Supporting information for

Catalytic dehydrative etherification and chlorination of benzyl alcohols in ionic liquids

Hassan A. Kalviri, Chad F. Petten and Francesca M. Kerton*

Chemistry Department, Memorial University of Newfoundland, St. John's, Newfoundland, A1B 3X7, Canada

To whom correspondence should be addressed. E-mail: fkerton@mun.ca

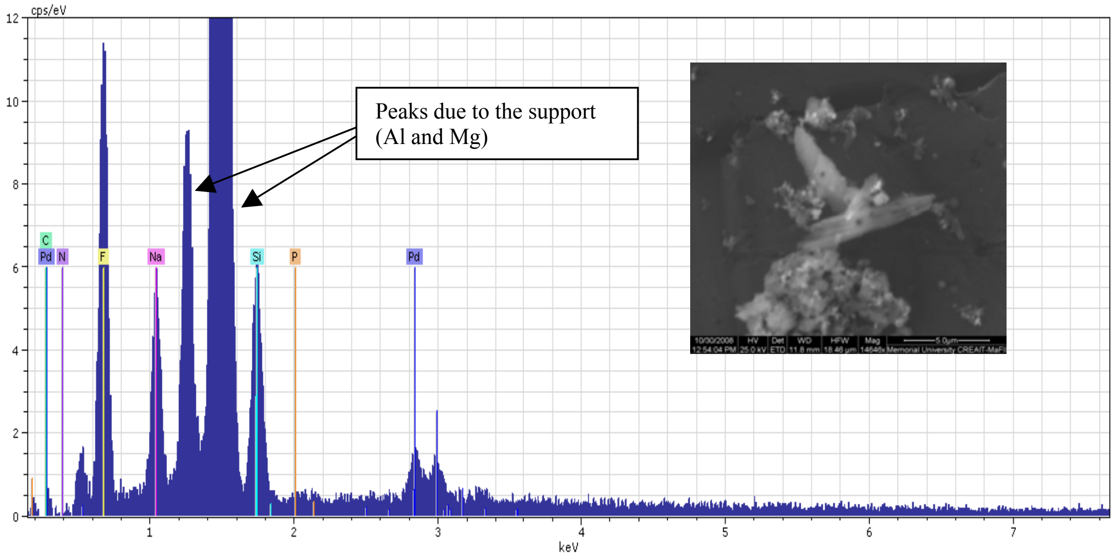
Contents:

General information:

$PdCl_2$ and $RuCl_3 \cdot xH_2O$ were purchased from Precious Metals Online. All reagents and [BMMIm]PF_6 were purchased from Alfa Aesar, while the ionic liquid [P_{66614}]DBS was a gift from Cytec Inc. [BMIm]Cl, [BMIm]BF_4 and [BMIm]PF_6 were prepared using literature procedures. (P. A. Z. Suarez, J. E. L. Dullius, S. Einloft, R. F. De Souza and J. Dupont, *Polyhedron*, 1996, **15**, 1217)

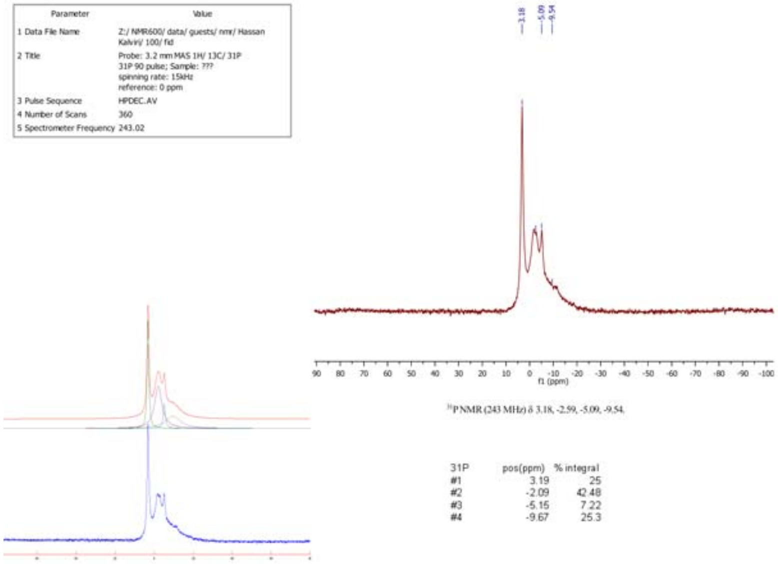
The (Scanning Electron Microscope) SEM images were obtained using a *FEI Quanta 400* environmental SEM. The system has an Energy Dispersive X-ray (EDX) analytical system from Roëntec.^{1}H-NMR spectra were acquired on a Bruker AVANCE 500MHz spectrometer. Solid-state ^{19}F-NMR and ^{31}P-NMR spectra were ran on a Bruker AVANCE II 600 spectrometer. An Anton Paar (Synthos 3000) microwave reactor was used to run the experiments under MW irradiation. In this reactor, a Rotor 64MG5 that is suitable to run the reactions in a 0.3 to 3.0 mL scale (up to 20 bar and 200 °C) was used. GC-MS spectra were recorded on an Agilent 7890A GC system coupled with an Agilent 5975C MS detector that was equipped with a capillary column DB-5 (column length: 30.0 m and column diameter: 0.25 mm).

