Supporting Information

Manganese Catalyzed Selective Hydrogenation of Cyclic Imides to Diols and Amines

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1. General information:

All experiments were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40-2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All non-deuterated solvents were refluxed over sodium/benzophenoneketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All solvents were degassed with argon and kept in the glove box over 4Å molecular sieves. Most of the chemicals used in the experiments were purified according to standard procedures (vacuum distillation). The complex **1**, **2**, **3**, **4**, **5** and **6** complexes were prepared according to the our reported procedures.[1-4] Most of the chemicals used in the catalytic reactions are commercially available and were purified according to standard procedure and some of them were prepared using the literature method.[5-10] NMR spectra were recorded using Bruker Avance III 7T, Avance III 9.4T and Avance III 11.7T NMR spectrometers. All spectra were recorded at 298 K, unless otherwise noted. ^{1}H NMR in $CDCl_3$ (7.26 ppm is solvent peak) solution and reported in ppm (δ). GC–MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30 m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas.

2. Experimental procedures:

(a) Procedure for the catalytic hydrogenation of cyclic imides:

#Catalytic hydrogenation of N-benzylphthalimide

In a N_2 glove box, 0.02 mmol of the Mn complex (**1**-**4** as mentioned in Table 1) and 0.03 mmol of ^{t}BuOK (if required) were added in 2 mL solvent to a 20 mL vial. This mixture was stirred for 3 min, then N-benzylphthalimide (1 mmol) and mesitylene (1 mmol, 120 mg, internal standard) were added to it and it was transferred to a 25 mL steel autoclave fitted with a Teflon sleeve. The autoclave was taken out of the glove box and pressurized with H_2 (pressure as specified in Table 1) and heated at the specified temperature with stirring (as specified in Table 1), after which the steel autoclave was cooled in an ice-bath for 30 min and the H_2 was vented off carefully. The cold solution was then filtered through Celite and the solution was analyzed by ^{1}H NMR spectroscopy and GC-MS. The conversion of cyclic imides and the yields of amines and diols were determined by GC-MS and ^{1}H NMR spectroscopy with respect to the internal standard (mesitylene).

Table S1: Optimization of the catalytic conditions for hydrogenation of N-benzylphthalimide.[a]

entry	[**Mn**]	H_2 (bar)	Temp (°C).	Solvent	T (h)	Conv. (%)[b]	yield (%) of diol/amine[b]
1	**1**	40	110	THF	24	-	-
2	**1**	40	130	THF	48	trace	-
3	**2**	40	110	THF	24	-	-
4	**2**	40	130	THF	36	43	35/40
5	**2**	40	130	THF	48	65	62/63
6	**3**	40	110	THF	24	-	-
7	**3**	40	130	THF	48	10	nd
8	**4**	40	130	THF	24	78	68/73
9	**4**	40	130	THF	36	90	75/87
10	**4**	**30**	**130**	**THF**	**48**	**>99**	**98(94)[c]/99(92)[c]**
11	**4**	20	130	THF	48	>99	65[d]/99
12	**4**	30	130	1,4-Dioxane	48	98	92 /97
13	**4**	30	130	Toluene	48	70	68/70
14	**4**	30	130	p-Xylene	48	66	60/63

[a]Reaction conditions: Catalyst [**Mn**] (0.02 mmol), ^{t}BuOK (0.03 mmol), N-benzylphthalimide (1 mmol), solvent (2 mL), H_2 (20-40 bar). [b]Conversion of N-benzylphthalimide and yields of diols and amines were determined by GCMS and/or ^{1}H NMR spectroscopy using mesitylene as an internal standard. [c]Isolated yields. [d]Phthalide is minor product.

