IRANIAN JOURNAL OF CATALYSIS

Hydrogen-bond catalysis

Compiled by Maryam Mansouri

Maryam Mansouri was born in 1996 in Ilam/Iran. Having graduated in the field of chemical industry engineering (2016) from Vali-asr University, Tehran, Iran, She continued Her M.Sc. in 2017 in Organic Chemistry under the supervision of Professor Davood Habibi. Her research interest is the design, synthesis, and characterization of task-specific biological-based catalysts and their applications in organic transformations.

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

E-mail: maryammansouri13751375@gmail.com

This feature focuses on a reagent chosen by a postgraduate, highlighting the uses and preparation of the reagent in current research.

Introduction

Hydrogen bonding (HB) is a ubiquitous force in nature. It plays a crucial role in biocatalysis. Not until recently have chemists begun to implement this force in catalysis, but already with extraordinary success. However, chemists have only recently attempted to harness the power of using hydrogen bonds to perform catalysis, and the field is relatively undeveloped compared to research in Lewis acid catalysis. Nevertheless, the development of chiral Brønsted acids as activation forces is a highly challenging task in asymmetric catalysis, presumably because much weaker hydrogen-bonding interactions between the promoter and substrates would be the source of stereochemical control. Recently, chemists have begun to appreciate the potential offered by hydrogen bonding as a force for electrophile activation in small-molecule-based catalysis. In particular, the utilization of chiral hydrogen-bond donors as promoters has been the subject of intense research, as evidenced by the number of research papers that have appeared. The majority of HB catalysts incorporate the thiourea and phosphoric amide functional group. The advantages of this type of hydrogen bond catalysts include air and water stability, ease of synthesis, modification, and activity over a wide range of substrates. HB catalysis is a type of organocatalyzed catalysis that relies on the use of hydrogen bonding interactions to accelerate and control organic reactions [1-2]. HB catalysts are often simple to make, relatively robust, and can be synthesized in high enantiomeric purity. New reactions catalyzed by hydrogen-bond donors are being discovered at an increasing pace, including asymmetric variants of common organic reactions useful for synthesis, such as aldol additions, Diels-Alder cycloadditions and Mannich reactions. HB catalysis can promote reactions through a variety of different mechanisms. During the course of a reaction, hydrogen bonding can be used to stabilize anionic intermediates and transition states. Alternatively, some catalysts can bind small anions, enabling the formation of reactive electrophilic cations. More acidic donors can act as general or specific acids, which activate electrophiles by protonation. A powerful approach is the simultaneous activation of both partners in a reaction, e.g. nucleophile and electrophile, termed "bifunctional catalysis". In all cases, the close association of the catalyst molecule to substrate also makes hydrogen-bond catalysis a

powerful method of inducing enantioselectivity [3-5]. Catalytic performance is done in several ways, including: (1) Stabilization of tetrahedral intermediates (2) Stabilization of anionic fragments (3) Anion binding (4) Protonation (5) Multifunctional strategies (**Fig. 1**) [6]. Important applications of hydrogen bonds include sequencing in DNA, as a biocatalyst in chemical reactions, as nuclei, and nuclear interactions to conduct the oxidation of α-C-H amines to amides and amino ketones. In addition to the catalytic activity in chemical reactions, hydrogen bonds can be used as electrophilic reducing the electron density and attacking the activated core. Hydrogen catalysts and enzymes is often used to speed up chemical and biological processes. Urea and thiourea are the most common structures that have similar units and can stabilize a variety of negatively charged intermediates, as well as engage in anion-binding catalysis. Bifunctional urea and thiourea catalysis are abundant in the literature. Guanidinium and amidinium ions are structural relatives of ureas and thioureas and can catalyze similar reactions but, because of their positive charge, they are stronger donors and much more acidic.

