

Rapid Organocatalytic Formation of Carbon Monoxide: Application towards Carbonylative Cross Couplings

Ben Zoller, Josef Zapp, Peter H. Huy*

Chem. Eur. J. **2020**, 226, 9632-9638

*Rostock University, Institute for Chemistry

Albert-Einstein Strasse 3a, 18059 Rostock, Germany

Email: peter.huy@uni-rostock.de - **Homepage:** www.peterhuylab.de

www.huy.chemie.uni-rostock.de - **Twitter:** @peterhuylab.de

www.peterhuylab.de



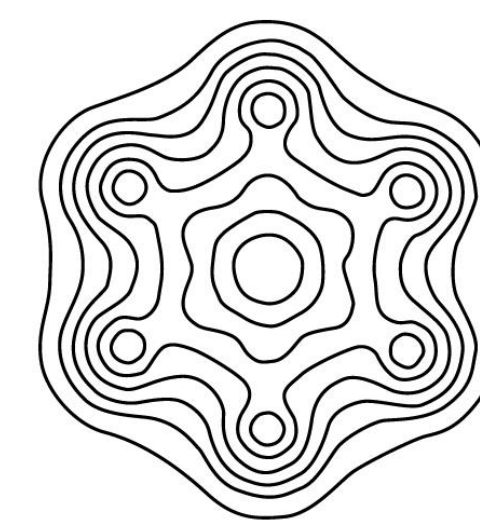
Chem. Eur. J. **2020**, 9632



Universität
Rostock



Traditio et Innovatio



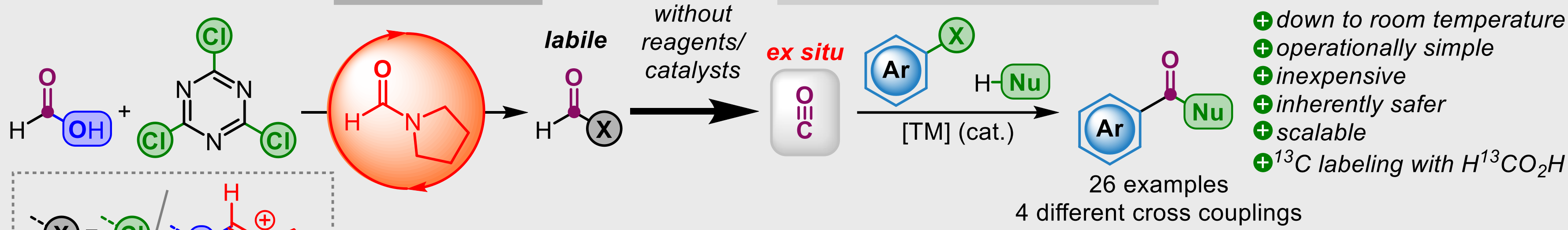
FCI
FONDS DER
CHEMISCHEN
INDUSTRIE



1. Abstract

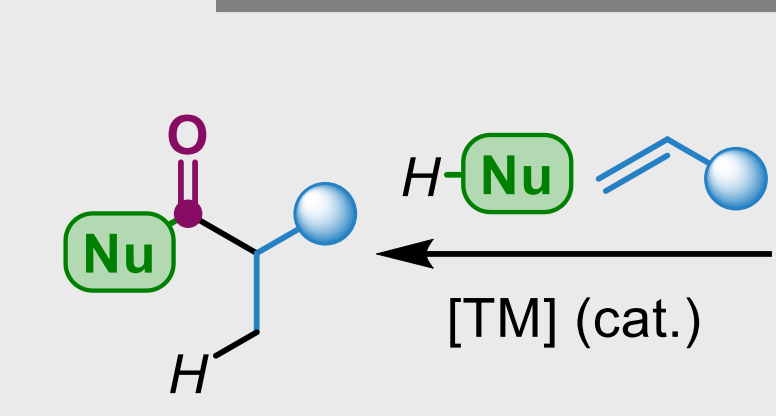
