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COMMUNICATION

Chirality-Driven Self-Assembly: Application Toward Renewable/Exchangeable Resin-Immobilized Catalysts

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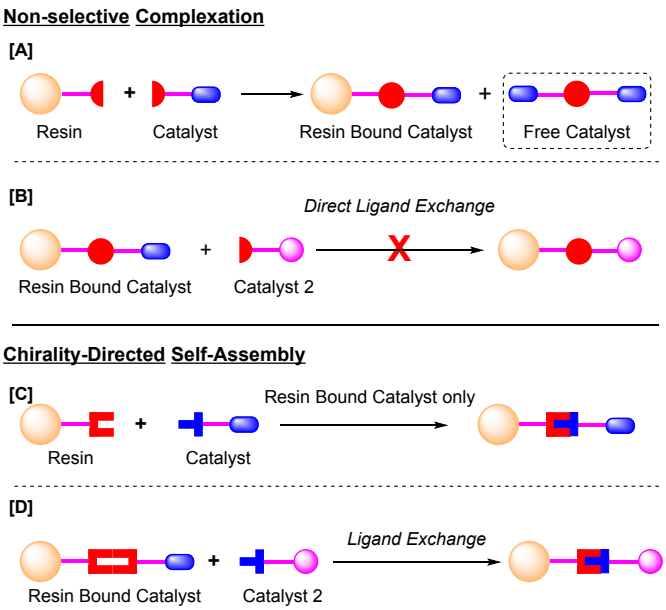
Resin-immobilized catalysts were prepared through chirality-driven self-assembly. The method allows the resin-immobilized catalyst to be regenerated under mild conditions and in-situ catalyst exchange to be carried out quantitatively. The uniqueness of the methodology was demonstrated by the preparation of a catalyst for TEMPO oxidation as well as a two-step sequential TEMPO oxidation/aldol condensation sequence enabled by facile catalyst exchange.

Catalyst recovery and recycling[1] is of significance in modern synthetic chemistry as the increase in environment awareness motivates scientists to develop and employ greener approaches.[2] Resin-immobilized catalysts have gained popularity due mostly to their facile recovery from the reaction media thus reducing cost and labour in preparing catalysts.[3] However, their recyclability and reusability is often limited by the functional integrity of the loaded catalyst, that is, the ability to regenerate and reuse the catalyst.[4,5] The exchangeability/renewability of damaged or poisoned catalysts plays a critical role in extending the life-span of supporting resins. Catalyst immobilization to a resin support is typically accomplished through either covalent[6] or non-covalent interactions.[7,8] The non-covalent immobilization of catalysts to the solid support reduces the number of synthetic steps, and the process is achieved through mild reaction conditions. For instance, phosphine ligands were anchored on the dendrimer support through multiple hydrogen bonds to urea adamantyl functional groups on the periphery of the dendrimer. The catalyst was successfully employed in the various Pd or Rh-catalyzed reactions.[9] The bis(imidazolium)-tagged 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) catalyst was immobilized onto cross-linked polymeric imidazolium solid supports via electrostatic interactions.[10] The loaded TEMPO effectively oxidized various primary and secondary alcohols, and immobilized catalysts were successfully recycled several times. Lastly, π-π stacking was employed for the immobilization of NHC-Pd and NHC-Ru catalysts onto the reduced graphene oxide (rGO) surface. It was used for the hydrogenation and nitro group reduction.[11]



Scheme 1. Non-selective (**A**,**B**) Versus Selective Self-assembly (**C**,**D**).

The relatively weak interactions among non-covalent often led to immobilized catalysts prone to leaching thus limiting their applications. In contrast, covalent immobilization has reduced the risk of catalyst leaching.[12] However, covalent immobilization process often involves lengthy preparation steps and demands strict compatible chemical/reaction conditions, resulting in lack of flexibility in catalyst design. Metal ligand complexation may provide an alternative to the current approaches. The comparatively higher bond strength of the metal-ligand interactions[13] is expected to enhance resistance

