

Plenary meeting, May 2021

EHLCATHOL

*Chemical transformation of enzymatic hydrolysis lignin (EHL)
with catalytic solvolysis to fuel commodities under mild conditions*



Homogeneous transition-metal catalysts for the reductive cleavage of C-O bonds in lignin model compounds

D. Savary, EPFL

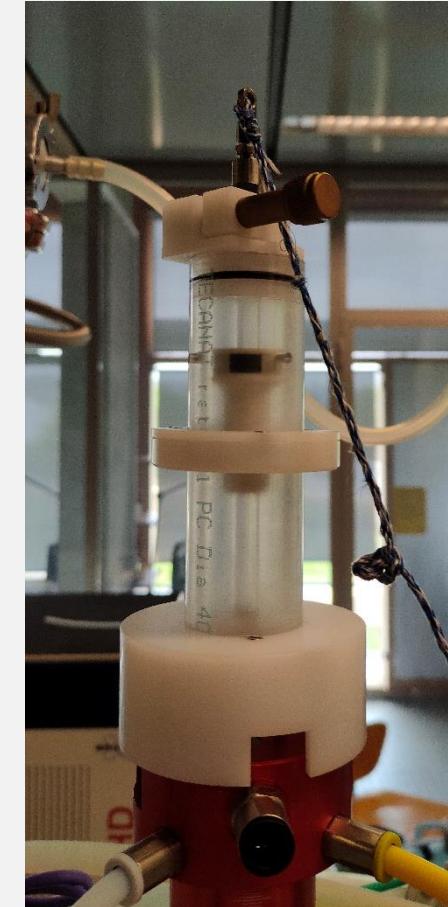
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Operando spectroscopy: high-pressure sapphire NMR tubes

