Accepted Article

Title: Reductive C-C Coupling from α,β-Unsaturated Nitriles by Intercepting Keteniminates

Authors: Lillian V. A. Hale, N. Marianne Sikes, and Nathaniel Kolnik Szymczak

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

WILEY-VCH

COMMUNICATION

Reductive C–C Coupling from α,β-Unsaturated Nitriles by Intercepting Keteniminates

Lillian V. A. Hale,[‡] N. Marianne Sikes,[‡] and Nathaniel K. Szymczak*[a]

Abstract: We present a new atom economic strategy to catalytically generate and intercept nitrile anion equivalents using hydrogen transfer catalysis. Addition of *α,β*-unsaturated nitriles to a pincer-based Ru–H complex affords structurally characterized κ-*N*-coordinated keteniminates via selective 1,4-hydride transfer. When generated *in situ* under catalytic hydrogenation conditions, electrophilic addition to the keteniminate was achieved using anhydrides to afford α-cyanoacetates in high yields. This work represents a new application of hydrogen transfer catalysis for selective 1,4 addition to *α,β*-unsaturated nitriles.
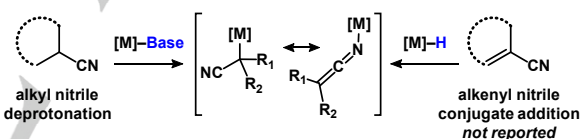
Nitrile anions are a diverse class of synthetic intermediates that provide access to highly functionalized products through nucleophilic addition and substitution reactions.[1] Analogous to enolates, nitrile anions are ambident nucleophiles that can react either as carbanions to provide *α*-functionalized cyano products,[1b-d] or as keteniminates to provide neutral ketenimines.[1d;2] Each product class has further synthetic utility as building blocks for natural products and pharmaceuticals; while *α*-cyano groups are easily derivatized, ketenimines further undergo nucleophilic, electrophilic, and/or cyclization reactions. To access the diverse chemical space of these nitrogen containing compounds, new methods to generate and control the reactivity of nitrile anions are highly desirable.

The synthetic utility of nitrile anions is hindered by a lack of catalytic strategies available to generate them *in situ* from simple pro-nucleophiles.[1b;1c;3] Alkyl nitriles are currently the major precursors to *C*- or *N*-metalated nitriles used in catalytic transformations (Scheme 1a, left).[1c] Base-assisted deprotonation of alkyl nitriles with transition-metal catalysts has been successfully applied in a number of α-functionalization reactions; however, significant challenges remain. Methods that deliver products with all-carbon quaternary centers and/or occur with high stereoselectivities are rare.[1b;1c;4] These challenges may be addressed by designing new catalytic methods using pro-nucleophiles with distinct modes of activation. α,β-Unsaturated nitriles can generate nitrile anions through conjugate addition (Scheme 1b, right) and are easily accessed from the corresponding ketone, aldehyde, or alkene in a single step.[5]

Lillian V. A. Hale, N, Marianne Sikes and Prof. Nathaniel K. Szymczak
    Department of Chemistry
    University of Michigan
    930 N. University, Ann Arbor, MI 48109
    E-mail: nszym@umich.edu

[‡] These authors contributed equally

Despite the potential for rapid multi-functionalization, this mode of activation is virtually unexplored for catalytic applications.
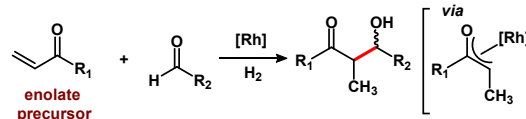
To contextualize the significance of expanding the pool of available pro-nucleophiles, it is useful to compare with well-established enolate chemistry; identifying new catalytic routes to form enolates or silyl enol ethers *in situ* has led to significant advances in selective reduction[6] and reductive C–C bond forming reactions.[7] In particular, Krische and co-workers have developed reductive C–C coupling reactions using hydrogen transfer catalysts and π-unsaturated substrates.[7c;7e] They reported that under catalytic hydrogenation conditions, α,β-unsaturated ketones generate enolates capable of participating in aldol condensations (Scheme 1b).[7b] Our current work parallels these discoveries based on α,β-unsaturated ketones and is the first example of using alkenyl nitriles as pro-nucleophiles for hydrogenative C–C bond forming reactions.

