Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting information for

Visible-Light triggered selective reduction of nitroarenes to azo compounds catalysed by Ag@organic molecular cage

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Content

1. Experimental section

1.1 Materials and instrumentation

The reagents and solvents employed were commercially available and used without further purification.

The powder diffractometer (XRD) patterns were collected by a D8 ADVANCEX-ray with Cu Kα radiation (λ = 1.5405 Å). The total surface areas of the catalysts were measured by the BET (Brunauer–Emmer–Teller) method using carbon dioxide adsorption at 195 K, this was done by the Micromeritics ASAP 2000 sorption/desorption analyzer. ICP-LC was performed on an IRIS InterpidII XSP and NU AttoM. HRTEM (High resolution transmission electron microscopy) analysis was performed on a JEOL 2100 Electron Microscope at an operating voltage of 200 kV. Gas chromatography (GC) analysis was performed on an Agilent 7890B GC (the product yield was determined by the peak area in GC). XPS spectra were obtained from PHI Versaprobe II. UV-vis absorption spectra were recorded at room temperature in quartz cells of 1 cm path length using a TU-1800 SPC spectrophotometer. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400-4000cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^{1}H NMR spectra were obtained on a Bruker AVANCE-400 spectrometer, and the chemical shifts are reported in δ relative to TMS. High-resolution ESI data were obtained using a Bruker Daltonics Inc. instrument.

1.2 Synthesis of 1

A DMF (2 mL) solution of *trans*-(1R,2R)-diaminocyclohexane (6.8 mg, 0.06 mmol) and 2-hydroxy-1,3,5-triformylbenzene (7.1 mg, 0.04 mmol) was heated at 90°C for 3 days in a Teflon-lined stainless steel autoclave (10 mL). After slowly cooling to room temperature, yellow block crystals were generated. The crystalline solids were then filtered off, washed with acetone. Yield, 85%. IR 3380, 3366, 2924, 2855, 1669, 1635, 1601, 1532, 1450, 1376, 1290, 1258, 1160, 1142, 1091, 1010, 947, 937, 866, 797, 766, 643 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.76-113.69 (4H, -OH), 8.66-8.37(4H, ortho-CH=N, Z isomers), 8.33-8.10 (4H, ortho-CH=N, E isomers), 8.10-7.91 (4H, para-CH=N), 7.91-7.67 (8H, Ar-H), 3.45-3.02 (12H, Cy, CH-N=), 1.88-1.25 (48H, Cy, -CH_2); ^{13}C NMR (400 MHz, $CDCl_3$) δ 164.26-160.12 (Ar, C-OH), 159.88-155.96 (para-CH=N), 155.28-152.02 (ortho-CH=N), 133.24-128.05 (Ar, C-H), 126.90-124.10 (para, Ar, **C**-C=N), 123.23-121.12 (Ar, **C**-(E)C=N), 118.80-117.42(Ar, **C**-(Z)C=N), 74.78-70.87 (Cy, CH-N), 32.90-31.17 (3-Cy, CH_2), 24.03-22.22 (4-Cy, CH_2); ESI-HR-MS calcd for $C_{72}H_{85}N_{12}O_4$ $[M+H]^+$: 1181.6817 found 1181.6656.

1.3 Synthesis of Ag@1

1 (10 mg) in CH_2Cl_2 (25mL) and $AgNO_3$ (22.5 mg) in MeOH (15 mL) were mixed and stirred vigorously for 10 h at room temperature. After removal of the solvent in vacuum, the obtained solids were washed several times with MeOH and CH_2Cl_2 (9.8 mg, 85%). The obtained **Ag(I)@1** (10 mg) was then stirred in MeOH (50 mL) at 80^{o}C for 10 h to generate **Ag@1** as an orange solid (9.8 mg). ICP measurement indicated that the encapsulated amount of Ag NPs in POC is 15.0 wt%. IR 3380, 3366, 2924, 2855, 1669, 1635, 1601, 1532, 1450, 1376, 1290, 1258, 1160, 1142, 1091, 1010, 947, 937, 866, 797, 766, 643 cm^{-1}.

1.4 Reduction nitrobenzene to azobenzene

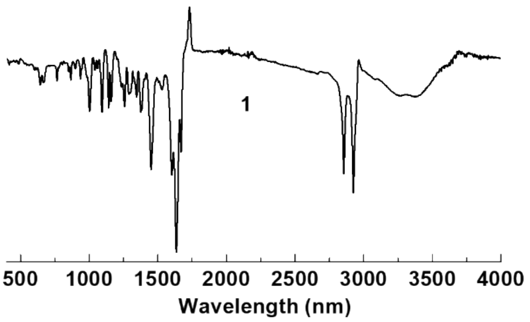
A mixture of nitrobenzene (120 μL, 1.18 mmol), NaOH (120mg, 3mmol) and Ag@1 (8 mg, 1.0 mol % Ag equiv) in EtOH (1 mL) was stirred at room temperature under visible light irradiation (λ =

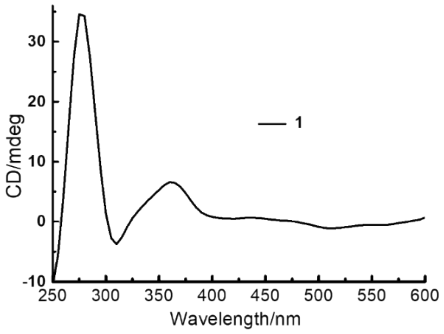
435nm, 300 W xenon with a power density of 2.5 W/cm^2) for 12 h in air (monitored by GC) to afford the corresponding product.

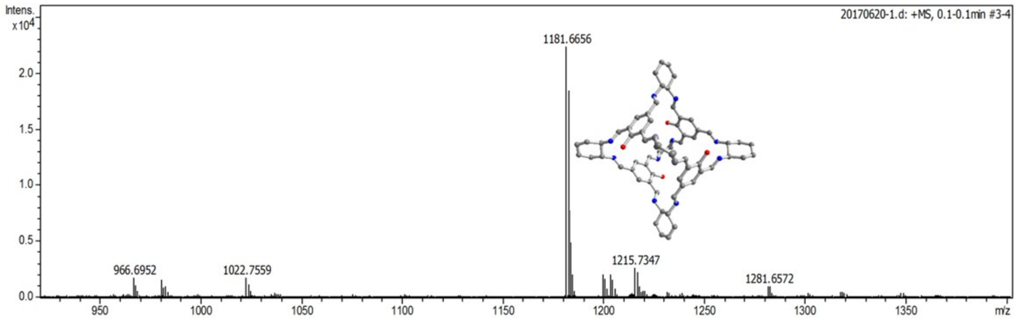
1.5 Reusability of Ag@1

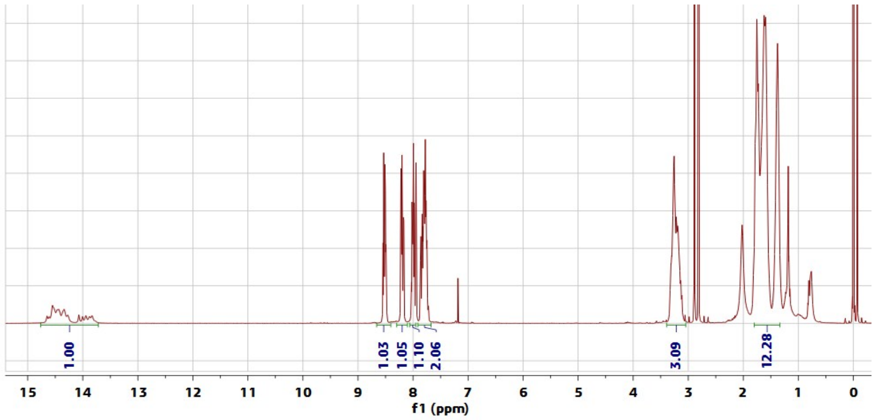
After reduction nitrobenzene to azobenzene, Ag@1 was separated via centrifugation and washed several times with ethanol-acetone mixture. After dried in vacuum, the Ag@1 was used directly for the next catalytic cycle.

