

Supporting Information for:

Highly Efficient Meerwein-Ponndorf-Verley Reductions Over a Robust Zirconium-Organoboronic Acid Hybrid

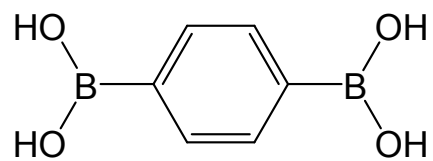
Jinliang Song,^{*a} Manli Hua,^{a,c} Xin Huang,^{a,c} Aurelia Visa,^b Tianbin Wu,^a Honglei Fan,^a Minqiang Hou,^a Zhaofu Zhang^a and Buxing Han^{*a,c}

^aBeijing National Laboratory for Molecular Science, CAS Key Laboratory of Colloid and Interface and Thermodynamics, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. E-mails: songjl@iccas.ac.cn, hanbx@iccas.ac.cn.

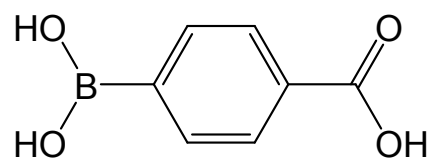
^bInstitute of Chemistry Timisoara of the Romanian Academy, 24 M. Viteazul Ave, 300223 Timisoara, Romania.

^cSchool of Chemistry and Chemical Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

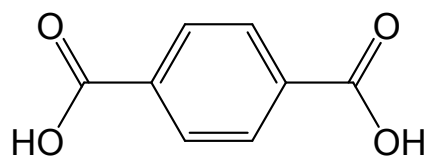
Materials. Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, 99.9% metals basis), benzaldehyde (99%), cyclohexanone (99%), boric acid (99.5%), 3-hydroxy-4-methoxybenzaldehyde (98%), and acetophenone (99%) were purchased from Innochem Scientific Ltd. 1,4-Benzenediboronic acid (98%), 4-carboxyphenylboronic acid (98%), zirconium(IV) oxide (ZrO_2 , 99%), *N,N*-dimethylformamide (99.9%), ethyl levulinate (98%), methyl levulinate (97%), furfural (99%), 4-methoxybenzaldehyde ($\geq 98\%$), 4-nitrobenzaldehyde (99%), cinnamaldehyde (99%), 3-phenylpropionaldehyde (95%), citronellal (97%), 2-octanone (99%), and zirconium 1,4-dicarboxybenzene MOF (UiO-66) were provided by J&K Scientific Ltd. 1,4-Benzenedicarboxylate acid (98+%), cyclohexanol (99%), 3,4-dimethoxybenzaldehyde (99%), 4-hydroxybenzaldehyde (98%), syringaldehyde (98+%), 4'-methoxyacetophenone (99%), 3',4'-dimethoxyacetophenone (98+%), 3',4',5'-trimethoxyacetophenone (99%), *n*-propanol (99+%), levulinic acid (LA, 98%), *tert*-butanol (99%), and 2-phenylacetophenone (97%) were purchased from Alfa Aesar. Butyl levulinate (98.0%), 2-phenoxyacetophenone (98%), and propyl levulinate (98%) were provided by TCI. 3'-Hydroxy-4'-methoxyacetophenone (97%) was purchased from Aladdin. *sec*-Butanol (99+%) was provided from Acros. Isopropyl alcohol (AR), methanol (AR), and ethanol (AR) were obtained from Sinopharm Chemical Reagent Beijing Co., Ltd. All reagents purchased from commercial sources were used as obtained without further purification.



1,4-Benzenediboronic acid
(BDB)



4-Carboxyphenylboronic acid
(CPB)



1,4-Benzenedicarboxylate acid
(BDC)

Scheme S1. The chemical structure of the used organic ligands.

