

Review

Recent Uses of *N,N*-Dimethylformamide and *N,N*-Dimethylacetamide as Reagents

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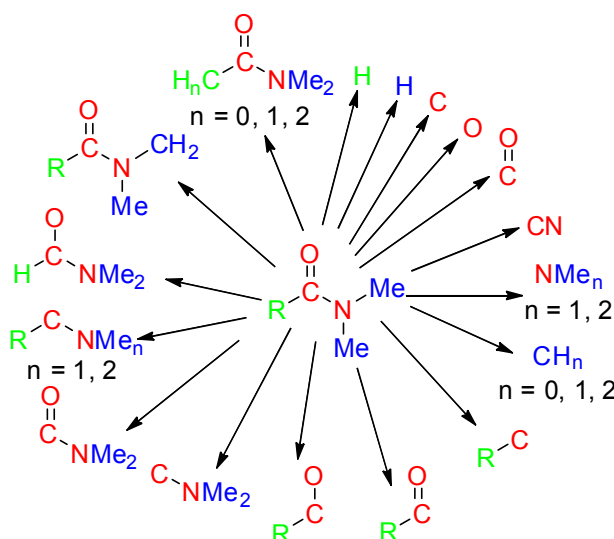


Abstract: *N,N*-Dimethylformamide and *N,N*-dimethylacetamide are multipurpose reagents which deliver their own H, C, N and O atoms for the synthesis of a variety of compounds under a number of different experimental conditions. The review mainly highlights the corresponding literature published over the last years.

Keywords: *N,N*-dimethylformamide; DMF; *N,N*-dimethylacetamide; DMAc; amination; amidation; thioamidation; formylation; carbonylation; cyanation; insertion; cyclization

1. Introduction

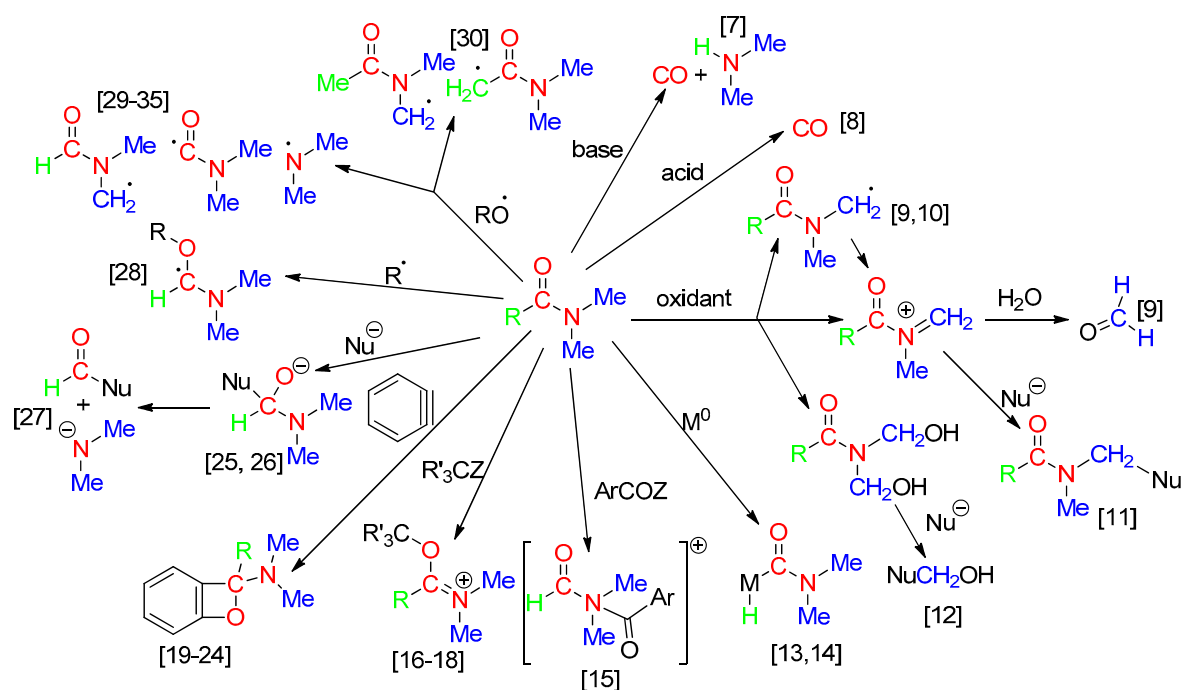
The organic, organometallic and bioorganic transformations are extensively carried out in *N,N*-dimethylformamide (DMF) or *N,N*-dimethylacetamide (DMAc). These two polar solvents are not only use for their dissolution properties, but also as multipurpose reagents. They participate in a number of processes and serve as a source of various building blocks giving one or more of their own atoms (Scheme 1).



Scheme 1. Fragments from DM (R = H or Me) used in synthesis.

In 2009, one of us reviewed the different roles of DMF, highlighting that DMF is much more than a solvent [1]. Subsequently, this topic has been documented by the teams of Jiao [2] and Sing [3].

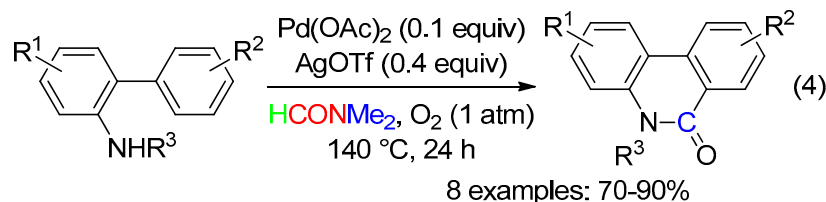
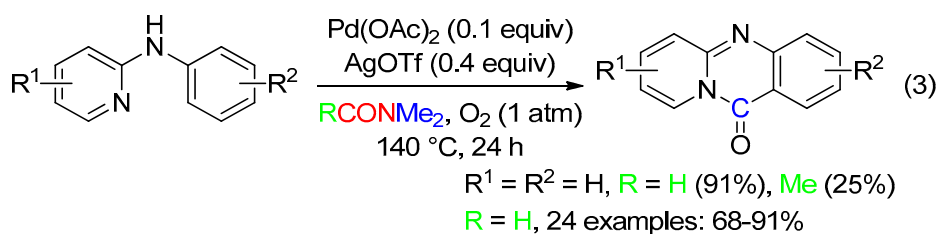
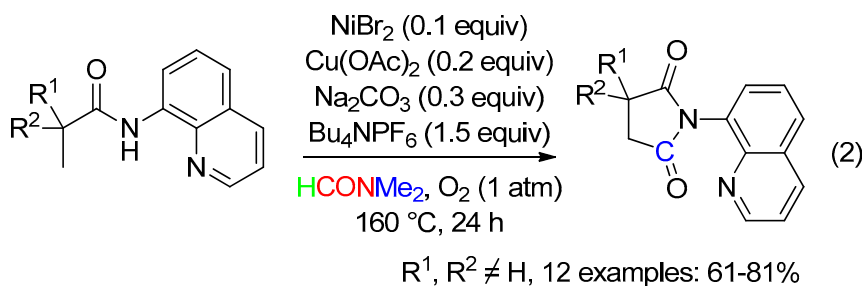
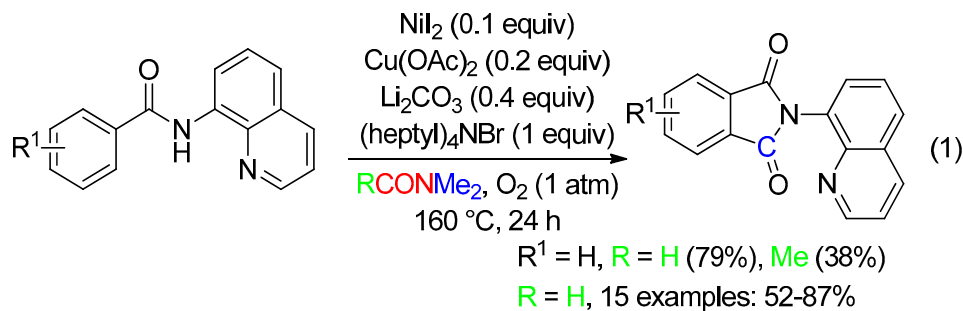
For of a book devoted to solvents as reagents in organic synthesis, we wrote a chapter summarizing the reactions consuming DMF and DMAc as carbon, hydrogen, nitrogen and/or oxygen sources [4]. This book chapter tentatively covered the literature up to middle 2015. The present mini-review focuses on recent reactions which involve DM (DM = DMF or DMAc) as a reagent although some key older papers are also included for context. Processes which necessitate the prerequisite synthesis of DM derivatives such as the Vilsmeier-Haack reagents [5] and DMF dimethyl acetal [6] are not surveyed, but a few reactions of the present review involve the in-situ formation of a Vilsmeier-type intermediate (Vilsmeier-type reagents have been extensively used. Search on 26 June 2018 for “Vilsmeier” with SciFinder led to 4379 entries). Color equations, based on literature proposals, are used to easily visualize the DM atom origin. When uncertainty is expressed by the authors or suspected by us, the atom is typed in *italic>*. Mechanistic schemes are not reported, but Scheme 2 [7–35] summarizes different proposed reactions of DM with the corresponding literature references, where DM acts as either a nucleophilic or electrophilic reagent, or leads to neutral, ionic or radical species. The review is divided in Sections depending on the DM fragment(s) which is (are) incorporated into the reaction product.



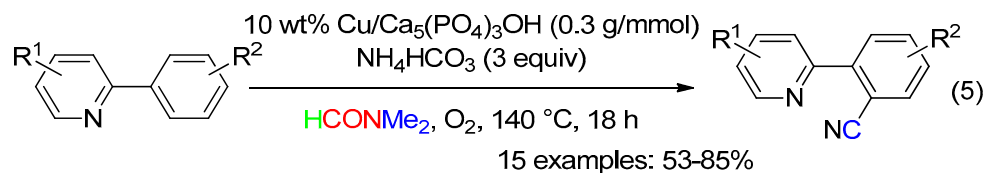
Scheme 2. Reactions of DM (R = H or Me).

2. C Fragment

Aerobic carbonylation under nickel/copper or palladium/silver synergistic catalysis occurred efficiently using the Me group of DMF as the C source, affording cyclic carbonylated compounds, via the directing group-assisted activation of a C(sp²)-H or C(sp³)-H bond (Equations (1) and (2) [36], Equations (3) and (4) [37]). Shifting from DMF to DMAc greatly decreased the yields (Equations (1) and (3)).

