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Synthesis of Enamides by Ruthenium-Catalyzed Reaction of Alkyl Azides with Acid Anhydrides in Ionic Liquid

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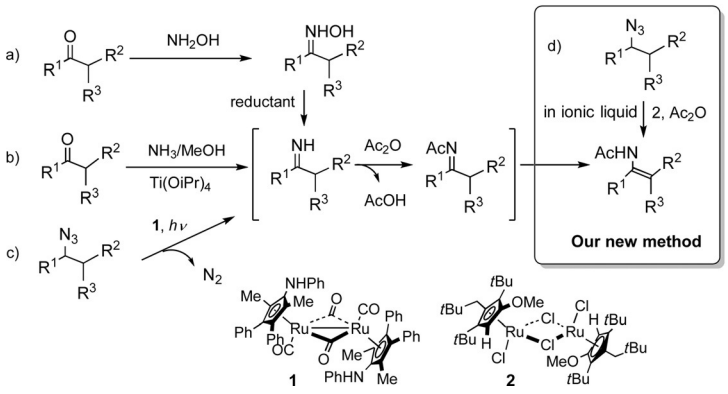
Enamides were synthesized by a ruthenium-catalyzed one-pot, one-step procedure from alkyl azides and acid anhydrides. The substrate scope includes not only secondary azides, but also primary aliphatic ones to give a wide range of enamides containing various functional groups. This one-step procedure was based on the newly discovered activity of Severin's diruthenium complex ([Cp^RuCl$_2$]$_2$: Cp^ = η^5-1-methoxy-2,4-di-*tert*-butyl-3-neopentylcyclopentadienyl) for the transformation of alkyl azides into the corresponding N–H imine intermediates in ionic liquids. The formation of ruthenium tetrazene complexes was observed in the stoichiometric reaction of Severin's complex with alkyl azides, which acted as the catalyst for the formation of N–H imine intermediates.

Enamides are key functional groups in numerous natural products and drug candidates[1] and serve as versatile intermediates in organic synthesis.[2] They have been utilized in pericyclic,[3] radical,[4] photochemical,[5] and transition-metal-catalyzed reactions,[6] including the well-known enantioselective hydrogenation reaction for the synthesis of chiral amines.[7] For these extensive applications, a number of methods have been devised for the synthesis of enamides.[8] Conventional ones include the addition of Grignard reagents to nitriles followed by reaction with acyl donors,[9] transition-metal-catalyzed cross-coupling reactions of vinyl electrophiles with amides,[10] direct condensation of amides with aldehydes and ketones,[11] and reductive acylation of ketoximes.[12] However, these methods frequently suffer from functional group tolerance, difficulties in preparing substrates, low yields, and/or the requirement of stoichiometric reductants or additives.

One of the most commonly employed procedures is the reductive acylation of ketoximes, which requires the transformation of ketones into ketoximes and subsequent reduction in the presence of acyl donors (Scheme 1 a). Recently, Reeves and co-workers developed a direct and redox-free synthesis of enamides from ketones, ammonia, and acetic anhydride with the aid of Ti(O*i*Pr)$_4$ (Scheme 1 b).[13] Although this is a one-pot process under mild conditions, the use of an excess amount of Ti(O*i*Pr)$_4$ requires a complicated workup procedure to remove titanium waste from the reaction mixture. As an innovative method overcoming the problem of stoichiometric reductants or additives, our group developed the synthesis of enamides from alkyl azides and acid anhydrides[14] that is based on Ru catalysis to transform alkyl azides into N–H imines (Scheme 1 c).[15] Diruthenium complex **1** shown in Scheme 1 c needs light to be activated, and the resulting activated species is deactivated by acetic acid. Thus, Scheme 1 c is a two-step process requiring the accumulation of the intermediate N–H imines before acylation with acetic anhydride. This two-step process limits the substrate scope, because unstable N–H imine intermediates suffer from side reactions such as rearrangements and self-condensation reactions.[16] Particularly, aliphatic N–H aldimines are too unstable to afford the corresponding enamides.



Scheme 1. Methods for the synthesis of *N*-acyl enamides through N–H imine intermediates.