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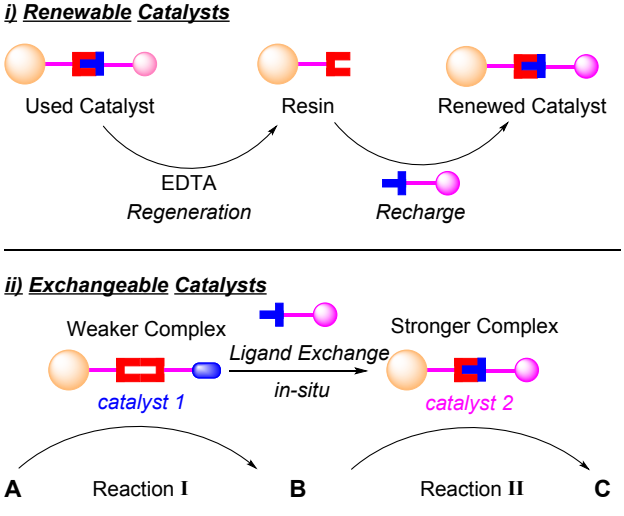
toward catalyst leaching, while its reversible nature still allows recharging or replacing catalysts under mild condition without damaging the structural integrity of the polymeric support.[14] Among the metal-ligand complexation strategies employed,[15] we believe chirality-directed self-assembly[16] using labile covalent, chelating methylene bis(oxazoline) (box) subunits provides a highly promising but underutilized approach. Appropriately designed, the formation of heterochiral metal-ligand complex can be highly favoured over homochiral complexes. We recently reported using this high selectivity to generate structurally distinct Janus dendrimers quantitatively in one-pot process.[17] Prior studies used the strategy to construct supramolecular chiral bidentate ligands in various asymmetric reactions.[18] We now report applying a similar approach to loading catalysts on to a solid resin support. As illustrated in Scheme 1, generation of undesirable unbound catalyst can be effectively eliminated. (Scheme 1, **A** vs. **C**) In addition, chirality-directed self-assembly allows *in situ* modification of loaded catalysts through direct ligand exchange. For example, the homochiral assembly, a thermodynamically weaker complex, can be efficiently and quantitatively transformed into the heterochiral assembly by exposure to the ligand with opposite chirality. This is a challenging task with traditional metal-ligand complexes using ligand combination that lacks significant differences in stability upon complexation with the metal (Scheme 1, **B** vs. **D**).

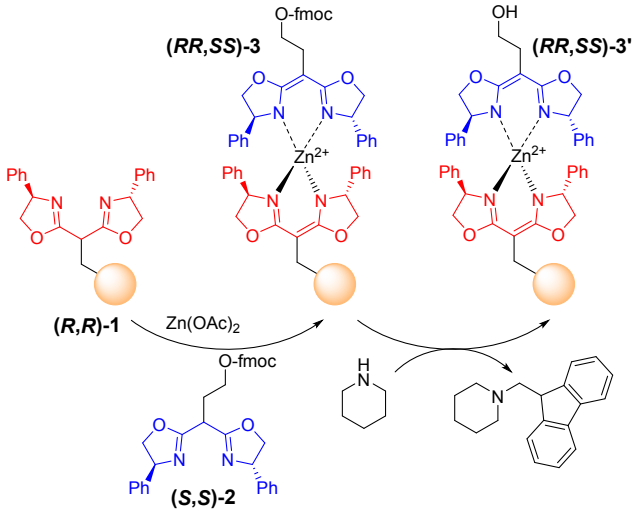
Our main objective for this study is to apply chirality-driven self-assembly for immobilizing catalysts onto a resin to generate renewable/exchangeable heterogeneous catalysts. Scheme 2-i illustrates the proposed application to a single-step renewable resin-immobilized catalyst and its facile regeneration and recharge. Scheme 2-ii illustrates a proposed sequential two-step catalysts sequence in which the resin undergoes facile *in situ* exchange to effect new catalytic activity.



Scheme 2 Renewability and Exchangeability of the Self-Assembly Based Resin Immobilized Catalysts.

The immobilization of chiral methylene bis(oxazoline) ((*R*,*R*)-BOX) ligand onto Wang resin (*R*,*R*)-**1** was achieved in one-step by following a known procedure from commercially available brominated Wang resin.[19] As shown in Scheme 3, the functional loading capacity of chiral BOX for self-assembly was measured spectroscopically using UV/Vis through the titration of fmoc-derived (*S*,*S*)-**2**, and determined to be 0.28 mmol per gram of resin.[20] The formation of the heterochiral Zn(II) complex (*RR*,*SS*)-**3** was also monitored by the FTIR analysis; the C=N bond stretch shifts from 1655 cm^{-1} ((*S*,*S*)-**2**) to 1600 cm^{-1} ((*RR*,*SS*)-**3**).[21] The shift in the C=N bond stretching band is similar to that observed with the free (i.e., unbound) heterochiral Zn(II) complexes formed in solution which results in a shift from 1654 cm^{-1} to 1599 cm^{-1}.

As mentioned above, the chirality-driven self-assembly enables facile construction of resin-immobilized catalyst which can be easily renewed without affecting integrity of the resin as catalytic activity deteriorated. To demonstrate simplicity in renewing immobilized catalyst, the resin-immobilized pyrrolidine catalyst[22] was subject to the catalyst renewal after

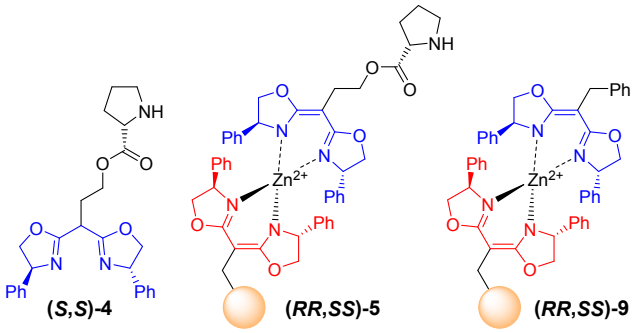


several use in aldol reaction.[23]

Scheme 3 One-Pot Preparation of fmoc-Derived Resin Used for Quantifying the Functional Capacity.

