Bisoxazoline-Lewis Acid Catalyzed Direct-Electron Demand *oxo*-Hetero-Diels-Alder Reactions of Pyridine-*N*-Oxide Aldehyde and Ketone Derivatives

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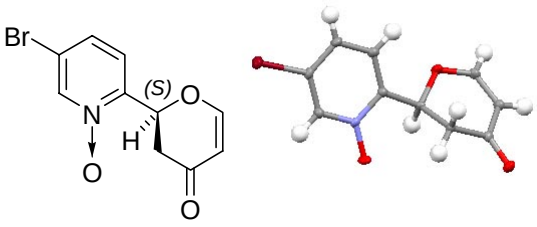
Supporting Information

Contents

General. The ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm relative to MeOH ($\delta = 3.34$) for ^{1}H NMR and relative to the central MeOH resonance ($\delta = 50.41$) for ^{13}C NMR. Purification of reaction products was carried out by flash chromatography (FC) using silica gel 60 (230-400 mesh). The enantiomeric excess (ee) was determined by HPLC. Optical rotation was measured on a polarimeter (Hg lamp 578, solvent MeOH). Mass spectra were recorded using electrospray (ES^{+}) ionisation techniques.

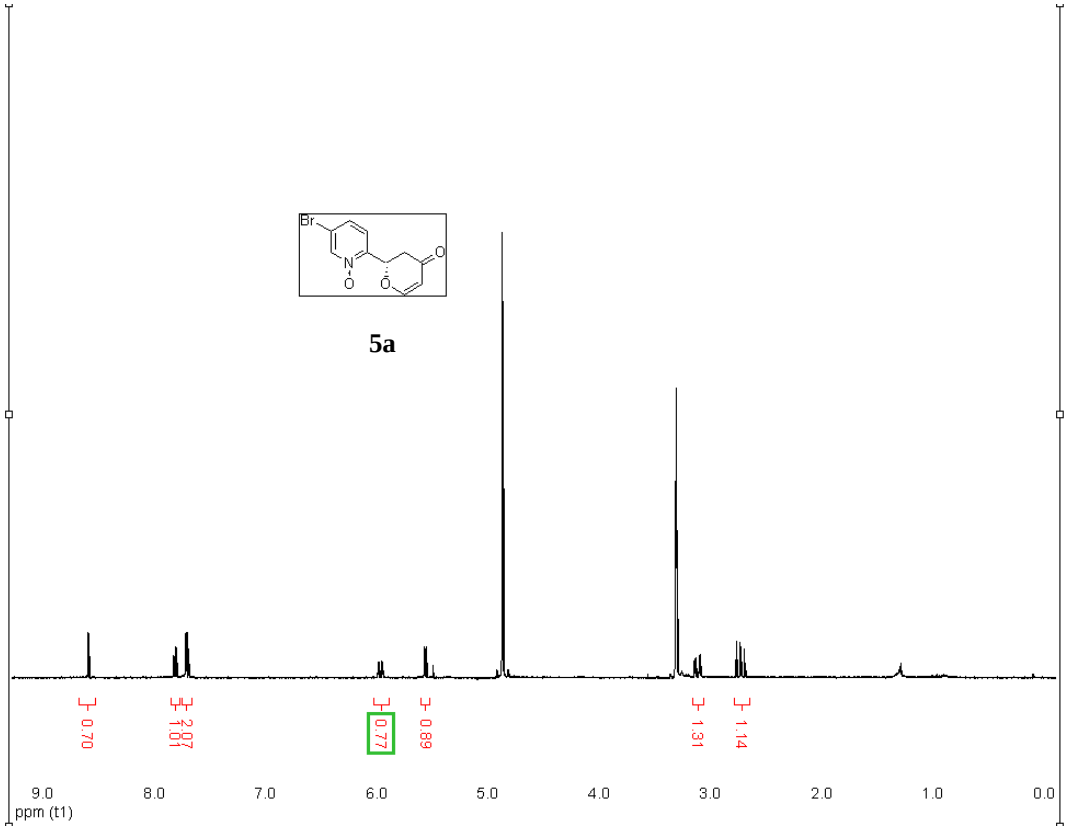
Materials: Bisoxazoline ligands and *N*-oxy-pyridine derivatives were prepared by the literature procedures.[1] Commercially available starting materials were used without further purification. Solvents were distilled prior to use: CH_2Cl_2 was dried and distilled from CaH_2 and THF, THF and toluene were distilled from sodium metal/benzophenone ketyl. All reactions were carried out in an inert atmosphere of Ar and in oven dried glassware.

Figure. X-ray Crystallographic Structure of **5a**.



X-Ray Data Compound 5a:

Formula	$C_{10}H_8BrNO_3$
