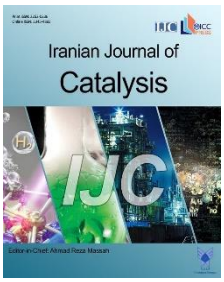


Volume 15, Issue 4, (2025) Article(1-6)

Iranian Journal of Catalysis (IJC)

https://doi.org/10.57647/j.ijc.2025.1504.50

Catalytic Applications of Chiral Covalent Organic Frameworks

Bahareh Vandaei

Faculty of Chemistry, Bu-Ali Sina University, Hamedan 6517838683, Iran

***Corresponding author:** Bahareh074.vandaei@gmail.com

Spotlight

Received:
20 October 2025

Revised:
9 August 2025

Accepted:
19 October 2025

Published online:
5 November 2025

Published in issue:
31 December 2025

Abstract

Bahareh Vandaei was born in 1995 in Hamedan, Iran. She received her B.Sc. in Applied Chemistry in 2020 and her M.Sc. in organic chemistry from the same university under the guidance of Dr. Meysam Yarie at Bu-Ali Sina University. She is currently working towards her Ph.D. under the supervision of Dr Maliheh Safaiee at Bu-Ali Sina University. Her research interest is the design, synthesis and characterization of porous organic polymers and their catalytic applications in organic reactions.

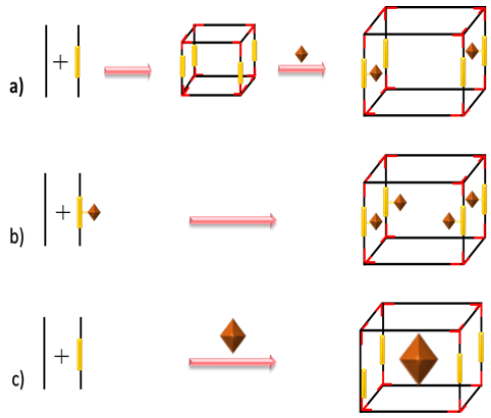
This feature focuses on a catalyst selected by a graduate student and highlights the application and preparation methodes of catalysts in current research.

1. Introduction

In recent decades, covalent organic frameworks (COFs) chemistry has emerged as one of the most exciting fields in chemistry. COFs are a class of regular organic structures composed of various organic units, including carbon, nitrogen, hydrogen, and boron, which are interconnected through covalent bonds. These unique materials have been widely applied in numerous research areas [1-3]. Due to their high stability, unique structural features, excellent tunability, and versatile performance, COFs have attracted considerable attention.COFs can form as 2D or 3D regular crystalline structures under thermodynamic control [4-8]. The creation of COFs by Yaghi and his team in 2005 has sparked a vibrant area of research in materials science, which has grown and developed at an impressive pace [9-12]. COFs can be utilized for various applications, including gas adsorption, sensing, proton conduction, energy storage, catalytic processes, and drug delivery [13–24]. Their properties include permanent porosity with a high specific surface area, low density, tunable pore diameter (ranging from micropore to mesopore size), and high stability in common solvents as well as under extremely acidic or alkaline conditions. Additionally, these compounds exhibit intrinsic catalytic activity, making them highly suitable for heterogeneous catalysis [25,26]. In recent years, the field of chiral science and technology, encompassing the synthesis, structural analysis, isolation, and applications of chiral compounds, has garnered increasing attention [27].

A careful selection of building blocks can lead to porous COFs with advantages such as structural diversity and ease of processing. These COFs also exhibit highly ordered pores, high electrical conductivity, mechanical processability, and superior chemical stability [28,29]. These attributes endow chiral covalent organic frameworks (CCOFs) with significant capabilities for chiral separation, chiral recognition, catalysis, chiral optics and asymmetric synthesis [30]. The advancement of CCOFs is crucial for the progress of chiral science. However, one ongoing challenge in developing CCOFs is achieving a balance between the asymmetry of the chiral monomers and the crystallinity of the materials. Therefore, precise control over chirality, functionality, and crystallinity is essential. To date, only a limited number of CCOFs have been reported, and their network topologies remain quite

