Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Cobalt(III)-Catalyzed Site-Selective C-H Amidation of Pyridones and Isoquinolones

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Table of Contents

1. General Information

Unless otherwise noted, the reagents (chemicals) were purchased from commercial sources, and used without further purification. Water was deionized before used. Analytical thin layer chromatography (TLC) was HSGF 254 (0.15-0.2 mm thickness). Compound spots were visualized by UV light (254 nm). Column chromatography was performed on silica gel FCP 200-300. NMR spectra were run on 400 or 500 MHz instrument. Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br). Low- and high-resolution mass spectra (LRMS and HRMS) were measured on spectrometer. Melting points were measured on melting point apparatus.

2. Experimental Procedures

General procedure for synthesis of 1-(2-Pyridyl)-2-pyiridones 1[1]

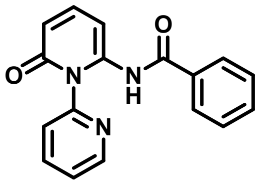
Synthesis of **1a** is representative. To a solution of 2-hydroxypyridine (950 mg, 10 mmol), copper(I) iodide (95 mg, 0.5 mmol), *N*,*N*'-dimethylethylenediamine (DMEDA, 0.1 mL, 1 mmol) and potassium phosphate (4.2 g, 20 mmol) in toluene (20 mL) were added 2-bromopyridine (1.9 mL, 20 mmol). The resulting mixture was stirred at 120 °C for 24 h under argon. Then the resulting mixture was cooled to room temperature and diluted with ethyl acetate. A small amount of ethylenediamine was added to dissolve the copper salts and then the mixture was filtered. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography (PE/EA = 2/1- 1/1) to give **1a** in 70% yield.

General procedures for cobalt(III)-catalyzed site-selective C-H amidation of pyridones.

Synthesis of **3a** is representative. A Schlenk tube equipped with a magnetic stir bar was charged with 2*H*-[1,2'-bipyridin]-2-one **1a** (0.2 mmol), phenyl oxazolone **2a** (0.60 mmol), $Cp^*Co(CO)I_2$ (10 mol%), $AgSbF_6$ (20 mol%) and KOAc (30 mol%) and then capped with septa. 2 mL of DCM was charged to the vial via syringe, and then the resulting mixture was stirred in a pre-heated oil bath at 90 °C for 12 h. After the reaction was completed, solvent was removed under vacuum and the residue was purified by silica gel column using 2% methanol in DCM as eluent to afford desired amidated product **3a** as a white solid.

_N_-(2-oxo-2_H_-[1,2'-bipyridin]-6-yl)benzamide (3a)

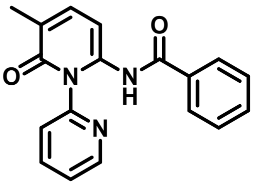
Compound **3a** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 56.5 mg, 97% yield. Mp: 153-155 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.30 (s, 1H), 8.58 – 8.50 (m, 1H), 7.90 (td, *J* = 7.7, 1.9 Hz, 1H), 7.60 (dd, *J* = 9.3, 7.1 Hz, 1H), 7.47 (dt, *J* = 8.6, 4.4 Hz, 3H), 7.42 – 7.33 (m, 4H), 6.51 – 6.45 (m, 1H), 6.39 (dd, *J* = 7.1, 1.0 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.8, 162.4, 150.4, 148.7, 141.0, 140.8, 138.0, 133.1, 131.9, 128.3, 127.3, 124.5, 124.0, 118.4, 104.0. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{17}H_{12}N_3O_2$: 290.0935, found: 290.0934.



3a

N-(3-methyl-2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (3b)

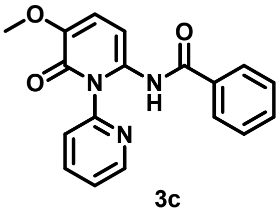
Compound **3b** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 56.8 mg, 93% yield. Mp: 195-198 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 8.55 – 8.53 (m, 1H), 7.89 (td, *J* = 7.6, 2.0 Hz, 1H), 7.50 – 7.44 (m, 4H), 7.41 – 7.34 (m, 4H), 6.28 (d, *J* = 7.6 Hz, 1H), 2.06 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.9, 162.6, 150.7, 148.7, 138.0, 137.8, 137.4, 132.9, 131.9, 128.3, 127.5, 127.3, 124.4, 123.9, 104.2, 16.7. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{18}H_{14}N_3O_2$: 304.1092, found: 304.1087.



3b

N-(3-methoxy-2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (3c)

Compound **3c** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 45.0 mg, 70% yield. Mp: 243-245 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 8.55 – 8.53 (m, 1H), 7.89 (td, *J* = 7.6, 2.0 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.41 – 7.32 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.27 (d, *J* = 8.0 Hz, 1H), 3.79 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.2, 157.5, 150.4, 148.8, 148.7, 138.1, 133.0, 131.8, 131.2, 128.3, 127.3, 124.2, 124.0, 113.2, 103.8, 55.8. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{18}H_{14}N_3O_3$: 320.1041, found: 320.1043.

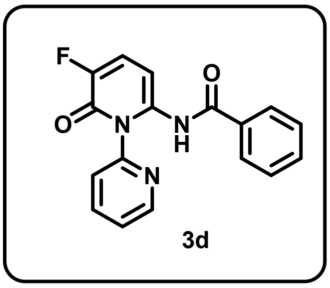


3c

N-(3-fluoro-2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (3d)

Compound **3d** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 41.2 mg, 73% yield. Mp: 242-243 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.32 (s, 1H), 8.57 – 8.56 (m, 1H), 7.94 (td, *J* = 8.0, 1.6 Hz, 1H), 7.61(t, *J* = 8.0 Hz, 1H), 7.51 – 7.41 (m, 5H), 7.39 – 7.36 (m, 2H), 6.37 - 6.34 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.0, 155.7 (d, *J* = 26.5 Hz), 150.6 (d, *J* = 245.7 Hz), 149.5, 149.0, 138.4, 136.2, 136.1, 132.7, 132.0, 131.2, 128.3, 128.2, 127.4, 127.3, 124.5, 124.2, 121.3 (d, *J* = 17.6 Hz), 102.8

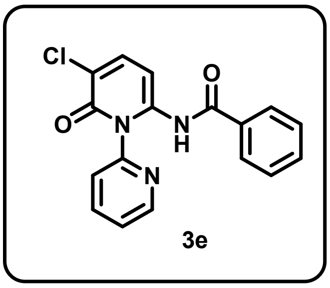
(d, *J* = 5.0 Hz). **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}FN_3O_2$: 308.0841, found: 308.0834.



3d

N-(3-chloro-2-oxo-2H-[1,2'-bipyridin]-6-yl)benzamide (3e)

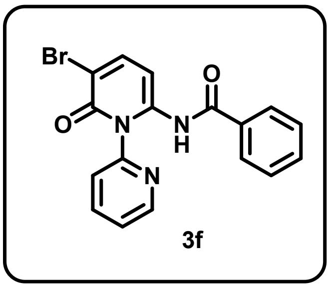
Compound **3e** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 63.8 mg, 98% yield. Mp: 229-231 °C. ^{1}**H NMR** (400 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.57 – 8.56 (m, 1H), 7.97 – 7.92 (m, 2H), 7.52 – 7.43 (m, 5H), 7.39 – 7.36 (m, 2H), 6.45 (d, *J* = 8.0 Hz, 1H). ^{13}**C NMR** (126 MHz, DMSO-d_6) δ 165.9, 158.4, 149.9, 148.9, 139.8, 139.0, 138.4, 132.6, 132.2, 128.4, 127.4, 124.5, 124.3, 122.9, 104.1. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}ClN_3O_2$: 324.0545, found: 324.0545.



3e

N-(3-bromo-2-oxo-2H-[1,2'-bipyridin]-6-yl)benzamide (3f)

Compound **3f** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 70.3 mg, 95% yield. Mp: 216-218 °C. ^{1}**H NMR** (400 MHz, DMSO-d_6) δ 10.36 (s, 1H), 8.57 – 8.55 (m, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.94 (td, *J* = 7.6, 2.0 Hz, 1H), 7.52 – 7.42 (m, 5H), 7.40 – 7.36 (m, 2H), 6.40 (dd, *J* = 8.0, 1.0 Hz, 1H). ^{13}**C NMR** (126 MHz, DMSO-d_6) δ 165.8, 158.5, 150.1, 148.9, 142.7, 140.6, 138.4, 132.7, 132.2, 128.4, 127.4, 124.5, 124.3, 113.3, 104.8. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}BrN_3O_2$: 368.0040, found: 368.0042.

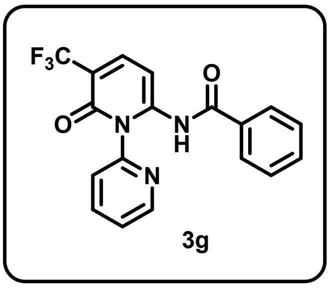


3f

N-(2-oxo-3-(trifluoromethyl)-2H-[1,2'-bipyridin]-6-yl)benzamide (3g)

Compound **3g** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 65.4 mg, 91% yield. Mp: 218-222 °C. ^{1}**H NMR** (400 MHz, DMSO-d_6) δ 10.48 (s, 1H), 8.58 – 8.60 (m, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.98 (td, *J* = 7.6, 2.0 Hz, 1H), 7.55 – 7.46 (m, 5H), 7.42 – 7.38 (m, 2H), 6.64 (d, *J* = 7.6 Hz, 1H). ^{13}**C NMR** (126 MHz, DMSO-d_6) δ 165.7, 158.7, 149.0, 145.4, 141.2 (q, *J* = 4.5 Hz), 138.4, 132.6, 132.4, 128.4, 127.5, 124.9, 124.7, 123.0 (q, *J* = 271.5 Hz), 116.1 (q, *J* = 30.4 Hz), 101.8. **HRMS** (ESI) [M-H]$^-$

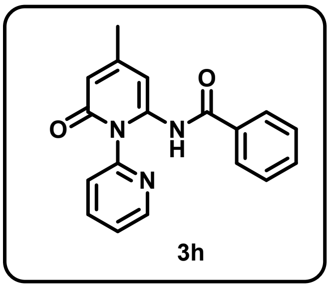
calcd for $C_{18}H_{11}F_3N_3O_2$: 358.0809, found: 358.0805.



3g

N-(4-methyl-2-oxo-2H-[1,2'-bipyridin]-6-yl)benzamide (3h)

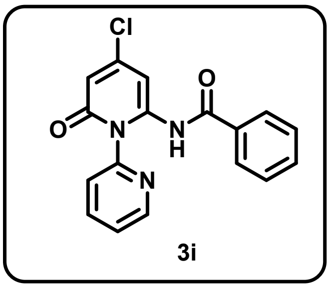
Compound **3h** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 56.2 mg, 92% yield. Mp: 190-193 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.24 (s, 1H), 8.54 – 8.53 (m, 1H), 7.89 (td, J = 6.4, 1.2 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.40 – 7.34 (m, 4H), 6.32 (d, J = 1.2 Hz, 1H), 6.26 (d, J = 1.2 Hz, 1H), 2.23 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.7, 162.1, 152.0, 150.3, 148.7, 139.5, 137.9, 132.9, 132.0, 128.3, 127.3, 124.6, 123.9, 116.9, 106.5, 21.0. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{18}H_{14}N_3O_2$: 304.1092, found: 304.1090.



3h

N-(4-chloro-2-oxo-2H-[1,2'-bipyridin]-6-yl)benzamide (3i)

Compound **3i** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 63.2 mg, 97% yield. Mp: 201-203 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.38 (s, 1H), 8.56 (m, 1H), 7.93 (m, 1H), 7.46 – 7.37 (m, 7H), 6.69 (s, 1H), 6.62 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.7, 161.0, 149.4, 148.9, 146.7, 141.6, 138.3, 132.6, 132.2, 128.4, 127.4, 124.7, 124.4, 116.7, 105.1. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}ClN_3O_2$: 324.0545, found: 324.0544.

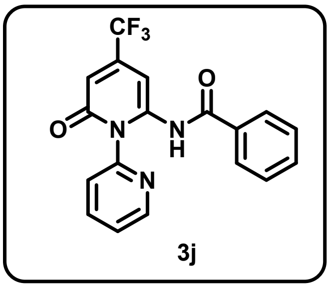


3i

N-(2-oxo-4-(trifluoromethyl)-2H-[1,2'-bipyridin]-6-yl)benzamide (3j)

Compound **3j** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 69.0 mg, 96% yield. Mp: 172-175 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.47 (s, 1H), 8.59 – 8.58 (m, 1H), 7.97 (td, J = 7.6, 1.6 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.49 – 7.45 (m, 4H), 7.42 – 7.38 (m, 2H), 6.96 (d, J = 0.8 Hz, 1H), 6.74 (d, J = 2.0 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.8, 161.2, 149.3, 149.0, 143.2, 140.5 (q, J = 36.0 Hz), 138.5, 132.6, 132.3, 128.4, 127.4, 124.6, 124.5, 122.3 (q, J = 274.4 Hz), 116.1, 98.5. **HRMS** (ESI)

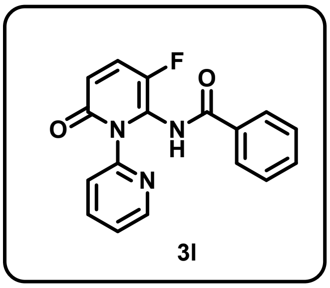
[M-H]$^-$ calcd for $C_{18}H_{11}F_3N_3O_2$: 358.0809, found: 358.0801.



3j

N-(5-fluoro-2-oxo-2H-[1,2'-bipyridin]-6-yl)benzamide (3l)

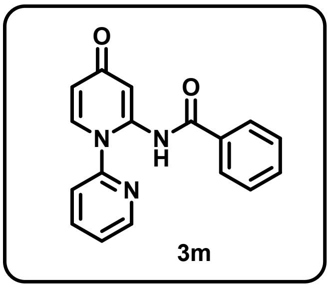
Compound **3l** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 53.2 mg, 86% yield. Mp: 195-199 °C. **^{1}H NMR** (500 MHz, DMSO-d_6) δ 10.32 (s, 1H), 8.56 (dd, J = 4.8, 1.8 Hz, 1H), 7.98 – 7.79 (m, 2H), 7.57 – 7.48 (m, 3H), 7.47 – 7.30 (m, 4H), 6.61 (dd, J = 10.2, 4.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.2, 160.7, 150.0, 149.5, 143.3 (d, J = 239.4 Hz), 138.9, 133.3 (d, J = 25.2 Hz), 132.8, 132.7, 128.9, 127.9, 127.5 (d, J = 23.9 Hz), 124.8, 124.7, 121.1 (d, J = 6.3 Hz). **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}FN_3O_2$: 308.0841, found: 308.0837.



3l

N-(4-oxo-4H-[1,2'-bipyridin]-2-yl)benzamide (3m)

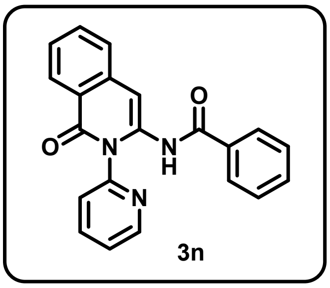
Compound **3m** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 38.5 mg, 66% yield. Mp: 143-146 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.29 (s, 1H), 8.55 – 8.54 (m, 1H), 7.90 (td, J = 7.6, 1.6 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.51 – 7.45 (m, 3H), 7.42 – 7.35 (m, 4H), 6.50 (d, J = 9.6 Hz, 1H), 6.37 (d, J = 8.0 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 165.8, 162.4, 150.3, 148.8, 140.8, 140.6, 138.0, 132.8, 132.0, 128.3, 128.2, 127.4, 127.3, 124.5, 124.0, 118.8, 104.2. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{12}N_3O_2$: 290.0923, found: 290.0929.



3m

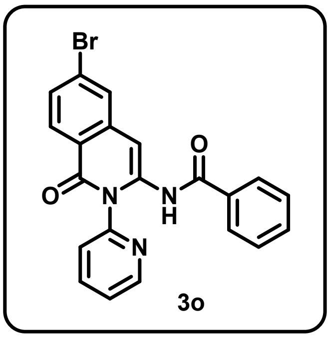
N-(1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3n)

Compound **3n** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 58.7 mg, 86% yield. Mp: 186-189 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.33 (s, 1H), 8.58 – 8.57 (m, 1H), 8.25 – 8.23 (m, 1H), 7.92 (td, J = 6.4, 1.6 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.60 – 7.57 (m, 1H), 7.51 – 7.48 (m, 3H), 7.45 – 7.37 (m, 4H), 6.81 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 166.2, 162.1, 150.6, 148.8, 138.0, 136.5, 1347, 133.3, 133.0, 131.9, 128.3, 127.3, 127.2, 127.1, 126.5, 124.7, 124.6, 123.9, 104.5. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{21}H_{14}N_3O_2$: 340.1092, found: 340.1088.


3n

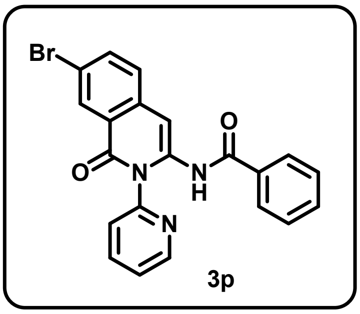
N-(6-bromo-1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3o)

Compound **3o** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 79.0 mg, 94% yield. Mp: °C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 10.40 (s, 1H), 8.58 (dd, *J* = 4.9, 1.7 Hz, 1H), 8.15 (d, *J* = 8.6 Hz, 1H), 8.10 (d, *J* = 1.9 Hz, 1H), 7.93 (td, *J* = 7.7, 1.9 Hz, 1H), 7.74 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.53 – 7.41 (m, 5H), 7.42 – 7.36 (m, 2H), 6.82 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 166.6, 162.1, 150.7, 149.3, 138.7, 138.6, 136.6, 133.3, 132.5, 130.5, 130.1, 129.2, 128.8, 127.9, 127.8, 125.2, 124.5, 123.9, 103.9. **HRMS** (ESI) [M+H]$^+$ calcd for $C_{21}H_{15}N_3O_2Br$: 420.0342, found: 420.0334.


3o

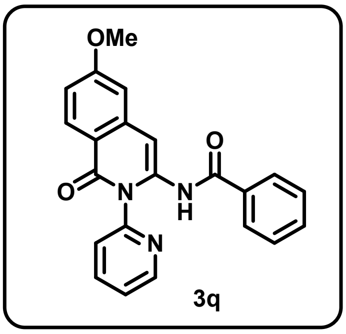
N-(7-bromo-1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3p)

Compound **3p** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 75.8 mg, 90% yield. Mp: 196-198°C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 10.36 (s, 1H), 8.59 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.32 (d, *J* = 2.1 Hz, 1H), 7.99 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.94 (td, *J* = 7.7, 2.0 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.54 – 7.42 (m, 5H), 7.42 – 7.36 (m, 2H), 6.87 (s, 1H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 166.6, 161.5, 150.7, 149.3, 138.7, 136.7, 136.0, 135.9, 133.4, 132.4, 129.9, 129.4, 128.8, 127.8, 126.5, 125.2, 124.6, 120.3, 104.5. **HRMS** (ESI) [M+H]$^+$ calcd for $C_{21}H_{15}N_3O_2Br$: 420.0342, found: 420.0333.


3p

N-(6-methoxy-1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3q)

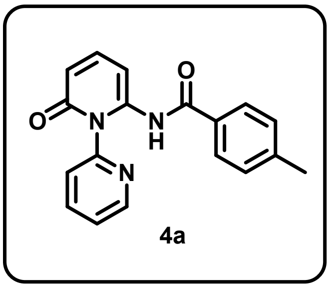
Compound **3q** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 73.5 mg, 99% yield. Mp: 237-240°C. **^{1}H NMR** (500 MHz, DMSO-*d*$_6$) δ 10.31 (s, 1H), 8.57 (dd, *J* = 5.1, 1.8 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H), 7.91 (td, *J* = 7.7, 1.9 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.45 – 7.35 (m, 4H), 7.27 (d, *J* = 2.5 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.73 (s, 1H), 3.93 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 166.5, 163.5, 162.2, 151.1, 149.2, 139.2, 138.4, 135.7, 133.5, 132.4, 129.9, 128.8, 127.8, 125.3, 124.3, 118.7, 116.7, 108.3, 104.8, 56.1. **HRMS** (ESI) $[M+H]^+$ calcd for $C_{22}H_{18}N_3O_3$: 372.1343, found: 372.1337.



3q

4-Methyl-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4a)

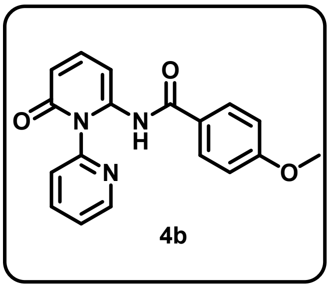
Compound **4a** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 40.3 mg, 66% yield. Mp: 172-175 °C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 10.16 (s, 1H), 8.54 – 8.53 (m, 1H), 7.89 (td, *J* = 6.0, 1.6 Hz, 1H), 7.61 – 7.58 (m, 1H), 7.40 – 7.36 (m, 4H), 7.17 (d, *J* = 6.0 Hz, 2H), 6.49 (d, *J* = 7.6 Hz, 1H), 6.36 (d, *J* = 5.6 Hz, 1H), 2.29 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 165.6, 162.3, 150.3, 148.7, 142.2, 140.8, 140.7, 138.0, 130.0, 128.9, 127.4, 124.5, 124.0, 118.6, 104.1, 20.9. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{18}H_{14}N_3O_2$: 304.1092, found: 304.1085.



4a

4-Methoxy-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4b)

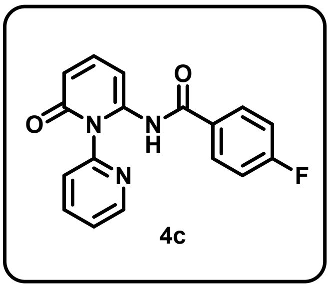
Compound **4b** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 55.9 mg, 87% yield. Mp: 206-209 °C. **^{1}H NMR** (500 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 8.70 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.95 (td, *J* = 7.8, 1.9 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.49 – 7.42 (m, 2H), 7.08 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.91 – 6.85 (m, 2H), 6.48 (dd, *J* = 9.2, 1.1 Hz, 1H), 3.83 (s, 3H). **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 163.2, 162.6, 162.1, 150.0, 148.1, 140.6, 139.2, 138.9, 128.4, 125.0, 125.0, 123.9, 115.9, 113.6, 98.2, 55.0. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{18}H_{14}N_3O_3$: 320.1041, found: 320.1037.



4b

4-Fluoro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4c)

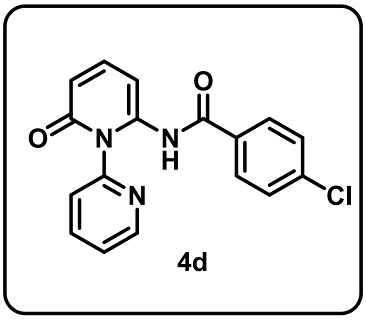
Compound **4c** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 60.0 mg, 97% yield. Mp: 211-213 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.34 (s, 1H), 8.54 – 8.53 (m, 1H), 7.89 (td, *J* = 6.4, 1.6 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.57 – 7.54 (m, 2H), 7.41 – 7.38 (m, 1H), 7.37 (dd, *J* = 6.4, 0.8 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 2H), 6.51 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.37 (dd, *J* = 6.0, 0.8 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 164.7, 164.2 (d, *J* = 249.5 Hz), 162.3, 150.3, 148.8, 140.8, 140.4, 138.0, 130.1 (d, *J* = 8.8 Hz), 129.3 (d, *J* = 2.5 Hz), 124.5, 124.0, 118.9, 115.4 (d, *J* = 21.4 Hz), 104.4. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{17}H_{11}FN_3O_2$: 308.0841, found: 308.0839.



4c

4-Chloro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4d)

Compound **4d** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 61.9 mg, 95% yield. Mp: 192-196 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.58 – 8.44 (m, 1H), 7.88 (td, *J* = 7.8, 1.9 Hz, 1H), 7.59 (dd, *J* = 9.3, 7.0 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 4H), 7.42 – 7.32 (m, 2H), 6.50 (dd, *J* = 9.3, 1.1 Hz, 1H), 6.38 – 6.30 (m, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 164.7, 162.3, 150.2, 148.7, 140.8, 140.3, 138.0, 136.9, 131.5, 129.2, 128.5, 124.5, 124.0, 118.9, 104.3. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{17}H_{11}ClN_3O_2$: 324.0545, found: 324.0542.