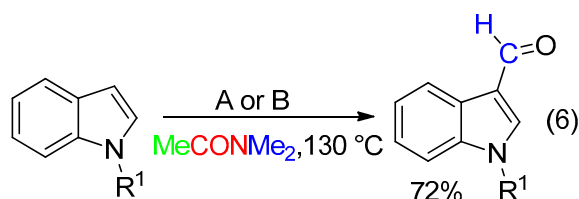


The Me group of DMF was also involved in the cyanation of the C(sp²)-H bond of arenes catalyzed with an heterogeneous copper catalyst (Equation (5)) [38].



3. CH Fragment

Treatment of indole at 130 °C with supraprostoichiometric amounts of CuI, *t*-BuOOH and AcOH in DMAc under air afforded the corresponding C3-formylation product (Equation (6)) [39]. Such a reaction also occurred with *N*-methylindole using CuI and CF₃CO₂H in DMAc under oxygen [40]. The CH fragment came from the NMe₂ moiety [39,40]. In DMF, both procedures led to C3-cyanation (see below, Equation (25)).



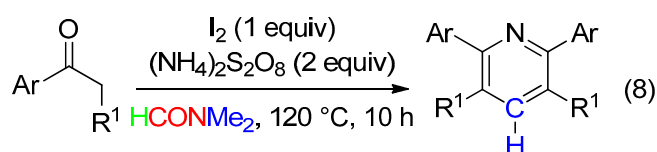
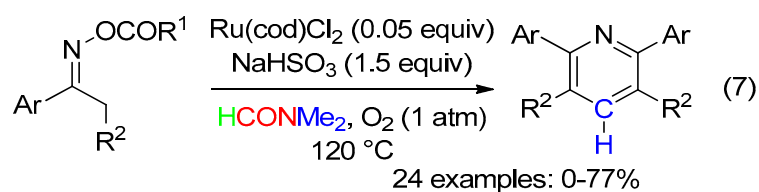
A. R¹ = H; CuI (1.2 equiv), *t*-BuOOH (2 equiv),

AcOH (8 equiv), air, 48 h: 72%

B. R¹ = Me; CuI (1 equiv), CF₃CO₂H (1.2 equiv)

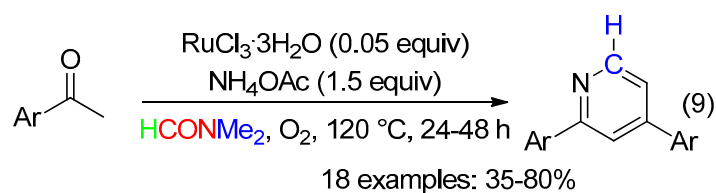
O₂ (1 atm), 36 h: 42%

Cycloadditions leading to symmetrical tetrasubstituted pyridines using the Me group of DMF as the CH source have been carried out using either ketoxime carboxylates with Ru catalysis (Equation (7)) [41], or arones with both iodine and ammonium persulfate mediation (Equation (8)) [42].



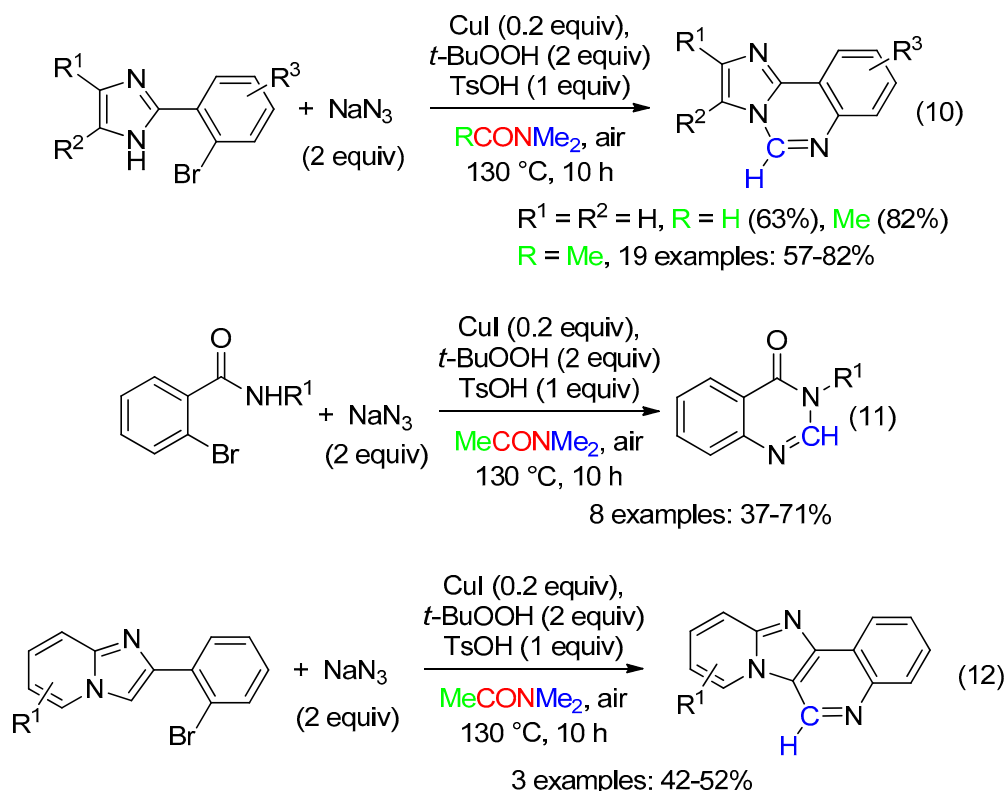
15 examples: 71-89%

2,4-Diarylpyridines were also synthesized from Ru-catalyzed reaction of acetophenones with ammonium acetate and DMF as source of the N and CH atoms, respectively (Equation (9)) [43].

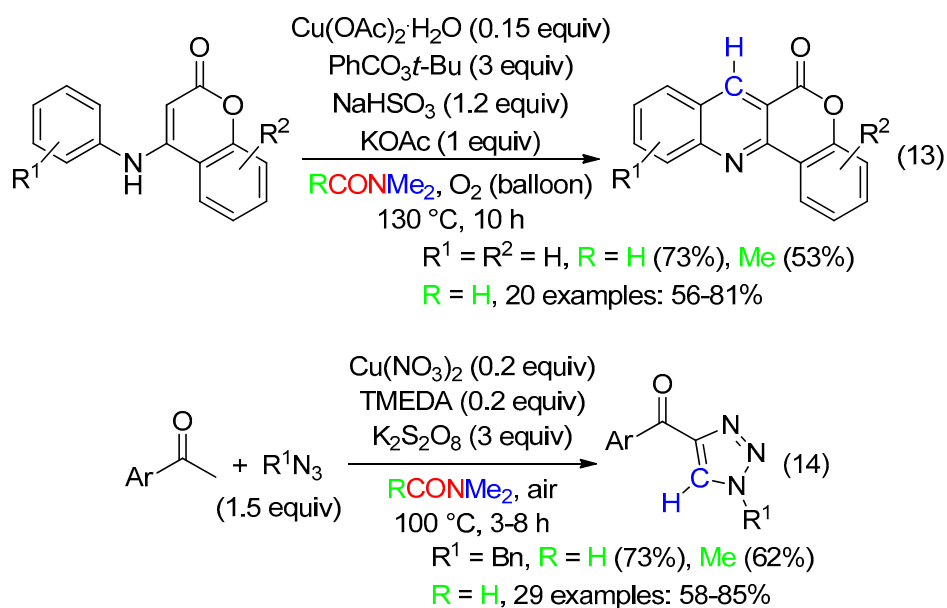


18 examples: 35-80%

With sodium azide as the nitrogen source, DMAc was superior to DMF to deliver the CH fragment of the copper-catalyzed domino reactions of aryl halides which led to imidazo [1,2-*c*]quinazolines, quinazolinones or imidazo[4,5-*c*]quinolones (Equations (10)–(12)) [44].

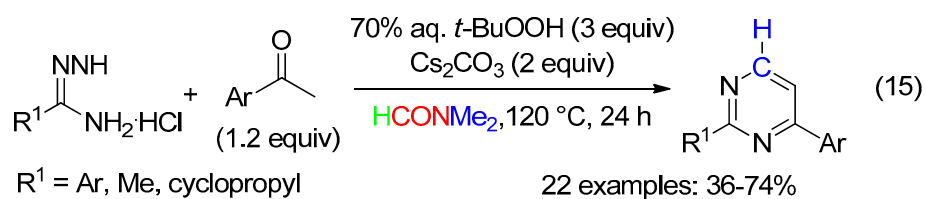


In contrast to the above examples, the Cu-catalyzed cyclization leading to 6*H*-chromeno[4,3-*b*]quinolin-6-ones (Equation (13)) with incorporation of a CH belonging to DMF occurred with low yield when *t*-BuOOH was the oxidant. Shifting to *t*-butyl perbenzoate allowed an effective reaction [45]. For the synthesis of 4-acyl-1,2,3-triazoles from Cu-catalyzed cycloaddition to acetophenones (Equation (14)), K₂S₂O₈ was superior to *t*-BuOOH, (*t*-BuO)₂ and (PhCO₂)₂ [46]. Yields decreased with DMAc instead of DMF (Equations (13) and (14)).

