

Supporting Information

Electrochemical Tandem Synthesis of Oximes from Alcohols Using KNO_3 as Nitrogen Source Mediated by Tin

Microspheres in Aqueous Medium

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General Remarks: ^1H NMR and ^{13}C NMR were recorded on a Bruker AC-300 FT (^1H : 300 MHz, ^{13}C : 75 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

1. Experimental Section.

Instruments: The instrument for electrolysis is dual display potentiostat (CJS-292) (made in China). Cyclic voltammetric (CV) experiments were carried out with a CHI660D system (USA CH Instruments) in a conventional three-electrode cell in the presence of supporting electrolyte. The anode electrode is Pt ($1.0 \times 1.0 \text{ cm}^2$) or a graphite (diameter 0.5 cm) while the cathode electrode is tin-doped indium oxide on glass (ITO; Nanbo Co. Ltd, Shenzhen, China). A saturated calomel electrode (SCE) were used as the reference electrode.

Representative procedures for oximation of alcohols:

An undivided cell was equipped with a magnet stirrer, platinum electrode as the working electrode and ITO as the counter electrode respectively. In the electrolytic cell a solution of alcohol (2 mmol), SnCl_2 (1 mmol), HCl (0.25 mL) and KNO_3 saturated solution (6 mL) was allowed to stir and electrolyze at a constant current of 25 mA for six hours until the quantity of the electricity 2.8 F/mol was passed at room temperature. Upon completion of the reaction, the mixture was diluted with ethyl acetate. The solvent was removed with the aid of a rotary evaporator. The residue was purified by column chromatography on silica gel, and the product was dried under high vacuum for at least 0.5h before it was weighed and characterized by NMR spectroscopy.

Crystal data of the product: 4-Br- $\text{C}_6\text{H}_4\text{CHNOH}$

The data collection for the above compound were performed on a Oxford Diffraction Gemini S Ultra CCD diffractometer equipped with graphite monochromated Mo- $\text{K}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation at room temperature. The structure was solved by direct methods and refined by full-matrix least-squares methods with SHELXL-97 programs. Crystallographic parameters: $\text{C}_7\text{H}_6\text{BrNO}$, $M = 200.04$, monoclinic, space group $P 2_1/c$, $a = 6.1832(7)$, $b = 4.7807(6)$, $c = 25.509(5) \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 94.353(15)^\circ$, $\gamma = 90.00^\circ$, $V = 751.87(19) \text{ \AA}^3$, $Z = 4$, $D_c = 1.767 \text{ g/cm}^3$, $F(000) = 392$. Goodness of fit: 1.024, $R1[I > 2\sigma(I)] = 0.0292$, $wR2[I > 2\sigma(I)] = 0.0670$, $R1$ (all data) = 0.0381, $wR2$ (all data) = 0.0718.

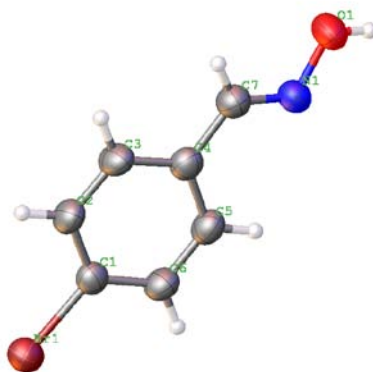


Figure S1 ORTEP draw of the crystal structure of the 4-Br-C₆H₄CHNOH with 30% thermal possibility.

Experimental details for the investigation of reaction mechanism:

Scheme S1

An undivided cell was equipped with a magnet stirrer, platinum electrode as the working electrode and ITO as the counter electrode respectively. In the electrolytic cell a solution of SnCl₂ (2 mmol), HCl (0.25 mL) and KNO₃ saturated solution (6 mL) was allowed to stir and electrolyze at a constant current of 25 mA for six hours until the quantity of the electricity 2.8 F/mol was passed in an undivided cell, which was equipped with a three-electrode system at room temperature. Upon completion of the reaction, the mixture was diluted with ethyl acetate. The solvent was removed with the aid of a rotary evaporator and the product was dried under high vacuum for at least 0.5h before it was characterized by NMR spectroscopy.

¹H-NMR (CDCl₃, 300 MHz, ppm): δ = 9.19 (s, 1 H), 2.13 (s, 2 H).