Scheme 1. (a) Formation of nitrile anions with alkyl nitrile or alkenyl nitrile pro-nucleophiles. (b) Hydrogen mediated reductive coupling using π-unsaturated substrates.

Although nitriles may undergo insertion into metal-hydrides to afford imine type products,[8] a second site of unsaturation may promote isomerization to form the resonance stabilized nitrile anion/keteniminate. We previously reported that HRu(bMepi)(PPh₃)₂ (**1,** bMepi = 1,3-bis(6'-methyl-2'-
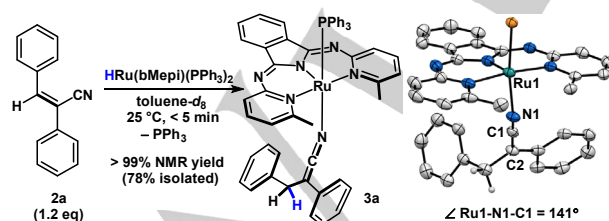
COMMUNICATION

pyridylimino)isoindoline)) is an excellent catalyst for reversible hydrogen transfer reactions of alcohols and amines.[9] For nitrile substrates, hydride insertion readily occurs to form imine coordinated species, and the catalytically active Ru–H can be directly (re)generated from H_2. **1** exhibits unique reactivity with amines and nitriles, and has a high binding affinity for the intermediate imine.[9d;10] We hypothesized that this reactivity would provide an entry point for evaluating hydrogenative C–C coupling with α,β-unsaturated nitriles.

We evaluated the insertion chemistry of α,β-unsaturated nitriles to Ru–H through stoichiometric addition of α-phenylcinnamonitrile (**2a**) to **1** (Scheme 2). When **2a** (1.2 equiv) was added to a toluene-d_8 solution of **1** at room temperature, quantitative conversion to a new species occurred within 5 minutes. ^{31}P NMR spectroscopy confirmed the disappearance of **1** (51 ppm), concomitant with the appearance of free PPh_3 and a new resonance at 39 ppm. **1** was also absent in the ^{1}H NMR spectrum, with no detectable H_2 or hydride-containing byproducts, consistent with a hydride insertion reaction. A phase sensitive [1]H–^{13}C correlation experiment (HSQC) revealed the presence of a –CH_2 group ([1]H δ: 3.20; [13]C δ: 34.7), consistent with hydride addition to the least substituted carbon of α-phenylcinnamonitrile (Figure S5).

X-ray diffraction of single crystals unambiguously confirmed the insertion product as the Ru-keteniminate complex **3a**. The *N*-coordinated keteniminate has an elongated C1−N1 bond of 1.190(7) Å and a shortened C1–C2 bond length of 1.369(7) Å. Analysis by IR spectroscopy revealed a bathochromic shift in the C–N stretching frequency between **2a** (v_{CN} = 2218 cm^{-1}) and **3a** (v_{CN} = 2210 cm^{-1}), consistent with C–N bond elongation upon formation of the C2=C1=N1 unit. These bond distances and IR frequencies are consistent with known metal-keteniminate complexes and reflect the electronic delocalization from the partially negative C2 atom into the adjacent C1–N1 group.[11][12][13] A distinct feature of **3a** is the bent Ru–N1–C1 angle (= 141°), which is highly unusual for metalated keteniminates — only four structurally characterized keteniminate complexes exhibit M–N–C1 angles <145°.[14],[13;15] Moreover, all reported κ-*N*-Ru-keteniminate complexes exhibit nearly linear coordination (Ru–N1–C1 Avg. 173°).[16] In addition to a *base-free* route to form a keteniminate, the unique binding mode to Ru offers a new framework to develop subsequent reactivity.[17]