All the chemical shifts are reported in ppm and all solution state NMR experiments were performed in acetone-D_6 except one experiment (Table 2, Entry 9, using [P_{66614}]DBS) in which chloroform-D was used as the deuterated solvent. In all quantification experiments, acetophenone was used as the internal standard (Fig S9). Table S1 shows the chemical shifts of the benzylic protons in the products that were documented in Tables 1 and 2. GC-MS was used to confirm the identities of products and the selectivity of the reactions. For several reactions (using Pd or Ru), the reaction product was extracted and an isolated yield calculated. Isolated yields were in general agreement with NMR yields. When $FeCl_3{\cdot}6H_2O$ was used as the catalyst, due to its paramagnetic nature, the reaction product was extracted using diethyl ether, concentrated and analysed using ^{1}H NMR spectroscopy and GC-MS.



Peaks due to the support (Al and Mg)

Fig S1. EDX analysis of the precipitate from reaction mixtures, when Y ≠ OMe. The inset image is an SEM image of the precipitate.



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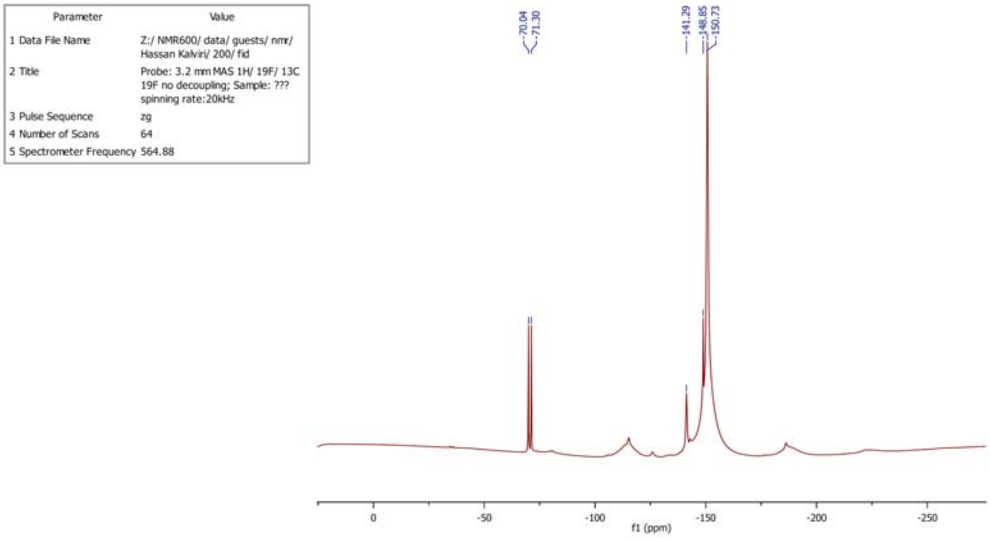
3 Pulse Sequence	HPDEC.AV
4 Number of Scans	360
5 Spectrometer Frequency	243.02

^{31}P NMR (243 MHz) δ 3.18, -2.59, -5.09, -9.54.

31P	pos(ppm)	% integral
#1	3.19	25
#2	-2.09	42.48
#3	-5.15	7.22
#4	-9.67	25.3

Fig S2. Solid-state ^{31}P-NMR spectrum of precipitate from reaction mixture



Parameter	Value
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3 Pulse Sequence	zg
4 Number of Scans	64
5 Spectrometer Frequency	564.88

^{19}F NMR (565 MHz, DMSO) δ -70.04, -71.30, -141.29, -148.85, -150.73.

