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无过渡金属参与甲基杂环化合物与醇的选择性有氧烯基化反应

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摘要 采用适当的碱, 在足量空气条件下, 不使用任何外加催化剂即可实现甲基杂环化合物与醇的高效高选择性烯基化反应, 得到烯基杂环产物. 控制实验显示, 醇在碱的作用下可被足量空气几乎完全氧化为羰基化合物, 进而与甲基杂环化合物反应得到烯基化产物; 由于存在足量空气, 使用较少量的碱以及相对烷基化反应较低的温度, 烯基杂环产物不能被体系中剩余的少量醇通过转移氢化还原, 使得烯基化反应具有很高的选择性. 因此, 本方法是一种较为实用的烯基杂环化合物的合成方法, 可与之前发展的少量空气下无过渡金属参与的甲基杂环化合物与醇的脱水烷基化反应形成互补.

关键词 醇; 烯基化反应; 甲基杂环化合物; 无过渡金属; 烯基杂环化合物

Transition Metal-Free Selective Aerobic Olefination of Methyl *N*-Heteroarenes with Alcohols

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Abstract By performing the reactions in the presence of adequate amount of air and a suitable base, selective olefination of methyl *N*-heteroarenes with alcohols can be effectively achieved without using any external catalyst. Control experiments revealed that, with adequate air, base can promote the aerobic oxidation of alcohols almost completely to carbonyl intermediates, which then condense with the methyl *N*-heteroarenes to afford the alkenyl *N*-heteroarene products. As the reaction is performed with adequate amount of air and a lower loading of the base at a lower temperature than that of the alkylation reaction, the generated alkenyl *N*-heteroarenes cannot be transfer hydrogenated to the alkylated products by the remained small amount of alcohol in the reaction mixture, which leads to a high selectivity of the olefination reaction. This method is thus a practical way for preparation of the alkenyl *N*-heteroarenes, being a complementary method to previous transition metal-free *C*-alkylation reaction of methyl *N*-heteroarenes with alcohols in the presence of small amount of air.

Keywords alcohol; olefination; methyl *N*-heteroarene; transition metal-free; alkenyl *N*-heteroarene

1 Introduction

Alcohols have been frequently utilized in organic synthesis in recent years, as they are considered to be a class of comparatively greener compounds having several advantages in comparison with other chemicals, especially the corresponding organohalides and carbonyl compounds.[1-4] Therefore, they have been extensively used in nucleophilic substitution reactions with various nucleophiles,[1] transition metal (TM)-catalyzed or TM-free dehydrative *N*- and *C*-alkylation reactions,[2-3] TM-catalyzed anaerobic dehydrogenative or aerobic oxidative imination reactions,[4] TM-catalyzed or TM-free anaerobic dehydrogenative or aerobic oxidative construction of heterocyclic skeletons,[5] as well as other types of transformations.

On the other hand, since *N*-heteroarene derivatives are useful building blocks in synthesis and ligand preparation, important structural motif in various natural products, pharmaceutically and biologically active molecules, and also key functionalities in materials, developing efficient and green methods for functionalization of *N*-heteroarenes is a hot topic in synthetic organic chemistry. In this domain, functionalization of methyl *N*-heteroarenes with alcohols has seldom been studied in comparison with the frequently-reported *N*- and *C*-alkylation and imination reactions of alcohols.[1-4] Only limited alkylation[6] and olefination[7]

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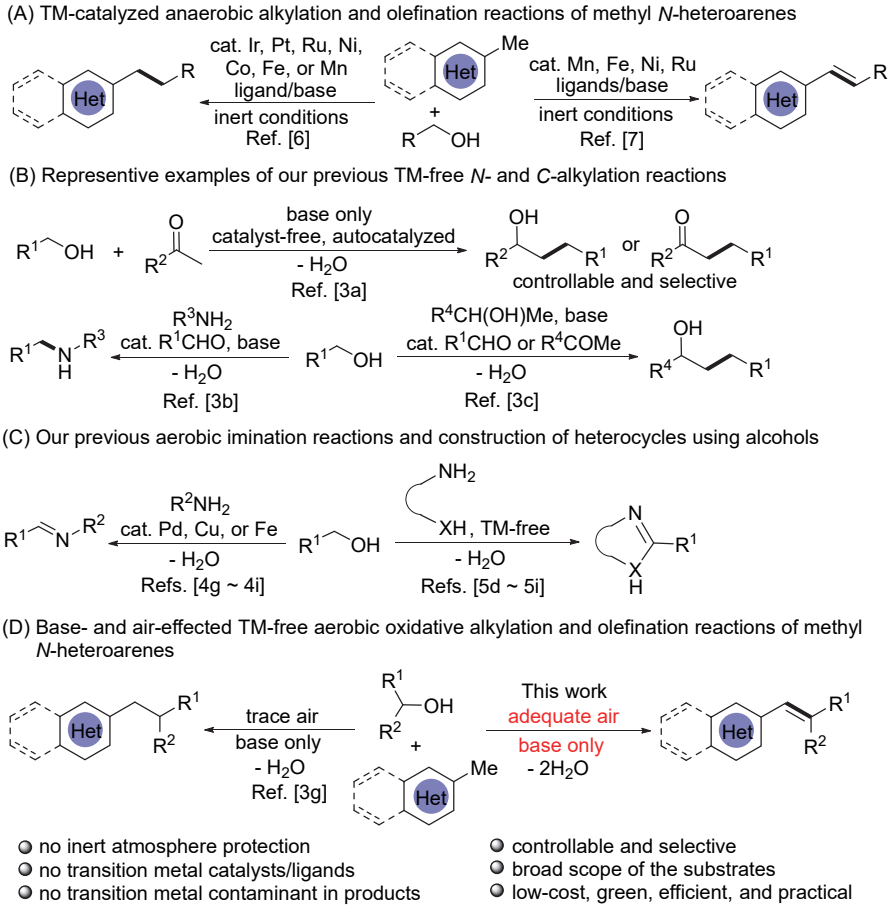
reactions of methyl *N*-heteroarenes with alcohols were reported so far (Scheme 1, A). Although these methods have some advantages for using alcohols as the substrate, they still have drawbacks such as requiring certain noble metal catalysts/ligands, strict anaerobic conditions, potential heavy metal residue contamination in products, limitation to primary alcohols, *etc*. Therefore, developing more environmentally friendly, simpler to operate, more practical, and more economical functionalization methods for methyl *N*-heteroarenes is still a highly desirable research in the field.

In our previous studies, we accidentally found the TM-catalyzed arobic dehydrative *N*- and *C*-alkylation reactions of alcohols.[8] During the studies, the crucial roles of both base and air in the reactions were also observed. Thus, as we gradually realized, many of the *N*- and *C*-alkylation reactions in effect could proceed smoothly without using any TM catalyst (Scheme 1, B),[3] which were further extended to the reactions of alcohols, amines, thiols and phosphites for TM-free green synthesis of ethers, secondary and tertiary amines, thioethers, and several class of organophosphorus compounds.[9] On the other hand, with adequate amount of air, the transfer hydrogenation step of the alkylation reaction could be interrupted and led to generation of unsaturated intermediates such as imines (Scheme 1, C, left)[4g-4i] rather than the alkylated products. Moreover, without using any TM catalyst, base alone could readily promote the aerobic oxidation of alcohols to carbonyl compounds,[3e,3g,5d-5i,10] which could then lead to TM-free construction of heterocycle compounds (Scheme 1, C, right).[5d-5i] Recently, we developed a TM-free aerobic *C*-alkylation reaction of methyl *N*-heteroarenes, which could afford *C*-alkylated products in high selectivity in the presence of small amount of air (Scheme 1, D, left).[3g] Now we find that, with adequate amount of air and a suitable amount of base, selectivity of the reaction can be switched completely to afford the olefinated products in high selectivity, providing a TM-free, simple and low cost, green and practical method for the synthesis of alkenyl *N*-heteroarene compounds (Scheme 1, D, right).

