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S1. General Information

General comments

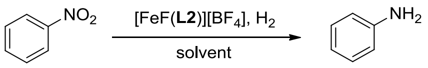
All reactions were carried out under argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros, Alfa Aesar and used without further purification. NMR data were recorded on Bruker ARX 400 and Bruker ARX 300 spectrometers. ^{13}C- and ^{1}H-NMR spectra were referenced to signals of the deutero solvents. The Gas chromatography analysis was performed on an Agilent HP-6890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. Gas chromatography-mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.25 mm i.d., 0.25 µm film thickness) using helium carrier gas. HRMS was performed on MAT 95XP (EI) and Agilent 6210 Time-of-Flight LC/MS (ESI).

All hydrogenation reactions were carried out in an eight-fold parallel reactor array with a reactor volume of 3.0 mL (Institute of Automation (IAT), Richard Wagner Str. 31/H. 8, 18119 Rostock-Warnemünde, Germany).

The in situ NMR-experiments were performed in a sapphire tube[1] on a BRUKER Avance 400 spectrometer using a broadband observe probe, which was properly tuned and matched each time. The integrals of the different spectra were measured and calibrated using standard NMR software (i.e. Topspin version 1.3, BRUKER, Germany).

S1. Reaction parameters

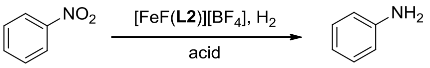
Table 1. Iron-catalyzed hydrogenation of nitrobenzene: Influence of solvents.[a]



Entry	solvent	conv. (%)[b]	yield (%)[b]	select. (%)
1	MeOH	31	25	79
2	EtOH	54	42	82
3	*i*-PrOH	51	49	96
4	*t*-AmOH	87	87	>99
5	THF	82	79	96
6	Toluene	14	9	69

[a] Reaction conditions: 0.5 mmol nitrobenzene, 2 mol% [FeF(**L2**)][BF_4], 120 °C, 2 h, 30 bar H_2, 1.5 mL solvent, 20 µL TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

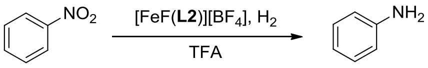
Table 2. Screening of different acids for the iron-tetraphos-catalyzed hydrogenation of nitrobenzene.[a]



entry	acid	conv. (%)[b]	yield (%)[b]	select. (%)
1	acetic acid	-	-	-
2	benzoic acid	-	-	-
3	p-toluenesulfonic acid	13	13	>99
4	benzenesulfonic acid	15	15	>99
5	triphenylacetic acid	-	-	-
6	Trifluoroacetic acid	54	54	>99
7	methanesulfonic acid	19	16	84
8	methanesulfonic acid anhydride	20	15	75
9	phosphoric acid	-	-	-
10	tetrafluoroboric acid (40% in H_2O)	30	27	90

[a] Reaction conditions: 0.5 mmol nitrobenzene, 1 mol% [FeF(**L2**)][BF_4], 120 °C, 2 h, 20 bar H_2, 1.5 mL *t*-AmOH, 50 mol% TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

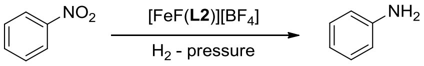
Table 3. Varying the TFA concentration for the iron-tetraphos-catalyzed hydrogenation of nitrobenzene.[a]



entry	TFA in mol%	conv. (%)[b]	yield (%)[b]	select. (%)
1	-	-	-	-
2	12.5	20	20	>99
3	25	32	31	97
4	50	54	52	96
5	100	74	68	92
6	150	77	70	91

[a] Reaction conditions: 0.5 mmol nitrobenzene, 1 mol% [FeF(**L2**)][BF_4], 120 °C, 2 h, 20 bar H_2, 1.5 mL *t*-AmOH, TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

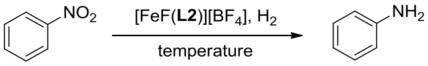
Table 4. Varying the hydrogen pressure for the iron-tetraphos-catalyzed hydrogenation of nitrobenzene.[a]



entry	H_2 pressure (in bar)	conv. (%)[b]	yield (%)[b]	select. (%)
1	2	11	9	82
2	5	23	20	87
3	10	45	43	96
4	20	54	53	98
5	30	51	48	94
6	40	43	42	98
7	60	33	33	>99

