Supplementary Material (ESI) for Green Chemistry

Supporting information

Mild and recyclable catalytic oxidation of pyridines to N-oxides with H_2O_2 in water mediated by a vanadium-substituted polyoxometalate

Yong Ding*, Wei Zhao, Wenfeng Song, Zhenxin Zhang, Baochun Ma*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China

Contents: **Pages**

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

Preparation of the active catalyst of $K_6[PW_9V_3O_{40}]\cdot 4H_2O$ [1]:

Firstly, $Na_8H[PW_9O_{34}]$ was synthesized from $Na_2WO_4\cdot 2H_2O$ and H_3PO_4 according to the ref. [2]. 0.61g sample of $NaVO_3$ was added to 20 ml (1.0 M) of sodium acetate/ acetic acid buffered at PH 4.8. Then, 4 g of $Na_8H[PW_9O_{34}]$ was added to the above solution and stirred at 25 ^oC for 48 h. The solution was treated with 3 g of solid KCl and stirred for 30 min. Methanol (50 ml) was added to produce precipitate. The solid was filtered and dried in air to give 4.1 g of tan-orange powder. IR spectrum (KBr, cm^{-1}): 1085, 1055, 962, 876, 788, 597, 509, 481. ^{31}P MAS NMR: -13.2 ppm. Calcd for $K_6[PW_9V_3O_{40}]\cdot 4H_2O$: K, 8.42; P, 1.11; V, 5.49; W, 59.41. Found: K, 8.49; P, 1.06; V, 5.38; W, 59.35.

The sample of peroxo species was synthesized as follows:

780 mg (280 μmol) of $K_6[PW_9V_3O_{40}]\cdot 4H_2O$ was dissolved in 21 ml (30% aq, 200 mmol) H_2O_2. (the molar ratio of H_2O_2/ $K_6[PW_9V_3O_{40}]\cdot 4H_2O$ is the same as the catalytic reaction condition). The solution was kept for 5-6 hours at room temperature with vigorous stirring. Finally, an orange powder solid was obtained after the aqueous solution was concentrated. IR spectrum (KBr, cm^{-1}): 1082, 954, 879, 794, 621, 552.

1.3 Characterization techniques

Infrared spectra were recorded on a Nicolet FTIR-360 FT-IR spectrometer. The catalysts were measured using 2–4% (w/w) KBr pellets prepared by manual grinding. Chemical elemental analysis of the catalysts was done on an ICP-atomic emission spectrometer (IRIS ER/S). ^{31}P MAS NMR spectra were recorded at 9.4 T on a Bruker Avance-400 wide bore spectrometer. The ^{31}P MAS NMR spectra of solid catalyst with high-power proton decoupling were performed at 161.9 MHz with BB MAS probe head using 4 mm ZrO_2 rotors and 3.8 μs pulse and 2 s repetition time and 4096 scans, with samples spun at 10 kHz and referenced to 85% H_3PO_4.GC analyses were performed on Shimadzu GC-9AM with a flame ionization detector equipped with FFAP capillary

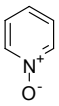
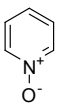
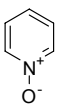
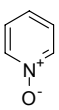
column (internal diameter = 0.25 mm, length = 30 m). GC-MS was recorded on Finnigan Trace DSQ (Thermo Electron Corporation) at an ionization voltage of 70 eV equipped with a DB-5 capillary column (internal diameter = 0.25 mm, film thickness = 0.25μm, length = 30m). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-400 and Varian mercury 300 MHz spectrometer with TMS as an internal standard and $CDCl_3$ as solvent.

1.4 Catalytic reaction

Catalyst (14 μmol), H_2O (1 ml), substrate (2 mmol), and H_2O_2 (10 mmol, 30% aq.) were charged in the reaction flask. The mixture was stirred at room temperature (298K) or 338K for 6-24 h. The reaction was detected by TLC accompanied with GC. After the reaction, the organic products were separated from the aqueous phase by extraction and then the organic layer was analyzed by GC with the internal standard method. The pure products were obtained by evaporation or column chromatography and analyzed by melting point, ^{1}H NMR and ^{13}C NMR. After separation of the products, re-addition of pyridines (2 mmol) and H_2O_2 (10 mmol, 30% aq.) to the aqueous phase containing the catalyst was carried out for the next oxidation cycle.

2. Catalyst reuse

Table S1 Oxidation of pyridine catalyzed by $K_6[PW_9V_3O_{40}]\cdot 4H_2O$ for different cycles [a]

Catalyst	Substrate	Product	Yield (%)	TON
Fresh			91	130
Cycle 1			92	131
Cycle 2			90	128
Cycle 3			89	127

[a] Reaction conditions: 2 mmol substrate, 10 mmol (30% aq.) H_2O_2, 14 μmol catalyst, 1 ml H_2O. Room temperature, 12 h. Yields were determined by GC analysis. TON= molar of product/molar of catalyst used.

3. Kinetics plot of conversion (%) vs time

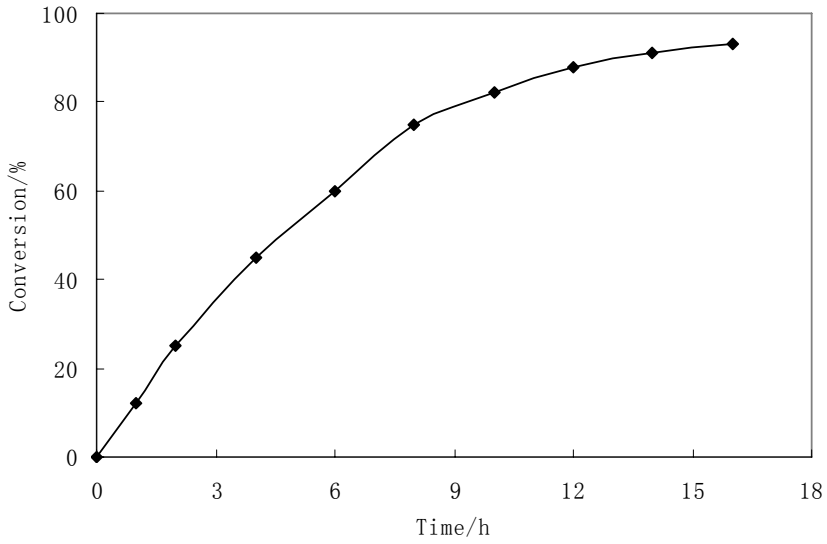


Fig. S1 kinetics plot of conversion (%) vs time in the oxidation of 4-picoline in water with H_2O_2 catalyzed by $K_6[PW_9V_3O_{40}]\cdot 4H_2O$.

Reaction conditions: 2 mmol substrate, 10 mmol (30% aq.) H_2O_2, 14 μmol catalyst, 1 ml H_2O, room temperature.

4. IR spectra

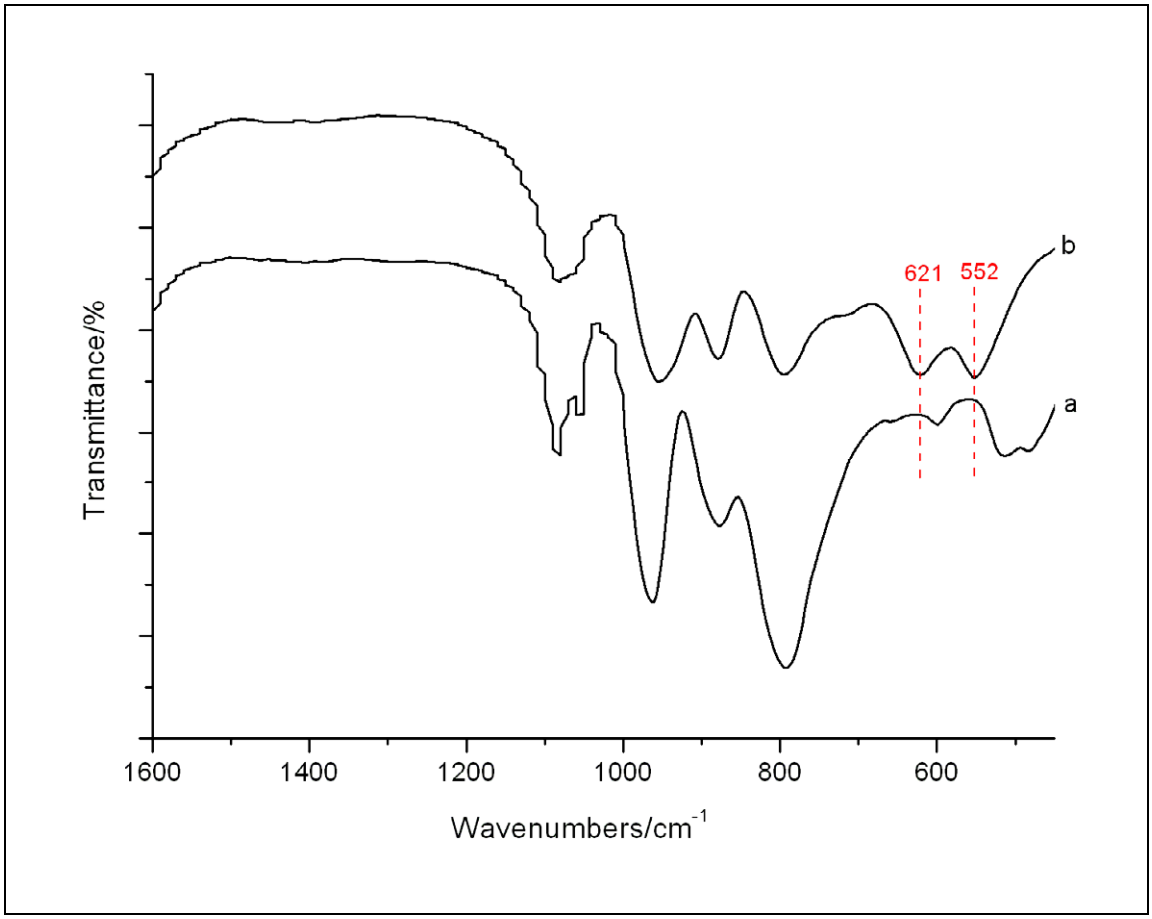
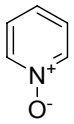
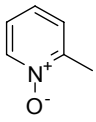


