RECENT PROGRESS IN THE MODIFICATION OF HETEROCYCLES BASED ON THE TRANSFORMATION OF DMSO

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Abstract. *Dimethyl sulfoxide has been widely used in organic synthesis as carbon source, sulfur source, oxygen source as well as oxidant and solvent. Recently, a large number of impressive methodologies for constructing highly functionalized heterocycles have been developed on the basis of transforming DMSO. This chapter summarized selected recent achievements covering from 2012 to 2022 on the preparation of heterocyclic compounds through DMSO-based heterocycle modification.*

Contents

1. Introduction
2. DMSO as source of CH
3. DMSO as source of CH_2
4. DMSO as source of CH_3
5. DMSO as source of SCH_3
6. DMSO as source of CH_2SCH_3
7. DMSO as source of $SOCH_3$
8. DMSO as source of CHO
9. DMSO as oxidant
10. Halogenation
11. Conclusion
Acknowledgement
References

1. Introduction

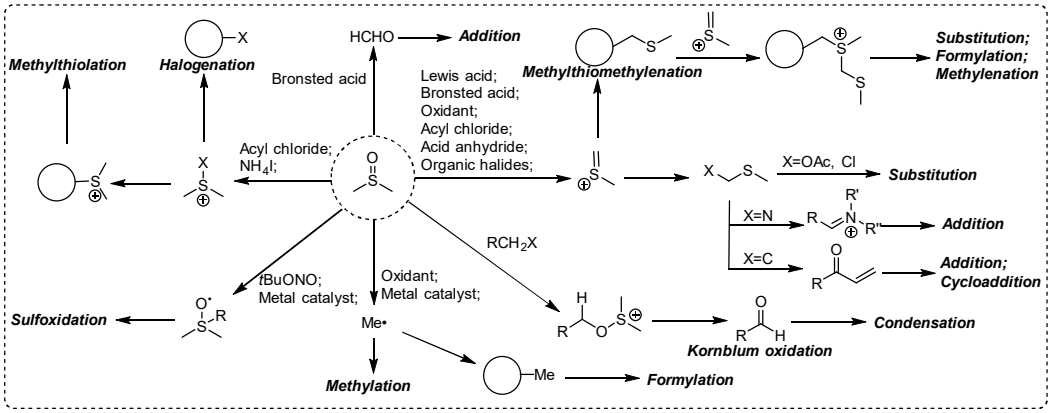
DMSO has been playing versatile roles in organic synthesis, as DMSO may act as carbon source, sulfur source, and oxygen source as well as solvent and oxidant for forming C–C and C–X bonds.[1-4] A series of functional groups can be introduced into the target molecules by the transformation of DMSO, including CH, CH_2, CH_3, SCH_3, CH_2SCH_3, $SOCH_3$ and CHO. Besides, DMSO is also a useful oxidant in a range of chemical transformations, and especially essential for the halogenation of various heteroarenes.

The direct modification of heterocycles is an alternative way for preparing functionalized heterocyclic compounds. Particularly, late-stage modification of natural products, drugs, privileged framework-containing molecules, and peptides is an easy and rapid method for generating complex and interesting molecules with potential applications.[5] DMSO-based organic transformations enable the efficient introduction of a variety of functional groups into the heterocycles. A vast number of choices for activating DMSO, such as Lewis acids, Bronsted acids, oxidants, organic halides, acid chlorides, acid anhydrides, *etc,* providing various active species for distinct conversions (Scheme 1).

The unique properties of DMSO have been highlighted in several pioneering oxidation reactions together with different activators, including Moffatt oxidation (DCC/HX/DMSO)[6], Parikn-Doering oxidation (SO_3/DMSO)[7], Swern oxidation (ClCOCOCl/DMSO)[8] and Kornblum oxidation[9]. Some other robust and practical DMSO-based reaction systems have also been frequently used such as HBr/DMSO and I_2/DMSO. Moreover, plenty of functional groups can be easily and selectively introduced, regardless of the single role or multiple roles that DMSO may have displayed in these reaction systems. Therefore, the DMSO-based heterocycle modification is definitely an attractive way for the construction of structurally diverse heterocyclic compounds.

In recent years, a large number of elegant methodologies have been reported focusing on the synthesis of heterocycles based on the utilization of DMSO. Therefore, in this regard, several impressive reviews have been published summarizing these achievements. The groups of Wu and Magolan have systematically

reviewed and discussed the organic reactions using DMSO as a synthon independently in 2016.[1-2] Later, the Mahdavi group classified the reactions using DMSO as a reagent coherently.[3] Maulide and co-workers have also well documented the unique chemistry of sulfoxides in their review.[4] Since increasing numbers of DMSO-based protocols with high efficiency have been reported, there is a great need to summarize recent achievements in the research field of heterocycle synthesis through DMSO-based modification pathways.



Scheme 1. Active species generated from DMSO for heterocycle modifications.

According to the role of DMSO in these organic reactions, this chapter is further subdivided to several sections including DMSO as the source of CH, DMSO as the source of CH_2, DMSO as the source of CH_3, DMSO as the source of SCH_3, DMSO as the source of CH_2SCH_3, DMSO as the source of $SOCH_3$, DMSO as the source of CHO, DMSO as the oxidant and halogenation. It should be noted that the DMSO-based direct synthesis of heterocycles from acyclic starting materials will not be discussed in this review due to the limited space, although a great number of relevant achievements have been reported in the past decades.

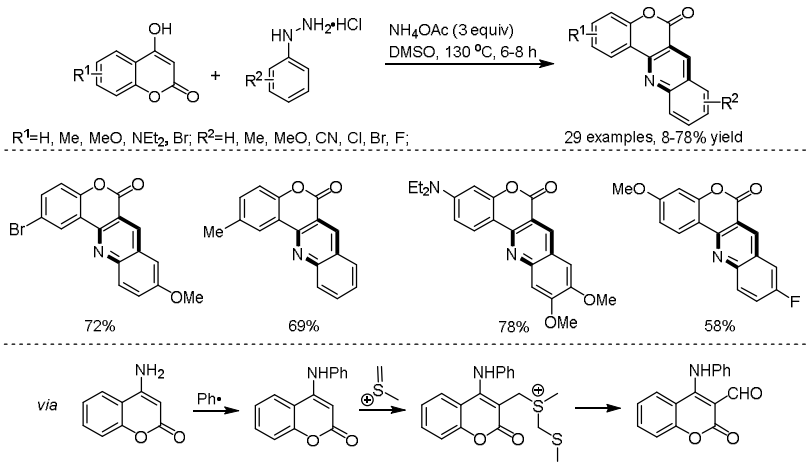
2. DMSO as source of CH

There are several reaction pathways for generating CH moiety from DMSO: through the formation of imine and a subsequent addition, through the formation of α,β-unsaturated ketones and a following cyclization, and through the *in situ* generation of aldehyde and a subsequent condensation. In general, the methine group generated from DMSO always appears in aromatic molecules and thus the incorporation of CH requires DMSO-involved generation of aromatic moieties.

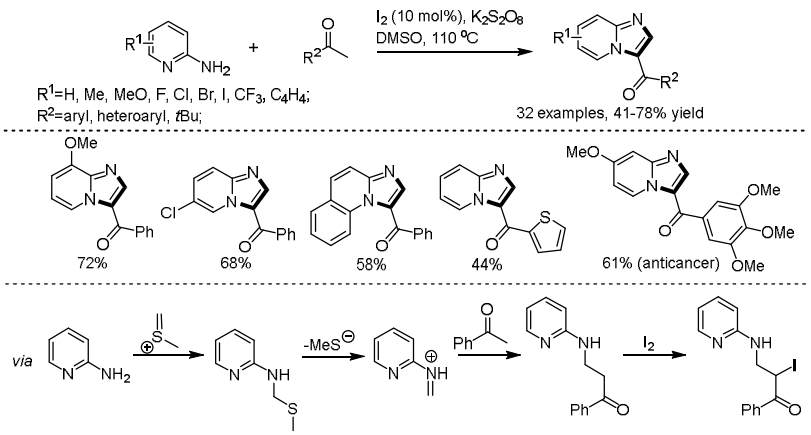
Chromene nucleus has been playing an essential role in the design of fluorescent heterocycles with great potential in medical chemistry and material chemistry. In particular, chromene-fused quinolines have been served as a key unit in biologically important natural products. The Sakhuja's group has developed an efficient NH_4OAc-mediated cascade approach for constructing 6*H*-chromeno[4,3-*b*]quinolin-6-ones with 4-hydroxycoumarins, arylhydrazine hydrochlorides in DMSO (Scheme 2, 29 examples, 8-78% yield).[10] 4-Aminophenyl coumarin has been identified as the key intermediate which was generated via aryl radical pathway. DMSO acted as the source of methine and the oxidant as well as the solvent. Various substrates can be compatible in this process affording corresponding chromeno-quinoline derivatives in moderate to good yields, except for arylhydrazine bearing electron withdrawing group such as CN group.

Imidazo[1,2-*a*]pyridines occur in a great number of pharmacologically important molecules as well as the research fields of organometallic chemistry and materials. Ma and co-workers have established a convenient iodine-catalyzed synthesis of highly functionalized imidazo[1,2-*a*]pyridine derivatives with methyl ketones and 2-amino-*N*-heterocycles by transforming DMSO (Scheme 3).[11] A series of biologically active 3-aroylimidazo[1,2-*a*]-*N*-heterocycles with diverse substituent patterns could be assembled in moderate to good yields (41-78%). $K_2S_2O_8$ served as the activator of DMSO and DMSO was employed as the source of methine. Anticancer candidate can be prepared in 61% yield by this one-pot process demonstrating its apparent efficiency and superiority compared with the reported three-step synthesis (20% totally). A plausible

methylthiomethylenation, elimination, α-C(sp^3)–H methylenation of ketones, iodination, annulation and oxidation cascade pathway was proposed by the authors.



Scheme 2. DMSO-based 6*H*-chromeno[4,3-*b*]quinolin-6-ones constructions.

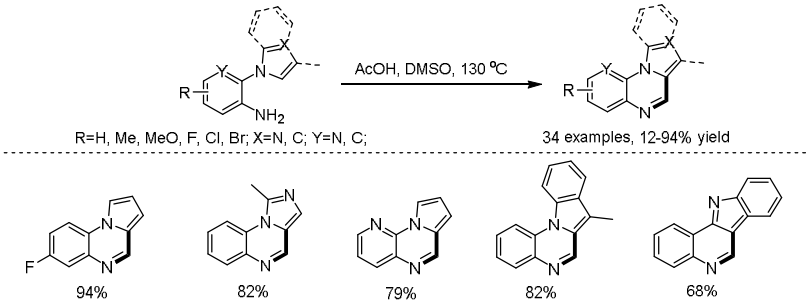


Scheme 3. Synthesis of 3-aroylimidazo[1,2-*a*]-*N*-heterocycles.

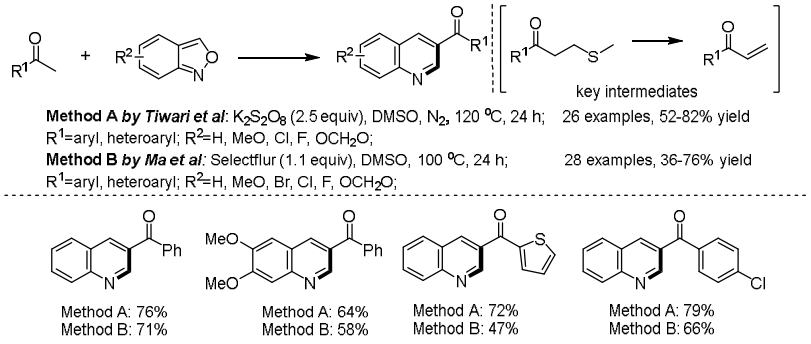
Pyrrolo[1,2-*a*]quinoxalines have shown extensive application in functional materials, pharmaceuticals and biological researches. Ma *et al.* have disclosed an efficient and green preparation of pyrrolo[1,2-*a*]quinoxalines under AcOH/DMSO reaction system (Scheme 4).[12] Other *N*-heterocycle-fused quinoxalines of interest such as indolo[1,2-*a*]quinoxalines, 1*H*-pyrrolo[3,2-*c*]quinoxalines and benzo[4,5]imidazo[1,2-*c*]quinazolines can also be readily produced under the same reaction conditions. This protocol features good functional group compatibility, environmental friendliness and high efficiency. DMSO served as the methine source and oxygen (from air) acted as the terminal oxidant.

