N, S-Codoped Carbon Shells Embedded with Ultrafine Co NPs for Reductive Amination with Formic Acid

Haotian Guo, [ad] Bowei Wang, [abc]* Pengzhi Qiu, [a] Ruixiao Gao, [a] Mingming Sun, [a] Ligong Chen, [abc]*

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300350, P. R. China.
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, P. R. China.
[c] Tianjin Engineering Research Center of Functional Fine Chemicals, Tianjin, P. R. China.
[d] Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States.

* Corresponding author. E-mail: bwwang@tju.edu.cn (Bowei Wang);

lgchen@tju.edu.cn (Ligong Chen)

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Number of Tables: 5

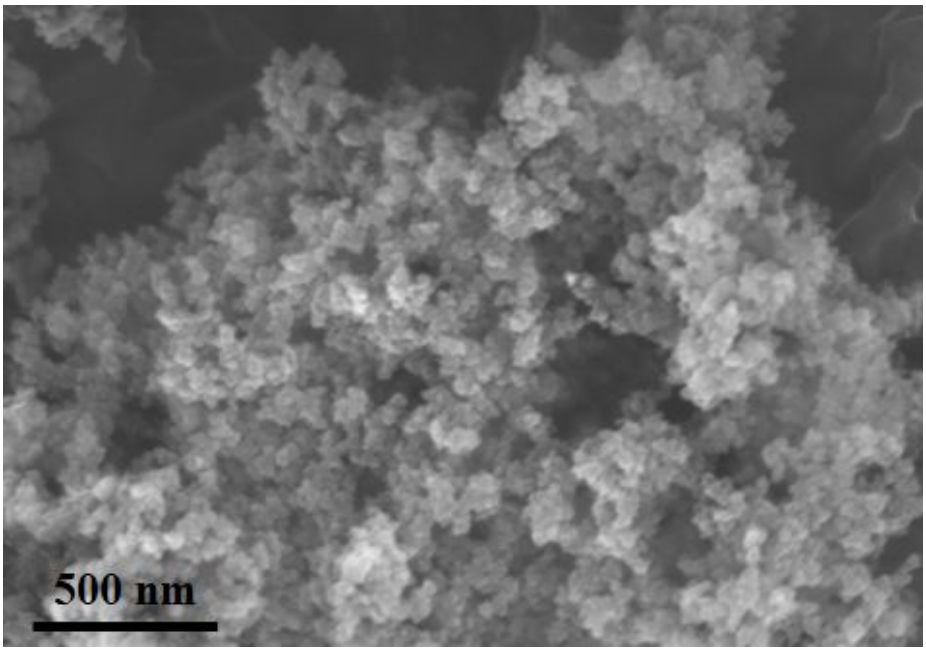


Fig. S1 The SEM image of SNW-1.

