Supporting Information for

Recyclable hydrotalcite catalysts for alcohol imination via acceptorless dehydrogenation

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SI-Experimental

Preparation of Mg: Al HT 3:1: Mg:Al HT 3:1 was prepared using three parts M^{2+} to two parts M^{3+} titrated together at a pH between 8-10. A standard procedure prepared two solutions. Solution 1 was that of deionozed H_2O, $Mg(NO_3)_2*6H_2O$ (0.15 mol), and $Al(NO_3)_3*9H_2O$ (0.05 mol). Solution 2 was that of deionozed H_2O, NaOH (0.4 mol), and $NaCO_3$(0.025 mol). Solution 1 was then titrated into solution 2 over a three to four hour period while stirring between 800 and 1200 rpm and then heated at 338K for 16-20 hours. The precipitate was then filtered and washed with room temperature deionized water until the pH of the filtrate was between 7 and 7.2. Once filtered the hydrotalcite was dried in an oven at 110°C for 24 hours. The dry hydrotalcite was then resuspended in deionized water, filtered, and dried again in the oven. For the samples that were calcined, they were placed in a furnace at 450°C for 24 hours and cooled in a desiccator before put into sample jars and stored.

Preparation of 15% M^x doped Mg:Al Hydrotalcite: M^x (M= Cu, Fe, Zn, Ni, Cr; x=2^+, 3^+) doped Mg:Al HT was prepared using three parts M^{2+} to two parts M^{3+} titrated together at pH>11. A standard procedure prepared three solutions. Solution 1 was that of deionozed H_2O, $Mg(NO_3)_2*6H_2O$, $Al(NO_3)_3*9H_2O$, and $M^x(NO_3)_x*YH_2O$. Solution 2 was that of deionozed H_2O and Na_2CO_3 (0.025 mol). Solution 3 was 1M NaOH. Solution 1 was then titrated into solution 2 over a three to four hour period with aliquots of Solution 3 added regularly. The system was left stirring between 800 and 1200 rpm through the titration and then heated at 338K for 16-20 hours. The precipitate was then filtered and washed with room temperature deionized water until the pH of the filtrate was between 7 and 7.2. Once filtered the hydrotalcite was dried in an oven at 110°C for 24 hours. The dry hydrotalcite was then resuspended in deionized water, filtered, and dried again in the oven. For the samples that were calcined, they were placed in a furnace at 450°C for 24 hours and cooled in a desiccator before put into sample jars and stored.

Table S1. Reports of hydrotalcite-like materials and their structural properties

Reference	Formula	BET (m^2/g)	Crystallite Å
Millange J. Mater. Chem. 2000, 1713-1720	$[Mg_3Al(OH)_8]\ [(CO_3)_{0.5}]\cdot 2H_2O$	N/A	337
V.K. Diez et. al J. Catalysis, 2003, 220-233	Mg_5AlO_x Mg_3AlO_x Mg_1AlO_x	184 238 231	N/A N/A N/A
Meloni, D. et. al. *J. Therm. Anal. Calorim.* 2012, 783-791	MgNiAl(0.22)* MgNiAl(0.47)* MgNiAl(4.05)*	154 359 282	a = 3.012; c= 22.162 a=3.039; c=22.046 a=3.051; c=22.918
Zhao, Y. et. al. Chem. Mater. 2002, 4286-4291	Mg_2Al^a Mg_3Al^a Mg_4Al^a	N/A N/A N/A	296 116 96
Sharma, S.K.; et. al. *Ind. Eng. Chem. Res.*	$Mg_{3.5}Al$	$75\text{-}85^b$	$180\text{-}290^c$

2007, 4856-4865			
Miyata, S. *Clays and Clay Miner.* 1980, 50-56	MgAl[a,d]	24	112-909 [e]
Takehira, K. *Catal. Surv. Asia*. 2007, 1-30	Mg_3-Al[a] Ni_2-Al[a] $Mg_{2.5}(Ni_{0.5})$–Al	91.3 99.9 121.2	N/A N/A N/A
Wu, J.S; et. al. *Turk. J. Chem.* **2011**, 881-891	Cu-Mg-Al_HTlc 1) 0% ethylene glycol 2) 5% 3) 10% 4) 15% 5) 20%	 1) N/A 2) N/A 3)136.92 4) N/A 5) N/A	 1)382.5 2)364.5 3)321.4 4)338.7 5)339.6
Tong, M.; Chen, H.; Yang, Z.; Wen, R. *Int. J. Mol. Sci.* ***2011***, 1756-1766	Zn-Al-Hts	43.48	N/A