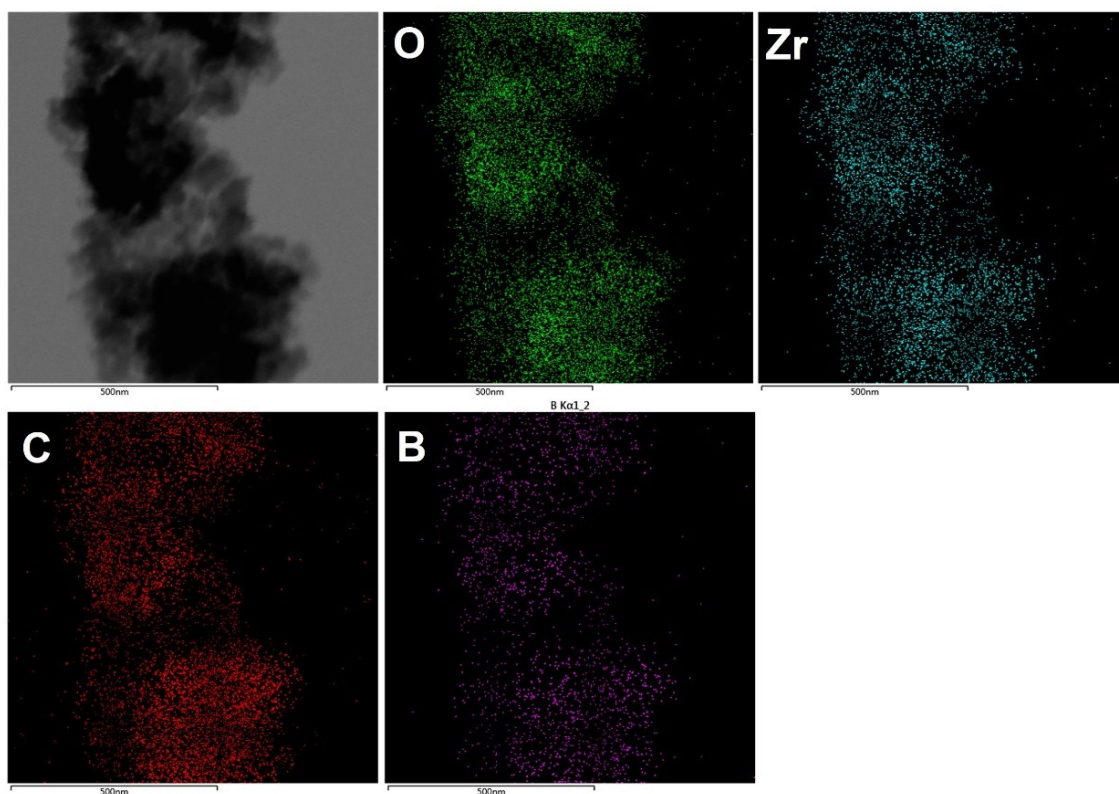


Fig. S1. Elemental distribution mappings for the prepared Zr-BDB.

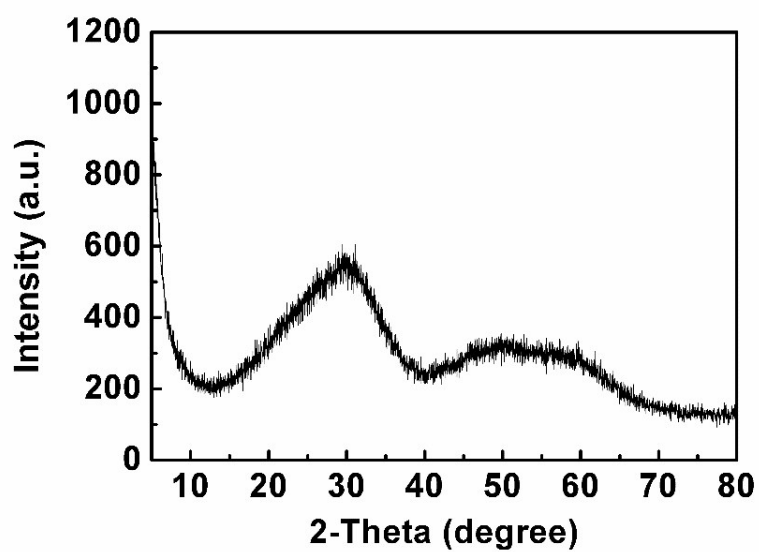
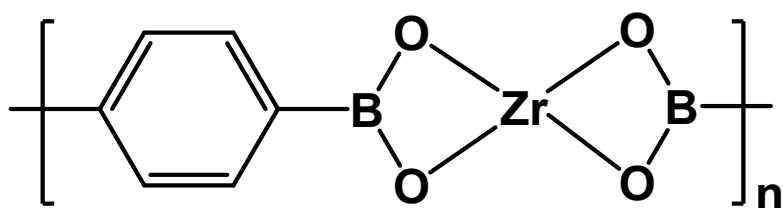


