Insights into the Mechanistic and Synthetic Aspects of the Mo/P-Catalyzed Oxidation of *N*-Heterocycles

Oleg V. Larionov,* David Stephens, Adelphe M. Mfuh, Hadi D. Arman, Anastasia S. Naumova, Gabriel Chavez, and Behije Skenderi

Department of Chemistry, University of Texas at San Antonio, One UTSA Circle, San Antonio, Texas, United States

X-ray Data Collection and Structure Solution Refinement. Crystals suitable for X-ray diffraction were mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream maintained by an X-Stream low-temperature apparatus. The data were collected at 98(2) K using a Rigaku AFC12/Saturn 724 CCD fitted with Mo Kα radiation (λ= 0.71073 Å).[1] Data collection and unit cell refinement were performed using *Crystal Clear* software. The total number of data were measured in the range (see table 3) using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors, see table 3,were accomplished with *Crystal Clear* and *ABSCOR*,[2] respectively. The structure, using *SHELXL-97*, was solved by direct methods and refined (on F^2) using full-matrix, least-squares techniques.[3],[4] All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. An electron density peak was used to identify the hydrogen atoms bound to the solvent molecule and the displacement parameters were set to 1.5 times the displacement parameters of the bonded atom. Compounds **26-29** have been assigned the following CCDC numbers: **26** (CCDC 981527), **27** (CCDC 981529), **28** (CCDC 981530), **29** (CCDC 981531).

Table 1. Selected bond distances for the molybdenum complexes 26-29 (Å).

Complex	O—O Mo [1]	O═Mo	N—O—Mo[2]	P—O—Mo[3]	N–Mo
26	1.925(3),1.949(3) [1.479(4)] 1.928(3),1.945(3) [1.482(4)]	1.688(2)	2.257(3) [1.341(4)] 2.114(2) [1.371(4)]		
29	1.920(4),1.919(4) [1.458(6)] 1.924(3),1.996(3) [1.470(5)]	1.669(4)	[1.345(10)]	2.023(4) [1.528(4)]	
27	1.933(2),1.960(2) [1.475(3)] 1.937(2),1.959(2) [1.481(3)]	1.687(2)	2.122(2) [1.354(3)] 2.195(2) [1.344(3)]		

28	1.944(6),1.981(6) [1.492(7)] 1.973(7),1.994(6) [1.501(7)]	1.725(6)	2.246(6) [1.373(8)]		2.263(6)

[1] The O–O bond distance is specified in brackets. [2] The N–O bond distance is specified in brackets. [3] The P–O bond distance is specified in brackets.

Table 2. Selected hydrogen bond distances and angles for the molybdenum complexes.

Complex	D-H(Å)	H---O(Å)	D---O(Å)	D-H---O(°)	Symmetry Operators
26 (O8-H8c---O6)	0.97(2)	2.06(7)	2.815(6)	133(7)	
26 (O8-H8b---O7)	0.98(2)	1.77(4)	2.695(6)	156(8)	x, 1+y, z
26 (C11-H11a--O8)	0.93	2.36	3.263(6)	163	
28 (C10-H10a---O5)	0.93	2.34	3.19(1)	152	-x,-y,-z
28 (C10-H1a---O4)	0.93	2.44	3.29(1)	153	1-x,1-y,1-z

Table 3. Crystallographic parameters for Mo complexes 26-29.

Parameter	**26**	**29**	**27**	**28**
Empirical formula	$C_{18}H_{16}MoN_2O_8$	$C_{40}H_{39}Mo_4N_4O_{32}P$	$C_{20}H_{18}MoN_2O_7$	$C_{10}H_8MoN_2O_6$
Formula weight	484.27	1502.48	494.30	348.12
Crystal system	Triclinic	orthorhombic	Triclinic	Triclinic
Space group	$P\bar{1}$	*Fddd*	$P\bar{1}$	$P\bar{1}$
a(Å)	7.3259(13)	12.468(3)	8.1944(14)	7.136(14)
b(Å)	7.9556(14)	24.565(5)	8.3391(14)	7.593(14)
c(Å)	15.181(3)	36.887(7)	15.475(3)	12.48(2)
α(°)	91.695(4)	90	95.507(3)	94.746(18)
β(°)	91.210(4)	90	96.472(3)	105.60(3)
γ(°)	97.655(4)	90	106.989(3)	112.22(3)
Volume(Å^3)	876.2(3)	11298(4)	995.6(3)	589.9(18)
Z	2	8	2	2
ρ(calc.)	1.835	1.767	1.649	1.960
λ	0.71073	0.71073	0.71073	0.71073
Temp.(K)	98(2)	98(2)	98(2)	98(2)
F(000)	488	5968	500	344
μ(mm^{-1})	0.803	0.992	0.705	1.137
T_{min}, T_{max}	0.729, 1.000	0.800, 1.000	0.702, 1.000	0.326, 1.000
$2\theta_{range}$(°)	5.16 to 55.00	4.94 to 52.00	4.74 to 55.00°	5.18 to 51.00°
Reflections Collected	6281	17628	7267	2879
Independent reflections	3401 [R(int) = 0.0613]	2771 [R(int)=0.0815]	4507 [R(int)=0.0466]	2161 [R(int) = 0.0705]
Data / restraints / parameters	3401 / 0 / 268	2771 / 0 / 184	4507 / 0 / 271	2161 / 0 / 172
wR(F^2 all data)	0.01053	0.1353	0.0860	0.1363
R(*F* obsd data)	0.0389	0.0545	0.0342	0.0601

GOOF on F^2	1.013	1.124	1.012	1.052
Observed data [I > 2σ(I)]	3185	2623	4261	1816
Largest and mean shift / s.u.	0.0015/ 0.000	0.002/ 0.000	0.001/ 0.000	0.000/ 0.000