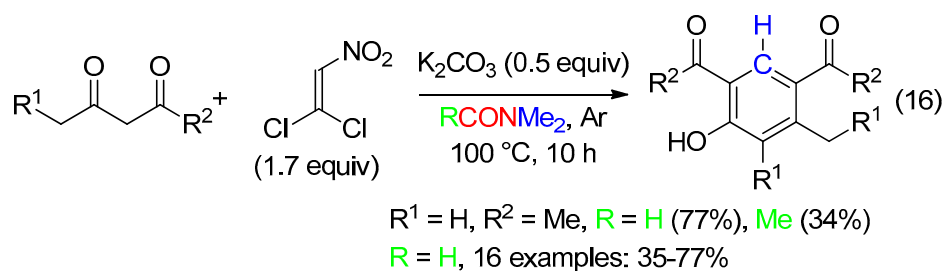


The insertion of a CH from the NMe₂ of DMF under metal-free conditions has been reported for the synthesis of cyclic compounds such as:

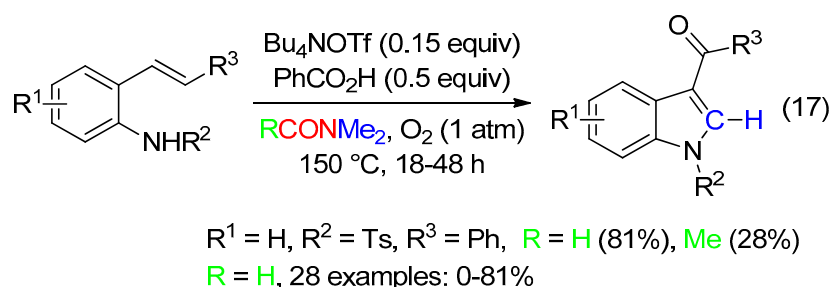
- pyrimidines from *t*-BuOOH-mediated reaction between acetophenones, amidines and DMF (Equation (15)) [47],



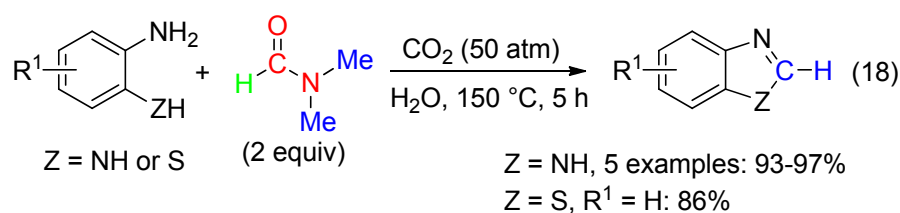
- substituted phenols also from three components cycloadditions (Equation (16)) [48],



- 3-acylindoles from 2-alkenylanilines (Equation (17)) [49],

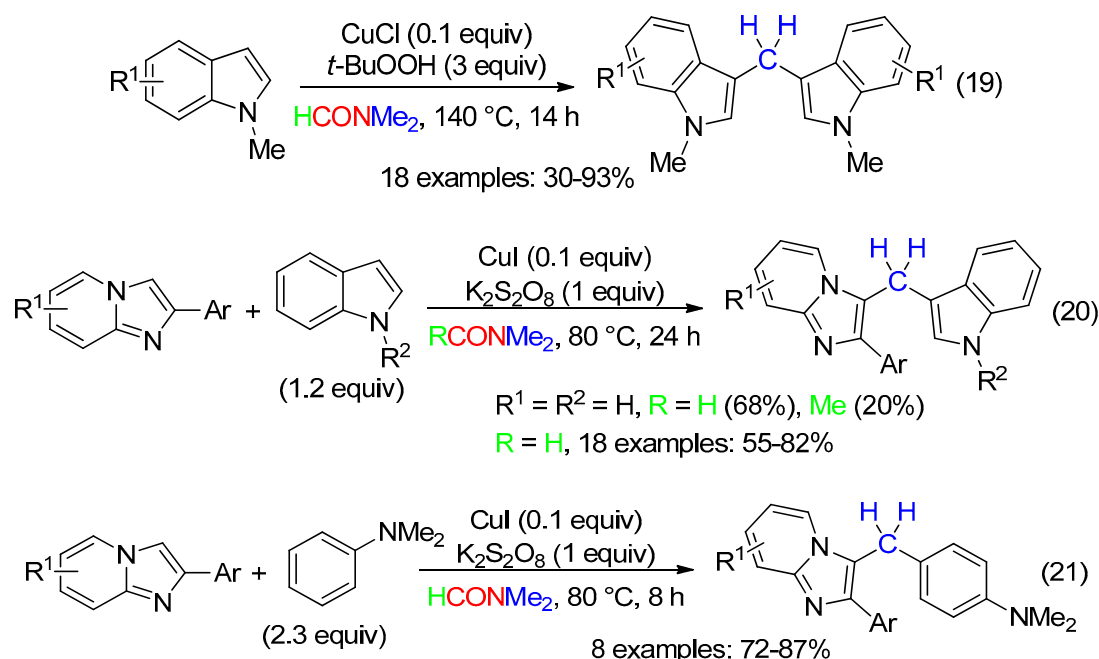


- benzimidazoles and benzothiazole from *o*-phenylenediamine or 2-aminobenzenethiol through carbon dioxide-mediated cyclization (Equation (18)) [50].

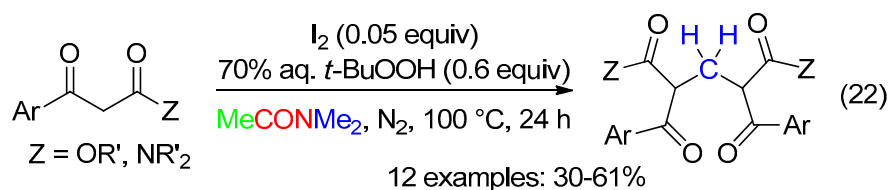


4. CH₂ Fragment

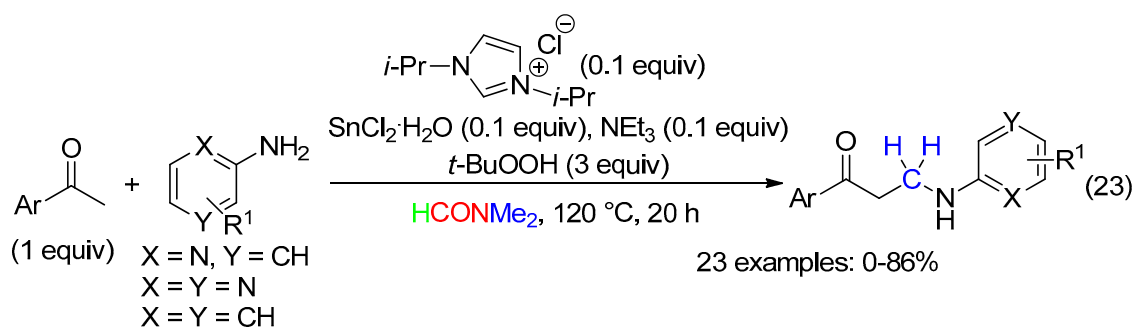
The coupling of indoles or imidazo[1,2-*a*]pyridines to afford heterodiarlylmethanes with DMF as the methylenating reagent occurred in fair to high yields with a Cu^I catalyst associated to *t*-BuOOH [51] or K₂S₂O₈ [52] (Equations (19)–(21)). Use of DMAc was less efficient.



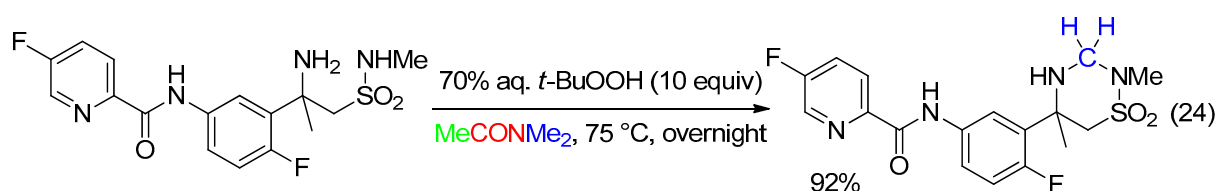
In DMAc, the $I_2/t\text{-BuOOH}$ association catalyzed the formation of methylene-bridged bis-1,3-dicarbonyl compounds from aryl β -ketoesters or β -ketoamides (Equation (22)). Lower yields were obtained with $I_2/K_2S_2O_8$ in DMAc or DMF [9]. Subjection 1,3-diphenylpropane-1,3-dione or ethyl 3-oxobutanoate to the $I_2/t\text{-BuOOH}/\text{DMAc}$ did not afford the bridged compounds.



A Mannich reaction leading to β -amino ketones with DMF as the formaldehyde source has been reported in the presence of $t\text{-BuOOH}$ and catalytic amounts of an N -heterocyclic carbene, SnCl_2 and NEt_3 (Equation (23)) [11].

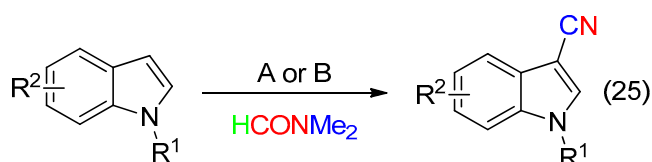


The study of an unexpected reaction due to the oxidation of DMAc with aqueous $t\text{-BuOOH}$ (Equation (24)) showed the formation of $\text{MeCONMe}(\text{CH}_2\text{OH})$ and $\text{MeCON}(\text{CH}_2\text{OH})_2$, these unusual species delivering the methylene group [12].

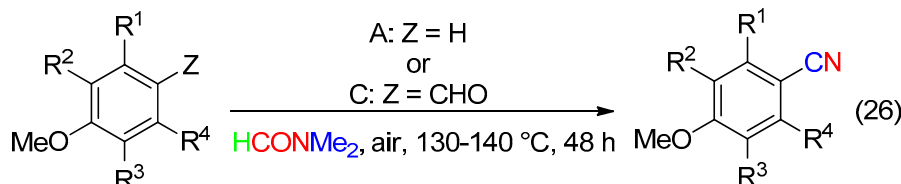


5. NC Fragment

While CuI under oxidative and acidic conditions led, in DMAc, to the C3-formylation of indole and *N*-methylindole (Equation (6)), reactions in DMF led to C3-cyanations (Equation (25)) [39,40]. Cyanation of electron-rich arenes and benzaldehydes was also carried out (Equation (26)) [39]. Monitoring the course of the reaction indicated a cyanation arising via the formyl compounds [39,40]. Moreover, 3-iodo indole could also be involved in the formation of the cyano product [40].

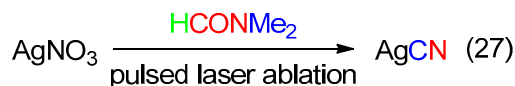


- A. $R^1 = \text{H}$; CuI (1.2 equiv), *t*-BuOOH (2 equiv), AcOH (4 equiv), air, 120–130 °C, 48 h; 15 examples: 30–86%
- B. $R^1 = \text{Me}$; CuI (1 equiv), $\text{CF}_3\text{CO}_2\text{H}$ (1.2 equiv), O_2 (1 atm), 130–150 °C, 36–96 h; 15 examples: 25–90%



- A. CuI (1.2 equiv), *t*-BuOOH (2 equiv), AcOH (4 equiv)
 $R^1 = R^4 = \text{OMe}$, $R^2 = R^3 = \text{H}$: 80%; $R^1 = \text{Me}$, $R^2 = \text{H}$, $R^3 = R^4 = \text{OMe}$: 35%;
 $R^1 = R^2 = R^3 = \text{H}$, $R^4 = \text{OMe}$: 51%
- C. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 equiv), *t*-BuOOH (2 equiv), AcOH (8 equiv)
 $R^1 = R^2 = R^3 = R^4 = \text{H}$: 70%; $R^1 = R^4 = \text{H}$, $R^2 = R^3 = \text{OMe}$: 90%

Laser ablation of silver nitrate in DMF led to silver cyanide (Equation (27)) [53].