Diol catalysts are thought to engage the substrate with a single hydrogen bond, with the other hydroxyl participating in an internal hydrogen bond. These are some of the earliest hydrogen bond catalysts investigated. They are most commonly used in stabilizing partial anionic charge in transition states, for example coordinating to aldehyde dienophiles in hetero-Diels-Alder reactions. Phosphoric acid catalysts are the most common strong acid catalysts and formed by chiral ion pairs with basic substrates such as imines [7].

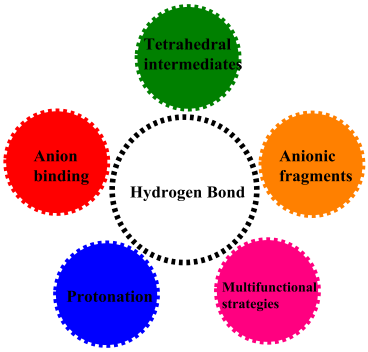


Fig. 1. How catalytic performance is done in several ways

Several mechanisms hydrogen bond Chemical reactions [15] (**Fig. 2**):

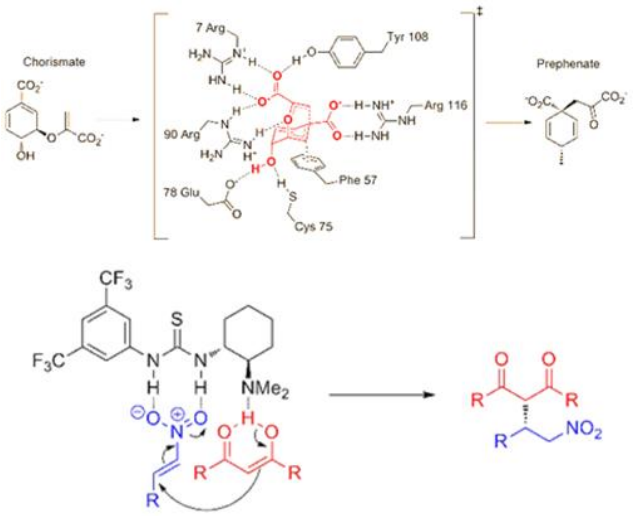


Fig. 2. Mechanisms hydrogen bond

An emerging strategy in the synthesis of new catalysts is to harness the strength of hydrogen bonds in the design of catalysts. Over the past decade, major advances in the analysis of organic acids by asymmetric Brønsted / hydrogen bond donors have been facilitated, including phosphoric acid, diol and Gvanydynym of urea and theories have been achieved. (**Fig. 3**) [8-13]. It has become clear that non-covalent interactions position of influence is in synthesis, catalytic process to design and develop drugs, diagnostic substances and molecules, reactions molecular biology. [14]. One of the most important non-covalent interactions is the ability to form hydrogen bonds. In addition, in synthetic chemical processes, scientists will be able to adjust the chemical interactions hydrogen bonds with the use of chemical bonds stereo. [15-16]. Therefore, it is not surprising that the analysis of hydrogen bond catalysis as an interesting topic of study has expanded rapidly and several review articles exist dealing with this field of analysis. [17-21]. Recently, we have reviewed various aspects of urea and its derivatives as powerful and influential catalytic active agents in a wide range of chemical processes [22].

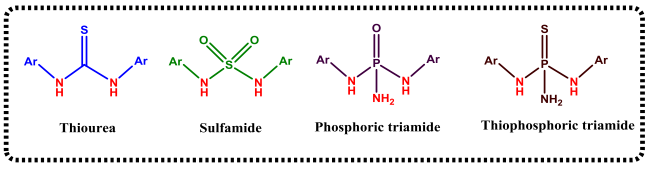
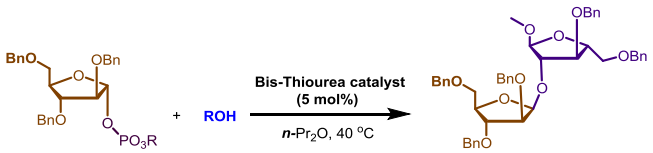


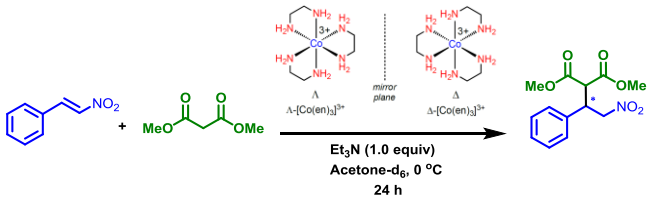
Fig. 3. The sulfamide, phosphoric triamide, and thiophosphoric triamide structures.