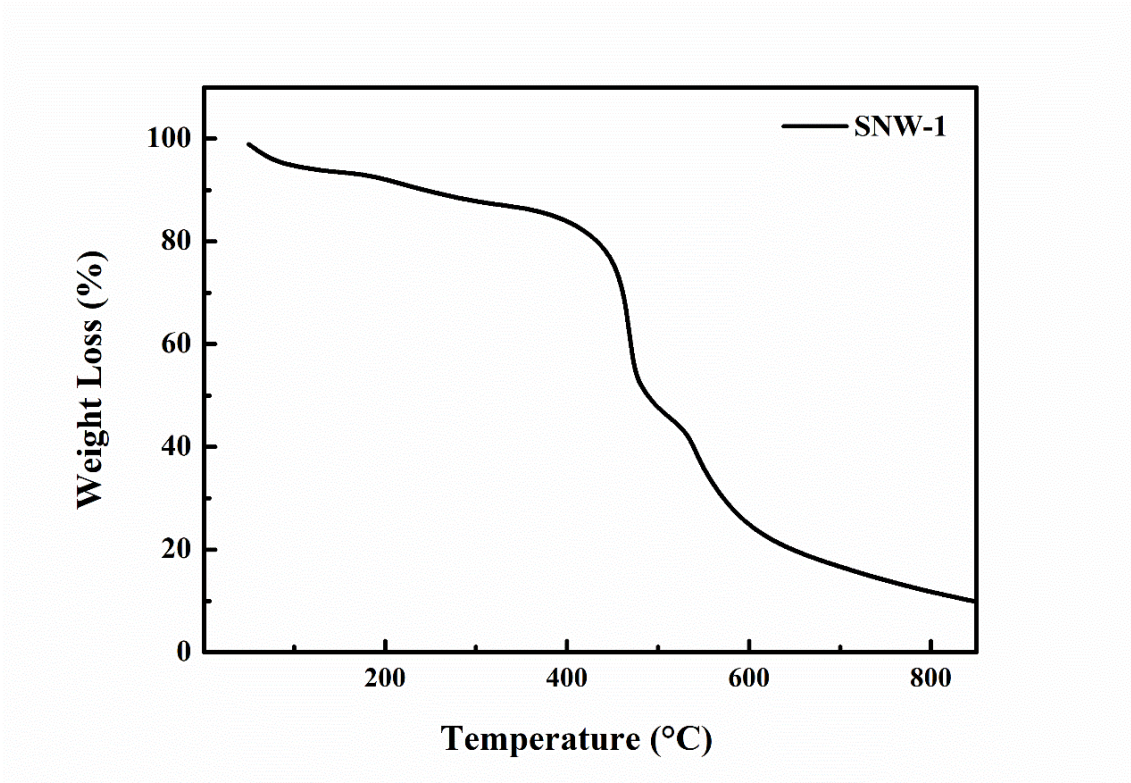


Fig. S2 The TGA curve of SNW-1.