Aliphatic N–H aldimines will be valuable intermediates for the synthesis of peptide natural products and bioactive molecules that contain an enamide functionality as an important structural motif.[1,8a,11d] Our search for new catalyst systems that can provide aliphatic N–H aldimines and retain catalytic activity under conditions for the subsequent acylation[17] led to the finding of chloride-bridged diruthenium complex **2**.[18] Complex **2** has shown catalytic activity for the transformation of benzyl

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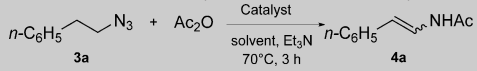
azide into hydrobenzamide. Although its substrate scope is described to be limited to primary benzylic azides, we were attracted by the probable intermediacy of N–H benzaldimine for the formation of hydrobenzamide.[19] Herein, we wish to report a newly discovered activity of **2** in ionic liquids; we found that efficient synthesis of the enamides involving aliphatic N–H aldimine intermediates is possible. In fact, a wide range of enamides can be prepared not only from primary aliphatic azides but also from secondary azides by a one-pot, one-step process (Scheme 1 d).

The transformation of 1-octyl azide (**3 a**) into *N*-(oct-1-enyl)acetamide (**4 a**) was examined under various conditions (Table 1). The yield of **4 a** was only 32% in the first attempt in THF (Table 1, entry 1). However, considering the scope limitation described in the previous report,[14] it was an unexpected and promising result. This finding supports the idea that the catalytic activity of **2** for the generation of octan-1-imine was retained to some extent under conditions for acylation. The yield increased slightly in dioxane (Table 1, entry 2). A considerable increase in the yield was observed for the reaction performed in the ionic liquid (butylmethylimidazolium chloride ([bmim]Cl)) (Table 1, entry 3). Although changing the chloride anion with tetrafluoroborate or hexafluorophosphate was not rewarding (Table 1, entries 4 and 5), increasing the length of the alkyl substituent improved the yield significantly (Table 1, entry 6). Remarkably, **4 a** was formed in quantitative yield in octylmethylimidazolium chloride ([omim]Cl) (Table 1, entry 7). The yield decreased on lowering the reaction temperature and on reducing the amount of catalyst **2**, acetic anhydride, or triethylamine (Table 1, entries 8–11). Analogous Ru^{III} complexes and other commercially available Ru^{II} complexes showed much lower catalytic activity than **2** (Table 1, entries 12–16). Geometrical selectivity was not so high: $E/Z \approx 58:42$–$74:26$.

Table 1. Transformation of *n*-octyl azide into *N*-(oct-1-enyl)acetamide.[a]



Entry	Catalyst	Solvent	Conversion of azide [%][b]	Yield[b] [%]	(*E*/*Z*)
1	**2**	THF	>99	32	(65:35)
2	**2**	dioxane	>99	41	(68:32)
3	**2**	[bmim]Cl	74	60	(58:42)
4	**2**	[bmim]BF_4	>99	52	(60:40)
5	**2**	[bmim]PF_6	17	trace	
6	**2**	[hmim]Cl	>99	90	(62:38)
7	**2**	[omim]Cl	>99	99	(58:42)
8	**2**	[omim]Cl	>99	65[c]	(74:26)
9	**2**	[omim]Cl	>99	90[d]	(60:40)
10	**2**	[omim]Cl	>99	70[e]	(64:36)
11	**2**	[omim]Cl	73	44[f]	(66:34)
12	$(CpRuCl_2)_2$	[omim]Cl	<5	trace	
13	$(Cp^*RuCl_2)_2$	[omim]Cl	29	29	(61:39)
14	$CpRuCl(PPh_3)_2$	[omim]Cl	5	trace	
15	$[(p\text{-cymene})RuCl_2]_2$	[omim]Cl	4	trace	
16	$RuCl_2(PPh_3)_3$	[omim]Cl	29	trace	

