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Noble metal-free upgrading of multi-unsaturated biomass derivatives at room temperature: Silyl species enable reactivity

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Biomass derivatives are a class of oxygen-rich organic compounds, which can be selectively upgraded to various valueadded molecules by partial or complete hydrogenation over metal catalysts. Here, we show that Cs₂CO₃, a low-cost commercial chemical, enables the selective reduction of dicarbonyl compounds including bio-derived carboxides to monohydric esters/amides, hydroxylamines or diols with high yields (82-99%) at room temperature using eco-friendly and equivalent hydrosilane as hydride donor. The *in-situ* formation of silyl ether enables the developed catalytic system to tolerate other unsaturated groups and permits a wide substrate scope with high selectivities. Spectroscopic and computational studies elucidate reaction pathways with an emphasis on the role of endogenous siloxane.

Introduction

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Catalytic hydrogenation of unsaturated carbon-containing bonds (C=C, C=N, C=O) in organic compounds with metal complexes or particles is a prolific approach that is extensively applied in petroleum, pharmaceutical, fine chemical, perfume and flavoring industries ¹. Noble (e.g., Au, Pt, Ru, Rh) and transition (e.g., Fe, Co, Ni, Cu) metals prevail in both heterogeneous and homogeneous catalytic hydrogenation processes as catalysts with favourable activity and selectivity ². The co-use of unique organic/inorganic ligands, suitable acidic species, or additional metallic additives with relatively harsh reaction conditions is a prerequisite to ensure good reactivity in the hydrogenation process, which on the other hand may lead to accelerated catalyst deactivation ³.

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Currently, much attention is being paid to the selective hydrogenation of unsaturated functionalities. For example, partial or complete reduction of oxygenates to alcohols or alkanes 4, regioselective reduction of polyols or polyenes ⁵, and selective hydrogenation of α, β -unsaturated carbonyl compounds ⁶ can be achieved using well-designed metal catalysts. Given the significance of selectivity in reduction reactions, it would be especially attractive to control the hydrogenation capability toward multi-unsaturated functional groups with similar redox potential. As the most abundant organic carbon source derived from photosynthesis, lignocellulosic biomass has been explored as promising renewable feedstock for producing a wide range of platform molecules that can compete with petroleum-based products ⁷. One of the bottlenecks for the efficient upgrade of biomass is the selective hydrogenation of oxygenated species that are rich in downstream derivatives such as sugar, organic acid, aromatic and furanic carbonyl compounds ⁸, especially those concurrently containing two or more different types of carbonyl groups. Levulinic acid (LA) and its esters are a class of biomass-derived dicarbonyl compounds ⁹, which can be selectively hydrogenated to value-added products, especially y-valerolactone (GVL) and 1,4pentanediol (1,4-PD) over metal catalysts ¹⁰. Significant progress has been achieved with metal-mediated biomass valorisation processes in the presence of excessive hydrogen donors along with high pressure and reaction temperature (Table S1), while the development of more benign and cost-effective catalytic systems would be desirable.

In most cases, precious or transition metal species coupled with suitable additives were reported to be efficient catalysts for the hydrogenation reactions ¹¹. Due to significantly enhanced sustainability, alkali carbonates, which are low-cost, pollution-free and obtainable from CO_2 ¹², seem better candidates for the

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hydrogenation reactions. In the present study, we present a sustainable carbonate-based catalytic process (Fig. 1) that is able to selectively hydrogenate dicarbonyl compounds and tolerate other unsaturated moieties by using environmentally benign, cheap, and air-stable hydrosilanes ¹³ as hydride source. The silyl ether species formed *in situ* in the hydrogenation process enable the control of selectivity in the reduction of multi-unsaturated carbonyl compounds that bear aldehyde/ketone, ester/amide, and aromatic/furanic groups.



Fig. 1. Selective hydrogenation of dicarbonyl compounds to hydroxy-ester/amide or diol/hydramine catalysed by alkali carbonates (M2CO3).

Results and discussion

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Controllable hydrogenation of bio-based ethyl levulinate

Initial screening studies were conducted to investigate the selective hydrogenation of ethyl levulinate (EL) to GVL or 1,4-PD over Cs_2CO_3 using triethoxysilane (EtO)₃SiH as reducing agent in the biomassderived solvent 2-methyltetrahydrofuran (MTHF), and the results are collected in Table 1. At room temperature (25 °C) in the presence of Cs_2CO_3 and 1.5 equiv. H⁻, 74% yield of GVL could be achieved from EL in 0.5 h, while the silyl ether **Si-1** (21%) was found to be the dominant byproduct (Table S2, entry 1). After post-treatment with ethanol under stirring at 25 °C for 2 h, the GVL yield increased to 87% by partial consumption of **Si-1** (10% yield; Table S2, entry 2). Upon further increase of the post-treatment temperature to 80 °C, a high GVL yield of 98% was obtained with a TOF value of 39.2 h⁻¹ (Table 1, entry 1), giving tetraethyl orthosilicate [Si(OEt)₄] as the co-product (Figs. S1 and S2).

