Homogeneous Catalysis

International Edition: DOI: 10.1002/anie.201702277
German Edition: DOI: 10.1002/ange.201702277

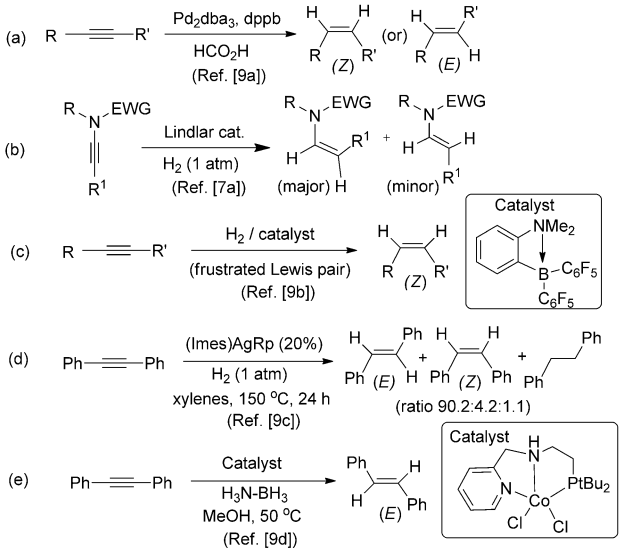
Ethanol as a Hydrogenating Agent: Palladium-Catalyzed Stereoselective Hydrogenation of Ynamides to Give Enamides

*Alla Siva Reddy and K. C. Kumara Swamy**

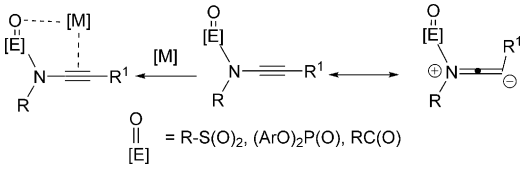
Abstract: *Ethanol is shown to act as a hydrogenating agent for ynamides under palladium catalysis. This behavior is different from the normally expected reaction of ethanol addition to alkynes. The reaction shows stereoselectivity for E enamides, which is in contrast to reports using other hydrogenating sources. The method was also extended to ynamines. Alternatively, the use of ethanol and ammonium formate as the hydrogenating source gives Z enamides. The role of ethanol in hydrogenation was demonstrated by means deuterium labeling experiment.*

Transition-metal-catalyzed hydrogenation of alkynes to give alkenes is an important reaction of vast synthetic utility.[1] Either a heterogeneous catalyst (Raney Ni, Lindlar catalyst, Pd/C)[2] or a homogeneous catalyst consisting of a Rh, Ru, or Ir complex[3] can be utilized to achieve this transformation using hydrogen gas as the hydrogenating agent. Two problems associated with many of these methods are 1) a lack of chemo- and stereoselectivity for the alkenes and 2) over-reduction of the resulting alkenes to alkanes.[4] While much of the literature is devoted to diaryl/dialkyl-substituted alkynes, ynamides have also emerged as important synthons.[5,6] Selected recent examples of hydrogenation of alkynes including ynamides are shown in Scheme 1. We are aware of only two reports on the catalytic hydrogenation of ynamides to give *Z* alkenes by using hydrogen gas and either Lindlar or a [Pd] catalyst.[7] With regard to general alkynes, Szymczak and co-workers recently described hydrogenation to give *Z* alkenes by using a borane-appended [Ru] catalyst, and Tokmic and Fout reported *E*-specific hydrogenation using a [Co] catalyst.[8] Apart from these, several other interesting reports on the semihydrogenation of alkynes are known.[9] Among the methods shown in Scheme 1, reaction (a) utilizes formic acid as the hydrogen source, and those in (b)–(d) involve hydrogen gas. In reaction (e), a $H_3B{:}NH_3$ adduct is utilized in methanol, which acts only as a solvent.

