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Selective synthesis of *N*-monomethyl amines with primary amines and nitro compounds

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N-Monomethyl amines are important building blocks in the synthesis of a range of valuable compounds, including dyes, surfactants, pharmaceuticals, agrochemicals, and materials. Furthermore, the *N*-methyl group plays an important role in various biological processes where some methylated drug candidates show enhanced activity compared to the non-methylated precursors as a result of the change in solubility, conformation, and metabolic activity. However, facile access to such compounds remains a fundamental challenge in organic synthesis owing to selectivity issues caused by overmethylation. Therefore, controllable synthesis of *N*-monomethyl amines by selective *N*-monomethylation of primary amines and nitro compounds is an important and challenging field in synthetic organic chemistry and catalysis. There is a need for a comprehensive review on catalytic *N*-monomethylation of primary amines and nitro compounds to motivate the advancements of this field. Herein, the development of *N*-monomethylation of primary amine and nitro compounds with homogeneous and heterogeneous catalysts is summarized. This article describes the development of the selective *N*-monomethylation of primary amines and nitro compounds by using various methylating agents, such as MeX, carbon dioxide, methanol, formaldehyde, formic acid and dimethyl carbonate. The basic principles and strategies to control selectivity of *N*-monomethylation of primary amines and nitro compounds with different methylating agents are also summarized. Finally, we will give some advice for future progress in this field. This review will promote the development of *N*-monomethylation of primary amines and other selective methylation.

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1. Introduction

N-Methylation is one of the most fundamental C–N bond forming reactions in organic chemistry and green chemistry.[1] It is well known that *N*-monomethylamine is a fundamental building block as an intermediate for the production of synthesis of pharmaceuticals, dyes, agrochemicals and so on (Scheme 1).[2] What's more, the *N*-methylation of amines is of

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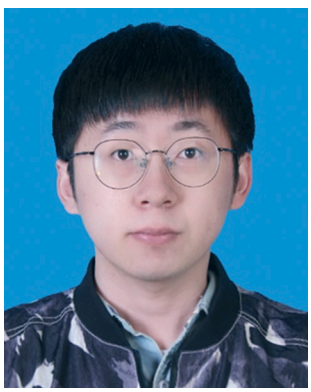

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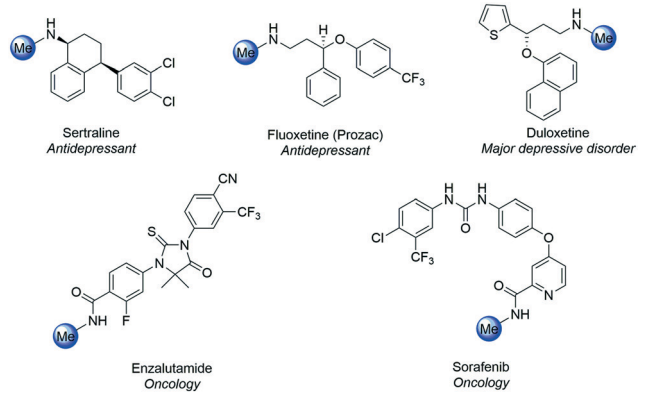

Scheme 1 Bioactive molecules bearing a *N*-methyl moiety.

significant importance to regulate the physicochemical properties of organic molecules including their biological and pharmaceutical activities.[3,4] In organic and medicinal chemistry, the introduction of methyl groups into molecular frameworks is an essential and ubiquitous process. Nevertheless, the highly selective synthesis of *N*-monomethylamines remains a tremendous challenge in synthetic organic and catalysis because *N*-monomethylamines possess higher reactivity than primary amines and are prone to further transform into *N*,*N*-dimethyl amines. Furthermore, overmethylation still presents a serious issue that is due to the increased nucleophilicity of the amine following monomethylation as well as the small size of the methyl group.[5] It is well-known that nitro compounds are cheap and readily available, and hydrogenation of nitroarenes is one of the most commonly used approaches to synthesize primary amines. Thus, it is attractive to perform the one-pot *N*-monomethylation reactions using nitro compounds as the flexible feedstock. Therefore, it is important to emphasize that precisely regulating selectivity of the single *N*-monomethylamine product is still a challenging limitation and it is urgent to design and prepare catalysts to solve the problem of overmethylation.

For the catalytic mechanism of *N*-monomethylation, there are generally two ideas at present (Fig. 1). The first idea is to completely consume the methylating reagent during the first step of methylation or not to proceed to the second step through kinetically regulating the reaction. The other idea is to adjust the structure and properties of the catalyst to control the adsorption and desorption steps of products and raw materials on the surface of the catalyst, so that the *N*-monomethylated product is easy to desorb from the surface of the catalyst, making it impossible to carry out *N*,*N*-dimethylation. In other words, the synthesis of *N*-monomethylamine is controlled by kinetic inhibition of *N*,*N*-dimethylation *via* nondominant adsorption and easy desorption of *N*-monomethylamine on the catalyst surface.

Traditional methylation reactions involve the use of flammable, explosive and toxic starting materials. This kind of method has many disadvantages, it not only needs high reaction temperature and a large amount of base, but also produces a lot of waste, and the selectivity and yield are not good. In contrast, newly developed methods have overcome this point and provide a mild strategy. A variety of methylating agents are employed as starting materials for the selective synthesis of *N*-monomethylamines, such as CO_2, methanol, HCHO, HCOOH and dimethyl carbonate (DMC). Therefore, the utilization of environmentally friendly and low-cost C1 carbon source to develop new methods of *N*-monomethylation that meet the needs of green environmental protection has become an important development direction in this research field.

Although the application of methylating reagents has made great progress in the *N*,*N*-dimethylation of primary amines and the *N*-methylation of secondary amines,[6–14] there are still problems with *N*-monomethylation and we could not find any reviews or books which systematically outlined the

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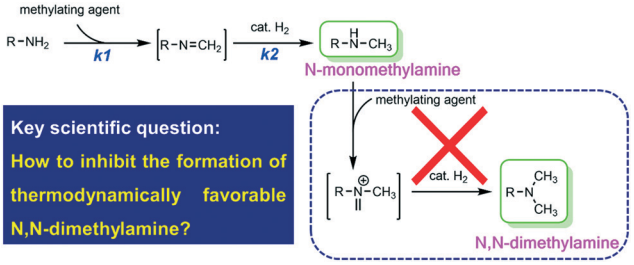


Fig. 1 Plausible catalytic mechanism of *N*-monomethylation.

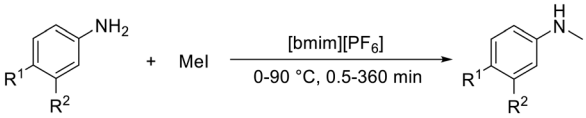
early adventures and recent advancements in selective *N*-monomethylation reactions of primary amines and nitro compounds. This review will summarize selective *N*-monomethylation of primary amines and nitro compounds using different methylating agents, such as MeX, CO_2, methanol, HCHO, HCOOH and dimethyl carbonate (DMC). As CO_2, methanol, HCHO and HCOOH are carbon one (C1) molecules, we believe that this review will provide a promising perspective of efficient utilization of C1 resource and promote the development of C1 chemistry. Furthermore, we also believe that this review will motivate the advancements of other selective methylation of reactions, such as methylation of C(sp^2)–H bond in (hetero)arenes, methylation of α-C(sp^3)–H bond in carbonyl compounds and attract a growing number of researchers to this field. We sincerely hope it can help researchers in the fields of organic synthesis, catalysis, and medicinal and biological chemistry, and play a positive role in the study of *N*-monomethylation.

2. *N*-Monomethylation with methylating agents

2.1 MeX as methylating agent

In the early days, researchers prepared *N*-alkylamines by reacting amines with halogenated reagents.[15] Although this method used dangerous and toxic methylation reagents and strong alkaline reaction media, it laid a good foundation for the green synthesis of *N*-methylated amine molecules. Of course, *N*-monomethylated amines could also be synthesized using MeX as a methylation reagent.

In 2006, Chiappe and co-workers reported the preparation of *N*-monomethylated substituted anilines with MeI in [bmim][PF_6] ionic liquids (ILs) for the first time.[16] Six examples of desired products could be obtained by reacting at 0–90 °C with up to 60% yield (Scheme 2). They found the best selectivity could be achieved in the solvent with the poorest H-bond acceptor anion and the least selectivity occurred when the anion was a good H-bond acceptor.



Scheme 2 *N*-Monomethylation of substituted anilines with MeI.

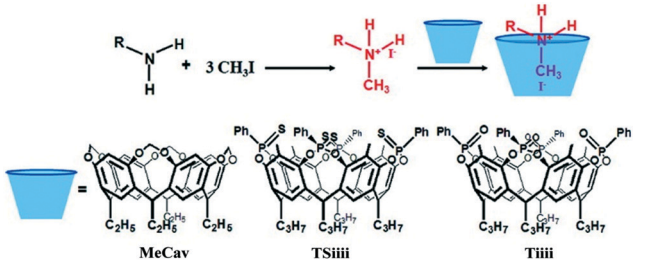
However, how to solve the narrow substrate scope and poor selectivity is the main challenge. In 2009, Dalcanale *et al.* presented an appropriate host to sequester the intermediate product when using MeI as methylation reagent, thus avoiding further methylation *in situ*.[17] 64–87% yields of *N*-monomethylamines could be obtained at 25–45 °C with Tiiii cavitands as sequestrating agents (Scheme 3). ^{31}P NMR showed that high association constants and specific complexation modes were the key factors when choosing an effective sequestrating agent.

In 2014, an important breakthrough for the selective *N*-monomethylation of primary amines with methyl triflate (MeOTf) was achieved by Legros and co-workers.[18] They used hexafluoroisopropanol (HFIP) as the solvent to interfere with amines and avoid overmethylation by the selective deactivation of secondary and tertiary amines through H-bonding. In the absence of catalyst, a variety of amines with different functional groups could be obtained in moderate to excellent yields, including glycine and L-valine ethyl ester (Scheme 4).

