Supporting Information

Superior Activity and Selectivity of Heterogenized Cobalt Catalysts for Hydrogenation of Nitroarenes

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1. General Remarks

N$_2$-Physisorption was performed on an Asap 2000 from Micromeritics. The samples were degassed for 24 hours at 300 °C and afterwards the measurement was performed at -196 °C. Inductively coupled plasma (ICP-OES) analysis was conducted with an instrument of SPECTRO Analytical Instruments, Model SPECTROFLAME. The pore structure and particle distribution of the catalyst samples were investigated via STEM imaging on a Hitachi HD-2700 electron microscope (CS-corrected, 200 kV, Cold FEG, EDX Octane T Ultra W 100 mm$^2$ SDD TEAM-Software). X-ray diffraction (XRD) was performed on a Siemens D5000 (Radiation/wavelength: Cu K-alpha, 0.15418 nm). Thermogravimetric analysis (TGA) was conducted on a STA 409 cell from Netzsch. X-ray photoelectron spectroscopy (XPS) data were obtained on a Phi5000 VersaProbe II spectrometer (ULVAC-Phi Inc., USA) using AlK$\alpha$ as the excitation source (1.486 keV) and operated at 50 W, 15 kV, 200 μm. Survey spectra were obtained by 187.5 eV energy, 0.8 eV step range, 100 ms/step. High resolution spectra were obtained by 23.5 eV energy, 0.1 eV step, 100 ms/step. The shift of the binding energy was corrected using C 1s level at 285 eV. Furthermore, the quantifications in at% show a relative error of 15% and was indexed to 100% with a Shirley-background and empiric device-optimized sensitivity factor.

Unless otherwise stated, reactions were performed in a 300 mL autoclave from Parr Instrument Company. Solvents were used directly without further purification. NMR-spectra were recorded on Bruker AV 300 and 400 spectrometers. Chemicals shifts (δ) are reported in ppm downfield of tetramethylsilane. The residual solvent signals were used as references for $^1$H and $^{13}$C NMR spectra (CDCl$_3$: δH = 7.26 ppm, δC = 77.12 ppm; DMSO-d$_6$: δH = 2.50 ppm, δC = 39.52 ppm).

2. Procedure for the Preparation of Catalysts

2.1. Synthesis of the hard-template

SBA-15 materials were synthesized according to the procedure of Zhao et al.$^1$ in order to use them as templates for the formation of nanostructured carbon. Ordered mesoporous silica templates were prepared using the surfactant EO$_{20}$PO$_{70}$EO$_{20}$ (P123), and TEOS as silica source. P123 (6.0 g) was completely dissolved in 2 M HCl (180 mL) overnight at room temperature. TEOS (12.6 mL) was added to the stirred mixture at 35 °C. The mixture was placed in the oven at 120 °C for 24 h. The white precipitates were filtered by vacuum filtration and washed twice with distilled water and twice with ethanol. The product was dried at 80 °C for 24 h and calcined at 550 °C for 6 h.
2.2. Synthesis of nanostructured carbon (CMK-3-CoPc)

Ordered mesoporous carbon materials (CMK-3) were formed using the same procedure as introduced by Ryoo et al.\textsuperscript{2} CMK-3 was synthesized with Cobalt phthalocyanine (CoPc) as a carbon source by replicating mesoporous silica SBA-15 (hard-template). The pores of SBA-15 were filled with CoPc via different impregnation methods (see 2.2.1-2.2.3). The mixture was then placed into an oven at 100 °C for 1 h, 350 °C for 1 h and subsequently carbonized at 990°C for 1 h under nitrogen atmosphere. To leach the silica template from the silica-Co-phthalocyanine composite, the resulting black powder was treated with 5 M NaOH solution at 100 °C for 24 h. The solution was then centrifuged at 6000 rpm for 15 minutes, followed by decantation of the supernatant solution. The sediment was dispersed in distilled water. Centrifugation was repeated ten times to ensure a neutral pH of the supernatant solution. The silica leaching step was then repeated. The replica was dried at 100 °C and ordered mesoporous carbon materials denoted as CMK-3-CoPc were obtained (see Scheme S1).

2.2.1  Grinding (solid/solid-impregnation; denoted as GR)

CoPc (1.0 g) was added to SBA-15 (1.0 g) and both materials were physically mixed together thoroughly via pestle and mortar until a homogeneous colored powder was formed.