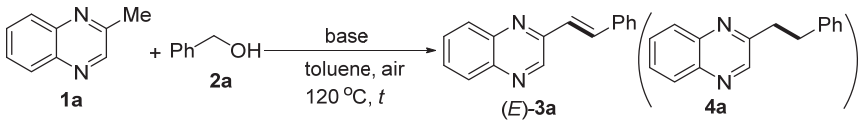
2 Results and discussion

In our previous study, to achieve a good *C*-alkylation method for the methyl *N*-heteroarene compounds,[3g] the reaction of 2-methyl quinoxaline (**1a**) and benzyl alcohol (**2a**) was initially heated with 0.5 equiv. of KOH at 120 ℃ in toluene in a 20 mL tube directly sealed in air (Table 1, Entry 1). However, in addition to the target alkylation product **4a**, the olefination product **3a** could also be produced in a considerable selectivity of 36%. We thus realized that a TM-free and green method may also be developed for the olefination of methyl *N*-heteroarenes. During the alkylation studies,[3g] more air, less base, and lower temper-



Scheme 1 Background of the research

Table 1 Condition optimization for TM-free aerobic olefination of methyl *N*-heteroarenes with alcohols[a]



Entry	Base (dosage/equiv.)	*t*/h	Conv.[b]/% of **1a**	Ratio of **3a**/**4a**[b]	Yield[c]/% of **3a**
1[d]	KOH (0.5)	15	51	36/64	18
2[d]	NaOH (0.5)	15	20	82/18	16
3[e]	KOH (0.5)	24	59	92/8	54
4	KOH (0.5)	24	59	>99/1	59
5	KOH (0.3)	24	45	>99/1	45
6[f]	KOH (0.3)	18	84	92/8	77
7[f]	KOH (0.4)	18	89	>99/1	89 (84)
8[f]	KOH (0.5)	18	91	>99/1	91 (85)
9[f]	**KOH (0.6)**	**18**	**96**	**>99/1**	**96 (87)**
10[f]	LiOH (0.6)	18	—	—	Trace
11[f]	NaOH (0.6)	18	55	87/13	48
12[f]	**CsOH (0.6)**	**18**	**93**	**>99/1**	**97 (86)**
13[f]	*t*-BuONa (0.6)	18	52	94/6	49
14[f]	*t*-BuOK (0.6)	18	75	97/3	73

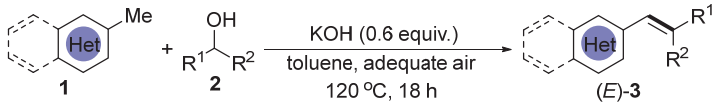
[a] Unless otherwise noted, the mixture of **1a** (0.5 mmol), **2a** (1.0 mmol) and a base in toluene (1 mL) was sealed under air in a 100 mL Schlenk tube and then heated at 120 ℃. [b] Conversion of **1a** and **3a**/**4a** ratios are based on gas chromatography-mass spectrometry (GC-MS) analysis. [c] GC yields (isolated yields in parenthesis) based on **1a**. The obtained **3a** was confirmed to be the (*E*)-isomer with >99/1 selectivity as determined by ^{1}H NMR analysis and by comparison with the literature data. [d] In 20 mL tube. [e] In 50 mL tube. [f] 1.5 mmol of **2a** was used.

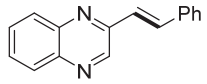
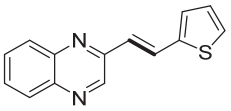
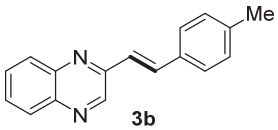
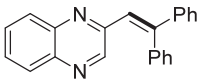
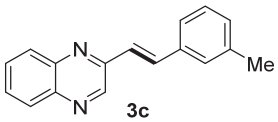
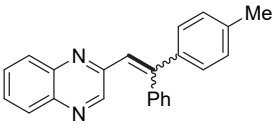
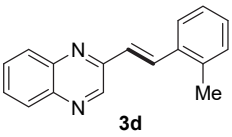
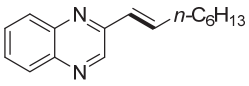
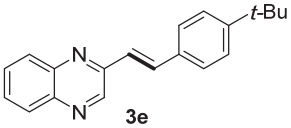
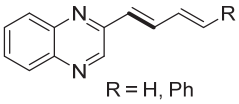
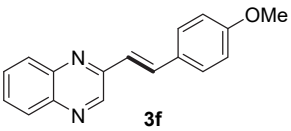
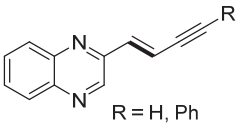
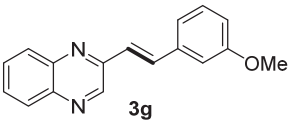
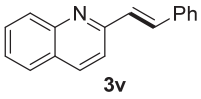
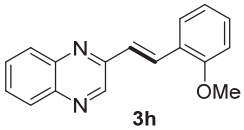
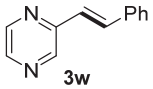
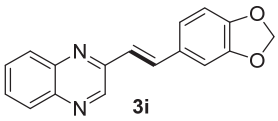
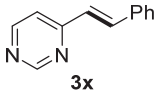
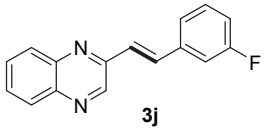
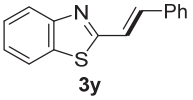
ature were found to benefit the generation of olefination product, other conditions were then investigated to enhance the yield and selectivity of **3a**. Firstly, other bases such as NaOH were also screened, but only lower yields of the product were obtained (Entry 2). KOH was then still used as the best base for the reaction. Prolonging the reaction time and performing the reaction in larger vessels containing more amounts of air could greatly enhance the selectivity for **3a** (Entries 3, 4). Thus, in a 100 mL reaction tube containing adequate amounts of air as the oxidant, **3a** could be obtained in >99% selectivity and moderate yield (Entry 4). Then, reduced KOH loading was found to lead to a lower yield of the product (Entry 5), whereas, increased **2a** loading could enhance the yield of **3a** with a slight drop in its selectivity (Entry 6). With these findings in mind, to ensure the high selectivity of **3a** and to enhance its yield simultaneously, higher loadings of KOH were investigated (Entries 7～9). The results showed that 0.6 equiv. of KOH could ensure almost complete conversion of **1a** to afford the highest yield of **3a** with a high selectivity of >99% (Entry 9). By comparison with the literature,[7] the obtained **3a** was determined to be the (*E*)-isomer in >99/1 selectivity. Then, various bases were also tested under the optimized conditions. LiOH was still not effective (Entry 10). NaOH, *t*-BuONa and *t*-BuOK gave improved but still not satisfactory results (Entries 11, 13, and 14). Only CsOH gave comparable yield and selectivity of **3a** with that of KOH (Entry 12). It should also be pointed out that, as we have proved in the previous alkylation reaction that it should be a TM-free reaction (see the control reactions using highly pure semiconductor grade KOH, with addition of TM catalysts, *etc*.),[3g] the present olefination reaction should also be a TM-free method.

With the best conditions in hand, the substrate scope of this TM-free olefination method was investigated. KOH was still chosen as the base for the reaction regarding its effectiveness, availability and economy. Similar to the above model reaction, **1a** also reacted efficiently with electron-rich and electron-deficient benzylic alcohols including those with bulky substituents and sterically more hindered *ortho*-substituted ones to afford the target (*E*)-2-alkenyl quinoxalines with good to high yields (Table 2, Entries 2～13). Both 1- and 2-naphthyl methanols afforded good yields of the products (Entries 14, 15). The reactions of heteroaryl methanols required prolonged reaction time to give moderate to good yields of the products (Entries 16～18).

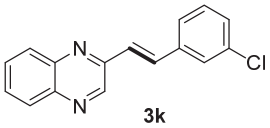
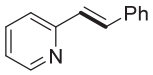
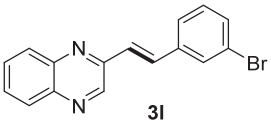
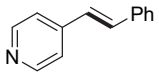
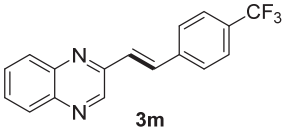
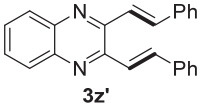
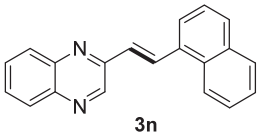
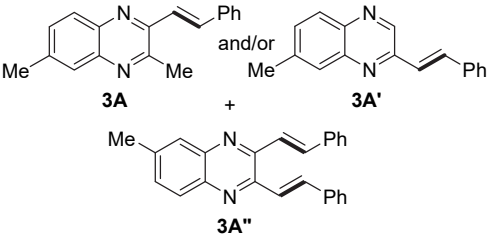
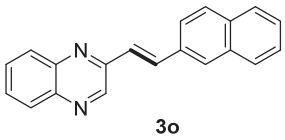
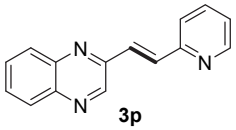
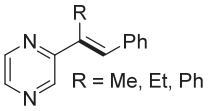
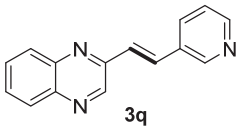
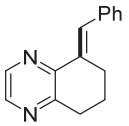
Unlike the TM-catalyzed anaerobic α-olefination methods that limited to primary alcohols,[7] this TM-free aerobic oxidative method could be extended to sterically more bulky secondary alcohols such as benzohydrols (Entries 19, 20). The substituted benzohydrol gave a mixture of *E*/*Z* isomers **3t**/**3t'** due to the weak sterical difference between the phenyl and tolyl groups (Entry 20). The less reactive aliphatic alcohols such as 1-heptanol could also be used in the method, affording a lower yield of the product (Entry 21). Most likely due to their sterical bulkiness and lower reactivities, these alcohols require a higher temperature (Entries 19, 21). In contrast, allylic alcohols such as allyl and cinnamyl alcohols and propargylic alcohols such as propargyl and 3-phenyl propargyl alcohols were not reactive in the reaction, giving no target products under the standard or modified conditions using either KOH or CsOH as the base (Entries 22, 23). Other methyl *N*-heteroarenes, such as 2-methyl quinoline, 2-methyl pyrazine, 2-methyl pyrimidine and 2-methyl benzothiazole, all afforded target

Table 2 Substrate scope for TM-free aerobic oxidative α-olefination of methyl *N*-heteroarenes with alcohols[a]