Weight, g mol^{-1}	270.08
Crystal system	monoclinic
Space Group	P 1 $2_1$1
Z	4
a, Å	7.1454(10)
b, Å	6.9176(10)
c, Å	10.0029(2)
α, °	90
β, °	98.29
γ, °	90
V, $Å^3$	489.265(14)
T, K	100
ρ, g cm^{-3}	1.833
μ, mm^{-1}	4.185
d_{min}, Å	0.65
N_{meas}, N_{uniq}	10810, 3692
R_{int}	0.0297
N_{obs}, N_{var}	3692, 136
$R_w(F^2)$, all data	0.04994
Goodness of fit	1.054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O
O
O
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2.07
1.01
0.77
0.89
1.31
1.14
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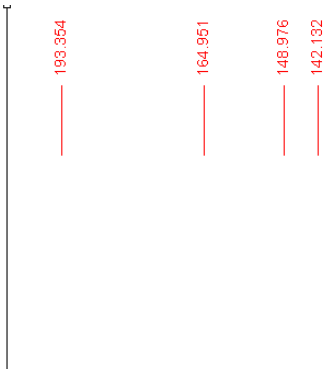
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

5a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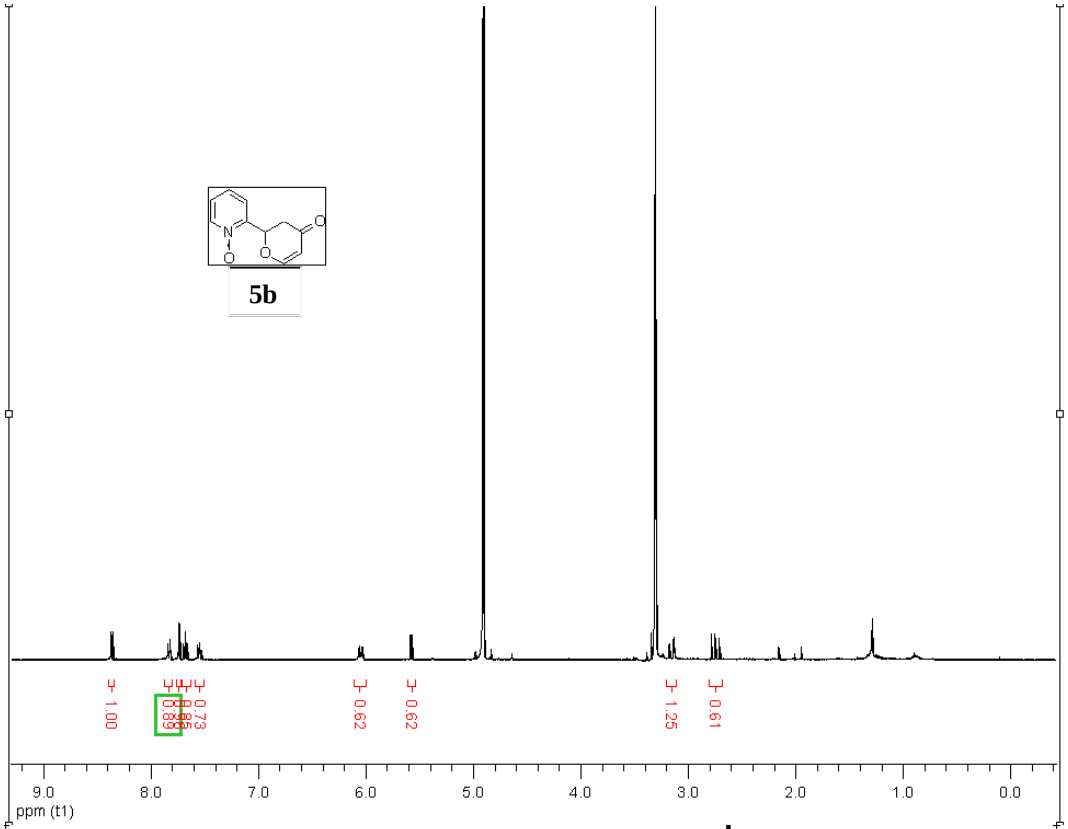
148.976
142.132

5a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1.89
1.89
1.89
0.73
0.62
0.62
1.25
0.91
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7.0
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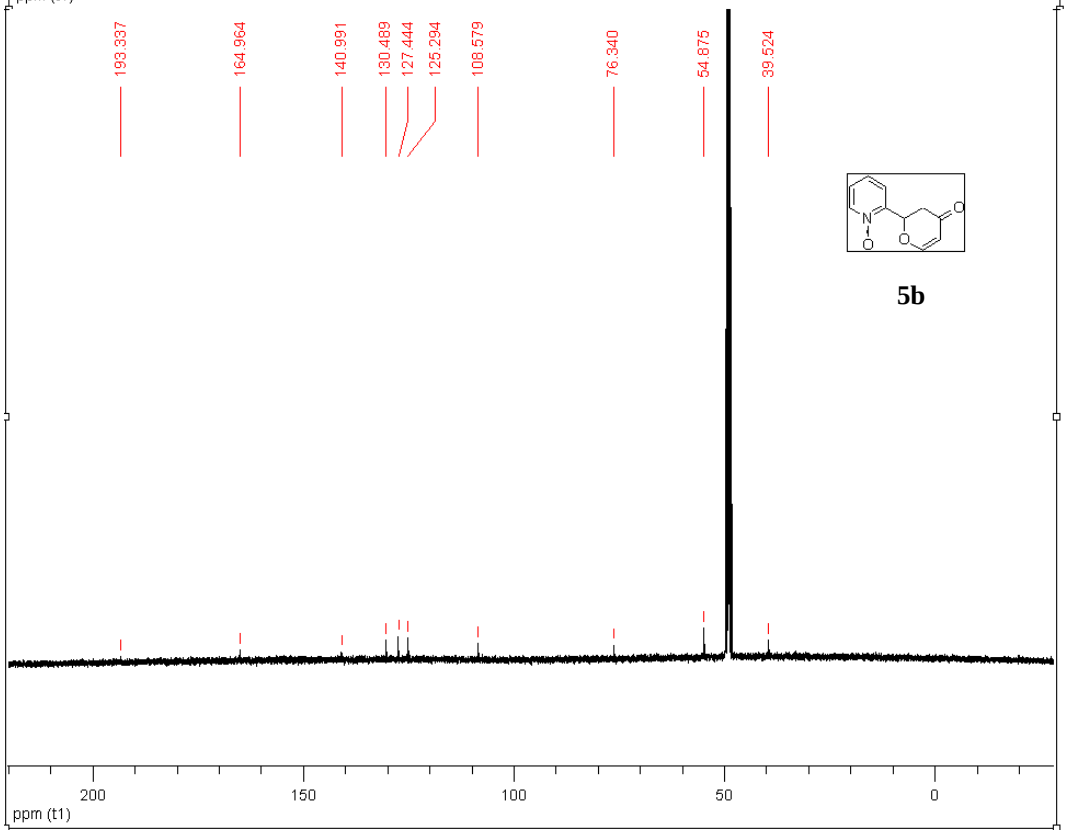
ppm (t1)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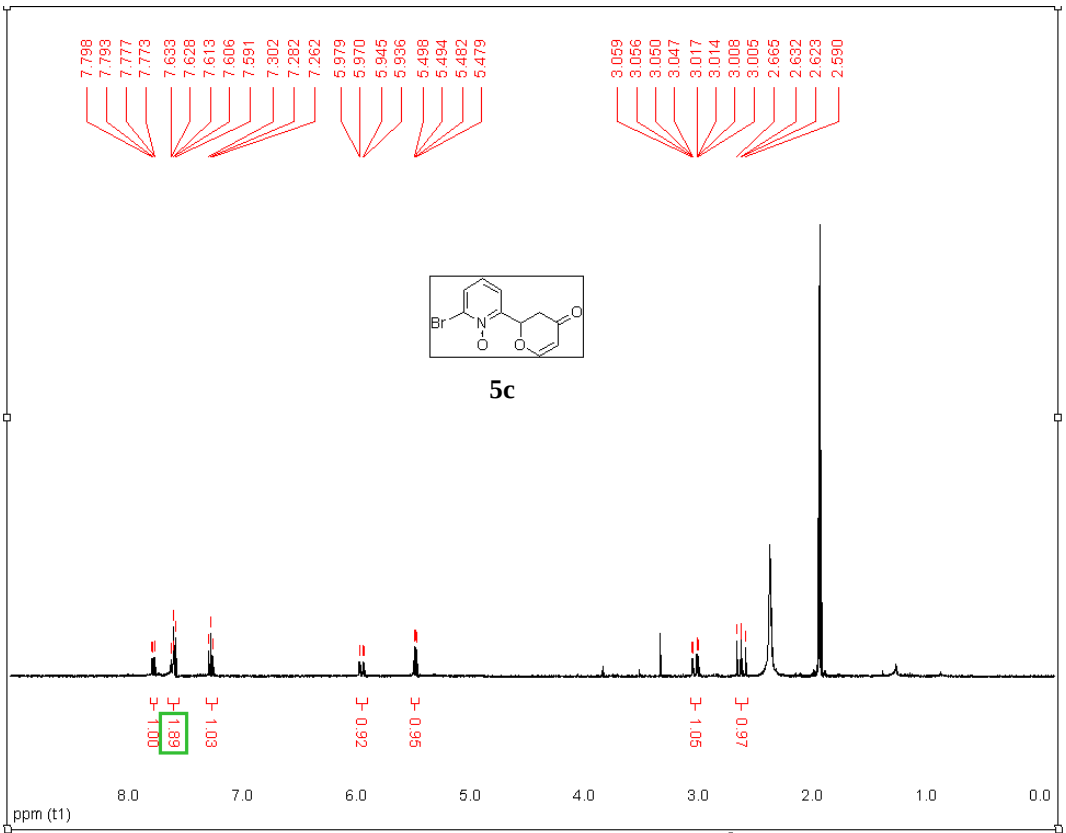
100
50
0
ppm (t1)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5.970
5.945
5.936
5.498
5.494
5.482
5.479
3.059
3.056
3.050
3.047
3.017
3.014
3.008
3.005
2.665
2.632
2.623
2.590
Br
N
O
O
O
5c
1.00
1.89
1.03
0.92
0.96
1.06
0.97
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4.0