2. IR, CD, ESI-MS, ^{1}H NMR and ^{13}C NMR spectra of 1









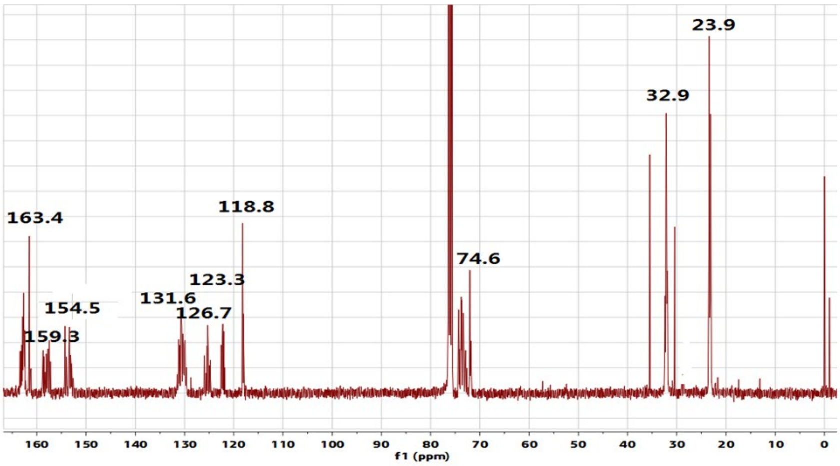


Fig. S1 IR, CD (positive Cotton effect at 277 and 361 nm, negative dichroic signal at 310 and 508 nm), ESI-MS ($C_{72}H_{85}O_4N_{12}$ $[M+H]^+$ calcd for 1181.6817, found 1181.6656), ^1H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (400 MHz, $CDCl_3$) spectra of **1**. The peaks at 7.20 ($CHCl_3$), 2.89 and 2.81 (DMF), 2.05 (acetone), 1.27 and 0.88 (grease) in the ^1H NMR spectrum, and 77.36 ($CHCl_3$), 36.53 (DMF), and 30.91 (acetone) in the ^{13}C NMR spectrum are attributed to the solvent molecules.

3. Single-crystal data of 1

Diffraction data for single crystals of **1** was collected at 293 (2) K on a Bruker Smart 1000 CCD diffractometer using Mo-Kα radiation (λ = 0.71073 Å) with the ω-2θ scan technique. An empirical absorption correction was applied to raw intensities.[1] The structure was solved by direct methods (SHELX-97) and refined with full-matrix least-squares technique on F^2 using the SHELX-97.[2] The hydrogen atoms were added theoretically, and riding on the concerned atoms and refined with fixed thermal factors. The details of crystallographic data and structure refinement parameters are summarized in Table S1. The selected bonds lengths and angles for **1** was shown in Table S2. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 1515347. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement for **1**.

Complexes	**1**
Empirical formula	$C_{72}H_{72}N_{12}O_{16}$
Formula weight	1361.42
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system, space group	Cubic, *F4132*
Unit cell dimensions	a = 24.8625(3) Å, alpha = 90deg.
	b = 24.8625(3) Å, beta = 90 deg.
	c = 24.8625(3) Å, gamma = 90 deg.
Volume	15368.6(3) $Å^3$
Z, calculated density	8, 1.117 Mg/m^3
Absorption coefficient	0.701 mm^{-1}

F(000)	5728
Crystal size	0.2 x 0.2 x 0.1 mm
Theta range for data collection	5.03 to 63.63 deg.
Limiting indices	--12<=h<=28, -10<=k<=28, -19<=l<=28
Reflections collected / unique	2795 / 1061 [*R*(int) = 0.0372]
Completeness to theta = 71.06	99.4 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1061 / 1 / 80
Goodness-of-fit on F^2	1.934
Final *R* indices [I>2sigma(I)]	*R*1 = 0.1800, w*R*2 = 0.4373
R indices (all data)	*R*1 = 0.1990, w*R*2 = 0.4528
Largest diff. peak and hole	0.649 and -0.563 e. Å^{-3}

Table S2. Selected bonds lengths and angles for **1**

1	N(1)-C(1)	1.270(10)	N(1)-C(4)	1.431(11)
	C(3)-C(2)#1	1.378(11)	C(3)-C(2)	1.406(11)
	C(3)-O(1)	1.408(16)	C(2)-C(3)#2	1.378(11)
	C(2)-C(1)	1.482(12)	C(5)-C(6)	1.360(9)
	C(5)-C(4)	1.508(12)	C(4)-C(4)#3	1.540(18)
	C(6)-C(6)#3	1.30(5)	C(1)-N(1)-C(4)	117.0(7)
	C(2)#1-C(3)-C(2)	119.8(8)	C(2)#1-C(3)-O(1)	118.8(8)
	C(2)-C(3)-O(1)	121.4(8)	C(3)#2-C(2)-C(3)	120.2(8)
	C(3)#2-C(2)-C(1)	120.1(7)	C(3)-C(2)-C(1)	119.6(7)
	C(6)-C(5)-C(4)	121.4(11)	N(1)-C(4)-C(5)	113.8(9)
	N(1)-C(4)-C(4)#3	109.6(6)	C(5)-C(4)-C(4)#3	103.6(8)
	N(1)-C(1)-C(2)	123.5(8)	C(6)#3-C(6)-C(5)	115(2)

Symmetry transformations used to generate equivalent atoms: #1 -y+1/2,-z+1/2,x+0, #2 z+0,-x+1/2,-y+1/2, #3 -x,-y+1,z+0.

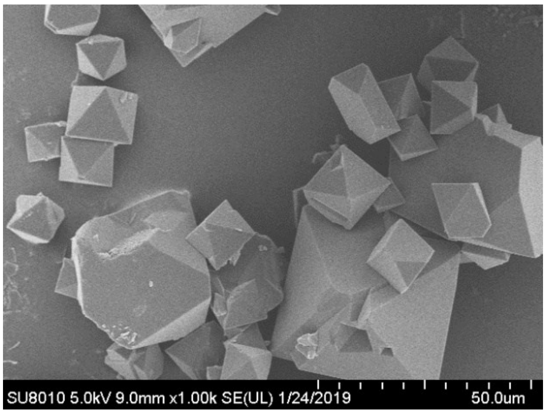


Fig. S2 SEM of **1**. All the crystals were obtained as the octahedral particles, indicating its pure phase.

4. TGA traces of 1 and Ag NPs@1

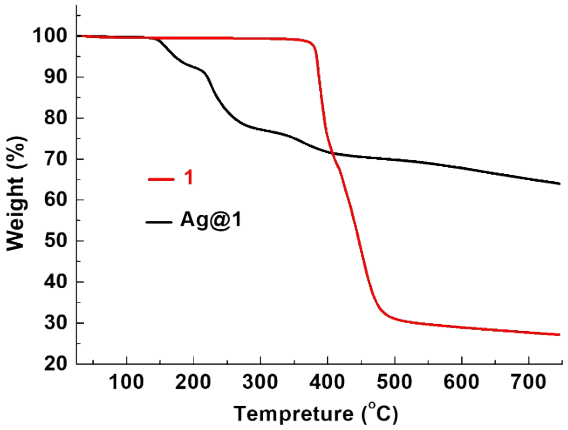


Fig. S3 TGA trace of **1** and **Ag@1**.

