Supplementary Materials

$ZrOCl_2$ as bifunctional and in-situ precursor materials for catalytic hydrogen transfer of bio-based carboxides

Jian He [a,b], Yufei Xu [b], Zhaozhuo Yu [b], Hu Li [b, *], Wenfeng Zhao [b], Hongguo Wu [b], Song Yang [b, *]

[a] *Key Laboratory of Hunan Forest Products and Chemical Industry Engineering, Jishou University, Zhangjiajie, 427000, PR China*

[b] *State Key Laboratory Breeding Base of Green Pesticide & Agricultural Bioengineering, Key Laboratory of Green Pesticide & Agricultural Bioengineering, Ministry of Education, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, Center for Research & Development of Fine Chemicals, Guizhou University, Guiyang, Guizhou 550025, China.*

Figure and Table captions:

Figure S1 GC spectra of reaction mixture (from FAOL-to-GVL conversion) obtained from different metal salts at 180 °C for 6 h.

Figure S2 Effect of reaction solvent on the tandem synthesis of GVL from FAOL. Reaction conditions: 2 mmol FAOL, 0.2 g $ZrOCl_2 \cdot 8H_2O$, 12 mL solvent, 200 °C, 6 h.

Figure S3 GC spectra of reaction mixture (from FF-to-GVL conversion) obtained from different reaction times at 180 °C (a); GC spectra of reaction mixture (from FF-to-GVL conversion) obtained from at different reaction temperatures with a reaction time of 8 h.

Figure S4 GVL yield profiles of the reaction mixture with or without $ZrOCl_2 \cdot 8H_2O$ catalyst (removed after 1 h) at 200 °C. Reaction conditions: 2 mmol FAOL, 0.2 g catalyst, 12 mL 2-propanol.

Figure S5 Recycling test in the transfer hydrogenation of FF to FAOL with ZrO_2-(C). Reaction conditions: 2 mmol FF, 0.1 g ZrO_2-(C), 10 mL 2-propanol, 170 °C, 3 h.

Figure S6 The SEM images of ZrO_2-(P) (prepared by precipitation method).

Figure S7 Images of contact angle of ZrO_2-(C) catalyst (A) and ZrO_2-(P) catalyst (B).

Table S1 Conversion of furfural (FF) or furfuryl alcohol (FAOL) into GVL over heterogeneous catalysts.

Table S2 Activity comparison in the conversion of levulinate into GVL with using alcohol as H-donor over Zr-based heterogeneous catalysts.