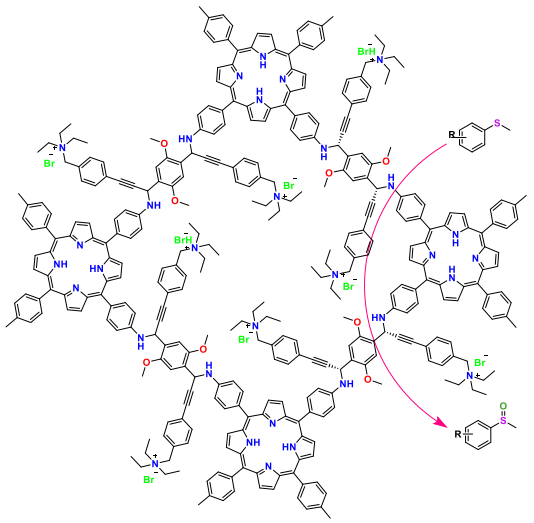
restricted. The synthetic methods for creating chiral COFs are generally categorized into three types: 1) post-synthesis, 2) direct synthesis and 3) cross-linking construction [31] (Scheme 1).
Strategies: post-Chiral COFs exhibit high activity and enantioselectivity for various asymmetric catalytic organic transformations [32]. They can encapsulate volatile radionuclides produced during the nuclear fission process, which pose threats to public safety and the environment [33]. Another catalytic advantage of chiral COFs is their stability, which is comparable to that of polymer catalysts. This study and review aim to provide an overview of COFs, focusing on their design, synthesis, and applications in asymmetric catalysis. This review also discusses chiral COFs, including case studies that demonstrate design strategies, structural features, and applications. In this spotlight, the catalytic performance of chiral COFs in asymmetric synthetic reactions is highlighted.



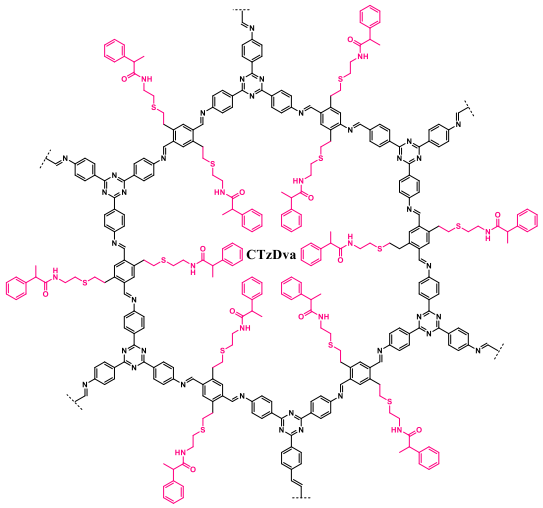
Scheme 1. The strategies to build CCOF: a) postmodification, b) presynthesis, pendant mode and c) chiral induction.

Abstract:

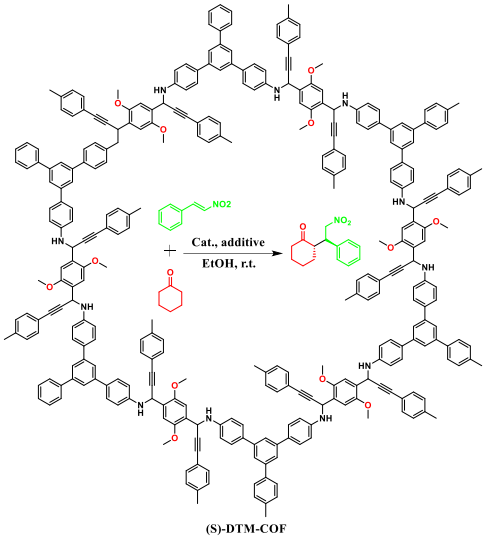
(A) In 2022, Zheng and co-workers reported a chiral organocovalent framework (CCOF) known as (R)-DTP-COF-QA, which was composed of porphyrin photosensitizers, chiral propargylamine linkers, and ammonium bromide phase transfer groups. Under optimal conditions, (R)-DTP-COF-QA catalyzed the enantiomeric oxidation of a wide range of sulfides to sulfoxides with yields ranging from 81% to 96% and enantiomeric excesses ranging from 77% to 99%. This CCOF also facilitated the photocatalytic synthesis of (R)-modafinil, a drug used to treat excessive sleepiness. Furthermore, it demonstrated excellent recyclability and stability over five steps [34].



