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Zinc−Zinc Bonded Decamethyldizincocene $Zn_2(\eta^5\text{-}C_5Me_5)_2$ as Catalyst for the Inter- and Intramolecular Hydroamination Reaction

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Supporting Information

13 pages

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Experimental Section.

General considerations: NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99 atom % D).

Hydroamination Reactions: The catalyst was weighed under argon in a NMR tube. C_6D_6 (≈ 0.5 mL) was condensed into the NMR tube, and the mixture was frozen at –196 °C. The reactant was injected onto the solid mixture, and the whole sample was melted and mixed just before insertion into the core of the NMR machine (t_0). The ratio between the reactant and the product was calculated by comparison of the integrals of the corresponding signals. Ferrocene was used as an internal standard for kinetic measurements.

Intramolecular hydroamination

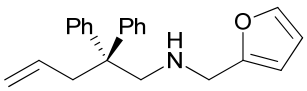
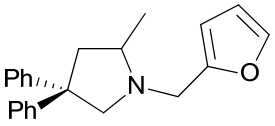
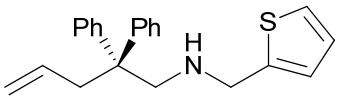
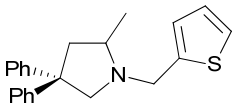
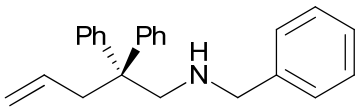
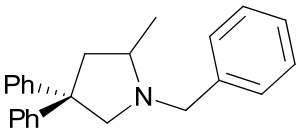
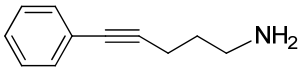
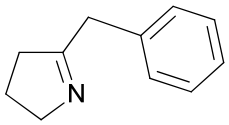
The substrates (2,2-diphenylpent-4-enyl)-furan-2-ylmethyl-amine,[1] (2,2-diphenyl-4-pentenyl)-thiophen-2-ylmethylamine,[2] benzyl(2,2-diphenyl-4-pentenyl)amine,[3] 5-phenyl-4-pentyn-1-amine[4] were synthesized according to literature procedures. The ^{1}H NMR spectra of 1-furan-2-ylmethyl-2-methyl-4,4-diphenyl-pyrrolidine,[1] 2-methyl-4,4-diphenyl-1-thiophen-2-ylmethylpyrrolidine,[5] 1-benzyl-2-methyl-4,4-diphenyl-pyrrolidine,[3] and 2-benzyl-1-pyrroline[4] conform to the literature.

Intermolecular hydroamination

The substrates were purchased from Aldrich, AlfaAesar and Acros.

The ^{1}H NMR spectra of *N*-(methylbenzylidene)aniline,[6] methylphenyl(1-phenylvinyl)amine,[7] *N*-(1-phenylethylidene)-4-chloroaniline,[8] 3-methoxy-*N*-(1-phenylethylidene)aniline,[9] *N*-(1-phenylethylidene)-2,4,6-trimethylaniline,[10] *N*-[1-(4-bromophenyl)ethylidene)]benzenamine,[11] *N,N*-dimethyl-4-[1-(phenylimino)]ethylaniline,[12] and *N*-[1-(4-methoxyphenyl)ethylidene]aniline[8] conform to the literature.

Table SI1 Intramolecular Hydroamination of Anilines and Alkynes Catalyzed by [(η^5-Cp*)$_2$Zn$_2$].[a]

entry	Substrate	Time / Conversion[b]	Product
1		40 min Quant.	
2		10 min Quant.	
3		30 min[c] Quant.	
4		9 h 85% (18% bypr) 14 h 94% (20% bypr)	

[a] *Reagents and Conditions*: Substrate (0.5 mmol), catalyst (2.5 mol%), [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (2.5 mol%), C$_6$D$_6$, 80 °C; [b] Determined by ^{1}H NMR; [c] reaction temperature: 40 °C; bypr = byproduct = enamine.

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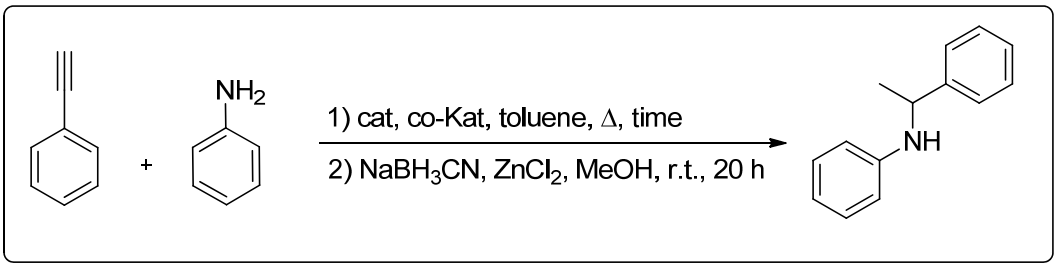
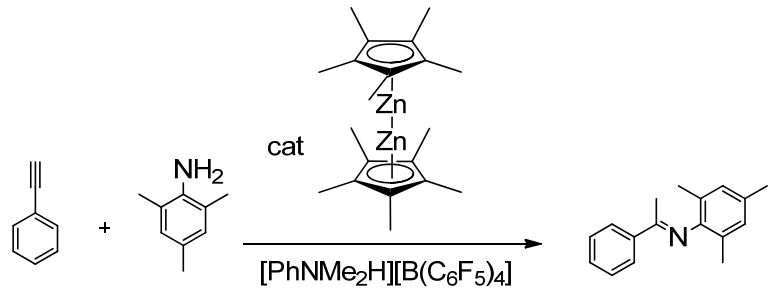
Figure S1.



Entry/ Ref.	Cat.	*T* [°C]	*t* [h] first step	Isolated Yield [%]	mol% cat.	Ratio amine/ alkyne
1	$[(\eta^5\text{-Cp*})_2Zn_2]$	80	15	89	2.5	1:1
2	$Zn(OTf)_2$	120	24	98	5	1.3:1[13]

Kinetics

Figure S2.