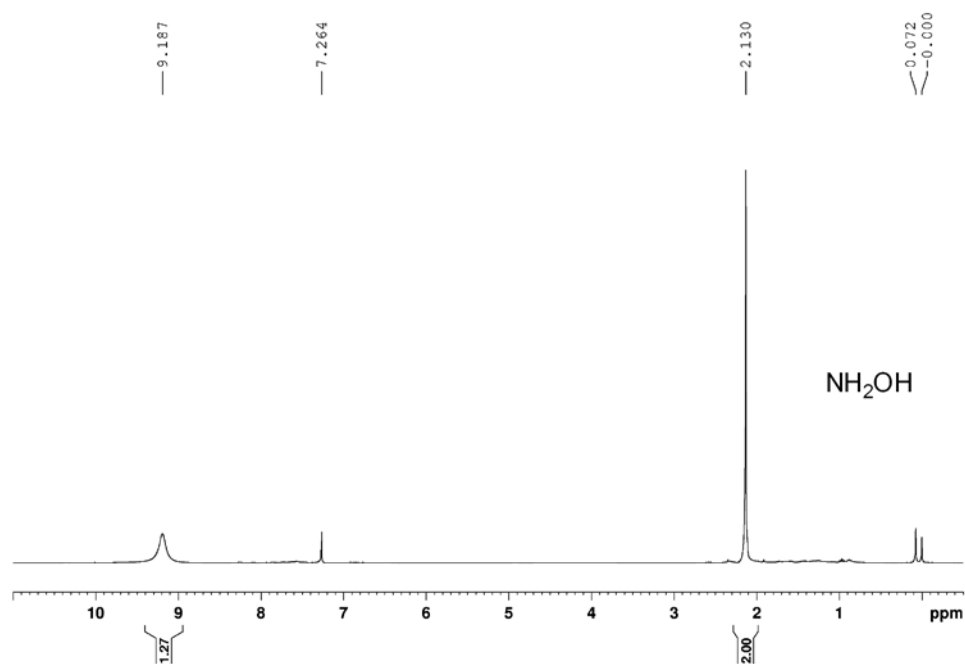
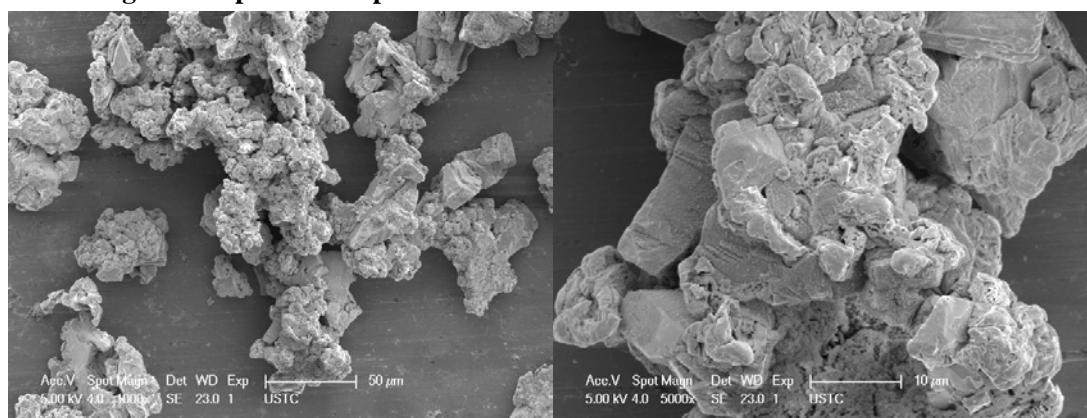