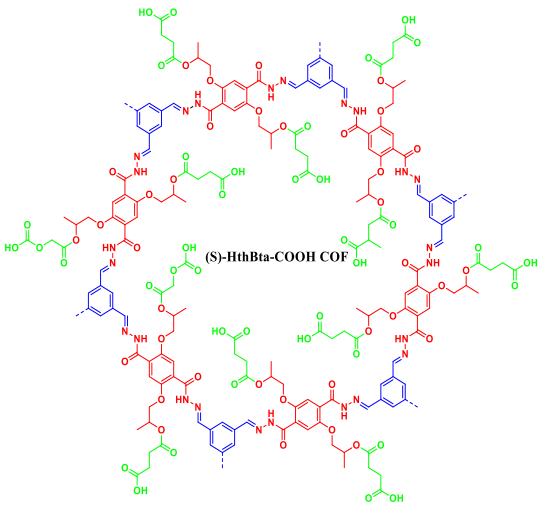
(B) In 2021, Guo and colleagues demonstrated a simple and effective “thiol-ene” click strategy for the synthesis of chiral COFs. First, the COF precursor, TzDva, was synthesized via the imine condensation reaction of Tz and Dva. The obtained TzDva and the chiral thiol derivative were reacted in a suitable solvent mixture of mesitylene/1,4-dioxane (5/5, v/v) to form chiral COFs in about 95.5% yield. The chiral COF CTzDva exhibited high thermal stability and good porosity. Using this synthesized CCOF on a CTzDva-based gas capillary column, it showed good separation of benzene/cyclohexane and racemates (citronellal and fenchone). This work provided a convenient strategy for the preparation of chiral COFs for the separation of racemates [35].



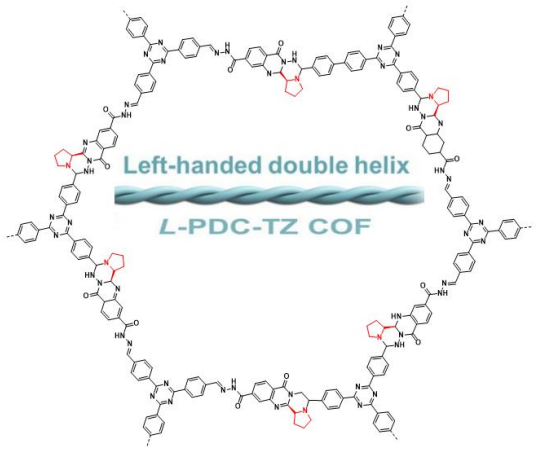
(C) In 2020, the Dong group reported the synthesis of CCOFs from prochiral monomers via catalytic asymmetry. Propargylamine-linked CCOFs can provide highly reusable chiral catalysts for the first time. This involved a three-component reaction during catalytic asymmetric polymerization using 2,5-dimethoxyterephthalaldehyde (DMTP), 1,3,5-tris(4-aminophenyl)benzene (TAPB), phenylacetylene (PA), and the catalyst (S)-DTP-COF. Notably, this synthesis strategy did not require harsh reaction conditions and avoided harmful solvents and extreme temperatures or pressures. It successfully carried out the Michael addition reaction in the presence of acid and ethanol with (S)-DTP-COF as the chiral catalyst [36].



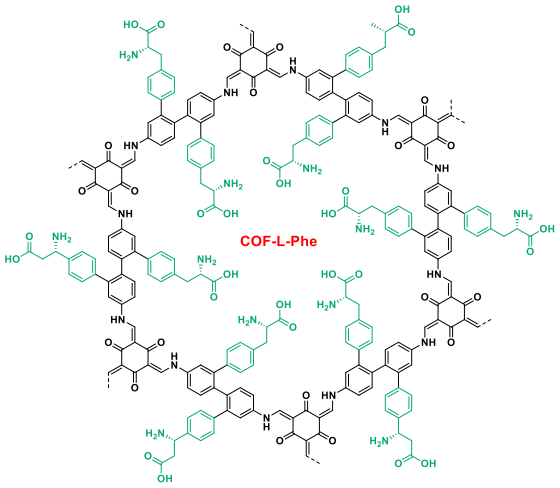
(D) In 2020, Cai and co-workers developed a novel synthesis of enantiomeric pairs of hydroxyl-functionalized hydrazone-linked 2D chiral COFs, named (S)- and (R)-HthBta-OH. Notably, the VCD spectra showed a chiral signal inversion from the positive cation effect of the (S)-Hth monomer to the negative cation effect of the (S)-HthBta-OH chiral COFs, which has never been reported in chiral COFs. Also, two catalysts, (S)- and (R)-HthBta-COOH, were prepared by post-synthesis modification of the corresponding hydroxyl-functionalized chiral COFs with succinic anhydride. These carboxyl-functionalized COFs, due to the high chemical specificity of the initial hydrazone-linked chiral COFs, retained homochirality and crystallinity without linker racemization and structural collapse after chemical modification. The resulting stable homochiral COFs, which are hydrazone-linked and have hydroxyl and carboxyl functional groups, can be used as good candidates for chiral chromatographic separation and asymmetric catalysis [37].