5. XPS spectrum of Ag@1

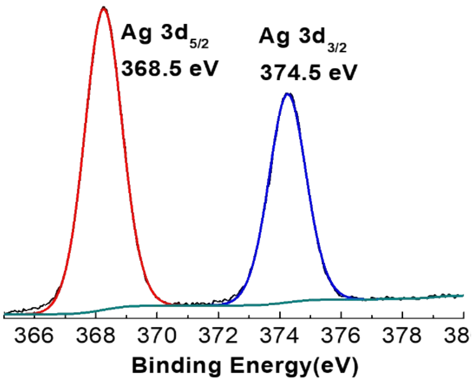


Fig. S4 XPS spectrum of **Ag@1**.

6. GC analysis for Table 1

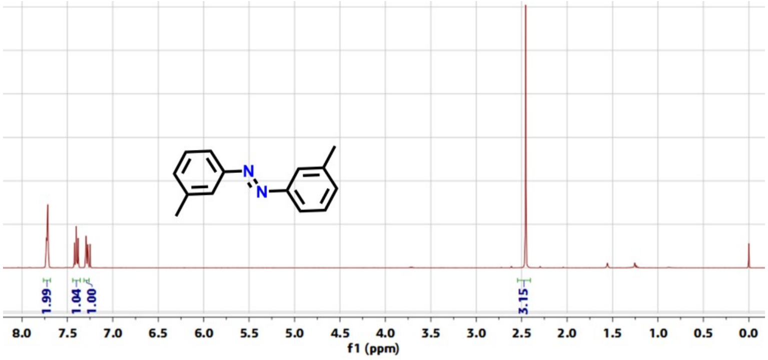


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) and ESI-MS of azobenzene.

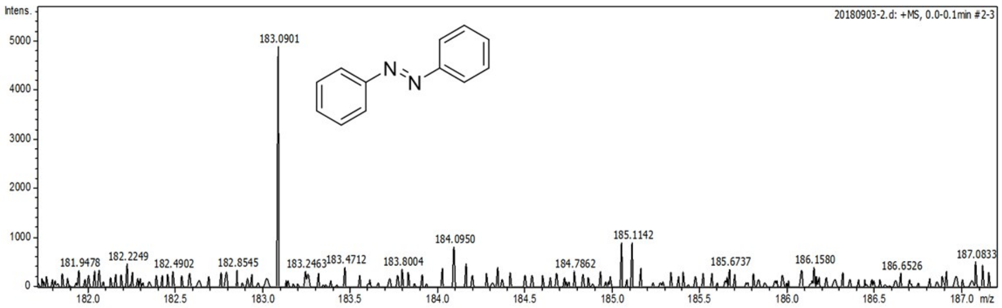
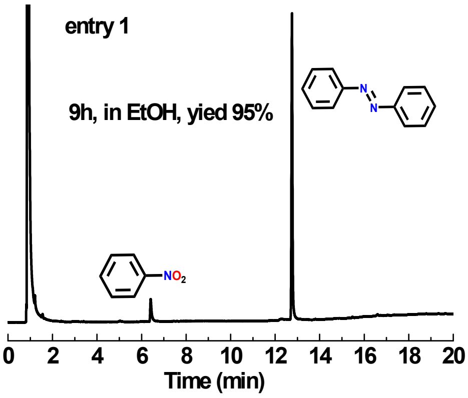
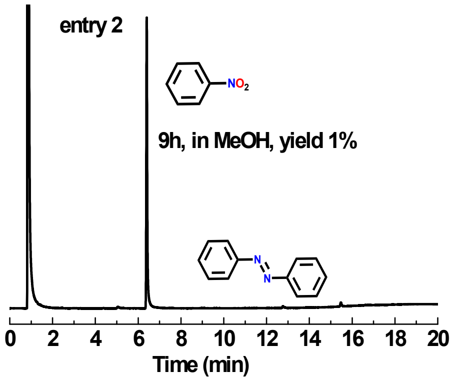
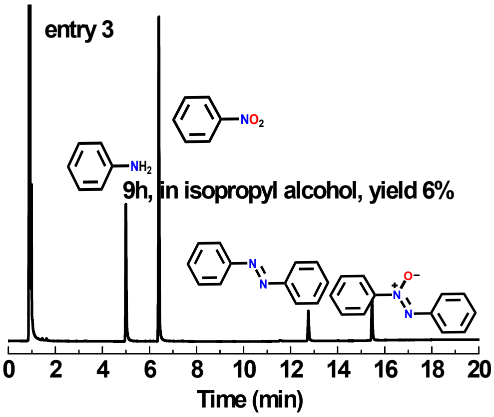
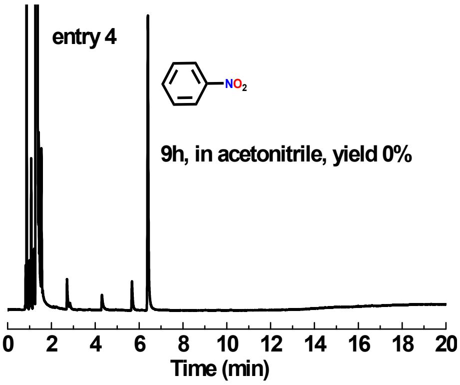


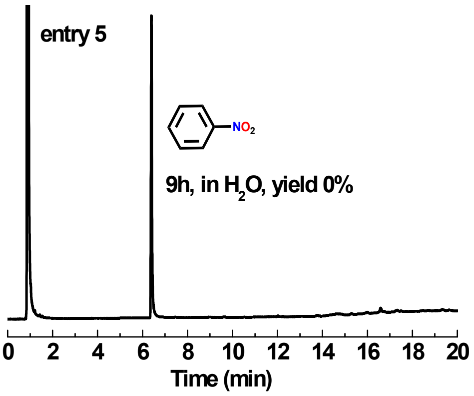
Fig. S6 MS (ESI): $C_{12}H_{11}N_2$ ($[M+H]^+$) calcd for 183.0922, Found: 183.0901.

