Supplementary Material (ESI) for Chemical Communications

Supporting information

Carbon Supported Pt Colloid as Effective Catalyst for Selective Hydrogenation of Nitroarenes to Arylhydroxylamines

*Zeming Rong, Wenqiang Du, Yue Wang and Lianhai Lu**

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116012, P. R. China

E-mail： lianhai@dlut.edu.cn

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1、Materials and Methods

All the solvents were analytic grade. ^{1}H-NMR were measured on a Bruker Avancell 400 spectrometer with chemical shifts reported as ppm(in DMSO-d_6, TMS as internal standard). Mass spectra were measured on a HP 1100 LC-MS spectrometer. The conversion and selectivity of product were analyzed on Waters 2695/2996 HPLC.

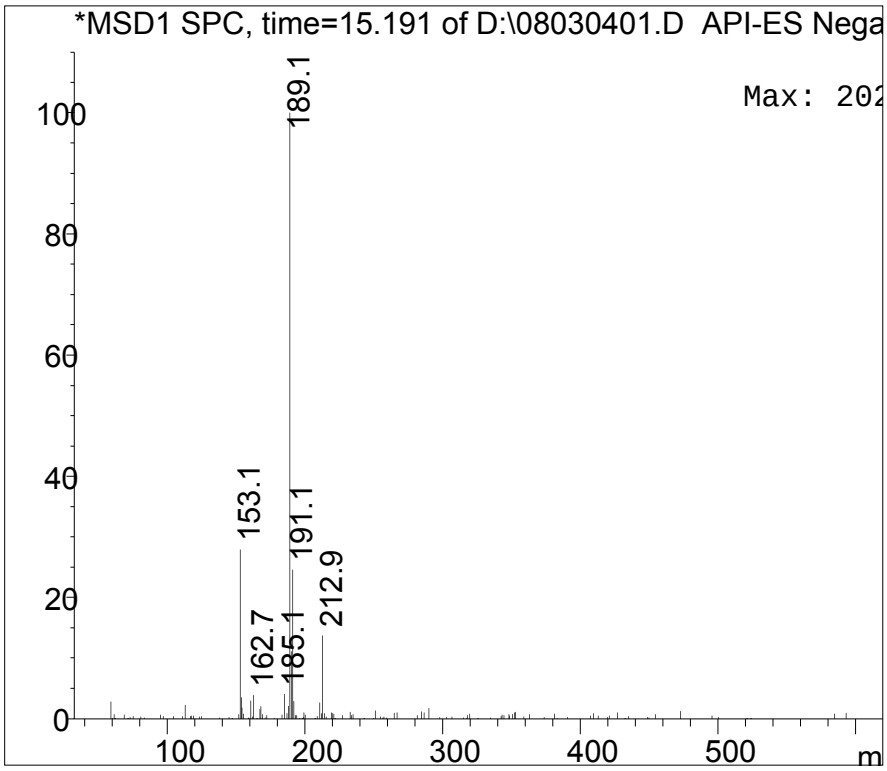
2、Experimental Procedures

The catalytic hydrogenation reaction was typically conducted in a stainless-steel autoclave reactor. For each run, a predetermined quantity of substrate and THF solvent was placed into the reactor (70ml capacity) together with an appropriate amount of catalyst. After the reactor was sealed, it was purged by flushing with 1.0MPa of N_2 for three times and then H_2 for three times. The reaction temperature was controlled by adding ice to the water bath and maintained within ±1K of the desired temperature. When the autoclave was cooled to a required temperature, it was pressurized with H_2 at the selected setting point. The reaction time was reckoned when the agitation started from this point. A constant pressure was maintained throughout the reaction period. The process of the reaction was monitored by HPLC. After completion of the reaction, the suspension was filtered of and the filtrate was purified by flash chromatography(silica gel, hexane : trichloromethane=2:3, v/v) under N_2 atmosphere to give the pure *N*-arylhydroxylamine.