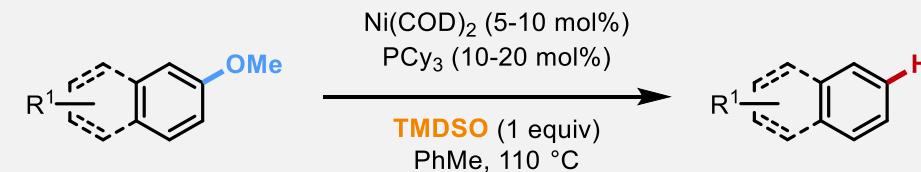


Operando spectroscopy: high-pressure sapphire NMR tubes

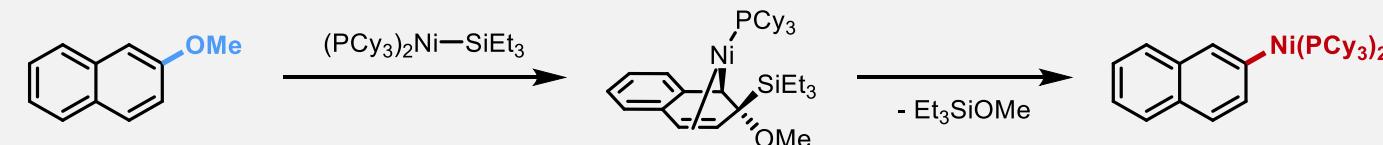


TM-catalysed reductive cleavage of C–O bonds: silanes

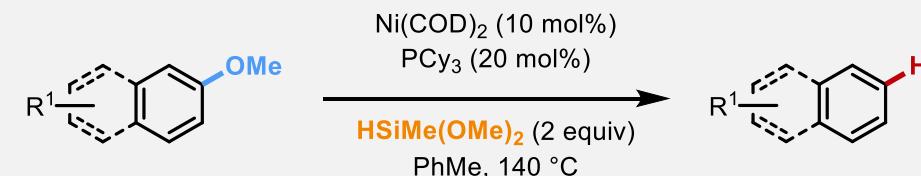
Martin^[a], JACS 2010



Martin and Gómez-Bengoa^[b], JACS 2013



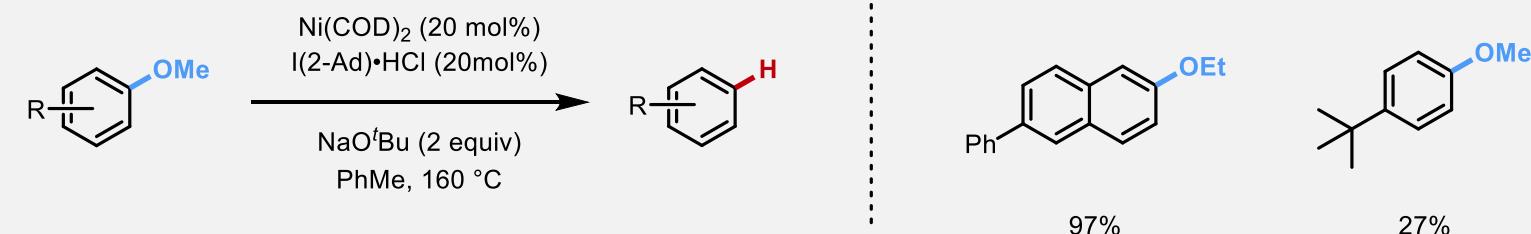
Tobisu and Chatani^[c], Chem. Comm. 2011



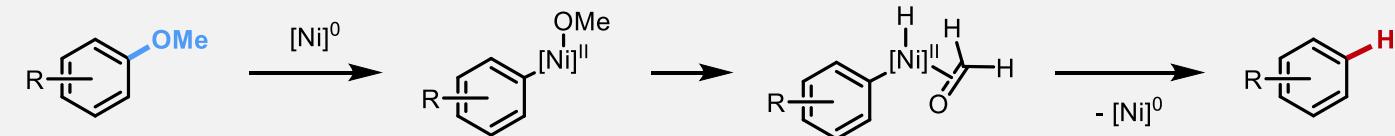
[a] P. Álvarez-Bercedo, R. Martin, *J. Am. Chem. Soc.* **2010**, *132*, 17352. [b] J. Cornella, E. Gómez-Bengoa, R. Martin, *J. Am. Chem. Soc.* **2013**, *135*, 1997. [c] M. Tobisu, K. Yamakawa, T. Shimasaki, N. Chatani, *Chem. Commun.* **2011**, *47*, 2946.

TM-catalysed reductive cleavage of C-O bonds: no external reductant

Tobisu and Chatani^[a], *ACS Catal.* **2018**



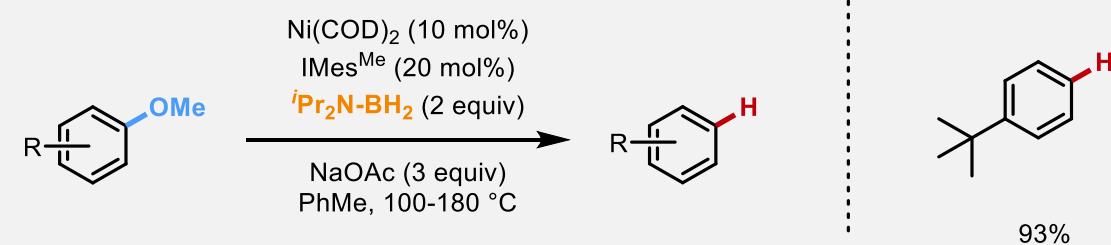
Proposed mechanism



[a] T. Igarashi, A. Haito, N. Chatani, M. Tobisu, *ACS Catal.* **2018**, *8*, 7475–7483.