2.2 CO_2 as methylating agent

Since the 20th century, fossil fuels have been highly polluting and non-renewable, which has had a bad impact on the environment. Therefore, carbon dioxide as a cheap, renewable, abundant and green C1 resource used to synthesize fine chemical raw materials has attracted considerable attention.[19] In particular, the conversion of CO_2 into high value-added fine chemicals is a hot research direction, so it has a wide range of application value in methylation.[20]

In 2013, Cantat and co-workers firstly presented IPrZnCl_2 catalyzed *N*-monomethylation of primary amines when using CO_2 and hydrosilanes as reductants.[21] This catalyst was an off-white solid and it was effective in promoting both a 6 electron reduction of carbon dioxide and the formation of a C–N bond. In the presence of 1 bar CO_2 and 2 equivalent $PhSiH_3$, *N*-monomethylamine with up to 67% yield could be obtained (Scheme 5). At the same time, Beller *et al.* reported Ru-catalyzed selective *N*-monomethylation of diamines.[22] Due to the high chemical similarity of the two amine moieties, this reaction represents a challenging task for traditional



Scheme 3 *N*-Monomethylation of primary amines in the presence of cavitands as sequestrating agents[17] (copyright 2009 American Chemical Society).

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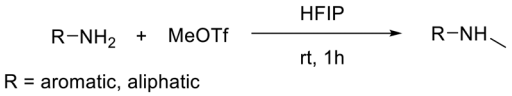
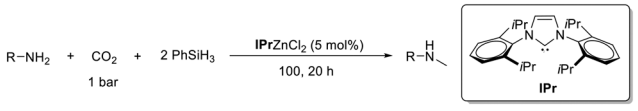


Scheme 4 *N*-Monomethylation of primary amines with MeOTf in HFIP.

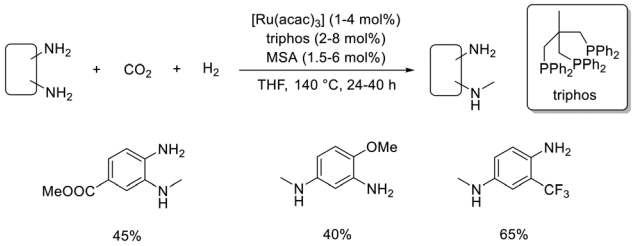
N-monomethylation methods. When $Ru(acac)_3$, triphos and methanesulfonic acid (MSA) were used as catalysts, 40–65% yields of diamines could be obtained (Scheme 6). They found the desired reaction site was more nucleophilic and less sterically hindered. Moreover, formamide (primary) and methanol (secondary) as intermediates was proposed. The formamide intermediate was favorably formed, and then rapidly reduced to the corresponding methylated product. These works exhibited the excellent performance and specific reaction sites of homogeneous catalysts for the *N*-monomethylation of primary amines and carbon dioxide.

In 2014, Shi's group reported the first heterogeneous catalytic *N*-monomethylation of aromatic primary amines with CO_2/H_2.[23] They prepared an active $Pd/ZrCuO_x$ catalyst by co-precipitation method and 49–79% yields of the corresponding products were synthesized. Further characterizations indicated CuO and ZrO_2 could be observed and palladium particles were highly dispersed in the bulk catalyst or on the catalyst surface.

Furthermore, this catalyst could be reused 3 times without obvious deactivation. However, the use of precious metal would increase the difficulty of industrialization and the cost of the target products, so it was urgent to develop non-noble metal. Subsequently, Shi and co-workers discovered $CuAlO_x$ catalyst exhibited excellent performance for the activation of carbon dioxide to generate high value-added products.[24] In the presence of 3.0 MPa CO_2 and 6.0 MPa H_2, 7 examples of amines could be transformed into *N*-monomethylamines in good to excellent yields at 160 °C. Challenging aliphatic amines could also undergo *N*-monomethylation under the same condition. For example, *N*-methyldodecan-1-amine can be obtained in 44% yield. Moreover, the crystal lattices of Cu (111) and Cu (200) could be clearly observed by HR-TEM. The line scan EDS analysis of the catalyst sample showed that it was composed of nano CuO_x particles deposited on the AlO_x plane (Fig. 2). Interestingly, nitrobenzene and aromatic nitrile derivatives can also be efficiently and selectively transformed into the corresponding *N*-methyl or *N*,*N*-dimethyl products with excellent yields. These works provide new insights for the preparation of heterogeneous catalysts to utilize and recycle CO_2.



Scheme 5 Zinc-catalyzed *N*-monomethylation of primary amines with CO_2.



Scheme 6 Ru-Catalyzed *N*-monomethylation of primary amines with CO_2.

2.3 MeOH as methylating agent

Methanol is an attractive reagent in the *N*-monomethylation of primary amines because it is easily available, inexpensive, and a renewable raw material. However, compared with other alcohols, methanol dehydrogenation is more demanding in terms of energy (for methanol, ΔH = +84 kJ mol^{-1}, for ethanol, ΔH = +68 kJ mol^{-1}).[25,26] Therefore, the utilization of methanol as a methylating agent is still a challenging task. During the reaction, using the mechanism of borrowing hydrogen,[27] methanol is first activated to formaldehyde after dehydrogenation, then it is condensed with amine to obtain the corresponding imine, and finally reduced to *N*-methylated amine *in situ* (Scheme 7). The methodology is attractive because of high atom efficiency and the formation of water as the only by-product. Therefore, methanol has become one of the most used reagents in current research and has a good development prospect.

2.3.1 Homogeneous catalyst system. In 1981, Grigg *et al.* described the first example of a homogeneous transition metal-catalyzed *N*-monomethylation of primary amines (Scheme 8), whereby $RhH(PPh_3)_4$ was shown to be effective

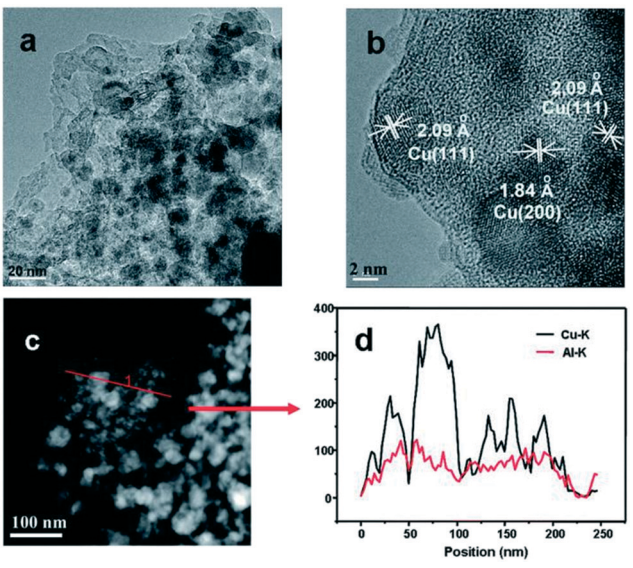


Fig. 2 TEM (a), HR-TEM (b) and line-scan EDS analysis (c) images of the $CuAlO_x$ catalyst sample (d)[24] (copyright 2014 Royal Society of Chemistry).

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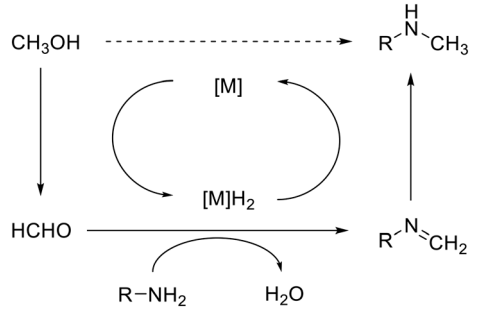
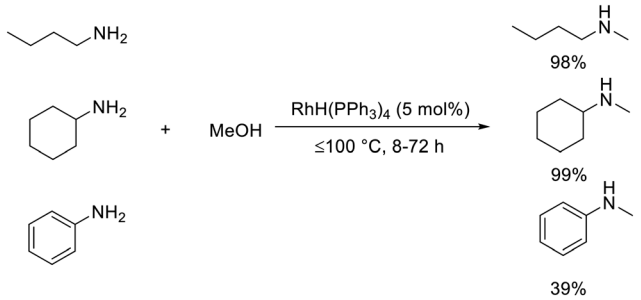


Scheme 7 Plausible mechanism of *N*-monomethylation of primary amines with MeOH.

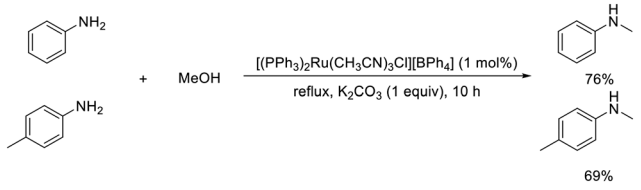


Scheme 8 $RhH(PPh_3)_4$ catalyzed *N*-monomethylation of primary amines with MeOH.

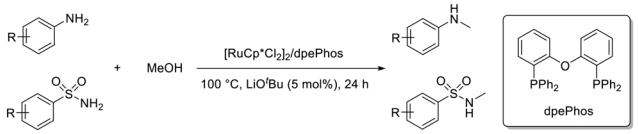
catalysts for preparation of *N*-monomethylamine from primary amine and methanol, albeit with 3 examples and low yield of *N*-methylaniline.[28] This research has laid a good foundation and created a precedent for the *N*-monomethylation reaction.

Bhattacharjee's group later reported $[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ catalyzed *N*-monomethylation of aniline and *p*-tolylamin, the corresponding products were obtained with 76% and 69% yields, respectively (Scheme 9).[29] Although the yield of aromatic amines increased, the substrate scope was still narrow.