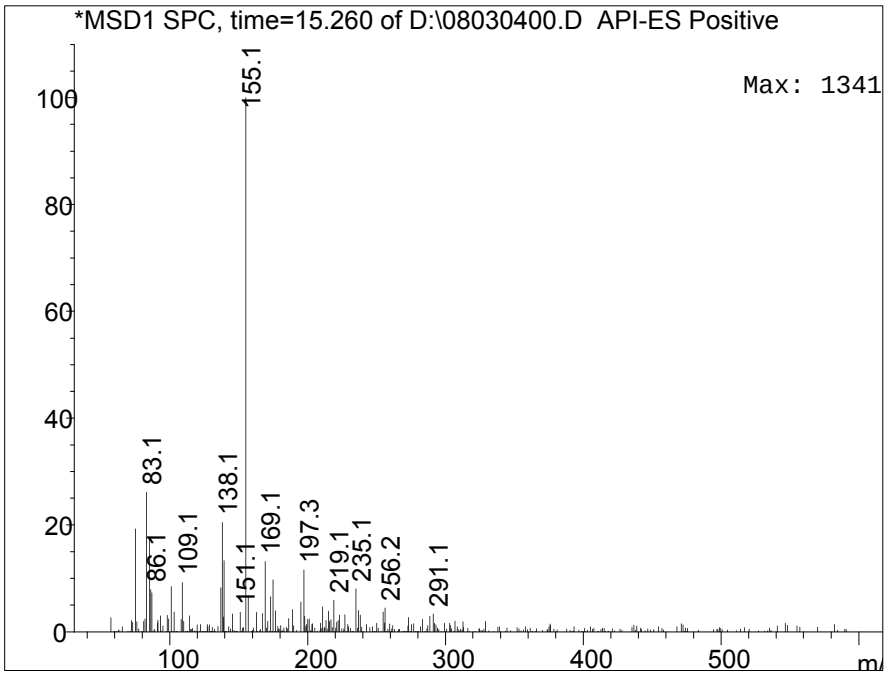
3、Analytical and spectral characterization data

***N*-(3-Nitro-phenyl)-hydroxylamine：**

^{1}H NMR(400MHz, DMSO-d_6): δ 8.87(s,-NH), δ 8.75 (s,-OH), δ 7.61(s,1H), δ 7.57(d, *J*=8.00 Hz,1H), δ 7.44(t,1H), δ 7.19(d, *J*=8.00 Hz,1H) ; MS(API-ES): m/z 155$[M+H]^+$ ，m/z 153$[M-H]^-$ ，m/z 189$[M+Cl]^-$



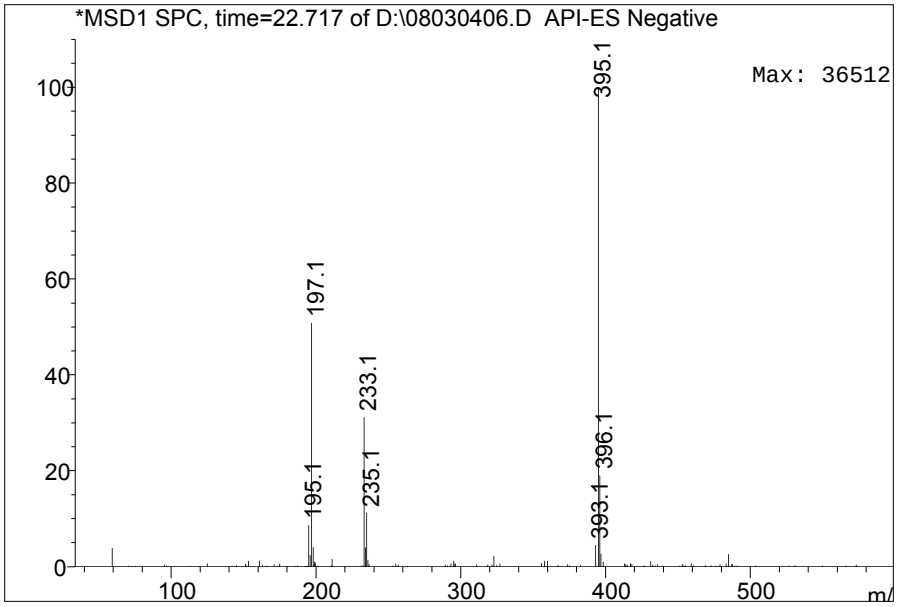
S-1 Mass spectra of *N*-(3-Nitro-phenyl)-hydroxylamine in Negative model



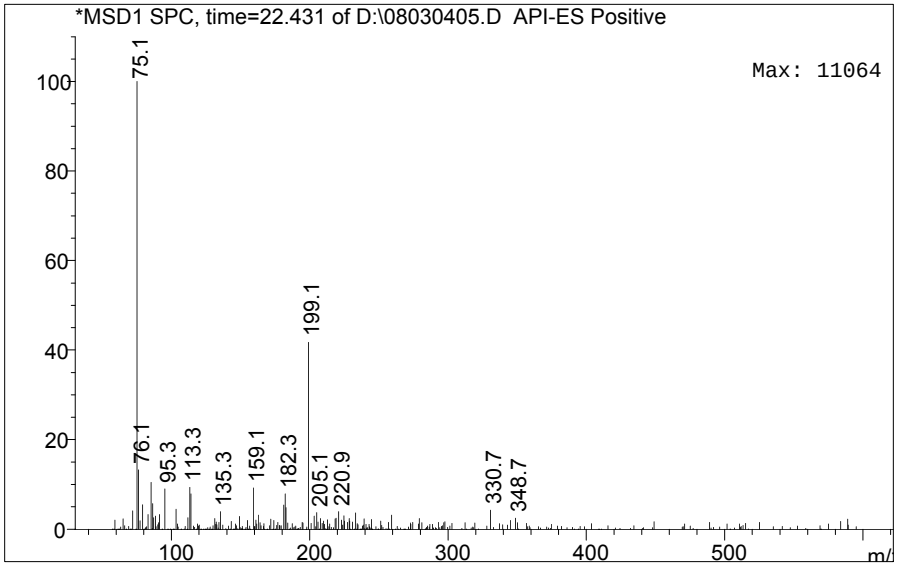
S-2 Mass spectra of *N*-(3-Nitro-phenyl)-hydroxylamine in Positive model