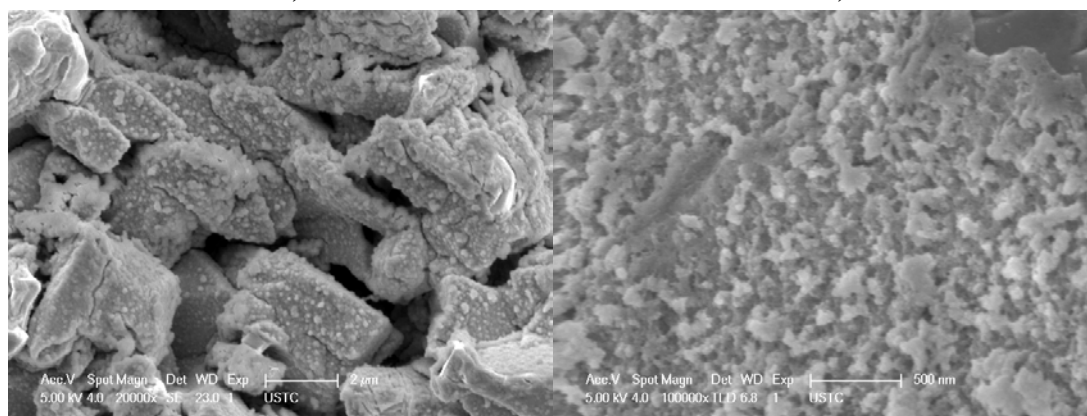
Figure S2

SEM images of Sn particles deposited from two kinds of electrodes.



a)

b)



c)

d)

Figure S3 SEM images of Sn particles deposited on graphite electrode with different sites. Scale bar: a) 50 μm ; b) 10 μm ; c) 2 μm ; d) 500 nm.

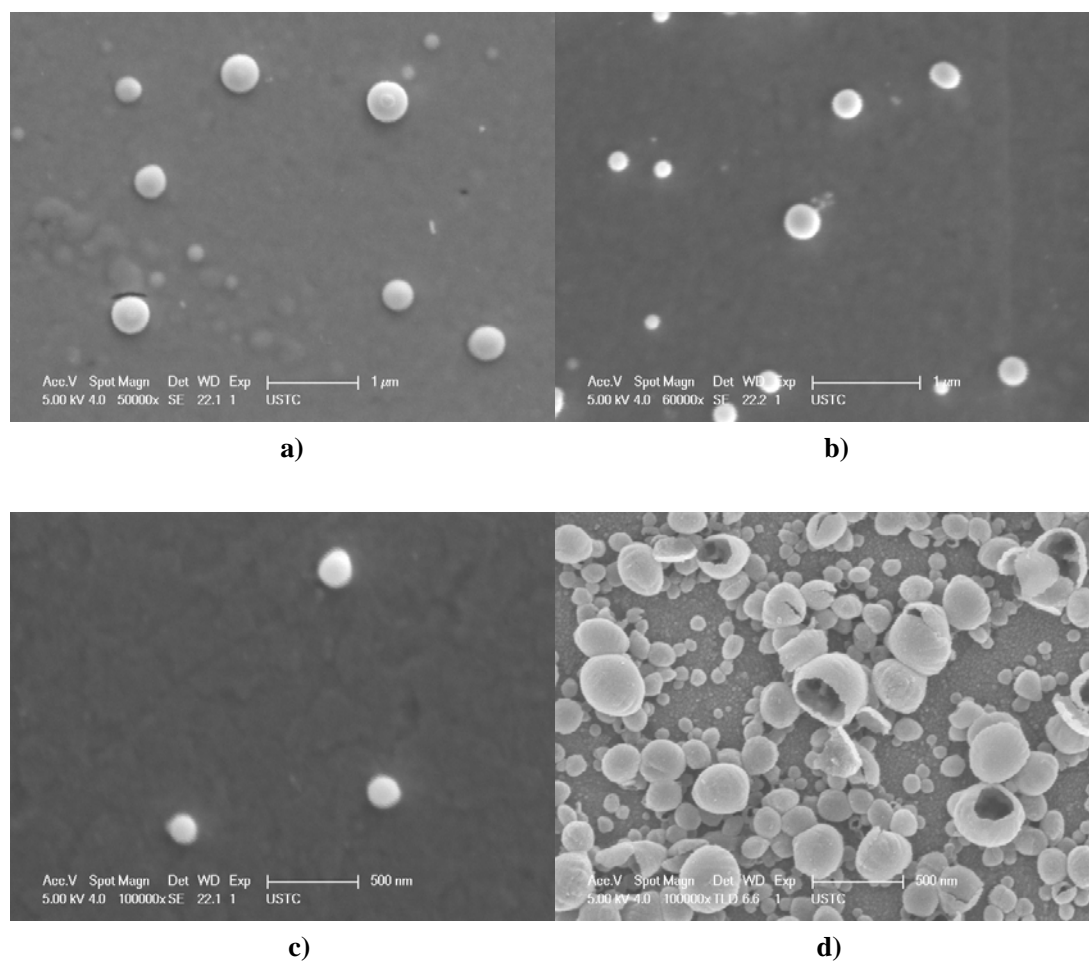
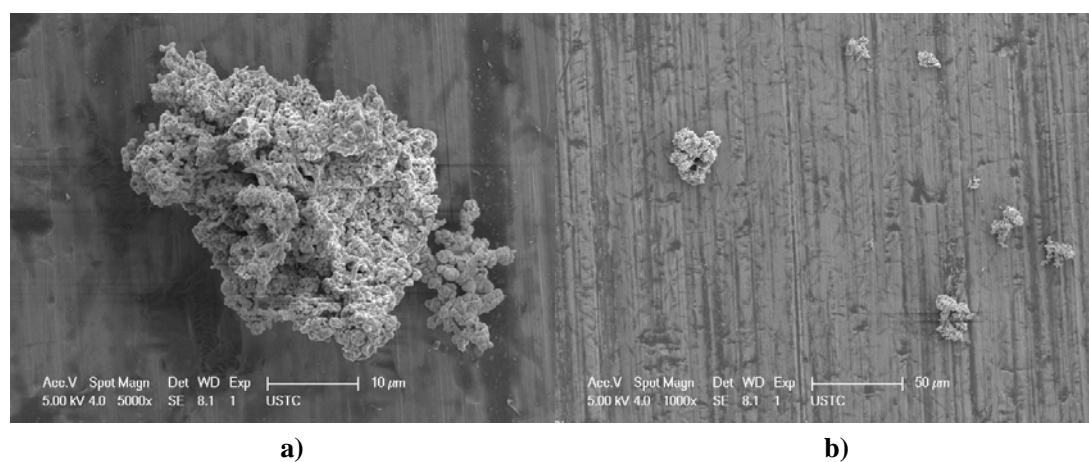
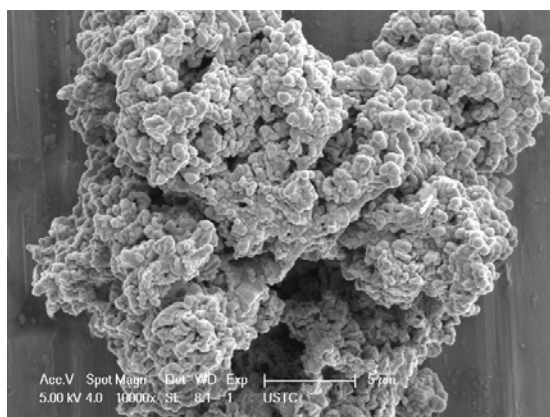