In addition to Cs_2CO_3 , other alkali carbonates including K_2CO_3 , Na_2CO_3 , and Li_2CO_3 were examined and proved almost inactive for the hydrogenation of EL with no more than 2% conversion (Table S2, entries 3-5). This finding seems to imply a positive role of cesium in the hydrogenation process. However, the inactivity of CsCl, CsNO₃ and CsOOCH (Table S2, entries 6-8) is contradictory to the speculation, which on the other hand indicates the activation effect of the carbonate. The co-addition of 18-crown-6 (10 mol%) significantly enhanced the performance of K_2CO_3 for the reaction (Table S2, entry 9) by increasing its solubility, clearly proving the dominant role of carbonate in the catalytic process. Although CsOH showed comparable activity to Cs_2CO_3 in terms of EL conversion, the selectivity toward GVL significantly dropped to 82% with 1,4-pentanediol (1,4-PD) as the primary byproduct (13% yield; Table 1, entry 2). This result further indicates that the appropriate

nucleophilicity of the dissociative carbonate is crucial for the pronounced reactivity in the selective hydrogenation of the dicarbonyl compound. In line with this finding, the type of solvent was illustrated to significantly influence the reactivity (Fig. S3), where MTHF is capable of dispersing Cs₂CO₃ and (EtO)₃SiH to enable their contact with the substrate EL. In contrast, more polar solvent (DMSO and acetonitrile) was not able to completely convert EL (Fig. S3), while less polar solvent (*n*-hexane) promoted the over-hydrogenation of GVL to afford corresponding acetal and 1,4-PD (Figs. S4 and S5). In the case of using tetrahydrofuran (THF) as the solvent with a structure quite similar to that of MTHF, GVL was found to be the predominant product after post-treatment at variable temperatures (Fig. S6), while GVL-derived acetals (2-ethoxy-5-methyltetrahydrofuran and triethyl (5-methyltetrahydrofuran-2-yl) silicate) without 1,4-PD and MTHF were detected by GC-MS (Fig. S7).

Both the type and dosage of hydrosilanes were found to directly affect both EL conversion and selectivity towards GVL or 1,4-PD. Among the tested hydrosilanes, (EtO)₃SiH exhibited the highest activity in the synthesis of GVL from EL, while the other hydrosilanes were either too active (with ca. 9% yield of 1,4-PD formed in the presence of PhSiH₃) or inert (e.g., Et₃SiH and Ph₂SiH₂) for the reaction (Table S3). 1.5 equiv. H⁻ of (EtO)₃SiH was most favorable for the formation of GVL (Fig. S8), while the use of larger excess of hydrosilane (2.5-5.5 equiv. H⁻) resulted in reduction of the ester group in either EL or GVL (Fig. S1), giving 1,4-PD as the major co-product in up to ca. 10% yield. Owing to its relatively low nucleophilicity, Cs₂CO₃ showed inferior activity relative to CsOH in the formation of 1,4-PD (yield: 4% vs 38%; Table 1, entries 3 and 4). However, a low carbon balance was observed in the latter case (89%), which could be ascribed to the presence of strongly basic OH⁻ causing undesired side reactions like condensation or the formation of stable intermediates such as 2-ethoxy-5-methyltetrahydrofuran (Fig. S9). It should be noted that an increased 1,4-PD yield of 71% with 21% GVL could be obtained with Cs₂CO₃ and 3.5 equiv. H⁻ of (EtO)₃SiH by prolonging the reaction time to 6 h (Fig. S10). When the more active phenylsilane (PhSiH₃) was used as a reducing agent in the presence of Cs₂CO₃, a 25% yield of 1,4-PD was obtained after 0.5 h, which is comparable to the yield (20%) achieved with (EtO)₃SiH after 2 h under otherwise identical conditions (Table 1, entries 5 and 6). With an extension of the reaction time to 6 h, an unprecedented high yield of 1,4-PD (95%) was attained using Cs₂CO₃ and PhSiH₃ (Table 1, entry 7). Although a slight increase of reaction temperature to 60 °C enhanced the reaction rate from 3.2 to 6.9 h⁻¹, the 1,4-PD yield together with the carbon balance was markedly reduced to ca. 87% (Table 1, entry 8), due to the formation of some unidentified products. These results demonstrate that room temperature (25 °C) was preferable to warrant high carbon balance through the reaction process, while the dosage and type of hydrosilane as well as the reaction time, were key factors determining the selectivity and product distribution.

For comparison, some previously reported results using metalbased catalysts for the production of GVL and 1,4-PD are listed in Table 1, entries 9-12 ¹⁴. The Pt/V_2O_5 catalyst could afford a yield of GVL (99%) comparable to our catalytic system (entry 9 vs entry 1), but

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harsher reaction conditions (130 °C, 6 h, and 5 MPa H₂) were required and the reaction rate was much lower (TOF: 16.5 h⁻¹ with Pt/V₂O₅ vs 39.2 h⁻¹ with Cs₂CO₃ at 25 °C). Even higher reaction temperature (160 ^oC), longer reaction time (10-24 h), or higher H₂ pressure (3-5 MPa) was required over metallic catalysts to produce 1,2-PD with yields of 48-93% and TOF values of 0.1-1.9 h⁻¹ (entries 10-12). It is also worth noting that the metal catalysts with serious leaching and toxicity issues are prone to cause the formation of cyclic ether or monoalcohol. For example, MTHF (19%), 2-pentanol (20%), and 1-pentanol (6%) were found to be the major byproducts using Pt-Mo/SiO₂ (39), thus greatly annihilating the selectivity toward 1,4-PD (48%; entry 11). In contrast, our catalytic system was able to selectively produce 1,4-PD in a higher yield of 95% with TOF of 3.2 h^{-1} (entry 7) by simply increasing the hydrosilane dosage from 1.5 to 3.5 equiv. of H⁻. This finding manifests the advantages of the Cs2CO3-promoted hydrosilylation process in the selective hydrogenation of EL, a dicarbonyl compound, into GVL or 1,4-PD at room temperature.