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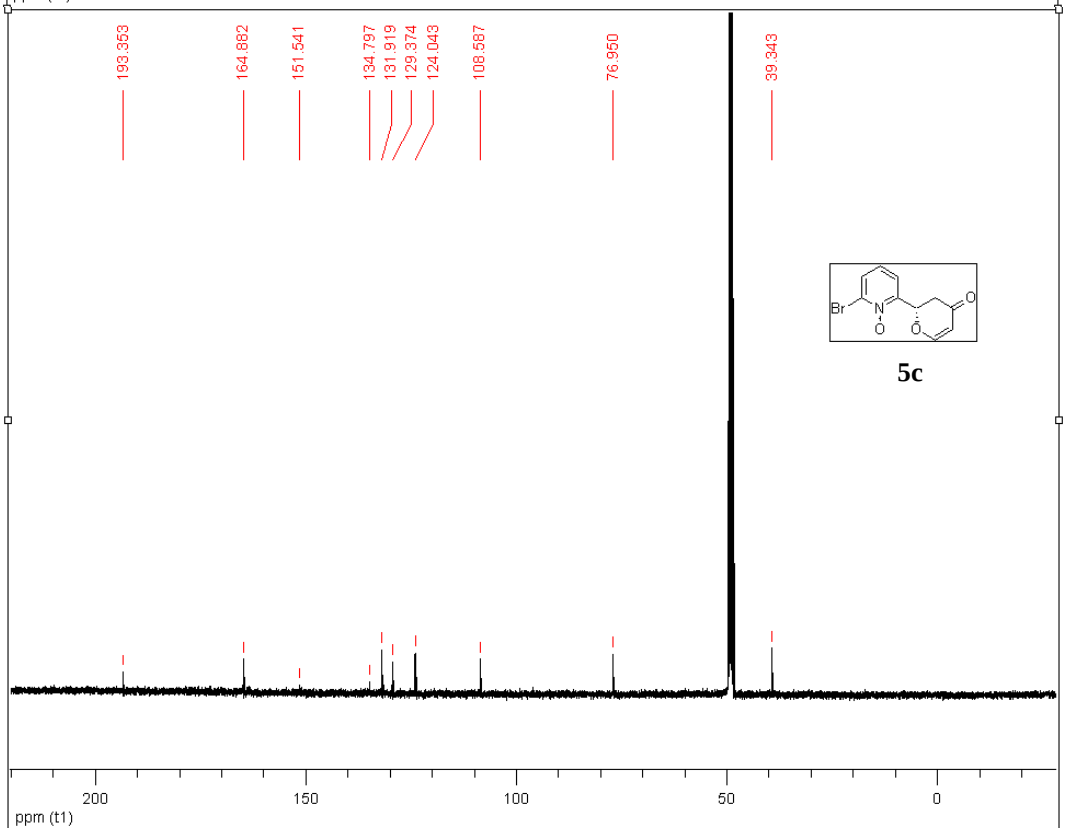
ppm (t1)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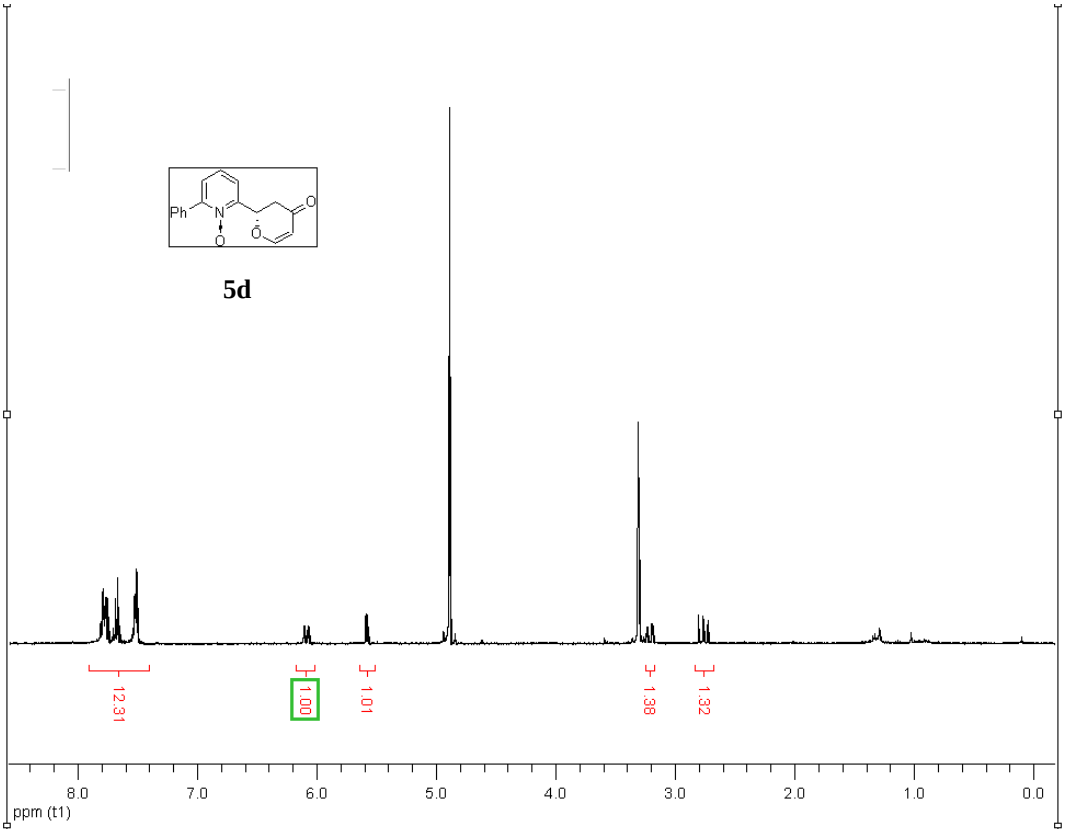
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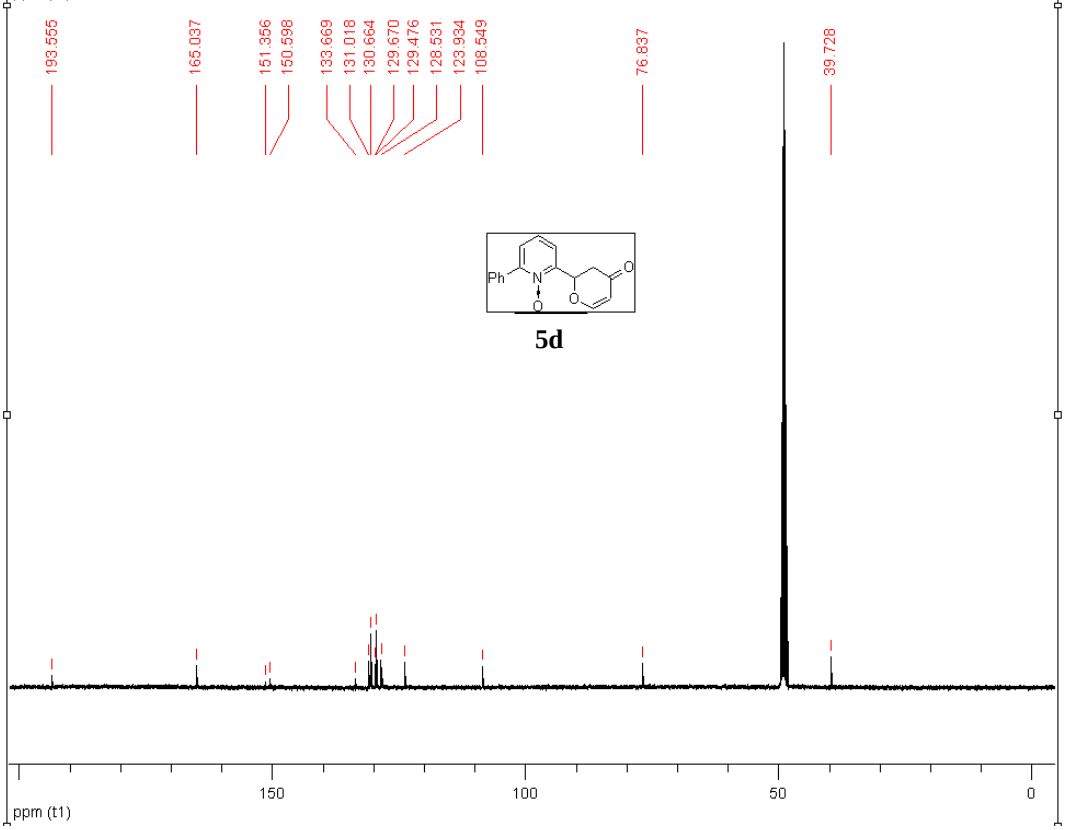
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76.837
39.728
Ph
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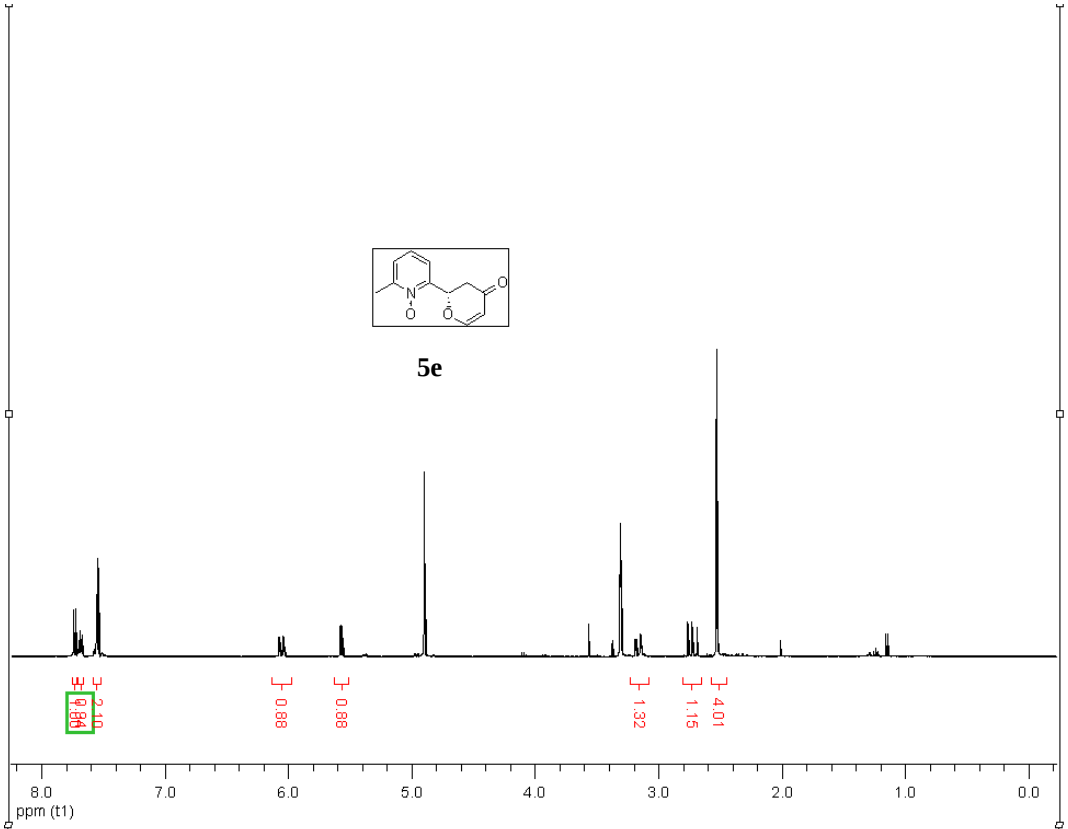
O
O
5d
150
100
50
0
ppm (t1)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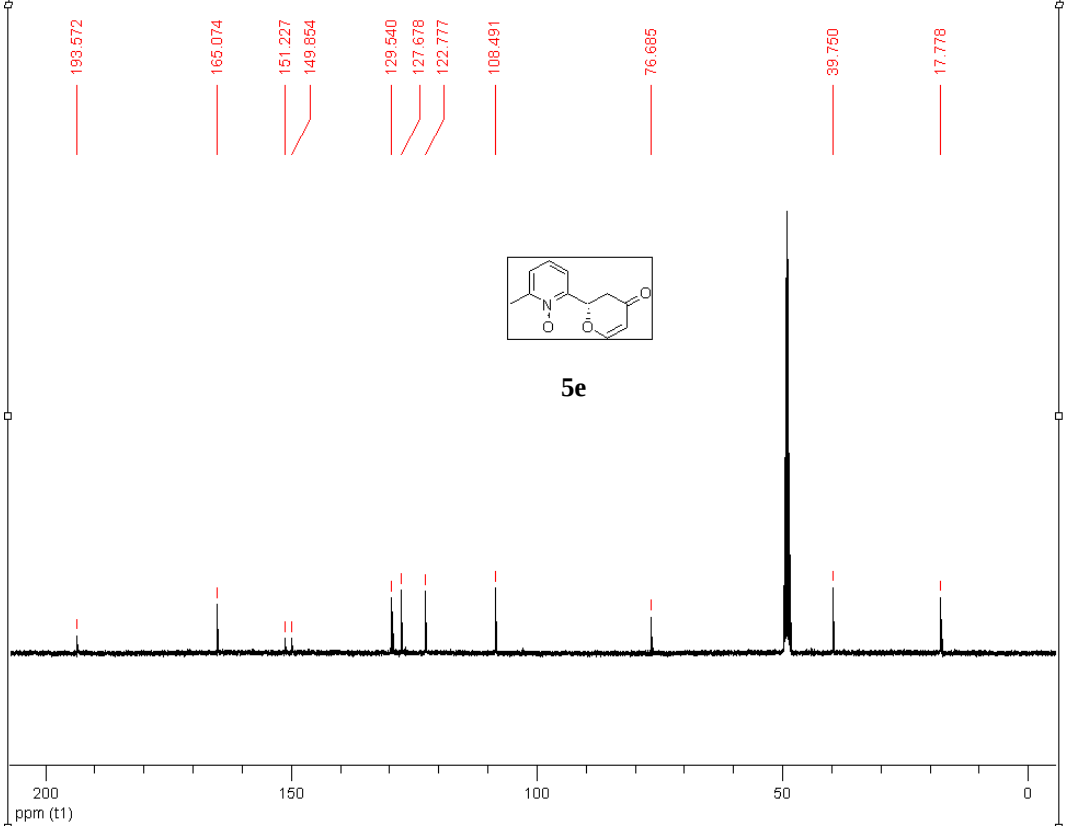
ppm (t1)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50
