

View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: C. Chen, Y. Huang, Z. Zhang, X. Dong and X. Zhang, *Chem. Commun.*, 2017, DOI: 10.1039/C7CC01228D.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/chemcomm

Journal Name



Cobalt-Catalyzed (Z)-Selective Semihydrogenation of Alkynes with Molecular Hydrogen

Received 00th January 20xx, Accepted 00th January 20xx

Caiyou Chen,^a Yi Huang,^a Zongpeng Zhang,^a Xiu-Qin Dong,^{*a} and Xumu Zhang^{*b,a}

catalyst.

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 29 March 2017. Downloaded by Fudan University on 29/03/2017 16:10:24

A cobalt-catalyzed highly (Z)-selective semihydrogenation of alkynes using molecular H₂ was developed using commercially available and cheap cobalt precursors. A variety of (Z)-alkenes were obtained in moderate to excellent selectivities [(Z)alkene/(E)-alkene/alkane ratio up to > 99:1:1)] and it was found that the readily available ethylenediamine ligand is crucial in determining the selectivity.

(Z)-Olefinic structures are widely found in many biologically and pharmaceutically active molecules and are manufactured in several fine and bulk chemical processes.^[1] Convenient methods have been developed for the preparation of (Z)alkenes, which include Wittig^[2], Peterson^[3] and Julia olefin metathesis^[5], olefination^[4], and cross-coupling reactions^[6]. However, selective semihydrogenation of readily available alkynes is the simplest and most straightforward approach for the preparation of (Z)-alkenes. To date, many transition-metal based catalysts have been intensively studied for the (Z)-selective semihydrogenation of alkynes, which include Pd,^[7] Rh,^[8] Au,^[9] Ru,^[10] Ni,^[11] Cu,^[12] V,^[13] Cr,^[14] Nb, ^[15] and even Fe ^[16] (Scheme 1a). However, the Lindlar's catalyst is still the common choice for the (Z)-selective semihydrogenation of alkynes since it is practical, general, and commercially available.^[1c,7a] Despite these superiorities, the Lindlar's catalyst has significant drawbacks, which suffers from isomerization of the (Z)-alkene to the (E)-alkene, shift of the double bond, over-reduction to the alkane, and poor stability.^[17] Moreover, the lead species and quinoline are often required which lead to harmful wastes and heavy metal residual in the products (Scheme 1b). $^{\left[17\right] }$ As a result, efforts into developing new and more efficient catalysts are highly desirable.





Scheme 1. Previous developed catalysts and drawbacks of Lindlar's

With regard to the development of new catalysts, it is of great value to use the nonprecious base metals to replace the noble metals. The base metal such as cobalt is elegant for its economic and environmental advantages, and more importantly, for its unusual reactivities and selectivities in hydrogenation reactions.^[18] However, few cobalt-based catalysts have been developed for the (Z)-selective semihydrogenation of alkynes. Very recently, Liu et al. developed a promising cobalt catalyst appended with pincer ligands and excellent selectivities were obtained in the semihydrogenation of a variety of alkynes.^[19] Importantly, the (Z) or (E) selectivity can be controlled by the ligands (Scheme 2a). However, ammonia borane was utilized as the hydrogen source, which is not ideal from the atom economic and environmental point of view. Recently, Fout et al. developed an unique cobalt catalyst using molecular H₂ as the hydrogen source.^[20] However, only the (E)-alkenes can be obtained (Scheme 2b). Regarding to the (Z)-selective cobalt-catalyzed semihydrogenation with molecular hydrogen, very recently Beller et al also reported a heterogeneous cobalt catalyst. However, the (Z)-selectivities achieved were only moderate.^[21] Herein, we report a cobalt-catalyzed highly (Z)-selective semihydrogenation of alkynes using molecular H₂ as the hydrogen source. Importantly, compared with the previous studies, in which the ligands and catalysts were synthesized in multiple steps, the cobalt catalyst we report herein is very simple and practical, which is generated in situ from the com-

^{a.} College of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei, 430072, P. R. China

^{b.} Department of Chemistry, South University of Science and Technology of China, Shenzhen, Guangdong, 518055, P. R. China.

xumu@whu.edu.cn; xiuqindong@whu.edu.cr

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

COMMUNICATION



Scheme 2. Examples of cobalt-catalyzed semihydrogenation of alkynes.

mercially available and cheap $Co(OAc)_2 \cdot (H_2O)_4$, NaBH₄ and ethylenediamine. Employing this readily available cobalt catalyst, a variety of alkynes with wide functional group tolerance were converted to the (*Z*)-alkenes in moderate to excellent selectivities (Scheme 2c).