The linear geometry of substituted keteniminates allow for facile electrophilic additions to the C2 site, resulting in products with new all-carbon quaternary centers. Highly substituted carbons are desirable motifs for drug design and multi-step syntheses.[18] When the electrophile is a carbonyl or acetate group, the resulting α-cyano compounds can be modified at either functional group to provide pharmaceutically relevant structural cores.[19] The most common entry point into α-cyano carbonyl products are through lithiated alkyl nitriles; however, in most cases, stoichiometric addition of lithium diisopropylamide (LDA) or *n*-BuLi is required to unmask the nucleophilic carbon.[4a;20] Silyl ketenimines are precursors to quaternary α-cyano carbonyl groups; however, stoichiometric base is also required.[2f] Interception of Ru-keteniminates with a carbonyl electrophile under hydrgonative reductive coupling conditions could provide α-functionalized cyano compounds while avoiding stoichiometric waste (eq 1).

The addition of carbonyl electrophiles to α,β-unsaturated nitriles in the presence of H_2 presents a key challenge: both C=C and C≡N groups are susceptible to hydrogenation using **1**. Prior to evaluating reductive coupling with **2a**, we interrogated hydrogenation reactivity using H_2 (100 psig) and **1** (1 mol %) (Table 1, entry 1). Complete hydrogenation of **2a** (0.25 mmol) to amine **6a** occurred at 80 °C.[21] Reductive C–C coupling was evaluated using anhydrides based on the precedent for their electrophilic addition to α-cyano carbanions.[2f;22] When di-*tert*-butyl dicarbonate (Boc$_2$O, 1 equiv) was added to the hydrogenation reaction above under analogous conditions (80 °C), acylation of **2a** occurred to provide **4a** in 29% yield and the remaining mixture (71%) was composed of hydrogenation products **5a** and **6a** (entry 2). Hydrogenative acylation was promoted with the addition of base, where 10 mol % LiO^{t}Bu at 80 °C increased the selectivity for **4a** over hydrogenation products (53:47; entry 3). Further optimization revealed that a higher temperature (100 °C), catalyst loading (2 mol % **1**) and concentration of Boc$_2$O (4 equiv) improved acylation selectivity, affording **4a** in 70% chemical yield (entry 4).

Scheme 2. Formation of Ru-keteniminate **3a** via selective 1,4-hydride transfer. The solid-state structure is displayed with 50% probability ellipsoids. PPh$_3$ phenyl groups and hydrogen atoms, except for the –CH$_2$ group, are omitted for clarity.

WILEY-VCH

COMMUNICATION

Table 1. Hydrogenative acylation of **2a** with **1**. Conversion and product ratios were determined by NMR analysis with PhSi(CH$_3$)$_3$ as an internal standard.
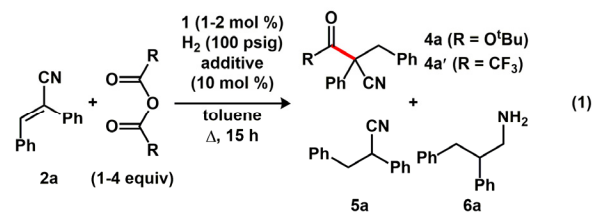

Entry	Temp (°C)	Additive (10 mol %)	Anhydride	% conv	4:5+6
1[a]	80	None	None	>99	0:99
2[b]	80	None	Boc$_2$O	>99	29:71
3[b]	80	LiO^{t}Bu	Boc$_2$O	>99	53:47
4[c]	100	LiO^{t}Bu	Boc$_2$O	>99	70:30
5[c]	100	None	(CF$_3$CO)$_2$O	>99	93:7
6[c]	100	DBU	Boc$_2$O	>99	95:5
7	100	DBU	Ac$_2$O	>99	89:11
8	100	DBU	(C$_6$H$_5$CO)$_2$O	>99	92:8

[a] reaction conditions: **1** (1 mol %) [b] reaction conditions: **1** (2 mol %), Boc$_2$O (2 equiv). [c] reaction conditions: **1** (2 mol %), Boc$_2$O or (CF$_3$CO)$_2$O (4 equiv)