In 2015, $[RuCp^*Cl_2]_2$/dpePhos catalyzed *N*-monomethylation of aromatic amines and sulfonamides using methanol was investigated by Seayad's group (Scheme 10).[30] This catalyst system was shown high catalytic performance with 5 mol% LiO^tBu base and given 73–98% yields with good tolerance to reducible functional groups under the optimized reaction conditions (100 °C, 24 h).



Scheme 9 $[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$ catalyzed *N*-monomethylation of aromatic amines with MeOH.



Scheme 10 $[RuCp^*Cl_2]_2$/dpePhos catalyzed *N*-monomethylation of aromatic amines and sulfonamides using MeOH.

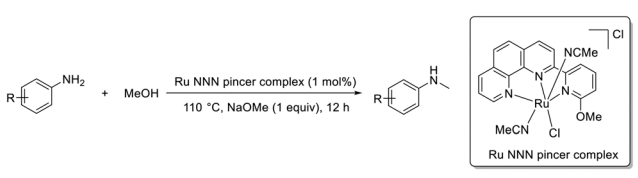
Furthermore, the catalytic intermediate Cp*Ru(dpePhos)H was shown to be active for methylation in the absence of base. However, aliphatic amines underwent overmethylation to produce *N*,*N*-dimethylation products under the same reaction conditions, which can be attributed to the more nucleophilic aliphatic amines.

This overmethylation phenomenon was also observed in Kundu's group, and 71–100% yields of *N*-monomethylation products could be obtained by using Ru^{II} NNN pincer complex and 1 equiv. NaOMe at 110 °C (Scheme 11).[31] Later, they found that a similar Ru^{II} NNN pincer complex could also make aromatic amines *N*-monomethylation and applied to other reactions, such as *N*-alkylation, amidation and synthesis of quinoline.[32] Furthermore, this catalyst system was also the first report of tandem reductive amination of nitro compounds with methanol to various *N*-methylamines.

In 2018, $RuHCl(CO)(PN^HP)$ (PN^HP = bis(2-diphenylphosphinoethyl)amine) was identified as an effective catalyst for *N*-monomethylation of aromatic amines with methanol (Scheme 12),[33] providing the desired products in 13–100% yields at 150 °C with a low catalyst loading (0.02–0.1 mol%) in the presence of KO^tBu (20–100 mol%).

At the same time, Hong's group reported the highly selective *N*-monomethylation of primary amines with methanol by using Ru-MACHO-BH catalyst (Scheme 13).[34] Interestingly, in the presence of hydrogen, various substrates including bio-related molecules, pharmaceuticals, aliphatic primary amines and aromatic amines were selectively monomethylated and the corresponding products were obtained in 34–99% yields without base.

They presented that H_2 as the reducing agent could retard the dehydrogenation of hemiaminal **A** and facilitate the hydrogenation of imine **B**, which will be formed by the dehydration of semiamine **A** (Scheme 14). It is believed that further methylation of the secondary amine could be kinetically prevented under suitable catalytic conditions as the formation of the charged iminium intermediate **D** could have a higher activation barrier than that of neutral imine **B**. Furthermore, the addition of H_2 inhibits the



Scheme 11 *N*-Monomethylation of amines with methanol, catalyzed by Ru^{II} NNN pincer complex.

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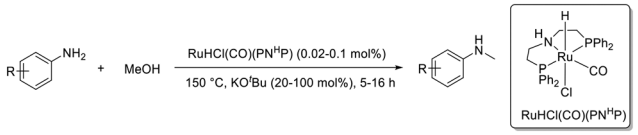
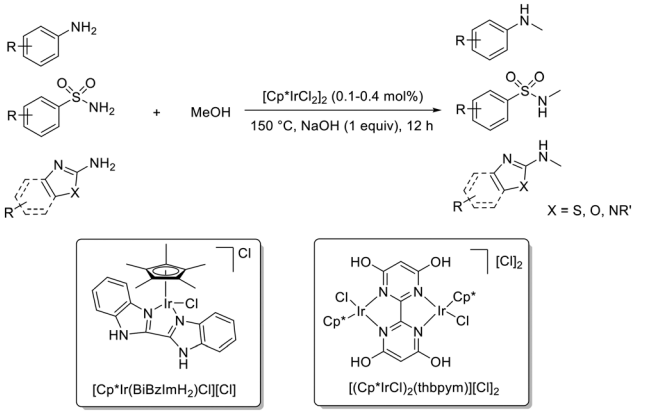


Scheme 12 RuHCl(CO)(PN^HP) catalyzed *N*-monomethylation of amines with methanol.

Scheme 13 Ru-MACHO-BH catalyzed *N*-monomethylation of primary amines with methanol.



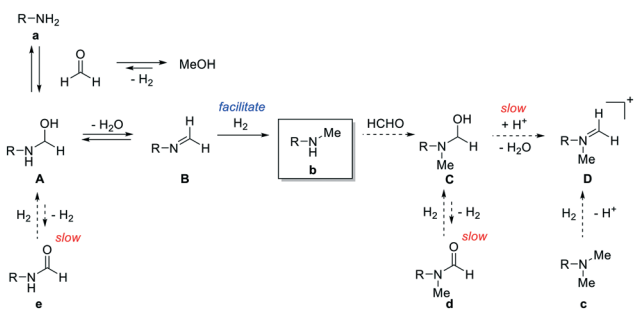
Scheme 15 Ir complex catalyzed *N*-monomethylation of aromatic primary amines with methanol.

dehydrogenation steps to generate **e** and **d**, rendering the dehydration pathways more productive. This work was the first utilization of hydrogen to improve the selectivity of the *N*-monomethylation of primary amine and methanol, and a novel explanation of the proposed reaction pathway was established through the control experiment of 1,2,3,4-tetrahydroisoquinoline and primary amine. These results indicate that primary amines are more reactive than secondary amines in methylation. Furthermore, it was indicated that not only was the suitable reaction temperature important for kinetically controlling the selectivity between *N*-monomethylation and *N*,*N*-dimethylation, but also the presence of hydrogen was essential to achieve selective dehydration over dehydrogenation of the hemiaminal intermediate.

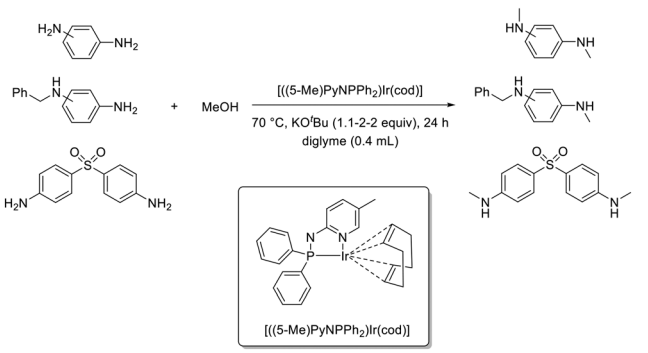
In 2012, Li *et al.* described $[Cp^*IrCl_2]_2$/NaOH (Cp* = pentamethylcyclopentadienyl) highly selective catalyzed *N*-monomethylation of aromatic primary amines (Scheme 15).[35] Arylsulfonamides and amino-azoles were explored for the first time and the corresponding products including arylamines could be obtained in 71–97% yields. Importantly, further experiment indicated that this catalyst system was only effective for the synthesis of *N*-monomethylated products and overmethylation could not be detected. Later they developed another Ir catalysts, [Cp*Ir(BiBzImH_2)Cl][Cl] could be used for *N*-monomethylation of a variety of amines with methanol in the presence of 0.3 equiv. of Cs_2CO_3 and a range of desirable products were obtained in 78–96% yields.[36] Interestingly, they recently proposed *N*-monomethylation of amines with methanol in aqueous solution by using [(Cp*IrCl)$_2$(thbpym)][Cl]$_2$ and KOH catalyst system.[37] Moreover, the presence of OH units in the bpym ligand was essential for the catalytic activity of the iridium complex and the corresponding *N*-monomethylated products could be observed in 77–94% yields.

Kempe's group simultaneously used a simple two-step method to synthesize an novel iridium catalyst [((5-Me)PyNPPh$_2$)Ir(cod)].[38] This catalyst was stabilized by an anionic P,N ligand and catalyzed the symmetrical and unsymmetrical monoalkylation of *para*-, *meta*-, and *ortho*-benzenediamines. There were 7 examples of *N*-monomethylation among them and the 80–97% yields could be obtained at 70 °C (Scheme 16).

In 2015, microwave heating promoted *N*-monomethylation of aromatic amines with methanol was reported by Crabtree's group for the first time.[39] Iridium bis(*N*-heterocyclic carbene) catalysts was developed and various functional groups of aromatic amines could be transformed with up to 95% yield (Scheme 17). Moreover, this catalytic system was also active for acceptorless dehydrogenation and transfer hydrogenation.



Scheme 14 Proposed reaction pathway.[34]



Scheme 16 [((5-Me)PyNPPh$_2$)Ir(cod)] catalyzed *N*-monomethylation of benzenediamines and 4,4′-sulfonyldianilines with methanol.

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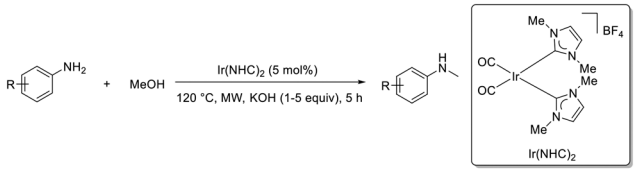
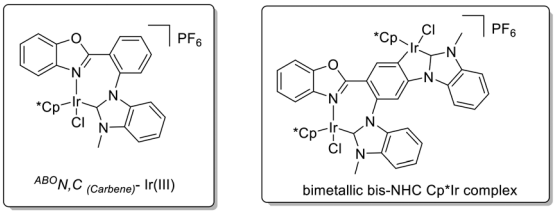


Scheme 17 Microwave-assisted *N*-monomethylation of substituted anilines catalyzed by Ir complex.