3-Hydroxyamino-5-nitro-benzoic acid：

^{1}H NMR(400MHz, DMSO-d_6): δ 13.53(s, COOH), δ 9.10 (s, NH), δ 8.94(s, OH),δ 7.99(s, 1H), δ 7.78(s, 1H), δ 7.73(s, 1H)；MS(API-ES): m/z 197 $[M-H]^-$, m/z 233 $[M+Cl]^-$, m/z395$[2M-H]^-$,m/z 199$[M+H]^+$,m/z221$[M+Na]^+$



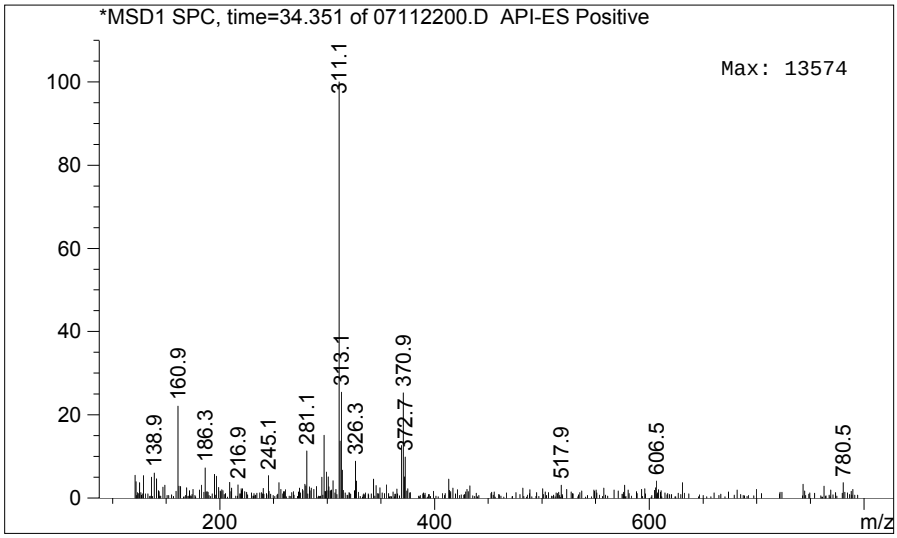
S-3 Mass spectra of 3-Hydroxyamino-5-nitro-benzoic in Negative model



S-4 Mass spectra of 3-Hydroxyamino-5-nitro-benzoic acid in Positive model

4-Chloro-3-hydroxyamino-5-nitro-benzoic acid isobutyl ester

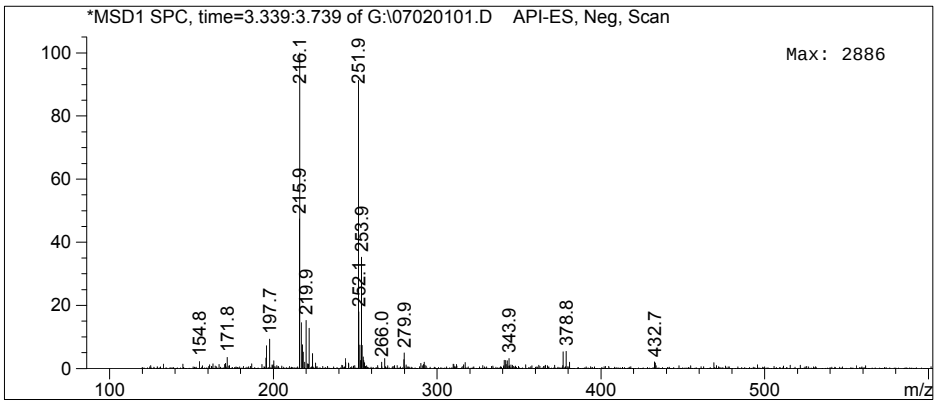
^{1}H NMR(400MHz, DMSO-d_6): δ 9.23 (1H,s,NH), δ 9.15 (1H,s,OH),δ 7.90(1H,s,Ph), δ 7.83 (1H,s,Ph), δ4.11(2H,d,CH_2) , δ2.15(1H,m,CH), δ0.97 (6H,d,CH_3), MS(API-ES): m/z 311$[M+Na]^+$