Organocatalysis

Carbonylative Transformations

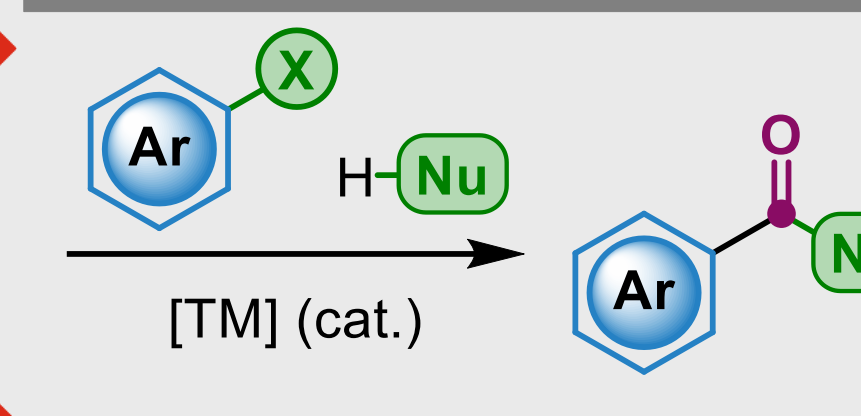


2. Motivation^[1,2]

Hydrocarbonylation

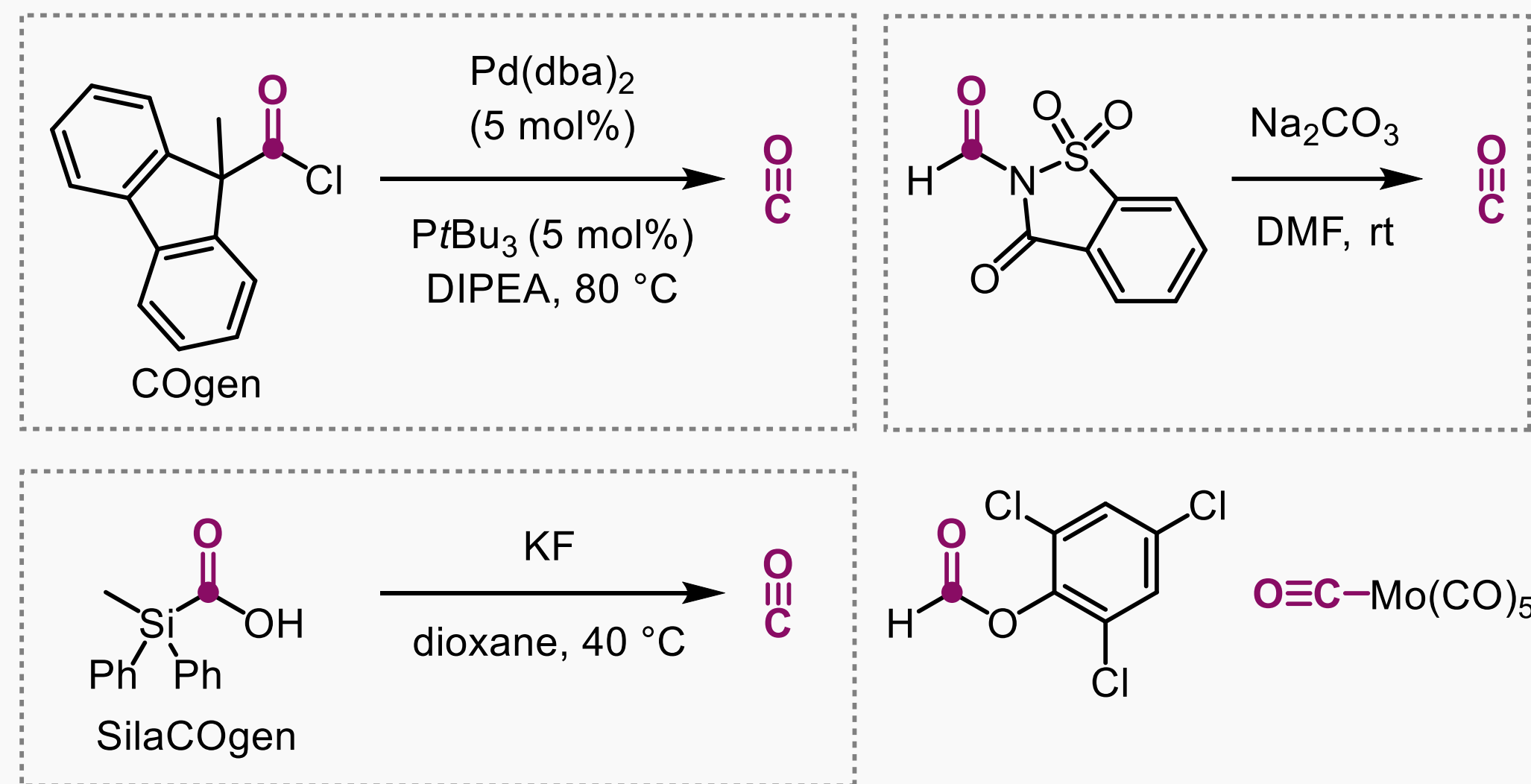


Carbonylative Cross Coupling

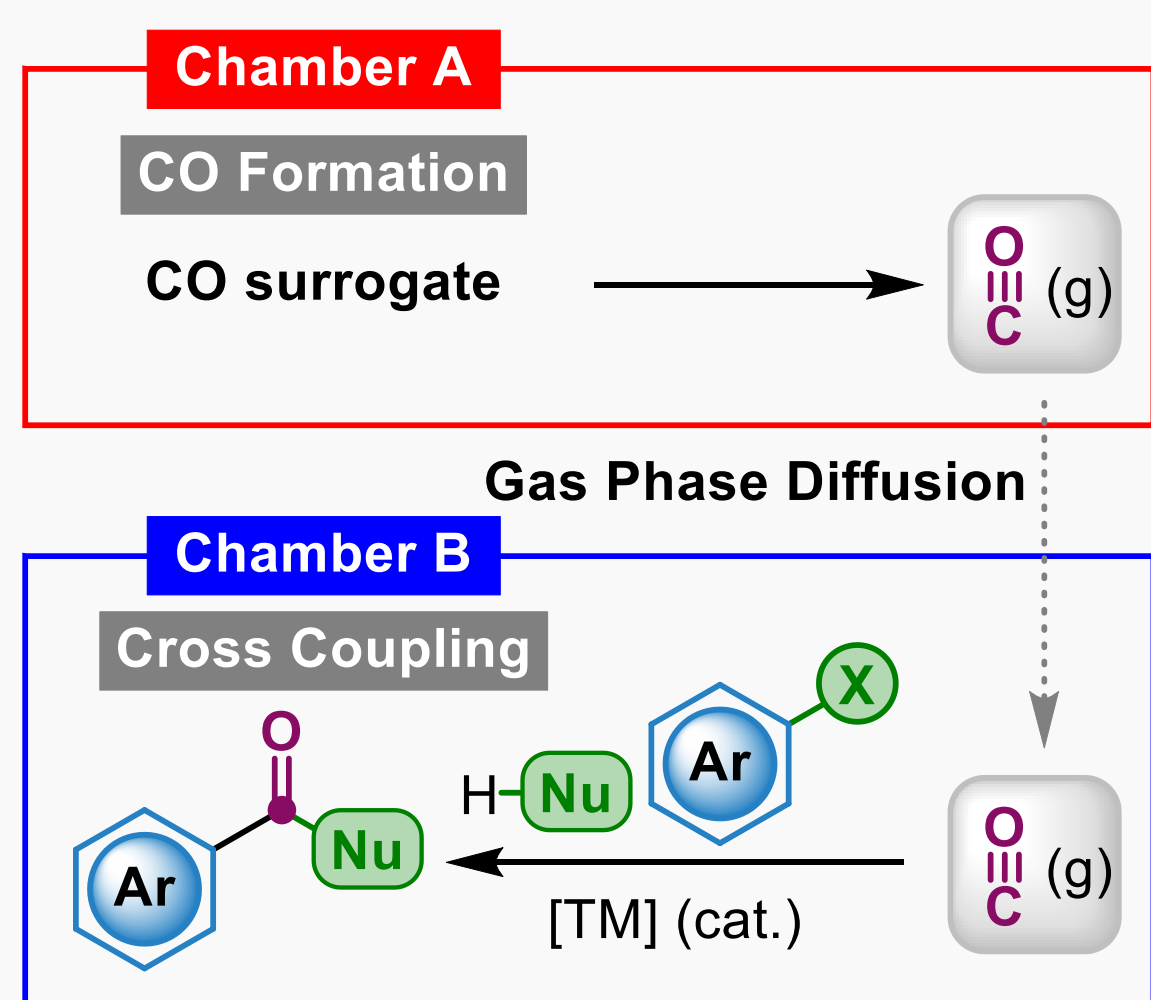


3. State of Knowledge

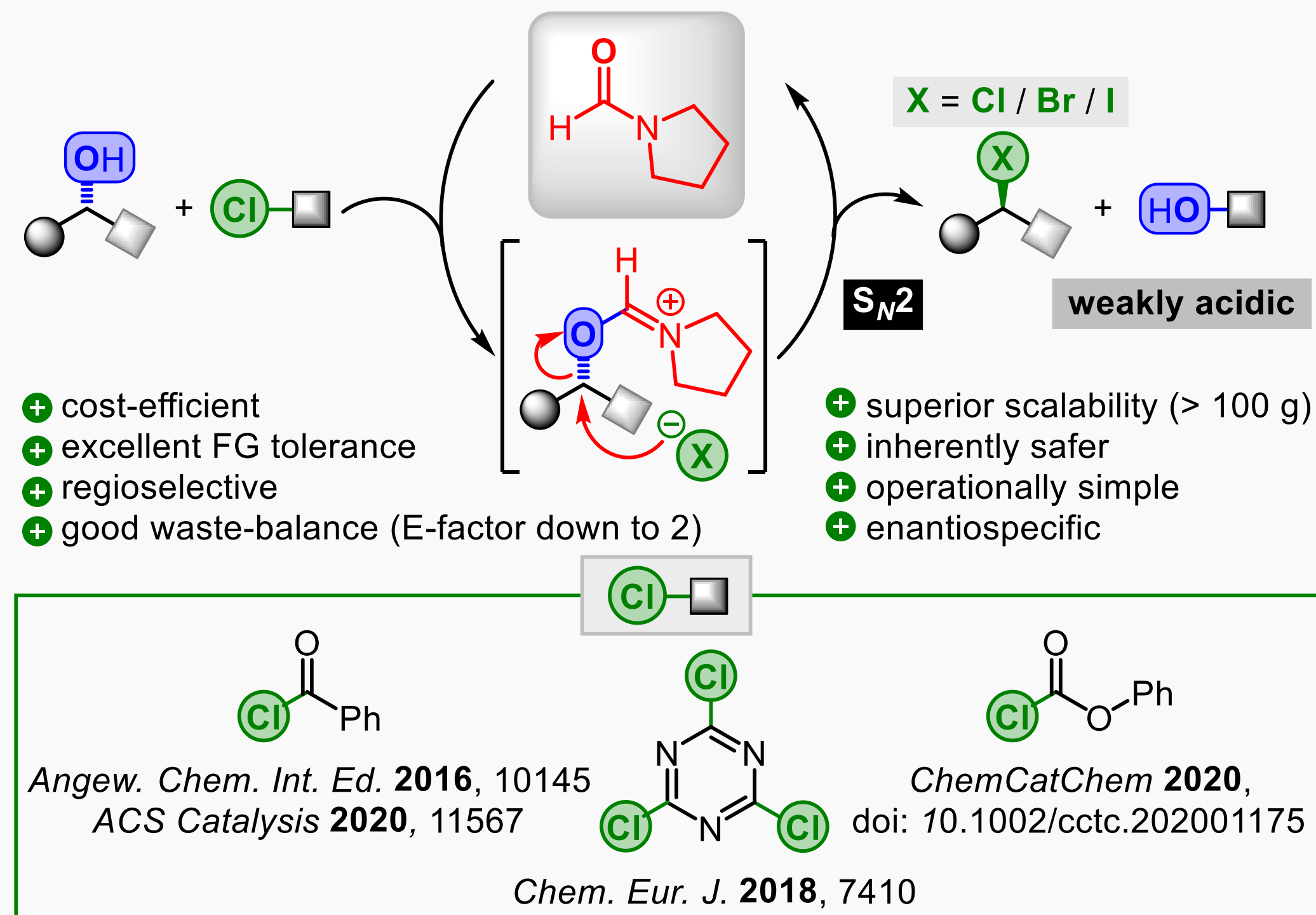
CO Surrogates^[2,3]