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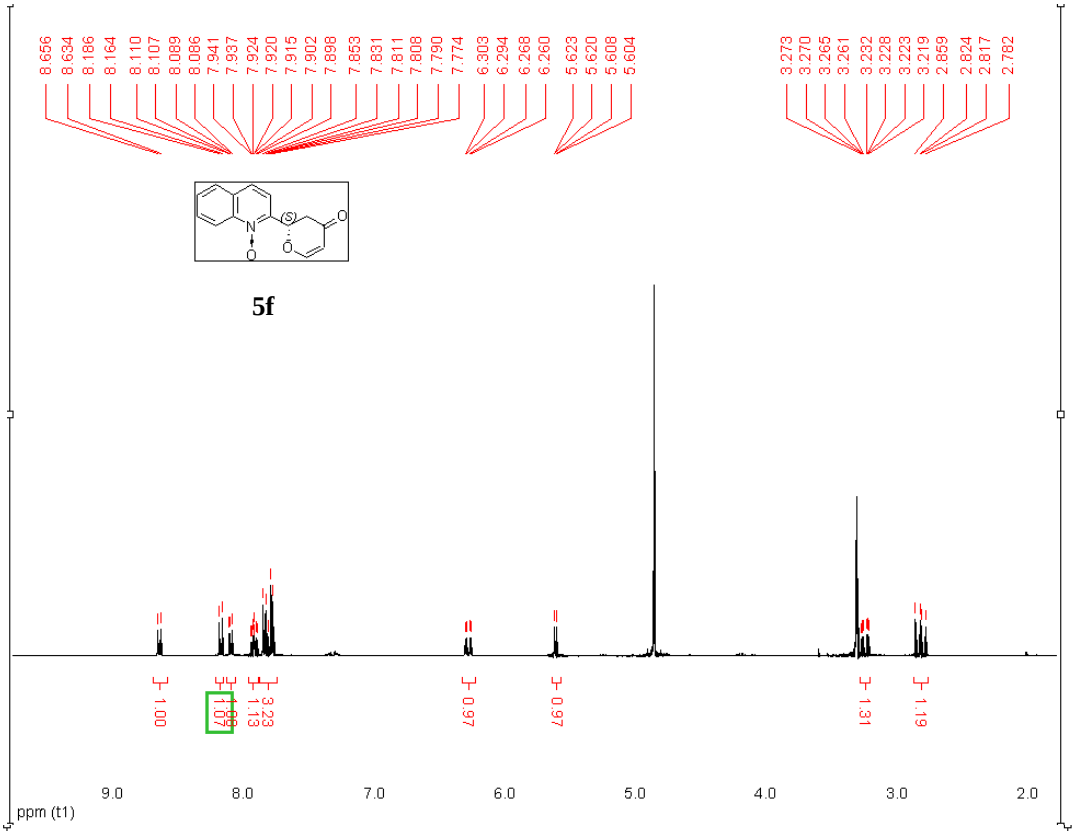
ppm (t1)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7.902
7.898
7.853
7.831
7.811
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7.790
7.774
6.303
6.294
6.268
6.260
5.623
5.620
5.608
5.604
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3.270
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3.223
3.219
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2.824
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1.13
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0.97
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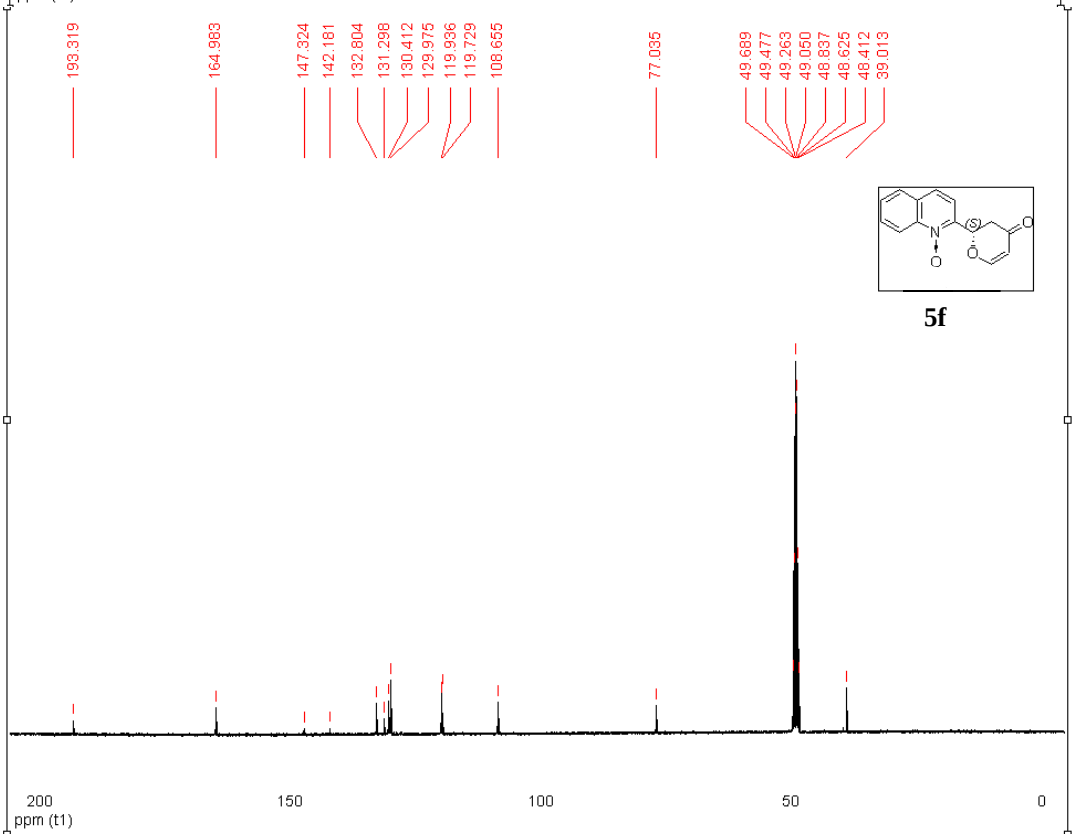
ppm (t1)

