Facile (3+2) Cycloaddition between an *N*-Heterocyclic Olefin and Nitrous Oxide at Ambient Conditions

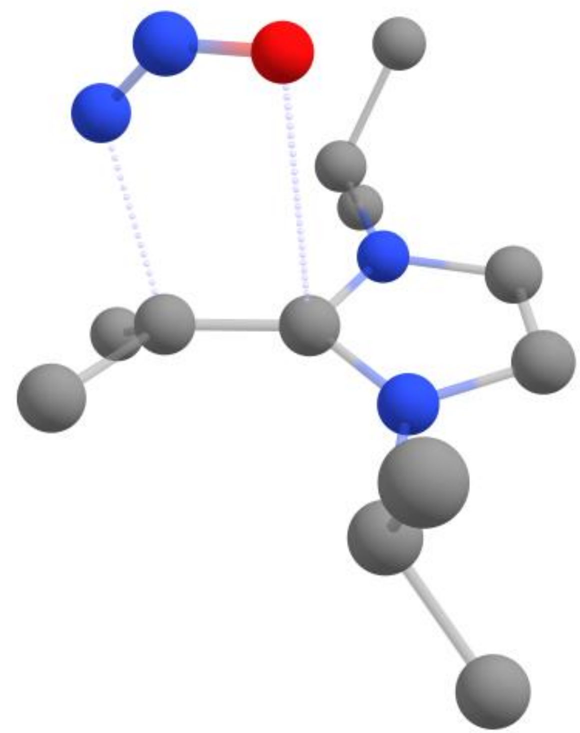
Seminar talk presented by

Jama Ariai

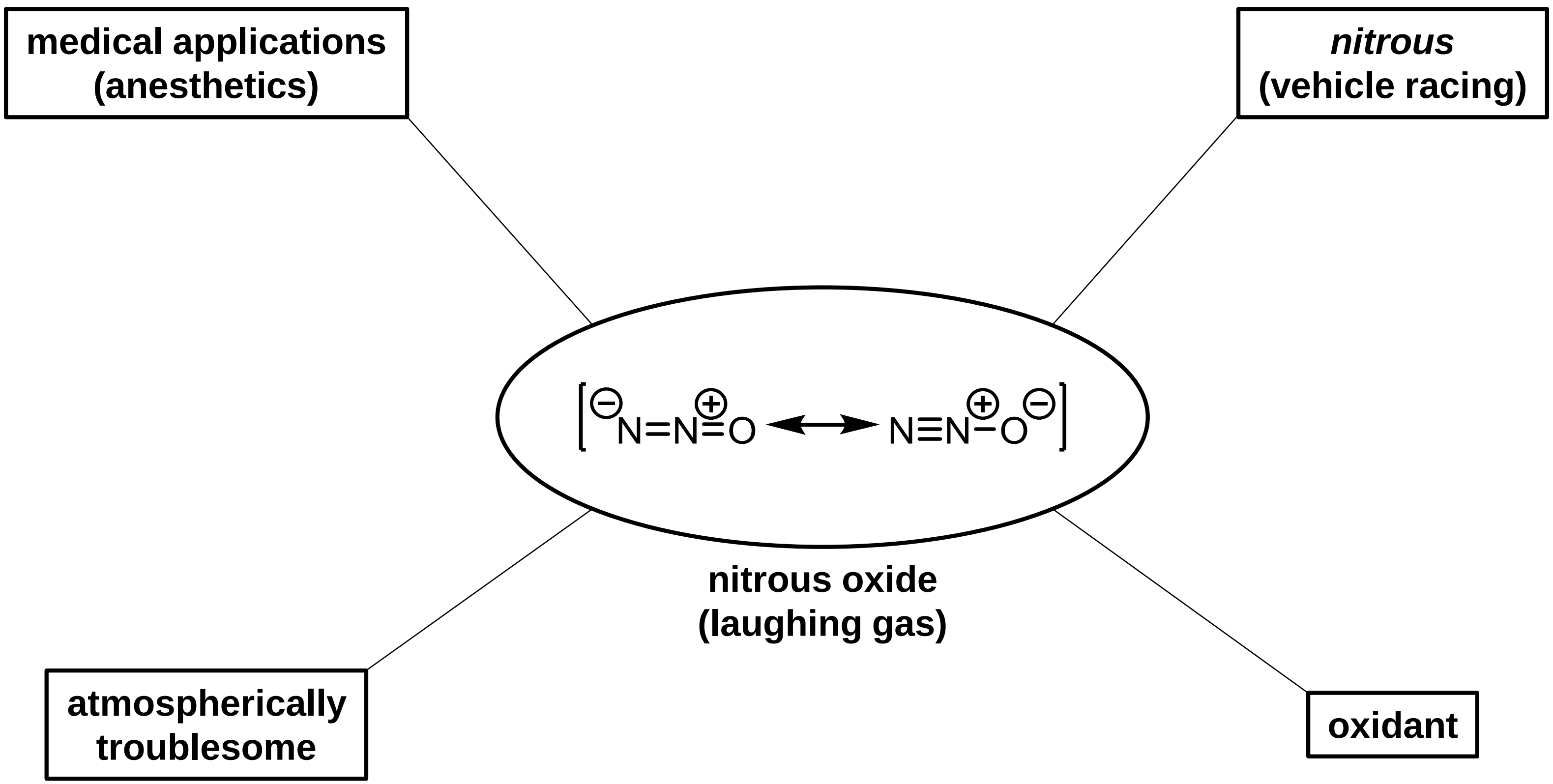
July 30th, 2021

Institute of Organic Chemistry

Justus Liebig University Giessen

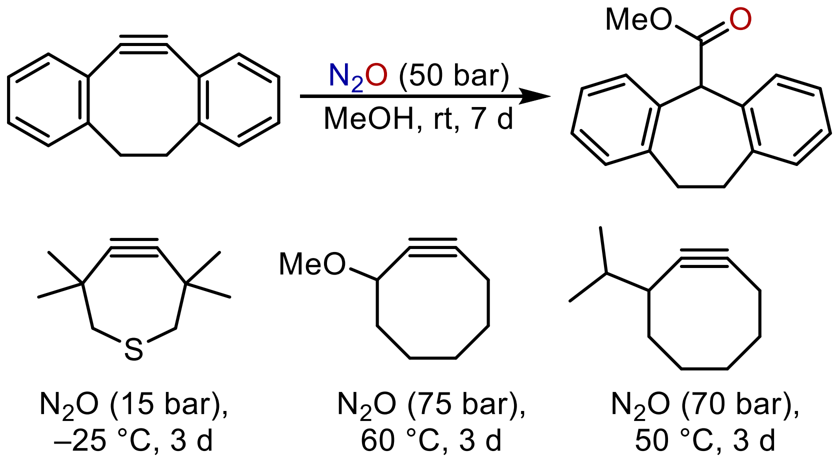


Introduction: Nitrous Oxide



Atmosphere: A. R. Ravishankara, J. S. Daniel, R. W. Portmann, *Science* **2009**, *326*, 123−125; D. J. Wuebbles, *Science* **2009**, *326*, 56−57. Oxidant: Y. Pang, M. Leutzsch, N. Nöthling, J. Cornella, *J. Am. Chem. Soc*. **2009**, *131*, 9918−9919; V. N. Parmon, G. I. Panov, A. Uriarte, A. S. Noskov, *Catal. Today* **2005**, *100*, 115−131; H. Tanaka, K. Hashimoto, K. Suzuki, Y. Kitaichi, M. Sato, T. Ikeno, T. Yamada, *Bull. Chem. Soc. Jpn*. **2004**, *77*, 1905−1914; R. Zeng, M. Feller, Y. Diskin-Posner, L. J. W. Shimon Y. Ben-David, D. Milstein, *J. Am. Chem. Soc*. **2018**, *140*, 7061−7064.

