A Comparison of Decamethyldizincocene [(η^5-Cp*)$_2$Zn$_2$], Decamethylzincocene [(η^5-Cp*)$_2$Zn], and Diethylzinc Et$_2$Zn as Precatalysts for the Intermolecular Hydroamination Reaction

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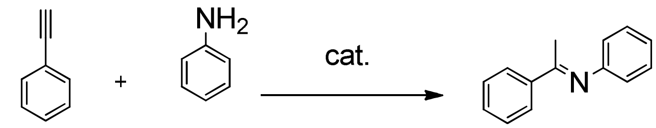
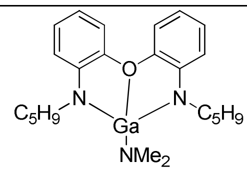
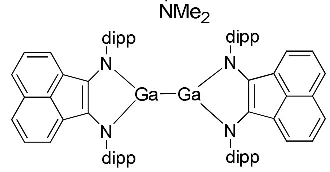
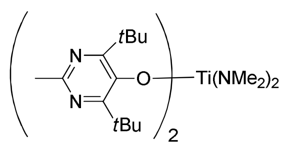
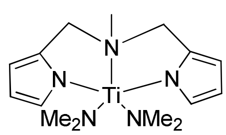
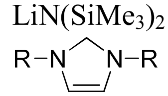
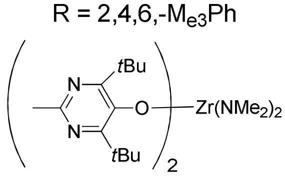
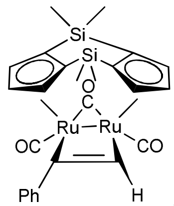
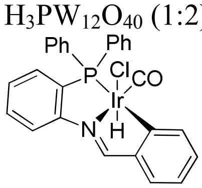
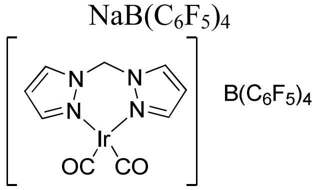
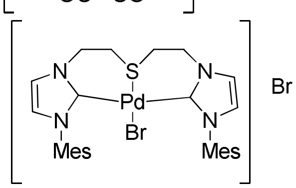
Supporting Information

21 pages

Table S1 Intermolecular Hydroamination of Phenylethyne with Aniline



Entry/ Ref.	Cat.	T [°C]	t [h]	Yield [%]	mol% cat.	Ratio amine/ alkyne
1	**[(η^5-Cp*)$_2$Zn$_2$] / [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (1:1)**	**60**	**9**	**95**	**2.5**	**1:1**
2	**[Cp*$_2$Zn] / [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (1:1)**	**60**	**9**	**quant. (9 % bypr)[c]**	**2.5**	**1:2**
3	**Et$_2$Zn**	**60**	**31**	**88% (3% bypr)[c]**	**2.5**	**1:2**
4[1]		100	20	22	5	1:1
			7	quant	10	
5[2]		90	16	99	2	1:1
6[3]	In(OTf)$_3$	110	3	90	10	1:1.1
7[4]		110	16	52	5	2:1
8[5]	[Ti(NMe$_2$)$_4$]	75	2	37	10	3:1
9[6]		75	8	26	10	3:1
10[7]	[Ti(NPh)(NHPh)$_2$]	100	24	80	10	3:2
11[8]	[Ti(NMe$_2$)$_4$] / LiN(SiMe$_3$)$_2$ /  R = 2,4,6,-Me$_3$Ph	100	2	52	10	3:1
12[4]		110	16	44	5	2:1

13[9]	$[Rh(cod)_2]BF_4$/3 PCy_3	RT	20	10	2.5	1:2
14[7]	$[V(\mu\text{-}NPh)(NMe_2)_2]_2$	100	24	48	10	3:2
15[10]	$[Np_3Ta{=}NCMe_3]$	135	2	77	5	1:1
16[10]	$[(PhCH_2)Ta{=}NCMe_3]^+$	135	2	66	5	1:3
17[11]	 / HBF_4 OEt_2	40	18	12	3.3	1:1
18[12]	$[Ru_3(CO)_{12}]$ / NH_4PF_6 (1:3)	100	12	84	0.1	1.1:1
19[13]	$[Ru(CO)_2(PPh_3)$(*o*-styryldiphenylphophine)] / NH_4PF_6 (1:2)	100	6	72	0.3	1:1
20[13]	$[Ru(CO)_2(PPh_3)_3]$ / NH_4PF_6 (1:2)	100	6	16	0.3	1:1
21[13]	$[Ru(CO)_3(PPh_3)_2]$ / NH_4PF_6 (1:2)	100	6	49	0.3	1:1
22[13]	$[RuH_2(CO)(PPh_3)_3]$ / NH_4PF_6 (1:2)	100	6	8	0.3	1:1
23[13]	$[Ru(CO)(PPh_3)_2$(*o*-styryldiphenylphophine)] / NH_4PF_6 (1:2)	100	6	10	0.3	1:1
24[13]	$[Ru(CO)_2(PPh_3)$(*o*-styryldiphenylphophine)] / $H_3PW_{12}O_{40}$ (1:2)	100	48	99	0.1	1:1
25[14]	 / $NaB(C_6F_5)_4$	110	12	95	1	1.2:1
26[15]		60	22	57	5	≈1:1
27[16]	 / triflic acid (1:5)	100	12	23	1	1:2

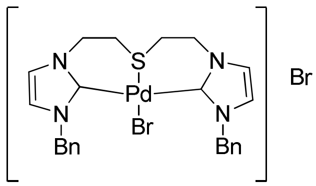
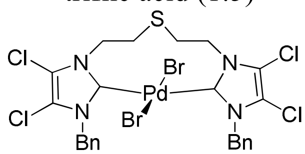
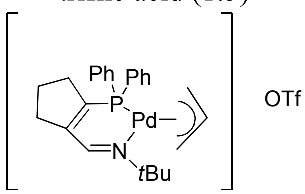
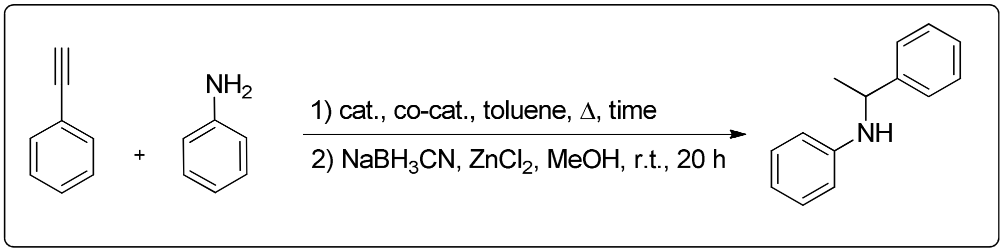
28[16]	 / triflic acid (1:5)	100	12	30	1	1:2
29[16]	 / triflic acid (1:5)	100	12	20	1	1:2
30[17]		70	22	75	5	1:10
31[18]	$PtBr_2$	100	10	27	0.13	1:1
32[19]	AgOTf	80	3	24	10	1:1
33[20]	$(Ph_3P)AuCH_3$ / $H_3PW_{12}O_{40}$ (1:5)	70	2	98	0.2	1:1.1
34[21]	$AuCl_3$/AgOTf 1:3	RT	12	35	5	1:2
35[22]	$Zn(OTf)_2$	120	24	99	5	1.3:1

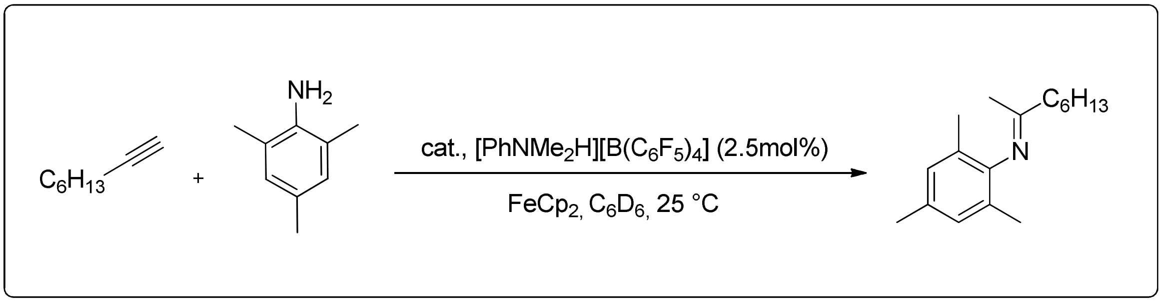
Figure S1.