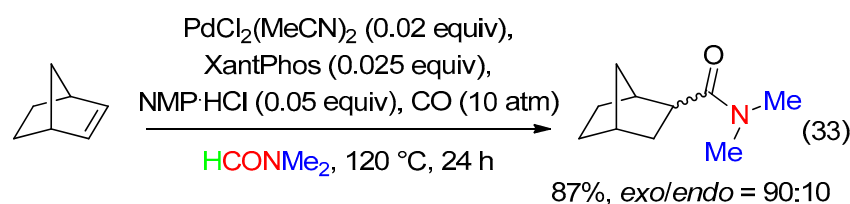
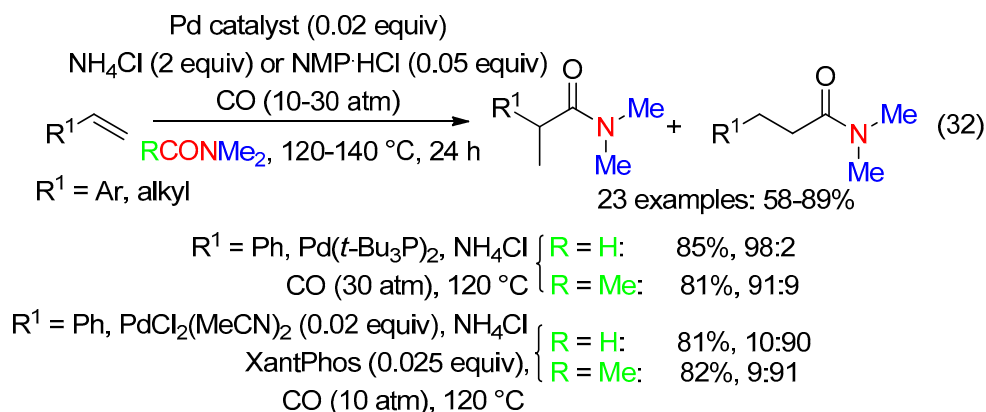


6. NMe₂ Fragment

This chapter is divided in sections corresponding to the type of function reacting with DM.

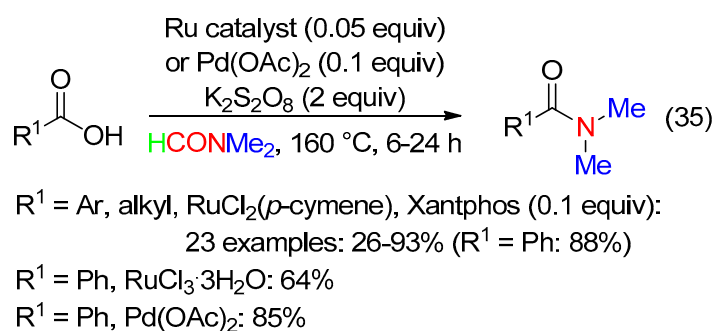
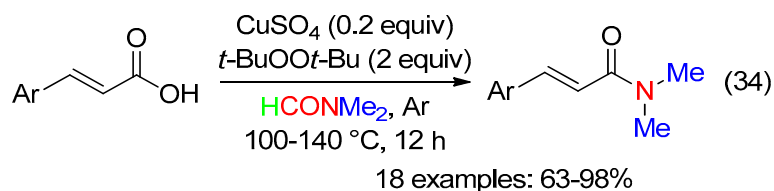
6.1. Aryl Halides

Refluxing chloropyridines in DM or DMAc afforded the corresponding aminopyridines (Equation (28)) [25]. The amination of aryl chlorides and 3-pyridinyl chloride with DMF occurred at room temperature in the presence of potassium *t*-butoxide and a carbenic palladium catalyst (Equation (29)) [27].



6.4. Acids

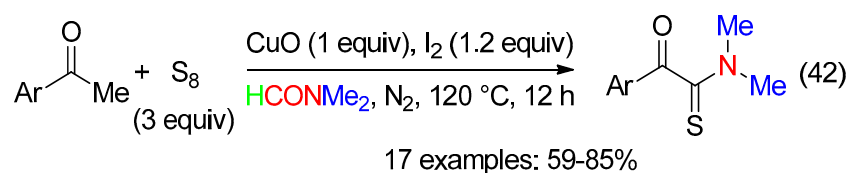
Copper, palladium and ruthenium catalysts associated to oxidants and DMF were used for the amidation of cinnamic acids [29] and carboxylic acids [55] (Equations (34) and (35)). *N,N*-Dimethylbenzamide was one of the products obtained from the Cu^{II}-catalyzed oxidation of flavonol [56].



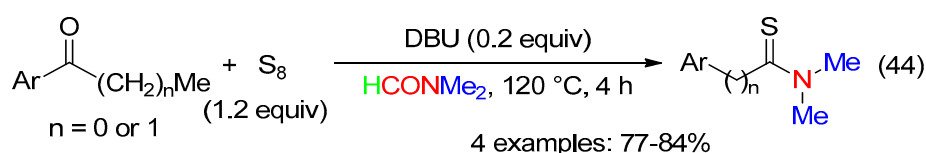
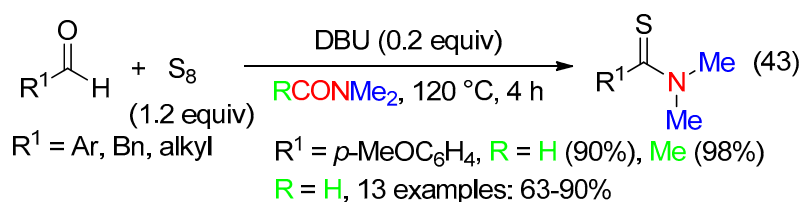
Metal-free conditions and DMF were used for:

- the amidation of acids promoted with propylphosphonic anhydride associated to HCl at 130 °C (Equation (36)) [15],
- the amination of acids employing a hypervalent iodine reagent at room temperature (Equation (37)) [35]. Mesityliodine diacetate was superior to the other hypervalent iodine reagents, while oxidants such as I₂, *t*-BuOOH, NaIO₄ or K₂S₂O₈ did not mediate the amidation reaction [35].

Copper oxide and iodine mediated the reaction of acetophenones with sulfur and DMF to afford α -arylketothioamides (Equation (42)) via the formation of α -iodoacetophenones [59].

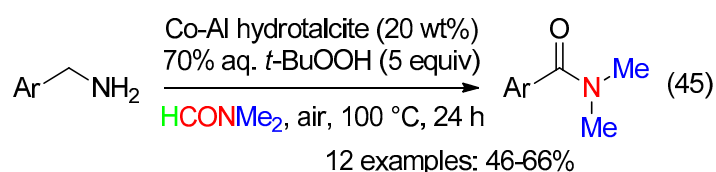


Elemental sulfur and the NMe₂ moiety of DMF or DMAc was also used for the DBU-promoted synthesis of thioamides from aldehydes (Equation (43)) or arones (Equation (44)) [60], the latter undergoing an efficient Willgerodt-Kindler reaction [61,62].



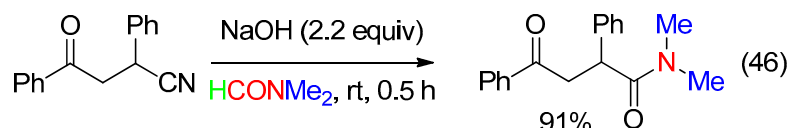
6.6. Benzyl Amines

The recyclable Co/Al catalysts used above in DMF for the amidation of benzaldehydes also led to benzamides from benzylamines and *t*-BuOOH (Equation (45)). These transformations would involve benzaldehydes as intermediates [58].



6.7. Nitriles

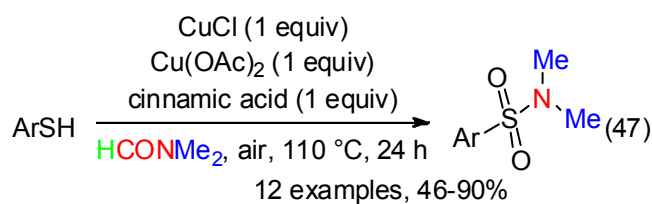
NaOH mediated, at room temperature, the efficient reaction of the CN group of 4-oxo-2,4-diphenylbutanenitrile with DMF to afford the corresponding γ -ketoamide (Equation (46)) [63]. Such compounds were also obtained from the domino reaction of chalcones with malononitrile and NaOH in DMF [63].



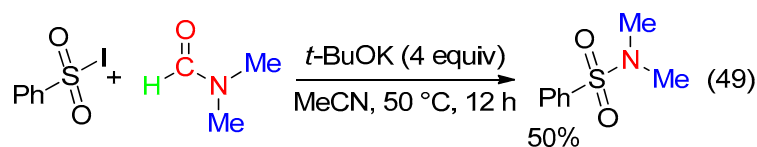
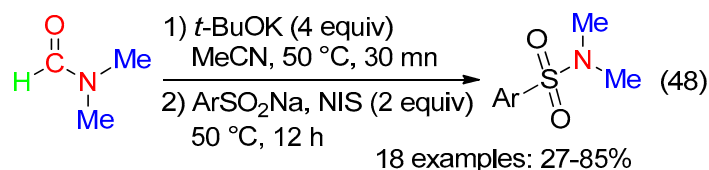
6.8. Sulfur Compounds

Sulfonamides were synthesized:

- from thiophenols, DMF and air via an oxygen-activated radical process mediated by copper salts and cinnamic acid (Equation (47)) [64],

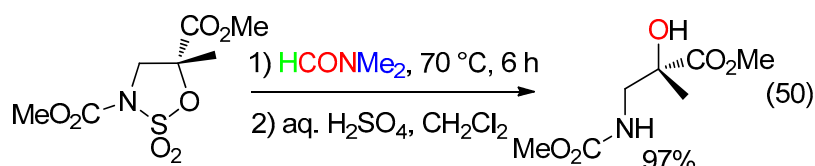


or reaction of sodium sulfonates with *N*-iodosuccinimide and DMF pretreated with *t*-BuOK (Equation (48)) via, probably, sulfonyl iodides (Equation (49)) [65].