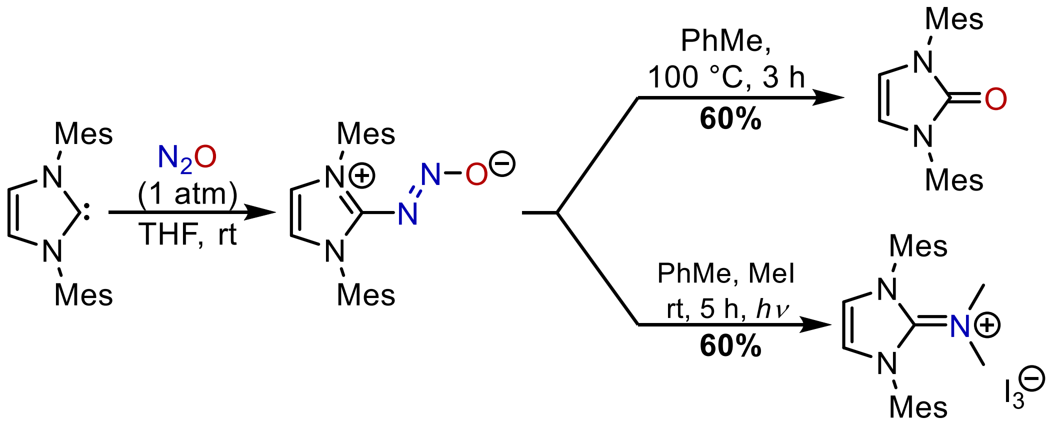
Introduction: Nitrous Oxide as 1,3-Dipolar in Cycloadditions

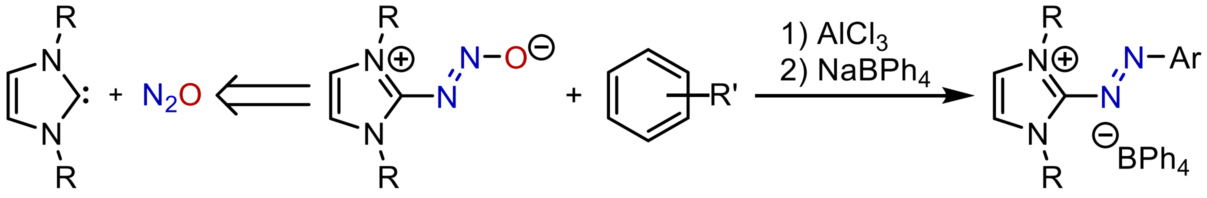


via (3+2) cycloaddition

K. Banert, O. Plefka, *Angew. Chem. Int. Ed.* **2011**, *50*, 6171−6174.

Introduction: Capture and Valorization of N_2O by NHCs

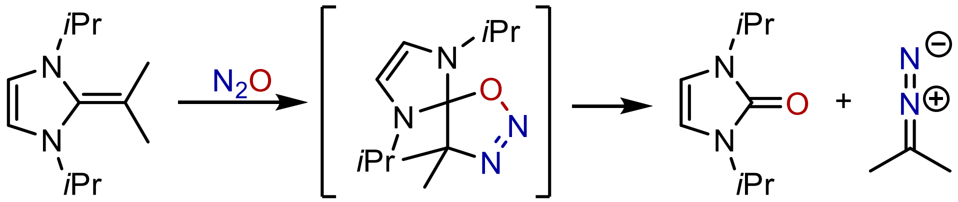




A. G. Tskhovrebov, E: Solari, M. D. Wodrich, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2012**, *51*, 232−234; A. G. Tskhovrebov, B. Vuichoud, E. Solari, R. Scopelliti, K. Severin, *J. Am. Chem. Soc.* **2013**, *135*, 9486−9492; A. G. Tskhovrebov, L. C. E. Naested, E: Solari, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* **2014**, *53*, 1−5.

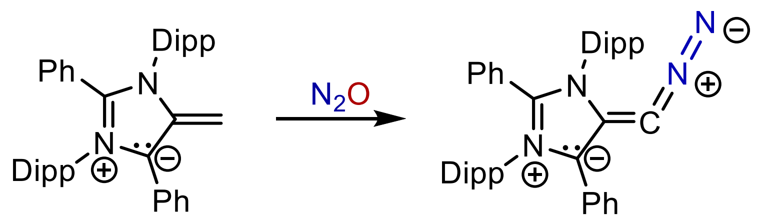
Working Hypothesis: Exposure of NHO to Ambient N_2O

Computations suggest:



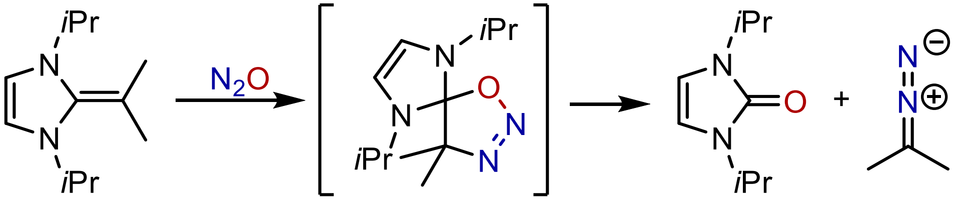
Isolable Diazoalkene by Exposure of N_2O to a Mesoionic NHO

Meanwhile ….



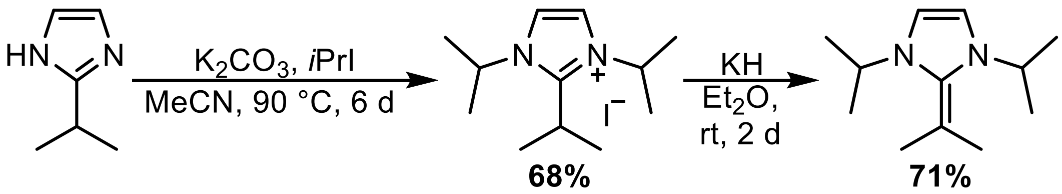
P. W: Antoni, C. Golz, J. J. Holstein, D. A. Pantazis, M. M. Hansmann, *Nat. Chem.* **2021**, *13*, 587−593.