Abstracts

(A) In 2020, Jacobsen. et al., [23] reported a new method for stereoselective Ofuranosylation reactions promoted by a precisely tailored bis-thiourea hydrogen-bond-donor catalyst.

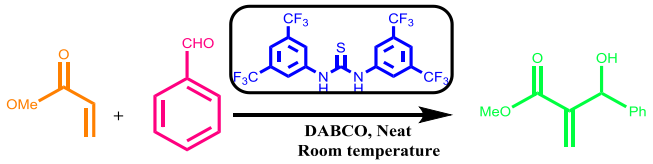


(B) The Chiral Tricationic tris(1,2-diphenylethylenediamine) Cobalt(III) Hydrogen Bond Donor Catalysts with Defined Carbon/Metal Configurations; Matched/Mismatched Effects upon Enantioselectivities with Enantiomeric Chiral Counter Anions [24] have been investigated.



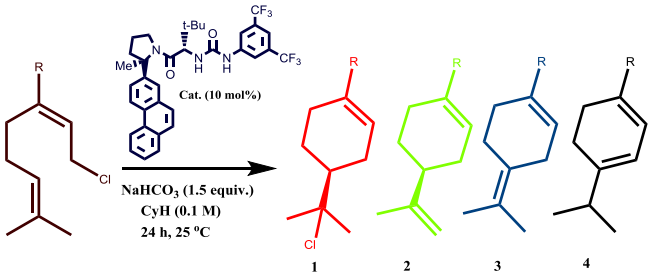
(C) New Architectures in Hydrogen Bond Catalysis:

The Baylis–Hillman reaction between methyl acrylate and benzaldehyde was also examined with catalysts. Urea have been used successfully to catalyze this transformation [25].



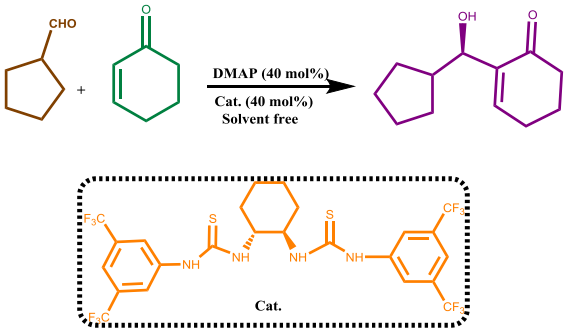
(D) Enantioselective Tail-to-Head Cyclizations Catalyzed by Dual-Hydrogen-Bond Donors:

The reactivity of the resulting carbocationic intermediates is then modulated through a combination of substrate preorganization5 and non-covalent stabilizing interactions3,6 in the enzyme active site, resulting in selective rearrangements and carbon-carbon bond-forming reactions that ultimately give rise to an extraordinarily diverse array of natural products [26].

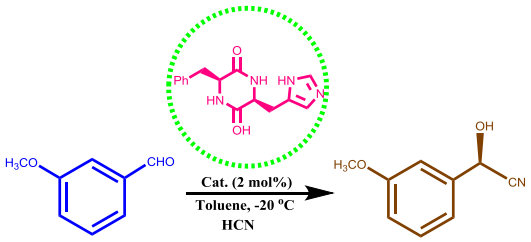


(E) Asymmetric Catalysis by Chiral Hydrogen-Bond Donors:

Thioureas incorporating additional acidic groups also show promise as bifunctional catalysts. Bis-thiourea mediates enantioselective Baylis–Hillman reactions of cyclohexanone with aldehydes in the presence of N, N-(dimethylamino) pyridine or imid azole [27].