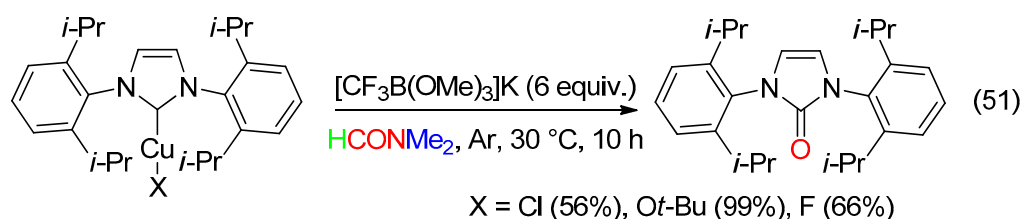


7. O Fragment

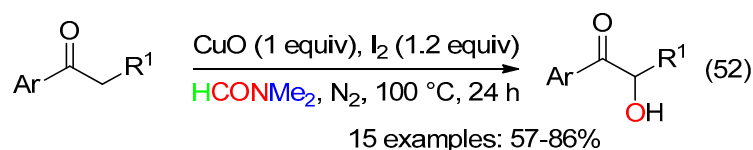
DMF delivered its oxygen atom to 1,2-cyclic sulfamidates via nucleophilic displacement at the quaternary center to afford, after hydrolysis, an aminoalcohol (Equation (50)) [17].



DMF was also the oxygen source leading to an imidazolinone from the reaction with the Cu-carbene complex and the borate salt depicted in Equation (51) [66].



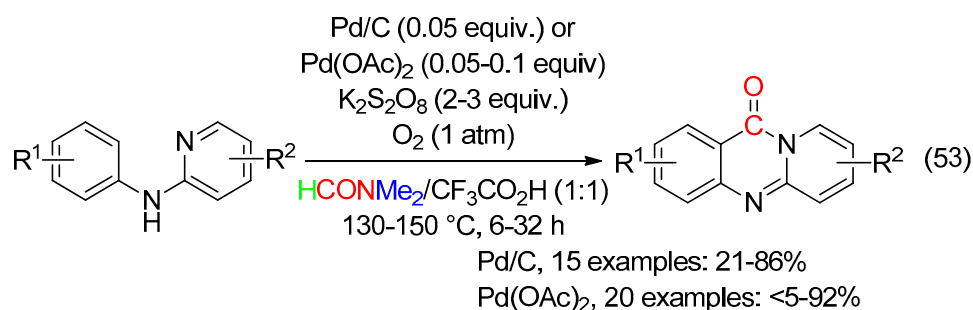
The I₂/CuO association allowed the α-hydroxylation of arones in abstracting, via the α-iodoarone, the oxygen atom of DMF (Equation (52)) [18].



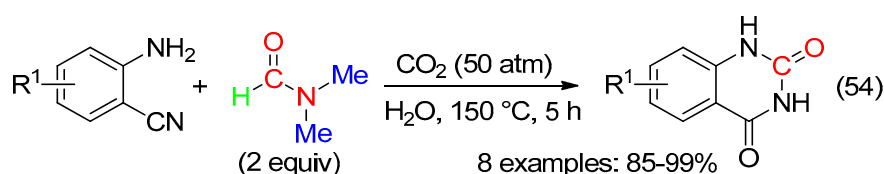
8. C=O Fragment

With DMF as the CO surrogate, quinazolinones have been prepared at 140–150 °C

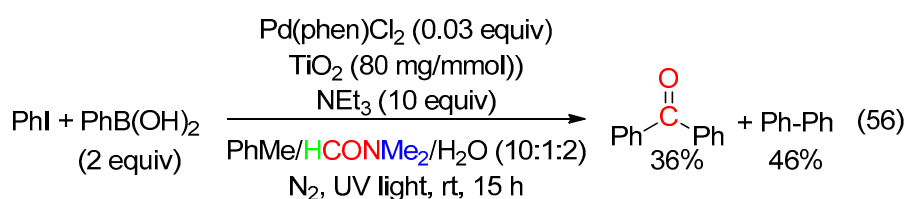
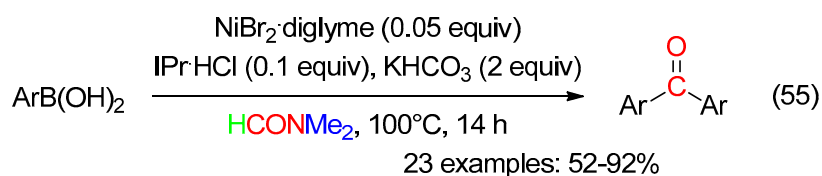
- via C(sp²)-H bond activation and annulation using Pd/C [67] or Pd(OAc)₂ [8], in the presence of K₂S₂O₈, CF₃CO₂H and O₂ (Equation (53)),



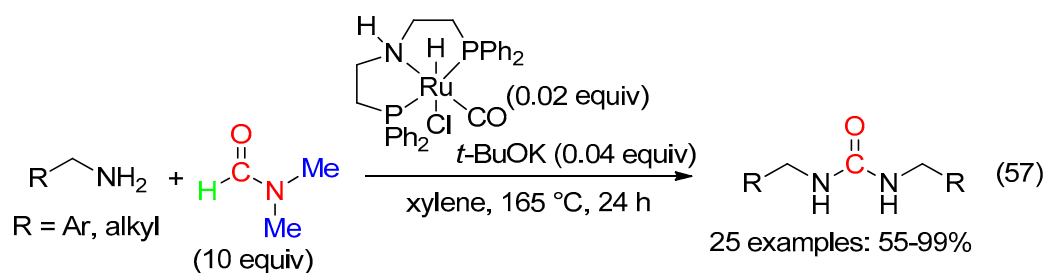
or carbon dioxide-mediated cyclization of 2-aminobenzonitrile (Equation (54)) [50]. This latter reaction would involve a Vilsmeier-Haack type intermediate and did not occur with DMAc.

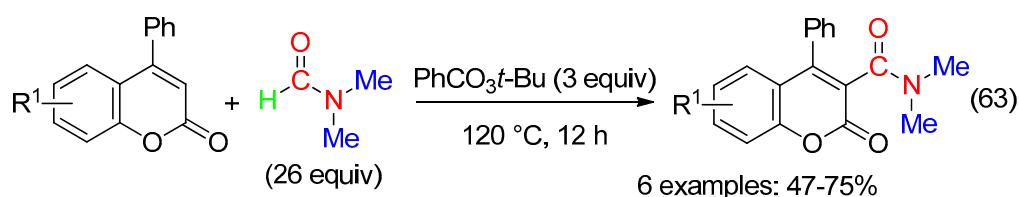


A carbonylative Suzuki-type reaction leading to diarylketones arose in DMF under Ni catalysis at 100 °C (Equation (55)), IPr = bis(2,6-diisopropylphenyl)imidazol-2-ylidene [13], or Pd catalysis and UV light assistance at room temperature (Equation (56)) [68].

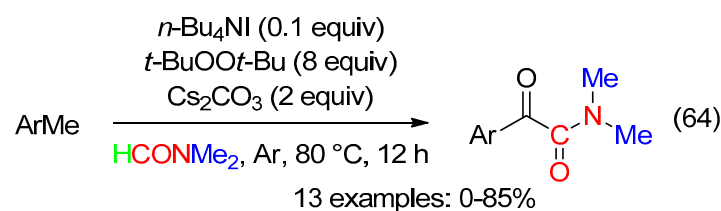


Catalytic amounts of a ruthenium pincer complex and *t*-BuOK led, at 165 °C, to symmetric and unsymmetric *N,N'*-disubstituted ureas from primary amines and DMF (Equation (57)) [69].

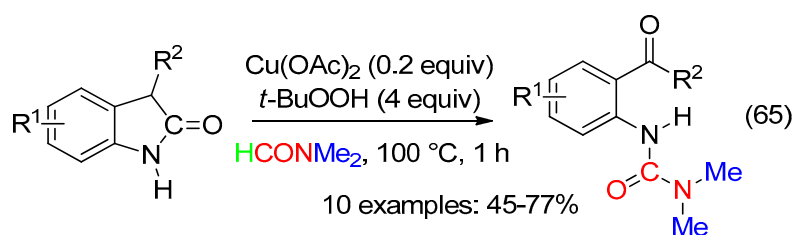




α -Ketoamides were obtained from the domino reaction of toluenes with DMF using $(t\text{-BuO})_2$, Cs_2CO_3 and catalytic amounts of $n\text{-Bu}_4\text{NI}$ (Equation (64)) [75].

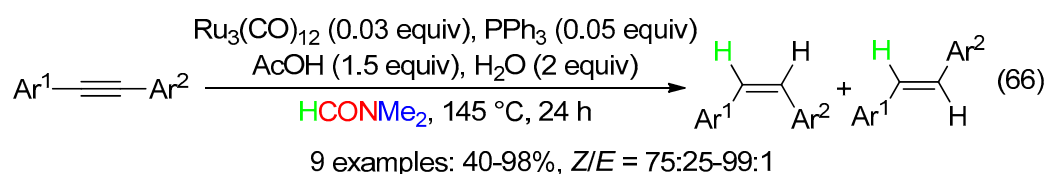


At 100 °C in DMF, Cu catalyst associated to $t\text{-BuOOH}$ led to unsymmetrical ureas from 2-oxindoles (Equation (65)) [76]. The peroxide would mediate the cleavage reaction, and was the oxygen source of the benzylic carbonyl. That resulted in a ketoamine which undergone the Cu-catalyzed reaction with DMF/ $t\text{-BuOOH}$, leading to the urea.

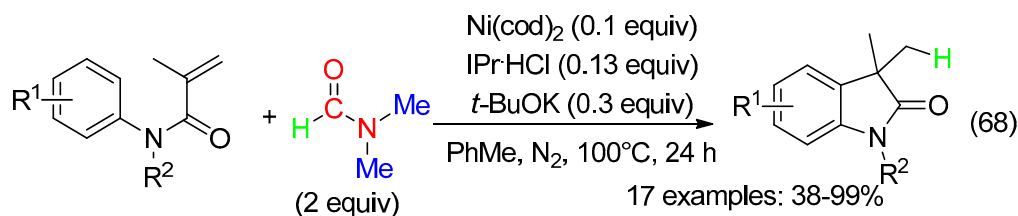
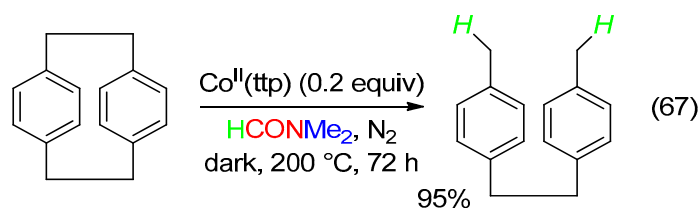


10. H Fragment

Semihydrogenation of diaryl alkynes occurred under Ru (Equation (66)) [77] and Pd [78] catalysis with DMF and water as hydrogen source.