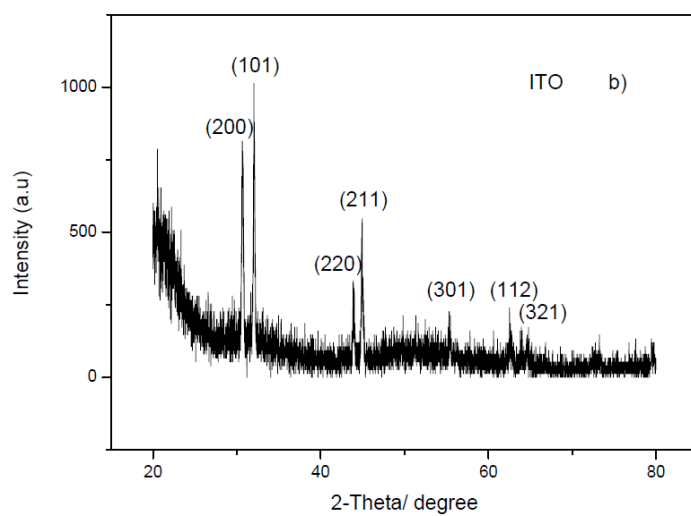
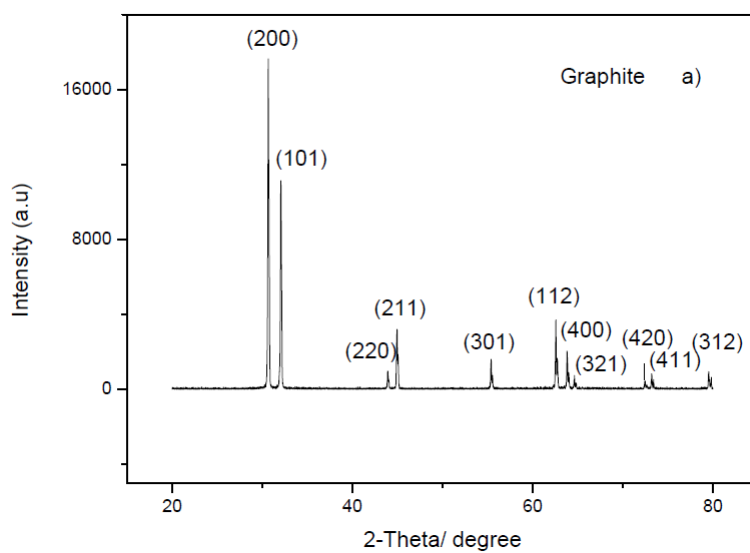
Figure S4 SEM images of Sn particles deposited on ITO electrode with different sites. Scale bar: a) 1 μm ; b) 1 μm ; c) 500 nm; d) 500 nm.





