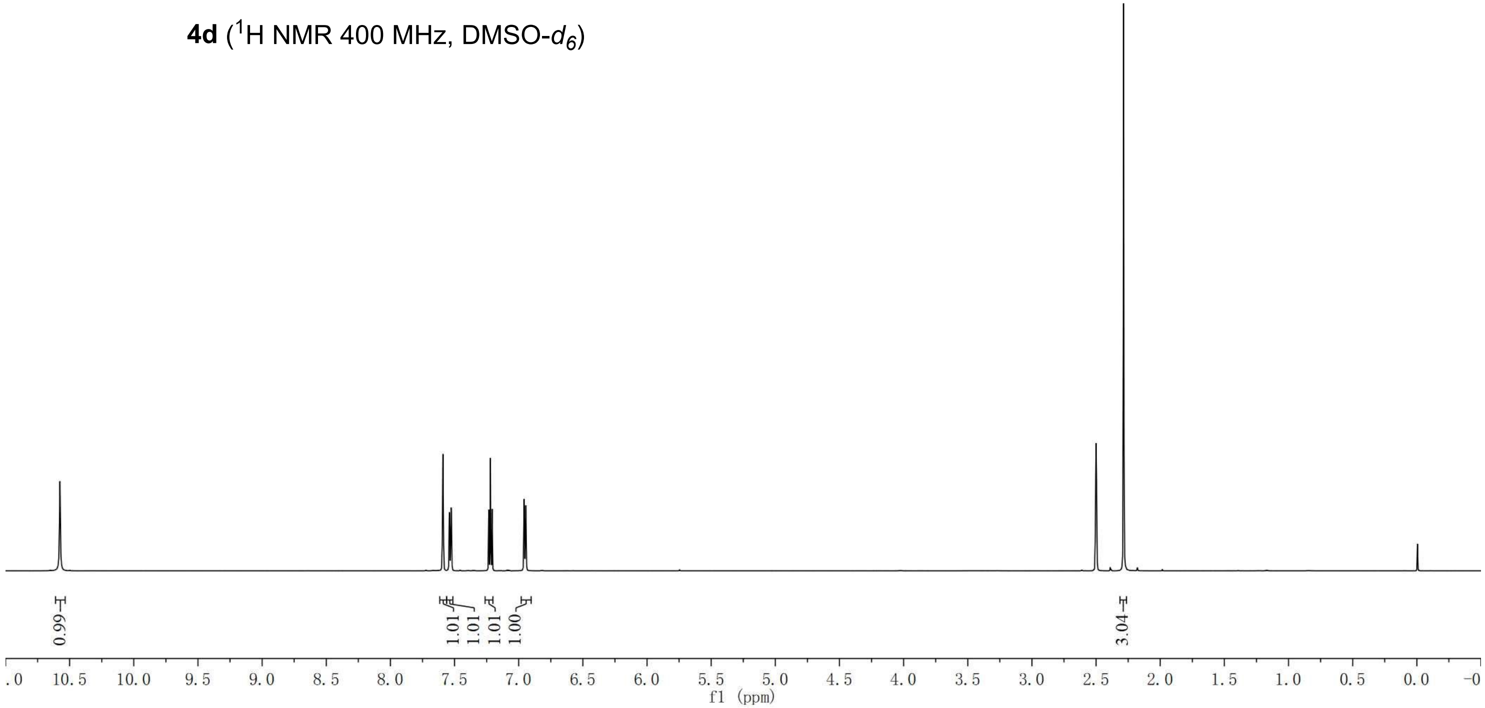

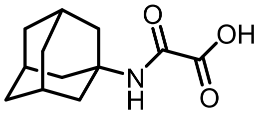

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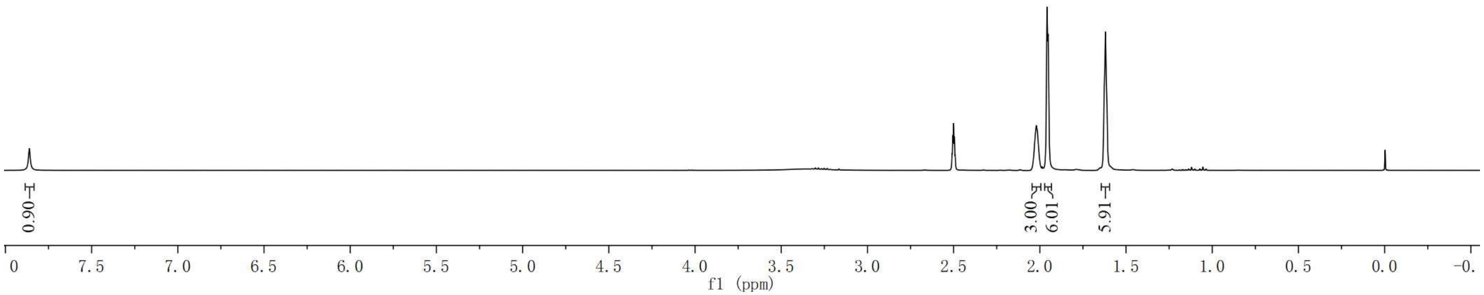

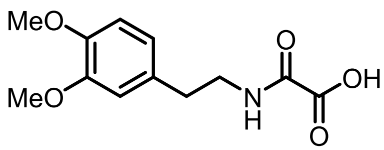

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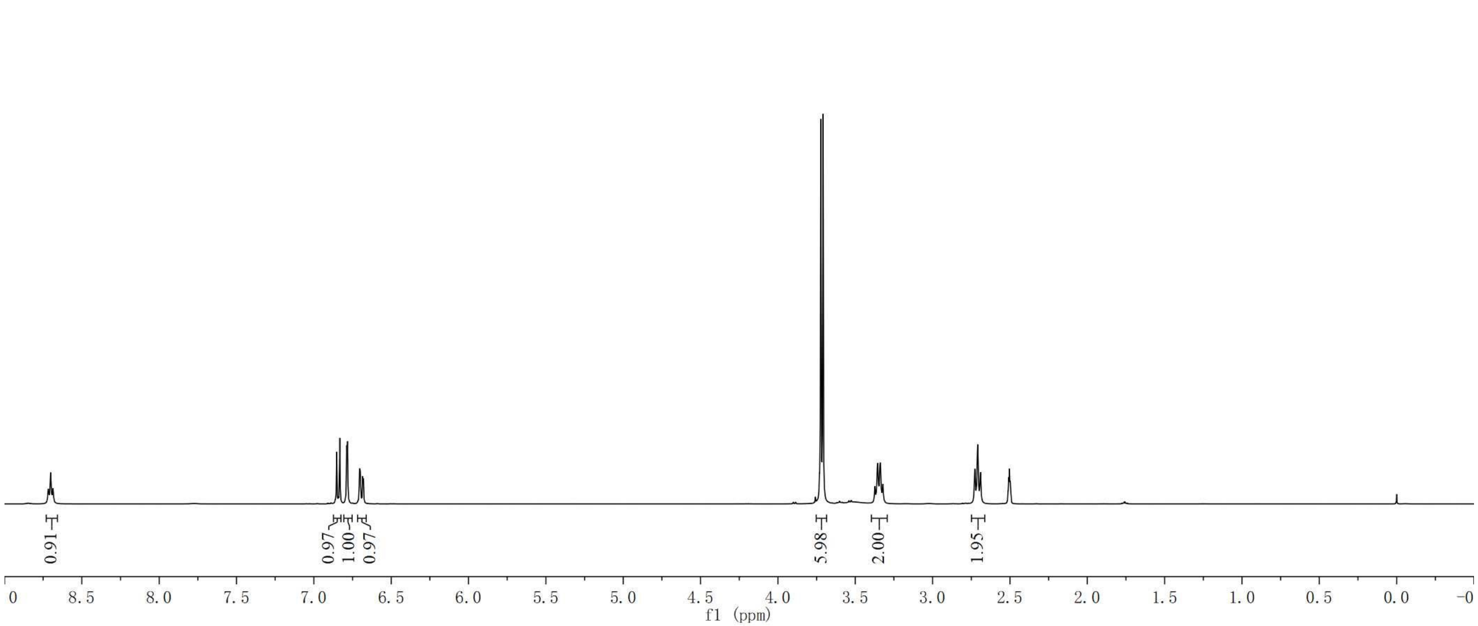

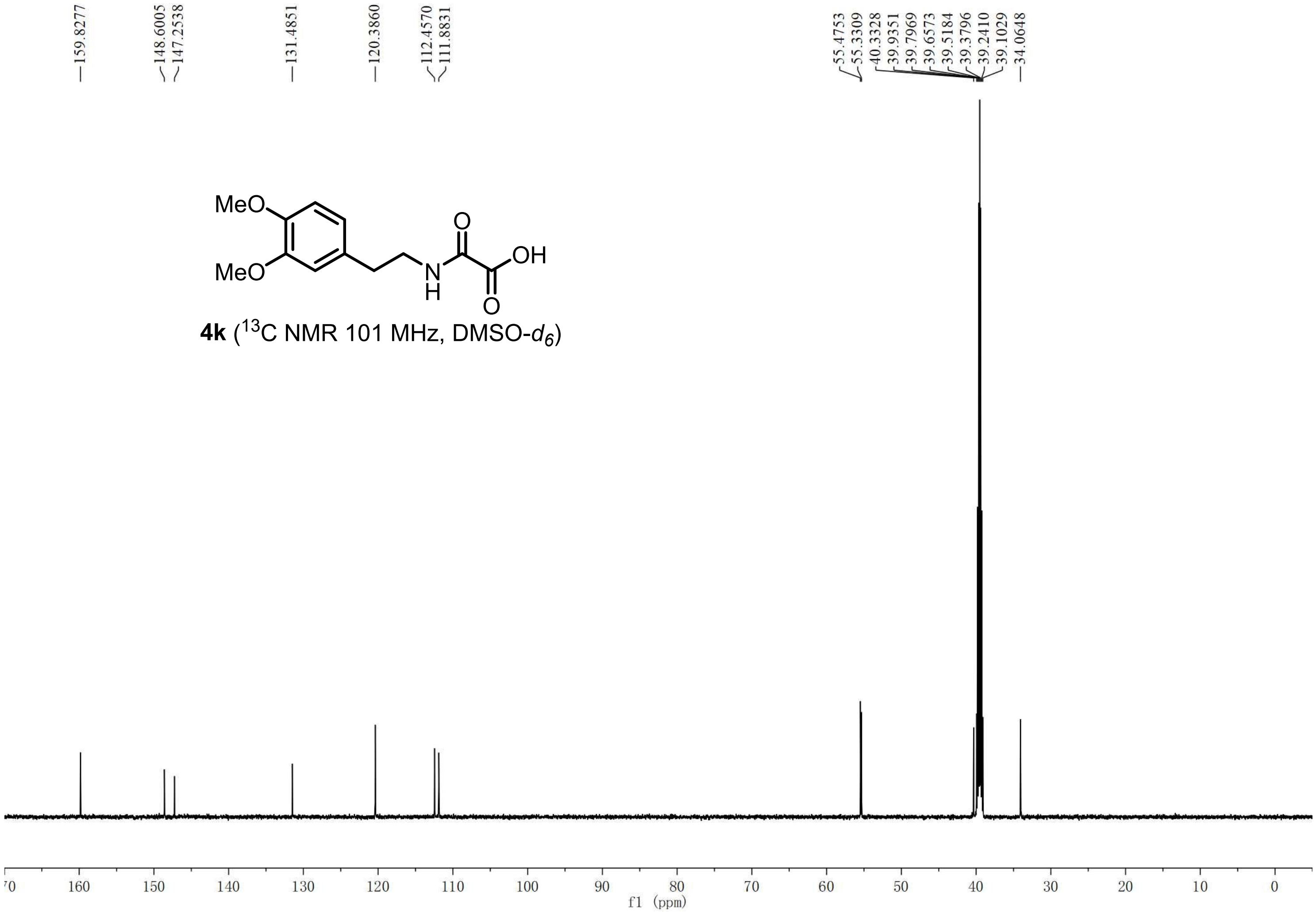

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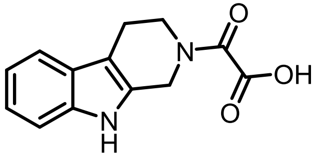

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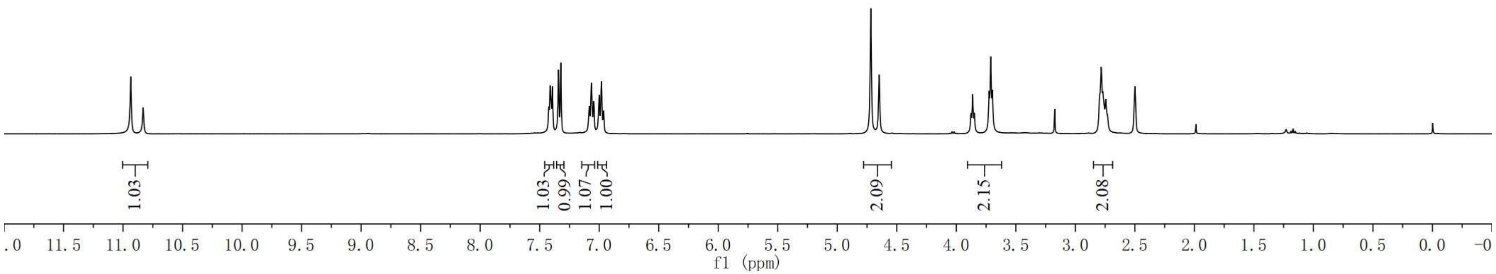

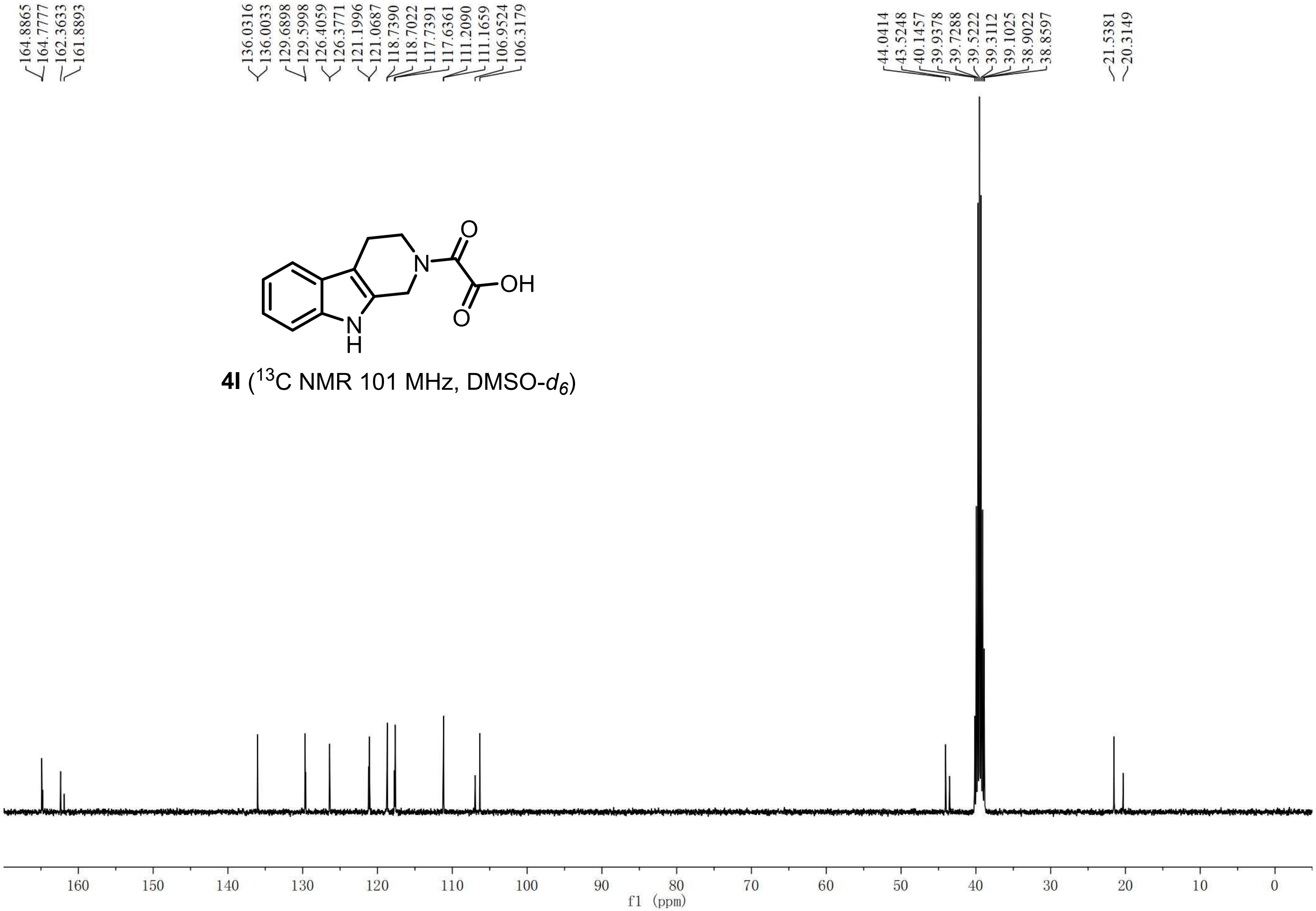

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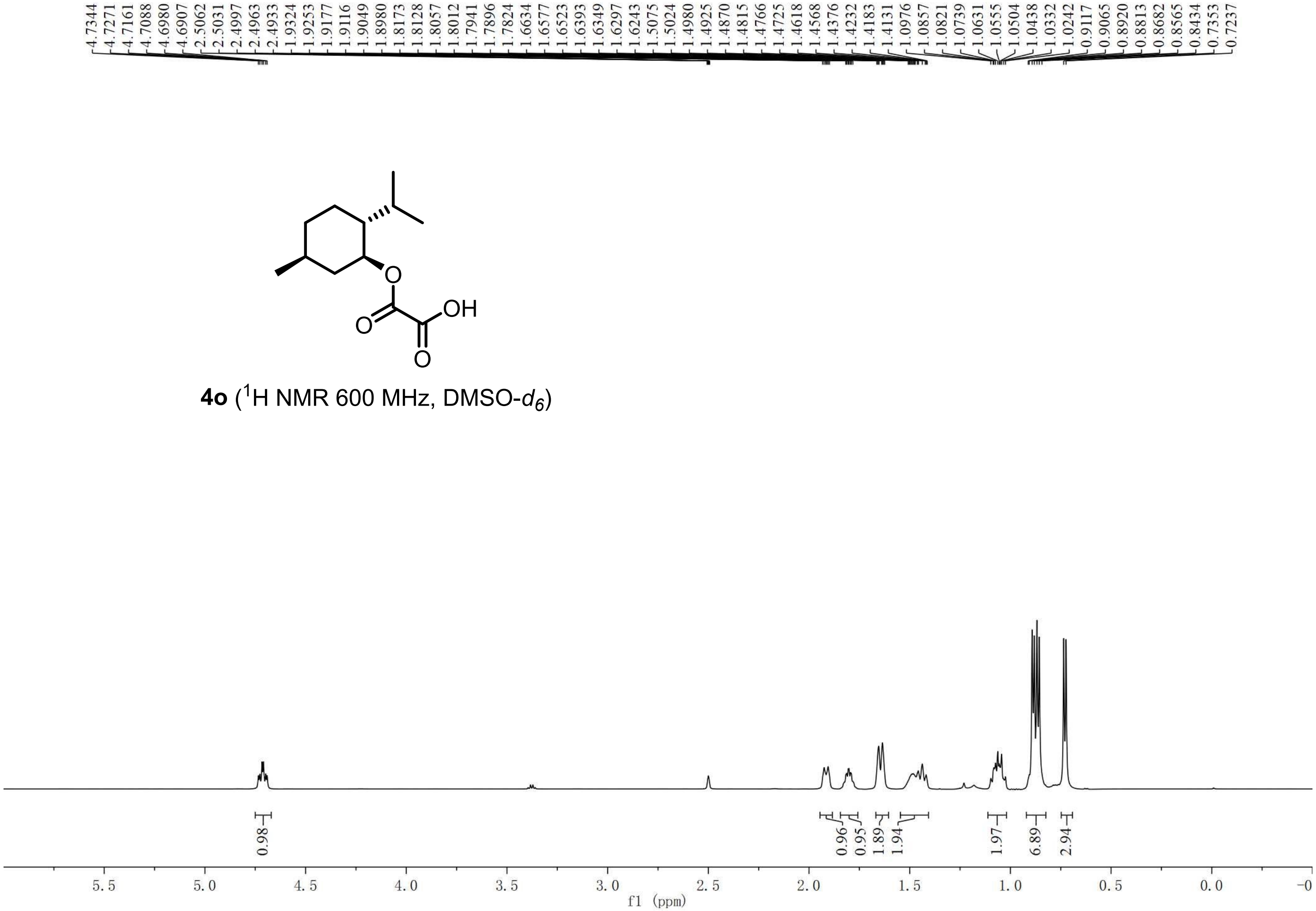

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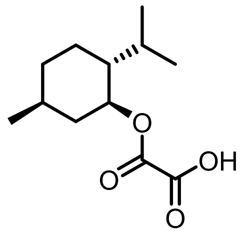

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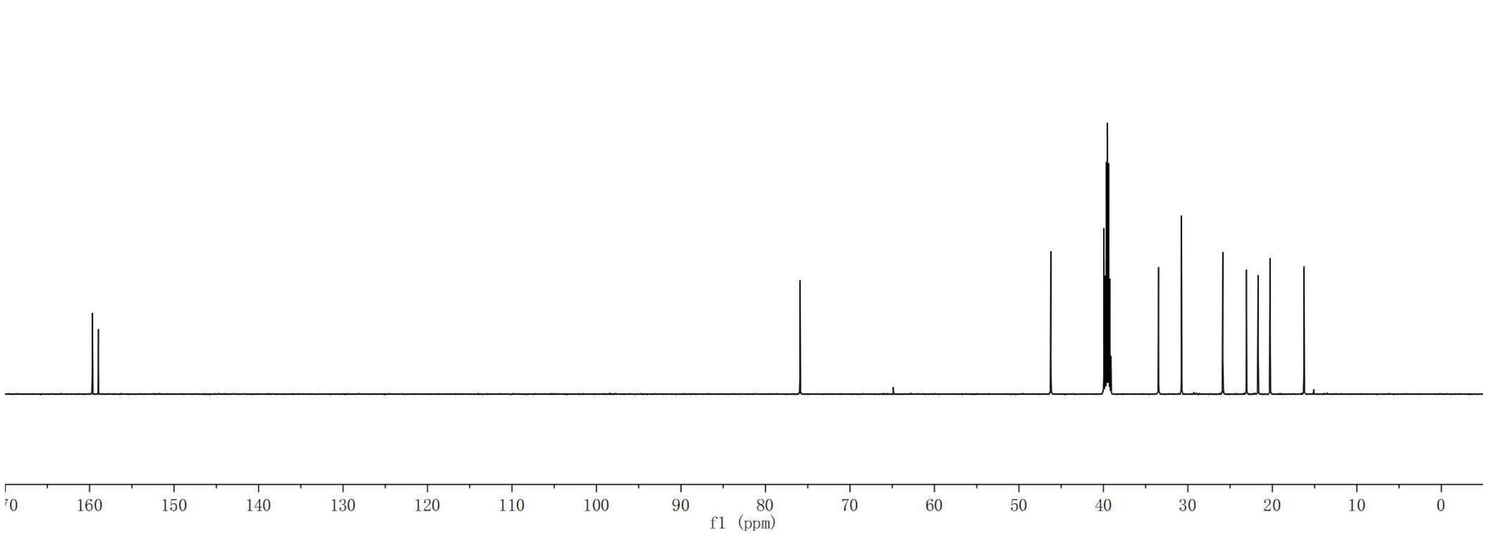

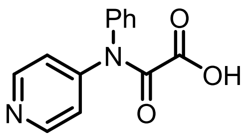

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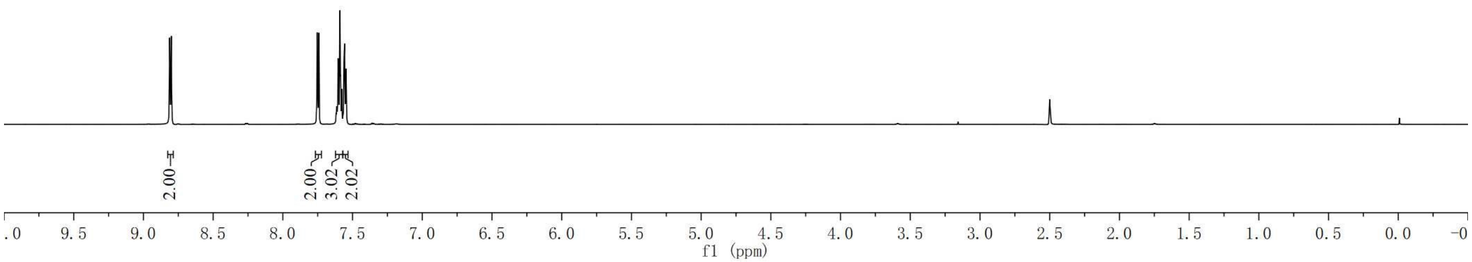

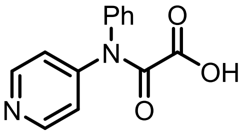

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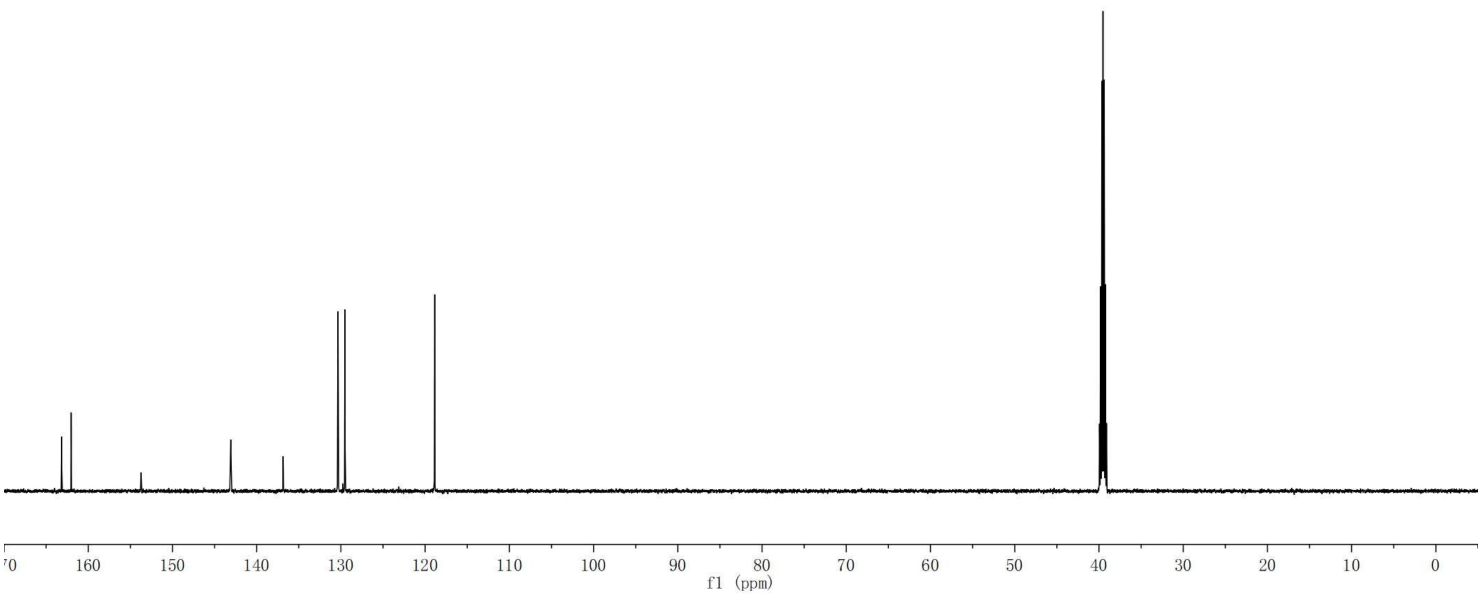

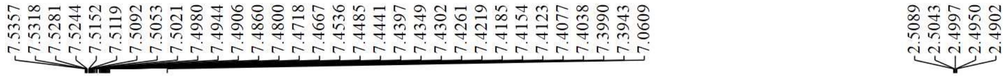

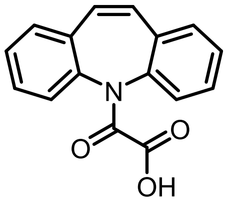

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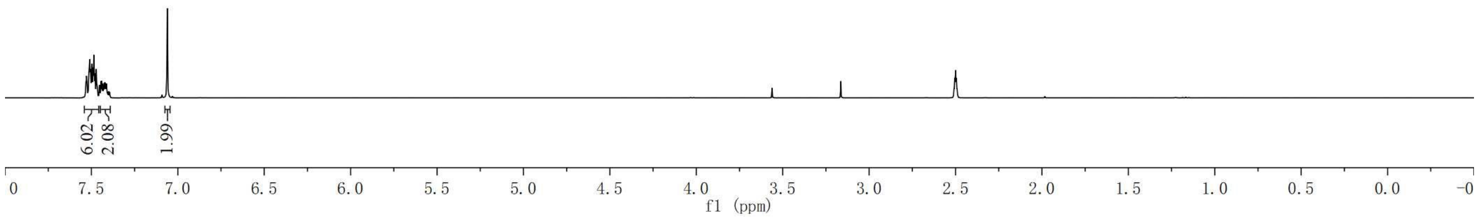

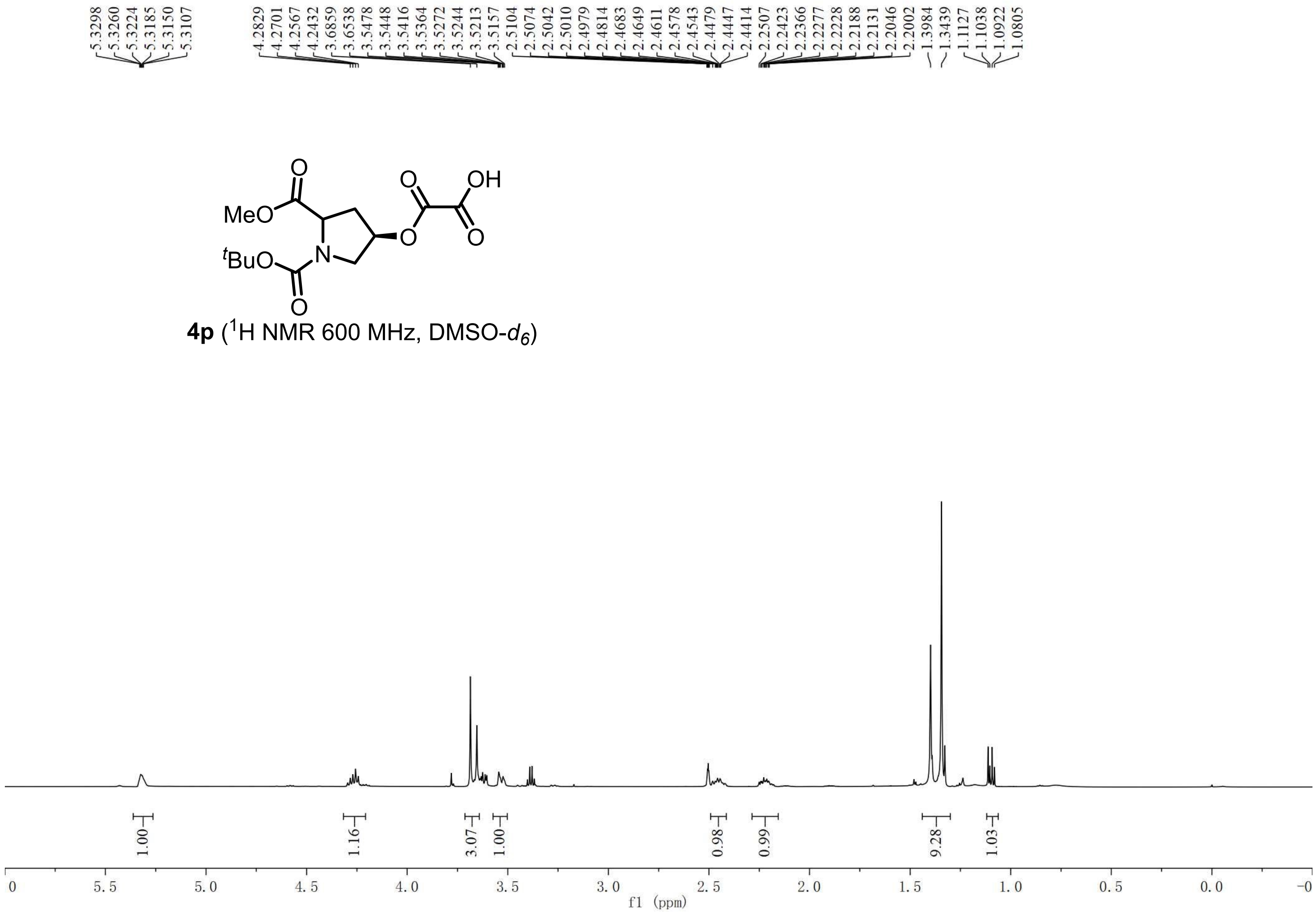

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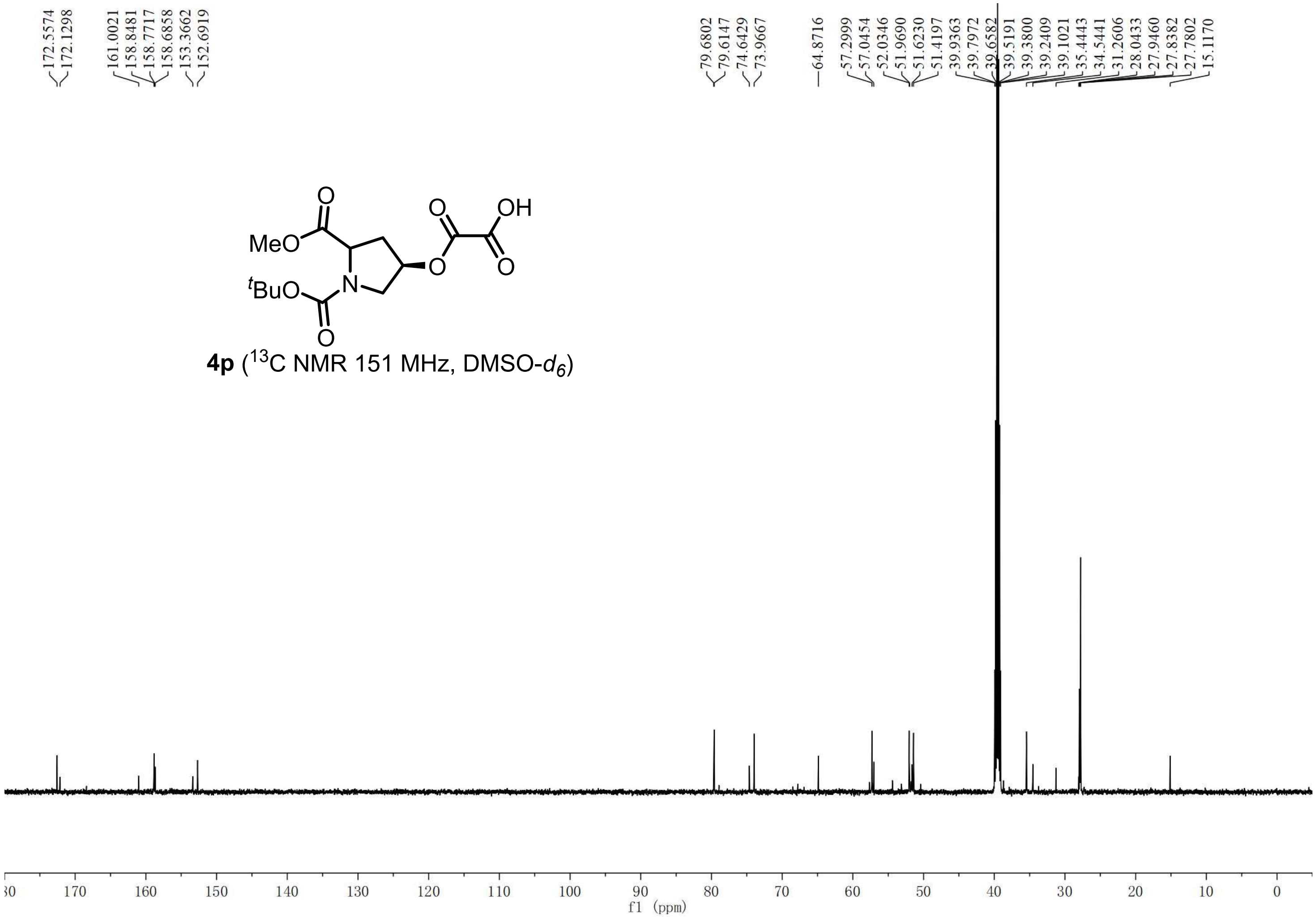