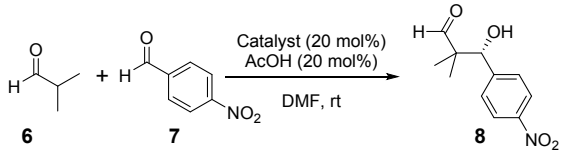
The self-assembled pyrrolidine derived resin (*RR*,*SS*)-**5** was prepared by using the same strategy for (*RR*,*SS*)-**3** in Scheme 3 by mixing an equimolar amount (0.28 mmol) of $Zn(OAc)_2$, (*S*,*S*)-BOX-pyrrolidine derivative (*S*,*S*)-**4** and the (*R*,*R*)-BOX functionalized resin (*R*,*R*)-**1** (Scheme 4). A variety of pyrrolidine derived catalysts have been successfully used to catalyse cross aldol reactions.[24] Those results serve as a useful benchmark against which the current strategy can be compared. For example, proline methyl ester catalyzes the condensation of isobutyraldehyde and 4-nitrobenzaldehyde under the conditions highlighted in Table 1 gave a good yield (92%) in modest reaction time (3 h) (entry 1). Under comparable conditions, the resin-immobilized pyrrolidine (*RR*,*SS*)-**5** performs nearly identically (91% yield, 6 h) (entry 2). The outcome of enantioselectivity (54%) was also identical between free and bound chiral pyrrolidine catalysts.[25] In contrast the resin lacking the crucial pyrrolidine subunit, (*RR*,*SS*)-**9**, gave only recovered starting materials unchanged after 3 days (entry 3). In addition, neither resin (*R*,*R*)-**1** itself nor 1:1 Zn(II)-BOX complex of resin (*R*,*R*)-**1** yielded aldol product **8** (entries 4 and 5). The pyrrolidine immobilized (*RR*,*SS*)-**5** can be recycled several times; the catalytic efficiency as well as enantioselectivity deteriorated after 8 recycles (entry 6). Pyrrolidine catalysts on (*RR*,*SS*)-**5** was renewed by first removing existing pyrrolidine under mild

reaction conditions through a treatment with EDTA solution.[18] The fresh pyrrolidine catalyst (*S*,*S*)-**4** was added to this recycled (*R*,*R*)-**1** to obtain renewed (*RR*,*SS*)-**5**. The catalytic efficiency was regained with a renewed (*RR*,*SS*)-**5**, maintaining the efficiency for several recycling (entries 7 and 8).



Scheme 4 Renewability and Exchangeability of the Self-Assembly Based Resin Immobilized Catalysts.

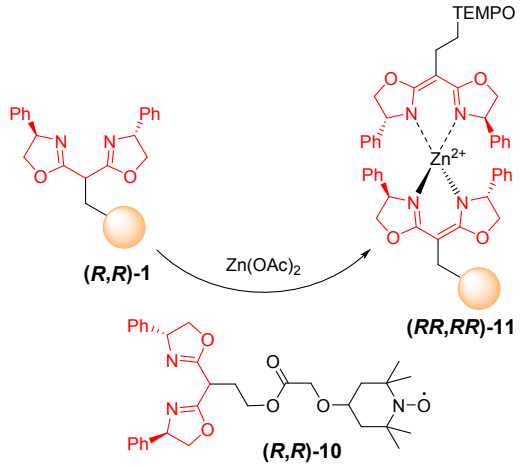
Table 1 Aldol Reactions of *p*-Nitrobenzaldehyde (**7**) and Isobutyl Aldehyde (**6**).[a]



entry	catalyst	Time (h)[b]	Yield (%)[c] **8**
1[d]	proline methyl ester	4	92
2[d]	(*RR*,SS)-**5**	6	91
3	(*RR*,SS)-**9**	72	trace
4	(*R*,*R*)-**1**	72	trace
5	(*R*,*R*)-**1** + $Zn(OAc)_2$	72	trace
6[e]	(*RR*,*SS*)-**5** Repeat #8	8	84
7[f]	(*RR*,*SS*)-**5** Renewed	6	90
8[f] [g]	(*RR*,*SS*)-**5** Renewed, repeat #3	6	92

[a] *p*-Nitrobenzaldehyde **7** (1.1 mmol), isobutyl aldehyde **6** (1.0 mmol), acetic acid (1.0 mmol) and catalyst (20 mol%) in DMF. [b] Monitored by GC. [c] An isolated yield after column purification (Hex:EtOAc = 6:4), [d] % ee = 54%, HPLC (Chiralpak AD-H, i-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} =10.71 min, t_{minor} = 12.07 min. [e] % ee = 46% [f] Regenerated catalyst was used. [g] The 3rd reaction cycle using the renewed catalyst.