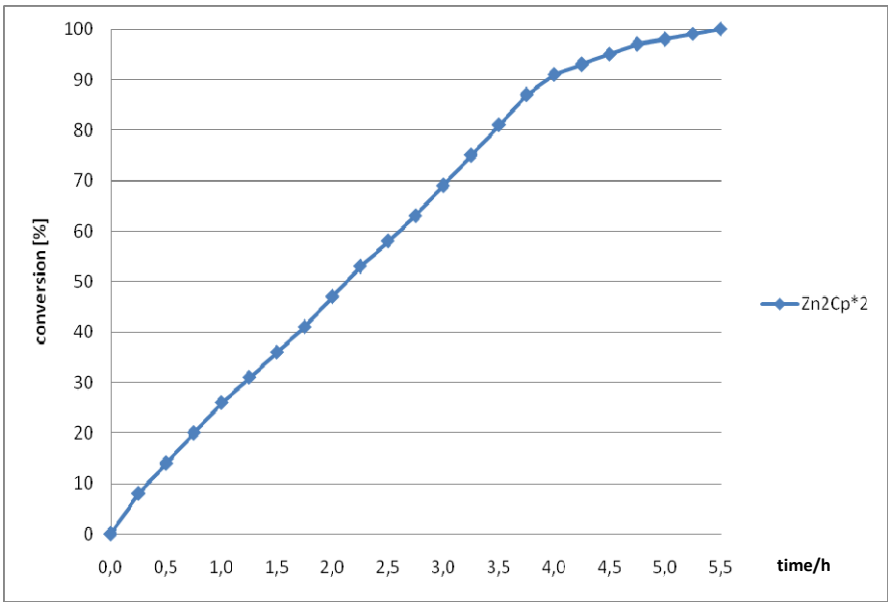
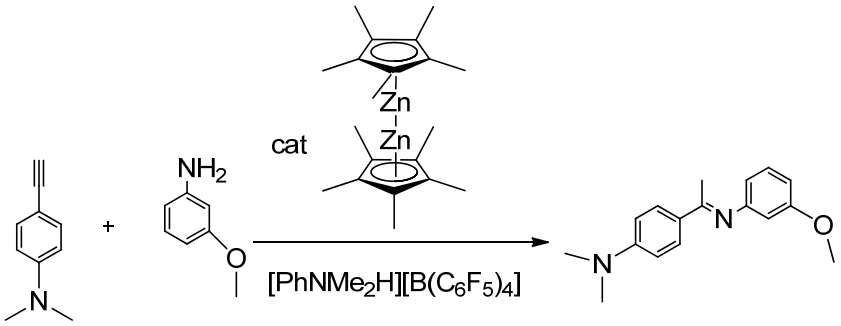
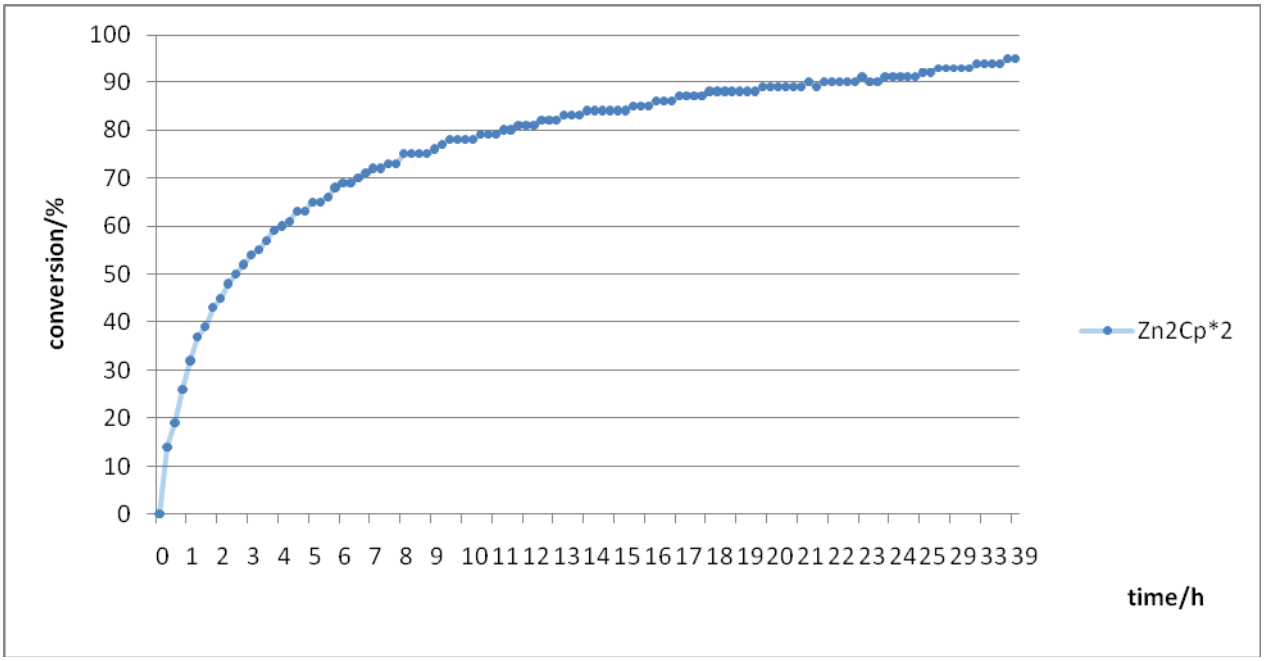


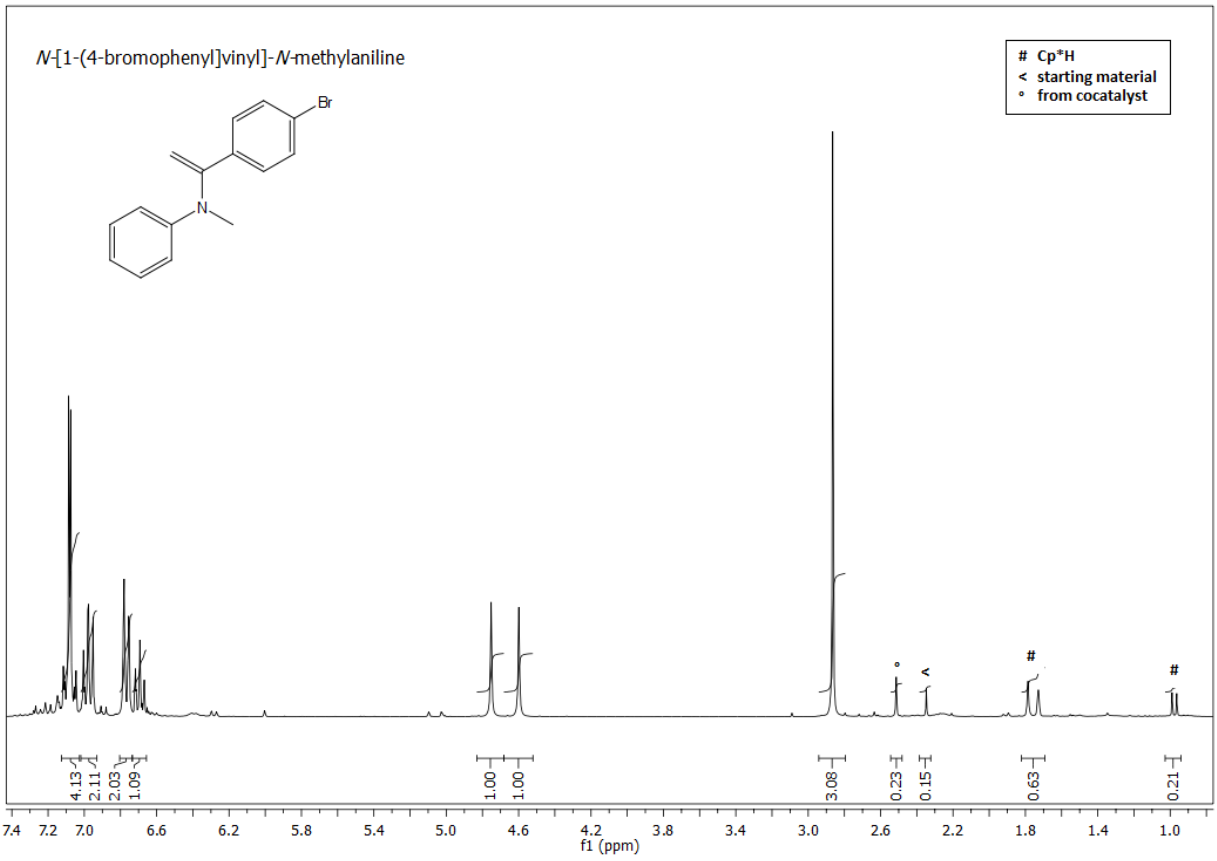
Figure S3.

