

Supporting Information for:

Catalytic system for pyridine oxidation to N-oxides under mild conditions based on polyoxomolybdate

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1. Experimental

1.1 Reagents

All chemicals were analytical grade, commercially available and used without further purification unless otherwise stated.

1.2 Preparation of catalyst $[(\text{NH}_4)_{42}[\text{Mo}^{\text{VI}}_{72}\text{Mo}^{\text{V}}_{60}\text{O}_{372}(\text{CH}_3\text{COO})_{30}(\text{H}_2\text{O})_{72}] (\{\text{Mo}_{132}\}) [9]$:

Firstly, 5.6 g (4.5 mmol) of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 2\text{H}_2\text{O}$ and 12.5 g (162 mmol) of $\text{CH}_3\text{COONH}_4$ were dissolved in 250 ml of water with stirring. 0.8 g (6.1 mmol) of $\text{N}_2\text{H}_4\text{H}_2\text{SO}_4$ was then added to the solution. The solution was then stirred for 10 min and the color changed to blue green. 83 mL of CH_3COOH (50%) was subsequently added. The deep green solution was kept at 293-298 K without further stirring for four days (color change to dark brown). The precipitated red-brown crystals were filtered through a glass frit (G2). The sample was washed with 90% ethanol, then with a 1:1 mixture of ethanol/diethyl ether and finally dried in air. The yield is about 3.2 g (about 50% yield based on molybdate). IR spectrum (KBr, cm^{-1}): 1624, 1540.9, 1401.8, 968.6, 937.0, 856.6, 794.8, 727.1, 631.6, 567.8, 512.8, 464.2, 438.5, 409.5.

1.3 Characterization techniques

Infrared spectra were recorded on a Nicolet 5700 FT-IR spectrometer using KBr pellets. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III-400 MHz spectrometer with TMS as an internal standard and CDCl_3 as solvent.

1.4 Catalytic reaction

Catalyst (0.01 mmol), H_2O (3 ml), absolute ethyl alcohol (2 ml), substrate (1 mmol), and H_2O_2 (5 mmol, 30 % aq.) were charged in the reaction flask. The mixture was then stirred at room temperature (298 K) for 6-24 h. The reaction was detected by TLC. After reaction, the organic

products were separated from the aqueous phase by extraction with dichloromethane. The aqueous phase containing the catalyst was carried out for the next oxidation cycle. The combined organic layers were dried over anhydrous Na_2SO_4 . After filtered and concentration, the dichloromethane solution was passed through a silica gel column using ethyl acetate and absolute ethyl alcohol as eluent to provide analytically pure N-oxides.

2. IR spectra

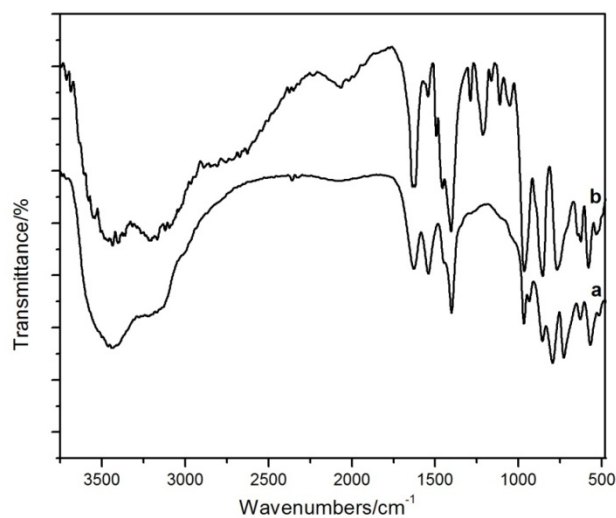


Figure S1 IR spectra of the catalyst before and after oxidation reaction: (a) the fresh catalyst; (b) the used catalyst.

