Copper(II) quinoxolinol imidazolium complexes in catalytic oxidation of benzylic and heterocyclic alcohols

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Supporting Information

Contents

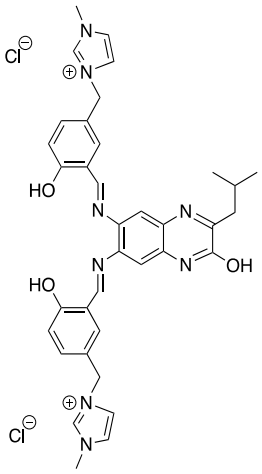
Instrumentation:

^{1}H-NMR and ^{13}C-NMR were recorded on JEOL ECS 400 MHz and 500MHz NMR spectrometer operating at 298 K. ^{1}H NMR spectra were referenced internally to the solvent resonances. NMR samples were dissolved in DMSO-d_6 as noted. The detection of Copper(II) complexes is hindered by Cu(II) paramagnetic properties.

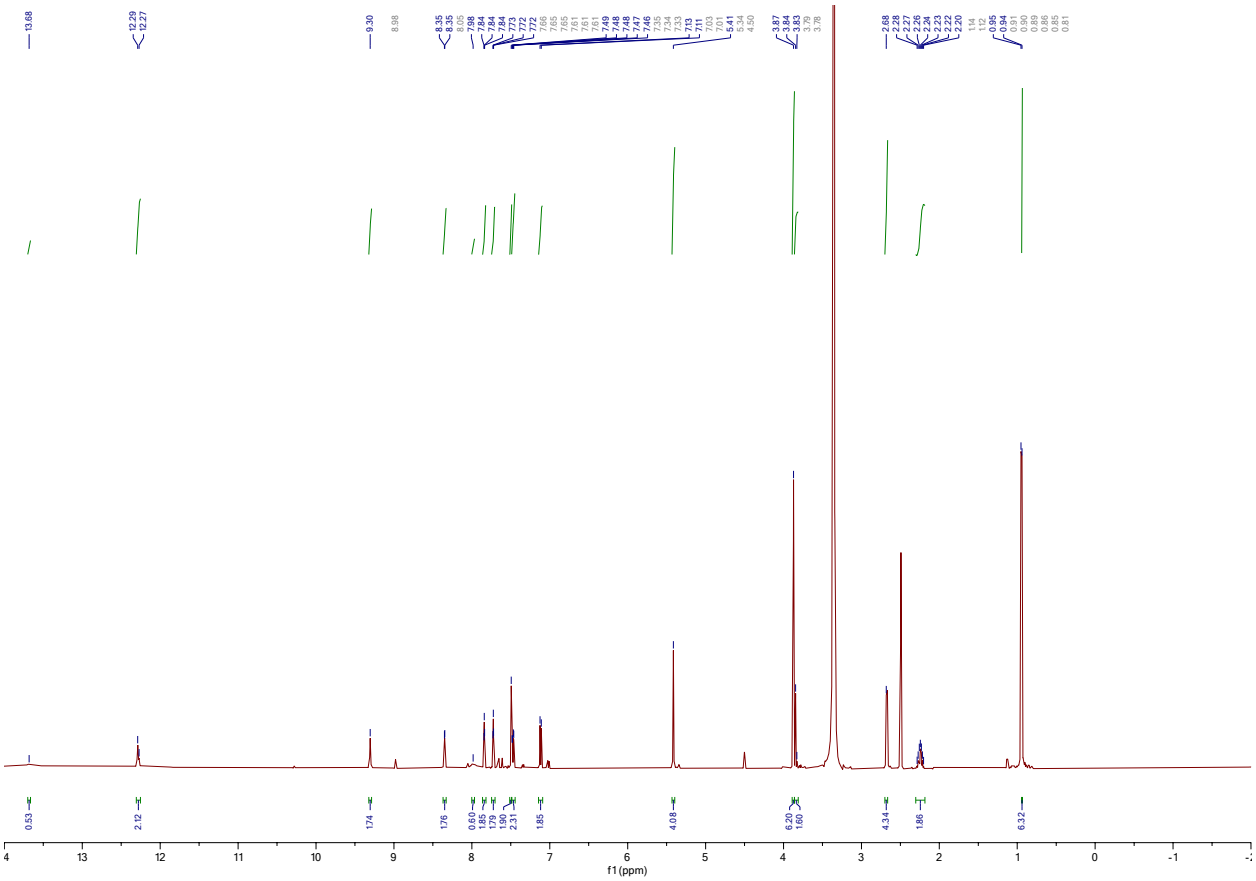
Solid-state IR spectra were collected on a Thermo Scientific Nicolet iS10 instrument equipped with a diamond ATR.

Solution-phase UV–vis data were obtained in 25 μM solutions using an Agilent Technologies Cary Series UV–vis Spectrophotometer. The samples were dissolved in methanol and placed in a 1 cm quartz cell. Data were collected from 200 to 800 nm.

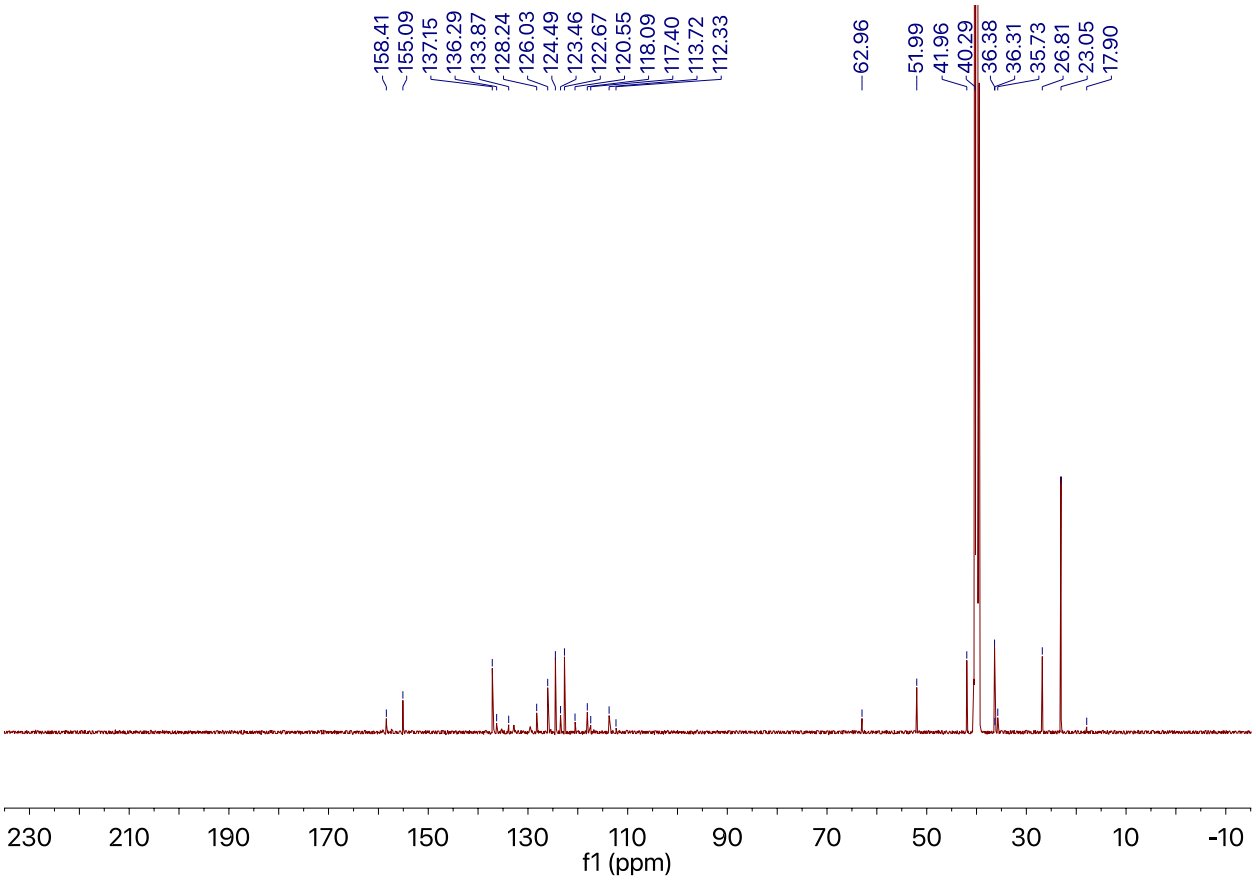
Characterization of new ligand L5



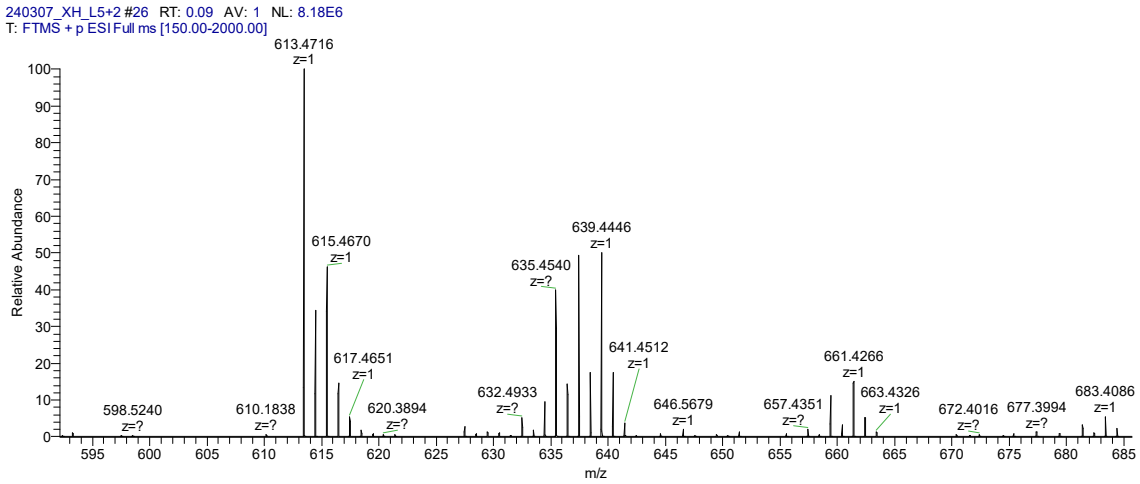
^{1}H-NMR(400 MHz, DMSO-d_6)

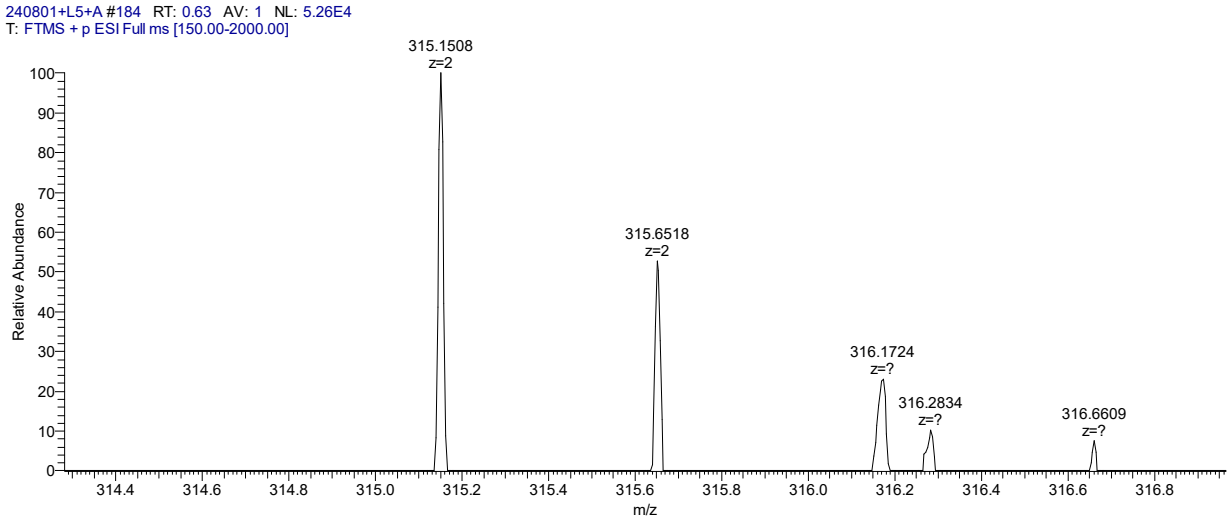


^{13}C-NMR(500 MHz, DMSO-d_6)



