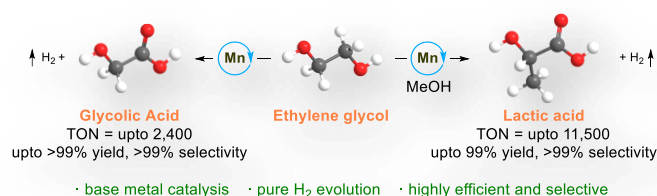


Manganese Catalyzed Reformation of Ethylene Glycol to Glycolic acid and Lactic Acid

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Manganese catalysis, Dehydrogenative coupling, Lactic Acid, Glycolic acid, Reformation, Sustainable synthesis, Hydrogen



ABSTRACT: Conversion of readily available feedstocks to valuable platform chemicals *via* a sustainable catalytic pathway has always been one of the key focuses of synthetic chemists. Cheaper, less toxic, and more abundant base metals as a catalyst for performing such transformations provide an additional boost. In this context, herein, we report a reformation of readily available feedstock, ethylene glycol, to value-added platform molecules, glycolic acid, and lactic acid. A bench stable base metal complex {[HN(C₂H₄PPh₂)₂]Mn(CO)₂Br}, **Mn-I**, known as Mn-^{Ph}MACHO, catalyzed the reformation of ethylene glycol to glycolic acid at 140 °C in high selectivity with a turnover number TON = 2400, surpassing previously used homogeneous catalysts for such a reaction. Pure hydrogen gas is evolved without the need for an acceptor. On the other hand, a bench stable Mn(I)-complex, {[^{tr}PN²P]Mn(CO)₂Br}, **Mn-III**, with a triazine backbone, efficiently catalyzed the acceptorless dehydrogenative coupling of ethylene glycol and methanol for the synthesis of lactic acid, even at a ppm level of catalyst loading, reaching the TON of 11,500. Detailed mechanistic studies were performed to elucidate the involvements of different manganese(I)-species during the catalysis.

INTRODUCTION

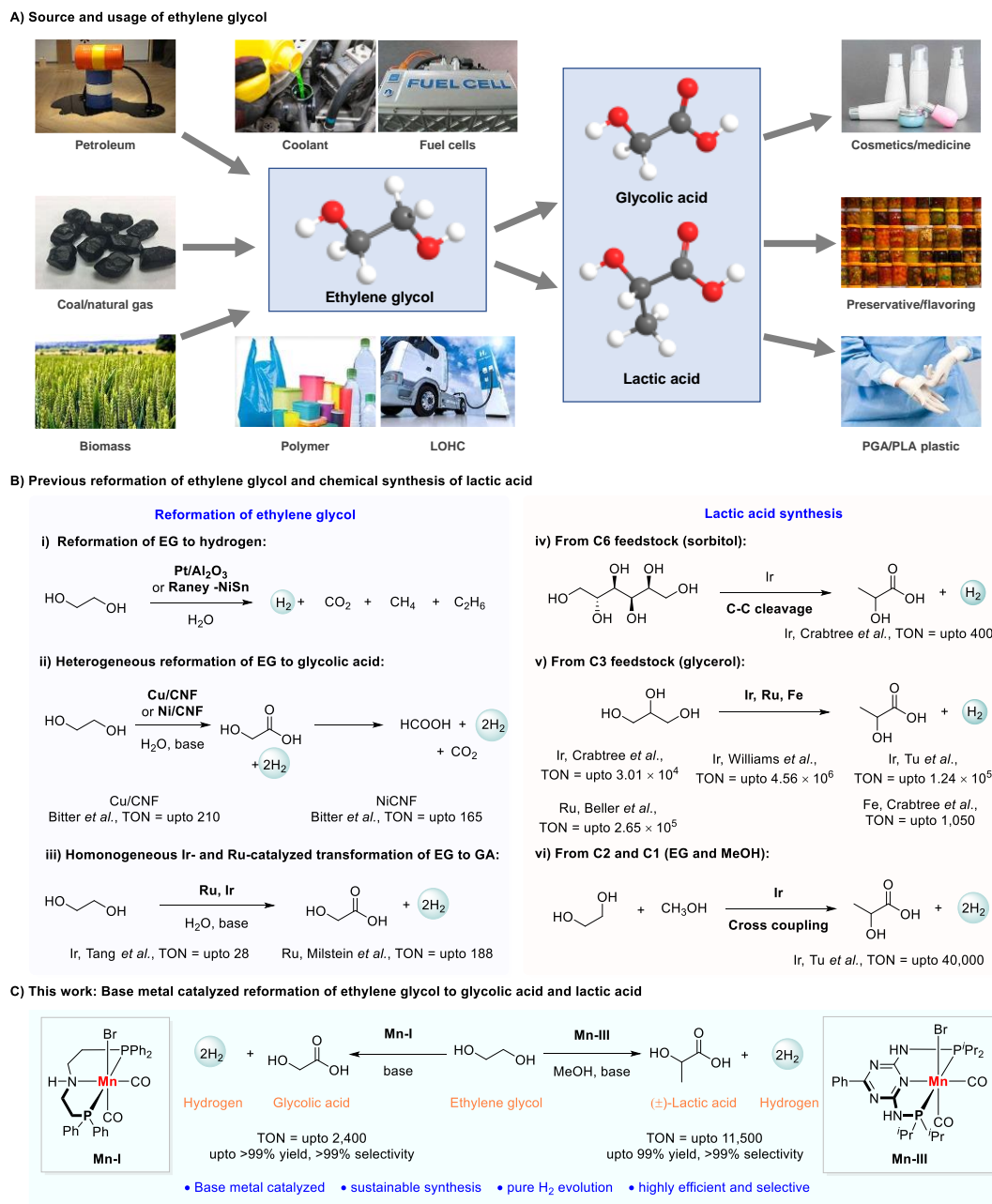
Converting widely accessible renewable feedstock into value-added products and alternative fuel sources is highly relevant in terms of synthetic output and sustainable chemical development.¹⁻⁸ In this context, ethylene glycol (EG) is readily available and cheaply sourced, both from biomass and fossil fuel-based resources, and is an excellent feedstock for such derivatization (Figure 1A).⁹⁻¹⁰ Industrially, EG has been utilized as a coolant, heat-transfer, anti-freeze agent, and precursor for blockbuster polymers.⁹⁻¹⁰ Recently, EG has also emerged as a promising candidate for hydrogen gas carriers with a theoretical hydrogen storage capacity (HSC) of 6.5 wt%.¹¹ Consequently, it has been considered a viable candidate for serving as a liquid organic hydrogen carrier (LOHC). On the contrary, the valorization of EG for synthesizing various value-added products is relatively finite.