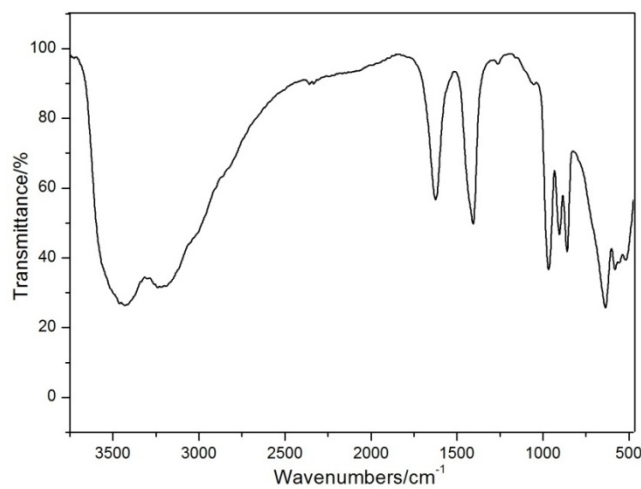


Figure S2 IR spectrum of the catalyst treated with H_2O_2

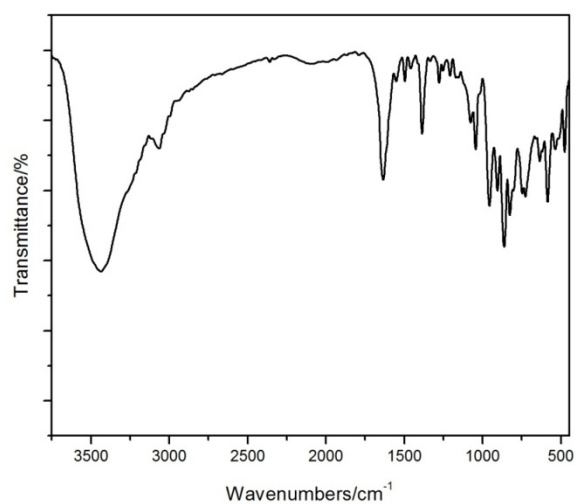
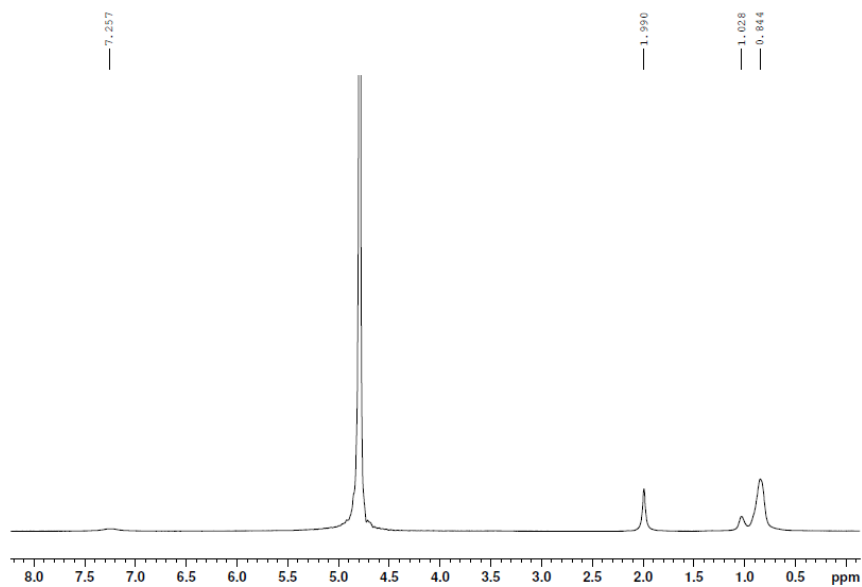
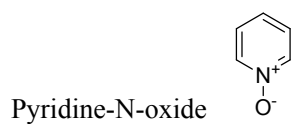


Figure S3 IR spectrum of the used catalyst precipitated from system after oxidation of quinoline

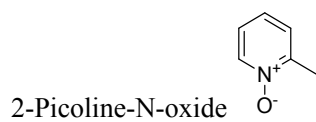
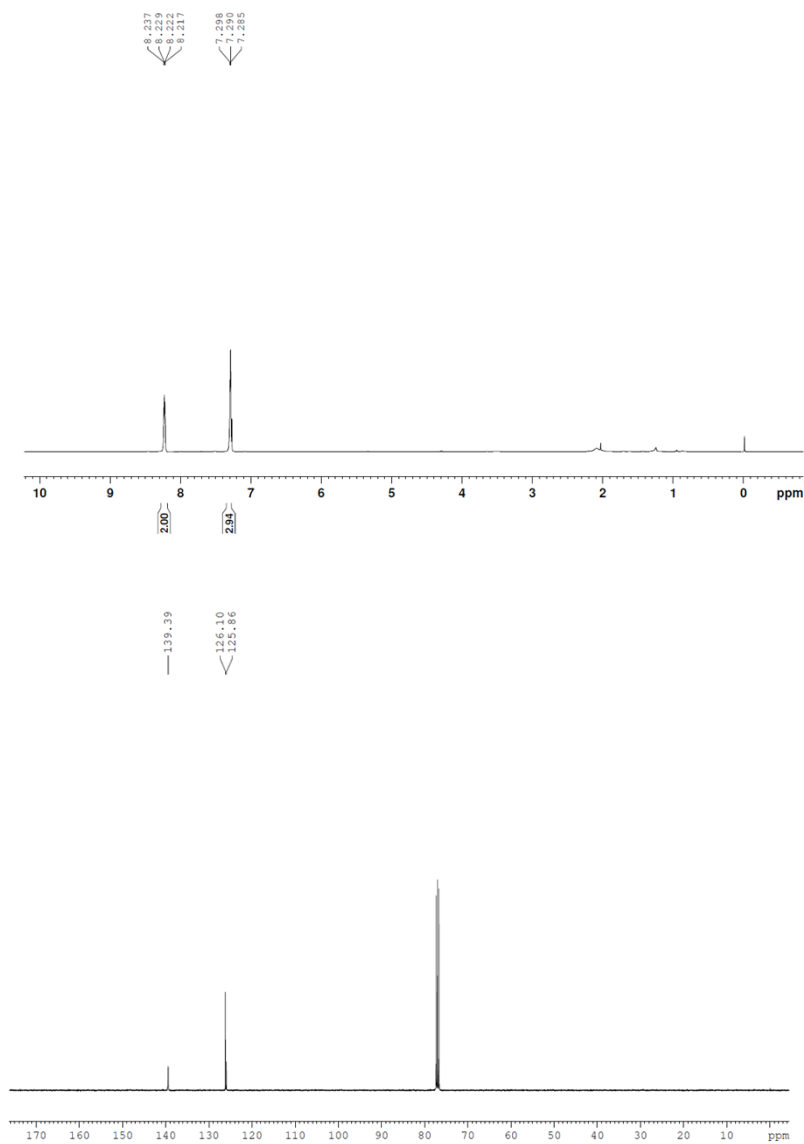
3. ¹H NMR spectra of fresh catalyst