Working Hypothesis: Exposure of NHO to Ambient N_2O

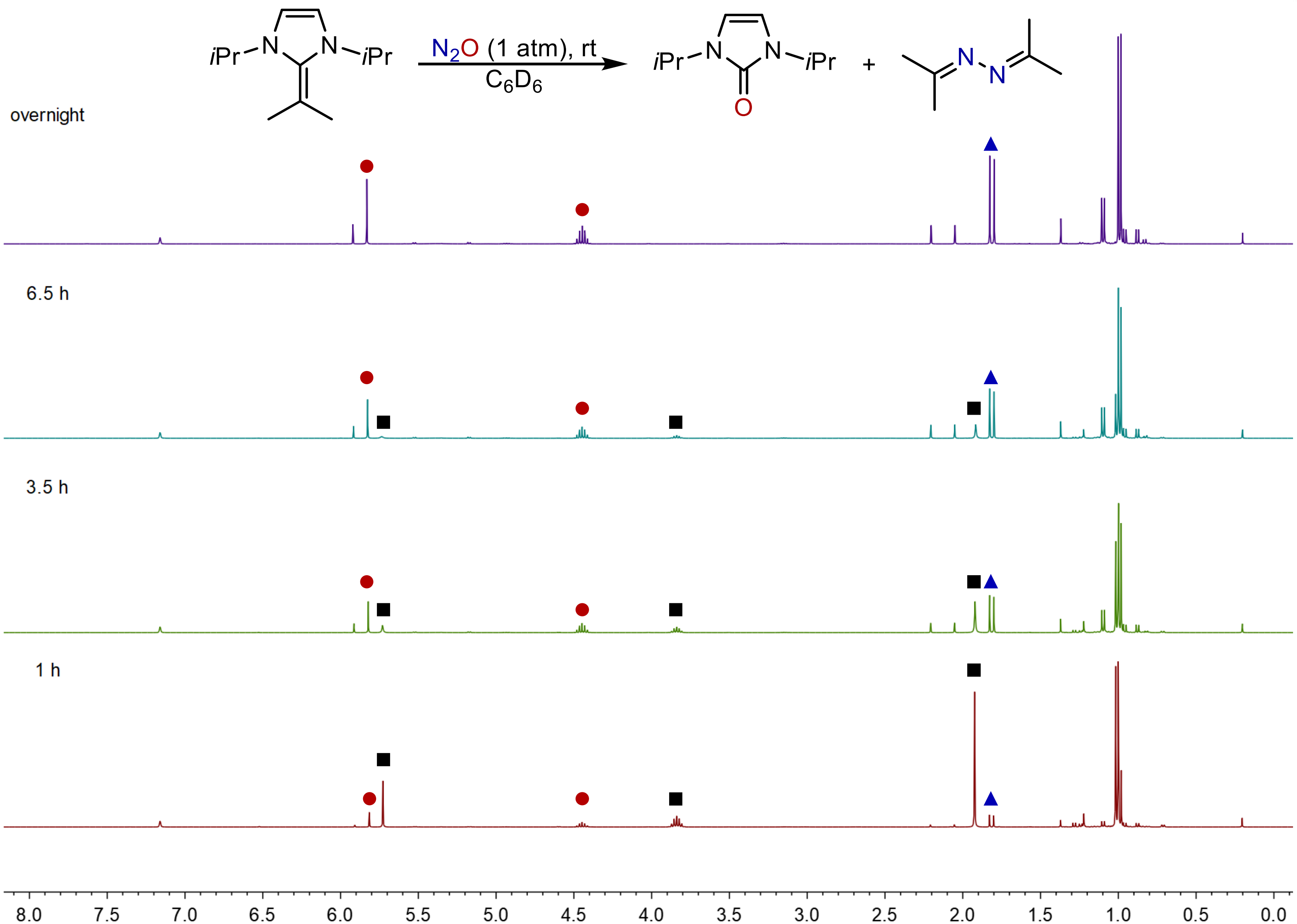


Manusscript submitted for publication.