c)

Figure S5 SEM images of Sn particles deposited on platinum electrode with different sites. Scale bar: a) 10 μm; b) 50 μm; c) 5 μm.



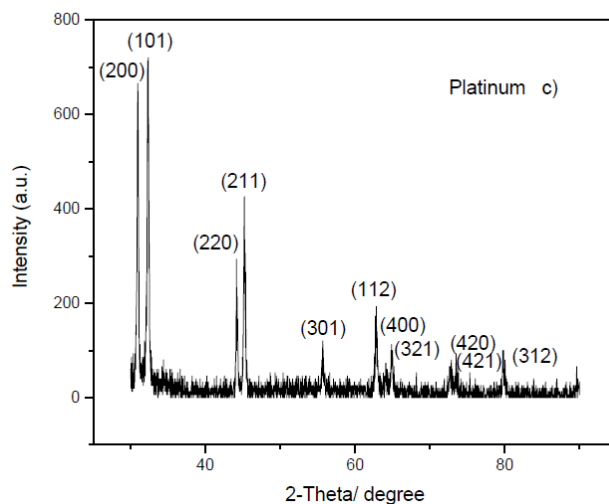


Figure S6 a) XRD pattern of the Sn produced on surface of the graphite electrode; b) XRD pattern of the Sn produced on surface of tin-doped indium oxide on glass (ITO); c) XRD pattern of the Sn produced on surface of platinum (XRD showed in situ produced Sn is all of β -phase on three electrodes).

2. Characterization data of all products.

General Remarks: ^1H NMR and ^{13}C NMR were recorded on a Bruker AC-300 FT (^1H : 300 MHz, ^{13}C : 75 MHz) using TMS as internal reference. The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. Infrared samples were recorded on a Perkin-Elmer 2000 FTIR spectrometer.

(E)-benzaldehyde oxime

^1H -NMR (CDCl_3 , 300 MHz, ppm): δ = 8.75 (s, 1 H), 8.17 (s, 1 H), 7.60-7.50 (m, 2 H), 7.40-7.30 (m, 3 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): δ = 150.5, 130.2, 128.9, 127.2; IR (liquid film, cm^{-1}): ν = 3304, 3063, 1498, 1449, 1302, 1210, 953, 870, 756, 692.

(E)-4-methylbenzaldehyde oxime

^1H -NMR (CDCl_3 , 300 MHz, ppm): δ = 8.13 (s, 1 H), 7.47 (d, J = 7.8 Hz, 2 H), 7.19 (d, J = 7.8 Hz, 2 H), 2.36 (s, 3 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): δ = 151, 140, 131, 129, 127, 21.6; IR (liquid film, cm^{-1}): ν = 3289, 2922, 1448, 1300, 1112, 960, 816, 714.

(E)-4-methoxybenzaldehyde oxime

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm): δ = 8.11 (s, 1 H), 7.52 (d, J = 8.7 Hz, 2 H), 6.91 (d, J = 8.7 Hz, 2 H), 3.84 (s, 3 H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz, ppm): δ = 150, 129, 114, 55; IR (liquid film, cm^{-1}): ν = 3353, 2929, 1606, 1513, 1303, 1253, 1174, 1030, 956, 874, 831.