The improved selectivity toward acylation with the addition of LiO^{t}Bu may be due to 1) base-assisted H$_2$ heterolysis, or 2) electrophilic activation of Boc$_2$O by Li$^+$. To determine whether a more activated electrophile further improves the reaction selectivity, we evaluated trifluoroacetic anhydride (CF$_3$CO)$_2$O in place of Boc$_2$O. Under base-free conditions, (CF$_3$CO)$_2$O provided excellent selectivity for the acylated product **4a′** (93: 7, entry 5). Anhydride reagents with decreased reactivity (such as Boc$_2$O) may be further activated with an appropriate nucleophile to promote hydrogenative acylation. We previously identified 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a compatible base under hydrogenation conditions with **1**.[23] When DBU was used in place of LiO^{t}Bu to activate Boc$_2$O, the selectivity for **4a** dramatically improved (95:5, entry 6). These data indicate that the electrophilicity of the acylating agent influences reaction selectivity. Finally, the reductive acylation reaction is general to several representative anhydride reagents and, in addition to Boc$_2$O and (CF$_3$CO)$_2$O, we observed high yields using both acetic anhydride (89%, entry 7) and benzoic anhydride (92%, entry 8).[24]

To assess the reaction scope and functional group compatibility, we examined α,β-unsaturated nitriles **2b-2h** with varying aryl and alkyl substitution (Scheme 3). Under optimized conditions with DBU and Boc$_2$O, diaryl α-cyanoacetates **4a-4e** were obtained in high isolated yields ranging from 78-95%. Alkyl substitution was also tolerated, although higher temperatures (150 °C) were required to obtain **4f** (84%) and **4g** (79%) from monoalkyl substituted alkenyl nitriles **2f** (R$_1$ = H, R$_2$ = C$_6$H$_6$) and

2g (R$_1$ = H, R$_2$ = CH$_3$) using DBU and (C$_6$H$_5$CO)$_2$O. In contrast, di-substituted 2,3-dimethylacrylonitrile (**2h**, R$_1$ = R$_2$ = CH$_3$) was reactive toward acylation with (C$_6$H$_5$CO)$_2$O at 100 °C to provide **4h** (81%).
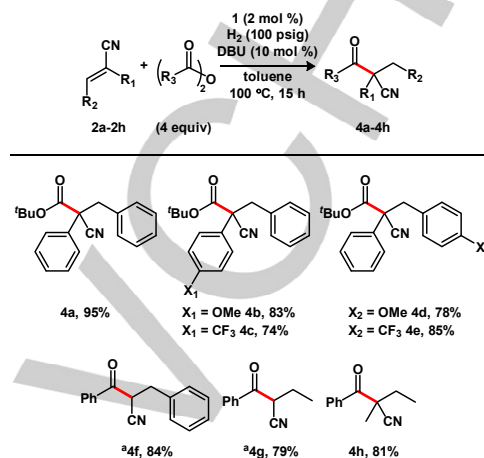
Scheme 3. Synthesis of α-cyanoacetates **4a-4h** with Boc$_2$O or ((C$_6$H$_5$CO)$_2$O), DBU and **1**. Isolated yields following chromatography are reported. [a]Reaction performed at 150 °C in mesitylene.

Finally, we examined the functional group compatibility of the hydrogenative acylation reaction using **1** in the presence of several common functional groups (eq 2, Table 2).[25] Using **2e** and Boc$_2$O, the NMR yield of **4e** was assessed under standard conditions in the presence of potentially reactive additives. Notably, most additives tested did not decrease the yield of **4e** (entries 2-6). One limitation, however, was the incompatibility with hydrogen acceptors such as 2-vinylnaphthalene (entry 7), consistent with competitive hydrogenation by **1**.
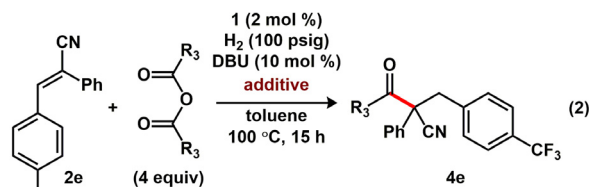

Table 2. Compatibility screening for hydrogenative acylation of **2e** in the presence of additives (1 equiv) containing common functional groups. R$_3$ = O^{t}Bu. Yields were determined by NMR spectroscopy using PhSi(CH$_3$)$_3$ as an internal standard.