Synthesis of NHOs

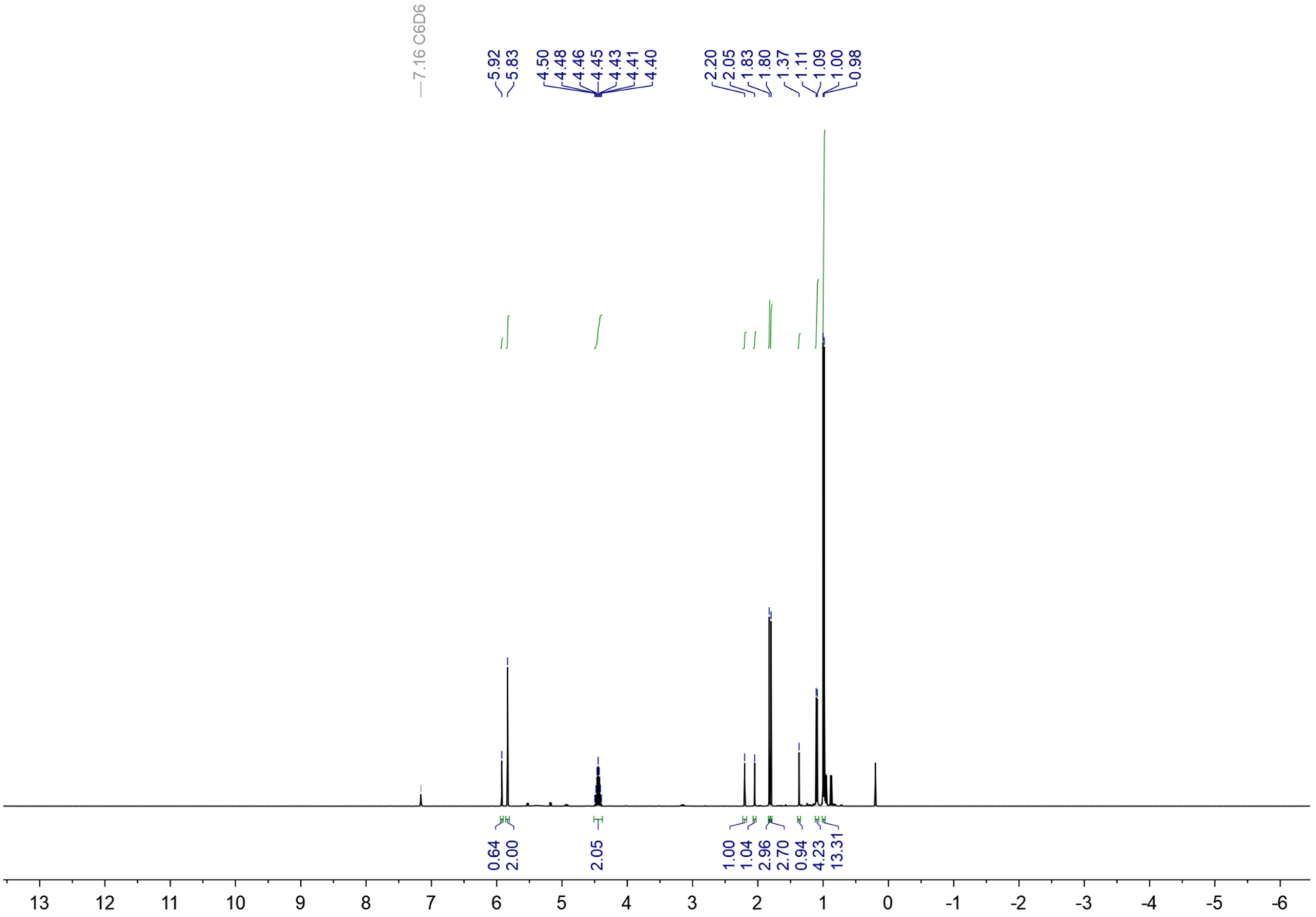


NHO + N_2O Monitored by ^1H NMR

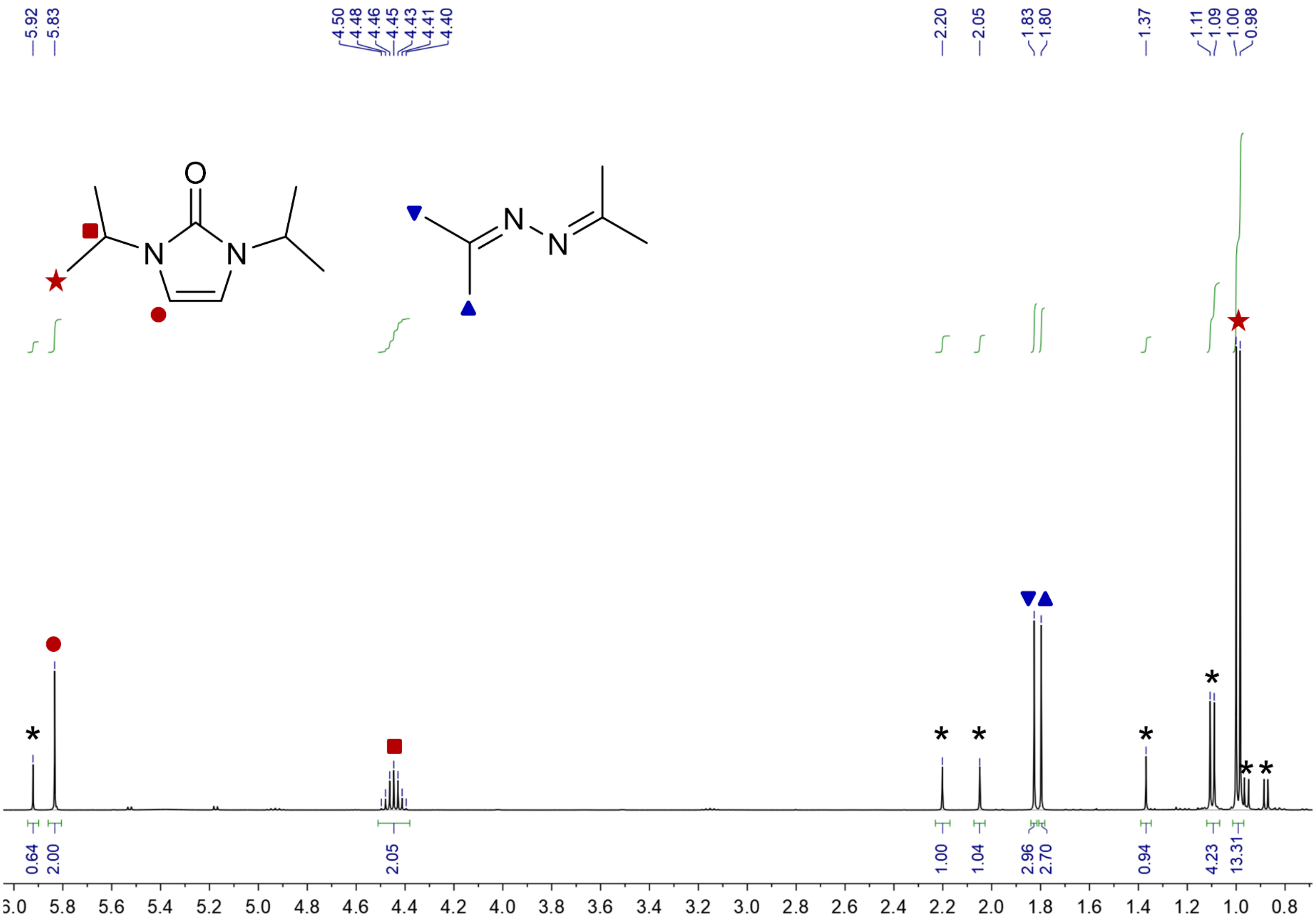


Manusscript submitted for publication.

^{1}H NMR Assignments after Exposure of NHO to Ambient N_2O



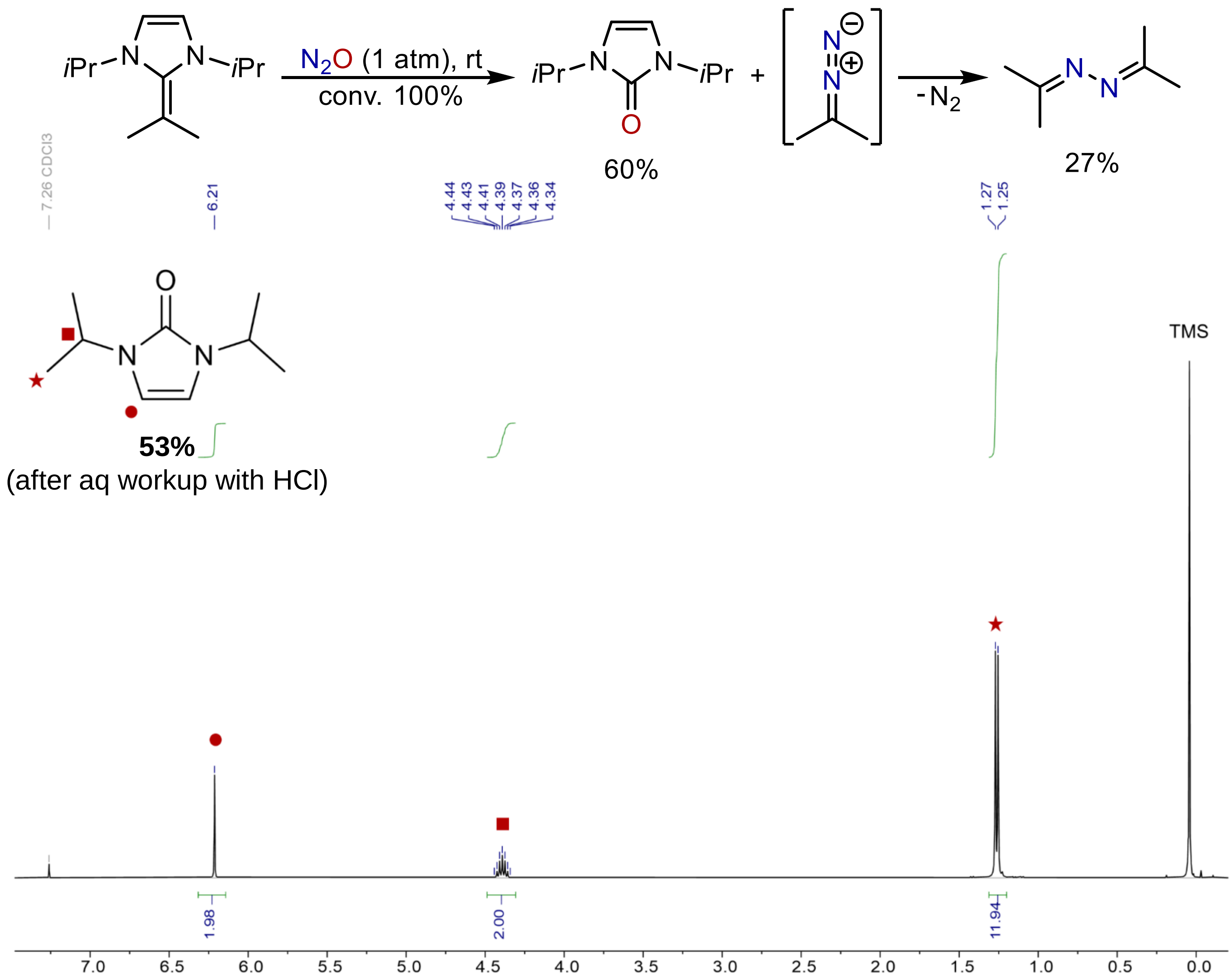
^{1}H NMR Assignments after Exposure of NHO to Ambient N_2O