The unusual reactivity of ynamides is presumably the result of formation of a reactive keteniminium ionic species[10] or coordination of the metal catalyst to the alkyne, and in some cases, to the heteroatom of the electron-withdrawing group (Scheme 2).[11] Numerous transformations involving ynamides have been explored in recent years for the generation of carbocycles, heterocycles, and enamides, among others.[12–14] The enamides thus obtained are versatile building blocks that are present in several natural products.[15] Our idea was to use inexpensive ethanol as the hydrogenating agent, since it can be oxidized to aldehyde with the elimination of hydrogen, thereby avoiding the more difficult-to-handle hydrogen gas. To the best of our knowledge, the use of ethanol as a hydrogenating agent in the catalytic reduction of alkynes is rather unknown.[4c] Alcohol/phenol addition to alkynes (hydroalkoxylation/aryloxyaltion) is lot more common.[16] Herein, we report easy-to-handle and inexpensive ethanol as the hydrogenating source. The use of either ethanol or an ethanol/ammonium formate system with an ynamide precursor is presented as an elegant stereoselective approach to either *E* or *Z* enamides through [Pd]-catalyzed hydrogenation.



Scheme 1. Selected examples of hydrogenation of alkynes or ynamides.

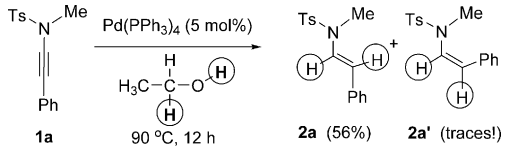


Scheme 2. Reactivity specificity of ynamides.

[*] A. Siva Reddy, Prof. K. C. Kumara Swamy
School of Chemistry, University of Hyderabad
Hyderabad-500046 (India)
E-mail: kckssc@uohyd.ac.in
kckssc@yahoo.com

Supporting information (including experimental details; optimization Tables S1 and S2; ORTEPS of **2a**, **2e**, and **2m**; and $^1H/^{13}C$ NMR/^{31}P spectra) and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/anie.201702277.

Our initial examination involved the reaction of *N*-alkynyl benzenesulfonamide **1a** with ethanol (used also as a solvent) in the presence of $Pd(PPh_3)_4$ (5 mol%) as the catalyst at 90°C for 12 h. We were delighted to obtain the *trans*-hydrogenated product **2a** in 56% yield (Scheme 3). The stereochemistry and structure of compound **2a** were confirmed by X-ray crystallography (Figure 1).[17]



Scheme 3. [Pd]-catalyzed hydrogenation of ynamide **1a** with ethanol.

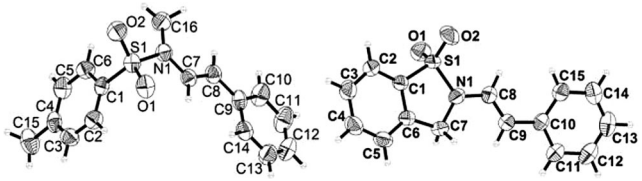
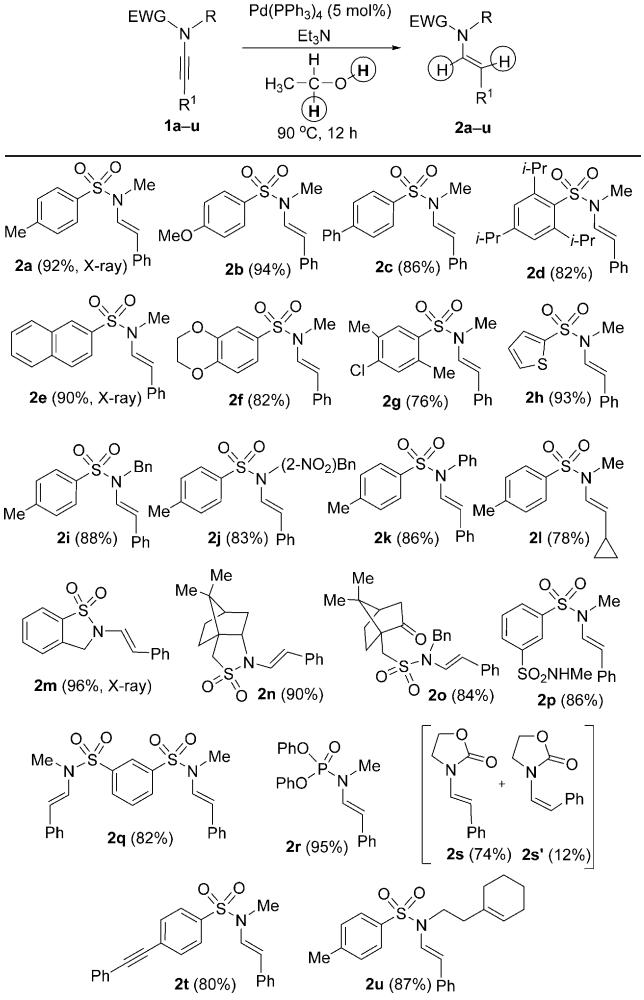