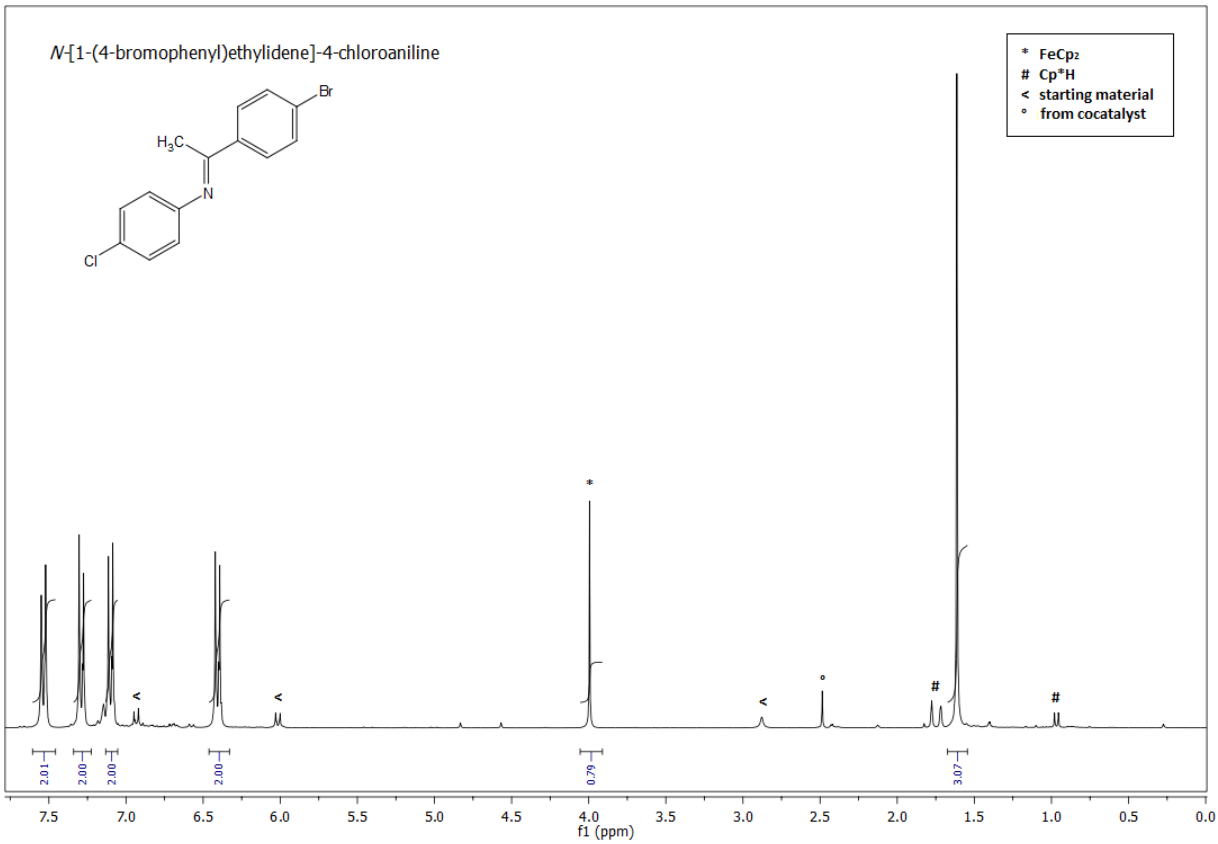

Zn
Zn
cat
NH2
O
N
[PhNMe2H][B(C6F5)4]
N
N
O

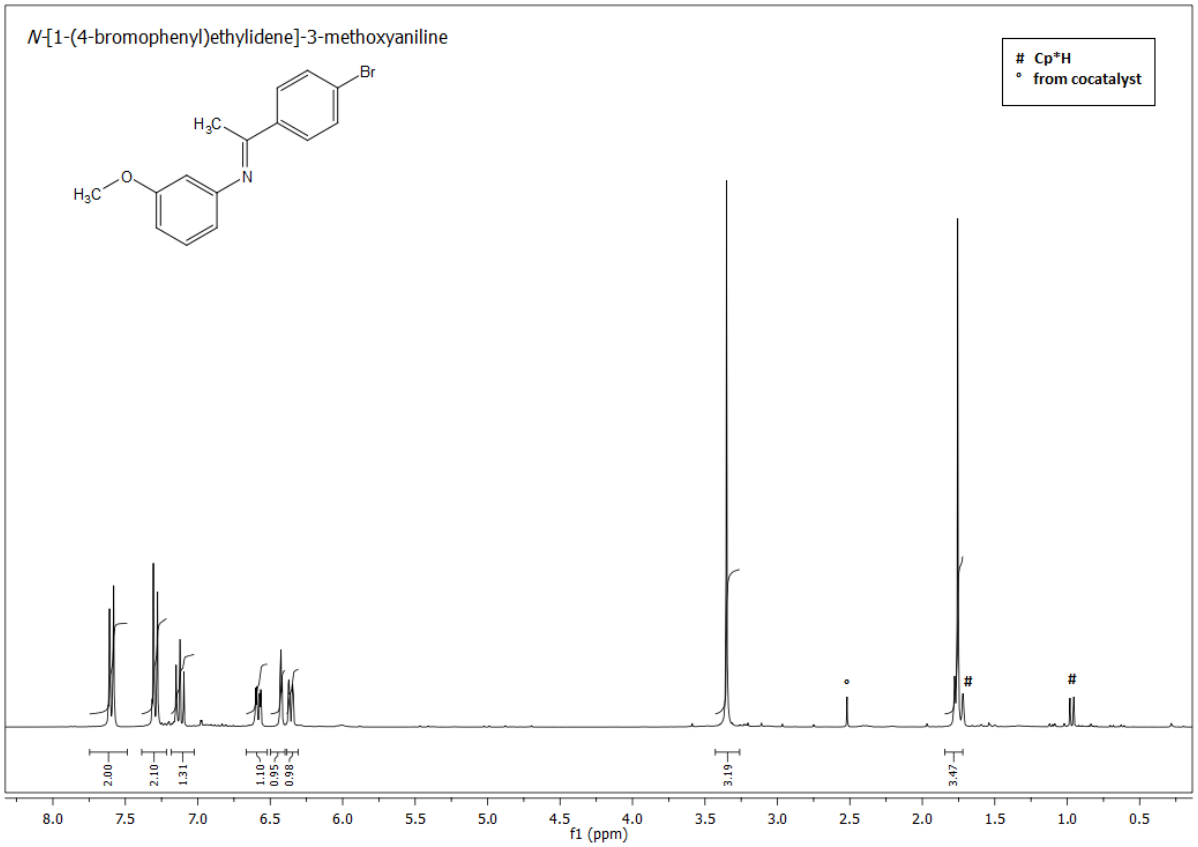

100
90
80
70
60
50
40
30
20
10
0
conversion/%
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 29 33 39
time/h
Zn2Cp*2