The investigation of the semihydrogenation was initiated by using 1,2-diphenylacetylene 1a as the standard substrate. To our delight, 1a was converted to the desired (Z)-1,2diphenylethylene 2a with good selectivity in the presence of the cobalt catalyst generated in situ from Co(OAc)₂·(H₂O)₄, NaBH₄ and ethylenediamine using molecular H₂, although the substrate was not fully converted (Table 1, entry 1). Screening of the cobalt precursor revealed that Co(II) species gave promising results while $Co_2(CO)_8$ didn't show any activity (Entries 2-4). $Co(OAc)_2 \cdot (H_2O)_4$ was selected as the precursor for the slightly higher activity. Screening of the ligands revealed that almost all the substrate was converted to the alkane without ethylenediamine or using 2,2'-bipyridine (Entries 5-6), demonstrating the key role of the ethylenediamine ligand in determining the selectivity. Further screening of the amine revealed that introducing substituents ligands on ethylenediamine gave slightly lower reactivity while the selectivity was not significantly influenced (Entries 7-10). Phosphine ligands were also tried, but relatively lower activity and selectivity were observed (Entries 11-12). It was found that solvent played an important role in the activity of the catalytic system. Changing the solvent from alcohol to THF, CH₂Cl₂ or toluene resulted in almost no activity of the catalyst (Entries 13-15). It was also found that water is helpful to increase the selectivity and much lower selectivity was observed when the reaction was conducted in the absence of water (Entry 16). It is likely that water may act as a weak coordinating ligand to slowdown the isomerization of (Z)alkene to (E)-alkene and the over-reduction. Considering this possibility, the weak coordinating solvent, THF, was added as a co-solvent to further increase the selectivity. To our delight,

	2	
	3	Co(BF ₄) ₂ •(H ₂ O)
es Ar = 1,3,5-trimethylphenyl	4	Co ₂ (CO) ₈
	5	Co(OAc) ₂ ·(H ₂ O)
\rightarrow R^1 R^2 (Z)-selective		Co(OAc) ₂ •(H ₂ O
 Simple and practical catalyst High (Z)-selectivity 	7	Co(OAc) ₂ •(H ₂ O
Wide substrate scope		Co(OAc) ₂ •(H ₂ O
vzed semibydrogenation of	9	Co(OAc) ₂ (H ₂ O
i i i i i i i i i i i i i i i i i i i	10	Co(OAc) ₂ •(H ₂ O)