[a] Reaction conditions: 0.5 mmol nitrobenzene, 1 mol% [FeF(**L2**)][BF_4], 120 °C, 2 h, 20 bar H_2, 1.5 mL *t*-AmOH, TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

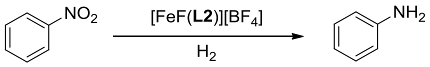
Table 5. Temperature dependence of the iron-tetraphos-catalyzed hydrogenation of nitrobenzene.[a]



entry	temperature (in °C)	conv. (%)[b]	yield (%)[b]	select. (%)
1	100	42	42	>99
2	120	71	69	97
5	140	68	66	97

[a] Reaction conditions: 0.5 mmol nitrobenzene, 1 mol% [FeF(**L2**)][BF_4], 120 °C, 2 h, 20 bar H_2, 1.5 mL *t*-AmOH, 100 mol% TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

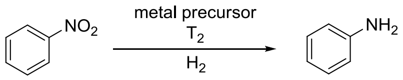
Table 6. Catalyst concentration for the iron-tetraphos-catalyzed hydrogenation of nitrobenzene.[a]



entry	Catalyst loading (in mol%)	conv. (%)[b]	yield (%)[b]	select. (%)
1	0.1	7	7	>99
2	0.5	33	33	>99
3	1.0	71	69	97
4	1.5	91	91	>99
5	2.0	100	>99	>99

[a] Reaction conditions: 0.5 mmol nitrobenzene, [FeF(**L2**)][BF_4], 120 °C, 2 h, 20 bar H_2, 1.5 mL *t*-AmOH, 100 mol% TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

Table 7. Different precursor for the hydrogenation of nitrobenzene.[a]