Fig. S2 IR spectra of (a) fresh catalyst of $K_6[PW_9V_3O_{40}]\cdot 4H_2O$ (b) the peroxo species

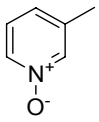
5. Characterization of oxidation products

Pyridine-N-oxide [3] 

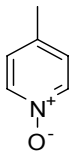
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97-7.96 (t, 2 H), 7.05-7.03 (m, 3 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 125.6 (2C), 125.8, 138.6 (2C).

2-Picoline-N-oxide [4] 

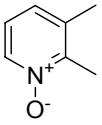
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.18 (d, J=6.4 Hz, 1 H), 7.12-7.08 (t, 2 H), 7.04-7.00 (m, 1 H), 2.30 (s, 3 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 16.6, 123.0, 125.9, 126.8, 138.4, 148.0.

3-Picoline-N-oxide [5] 

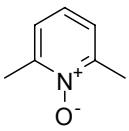
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, J=9.6 Hz, 2 H), 7.16-7.07 (m, 2 H), 2.28 (s, 3 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ18.2, 125.3, 127.3, 136.5, 136.8, 139.3.

4-Picoline-N-oxide [4] 

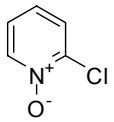
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.10 (d, J=6.8 Hz, 2 H) 7.08 (d, J=6.4 Hz, 2 H), 2.34 (s, 3 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 19.9, 126.4 (2C), 137.5, 138.3 (2C).

2,3-Lutidine-N-oxide 

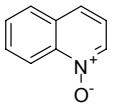
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.09 (d, J=4.8 Hz, 1 H), 6.98-6.93 (m, 2 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 13.6, 19.4, 121.9, 127.0, 134.8, 137.0, 148.2.

2,6-Lutidine-N-oxide 

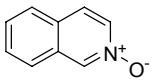
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.13 (d, J=7.6 Hz, 2 H), 7.08-7.05 (m, 1 H), 2.52 (s, 6 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ17.5, 17.6, 123.5, 125.3, 148.6.

2-Chloropyridine-N-oxide [4] 

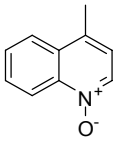
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.35 (s, 1 H), 7.53 (s, 1 H), 7.24 (s, 2 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 123.9, 126.2, 127.2, 140.8, 142.2.

Quinoline-N-oxide [5] 

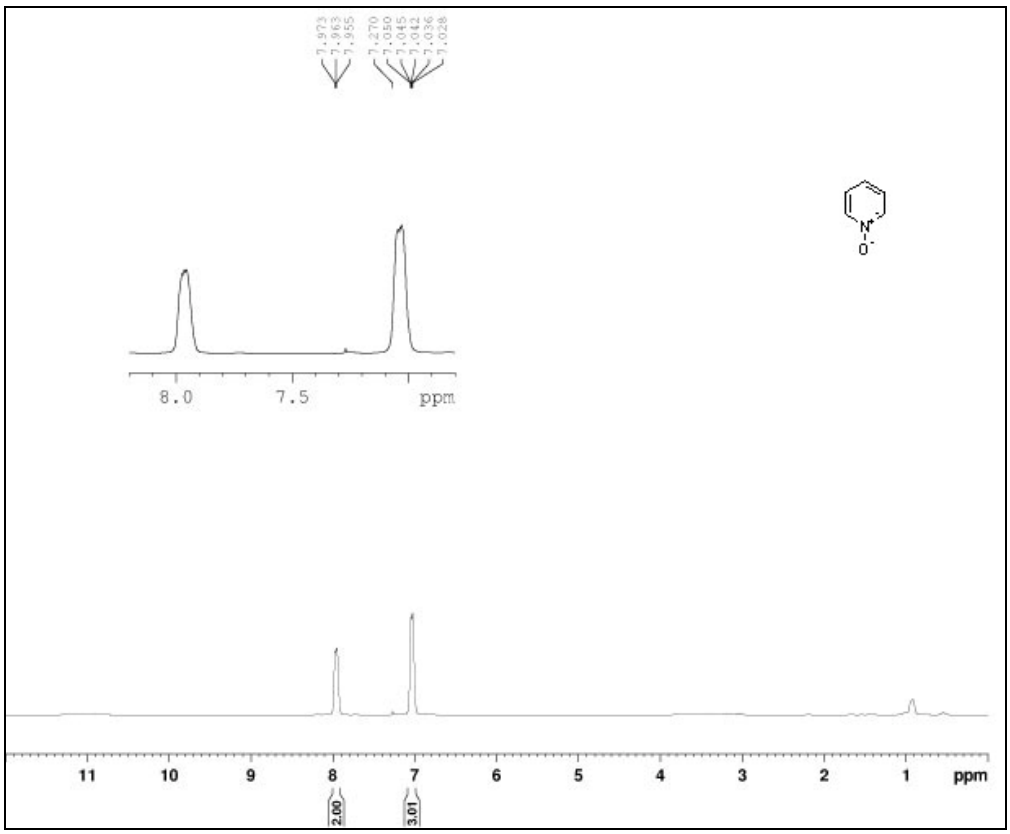
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.76 (d, J=8.8 Hz, 1 H), 8.55 (d, J=6 Hz, 1 H), 7.82 (d, J=8 Hz, 1 H), 7.80-7.75 (m, 2 H), 7.68-7.64 (m, 1 H), 7.31-7.29 (m, 1 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ118.7, 120.3, 125.6, 127.4, 127.9, 129.6 (2C), 135.0, 140.4.

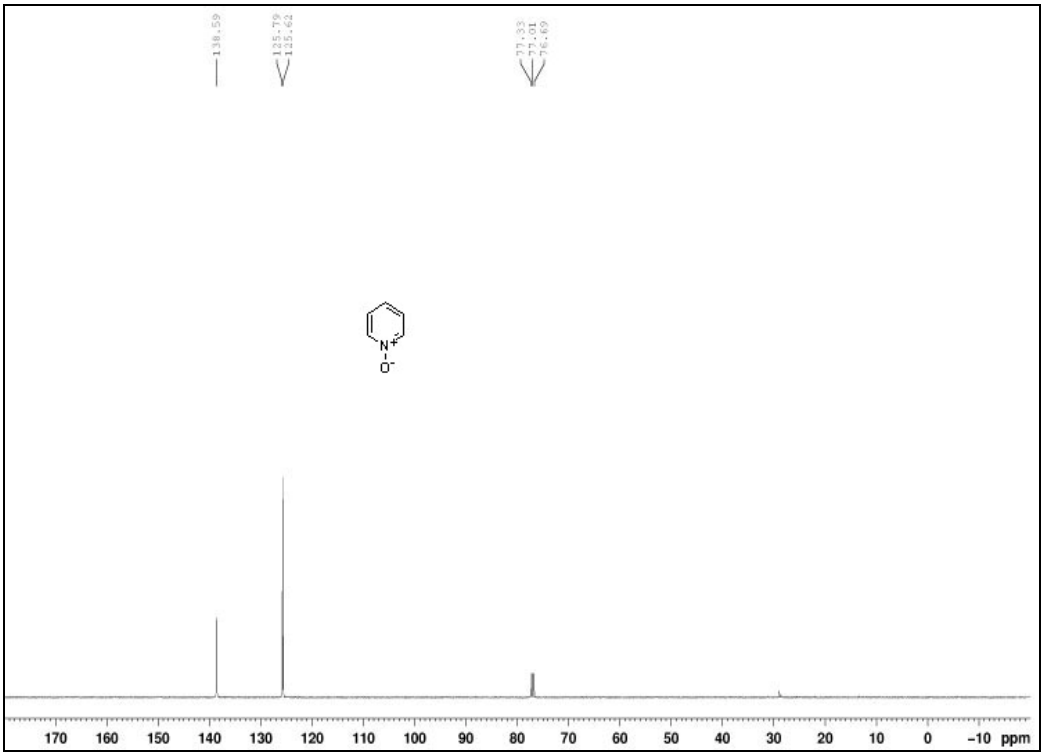
Isoquinoline-N-oxide [5] 