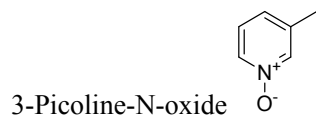
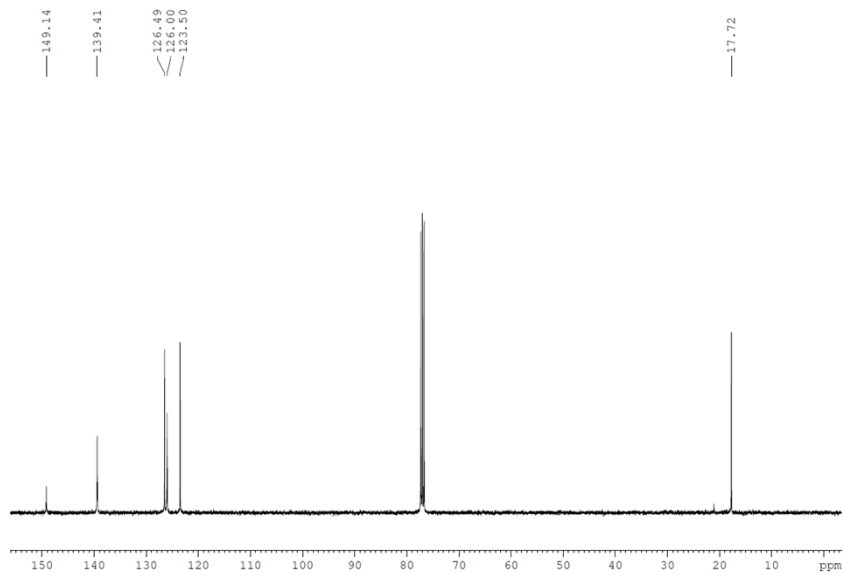
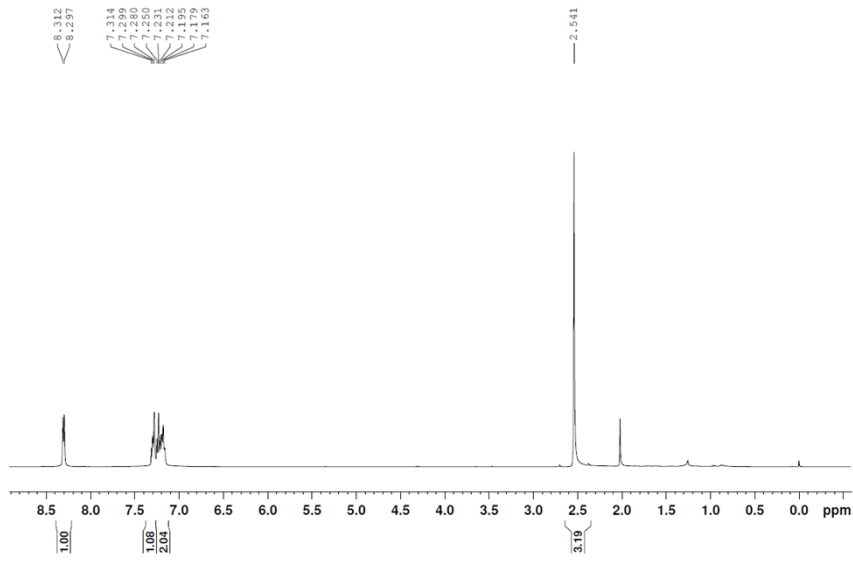
4. Characterization of oxidation products