 Table 1. Screening of the reaction conditions. a
 View Article Online

 DOI: 10.1039/C7CC01228D

$[Co]/NaBH_4$ $\underline{Ligand} = p_{h} + Ph + $							
-	1a H ₂ 1a rt,	(2 bar) 2a 12 h	3a		4a		
Entry	Со	Ligand	Solvent	Conv% ^b	Z/E/Alkane ^c		
1	Co(OAc) ₂ •(H ₂ O) ₄	$H_2N^{NH_2}$	EtOH/H ₂ O	86	21: 1 : 2		
2	CoCl ₂	$H_2N^{NH_2}$	EtOH/H ₂ O	52	21 : 1 : 1		
3	$Co(BF_4)_2 \cdot (H_2O)_6$	$_{H_2N} \checkmark ^{NH_2}$	EtOH/H ₂ O	78	20 : 1 : 2		
4	Co ₂ (CO) ₈	$_{H_2N} \checkmark ^{NH_2}$	EtOH/H ₂ O	0	nd		
5	$Co(OAc)_2 \cdot (H_2O)_4$	no	EtOH/H ₂ O	>99	0: 0 : > 99		
6	Co(OAc) ₂ •(H ₂ O) ₄	2,2'-bipyridine	EtOH/H ₂ O	>99	0: 0 : > 99		
7	Co(OAc) ₂ •(H ₂ O) ₄		EtOH/H ₂ O	78	22 : 1 : 3		
8	Co(OAc) ₂ •(H ₂ O) ₄	IMeN NMel	H EtOH/H ₂ O	41	21: 1 : 2		
9	Co(OAc) ₂ •(H ₂ O) ₄	H ₂ N ^{NMe} 2	EtOH/H ₂ O	54	25: 1 : 3		
10	Co(OAc) ₂ •(H ₂ O) ₄	Me ₂ N ^{NMe} 2	EtOH/H ₂ O	43	19 :1 : 3		
11 ^d	$Co(OAc)_2 (H_2O)_4$	PPh ₃	EtOH/H ₂ O	46	19 :1 : 3		
12 ^e	Co(OAc) ₂ •(H ₂ O) ₄	DPPP	EtOH/H ₂ O	16	17: 1 : 1		
13	$Co(OAc)_2$ $(H_2O)_4$	$_{H_2N} \checkmark ^{NH_2}$	THF/H ₂ O	4	10 : 1 : 0.3		
14	Co(OAc) ₂ •(H ₂ O) ₄	$H_2N^{NH_2}$	CH_2CI_2	trace	nd		
15	Co(OAc) ₂ •(H ₂ O) ₄	$_{\text{H}_2\text{N}} \swarrow^{\text{NH}_2}$	Toluene	8	11 : 1 : 1		
16	Co(OAc) ₂ •(H ₂ O) ₄	$_{\text{H}_2\text{N}} \swarrow^{\text{NH}_2}$	EtOH	93	12 : 1 : 2		
17 ^f	Co(OAc) ₂ •(H ₂ O) ₄	$_{\text{H}_2\text{N}} \swarrow^{\text{NH}_2}$	EtOH/THF/H ₂ O	78	25 : 1 : 2		
18 ^{f,g}	Co(OAc) ₂ •(H ₂ O) ₄	$_{\text{H}_2\text{N}} \swarrow^{\text{NH}_2}$	EtOH/THF/H ₂ O	88	23 : 1 : 2		
19 ^{f,g,ł}	[∩] Co(OAc) ₂ ·(H ₂ O) ₄	$_{H_2N} \checkmark ^{NH_2}$	EtOH/THF/H ₂ O	> 99	21 : 1 : 3		
20 ⁱ	Co(OAc) ₂ •(H ₂ O) ₄	$H_2N^{NH_2}$	EtOH/THF/H ₂ O	22	nd		
21 ^j	Co(OAc) ₂ ·(H ₂ O) ₄	H ₂ N ^{NH₂}	EtOH/THF/H ₂ O	5	nd		

^{*a*} The reaction was conducted in 0.5 mmol scale, solvent/H₂O = 2.0 mL/0.1 mL, Co = 1 mol%, NaBH₄ = 2 mol%, ligand = 8 mol%, H₂ = 2 bar, time = 12 h; ^{*b*} Conversion of the substrate, determined by ¹H NMR; ^{*c*} Determined by ¹H NMR; ^{*d*} PPh₃ = 4 mol%; ^{*c*} DPPP = 1,3-bis(diphenylphosphanyl)propane, 2 mol%; ^{*f*} EtOH:THF:H₂O = 1.0 mL:1.0 mL : 0.1 mL; ^{*g*} time = 24 h; ^{*h*} H₂ = 3 bar; ^{*i*} EtOH:THF:H₂O = 1.0 mL:1.0 mL : 0.1 mL, time = 24 h, H₂ = 3 bar, conducted outside the glovebox; ^{*i*} EtOH:THF:H₂O = 1.0 mL:1.0 mL; using non-degassed solvent.

slightly higher selectivity was observed while the activity was not significantly influenced (Entry 17). And importantly, the use of THF as a co-solvent addressed the problem of the low solubility of many substrates in alcohol. In order to ensure full conversion of the substrate, reaction time and H₂ pressure were increased. To our delight, the substrate was fully converted while the selectivity remained high (Entries 18-19). It should be noted that the catalytic system is sensitive to air. Conducting the reaction outside the golve box or using non-degassed solvent resulted in low conversions (Entries 20-21).