Entry	Product	Yield/%	Entry	Product	Yield/%
1	 **3a**: (>99/1 *E*-isomer)[b] (>99/1 olefination sel.)[b]	87	18	 **3r**	53 (71, 24 h)
2	 **3b**	60	19[e]	 **3s**	49
3	 **3c**	64	20[c,e]	 **3t/3t'** (*E*/*Z* or *Z*/*E*: 54/46)	34
4	 **3d**	73	21[e]	 **3u**	27
5	 **3e**	75	22[e]	 R = H, Ph	—
6	 **3f**	69	23[e]	 R = H, Ph	—
7	 **3g**	66	24	 **3v**	19 (74,[c,f] 88[g])
8	 **3h**	75	25	 **3w**	43 (65, 24 h)[c]
9	 **3i**	67	26	 **3x**	87
10	 **3j**	72	27	 **3y**	82

Continued

Entry	Product	Yield/%	Entry	Product	Yield/%
11	 **3k**	70	28[e]		Trace
12	 **3l**	51	29[e]		Trace
13	 **3m**	40 (80)[c]	30	 **3z'**	16
14	 **3n**	83	31	 **3A** + **3A'** and/or **3A"**	39 (**3A**+**3A'**), 7 (**3A"**)[c,f]
15	 **3o**	73			
6[d]	 **3p**	55	32[c,f]	 R = Me, Et, Ph	—
17	 **3q**	38 (61, 36 h)[c]	33[c,f]		—

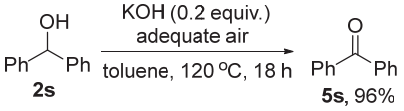
[a] Unless otherwise noted, **1a** (0.5 mmol), **2a** (1.5 mmol) and KOH (0.6 equiv.) in toluene (1 mL) were sealed under air in a 100 mL Schlenk tube and then heated at 120 ℃ for 18 h. Isolated yields based on **1a**. [b] *E*/*Z* selectivity determined by ^{1}H NMR. Olefination selectivity determined by GC-MS. [c] KOH (1.0 equiv.). [d] 100 ℃, 36 h. [e] 160 ℃, 24 h. [f] 140 ℃, 24 h. [g] CsOH (0.4 equiv.), xylene, 140 ℃, 12 h.

products with good to high yields under the standard or modified conditions (Entries 24～27). However, no product or only trace products could be observed in the reactions of other methyl *N*-heteroarenes such as 2-methyl pyridine and 4-methyl pyridine under standard or modified conditions using either KOH or CsOH as the base (Entries 28, 29), most possibly due to their low reactivities in the reaction.

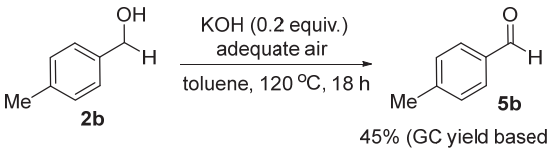
For substituted methyl *N*-heteroarenes, 2,3-dimethyl quinoxaline did not give mono-olefinated product under the standard conditions, but bis-olefinated **3z'** in a low yield (Entry 30). For 2,3,7-trimethyl quinoxaline, only trace products were observed under the standard conditions, whereas a mixture of the mono-olefinated products (39%) and a bis-olefinated product (7%) could be obtained in low yields under modified conditions (Entry 31). For *N*-heteroarenes with longer alkyl chains such as 2-ethyl pyrazine, 2-propyl pyrazine, 2-benzyl pyrazine, and 5,6,7,8-tetrahydroquinoxaline, most likely due to similar steric and electron-donating effect of the substituents, only trace products could be observed under elevated conditions (Entries 32, 33). The above results revealed the relatively broad substrate scope of the TM-free olefination method.

The reason why the above TM-free olefination reaction could afford high selectivity of the alkenyl *N*-heteroarene products was then studied. As shown in Eq. 1, in the presence of adequate amount of air and a catalytic amount of KOH, almost a quantitative yield of diphenyl ketone **5s** could be produced from benzohydrol **2s** under the standard conditions. Similarly, a considerable yield of substituted benzaldehyde **5b** could also be generated under the same

conditions from the corresponding alcohol **2b** (Eq. 2). Herein, in the absence of **1a**, the relatively lower yield of **5b** should be due to **2b** side reactions (such as Cannizzaro reaction) in the presence of a strong base at heating, but the conversion of **2b** should also be high. These results consist well with our previous findings[3e,3g,5d-5i] as well as the literature reports.[10] It not only revealed the crucial role of adequate air in generating the large amount of carbonyl intermediates needed in the next condensation step, but also explained the high conversions of the starting alcohols in the reaction. Consequently, the small amount of alcohol remained in the reaction mixture should be too few to reduce the unsaturated alkenyl *N*-heteroarenes. Besides, as the alkylation of methyl *N*-heteroarenes generally requires a higher temperature of 140 ℃ and a higher loading of base (generally 1.0 equiv.) to ensure an efficient and complete transfer hydrogenation step,[3g] the lower temperature of 120 ℃ and lower loading of KOH (0.6 equiv. only) under the present conditions should be not enough for the alkylation to effectively occur to compete with the olefination reaction. Therefore, under the present conditions, the alkylated *N*-heteroarenes should be generated in only a very low selectivity and hence the olefination occurs as the major reaction to afford high selectivity of the alkenyl *N*-heteroarenes as the major products.



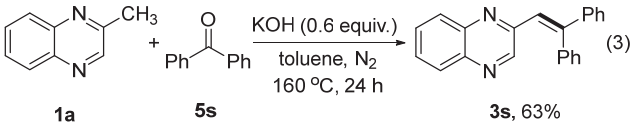
(1)



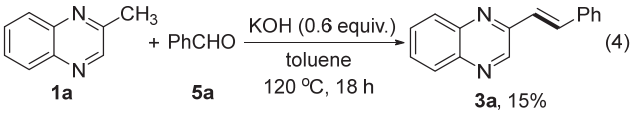
(2)

45% (GC yield based on 0.5 mmol of **1a was** used in the olefination reaction)

Then the condensation step, a known method for preparing alkenyl *N*-heteroarenes,[13] was also investigated. Under the optimized conditions (Table 2, Entry 19), the reaction of 2-methyl quinoxaline **1a** and ketone **5s** smoothly afforded the target **3s** in a yield comparable to that of the olefination reaction (Eq. 3), confirming the condensation step. In contrast, the reaction of **1a** and benzaldehyde **5a** only afforded a low yield of **3a** (Eq. 4), which should be due to the inevitable side-reactions of **5a** such as the Cannizzaro reaction under the strong basic and heating conditions. Indeed, considerable amounts of $PhCH_2OH$ (**2a**), one of the Cannizzaro products, was observed by GC-MS analysis of the reaction mixture. Thus, most likely, the Cannizzaro side-reaction and neutralization of KOH by *in situ* generated PhCOOH, the other Cannizzaro product, led to the ineffective reaction and the low yield of **3a**. This much lower yield of **3a** (15%, Eq. 4) than that of the model olefination reaction (87%, Table 1, Entry 9) showed that the *in situ* generated benzaldehyde could react with **1a** in a much more effective way than the added external benzaldehyde. For one reason, obviously, the externally added benzaldehyde is labile and prone to undergo side reactions under the strong basic and heating conditions, which can greatly decrease the product yield. For the other reason, more importantly, the *in situ* generated benzaldehyde should remain in a relatively low concentration and be quickly reacted up by the higher concentration methyl *N*-heteroarene to give the product, through which the side reactions of the *in situ* generated benzaldehyde can be inhibited. These results further implied that alcohols should be the more preferable substrates than the less stable aldehydes in the preparation of the alkenyl *N*-heteroarene compounds.



(3)

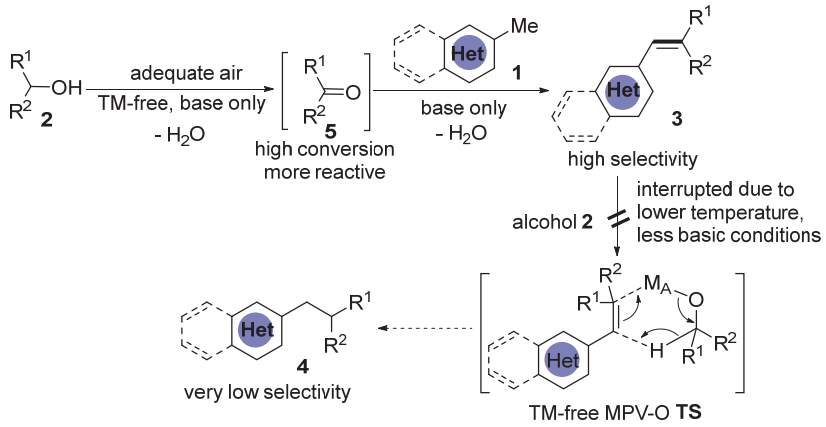


(4)