Interestingly, when LA instead of EL was used as substrate, a good GVL yield of 93% (Table 1, entry 13) was also obtained under the

optimal reaction conditions, indicating that the developed catalytic system can be potentially used for the reduction of biomass-derived organic acids. As one of the promising silanes used for hydrogenation, polymethylhydrosiloxane (PMHS) is a polymeric byproduct of the silicone industry, which is non-toxic, inexpensive, safe, and water/air insensitive ¹⁵. Although a low GVL yield (25%) was obtained using PMHS after a short reaction time of 0.5 h (Table S3), the yield could be improved to ca. 90% over our developed catalytic system by prolonging the reaction time to 2 h (Table 1, entry 14). In order to examine the feasibility of the developed catalytic system in practical production, the reaction was scaled up from 2 to 50 mL, and the amount of EL was accordingly increased from 144 mg to 3.6 g. Although the substrate was scaled up from milligram to gram by 25fold, GVL and 1,4-PD could be obtained in good yields of 90 and 82% with 5 mol% Cs₂CO₃ at 25 °C using 1.5 equiv. H⁻ of (EtO)₃SiH and 3.5 equiv. H⁻ of PhSiH₃ after 1 h and 8 h, respectively. These results demonstrate the great potential of the Cs₂CO₃-hydrosilane catalytic system for industrial application.

			OEt (EtO) ₃ Si Cs ₂ CO	OSi(C iH ³ Si-	DEt) ₃ OEt 1 O EtOH	2[H] (EtO) ₃ SiH Cs ₂ CO ₃	OSi(C	DEt) ₃ OS OS OS OS OS OS OS OS	Si(OEt) ₃ DH	- , , -		
				~	⋛⁰			н ∽∕~	_OH			
				GV	'L			1,4-PD				
Entry	Catalyst	Hydrogen-donor		Temp	Time	EL conv.	Product yield (%)		CB ^a	TOF ^b		
		Туре	H ⁻ dosage	(ºC)	(h)	(%)	Si-1	GVL	Si-2	1,4-PD	(%)	(h⁻¹)
1	Cs_2CO_3	(EtO)₃SiH	1.5 equiv.	25	0.5	>99	<1	98	<1	0	99	39.2
2	CsOH	(EtO)₃SiH	1.5 equiv.	25	0.5	100	0	82	2	13	97	32.8
3	Cs_2CO_3	(EtO)₃SiH	3.5 equiv.	25	0.5	100	0	92	3	4	99	36.8
4	CsOH	(EtO)₃SiH	3.5 equiv.	25	0.5	100	0	51	<1	38	89	20.4
5	Cs_2CO_3	(EtO)₃SiH	3.5 equiv.	25	2	100	0	77	1	20	98	7.7
6	Cs ₂ CO ₃	$PhSiH_3$	3.5 equiv.	25	0.5	99	<1	72	1	25	>99	28.8
7	Cs_2CO_3	PhSiH₃	3.5 equiv.	25	6	100	0	2	<1	95	97	3.2
8	Cs ₂ CO ₃	PhSiH₃	3.5 equiv.	60	2.5	100	0	<1	0	87	87	6.9
9 ^c	Pt/V_2O_5	5 MPa H_2	-	130	6	>99	-	99	-	1	100	16.5
10 ^c	Pt-Mo/HAP	3 MPa H_2	-	130	24	>99	-	<1	-	93	94	1.9
11 ^d	Pt-Mo/SiO ₂	5 MPa H_2	-	130	24	>99	-	0	-	48	93	1.0
12 ^e	CuAlZn	4 MPa H_2	-	160	10	100	-	17	-	82.9	99.9	0.1
13 ^f	Cs_2CO_3	(EtO)₃SiH	1.5 equiv.	25	0.5	95	0	93	<1	0	98	37.2
14 ^g	Cs_2CO_3	PMHS	1.5 equiv.	25	2	96	<1	90	<1	2	97	9.0

Table 1. Selective hydrogenation of ethyl levulinate (EL) to y-valerolactone (GVL) and 1,4-pentanediol (1,4-PD) via silyl ethers (Si-1 and Si-2).

Reaction conditions: 1 mmol EL, 1.5 or 3.5 equiv. H⁻, 5 mol% catalyst, 2 mL MTHF; After the reaction, 2 mL ethanol was added into the reaction mixture and stirred at 80 °C for 2 h. ^{*a*} CB: Carbon balance; ^{*b*} TOF (turnover frequency) is defined as (mole of primary product) / (mole of active species × time); ^{*c*} Ref. (14*a*); ^{*d*} Ref. (14*b*); ^{*e*} Ref. (14*b*); ^{*f*} LA instead of EL was used as substrate; ^{*a*} Polymethylhydrosiloxane (PMHS) was used as reducing agent.

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NMR study of reaction pathways

To elucidate the reaction pathways, in situ NMR studies were conducted to monitor the product distribution during the reduction process of EL to GVL in the presence of Cs₂CO₃ with (EtO)₃SiH. The in situ ¹³C NMR spectra of the EL hydrogenation (Fig. 2A) display that the silyl ether (Si-1) and ethyl 4-hydroxypentanoate (EHP) are possibly key intermediates to the final product GVL. EL was almost completely converted in 0.5 h even without magnetic stirring, where Si-1 was observed as the first intermediate, followed by gradual degradation to EHP (Fig. S11). On the other hand, the absence of signals in the olefinic region in the in situ ¹³C NMR spectra of the reaction mixture (Fig. 2B) validates the initial occurrence of the hydrogenation step, rather than a possible initial cyclization of EL to form α -angelica lactone (Fig. 3). After reacting for different intervals (3-60 min), the characteristic regions belonging to EHP and GVL in ex situ NMR spectra of the reaction mixture guenched by methanol were recorded (Fig. S12). Clearly, better selectivity toward GVL was observed after methanol treatment, as compared with the in situ obtained results (Fig. 2A) in the NMR tube. This finding verifies the importance of the post-treatment process (e.g., with ethanol) at the specific temperature (ca. 80 °C) to accomplish the following cyclization step, thus exclusively giving GVL.