TM-catalysed reductive cleavage of C-O bonds: another reductant

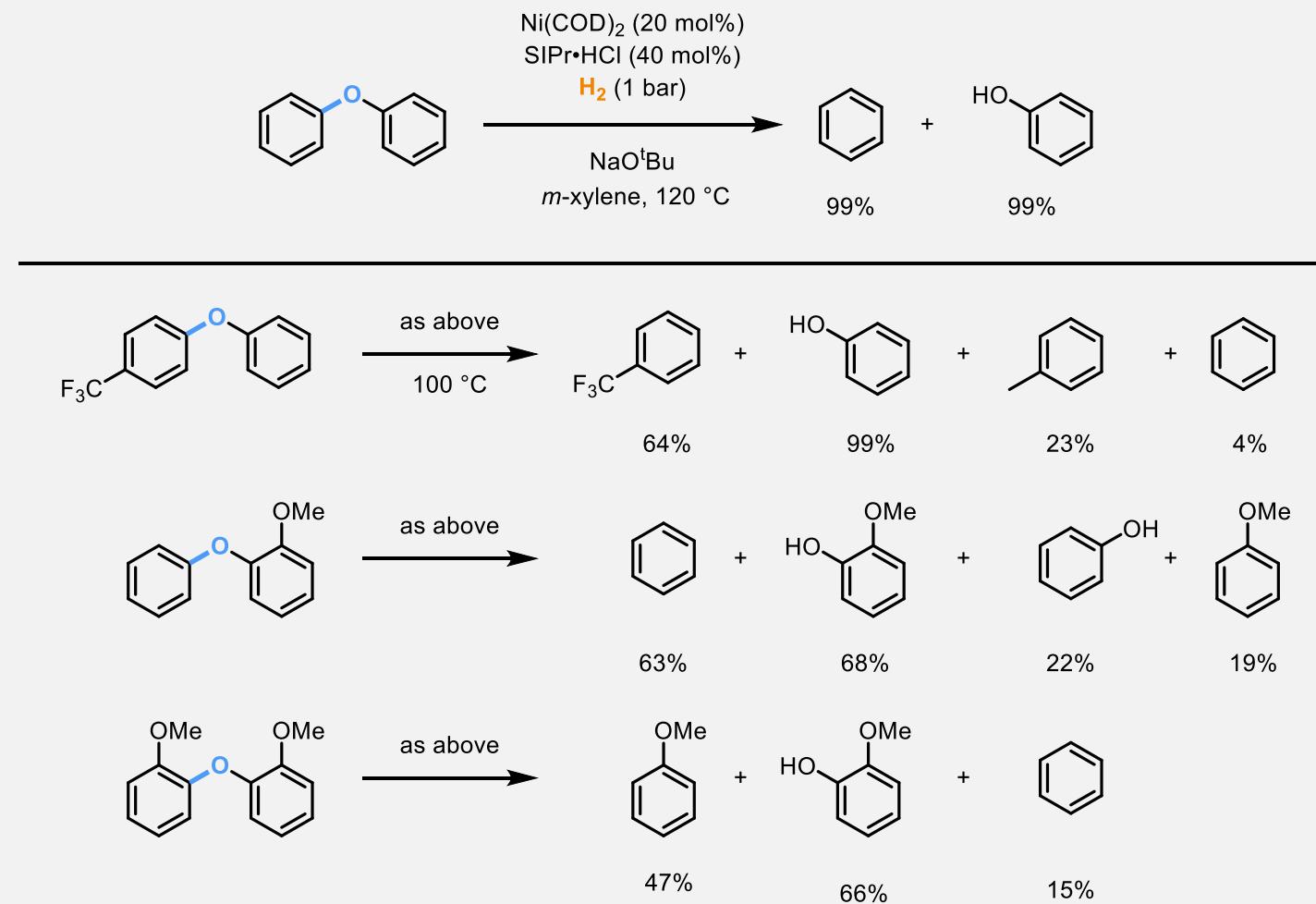
Tobisu and Chatani^[a], *ACS Catal.* **2018**



[a] T. Igarashi, A. Haito, N. Chatani, M. Tobisu, *ACS Catal.* **2018**, *8*, 7475.