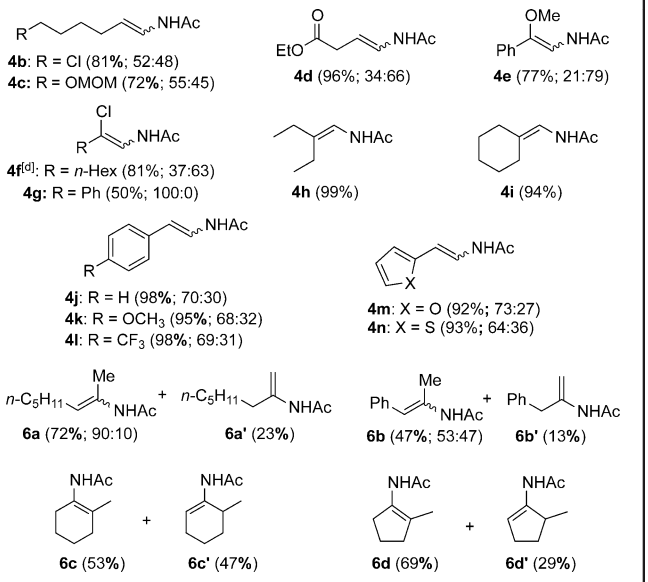
[a] Reaction conditions: A solution of *n*-octyl azide (0.25 mmol), catalyst (2.0 mol%), Et_3N (0.50 mmol), and Ac_2O (0.50 mmol) in solvent (1.0 mL) was stirred at 70 °C for 3 h. Cp = η^5-cyclopentadienyl, Cp* = η^5-pentamethylcyclopentadienyl. [b] Determined by ^1H NMR spectroscopy by using dibromomethane as an internal standard. [c] At 50 °C. [d] **2** (1.0 mol%). [e] Ac_2O (1.2 equiv.). [f] Et_3N (2.0 mol%).

With the conditions optimized in Table 1, we explored the substrate scope for aliphatic azides (Table 2). Various functional groups were compatible with the catalyst system: chloride (see product **4 b**), methoxymethyl ether (see product **4 c**), and ester groups (see product **4 d**). β-Methoxy-substituted enamide **4 e** was obtained in good yield, which is a useful precursor for the synthesis of β-amino alcohols.[12h,20] β-Chloro enamides **4 f** and **4 g** were obtained in moderate to good yields and have been used as important building blocks in the synthesis of chartellines.[21]

Acyclic **4 h** and cyclic β-branched enamide **4 i** were formed in high yields. Enamides **4 j**–**l** conjugated with aryl rings and enamides **4 m** and **4 n** conjugated with heteroaromatic rings were obtained in almost quantitative yields. The electronic effects of the substituents in the aromatic rings of **4 j**–**l** were not significant for enamide formation.

In the transformation of linear secondary aliphatic azides **5**, corresponding enamides **6** were formed as mixtures of regioisomers and geometric isomers. From 2-azidooctane, trisubstituted enamide **6 a** was obtained as a 90:10 *E*/*Z* mixture in 72% combined yield with minor regioisomer **6 a′** in 23% yield. Conjugation to the phenyl ring was not beneficial to the reaction efficiency or to the product selectivity in the transformation of (2-azidopropyl)benzene; **6 b** was obtained as a 53:47 *E*/

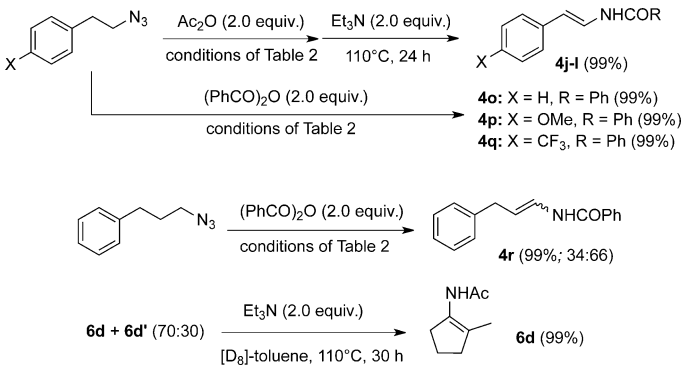
Table 2. Synthesis of enamides from aliphatic azides.[a–c]



[a] Reaction conditions: A solution of **3** (0.25 mmol), **2** (2.0 mol%), Et_3N (0.50 mmol), and Ac_2O (0.50 mmol) in [omim]Cl (1.0 mL) was stirred at 70 °C for 3 h. MOM = methoxymethyl. [b] Reactions conditions: A solution of **5** (0.25 mmol), **2** (2.0 mol%), Et_3N (0.50 mmol), and Ac_2O (0.50 mmol) in [omim]Cl (1.0 mL) was stirred at 70 °C for 12 h. [c] Yields of isolated products are given; *E*/*Z* ratios are given in parentheses. [d] 1 h at 60 °C.