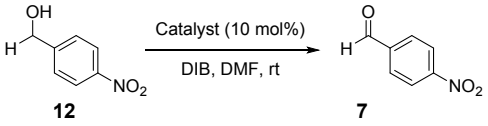
The heterochiral Zn(II) BOX was used as a catalyst immobilization in above studies. Interestingly, we found that an efficient resin-bound catalyst can also be obtained with the weaker homochiral Zn(II) complex. For example, the resin-immobilized TEMPO catalyst[26] was prepared, and the resulting resin-bound catalyst was evaluated in the oxidation of a prototypical alcohol, *p*-nitrobenzyl alcohol, using DIB as TEMPO oxidant to generate *N*-oxoammonium cation (Scheme 5, Table 2). The preparation of (*RR*,*RR*)-**11** required three mole equivalents of (*R*,*R*)-**10**, followed by washing step to remove



unbound TEMPO-BOX homochiral Zn(II) complex (*RR*,*RR*)-Zn(II) **10**.[27]

Scheme 5 A One-pot Preparation of Resin Immobilized TEMPO catalyst (*RR*,*RR*)-**11**.

Table 2 TEMPO Oxidation of *p*-Nitrobenzalcohol **12**.[a]



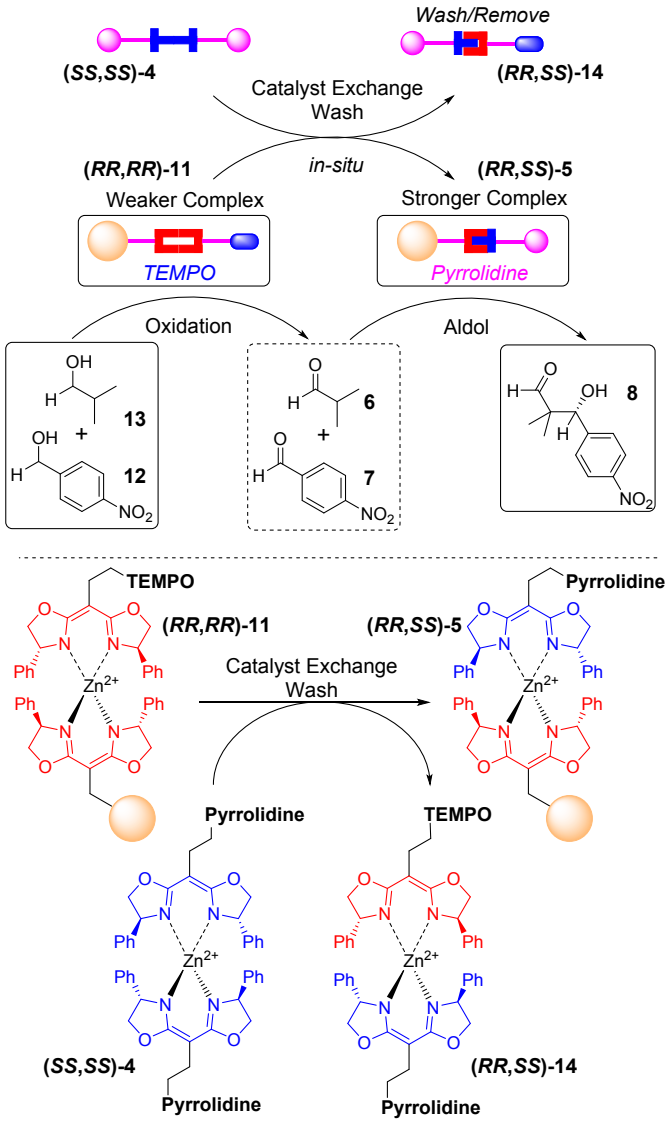
entry	catalyst	Time (h)[b]	**7** Yield (%)[c]
1	TEMPO	4	>98
2	(*RR*,*RR*)-**11**	5.5	>98
3	(*R*,*R*)-**1**	24	0
4	(*R*,*R*)-**1** + $Zn(OAc)_2$	24	0
5[d]	(*RR*,*RR*)-**11** Repeat #8	8	87
6[d][e]	(*RR*,*RR*)-**11** Renewed, Repeat #3	5.5	>98

[a] *p*-Nitrobenzaldehyde **7** (1.0 mmol), DIB (1.02 mmol) and catalyst (20 mol%) in DMF. [b] Monitored by GC. [c] An isolated yield after column purification (Hex:EtOAc = 7:3 to 5:5). [d] Renewed catalyst was used. [e] 3rd reaction cycle using the renewed catalyst.