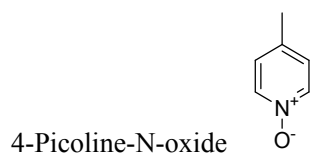
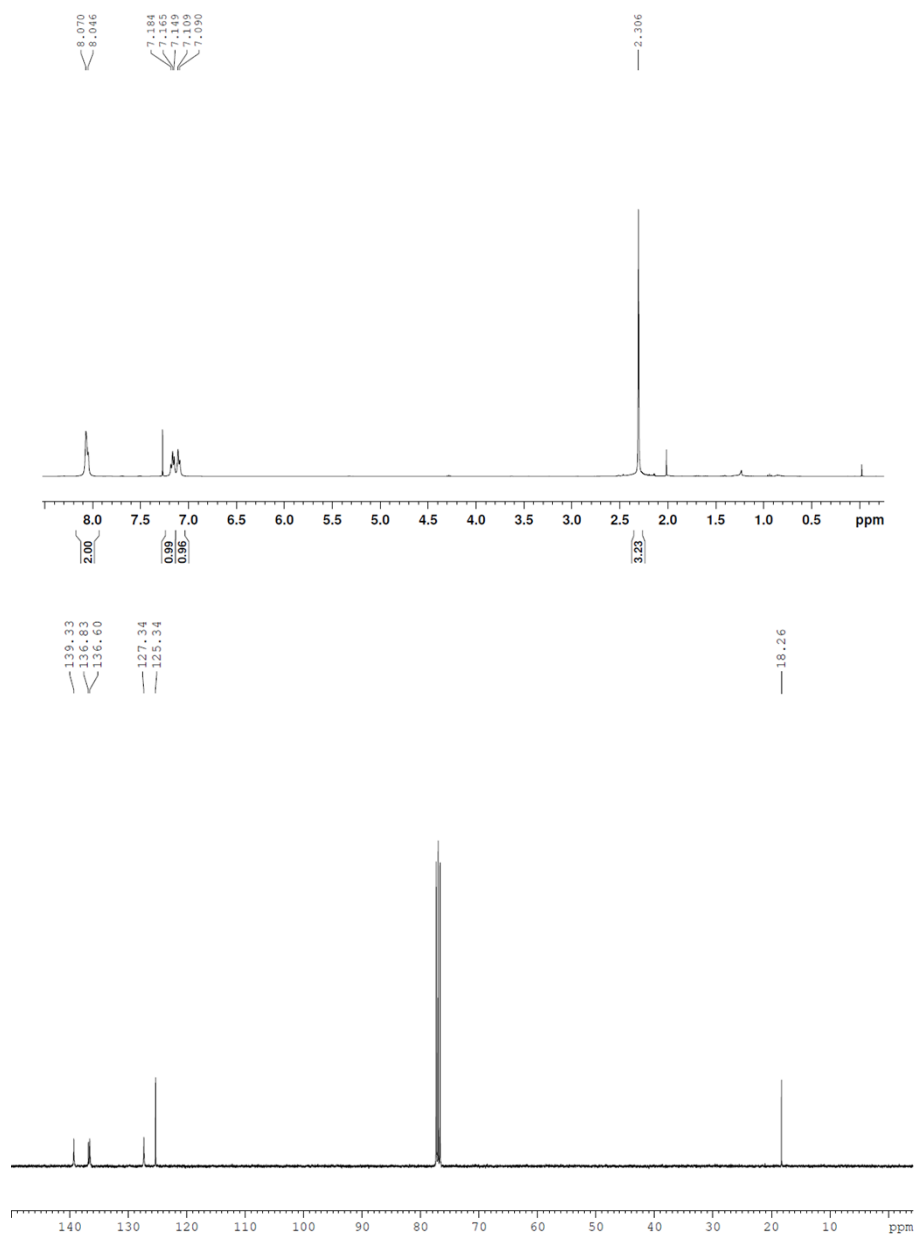
^1H NMR (CDCl_3 , 400 MHz) δ 8.24-8.22 (m, 2 H), 7.30-7.28 (m, 3 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 125.9 (2C), 126.1, 139.4 (2C).