Z mixture in 47% combined yield with minor regioisomer **6b′** in 13% yield. Enamides were obtained quantitatively in combined yields in the transformation of cyclic secondary aliphatic azides **5c** and **5d**, although the regioselectivity was low. There was negligible regioselectivity in the formation of cyclohexenylacetamides **6c** and **6c′**, whereas moderate regioselectivity was observed in the formation of the cyclopentenylacetamides to give tetrasubstituted enamide **6d** as the major product.

Notably, the *E*/*Z* mixtures of *N*-acetyl enamides **4j–l** formed in the reactions of (2-azidoethyl)benzene derivatives were converted quantitatively into the *E* isomers by heating the mixtures at 110 °C for 24 h (Scheme 2).[22] It is also notable that *E*



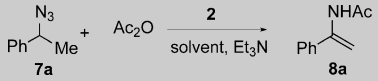
Scheme 2. Thermal isomerization of *N*-acyl enamides.

isomers **4o–q** were formed exclusively by the use of benzoic anhydride instead of acetic anhydride under the conditions of Table 2. However, breaking the conjugation to the phenyl ring as in **4r** diminished the selectivity, and slow decomposition or incomplete isomerization was observed in the heat treatment of *E*/*Z* mixtures of other enamides. The thermal isomerization of cyclopentenylacetamide **6d′** into **6d** in toluene at 110 °C was successful, but slow decomposition of **6c** and **6c′** was observed at 110 °C in the presence of triethylamine.

The transformation of benzylic azides, in contrast to that of aliphatic azides, was more facile in [bmim]Cl than in ionic liquids having longer alkyl chains such as hexylmethylimidazolium chloride ([hmim]Cl) and [omim]Cl (Table 3, entries 1–3). The reaction efficiency in [bmim]BF_4 was as good as that in [bmim]Cl (Table 3, entry 4), whereas that in [bmim]PF_6 was mediocre (Table 3, entry 5). Enamide **8a** was formed in quantitative yield even with 1.0 mol% of **2**, 1.2 equivalents of acetic anhydride, and 2.0 mol% of triethylamine (Table 3, entry 6). A large-scale reaction proceeded smoothly with 0.10 mol% of **2** and 0.20 mol% of Et_3N to give **8a** in 91% yield (Table 3, entry 7). Interestingly, THF was also a good reaction medium for the transformation (Table 3, entry 8).

A wide range of benzylic azides were successfully transformed into the corresponding enamides (Table 4). A small steric effect was observed in the formation of **8b** having a 2-methylphenyl group, whereas there was no clear trend of the electronic effect in the formation of **8d–g**. Various functional groups were compatible with the reaction conditions: alkoxy (see product **8e**), ester (see product **8f**), nitro (see product

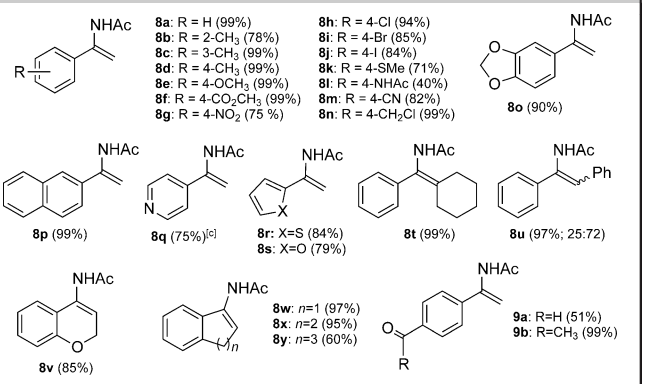
Table 3. Transformation of (1-azidoethyl)benzene into *N*-(1-phenylvinyl)-acetamide.[a]



Entry	**2** [mol%]	Solvent	Ac_2O [equiv.]	Et_3N [equiv.]	Yield [%][b]
1	2.0	[omim]Cl	2.0	2.0	70
2	2.0	[hmim]Cl	2.0	2.0	70
3	2.0	[bmim]Cl	2.0	2.0	99
4	2.0	[bmim]BF_4	2.0	2.0	99
5	2.0	[bmim]PF_6	2.0	2.0	73
6	1.0	[bmim]Cl	1.2	0.020	99
7[c]	0.10	[bmim]Cl	1.2	0.0020	91[d]
8	2.0	THF	2.0	2.0	99

[a] Reaction conditions: A solution of (1-azidoethyl)benzene (0.25 mmol), **2**, Et_3N, and Ac_2O in solvent (1.0 mL) was stirred at 70 °C for 3 h. [b] Determined by ^1H NMR spectroscopy by using dibromomethane as an internal standard. [c] (1-Azidoethyl)benzene (1.0 g, 7.0 mmol). [d] Yield of isolated product.