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27.8382
27.7802
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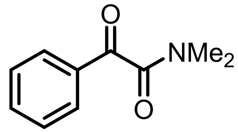
4p (13C NMR 151 MHz, DMSO-d6)
f1 (ppm)



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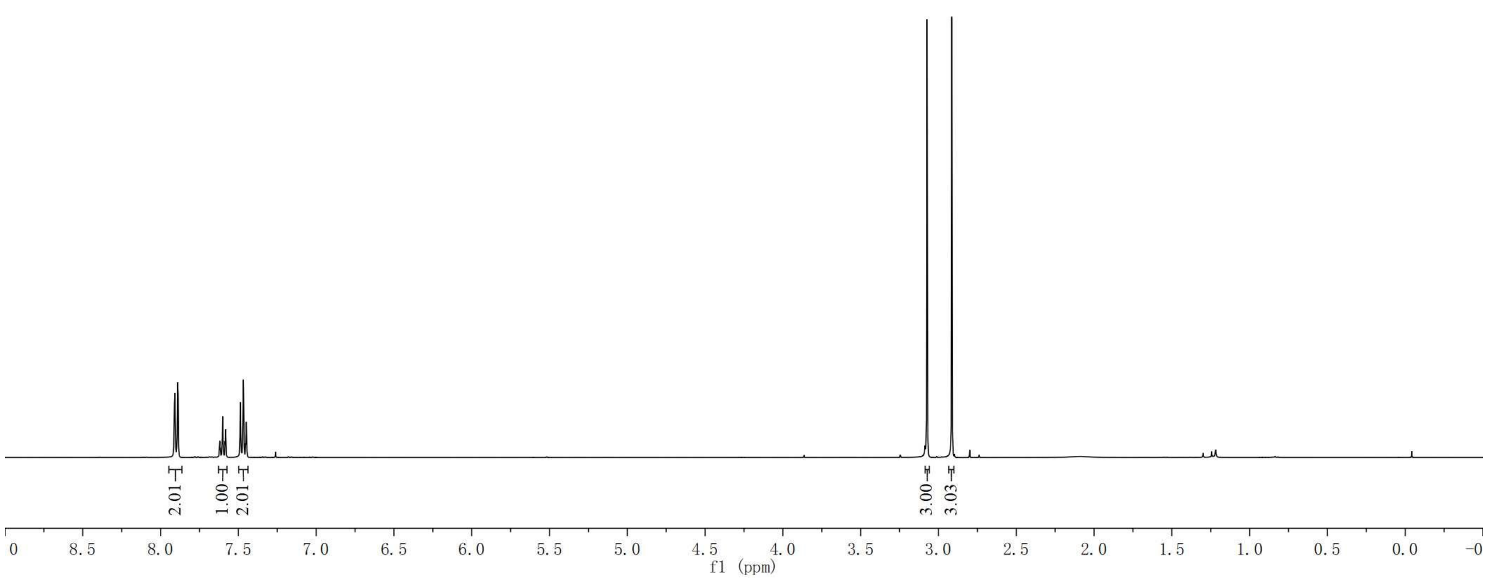

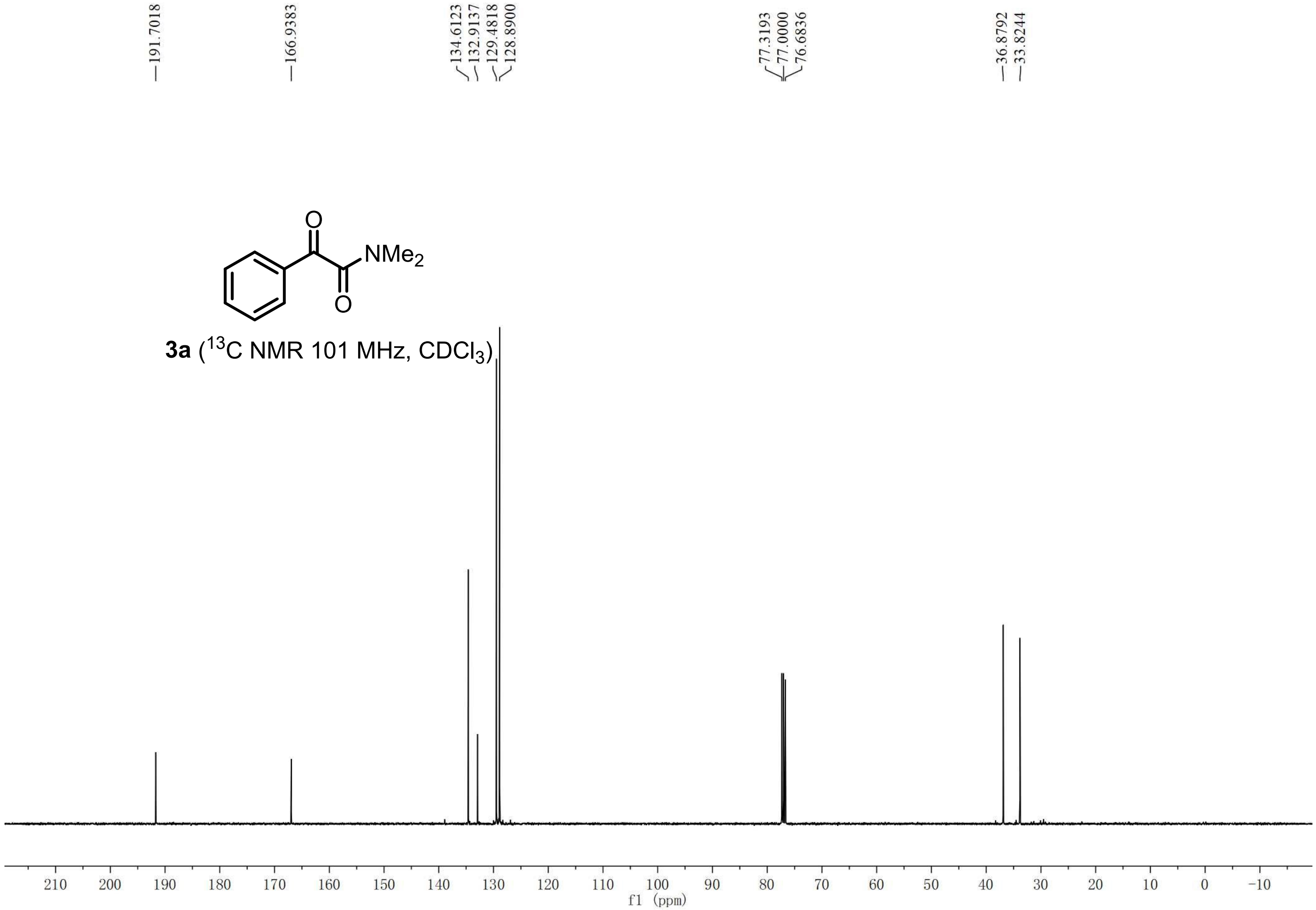

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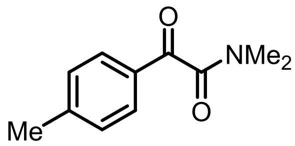

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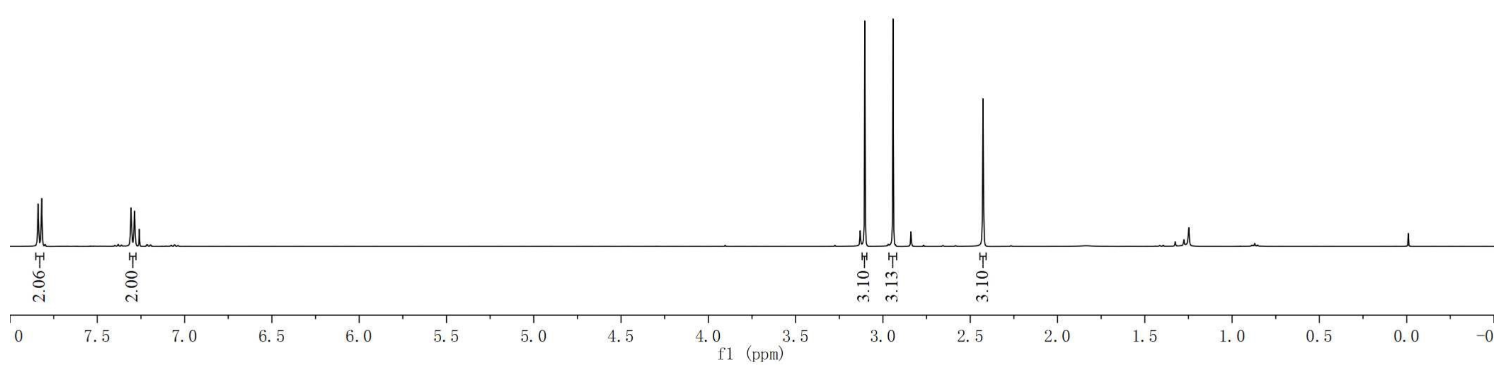

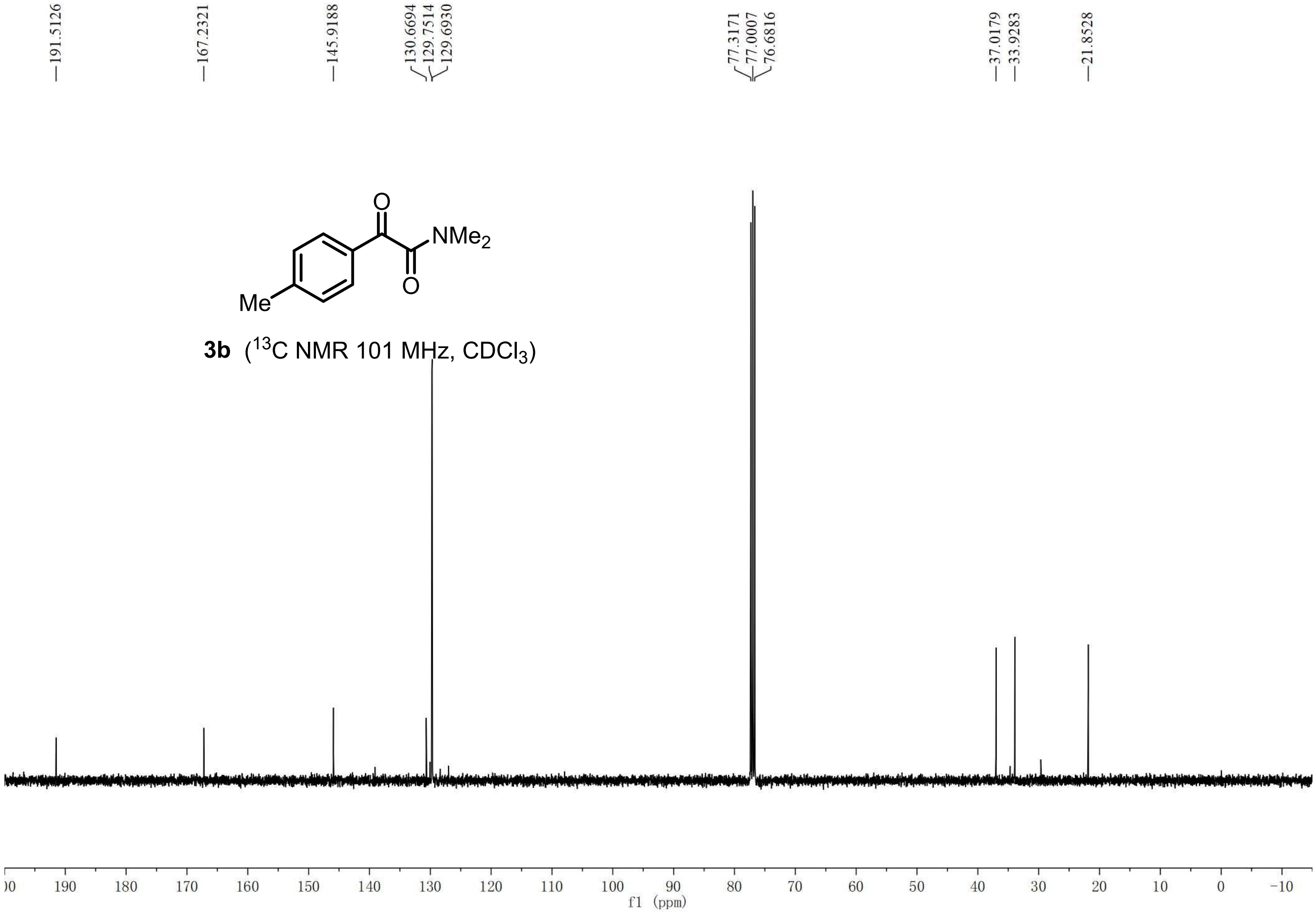

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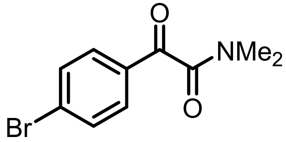

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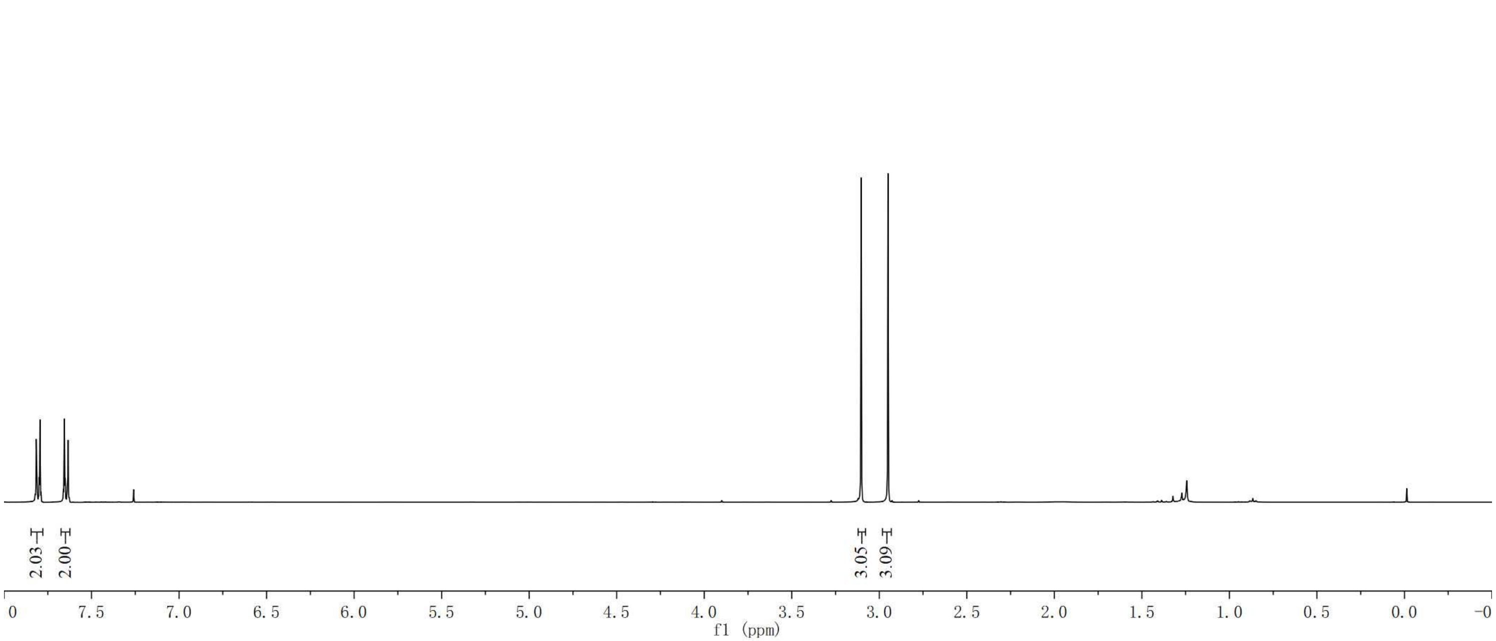

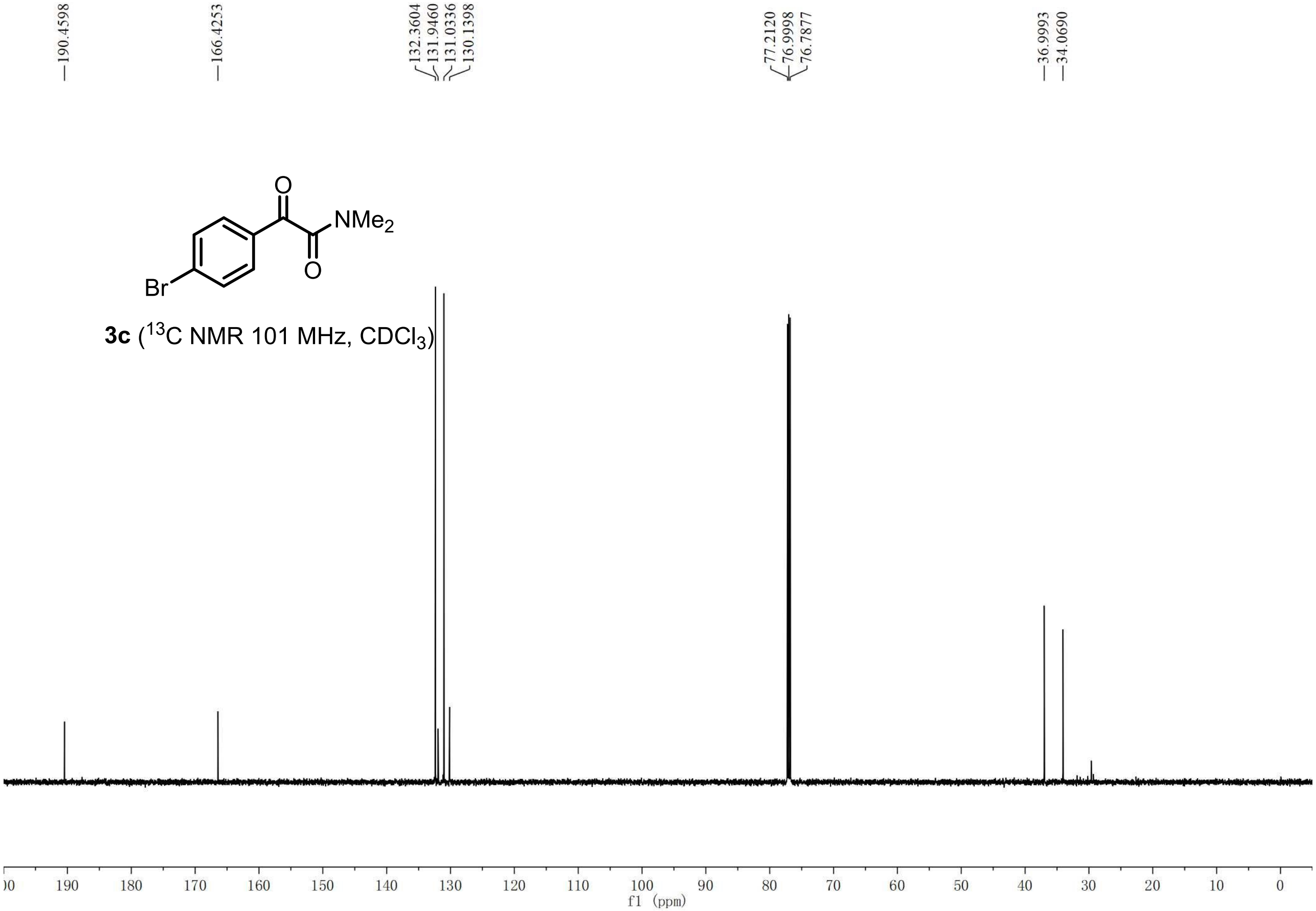

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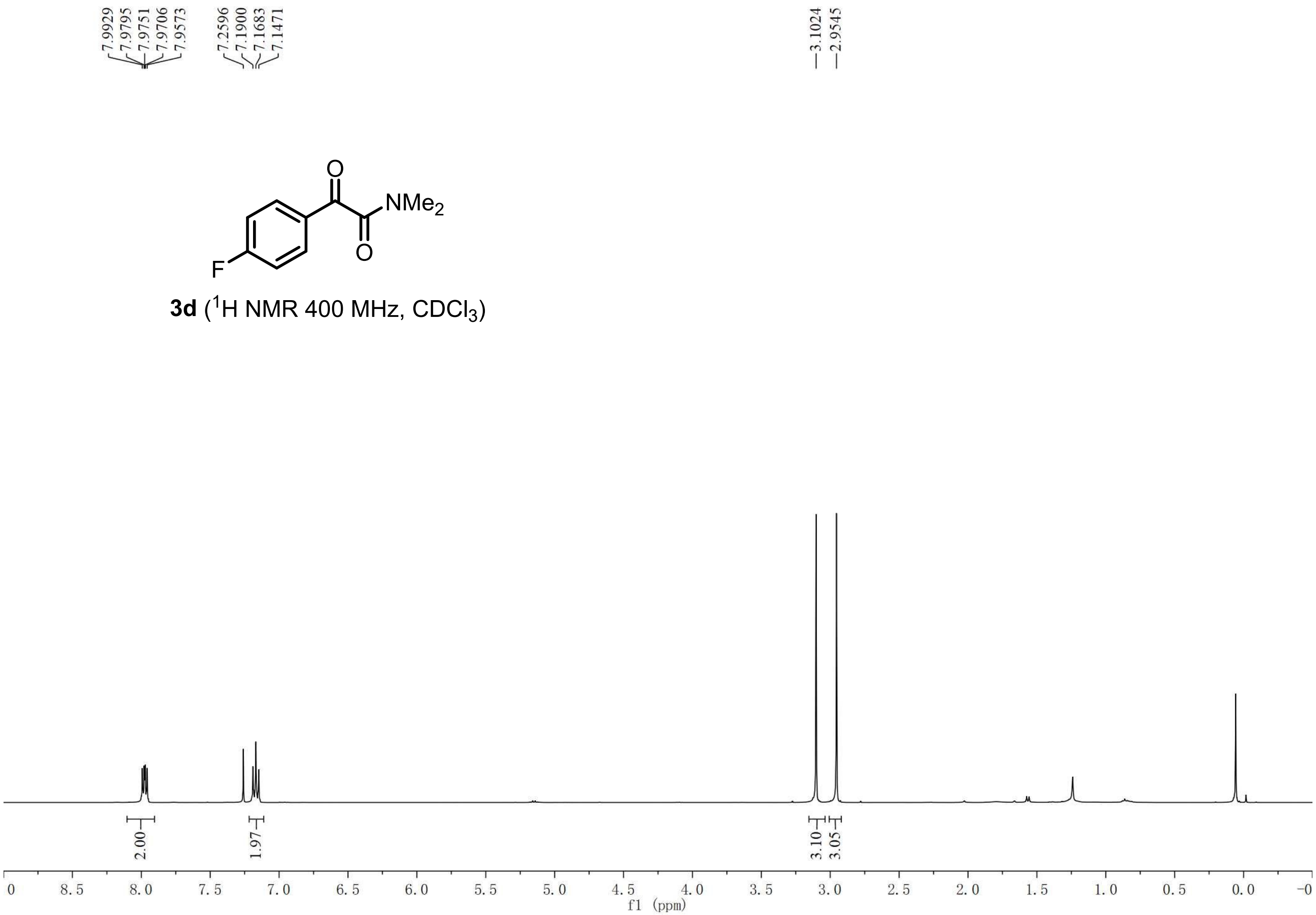

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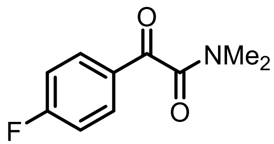

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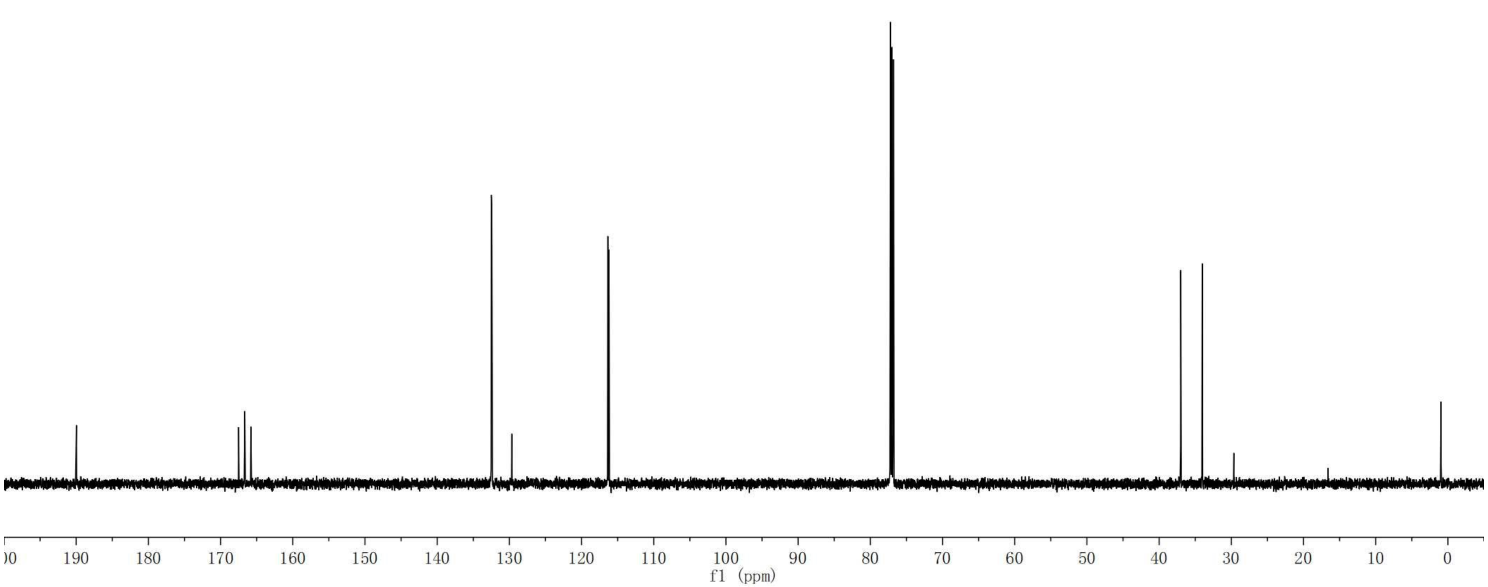

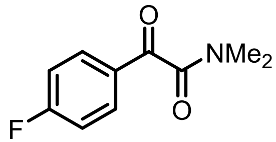

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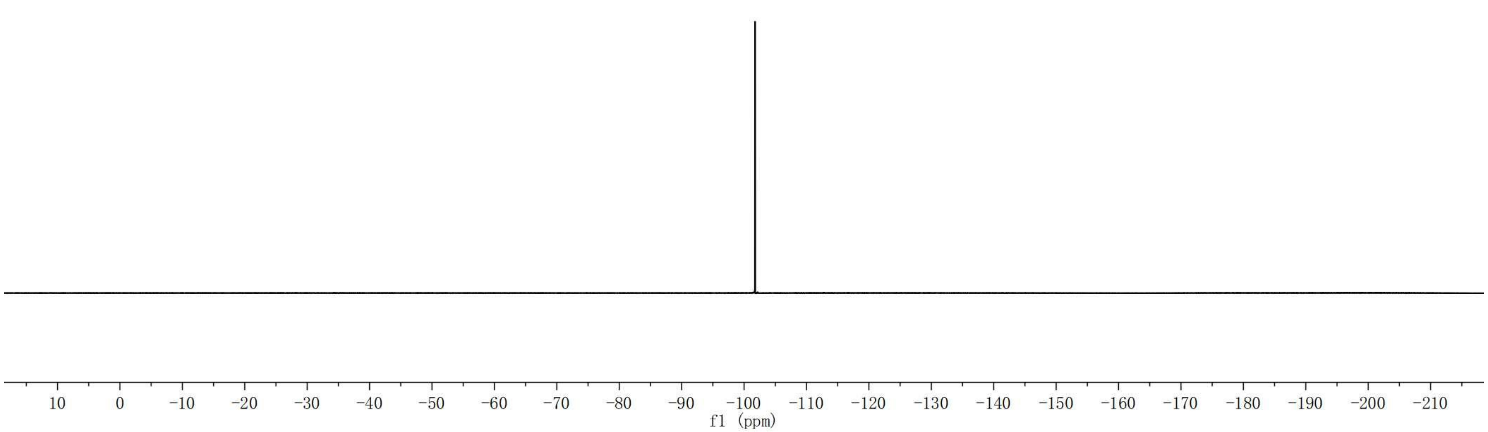

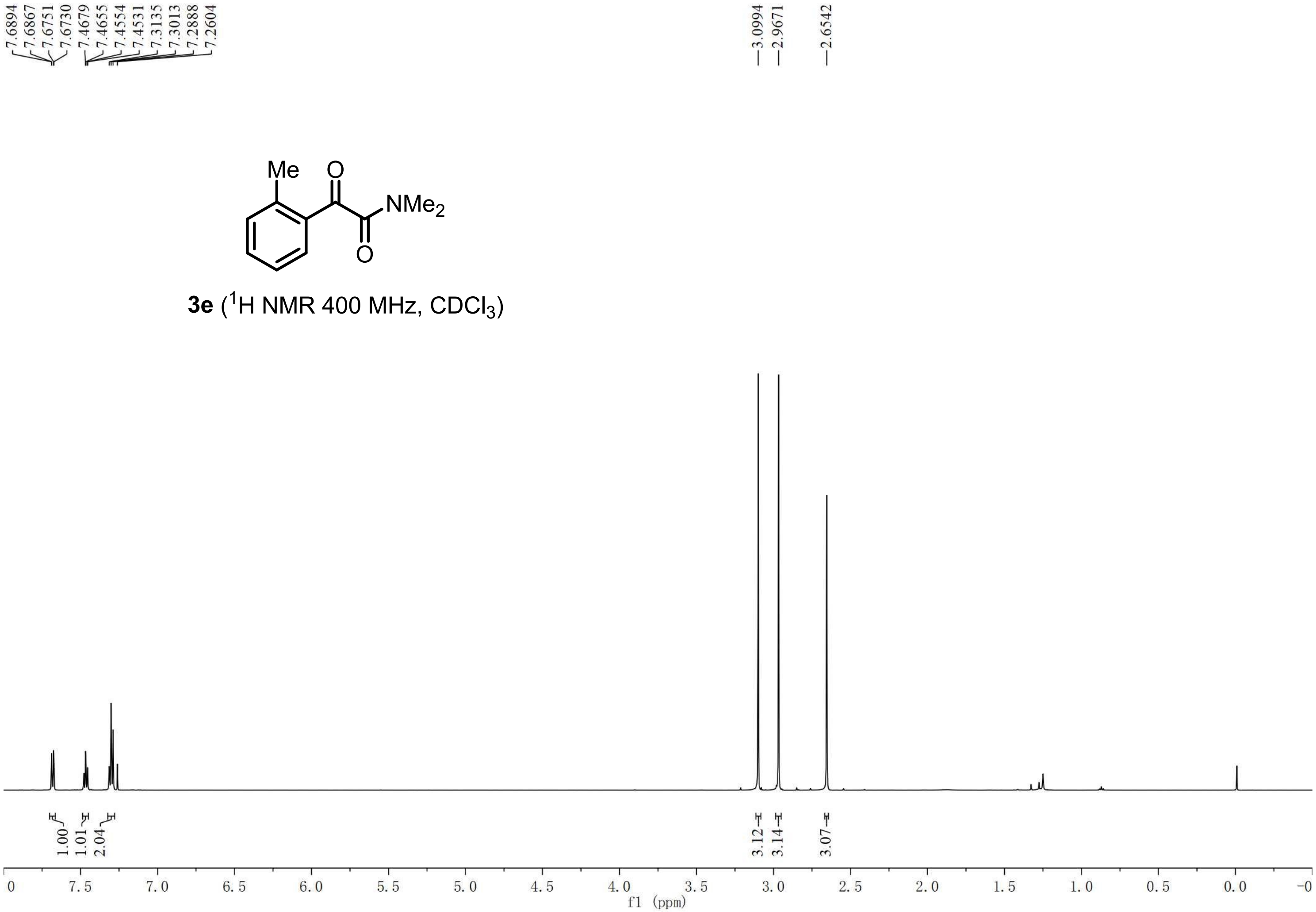

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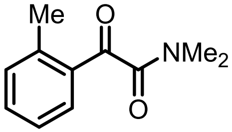
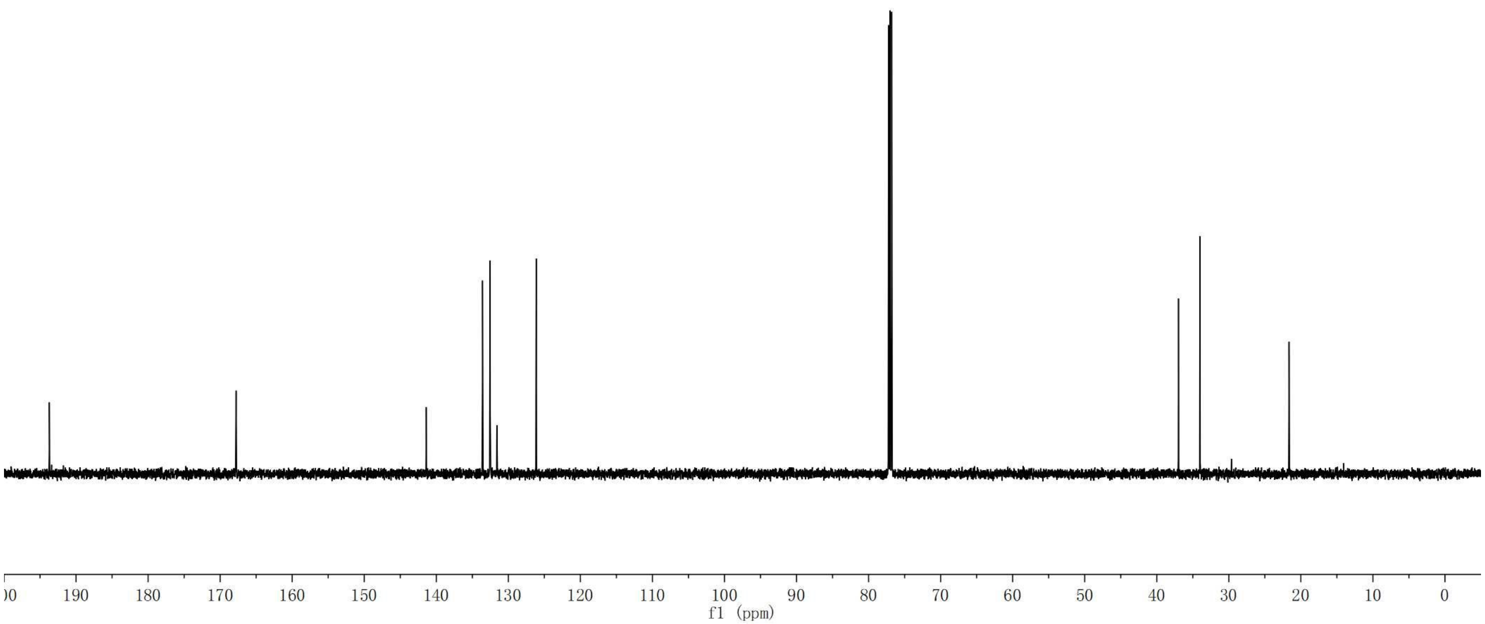
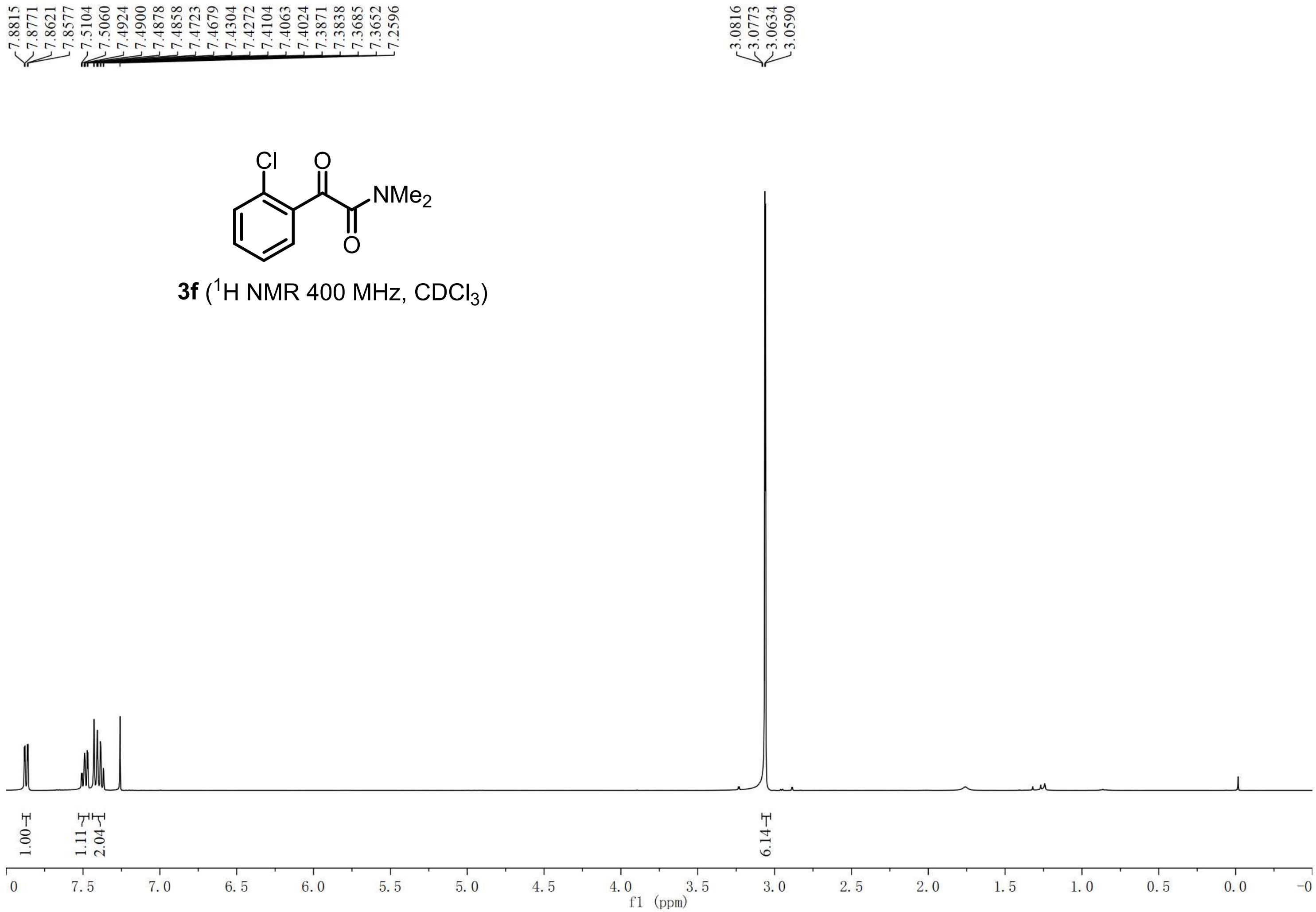


