catalysts

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Supplementary Information

"Doing more with less": Ni(II)@ORMOSIL, a novel sol-gel pre-catalyst for the reduction of nitrobenzene

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Figure S1. Raw wet 1% Ni(II)@ORMOSIL, metal ORMOSIL gel.

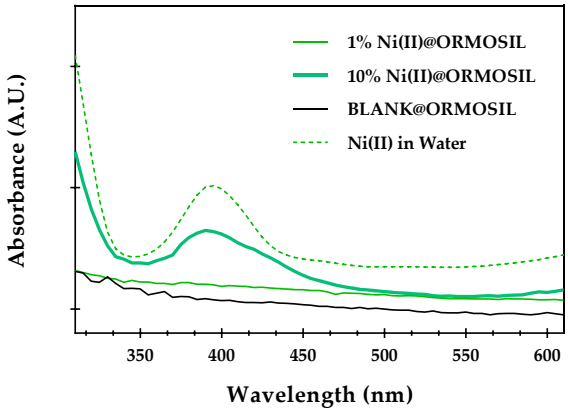


Figure S2. The overlayed spectra of 0.14M $NiCl_2 \cdot 6H_2O$. Dashed green: in water. Black: 0.2 gr of Blank@ORMOSIL. Light green: 0.2 gr 1.0 % Ni(II)@ORMOSIL. Dark green: 0.2 gr of 10% Ni(II)@ORMOSIL.

Table S1: XPS surface analysis elemental composition of of 1.0% Ni(II)@ORMOSIL.

Name	Peak BE	FWHM	Area	Atomic %
Si2p	103.8	2.84	60415.9	21.7
C1s	284.9	3.17	84089.5	30.3
O1s	533.2	2.77	318810.8	47.7
Ni2p	854.8	0.03	8878.9	0.3

Table S2. Metal phases found in 10% Ni(II)@ORMOSIL

Substance	2θ°	Miller Index	File No.

$3Ni(OH)_2*2H_2O$	33,7	1,1,0	00-022-0444
	59,6	3,0,0	
$Ni_3Si_4O_{10}(OH)_2*5H_2O$	33,7	1,0,3	00-043-0664
	60.9	3,0,0	

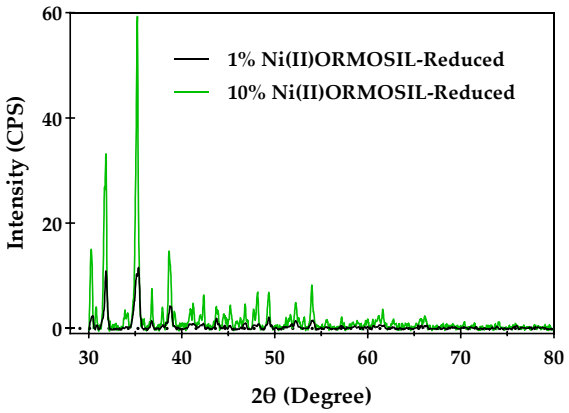


Figure S3. Diffractogram of 1% Ni(II)@ORMOSIL-Reduced, 10% Ni(II)@ORMOSIL-Reduced.

Table S3. Metal phases found in 1% Ni(II)@ORMOSIL-Reduced, 10% Ni(II)@ORMOSIL-Reduced

Substance	2θ°	Miller Index	File No.
$Na_2B_4O_5(OH)_4 \cdot 8H_2O$	29,96	2,2,2	
	30.5	4,0,0	
	31.38	0,0,4	
	31.56	2,3,1	
	34.8	4,1,1	
	34.95	-2,3,3	00-033-1215
	34.95	4,2,0	
	36,5	3,3,1	
	38.35	4,0,2	
	38.42	3,1,3	
	38.52	-2,4,2	