With the optimized reaction conditions established, a series of substrates was smoothly hydrogenated to the Z-alkenes with moderate to excellent selectivities (11:1:1~>99:1:1 Z/E/A

Journal Name

Published on 29 March 2017. Downloaded by Fudan University on 29/03/2017 16:10:24

Journal Name

COMMUNICATION

Table 2. Substrate scope of the cobalt-catalyzedsemihydrogenation a



^{*a*} The reaction was conducted in 0.5 mmol scale, EtOH/THF/H₂O = 1.0 mL/1.0 mL/0.1 mL, ethylenediamine/NaBH₄/Co = 8:2:1, H₂ = 3 bar, conversion of the substrate and the Z/E/A ratio were determined by ¹H NMR or GC analysis, *Z*/*E*/A is the ratio of (*Z*)-alkene/(*E*)-alkene/alkane, S/C is the substrate/catalyst ratio.

ratio, 77%~98% Z-alkene yield). Good selectivities were obtained in the semihydrogenation of non-functionalized diaryl-substituted alkynes (Table 2, 2a-2d), although a slightly lower selectivity was observed when the electron-withdrawing fluorine atom was introduced on the para position (2d). However, in the semihydrogenation of the alkyne attached with aryl and alkyl substituents, the selectivity was relatively the selectivity lower (2e). Nevertheless. of the semihydrogenation of the dialkyl-substituted alkyne still remained high (2f). Substrate scope was then investigated in the semihydrogenation of a variety of functionalized alkynes. A series of (Z)-3-substituted protected allylic amines were obtained with very high selectivities, regardless of whether the substituents on the aromatic ring is electron-donating or electron-withdrawing (2g-2l). A number of (Z)-3-substituted allylic alcohols was also smoothly obtained with high



Scheme 3. Gram scale semihydrogenation of the functionalized alkynes 1g and 1m; except for the catalyst loading, the reaction conditions are the same as described in Table 2.



Scheme 4. Measurement of the reaction rates.

selectivity (2m-2v). Especially, when the weak coordinating methoxy group was introduced, excellent selectivities were observed (2n-2p). Moreover, the reaction also tolerated functional groups such as acetyl (2s) and cyano (2t). It is noteworthy that, compared with the nonfunctionalized alkynes, the selectivities observed in the semihydrogenation of the functionalized alkynes are distinctly higher. This is probably because that the amine and alcohol moieties in the functionalized alkynes could act as weak coordinating groups to slowdown the isomerization and over-reduction. However, if the coordinating ability of the functional group (such as dimethyl amine or thiophene) is too strong, the catalyst could be poisoned, which afforded low conversions (2w-2x).

In order to further demonstrate the practical utility of the current method, the semihydrogenation of the functionalized substrates **1g** and **1m** was conducted in gram scale. To our delight, the reaction proceeded smoothly to give the desired (*Z*)-product in high yield and selectivity (Scheme 3).

In an effort to reveal the reactivity order of the functionalized and nonfunctionalized alkynes, we measured



Scheme 5. Control experiments using MeOD, D₂O and D₂.

COMMUNICATION

the reaction rate of each substrate separately. As shown in scheme 4, when the reaction was stopped after 4 h with 1 mol% catalyst, 3-phenyl-propargyl alcohol **1m** exhibited the highest rate. To the contrary, the reaction rate of 3-substituted protected propargylamine **1g** was the lowest. It is notable that the reaction rate of 2-butylphenylacetylene **1e** is distinctly higher than that of 1,2-diphenylacetylene **1a**, which is probably due to the electron-richer feature of the former.

Control experiments were also conducted using deuterated methanol and water to determine whether the alcohol solvent and water serve as hydrogen donors. As shown in Scheme 5, no deuterated products were observed when deuterated methanol or water was used as co-solvents (Scheme 5a-5b). This result suggests that alcohol solvent and water do not serve as hydrogen donors. Furthermore, when the reaction was conducted using D₂, for all of the three products (2a', 3a', and 4a'), the deuterium incorporation was higher than 95% (Scheme 5c). As a result, H₂ was considered to be the sole hydrogen source and the transfer hydrogenation mechanism was ruled out.