Fig. S2. XRD pattern of the prepared Zr-BDB.



Scheme S2. The most plausible connectivity pattern between Zr^{4+} and BDB.

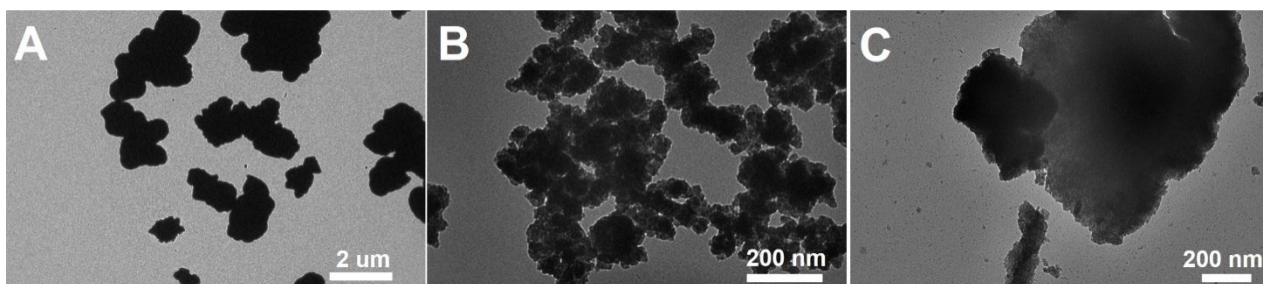


Fig. S3. TEM images. (A) Zr-CPB, (B) Zr-BDC, and (C) Zr-B.

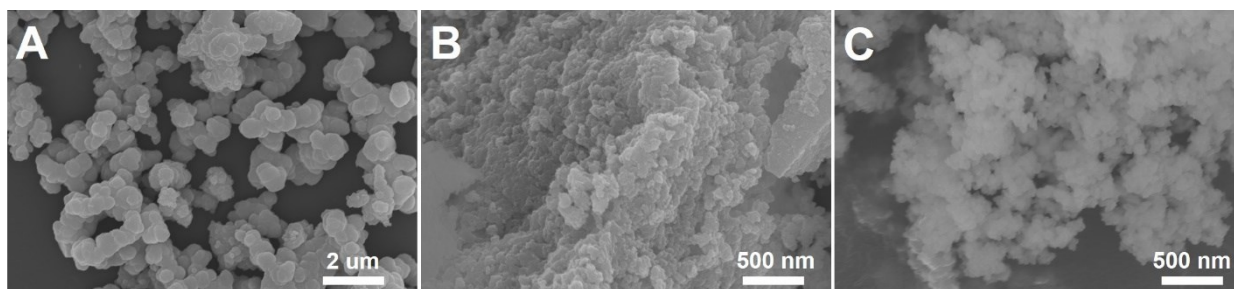


Fig. S4. SEM images. (A) Zr-CPB, (B) Zr-BDC, and (C) Zr-B.