Figure 1. Structures of compounds **2a** (left) and **2m** (right).[17]

Encouraged by the above result, we turned our attention to improve the yield of product **2a** (Table S1 in the Supporting Information). As expected, there was no reaction in aprotic solvents like toluene, THF, and DMSO. There was also no formation of the desired product in the absence of the catalyst. The primary alcohols ^{n}PrOH and ^{n}BuOH also worked well. The reaction rate was slower in ^{i}PrOH and no product was detected when using ^{t}BuOH as the solvent. Thus only alcohols possessing at least one hydrogen substituent on the α-carbon atom are suitable for the hydrogenation process. Intriguingly, in the presence of K_2CO_3 as a base, we noticed the formation of a *cis*-hydrogenated product as the major isomer, albeit in only 36% yield (after isolation). To our delight, the reaction proceeded smoothly when using either Et_3N or pyridine as the base, affording the desired product in 92% yield with excellent stereoselectivity. [Pd] catalysts that do not contain phosphine failed to produce product **2a**. Pd/C and $Pd_2(dba)_3$ were less efficient as catalysts for this transformation. More importantly, no product formation was seen at room temperature. This may be due to the requirement of a higher dissociation energy for hydride-ion transfer. Although decreasing the catalyst loading to 3 mol% reduced the product yield when keeping the reaction time of 12 h, increasing the duration to 36–48 h afforded better yield of the product even with 2 mol% of the catalyst (i.e., a substrate/catalyst ratio of 50:1). The optimal conditions for this transformation were **1a** (0.2 mmol), $Pd(PPh_3)_4$ (5 mol%), Et_3N (0.6 mmol) in ethanol (1 mL) at 90°C for 12 h (see Table S1 in the Supporting Information).

Various types of ynamides were transformed into the corresponding *E* enamides **2a–u** in good to excellent yields with high stereoselectivity when using ethanol as the hydrogenating source (Table 1). Even the sterically crowded ynamides **1d–f** furnished the corresponding products **2d–f** in good yields. Altering the substituents on the nitrogen atom of the ynamide from aliphatic to aromatic was also tolerated and delivered the enamides **2i–2k**. The reaction is compatible with cyclic sulfonamide derived ynamides to give the enamides **2m**,**n**. Chemoselectivity is demonstrated by the retention of the carbonyl group as in product **2o** (or **2s**). The ynamide **1p**, which has a free sulfonamide functionality, also worked to provide the product **2p**. Interestingly, hydrogenation of two different C≡C bonds can also be accomplished readily, as shown by the isolation of **2q** in good yield. Replacing the sulfonyl group with a phosphoryl group does not affect the stereoselectivity, and affords the product **2r** in excellent yield. The carbamate-derived ynamide slightly reduced the stereoselectivity, but with a good overall yield of **2s**. The functional-group tolerance is demonstrated by selective hydrogenation of the ynamide functionality in the presence of non-activated alkynyl and alkenyl groups, as shown by the isolation of products **2t** and **2u**. Additionally, the enamide product does not become over-hydrogenated, even after 48 h. The struc-

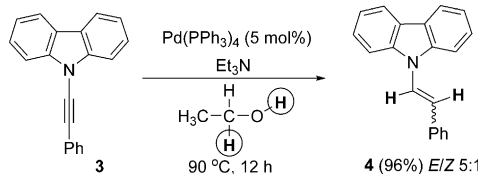
Table 1: Scope of the hydrogenation of ynamides by ethanol to give *E* enamides.[a]



[a] Conditions: **1** (0.2 mmol), $Pd(PPh_3)_4$ (5 mol%), Et_3N (0.6 mmol) in ethanol (1 mL) at 90°C for 12 h. Yields of isolated product after column chromatography are given in parenthesis. For the preparation of compound **2q**, we used $Pd(PPh_3)_4$ (10 mol%) and Et_3N (1.2 mmol).

tures of compounds **2m** and **2e** were confirmed by X-ray crystallography (Figure 1, right and Figure S2 in the Supporting Information).