3-Substituted quinolines have exhibited a wide range of biological activities in pharmacological and medicinal researches as well as herbicidal activity in agrochemistry. The Tiwari's group has disclosed an efficient construction of 3-substituted quinolines with readily available acetophenones and anthranils by the employment of a $K_2S_2O_8$/DMSO reaction system (Scheme 5).[13] Various aryl and heteroaryl methyl ketones could be compatible in this process. All anthranils bearing electron-withdrawing and electron-donating groups could be tolerated. Moderate to good yields were obtained in most cases (26 examples, 52-82% yields). Later,

Ma and co-workers have developed a selectfluor/DMSO reaction system for the synthesis of 3-acylquinolines with acetophenones and anthranils.[14] Selectfluor was applied as the activator of DMSO (28 examples, 36-76% yields). This process features easy availability of starting material, broad substrate generality and mild reaction conditions. In both protocols, DMSO has been used as methine source and solvent. *In situ*-generated thioether from acetophenone and α,β-unsaturated ketone formed by elimination were proposed as the key intermediates for both processes.



Scheme 4. Synthesis of pyrrolo[1,2-*a*]quinoxalines.



Scheme 5. Synthesis of 3-acylquinolines with acetophenones and anthranils.

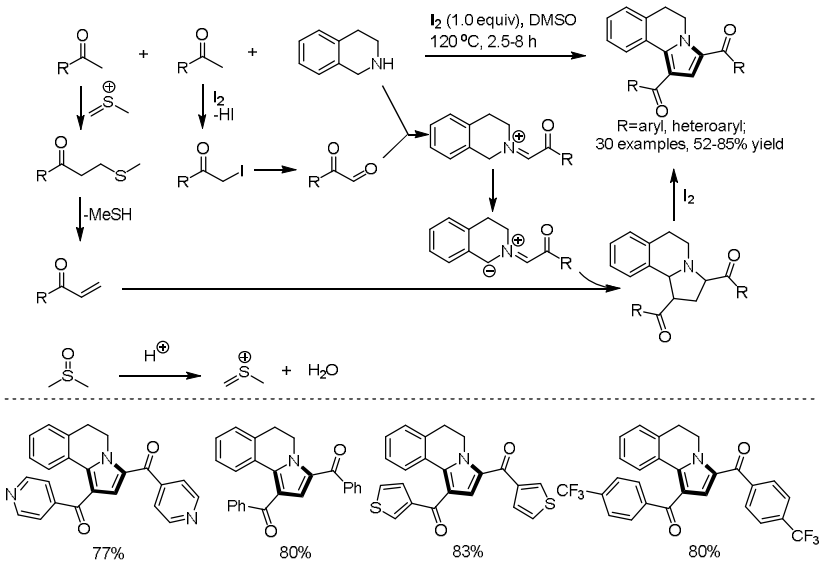
Wu and Yang have established an efficient iodine-promoted formal [2+1+1+1]-cycloaddition for constructing pyrrolo[2,1-*a*]isoquinolines with arylmethyl ketones and tetrahydroisoquinoline (Scheme 6).[15] As demonstrated by the authors, DMSO played several roles in this reaction system: source of CH, oxidant for the generation of aryl glyoxal via Kornblum oxidation, and solvent. A dipolar cycloaddition of *in situ*-generated azomethine ylide and α,β-unsaturated ketone was proposed as the key step for this cascade sequence. A wide range of substituted acetophenones can be tolerated in this process affording highly functionalized pyrrolo[2,1-*a*]isoquinolines (30 examples, 52-85% yields). Notably, heterocyclic moieties can be easily incorporated into the products, including 2-thienyl, 3-thienyl, 3-pyridyl, 4-pyridyl and 2-benzofuranyl groups.

3. DMSO as source of CH_2

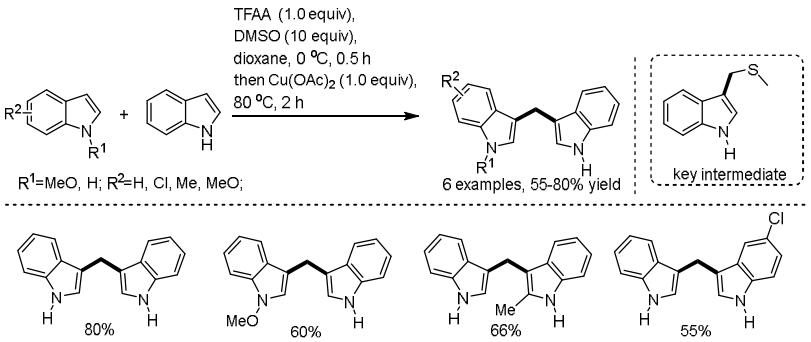
The formation of imine followed by Mannich addition and sulfonium intermediate based replacement can be regarded as two main pathways for the incorporation of CH_2 into heterocycles with DMSO. In addition, the generation of aldehyde and the following aldol addition/substitution may also be involved in the formation of methylene group.

Promising biological and pharmaceutical activities including cancer cell growth inhibition, antifungal and antibacterial activities have been identified in 3,3´-bisindolylmethanes derivatives. Ishikura and co-workers prepared 3,3´-bisindolylmethanes through a copper-mediated intermolecular Pummerer reaction.

Both symmetric and non-symmetric methylene-bridged indoles can be produced in moderate to good yields (6 examples, 55-80% yield).[16] In this process, TFAA has been used as the activator of DMSO and the methylthiomethylenation product has been proposed as a key intermediate for this transformation (Scheme 7).



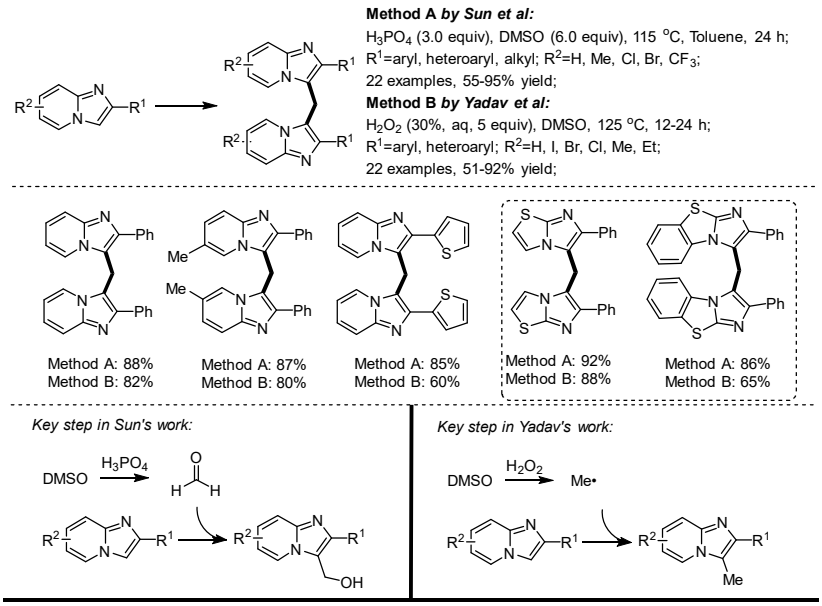
Scheme 6. Formal [2+1+1+1]-cycloaddition for constructing pyrrolo[2,1-*a*]isoquinolines.



Scheme 7. DMSO-based synthesis of bisindolylmethanes.

Since fused imidazoheterocycles have displayed frequent presence in pharmaceutically important molecules exhibiting a wide range of biological activities, the functionalization of imidazoheterocycles has attracted increasing attentions. In 2016, two independent reports for the construction of 3,3'- bisimidazopyridinylmethanes on the basis of transforming DMSO have been developed by the groups of Sun and Yadav respectively (Scheme 8).[17-18] H_3PO_4 has been used as the activator of dimethyl sulfoxide by Sun and co-workers allowing access to a series of symmetrical methylene-bridged imidazoheterocycles (22 examples, 55-95% yield).[16] On the basis of their results, the authors proposed that the reaction underwent through a cascade sequence including H_3PO_4 promoted generation of HCHO from DMSO, aldol reaction of heterocycle with HCHO and a final substitution reaction.

In Yadav's work, H_2O_2 has been applied as an activator for the methylenation of imidazo[1,2-*a*]pyridines.[18] Broad substrate scope and good yields were also reached in this process (22 examples, 51-92% yield). It is worthy noted that unsymmetrical imidazoheterocycles can also be accessed in good yields by the H_2O_2/DMSO reaction system. A radical methylation of imidazo[1,2-*a*]pyridine was proposed as the key step in this reaction by the authors, which was followed by a radical sp^3 C–H activation providing the final methylene-bridged product. Notably, both protocols can be expanded to the synthesis of methylene-bridged imidazo[2,1-*b*]thiazoles and imidazo[2,1-*b*]benzothiazoles.



Scheme 8. DMSO-based synthesis of 3,3'-bisimidazopyridinylmethanes.

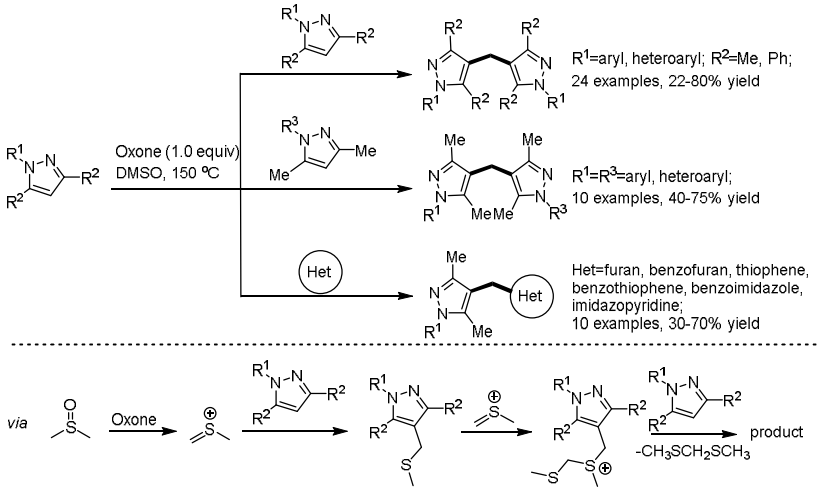
The Sawant's group has employed oxone as the activator of DMSO for the synthesis of novel methylene-bridged bis-heterocyclic scaffold through Csp^2-Csp^3-Csp^2 bond construction (Scheme 9).[19] A wide range of *N*-arylated pyrazole can be compatible in this process delivering symmetric bis-pyrazole derivatives in acceptable to good yields (24 examples, 22-80% yield). Unsymmetric bis-pyrazoles have also been readily prepared by this approach (10 examples, 40-75% yield).

Interestingly, under the reaction system, pyrazole was functionalized with various heterocycle rings, including furan, benzofuran, thiophene, benzothiophene, benzoimidazole, and imidazopyridine with a methylene linker (10 examples, 30-70% yield). The authors proposed that a methylthiomethylenation product generated with thionium ion intermediate and pyrazole should be the key intermediate. The thioether would undergo further addition with thionium ion and a subsequent replacement with another molecule of pyrazole gave the final product.