3e (^{13}C NMR 101 MHz, $CDCl_3$)





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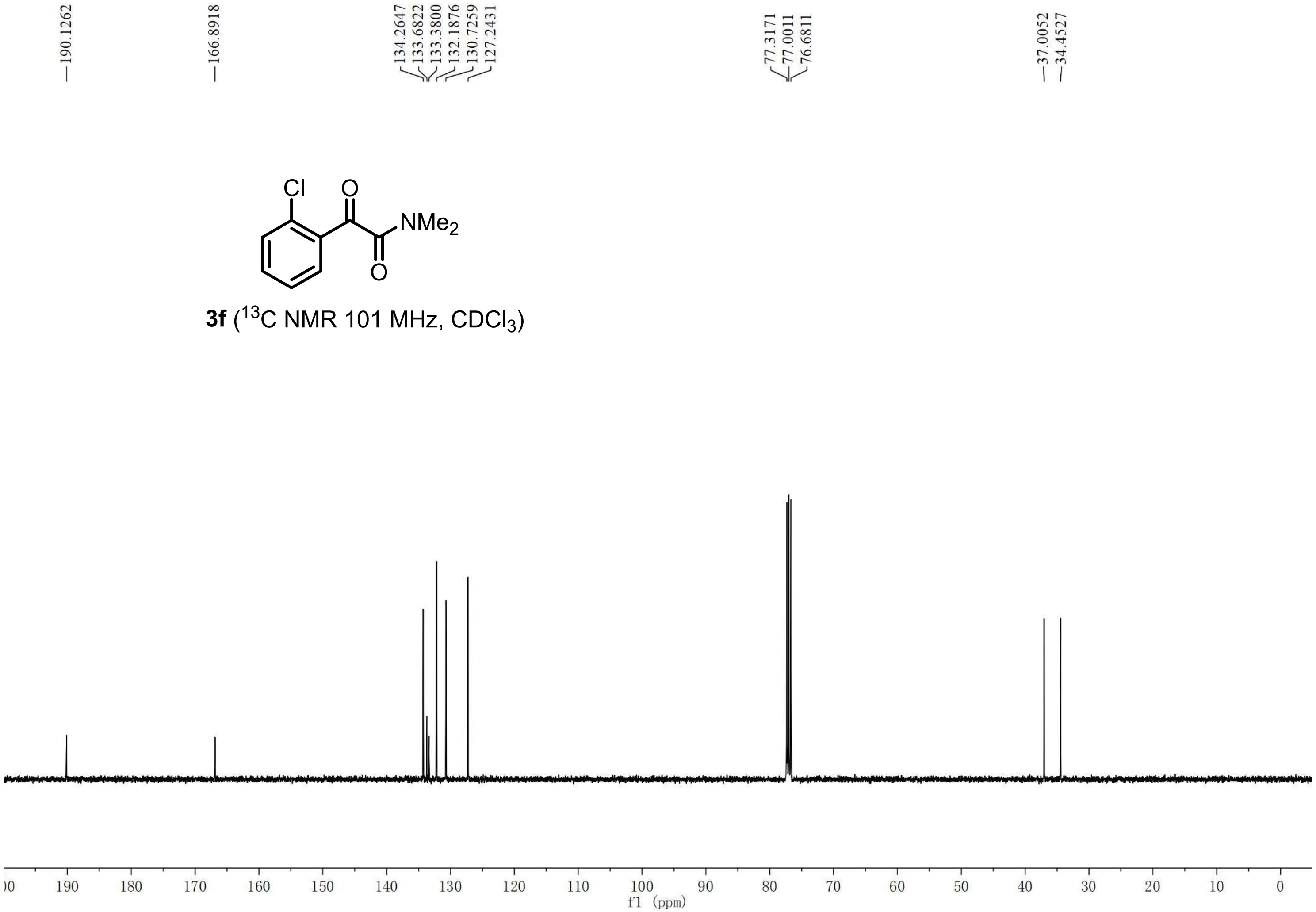

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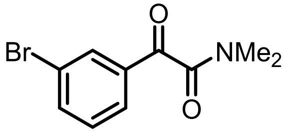

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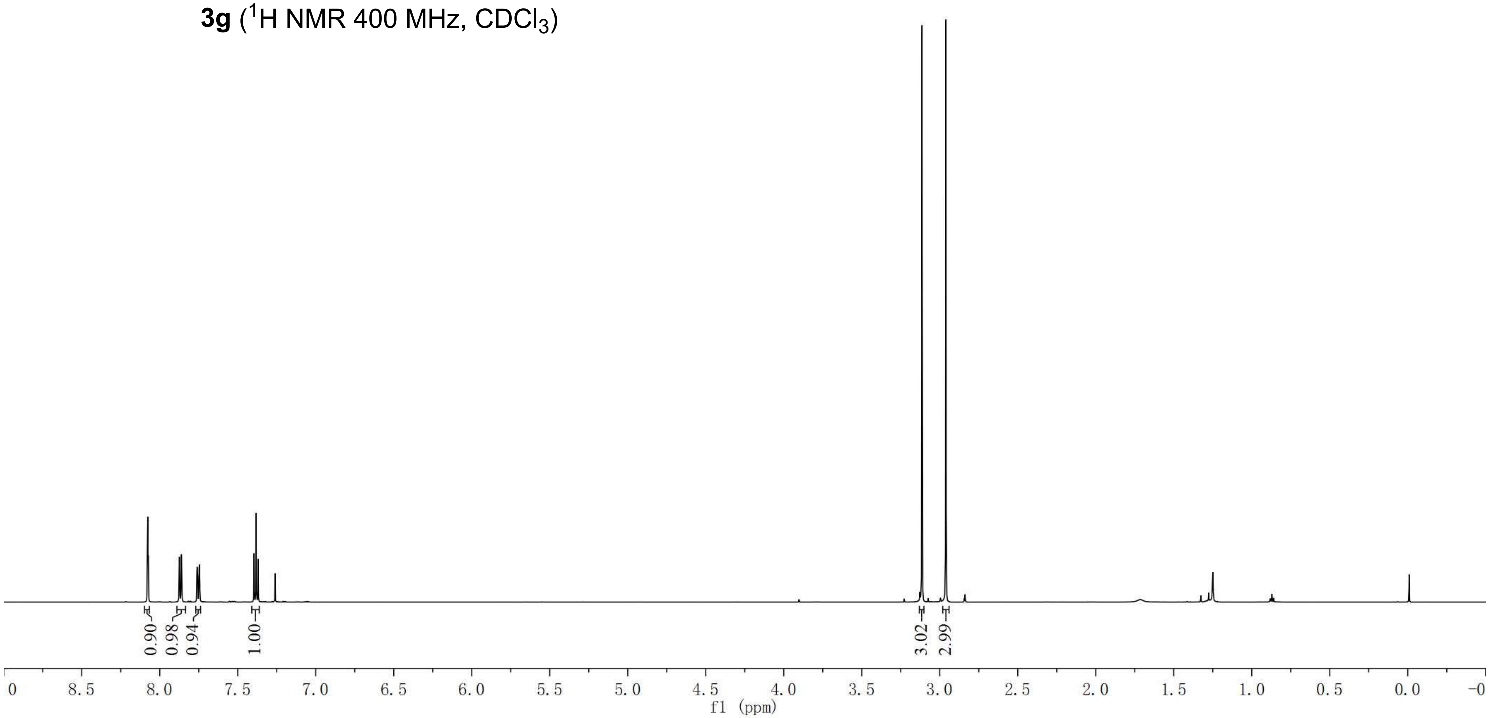
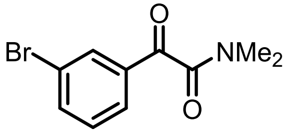
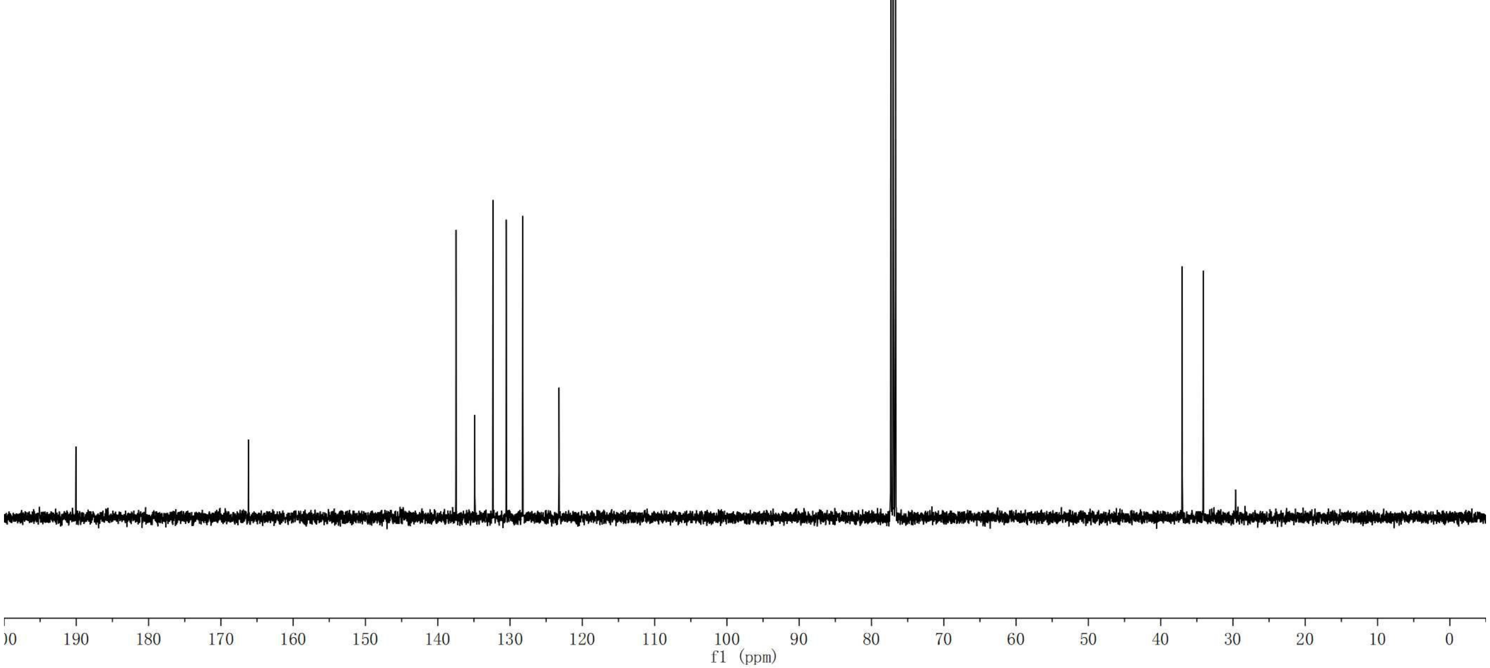
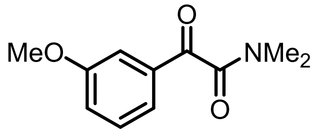




3g (^{13}C NMR 101 MHz, $CDCl_3$)





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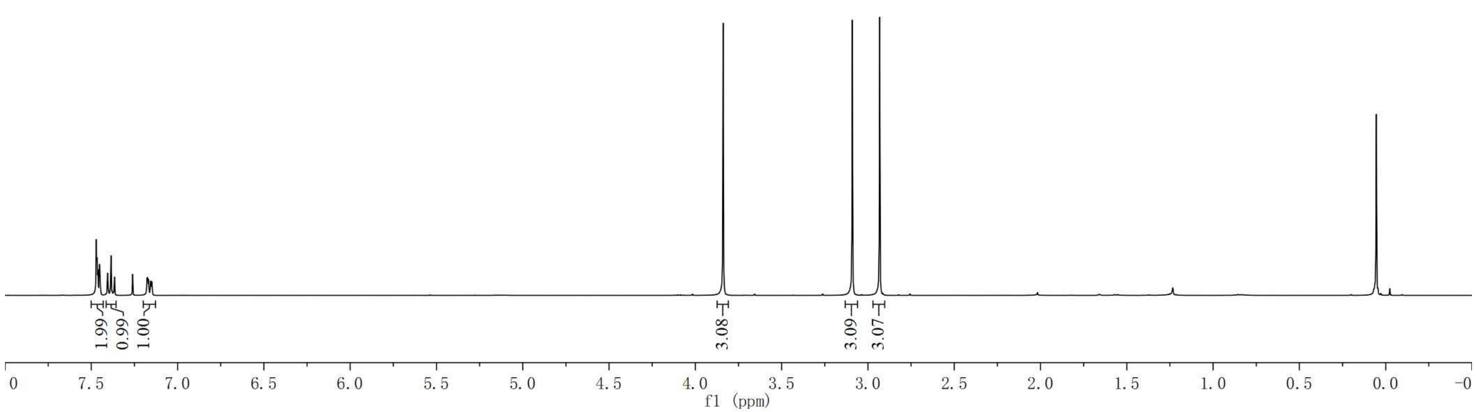

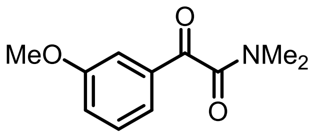

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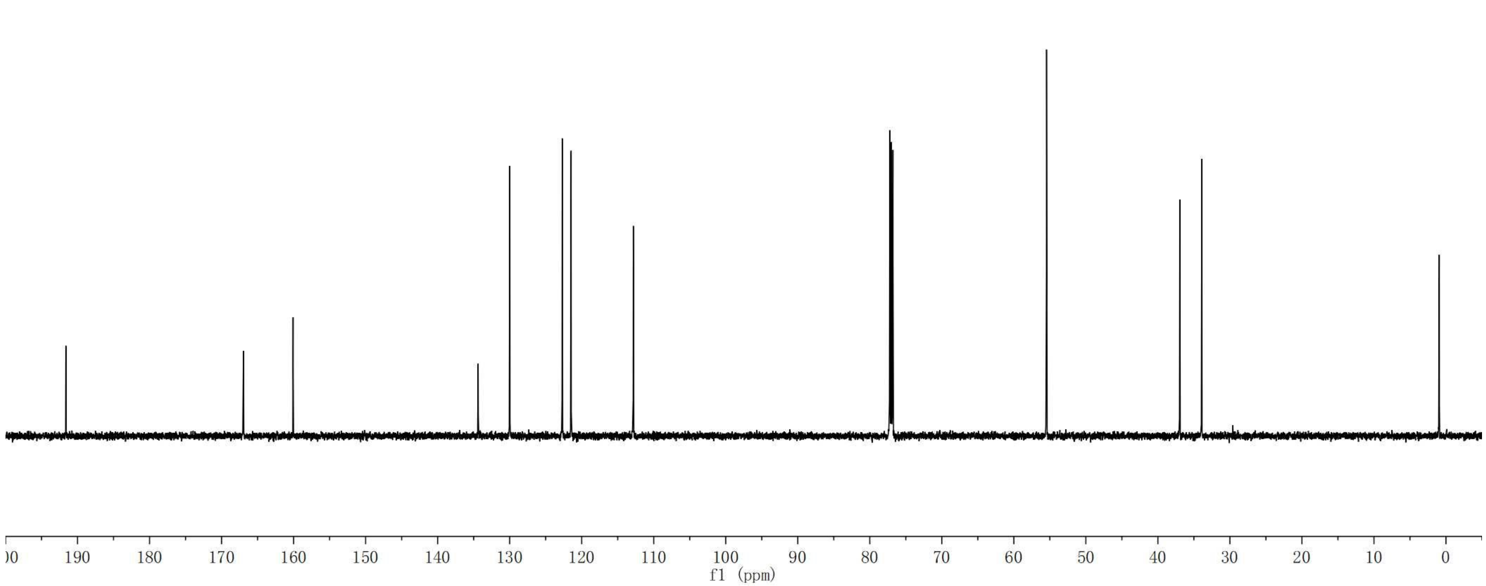
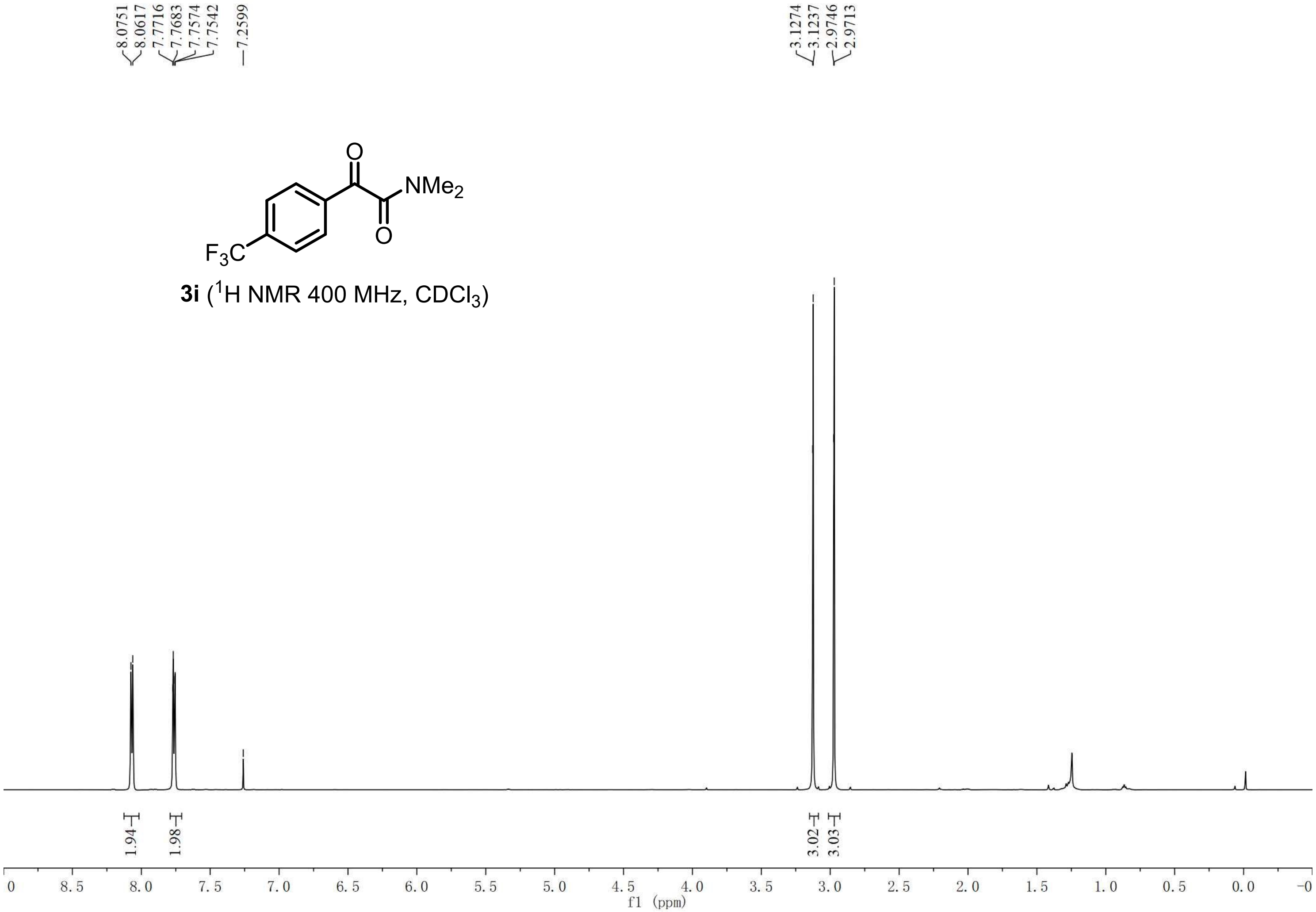
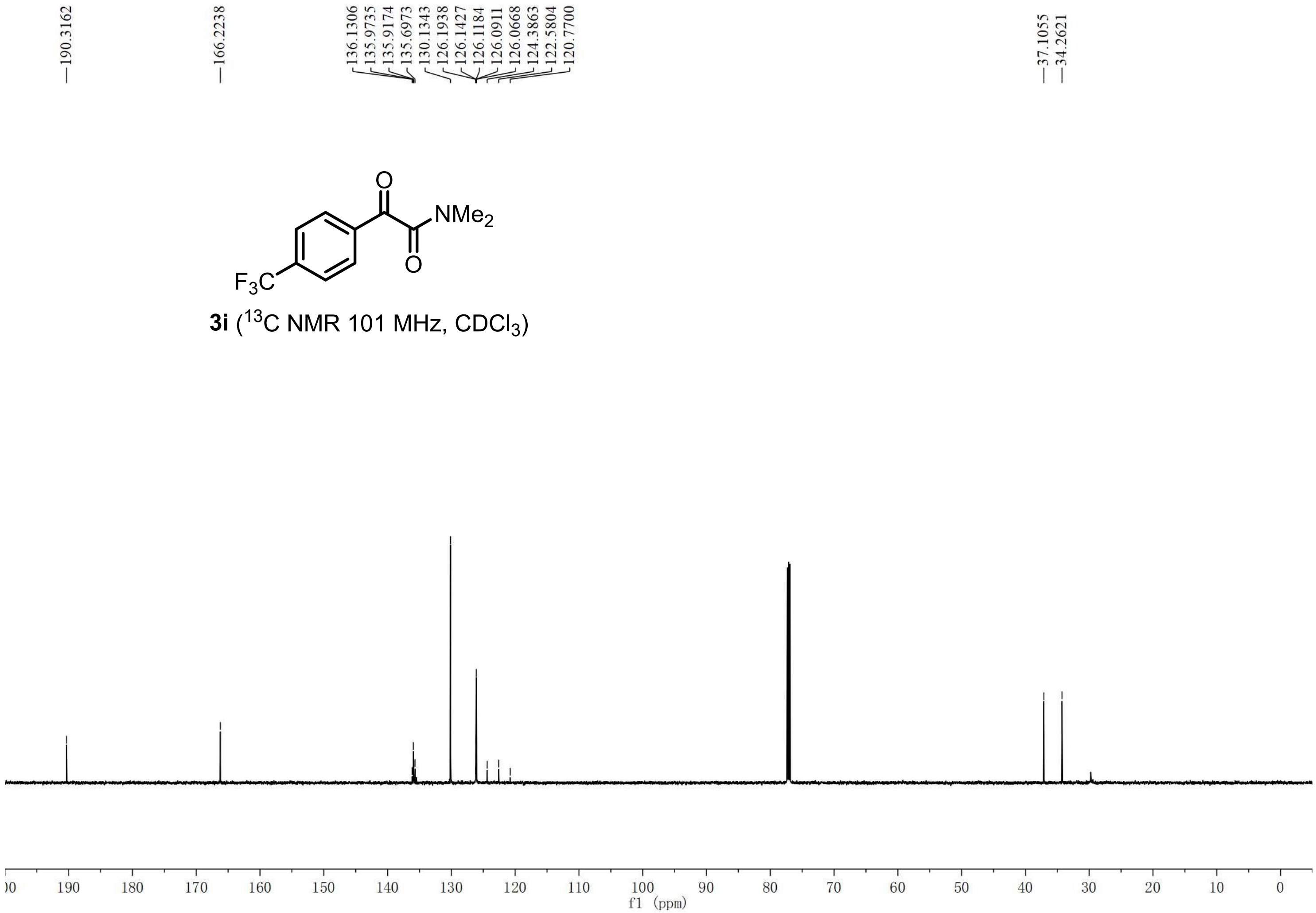
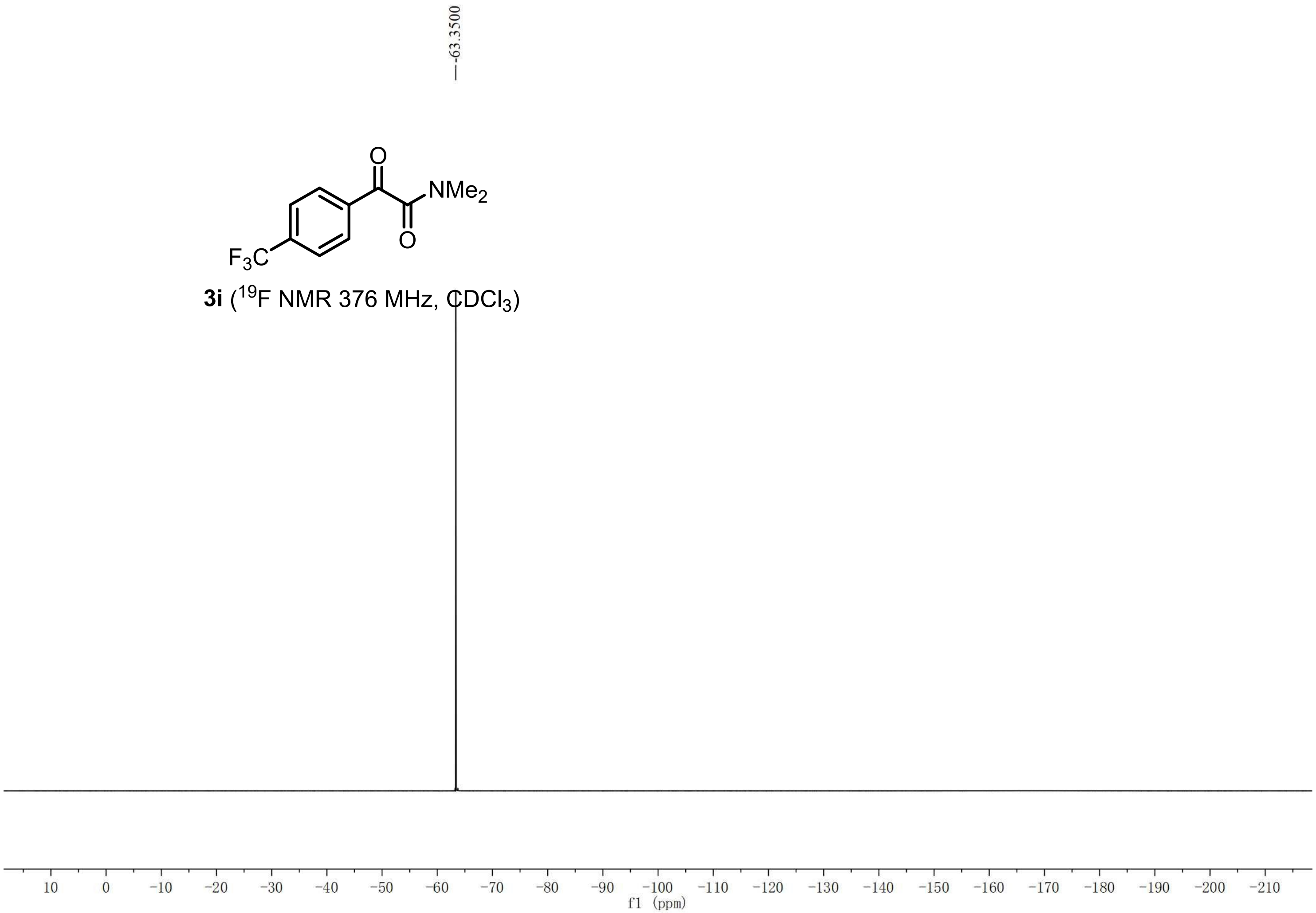




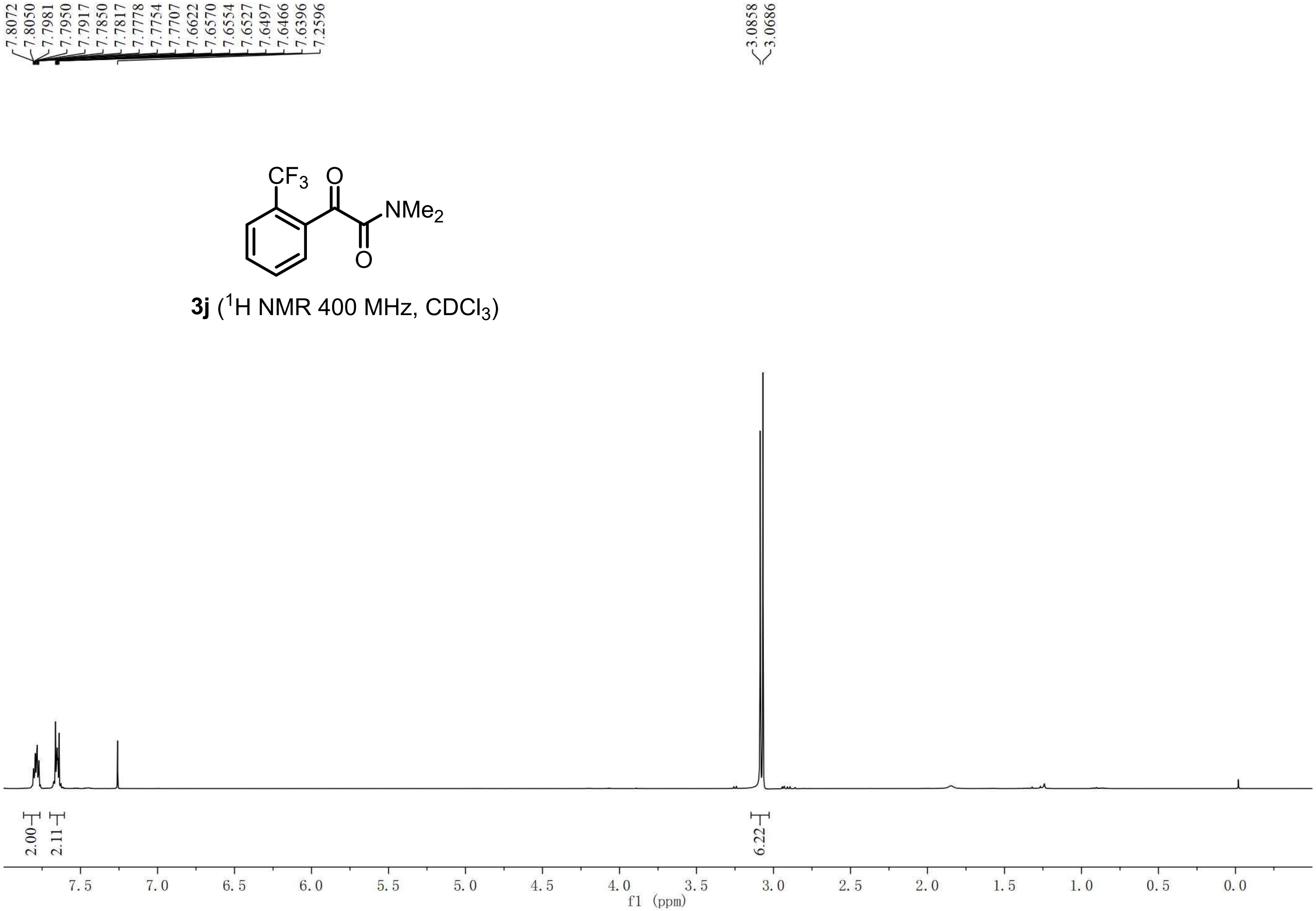
3i (^{1}H NMR 400 MHz, $CDCl_3$)



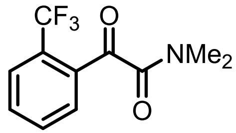
3i (^{13}C NMR 101 MHz, $CDCl_3$)