It is important to note that the carbazole-derived ynamine substrate **3** also afforded the enamine **4** in 96% yield of isolated product, with the *E* isomer still predominating (Scheme 4).

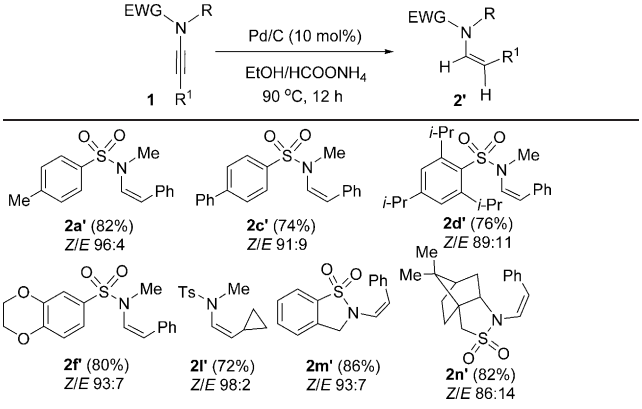


Scheme 4. Hydrogenation of ynamine **3** with ethanol.

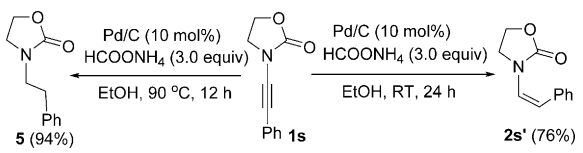
During optimization of the above reaction, it was noted that using Pd/C or $Pd_2(dba)_3$ as the catalyst preferentially led to only very small quantities of the *Z* isomer (Table S1, entries 19–20), with most of the starting ynamide unreacted. We surmised that the addition of other hydrogenating source may increase the yield of this isomer. Aqueous formic acid led primarily to the addition product with water. Pleasingly, using EtOH/NH_4OOCH as the hydrogenating source afforded *Z* enamides with high stereoselectivity. This route was then utilized to obtain several *Z* enamides (**2a′**, **2c′**, **2d′**, **2f′**, **2l′**, **2m′**, and **2n′**; Table 2). Since the yield was lower when THF (or toluene or CH_3CN) was used in place of EtOH, we believe that the latter plays a synergistic role in hydrogenation. In these cases, there was no over-hydrogenation even after 48 h. The ynamide **1s** was lot more reactive, and afforded a good yield of **2s′** even at RT; at 90 °C, fully reduced product **5** was obtained in high yields (Scheme 5).

For the reaction shown in Scheme 3, replacing ethanol with methanol led to predominantly **2a**, along with small amounts of the (competitive) methanol addition product **6** (Scheme 6a). Use of CH_3OD (or C_2H_5OD) led to the isolation of **2a**-d_1 (Scheme 6b). The reaction using CD_3OD did not proceed, probably for kinetic reasons. A plausible

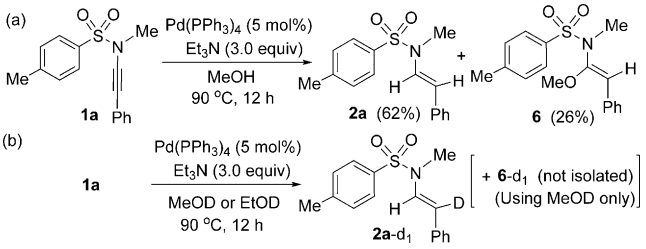
Table 2: Scope of the *Z*-selective hydrogenation of ynamides.[a]



[a] Conditions: **1** (0.2 mmol), Pd/C (10 mol%), $HCOONH_4$ (0.6 mmol) in EtOH (1 mL) at 90 °C for 12 h. Yields of isolated product after column chromatography are given in parenthesis.