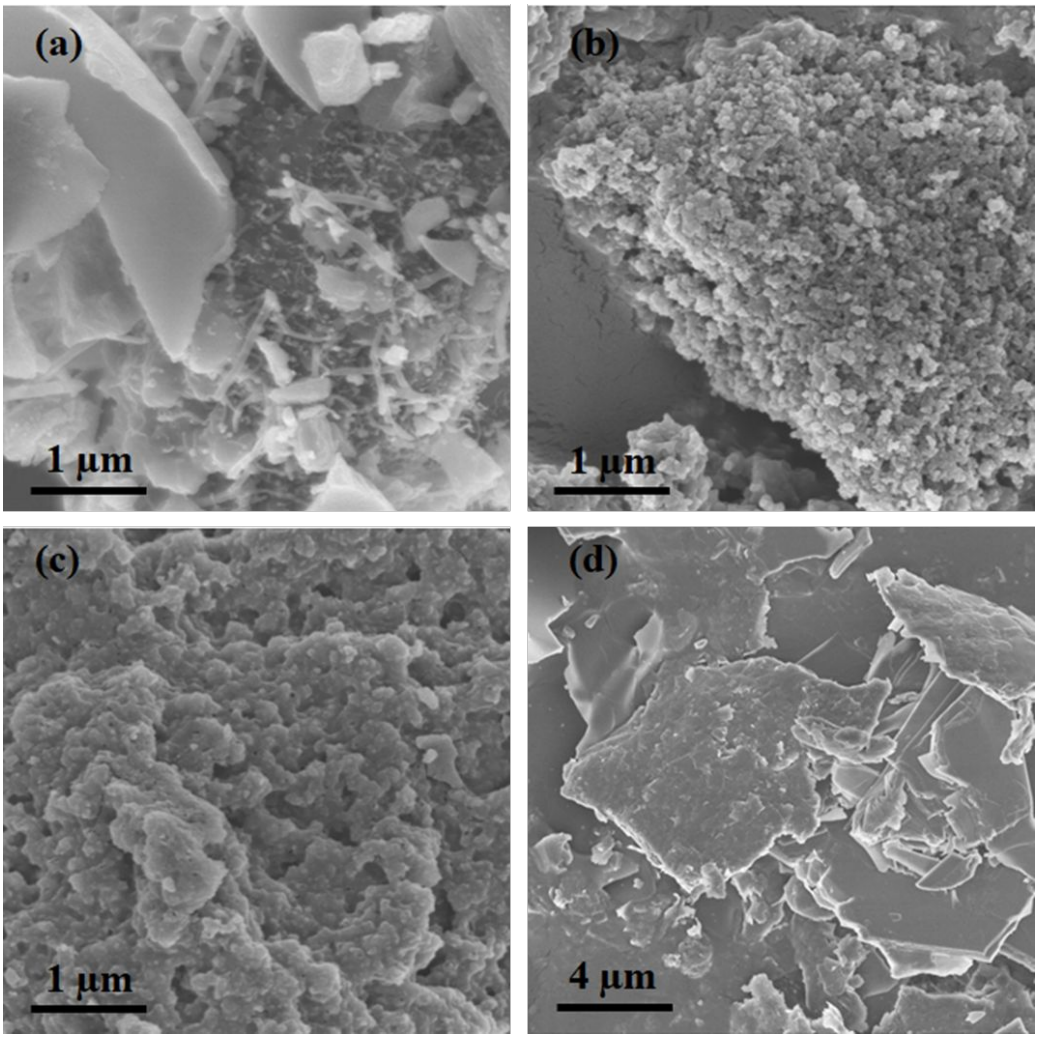


Fig. S3 The SEM images of Co@NSC-0 (a), Co@NSC-1 (b), Co@NSC-3 (c) and Co@NSC-7 (d).

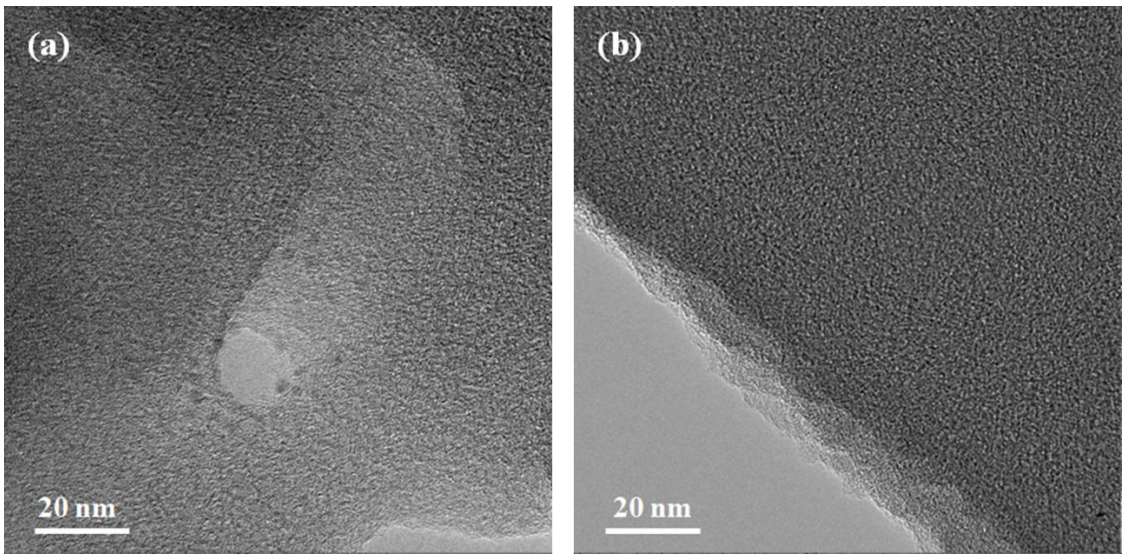


Fig. S4 The TEM images of Co@NSC-1 (a) and Co@NSC-7.