The resin-immobilized TEMPO catalyst (*RR*,*RR*)-**11** oxidized alcohol **12** in 5.5 hours, which is comparable in efficiency relative to the free TEMPO catalyst (Table 2, entry 1 vs. entry 2). As is the case in aldol reaction, resin (*R*,*R*)-**1** as well as 1:1 Zn(II) complex of (*R*,*R*)-**1**-Zn(II) did not oxidize the alcohol (entries 2 vs. 3 and 4). The (*RR*,*RR*)-**11** can be re-used several times before catalytic efficiency started deteriorating (entry 5). As is the case in pyrrolidine catalyst (*RR*,*SS*)-**5**, the catalytic efficiency of (*RR*,*RR*)-**11** can be recovered by regenerating TEMPO on the resin. The renewed catalytic activity was identical to its original (*RR*,*RR*)-**11** (entry 1 vs. 6).

A two-step sequential oxidation/aldol reaction[28] was next examined as a model reaction sequence that exploits catalyst

exchange. The overall strategy is summarized in Scheme **6**. When the oxidation and aldol reactions were conducted with free catalysts (TEMPO and pyrrolidine) sequentially in one pot, the oxidation step went smoothly, however, the aldol reaction was sluggish due to the generation of *N*-oxoammonium cation from TEMPO and excess (diacetoxyiodo)benzene (DIB). These by-products deactivate the pyrrolidine catalyst (Table 3, entry 2). The two catalysts are incompatible,[29] and TEMPO and its reaction by-products must be removed prior to the pyrrolidine catalysis. Using the TEMPO catalyst (*RR*,*RR*)-**11**, oxidations of both alcohols (i.e., isobutanol and *p*-nitrobenzyl alcohol) underwent smoothly. Upon completion of oxidation step, pyrrolidine catalyst (*RR*,*SS*)-**5** was generated through a ligand exchange between (*RR*,*RR*)-**11** and (*SS*,*SS*)-**4.** The exchanged resin was simply washed several times to remove the TEMPO containing complex (*RR*,*SS*)-**14**. The two-step sequence gave the final aldol product in 80% overall isolated yield with 54% ee (Table 3, entry 1).



Scheme 6 Sequential Oxidation/Aldol Reaction Using Catalyst Exchangeable Resin.

Several control experiments provided further information about the reactions. If the resins were not washed upon ligand exchange to remove TEMPO containing unbound (*RR*,*SS*)-**14**, only trace amount of aldol adduct was obtained (entry 3). Use of the catalytically inert Bn-BOX (*SS*,*SS*)-**9** instead of pyrrolidine (*SS*,*SS*)-**4** at ligand exchange step yielded no aldol product after 72 hours. (entry 4) When TEMPO catalyst (*RR*,*SS*)-**11** was assembled through heterochiral Zn(II) assembly using opposite enantiomer of BOX ligand (*S*,*S*)-**10** instead of (*R*,*R*)-**10**, the second aldol step failed to take place as pyrrolidine (*SS*,*SS*)-**4** was unable to replace heterochiral Zn(II) complex bound TEMPO on resin (*RR*,*SS*)-**11** (entry 5). The pyrrolidine catalyst (*RR*,*SS*)-**5** can be transformed back to the initial non-catalytic resin (*R*,*R*)-**1** through Zn(II) complex disassembly by the EDTA solution. It is noteworthy to mention that the detached BOX-pyrrolidine (*S*,*S*)-**4** ligand was recovered through extraction of EDTA solution. The second-round sequential reactions with regenerated catalytic resin yielded aldol product in similar overall yield as well as enantioselectivity (entry 6).

Table 3. Sequential Oxidation-Aldol Reaction[a]

entry	Oxidation Catalyst	Aldol Catalyst	Time (h)[b] [c] Ox/Aldol	Yield (%)[d] **8**
1[e]	(*RR*,*RR*)-**11**	(*RR*,*SS*)-**5**	9/12	80
2[f]	TEMPO	proline methyl ester	9/72	21
3[g]	(*RR*,*RR*)-**11**	(*RR*,*SS*)-**5**	9/72	25
4	(*RR*,*SS*)-**9**	(*RR*,*SS*)-**5**	72/72	0
5	(*RR*,*SS*)-**11**	No exchange	9/72	trace
6[e][h]	(*RR*,*RR*)-**11**	(*RR*,*SS*)-**5**	9/12	81

[a] Oxidation: *p*-nitrobenzyl alcohol (**12**) (1.0 mmol), isobutyl alcohol (**13**) (1.0 mmol), DIB (2.04 mmol) and catalyst (0.2 mmol) followed by aldol reaction. [b] Total reaction time not including catalyst isolation/exchange/wash processes (approx. 30 min). [c] Reaction time for oxidation and aldol steps are longer due to lower catalytic loading (oxidation) and diluted reaction condition (aldol). [d] Isolated yield of **8**. [e] % ee = 54%, HPLC (Chiralpak AD-H, i-PrOH/hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm): t_{major} =10.71 min, t_{minor} = 12.07 min% ee = 54%, [f]Pyrrolidine **9** was added upon completion of oxidation by **13**. [g] Resins were not washed after ligand exchange process. [h] Second-round sequential reaction.