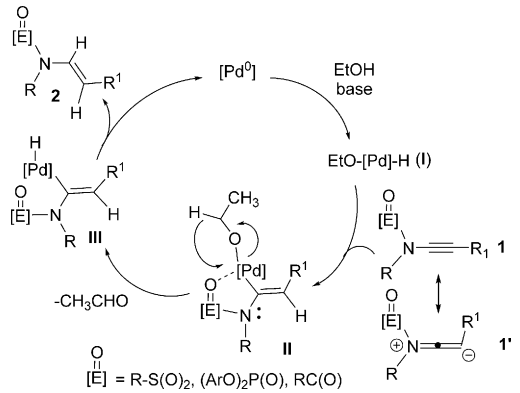


Scheme 5. Hydrogenation (*Z*-specific/full) of ynamide **1s**.



Scheme 6. Control experiments.

catalytic cycle for the formation of compounds **2a–s**, based on control experiments and earlier reports,[18] is shown in Scheme 7. The ynamide likely exists as the alkyne (**1**) and keteniminium (**1′**) resonance forms. The in situ formed [Pd]



Scheme 7. Proposed pathway for the formation of **2**.

intermediate **I** undergoes addition to **1′** to give intermediate **II**. It is likely that in **II**, the metal is coordinated to the sulfonyl/phosphoryl oxygen atom. Steric interactions between the nitrogen lone pair and R^1/H group may be responsible for the *trans* stereoselectivty, with the hydrogen preferring the opposite side of Pd. In general, we did not observe isomerization or over-hydrogenation. In the X-ray structures of **2a**, **2e**, and **2m**, the N–C(*H*)= hydrogen atom is close to one of the sulfonyl oxygen atoms (< 2.87 Å), which may explain the stereochemistry to some degree, but more data is required to establish this feature. Species **II** undergoes hydride shift with subsequent elimination of acetaldehyde to give intermediate **III**. Isolation of deuterated compound **2a**-d_1 is consistent with the intermediacy of **II**. The lack of reaction with ^{t}BuOH suggests a requirement for β-hydride shift. Finally, **III** undergoes reductive elimination to afford **2**, thereby thus regenerating the active [Pd^0] catalyst.

In conclusion, we have shown that ethanol can act as the hydrogenating agent in the palladium-catalyzed reaction of

ynamides, a synthetically versatile class of alkynes. The reaction is operationally simple and affords *E* enamides in a highly stereoselective manner. A complementary palladium-catalyzed reaction involving EtOH/NH_4OOCH gives *Z*-selective hydrogenation. This method is also applicable to phosphoryl-and carbamate-derived ynamides and ynamines.

Acknowledgements

We thank DST and UGC, New Delhi (FIST, IRHPA, J C Bose Fellowship, UPE-II and CAS programs) for support. ASR thanks UGC for fellowship.

Conflict of interest

The authors declare no conflict of interest.

Keywords: enamides · ethanol · hydrogenation · palladium · ynamides

[1] a) A. M. Kluwer, C. J. Elsevier in *Handbook of Homogeneous Hydrogenation*, *Vol. 1* (Eds.: J. G. de Vries, C. J. Elsevier), Wiley-VCH, Weinheim, **2007**, pp. 375; b) S. Siegel in *Comprehensive Organic Synthesis*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, pp. 417; c) A. Fedorov, H.-J. Liu, H.-K. Lo, C. Copéret, *J. Am. Chem. Soc.* **2016**, *138*, 16502; d) S. Furukawa, T. Komatsu, *ACS Catal.* **2016**, *6*, 2121; e) R. M. Drost, T. Bouwens, N. P. van Leest, B. de Bruin, C. J. Elsevier, *ACS Catal.* **2014**, *4*, 1349.

[2] a) S. Nishimura, *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley-Interscience, New York, **2001**; b) H.-U. Blaser, A. Schnyder, H. Steiner, F. Rössler, P. Baumeister in *Handbook of Heterogeneous Catalysis*, *Vol. 7*, 2nd ed. (Eds.: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp), Wiley-VCH, Weinheim, **2008**, p. 3284; c) H. Lindlar, *Helv. Chim. Acta* **1952**, *35*, 446; d) J. R. Weir, B. A. Patel, R. F. Heck, *J. Org. Chem.* **1980**, *45*, 4926; e) T. Mitsudome, T. Urayama, K. Yamazaki, Y. Maehera, J. Yamasaki, K. Gohara, Z. Maeno, T. Mizugaki, K. Jitsukawa, K. Kaneda, *ACS Catal.* **2016**, *6*, 666.