Entry	Additive (1 eq)	% conv	% yield
1	None	>99	86
2	N-benzylpyrrole	>99	88
3	2,4,6-collidine	>99	88
4	methyl benzoate	>99	86

COMMUNICATION

5	N-methyl-N-phenylacetamide	>99	87
6	chlorobenzene	>99	86
7	2-vinylnapthalene	57	0

Because saturated nitriles are products under hydrogenation conditions with **1** and α,β-unsaturated nitriles, a feasible pathway to α-cyanoacetate products may first involve C=C hydrogenation followed by deprotonation of the acidic α-C–H bond (by base or **1**) prior to acylation. To evaluate this possibility, we subjected saturated nitrile **5a** to our reaction conditions (Scheme 4). No **4a** was formed as assessed by NMR spectroscopy (see Figures S54-56). This suggests that **5a** does not undergo a base-assisted acylation. We attribute this result to competitive activation of the Boc$_2$O by DBU compared to deprotonation.[26] We also found that stoichiometric reactions between **3a** and Boc$_2$O quantitatively affords **4a**, and that **3a** is a competent pre-catalyst. Under analogous conditions, **3a** provided identical yields of **4a** compared to reactions employing **1**, consistent with the intermediacy of **3a** during catalysis. Collectively, these results suggest that **1** provides a unique entry point to nitrile anions for catalysis, which is distinct from the previously reported deprotonation pathways of alkyl nitriles. Selective 1,4-hydride addition to α,β-unsaturated nitriles is a key step for generating catalytically competent keteniminate intermediates for hydrogenative C–C coupling reactions.
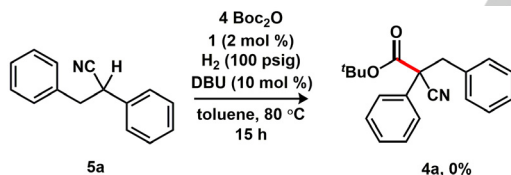
Scheme 4. Acylation of **5a** does not proceed under reductive C–C coupling conditions with **1** and DBU.

This work has introduced a new strategy to use catalytic hydrogen mediated reductive coupling to generate and intercept nitrile nucleophiles. Hydride transfer to *α,β*-unsaturated nitriles from **1** affords Ru-keteniminates that can be converted to α-cyanoacetate products under a H$_2$ atmosphere using catalytic DBU and **1**. Hydrogenative acylation enables the use of *α,β*-unsaturated nitriles as a new substrate class to access products containing all-carbon quaternary centers. Mechanistically distinct modes of nitrile activation are needed to discover new reactivity that parallels their oxygen containing counterparts. We predict that the diverse reactivity available to keteniminates and nitrile carbanions may be accessible following H$^-$ insertion by **1** to *α,β*-unsaturated nitriles. Current work is focused on exploring the scope in substrate and electrophile, as well as enantioselective acylation protocols.

[1] (a) M. S. Singh, *Reactive intermediates in organic chemistry: structure, mechanism, and reactions*, Wiley-VCH, Weinheim, Germany, **2014**; (b) L. Rosa, P. Claudio, *Angew. Chem. Int. Ed.* **2015**, *54*, 13170-13184; (c) A. C. Bissember, M. G. Gardiner, T. S. Wierenga, *J. Organomet. Chem.* **2018**, *869*, 213-226; (d) X. Yang, F. F. Fleming, *Acc. Chem. Res.* **2017**, *50*, 2556-2568; (e) S. Gronert, in *Reactive Intermediate Chemistry* (Eds.: R. A. Moss, M. S. Platz, J. Maitland Jones), John Wiley & Sons, Inc, Hoboken, New Jersey, **2004**, pp. 69-119; (f) Z. Rappoport, Editor, *Chemistry of Cyano-Group (Chemistry of Functional Group)*, Interscience, **1970**.