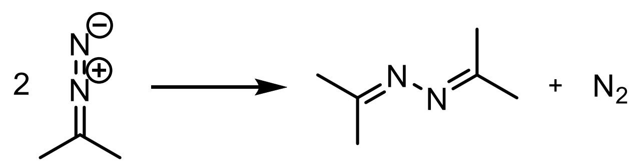
* = unidentified byproduct

Exposure of NHO to Ambient N_2O

in-situ yields determined by ^{1}H NMR with mesitylene as internal standard

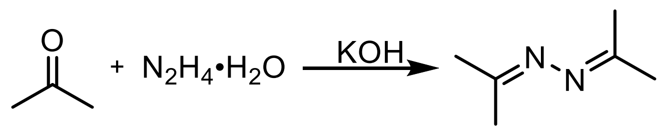


Disproportion of Diazoalkanes to Azines in the Presence of Base/Nuc



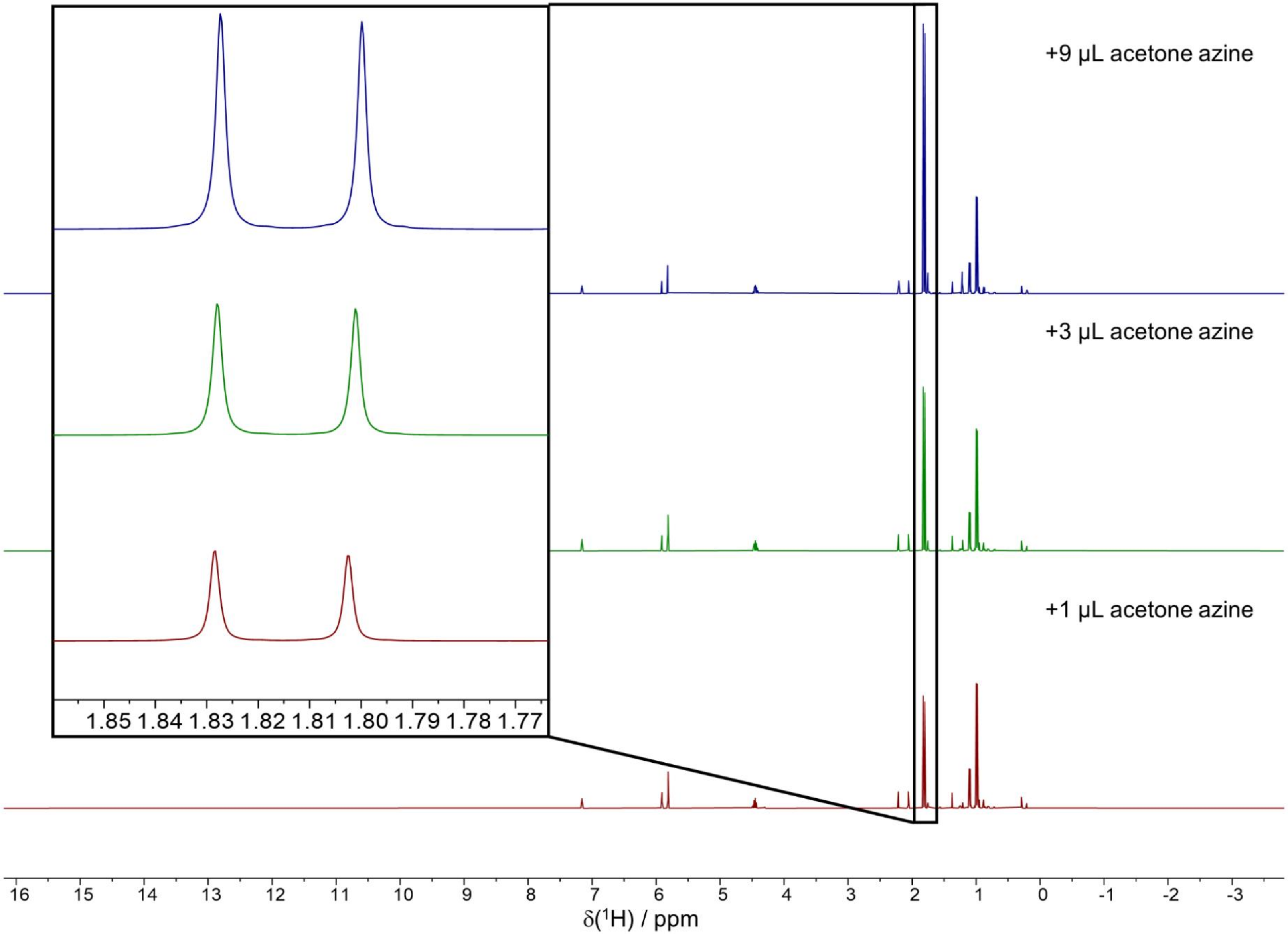
M. Regitz, *Angew. Chem. Int. Ed. Engl.* **1967**, *6*, 733−749; L. J. McDowell, M. M. Khodaei, D. Bethell, *Org. Biomol. Chem.* **2003**, *1*, 995−1003.

Identification of Acetone Azine by Spiking Experiments



A. C. Day, M. C. Whiting, *Org. Synth.* **1970**, *50*, 3.

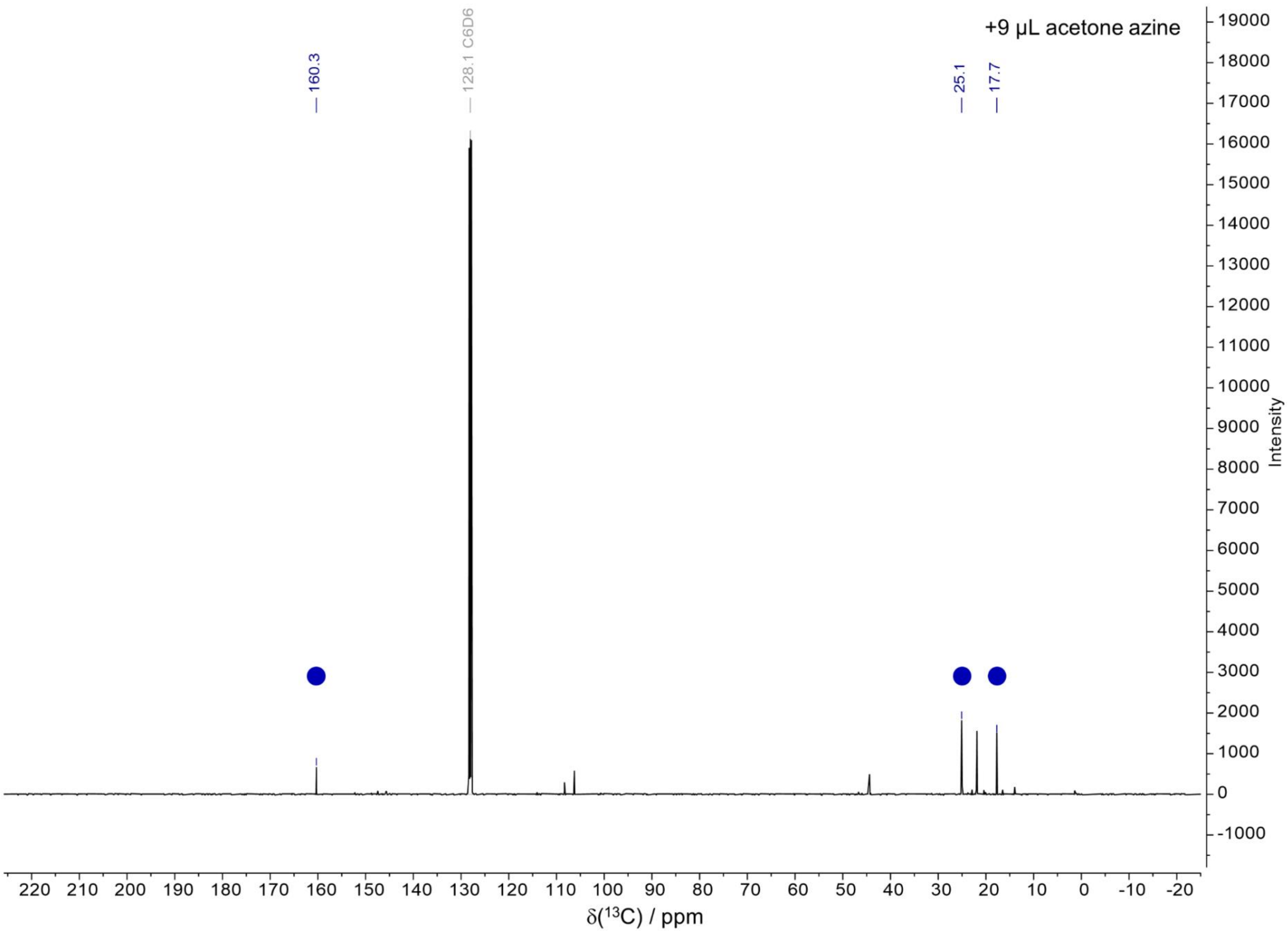
Identification of Acetone Azine by Spiking Experiments



A. C. Day, M. C. Whiting, *Org. Synth.* **1970**, *50*, 3.

Manusscript submitted for publication.