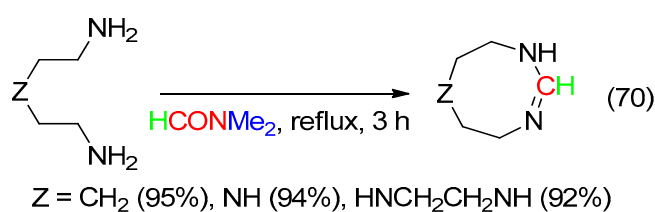
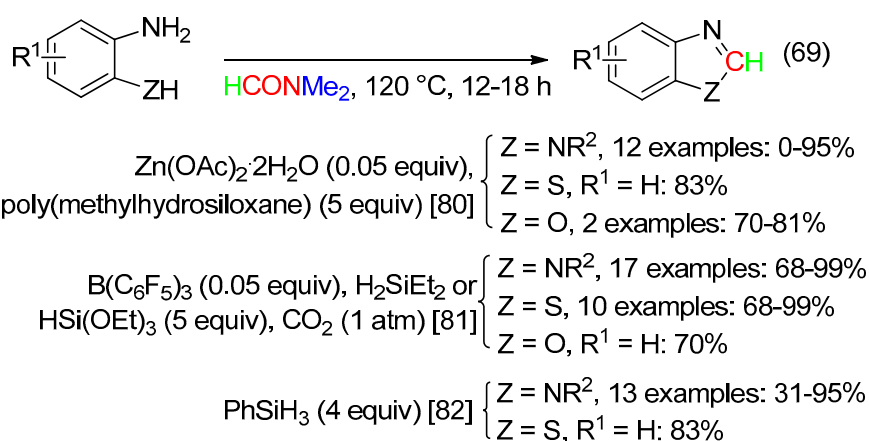


Cobalt porphyrins catalyzed the hydrogenation transfer from DMF to the $\text{C}(\text{sp}^3)\text{-C}(\text{sp}^3)$ bond of [2.2]paracyclophane (Equation (67)) [79]. DMF was also involved in the Ni-catalyzed intramolecular hydroarylations depicted in Equation (68) [14].

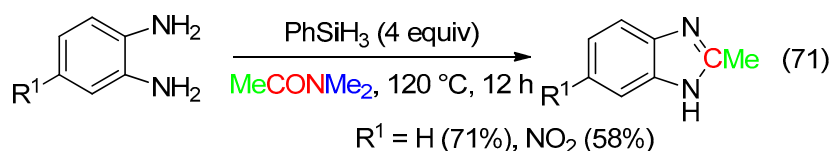


11. RC Fragment

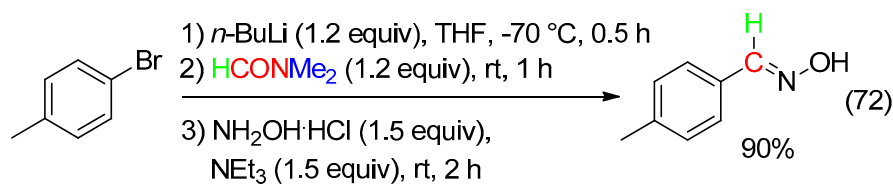
New metal-catalyzed and metal-free conditions involving the CH of the formyl group of DMF have been reported for cyclizations leading to heterocycles (Equations (69) [80–82] and (70) [83]).



2-Methylbenzimidazoles were obtained from PhSiH₃-assisted delivery of the CMe of DMAc to benzene-1,2-diamines (Equation (71)) [82].

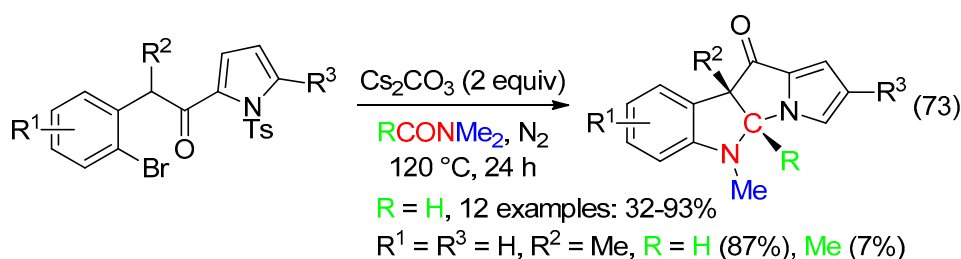


Addition of *p*-tolyllithium to DMF followed by reaction with hydroxylamine hydrochloride afforded 4-methylbenzaldehyde oxime (Equation (72)). The latter underwent cycloaddition with diphenylphosphoryl azide or, in the presence of Oxone[®], with diethylacetylene dicarboxylate to provide the corresponding 5-aryltetrazole or 3-arylisoxazole, respectively [84].



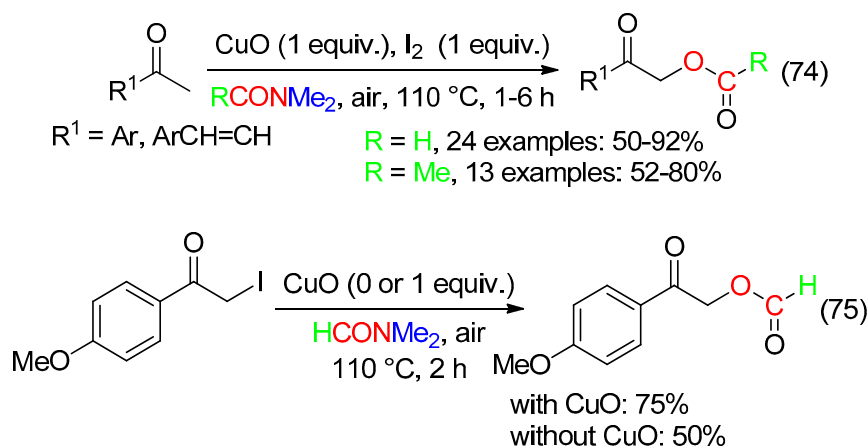
12. RCNMe₂ Fragment

Dihydropyrrolizino[3,2-*b*]indol-10-ones were isolated in fair to high yields from a Cs₂CO₃-promoted domino reaction leading to the formation of three bonds with incorporation of the HCNMe of DMF. Such a reaction-type with incorporation of the MeCNMe also occurred in DMAc but with a low yield (Equation (73)) [26].

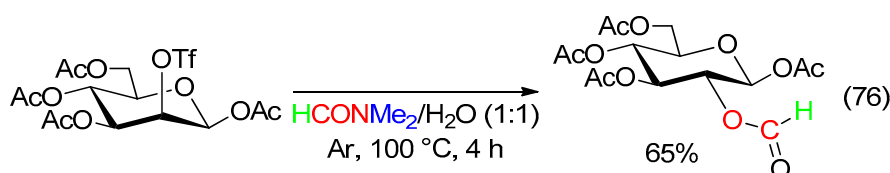


13. RC-O Fragment

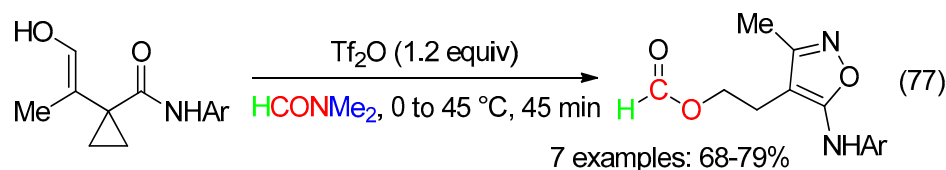
A 1:1 mixture of CuO and I₂ led the α-formyloxylation or α-acetoxylation of methylketones by DMF or DMAc, respectively (Equation (74)). α-Iodoketones would be the intermediates as indicated by the reaction of 2-iodo-1-(4-methoxyphenyl)ethanone (Equation (75)). Traces of water delivered the carbonyl oxygen [16].



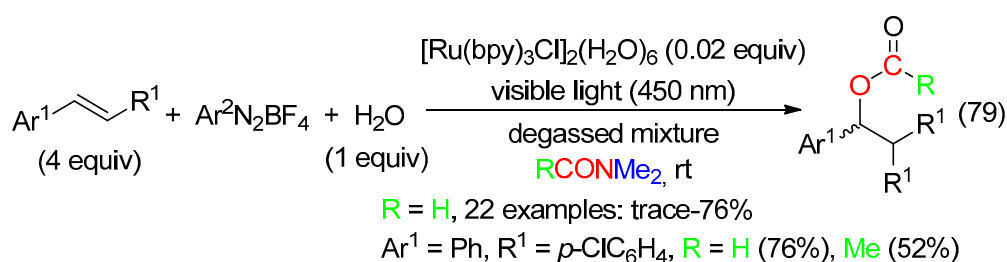
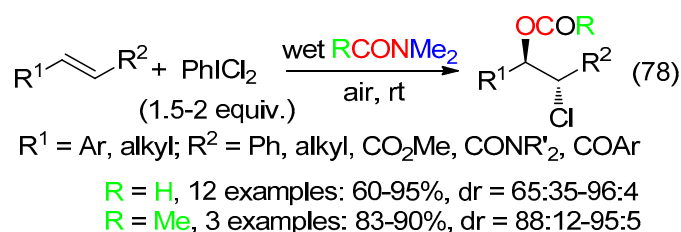
Stereoinversion of the secondary alcohols of a number of carbocyclic substrates was carried out via their triflylation followed by treatment with aqueous DMF (Equation (76)) and subsequent methanolysis [85]. A one pot stereoinversion process was reported.



The formyl group of DMF was involved in the triflic anhydride-mediated domino reaction depicted in Equation (77) [86].

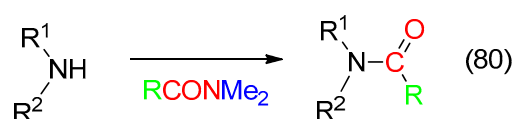


Chloroformyloxylation and chloroacetoxylation of olefinic substrates were performed with PhICl_2 and either wet DMF or DMAc (Equation (78)) [87]. Styrenes suffered also difunctionalization using aryl diazonium salts and Ru photocatalysis in wet DM (Equation (79)) [28].



14. RC=O Fragment

Metal-catalyzed or CO_2 -mediated C–N and N–H bond metathesis reactions between primary or secondary amines and DM provided the transamidation products, that is formamides or acetamides (Equation (80)) [88–91].