[2] (a) D. S. Watt, *Synth. Commun.* **1974**, *4*, 127-131; (b) G. R. Krow, *Angew. Chem. Int. Ed.* **1971**, *10*, 435-449; (c) P. Lu, Y. Wang, *Chem. Soc. Rev.* **2012**, *41*, 5687-5705; (d) A. D. Allen, T. T. Tidwell, *Chem. Rev.* **2013**, *113*, 7287-7342; (e) S. E. Denmark, T. W. Wilson, *Angew. Chem. Int. Ed.* **2012**, *51*, 9980-9992; (f) A. H. Mermerian, G. C. Fu, *Angew. Chem. Int. Ed.* **2005**, *44*, 949-952.

[3] X.-Q. Chu, D. Ge, Z.-L. Shen, T.-P. Loh, *ACS Catal.* **2018**, *8*, 258-271.

[4] (a) A. Goto, K. Endo, Y. Ukai, S. Irle, S. Saito, *Chem. Commun.* **2008**, 2212-2214; (b) A. Goto, H. Naka, R. Noyori, S. Saito, *Chem. Asian J.* **2011**, *6*, 1740-1743; (c) D. Sureshkumar, V. Ganesh, N. Kumagai, M. Shibasaki, *Chem. Eur. J.* **2014**, *20*, 15723-15726; (d) S. Chakraborty, Y. J. Patel, J. A. Krause, H. Guan, *Angew. Chem. Int. Ed.* **2013**, *52*, 7523-7526.

[5] (a) B. A. D'Sa, P. Kisanga, J. G. Verkade, *J. Org. Chem.* **1998**, *63*, 3961-3967; (b) D.-W. Gao, E. V. Vinogradova, S. K. Nimmagadda, J. M. Medina, Y. Xiao, R. M. Suciu, B. F. Cravatt, K. M. Engle, *J. Am. Chem. Soc.* **2018**, *140*, 8069-8073.

[6] Y. Zhou, J. S. Bandar, R. Y. Liu, S. L. Buchwald, *J. Am. Chem. Soc.* **2018**, *140*, 606-609.

[7] (a) R. R. Huddleston, M. J. Krische, *Org. Lett.* **2003**, *5*, 1143-1146; (b) H.-Y. Jang, R. R. Huddleston, M. J. Krische, *J. Am. Chem. Soc.* **2002**, *124*, 15156-15157; (c) A. Hassan, M. J. Krische, *Org. Process Res. Dev.* **2011**, *15*, 1236-1242; (d) R. R. Huddleston, M. J. Krische, *Synlett* **2003**, *2003*, 0012-0021; (e)M.-Y. Ngai, J.-R. Kong, M. J. Krische, *J. Org. Chem.* **2007**, *72*, 1063-1072; (f) C. Bee, S. B. Han, A. Hassan, H. Iida, M. J. Krische, *J. Am. Chem. Soc.* **2008**, *130*, 2746-2747; (g) C.-K. Jung, M. J. Krische, *J. Am. Chem. Soc.* **2006**, *128*, 17051-17056.

[8] R. Reguillo, M. Grellier, N. Vautravers, L. Vendier, S. Sabo-Etienne, *J. Am. Chem. Soc.* **2010**, *132*, 7854-7855.

[9] (a) K.-N. T. Tseng, J. W. Kampf, N. K. Szymczak, *Organometallics* **2013**, *32*, 2046-2049; (b) K.-N. T. Tseng, A. M. Rizzi, N. K. Szymczak, *J. Am. Chem. Soc.* **2013**, *135*, 16352-16355; (c) K.-N. T. Tseng, S. Lin, J. W. Kampf, N. K. Szymczak, *Chem. Commun.* **2016**, *52*, 2901-2904; (d) L. V. A. Hale, N. K. Szymczak, *J. Am. Chem. Soc.* **2016**, *138*, 13489-13492; (e) K.-N. T. Tseng, J. W. Kampf, N. K. Szymczak, *ACS Catal.* **2015**, *5*, 5468-5485.

[10] L. V. A. Hale, T. Malakar, K.-N. T. Tseng, P. M. Zimmerman, A. Paul, N. K. Szymczak, *ACS Catal.* **2016**, *6*, 4799-4813.