(E) Tang et al. (2023) reported the synthesis of an enantiomeric pair of chiral helical COFs, namely L-PDC-TZ COF and D-PDC-TZ COF. The chiral framework consists of a novel amine bond and a hydrazone bond formed between the multifunctional L/D-PDC and benzaldehyde (BA). Interestingly, by adjusting the amount of acetic acid used in the synthesis, the COF nanostructures can be switched between two opposing helices, thereby enabling control of the chirality and helicity of the framework. This work provides a new example of template-free self-assembly of chiral nanofibrous COF double helices. They also demonstrate the modulated chiroptic properties of chiral nanofibrous COF helices. By transferring chirality to chiral fluorescent molecular absorbers, the helical COF nanostructures can effectively induce circularly polarized luminescence with the highest luminescence asymmetric coefficient (glum) of up to about 0.01 [38].



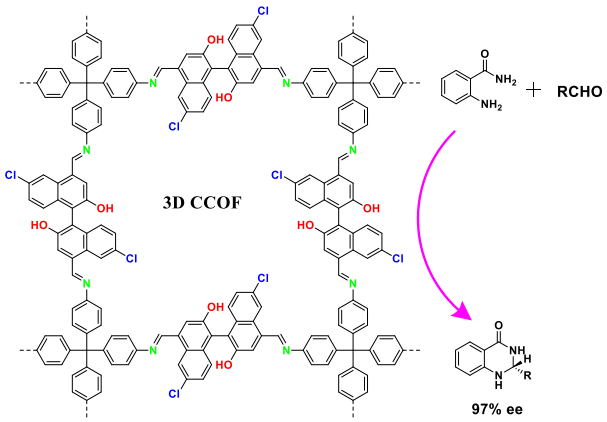
(F) In 2023, Tan and co-workers synthesized a brominated functionalized COF (COF-Br). This COF has high crystallinity and stability. Brominated COF (COF-Br) was synthesized using 2,4,6-trihydroxybenzene-1,3,5-tricarbaldehyde (Tp) and 3,30-dibromo-[1,10-biphenyl]-4,40-diamine (BD) via Schiff base condensation. Then, a new chiral COF (COF-L Phe) was constructed by mixing COF-Br with L-BPA via Suzuki-Miyaura cross-coupling reaction. Also, capillary columns modified with COF-L-Phe were successfully used for the separation of racemic phenylalanine using capillary electrochromatography. The results of adsorption and arteriole electrochromatography experiments showed that COF-L-Phe has a favorable chiral separation potential for D- and L-Phe [39].



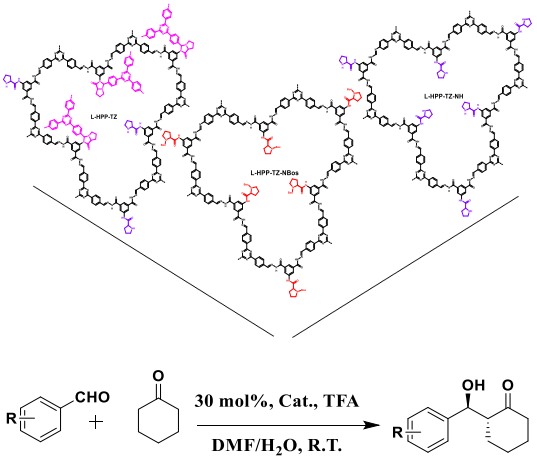
ee% Values of each amino acid on different materials

