

Supporting Information

Catalyst-free Transamidation of Aromatic Amines with Formamide Derivatives and Tertiary Amides with Aliphatic Amines

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1. General information

Preparative thin-layer chromatography was performed for product purification using Sorbent Silica Gel 60 F254 TLC plates and visualized with ultraviolet light. IR spectra were recorded on a new Fourier transform infrared spectroscopy. ^1H , ^{13}C and ^{19}F NMR spectra were recorded on 400, 100, 377 MHz NMR spectrometer using CDCl_3 as solvent unless otherwise stated. HRMS were made by means of ESI. Melting points were measured on micro melting point apparatus and uncorrected. Unless otherwise noted, all reagents were weighed and handled in air, and all reactions were carried out in a 25 mL sealed tube under an atmosphere of air. Unless otherwise noted, all reagents were purchased from reagent company, and used without further purification.

2. Experimental procedure and characterization data for products

A typical experimental procedure: A solution of aromatic or heterocyclic amine (1 mmol), and formamide (10 mmol, 10 equiv.) under neat conditions were stirred in a 25 mL sealed tube under an atmosphere of air or argon at 150 °C for 24 h. After the mixture was cooled to room temperature, 20 mL water was added, and extracted with ethyl acetate (4 X 20 mL). The combined organic layers were dried with anhydrous Na_2SO_4 . After filtering, the solvent was evaporated under vacuum, and the crude product was purified by preparative TLC or column chromatography (silica gel,

petroleum ether/EtOAc) to obtain the pure product.

3. Gram scale reaction and applications

Gram scale preparation of *N*-*p*-tolylformamide (Scheme 2, A):

A solution of *p*-toluidine (**1a**, 1 g, 9.34 mmol) and formamide (3.71 mL, 93.4 mmol) was stirred in a sealed microwave reaction tube (120 mL) under an atmosphere of air at 150 °C for 33 h. The mixture was cooled to room temperature, and 20 mL water was added. The mixture was extracted with EtOAc (4 X 20 mL). The combined organic layers were dried with anhydrous Na₂SO₄. After filtering, the solvent was evaporated under vacuum, and the crude product was purified by column chromatography (silica gel, petroleum ether/EtOAc 3:1 with 1% Et₃N) to obtain the pure product in a yield of 98% (1.24 g).

Gram scale preparation of acetaminophen (Scheme 2, B):

A solution of 4-aminophenol (1 g, 9.16 mmol) and acetamide (5.47 g, 91.64 mmol) was stirred in a sealed microwave reaction tube (120 mL) under an atmosphere of argon at 150 °C for 72 h. The mixture was cooled to room temperature, and water (20 mL) was added; the mixture was extracted with EtOAc (4 X 20 mL). The combined organic layers were dried with anhydrous Na₂SO₄. After filtering, the solution was evaporated under vacuum, and the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc 1:3 with 1% Et₃N) to obtain the pure product in a yield of 96% (1.34 g).

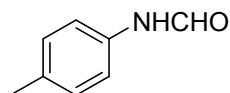
The simplified purification process for the preparation of acetaminophen (Scheme 2, B): After the reaction completed, the mixture was diluted with water (20 mL), then extracted with EtOAc. The EtOAc layer was washed with 0.5 M hydrochloric acid. The organic layer was dried over anhydrous Na₂SO₄ and concentrated under vacuum to obtain pure acetaminophen in a yield of 92% (1.28 g).

The synthesis of BMY 30123

To a mixture of tretinoin (0.3 g, 1 mmol), acetaminophen (0.18 g, 1.2 mmol), DMAP (0.063 g, 0.5 mmol) and DCC (0.43 g, 2 mmol) was added in dry CH₂Cl₂ (15 mL). To this mixture was added in dry DMF (2 mL) and stirred under an atmosphere of air at room temperature for 4 h. After completion, 20 mL water was added, and extracted with CH₂Cl₂ (4 X 15 mL). The combined organic layers were dried with anhydrous Na₂SO₄. After filtering, the solvent was evaporated under vacuum, and the residue was purified by column chromatography (silica gel, petroleum ether/EtOAc 1:1 with 1% Et₃N) to obtain the pure product in a yield of 72% (0.312 g).

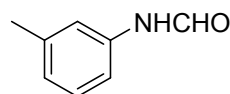
4. Characterization data for desired products

N-p-tolylformamide (3a)^[1]



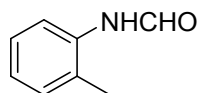
Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow solid; Isolated yield 89% (120.3 mg); Mp 54-56 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.63 (major rotamer, d, J = 11.6 Hz, 0.55H), 8.49 (major rotamer, br s, 0.51H), 8.33 (minor rotamer, s, 0.45H), 7.64 (minor rotamer, br s, 0.42H), 7.42 (d, J = 8.4 Hz, 0.92H), 7.16-7.11 (m, 2.00H), 6.99 (d, J = 8.4 Hz, 1.08H), 2.32 (d, J = 7.6 Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 163.1, 134.6, 134.1, 129.8, 118.7, 20.5, major rotamer 159.7, 134.3, 134.0, 129.2, 120.0, 20.6; IR (KBr) 3198, 2363, 1893, 1521, 1402, 1252, 1148, 939, 868, 816, 522 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{NO}$ 136.0757, found 136.0758.

N-m-tolylformamide (3b)^[2]



Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow oil; Isolated yield 80% (108.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.32 (major rotamer, br s, 0.51H), 8.68 (major rotamer, d, J = 11.2 Hz, 0.54H), 8.52 (minor rotamer, br s, 0.46H), 8.30 (minor rotamer, d, J = 2.0 Hz, 0.46H), 7.40 (s, 0.47H), 7.34 (d, J = 8.0 Hz, 0.49H), 7.22- 7.15 (m, 1.00H), 6.97 (d, J = 7.6 Hz, 0.53H), 6.93-6.90 (m, 1.51H), 2.30 (d, J = 13.2 Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 163.2, 139.6, 136.6, 129.3, 125.8, 119.2, 115.5, 21.2, minor rotamer 159.7, 138.8, 136.8, 128.7, 125.3, 120.6, 117.1, 21.3; IR (KBr) 3250, 1938, 1398, 1204, 1129, 1096, 1040, 899, 861, 783, 693, 495 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{HCO}_2\text{H}-\text{H}]^-$ calcd for $\text{C}_9\text{H}_{10}\text{NO}_3$ 180.0666, found 180.0663.

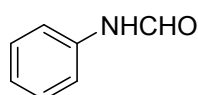
N-o-tolylformamide (3c)^[3]



Purified by TLC; R_f 0.4 (PE:EA = 3:1); Brown solid; Isolated yield 60% (82.0 mg); Mp 55-57 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.55 (major rotamer, d, J = 11.2 Hz,

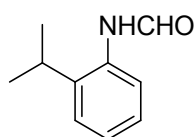
0.65H), 8.45 (minor rotamer, d, $J = 1.6$ Hz, 0.35H), 7.95-7.89 (m, 0.95H), 7.25-7.08 (m, 4.00H), 2.30 (d, $J = 9.2$ Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 163.8, 135.0, 131.1, 129.9, 126.9, 125.9, 120.8, 17.6, minor rotamer 159.6, 134.5, 130.4, 129.1, 126.5, 125.4, 123.1, 17.6; IR (KBr) 3183, 2878, 2359, 1692, 1592, 1535, 1547, 1402, 1297, 1156, 1047, 753 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{NO}$ 136.0757, found 136.0755.

***N*-phenylformamide (3d)^[1]**



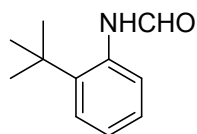
Purified by TLC; R_f 0.4 (PE:EA = 2:1); Yellow oil; Isolated yield 83% (100.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.70 (major rotamer, d, $J = 11.6$ Hz, 0.53H), 8.39 (minor rotamer, s, 0.47H), 8.14 (major rotamer, br, 0.49H), 7.56-7.54 (m, 0.90H), 7.39-7.32 (m, 2.39H), 7.20 (t, $J = 7.4$ Hz, 0.55H), 7.15 (t, $J = 7.6$ Hz, 0.50H), 7.11-7.09 (m, 1.05H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 163.1, 136.7, 129.4, 125.0, 118.5, major rotamer 159.8, 136.9, 128.8, 124.5, 120.0; IR (KBr) 3243, 2878, 2363, 1946, 1603, 1543, 1178, 1148, 1077, 1029, 906, 693, 518 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_8\text{NO}$ 122.0600, found 122.0602.

***N*-(2-isopropylphenyl)formamide (3e)^[4]**



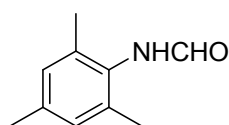
Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow solid; Isolated yield 77% (125.4 mg); Mp 65-67 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, $J = 12.0$ Hz, 1.00H), 8.22 (major rotamer, br d, $J = 8.4$ Hz, 0.66H), 7.77 (minor rotamer, br d, $J = 5.2$ Hz, 0.28H), 7.36-7.20 (m, 3.30H), 7.13 (d, $J = 7.6$ Hz, 0.70H), 3.17-3.03 (m, 1.00H), 1.26 (d, $J = 6.8$ Hz, 6.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 164.2, 141.2, 133.5, 126.6, 126.3, 122.6, 27.6, 23.0, minor rotamer 159.9, 140.2, 132.8, 126.8, 125.6, 124.6, 27.7, 22.9; IR (KBr) 3138, 2363, 1685, 1525, 1454, 1402, 1293, 1081, 757, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{HCO}_2\text{H}-\text{H}]^-$ calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3$ 208.0979, found 208.0973.

***N*-(2-(*tert*-butyl)phenyl)formamide (3f)^[5]**



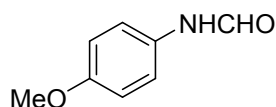
Purified by TLC; R_f 0.2 (PE:EA = 3:1); Yellow solid; Isolated yield 62% (109.5 mg); Mp 73-75 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.45 (minor rotamer, s, 0.24H), 8.37 (major rotamer, d, J = 11.2 Hz, 0.76H), 8.02 (major rotamer, br d, J = 8.0 Hz, 0.70H), 7.62-7.59 (m, 0.47H), 7.45-7.41 (m, 1.00H), 7.27-7.17 (m, 2.00H), 7.11-7.09 (m, 0.77H), 1.43 (s, 9.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 164.1, 143.6, 134.4, 127.1, 127.0, 126.6, 126.3, 34.7, 30.6, minor rotamer 160.1, 143.0, 133.6, 128.2, 127.0, 126.5, 126.3, 34.5, 30.4; IR (KBr) 3161, 2967, 2837, 2363, 1692, 1513, 1402, 1293, 1055, 898, 760, 503 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{16}\text{NO}$ 178.1226, found 178.1228.

***N*-mesitylformamide (3g)^[6]**



Purified by column chromatography; R_f 0.5 (PE:EA = 3:1); Yellow solid; Isolated yield 72% (119.2 mg); Mp 187-189 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.37 (minor rotamer, s, 0.49H), 8.05 (major rotamer, d, J = 12.0 Hz, 0.51H), 7.08 (br d, J = 8.8 Hz, 0.53H), 6.92 (d, J = 14.0 Hz, 2.00H), 2.27 (d, J = 13.2 Hz, 6.00H), 2.21 (s, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 165.1, 137.4, 134.9, 129.7, 128.9, 20.9, 18.4, major rotamer 159.6, 137.5, 135.1, 130.4, 129.3, 20.8, 18.6; IR (KBr) 3153, 2292, 1655, 1536, 1402, 1260, 1115, 883, 757, 552 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{NNaO}$ 186.0889, found 186.0889.

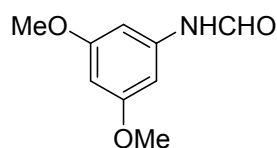
***N*-(4-methoxyphenyl)formamide (3h)^[7]**



Purified by TLC; R_f 0.4 (PE:EA = 1:1); Yellow solid; Isolated yield 98% (148.2 mg); Mp 76-78 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.80 (minor rotamer, br d, J = 10.4 Hz,

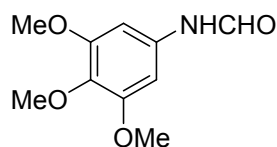
0.45H), 8.52 (minor rotamer, d, $J = 11.6$ Hz, 0.46H), 8.28 (major rotamer, s, 0.54H), 8.11 (major rotamer, br, 0.50H), 7.45 (d, $J = 8.8$ Hz, 1.06H), 7.04 (d, $J = 8.8$ Hz, 0.94H), 6.89-6.83 (m, 2.00H), 3.78 (d, $J = 8.8$ Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 163.4, 157.3, 129.6, 121.7, 114.6, 55.3, major rotamer 159.5, 156.4, 130.0, 121.2, 113.9, 55.2; IR (KBr) 3131, 2840, 2050, 1894, 1684, 1551, 1402, 1312, 1182, 1033, 835, 634 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{NO}_2$ 152.0706, found 152.0705.

***N*-(3,5-dimethoxyphenyl)formamide (3i)^[8]**



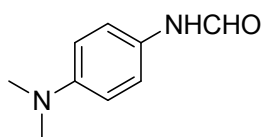
Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 98% (177.4 mg); Mp 78-82 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.91 (major rotamer, d, $J = 10.8$ Hz, 0.55H), 8.70 (major rotamer, d, $J = 11.2$ Hz, 0.55H), 8.32 (minor rotamer, s, 0.45H), 8.12 (minor rotamer, br s, 0.44H), 6.80 (d, $J = 1.6$ Hz, 0.91H), 6.27-6.24 (m, 2.09H), 3.76 (d, $J = 10.4$ Hz, 6.00H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 162.8, 159.4, 138.7, 98.3, 96.8, 55.2, major rotamer 161.5, 160.9, 138.5, 97.0, 96.6, 55.3; IR (KBr) 3138, 2352, 2285, 1685, 1603, 1402, 1208, 1156, 1066, 831 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{NO}_3$ 182.0812, found 182.0810.

***N*-(3,4,5-trimethoxy)phenylformamide (3j)^[8]**



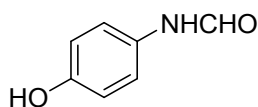
Purified by column chromatography; R_f 0.4 (PE:EA = 1:3); Yellow oil; Isolated yield 99% (208.3 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.62 (minor rotamer, d, $J = 11.2$ Hz, 0.41H), 8.34 (major rotamer, s, 0.59H), 8.27 (minor rotamer, br, 0.38H), 7.68 (major rotamer, br, 0.59H), 6.86 (s, 1.18H), 6.32 (s, 0.82H), 3.86-3.82 (m, 9.00H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 163.0, 153.9, 135.5, 133.0, 97.0, 61.0, 56.2, major rotamer 159.5, 153.2, 134.6, 133.5, 97.7, 61.0, 56.0; IR (KBr) 3437, 2900, 2095, 1692, 1513, 1394, 1312, 1238, 1129, 995, 604 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{NO}_4$ 212.0917, found 212.0911.

***N*-(4-(dimethylamino)phenyl)formamide (3k)^[5]**



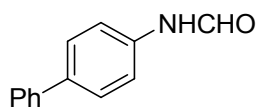
Purified by column chromatography; R_f 0.6 (PE:EA = 1:3); Brown solid; Isolated yield 73% (119.5 mg); Mp 106-108 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.44 (major rotamer, d, J = 11.6 Hz, 0.52H), 8.29 (minor rotamer, d, J = 2.0 Hz, 0.48H), 7.80 (major rotamer, br s, 0.50H), 7.40-7.36 (m, 0.92H), 7.29 (minor rotamer, br, 0.40H), 7.01-6.97 (m, 1.06H), 6.72-6.68 (m, 2.05H), 2.93 (d, J = 8.0 Hz, 6.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 163.4, 148.9, 125.8, 122.0, 113.2, 40.7, minor rotamer 159.0, 148.1, 126.6, 121.7, 112.9, 40.8; IR (KBr) 3131, 2810, 2281, 1700, 1532, 1402, 1308, 1223, 1066, 813, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{13}\text{N}_2\text{O}$ 165.1022, found 165.1015.

***N*-(4-hydroxyphenyl)formamide (3l)^[3]**



Purified by TLC; R_f 0.3 (PE:EA = 1:3); Brown solid; Isolated yield 99% (136.2 mg); Mp 135-137 °C; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 9.17 (br s, 0.97H), 8.58 (minor rotamer, d, J = 11.6 Hz, 0.25H), 8.43 (br s, 0.84H), 8.30 (major rotamer, d, J = 1.6 Hz, 0.75H), 7.49 (d, J = 8.8 Hz, 1.51H), 7.09 (d, J = 8.4 Hz, 0.49H), 6.84 (d, J = 8.8 Hz, 0.48H), 6.80 (d, J = 8.8 Hz, 1.52H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ minor rotamer 163.5, 155.6, 130.6, 121.8, 116.8, major rotamer 159.8, 154.7, 131.2, 122.0, 116.0; IR (KBr) 3794, 3727, 3146, 2352, 1879, 1666, 1402, 1249, 831, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_8\text{NO}_2$ 138.0550, found 138.0549.

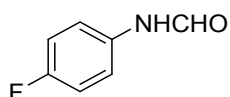
***N*-([1,1'-biphenyl]-4-yl) formamide (3m)^[9]**



Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 99% (196.0 mg); Mp 183-185 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.74 (minor

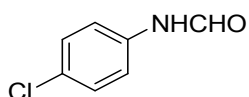
rotamer, d, $J = 11.6$ Hz, 0.46H), 8.43 (major rotamer, s, 0.54H), 7.64-7.57 (m, 5.72H), 7.48-7.33 (m, 3.54H), 7.16 (d, $J = 8.0$ Hz, 1.03H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 162.5, 140.3, 138.3, 135.9, 128.8, 127.7, 127.2, 126.8, 120.3, minor rotamer 159.0, 140.0, 137.7, 136.1, 128.9, 128.4, 127.4, 126.8, 119.0; IR (KBr) 3235, 2352, 2290, 1651, 1402, 1081, 835, 760, 690, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{HCO}_2\text{H}-\text{H}]^-$ calcd for $\text{C}_{14}\text{H}_{12}\text{NO}_3$ 242.0823, found 242.0807.

***N*-(4-fluorophenyl)formamide (3n)^[1]**



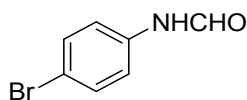
Purified by TLC; R_f 0.5 (PE:EA = 1:1); Brown solid; Isolated yield 90% (125.0 mg); Mp 66-68 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.94 (minor rotamer, br s, 0.36H), 8.59 (minor rotamer, d, $J = 11.2$ Hz, 0.40H), 8.33 (major rotamer, d, $J = 1.2$ Hz, 0.60H), 8.18 (major rotamer, br s, 0.46H), 7.53-7.50 (m, 1.15H), 7.11-6.98 (m, 2.81H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 163.1, 160.3 (d, $J = 243.3$ Hz), 132.7 (d, $J = 2.8$ Hz), 121.0 (d, $J = 8.2$ Hz), 116.5 (d, $J = 22.8$ Hz), major rotamer 159.5 (d, $J = 242.8$ Hz), 159.3, 132.9 (d, $J = 2.9$ Hz), 121.8 (d, $J = 7.9$ Hz), 115.7 (d, $J = 22.4$ Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -116.94 (minor rotamer, s), -117.08 (major rotamer, s); IR (KBr) 3124, 2285, 1685, 1513, 1402, 1312, 1223, 1160, 835, 596, 521 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_7\text{FNO}$ 140.0506, found 140.0504.

***N*-(4-chlorophenyl)formamide (3o)^[1]**



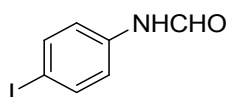
Purified by TLC; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 81% (125.7 mg); Mp 103-105 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.85 (minor rotamer, d, $J = 9.2$ Hz, 0.32H), 8.66 (minor rotamer, d, $J = 11.2$ Hz, 0.45H), 8.36 (major rotamer, d, $J = 1.2$ Hz, 0.55H), 7.92 (major rotamer, br s, 0.41H), 7.50 (d, $J = 8.8$ Hz, 1.16H), 7.34-7.27 (m, 2.04H), 7.05 (d, $J = 8.8$ Hz, 0.84H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 162.7, 135.3, 130.7, 129.8, 120.0, major rotamer 159.2, 135.4, 130.7, 129.1, 121.2; IR (KBr) 3138, 1685, 1402, 1308, 1092, 1014, 872, 831, 746, 526 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_7\text{ClNO}$ 156.0211, found 156.0206.

***N*-(4-bromophenyl)formamide (3p)^[3]**



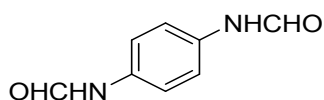
Purified by column chromatography; R_f 0.6 (PE:EA = 1:1); Yellow solid; Isolated yield 73% (145.6 mg); Mp 117-119 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (minor rotamer, d, J = 11.2 Hz, 0.42H), 8.51 (minor rotamer, d, J = 10.0 Hz, 0.37H), 8.38 (major rotamer, d, J = 1.6 Hz, 0.58H), 7.57 (major rotamer, br s, 0.50H), 7.49-7.45 (m, 3.18H), 6.99 (d, J = 8.8 Hz, 0.82H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 162.4, 135.8, 132.8, 120.3, 118.2, major rotamer 159.0, 135.9, 132.1, 121.5, 117.4; IR (KBr) 3116, 2289, 1677, 1593, 1491, 1402, 1305, 1074, 1010, 824, 742, 514 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_7\text{BrNO}$ 199.9706, found 199.9703.

***N*-(4-iodophenyl)formamide (3q)^[2]**



Purified by column chromatography; R_f 0.6 (PE:EA = 1:1); Brown solid; Isolated yield 71% (174.8 mg); Mp 93-95 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (minor rotamer, d, J = 11.2 Hz, 0.43H), 8.39 (major rotamer, d, J = 1.6 Hz, 0.57H), 8.35 (minor rotamer, br, 0.40H), 7.67-7.62 (m, 2.00H), 7.46 (major rotamer, br s, 0.55H), 7.33 (d, J = 8.8 Hz, 1.18H), 6.87 (d, J = 8.8 Hz, 0.82H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 162.4, 138.6, 136.5, 120.4, 88.6, major rotamer 159.1, 138.0, 136.6, 121.8, 88.1; IR (KBr) 3168, 2289, 1901, 1692, 1484, 1402, 1305, 1144, 1006, 809, 693, 507 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_7\text{H}_7\text{INO}$ 247.9567, found 247.9567.

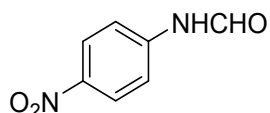
***N*-(4-formylaminophenyl)formamide (3r)^[10]**



Purified by column chromatography; R_f 0.3 (PE:EA = 1:3); Brown solid; Isolated yield 91% (149.8 mg); Mp 124-126 °C; ^1H NMR (400Hz, $(\text{CD}_3)_2\text{SO}$) δ 10.14-10.06 (m, 2.00H), 8.69 (minor rotamer, d, J = 11.2 Hz, 0.46H), 8.23 (major rotamer, d, J = 1.6 Hz, 1.54H), 7.54-7.52 (m, 3.10H), 7.15-7.13 (m, 0.90H); ^{13}C NMR (100Hz, $(\text{CD}_3)_2\text{SO}$) δ minor rotamer 162.4, 134.4, 120.2, 118.9, major rotamer 159.3, 134.0, 119.6, 118.3; IR (KBr) 3138, 2352, 2285, 1670, 1521, 1402, 1100, 831, 527, 455

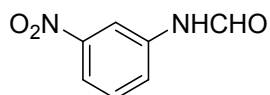
cm⁻¹; HRMS (ESI): m/z [M-H]⁻ calcd for C₈H₇N₂O₂ 163.0513, found 163.0517.

***N*-(4-nitrophenyl)formamide (3s)**^[7]



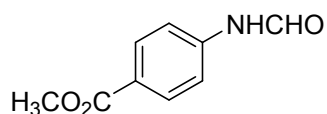
Purified by column chromatography; R_f 0.3 (PE:EA = 1:7); Yellow solid; Isolated yield 26% (42.6 mg); Mp 193-195 °C; ¹H NMR (400 MHz, (CD₃)₂SO) δ 10.15 (major rotamer, s, 0.75H), 10.07 (minor rotamer, d, *J* = 10.4 Hz, 0.25H), 8.67 (minor rotamer, d, *J* = 10.8 Hz, 0.22H), 8.21 (major rotamer, d, *J* = 1.6 Hz, 0.78H), 7.96 (d, *J* = 13.2 Hz, 0.59H), 7.52 (d, *J* = 6.0 Hz, 2.23H), 7.21-7.12 (m, 1.18H); ¹³C NMR (100 MHz, (CD₃)₂SO) δ major rotamer 163.2, 159.5, 134.1, 119.8, 118.4, minor rotamer 162.6, 159.5, 134.4, 120.4, 119.0; IR (KBr) 3146, 2352, 2259, 1651, 1402, 1111, 1029, 828, 768, 529 cm⁻¹; HRMS (ESI): m/z [M+NH₃-H]⁻ calcd for C₇H₈N₃O₃ 182.0571, found 182.0563.

***N*-(3-nitrophenyl)formamide (3t)**^[11]



Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 80% (132.4 mg); Mp 134-136 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.82 (minor rotamer, d, *J* = 11.2 Hz, 0.25H), 8.48 (major rotamer, d, *J* = 1.2 Hz, 0.75H), 8.41 (t, *J* = 2.2 Hz, 0.75H), 8.08-7.94 (m, 2.32H), 7.60-7.41 (m, 2.07H); ¹³C NMR (100 MHz, CDCl₃) δ minor rotamer 161.4, 148.6, 137.8, 130.9, 124.0, 119.8, 113.0, major rotamer 158.9, 148.6, 137.8, 130.1, 125.5, 119.5, 114.6; IR (KBr) 3161, 2285, 1666, 1528, 1402, 1353, 1088, 887, 798, 738, 667, 529 cm⁻¹; HRMS (ESI): m/z [M+K]⁺ calcd for C₇H₆N₂KO₃ 205.0010, found 205.0007.

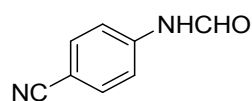
methyl 4-formamidobenzoate (3u)^[1]



Purified by TLC; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 50% (90.4 mg); Mp 116-118 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.85 (minor rotamer, d, *J* = 11.6 Hz,

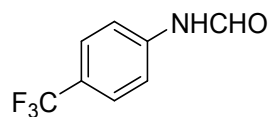
0.41H), 8.45 (major rotamer, d, $J = 1.6$ Hz, 0.59H), 8.04 (t, $J = 8.2$ Hz, 2.03H), 7.94 (minor rotamer, br, 0.33H), 7.64 (d, $J = 8.8$ Hz, 1.17H), 7.38 (major rotamer, br s, 0.58H), 7.13 (d, $J = 8.8$ Hz, 0.80H), 3.92 (d, $J = 4.0$ Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 166.5, 159.0, 140.9, 130.9, 126.2, 119.1, 52.1, minor rotamer 166.3, 161.8, 140.8, 131.6, 126.6, 117.2, 52.2; IR (KBr) 3153, 2289, 1730, 1614, 1525, 1402, 1282, 1193, 1115, 850, 764, 690, 526 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{10}\text{NO}_3$ 180.0655, found 180.0662.

***N*-(4-cyanophenyl)formamide (3v)**^[12]



Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 57% (83.0 mg); Mp 183-185 $^{\circ}\text{C}$; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.65 (major rotamer, s, 0.75H), 10.53 (minor rotamer, d, $J = 10.0$ Hz, 0.25H), 9.00 (minor rotamer, d, $J = 10.8$ Hz, 0.24H), 8.38 (major rotamer, s, 0.76H), 7.71-7.75 (m, 3.50H), 7.38 (d, $J = 8.4$ Hz, 0.50H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ minor rotamer 162.7, 142.9, 133.8, 118.9, 117.1, 105.2, major rotamer 160.4, 142.3, 133.4, 119.3, 117.1, 105.4; IR (KBr) 3437, 2259, 1651, 1402, 1215, 1402, 1029, 828, 630, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{K}]^+$ calcd for $\text{C}_8\text{H}_6\text{N}_2\text{KO}$ 185.0112, found 185.0114.

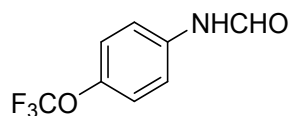
***N*-(4-(trifluoromethyl)phenyl)formamide (3w)**^[2]



Purified by TLC; R_f 0.3 (PE:EA = 3:1); Yellow solid; Isolated yield 30% (56.3 mg); Mp 56-58 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.93 (minor rotamer, br d, $J = 10.0$ Hz, 0.39H), 8.82 (minor rotamer, d, $J = 11.2$ Hz, 0.42H), 8.43 (major rotamer, d, $J = 1.6$ Hz, 0.58H), 7.92 (major rotamer, br s, 0.54H), 7.69 (d, $J = 8.4$ Hz, 1.14H), 7.63-7.57 (m, 2.02H), 7.21 (d, $J = 8.4$ Hz, 0.84H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 162.3, 139.9, 127.1 (q, $J = 3.7$ Hz), 126.6 (q, $J = 32.7$ Hz), 123.8 (q, $J = 270.0$ Hz), 117.9, major rotamer 159.3, 139.9, 126.6 (q, $J = 32.7$ Hz), 126.3 (q, $J = 3.7$ Hz), 123.9 (q, $J = 270.0$ Hz), 119.6; ^{19}F NMR (377 MHz, CDCl_3) δ -62.22 (major rotamer, s), -62.26 (minor rotamer, s); IR (KBr) 3138, 2285, 1685, 1618, 1543, 1402,

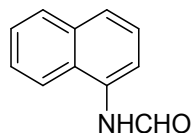
1327, 1115, 824, 734, 529 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_8\text{H}_7\text{F}_3\text{NO}$ 190.0474, found 190.0472.

***N*-(4-(trifluoromethoxy)phenyl)formamide (3x)^[1]**



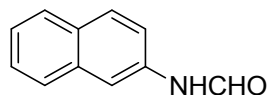
Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow oil; Isolated Yield 78% (160.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 9.04 (minor rotamer, br d, J = 10.4 Hz, 0.37H), 8.68 (minor rotamer, d, J = 11.6 Hz, 0.39H), 8.37 (major rotamer, d, J = 1.6 Hz, 0.61H), 8.22 (major rotamer, br s, 0.56H), 7.59 (d, J = 9.2 Hz, 1.20H), 7.22 (d, J = 8.8 Hz, 0.77H), 7.18-7.13 (m, 2.03H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 163.0, 145.5, 135.5, 121.7, 119.9, 120.4 (d, J = 253.3 Hz), minor rotamer 159.6, 146.3, 135.5, 122.5, 121.3, 120.4 (d, J = 253.3 Hz); ^{19}F NMR (377 MHz, CDCl_3) δ -58.23 (major rotamer, s), -58.29 (minor rotamer, s); IR (KBr) 3138, 2285, 1685, 1510, 1402, 1274, 1163, 850, 753, 529 cm^{-1} ; HRMS (ESI): m/z $[M+\text{Na}]^+$ calcd for $\text{C}_8\text{H}_6\text{F}_3\text{NNaO}_2$ 228.0243, found 228.0243.

***N*-(naphthalen-1-yl)formamide (3y)^[10]**



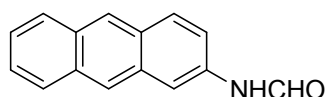
Purified by column chromatography; R_f 0.3 (PE:EA = 2:1); Yellow solid; Isolated yield 74% (126.3 mg); Mp 145-147 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.90 (major rotamer, d, J = 8.8 Hz, 0.67H), 8.64 (major rotamer, d, J = 10.8 Hz, 0.75H), 8.61 (br s, minor rotamer, 0.25H), 8.04 (d, J = 8.0 Hz, 0.74H, HAr), 8.00 (d, J = 7.6 Hz, 0.29H), 7.91-7.78 (m, 2.32H), 7.71 (d, J = 8.0 Hz, 0.28H), 7.61-7.50 (m, 2.05H), 7.46 (t, J = 8.0 Hz, 1.05H), 7.31 (d, J = 7.2 Hz, 0.72H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 164.2, 134.2, 132.2, 128.5, 127.7, 127.0, 126.8, 126.1, 125.5, 121.3, 118.9, minor rotamer 159.7, 134.0, 132.2, 128.8, 127.7, 127.0, 126.5, 126.2, 125.7, 120.9, 120.4; IR (KBr) 3750, 3429, 3138, 2285, 1651, 1402, 1275, 1111, 749, 529 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{NO}$ 172.0757, found 172.0751.

***N*-(naphthalene-2-yl)formamide (3z)^[13]**



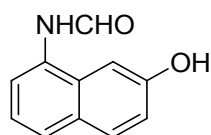
Purified by column chromatography; R_f 0.3 (PE:EA = 2:1); Yellow solid; Isolated yield 85% (145.7 mg); Mp 134-136 °C; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.45-10.40 (m, 0.98H), 8.98 (minor rotamer, d, J = 10.8 Hz, 0.24H), 8.41 (major rotamer, s, 0.76H), 8.34 (s, 0.74H), 7.88-7.78 (m, 3.02H), 7.69 (s, 0.25H), 7.59 (d, J = 8.8 Hz, 0.75H), 7.49-7.38 (m, 2.22H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ minor rotamer 162.8, 136.1, 133.6, 130.0, 129.3, 127.6, 127.0, 126.7, 124.7, 118.6, 112.9, major rotamer 159.9, 135.9, 133.4, 129.9, 128.6, 127.5, 127.3, 126.6, 124.8, 119.7, 115.5; IR (KBr) 3146, 2289, 1730, 1681, 1558, 1402, 1297, 850, 824, 742, 481 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{NO}$ 172.0757, found 172.0751.

***N*-(anthracen-2-yl)formamide (3a)**^[14]



Purified by column chromatography; R_f 0.3 (PE:EA = 3:1); Brown solid; Isolated yield 96% (105.5 mg); Mp 245-247 °C; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.47 (major rotamer, s, 0.63H), 10.42 (minor rotamer, d, J = 11.2 Hz, 0.19H), 9.02 (minor rotamer, d, J = 10.8 Hz, 0.20H), 8.51 (d, J = 6.4 Hz, 1.52H), 8.46 (s, 0.71H), 8.41 (d, J = 1.2 Hz, 0.85H), 8.10-8.02 (m, 2.70H), 7.97 (dd, J = 13.6, 0.8 Hz, 0.73H), 7.69 (br s, 0.22H), 7.97 (dd, J = 9.2, 1.6 Hz, 0.70H), 7.51-7.45 (m, 2.30H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ major rotamer 162.9, 135.2, 131.7, 131.5, 130.5, 129.1, 128.6, 128.1, 127.7, 125.9, 125.7, 125.1, 125.1, 120.6, 114.3, minor rotamer 160.0, 135.5, 131.8, 131.6, 130.4, 129.8, 128.7, 128.1, 127.7, 126.2, 125.8, 125.1, 124.6, 119.5, 111.4; IR (KBr) 3422, 2352, 2255, 2128, 1692, 1402, 1308, 1029, 828, 764 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+2\text{H}_2\text{O}-\text{H}]^-$ calcd for $\text{C}_{15}\text{H}_{14}\text{NO}_3$ 256.0979, found 256.0962.

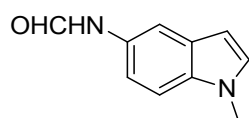
***N*-(7-hydroxy-[1]naphthyl)-formamide (3zb)**^[15]



Purified by column chromatography; R_f 0.2 (PE:EA = 1:1); Brown solid; Isolated yield 89% (167.5 mg); Mp 205-208 °C; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{SO}$) δ 10.26

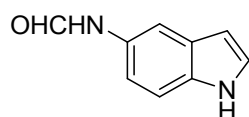
(minor rotamer, d, $J = 10.4$ Hz, 0.35H), 10.09 (major rotamer, s, 0.63H), 9.91 (minor rotamer, s, 0.38H), 9.87 (major rotamer, s, 0.62H), 8.47-8.44 (m, 0.98H), 7.81-7.78 (m, 1.66H), 7.69 (d, $J = 8.0$ Hz, 0.38H), 7.63 (d, $J = 8.0$ Hz, 0.65H), 7.33 (s, 1.00H), 7.29-7.22 (m, 1.42H), 7.14 (dd, $J = 8.8, 2.0$ Hz, 1.02H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{SO}$) δ minor rotamer 164.1, 155.8, 131.9, 129.8, 129.6, 128.5, 125.8, 122.3, 119.9, 119.0, 104.2, major rotamer 160.2, 155.7, 131.0, 130.0, 129.6, 128.4, 125.0, 122.1, 120.5, 118.7, 103.8; IR (KBr) 3750, 3675, 3138, 2348, 2285, 1670, 1402, 1111, 995, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{10}\text{NO}_2$ 188.0706, found 188.0711.

***N*-(1-methyl-1*H*-indol-5-yl)formamide (3zc)**



Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 86% (149.4 mg); Mp 94-96 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.57 (major rotamer, d, $J = 11.6$ Hz, 0.62H), 8.39 (minor rotamer, s, 0.38H), 7.86 (minor rotamer, d, $J = 1.6$ Hz, 0.41H), 7.78 (major rotamer, br, 0.58H), 7.35 (d, $J = 2.0$ Hz, 0.62H), 7.31-7.25 (m, 2.03H), 7.11 (d, $J = 3.2$ Hz, 0.58H), 7.06 (d, $J = 2.8$ Hz, 0.38H), 6.97 (dd, $J = 8.8, 2.0$ Hz, 0.57H), 6.47-6.45 (m, 0.95H), 3.79 (d, $J = 9.6$ Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 163.8, 134.8, 130.2, 128.8, 128.7, 115.4, 112.7, 110.0, 100.8, 32.9, minor rotamer 159.2, 134.2, 129.7, 129.2, 128.3, 115.5, 112.2, 109.3, 101.0, 32.8; IR (KBr) 3116, 2289, 1681, 1495, 1402, 1308, 1081, 876, 801, 727, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}$ 175.0866, found 175.0865.

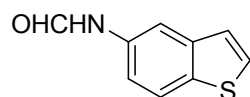
***N*-(1*H*-indol-5-yl)formamide (3zd)**



Purified by column chromatography; R_f 0.3 (PE:EA = 1:1); Yellow solid; Isolated yield 82% (132.5 mg); Mp 157-159 $^{\circ}\text{C}$; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 10.28 (major rotamer, br, 0.52H), 9.19 (minor rotamer, s, 0.48H), 8.69-8.66 (m, 0.30H), 8.36 (major rotamer, s, 0.70H), 8.18 (br d, $J = 11.6$ Hz, 0.27H), 8.04 (s, 0.63H), 7.44-7.32 (m, 2.88H), 7.02 (dd, $J = 8.6, 1.8$ Hz, 0.32H), 6.46-6.44 (m, 0.90H), 3.17 (s,

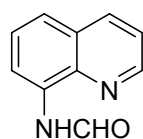
0.79H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ minor rotamer 163.6, 134.9, 131.0, 129.5, 127.0, 115.7, 112.9, 111.5, 102.3, major rotamer 159.6, 134.2, 131.6, 128.9, 126.5, 115.6, 112.0, 111.9, 102.4; IR (KBr) 3757, 3138, 2285, 1681, 1480, 1402, 1327, 1096, 805, 764, 731, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_9\text{N}_2\text{O}$ 161.0709, found 161.0709.

***N*-(1-benzothiophen-5-yl)formamide (3ze)**



Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 93% (163.9 mg); Mp 79-81°C; ^1H NMR (400 MHz, CDCl_3) δ 8.96 (minor rotamer, br d, J = 10.4 Hz, 0.46H), 8.73 (minor rotamer, d, J = 11.2 Hz, 0.49H), 8.39 (major rotamer, d, J = 2.0 Hz, 0.51H), 8.18 (d, J = 2.0 Hz, 0.50H), 8.00 (major rotamer, br s, 0.49H), 7.81 (d, J = 8.8 Hz, 0.50H), 7.75 (d, J = 8.4 Hz, 0.50H), 7.52 (d, J = 2.0 Hz, 0.50H), 7.50 (d, J = 5.6 Hz, 0.50H), 7.43 (d, J = 5.2 Hz, 0.50H), 7.35 (dd, J = 8.8, 2.0 Hz, 0.50H), 7.25 (dd, J = 10.8, 5.6 Hz, 1.00H), 7.09 (dd, J = 8.4, 2.0 Hz, 0.50H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 163.2, 140.4, 136.7, 133.5, 128.5, 123.6, 123.5, 116.8, 113.5, major rotamer 159.2, 140.1, 135.9, 133.6, 127.8, 123.8, 122.8, 117.4, 114.8; IR (KBr) 3739, 3437, 3153, 2285, 1674, 1525, 1402, 1279, 1088, 753, 693, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{NH}_3-\text{H}]^-$ calcd for $\text{C}_9\text{H}_9\text{N}_2\text{OS}$ 193.0436, found 193.0435.

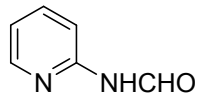
***N*-(8-quinolinyl)formamide (3zf)^[16]**



Purified by column chromatography; R_f 0.4 (PE:EA = 3:1); White solid; Isolated yield 64% (110.1 mg); Mp 157-159 °C; ^1H NMR (400 MHz, CDCl_3) δ 9.81 (major rotamer, s, 0.79H), 9.47 (minor rotamer, br s, 0.10H), 9.14 (minor rotamer, d, J = 12.0 Hz, 0.11H), 8.83 (d, J = 4.0 Hz, 0.99H), 8.78-8.74 (m, 0.87H), 8.71 (major rotamer, s, 0.89H), 8.19 (d, J = 8.0 Hz, 0.99H), 7.59-7.47 (m, 3.13H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 160.5, 148.9, 137.9, 136.0, 133.8, 128.5, 126.5, 122.5, 121.6, 110.9, major rotamer 159.2, 148.3, 138.1, 136.2, 133.4, 127.8, 127.1, 122.1, 121.6, 117.4; IR (KBr) 3757, 3131, 2285, 1655, 1543, 1402, 1327, 820, 749, 629 cm^{-1} ;

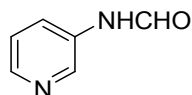
HRMS (ESI): m/z $[M+HCO_2H-H]^-$ calcd for $C_{11}H_9N_2O_3$ 217.0619, found 217.0600.

***N*-(pyridin-2-yl) formamide (3zg)^[7]**



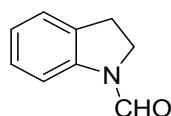
Purified by TLC; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 37% (44.0 mg); Mp 34-36 °C; 1H NMR (400 MHz, $CDCl_3$) δ 10.30 (minor rotamer, br s, 0.41H), 10.11 (major rotamer, br s, 0.59H), 9.34 (minor rotamer, d, J = 10.4 Hz, 0.43H), 8.55 (major rotamer, s, 0.57H), 8.35 (d, J = 4.4 Hz, 1.00H), 8.28 (d, J = 8.4 Hz, 0.57H), 7.76 (t, J = 7.8 Hz, 0.57H), 7.69 (t, J = 7.8 Hz, 0.43H), 7.13-7.07 (m, 1.00H), 6.95 (d, J = 8.0 Hz, 0.43H); ^{13}C NMR (100 MHz, $CDCl_3$) δ minor rotamer 163.1, 151.0, 148.5, 138.7, 119.8, 110.5, major rotamer 159.6, 150.9, 147.3, 138.9, 120.1, 115.1; IR (KBr) 3750, 3198, 2300, 1685, 1480, 1439, 1301, 1249, 1152, 999, 779, 525, 484 cm^{-1} ; HRMS (ESI): m/z $[M+K]^+$ calcd for $C_6H_6N_2KO$ 161.0112, found 161.0107.

***N*-(pyridin-3-yl)formamide (3zh)^[17]**



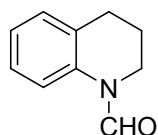
Purified by TLC; R_f 0.2 (PE:EA = 1:1); Yellow solid; Isolated yield 82% (100.1 mg); Mp 90-93 °C; 1H NMR (400 MHz, $CDCl_3$) δ 9.79-9.51 (m, 1.00H), 8.76 (minor rotamer, d, J = 11.2 Hz, 0.25H), 8.67 (major rotamer, s, 0.75H), 8.52 (d, J = 2.0 Hz, 0.23H), 8.47 (s, 1.00H), 8.35 (d, J = 3.6 Hz, 0.77H), 8.23 (d, J = 8.4 Hz, 0.77H), 7.54 (d, J = 8.4 Hz, 0.23H), 7.36-7.30 (m, 1.00H); ^{13}C NMR (100 MHz, $CDCl_3$) δ minor rotamer 162.5, 146.0, 140.4, 134.0, 126.0, 124.3, major rotamer 160.0, 144.9, 140.7, 134.6, 127.7, 124.0; IR (KBr) 3742, 3138, 2285, 1685, 1543, 1402, 1290, 1152, 805, 705, 630, 514 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_6H_7N_2O$ 123.0553, found 123.0556.

***N*-formylindoline (3zi)^[18]**



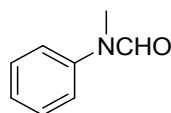
Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow solid; Isolated yield 92% (135.2 mg); Mp 63-65 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.89 (major rotamer, s, 0.81H), 8.48 (minor rotamer, s, 0.19H), 8.05 (d, J = 8.0 Hz, 0.19H), 7.22 (d, J = 7.6 Hz, 0.82H), 7.19-7.12 (m, 2.00H), 7.05-7.01 (m, 1.00H), 4.09-3.99 (m, 2.00H), 3.17-3.09 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 159.1, 140.9, 131.8, 127.3, 124.6, 124.3, 116.3, 46.7, 27.4, major rotamer 157.3, 140.8, 131.7, 127.3, 125.8, 124.0, 109.1, 44.4, 26.9; IR (KBr) 3742, 3496, 3138, 2352, 1666, 1595, 1495, 1402, 1297, 1174, 1096, 798, 753, 686 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{10}\text{NO}$ 148.0757, found 148.0753.

3,4-dihydroquinoline-1(2H)-carbaldehyde (3zj)^[18]



Purified by TLC; R_f 0.5 (PE:EA = 3:1); Yellow oil; Isolated yield 81% (130.7 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.78 (major rotamer, s, 0.93H), 8.32 (minor rotamer, s, 0.07H), 7.21-7.06 (m, 4.03H), 3.80 (major rotamer, t, J = 6.0 Hz, 1.84H), 3.66-3.64 (minor rotamer, m, 0.16H), 2.91-2.88 (minor rotamer, m, 0.16H), 2.80 (major rotamer, t, J = 6.4 Hz, 1.84H), 2.05-1.99 (minor rotamer, m, 0.16H), 1.97-1.91 (major rotamer, m, 1.84H); ^{13}C NMR (100 MHz, CDCl_3) δ minor rotamer 161.3, 137.0, 129.1, 128.7, 126.0, 122.1, 116.8, 46.0, 26.8, 22.9, major rotamer 160.9, 137.0, 129.4, 128.7, 126.9, 124.3, 116.8, 40.1, 26.9, 22.1; IR (KBr) 3466, 3138, 2945, 2285, 1684, 1603, 1402, 1368, 1204, 1122, 1062, 917, 764, 544 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{NO}$ 162.0913, found 162.0914.

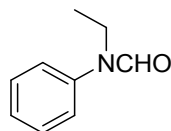
N-methyl-N-phenylformamide (3zk)^[7]



Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow oil; Isolated yield 60% (81.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.48 (major rotamer, s, 0.96H), 8.36 (minor rotamer, s, 0.04H), 7.44-7.40 (m, 2.10H), 7.30-7.26 (m, 1.00H), 7.18 (d, J = 8.0 Hz, 1.90H), 3.36 (minor rotamer, s, 0.17H), 3.32 (major rotamer, s, 2.83H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 162.2, 141.9, 129.4, 126.2, 122.1, 31.9, minor rotamer 162.1, 141.9, 128.9, 126.1, 123.4, 36.7; IR (KBr) 3750, 3138, 2244, 1946, 1681, 1599, 1498,

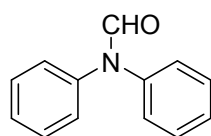
1402, 1363, 1271, 1118, 1029, 764, 537 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{NO}$ 136.0757, found 136.0753.

***N*-ethylformanilide (3zl)^[19]**



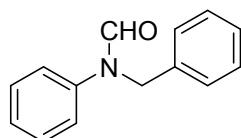
Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow oil; Isolated yield 62% (92.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.36 (s, 1.00H), 7.44-7.40 (m, 2.00H), 7.33-7.29 (m, 1.18H), 7.18 (d, J = 7.6 Hz, 1.82H), 3.87 (q, J = 7.2 Hz, 2.00H), 1.17 (t, J = 7.2 Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 161.9, 140.6, 129.5, 126.7, 124.1, 39.9, 12.9, minor rotamer 161.9, 140.6, 129.1, 126.0, 124.1, 44.8, 14.9; IR (KBr) 3750, 3138, 2878, 2348, 1681, 1595, 1498, 1256, 1129, 1088, 1036, 616, 768, 701, 552 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{NO}$ 150.0913, found 150.0914.

***N,N*-diphenylformamide (3zm)^[3]**



Purified by TLC; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 32% (62.6 mg); Mp 65-67 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.67 (s, 1.00H), 7.43-7.38 (m, 4.03H), 7.33-7.26 (m, 4.47H), 7.18-7.16 (m, 1.81H); ^{13}C NMR (100 MHz, CDCl_3) δ major rotamer 161.7, 141.7, 129.7, 127.0, 125.0, minor rotamer 161.7, 139.6, 129.1, 126.8, 126.1; IR (KBr) 3753, 3138, 2285, 1689, 1595, 1402, 1267, 1133, 697, 578, 529, 421 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{12}\text{NO}$ 198.0913, found 198.0918.

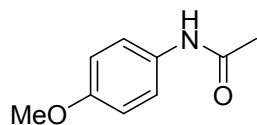
***N*-benzyl-*N*-phenylformamide (3zn)^[19]**



Purified by TLC; R_f 0.5 (PE:EA = 5:1); Yellow solid; Isolated yield 62% (129.9 mg); Mp 45-47 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.56 (s, 1.00H), 7.36-7.22 (m, 8.30H), 7.11-7.09 (m, 2.00H), 5.00 (s, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.4, 140.9,

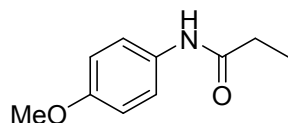
136.6, 129.5, 128.5, 127.8, 127.4, 126.8, 124.0, 48.8; IR (KBr) 3742, 3138, 2352, 1674, 1495, 1402, 1264, 1081, 962, 764, 698, 537 cm^{-1} ; HRMS (ESI): m/z $[M+H]^+$ calcd for $\text{C}_{14}\text{H}_{14}\text{NO}$ 212.1070, found 212.1065.

***N*-(4-methoxyphenyl)acetamide (3zo)**^[20]



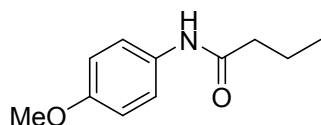
Purified by column chromatography; R_f 0.3 (PE:EA = 2:1); Brown solid; Isolated yield 83% (136.8 mg); Mp 126-128 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (br, 1.00H), 7.38 (d, J = 8.4 Hz, 2.00H), 6.83-6.80 (m, 2.00H), 3.77 (d, J = 2.8 Hz, 3.00H), 2.11 (d, J = 4.8 Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.8, 156.2, 131.1, 122.0, 113.9, 55.3, 24.0; IR (KBr) 3750, 3135, 2352, 1651, 1513, 1402, 1115, 1029, 839, 772, 522, 421 cm^{-1} ; HRMS (ESI): m/z $[M+\text{NH}_4]^+$ calcd for $\text{C}_9\text{H}_{15}\text{N}_2\text{O}_2$ 183.1128, found 183.1134.

***N*-(4-methoxyphenyl)-propanamide (3zp)**^[20]



Purified by column chromatography; R_f 0.4 (PE:EA = 2:1); Brown solid; Isolated yield 93% (166.6 mg); Mp 77-79 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 9.2 Hz, 2.00H), 7.36 (br s, 0.91H), 6.84 (d, J = 8.8 Hz, 2.00H), 3.78 (s, 3.00H), 2.36 (q, J = 7.6 Hz, 2.00H), 1.23 (t, J = 7.6 Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 172.1, 156.2, 131.1, 121.8, 114.0, 55.4, 30.4, 9.7; IR (KBr) 3683, 3317, 2840, 2289, 1882, 1659, 1539, 1402, 1301, 1249, 1178, 1033, 828, 701, 522 cm^{-1} ; HRMS (ESI): m/z $[M+\text{NH}_3-\text{H}]^-$ calcd for $\text{C}_{10}\text{H}_{15}\text{N}_2\text{O}_2$ 195.1134, found 195.1140.

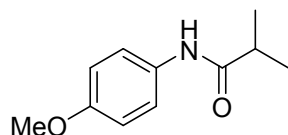
***N*-(4-methoxyphenyl)butanamide (3zq)**^[21]



Purified by column chromatography; R_f 0.5 (PE:EA = 2:1); Yellow solid; Isolated yield 63% (122.6 mg); Mp 86-88 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, J = 8.8 Hz, 2.00H), 7.23 (br s, 0.89H), 6.84 (d, J = 9.2 Hz, 2.00H), 3.78 (s, 3.00H), 2.31 (q, J = 7.4 Hz, 2.00H), 1.80-1.71 (m, 2.39H), 1.00 (t, J = 7.4 Hz, 3.00H); ^{13}C NMR (100

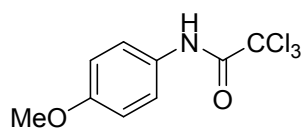
MHz, CDCl₃) δ 171.1, 156.3, 131.0, 121.7, 114.1, 55.5, 39.5, 19.1, 13.7; IR (KBr) 3288, 3198, 2963, 2863, 2878, 2363, 1879, 1659, 1402, 1300, 1252, 1033, 828, 522 cm⁻¹; HRMS (ESI): m/z [M+Li]⁺ calcd for C₁₁H₁₅NLiO₂ 200.1257, found 200.1254.

***N*-(4-methoxyphenyl)isobutyramide (3zr)^[22]**



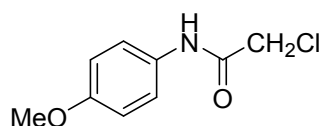
Purified by column chromatography; R_f 0.2 (PE:EA = 3:1); Yellow solid; Isolated yield 42% (81.2 mg); Mp 102-104 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, J = 8.8 Hz, 2.00H), 7.38 (br s, 1.00H), 6.83 (d, J = 8.4 Hz, 2.00H), 3.78 (s, 3.00H), 2.54-2.44 (m, 0.96H), 1.23 (d, J = 6.8 Hz, 6.00H); ¹³C NMR (100 MHz, CDCl₃) δ 175.2, 156.2, 131.2, 121.7, 114.0, 55.4, 36.4, 19.6; IR (KBr) 3138, 2971, 2348, 1655, 1607, 1402, 1297, 1245, 1103, 1033, 828, 731, 526 cm⁻¹; HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₁H₁₅NNaO₂ 216.0995, found 216.0994.

2,2,2-trichloro-*N*-(4-methoxyphenyl)acetamide (3zs)



Purified by column chromatography; R_f 0.6 (PE:EA = 5:1); Yellow solid; Isolated yield 33% (87.9 mg); Mp 106-108 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.27 (br s, 0.90H), 7.49 (d, J = 9.2 Hz, 2.00H), 6.93 (d, J = 8.8 Hz, 2.00H), 3.82 (s, 3.00H); ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 157.6, 128.8, 122.1, 114.4, 92.8, 55.5; IR (KBr) 3138, 2289, 1692, 1543, 1402, 1245, 1033, 880, 835, 749, 649, 522 cm⁻¹; HRMS (ESI): m/z [M+Na]⁺ calcd for C₉H₈Cl₃NNaO₂ 289.9513, found 289.9503.

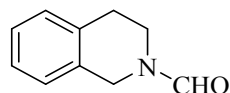
***N*-(4-methoxyphenyl)-2-chloroacetamide (3zt)^[23]**



Purified by column chromatography; R_f 0.4 (PE:EA = 3:1); Yellow solid; Isolated yield 43% (85.3 mg); Mp 117-119 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (br s, 0.95H), 7.44 (d, J = 8.8 Hz, 2.00H), 6.89 (d, J = 9.2 Hz, 2.00H), 4.18 (s, 2.00H), 3.80 (s, 3.00H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 157.0, 129.7, 122.1, 114.2, 55.4,

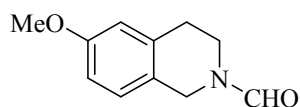
42.8; IR (KBr) 3138, 2352, 1662, 1543, 1402, 1252, 1029, 831, 790, 522 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_9\text{H}_{10}\text{ClNNaO}_2$ 222.0298, found 222.0289.

2-formyl-1,2,3,4-tetrahydroisoquinoline (3A)^[24]



Purified by TLC; R_f 0.3 (PE:EA = 3:1); Yellow oil; Isolated yield 74% (119.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.25 (minor rotamer, s, 0.36H), 8.19 (major rotamer, s, 0.64H), 7.22-7.08 (m, 4.00H), 4.68 (major rotamer, s, 1.24H), 4.54 (minor rotamer, s, 0.75H), 3.78 (minor rotamer, t, J = 6.2 Hz, 0.74H), 3.64 (major rotamer, t, J = 5.8 Hz, 1.27H), 2.92-2.85 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.6 (major rotamer), 161.1 (minor rotamer), 134.3 (minor rotamer), 133.4 (major rotamer), 132.1 (minor rotamer), 131.7 (major rotamer), 129.1 (minor rotamer), 128.8 (major rotamer), 127.0, 126.6-126.4 (m), 125.8, 47.2 (minor rotamer), 43.1 (major rotamer), 42.2 (major rotamer), 37.9 (minor rotamer), 29.6 (major rotamer), 27.8 (minor rotamer); IR (neat) 3151, 3025, 2931, 2862, 1672, 1584, 1498, 1439, 1400, 1343, 1318, 1282, 1228, 1197, 1164, 1109, 1049, 930, 882, 814, 751, 710, 675, 606, 477 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{11}\text{NNaO}$ 184.0733, found 184.0733.

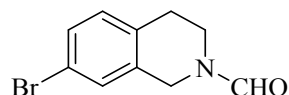
2-formyl-1,2,3,4-tetrahydro-6-methoxyisoquinoline (3B)^[24]



Purified by TLC; R_f 0.3 (PE:EA = 3:1); Yellow solid; Isolated yield 74% (71.0 mg); Mp 63-64 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.22 (minor rotamer, s, 0.40H), 8.17 (major rotamer, s, 0.60H), 7.04-6.99 (m, 1.00H), 6.78-6.74 (m, 1.00H), 6.65 (d, J = 10.0 Hz, 1.00H), 4.60 (major rotamer, s, 1.24H), 4.47 (minor rotamer, s, 0.77H), 3.77-3.73 (m, 3.76H), 3.61 (major rotamer, t, J = 5.8 Hz, 1.24H), 2.87-2.81 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.5 (major rotamer), 161.1 (minor rotamer), 158.4 (minor rotamer), 158.1 (major rotamer), 135.6 (minor rotamer), 134.7 (major rotamer), 127.6 (major rotamer), 126.8 (minor rotamer), 124.3 (minor rotamer), 123.7 (major rotamer), 113.6 (minor rotamer), 113.5 (major rotamer), 112.9 (major rotamer), 112.7 (minor rotamer), 55.2 (s), 46.8 (minor rotamer), 43.1 (major rotamer), 41.7 (major rotamer), 37.8 (minor rotamer), 29.9 (major rotamer), 28.2 (minor

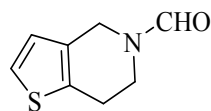
rotamer); IR (neat) 3140, 1672, 1612, 1508, 1402, 1312, 1277, 1262, 1241, 1119, 1036, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{HCO}_2\text{H}-\text{H}]^-$ calcd for $\text{C}_{12}\text{H}_{14}\text{NO}_4$ 236.0928, found 236.0921.

7-bromo-3,4-dihydroisoquinoline-2(1H)-carbaldehyde (3C)^[24]



Purified by TLC; R_f 0.5 (PE:EA = 3:1); Yellow solid; Isolated yield 93% (222.5 mg); Mp 58-60 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.24 (minor rotamer, s, 0.37H), 8.19 (major rotamer, s, 0.63H), 7.34-7.26 (m, 2.00H), 7.02 (t, J = 8.8 Hz, 1.00H), 4.66 (major rotamer, s, 1.31H), 4.52 (minor rotamer, s, 0.72H), 3.78 (minor rotamer, t, J = 6.2 Hz, 0.72H), 3.65 (major rotamer, t, J = 5.8 Hz, 1.32H), 2.86 (major rotamer, t, J = 5.8 Hz, 1.28H), 2.82 (minor rotamer, t, J = 6.0 Hz, 0.80H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.6 (major rotamer), 161.0 (minor rotamer), 134.2 (minor rotamer), 133.8 (major rotamer), 133.3 (minor rotamer), 132.4 (major rotamer), 130.8 (minor rotamer), 130.5 (major rotamer), 130.1 (minor rotamer), 129.7 (major rotamer), 129.4 (major rotamer), 128.7 (minor rotamer), 120.2 (major rotamer), 119.9 (minor rotamer), 46.8 (minor rotamer), 42.9 (major rotamer), 41.8 (major rotamer), 37.7 (minor rotamer), 29.2 (major rotamer), 27.4 (minor rotamer); IR (neat) 3140, 1672, 1402, 1191, 1157, 1116, 1075, 1051, 932, 829, 531 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{BrN}_2\text{O}$ 257.0284, found 257.0275.