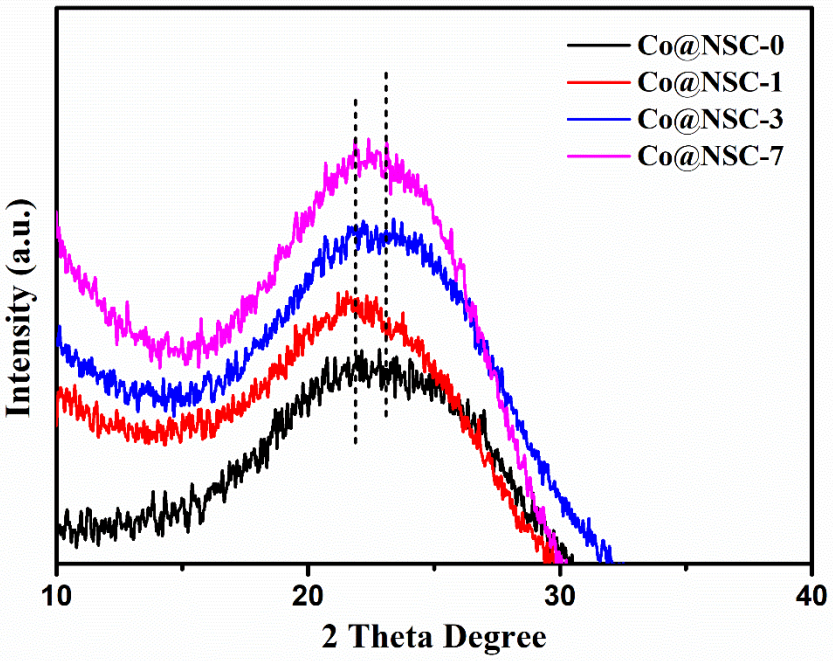


Fig. S5 The enlarged peak shift in XRD patterns of Co@NSC-x.

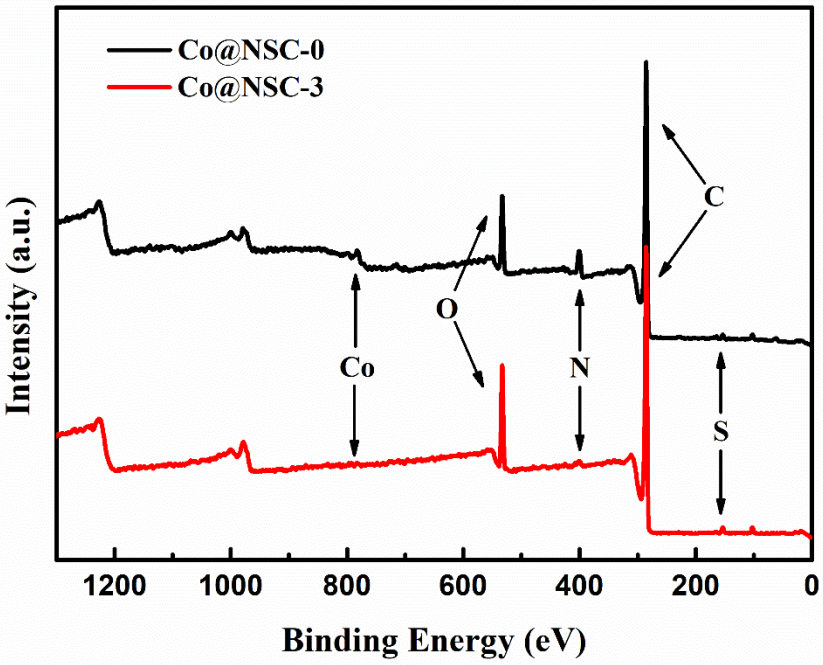


Fig. S6 The full survey spectra of Co@NSC-0 and Co@NSC-3.