* = () indicate ratio of Mg^{2+}/Ni^{2+}

[a] belong to general formula of$[M^{(II)}_{1-x}M^{(III}{}_{)x}(OH)_2]^{x+}(A^{n-}{}_{x/n})\ {}_mH_2O$(typically $[Mg_{1-x}Al_x(OH)_2]^{x+}(CO_3)_{x/2}\cdot yH_2O$ made via constant pH method)

[b] depending on aging time (75-7hr : 85-3hr)

[c] depending on hydrothermal treatment temp (aging temp), where 70°C = 180 and 140°C =290

[d] ratio = Al/(Mg+Al) = 0.250

[e] depending on hydrothermal treatment temp/time (112 = 0 hr at 40°C and 909 = 48hr at 150°C)

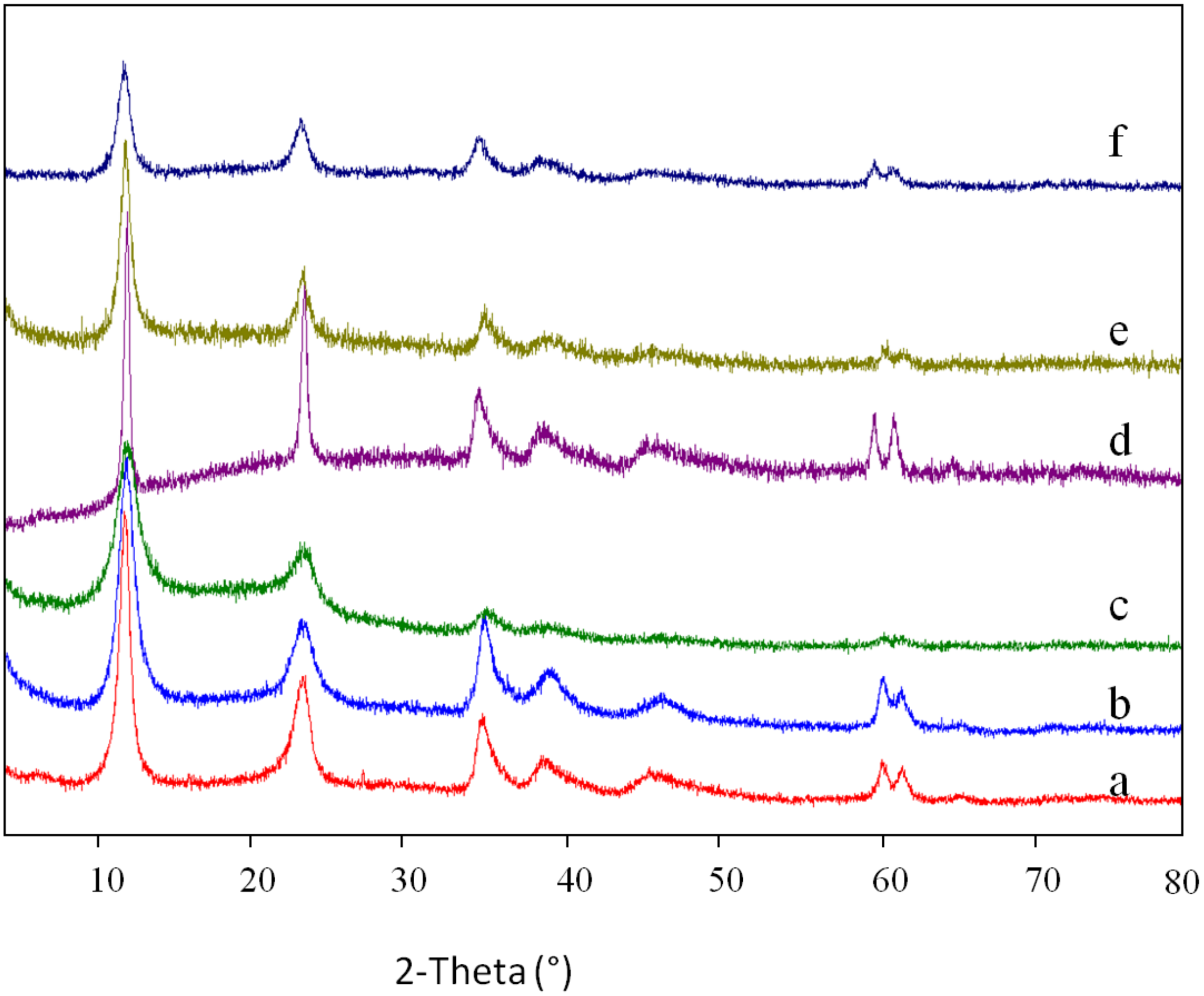


Figure S1: PXRD patterns of (a) HT*1*, (b) HT*2*, (c) HT*3*, (d) HT*4*, (e) HT*5*, (f) HT*6*