Based on the above findings, a possible reaction path was proposed for the present TM-free selective aerobic oxidative *α*-olefination reaction of methyl *N*-heteroarenes and alcohols. As shown in Scheme 2, with adequate amount of air, catalytic amount of base alone can readily promote the aerobic oxidation of alcohols **2** to carbonyl compounds **5** in high conversions, with only a very small amount of unreacted alcohol remained in the reaction mixture. This step should occur with base-mediated deprotonation of the alcohol to its alkoxide first, which is then oxidized by air to **5**.[10] The *in situ* gradually-generated **5** (in low concentration) may quickly be reacted up by substrate methyl *N*-heteroarenes **1** (in higher concentration) to afford alkenyl *N*-heteroarenes **3** via dehydrative condensation in the presence of the base. As both the base loading/concentration and reaction temperature are lower than those of the alkylation reaction,[3g] the generated alkenyl *N*-heteroarenes cannot be effectively transfer hydrogenated by the remained small amount of unreacted alcohol, so that the alkylated byproducts **4** are usually produced in very low yields. As a result, the target alkenyl *N*-heteroarene compounds **3** can be obtained in high selectivity. On the contrary, in case the reaction was performed with small amount of air, at a high temperature with more base,[3g] only small amount of the alcohol **2** could be oxidized to carbonyl compounds **5** and then transformed into alkenyl *N*-heteroarenes **3** with large amounts of the alcohol remained unreacted in the reaction mixture. Then the alkenyl *N*-heteroarenes **3** could be gradually transfer hydrogenated into the alkylated products **4**, most possibly via a six-membered TM-free Meerwein-Pondorf-Verley-Oppenauer (MPV-O) transition states **TS** (Scheme 2).[3,12]

3 Conclusions

In conclusion, by performing the reactions in the pres-



Scheme 2 Proposed reaction path

ence of adequate amount of air and a suitable base, selective olefination of methyl *N*-heteroarenes with alcohols can be effectively achieved without using any external catalyst. Control experiments revealed that, in the presence of adequate amount of air, base alone can promote the aerobic oxidation of alcohols to carbonyl intermediates almost completely, which then effectively condense with the methyl *N*-heteroarenes to afford the alkenyl *N*-heteroarene products. As the reaction is performed with adequate amount of air and a lower loading of the base at a lower temperature than that of the alkylation reaction, the generated alkenyl *N*-heteroarenes cannot be transfer hydrogenated to the alkylated products by the small amount of unreacted alcohol remained in the reaction mixture, which consequently leads to a high selectivity of the olefination reaction. This method has advantages of requiring no TM catalysts/ligands and no inert atmosphere protection, broad substrate scope, simple operation, low cost, no TM contaminant in the products, and thus can be an environmentally benign and practical way for preparation of the alkenyl *N*-heteroarene compounds.

4 Experimental section

4.1 General information

Unless otherwise noted, all chemicals including solvents were purchased from Aladdin Biochemical, Energy Chemical, Alfa Aesar, TCI, or other chemical companies and used without further purification. Benzaldehyde (**5a**) purified by vacuumn distillation was used in the condensation reactions. Unless otherwise specified, all reactions were carried out in sealed Schlenk tubes (100 mL) under air or N_2 atmosphere and monitored by thin-layer chromatography (TLC) and/or GC-MS. The products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance-III 500 instrument (500 MHz for ^{1}H NMR and 125.4 MHz for ^{13}C NMR spectroscopies) or a Zhongke-Niujin WNMR-1-400 instrument (400 MHz for ^{1}H NMR) using $CDCl_3$ as the solvent and Me_4Si (δ 0) as internal standard. Mass spectra were measured on a Shimadzu GC-MS-QP2010 Plus spectrometer (EI). High Resolution Mass Spectra (HRMS) were measured on a Bruker micrOTOF-Q II instrument (ESI) at Wenzhou University. Melting points of the solid products were measured on a WRS-1B apparatus (Shanghai Shenguang).

4.2 Typical procedure for TM-free aerobic oxidative α-olefination of methyl *N*-heteroarenes with alcohols.

A methyl *N*-heteroarene compound **1** (0.5 mmol), an alcohol **2** (1.5 mmol), KOH (0.6 equiv.), and toluene (1 mL) were added to a 100 mL Schlenk tube and the tube directly sealed under air. The mixture was then heated at 120 ℃ for 18 h and monitored by TLC and/or GC-MS. After completion of the reaction, the reaction mixture was condensed by rotary evaporation and the residue purified by flash column chromatography to give the olefination product **3**.

(*E*)-2-(2-Phenyl)vinyl quinoxaline (**3a**):[13] Brown solid, m.p. 100～103 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.07 (d, J=7.5 Hz, 2H), 7.88 (d, J=16.5 Hz, 1H), 7.78～7.74 (m, 1H), 7.72～7.69 (m, 1H), 7.66 (d, J=7.5 Hz, 2H), 7.44～7.40 (m, 3H), 7.38～7.36 (m, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 150.7, 144.4, 142.5, 141.6, 136.5, 136.1, 130.3, 129.3, 129.23, 129.20, 129.18, 128.9, 127.5, 125.4; MS (EI) *m*/*z* (%): 232 (47), 231 (100), 209 (6), 208 (9), 207 (42), 204 (8), 115 (8), 102 (13), 96 (8), 77 (7), 76 (8), 73 (9).

(*E*)-2-(2-*p*-Tolyl)vinyl quinoxaline (**3b**):[14] Brown solid, m.p. 196～198 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.04 (s, 1H), 8.07～8.05 (m, 2H), 7.85 (d, J=16.5 Hz, 1H), 7.77～7.74 (m, 1H), 7.71～7.68 (m, 1H), 7.56 (d, J=8.0 Hz, 2H), 7.34 (d, J=16.5 Hz, 1H), 7.26～7.23 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 150.7, 144.5, 142.5, 141.5, 139.5, 136.5, 133.3, 130.3, 129.7, 129.2, 127.5, 124.4, 21.4; MS (EI) *m*/*z* (%): 246 (30), 245 (51), 231 (18), 209 (13), 208 (21), 207 (100), 191 (14), 133 (14), 115 (11), 96 (16), 76 (7), 73 (22).

(*E*)-2-(2-*m*-Tolyl)vinyl quinoxaline (**3c**): Brown solid, m.p. 153～155 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.04 (s, 1H), 8.07 (d, J=8.5 Hz, 2H), 7.84 (d, J=16.5 Hz, 1H), 7.77～7.72 (m, 1H), 7.72～7.67 (m, 1H), 7.46 (d, J=11.5

Hz, 2H), 7.37 (d, J=16.5 Hz, 1H), 7.33～7.28 (m, 1H), 7.17 (d, J=7.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 150.6, 144.4, 142.3, 141.5, 138.5, 136.8, 135.9, 130.4, 130.2, 129.3, 129.1, 129.0, 128.8, 128.2, 125.0, 124.7, 21.4; MS (EI) m/z (%): 246 (13), 245 (23), 231 (12), 209 (13), 208 (18), 207 (100), 191 (13), 133 (14), 115 (9), 96 (15), 73 (17); HRMS calcd for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1230, found 247.1221.

(*E*)-2-(2-*o*-Tolyl)vinyl quinoxaline (**3d**): White solid, m.p. 126～128 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.04 (s, 1H), 8.15 (d, J=16.1 Hz, 1H), 8.11～8.07 (m, 2H), 7.79～7.67 (m, 3H), 7.31 (d, J=16.2 Hz, 1H), 7.28～7.21 (m, 3H), 2.54 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 150.7, 144.5, 142.2, 141.6, 137.1, 135.0, 134.4, 130.8, 130.4, 129.3, 129.14, 129.06, 126.4, 126.2, 125.9, 20.0; MS (EI) m/z (%): 246 (66), 245 (100), 231 (85), 208 (9), 207 (44), 128 (17), 116 (16), 115 (45), 103 (11), 102 (11), 77 (10), 76 (15), 73 (9), 50 (9); HRMS Calcd for $C_{17}H_{15}N_2$ $[M+H]^+$ 247.1230, found 247.1221.

(*E*)-2-(2-*p*-*tert*-Butylphenyl)vinyl quinoxaline (**3e**): White solid, m.p. 123～124 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.07 (d, J=12.0 Hz, 2H), 7.86 (d, J=16.5 Hz, 1H), 7.74～7.72 (m, 1H), 7.72～7.65 (m, 1H), 7.60 (d, J=8.5 Hz, 2H), 7.45 (d, J=8.5 Hz, 2H), 7.36 (d, J=16.5 Hz, 1H), 1.35 (s, 9H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 152.8, 150.7, 144.4, 142.2, 141.5, 136.5, 133.2, 130.4, 129.2, 129.1, 129.0, 127.3, 125.9, 124.4, 34.9, 31.2; MS (EI): m/z (%) 288 (71), 287 (83), 274 (12), 273 (65), 272 (10), 271 (9), 257 (11), 232 (28), 231 (100), 207 (13), 129 (21), 128 (13), 122 (18), 102 (12), 77 (11), 76 (15); HRMS calcd for $C_{20}H_{21}N_2$ $[M+H]^+$ 289.1699, found 289.1694.