[3] a) H. Takaya, R. Noyori in *Comprehensive Organic Synthesis*, *Vol. 8* (Eds.: B. M. Trost, I. Fleming), Pergamon, Oxford, **1991**, p. 443; b) S. Furukawa, A. Yokoyama, T. Komatsu, *ACS Catal.* **2014**, *4*, 3581; c) C. Kohrt, G. Wienhöfer, C. Preibbenow, M. Beller, D. Heller, *ChemCatChem* **2013**, *5*, 2818; d) K. T. Neumann, S. Klimczyk, M. N. Burhardt, B. Bang-Andersen, T. Skrydstrup, A. T. Lindhardt, *ACS Catal.* **2016**, *6*, 4710; e) J. Navarro, M. Sagi, E. Sola, F. J. Lahoz, I. T. Dobrinovitch, A. Katho, F. Joo, L. A. Oro, *Adv. Synth. Catal.* **2003**, *345*, 280.

[4] a) H. Sajiki, S. Mori, T. Ohkubo, T. Ikawa, A. Kume, T. Maegawa, Y. Monguchi, *Chem. Eur. J.* **2008**, *14*, 5109; b) T. Mitsudome, Y. Takahashi, S. Ichikawa, T. Mizugaki, K. Jitsukawa, K. Kaneda, *Angew. Chem. Int. Ed.* **2013**, *52*, 1481; *Angew. Chem.* **2013**, *125*, 1521; c) K. Tani, A. Iseki, T. Yamagata, *Chem. Commun.* **1999**, 1821.

[5] Reviews: a) C. A. Zificsak, J. A. Mulder, R. P. Hsung, C. Rameshkumar, L.-L. Wei, *Tetrahedron* **2001**, *57*, 7575; b) K. A. Dekorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang, R. P. Hsung, *Chem. Rev.* **2010**, *110*, 5064; c) G. Evano, A. Coste, K. Jouvin, *Angew. Chem. Int. Ed.* **2010**, *49*, 2840; *Angew. Chem.* **2010**, *122*, 2902; d) G. Evano, K. Jouvin, A. Coste, *Synthesis* **2013**, 0017; e) X.-N. Wang, H.-S. Yeom, L.-C. Fang, S. He, Z.-X. Ma, B. L. Kedrowski, R. P. Hsung, *Acc. Chem. Res.* **2014**, *47*, 560; f) T. Lu, R. P. Hsung, *Arkivoc* **2014**, *i*, 127; g) F. Pan, C. Shu, L.-W. Ye, *Org. Biomol. Chem.* **2016**, *14*, 9456.

[6] a) A. Siva Reddy, K. C. Kumara Swamy, *Org. Lett.* **2015**, *17*, 2996; b) A. Siva Reddy, A. Leela Siva Kumari, S. Saha, K. C. Kumara Swamy, *Adv. Synth. Catal.* **2016**, *358*, 1625; c) A. Leela Siva Kumari, A. Siva Reddy, K. C. Kumara Swamy, *Org. Lett.* **2016**, *18*, 5752.

[7] a) X. Zhang, Y. Zhang, J. Huang, R. P. Hsung, K. C. M. Kurtz, J. Oppenheimer, M. E. Petersen, I. K. Sagamanova, L. Shen, M. R. Tracey, *J. Org. Chem.* **2006**, *71*, 4170; b) F.-X. Felpin, E. Fouquet, *Chem. Eur. J.* **2010**, *16*, 12440.

[8] a) K.-N. T. Tseng, J. W. Kampf, N. K. Szymczak, *J. Am. Chem. Soc.* **2016**, *138*, 10378; b) K. Tokmic, A. R. Fout, *J. Am. Chem. Soc.* **2016**, *138*, 13700.

[9] a) R. Shen, T. Chen, Y. Zhao, R. Qiu, Y. Zhou, S. Yin, X. Wang, M. Goto, L.-B. Han, *J. Am. Chem. Soc.* **2011**, *133*, 17037; b) K. Chernichenko, Á. Madarász, I. Pápai, M. Nieger, M. Leskelä, T. Repo, *Nat. Chem.* **2013**, *5*, 718; c) M. K. Karunananda, N. P. Mankad, *J. Am. Chem. Soc.* **2015**, *137*, 14598; d) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, *J. Am. Chem. Soc.* **2016**, *138*, 8588.