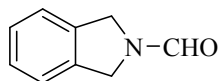
5-formyl-4,5,6,7-tetrahydrothieno[3,2-c]pyridine (3D)^[24]



Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow oil; Isolated yield 89% (149.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.24 (minor rotamer, s, 0.38H), 8.20 (major rotamer, s, 0.62H), 7.17-7.15 (m, 1.00H), 6.80 (t, J = 4.4 Hz, 1.00H), 4.60 (major rotamer, s, 1.28H), 4.47 (minor rotamer, s, 0.74H), 3.86 (minor rotamer, t, J = 5.8 Hz, 0.74H), 3.69 (major rotamer, t, J = 5.8 Hz, 1.28H), 2.93 (major rotamer, t, J = 5.8 Hz, 1.26H), 2.88 (minor rotamer, t, J = 5.8 Hz, 0.75H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.7 (major rotamer), 161.4 (minor rotamer), 133.8 (minor rotamer), 132.1 (major rotamer), 130.8 (major rotamer), 130.7 (minor rotamer), 125.0 (major rotamer), 124.3

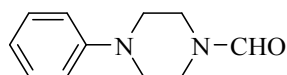
(minor rotamer), 123.8 (s), 45.7 (minor rotamer), 43.7 (major rotamer), 40.6 (major rotamer), 37.9 (minor rotamer), 25.8 (major rotamer), 24.4 (minor rotamer); IR (neat) 3129, 1705, 1670, 1433, 1402, 1314, 1176, 1043, 1018, 824, 706, 593, 567 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_8\text{H}_{13}\text{N}_2\text{SO}$ 185.0743, found 185.0735.

2-formyl-1,3-dihydro-isoindole (3E)^[24]



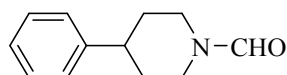
Purified by TLC; R_f 0.2 (PE:EA = 3:1); Black oil; Isolated yield 80% (58.8 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.42 (s, 1.00H), 7.31-7.27 (m, 4.00H), 4.89 (s, 2.00H), 4.76 (s, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.5 (s), 135.9 (s), 135.2 (s), 128.0 (s), 127.7 (s), 123.2 (s), 122.8 (s), 51.4 (s), 49.8 (s); IR (neat) 3140, 1668, 1465, 1402, 1159, 1092, 747, 608, 531, 416 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Cl}]^-$ calcd for $\text{C}_9\text{H}_9\text{ClNO}$ 182.0367, found 182.0368.

4-phenylpiperazine-1-carboxaldehyde (3F)^[24]



Purified by TLC; R_f 0.2 (PE:EA = 3:1); Yellow solid; Isolated yield 80% (151.8 mg); Mp 86-87 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.08 (s, 1.00H), 7.30-7.27 (m, 2.00H), 6.94-6.90 (m, 3.00H), 3.69 (t, J = 5.2 Hz, 2.00H), 3.51 (t, J = 5.0 Hz, 2.00H), 3.15 (dt, J = 15.2, 5.2 Hz, 4.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.6 (s), 150.8 (s), 129.1 (s), 120.7 (s), 116.9 (s), 50.3 (s), 49.2 (s), 45.4 (s), 39.8 (s); IR (neat) 3131, 1664, 1402, 1152, 1115, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{KO}$ 229.0738, found 229.0742.

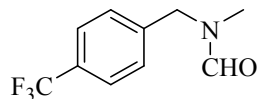
4-phenylpiperidine-1-carbaldehyde (3G)^[24]



Purified by TLC; R_f 0.2 (PE:EA = 3:1); Yellow solid; Isolated yield 91% (86.2 mg); Mp 98-99 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1.00H), 7.31 (t, J = 7.4 Hz, 2.00H), 7.24-7.18 (m, 3.00H), 4.56 (d, J = 13.6 Hz, 1.00H), 3.73 (d, J = 13.2 Hz, 1.00H), 3.19 (td, J = 12.9, 2.6 Hz, 1.00H), 2.81-2.67 (m, 2.00H), 1.92 (t, J = 15.8 Hz, 2.00H), 1.67-1.54 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8 (s), 144.8 (s), 128.5 (s), 126.6 (s), 126.5 (s), 46.4 (s), 42.8 (s), 40.1 (s), 33.8 (s), 32.3 (s); IR (neat)

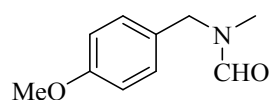
3140, 1675, 1653, 1402, 1170, 1064, 759, 699, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{12}\text{H}_{15}\text{NNaO}$ 212.1046, found 212.1048.

***N*-methyl-*N*-[[4-(trifluoromethyl)phenyl]methyl]methanamide (3H)^[24]**



Purified by TLC; R_f 0.3 (PE:EA = 3:1); Yellow oil; Isolated yield 70% (75.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.31 (minor rotamer, s, 0.48H), 8.19 (major rotamer, s, 0.52H), 7.63 (dd, J = 18.2, 8.2 Hz, 2.00H), 7.36 (dd, J = 12.6, 8.2 Hz, 2.00H), 4.59 (major rotamer, s, 1.07H), 4.48 (minor rotamer, s, 0.96H), 2.89 (major rotamer, s, 1.64H), 2.80 (minor rotamer, s, 1.42H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.9 (minor rotamer), 162.8 (major rotamer), 140.2 (major rotamer), 140.0 (minor rotamer), 130.3 (major rotamer, dd, J = 51.2, 32.3 Hz), 128.5 (major rotamer), 127.7 (minor rotamer), 126.0 (minor rotamer, q, J = 3.7 Hz), 125.8 (major rotamer, q, J = 3.7 Hz), 125.5 (major rotamer), 125.3 (minor rotamer), 122.8 (major rotamer), 122.6 (minor rotamer), 53.1 (minor rotamer), 47.5 (major rotamer), 34.3 (major rotamer), 29.7 (minor rotamer); ^{19}F NMR (377 MHz, CDCl_3) δ -62.53 (major rotamer, s), -62.58 (minor rotamer, s); IR (neat) 3140, 2361, 2343, 1675, 1621, 1402, 1327, 1165, 1113, 1068, 1019, 848, 818, 527 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{F}_3\text{N}_2\text{O}$ 235.1053, found 235.1067.

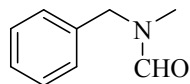
***N*-(4-methoxybenzyl)-*N*-methylformamide (3I)^[24]**



Purified by TLC; R_f 0.4 (PE:EA = 2:1); Yellow oil; Isolated yield 99% (88.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.22 (major rotamer, s, 0.58H), 8.08 (minor rotamer, s, 0.42H), 7.14 (minor rotamer, d, J = 8.4 Hz, 0.86H), 7.08 (major rotamer, d, J = 8.4 Hz, 1.15H), 6.86-6.81 (m, 2.00H), 4.41 (minor rotamer, s, 0.86H), 4.28 (major rotamer, s, 1.20H), 3.76 (major rotamer, s, 1.78H), 3.75 (minor rotamer, s, 1.23H), 2.78 (minor rotamer, s, 1.30H), 2.71 (major rotamer, s, 1.75H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.5 (major rotamer), 162.4 (minor rotamer), 159.3 (major rotamer), 159.0 (minor rotamer), 130.3, 129.5 (minor rotamer), 128.7 (major rotamer), 128.0 (minor rotamer), 127.5 (major rotamer), 114.1 (major rotamer), 113.9 (minor rotamer), 113.5,

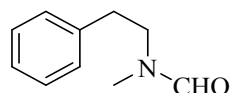
55.2 (major rotamer, d, $J = 4.4$ Hz), 52.8 (minor rotamer), 47.0 (major rotamer), 44.7 (minor rotamer), 33.8 (minor rotamer), 29.1 (major rotamer); IR (neat) 3140, 1671, 1612, 1515, 1402, 1303, 1249, 1176, 1079, 1032, 846, 814, 559, 522 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{NH}_4]^+$ calcd for $\text{C}_{10}\text{H}_{17}\text{N}_2\text{O}_2$ 197.1285, found 197.1304.

***N*-methyl-*N*-benzylformamide (3J)**^[24]



Purified by TLC; R_f 0.3 (PE:EA = 3:1); Yellow oil; Isolated yield 80% (119.3 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.29 (major rotamer, s, 0.57H), 8.17 (minor rotamer, s, 0.43H), 7.40-7.20 (m, 5.00H), 4.53 (minor rotamer, s, 0.84H), 4.40 (major rotamer, s, 1.16H), 2.85 (minor rotamer, s, 1.30H), 2.79 (major rotamer, s, 1.75H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.8 (major rotamer), 162.6 (minor rotamer), 135.9 (minor rotamer), 135.6 (major rotamer), 128.9 (major rotamer), 128.7 (minor rotamer), 128.2 (major rotamer), 128.1 (minor rotamer), 127.6 (minor rotamer), 127.4 (major rotamer), 53.5 (major rotamer), 47.7 (minor rotamer), 34.1 (minor rotamer), 29.4 (major rotamer); IR (neat) 3122, 1664, 1402, 1379, 1140, 1066, 1081, 705, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{CH}_3\text{CO}_2\text{H}-\text{H}]^-$ calcd for $\text{C}_{11}\text{H}_{14}\text{NO}_3$ 208.0979, found 208.0971.

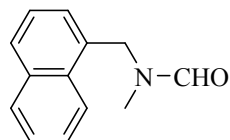
***N*-methyl-*N*-phenethyl-formamide (3K)**^[24]



Purified by TLC; R_f 0.3 (PE:EA = 2:1); Yellow oil; Isolated yield 99% (80.9 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (minor rotamer, s, 0.37H), 7.80 (major rotamer, s, 0.63H), 7.33-7.22 (m, 4.00H), 7.14 (d, $J = 7.2$ Hz, 1.00H), 3.56 (minor rotamer, t, $J = 7.6$ Hz, 0.79H), 3.47 (major rotamer, t, $J = 7.0$ Hz, 1.25H), 2.90-2.82 (m, 5.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.6 (major rotamer), 162.4 (minor rotamer), 138.5 (minor rotamer), 137.6 (major rotamer), 128.7 (major rotamer), 128.7 (minor rotamer), 128.6 (major rotamer), 128.5 (minor rotamer), 126.7 (major rotamer), 126.4 (minor rotamer), 51.2 (major rotamer), 45.9 (minor rotamer), 35.0 (minor rotamer), 34.7 (major rotamer), 33.1 (minor rotamer), 29.7 (minor rotamer); IR (neat) 3140, 1666, 1402, 1152, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{14}\text{NO}$

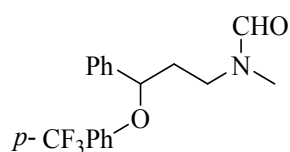
164.1070, found 164.1071.

***N*-methyl-*N*-(naphthalen-1-ylmethyl)methanamide (3L)**^[24]



Purified by TLC; R_f 0.4 (PE:EA = 2:1); Yellow oil; Isolated yield 86% (171.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.38 (minor rotamer, s, 0.40H), 8.18 (major rotamer, s, 0.61H), 8.10 (d, J = 8.0 Hz, 0.61H), 7.91-7.82 (m, 2.46H), 7.55-7.30 (m, 4.00H), 4.98 (major rotamer, s, 1.20H), 4.87 (minor rotamer, s, 0.77H), 2.85 (minor rotamer, s, 1.20H), 2.74 (major rotamer, s, 1.78H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.3 (minor rotamer), 162.4 (major rotamer), 133.9, 131.6, 131.3 (major rotamer), 131.3 (minor rotamer), 131.1 (minor rotamer), 131.0 (major rotamer), 129.2 (minor rotamer), 129.0 (major rotamer), 128.9 (minor rotamer), 128.7 (major rotamer), 127.8 (minor rotamer), 126.8 (minor rotamer), 126.2 (major rotamer), 125.6 (minor rotamer), 125.2 (minor rotamer), 123.9 (major rotamer), 122.4 (minor rotamer), 51.1 (minor rotamer), 45.9 (major rotamer), 34.1 (major rotamer), 30.1 (minor rotamer); IR (neat) 3140, 1672, 1510, 1402, 1258, 1161, 1081, 803, 779, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{14}\text{NO}$ 200.1070, found 200.1069.

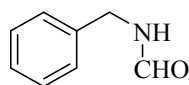
***N*-formylfluoxetine (3M)**^[24]



Purified by TLC; R_f 0.5 (PE:EA = 2:1); Yellow oil; Isolated yield 76% (128.3 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.02 (minor rotamer, s, 0.41H), 7.99 (major rotamer, s, 0.59H), 7.43 (d, J = 8.8 Hz, 2.00H), 7.37-7.27 (m, 5.00H), 6.90-6.86 (m, 2.00H), 5.20 (minor rotamer, dd, J = 8.8, 4.4 Hz, 0.42H), 5.14 (major rotamer, dd, J = 8.8, 4.0 Hz, 0.61H), 3.59-3.52 (major rotamer, m, 1.42H), 3.42-3.35 (minor rotamer, m, 0.62H), 2.94 (minor rotamer, s, 1.21H), 2.90 (major rotamer, s, 1.84H), 2.27-2.17 (m, 1.06H), 2.15-2.04 (m, 1.15H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.7 (major rotamer), 162.6 (minor rotamer), 160.1 (minor rotamer), 159.8 (major rotamer), 140.4 (minor rotamer), 139.8 (major rotamer), 129.0 (major rotamer), 128.8 (minor rotamer), 128.2

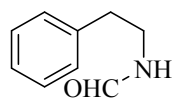
(major rotamer), 128.0 (minor rotamer), 126.9-126.7 (m), 125.6 (minor rotamer), 125.5 (major rotamer), 123.3-122.7 (m), 115.7 (minor rotamer), 115.6 (major rotamer), 78.1 (minor rotamer), 76.9 (major rotamer), 45.9 (major rotamer), 41.5 (minor rotamer), 36.9 (major rotamer), 35.8 (minor rotamer), 34.8 (minor rotamer), 29.5 (major rotamer); ^{19}F NMR (377 MHz, CDCl_3) δ -61.52 (minor rotamer, s), -61.59 (major rotamer, s); IR (neat) 3140, 1675, 1616, 1519, 1329, 1251, 1161, 1113, 1068, 837, 703, 527 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{NNaO}_2$ 360.1182, found 360.1178.

***N*-benzylformamide (3N)**^[24]



Purified by TLC; R_f 0.4 (PE:EA = 3:1); Yellow solid; Isolated yield 75% (101.3 mg); Mp 54-58 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.25 (major rotamer, s, 0.87H), 8.16 (minor rotamer, d, J = 12.0 Hz, 0.13H), 7.35-7.27 (m, 5.00H), 6.08 (br s, 1.00H), 4.48 (major rotamer, d, J = 6.0 Hz, 1.73H), 4.41 (minor rotamer, d, J = 6.4 Hz, 0.34H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7 (minor rotamer), 161.0 (major rotamer), 137.5 (major rotamer), 137.4 (minor rotamer), 128.9 (minor rotamer), 128.7 (major rotamer), 127.9 (minor rotamer), 127.7 (major rotamer), 127.6 (major rotamer), 126.9 (minor rotamer), 45.6 (minor rotamer), 42.1 (major rotamer); IR (neat) 3140, 1666, 1402, 699, 526 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{10}\text{NO}$ 136.0757, found 136.0747.

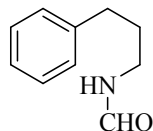
***N*-(2-phenylethyl)formamide (3O)**^[24]



Purified by TLC; R_f 0.3 (PE:EA = 2:1); Yellow oil; Isolated yield 86% (128.0 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.10 (major rotamer, s, 0.84H), 7.89 (minor rotamer, d, J = 12.0 Hz, 0.16H), 7.32-7.20 (m, 5H), 5.83 (br s, 1.00H), 3.59-3.46 (m, 2.00H), 2.86-2.82 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.5 (minor rotamer), 161.2 (major rotamer), 138.4 (major rotamer), 137.5 (minor rotamer), 128.8-128.6 (m), 126.8 (minor rotamer), 126.6 (major rotamer), 43.1 (minor rotamer), 39.1 (major rotamer), 37.6 (minor rotamer), 35.4 (major rotamer); IR (neat) 3140, 1670, 1402, 1154, 689, 527 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_9\text{H}_{11}\text{NNaO}$ 172.0733,

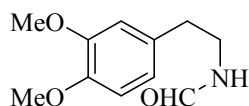
found 172.0741.

***N*-formyl-3-phenylpropylamine (3P)**^[24]



Purified by TLC; R_f 0.1 (PE:EA = 3:1); Yellow oil; Isolated yield 99% (161.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.13 (major rotamer, s, 0.82H), 7.99 (minor rotamer, d, J = 12.0 Hz, 0.18H), 7.32-7.17 (m, 5.00H), 6.04 (br s, 1.00H), 3.31 (major rotamer, q, J = 6.8 Hz, 1.64H), 3.20 (minor rotamer, q, J = 6.8 Hz, 0.36H), 2.68-2.64 (m, 2.00H), 1.89-1.82 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.8 (minor rotamer), 161.3 (major rotamer), 141.1 (major rotamer), 140.5 (minor rotamer), 128.5 (minor rotamer), 128.4 (major rotamer), 128.3 (major rotamer), 126.2 (minor rotamer), 126.0 (major rotamer), 41.0 (minor rotamer), 37.7 (major rotamer), 33.0 (major rotamer), 32.4 (minor rotamer), 32.4 (minor rotamer), 31.0 (major rotamer); IR (neat) 3122, 1666, 1402, 1154, 1113, 749, 701, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{NNaO}$ 186.0889, found 186.0897.

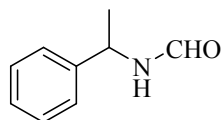
***N*-[2-(3,4-dimethoxyphenyl)ethyl]formamide (3Q)**^[24]



Purified by TLC; R_f 0.1 (PE:EA = 2:1); Yellow oil; Isolated yield 86% (180.1 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (major rotamer, s, 0.85H), 7.87 (minor rotamer, d, J = 12.0 Hz, 0.15H), 6.79-6.65 (m, 3.00H), 5.93 (br s, 1.00H), 3.83 (major rotamer, s, 3.73H), 3.82 (minor rotamer, s, 2.25H), 3.51 (major rotamer, q, J = 6.4 Hz, 1.64H), 3.41 (minor rotamer, q, J = 6.4 Hz, 0.36H), 2.77-2.71 (m, 2.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.5 (minor rotamer), 161.2 (major rotamer), 148.9 (minor rotamer), 148.8 (major rotamer), 147.7 (minor rotamer), 147.5 (major rotamer), 130.8 (major rotamer), 130.0 (minor rotamer), 120.8 (minor rotamer), 120.5 (major rotamer), 111.8 (minor rotamer), 111.7 (major rotamer), 111.3 (minor rotamer), 111.2 (major rotamer), 55.9 (major rotamer), 55.7 (minor rotamer), 43.2 (minor rotamer), 39.2 (major rotamer), 37.2 (minor rotamer), 34.9 (major rotamer); IR (neat) 3140, 3006,

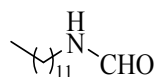
2941, 2838, 1668, 1610, 1593, 1519, 1467, 1400, 1265, 1238, 1195, 1159, 1142, 1029, 937, 859, 811, 810, 766, 632 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{11}\text{H}_{16}\text{NO}_3$ 210.1125, found 210.1122.

***N*-(1-phenylethyl)formamide (3R)**^[24]



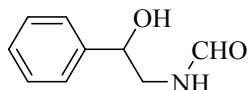
Purified by TLC; R_f 0.4 (PE:EA = 2:1); Yellow oil; Isolated yield 50% (75.2 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.11 (s, 1.00H), 7.38-7.25 (m, 5.00H), 6.33 (br s, 1.00H), 5.22-5.15 (major rotamer, m, 0.82H), 4.71-4.64 (minor rotamer, m, 0.19H), 1.55 (minor rotamer, d, J = 6.8 Hz, 0.53H), 1.50 (major rotamer, d, J = 6.8 Hz, 2.47H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.3, 142.5, 128.8 (minor rotamer), 128.6 (major rotamer), 127.7 (minor rotamer), 127.4 (major rotamer), 126.0 (major rotamer), 125.7 (minor rotamer), 51.6 (minor rotamer), 47.5 (major rotamer), 23.5 (minor rotamer), 21.7 (major rotamer); IR (neat) 3100, 1662, 1534, 1497, 1402, 1238, 1118, 762, 698, 609, 537 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{NO}$ 150.0913, found 150.0912.

***N*-(dodecyl)formamide (3S)**^[24]



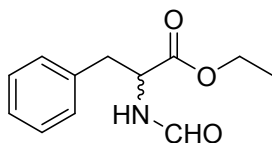
Purified by TLC; R_f 0.2 (PE:EA = 2:1); Gray solid; Isolated yield 73% (155.6 mg); Mp 33-35 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (major rotamer, s, 0.82H), 8.03 (minor rotamer, d, J = 12.0 Hz, 0.18H), 5.63 (br s, 1.00H), 3.28 (major rotamer, q, J = 6.8 Hz, 1.66H), 3.20 (minor rotamer, q, J = 6.8 Hz, 0.44H), 1.53-1.48 (m, 2.00H), 1.29-1.24 (m, 18.00H), 0.87 (t, J = 6.8 Hz, 3.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.7 (minor rotamer), 161.0 (major rotamer), 41.8 (minor rotamer), 38.2 (major rotamer), 31.9 (major rotamer), 31.2 (minor rotamer), 29.6-29.1 (m), 26.8 (major rotamer), 26.3 (minor rotamer), 22.6, 14.1; IR (neat) 3122, 1670, 1401, 1150, 1113, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{K}]^+$ calcd for $\text{C}_{13}\text{H}_{27}\text{NKO}$ 252.1724, found 252.1724.

***N*-(2-hydroxy-2-phenylethyl)formamide (3T)**^[24]



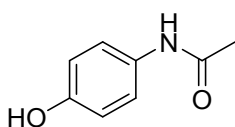
Purified by TLC; R_f 0.1 (PE:EA = 2:1); Yellow oil; Isolated yield 58% (47.5 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.09 (major rotamer, s, 0.83H), 7.86 (minor rotamer, d, J = 12.0 Hz, 0.17H), 7.34-7.27 (m, 5.00H), 6.35 (br s, 1.00H), 4.80 (major rotamer, dd, J = 8.6, 3.4 Hz, 0.84H), 4.70 (minor rotamer, dd, J = 7.4, 3.8 Hz, 0.18H), 3.73-3.67 (major rotamer, m, 1.80H), 3.45-3.37 (minor rotamer, m, 0.19H), 3.33-3.27 (m, 1.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.4 (minor rotamer), 162.2 (major rotamer), 141.4 (major rotamer), 140.8 (minor rotamer), 128.7 (minor rotamer), 128.5 (major rotamer), 128.2 (minor rotamer), 128.0 (major rotamer), 125.8 (minor rotamer), 125.8 (major rotamer), 73.3 (minor rotamer), 72.9 (major rotamer), 49.2 (minor rotamer), 45.7 (major rotamer); IR (neat) 3140, 1670, 1523, 1495, 1402, 1239, 1198, 1096, 915, 755, 703, 533 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_9\text{H}_{12}\text{NO}_2$ 166.0863, found 166.0860.

ethyl formylphenylalaninate (3U)^[25]



Purified by TLC; R_f 0.8 (PE:EA = 1:9); Yellow oil; Isolated yield 58% (128.6 mg); ^1H NMR (400 MHz, CDCl_3) δ 8.12 (s, 1.00H), 7.30-7.24 (m, 3.21H), 7.16-7.11 (m, 2.03H), 6.48 (br s, 0.98H), 4.95-4.90 (m, 0.93H), 4.18 (q, J = 7.2 Hz, 1.96H), 3.18-3.08 (m, 2.00H), 1.25 (t, J = 7.0 Hz, 3.39H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.1, 160.7, 135.5, 129.1, 128.3, 126.9, 61.4, 51.7, 37.6, 13.9; IR (KBr) 3891, 3135, 2572, 1741, 1662, 1532, 1402, 1204, 1092, 1029, 861, 749, 701, 574 cm^{-1} ; Chiral HPLC analysis (Chiralcel OJ-H, $i\text{PrOH}$: $n\text{-Hex}$ = 10:90, flow rate = 0.5 mL/min, λ = 254 nm), t_{r1} = 24.139, t_{r2} = 29.859. ee = 3.6%; $[\alpha]_{20}^{25} = +7.8$ (c 0.4, CHCl_3) [ref.²⁵ $[\alpha]_{20}^D = +76.0$ (c 0.55, CHCl_3)]. HRMS (ESI): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{16}\text{NO}_3$ 222.1125, found 222.1117.

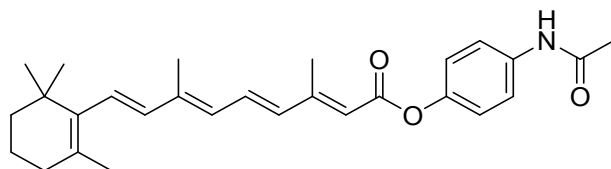
acetaminophen^[26]



Purified by column chromatography; R_f 0.3 (PE:EA = 1:3); Brown solid; Isolated

yield 96% (1.34 g); Mp 173-175 °C; ^1H NMR (400 MHz, $(\text{CD}_3)_2\text{CO}$) δ 8.95 (br s, 0.53H), 8.17 (br s, 0.45H), 7.45-7.43 (m, 2.00H), 6.77-6.73 (m, 2.00H), 2.02 (s, 3.00H); ^{13}C NMR (100 MHz, $(\text{CD}_3)_2\text{CO}$) δ 168.3, 154.2, 132.7, 121.7, 115.8, 24.0; IR (KBr) 3791, 3138, 2285, 1711, 1402, 1153, 1081, 969, 828, 723, 522 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_8\text{H}_9\text{NNaO}_2$ 174.0526, found 174.0527.

BMV 30123^[27]



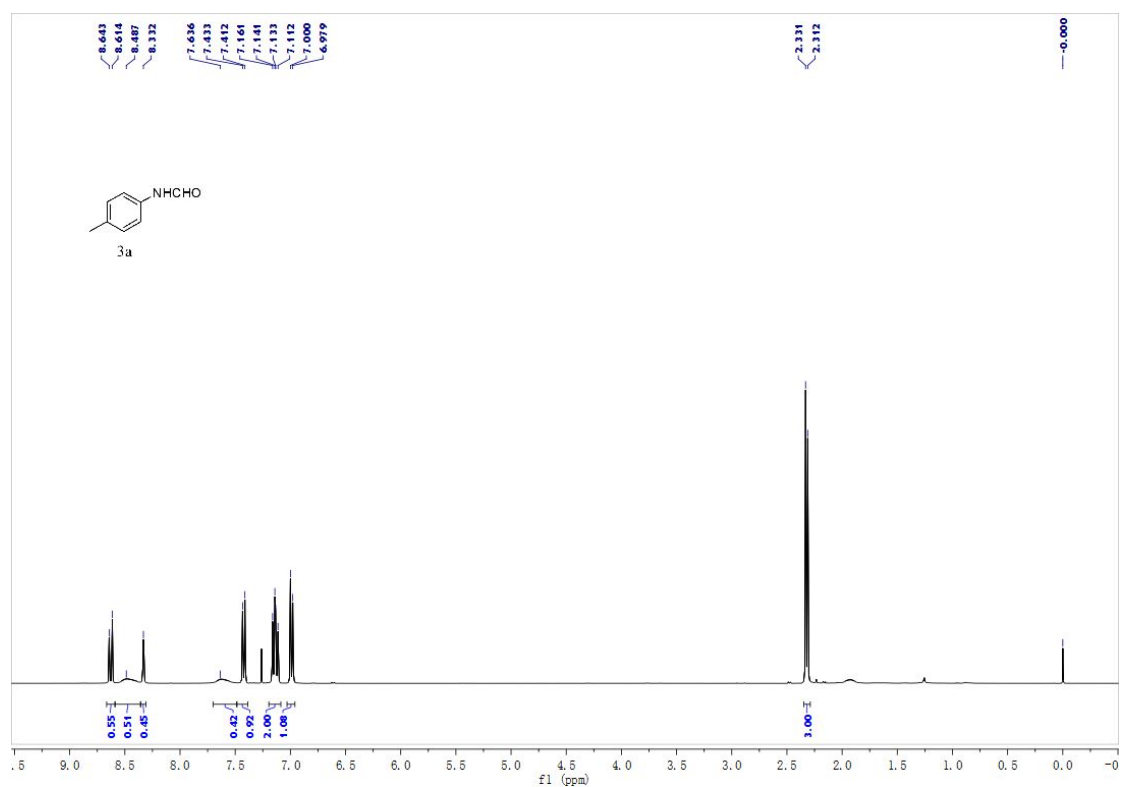
Purified by column chromatography; R_f 0.5 (PE:EA = 1:1); Yellow solid; Isolated yield 72% (0.312 g); Mp 185-187 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (br d, J = 11.6 Hz, 1.00H), 7.48 (d, J = 8.8 Hz, 2.00H), 7.12-7.03 (m, 3.00H), 6.39-6.30 (m, 2.00H), 6.20-6.14 (m, 2.00H), 5.98 (s, 1.00H), 2.41 (s, 3.00H), 2.14 (s, 3.00H), 2.03 (s, 5.00H), 1.73 (s, 3.00H), 1.64-1.61 (m, 2.00H), 1.49-1.46 (m, 2.00H), 1.04 (s, 6.00H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.6, 165.8, 157.0, 155.7, 146.8, 140.5, 137.6, 137.1, 135.5, 134.6, 132.1, 130.2, 129.3, 129.2, 122.0, 120.9, 117.0, 49.1, 39.6, 34.2, 33.9, 33.1, 28.9, 25.5, 24.9, 24.3, 21.7, 19.2, 14.1, 12.9; IR (KBr) 3138, 2259, 1662, 1505, 1402, 1260, 1122, 1029, 753, 529 cm^{-1} ; HRMS (ESI): m/z $[\text{M}+\text{HCO}_2\text{H}-\text{H}]^-$ calcd for $\text{C}_{29}\text{H}_{36}\text{NO}_5$ 478.2599, found 478.2593.

5. References

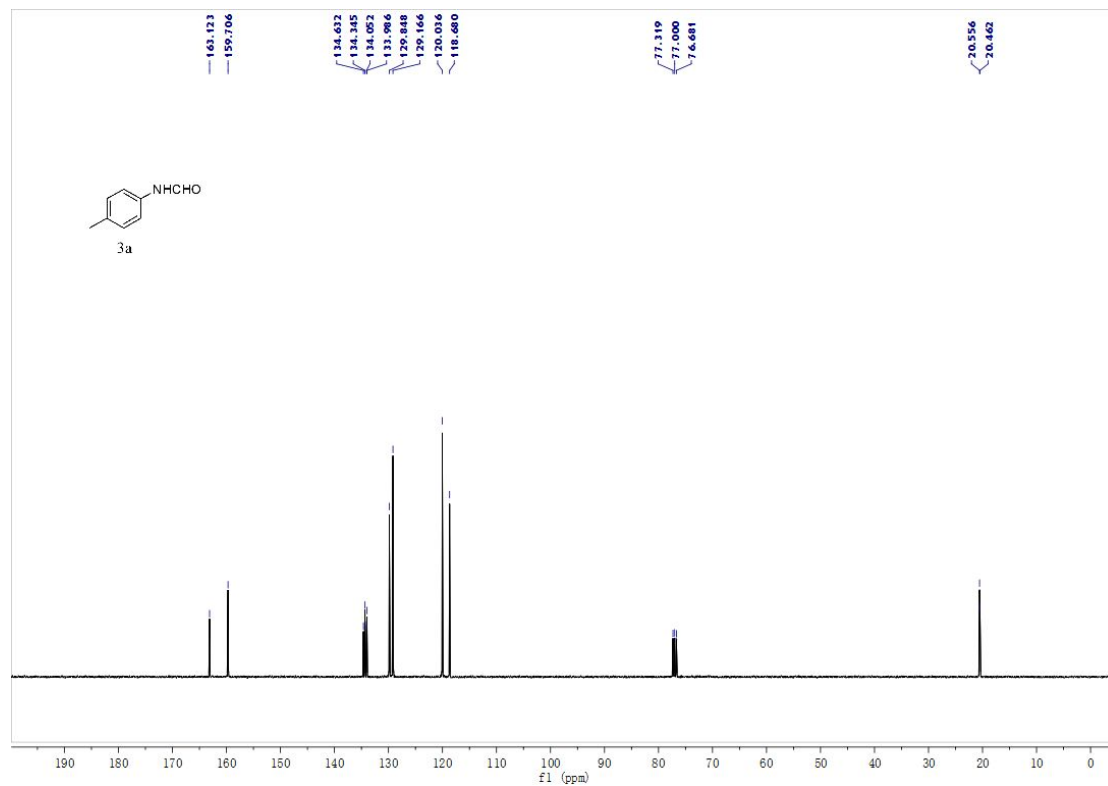
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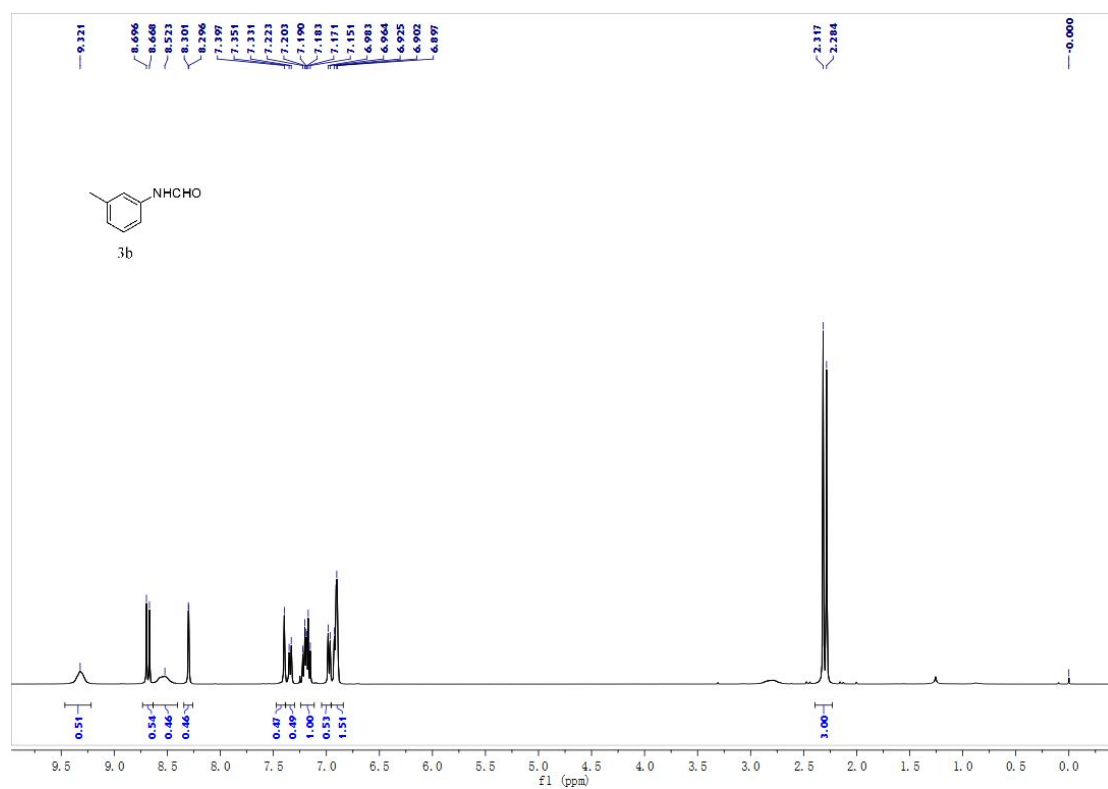
6. Copies of ^1H , ^{13}C and ^{19}F NMR spectra