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[22]

Kinetics

Figure S2.



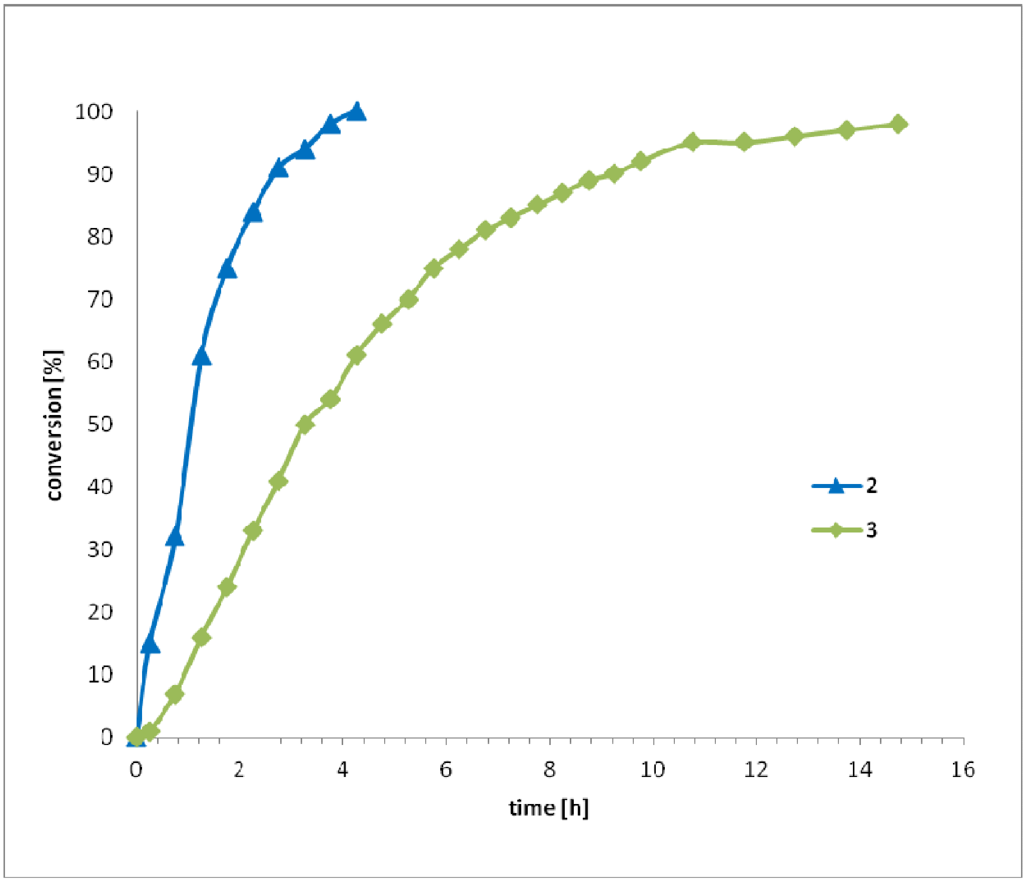
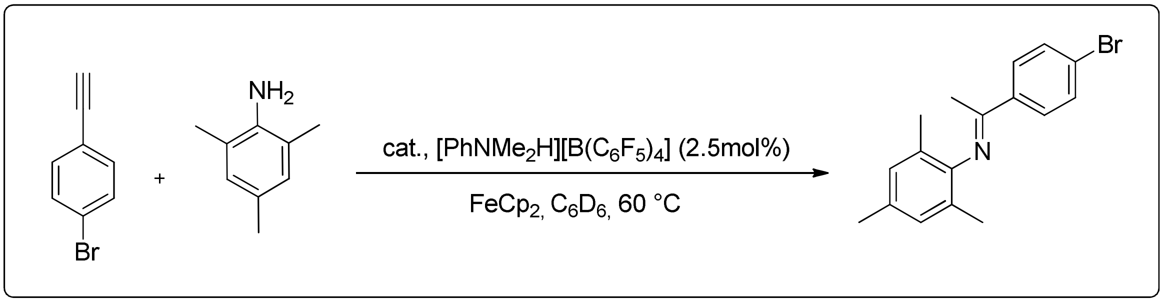
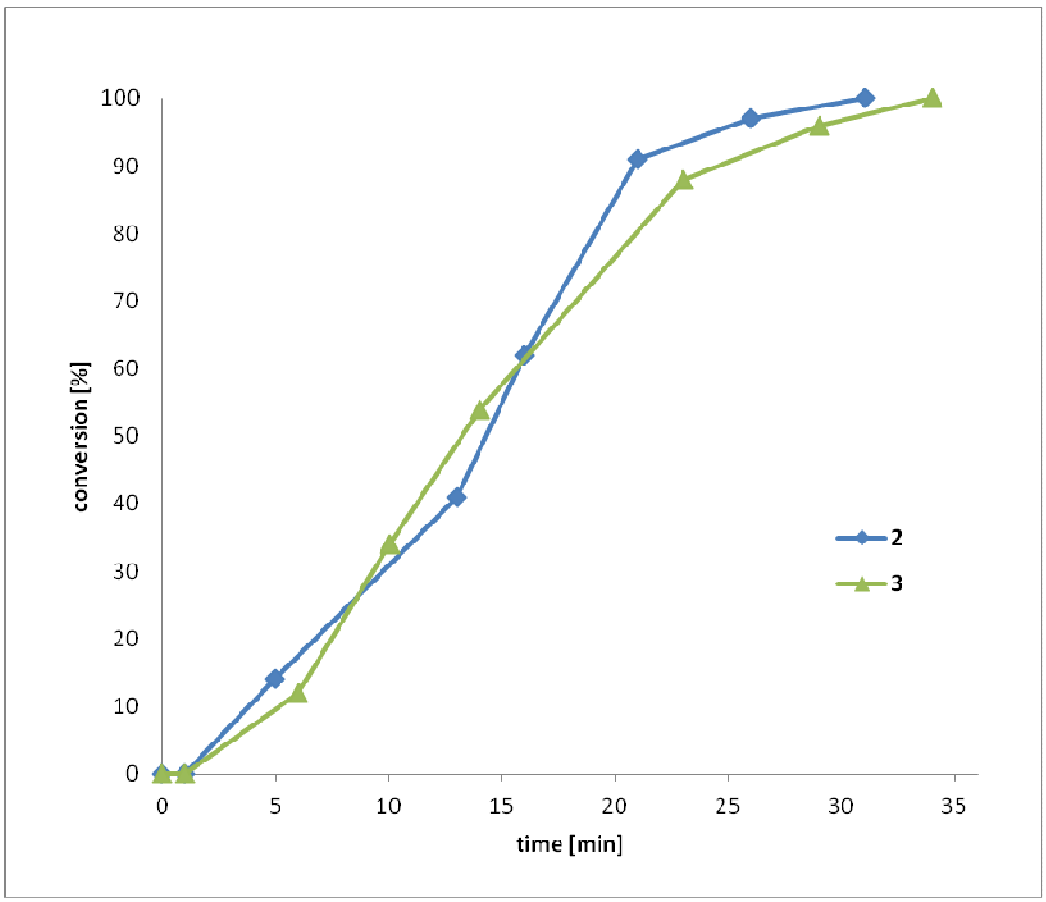


Figure S3.


NH2
Br
+
cat., [PhNMe2H][B(C6F5)4] (2.5mol%)
FeCp2, C6D6, 60 °C
N
Br


conversion [%]
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
time [min]
2
3

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.

Hydroamination reaction

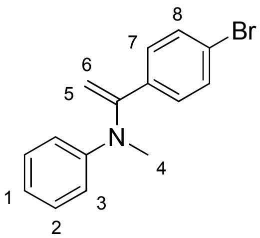
The substrates were purchased from Aldrich, AlfaAesar and Acros.

The ^{1}H NMR spectra of *N*-(methylbenzylidene)aniline,[23] methylphenyl(1-phenylvinyl)amine,[24] *N*-(1-phenylethylidene)-4-chloroaniline,[25] *N*-(1-phenylethylidene)- 2,4,6-trimethylaniline,[26] *N*-[1-(4-bromophenyl)ethylidene)]benzamine,[27] *N,N*-dimethyl-4-[1-(phenylimino)]ethylaniline,[28] *N*-[1-(1-cyclohexene-1-yl)ethylidene]benzamine,[29] *N*-(1-methyl-heptylidene)-benzamine,[30] 4-chlor-*N*-(1-methylheptylidene)-benzamine,[31] and *N*-(1-phenyl-ethylidene)-benzmethanamine[32] conform to the literature.