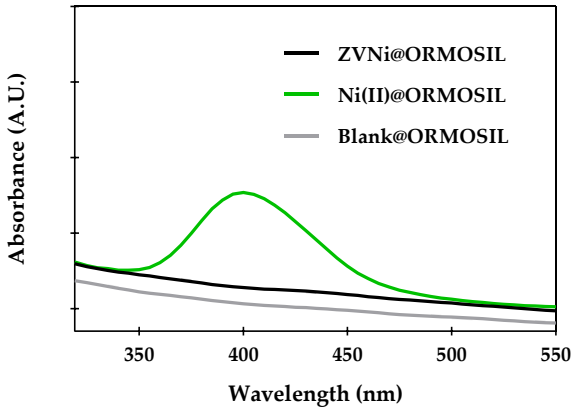
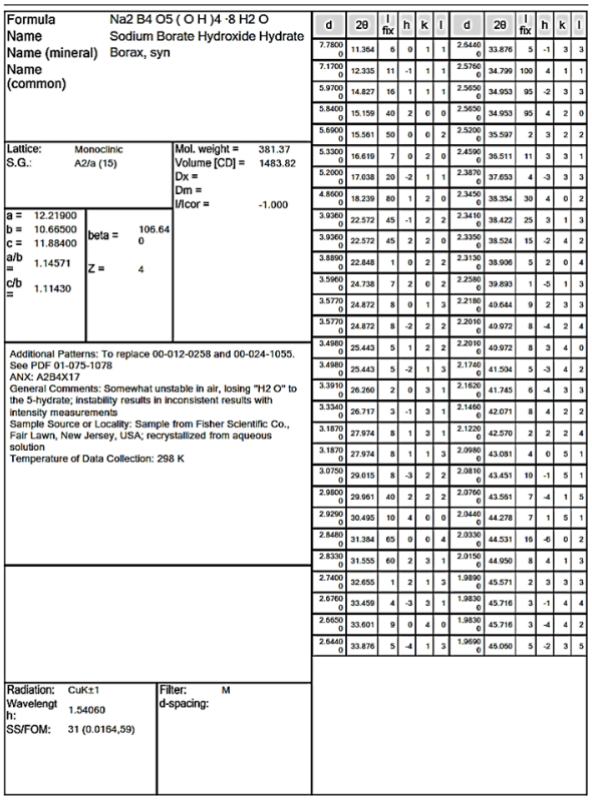


Figure S4. UV-vis spectrum; Blank@ORMOSIL-grey, 10 % Ni(II)@ORMOSIL-green, 10% ZVNi@ORMOSIL-black.



Formula	Na2 B4 O5 (O H)4 ·8 H2 O
Name	Sodium Borate Hydroxide Hydrate
Name (mineral)	Borax, syn
Name (common)	

Lattice:	Monoclinic	Mol. weight =	381.37
S.G.:	A2/a (15)	Volume [CD] =	1483.82
		Dx =	
		Dm =	
		I/Icor =	-1.000

a =	12.21900	beta =	106.640
b =	10.66500		
c =	11.88400		
a/b =	1.14571	Z =	4
c/b =	1.11430		

Additional Patterns: To replace 00-012-0258 and 00-024-1055. See PDF 01-075-1078
ANX: A2B4X17
General Comments: Somewhat unstable in air, losing "H2 O" to the 5-hydrate; instability results in inconsistent results with intensity measurements
Sample Source or Locality: Sample from Fisher Scientific Co., Fair Lawn, New Jersey, USA; recrystallized from aqueous solution
Temperature of Data Collection: 298 K

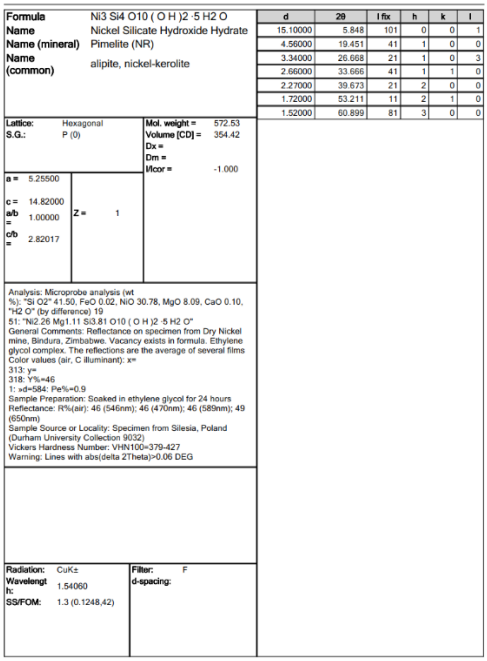
Radiation:	CuK±1	Filter:	M
Wavelength:	1.54060	d-spacing:	
SS/FOM:	31 (0.0164,59)		