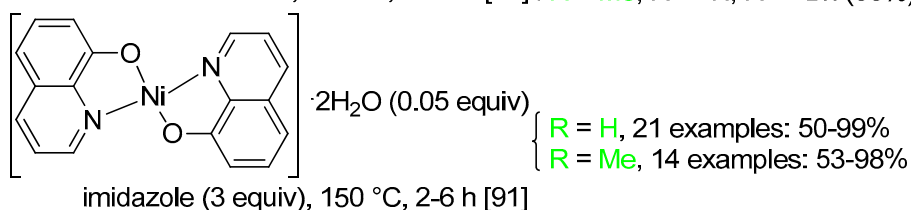
$\text{R}^1 = \text{Ar}$, alkyl, Bn; $\text{R}^2 = \text{H}$, alkyl, Bn

CO_2 (1 bar), 100 °C, 24–48 h [88]: $R = \text{H}$, 23 examples: 68–99%

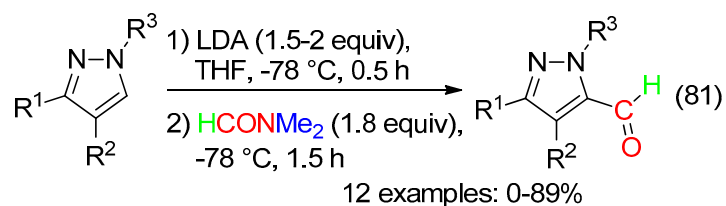
CeO_2 (cat), 150 °C, 24 h [89]: $R = \text{H}$, 17 examples: 49–99%

$\text{Nd}_2\text{Na}_8(\text{OCH}_2\text{CF}_3)_{14}(\text{THF})_6$ (0.04 equiv) $R = \text{H}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Bn}$ (78%), $(\text{CH}_2)_{10}\text{Me}$ (76%)

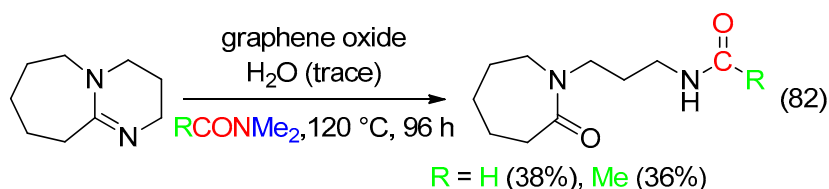
Ar, 120 °C, 5–10 h [90] $R = \text{Me}$, $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Bn}$ (86%), $(\text{CH}_2)_{10}\text{Me}$ (83%)



Formylation of aromatic substrates resulted from their treatment with LDA [92] or *n*-BuLi [93] and, subsequently, DMF (Equation (81)).

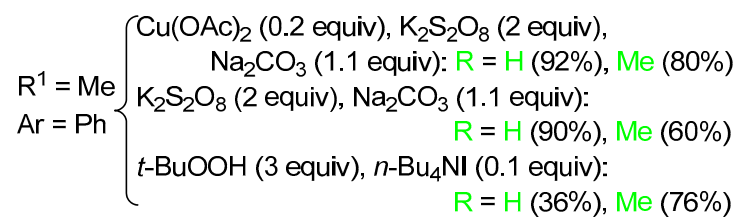
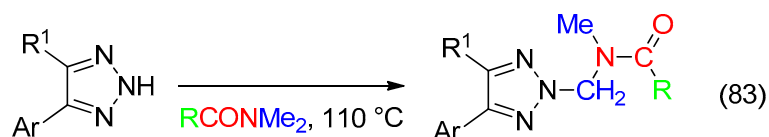


Graphene oxide reacted with DBU and DM to afford, in presence of trace of water, *N*-(3-(2-oxoazepan-1-yl)propyl)formamide or the corresponding acetamide (Equation (82)) [94].

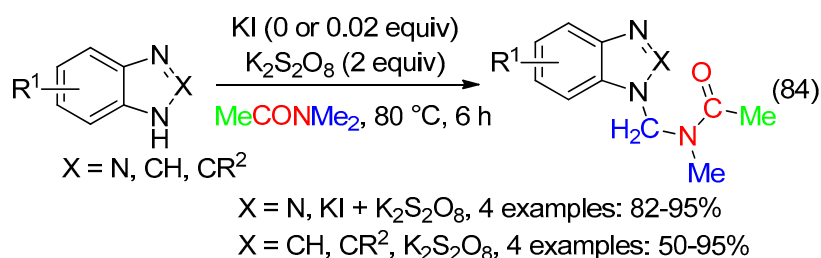


15. $RC=ON(CH_2)Me$ Fragment

N-Amidoalkylation of imidazoles and 1,2,3-triazoles with DM effectively arose under various experimental conditions (Equations (83) [95] and (84) [10]).

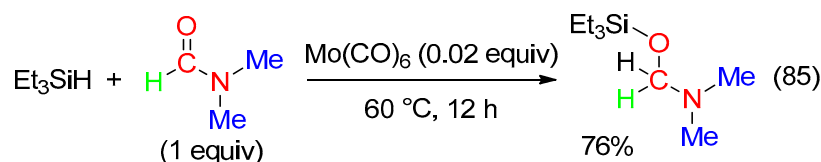


$Cu(OAc)_2$ (0.2 equiv), $K_2S_2O_8$ (2 equiv), Na_2CO_3 (1.1 equiv),
34 examples: 47-94%



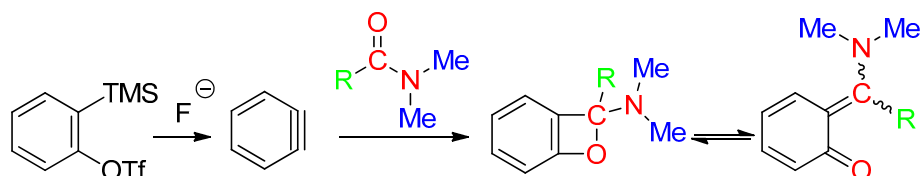
16. $HC-ONMe_2$ Fragment

Catalysis with $Mo(CO)_6$ of the reduction of DMF with triethylsilane afforded a siloxymethylamine (Equation (85)), which was used as a Mannich reagent [96].

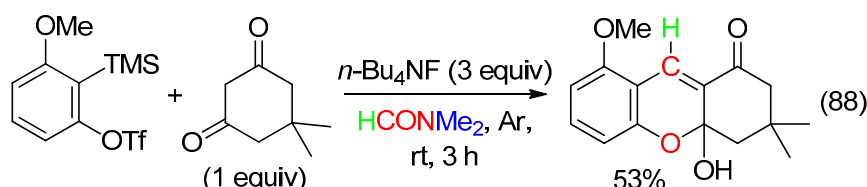
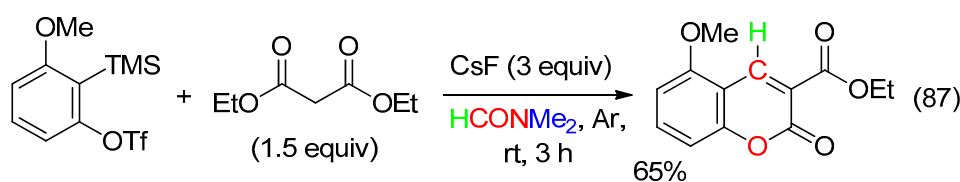
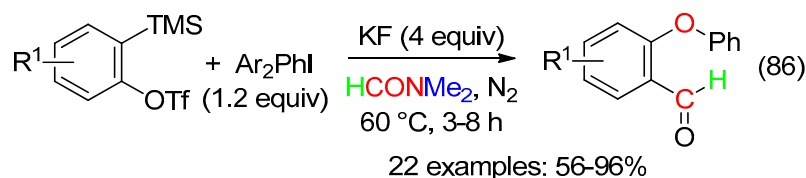


17. RC and O Fragment

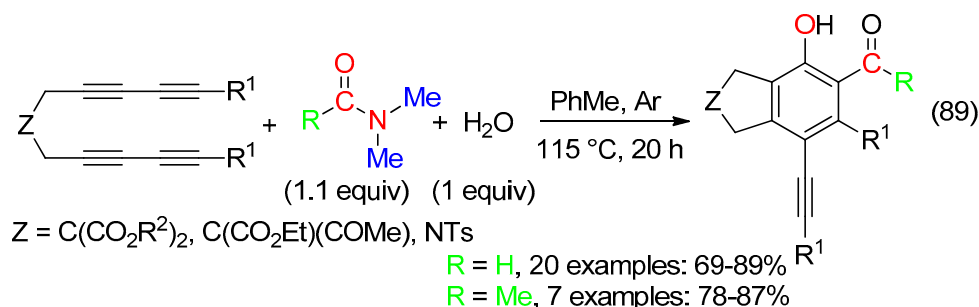
Arynes, which are easily obtained from, for example 2-(trimethylsilyl)phenyl trifluoromethanesulfonate, undergone a [2 + 2] cyclization with DM giving a benzoxetene and its isomer, the *ortho*-quinone methide (Scheme 3). Trapping of these intermediates provides various products, which contain the formyl or acetyl CH part and the O atom of DM (Equations (86) [19], (87) [20], (88) [21] and (89) [97]), or the HCNMe₂ and O fragments of DMF (see Section 18).



Scheme 3. Aryne formation and reaction with DM.



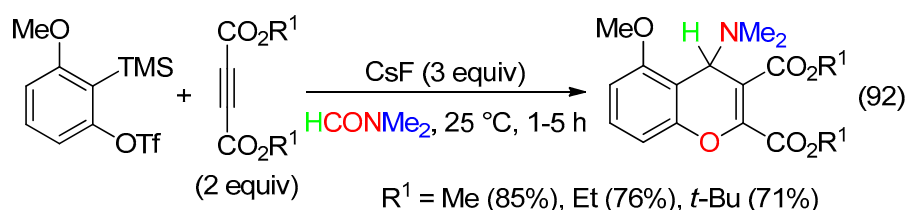
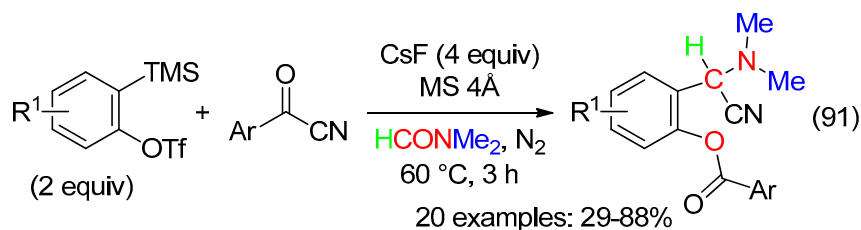
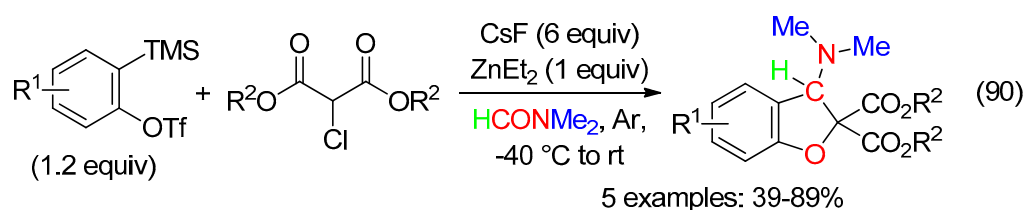
At 115 °C in wet toluene, the hexadehydro-Diels–Alder of tetraynes depicted in Equation (89) was in-situ followed by [2 + 2] cycloaddition reaction with DM leading to multifunctionalized salicylaldehydes and salicylketones [97].