Materials	Phenylalanine(%)	Tryptophan(%)
COF-Br	4.39	7.76
COF-L-Phe	18.03	7.55

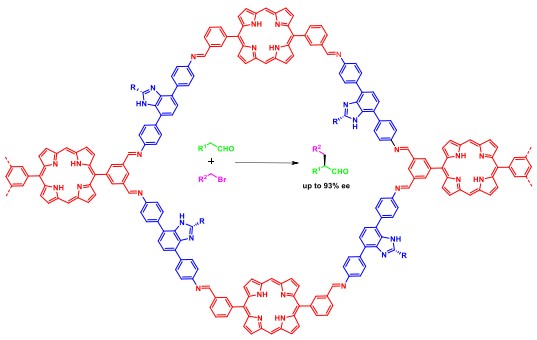
(G) In 2021, Kuiwei and colleagues prepared a 3D CCOF catalyst by incorporating homogeneous catalysts into COFs, creating heterogeneous catalysts with enhanced activity and selectivity. Two 3D CCOFs were formed through the condensation of a tetrahedral tetraamine with two linear dialdehydes derived from 1,1'-binaphthol (BINOL) compounds, which lack enantioselectivity but can induce high enantioselectivity properties in 3D COFs through structural methods in rigid pores. During the reaction process, they synthesized enantioselectivity from aldehydes and anthranilamides in the catalytic synthesis of dihydroquinazoline. The arrangement of BINOL hydroxyl groups within the channels results in much higher acidity compared to the free acids, and they can act as heterogeneous Brønsted catalysts [40].



(H) In 2024, Cai and colleagues were able to synthesize a series of three chiral COFs linked to cloverleaf hydrazone, each with a variable number of accessible chiral pyrrolidine catalytic sites. The catalytic efficiency of these COFs in the asymmetric aldol reaction between cyclohexanone and 4-nitrobenzaldehyde correlated well with the number of accessible pyrrolidine sites in the frameworks. L-HPP-TZ-NH2, which contained the largest number of active pyrrolidine-NH2 sites in the valve channels, showed the highest catalytic activity (97% yield) and chiral selectivity (83% ee and 1:8.5 dr) for catalyzing the reactions between cyclohexanone and nitrobenzaldehydes. L-HPP-TZ-NBoc and LHPP-TZ with fully and partially blocked pyrrolidine-NH2 sites in the pores, respectively, showed poor chiral catalytic performance [41].



(I) In 2023, Liu and co-workers reported a general strategy for the successful synthesis of several photoactive CCOFX (X = 1-5 and 1-Boc). Photoactive porphyrin building blocks and various chiral secondary amine-based catalytic centers were immobilized on the pore walls of CCOFX via benzimidazole linkers. The porphyrin units act as light-harvesting antennae to generate photoinduced charge carriers for bromide activation during the photocatalytic asymmetric alkylation of aldehydes. Also, various aldehydes are activated by the chiral secondary amine to form products with high yields (up to 97%) and ee values (up to 93%). The CCOF catalysts demonstrated excellent conversion and stereoselectivity in the asymmetric alkylation of aldehydes under visible light irradiation, along with good recyclability [42].



Authors Contribution
All authors have contributed equally to prepare the paper.

Availability of data and materials
The data that support the findings of this study are available from the corresponding author, upon reasonable request.

Conflict of interests
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] T. Sun, J. Xie, W. Guo, D. S. Li, Q. Zhang, Adv. Energy Mater., 10(2020):1904199.
DOI: https://doi.org/10.1002/aenm.201904199.

[2] E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Hene, D. Jiang, Sci., 357(2017):673-676.
DOI: https://doi.org/10.1126/science.aan0202.

[3] B. Zhang, M. Wei, H. Mao, X. Pei, S. A. Alshmimri, J. A. Reimer, O. M. Yaghi., J. Am. Chem. Soc., 140(2018):12715-12719.
DOI: https://doi.org/10.1021/jacs.8b08374.

[4] H. Wang, Z. Zeng, P. Xu, L. Li,G. Zeng,R. Z. Xiao, D. Tang , Huang, L. Tang, C. Lai, D. Jiang, Y. Liu, H. Yi, L. Qin, S. Ye, X. Ren, W. Tang, Chem. Soc. Rev., 48(2019):488-516.
DOI: https://doi.org/10.1039/C8CS00376A.

[5] E. Jin, M. Asada, Q. Xu, S. Dalapati, M. A. Addicoat, M. A. Brady, H. Xu, T. Nakamura, T. Heine, Q. Chen, D. Jiang, Sci., 357(2017):673-676.
DOI: https://doi.org/10.1126/science.aan0202.