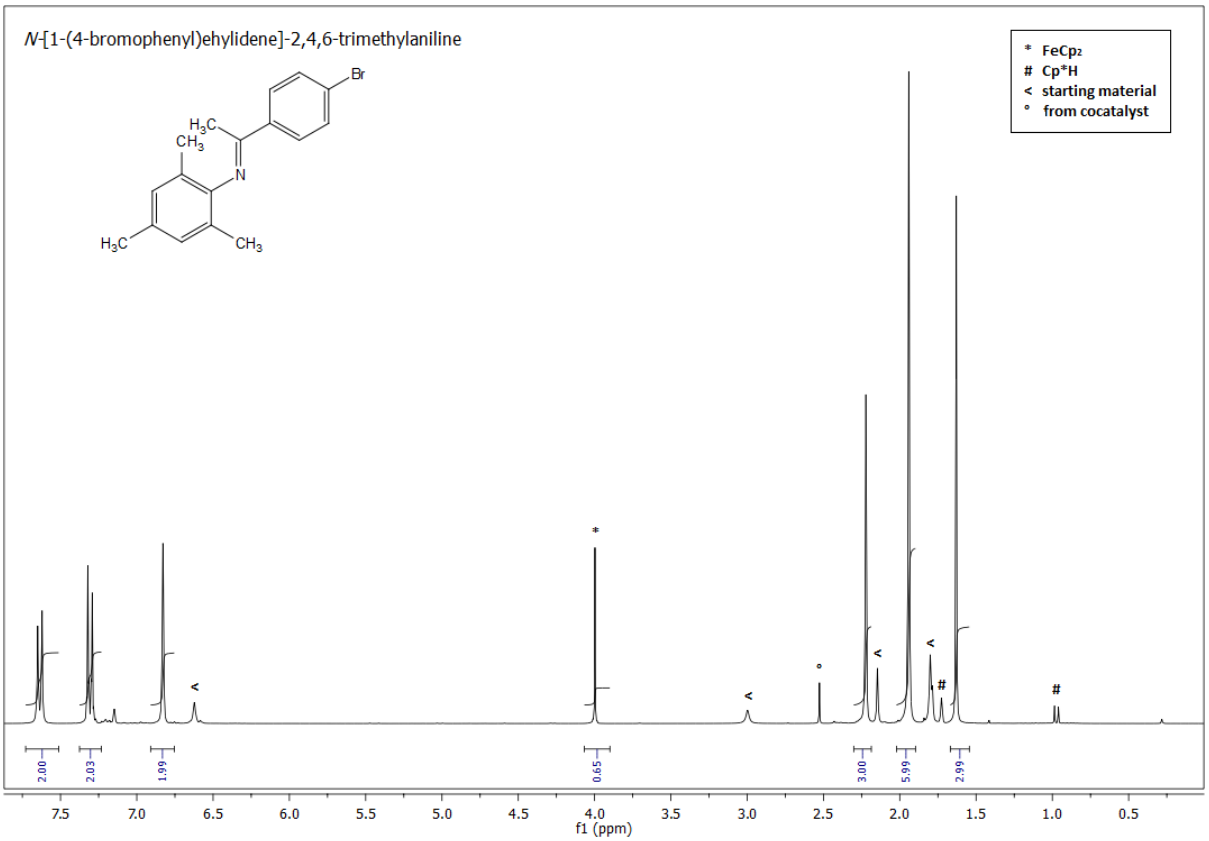
NMR

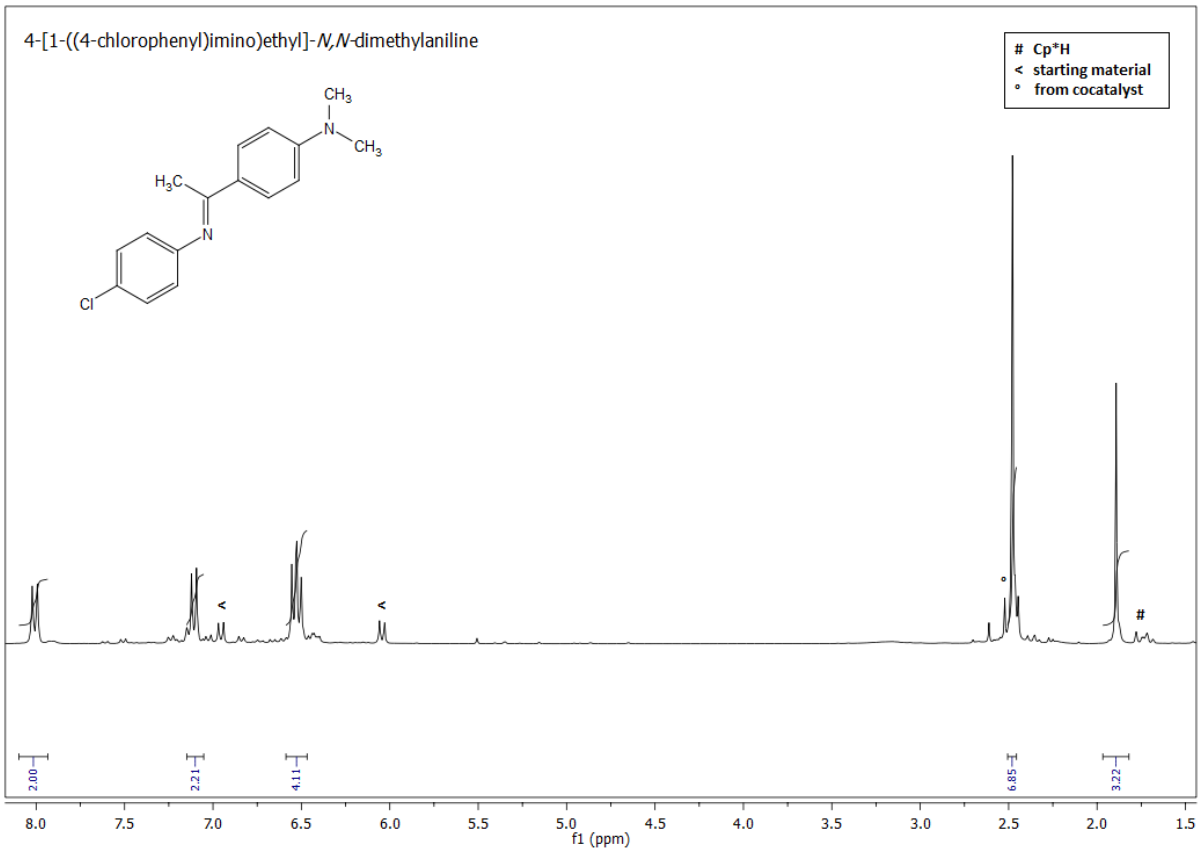
The NMR spectra shown are taken directly from NMR scale reactions without further purification to shown the high conversion and not the absolute purity of the samples. Therefore traces of the catalyst, the cocatalyst, and the internal standard (Cp_2Fe) and in some cases also small traces of the starting materials are seen in the spectra.