$wR_2 = \{ \Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2] \}^{1/2}$

$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

References

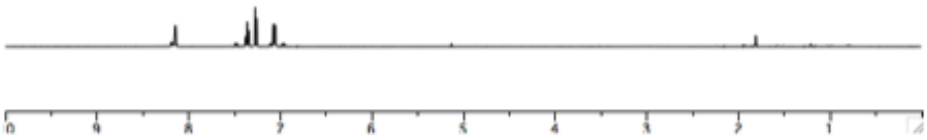
1 *CrystalClear*, User Manual. Rigaku/MSC Inc., Rigaku Corporation, The Woodlands, TX, 2005

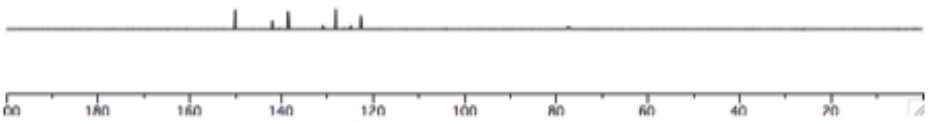
2 Higashi, *ABSCOR*, Rigaku Corporation, Tokyo, Japan, 1995

3 Sheldrick, G. M. *SHELXS97*. Program for the Solution of Crystal Structures. University of Göttingen, Germany, **1997**.

4 Sheldrick, G. M. *SHELXL97*, Program for crystal structure analysis. University of Göttingen, Germany, **1997**.

2-Bromopyridine 1-oxide (5)