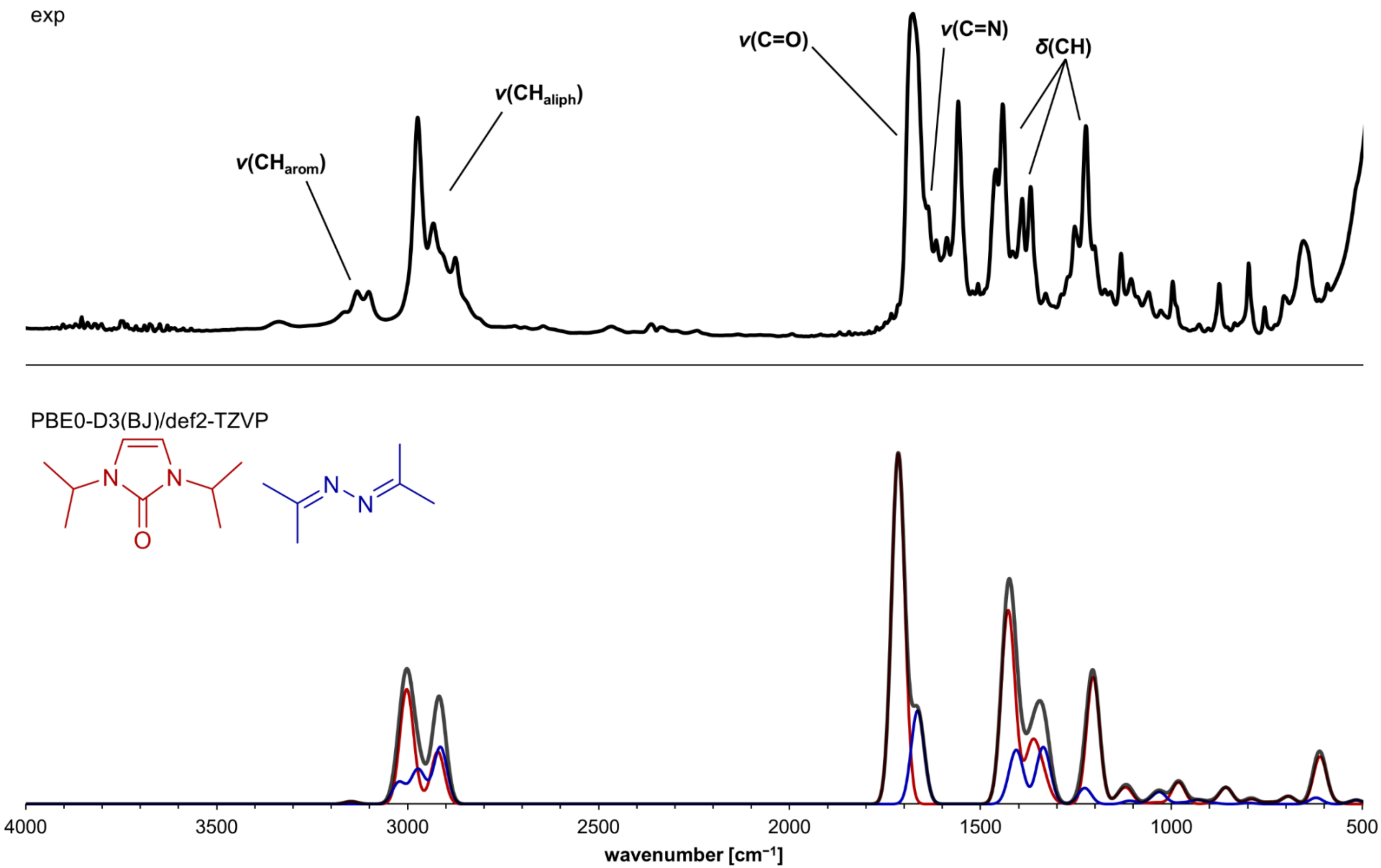
Identification of Acetone Azine by Spiking Experiments



A. C. Day, M. C. Whiting, *Org. Synth.* **1970**, *50*, 3.

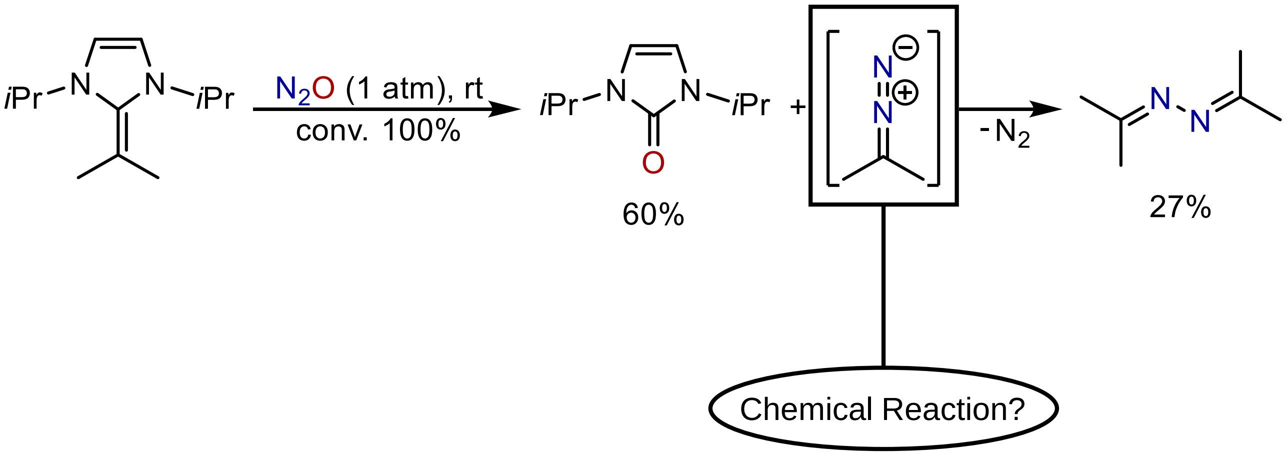
Manusscript submitted for publication.

Infrared Spectroscopy after Exposure of NHO to Ambient N_2O



PBE0: C. Adamo, V. Barone, *J. Chem. Phys*. **1999**, *110*, 6158−6170; M. Ernzerhof, G. E. Scuseria, *J. Chem. Phys*. **1999**, *110*, 5029−5036. D3(BJ): S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; S. Grimme, S. Ehrlich, L. Goerigk *J. Comput. Chem.* **2011**, *32*, 1456−1465. Basis set: F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297−3305. Scaling factor: M. K. Kesharwani, B. Brauer, J. M. L. Martin *J. Phys. Chem. A* **2015**, *119*, 1701−1714. ORCA: F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73−78; F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327.

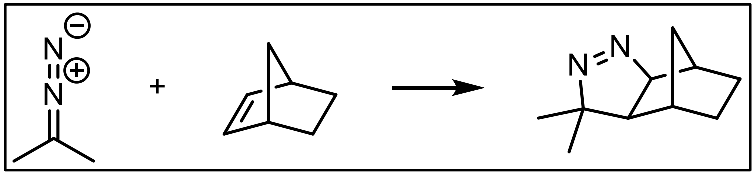
Trapping of 2-Diazopropane by 1,3-Dipolar Cycloaddition



M. Christl, E. Brunn, W. R. Roth, H.-W. Lennartz, *Tetrahedron* **1989**, *45*, 29905−2915.

Trapping of 2-Diazopropane by 1,3-Dipolar Cycloaddition

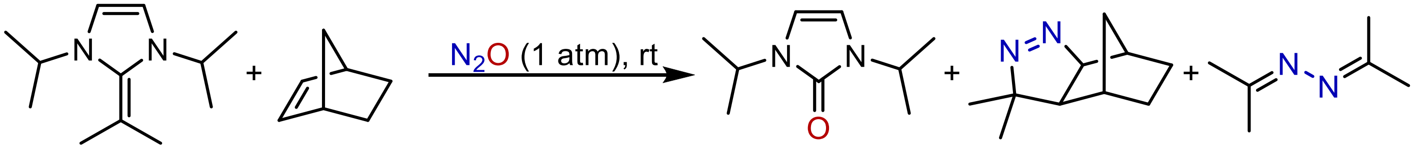
literature known



M. Christl, E. Brunn, W. R. Roth, H.-W. Lennartz, *Tetrahedron* **1989**, *45*, 29905−2915.

Trapping of 2-Diazopropane by 1,3-Dipolar Cycloaddition

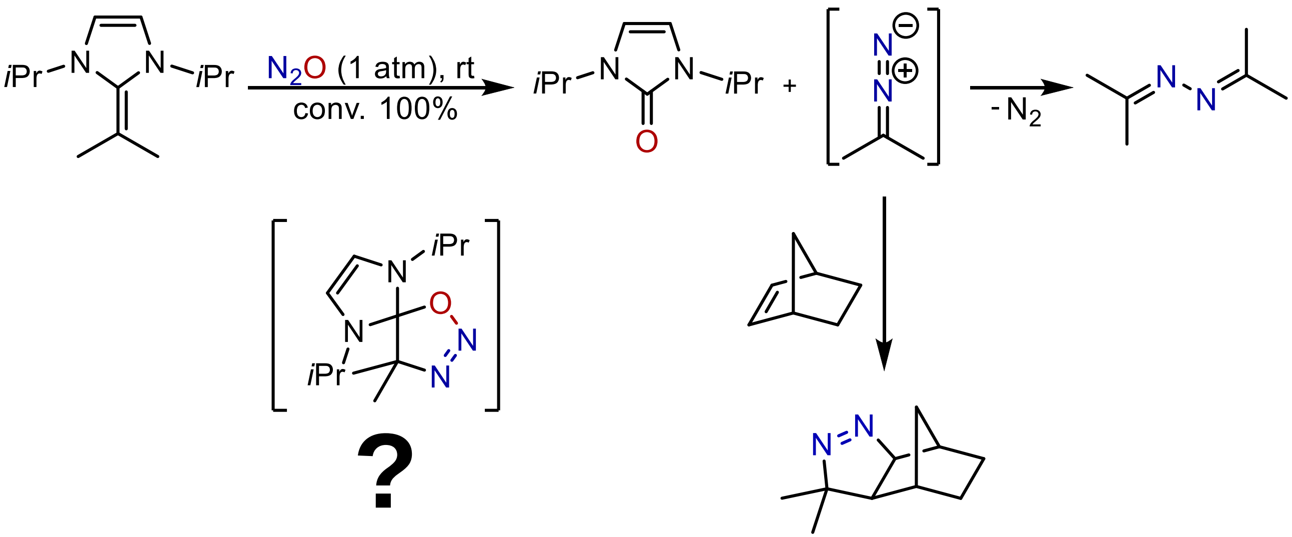
in-situ yields determined by ^{1}H NMR with mesitylene as internal standard