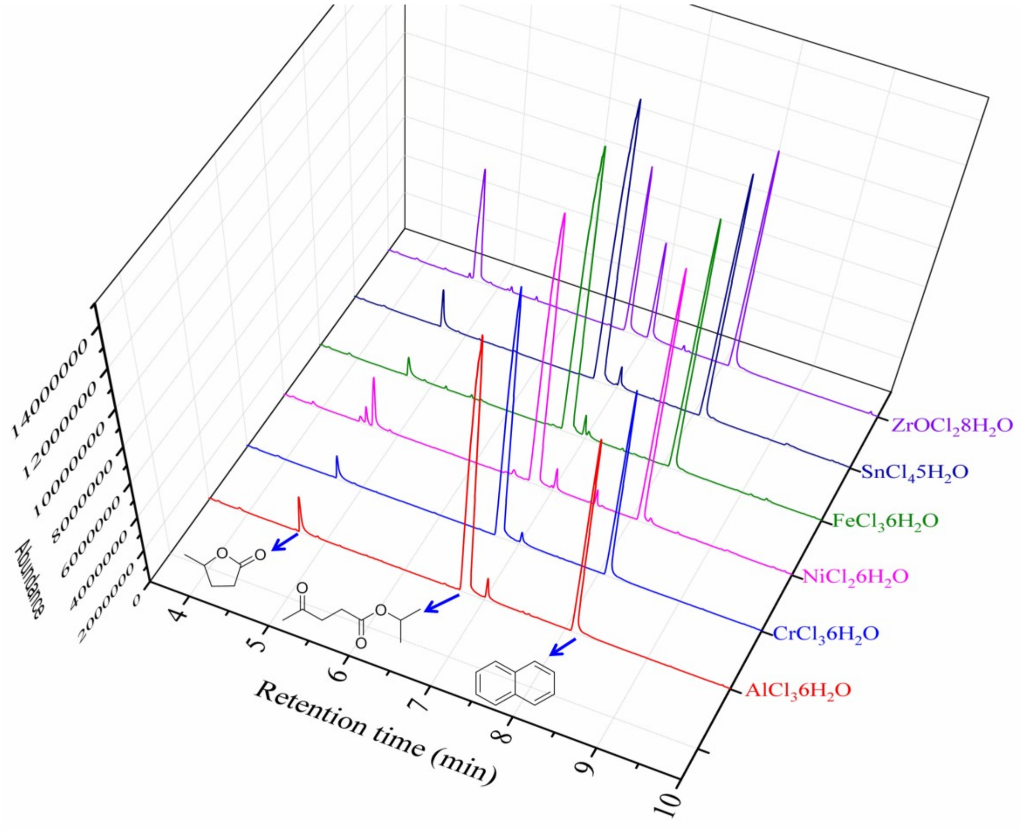

Figure S1 GC spectra of reaction mixture (from FAOL-to-GVL conversion) obtained from different metal salts at 180 °C for 6 h.

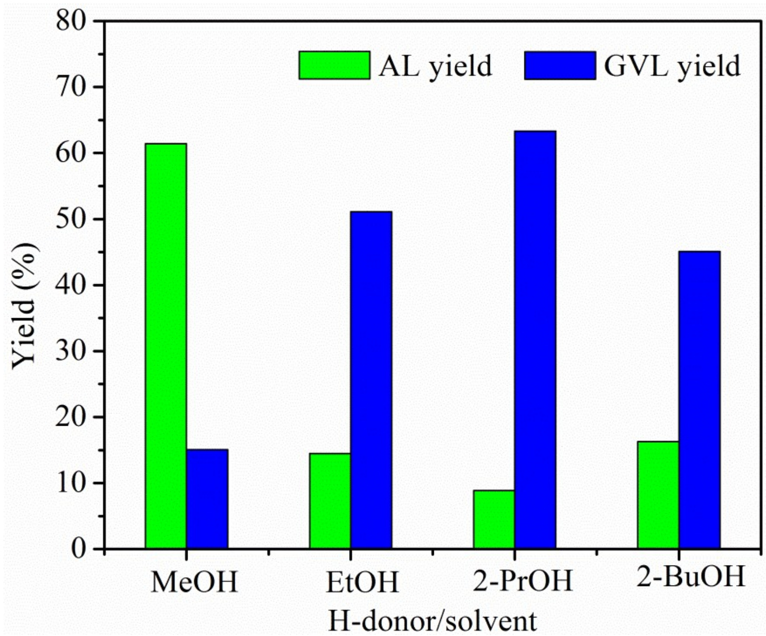

Figure S2 Effect of reaction solvent on the tandem synthesis of GVL from FAOL. Reaction conditions: 2 mmol FAOL, 0.2 g $ZrOCl_2·8H_2O$, 12 mL solvent, 200 °C, 6 h.