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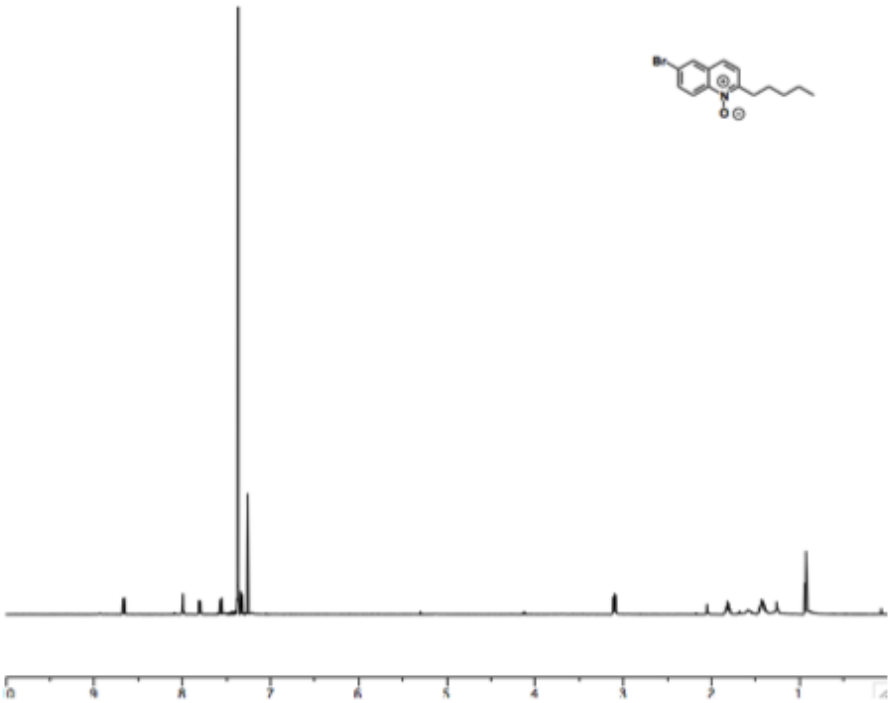
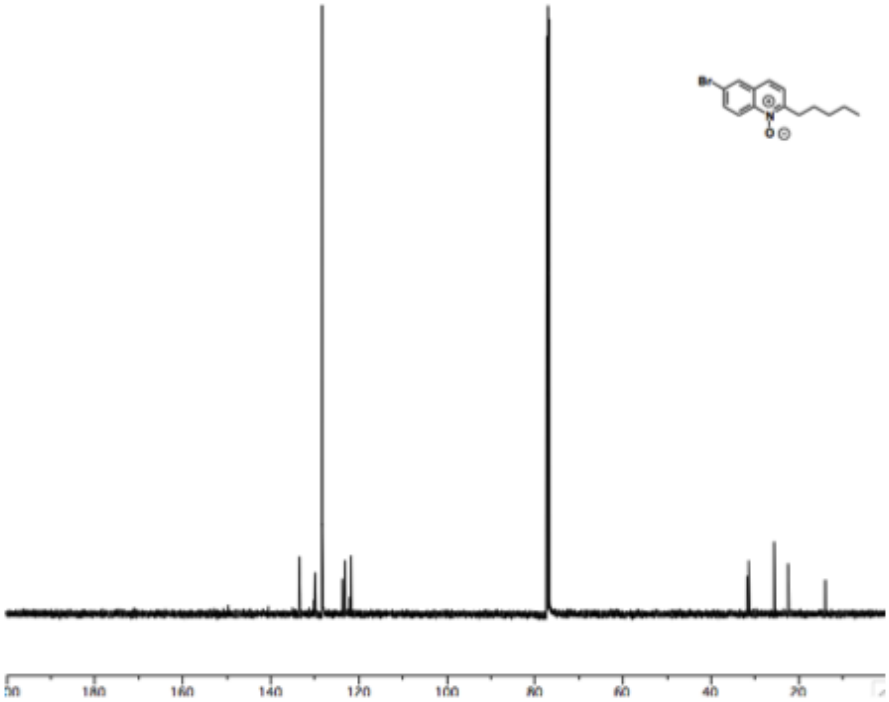
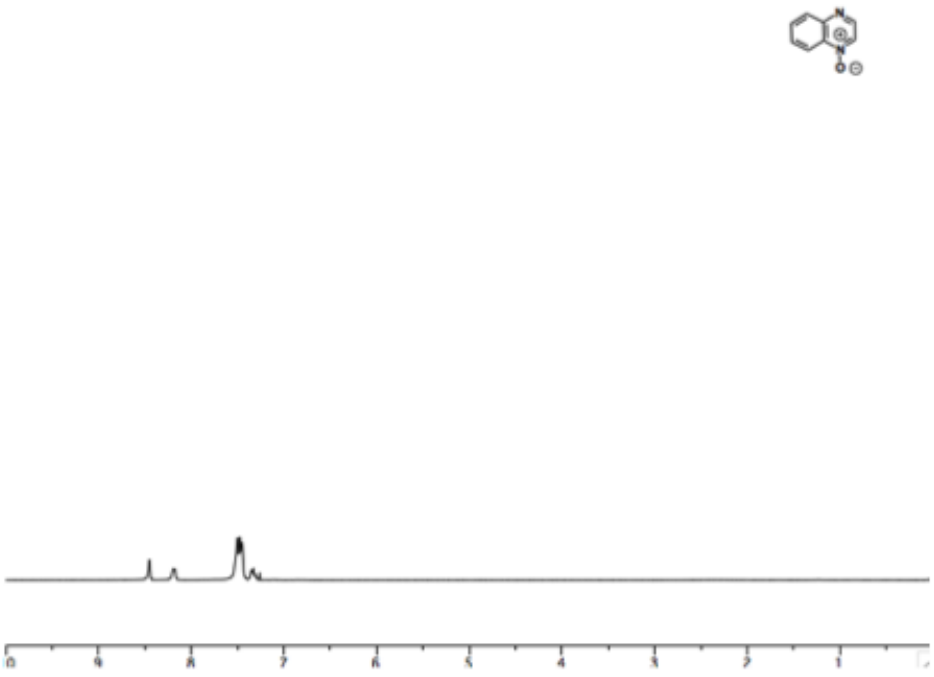
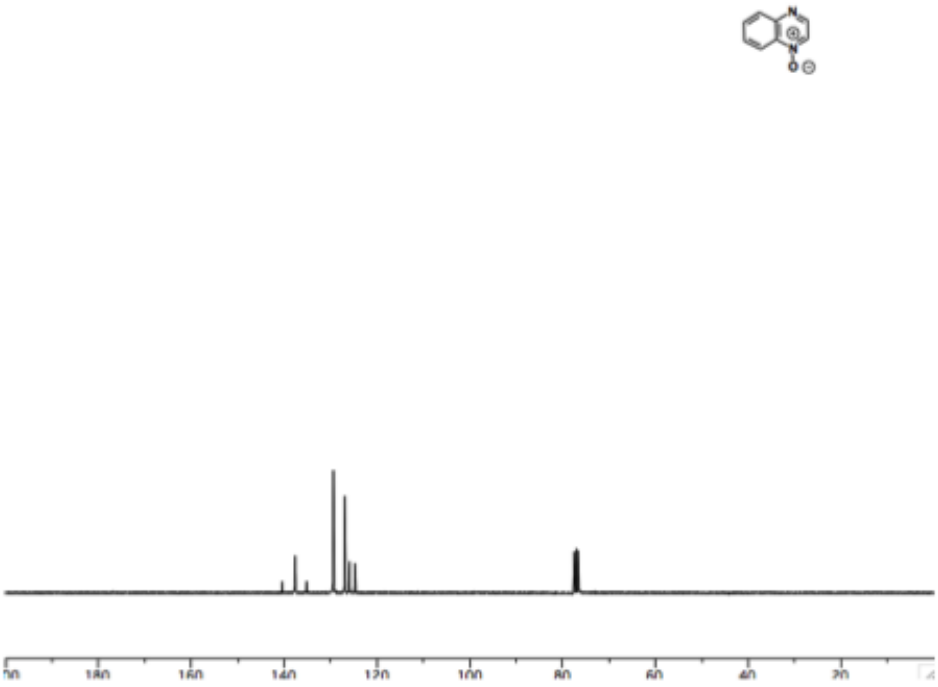