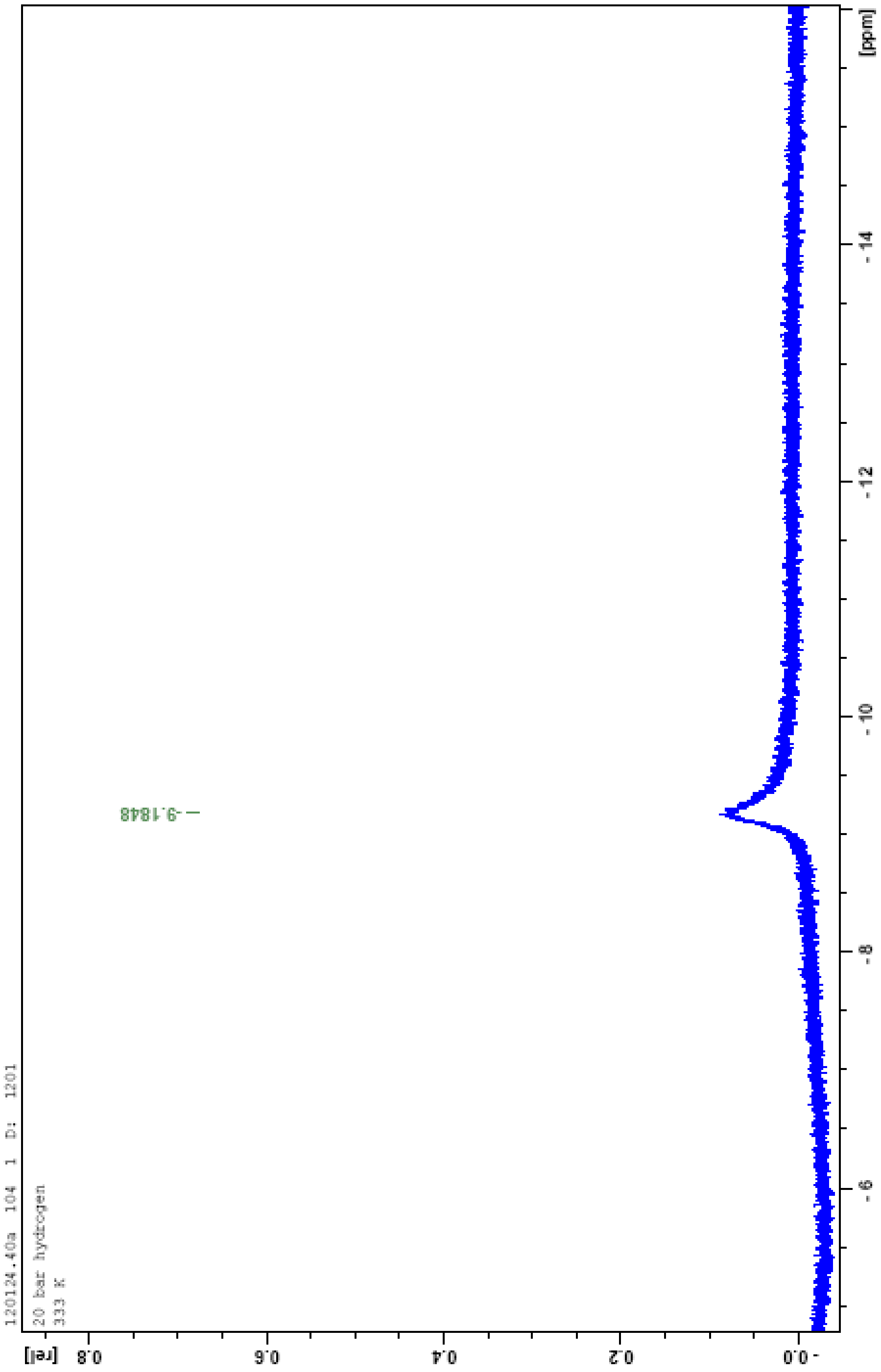


entry	precursor	conv. (%)[b]	yield (%)[b]	select. (%)
1	$Fe(BF_4)_2 \cdot 6H_2O$	66	66	>99
2	$Fe(acac)_2$	51	48	94
3	$Fe(acetate)_2$	54	51	94
4	$FeCl_2 \cdot 4H_2O$	-	-	-
5	$Cu(BF_4)_2 \cdot xH_2O$	-	-	-
6	$Co(BF_4)_2 \cdot 4H_2O$	-	-	-

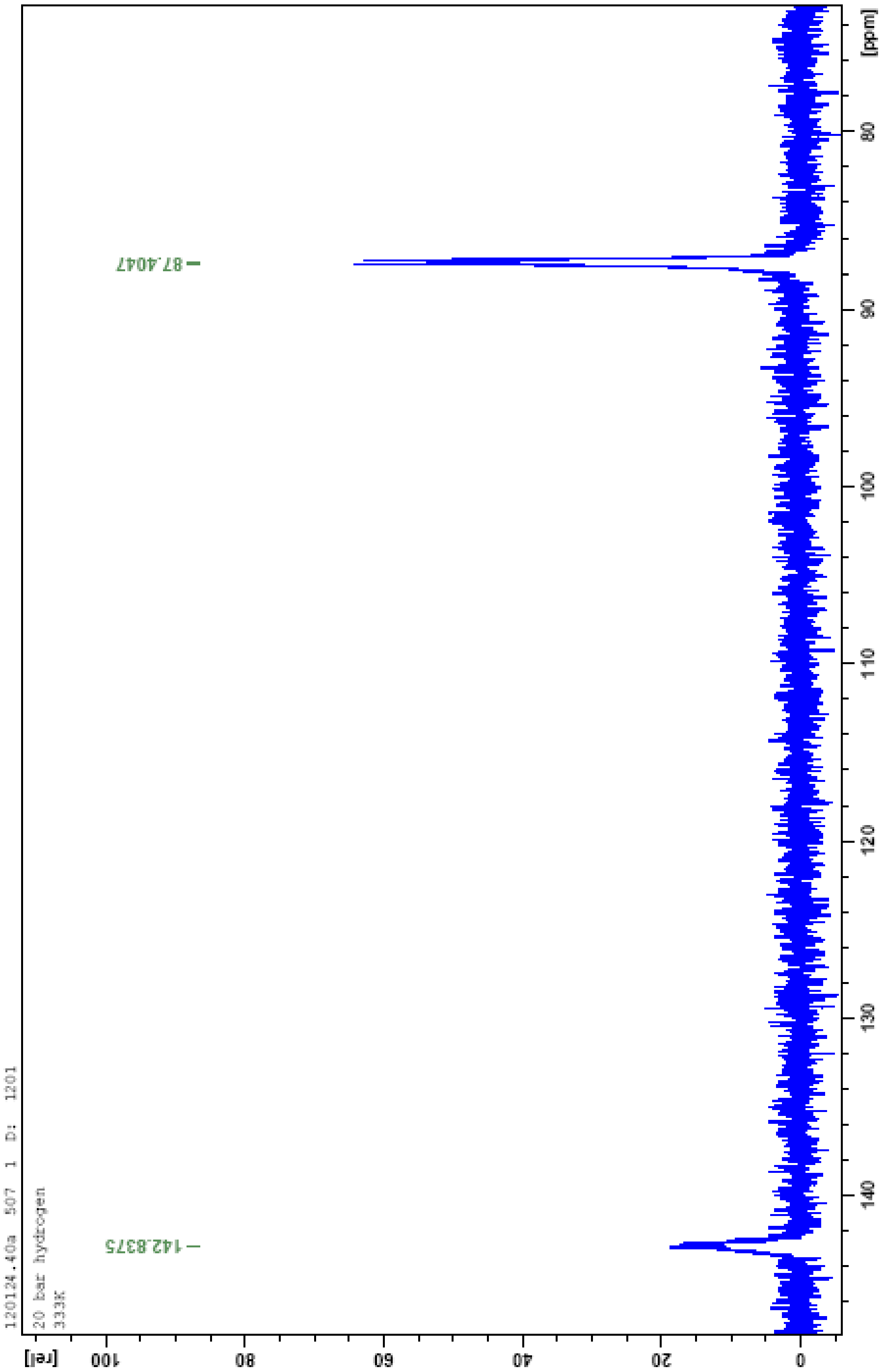
[a] Reaction conditions: 0.5 mmol nitrobenzene, 1 mol% precursor/ **L2**, 120 °C, 2 h, 20 bar H_2, 1.5 mL *t*-AmOH, 50 mol% TFA. [b] Determined by GC using *n*-hexadecane as an internal standard.

