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An efficient method to prepare aryl acetates by the carbonylation of aryl methyl ethers or phenols†

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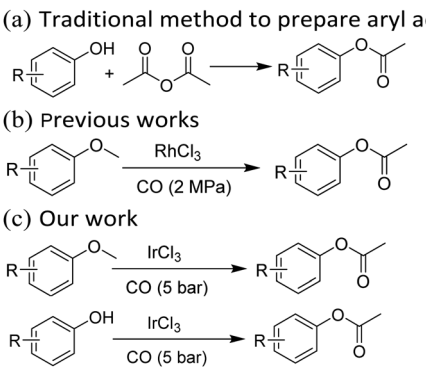
Synthesis of valuable chemicals from lignin based compounds is critical for the application of biomass. Here, we develop a method of preparing aryl acetates by the carbonylation of aryl methyl ethers or phenols under low CO pressure. Good to excellent yields of aryl acetates were obtained using different substrates, and a possible reaction mechanism was proposed by conducting a series of control experiments. This method may provide a potential way for the utilization of lignin.

Introduction

With the depletion of fossil fuels, renewable resources such as biomass are expected to serve as feedstock in the preparation of energy and chemicals.[1] Lignin, consisting of methoxylated phenylpropanoid units, is the only large volume renewable feedstock that comprises aromatics.[2] In consideration of the importance of aromatic compounds in many key commercial chemicals, the transformation of lignin and its derivatives has attracted much attention.[3] However, the utilization of lignin to prepare various valuable chemicals remains challenging because of its natural complexity and notorious inactive properties.[4] In general, two steps need to be performed before the application of lignin: depolymerization of lignin and transformation of depolymerization products into value-added compounds. At present, much attention has been paid to the depolymerization of lignin. Phenols and aryl methyl ethers were obtained in most of the reported processes.[5] Therefore, the conversion of phenols and aryl methyl ethers into valuable chemicals is significant to the emergence of a sustainable industry based on lignin.

Aryl acetates are important intermediates in the pharmaceutical industry. Many functional medicines prepared from aryl acetates are making a significant contribution to the clinic treatment of hepatitis and cholecystitis, and besides, they are also effective in the detection of cancer.[6] Hence, the efficient preparation of aryl acetates is of great importance. In traditional studies, acetic anhydride or acyl halides were used as starting materials in the presence of base (such as NaOH). Such methods are less environmentally friendly and corrosive (Scheme 1a).[7] In 1995, the acylation of anisole with carboxylic acids was reported, HZSM-5 zeolite was used as a catalyst, phenyl carboxylic ester and 4-acyl anisole were obtained at different temperatures.[8] In addition, a new acetylation procedure was developed. Demethylation of aryl methyl ethers with BBr_3 and acetylation of phenols with acetic acid were combined, and this method would be useful in the functional group changing from OMe to OAc.[9] As a cheap and abundant C1 resource, carbon monoxide (CO) has attracted much attention in recent years.[10] However, to the best of our knowledge, there were only a few studies reported on preparing aryl acetates with CO as feedstock. The carbonylation of aryl methyl ethers to synthesise aryl acetates was reported by Mei;[11] LiI and $LiBF_4$ were employed to promote the cleavage of ether bonds, and good yields of aryl acetates were



Scheme 1 Synthesis of aryl acetates.

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obtained. However, to our surprise, the phenolic hydroxyl group was not favorable for the transformation into esters in the current reaction system, although 2 MPa CO was used (Scheme 1b).

Here, we reported a new efficient catalytic system to prepare aryl acetates with good yields using phenols or aryl methyl as the starting materials. The reactions performed quite well at low pressure (5 bar of CO). Compared with the traditional methods, this method may be more economical and environmentally friendly. Considering that the phenolic hydroxyl group and the methoxy group are the main functional groups in the depolymerization products of lignin, the reported method is a potential way to the utilization of lignin.