#(Table 2): Genaral procedure for the ctalaytic hydrogenation of cyclic imides

In a N_2 glove box, 11 mg (0.02 mmol) of complex **4** and 3.5 mg (0.03 mmol) of ^{t}BuOK in 2 mL of THF were added to a 20 mL vial. To this suspension, 1 mmol cyclic imide and mesitylene (1 mmol, 120 mg, internal standard) were added and placed in a 25 mL steel autoclave fitted with a Teflon sleeve. The autoclave was pressurized with H_2 (30 bar, amount of hydrogen gas was aproximatly 30 mmol) and heated at 130 °C for 48h, after which the steel autoclave was cooled in an ice-bath for 30 min and the H_2 was vented off carefully. The cold solution was then filtered through Celite and the solution was analyzed by ^{1}H NMR spectroscopy and GC-MS. The conversion of carbamates and the yields of amines and alcohols were determined by GC-MS and ^{1}H NMR spectroscopy with respect to the internal standard (mesitylene). Isolation of products were done by colloum chromatography.

3. Analysis of organic compounds

Identification of the products were confirmed by the GC-MS. Conversion of cyclic imides, yields of diol and amine were determined by the GC-MS and ^{1}H NMR spectroscopy using mesitylene as an internal standard. The qualitative analysis (retention time) of the products (diols and amines) were performed in comparison to the corresponding authentic samples (commercially purchased). For quantitative analysis, a response factor was determined by injecting different concentration ratio of either diol or amine and the internal standard, mesitylene, following the same procedure used earlier by us.[11] GC–MS was carried out on HP 6890 (flame ionization detector and thermal conductivity detector) and HP 5973 (MS detector) instruments equipped with a 30m column (Restek 5MS, 0.32 mm internal diameter) with a 5% phenylmethylsilicone coating (0.25 mm) and helium as carrier gas.

(a) Representative GC-MS spectra of the crude reaction mixtures of catalytic hydrogenation of cyclic imides:

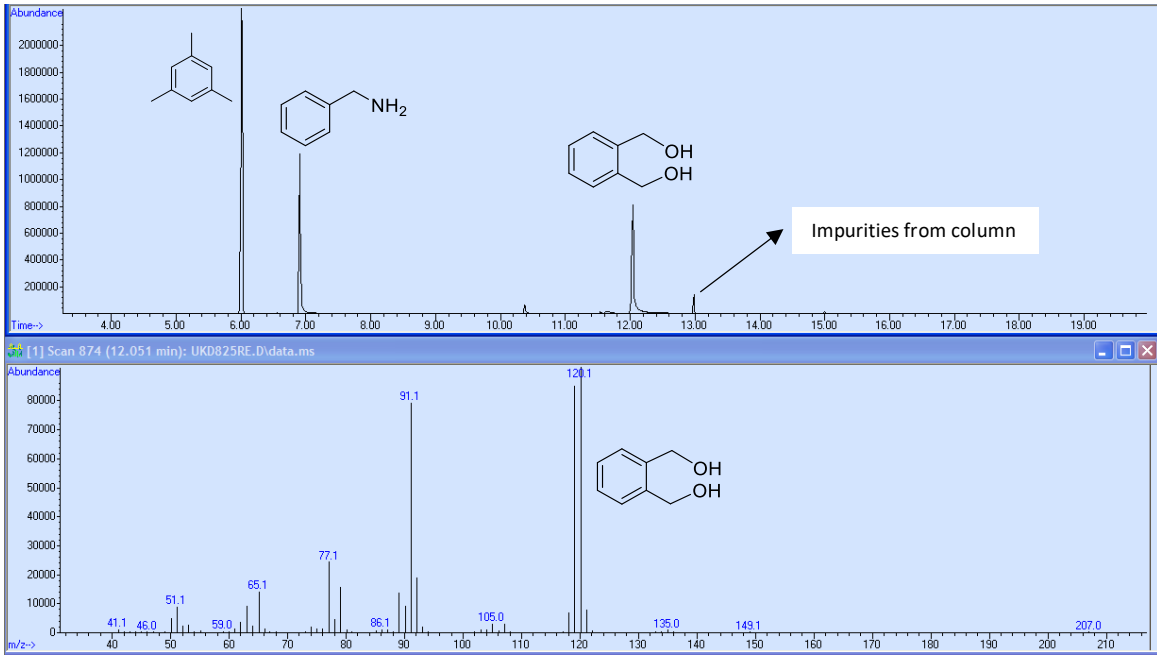

Figure S1. GC-MS spectrum of the crude reaction mixtures of hydrogenation of N-benzylphthalimide (Table 1, entry 7) with mesitylene as internal standard.