Table 4. Synthesis of enamides from benzylic azides.[a,b]

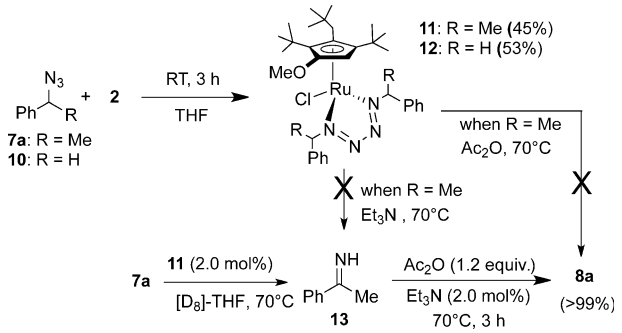


[a] Reaction conditions: A solution of benzylic azide **7** (0.25 mmol), **2** (1.0 mol%), Et_3N (2.0 mol%), and Ac_2O (0.30 mmol) in [bmim]Cl (1.0 mL) was stirred at 70 °C for 3 h. [b] Yields of isolated products are given; *E*/*Z* ratios are given in parentheses. [c] Reaction performed in THF.

8g), halide (see products **8h–j**), thioether (see product **8k**), amide (see product **8l**), and cyano groups (see product **8m**). Noticeably, the chloromethyl group labile toward nucleophiles in **8n** and the acetal group labile toward acids in **8o** remained intact during the transformation. Naphthyl (see product **8p**) and heteroaromatic enamides (see product **8q–s**) were also obtained in good yields. β,β-Disubstituted derivative **8t** was formed in quantitative yield. β-Monosubstituted derivative **8u** was produced as a mixture of geometrical isomers in quantitative yield. Benzocyclic enamides **8v–y** were obtained from the corresponding benzocyclic azides in good to excellent yields. Notable examples are **9a** and **9b**, which cannot be afforded by conventional enamide synthesis by employing carbonyl substrates and/or nucleophilic reagents.

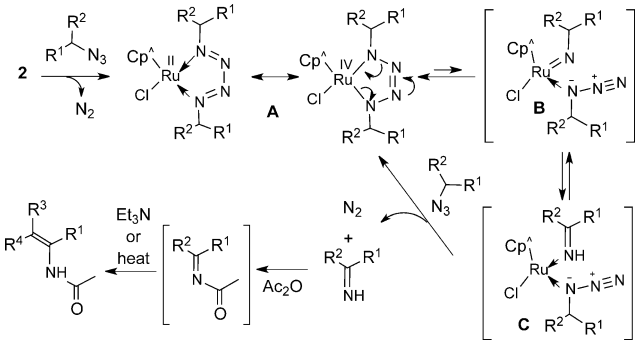
Interestingly, diruthenium complex **2** was first reported by Severin's group,[23] and the formation of ruthenium tetrazene complex **12** was also reported by the group in the reaction of

benzyl azide with **2**.[18] We observed the formation of a diastereomeric mixture of analogous tetrazene complexes **11** in the reaction of **2** with **7a** (Scheme 3). In fact, **11** acted as the catalyst for the conversion of **7a** into N–H ketimine **13**, which was characterized by ^{1}H NMR spectroscopy and converted into *N*-(1-phenylvinyl)acetamide (**8a**) in quantitative yield in a subsequent reaction with acetic anhydride.[14] However, **11** was intact under conditions involving heating at 70 °C in the presence of acetic anhydride. In contrast, in the presence of triethylamine at 70 °C **11** decomposed into a complex mixture, in which ketimine **13** was not observed.[24]



Scheme 3. Formation of Ru–tetrazene complexes and their activities.

On the basis of the results in Scheme 3, we propose a pathway involving ruthenium tetrazene complex **A** as the key intermediate for the formation of enamides (Scheme 4). Tetrazene complex **A** would be in equilibrium with less-stable intermediates **B** and **C**. By tautomerization, **B** is converted into **C** having an N–H imine ligand. The N–H imine is liberated from intermediate **C** in the presence of an external azide substrate. Then, acetic anhydride reacts with the in situ generated N–H imine to form an *N*-acetyl imine intermediate, which isomerizes to the corresponding enamide with the aid of triethylamine or by heating.[14]



Scheme 4. A plausible reaction pathway for the formation of enamides.