Fig S3. Solid-state ^{19}F-NMR spectrum of precipitate from reaction mixture

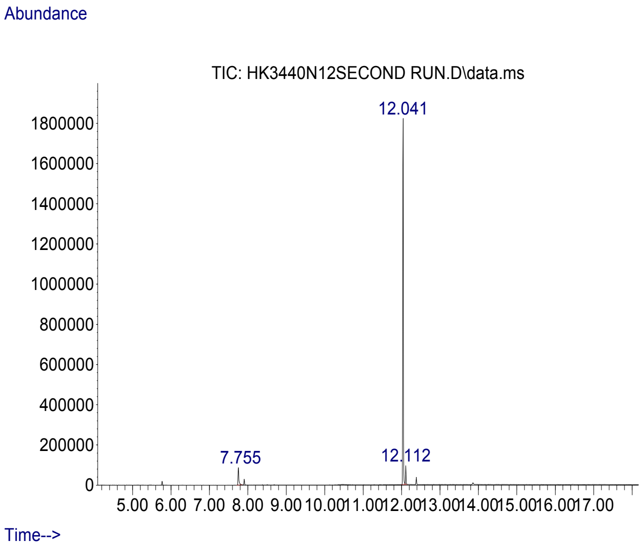

Fig S4. GC trace for the reaction of 4-methoxybenzyl alcohol under MW condition for a prolonged reaction time (20 minutes, $Pd(CH_3CN)_2Cl_2$). Retention times: t (7.75) for 4-methoxybenzyl alcohol and t (12.04) for 4,4´-dimethoxydiphenyl methane (**4**)

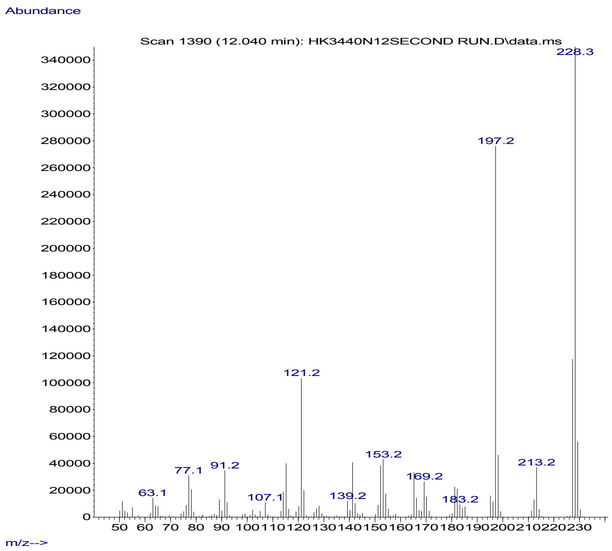

Fig S5. MS spectrum for 4,4´-dimethoxydiphenyl methane (**4**), related to Fig. S4

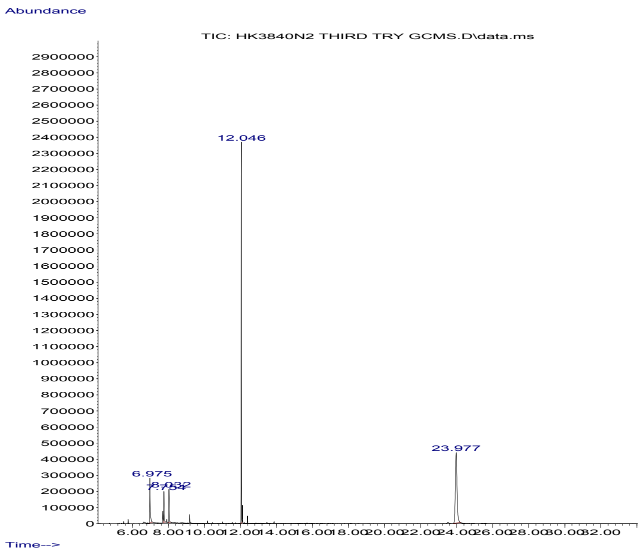

Fig S6. GC trace for the reaction of 4-methoxybenzyl alcohol with $PdCl_2$ as the catalyst (MW 9 minutes). Retention times: t (12.05) for 4,4′-dimethoxydiphenyl methane (**4**) and t (23.98) for [4-methoxy-3-(4-methoxybenzyl)phenyl](4-methoxyphenyl)methane (**6**)