S-5 Mass spectra of 4-Chloro-3-hydroxyamino-5-nitro-benzoic acid isobutyl ester in Positive model

2-(3-Hydroxyamino-benzenesulfonyl)-ethanol:

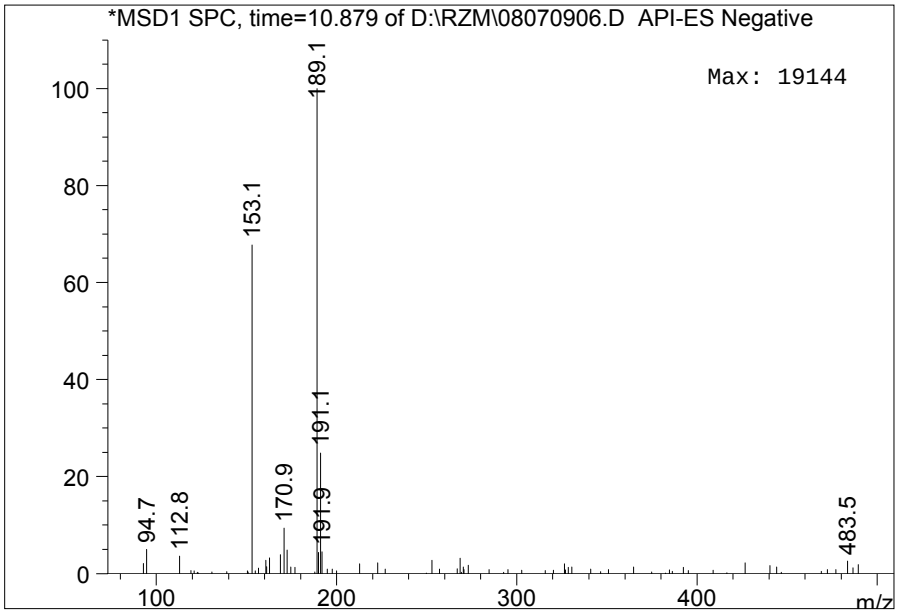
^{1}H NMR(400MHz, DMSO-d_6): δ 8.74 (1H,s,NH), δ 8.63(1H,s,OH),δ 7.41(1H,t,Ph), δ 7.30(1H,s,Ph), δ 7.23(1H,d,Ph), δ 7.10(1H,d,Ph), δ 3.65(2H,q,CH_2), δ3.36 (2H,t,CH_2); MS(API-ES): m/z216 $[M-H]^-$, m/z252 $[M+Cl]^-$



S-6 Mass spectra of 2-(3-Hydroxyamino-benzenesulfonyl)-ethanol in Negative model

***N*-(2-Nitro-phenyl)-hydroxylamine**

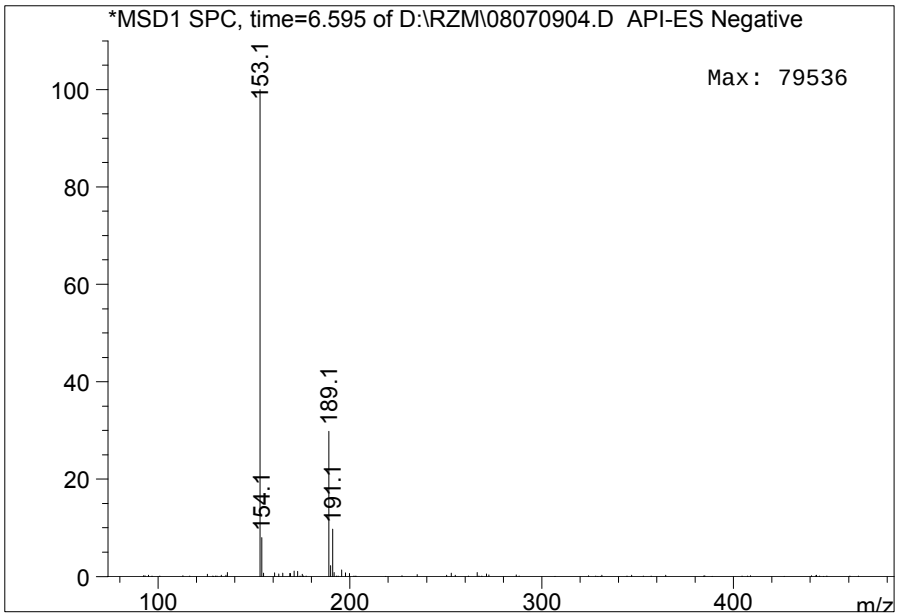
MS(API-ES): m/z153 $[M-H]^-$, m/z189 $[M+Cl]^-$