TM-catalysed reductive cleavage of C-O bonds: H₂

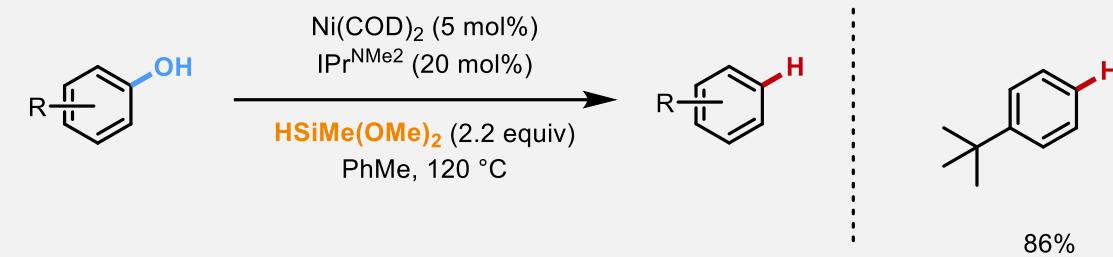
Hartwig^[a], *Science* 2011



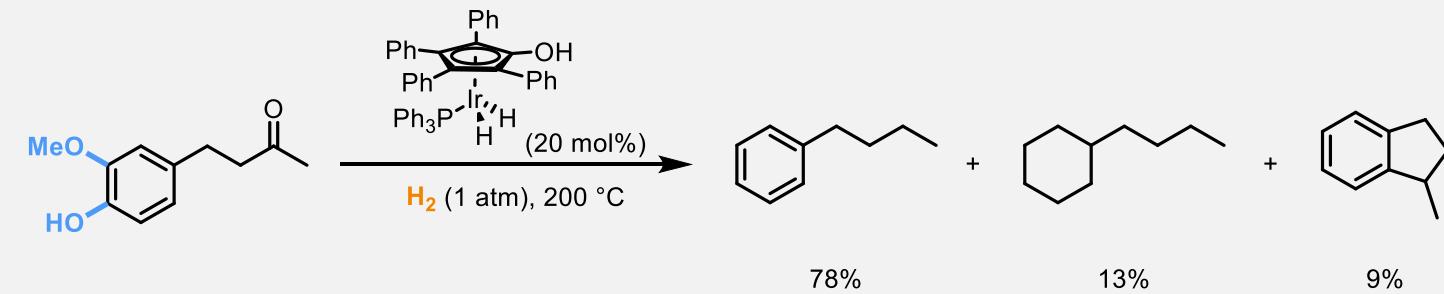
[a] A. G. Sergeev, J. F. Hartwig *Science* 2011, 332, 439.