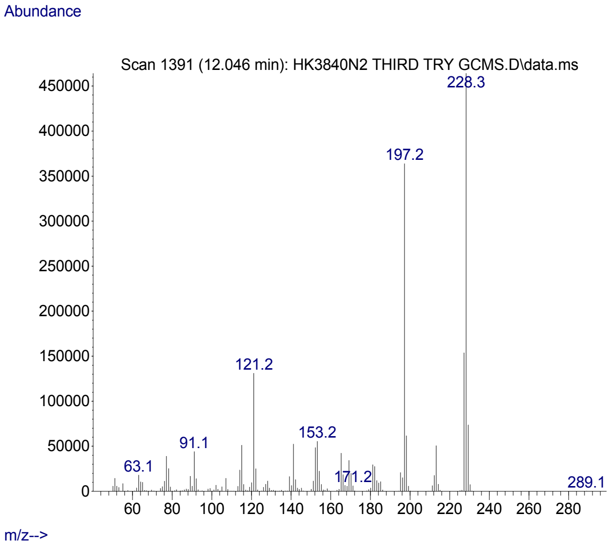

Fig S7. MS spectrum for 4,4′-dimethoxydiphenyl methane (**4**), related to Fig. S6

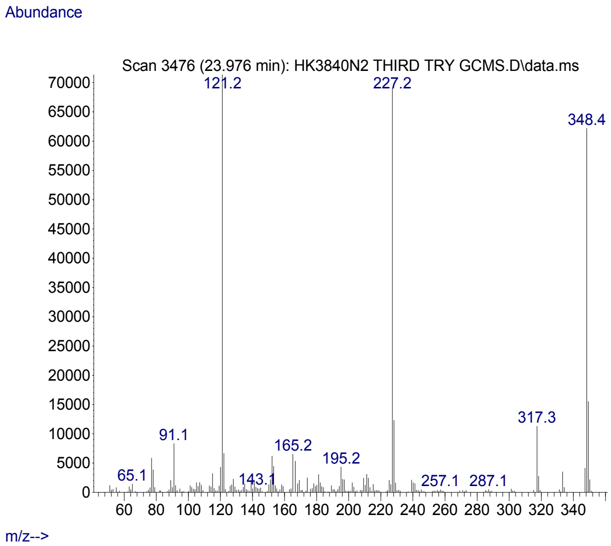

Fig S8. MS spectrum for [4-methoxy-3-(4-methoxybenzyl)phenyl](4-methoxyphenyl)methane (**6**), related to Fig. S6

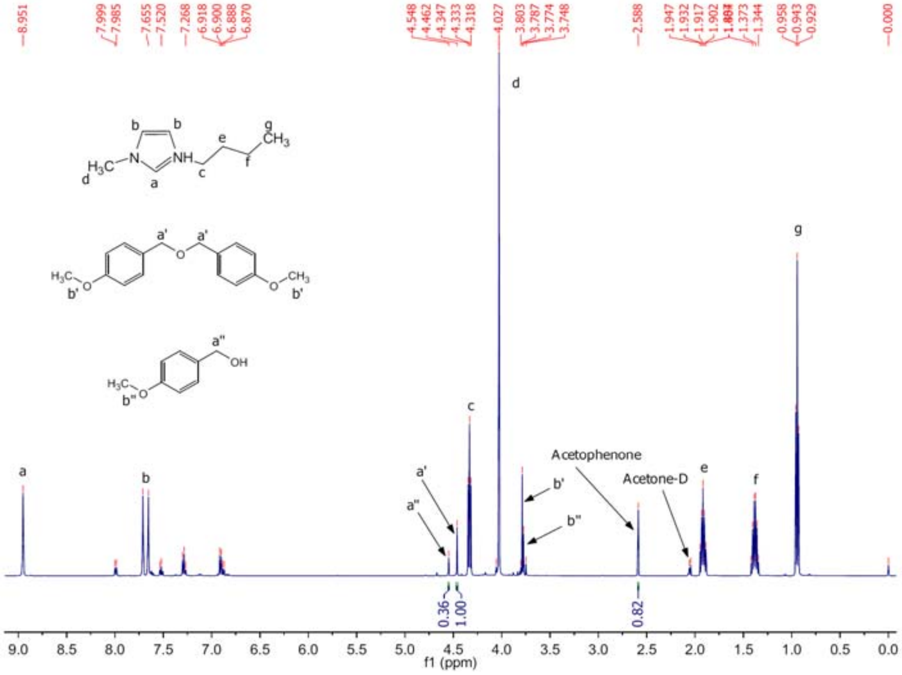

Fig S9. ^{1}H-NMR spectrum of the reaction related to Table 2, entry 4.

Table S1. Chemical shifts of the benzylic protons in the ether products (Table 2). Deuterated solvent: acetone-D_6 except for entry 7 where chloroform-D was used.

Entry	1	2	3	4	5	6	7	8
Y in different substrates	H	Cl	CH_3	OCH_3	NO_2	Br	OCH_3 in $[P_{66614}]$DBS	H in [BMMIm]PF_6
Chemical shifts for benzylic protons in ethers (ppm)	4.58	4.58	4.50	4.45	-	4.57	4.46	4.58