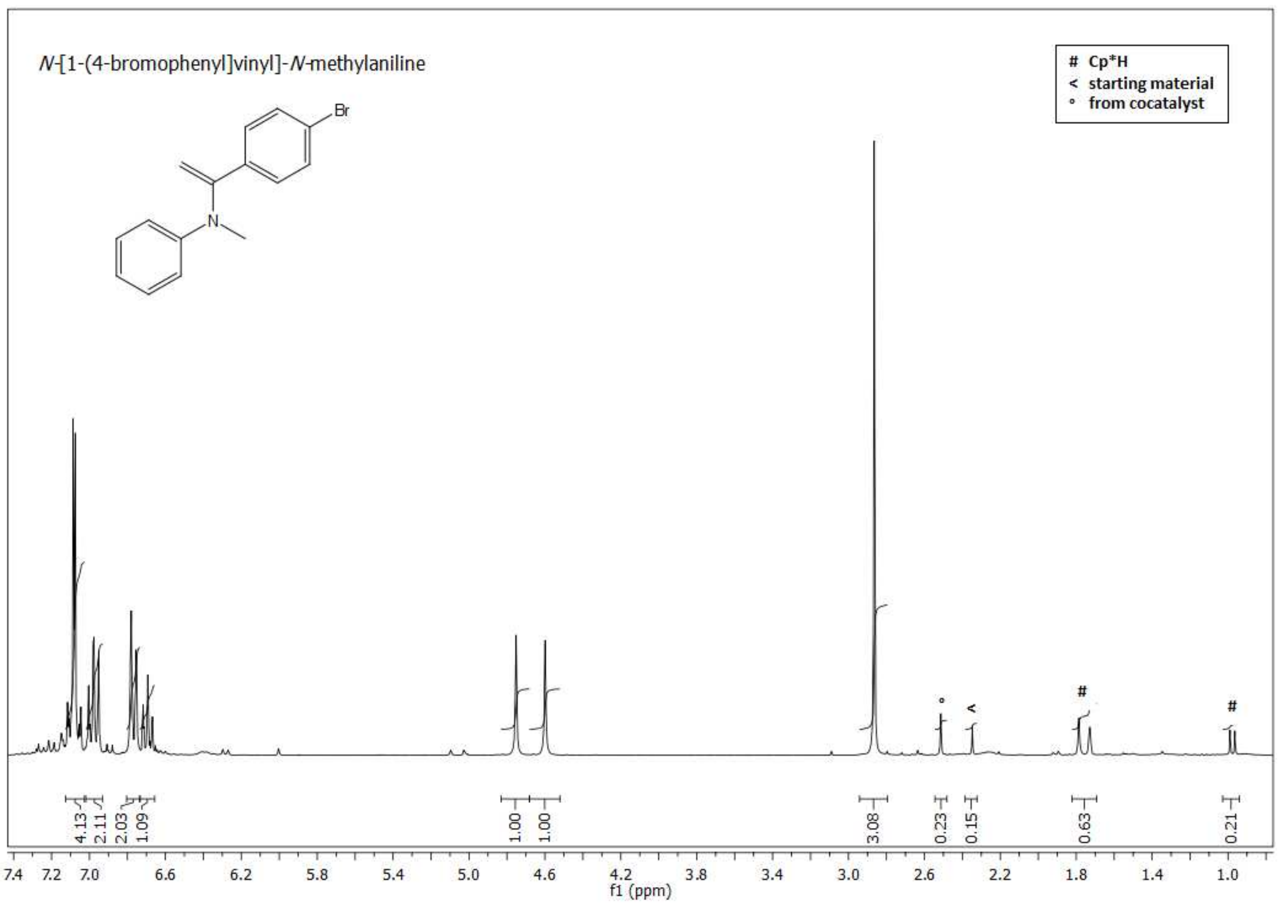
The NMR spectra shown were taken directly from NMR scale reactions without further purification to shown the high conversion and not the absolute purity of the samples. Therefore traces of the catalyst, the cocatalyst, and the internal standard (Cp_2Fe) and in some cases also small traces of the starting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

NMR

N-[1-(4-bromophenyl)vinyl]-*N*-methylaniline

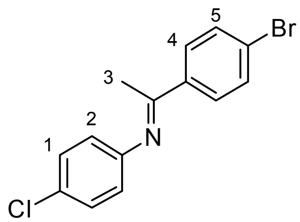


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 2.86 (s, 3 H, H-4); 4.60 (s, 1 H, H-5); 4.75 (s, 1 H, H-6); 6.69 (t, $^3J_{H\text{-}H}$ = 6.0 Hz, 1 H, H-1); 6.75 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-3); 6.95 (m, 2 H, H_{ar}); 7.05-7.15 (m, 4 H, H_{ar}).

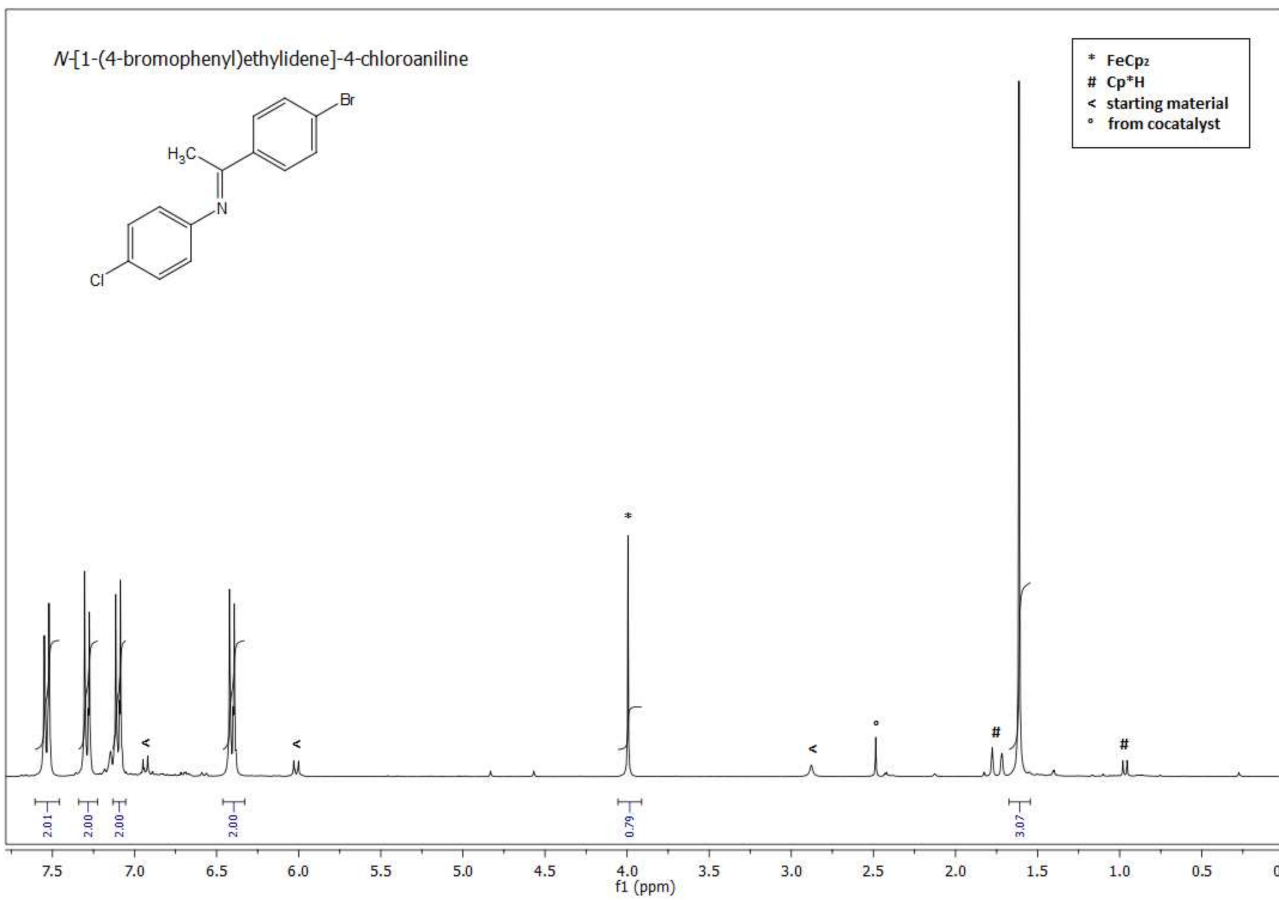


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 40.79; 100.05; 121.01; 121.20; 127.39; 128.73; 128.94; 131.27; 133.39; 148.65; 152.53.