Glycolic acid (GA) and lactic acid (LA), having both hydroxy and acid functional groups, are highly demanded with widespread applications ranging from food, skincare, cosmetics, pharmaceuticals, textile, and polymer (Figure 1A).¹²⁻¹⁵ Furthermore, they are widely used to produce various green solvents and commodity chemicals.¹⁴ More intriguingly, both these acids are precursors of widely used biodegradable and biocompatible polymer polyglycolic acid (PGA) and polylactic acid (PLA).¹⁶⁻¹⁷ Owing to their diverse applications, the global market for LA

in 2022 is estimated to cross 4×10^5 tons per year, and for GA to exceed 400 million USD by 2024.^{14, 18} While the current manufacturing protocol for LA is based on conventional chemocatalysis and fermentative methods, the current production of GA largely depends on high-pressure formaldehyde carbonylation using CO at cryogenic conditions, or hydrolysis of chloroacetic acid or methyl 2-hydroxyacetate, cyanidation, transesterification, and enzymatic reaction.¹⁹⁻²¹ Although used industrially, these reactions suffer from major sustainability issues like stoichiometric waste generation, multi-step purification, separation, and toxic reagents requirement. Alternatively, an environmentally benign direct conversion of readily available renewable biomass, like EG, to GA and LA under mild and atom economic conditions is valued as highly desirable.²¹⁻²⁵ However, it is less explored to date.

Contextually, Dumesic demonstrated the first reformation of aqueous EG to H₂, CO₂, and short alkanes at elevated temperatures using Pt/Al₂O₃ and Raney-NiSn (Figure 1B).^{26,27} Bitter attempted carbon nanofiber (CNF) supported Cu, and Ni nanoparticles promoted conversion of EG to GA and H₂.²³ However, further decomposition of GA to formic acid, H₂, and CO₂ was observed. Independently, Cole-Hamilton²⁸ and Beller²⁹ disclosed the reformation of EG to H₂; however, the formation of GA was not confirmed. A homogeneous Rh-catalyzed oxidative dehydrogenation of alcohols and polyalcohols, including EG, to carboxylic acids in the presence of sacrificial hydrogen acceptors such as ketones or methyl methacrylate was developed.²²

Figure 1 (A) Source and Usage of Ethylene Glycol. (B) Previous Reformation of Ethylene Glycol and Lactic Acid Synthesis. (C) Manganese Catalyzed Reformation of Ethylene Glycol to Glycolic acid and Lactic Acid.



Recently, homogeneous iridium- (turn over number, TON up to 28) and ruthenium-catalyzed (TON up to 188) reformation of EG to GA were independently developed by Tang,²⁴ and Milstein,²¹ respectively (Figure 1B). However, the need for sacrificial hydrogen acceptor, scarce noble metals, poor selectivity, and low TON somewhat limits the scope of these reactions.

Contemporarily, the reconstruction of C6 (sorbitol)³⁰ and C3 (glycerol)^{29, 31-34} sources had offered an appealing chemical route for the synthesis of LA (Figure 1B). Nonetheless, low selectivity due to undesired C-C bond cleavage and low atom economy remain the key issues. As an alternative, a dehydrogenative coupling (DHC) between EG and MeOH can be carried out to synthesize this platform molecule. The protocol,

however, comes with the challenge that the catalyst needs to be highly selective for EG and MeOH dehydrogenation and cross-coupling of *in situ* generated glycolaldehyde and formaldehyde. At the same time, the unproductive homo-coupling of aldehydes, overoxidation, esterification, or polymerization of EG must be suppressed. To the best of our knowledge, only one iridium-*N*-heterocyclic carbene complex successfully realized the DHC of EG and MeOH to LA in high yields and selectivities (Figure 1B).²⁵ Nevertheless, the synthesis of LA and also GA from readily available natural resources utilizing non-noble metal catalysts with high yield and selectivity is the need of the hour.^{14, 21-24}

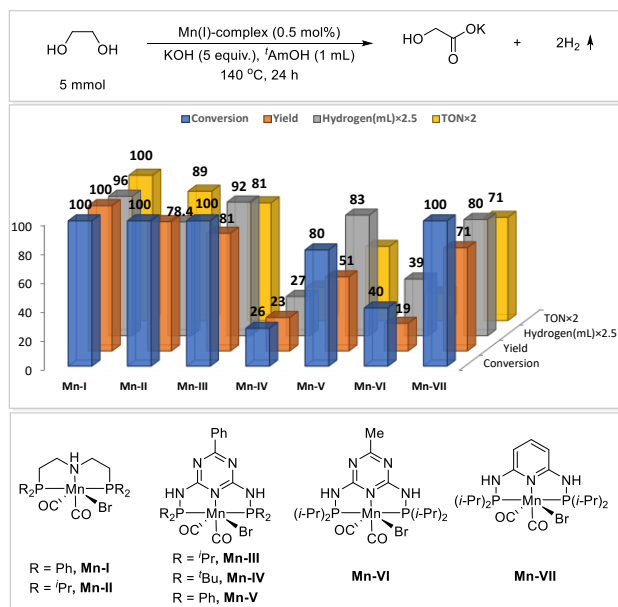
Recently, molecularly defined complexes of the third most abundant metal manganese have emerged as a powerful

catalyst for various hydrogen transfer reactions.³⁵⁻⁴³ In this aspect, several groups, including ours, have also been involved in developing manganese-catalyzed hydrogen transfer mediated acceptorless dehydrogenative coupling and borrowing hydrogenation reactions.⁴⁴⁻⁵³ Manganese catalyzed reformation leading to the generation of value-added products has started gathering keen interest.⁵⁴⁻⁵⁹ In our continuous quest to develop sustainable manganese-based catalytic systems, herein, we report homogeneous manganese(I)-complexes for the reformation of EG to highly demanded GA and LA molecules with the generation of pure hydrogen gas (Figure 1C). Encouragingly, the catalysts operate at a lower temperature and exhibit excellent yields and selectivities for GA and LA, suppressing all possible byproducts, with TON up to 2400 for GA (highest reported till date) and 11,500 for LA, respectively. To the best of our knowledge, manganese-catalyzed reformation of EG to GA and LA has not been reported thus far.