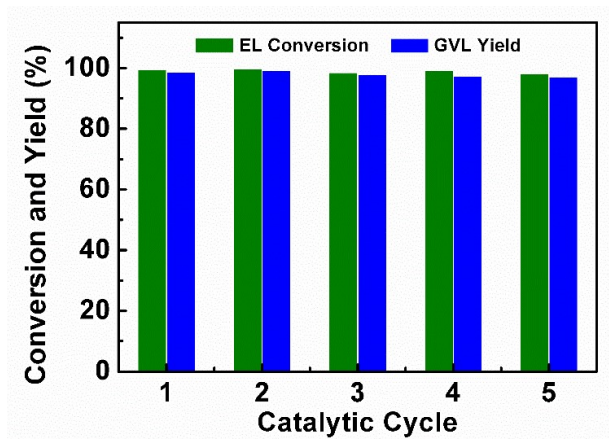


Fig. S5. Reusability of Zr-BDB. Reaction conditions: EL, 1 mmol; isopropyl alcohol, 5 g; the amount of Zr-BDB, 0.2 g; reaction temperature, 130 °C; reaction time, 6 h.

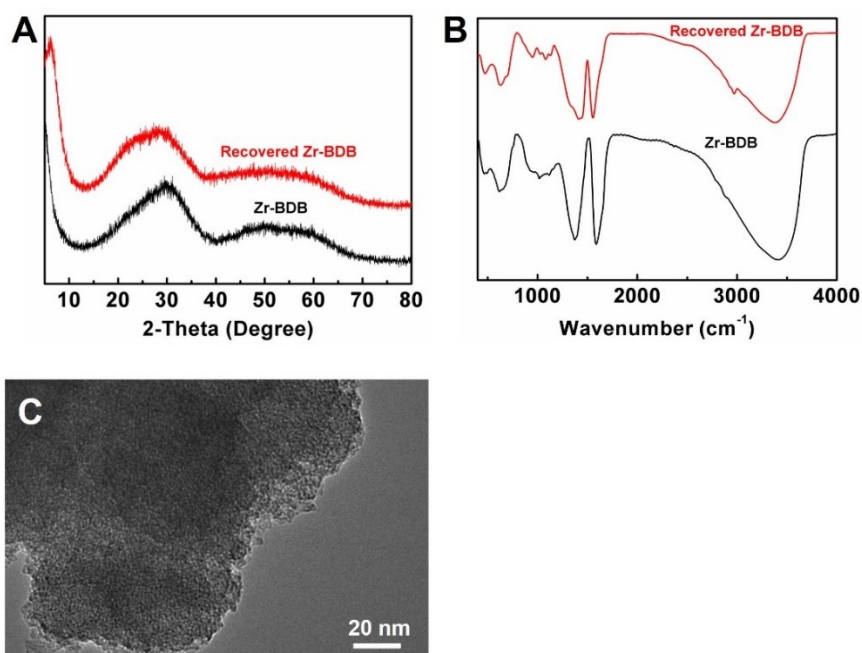


Fig. S6. Characterization of the recovered Zr-BDB after five catalytic cycles. (A) XRD patterns, (B) FT-IR spectra, and (C) HR-TEM image.