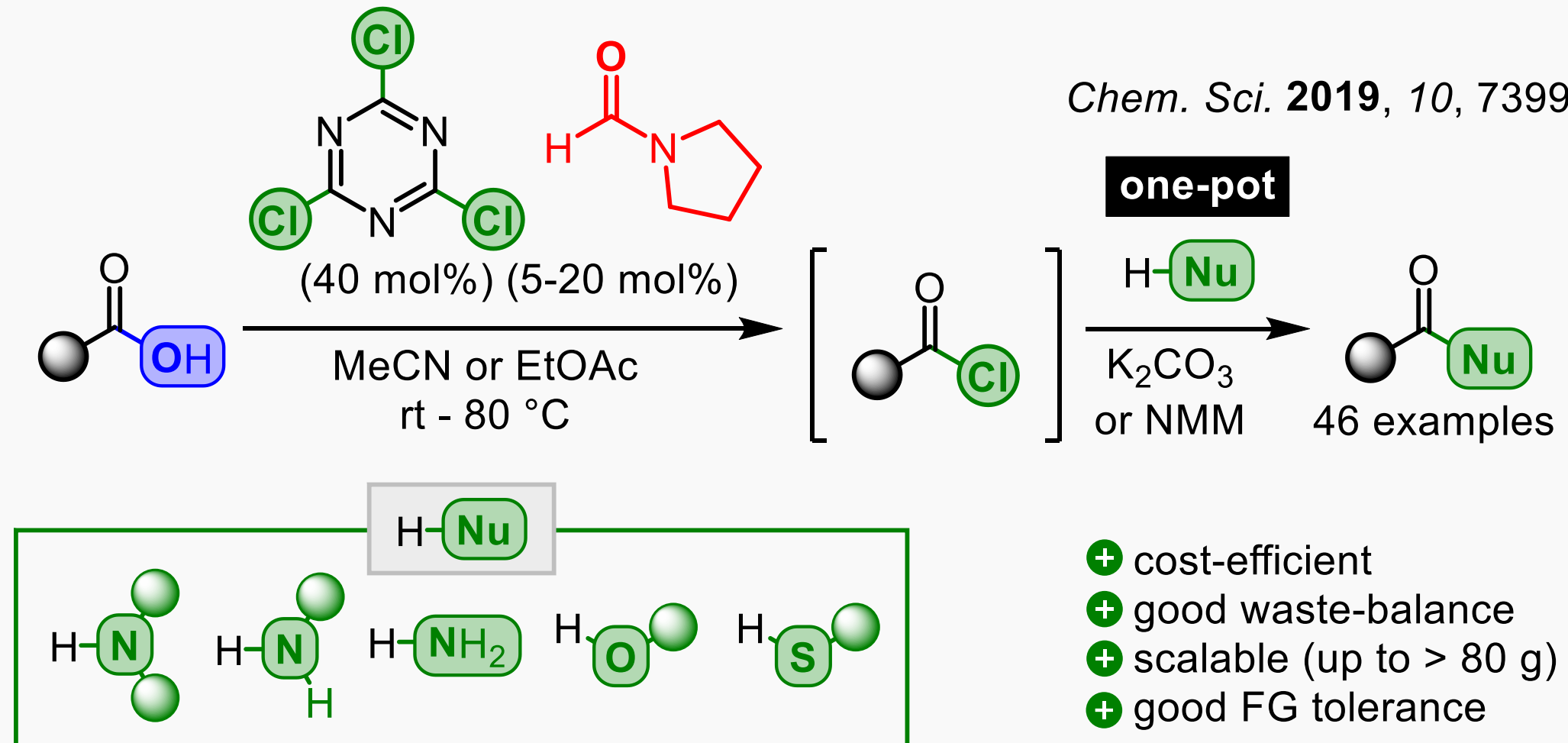
Commercial COware from SyTracks (Skrydstrup)^[2,4]



Formamide Catalyzed Activations of Alcohols^[5,6]



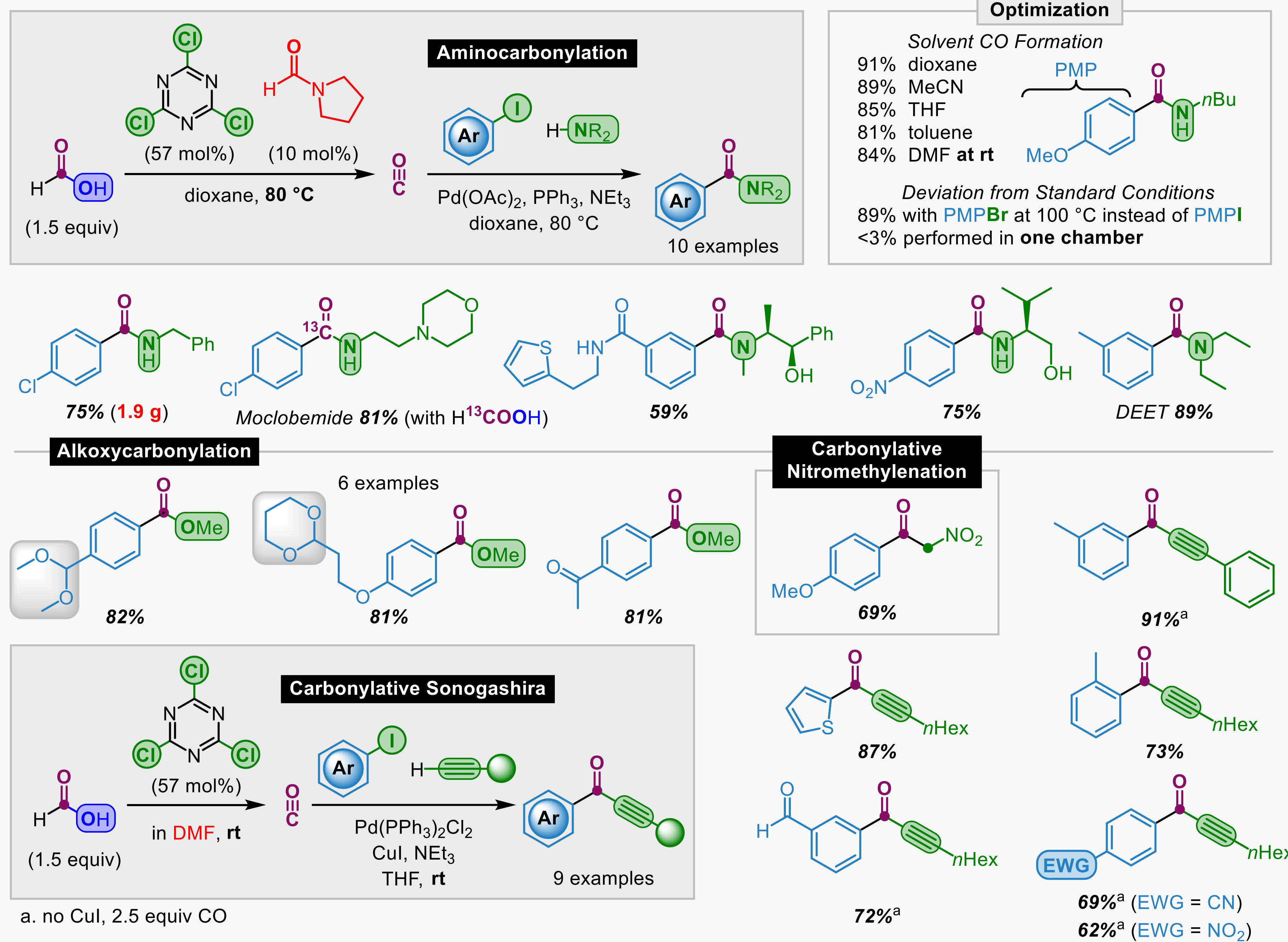
Formamide Catalyzed Activation of Acids^[7]