Fig. 2. In situ ¹³C NMR spectra for the hydrogenation of ethyl levulinate (EL). (A) Formation of γ -valerolactone (GVL) via the silyl ether (Si-1) and ethyl 4hydroxypentanoate (EHP); (B) Olefinic region in ¹³C NMR spectra of the reaction mixture. Reaction conditions: 1 mmol EL, 1.5 equiv. H⁻ of (EtO)₃SiH, 5 mol% Cs₂CO₃, 2 mL MTHF, 25 °C.



The simultaneous presence of the intermediates EHP and Si-1 in the reaction mixture can also be distinguished by the ¹H-¹³C HMBC spectra of the reaction mixture (Fig. 4A). The Si attachment in Si-1 can be affirmed by 1H-29Si HMBC (Fig. 4A). To some extent, the stable intermediates are not favorable for directly producing GVL from EL, due to the requirement of secondary post-treatment. Fortunately, the reaction rate is significantly enhanced after a specific period (ca. 15-30 min) of the steady reaction process, as shown in Fig. 4B. The formation of the intermediates as well as the siloxane Si(OEt)₄ is most likely to promote the dissolution of the catalytically active species (carbonate), thus leading to rapid or runaway reaction. Furthermore, the incorporation of hydride from the hydrosilane into the substrate EL can be illustrated by comparison of the obtained ¹H NMR spectra (Fig. S13) using normal Ph₂SiH₂ and deuterium-labeled Ph₂SiD₂ as reducing agents. Kinetic isotope effect (KIE) study disclosed a significant difference in $k_{\rm H}/k_{\rm D}$ value (ca. 2.4) when the hydride was supplied either by Ph₂SiH₂ or Ph₂SiD₂, further supporting that the relative activity of the employed hydrosilane plays a key role in the selective hydrogenation. On the other hand, ¹H-¹³C HSQC NMR spectra of the reaction mixture after post-treatment with methanol-d₄ at 60 °C for 2 h demonstrated the complete conversion of the intermediates into GVL (Fig. S14), which is in agreement with the corresponding ¹³C NMR spectra (Figs. S15 and S16).

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Fig. 4. In situ NMR spectra of the reaction mixture for ethyl levulinate (EL) conversion. (A) In situ ¹H-¹³C/²⁹Si HMBC spectra of the intermediates [ethyl 4-hydroxypentanoate (EHP) and silyl ether (Si-1)], and (B) In situ time-series of ¹³C NMR spectra for the hydrogenation of ethyl levulinate (EL) to the intermediates [silyl ether (Si-1) and ethyl 4-hydroxypentanoate (EHP)]; Tetraethyl orthosilicate is the asterisk in ¹H-²⁹Si HMBC spectrum (top).

Upgrade of carbonate

Although the used catalyst Cs₂CO₃ is cheap, widely available and eco-friendly, attempts were made to investigate its recoverability for potential recycling or further upgrading. Initially, the effect of Cs₂CO₃ dosage on the conversion of EL to GVL was studied, where no more than 80% yields of GVL were obtained using less than 5 mol% Cs₂CO₃ (Fig. S17). This relatively low yield shows the importance of using sufficient Cs₂CO₃ (5 mol%) for good catalytic performance. However, the amount of Cs₂CO₃ (separated out by centrifugation) was decreased by around 68% after the first cycle of the reaction. Notably, the recovered solids were characterized by STEM (Fig. S18) to be Cs₂CO₃ with additional silicon compounds, thus underlining the difficulty in completely recycling the catalyst. TEM images of both fresh and recovered Cs₂CO₃ pre-dispersed into THF indicated the formation of nano-sized particles (Fig. S19), which is in agreement with the superior catalytic results of the alkali carbonate salts being more soluble (Table S2, entries 1-5). Instead, the addition of ethanol (2 mL) into the liquid mixture after the reaction led to full conversion of the residual carbonate in both solid and leached states into formate (>95% yields) in 2 h (Fig. S20), which was confirmed by ¹H NMR through detection of a singlet with a chemical shift of about 8.6 ppm belonging to ¹HCOO- (Fig. S21). Therefore, it would be more preferable to co-synthesize the expected products together with the value-added formate by post-treatment with ethanol.

Selective hydrogenation of dicarbonyl compounds to hydroxy esters and diols

Cyclic ether or mono-alcohol is typically formed in the synthesis of diols from dicarbonyl compounds ^{14b,16}. To examine the versatility of the catalytic system developed in this study, the substrate scope was further expanded to other dicarbonyl compounds (Table 2). Both diketones and dialdehydes could be selectively reduced to diols with yields of 87-95% in 0.5-1 h (entries 1-3). The exclusive selectivity toward the diols further indicates the intact C-O bond during the processes of reduction and post-treatment, which is unambiguously attributed to the formation of silvl ether under the mild reaction conditions. Apart from the aromatic ring, the nitro group was also intact during the hydrogenation process (entry 4). This makes the catalytic system capable of exclusively producing alcohols with good compatibility to other multi-unsaturated functional groups. By prolonging the reaction time to 6 h and increasing hydrosilane dosage to 2.5 equiv. H⁻ of PhSiH₃, methyl benzoate and methyl p-methyl benzoate could be hydrogenated to benzyl alcohol (96% yield, entry 5) and p-methylbenzyl alcohol (>99% yield, entry 6), respectively. In the presence of both aldehyde/ketone and ester, the selective reduction of aldehyde or ketone to alcohol without affecting the ester group could be achieved (entries 7, 9 and 11). Importantly, both the presented carboxides could be reduced to diols in high yields of 88-96% from those dicarbonyl compounds containing aldehyde/ketone and ester groups (entries 8, 10 and 12).

Table 2. Selective reduction of carbonyl compounds bearing multi-unsaturated groups to alcohols via silyl ethers.