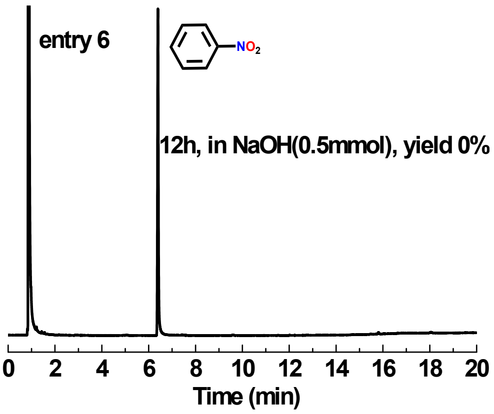


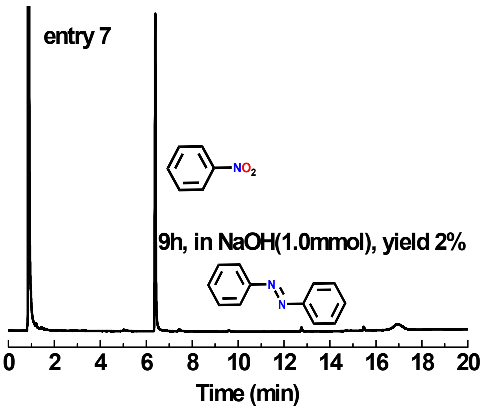


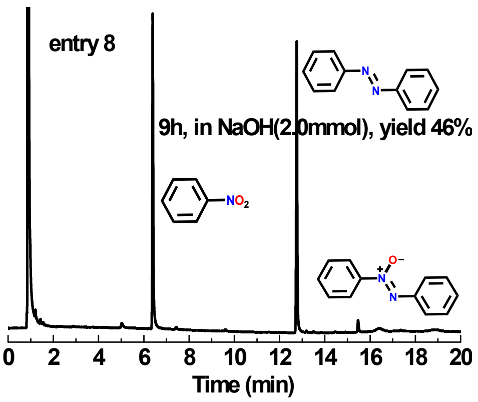


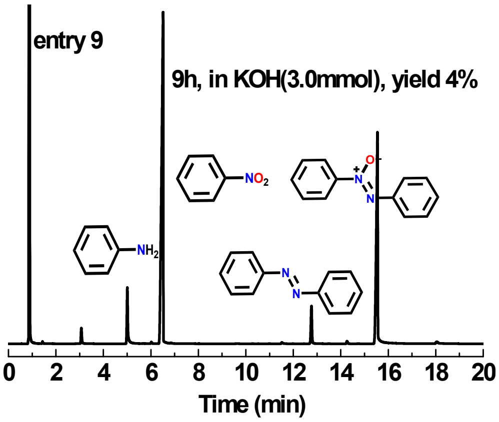


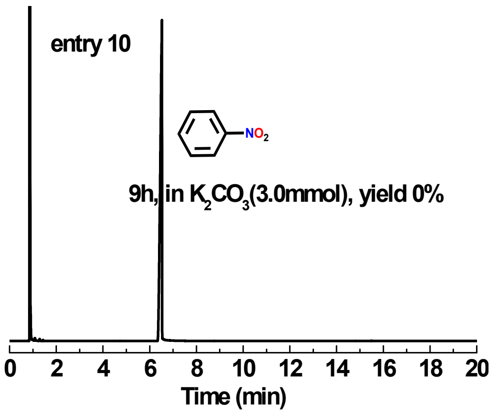





entry 7
9h, in NaOH(1.0mmol), yield 2%
NO$_2$
N
N
0 2 4 6 8 10 12 14 16 18 20
Time (min)


entry 8
9h, in NaOH(2.0mmol), yield 46%
NO$_2$
N
N
O−
+N
0 2 4 6 8 10 12 14 16 18 20
Time (min)


entry 9
9h, in KOH(3.0mmol), yield 4%
NH$_2$
NO$_2$
N
N
O−
+N
0 2 4 6 8 10 12 14 16 18 20
Time (min)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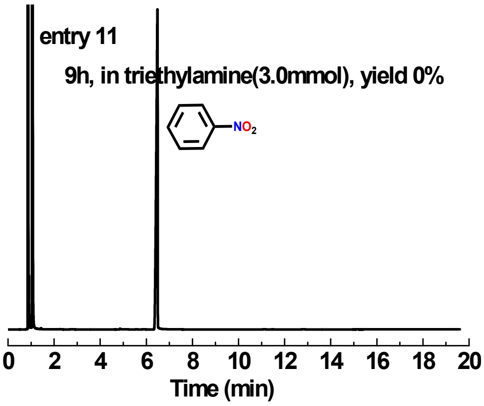
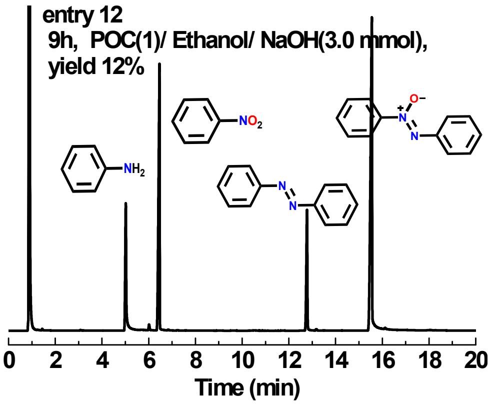
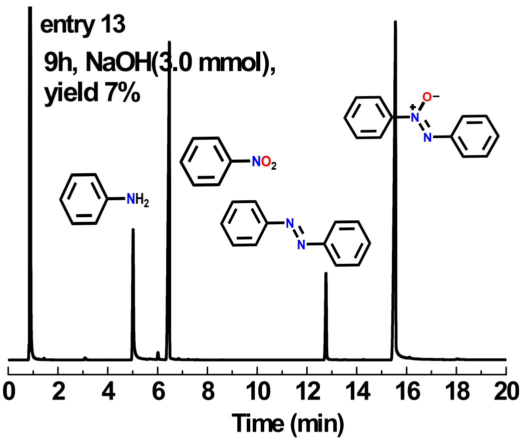
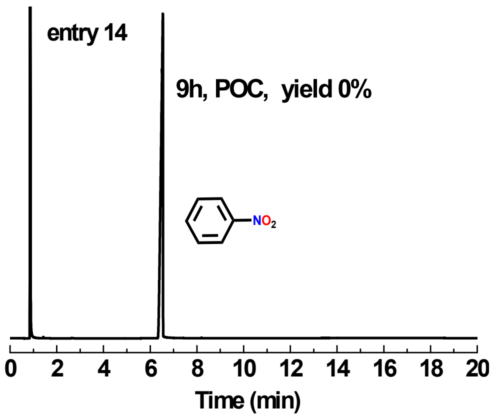
9h, in K$_2$CO$_3$(3.0mmol), yield 0%
NO$_2$
0 2 4 6 8 10 12 14 16 18 20
Time (min)


entry 11
9h, in triethylamine(3.0mmol), yield 0%
NO$_2$
0 2 4 6 8 10 12 14 16 18 20
Time (min)


entry 12
9h, POC(1)/ Ethanol/ NaOH(3.0 mmol),
yield 12%
NH$_2$
NO$_2$
N
N
O−
+N
0 2 4 6 8 10 12 14 16 18 20
Time (min)


entry 13
9h, NaOH(3.0 mmol),
yield 7%
NH$_2$
NO$_2$
N
N
O−
+N
0 2 4 6 8 10 12 14 16 18 20
Time (min)


entry 14
9h, POC, yield 0%
NO$_2$
0 2 4 6 8 10 12 14 16 18 20
Time (min)