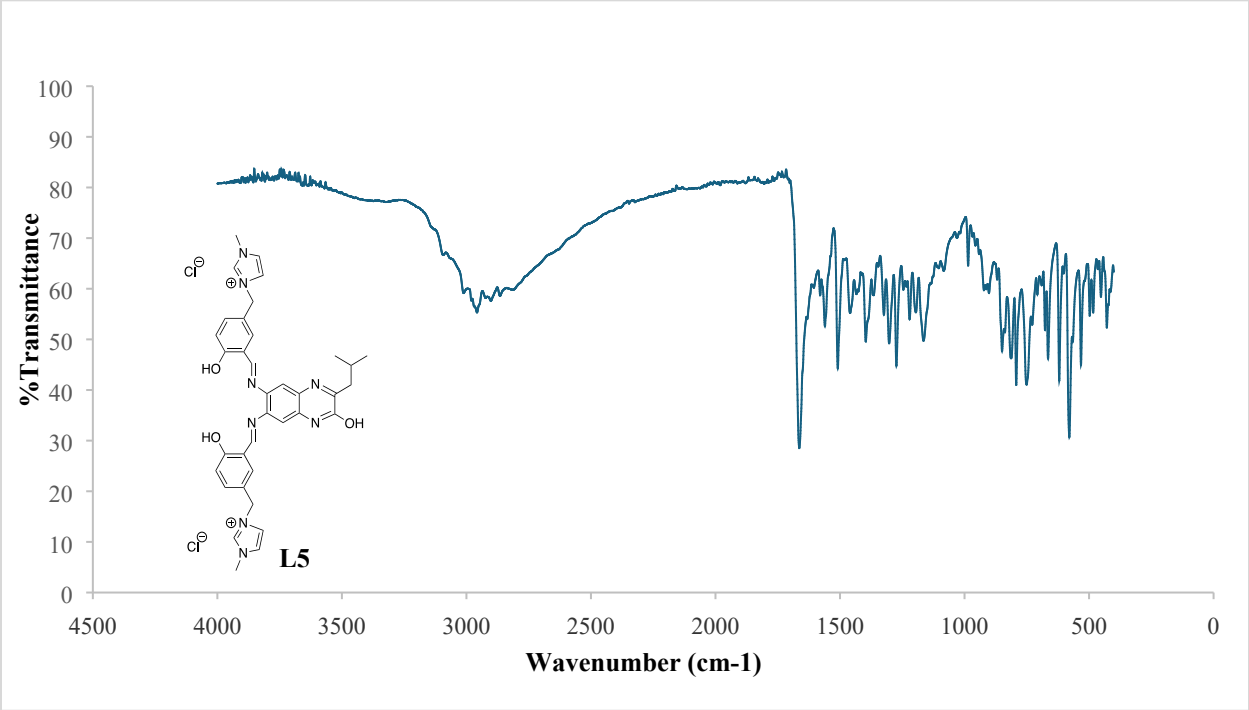
Mass spectrum



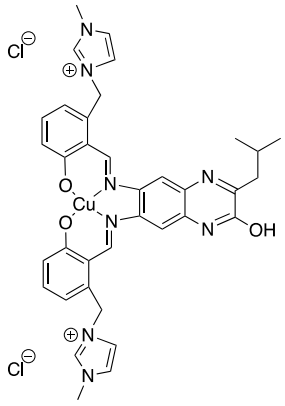


The peak at 613.4716 is accounted for by the molecular formula of $[C_{36}H_{38}N_8O_3]^{2+}$, which is as expected m/z 630.3066 minus one hydroxyl group. The peak at 315.1508 is accounted for m/2 by the molecular formula of $[C_{36}H_{38}N_8O_3]^{2+}$, which is the expected at 315.1533.

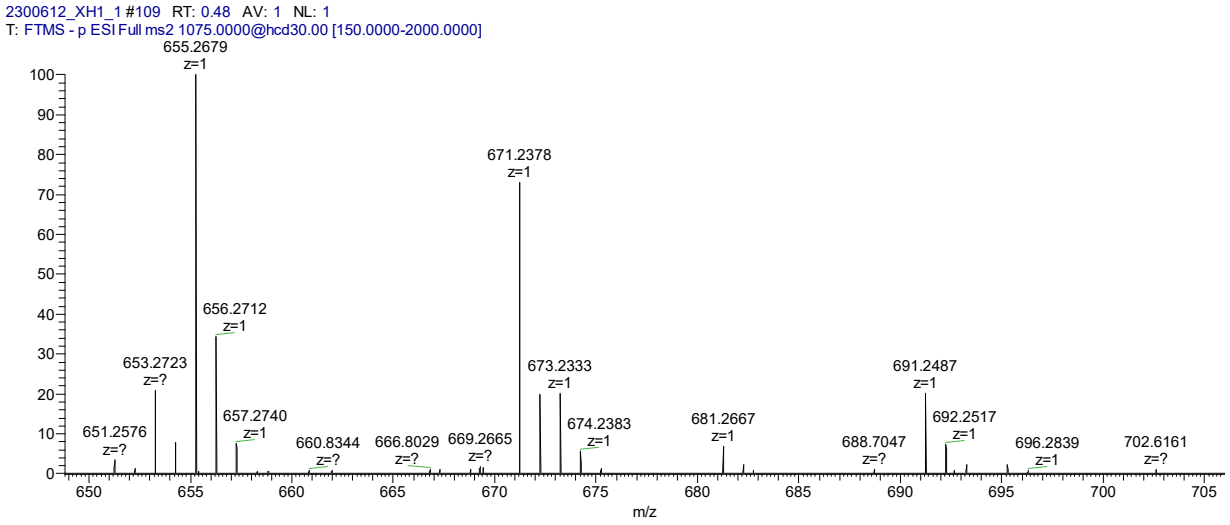
IR spectroscopy

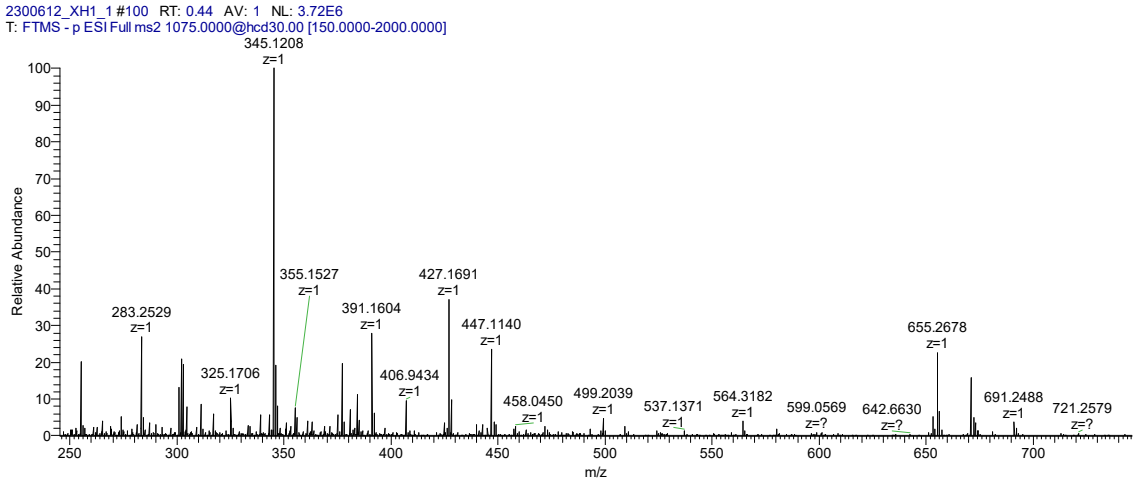


Characterization of new copper-L5 complex



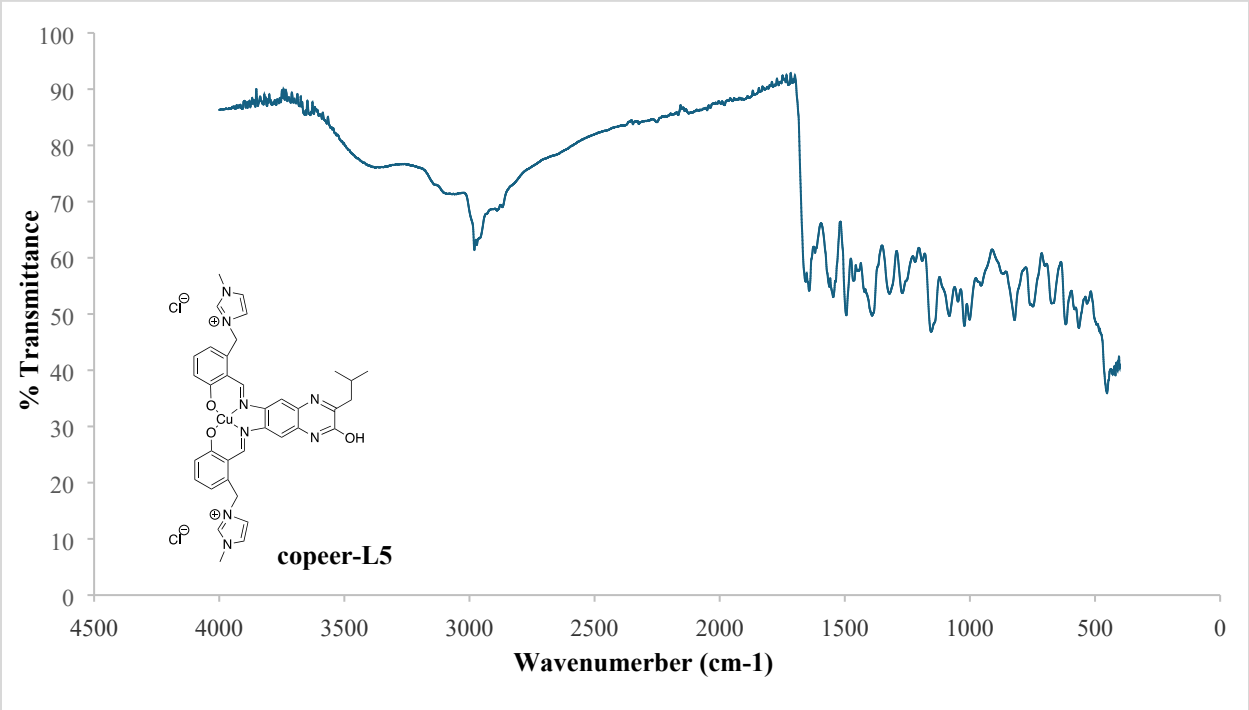
Mass spectrum



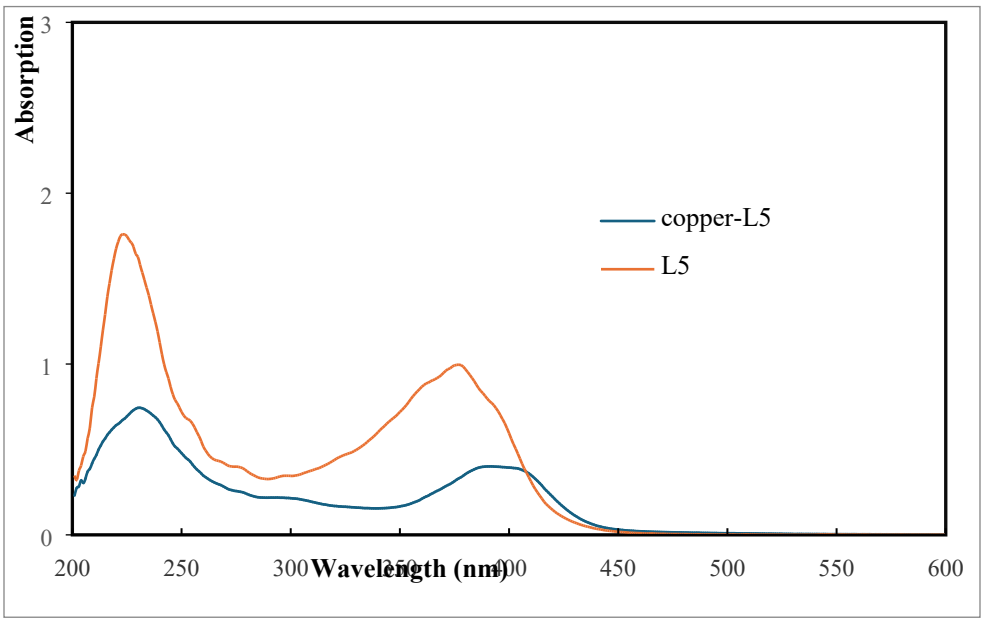


The peak at 691.2487 is accounted for by the molecular formula of of $[C_{36}H_{36}CuN_8O_3^{2+}]^{2+}$, which is as expected m/z at 691.2488. The peak at 655.2679 is as expected m/z minus two hydroxyl group. The peak at 345.1208 is accounted for m/2 by the molecular formula of $[C_{36}H_{36}CuN_8O_3^{2+}]^{2+}$, which is the expected at 345.1244.

IR spectroscopy



UV-Vis spectra of L5 ligand and copper-L5 complex. Samples were prepared as 25 μM solution in MeOH.

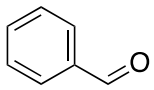


In the UV-Vis spectra in MeOH, the L5 had an absorption band at 226 nm (69000 $M^{-1}cm^{-1}$) due to its conjugation structure, and the ligand absorption at 380 nm (38000 $M^{-1}cm^{-1}$) can be ascribed to the electron excitation from the HOMO to the LUMO. Upon binding of Cu(II), the copper-L5 exhibited two absorptions. The one at 235 nm (28700 $M^{-1}cm^{-1}$) can be ascribed to the electron excitation from the HOMO of complex to the LUMO, while the other at 395 nm (15900 $M^{-1}cm^{-1}$) is typical of a ligand-to-metal charge transfer(LMCT) transition.