In conclusion, we discovered unprecedented catalytic activity of Severin's diruthenium complex ([Cp^RuCl$_2$]$_2$: Cp^ = η^5-1-methoxy-2,4-di-*tert*-butyl-3-neopentylcyclopentadienyl) in ionic liquids for the synthesis of enamides from primary azides and from secondary azides. The one-step synthetic process is much more convenient than any other known method, is highly efficient, and provides a wide range of enamides containing various functional groups. A large-scale reaction was demonstrated in nonflammable ionic liquid to diminish safety concerns associated with the use of organic azides as substrates.[25]

Experimental Section

General procedure

A flame-dried J-Young flask filled with argon gas was charged with ruthenium catalyst **2** (6.3 mg, 0.10 mol%), dried and degassed [bmim]Cl (5.0 mL), **7a** (1.0 g, 7.0 mmol), Et$_3$N (2.0 μL, 0.20 mol%), and Ac$_2$O (790 μL, 1.2 equiv.). The mixture was stirred at 70 °C for 24 h and was then extracted with dichloromethane (15 mL × 3). The organic layer was dried with anhydrous sodium sulfate, concentrated, and purified by column chromatography to give *N*-(1-phenylvinyl)acetamide (1.0 g, 91%).

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Keywords: azides · enamides · imines · ionic liquids · ruthenium

[1] L. Yet, *Chem. Rev.* **2003**, *103*, 4283 – 4306.
[2] a) D. R. Carbery, *Org. Biomol. Chem.* **2008**, *6*, 3455 – 3460; b) K. Gopalaiah, H. B. Kagan, *Chem. Rev.* **2011**, *111*, 4599 – 4657; c) R. Matsubara, S. Kobayashi, *Acc. Chem. Res.* **2008**, *41*, 292 – 301.
[3] a) Y. Huang, T. Iwama, V. H. Rawal, *J. Am. Chem. Soc.* **2000**, *122*, 7843 – 7844; b) R. J. Huntley, R. L. Funk, *Org. Lett.* **2006**, *8*, 3403 – 3406; c) M. Barbazanges, C. Meyer, J. Cossy, *Org. Lett.* **2007**, *9*, 3245 – 3248; d) P. M. Ylioja, A. D. Mosley, C. E. Charlot, D. R. Carbery, *Tetrahedron Lett.* **2008**, *49*, 1111 – 1114.
[4] a) B. Quiclet-Sire, F. Wendeborn, S. Z. Zard, *Chem. Commun.* **2002**, 2214 – 2215; b) T. Taniguchi, K. Iwasaki, M. Uchiyama, O. Tamura, H. Ishibashi, *Org. Lett.* **2005**, *7*, 4389 – 4390; c) T. Taniguchi, G. Tanabe, O. Muraoka, H. Ishibashi, *Org. Lett.* **2008**, *10*, 197 – 199.
[5] a) W. Adam, S. G. Bosio, N. J. Turro, *J. Am. Chem. Soc.* **2002**, *124*, 14004 – 14005; b) J. Sivaguru, H. Saito, T. Poon, T. Omonuwa, R. Franz, S. Jockusch, C. Hooper, Y. Inoue, W. Adam, N. J. Turro, *Org. Lett.* **2005**, *7*, 2089 – 2092.
[6] a) T. J. Harrison, B. O. Patrick, G. R. Dake, *Org. Lett.* **2007**, *9*, 367 – 370; b) J. Mo, L. Xu, J. Xiao, *J. Am. Chem. Soc.* **2005**, *127*, 751 – 760; c) Z. Song, T. Lu, R. P. Hsung, Z. F. Al-Rashid, C. Ko, Y. Tang, *Angew. Chem. Int. Ed.* **2007**, *46*, 4069 – 4072; *Angew. Chem.* **2007**, *119*, 4147 – 4150.
[7] a) X.-B. Jiang, L. Lefort, P. E. Goudriaan, A. H. M. de Vries, P. W. N. M. van Leeuwen, J. G. de Vries, J. N. H. Reek, *Angew. Chem. Int. Ed.* **2006**, *45*, 1223 – 1227; *Angew. Chem.* **2006**, *118*, 1245 – 1249; b) T. C. Nugenta, M. El-Shazly, *Adv. Synth. Catal.* **2010**, *352*, 753 – 819.
[8] a) T. Kuranaga, Y. Sesoko, M. Inoue, *Nat. Prod. Rep.* **2014**, *31*, 514 – 532; b) J. R. Dehli, J. Legros, C. Bolm, *Chem. Commun.* **2005**, 973 – 986.
[9] a) S. Enthaler, B. Hagemann, K. Junge, G. Erre, M. Beller, *Eur. J. Org. Chem.* **2006**, 2912 – 2917; b) C. G. Savarin, G. N. Boice, J. A. Murry, E. Corley, L. DiMichele, D. Hughes, *Org. Lett.* **2006**, *8*, 3903 – 3906.
[10] a) Y. Bolshan, R. A. Batey, *Angew. Chem. Int. Ed.* **2008**, *47*, 2109 – 2112; *Angew. Chem.* **2008**, *120*, 2139 – 2142; b) Y. Bolshan, R. A. Batey, *Tetrahedron* **2010**, *66*, 5283 – 5294; c) R. S. Coleman, P.-H. Liu, *Org. Lett.* **2004**, *6*, 577 – 580; d) L. Jiang, G. E. Job, A. Klapars, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 3667 – 3669; e) A. Klapars, K. R. Campos, C.-y. Chen, R. P. Vola-