Experimental

Chemicals

CO (99.99%) was purchased from Nanjing Tianze Co. Ltd, $IrCl_3$ was obtained from Energy Chemical Co. Ltd, and other chemicals were purchased from commercial companies and no further purification was done.

Carbonylation of aryl methyl ethers or phenols

The reaction was carried out in a high-pressure autoclave (50 mL) with a magnetic stirrer. In a typical experiment, 2 mmol aryl methyl ethers or phenols, 2 mol% $IrCl_3$, 5 mol% PPh_3 and 3 mmol CH_3I were loaded into a reactor. Subsequently, the reactor was purged with CO to remove air, and then, CO was charged into an autoclave to 5 bar. Finally, the reactor was heated to 180 °C and stirred for 20 hours. After the reaction, the reactor was cooled to room temperature. Silica gel column chromatography was used to purify the products with petroleum ether and ethyl acetate mixture as the eluent. GC–MS, ^1H and ^{13}C NMR were employed to characterize the products.

Analysis methods

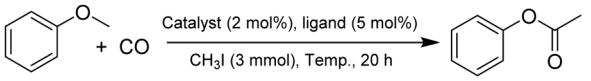
GC-2014 (Shimadzu, Japan) equipped with an RTX-5 column (30 m × 250 μm) was used to determine the yields of the products. GCMS-QP 2030 NX (Shimadzu, Japan) and Bruker Avance II 400 MHz NMR spectrometers were employed to prove the structure of the reaction products.

Results and discussion

Optimization of the reaction conditions

In a first reaction, the carbonylation of anisole to phenylacetate was used as a probe reaction to optimize the conditions (Table 1). Up to 93% yield of phenylacetate can be obtained in the presence of 2 mol% $IrCl_3$ (entry 1). The control reaction in the absence of IrCl3 cannot happen at all (entry 2). The decrease of the reaction temperature was attempted and a lower yield of 47% was obtained at 150 °C (entry 3). In addition, the dosage of $IrCl_3$ was also explored. 82% yield of phenylacetate can be obtained with 1 mol% catalyst (entry 4). The pressure of CO is of great importance to the carbonylation reaction. Hence, the effect of the CO pressure on the yield of phenylacetate was investigated. The higher pressure of CO cannot further increase the yield of phenylacetate. But, there was no phenylacetate generated when the pressure of CO was as low as 1 bar (entries 5 and 6). $CoCl_2$ and $NiCl_2$ were employed to investigate the catalytic performances and the results indicated that both $CoCl_2$ and $NiCl_2$ have no catalytic activity under the standard conditions (entries 7 and 8). The solvent has a remarkable influence on the yield of phenylacetate. MeCN gave the best result among the solvents investigated here (entries 9–13). Additionally, $[Ir(COD)Cl]_2$ was employed to catalyze the reaction; however, there was no clear difference between $IrCl_3$ and $[Ir(COD)Cl]_2$ (entry 14). The ligand is of great importance to change the electron density of the metal. Therefore, the effect of different ligands on the yields of phenylacetate was explored (Fig. 1). The results indicated that PPh_3 was more suitable for

Table 1 Optimization of the reaction conditions[a]



Entry	Catalyst	Solvent	Yield[g]/(%)
1	$IrCl_3$	MeCN	93
2	—	MeCN	0
3[b]	$IrCl_3$	MeCN	47
4[c]	$IrCl_3$	MeCN	82
5[d]	$IrCl_3$	MeCN	93
6[e]	$IrCl_3$	MeCN	0
7	$CoCl_2$	MeCN	0
8	$NiCl_2$	MeCN	0
9	$IrCl_3$	Benzene	88
10	$IrCl_3$	Toluene	86
11	$IrCl_3$	DMF	0
12	$IrCl_3$	1,4-Dioxane	0
13	$IrCl_3$	Heptane	80
14	$[Ir(COD)Cl]_2$	MeCN	92
15[f]	$IrCl_3$	MeCN	17

[a] Standard conditions: 2 mmol anisole, 2 mol% $IrCl_3$ as a catalyst, 5 mL of solvent, 5 mol% PPh_3, 3 mmol CH_3I, 5 bar CO, 180 °C, 20 h. Yields were determined by GC and GC–MS. [b] 150 °C. [c] 1 mol% $IrCl_3$ was used. [d] 10 bar CO. [e] 1 bar CO. [f] 3 mmol HI was used instead of CH_3I. [g] GC yield.