[6] X. Guan, H. Li, Y. Ma, M. Xue, Q. Fang, Y. Yan,V. Valtchen, S. Qiu, Nat. chem., 11(2019):587-594.
DOI:https://doi.org/10.1038/s41557-019-0238-5.

[7] C. S. Diercks, O. M. Yaghi, Sci., 355(2017): eaal1585.
DOI: https://doi.org/10.1126/science.aal1585.

[8] H. R. Abuzeid, A. F. EL-Mahdy, S. W. Kuo, Gaint., 6(2021):100054.
DOI: https://doi.org/10.1016/j.giant.2021.100054.

[9] S. Y. Ding, J. Gao, Q. Wang, Y. Zhang, W. G. Song, C. Y. Su, W. Wang, J. Am. Chem. Soc., 133(2011):19816-19822.
DOI: https://doi.org/10.1021/ja206846p.

[10] Y. Zhi, Z. Wang, H.L. Zhang, Q. Zhang, Small, 16(2020):2001070.
DOI: https://doi.org/10.1002/smll.202001070.

[11] H. Wang, Z. Zeng, P. Xu, L. Li, G. Zeng, R. Xiao, Z. Tang, D. Huang, L. Tang, C. Lai, D. Jiang, Y. Lin, H. Yi, L. Qin, S. Ye, X. Ren,W. Tang, Chem. Soc. Rev., 48(2019):488-516.
DOI: https://doi.org/10.1039/C8CS00376A.

[12] J. L. Segura, M. J. Mancheño, F. Zamora, Chem. Soc. Rev., 45(2016):5635-5671.
DOI: https://doi.org/10.1039/C5CS00878F.

[13] A. M. Evans, L. R. Parent, N. C. Flanders, R. P. Bisbey, E. Vitaku, M. S. Kirschner, R. D. Schaller, L. X. Chen, N. C. Gianneschi, W. R. Dichtel, Sci., 361(2018):52-57.
DOI: https://doi.org/10.1126/science.aar7883.

[14] Y. Zeng, R. Zou, Y. Zhao, Adv. Mater., 28(2019):2855-2873.
DOI: https://doi.org/10.1002/adma.201505004.

[15] S. S. Han, H. Furukawa, O. M. Yaghi, W. A. Goddard Iii, J. Ame. Chem. Soc., 130(2008):11580-11581.
DOI: https://doi.org/10.1021/ja803247y.

[16] Q. Hao, Z. J. Li, C. Lu, B. Sun, Y. W. Zhong, L. J. Wan, D.Wang, J. Ame. Chem. Soc., 141(2019):19831-19838.
DOI: https://doi.org/10.1021/jacs.9b09956.

[17] X. Liu, D. Huang, C. Lai, G. Zeng, L. Qin, H. Wang, H. Yi, B. Li, S. Liu, M. Zhang, R. Deng, Y. Fu, L. Li,W. Xue, S. Chen, Chem. Soc. Rev., 48(2019):5266-5302.
DOI: https://doi.org/10.1039/C9CS00299E.

[18] F. Yu, W. Liu, B. Li, D. Tian, J. L. Zuo, Q. Zhang, Angew. Chem. Int. Ed., 58(2019):16101-16104.
DOI: https://doi.org/10.1002/anie.201909613.

[19] S. Chandra, T. Kundu, S. Kandambeth, R. BabaRao, Y. Marathe, S. M. Kunjir, R. J. Banerjee,. Ame. Chem. Soc., 136(2014):6570-6573.
DOI: https://doi.org/10.1021/ja502212v.

[20] H. Xu, S. Tao, D. Jiang, Nature materials., 15(2016):722-726.
DOI: https://doi.org/10.1038/nmat4611.

[21] C. Wu, Y. Liu, H. Liu, C. Duan, Q. Pan, F. J. Zhu, F. Hu, X. Ma, T. Jiu, Z. Li, Y. Zhao, J. Ame. Chem. Soc., 140(2018):10016-10024.
DOI: https://doi.org/10.1021/jacs.8b06291.

[22] S. Wu, M. Li, H. Phan, D. Wang, T. S. Herng, J. Ding, Z. Lu, J. Wu, Angew. Chem. Int. Ed., 57(2018):8007-8011.

DOI: https://doi.org/10.1002/anie.201801998.

[23] Q. Fang, J. Wang, S. Gu, R. B. Kaspar, Z. Zhuang, J. Zheng, H. Guo, S. Qiu, Y. Yan, J. Ame. Chem. Soc., 137(2015):8352-8355.
DOI: https://doi.org/10.1021/jacs.5b04147.