RESULTS AND DISCUSSION

Manganese-catalyzed reformation of EG to GA. For the reformation of EG to GA, we commenced our investigation by screening various bench stable manganese(I)-pincer-complexes **Mn-I** to **Mn-VII** as catalysts. The complexes have previously been utilized for diverse waste-free redox transformations.^{45-46, 60-63} In a typical reaction, 5 mmol of EG was treated with 0.5 mol% of manganese(I)-complex in the presence of KOH in *t*-AmOH at 140 °C (Scheme 1). Progress of the reaction was monitored by measuring the evolved hydrogen.

Scheme 1. Evaluation of Manganese(I)-Complexes for Reformation of EG to GA and Hydrogen.^a



^a Reaction conditions: EG (5 mmol), Mn(I)-complex (0.5 mol%), KOH (25 mmol), *t*-AmOH (1 mL) at 140 °C for 24 h under Ar in a 100 mL reaction tube with sidearm. Conversion, yield, and selectivity were determined by ¹H NMR analysis using sodium acetate as an internal standard. Hydrogen volume was measured using an inverted burette.

Much to our delight, among the tested Mn(I)-complexes, **Mn-I**, stabilized by the ^{Ph}MACHO ligand, gave the highest volume of hydrogen (240 mL, TON >198). ¹H NMR analysis of the reaction mixture indicated complete conversion of EG and exclusive formation of glycolate (>99% yield). Although **Mn-II**, **Mn-III**, and **Mn-VII** resulted in full conversion of EG, the selectivity for GA was measured to be slightly less (up to 89% yield and TON = 178). Complexes **Mn-IV** with a bulky ^{Bu} phosphine ligand and **Mn-VI** were noticed to be less active for this reaction (up to 23% yield and TON = 46).

Encouraged by these promising results, we screened various reaction parameters to improve the reaction's efficiency (Table 1). Monitoring the reaction time indicated that the reaction was completed at 9h (Entries 1-3). The use of bases other than KOH was found to be detrimental to the reaction (entries 4-5). The equivalency of the base used was also crucial, and lowering the equivalency resulted in a decrease in the yield (entries 6-7). The reaction was susceptible to *t*-AmOH as other mediums performed poorly (entries 8-9). Notably, the reaction was also found to proceed smoothly at 130 °C without compromising yield and selectivity (entry 10). Control experiments demonstrated the importance of the catalyst and base (entries 11-12). Further details of reaction optimization are tabulated in Tables S1-S5.

Table 1. Optimization Studies for the Mn-I Catalyzed Reformation of EG to GA.^a

$\text{HOCH}_2\text{CH}_2\text{OH} \xrightarrow[\text{base, Solvent}]{\text{Mn-I (0.04 - 0.5 mol\%)}} \text{HOCH}_2\text{COOK} + 2\text{H}_2 \uparrow$ 130 - 140 °C, 6 - 24 h						
Entry	Solvent	Base (x equiv.)	Time (h)	Yield (GA)	Hydrogen (mL)	TON (GA)
1	<i>t</i> -AmOH	KOH (5)	24	>99%	240	>198
2	<i>t</i> -AmOH	KOH (5)	6	82%	192	164
3	<i>t</i> -AmOH	KOH (5)	9	>99%	230	>198
4	<i>t</i> -AmOH	NaOH (5)	9	15%	179	30
5	<i>t</i> -AmOH	Ba(OH) ₂ ·8H ₂ O (5)	9	n.d.	n.d.	n.d.
6	<i>t</i> -AmOH	KOH (4)	9	98%	208	196
7	<i>t</i> -AmOH	KOH (3)	9	61%	130	122
8	THF	KOH (5)	9	10%	25	20
9	toluene	KOH (5)	9	n.d.	n.d.	n.d.
10 ^b	<i>t</i> -AmOH	KOH (5)	9	>99%	235	>198
11	<i>t</i> -AmOH	-	9	n.d.	n.d.	n.d.
12 ^c	<i>t</i> -AmOH	KOH (5)	9	n.d.	n.d.	n.d.
13 ^d	<i>t</i> -AmOH	KOH (5)	12	96%	925	2400

^a Reaction conditions: EG (5 mmol), **Mn-I** (0.5 mol%), base, solvent (1 mL) at 140 °C for 6-24 h under Ar in a 100 mL reaction tube with a sidearm. Conversion, yield, and selectivity were determined by ¹H NMR analysis using sodium acetate as an internal standard. Hydrogen volume was measured using an inverted burette. ^b At 130 °C. ^c No catalyst. ^d EG (20 mmol), **Mn-I** (0.04 mol%), *t*-AmOH (4 mL) for 12 h at 140 °C under Ar. n.d. = not determined.

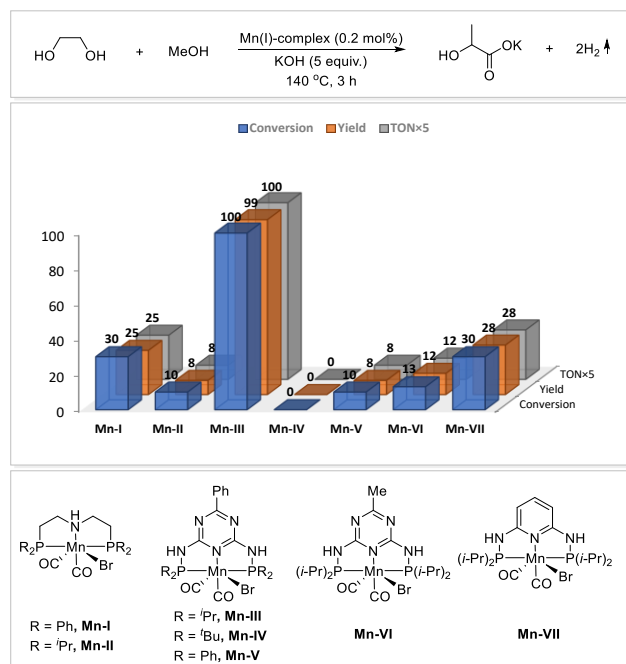
Pleasingly, a scale-up reaction with 0.04 mol% loading of **Mn-I** gave GA in 96% yield with the generation of 0.93 L of hydrogen reaching a TON of 2400 (Table 1, entry 13). To the best of our knowledge, it represents the highest TON for the EG reformation to GA reported to date using a molecularly defined metal complex. Notably, the gas chromatography analysis of the evolved gas showed that the pure hydrogen was evolved (SI, Section 11.13). It thus provides the possibility of being used as a clean energy source. Any further scale-up

reaction was not performed due to the limitation of the reaction vessel.