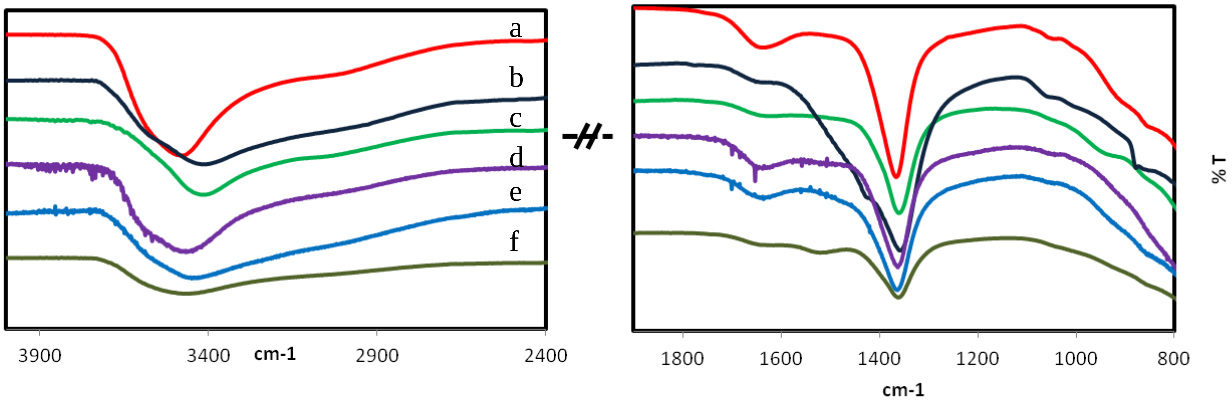
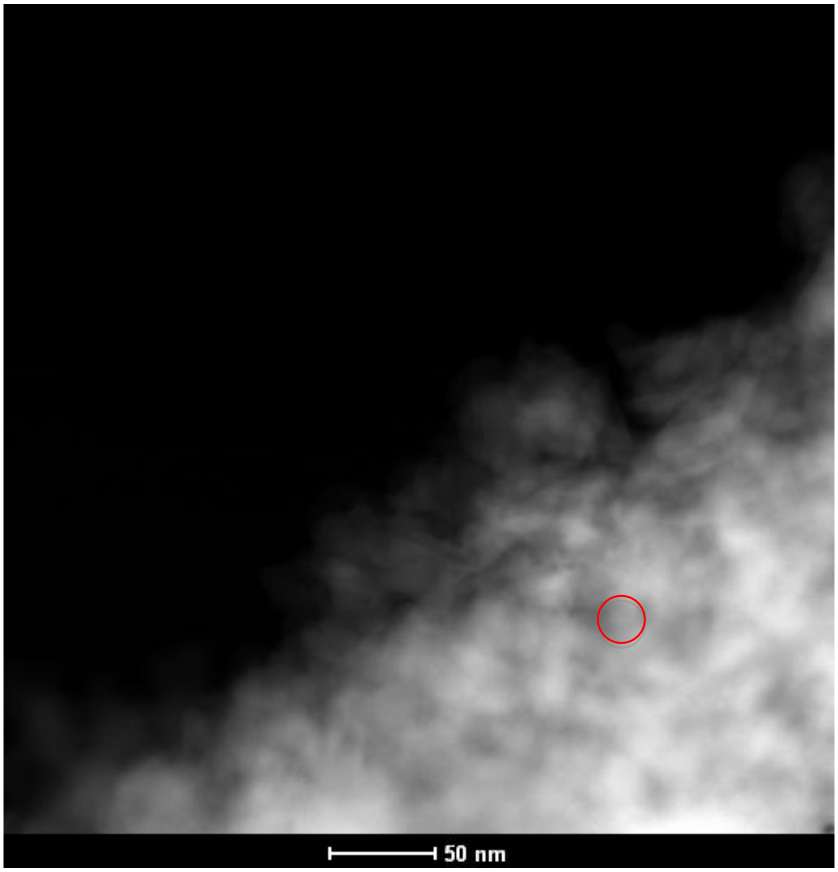