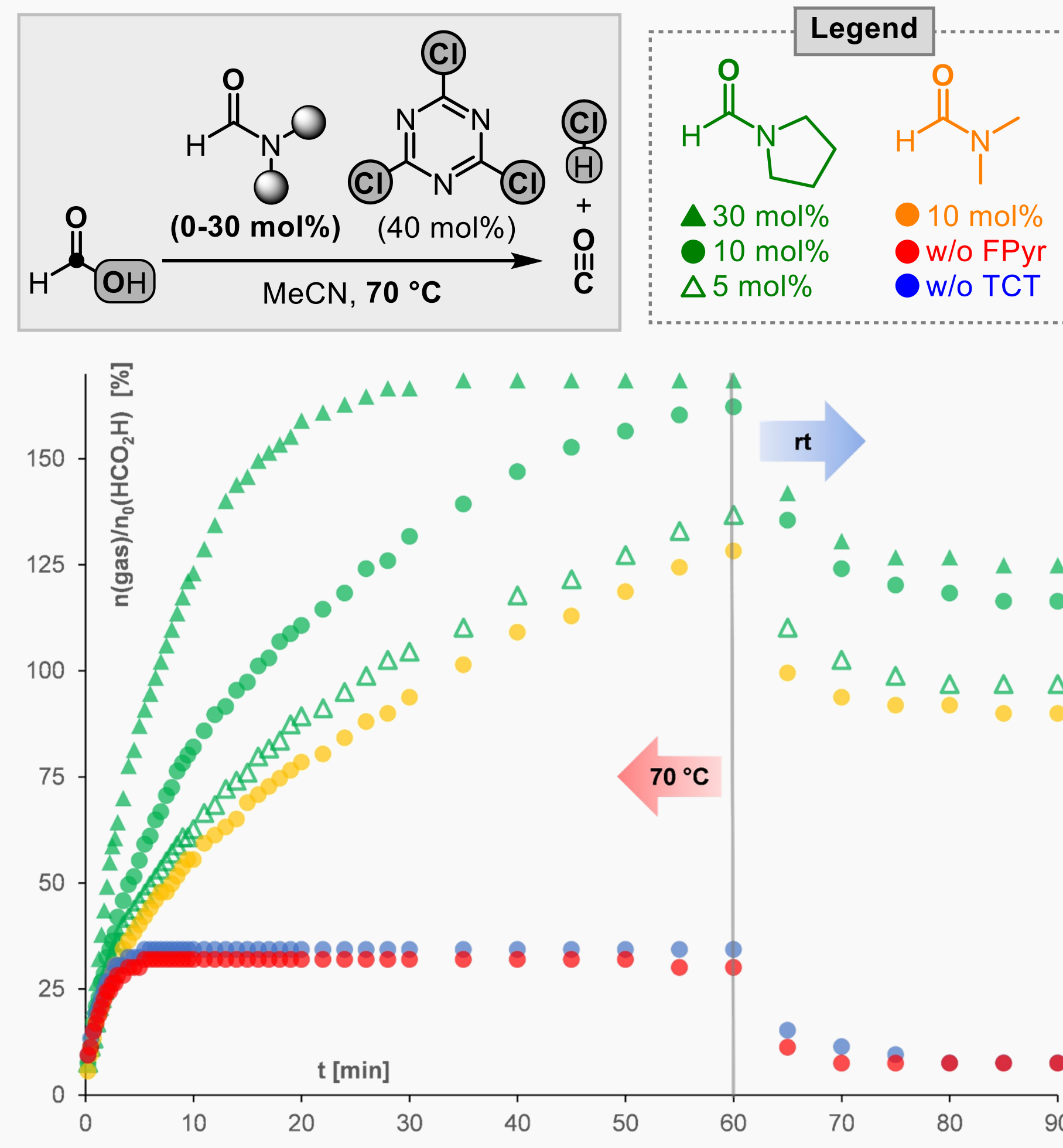
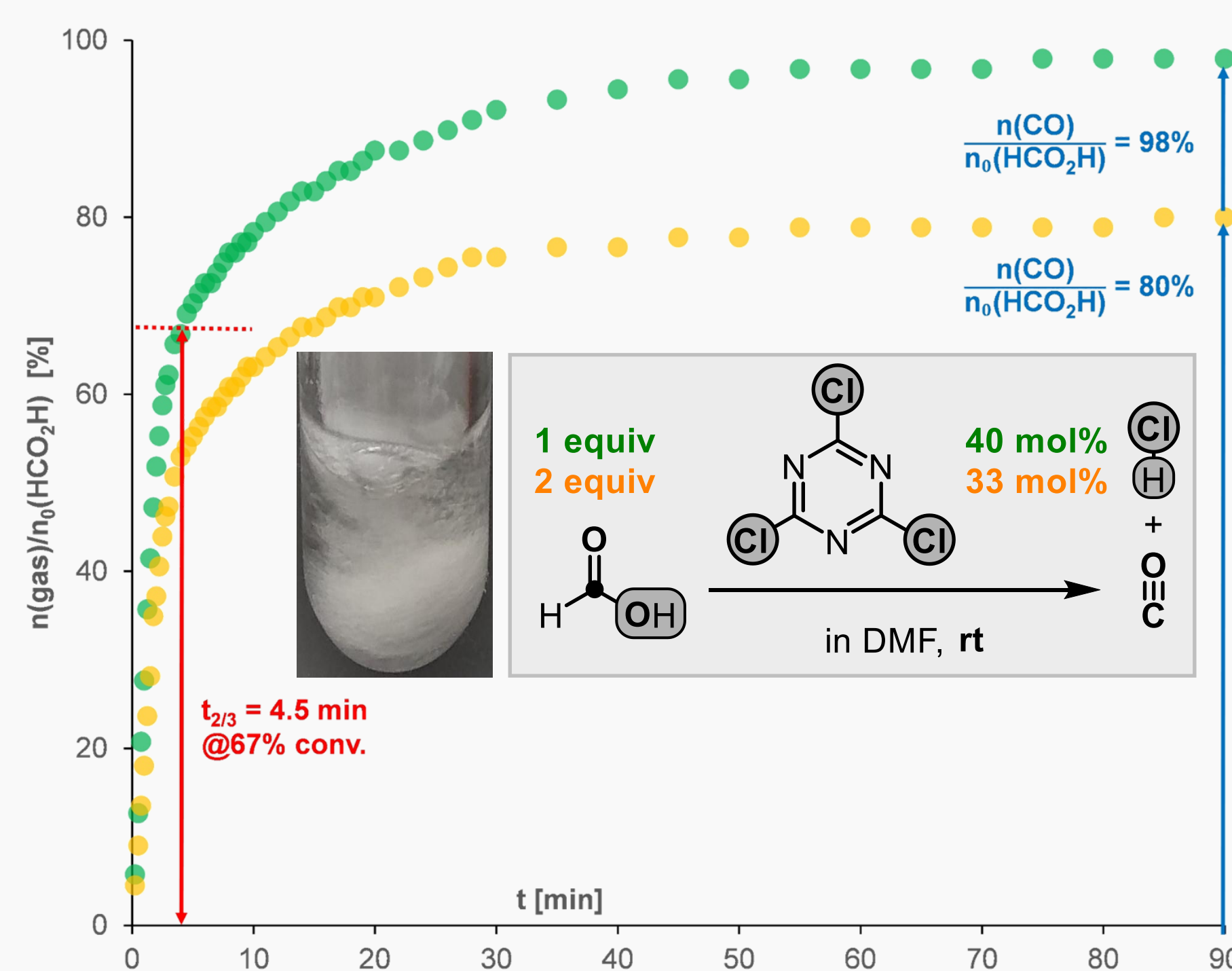
References