***N*-[1-(4-bromophenyl)ethylidene]-4-chloroaniline**

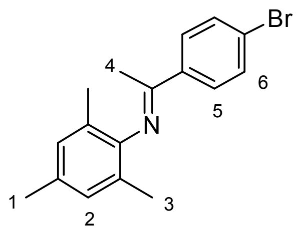


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.61 (s, 3 H, H-3); 6.39 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-2); 7.09 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-1); 7.28 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-5); 7.52 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-4).

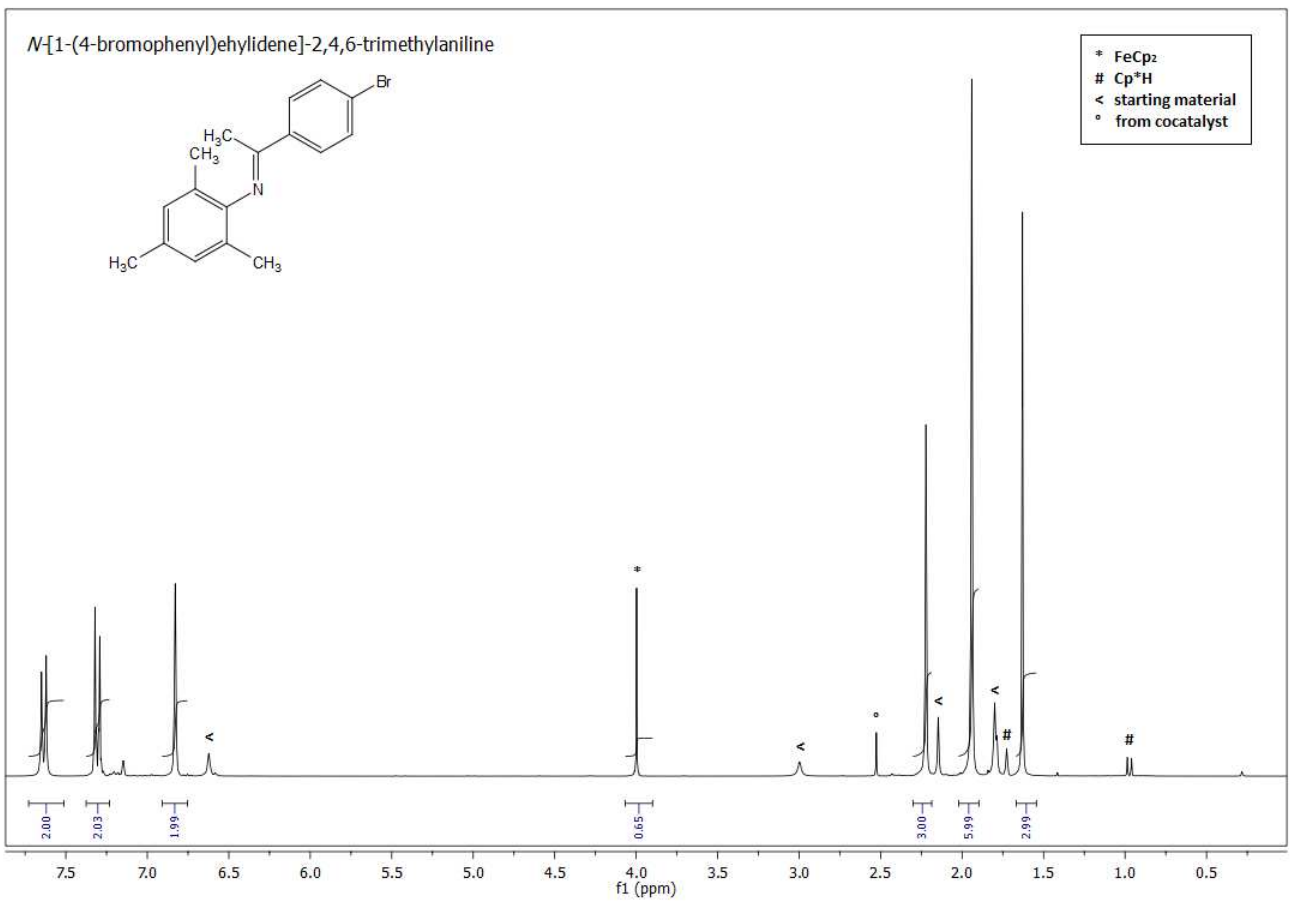


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 16.30; 120.72; 125.26; 128.83; 129.00; 131.34; 131.45; 137.79; 149.92; 164.14.

***N*-[1-(4-bromophenyl)ethylidene]-2,4,6-trimethylaniline**

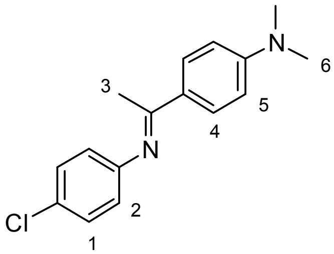


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.63 (s, 3 H, H-4); 1.94 (s, 6 H, H-3); 2.22 (s, 3 H, H-1); 6.83 (s, 2 H, H-2); 7.29 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-6); 7.62 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-5).

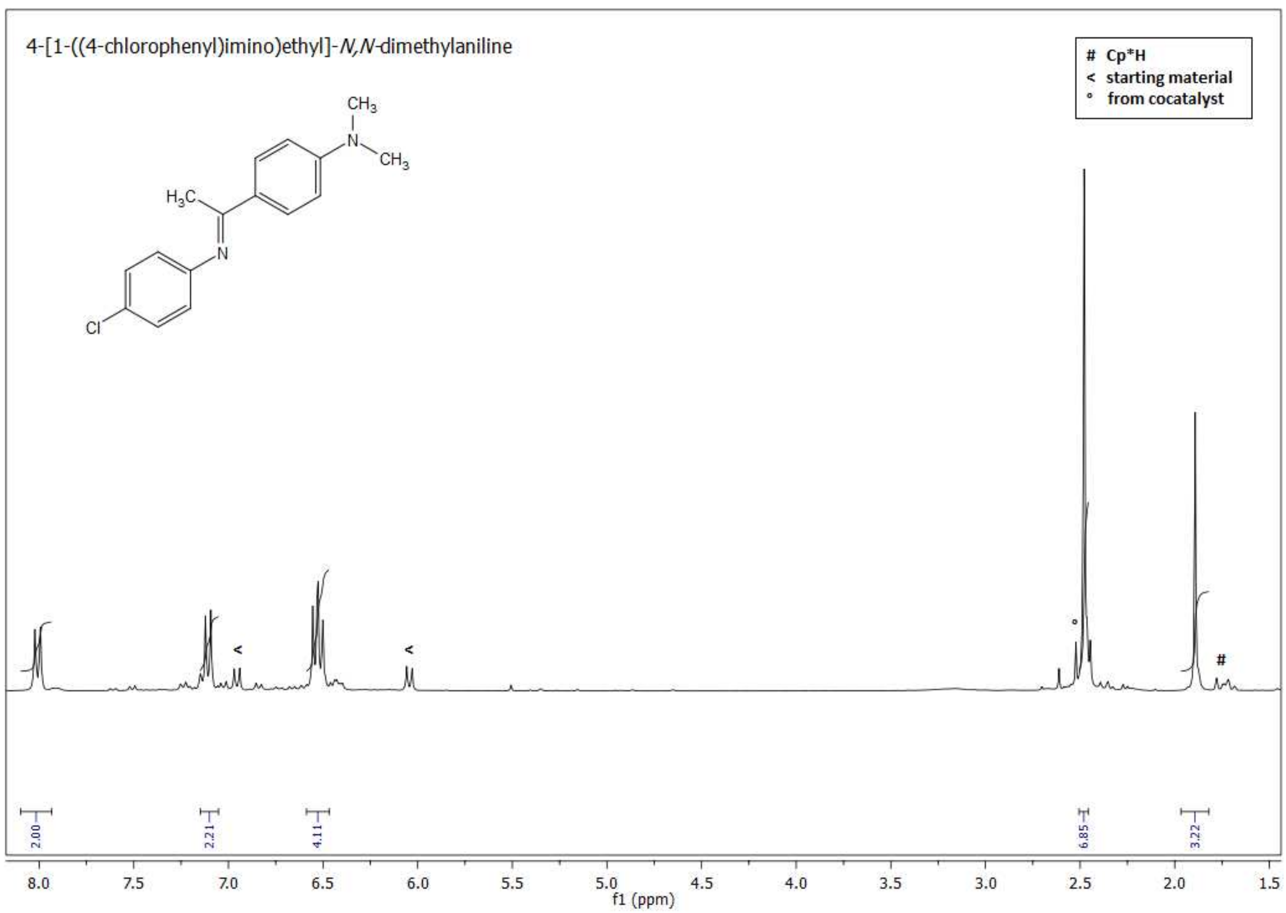


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 16.38; 17.72; 20.58; 124.87; 125.07; 128.70; 128.71; 131.32; 131.72; 137.80; 146.59; 163.55.

