Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Amination and Dehydration of 1,3-Propanediol by Hydrogen Transfer: Reactions of a Bio-Renewable Platform Chemical

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Synthetic Procedures.
^{1}H NMR were recorded at 25 °C using a Bruker DPX300 or DPX500 spectrometer. Catalysts **1** and **2** were prepared by a modification of a literature procedure for [Cp*IrCl$_2$(NHC)] complexes.[1] Filtration through celite had to be repeated many times to remove contamination by silver.
Analysis of **2**.

^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 7.10 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H* imidazole), 6.95 (d, $^3J_{HH}$ = 2.0 Hz, 1H, C*H* imidazole), 4.64 (m, 1H, *n*-Bu), 3.99 (s, 3H, NCH_3), 2.05 (m, 1H, *n*-Bu), 1.68 (m, 2H, *n*-Bu), 1.58 (s, 15H, Cp*), 1.49 (m, 2H, *n*-Bu), 0.995 (t, $^3J_{HH}$ = 7.4 Hz, 3H, *n*-Bu).
Anal. Calcd for $C_{18}H_{29}Cl_2IrN_2$: C, 40.29; H, 5.45; N, 5.22. Found: C, 40.34; H, 5.58; N, 5.08.
EI + Ms (VG Autospec X). *m*/*z*: 537 $[M]^+$.

Catalytic Procedures.
The amination of 1,3-propanediol was performed as detailed previously,[2] Employing the quantities detailed in the manuscript (Table 1).

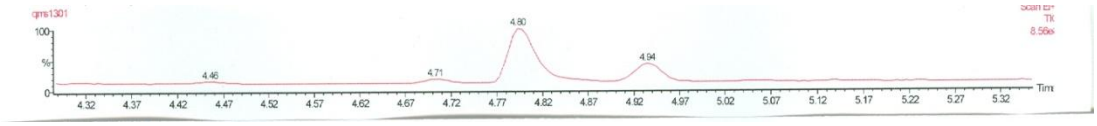
Work-up of the toluene reactions (Table 1 and 2, entries 1 and 2): The reaction mixture was cooled to room temperature and diluted with CH_2Cl_2 (2mL). Salts and catalyst were removed by filtration through a plug of silica. The solvent was removed *in vacuo*. TLC (ethyl acetate / hexane 1:3) revealed 6 products, presumed to be aniline, 1,3-propanediol, **3**, **4**, **5** and an unknown. The ^{1}H NMR analysis of the composition of the toluene solution detailed Tables 1 and 2 (entry 2) was verified by GC/MS (using a 30 m BP5 capillary column), the conversion was calculated (values calculated by ^{1}H NMR in parenthesis) as 68% (71) and the composition as 90% (89) mono-amine **3**, 8% (8) di-amine **4**, 2% (3) *N*-propyl aniline **5**. *N*-allyl aniline was also detected in solution, this was not apparent by NMR, and is assumed to be the unknown detected by TLC.

Work-up of the $N_{1,8,8,8}NTf_2$ reactions (Table 1 and 2, entries 3 – 6): The reaction was cooled to room temperature and quenched by adding H_2O (1.0 mL). The product was extracted with hexane / diethyl ether (3:1, 6 x 5.0 mL) at 0 °C. The mixture is triphasic and composition must be cross referenced against the composition of the crude ionic liquid solution to avoid erroneous results due to selective extraction.

Dehydration in the Absence of Aniline.