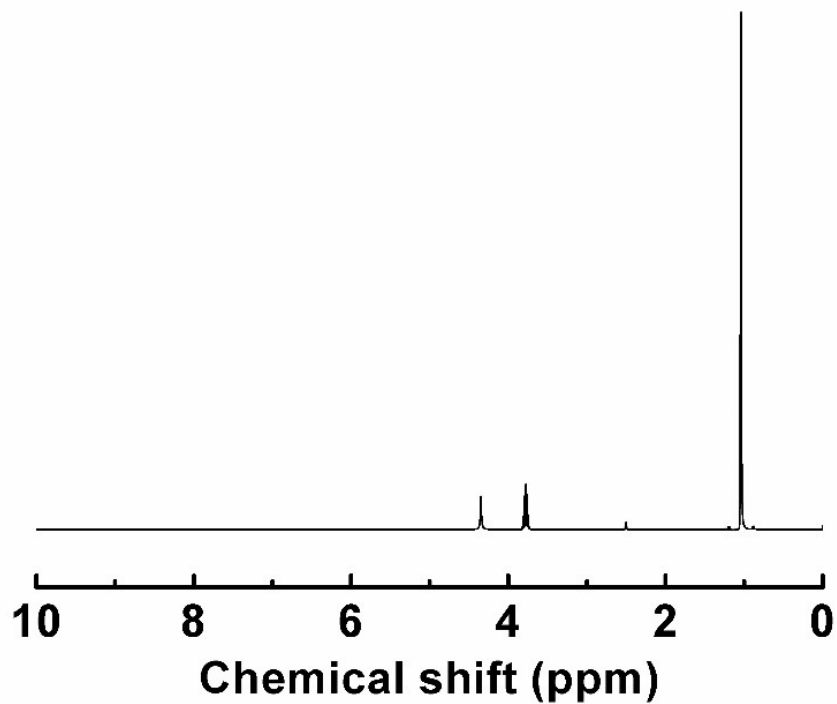


Fig. S7. ¹H NMR spectra of isopropyl alcohol in DMSO-*d*₆.

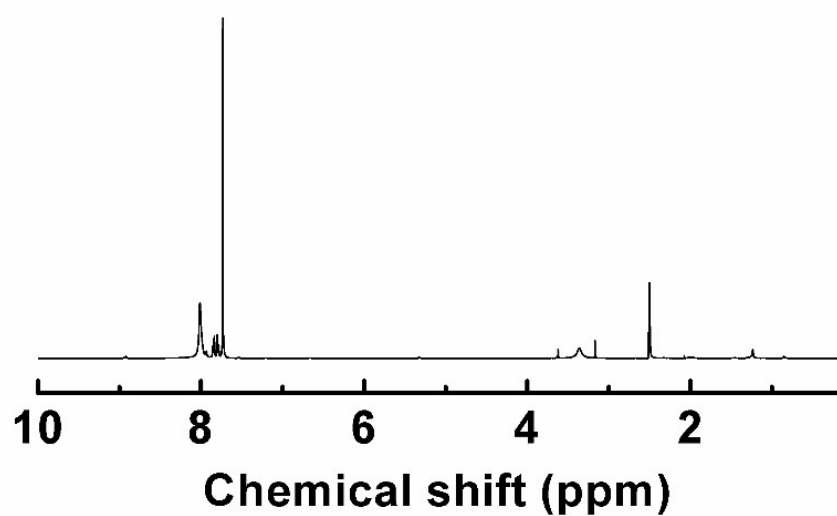


Fig. S8. ¹H NMR spectra of 1,4-benzenediboronic acid in DMSO-*d*₆.