(*E*)-2-(2-*p*-Methoxyphenyl)vinyl quinoxaline (**3f**):[7g] Brown solid, m.p. 123～124 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.02 (s, 1H), 8.07～8.03 (m, 2H), 7.83 (d, J=16.0 Hz, 1H), 7.77～7.72 (m, 1H), 7.72～7.66 (m, 1H), 7.61 (d, J=8.0 Hz, 2H), 7.25 (d, J=16.0 Hz, 1H), 6.96 (d, J=8.0 Hz, 2H), 3.86 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 160.6, 151.0, 144.4, 142.5, 141.4, 136.1, 130.3, 129.13, 129.05, 128.99, 128.96, 128.8, 123.1, 114.4, 55.4; MS (EI) m/z (%): 262 (60), 261 (70), 231 (11), 219 (23), 218 (19), 209 (15), 208 (30), 207 (100), 191 (23), 116 (10), 103 (11), 96 (17), 76 (14), 73 (22), 70 (14), 61 (14).

(*E*)-2-(2-*m*-Methoxyphenyl)vinyl quinoxaline (**3g**):[15] Brown solid, m.p. 44～46 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.09～8.04 (m, 2H), 7.84 (d, J=16.0 Hz, 1H), 7.79～7.74 (m, 1H), 7.74～7.68 (m, 1H), 7.39～7.32 (m, 2H), 7.26 (d, J=8.0 Hz, 1H), 7.19 (s, 1H), 6.93 (d, J=8.0 Hz, 1H), 3.87 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 160.0, 150.6, 144.4, 142.5, 141.6, 137.4, 136.3, 130.3, 129.9, 129.3, 129.2, 125.7, 120.3, 115.3, 112.3, 55.3; MS (EI) m/z (%): 262 (15), 261 (25), 209 (20), 207 (100), 191 (12), 147 (6), 133 (12), 96 (15), 89 (5), 73 (21).

(*E*)-2-(2-*o*-Methoxyphenyl)vinyl quinoxaline (**3h**):[7g] Brown solid, m.p. 64～66 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.09 (s, 1H), 8.19 (d, J=16.5 Hz, 1H), 8.11～8.03 (m, 2H), 7.76～7.71 (m, 1H), 7.71～7.65 (m, 2H), 7.45 (d, J=16.5 Hz, 1H), 7.35～7.31 (m, 1H), 7.03～6.97 (m, 1H), 6.94 (d, J=8.5 Hz, 1H), 3.93 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 157.8, 151.2, 144.4, 142.3, 141.4, 131.8, 130.5, 130.2, 129.09, 129.05, 127.7, 125.9, 125.0, 120.9, 111.1, 55.6; MS (EI) m/z (%): 262 (6), 265 (5), 232 (8), 231 (100), 207 (34), 131 (10).

(*E*)-2-(2-Benzo[*d*][1,3]dioxol-5-yl)vinyl quinoxaline (**3i**): Brown solid, m.p. 135～137 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.06 (s, 1H), 8.14 (d, J=8.0 Hz, 1H), 8.09 (d, J=8.0 Hz, 1H), 7.86 (d, J=16.0 Hz, 1H), 7.79～7.75 (m, 1H), 7.75～7.68 (m, 1H), 7.31～7.19 (m, 2H), 7.14 (d, J=8.0 Hz, 1H), 6.87 (d, J=8.0 Hz, 1H), 6.03 (s, 2H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 150.8, 148.8, 148.4, 144.4, 142.5, 141.5, 136.1, 130.6, 130.2, 129.14, 129.08, 129.0, 123.5, 123.3, 108.6, 106.1, 101.4; MS (EI) m/z (%): 276 (44), 275 (64), 253 (11), 209 (14), 208 (26), 207 (100), 191 (13), 96 (17), 73 (23), 58 (21); HRMS calcd for $C_{17}H_{13}N_2O_2$ $[M+H]^+$ 277.0972, found 277.0974.

(*E*)-2-(2-*m*-Fluoropheyl)vinyl quinoxaline (**3j**):[16] Brown solid, m.p. 94～96 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.03 (s, 1H), 8.09 (d, J=10.5 Hz, 2H), 7.84 (d, J=16.5 Hz, 1H), 7.80～7.75 (m, 1H), 7.75～7.70 (m, 1H), 7.42 (d, J=7.5 Hz, 1H), 7.41～7.33 (m, 3H), 7.08～7.04 (m, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 164.1, 162.2, 150.0, 144.4, 142.2, 141.6, 138.2 (d, J=7.7 Hz), 135.3, 130.6, 130.4 (d, J=8.3 Hz), 129.6, 129.1 (d, J=11.1 Hz), 126.3, 123.4, 116.1 (d, J=21.5 Hz), 113.8 (d, J=22.0 Hz); MS (EI) m/z (%): 250 (28), 249 (56), 209 (13), 208 (20), 207 (100), 191 (11), 147 (7), 133 (15), 125 (6), 96 (19), 73 (20), 50 (6).

(*E*)-2-(2-*m*-Chlorophenyl)vinyl quinoxaline (**3k**):[17] Brown solid, m.p. 104～106 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.04 (s, 1H), 8.09 (d, J=8.0 Hz, 2H), 7.83 (d, J=16.5 Hz, 1H), 7.80～7.72 (m, 2H), 7.65 (s, 1H), 7.53 (d, J=7.0 Hz, 1H), 7.39 (d, J=19.5 Hz, 1H), 7.36～7.32 (m, 2H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 149.9, 144.4, 142.1, 141.7, 137.8, 135.1, 134.9, 130.1, 129.7, 129.2, 129.1, 127.3, 126.3, 125.7; MS (EI) m/z (%): 267 (18), 266 (15), 265 (32), 231 (7), 209 (11), 208 (19), 207 (100), 191 (12), 133 (13), 96 (15), 73 (24).

(*E*)-2-(2-*m*-Bromophenyl)vinyl quinoxaline (**3l**):[18] Brown solid, m.p. 123～125 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.05 (s, 1H), 8.13～8.09 (m, 2H), 7.86～7.69 (m, 4H), 7.58 (d, J=7.5 Hz, 1H), 7.49 (d, J=7.5 Hz, 1H), 7.41 (d, J=16.5 Hz, 1H), 7.33～7.27 (m, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 150.1, 144.4, 142.5, 141.8, 138.2, 134.7, 131.9, 130.438, 130.436, 130.2, 129.5, 129.3, 129.2, 126.6, 126.0, 123.1; MS (EI) m/z (%): 311 (33), 310 (23), 309 (33), 282 (11), 281 (43), 231 (20), 230 (11), 209 (12), 208 (22), 207 (100), 191 (11), 133 (14), 115 (18), 102 (12), 96 (12), 77 (11), 76 (13), 75 (9), 73 (24).

(*E*)-2-(2-*p*-Trifluoromethylphenyl)vinyl quinoxaline (**3m**):[6h] Brown solid, m.p. 169～171 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.07 (s, 1H), 8.12 (d, J=7.5 Hz, 2H), 7.91 (dd, J=16.3, 2.6 Hz, 1H), 7.82～7.76 (m, 4H), 7.70 (d, J=7.5 Hz, 2H), 7.47 (dd, J=16.3, 2.8 Hz, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 149.8, 144.4, 142.4, 141.8, 139.3, 134.6, 130.8, 130.5, 129.7, 129.24, 129.19, 127.5, 125.8 (q,

J=3.7 Hz), 125.1, 122.9; MS (EI) *m*/*z* (%): 300 (52), 299 (100), 231 (18), 102 (9), 76 (22).

(*E*)-2-(2-*α*-Naphthalenyl)vinyl qinoxaline (**3n**):[14] Brown solid, m.p. 105～107 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 9.08 (s, 1H), 8.71 (d, *J*=16.0 Hz, 1H), 8.33 (d, *J*=8.5 Hz, 1H), 8.13～8.08 (m, 2H), 7.89 (dd, *J*=12.5, 6.5 Hz, 3H), 7.79～7.74 (m, 1H), 7.74～7.69 (m, 1H), 7.63～7.58 (m, 1H), 7.55～7.51 (m, 2H), 7.43 (d, *J*=16.0 Hz, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 150.6, 144.7, 142.5, 141.7, 133.8, 133.5, 133.4, 131.5, 130.3, 129.6, 129.4, 129.3, 129.2, 128.8, 127.9, 126.6, 126.1, 125.6, 124.4, 123.6; MS (EI) *m*/*z* (%): 282 (20), 281 (50), 209 (13), 208 (20), 207 (100), 191 (17), 147 (7), 96 (17), 73 (24), 70 (11), 61 (15).

(*E*)-2-(2-*β*-Naphthalenyl)vinyl quinoxaline (**3o**): Brown solid, m.p. 141～143 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 9.08 (s, 1H), 8.08 (d, *J*=9.5 Hz, 2H), 8.06～8.01 (m, 2H), 7.90～7.82 (m, 4H), 7.79～7.75 (m, 1H), 7.77～7.71 (m, 1H), 7.56～7.45 (m, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 150.7, 144.5, 142.5, 141.6, 136.5, 133.8, 133.6, 133.5, 130.3, 129.3, 129.20, 129.17, 128.8, 128.7, 128.4, 127.8, 126.8, 126.6, 125.5, 123.4; MS (EI) *m*/*z* (%): 282 (10), 281 (17), 231 (30), 209 (14), 208 (27), 207 (100), 191 (11), 133 (14), 96 (16), 73 (16); HRMS calcd for $C_{20}H_{15}N_2$ $[M+H]^+$ 283.1230, found 283.1229.