d	2θ	I fix	h	k	l	d	2θ	I fix	h	k	l
7.7800	11.364	6	0	1	1	2.6440	33.876	5	-1	3	3
7.1700	12.335	11	-1	1	1	2.5760	34.799	100	4	1	1
5.9700	14.827	16	1	1	1	2.5650	34.953	95	-2	3	3
5.8400	15.159	40	2	0	0	2.5650	34.953	95	4	2	0
5.6900	15.561	50	0	0	2	2.5200	35.597	2	3	2	2
5.3300	16.619	7	0	2	0	2.4590	36.511	11	3	3	1
5.2000	17.038	20	-2	1	1	2.3870	37.653	4	-3	3	3
4.8600	18.239	80	1	2	0	2.3450	38.354	30	4	0	2
3.9360	22.572	45	-1	2	2	2.3410	38.422	25	3	1	3
3.9360	22.572	45	2	2	0	2.3350	38.524	15	-2	4	2
3.8890	22.848	1	0	2	2	2.3130	38.906	5	2	0	4
3.5960	24.738	7	2	0	2	2.2580	39.893	1	-5	1	3
3.5770	24.872	8	0	1	3	2.2180	40.644	9	2	3	3
3.5770	24.872	8	-2	2	2	2.2010	40.972	8	-4	2	4
3.4980	25.443	5	1	2	2	2.2010	40.972	8	3	4	0
3.4980	25.443	5	-2	1	3	2.1740	41.504	5	-3	4	2
3.3910	26.260	2	0	3	1	2.1620	41.745	6	-4	3	3
3.3340	26.717	3	-1	3	1	2.1460	42.071	8	4	2	2
3.1870	27.974	8	1	3	1	2.1220	42.570	2	2	2	4
3.1870	27.974	8	1	1	3	2.0980	43.081	4	0	5	1
3.0750	29.015	8	-3	2	2	2.0810	43.451	10	-1	5	1
2.9800	29.961	40	2	2	2	2.0760	43.561	7	-4	1	5
2.9290	30.495	10	4	0	0	2.0440	44.278	7	1	5	1
2.8480	31.384	65	0	0	4	2.0330	44.531	16	-6	0	2
2.8330	31.555	60	2	3	1	2.0150	44.950	8	4	1	3
2.7400	32.655	1	2	1	3	1.9890	45.571	2	3	3	3
2.6760	33.459	4	-3	3	1	1.9830	45.716	3	-1	4	4
2.6650	33.601	9	0	4	0	1.9830	45.716	3	-4	4	2
2.6440	33.876	5	-4	1	3	1.9690	46.050	5	-2	3	5

Figure S5: Powder diffraction file for $Na_2B_4O_5(OH)_4{\cdot}8H_2O$ (#PDF-033-1215)

d	2θ	I fix	h	k	l
1.96900	46.060	5	-1	3	5
1.95000	46.535	9	3	4	2
1.95000	46.535	9	6	0	0
1.91300	47.490	12	2	1	5
1.91300	47.490	12	-3	3	5
1.89800	47.889	11	0	0	6
1.85500	49.071	9	5	3	1
1.85500	49.071	9	-2	2	6
1.83300	49.699	12	6	2	0
1.79000	50.978	4	-4	4	4
1.77700	51.378	5	4	3	3
1.77700	51.378	5	0	6	0
1.75800	51.974	10	1	6	0
1.75800	51.974	10	-6	3	1
1.74800	52.294	3	2	4	4
1.74800	52.294	3	-4	5	1
1.73100	52.847	2	-6	3	3
1.70500	53.717	8	2	5	3
1.70500	53.717	8	2	3	5
1.70100	53.853	11	2	6	0
1.70100	53.853	11	-7	1	3
1.66130	55.249	2	-3	1	7
1.65850	55.350	2	-7	2	2
1.65850	55.350	2	1	6	2
1.61590	56.940	2	-4	1	7
1.61590	56.940	2	-6	4	2
1.59520	57.748	1	7	2	0
1.58410	58.191	1	-2	5	5
1.58410	58.191	1	-1	5	5
1.57400	58.601	2	7	1	1
1.57400	58.601	2	6	4	0
1.54570	59.782	2	-5	1	7
1.54570	59.782	2	0	4	6
1.53130	60.402	2	5	2	4
1.53130	60.402	2	-2	3	7
1.51970	60.912	3	4	6	0
1.51970	60.912	3	-3	3	7
1.51770	61.001	3	-2	6	4
1.51770	61.001	3	-1	3	7
1.50830	61.422	3	0	6	4
1.48530	62.479	2	-4	3	7
1.45380	63.991	1	-4	0	8
1.43030	65.171	5	-5	3	7
1.43030	65.171	5	6	3	3
1.42330	65.532	4	0	0	8
1.41530	65.949	3	2	4	6
1.36080	68.952	2	-6	3	7
1.36080	68.952	2	-5	2	8

Figure S6: Powder diffraction file for $Na_2B_4O_5(OH)_4{\cdot}8H_2O$ (continued) (#PDF-033-1215)



Formula	Ni3 Si4 O10 (O H)2 ·5 H2 O
Name	Nickel Silicate Hydroxide Hydrate
Name (mineral)	Pimelite (NR)
Name (common)	alipite, nickel-kerolite

Lattice:	Hexagonal
S.G.:	P (0)