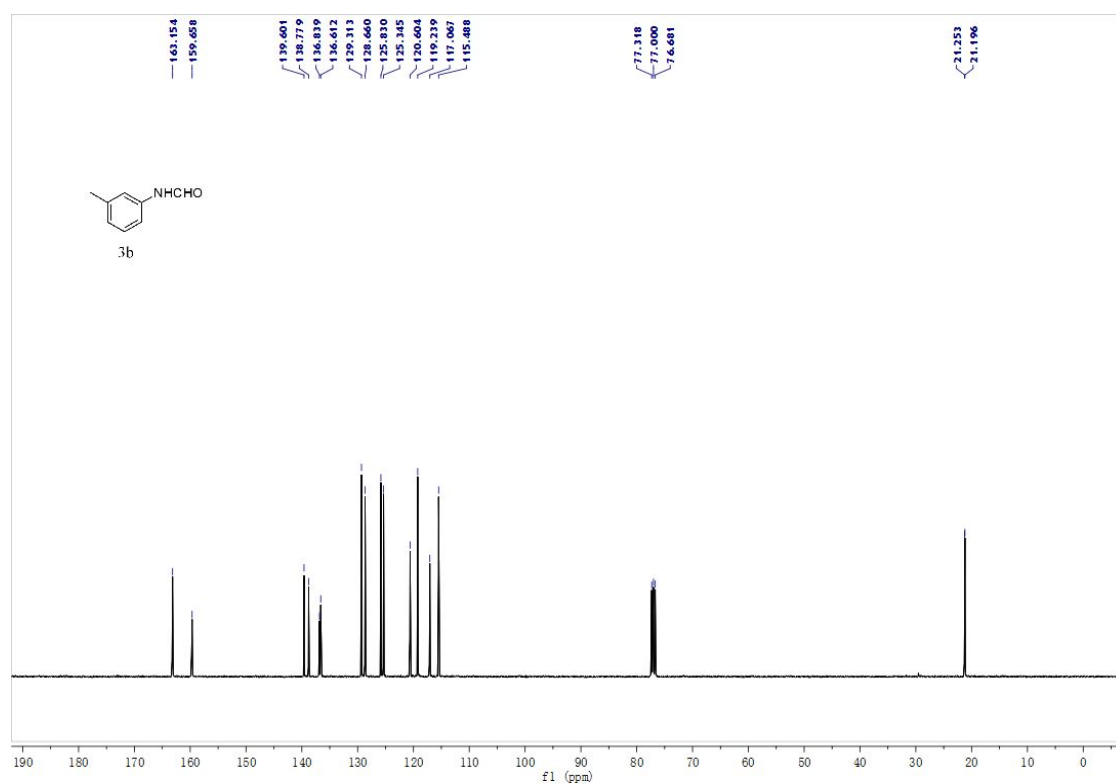
^1H NMR spectra of **3a**



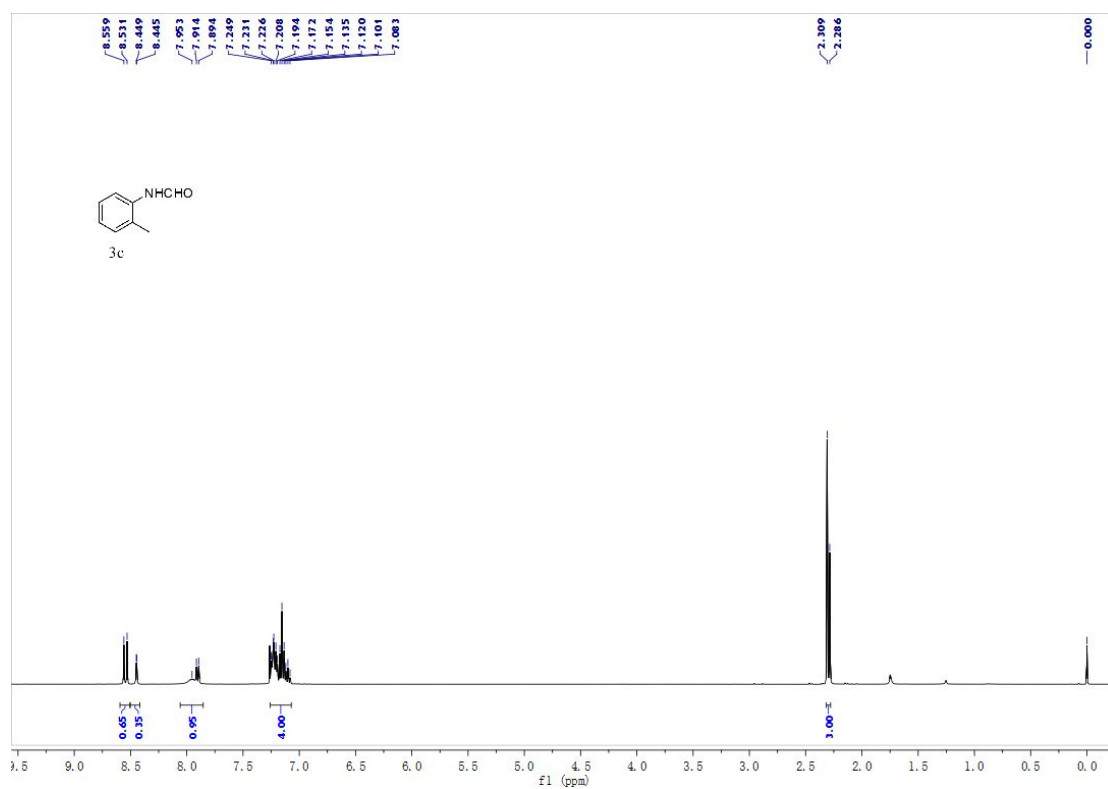
^{13}C NMR spectra of **3a**



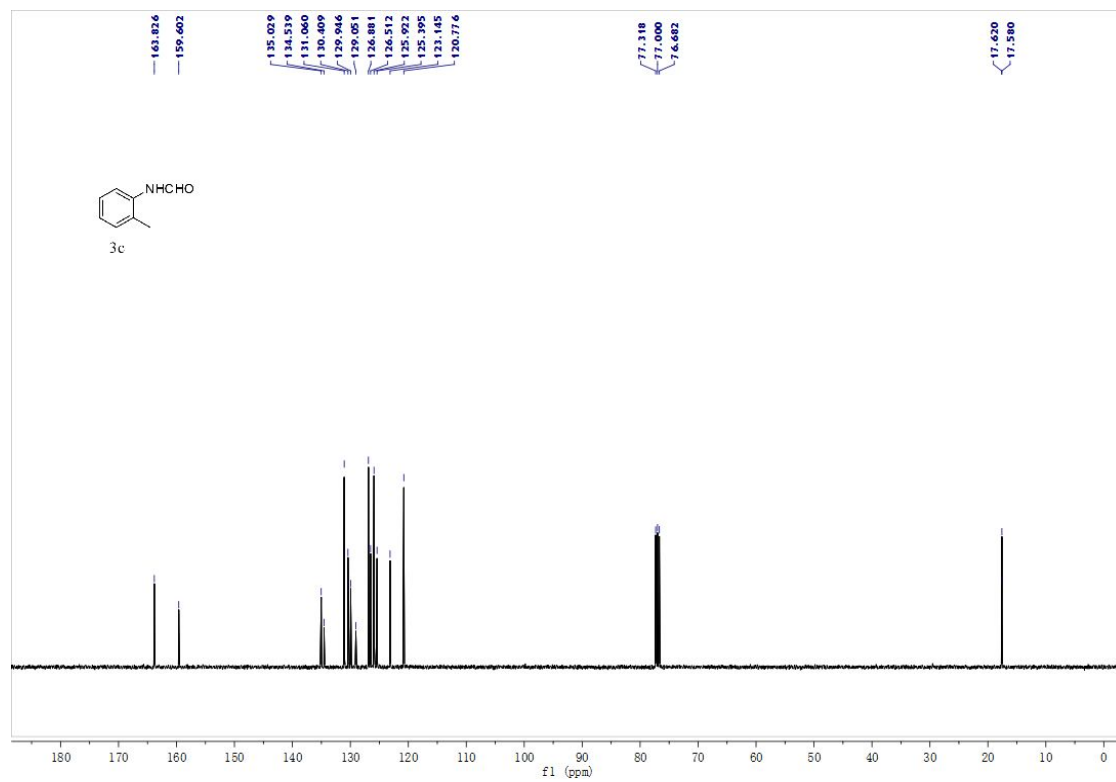
¹H NMR spectra of **3b**



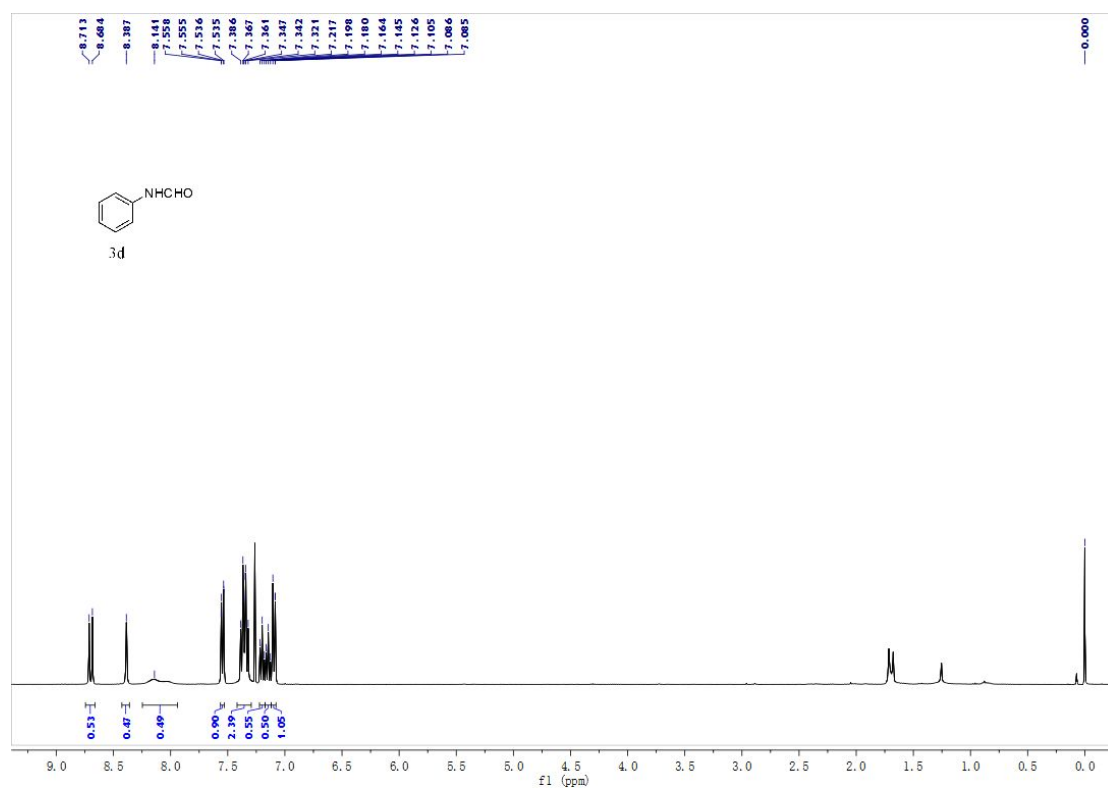
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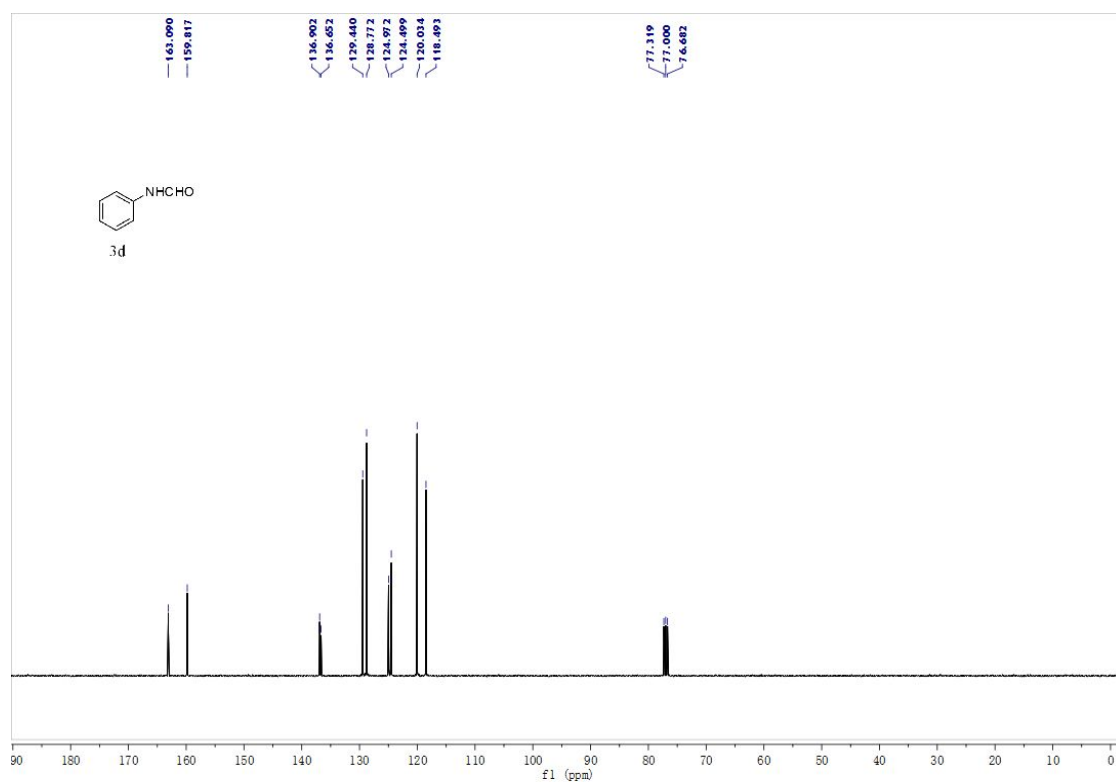
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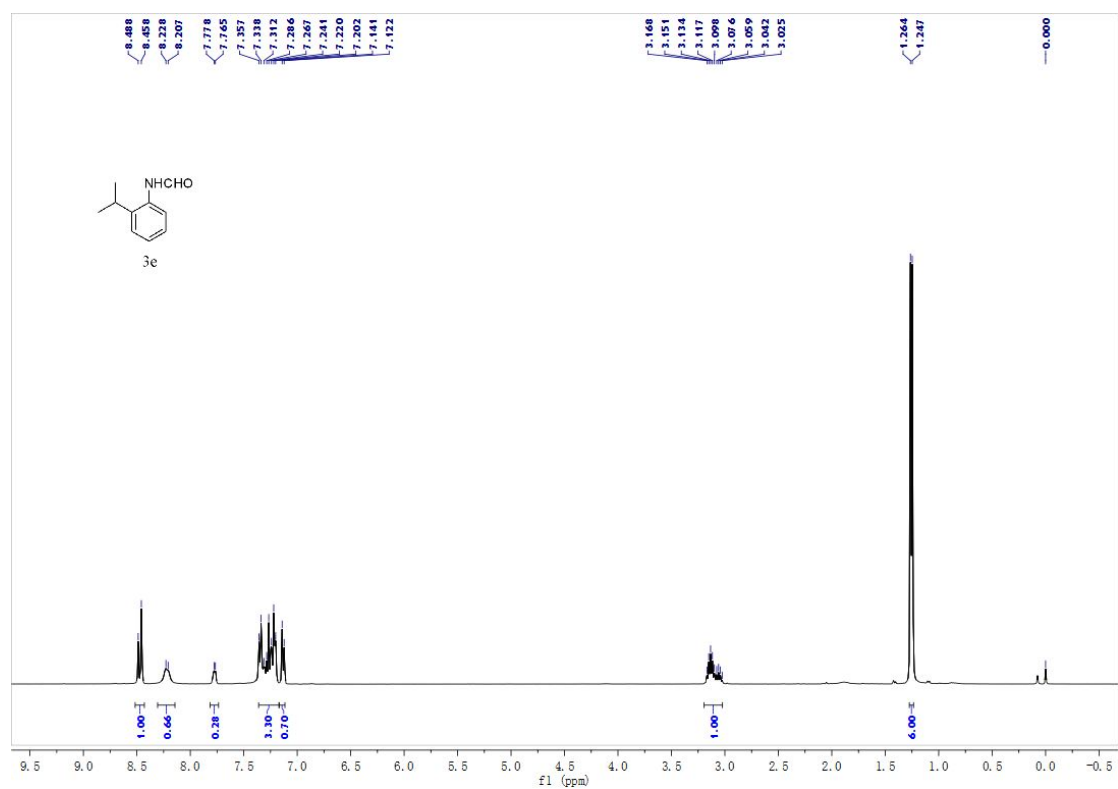
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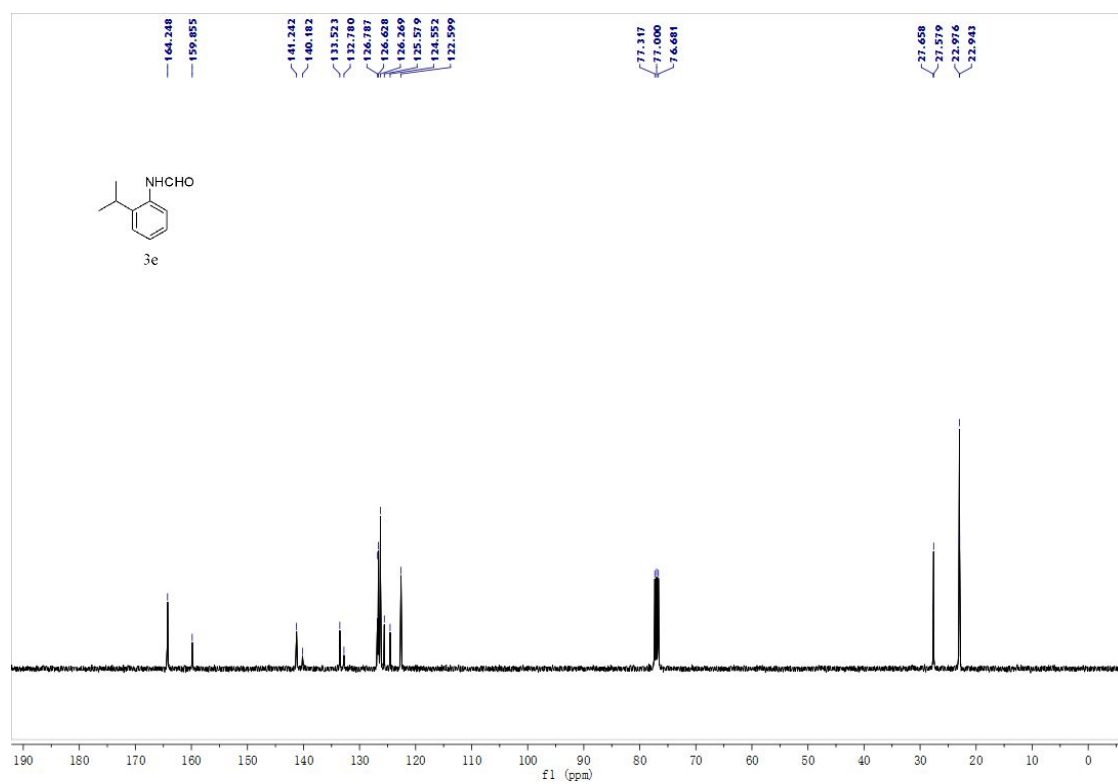
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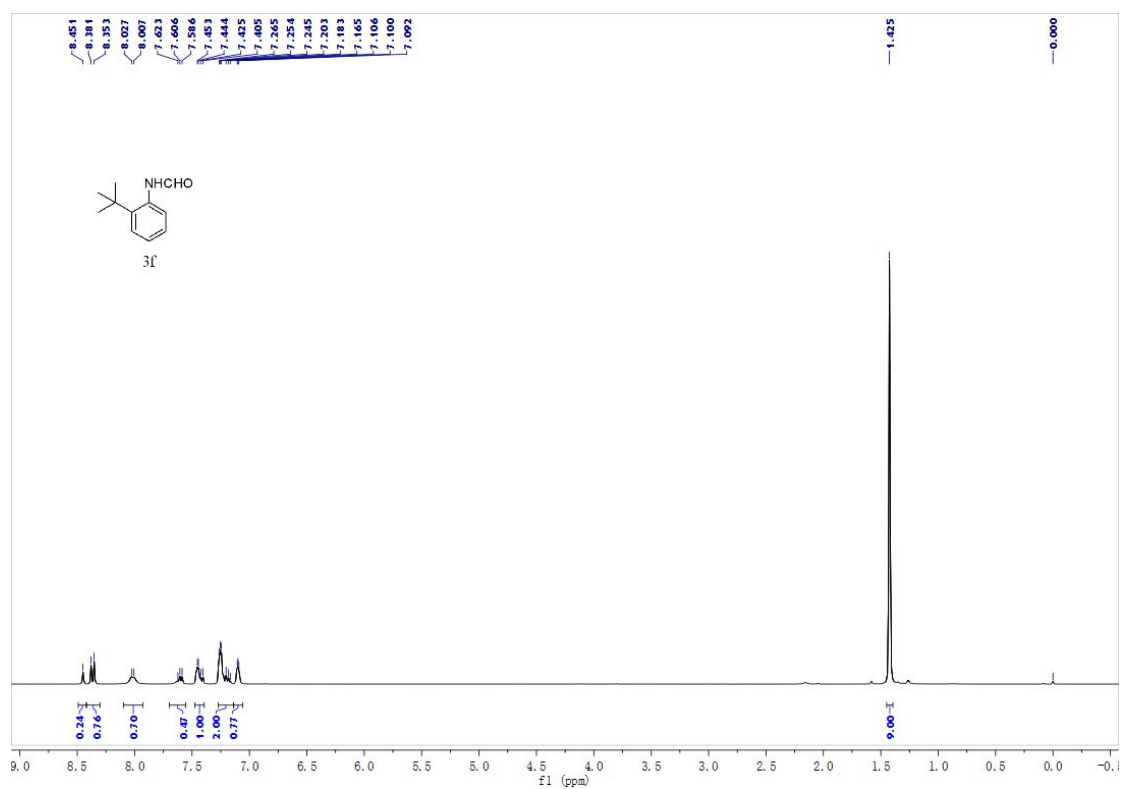
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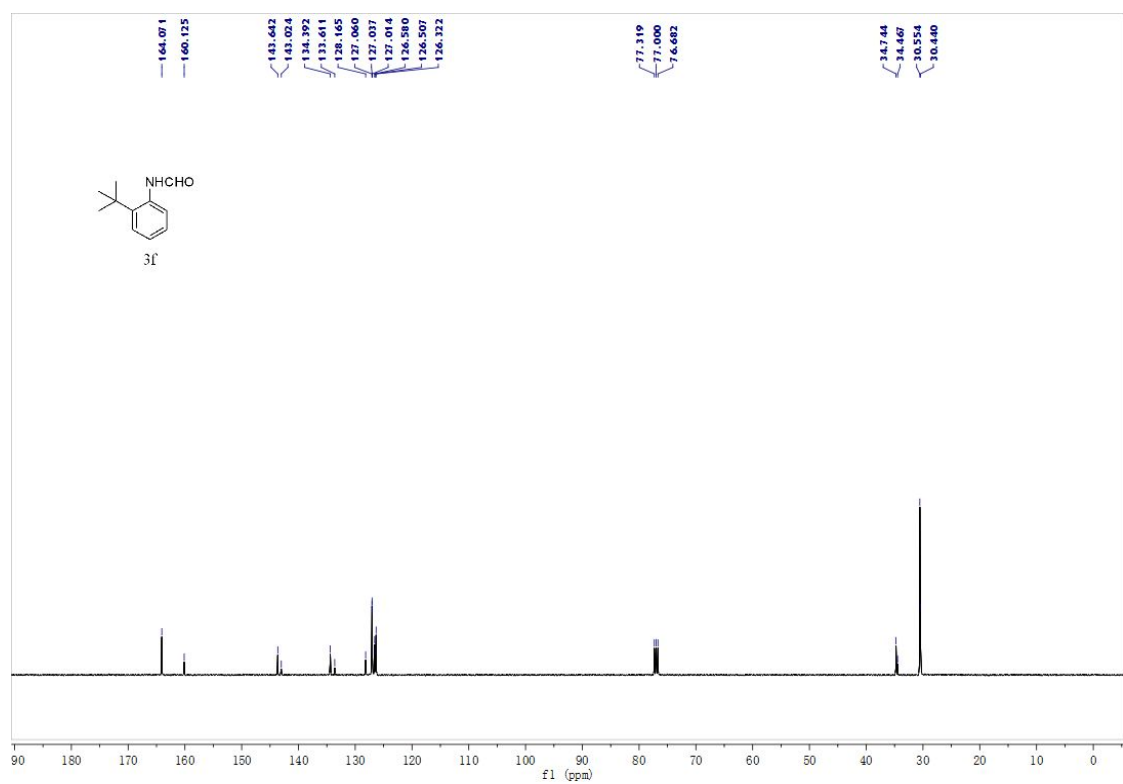
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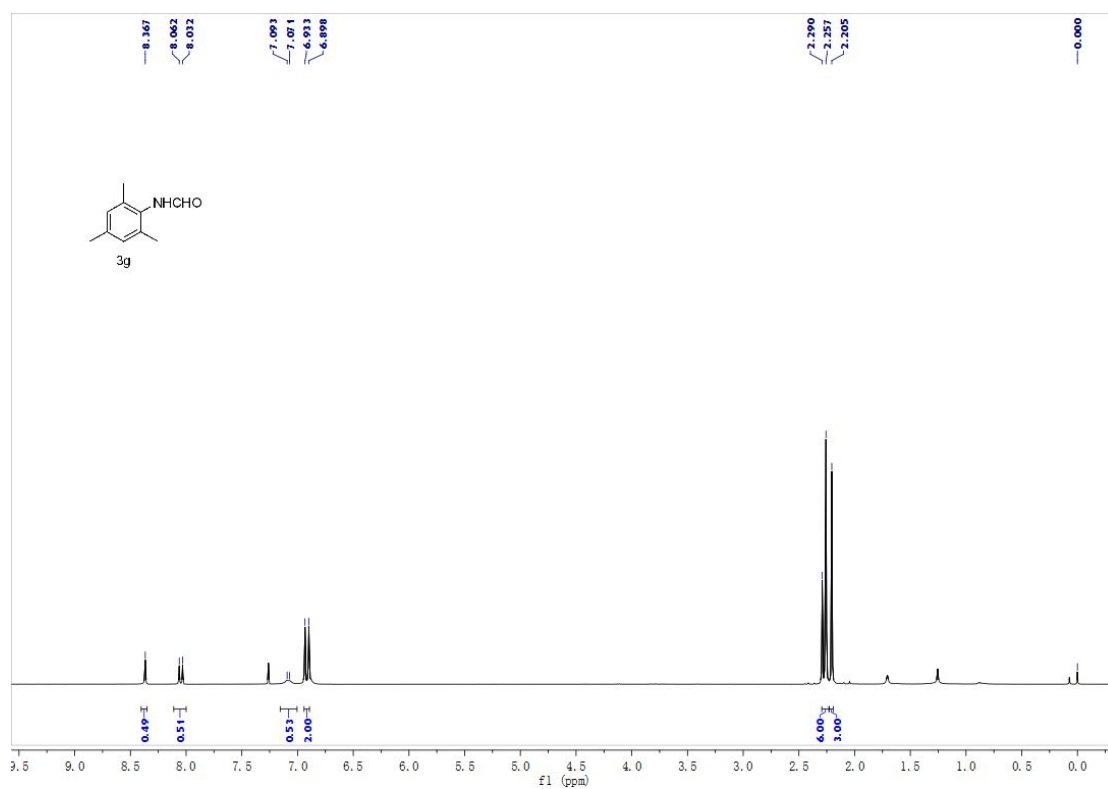
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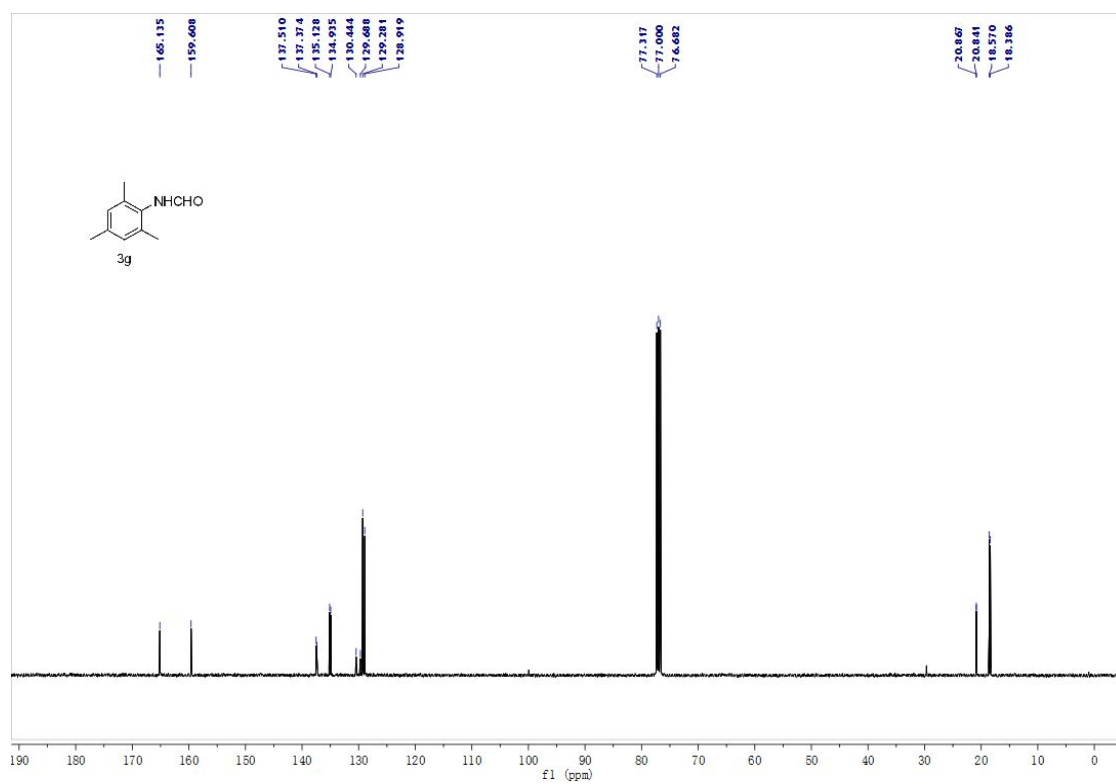
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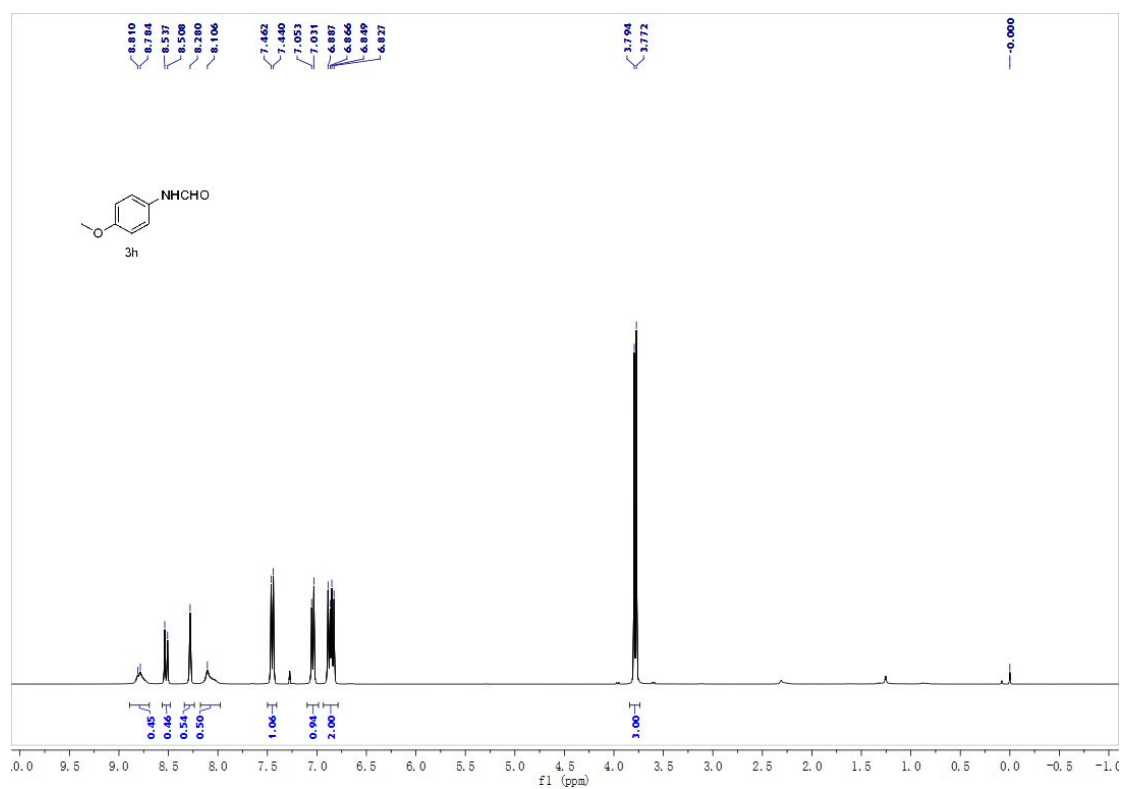
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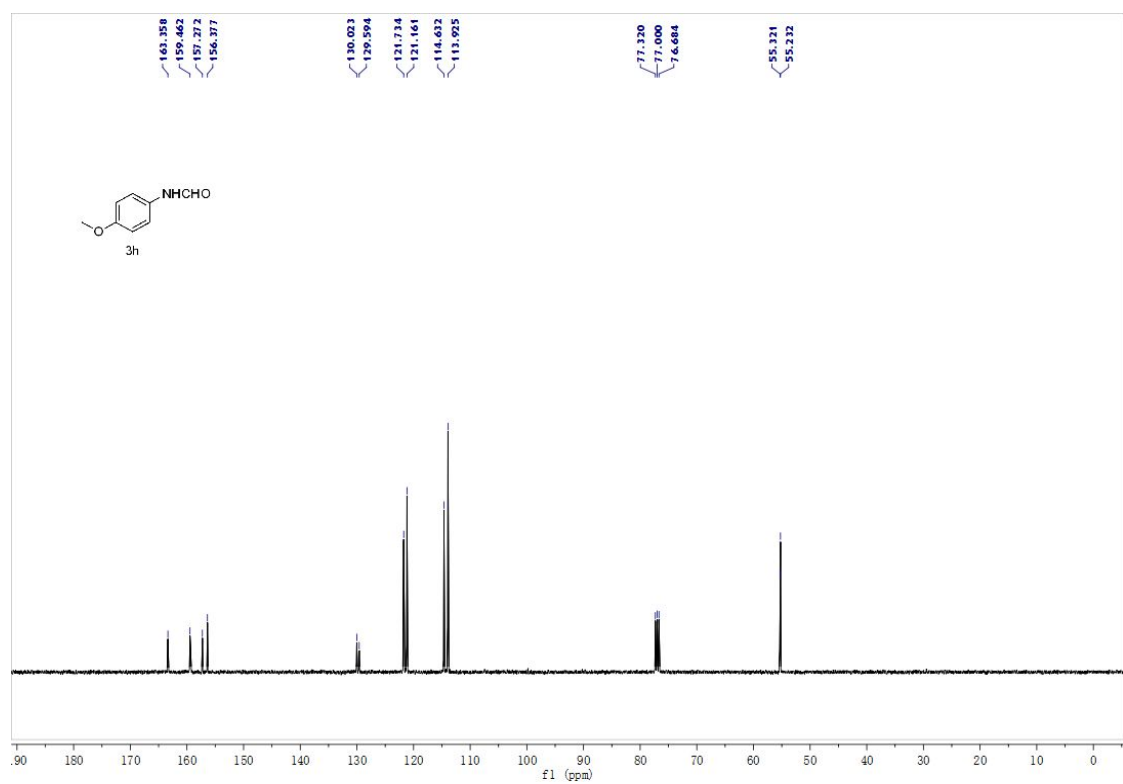
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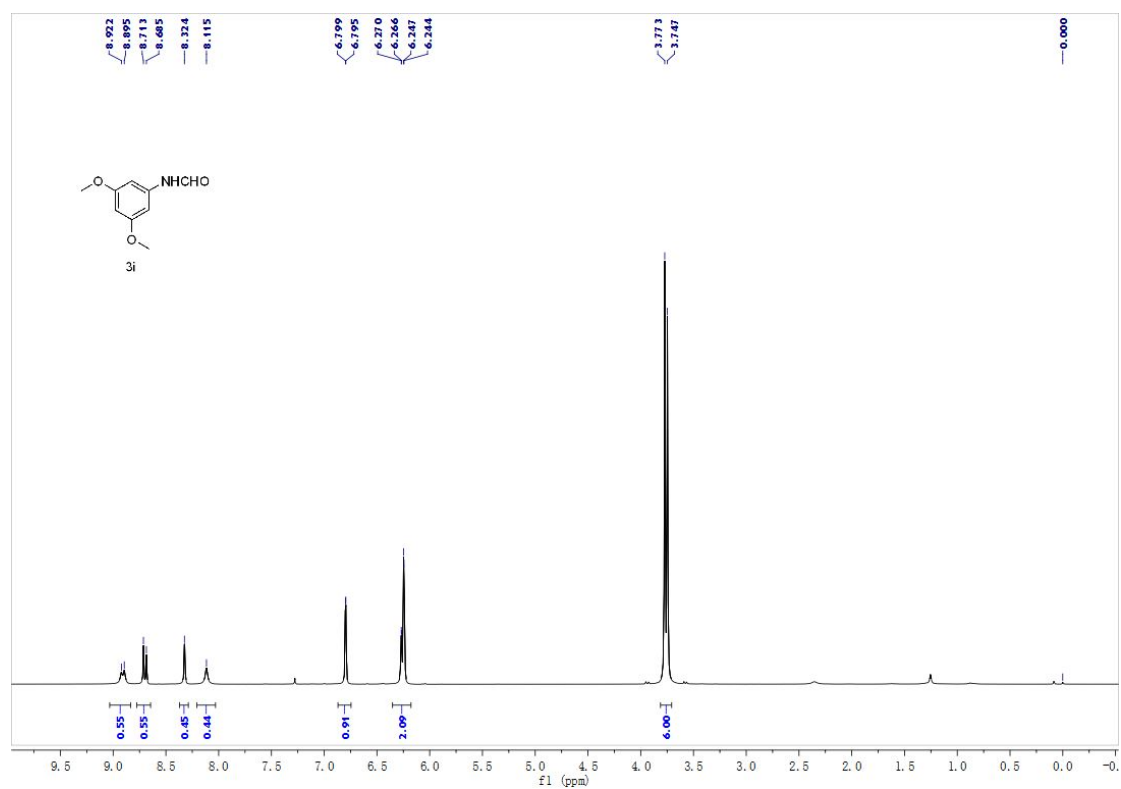
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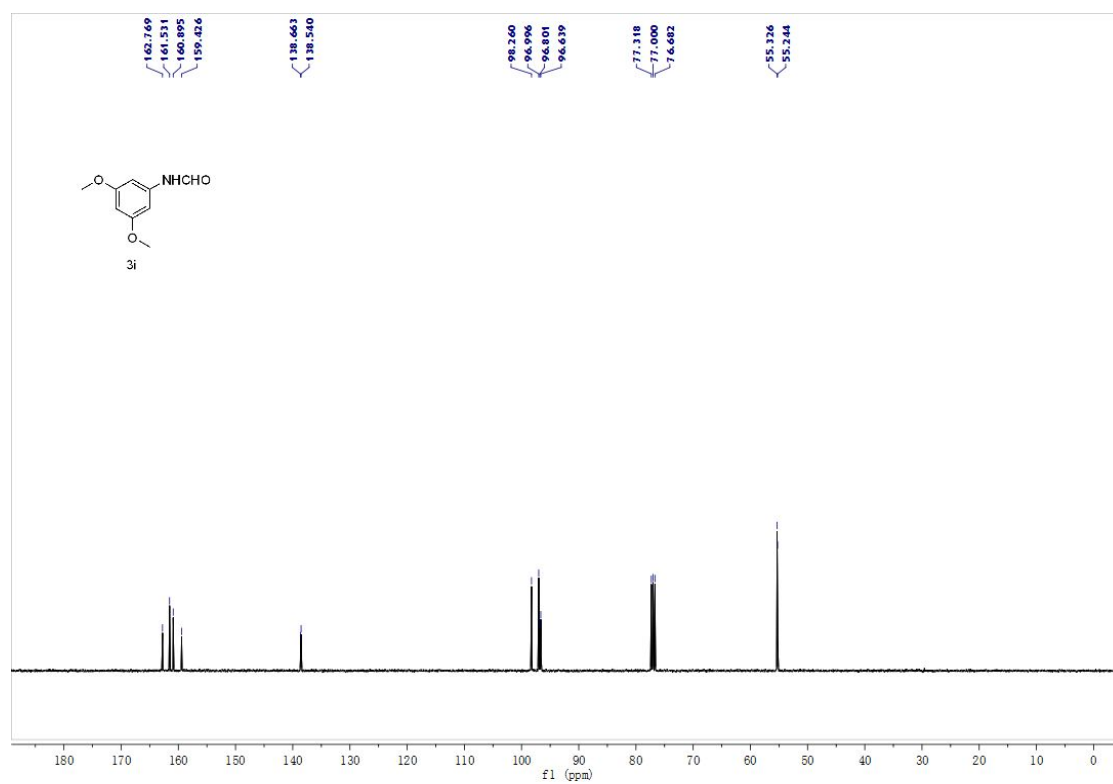
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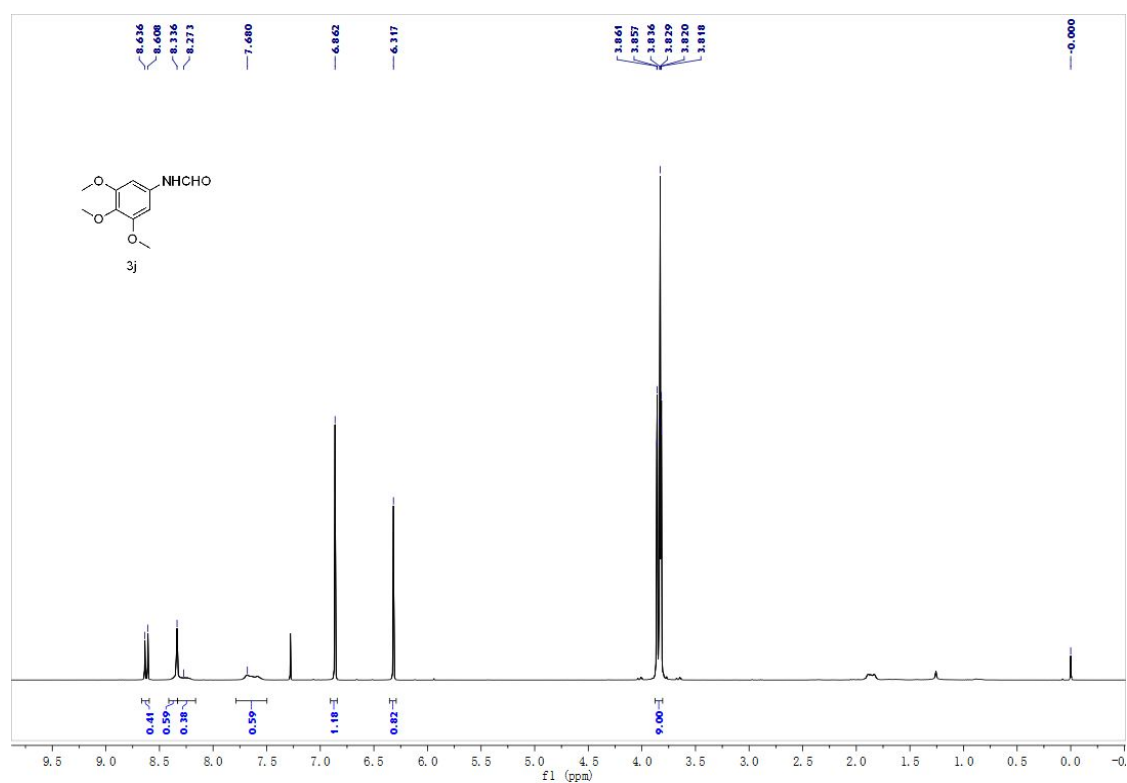
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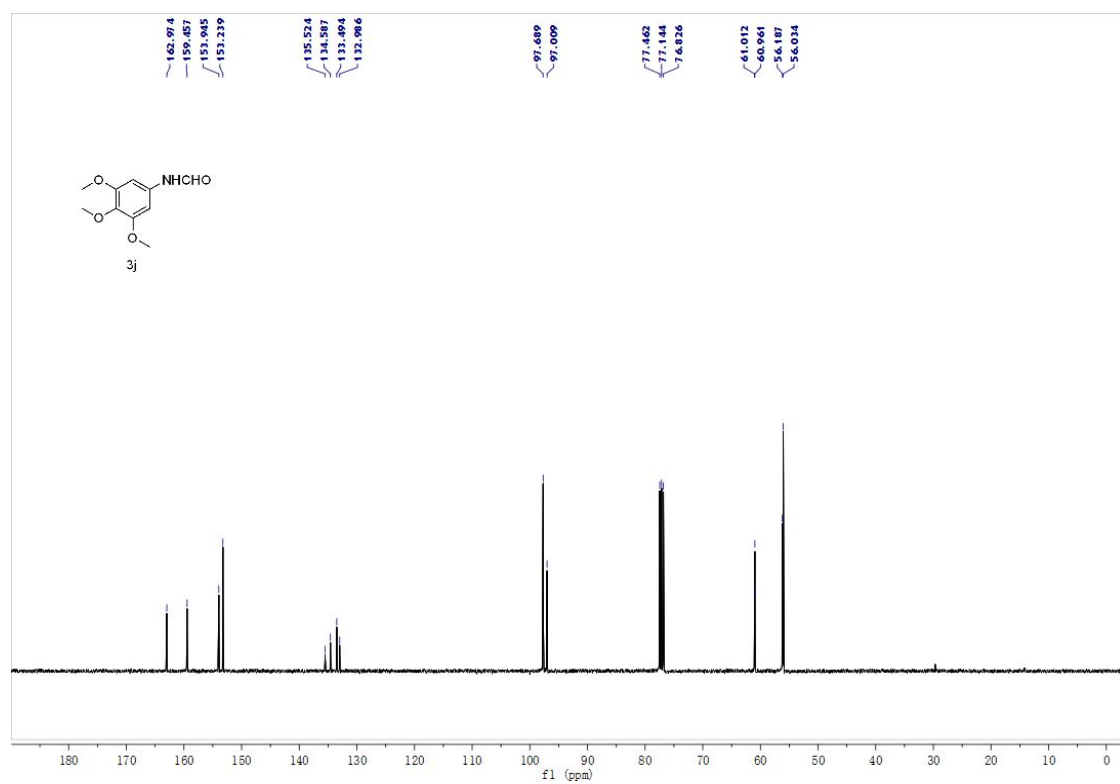
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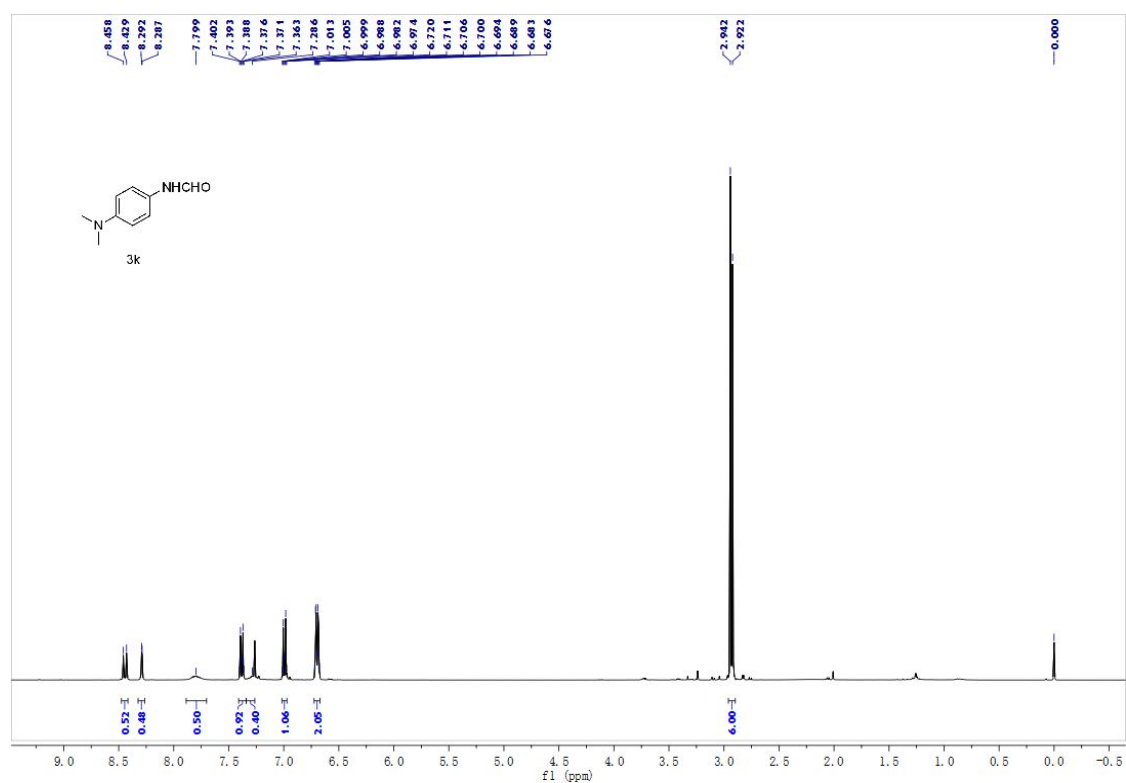
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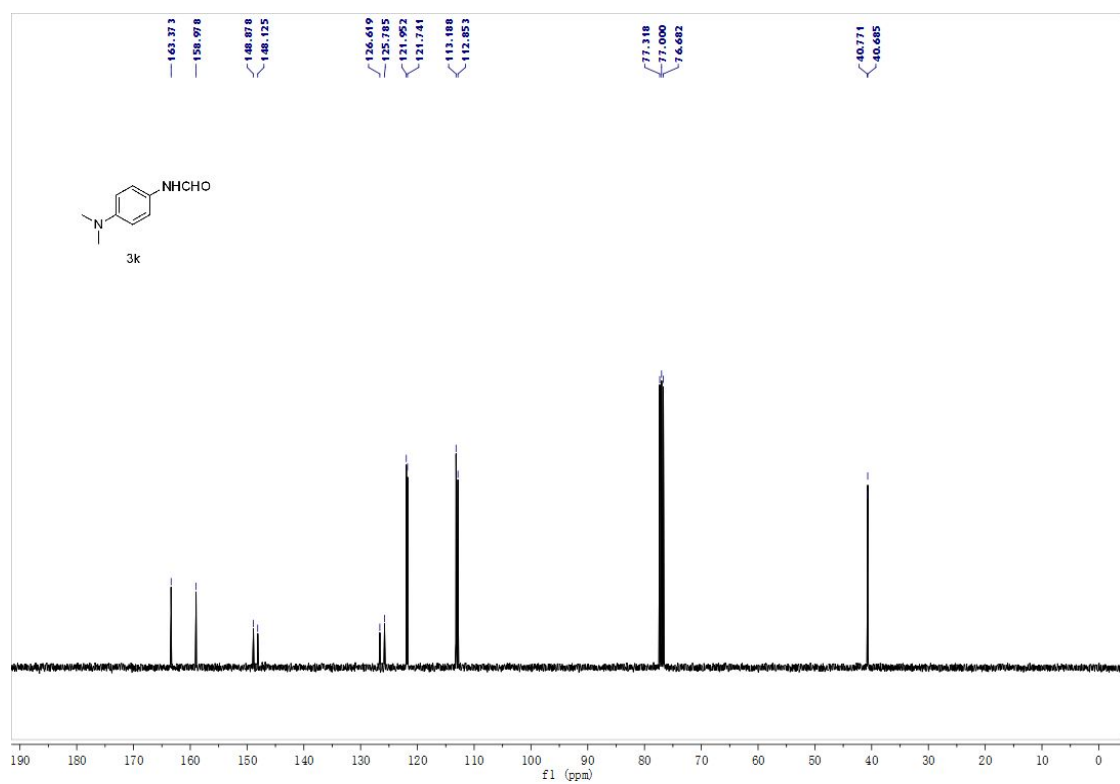
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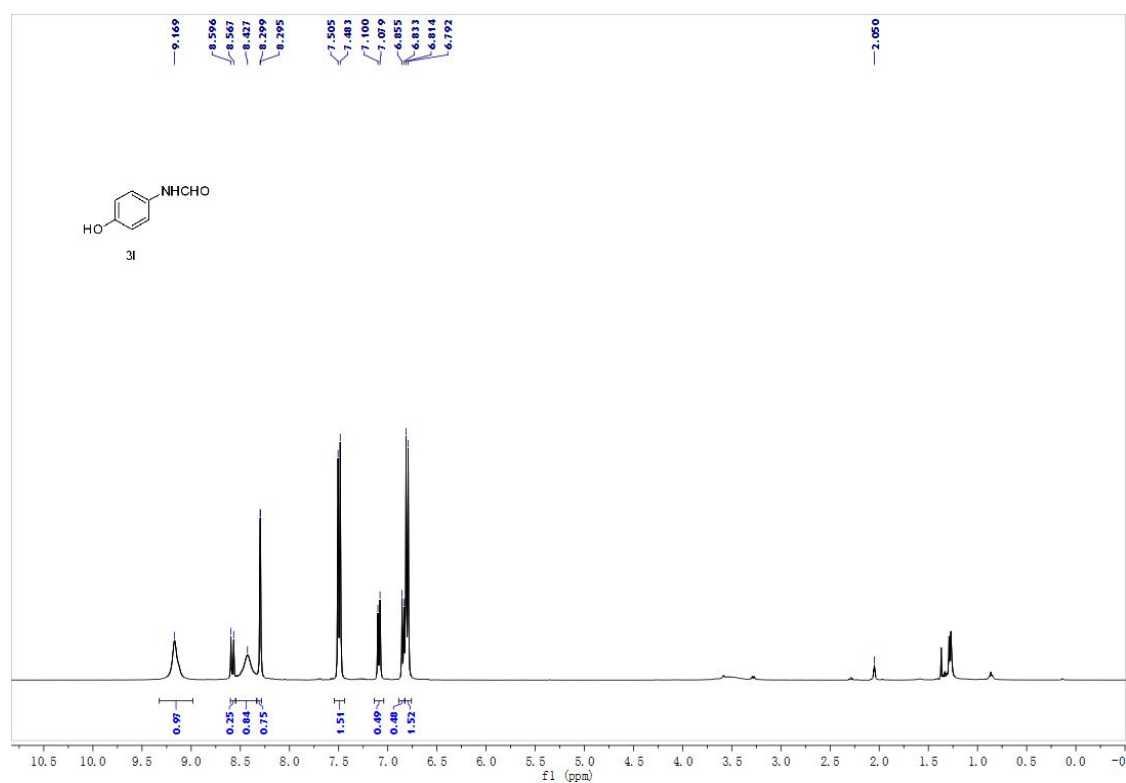
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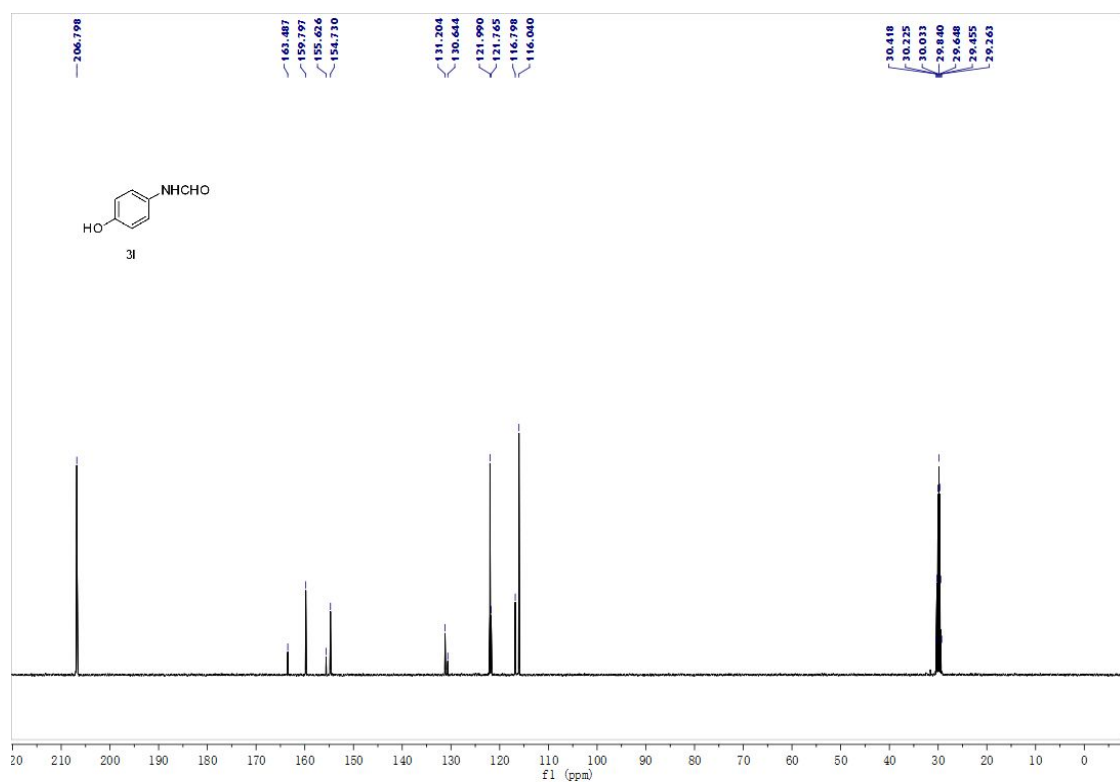
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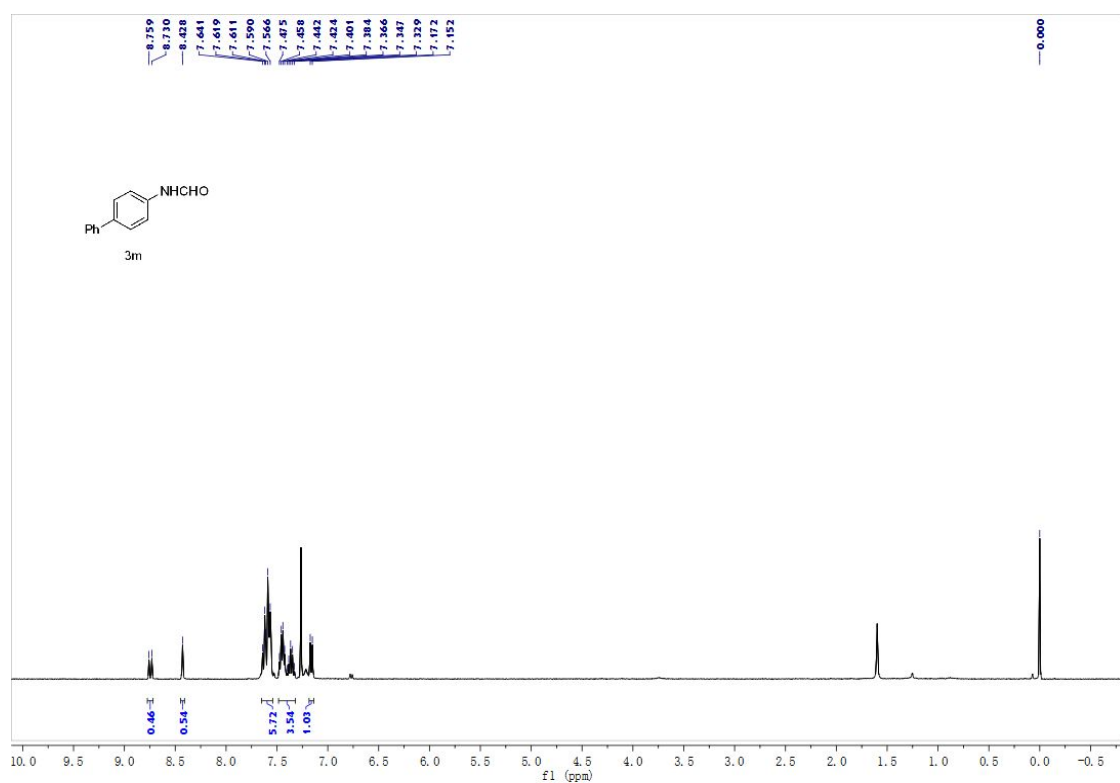
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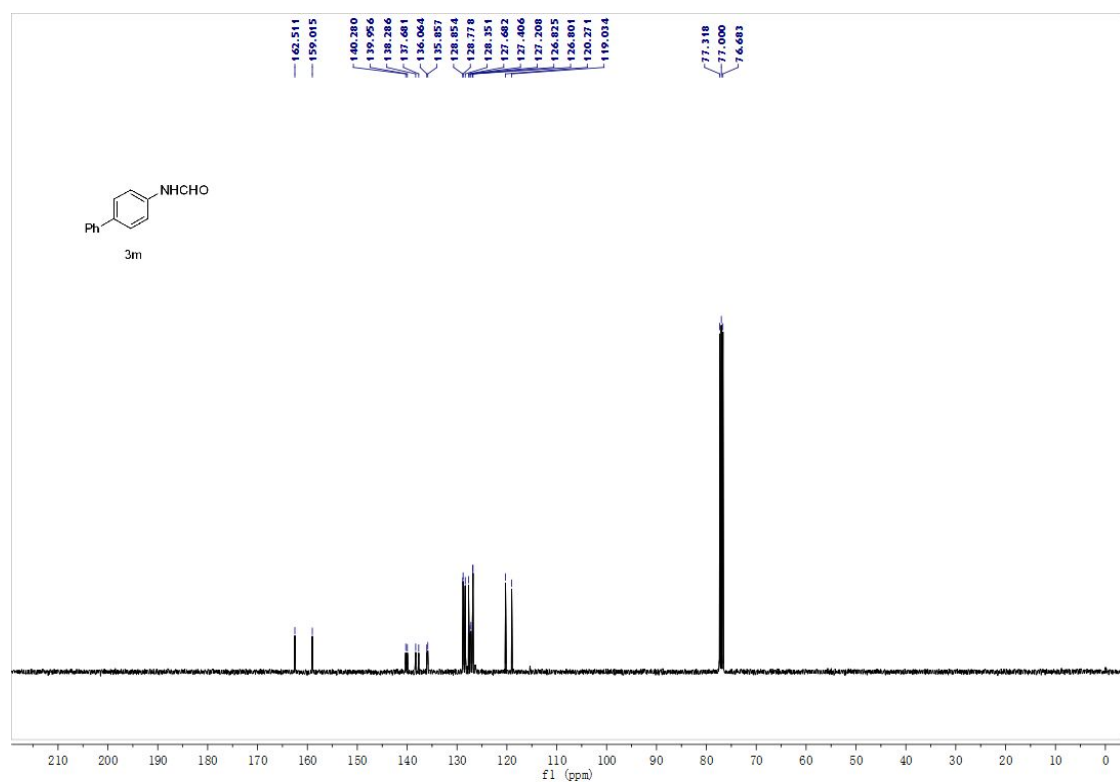
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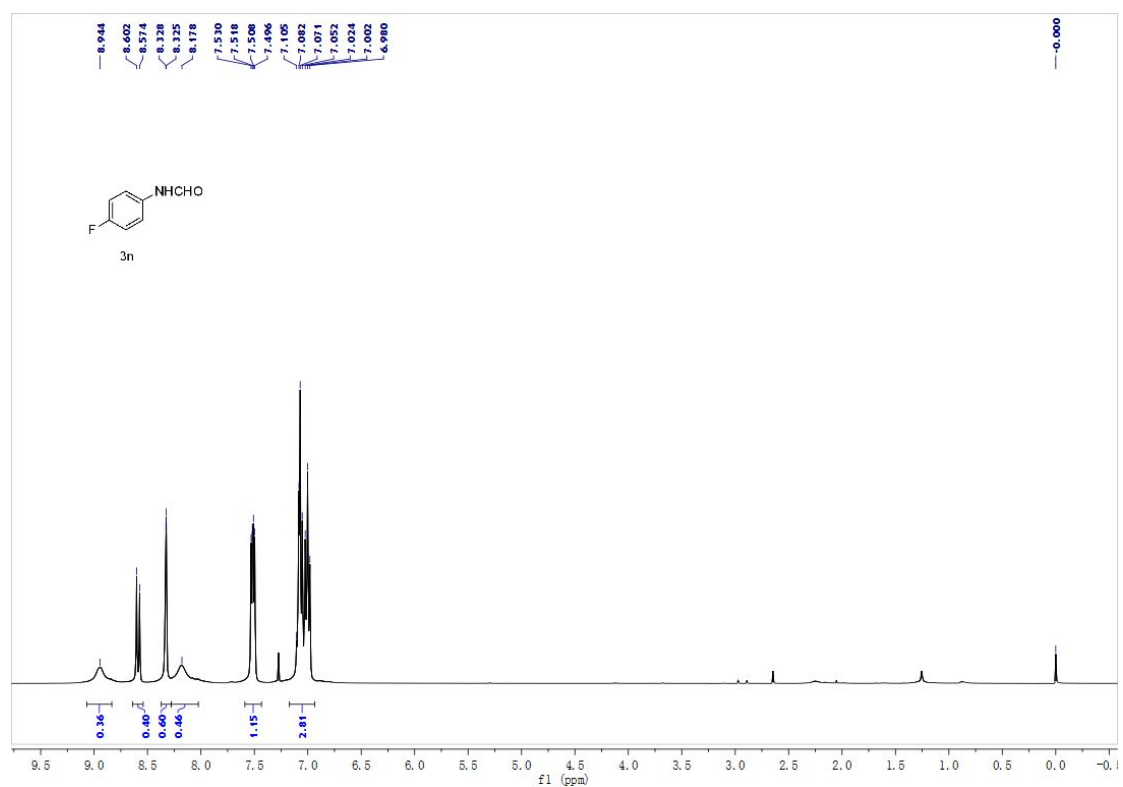
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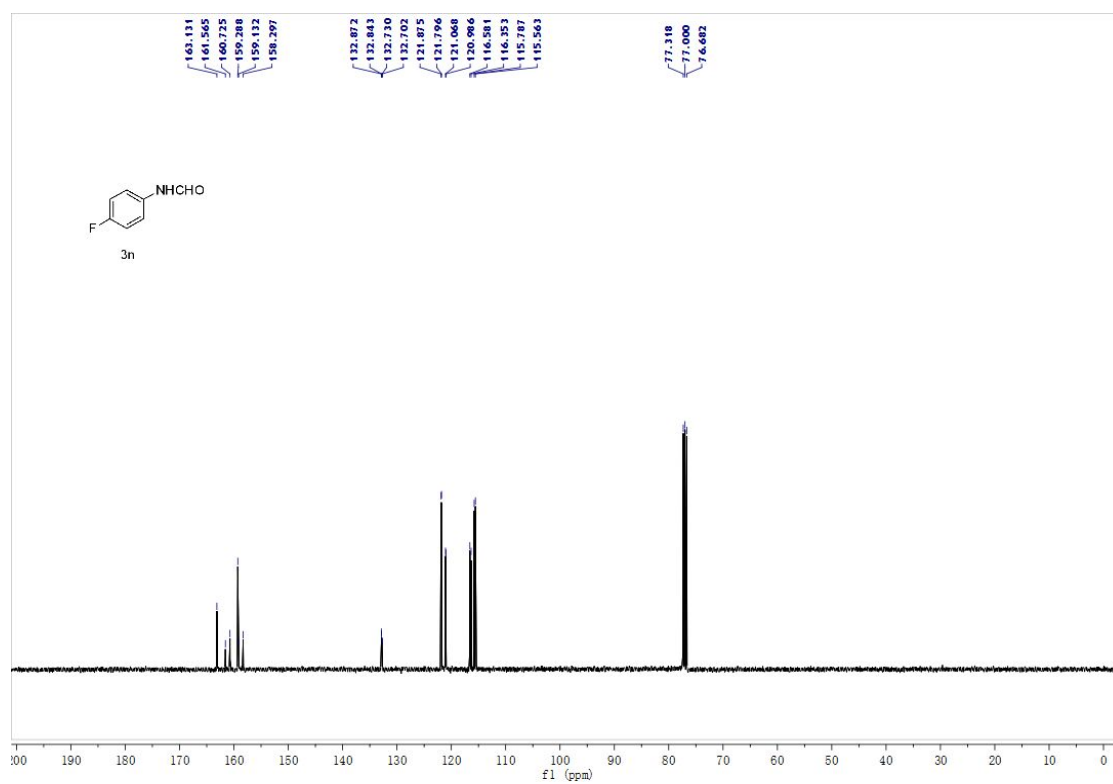
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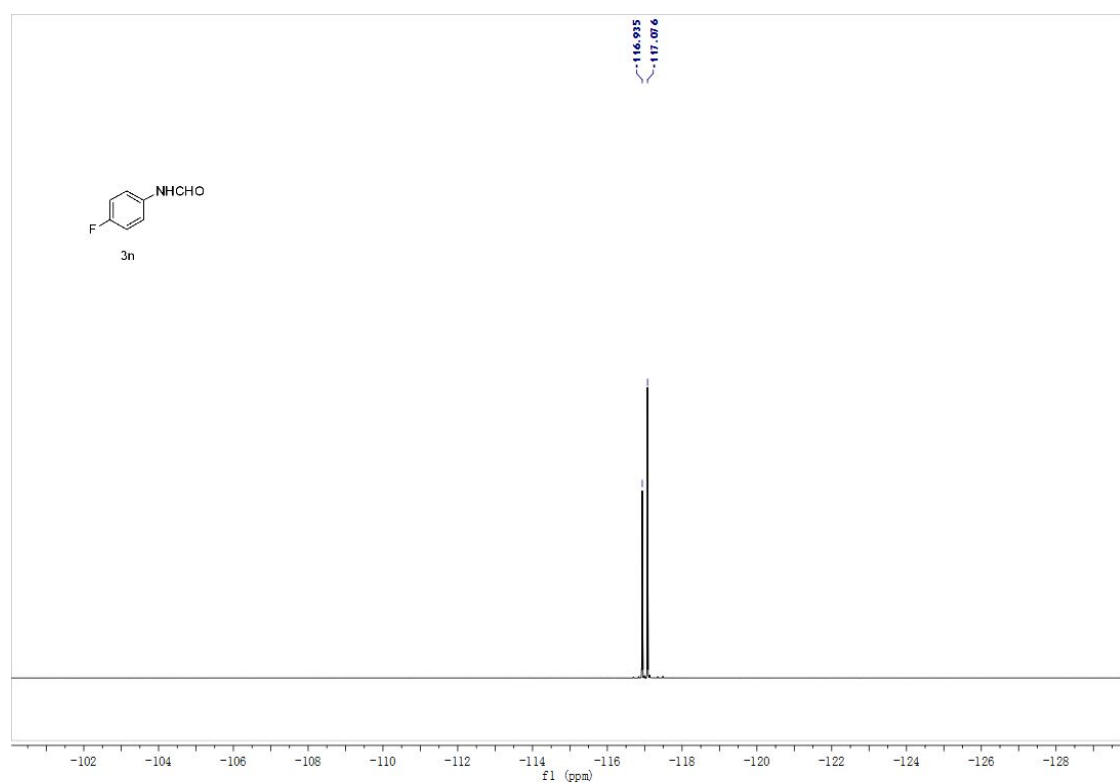
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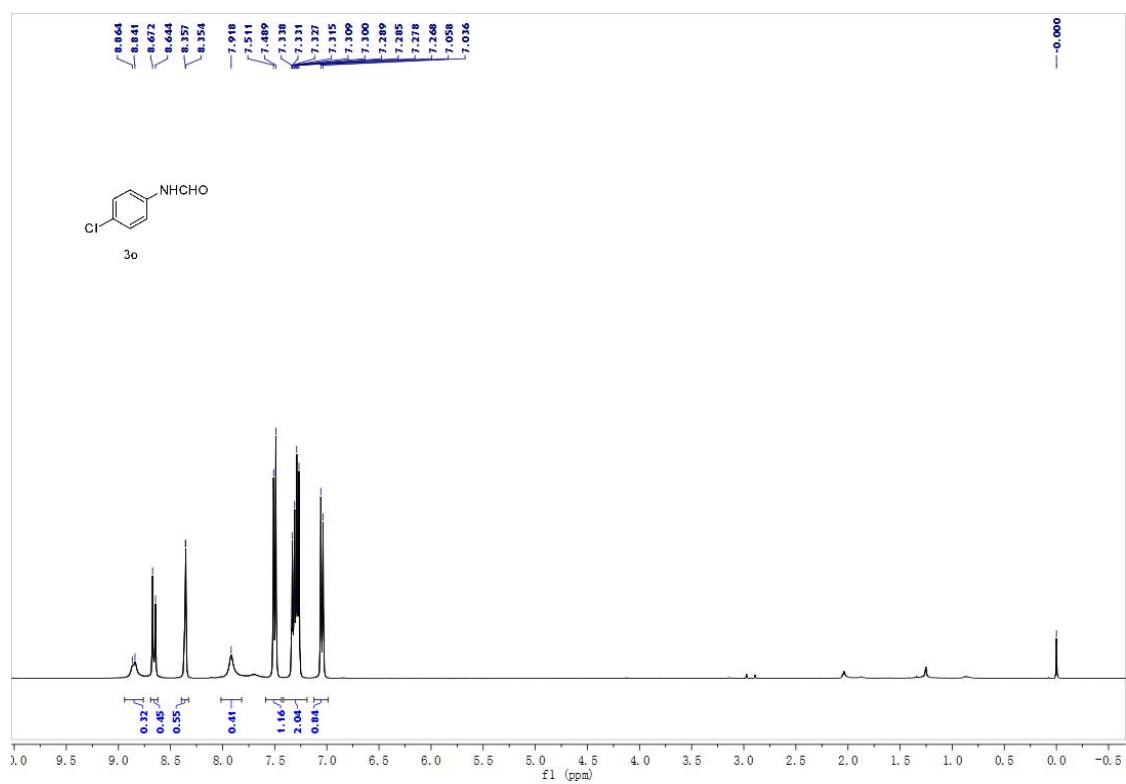
¹H NMR spectra of **3n**