Scheme 19 Structural formula of Ir complex.

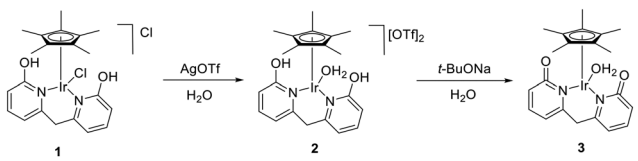
In 2018, [Cp*Ir-($HOC_5H_3CH_2C_5H_3OH$)Cl][Cl] (**1**) was developed for *N*-monomethylation of aromatic primary amines with methanol in 62–94% yields by Chen *et al.*[40] Interestingly, simply modifying the (**1**) complex can get [Cp*Ir($HOC_5H_3CH_2C_5H_3OH$)(H_2O)][OTf]$_2$ (**2**) and [Cp*Ir-(OC_5H_3-$CH_2C_5H_3O$)(H_2O)] (**3**) complexes (Scheme 18). And *N*-methylaniline could also be synthesized efficiently with 0.3 equiv. Cs_2CO_3 at 120 °C. Moreover, (**1**) complex could also catalyze selective monomethylation of propiophenone derivatives using methanol.

In 2019, Hou's group prepared several novel chelated cyclometalated Ir complexes ^{ABO}N,P, ^{ABO}N,O, ^{ABO}N,C$_{(Carbene)}$ based on a rigid and tunable 2-arylbenzo[*d*]oxazole backbone and ^{ABO}N,C$_{(Carbene)}$ (Scheme 19) exhibited the best activity in *N*-monomethylation of aromatic amines with methanol.[41] Various substrates covering electron-rich/deficient aromatic amines at *para*-, *meta*- and *ortho*-position, heterocyclic amines, and many functional groups could be converted into *N*-monomethylated products in 64–99% yields with 1 equiv. KO^{t}Bu at 130 °C. Recently, they developed bimetallic bis-NHC Cp*Ir complex (Scheme 19) and *N*-monomethylamine could be obtained in moderate to excellent yields under similar reaction conditions.[42] Moreover, just simply extending the reaction time, the corresponding *N*-monomethylated product was synthesized with nitrobenzene and methanol in one step with a yield of 62–94%. Further kinetic experiment results and DFT calculations proved that the presence of a bimetallic synergistic effect between the two Ir centers.

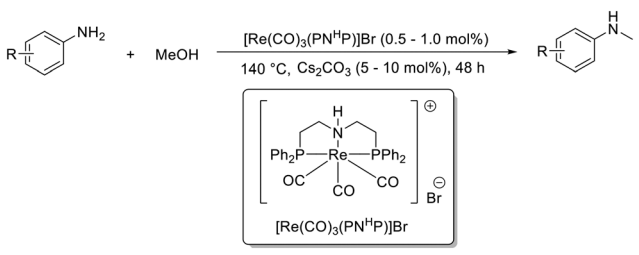
In 2018, the first example of rhenium-catalyzed *N*-monomethylation of aromatic amines with methanol was reported by Sortais's group.[43] They synthetized new rhenium complexes bearing aliphatic tridendate PNP ligands with various substituents on the phosphorus atom by using one equivalent of ligand with one equivalent of [$ReBr(CO)_5$] in toluene at 100 °C. Furthermore, this catalytic system required only 5–10 mol% Cs_2CO_3 base to obtain the corresponding products with up to 95% isolated yield (Scheme 20). Moreover, the mechanism of the reaction was studied by DFT calculations. The results not only showed the importance of the metal catalysis process to kinetics, but also the role of the formation of imine intermediates.

Obviously, precious metal-based complexes are highly effective catalysts for *N*-monomethylation of amines and methanol. However, due to economic pressure and the common concept of sustainable development, the replacement of these noble metals by Earth-abundant non-noble metal has gradually become a challenging and attractive topic. In 2016, the defined PNP manganese pincer complex catalyzed the chemoselective *N*-monomethylation of primary amines using methanol under mild conditions was reported by Beller *et al.* for the first time (Scheme 21).[44] In the presence of 1 equiv. KO^{t}Bu, various anilines gave the *N*-monomethylated products in 52–94% yields at 100 °C. This study was also one of the earliest examples of using non-noble metal homogeneous catalyst to catalyze *N*-monomethylation with methanol as a methylation reagent and provided new insights for the design of non-noble metal homogeneous catalysts. One year later, they developed [Mn(PNP^{iPr})$(CO)_2$Br] catalyst (Scheme 21) and substrates with functional groups such as ketones, double bonds or amides could be transformed into the corresponding products in good yields at 100 °C and 0.5 equiv. KO^{t}Bu.[45] Sortais's group simultaneously used a tridentate PN^{3}P manganese pre-catalyst (Scheme 21) for *N*-monomethylation with methanol.[46] Under catalytic amount of KO^{t}Bu (20 mol%), various aniline derivatives were methylated in good to excellent yields. Moreover, they clarified the catalytic mechanism through X-ray diffraction studies to isolate and characterize the de-aromatized manganese intermediate.

In 2017, Liu's group reported *N*-monomethylation reaction catalyzed by the commercially available Co(acac)$_2$ and a tetradentate phosphine ligand P($CH_2CH_2PPh_2$)$_3$ (Scheme 22) for the first time.[47] In the presence of 1 equiv. K_3PO_4, 82–



Scheme 18 Synthesis of complexes **2** and **3**.



Scheme 20 Re-Catalyzed *N*-monomethylation of aromatic primary amines with methanol.

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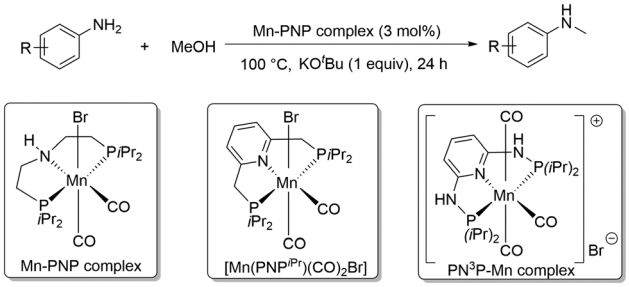
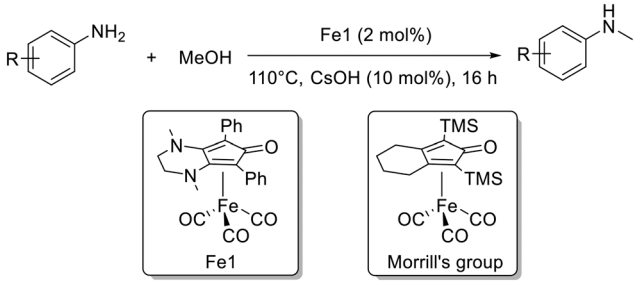


Scheme 21 Mn complex catalyzed *N*-monomethylation of aromatic primary amines with methanol.



Scheme 23 Fe-Catalyzed *N*-monomethylation of aromatic primary amines with methanol.

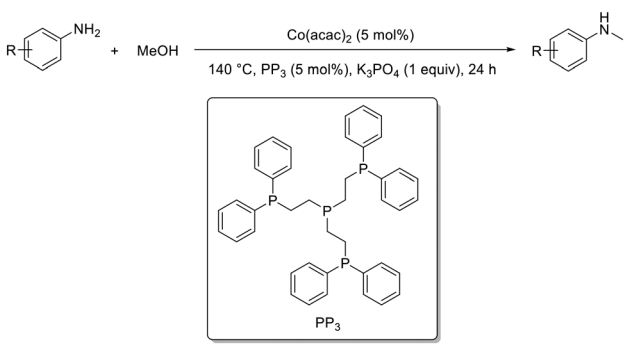
95% yields of the corresponding *N*-monomethylated products could be obtained at 140 °C. Control experiments and deuterium-labeling experiments showed a hydrogen-borrowing process in reaction mechanism. Although non-noble metal homogeneous catalyst with these complexes paved the way to more sustainable processes, they are based on expensive phosphorus ligands.

In order to solve the above problem, Renaud and Poater *et al.* identified that an iron(0) complex bearing a cyclopentadienone ligand exhibited catalytic activity for *N*-monomethylation of aromatic primary amines with methanol (Scheme 23) in 2018.[48] Moreover, the CsOH just required a catalytic equivalent to obtain the corresponding products with up to 99% yield at 110 °C. Further experimental work and DFT calculations suggested molecular hydrogen acted not only as a reducing agent but also as an additive to displace thermodynamic equilibria. At the same time, Morrill's group reported a similar Fe complex catalyst for *N*-monomethylation (Scheme 23).[49] In the presence of 2 equiv. K_2CO_3, the products in good to excellent yields could be obtained at 80–110 °C with Me_3NO as activator. In addition, various ketones, indoles, oxindoles, amines, and sulfonamides could also be mono- or dimethylated under similar reaction conditions.

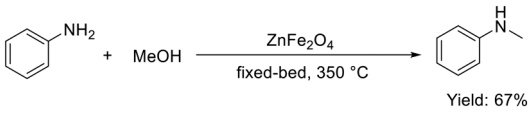
2.3.2 Heterogeneous catalyst system. At present, the development of *N*-monomethylation of amines with methanol catalyzed by homogeneous catalysts is gradually improving and showing excellent catalytic performance, but the catalyst cannot be easily separated and reused, which makes it difficult to achieve green economy and large-scale industrial applications. Therefore, scientists have gradually developed heterogeneous catalysts to solve the above problems.