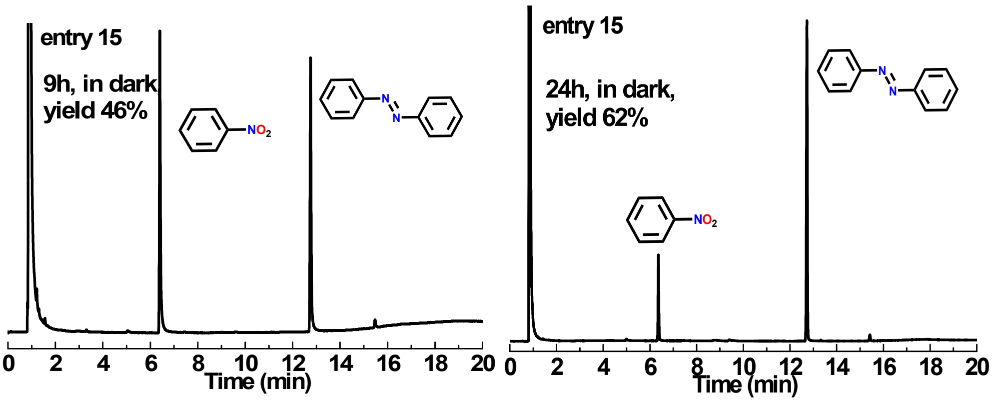
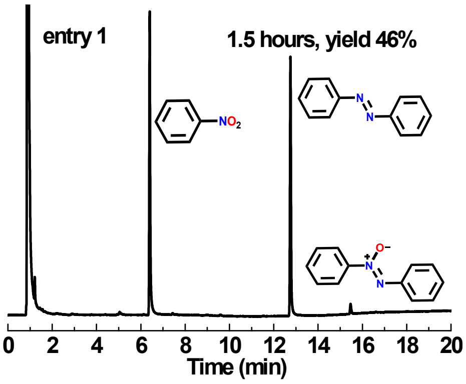
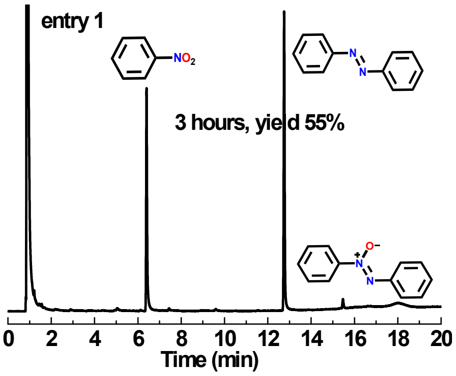
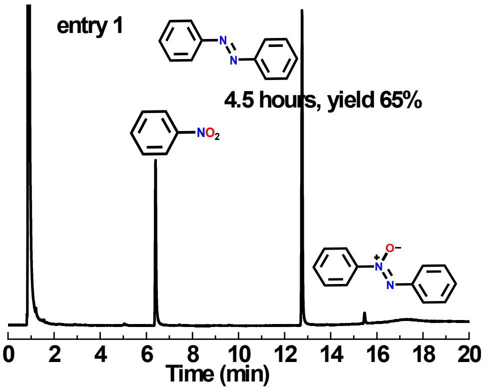


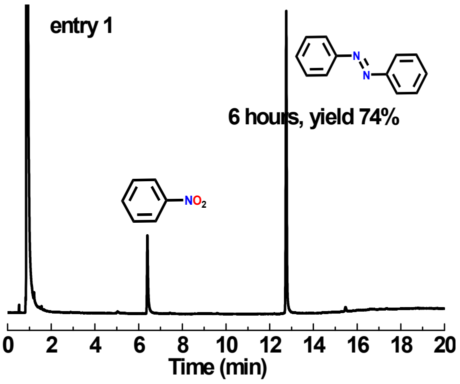
Fig. S7 GC analysis for Table 1.

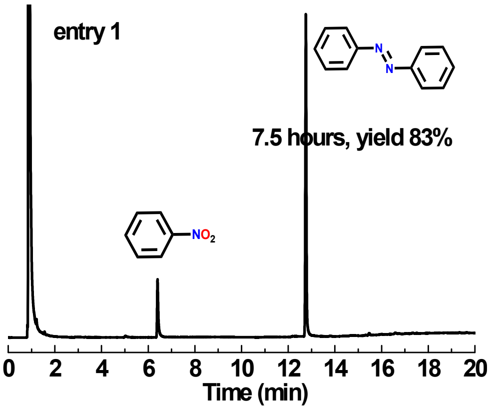
7. GC analysis for the relationship between reaction time and yield

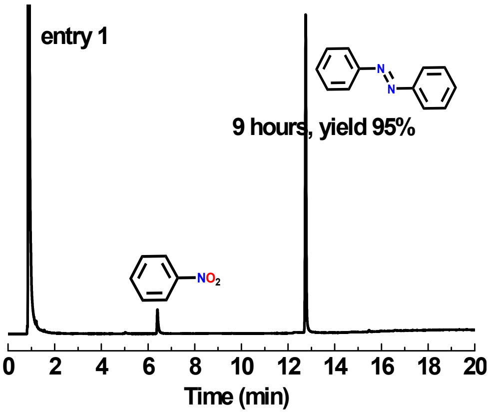












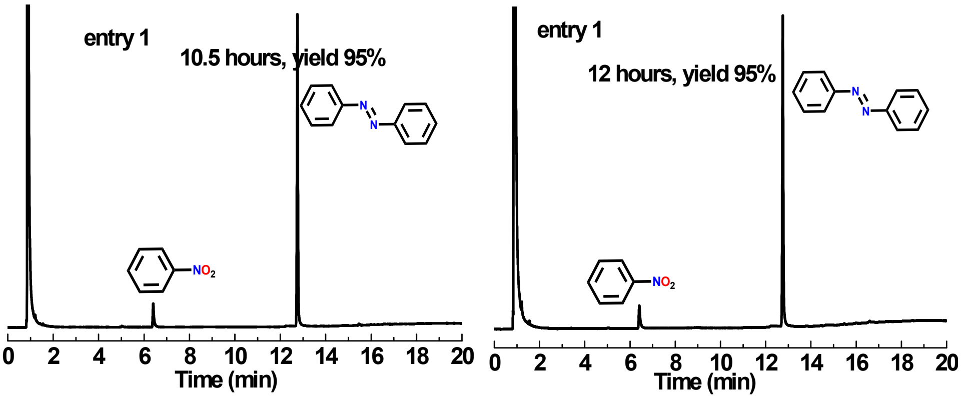


Fig. S8 GC analysis for the relationship between reaction time and yield (Table 1, entry 1).

8. GC analysis for repetitive catalytic runs

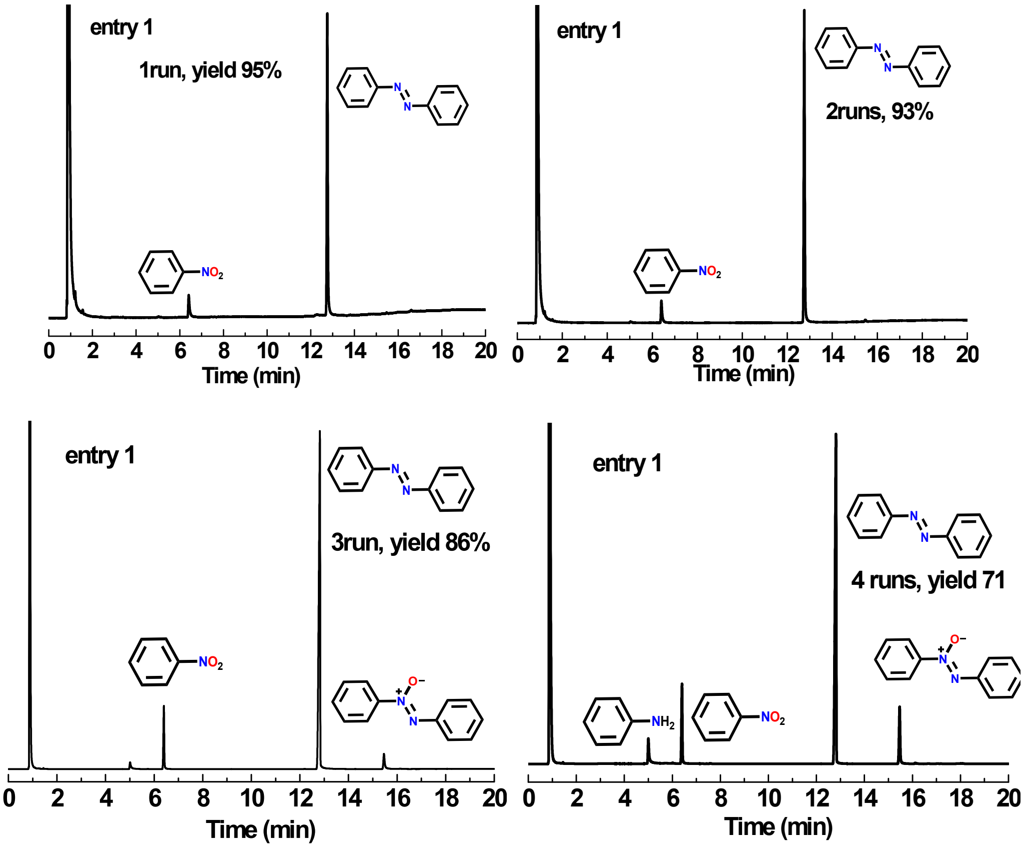


Fig. S9 GC analysis for four catalytic runs on the model reaction (Table 1, entry 1).