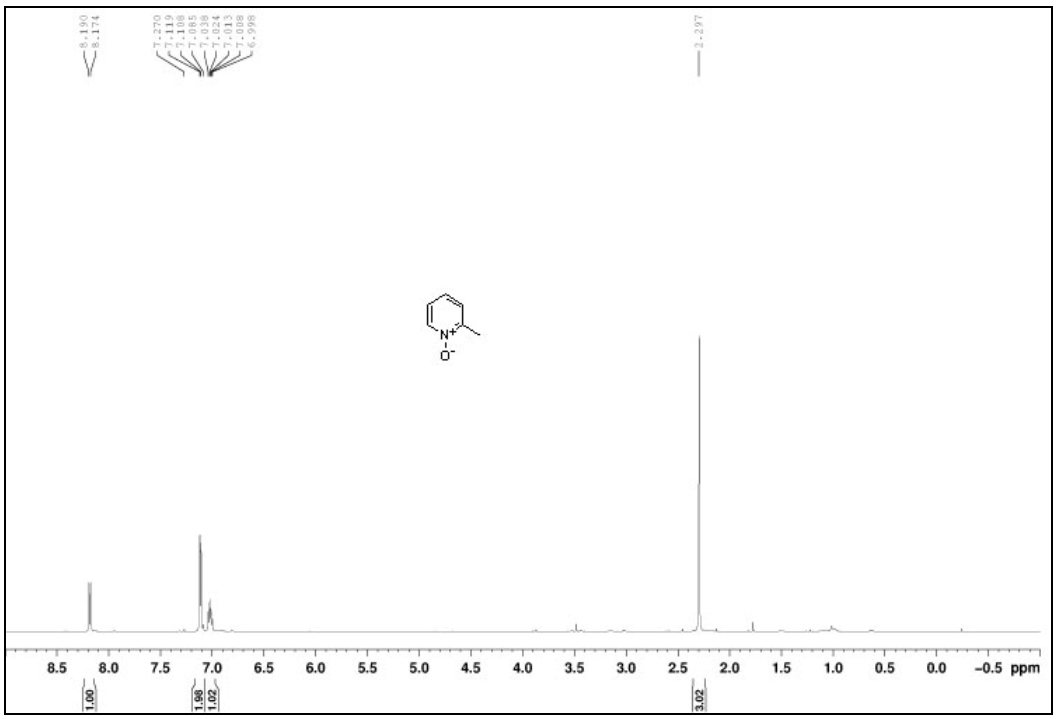
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.80 (s, 1 H), 8.16-8.14 (m, 1 H), 7.77-7.76 (m, 1 H), 7.74-7.72 (m, 1 H), 7.67 (d, J=7.2 Hz, 1 H), 7.63-7.57 (m, 2 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 124.2 (2C), 125.1, 126.5, 129.0, 129.2, 129.3, 129.4, 136.4.

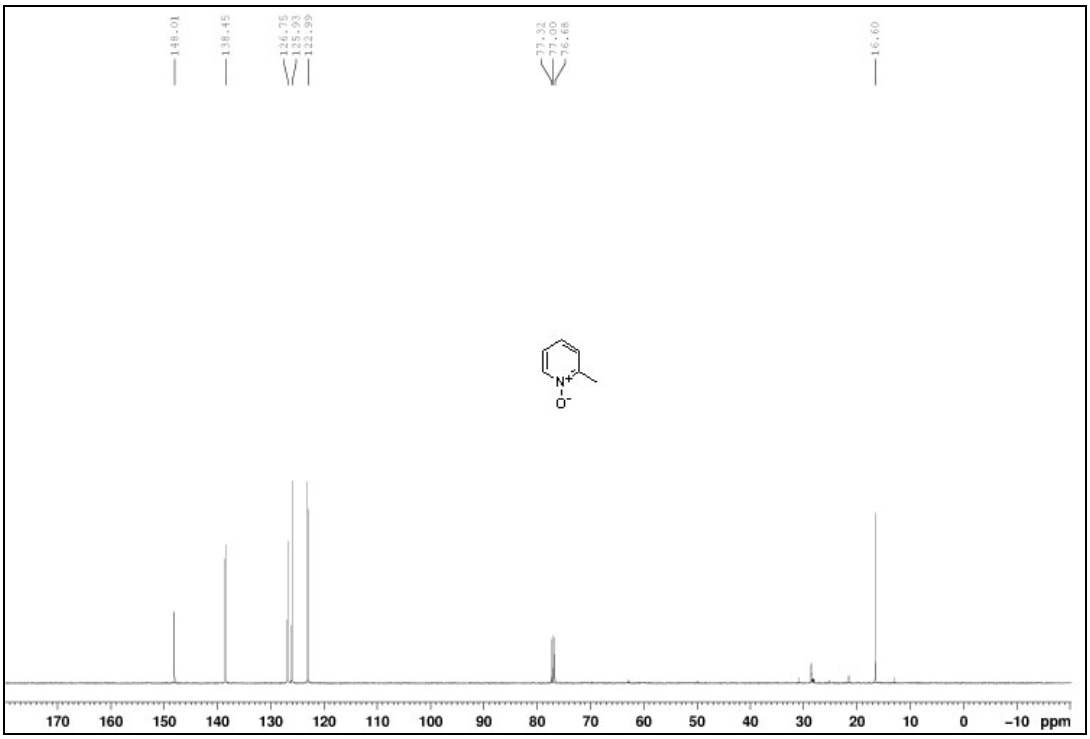
4-Methyl-quinoline-N-oxide 

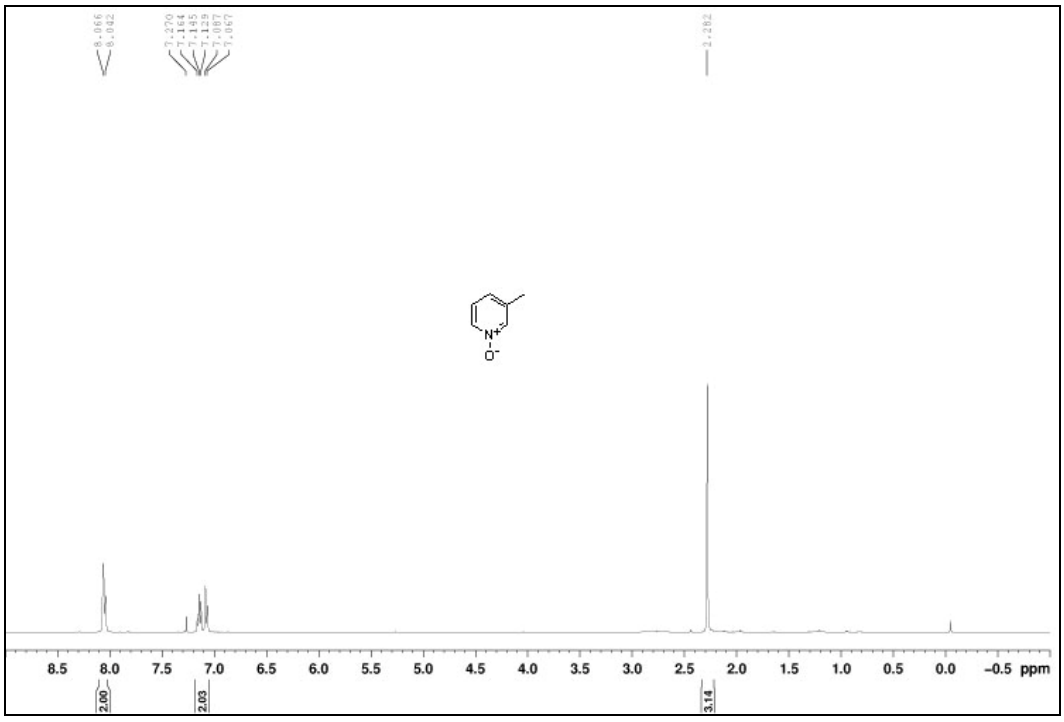
^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.78 (d, J=8.4 Hz, 1 H), 8.46 (d, J=6 Hz, 1 H), 7.94 (d, J=8 Hz, 1 H), 7.76-7.72 (t, 1 H), 7.67-7.63 (t, 1 H), 7.20 (d, J=6.4 Hz, 1 H), 2.64 (s, 3 H); ^{13}C NMR($CDCl_3$, 400 MHz) δ 18.2, 120.2, 121.3, 124.6, 128.3, 129.7, 130.0, 134.5, 134.9,140.8.