As early as 1999, Rao's group reported $Zn_{1-x}Ni_xFe_2O_4$ (x = 0, 0.2, 0.5, 0.8 and 1) catalyzed *N*-monomethylation of aniline in a fixed-bed down-flow reactor.[50] When the molar ratio of methanol to aniline was 7, the yield of *N*-methyl aniline catalyzed by $ZnFe_2O_4$ (ZF-1) was nearly 67% at 350 °C (Scheme 24). With the increasing of content of Ni, Ni^{2+} ions isomorphically replace acidic Fe^{3+} ions from the active O-sites to T-sites, leading to a progressive diminishing in the activity. It could also be said that the distribution of cations in the spinel lattice would affect its acidic–basic properties and the Lewis acid sites, thereby affecting the catalytic performance. Later, they further developed $Zn_{0.8}Co_{0.2}Fe_2O_4$ catalyst and 72% yield of *N*-methyl aniline could also be obtained at a methanol to aniline molar ratio of 5.[51]

Ikariya *et al.* firstly used supercritical methanol ($scCH_3OH$) to study the effects of conventional solid acids (H-mordenite, β-zeolite, amorphous silica–alumina) and acid–base bifunctional catalysts (Cs–P–Si mixed oxide and γ-alumina) on the selective *N*-methylation of bifunctionalized amines in a continuous flow fixed-bed reactor.[52,53] They found Cs–P–Si exhibited the most efficient catalyst performance in terms of selectivity and reactivity at 300 °C and 8.2 MPa. Importantly, various diamines could be transformed into *N*-methyl diamines with up to 58% yield for the first time (Scheme 25). Magic-angle spinning NMR spectroscopy and X-ray diffraction analysis showed that the acidic and basic sites of the Cs–P–Si mixed oxide catalyst originated from P_2O_5/SiO_2 and Cs/SiO_2, respectively. Moreover, the weak acid–base sites on the surface of the catalyst were attributed to three kinds of cesium phosphates on SiO_2, which might be the cause of selective *N*-methylation. Luque's group later also drew a similar conclusion that weak to moderate acid sites seemed



Scheme 22 Cobalt-catalyzed *N*-monomethylation of aromatic primary amines with methanol.



Scheme 24 $ZnFe_2O_4$ catalyzed *N*-monomethylation of aniline with methanol.

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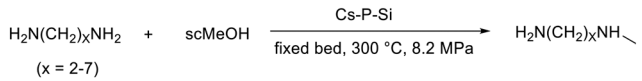


Scheme 25 Cs–P–Si catalyzed *N*-monomethylation of diamines with supercritical methanol.

to be responsible for *N*-methylation of aniline.[54] The conversion of aniline between 10 and 20% and a *N*-methylaniline selectivity higher than 70% were achieved when using Al-MCM-41 as catalyst.

In 2013, an important breakthrough for the selective *N*-monomethylation of 2-(pyridin-2-yl)ethanamine with an air- and moisture-stable $NiCuFeO_x$ catalyst was achieved by Shi and co-workers.[55] *N*-methyl-2-(pyridin-2-yl)-ethanamine could be synthesized that was used as a drug for Meniere's disease and vertigo, and 79% yield could be obtained at the temperature of the xylene reflux. TEM characterization showed that the catalyst was composed of nanoparticles with a size of 20 to 30 nm (Fig. 3) and the morphology and crystal lattices of the catalyst were maintained before and after use. Furthermore, the catalyst could be recycled 5 times without obvious deactivation.

In 2017, Tu's group prepared *N*-heterocyclic carbene iridium (NHC–Ir) coordination assemblies as highly efficient solid molecular catalysts for *N*-monomethylation of aromatic primary amine.[56] In the presence of 1 equiv. KO^{t}Bu, 72–99% yields of the corresponding *N*-monomethylated products containing competitive groups including olefins, ketones, nitriles, free hydroxyls and bioactive molecules with up to 2.0 × 10^4 turnover numbers (TON) could be obtained at 130 °C

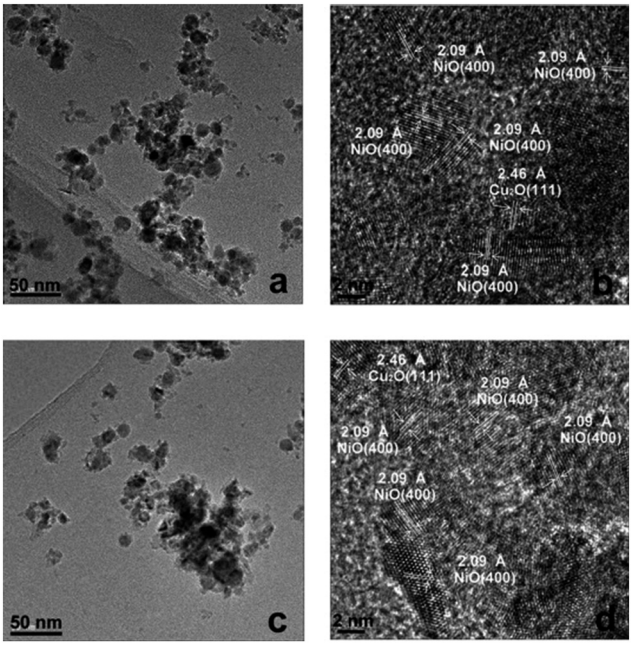
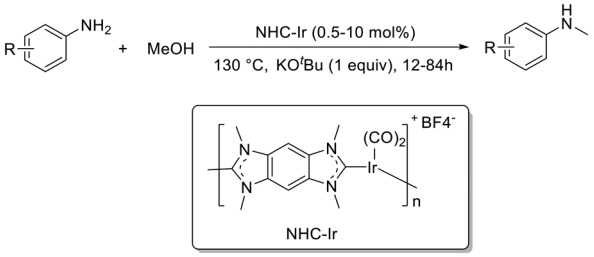


Fig. 3 TEM and HR-TEM images of $NiCuFeO_x$ a and b) before and c and d) after use[55] (copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).



Scheme 26 NHC–Ir catalyzed *N*-monomethylation of aromatic primary amine with methanol.

(Scheme 26). Moreover, the catalyst could be reused up to 23 times.

At the same time, Obora and co-workers reported *N*-monomethylation of methanol and anilines catalyzed by DMF-stabilized Ir nanoclusters (NCs).[57] In the presence of 0.5 equivalent of Cs_2CO_3, aniline, *p*-toluidine and *p*-chloroaniline could produce the corresponding *N*-monomethylated products with yields of 78%, 80% and 87% at 150 °C, respectively. Importantly, a high TON of 310 000 was achieved for the *N*-monomethylation of aniline when the catalyst loading was reduced. The diameters of the NCs were about 1–1.5 nm (Fig. 4) by high resolution transmission electron microscopy (HR-TEM). In addition, ^{1}H-NMR, TG-DTA, and FT-IR results indicated that DMF molecules protected the surface of the Ir NCs.

Later, another kind of iridium nanoparticles encapsulated within yolk–shell-structured mesoporous carbon nanospheres (Ir@YSMCNs) exhibited good efficiency for the *N*-monomethylation of aromatic primary amine.[58] Seven different primary aromatic amines could be converted into corresponding products in 74–95% yields at 170 °C in the presence of 1 equivalent of KO^{t}Bu base. Moreover, the catalyst could be reused for 3 times without any activity loss. XRD and TEM indicated that Ir was highly dispersed and had good thermal stability, and there was no significant difference in morphology between fresh catalyst and recycled catalyst (Fig. 5).

In 2019, Shimizu and Siddiki *et al.* prepared Pt/C by wet impregnation method and realized *N*-monomethylation of aliphatic amines under 4 MPa H_2 and *N*-monomethylation of

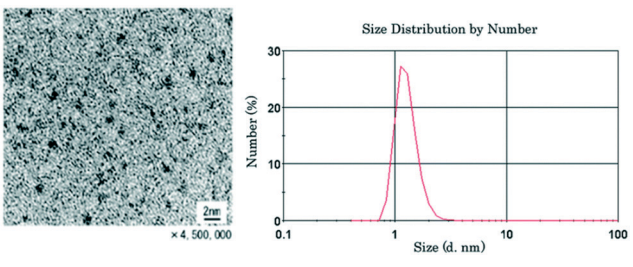


Fig. 4 Left: Transmission electron microscopy image of DMF-stabilized Ir nanoclusters (NCs). Bar length: 2 nm. Right: Dynamic light scattering spectrum of Ir NCs[57] (copyright 2017 Royal Society of Chemistry).

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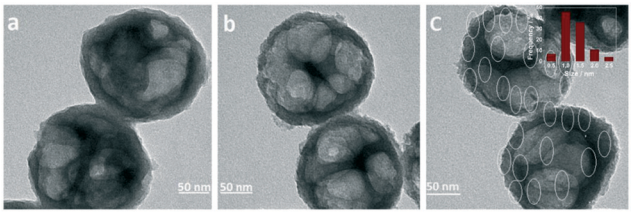
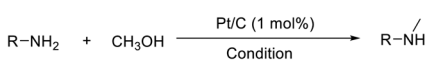


Fig. 5 TEM images of Ir@YSMCNs, a) fresh catalyst; b) catalyst for 2th run; c) catalyst for 4th run[58] (copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim).

aromatic amines under N_2 atmosphere (Scheme 27) in good to excellent yields for the first time.[59] This catalyst could be reused 4 times and applied to dimethylation of aliphatic amines. Further kinetic results combined with density functional theory (DFT) calculations showed that the moderate metal–hydrogen bond strength of Pt led to high catalytic performance of Pt/C.

At the same time, commercial Pd/C was also used for selective *N*-monomethylation of aniline derivatives with methanol.[60,61] Hou's group systematically studied the *N*-monomethylation reaction and 58–92% yields of *N*-monomethylated aromatic amines could be obtained with the presence of 2 equiv. CH_3ONa at 150 °C. Furthermore, Pd/C could be easily recovered and reused more than five times with a slight decrease in activity and 4 examples of gram-scale experiments were also successfully performed.