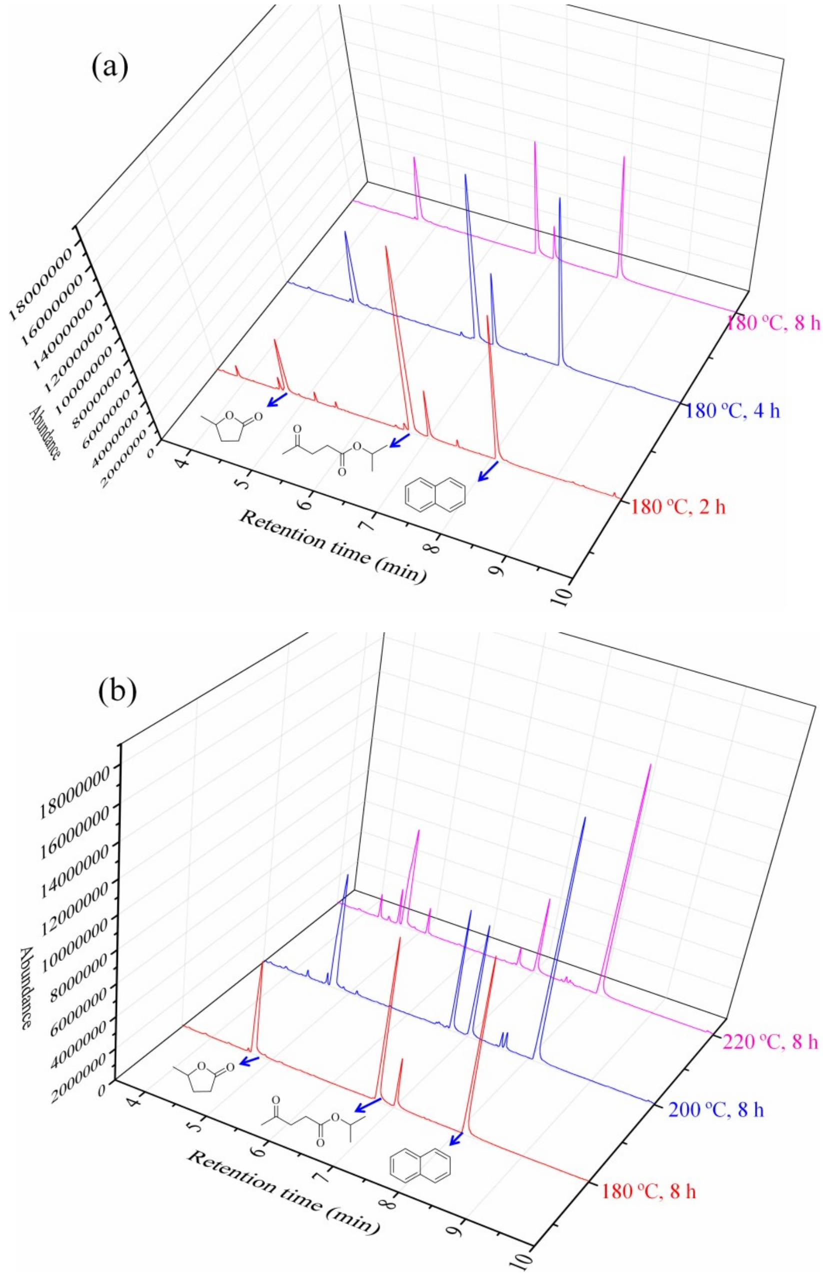

Figure S3 GC spectra of reaction mixture (from FF-to-GVL conversion) obtained from different reaction times at 180 °C (a); GC spectra of reaction mixture (from FF-to-GVL conversion) obtained from at different reaction temperatures with a reaction time of 8 h.

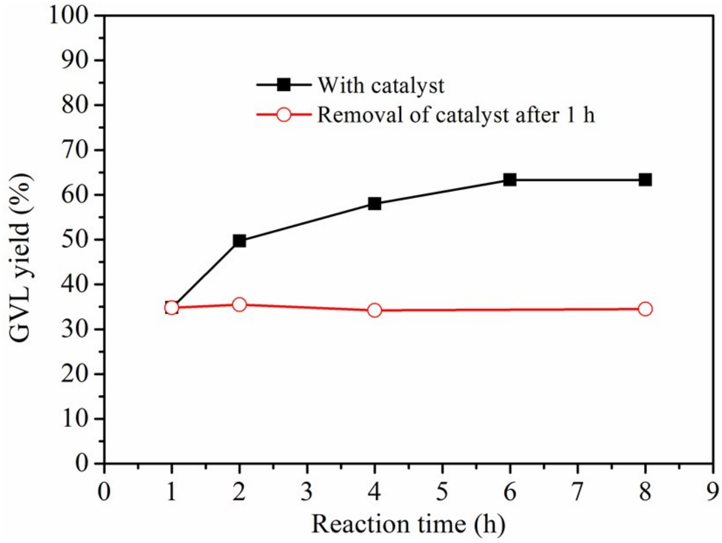

Figure S4 GVL yield profiles of the reaction mixture with or without $ZrOCl_2{\cdot}8H_2O$ catalyst (removed after 1 h) at 200 °C. Reaction conditions: 2 mmol FAOL, 0.2 g catalyst, 12 mL 2-propanol.