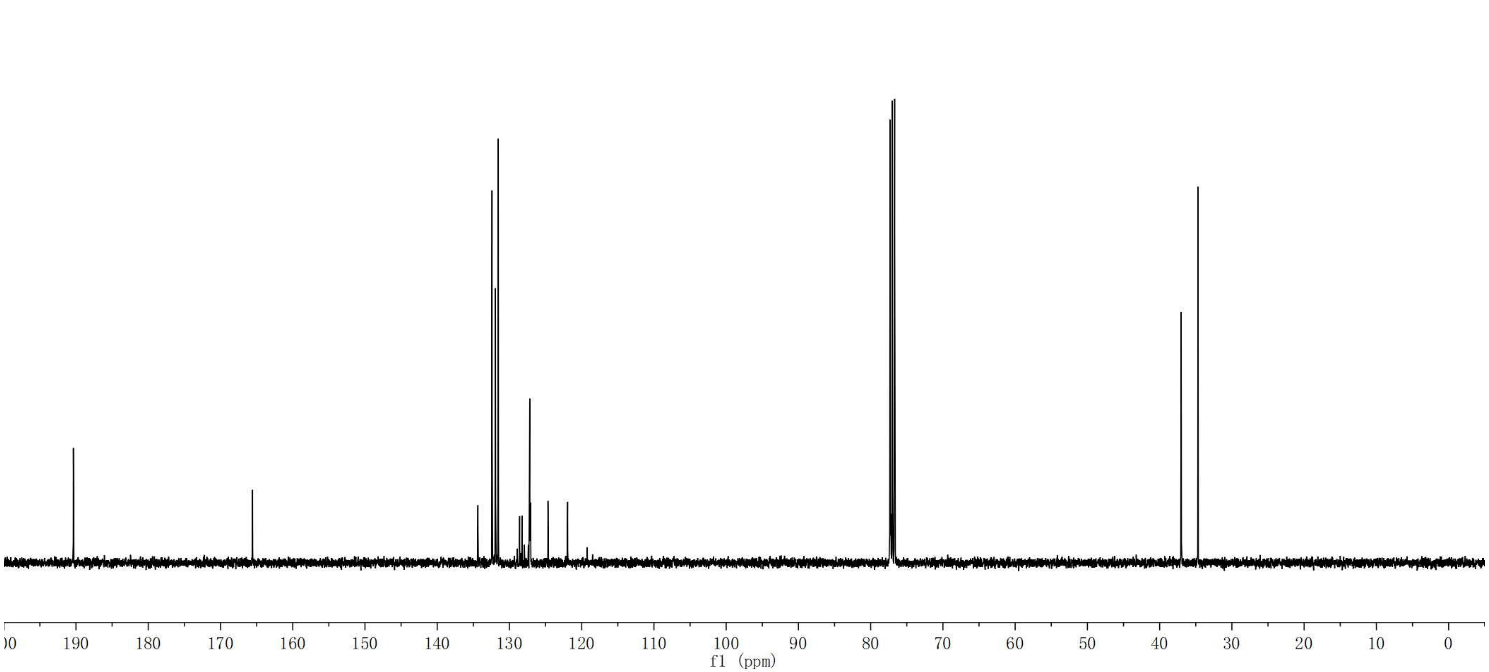
3i (^{19}F NMR 376 MHz, $CDCl_3$)

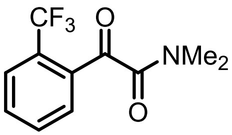


3j (^{1}H NMR 400 MHz, $CDCl_3$)

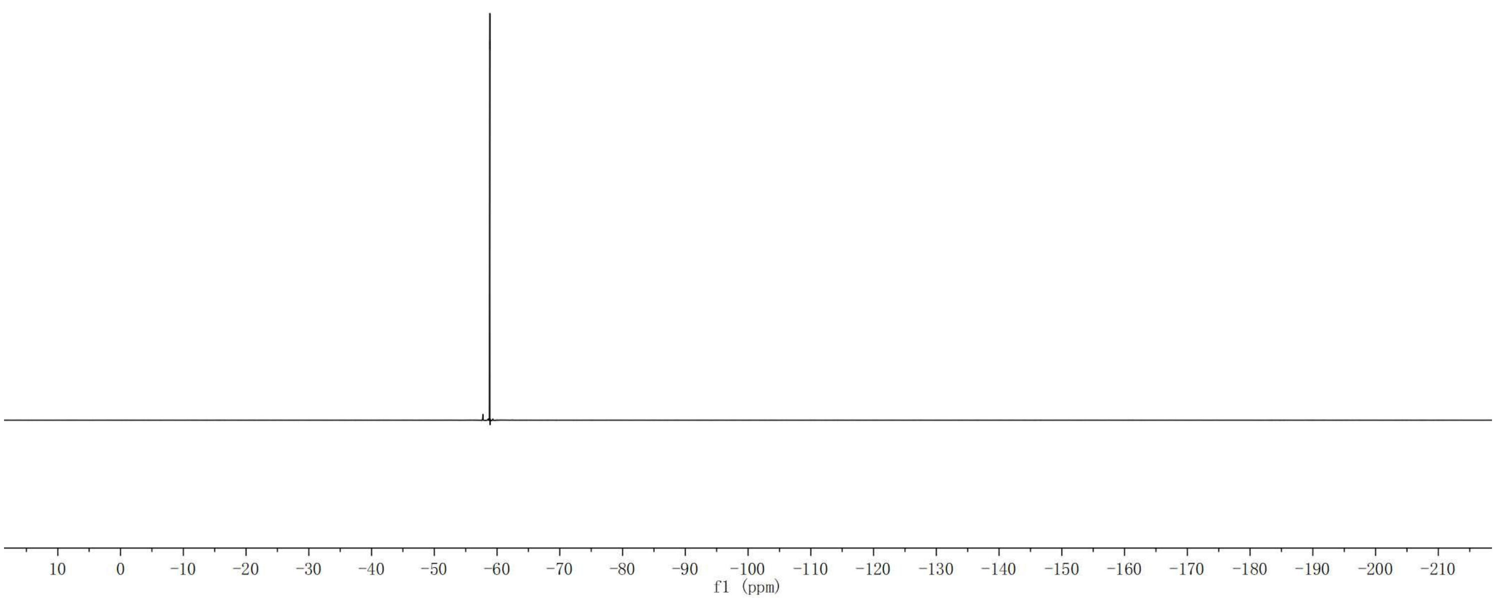


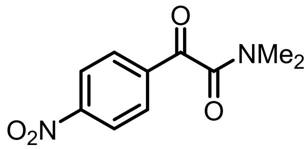
3j (^{13}C NMR 101 MHz, $CDCl_3$)



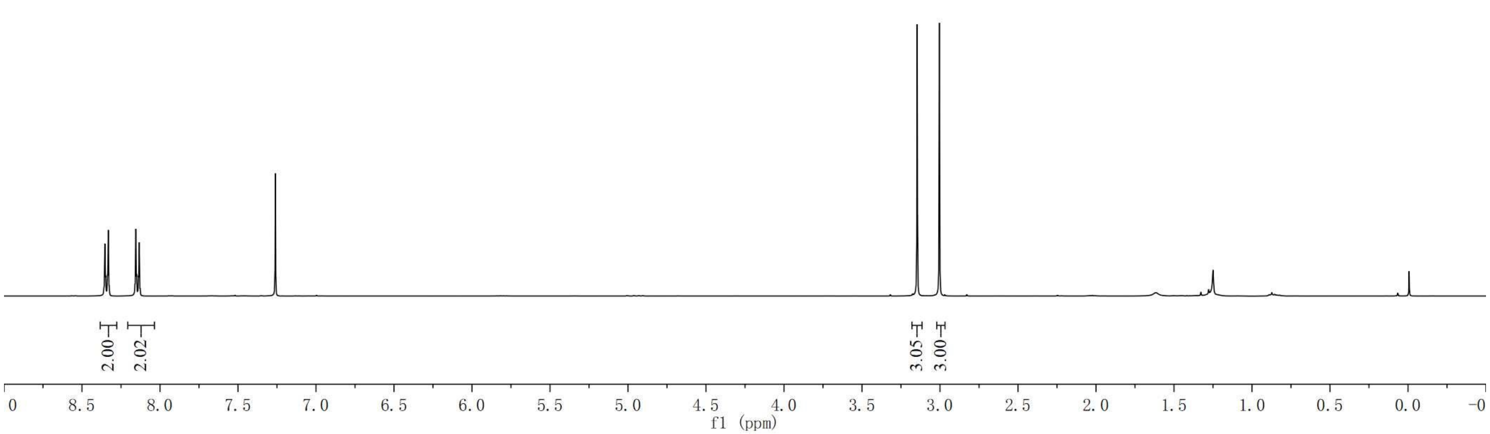


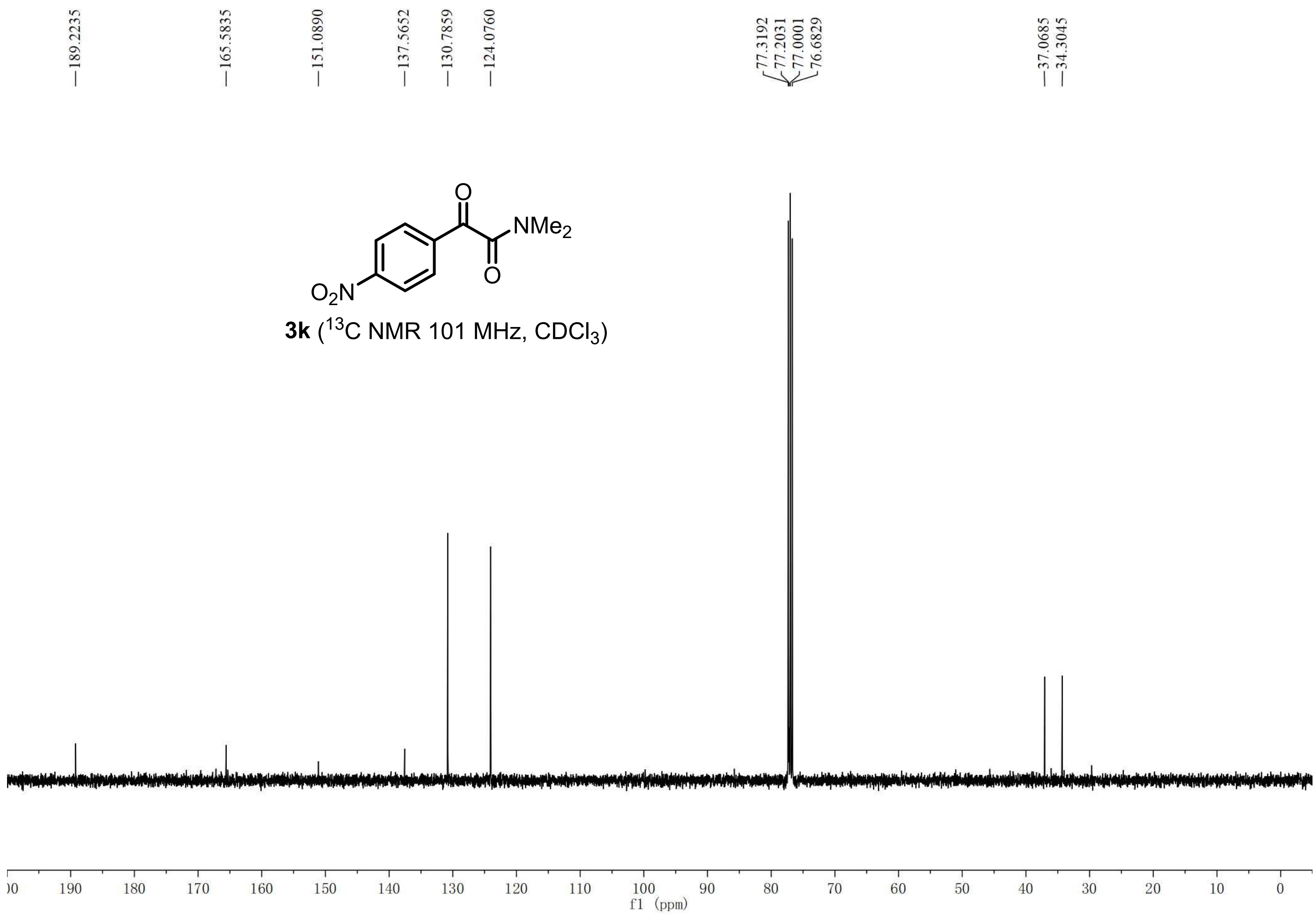
3j (^{19}F NMR 376 MHz, $CDCl_3$)



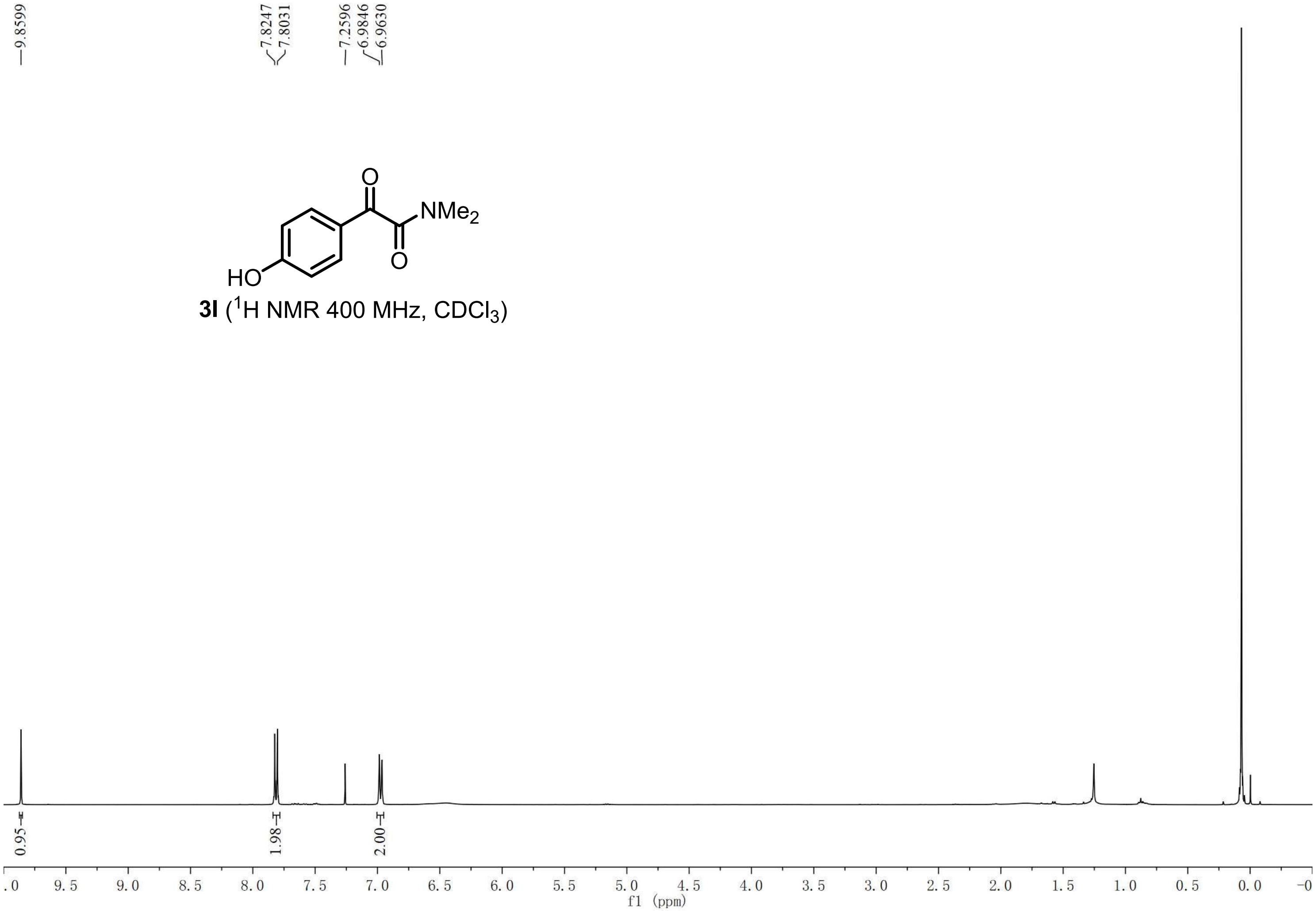


3k (^{1}H NMR 400 MHz, $CDCl_3$)

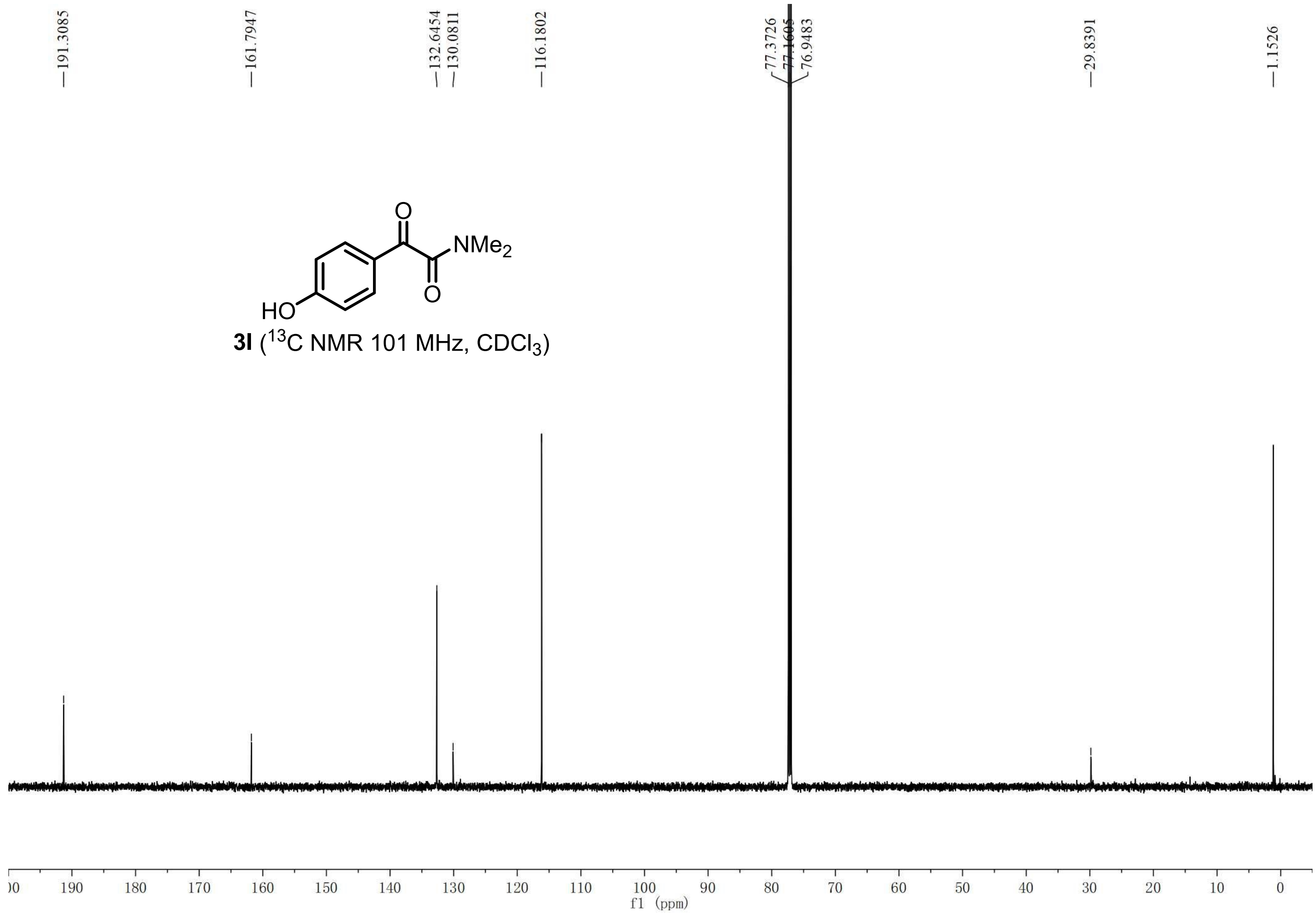


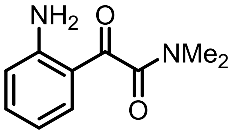


189.2235
165.5835
151.0890
137.5652
130.7859
124.0760
77.3192
77.2031
77.0001
76.6829
37.0685
34.3045
NMe2
O2N
O
O
3k (13C NMR 101 MHz, CDCl3)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

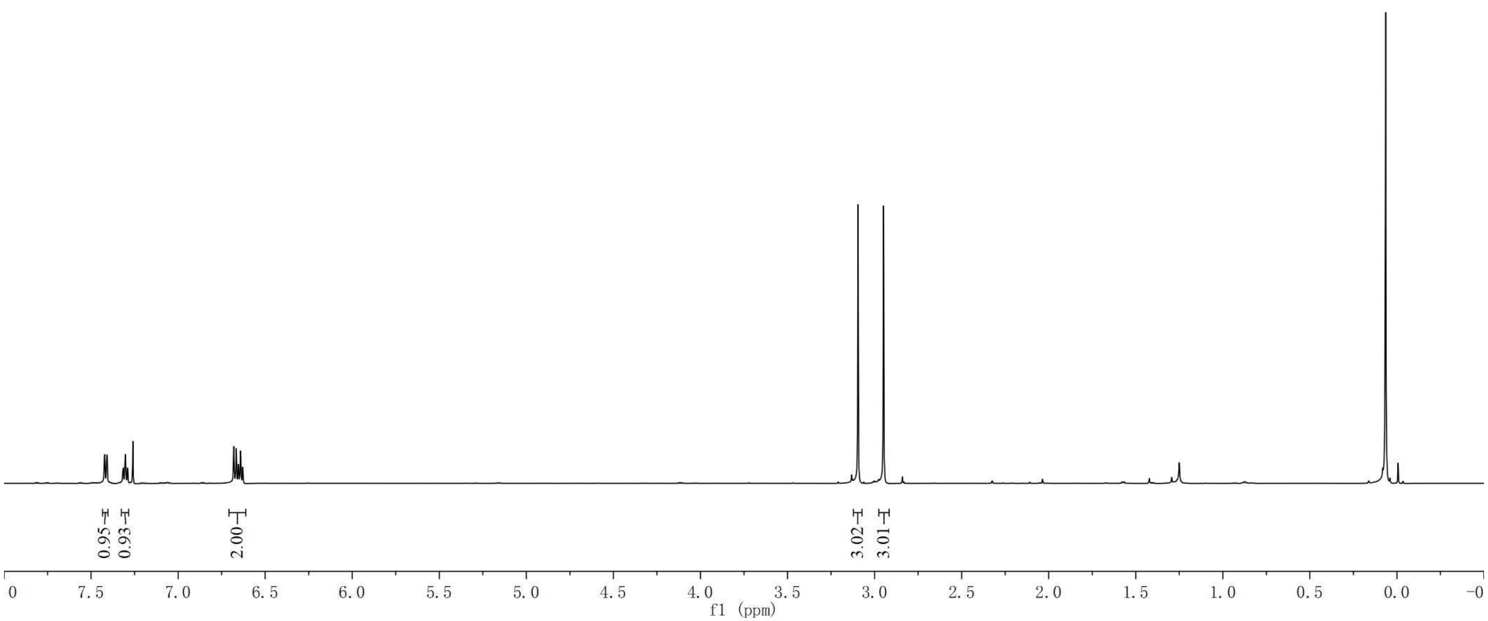


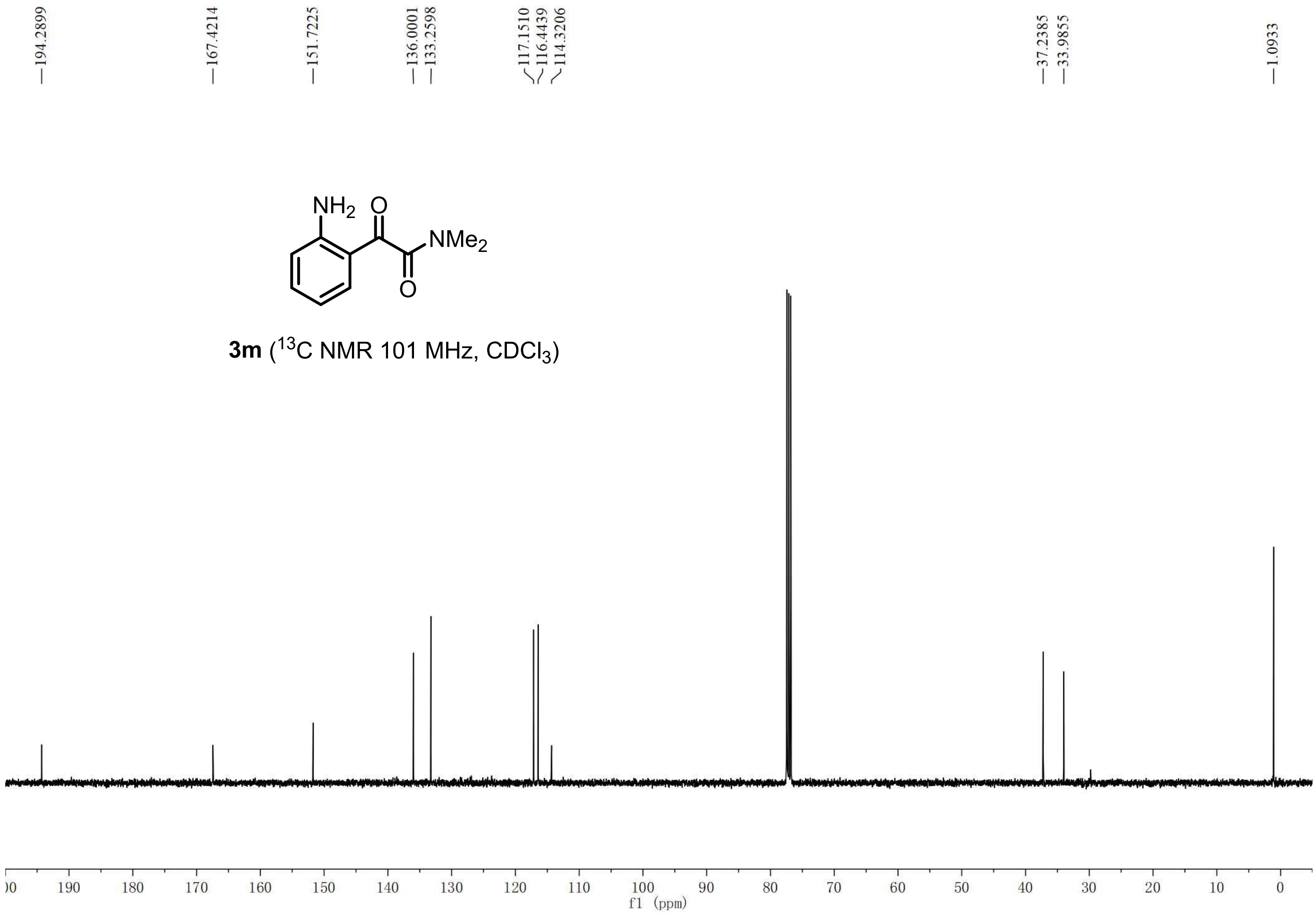
3l (^{1}H NMR 400 MHz, $CDCl_3$)


191.3085
161.7947
132.6454
130.0811
116.1802
77.3726
77.1605
76.9483
29.8391
1.1526
NMe2
HO
O
3l (13C NMR 101 MHz, CDCl3)
f1 (ppm)

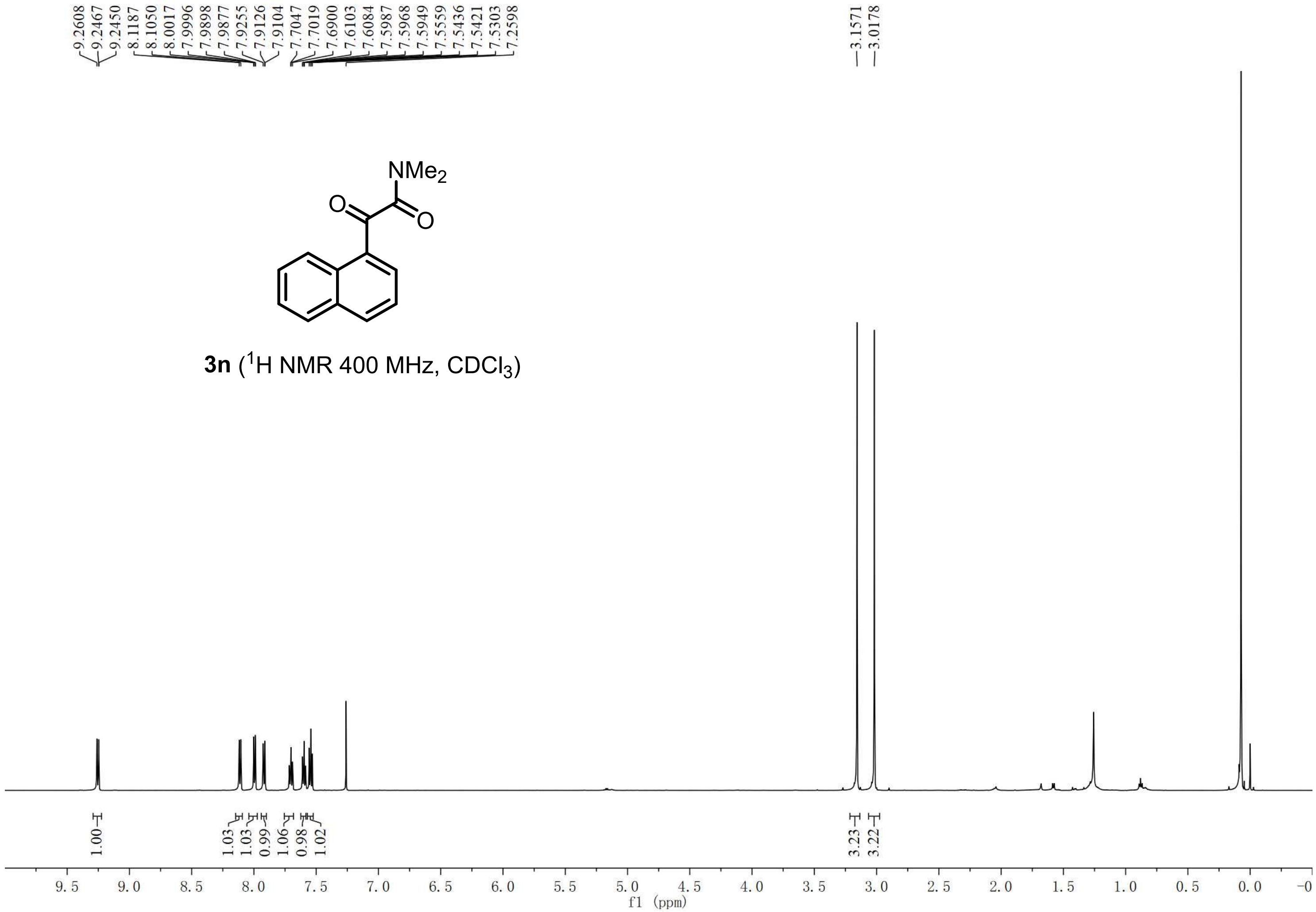


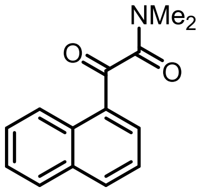
3m (^{1}H NMR 400 MHz, $CDCl_3$)



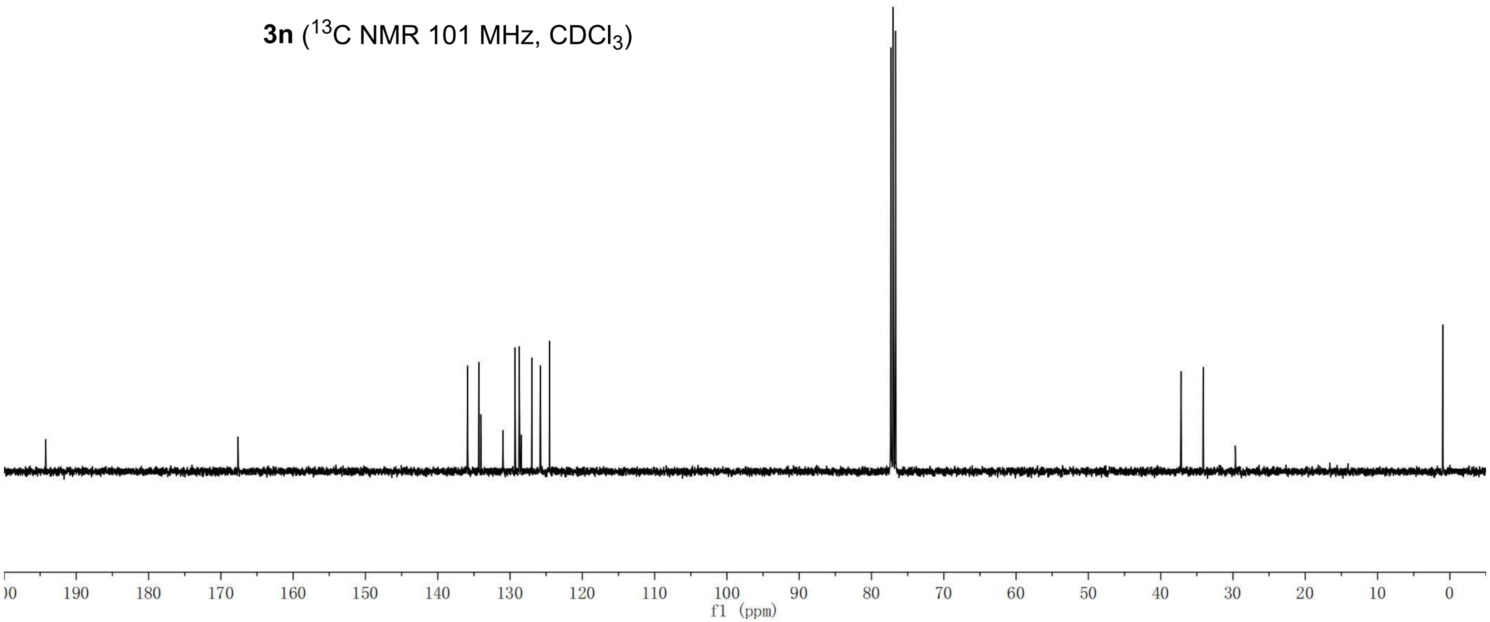


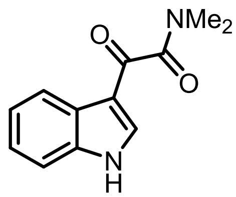
3m (^{13}C NMR 101 MHz, $CDCl_3$)


9.2608
9.2467
9.2450
8.1187
8.1050
8.0017
7.9996
7.9898
7.9877
7.9255
7.9126
7.9104
7.7047
7.7019
7.6900
7.6103
7.6084
7.5987
7.5968
7.5949
7.5559
7.5436
7.5421
7.5303
7.2598
3.1571
3.0178
NMe2
O
O
3n (1H NMR 400 MHz, CDCl3)
1.00
1.03
1.03
0.99
1.06
0.98
1.02
3.23
3.22
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
f1 (ppm)