2.2.2  Wet Impregnation (denoted as WI)

CoPc (1.0 g) was dissolved in ethanol (50 mL) and SBA-15 (1.0 g) was added to the solution. The mixture was heated up to 60 °C for 24 h and stirred until the solution turned colorless. The solvent was evaporated under reduced pressure.

2.2.3. Incipient Wetness Impregnation (denoted as IWI)

SBA-15 (1.0 g) was impregnated with CoPc (1.0 g) dissolved in ethanol (2 mL). The metal solution was added dropwise to SBA-15, thus only wetting the solid template by the incipient wetness principle.


3. Characterization of the Catalysts

3.1. Thermogravimetric analysis

![Figure S1](image1.png)

**Figure S1.** Thermogravimetric analysis (TGA) for CMK-3-CoPc-WI.

3.2. X-ray Photoelectron Spectroscopy (XPS)

![Figure S2](image2.png)

**Figure S2.** XPS survey scan for CoPc (template-free) and CMK-3-CoPc-WI prior and after 5 catalytic cycles. The survey spectra indicate that no other metallic or inorganic contaminants are present. The In 3d signal (marked by *) originates from the Indium-foil used for fixation of the powder sample.
**Figure S3.** XPS C 1s (left) and O 1s spectra (right) for CoPc (template-free) and CMK-3-CoPc-WI prior and after 5 catalytic cycles; O 1s species can be assigned as follows: (O 1s-1, red) O=C-N, C=O (aromatic); (O 1s-2, blue) C-O-C (aromatic), epoxy-, O-C-O, C=O (aliphatic), H$_2$O; (O 1s-3, green) H$_2$O, O$_2$/C; (O 1s-4, light blue) O$_2$/C; (O 1s-5, magenta) CoO.
**Figure S4.** XPS N 1s (left) and Co 2p spectra (right) for CoPc (template-free) and CMK-3-CoPc-WI prior and after 5 catalytic cycles; Co 2p$_{3/2}$ spectra were curve fitted based on the literature peak set of CoO and Co$_2$O$_4$ multiplets (M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. St. C. Smart, *Appl. Surf. Sci.* 2011, **257**, 2717-2730).
4. General Procedure for the Hydrogenation of nitroarene (GR)

In a 4 mL vial fitted with magnetic stirring bar and septum cap, cobalt catalyst (30 mg) was added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. Solvent (2-methyltetrahydrofuran (MTHF)/H₂O 1.5 mL/0.5 mL) and nitroarene (0.5 mmol) were added, independently. The vials (up to eight) were placed into a 300 mL steel Parr autoclave. The autoclave was flushed with hydrogen 10 times at 20 bar and finally pressurized to the desired value (20 bar). Then it was placed into an aluminium block and heat to the desired temperature (40 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and dodecane (89 mg, 0.52 mmol) was added to the crude reaction mixture as internal standard, then diluted with aceton. The reaction mixture was centrifuged and the liquid was analysed at the GC-FID.

5. Procedure for Catalyst Recycling

In a 4 mL vial fitted with magnetic stirring bar and septum cap, cobalt catalyst (30 mg) was added. Then, a needle was inserted in the septum which allows gaseous reagents to enter. Solvent (MTHF/H₂O 1.5 mL/0.5 mL) and nitroarene (0.5 mmol) were added, independently. The vials (up to eight) were placed into a 300 mL steel Parr autoclave. The autoclave was

**Figure S5.** STEM analysis of different regions within the recycled catalyst CMK-3-CoPc-WI-(recyc.) after 5 successive runs.
flushed with hydrogen 10 times at 20 bar and finally pressurized to the desired value (20 bar). Then it was placed into an aluminium block and heat to the desired temperature (40 °C) from room temperature. At the end of the reaction, the autoclave was quickly cooled down at room temperature with an ice bath and vented. Finally, the samples were removed from the autoclave, and dodecane (89 mg) was added to the crude reaction mixture as internal standard, and then diluted with aceton. The reaction mixture was centrifuged and the liquid was analysed at the GC-FID. The catalyst was isolated by centrifugation and reused for next reaction.
6. ICP-OES analysis

ICP-OES Analyse
A. Simmula, vertreten durch: K. Struve Tel. 323
Analysergebnis/Kurzbericht

AUFTRAG

4
Anzahl der Proben: 5 Flüssig
Auftragsnummer: 8459
Auftraggeber: Wu, Li

Institution: LIKAT

Probenvorbereitung: ohne
durch Auftraggeber in HCL aufgeschlossen und verdünnt vorliegend.