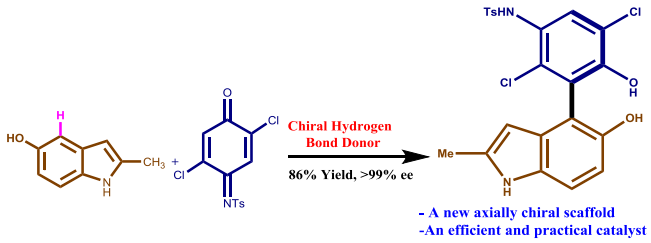
(F) The hydrocyanation of aldehydes developed by Inoue in 1981 was among the first-reported highly enantioselective oligopeptide-catalyzed reactions. The diketopiperazine cyclo (l-phenylalanine-l-histidine) was found to mediate asymmetric hydrocyanation of a variety of aldehydes, with particularly high enantiomeric excess observed using electron-rich benzaldehyde substrates [27-28].



(G) An Atropo-enantioselective Synthesis of Benzo-Linked Axially Chiral Indoles via Hydrogen-Bond Catalysis:

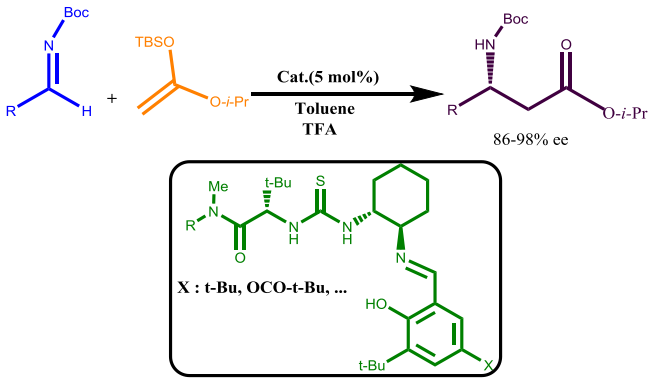
1- Constructing axial chirality via hydrogen-bond catalysis.

2- The first example of constructing axial chirality through functionalization of indoles in the carbocyclic ring [29].

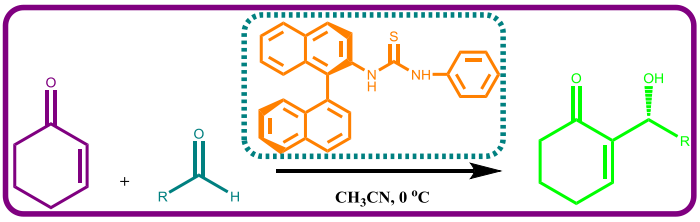


(H) Monofunctional Thiourea Catalysts:

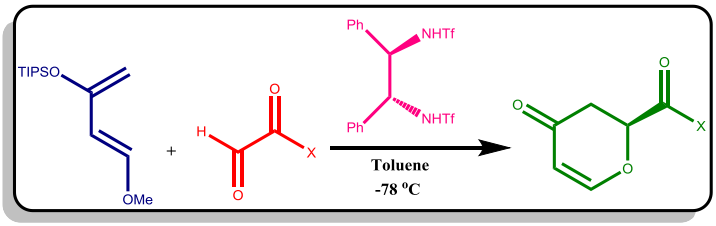
Thioures have been extensively investigated in molecular recognition due to their ability to form hydrogen bonds. Curran et al. observed the alteration of the stereoselectivity by use of a urea derivative in 1994. A similar catalyst is applicable to the asymmetric Mannich-type reaction of N-Boc-aldimines with silylketene acetals. The corresponding b-amino esters were obtained in 86–98% ee [30-31].