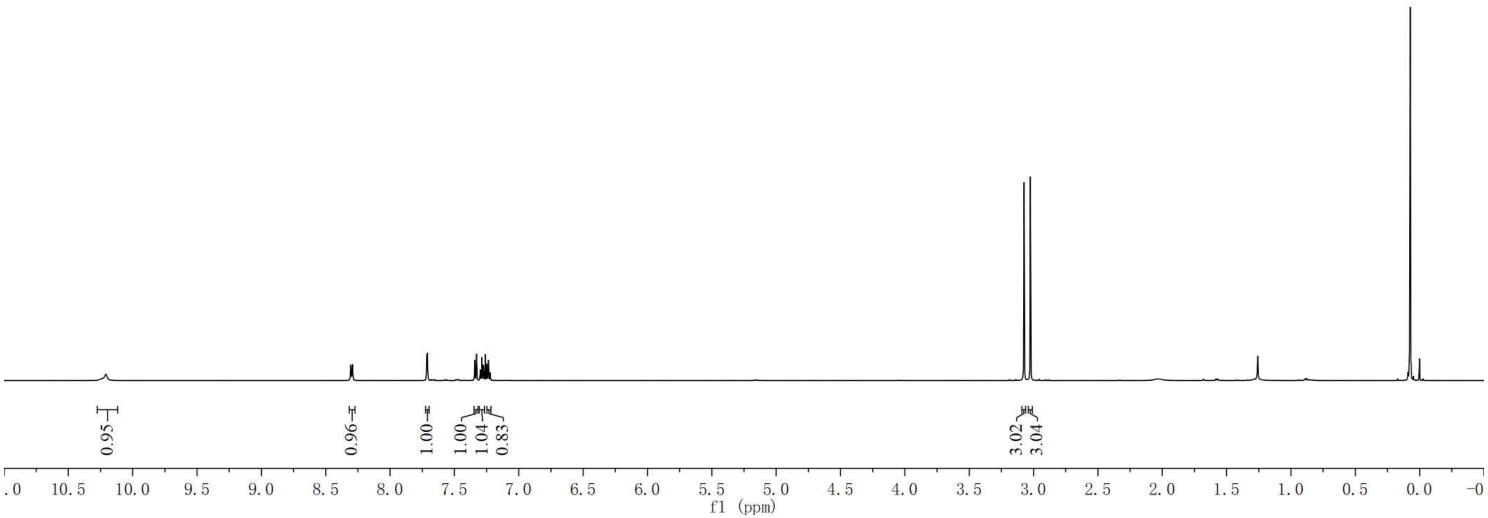


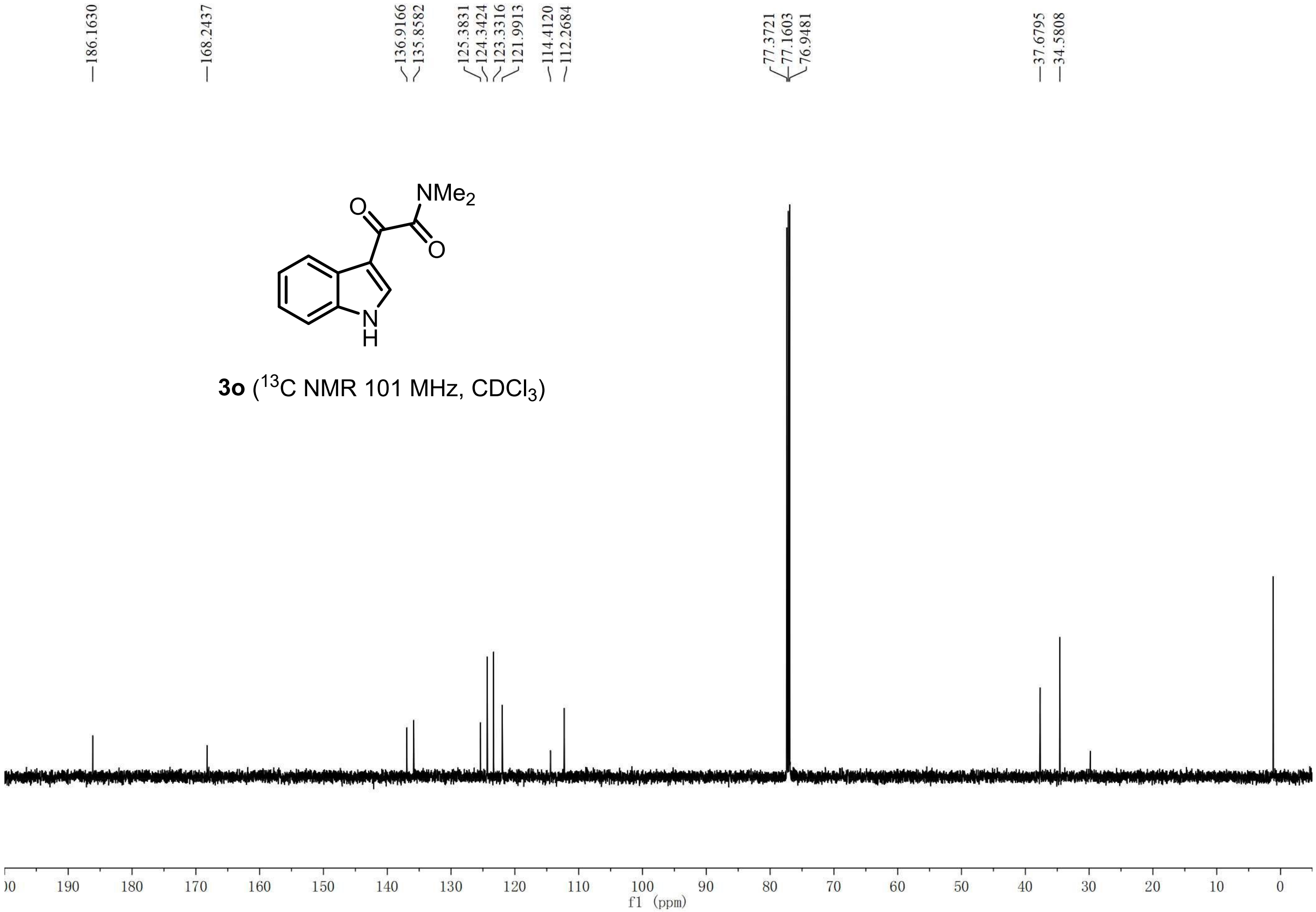
3n (^{13}C NMR 101 MHz, $CDCl_3$)





3o (^{1}H NMR 400 MHz, $CDCl_3$)

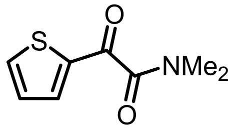




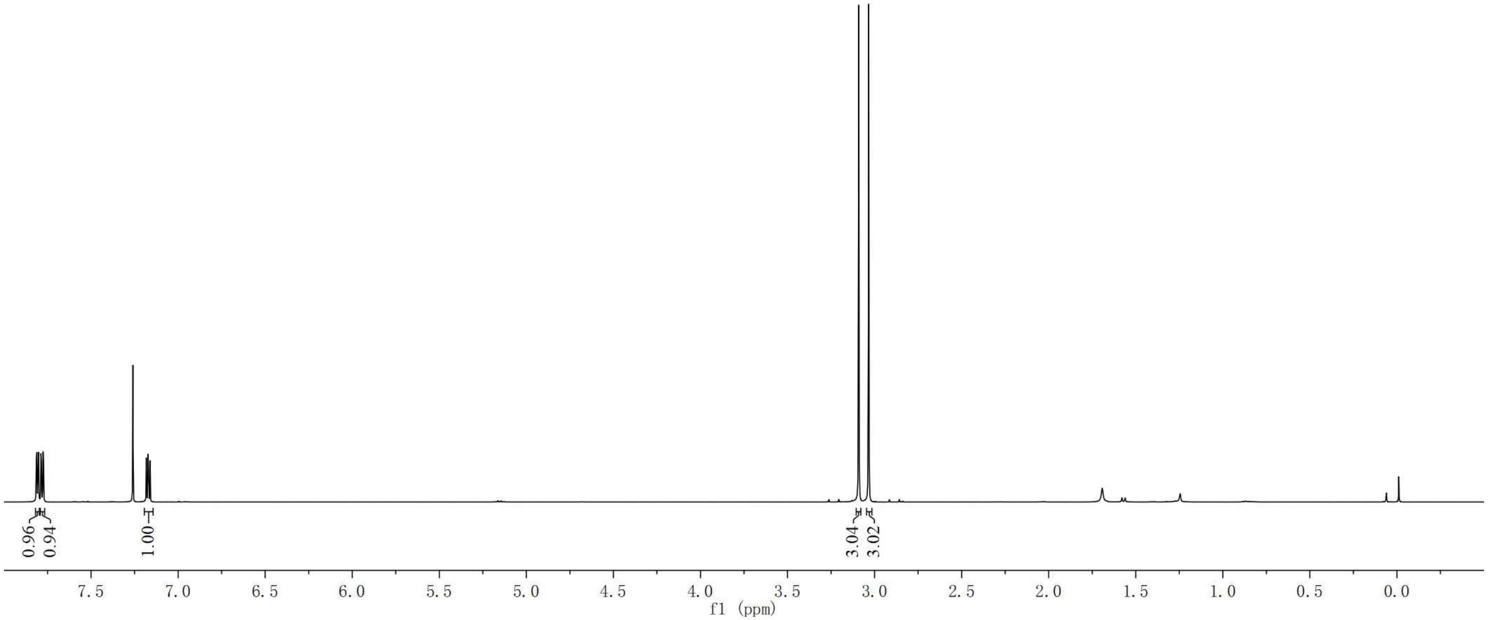
3o (^{13}C NMR 101 MHz, $CDCl_3$)

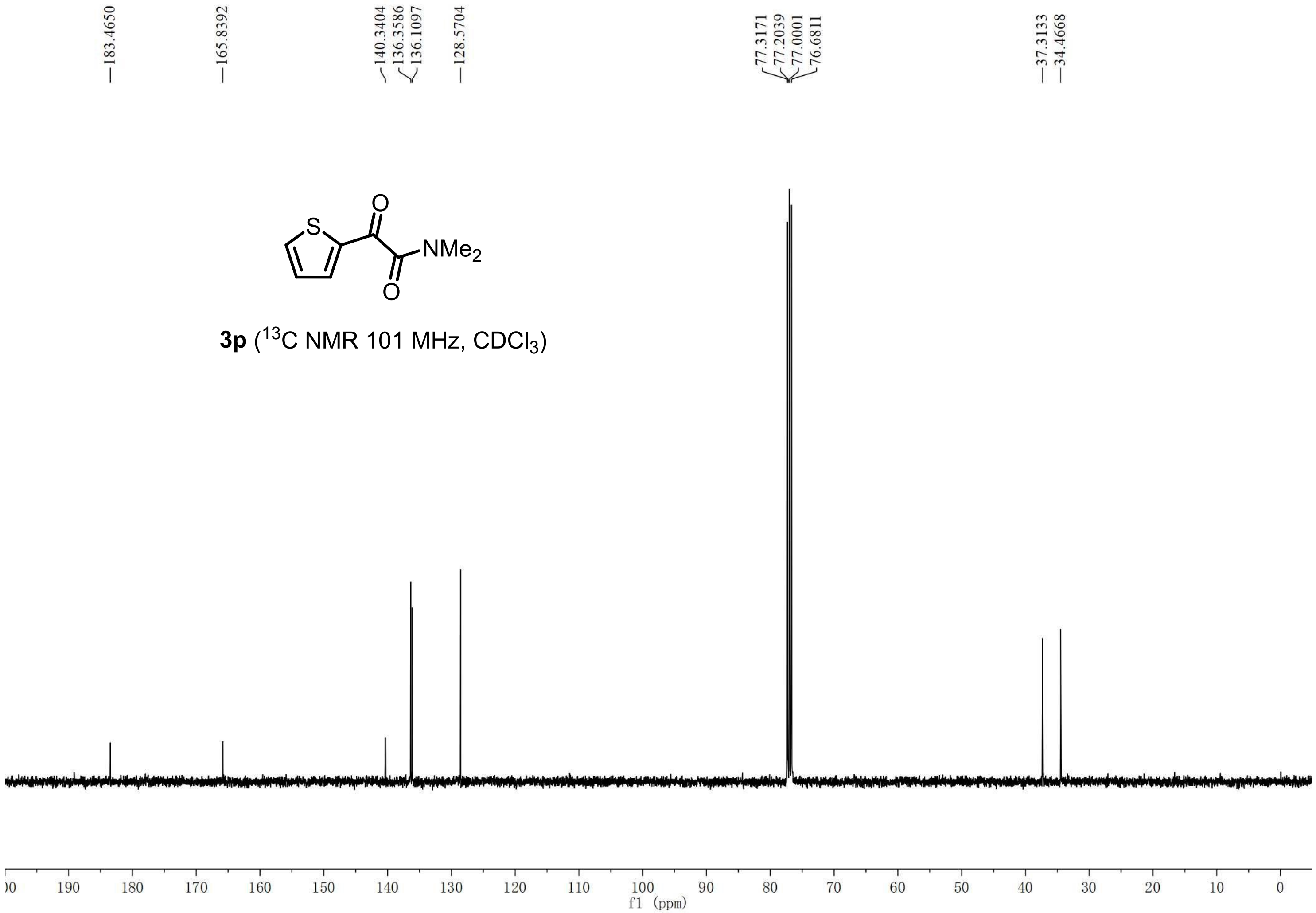
7.8141
7.8113
7.8046
7.8016
7.7879
7.7850
7.7757
7.7728
7.2599
7.1827
7.1730
7.1704
7.1608

3.0910
3.0339

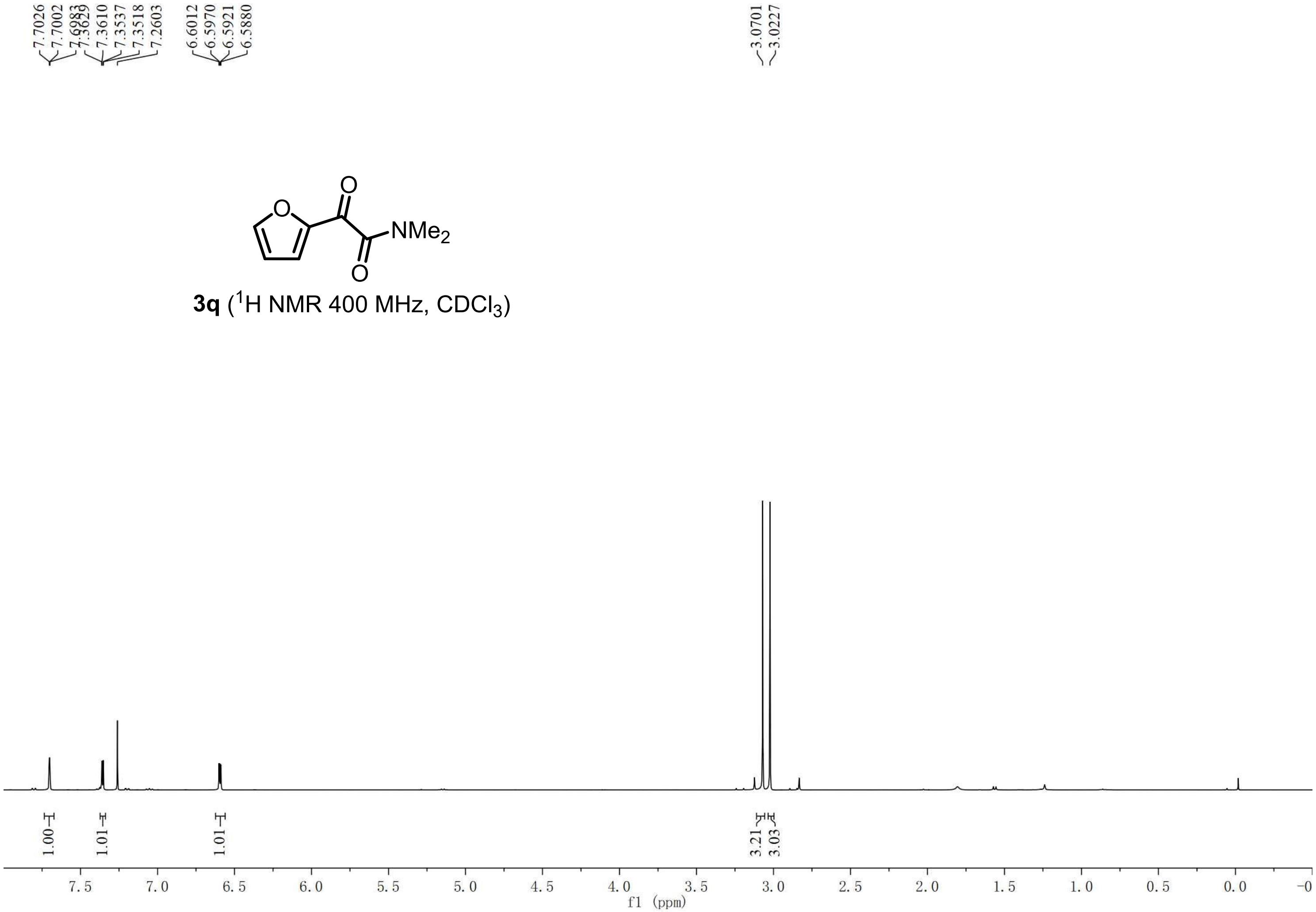


3p (^{1}H NMR 400 MHz, $CDCl_3$)

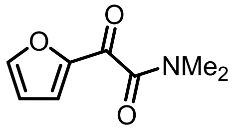




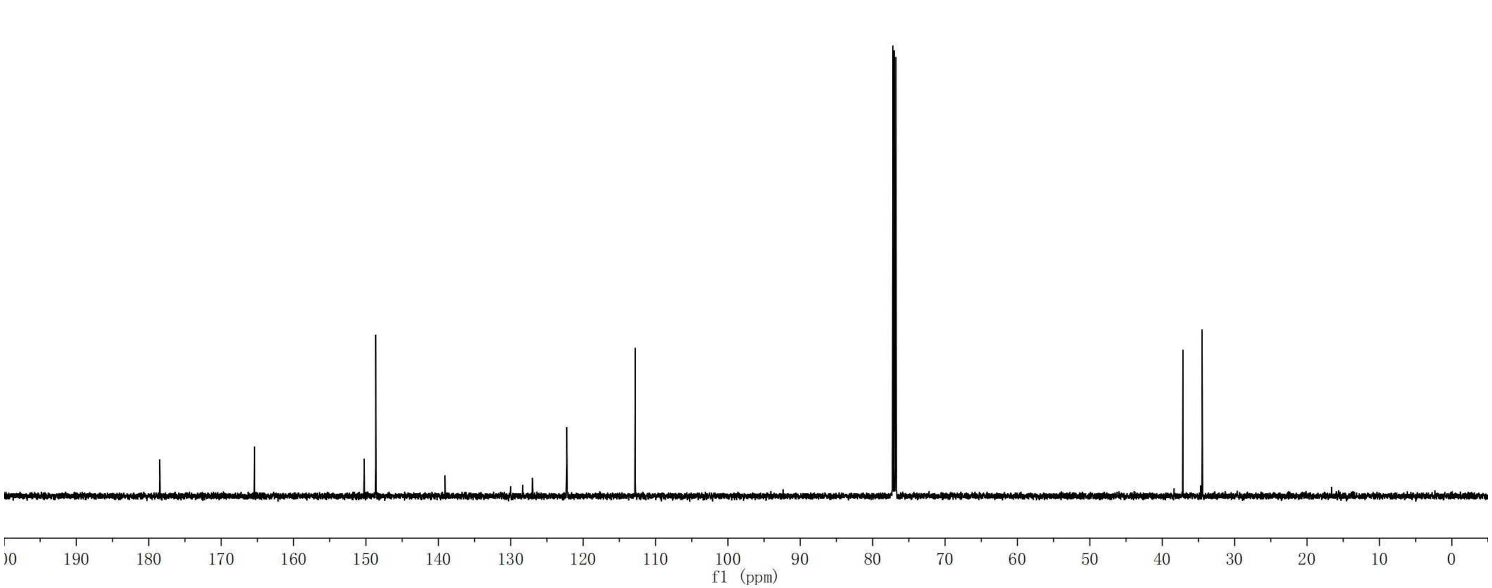
3p (^{13}C NMR 101 MHz, $CDCl_3$)

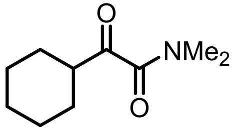


3q (^{1}H NMR 400 MHz, $CDCl_3$)

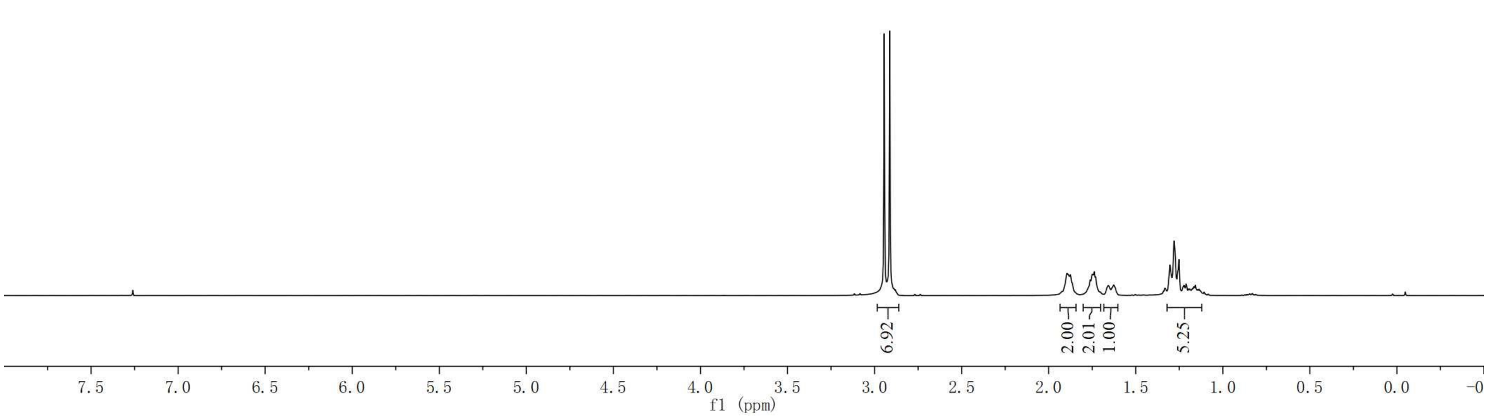


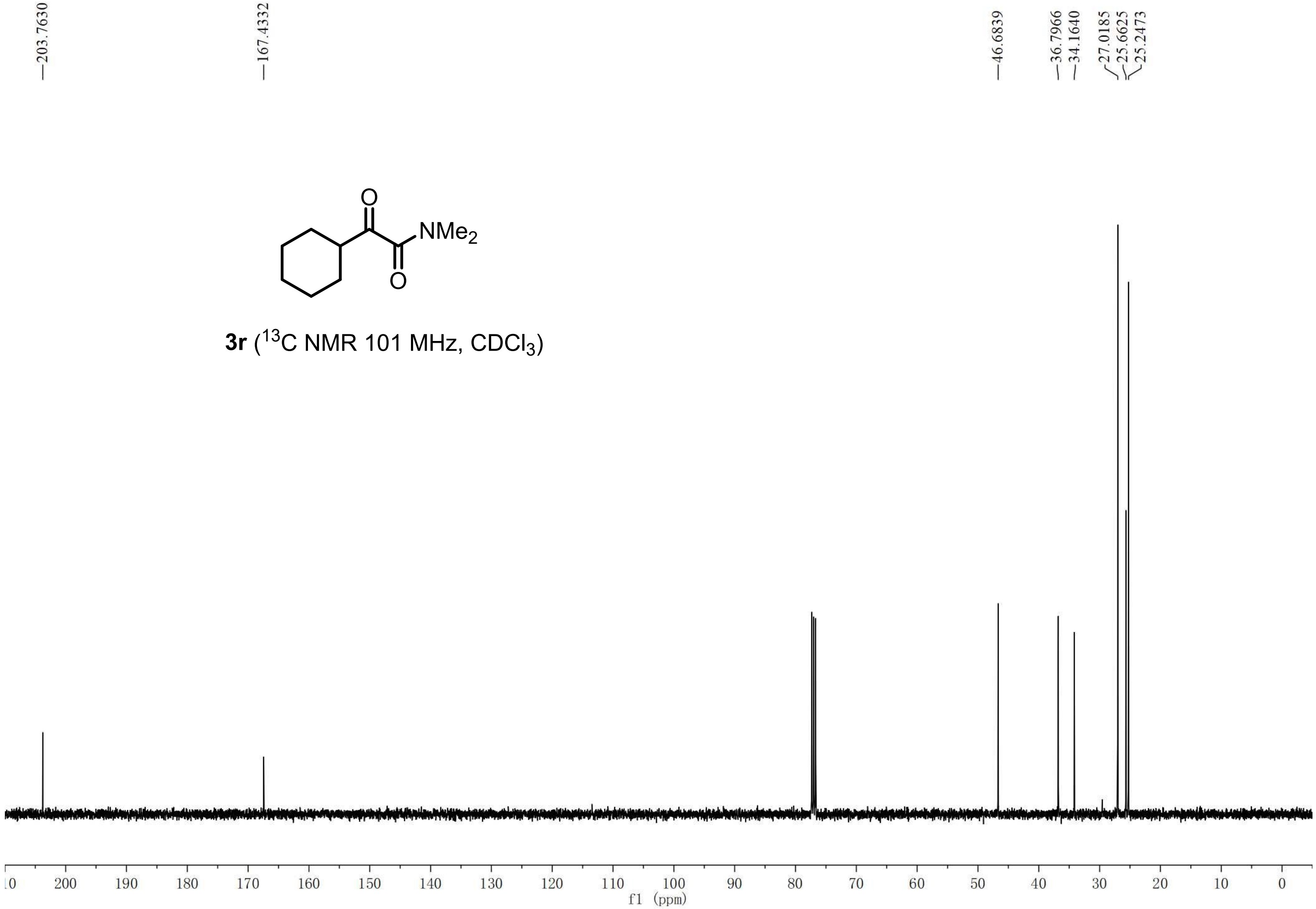
3q (^{13}C NMR 101 MHz, $CDCl_3$)



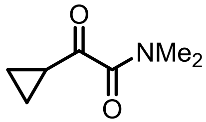


3r (^{1}H NMR 400 MHz, $CDCl_3$)

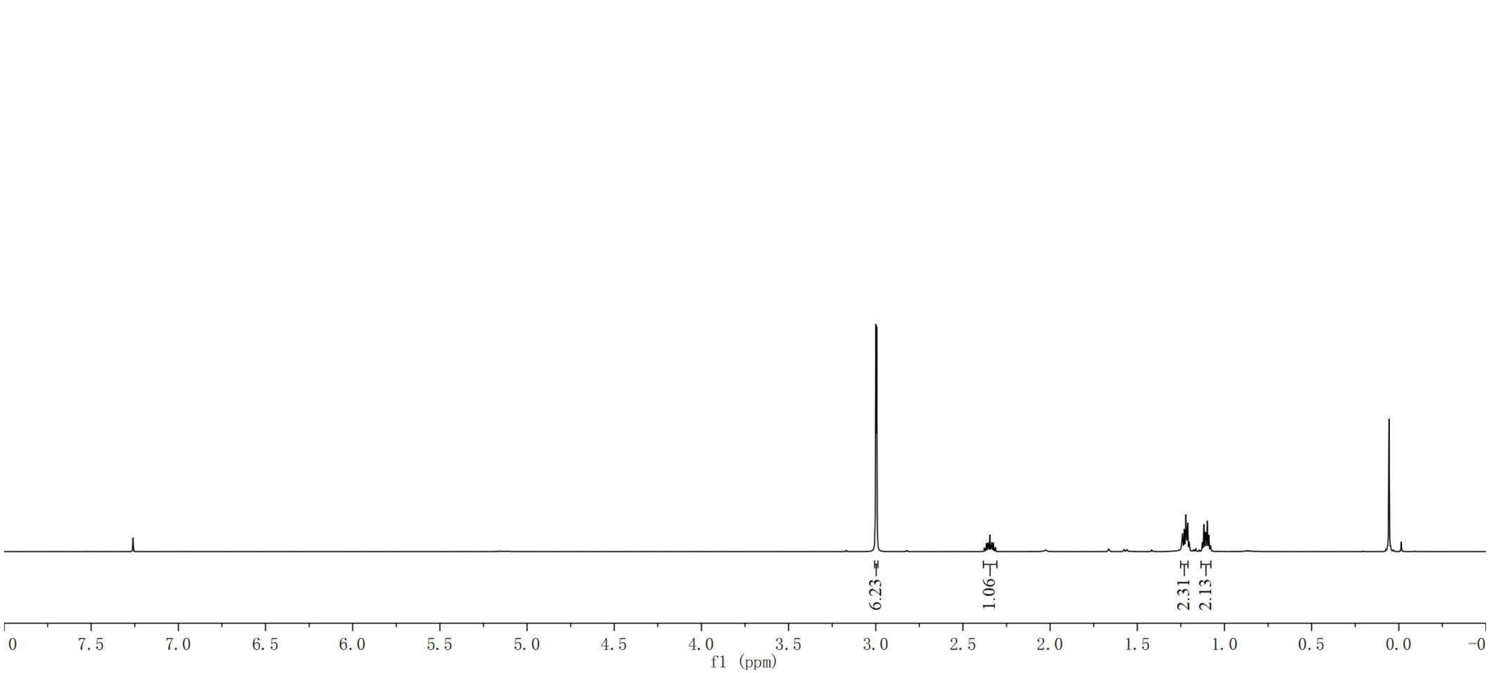


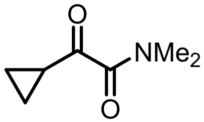


3r (^{13}C NMR 101 MHz, $CDCl_3$)

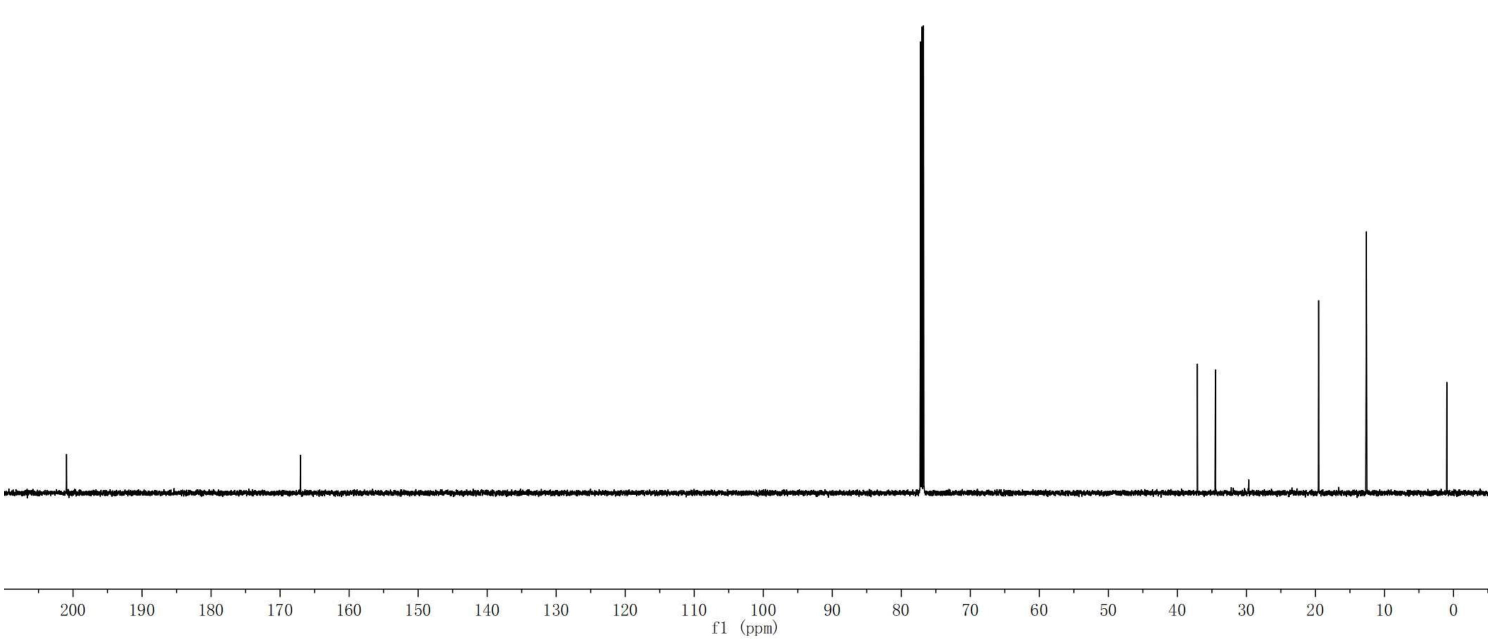


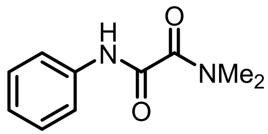
3s (^{1}H NMR 400 MHz, $CDCl_3$)



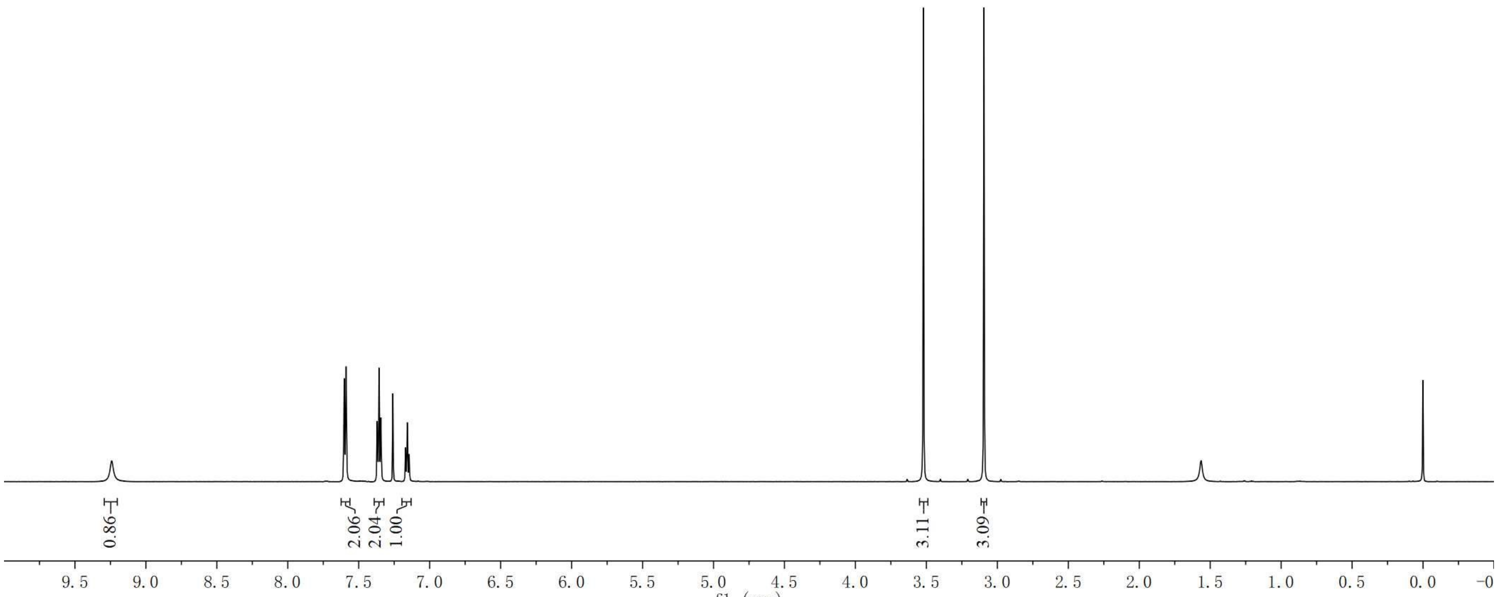


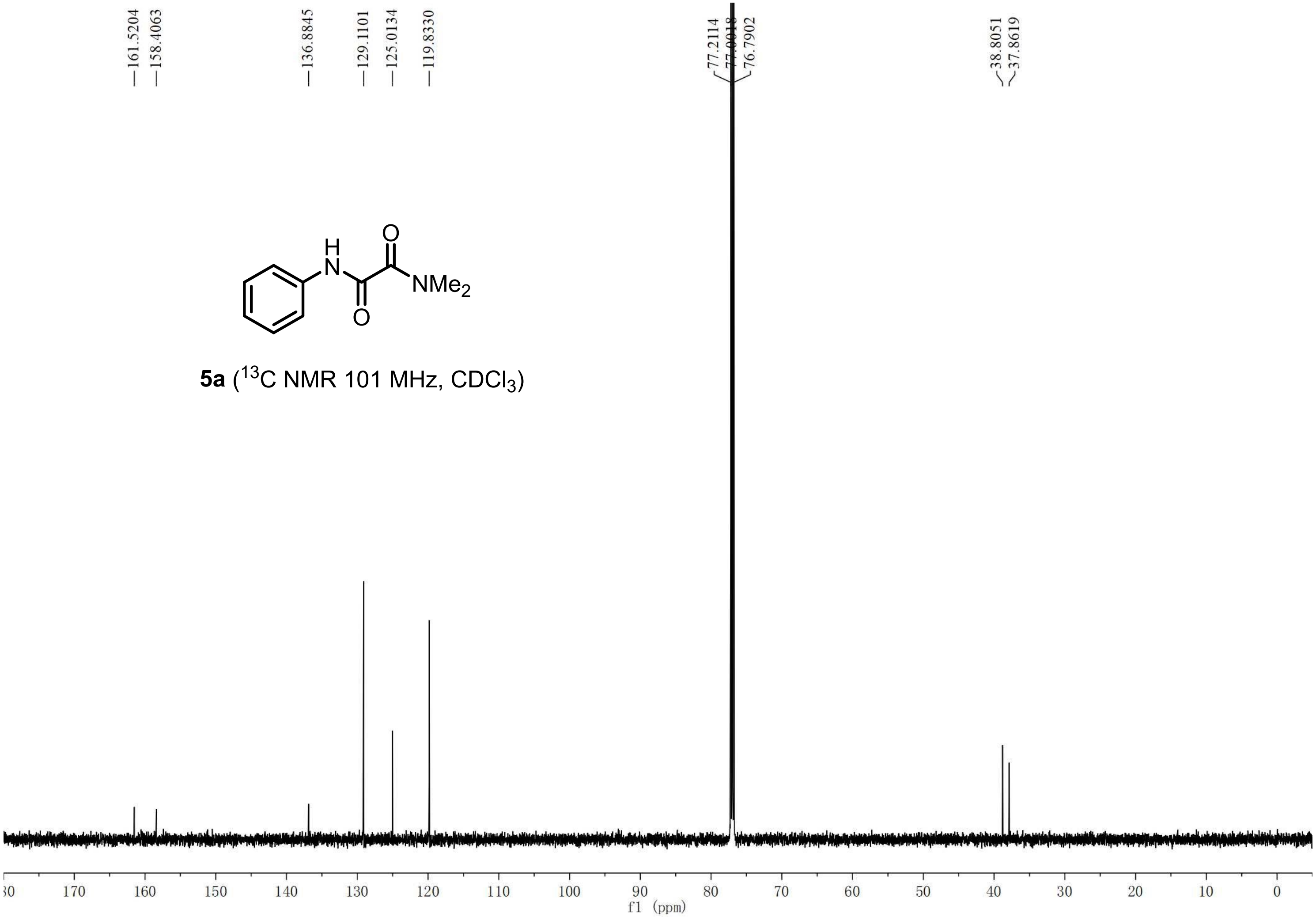
3s (^{13}C NMR 101 MHz, $CDCl_3$)