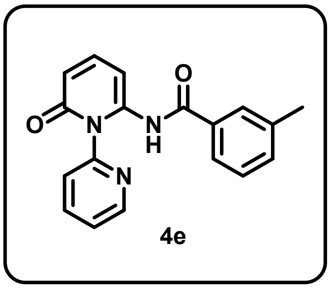


4d

3-Methyl-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4e)

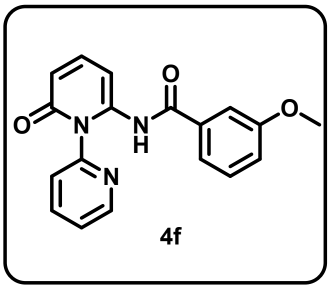
Compound **4e** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 56.8 mg, 93% yield. Mp: 138-141 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 8.56 (ddd, *J* = 4.8, 1.9, 0.8 Hz, 1H), 7.92 (td, *J* = 7.7, 1.9 Hz, 1H), 7.61 (dd, *J* = 9.3, 7.1 Hz, 1H), 7.46 – 7.35 (m, 2H), 7.34 – 7.28 (m, 1H), 7.28 – 7.21 (m, 3H), 6.50

(dd, *J* = 9.3, 1.1 Hz, 1H), 6.37 (dt, *J* = 7.1, 0.9 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 165.8, 162.3, 150.3, 148.7, 140.8, 140.6, 138.0, 137.6, 132.8, 132.6, 128.2, 127.9, 124.5, 124.4, 124.0, 118.6, 104.0, 20.8. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{18}H_{14}N_3O_2$: 304.1092, found: 304.1088.


4e

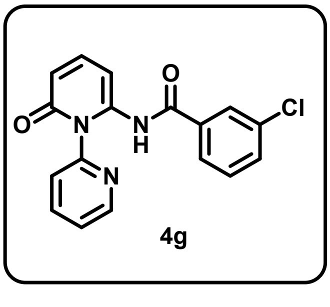
3-Methoxy-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4f)

Compound **4f** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 63.0 mg, 98% yield. Mp: 97-99 °C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 10.25 (s, 1H), 8.57 – 8.55 (m, 1H), 7.90 (td, *J* = 8.0, 2.0 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.44 – 7.40 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.95 – 6.94 (m, 1H), 6.51 (dd, *J* = 9.2, 1.2 Hz, 1H), 6.37 (dd, *J* = 6.8, 1.2 Hz, 1H), 3.72 (s, 3H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 165.5, 162.3, 158.9, 150.2, 148.8, 140.8, 140.4, 138.1, 134.3, 129.5, 124.5, 124.0, 119.5, 118.8, 117.9, 112.3, 104.2, 55.2. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{18}H_{14}N_3O_3$: 320.1041, found: 320.1037.


4f

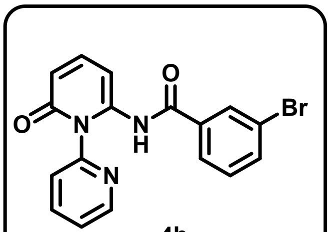
3-Chloro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4g)

Compound **4g** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 63.8 mg, 98% yield. Mp: 179-182 °C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$)δ 10.46 (s, 1H), 8.56 (ddd, J = 4.8, 1.9, 0.8 Hz, 1H), 7.92 (td, *J* = 7.7, 1.9 Hz, 1H), 7.66 – 7.56 (m, 2H), 7.47 – 7.41 (m, 4H), 7.38 (dt, *J* = 7.9, 1.0 Hz, 1H), 6.53 (dd, *J* = 9.3, 1.1 Hz, 1H), 6.38 (dd, *J* = 7.0, 1.1 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 164.5, 162.3, 150.2, 148.8, 140.8, 140.1, 138.1, 134.8, 133.1, 131.9, 130.5, 127.2, 126.1, 124.6, 124.1, 119.1, 104.5. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}ClN_3O_2$: 324.0545, found: 324.0540.


4g

3-Bromo-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4h)

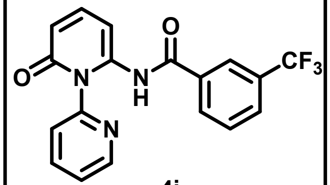
Compound **4h** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 73.3 mg, 99% yield. Mp: 191-194 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.45 (s, 1H), 8.56 – 8.54 (m, 1H), 7.91 (td, *J* = 8.0, 2.0 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 (d, *J* = 1.6 Hz, 1H), 7.49 – 7.46 (m, 1H), 7.44 – 7.40 (m, 1H), 7.38 – 7.34 (m, 2H), 6.52 (dd, *J* = 9.2, 1.2 Hz, 1H), 6.37 (dd, *J* = 7.2, 1.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 164.4, 162.3, 150.2, 148.8, 140.8, 140.1, 138.1, 135.0, 134.7, 130.7, 130.0, 126.4, 124.5, 124.1, 121.5, 119.0, 104.2. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{17}H_{11}BrN_3O_2$: 368.0040, found: 368.0037.



4h

***N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)-3-(trifluoromethyl)benzamide (4i)**

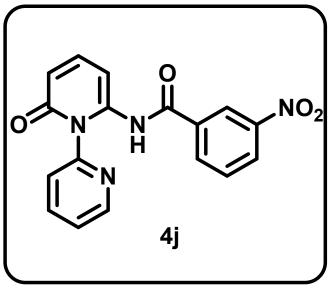
Compound **4i** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 67.6 mg, 94% yield. Mp: 151-153 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.59 (s, 1H), 8.55 – 8.53 (m, 1H), 7.93 – 7.88 (m, 2H), 7.77 (d, *J* = 7.6 Hz 1H), 7.70 (s, 1H), 7.67 – 7.60 (m, 2H), 7.43 – 7.40 (m, 1H), 7.39 – 7.37 (m, 1H), 6.53 (dd, *J* = 9.6, 1.2 Hz, 1H), 6.40 (dd, *J* = 6.8, 1.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 164.5, 162.3, 150.2, 148.7, 140.8, 140.0, 138.1, 133.8, 131.4, 129.8, 129.0 (q, *J* = 31.9 Hz), 128.6 (q, *J* = 3.4 Hz), 124.5, 124.0, 123.9 (q, *J* = 4.0 Hz), 123.7 (q, *J* = 272.9 Hz), 119.1, 104.4. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{18}H_{11}F_3N_3O_2$: 358.0809, found: 358.0807.



4i

3-Nitro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4j)

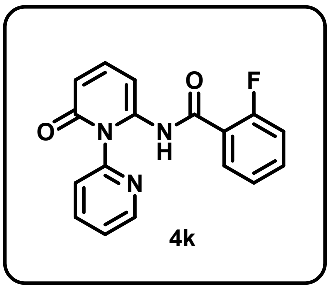
Compound **4j** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 27.6 mg, 41% yield. Mp: 216-220 °C. **^{1}H NMR** (400 MHz, DMSO-d_6) δ 10.73 (s, 1H), 8.56 – 8.54 (m, 1H), 8.37 – 8.34 (m, 1H), 8.25 (t, *J* = 2.0 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.71 (t, *J* = 8.0 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.43 – 7.38 (m, 2H), 6.54 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.41 (dd, *J* = 7.2, 1.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 163.9, 162.2, 150.1, 148.8, 147.5, 140.8, 139.9, 138.1, 134.2, 133.7, 130.3, 126.6, 124.5, 124.1, 122.1, 119.2, 104.4. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{17}H_{11}N_4O_4$: 335.0786, found: 335.0781.



4j

2-Fluoro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4k)

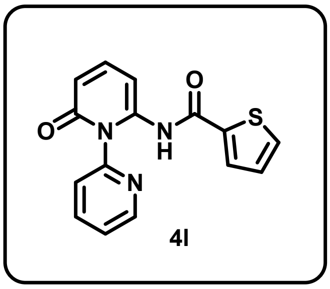
Compound **4k** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 27.6 mg, 41% yield. Mp: 216-220 °C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 10.03 (s, 1H), 8.62 – 8.61 (m, 1H), 7.98 (td, *J* = 6.4, 1.6 Hz, 1H), 7.62 – 7.59 (m, 1H), 7.52 – 7.50 (m, 2H), 7.43 (dd, *J* = 6.0, 1.2 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.22 – 7.17 (m, 1H), 6.51 – 6.47 (m, 2H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 162.5, 162.1, 158.9 (d, *J* = 251.2 Hz), 150.0, 149.1, 140.9, 139.8, 138.4, 133.4 (d, *J* = 8.7 Hz), 129.9 (d, *J* = 1.1 Hz), 124.6, 124.5 (d, *J* = 3.5 Hz), 124.3, 122.2 (d, *J* = 13.7 Hz), 118.3, 116.2 (d, *J* = 22.1 Hz), 103.0. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{17}H_{11}FN_3O_2$: 308.0841, found: 308.0837.



4k

***N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)thiophene-2-carboxamide (4l)**

Compound **4l** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 57.1 mg, 96% yield. Mp: 159-162 °C. **^{1}H NMR** (400 MHz, DMSO-*d*$_6$) δ 10.27 (s, 1H), 8.54 – 8.52 (m, 1H), 7.90 (td, *J* = 6.0, 1.6 Hz, 1H), 7.76 – 7.75 (m, 1H), 7.62 – 7.58 (m, 1H), 7.49 (dd, *J* = 3.2, 1.2 Hz, 1H), 7.41 – 7.36 (m, 2H), 7.07 – 7.05 (m, 1H), 6.51 (dd, *J* = 7.6, 1.2 Hz, 1H), 6.38 (dd, *J* = 5.6, 1.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-*d*$_6$) δ 162.3, 160.1, 150.2, 148.8, 140.8, 139.9, 138.1, 137.4, 132.4, 129.7, 128.0, 124.4, 124.0, 118.9, 104.4. **HRMS** (ESI) [M-H]$^-$ calcd for $C_{15}H_{10}SN_3O_2$: 296.0499, found: 296.0497.

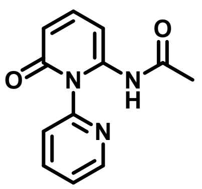


4l

***N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)acetamide (4m)**

Compound **4m** was prepared as described in general procedure for cobalt(III)-catalyzed site-selective C-H amidation of pyridones. White solid, 43.1 mg, 94% yield. Mp: 196-198 °C. **^{1}H NMR**

(400 MHz, DMSO-d_6) δ 9.54 (s, 1H), 8.60 – 8.58 (m, 1H), 7.97 (td, *J* = 8.0, 2.0 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.51 – 7.48 (m, 1H), 7.34 – 7.31 (m, 1H), 6.40 (dd, *J* = 9.2, 1.2 Hz, 1H), 6.30 (dd, *J* = 7.2, 1.2 Hz, 1H). **^{13}C NMR** (126 MHz, DMSO-d_6) δ 168.7, 162.2, 150.0, 149.0, 140.8, 140.4, 138.2, 124.4, 124.1, 117.8, 103.1, 22.3. **HRMS** (ESI) $[M-H]^-$ calcd for $C_{12}H_{10}N_3O_2$: 228.0779, found: 228.0774.

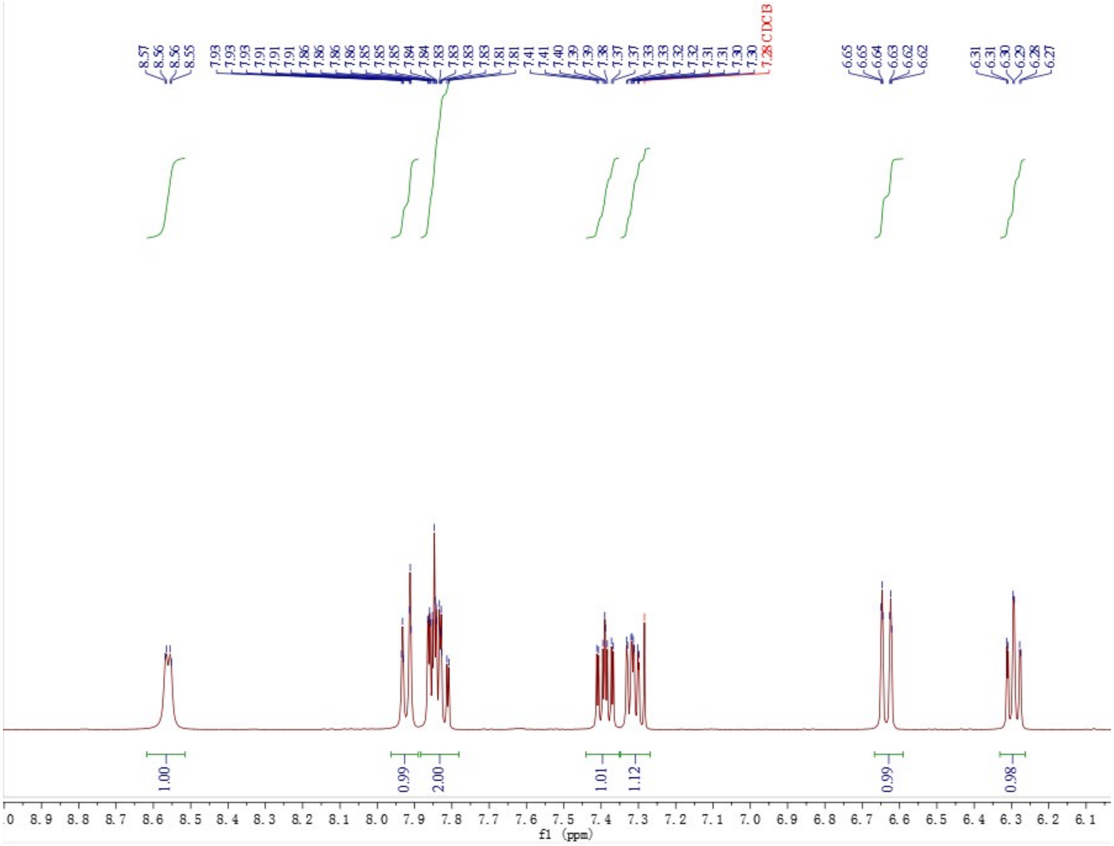


4m

3. Mechanistic Investigations

H/D exchange experiments

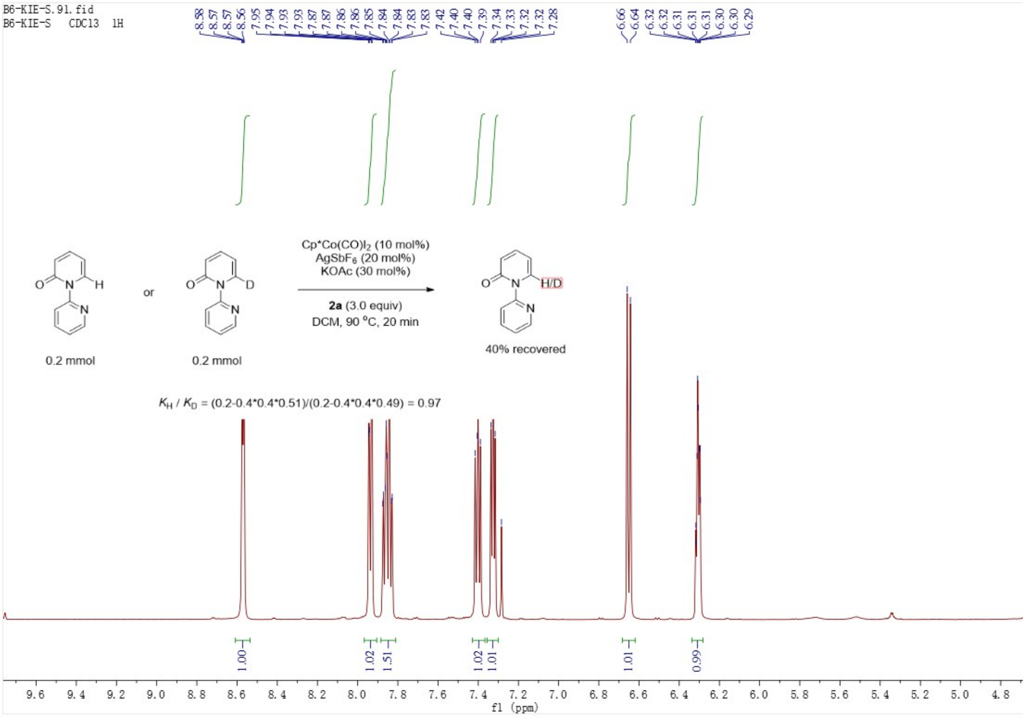
The dry sealed tube was charged with **1a** (0.2 mmol), Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%), KOAc (30 mol%) and CD_3OD (2 mol) were dissolved in DCM (2 mL). The resulting mixture was stirred at 90 °C for 12 h. Then the solvent was removed under vacuum and ^{1}H NMR indicated that the C6-H was not deuterated.



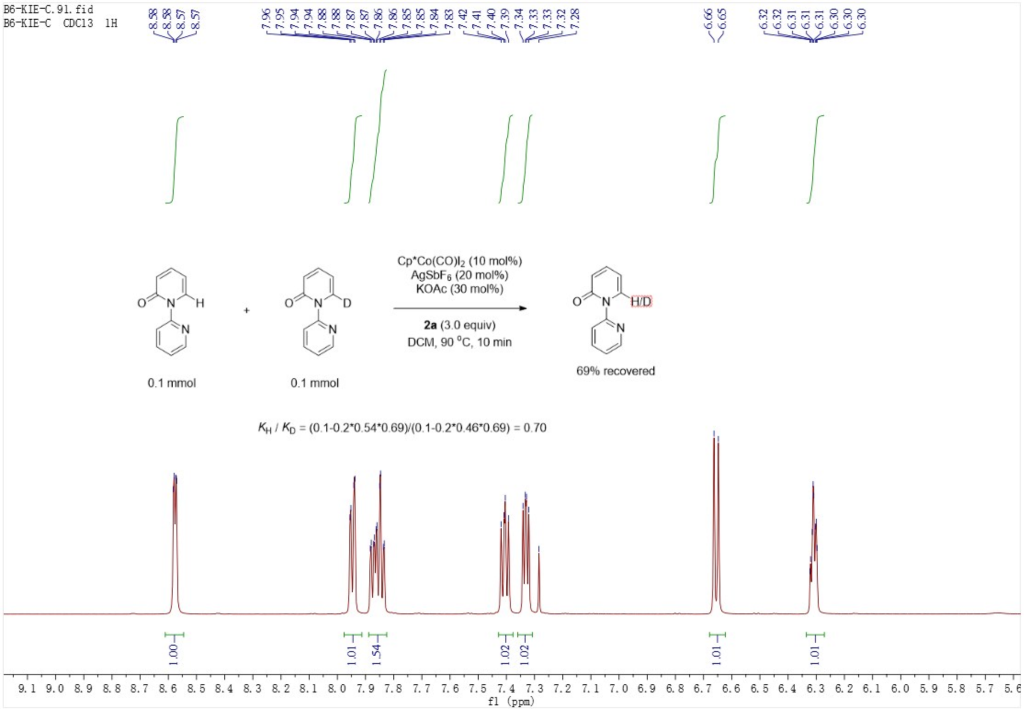
Scheme S1 H/D exchange experiment

KIE experiments

A mixture of 2*H*-[1,2'-bipyridin]-2-one **1a** (0.20 mmol) or deuterium-labeled compound [D_1]-**1a** (0.20 mmol), phenyl oxazolone **2a** (0.6 mmol), Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%), KOAc (30 mol%) and DCM (2 mL) were added into a dry sealed tube. The reactions were stirred at 90 °C in parallel for 20 min. After cooling to room temperature, these two reactions were combined and the solvent was removed under vacuum. The residue was purified by flash chromatography using 2% methanol in DCM as eluent. 40% starting material was recovered and the KIE value was determined to be 0.97.



A mixture of 2*H*-[1,2'-bipyridin]-2-one **1a** (0.10 mmol) and deuterium-labeled compound [D$_1$]-**1a** (0.10 mmol), phenyl oxazolone **2a** (0.6 mmol), Cp*Co(CO)I$_2$ (10 mol%), AgSbF$_6$ (20 mol%), KOAc (30 mol%) and DCM (2 mL) were added into a dry sealed tube. The solution was stirred at 90 °C for 10 min. Then the solvent was removed under vacuum and the residue was purified by flash chromatography using 2% methanol in DCM as eluent. 69% starting material was recovered and the KIE value was determined to be 0.70.



Competition experiments

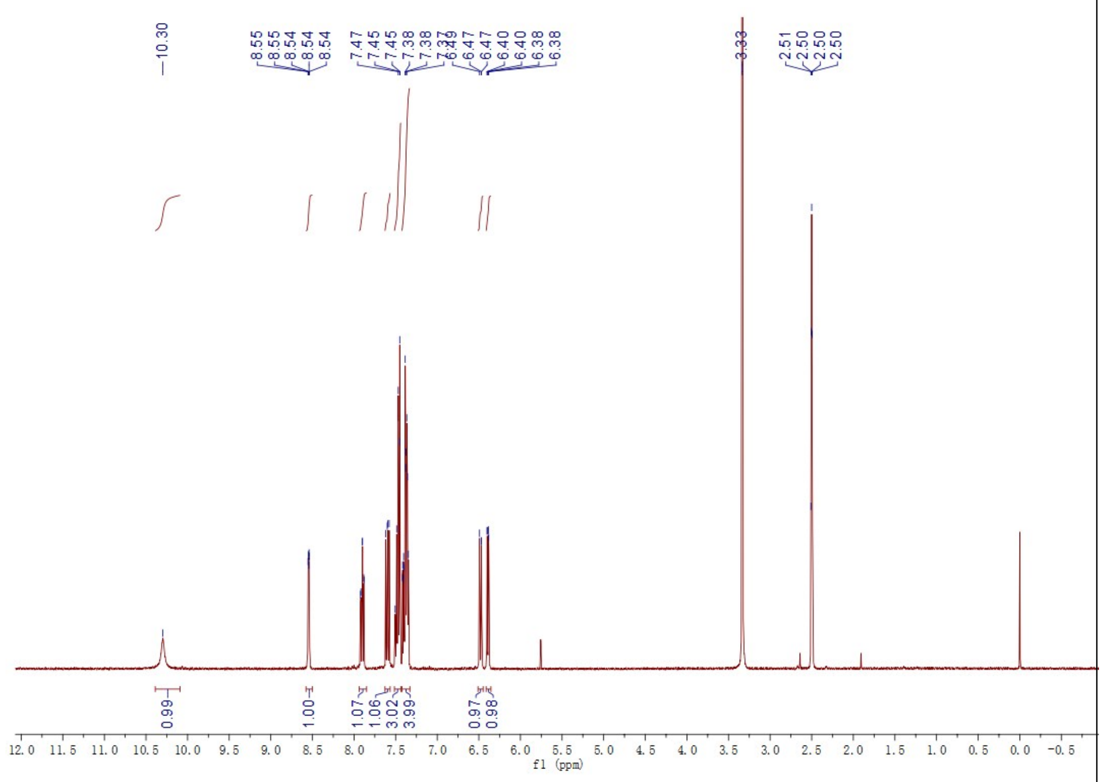
A Schlenk tube equipped with a magnetic stir bar was charged with pyridones **1b** (0.1 mmol) and **1g** (0.1 mmol), phenyl oxazolone **2a** (0.3 mmol), Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%) and KOAc (30 mol%) and then capped with septa. 2 mL of DCM was charged to the vial via syringe, and then the resulting mixture was stirred in a pre-heated oil bath at 90 °C for 1 h. After the reaction was completed, the solvent was removed under vacuum and the residue was purified by silica gel column using 2% methanol in DCM as eluent to afford desired amidated product **3b** in 75% yield and trace amount of **3g** was detected by LC-MS.

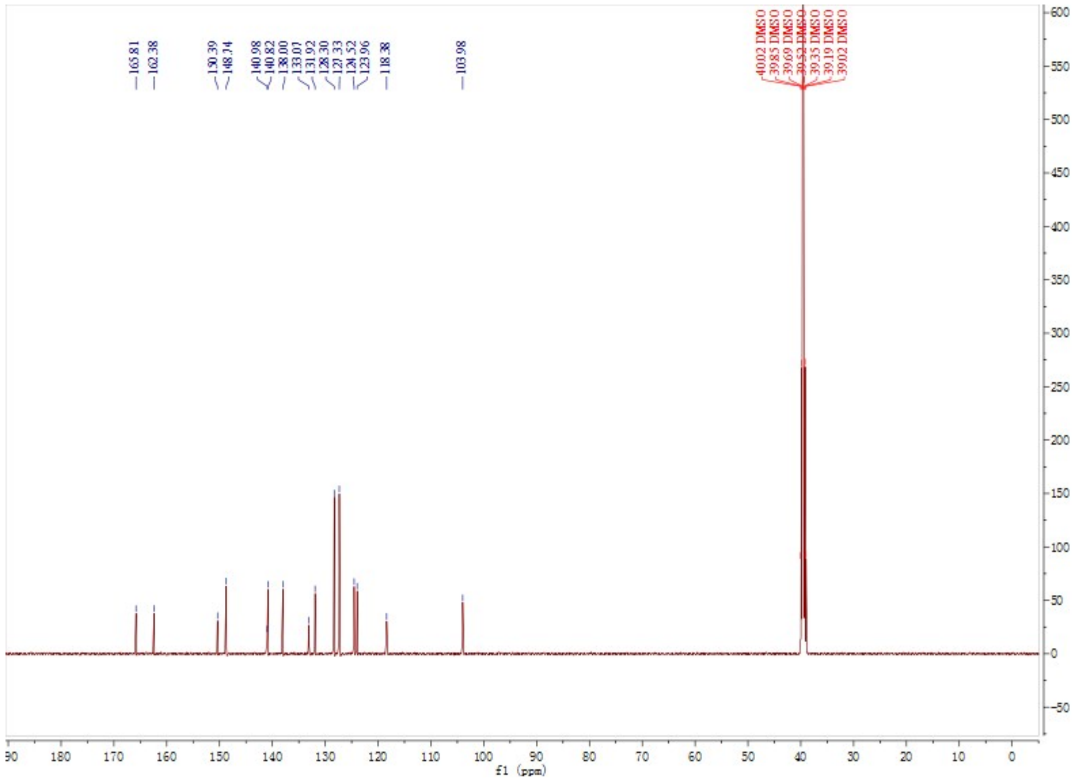
4. References

(1) a) R. Odani, K. Hirano, T. Satoh and M. Miura, *Angew. Chem. Int. Ed.*, 2014, **53**, 10784; b) V. Smout, A. Peschiulli, S. Verbeeck, E. A. Mitchell, W. Herrebout, P. Bultinck, C. M. Vande Velde, D. Berthelot, L. Meerpoel, B. U. Maes, *J. Org. Chem.,* 2013, **78**, 9803; c) P. Peng, J. Wang, C. Li, W. Zhu, H. Jiang, H. Liu, *Rsc Advances,* 2016, **6**, 57441.