Mol. weight =	572.53
Volume [CD] =	354.42
Dx =	
Dm =	
I/Icor =	-1.000

a =	5.25500
c =	14.82000
a/b =	1.00000
c/b =	2.82017
Z =	1

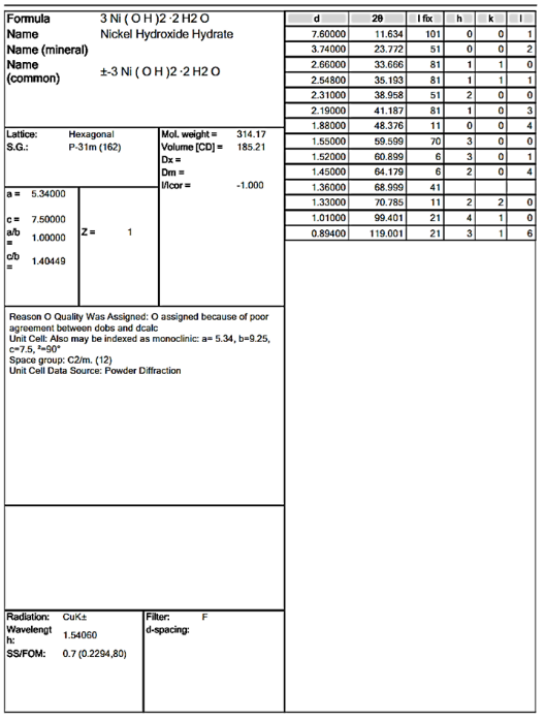
Analysis: Microprobe analysis (wt %): "Si O2" 41.50, FeO 0.02, NiO 30.78, MgO 8.09, CaO 0.10, "H2 O" (by difference) 19
51: "Ni2.26 Mg1.11 Si3.81 O10 (O H)2 ·5 H2 O"
General Comments: Reflectance on specimen from Dry Nickel mine, Bindura, Zimbabwe. Vacancy exists in formula. Ethylene glycol complex. The reflections are the average of several films
Color values (air, C illuminant): x=
313: y=
318: Y%=46
1: >d=584: Pe%=0.9
Sample Preparation: Soaked in ethylene glycol for 24 hours
Reflectance: R%(air): 46 (546nm); 46 (470nm); 46 (589nm); 49 (650nm)
Sample Source or Locality: Specimen from Silesia, Poland (Durham University Collection 9032)
Vickers Hardness Number: VHN100=379-427
Warning: Lines with abs(delta 2Theta)>0.06 DEG

Radiation:	CuKα
Wavelength:	1.54060
SS/FOM:	1.3 (0.1248,42)

Filter:	F
d-spacing:	

d	2θ	I fix	h	k	l
15.10000	5.848	101	0	0	1
4.56000	19.451	41	1	0	0
3.34000	26.668	21	1	0	3
2.66000	33.666	41	1	1	0
2.27000	39.673	21	2	0	0
1.72000	53.211	11	2	1	0
1.52000	60.899	81	3	0	0

Figure S7: Powder diffraction file for $Ni_3Si_4O_{10}(OH)_2 \cdot 5H_2O$(#PDF-00-043-0664)



Formula	3 Ni (O H)2 ·2 H2 O
Name	Nickel Hydroxide Hydrate
Name (mineral)	
Name (common)	±-3 Ni (O H)2 ·2 H2 O

Lattice:	Hexagonal
S.G.:	P-31m (162)

Mol. weight =	314.17
Volume [CD] =	185.21
Dx =	
Dm =	
I/Icor =	-1.000

a =	5.34000
c =	7.50000
a/b =	1.00000
c/b =	1.40449
Z =	1

Reason O Quality Was Assigned: O assigned because of poor agreement between dobs and dcalc
Unit Cell: Also may be indexed as monoclinic: a= 5.34, b=9.25, c=7.5, ß=90°
Space group: C2/m. (12)
Unit Cell Data Source: Powder Diffraction

Radiation:	CuKα
Wavelength:	1.54060
SS/FOM:	0.7 (0.2294,80)

Filter:	F
d-spacing:	

d	2θ	I fix	h	k	l
7.60000	11.634	101	0	0	1
3.74000	23.772	51	0	0	2
2.66000	33.666	81	1	1	0
2.54800	35.193	81	1	1	1
2.31000	38.958	51	2	0	0
2.19000	41.187	81	1	0	3
1.88000	48.376	11	0	0	4
1.55000	59.599	70	3	0	0
1.52000	60.899	6	3	0	1
1.45000	64.179	6	2	0	4
1.36000	68.999	41			
1.33000	70.785	11	2	2	0
1.01000	99.401	21	4	1	0
0.89400	119.001	21	3	1	6

Figure S8: Powder diffraction file for $3Ni(OH)_2 \cdot 2H_2O$ (#PDF-00-022-0444)

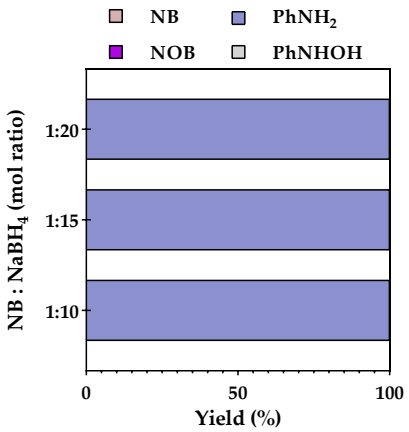


Figure S9: Product distribution of NB reduction, the catalyst load effect. The reaction suspensions contained 0.20 g 0.2% Ni(II)@ORMOSIL catalyst at ambient conditions. Reaction time 60 min. 10 mM [NB], 100,150,200 mM [$NaBH_4$], reaction medium: 10% Acetonitrile.