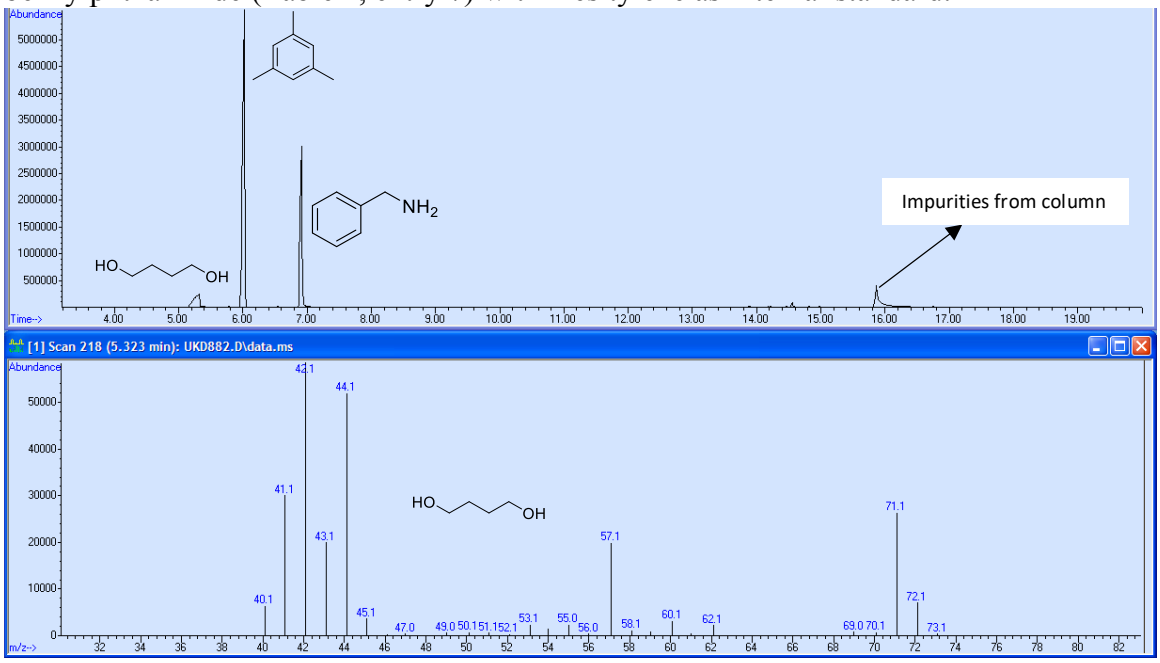

Figure S2. GC-MS spectrum of the crude reaction mixtures of hydrogenation of N-benzylsuccinimide (Table 2, entry 10) with mesitylene as internal standard.