9. TEM, SEM images and XRPD pattern of Ag@1 after 3 catalytic runs

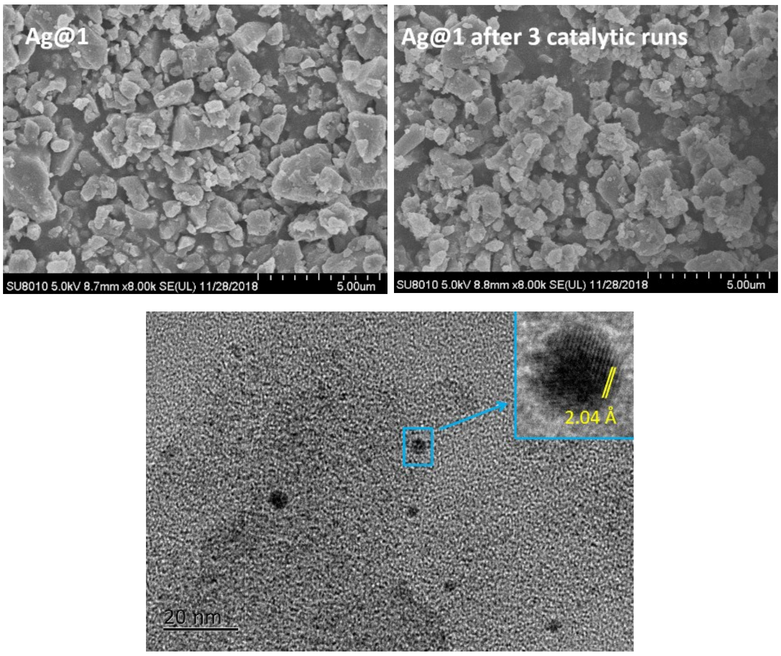


Fig. S10 TEM image of **Ag@1** after three catalytic runs on the model reaction, and SEM images before and after catalytic runs (Table 1, entry 1).

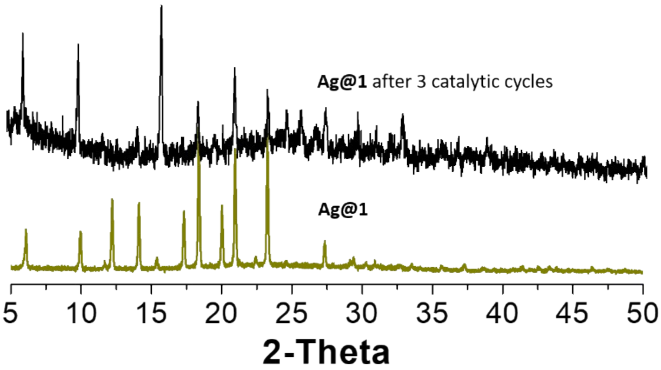
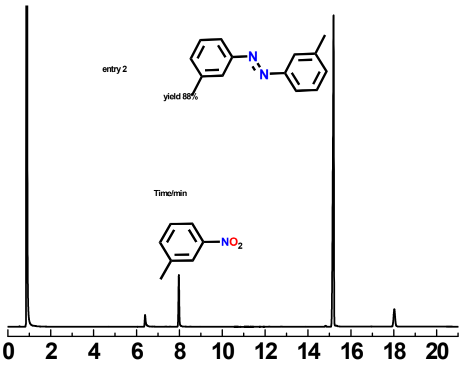
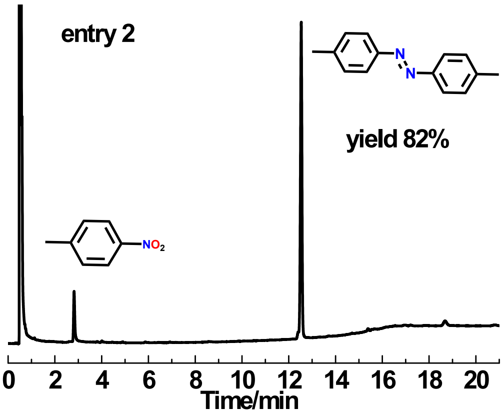
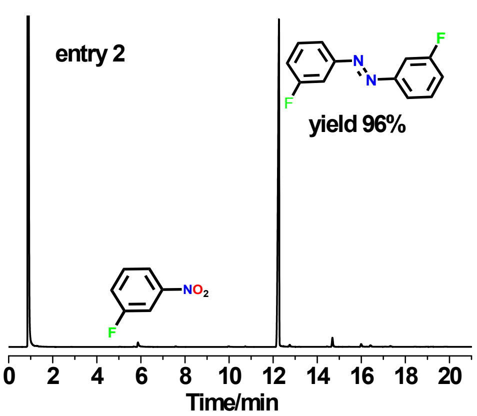


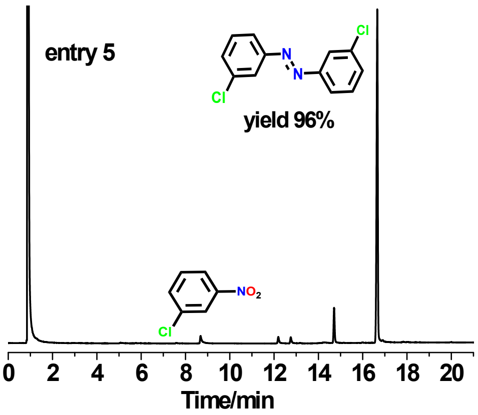
Fig. S11 XRPD pattern of **Ag@1** after three catalytic runs on the model reaction (Table 1, entry 1).