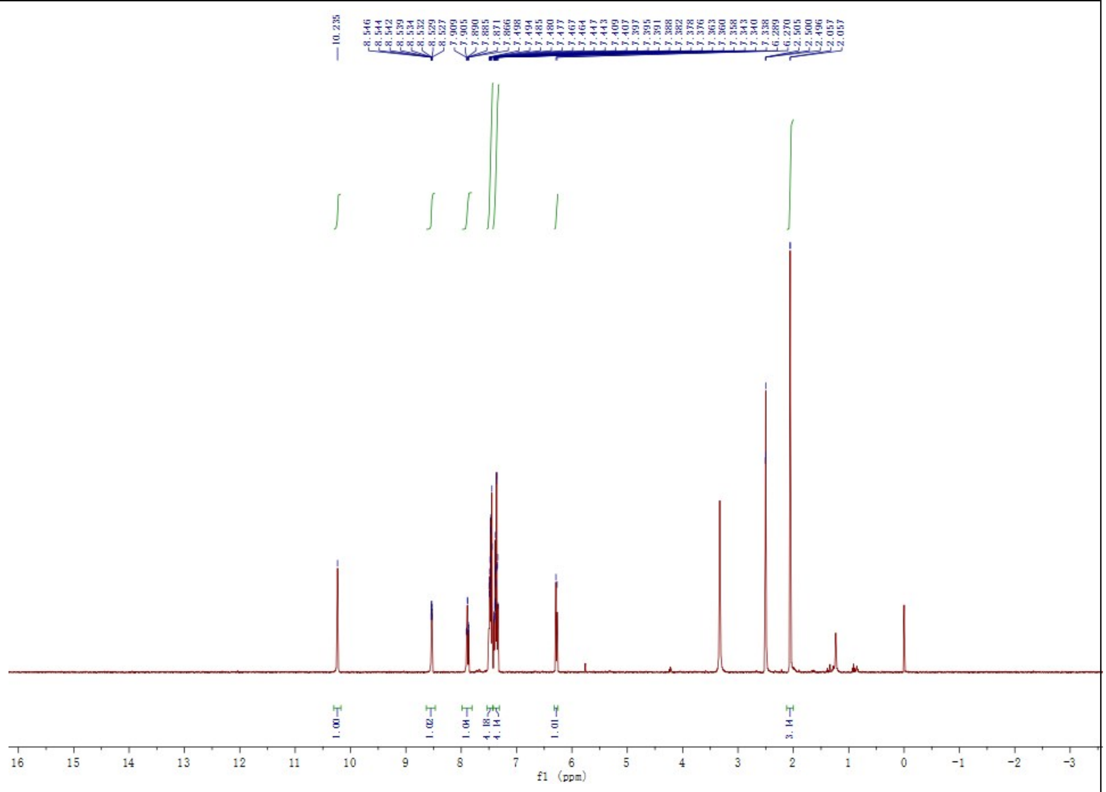
5. NMR spectra

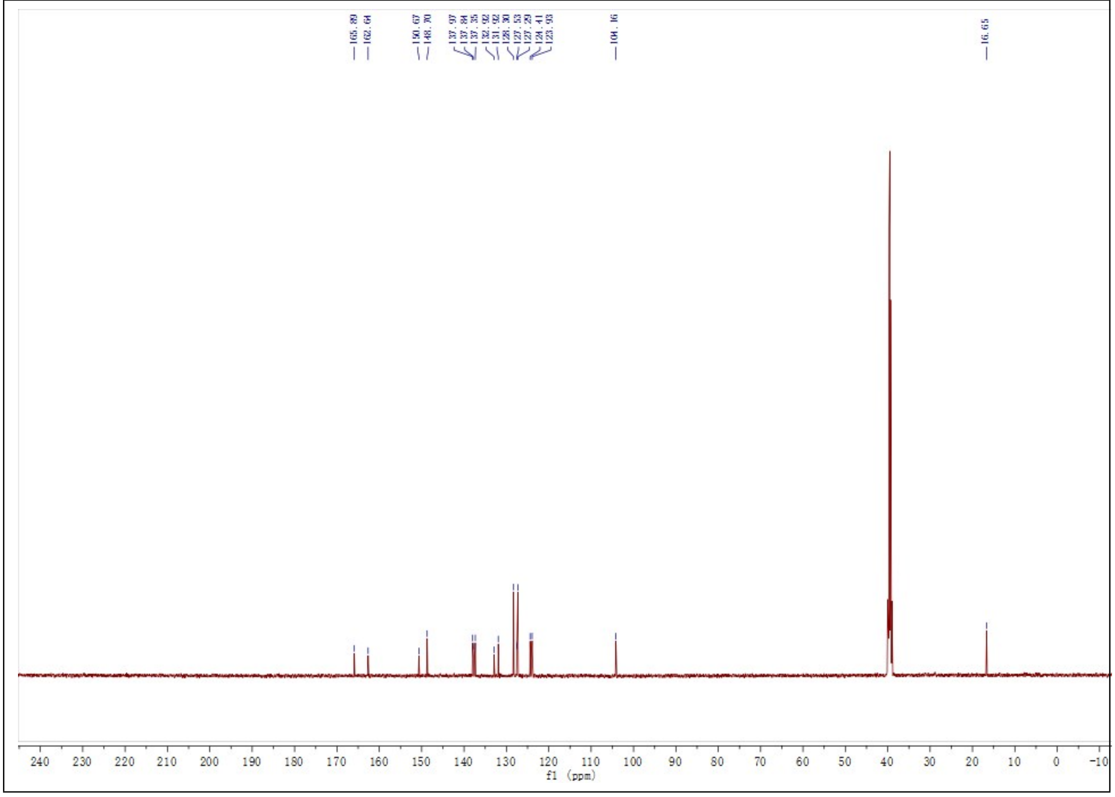
***N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (3a)**





N-(3-methyl-2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (3b)





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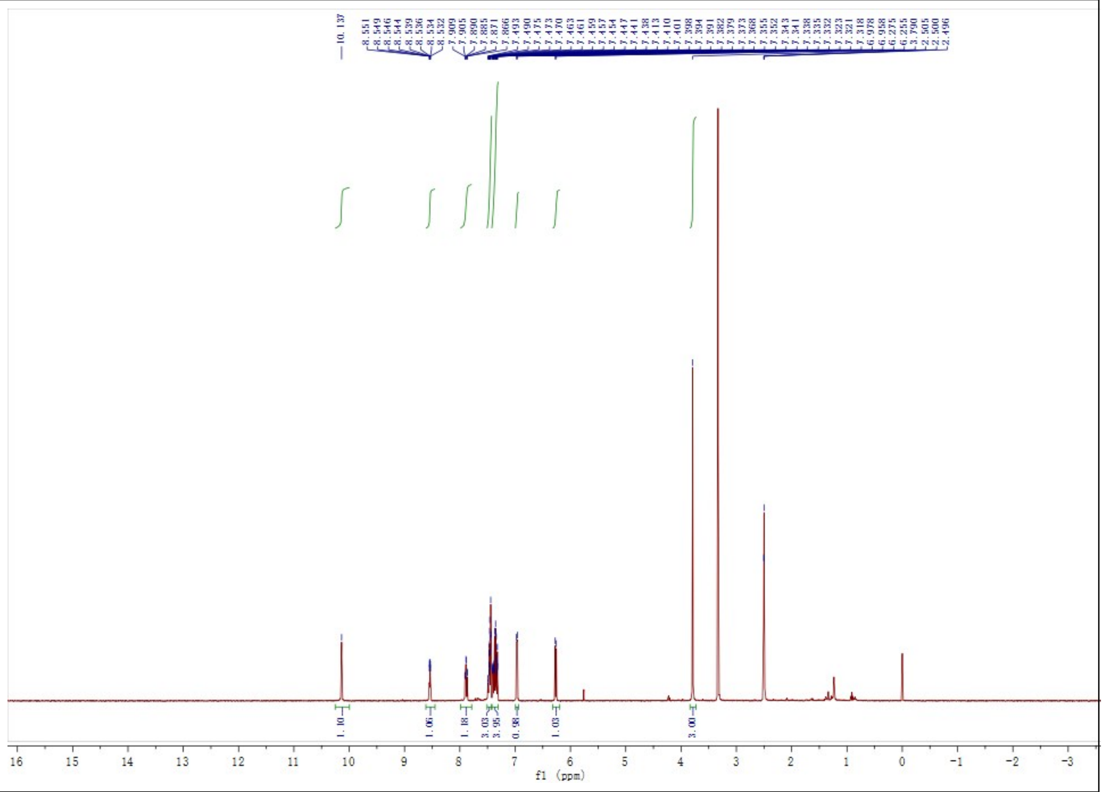

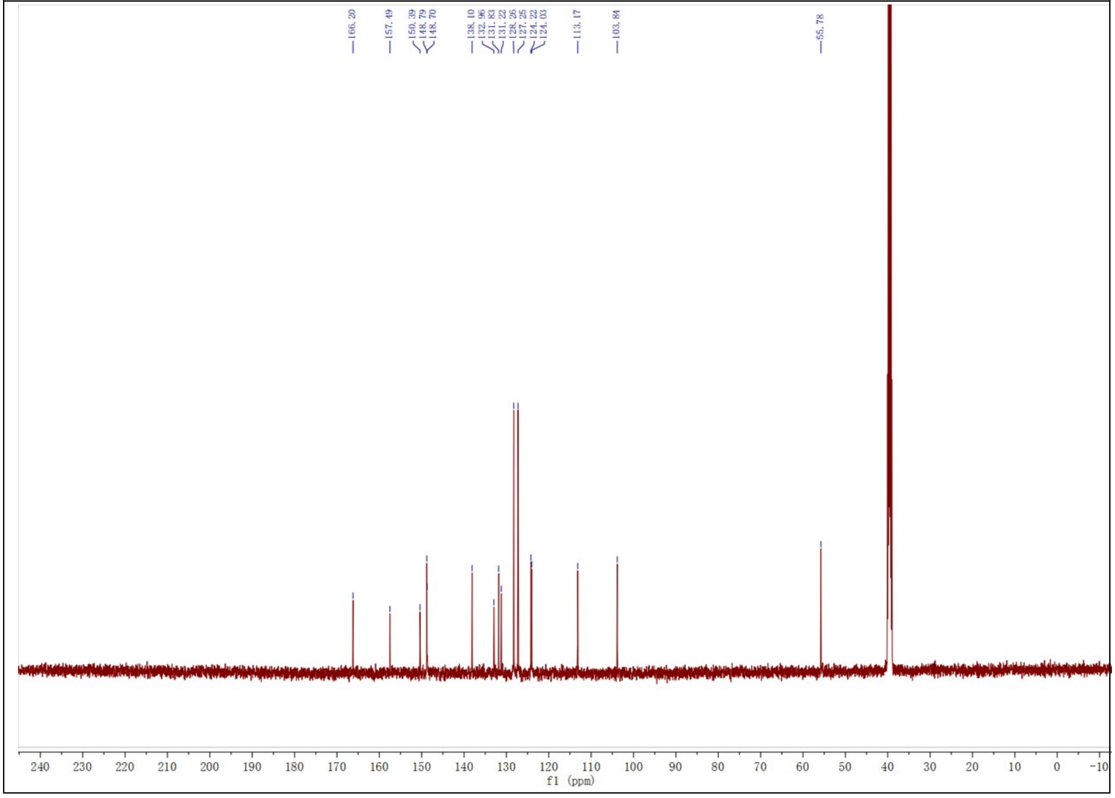

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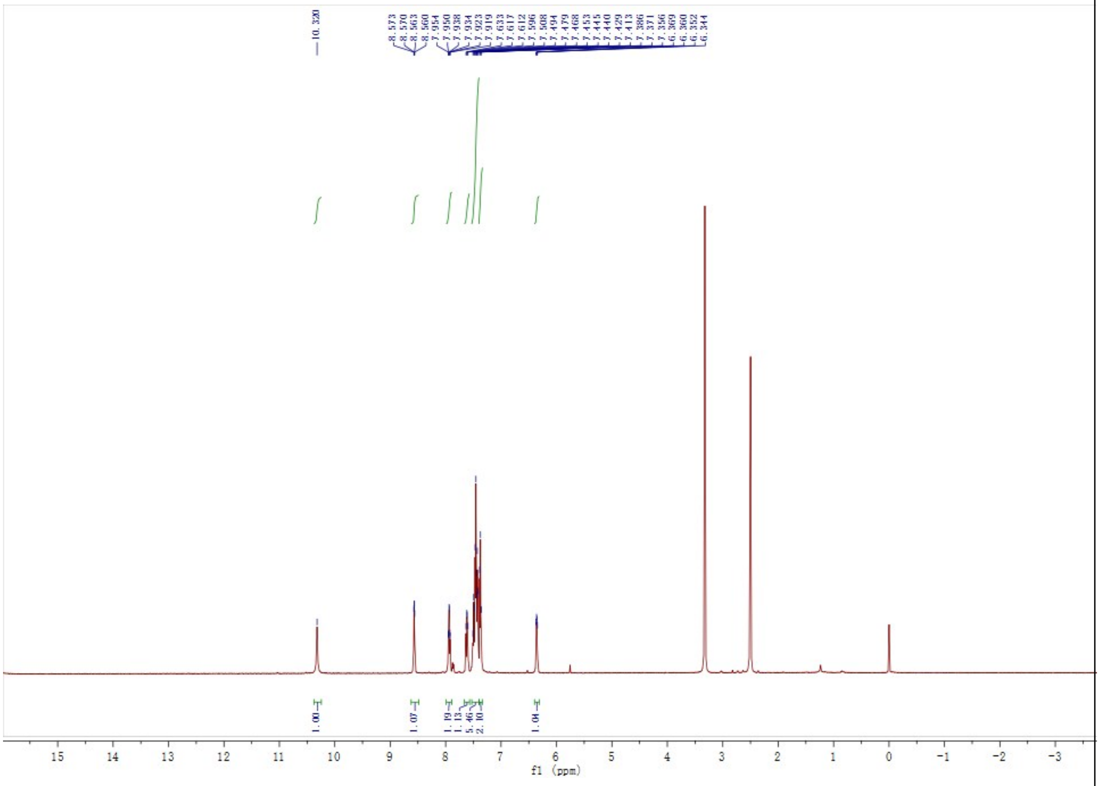

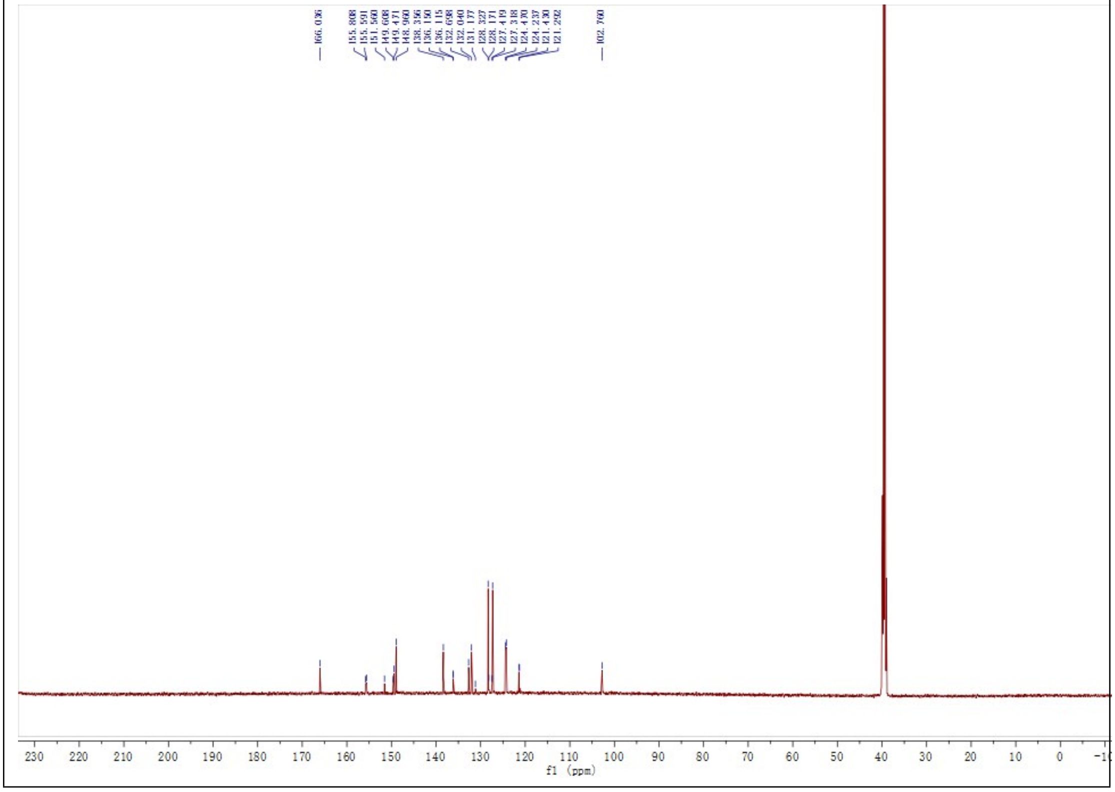

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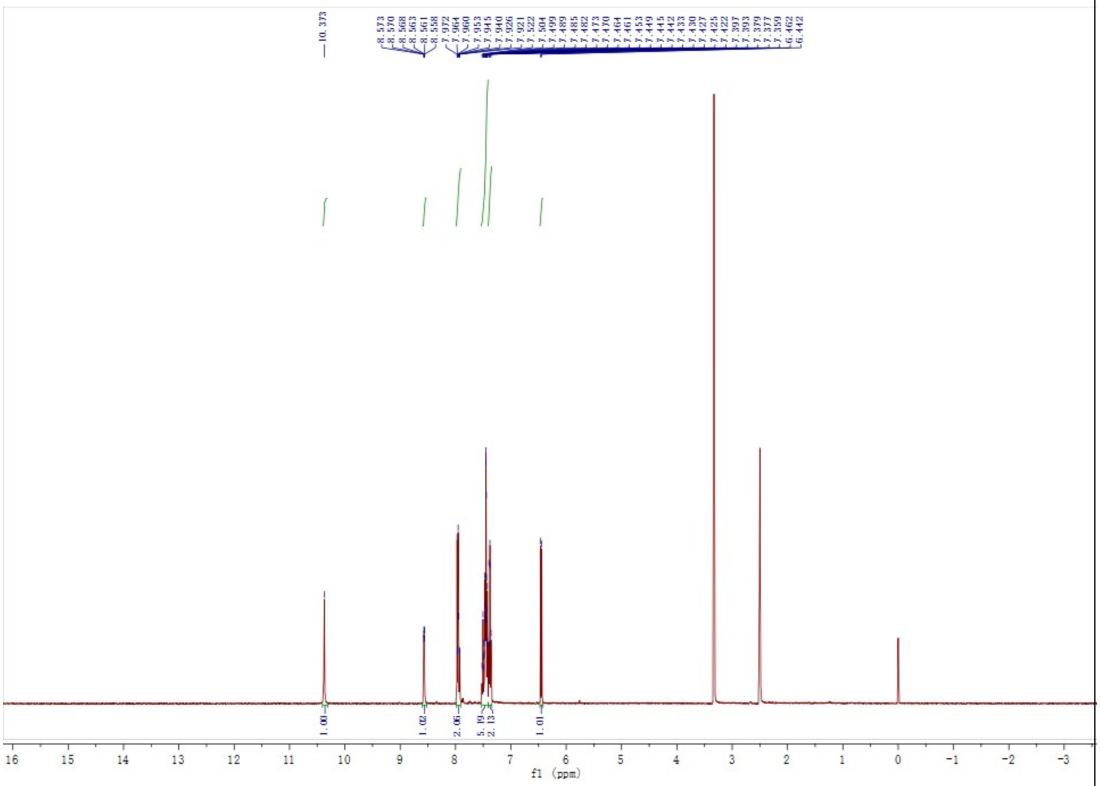

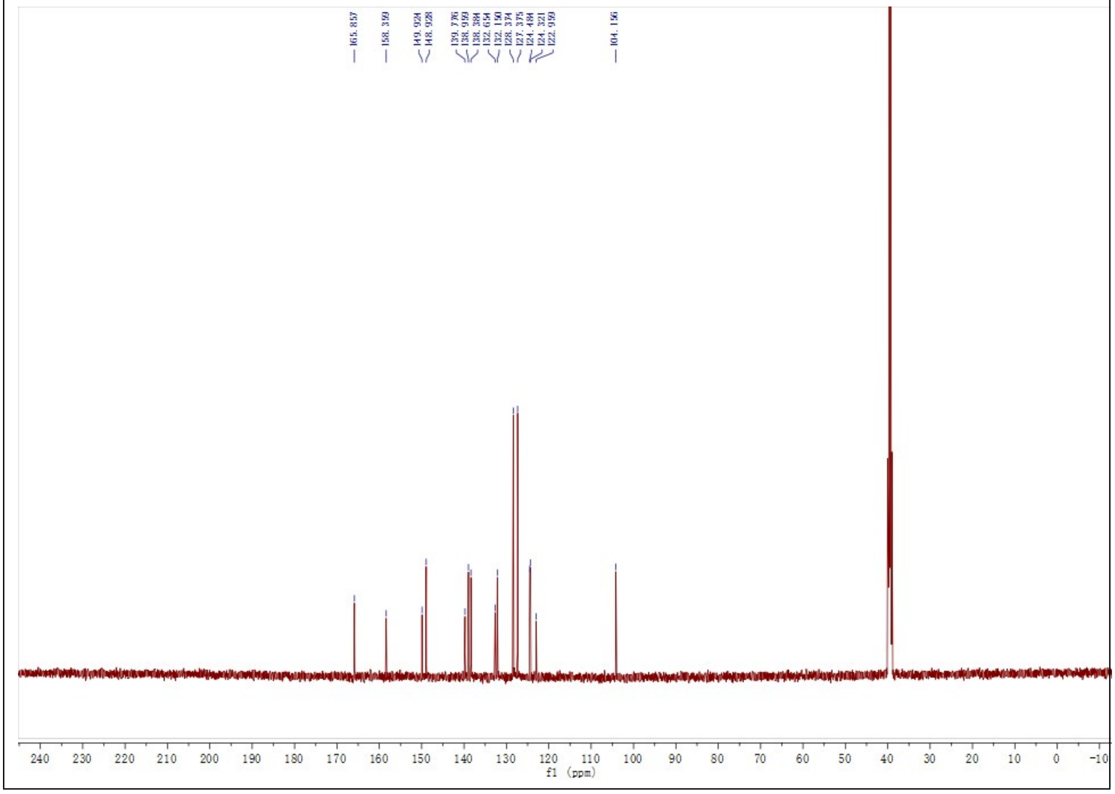

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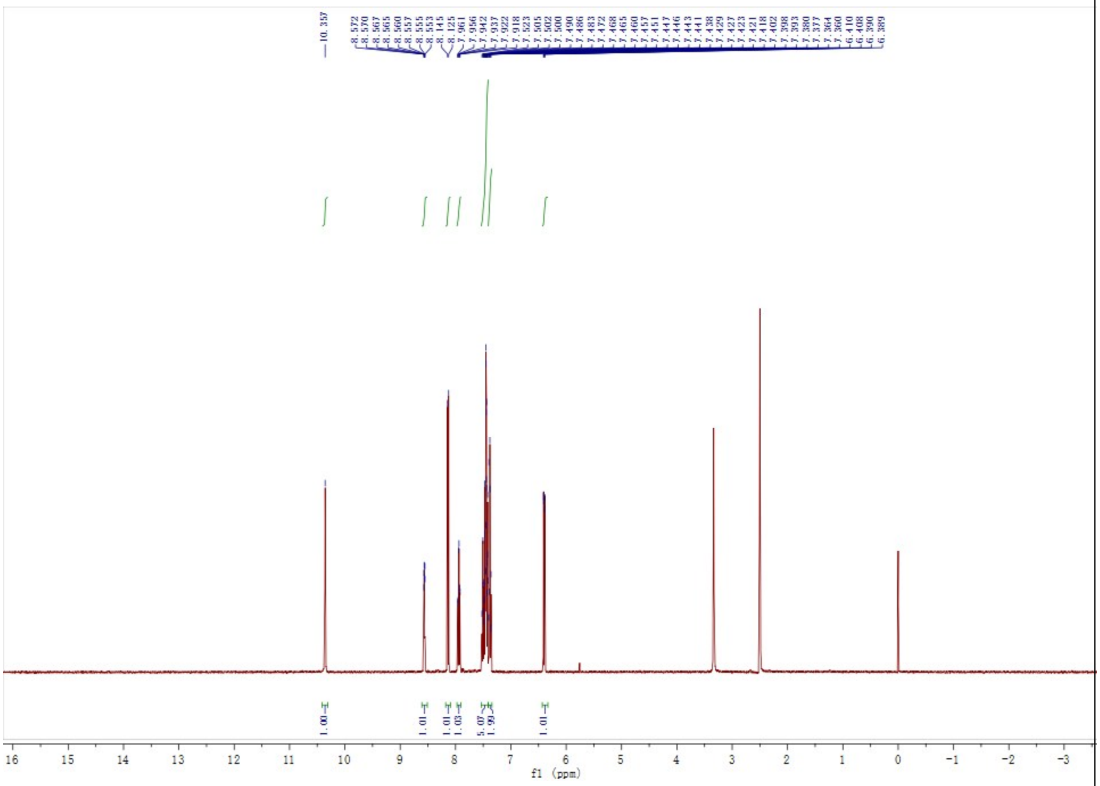