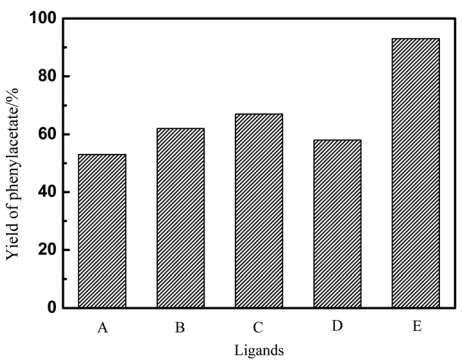


Fig. 1 Yields of phenylacetate catalyzed by $IrCl_3$ with different ligands. Reaction conditions: 2 mmol anisole, 2 mol% $IrCl_3$, 5 mL MeCN, 5 mol% ligand, 3 mmol CH_3I, 5 bar CO, 180 °C, 20 h. (A) No ligand, (B) 2,4,6-collidine, (C) 1,3-bis(diphenylphosphino)propane, (D) 2,2′-bipyridine, and (E) PPh_3.

the preparation of phenylacetate even when only 2 mmol% $IrCl_3$ was used.

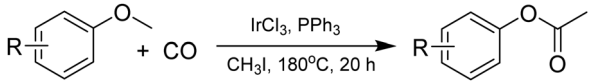
Scope of substrates

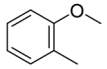
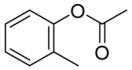
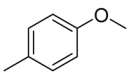
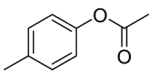
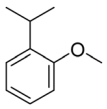
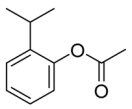
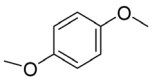
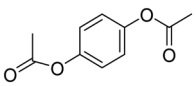
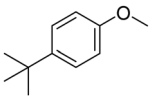
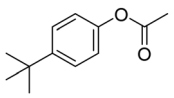
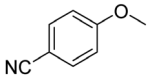
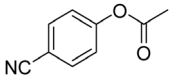
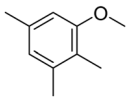
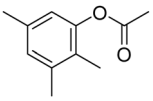
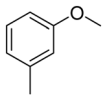
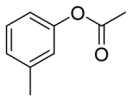
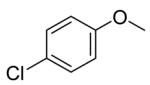
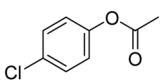
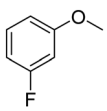
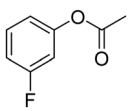
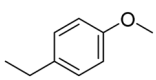
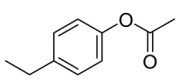
Scope of aryl methyl ethers. With the optimized reaction conditions in hand, a variety of aryl methyl ethers containing different functional groups were employed to investigate the scope of substrates (Table 2). In general, the corresponding aryl acetates were obtained with good to excellent yields. A variety of substituents, such as methyl (entries 1, 2, 7 and 8), isopropyl (entry 3), *tert*-butyl (entry 5), –CN (entry 6) and halogens (entries 9 and 10), were tolerated. The substrates with an electron-donating or an electron-withdrawing group have no significant influence on the yields of the target products.

Scope of phenols

As we all know, the phenolic hydroxyl group is also an important part of lignin. Hence, a variety of phenols with different functional groups were adopted to investigate the reaction of the phenolic hydroxyl group (Table 3). To our delight, the corresponding aryl acetates were obtained with excellent yields. However, compared with using aryl methyl ethers as substrates, CH_3I was consumed to produce aryl acetate when phenols were adopted.