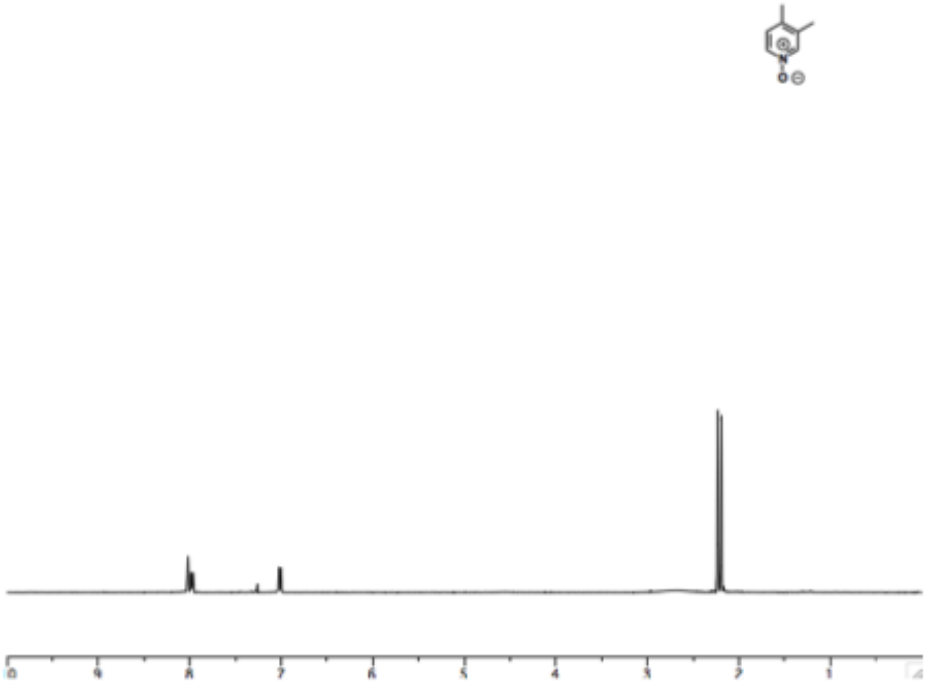


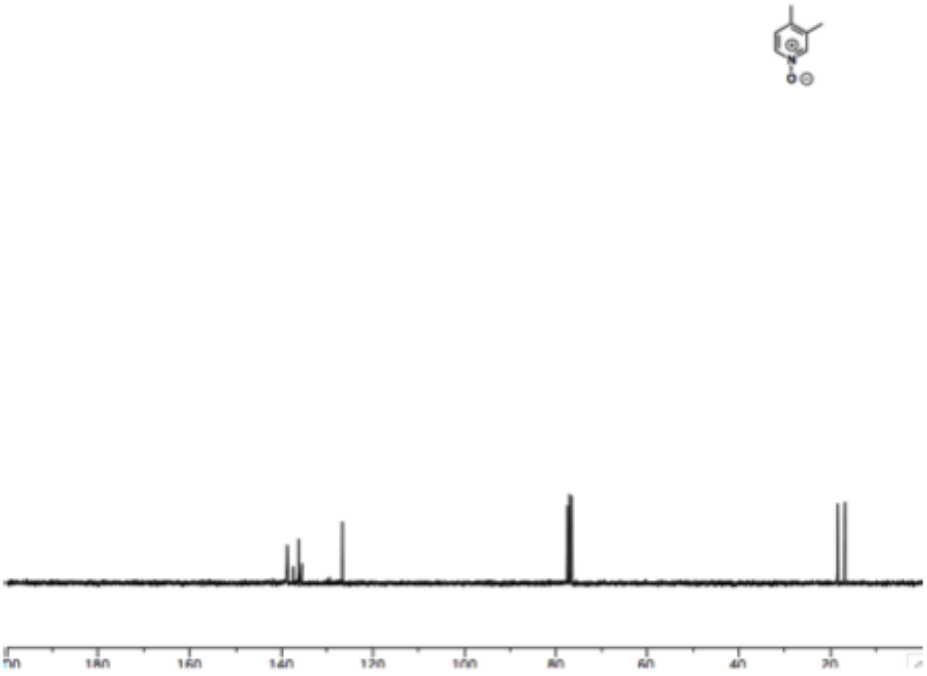
Quinoxaline 1-oxide (8)





3,4-Dimethylpyridine 1-oxide (10)





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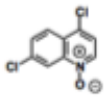
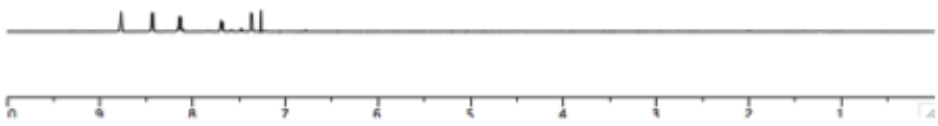
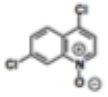
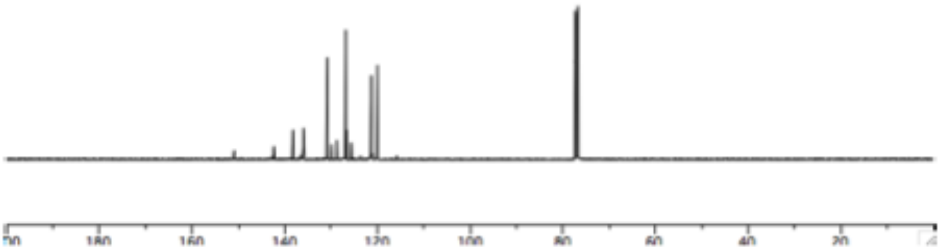
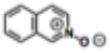


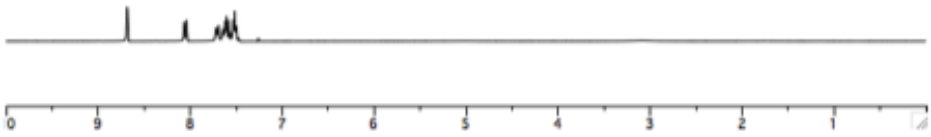


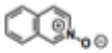


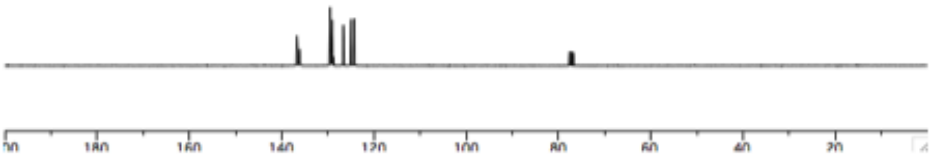


Isoquinoline 2-oxide (15)