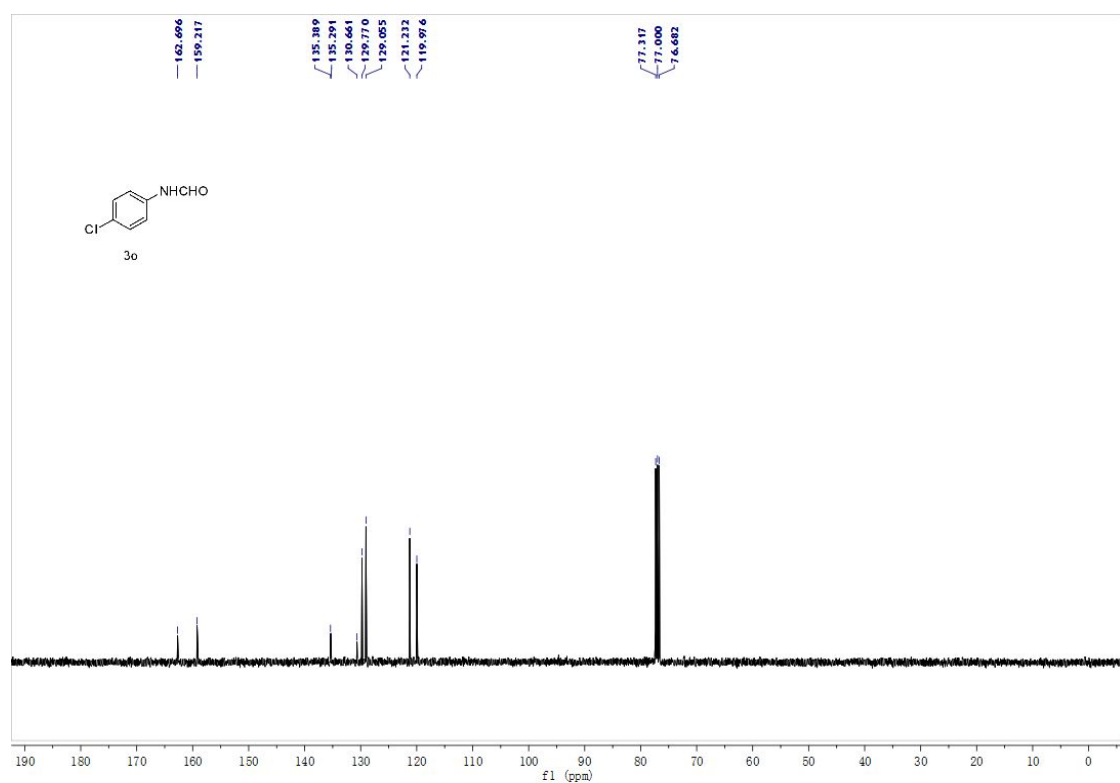
¹³C NMR spectra of **3n**



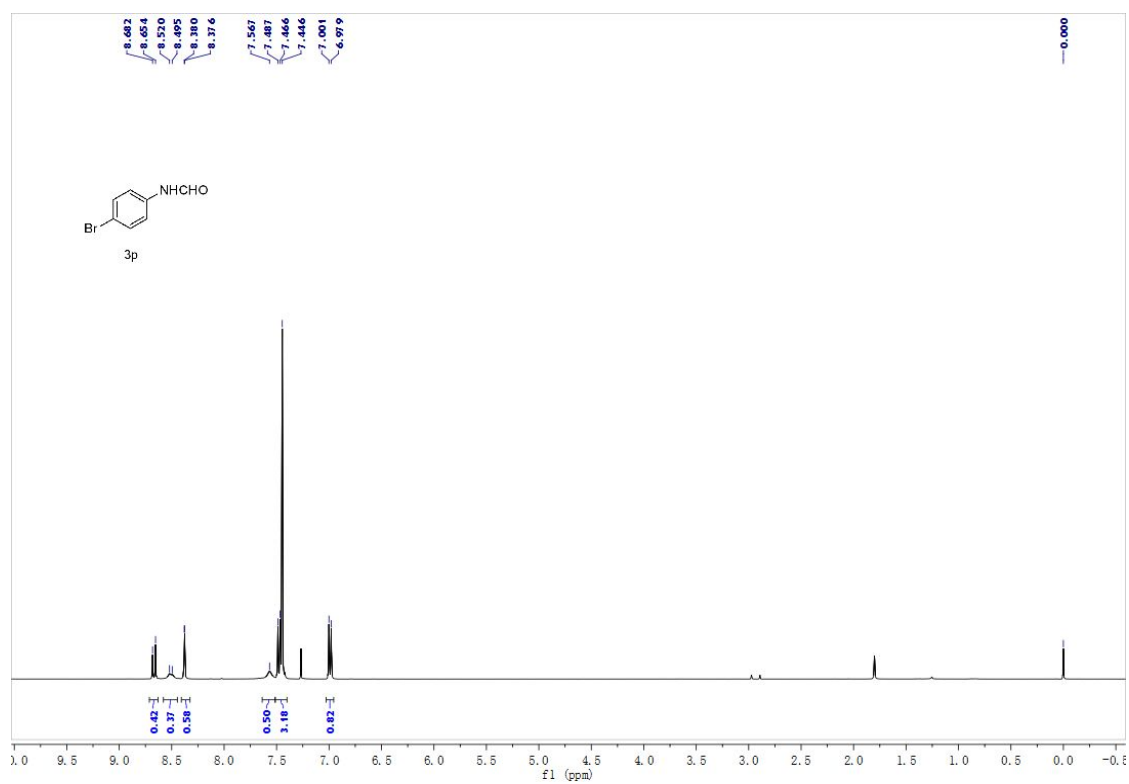
^{19}F NMR spectra of **3n**



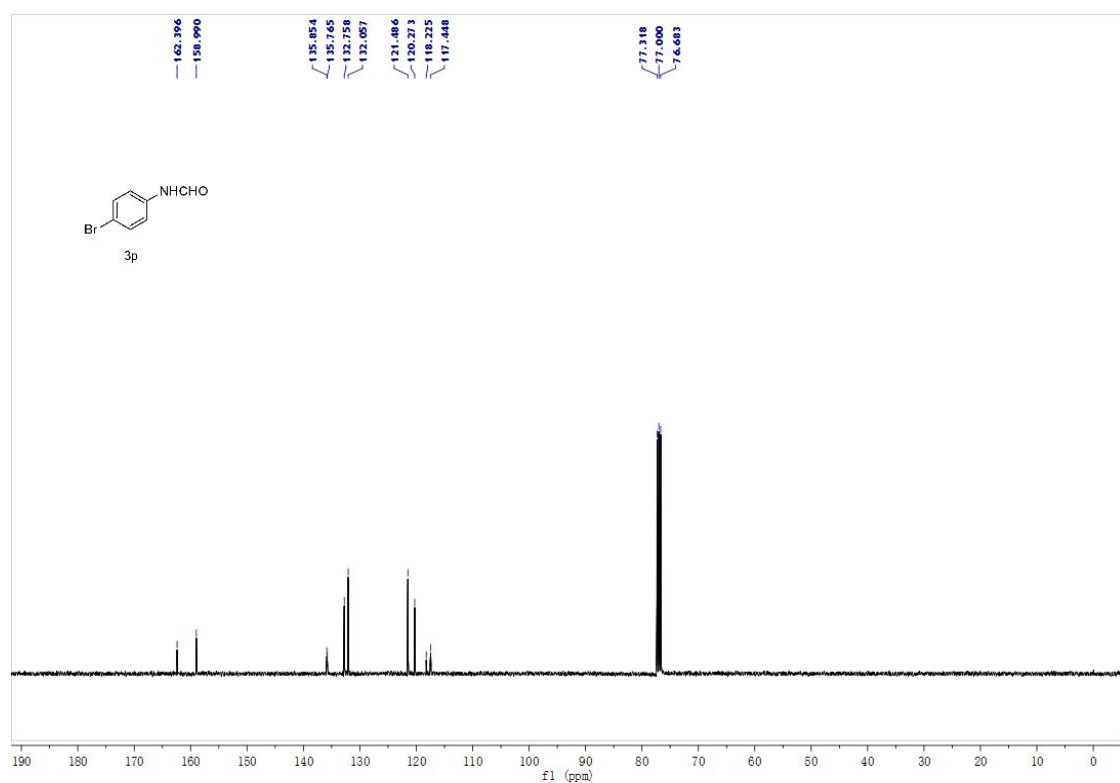
^1H NMR spectra of **3o**



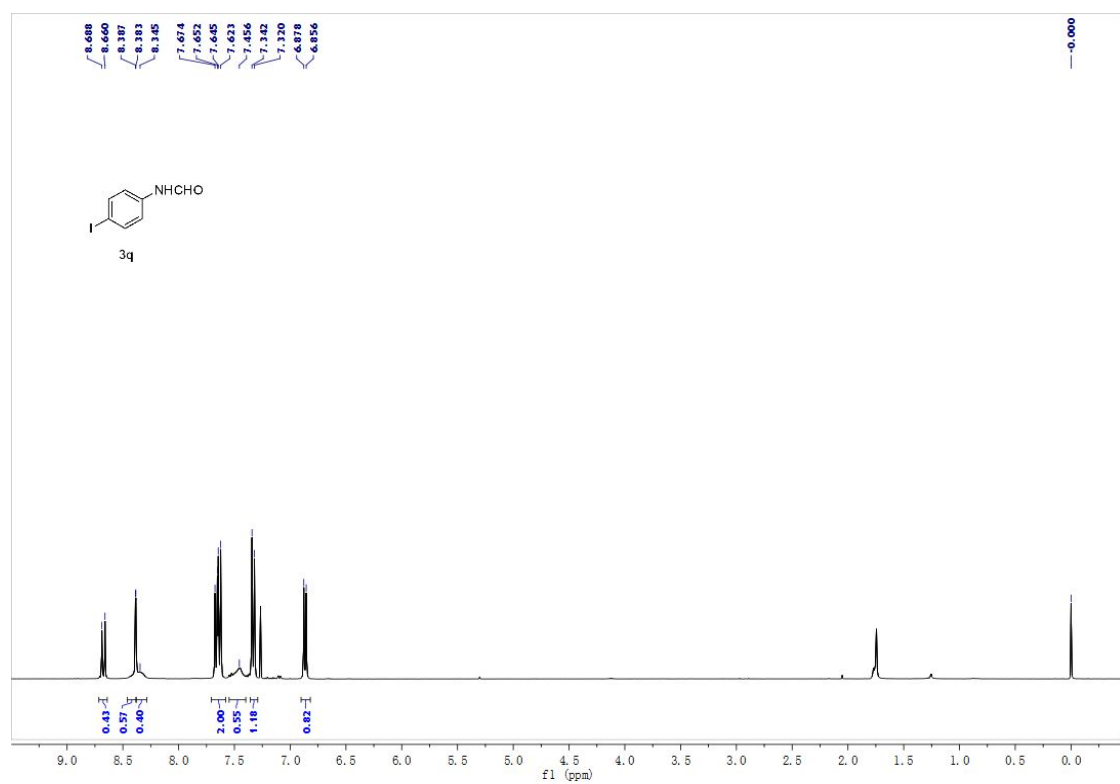
¹³C NMR spectra of **3o**



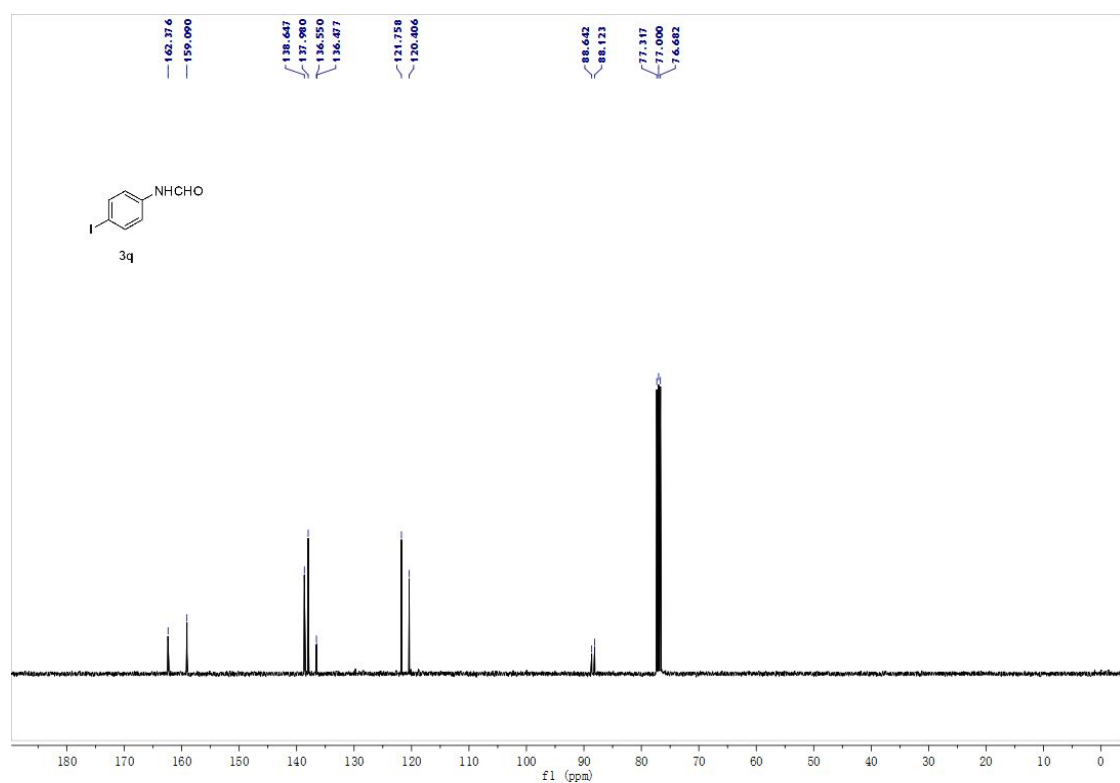
¹H NMR spectra of **3p**



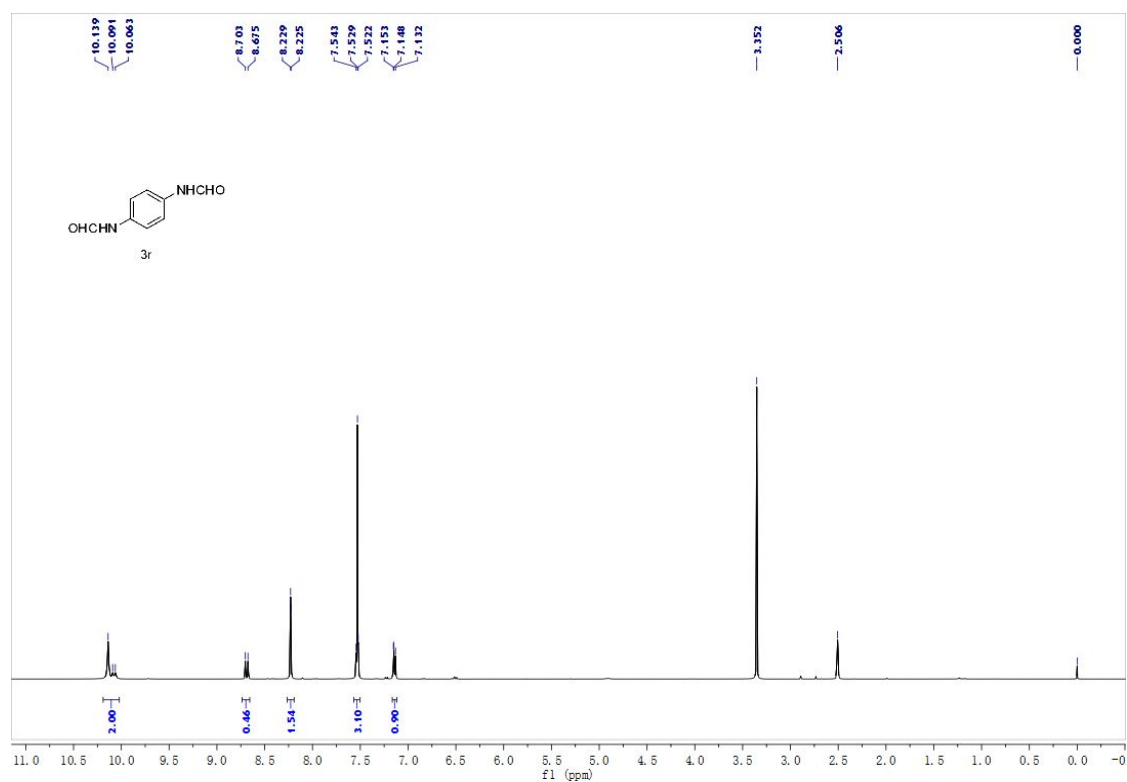
¹³C NMR spectra of **3p**



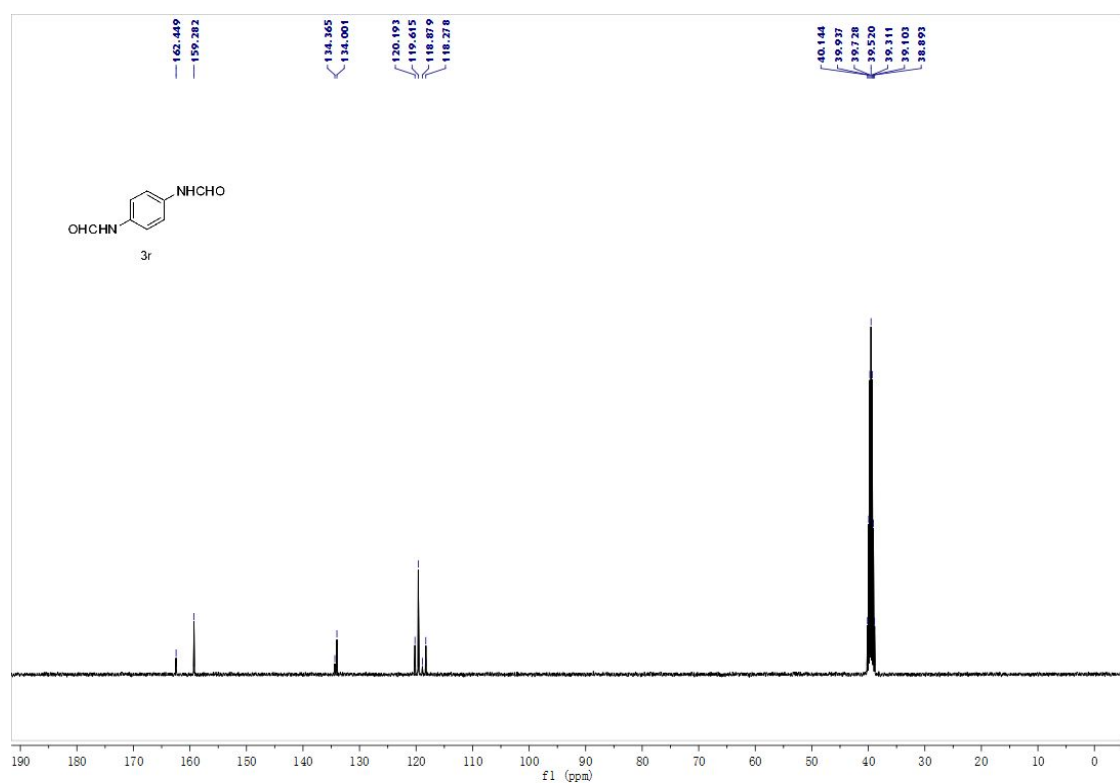
¹H NMR spectra of **3q**



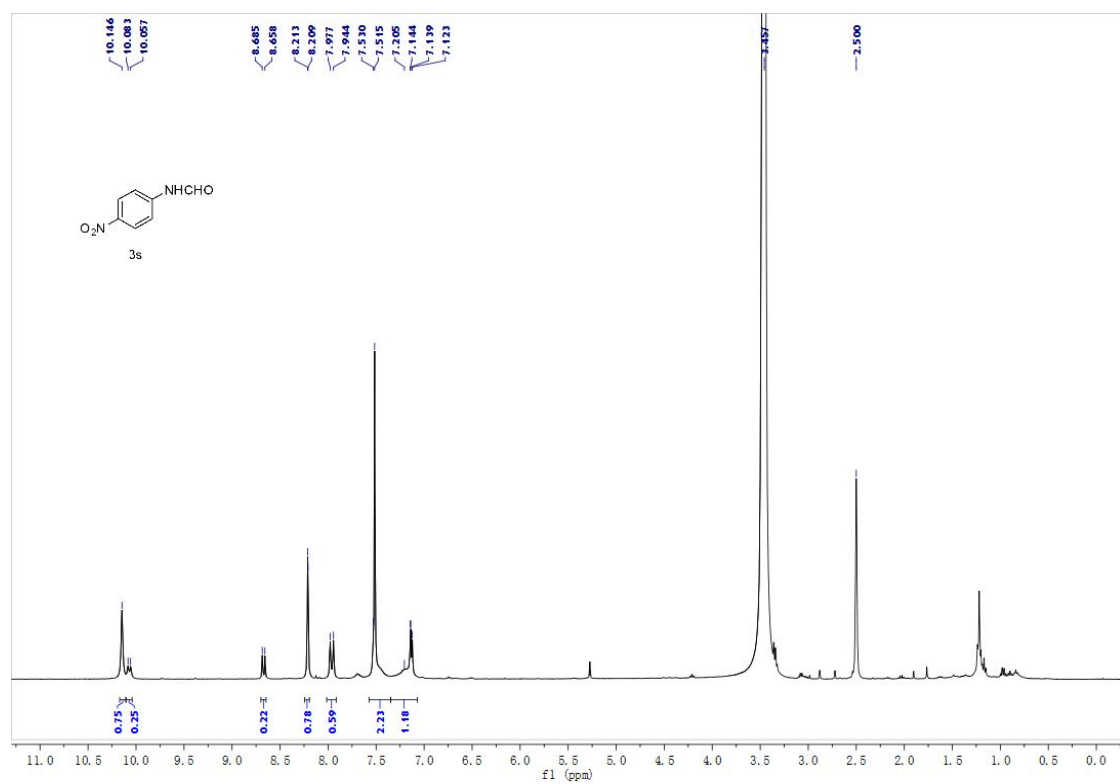
¹H NMR spectra of **3q**



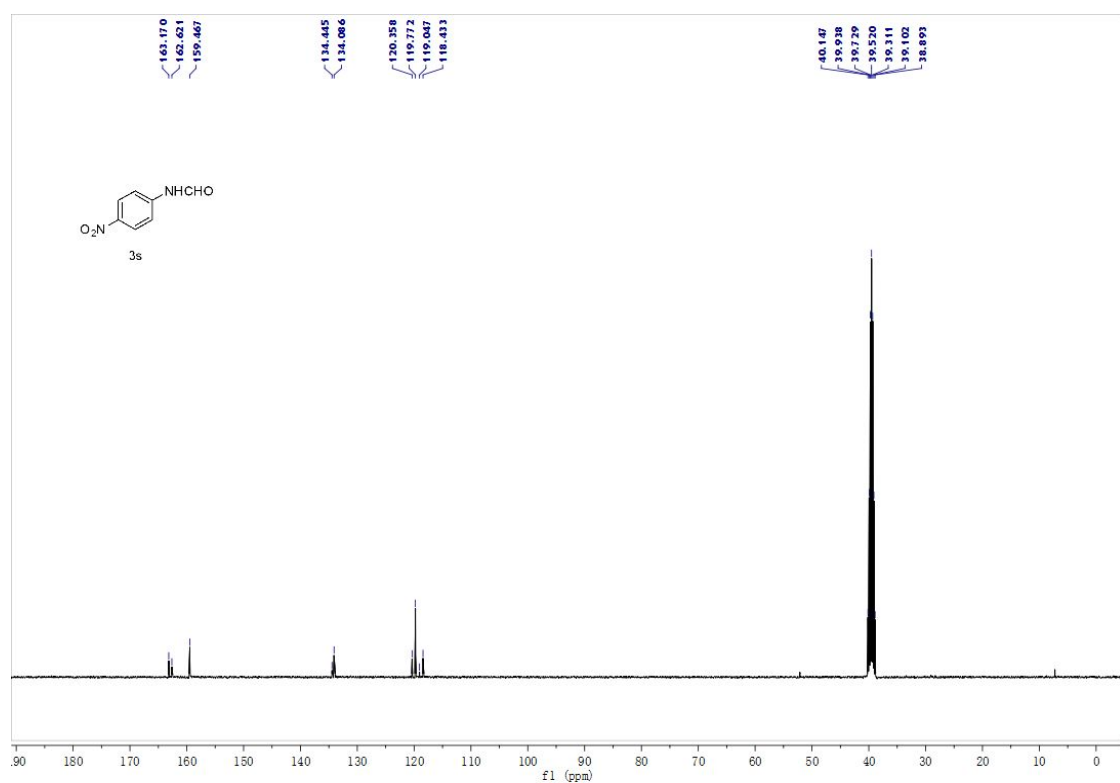
¹H NMR spectra of **3r**



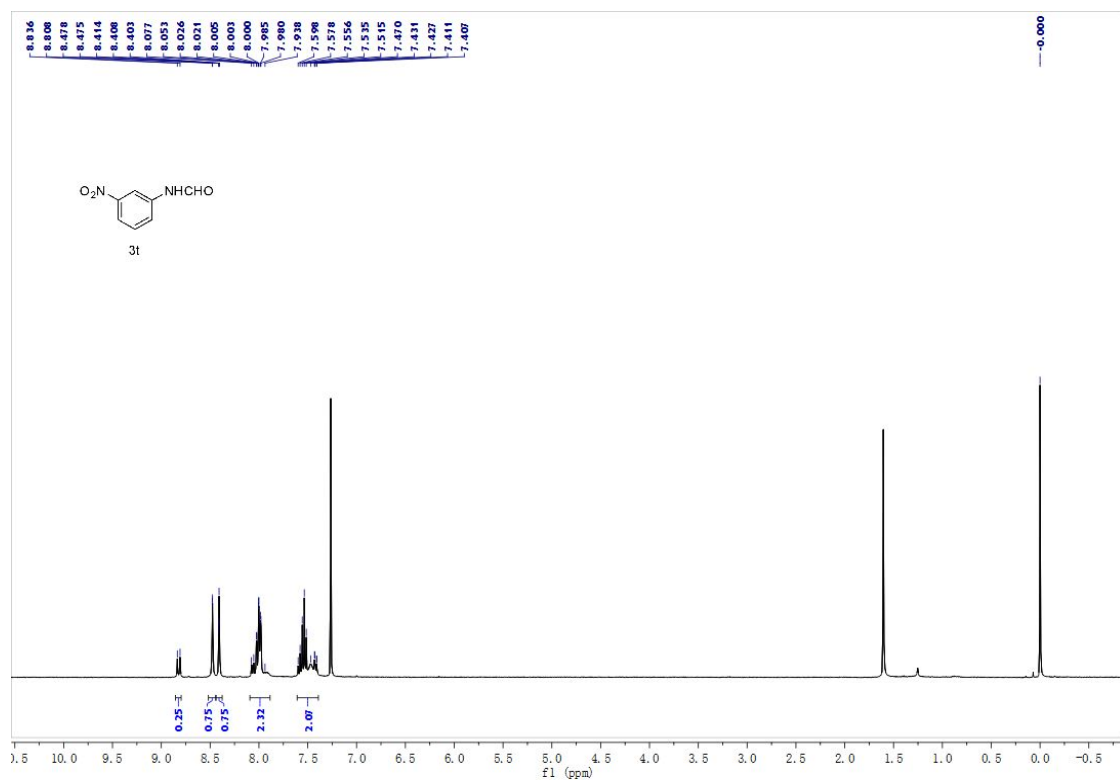
¹³H NMR spectra of **3r**



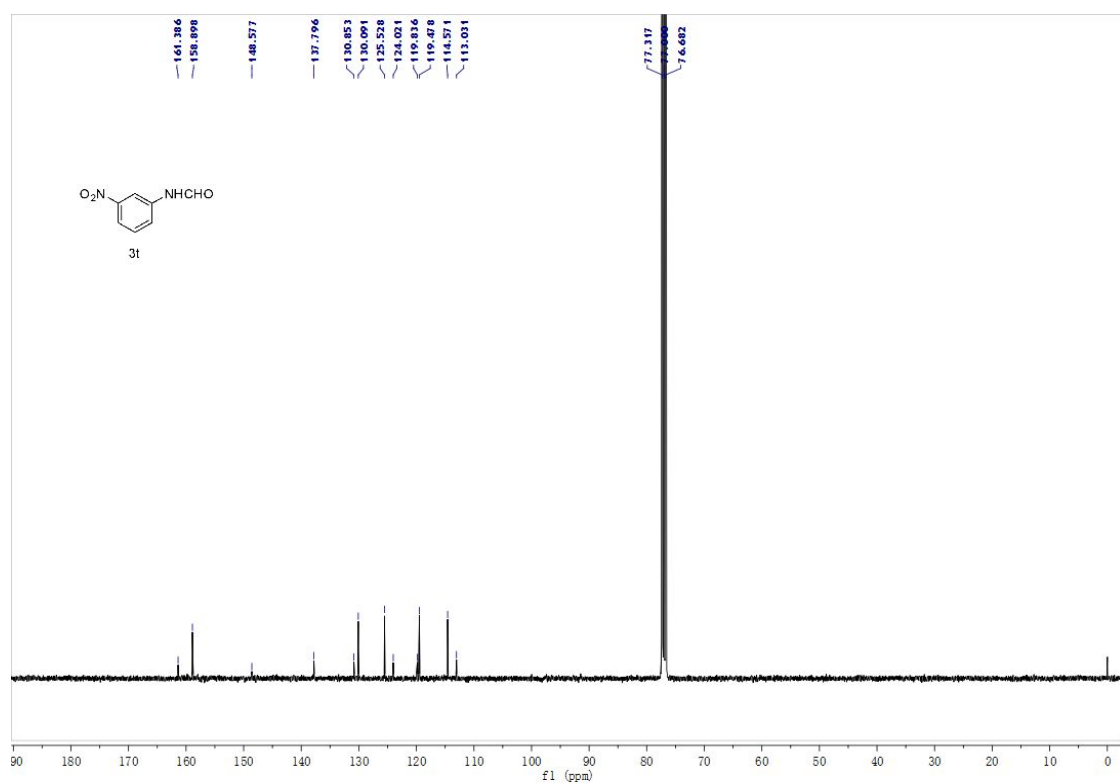
¹H NMR spectra of **3s**



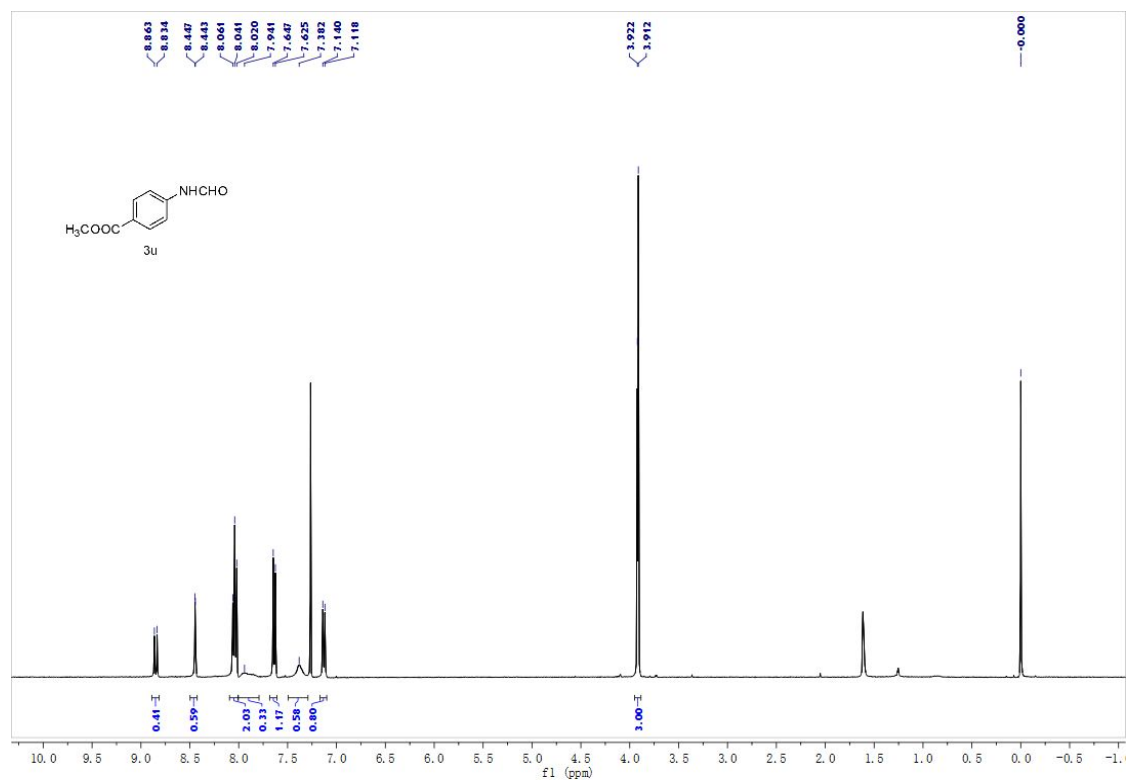
¹³C NMR spectra of **3s**



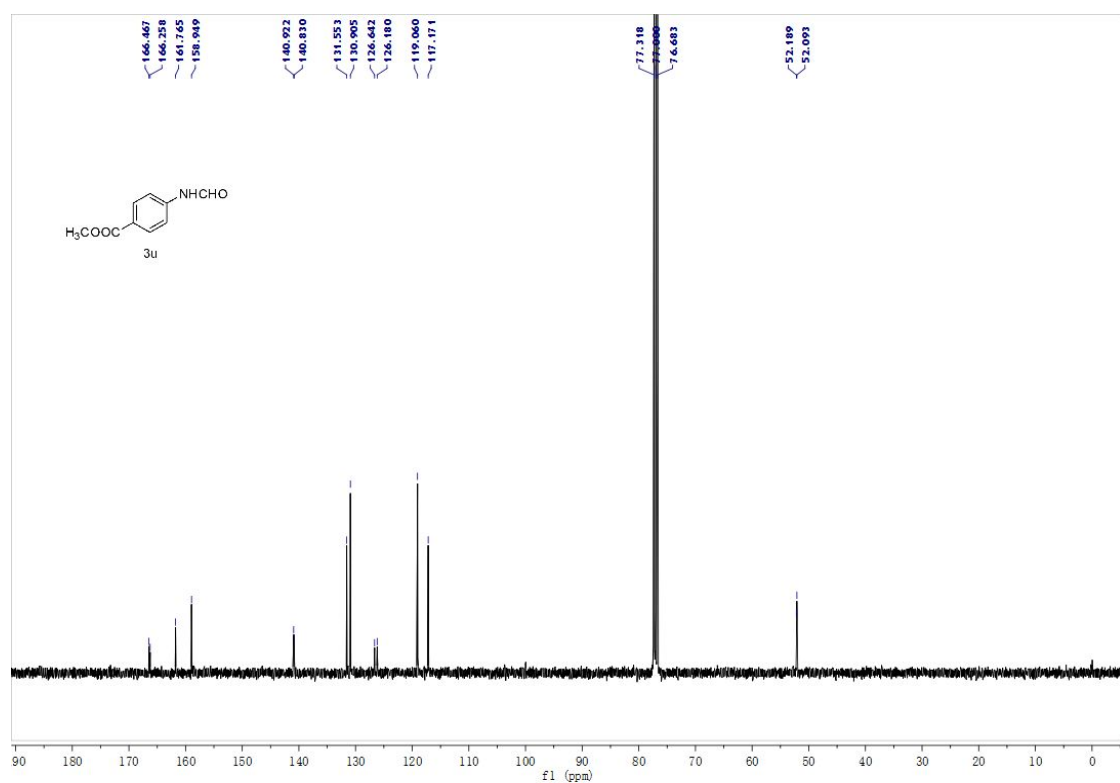
¹H NMR spectra of **3t**



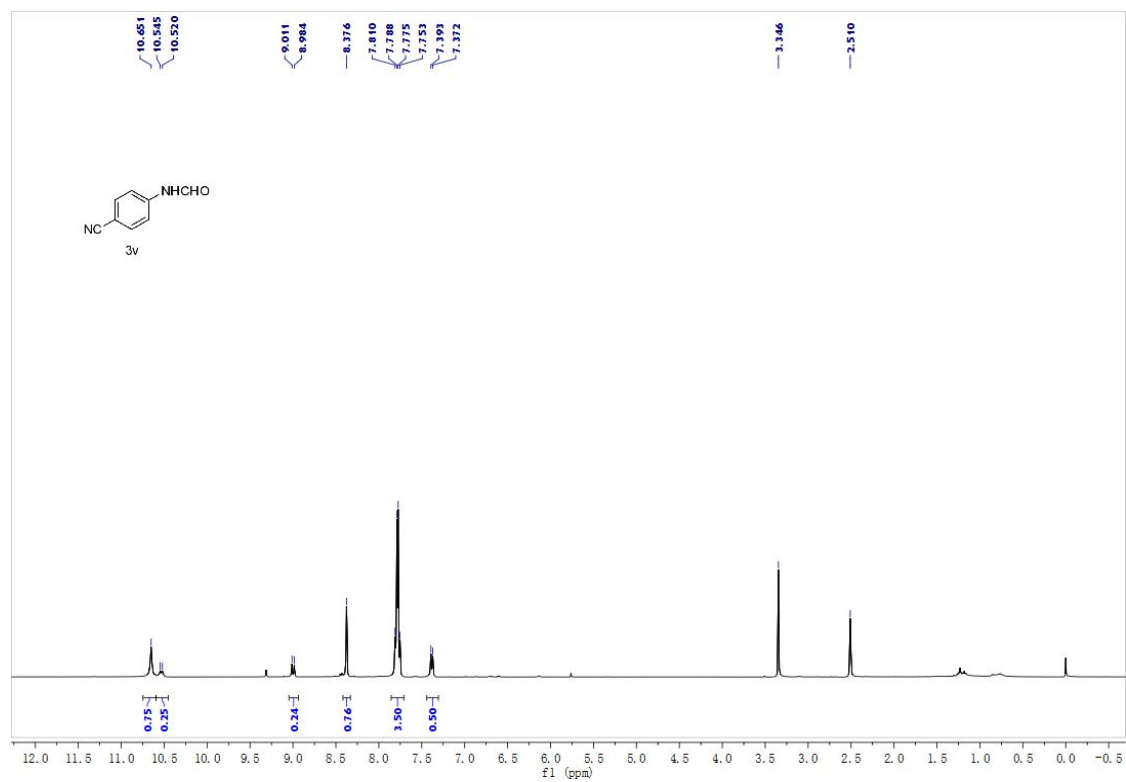
¹³C NMR spectra of **3t**



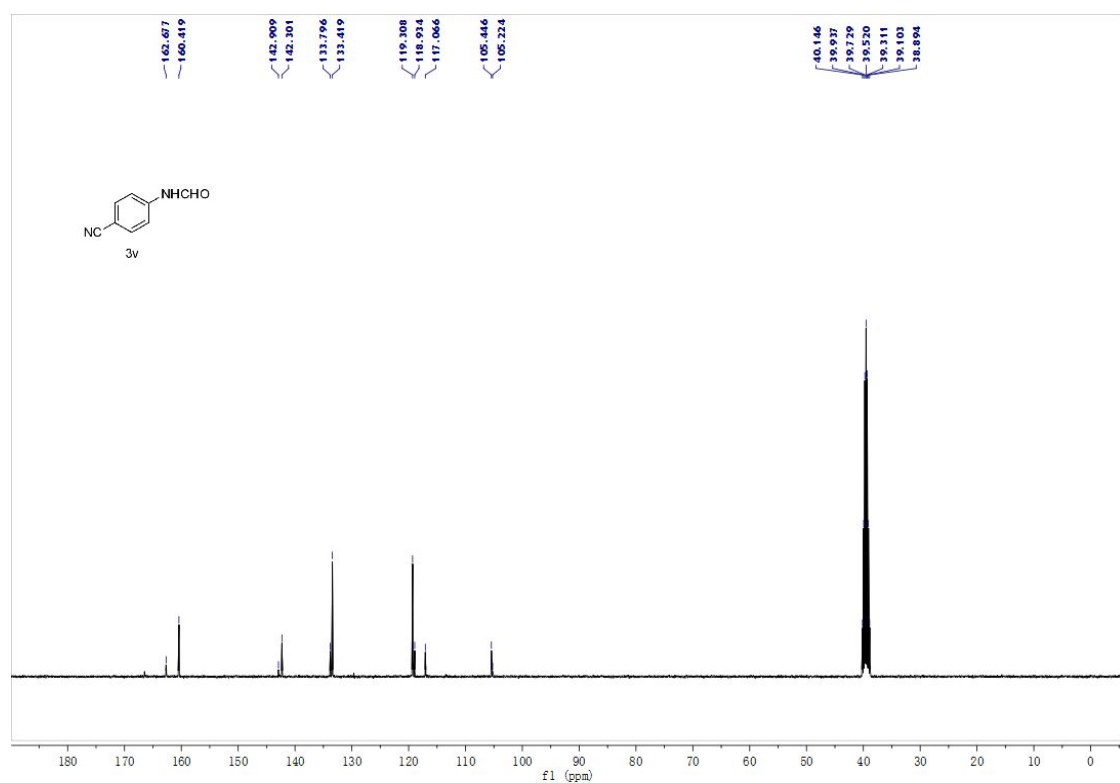
¹H NMR spectra of **3u**



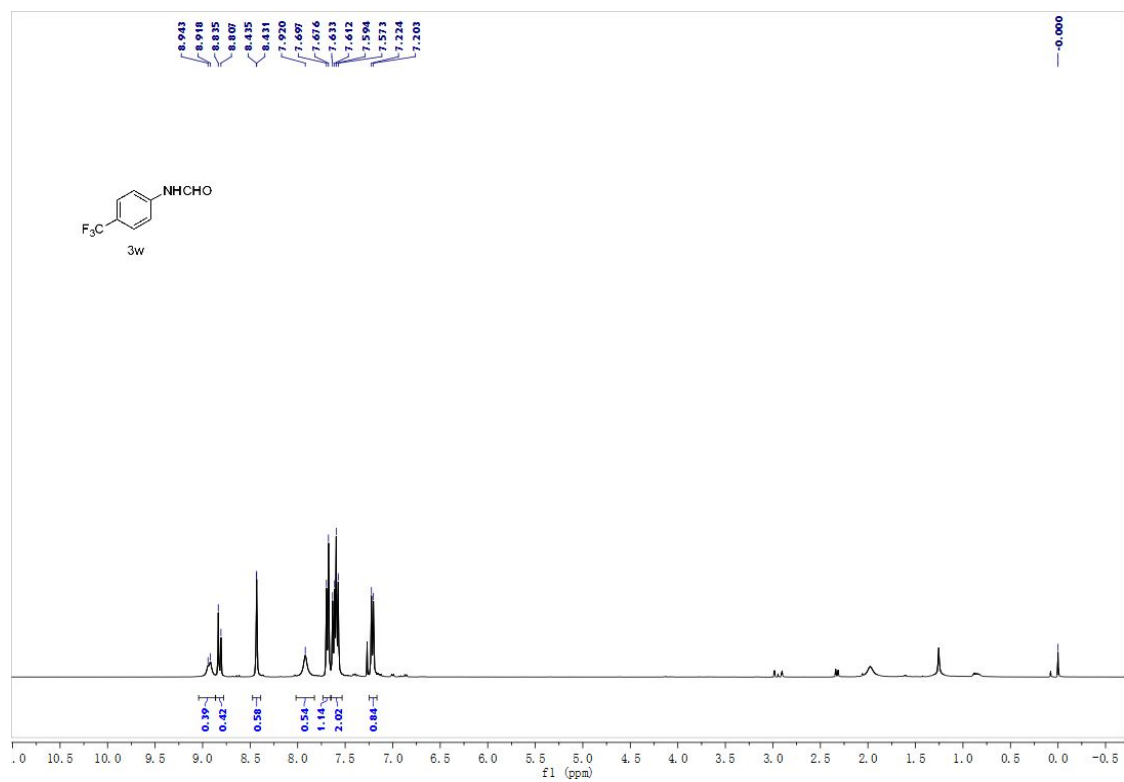
¹³C NMR spectra of **3u**



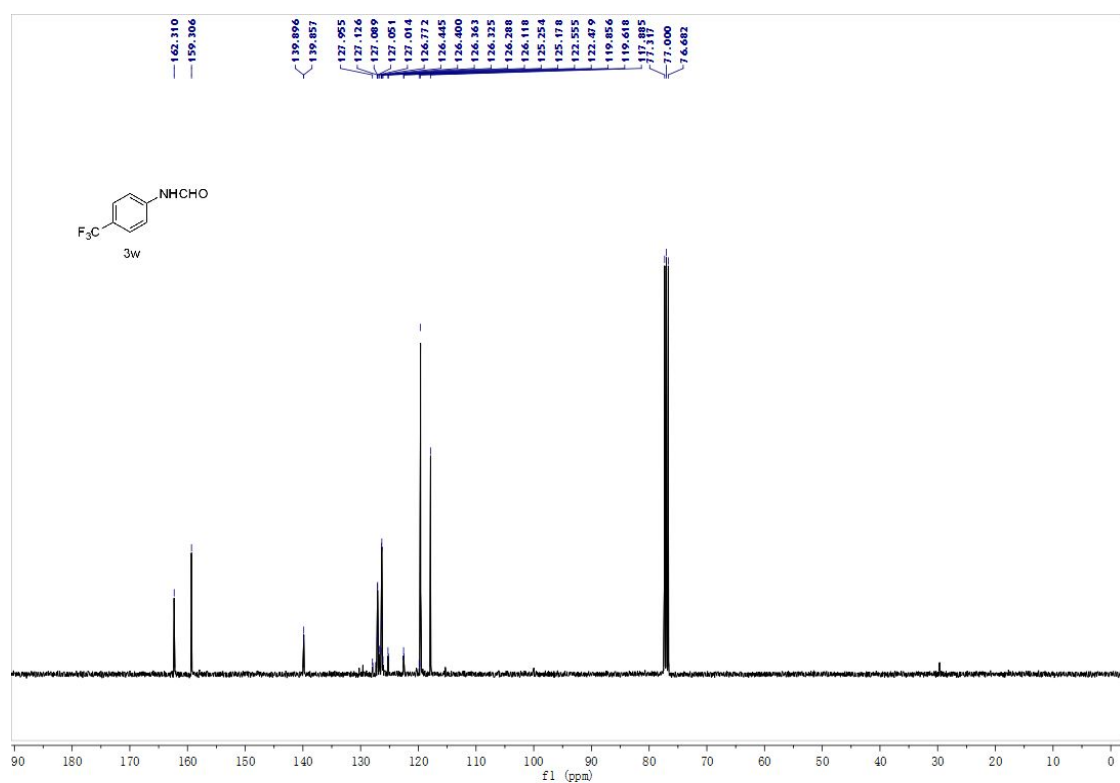
¹H NMR spectra of **3v**



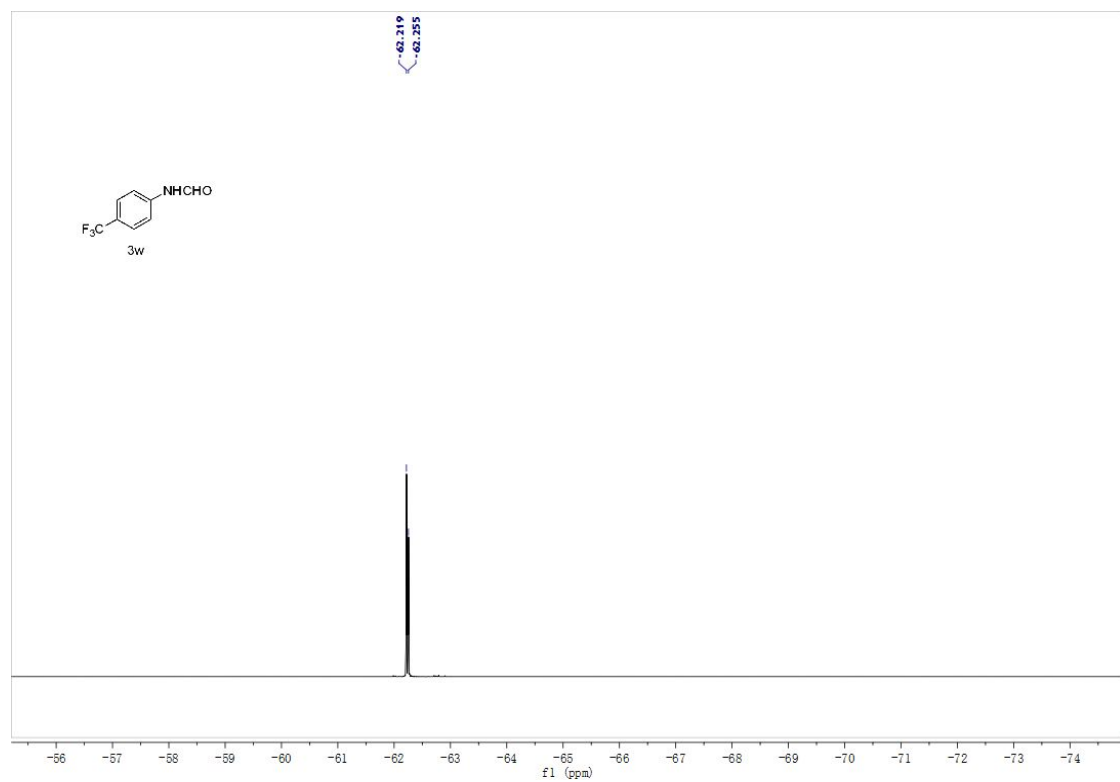
¹³C NMR spectra of **3v**



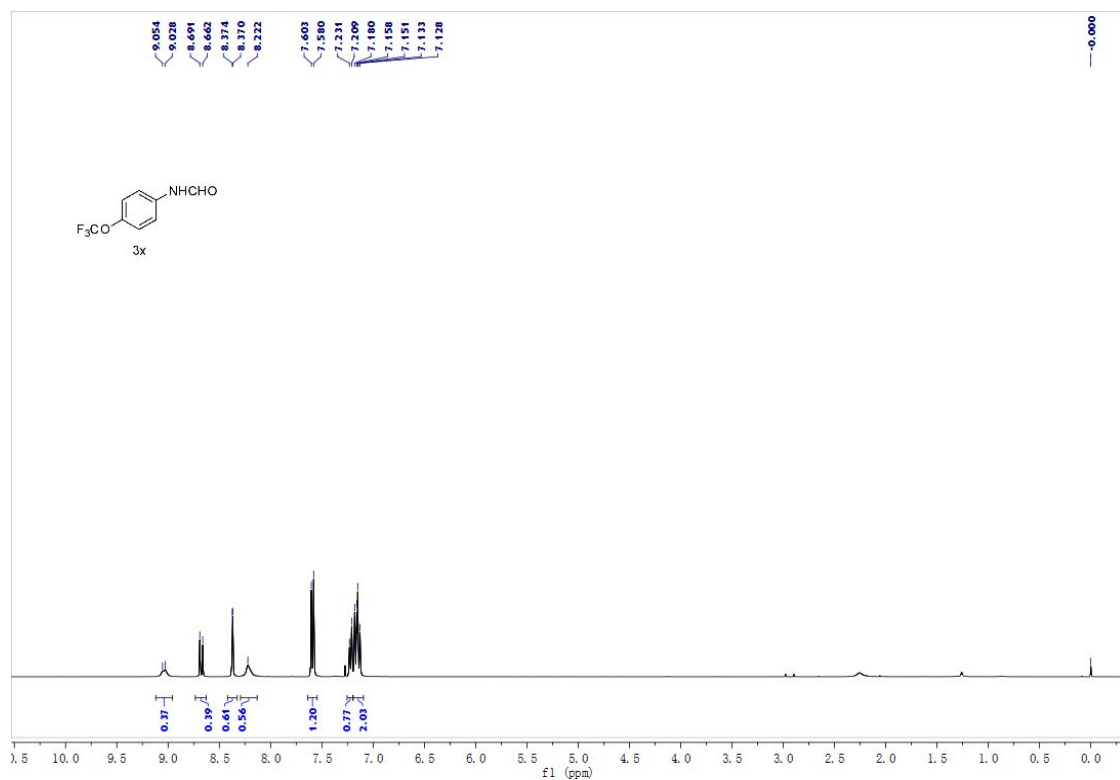
¹H NMR spectra of **3w**



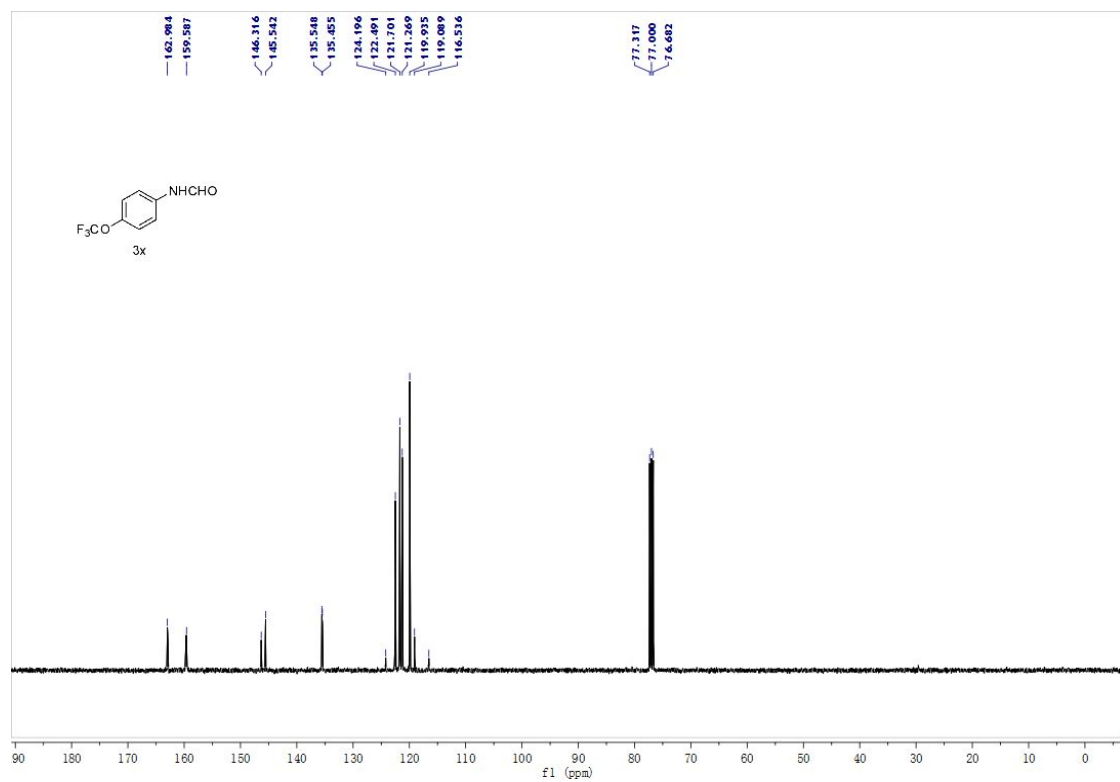
¹³C NMR spectra of **3w**



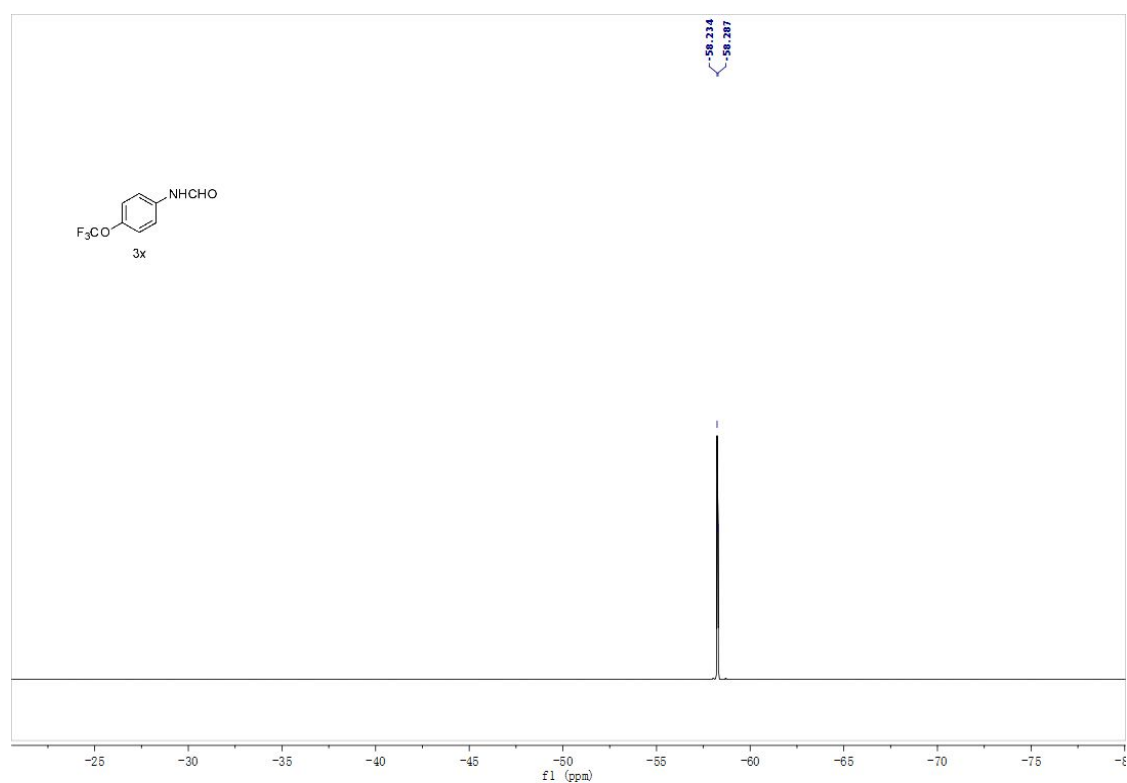
¹⁹F NMR spectra of **3w**



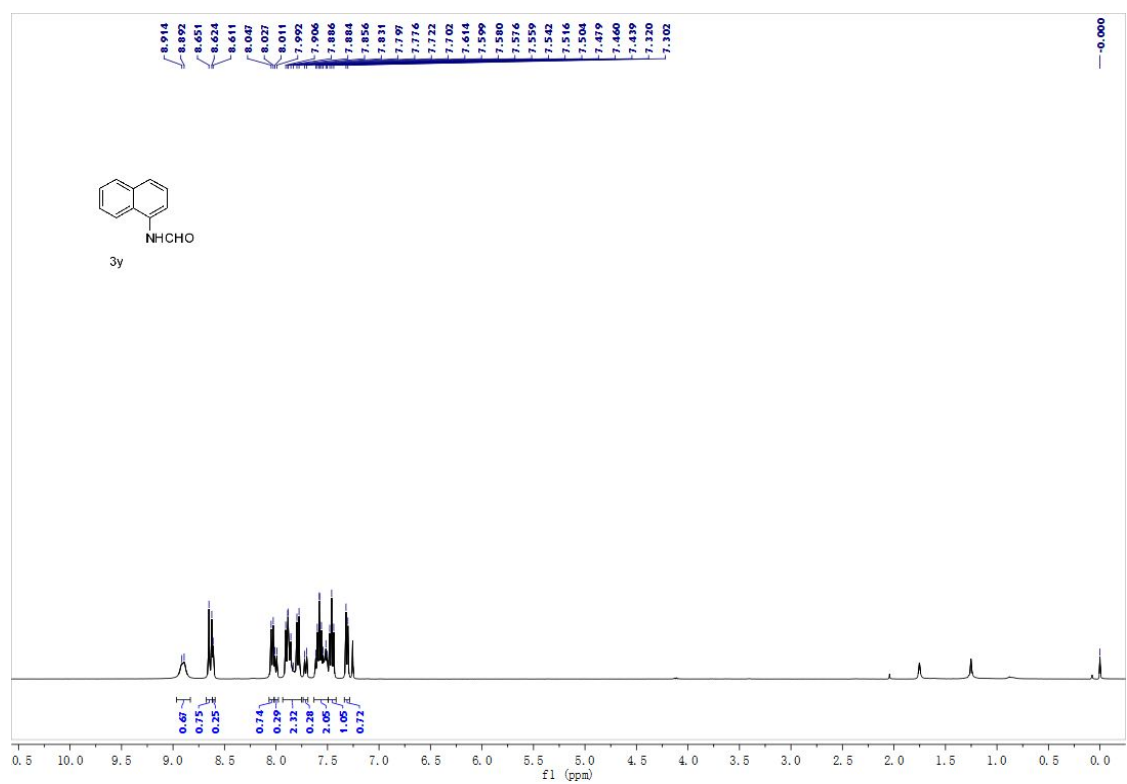
¹H NMR spectra of **3x**



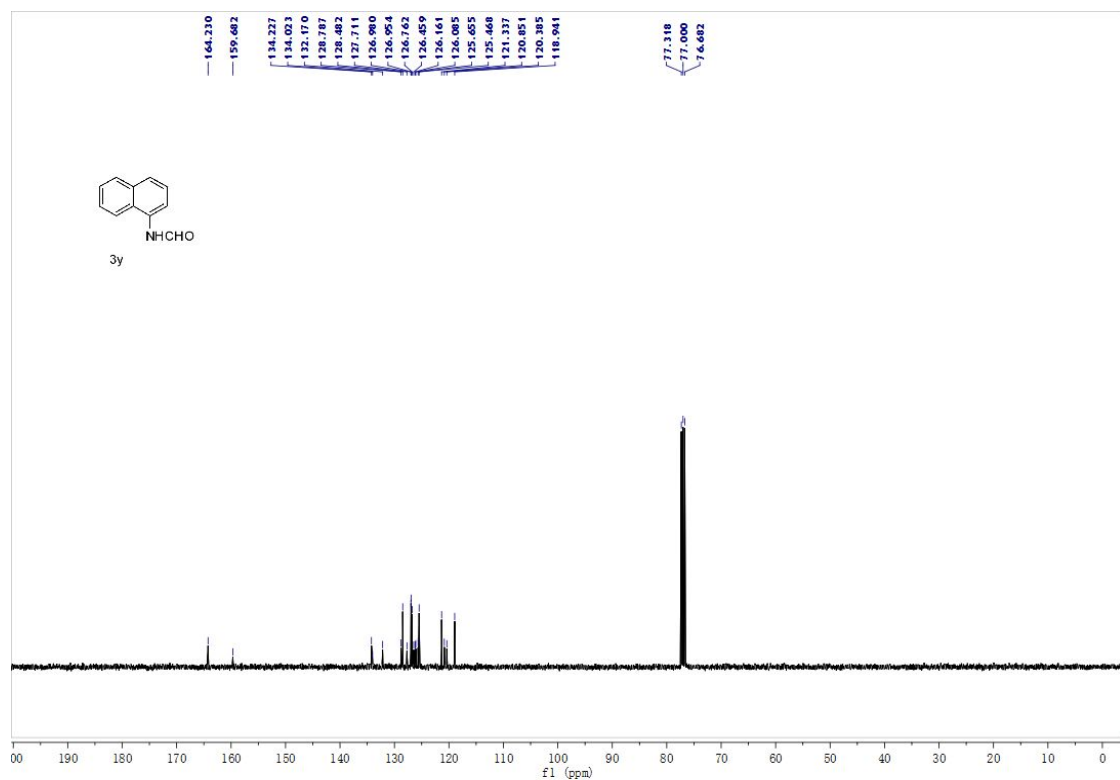
¹³C NMR spectra of **3x**



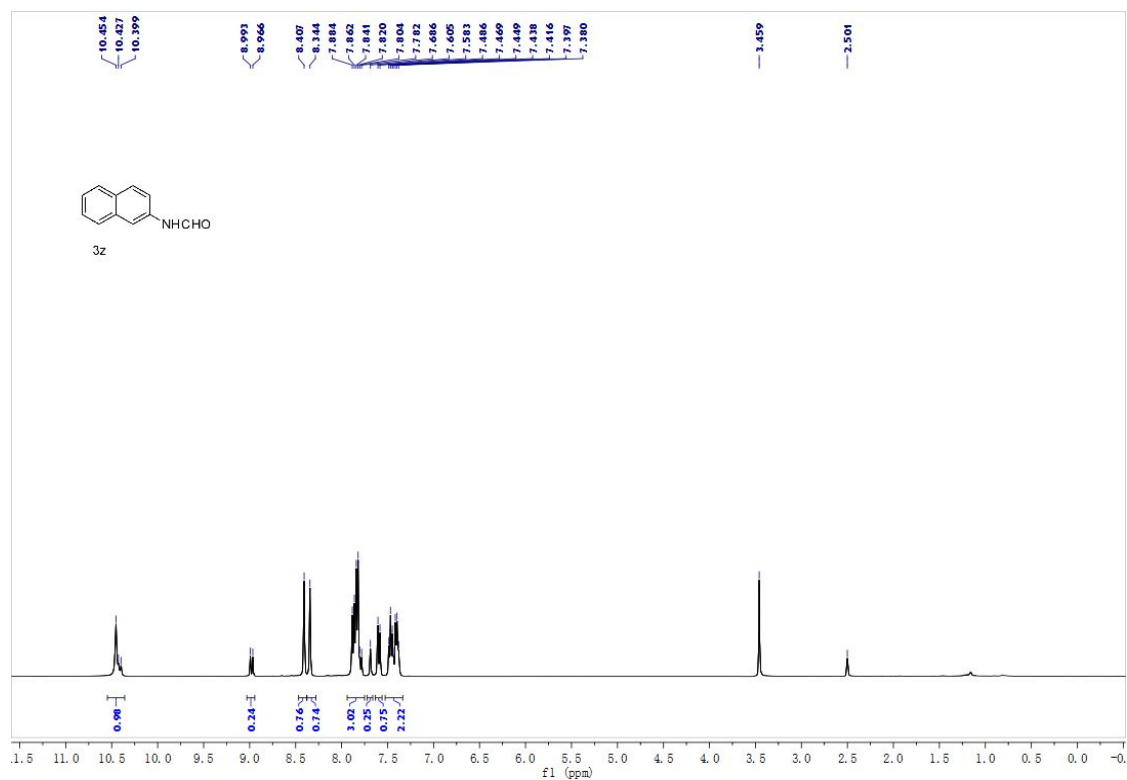
¹⁹F NMR spectra of **3x**



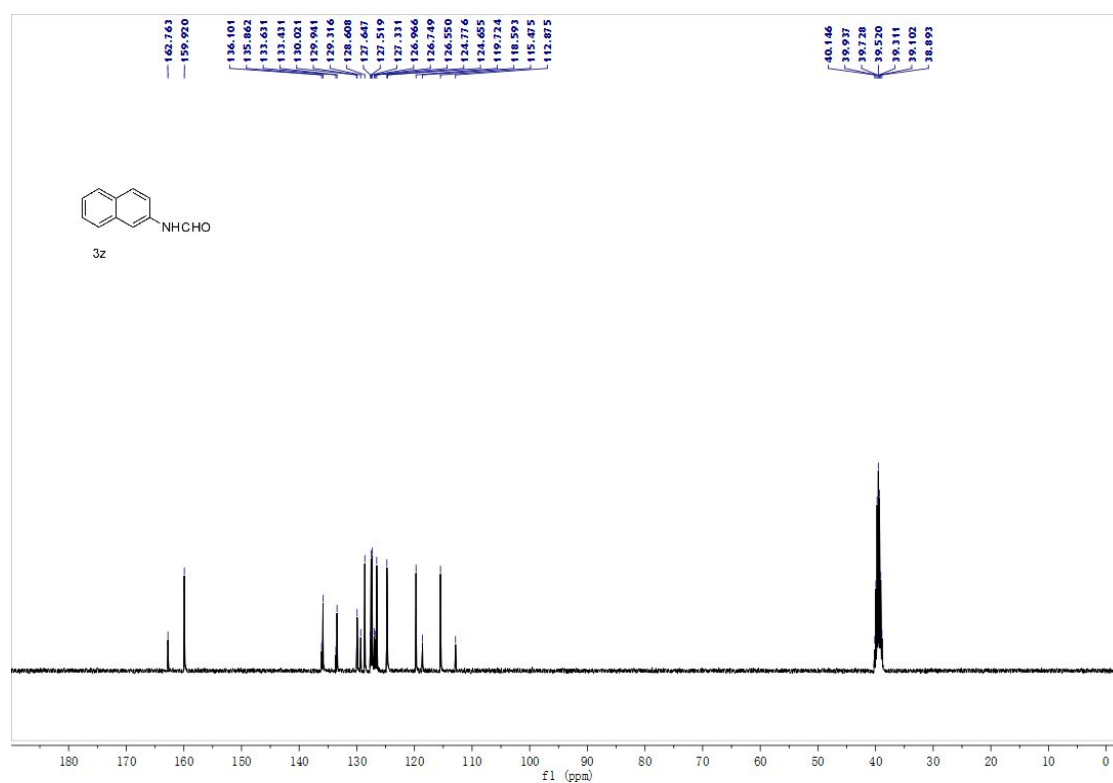