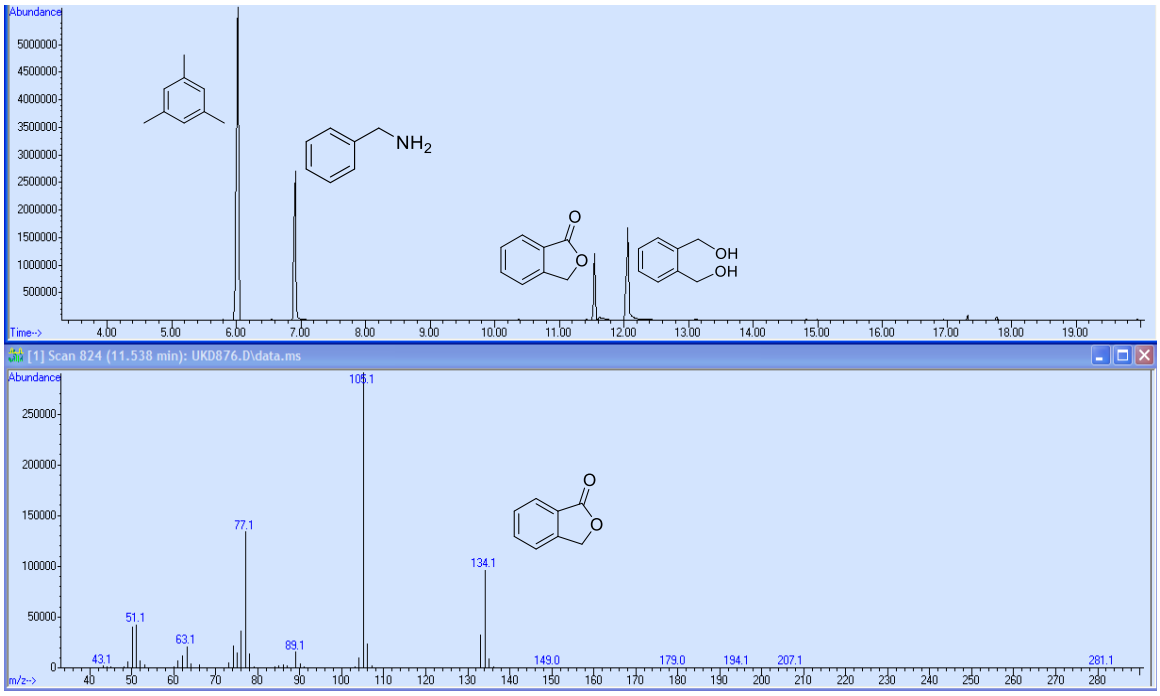

Figure S3. GC-MS spectrum of the crude reaction mixtures of low pressure hydrogenation of N-benzylphthalimide (scheme 3c) with mesitylene as internal standard.

(b) Representative NMR data of some isolated compounds and ^{1}H NMR spectra of the crude reaction mixtures of catalytic hydrogenation of cyclic imides:

1,2-Benzenedimethanol
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 3.20 (s, 2H), 4.65 (s, 4H), 7.26-7.30 (m, 4H). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ = 64.1, 128.6, 129.7, 139.4.

1,4-Butanediol
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.55 (m, 4H), 3.52 (m, 4H). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ = 29.7, 62.4.

Benzylamine
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.31 (s, 2H), 3.79 (s, 4H), 7.14-7.27 (m, 5H). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ = 46.5, 126.7, 127.0, 128.5, 143.4.

Hexylamine
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.82 (t, J = 7.0 Hz, 3H), 0.96 (s, 2H), 1.22-1.29 (m, 6H), 1.35-1.41 (m, 2H), 2.61 (t, J = 7.0 Mz, 2H). ^{13}C{1H} NMR ($CDCl_3$, 125 MHz): δ = 13.9, 22.6, 26.5, 31.7, 33.9, 42.3.