Conclusions

In summary, we demonstrated a highly versatile approach in assembling resin-bound catalysts using chirality-directed self-assembly. The assembled catalyst is stable in the temperature range typically used in synthesis, yet the loaded catalyst can be easily detached from resin under mild conditions through a ligand exchange. Therefore, a facile regeneration of resin-immobilized catalysts is possible without negatively impacting on the functional/structural frameworks of the chiral BOX functionalized resin. In addition, by taking advantage of the stability differences between homochiral and heterochiral Zn(II) BOX complexes, resin-bound catalysts through a homochiral complex bridge can be easily swapped by simply adding a new catalyst that is bound to a homochiral BOX of the opposite enantiomer. Catalyst exchange on the resin allows the same

resin to be used in sequential operations without preparing multiple sets of resin-immobilized catalysts. The simplicity in assembly enables one to build a large library of resin-immobilized catalysts in very short period of time. In addition, the application of this concept is not limited to the resin-immobilized catalyst, and it can be employed in connecting two functional groups together. Further applications generating a multi-functional resin-immobilized catalysts are under development.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 a) M. Miceli, P. Frontera, A. Macario, A. Malara, *Catalysts*, 2021, **11**, 591-607. b) Z.D. Susam, C. Tanyeli, Cihangir, *Asian J. Org. Chem*. **2021**, *10*, 1251-1266. c) M. Liu, J. Wu, H. Hou, *Chem. Eur. J*. **2019**, *25*, 2935-2948. d) R. Ye, A.V. Zhukhovitskiy, C.V. Deraedt, F.D. Toste, G.A. Somorjai, *Acc. Chem. Res*. **2017**, *50*, 1894-1901. e) C. Moberg, *Acc. Chem. Res*. **2016**, *49*, 2736-2745.

2 a) A, Molnar, A. Papp, *Coord. Chem*. Reviews **2017**, *349*, 1-65. b) R.A. Sheldon, *Chem.Soc.Rev*. **2012** *41*, 1437-1451. c) P.T. Anastas, N. Eghbali, *Chem.Soc.Rev*. **2010**. *39*, 301-312.

3 a) H. Zhang, H. Li, C.C. Xu, S. Yang, *ACS Catal*. **2019**, *9*, 10990-11029. b) P. Munnik, P.E. de Jongh, K.P. de Jong, *Chem. Rev*. **2015**, *115,* 6687-6718. c) E. Barak-Kulbak, K. Goren, M. Portnoy, *Pure Appl. Chem.* **2014**, *86*, 1805-1818. d) M. Benaglia, A. Puglisi, F. Cozzi, Franco, *Chem. Rev* **2003**, *103*, 3401-3429.

4 a) A.F. Trindade, P.M.P.Goisand, C.A.M. Afonso, *Chem. Rev*., **2009**, *109*, 418–514 b) J. Luand, P.H.Toy, *Chem. Rev*., **2009**, *109*, 815–838. c) M. Heitbaum, F.Gloriusand I. Escher, *Angew.Chem.,Int. Ed*., **2006**, *45*, 4732–4762. d) F. Cozzi, *Adv. Synth. Catal*., **2006**, *348*, 1367–1390. e) M. Benaglia, *New J. Chem*., **2006**, *30*, 1525–1533.

5 a) L. Lebreton, M. Egger, B. Slat, *Sci. Rep*. **2019**, *9*, 1-10. b) R.A. Sheldon, J.M. Woodley, *Chem. Rev*. **2018**, *118*, 801-838. c) J.R. Jambeck, R. Geyer, C. Wilcox, T.R. Siegler, M. Perryman, A. Andrady, R. Narayan, K.L. Law, *Science* **2015**, *347*, 768-771.

6 a) F. Moccia, L. Rigamonti, A. Messori, V. Zanotti, R. Mazzoni, *Molecules* **2021**, 26, 2728-2754. b) J. Lu, P.H. Toy, *Chem.Rev*. **2009**, *109*, 815-838. c) X.S. Zhao, X.Y. Bao, W. Guo, F.Y. Lee, *Mater. Today* **2006**, *9*, 32-39. d) P. McMorn, G. J. Hutchings, *Chem. Soc. Rev*. **2004**, *33*, 108. e) N.E. Leadbeater, M. Marco, *Chem.Rev*. **2002**, *102*, 3217-3274. f) C.A. McNamara, M.J. Dixon, M. Bradley, *Chem.Rev*. **2002**, *102*, 3275-3300. g) D.E. De Vos, I.F.J. Vankelecom, P.A. Jacobs, *Chiral Catalysts Immobilization and Recycling*; Wiley-VCH: Weinheim, **2000**.

7 a) M. Lombardo, C. Trombini, *RSC Green Chem*. **2009**, *3*, 1-79. b) P. Barbaro, F. Liguori, *Chem. Rev*. **2009**, *109*, 515-529. c) M. Heitbaum, F. Glorius, I. Escher, Angew. Chem., Int. Ed. **2006**, *45*, 4732-4762. d) J. Horn, F. Michalek, C.C. Tzschucke, W. Bannwarth, *Top. Curr. Chem*. **2004**, 242, 43-75.