Figure S2: FT-IR spectra of (a) HT*1*, (b) HT*6*, (c) HT*3*, (d) HT*4*, (e) HT*2*, (f) HT*5*


50 nm

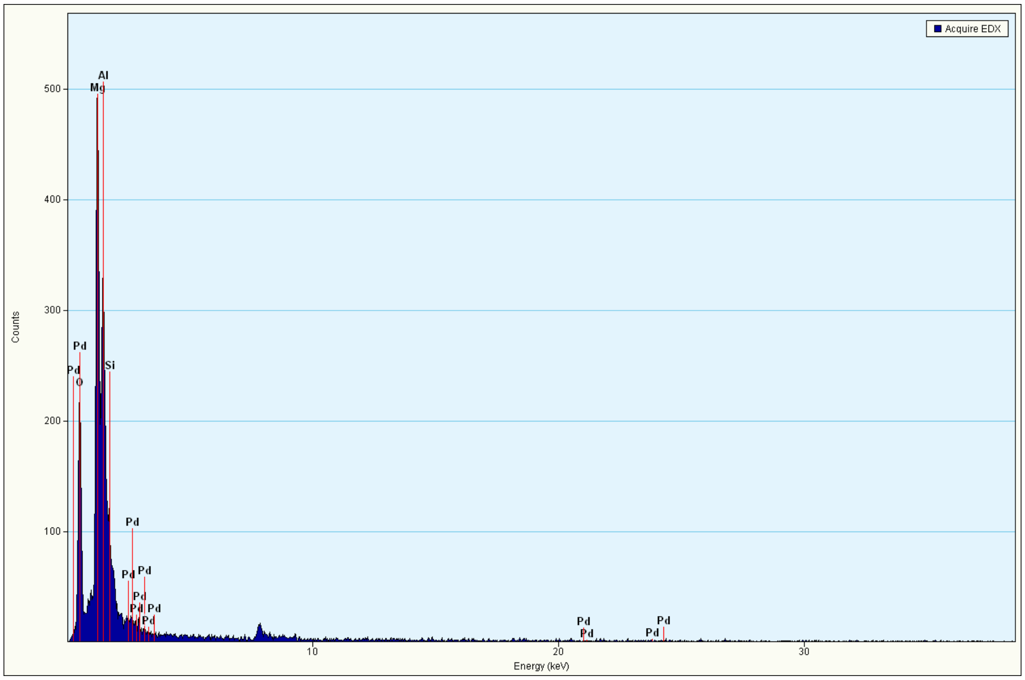


Figure S3. STEM image of Pd/HT***1*** with EDX of the region indicated with red circle.