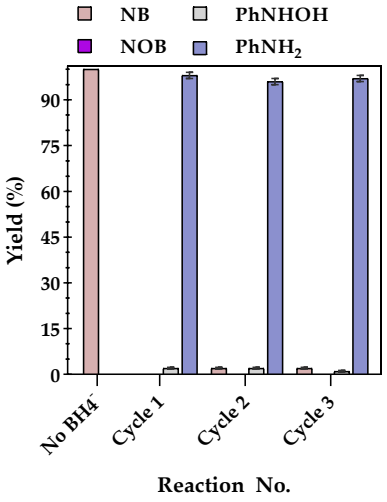


Figure S10: Repeated use in Nitrobenzene (NB) reductions performed in by different catalysts [NB] = 10 mM, [$NaBH_4$] = 60 mM, reaction medium (9:1) (H_2O: ACN) for 60 min with 0.20 g catalyst (a)Ni(II)@ORMOSIL.

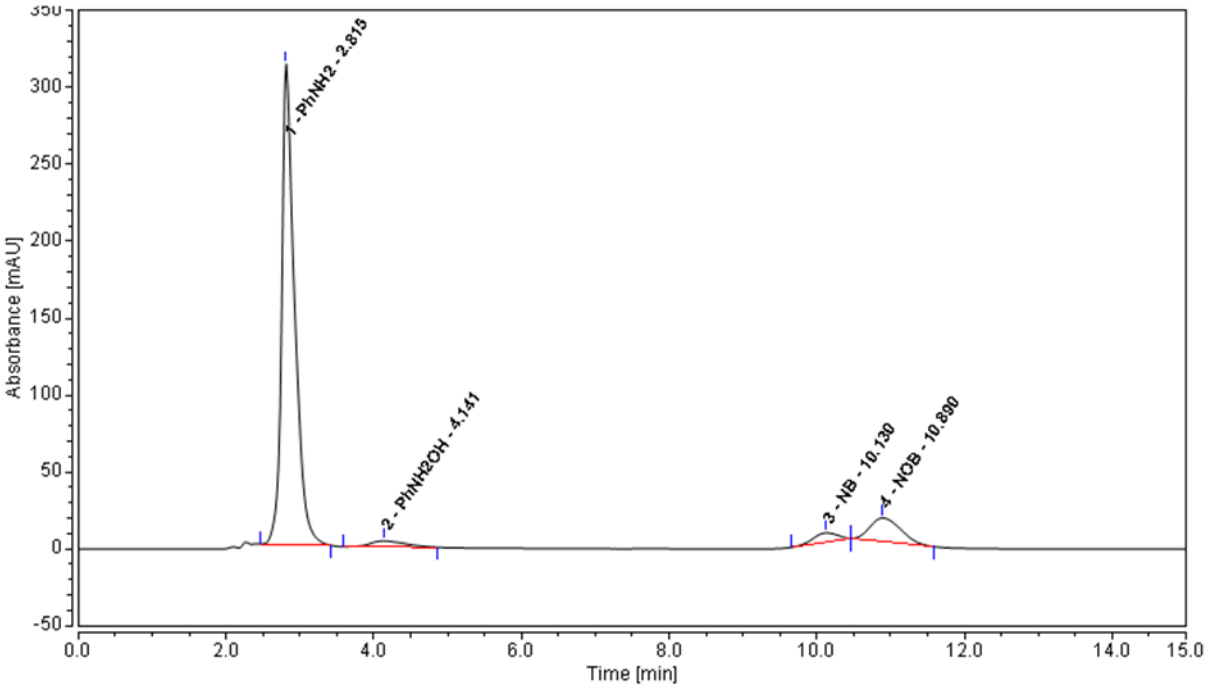
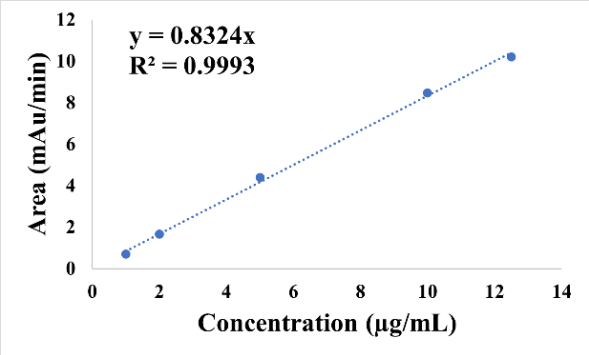
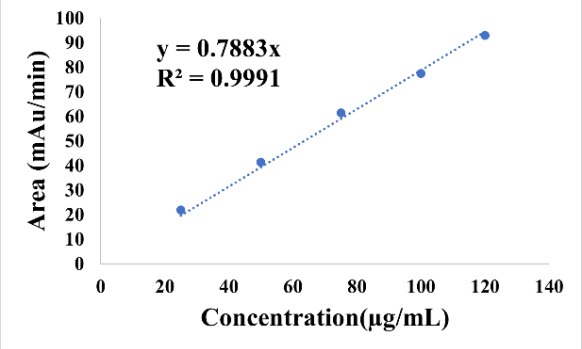