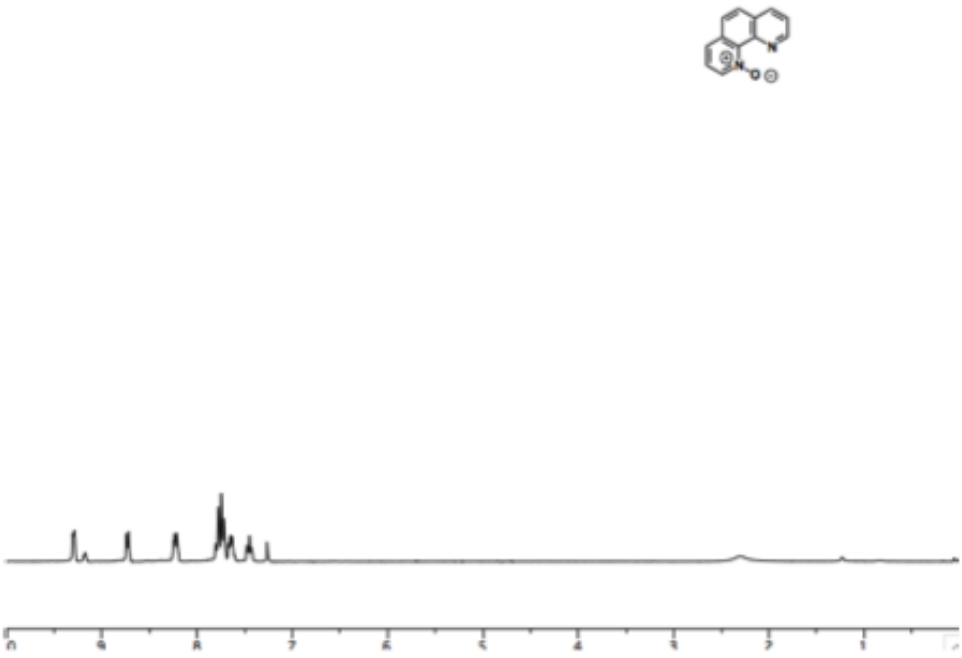


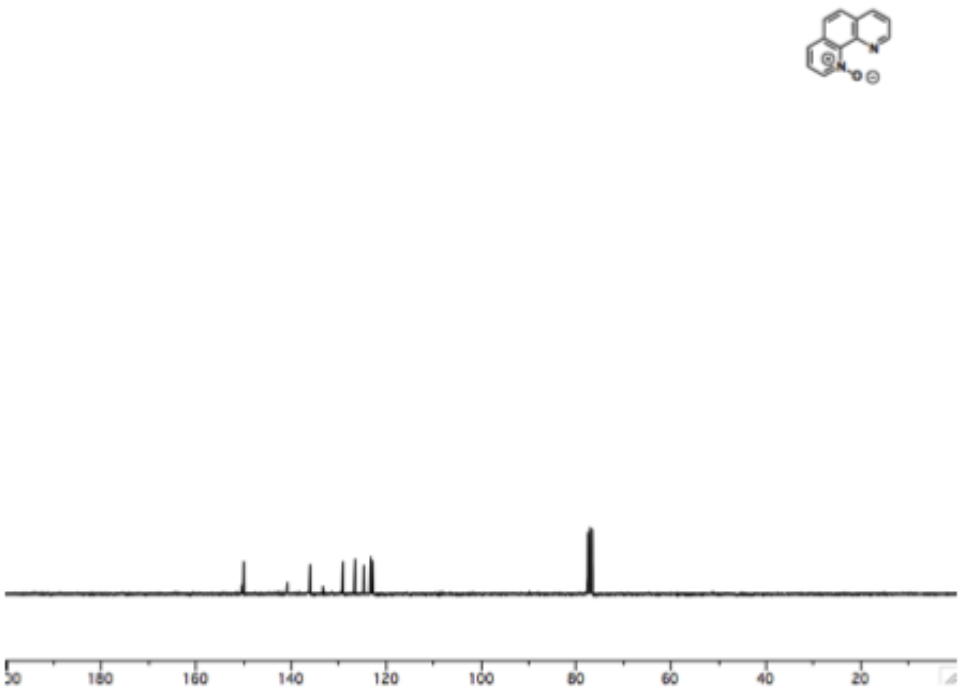






1,10-Phenanthroline 1-oxide (16)