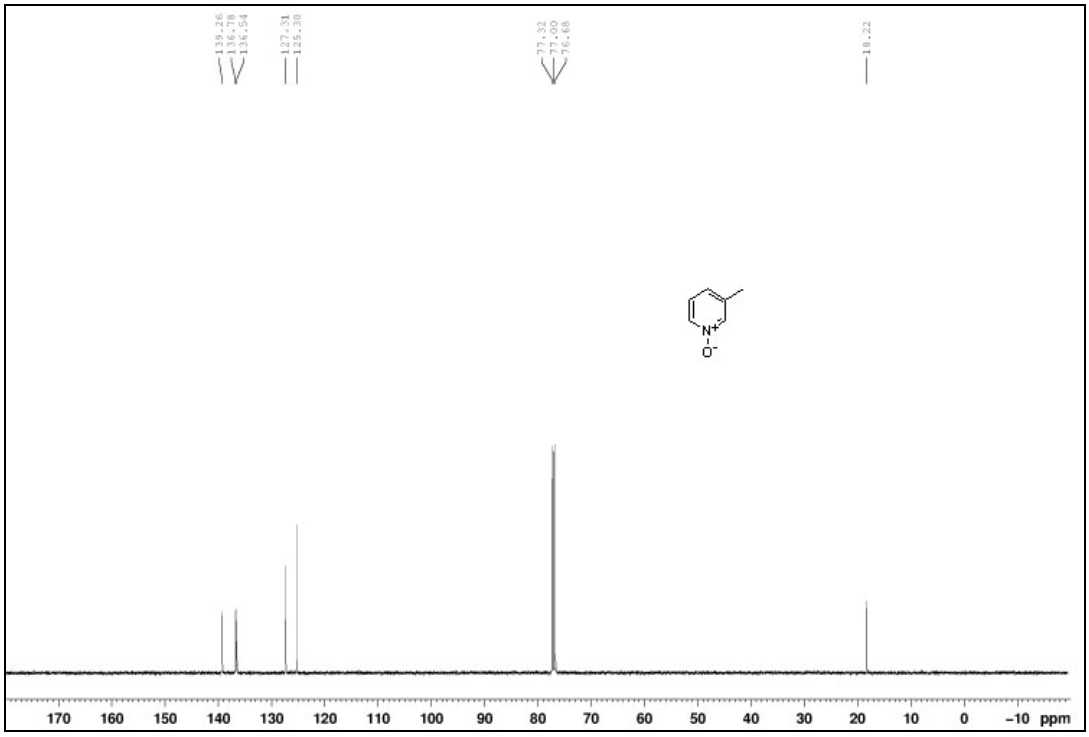

7.973
7.963
7.955
7.270
7.059
7.045
7.042
7.036
7.028
8.0
7.5
ppm
11
10
9
8
7
6
5
4
3
2
1
ppm
2.00
3.01

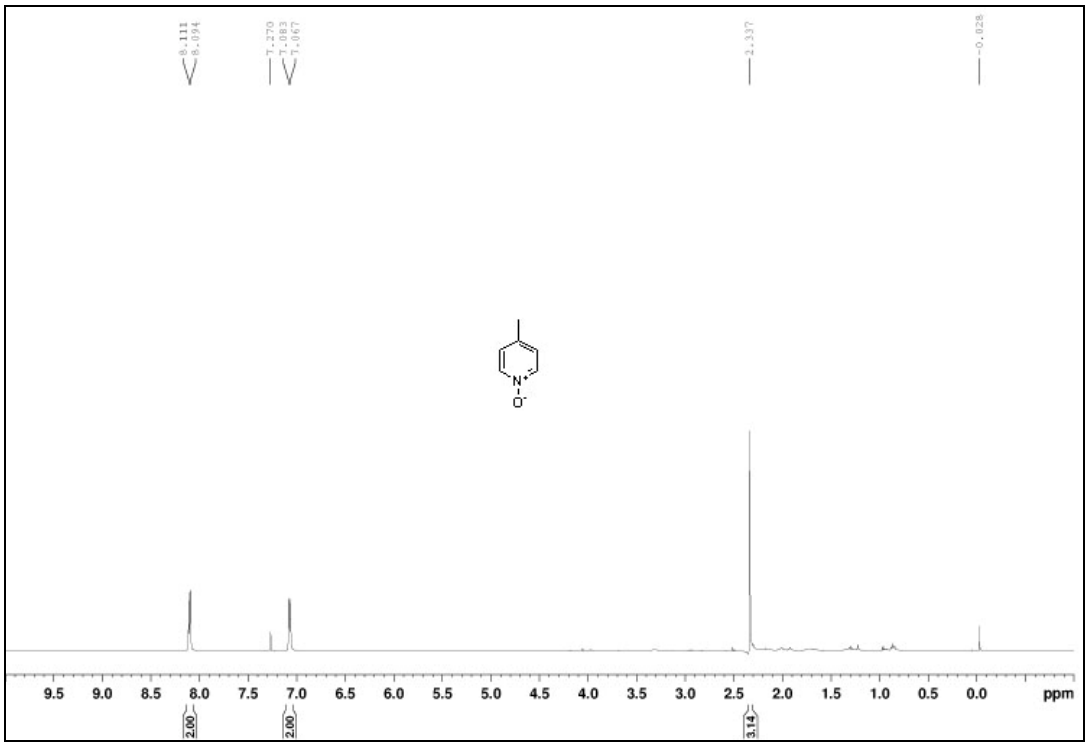

138.59
125.79
125.62
77.33
77.01
76.69
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10 ppm

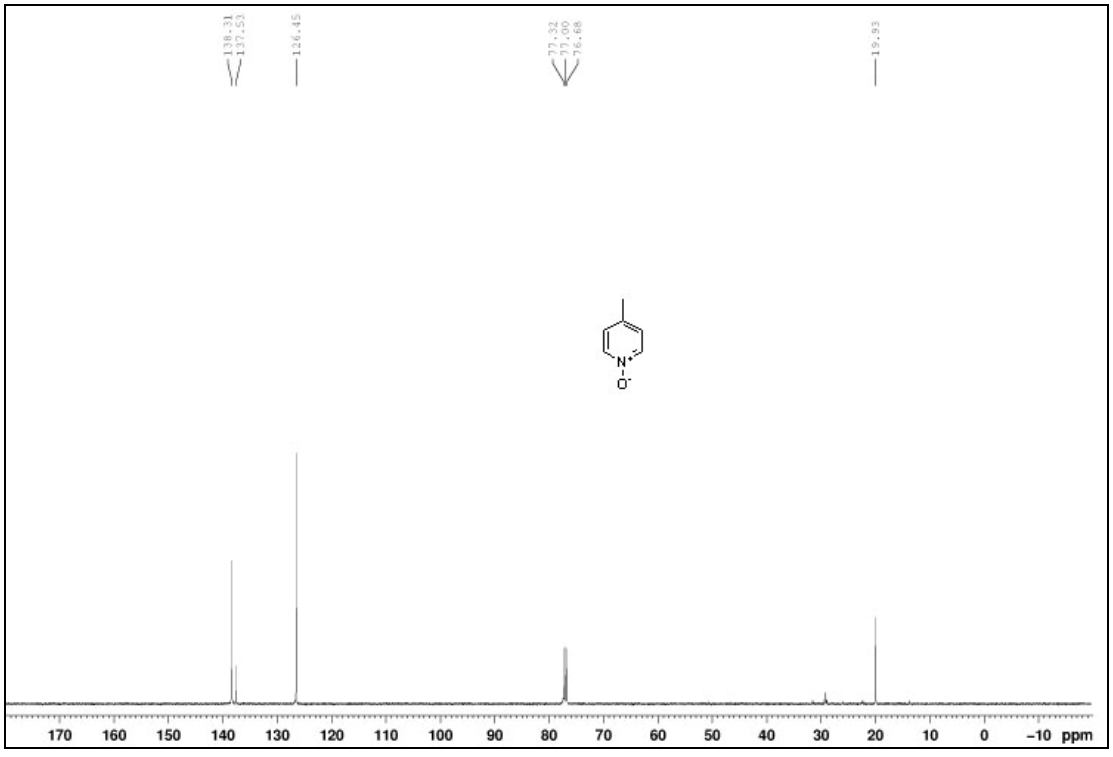

8.190
8.174
7.370
7.111
7.109
7.105
7.085
7.038
7.024
7.015
7.008
6.998
2.297
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
1.89
1.02
3.02