nte, *Org. Lett.* **2005**, *7*, 1185 – 1188; f) X. Pan, Q. Cai, D. Ma, *Org. Lett.* **2004**, *6*, 1809 – 1812; g) R. Shen, J. A. Porco, *Org. Lett.* **2000**, *2*, 1333 – 1336; h) D. J. Wallace, K. R. Campos, C. S. Shultz, A. Klapars, D. Zewge, B. R. Crump, B. D. Phenix, J. C. McWilliams, S. Krska, Y. Sun, C.-y. Chen, F. Spindler, *Org. Process Res. Dev.* **2009**, *13*, 84 – 90; i) D. J. Wallace, D. J. Klauber, C.-y. Chen, R. P. Volante, *Org. Lett.* **2003**, *5*, 4749 – 4752.

[11] a) J. Chen, W. Zhang, H. Geng, W. Li, G. Hou, A. Lei, X. Zhang, *Angew. Chem. Int. Ed.* **2009**, *48*, 800 – 802; *Angew. Chem.* **2009**, *121*, 814 – 816; b) J. Genovino, B. Lagu, Y. Wang, B. B. Toure, *Chem. Commun.* **2012**, *48*, 6735 – 6737; c) D. M. Tschaen, L. Abramson, D. Cai, R. Desmond, U.-H. Dolling, L. Frey, S. Karady, Y.-J. Shi, T. R. Verhoeven, *J. Org. Chem.* **1995**, *60*, 4324 – 4330; d) A. Bayer, M. E. Maier, *Tetrahedron* **2004**, *60*, 6665 – 6677.

[12] a) M. J. Burk, G. Casy, N. B. Johnson, *J. Org. Chem.* **1998**, *63*, 6084 – 6085; b) Z.-H. Guan, K. Huang, S. Yu, X. Zhang, *Org. Lett.* **2009**, *11*, 481 – 483; c) Z.-H. Guan, Z.-Y. Zhang, Z.-H. Ren, Y.-Y. Wang, X. Zhang, *J. Org. Chem.* **2011**, *76*, 339 – 341; d) K. Murugan, D.-w. Huang, Y.-T. Chien, S.-T. Liu, *Tetrahedron* **2013**, *69*, 268 – 273; e) W. Tang, A. Capacci, M. Sarvestani, X. Wei, N. K. Yee, C. H. Senanayake, *J. Org. Chem.* **2009**, *74*, 9528 – 9530; f) Q.-S. Wang, J.-H. Xie, W. Li, S.-F. Zhu, L.-X. Wang, Q.-L. Zhou, *Org. Lett.* **2011**, *13*, 3388 – 3391; g) H. Zhao, C. P. Vandenbossche, S. G. Koenig, S. P. Singh, R. P. Bakale, *Org. Lett.* **2008**, *10*, 505 – 507; h) G. Zhu, A. L. Casalnuovo, X. Zhang, *J. Org. Chem.* **1998**, *63*, 8100 – 8101.