[24] C. Liu, W. Zhang, Q. Zeng, S. Lei, Chem. Eur. J., 22(2016):6768-6773.
DOI: https://doi.org/10.1002/chem.201601199.

[25] H. Hu, Q.Yan, R. Ge, Y. Gao, Chinese. J. Catal, 39(2018):1167-1179.
DOI: https://doi.org/10.1016/S1872-2067(18)63057-8.

[26] J. Liu, N. Wang, L. Ma, Chem. Asian. J., 15(2020):338-351.
DOI: https://doi.org/10.1002/asia.201901527.

[27] X. Han, C. Yuan, B. Hou, L. Liu, H. Li, Y. Liu, Y.Cui, Chem. Soc. Rev., 49(2020):6248-6272.
DOI: https://doi.org/10.1039/D0CS00009D.

[28] X. Wu, X. Han, Y. Liu, Y. Liu, Y. Cui, J. Am. Chem. Soc., 140(2018):16124-16133.
DOI: https://doi.org/10.1021/jacs.8b08452.

[29] X. Guan, H. Li, Y. Ma, M. Xue, Q. Fang, Y. Yan, V. Valtchev, S. Qiu, Nat. chem., 11(2019):587-594.
DOI: https://doi.org/10.1038/s41557-019-0238-5.

[30] G. Liu, J. Sheng, Y. Zhao, Sci. China Chem., 60(2017):1015-1022.
DOI: https://doi.org/10.1007/s11426-017-9070-1.

[31] S. C. Yu, L. Cheng, L. Lius. Organic Materials., 3(2021):245-253.
DOI: https://doi.org/10.1055/a-1400-5581.

[32] H. Zhang, L. L. Lou, K. Yu, S. Liu, Small., 17(2021):2005686.
DOI: https://doi.org/10.1002/smll.202005686.

[33] Y.Sun, S. Song, D. Xiao, L.Gan, Y. Wang, ACS omega., 5(2020):24262-24271.
DOI: https://doi.org/10.1021/acsomega.0c02382.

[34] H. Zheng, & W. Lin, Chem Catal., 2(2022):2820-2822.
DOI: https://doi.org/10.1016/j.checat.2022.10.014.

[35] J. X. Guo, C. Yang, & X. P. Yan, J. Mater. Chem. A., 9(2021):21151-21157.
DOI: https://doi.org/10.1039/D1TA04621G.

[36] J. C. Wang, X. Kan, J. Y. Shang, H. Qiao, Y. B. Dong, J. Ame. Chem. Soc., 142(2020):16915-16920.
DOI: https://doi.org/10.1021/jacs.0c07461.

[37] Y. Yan, X. Li, G. Chen, K. Zhang, X. Tang, S. Zhang, S. Zheng, J. Fan, W. Zhang & S. Cai, Chin. Chem. Lett., 32(2021):107-112.
DOI: https://doi.org/10.1016/j.cclet.2020.11.063.

[38] X. Tang, X. Liao, X. Cai, J. Wu, X. Wu, Q. Zhang, & Y. Liu, Angew. Chem. Int. Ed., 62(2023):e202216310.
DOI: https://doi.org/10.1002/anie.202216310.

[39] D. Tan, T. Wang, J. Hu, D. Deng, T. Li, & R. Li, NJC., 47(2023):6378-6384.
DOI: https://doi.org/10.1039/D2NJ05811A.

[40] B. Hou, S. Yang, K. Yang, X. Han, X. Tang, Y. Liu, J. Jiang, Y. Cui, Angew. Chem. Int. Ed., 60(2021):6086-6093.
DOI: https://doi.org/10.1002/anie.202013926

[41] K. Zhang, X. Tang, X. Yang, J. Wu, B. Guo, R. Xiao, S. Zheng, H. Jiang, J. Fan, W. Zhang, Y. Liu, & S. Cai, ACS Appl. Mater. Interfaces., 16(2024):10661-10670.
DOI: https://doi.org/10.1021/acsami.3c17048.

[42] T. He, R. Liu, , S. Wang, I. K. W. On, Y. Wu, Y. Xing, W. Yang, J. Gao, & Y. Zhao, J. Am. Chem. Soc., 145(2023):18015-18021.
DOI: https://doi.org/10.1021/jacs.3c05732.