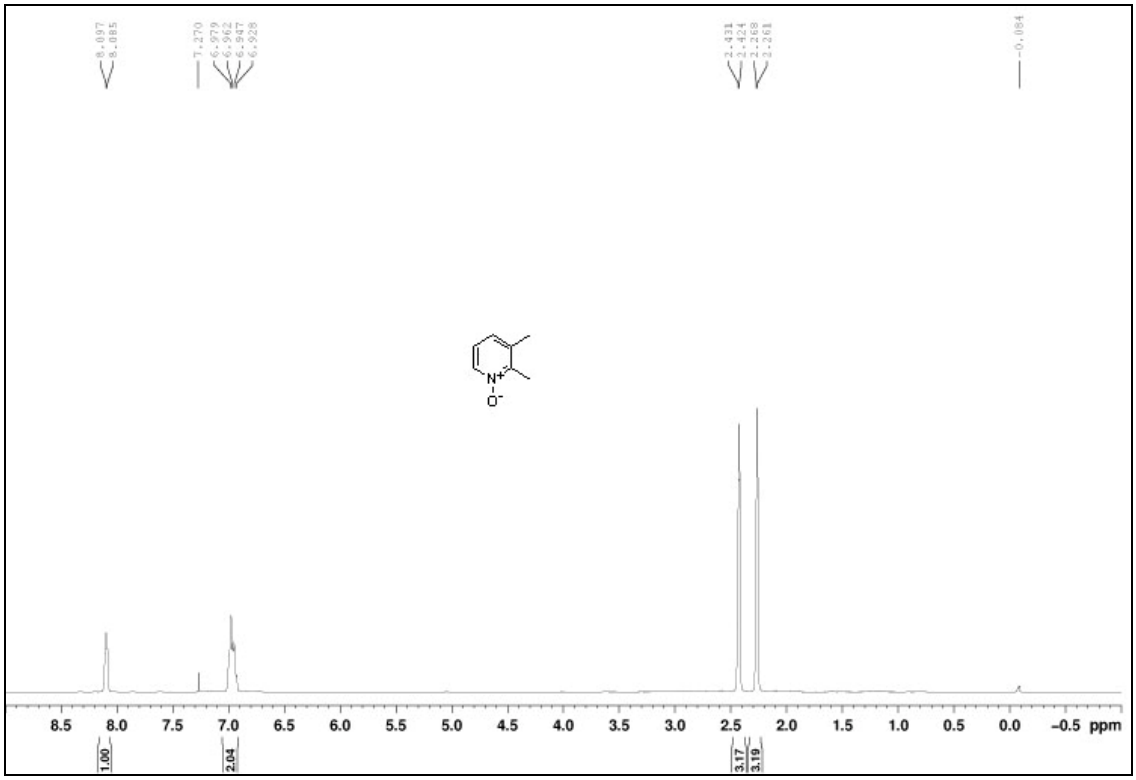

148.01
138.45
126.75
125.03
122.99
77.32
77.00
76.68
16.60
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

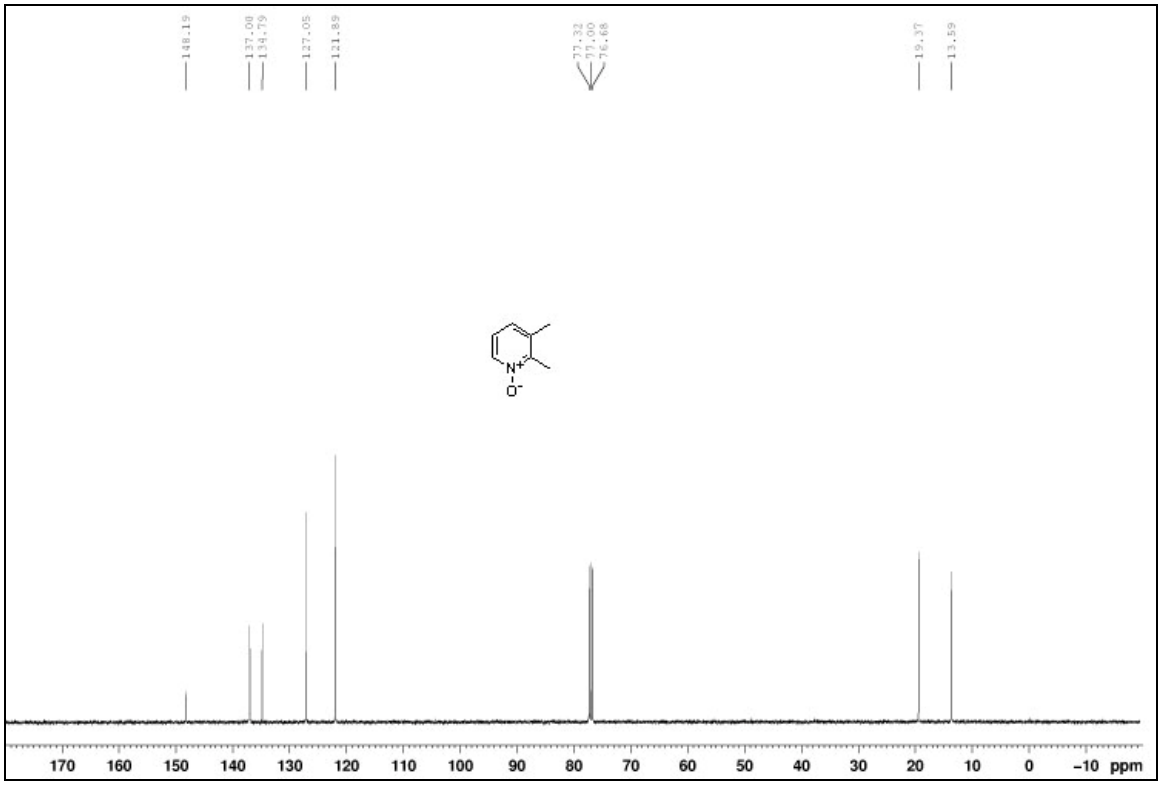

8.066
8.042
7.220
7.164
7.145
7.129
7.087
7.067
2.282
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.00
2.03
3.14

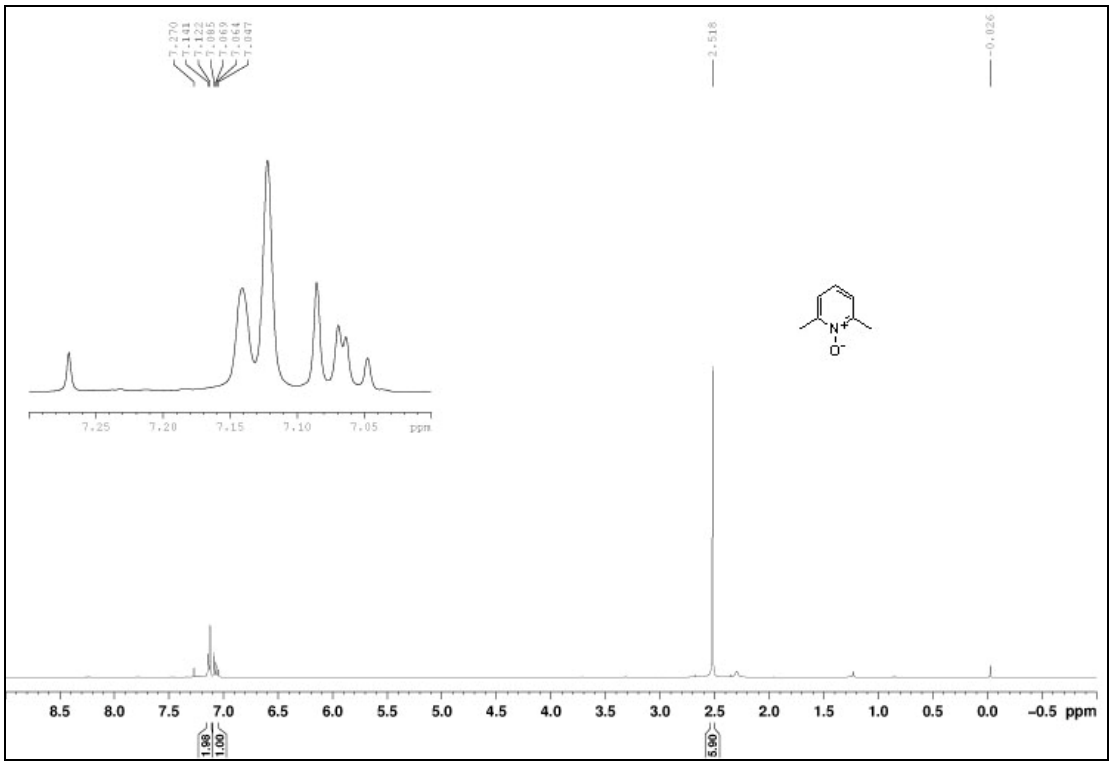

139.26
136.78
136.54
127.31
125.30
77.32
77.00
76.68
18.22
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