General Procedures for ^{1}H NMR of crude oxidation products:

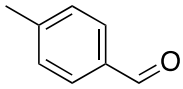
For each oxidation reaction, 0.5 mmol alcohol, copper-L5 complex(1 mol %, 3.46 mg), and TBHP (3.5 equivalents, 170 uL) were sequentially added to a 20 ml scintillation vial with a stirring bar into 5 ml CH_3CN. The progress was monitored after the reaction was stirred at 70℃ for 1h, 4h, 8h, 12h, 24h, and 48h. Yields (%) are recorded by GC-MS based on the starting alcohol. The reaction mixtures were filtered through small glass pipette containing celite and dried in the vacuum oven overnight. Crude ^{1}H NMR of oxidation products were operated by the spectrometer under 400 MHz in CHLOROFORM-D.

Characterization of crude products



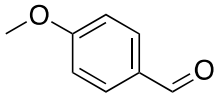
1, 4h, 65%

Benzaldehyde(1): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.38 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 14H), 7.61 (s, 5H), 7.48 (s, 5H), 5.36 (s, 1H), 1.71 – 0.91 (m, 9H).



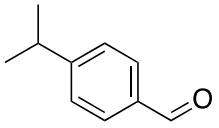
2, 4h, 54%

4-methylbenzaldehyde(2): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.06 (d, *J* = 26.0 Hz, 1H), 8.02 (s, 2H), 7.95 (s, 2H), 5.30 (s, 3H), 2.35 (s, 3H), 1.42 – 1.10 (m, 9H).



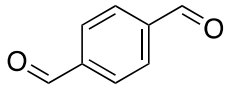
3, 4h, 55%

4-methoxybenzaldehyde(3): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.16 – 7.96 (m, 2H), 7.07 – 6.80 (m, 2H), 3.88 (s, 3H).



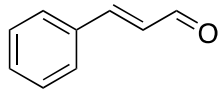
4, 4h, 56%

4-isopropylbenzaldehyde(4): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.54 (dd, *J* = 13.7, 7.7 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.26 (dt, *J* = 14.1, 5.9 Hz, 2H), 5.45 – 5.27 (m, 1H), 1.28 – 1.23 (m, 6H).



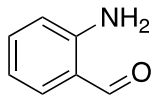
5, 24h, 56%

Terephthalaldehyde(5): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.12 – 10.08 (m, 1H), 10.01 (d, *J* = 11.1 Hz, 1H), 7.36 (s, 3H), 4.69 (s, 2H).



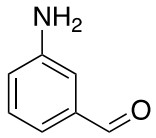
6, 4h, 82%

cinnamaldehyde(6): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.15 (s, -1H), 7.25 (s, 4H), 6.50 (s, 1H), 6.46 (s, 1H), 3.82 – 3.68 (m, 3H), 2.19 (s, 1H), 1.69 – 1.14 (m, 9H).



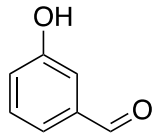
7, 8h, 86%

2-aminobenzaldehyde(7): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.08 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.03 – 7.85 (m, 1H), 7.74 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.64 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.12 (d, *J* = 25.8 Hz, 1H), 4.96 (s, 3H).



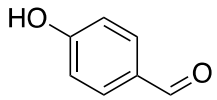
8, 12h, 40%

3-aminobenzaldehyde(8): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.15 – 9.81 (m, 1H), 8.73 (t, *J* = 1.9 Hz, 1H), 8.55 (s, 1H), 8.23 (s, 2H), 8.14 – 7.49 (m, 16H), 6.78 – 6.56 (m, 1H), 4.81 (s, 8H), 2.02 – 1.15 (m, 9H).



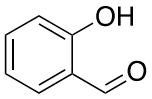
9, 4h, 23%

3-hydroxybenzaldehyde(9): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.58 (s, 1H), 9.95 (s, 1H), 7.51 (s, 1H), 7.43 (s, 1H), 6.98 (s, 1H), 6.76 (s, 1H), 4.65 (s, 1H), 1.24 (s, 9H).



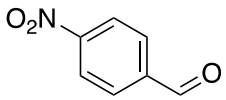
10, 4h, 33%

4-hydroxybenzaldehyde(10): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.86 (s, 1H), 7.92 – 7.72 (m, 2H), 6.78 (s, 2H), 2.00 (s, 2H), 1.25 (d, *J* = 9.9 Hz, 9H).



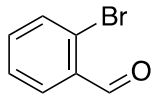
11, 4h, 29%

2-hydroxybenzaldehyde(11): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 11.37 (s, 1H), δ 11.35 (s, 1H), δ 7.51 (s, 2H), 6.98 (s, 1H), 6.75 (d, *J* = 1.4 Hz, 1H), 1.25 (d, *J* = 8.9 Hz, 9H).



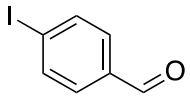
12, 8h, 43%

4-nitrobenzaldehyde(12): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.15 (s, 1H), 8.39 (dd, *J* = 7.0, 1.7 Hz, 2H), 8.09 – 8.05 (m, 2H), 4.84 (s, 8H), 2.16 (s, 1H), 1.49 – 1.15 (m, 9H).



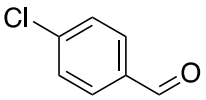
13, 4h, 76%

2-bromobenzaldehyde(13): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.39 (m, 1H), 7.16 (s, 1H), 7.13 – 7.06 (m, 1H), 4.57 (t, *J* = 7.0 Hz, 1H), 3.76 (s, 1H), 3.21 (t, *J* = 7.0 Hz, 1H), 2.04 – 0.59 (m, 9H).



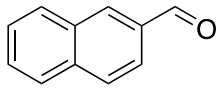
14, 4h, 84%

4-iodobenzaldehyde(14): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.07 (s, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.89 (d, *J* = 1.6 Hz, 2H), 5.39 (d, *J* = 2.2 Hz, 3H), 1.47 – 1.02 (m, 9H).



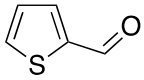
15, 4h, 65%

4-chlorobenzaldehyde(15): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.99 (s, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 5.25 (s, 1H), 2.17 (s, 4H), 1.34 – 0.69 (m, 9H).



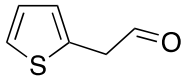
16, 8h,70%

2-naphthaldehyde(16): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.17 (s, 1H), 8.34 (s, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.94 (s, 1H), 7.88 (s, 1H), 7.64 (d, *J* = 1.3 Hz, 1H), 7.58 (s, 2H), 7.51 (d, *J* = 1.6 Hz, 1H), 3.98 (s, 1H), 1.59 – 0.90 (m, 3H).



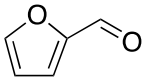
17, 4h, 99%

thiophene-2-carbaldehyde(17): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.52 (s, 1H), 7.89 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.64 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.15 – 7.13 (m, 1H).



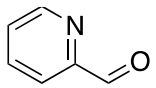
18, 4h, 54%

2-(thiophen-2-yl)acetaldehyde(18): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 7.87 (d, *J* = 1.3 Hz, 1H), 7.63 (d, *J* = 1.3 Hz, 1H), 7.14 – 7.11 (m, 2H), 1.99 (s, 1H), 1.35 (s, 9H).



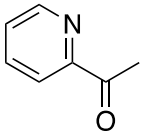
19, 8h, 87%

furan-2-carbaldehyde(19): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 8.05 (d, *J* = 5.2 Hz, 1H), 7.87 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.62 (dd, *J* = 4.9, 1.3 Hz, 1H), 7.14 – 7.12 (m, 1H), 6.94 (ddd, *J* = 4.9, 3.4, 1.4 Hz, 1H), 4.57 – 2.86 (m, 12H), 1.99 (s, 9H).



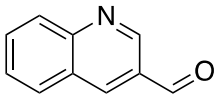
20, 8h, 97%

2-pyridinecarboxaldehyde(20): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.26 (d, *J* = 12.9 Hz, 1H), 8.76 (d, *J* = 20.5 Hz, 1H), 8.63 (s, 1H), 8.37 – 8.30 (m, 1H), 8.18 (d, *J* = 6.0 Hz, 1H), 5.42 (s, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 2.16 (s, 4H), 1.57 – 0.95 (m, 9H).



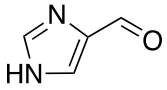
21, 4h, 99%

1-(pyridin-2-yl)ethan-1-one(21): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.15 (s, 1H), 8.65 – 8.60 (m, 1H), 8.59 (d, *J* = 4.8 Hz, 1H), 8.10 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 5.00 (s, 1H), 2.16 (s, 3H), 1.83 – 1.57 (m, 9H).



22, 4h, 78%

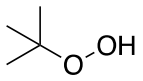
quinoline-3-carbaldehyde(22): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 10.20 (s, 1H), 9.31 (d, *J* = 2.1 Hz, 1H), 8.60 (d, *J* = 1.9 Hz, 1H), 8.10 (s, 1H), 7.96 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 4.88 (s, 3H).



23, 8h, 67%

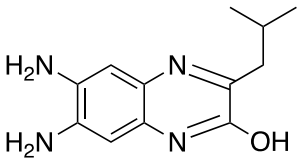
1*H*-imidazole-4-carbaldehyde(23): ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.75 (s, 1H), 7.84 (s, 1H), 7.51 (s, 1H), 6.98 (s, 1H), 2.00 (s, 1H), 1.50 – 0.87 (m, 9H).

Characterization of possible impurities:

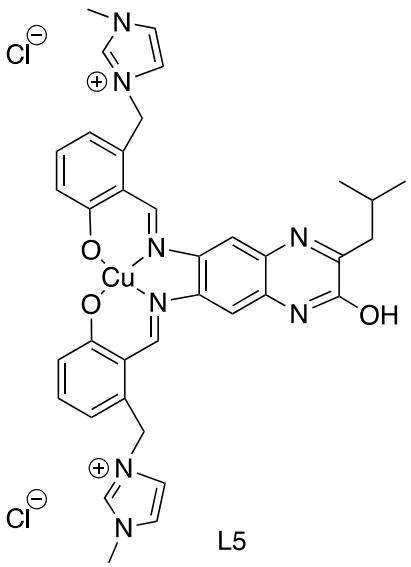


oxidant

tert-Butyl hydroperoxide: ^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 4.74 (s, 1H), 1.22 (s, 9H).



6,7-diamino-3-isobutylquinoxalin-2-ol: ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.70 (s, 1H), 6.74 (s, 1H), 6.30 (s, 1H), 5.34 (s, 2H), 4.56 (s, 2H), 2.09 (dp, *J* = 13.6, 6.8 Hz, 1H), 0.85 (d, *J* = 6.6 Hz, 6H).