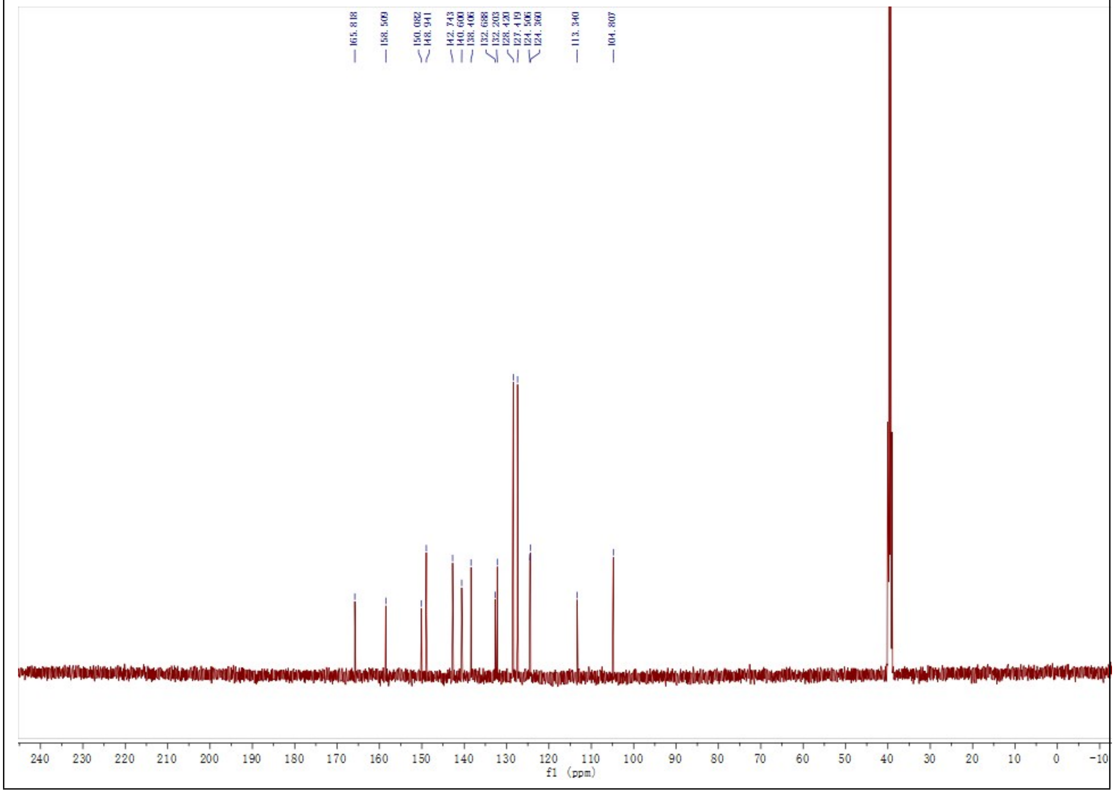

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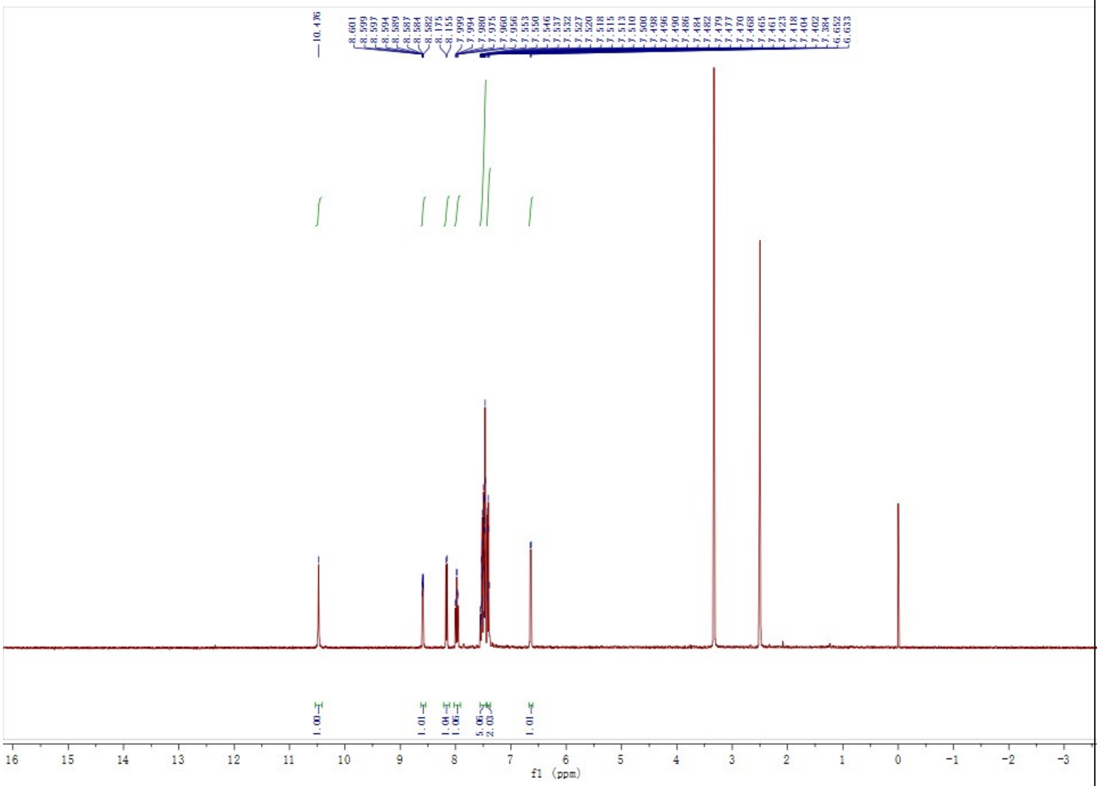

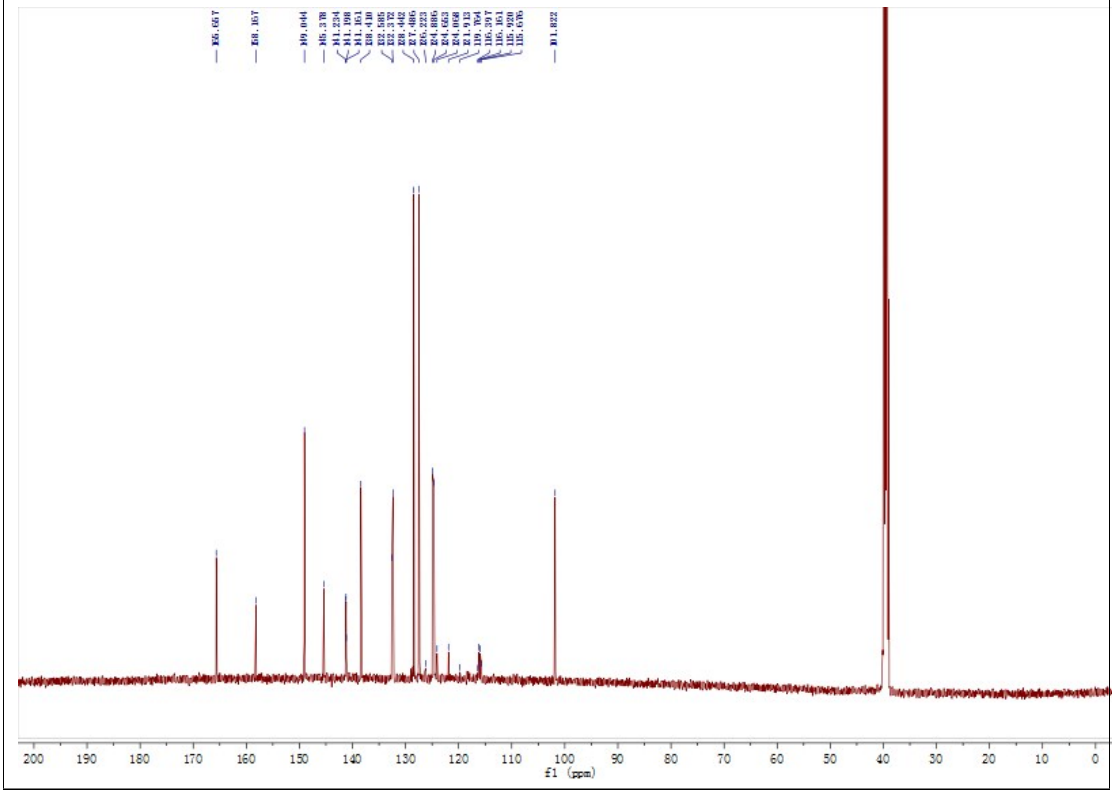

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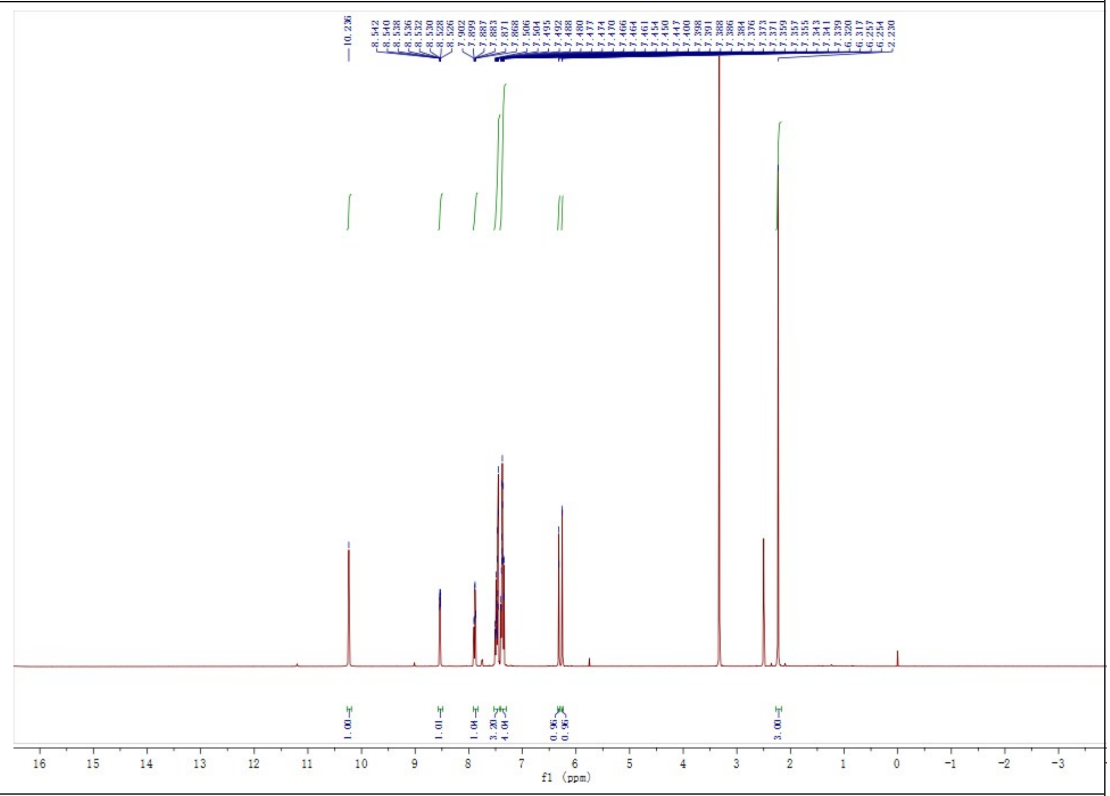

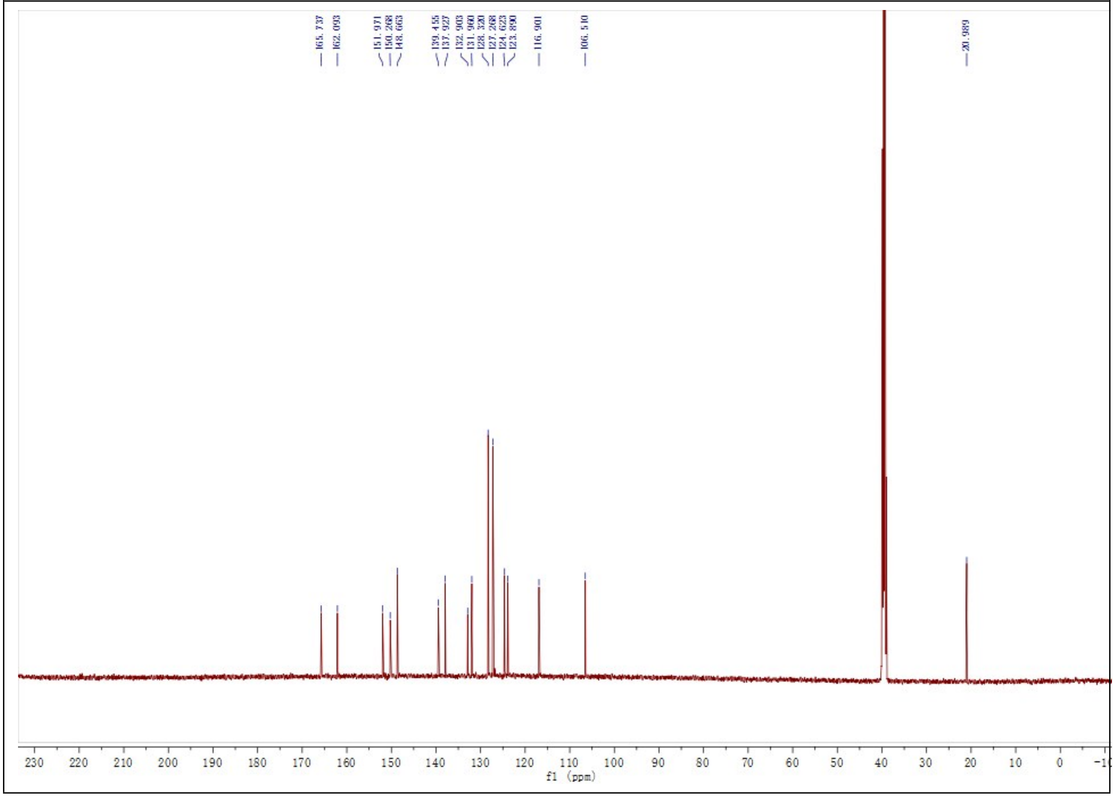

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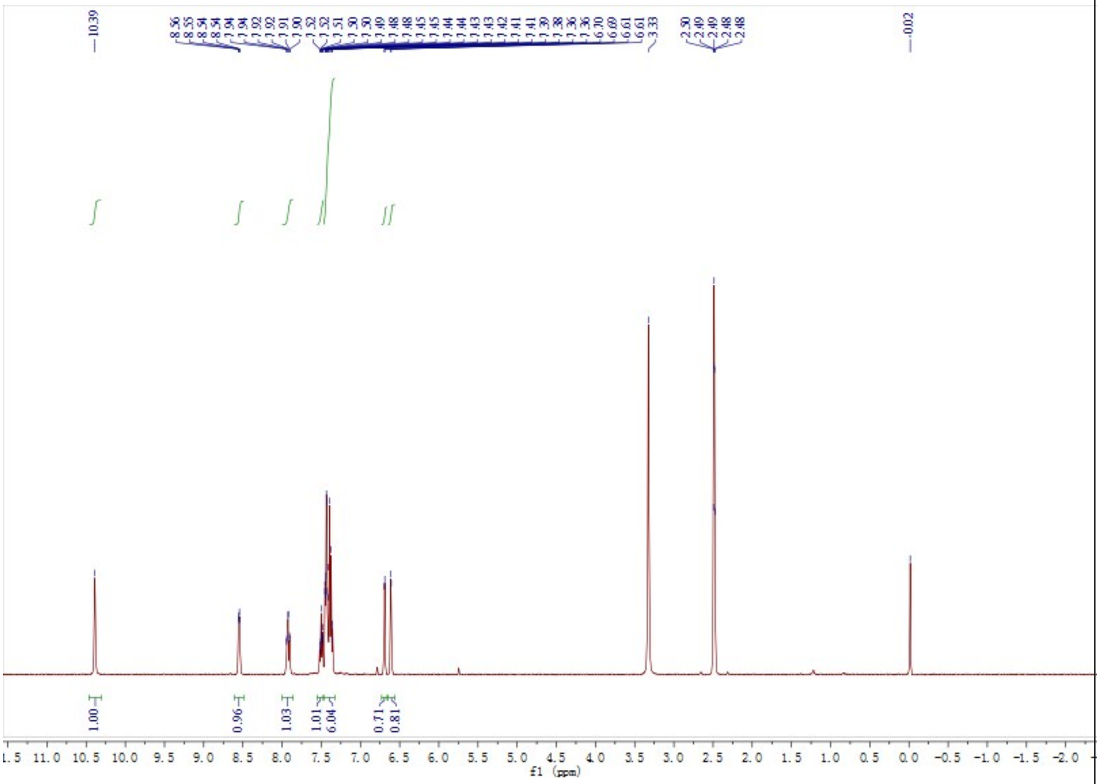

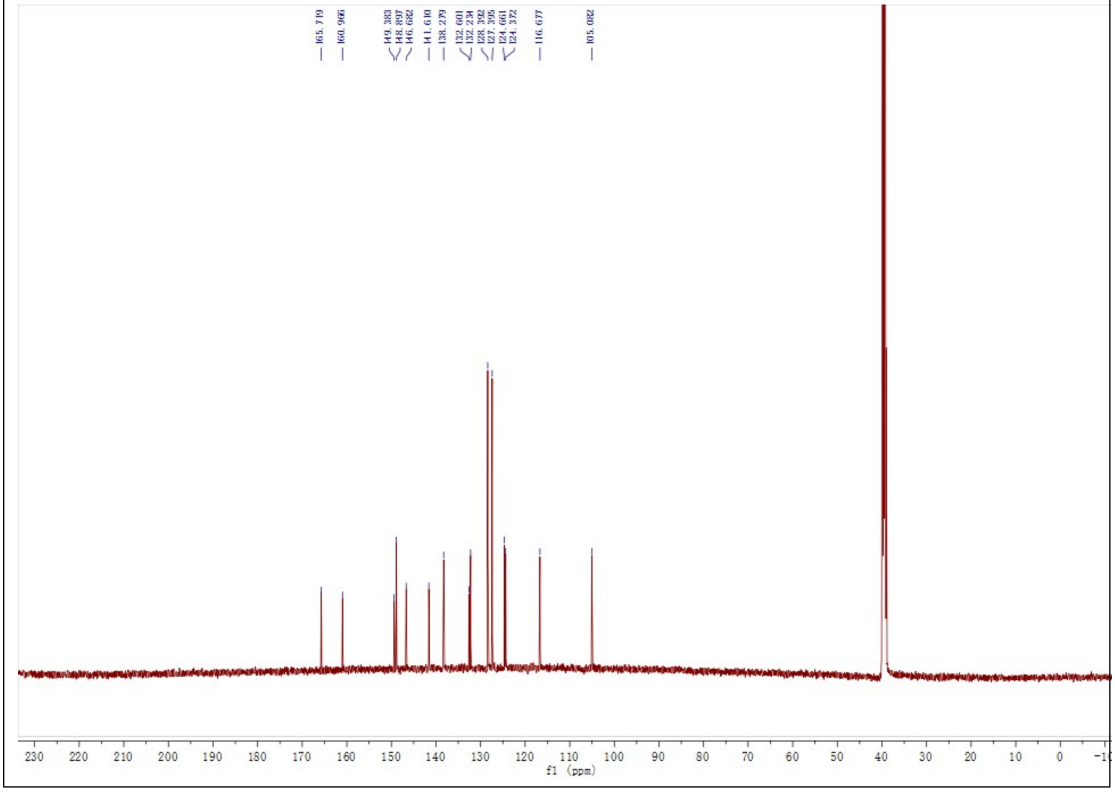

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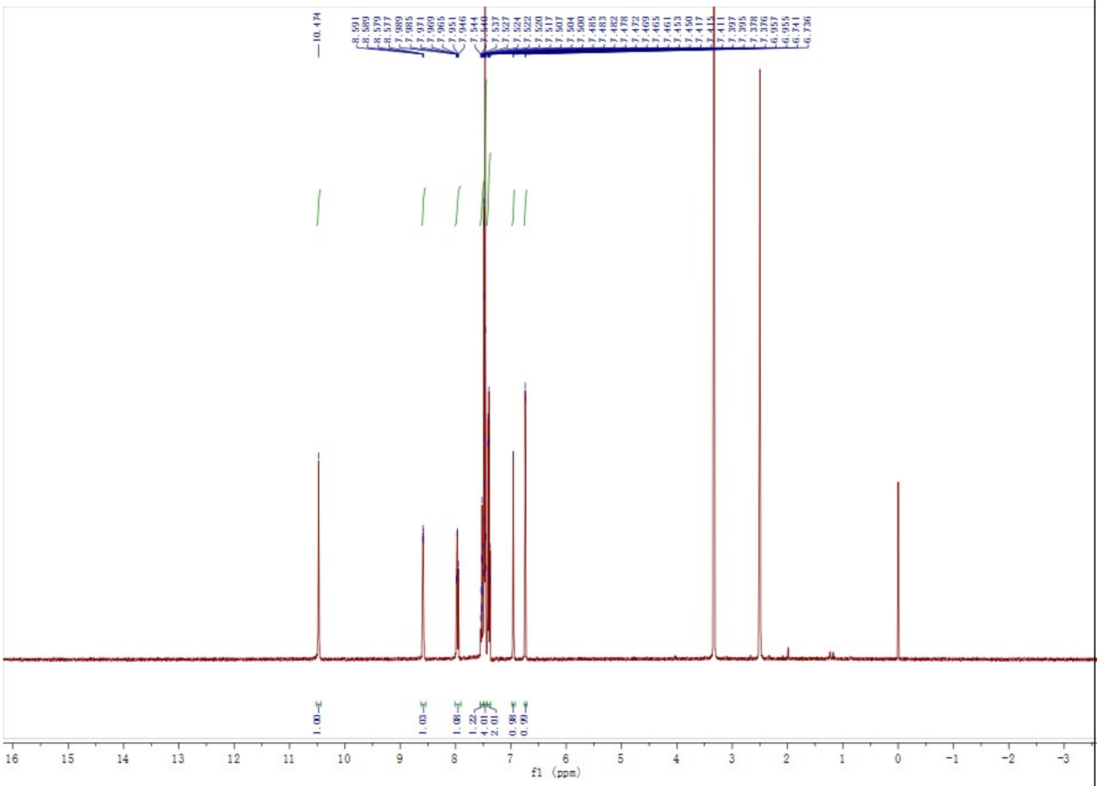