4-[1-((4-chlorophenyl)imino)ethyl]-*N*,*N*-dimethylaniline

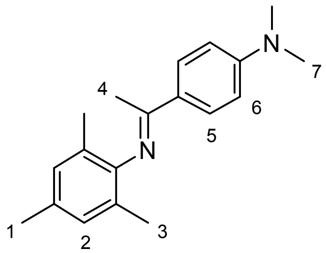


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.89 (s, 3 H, H-3); 2.48 (s, 6 H, H-6); 6.50 (m, 4 H, H-5, H-2); 7.09 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-1); 7.99 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-4).

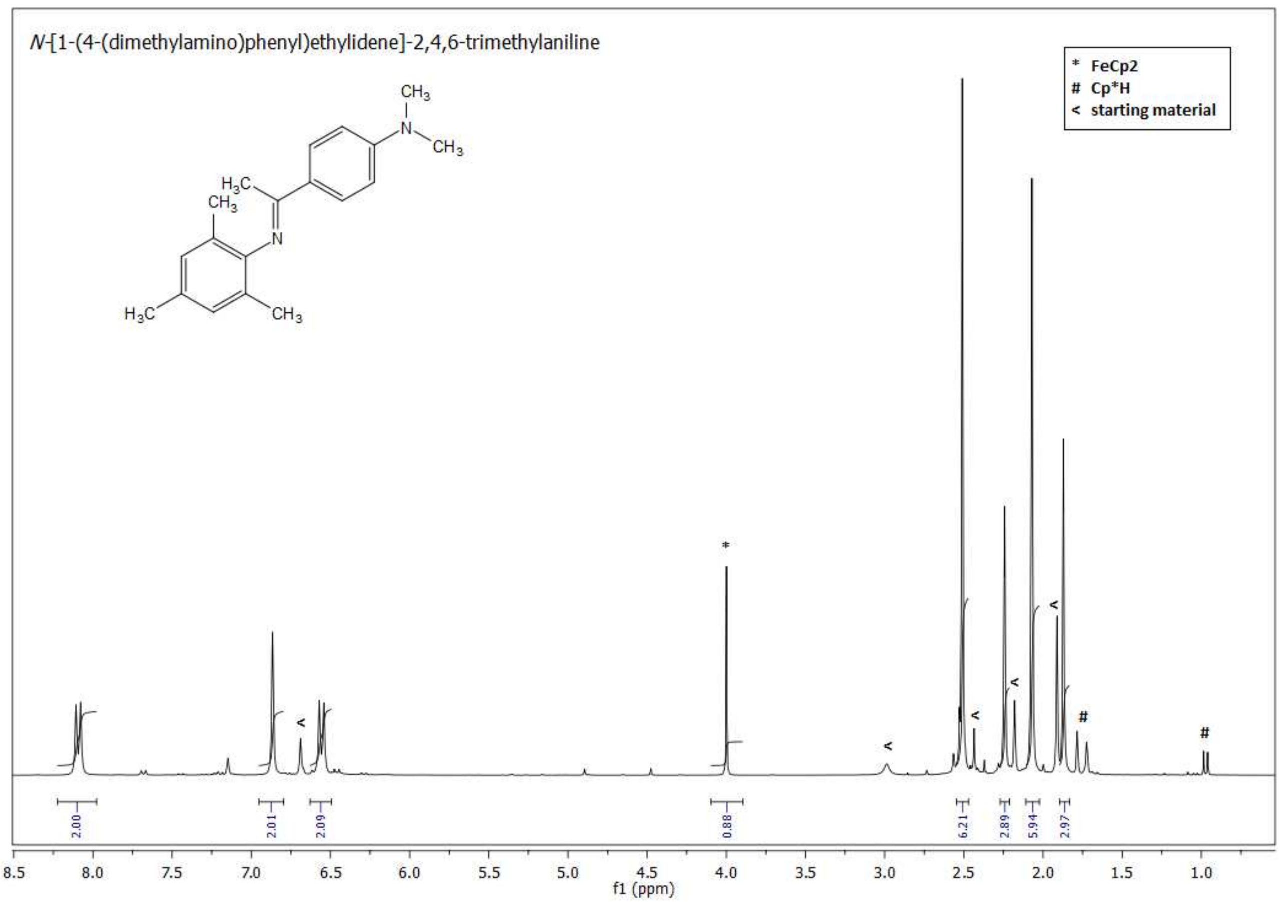


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 16.20; 39.34; 111.12; 121.39; 128.84; 129.24; 133.17; 151.41; 151.87; 164.16.

***N*-[1-(4-(dimethylamino)phenyl)ethylidene]-2,4,6-trimethylaniline**

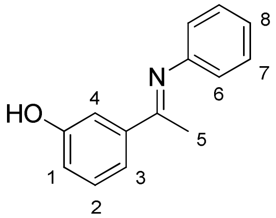


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.87 (s, 3 H, H-4); 2.07 (s, 6 H, H-3); 2.24 (s, 3 H, H-1); 2.51 (s, 6 H, H-7); 6.54 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-6); 6.87 (s, 2 H, H-2); 8.08 (d, $^3J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-5).