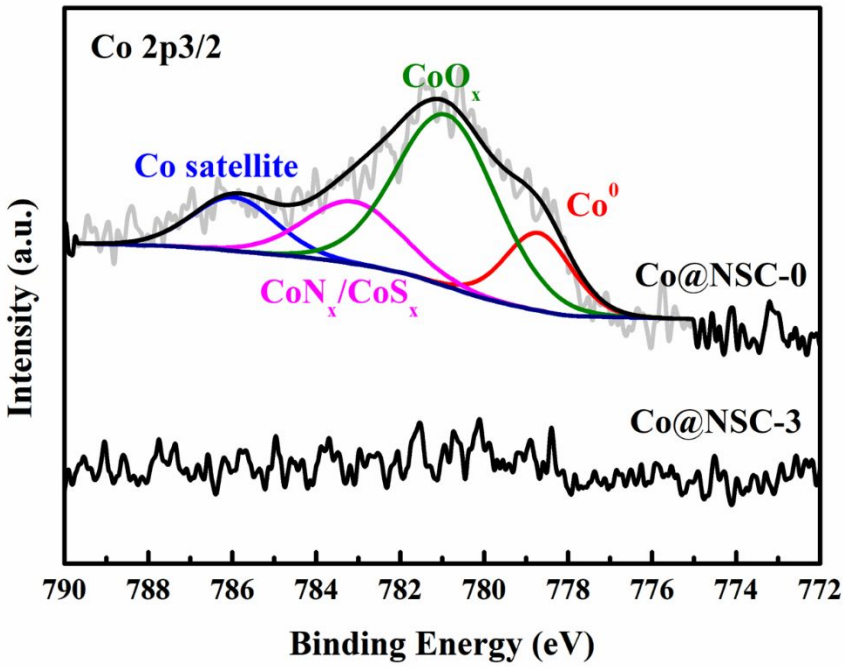


Fig. S7 The Co2p3/2 spectra of Co@NSC-0 and Co@NSC-3.

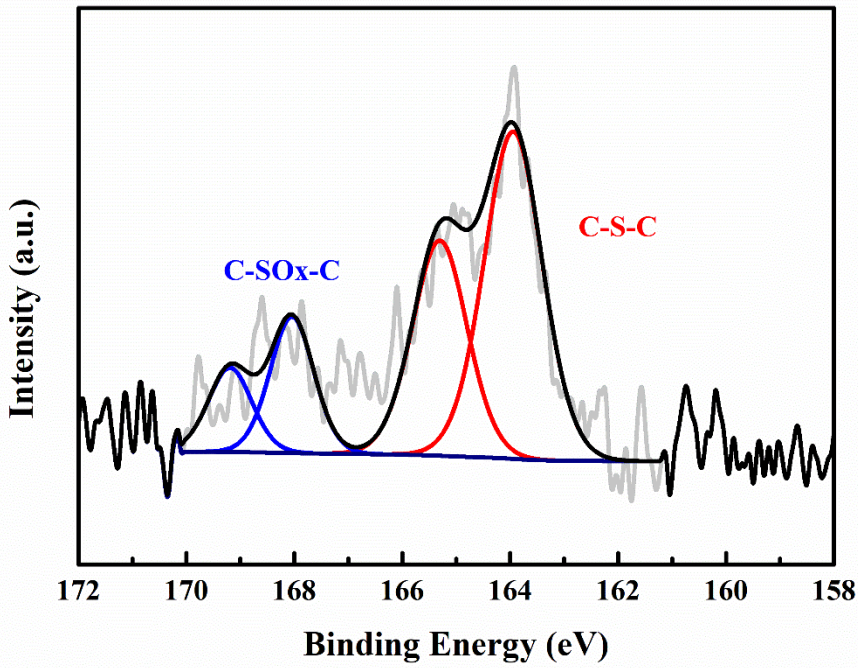


Fig. S8 The S2p spectrum of Co@NSC-1.