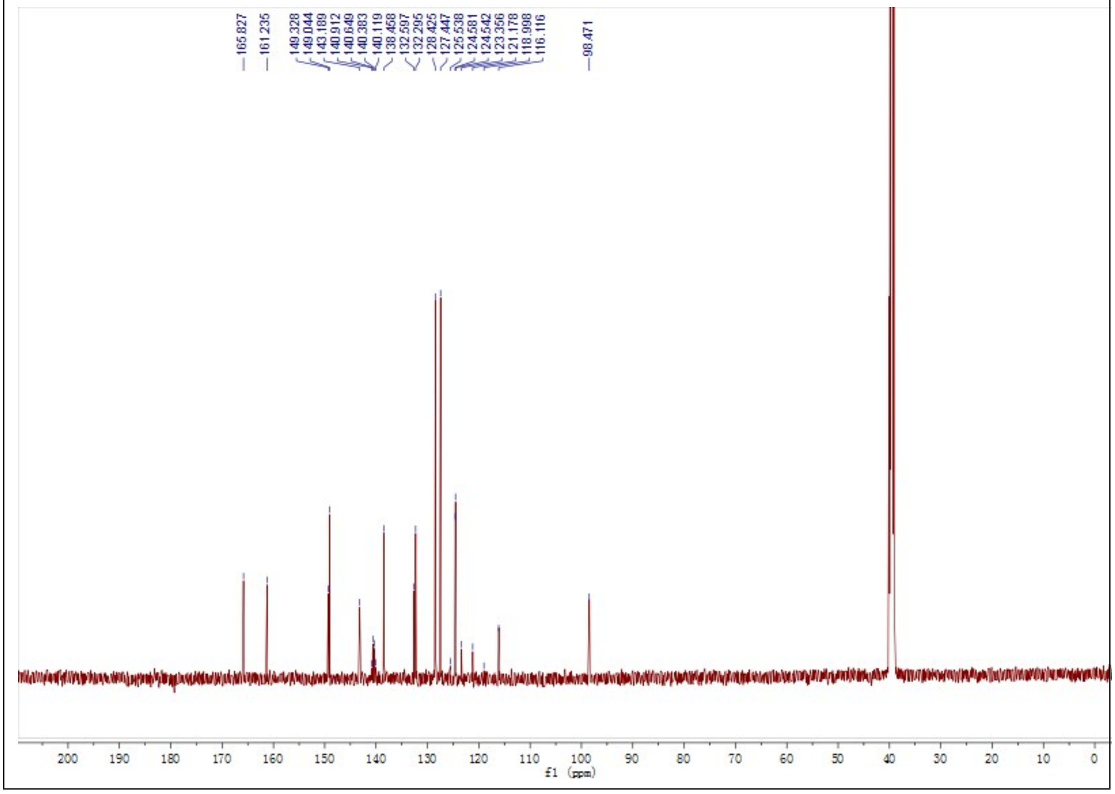

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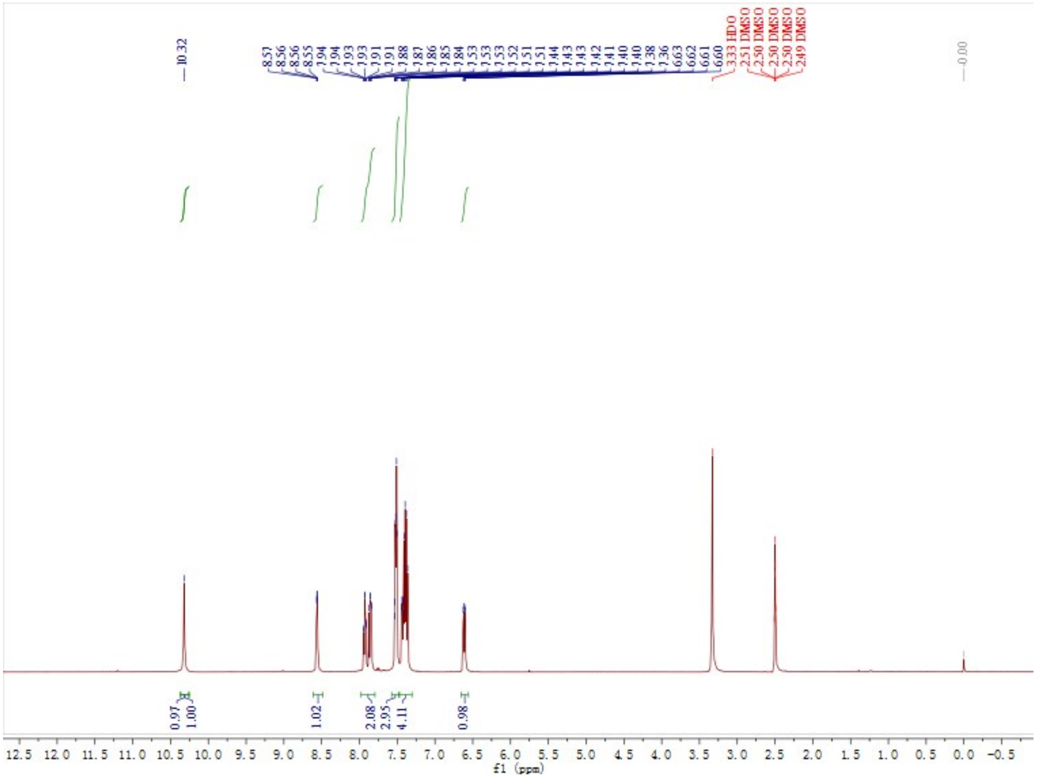
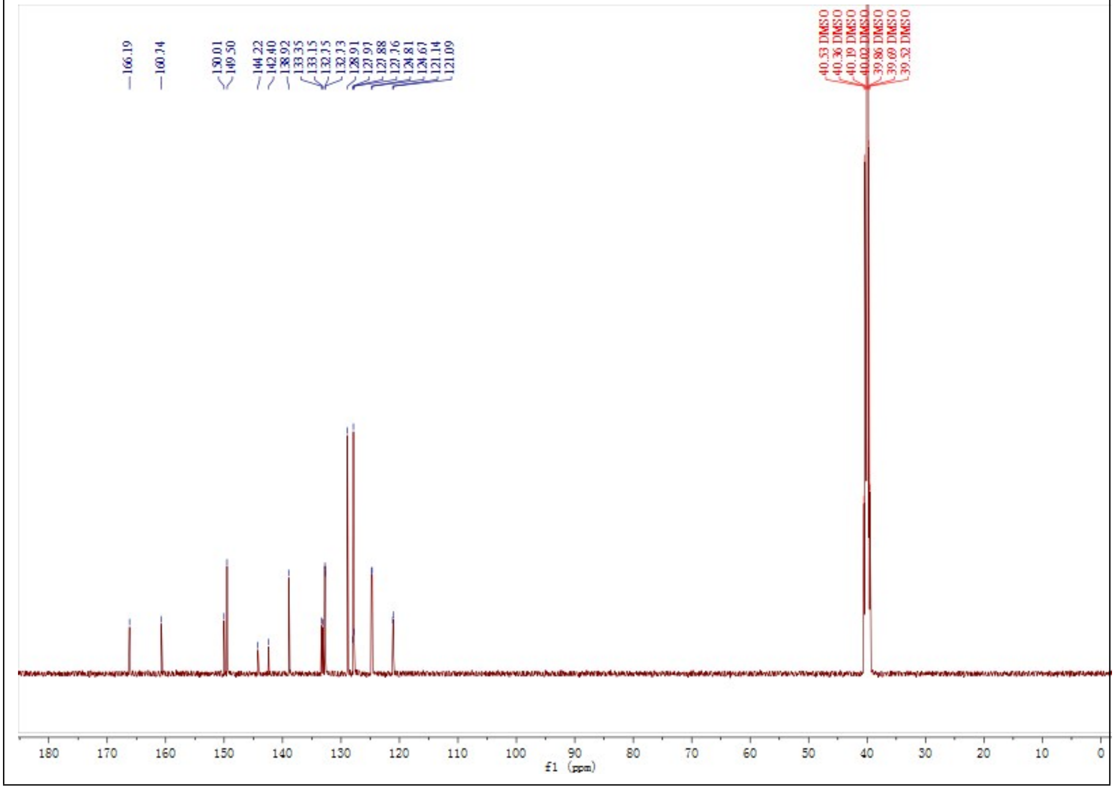
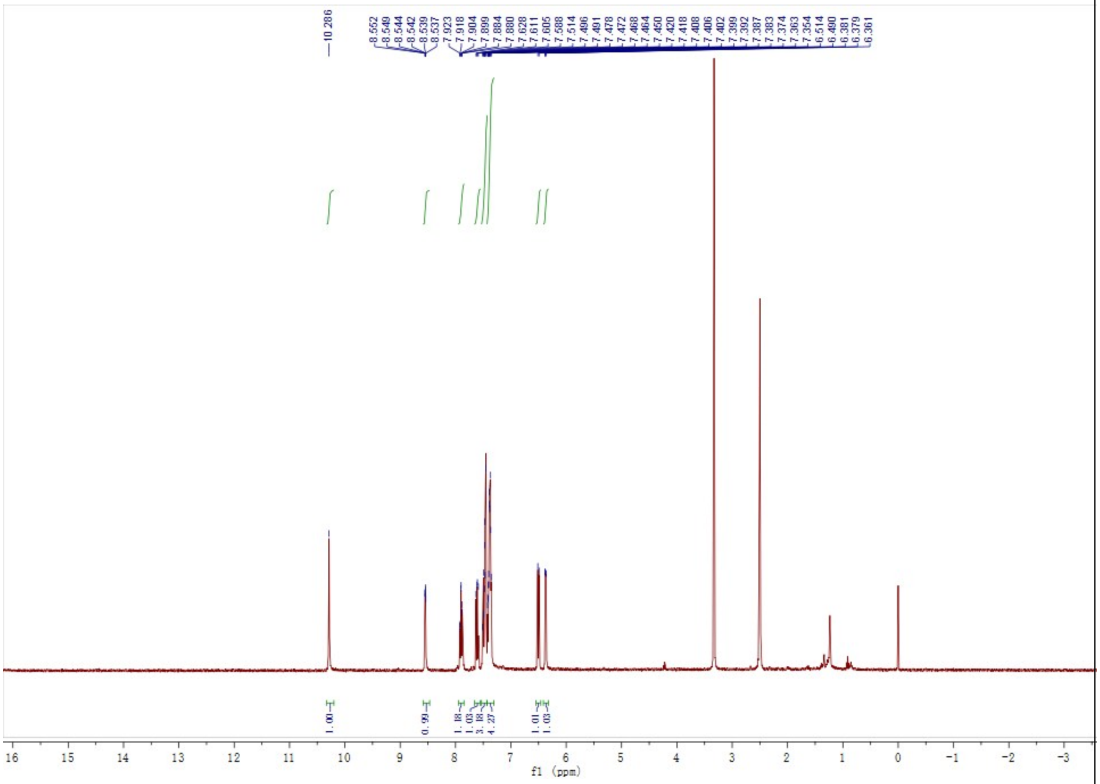
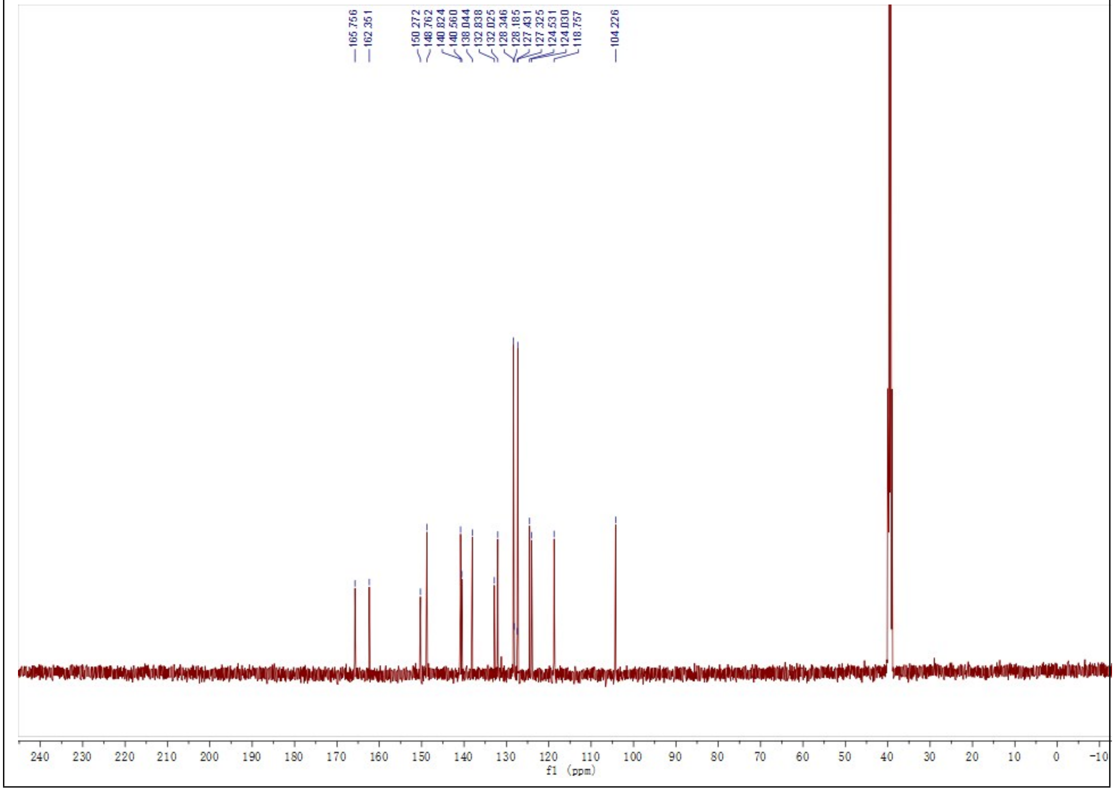


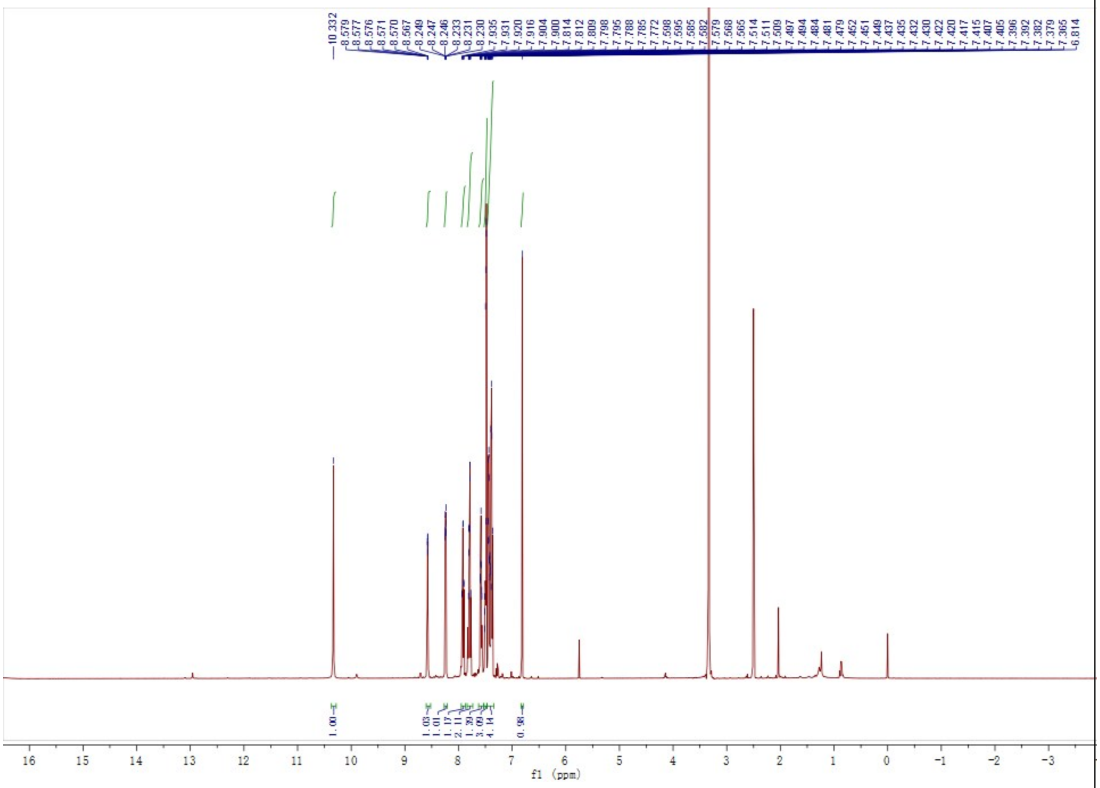


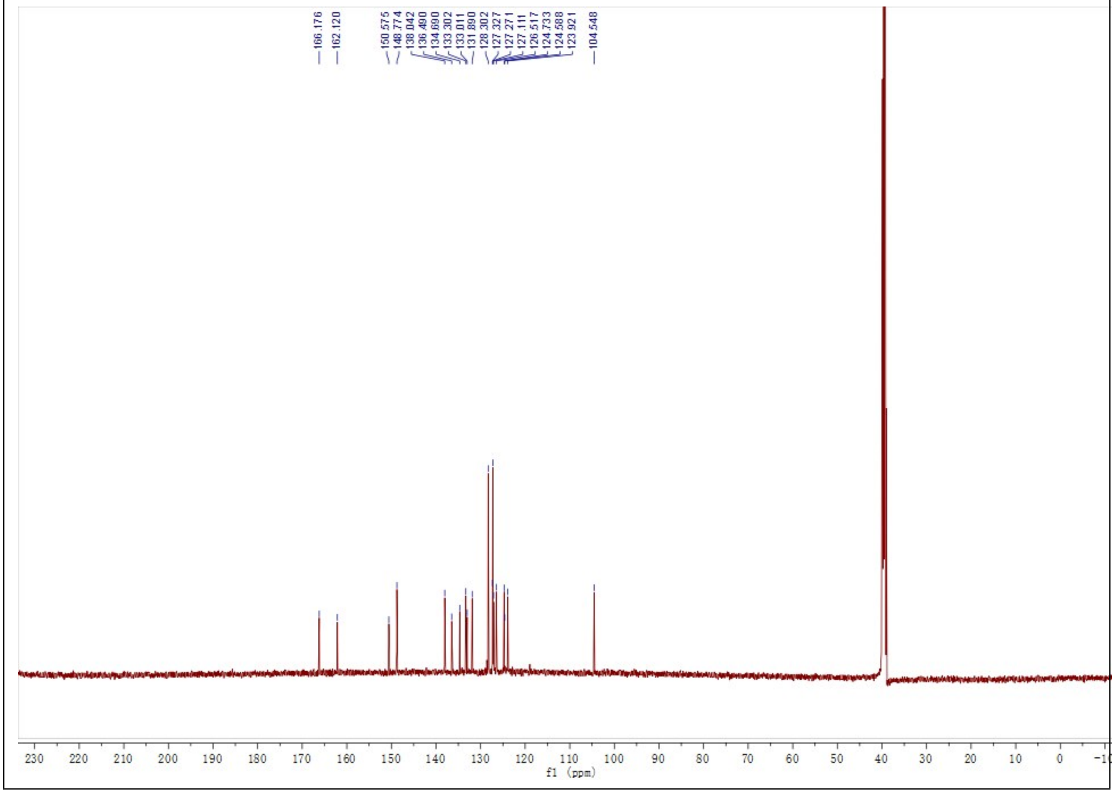
N-(4-oxo-4*H*-[1,2'-bipyridin]-2-yl)benzamide (3m)



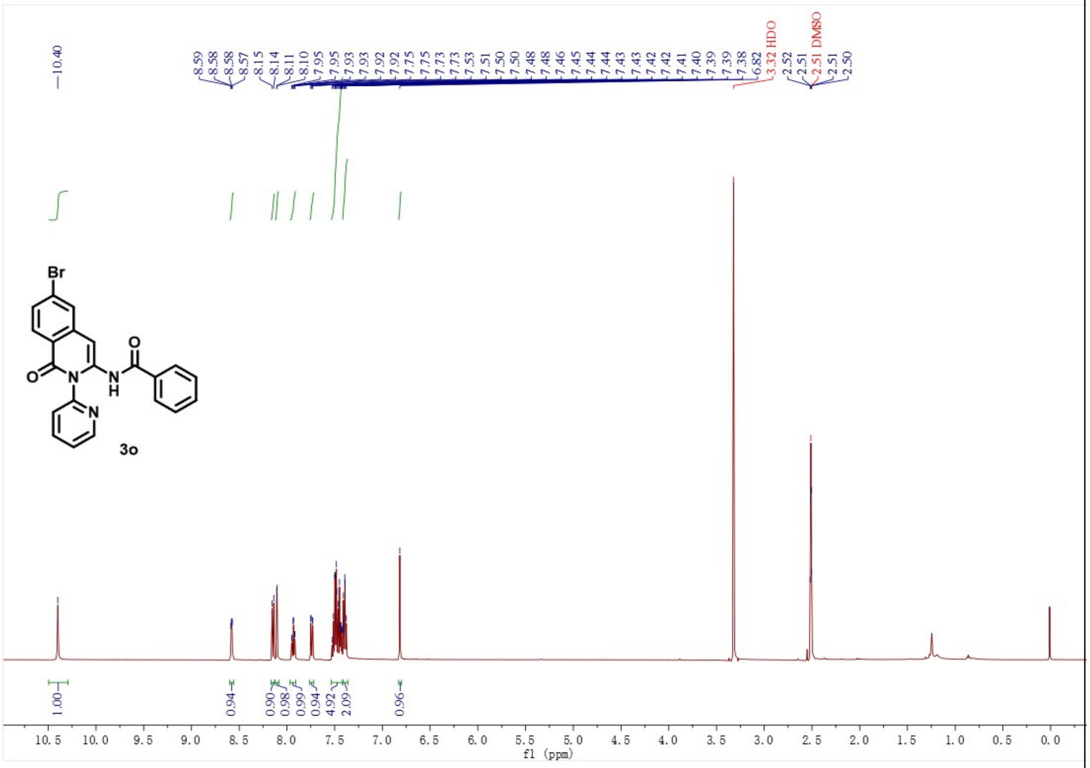


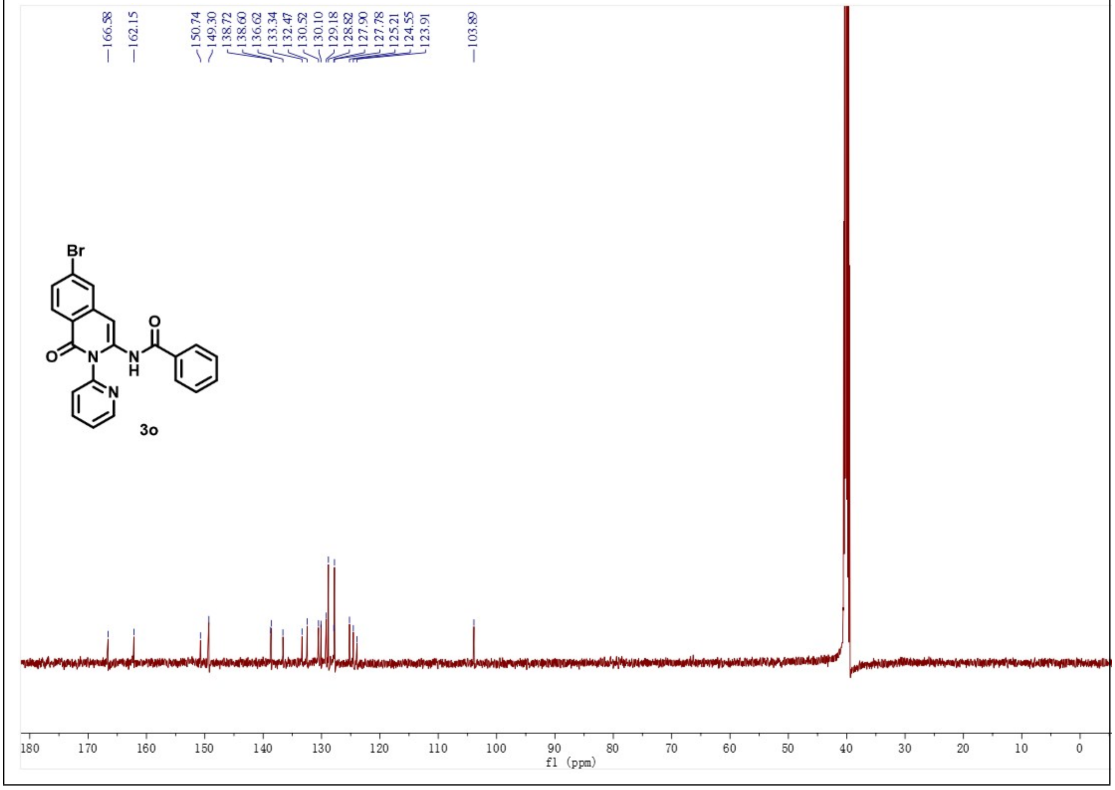
***N*-(1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3n)**