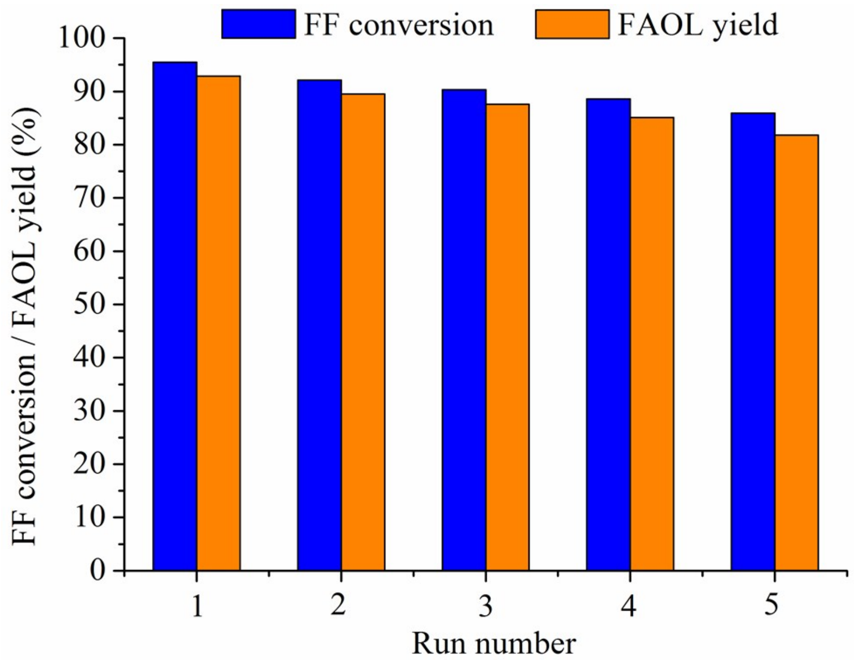

Figure S5 Recycling test in the transfer hydrogenation of FF to FAOL with ZrO_2-(C). Reaction conditions: 2 mmol FF, 0.1 g ZrO_2-(C), 10 mL 2-propanol, 170 °C, 3 h (after each run, the used catalyst was collected by centrifugation, washed with ethanol and then calcinated at 550 °C in air for 2 h).

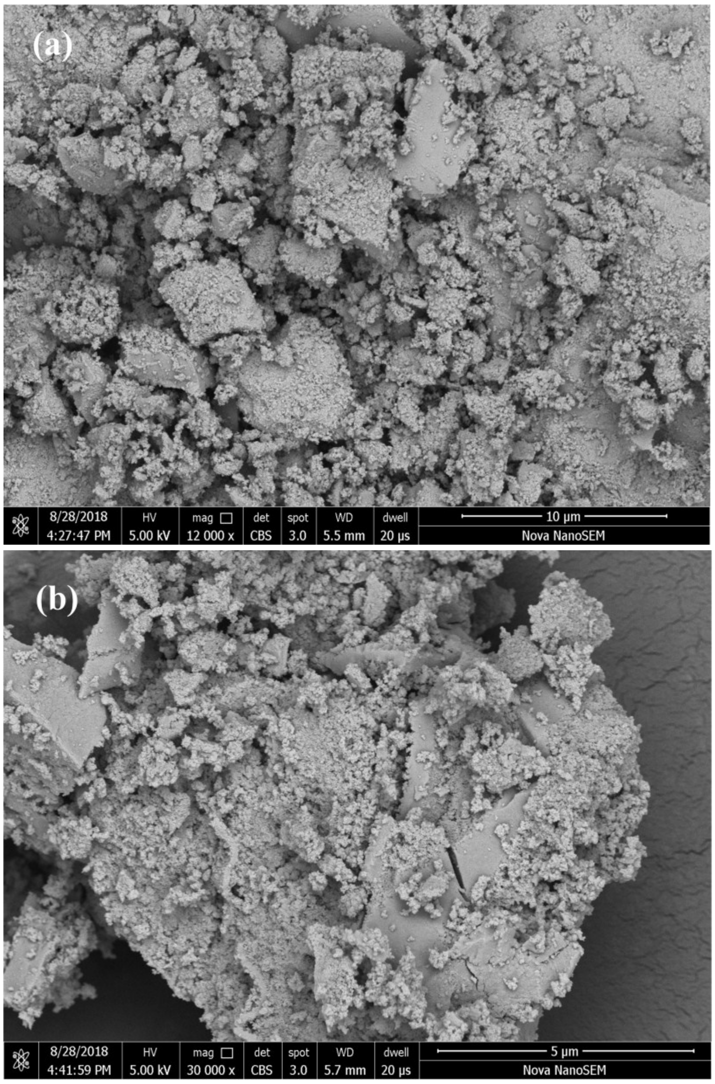

Figure S6 The SEM images of ZrO_2-(P) (prepared by precipitation method).