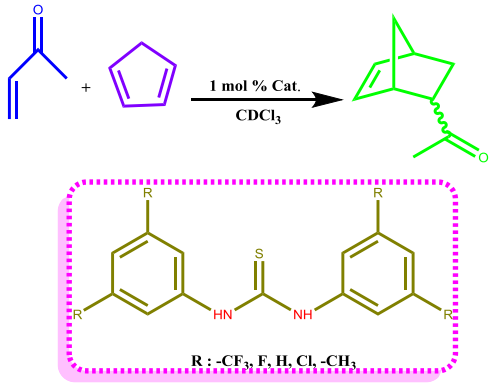
(I) Wang et al. developed the bifunctional thiourea, bearing a binaphthyl backbone and an amine moiety, which catalyzed the Morita–Baylis–Hillman reaction of cyclohexenone with a wide range of aldehydes [32].



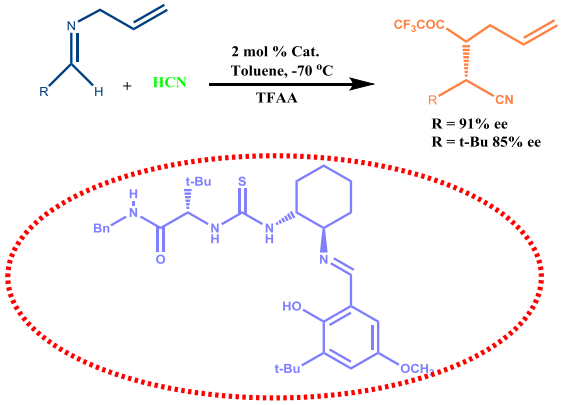
(J) Mikami et al. reported that the Bis-sulfonamide derived from 1,2-diamino-1,2-diphenylethane 14 proved to be effective as a catalyst for the hetero-Diels– Alder reaction of DanishefskyKs diene with glyoxylate [33].



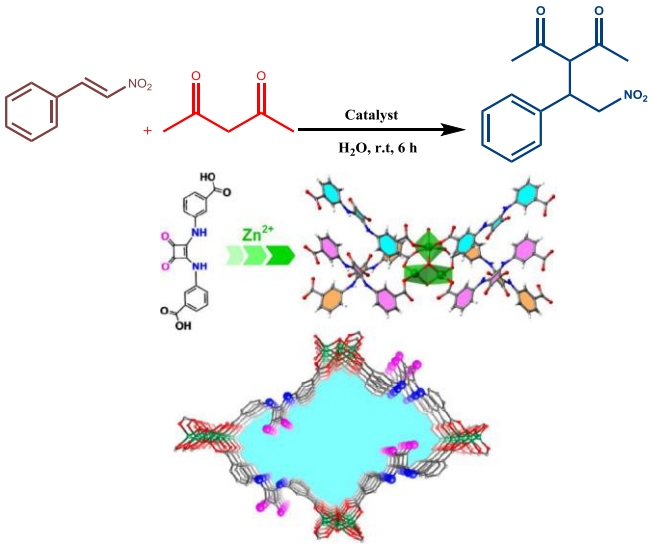
(K) Metal-Free, Noncovalent Catalysis of Diels ± Alder Reactions by Neutral Hydrogen Bond Donors in Organic Solvents and in Water: To screen catalyst efficiencies, we carried out a series of Diels -Alder reactions of cyclopentadiene with several unsaturated carbonyl compounds catalyzed by thiourea derivatives and without an additive in deuterated chloroform. Chloroform is a hydrogen-bond donor and is known to accelerate Diels-Alder reactions [34].



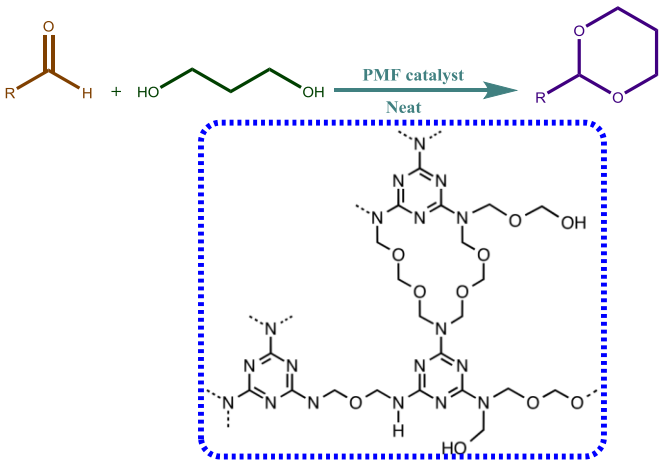
(L) Small-Molecule H-Bond Donors in Asymmetric Catalysis: In 1998, Sigman and Jacobsen reported that urea and thiourea derivatives catalyze enantioselective hydrocyanation reactions of imines derived from both aromatic and aliphatic aldehydes [35].