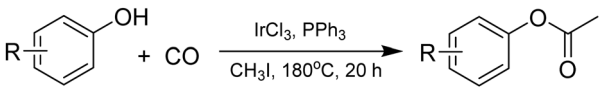
Table 2 Scope of aryl methyl ethers



Entry	Substrates	Products	Yields/(%)
1			90
2			95
3			92
4			78
5			75
6			92
7[a]			65
8			83
9			85
10			78
11			83

Conditions: 2 mmol aryl methyl ethers, 2 mol% $IrCl_3$, 5 mL MeCN, 5 mol% PPh_3, 3 mmol CH_3I, 5 bar CO, 180 °C, 20 h. Isolated yields were reported. [a] Yield was determined by ^1H NMR.

Table 3 Scope of phenols



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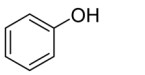
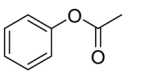
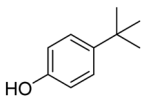
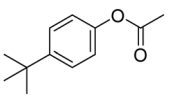
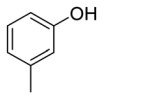
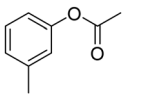
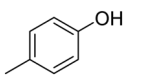
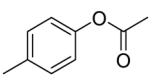
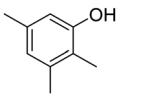
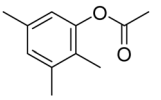
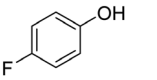
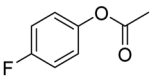
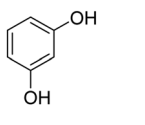
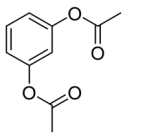
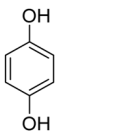
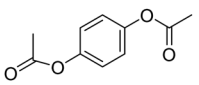
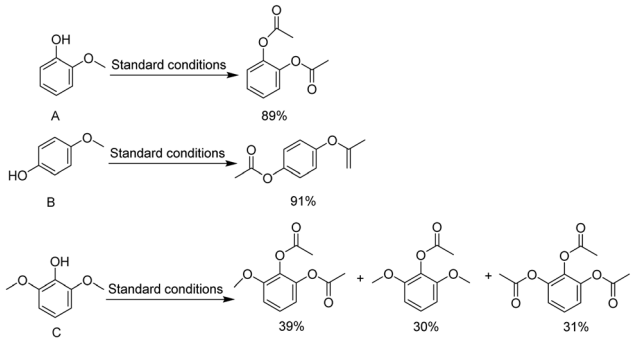
1			95
2			79
3			93
4			91
5[a]			66
6			88
7[b]			73
8[b]			75
9[a]			76
10[a]			57

Conditions: 2 mmol phenols, 2 mol% $IrCl_3$, 5 mL MeCN, 5 mol% PPh_3, 3 mmol CH_3I, 5 bar CO, 180 °C, 20 h. Isolated yields were reported. [a] Yield was determined by ^1H NMR. [b] 1 mmol substrate was used.



Scheme 2 Reactions with the lignin monomers A, B and C.

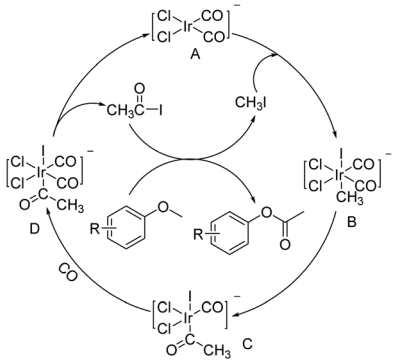


Fig. 2 Proposed mechanism.