	O PhSiH ₃	OSiH ₂ Ph E	toh C	н	
R	R^2 Cs ₂ CO ₃	$R^1 R^2$	R ¹	R ²	
A	ldehyde Ketone Ester	Silyl ether	Alcohol		
Entry	Substrate	Hydride (H⁻ equiv.)	Time (h)	Alcohol yield (%)	
1		2.5	1	92	
2		2.5	1	87	
3		2.5	1	95	
4	0 ₂ N-	2.5	1.5	97	
5	OMe	2.5	6	96	
6		2.5	12	>99	
7	<u>م</u>	1.5	0.5	98	
8	OMe	3.5	24	96	
9	\sim	1.5	1	94	
10	/ Come	3.5	24	91	
11		1.5	1	85	
12	OCEt	3.5	24	88	

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Reaction conditions: 1 mmol substrate, 1.5-3.5 equiv. H⁻ of PhSiH₃, 5 mol% Cs₂CO₃, 2 mL MTHF, 25 °C; After the reaction, 2 mL ethanol was added to the liquid mixture and stirred at 80 °C for 2 h.

Selective hydrogenation of multi-unsaturated amides

Pyrrolidones are a class of amides extensively applied as solvents and feedstocks for fibers or surfactants ¹⁷. In the present study, starting from levulinic acid (LA) and amines, a variety of N-substituted lactams (i.e., pyrrolidones) could be synthesized in good yields of 85-92% at 120 °C using formic acid both as an acid and as hydrogen source in the absence of a catalyst (Table S4). The results are comparable to those obtained over metal catalysts such as Ir and Ni in the production of lactams ^{17,18}. In general, the controllable reduction of lactams is one of the promising ways to produce cyclamines. However, the cleavage of C-N bonds often occurs over metal (e.g., Ru, Mn, and Fe) catalysts during the hydrogenation process, simultaneously giving amines and alcohols as products ¹⁹. Typically, the lactam is more inert towards reduction compared with the ester analogue ^{11e}, while extension of the reaction time to 24-36 h could yield 81-99% cyclamine with selectivity of 95-100% in the presence of the hydrosilane/Cs₂CO₃ catalytic system at room temperature (Table 3). Notably, this catalytic system is compatible with aliphatic and aromatic N-substitutes, and it does not interfere with halogen substituent resulting in hydrodechlorination reaction.

Table 3. Selective hydrogenation of *N*-substituted lactams derived from levulinic acid.



Reaction conditions: 1 mmol substrate, 3 equiv. H $^\circ$ of PhSiH₃, 5 mol% Cs₂CO₃, 2 mL MTHF, 25 °C; After the reaction, 2 mL ethanol was added to the reaction mixture and stirred at 80 °C for 2 h.

With respect to the amides bearing multi-unsaturated groups, the substrate scope was also investigated at 25 $^\circ\text{C}$ for the selective

hydrogenation (Table 4). Either aldehyde or ketone could be hydrogenated to alcohol with yields of 97 or 94% in 1 or 2 h, respectively (entries 1 and 3), while the amide was almost unreacted (<1%). After reacting for 24 or 30 h with 4.5 equiv. H⁻ of PhSiH₃, the hydrogenation of amide to amine proceeded giving hydramine in ~90% yield (entries 2 and 4). This finding indicates that the initial reduction of aldehydes or ketones to corresponding silyl ethers was kinetically favorable and proceeded to completion relatively rapidly. On the other hand, hydrogenation of the amide group was most likely thermodynamically controlled, where an increase of the reaction temperature from 25 to 60 °C significantly shortened the reaction time from 24-30 h to 6-8 h with comparable hydramine yields (entries 2 and 4). Even in the presence of other unsaturated functional groups (e.g., -NO₂ and -CN), the amide compounds were selectively reduced at room temperature (entries 5 and 6), leaving the other functional groups intact. This unprecedented selectivity toward hydrogenates shows great potential in the controllable reduction of multiunsaturated carbonyl compounds. Thus, the reaction system permits selective reduction of amides under mild conditions, which is an enduring challenge in pharmaceutical processes ²⁰. Overall, the chemistries described herein thus have the potential to impact on the upgrading of biomass-derived chemicals and on fine chemical production.

Table 4. Selective reduction of amides bearing other unsaturated groups to cyclic amines



Reaction conditions: 1 mmol substrate, 1.5-4.5 equiv. H⁻ of PhSiH₃, 5 mol% Cs₂CO₃, 2 mL MTHF, 25 °C; After the reaction, 2 mL ethanol was added into the reaction mixture and stirred at 80 °C for 2 h. ^{*a*} Data in the parenthesis were obtained at 60 °C under otherwise identical conditions.

ARTICLE

Computational study of representative reaction pathways

Regarding the selective synthesis of GVL and 1,4-PD from EL in the presence of Cs₂CO₃ and (EtO)₃SiH, the in situ formed silvl ethers Si-1 and Si-2 were verified to be the key intermediates (vide supra), respectively. In particular, the efficiency in the consecutive addition of one to three equiv. hydrides to EL seemed essential for the formation of the silvl ethers (Fig. S22). DFT calculation was conducted to examine the free energies of the dominant products involved in the reaction pathways, and the resulting energy profiles are shown in Fig. S23. Both Si-1 and Si-2 were found to have lower free energy (-17.20 and -15.38 kcal/mol, respectively) than the starting material EL. These two silyl ethers with moderate stability can not only remain intact during the reaction process under mild conditions, but can also be further degraded to remove the siloxane moiety at elevated temperature, rendering them ideal precursors of GVL and 1,4-PD. It should be noted that EL acetal derived from Si-1 was calculated to have a higher free energy (-2.87 kcal/mol, Fig. S22), implying that the dominant barrier toward 1,4-PD from EL was the ester hydrogenation step. This finding is consistent with the experimental results, where Si-1 (precursor of GVL) can be rapidly and quantitatively formed in 0.5 h, while approximately 6 h are required to obtain Si-2 (precursor of 1,4-PD).