TM-catalysed reductive cleavage of C-O bonds : phenols

Nakao^[a], *Chem. Lett.* **2016**

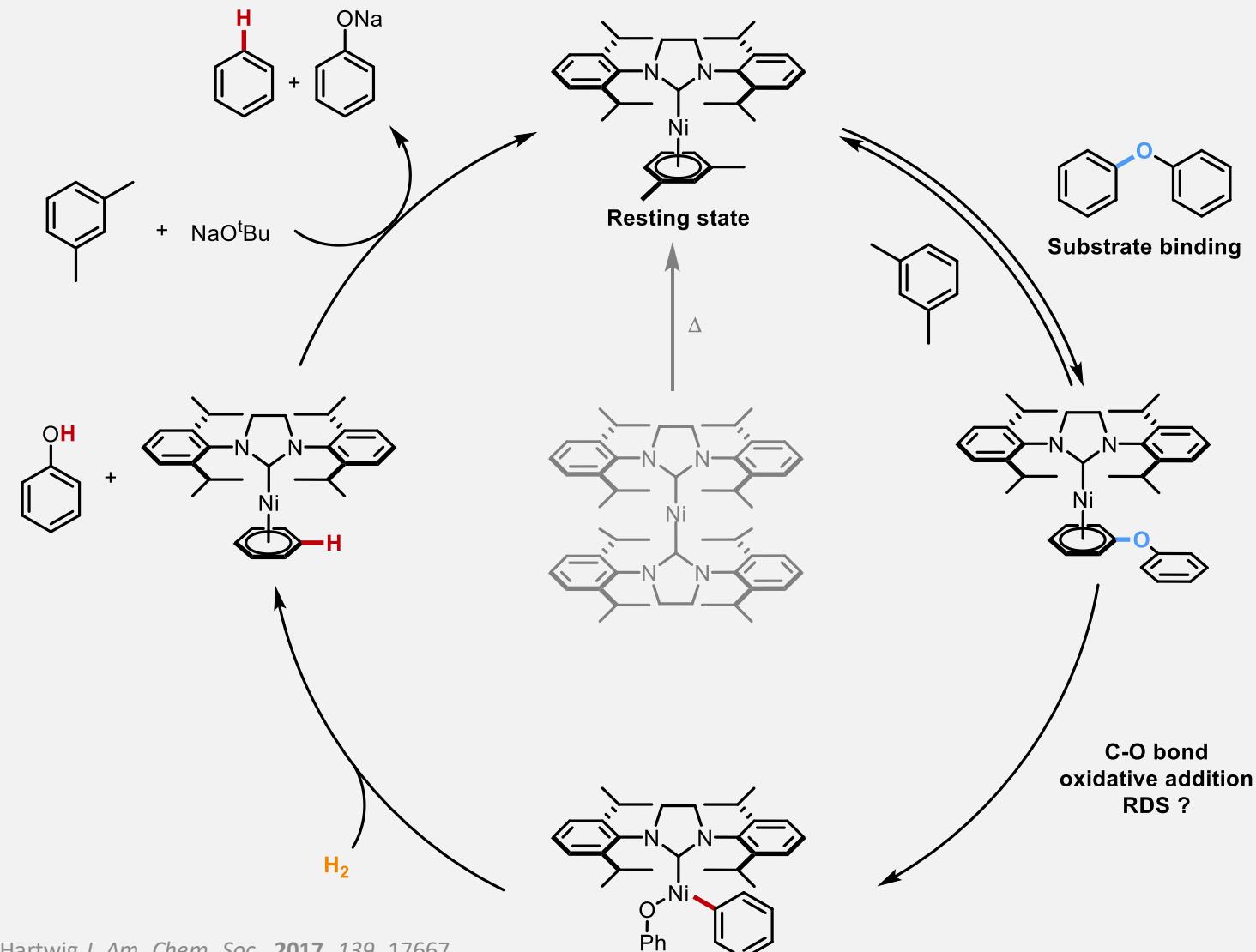


Nozaki^[b], *Nat. Commun.* **2015**



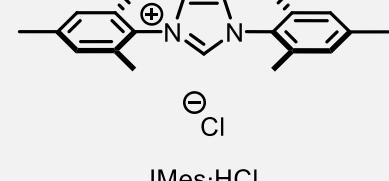
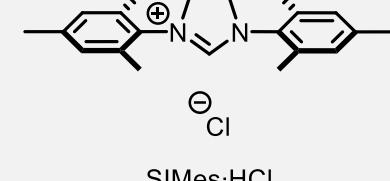
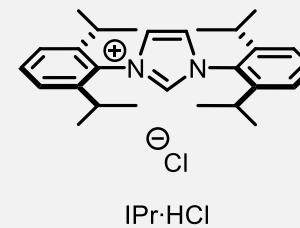
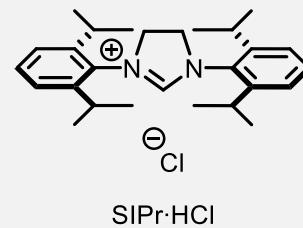
[a] A. Ohgi, Y. Nakao, *Chem. Lett.* **2016**, 45, 45. [b] S. Kusumoto, K. Nozaki, *Nat. Commun.* **2015**, 6, 1.