Conclusions

Published on 29 March 2017. Downloaded by Fudan University on 29/03/2017 16:10:24

In conclusion, a cobalt-catalyzed highly (*Z*)-selective semihydrogenation of alkynes using molecular H_2 was developed. Notably, this reaction system is very practical using commercially available and cheap cobalt precursor and ethylenediamine ligand. A variety of (*Z*)-alkenes were obtained in moderate to excellent reactivities and selectivities. It was found that the ethylenediamine ligand is crucial in determining the selectivity. The reactivity order of each kind of substrate was determined by measuring the reaction rate separately. And control experiments revealed that H_2 was the sole hydrogen source. Further studies are underway to reveal the mechanism of this cobalt-catalyzed semihydrogenation.

This work was supported by the grant from Wuhan University (203273463, 203600400006), the support of the Important Sci-Tech Innovative Project of Hubei Province (2015ACA058), the National Natural Science Foundation of China (Grant No. 21372179, 21432007, 21502145) and Natural Science Foundation of Hubei Province (Grant No. 2016CFB449).

Notes and references

- a) J. Burwell, L. Robert, *Chem. Rev.* 1957, **57**, 895-934; b) E. N. Marvell, T. Li, *Synthesis* 1973, **8**, 487; c) C. Oger, L. Balas, T. Durand, J. Galano, *Chem. Rev.* 2013, **113**, 1313-1350; d) A. M. Kluwer, T. S. Koblenz, T. Jonischkeit, K. Woelk, C. J. Elsevier, *J. Am. Chem. Soc.* 2005, **127**, 15470-15480.
- 2 a) G. Wittig, U. Schöllkopf, *Chem. Ber.* 1954, **87**, 1318-1330; b)
 B. E. Maryanoff, A. B. Reitz, *Chem. Rev.* 1989, **89**, 863-927; c)
 W. S. Wadsworth, W. D. Emmons, *J. Am. Chem. Soc.* 1961, **83**, 1733-1738.
- 3 D. J. Peterson, J. Org. Chem. 1968, 33, 780-784.
- 4 P. R. Blakemore, J. Chem. Soc. 2002, 2563-2585.
- 5 a) B. K. Keitz, K. Endo, P. R. Patel, M. B. Herbert, R. H. Grubbs, J. Am. Chem. Soc. 2012, **134**, 693-699; b) F. Z. Dörwald, In Handbook of Metathesis. Vol. 1; R. H. Grubbs, Ed.; Wiley-VCH Verlag: Hoboken, NJ, 2004; Vol. 43, pp 395-396.