¹H NMR spectra of **3y**



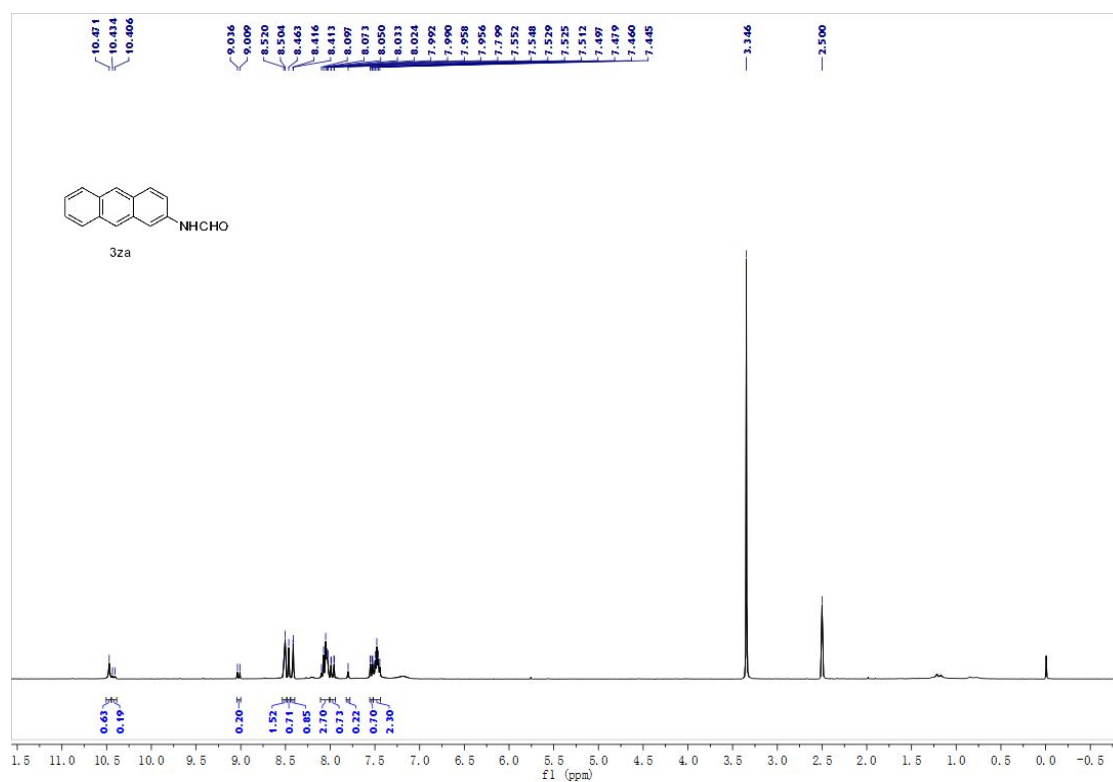
¹³C NMR spectra of **3y**



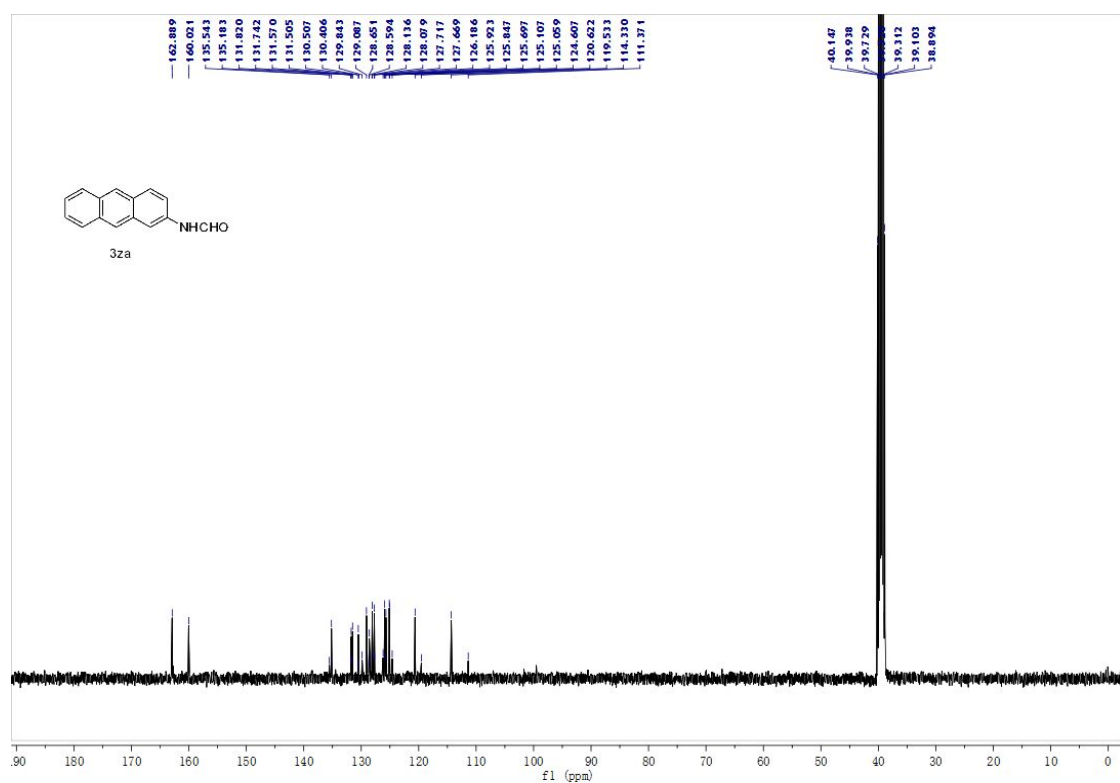
¹H NMR spectra of **3z**



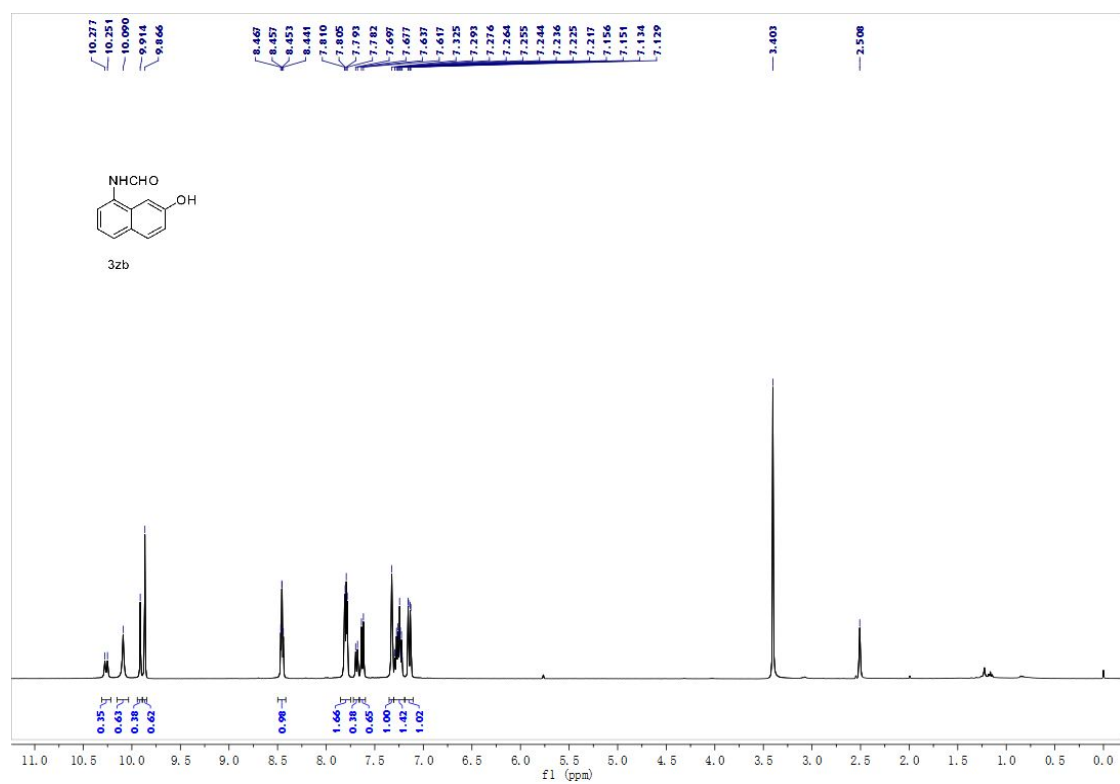
¹³C NMR spectra of **3z**



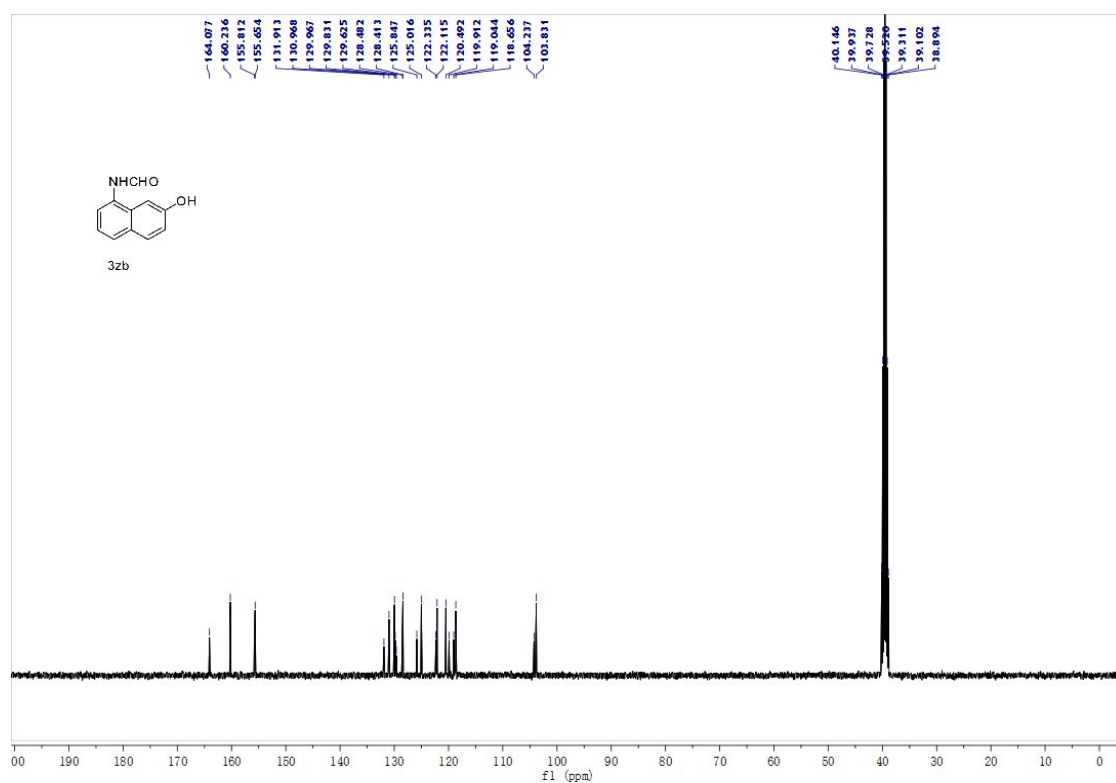
¹H NMR spectra of **3za**



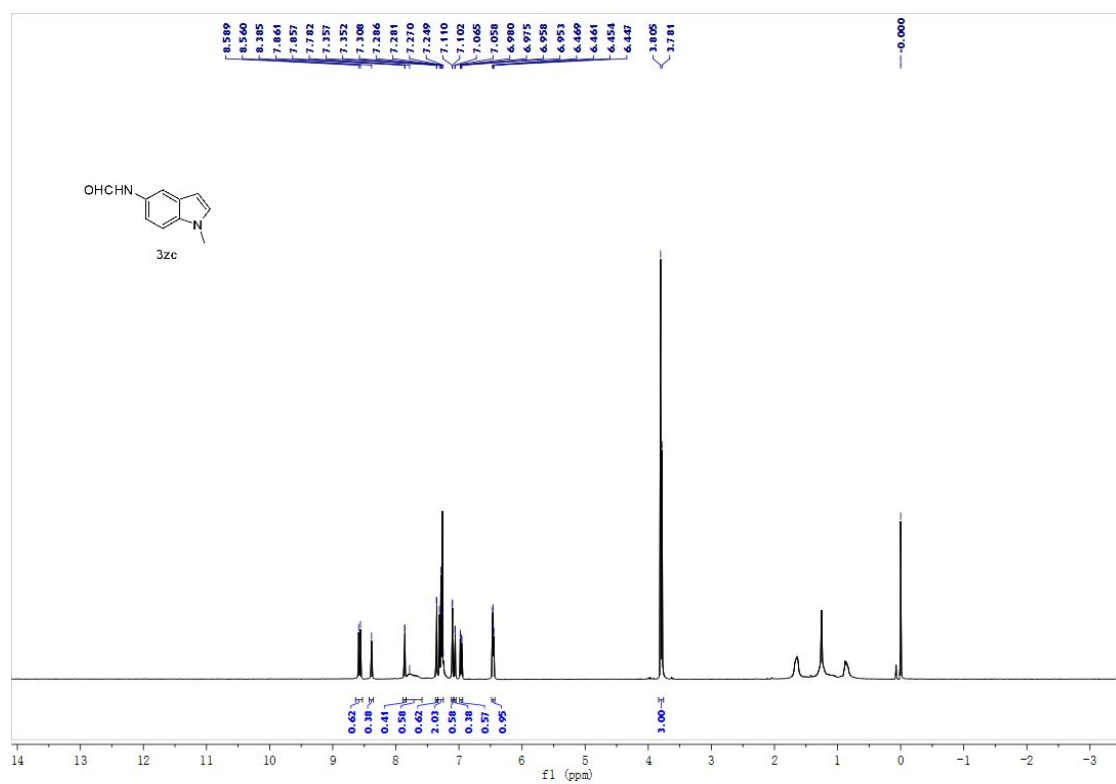
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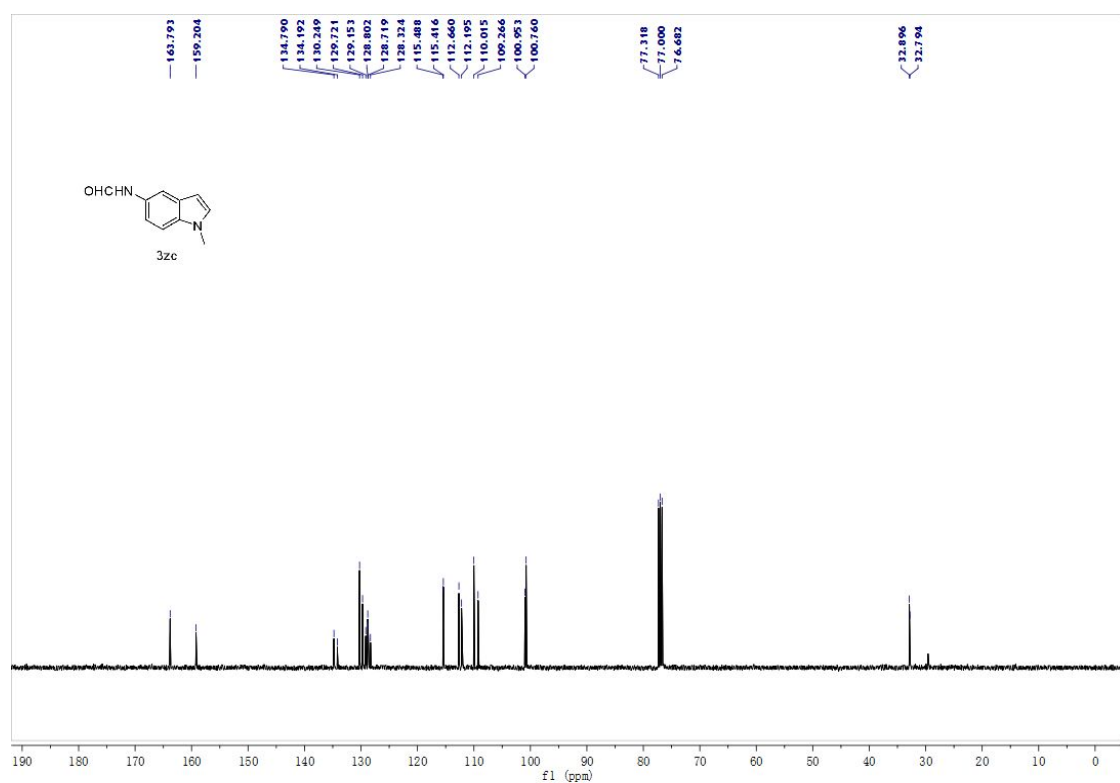
¹H NMR spectra of **3zb**



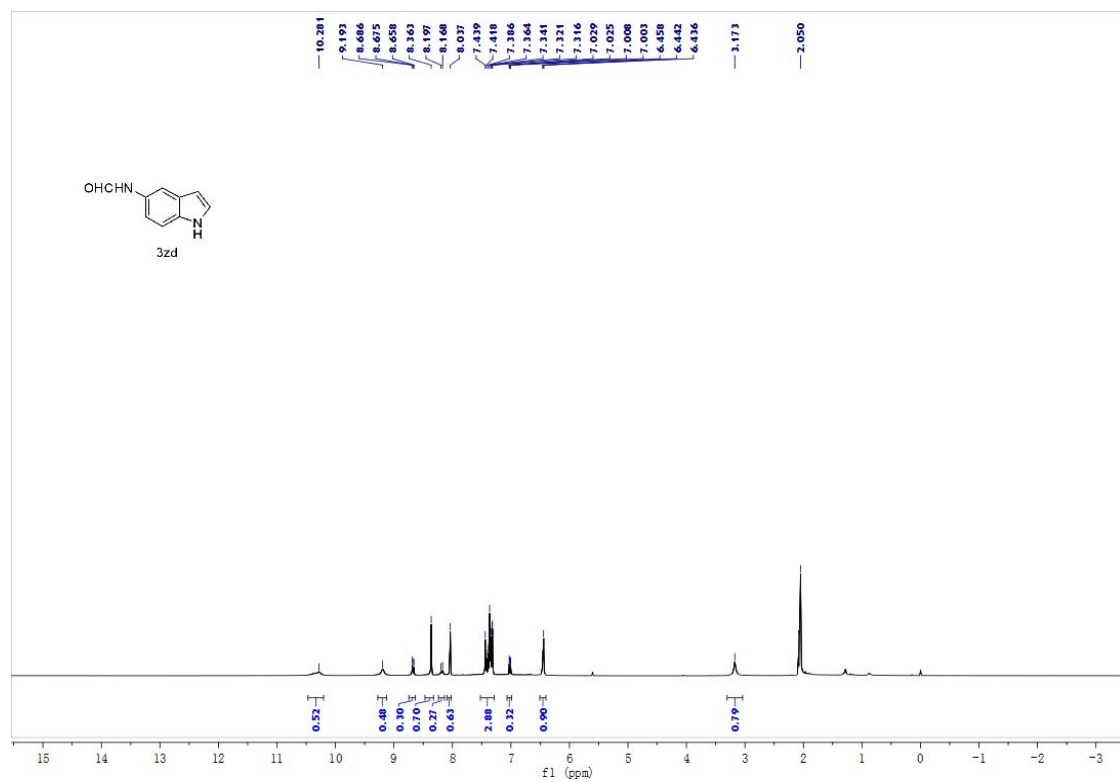
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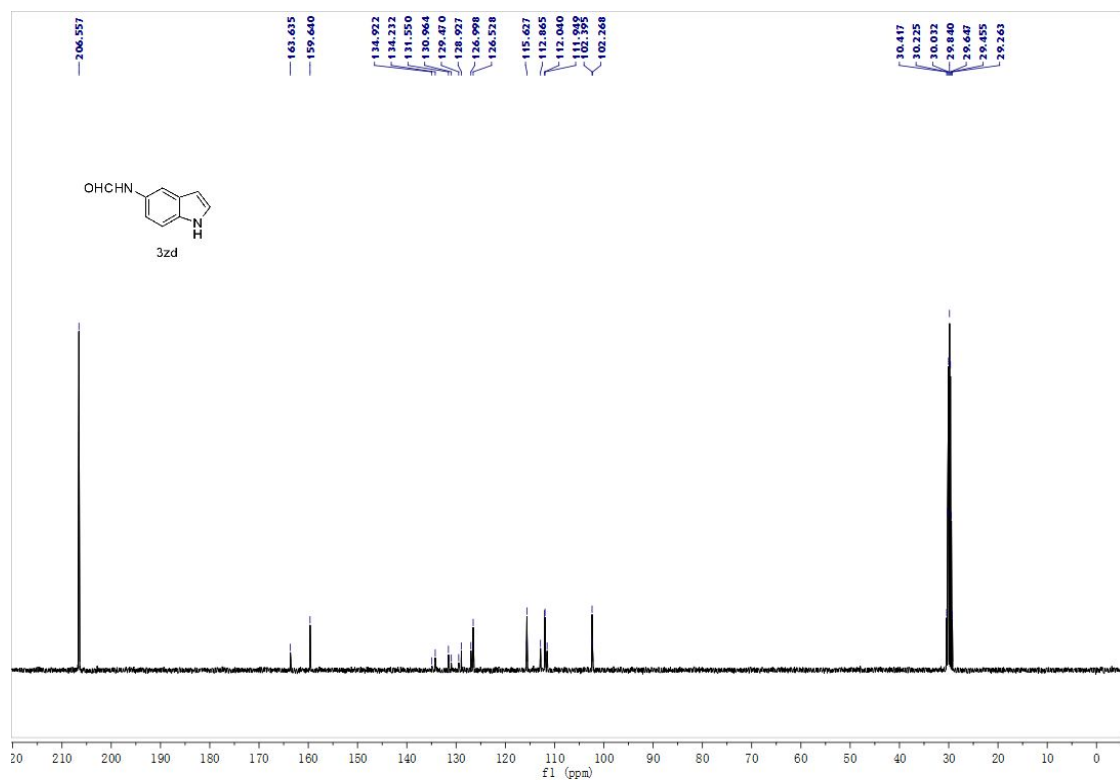
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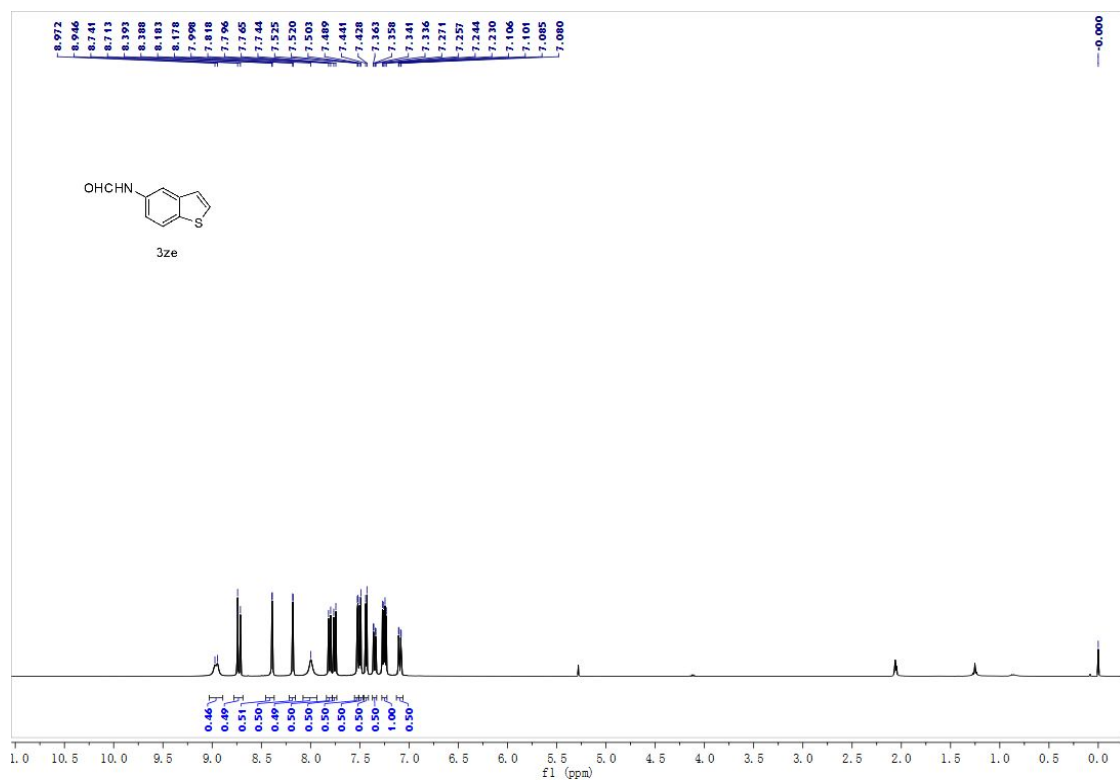
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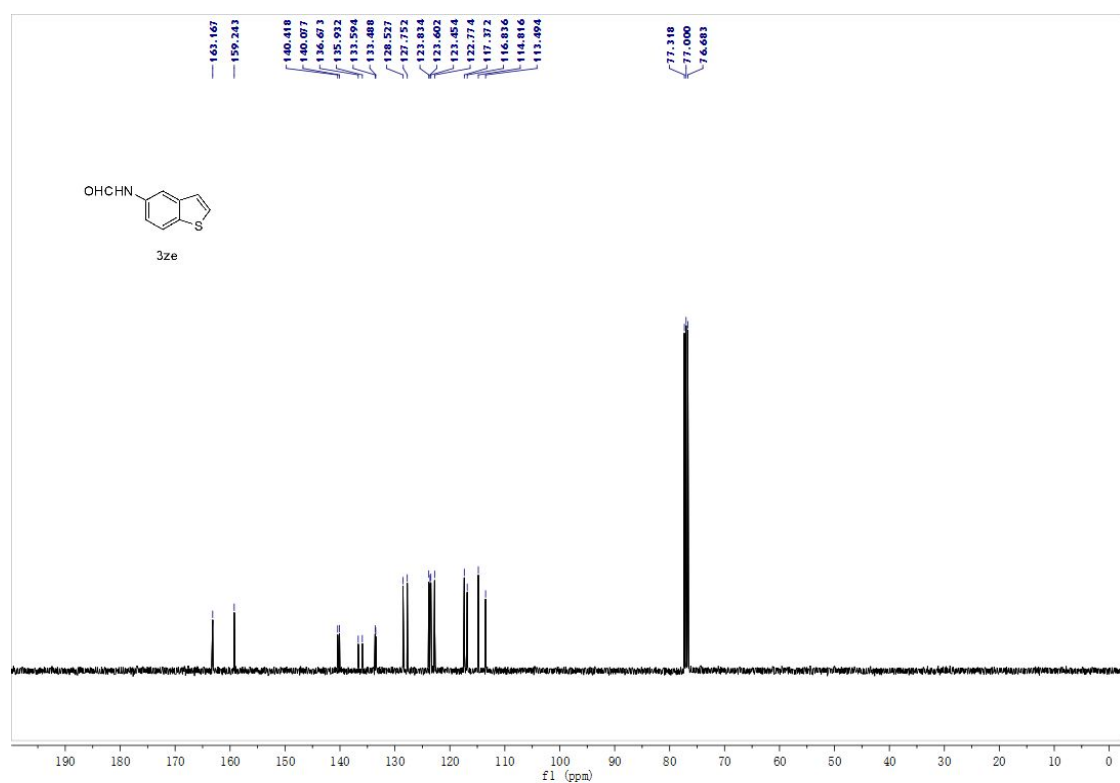
¹H NMR spectra of **3zd**



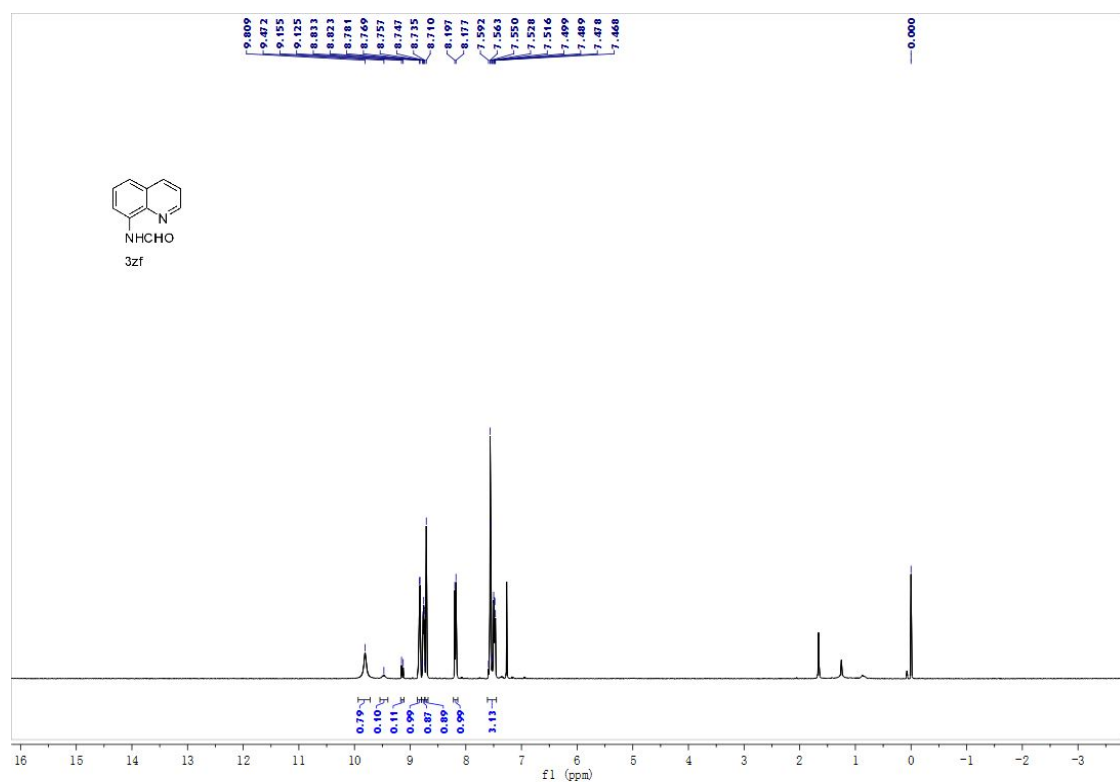
¹³C NMR spectra of **3zd**



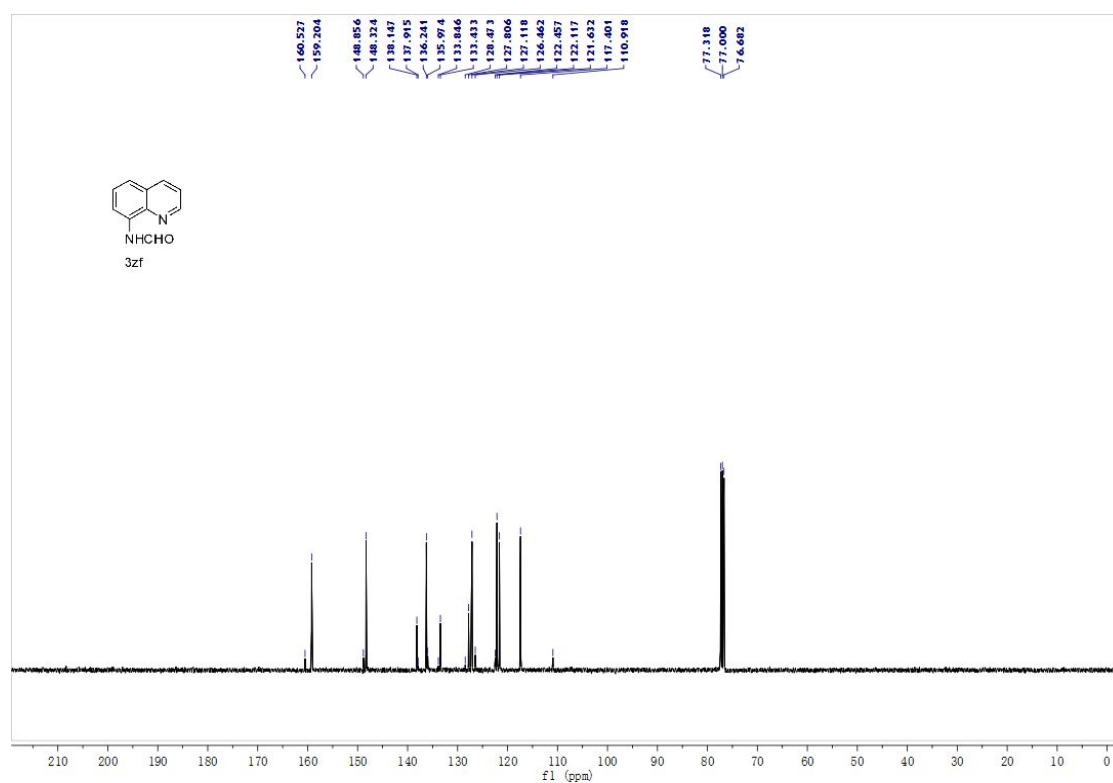
¹H NMR spectra of **3ze**



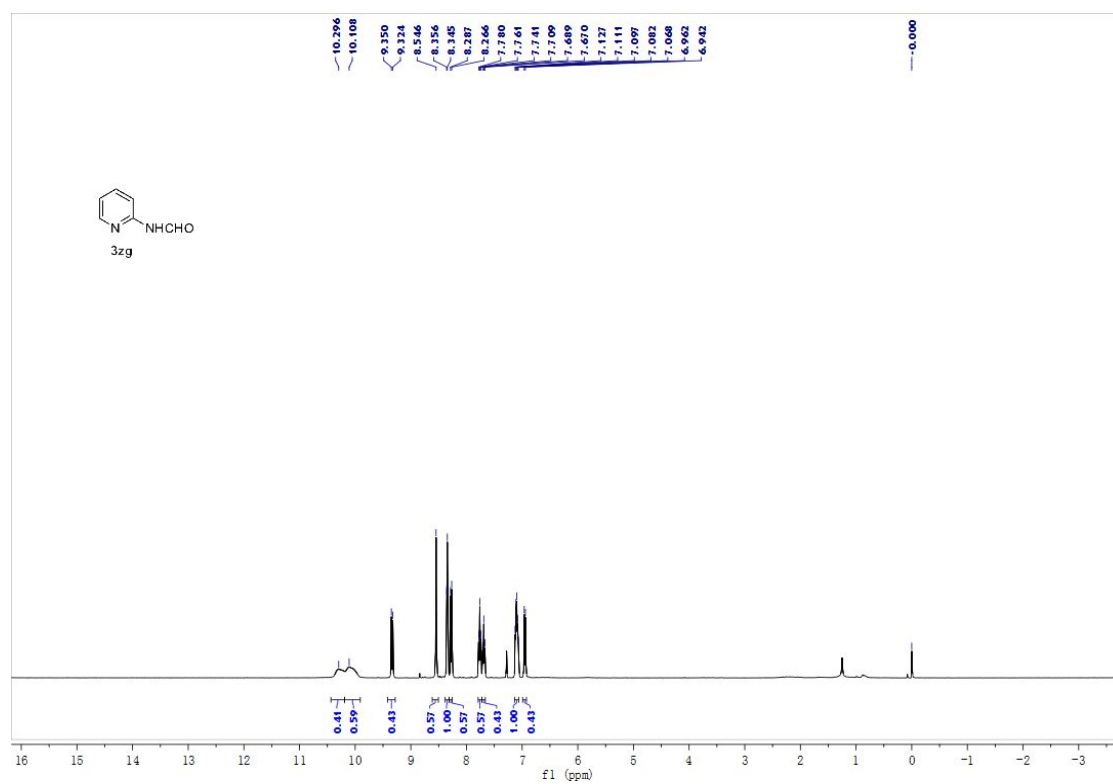
¹³C NMR spectra of **3ze**



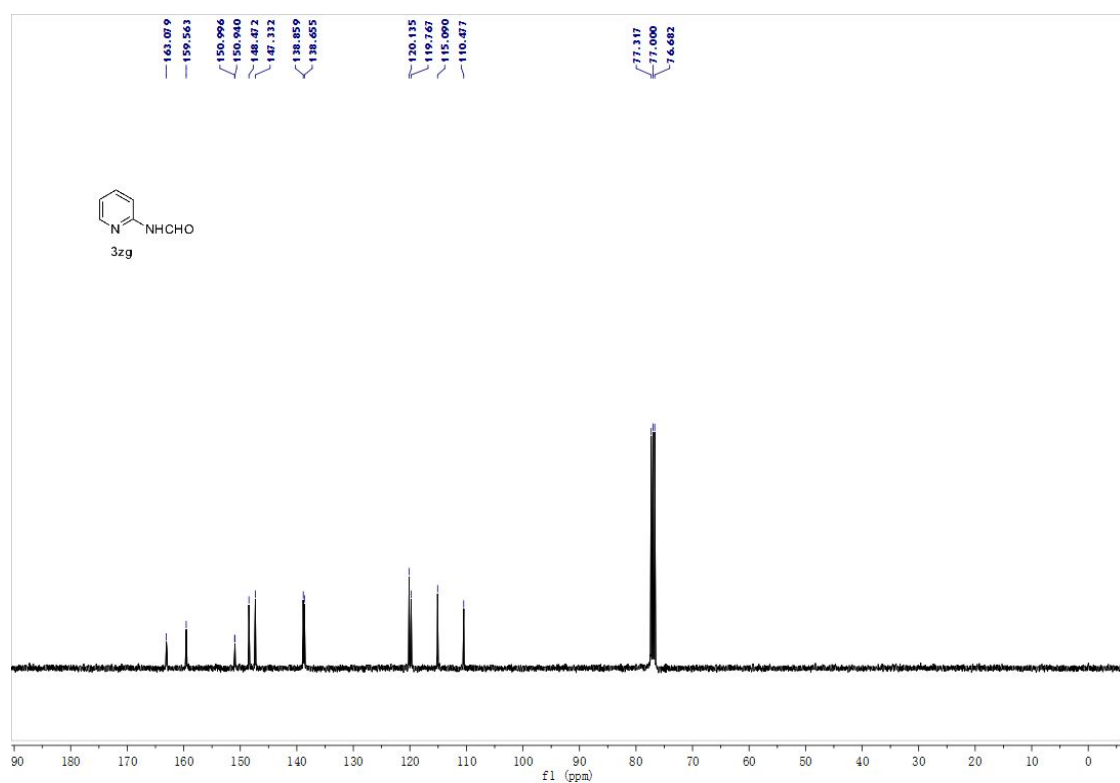
¹H NMR spectra of **3zf**



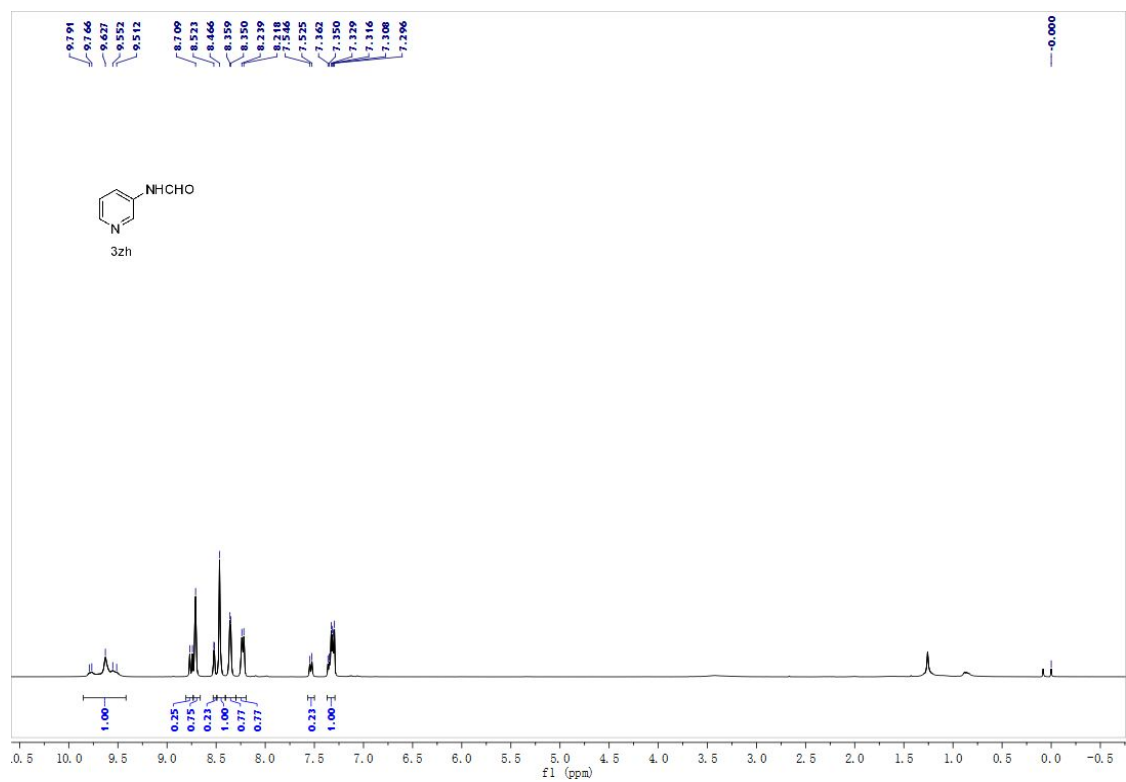
¹³C NMR spectra of **3zf**



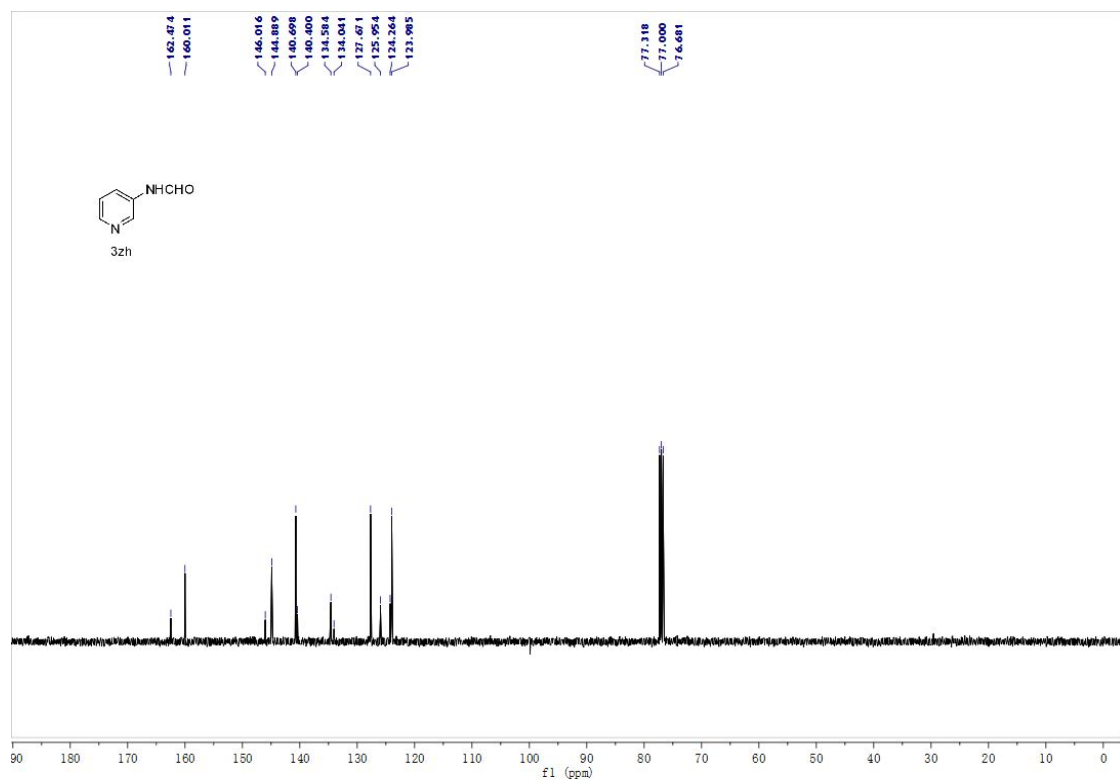
¹H NMR spectra of **3zg**



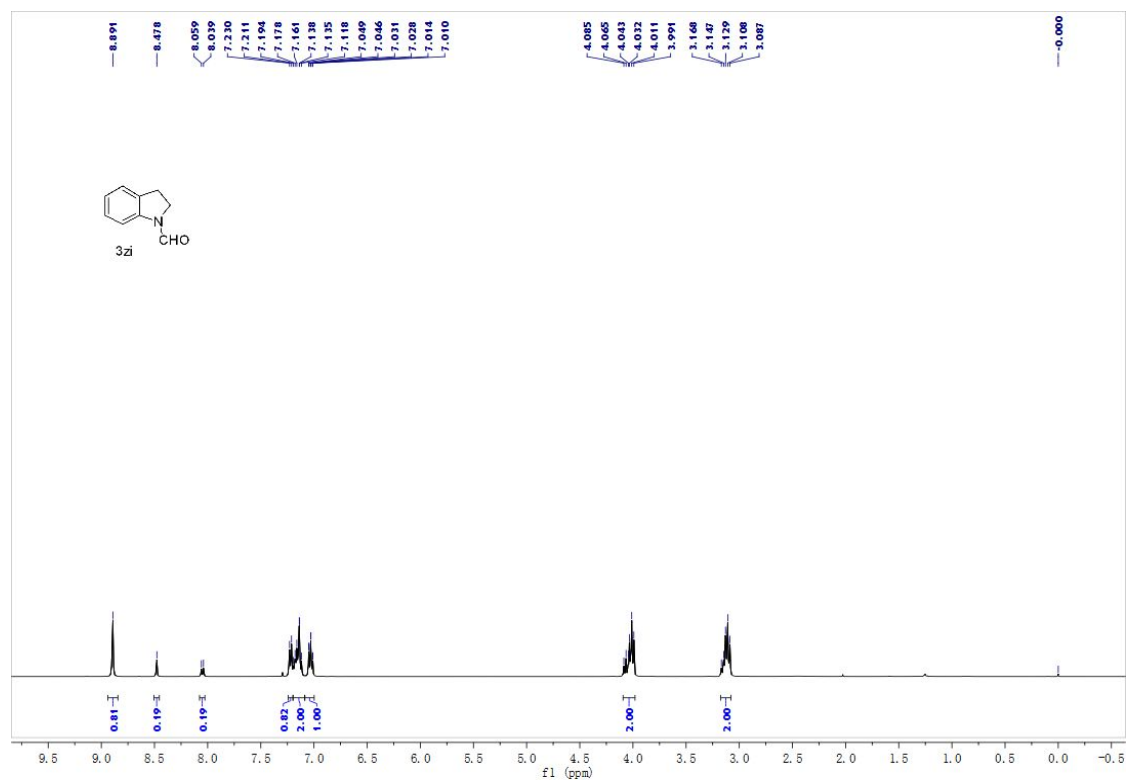
¹³C NMR spectra of **3zg**



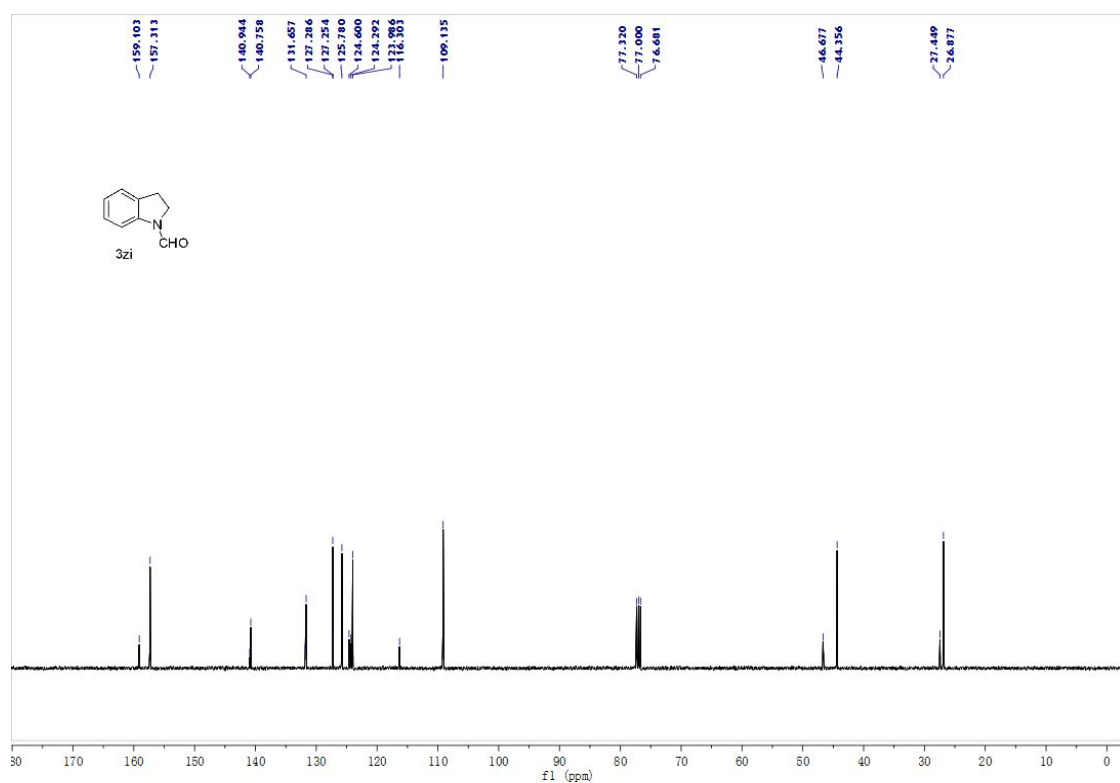
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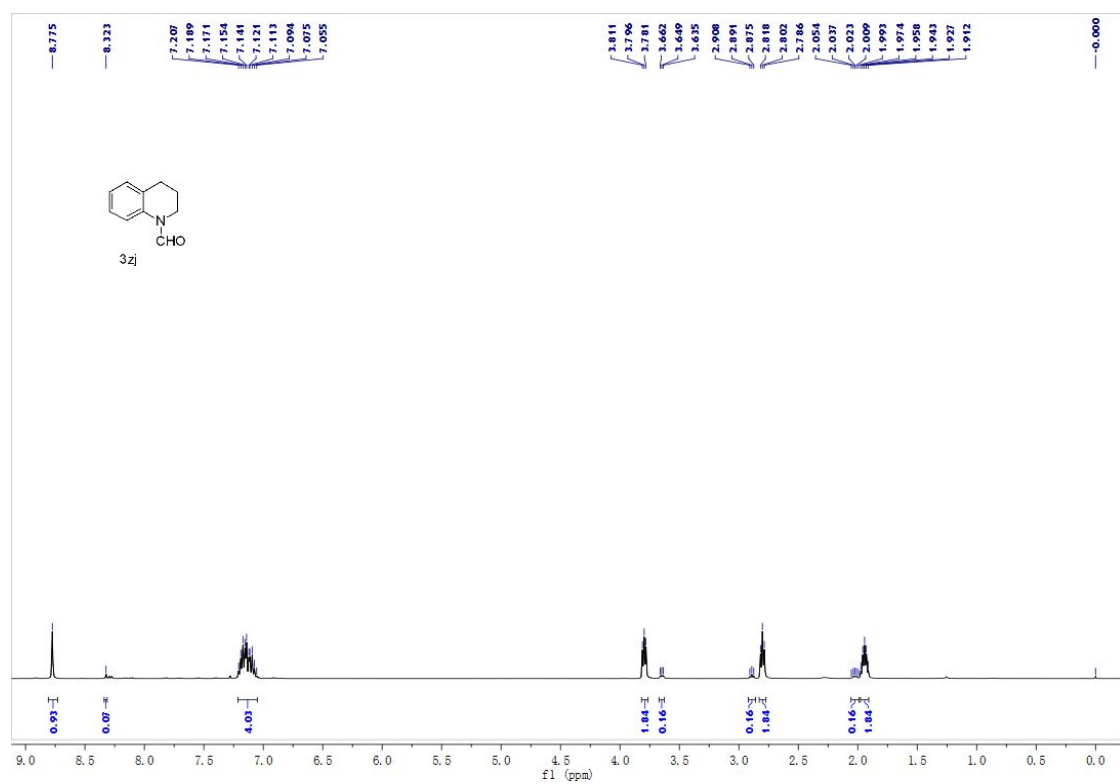
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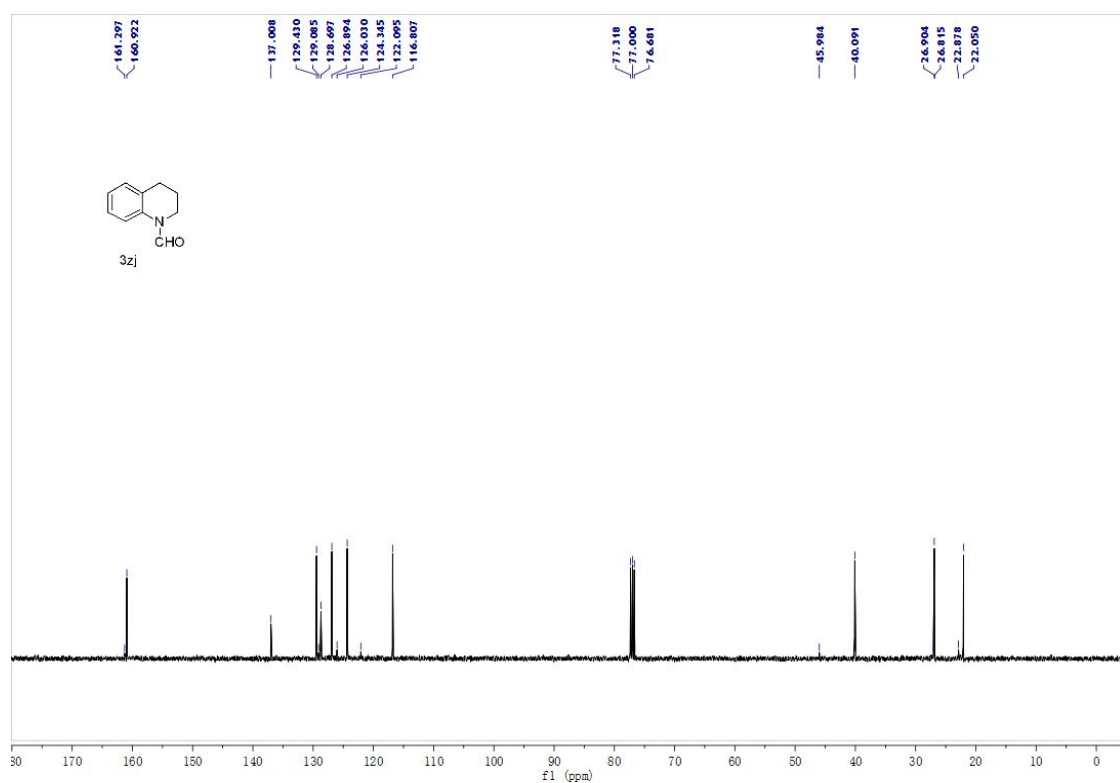
¹H NMR spectra of **3zi**



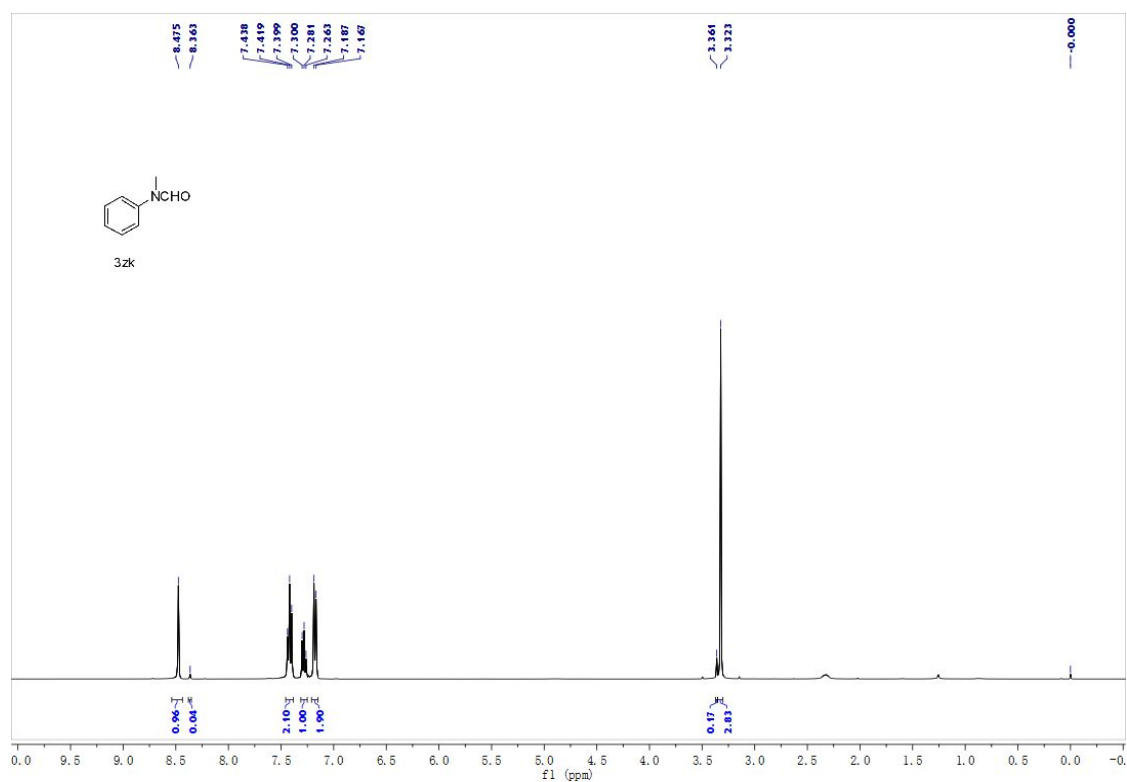
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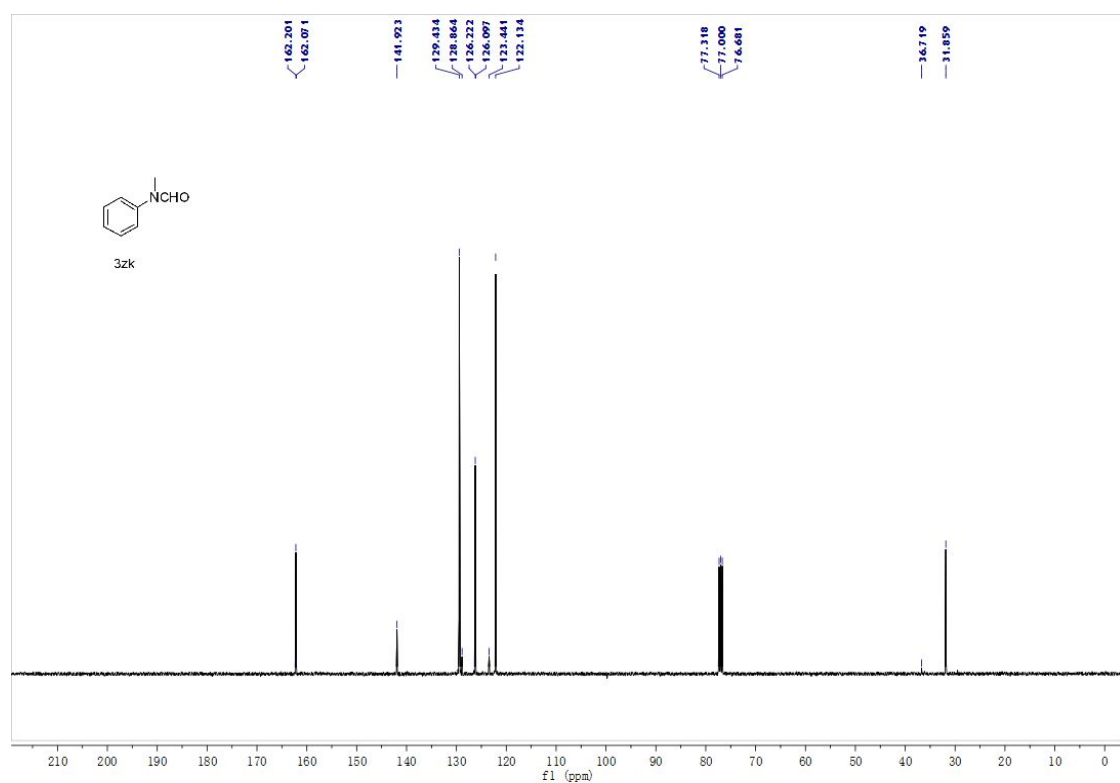
¹H NMR spectra of **3zj**