Reaction coordinate (R)

Fig. 5. DFT calculation results of silyl ether *in situ* formed from the lactone and lactam using PhSiH₃ as H-donor. Energy profiles for reduction of (A) γ -valerolactone (GVL) to 2-methyltetrahydrofuran (MTHF) and (B) 1,5-dimethyl-2-pyrrolidinone (DPO) to 1,2-dimethylpyrrolidine (DPI) via corresponding silyl ethers. The optimized transition state (TS1) structures are shown in blue.

In addition, we note that a significant difference in product distribution was obtained when lactone and lactam were used as substrates with PhSiH₃ as the hydrogen source for reduction (Fig. S24).

In the case of a lactone (e.g., GVL), a diol (1,4-PD) was prone to be obtained, while the complete reduction of lactam (e.g., 1,5-dimethyl-2-pyrrolidinone (DPO)) gave cyclamine (1,2-dimethylpyrrolidine (DPI)) as the predominant product. DFT calculation demonstrated the significance of the type of silvl ethers formed in situ (i.e., GVL/DPO acetals) along with its preceding optimized transition state (TS1) in the selectivity control (Fig. 5). The TS1 free energy for initial reduction of GVL was found to be slightly higher than for initial hydrogenation of DPO (57.52 vs 55.25 kcal/mol), indicating the need of a relatively higher energy barrier to form a GVL-derived acetal: (5methyltetrahydrofuran-2-yl)oxy phenylsilane. Moreover, the stability of this compound was higher than that of the corresponding intermediate (DPO-derived acetal), in view of their free energies (-1.86 vs +5.96 kcal/mol). This finding rationalizes the difficulty in the synthesis of MTHF from GVL, which is in agreement with the experimental results. In fact, 1,4-PD was detected to be the main product from the reduction of GVL, showing that the cyclic C-O bond was more easily broken than the exocyclic one of the GVL acetal during the hydrosilylation process, as illustrated in Fig. S24. In contrast, the exocyclic C-O bond of the DPO-derived acetal was susceptible to cleavage, affording the cyclamine (DPI) as the principal product. The presence of competing reaction pathways dependent on the structures of in situ formed silyl ethers makes the product distribution controllable.

Conclusions

In summary, an economic and green catalytic system composed of Cs₂CO₃, hydrosilane and the bio-based solvent MTHF has been developed for room-temperature reduction of dicarbonyl compounds into monohydric esters or diols in 85-99% yield using 1.5-3.5 equiv. H⁻. Especially, the cyclization/lactonization of ethyl 4-hydroxypentanoate (EHP) or its silyl ether (Si-1) formed in situ from biomass-derived ethyl levulinate (EL) can take place through a facile post-treatment process, quantitatively giving the valuable platform molecule y-valerolactone (GVL). The process exhibits a TOF value (39.2 h⁻¹) that is superior to previous results obtained using metal catalysts. By the appropriate increase of the hydrosilane dosage and by extension of the reaction time, 1,4-pentanediol (1,4-PD) instead of GVL can become the dominant product (up to 95% yield), while cyclic ether formation (selfetherification) or monohydric alcohol formation (over-hydrogenation) are absent. The in situ formation of silyl ether is most likely responsible for the pronounced performance and selectivity toward different types of carbonyl species, as demonstrated by in situ NMR and computational studies. Despite requiring longer reaction time, a variety of monohydric amides and hydroxylamines can be synthesized from corresponding dicarboxides, while the concurrent other unsaturated species remain intact. The high selectivity and benign reaction conditions render our catalytic system a promising alternative to precious metal catalysts in the specific reduction of carbonyl groups. In addition, the concept of in-situ generating labile silyl ether between the reactant and hydride bears promise in the

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switchable reduction or transformation of specific species from multifunctional groups in both biomass feedstock and relevant molecules.

Experimental

Materials

Tetrahydrofuran- d_8 (99.5 atom % D), methanol- d_4 (99.8 atom % D), diphenylsilane- d_2 (97 atom % D), and Amberlyst-15 (hydrogen ion form, wet) were purchased from Shanghai Sigma-Aldrich Trading Co. Ltd. Cesium carbonate (Cs₂CO₃, 99%), 2-methyltetrahydrofuran (MTHF, 99%), 18-crown-6 (99%), triethoxysilane [(EtO)₃SiH, 95%], phenylsilane (PhSiH₃, 97%), ethyl levulinate (EL, 99%), γ -valerolactone (GVL, 98%), 1,4-pentanediol (1,4-PD, 99%), naphthalene (99%), and xylene (99%) were purchased from Beijing InnoChem Science & Technology Co., Ltd.

Reduction of multi-unsaturated carbonyl compounds

All the reduction reactions were carried out in Ace pressure tubes (10 mL). In a typical procedure, 1 mmol carbonyl compound, 1-5.5 equiv. H⁻ of hydrosilane, 5 mol% Cs_2CO_3 , and 2 mL MTHF were added into the tube. After stirring (500 rpm) at room temperature (25 °C) for a specific reaction time, 2 mL ethanol was added into the reaction mixture and stirring continued at 80 °C for another 2 h. The resulting solution was collected and subjected to product analysis.

Product analysis

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Dominant products were identified by GC-MS (Agilent 6890N combined with 5973 MS), whereas the quantification of liquid products was performed by GC (Agilent 7890B) fitted with flame ionization detector (FID) and HP-5 column (30 m × 0.320 mm × 0.25 μ m) using naphthalene as internal standard and referring to standard curves. The content of formate was determined by ¹H NMR using xylene as an internal standard.