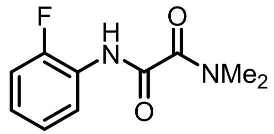


5a (^{1}H NMR 400 MHz, $CDCl_3$)

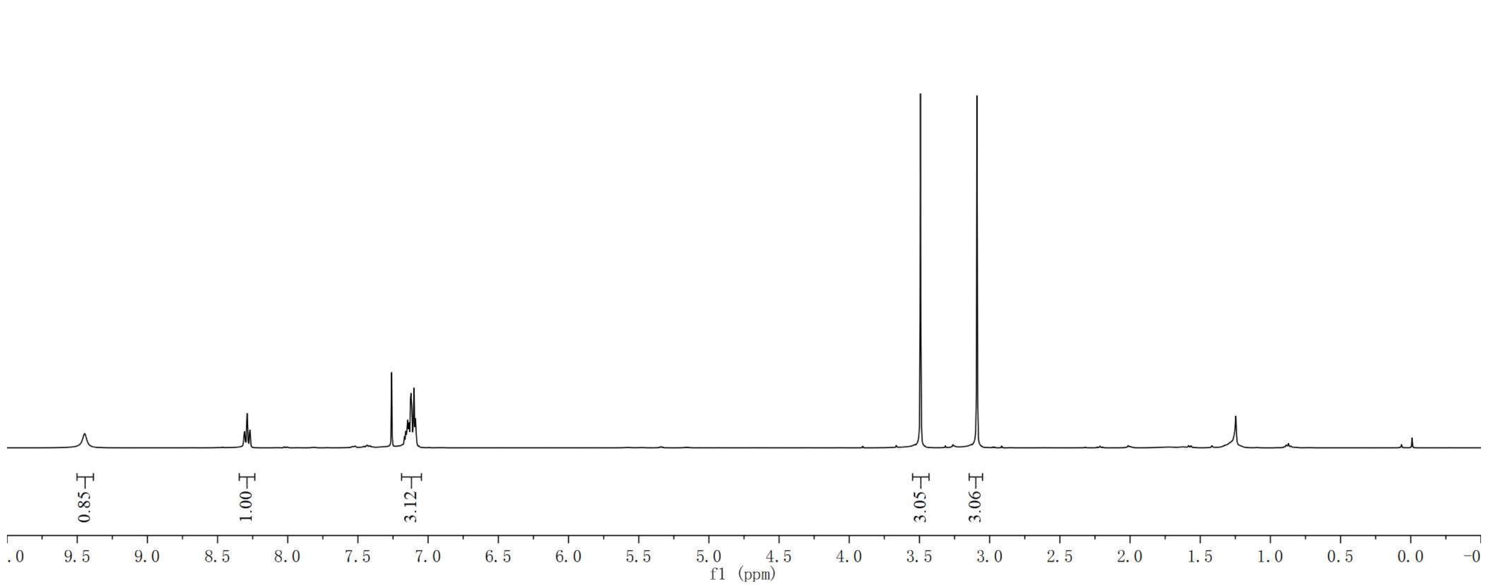


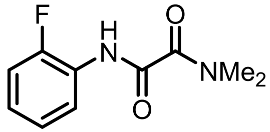


5a (^{13}C NMR 101 MHz, $CDCl_3$)

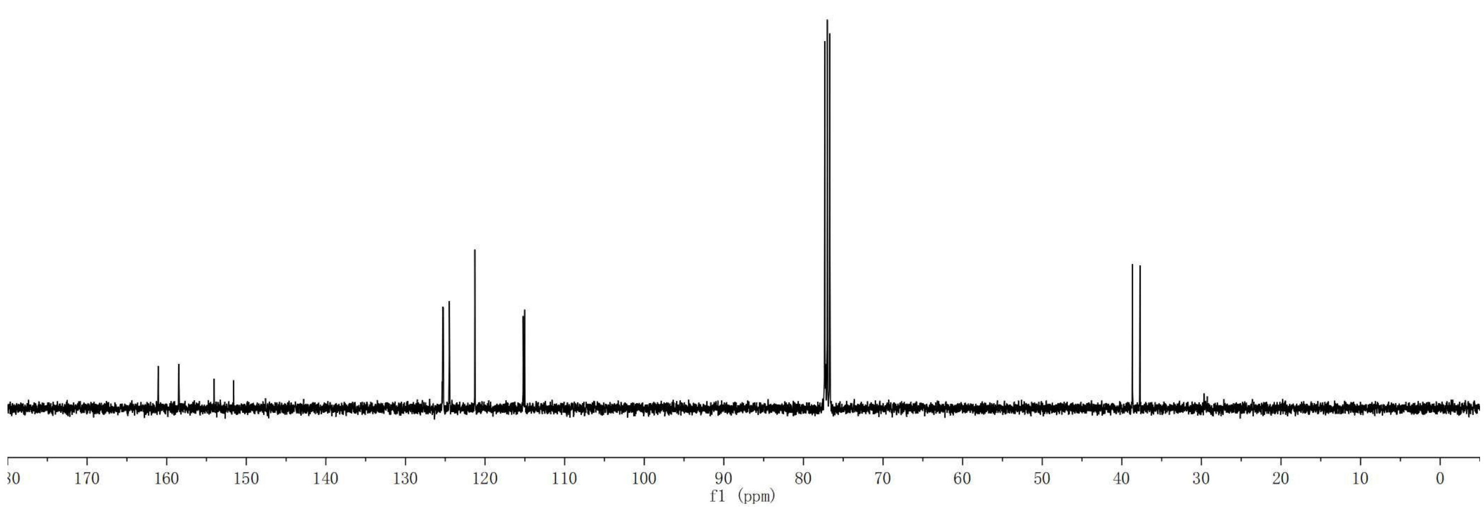


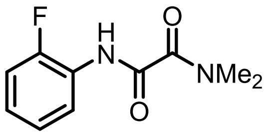
5b (^{1}H NMR 400 MHz, $CDCl_3$)



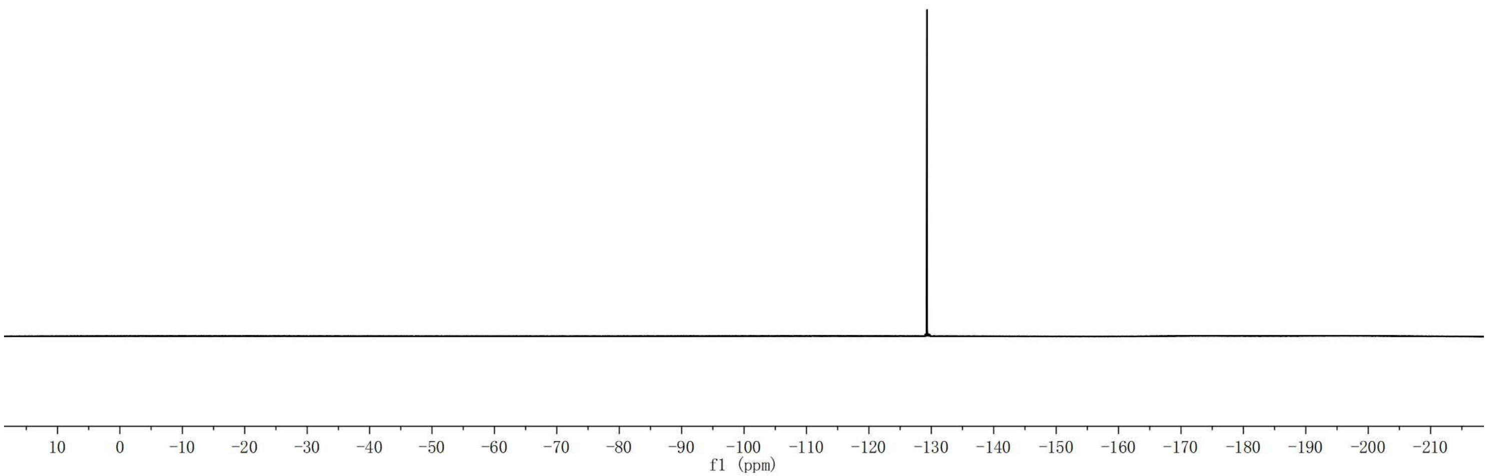


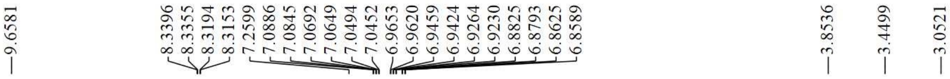
5b (^{13}C NMR 101 MHz, $CDCl_3$)

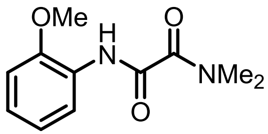




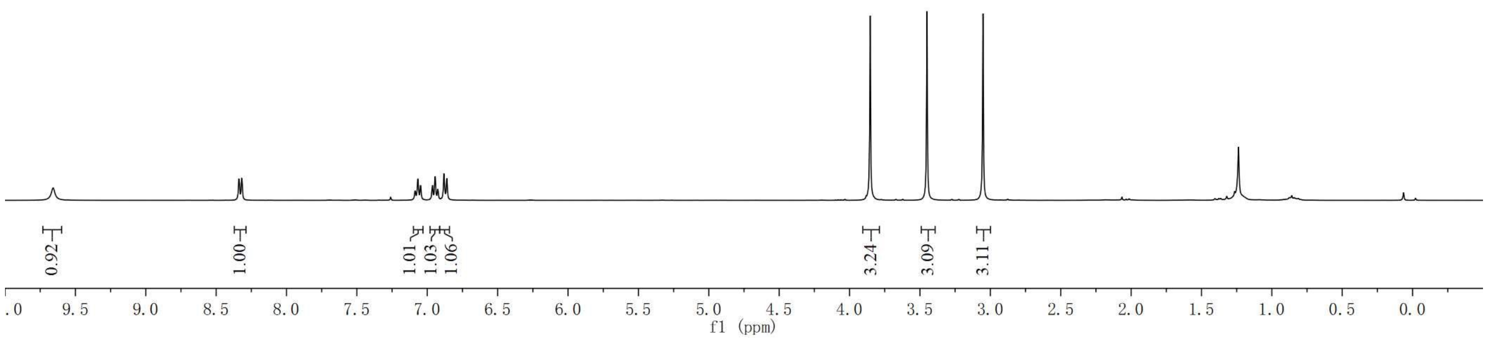
5b (^{19}F NMR 376 MHz, $CDCl_3$)

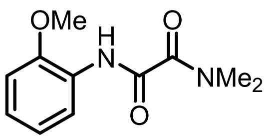




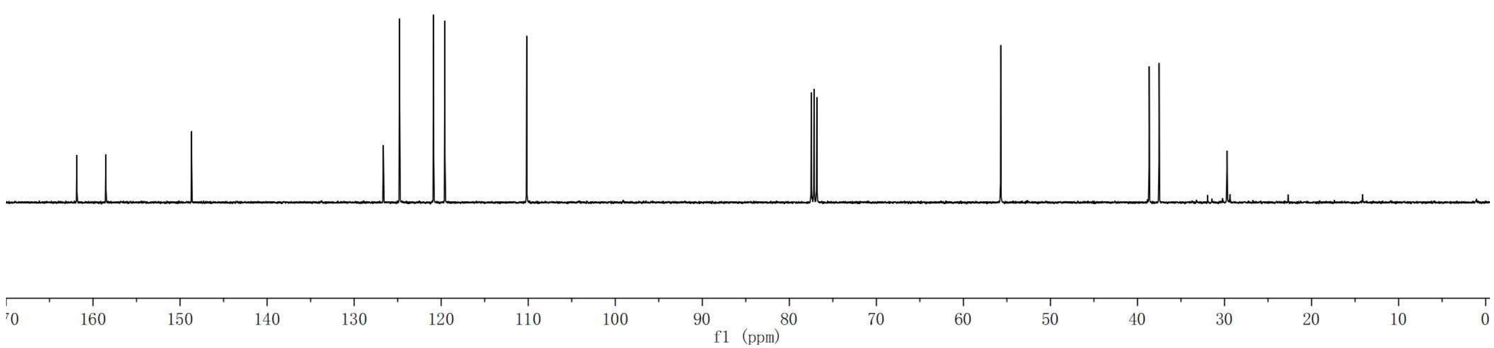


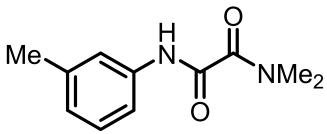
5c (^{1}H NMR 400 MHz, $CDCl_3$)



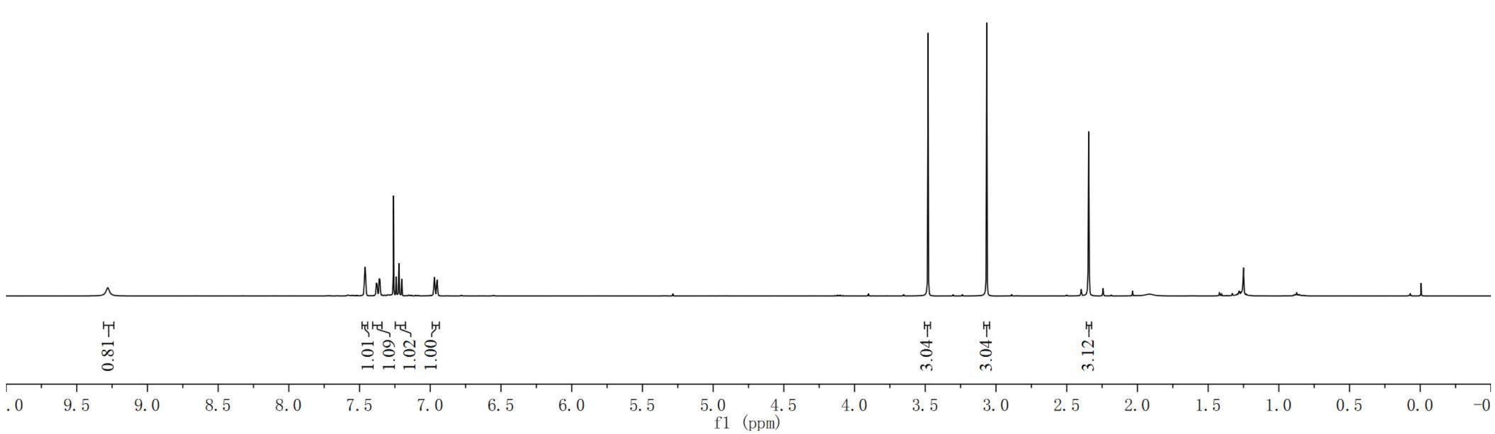


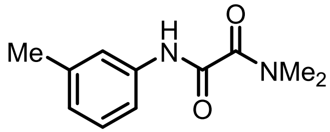
5c (^{13}C NMR 101 MHz, $CDCl_3$)



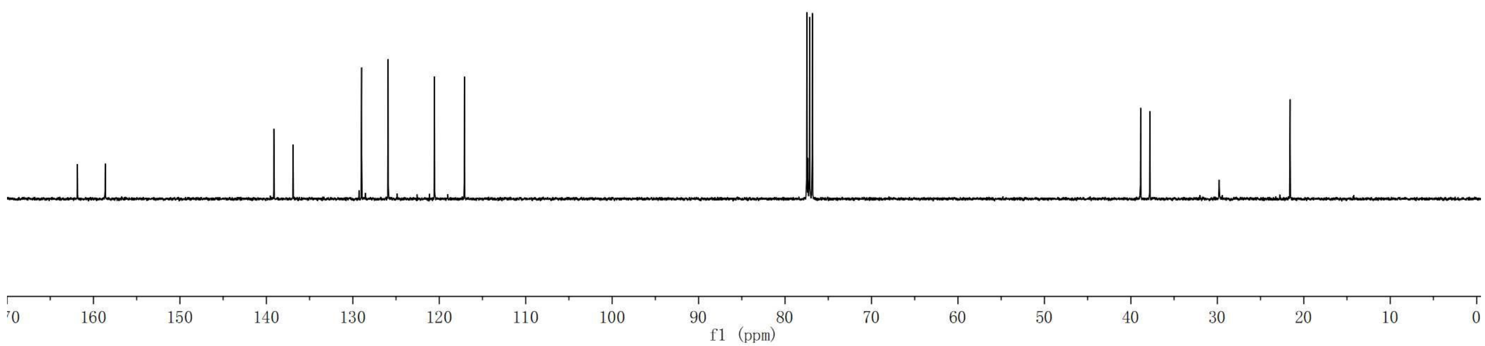


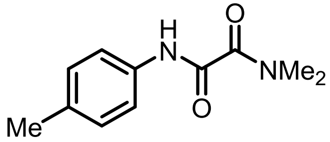
5d (^{1}H NMR 400 MHz, $CDCl_3$)



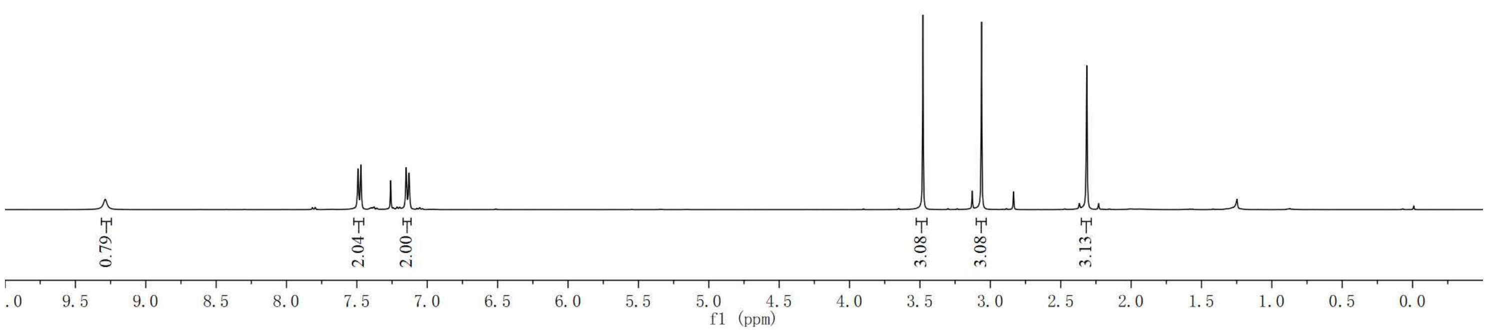


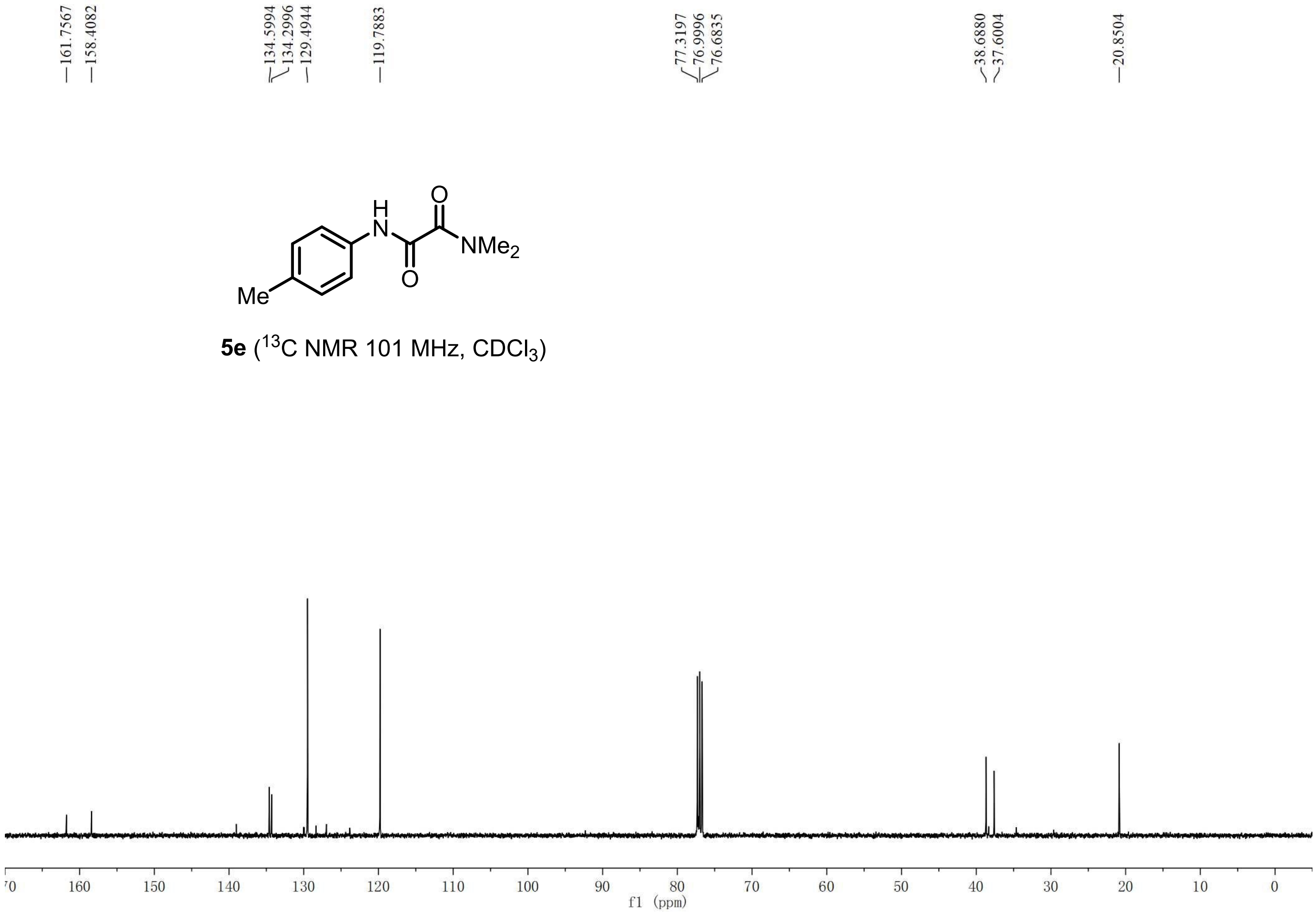
5d (^{13}C NMR 101 MHz, $CDCl_3$)



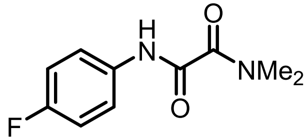


5e (^{1}H NMR 400 MHz, $CDCl_3$)

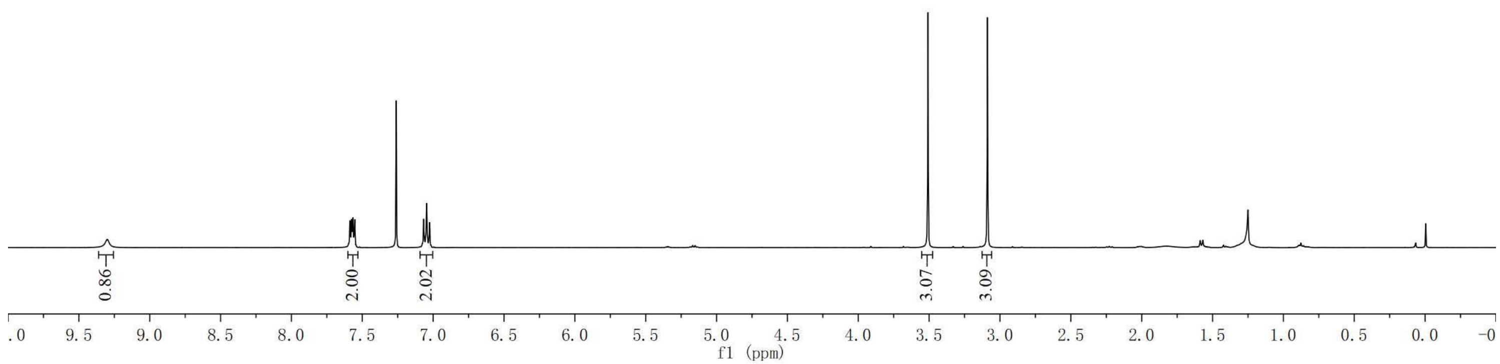


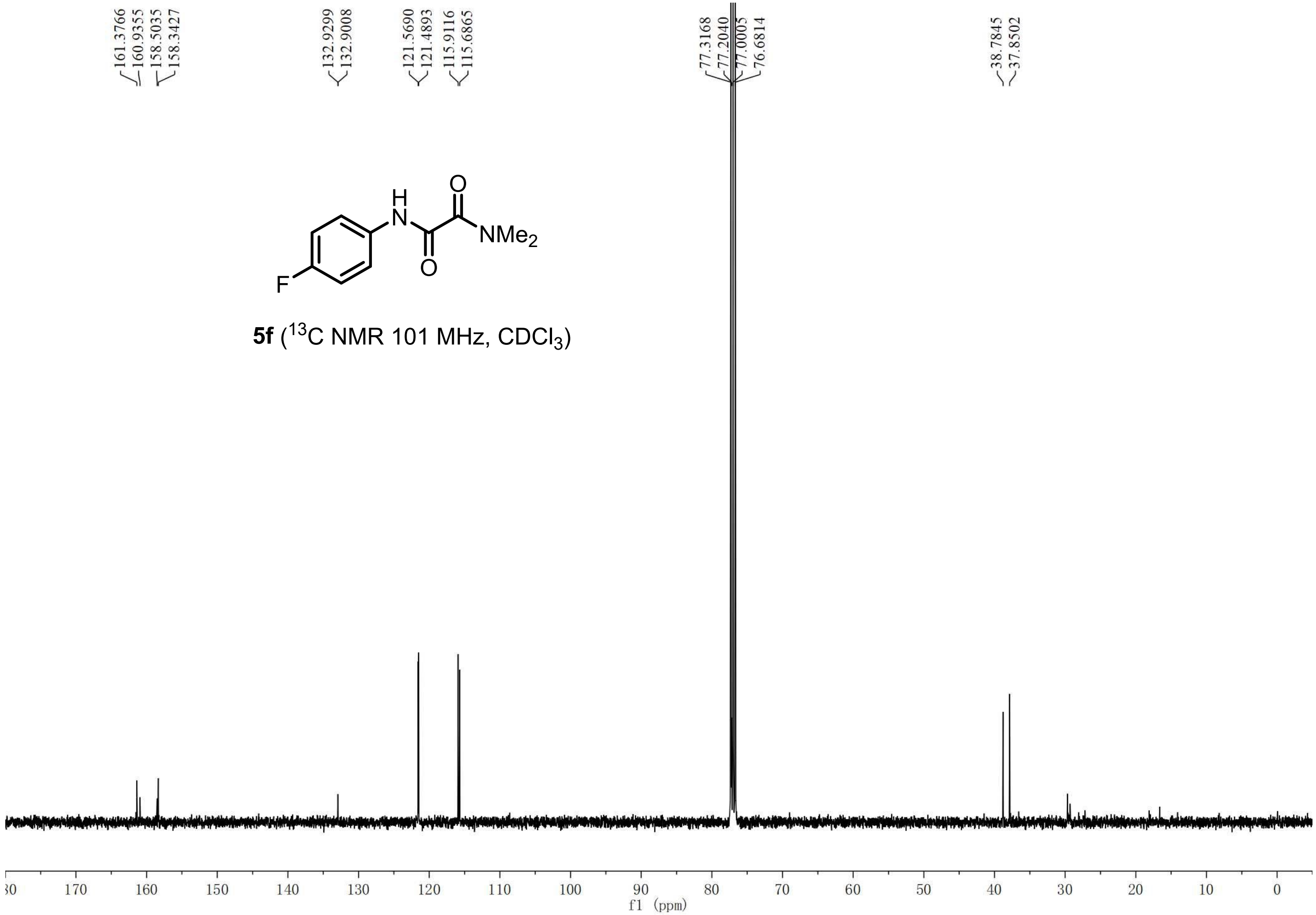


5e (^{13}C NMR 101 MHz, $CDCl_3$)

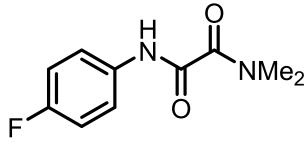


5f (^{1}H NMR 400 MHz, $CDCl_3$)

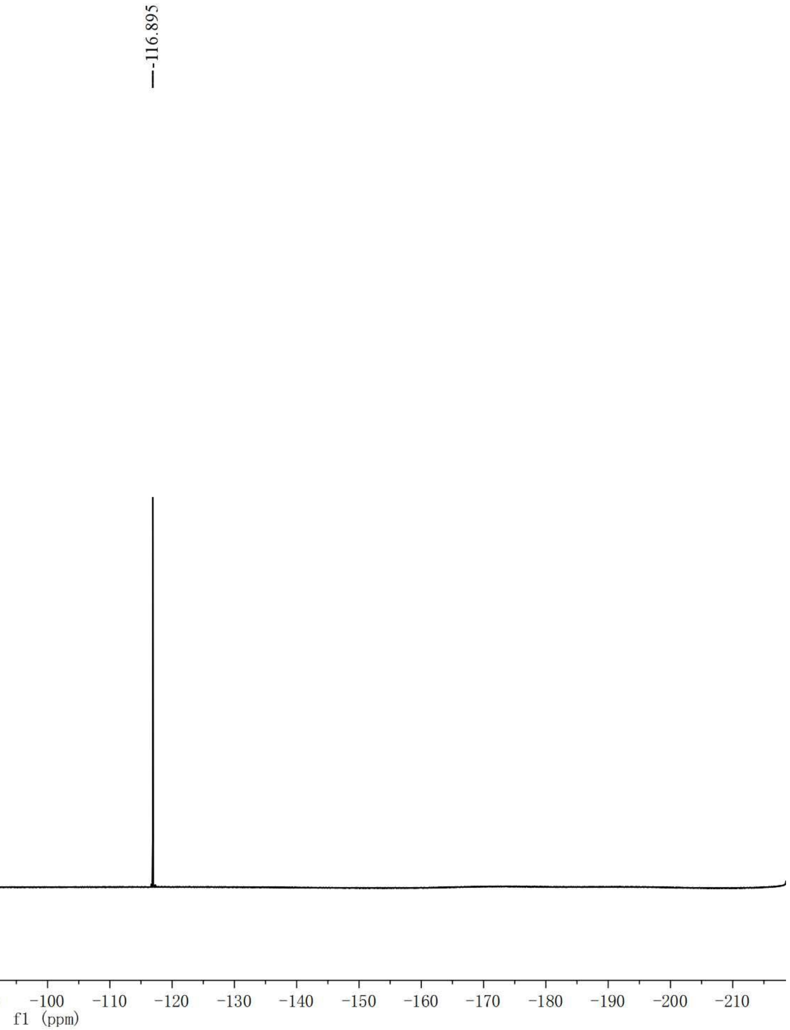


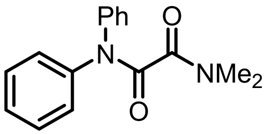


5f (^{13}C NMR 101 MHz, $CDCl_3$)

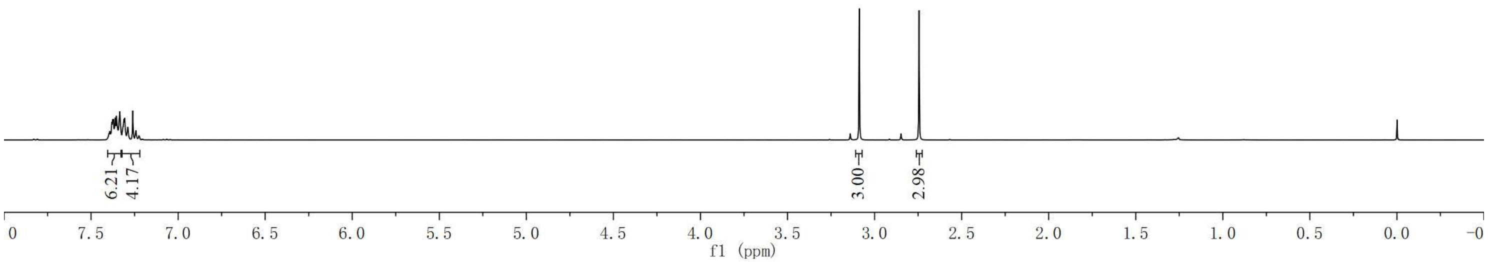


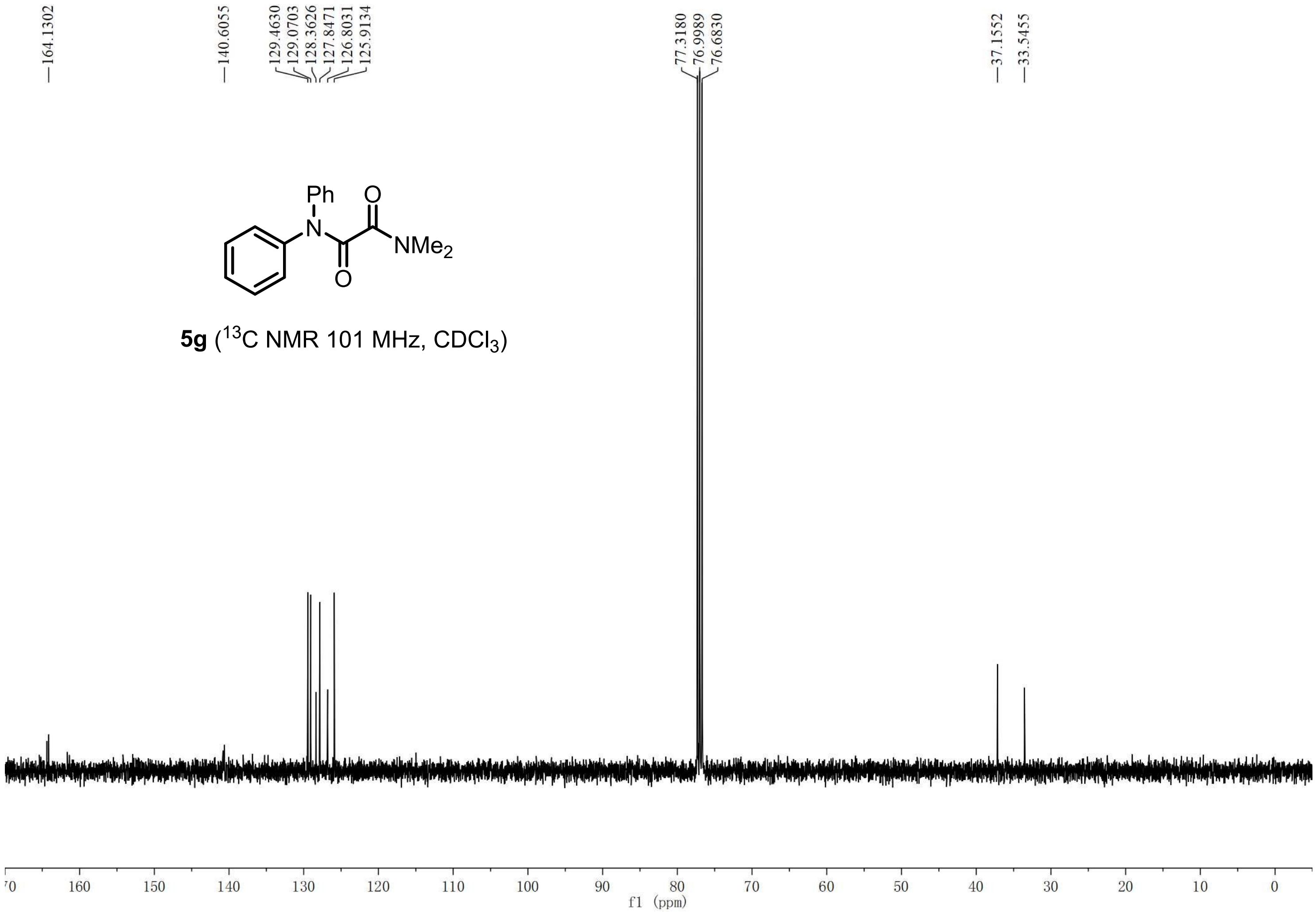
5f (^{19}F NMR 376 MHz, $CDCl_3$)