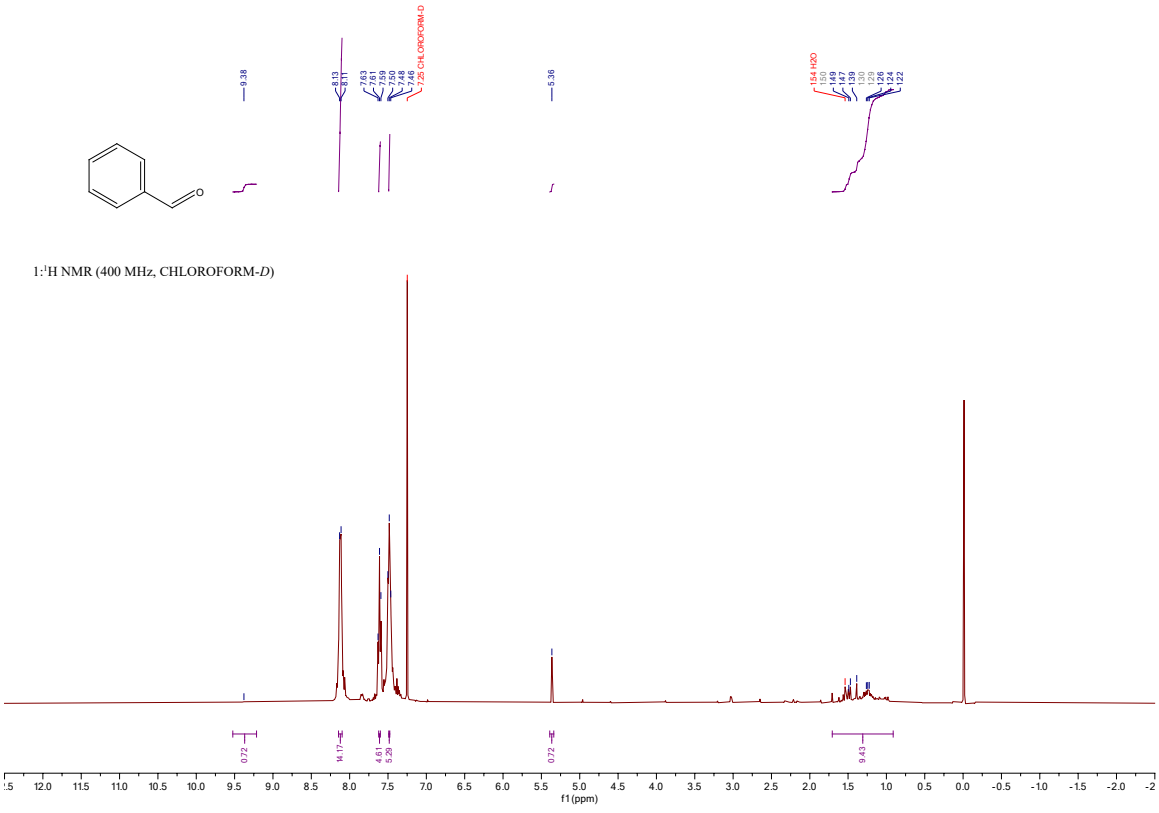


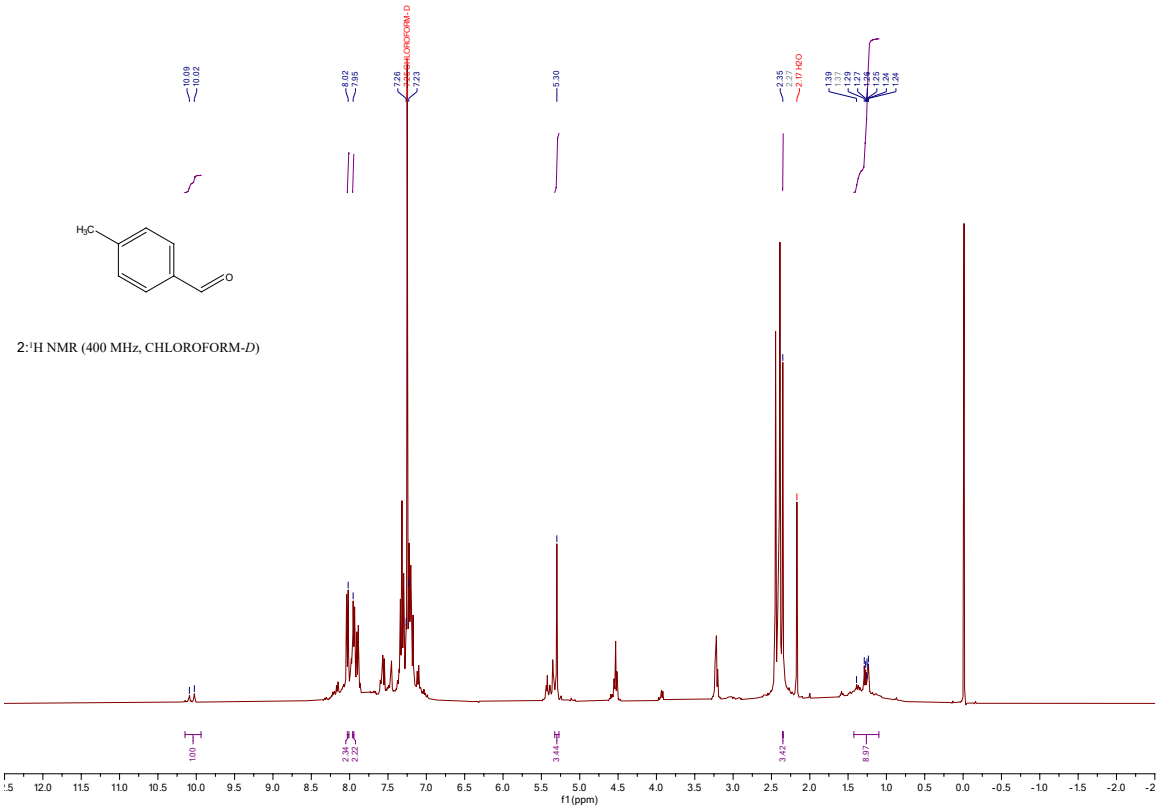
L5 (characterization as below)

^{1}H NMR (400 MHz, DMSO-

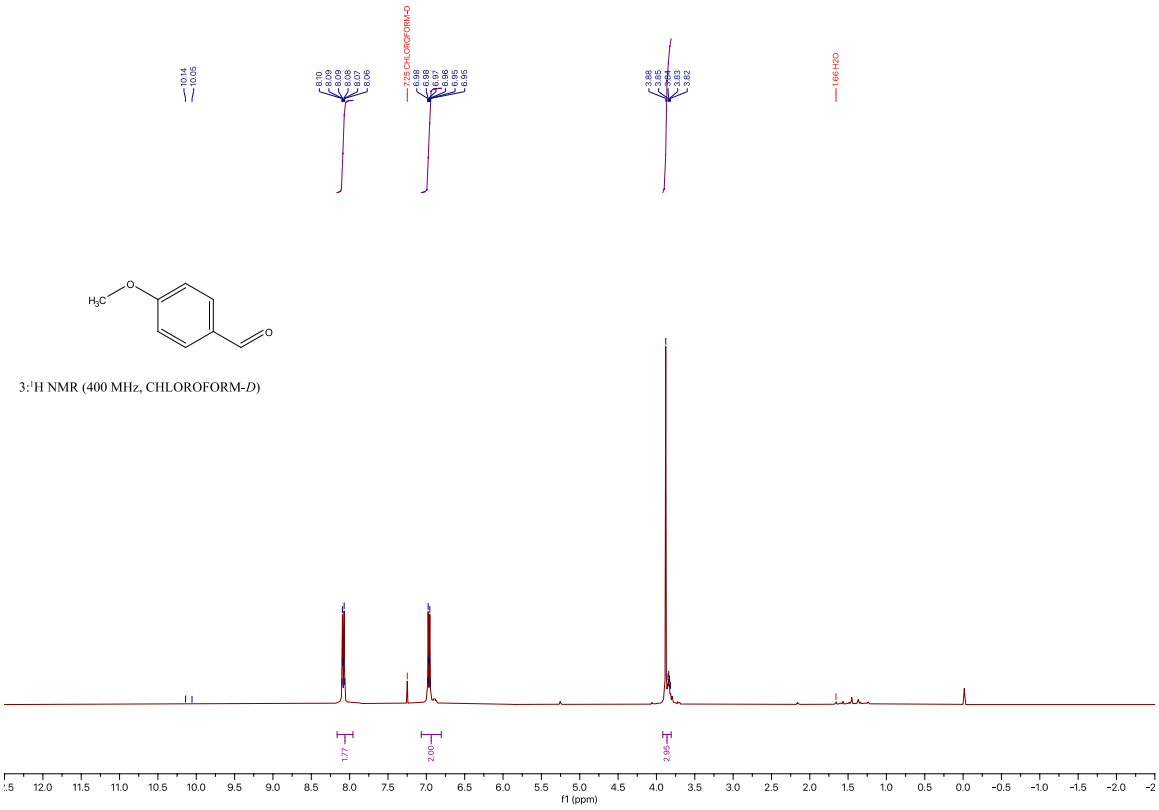
$_6$) δ 12.27 (s, 2H), 9.24 (s, 2H), 8.24 (s, 2H), 7.93 (d, J = 38.1 Hz, 2H), 7.84 (s, 2H), 7.66 (s, 2H), 7.49 (s, 2H), 7.45 – 7.37 (m, 2H), 7.09 (d, J = 38.1 Hz, 2H), 5.38 (s, 4H), 3.84 (s, 6H), 2.43 (d, J = 2.0 Hz, 1H), 2.21 (hept, J = 6.9 Hz, 2H), 0.91 – 0.89 (m, 6H).

Scanned copies of ^{1}H NMR

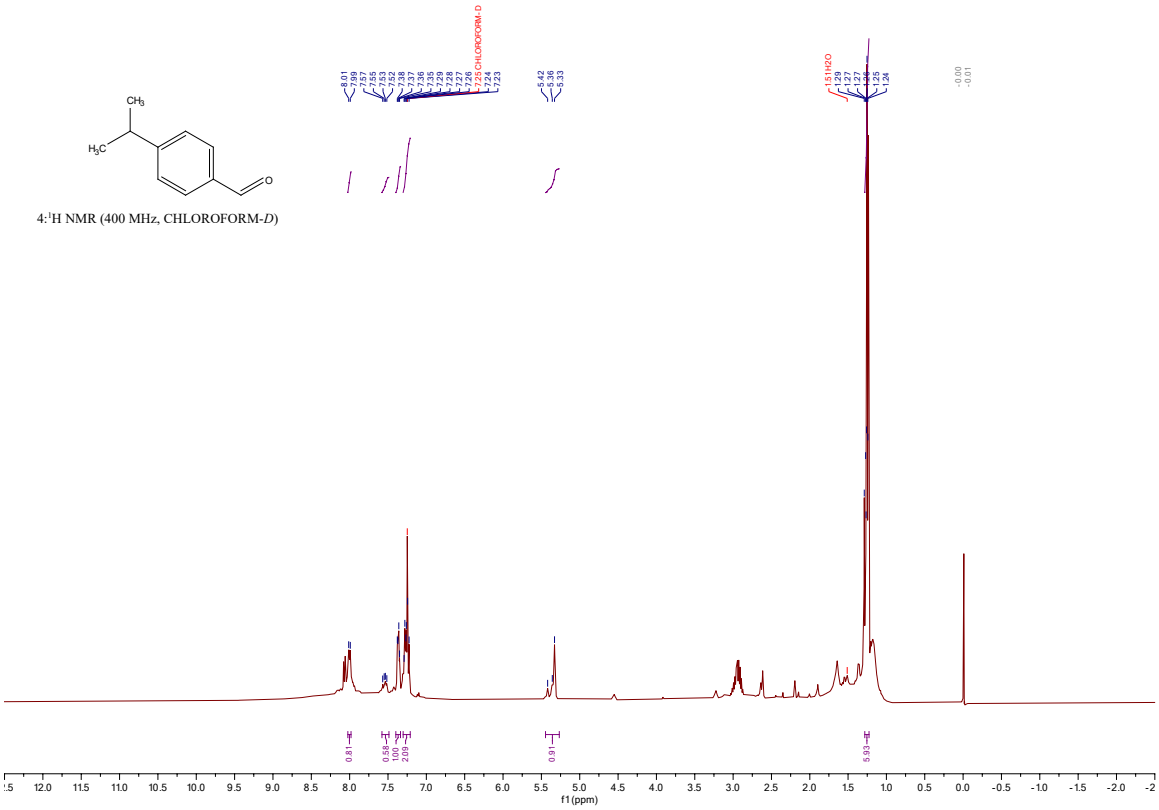




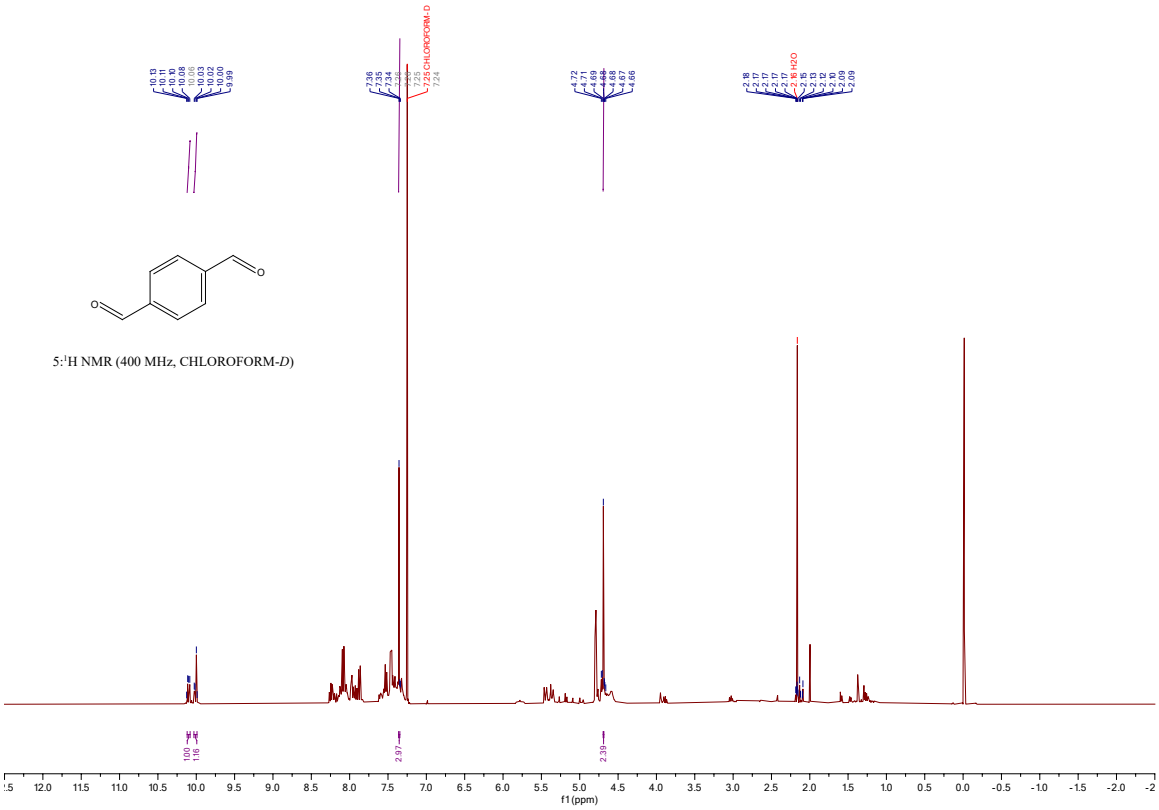
2: ^{1}H NMR (400 MHz, CHLOROFORM-*D*)