100% conv. 61% conv. 62% 49% 7%

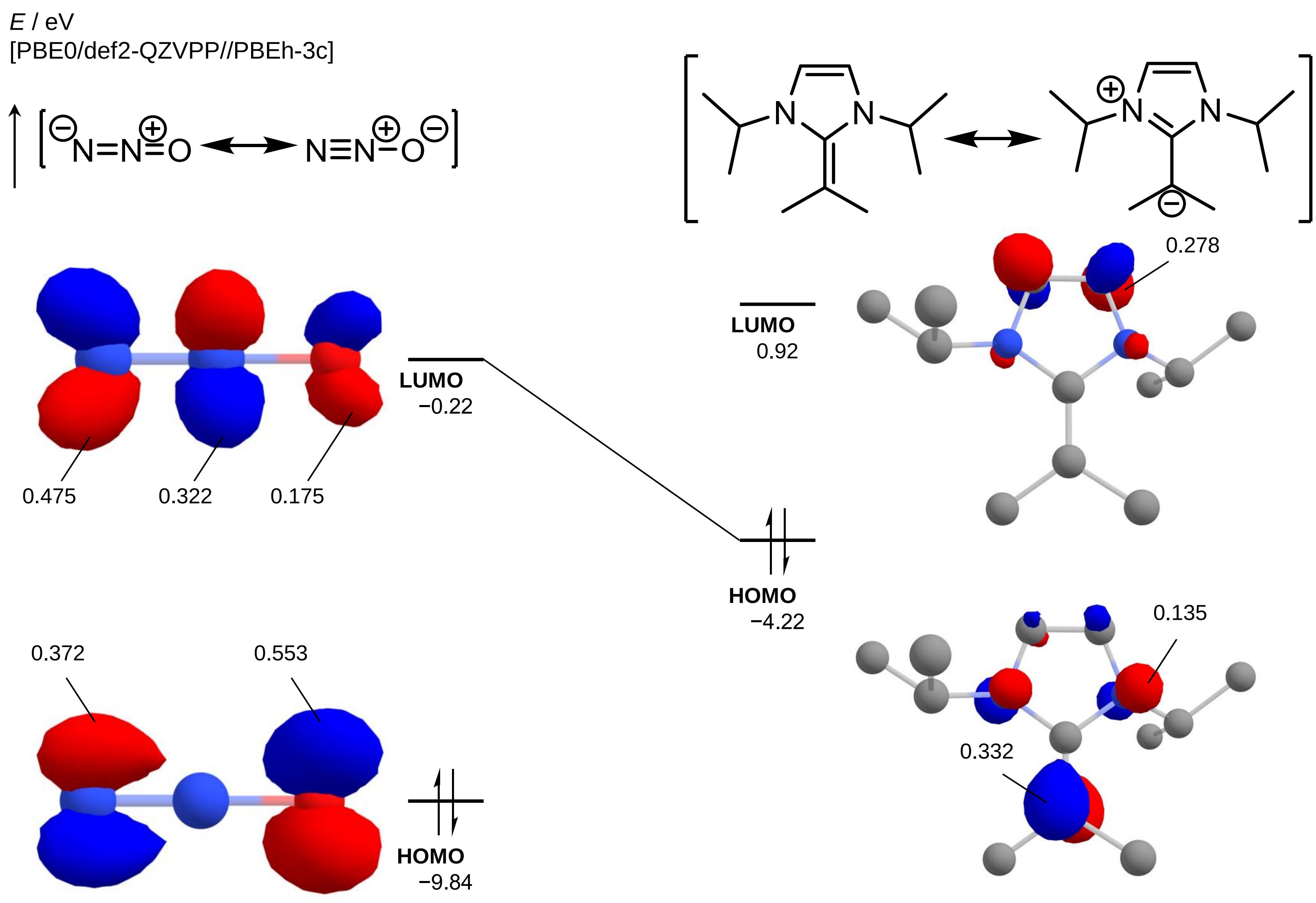
M. Christl, E. Brunn, W. R. Roth, H.-W. Lennartz, *Tetrahedron* **1989**, *45*, 29905−2915.

Trapping of 2-Diazopropane by 1,3-Dipolar Cycloaddition



Manusscript submitted for publication.