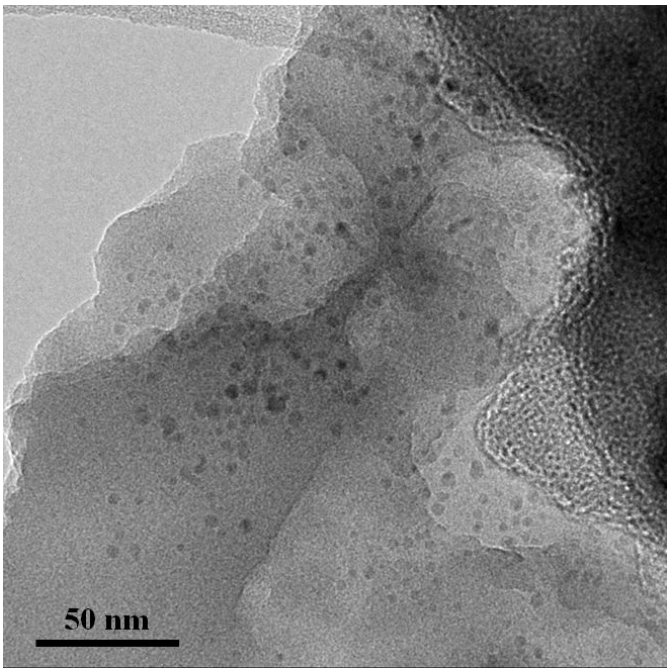


Fig. S9 The TEM image of used catalyst.

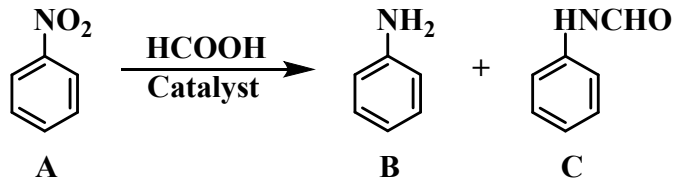
Table S1 The contents of N, S and Co in Co@NSC-x samples.

	C(wt%)[a]	H(wt%)[a]	N(wt%)[a]	S(wt%)[a]	Co(wt%)[b]
SNW-1	37.31	4.30	43.71	3.00	-
Co@NSC-0	60.58	1.57	9.63	1.27	5.71
Co@NSC-1	67.98	1.72	5.08	1.14	2.02
Co@NSC-3	69.01	2.02	3.42	0.85	1.14
Co@NSC-7	72.98	1.83	3.92	0.40	0.52

[a] detected by elemental analysis;

[b] detected by ICP-OES.

Table S2 The evaluation by CTH of nitrobenzene with formic acid[a]



Entry	Catalyst	Conv.(%)	Sel.B(%)
1	Co@NSC-0	38	100
2	Co@NSC-1	99	100
3	Co@NSC-3	97	100
4	Co@NSC-7	20	100

[a] Reaction conditions: nitrobenzene (0.5 mmol), solvent (5 mL), catalyst (20 mg), formic acid (1.5 mmol), time (2 h) and temperature (110 °C); GC analysis using n-dodecane as an internal standard;

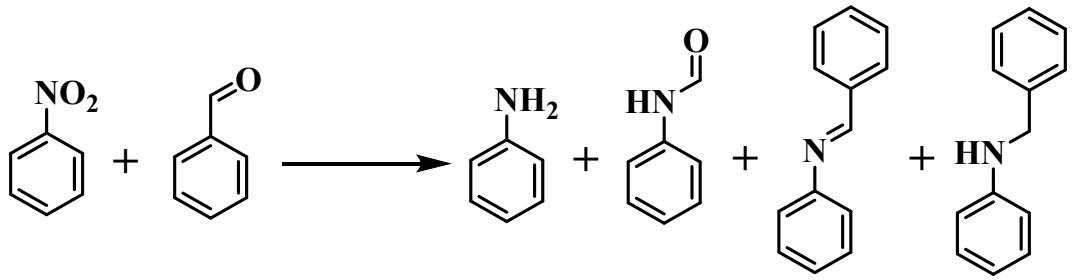
Table S3 Comparison of the catalytic activity of Co@NSC-3 with recent reported Co-based catalysts for CTH of nitrobenzene.