5f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49.689
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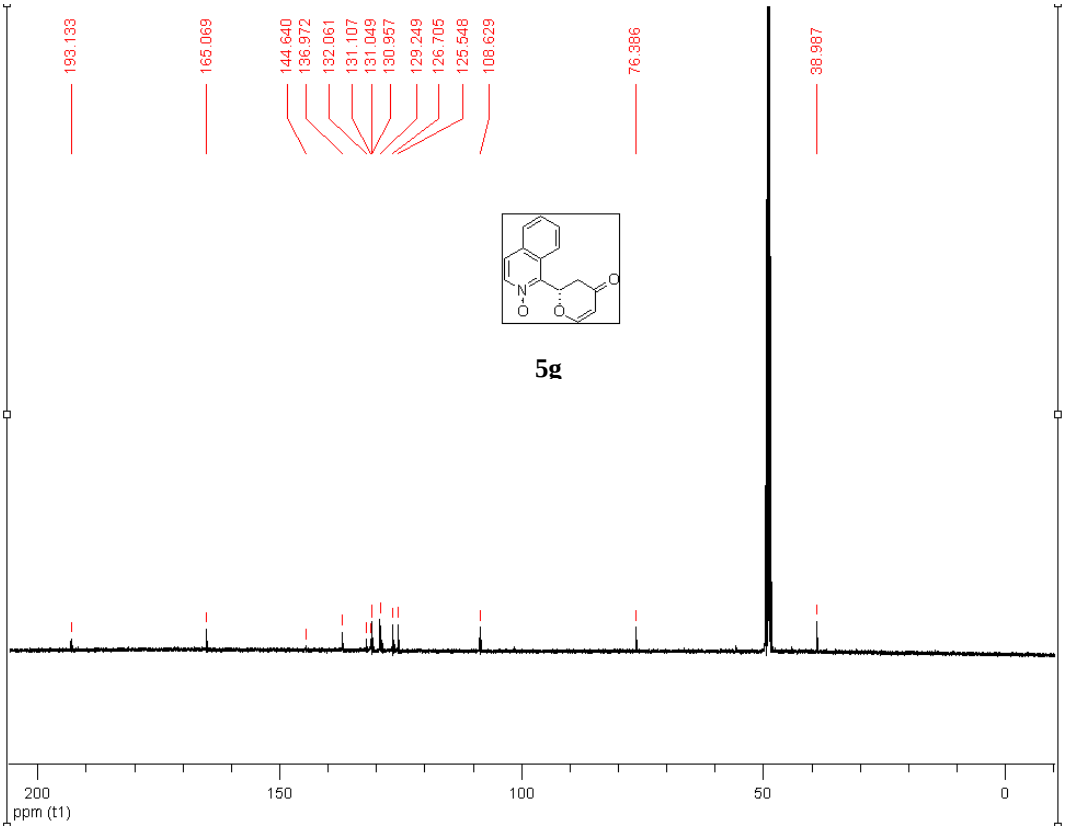
5f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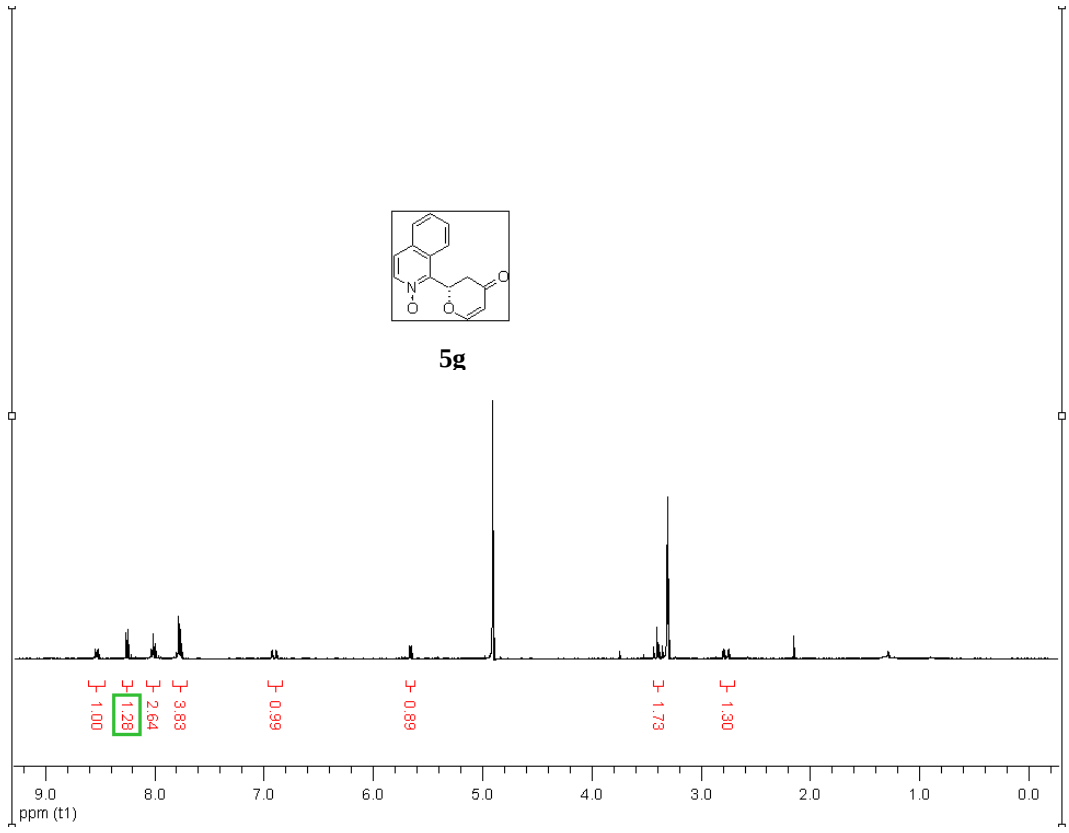
5g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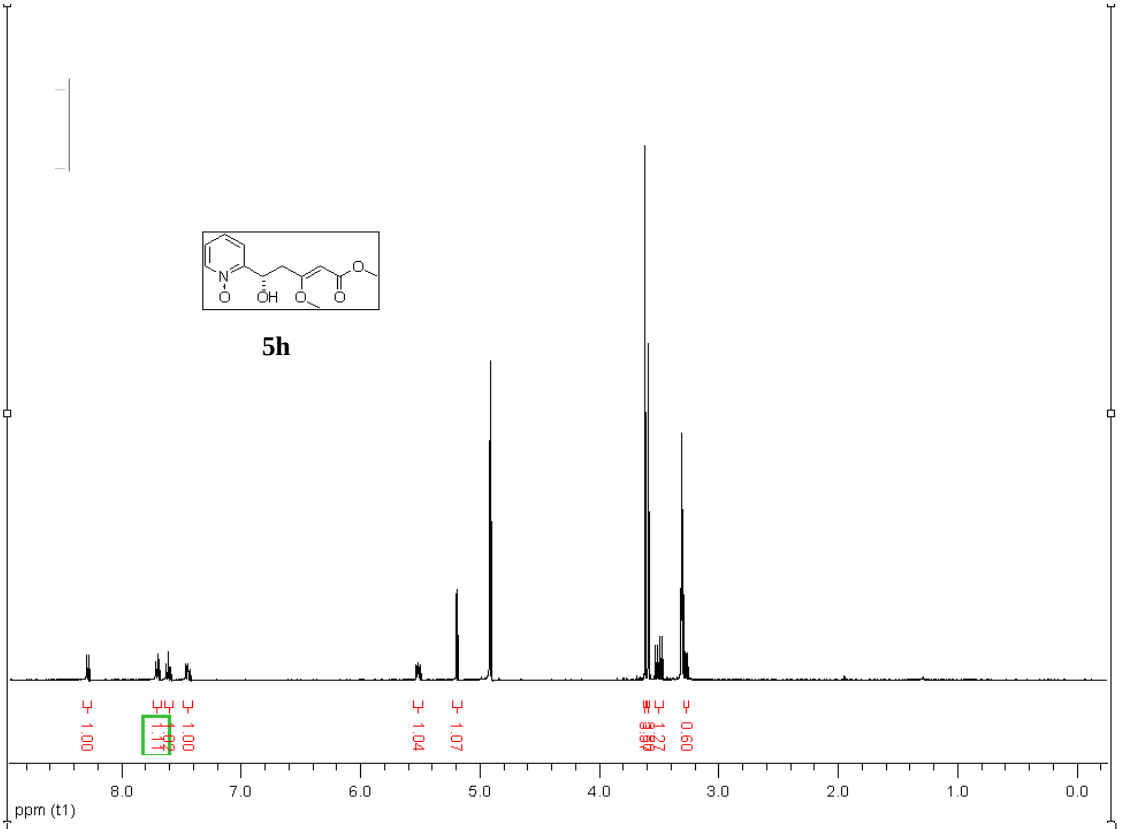
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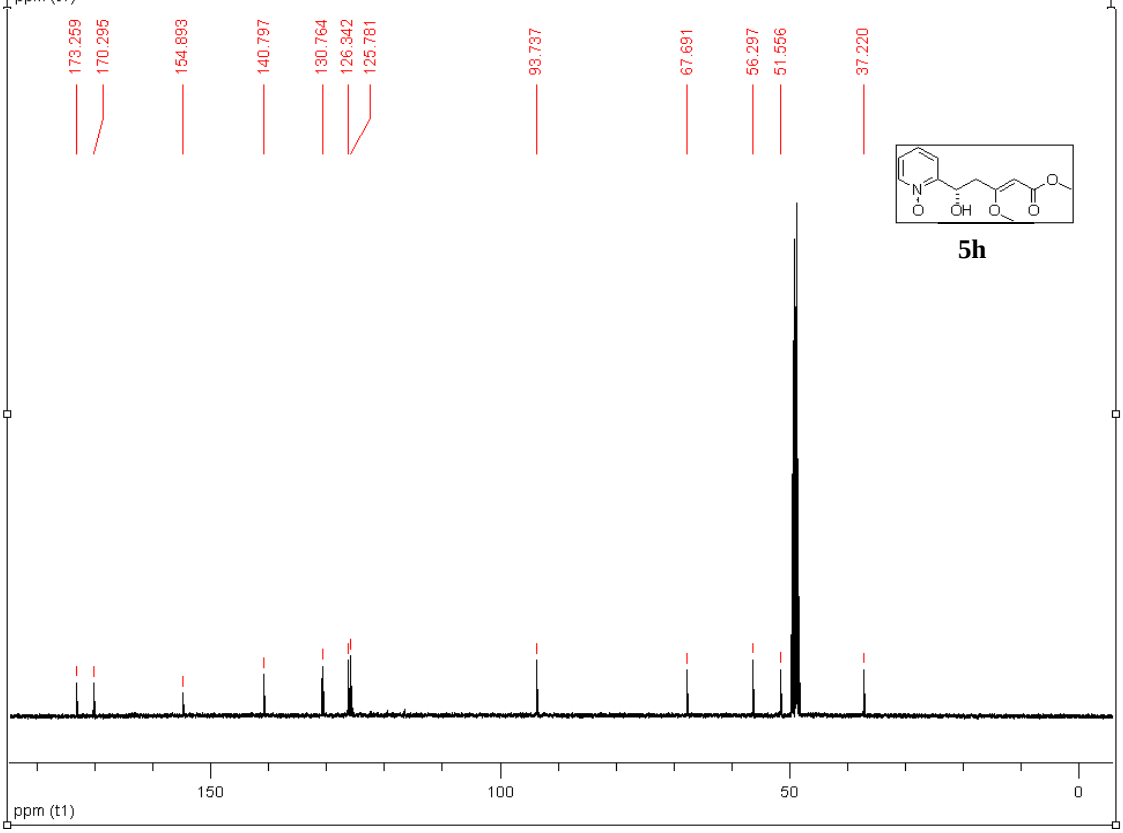
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50
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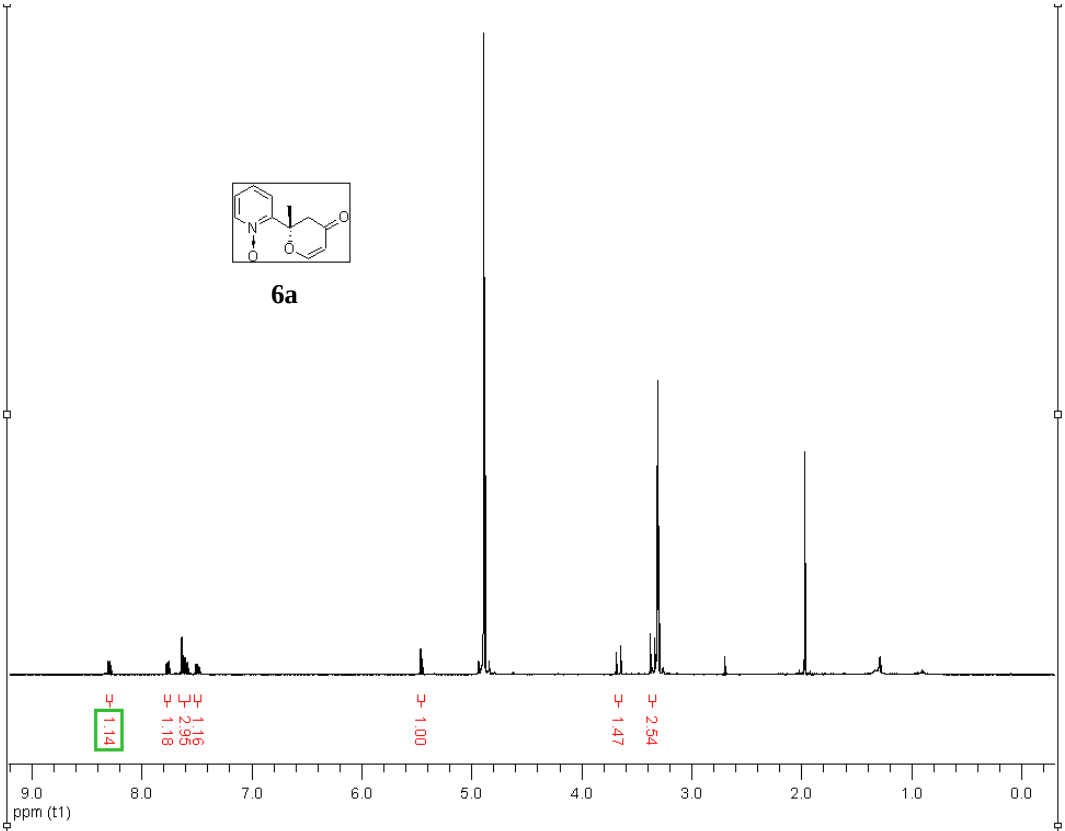
ppm (t1)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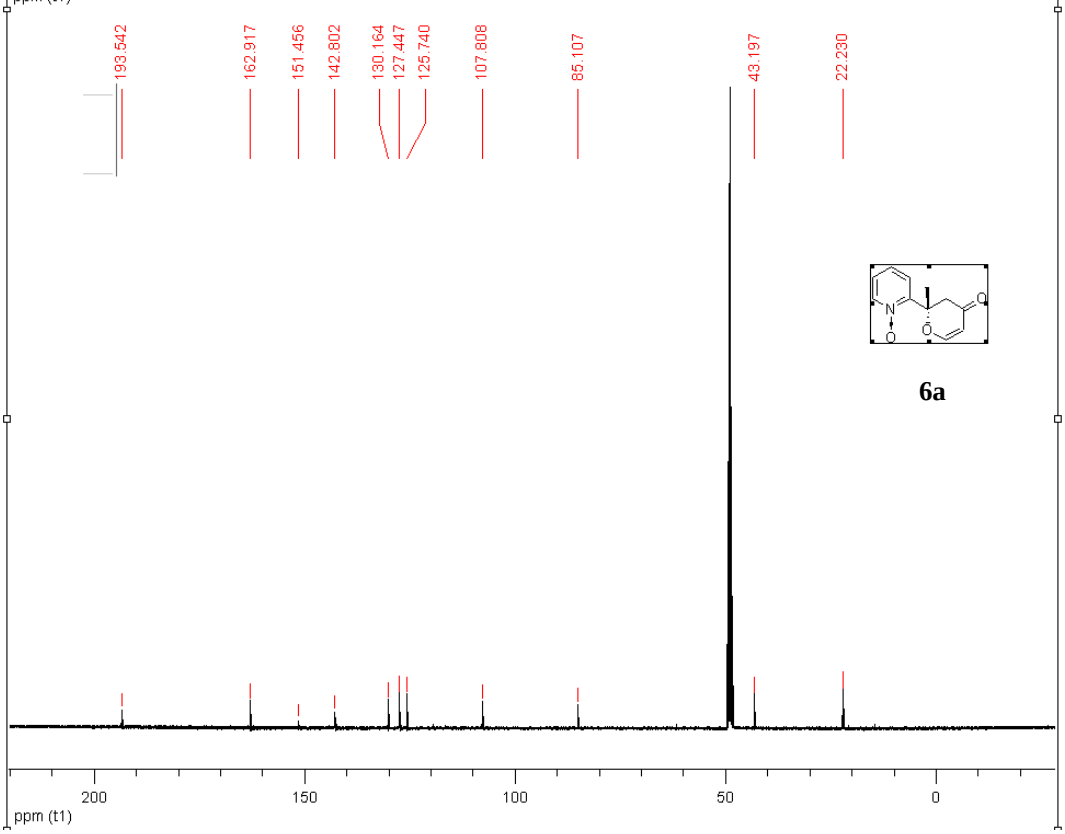