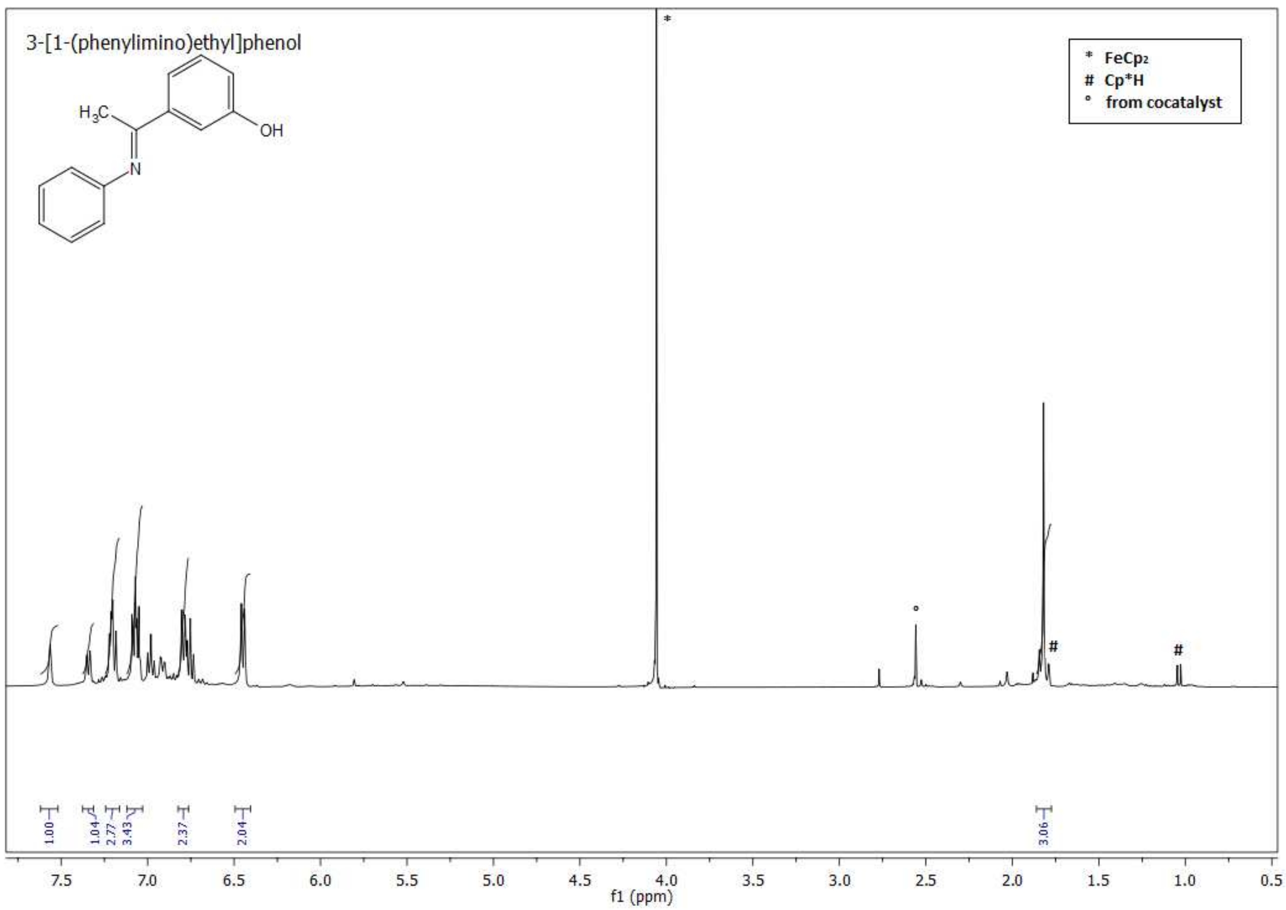


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 16.33; 17.97; 20.63; 39.46; 111.28; 125.65; 128.60; 130.77; 133.16; 147.74; 151.81; 163.42.

3-[1-(phenylimino)ethyl]phenol

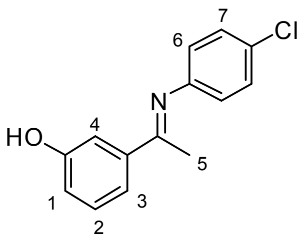


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.82 (s, 3 H, H-5); 6.45 (d, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 2 H, H-6); 6.77 (d, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 1 H, H-1); 7.07 (t, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 2 H, H-2, H-8,); 7.15-7.25 (m, 2 H, H-7); 7.32 (d, $^{3}J_{H\text{-}H}$ = 6.0 Hz, 1 H, H-3,); 7.01 (s br, 1 H, OH); 7.56 (s, 1 H, H-4).

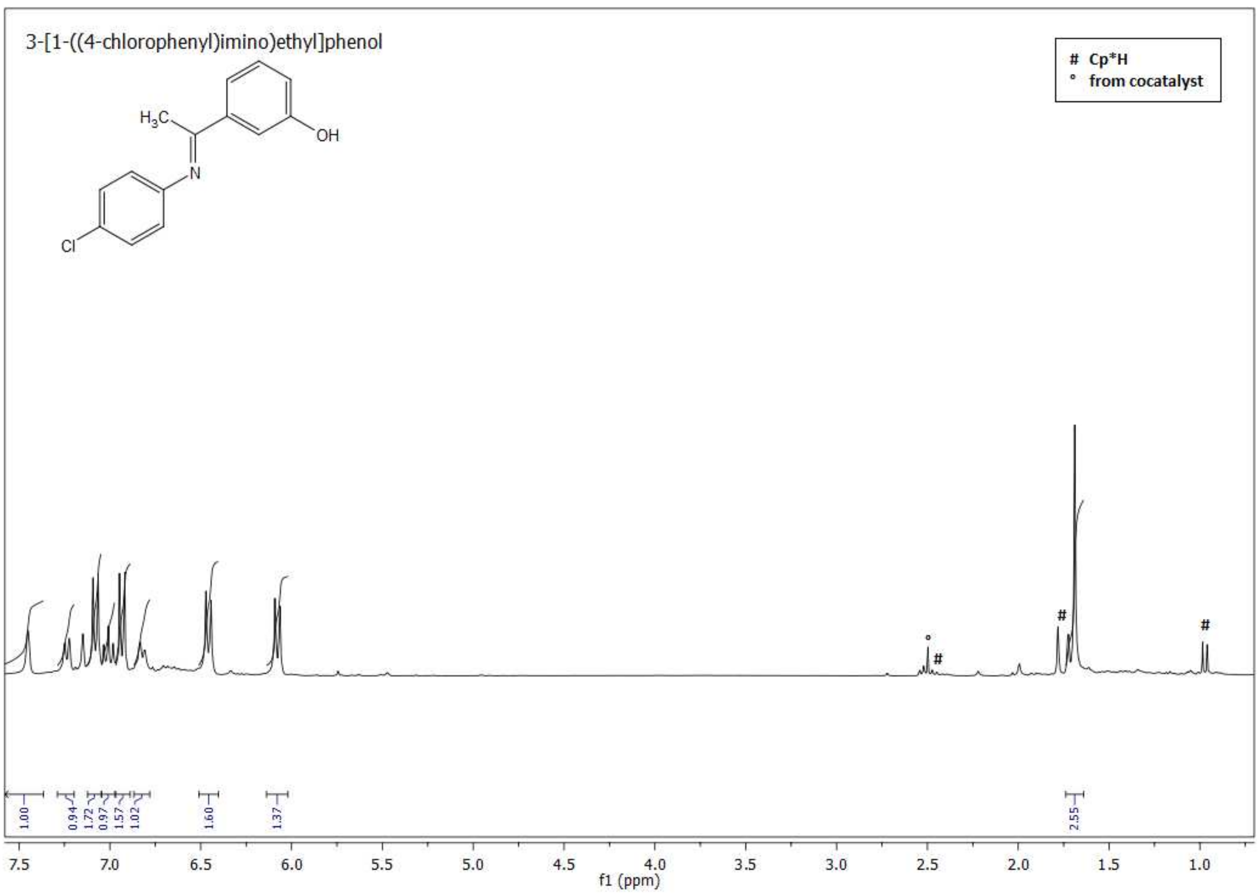


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 17.94; 116.44; 120.05; 123.42; 124.17; 129.21; 129.63; 140.31; 149.94; 156.23; 169.49.

3-[1-((4-chlorophenyl)imino)ethyl]phenol

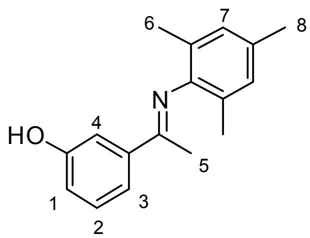


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.69 (s, 3 H, H-5); 6.07 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 1 H, H-1); 6.46 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-6); 6.93 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 1 H, H-3); 7.01 (t, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 1 H, H-2); 7.02 (s br, 1 H, OH); 7.07 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 1 H, H-7); 7.45 (s, 1 H, H-4).