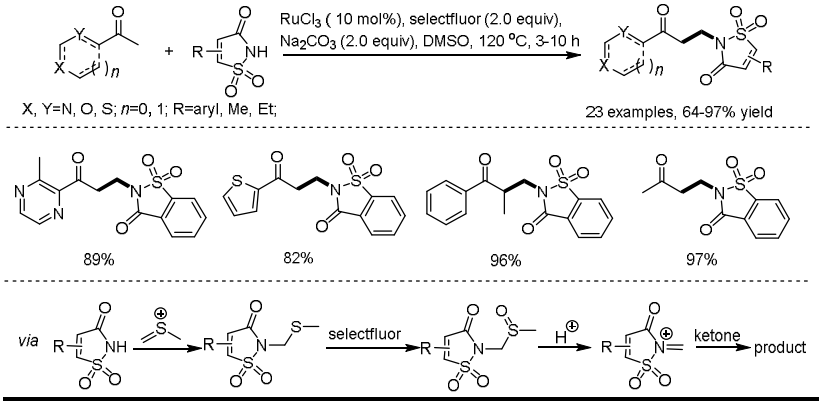
Sun, Liu, Wang and co-workers developed a Ru-catalyzed synthesis of heterocycle-containing β-amino ketones using DMSO as the methylene source and solvent (Scheme 10).[20-21] Various cyclic sulfonyl imides and acetophenones acted as suitable candidates for this process, affording Mannich-type adducts in moderate to good yields (23 examples, 64-97% yield). Mechanistic studies revealed that cleavage of C–S bond in DMSO may be the rate-limiting step. Selectfluor served as the oxidant, which was used for the oxidation of thioether intermediate to sulfoxide intermediate.

The Cui's group developed an iron-catalyzed aminomethylenation of pyrrolo[2,1-*a*]isoquinolines with amines and DMSO (Scheme 11).[22] A series of modified pyrrolo[2,1-*a*]isoquinolines can be obtained in low to good yields (26 examples, 17-72% yield). Both primary amines (2-aminopyridine, aniline) and secondary amines (morpholine, piperidine) could be compatible in this process. The obtained product can be easily

cyclized to lactam derivative by the treatment with KO*t*Bu. The mechanistic investigation indicated that methylthiomethylenation product may serve as a key intermediate, which would undergo addition with sulfonium ion and further replacement with amine to deliver the final product.



Scheme 9. Methylene-bridged bis-heterocycle synthesis.



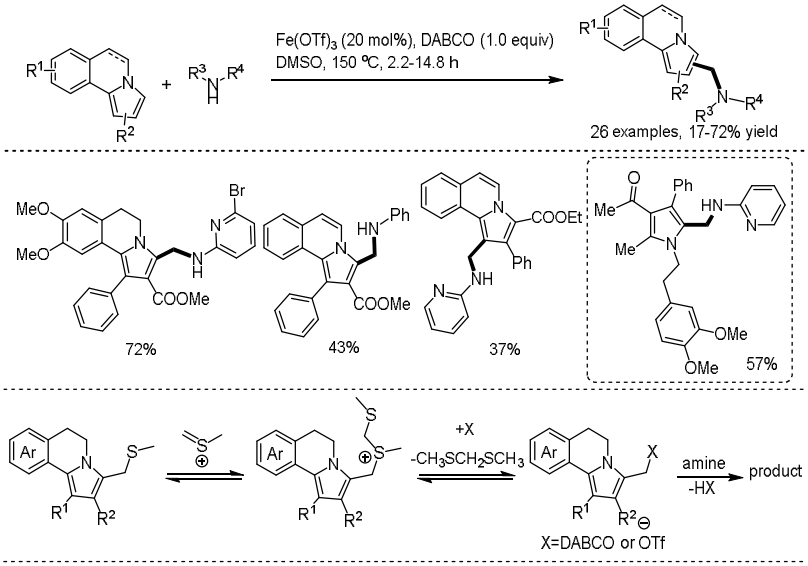
Scheme 10. DMSO-based synthesis of β-amino ketones.

In another continuing program of modifying pyrrolo[2,1-*a*]isoquinoline derivatives, Cui and co-workers used ammonium acetate as activator of DMSO (Scheme 12).[23] Both methylthiomethylenation product and methylene-bridged bis-pyrrolo[2,1-*a*]isoquinoline can be obtained under the reaction conditions. It was found that the chemoselectivity was controlled by the amount of activator and the reaction concentration.

Later, Cui and co-workers utilized acetyl chloride as activator of DMSO for generating active species to tether two molecules of pyrrolo[2,1-*a*]isoquinolines under a mild reaction condition.[24] A variety of pyrrolo[2,1-*a*]isoquinoline derivatives and multisubstituted pyrroles could be bridged with a methylene moiety (22 examples, 17-94% yield). Pleasingly, unsymmetric methylenated pyrrolo[2,1-*a*]isoquinoline was synthesized by monohydrolysis and amidation.

On the basis of the obtained results and previous reports, the authors proposed that leaving groups tethered pyrrolo[2,1-*a*]isoquinolines with a methylene might be key intermediates for this transformation. Nucleophilic replacement of these intermediates with another molecule of pyrrolo[2,1-*a*]isoquinoline would

lead to the formation of corresponding methylenation product. Unfortunately, other important *N*-heteroarenes such as indole, protected tryptamine and benzoimidazole failed to provide the desired methylene-bridged dimers under the reaction conditions, probably because of their lower instability in the acidic reaction system or the weaker nucleophilicity.



Scheme 11. Iron-catalyzed aminomethylenation of pyrrolo[2,1-*a*]isoquinolines.

4. DMSO as source of CH_3

Methyl group can be introduced into heterocycles by the Me transfer via the formation of palladium/DMSO/*N*-oxide complex. Another efficient pathway is the reduction of *in situ*-generated imines which were derived from thioethers via methylthiomethylenation.

Deng and Li have developed a palladium-catalyzed methylation of isoquinoline *N*-oxides though C–H oxidation (Scheme 13).[25] This is the first example of employing dialkyl sulfoxides as the sources of alkyl groups for constructing 1-alkylated isoquinolines. A series of functional groups such as F, Cl, MeO, OCH_2O, CF_3 and aryl groups were well tolerated in this process, yielding the desired 1-methylisoquinolines in moderate to good yields (14 examples, 51-79% yields). This methodology could also be extended to the use of quinoline *N*-oxide as substrate and dibutyl sulfoxide as alkyl source. Oxidative cleavage of the C–S bond of DMSO after C–H oxidation-carbopalladation-complexation and a subsequent methyl insertion was proposed as the reaction pathway.

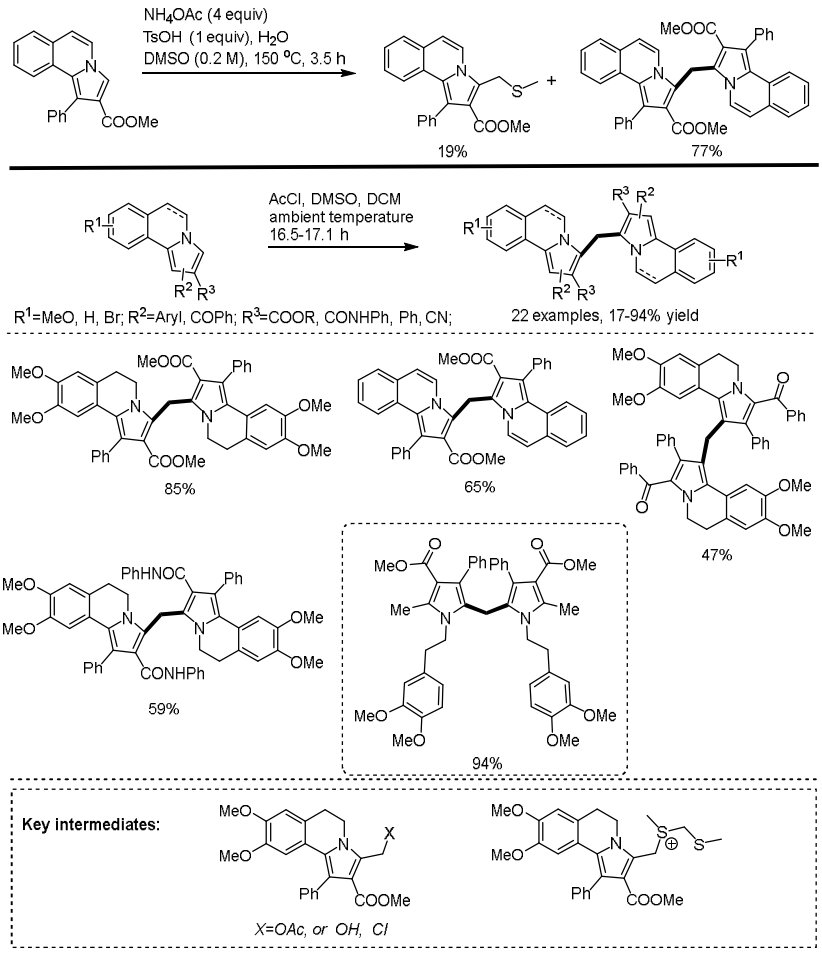
Methylation of *N*-containing heterocycle has been demonstrated to be a useful tool for the construction of pharmaceutically important molecules. Xiao and Wang developed a catalyst-free amine methylation approach by using DMSO as the methyl source.[26] Diverse aromatic amines could be well methylated with this reaction system (Scheme 14). A thioether was proposed by the authors as the key intermediate for the methylation process. Notably, this reaction can be utilized for the synthesis of Galipine in good yield at multigram scale.

5. DMSO as source of SCH_3

Incorporation of SMe group into heterocyclic molecules from DMSO can be realized by formation of iododimethylsulfonium/substitution/demethylation cascade and palladium catalyzed C–H activation.

Xu, Yu and Gao realized a Lewis-acid-catalyzed, Cu^{II}-mediated construction of heteroaryl thioethers with DMSO serving as an effective methylthiolation reagent (Scheme 15).[27] The use of AgF as catalyst afforded a series of heterocyclic methyl thioethers in moderate to excellent yields (6 examples, 60-95% yield).

Thiazoles, azoles, imidazole and oxadiazole could all be functionalized readily through this process regardless of their electronic property and the presence of sensitive functional groups. It was found that $NiCl_2$ and FeF_2 could also be utilized as catalyst for this reaction, but relatively lower yields were obtained compared with the reactions under the catalysis of AgF. The authors suggested that copper acetate might be able to trap the *in situ*-generated methylmercaptan from the thermal decomposition of DMSO.

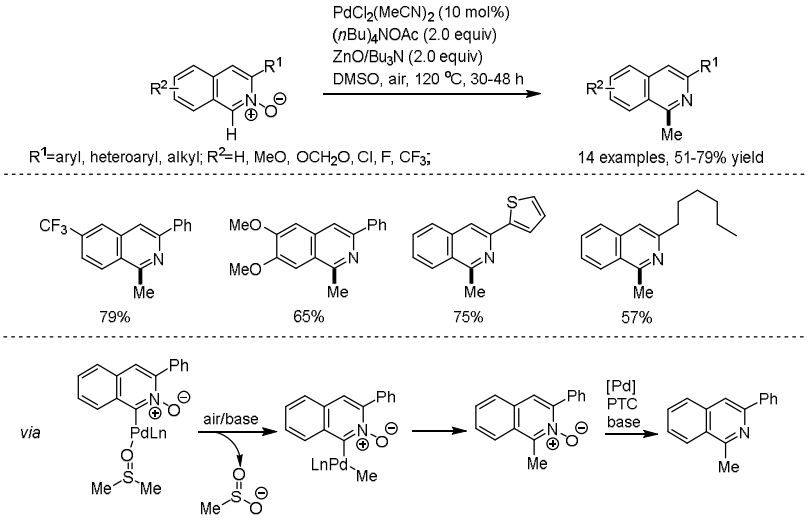


Scheme 12. DMSO-based methylenation of pyrrolo[2,1-*a*]isoquinoline.