Entry	Catalyst	FA (eq)	T (°C)	t (h)	Co ($_{wt}$%)	Y_{AN}[a] (%)	CP[b] (h^{-1})	Ref.
1	Co_3O_4-NGr@C	3.5	100	15	3.05	96	3.20	[1]
2	Co@CN-800	3	110	10	23.9	100	0.62	[2]
3	Co@NC-600	9.78	90	6	9.3	99.9	1.32	[3]
4	Co@NPC-800	4	120	24	3.54	90	0.69	[4]
5	Co-NSPC-850	3	110	3	10.02	99	4.85	[5]
6	Co-Nx/C-800-AT	3	110	12	0.25	>99	48.59	[6]
7	**Co@NSC-3**	**3**	**110**	**3**	**1.12**	**97**	**41.76**	**This work**

[a] Y_{AN} means yield of aniline.

[b] CP means catalyst productivity, which is calculated by moles of nitrobenzene consumed divided by total moles of cobalt per hour.

Table S4 The solvent selection for one-pot hydrogenation and reductive amination[a].



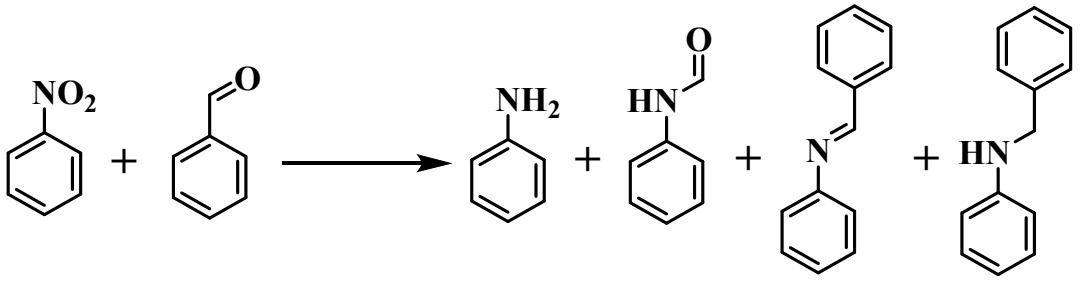
A **B** **C** **D** **E** **F**

Entry	Solvent	Conv.A(%)	Sel.C(%)	Sel.D(%)	Sel.E(%)	Sel.F(%)
1	toluene	94.8	10.7	0.9	74.9	13.5
2	THF	79.7	3.0	1.3	67.2	28.5
3	1,4-Dioxane	8.9	2.0	19.9	77.2	0.9
4	n-Hexane	28.5	3.9	0.0	87.8	8.3
5	isopropanol	75.9	3.4	0.4	65.9	30.3
6	DMF	92.8	43.1	0.6	17.2	39.1
7	H_2O	95.2	48.2	0	17.0	34.8
8	THF/H2O[b]	100	25.1	2.5	18.5	53.9

[a] Reaction conditions: nitrobenzene (0.5 mmol), benzaldehyde (1 mmol), Co@NSC-3 (20 mg), solvent (5 mL), formic acid (2 mmol) and 150 ℃; Conversion and the selectivity were calculated based on nitro compounds, and GC analysis using n-dodecane as an internal standard.

[b] V_{THF}/V_{H2O}=10:1

Table S5 The optimization of one-pot hydrogenation and reductive amination[a].



A **B** **C** **D** **E** **F**

Entry	T	FA(eq.)	Conv.A(%)	Sel.C(%)	Sel.D(%)	Sel.E(%)	Sel.F(%)
1	110	4	100	33.4	3.5	54.3	8.8
2	130	4	100	19.9	2.6	40.1	37.4
3	150	4	100	25.1	2.5	18.5	53.9
4	170	4	100	26.5	0.7	9.3	63.4
5	170	5	100	1.4	2.0	7.0	89.6
6	170	6	100	3.3	1.0	0.7	94.9

[a] Reaction conditions: nitrobenzene (0.5 mmol), benzaldehyde (1 mmol), Co@NSC-3 (20 mg), THF/H_2O (V_{THF}/V_{H2O}=10:1, 5 mL); Conversion and selectivity were calculated based on nitro compounds, and GC analysis using n-dodecane as an internal standard.

Reference

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