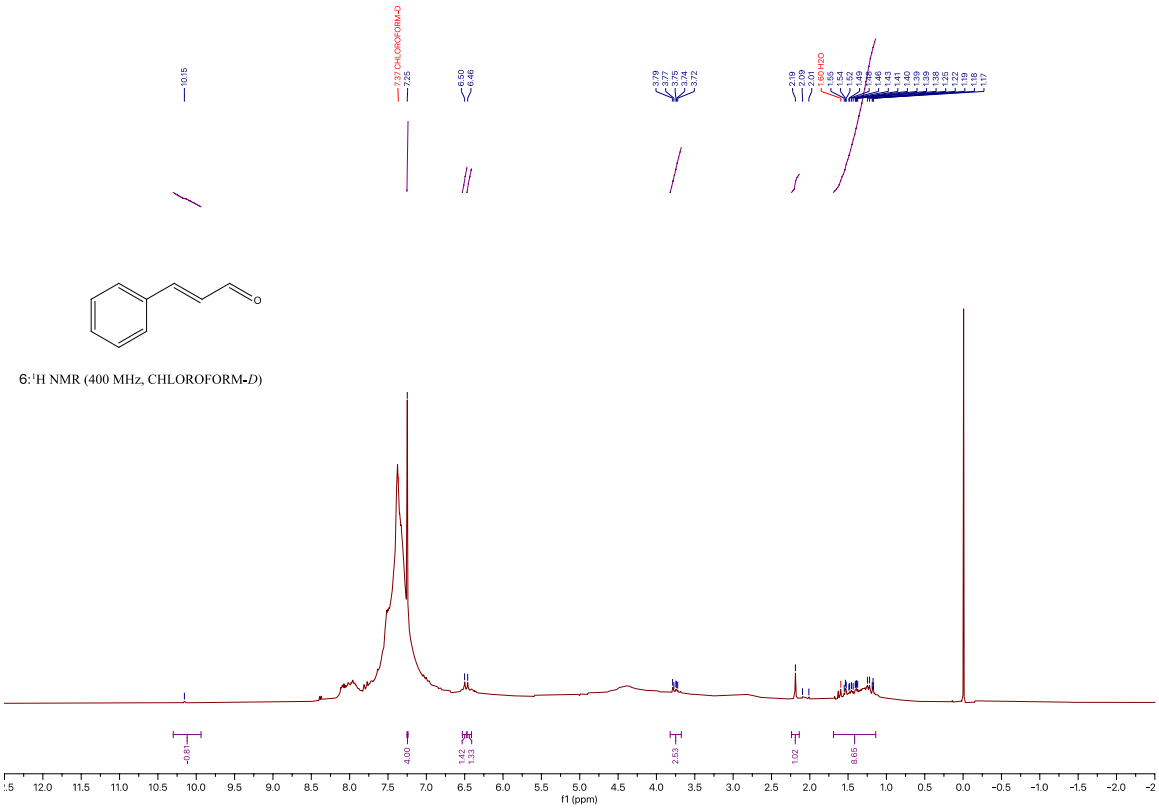
3:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



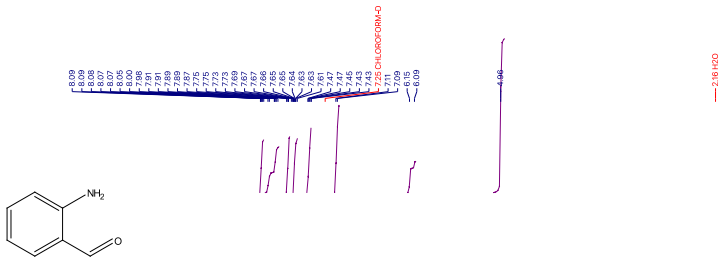
4:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



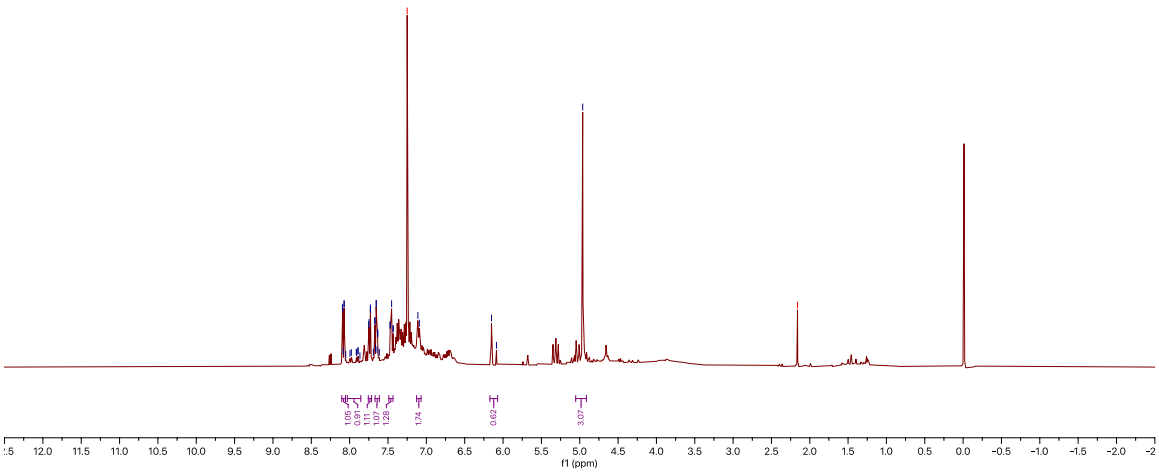
5:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



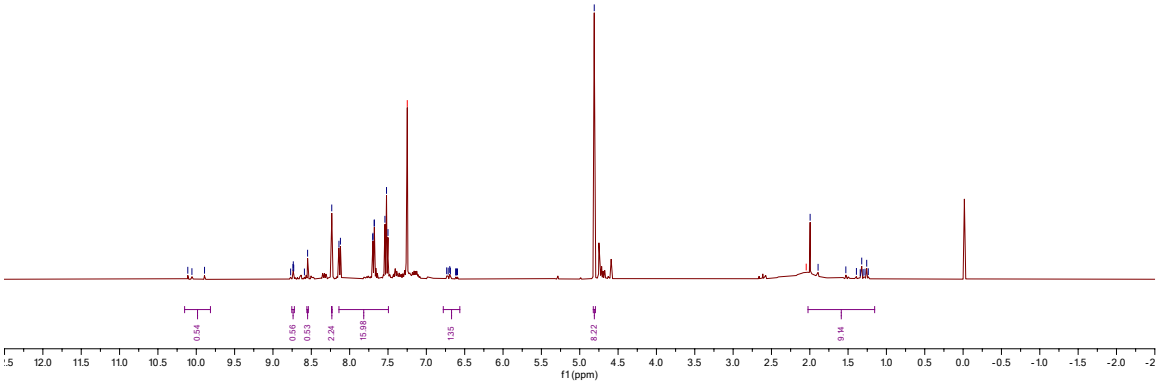
6:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

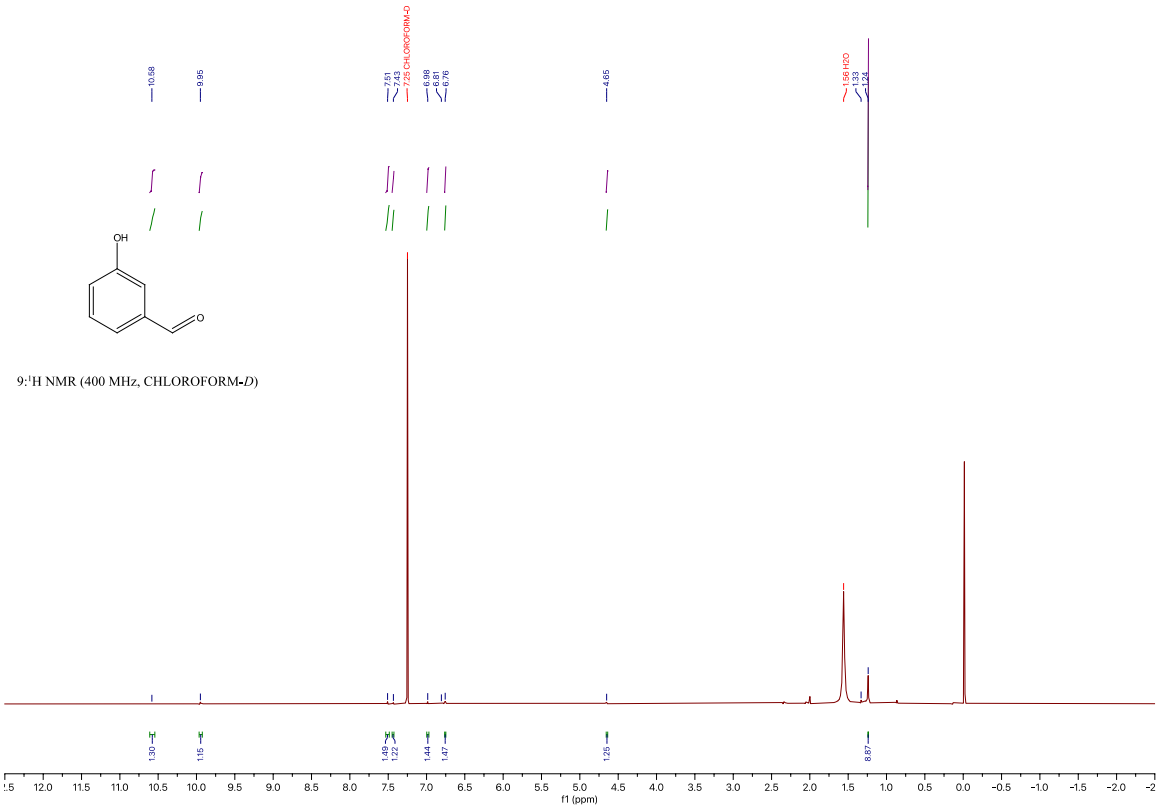


7:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

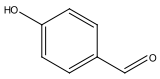


8: ^{1}H NMR (400 MHz, CHLOROFORM-*D*)