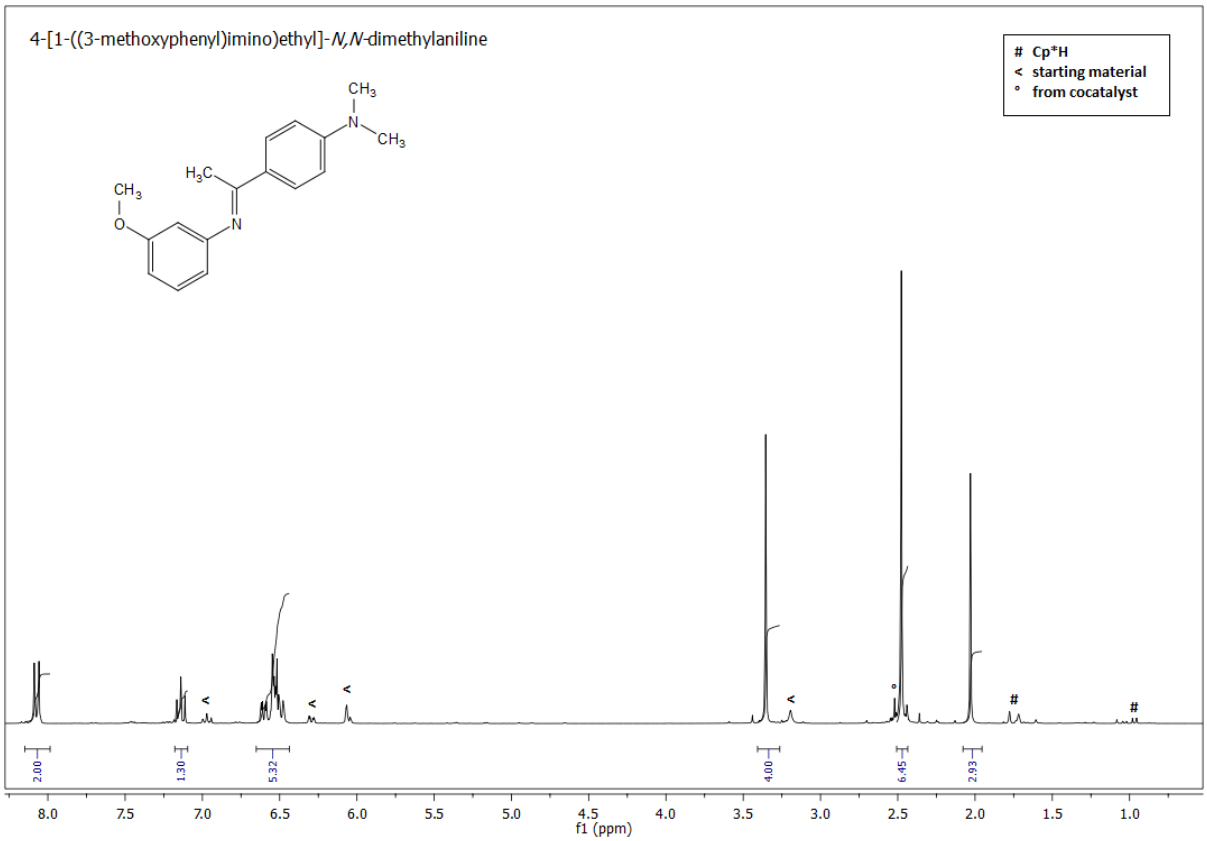


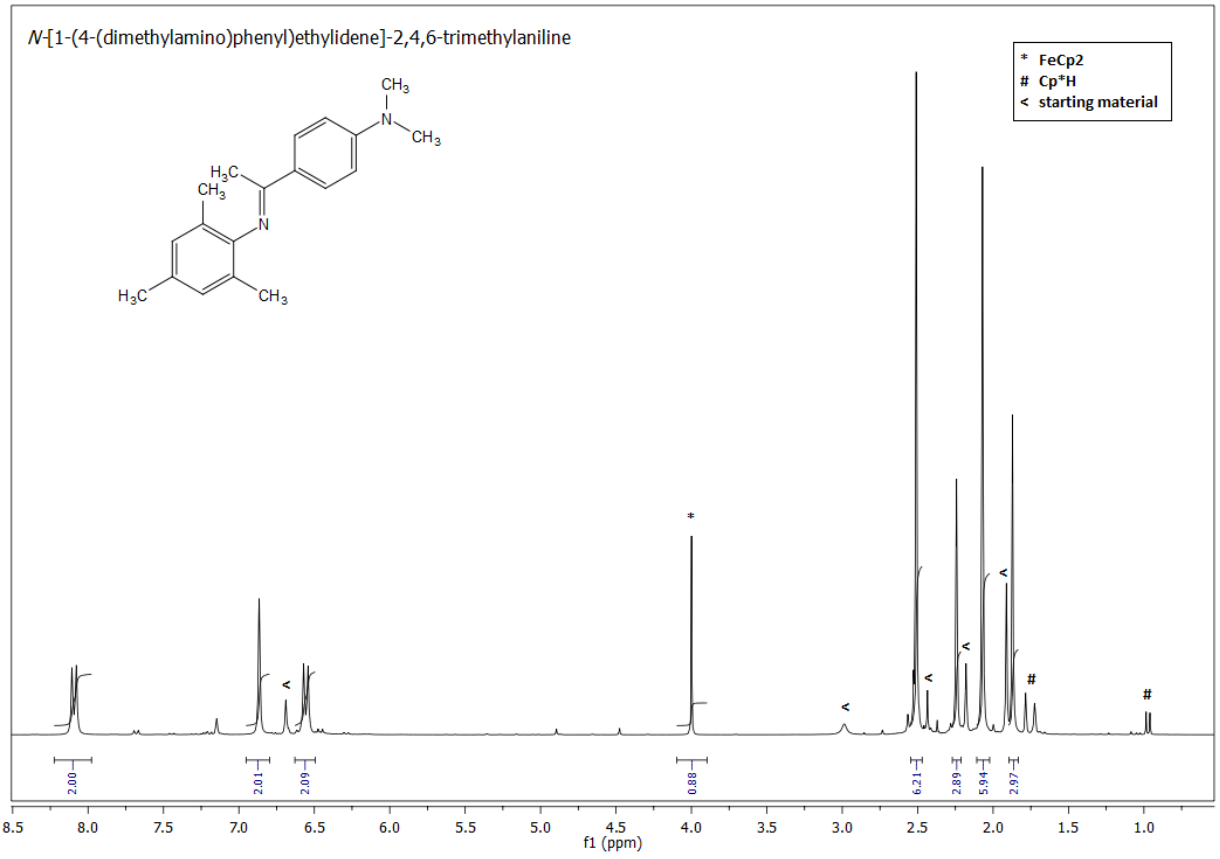

N-[1-(4-bromophenyl)ethylidene]-4-chloroaniline
Br
H3C
N
Cl
* FeCp2
# Cp*H
< starting material
° from cocatalyst
2.01
2.00