8 a) B. Zhang, J.N. Reek, Chem. Asian J. **2021**, *16*, 3851-3863. b) V. I. Parvulescu, H. Garcia, *Catal. Sci. Technol*. **2018**, *8*, 4834-4857

9 a) R. Chen, R. P. Bronger, P. C. Kamer, P. W. van Leeuwen, J. N. Reek, *J.Am. Chem. Soc*. **2004**, *126*, 14557–14566. b) D. de Groot, B. F. de Waal, J. N. Reek, A. P. Schenning, P. C. Kamer, E. W. Meijer, P. W. van Leeuwen, *J. Am. Chem. Soc*. **2001**, *123*, 8453–8458.

10 H. A. Beejapur, F. Giacalone, R. Noto, P. Franchi, M. Lucarini, M. Gruttadauria, *ChemCatChem*. **2013**, *5*, 2991–2999.

11 a) S. Sabater, J. A. Mata, E. Peris, *Organometallics* **2015**, 34, 1186–1190. b) S. Ruiz-Botella, E. Peris, *Chem. Eur. J.* **2015**, *21*, 15263–15271. c) S. Sabater, J. A. Mata, E. Peris, *ACS Catal*. **2014**, *4*, 2038–2047.

12 a) J. Luand, P.H. Toy, *Chem. Rev*., **2009**, *109*, 815–838. b) A. Corma, H. Garcia, *Adv. Synth. Catal*., 2006, 348, 1391–1412. c) D. Astruc, F. Lu, J.R. Aranzaes, *Angew. Chem., Int. Ed*., **2005**, *44*, 7852–7872. d) Y.C. Chen, T.F. Wu, L. Jiang, J.G. Deng, H. Liu, J. Zhu, Y.Z. Jiang, *J. Org. Chem*., **2005**, *70*, 1006–1010.

13 M. Gruttadauria, F. Giacalone, R. Noto, GreenChem., **2013**, *15*, 2608-2618.

14 a) S.H. Cho, B.Q. Ma, S.T. Nguyen, J.T.; Hupp, T.E. Albrecht-Schmitt, *Chem. Commun*. **2006**, 2563-2565. b) C.D. Wu, A. Hu, L. Zhang, W.B. Lin, *J. Am. Chem. Soc*. **2005**, *127*, 8940-8941. c) J.W. Yang, H.Y. Han, E.J. Roh, S.G. Lee, C.E. Song, *Org. Lett*. **2002**, 4, 4685-4688. d) T. Nagashima, H.M.L. Davies, *Org. Lett*. **2002**, *4*, 1989-1992 e) G. Gerstberger, C. Palm, R. Anwander, *Chem. Eur. J*. **1999**, *5*, 997-1005. f) J.M. Fraile, J.I. Garcı´a, B. La´zaro, J.A. Mayoral, *Chem. Commun*.**1998**, 1807-08.

15 a) A.M. Kluwer, C. Simons, Q. Knijnenburg, J.I. van der Vlugt, B. de Bruinand, J.N. Reek, *Dalton Trans*., **2013**, *42*, 3609–3616. b) F. Marras, P.W. van Leeuwen, J.N. Reek, *Chem.–Eur. J*., **2011**, 17, 7460–7471.c) B.W.T. Gruijters, M.A.C. Broeren, F.L. van Delft, R. P. Sijbesma, P.H.H. Hermkens, F.P.J.T. Rutjes, *Org. Lett*., **2006**, *8*, 3163–3166.

16 a) J.M. Takacs, S.A. Moteki, D.S. Reddy, *Supramolecular Catalysis* (Eds.: P.W.N.M. van Leeuwen) Wiley-VCH, Weinheim, **2008**, pp. 235-253. b) J.M. Atkins, S.A. Moteki, S.G. DiMagno, J.M. Takacs, *Org. Lett*. **2006**, *8*, 2759-2762. c) J.M. Takacs, P.M. Hrvatin, J.M. Atkins, D.S. Reddy, J.L. Clark, *New J. Chem*. 2005, *29*, 263-265.

17 J. Zhou, A.M. Cole, E.M. Menuey, K.V. Kilway, S.A. Moteki, *Chem. Commun.* **2021**, *57*, 6404-6407.

18 a) N.C. Thacker, S.A. Moteki, J.M. Takacs, *ACS Catal*. **2012**, *2*, 2743-2752. b) S.A. Moteki, K. Toyama, Z. Liu, J. Ma, Jing; A.E. Holmes, J.M. Takacs, *Chem. Commun*. **2012**, *48*, 263-265. c) S.A. Moteki, J.M. Takacs, *Angew. Chem., Int. Ed*. **2008**, *47*, 894-897. d) J.M. Takacs, D.S. Reddy, S.A. Moteki, D. Wu, H. Palencia, *J. Am. Chem. Soc*. **2004**, *126*, 4494-4495.