[10] a) C. Theunissen, B. Métayer, N. Henry, G. Compain, J. Marrot, A. Martin-Mingot, S. Thibaudeau, G. Evano, *J. Am. Chem. Soc.* **2014**, *136*, 12528; b) M. Lecomte, G. Evano, *Angew. Chem. Int. Ed.* **2016**, *55*, 4547; *Angew. Chem.* **2016**, *128*, 4623; c) D. V. Patil, S. W. Kim, Q. H. Nguyen, H. Kim, S. Wang, T. Hoang, S. Shin, *Angew. Chem. Int. Ed.* **2017**, *56*, 3670 – 3674; *Angew. Chem.* **2017**, *129*, 3724 – 3728; d) H. V. Adcock, E. Chatzopoulou, P. W. Davies, *Angew. Chem. Int. Ed.* **2015**, *54*, 15525; *Angew. Chem.* **2015**, *127*, 15745; e) K. A. Dekorver, R. P. Hsung, W.-Z. Song, X.-N. Wang, M. C. Walton, *Org. Lett.* **2012**, *14*, 3214.

[11] a) B. Gourdet, H. W. Lam, *J. Am. Chem. Soc.* **2009**, *131*, 3802; b) Y. Minko, M. Pasco, L. Lercher, M. Botoshansky, I. Marek, *Nature* **2012**, *490*, 522; c) Y. Fukudome, H. Naito, T. Hata, H. Urabe, *J. Am. Chem. Soc.* **2008**, *130*, 1820; d) W. Gati, M. M. Rammah, M. B. Rammah, F. Couty, G. Evano, *J. Am. Chem. Soc.* **2012**, *134*, 9078; e) E. Romain, C. Fopp, F. Chemla, F. Ferreira, O. Jackowski, M. Oestreich, A. Perez-Luna, *Angew. Chem. Int. Ed.* **2014**, *53*, 11333; *Angew. Chem.* **2014**, *126*, 11515.

[12] a) S. Kramer, Y. Odabachian, J. Overgaard, M. Rottlander, F. Gagosz, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2011**, *50*, 5090; *Angew. Chem.* **2011**, *123*, 5196; b) E. Rettenmeier, A. M. Schuster, M. Rudolph, F. Rominger, C. A. Gade, A. S. K. Hashmi, *Angew. Chem. Int. Ed.* **2013**, *52*, 5880; *Angew. Chem.* **2013**, *125*, 5993; c) L. Chen, J. Cao, Z. Xu, Z.-J. Zheng, Y.-M. Cui, L.-W. Xu, *Chem. Commun.* **2016**, *52*, 9574; d) R. B. Dateer, B. S. Shaibu, R. S. Liu, *Angew. Chem. Int. Ed.* **2012**, *51*, 113; *Angew. Chem.* **2012**, *124*, 117.

[13] a) D. Fujino, H. Yorimitsu, A. Osuka, *J. Am. Chem. Soc.* **2014**, *136*, 6255; b) R. N. Straker, Q. Peng, A. Mekareeya, R. S. Paton, E. A. Anderson, *Nat. Commun.* **2016**, *7*, 10109; c) S. N. Karad, R.-S. Liu, *Angew. Chem. Int. Ed.* **2014**, *53*, 9072; *Angew. Chem.* **2014**, *126*, 9218; d) B. Witulski, C. Alayrac, L. Tevzadze-Saeftel, *Angew. Chem. Int. Ed.* **2003**, *42*, 4257; *Angew. Chem.* **2003**, *115*, 4392; e) S. Couty, C. Meyer, J. Cossy, *Angew. Chem. Int. Ed.* **2006**, *45*, 6726; *Angew. Chem.* **2006**, *118*, 6878; f) W.-B. Shen, X.-Y. Xiao, Q. Sun, B. Zhou, X.-Q. Zhu, J.-Z. Yan, X. Lu, L.-W. Ye, *Angew. Chem. Int. Ed.* **2017**, *56*, 605; *Angew. Chem.* **2017**, *129*, 620; g) S. E. Kiruthika, A. Nandakumar, P. T. Perumal, *Org. Lett.* **2014**, *16*, 4424.