ANALYSE

Elemente: Co
durchgeführt von: K. Struve

Ergebnis: 09.11.2017

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Bemerkungen:

Unterschrift/ Datum: Struve, 16.11.2017

Anlagen( Erläuterungen)/ Abbildungen
7. Characterization Data for the Products

According to **GP**, catalyst (31 mg), 1-methyl-4-nitrobenzene 1b (68 mg, 0.50 mmol), in MTHF/H2O (1.5 mL/0.5 mL), H2 (20 bar), at 40 °C for 24 h. The product 2b (49 mg, 0.46 mmol, 92%) was obtained as a solid.

1H NMR (300 MHz, CDCl3) δ 7.08–6.89 (m, 2H), 6.69–6.54 (m, 2H), 3.32 (s, 3H), 2.25 (s, 3H).

13C NMR (75 MHz, CDCl3) δ 143.78, 129.87, 128.02, 115.47, 20.58.

According to **GP**, catalyst (31 mg), 1-chloro-4-nitrobenzene 1c (79 mg, 0.50 mmol), in MTHF/H2O (1.5 mL/0.5 mL), H2 (20 bar), at 40 °C for 24 h. The product 2c (63 mg, 0.49 mmol, 98%) was obtained as a solid.

1H NMR (300 MHz, CDCl3) δ 7.15–7.04 (m, 2H), 6.65–6.53 (m, 2H), 3.55 (s, 2H).

13C NMR (75 MHz, CDCl3) δ 145.46, 129.87, 123.66, 116.77.

According to **GP**, catalyst (31 mg), 1-bromo-4-nitrobenzene 1d (100 mg, 0.50 mmol), in MTHF/H2O (1.5 mL/0.5 mL), H2 (20 bar), at 40 °C for 24 h. The product 2d (83 mg, 0.49 mmol, 98%) was obtained as a solid.

1H NMR (300 MHz, CDCl3) δ 7.41–7.10 (m, 2H), 6.77–6.43 (m, 2H), 3.59 (s, 2H).

13C NMR (75 MHz, CDCl3) δ 145.52, 132.08, 116.81, 110.24.

According to **GP**, catalyst (30 mg), 1-methoxy-4-nitrobenzene 1e (80 mg, 0.52 mmol), in MTHF/H2O (1.5 mL/0.5 mL), H2 (20 bar), at 40 °C for 24 h. The product 2e (65 mg, 0.52 mmol, 99%) was obtained as a liquid.
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.75 (d, $J = 8.9$ Hz, 2H), 6.64 (d, $J = 8.9$ Hz, 2H), 3.74 (s, 3H), 3.39 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.88, 140.04, 116.50, 114.90, 55.81.

$^{2f} 99\%$

According to GP, catalyst (30 mg), 1-ethoxy-4-nitrobenzene $1f$ (86 mg, 0.51 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product $2f$ (70 mg, 0.51 mmol, 99%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.84–6.69 (m, 2H), 6.63 (d, $J = 8.7$ Hz, 2H), 3.95 (q, $J = 7.0$ Hz, 2H), 3.34 (s, 2H), 1.37 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 152.16, 139.99, 116.50, 115.75, 64.12, 15.06.

$^{2g} 94\%$

According to GP, catalyst (31 mg), 1-nitro-3-(trifluoromethyl)benzene $1g$ (95 mg, 0.50 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product $2g$ (75 mg, 0.47 mmol, 94%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.18–7.09 (m, 1H), 6.88 (ddq, $J = 7.7$, 1.6, 0.8 Hz, 1H), 6.78 (ddt, $J = 2.3$, 1.5, 0.7 Hz, 1H), 6.70 (ddq, $J = 8.0$, 2.3, 0.7 Hz, 1H), 3.69 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 146.85, 131.74 (d, $J = 31.9$ Hz), 129.86, 126.14, 122.53, 119.00–116.34(m), 115.12 (q, $J = 4.0$ Hz), 111.43 (q, $J = 3.9$ Hz).