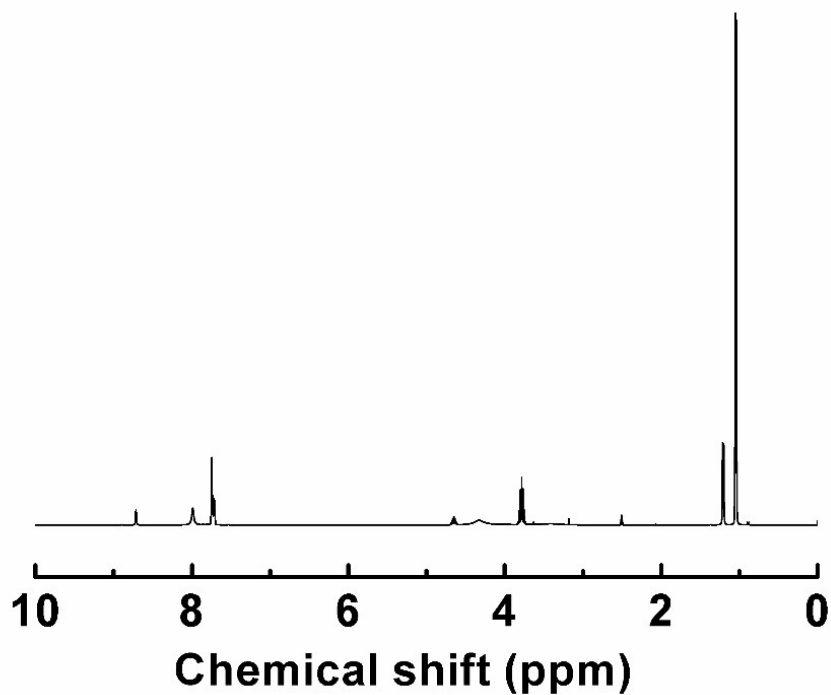
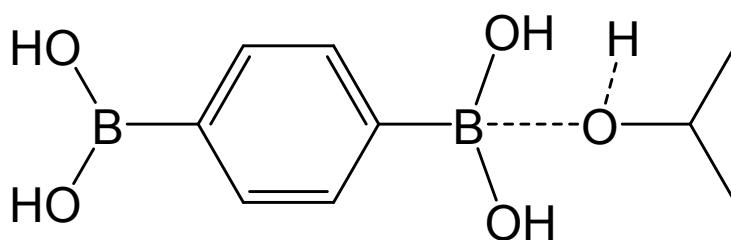


Fig. S9. ^1H NMR spectra of the mixture of isopropyl alcohol and 1,4-benzenediboronic acid in $\text{DMSO-}d_6$.



Scheme S3. The possible mode for the activation of isopropyl alcohol by the borate group.

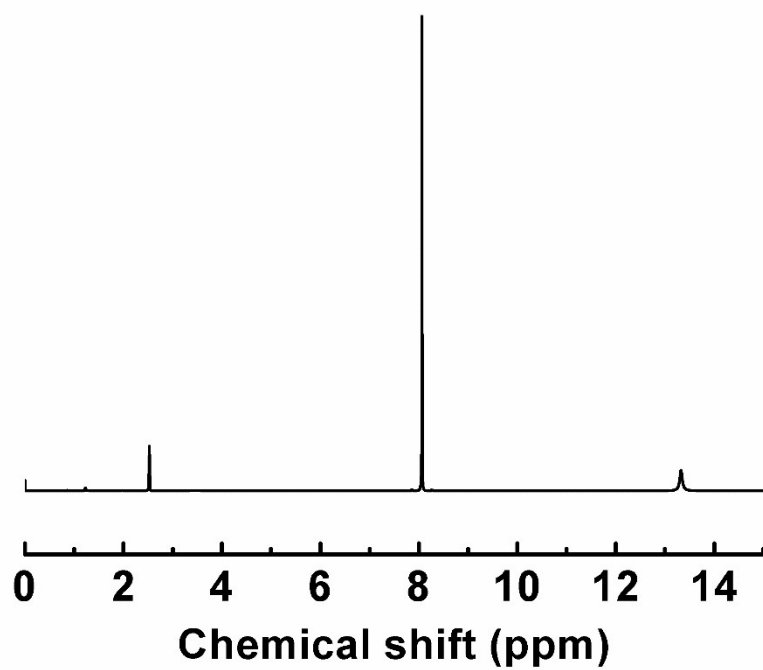


Fig. S10. ^1H NMR spectra of BDC in $\text{DMSO-}d_6$.