S-7 Mass spectra of *N*-(2-Nitro-phenyl)-hydroxylamine in Negative model

***N*-(4-Nitro-phenyl)-hydroxylamine**：

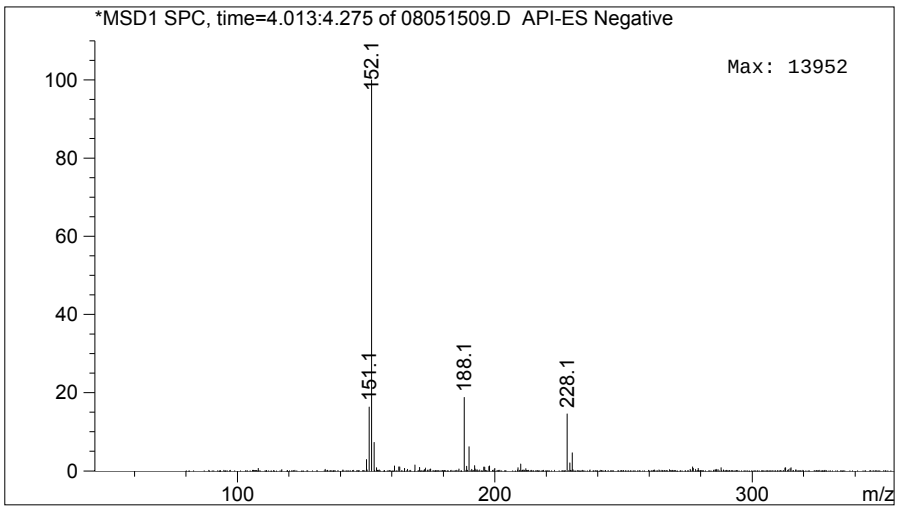
MS(API-ES): m/z153 $[M-H]^-$, m/z189 $[M+Cl]^-$, m/z 155$[M+ H]^+$ ， m/z 177$[M+ Na]^+$



S-8 Mass spectra of *N*-(4-Nitro-phenyl)-hydroxylamine in Negative model

2-Hydroxyamino-benzoic acid：

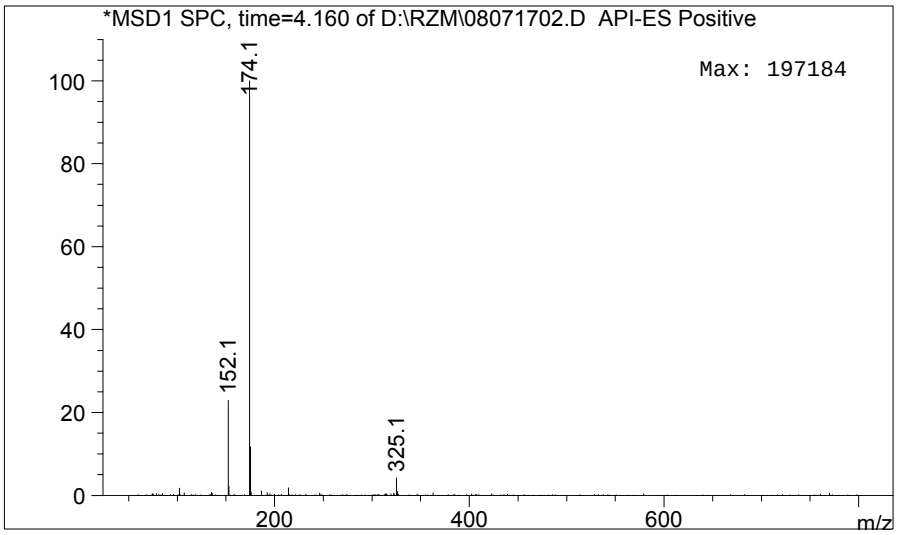
MS(API-ES): m/z152 $[M-H]^-$, m/z188 $[M+Cl]^-$



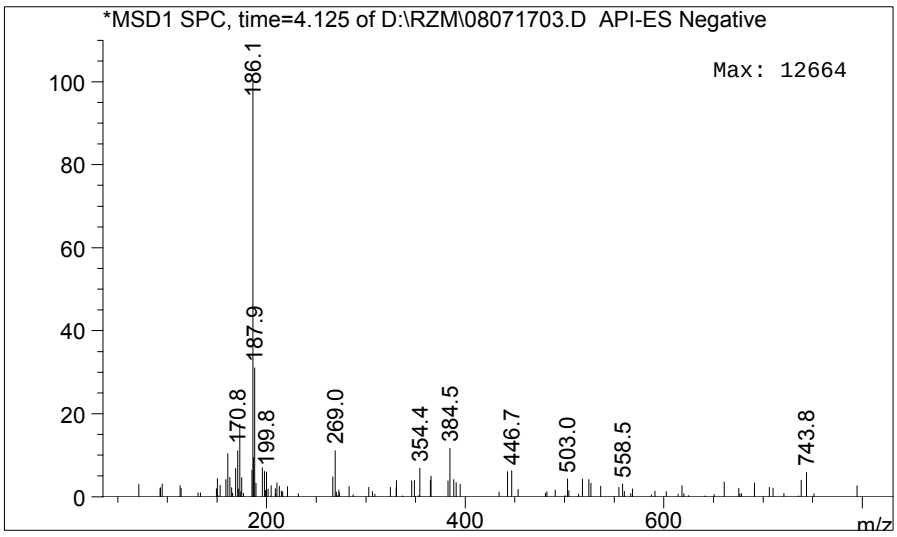
S-9 Mass spectra of 2-Hydroxyamino-benzoic acid in Negative model