- 6 B. M. Trost, Z. T. Ball, T. Jöge, J. Am. Chem. Soc. 2002, 124 7922-7923. DOI: 10.1039/C7CC01228D
- For representative examples, see: a) H. Lindlar, *Helv. Chim.* Acta 1952, **35**, 446-450; b) B. M. Trost, R. Braslau, *Tetrahedron Lett.* 1989, **30**, 4657-4660; c) L. L. Wei, L. M. Wei,
 W. B. Pan, S. P. Leou, M. J. Wu, *Tetrahedron Lett.* 2003, **44**, 1979-1981; d) M. Crespo-Quesada, F. Cardenas-Lizana, A. Dessimoz, L. KiwiMinsker, *ACS Catal.* 2012, **2**, 1773-1786; e)
 R. M. Drost, T. Bouwens, N. P. van Leest, B. Bruin, C. J. Elsevier, *ACS Catal.* 2014, **4**, 1349-1357; f) J. Zhong, Q. Liu, C.
 Wu, Q. Meng, X. Gao, Z. Li, B. Chen, C. Tunga, L. Wu, *Chem. Commun.*, 2016, **52**, 1800-1803; g) S. Yang, C. Cao, L. Peng, J.
 Zhang, B. Han, W. Song, *Chem. Commun.*, 2016, **52**, 3627-3630; h) T. Mitsudome, T. Urayama, K. Yamazaki, Y. Maehara, J. Yamasaki, K. Gohara, Z. Maeno, T. Mizugaki, K. Jitsukawa, K.
 Kaneda, *ACS Catal.* 2016, **6**, 666-670.
- 8 For representative example, see: R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* 1976, **98**, 2143-2147.
- 9 For representative examples, see: a) L. Shao, X. Huang, D. Teschner, W. Zhang, ACS Catal. 2014, 4, 2369-2373; b) G. Li, R. Jin, J. Am. Chem. Soc. 2014, 136, 11347-11354. c) E. Vasilikogiannaki, I. Titilas, G. Vassilikogiannakis, M. Stratakis, Chem. Commun. 2015, 51, 2384-2387; d) T. Mitsudome, M. Yamamoto, Z. Maeno, T. Mizugaki, K. Jitsukawa, K. Kaneda, J. Am. Chem. Soc. 2015, 137, 13452-11354; e) S. Liang, G. B. Hammond, B. Xu, Chem. Commun., 2016, 52, 6013-6016.
- 10 For representative example, see: M. Niu, Y. Wang, W. Li, J. Jiang, Z. Jin, *Catal. Commun.* 2013, **38**, 77-81.
- 11 For representative examples, see: a) C. A. Brown, V. K. Ahuja, J. Chem. Soc., Chem. Commun. 1973, 15, 553-554; b) J. A. Schreifels, P. C. Maybury, W. E. Swartz, J. Org. Chem., 1981, 46, 1263-1269; c) G. Zhu, X. Lu, J. Org. Chem., 1995, 60, 1087-1089; d) F. Studt, F. Abild-Pedersen, T. Bligaard, R. Z. Sørensen, C. H. Christensen, J. K. Nørskov, Science 2008, 320, 1320-1322; e) E. Richmond, J. Moran, J. Org. Chem. 2015, 80, 6922-6929;
- 12 For representative examples, see: a) K. Semba, T. Fujihara, T. Xu, J. Terao, Y. Tsuji, Adv. Synth. Catal. 2012, **354**, 1542-1550;
 b) N. O. Thiel, J. F. Teichert, Org. Biomol. Chem., 2016, **14**, 10660–10666; c) F. Pape, N. O. Thiel, J. F. Teichert, Chem. Eur. J. 2015, **21**, 15934 15938; d) A. M Whittaker, G. Lalic, Org. Lett., 2013, **15**, 1112–1115.
- For representative example, see: H. S. La Pierre, J. Arnold, F. D. Toste, Angew. Chem., Int. Ed., 2011, 50, 3900-3903.
- 14 For representative example, see: M. Sodeoka, M. Shibasaki, J. Org. Chem. 1985, **50**, 1147-1149.
- 15 For representative examples, see: a) T. L. Gianetti, N. C. Tomson, J. Arnold, R. G. Bergman, J. Am. Chem. Soc. 2011, 133, 14904-14907; b) Y. Satoh, Y. Obora, J. Org. Chem. 2011, 76, 8569–8573.
- 16 For representative examples, see: a) L. Ilies, T. Yoshida, E. Nakamura, J. Am. Chem. Soc., 2012, 134, 16951-16954; b) D. Srimani, Y. Diskin-Posner, Y. Ben-David and D. Milstein, Angew. Chem., Int. Ed., 2013, 52, 14131-14134.
- 17 R. Chinchilla, C. Najera, Chem. Rev., 2014, **114**, 1783-1826.
- 18 a) P. J. Chirik, Acc. Chem. Res. 2015, 48, 1687-1695; b) R. H.
 Morris, Acc. Chem. Res. 2015, 48, 1494-1502. (c) T. Zell, D.
 Milstein, Acc. Chem. Res. 2015, 48, 1979-1994.
- 19 a) S. Fu, N.-Y. Chen, X. Liu, Z. Shao, S.-P. Luo, Q. Liu, J. Am. Chem. Soc. 2016, 138, 8588-8594.
- 20 K. Tokmic, A. R. Fout, J. Am. Chem. Soc. 2016, 138, 13700-13705.
- 21 F. Chen, C. Kreyenschulte, J. Radnik, H. Lund, A.-E. Surkus, K. Junge, M. Beller, ACS Catal. 2017, 7, 1526-1532.

Journal Name