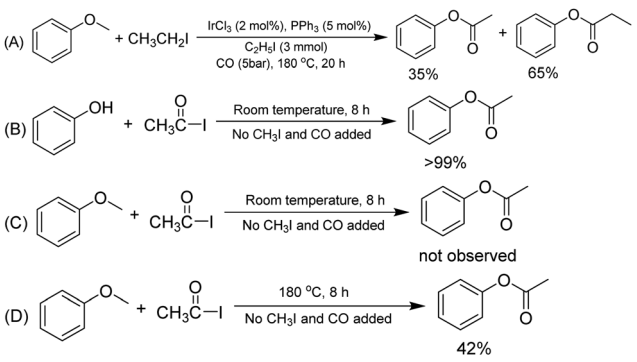
Reactions with lignin monomers

To demonstrate the ability of the catalytic system to promote the conversion from lignin based materials to aryl acetate, the lignin monomers guaiacol (A), 4-methoxyphenol (B) and syringol (C) were investigated in our experiments (Scheme 2). 89% yield of 1,2-phenylene diacetate was obtained when guaiacol was used. Both the phenolic hydroxyl group and the methoxy group can convert to ester at the same time. Compared with guaiacol, a similar result was obtained when 4-methoxyphenol was employed, and 91% yield of the corresponding product was obtained under standard reaction conditions. For the reaction of syringol, there products with a ratio of 39 : 30 : 31 can be obtained. More CH_3I are required if we want to increase the selectivity of the triple-ester product (49% yield of triple-ester product when 5 mmol CH_3I was used).

Reaction mechanism

Several control experiments were performed to gain more mechanistic insight into the reaction pathway. Under standard conditions, 3 mmol of CH_3I was added. In order to confirm the cleavage of ether bonds, iodoethane was added. It was interesting to find that there was still 35% of phenylacetate existing in the reaction solution, and the other product was phenyl propionate. Hence, we can conclude that CH_3I is not consumed in the reaction system. The methoxy group in anisole will transform to CH_3I *in situ* (Scheme 3A). Subsequently, according to the literature reported by Voronkov,[12] acetyl iodide was employed to explore the reaction pathway. When there were no CH_3I and CO in our experiments, phenylacetate was obtained at room temperature with phenol as the substrate (Scheme 3B). However, no phenylacetate was formed at room temperature when anisole was used. When the same reaction was performed at 180 °C, phenylacetate can be produced (Schemes 3C and D). The high dissociation energy of the C–O bond may be responsible for the difference.[13]

Based on the control experiments and previous studies,[14] a possible reaction mechanism was proposed (Fig. 2). $[Ir(CO)_2Cl_2]^-$ was generated *in situ* by the reaction between $IrCl_3$ and CO. The oxidative addition of CH_3I with A happens, which might be the rate-determining step in the carbonylation process. Then, an acetyl group (C) was generated from B with the migration of methyl, and coordination of CO occurred immediately. Subsequently, the complex D underwent reductive elimination to produce the acetyl iodide and catalytic active species A. Finally, acetyl iodide can react with aryl methyl ethers to produce aryl acetate, and CH_3I was regenerated *in situ*.



Scheme 3 Controlled experiments.

Conclusions

In conclusion, we have developed a new catalytic system for the preparation of aryl acetates under low CO pressure. Good to excellent yields of aryl acetates can be obtained with different phenols, aryl methyl ethers and lignin based materials. This method may provide an effective way for the preparation of aryl acetates and the utilization of lignin.

Conflicts of interest

We have no conflicts of interest to declare.

Acknowledgements

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Notes and references

1 (*a*) J. Zakzeski, P. C. A. Bruijnincx, A. L. Jongerius and B. M. Weckhuysen, *Chem. Rev.*, 2010, **110**, 3552–3599; (*b*) X. Wu, W. Jiao, B. Z. Li, Y. M. Li, Y. H. Zhang, Q. R. Wang and T. Yi, *Chin. J. Catal.*, 2017, **38**, 1216–1228; (*c*) W. Schutyser, T. Renders, S. Van den Bosch, S. F. Koelewijn, G. T. Beckham and B. F. Sels, *Chem. Soc. Rev.*, 2018, **47**(3), 852–908; (*d*) W. Lan, M. T. Amiri, C. M. Hunston and J. S. Luterbacher, *Angew. Chem., Int. Ed.*, 2018, **57**(5), 1356–1360; (*e*) R. A. Sheldon, *Green Chem.*, 2016, **18**(11), 3180–3183; (*f*) X. W. Liu, H. Y. Zhang, C. L. Wu, Z. H. Liu, Y. Chen, B. Yu and Z. M. Liu, *New J. Chem.*, 2018, **42**(2), 1223–1227.