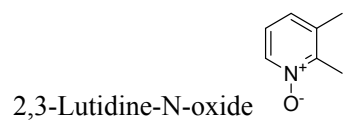
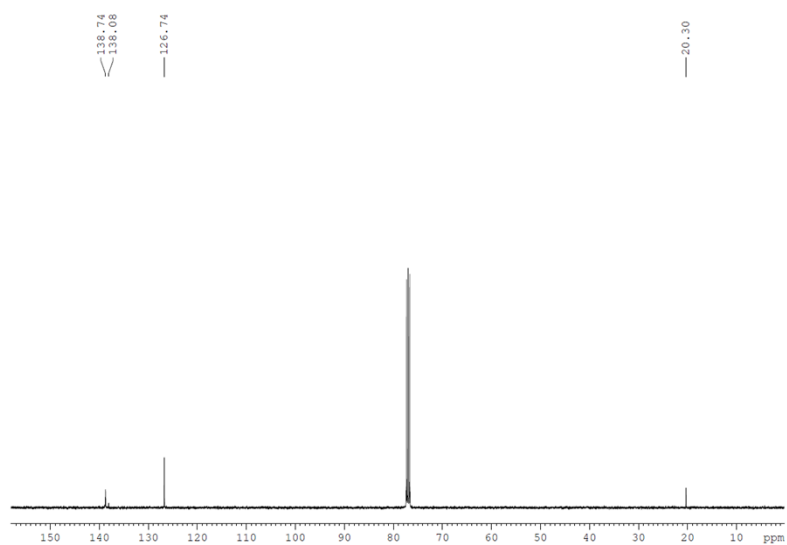
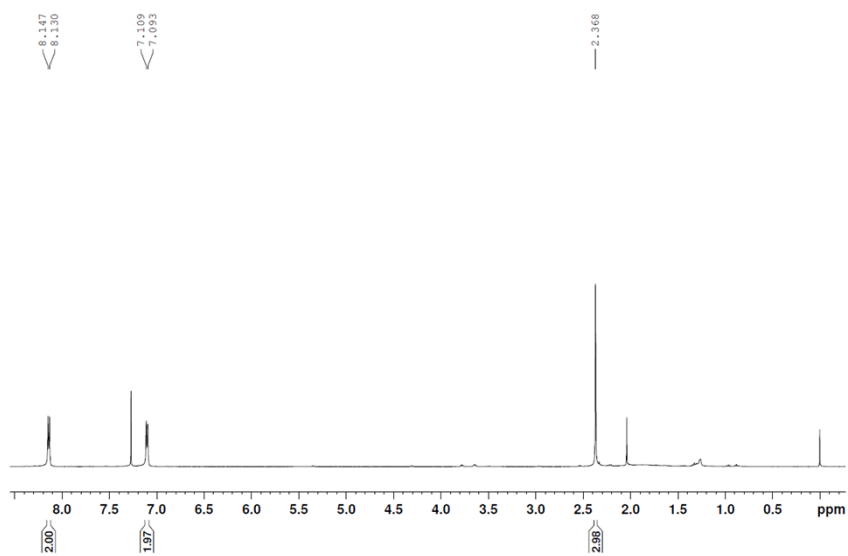
^1H NMR (CDCl_3 , 400 MHz) δ 8.30 (d, $J=6$ Hz, 1 H), 7.31-7.28 (m, 1 H), 7.25-7.16 (m, 2 H), 2.54 (s, 3 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 17.7, 123.5, 126.0, 126.5, 139.4, 149.1.



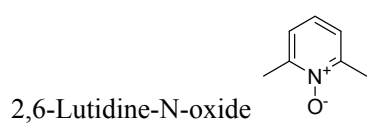
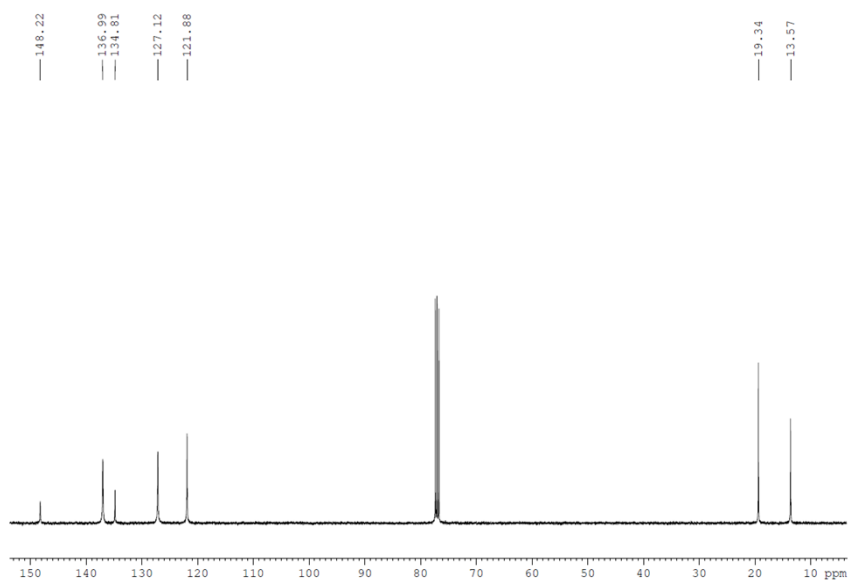
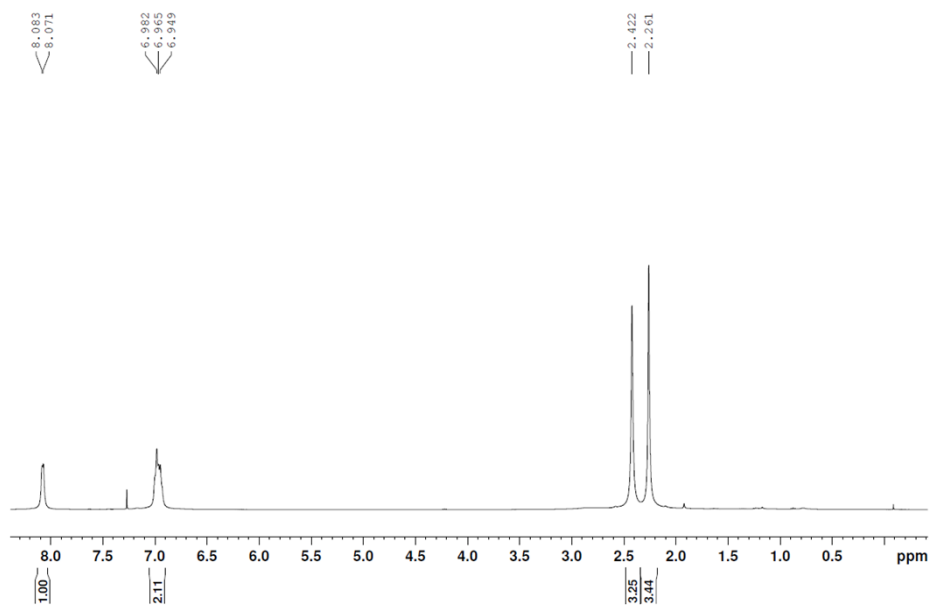
^1H NMR (CDCl_3 , 400 MHz) δ 8.06 (d, $J=9.4$ Hz, 2 H), 7.18-7.09 (m, 2 H), 2.31 (s, 3 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 18.3, 125.3, 127.3, 136.6, 136.8, 139.3.