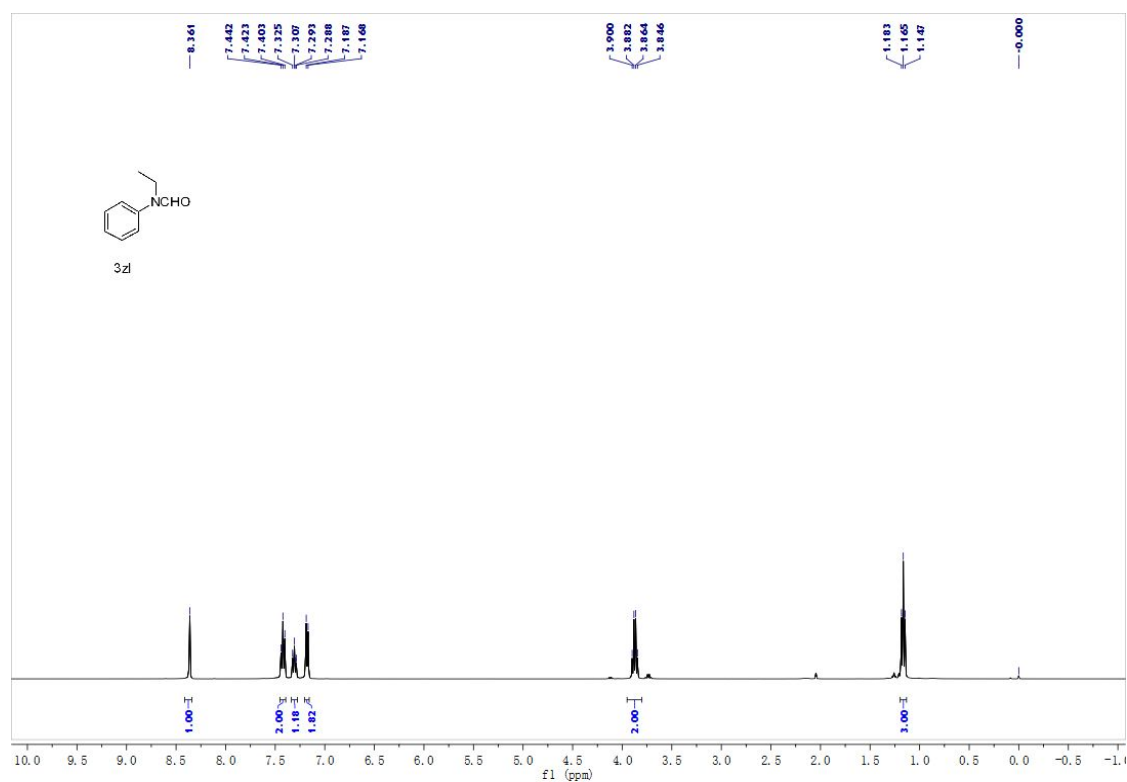
¹³C NMR spectra of **3zj**



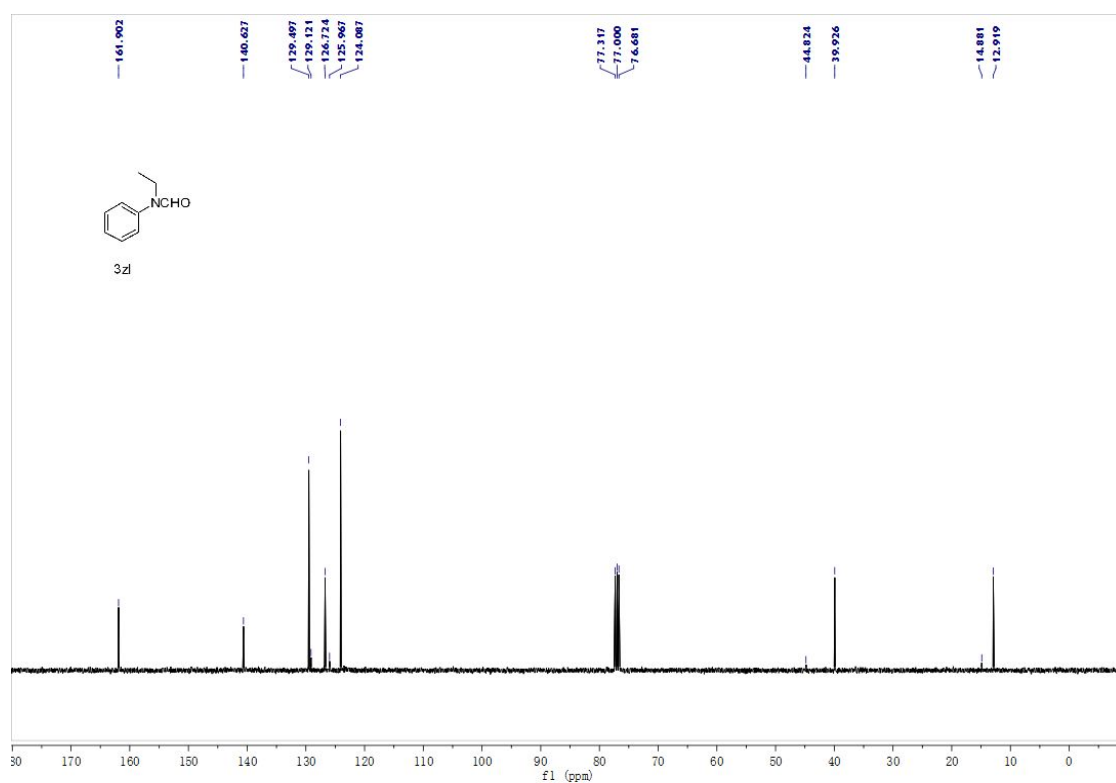
¹H NMR spectra of **3zk**



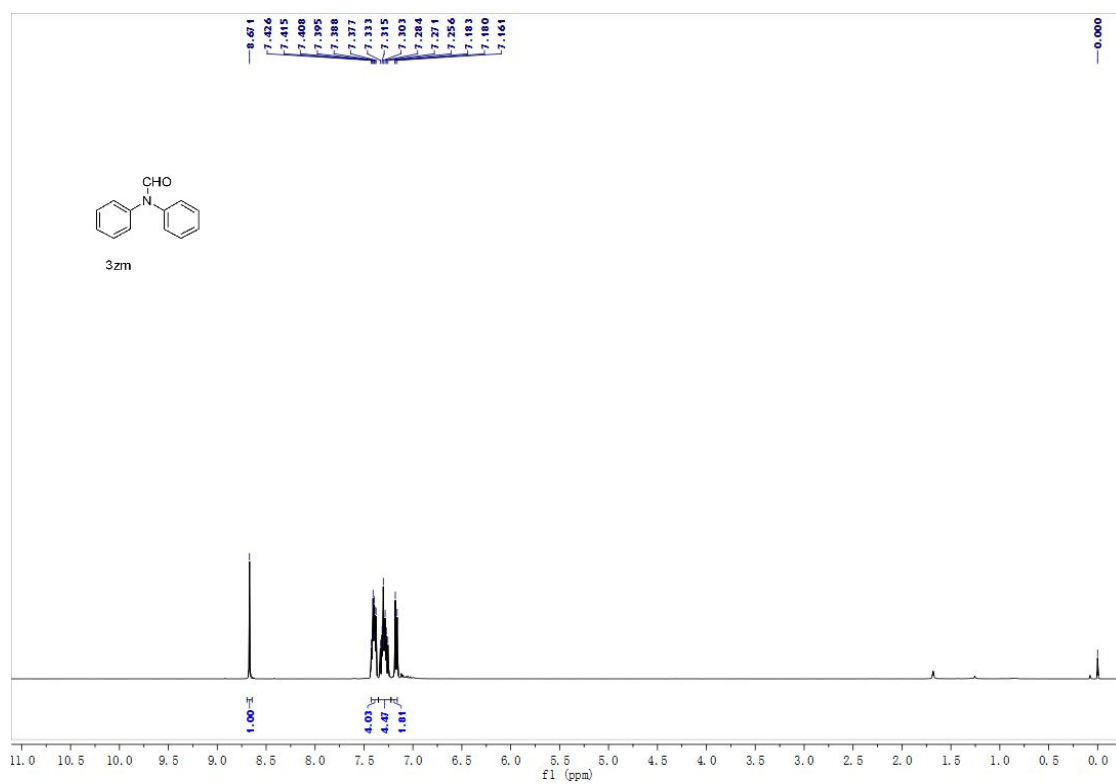
¹³C NMR spectra of **3zk**



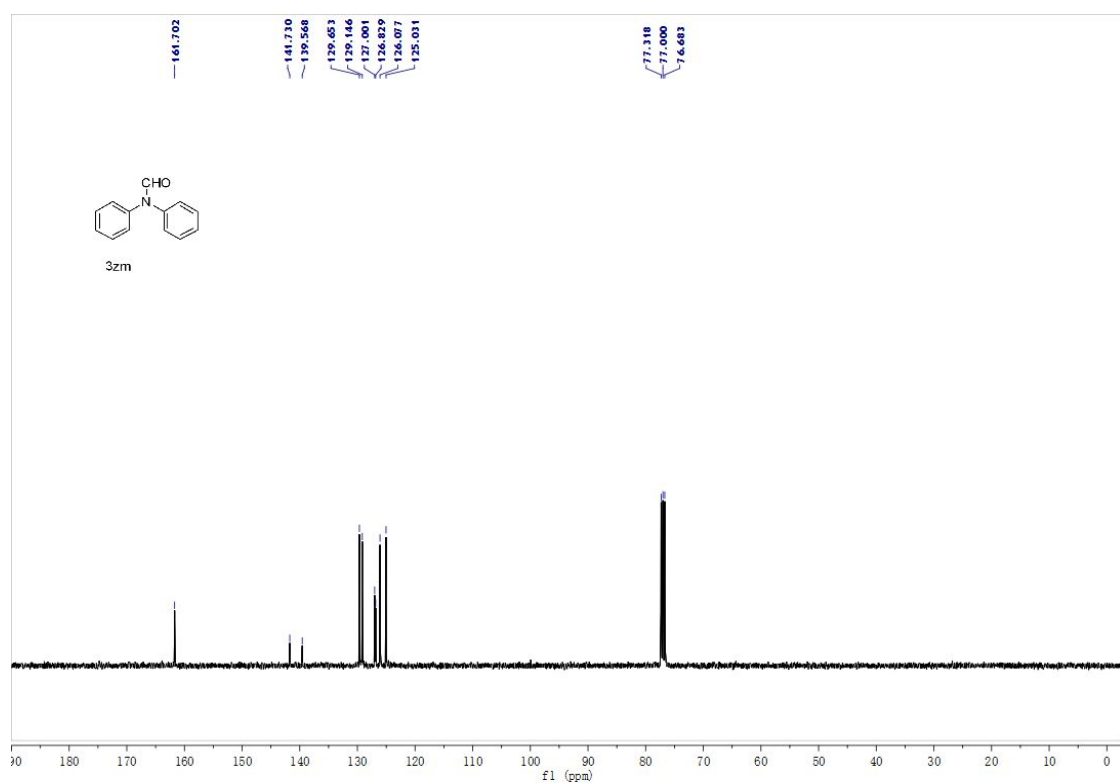
¹H NMR spectra of **3zl**



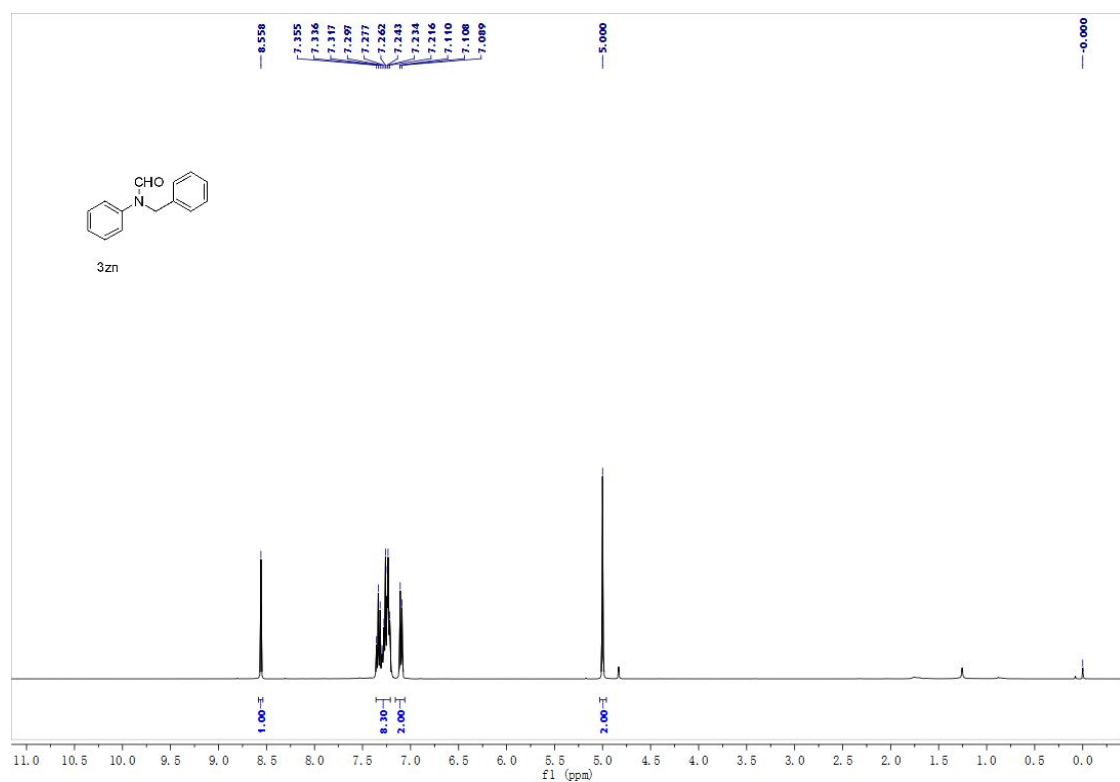
¹³C NMR spectra of **3zl**



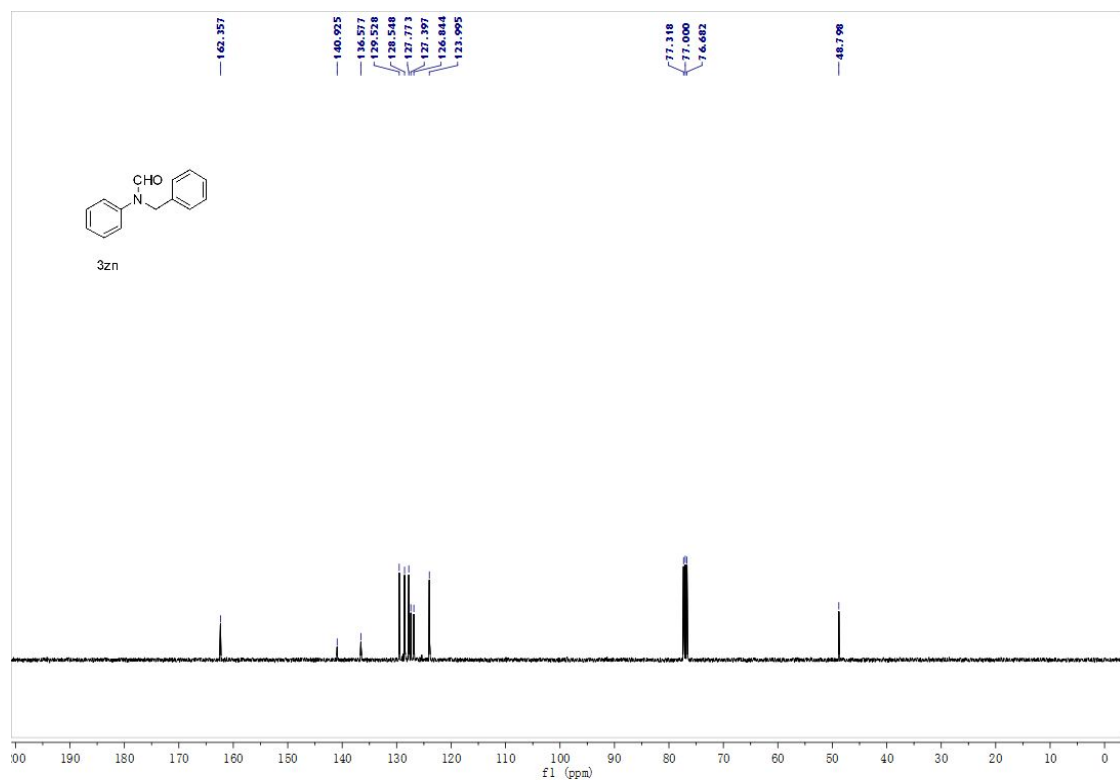
¹H NMR spectra of **3zm**



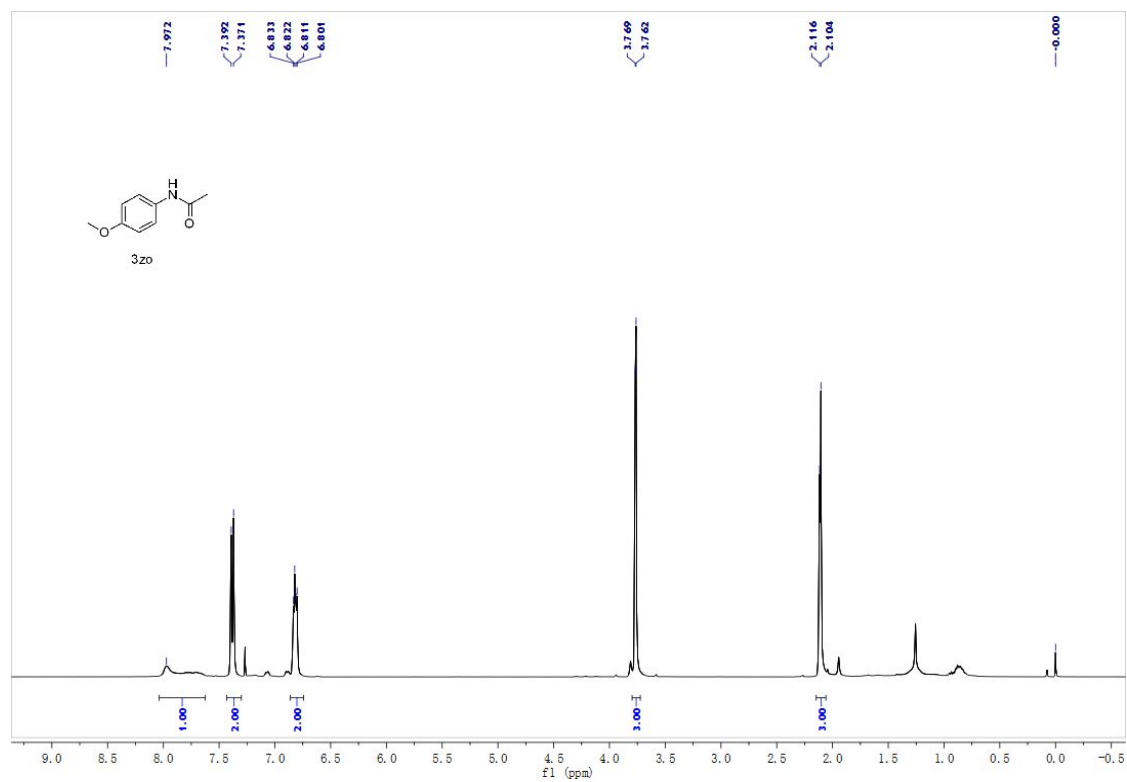
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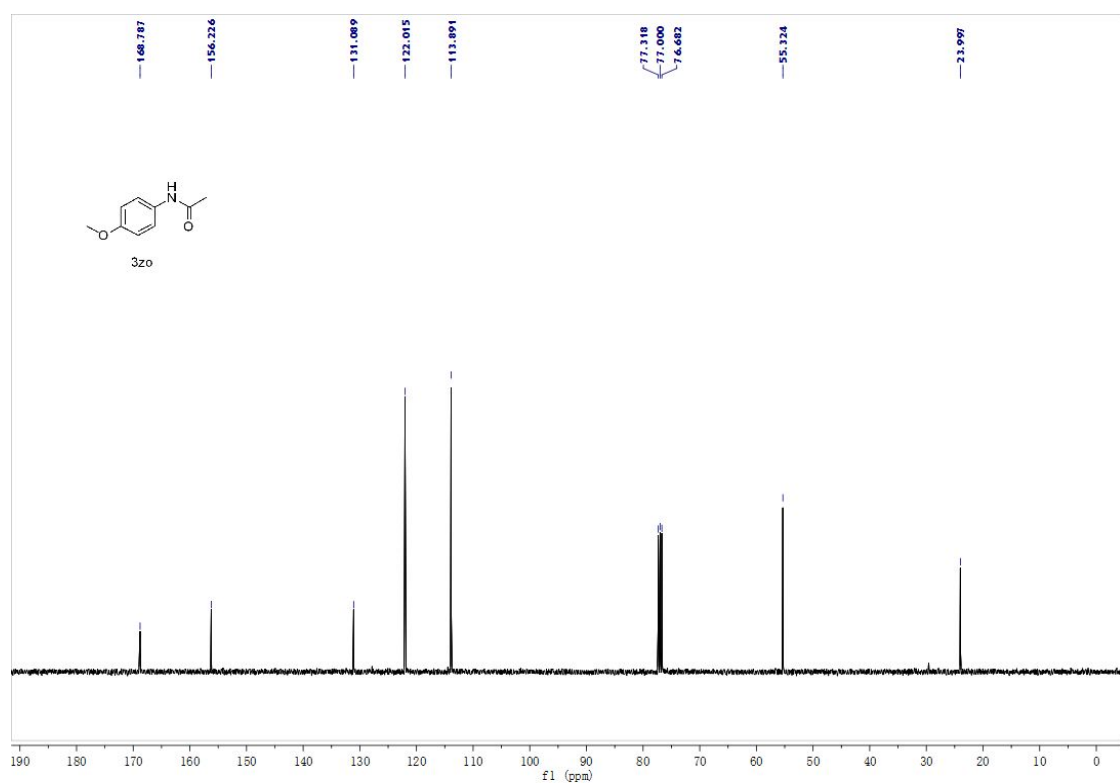
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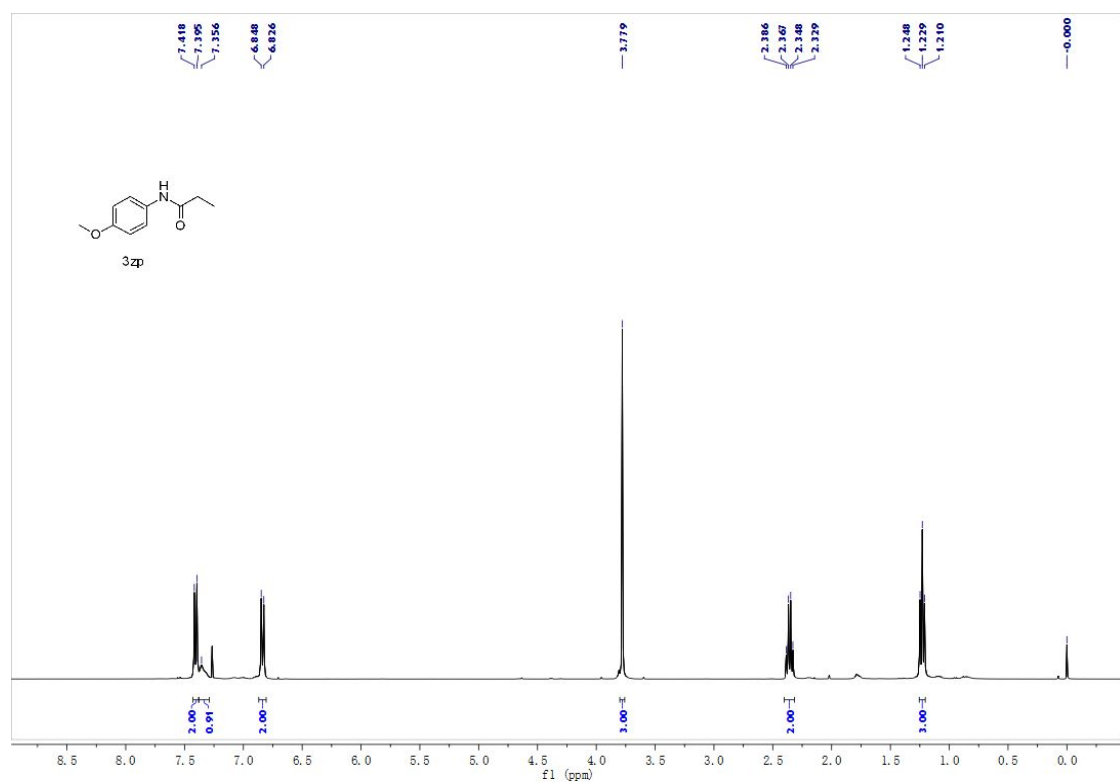
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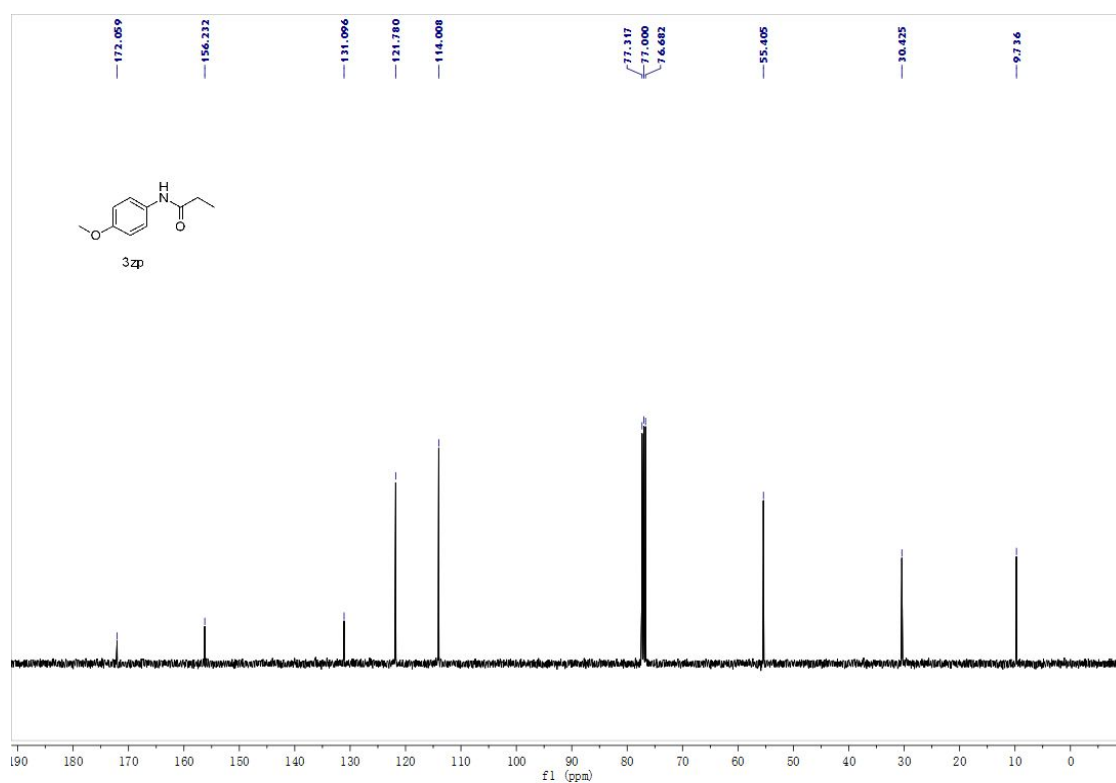
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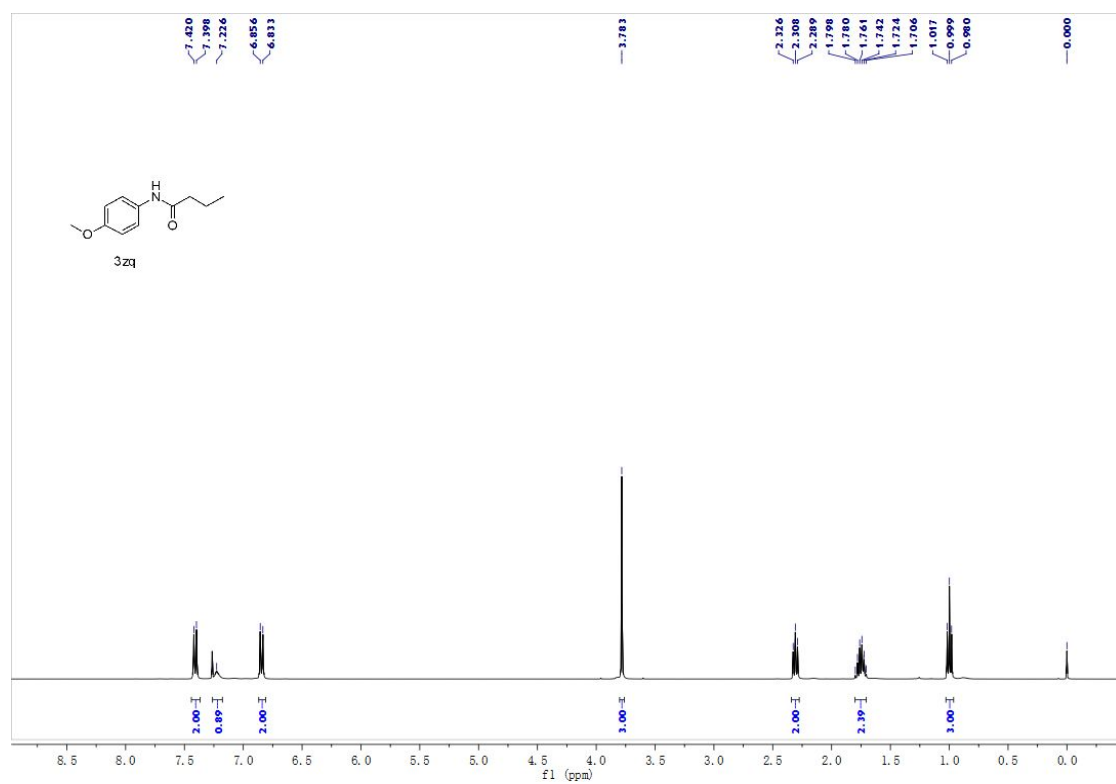
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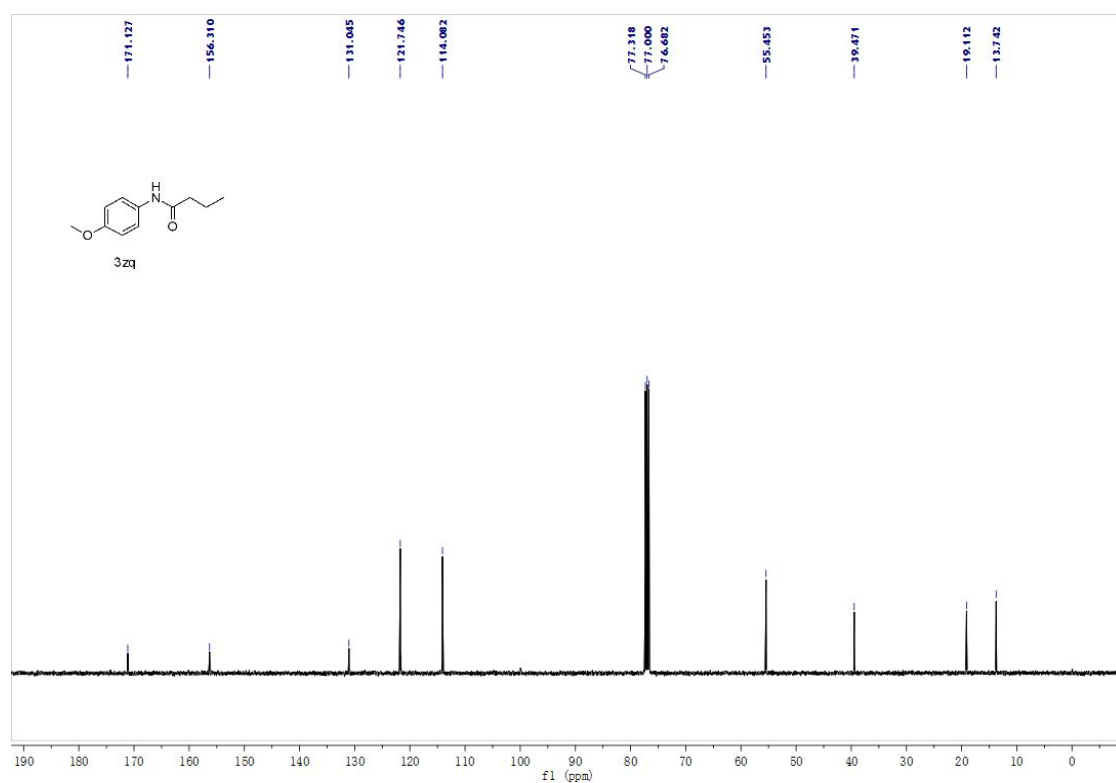
¹H NMR spectra of **3zp**



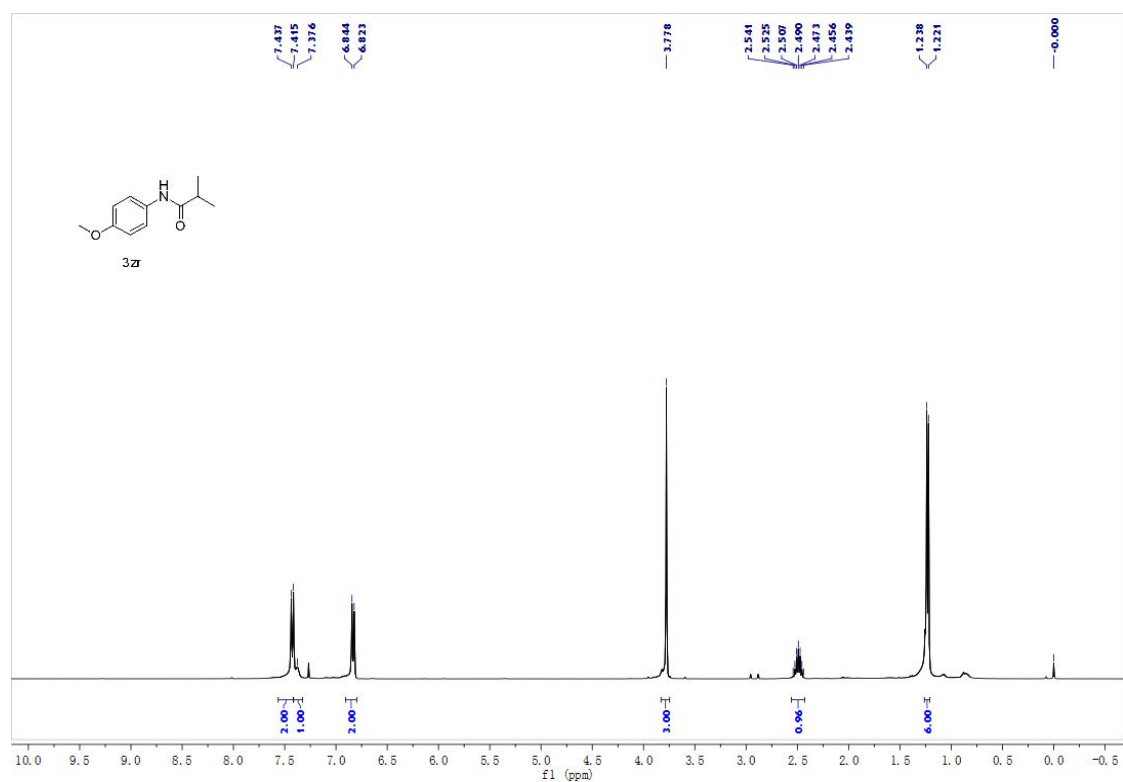
¹³C NMR spectra of **3zp**



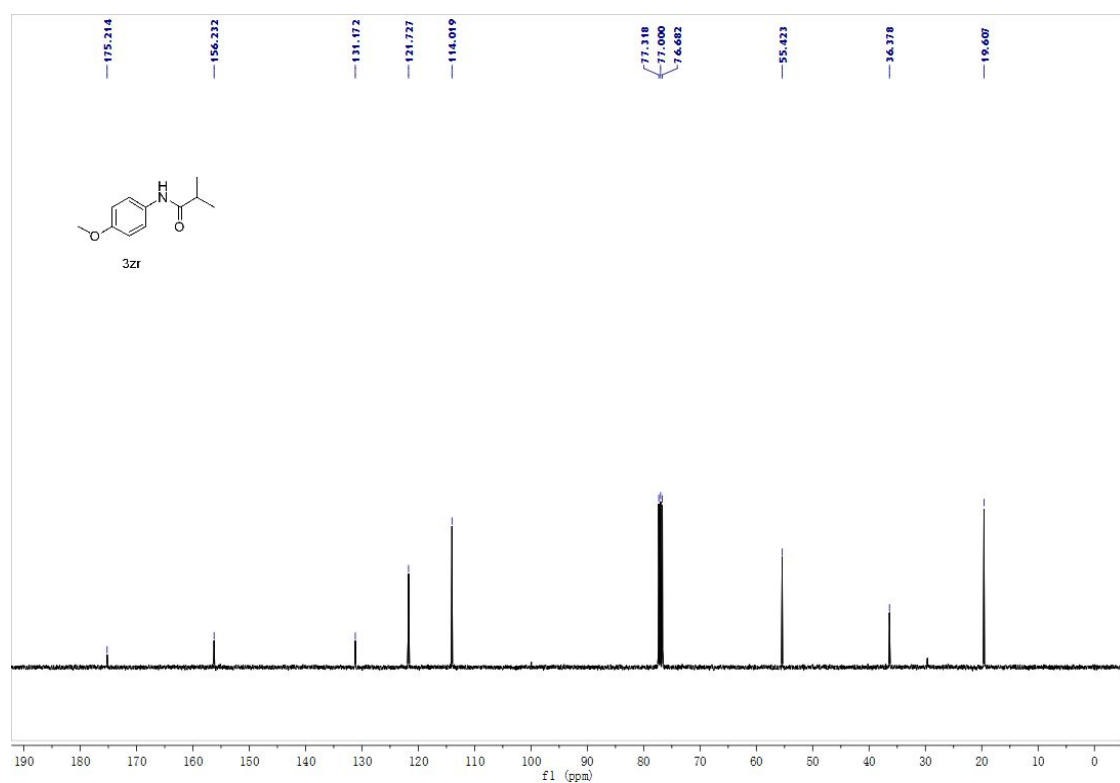
¹H NMR spectra of **3zq**



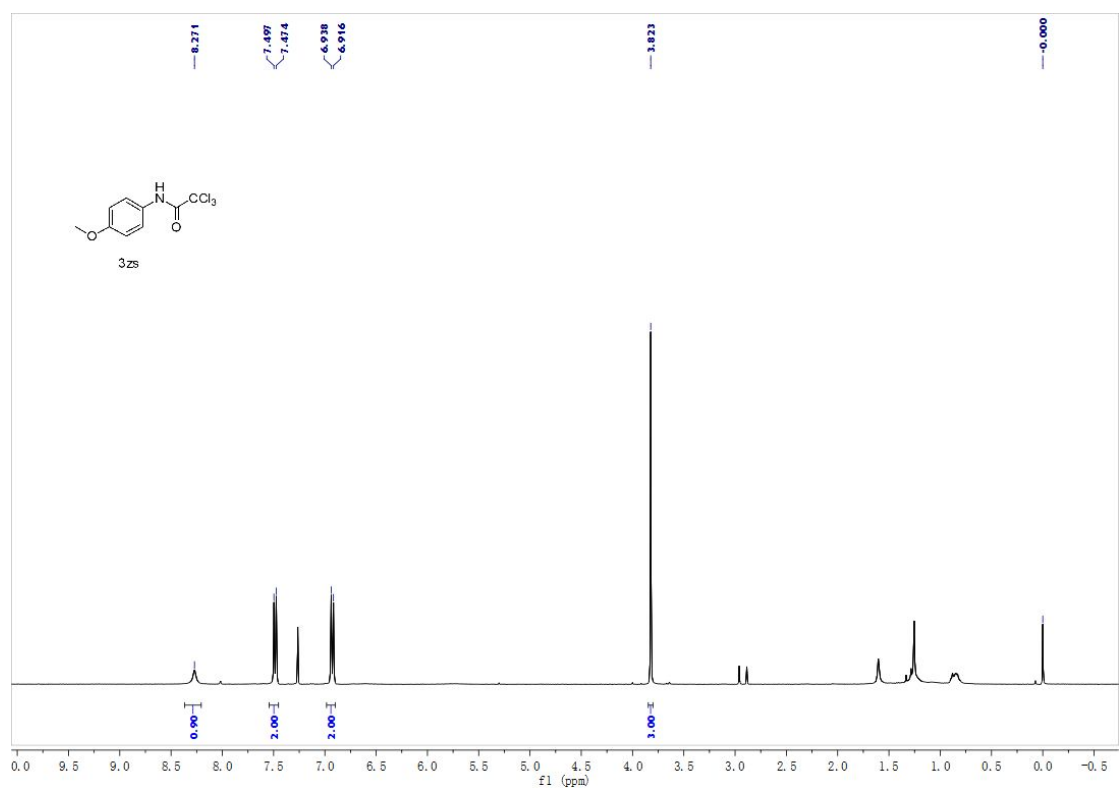
¹³C NMR spectra of **3zq**



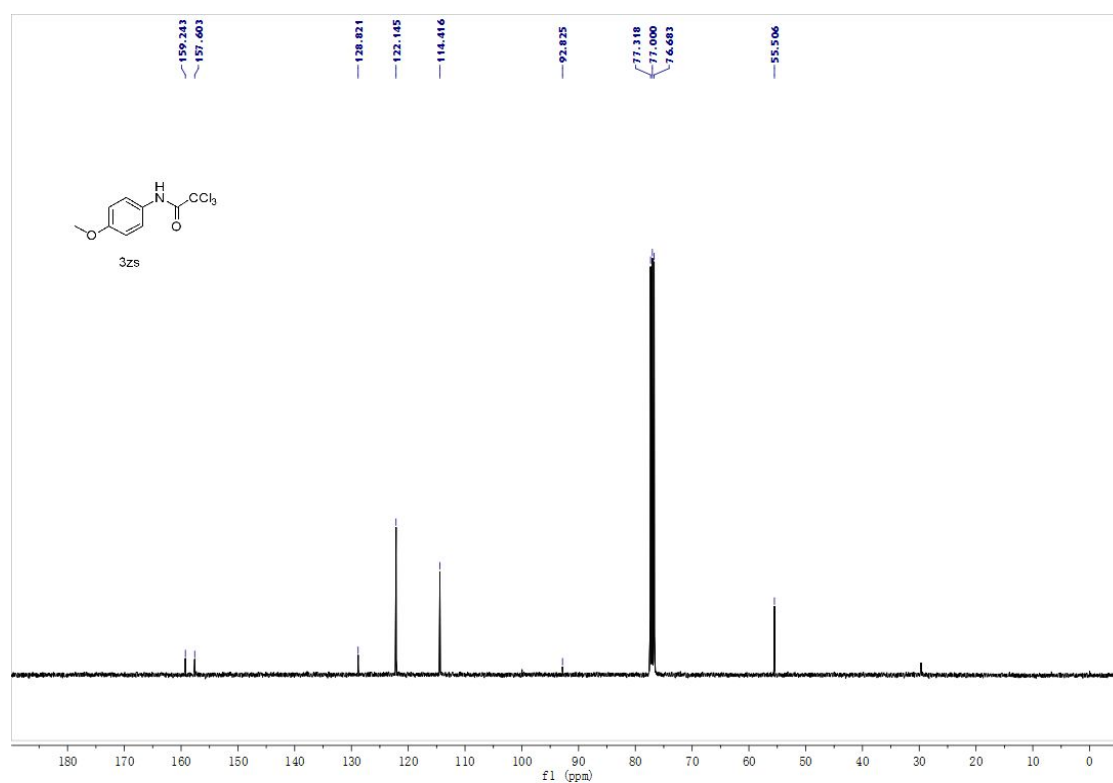
¹H NMR spectra of **3zr**



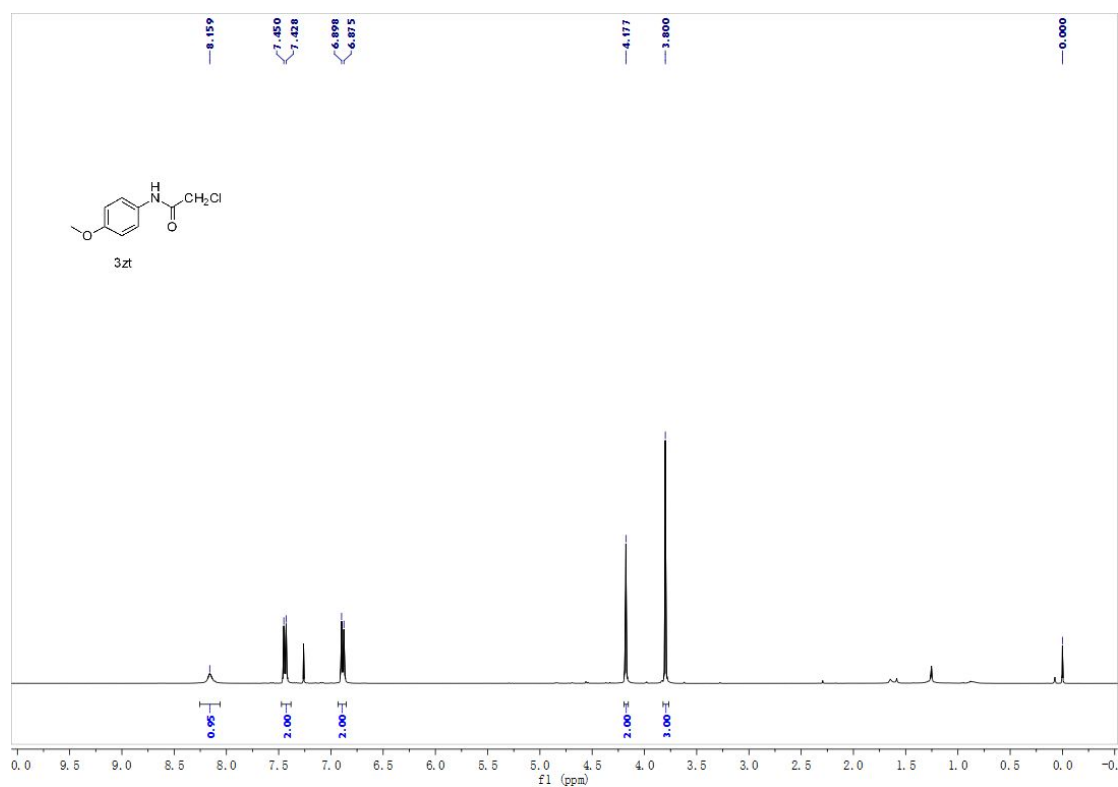
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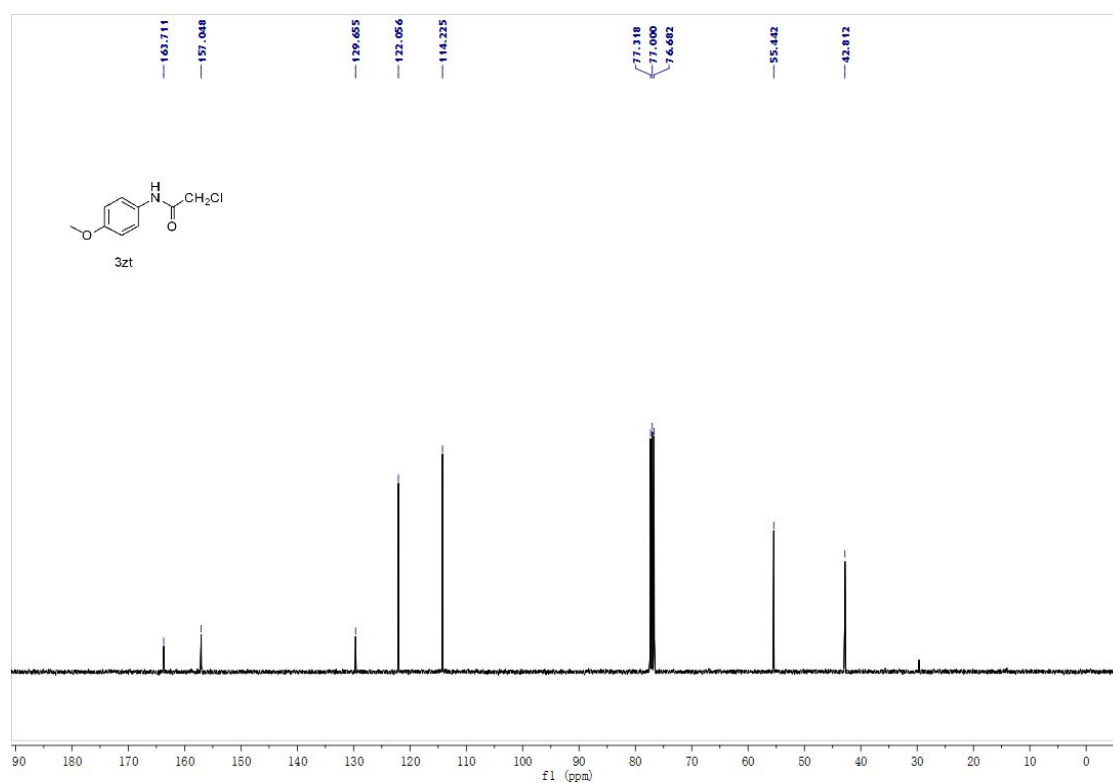
¹H NMR spectra of **3zs**