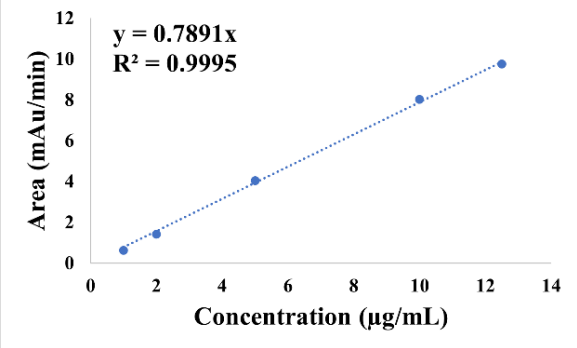
Figure S11: Typical chromatogram for NB reduction that is illustrated in figure 11b


y = 0.8324x
R² = 0.9993
Area (mAu/min)
Concentration (µg/mL)

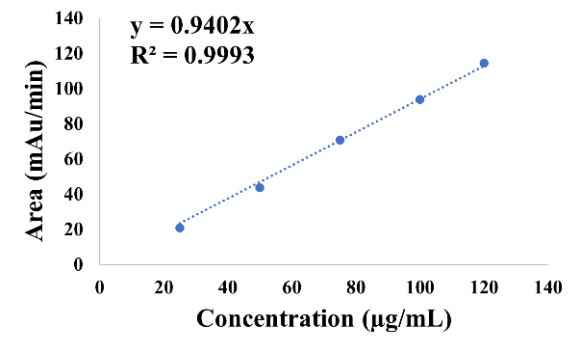
(a)


y = 0.7883x
R² = 0.9991
Area (mAu/min)
Concentration(µg/mL)

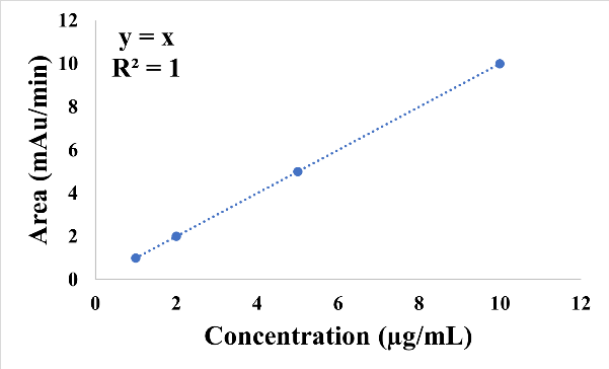
(b)


y = 0.7891x
R² = 0.9995
Area (mAu/min)
Concentration (µg/mL)

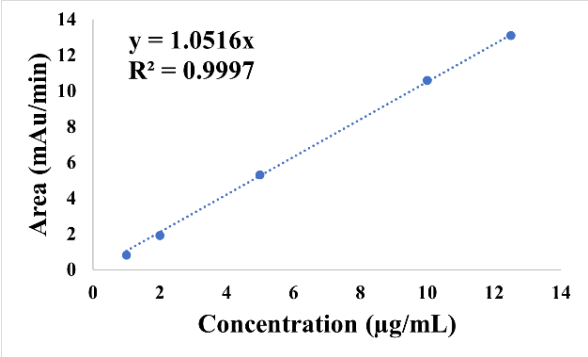
(c)


y = 0.9402x
R² = 0.9993
Area (mAu/min)
Concentration (µg/mL)

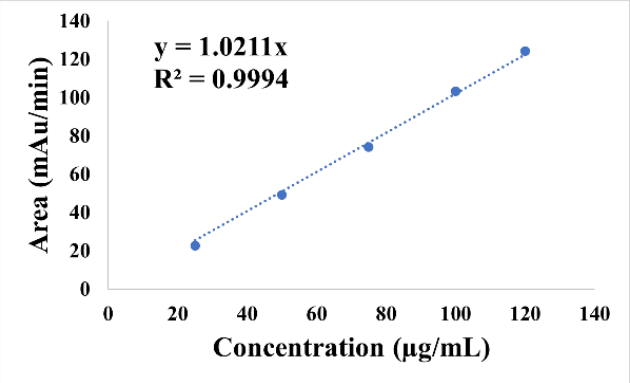
(d)


y = x
R² = 1
Area (mAu/min)
Concentration (µg/mL)