Further, a catalyst recyclability test was performed to test the robustness of **Mn-I** in catalyzing the reformation of EG to GA and hydrogen (SI, section 6). The catalyst was found to be active for three cycles (on 10 mmol of EG run), and a total of 1.3 L of hydrogen evolution was observed over a period of 72 h. After three cycles, the catalytic activity decreased.

Manganese-catalyzed dehydrogenative coupling of EG and MeOH for the synthesis of LA. We next extended the protocol towards synthesizing LA by the dehydrogenative coupling of EG and MeOH. For the DHC reaction, 5 mmol of EG was treated with 0.2 mol% of the previously used manganese(I)-complexes and KOH in MeOH at 140 °C (Scheme 2). Gratifyingly, amongst the different manganese(I)-complexes tested, (ⁱPrPN⁵P)Mn(I)-complex **Mn-III** with a triazine backbone gave a quantitative lactate yield (TON = 495). Other tested manganese complexes **Mn-I**, **Mn-II**, and **Mn-IV** – **Mn-VII**, which were efficient for EG reformation to GA, were found to be ineffective (TON up to 140) under these conditions, elaborating the need for appropriate catalyst design.

Scheme 2. Evaluation of Manganese(I)-Complexes for the Dehydrogenative Coupling of EG and MeOH to Yield LA.^a



^a Reaction conditions: EG (5 mmol), Mn(I)-complex (0.2 mol%), KOH (25 mmol), MeOH (4 mL) at 140 °C for 3 h under Ar in a 15 mL Schlenk tube. Conversion, yield, and selectivity were determined by ^1H NMR analysis using sodium acetate as an internal standard.

With the suitable manganese(I)-catalyst in hand, we then screen other reaction conditions to optimize the LA production (Table 2). The reaction was found to be sensitive to bases. Besides KOH, other bases performed poorly under these conditions (entries 1-4). Lowering the equivalency of KOH also made the reaction sluggish and led to a slightly diminished yield of the desired product (entries 5-6). The MeOH equivalency was then varied. Notably, it was found that up to 5

equivalent of MeOH gives a quantitative yield of lactate (entries 7-9). A slightly lower conversion and yield were obtained when 2.5 equivalent of MeOH was used (entry 10). Controlled reactions in the absence of either the base or the catalyst resulted in no consumption of the EG, thereby stressing the need for both (entries 11-12).

Inspired by these promising results, we have lowered the catalyst concentration to boost the LA production. When a six-fold lower loading of **Mn-I** was used, a TON 3030 with a high turnover frequency TOF = 1010 h⁻¹ was reached with maintaining high selectivity for LA (entry 13). Notably, lowering the catalyst loading to as low as 195 ppm also gave the desired product in a high 97% yield with TON = 11,500 within 72 h (entry 14).

Table 2. Optimization Studies for the Mn-III Catalyzed LA Synthesis via DHC of EG and MeOH.^a

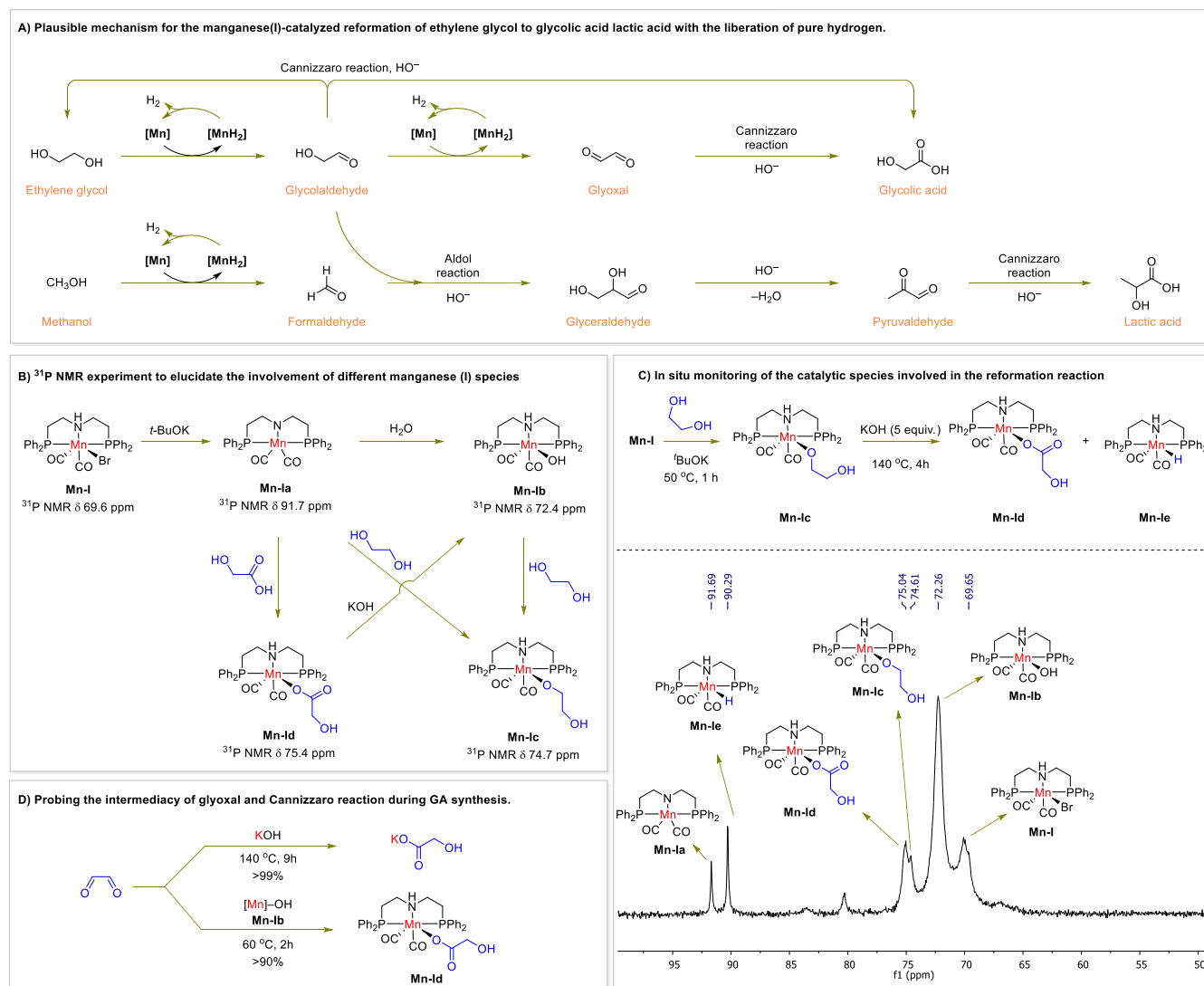
$\text{HO-CH}_2\text{-CH}_2\text{-OH} + \text{MeOH} \xrightarrow[\text{base, 140 }^{\circ}\text{C, 3-72 h}]{\text{Mn-III (0.008-0.2 mol\%)}} \text{HO-CH}_2\text{-COOH} + 2\text{H}_2\uparrow$							
Entry	MeOH equiv.	Base (x equiv.)	Time (h)	Conversion (EG)	Yield (LA)	TON (LA)	
1	20	KOH (5)	3	100%	99%	495	
2	20	NaOH (5)	3	6%	4%	20	
3	20	Ca(OH) ₂ (5)	3	16%	5%	25	
4	20	Ba(OH) ₂ ·8H ₂ O (5)	3	n.d.	n.d.	n.d.	
5	20	KOH (4)	3	87%	81%	405	
6	20	KOH (3)	3	85%	76%	380	
7	15	KOH (5)	3	100%	99%	495	
8	10	KOH (5)	3	100%	99%	495	
9	5	KOH (5)	3	100%	99%	495	
10	2.5	KOH (5)	3	96%	77%	375	
11	5	-	3	n.d.	n.d.	n.d.	
12 ^b	5	KOH (5)	3	n.d.	n.d.	n.d.	
13 ^c	5	KOH (5)	3	100%	99%	3030	
14 ^d	5	KOH (5)	72	93%	92%	11,500	