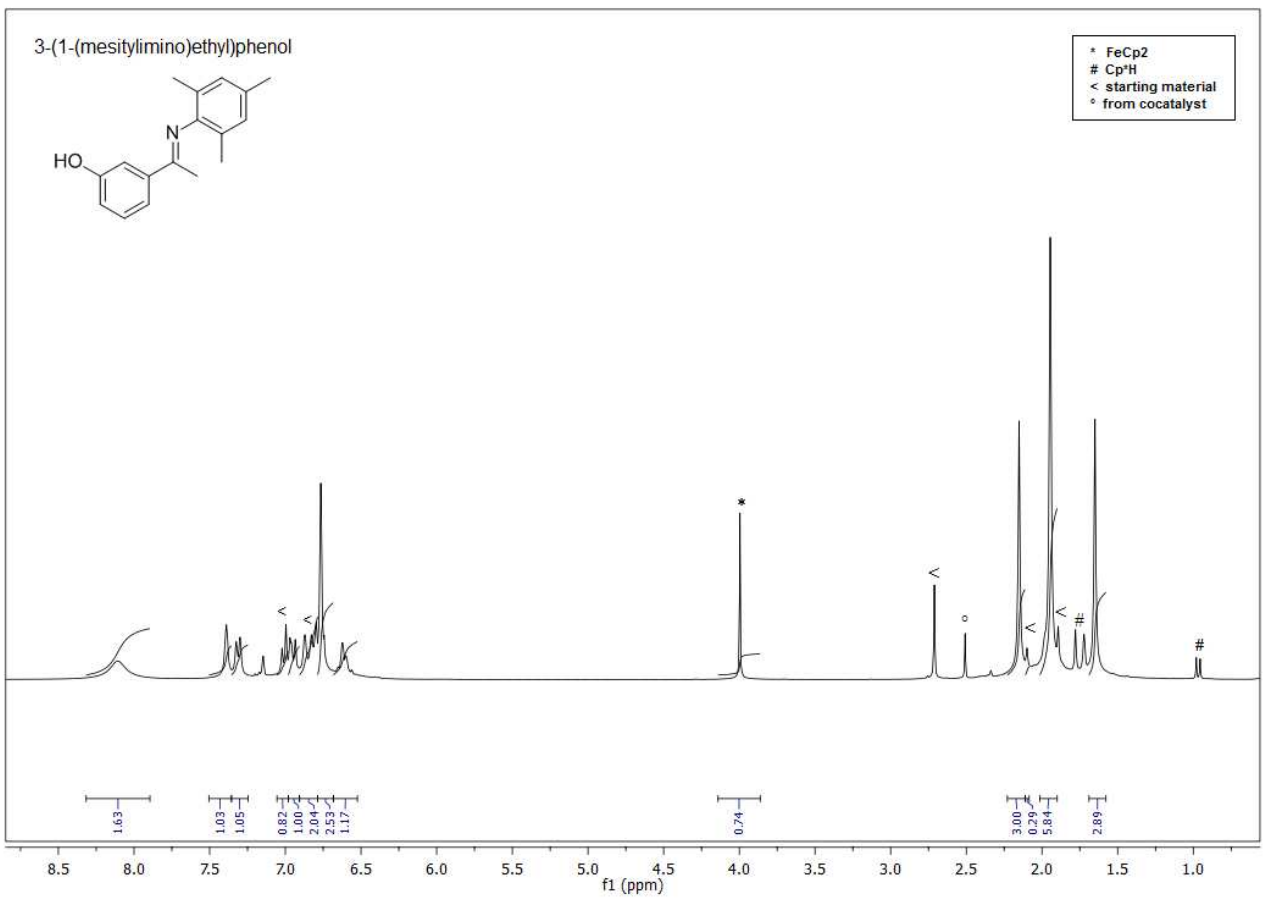


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 17.72; 114.36; 117.13; 119.53; 121.41; 129.04; 129.23; 129.65; 129.73; 148.78; 156.58; 169.19.

3-(1-(mesitylimino)ethyl)phenol

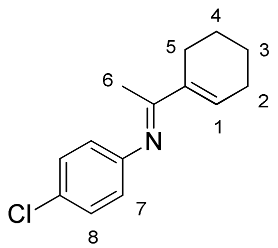


[1]H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.65 (s, 3 H, H-5); 1.95 (s, 6 H, H-6); 2.16 (s, 3 H, H-8); 6.78 (s, 2 H, H-7); 6.20-6.90 (m, 2 H, H-1, OH); 7.00 (t, $^3J_{H\text{-}H}$ = 9.0 Hz, 1 H, H-2); 7.33 (d, $^3J_{H\text{-}H}$ = 6.0 Hz, 1 H, H-3); 7.44 (s, 1 H, H-4).

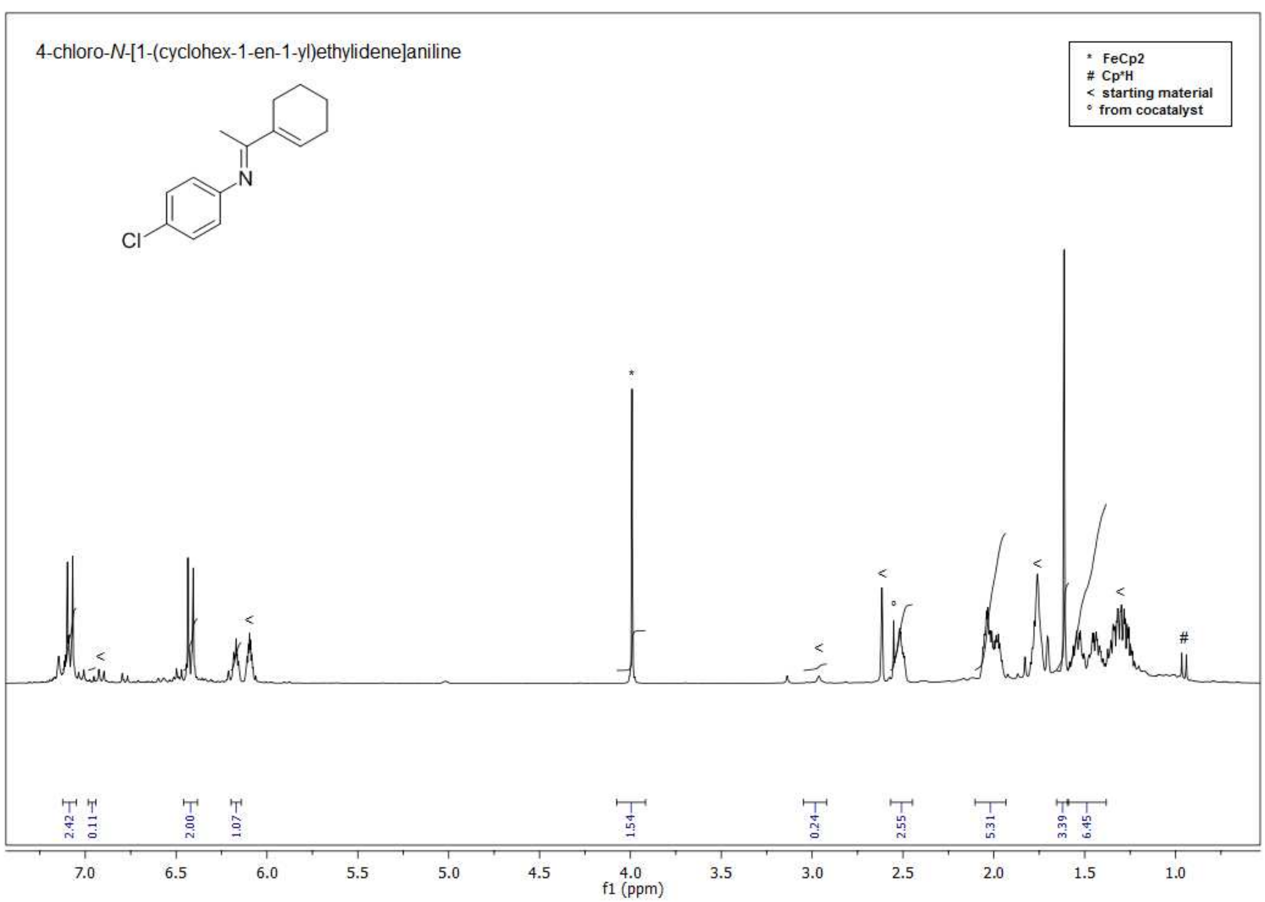


[13]C{[1]H} NMR (C_6D_6, 100 MHz): δ (ppm) = 17.63; 17.79; 20.50; 114.50; 118.48; 119.04; 126.30; 129.00; 129.46; 129.72; 132.85; 145.10; 156.79; 169.62.

4-chloro-*N*-[1-(cyclohex-1-en-1-yl)ethylidene]aniline

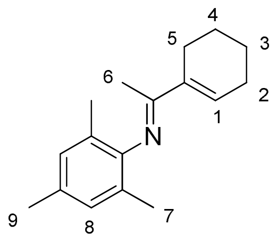


^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.40-1.61 (m, 4 H, H-3, H-4); 1.61 (s, 3 H, H-6); 1.92-2.09 (m, 2 H, H-5); 2.42-2.55 (m, 2 H, H-2); 6.14-6.23 (m, 1 H, H-1); 6.43 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-7); 7.10 (d, $^{3}J_{H\text{-}H}$ = 9.0 Hz, 2 H, H-8).