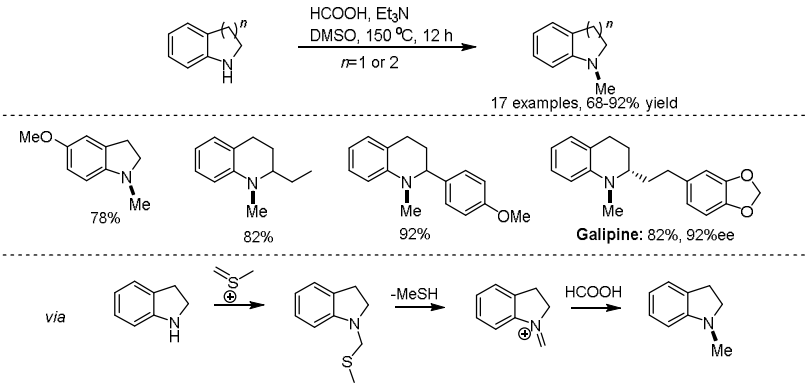
Ge and Zhou reported a non-radical regioselective sulfenylation of flavones under NH_4I/DMSO reaction system (Scheme 16).[28] Flavone-containing methyl thioethers were prepared in moderate to good yields (12 examples, 55-82% yield). Various functional groups including Me, OH, Cl, Br, CN and NO_2 on flavone were tolerated. A key iododimethylsulfonium intermediate was proposed to be generated *in situ* from NH_4I and DMSO. Flavone as a nucleophile would attack the iododimethylsulfonium intermediate. Further demethylation and deprotonation gave the final methylthiolation product.

The Batra's group have also developed a Pd-catalyzed functionalization of 1-aroyl-β-carbolines using DMSO as the source of thiomethyl group (6 examples, 52-70% yield).[29] By employing β-carboline as a directing group, *ortho*-selective Csp^2–H activation can be achieved by an oxidative Heck reaction (Scheme

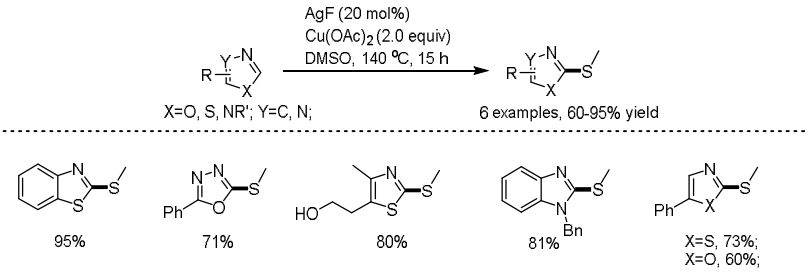
17). Beside of serving as an oxidant for the recycle of palladium catalyst, copper acetate was also proposed to act as the oxidant for the generation of 1,2-dimethyldisulfane from methyl mercaptan.



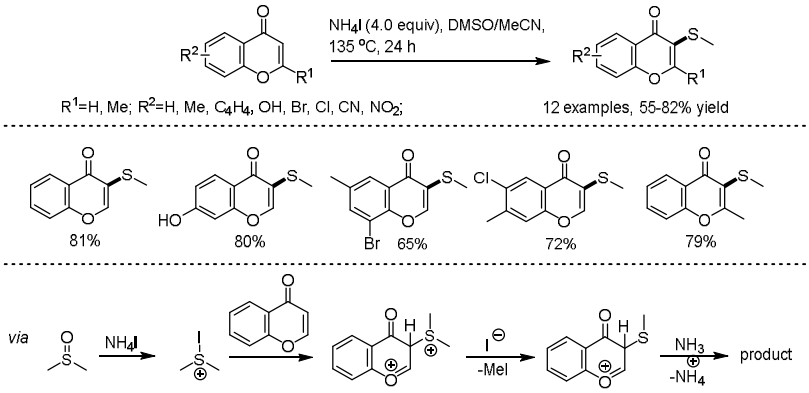
Scheme 13. Pd-catalyzed methylation of isoquinoline *N*-oxides.



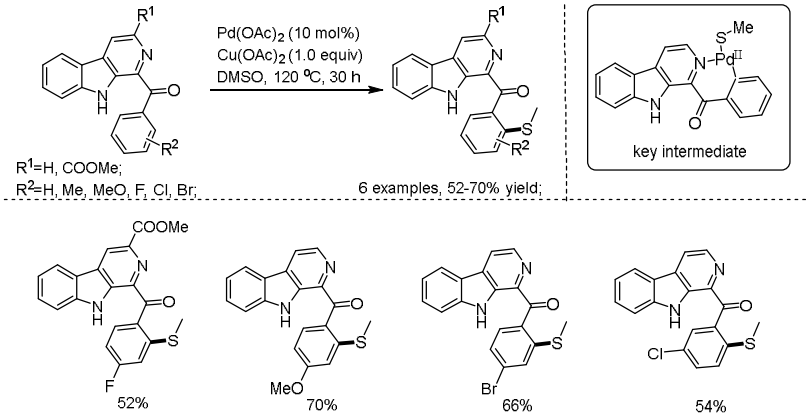
Scheme 14. DMSO-based methylation of *N*-containing heterocycle.



Scheme 15. Lewis-acid-catalyzed methylthiolation of heterocycles.



Scheme 16. Sulfenylation of flavones with NH_4I/DMSO.



Scheme 17. Pd-catalyzed methylthiolation of 1-aroyl-β-carbolines.

6. DMSO as source of CH_2SCH_3

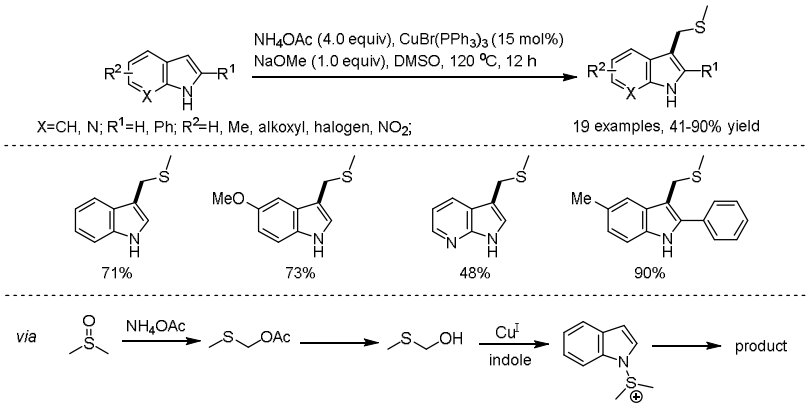
Since methyl(methylene)sulfonium is a common intermediate in a DMSO-based reaction system in the presence of various activators, both direct addition with the sulfonium intermediate and replacement of sulfonium intermediate-derived adducts are able to achieve the goal of introducing CH_2SCH_3 moiety.

The Huang's group disclosed a facile $CuBr(PPh_3)_3$-catalyzed and NH_4OAc-induced intermolecular Pummerer-type reaction with indoles and dimethylsulfoxide (Scheme 18).[30] A range of N1-free indoles bearing various functional groups can be applied in this process affording methylthiomethyl-substituted indoles in moderate to good yields (19 examples, 41-90% yield). On the basis of the experimental results, methylthiomethyl acetate was proposed by the authors to be a key intermediate, which was generated by the activation of DMSO with NH_4OAc. Methylthiomethanol was then formed through amminolysis and further yielded reactive species in the presence of copper catalyst, which was then trapped by indole to give indole 1-sulfonium ylide intermediate. A final [2,3]-sigmatropic rearrangement gave the desired thioether.

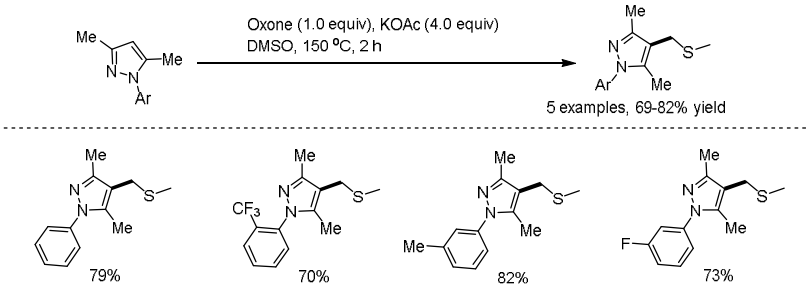
The Sawant's group also prepared a series of methylthiomethyl substituted pyrazoles using oxone as the activator of DMSO (Scheme 19).[19] The *in situ*-generated thionium ion intermediate could be trapped by *N*-arylated pyrazoles, leading to the formation of corresponding thioethers. On the basis of experimental, analytical (LC-MS) and computational (DFT) analysis, the authors claimed that the obtained thioethers could act as intermediate for further formation of methylene-bridged pyrazole.

The Cui's group modified a variety of pyrrolo[2,1-*a*]isoquinolines and pyrrolo[1,2-*a*]quinolines through methylthiomethylenation under NH_4OAc/DMSO reaction system (Scheme 20).[23] The corresponding

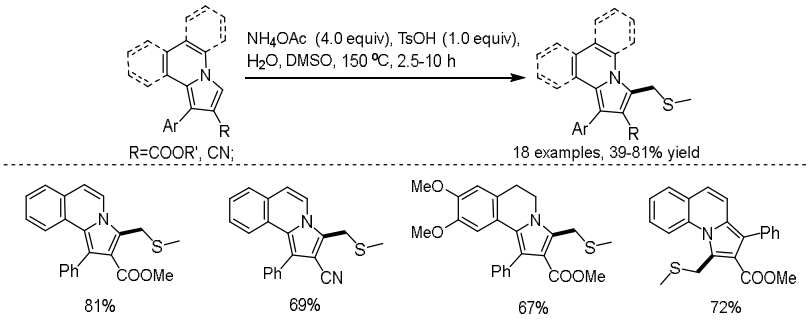
thioethers were obtained in acceptable to good yields (18 examples, 39-81% yield). In this reaction system, ammonium acetate served as the activator of DMSO. A sulfonium ion should be the *in situ*-formed key intermediate, which would be trapped by the *N*-heterocycles to give methylthiomethyl substituted products.



Scheme 18. $CuBr(PPh_3)_3$-catalyzed and NH_4OAc-induced methylthiomethylenation of indoles.



Scheme 19. Oxone-mediated methylthiomethylation of pyrazoles.



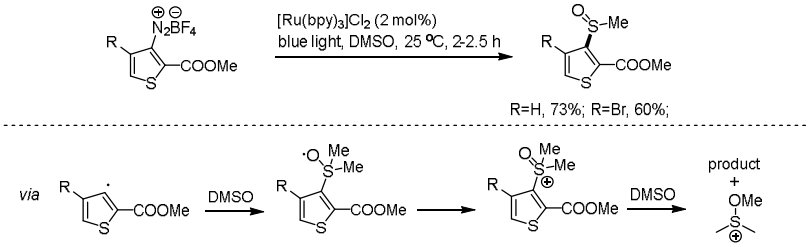
Scheme 20. Methylthiomethylenation of pyrrolo[2,1-*a*]quinolines with NH_4OAc/DMSO.

7. DMSO as source of $SOCH_3$

The reported DMSO-based methylsulfoxidation approaches require the generation of aryl radical. Radical type addition with DMSO/oxidation/demethylation with DMSO is a common reaction pathway for these reactions.

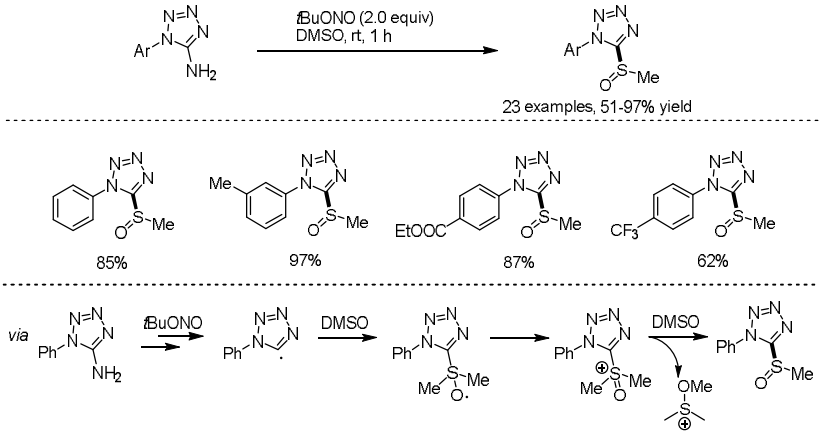
The Rastogi's group prepared thienyl incorporated methylsulfoxides through visible light-induced methylsulfoxidation of heteroaryl diazonium salts with DMSO as the source of methylsulfinyl group (Scheme

21).[31] Functionalization of a wide range of aryl diazonium salts was also realized by this method, giving the corresponding aryl methyl sulfoxides in moderate to good yields. Heteroaryl radical was proposed to be generated from the diazonium salt in the presence of excited state $Ru(bpy)_3^{2+*}$ and would be captured by a molecule of DMSO. A subsequent oxidation to sulfoxide cation and further transfer of one methyl group to DMSO by nucleophilic attack provided the desired product.