(*E*)-2-(2-Pyridin-2-yl)vinyl quinoxaline (**3p**): Yellow solid, m.p. 118～120 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 9.06 (s, 1H), 8.69 (d, *J*=4.5 Hz, 1H), 8.09 (dd, *J*=9.0, 3.0 Hz, 2H), 8.01～7.87 (m, 2H), 7.83～7.68 (m, 3H), 7.54 (d, *J*=8.0 Hz, 1H), 7.36～7.17 (m, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 154.3, 150.1, 150.0, 145.1, 142.5, 141.9, 136.8, 135.3, 130.3, 129.6, 129.4, 129.2, 128.9, 123.5, 123.3; MS (EI) *m*/*z* (%): 233 (8), 232 (14), 209 (19), 208 (20), 207 (100), 191 (14), 133 (14), 96 (11), 73 (19); HRMS calcd for $C_{15}H_{12}N_3$ $[M+H]^+$ 234.1026, found 234.1019.

(*E*)-2-(2-Pyridin-3-yl)vinyl quinoxaline (**3q**): Yellow solid, m.p. 113～115 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 9.04 (s, 1H), 8.88 (d, *J*=2.0 Hz, 1H), 8.59 (dd, *J*=5.0, 1.5 Hz, 1H), 8.18～8.05 (m, 2H), 7.97 (d, *J*=3.5 Hz, 1H), 7.88 (d, *J*=16.5 Hz, 1H), 7.83～7.69 (m, 2H), 7.44 (d, *J*=16.5 Hz, 1H), 7.37 (dd, *J*=8.0, 5.0 Hz, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 149.76, 149.73, 149.2, 144.4, 142.4, 141.8, 133.5, 132.4, 131.8, 130.5, 129.6, 129.24, 129.17, 127.2, 123.8; MS (EI) *m*/*z* (%): 233 (45), 232 (80), 209 (11), 208 (26), 207 (100), 205 (15), 191 (9), 177 (10), 133 (14), 103 (16), 96 (13), 78 (15), 77 (11), 76 (16), 73 (15), 70 (17), 61 (15), 51 (6); HRMS calcd for $C_{15}H_{12}N_3$ $[M+H]^+$ 234.1026, found 234.1019.

(*E*)-2-(2-Thiophen-2-yl)vinyl quinoxaline (**3r**): Brown solid, m.p. 97～99 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.94 (s, 1H), 8.10～7.95 (m, 3H), 7.78～7.72 (m, 1H), 7.70～7.62 (m, 1H), 7.34～7.28 (m, 2H), 7.28 (d, *J*=3.5 Hz, 1H), 7.16 (d, *J*=16.0 Hz, 1H), 7.07 (dd, *J*=5.0, 3.5 Hz, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 150.2, 144.5, 142.3, 141.6, 141.5, 130.4, 129.4, 129.23, 129.20, 129.1, 129.0, 128.1, 127.0, 124.1; MS (EI) *m*/*z* (%): 238 (18), 237 (36), 209 (13), 208 (19), 207 (100), 191 (13), 133 (12), 96 (14), 73 (22); HRMS calcd for $C_{14}H_{11}N_2S$ $[M+H]^+$ 239.0637, found 239.0636.

2-(2,2-Diphenyl)vinyl quinoxaline (**3s**): Brown solid, m.p. 76～78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.17 (s, 1H), 8.02 (dd, *J*=8.2, 1.2 Hz, 1H), 7.97 (dd, *J*=8.2, 1.2 Hz, 1H), 7.80～7.67 (m, 2H), 7.50～7.45 (m, 2H), 7.43～7.38 (m, 6H), 7.33 (s, 1H), 7.29 (dd, *J*=7.2, 1.8 Hz, 2H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 152.5, 149.5, 145.9, 142.3, 141.7, 140.1, 139.3, 130.3, 129.9, 129.3, 129.1, 129.0, 129.0, 128.81, 128.79, 128.4, 128.1, 126.1; MS (EI) *m*/*z* (%): 308 (100), 307 (13), 281 (15), 208 (8), 207 (37), 191 (5), 133 (4), 73 (8), 55 (17); HRMS calcd for $C_{22}H_{17}N_2$ $[M+H]^+$ 309.1386, found 309.1392.

(*E*/*Z*)-2-(2-Phenyl-2-*p*-tolyl)vinyl quinoxaline (**3t/3t'**, *E*/*Z* or *Z*/*E*: 54/46): Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.17 or *δ* 8.11 (s, 1H), 8.01～7.89 (m, 2H), 7.67～7.65 (m, 2H), 7.46～7.29 (m, 5H), 7.26～7.25 (m, 2H), 7.18～7.13 (m, 3H), 2.38 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 152.8 or 152.6, 149.7 or 149.5, 146.04 or 145.96, 142.4 or 142.3, 142.0, 140.0, 139.4, 139.0 or 138.9, 138.8, 136.2, 130.3 or 130.2, 129.90 or 129.88, 129.28 or 129.25, 129.2 or 129.1, 128.97 or 128.95, 128.92 or 128.90, 128.8 or 128.7, 128.4, 128.2, 128.1, 125.9 or 125.3, 21.4 or 21.3; MS (EI) *m*/*z* (%): 322 (50), 321 (100), 307 (14), 245 (14), 209 (16), 208 (28), 207 (89), 191 (16), 178 (11), 167 (11), 153 (14), 152 (10), 133 (11), 119 (10), 96 (11), 78 (13), 77 (10), 73 (8); HRMS calcd for $C_{23}H_{19}N_2$ $[M+H]^+$ 323.1543, found 323.1547.

(*E*)-2-(2-*n*-Hexyl)vinyl quinoxaline (**3u**): Brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.93 (s, 1H), 8.03 (dd, *J*=14.5, 8.0 Hz, 2H), 7.76～7.70 (m, 1H), 7.70～7.65 (m, 1H), 7.07～7.00 (m, 1H), 6.71 (d, *J*=16.0 Hz, 1H), 2.37 (q, *J*=7.0 Hz, 2H), 1.59～1.54 (m, 2H), 1.48～1.28 (m, 6H), 0.90 (t, *J*=6.0 Hz, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 151.0, 143.9, 142.3, 141.4, 140.7, 130.1, 129.1, 128.9, 127.8, 33.3, 31.7, 29.0, 28.7, 22.6, 14.1; MS (EI): *m*/*z* (%): 240 (13), 209 (15), 208 (24), 207 (100), 191 (11), 183 (49), 169 (38), 157 (13), 156 (13), 144 (17), 96 (15), 77 (11), 61 (10); HRMS calcd for $C_{16}H_{21}N_2$ $[M+H]^+$ 241.1699, found 241.1698.

(*E*)-2-(2-Phenyl)vinyl quinoline (**3v**):[19] White solid, m.p. 96～98 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) *δ*: 8.12 (d, *J*=8.5 Hz, 1H), 8.08 (d, *J*=8.5 Hz, 1H), 7.80 (d, *J*=8.0 Hz, 1H), 7.72～7.63 (m, 5H), 7.52～7.48 (m, 1H), 7.43～7.39 (m, 3H), 7.35～7.29 (m, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 156.0, 148.3, 136.6, 136.3, 134.5, 129.7, 129.3, 129.1, 128.8, 128.6, 127.5, 127.4, 127.3, 126.2, 119.3; MS (EI) *m*/*z* (%): 231 (43), 230 (100), 228 (8), 207 (38), 191 (6), 115 (12), 114 (10), 102 (12), 96 (7), 77 (7), 73 (9).

(*E*)-2-(2-Phenyl)vinyl pyrazine (**3w**):[7b] White solid, m.p. 93～95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 8.69 (s, 1H), 8.58 (s, 1H), 8.45 (s, 1H), 7.79 (d, *J*=16.0 Hz, 1H), 7.63 (d, *J*=7.0 Hz, 2H), 7.46～7.41 (m, 2H), 7.40～7.35 (m, 1H), 7.20 (d, *J*=16.0 Hz, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) *δ*: 151.3, 144.3, 143.7, 142.7, 136.0, 135.3, 129.0, 128.8, 127.3, 124.0; MS (EI) *m*/*z* (%): 182 (24), 181 (100), 154 (4), 129 (4), 128 (8), 127 (8), 102 (7), 78 (3), 77 (5), 70 (4).

(*E*)-4-(2-Phenyl)vinyl pyrimidine (**3x**):[7b] Brown solid, m.p. 104～106 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 9.17 (s, 1H), 8.67 (s, 1H), 7.90 (d, J=16.0 Hz, 1H), 7.60 (d, J=7.0 Hz, 2H), 7.42～7.32 (m, 4H), 7.05 (d, J=16.0 Hz, 1H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 162.4, 158.6, 157.1, 137.8, 135.5, 129.6, 127.7, 125.4, 118.7; MS (EI) *m*/*z* (%): 182 (22), 181 (100), 154 (9), 128 (16), 127 (11), 96 (5), 91 (5), 77 (12), 73 (7).