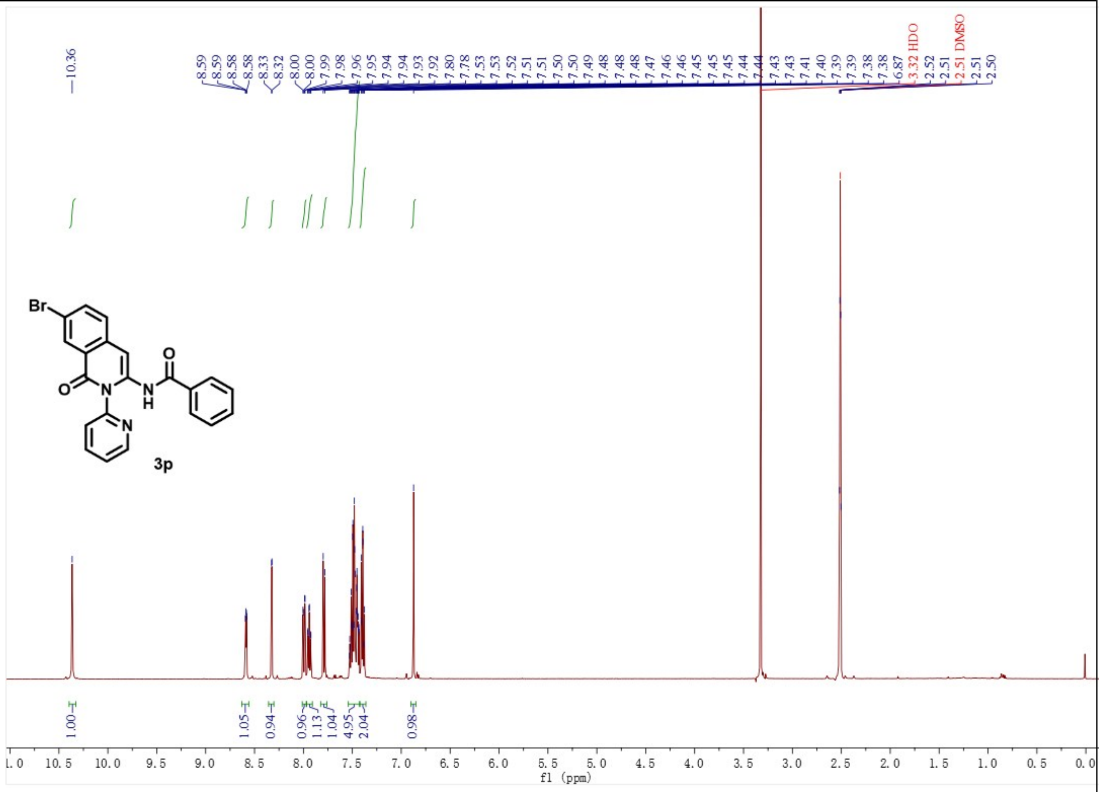


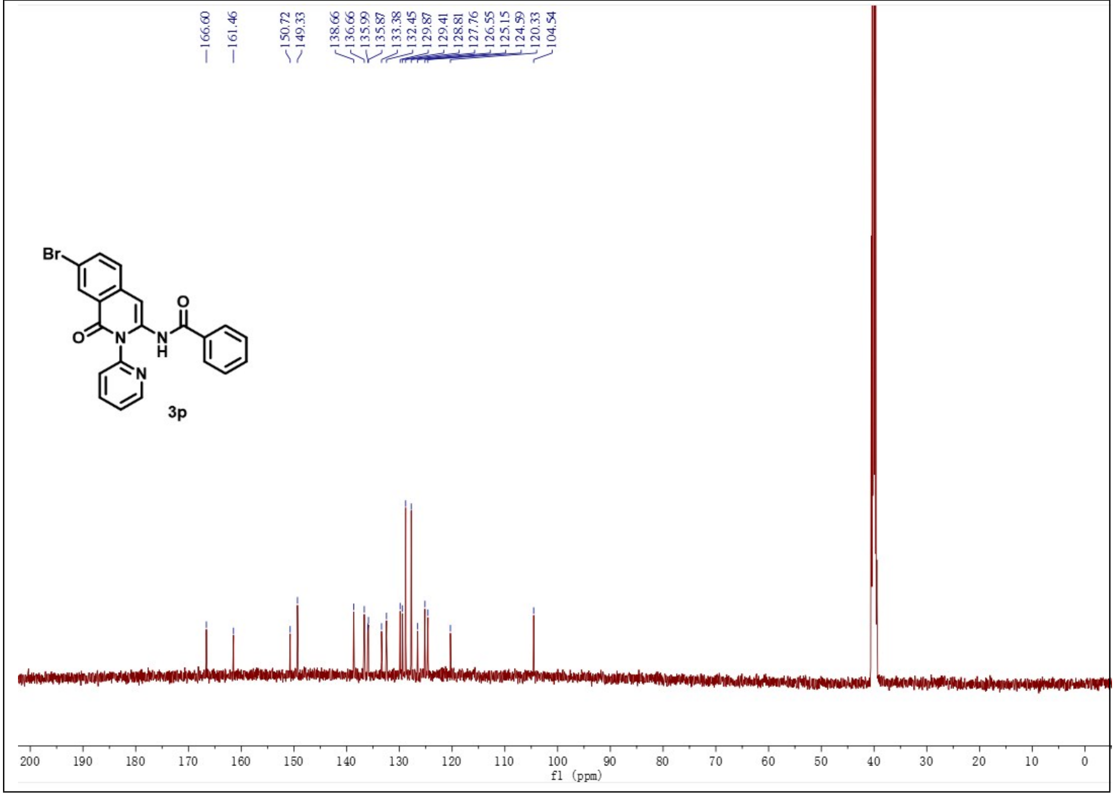
N-(6-bromo-1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3o)





N-(7-bromo-1-oxo-2-(pyridin-2-yl)-1,2-dihydroisoquinolin-3-yl)benzamide (3p)





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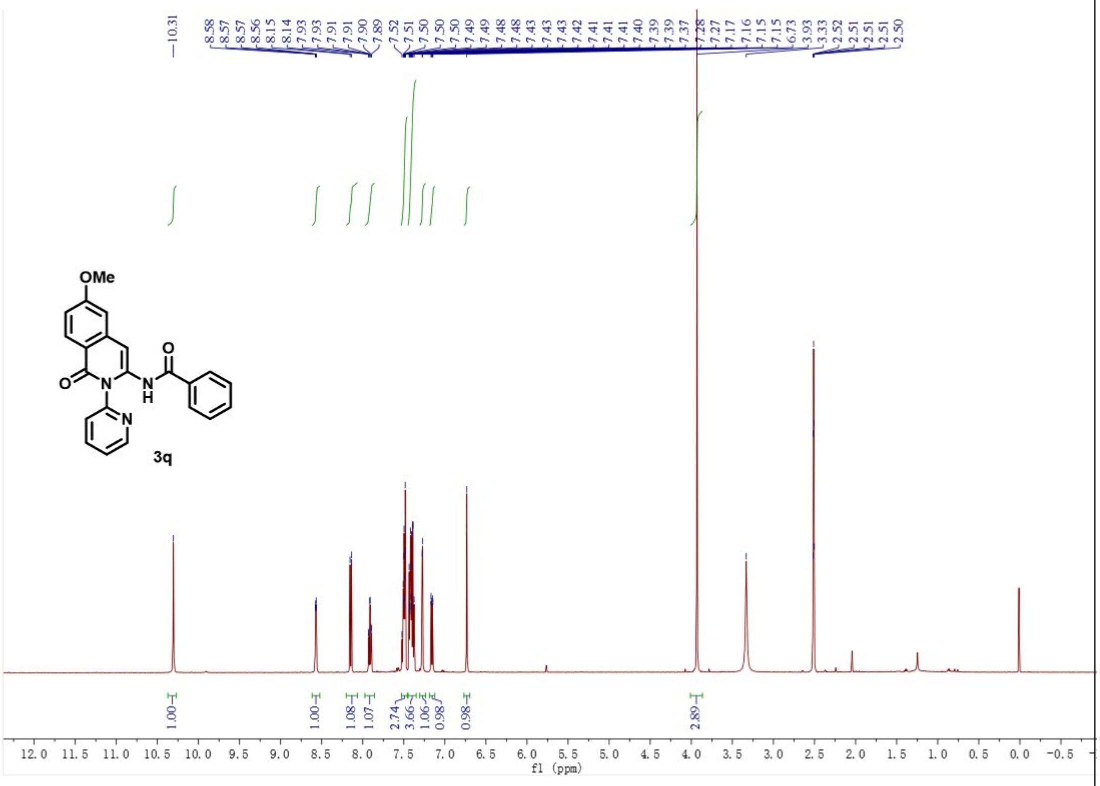
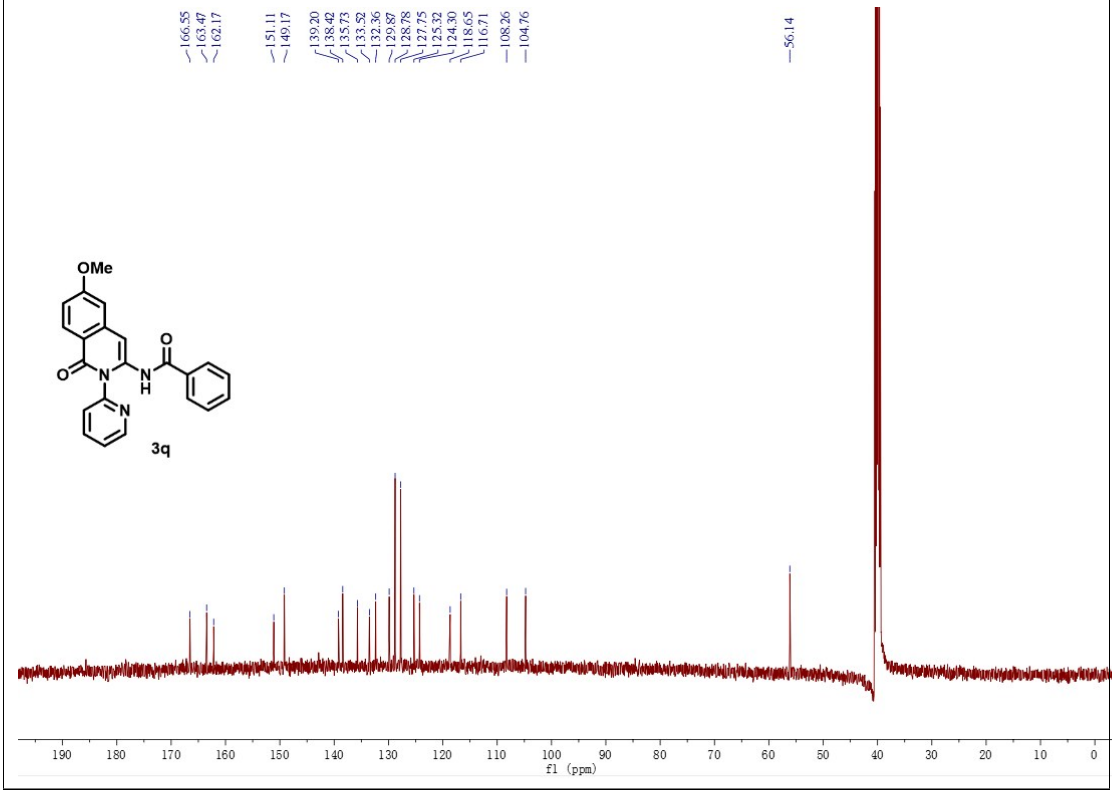
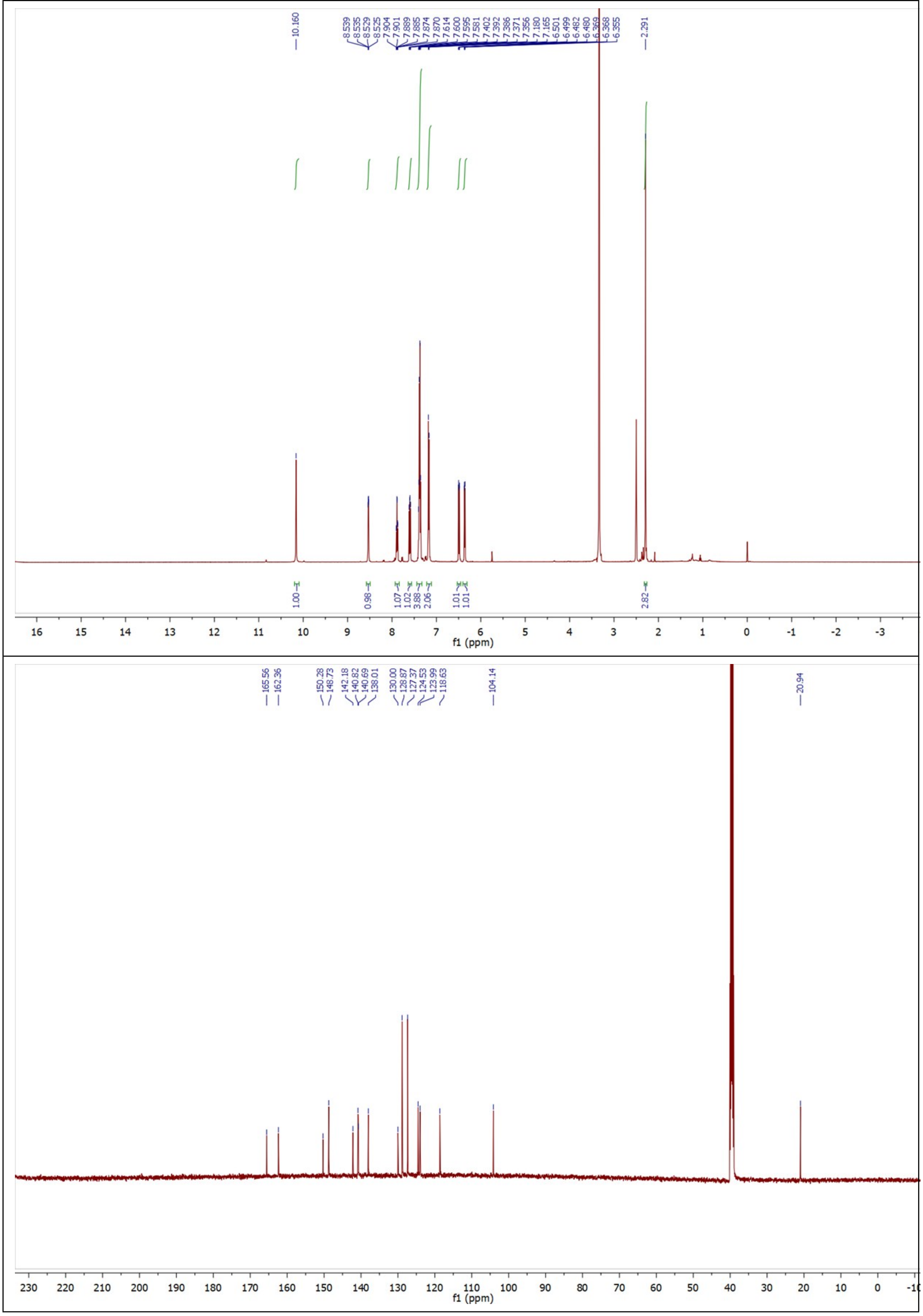
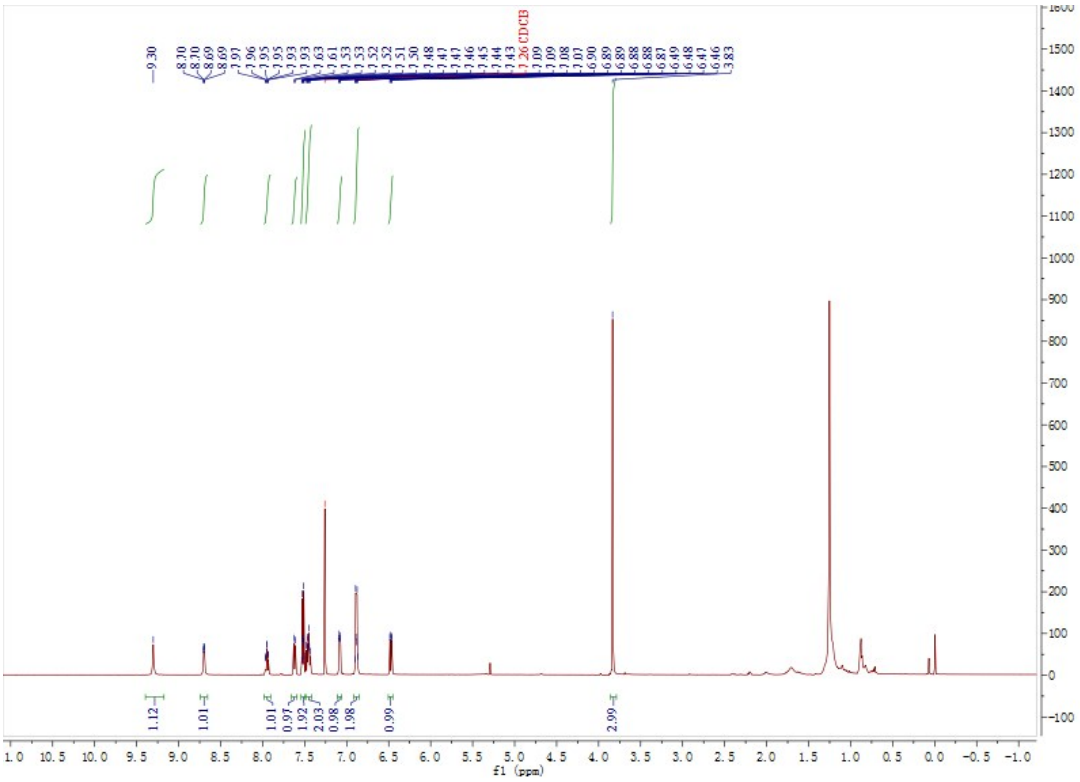


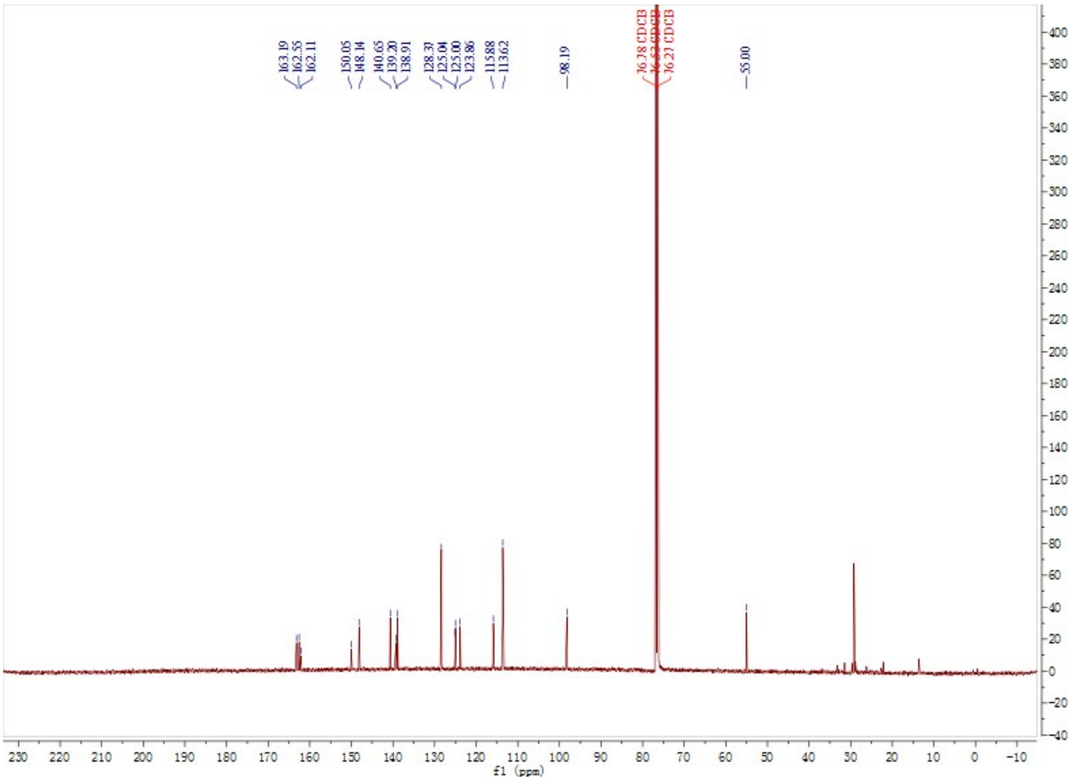


4-Methyl-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4a)

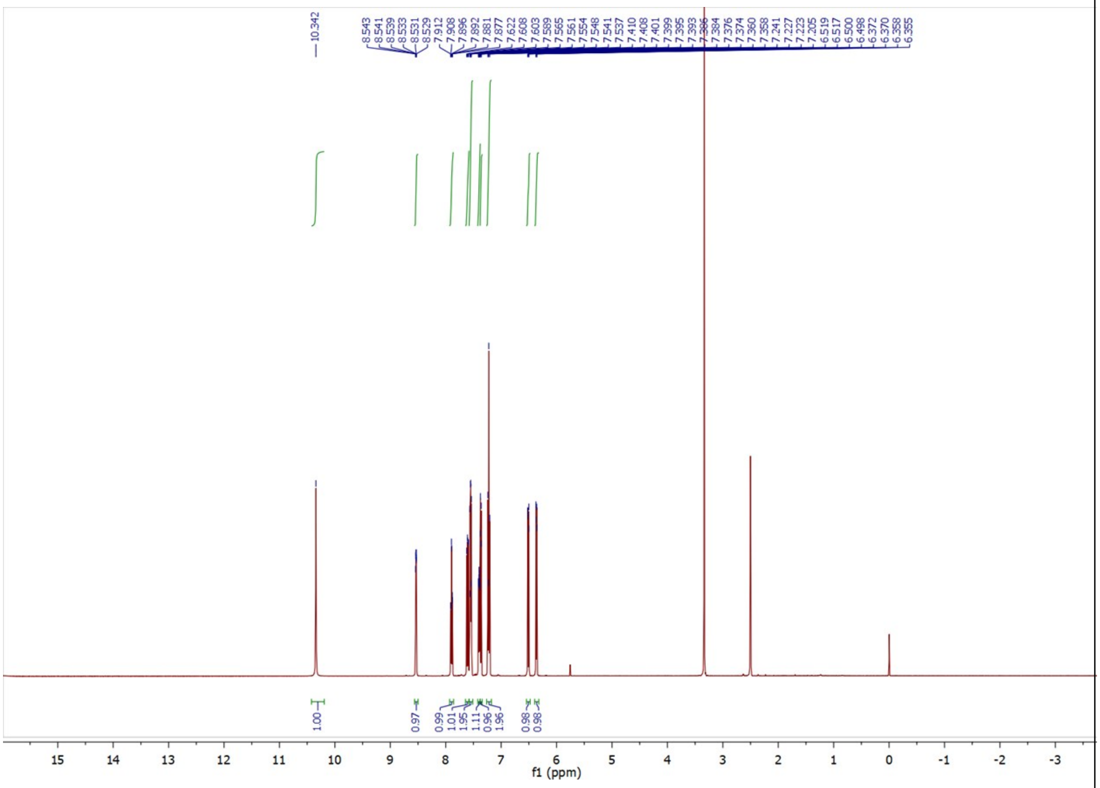


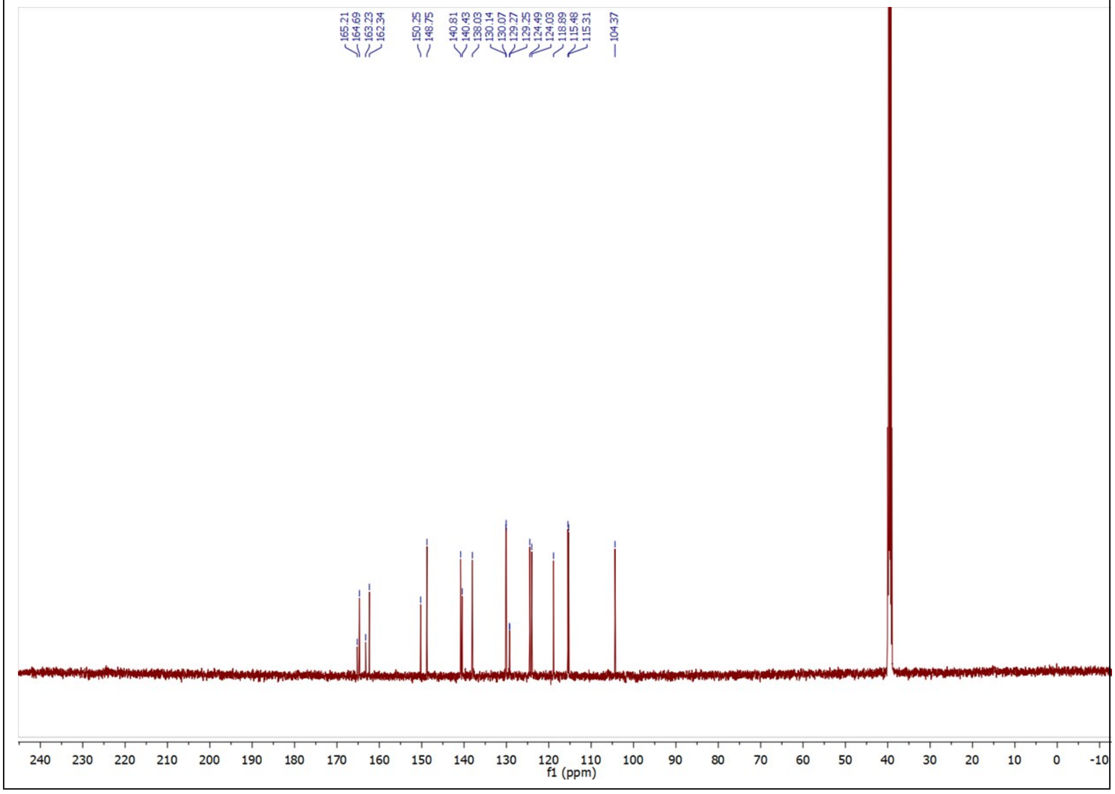
4-Methoxy-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4b)