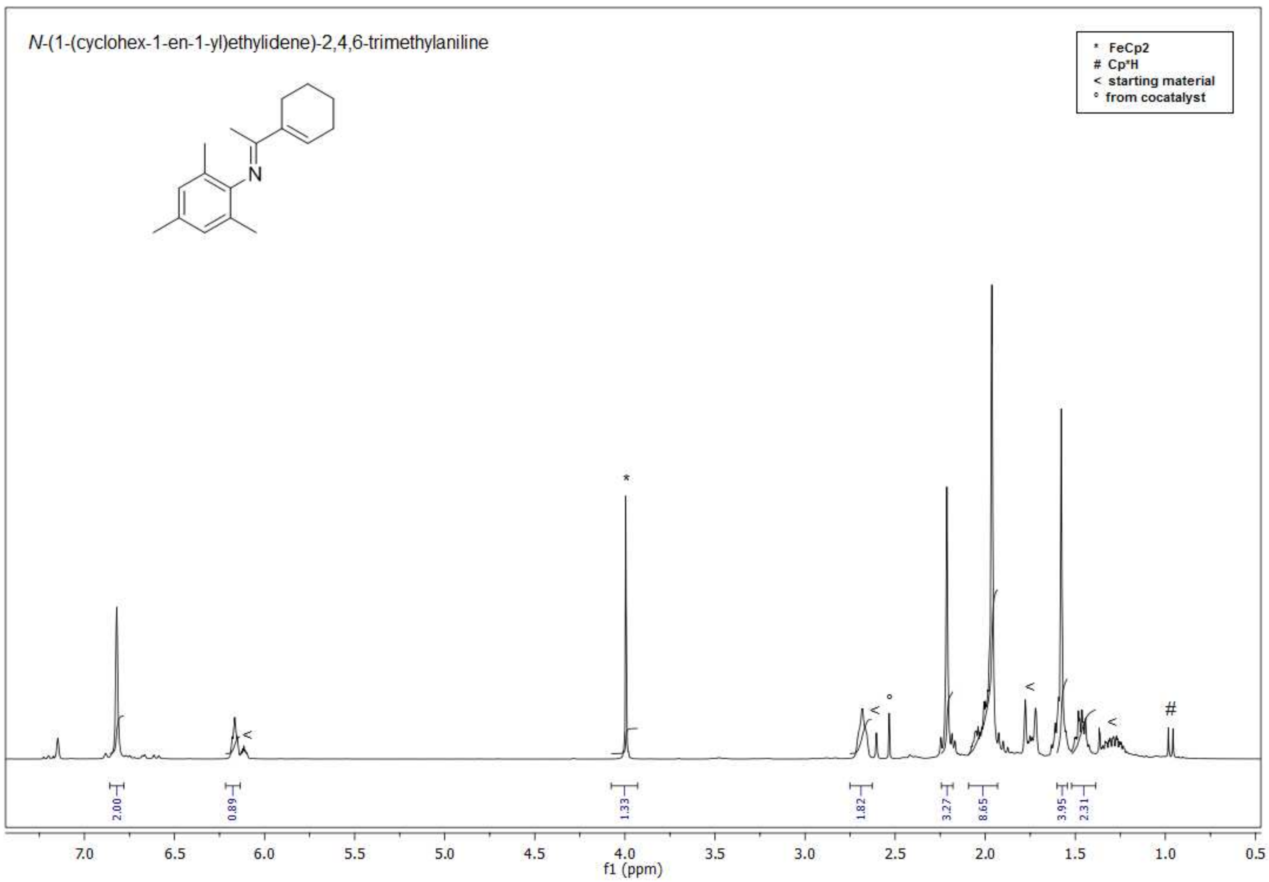


^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 15.08; 21.27; 22.03; 24.60; 26.04; 120.66; 128.76; 128.85; 133.57; 139.42; 150.97; 166.06.

***N*-(1-(cyclohex-1-en-1-yl)ethylidene)-2,4,6-trimethylaniline**

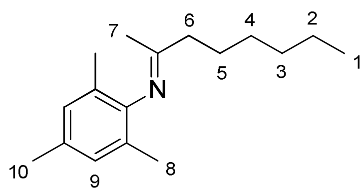


[1]H NMR (C_6D_6, 300 MHz): δ (ppm) = 1.32-1.53 (m, 4 H, H-3, H-4); 1.57 (s, 3 H, H-6); 1.94 (s, 6 H, H-7); 1.97-2.13 (m, 2 H, H-5); 2.20 (s, 3 H, H-9); 2.61-2.70 (m, 2 H, H-2); 6.12-6.26 (m, 1 H, H-1); 6.80 (s, 2 H, H-8).

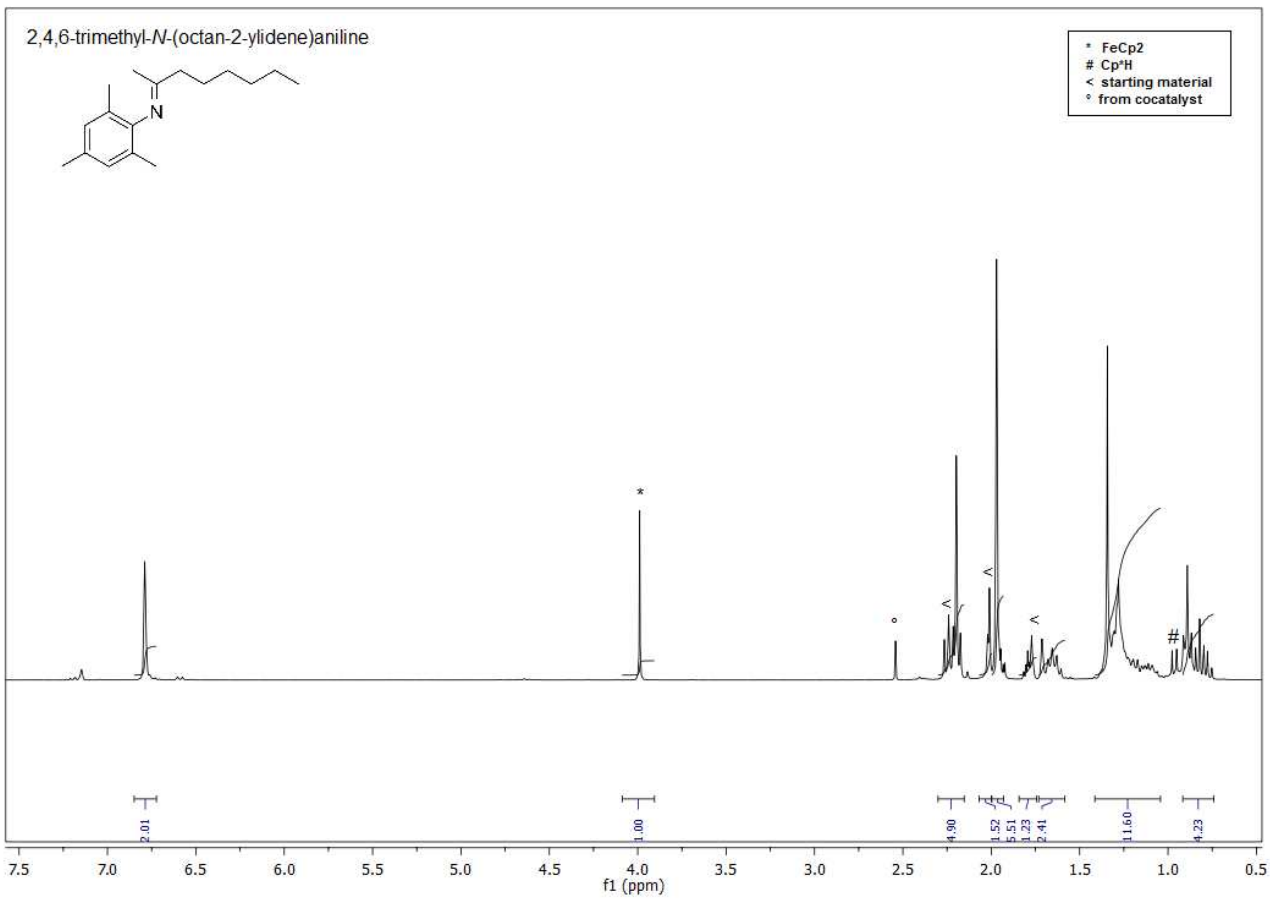


[13]C{[1]H} NMR (C_6D_6, 100 MHz): δ (ppm) = 15.15; 17.78; 21.26; 22.03; 22.10; 24.79; 25.96; 128.53; 128.87; 130.93; 132.24; 135.68; 147.27; 165.47.

2,4,6-trimethyl-*N*-(octan-2-ylidene)aniline



^{1}H NMR (C_6D_6, 300 MHz): δ (ppm) = 0.75-0.95 (m, 3 H, H-1); 1.05-1.35 (m, 8 H, H-2, H-3, H-4, H-5); 1.34 (s, 3 H, H-7); 1.58-1.83 (m, 2 H, H-6); 1.97 (s, 6 H, H-8); 2.20 (s, 3 H, H-10); 6.79 (s, 2 H, H-9).



^{13}C{^{1}H} NMR (C_6D_6, 100 MHz): δ (ppm) = 13.93; 17.70; 19.07; 20.48; 22.67; 26.19; 29.20; 31.79; 40.52; 125.06; 128.59; 130.93; 146.85; 170.01.

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