Hydrogenolysis diaryl ethers: proposed mechanism



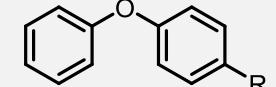
[a] N. I. Saper, J. F. Hartwig *J. Am. Chem. Soc.* 2017, 139, 17667.

In situ formation of the catalyst, preliminary screening

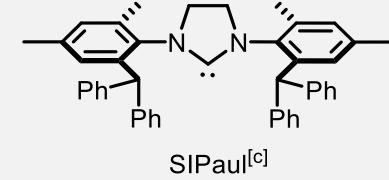
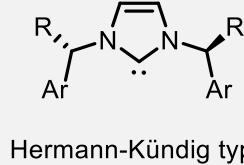
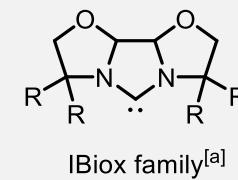


- NHC ligands (SIPr, IPr, SIMes, IMes,...)
- Nickel sources ($\text{NiCl}_2\text{-glyme}$, NiOTf_2 , $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$, ...)
- Solvents (*m*-xylene, *o*-xylene, toluene, THF,...)
- Bases (NaO^tBu , KO^tBU , Cs_2CO_3 , CsOPiv , K_3PO_4 , ...)
- H_2 pressure (1-10 bar)
- No better conditions found so far

Model compounds



$\text{R} = -\text{H}, -\text{Et}, -\text{OMe}, -\text{CF}_3, -\text{OCF}_3, \dots$

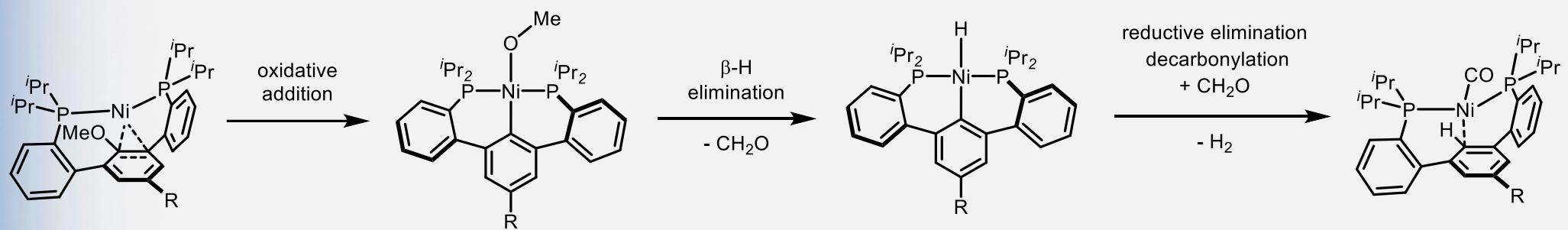


[a] S. Würtz, C. Lohre, R. Fröhlich, K. Bergander, F. Glorius *J. Am. Chem. Soc.* **2009**, *131*, 8344. [b] W. A. Herrmann, L. J. Goossen, C. Köcher, A. G. R. J. Artus *Angew. Chem. Int. Ed.* **1996**, *35*, 2805; E. P. Kündig, T. M. Seidel, Y.-X. Jia, G. Bernardinelli, *Angew. Chem. Int. Ed.* **2007**, *46*, 8484. [c] G. Laidlaw, S. H. Wood, A. R. Kennedy, D. J. Nelson *Z. Anorg. Allg. Chem.* **2019**, *645*, 105.

Different reaction set-up



Reductive cleavage of diaryl ethers: alternative mechanism



[a] P. Kelley, S. Lin, G. Edouard, M. W. Day, T. Agapie *J. Am. Chem. Soc.* **2012**, *134*, 5480.

Thank you for your
attention!