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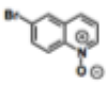
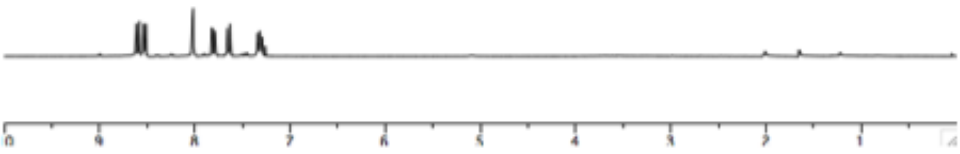
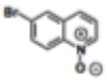
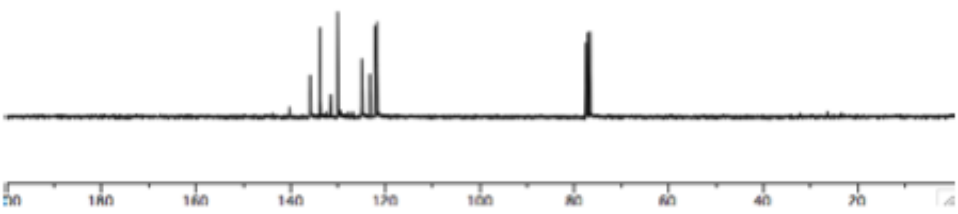
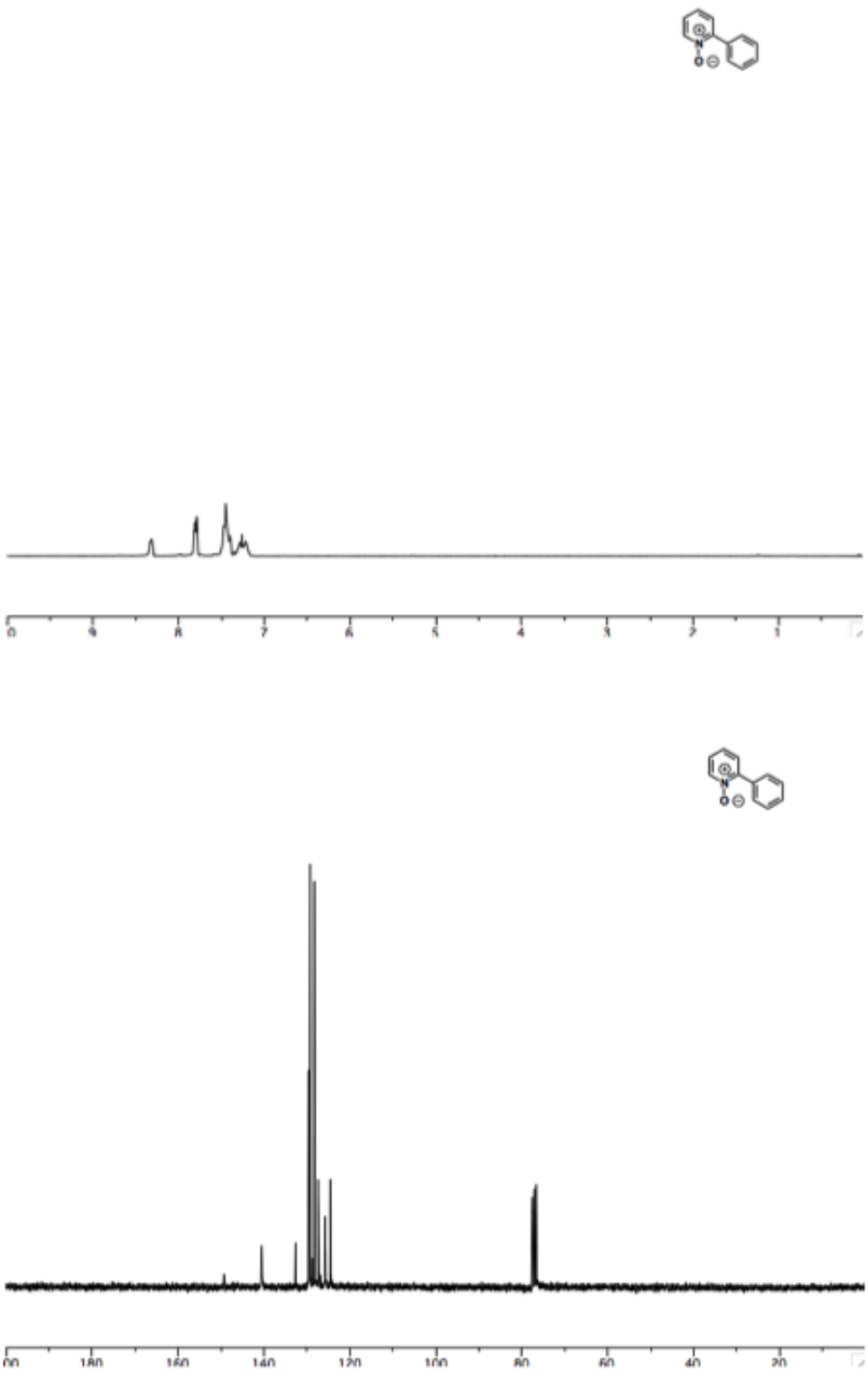