- [1] Selected reviews on carbonylations: (a) I. Ojima, *Chem. Rev.* **1988**, 88, 1011-1030; (b) A. Brennfürer, H. Neumann, M. Beller, *ChemCatChem* **2009**, 1, 28-41; (c) R. Franke, D. Selent, A. Börner, *Chem. Rev.* **2012**, 112, 5675-5732; (d) X.-F. Wu, H. Neumann, M. Beller, *ChemSusChem* **2013**, 6, 229-241; (e) X.-F. Wu, X. Fang, L. Wu, R. Jackstell, H. Neumann, M. Beller, *Acc. Chem. Res.* **2014**, 47, 1041-1053; (f) L. Wu, X. Fang, Q. Liu, R. Jackstell, M. Beller, X.-F. Wu, *ACS Catal.* **2014**, 4, 2977-2989; (g) Y. Bai, D. C. Davis, M. Dai, *J. Org. Chem.* **2017**, 82, 2319-2328; (h) Y. Li, Y. Hu, X.-F. Wu, *Chem. Soc. Rev.* **2018**, 47, 172-194; (i) J. B. Peng, H.-Q. Geng, X.-F. Wu, *Chem* **2019**, 5, 526-552; (j) J.-B. Peng, F.-P. Wu, X.-F. Wu, *Chem. Rev.* **2019**, 119, 2090-2127.
- [2] Selected reviews on CO surrogates: (a) L. Wu, Q. Liu, R. Jackstell, M. Beller, *Angew. Chem. Int. Ed.* **2014**, 53, 6310-6320; (b) H. Konishim, K. Manabe, *Synlett* **2014**, 25, 1971-1986; (c) S. D. Friis, A. T. Lindhardt, T. Skrydstrup, *Acc. Chem. Res.* **2016**, 49, 594-605; (d) J. Cao, Z.-J. Zheng, Z. Xu, L.-W. Xu, *Coord. Chem. Rev.* **2017**, 336, 43-53; (e) D. U. Nielsen, K. T. Neumann, A. T. Lindhardt, T. Skrydstrup, *J. Label. Compd. Radiopharm.* **2018**, 61, 949-987; (f) D. U. Nielsen, K. T. Neumann, T. Skrydstrup, *Chimia* **2018**, 72, 606-609; (g) H. Konishi, *Chem. Pharm. Bull.* **2018**, 66, 1-19; (h) K. Mondal, P. Halder, G. Gopalan, P. Sasikumar, K. V. Radhakrishnan, P. Das, *Org. Biomol. Chem.* **2019**, 17, 5212-5222; (i) L. Åkerbladh, L. R. Odell, M. Larhed, *Synlett* **2019**, 30, 141-15; (j) J. Demaerel, C. Verseyer, W. M. De Borggraeve, *React. Chem. Eng.* **2020**, 5, 615-631.
- [3] Examples for formic acid as CO surrogate: (a) J.-P. Simonato, T. Walter, P. Métivier, *J. Mol. Catal. A* **2001**, 171, 91-94; (b) J.-P. Simonato, *J. Mol. Catal. A* **2003**, 197, 61-64;