2.00
2.00
0.79
3.07
f1 (ppm)

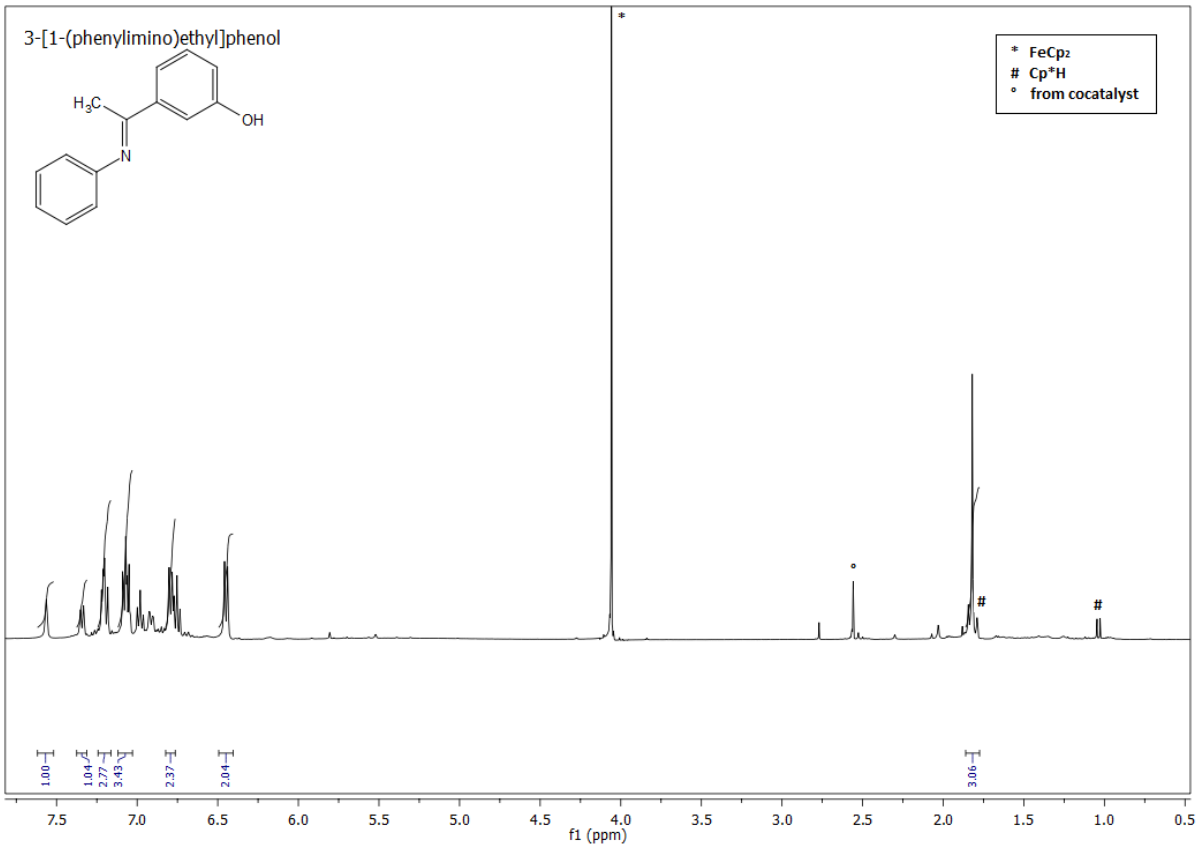

N-[1-(4-bromophenyl)ethylidene]-3-methoxyaniline
Br
H3C
O
H3C
N
Cp*H
° from cocatalyst
2.00
2.10
1.31
1.10
0.95
0.98
3.19
3.47
f1 (ppm)