$^{2h} 98\%$

According to GP, catalyst (29 mg), (3-nitrophenyl)methanol $1h$ (77 mg, 0.50 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product $2h$ (60 mg, 0.49 mmol, 98%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.20–7.05 (m, 1H), 6.76–6.68 (m, 2H), 6.61 (dddt, $J = 7.9$, 2.4, 1.0, 0.4 Hz, 1H), 4.59 (q, $J = 0.6$ Hz, 2H), 2.83 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 146.76, 142.37, 129.65, 117.24, 114.53, 113.71, 65.49.

$^{2i} 96\%$
According to GP, catalyst (31 mg), 3-nitroaniline 1i (71 mg, 0.51 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2i (53 mg, 0.49 mmol, 96%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 6.92–6.76 (m, 1H), 6.02 (dd, $J = 7.9, 2.2$ Hz, 2H), 5.91 (td, $J = 2.2, 0.4$ Hz, 1H), 3.42 (s, 4H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 147.59, 130.20, 105.99, 102.03.

\[ \text{NH}_2 \]

2j 90%

According to GP, catalyst (32 mg), 1-fluoro-2-nitrobenzene 1j (72 mg, 0.51 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2j (51 mg, 0.46 mmol, 90%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.06 – 6.89 (m, 2H), 6.87–6.61 (m, 2H), 3.67 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.41, 150.25, 134.59 (d, $J = 12.6$ Hz), 124.54 (d, $J = 3.6$ Hz), 118.73 (d, $J = 6.8$ Hz), 117.04 (d, $J = 3.5$ Hz), 115.44, 115.20.

\[ \text{NH}_2 \]

2k 99%

According to GP, catalyst (30 mg), 1-chloro-2-nitrobenzene 1k (82 mg, 0.52 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2k (66 mg, 0.52 mmol, 99%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.16 (ddd, $J = 8.0, 1.5, 0.3$ Hz, 1H), 7.02–6.94 (m, 1H), 6.69 (ddd, $J = 8.0, 1.5, 0.3$ Hz, 1H), 6.61 (ddd, $J = 8.0, 7.3, 1.5$ Hz, 1H), 3.58 (t, $J = 6.1$ Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 129.55, 127.75, 119.17, 116.01.

\[ \text{NH}_2 \]

2l 99%

According to GP, catalyst (30 mg), 2-nitrobenzamide 1l (82 mg, 0.49 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2l (67 mg, 0.49 mmol, 99%) was obtained as a solid.

$^1$H NMR (400 MHz, DMSO-d$_6$) δ 7.73 (s, 1H), 7.53 (dd, $J = 8.1, 1.6$ Hz, 1H), 7.20–7.10 (m, 1H), 7.07 (s, 1H), 6.68 (d, $J = 8.3$ Hz, 1H), 6.56 (s, 2H), 6.48 (t, $J = 7.5$ Hz, 1H).

$^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 171.76, 150.64, 132.35, 129.21, 116.86, 114.83, 114.12.
According to GP, catalyst (30 mg), 1-ethoxy-2-nitrobenzene 1m (81 mg, 0.49 mmol), in MTHF/H₂O (1.5 mL/0.5 mL), H₂ (20 bar), at 40 °C for 24 h. The product 2m (60 mg, 0.44 mmol, 90%) was obtained as a liquid.

H NMR (400 MHz, CDCl₃) δ 6.83–6.70 (m, 3H), 4.07 (q, J = 7.0 Hz, 2H), 3.70 (s, 2H), 1.44 (t, J = 7.0 Hz, 3H).

C NMR (101 MHz, CDCl₃) δ 146.81, 136.12, 121.05, 118.70, 115.30, 111.57, 63.84, 15.10.

According to GP, catalyst (29 mg), 4-chloro-1-methyl-2-nitrobenzene 1n (85 mg, 0.50 mmol), in MTHF/H₂O (1.5 mL/0.5 mL), H₂ (20 bar), at 40 °C for 24 h. The product 2n (70 mg, 0.50 mmol, >99%) was obtained as a liquid.

H NMR (300 MHz, CDCl₃) δ 6.99–6.88 (m, 1H), 6.67 (d, J = 7.3 Hz, 2H), 3.60 (s, 2H), 2.12 (s, 3H).

C NMR (75 MHz, CDCl₃) δ 145.69, 132.17, 131.42, 120.72, 118.40, 114.63, 16.91.