^a Reaction conditions: EG (5 mmol), **Mn-III** (0.2 mol%), KOH (25 mmol), MeOH (1 mL) for 3 h at 140 °C under Ar. Conversion, yield, and selectivity were determined by ^1H NMR analysis using sodium acetate as an internal standard. ^b No catalyst, ^c **Mn-III** (0.033 mol%). ^d EG (20 mmol), **Mn-III** (0.008 mol%, 195 ppm), MeOH (4 mL) for 72 h.

Mechanistic studies. A plausible working model for the reformation of EG to GA and LA with pure hydrogen production is depicted in Scheme 3A.^{24, 32} Ethylene glycol dehydrogenation occurs in the presence of manganese catalysts leading to the formation of glycolaldehyde with the liberation of hydrogen. In the absence of methanol, glycolaldehyde will undergo another cycle of dehydrogenation, leading to glyoxal formation. Subsequently, intramolecular Cannizzaro reaction of the *in-situ* generated glyoxal under basic conditions leads to the formation of the glycolate product. Alternatively, glycolaldehyde could also be converted to glycolate *via* an intermolecular Cannizzaro reaction.

A set of control and mechanistic experiments were then carried out to get inside the reformation reaction. Initially, several ^{31}P NMR experiments were performed to elucidate the involvement of relevant manganese intermediates in the reaction (Scheme 3B, SI Section 11.3). Treatment of the manganese precatalyst, **Mn-I** with base leads to the formation of Mn(I)-amido complex **Mn-Ia** following dehydrobromination.⁶⁴ **Mn-Ia** on treatment with excess water and ethylene

Scheme 3. A Plausible Mechanism for Reformation of Ethylene Glycol to Glycolic acid and Lactic Acid and Mechanistic Studies.



glycol forms the Mn(I)-hydroxy complex **Mn-Ib** and the Mn(I)-alkoxy complex **Mn-Ic**, respectively. The synthesis of the complexes similar to **Mn-Ib,c** have previously been reported.⁶⁵ Again, the alkoxy complex **Mn-Ic** was formed when the hydroxide **Mn-Ib** was reacted with excess ethylene glycol. Additionally, the treatment of **Mn-Ia** with GA leads to the formation of Mn(I)-glycolato complex **Mn-Id**. When treated with an excess amount of KOH, the latter liberates the hydroxide complex **Mn-Ib** and potassium glycolate.

We believe that the ethylene glycol dehydrogenation reaction occurred *via* the intermediacy of the alkoxy intermediate **Mn-Ic**, formed directly from the amido complex **Mn-Ia** or *via* the hydroxide **Mn-Ib** (Scheme 3B). To elucidate the involvement of the alkoxy complex **Mn-Ic**, we have generated it *in situ* from **Mn-I** by treating it with base and EG. When thus formed, **Mn-Ic** was reacted with an excess KOH at 140 °C for 4 h, we have observed the formation of manganese(I)-glycolato **Mn-Id** and the manganese(I)-hydride **Mn-Ie** along with the intermediates **Mn-Ia,b** (Scheme 3C). Additionally, the above experiments (Scheme 3B,C) highlight the existence of the complexes **Mn-Ia-e** in solution during the catalysis.

Furthermore, the alkoxy complex **Mn-Ic** was synthesized separately and used for catalytic and stoichiometric EG reformation reactions (SI, Section 11.8-11.10). Under these conditions, 95% and 93% yields of GA, respectively, were obtained. It further suggested the intermediacy of **Mn-Ic**. Moreover, independently synthesized the manganese(I)-hydroxide **Mn-Ib** could also catalyze the reformation reaction in similar efficiencies (71% yield, SI section 11.12), suggesting its intermediacy during the reaction.

Kinetics studies for the **Mn-I** catalyzed EG reformation to GA were then performed to shed more light on the mechanism (See SI, Section 11.6). The hydrogen evolution over time was measured using an inverted burette to determine the initial rates. For the reaction performed at $[\text{EG}] = 1.67 \text{ M}$, $[\text{KOH}] = 8.33 \text{ M}$, the initial rate for the hydrogen evolution was found to increase linearly with the increasing concentration of **Mn-I** (0.005-0.01 M), indicating the first-order kinetics. Different initial concentrations of EG (1.67-6.67 M) were noticed to impart minimal effect on the reaction rate. This suggested that the **Mn-I** catalyzed dehydrogenation of ethylene glycol is a fast and facile step and might not contribute to the overall

reaction rate. Notably, when the reaction was conducted with the varying initial concentration of KOH (8.33–13.3 M), the reaction was found to be second-order with [KOH]. This indicated the executive role of the base during the ethylene glycol dehydrogenation and Cannizzaro reaction.