2 (*a*) C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon and M. Poliakoff, *Science*, 2012, **337**, 695–699; (*b*) Y. Jing, L. Dong, Y. Guo, X. Liu and Y. Wang, *ChemSusChem*, 2020, **13**, 1–19; (*c*) M. Wang and F. Wang, *Adv. Mater.*, 2019, **31**(50), e1901866; (*d*) Y. S. Guan, W. Zhao, K. S. Liu, T. T. Guo, D. K. Wang, M. Y. Cui, S. Y. Fu, X. Fan and X. Y. Wei, *New J. Chem.*, 2020, **44**(34), 14411–14420.

3 (*a*) J. G. Zhang, L. Lombardo, G. Gozaydin, P. J. Dyson and N. Yan, *Chin. J. Catal.*, 2018, **39**(9), 1445–1452; (*b*) H. Wu, J. Song, C. Xie, C. Wu, C. Chen and B. Han, *ACS Sustainable Chem. Eng.*, 2018, **6**(3), 2872–2877; (*c*) H. Wang, Y. F. Zhao, Z. G. Ke, B. Yu, R. P. Li, Y. Y. Wu, Z. P. Wang, J. J. Han and Z. M. Liu, *Chem. Commun.*, 2019, **55**, 3069–3072.

4 (*a*) Q. Song, J. Y. Cai, J. J. Zhang, W. Q. Yu, F. Wang and J. Xu, *Chin. J. Catal.*, 2013, **34**(4), 651–658; (*b*) P. J. Deuss and K. Barta, *Coord. Chem. Rev.*, 2016, **306**, 510–532; (*c*) C. Zhang and F. Wang, *Acc. Chem. Res.*, 2020, **53**(2), 470–484; (*d*) C. J. Cooper, S. Alam, V. D. P. N. Nziko, R. C. Johnston, A. S. Ivanov, Z. Mou, D. B. Turpin, A. W. Rudie, T. J. Elder, J. J. Bozell and J. M. Parks, *ACS Sustainable Chem. Eng.*, 2020, **8**(18), 7225–7234.

5 (*a*) C. Chio, M. Sain and W. Qin, *Renewable Sustainable Energy Rev.*, 2019, **107**, 232–249; (*b*) S. Song, J. Zhang, G. Gozaydin and N. Yan, *Angew. Chem., Int. Ed.*, 2019, **58**(15), 4934–4937; (*c*) P. Asawaworarit, P. Daorattanachai, W. Laosiripojana, C. Sakdaronnarong, A. Shotipruk and N. Laosiripojana, *Chem. Eng. J.*, 2019, **356**, 461–471; (*d*) X. Wu, X. Fan, S. Xie, J. Lin, J. Cheng, Q. Zhang, L. Chen and Y. Wang, *Nat. Catal.*, 2018, **1**(10), 772–780; (*e*) L. Shuai, M. T. Amiri, Y. M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph and J. S. Luterbacher, *Science*, 2016, **354**, 329–333; (*f*) A. Rahimi, A. Ulbrich, J. J. Coon and S. S. Stahl, *Nature*, 2014, **515**, 249–252; (*g*) C. S. Lancefield, O. S. Ojo, F. Tran and N. J. Westwood, *Angew. Chem., Int. Ed.*, 2015, **54**(1), 258–262; (*h*) Y. Xu, Z. F. Peng, Y. X. Yu, D. L. Wang, J. G. Liu, Q. Zhang and C. G. Wang, *New J. Chem.*, 2020, **44**(13), 5088–5096.

6 (*a*) D. Samid, Z. Ram, W. R. Hudgins, S. Shack, L. Liu, S. Walbridge, E. H. Oldfield and C. E. Myers, *Cancer Res.*, 1994, **54**(4), 891–895; (*b*) R. van Putten, E. A. Uslamin, M. Garbe, C. Liu, A. Gonzalez-de-Castro, M. Lutz, K. Junge, E. J. M. Hensen, M. Beller, L. Lefort and E. A. Pidko, *Angew. Chem., Int. Ed.*, 2017, **56**(26), 7531–7534.