(*E*)-2-(2-Phenyl)vinyl benzo[*d*]thiazole (**3y**):[20] White solid, m.p. 117～119 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.99 (d, J=8.1 Hz, 1H), 7.82 (d, J=7.9 Hz, 1H), 7.55 (d, J=7.2 Hz, 2H), 7.50 (d, J=16.2 Hz, 1H), 7.45 (t, J=7.6 Hz, 1H), 7.42～7.30 (m, 5H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 167.0, 153.9, 137.7, 135.4, 134.4, 129.5, 129.0, 127.4, 126.4, 125.4, 123.0, 122.1, 121.5; MS (EI) *m*/*z* (%): 237 (15), 236 (43), 209 (13), 207 (100), 191 (13), 147 (7), 133 (13), 96 (17), 91 (7), 73 (23), 69 (6).

2,3-Di((*E*)-styryl)quinoxaline (**3z'**):[21] Brown solid, m.p. 195～197 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.0～7.95 (m, 4H), 7.66 (dd, J=17.3, 11.6 Hz, 8H), 7.43 (t, J=7.4 Hz, 4H), 7.36 (t, J=7.1 Hz, 2H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 149.1, 141.7, 137.9, 136.5, 129.5, 129.1, 128.9, 128.9, 127.6, 122.7; MS (EI) *m*/*z* (%): 234 (21), 233 (21), 281 (36), 257 (22), 231 (10), 209 (16), 208 (24), 207 (100), 204 (14), 191 (14), 177 (9), 167 (9), 165 (13), 133 (13), 110 (27), 102 (11), 96 (15), 78 (12), 77 (13), 73 (12).

(*E*)-3,6-Dimethyl-2-styrylquinoxaline and/or (*E*)-3,7-dimethyl-2-styrylquinoxaline (**3A** + **3A'**): Brown solid, m.p. 131～133 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.04～7.70 (m, 3H), 7.66 (d, J=7.4 Hz, 2H), 7.54～7.38 (m, 4H), 7.35 (t, J=6.8 Hz, 1H), 2.85 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 152.4, 151.6, 149.6, 148.9, 141.5, 141.3, 139.9, 139.74, 139.68, 139.49, 131.48, 131.45, 129.02, 128.96, 128.8, 128.5, 127.84, 127.80, 127.58, 127.55, 127.3, 122.8, 23.1 (d, J=4.2 Hz), 23.0 (d, J=3.8 Hz), 21.9 (d, J=4.1 Hz), 21.8 (d, J=3.8 Hz); MS (EI) *m*/*z* (%): 260 (78), 259 (100), 246 (13), 245 (66), 218 (17), 207 (45), 183 (31), 129 (10), 115 (15), 102 (20), 91 (12), 90 (17), 89 (48), 77 (13), 73 (12), 63 (15); HRMS calcd for $C_{18}H_{17}N_2$ $[M+H]^+$ 261.1386, found 261.1384.

6-Methyl-2,3-di((*E*)-styryl)quinoxaline (**3A''**):[22] Brown solid, m.p. 206～208 ℃; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.02～7.79 (m, 4H), 7.69 (d, J=7.6 Hz, 4H), 7.64 (s, 1H), 7.52 (d, J=8.2 Hz, 1H), 7.37 (ddd, J=53.1, 30.4, 16.1 Hz, 7H), 2.59 (s, 3H); ^{13}C NMR (125.4 MHz, $CDCl_3$) δ: 148.9, 148.3, 141.7, 140.2, 140.1, 137.6, 137.3, 136.63, 136.59, 132.0, 129.01, 128.95, 128.9, 128.61, 128.55, 128.4, 127.8, 127.59, 127.56, 122.8, 21.9; MS (EI) *m*/*z* (%): 348 (71), 347 (77), 346 (6), 333 (4), 272 (11), 271 (44), 270 (13), 269 (7), 257 (13), 245 (11), 218 (10), 209 (11), 208 (18), 207 (100), 193 (7), 191 (7), 177 (6), 173 (6), 167 (10), 166 (7), 165 (7), 147 (6), 135 (5), 133 (8), 115 (7), 103 (6), 102 (7), 96 (4), 91 (7), 89 (7), 77 (10), 73 (4).

Supporting Information Details of the control reactions and ^{1}H NMR and ^{13}C NMR spectra of the products. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

References

[1] (a) Lee, D.-H.; Kwon, K.-H.; Yi, C. S. *Science* **2011**, *333*, 1613.
(b) Skucas, E.; Ngai, M.-Y.; Komanduri, V.; Krische, M. J. *Acc. Chem. Res.* **2007**, *40*, 1394.
(c) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. P. *Chem. Rev.* **2009**, *109*, 2551.
(d) Zhang, S.-Y.; Zhang, F.-M.; Tu, Y.-Q. *Chem. Soc. Rev.* **2011**, *40*, 1937.
(e) Muzart, J. *Tetrahedron* **2005**, *61*, 4179.
(f) Detz, R. J.; Hiemstra, H.; van Maarseveen, J. H. *Eur. J. Org. Chem.* **2009**, *2009*, 6263.
(g) Emer, E.; Sinisi, R.; Capdevila, M. G.; Petruzziello, D.; Vincentiis, F. D.; Cozzi, P. G. *Eur. J. Org. Chem.* **2011**, *2011*, 647.
(h) Bandini, M.; Cera, G.; Chiarucci, M. *Synthesis* **2012**, 504.
(i) Chen, L.; Yin, X.-P.; Wang, C.-H.; Zhou, J. *Org. Biomol. Chem.* **2014**, *12*, 6033.

[2] (a) Watson, A. J. A.; Williams, J. M. J. *Science* **2010**, *329*, 635.
(b) Guillena, G.; Ramón, D. J.; Yus, M. *Chem. Rev.* **2010**, *110*, 1611.
(c) Dobereiner, G. E.; Crabtree, R. H. *Chem. Rev.* **2010**, *110*, 681.
(d) Bähn, S.; Imm, S.; Neubert, L.; Zhang, M.; Neumann, H.; Beller, M. *ChemCatChem* **2011**, *3*, 1853.
(e) Obora, Y. *ACS Catal.* **2014**, *4*, 3972.
(f) Yang, Q.; Wang, Q.; Yu, Z. *Chem. Soc. Rev.* **2015**, *44*, 2305.
(g) Huang, F.; Liu, Z.; Yu, Z. *Angew. Chem., Int. Ed.* **2016**, *55*, 862.
(h) Fujita, K.-I.; Yamaguchi, R. *Synlett* **2005**, 560.
(j) Corma, A.; Navas, J.; Sabater, M. J. *Chem. Rev.* **2018**, *118*, 1410.
(k) Irrgang, T.; Kempe, R. *Chem. Rev.* **2019**, *119*, 2524.
(i) Ma, X.; Su, C.; Xu, Q. *Top. Curr. Chem.* **2016**, *374*, article 27.

[3] (a) Xu, Q.; Chen, J.; Tian, H.; Yuan, X.; Li, S.; Zhou, C.; Liu, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 225.
(b) Xu, Q.; Li, Q.; Zhu, X.; Chen, J. *Adv. Synth. Catal.* **2013**, *355*, 73.
(c) Xu, Q.; Chen, J.; Liu, Q. *Adv. Synth. Catal.* **2013**, *355*, 697.
(d) Li, S.; Li, X.; Li, Q.; Yuan, Q.; Shi, X.; Xu, Q. *Green Chem.* **2015**, *17*, 3260.
(e) Li, X.; Li, S.; Li, Q.; Dong, X.; Li, Y.; Yu, X.; Xu, Q. *Tetrahedron* **2016**, *72*, 264.
(f) Chen, J.; Li, Y.; Li, S.; Liu, J.; Zheng, F.; Zhang, Z.; Xu, Q. *Green Chem.* **2017**, *19*, 623.
(g) Chen, T.; Han, F.; Li, S.; Liu, J.; Chen, J.; Xu, Q. *Chin. J. Org. Chem.* **2022**, *42*, 2914 (in Chinese).
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[4] (a) Gnanaprakasam, B.; Zhang, J.; Milstein, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 1468.
(b) Cano, R.; Ramón, D. J.; Yus, M. *J. Org. Chem.* **2011**, *76*, 5547.
(c) Zhang, G.; Hanson, S. K. *Org. Lett.* **2013**, *15*, 650.
(d) Sun, H.; Su, F.-Z.; Ni, J.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Angew. Chem., Int. Ed.* **2009**, *48*, 4390.
(e) Kang, Q.; Zhang, Y. *Green Chem.* **2012**, *14*, 1016.
(f) Soulé, J.-F.; Miyamura, H.; Kobayashi, S. *Chem. Commun.* **2013**, *49*, 355.
(g) Jiang, L.; Jin, L.; Tian, H.; Yuan, X.; Yu, X.; Xu, Q. *Chem. Commun.* **2011**, *47*, 10833.
(h) Tian, H.; Yu, X.; Li, Q.; Wang, J.; Xu, Q. *Adv. Synth. Catal.* **2012**, *354*, 2671.
(i) Zhang, E.; Tian, H.; Xu, S.; Yu, X.; Xu, Q. *Org. Lett.* **2013**, *15*, 2704.