***N*-(4-Acetyl-phenyl)-hydroxylamine：**

MS(API-ES): m/z152 $[M+H]^+$, m/z174 $[M+Na]^+$，m/z325$[2M+Na]^+$，m/z186 $[M+Cl]^-$



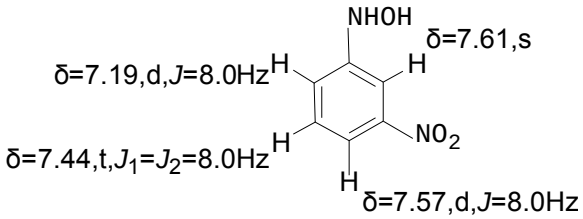
S-10 Mass spectra of *N*-(2-Acetyl-phenyl)-hydroxylamine in Positive model



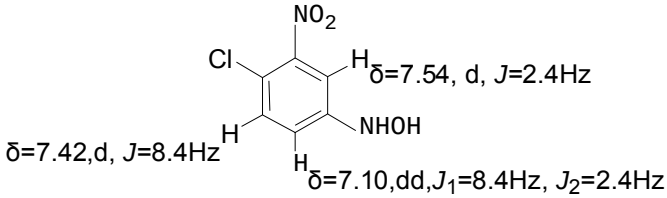
S-11 Mass spectra of *N*-(2-Acetyl-phenyl)-hydroxylamine in Negative model