19 E.P. Carreiro, N.M.M. Moura, A.J. Burke, Anthony J. *Eur. J. Org. Chem.* **2012**, *3*, 518-528.

20 K. R. Buszek, N. Brown, Neil, *J. Org. Chem*. **2007**, *72*, 3125-3128.

21 a) L. Carneiro, A. R. Silva, P. S. Shuttleworth, V. Budarin, J. H. Clark, *Molecules* **2014**, *19*, 11988-11998. b) A.R. Silva, V. Guimaraes, A.P. Carvalho, J. Pires, *Catal. Sci. Technol*. **2013**, *3*, 659-672.

22 a) S. Toma, *RSC Green Chem*. **2012**, *15*, 18-57. b) R.D. Carpenter, J.C. Fettinger, K.S. Lam, M.J. Kurth, *Angew. Chem., Int. Ed*. **2008**, *47*, 6407-6410.

23 a) A. Martinez, K. Zumbansen, A. Dohring, M. Gemmeren, B. List, *Synlett* **2014**, 25, 932-934. b) T. Kano, H. Sugimoto, K. Maruoka, *J. Am. Chem. Soc.* **2011**, *133*, 18130-18133. c) B. List,

L. Hoang, H.J. Martin, *PNAS* **2004**, *101*, 5839-5842. d) N. Mase, F. Tanaka, C.F. Barbas, *Org. Lett*. **2003**, 5, 4369-4372. e) B. List, R.A. Lerner, C.F. Barbas III, *J. Am. Chem. Soc.* **2000**, *122*, 2395-2396.

24 a) H. Yang, D. Liu, Q. Yu, S. Xia, D. Yu, M. Zhang, B. Sun, F. Zhang, *Eur. J. Org. Chem.* **2019**, *2019*, 852-856. b) D. Limnios, C. Kokotos, *RSC Adv.* **2013**, *3*, 4496-4499 c) M. Marigo, P. Melchiorre, *ChemCatChem* **2010**, *2*, 621-623. d) C. Zheng, Y. Wu, X. Wang, G. Zhao, *Adv. Syn. Catal*. **2008**, 350, 2690-2694. e) S. Chimni, D. Mahajan, *Tetrahedron* **2005**, *61*, 5019-5025. f) A. Cordova, W. Notz, C.F. Barbas, *Chem. Commun*. **2002**, 3024-3025.

25 The % enantiomeric excess using L-proline under the same condition was 80%.

26 a) T. Sun, H. Liang, S. Liu, E. Tang, C. Fu, *J. Nanoparticle Res.* **2020**, *22*, 163. b) Z. Zheng, J. Wang, M. Zhang, L. Xu, J. Ji, *ChemCatChem* **2013**, *5*, 307-312. c) K. Saito, K. Hirose, T. Okayasu, H. Nishide, M.T.W Hearn, *RSC Adv*. **2013**, *3*, 9752-9756. d) Y. Suzuki, M. Iinuma, K. Moriyama, H. Togo, *Synlett* **2012**, 23, 1250-1256. e) T. Fey, H. Fischer, S. Bachmann, K. Albert, C. Bolm, *J. Org. Chem*. **2001**, *66*, 8154-8159.

27 a) T. Okada, T. Asawa, Y. Sugiyama, T. Iwai, M. Kirihara, Y. Kimura, *Tetrahedron*, **2016**, 72, 2818-2827. b) H.A. Beejapur, V. Campisciano, F. Giacalone, M. Gruttadauria, *Adv. Syn. Catal.*, **2015**, 357, 51-58. c) H.A. Beejapur, F. Giacalone, R. Noto, P. Franchi, M. Lucarini, M. Gruttadauria, *ChemCatChem*, **2013**, *5*, 2991-2999. d) C. Zhu, Y. Wei, Yunyang, *Adv. Syn. Catal.*, **2012**, 354, 313-320. e) N. Lu, Y.C. Lin, *Tetrahedron Lett.*, **2007**, 48, 8823-8828. f) G.R. Karimipour, H.A. Shadegan, R. Ahmadpour, *J. Chem. Res*. **2007**, *4*, 252-256.

28 a) Y. Wang, C. Wang, Q. Cheng, Y. Su, H. Li, R. Xiao, C. Tan, G. Liu, *Green Chem.* **2021**, *23*, 7773-7779. b) H. Fan, Y. Yang, J. Song, G. Ding, C. Wu, G. Yang, B. Han, *Green Chem*. **2014**, *16*, 600-604. c) K. Akagawa, S. Takigawa, E. Mano, K. Kudo, *Tetrahedron Lett*. **2011**, 52, 770-773.

29 a) Y. Ueda, H. Ito, D. Fujita, M. Fujita, Makoto, *J. Am. Chem. Soc*. **2017**, *139*, 6090-6093. b) Y. Sasano, S. Nagasawa, M. Yamazaki, M. Shibuya, J. Park, Y. Iwabuchi, *Angew. Chem., Int. Ed*. **2014**, 53, 3236-3240