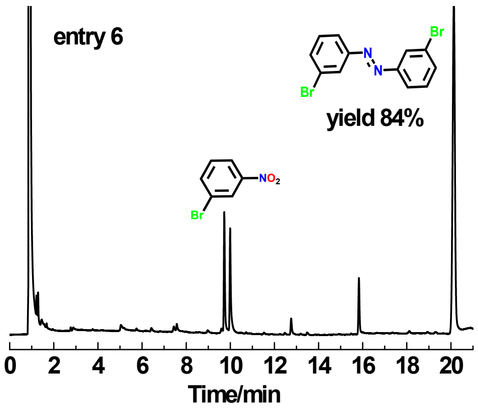
10. GC analysis and ^{1}H NMR spectra for Ag@1 promoted selective reduction based on different substituted nitrobenzenes

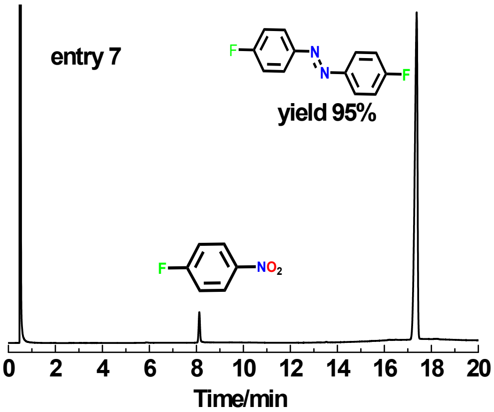


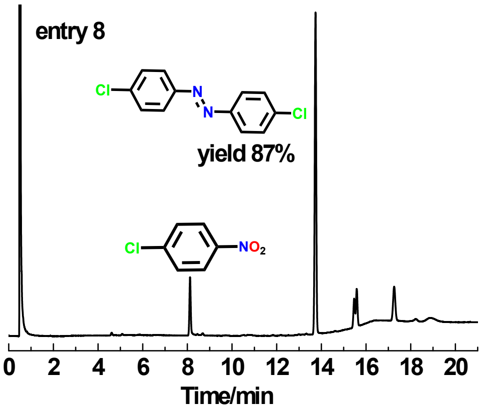


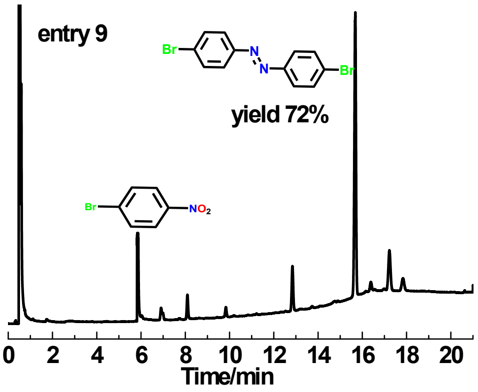

entry 2
N
N
F
F
yield 96%
NO2
F
0 2 4 6 8 10 12 14 16 18 20
Time/min

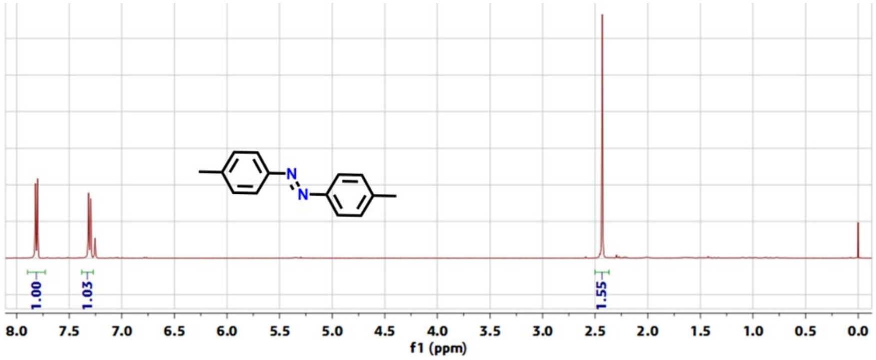

entry 5
N
N
Cl
Cl
yield 96%
NO2
Cl
0 2 4 6 8 10 12 14 16 18 20
Time/min

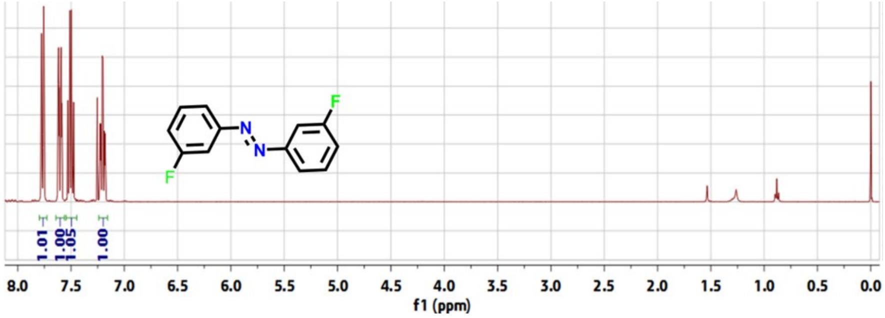

entry 6
N
N
Br
Br
yield 84%
NO2
Br
0 2 4 6 8 10 12 14 16 18 20
Time/min

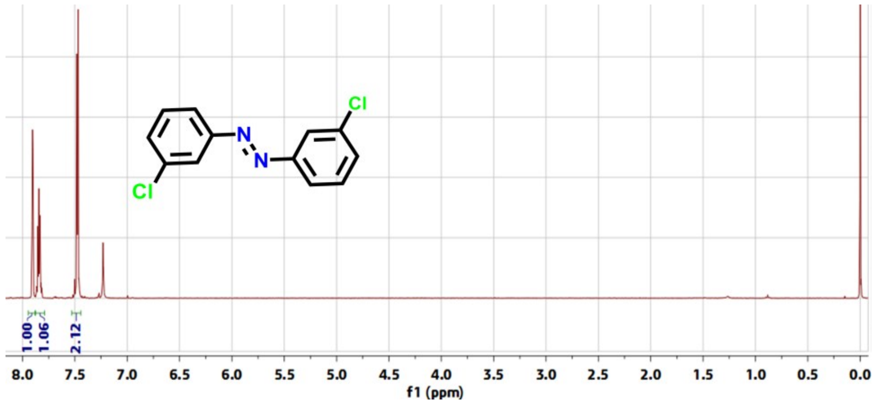

entry 7
F
N
N
F
yield 95%
F
NO2
0 2 4 6 8 10 12 14 16 18 20
Time/min

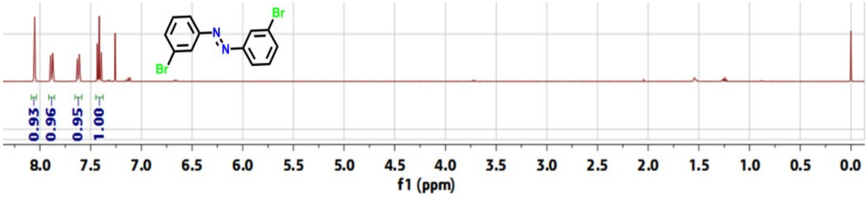

entry 8
Cl
N
N
Cl
yield 87%
Cl
NO2
0 2 4 6 8 10 12 14 16 18 20
Time/min

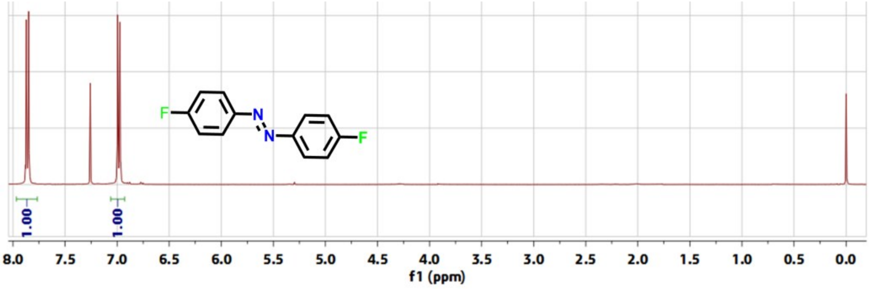

entry 9
Br
N
N
Br
yield 72%
Br
NO2
0 2 4 6 8 10 12 14 16 18 20
Time/min


N
N
1.00
1.03
1.55
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
N
N
F
1.01
1.00
1.05
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
N
N
Cl
1.00
1.06
2.12
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Br
N
N
Br
0.93
0.96
0.95
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
N
N
F
1.00
1.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