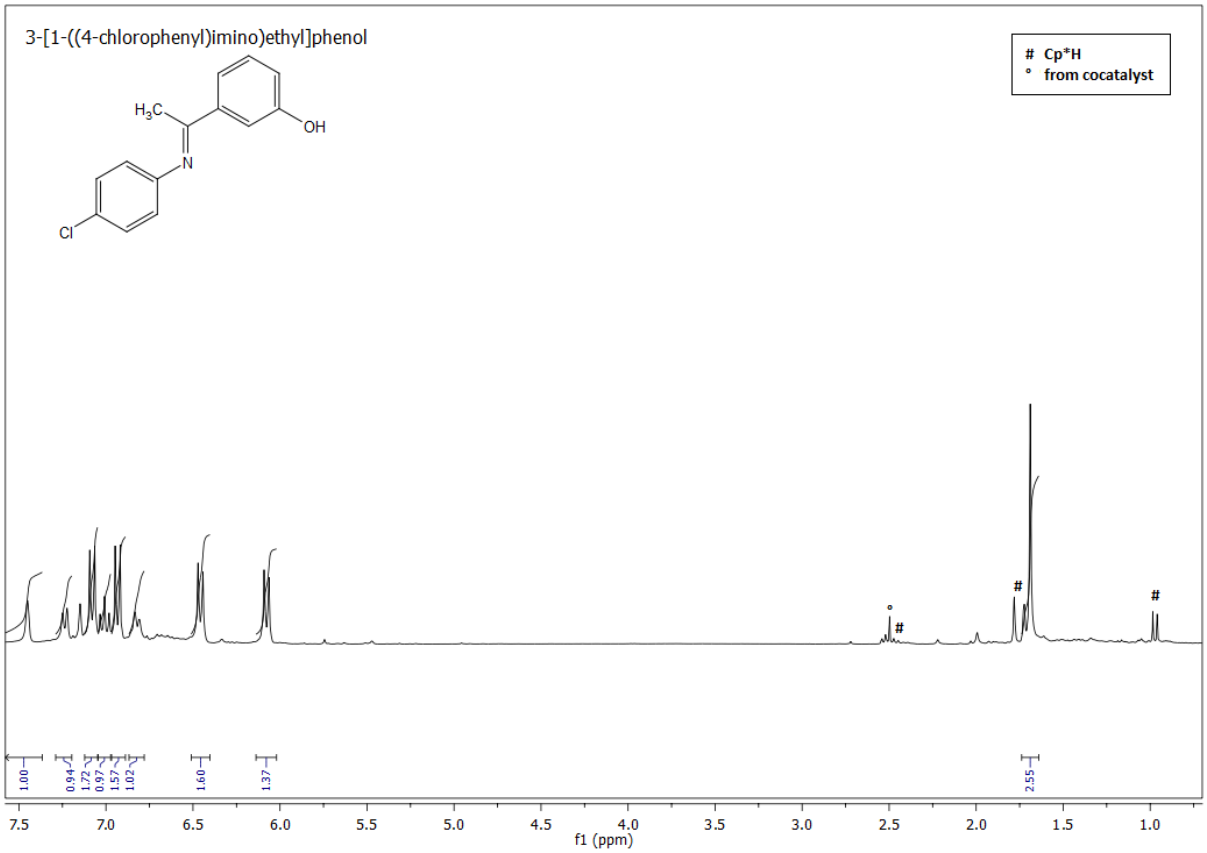

N-[1-(4-bromophenyl)ehylidene]-2,4,6-trimethylaniline
* FeCp2
# Cp*H
< starting material
° from cocatalyst
f1 (ppm)

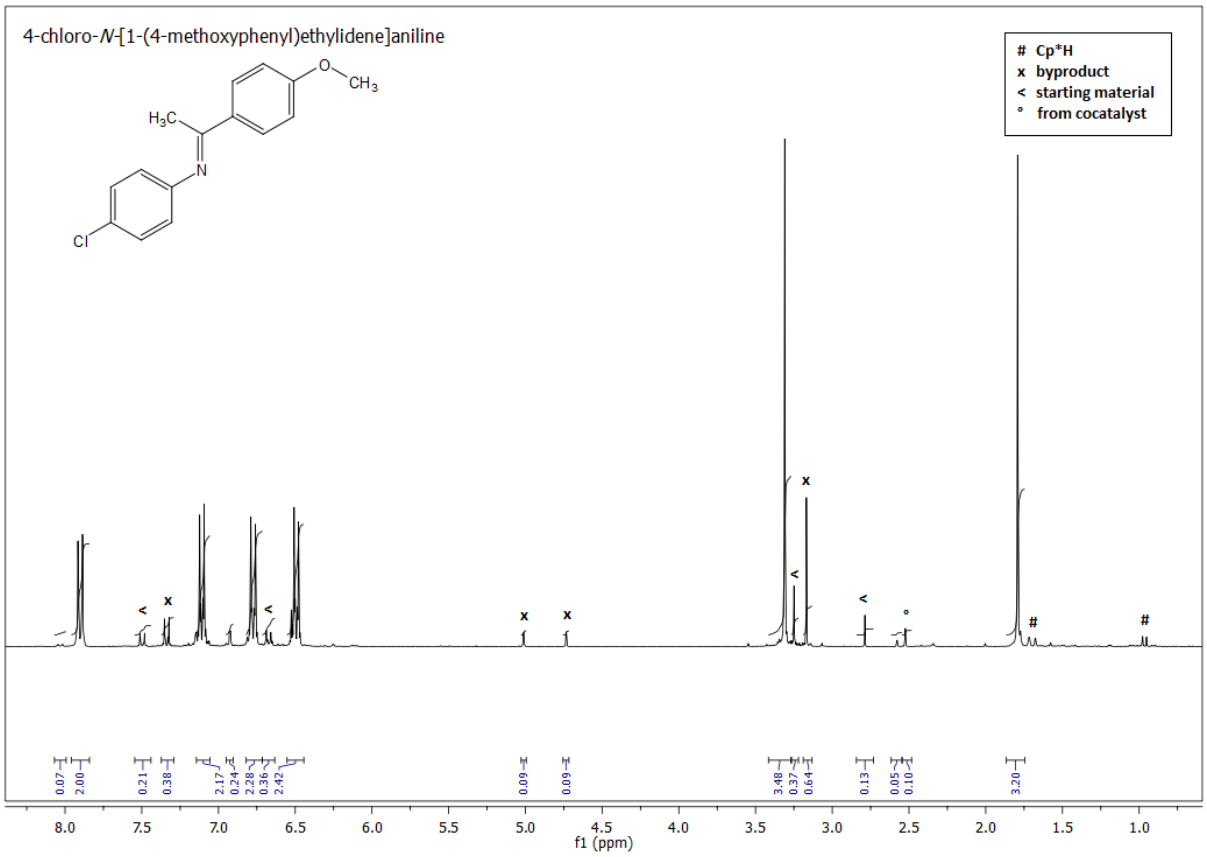

4-[1-((4-chlorophenyl)imino)ethyl]-N,N-dimethylaniline
Cp*H
< starting material
° from cocatalyst
f1 (ppm)