Scheme 21. Photo-induced methylsulfoxidation of heteroaryl diazonium salts with DMSO.

Zhang and Wu reported an efficient *tert*-butyl nitrite mediated methylsulfoxidation of various tetrazole-amines with DMSO (Scheme 22).[32] A wide range of functionalized aromatics were readily introduced into the methylsulfinylated tetrazoles under a very mild reaction condition (23 examples, 51-97% yield). Interestingly, selective cleavage of the C-SO bond was observed by using methylsulfinylethane and 2-methyl-2-methylsulfinylpropane. Methylsulfoxide was obtained in both cases in moderate yield. It was found that *tert*-butyl nitrite has played dual roles in diazotization and synergistic generation of heteroaryl radical. Promisingly antifungal activities were identified in the preliminary bioactivity evaluation.



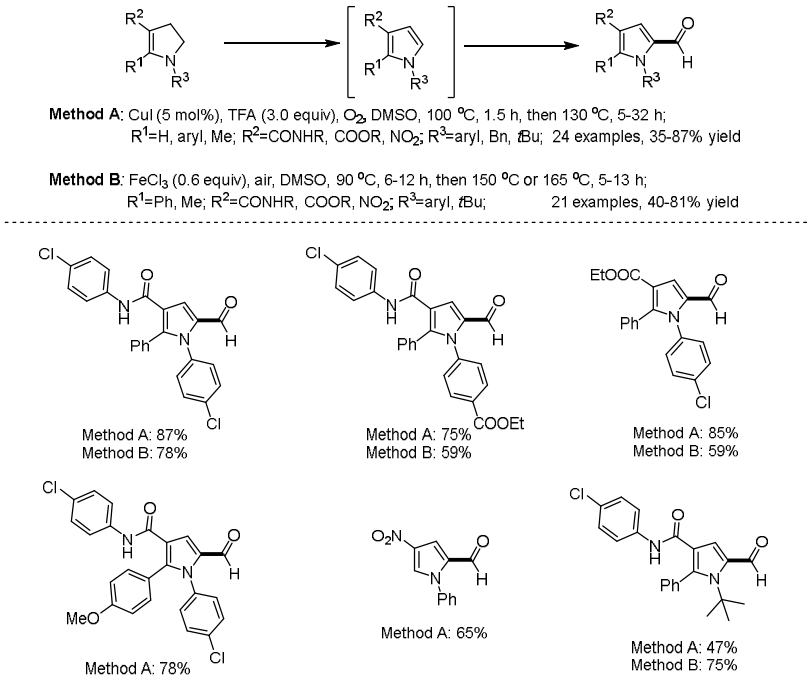
Scheme 22. *t*BuONO mediated methylsulfoxidation of tetrazole-amines with DMSO.

8. DMSO as source of CHO

Two main pathways were involved in the DMSO-based formylation of heterocycles: oxidation of the just introduced methyl group to aldehyde and Kornblum oxidation of the *in situ*-formed intermediates. It should be noted that the methyl group and *in situ*-formed intermediate were also generated by transforming DMSO.

α-Formylpyrroles have been extensively used as key building blocks for construction of linked polycyclic systems of great importance such as porphyrin derivatives and highly functionalized fused pyrrole derivatives. Zhang and Zhang developed a convenient copper-catalyzed oxidation/formylation cascade sequence of multisubstituted 2,3-dihydro-1*H*-pyrroles (Scheme 23).[33] Copper salts acted as the oxidant of 2,3-dihydro-1*H*-pyrrole producing aromatized pyrrole for the subsequent DMSO-involved formylation. TFA

was employed as the activator of DMSO for the generation of thionium ion as a key active species. Various functional groups can be incorporated into the products affording moderate to good yields (24 examples, 35-87% yields).



Scheme 23. Copper- and iron-catalyzed oxidation/formylation cascade sequence.

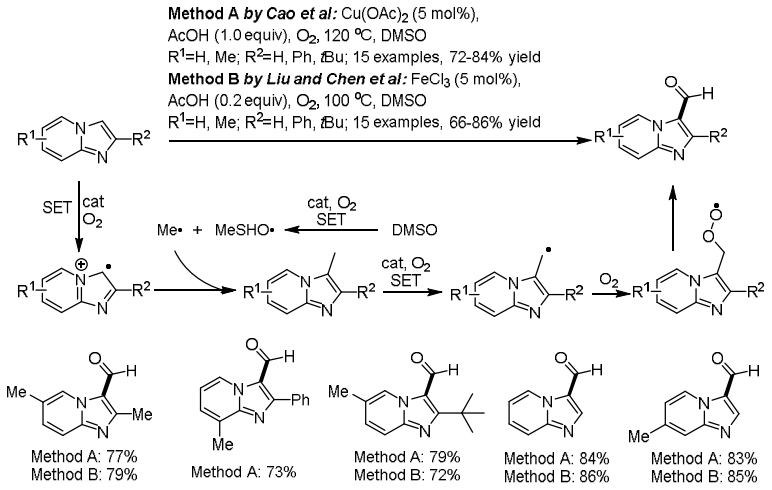
Later, the same group reported an iron-mediated synthesis of highly functionalized α-formylpyrroles in DMSO under air atmosphere.[34] A plausible radical reaction pathway including iron-promoted oxidation of 2,3-dihydro-1*H*-pyrrole, methylation and oxidation of methyl group to carbonyl group was proposed on the basis of the obtained results and further control experiments. A wide range to substrates were also tolerated in this process affording corresponding multisubstituted α-formylpyrroles in moderate to good yields (21 examples, 40-81% yields). In both procedures, DMSO served as the carbonyl source and solvent.

Imidazo[1,2-*a*]pyridine as a privileged framework is present in numerous natural products and drugs including necopidem, zolimidine, saripidem, zolimidine, olprinone and alpidem *etc.* The Cao's group has reported a Cu-catalyzed, dimethyl sulfoxide-involved C3-formylation of imidazo[1,2-*a*]pyridines (Scheme 24).[35] A series of imidazo[1,2-*a*]pyridine derivatives were formylated readily under this reaction system in good yields (15 examples, 72-84% yields) using DMSO as carbonyl source and molecular oxygen as the terminal oxidant. On the basis of their results and further control experiments, a plausible radical reaction pathway was proposed. Methyl radical would be generated under the catalysis of copper salts through single electron-transfer oxidation. A subsequent methylation of imidazo[1,2-*a*]pyridine and a final oxidation of methylated imidazo[1,2-*a*]pyridine provided the desired product.

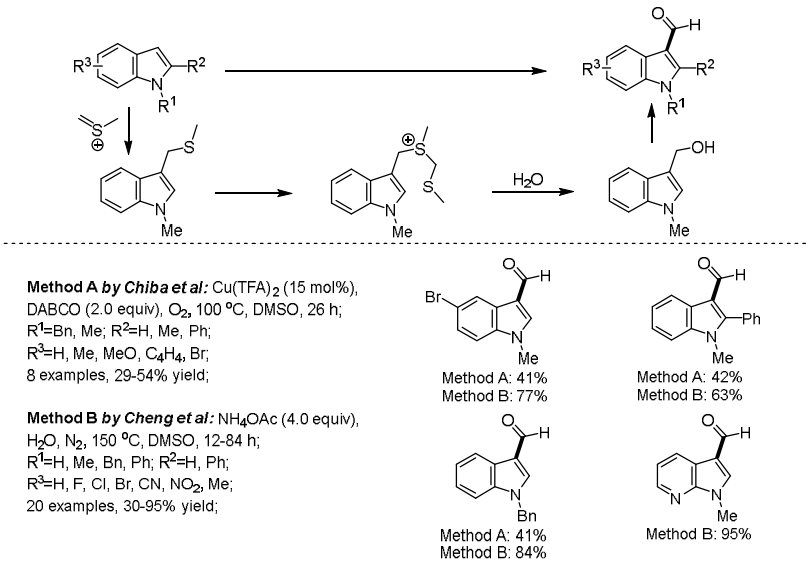
Later in 2016, Liu and Chen developed an iron-catalyzed formylation of imidazo[1,2-*a*]pyridine employing DMSO as carbonyl source and molecular oxygen as terminal oxidant (Scheme 24).[36] The reaction conditions were also general, providing the corresponding 3-formyl imidazo[1,2-*a*]pyridines in good yields (15 examples, 66-86% yields). A similar radical reaction pathway was also proposed based on their results.

Possessing a privileged framework, acyl indole and its derivatives have been used as valuable building blocks and also served as key structural unit in natural products and pharmaceutically important molecules. When studying the Cu-catalyzed aerobic oxidation of methyl/methylene-substituted indoles with DABCO and

DMSO, Chiba and co-workers developed a copper-catalyzed direct formylation of indoles using a $Cu(TFA)_2$/DABCO/DMSO reaction system (Scheme 25). C3 formylation of indoles and C2 formylation of pyrrole were obtained in low to moderate yields (8 examples, 29-54% yields).[37]



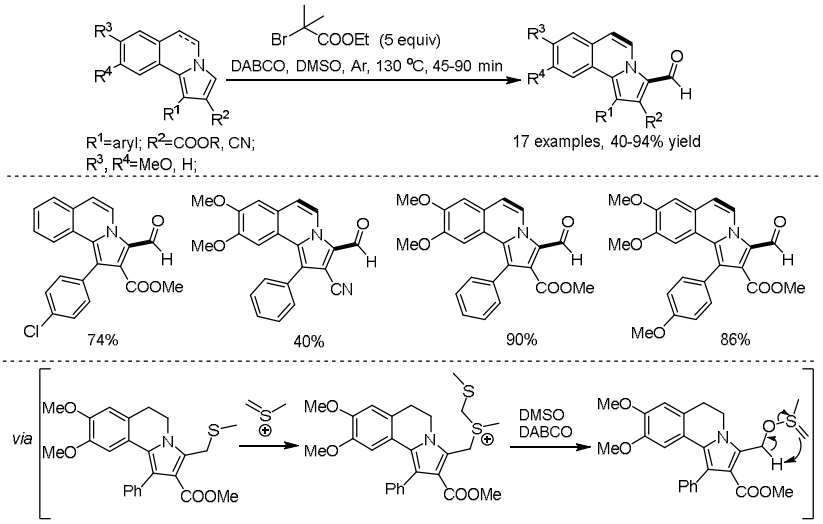
Scheme 24. DMSO-based formylation of imidazo[1,2-*a*]pyridines.



Scheme 25. DMSO-based formylation of indoles.

In 2013, the Cheng's group established a NH_4OAc mediated formylation of indoles by using water as key nucleophile and DMSO as the carbonyl source via sequential traditional and unusual Pummerer reaction pathways.[38] This reaction features good functional group tolerance, high yield and easily accessible starting material (20 examples, 30-95% yields). The authors proposed that the reaction proceeded through methylthiomethylenation, nucleophilic substitution and oxidation cascade sequence.