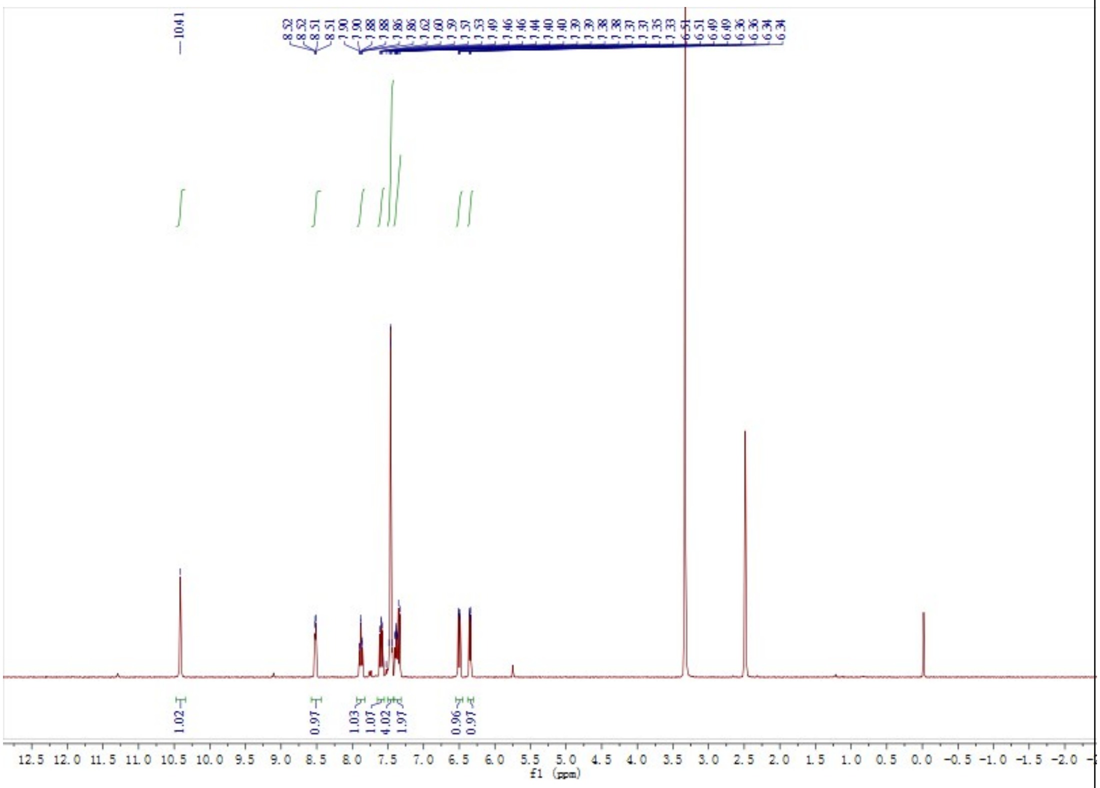


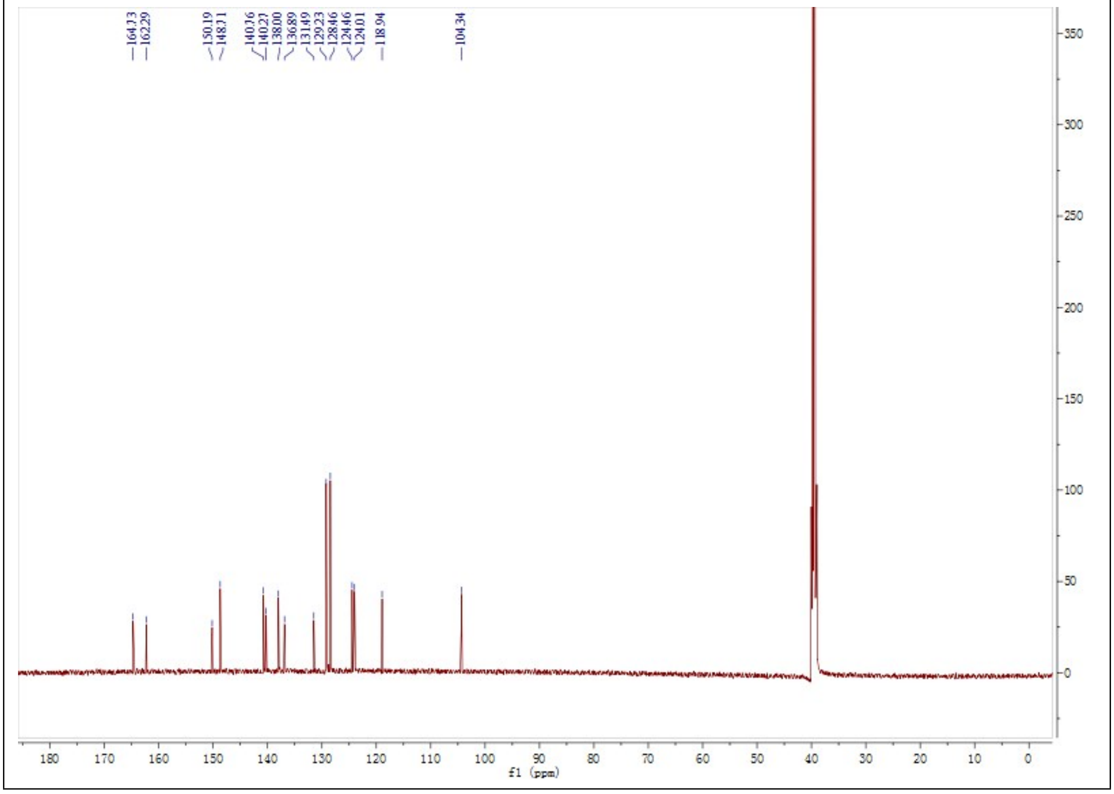
4-Fluoro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4c)



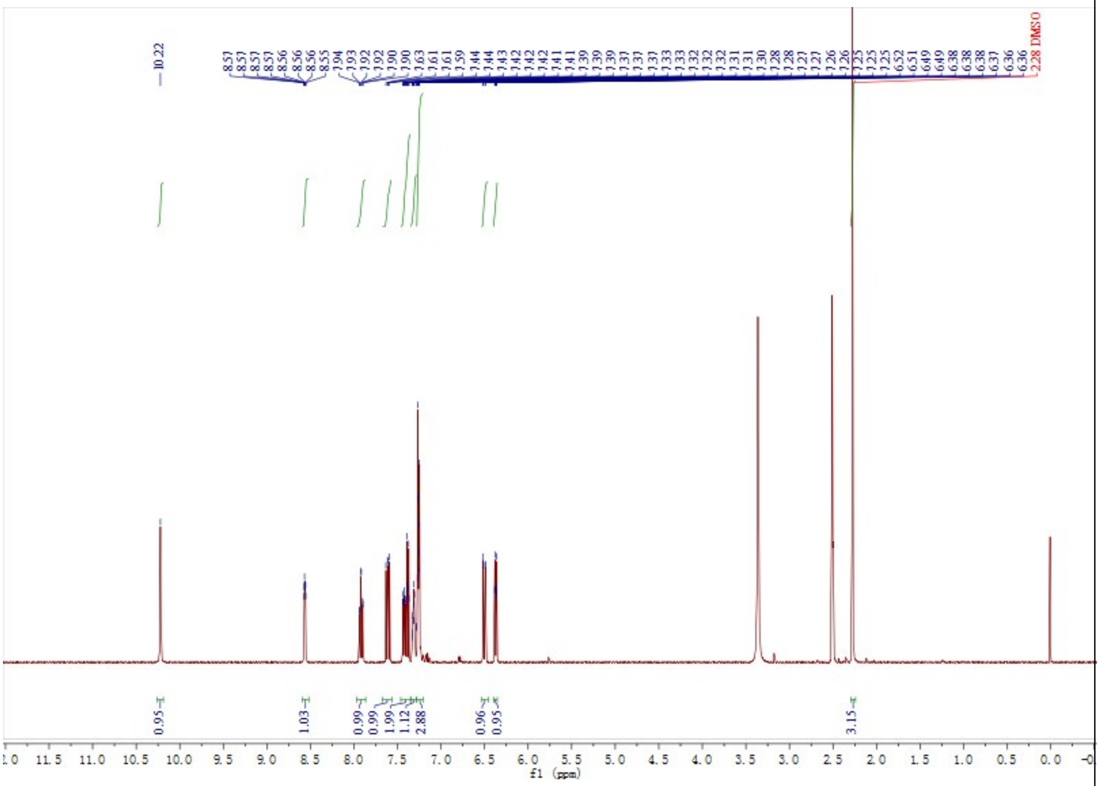


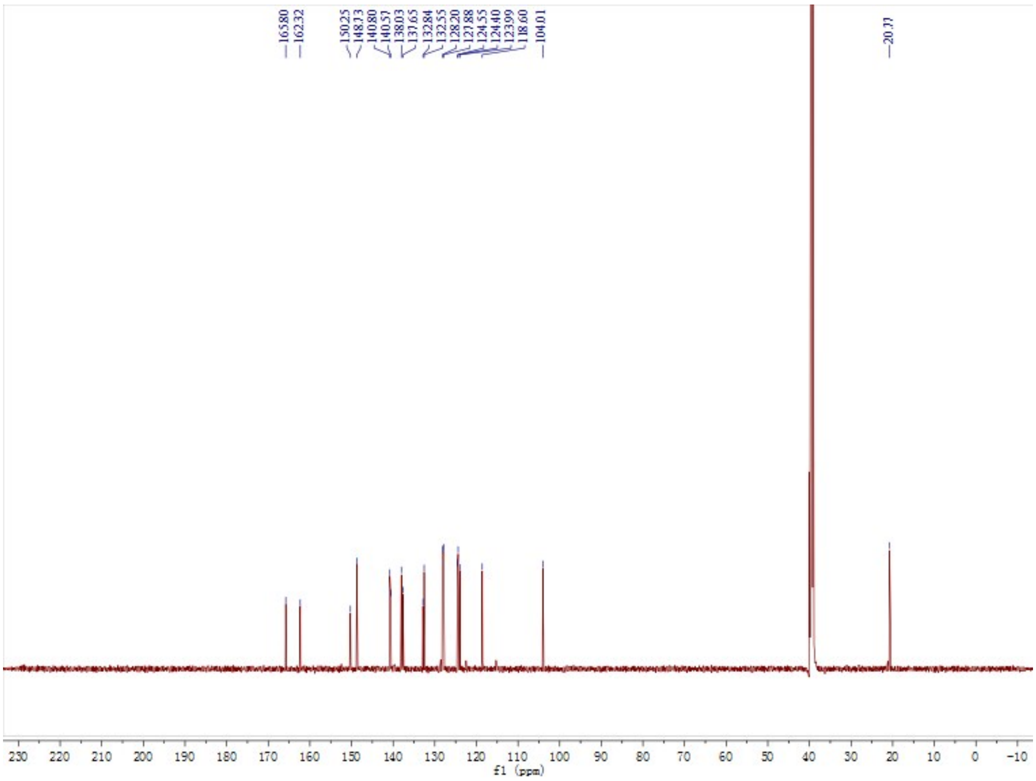
4-Chloro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4d)





3-Methyl-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4e)





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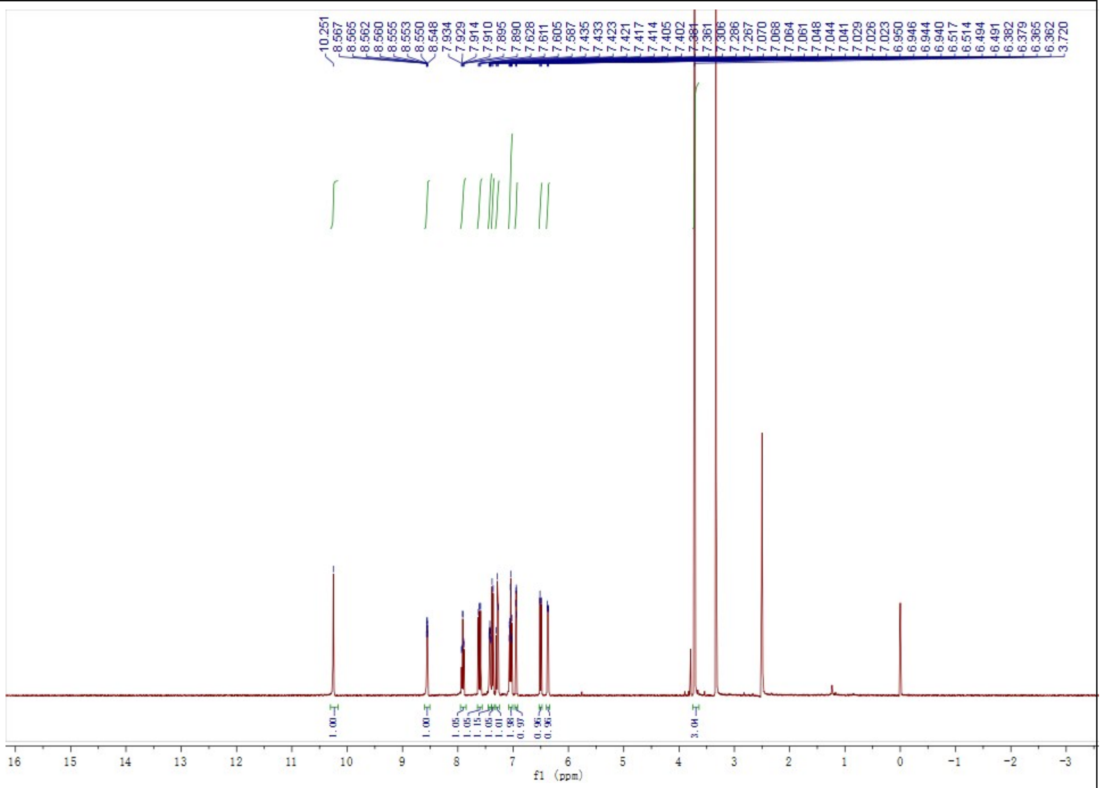

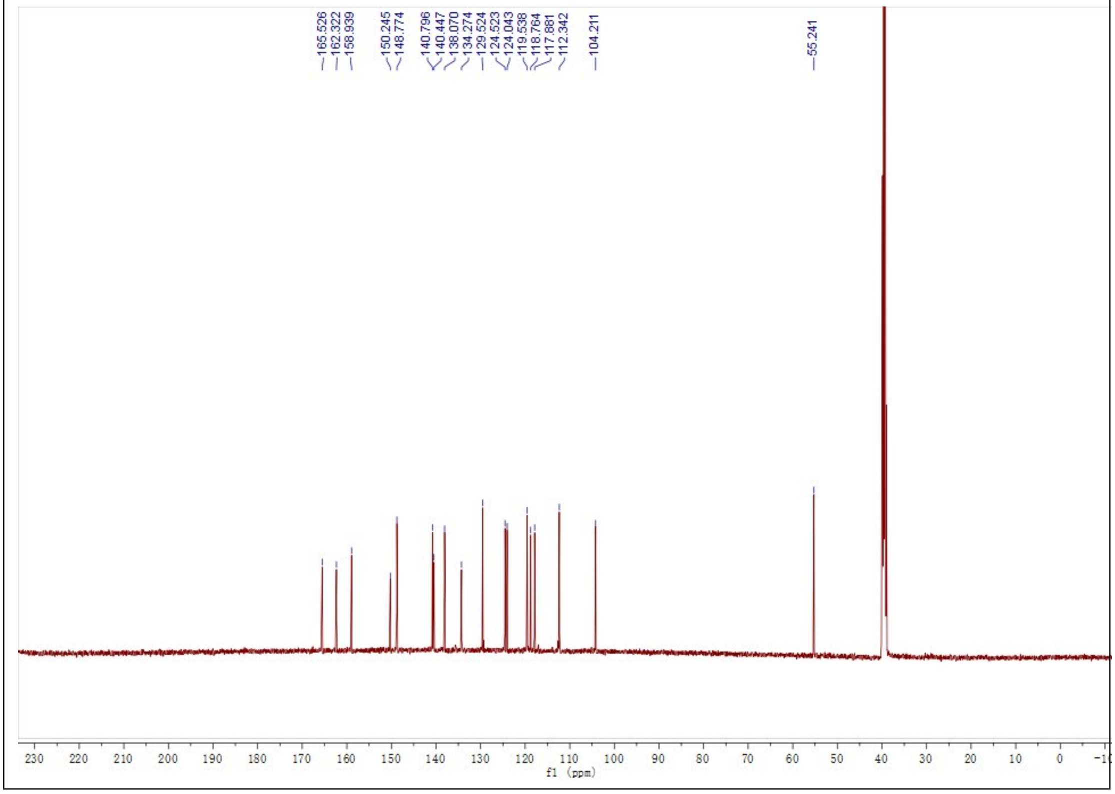

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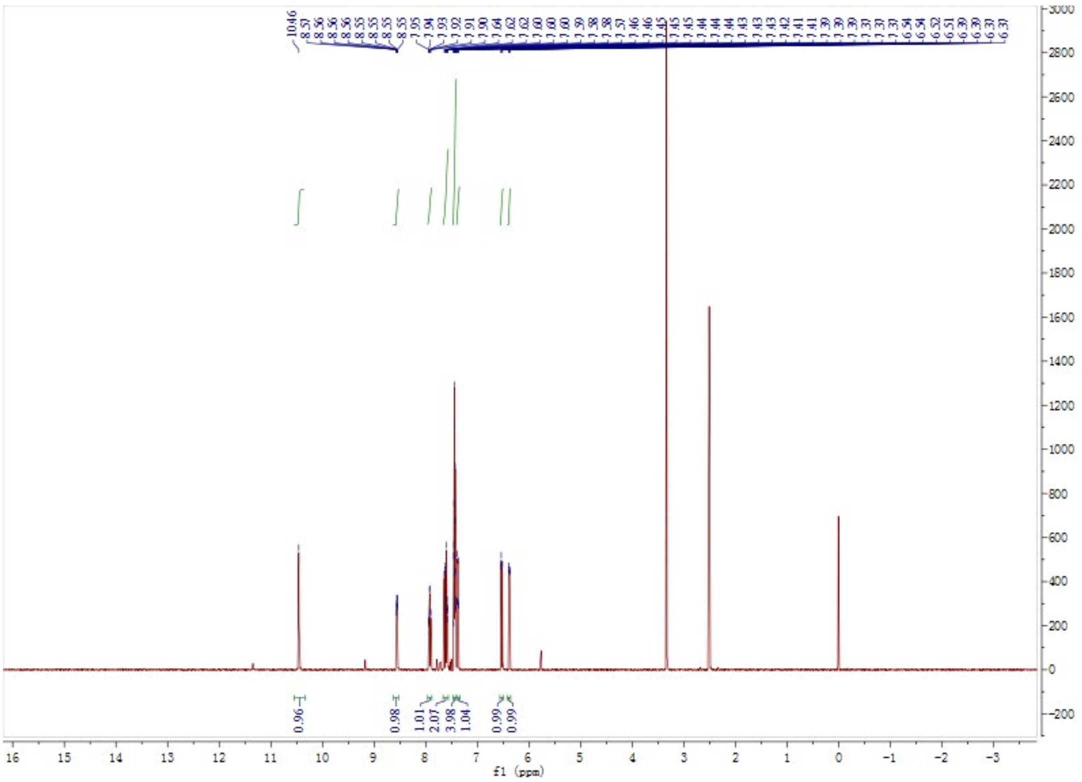
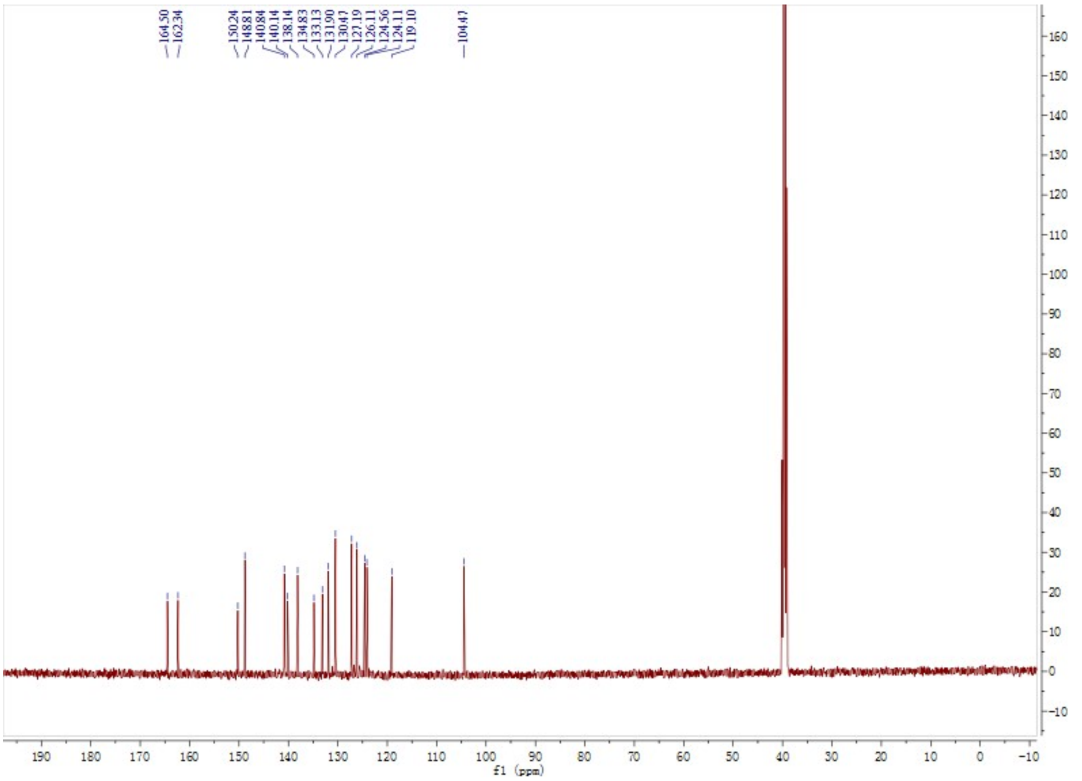
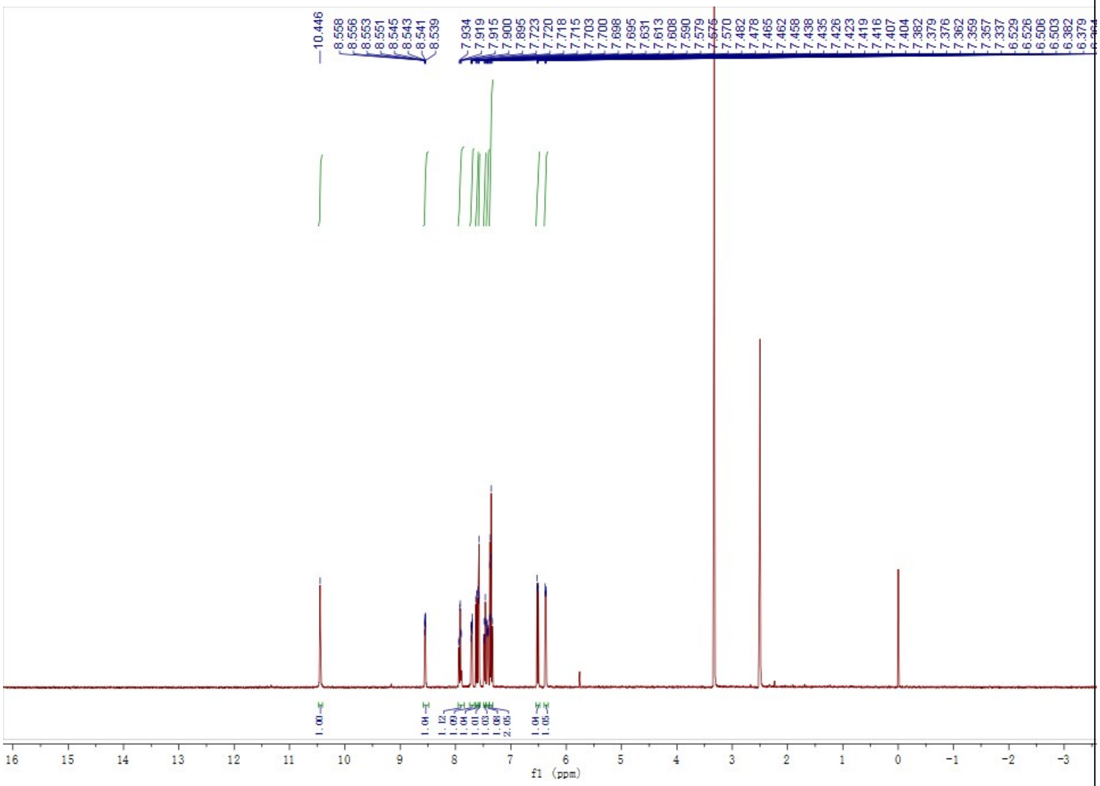
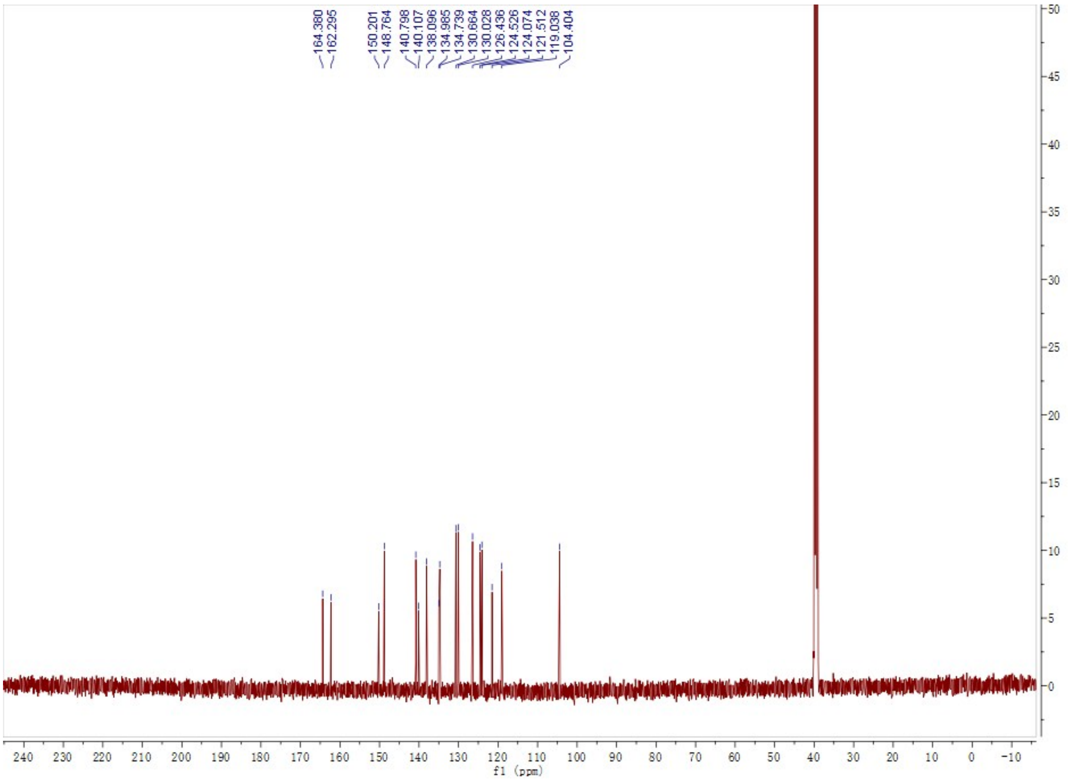