According to GP, catalyst (30 mg), 1-bromo-4-methyl-2-nitrobenzene 1o (105 mg, 0.49 mmol), in MTHF/H₂O (1.5 mL/0.5 mL), H₂ (20 bar), at 40 °C for 24 h. The product 2o (90 mg, 0.49 mmol, >99%) was obtained as a liquid.

H NMR (300 MHz, CDCl₃) δ 7.30 (d, J = 8.1 Hz, 1H), 6.68–6.58 (m, 1H), 6.54–6.42 (m, 1H), 3.98 (s, 2H), 2.26 (s, 3H).

C NMR (75 MHz, CDCl₃) δ 143.72, 138.48, 132.30, 120.68, 116.64, 106.30, 21.12.
According to GP, catalyst (29 mg), 3-nitropyridine 1q (62 mg, 0.50 mmol), in MTHF/H₂O (1.5 mL/0.5 mL), H₂ (20 bar), at 40 °C for 24 h. The product 2q (45 mg, 0.48 mmol, 98%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl₃) δ 8.05 (dd, $J = 2.8, 0.8$ Hz, 1H), 7.96 (dd, $J = 4.7, 1.5$ Hz, 1H), 7.03 (ddd, $J = 8.2, 4.6, 0.8$ Hz, 1H), 6.93 (ddd, $J = 8.2, 2.8, 1.5$ Hz, 1H), 3.61 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl₃) δ 144.23, 138.83, 127.53, 120.47, 113.31, 112.34, 23.65.

$^2$q 98%

According to GP, catalyst (31 mg), 8-nitroquinoline 1r (87 mg, 0.50 mmol), in MTHF/H₂O (1.5 mL/0.5 mL), H₂ (20 bar), at 40 °C for 24 h. The product 2r (71 mg, 0.49 mmol, 98%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl₃) δ 8.76 (dd, $J = 4.2, 1.7$ Hz, 1H), 8.06 (ddd, $J = 8.3, 1.7, 0.4$ Hz, 1H), 7.42–7.28 (m, 2H), 7.15 (dd, $J = 8.2, 1.3$ Hz, 1H), 6.93 (dd, $J = 7.5, 1.3$ Hz, 1H), 4.82 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl₃) δ 147.41, 144.01, 138.37, 136.16, 128.94, 127.49, 121.38, 116.08, 110.19.

$^2$r 98%

According to GP, catalyst (31 mg), 4-nitrobenzo[c][1,2,5]thiadiazole 1s (97 mg, 0.54 mmol), in MTHF/H₂O (1.5 mL/0.5 mL), H₂ (20 bar), at 40 °C for 24 h. The product 2s (80 mg, 0.53 mmol, >99%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl₃) δ 7.42–7.28 (m, 2H), 6.59 (ddd, $J = 6.8, 1.4, 0.5$ Hz, 1H), 4.69 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl₃) δ 155.87, 147.88, 139.01, 131.30, 110.11, 106.70.

$^2$s >99%
According to GP, catalyst (31 mg), 4-nitrobenzonitrile 1t (76 mg, 0.51 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2t (60 mg, 0.51 mmol, >99%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.38 (d, J = 8.5 Hz, 2H), 6.63 (d, J = 8.4 Hz, 2H), 4.20 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 150.66, 133.82, 120.33, 114.48, 99.90.

According to GP, catalyst (30 mg), 1-(4-nitrophenyl)ethan-1-one 1u (84 mg, 0.51 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2u (65 mg, 0.48 mmol, 94%) was obtained as a solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.91–7.62 (m, 2H), 6.75–6.45 (m, 2H), 4.10 (s, 2H), 2.48 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.68, 151.43, 130.86, 127.70, 113.75, 26.12.

According to GP, catalyst (30 mg), (4-nitrophenyl)(phenyl)methanone 1v (108 mg, 0.48 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2v (90 mg, 0.46 mmol, 95%) was obtained as a solid.

$^1$H NMR (400 MHz, DMSO-$d_6$) δ 7.60–7.48 (m, 5H), 6.63 (d, J = 8.3 Hz, 2H), 6.19 (s, 2H).

$^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 193.88, 154.26, 139.54, 133.06, 131.47, 129.23, 128.63, 124.18, 113.02.