NMR spectroscopic study

¹H, ¹³C and 2D ¹H-¹³C HSQC NMR spectra of the liquid mixtures were obtained with normal hydrosilanes in deuterated solvents (typically, MTHF- d_{10}) or in protonated solvents containing 5% DMSO- d_6 as lock substance on a Bruker Avance III 800 MHz spectrometer equipped with a TCI cryoprobe. *Ex situ* samples of reaction progress were obtained by quenching reactions with methanol- d_4 at indicated times. For the isotope-labeling study, ¹H, ¹³C, DEPT-135 and ¹H-¹³C HSQC NMR spectra of the reaction mixtures, which were obtained using deuterium reagents (diphenylsilane- d_2 and THF- d_8 with or without CD₃OD post-treatment), were recorded on a JEOL-ECX 500 NMR spectrometer.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- a) D. Wang, D. Astruc, *Chem. Rev.* 2015, **115**, 6621-6686; b) J.H. Xie, S.F. Zhu, Q.L. Zhou, *Chem. Rev.* 2011, **111**, 1713-1760; c) J. Pritchard, G.A. Filonenko, R. van Putten, E.J.M. Hensen, E.A. Pidko, *Chem. Soc. Rev.* 2015, **44**, 3808-3833.
- a) R. M. Bullock, *Science* 2013, **342**, 1054-1055; b) A. Corma, P. Serna, *Science*, 2006, **313**, 332-334; c) P. Ryabchuk, G. Agostini, M.M. Pohl, H. Lund, A. Agapova, H. Junge, K. Junge, M. Beller, *Sci. Adv.* 2018, **4**, eaat0761.
- a) K. Manna, T. Zhang, M. Carboni, C.W. Abney, W. Lin, *J. Am. Chem. Soc.* 2014, **136**, 13182-13185; b) H. Li, Z. Fang, R.L. Smith, S. Yang, *Prog. Energ. Combust.* 2016, **55**, 98-194; c) M. Naruto, S. Saito, Nat. Commun. 2015, 6, 8140; d) T.J. Korstanje, J.I. van der Vlugt, C.J. Elsevier, B. de Bruin, *Science* 2015, **350**, 298-302; e) K. Yuan, T. Song, D. Wang, X. Zhang, X. Gao, Y. Zou, H. Dong, Z. Tang, W. Hu, *Angew. Chem. Int. Ed.* 2018, **57**, 5708-5713; f) R.C. Cammarota, C.C. Lu, *J. Am. Chem. Soc.* 2015, **137**, 12486-12489; g) L. Wang, E. Guan, J. Zhang, J. Yang, Y. Zhu, Y. Han, M. Yang, C. Cen, G. Fu, B.C. Gates, F.S. Xiao, *Nat. Commun.* 2018, **9**, 1362.
- a) C. Pilar Jiménez-Gómez, J.A. Cecilia, D. Durán-Martín, R. Moreno-Tost, J. Santamaría-González, J. Mérida-Robles, R. Mariscal, P. Maireles-Torres, J. Catal. 2016, **336**, 107-115; b) G.W. Huber, J.N. Chheda, C.J. Barrett, J.A. Dumesic, Science 2005, **308**, 1446-1450; c) C. Zhao, Y. Kou, A.A. Lemonidou, X. Li, J.A. Lercher, Angew. Chem. Int. Ed. 2009, **48**, 3987-3990.
- a) Q. Meng, M. Hou, H. Liu, J. Song, B. Han, *Nat. Commun.* 2017,
 8, 14190; b) M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, K. Tomishige, *Angew. Chem. Int. Ed.* 2018, 57, 8058-8062.
- a) W. Liu, Y. Jiang, K.H. Dostert, C.P. O'Brien, W. Riedel, A. Savara, S. Schauermann, A. Tkatchenko, *Sci. Adv.* 2017, 3, e1700939; b) Y. Zhu, H. Qian, B.A. Drake, R. Jin, *Angew. Chem. Int. Ed.* 2010, 49, 1295-1298.
- a) C.O. Tuck, E. Pérez1, I.T. Horváth, R.A. Sheldon, M. Poliakoff, Science 2012, **337**, 695-699; b) Y.S. Jang, B. Kim, J.H. Shin, Y.J. Choi, S. Choi, C.W. Song, J. Lee, H.G. Park, S.Y. Lee, Biotechnol. Bioeng. 2012, **109**, 2437-2459; c) H. Li, A. Riisager, S. Saravanamurugan, A. Pandey, R.S. Sangwan, S. Yang, R. Luque, ACS Catal. 2018, **8**, 148-187; d) H. Li, R.L. Smith, Nat. Catal. 2018, **1**, 176-177.
- a) Y. Román-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, *Nature* 2007, **447**, 982-985; b) J.N. Chheda, G.W. Huber, J.A. Dumesic, *Angew. Chem. Int. Ed.* 2007, **46**, 7164-7183; c) D.M. Alonso, S.G. Wettstein, J.A. Dumesic, *Green Chem.* 2013, **15**, 584-595.
- a) W. Deng, Y. Wang, N. Yan, *Curr. Opin. Green Sustain. Chem.* 2016, **2**, 54-58; b) H. Li, Z. Fang, J. Luo, S. Yang, *Appl. Catal. B: Environ.* 2017, **200**, 182-191.
- a) Z. Zhang, ChemSusChem 2016, 9, 156-171; b) B. Banerjee, R. Singuru, S.K. Kundu, K.Dhanalaxmi, L. Bai, Y. Zhao, B.M. Reddy, A. Bhaumik, J. Mondal, Catal. Sci. Technol. 2016, 6, 5102-5115; c) S. Pendem, I. Mondal, A. Shrotri, B. S. Rao, N. Lingaiah, J. Mondal, Sustainable Energy Fuels 2018, 2, 1516-1529; d) K. Dhanalaxmi,