To probe the intermediacy of glyoxal and base-mediated Cannizzaro reaction, we have studied the reactions of glyoxal with KOH, and 99% yield of potassium glycolate was observed in 9h (Scheme 3D, SI, section 11.1). A similar reaction, when performed with the Mn(I)-hydroxide **Mn-1b**, formation of manganese glycolate **Mn-1d**, was noticed in >90% yield (Scheme 3D, SI section 11.4.3). During the catalysis, **Mn-1d** might be converted to manganese(I)-hydroxide **Mn-1b** and potassium glycolate in the presence of KOH to close the cycle. The conversion of **Mn-1d** to **Mn-1b** and potassium glycolate was observed as discussed earlier (Scheme 3B).

Furthermore, the EG reformation reaction rates were measured at different reaction temperatures (120 to 140 °C, SI Section 11.7). From the Eyring analysis, we have calculated overall barrier $\Delta G^\ddagger_{(298)} = 103.7 \text{ kJ mol}^{-1}$ with $\Delta H^\ddagger = +62.4 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -138.6 \text{ J mol}^{-1} \text{ K}^{-1}$. The negative value of entropy of activation suggested the involvement of the associative pathway.

During the LA synthesis *via* DHC reaction in the presence of MeOH, both EG and MeOH undergo dehydrogenation to the glycolaldehyde and formaldehyde, respectively, with the liberation of hydrogen (Scheme 3A). In this regard, **Mn-III** mediated dehydrogenation of MeOH to formaldehyde has previously been reported.^{61,66} A cross-aldol condensation of *in situ* generated glycolaldehyde and formaldehyde in the presence of a base gives glyceraldehyde. Subsequent dehydration of the glyceraldehyde results in pyruvaldehyde, which undergoes intramolecular Cannizzaro reaction under alkaline conditions, leading to the formation of LA.

CONCLUSION

A sustainable approach to synthesizing two valuable platform molecules, glycolic acid, and lactic acid, from readily available renewable resource ethylene glycol has been disclosed. The reformation has been carried out using Earth-abundant transition metal catalysts. A high TON and selectivity for the synthesis of both GA and LA were obtained. Pure hydrogen gas is liberated during the acceptorless reformation process. As a future outlook, we believe that this report will open a new avenue towards sustainably obtaining value-added products and serve as a milestone towards making synthetic chemistry more environment-friendly.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures, analytical and kinetic data, NMR spectra (pdf)

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All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

1. Centi, G.; Santen, v., R.A. *Catalysis for renewables : from feedstock to energy production*. Wiley-VCH: Weinheim, 2007.
2. Trost, B. The atom economy--a search for synthetic efficiency. *Science* **1991**, 254 (5037), 1471-1477.
3. Newhouse, T.; Baran, P. S.; Hoffmann, R. W. The economies of synthesis. *Chem. Soc. Rev.* **2009**, 38 (11), 3010-3021.
4. Goldstein, I. S. *Organic Chemicals from Biomass*. CRC Press: 1981; p 144.
5. Kersten, S.; Van Swaaij, W.; Lefferts, L.; Seshan, K., *Catalysis for renewables: from feedstock to energy production*. 2007.
6. Ragauskas, A. J.; Williams, C. K.; Davison, B. H.; Britovsek, G.; Cairney, J.; Eckert, C. A.; Frederick, W. J.; Hallett, J. P.; Leak, D. J.; Liotta, C. L.; Mielenz, J. R.; Murphy, R.; Templer, R.; Tschaplinski, T. The Path Forward for Biofuels and Biomaterials. *Science* **2006**, 311 (5760), 484-489.
7. Li, C.; Zhao, X.; Wang, A.; Huber, G. W.; Zhang, T. Catalytic Transformation of Lignin for the Production of Chemicals and Fuels. *Chem. Rev.* **2015**, 115 (21), 11559-11624.
8. Klass, D. L. *Biomass for renewable energy, fuels, and chemicals*. Elsevier: 1998.
9. Yue, H.; Zhao, Y.; Ma, X.; Gong, J. Ethylene glycol: properties, synthesis, and applications. *Chem. Soc. Rev.* **2012**, 41 (11), 4218-4244.
10. Wang, A.; Zhang, T. One-Pot Conversion of Cellulose to Ethylene Glycol with Multifunctional Tungsten-Based Catalysts. *Acc. Chem. Res.* **2013**, 46 (7), 1377-1386.
11. Zou, Y.-Q.; von Wolff, N.; Anaby, A.; Xie, Y.; Milstein, D. Ethylene glycol as an efficient and reversible liquid-organic hydrogen carrier. *Nat. Catal.* **2019**, 2 (5), 415-422.
12. J. Kubitschke, H. L., H. Strutz *Carboxylic Acids, Aliphatic in Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH: Weinheim, 2014.
13. Holm, M. S.; Saravanamurugan, S.; Taarning, E. Conversion of Sugars to Lactic Acid Derivatives Using Heterogeneous Zeotype Catalysts. *Science* **2010**, 328 (5978), 602-605.
14. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Makshina, E.; Sels, B. F. Lactic acid as a platform chemical in the biobased

economy: the role of chemocatalysis. *Energy Environ. Sci.* **2013**, *6* (5), 1415-1442.

15. Castillo Martinez, F. A.; Balciunas, E. M.; Salgado, J. M.; Domínguez González, J. M.; Converti, A.; Oliveira, R. P. d. S. Lactic acid properties, applications and production: A review. *Trends Food Sci. Technol.* **2013**, *30* (1), 70-83.

16. Wang, Y. Bioadaptability: An Innovative Concept for Biomaterials. *J. Mater. Sci. Technol.* **2016**, *32* (9), 801-809.

17. Gentile, P.; Chiono, V.; Carmagnola, I.; Hatton, P. V. An Overview of Poly(lactic-co-glycolic) Acid (PLGA)-Based Biomaterials for Bone Tissue Engineering. *Int. J. Mol. Sci.* **2014**, *15* (3), 3640-3659.

18. Glycolic Acid Market-Forecasts from 2018 to 2023. <https://www.researchandmarkets.com/reports/4542547/glycolic-acid-market-forecasts>.

19. Lee, S. Y.; Kim, H. U.; Chae, T. U.; Cho, J. S.; Kim, J. W.; Shin, J. H.; Kim, D. I.; Ko, Y.-S.; Jang, W. D.; Jang, Y.-S. A comprehensive metabolic map for production of bio-based chemicals. *Nat. Catal.* **2019**, *2* (1), 18-33.