Since pyrrolo[2,1-*a*]isoquinoline is a key structural unit in a large number of natural products of great interest such as lamellarin alkaloids, the direct modification of pyrrolo[2,1-*a*]isoquinoline derivatives can be an efficient way for yielding useful molecules. During the study of modifying pyrrolo[2,1-*a*]isoquinoline through radical pathway, Cui and co-workers found that ethyl bromoisobutyrate could act as the activator of DMSO and thus promote the formylation of pyrrolo[2,1-*a*]isoquinolines (Scheme 26).[39] A series of electron-rich pyrrolo[2,1-*a*]isoquinoline derivatives could be compatible in this process, yielding the corresponding aldehydes in moderate to good yields (17 examples, 40-94% yields). On the basis of obtained results and previous reports, a plausible reaction pathway was proposed involving methylthiomethylenation, addition with sulfonium intermediate and a final Kornblum oxidation.



Scheme 26. Ethyl bromoisobutyrate mediated formylation of pyrrolo[2,1-*a*]isoquinolines.

9. DMSO as oxidant

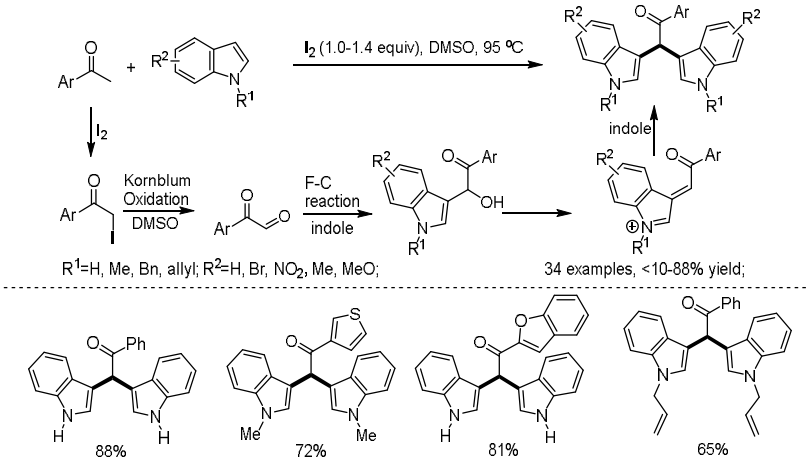
Kornblum oxidation can be found as an important step in most cases with DMSO as an oxidant. Generally, Friedel-Crafts type addition and condensation of the *in situ*-genetated aldehydes would provide necessary intermediates for further transformations.

The Wu's group realized a molecular iodine-promoted synthesis of 2,2-bisindolyl-1-arylethanones using DMSO as the oxidant in 2012 (Scheme 27).[40] A series of mechanism-different reactions including iodination, Kornblum oxidation and Friedel-Crafts reactions could be assembled in a single reactor by rational design. A large number of readily accessible aryl methyl ketones and substituted indoles could be tolerant in this process (34 examples, <10-88% yield). As demonstrated by the authors, molecular iodine played two roles: as iodination reagent for the subsequent Kornblum oxidation, and as Lewis acid for activating the *in situ*-formed aryl glyoxal for Friedel-Crafts reaction.

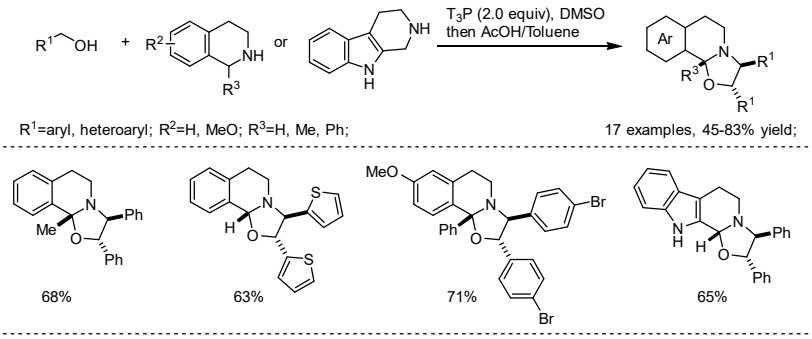
Mantelingu and co-workers reported a novel synthesis of tetrahydro-2*H*-oxazolo[2,3-*a*]isoquinolines with tetrahydroisoquinolines and benzyl alcohols (Scheme 28).[41] This one-pot process was proposed to occur through oxidation of benzyl alcohols to aldehydes by T_3P/DMSO and a subsequent acetic acid-mediated [3+2]-cycloaddition. This method can be expanded to heterocyclic alcohols and tetrahydro-β-carboline. In general, moderate to good yields were afforded (17 examples, 45-83% yield).

As chromone is a privileged framework in drug discovery, Zhu and Wu intended to replace coumarin with chromone in the key structure of lamellarin alkaloids to produce new isomeric derivatives.[42] The authors established an iodine-mediated cascade sequence for constructing chromone-fused pyrrolo[2,1-*a*]isoquinolines and indolizino[8,7-*b*]indoles with *o*-acetylphenoxyacrylates, tetrahydroisoquinolines and noreleagnines (Scheme 29). They logically designed a tandem iodination/Kornblum oxidation/condensation/intramolecular dipolar cycloaddition/aromatization reaction.

Notably, both pharmaceutically important skeletons, L-menthol and DL-α-tocopherol, could be readily incorporated into the products. In general, moderate to good yields were obtained with good functional group compatibility (42 examples, 34-75% yield).



Scheme 27. DMSO-based synthesis of 2,2-bisindolyl-1-arylethanones.



Scheme 28. DMSO-based synthesis of tetrahydro-2*H*-oxazolo[2,3-*a*]isoquinolines.

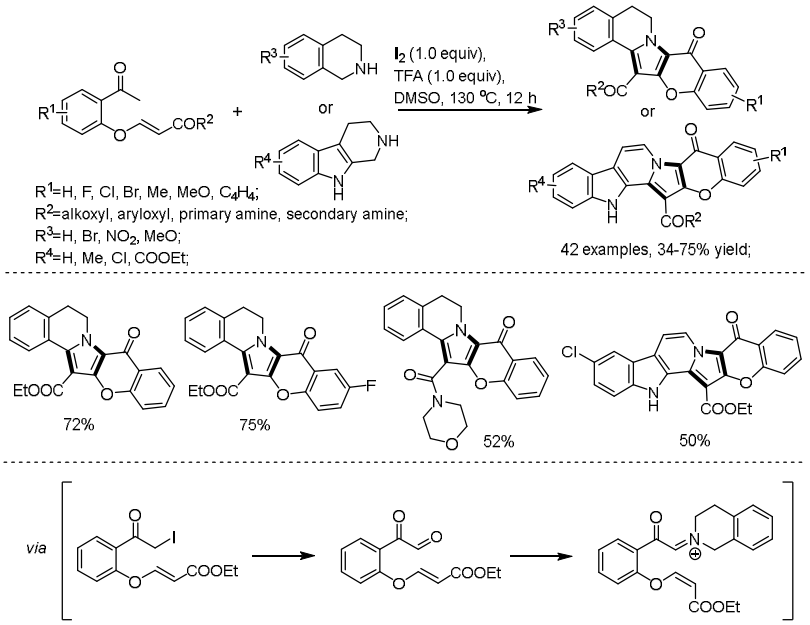
Wu and co-workers designed an elegant iodine-promoted synthesis of 1,2,3-triaroylindolizines with high efficiency from commercially available methyl ketones and pyridines in 2012 (Scheme 30).[43] Three key intermediates were proposed for this convergent domino reaction, including an aryl glyoxal (generated by iodination/Kornblum oxidation), an azomethine ylide (formed from pyridine and α-iodoacetophenone), and a key dipolarophile (*in situ*-generated by the condensation of azomethine ylide and aryl glyoxal). Various aromatic and heteroaromatic methyl ketones, substituted pyridines as well as quinoline and isoquinoline were compatible in this process (30 examples, 8-93% yield).

The Batra's group developed a highly efficient iodine-promoted oxidative Pictet-Spengler reaction for constructing 1-aroyl-β-carbolines from terminal alkynes and tryptamines in 2017 (Scheme 31).[29]

Terminal alkynes were used as 2-oxoaldehydes surrogate in a reaction system with I_2/DMSO through iodination/Kornblum oxidation. This protocol proved to be very general (42 examples, 68-96% yield). A large number of aryl alkynes, heteroaryl alkynes and substituted tryptamines could be used as suitable candidate for this process. It is worth noting that pyrrole- and indole-based substrates could also be compatible in this reaction providing pyrrolo[1,2-*a*]quinoxaline-incorporated molecules in good yields.

Ablajan and co-workers developed the iodine/TBHP promoted acylation of benzothiazoles in 2020 (Scheme 32).[44] This acylation process was proposed to take place through a cascade sequence including

oxidation of aryl methyl ketone to aryl glyoxal, hydrolysis of benzothiazole, condensation of 2-aminothiophenols with aryl glyoxal, cyclization and aromatization. A range of functionalized 2-acylbenzothiazoles were prepared using the I_2/TBHP/DMSO system (20 examples, 78-92% yield). Compared with previous studies, this protocol features shorter reaction time, lower temperature, metal-free and ligand-free conditions.



Scheme 29. DMSO-based synthesis of chromone-fused pyrrolo[2,1-*a*]isoquinolines and indolizino[8,7-*b*]indoles.

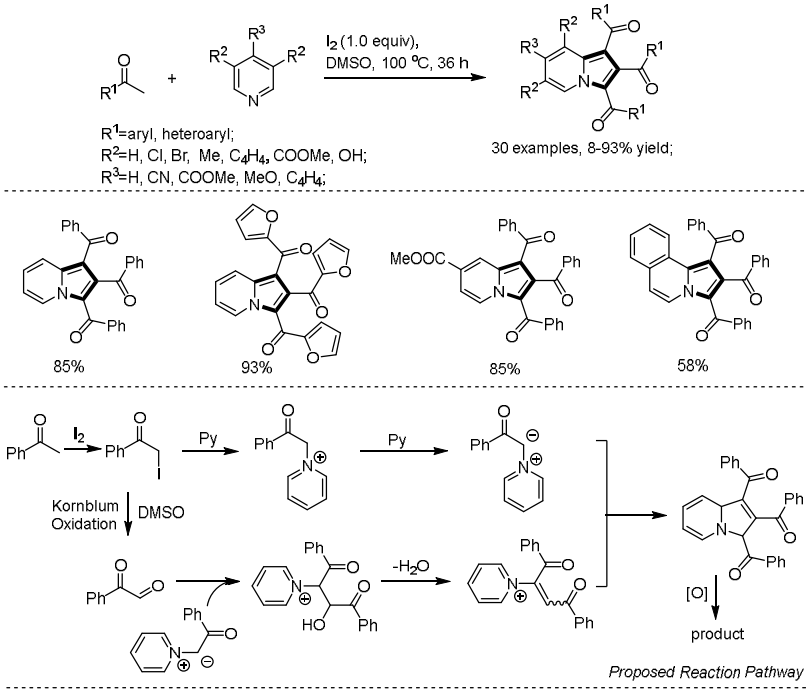
Three efficient DMSO-involved regioselective C3-modifications of indoles to 1,2-dicarbonylated molecules were developed recently (Scheme 33). Using a molecular iodine/pyrrolidine/DMSO system, the Wu's group constructed indolyl diketones scaffolds with indoles and methyl ketones in good yields (24 examples, up to 88% yield).[45] Two plausible reaction pathways were proposed by the authors. Glyoxal intermediate would be formed by iodination of methyl ketone and a following Kornblum oxidation. Friedel-Crafts reaction of glyoxal intermediate or *in situ*-generated iminium ion and a subsequent oxidation of the adduct with molecular iodine gave the dicarbonylated indoles.

By the direct use of aryl glyoxal monohydrate, Ahmed and Vishwakarma developed a convenient functionalization of indoles and pyrroles through C-3 dicarbonylation.[46] Various indoles and pyrroles could be transformed to 1,2-diketones in moderate to good yields under the catalysis of morpholine in DMSO (24 examples, 55-85% yield). As proposed by the authors on the basis of their results, DMSO could act as the oxidant for the oxidation of Friedel-Crafts type product to 1,2-diketone.

