Supporting Information for

Selective Cleavage of Allyl and Propargyl Ethers to

Alcohols Catalyzed by $\text{Ti}(\text{O-}i\text{-Pr})_4/\text{MX}_n/\text{Mg}$

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**^1H and ^{13}C NMR spectra of allyl- and propargyl ethers 1, 3 and 4,
esters 8-10, and bezen derivatives 2a and 2b.**

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Compounds

In Figure 1: **3a 3b 3d 3f 3j 3k 4a 4b 4e 4f 4g 4h 4i 4j 4k**

In Figure 2: **8 9 10**

In Scheme 6: 1-Allyloxymethyl-4-benzyloxybenzene

(4-Benzyloxyphenyl)-methanol

1-Benzyloxy-4-methylbenzene (^1H NMR)

1-Chloromethyl-4-benzyloxybenzene (^1H NMR)

In Scheme 1: **2a and 2b**

NMR spectra were recorded by use of a solution in CDCl₃ at 600 MHz for ¹H and 150 MHz for ¹³C, respectively, on JEOL JNM-ECA600 spectrometers. The substrate ethers **1**,¹ **3**,² **4**³ and esters **8-10**⁴ were prepared from the corresponding alcohol according to conventional reaction conditions and the following purification by column chromatography,⁵ and their NMR spectra are attached in the following pages. The product alcohols which were obtained by the present deallylation and/or depropargylation of ethers **3**, **4** or esters **8-10** are the known compounds, many of which are commercially available, and were characterized by comparison of their NMR spectra with those of the corresponding parent alcohols and TLC analysis. The benzene derivatives **2a-d** which were obtained from alkyne **1a**, **1b**, phenylacetylene or 1-hexyne were identical to the authentic samples prepared previously by us.¹

This file includes NMR spectra of the following compounds:

- (1) Saino, N.; Kogure, D.; Kase, K.; Okamoto, S. *J. Organomet. Chem.* **2006**, *691*, 3129. Saino, N.; Amemiya, F.; Tanabe, E.; Kase, K.; Okamoto, S. *Org. Lett.* **2006**, *8*, 1439. Saino, N.; Kogure, D.; Okamoto, S. *Org. Lett.* **2005**, *7*, 3065.
- (2) (a) For allyl ethers, see: Lee, K. Y.; Lee, M. J.; Kim, J. N. *Tetrahedron* **2005**, *61*, 8705. (b) Ranu, B. C.; Dutta, J.; Guchhait, S. K. *J. Org. Chem.* **2001**, *66*, 5624. (c) Dunn, J. A.; Pauson, P. L. *J. Organomet. Chem.* **1991**, *419*, 383. (d) Schneiderova, L.; Strouf, O.; Gruner, B.; Pouzar, V.; Drasar, P.; Hampl, R.; Kimlova, I. *Collect. Czech. Chem. Commun.* **1992**, *57*, 463. (e) Ashim, R.; Sahabuddin, S.; Basudeb, A.; Sukhendu, B. M. *Tetrahedron* **2005**, *61*, 365.
- (3) For propargyl ethers, see: (a) Gozzo, F. C.; Fernandes, S. A.; Rodrigues, D. C.; Eberlin, M. N.; Marsaioli, A. J. *J. Org. Chem.* **2003**, *68*, 5493. (b) Haight, A. R.; Stoner, E. J.; Peterson, M. J.; Grover, V. K. *J. Org. Chem.* **2003**, *68*, 8092. (c) Bartoli, G.; Cupone, G.; Dalpozzo, R.; De Nino, A.; Maiuolo, L.; Marcantoni, E.; Procopio, A. *Synlett* **2001**, 1897. (d) Bailey, W. F.; England, M. D.; Mealy, M. J.; Thongsornkleeb, C.; Teng, L. *Org. Lett.* **2000**, *2*, 489. (e) Taniguchi, T.; Ogasawara, K. *Angew. Chem., Int. Ed.* **1998**, *37*, 1136.
- (4) (a) Iwasaki, F.; Koyanagi, S.; Tsucha, S. *Jpn. Kokai Tokkyo Koho*, 06340590, 13 Dec 1994. (b) Genet, J. P.; Blart, E.; Savignac, M.; Lemeune, S.; Lemaire-Audoire, S.; Paris, J. M.; Bernard, J. *Tetrahedron* **1994**, *50*, 497. See also ref 3d.
- (5) Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis*, 3rd ed.; Wiley: New York, 1999.

¹H NMR of 3a

^{13}C NMR of **3a**

^1H NMR of **3b**

¹³C NMR of **3b**

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^{13}C NMR of **3d**

^1H NMR of **3f**

^{13}C NMR of **3f**

^1H NMR of **3j**

^{13}C NMR of **3j**

^1H NMR of **3k**

^{13}C NMR of **3k**

¹H NMR of 4a

^{13}C NMR of **4a**

¹H NMR of **4b**

^{13}C NMR of **4b**

^1H NMR of **4e** (a mixture of *E* and *Z* isomers)

^{13}C NMR of **4e** (a mixture of *E* and *Z* isomers)

^1H NMR of **4f**

¹³C NMR of **4f**

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^1H NMR of **4h**

¹³C NMR of **4h**

^1H NMR of **4i**

^{13}C NMR of **4i**

¹H NMR of **4j**

^{13}C NMR of **4j**

^1H NMR of **4k**

^{13}C NMR of **4k**

^1H NMR of **8**

^{13}C NMR of **8**

^1H NMR of **9**

¹³C NMR of **9**

^1H NMR of **10**

^{13}C NMR of **10**

^1H NMR of 1-allyloxymethyl-4-benzyloxybenzene

^{13}C NMR of 1-Allyloxymethyl-4-benzyloxybenzene

^1H NMR of (4-benzyloxyphenyl)-methanol

^{13}C NMR of (4-benzyloxyphenyl)-methanol

^1H NMR of 1-benzyloxy-4-methylbenzene

^1H NMR of 1-chloromethyl-4-benzyloxybenzene

¹H NMR (500MHz, CDCl₃) of **2a**

¹³C NMR (125MHz, CDCl₃) of **2a**