20. Prager, L.; Dowideit, P.; Langguth, H.; Schuchmann, H.-P.; von Sonntag, C. Hydrolytic removal of the chlorinated products from the oxidative free-radical-induced degradation of chloroethylenes: acid chlorides and chlorinated acetic acids. *J. Chem. Soc., Perkin Trans. 2* **2001**, (9), 1641-1647.

21. Zou, Y.-Q.; von Wolff, N.; Rauch, M.; Feller, M.; Zhou, Q.-Q.; Anaby, A.; Diskin-Posner, Y.; Shimon, L. J. W.; Avram, L.; Ben-David, Y.; Milstein, D. Homogeneous Reforming of Aqueous Ethylene Glycol to Glycolic Acid and Pure Hydrogen Catalyzed by Pincer-Ruthenium Complexes Capable of Metal-Ligand Cooperation. *Chem. Eur. J.* **2021**, *27* (14), 4715-4722.

22. Trincado, M.; Kühlein, K.; Grützmacher, H. Metal-Ligand Cooperation in the Catalytic Dehydrogenative Coupling (DHC) of Polyalcohols to Carboxylic Acid Derivatives. *Chem. Eur. J.* **2011**, *17* (42), 11905-11913.

23. van Haasterecht, T.; van Deelen, T. W.; de Jong, K. P.; Bitter, J. H. Transformations of polyols to organic acids and hydrogen in aqueous alkaline media. *Catal. Sci. Tech.* **2014**, *4* (8), 2353-2366.

24. Zhan, Y.; Hou, W.; Li, G.; Shen, Y.; Zhang, Y.; Tang, Y. Oxidant-Free Transformation of Ethylene Glycol toward Glycolic Acid in Water. *ACS Sustainable Chem. Eng.* **2019**, *7* (21), 17559-17564.

25. Wu, J.; Shen, L.; Chen, Z.-N.; Zheng, Q.; Xu, X.; Tu, T. Iridium-Catalyzed Selective Cross-Coupling of Ethylene Glycol and Methanol to Lactic Acid. *Angew. Chem. Int. Ed.* **2020**, *59* (26), 10421-10425.

26. Cortright, R. D.; Davda, R. R.; Dumesic, J. A. Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature* **2002**, *418* (6901), 964-967.

27. Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. Raney Ni-Sn Catalyst for H₂ Production from Biomass-Derived Hydrocarbons. *Science* **2003**, *300* (5628), 2075-2077.

28. Morton, D.; Cole-Hamilton, D. J. Molecular hydrogen complexes in catalysis: highly efficient hydrogen production from alcoholic substrates catalysed by ruthenium complexes. *J. Chem. Soc. Chem. Commun.* **1988**, (17), 1154-1156.

29. Li, Y.; Nielsen, M.; Li, B.; Dixneuf, P. H.; Junge, H.; Beller, M. Ruthenium-catalyzed hydrogen generation from glycerol and selective synthesis of lactic acid. *Green Chem.* **2015**, *17* (1), 193-198.

30. Manas, M. G.; Campos, J.; Sharninghausen, L. S.; Lin, E.; Crabtree, R. H. Selective catalytic oxidation of sugar alcohols to lactic acid. *Green Chem.* **2015**, *17* (1), 594-600.

31. Lu, Z.; Demianets, I.; Hamze, R.; Terrile, N. J.; Williams, T. J. A Prolific Catalyst for Selective Conversion of Neat Glycerol to Lactic Acid. *ACS Catal.* **2016**, *6* (3), 2014-2017.

32. Sharninghausen, L. S.; Campos, J.; Manas, M. G.; Crabtree, R. H. Efficient selective and atom economic catalytic conversion of glycerol to lactic acid. *Nat. Commun.* **2014**, *5* (1), 5084.

33. Sharninghausen, L. S.; Mercado, B. Q.; Crabtree, R. H.; Hazari, N. Selective conversion of glycerol to lactic acid with iron pincer precatalysts. *Chem. Commun.* **2015**, *51* (90), 16201-16204.

34. Sun, Z.; Liu, Y.; Chen, J.; Huang, C.; Tu, T. Robust Iridium Coordination Polymers: Highly Selective, Efficient, and Recyclable Catalysts for Oxidative Conversion of Glycerol to Potassium Lactate with Dihydrogen Liberation. *ACS Catal.* **2015**, *5* (11), 6573-6578.

35. Maji, B.; Barman, M. K. Recent Developments of Manganese Complexes for Catalytic Hydrogenation and Dehydrogenation Reactions. *Synthesis* **2017**, *49* (15), 3377-3393.

36. Gorgas, N.; Kirchner, K. Isoelectronic Manganese and Iron Hydrogenation/Dehydrogenation Catalysts: Similarities and Divergences. *Acc. Chem. Res.* **2018**, *51* (6), 1558-1569.

37. Mukherjee, A.; Milstein, D. Homogeneous Catalysis by Cobalt and Manganese Pincer Complexes. *ACS Catal.* **2018**, *8* (12), 11435-11469.

38. Hu, Y.; Wang, C. Manganese-Catalyzed C-H Olefination Reactions. *ChemCatChem* **2019**, *11* (4), 1167-1174.

39. Waiba, S.; Maji, B. Manganese Catalyzed Acceptorless Dehydrogenative Coupling Reactions. *ChemCatChem* **2020**, *12* (7), 1891-1902.

40. Das, K.; Barman, M. K.; Maji, B. Advancements in multifunctional manganese complexes for catalytic hydrogen transfer reactions. *Chem. Commun.* **2021**.

41. Maji, M.; Panja, D.; Borthakur, I.; Kundu, S. Recent advances in sustainable synthesis of N-heterocycles following acceptorless dehydrogenative coupling protocol using alcohols. *Org. Chem. Front* **2021**, *8* (11), 2673-2709.

42. Wang, Y.; Wang, M.; Li, Y.; Liu, Q. Homogeneous manganese-catalyzed hydrogenation and dehydrogenation reactions. *Chem* **2021**, *7* (5), 1180-1223.

43. Filonenko, G. A.; van Putten, R.; Hensen, E. J. M.; Pidko, E. A. Catalytic (de)hydrogenation promoted by non-precious metals – Co, Fe and Mn: recent advances in an emerging field. *Chem. Soc. Rev.* **2018**, *47* (4), 1459-1483.

44. Chakraborty, S.; Das, U. K.; Ben-David, Y.; Milstein, D. Manganese Catalyzed α -Olefination of Nitriles by Primary Alcohols. *J. Am. Chem. Soc.* **2017**, *139* (34), 11710-11713.