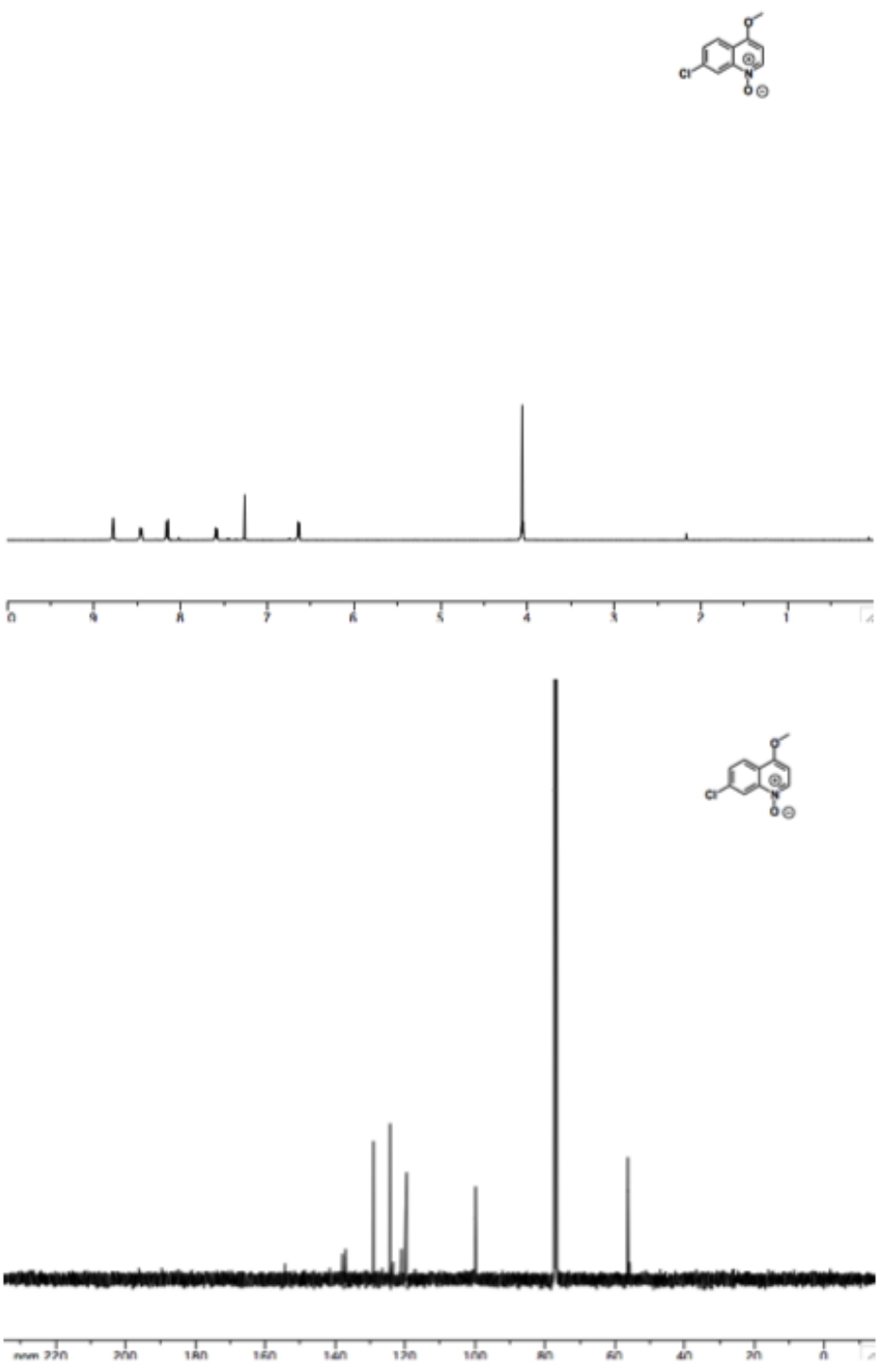




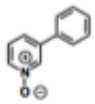
2-Phenylpyridine 1-oxide (19)

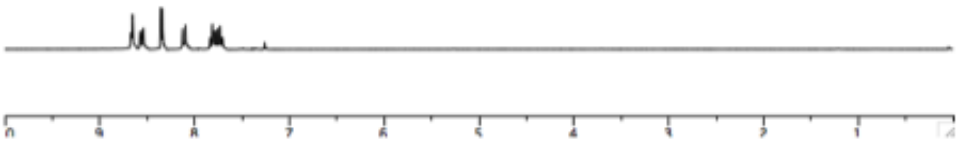


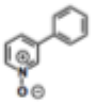
7-Chloro-4-methoxyquinoline 1-oxide (20)

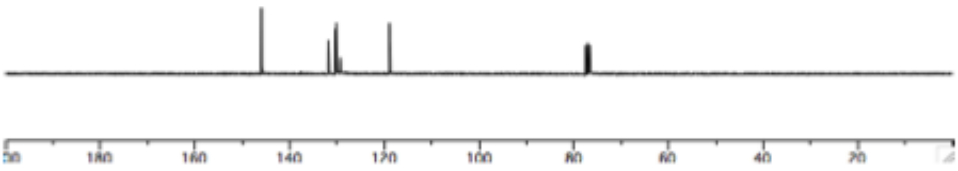


3-Phenylpyridine 1-oxide (21)