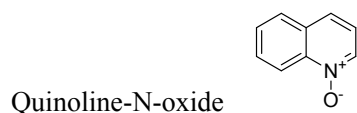
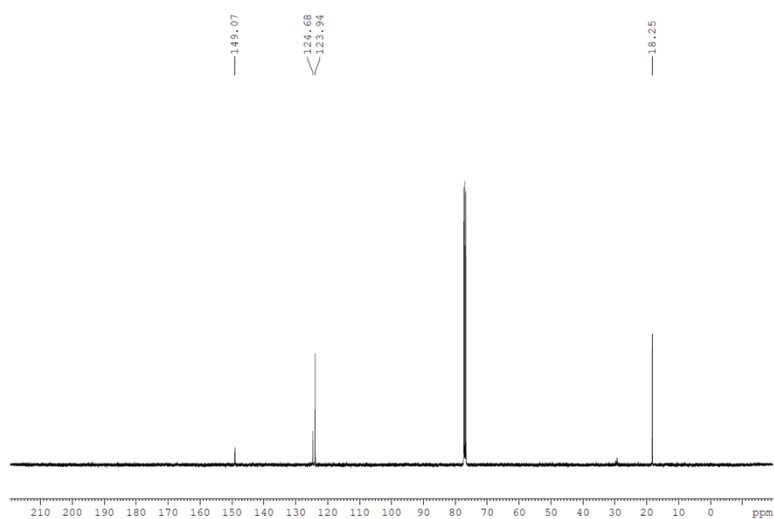
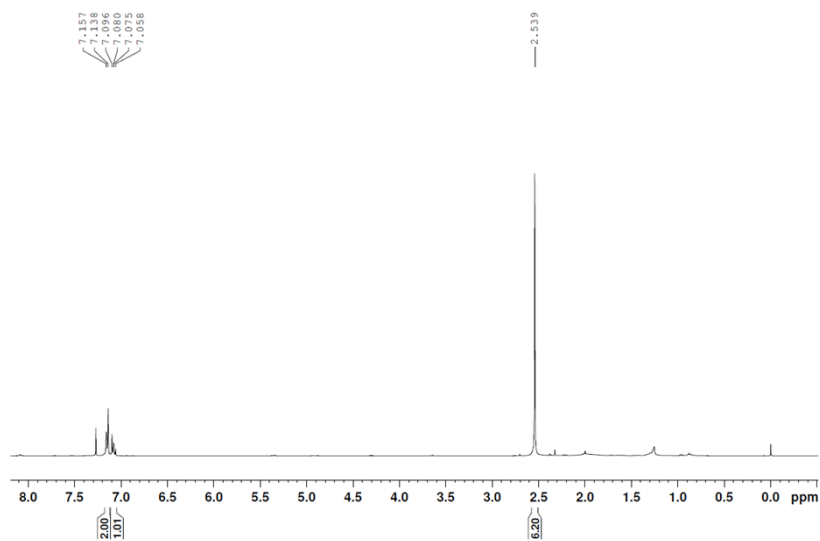
¹H NMR (CDCl₃, 400 MHz) δ 8.14 (d, J=6.8 Hz, 2 H) 7.10 (d, J=6.6 Hz, 2 H), 2.37 (s, 3 H); ¹³C NMR(CDCl₃, 100 MHz) δ 20.3, 126.7 (2C), 138.1, 138.7 (2C).