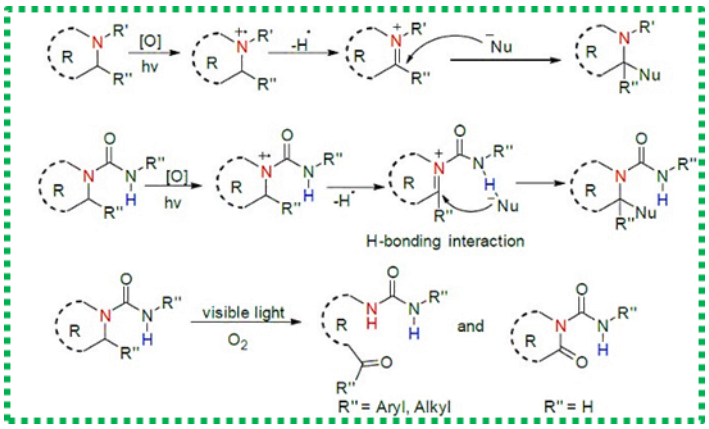
(M) Nanoporous Metal–organic Framework as Renewable Hydrogen-Bonding Catalyst in Water: Representation of the interaction between Zn–DBDA and β-nitrostyrene/Hacac computed by molecular force field-based calculations (A). Proposed mechanism of Michael addition catalyzed by Zn–DBDA (B and C) [36].



(N) Mesoporous Poly-melamine-formaldehyde (mPMF) a Highly Efficient Catalyst for Chemo selective Acetalization of Aldehydes: The substrate scope for acetalization in PDO over m-PMF was examined. The reaction was found to be chemo selective to aldehydes, and did not occur with ketones. Thus, this mild protocol could be useful for the protection of aldehydes in the presence of ketones and acid-sensitive groups. Generally, the protocol worked well for various aryl aldehydes [37].



(O) Hydrogen Bond Directed Aerobic Oxidation of Amines by Photoredox Catalysis: Wang reported H-bond oxidation interactive guidance for α-C-H amines and amino hoping to ketones catalyzed by an organic photocatalysts [38].