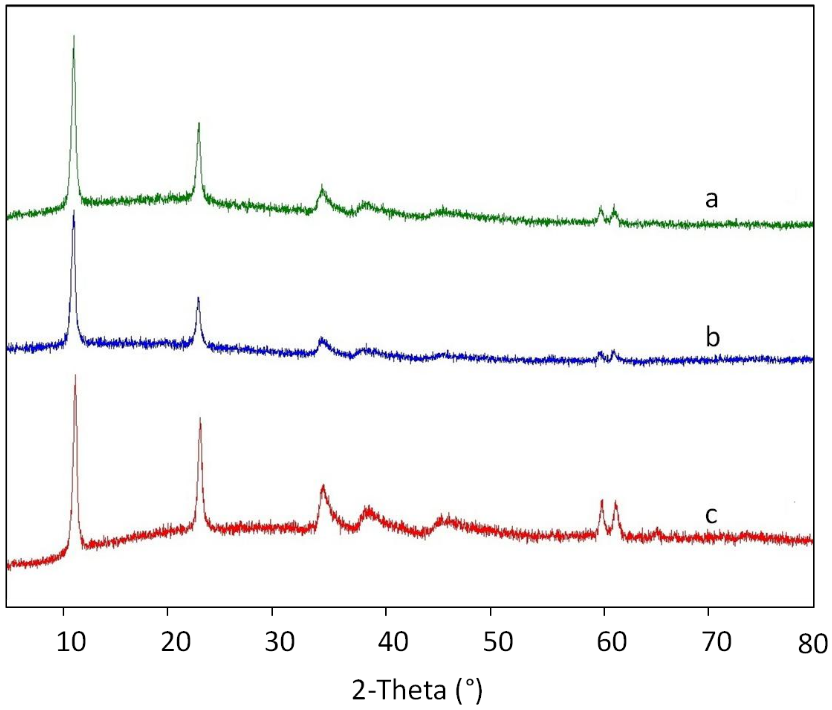


Figure S4. PXRD patterns of (a) HT***4***, (b) HT***4*** washed and dried after 1 cycle of the coupling reaction between benzyl alcohol and p-anisidine and (c) HT***4*** washed and dried after cycle 2

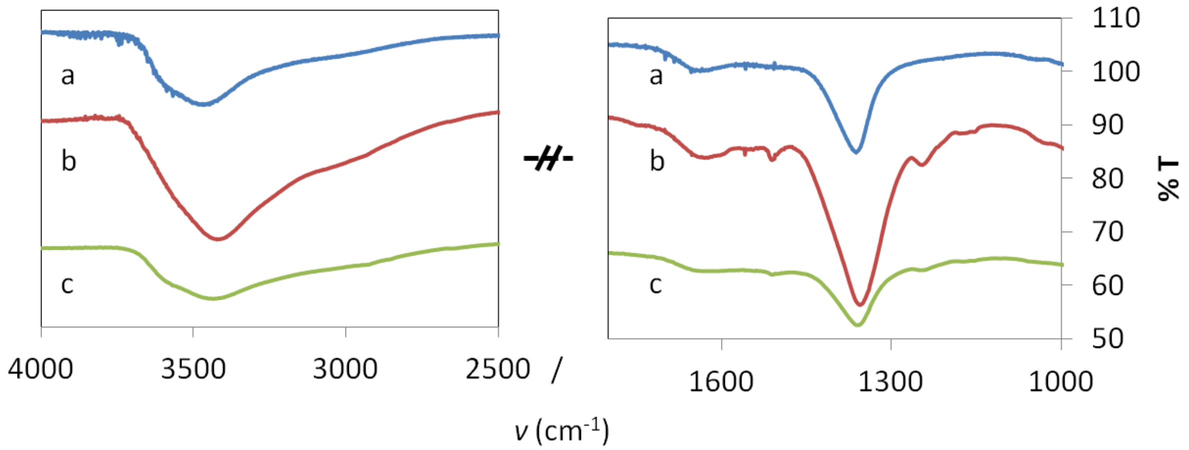
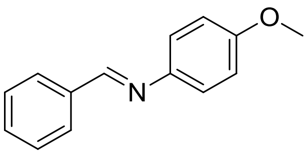
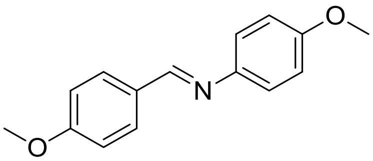


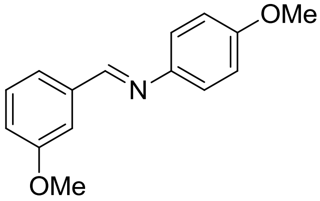
Figure S5: FT-IR spectra of (a) HT***4***, (b) HT***4*** washed and dried after 1 cycle of the coupling reaction between benzyl alcohol and p-anisidine and (c) HT***4*** washed and dried after cycle 2



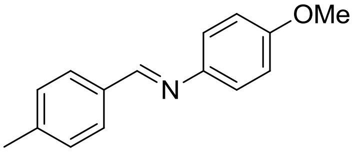
4-methoxy-*N*-(phenylmethylene)benzenamine. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.48 (s, 1H), 7.89 (m, 2H), 7.46 (m, 3H), 7.25 (d, 2H), 6.95 (d, 2H), 3.83(s, 3H). ^{1}H NMR is consistent with spectra reported by Lan, Y.-S..[1]



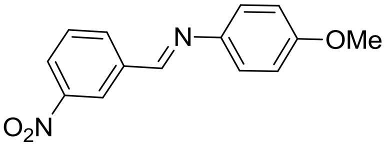
4-methoxy-N-[(4-methoxyphenyl)methylene]-benzenamine. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.40 (s, 1H), 7.82 (d, 2H), 7.19 (d, 2H), 6.96 (m, 4H), 3.86 (s, 3H), 3.82 (s, 3H). ^{1}H NMR is consistent with spectra reported by Bennett, J.S.[2]