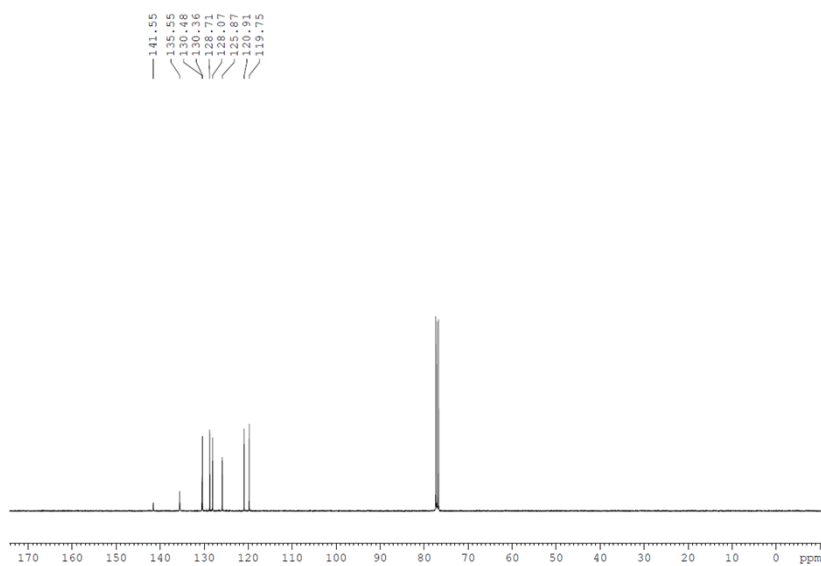
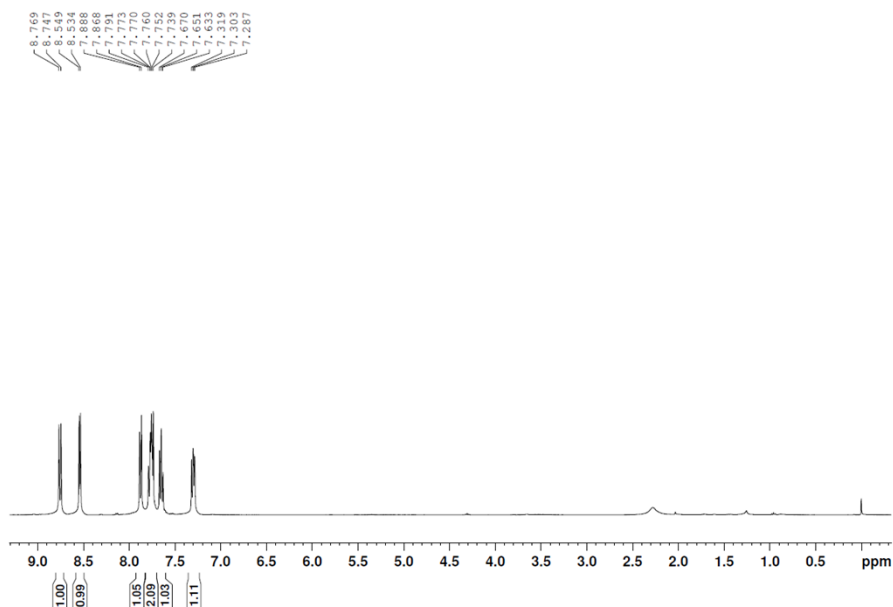
^1H NMR (CDCl_3 , 400 MHz) δ 8.08 (d, $J=4.7$ Hz, 1 H), 6.98-6.95 (m, 2 H), 2.42 (s, 3 H), 2.26 (s, 3 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 13.6, 19.3, 121.9, 127.1, 134.8, 137.0, 148.2.



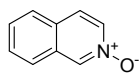
^1H NMR (CDCl_3 , 400 MHz) δ 7.15 (d, $J=7.6$ Hz, 2 H), 7.10-7.06 (m, 1 H), 2.54 (s, 6 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 18.3(2C), 123.9(2C), 124.7, 149.1(2C).