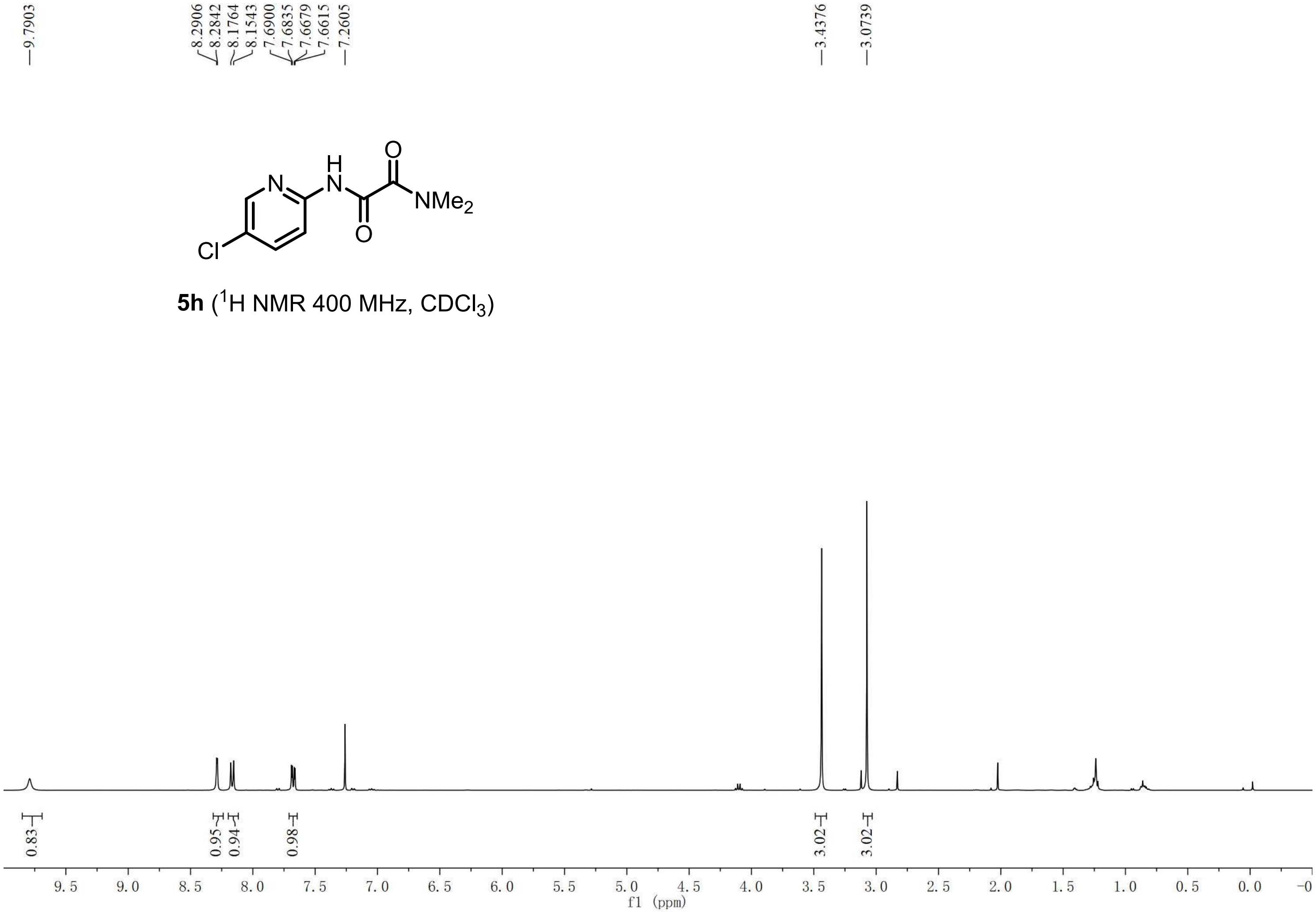


5g (^{1}H NMR 400 MHz, $CDCl_3$)

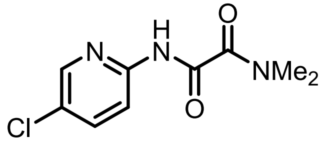




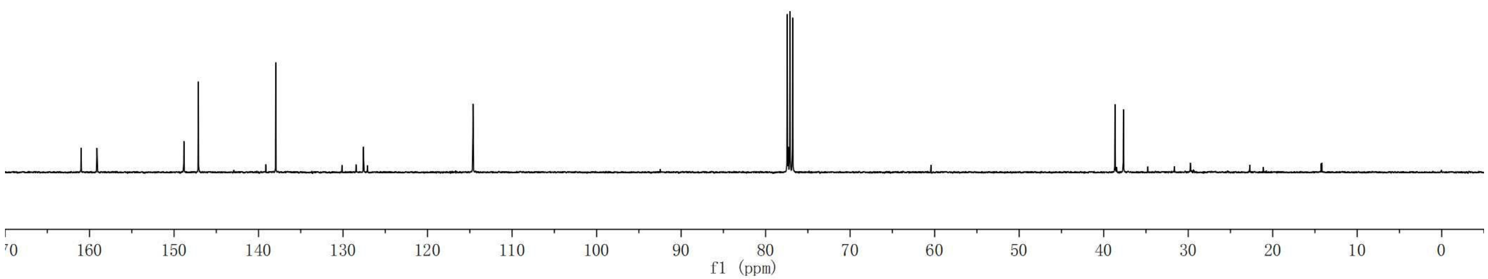
5g (^{13}C NMR 101 MHz, $CDCl_3$)

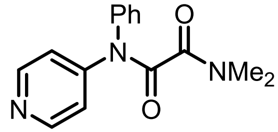


5h (^{1}H NMR 400 MHz, $CDCl_3$)

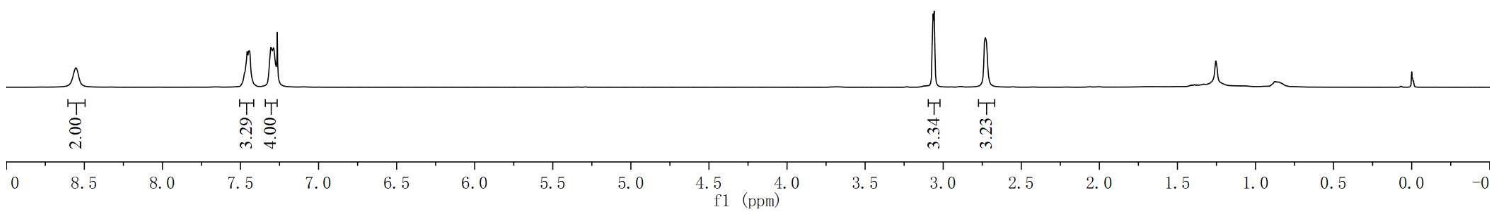


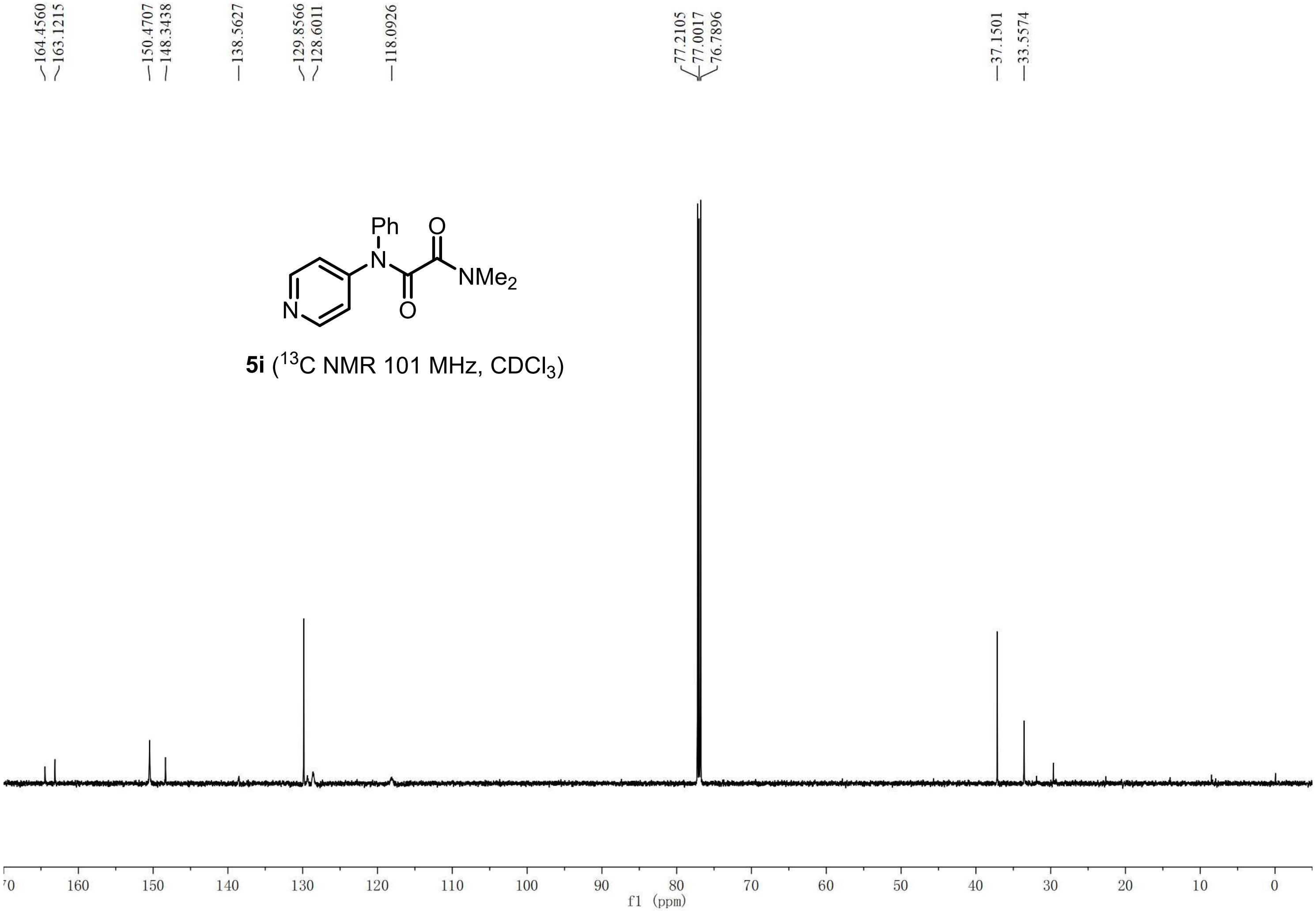
5h (^{13}C NMR 101 MHz, $CDCl_3$)



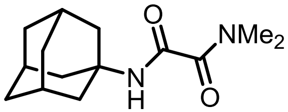


5i (^{1}H NMR 400 MHz, $CDCl_3$)

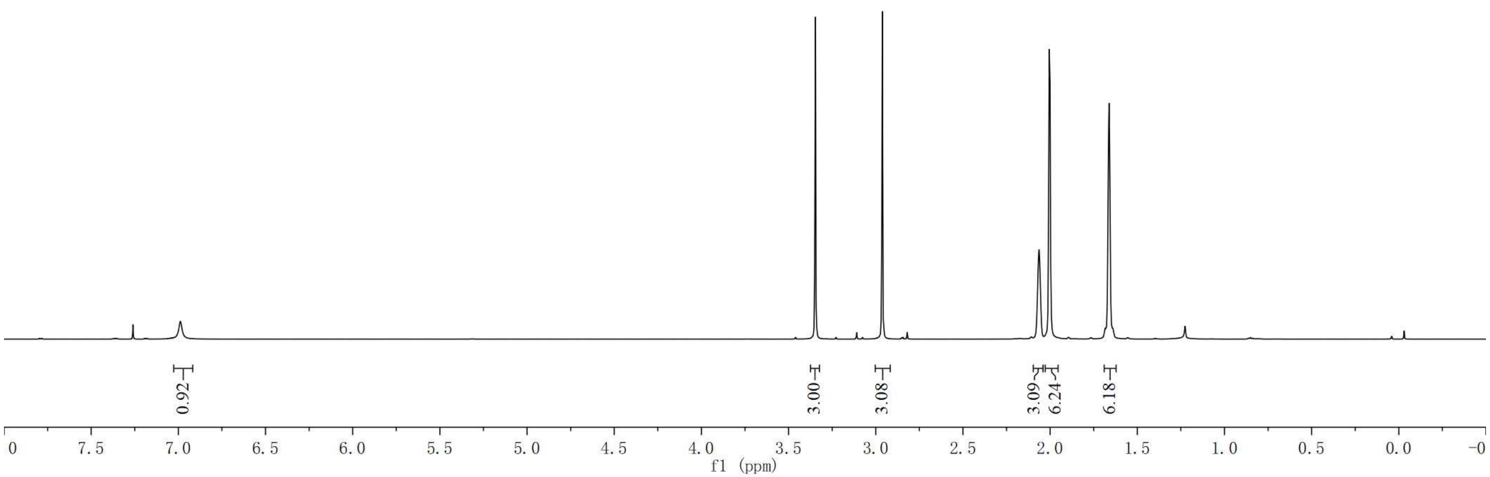


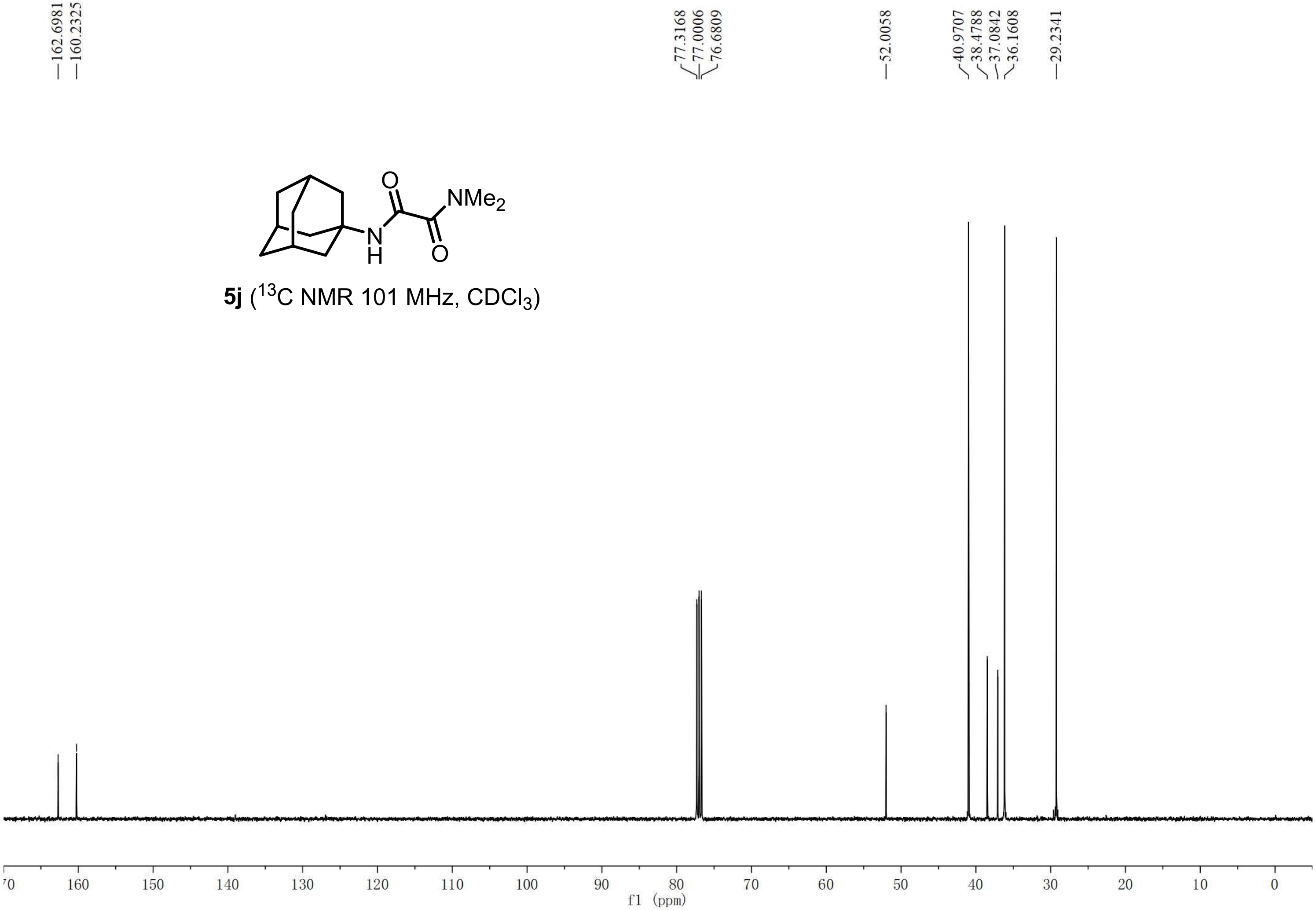


5i (^{13}C NMR 101 MHz, $CDCl_3$)

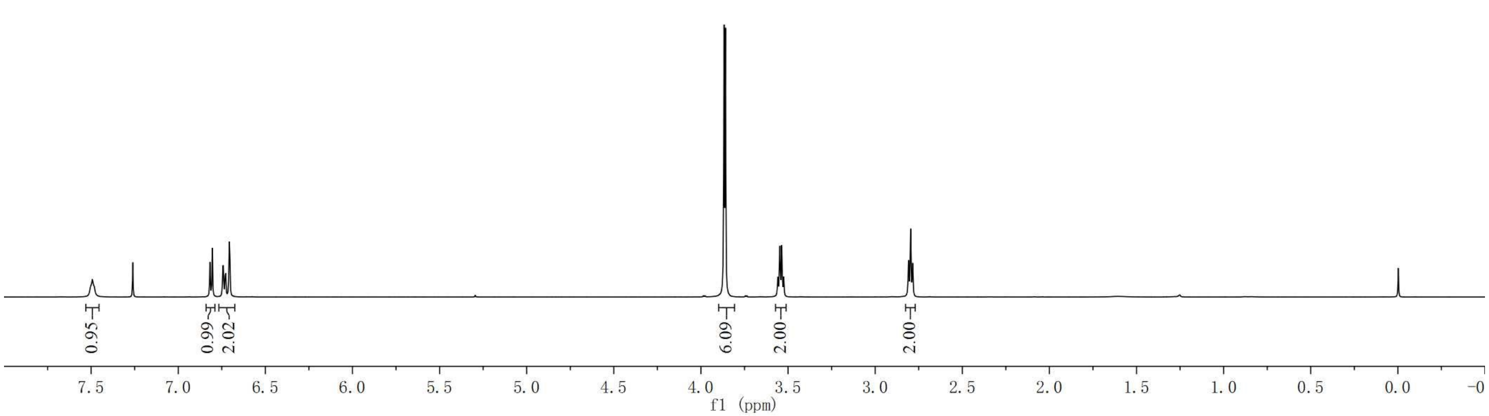


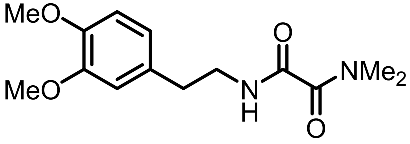
5j (^1H NMR 400 MHz, $CDCl_3$)



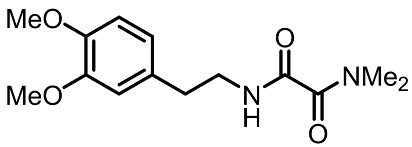


5j (^{13}C NMR 101 MHz, $CDCl_3$)

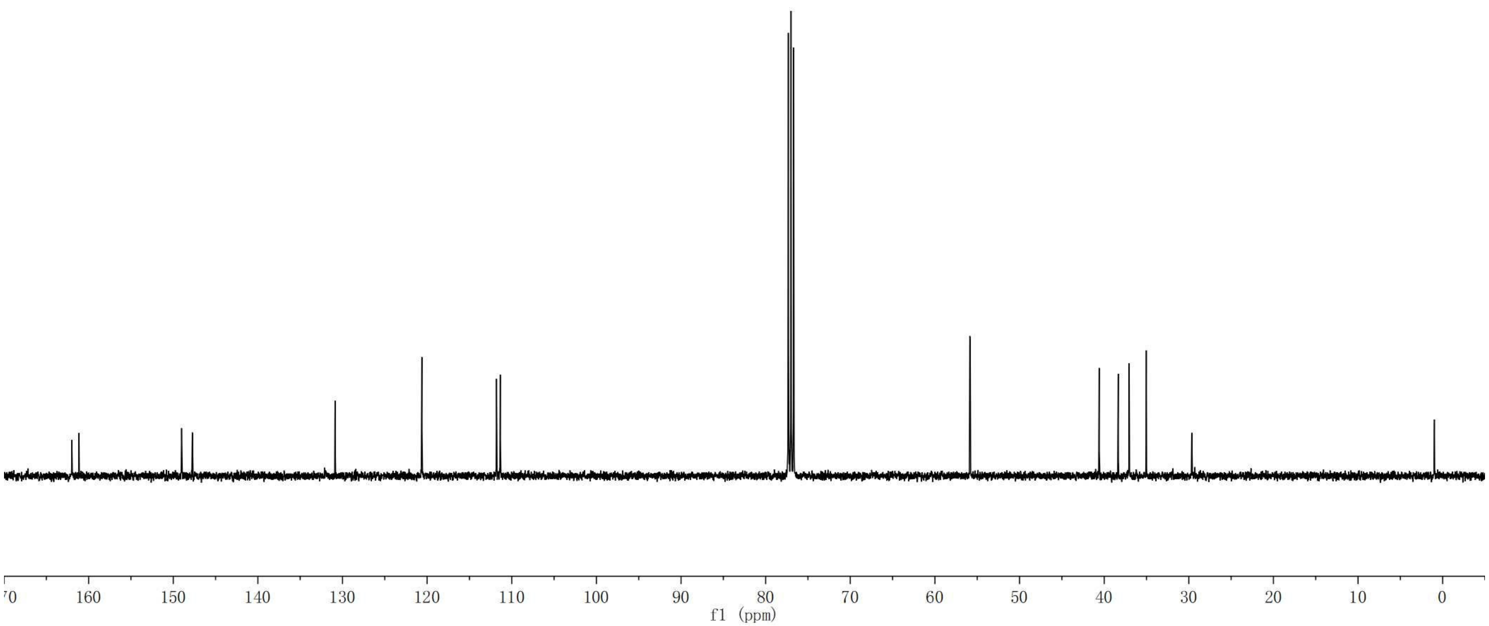




5k (^{1}H NMR 400 MHz, $CDCl_3$)



5k (^{13}C NMR 101 MHz, $CDCl_3$)



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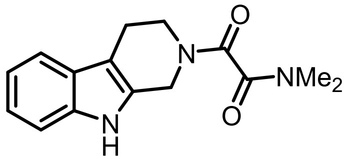
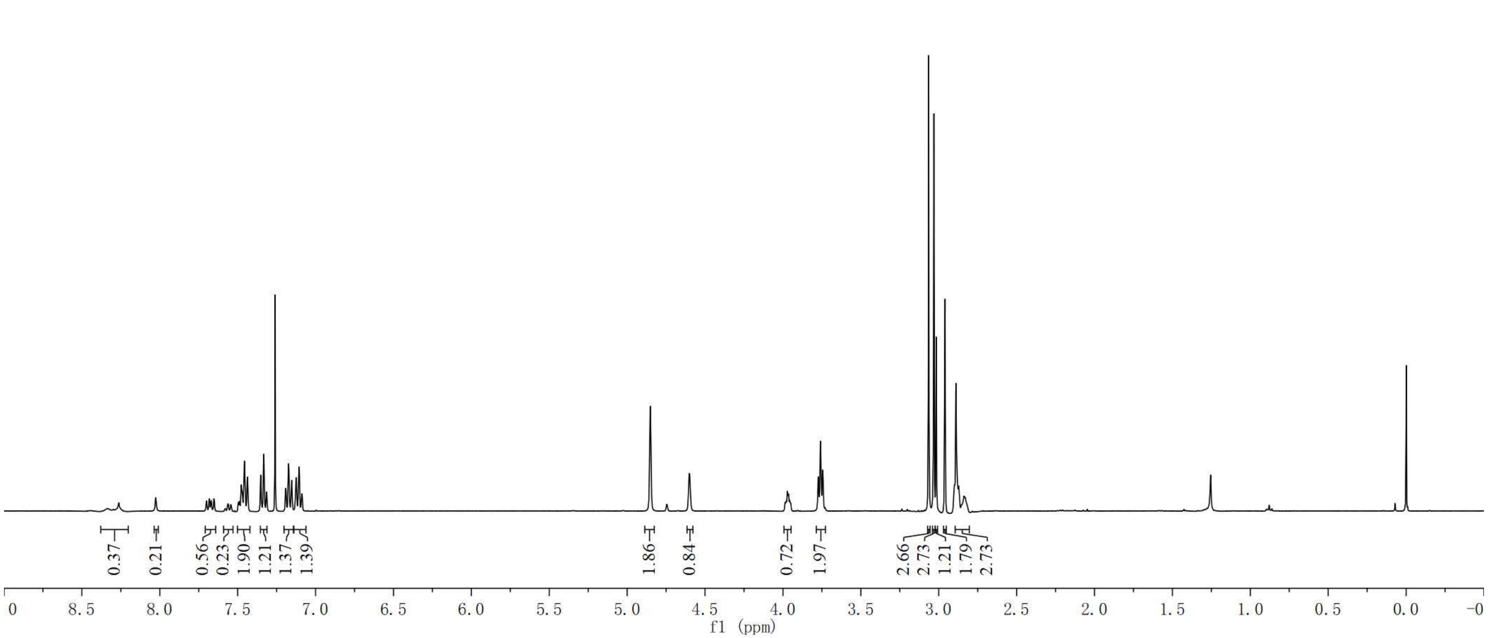
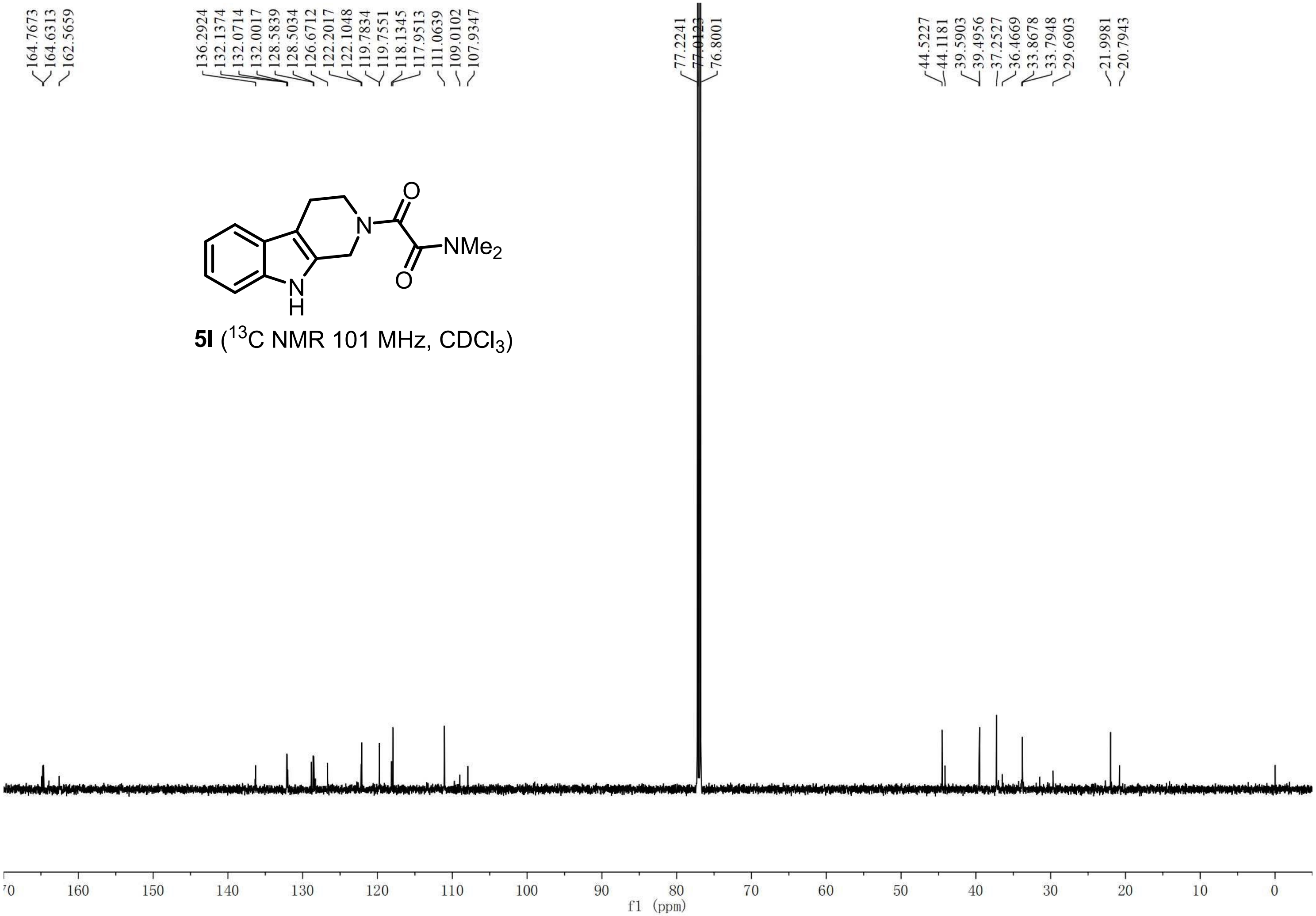
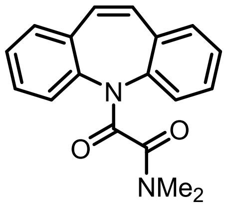


5l (^{1}H NMR 400 MHz, $CDCl_3$)

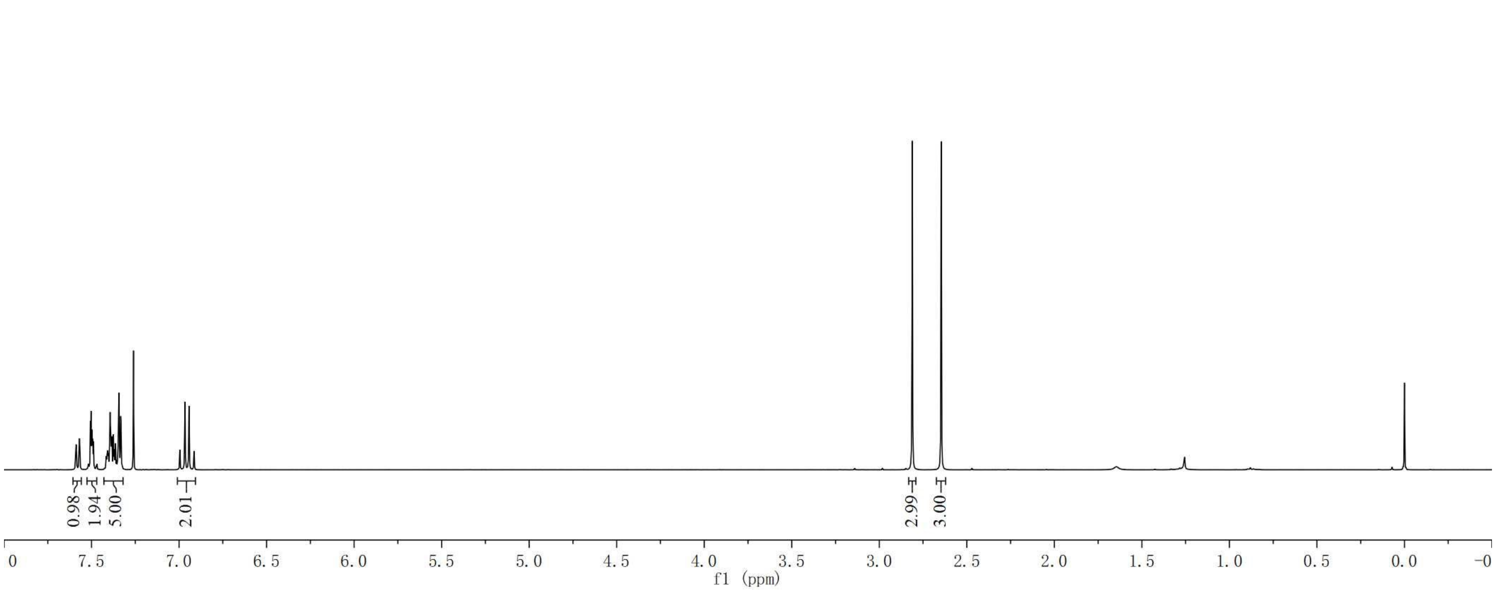


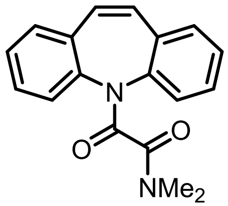


5l (^{13}C NMR 101 MHz, $CDCl_3$)