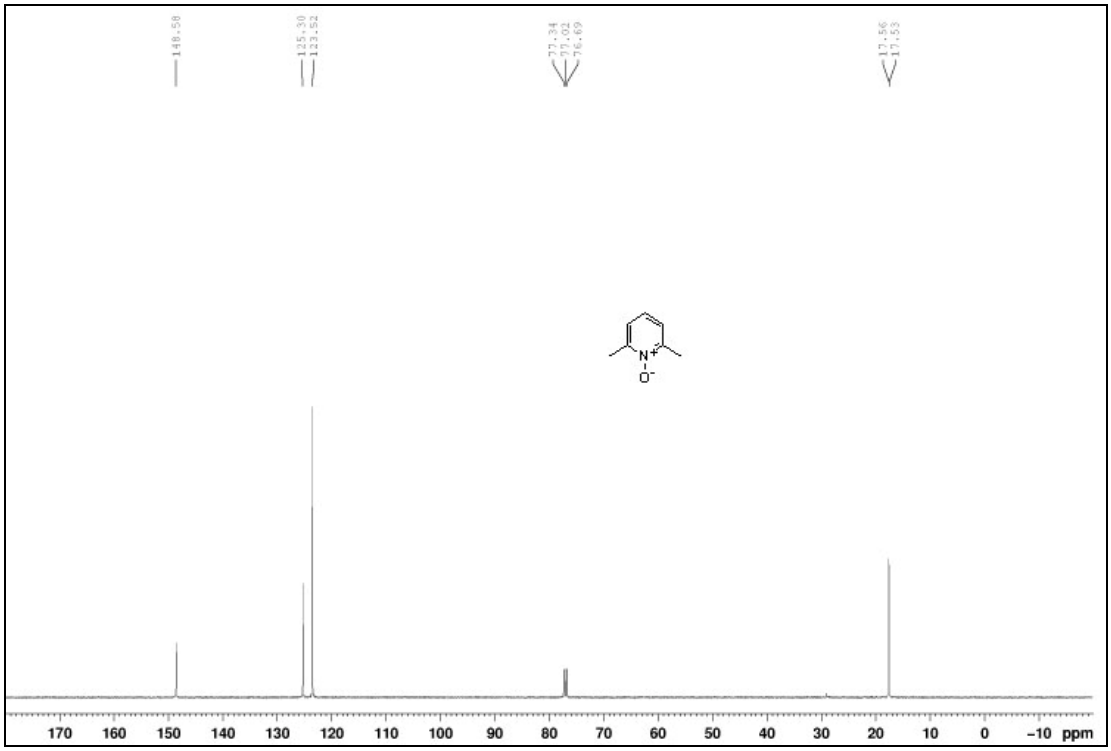

8.111
8.094
7.270
7.083
7.067
2.337
-0.028
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.00
2.00
3.14

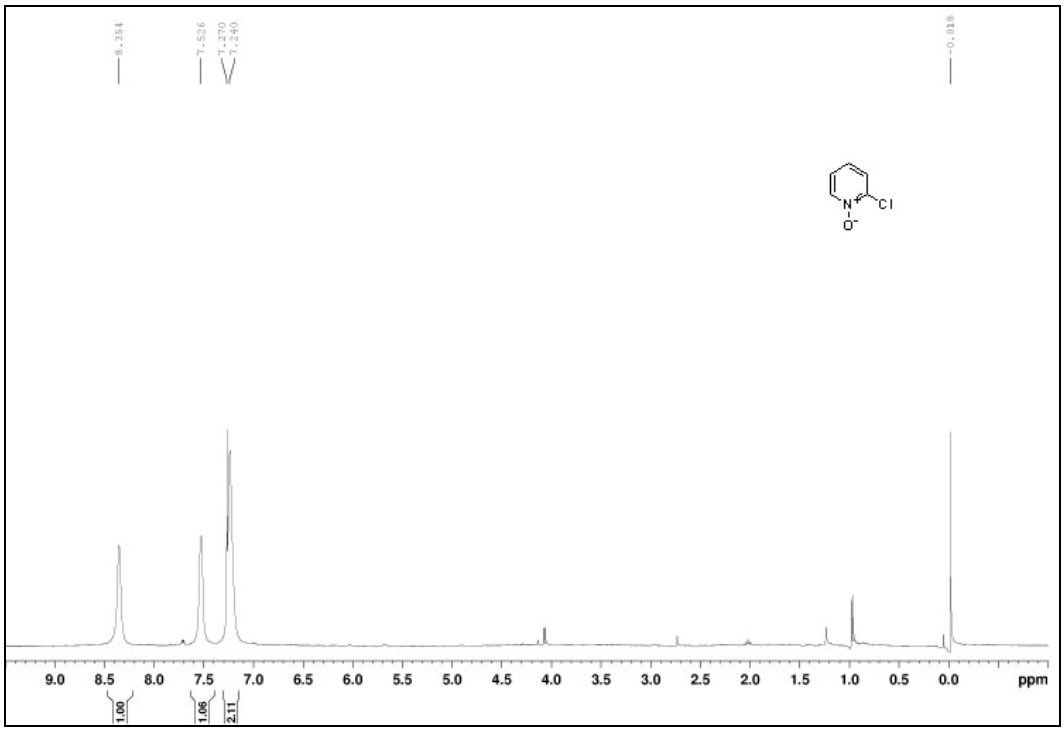

138.31
137.53
126.45
77.32
77.00
76.68
19.93
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

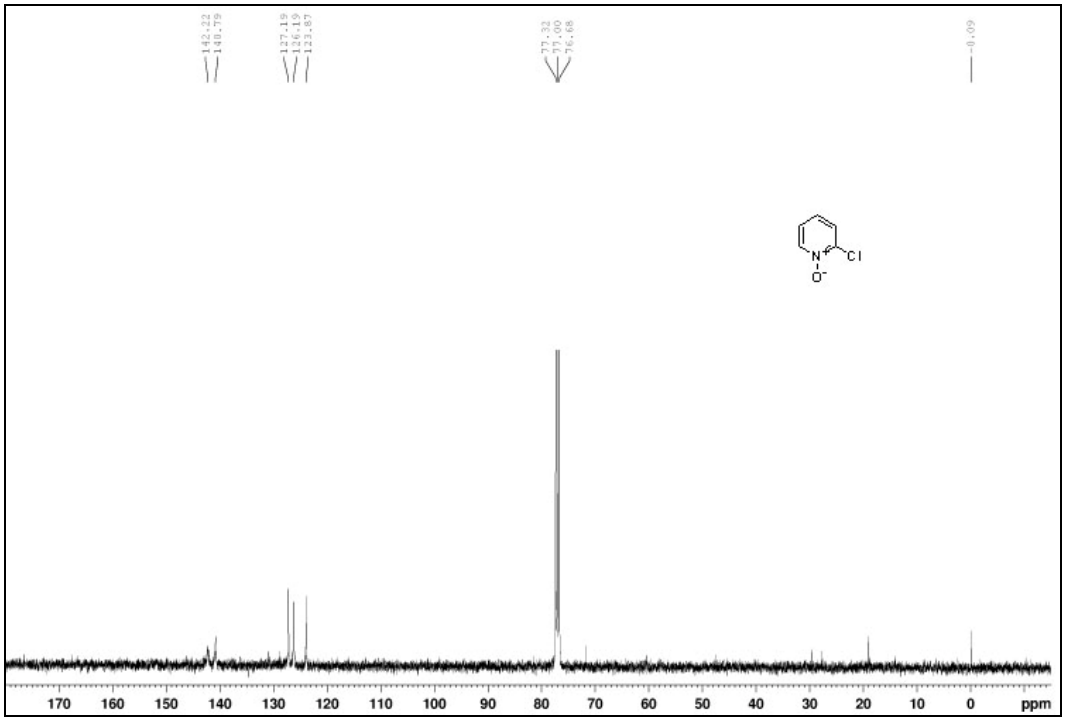

8.097
8.085
7.270
6.979
6.962
6.947
6.928
2.431
2.424
2.268
2.261
-0.084
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.00
2.04
3.17
3.19