7 Z. Liu, Q. Ma, Y. Liu and Q. Wang, *Org. Lett.*, 2014, **16**(1), 236–239.

8 Q. L. Wang, Y. Ma, X. Ji, H. Yan and Q. Qiu, *J. Chem. Soc., Chem. Commun.*, 2015, **22**, 2307–2308.

9 H. T. Balaydin, *J. Chem. Res.*, 2012, **36**, 238–240.

10 (*a*) K. Y. Ye, G. Kehr, C. G. Daniliuc, L. Liu, S. Grimme and G. Erker, *Angew. Chem., Int. Ed.*, 2016, **55**(32), 9216–9219; (*b*) H. R. Sharpe, A. M. Geer, L. J. Taylor, B. M. Gridley, T. J. Blundell, A. J. Blake, E. S. Davies, W. Lewis, J. McMaster, D. Robinson and D. L. Kays, *Nat. Commun.*, 2018, **9**(1), 3757; (*c*) Y. Pang, J. Li, Z. Wang, C. S. Tan, P. L. Hsieh, T. T. Zhuang, Z. Q. Liang, C. Zou, X. Wang, P. De Luna, J. P. Edwards, Y. Xu, F. Li, C. T. Dinh, M. Zhong, Y. Lou, D. Wu, L. J. Chen, E. H. Sargent and D. Sinton, *Nat. Catal.*, 2019, **2**(3), 251–258; (*d*) Y. Shi, J. Wang, Z. Y. Zhang, Y. Gao, C. N. Hao, X. Y. Xia and Q. Gu, *Nat. Commun.*, 2016, **7**(1), 13789; (*e*) K. Cai, S. Huang, Y. Li, Z. Cheng, J. Lv and X. Ma, *ACS Sustainable Chem. Eng.*, 2019, **7**(2), 2027–2034; (*f*) G. M. Yee, M. A. Hillmyer and I. A. Tonks, *ACS Sustainable Chem. Eng.*, 2018, **6**(8), 9579–9584.

11 Q. Q. Mei, Y. D. Yang, H. Y. Liu, S. P. Li, H. Z. Liu and B. X. Han, *Sci. Adv.*, 2018, **4**(5), eaaq0266.

12 M. G. Voronkov, A. A. Trukhina and N. N. Vlasova, *Russ. J. Org. Chem.*, 2002, **38**(11), 1579–1581.

13 (*a*) J. He, C. Zhao, D. Mei and J. A. Lercher, *J. Catal.*, 2014, **309**, 280–290; (*b*) M. C. Haibach, N. Lease and A. S. Goldman, *Angew. Chem., Int. Ed.*, 2014, **53**(38), 10160–10163; (*c*) M. Wang, Y. Zhao, D. Mei, R. M. Bullock, O. Y. Gutierrez, D. M. Camaioni and J. A. Lercher, *Angew. Chem., Int. Ed.*, 2020, **59**(4), 1445–1449.

14 (*a*) A. Haynes, P. M. Maitlis, G. E. Morris, G. J. Sunley, H. Adams, P. W. Badger, C. M. Bowers, D. B. Cook, P. I. P. Elliott, T. Ghaffar, H. Green, T. R. Griffin, M. Payne, J. M. Pearson, M. J. Taylor, P. W. Vickers and R. J. Watt, *J. Am. Chem. Soc.*, 2004, **126**, 2847–2861; (*b*) A. Haynes, A. J. H. M. Meijer, J. R. Lyons and H. Adams, *Inorg. Chem.*, 2009, **48**, 28–35; (*c*) Q. Mei, H. Liu, X. Shen, Q. Meng, H. Liu, J. Xiang and B. Han, *Angew. Chem., Int. Ed.*, 2017, **56**(47), 14868–14872.