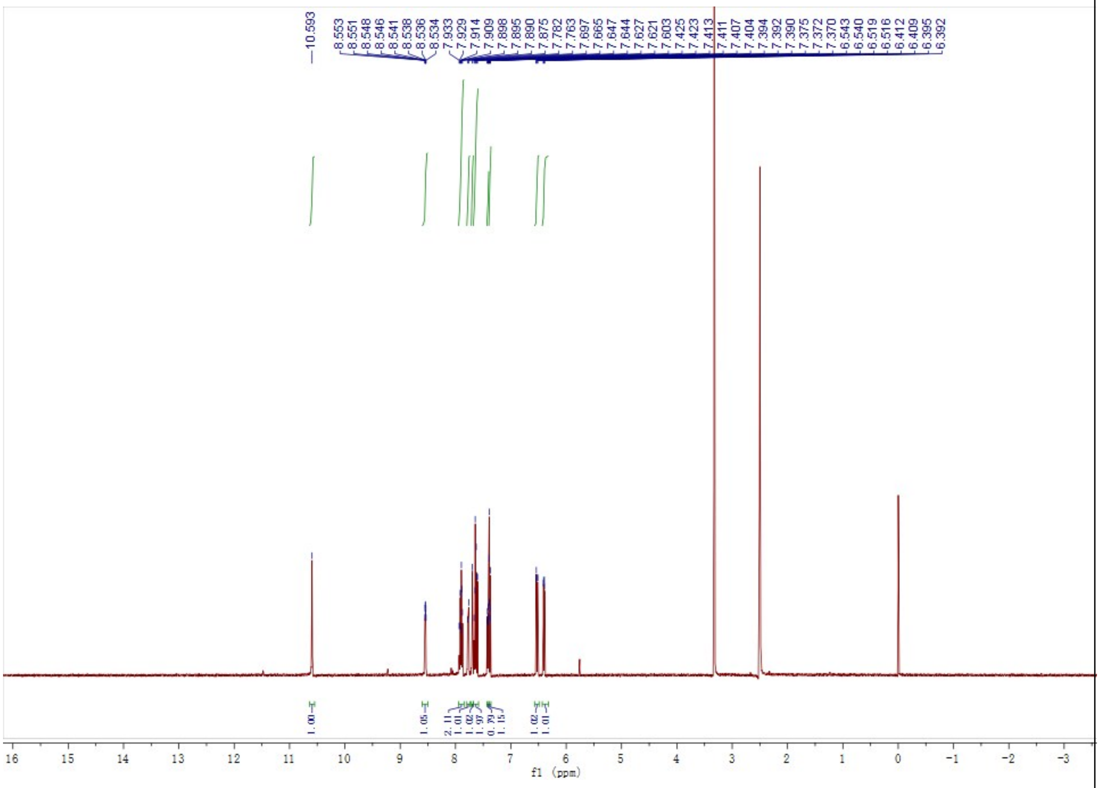


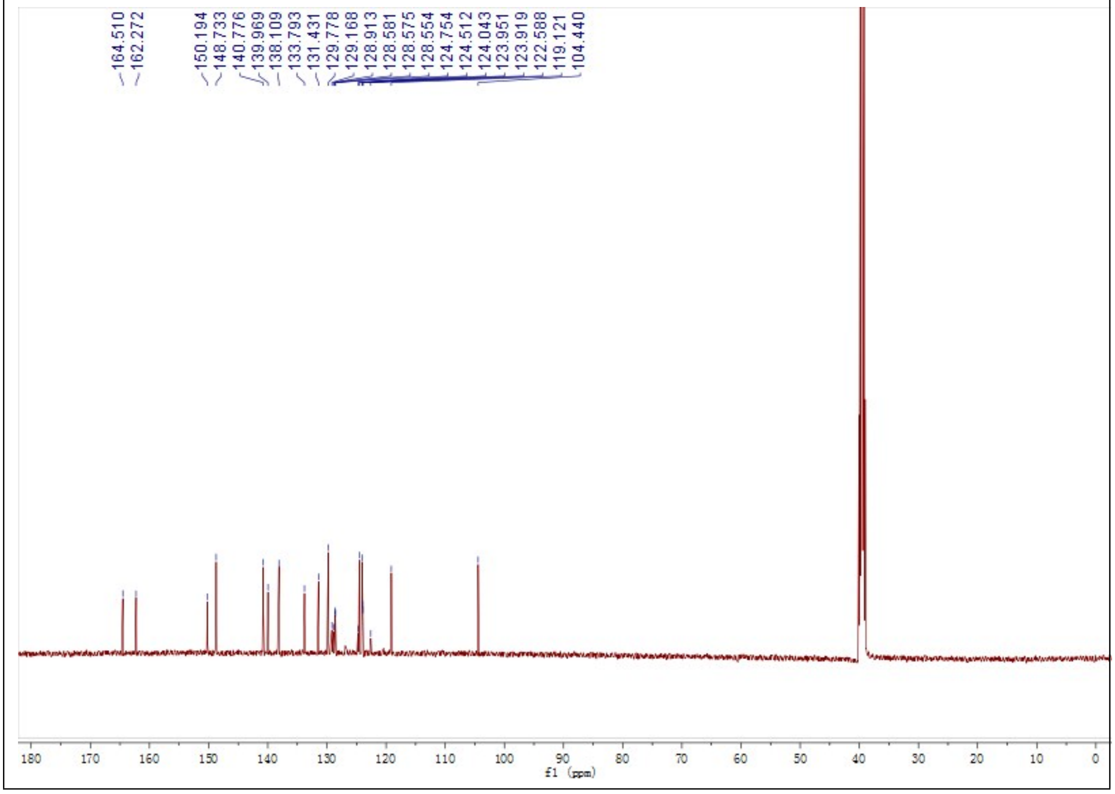
3-Bromo-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4h)



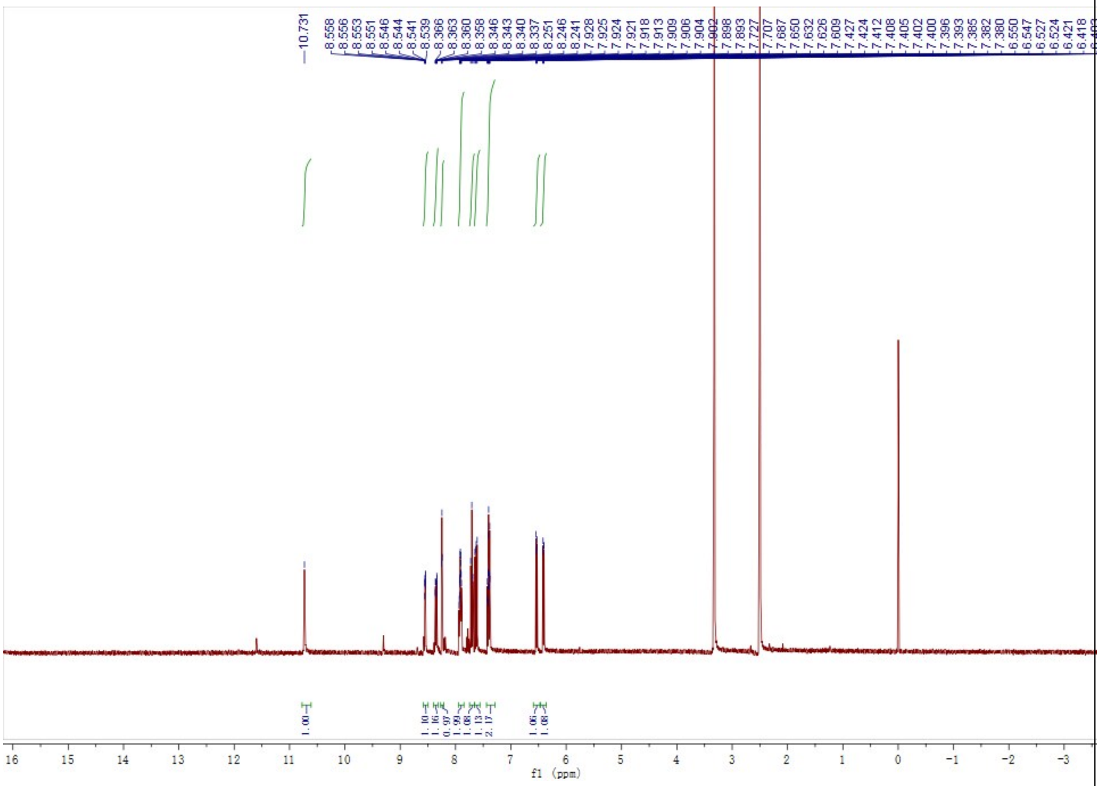


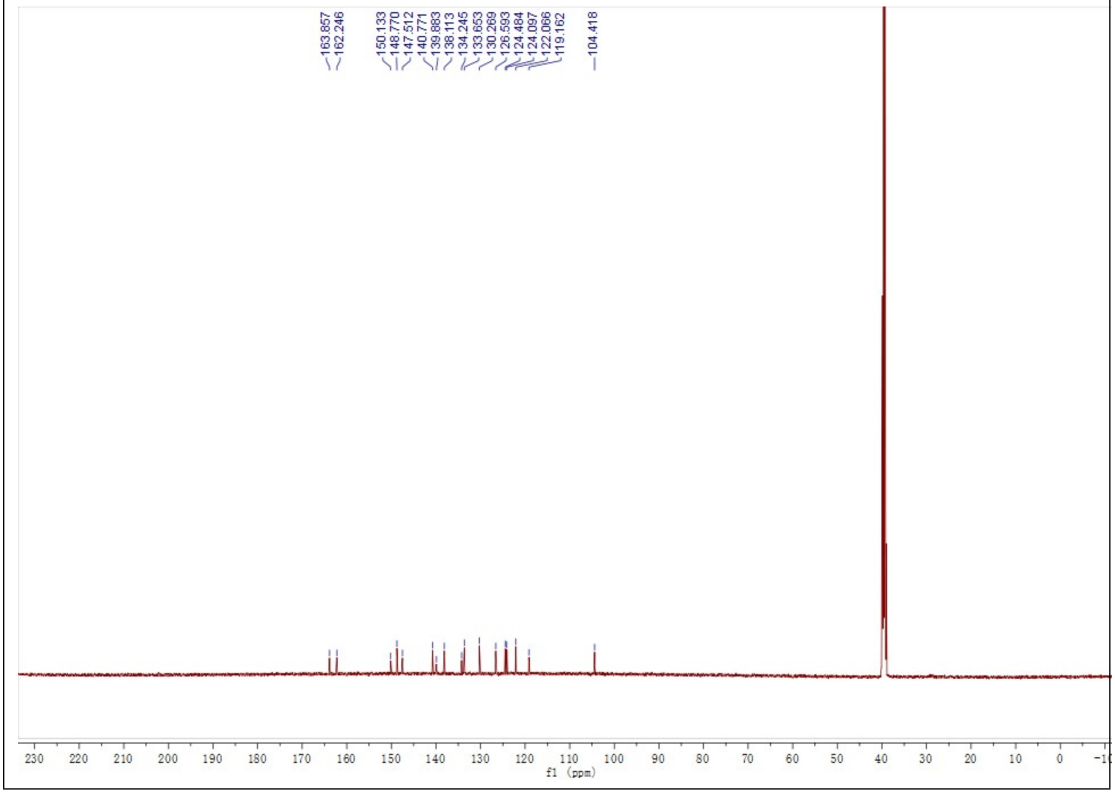
_N_-(2-oxo-2_H_-[1,2'-bipyridin]-6-yl)-3-(trifluoromethyl)benzamide (4i)



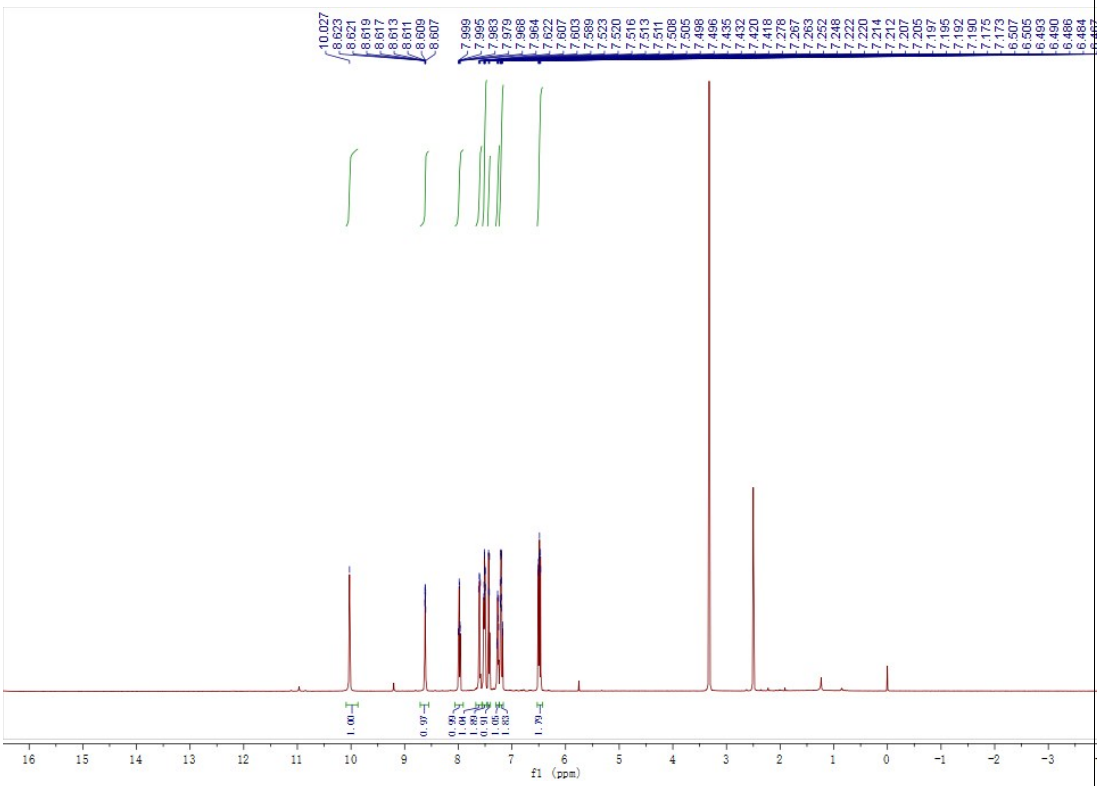


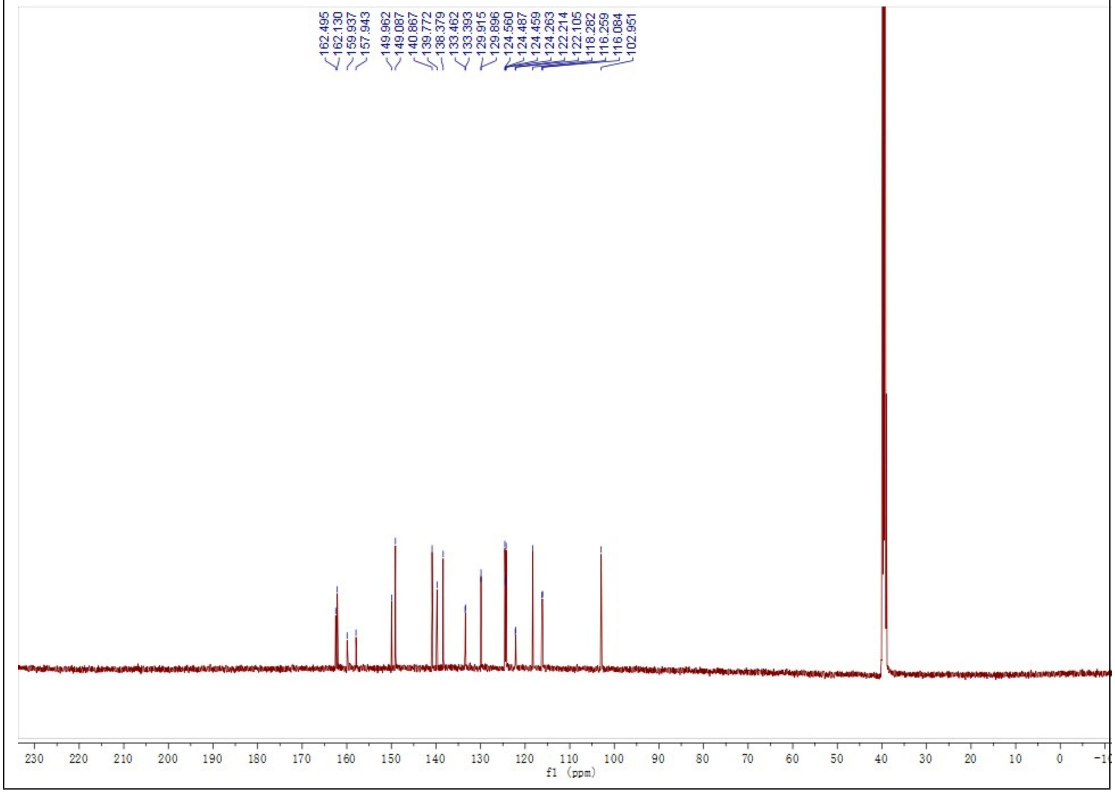
3-Nitro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4j)



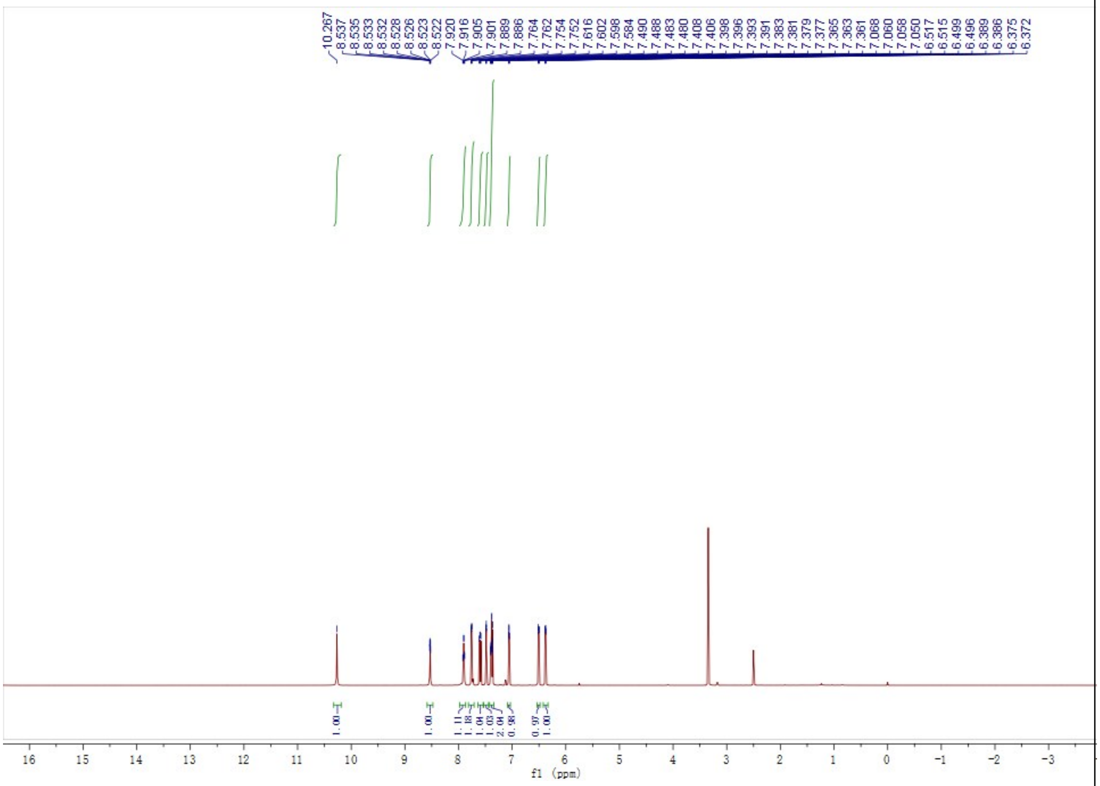


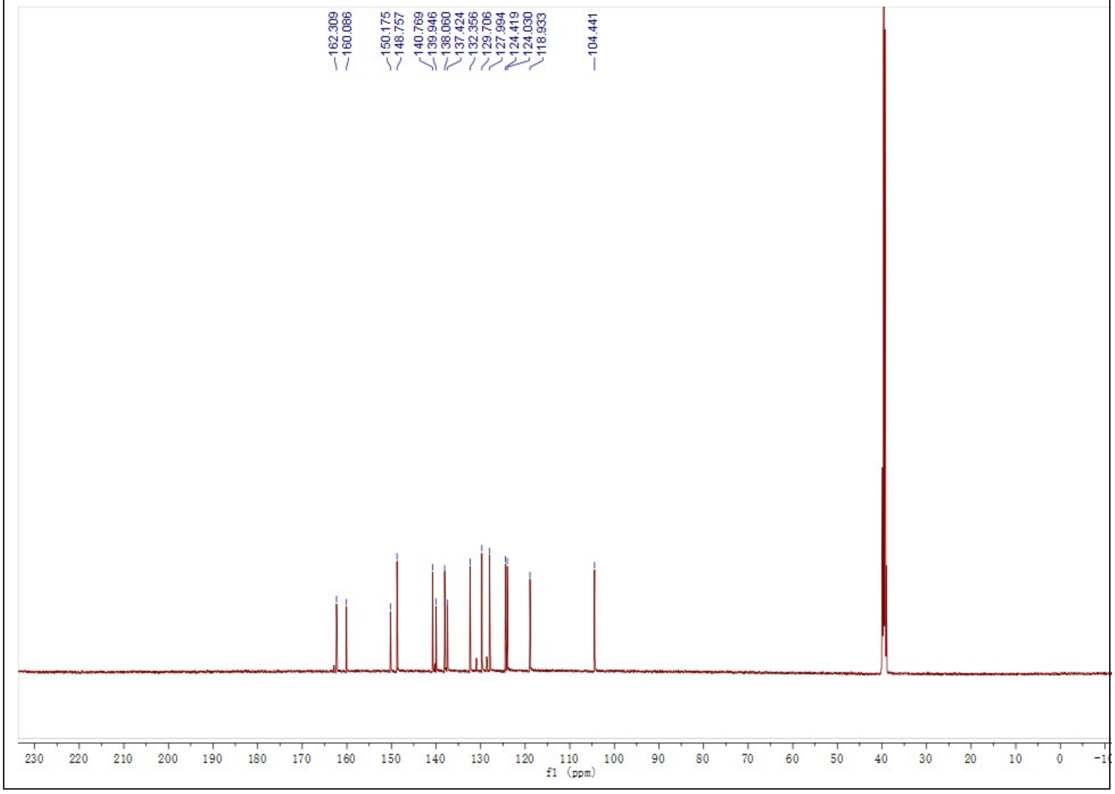
2-Fluoro-*N*-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)benzamide (4k)





N-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)thiophene-2-carboxamide (4l)





N-(2-oxo-2*H*-[1,2'-bipyridin]-6-yl)acetamide (4m)