S3. In situ NMR-experiments

H-NMR spectra at 20 bar and 233 K



P-NMR spectra at 20 bar and 233 K



S4. Preparation of the defined complexes

$Fe(BF_4)_2 \cdot 6H_2O$ and **L1** were purchased from Sigma-Aldrich. The ligand **L2** was synthesized according to the Literature.[2] The molecular defined complexes [FeF(**L1**)][BF_4] was synthesized according to literature protocols.[3] Synthesis for [FeF(**L2**)][BF_4] :

186 mg $Fe(BF_4)_2 \cdot 6H_2O$ (0.276 mmol) and 450 mg of the ligand **L2** (1 equiv) were solved in 25 mL THF and slowly a purple precipitate occurred. After stirring for 20 min 500 mg (93%) of [FeF(**L2**)][BF_4] could be isolated. The complex is paramagnetic. HRMS: calculated: $C_{54}H_{42}FFeP_4$: 889.15662; found: 889.15626

S5. General Procedure for hydrogenation of nitroarene

General procedure for the hydrogenation of nitrobenzene: 9.8 mg [FeF(T_2)][BF_4] (2 mol%) are placed in an autoclave under argon atmosphere. 1.5 mL t-AmOH, 52 µL nitrobenzene (0.5 mmol) and 40 µL TFA (0.5 mmol) are added. The argon atmosphere is replaced by 20 bar of hydrogen. The autoclave is heated to 120 °C for 2 h while the solution is continuously stirred. After cooling to room temperature, 100 µL *n*-hexadecane are added as an internal standard for GC-analysis. The reaction solution is neutralized with a saturated $NaHCO_3$-solution. A sample is taken for GC-analysis, conversions and yields are determined by comparison with authentic samples.

S6. References

[1] D. C. Roe, *J. Magn. Reson.* **1985**, *63*, 388.

[2] B. Chiswell and L. M. Venanzi, *J. Chem. Soc. A*, **1966**, 417-419.

[3] C. Bianchini, M. Peruzzini, A. Ceccanti, F. Laschi, P. Zanello, *Inorg. Chim. Acta* **1997**, *259*, 61-70.