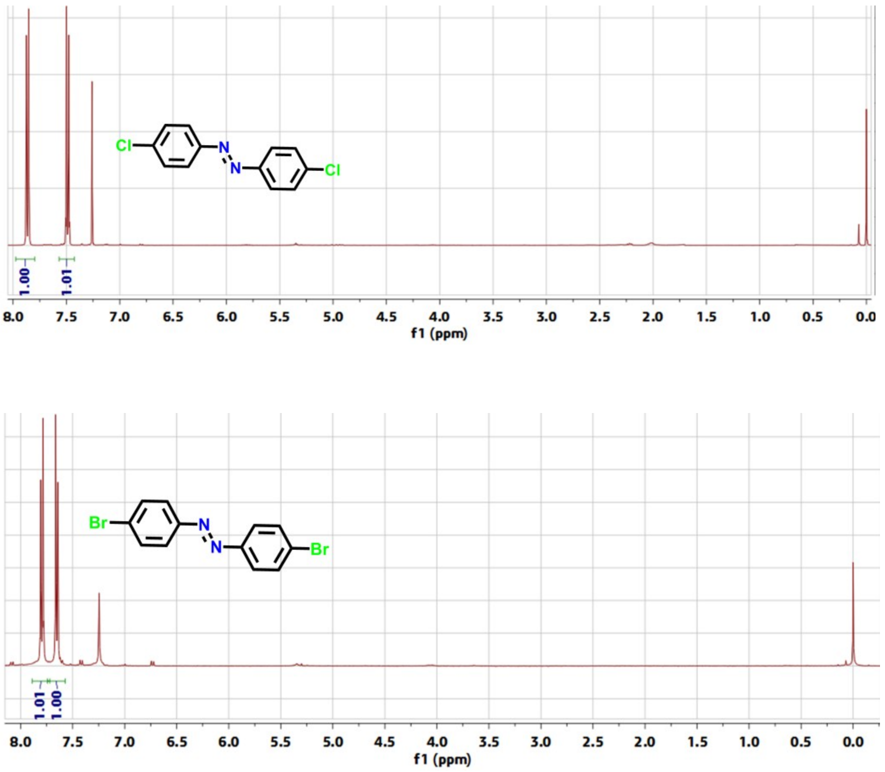
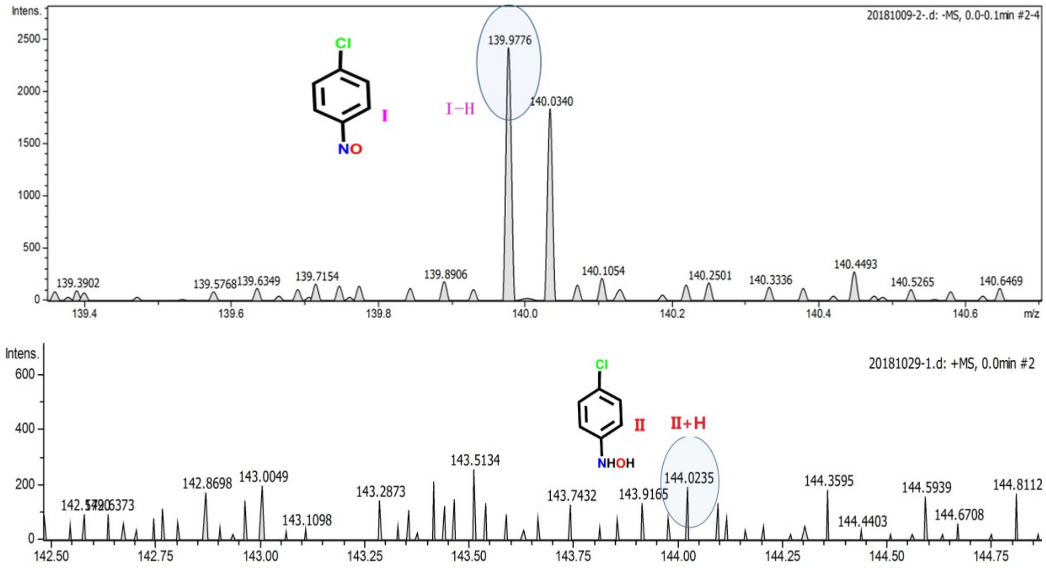


Fig. S12 GC analysis and ^{1}H NMR spectra (400 MHz, CDCl$_3$) for **Ag@1** promoted selective reduction based on different substituted nitrobenzenes (for Table 3).

11. ESI-MS spectra for the reaction mechanism study



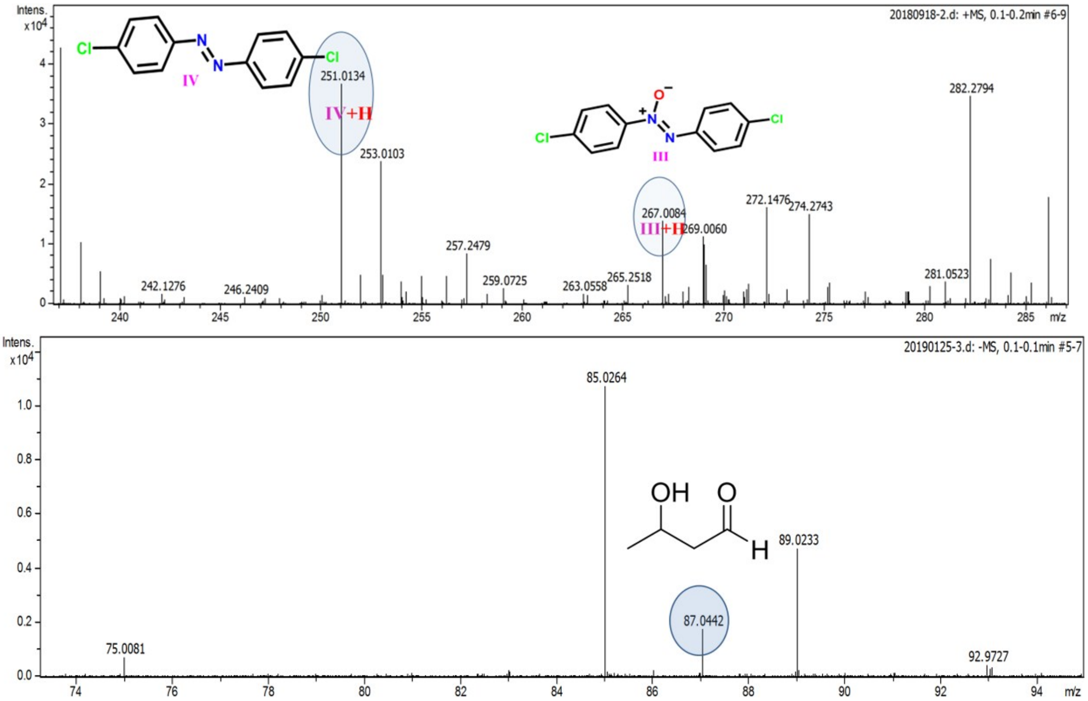


Fig. S13 ESI-MS spectra for the reaction mechanism study.

12. References

1. G. M. Sheldrick. SHELXS 97, Program for the Solution of Crystal Structures, University of Götingen, Germany, 1997.
2. G. M. Sheldrick. SHELXL 97, Program for the Refinement of Crystal Structures, University of Götingen: Germany, 1997.