45. Peña-López, M.; Piehl, P.; Elangovan, S.; Neumann, H.; Beller, M. Manganese-Catalyzed Hydrogen-Autotransfer C-C Bond Formation: α -Alkylation of Ketones with Primary Alcohols. *Angew. Chem. Int. Ed.* **2016**, *55* (48), 14967-14971.

46. Mukherjee, A.; Nerush, A.; Leitus, G.; Shimon, L. J. W.; Ben David, Y.; Espinosa Jalapa, N. A.; Milstein, D. Manganese-Catalyzed Environmentally Benign Dehydrogenative Coupling of Alcohols and Amines to Form Aldimines and H₂: A Catalytic and Mechanistic Study. *J. Am. Chem. Soc.* **2016**, *138* (13), 4298-4301.

47. Elangovan, S.; Neumann, J.; Sortais, J.-B.; Junge, K.; Darcel, C.; Beller, M. Efficient and selective N-alkylation of amines with alcohols catalysed by manganese pincer complexes. *Nat. Commun.* **2016**, *7*, 12641.

48. Barman, M. K.; Waiba, S.; Maji, B. Manganese-Catalyzed Direct Olefination of Methyl-Substituted Heteroarenes with Primary Alcohols. *Angew. Chem. Int. Ed.* **2018**, *57* (29), 9126-9130.

49. Jana, A.; Reddy, C. B.; Maji, B. Manganese Catalyzed α -Alkylation of Nitriles with Primary Alcohols. *ACS Catal.* **2018**, *8* (10), 9226-9231.

50. Das, K.; Kumar, A.; Jana, A.; Maji, B. Synthesis and characterization of N,N-chelate manganese complexes and applications in CN coupling reactions. *Inorg. Chim. Acta* **2020**, *502*, 119358.

51. Jana, A.; Das, K.; Kundu, A.; Thorve, P. R.; Adhikari, D.; Maji, B. A Phosphine-Free Manganese Catalyst Enables

Stereoselective Synthesis of (1 + n)-Membered Cycloalkanes from Methyl Ketones and 1,n-Diols. *ACS Catal.* **2020**, *10* (4), 2615-2626.

52. Waiba, S.; Jana, S. K.; Jati, A.; Jana, A.; Maji, B. Manganese complex-catalysed α -alkylation of ketones with secondary alcohols enables the synthesis of β -branched carbonyl compounds. *Chem. Commun.* **2020**, *56* (60), 8376-8379.

53. Fu, S.; Shao, Z.; Wang, Y.; Liu, Q. Manganese-Catalyzed Upgrading of Ethanol into 1-Butanol. *J. Am. Chem. Soc.* **2017**, *139* (34), 11941-11948.

54. Kar, S.; Goeppert, A.; Kothandaraman, J.; Prakash, G. K. S. Manganese-Catalyzed Sequential Hydrogenation of CO₂ to Methanol via Formamide. *ACS Catal.* **2017**, *7* (9), 6347-6351.

55. Ryabchuk, P.; Stier, K.; Junge, K.; Checinski, M. P.; Beller, M. Molecularly Defined Manganese Catalyst for Low-Temperature Hydrogenation of Carbon Monoxide to Methanol. *J. Am. Chem. Soc.* **2019**, *141* (42), 16923-16929.

56. Kaithal, A.; Werlé, C.; Leitner, W. Alcohol-Assisted Hydrogenation of Carbon Monoxide to Methanol Using Molecular Manganese Catalysts. *JACS Au* **2021**, *1* (2), 130-136.

57. Kaithal, A.; Hölscher, M.; Leitner, W. Carbon monoxide and hydrogen (syngas) as a C1-building block for selective catalytic methylation. *Chem. Sci.* **2021**, *12* (3), 976-982.

58. Kaithal, A.; Chatterjee, B.; Werle, C.; Leitner, W. Acceptorless dehydrogenation of methanol to carbon monoxide and hydrogen using molecular catalysts. *Angew. Chem. Int. Ed.* **2021**, *n/a* (n/a).

59. Andérez-Fernández, M.; Vogt, L. K.; Fischer, S.; Zhou, W.; Jiao, H.; Garbe, M.; Elangovan, S.; Junge, K.; Junge, H.; Ludwig, R.; Beller, M. A Stable Manganese Pincer Catalyst for the Selective Dehydrogenation of Methanol. *Angew. Chem. Int. Ed.* **2017**, *56* (2), 559-562.

60. Mastalir, M.; Glatz, M.; Pittenauer, E.; Allmaier, G.; Kirchner, K. Sustainable Synthesis of Quinolines and Pyrimidines Catalyzed by Manganese PNP Pincer Complexes. *J. Am. Chem. Soc.* **2016**, *138* (48), 15543-15546.

61. Deibl, N.; Kempe, R. Manganese-Catalyzed Multicomponent Synthesis of Pyrimidines from Alcohols and Amidines. *Angew. Chem. Int. Ed.* **2017**, *56* (6), 1663-1666.

62. Garbe, M.; Junge, K.; Beller, M. Homogeneous Catalysis by Manganese-Based Pincer Complexes. *Eur. J. Org. Chem.* **2017**, *2017* (30), 4344-4362.

63. Kallmeier, F.; Dudziec, B.; Irrgang, T.; Kempe, R. Manganese-Catalyzed Sustainable Synthesis of Pyrroles from Alcohols and Amino Alcohols. *Angew. Chem. Int. Ed.* **2017**, *56* (25), 7261-7265.

64. Wang, Y.; Zhu, L.; Shao, Z.; Li, G.; Lan, Y.; Liu, Q. Unmasking the Ligand Effect in Manganese-Catalyzed Hydrogenation: Mechanistic Insight and Catalytic Application. *J. Am. Chem. Soc.* **2019**, *141* (43), 17337-17349.

65. Shao, Z.; Wang, Y.; Liu, Y.; Wang, Q.; Fu, X.; Liu, Q. A general and efficient Mn-catalyzed acceptorless dehydrogenative coupling of alcohols with hydroxides into carboxylates. *Org. Chem. Front* **2018**, *5* (8), 1248-1256.

66. Schlagbauer, M.; Kallmeier, F.; Irrgang, T.; Kempe, R. Manganese-Catalyzed β -Methylation of Alcohols by Methanol. *Angew. Chem. Int. Ed.* **2020**, *59* (4), 1485-1490.