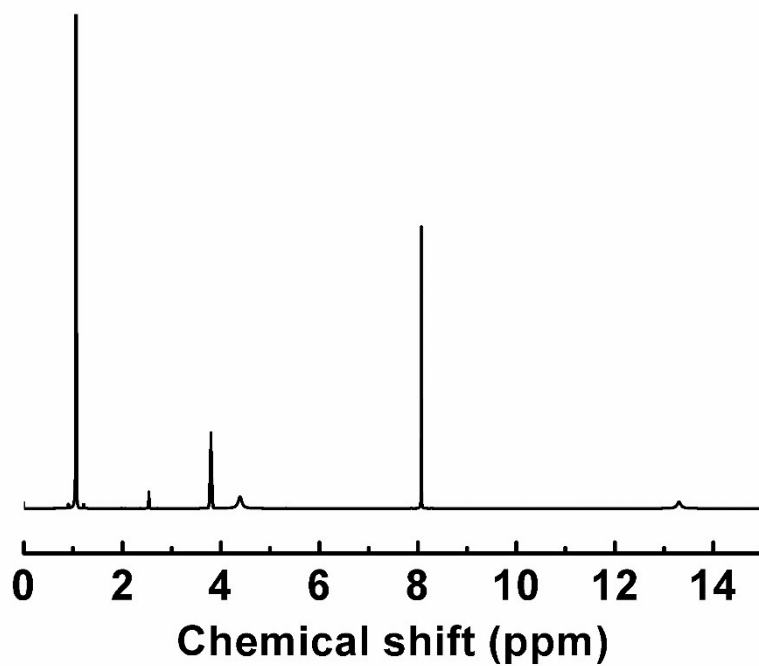


Fig. S11. ^1H NMR spectra of the mixture of isopropyl alcohol and BDC in $\text{DMSO-}d_6$.

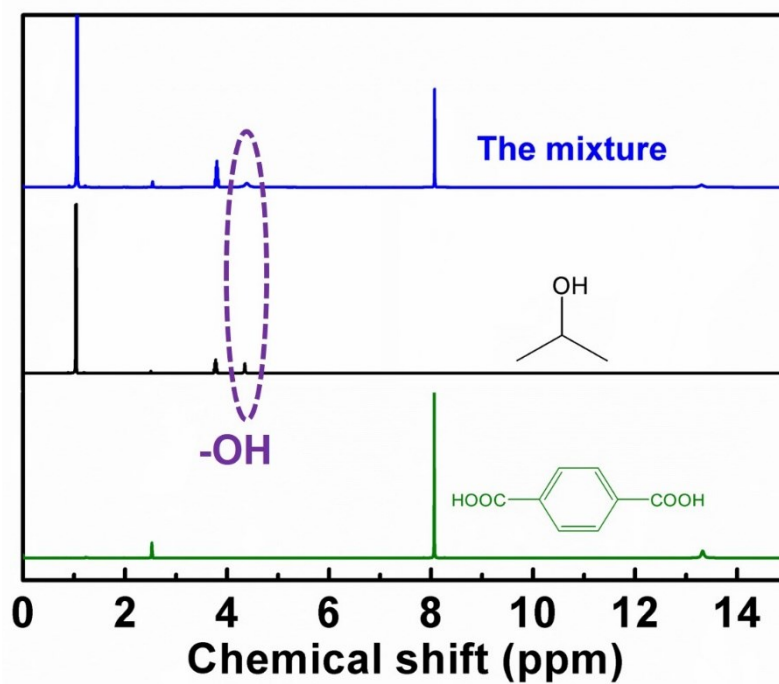
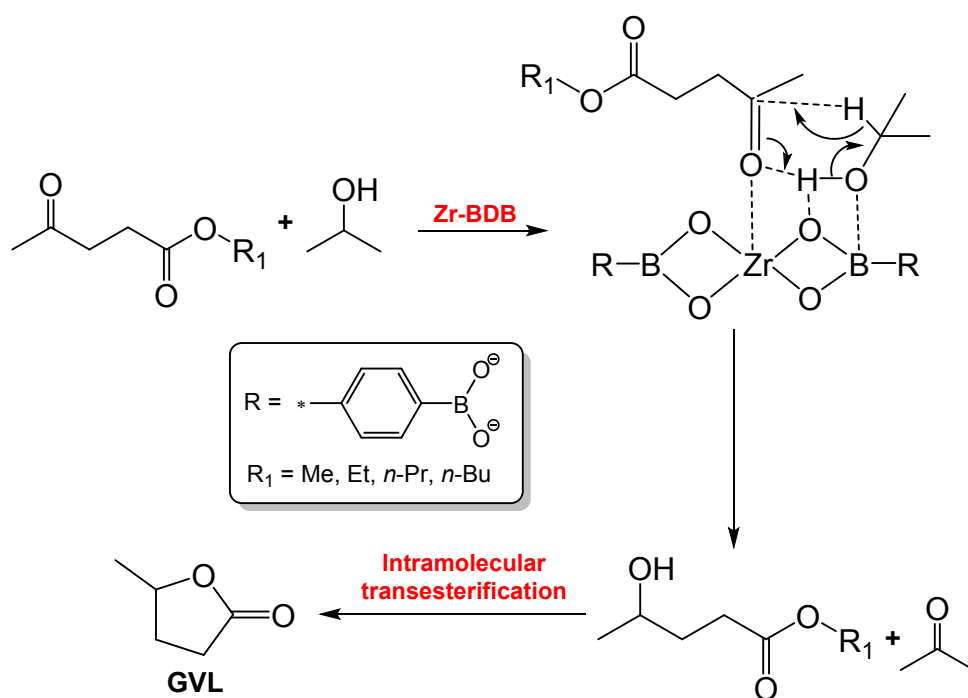