[5] (a) Yamaguchi, R.; Fujita, K-I.; Zhu, M. *Heterocycles* **2010**, *81*, 1093.
(b) Nandakumar, A.; Midya, S. P.; Landge, V. G.; Balaraman, E. *Angew. Chem., Int. Ed.* **2015**, *54*, 11022.
(c) Chelucci, G. *Coord. Chem. Rev.* **2017**, *331*, 37.
(d) Shi, X.; Guo, J.; Liu, J.; Ye, M.; Xu, Q. *Chem.-Eur. J.* **2015**, *21*,

9988.
(e) Yao, S.; Zhou, K.; Wang, J.; Cao, H.; Yu, L.; Wu, J.; Qiu, P.; Xu, Q. *Green Chem.* **2017**, *19*, 2945.
(f) Wang, Q.; Lv, M.; Liu, J.; Li, Y.; Xu, Q.; Zhang, X.; Cao, H. *ChemSusChem* **2019**, *12*, 3043.
(g) Liu, H.; Han, F.; Li, H.; Liu, J.; Xu, Q. *Org. Biomol. Chem.* **2020**, *18*, 7079.
(h) Wang, Q.; Zhang, X.; Han, F.; Liu, J.; Xu, Q. *ChemSusChem* **2021**, *14*, 2866.
(i) Wang, Q.; Zhu, B.; Zhang, X.; Shi, G.; Liu, J.; Xu, Q. *Asian J. Org. Chem.* **2022**, *11*, e202200056.

[6] (a) Blank, B.; Kempe, R. *J. Am. Chem. Soc.* **2010**, *132*, 924.
(b) Obora, Y.; Ogawa, S.; Yamamoto, N. *J. Org. Chem.* **2012**, *77*, 9429.
(c) Chaudhari, C.; Siddiki, S. M. A. H.; Shimizu, K. *Tetrahedron Lett.* **2013**, *54*, 6490.
(d) Feng, T.; Li, H.; Young, D.; Lang, J. *J. Org. Chem.* **2017**, *82*, 4113.
(e) Rana, J.; Babu, R.; Subaramanian, M.; Balaraman, E. *Org. Chem. Front.* **2018**, *5*, 3250.
(f) Vellakkaran, M.; Das, J.; Bera, S.; Banerjee, D. *Chem. Commun.* **2018**, *54*, 12369.
(h) Mishra, A.; Dwivedi, A. D.; Shee, S.; Kundu, S. *Chem. Commun.* **2020**, *56*, 249.
(h) Kabadwal, L. M.; Bera, S.; Banerjee, D. *Chem. Commun.* **2020**, *56*, 4777.
(i) Onoda, M.; Fujita, K.-I. *Org. Lett.* **2020**, *22*, 7295.
(j) Jana, A.; Kumar, A.; Maji, B. *Chem. Commun.* **2021**, *57*, 3026.

[7] (a) Zhang, G.; Irrgang, T.; Dietel, T.; Kallmeier, F.; Kempe, R. *Angew. Chem., Int. Ed.* **2018**, *57*, 9131.
(b) Barnan, M. K.; Waiba, S.; Maji, B. *Angew. Chem., Int. Ed.* **2018**, *57*, 9126.
(c) Das, J.; Vellakkaran, M.; Sk, M.; Banerjee, D. *Org. Lett.* **2019**, *21*, 7514.
(d) Ramalingam, B. M.; Ramakrishna, I.; Baidya, M. *J. Org. Chem.* **2019**, *84*, 9819.
(e) Das, J.; Vellakkaran, M.; Banerjee, D. *Chem. Commun.* **2019**, *55*, 7530.
(f) Su, C.; Zeng, M.; Zhang, C.; Cui, D.-M. *Eur. J. Org. Chem.* **2020**, *2020*, 4942.
(g) Hazra, S.; Tiwari, V.; Verma, A.; Dolui, P.; Elias, A. N. J. *Org. Lett.* **2020**, *22*, 5496.
(h) Zhang, Z.; Ma, Y.; Dai, S.; Li, L.; Zhang, Y.; Li, H. *Tetrahedron Lett.* **2020**, *61*, 151885.
(i) Zhang, C.; Li, Z.; Fang, Y.; Jiang, S.; Wang, M.; Zhang, G. *Tetrahedron* **2020**, *76*, 130968.

[8] (a) Feng, S.; Liu, C.; Li, Q.; Yu, X.; Xu, Q. *Chin. Chem. Lett.* **2011**, *22*, 1021.
(b) Liu, C.; Liao, S.; Li, Q.; Feng, S.; Sun, Q.; Yu, X.; Xu, Q. *J. Org. Chem.* **2011**, *76*, 5759.
(c) Yu, X.; Liu, C.; Jiang, L.; Xu, Q. *Org. Lett.* **2011**, *13*, 6184.
(d) Li, Q.; Fan, S.; Sun, Q.; Tian, H.; Yu, X.; Xu, Q. *Org. Biomol. Chem.* **2012**, *10*, 2966.
(e) Liao, S.; Yu, K.; Li, Q.; Tian, H.; Zhang, Z.; Yu, X.; Xu, Q. *Org. Biomol. Chem.* **2012**, *10*, 2973.
(f) Yu, X.; Jiang, L.; Li, Q.; Xie, Y.; Xu, Q. *Chin. J. Chem.* **2012**, *30*, 2322.
(g) Xu, Q.; Li, Q. *Chin. J. Org. Chem.* **2013**, *33*, 18 (in Chinese).
(徐清, 李强, 有机化学, **2013**, *33*, 18.)

[9] (a) Xu, Q.; Xie, H.; Chen, P.; Yu, L.; Chen, J.; Hu, X. *Green Chem.* **2015**, *17*, 2774.
(b) Xu, Q.; Xie, H.; Zhang, E.-L.; Ma, X.; Chen, J.; Yu, X.-C.; Li, H. *Green Chem.* **2016**, *18*, 3940.
(ch) Ma, X.; Yu, L.; Su, C.; Yang, Y.; Li, H.; Xu, Q. *Adv. Synth. Catal.* **2017**, *359*, 1649.
(d) Yang, Y.; Ye, Z.; Zhang, X.; Zhou, Y.; Ma, X.; Cao, H.; Bao, J.; Li, H.; Yu, L.; Xu, Q. *Org. Biomol. Chem*. **2017**, *15*, 9638.
(e) Ma, X.; Xu, Q.; Li, H.; Su, C.; Yu, L.; Zhang, X.; Cao, H.; Han, L.-B. *Green Chem*. **2018**, *20*, 3408.
(f) Ma, X.; Yu, J.; Yan, R.; Yan, M.; Xu, Q. *J. Org. Chem.* **2019**, *84*, 11294.

[10] For similar findings from other groups: (a) Zhang, W.; Liu, M.; Wu, H.; Ding, J.; Cheng, J. *Tetrahedron Lett.* **2008**, *49*, 5336.
(b) Wang, X.; Wang, D. Z. *Tetrahedron* **2011**, *67*, 3406.
(c) Donthiri, R. R.; Patil, R. D.; Adimurthy, S. *Eur. J. Org. Chem.* **2012**, *2012*, 4457.
(d) Xu, J.; Zhuang, R.; Bao, L.; Tang, G.; Zhao, Y. *Green Chem.* **2012**, *14*, 2384.

[11] (a) Pascal, L.; Eynde, J. J. V.; Haverbeke, Y. V.; Dubois, P. *Lett. Org. Chem.* **2004**, *1*, 112.
(b) Eynde, J. J. V.; Pascal, L.; Haverbeke, Y. V.; Dubois, P. *Synth. Commun.* **2001**, *31*, 3167.
(c) Jaung, J.-y.; Matsuoka, M.; Fukunishi, K. *Dyes Pigm.* **1996**, *31*, 141.

[12] For reviews on TM-free MPV-O type transfer hydrogenation reactions of alcohols: (a) Cha, J. S. *Org. Process Res. Dev.* **2006**, *10*, 1032.
(b) de Graauw, C. F.; Peters, J. A.; van Bekkum, H.; Huskens, J. *Synthesis* **1994**, 1007.

[13] Taylor, E. C.; Martin, S. F. *J. Am. Chem. Soc.* **1972**, *94*, 2874.

[14] Tang, W.-J.; Xu, L.-J.; Fan, Q.-H.; Wang, J.; Fan, B.-M.; Zhou, Z.-Y.; Lam, K. H.; Chan, A. S. C. *Angew. Chem., Int. Ed*. **2009**, *48*, 9135.

[15] Gulakova, E. N.; Sitin, A. G.; Kuzmina, L. G.; Fedorova, O. A. *Russ. J. Org. Chem.* **2011**, *47*, 245.

[16] Girase, T. R.; Patil, K. J.; Kapdi, A. R.; Gupta, G. R. *ChemistrySelect* **2020**, *5*, 4251.

[17] Jonsson, A.; Stene, P.; Willman, N. *Acta Pharm. Suec.* **1968**, *5*, 237.

[18] Fu, S.-H.; Wang, L.; Dong, H.-X.; Yu, J.-Q.; Xu, L.-B.; Xiao, J. *Tetrahedron Lett.* **2016**. 57, 4533.

[19] Wendlandt, A. E.; Stahl, S. S. *J. Am. Chem. Soc.* **2014**, *136*, 11910.

[20] Bahrami, K.; Khodaei, M. M.; Nejati, A. *Green Chem.* **2010**, *12*, 1237.

[21] Thirumurugan, P.; Muralidharan, D.; Perumal, P. T. *Dyes Pigm.* **2009**, *81*, 245.

[22] Bennett, G. M.; Willis, G. H. *J. Chem. Soc.* **1928**, 1960.

(Zhao, C.)