(e)


y = 1.0516x
R² = 0.9997
Area (mAu/min)
Concentration (µg/mL)

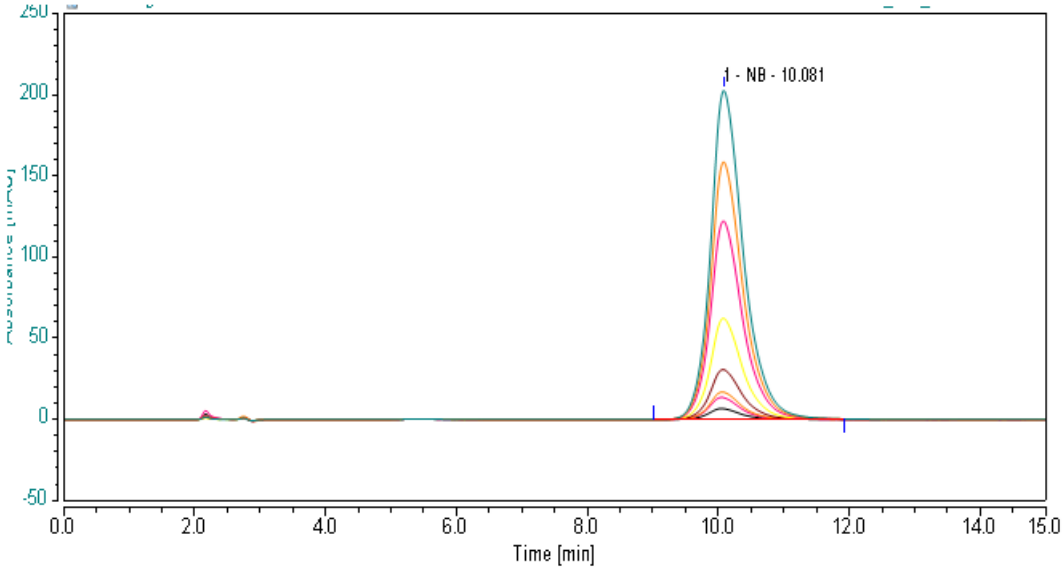
(f)



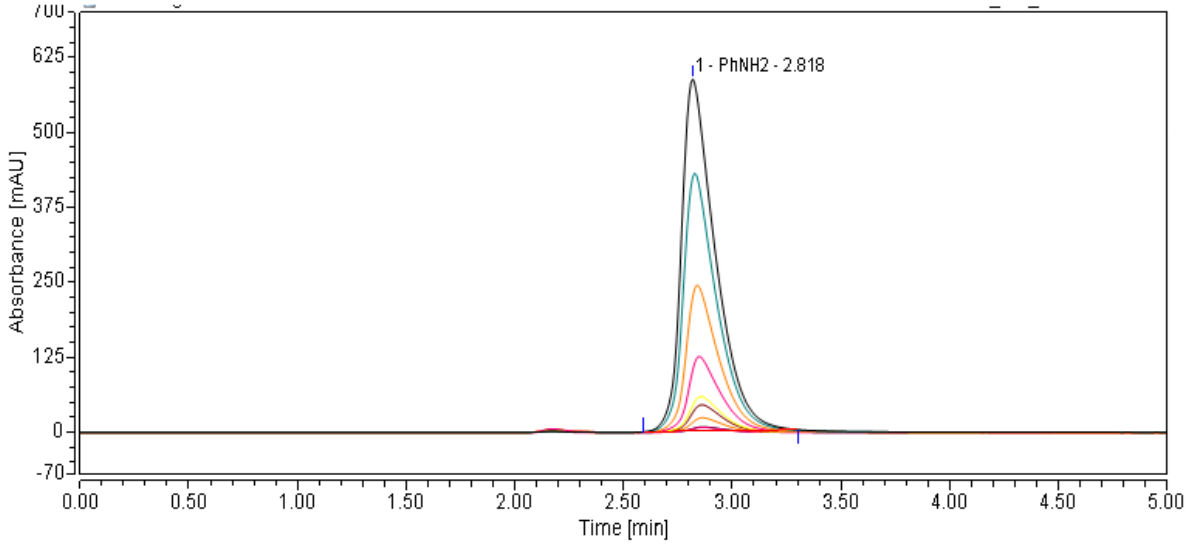
(g)

Figure S12. Calibration curves obtained as linear regressions for (a) Aniline ($PhNH_2$) concentration in the range (1-12.5) µg/mL, (b) Aniline ($PhNH_2$) concentration in the range (25-120) µg/mL, (c) Nitrobenzene (NB) concentration in the range (1-12.5) µg/mL, (d) Nitrobenzene (NB) concentration in the range (25-120) µg/mL, (e) Nitrobenzene (NOB) concentration in the range (1-10) µg/mL, f) Phenylhyrdoxylamine (PhNHOH) concentration in the range (1-12.5) µg/mL, (g) Phenylhyrdoxylamine (PhNHOH) concentration in the range (25-120) µg/mL.