[11] (a) Perst, H. in *Category 3, Compounds with Four and Three Carbon Heteroatom Bonds; Three Carbon—Heteroatom Bonds: Ketenes and Derivatives, Vol. 23*, 1st. Edition, (Ed.: R. L. Danheiser) Georg Thieme Verlag, Stuttgart, **2006**; (b) T. Naota, A. Tannna, S.-I. Murahashi, *J. Am. Chem. Soc.* **2000**, *122*, 2960-2961.

COMMUNICATION

[12] Hydride insertion to afford Ru-coordinated keteniminates with similar spectroscopic features was general for other α-phenyl substituted alkenyl nitriles. For instance, varying the para substituent of either phenyl group with OMe or CF_3 provided Ru-keteniminate products with similar IR stretches and ^{1}H, ^{31}P, and ^{13}C resonances to **3a** (See SI, section III).

[13] L. Becker, M. Haehnel, A. Spannenberg, P. Arndt, U. Rosenthal, *Chem. Eur. J.* **2015**, *21*, 3242-3248.

[14] Cambridge Structural Database, version 5.38, August 2018

[15] (a) D. A. Culkin, J. F. Hartwig, *J. Am. Chem. Soc.* **2002**, *124*, 9330-9331; (b) K. Chainok, S. M. Neville, C. M. Forsyth, W. J. Gee, K. S. Murray, S. R. Batten, *CrystEngComm* **2012**, *14*, 3717-3726; (c) W. X. Jing-Min Shi, Su-Qiao Lu, Chang-Ju Wu, Jie-Chao Ge, Zhi-De Zhang, *Chinese J. Struc. Chem.* **2002**, 640-642.

[16] For comparison, N-aryl and N-alkyl ketenimines typically have C–N–R (R = Ar or alkyl) bond angles between 117-129°. See reference 11a

[17] No reactivity studies have been reported based on known discrete Ru-ketenimine complexes. **3a** was investigated using density functional theory. See SI for the optimized structure, NBO analysis, and depiction of the HOMO for **3a** (Figure S11-S12).

[18] S.F Martin, *Tetrahedron.* **1980**, *36*, 419-460.

[19] (a) H. U. Blaser, F. Spindler, M. Studer, *Appl. Catal., A* **2001**, *221*, 119; (b) S. Sugimura, T. Osawa, S. Nakagawa, T. Harada, A. Tai, *Stud. Surf. Sci. Catal.* **1996**, *101*, 231; (c) S. Nakagawa, T. Sugimura, A. Tai, *Chem. Lett.* **1997**, 859.

[20] B. R. Pitta, O. W. Steward, F. F. Fleming, *J. Org. Chem.* **2018**, *83*, 2753-2762.

[21] See SI Section IV for further details about hydrogenation reactivity

[22] P. Hudhomme, *Synlett* **2010**, *2010*, 1331-1332.

[23] J. B. Geri, J. L. Ciatti, N. K. Szymczak, *Chem. Commun.* **2018**, *54*, 7790-7793.

[24] Ketones, amides, aldehydes, benzyl bromide, benzyl chloride, and bromohexane failed to give any acylated product.

[25] K. D. Collins, F. Glorius, *Nature Chemistry* **2013**, *5*, 597.

[26] W.C Shieh, S. Dell, O. Repič. *J. Org. Chem.* **2002**, *67*, 2188-2191.

WILEY-VCH

COMMUNICATION

Entry for the Table of Contents

COMMUNICATION
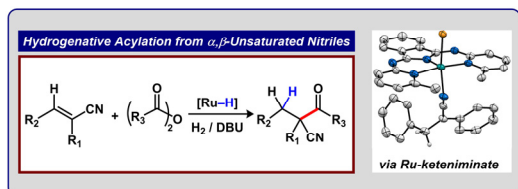
We present a new application of hydrogen transfer catalysis to intercept keteniminate intermediates from *α,β*-unsaturated nitriles for a net hydrogenative acylation reaction.

Lilian V. A. Hale, N. Marianne Sikes, and Nathaniel K. Szymczak*

Page No. – Page No.

Reductive C–C Coupling from α,β-Unsaturated Nitriles by Intercepting Keteniminates