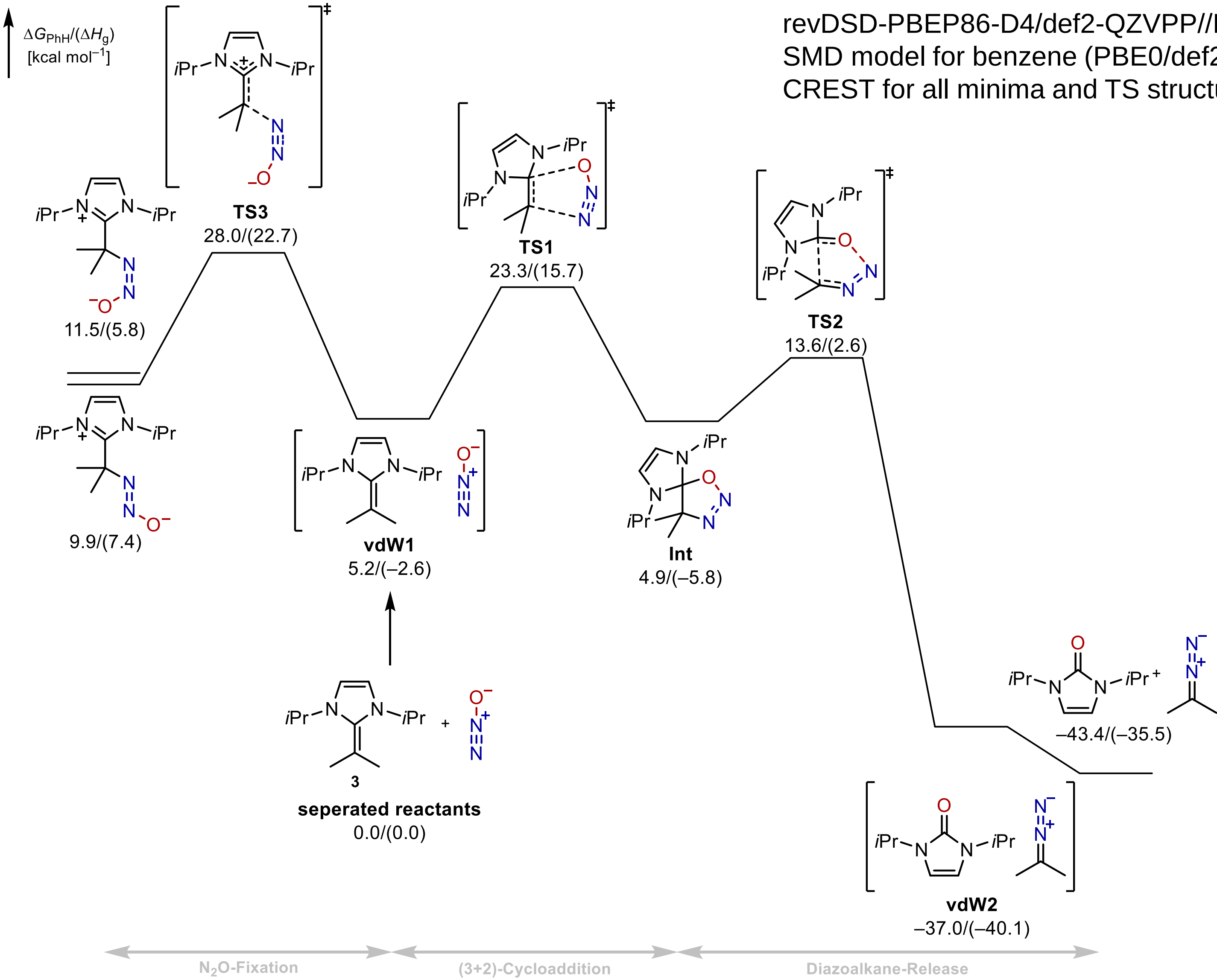
NHO + N_2O Monitored by ^1H NMR



PBE0: C. Adamo, V. Barone, *J. Chem. Phys*. **1999**, *110*, 6158−6170; M. Ernzerhof, G. E. Scuseria, *J. Chem. Phys*. **1999**, *110*, 5029−5036. Basis set: F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297−3305. PBEh-3c: S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, *J. Chem. Phys*. **2015**, *143*, 54107. Gaussian: M. J. Frisch *et al.*, Gaussian 16 (Revision C.01), Gaussian Inc., Wallingford, CT, 2019.

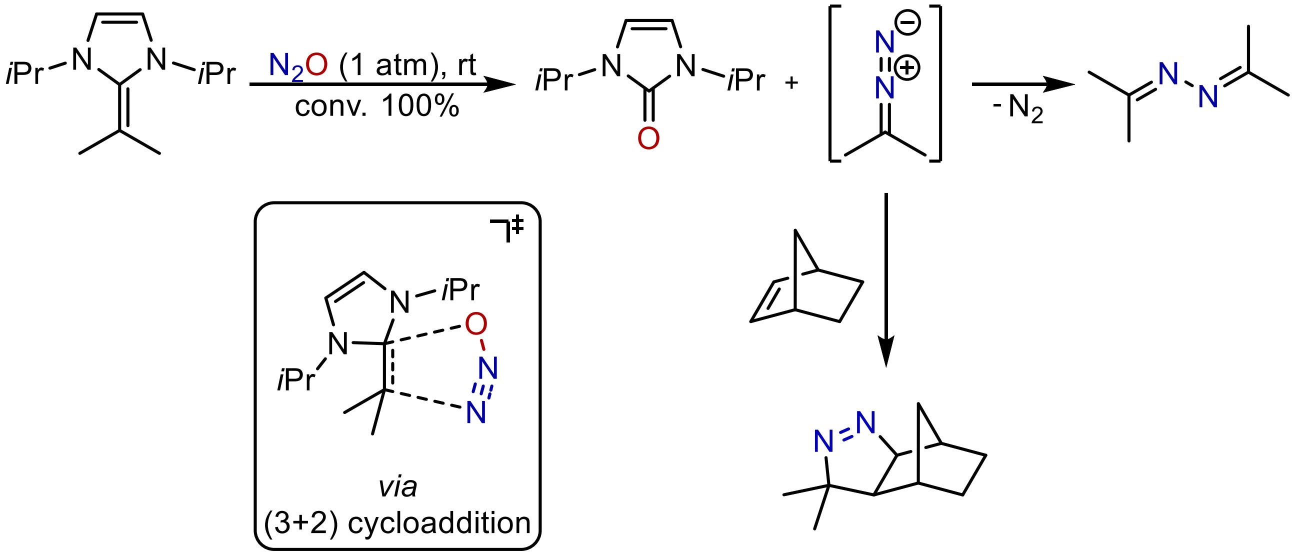
Potential Energy Surface: NHO + N_2O

revDSD-PBEP86-D4/def2-QZVPP//PBEh-3c
SMD model for benzene (PBE0/def2-SVP)
CREST for all minima and TS structures



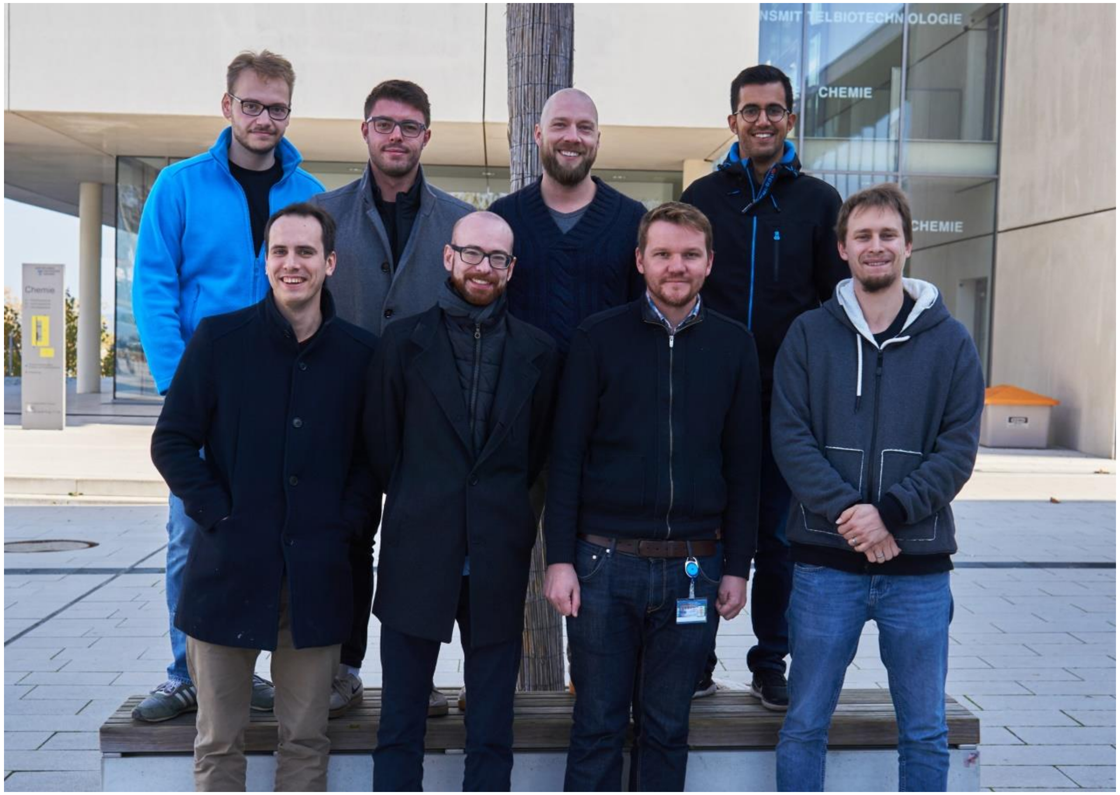
revDSD-PBEP86-D4: G. Santra, N. Sylvetsky, J. M. L. Martin, *J. Phys. Chem. A* **2019**, *123*, 5129−5143; G. Santra, J. M. L. Martin, *Isr. J. Chem.* **2020**, *60*, 787−804. PBEh-3c: S. Grimme, J. G. Brandenburg, C. Bannwarth, A. Hansen, *J. Chem. Phys*. **2015**, *143*, 54107. SMD: A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378−6396. Basis set: F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys*. **2005**, *7*, 3297−3305. CREST: S. Grimme, *J. Chem. Theory Comput*. **2019**, *15*, 2847−2862; P. Pracht, F. Bohle, S. Grimme, *Phys. Chem. Chem. Phys*. **2020**, *22*, 7169−7192. ORCA: F. Neese, *WIREs Comput. Mol. Sci.* **2012**, *2*, 73−78; F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327.

Exposure of NHO to Ambient N_2O releases 2-Diazopropane



Thank you …

- Dr. Urs Gellrich
- Tizian, Max, Felix, Arthur
- Lars, Schindler Group
- Dr. Dennis Gerbig
- Dr. Jonathan Becker
- Dr. Heike Hausmann, OC-Analytics
- Schreiner, Göttlich, and Wegner Group



FCI
FONDS DER
CHEMISCHEN
INDUSTRIE