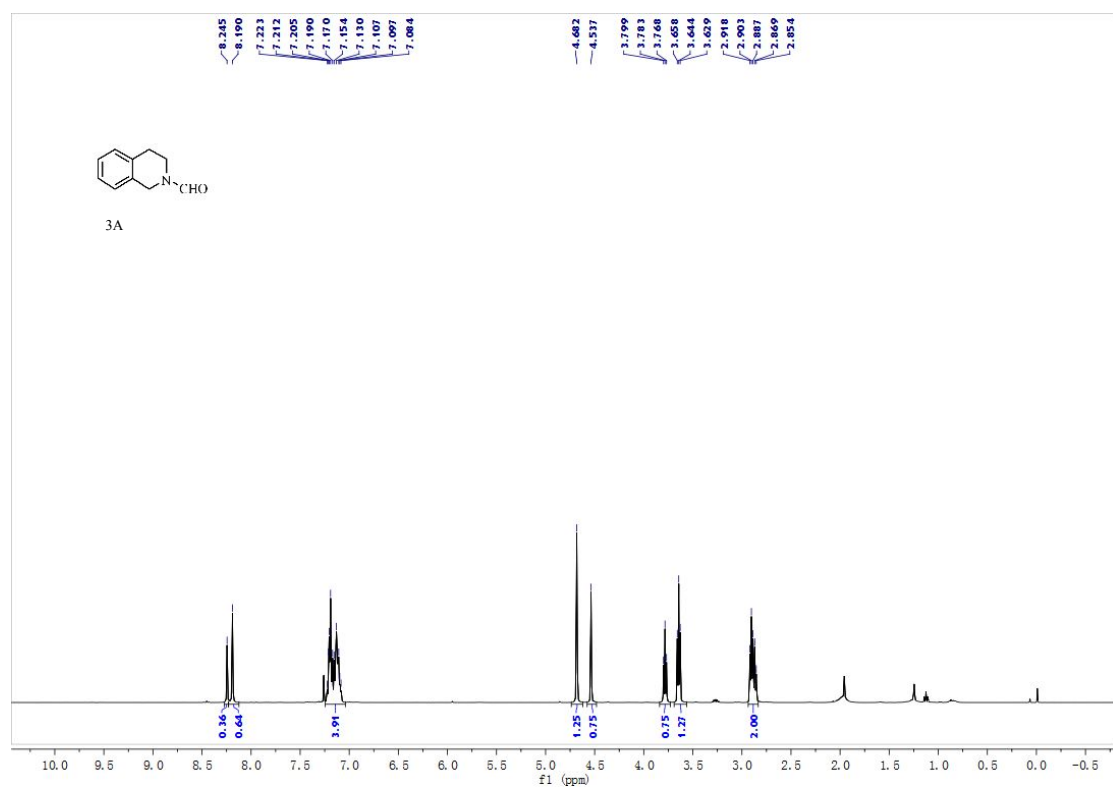
¹³C NMR spectra of **3zs**



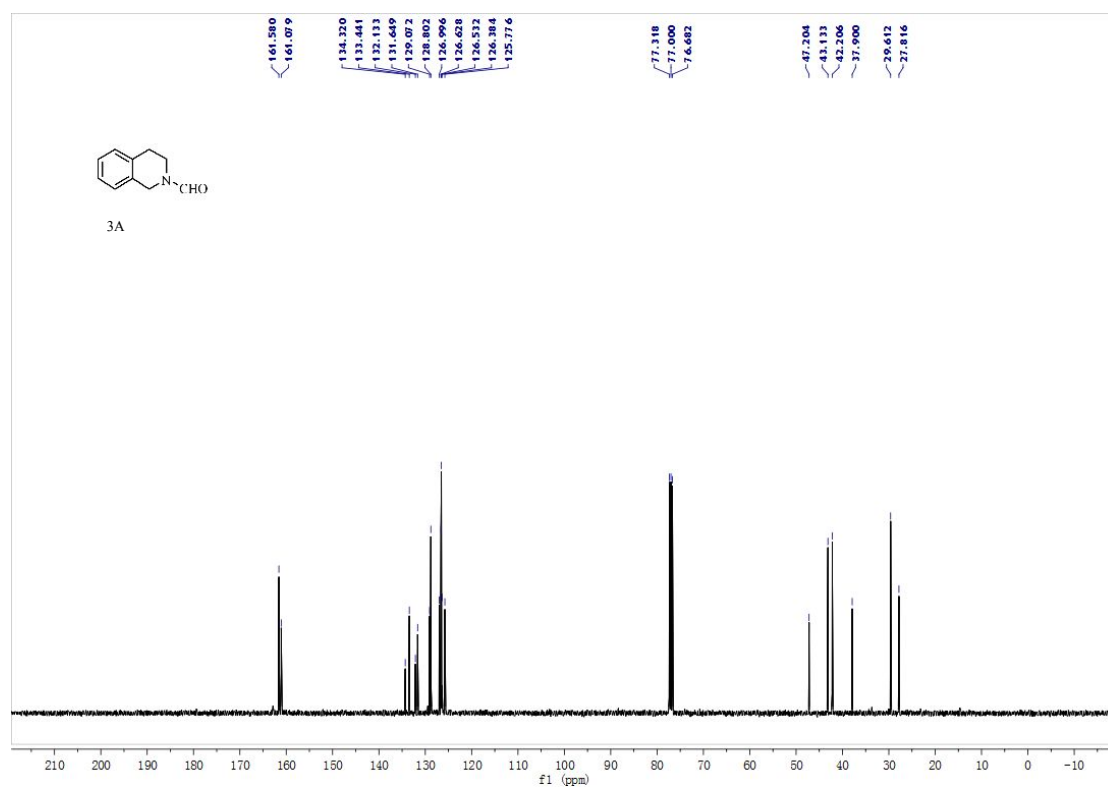
¹H NMR spectra of **3zt**



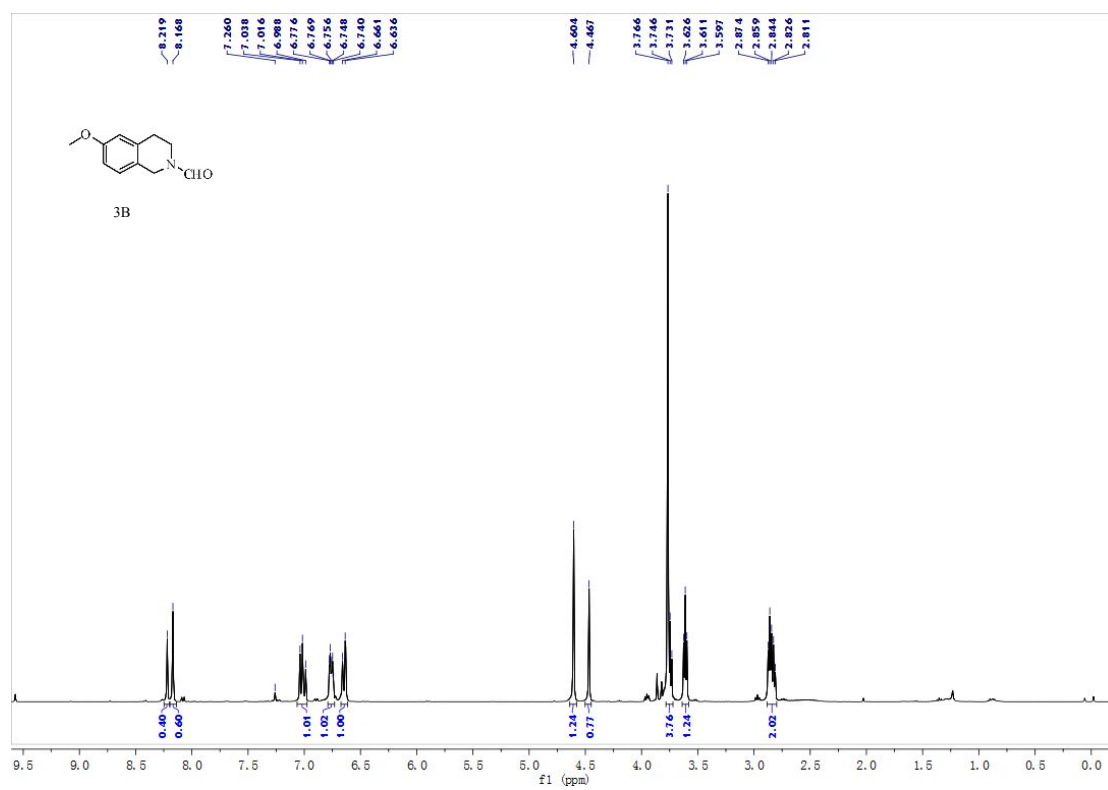
¹³C NMR spectra of **3zt**



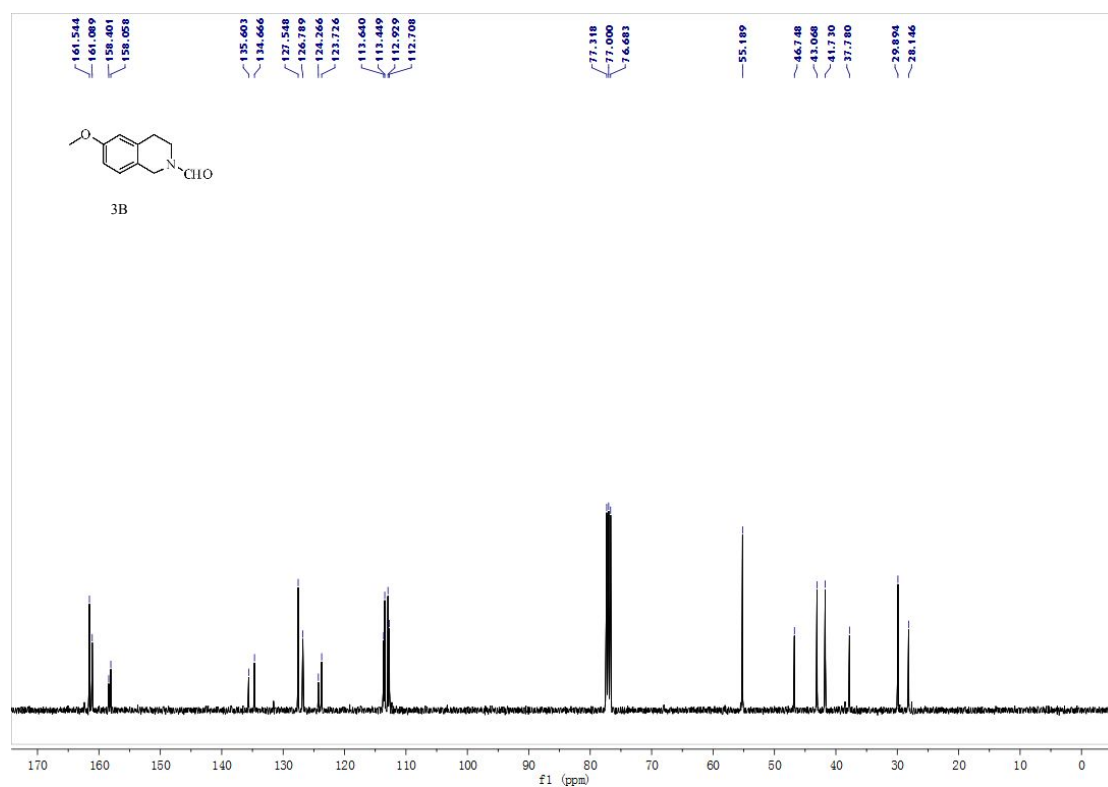
¹H NMR spectra of **3A**



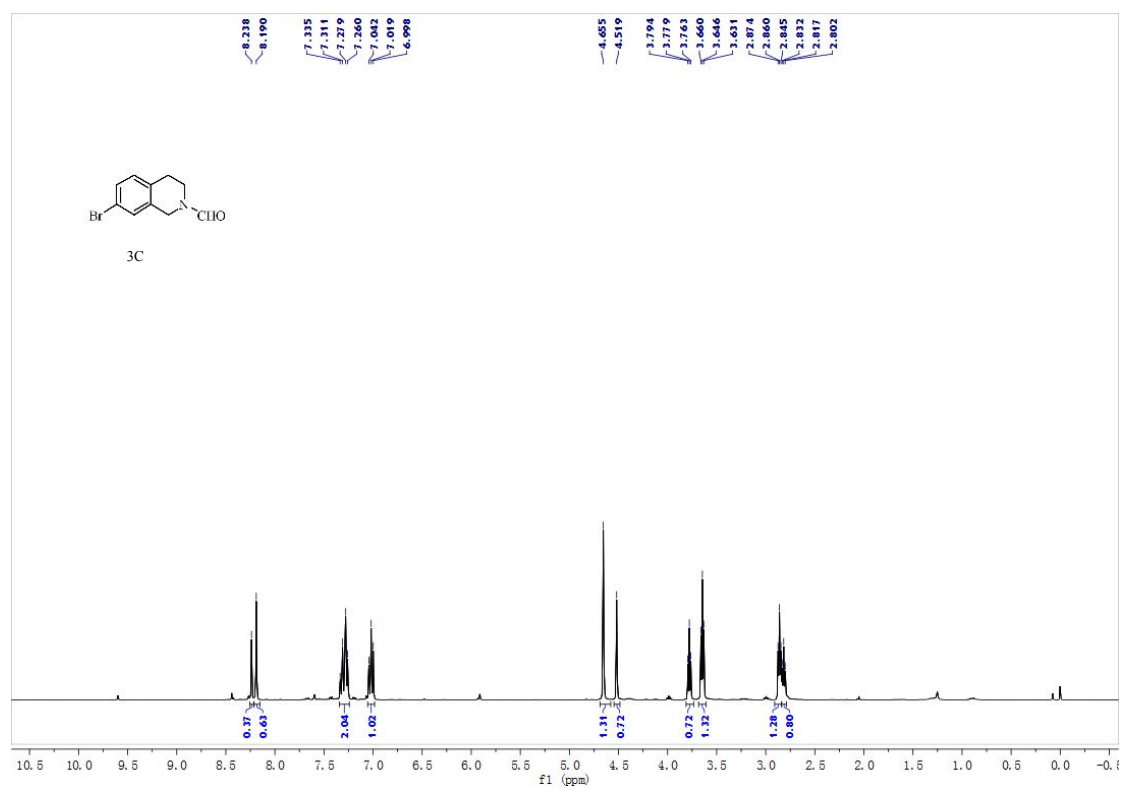
¹³C NMR spectra of 3A



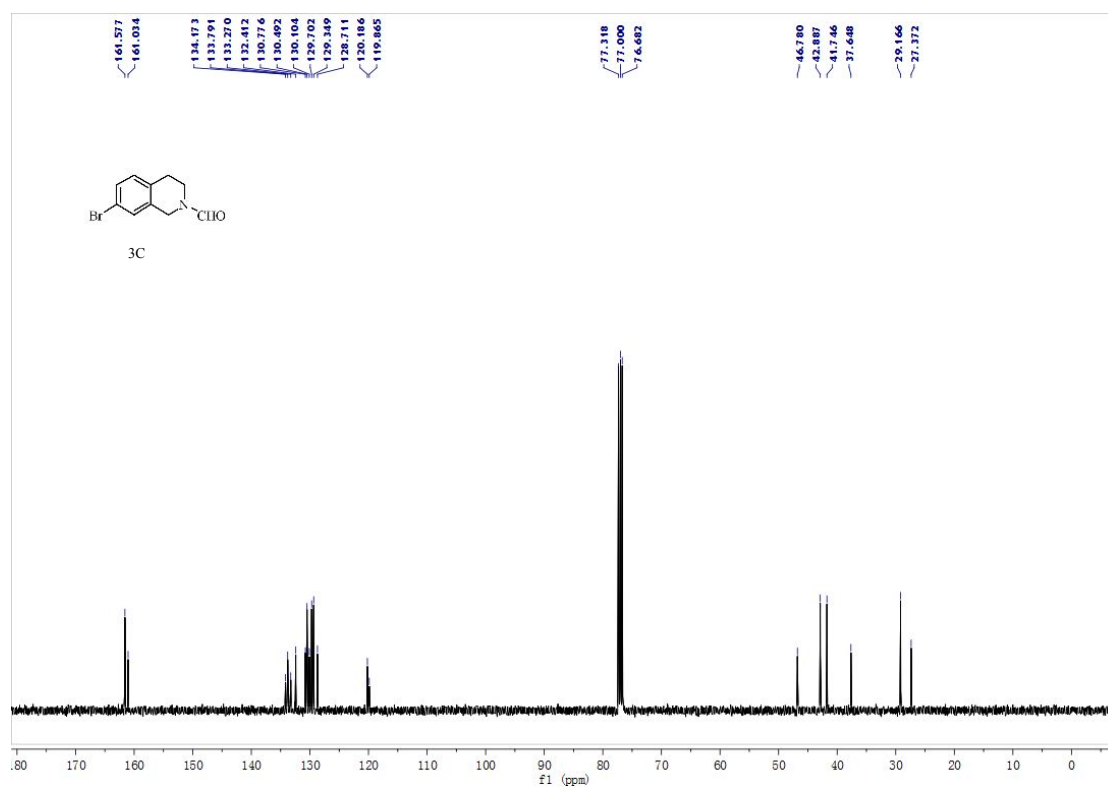
¹H NMR spectra of 3B



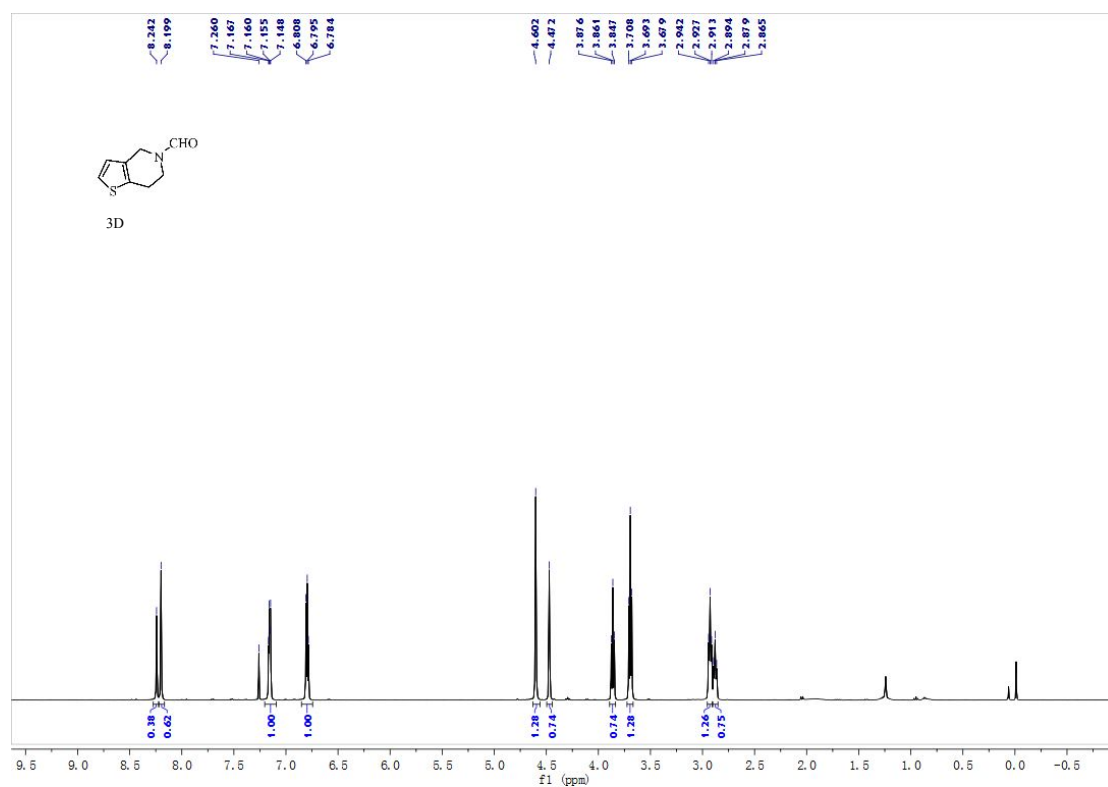
¹³C NMR spectra of **3B**



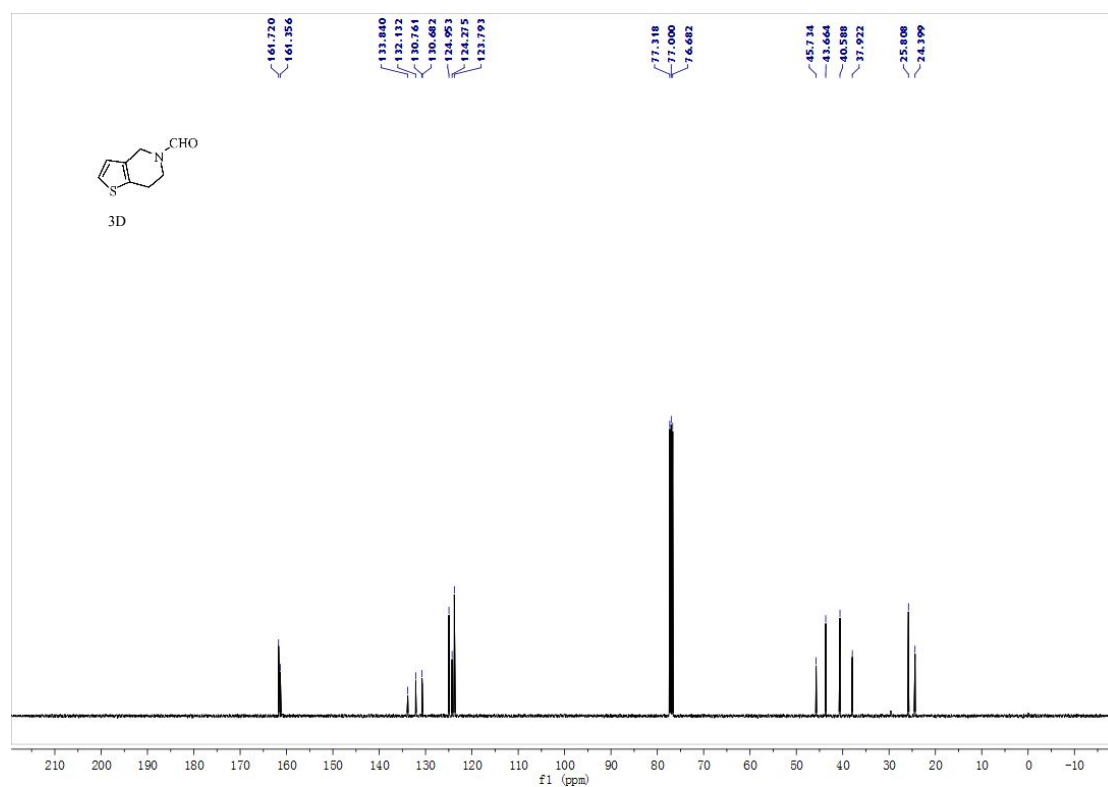
¹H NMR spectra of **3C**



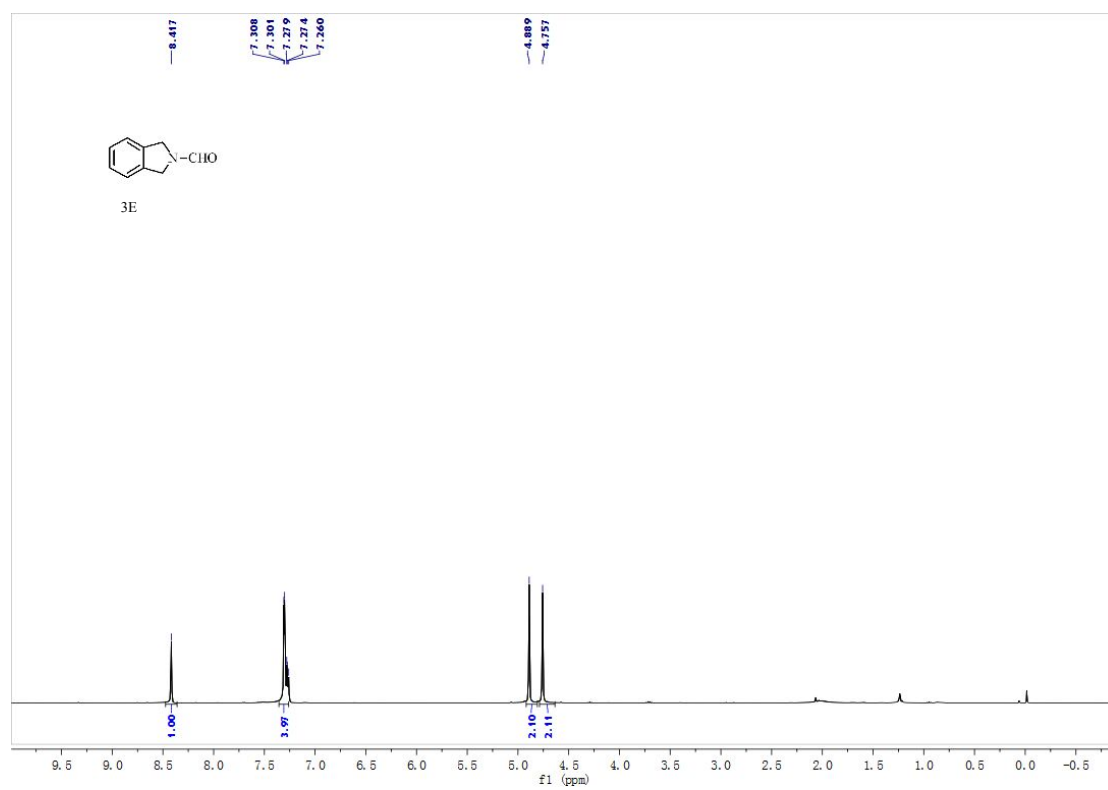
¹³C NMR spectra of **3C**



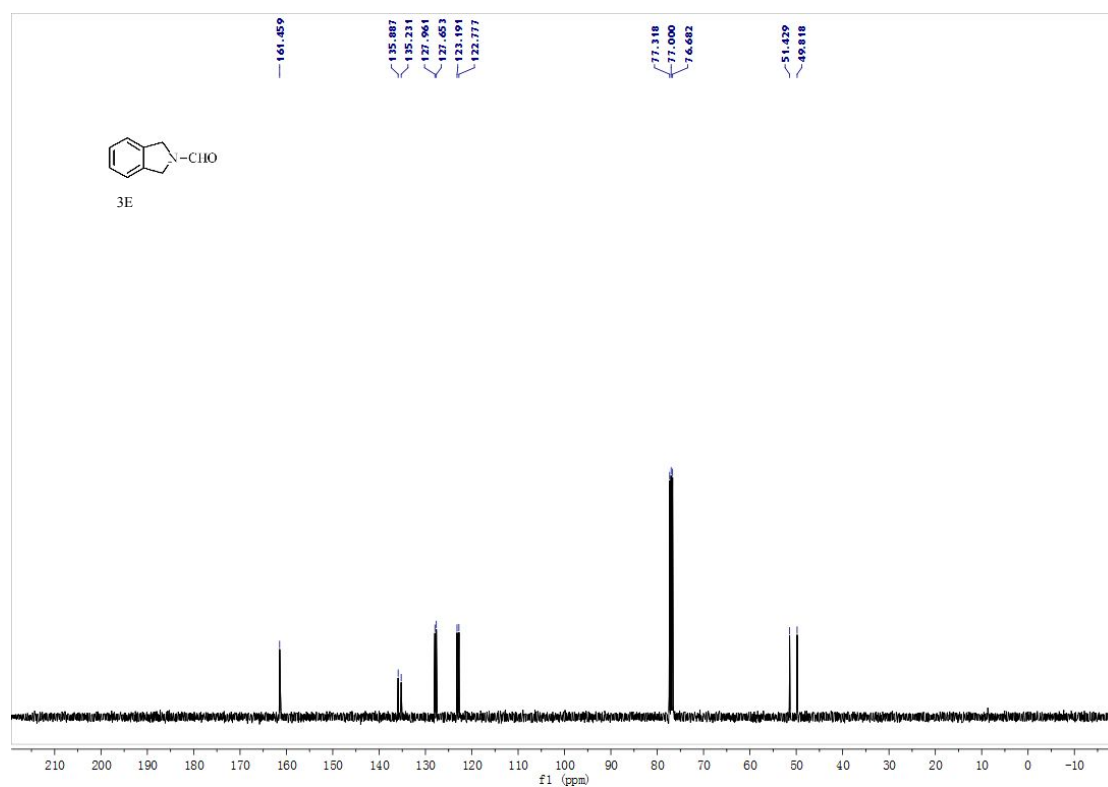
¹H NMR spectra of **3D**



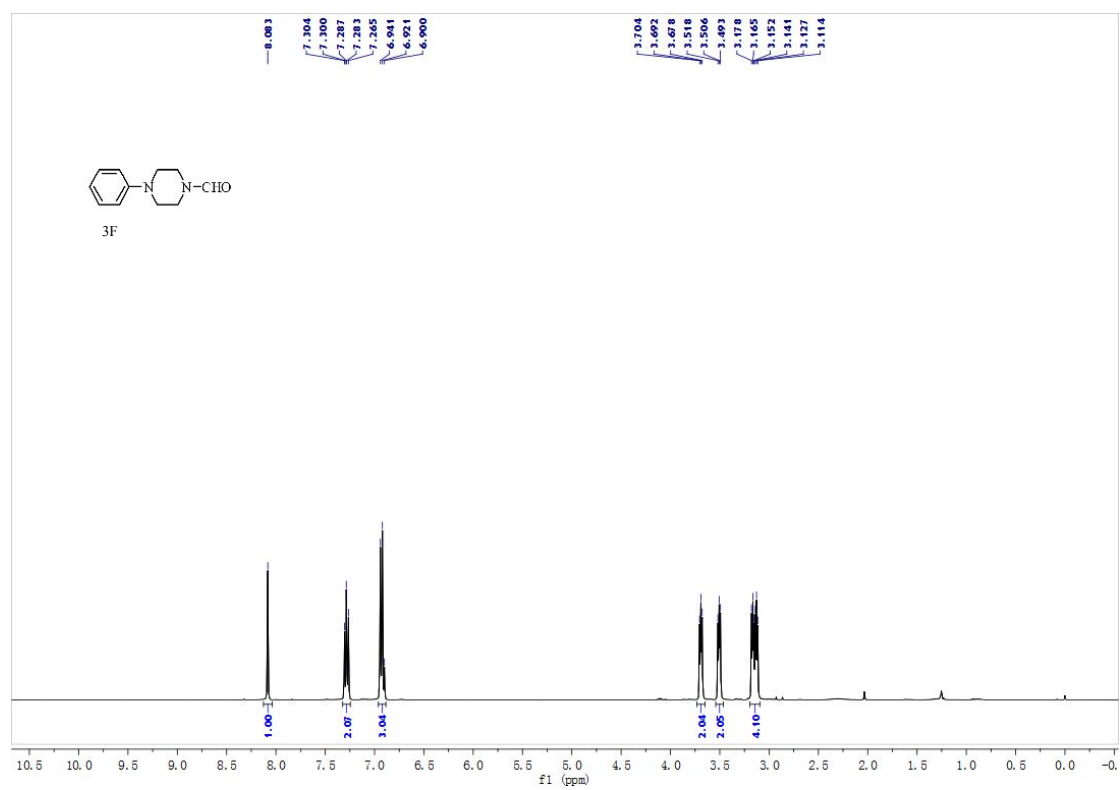
¹³C NMR spectra of **3D**



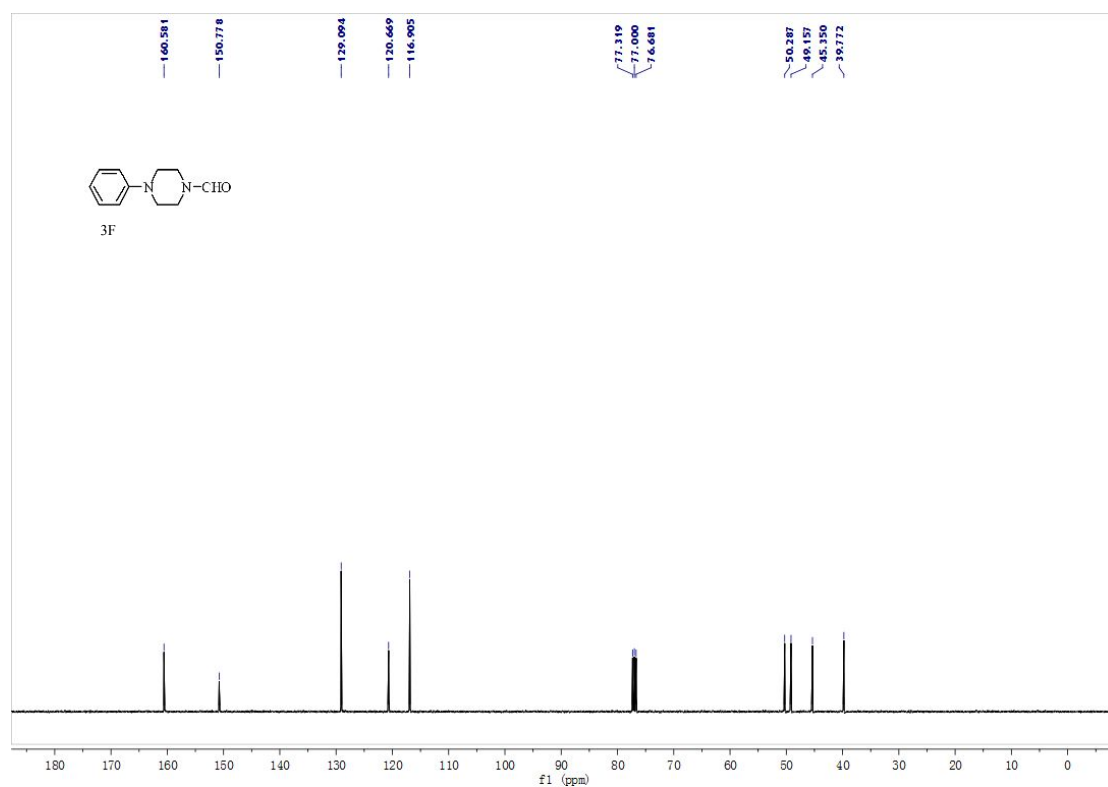
¹H NMR spectra of **3E**



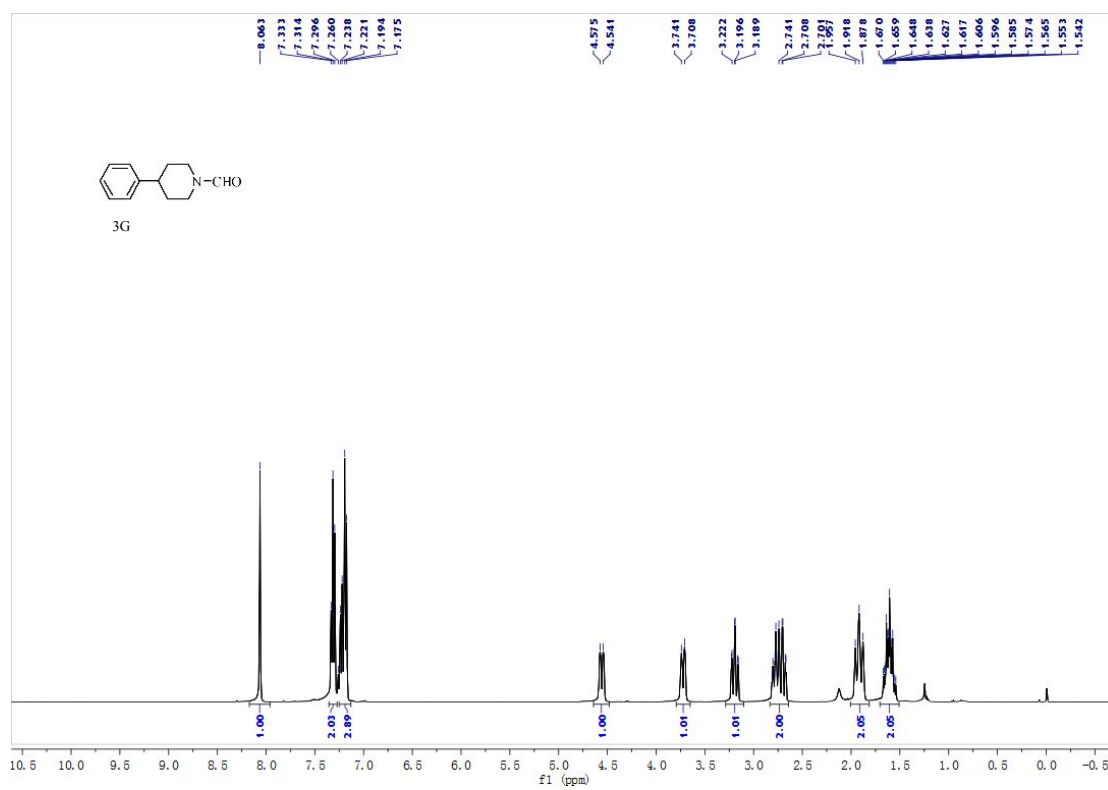
¹³C NMR spectra of **3E**



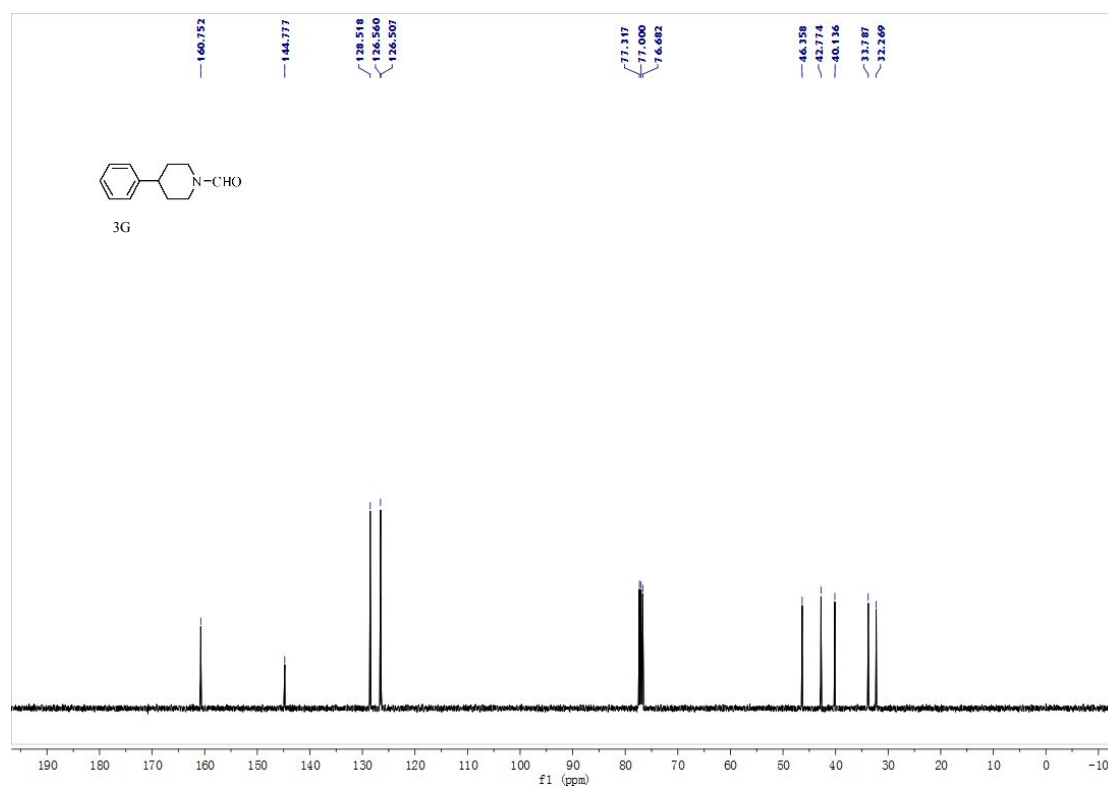
¹H NMR spectra of **3F**



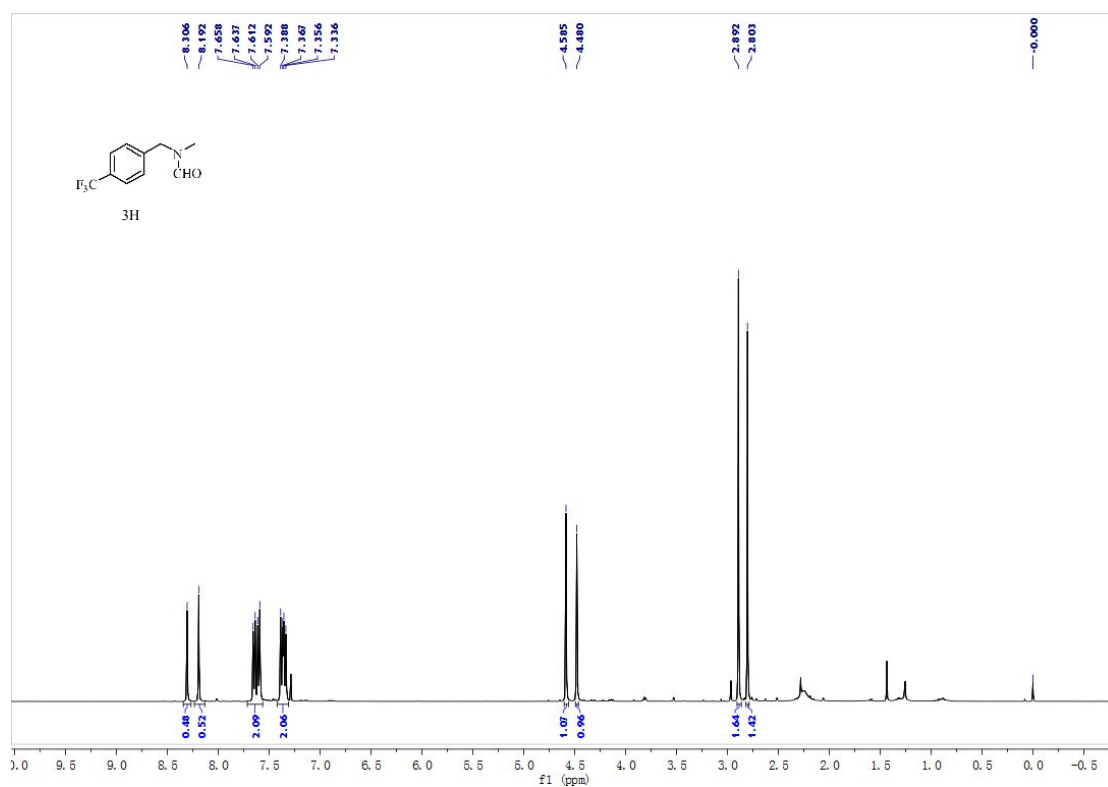
¹³C NMR spectra of **3F**



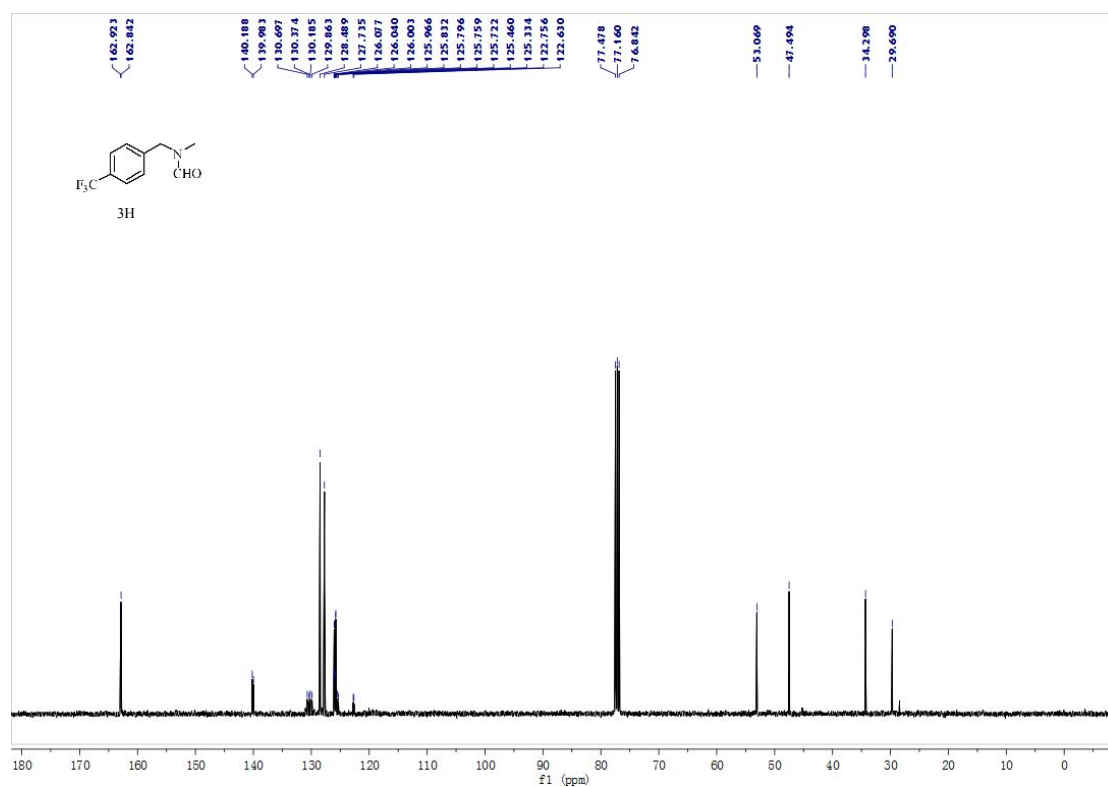
¹H NMR spectra of **3G**



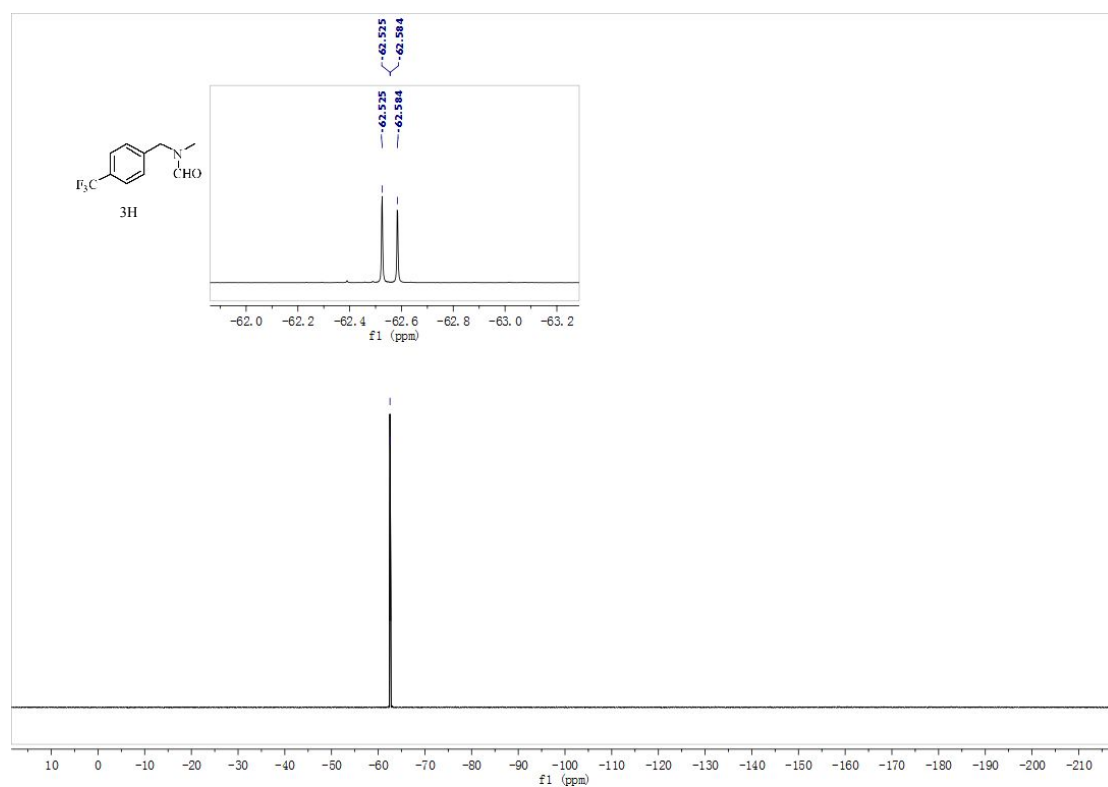
¹³C NMR spectra of **3G**



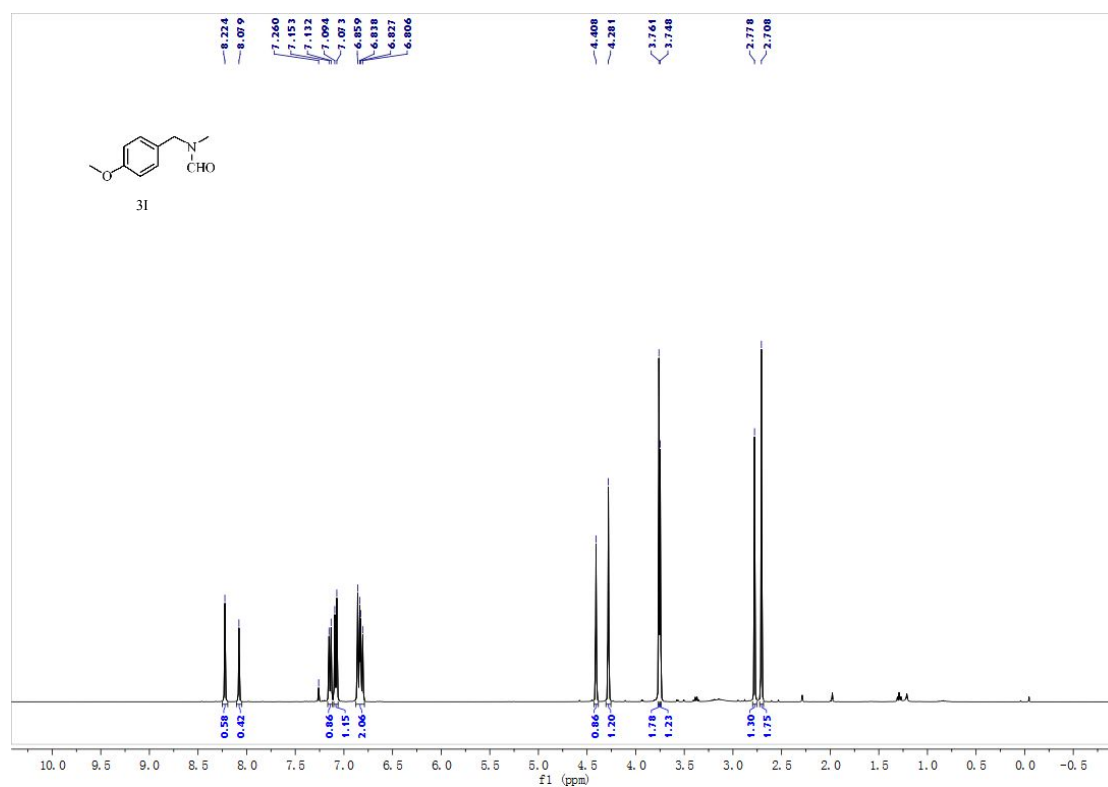
¹H NMR spectra of **3H**



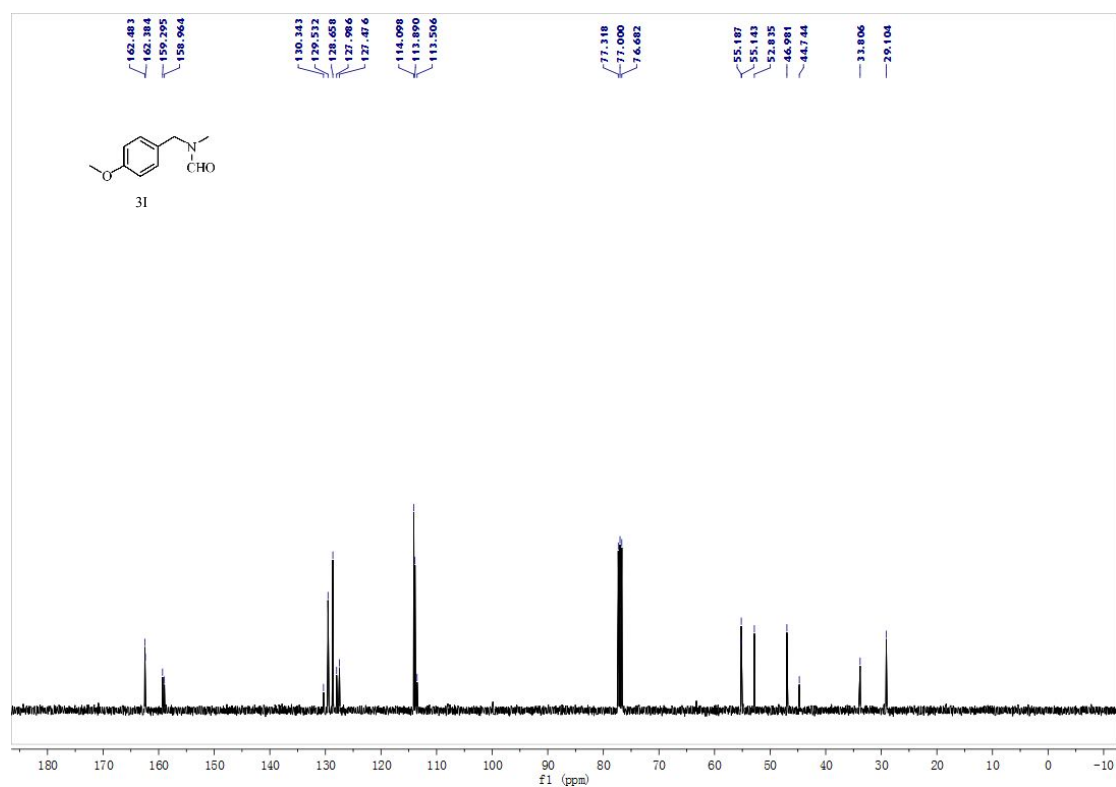
¹³C NMR spectra of **3H**



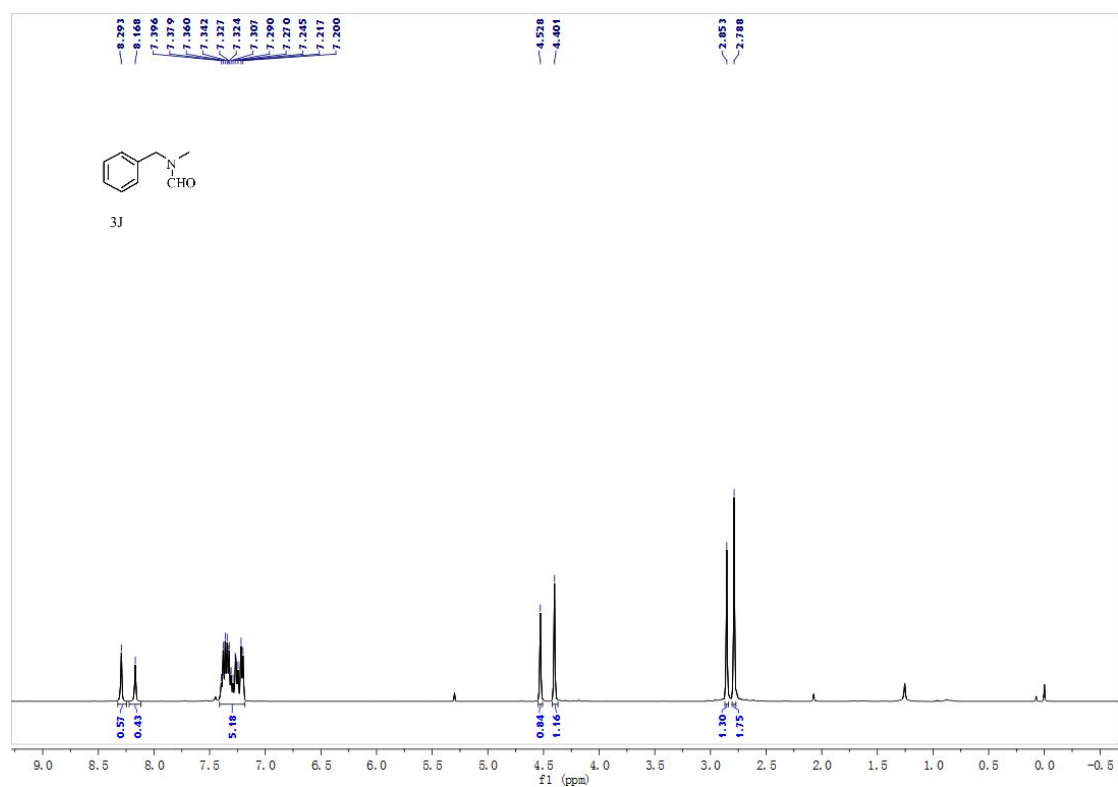
¹⁹F NMR spectra of **3H**



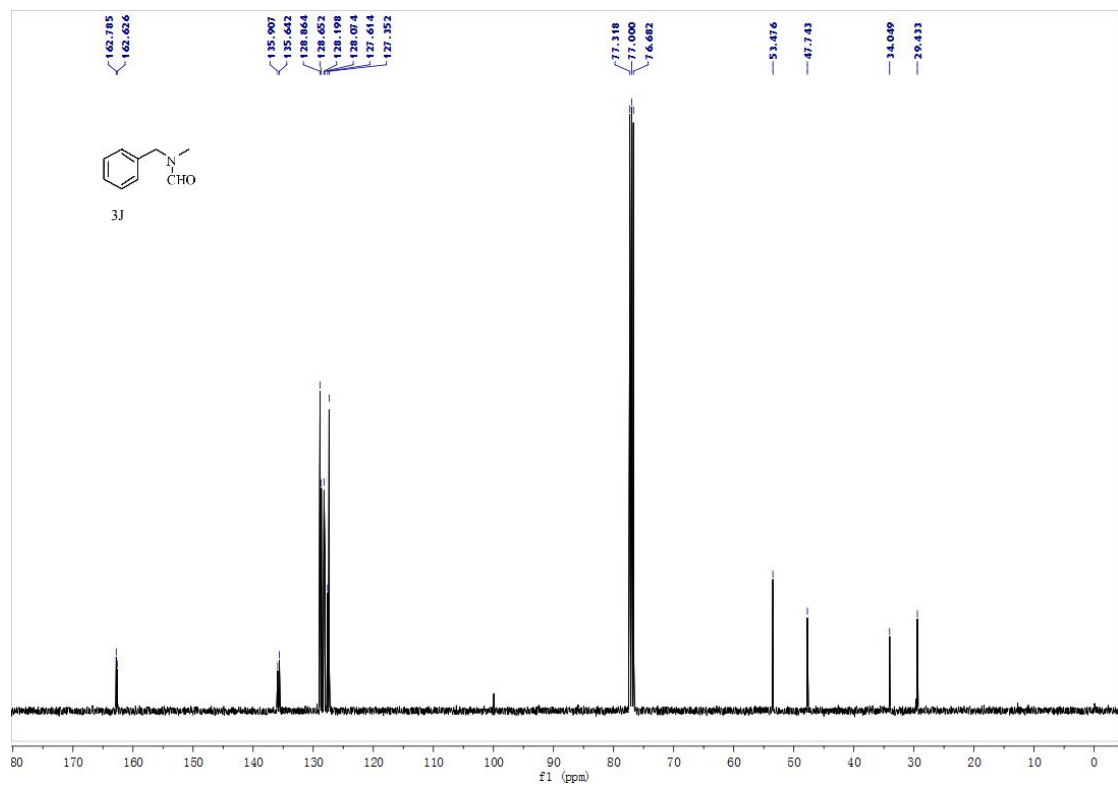
¹H NMR spectra of **3I**



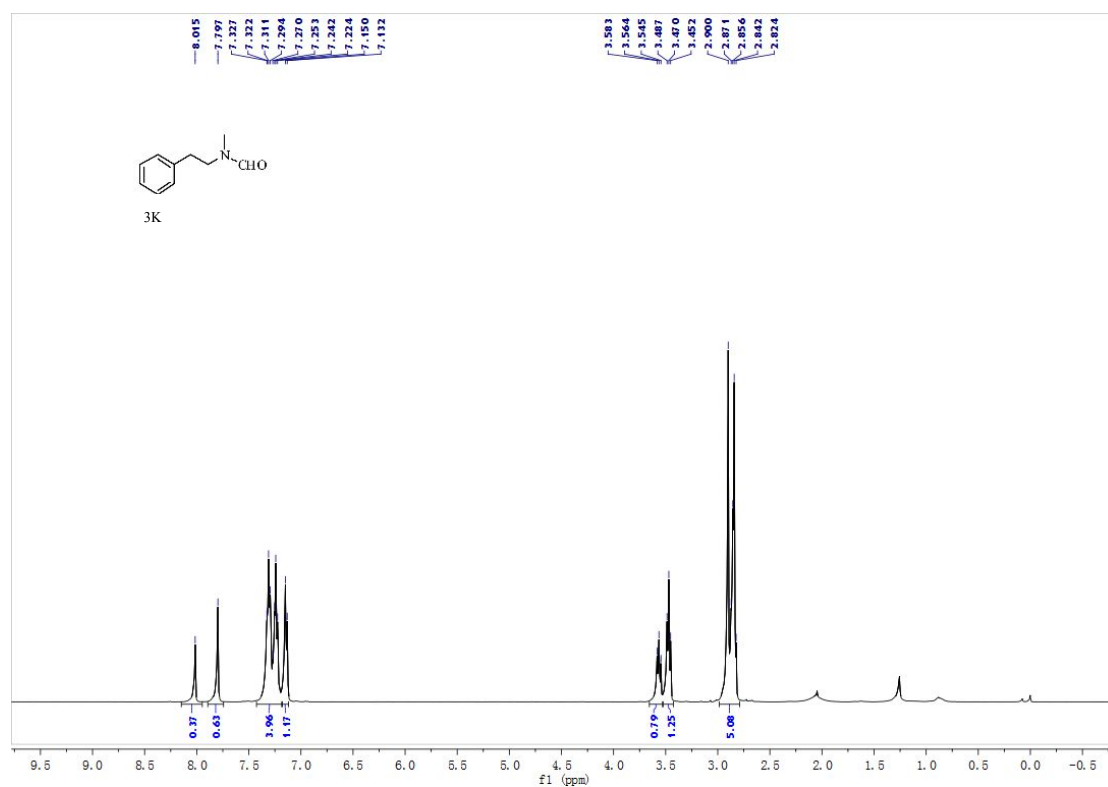
¹³C NMR spectra of **3I**



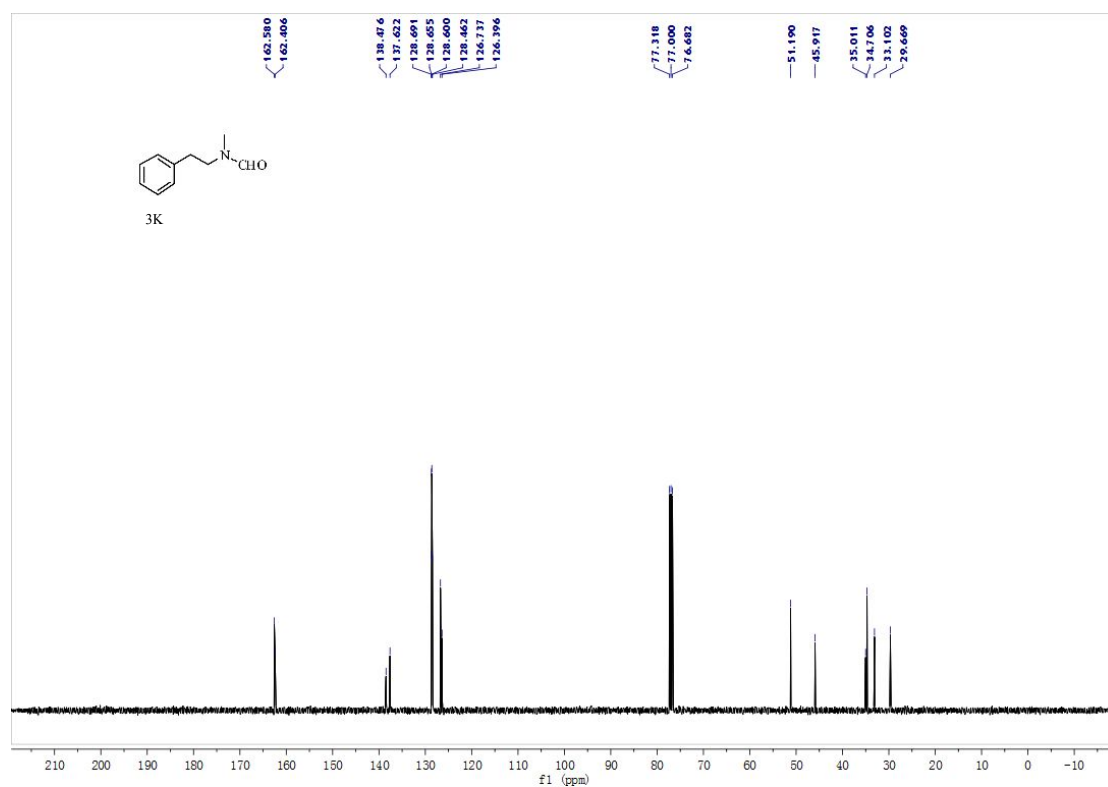
¹H NMR spectra of **3J**



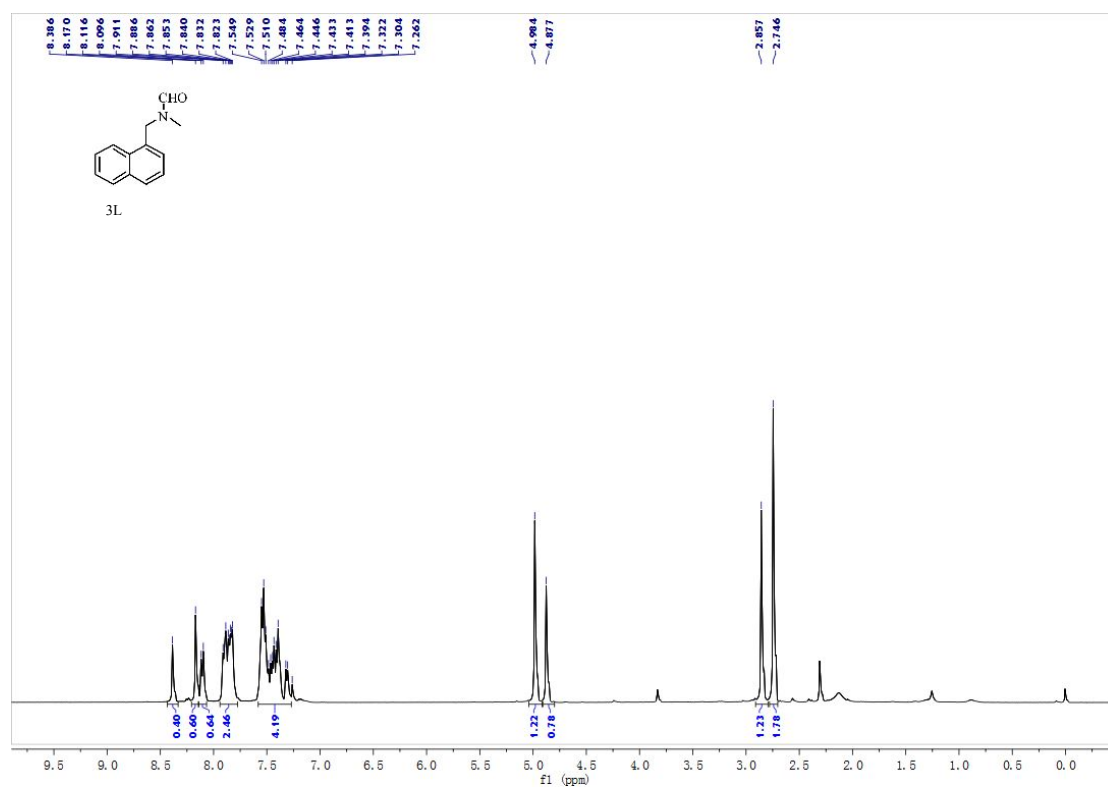
¹³C NMR spectra of **3J**



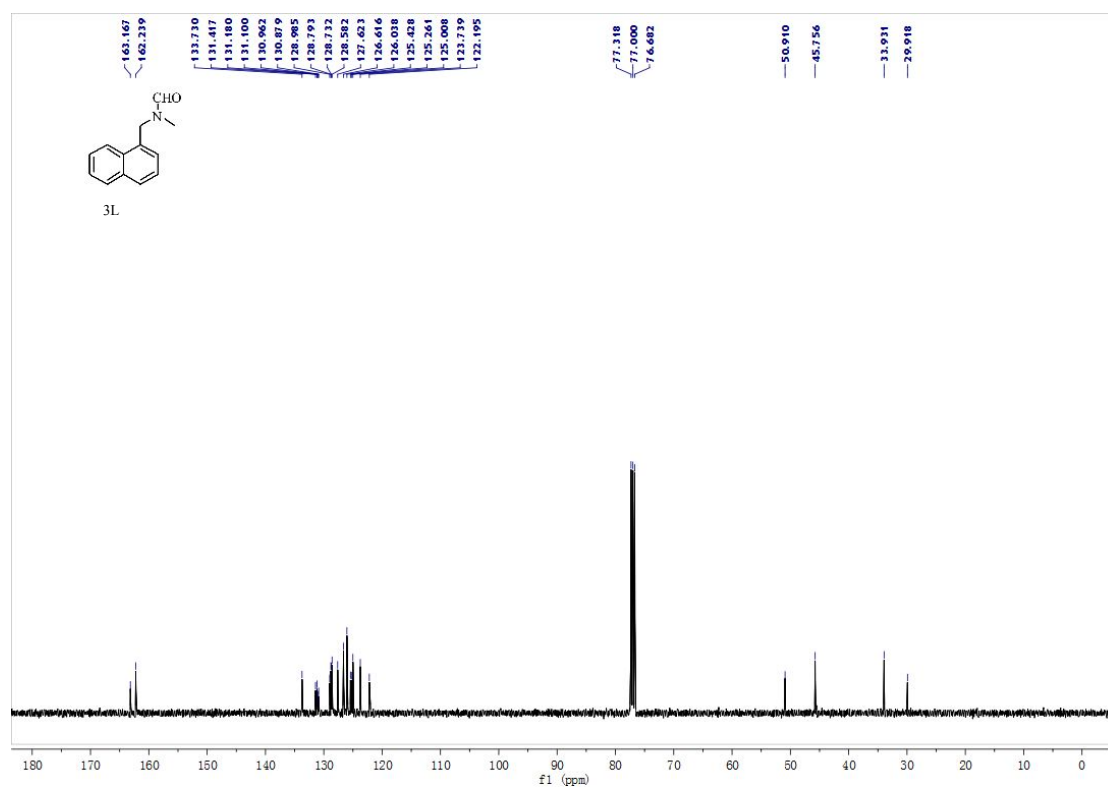