References

[1] E. N. Jacobsen, R. R. Knowles. Proc. Natl. Acad. Sci. 48 (2010) 20678–20685.
[2] E. N. Jacobsen, M. S. Taylor. Angew. Chem. Int. Ed. 45 (2010) 1521–1539.
[3] A. Doyle, G. Abigail, E.N. Jacobsen. Chem. Rev. 12 (2007) 5713–5743.
[4] O. Kirk, L. S. Conrad. Angew. Chem. Int. Ed. 38 (199) 977-979.
[5] A. G. Doyle, E. N. Jacobsen. Chem. Rev. 107 (2007) 5713.
[6] M. Rueping, A. P. Antonchick, T. Theissmann, Angew. Chem. Int. Ed. 45(2006) 6751-6755.
[7] Y. Huang, A. K. Unni, A. N. Thadani, V. H. Rawal, Nature Chem. 424 (2003) 146-146.
[8] J. Shen, T. T. Nguyen, T. P. Goh, W. Ye, X. Fu, J. Xu, C. H. Tan. J. Am. Chem. Soc. 128 (2006) 13692-13692.
[9] P. Vachal, E. N. Jacobsen. J. Am. Chem. Soc. 124 (2002) 10012-10014.
[10] Y. Huang, V. H. Rawal. J. Am. Chem. Soc. 124 (2002) 9662-9663.
[11] J. Tsuji, I. Shimizu, H. Suzuki, Y. Naito. J. Am. Chem. Soc. 17 (1979) 5070-5072.
[12] L. Zeng, J. Xu, D. Zhang, Z. Yan, G. Cheng, W. Rao, L. Gao. Angew. Chem. Int. Ed. 59 (2020) 21890-21894.
[13] S. C. Pan, J. Zhou, B. List. Angew. Chem. Int. Ed. 6 (2007) 5027-5029.
[14] T. Kamran, T. Mahmudov, V. Gurbanov, I. Guseinov, M. Fátima C. Guedes da Silva. Coor. Chem. Rev. 387 (2019) 32–46.
[15] T. N. C. Wells, A. R. Fersht, Nature. 316 (1985) 656 –657.
[16] Y.N. Wang, L.Q. Lu, W.J. Xiao. Chem. Asian J. 13(2018) 2174-2183.
[17] M. Zabka, R. Sebesta. Molecules. 20 (2015) 15500-15524.
[18] A. Franconetti, G. de Gonzalo. ChemCatChem. 10 (2018) 5554–5572.
[19] T. Gasperi, M. Miceli, J .Marc. Molecules. 22(2017) 22, 1636-1636.
[20] D. Herschlag, M. Pinney. Biochemistry. 9 (2018) 3338-3352.
[21] R. Nilesh Mote, H. Samir. Chikkali, Chem. Asian J. 13 (2018) 3623-3646.

[22] B. Atashkar, M. A. Zolfigol, S. Mallakpour, Mol. Catal. 452 (2018) 192–246.
[23] A. B. Mayfield, J. B. Metternich, A. H. Trotta, E. N. Jacobsen. J. A. Chem. Soc. 8 (2020) 4061-4069.
[24] C. Q. Kabes, W. J. Maximuck, S. K. Ghosh, A. Kumar, N. Bhuvanesh, J. A. Gladysz. ACS Catalysis. 10 (2020) 3249-3263.
[25] A. A. Rodriguez, H. Yoo, J. W. Ziller, K. J. Shea. Tetrahedron lett. 50 (2009) 6830-6833.
[26] D. A. Kutateladze, D. A. Strassfeld, E. N. Jacobsen. 15 (2020) 6951-6956.
[27] M. S. Taylor, E. N. Jacobsen. 10 (2006) 1520-1543.
[28] a) S. Inoue, J.-I. Oku, J. Chem. Soc. Chem. Commun. 10 (1981) 229-230. b) K. Tanaka, A. Mori, S. Inoue, J. Org. Chem. 55 (1990) 181–185.
[29] J. Y. Liu, X. C. Yang, Z. Liu, Y. C. Luo, H. Lu, Y. C. Gu, P. F. Xu. 21 (2019) 5219-5224.
[30] T. Akiyama, J. Itoh, K. Fuchibe, Adv. Synth. Catal. 9 (2006), 999-1010.
[31] D. P. Curran, L. H. Kuo, J. Org. Chem. 12 (1994) 3259-3261.
[32] J. Wang, H. Li, X. Yu, L. Zu, W. Wang, Org. Lett. 7 (2005) 4293-4296.
[33] T. Tonoi, K. Mikami, Tetrahedron Lett. 46 (2005) 6355-6358.
[34] A. Wittkopp, P. R. Schreiner, Chem. Eur. J. 9 (2003), 407-414.
[35] A. G Doyle, E. N. Jacobsen, Chem. Rev. 12(2007), 5713-5743.
[36] Y. Liu, J. Ma, P, Wu, J. J, Zheng, X. Tian, M. Jiang, J. Wang, Dalton Trans. 48(2019), 11855-11861.
[37] M. X. Tan, L. Gu, N. Li, J. Y. Ying, Y. Zhang, Green Chem.. 15(2013), 1127-1132.
[38] H. Wang, Y. Man, K. Wang, X. Wan, L. Tong, N. Li, B. Tang, chem.com. 1 (2018), 1-8.