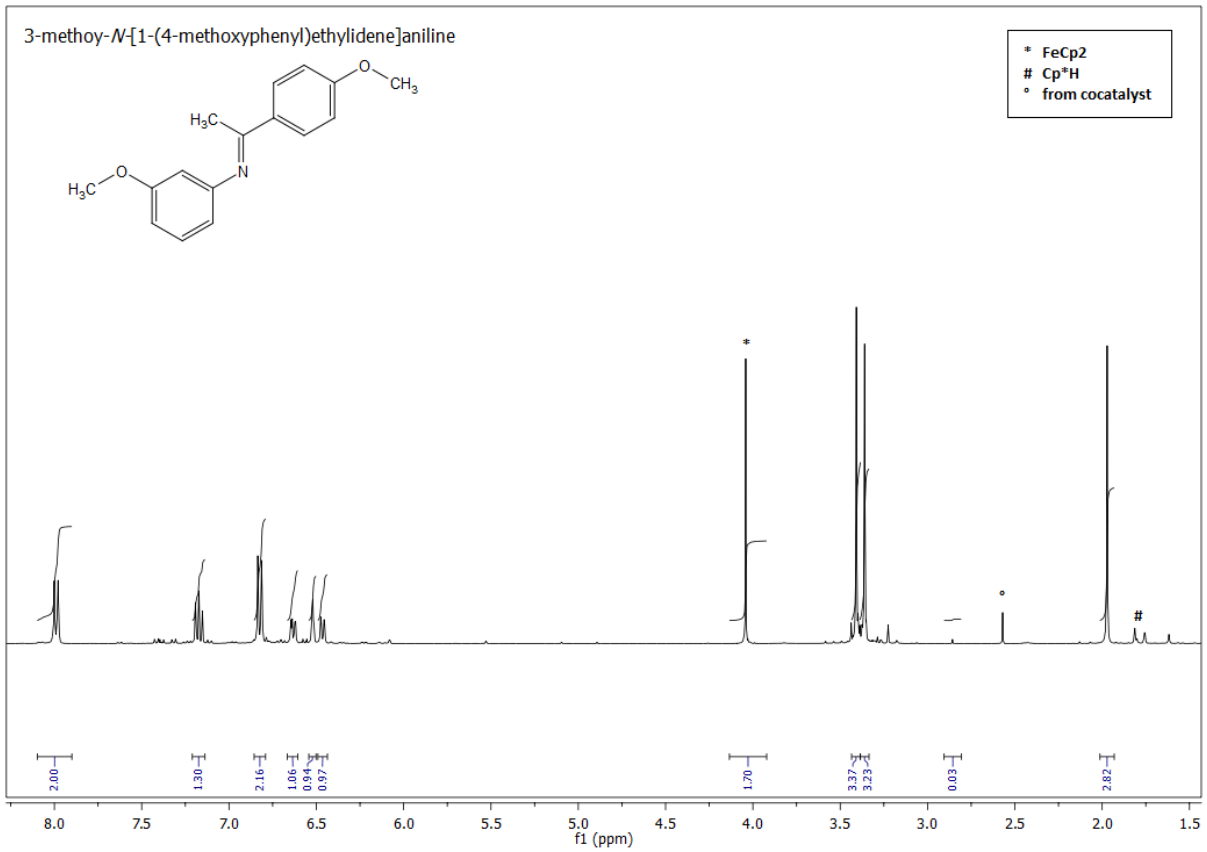

4-[1-((3-methoxyphenyl)imino)ethyl]-N,N-dimethylaniline
Cp*H
< starting material
° from cocatalyst
f1 (ppm)


N-[1-(4-(dimethylamino)phenyl)ethylidene]-2,4,6-trimethylaniline
* FeCp2
# Cp*H
< starting material
f1 (ppm)


3-[1-(phenylimino)ethyl]phenol
H3C
OH
N
* FeCp2
# Cp*H
° from cocatalyst
1.00
1.04
2.77
3.43
2.37
2.04
3.06
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
f1 (ppm)


3-[1-((4-chlorophenyl)imino)ethyl]phenol
H3C
OH
N
Cl
Cp*H
° from cocatalyst
1.00
0.94
1.72
0.97
1.57
1.02
1.60
1.37
2.55
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
f1 (ppm)


4-chloro-N-[1-(4-methoxyphenyl)ethylidene]aniline
Cp*H
x byproduct
< starting material
° from cocatalyst
f1 (ppm)


3-methoy-N-[1-(4-methoxyphenyl)ethylidene]aniline
* FeCp2
# Cp*H
° from cocatalyst
f1 (ppm)

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1. M. Dochnahl, K. Löhnwitz, J.-W. Pissarek, M. Biyikal, S. R. Schulz, S. Schön, N. Meyer, P. W. Roesky and S. Blechert, *Chemistry - A European Journal*, 2007, **13**, 6654-6666.
2. C. F. Bender, W. B. Hudson and R. A. Widenhoefer, *Organometallics*, 2008, **27**, 2356-2358.
3. C. F. Bender and R. A. Widenhoefer, *Journal of the American Chemical Society*, 2005, **127**, 1070-1071.
4. Y. Li and T. J. Marks, *Journal of the American Chemical Society*, 1996, **118**, 9295-9306.
5. N. Meyer, K. LÃ¶hnwitz, A. Zulys, P. W. Roesky, M. Dochnahl and S. Blechert, *Organometallics*, 2006, **25**, 3730-3734.
6. R. Torregrosa, I. M. Pastor and M. Yus, *Tetrahedron*, 2005, **61**, 11148-11155.
7. J. Barluenga, M. A. Fernández, F. Aznar and C. Valdés, *Chemistry – A European Journal*, 2004, **10**, 494-507.
8. T. Imamoto, N. Iwadate and K. Yoshida, *Organic Letters*, 2006, **8**, 2289-2292.
9. X.-Y. Liu, P. Ding, J.-S. Huang and C.-M. Che, *Organic Letters*, 2007, **9**, 2645-2648.
10. K. P. G. V. Shanbhag, S. B. Halligudi, *The Open Organic Chemistry Journal*, 2008, **2**, 52-57.
11. Z. Han, Z. Wang, X. Zhang and K. Ding, *Angewandte Chemie International Edition*, 2009, **48**, 5345-5349.
12. A. R. Katritzky, X. Lan and J. N. Lam, *Chemische Berichte*, 1991, **124**, 1431-1434.
13. K. Alex, A. Tillack, N. Schwarz and M. Beller, *ChemSusChem*, 2008, **1**, 333-338.