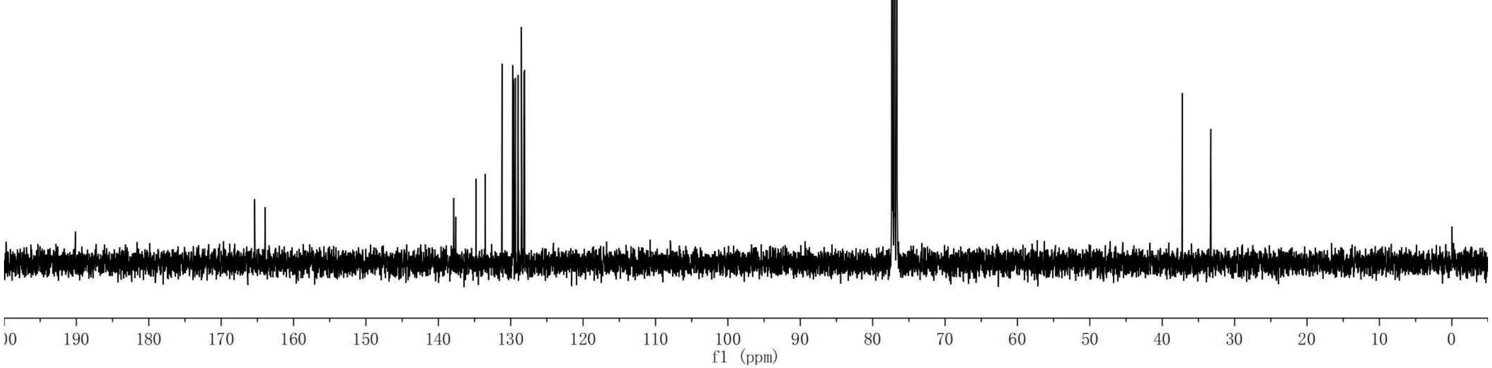


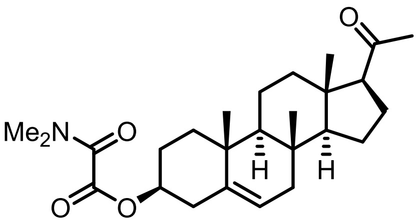
5m (^1H NMR 400 MHz, $CDCl_3$)



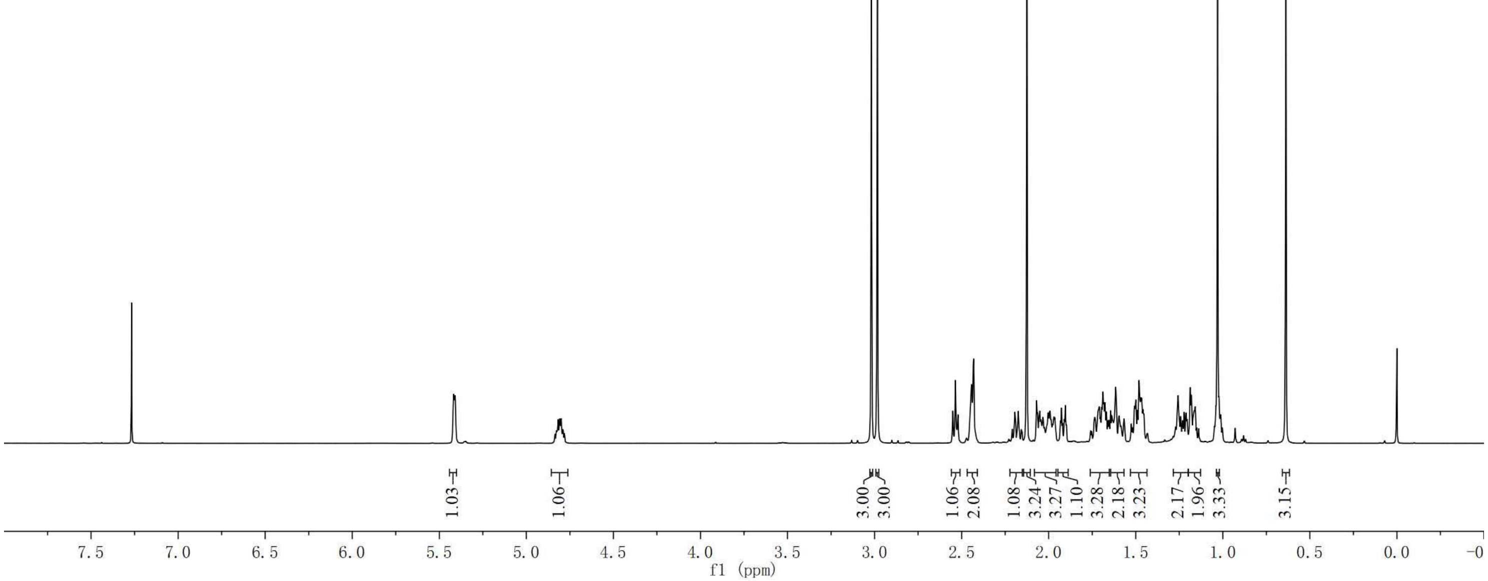


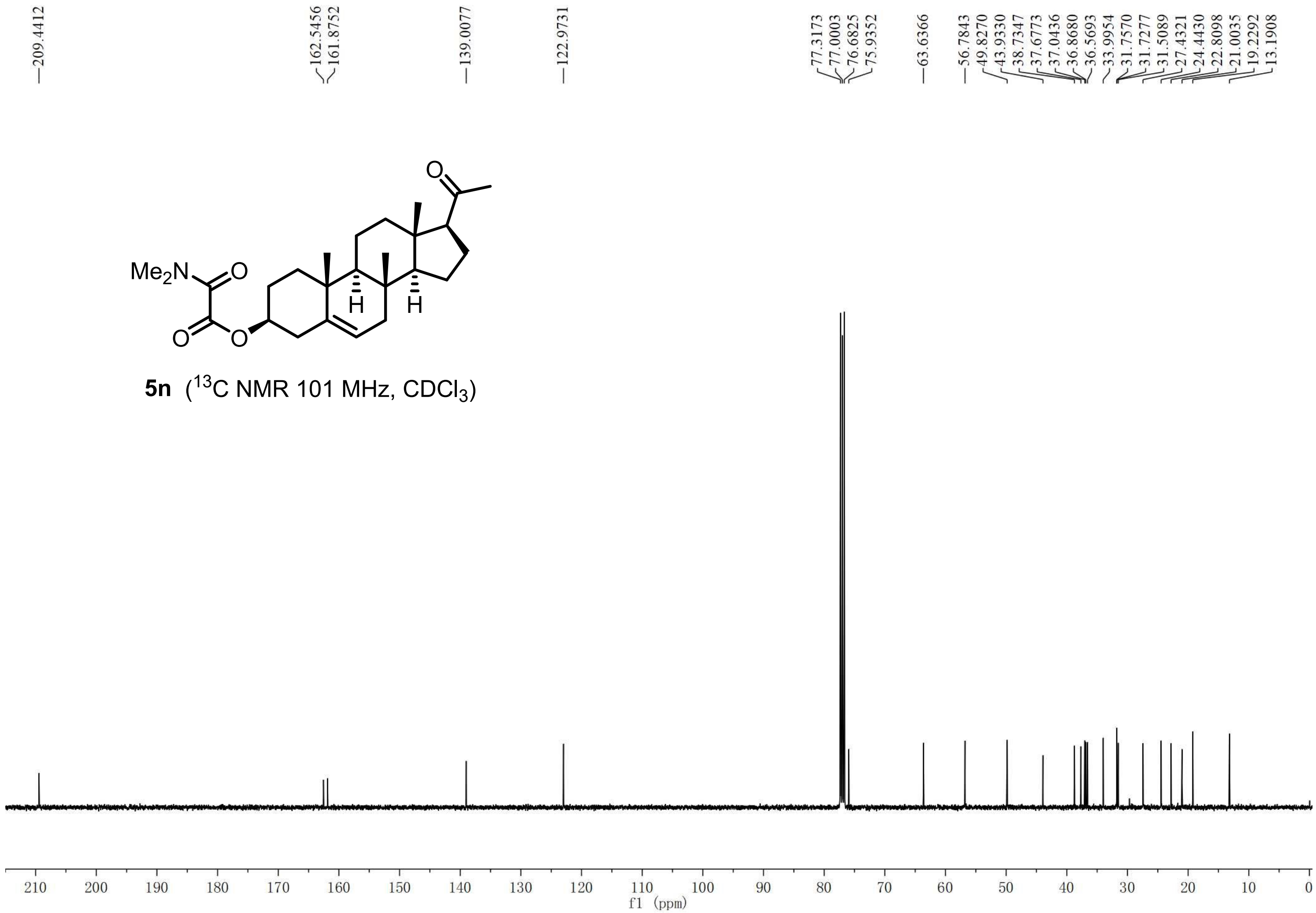
5m (^{13}C NMR 101 MHz, $CDCl_3$)



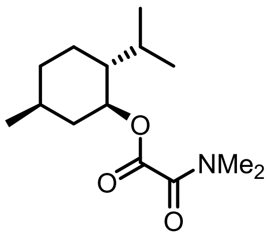


5n (^{1}H NMR 400 MHz, $CDCl_3$)

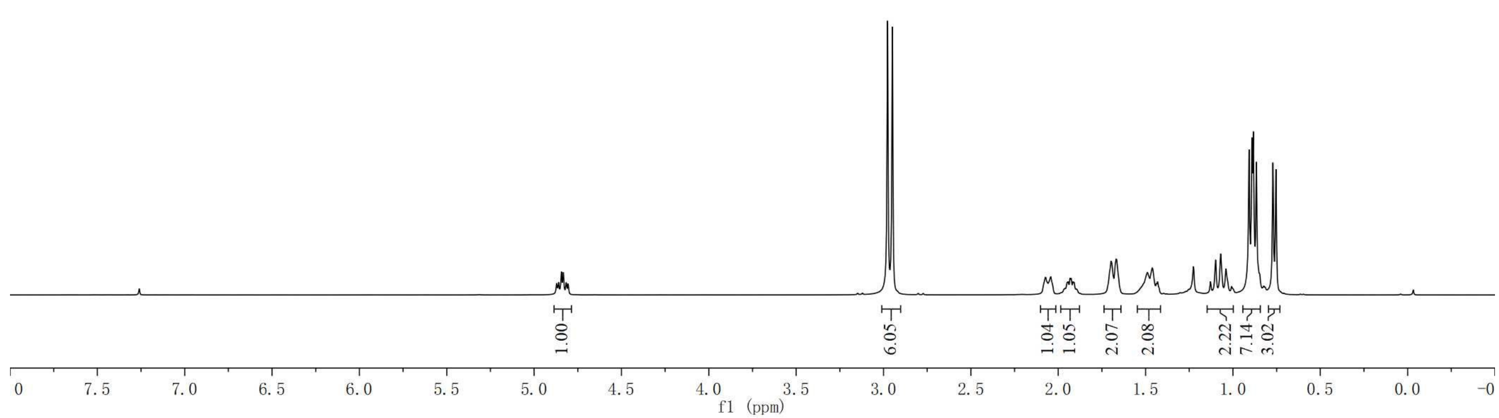


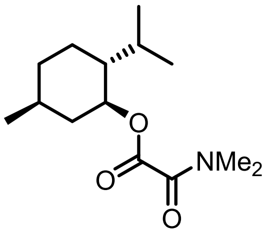


5n (^{13}C NMR 101 MHz, $CDCl_3$)

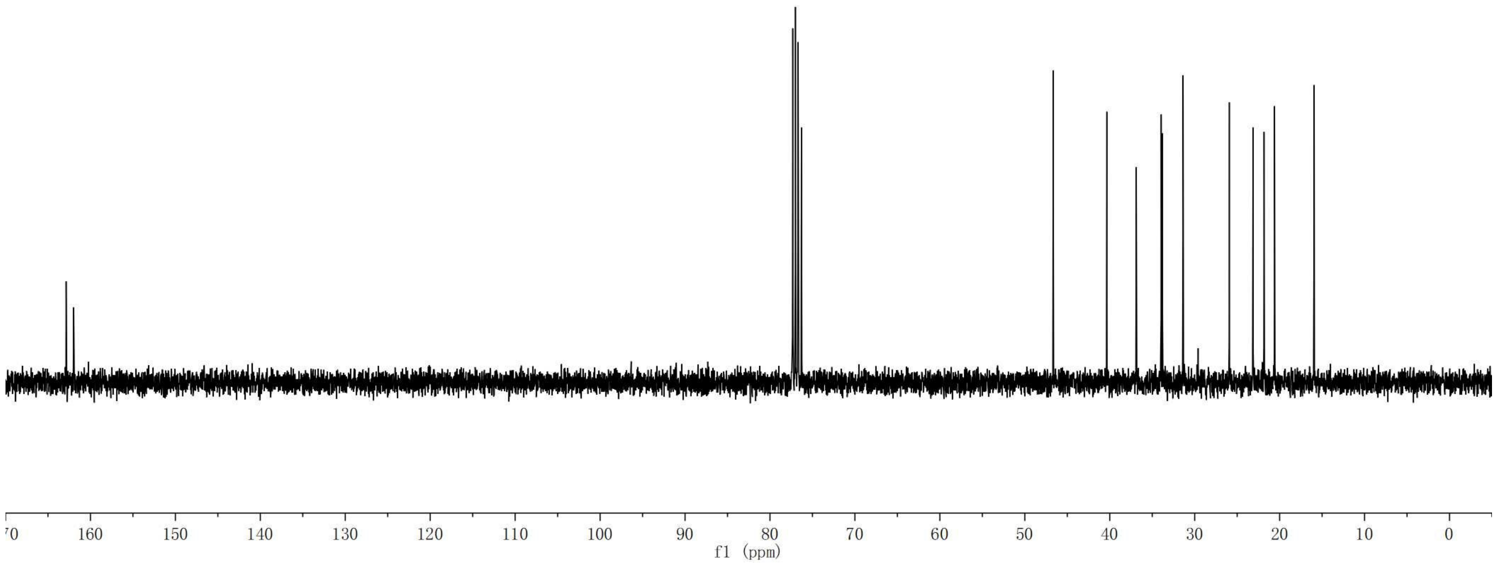


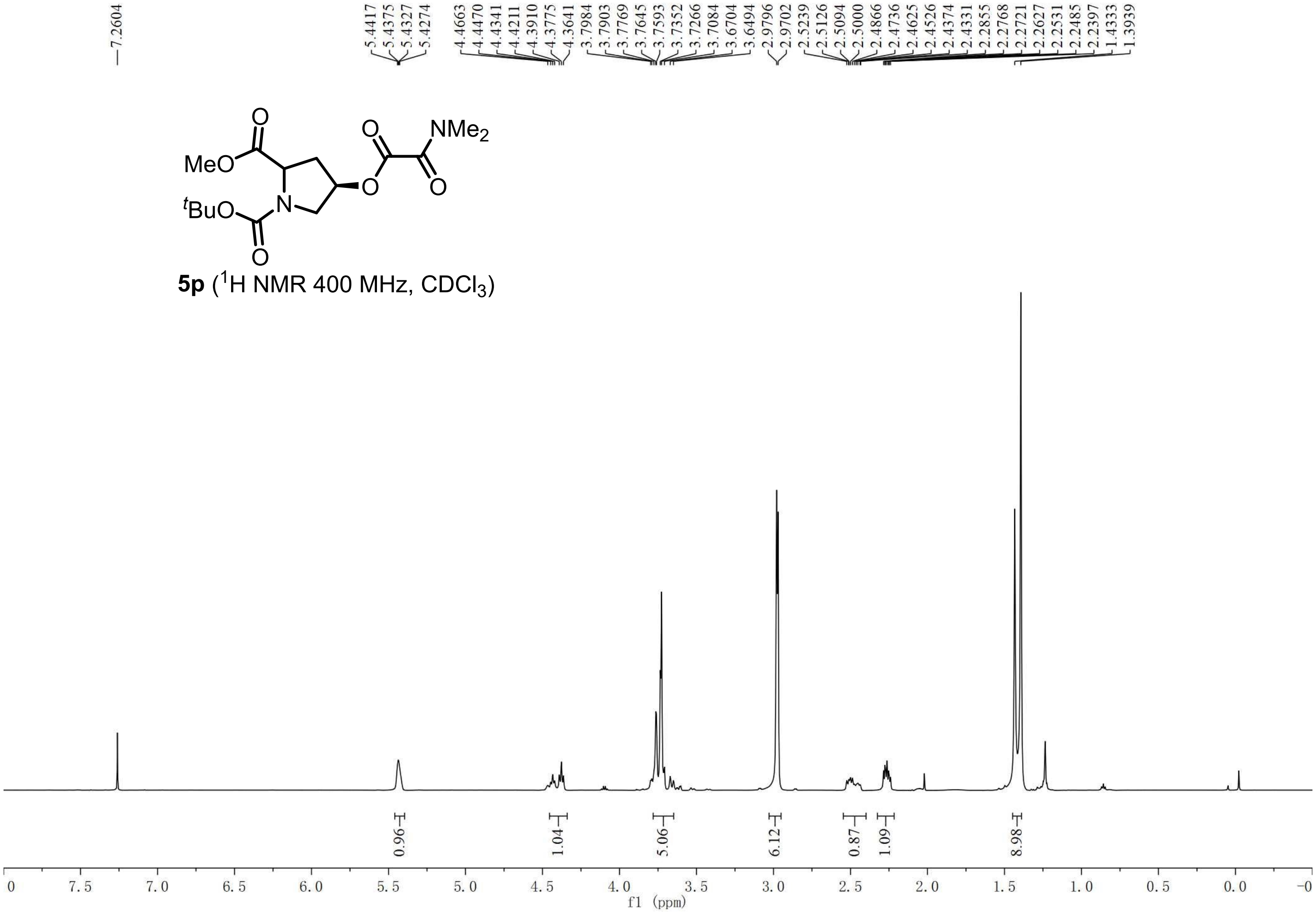
5o (^{1}H NMR 400 MHz, $CDCl_3$)



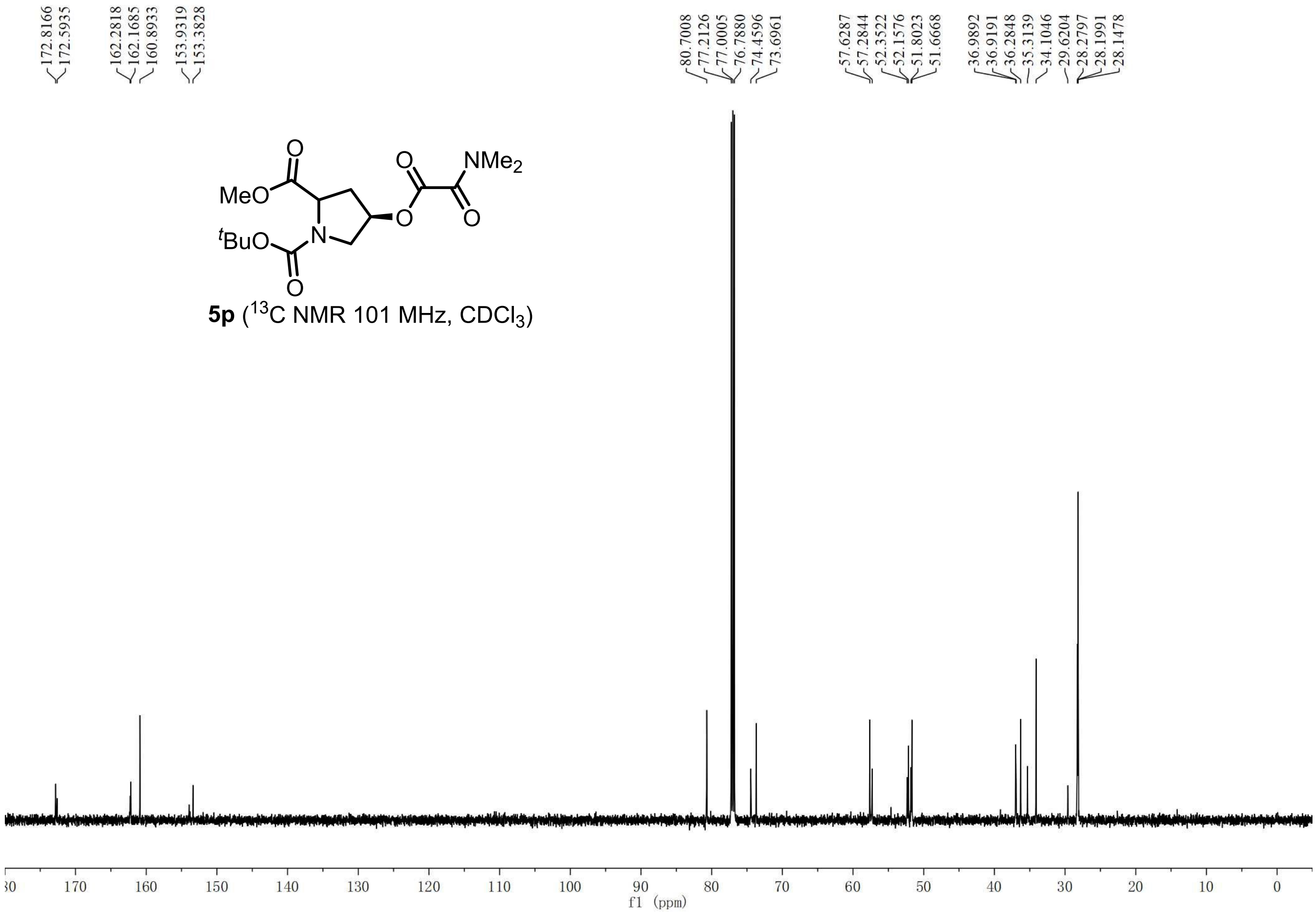


5o (^{13}C NMR 101 MHz, $CDCl_3$)

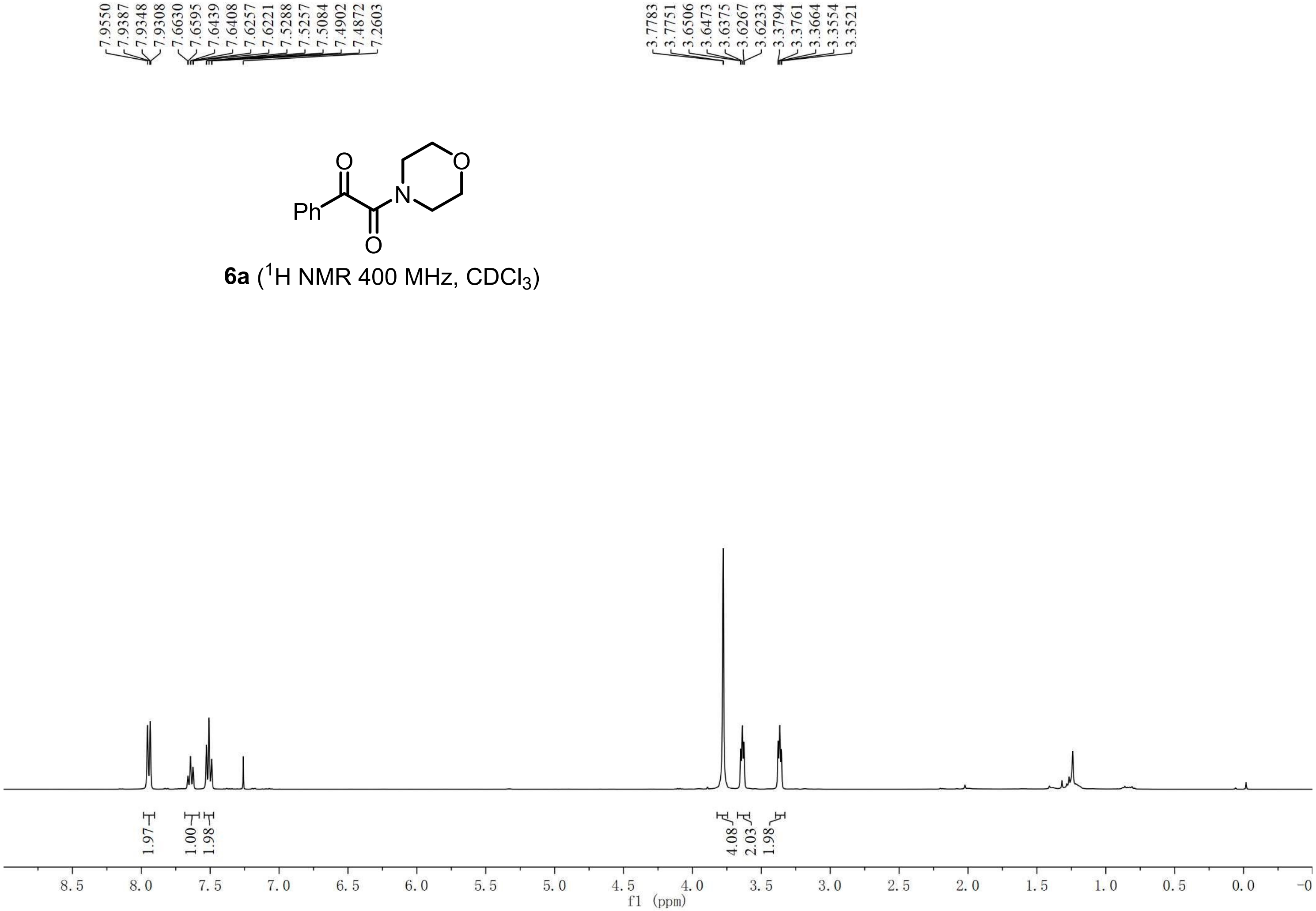




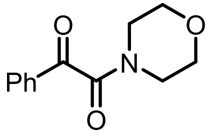
5p (^{1}H NMR 400 MHz, $CDCl_3$)



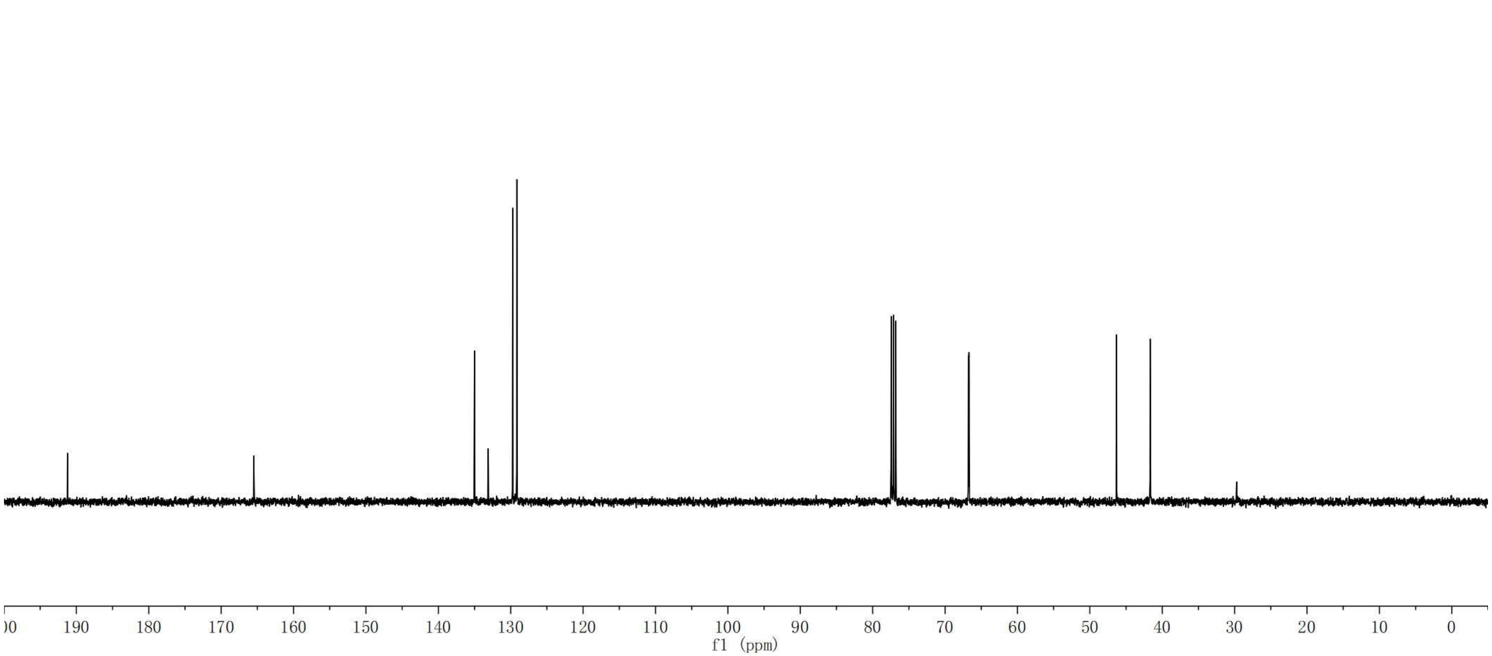
5p (^{13}C NMR 101 MHz, $CDCl_3$)

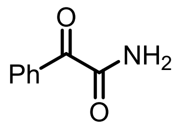


6a (^{1}H NMR 400 MHz, $CDCl_3$)

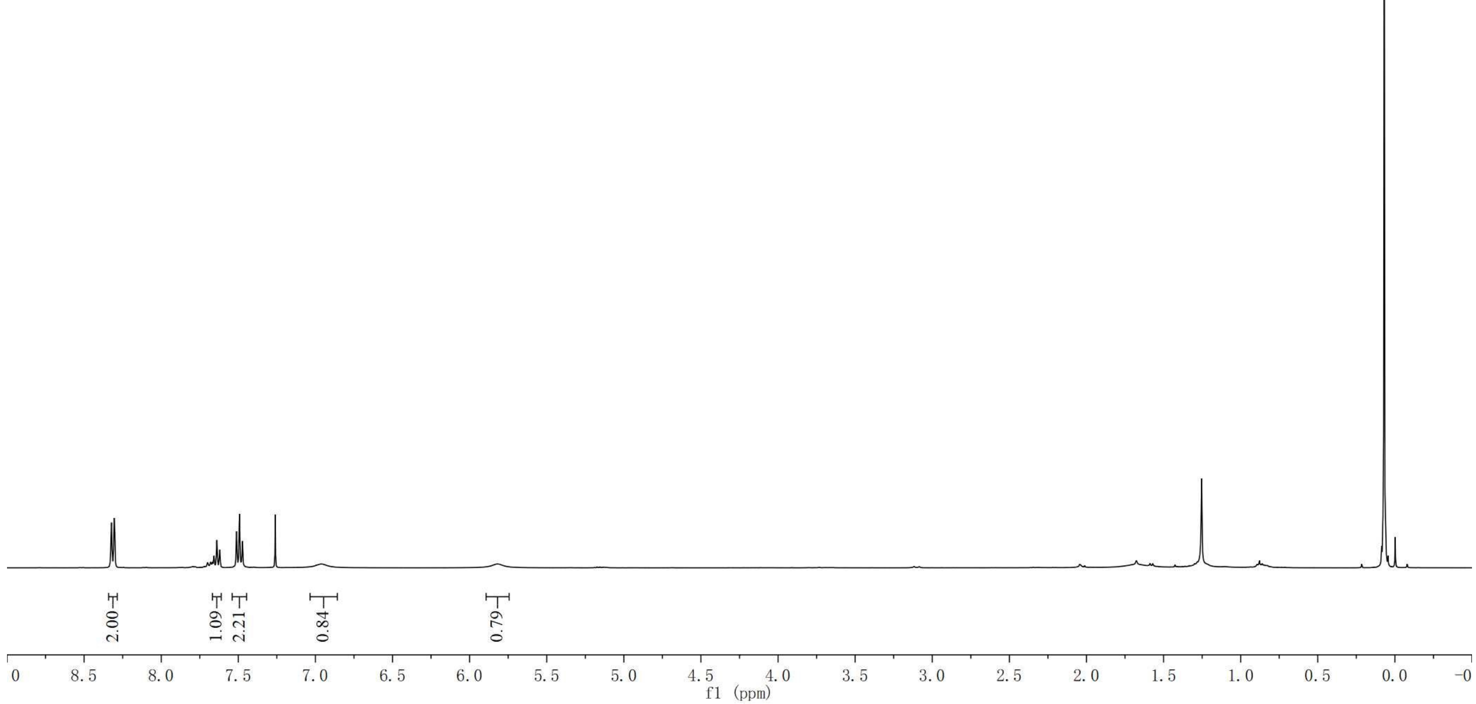


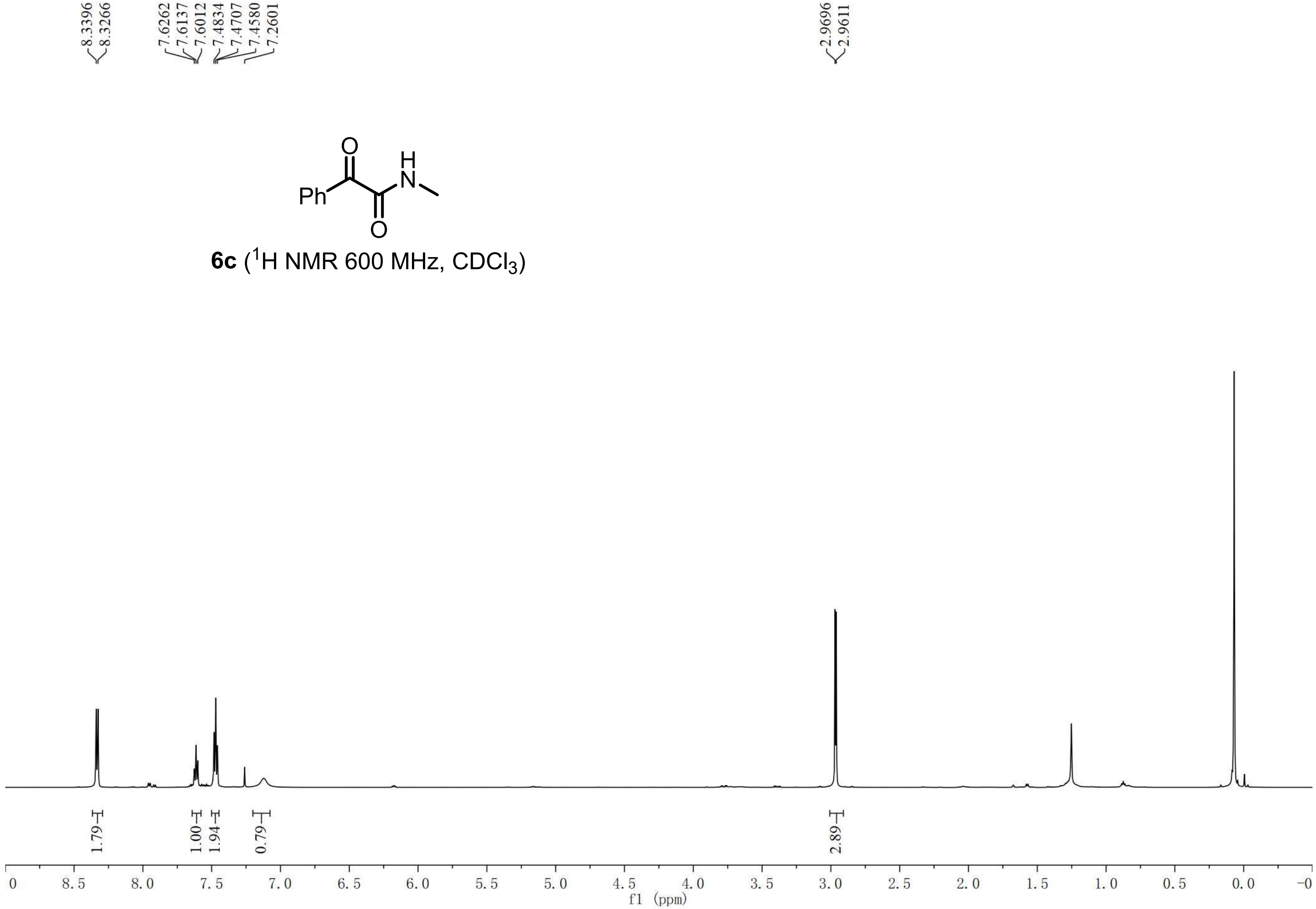
6a (^{13}C NMR 101 MHz, $CDCl_3$)



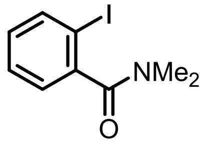


6b (^{1}H NMR 400 MHz, $CDCl_3$)





6c (^{1}H NMR 600 MHz, $CDCl_3$)



7a (^{1}H NMR 400 MHz, $CDCl_3$)