***N*-(4-Chloro-3-nitro-phenyl)-hydroxylamine and *N*-(2-Chloro-5-nitro-phenyl)-hydroxylamine**

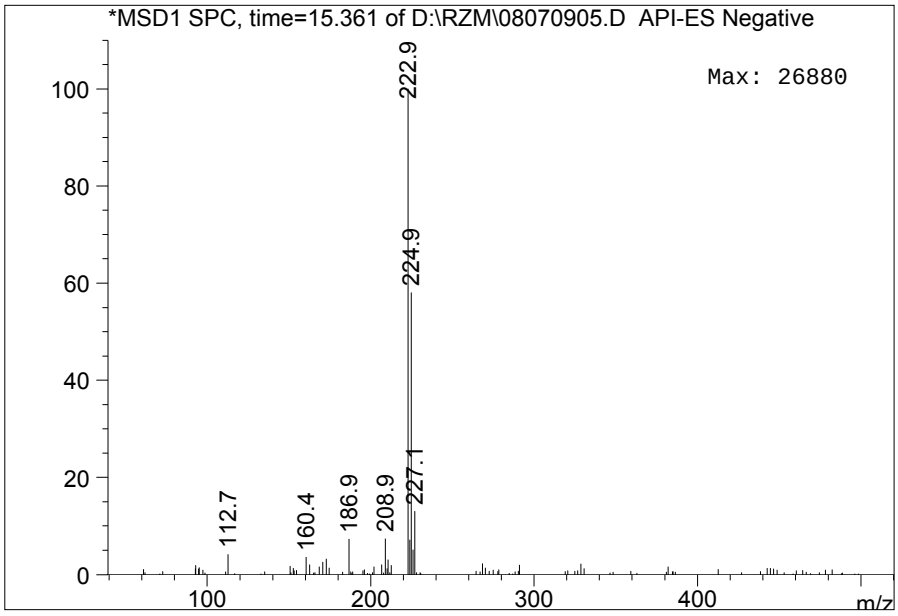
***N*-(3-Nitro-phenyl)-hydroxylamine:**



***N*-(4-Chloro-3-nitro-phenyl)-hydroxylamine:**

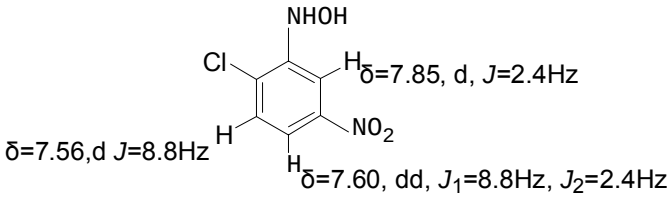


MS(API-ES): m/z187$[M-H]^-$, m/z223 $[M+Cl]^-$

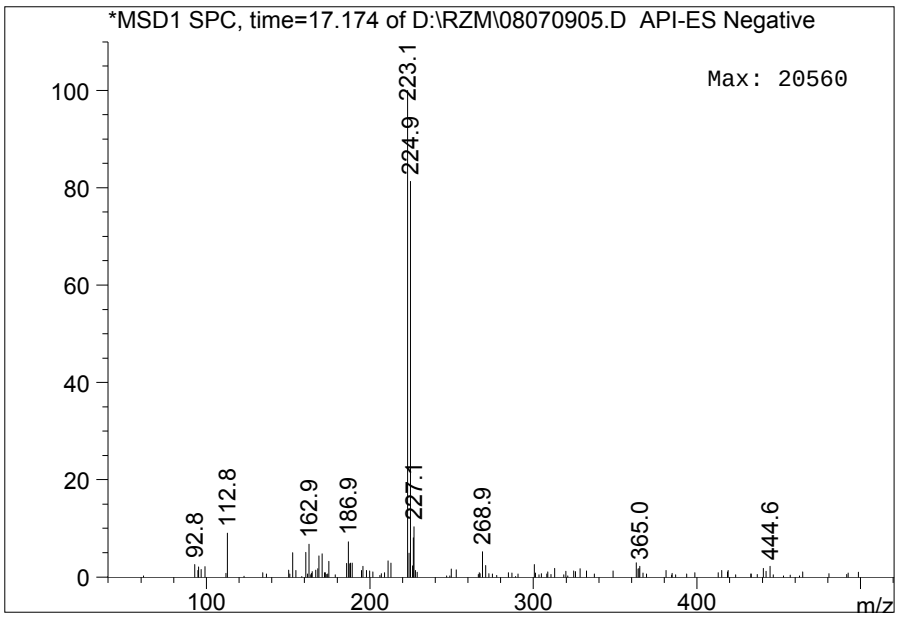


S-12 Mass spectra of *N*-(4-Chloro-3-nitro-phenyl)-hydroxylamine in Negative model

***N*-(2-Chloro-5-nitro-phenyl)-hydroxylamine**



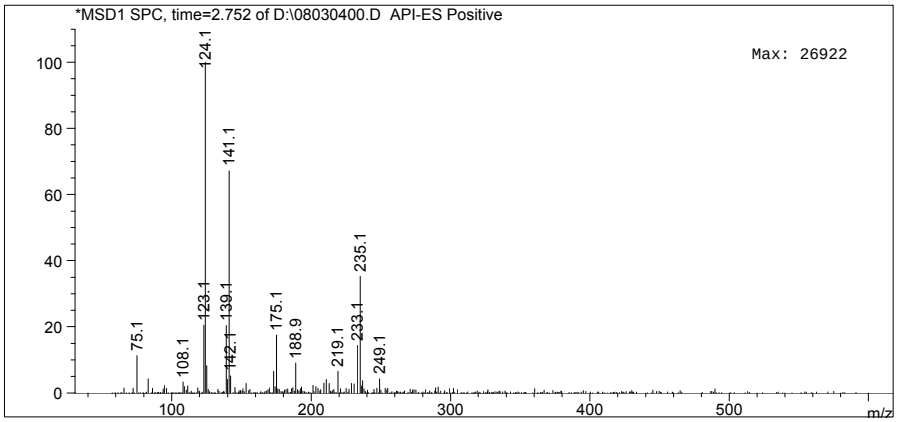
MS(API-ES): m/z187$[M-H]^-$, m/z223 $[M+Cl]^-$



S-13 Mass spectra of *N*-(2-Chloro-5-nitro-phenyl)-hydroxylamine in Negative model

***m*-dihydroxylamino-benzene:**

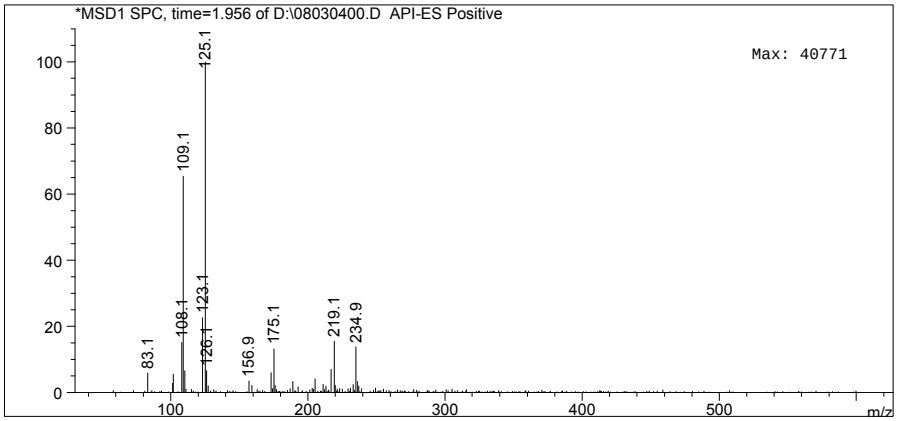
MS(API-ES): m/z 141 $[M+H]^+$,



S-14 Mass spectra of *m*-dihydroxylamino-benzene in Positive model

N-(3-Amino-phenyl)-hydroxylamine:

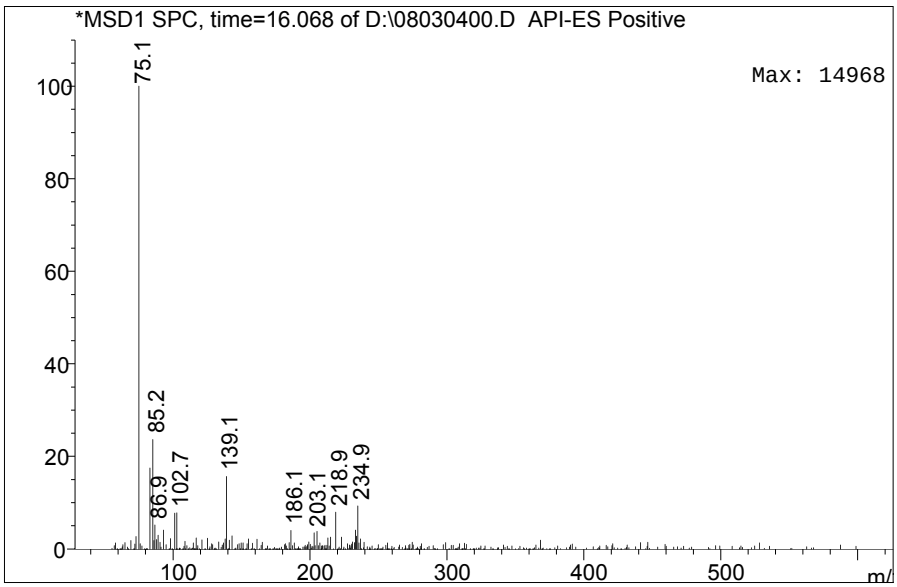
MS(API-ES): m/z 125 $[M+H]^+$



S-15 Mass spectra of N-(3-Amino-phenyl)-hydroxylamine in Positive model

3-Nitro-phenylamine:

MS(API-ES): m/z 139 $[M+H]^+$



S-16 Mass spectra of 3-Nitro-phenylamine in Positive model

4、Preparation and characterization of catalyst

The preparation procedure of Pt/C catalyst was typically as follows: 0.531 g $H_2PtCl_6 \cdot 6H_2O$ was added to 200 ml deionized water containing 9.2×10^{-5} mol Brij 35 and 8.04×10^{-5} mol Tween 20. Under vigorous stirring, 0.195 g $NaBH_4$ in 80 ml H_2O was dropwisely added to the solution. The color of solution changed into dark black soon after adding the reducing agent. Then, 10g active carbon powder was added to the colloid solution. After stirring for 30min, the Pt/C catalyst was obtained by filtration, washing, and drying in vacuum oven at room temperature for overnight.

For the structural characteristics, surface morphology of the Pt colloid on C and its electrochemical activity, please refer to *J. Nanoparticle Research,* 2008,10(1215-1220), "Binary-surfactant (Brij 35 + Tween 20) assisted preparation of highly dispersed Pt nanoparticles on carbon" by *Dong-Ha Lim, **Lianhai Lu**, Dong-Hyeok Choi, Dal-Ryung Park, and Ho-In Lee*.

5、Comparison of different catalyst and solvent

Table S-1. Chemoselective hydrogenation of *m*-DNB to *m*-hydroxylamino-nitrobenzene over different catalyst and solvent

Catalyst	weight(g)	Solvent	t/min	Conv./%[a]	Sele./%[a]
3.5wt%Ru/C	0.5	THF	475	95.1	70.0
3.5wt%Pd/C	0.2	THF	80	99.2	87.4
Raney Ni	0.5	THF	180	98	88.2
2 wt%Pt/Al_2O_3[b]	0.2	THF	150	100	90.7
2wt%Pt/C[c]	0.2	THF	240	100	90.9
2wt%Pt/C	0.05	THF	190	100	92.3
2wt%Pt/C	0.05	Ethanol	160	97	80.7
2wt%Pt/C	0.05	Methanol	73	100	91.0

Reduction conditions: 10mmol substrate, 30ml solvent at 283.15K and 0.1MPa.

a The conversion and selectivity(*N*-(3-Nitro-phenyl)-hydroxylamine) were determined by HPLC.

b Commercial Pt/ Al_2O_3 from Dalian Tongyong Chemicals, China

c Commercial Pt/C from Donggang Chemicals, China

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