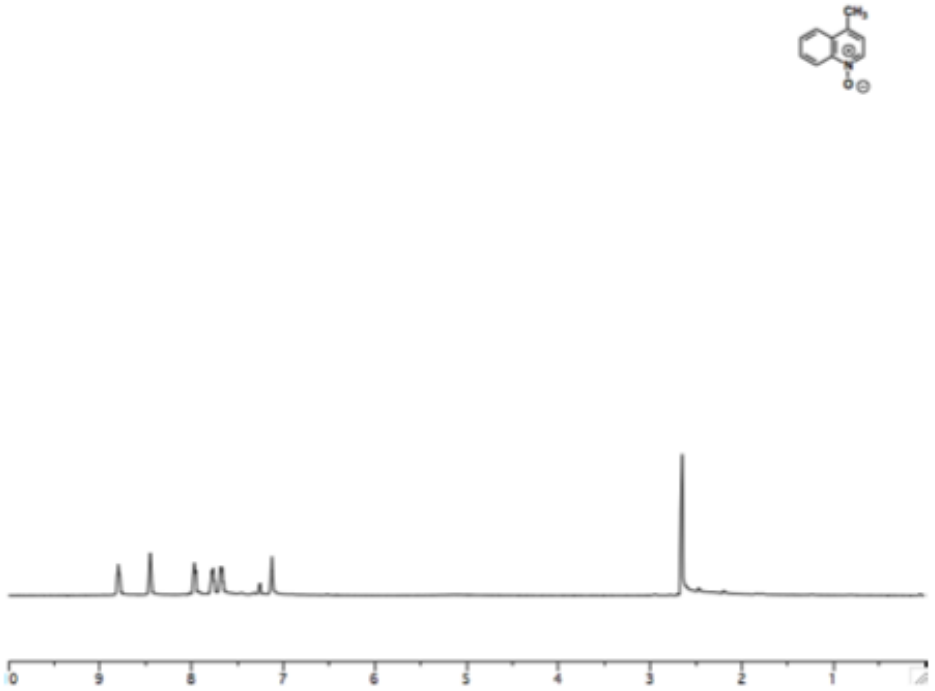


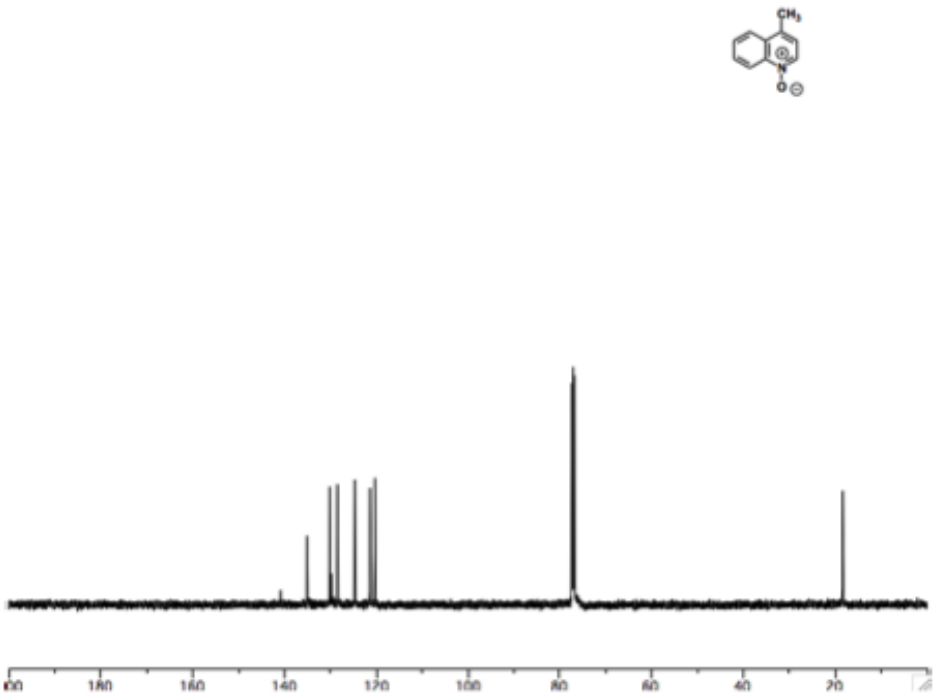






4-Methylquinoline 1-oxide (23)





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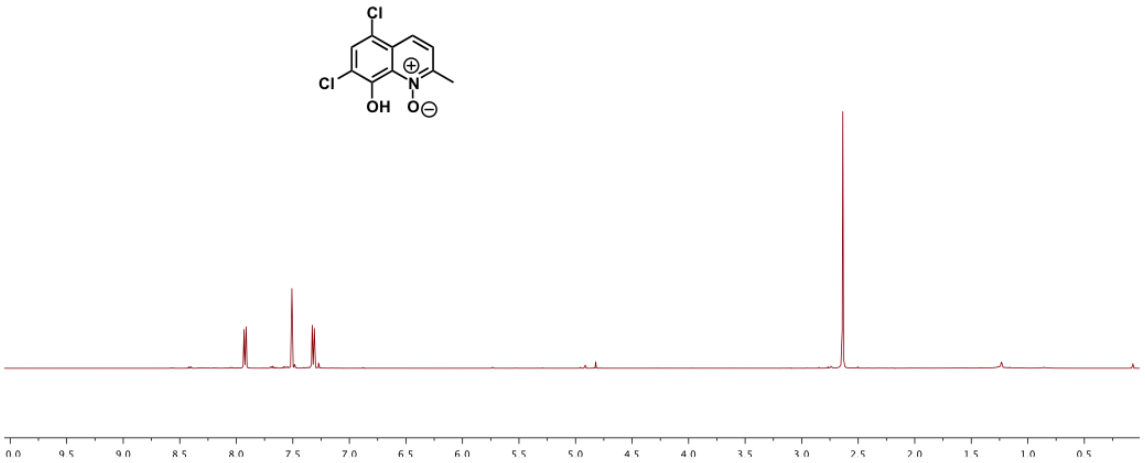

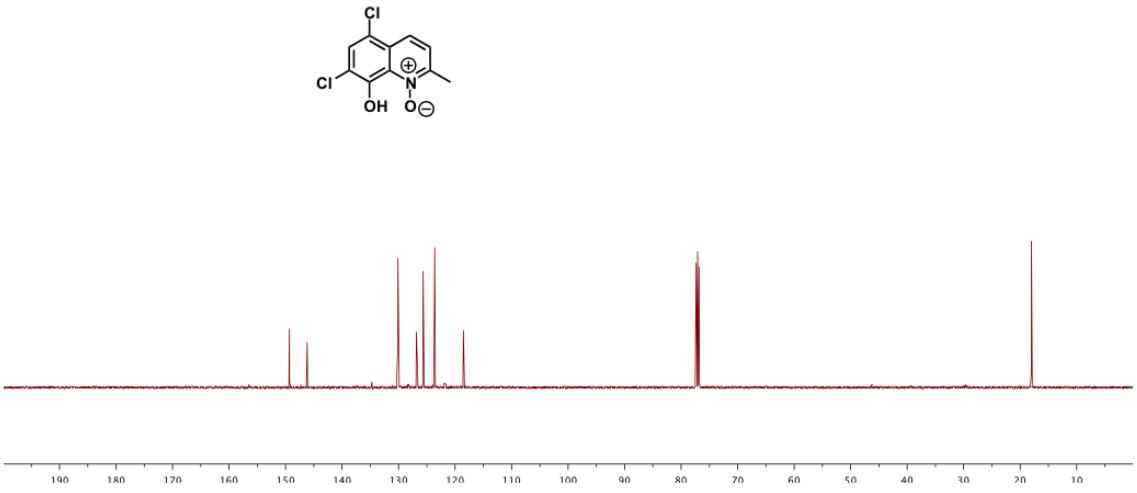

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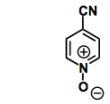
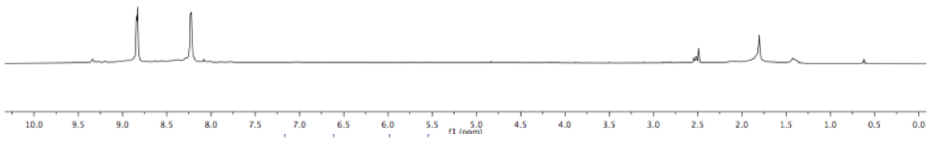
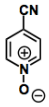


4-cyanopyridine 1-oxide





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