[14] a) P. Valenta, P. J. Carroll, P. J. Walsh, *J. Am. Chem. Soc.* **2010**, *132*, 14179; b) J. A. Mulder, K. C. M. Kurtz, R. P. Hsung, H. Coverdale, M. O. Frederick, L. Shen, C. A. Zificsak, *Org. Lett.* **2003**, *5*, 1547; c) D. L. Smith, W. R. F. Goundry, H. W. Lam,

Chem. Commun. **2012**, *48*, 1505; d) Y. Yang, L. Wang, J. Zhang, Y. Jin, G. Zhu, *Chem. Commun.* **2014**, *50*, 2347; e) S. Xu, J. Liu, D. Hu, X. Bi, *Green Chem.* **2015**, *17*, 184; f) A. Hentz, P. Ratailleau, V. Gandon, K. Cariou, R. H. Dodd, *Angew. Chem. Int. Ed.* **2014**, *53*, 8333; *Angew. Chem.* **2014**, *126*, 8473.

[15] a) B. Gourdet, H. W. Lam, *Angew. Chem. Int. Ed.* **2010**, *49*, 8733; *Angew. Chem.* **2010**, *122*, 8915; b) M. Nakanishi, C. Minard, P. Retailleau, K. Cariou, R. H. Dodd, *Org. Lett.* **2011**, *13*, 5792; c) D. R. Carbery, *Org. Biomol. Chem.* **2008**, *6*, 3455; d) R. Matsubara, S. Kobayashi, *Acc. Chem. Res.* **2008**, *41*, 292; e) Z.-X. Ma, J. B. Feltenberger, R. P. Hsung, *Org. Lett.* **2012**, *14*, 2742; f) Z. Song, T. Lu, R. P. Hsung, Z. F. Al-Rashid, C. Ko, Y. Tang, *Angew. Chem. Int. Ed.* **2007**, *46*, 4069; *Angew. Chem.* **2007**, *119*, 4147.

[16] a) R. M. P. Veenboer, S. Dupuy, S. P. Nolan, *ACS Catal.* **2015**, *5*, 1330; b) Y. Oonishi, A. Gómez-Suárez, A. R. Martin, S. P. Nolan, *Angew. Chem. Int. Ed.* **2013**, *52*, 9767; *Angew. Chem.* **2013**, *125*, 9949; c) D. Fujino, H. Yorimitsu, A. Osuka, *J. Am. Chem. Soc.* **2014**, *136*, 6255.

[17] CCDC 1532243, 1532244 and 1532245 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

[18] a) Y. Kim, R. B. Dateer, S. Chang, *Org. Lett.* **2017**, *19*, 190; b) P. R. Walker, C. D. Campbell, A. Suleman, G. Carr, E. A. Anderson, *Angew. Chem. Int. Ed.* **2013**, *52*, 9139; *Angew. Chem.* **2013**, *125*, 9309; c) R. Kawahara, K. Fujita, R. Yamaguchi, *J. Am. Chem. Soc.* **2012**, *134*, 3643.

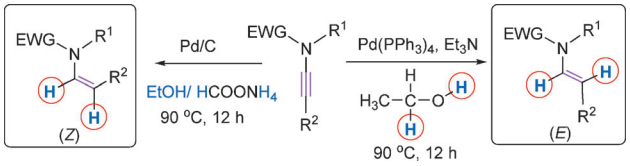
Manuscript received: March 2, 2017
Final Article published: ■■ ■■, ■■■■

Communications

Homogeneous Catalysis

A. Siva Reddy,
K. C. Kumara Swamy* ——— ▮▮▮▮–▮▮▮▮

Ethanol as a Hydrogenating Agent: Palladium-Catalyzed Stereoselective Hydrogenation of Ynamides to Give Enamides



One for the road: Ethanol acts as a hydrogenating agent for ynamides under palladium catalysis. This behavior is different from the normally expected addition of ethanol to alkynes. The reactions shows stereoselectivity for *E* enamides, which is in contrast to reports using other hydrogenating sources, and the method was also extended to ynamines. Alternatively, the use of ethanol/ammonium formate as the hydrogenating source gives *Z* enamides.