(E)-4-(trifluoromethyl)benzaldehyde oxime

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm): δ = 8.18 (s, 1 H), 8.00 (s, 1 H), 7.80-7.50 (m, 4 H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz, ppm): δ = 149.2, 127.4, 125.9, 125.9, 125.8, 125.8; IR (liquid film, cm^{-1}): ν = 3355, 2928, 1618, 1412, 1325, 1168, 1128, 1067, 968, 837.

(E)-4-fluorobenzaldehyde oxime

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm): δ = 8.12 (s, 1 H), 7.60-7.50 (m, 2 H), 7.20-7.00 (m, 2 H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz, ppm): δ = 165.0, 162.5, 149.3, 128.9, 128.8, 116.0, 115.8; IR (liquid film, cm^{-1}): ν = 3262, 1605, 1511, 1323, 1294, 1241, 972, 878, 827.

(E)-4-bromobenzaldehyde oxime

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm): δ = 8.09 (s, 1 H), 7.70-7.30 (m, 4 H); $^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz, ppm): δ = 149.5, 132.1, 128.5; IR (liquid film, cm^{-1}): ν = 3202, 2922, 1493, 1393, 1317, 1067, 970, 871, 820.

(E)-4-chlorobenzaldehyde oxime

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz, ppm): δ = 8.13 (s, 1 H), 8.11 (s, 1 H), 7.55-7.50 (m, 2 H), 7.40-7.30

(m, 3 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): $\delta = 149.5, 129.2, 128.4$; IR (liquid film, cm^{-1}): $\nu = 3312, 2924, 1494, 1089, 972, 874, 825, 696, 506$.

(E)-2-chlorobenzaldehyde oxime

^1H -NMR (CDCl_3 , 300 MHz, ppm): $\delta = 8.57$ (s, 1 H), 7.84 (d, $J = 2.0$ Hz, 1 H), 7.83-7.20 (m, 3 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): $\delta = 147, 133, 130, 129, 127, 126$; IR (liquid film, cm^{-1}): $\nu = 3288, 2929, 1483, 1436, 1316, 1279, 1206, 1045, 973, 749, 705$.

(E)-3-chlorobenzaldehyde oxime

^1H -NMR (CDCl_3 , 300 MHz, ppm): $\delta = 8.11$ (s, 1 H), 7.58 (s, 1 H), 7.57-7.30 (m, 3 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): $\delta = 149.4, 135, 134, 130, 127, 125$; IR (liquid film, cm^{-1}): $\nu = 3303, 2925, 1566, 1481, 1317, 1208, 1077, 954, 873, 781, 710, 675$.

(E)-acetophenone oxime

^1H -NMR (CDCl_3 , 300 MHz, ppm): $\delta = 7.80$ -7.50 (m, 2 H), 7.50-7.20 (m, 3 H), 2.30 (s, 3 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): $\delta = 156.2, 136.7, 129.4, 128.7, 126.2, 12.5$; IR (liquid film, cm^{-1}): $\nu = 3249, 1449, 1370, 1302, 1005, 925, 764$.

Cyclohexanone oxime

^1H -NMR (CDCl_3 , 300 MHz, ppm): $\delta = 2.54$ -2.49 (m, 2 H), 2.30-2.10 (m, 2 H), 1.80-1.60 (m, 6 H); ^{13}C -NMR (CDCl_3 , 75 MHz, ppm): $\delta = 161, 32.3, 27.0, 25.9, 25.7, 24.6$; IR (liquid film, cm^{-1}): $\nu = 3188, 3112, 2932, 2860, 1664, 1449, 993, 962, 900, 794$.

4-(hydroxyimino)cyclohexa-2, 5-dienone

$^1\text{H-NMR}$ (CD_3COCD_3 , 300 MHz, ppm): $\delta = 7.74$ (s, 2 H), 6.76 (s, 4 H); $^{13}\text{C-NMR}$ (CD_3COCD_3 , 75 MHz, ppm): $\delta = 151, 116$; IR (liquid film, cm^{-1}): $\nu = 3161, 3030, 1513, 1460, 1194, 832, 760, 524$.

3. NMR Spectra of all products.