However, heterogeneous catalysts catalyzed *N*-monomethylation often required high temperature and a large amount of base. It is urgent to find a catalytic system with low pressure, low temperature and no other environment-friendly additives. Recently, the utilization of CH_3OH for photocatalytic *N*-monomethylation was reported for the first time.[62] Zhang and Wang's group prepared Pd nanoparticle loaded CN (carbon nitride) based Mott–Schottky catalysts through a facile conventional wet impregnation method. Pd-3@CN (3 represents the original mass ratio of metal species to the CN substrate) exhibited good catalytic performance and the yield of *N*-monomethylated products was as high as 77% at 55 °C. The optimized Pd-3@CN also showed good selectivity and stable conversion efficiency after recycling 4 times. Transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) observations confirmed that Pd nanoparticles were evenly dispersed on carbon nitride with an average diameter of 4–6 nm (Fig. 6). Although the yield and selectivity of *N*-monomethylation reported this time were low, it provided a possible low-temperature and high-selectivity synthesis method in the future.



R = aliphatic; Condition 1: 130 °C, NaOH (1 equiv), H_2 (4 MPa), 24-36h; Yield: 74-86%

R = aromatic; Condition 2: 140 °C, NaOH (0.1 equiv), N_2 (0.1 MPa),15h; Yield: 81-98%

Scheme 27 Pt/C catalyzed *N*-monomethylation of primary amine with methanol.

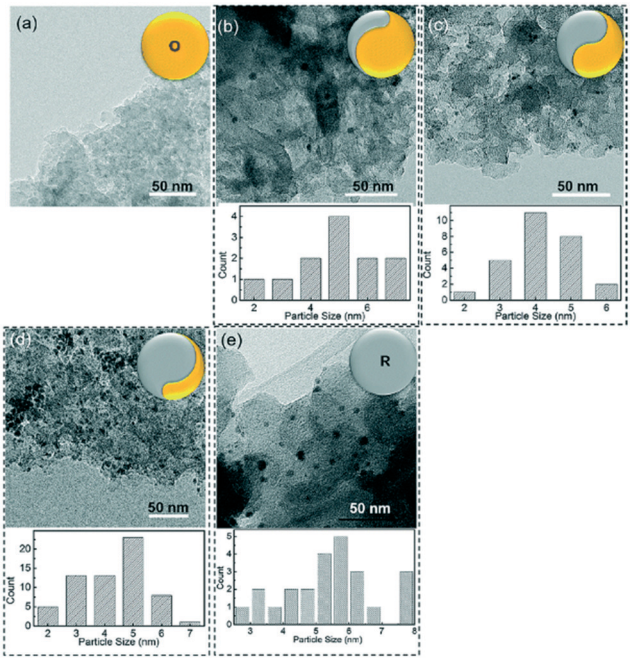
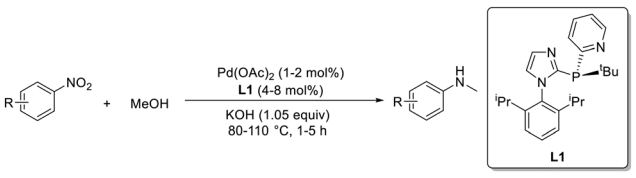


Fig. 6 TEM images of pristine CN (a), Pd-1@CN (b), Pd-3@CN (c), Pd-9@CN (d) and Pd-3@C (e) respectively[62] (copyright 2020 Royal Society of Chemistry).

2.3.3 *N*-Monomethylation of nitro compounds with methanol. Beller's group developed the first palladium-catalyzed *N*-monomethylation of nitroarenes with methanol (Scheme 28).[63] A novel bifunctional ligands L1 was synthesized, which combined the advantages of N atom of the pyridyl ring that cooperative action between the metal center and the nitrogen atom of the ligand enabled the (de) hydrogenation process, and state-of-the-art sterically hindered (hetero)arylphosphines for C–N bond formation. 54–87% yields of corresponding products could be obtained and this methodology could be easily combined with further functionalizations using the same catalyst.

At the same time, it was found that the API (amino-pyridine-imino) ligand can enable ruthenium catalyzed efficiently one-pot *N*-monomethylation of nitroarenes with methanol to produce *N*-monomethylated amines (Scheme 29).[64] Yang *et al.* expanded the reaction substrates to broad-spectrum nitroarenes in 45–88% yields, including pharmaceutically relevant nitro compounds with good tolerance to a set of functional groups. Mechanism studies showed that methanol was served as both a hydrogen source and a methylating agent.



Scheme 28 Pd-Catalyzed *N*-monomethylation of nitroarene with methanol.

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Scheme 29 Ru-Catalyzed *N*-monomethylation of nitroarene with methanol.

In 2020, compound $[IrBr(CO)_2(\kappa C\text{-}^tBuImCH_2PyCH_2OMe)]$ featuring a flexible pyridine/OMe functionalized NHC ligand κ^1C coordinated was prepared for *N*-monomethylation of nitroarene with methanol.[65] 12 examples of nitroarenes could be efficiently *N*-monomethylated to afford their corresponding *N*-monomethyl amines in high yields with good tolerance of various functional groups including heterocyclic or sterically hindered derivatives (Scheme 30). Mechanism involving nitrosobenzene and *N*-phenylhydroxylamine intermediates was proposed. Morrill's group simultaneously reported a well-defined bench stable Mn PN^3P pincer precatalyst based upon an earth-abundant first row transition metal for the one-pot conversion of nitroarenes into *N*-methylarylamines.[66] In the presence of 2 equivalent of KOH, 25–83% yields of *N*-monomethylamines can be obtained at 110 °C.

At the same time, Tu and Xu's group synthesized a series of *N*-heterocyclic carbene–iridium (NHC–Ir) coordination assemblies based on bispyrenoimidazolium salts as efficient solid molecular catalysts in selective mono-*N*-methylation of nitroarenes with methanol.[67] In the presence of 1 equivalent of KO^{t}Bu, a broad substrate scope of nitroarenes could be efficiently *N*-monomethylated to afford their corresponding *N*-monomethyl amines in 48–99% yields with good tolerance of various functional groups at 130 °C. Moreover, DFT calculations disclosed a redox neutral Ir(I)/Ir(I) process with a synergetic participation of the solvated base in support of the observed robustness, reusability, but extremely high catalytic activity of the catalytic system (Fig. 7). What's more, the robust NHC–Ir assemblies were found to be readily recovered and reused for more than 10 runs without loss of their catalytic activity and selectivity. Liu and co-workers achieved a continuous mode of selective *N*-methylations of nitroarenes with methanol under the exogenous base-free condition.[68] By simply changing the reaction conditions, Cu/Al_2O_3 catalyzed *N*-monomethylation can obtain the corresponding product with yields of 72–89%. Characterization displayed that the surface enrichment and high dispersion of metal Cu, and the well-developed pore system of the catalyst were responsible for the high performance.

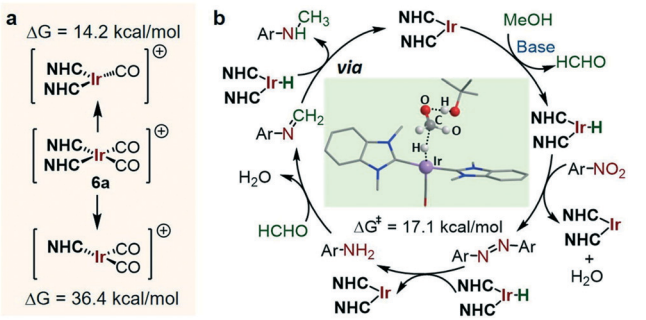


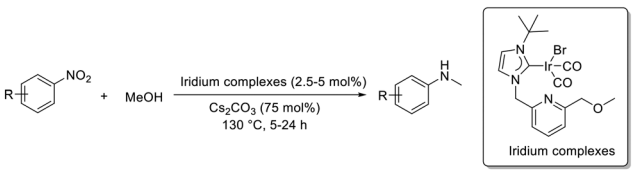
Fig. 7 (a) The DFT calculated free energy changes for the ligand detachment from NHC–Ir complex. (b) Proposed reaction mechanism. The DFT calculated value for dehydrogenation transition state represents the relative free energy with respect to NHC–Ir complex and methanol[67] (copyright 2020 Elsevier).

Recently, Natte and co-workers demonstrated the use of $RuCl_3{\cdot}xH_2O$ as a ligand-free catalyst for selective *N*-monomethylation of amines and nitroarenes with methanol (Scheme 31).[69] In the presence of KO^{t}Bu, 19–94% yields of *N*-monomethylamines can be synthesized when aliphatic/aromatic amines were used as substrates. In addition, 5 examples of nitroarenes can be directly one pot converted into the corresponding products in 26–82% yields. However, the direct *N*-monomethylation of aliphatic nitro compounds has still been a challenge so far.

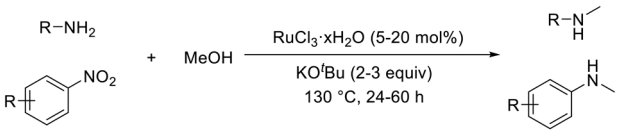
2.4 HCHO as methylating agent

As a priority indoor pollutant, formaldehyde has a wide range of sources. Long-term exposure to formaldehyde gas can cause allergenic, teratogenic, and carcinogenic effects, and seriously threaten people's lives.[70] Therefore, the removal of formaldehyde in an efficient and non-toxic way has become an urgent problem to be solved. The reductive amination using formaldehyde in the presence of a suitable reductant (Eschweiler–Clarke methylation) prevails in the industrial production of *N*-methyl amines. In particular, the conversion of formaldehyde into high value-added chemicals through catalytic chemistry has attracted widespread attention.