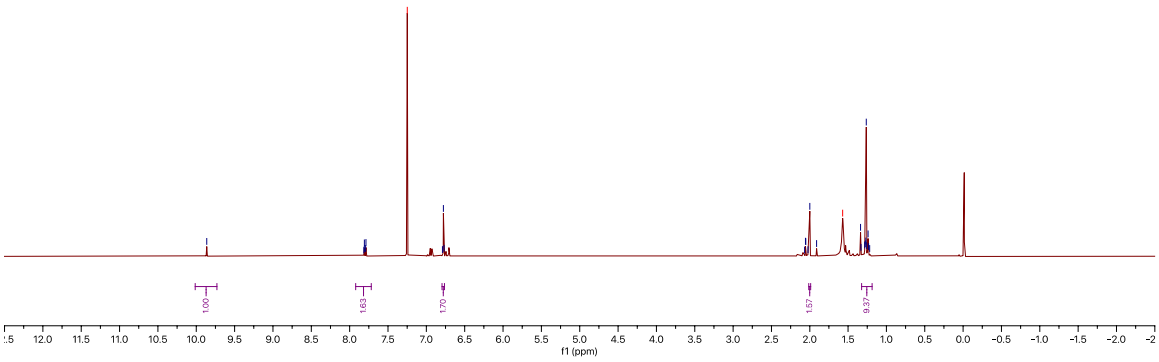


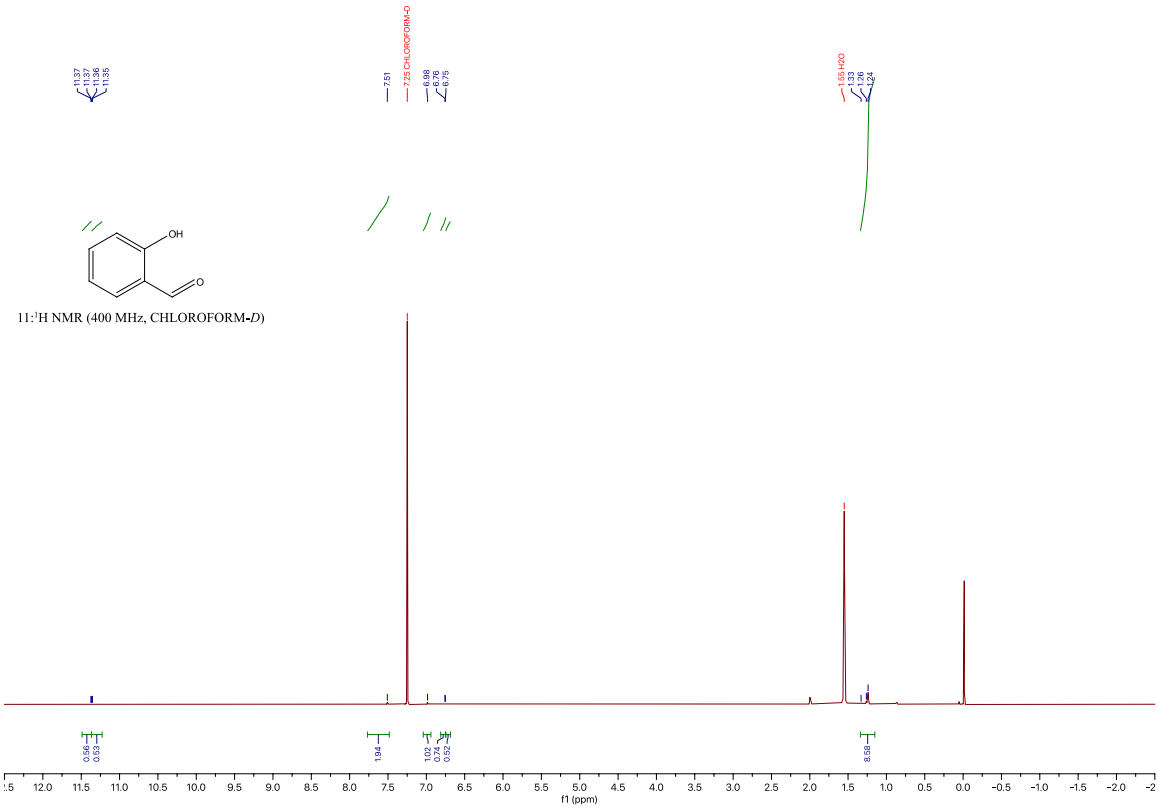


9:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

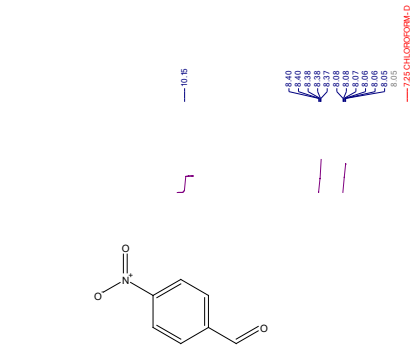


10:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

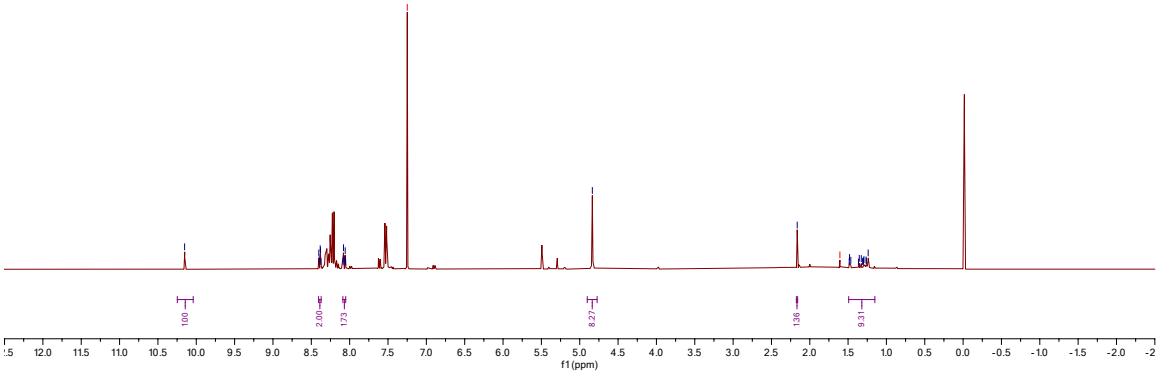


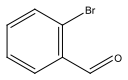


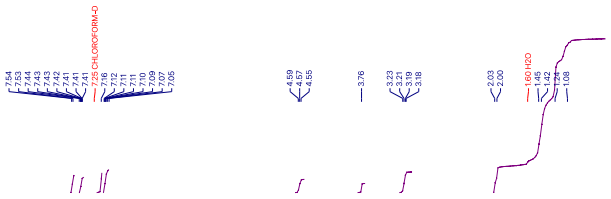
11:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



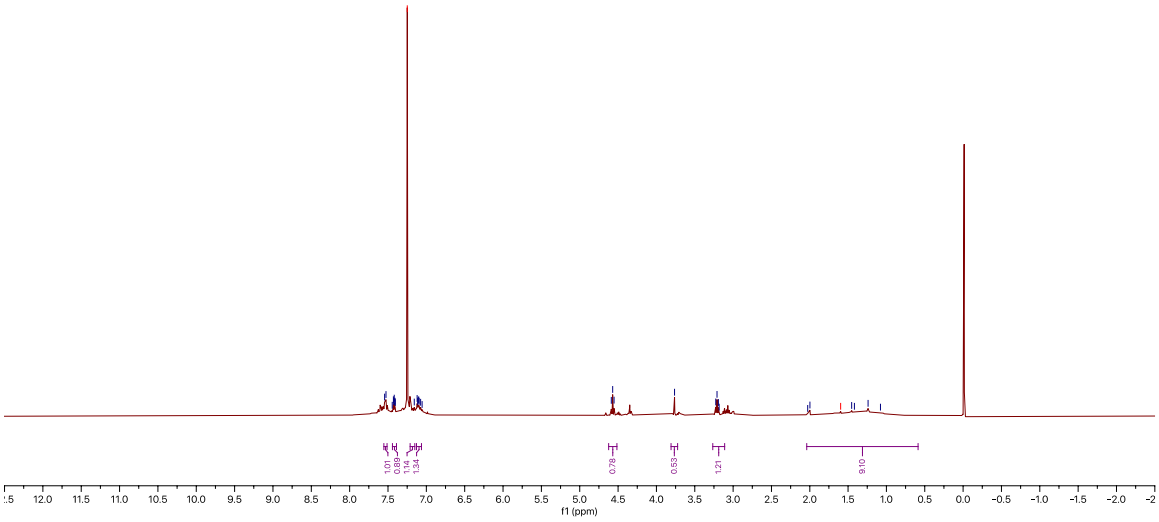
12:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