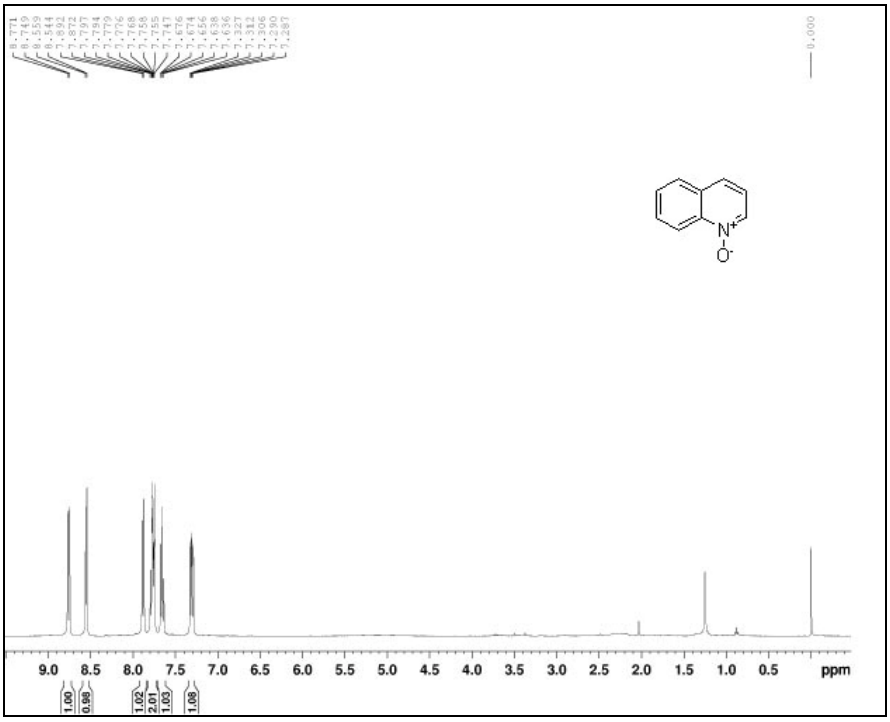

148.19
137.00
134.79
127.05
121.89
77.32
77.00
76.68
19.37
13.59
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

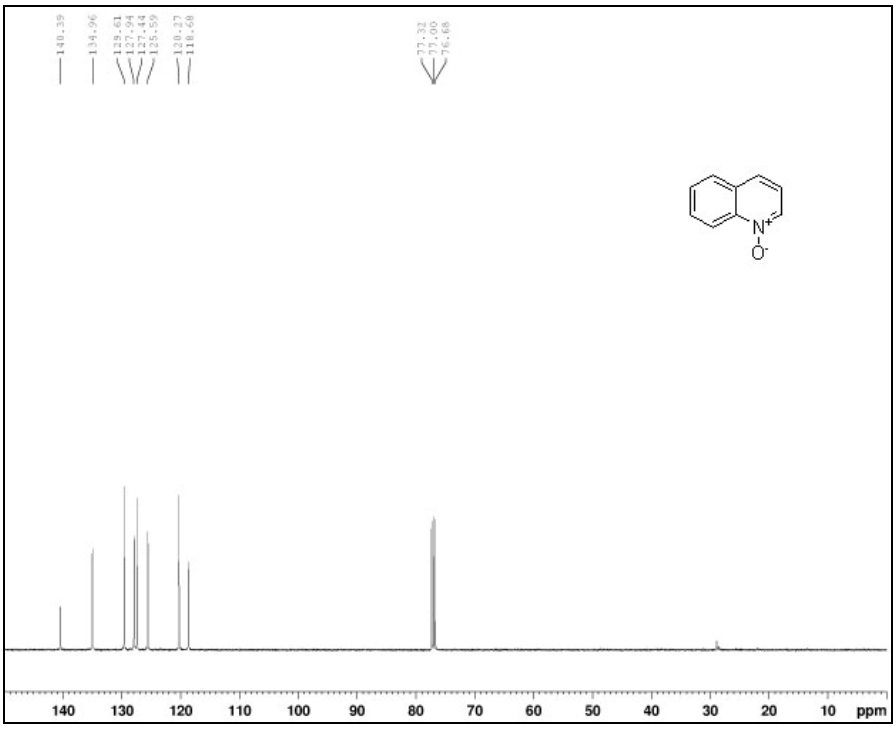

7.270
7.141
7.122
7.105
7.085
7.069
7.064
7.047
2.518
-0.026
7.25
7.20
7.15
7.10
7.05
ppm
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5 ppm
1.98
1.00
5.60

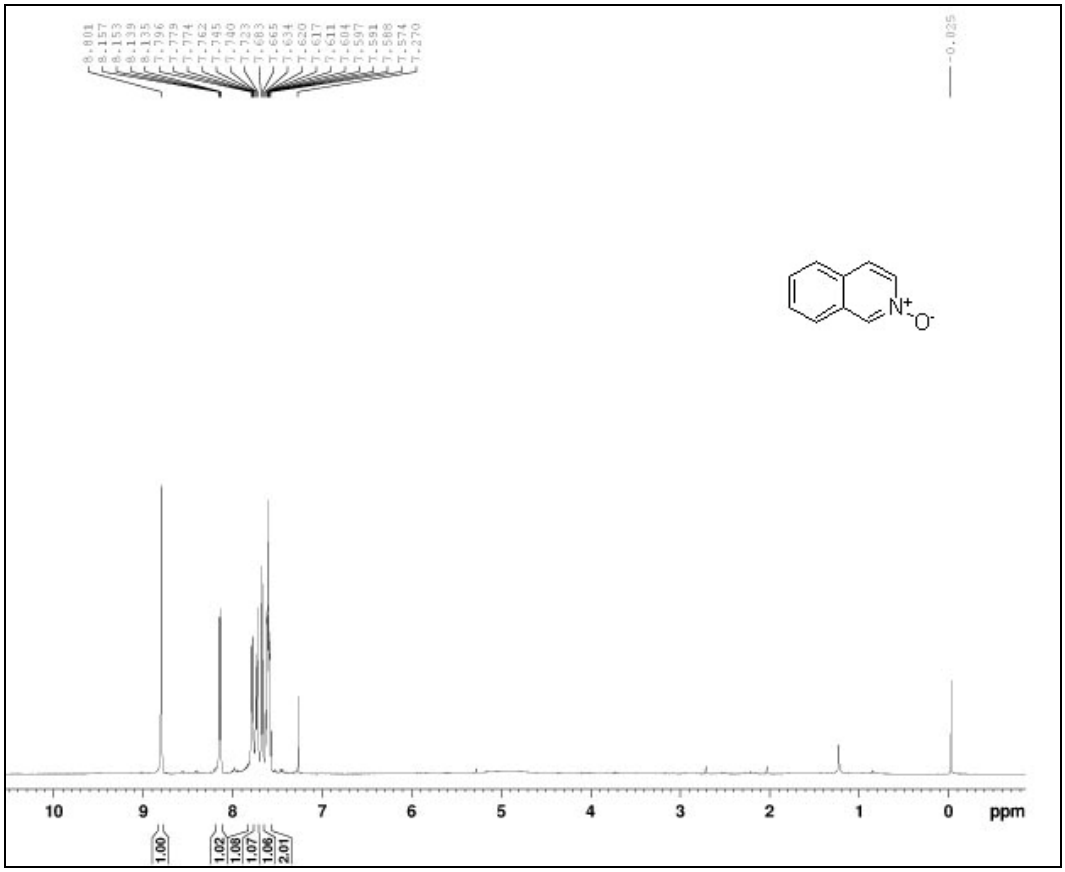

148.58
125.30
123.52
77.34
77.02
76.69
17.56
17.53
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10 ppm