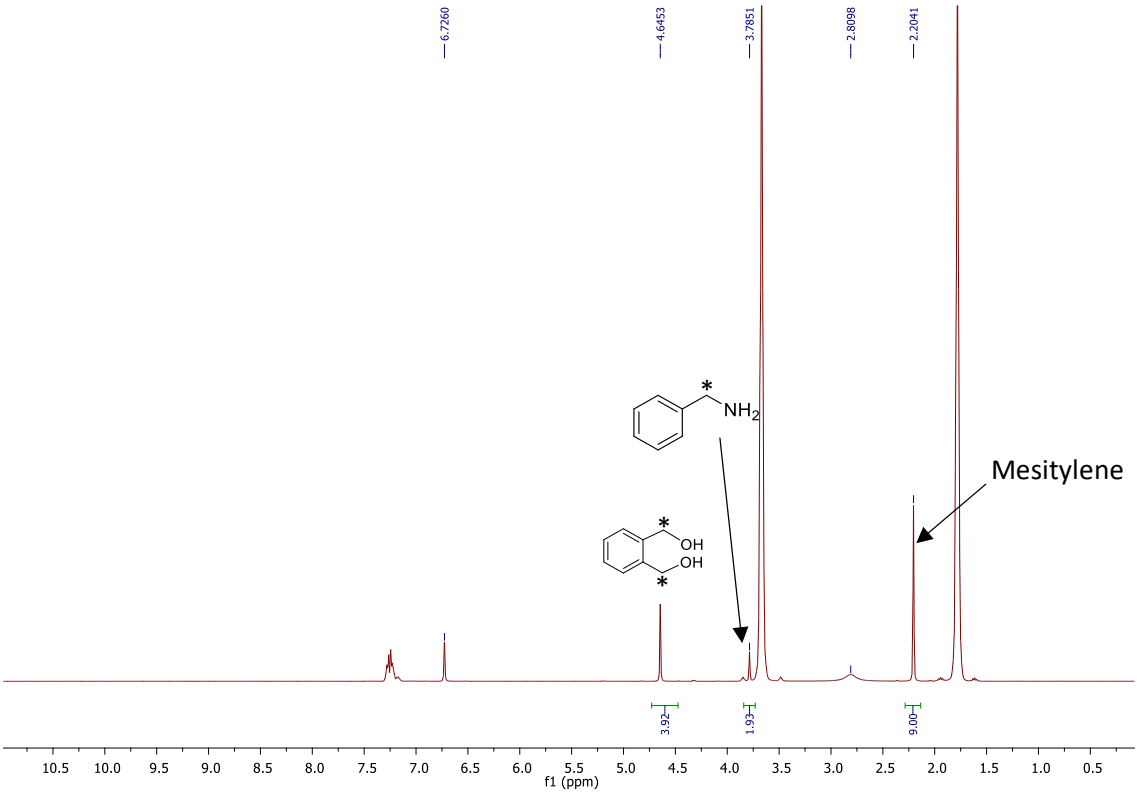

Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of the crude reaction mixture of hydrogenation of N-benzylphthalimide (Table 1, entry 7).

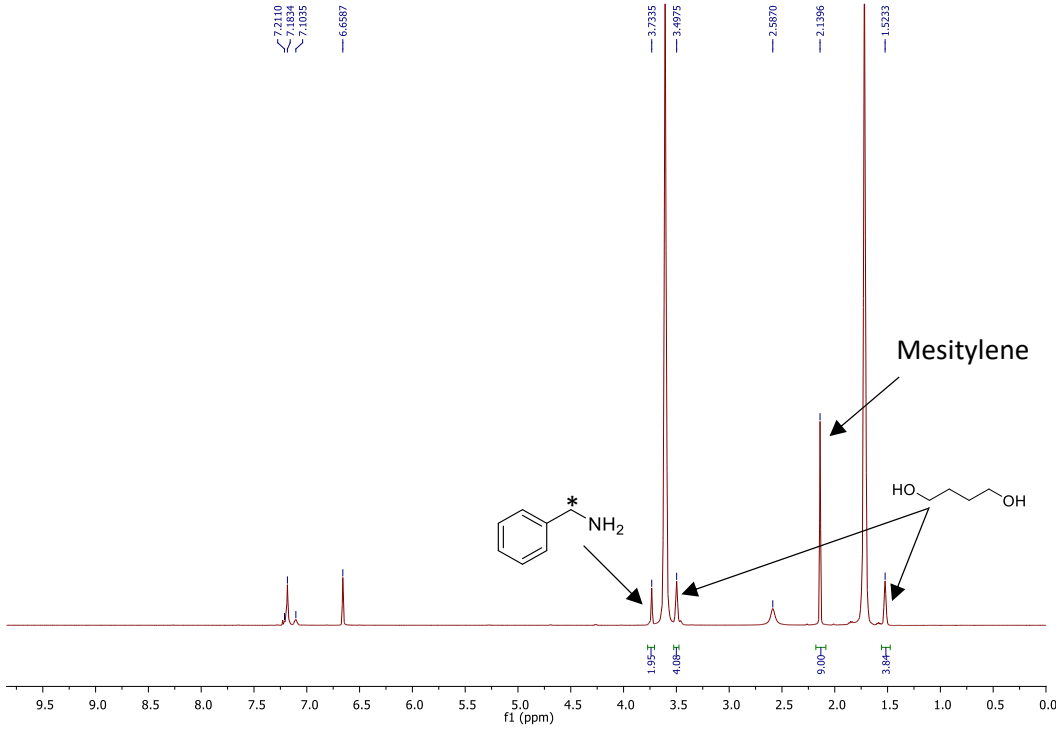

Figure S5. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of the crude reaction mixture of hydrogenation of N-benzylsuccinimide (Table 2, entry 10).

3. References:

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