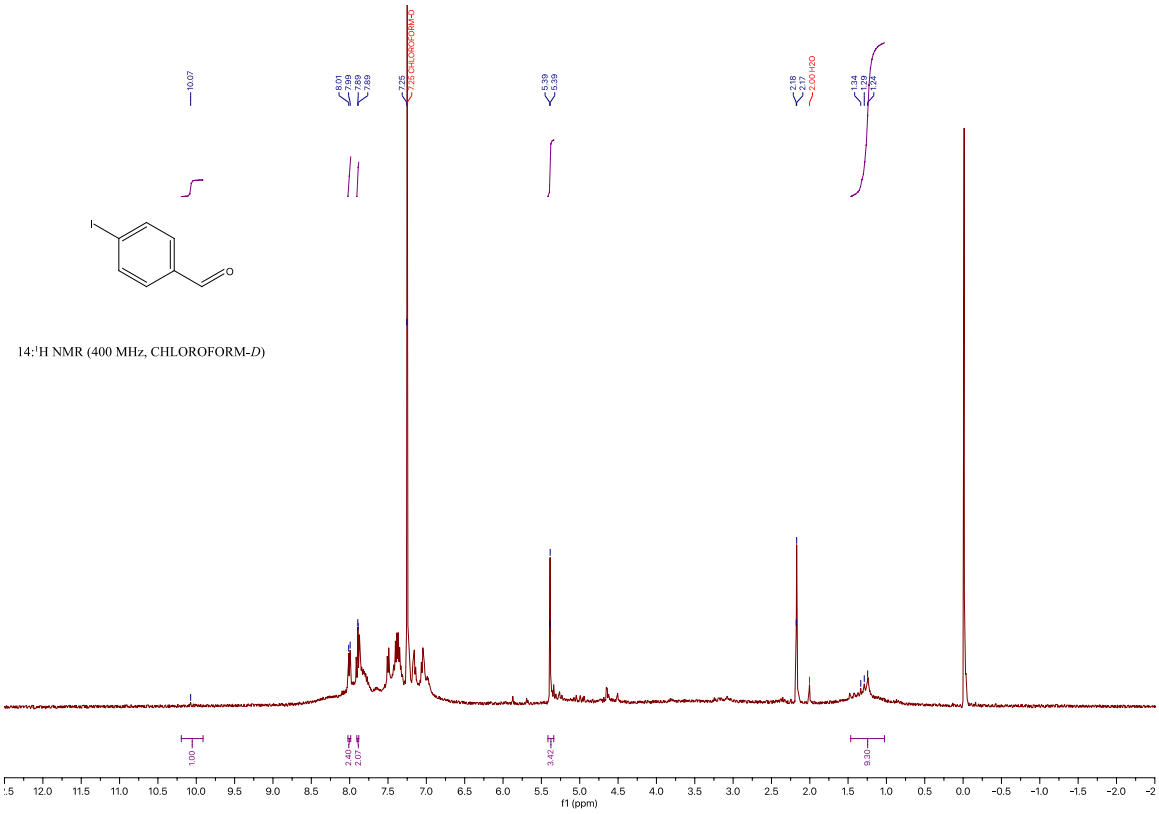




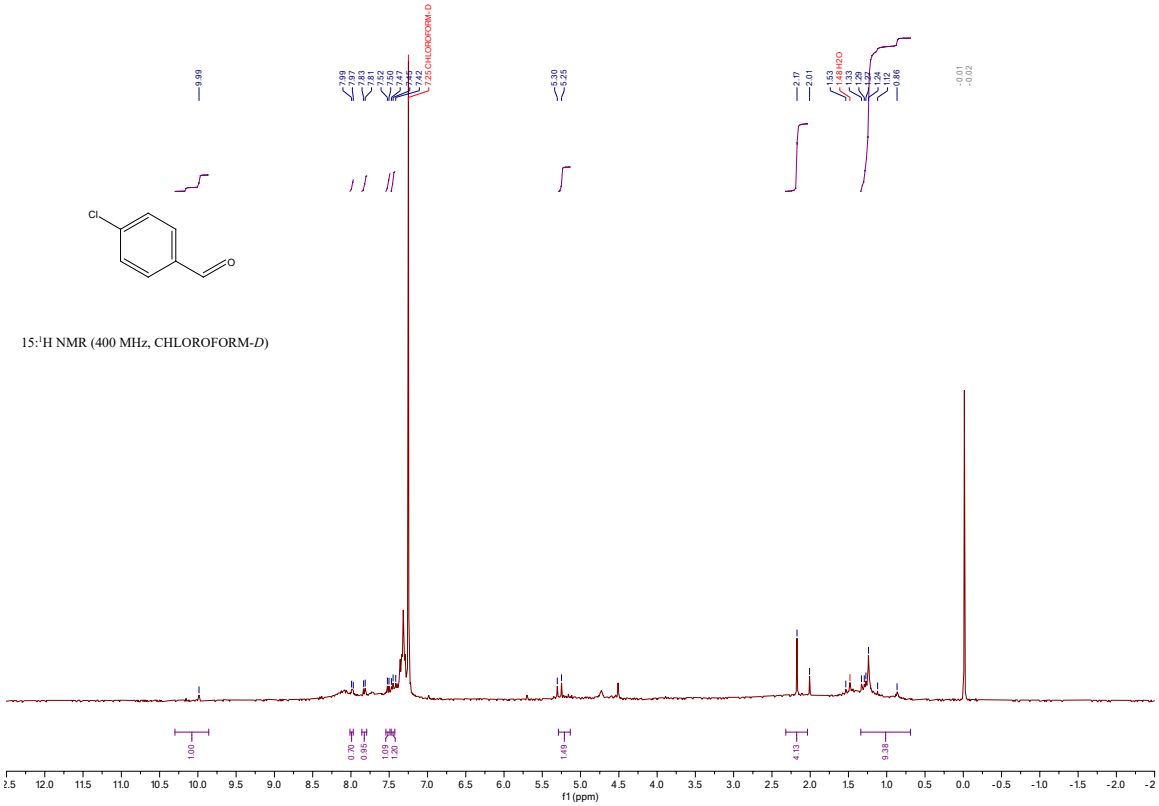


13:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

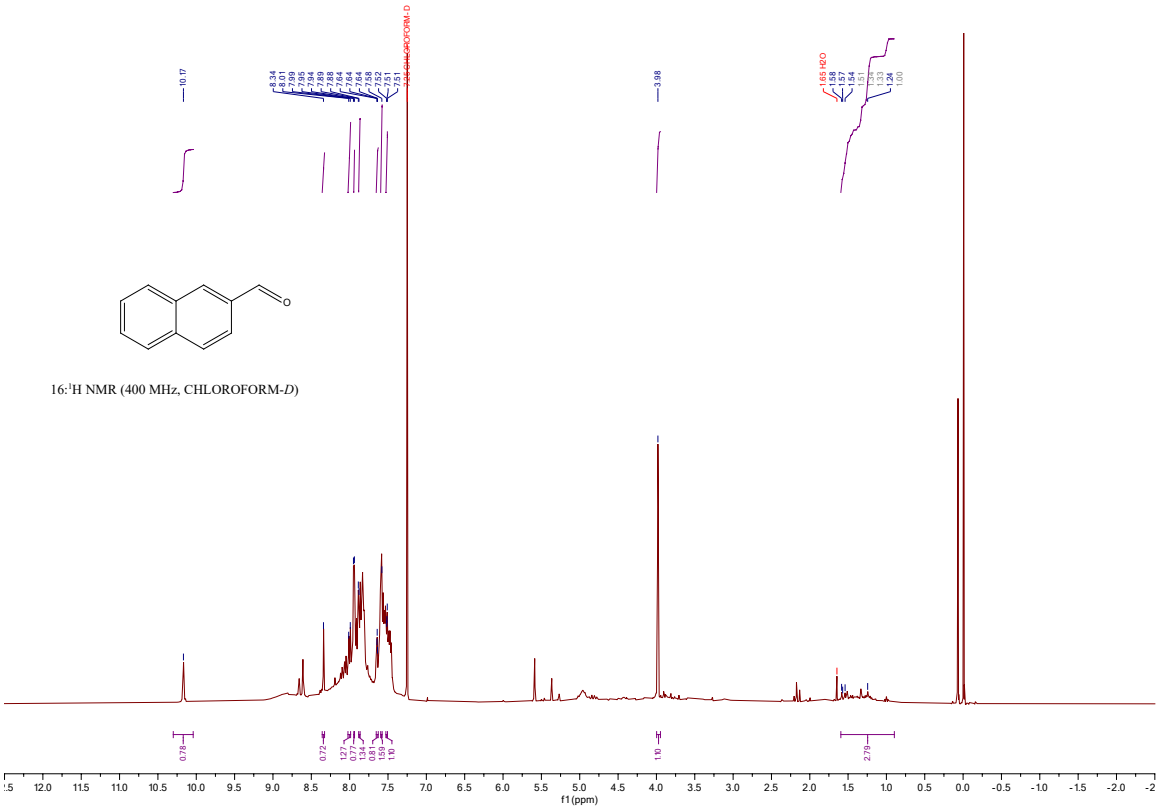




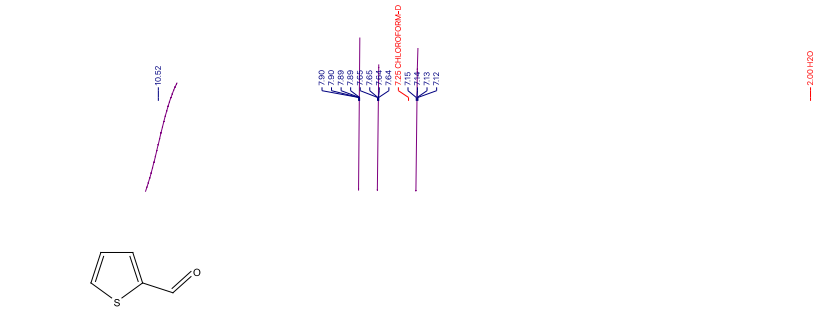
14:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



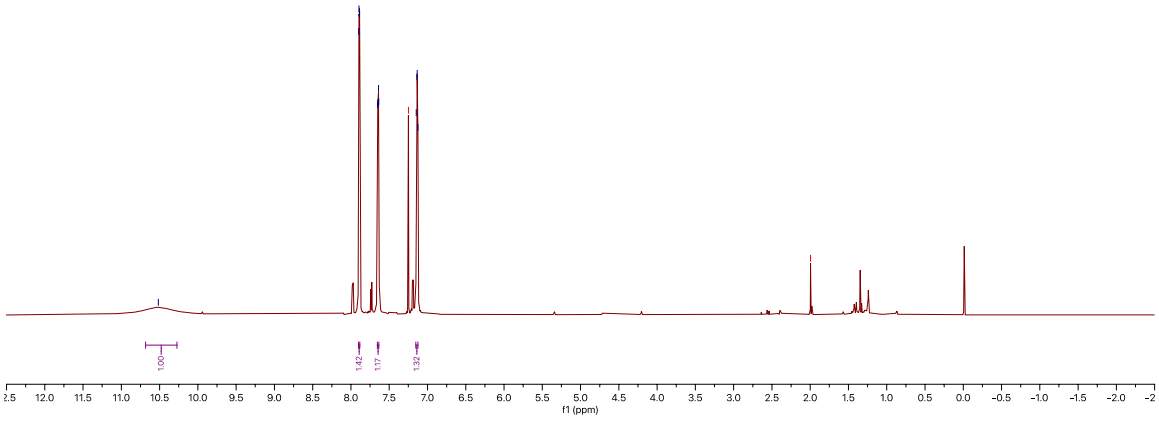
15:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

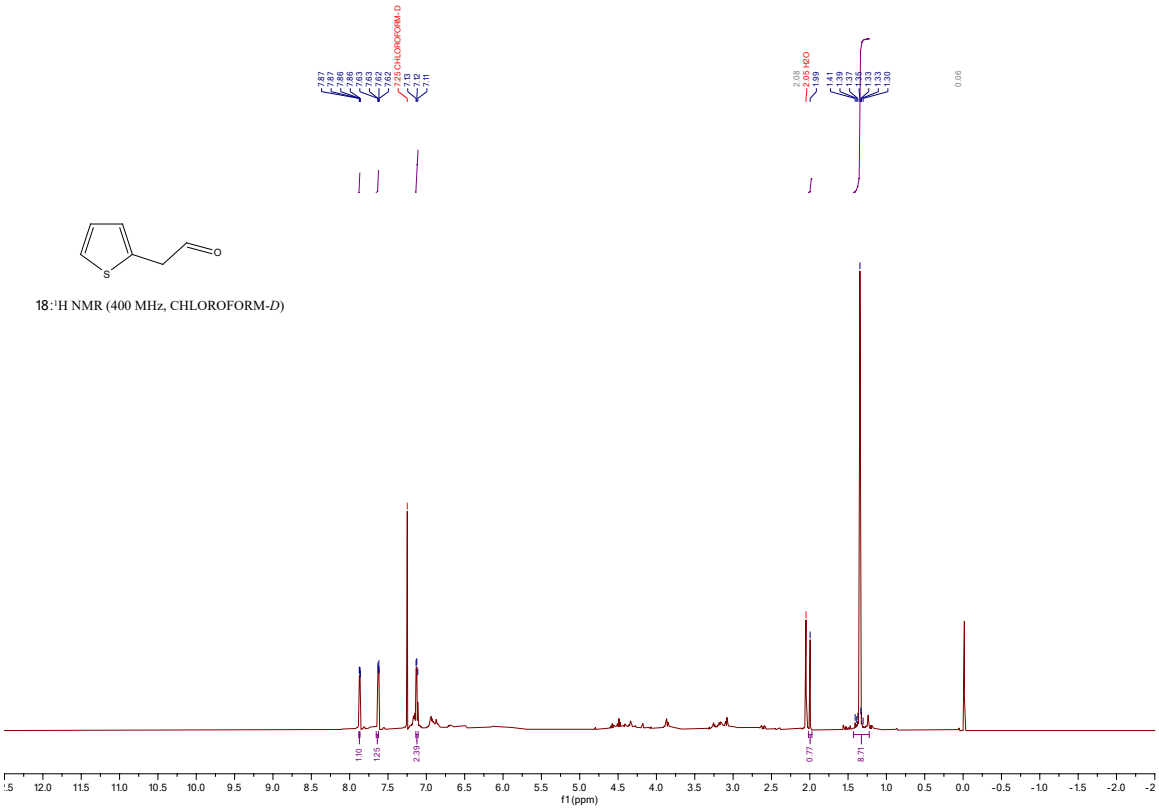


16:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

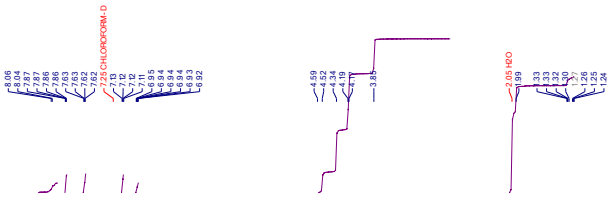


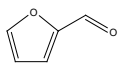
17:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



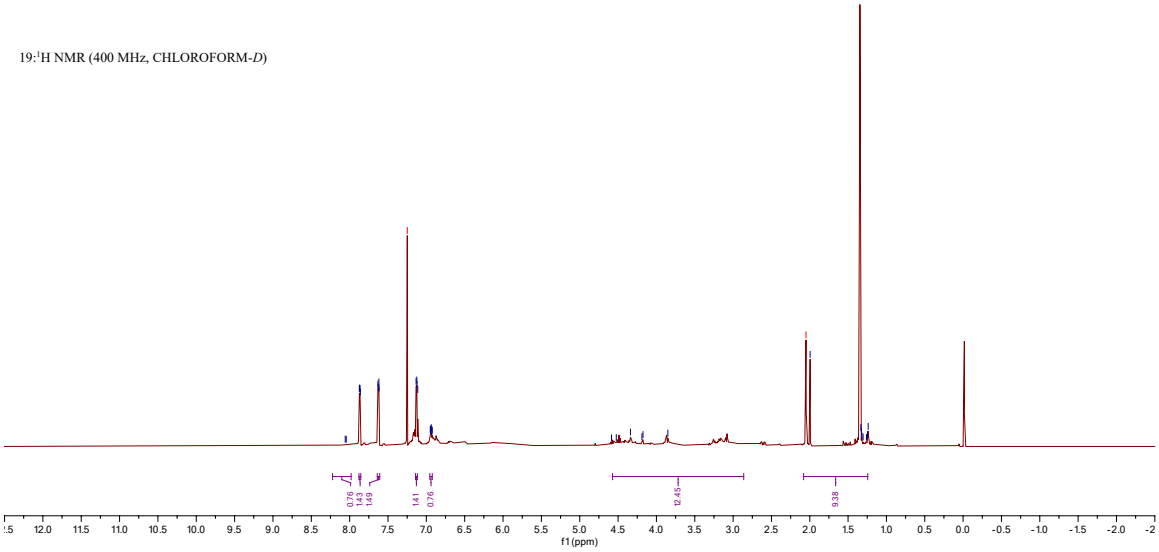


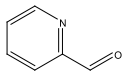
18:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

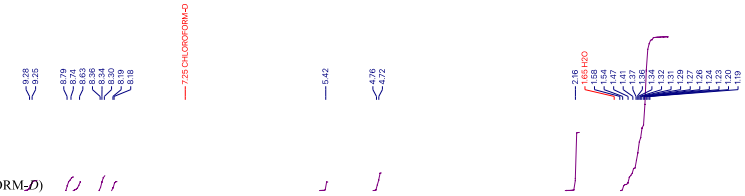




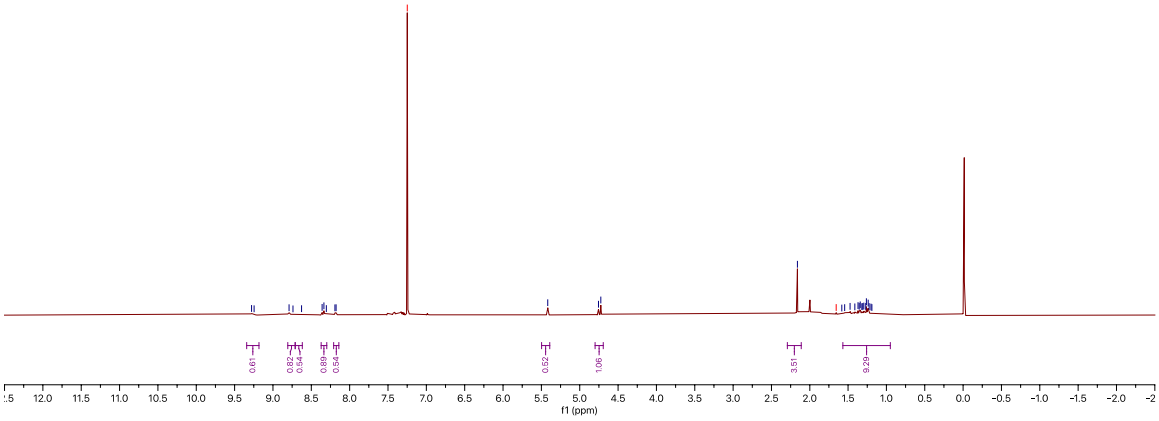
19.[1]H NMR (400 MHz, CHLOROFORM-*D*)