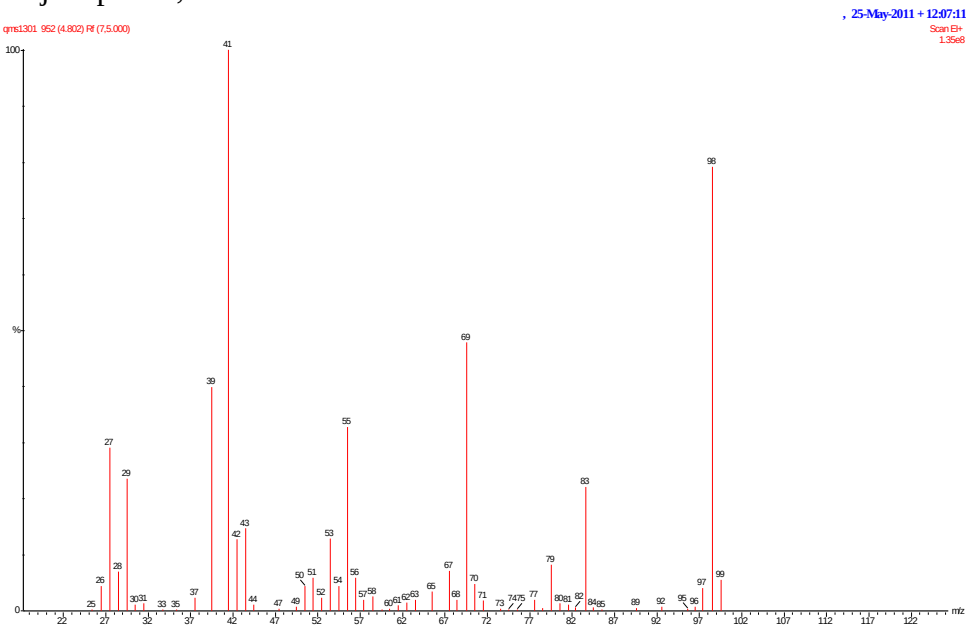
The procedure was adapted from the literature procedure[2] for *N*-alkylation by removing the amine from the reaction solution. Reactions were carried out in sealed tubes under a nitrogen atmosphere. A solution was prepared of K_2CO_3 (0.0210 g), toluene (1.5 mL), 4Å molecular sieves (0.0900g), catalyst (0.0150 millimoles), and 1,3-propanediol (0.1080 mL). A stir bar was added, the top was crimped shut, and the vessel was purged with nitrogen before being put in an oil bath at 115 °C. After running for 24 hours, the solution was allowed to cool and settle. Trap-to-trap vacuum distillation (TTVD) was used to concentrate the product solution. GC/MS was used to analyze the products of reaction.

GC Trace:

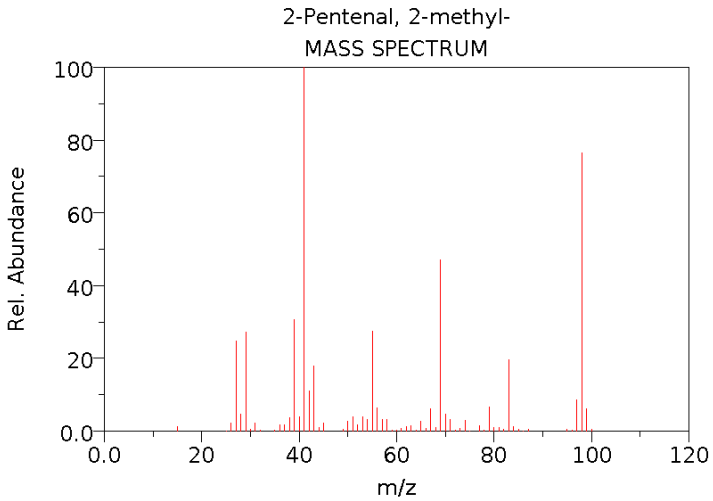


MS Analyses:

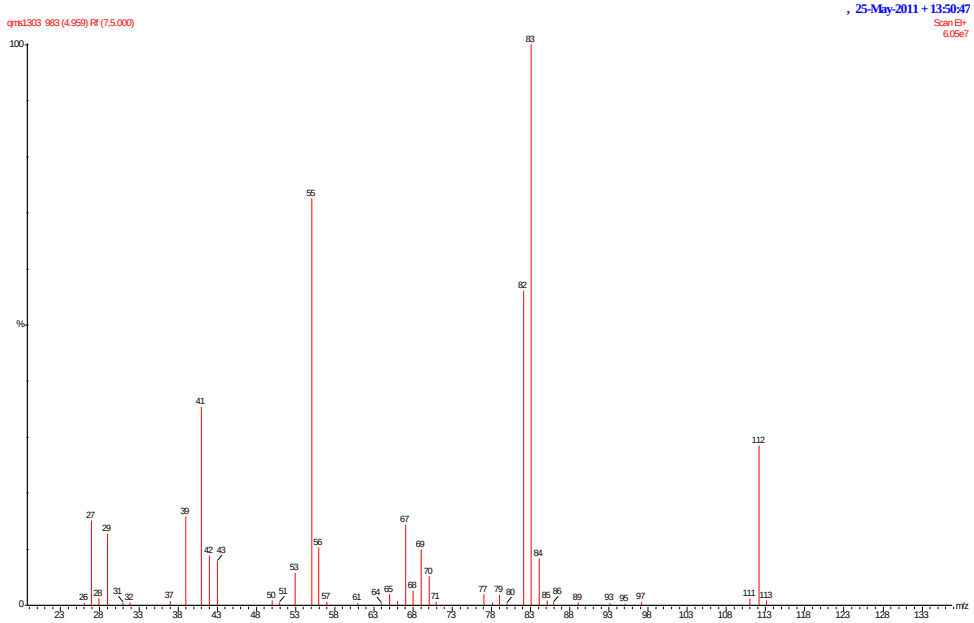
Major species, retention time 4.80:



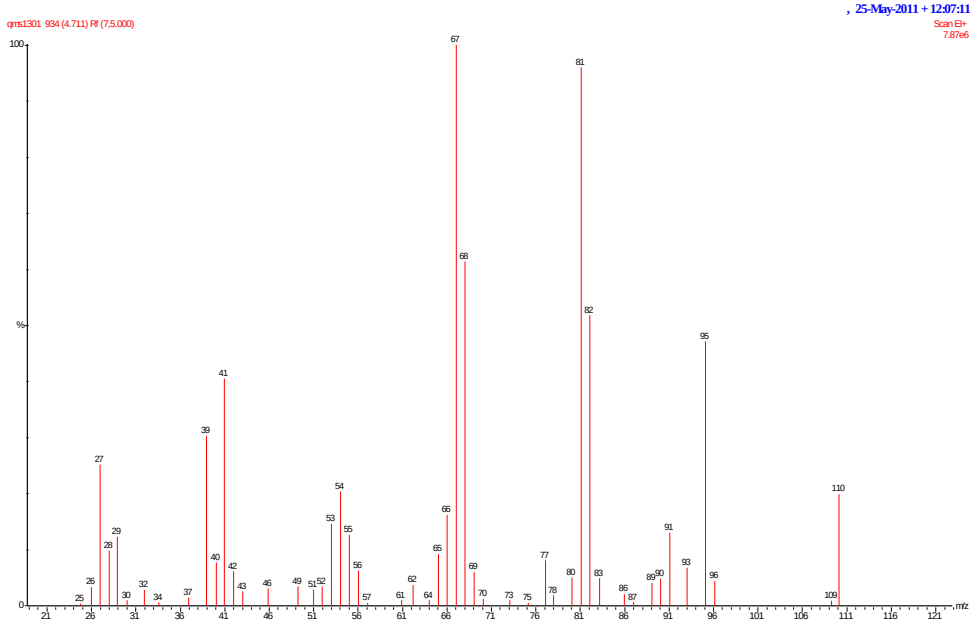
Predicted spectrum for 2-methylpentenal:



Minor Species, retention time 4.94:



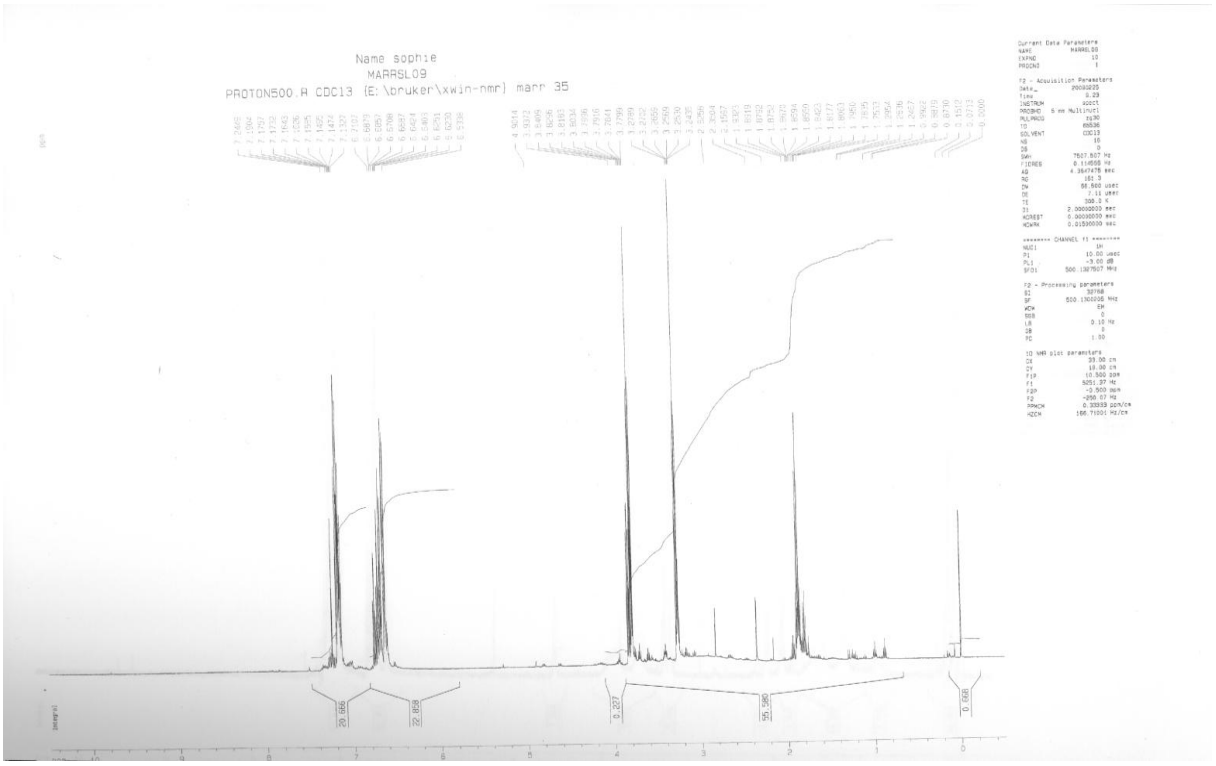
Trace Species, retention time 4.71:



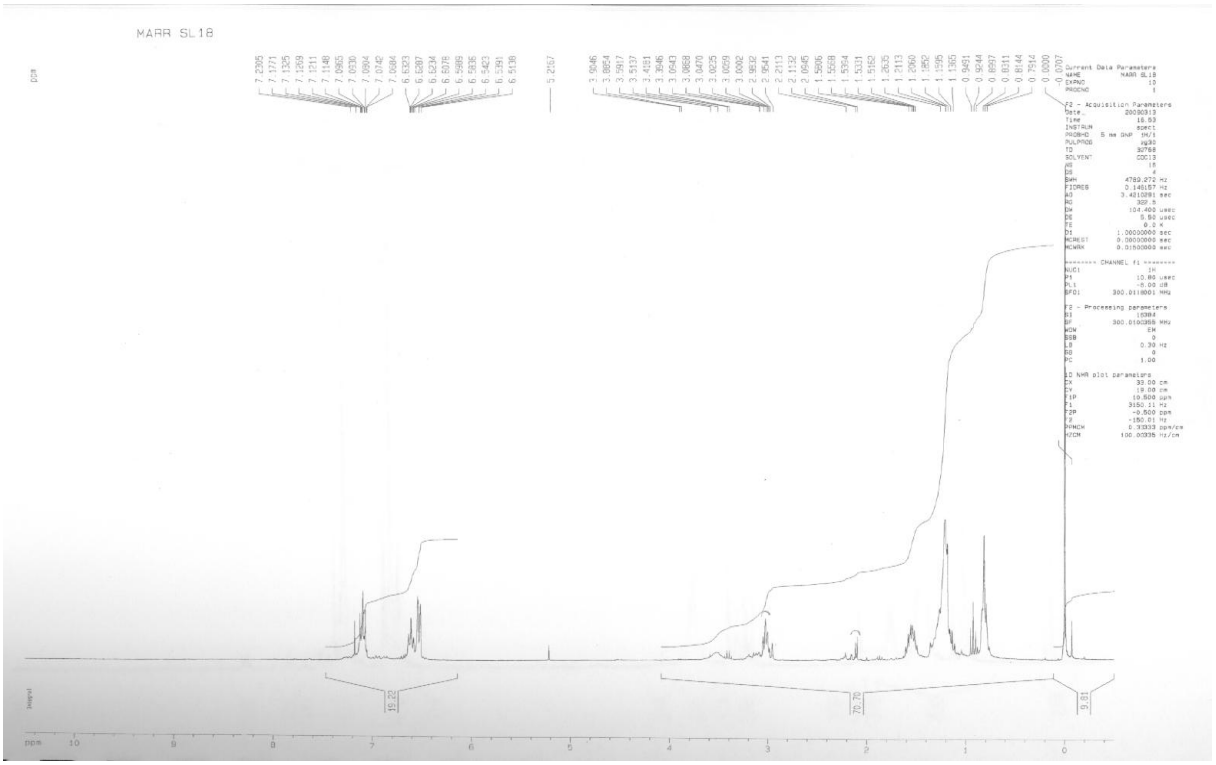
References

1. Rosa Corberán, M. Sanaú and E. Peris, *J. Am. Chem. Soc*. 2006, **128**, 3974 – 397.
2. S. Liu, M. Rebros, G. Stephens, A. C. Marr, *Chem. Commun.* 2009, 2308 – 2310 and supplementary data.

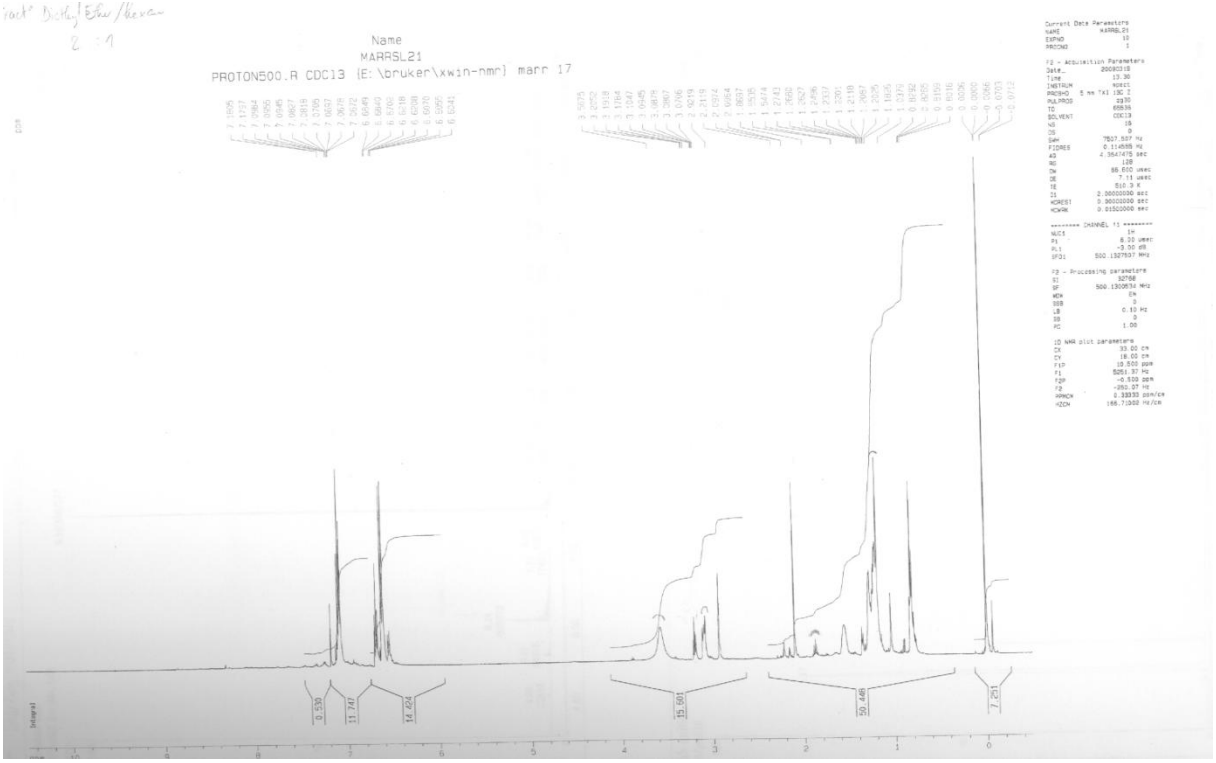
Appendix: NMR Spectra of Products, predominantly 3, 5 and 4 respectively.



NMR of products of the reaction of aniline and 1,3-propanediol under conditions for Table 1 and 2, entry 2.



NMR of products of the reaction of aniline and 1,3-propanediol under conditions for Table 1 and 2, entry 5.



NMR of products of the reaction of aniline and 1,3-propanediol under conditions for Table 1 and 2, entry 6.