4. Application towards Carbonylative Cross Couplings (selected examples)



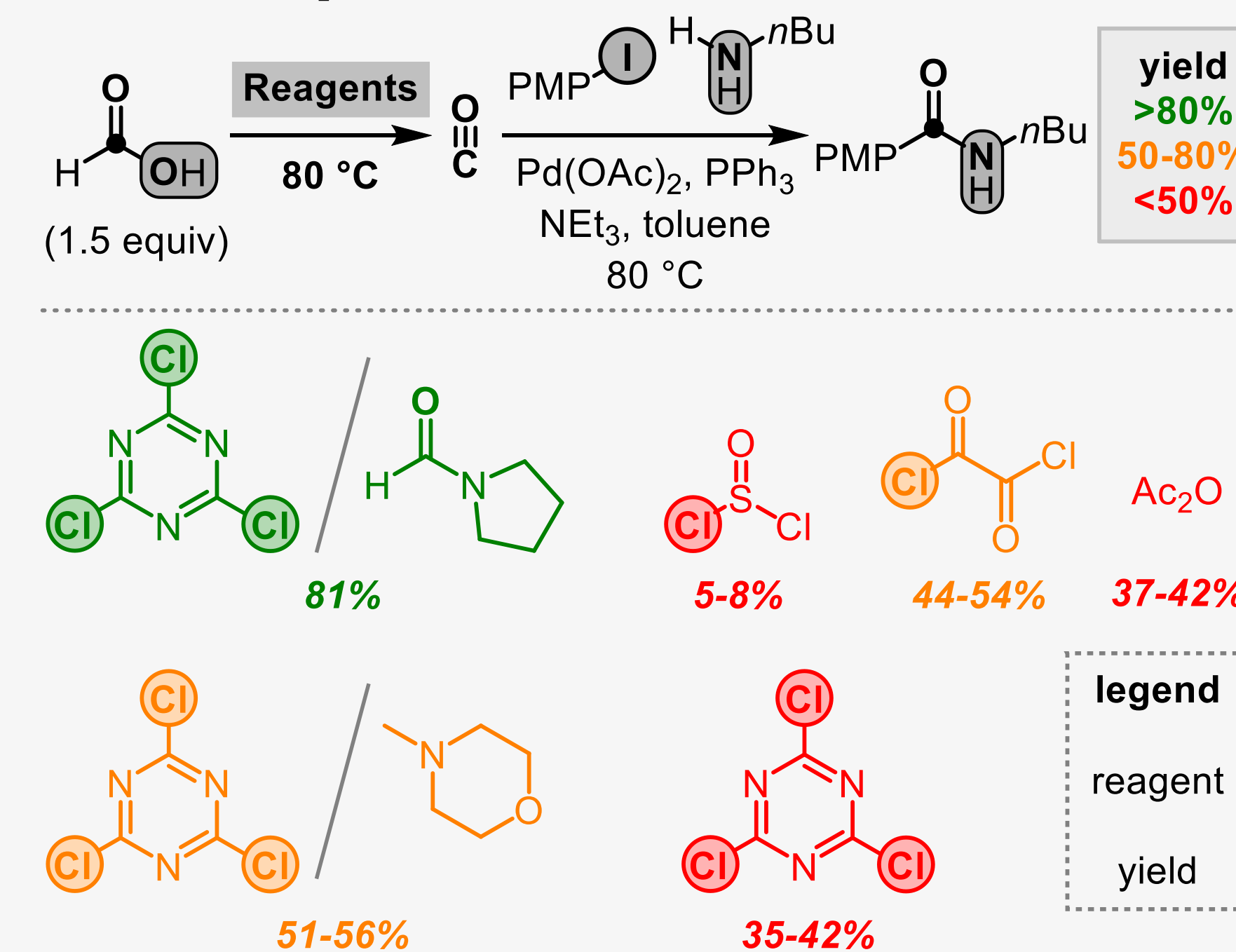
5. Gas Volumetry



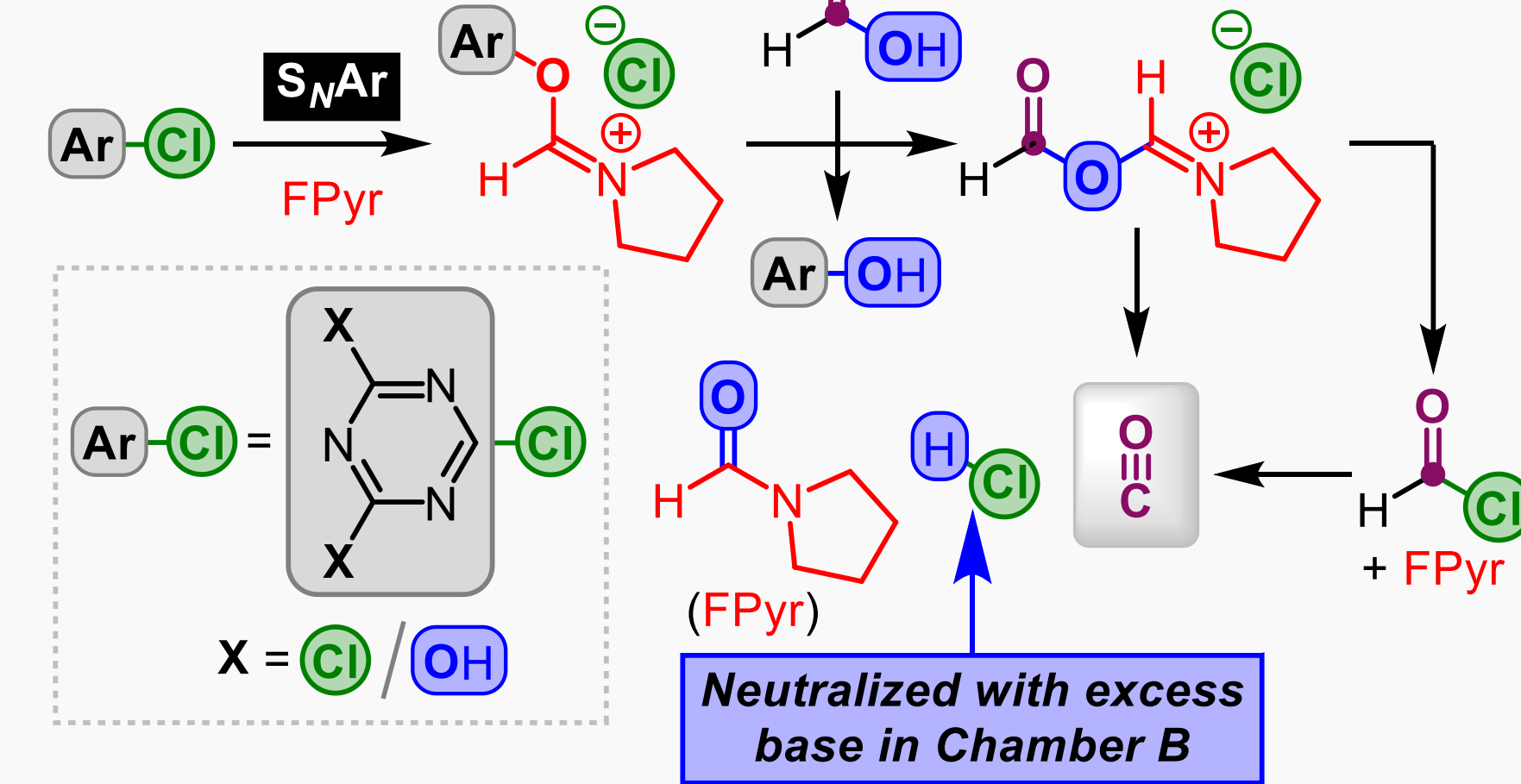
Acknowledgement

- Fonds of the Chemical Industry for a Liebig-fellowship
- German Research Foundation (DFG)

6. Comparison Reactions



7. Mechanism



- [3] continued: (c) S. Korsager, R. H. Taaning, T. Skrydstrup, *J. Am. Chem. Soc.* **2013**, 135, 2891-2894; (d) Y. Wang, W. Rena, Y. Shi, *Org. Biomol. Chem.* **2015**, 13, 8416-8419; (e) X. Qi, L.-B. Jiang, C.-L. Li, R. Li, X.-F. Wu, *Chem. Asian J.* **2015**, 10, 1870-1873; (f) C. Verseyer, S. Van Mileghem, B. Egle, P. Gilles, W. M. De Borggraeve, *React. Chem. Eng.* **2016**, 1, 142-146; (g) J.-B. Peng, F.-P. Wu, C.-L. Li, X. Qi, X.-F. Wu, *Eur. J. Org. Chem.* **2017**, 1434-1437; (h) R. Sang, P. Kucmierzcyk, K. Dong, R. Franke, H. Neumann, R. Jackstell, M. Beller, *J. Am. Chem. Soc.* **2018**, 140, 5217-5223.
- [4] https://www.sytracks.com/
- [5] Reviews on Lewis-base catalyzed S_N -reactions: (a) J. An, R. M. Denton, T. H. Lambert, E. D. Nacsas, *Org. Biomol. Chem.* **2014**, 12, 2993-3003; (b) P. H. Huy, T. Hauch, I. Filbrich, *Synlett* **2016**, 27, 2631-2636; (c) P. H. Huy, *Eur. J. Org. Chem.* **2020**, 10-27.
- [6] P. H. Huy, S. Motsch, S. M. Kappler *Angew. Chem.* **2016**, 128, 10300-10304; *Angew. Chem. Int. Ed.* **2016**, 55, 10145-10149; (b) P. H. Huy, I. Filbrich, *Chem. Eur. J.* **2018**, 24, 7410-7416; (c) B. Zoller, T. Stach, P. H. Huy, *ChemCatChem* **2020**, doi: 10.1002/cctc.202001175; (d) C. Kohlmeier, S. Schäfer, P. H. Huy, G. Hilt, *ACS Catalysis* **2020**, 10, 11567-11577.
- [7] P. H. Huy, C. Mbouhom, *Chem. Sci.* **2019**, 10, 7399-7406.