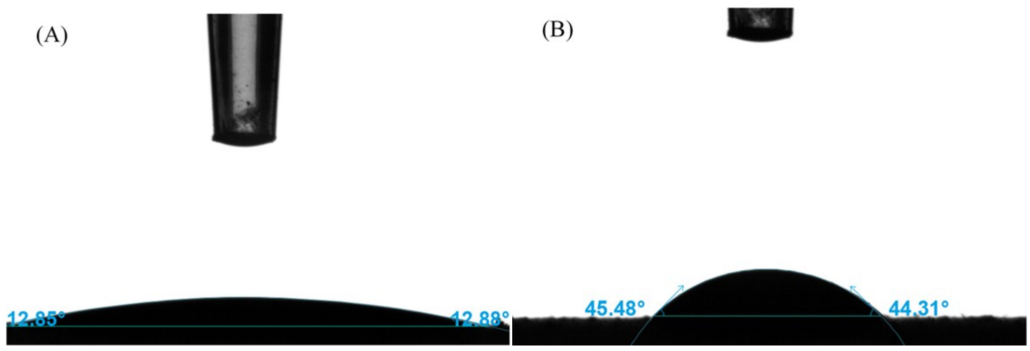

Figure S7 Images of contact angle of ZrO_2-(C) catalyst (A) and ZrO_2-(P) catalyst (B).

Table S1 Conversion of furfural (FF) or furfuryl alcohol (FAOL) into GVL over heterogeneous catalysts.

Entry	Substrate	Catalyst	H-donor	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)	Ref.
1[a]	FAOL	PDVB-IL + Co/TiO_2	H_2 (3MPa)	150 + 130	12 + 6	>99	69	S1
2	FAOL	γ-Fe_2O_3-HZSM-5	2-propanol	130	8	100	97	S2
3	FF	Zr-Beta + Al-MFI-ns	2-butanol	120	24	100	62	S3
4	FF	ZrAl-TUD	2-butanol	120	24	88	1	S4
5	FF	Au/ZrO_2 + ZSM-5	2-propanol	120	24	100	77.5	S5
6	FF	Sn-Al-Beta	2-butanol	180	24	100	60.5	S6
7	FF	Zr-Al-Beta	2-propanol	170	24	100	22.6	S7
8	FF	Meso-Zr-Al-beta	2-propanol	120	24	99	90	S8
9	FF	30 TiO_2/beta-NS	2-butanol	90	40	83	44	S9
10	FF	Hf-MOF-808 + Al-Beta	2-butanol	120	6	98	51	S10
11	FF	ZrO_2-SBA-15	2-propanol	170	7	100	37	S11
12	FF	HPW/Zr-Beta	2-propanol	180	24	100	68	S12
13	FAOL	$ZrOCl_2·8H_2O$	2-propanol	200	6	>99	63.3	This work
14	FF	$ZrOCl_2·8H_2O$	2-propanol	200	8	>99	52.1	This work

[a] The reaction was firstly conducted over PDVB-IL at 150 °C for 12 h, and then conducted over Co/TiO_2 at 130 °C for 6 h.

[S1]H. Zhou, J. Song, X. Kang, J. Hu, Y. Yang, H. Fan, Q. Meng, B. Han, *RSC Adv*., **2015**, 5, 15267-15273.

[S2] T. M. Lima, C. G. S. Lima, A. K. Rathi, M. B. Gawande, J. Tucek, E. A. Urquieta-González, R. Zbořil, M. W. Paixão, R. S. Varma, *Green Chem*., **2016**, 18, 5586-5593.

[S3] L. Bui, H. Luo, W. R. Gunther, Y. Román-Leshkov, *Angew. Chem. Int. Ed*., **2013**, 52, 8022-8025.

[S4] M. M. Antunes, S. Lima, P. Neves, A. L. Magalhães, E. Fazio, F. Neri, M. T. Pereira, A. F. Silva, C. M. Silva, S. M. Rocha, M. Pillinger, A. Urakawa, A. A. Valente, *Appl. Catal. B: Environ*., **2016**, 182, 485-503.

[S5] S. Zhu, Y. Xue, J. Guo, Y. Cen, J. Wang, W. Fan, *ACS Catal*., **2016**, 6, 2035-2042.