In 2007, Rhee and co-workers illustrated *N*-monomethylation of aniline with formaldehyde for the first time.[71] 0.1 equivalent Pd/C catalyst in aqueous 2-propanol solvent with ammonium formate as *in situ* hydrogen donor was used, and 45% yield of *N*-methylaniline could be



Scheme 30 Ru-Catalyzed *N*-monomethylation of nitroarene with methanol.



Scheme 31 Ru-Catalyzed *N*-monomethylation of amines and nitroarenes with methanol.

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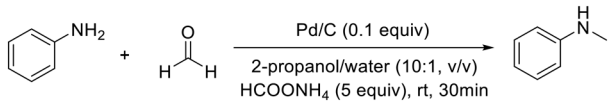
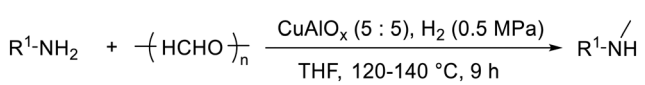


Scheme 32 Pd/C catalyzed *N*-monomethylation of primary amine with HCHO.

obtained at room temperature (Scheme 32). Later, Lemaire and Métay reported a similar catalytic system and broaden the scope of substrates.[72] In the presence of calcium hydride (60 mol%) as a source of hydrogen and Pd/C (2 mol%) as catalyst, various substrates including cyclohexylamine can be converted into *N*-monomethylamines and obtained with up to 91% yield.

However, the employment of $HCOONH_4$ and CaH_2 as reductants reduced the possibility of industrial applications. In order to significantly increase the appeal of this method in industrial applications. Shi's group described the selective synthesis of *N*-monomethyl amines with paraformaldehyde and H_2 in the presence of a simple $CuAlO_x$ catalyst for the first time.[73] A variety of amines, including primary aromatic amines, benzylamine and cyclohexylamine, as well as secondary amines, have been shown to be compatible with this reaction (Scheme 33). Furthermore, this catalyst can be reused 3 times. A series of characterizations showed that only a small amount of CuO_x was formed in $CuAlO_x$ (5 : 5), and the main copper species was metallic copper that might be the active species for this reaction.

Later, they developed one-pot *N*-monomethylation reactions using nitro compounds for the first time.[74] In the presence of Pd/TiO_2 catalyst, the synthesis of *N*-monomethylamine was controlled by kinetic inhibition of *N*,*N*-dimethylation *via* nondominant adsorption and easy desorption of *N*-monomethylamine on the catalyst surface (Fig. 8). NH_3/Me_2NH-TPD showed that the superior selectivity should be attributed to the preferential adsorption of the primary amine over *N*-monomethylamine on the Pd/TiO_2 surface. NH_3-TPD and H_2-TPR tests indicated the good H_2 activation ability and high amine adsorbing capacity of the catalyst, which might lead to excellent catalytic activity. A variety of nitroarenes containing methyl, methoxyl, hydroxyl, fluoride, trifluoromethyl, ester, and amide substituents were applicable to this reductive *N*-monomethylation, providing the corresponding products in 64–93% yields with a mono : di ratio of 16 : 1 to 72 : 1. Furthermore, the potential synthetic utility of this protocol in pharmaceutical was illustrated by *N*-monomethylation of drug molecules, such as cilnidipine, nimesulide, procaine, and methyl aminosalicylate. This work offers a straightforward, step economic, and clean



Scheme 33 $CuAlO_x$ catalyzed *N*-monomethylation of primary amine with paraformaldehyde and H_2.

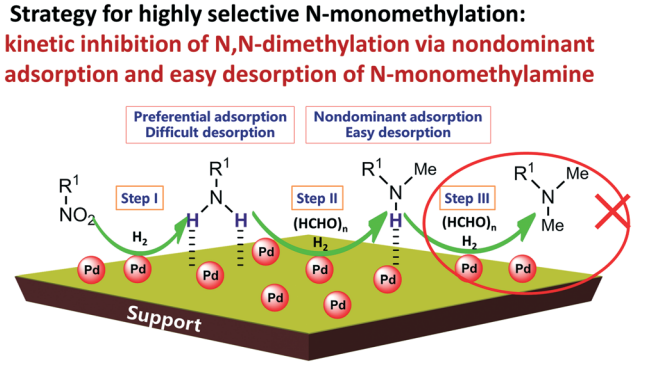


Fig. 8 Strategy for highly selective *N*-monomethylation of nitroarenes with $HCHO/H_2$ (ref. 74) (copyright 2018 American Chemical Society).

methodology for the selective synthesis of *N*-monomethylamines.

2.5 HCOOH as methylating agent

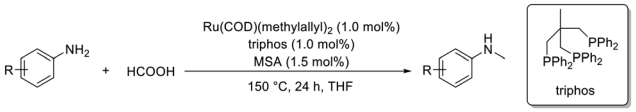
Formic acid (FA) is non-corrosive, nontoxic, and a single-carbon carboxylic acid that is produced industrially through several routes from methanol.[75] Therefore, using HCOOH as a unique carbon and hydrogen source for the methylation of amines is green and environmentally friendly.[76,77]

In 2014, Cantat and co-workers reported the first example of *N*-monomethylation of primary amines with HCOOH.[78] In the presence of 1.0 mol% $Ru(COD)(methylallyl)_2$, 1.0 mol% triphos and 1.5 mol% MSA (methanesulfonic acid), 11 kinds of substrates can be converted into *N*-monomethylamines and obtained with up to 71% yield (Scheme 34). In addition, the computed (DFT) pathways indicated that the methylation of the N–H bond with HCOOH involves the formation of a formamide intermediate which is reduced to an iminium species, prior to its reduction to a $N–CH_3$ group. However, there are few examples of formic acid directly used as *N*-monomethylation. Therefore, there is huge room for development of homogeneous and heterogeneous catalysts.

2.6 DMC as methylating agent

Dimethyl carbonate (DMC) has been demonstrated an ideal vector of both CO_2 and the methyl function, it is also an environmentally sustainable compound and an inexpensive and green methylating reagent that is commonly utilized in the methylation of carboxylic acids, arylacetonitriles, phenols, indoles, and benzimidazoles.[79]

As early as 1987, Tundo and co-workers reported that *N*-monomethylation of aniline with dimethyl carbonate (DMC) gave a 60.5% of *N*-methylaniline at 91.4% aniline



Scheme 34 Ru catalyzed *N*-monomethylation of primary amine with formic acid.

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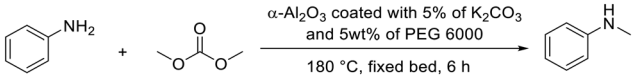
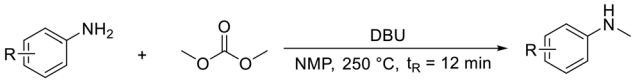


Scheme 35 *N*-Monomethylation of aniline with dimethyl carbonate.

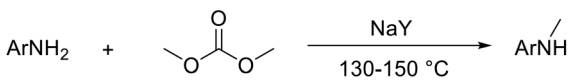


Scheme 37 *N*-Monomethylation of aromatic amines with dimethyl carbonate under continuous flow conditions.

conversion (DMC/aniline = 10), using α-Al_2O_3 coated with 5% of K_2CO_3 and 5 wt% of polyethylene glycol (PEG 6000) as the catalyst (Scheme 35).[80] Later, Ono and Fu studied the *N*-monomethylation of aniline with dimethyl carbonate over alkali cation exchanged zeolites.[81] When KY was used as the catalyst at 180 °C, the conversion of aniline was 99.6%, and the selectivity of *N*-methyl aniline was 93.5%. However, they all required high energy and temperature.

In 1997, Selva's group investigated Y- and X-type zeolites catalyzed the reaction of dimethyl carbonate (DMC) with different primary aromatic amines under batch conditions (autoclave).[82] The corresponding mono-*N*-methyl derivatives [$ArNH(CH_3)$] in 66–84% yields could be obtained even when they are deactivated by either electronic effects or steric hindrance (Scheme 36). The unusual mono-*N*-alkyl selectivity observed was likely to be attributable to a synergic effect between the double reactivity of DMC (acting both as a methylating and as a reversible methoxycarbonylating agent) and the dual acid–base properties of zeolite. Furthermore, the reaction mechanism involving carbamates ($ArNHCO_2CH_3$) and *N*-methylcarbamates [$ArN(CH_3)CO_2CH_3$] as intermediates was proposed. Later, they found the mono-*N*-alkyl selectivity is independent of concentration and polarity factors in the presence of triglyme as a solvent.[83] In addition, the mono-*N*-methyl selectivity was explained by the adsorption pattern of reagents within the zeolite pores: a $B_{Al}2$ displacement of the amine on methyl alkyl carbonate should occur aided by the geometric features of the NaY supercavities.[84]

However, *N*-monomethylation of aromatic amines with dimethyl carbonate catalyzed by zeolite all required DMC in solvent quantities, and the heating temperature need to exceed the boiling point of DMC (b.p. = 90 °C) and produced the stoichiometric amount of CO_2. Jamison and co-workers achieved selective *N*-monomethylation of anilines under continuous flow conditions in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU).[85] Both electron-rich and electron-deficient anilines could be tolerated and produce an intermediate in the synthesis of diazepam in good yields (Scheme 37). However, the *N*-monomethylation of aliphatic amines with DMC is still a huge challenge at present, and this problem needs to be solved in the future.



Ar = *p*-$O_2NC_6H_4$, *p*-NCC_6H_4, *o*-$CH_3O_2CC_6H_4$, 2,6-$(CH_3)_2C_6H_3$

Scheme 36 NaY catalyzed *N*-monomethylation of aromatic amines with dimethyl carbonate.