According to GP, catalyst (30 mg), 1-nitro-3-vinylbenzene 1w (75 mg, 0.50 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2w (60 mg, 0.50 mmol, >99%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.13 (t, J = 7.8 Hz, 1H), 6.84 (dt, J = 7.6, 1.3 Hz, 1H), 6.78–6.49 (m, 3H), 5.72 (dd, J = 17.6, 1.0 Hz, 1H), 5.22 (dd, J = 10.9, 1.0 Hz, 1H), 3.54 (s, 2H).
According to GP, catalyst (30 mg), ethyl (E)-3-(4-nitrophenyl)acrylate 1x (107 mg, 0.48 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2x (92 mg, 0.48 mmol, 99%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.61 (d, $J = 15.9$ Hz, 1H), 7.40–7.16 (m, 2H), 6.75–6.55 (m, 2H), 6.25 (d, $J = 15.9$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.93 (s, 2H), 1.33 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 167.80, 148.75, 144.97, 129.90, 124.70, 114.92, 113.67, 60.23, 14.43.

According to GP, catalyst (31 mg), (E)-1-nitro-4-styrylbenzene 1y (108 mg, 0.48 mmol), in MTHF/H$_2$O (1.5 mL/0.5 mL), H$_2$ (20 bar), at 40 °C for 24 h. The product 2y (93 mg, 0.47 mmol, 98%) was obtained as a liquid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.58–7.50 (m, 2H), 7.41 (dddt, $J = 8.1, 4.7, 2.1, 0.7$ Hz, 4H), 7.32 – 7.24 (m, 1H), 7.11 (d, $J = 16.3$ Hz, 1H), 6.99 (d, $J = 16.3$ Hz, 1H), 6.76–6.66 (m, 2H), 3.96 – 3.50 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) δ 146.26, 138.04, 128.79, 128.74, 128.05, 127.84, 126.97, 126.19, 125.16, 115.29.
9. $^1$H NMR and $^{13}$C NMR Spectra of Products

Original spectra for 2b:

\[
\text{PROTON CDCl}_3 \ (\text{C:BrukerTopSpin3.5pfd}) \ 1709 \ 21
\]

\[
\text{C13CPD CDCl}_3 \ (\text{C:BrukerTopSpin3.5pfd}) \ 1709 \ 21
\]
Original spectra for 2c:

\[ \text{Cl} \quad \text{NH}_2 \quad 2c \]
Original spectra for 2d:
Original spectra for 2e:

1H NMR (CDCl3, 400 MHz) - F1 (ppm): 11.00 (s, 1H, NH), 7.65 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 6.70 (s, 2H), 3.80 (s, 3H), 2.40 (s, 3H).

13C NMR (CDCl3, 100 MHz) - F1 (ppm): 170.9 (s), 150.2 (s), 140.3 (s), 111.2 (s), 66.5 (t), 32.0 (t), 20.1 (t).

Structural formula:

```
\begin{.gnu}
  \label{fig:structure}
  \begin{center}
    \includegraphics[width=0.5\textwidth]{structure.png}
  \end{center}
\end{gnu}
```
Original spectra for 2f:

1H/13C  11.02
Li/Wu-2-928
PROTON CDCl3 (C:\Bruker\TopSpin3.5\pk) 1709 29

\[
\text{EtO} \quad \text{2f} \quad \text{NH}_2
\]

1H/13C  11.02
Li/Wu-2-928
C13CPD CDCl3 (C:\Bruker\TopSpin3.5\pk) 1709 29
Original spectra for 2g:
Original spectra for 2h:

![Chemical structure of 2h]

NH₂

OH

170919.f325.10.fid
Li/Wu-2-924
PROTON C2D3 (C:/Bruker/TopSpin3.5/pl6) 1709 25

170919.f325.11.fid
Li/Wu-2-924
C13CPD C2D3 (C:/Bruker/TopSpin3.5/pl6) 1709 25
Original spectra for 2i:
Original spectra for 2j:

\[
\begin{align*}
&\text{NH}_2 \\
&F
\end{align*}
\]

171113.f3 2j

PROTON CDCl3 {C:\Bruker\TopSpin3.5pl6}
Original spectra for 2k:

1H NMR (CDCl3) 8.50 (d, J = 8.7 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.25 (t, J = 7.6 Hz, 1H), 4.00 (s, 3H).
Original spectra for 2l:

Wu Li WU-2-976
AuH DMSO (C:\Bruker\TopSpin3.5Spl) 1709 10

NH₂

NH₂

O
Original spectra for 2m:

1H NMR, 400 MHz
Wu Li WU-2-970
Au1H CDCl3 (C:\Bruker\TopSpin3.5pl6) 1709 12

\[
\text{NH}_2
\]
\[
\text{OEt}
\]

2m
Original spectra for 2n:

Cl\(\text{NH}_2\)

Me

2n
Original spectra for 2o:

170915.f319.10.fid
Wu Li WU-2-914
PROTON CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1709 19

\[\text{Me} \quad \text{NH}_2 \quad \text{Br} \quad 2o\]

L/0913.11.08
Wu Li WU-2-914
C13CPD CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1709 19
Original spectra for 2p:

1H/13C
Li/Wu-2-953
PROTON C2D3 (C:\Bruker\TopSpin3.5\pk) 1709 36

\[
\begin{align*}
\text{Me} & \quad \text{Br} \\
\text{NH}_2 & \quad 2p
\end{align*}
\]
Original spectra for 2r:

![N-attached 2r molecule with NH2 group]

**Proton Spectrums**

- **1H**: ppm values range from 0.0 to 12.0.
- **13C**: ppm values range from 18.0 to 170.0.

**Carbon Spectrums**

- ppm values range from 1.0 to 200.0.

**Deconvoluted Peaks**

- **1H**: ppm values range from 0.0 to 12.0.
- **13C**: ppm values range from 18.0 to 170.0.

**Nomenclature**

- **NH**: 2r
- **NH2**: 2r
Original spectra for 2s:

\[
\text{NH}_2
\]

2s
Original spectra for 2t:

170915.f318.10.fid
Wu Li
WU-2-913
PROTON CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1709 18

NH₂
2t

170915.f318.11.fid
Wu Li
WU-2-913
C13CPD CDCl3 (C:\Bruker\TopSpin3.5\pl6) 1709 18
Original spectra for 2u:

1H and 13C spectra for compound 2u.

Chemical shifts in ppm for protons (f1) and carbon (f2) nuclei.

- Proton spectrum with peaks at various ppm values.
- Carbon spectrum with peaks at various ppm values.

Structural formula of 2u:

![Structural formula of 2u](image)
Original spectra for 2v:

1H and 13C NMR spectra for compound 2v.

Wu Li, WU-2-981
Au1H DMSO (C:\Bruker\TopSpin3.5pl6) 1709 6

NH$_2$

O

Ph

2v
Original spectra for 2w:

\[
\text{\text{NH}_2}
\]

2w

\[
\begin{align*}
\text{f1 (ppm)} & \quad 0.0 & 0.5 & 1.0 & 1.5 & 2.0 & 2.5 & 3.0 & 3.5 & 4.0 & 4.5 & 5.0 & 5.5 & 6.0 & 6.5 & 7.0 & 7.5 & 8.0 & 8.5 & 9.0 & 9.5 & 10.0 & 10.5 & 11.0 & 11.5 & 12.0 \\
\end{align*}
\]

\[
\begin{align*}
l_1/\text{Wu-2-935} & \quad \text{PROTON CDCl}_3 \quad \{C:\text{Bruker/TopSpin3.5pl6}\} \\
\end{align*}
\]
Original spectra for 2x:
Original spectra for 2y:

![Spectra Image]

Ph

2y

NH₂

[Chemical Structures]

170919.f333.10.fid

Li/Wu-2-933

PROTON

CDCl₃

{C:\Bruker\TopSpin3.5pl6}

170933

1.61 1.90 0.97 1.01 1.05 3.89 1.94 3.66 3.68 3.70 3.70 3.72 6.69 6.70 6.71 6.73 6.73 6.74 6.96 7.02 7.08 7.13 7.26 7.26 7.26 7.28 7.28 7.29 7.29 7.30 7.31 7.31 7.37 7.38 7.38 7.38 7.39 7.39 7.39 7.40 7.40 7.41 7.41 7.41 7.42 7.42 7.42 7.43 7.43 7.43 7.44 7.52 7.52 7.53 7.53 7.53 7.54 7.54 7.54 7.55 7.55 7.56 7.56 7.56 7.56 7.57

170919.f333.11.fid

Li/Wu-2-933

C13CPD

CDCl₃

{C:\Bruker\TopSpin3.5pl6}

170933

76.74 77.16 77.58 115.29 125.16 126.19 126.97 127.84 128.05 128.69 128.79 138.04 146.26

NH₂

Ph

2y