[13] J. T. Reeves, Z. Tan, Z. S. Han, G. Li, Y. Zhang, Y. Xu, D. C. Reeves, N. C. Gonnella, S. Ma, H. Lee, B. Z. Lu, C. H. Senanayake, *Angew. Chem. Int. Ed.* **2012**, *51*, 1400 – 1404; *Angew. Chem.* **2012**, *124*, 1429 – 1433.

[14] J. Han, M. Jeon, H. K. Pak, Y. H. Rhee, J. Park, *Adv. Synth. Catal.* **2014**, *356*, 2769 – 2774.

[15] a) J. H. Lee, S. Gupta, W. Jeong, Y. H. Rhee, J. Park, *Angew. Chem. Int. Ed.* **2012**, *51*, 10851 – 10855; *Angew. Chem.* **2012**, *124*, 11009 – 11013; b) M. Jeon, S. Gupta, Y.-W. Im, Y. H. Rhee, J. Park, *Asian J. Org. Chem.* **2015**, *4*, 316 – 319; c) W. Jeong, J. Kim, J. Park, Y. H. Rhee, *Eur. J. Org. Chem.* **2014**, 7577 – 7581; d) S. Gupta, J. Han, Y. Kim, S. W. Lee, Y. H. Rhee, J. Park, *J. Org. Chem.* **2014**, *79*, 9094 – 9103; e) W. Jeong, J. H. Lee, J. Kim, W. J. Lee, J.-H. Seong, J. Park, Y. H. Rhee, *RSC Adv.* **2014**, *4*, 20632 – 20635; f) J. Han, Y. H. Rhee, J. Park, *Bull. Korean Chem. Soc.* **2014**, *35*, 3433 – 3436; g) d.-G. Kim, W. Jeong, W. J. Lee, S. Kang, H. K. Pak, J. Park, Y. H. Rhee, *Adv. Synth. Catal.* **2015**, *357*, 1398 – 1404.

[16] a) G.-M. Chen, H. C. Brown, *J. Am. Chem. Soc.* **2000**, *122*, 4217 – 4218; b) D. R. Boyd, R. Hamilton, N. T. Thompson, M. E. Stubbs, *Tetrahedron Lett.* **1979**, *20*, 3201 – 3204.

[17] Effenberger and co-workers has reported a rhenium-catalyzed reaction of α-azido ketones with acetic anhydride to give the corresponding enamides: F. Effenberger, T. Beisswenger, R. Az, *Chem. Ber.* **1985**, *118*, 4869 – 4876.

[18] J. Risse, R. Scopelliti, K. Severin, *Organometallics* **2011**, *30*, 3412 – 3418.

[19] C.-H. Chou, L.-T. Chu, S.-J. Chiu, C.-F. Lee, Y.-T. She, *Tetrahedron* **2004**, *60*, 6581 – 6584.

[20] a) J. C.-D. Le, B. L. Pagenkopf, *J. Org. Chem.* **2004**, *69*, 4177 – 4180; b) W. Li, J. P. Waldkirch, X. Zhang, *J. Org. Chem.* **2002**, *67*, 7618 – 7623; c) M. Ramanathan, D.-R. Hou, *Tetrahedron Lett.* **2010**, *51*, 6143 – 6145.

[21] P. S. Baran, R. A. Shenvi, *J. Am. Chem. Soc.* **2006**, *128*, 14028 – 14029.

[22] The thermal isomerization of *N*-benzoyl secondary enamides has been reported, see: L. J. Gooßen, K. S. M. Salih, M. Blanchot, *Angew. Chem. Int. Ed.* **2008**, *47*, 8492 – 8495; *Angew. Chem.* **2008**, *120*, 8620 – 8623.

[23] S. Gauthier, E. Solari, B. Dutta, R. Scopelliti, K. Severin, *Chem. Commun.* **2007**, 1837 – 1839.

[24] Triethylamine is effective for the isomerization of *N*-acylimines to the corresponding enamides; see Ref. [14].

[25] ***Caution:*** We have not observed any explosion during our experiments with organic azides. However, organic azides are known to be toxic and can decompose with the input of heat, light, and shock. For the safe handling of azides, see Ref. [77] of the following review: H. C. Kolb, M. G. Finn, K. B. Sharpless, *Angew. Chem. Int. Ed.* **2001**, *40*, 2004 – 2021; *Angew. Chem.* **2001**, *113*, 2056 – 2075.

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