3. Summary and outlook

This account has provided a brief survey of work in the sustainable synthesis of *N*-monomethyl amines by reaction of primary amines or nitro compounds with MeX, CO_2, methanol, HCHO, HCOOH and dimethyl carbonate (DMC). A series of homogeneous catalysts and heterogeneous catalysts have been successfully developed for selective *N*-monomethylation of primary amines and nitro compounds and good to excellent catalytic activity and selectivity have been obtained. In order to facilitate readers to read and compare the performance of each catalyst, we finally summarized the catalytic performance for selective *N*-monomethylation of primary amines with different catalysts, as shown in Tables 1 and 2.

Although remarkable advances have been achieved in sustainable catalytic synthesis of primary amines, there is still a significant amount of work to be done in this field. Firstly, *N*-monomethylation of primary aliphatic amines remains a challenging work. Thus, it is desired to develop highly efficient catalyst system for *N*-monomethylation of primary aliphatic amines. Furthermore, it is found that Ru homogeneous catalysts and methanol reagents have been studied a lot, but a large number of reports are lacking on non-noble metal catalysts such as Fe and Mn. Therefore, it is urgent to develop non-noble metal catalyst systems to achieve highly selective *N*-monomethylation of primary amines. Secondly, the design and preparation of efficient heterogeneous catalytic materials will be the hotspot of *N*-monomethylation in the future. For example, the bimetallic catalysts can be extensively studied to investigate the synergistic and inhibitory effects of metals on different supports. In addition, single-atom catalysts acted by 100% utilization of active sites could obtain superior activity even comparable to the homogeneous analogues, which can also be used to achieve *N*-monomethylation reactions.[86] Moreover, fabrication of catalytic materials that mergers the advantages of homogeneous catalysis with defined active sites, excellent activity, and selectivity and heterogeneous catalysis with facile recyclability will provide new opportunities for *N*-monomethylation of primary amines and nitro compounds.[87] Finally, much more effort should be directed to explore the origin of the structure–performance relationship, and reaction mechanism of *N*-monomethylation by *in situ* characterization techniques and theoretical calculations should be strengthened, which would benefit the judicious design and synthesis of catalysts with desired properties suitable for practical applications. We sincerely hope that this review can help researchers in the fields of

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Table 1 Summary of catalysts for selective *N*-monomethylation of primary amines with CH_3OH

Catalysts	Reaction conditions	*T* (°C)	Yield (%)	Year[ref.]
$RuCl_3{\cdot}xH_2O$	KO^{t}Bu (2–3 equiv.), 24–60 h	130	19–94	2021 (ref. 69)
Bis-NHC–Ir	KO^{t}Bu (1 equiv.), 4 h	130	56–99	2020 (ref. 42)
$[(Cp^*IrCl)_2(thbpym)][Cl]_2$	KOH (1 equiv.), 12 h	130	77–94	2020 (ref. 37)
Pd-3@CN	H_2 (1 bar), hγ, 4–36 h	55	0–77	2020 (ref. 62)
Pd/C	CH_3ONa (2 equiv.), 12–18 h	150	58–92	2019 (ref. 60)
Pd/C	KO^{t}Bu (2 equiv.), 12–30 h	130	91–98	2019 (ref. 61)
Pt/C	NaOH (0.1 equiv.), 15 h; H_2 (4 MPa), NaOH (1 equiv.), 36 h	130–140	81–98	2019 (ref. 59)
$^{ABO}N,C_{(Carbene)}$–Ir(III)	KO^{t}Bu (1 equiv.), 12–24 h	130	64–99	2019 (ref. 41)
Ir@YSMCNs	KO^{t}Bu (1 equiv.), 24–72 h	170	74–95	2019 (ref. 58)
Cp–Fe(0)	Me_3NO, K_2CO_3 (2 equiv.), 24–96 h	80	54–95	2018 (ref. 49)
$[Re(CO)_3(PN^HP)]Br$	Cs_2CO_3 (5–10 mol%), 48 h	140	0–95	2018 (ref. 43)
$RuHCl(CO)(PN^HP)$	KO^{t}Bu (20–100 mol%), 5–16 h	150	13–100	2018 (ref. 33)
NNN–Ru(II)	NaOMe (1 equiv.), 24 h	110	74–86	2018 (ref. 32)
Cp–Fe(0)	CsOH (10 mol%), 16 h	110	58–99	2018 (ref. 48)
$[Cp^*Ir\text{-}(HOC_5H_3CH_2C_5H_3OH)Cl][Cl]$	K_2CO_3 (0.3 equiv.), 12 h	120	62–94	2018 (ref. 40)
Ru-MACHO-BH	H_2 (4 MPa), 24 h	120	34–99	2018 (ref. 34)
Ru^{II} NNN pincer	NaOMe (1 equiv.), 12 h	110	71–100	2017 (ref. 31)
Ir NCs	Cs_2CO_3 (0.5 equiv.), 24 h	150	78–87	2017 (ref. 57)
$[Mn(PNP^{iPr})(CO)_2Br]$	KO^{t}Bu (0.5 equiv.), 16 h	100	51–95	2017 (ref. 45)
$Co(acac)_2$, PPh_3	K_3PO_4 (1 equiv.), 24 h	140	82–95	2017 (ref. 47)
$[Cp^*Ir(BiBzImH_2)Cl][Cl]$	Cs_2CO_3 (0.3 equiv.), 12 h	120	78–96	2017 (ref. 36)
NHC–Ir	KO^{t}Bu (1 equiv.), 12–84 h	130	72–99	2017 (ref. 56)
PN^3P-Mn	KO^{t}Bu (20 mol%), toluene, 24 h	120	0–98	2017 (ref. 46)
Mn–PNP	KO^{t}Bu (1 equiv.), 24 h	100	52–94	2016 (ref. 44)
$[RuCp^*Cl_2]_2$/dpePhos	LiO^{t}Bu (5 mol%), 24 h	100	73–98	2015 (ref. 30)
$Ir(NHC)_2$	KOH (1–5 equiv.), MW, 5 h	120	0–95	2015 (ref. 39)
$NiCuFeO_x$	Xylene, 24 h	Reflux (137)	79	2013 (ref. 55)
$[((5\text{-Me})PyNPPh_2)Ir(cod)]$	KO^{t}Bu (1.1–2.2 equiv.), diglyme, 24–48 h	70	80–97	2012 (ref. 38)
$[Cp^*IrCl_2]_2$	NaOH (1 equiv.), 12 h	150	71–97	2012 (ref. 35)
$[(PPh_3)_2Ru(CH_3CN)_3Cl][BPh_4]$	K_2CO_3 (1 equiv.), 10 h	Reflux (65)	69–76	2007 (ref. 29)
Al-MCM-41	Fixed-bed	300	13	2007 (ref. 54)
Cs–P–Si	Fixed-bed, 8.2 MPa	300	20–58	2004 (ref. 52, 53)
$Zn_{0.8}Co_{0.2}Fe_2O_4$	Fixed-bed	350	72	2000 (ref. 51)
$ZnFe_2O_4$	Fixed-bed	350	67	1999 (ref. 50)
$RhH(PPh_3)_4$	8–72 h	≤100	39–99	1981 (ref. 28)

Table 2 Summary of catalysts for selective *N*-monomethylation of primary amines with other methylation reagents

Catalysts	Methylation reagents	Reaction conditions	*T* (°C)	Yield (%)	Year[ref.]
None	MeOTf	Hexafluoroisopropanol, 1 h	rt	52–96	2014 (ref. 18)
Tiiii	MeI	5 h	25–45	64–87	2009 (ref. 17)
$[bmim][PF_6]$	MeI	0.5–360 min	0–90	29–60	2006 (ref. 16)
$Pd/CuZrO_x$	CO_2 (1 MPa)	Octane, H_2 (2.5 MPa), 30 h	150	49–79	2014 (ref. 23)
$CuAlO_x$	CO_2 (3 MPa)	Hexane, H_2 (6–7 MPa), 24–48 h	160	43–86	2014 (ref. 24)
$Ru(acac)_3$	CO_2 (2 MPa)	THF, H_2 (6 MPa), triphos, methanesulfonic acid, 5 h	140	13–90	2013 (ref. 22)
$IPrZnCl_2$	CO_2 (1 bar)	$PhSiH_3$ (2 equiv.), 20 h	100	0–67	2013 (ref. 21)
Pd/TiO_2	HCHO	1,4-Dioxane, H_2 (1 MPa), 24 h	60	64–95	2018 (ref. 74)
$CuAlO_x$	HCHO	THF, H_2 (0.5 MPa), 9 h	120–140	61–89	2017 (ref. 73)
Pd/C	HCHO	Toluene, CaH_2 (60 mol%), 16 h	30	0–91	2016 (ref. 72)
Pd/C	HCHO	2-Propanol/water (10 : 1, v/v), $HCOONH_4$ (5 equiv.), 30 min	rt	45	2007 (ref. 71)
$Ru(COD)(methylallyl)_2$	HCOOH	THF, triphos, methanesulfonic acid, 24 h	150	13–71	2014 (ref. 78)
DBU	DMC	NMP, t_R = 12 min	250	19–79	2018 (ref. 85)
NaY	DMC/MEC	Xylene/diglylene, 6–4680 min	90–150	43–100	2005 (ref. 84)
NaY	DMC	Triglyme, 90–660 min	130–160	68–94	2001 (ref. 83)
NaY	DMC	150–420 min	150	66–84	1997 (ref. 82)
KY	DMC	Fixed-bed	180	93	1993 (ref. 81)
α-Alumina coated with 5% of K_2CO_3 and 5 wt% of PEG 6000	DMC	Fixed-bed	180	60.5	1987 (ref. 80)

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organic synthesis, catalysis, medicinal and biological chemistry, and play a positive role in the study of *N*-monomethylation.

Conflicts of interest

There are no conflicts to declare.

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