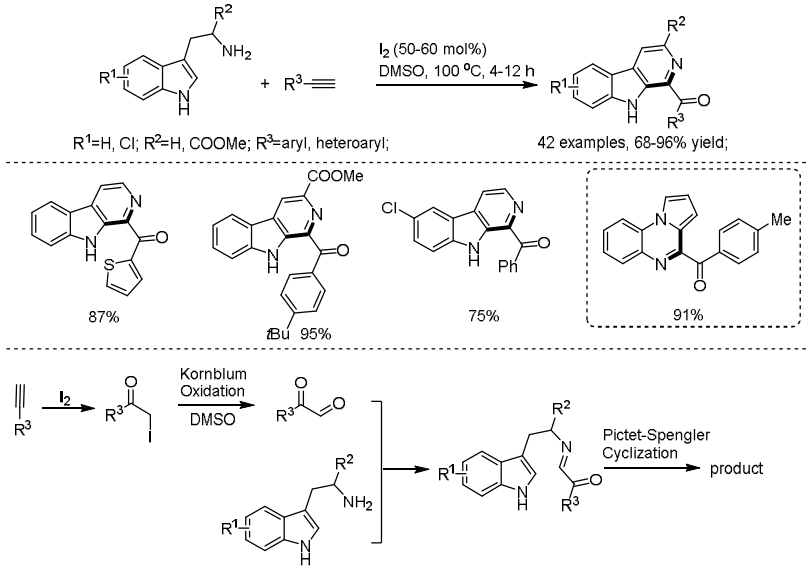
The Guo's group also reported a novel synthesis of C-3 dicarbonyl indoles through oxidative cross-coupling of styrenes and indoles using a KI/TBHP/DMSO system.[47] A variety of styrenes and indoles were tolerated in this reaction, leading to the formation of diketones in moderate to good yields (19 examples, 47-91% yield). α-Iodoacetophenone was proposed to be generated and a following Kornblum oxidation resulted in the formation of aryl glyoxal intermediate. The Friedel-Crafts type reaction of indole and aryl glyoxal was also proposed as a key step for this catalytic cycle.

Inspired by the previous achievements, Cui and co-workers realized a DMSO-involved modification of pyrrolo[2,1-*a*]isoquinolines through dicarbonylation with DMSO as oxidant and arylacyl bromide as the carbonyl source (Scheme 34).[48] Low to good yields could be obtained by modifying a series of

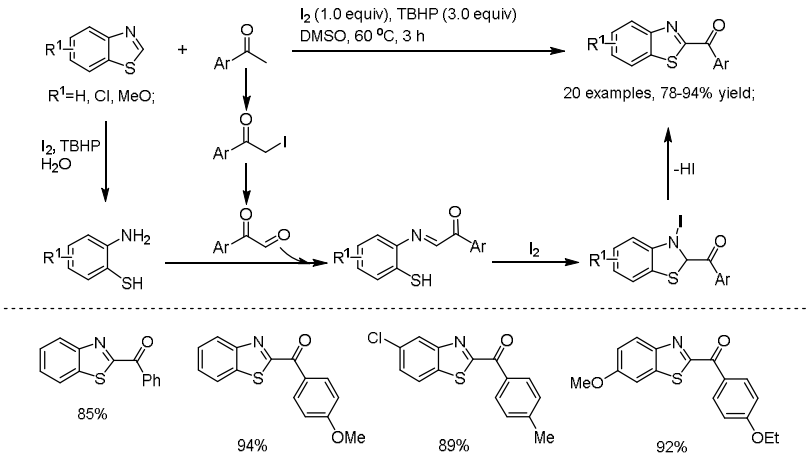
pyrrolo[2,1-*a*]isoquinoline derivatives (15 examples, 12-73% yield). However, this methodology was limited to the use of electron-deficient arylacyl bromides. Kornblum oxidation of arylacyl bromides and a subsequent Friedel-Crafts reaction were proposed as the key steps for this transformation.



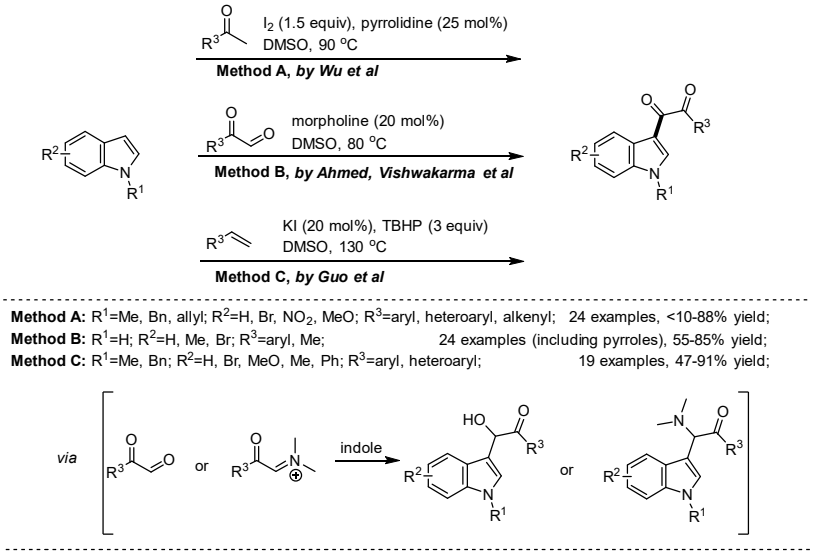
Scheme 30. Iodine-promoted synthesis of 1,2,3-triaroylindolizines.



Scheme 31. Iodine-promoted synthesis of 1-aroyl-β-carbolines.



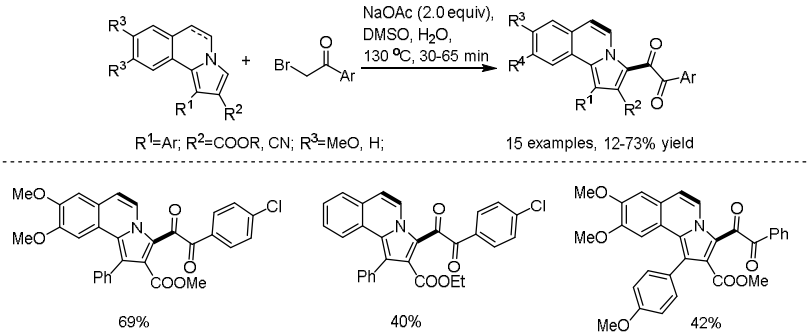
Scheme 32. Iodine/TBHP promoted acylation of benzothiazoles.



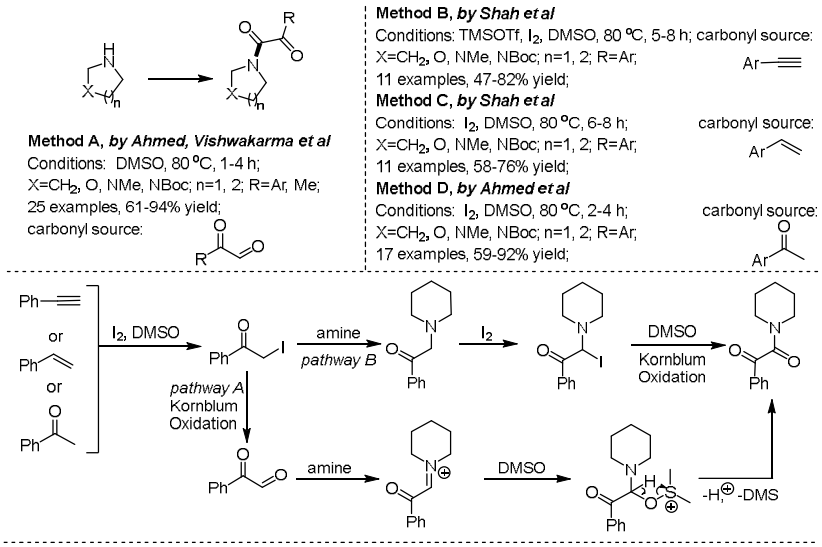
Scheme 33. DMSO-based dicarbonylation of indoles.

Recently, several DMSO-involved amide synthesis reaction systems have been developed by transforming cyclic amines to functionalized ketoamides (Scheme 35). Ahmed and Vishwakarma established a novel synthesis of α-ketoamides through a DMSO-promoted oxidative amidation with 2-oxoaldehydes and amines.[49] Both aliphatic and aromatic α-ketoamides could be prepared with various cyclic amines under this reaction system in moderate to excellent yields (Method A, 25 examples, 61-94% yield).

Later, the Shah's group applied terminal alkynes as the carbonyl source under a catalytic system TMSOTf/I_2/DMSO for the dicarbonylation of secondary amines.[50] Aryl glyoxal was proposed to be generated by trifluoromethylation/iodination/Kornblum oxidation of terminal alkynes in this process. Pyrrolidine, piperidine, morpholine, *N*-methyl piperazine and *N*-Boc piperazine were well tolerated in this reaction (Method B, 11 examples, 47-82% yield).



Scheme 34. DMSO-based dicarbonylation of pyrrolo[2,1-*a*]isoquinolines.



Scheme 35. DMSO-based diketonization of cyclic amines.

Shah and co-workers further considered terminal alkenes as carbonyl source for diketonization of amines.[51] A variety of α-ketoamides were successfully prepared with terminal alkenes and amines (Method C, 11 examples, 58-76% yield). α-Iodoketone was suggested to be the key intermediate for this reaction, which then underwent a Kornblum oxidation/condensation/oxidation sequence.

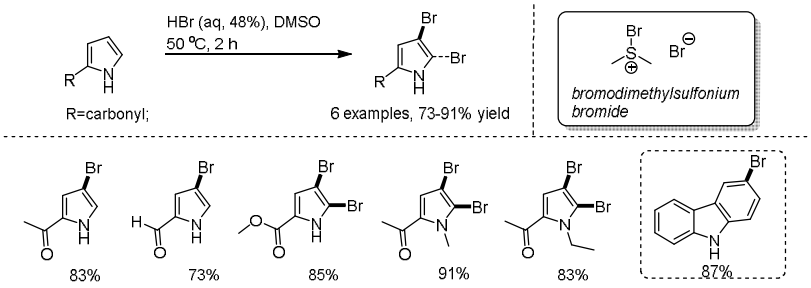
Ahmed and co-workers also reported another alternative way for the construction of α-ketoamides.[52] Commercially available arylmethylketones were used as carbonyl source using a I_2/DMSO system. This procedure also features good functional group compatibility (Method D, 17 examples, 59-92% yield). It should be noted that besides the well-recognized iodination/Kornblum oxidation/condensation/oxidation cascade sequence as predominant pathway (pathway A), a *N*-nucleophilic substitution-based pathway B was also proposed by the authors.

10. Halogenation

Several efficient DMSO-involved halogenation reaction systems have been developed such as HBr/DMSO, DXDMH/DMSO, NCS/DMSO, XCH_2CH_2X/DMSO and α-brominated carbonyl compounds/DMSO. Halogenated dimethylsulfonium intermediates can be popularly formed as an active

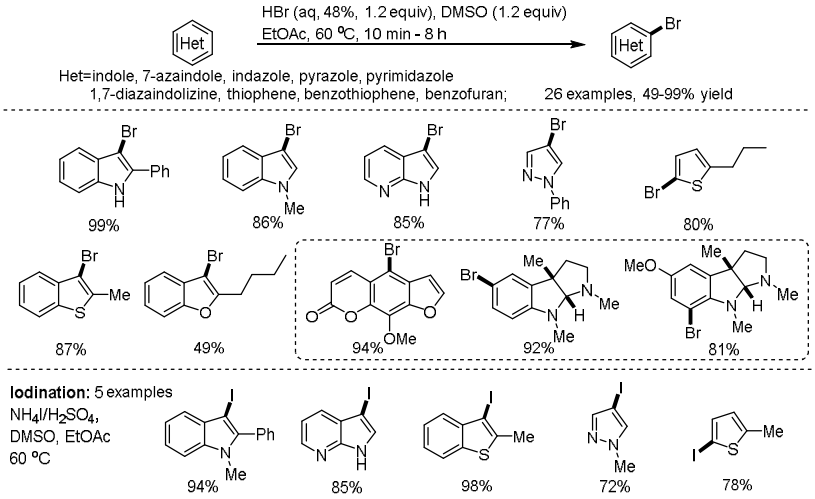
halogenation species. Molecular bromine may also be produced in some cases as brominating reagents. In addition, DMSO can also be used as catalyst in chlorination reaction together with NCS.