Fig. S12. Comparison on the ^1H NMR spectra of isopropyl alcohol, BDC, and their mixture in $\text{DMSO-}d_6$.



Scheme S4. Possible mechanism for the Zr-BDB-catalyzed MPV reaction of various levulinate esters.

Table S1. Results of N₂ adsorption-desorption examinations for different catalysts.

Entry	Sample ^a	BET surface area (m ² /g) ^b	Pore volume (cm ³ /g) ^c	Pore diameter (nm) ^d
1	Zr-BDB	271	0.24	3.4
2	Zr-CPB	3.6	0.01	10.6
3	Zr-BDC	736	0.46	4.0
4	Zr-B	445	0.17	2.8
5 ^e	Zr-BDB	256	0.22	3.6

^aThe samples were degassed at 120 °C for 24 h. ^bSurface area based on multipoint BET method. ^cPore volume based on BJH method. ^dPore diameter based on BJH method. ^eThe recovered Zr-BDB after five catalytic cycles.

Table S2. Influence of various alcohols (as the hydrogen donor) on MPV reaction of EL to produce GVL.^a

Entry	Alcohol	Conversion (%) ^b	GVL Yield(%) ^b	Selectivity (%)
1	Isopropyl alcohol	99.5	98.7	99.2
2	sec-Butyl alcohol	99.6	97.9	98.3
3	Methanol	64.9	2.1	3.2 ^c
4	Ethanol	59.7	58.6	98.2
5	<i>n</i> -Propanol	64.4	62.1	96.4
6	<i>tert</i> -Butanol	10.5	8.6	81.9

^aReaction conditions: EL, 1 mmol; Zr-BDB, 0.2 g; alcohol, 5 g; reaction temperature, 130 °C; reaction time, 6 h. ^bThe conversion and yield were determined by GC using cyclohexanol as the internal standard. ^cThe by-product was methyl levulinate from the transesterification of EL and methanol.

Table S3. CO₂-TPD results for different catalysts.

Entry	Catalyst	Basicity (mmol/g)
1	Zr-BDB	2.4
2	Zr-CPB	2.7
3	Zr-BDC	3.1
4	UiO-66	3.3
5	Zr-B	3.7
6	ZrO ₂	0.05