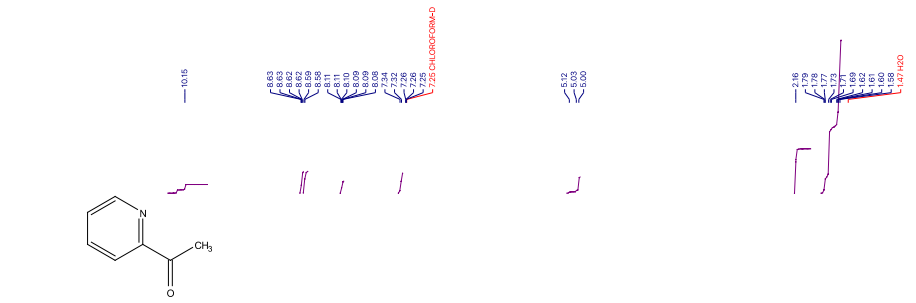




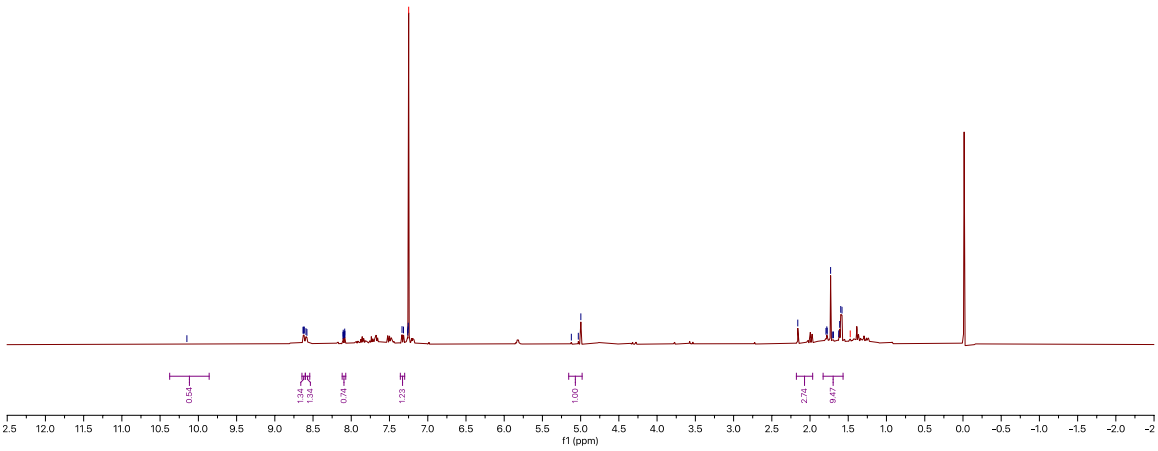


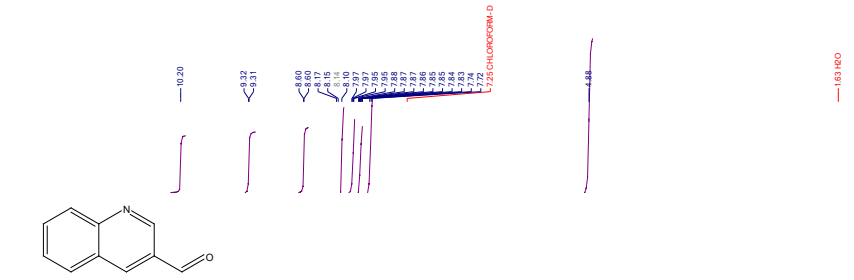
20:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



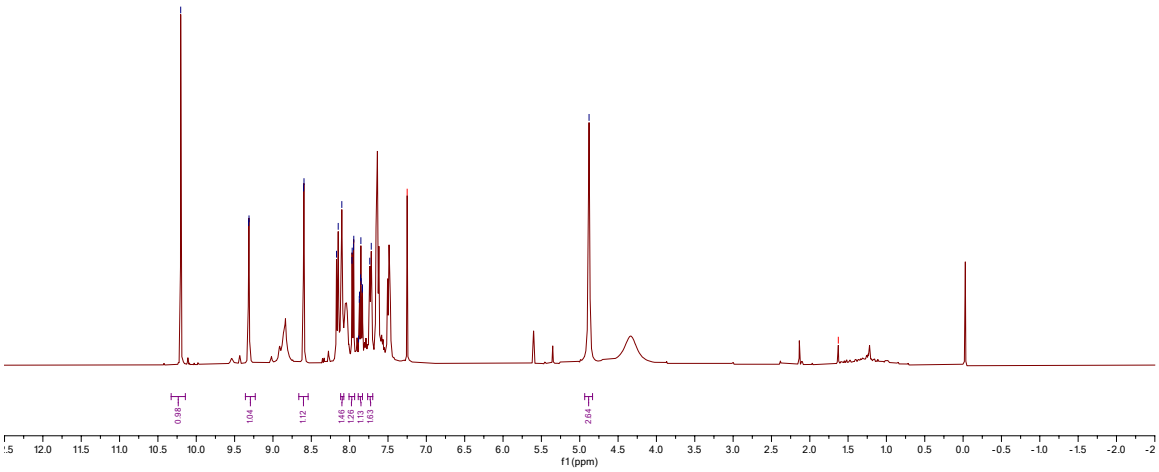


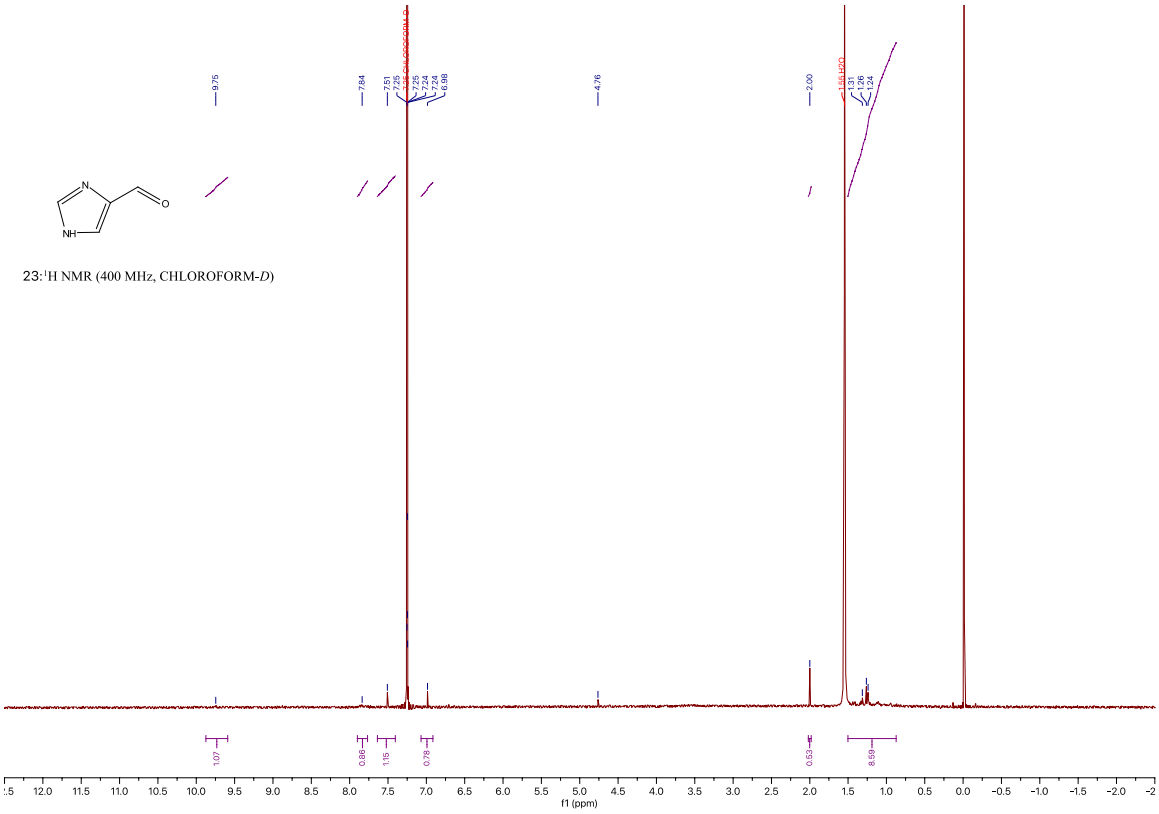
21:^{1}H NMR (400 MHz, CHLOROFORM-*D*)



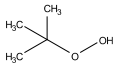


22:^{1}H NMR (400 MHz, CHLOROFORM-*D*)

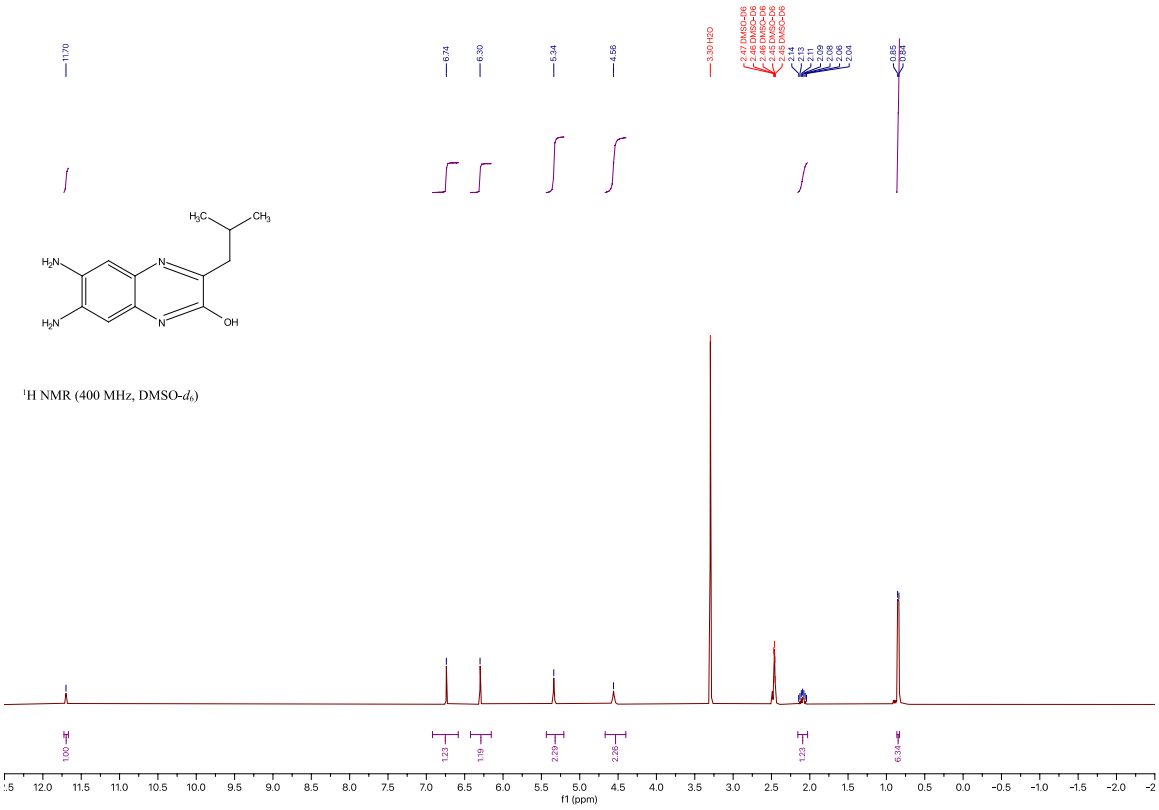




23: ^{1}H NMR (400 MHz, CHLOROFORM-*D*)



TBHP (oxidant)
^{1}H NMR (400 MHz, CHLOROFORM-*D*)

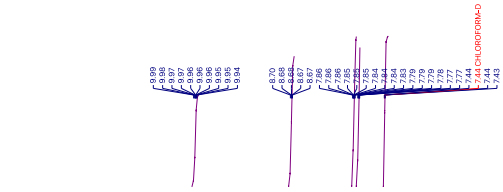


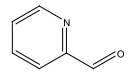
^{1}H NMR (400 MHz, DMSO-d_6)

Gram scale-2-pyridinecarboxaldehyde

Experimental procedures: To a 50 mL round-bottomed flask charged with a stirring bar was sequentially added 2-pyridine methanol (10 mmol), copper-L5 (1mol %), CH_3CN (25 mL), and t-BuOOH (35 mmol). After the reaction was stirred at 70 °C for 4 h, the reaction mixture was extracted with ethyl acetate (EtOAc) 3 times, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography with hexane/ethyl acetate (3:1, v/v) as eluent to yield 1.38 g yellowish oil isolated as the product (83%).

^{1}H NMR (400 MHz, CHLOROFORM-*D*) δ 9.97 (qd, *J* = 4.8, 2.4 Hz, 1H), 8.72 – 8.65 (m, 1H), 7.88 – 7.82 (m, 1H), 7.82 – 7.77 (m, 1H), 7.45 – 7.39 (m, 1H).





^{1}H NMR (400 MHz, CHLOROFORM-*D*)