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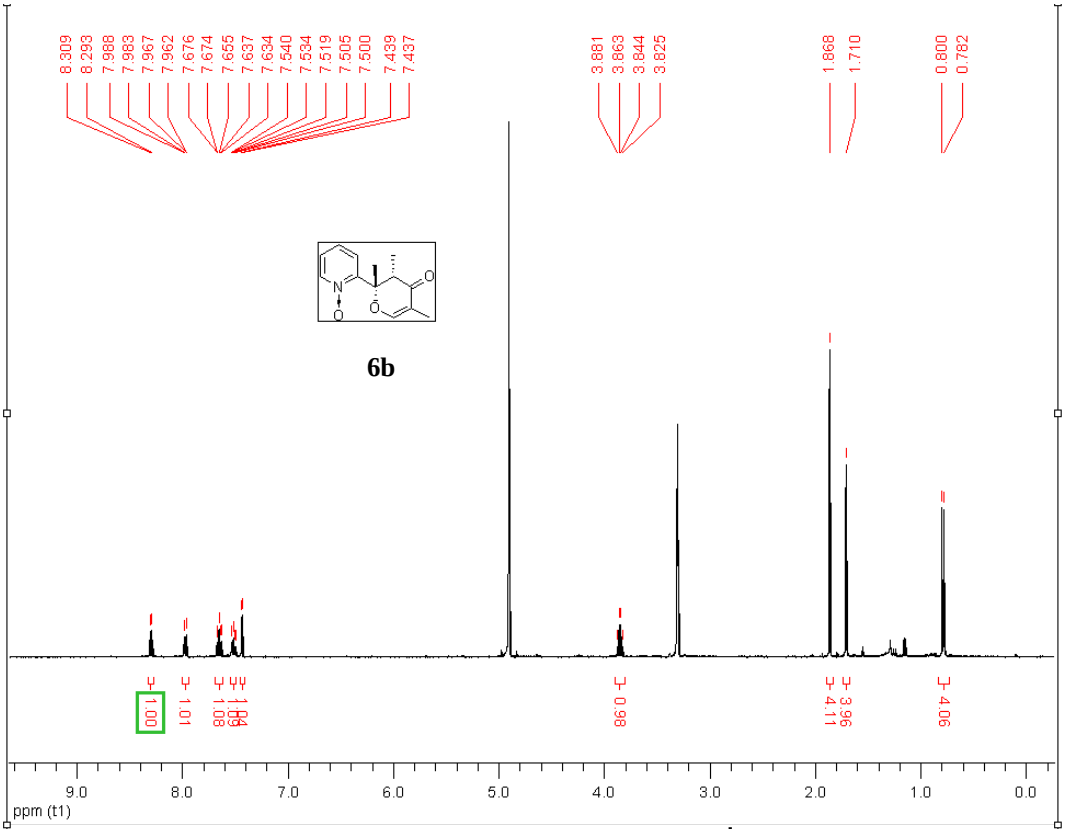
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1.08
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1.11
0.98
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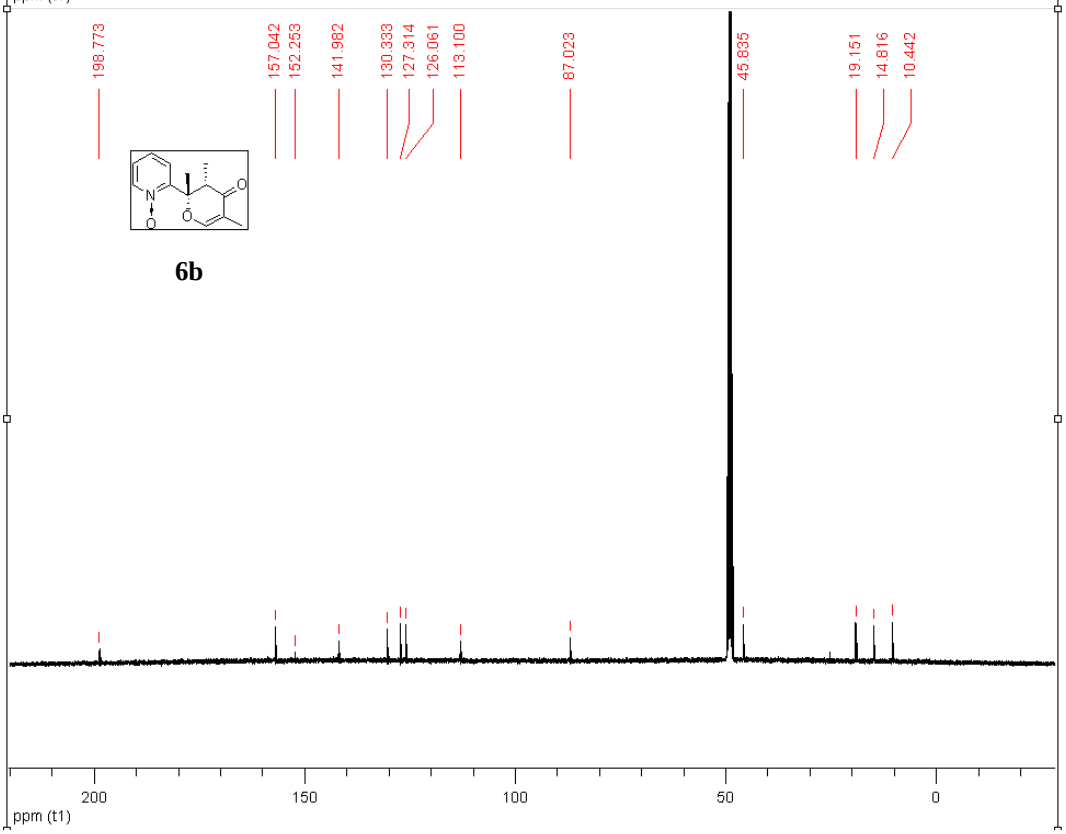
6b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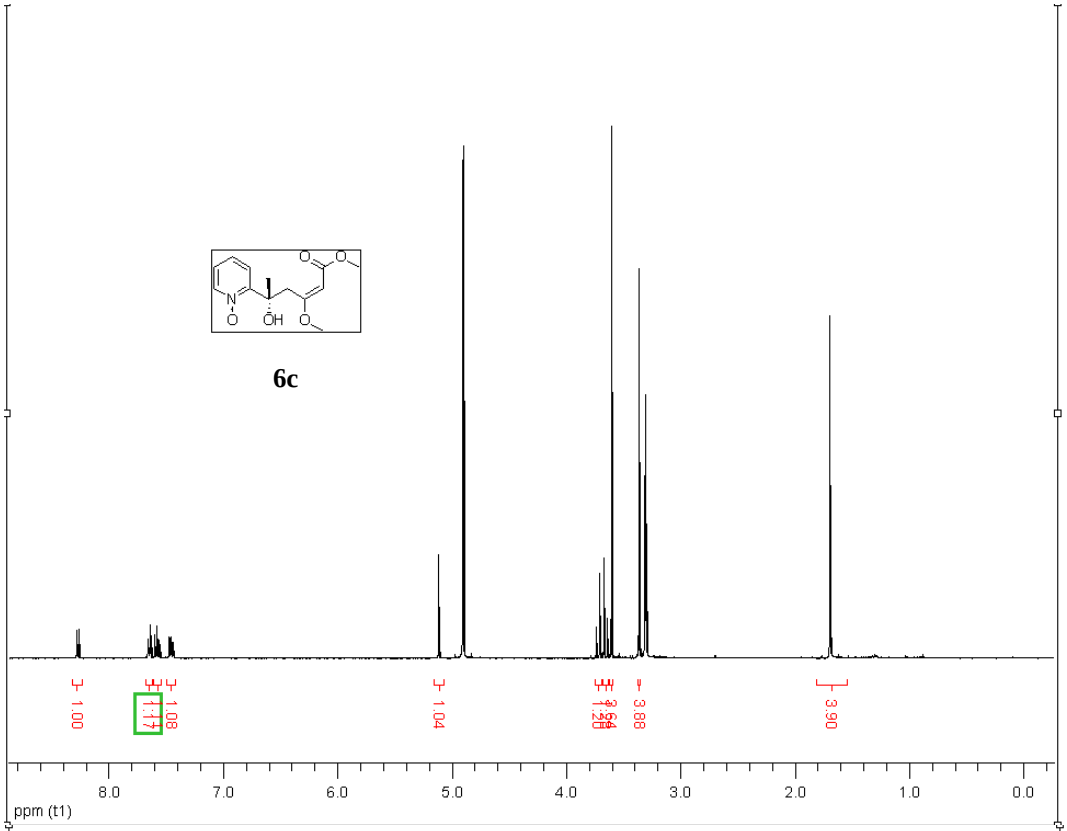
6b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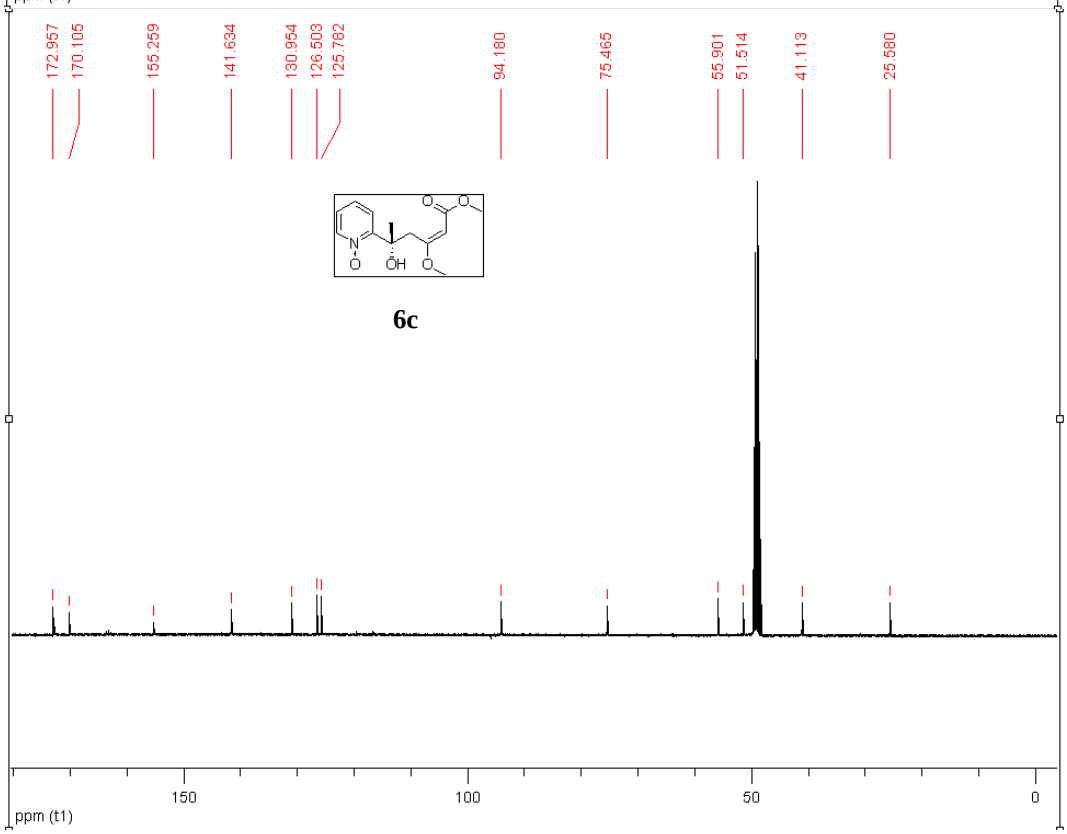
6c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55.901
51.514
41.113
25.580
150
100
50
0
ppm (t1)

6c

References

1. Landa, A.; Minkkilä, A.; Blay, G.; Jørgensen, K. A. *Chem. Eur. J.* **2006**, *12*, 3472.