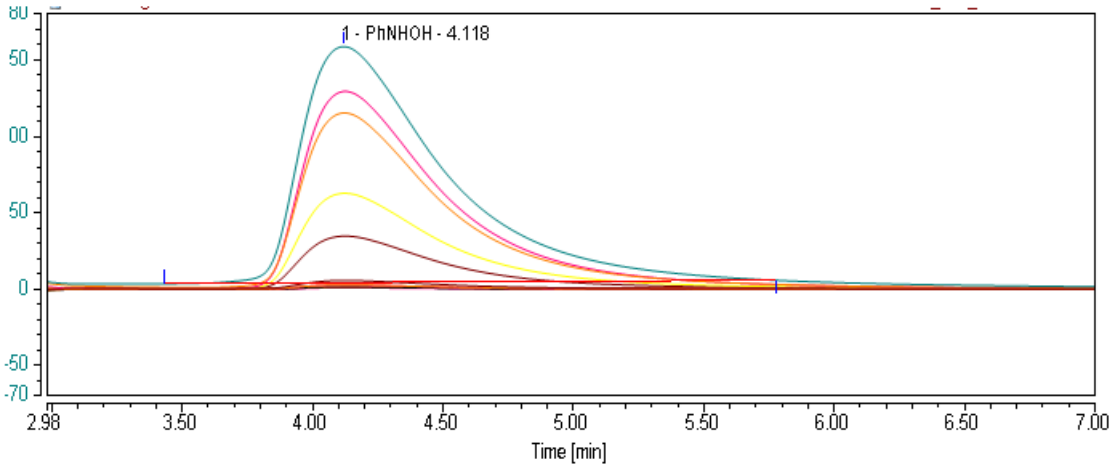
* The calibration curves in figure S12 describe the suitable concentration ranges for calculating the yields obtained in the reduction experiments.



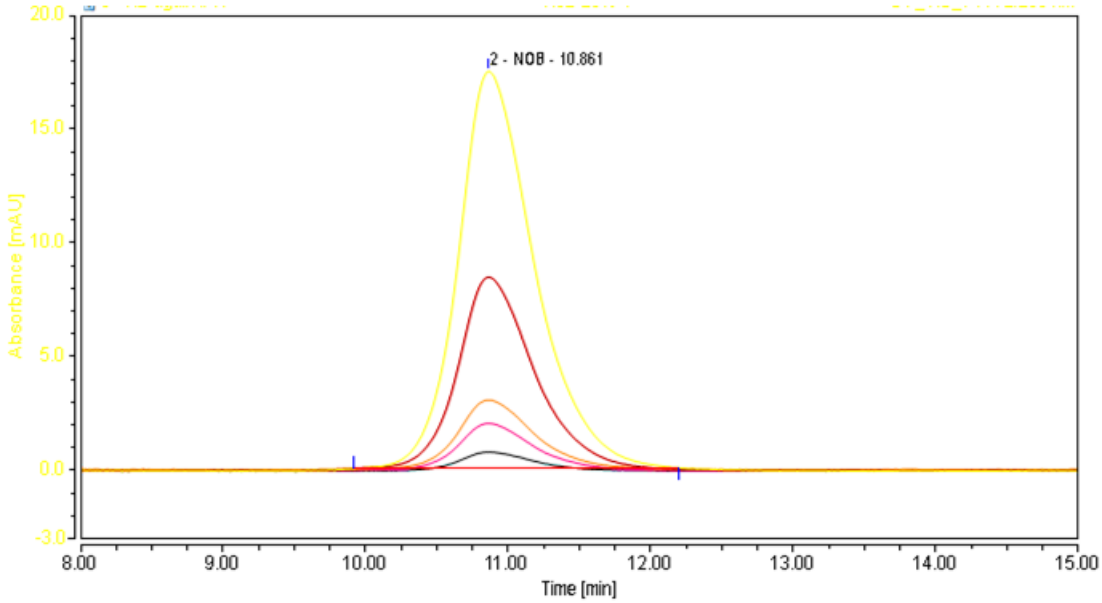
(a)



(b)



(c)



(d)

Figure S13: Typical chromatograms demonstrating specific elution times; (a) NB retention time (8.9-11.0) min., (b) $PhNH_2$ retention time (2.5-3.2) min., (c) PhNHOH retention time (3.7-4.7) min., (d)NOB retention time (9.9-12.0) minutes.

Figure S13 demonstrates typical retention times of standards solutions in the concentration range of the standard curves presented in Fig. S12.