Electrophilic bromination of pyrrole derivatives and carbazole have been realized by the group of Dai, utilizing HBr/DMSO as the bromination reagent (Scheme 36).[53] The selectivity of mono- and di-bromination of pyrroles was dependent on the substituents on the pyrrolic ring. For example, the presence of methyl and ethyl groups at the N-1 position facilitated the di-bromination. The *in situ*-formed bromodimethylsulfonium bromide was proposed as the key brominating reagent.



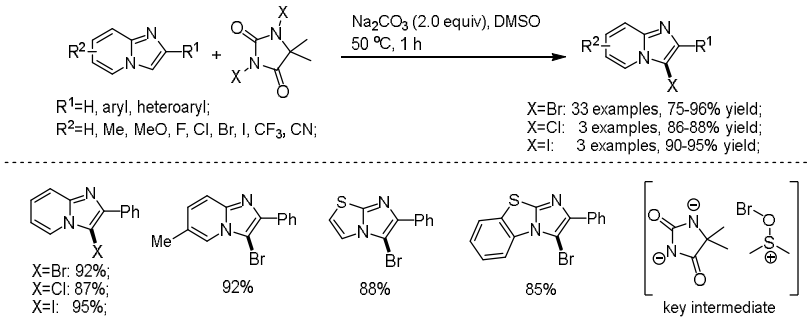
Scheme 36. Bromination of pyrroles with HBr/DMSO reaction system.

Jiao and co-workers established an efficient and practical halogenation system with DMSO/HX for halogenation of heteroarenes (Scheme 37).[54] It is noteworthy noted that only 1.2 equivalents of DMSO/HBr were used in most cases. Various heterocyclic compounds could be tolerated, including indole, 7-azaindole, indazole, pyrazole, pyrimidazole, 1,7-diazaindolizine, thiophene, benzothiophene, benzofuran (26 examples, 49-99% yield). Notably, late-stage functionalization of natural products and drugs such as (+)-δ-Tocopherol, Xanthotoxin, Esermethole, Desoxyeseroline, and Sinomenine by bromination were achieved with good compatibility of a range of functional groups. Iodination of heteroarenes could also be accomplished with ammonium iodate as iodine source (5 examples, 72-98% yield). On the basis of the experimental results, the authors proposed that *in situ*-generated X_2 or $DMS{\cdot}X_2$ might be the real halogenation reagent and DMSO served as an oxidant in the system.



Scheme 37. Halogenation of heterocycles with HX/DMSO/EtOAc.

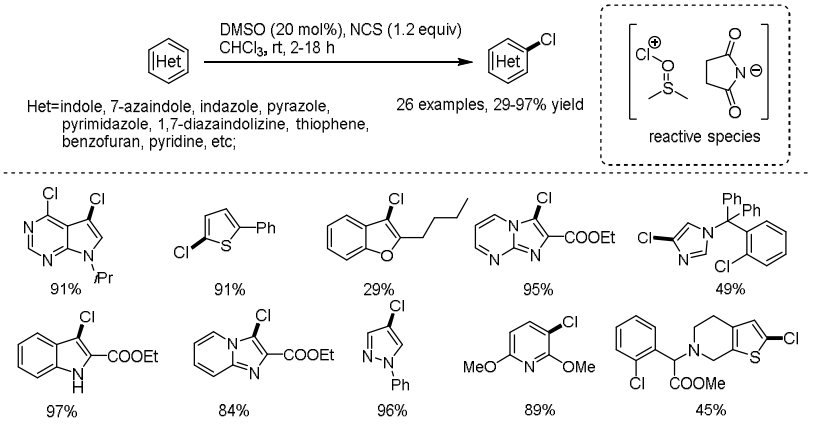
Jiang and Gui developed a convenient halogenation of imidazo[1,2-*a*]pyridines with DXDMH (X=Cl, Br and I) with DMSO as a solvent and an oxidant (Scheme 38).[55] A wide range of imidazo[1,2-*a*]pyridines, regardless of the presence of electron-rich and electron-deficient substituents, could be readily brominated (33 examples, 75-96% yield). Chlorination and iodination could also be achieved using suitable halogenation source. Bromosulfoxonium cation and dimethylhydantoin counteranion were proposed to be the key intermediates for this bromination process.



Scheme 38. Halogenation of imidazo[1,2-*a*]pyridines with DXDMH (X=Cl, Br and I)/DMSO.

Chlorination can be used for modification of bioactive molecules by changing the physiological properties and improving the pharmacokinetic and pharmacological profiles. The Jiao's group successfully chlorinated a wide range of heteroarenes as well as complex natural products, drugs and peptides through a DMSO-catalyzed late-stage aromatic chlorination (Scheme 39, 26 examples, 29-97% yield).[56]

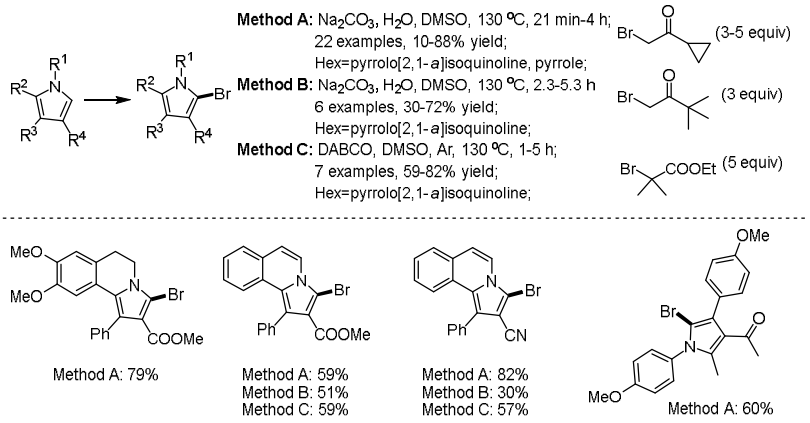
Various heteroarenes including indole, 7-azaindole, indazole, pyrazole, pyrimidazole, 1,7-diazaindolizine, thiophene, benzofuran, and pyridines could be used. In contrast, only trace to very little amount of chlorinated products can be detected in the absence of DMSO. *N*-chlorosuccinimide as chloro source could be activated by DMSO to form active Cl^+ species. This process features mild reaction conditions, good functional group compatibility, and easy-availability and stability of catalyst and reagents.



Scheme 39. DMSO-catalyzed late-stage aromatic chlorination.

Cui and co-workers realized the functionalization of a series of pyrrolo[2,1-*a*]isoquinolines and pyrroles using the combination of 2-bromo-1-cyclopropylethan-1-one and dimethylsulfoxide as brominating reagent (Scheme 40).

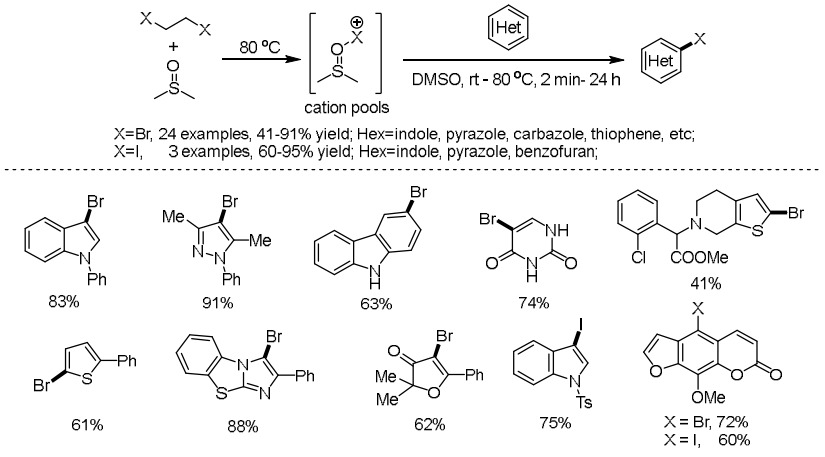
A range of pyrrolo[2,1-*a*]isoquinolines and pyrroles were successfully brominated (22 examples, 10-88% yield).[39,57] It was found that 1-bromo-3,3-dimethylbutan-2-one and ethyl 3-bromo-3-methyl-2-oxobutanoate could also be used as bromine source. It should be noted that the formylation products would be formed if using electron-rich pyrrolo[2,1-*a*]isoquinolines under a ethyl bromoisobutyrate/DMSO system. The chemoselectivity was controlled by the structure of the substrates.



Scheme 40. DMSO-based bromination of pyrrolo[2,1-*a*]isoquinolines.

Although the combination of MeI/DMSO has always been used as alkylation reagent, 1,2-dihaloethanes can be used for halogenation in the presence of DMSO surprisingly. The Panda's group established an efficient halogenation of heteroarenes through a halogen cation pools strategy (Scheme 41).[58] A DMSO-stabilized cation pools could be generated *in situ* using 1,2-dihaloethanes as halogen source. Monohalogenation could be realized by performing the reaction at room temperature. However, polyhalogenation would be achieved by raising the reaction temperature. It is worthy noted that this process could be expanded to the late stage functionalization of commonly marketed drugs by halogenation.

Heteroarenes such as indole, pyrazole, carbazole, thiophene as well as xanthotoxin and clopidogrel were all compatible in this system, giving the corresponding products in moderate to excellent yields (X=Br, 24 examples, 41-91% yield; X=I, 3 examples, 60-95% yield). The halogenation of arenes could also be achieved under the current reaction system.



Scheme 41. Halogenation of heteroarenes with 1,2-dihaloethane/DMSO.

Conclusion

By the logical design of DMSO-based reaction systems, various functional groups including CH, CH_2, CH_3, SCH_3, CH_2SCH_3, $SOCH_3$ and CHO have been readily incorporated into heterocycles, providing structurally diverse molecules. DMSO has been widely used in these organic reactions as carbon source, oxygen source and sulfur source as well as solvent. Besides, DMSO has also played an important role in some other transformations by oxidation of organic halides to aldehydes through Kornblum oxidation, oxidation of alcohols to aldehyde and oxidation of organic halide to generate positive halogenation species. Furthermore, DMSO can be even applied as catalyst for chlorination reaction of numerous heteroarenes by activating *N*-chlorosuccinimide to *in situ* generate active Cl^+ species.

Although great achievements have been made in the field of DMSO-based organic synthesis, improvements are expected in future studies. 1) Since stoichiometric amounts of activators are needed in most cases, too many chemical wastes are produced. Considering this situation, catalytic version of DMSO activation would be an attractive alternative. Though several catalytic DMSO-based transformations involving Ru, Ag, Cu, Pd or Fe catalysis have been developed, this research field is far less explored and more efforts should be paid in the future. 2) As one of the significant advantages of DMSO-based reaction systems is its flexibility, more selective reaction systems can be designed. The change of only one parameter may successfully provide different products. This strategy has already been used in the modification of pyrrolo[2,1-*a*]isoquinolines. The types of activators, the amount of activator, reaction temperature and the additives all have significant influence on the layout of products. 3) More heterocycles, especially privileged frameworks and core-structures of important natural products and drugs, should be utilized in the DMSO-based modification systems. This may be an easy, rapid and low-cost way for providing useful molecules with potential applications. Additionally, the established DMSO-involved reaction systems might inspire chemists for logical design of new chemistry of sulfoxides.[59]

The combination of new science and technology would also be a hopeful way for DMSO-based methodology development. For example, photo-induced and electrochemical transformations would provide more unprecedented organic reactions. Several outstanding reports through this strategy have realized amazing functionalization under mild reaction conditions. More wonderful and exciting breakthroughs are expected in the future.

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