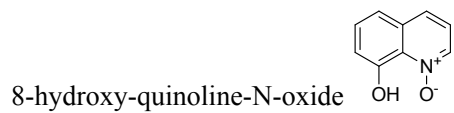
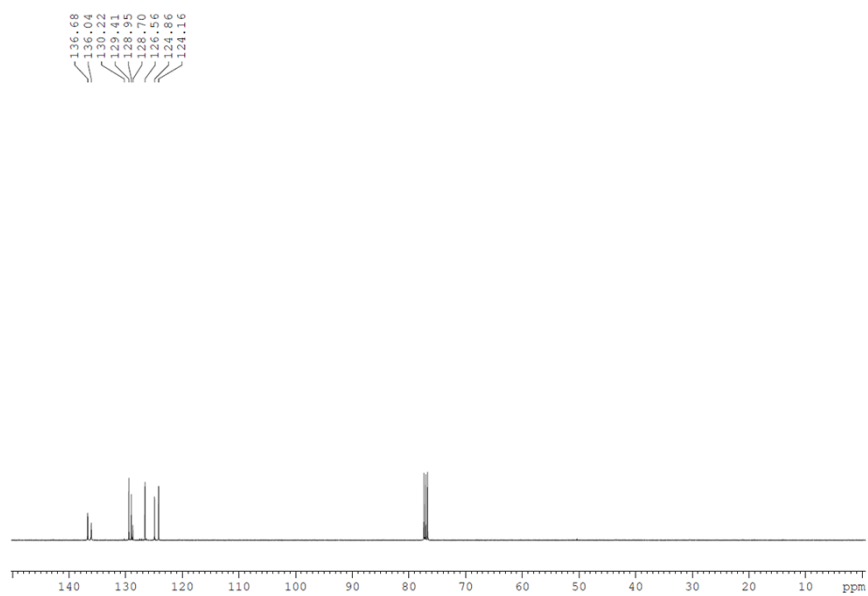
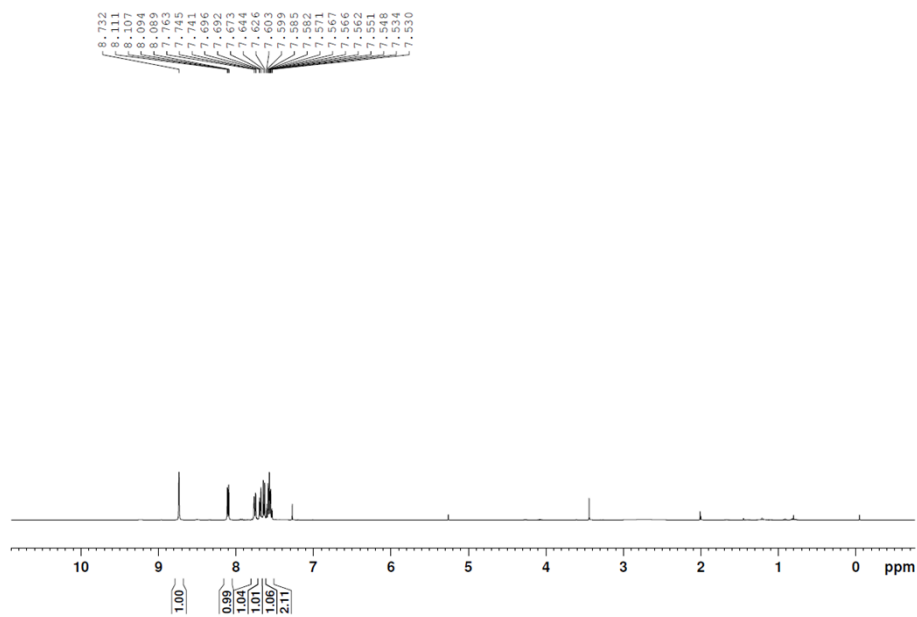
^1H NMR (CDCl_3 , 400 MHz) δ 8.76 (d, $J=8.8$ Hz, 1 H), 8.54 (d, $J=6$ Hz, 1 H), 7.88 (d, $J=8.2$ Hz, 1 H), 7.79-7.74 (m, 2 H), 7.67-7.63 (m, 1 H), 7.32-7.29 (m, 1 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 119.7, 120.9, 125.9, 128.1, 128.7, 130.4, 130.5, 135.5, 141.5.



Isoquinoline-N-oxide



^1H NMR (CDCl_3 , 400 MHz) δ 8.73 (s, 1 H), 8.10 (dd, $J=1.8, 7.1$ Hz 1 H), 7.76-7.74 (m, 1 H), 7.70-7.63 (m, 2 H), 7.60-7.53 (m, 2 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 124.2, 124.9, 126.6, 128.7, 129.0, 129.4, 130.2, 136.0, 136.7.



^1H NMR (CDCl_3 , 400 MHz) δ 15.0 (s, 1 H), 8.17 (d, $J=5.8$ Hz, 1 H), 7.71 (d, $J=8.5$ Hz, 1 H), 7.43-7.39 (m, 1 H), 7.19-7.15 (m, 2 H), 6.99 (d, $J=7.8$ Hz, 1 H); ^{13}C NMR(CDCl_3 , 100 MHz) δ 113.9, 115.7, 119.4, 128.6, 129.0, 129.6, 131.3, 133.5, 153.1.