¹H NMR spectra of 3K



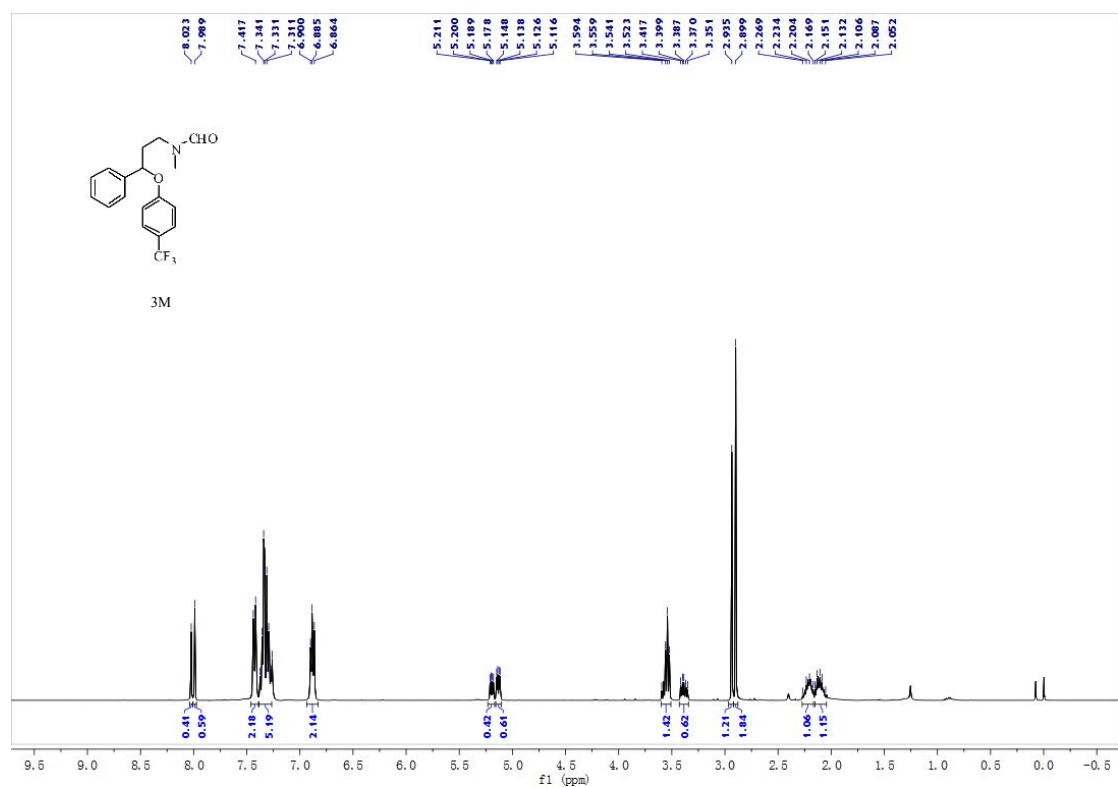
¹³C NMR spectra of 3K



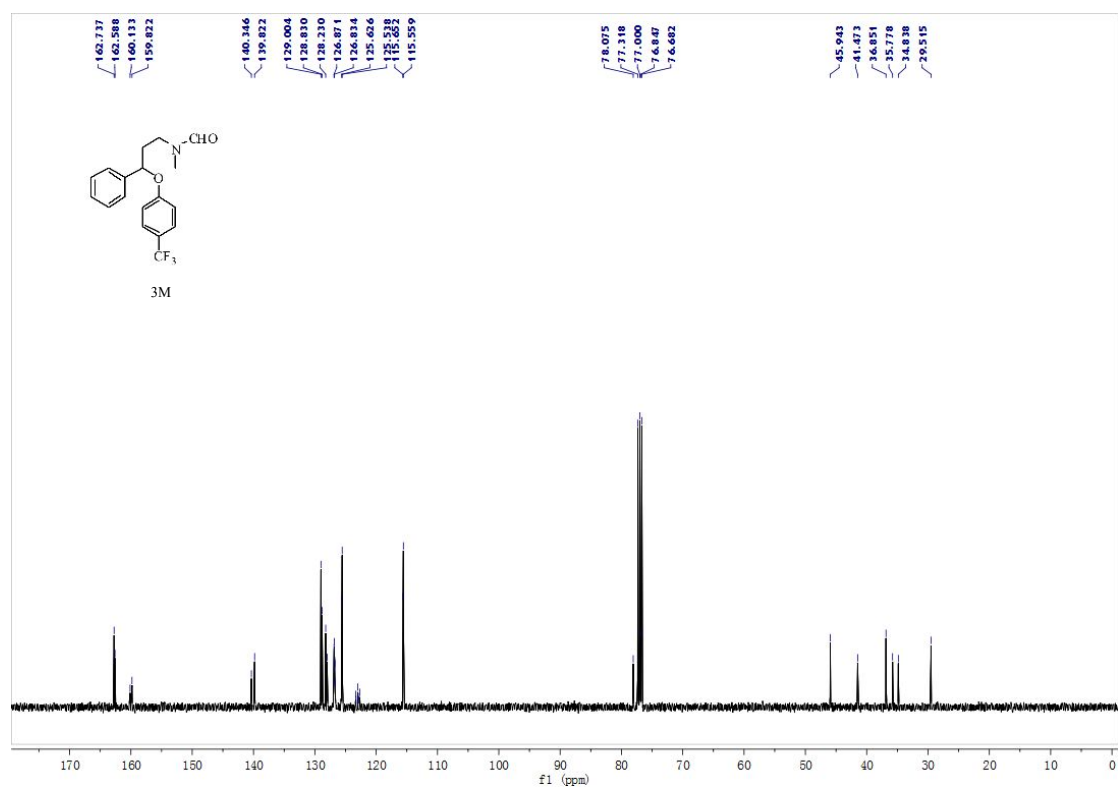
¹H NMR spectra of **3L**



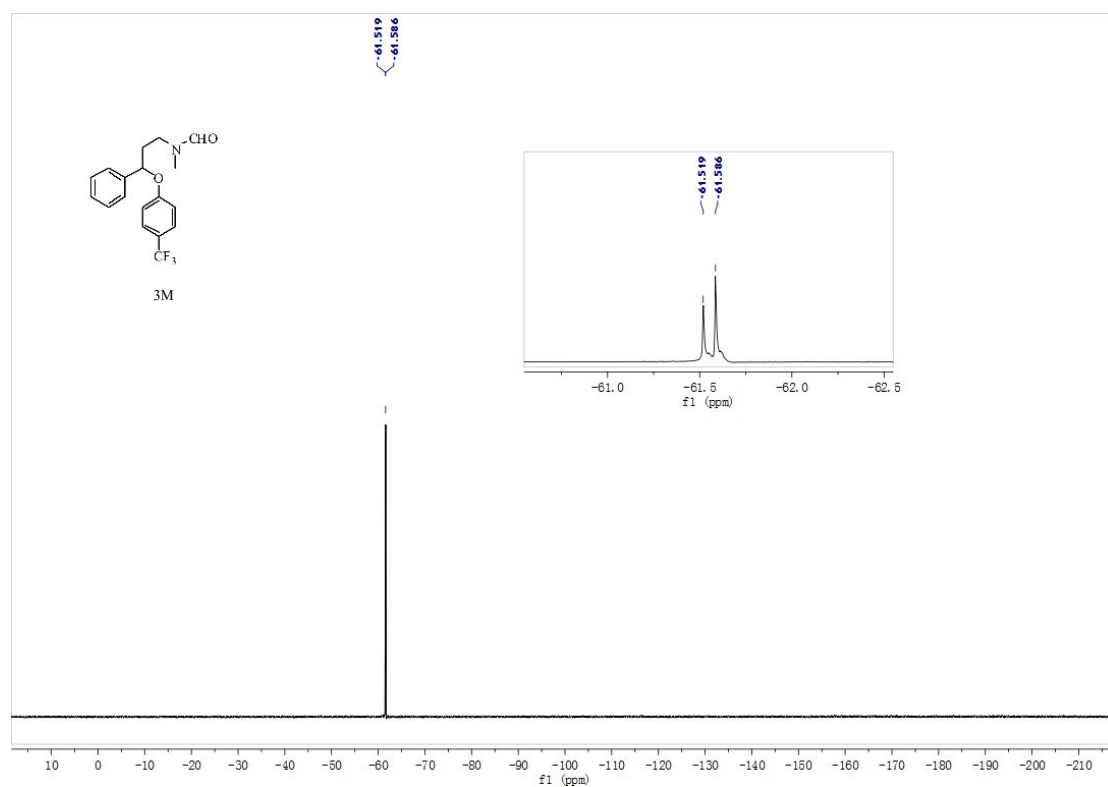
¹³C NMR spectra of **3L**



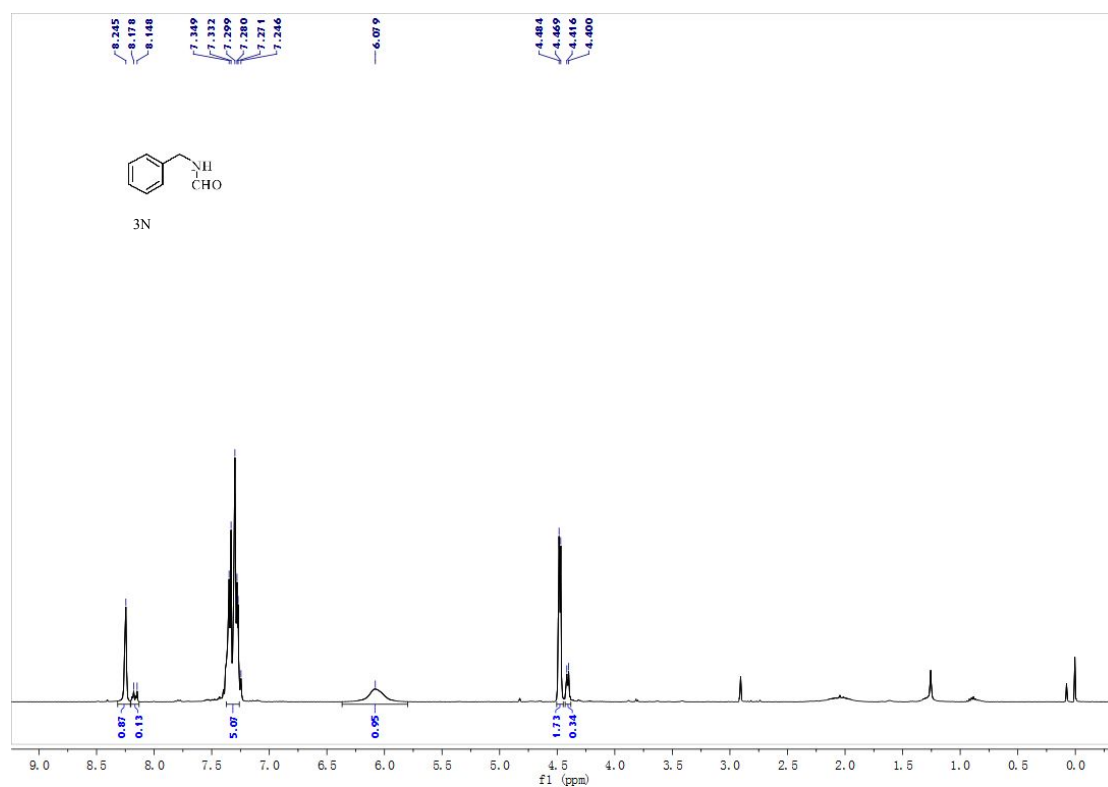
¹H NMR spectra of **3M**



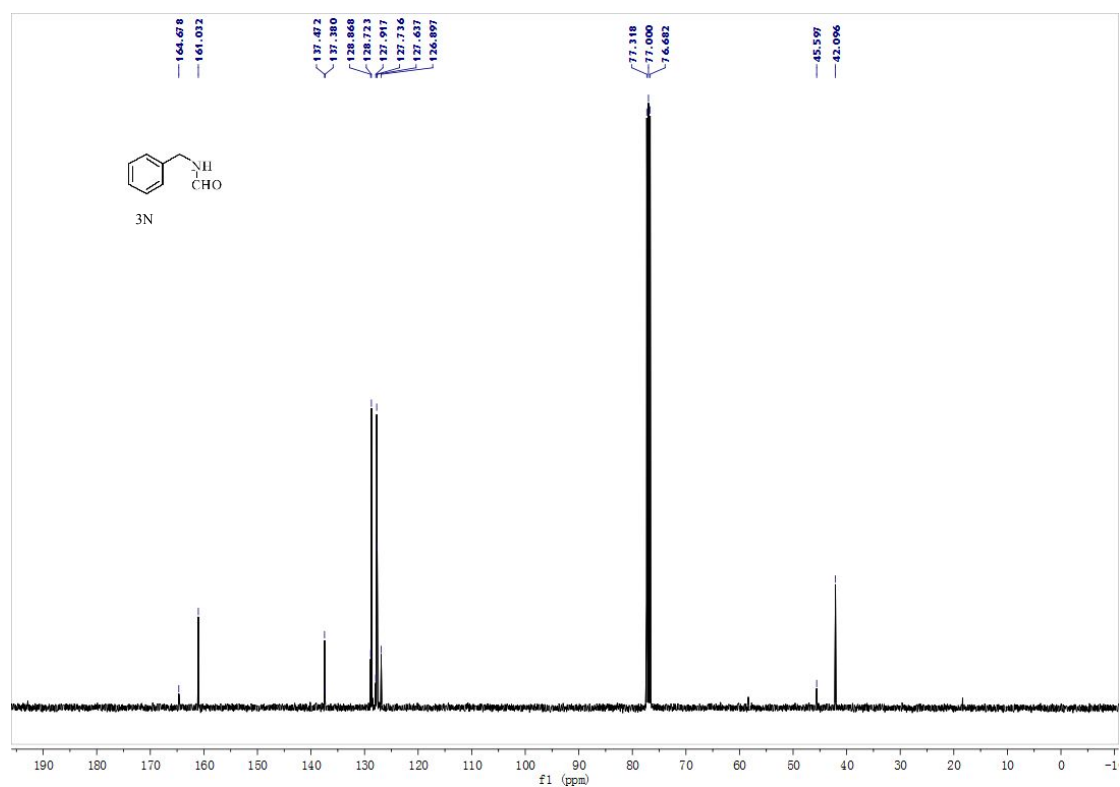
¹³C NMR spectra of **3M**



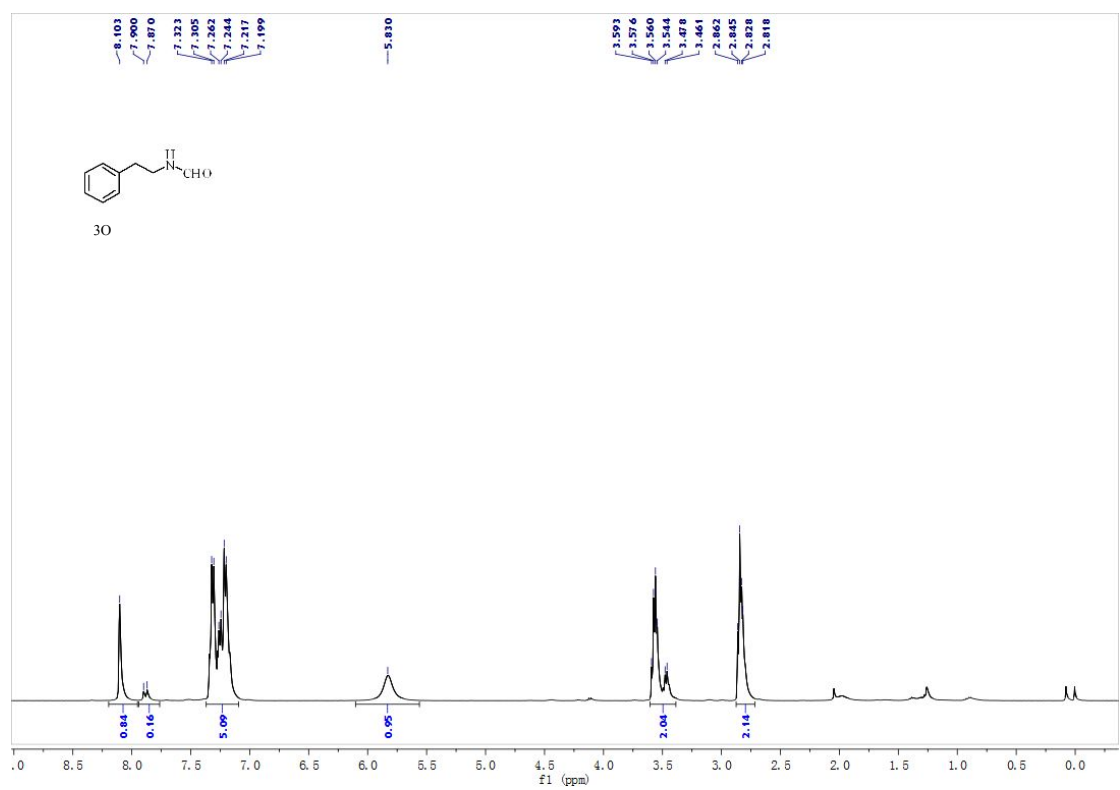
¹⁹F NMR spectra of 3M



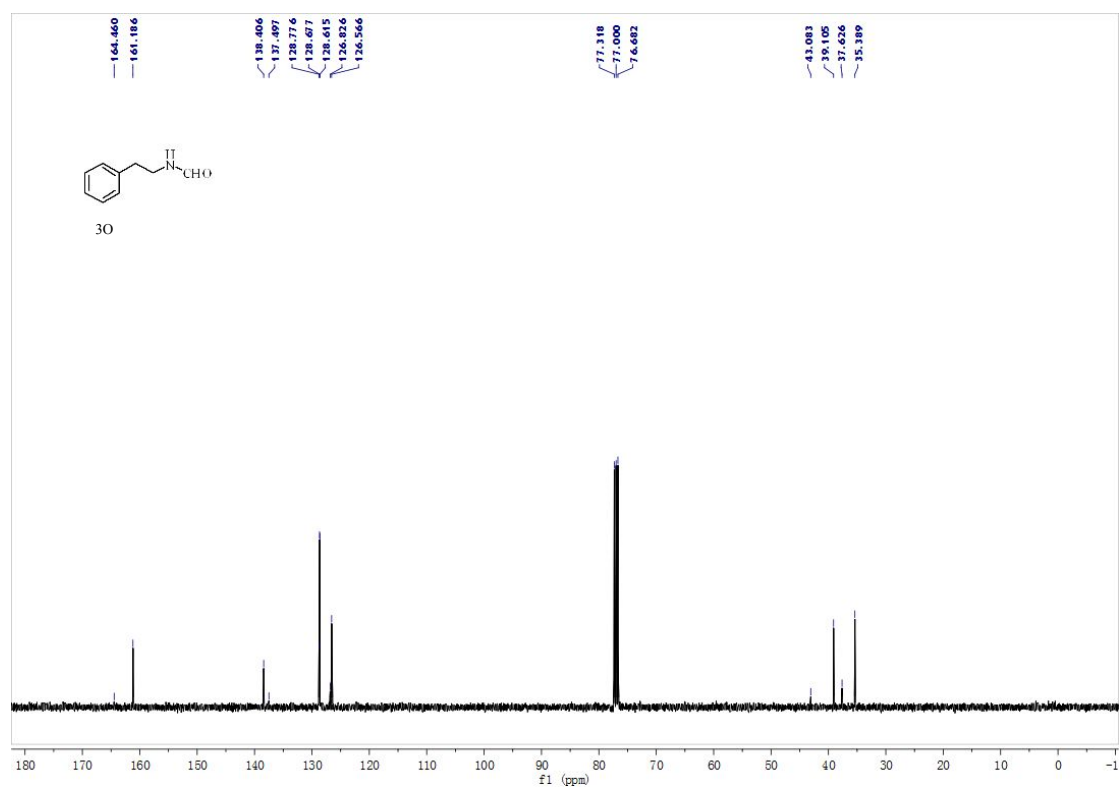
¹H NMR spectra of 3N



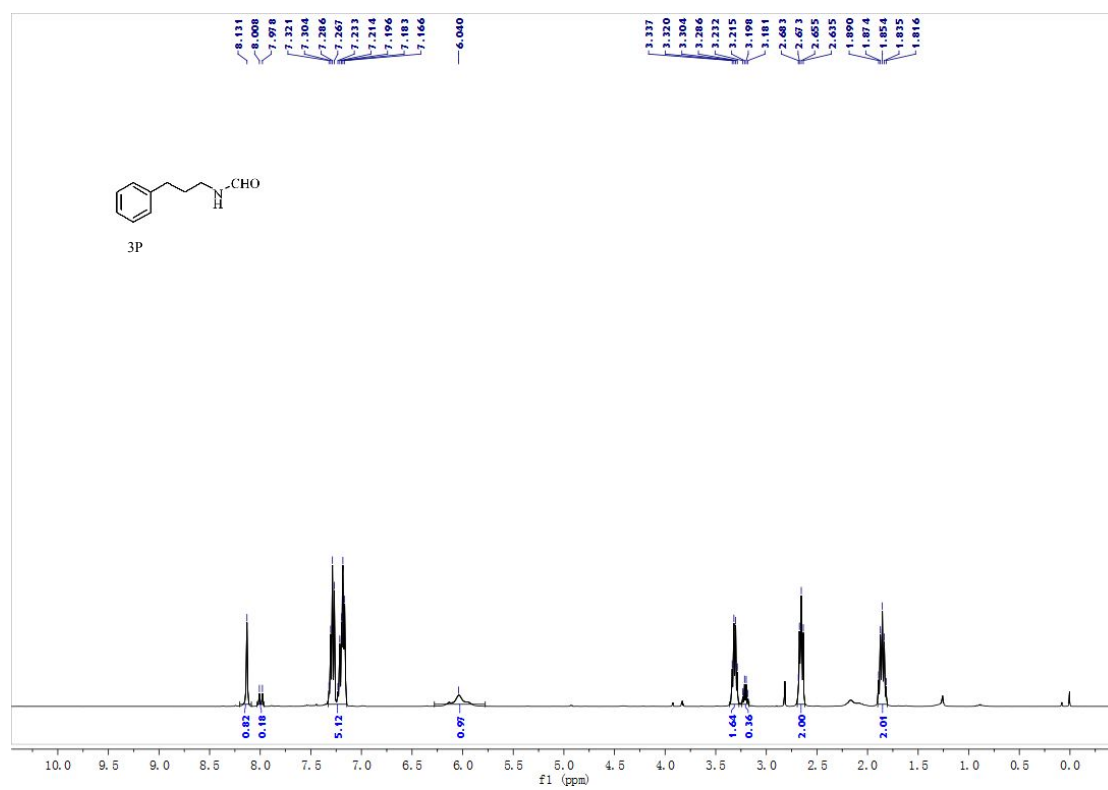
¹³C NMR spectra of **3N**



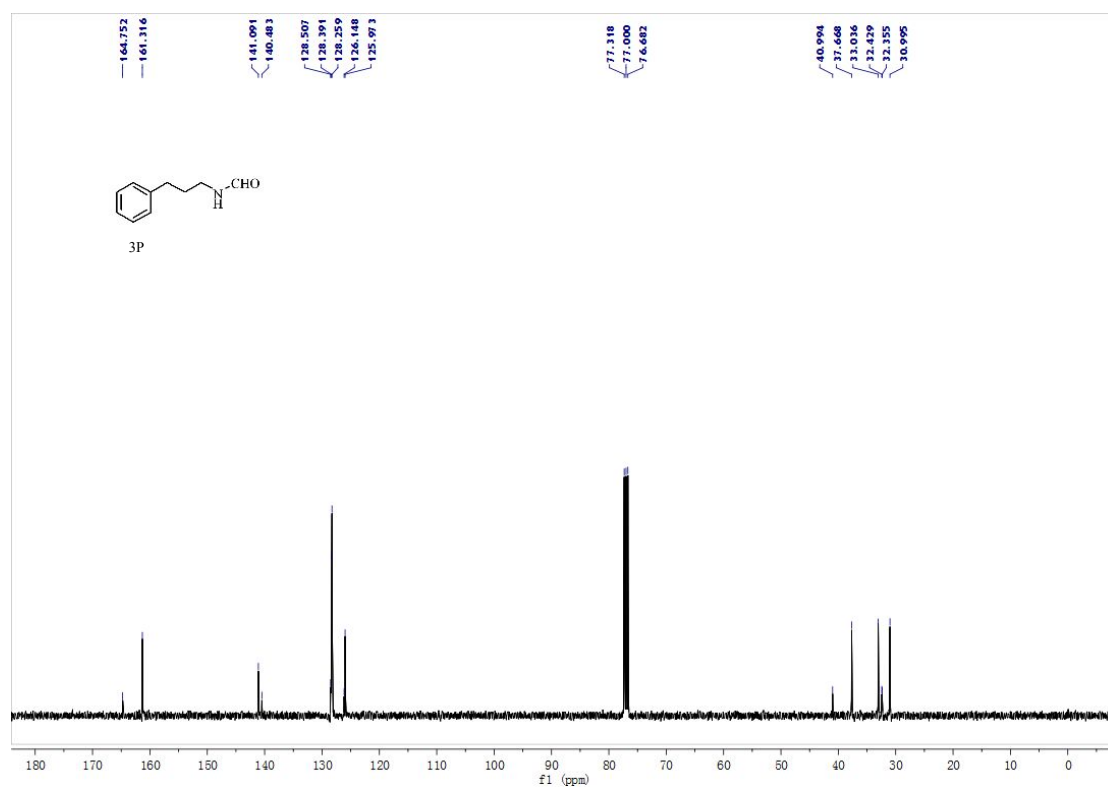
¹H NMR spectra of **3O**



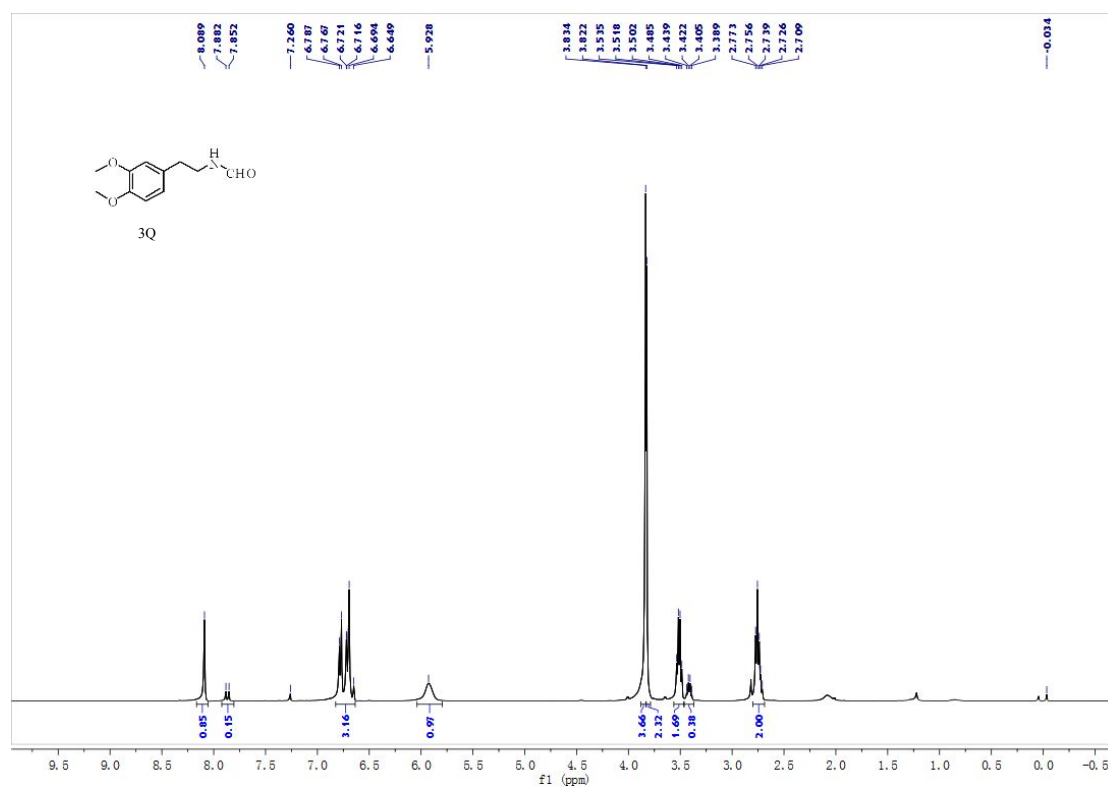
¹³C NMR spectra of **30**



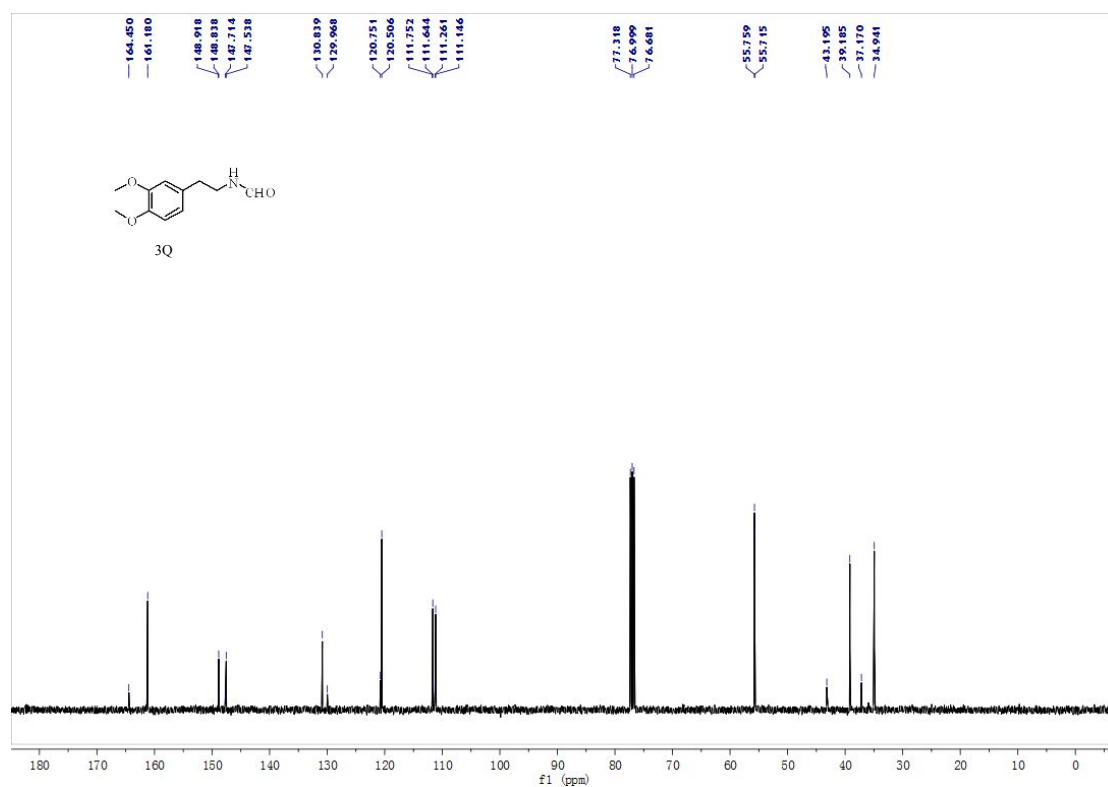
¹H NMR spectra of **3P**



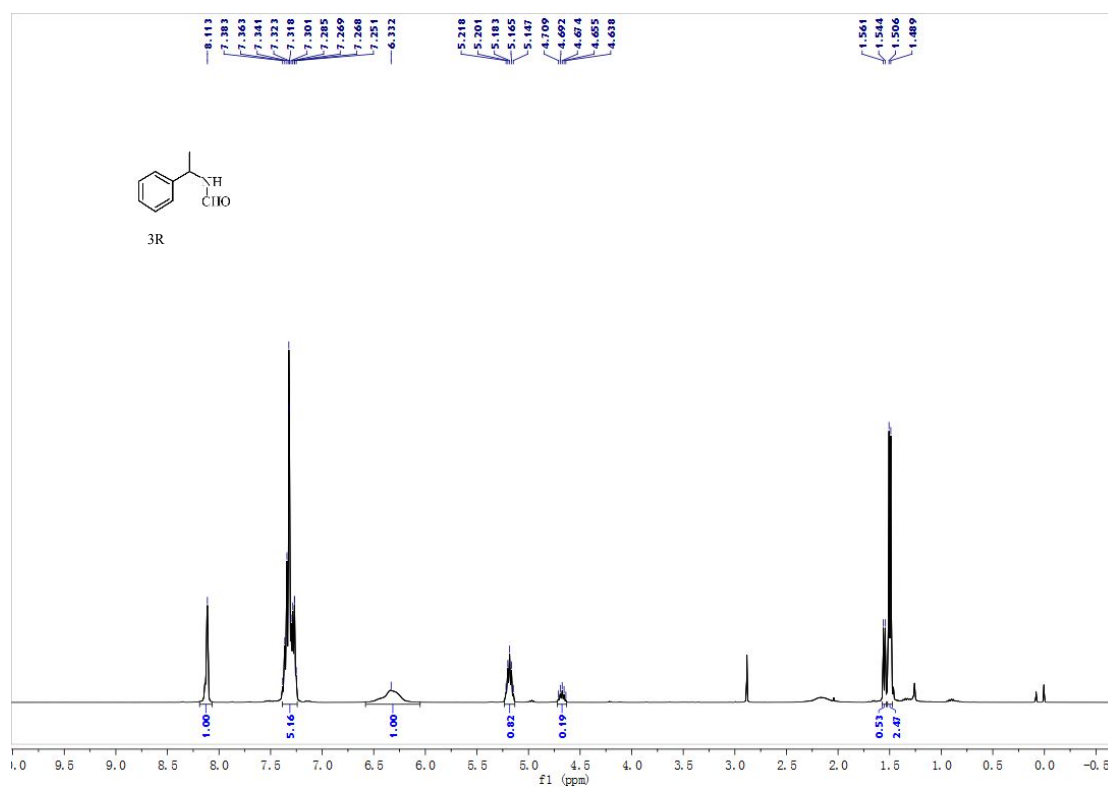
¹³C NMR spectra of **3P**



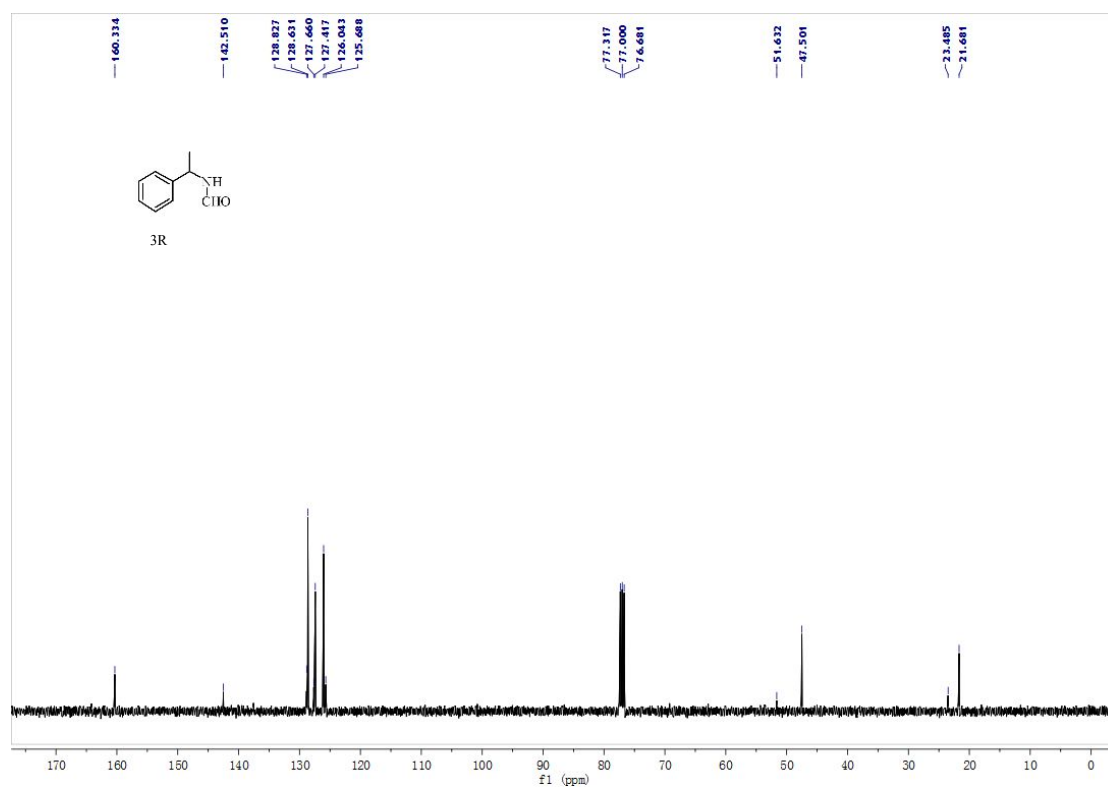
¹H NMR spectra of **3Q**



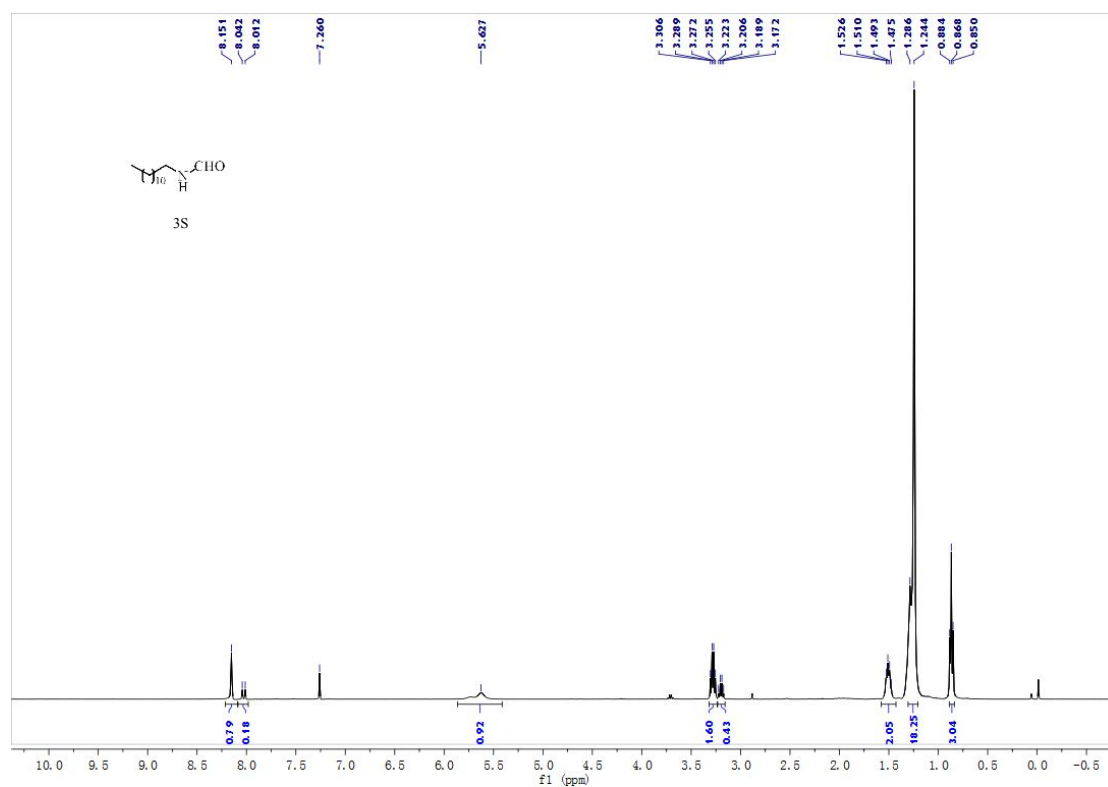
¹³C NMR spectra of **3Q**



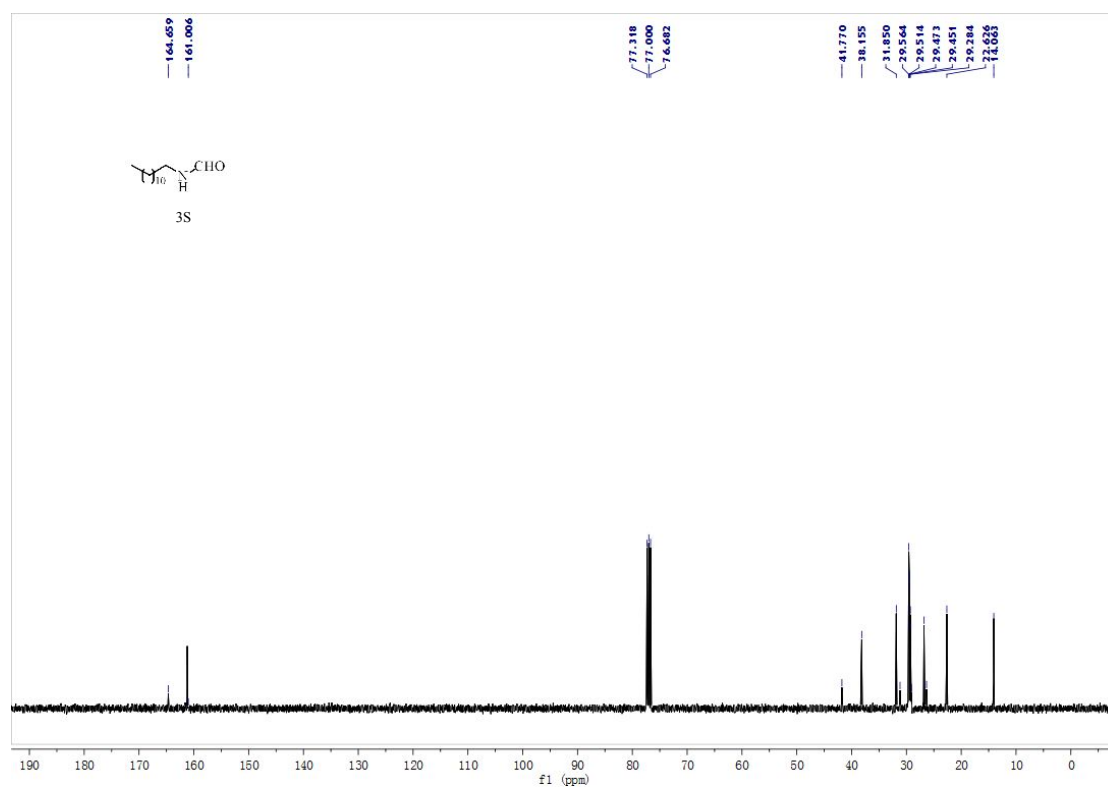
¹H NMR spectra of **3R**



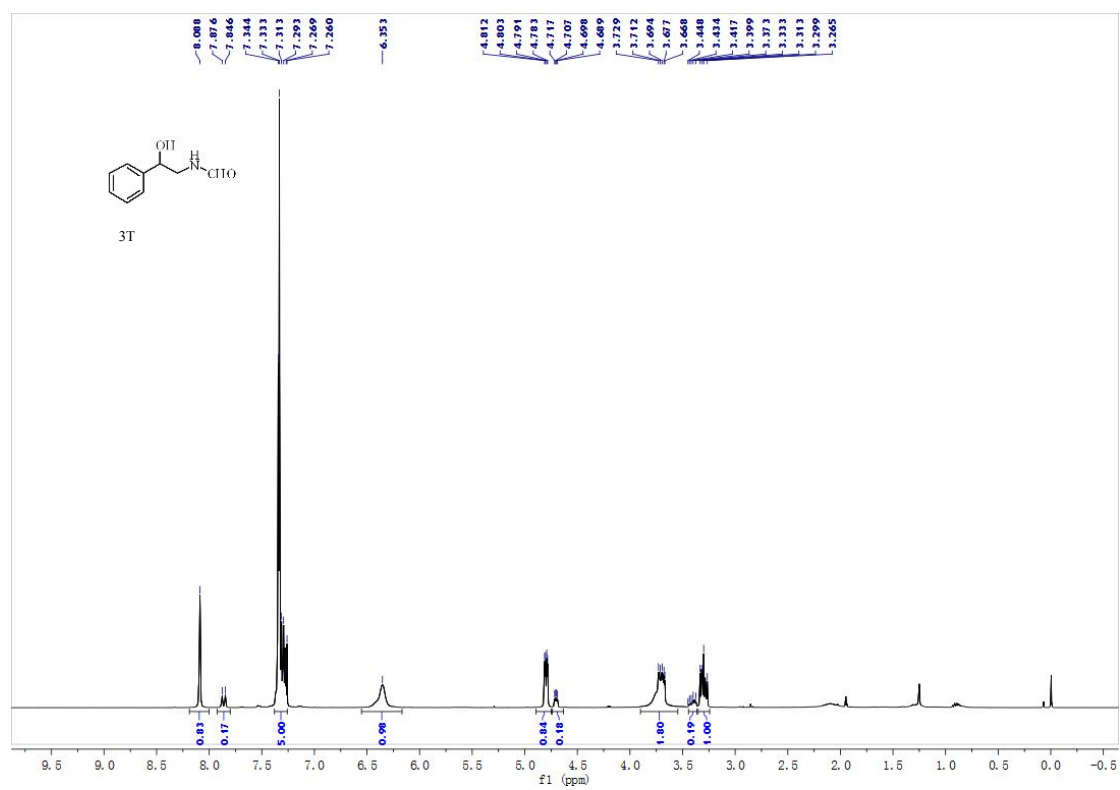
¹³C NMR spectra of **3R**



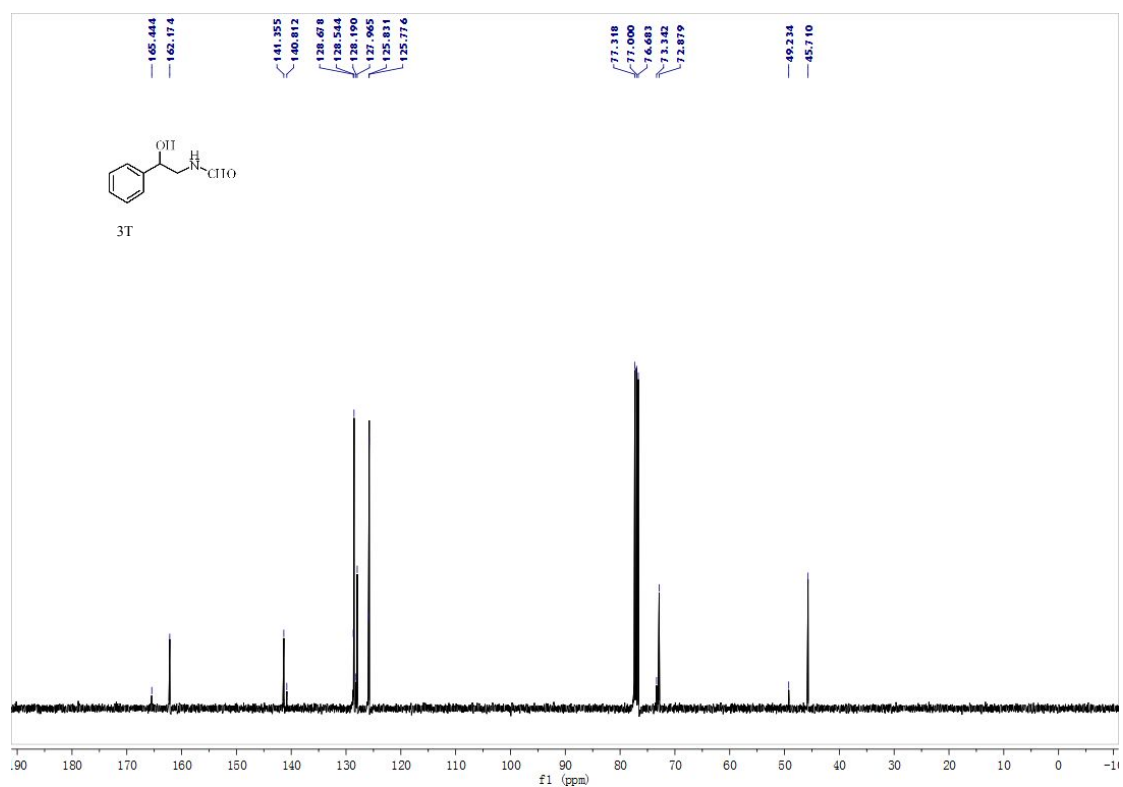
¹H NMR spectra of **3S**



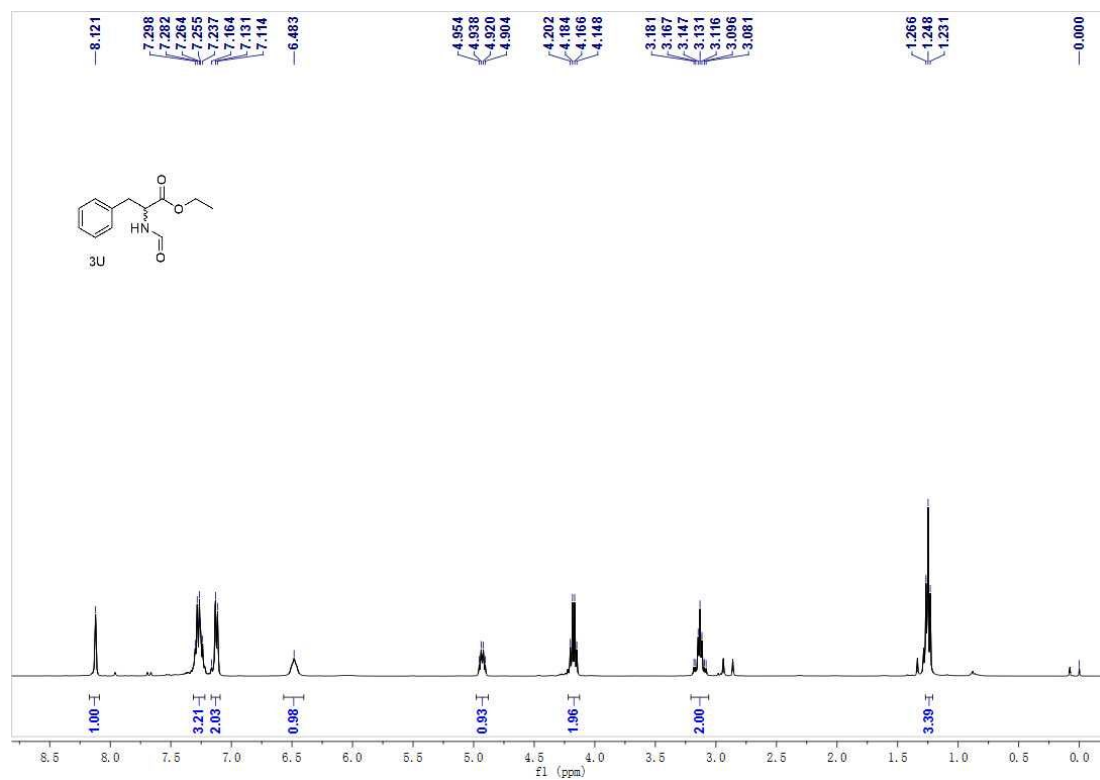
¹³C NMR spectra of **3S**



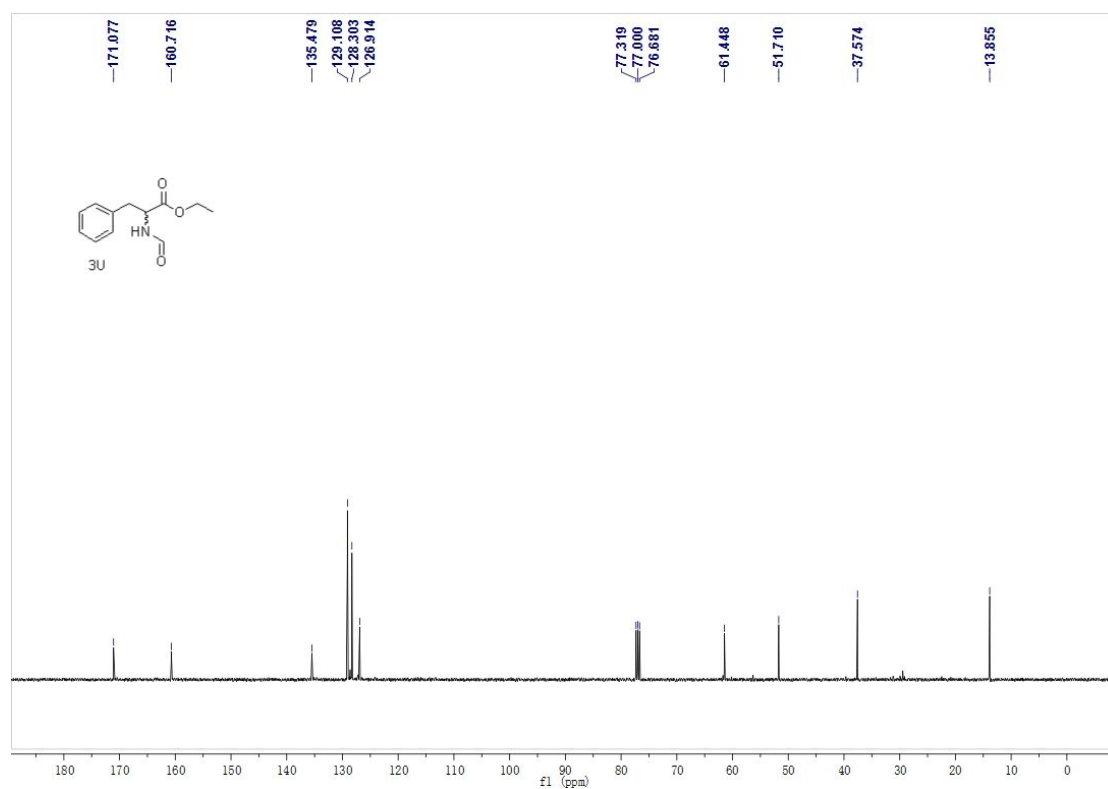
¹H NMR spectra of **3T**



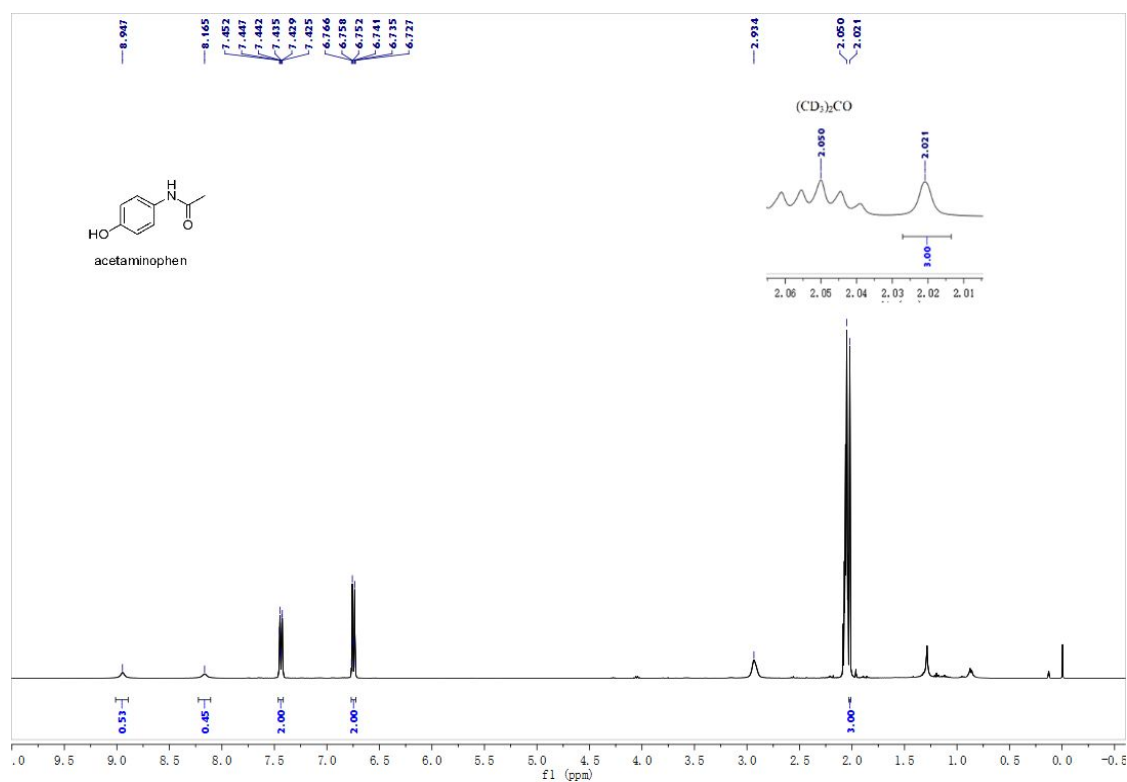
¹³C NMR spectra of **3T**



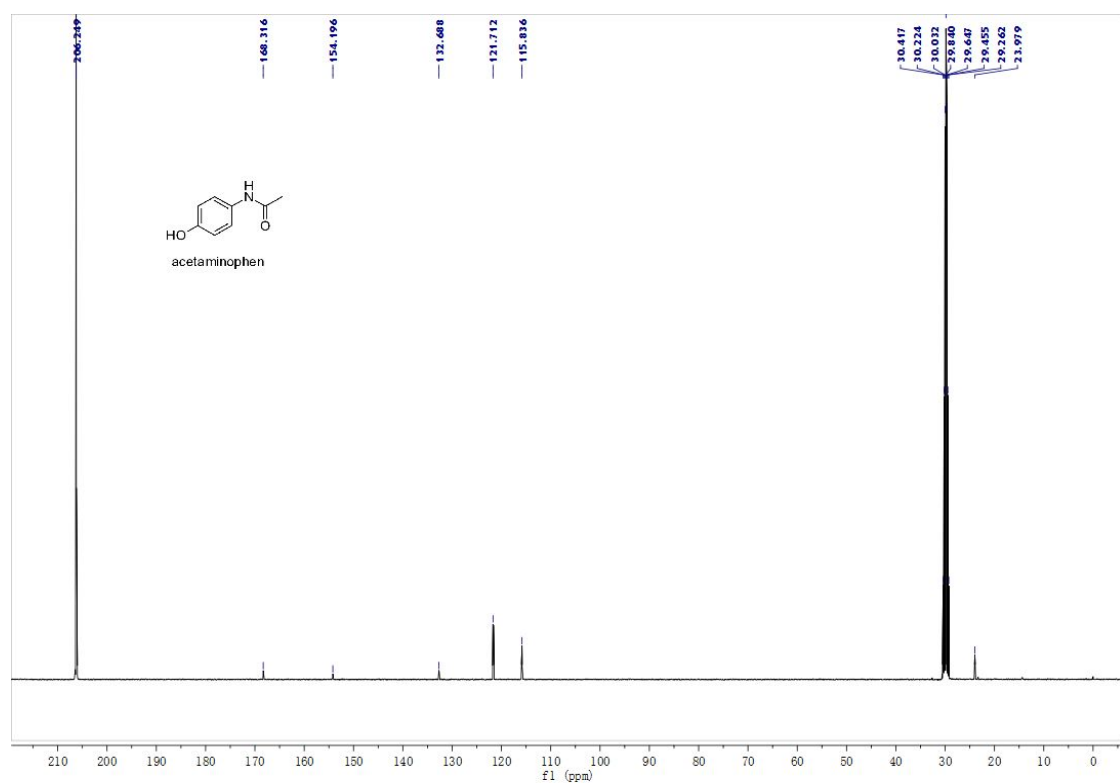
¹H NMR spectra of **3U**



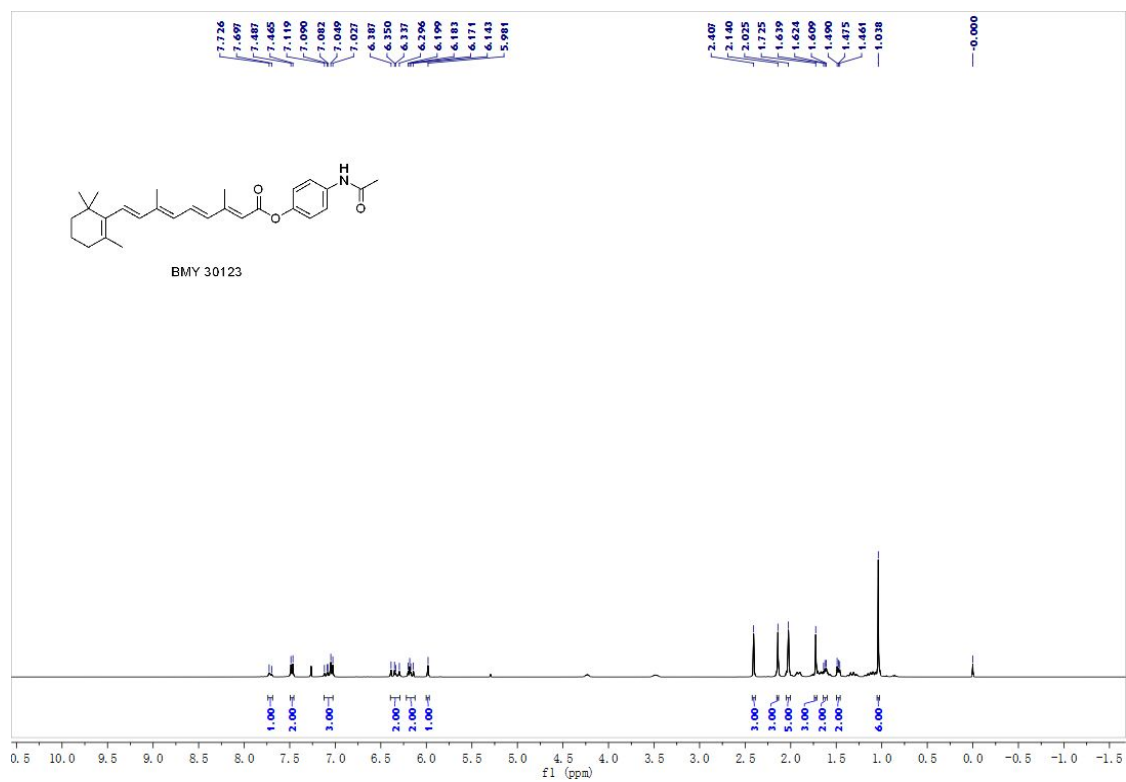
¹³C NMR spectra of **3U**



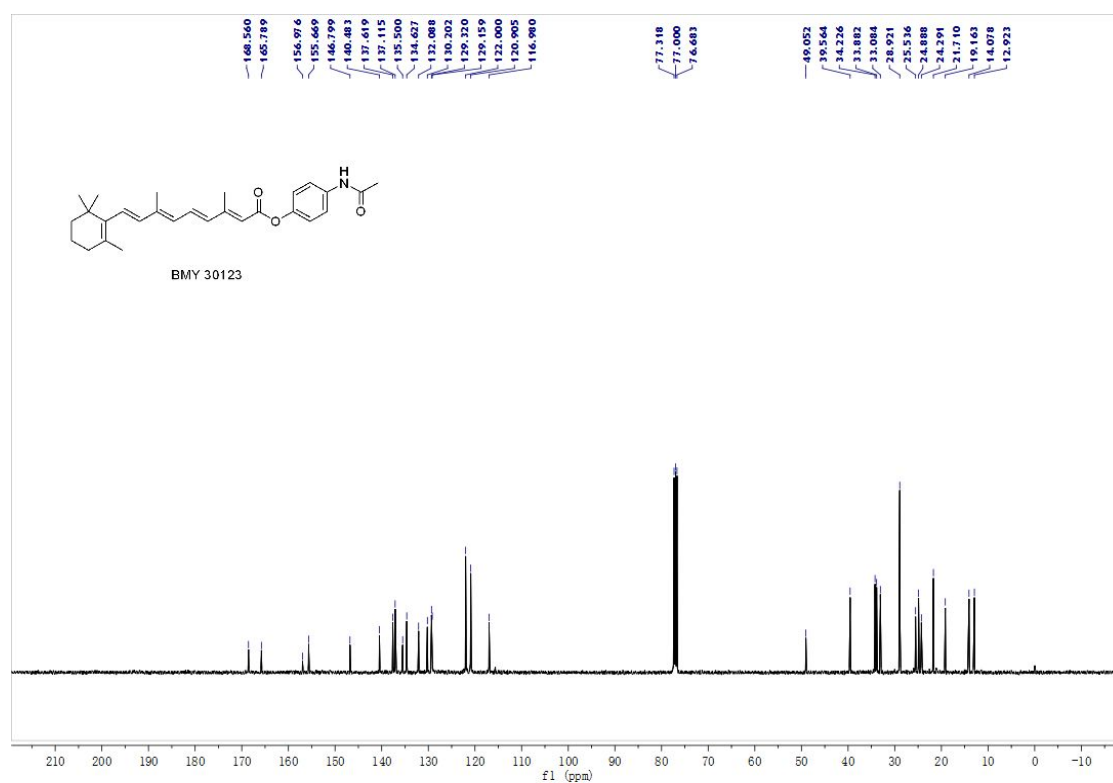
¹H NMR spectra of **acetaminophen**



¹³C NMR spectra of acetaminophen



¹H NMR spectra of **BMY 30123**



¹³C NMR spectra of **BMY 30123**