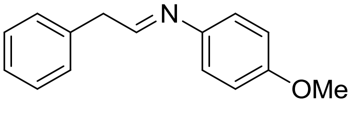
4-methoxy-N-[(3-methoxyphenyl)methylene]-benzenamine. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.44 (s, 1H), 7.51 (s, 1H), 7.39 (m, 2H), 7.22 (d, 2H), 7.03 (d. 1H), 6.94 (2, 2H), 3.88 (s, 3H), 3.82 (s, 3H). ^{1}H NMR is consistent with spectra reported by Cainelli, G.[3]



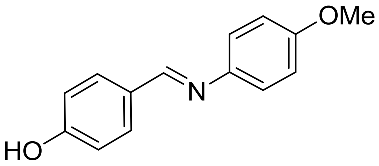
4-methoxy-*N*-[(4-methylphenyl)methylene]- Benzenamine. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.43 (s, 1H), 7.77 (d, 2H), 7.23 (m, 4H), 6.93 (d, 2H), 3.82 (s, 3H), 3.67 (s, 3H^{1}H NMR is consistent with spectra reported by Gopalakrishnan, M.[4]



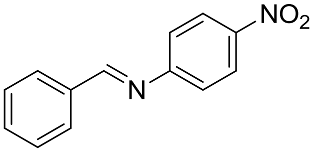
4-methoxy-*N*-[(3-nitrophenyl)methylene]- Benzenamine. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.63 (s, 1H), 8.47 (s, 1H), 8.19 (d, 1H), 8.12 (d, 1H), 7.54 (t, 1H), 7.20 (d, 2H), 6.89 (d, 2H), 3.76 (s, 3H). ^{1}H NMR is consistent with spectra reported by Cao, C.[5]



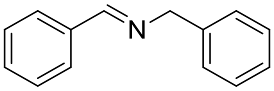
4-methoxy-*N*-(2-phenylethylidene)- Benzenamine. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.32 (t, 1H), 7.59 (m, 2H), 7.47 (m, 3H), 6.97 (d, 2H), 6.85 (d, 2H), 3.81 (s, 3H), 3.52 (d, 2H). ^{1}H NMR is consistent with spectra reported by Tomioka, K.[6]



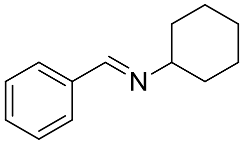
[[(4-methoxyphenyl)imino]methyl]-Phenol. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.34 (s, 1H), 7.71 (d, 2H), 7.28 (d, 2H), 6.91 (d, 2H), 6.42 (d, 2H), 3.78 (s, 3H). ^{1}H NMR is consistent with spectra reported by Chen, L-X.[7]



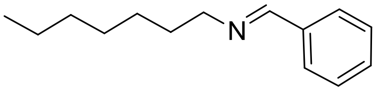
4-nitro-*N*-(phenylmethylene)-Benzenamine. NMR (CDCl$_3$, 400 MHz): δ 8.38 (s, 1H), 8.26 (d, 2H), 8.03 (d, 2H), 7.9 (dd, 2H), 7.51 (m, 3H). ^{1}H NMR is consistent with spectra reported by Naeimi, H.[8]



***N*-(phenylmethylene)- Benzenemethanamine.** NMR (CDCl$_3$, 400 MHz): δ 8.27 (s, 1H), 7.65 (m, 2H), 7.5-7.1 (m, 8H), 3.76 (s, 2H). ^{1}H NMR is consistent with spectra reported by Esteruelas, M.A.[9]



***N*-(phenylmethylene)-Cyclohexanamine**. NMR (CDCl$_3$, 400 MHz): δ 8.13 (s, 1H), 7.71 (m, 2H), 6.98 (m, 3H), 3.11 (m, 1H), 1.82-1.63 (m, 10H) ^{1}H NMR is consistent with spectra reported by Esteruelas, M.A. [9]



***N*-(phenylmethylene)-1-Heptanamine**. NMR ($CDCl_3$, 400 MHz): δ 8.32 (s, 1H), 7.79 (m, 2H), 7.46 (m, 3H), 3.67 (m, 2H), 1.77 (m, 2H), 1.37 (m, 8H), 0.96 (m, 3.29). ^{1}H NMR is consistent with spectra reported by Liu, L. H.[10]

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