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Journal Name

R. Singuru, S. Mondal, L. Bai, B. M. Reddy, A. Bhaumik, J. Mondal, ACS Sustainable Chem. Eng. 2017, 5, 1033-1045; e) D.
Ren, X. Wan, F. Jin, Z. Song, Y. Liu, Z. Huo, Green Chem. 2016, 18, 5999-6003; f) T. Mizugaki, Y. Nagatsu, K. Togo, Z. Maeno, T.
Mitsudome, K. Jitsukawa, K. Kaneda, Green Chem. 2015, 17, 5136-5139; g) J. Cui, J. Tan, Y. Zhu, F. Cheng, ChemSusChem 2018, 11, 1316-1320; h) S. C. Patankar, G. D. Yadav, ACS Sustainable Chem. Eng. 2015, 3, 2619-2630.

- a) S.G. Wettstein, D.M. Alonso, Y. Chong, J.A. Dumesic, *Energy Environ. Sci.* 2012, **5**, 8199-8203; b) W. Luo, M. Sankar, A.M. Beale, Q. He, Christopher J. Kiely, Pieter C.A. Bruijnincx, B.M. Weckhuysen, *Nat. Commun.* 2015, **6**, 6540; c) A. Primo, P. Concepción, A. Corma, *Chem. Commun.* 2011, **47**, 3613-3615; d) T. Mizugaki, Y. Nagatsu, K. Togo, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *Green Chem.* 2015, **17**, 5136-5139; e) D. Addis, S. Das, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* 2011, **50**, 6004-6011; f) A. Volkov, K.P.J. Gustafson, C.W. Tai, O. Verho, J.E. Bäckvall, H. Adolfsson, *Angew. Chem. Int. Ed.* 2015, **54**, 5122-5126; g) H. Li, W. Zhao, Z. Fang, *Appl. Catal. B: Environ.* 2017, **215**, 18-27.
- 12. F. Lehmann, Synlett 2004, 2447-2448.
- a) X. Y. Li, R. Shang, M. C. Fu, Y. Fu, *Green Chem.* 2015, **17**, 2790-2793; b) W. Zhao, T. Yang, H. Li, W. Wu, Z. Wang, C. Fang, S. Saravanamurugan, S. Yang, *ACS Sustainable Chem. Eng.* 2017, **5**, 9640-9644; c) X. F. Liu, C. Qiao, X. Y. Li, L. N. He, *Green Chem.* 2017, **19**, 1726-1731; d) H. Li, W. Zhao, A. Riisager, S. Saravanamurugan, Z. Wang, Z. Fang, S. Yang, *Green Chem.* 2017, **19**, 2101-2106; e) C. Wu, X. Luo, H. Zhang, X. Liu, G. Ji, Z. Liu, *Z. Liu, Green Chem.* 2017, **19**, 3525-3529; f) H. Li, W. Zhao, S. Saravanamurugan, W. Dai, J. He, S. Meier, S. Yang, A. Riisager, *Commun. Chem.* 2018, **1**, 32; g) C. Xu, B. Huang, T. Yan, M. Cai, *Green Chem.* 2018, **20**, 391-397; h) R. A. Pramudita, K. Motokura, *Green Chem.* 2018, DOI: 10.1039/C8GC02052C.
- a) T. Mizugaki, Y. Nagatsu, K. Togo, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *Green Chem.* 2015, **17**, 5136-5139; b) T. Mizugaki, K. Togo, Z. Maeno, T. Mitsudome, K. Jitsukawa, K. Kaneda, *ACS Sustain. Chem. Eng.* 2016, **4**, 682-685; c) D. Ren, X. Wan, F. Jin, Z. Song, Y. Liu, Z. Huo, *Green Chem.* 2016, **18**, 5999-6003.
- a) K. K. Senapati, Polymethylhydrosiloxane (PMHS), *Synlett* 2005,
 12, 1960-1961; b) D. B. Nale, B. M. Bhanage, *Green Chem.* 2015,
 17, 2480-2486; c) J. A. Caetano, A. C. Fernandes, *Green Chem.* 2018, 20, 2494-2498.
- M. Chia, Y. J. Pagán-Torres, D. Hibbitts, Q. Tan, H. N. Pham, A. K. Datye, M. Neurock, R. J. Davis, J. A. Dumesic, *J. Am. Chem. Soc.* 2011, **133**, 12675-12689.
- 17. S. Wang, H. Huang, C. Bruneau, C. Fischmeister, *ChemSusChem* 2017, **10**, 4150-4154;
- G. Gao, P. Sun, Y. Li, F. Wang, Z. Zhao, Y. Qin, F. Li, ACS Catal. 2017, 7, 4927-4935.
- a) J. R. Cabrero-Antonino, E. Alberico, K. Junge, H. Junge, M. Beller, *Chem. Sci.* 2016, **7**, 3432-3442; b) N. M. Rezayee, D. C. Samblanet, M. S. Sanford, *ACS Catal.* 2016, **6**, 6377-6383; c) V. Papa, J. R. Cabrero-Antonino, E. Alberico, A. Spanneberg, K. Junge, H. Junge, M. Beller, *Chem. Sci.* 2017, **8**, 3576-3585.
- a) J.M. Woodley, *Trend. Biotechnol.* 2008, **26**, 321-327; b) N. L. Lampland, M. Hovey, D. Mukherjee, A.D. Sadow, *ACS Catal.* 2015, **5**, 4219-4226; c) Y.Q. Zou, S. Chakraborty, A. Nerush, D. Oren, Y. Diskin-Posner, Y. Ben-David, D. Milstein, *ACS Catal.* 2018, **8**, 8014-8019.



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