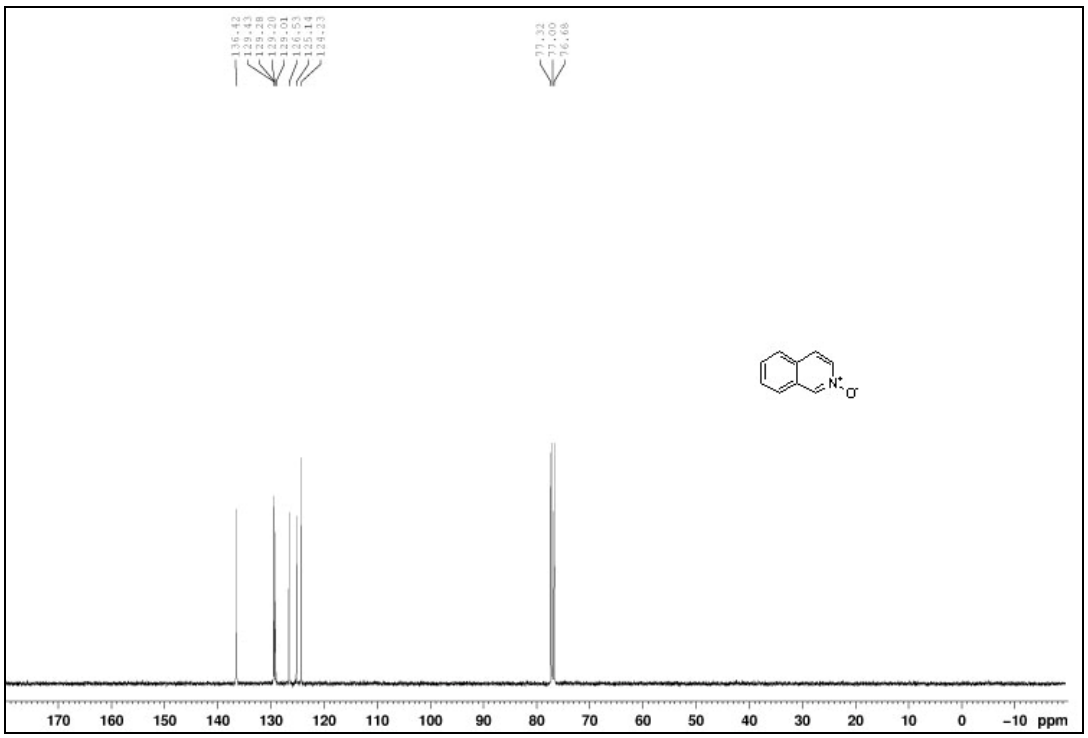

8.354
7.526
7.270
7.240
0.018
Cl
N+
O-
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.06
2.11

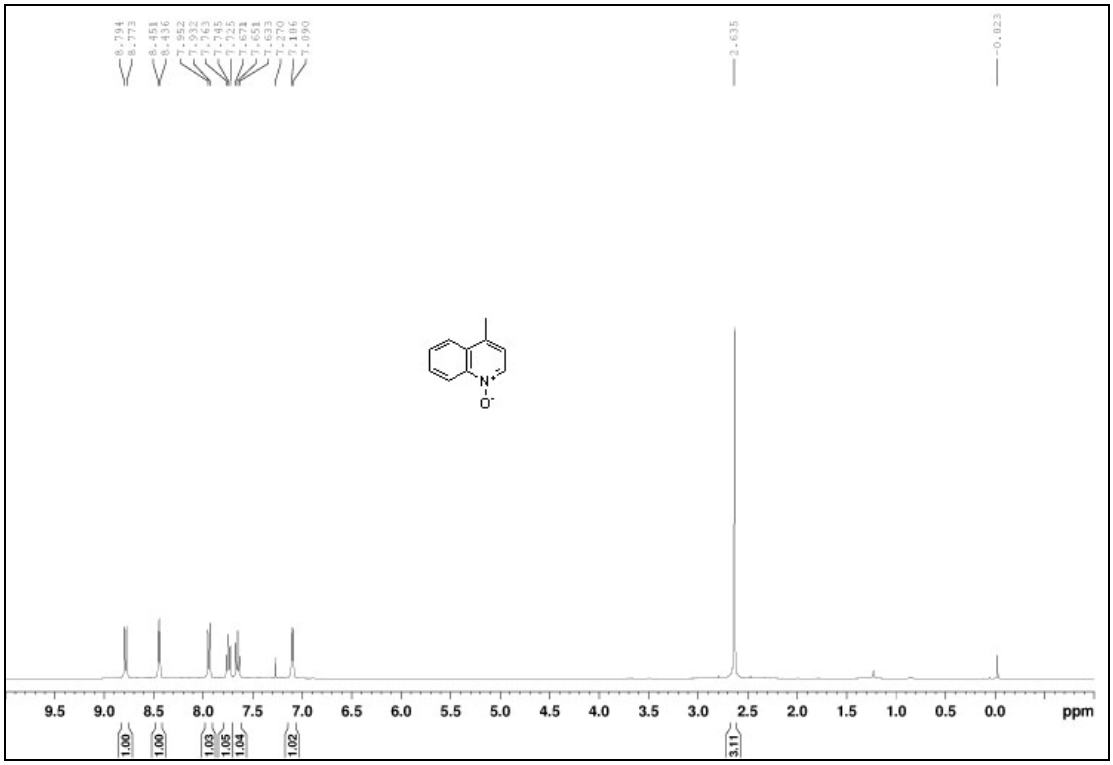

142.22
140.79
127.19
126.69
125.67
77.32
77.00
76.68
0.09
Cl
N+
O-
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

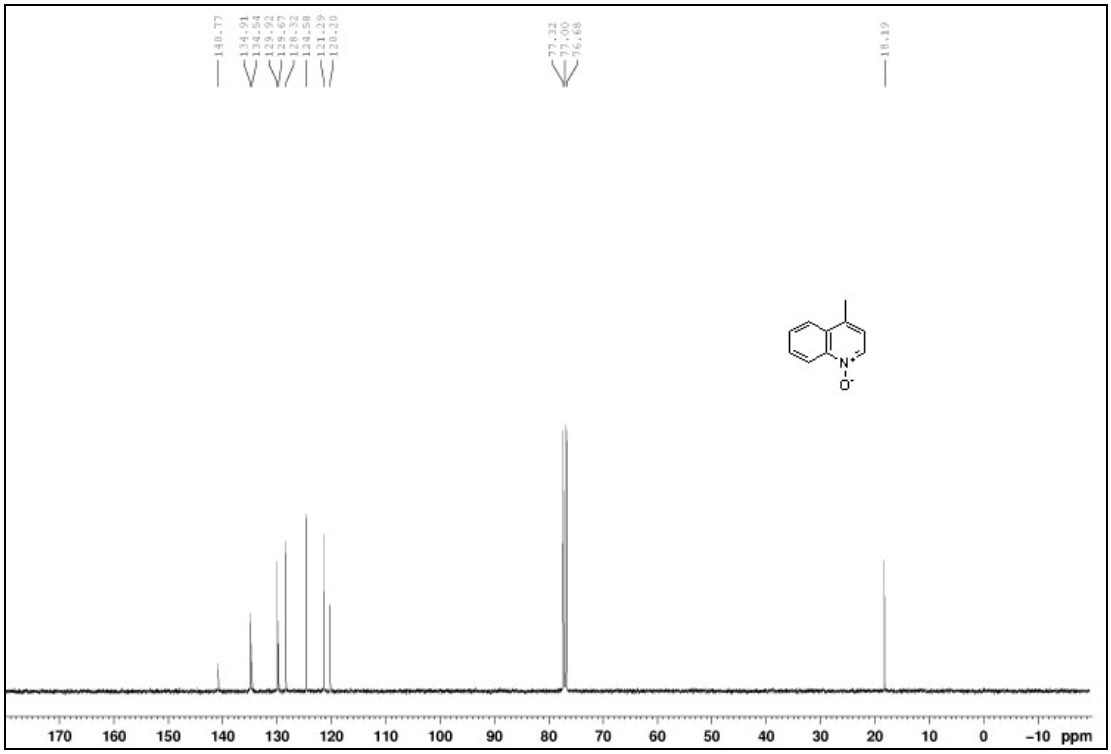

8.771
8.749
8.559
8.544
7.892
7.872
7.787
7.784
7.779
7.776
7.768
7.756
7.755
7.747
7.676
7.674
7.656
7.638
7.636
7.627
7.312
7.306
7.290
7.287
0.000
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00
0.98
1.02
2.01
1.03
1.08


140.39
134.96
129.61
127.94
127.44
125.89
120.27
118.69
77.32
77.00
76.68
140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


8.801
8.157
8.153
8.139
8.135
7.796
7.779
7.774
7.762
7.745
7.740
7.723
7.683
7.665
7.634
7.620
7.617
7.611
7.604
7.597
7.591
7.588
7.574
7.270
-0.025
N+
O-
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
1.08
1.07
1.06
2.01


136.42
129.43
129.28
129.20
129.01
126.63
125.14
124.23
77.32
77.00
76.68
N+
O-
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm


8.794
8.773
8.451
8.436
7.952
7.932
7.763
7.745
7.725
7.671
7.651
7.573
7.186
7.090
2.635
-0.023
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.00
1.00
1.03
1.05
1.04
1.02
3.11


140.77
134.91
134.54
129.42
128.57
128.32
124.58
121.29
120.20
77.32
77.00
76.68
18.19
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 ppm

6. References

[1] P. J. Domaille, *J. Am. Chem. Soc.*,1984, **106**, 7677.

[2] R. G. Finke, M. W. Droege and P. J. Domaille, *Inorg. Chem.*,1987, **26**, 3886.

[3] F. A. L. Anet and I. Yavari, J. Org. Chem. 1976, **41**, 3589.

[4] S. A. Sojka, *J. Org. Chem.* 1978, **44**, 307.

[5] C. Copéret, H. Adolfsson, T.-A. V. Khuong, A. K. Yudin and K. B. Sharpless, *J. Org. Chem.* 1998, **63**, 1740.