[S6] H. P. Winoto, B. S. Ahn, J. Jae, *J. Ind. Eng. Chem*., **2016**, 40, 62-71.

[S7] B. Hernández, J. Iglesias, G. Iglesias, M. Iglesias, C. López-Aguado, J. L. G. Fierro, P. Wolf, I. Hermans, J. A. Melero, *Green Chem*., **2016**, 18, 5777-5781.

[S8] S. Song, L. Di, G. Wu, W. Dai, N. Guan, L. Li, *Appl. Catal. B: Environ*., **2017**, 205, 393-403.

[S9] J. Han, J. Cho, J. Kim, R. Ryoo, *ACS Catal*., **2018**, 8, 876-879.

[S10] S. Rojas-Buzo, P. García-García, A. Corma, *ChemSusChem*, **2018**, 11, 432-438.

[S11] J. Iglesias, J. A. Melero, G. Morales, M. Paniagua, B. Hernández, A. Osatiashtiani, A. F. Lee, K. Wilson, *Catal. Sci. Technol*., **2018**, 8, 4485-4493.

[S12] H. P. Winoto, Z. A. Fikri, J. Ha, Y. Park, H. Lee, D. J. Suh, J. Jae, *Appl. Catal. B: Environ*., **2019**, 241, 588-597.

Table S2 Activity comparison in the conversion of levulinate into GVL with using alcohol as H-donor over Zr-based heterogeneous catalysts.

Entry	Substrate	Catalyst	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)	Ref.
1	Butyl levulinate	ZrO_2	180	4	93.2	80.5	S12
2	Ethyl levulinate	Al_7Zr_3-300	220	4	95.5	83.2	S13
3	Ethyl levulinate	ZrFeO(1:1)-300	230	0.5	94.2	86.7	S14
4	Ethyl levulinate	Zr-HBA	200	1	100	96.8	S15
5	Methyl levulinate	Zr- UiO-66-S_{60}	140	24	99	85	S16
6	Ethyl levulinate	Zr_1B_1	200	4	95.1	88.5	S17
7	Ethyl levulinate	UiO-66(Zr)	200	2	100	92.7	S18
8	Ethyl levulinate	Zr-PhyA	150	6	100	96.7	S19
9	Methyl levulinate	UiO-66 (Zr)	240	1 (TOS)	83	73.9	S20
10	Butyl levulinate	ZrPO-1.00	210	2	98.1	95.7	S21
11	Methyl levulinate	ZrO_2-(C)	190	6	95.9	87.3	This work

[S12] M. Chia, J. A. Dumesic, *Chem. Commun*., **2011**, 47, 12233-12235.

[S13] J. He, H. Li, Y. Lu, Y. Liu, Z. Wu, D. Hu, S. Yang, *Appl. Catal. A: Gen*., **2016**, 510, 11-19.

[S14] H. Li, Z. Fang, S. Yang, *ACS Sustainable Chem. Eng*., **2016**, 4, 236-246.

[S15] J. Song, L. Wu, B. Zhou, H. Zhou, H. Fan, Y. Yang, Q. Meng, B. Han, *Green Chem*., **2015**, 17, 1626-1632.

[S16] Y. Kuwahara, H. Kango, H. Yamashita, *ACS Sustainable Chem. Eng*., **2017**, 5, 1141-1152.

[S17] J. He, H. Li, Y. Liu, W. Zhao, T. Yang, W. Xue, S. Yang, *J. Ind. Eng. Chem*., **2016**, 43, 133-141.

[S18] A. H. Valekar, K. Cho, S. K. Chitale, D. Hong, G. Cha, U. Lee, D. W. Hwang, C. Serre, J. Chang, Y. K. Hwang, *Green Chem*., **201**6, 18, 4542-4552.

[S19] J. Song, B. Zhou, H. Zhou, L. Wu, Q. Meng, Z. Liu, B. Liu, *Angew. Chem. Int. Ed*., **2015**, 54, 9399-9403.

[S20] W. Ouyang, D. Zhao, Y. Wang, A. M. Balu, C. Len, R. Luque, *ACS Sustainable Chem. Eng*., **2018**, 6, 6746-6752.

[S21] F. Li, L. J. France, Z. Cai, Y. Li, S. Liu, H. Lou, J. Long, X. Li, *Appl. Catal. B: Environ*., **2017**, 214, 67-77.