18. RCNMe₂ and O Fragment

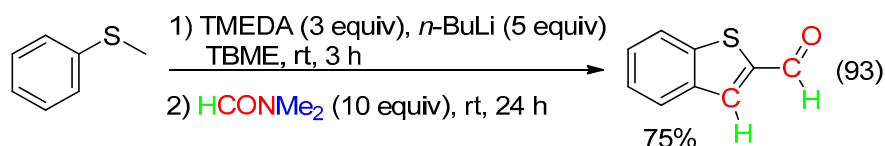
All atoms of DMF were inserted in the polyfunctionalized compounds produced from domino reactions involving formation of arynes, cycloaddition with DMF and subsequent trapping

with α -chloro β -diesters (Equation (90)) [22], aroyl cyanides (Equation (91)) [23] or diesters of acetylenedicarboxylic acid (Equation (92)) [24].



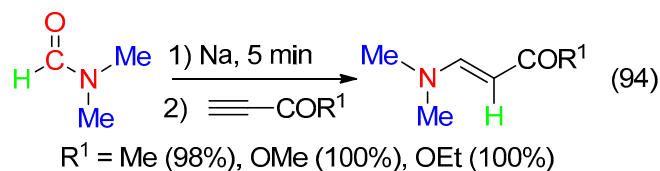
19. HC=O and HC Fragment

Lithium thioanisole biscalbanion reacted with two molecules of DMF to afford benzo[*b*]thiophene-2-carbaldehyde (Equation (93)) [98].



20. H and NMe₂ Fragment

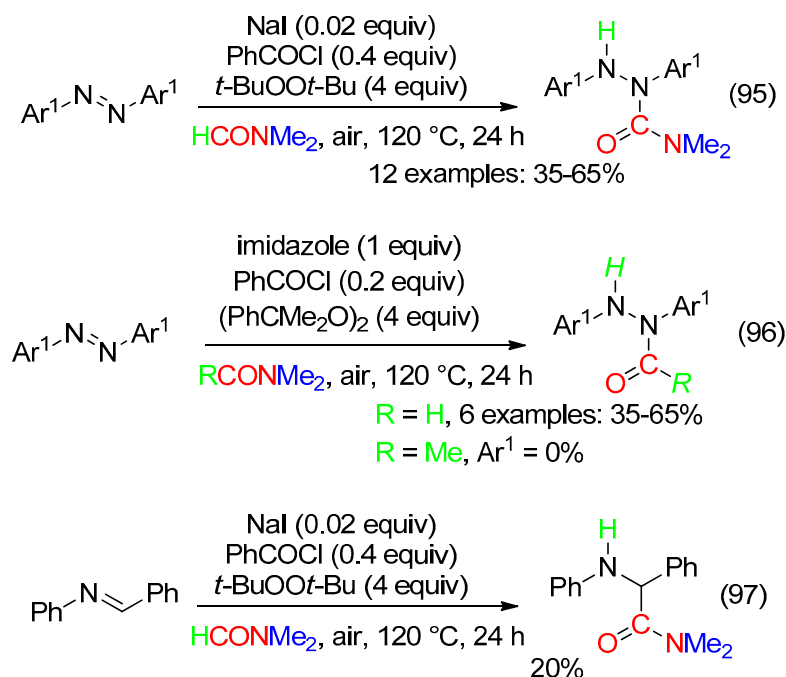
The reaction of DMF with sodium and subsequent addition of terminal activated alkynes afforded the corresponding hydroamination compounds (Equation (94)) [99].



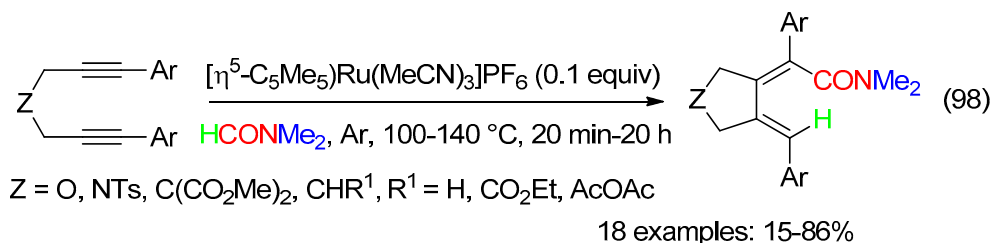
21. H and C=ONMe₂ Fragment

Semicarbazides have been synthesized from additions, mediated with $(t\text{-BuO})_2$ and catalytic amounts of both NaI and PhCOCl, of the H and CONMe₂ moieties of DMF to the extremities of the N=N bond of azoarenes (Equation (95)) [100]. The role of NaI and PhCOCl is not clear and, furthermore, exchange of NaI for imidazole led to formylhydrazines (Equation (96)) [100]. The corresponding acetylhydrazine was not formed in DMAc (Equation (96)). The $(t\text{-BuO})_2$ /NaI/PhCOCl/DMF system

led to the addition of H and CONMe₂ to the N=C bond of *N*-benzylideneaniline but with low yield (Equation (97)) [100].

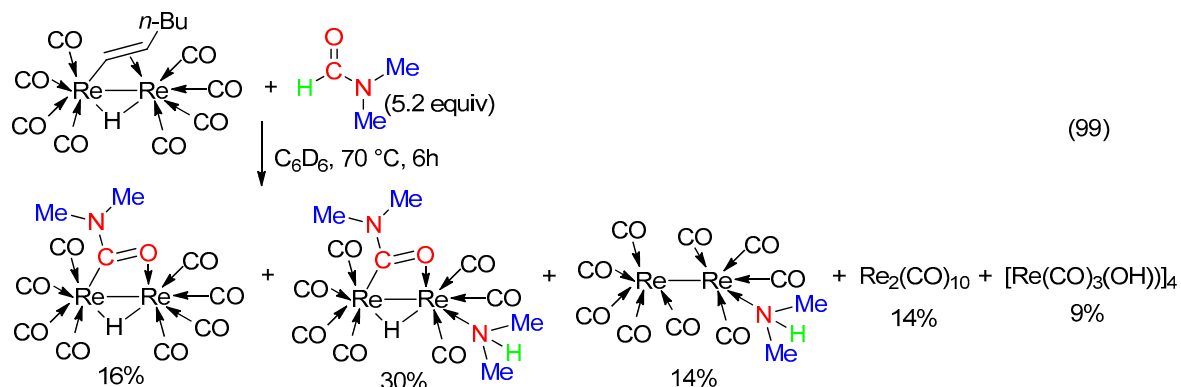


The Ru-catalyzed hydrocarbamoylative cyclization of 1,6-diynes proceeded in DMF to afford cyclic $\alpha,\beta,\delta,\gamma$ -unsaturated amides (Equation (98)) [101–103].



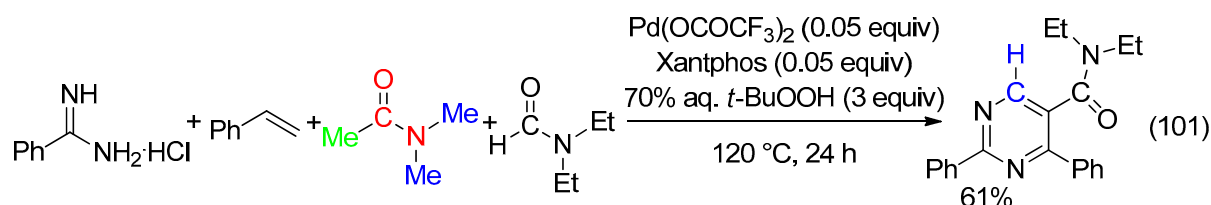
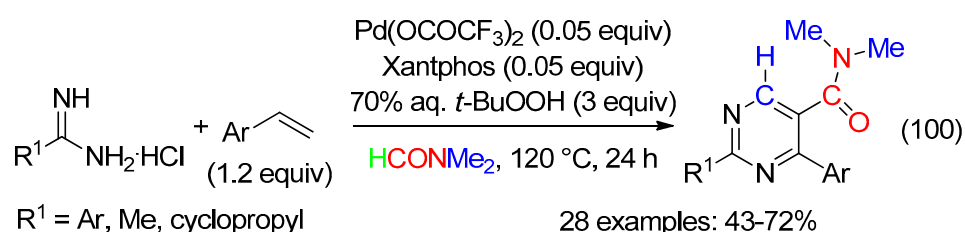
22. H, C=ONMe₂ and NMe₂ Fragment

Re₂(CO)₈[μ - η^2 -C(H)=C(H)Bu](μ -H) undergone reaction with DMF leading to hexenyl/CONMe₂ and CO/HNMe₂ exchange of ligands (Equation (99)) [104].



23. C=ONMe₂ and CH Fragment

Couplings between amidines, styrenes and fragments of two molecules of DMF in the presence of *t*-BuOOH and a Pd^{II} catalyst provided pyrimidine carboxamides (Equation (100)) [105]. DMAc may also be the CH source as exemplified with the formation of the *N,N*-diethyl-2,4-diphenylpyrimidine-5-carboxamide when *N,N*-diethylformamide was the source of the amide moiety (Equation (101)).



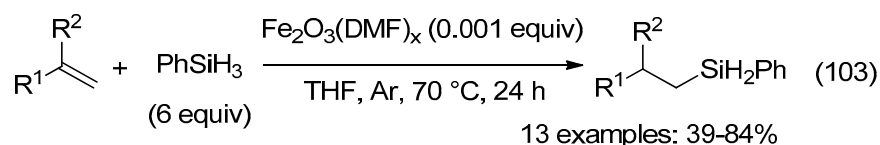
24. Reducing or Stabilizing Agent

DMF is a powerful reducing agent of metal salts, hence its use for the preparation of metal colloids [106]. In wet DMF, PdCl₂ led to carbamic acid and Pd(0) nanoparticles (Equation (102)) [107]. The latter have been associated with the metal-organic framework Cu₂(BDC)₂(DABCO) (BDC = 1,4-benzenedicarboxylate), leading to a catalytic system with high activity and recyclability for the aerobic oxidation of benzyl alcohols to aldehydes [108] and Suzuki-Miyaura cross-coupling reactions [107].

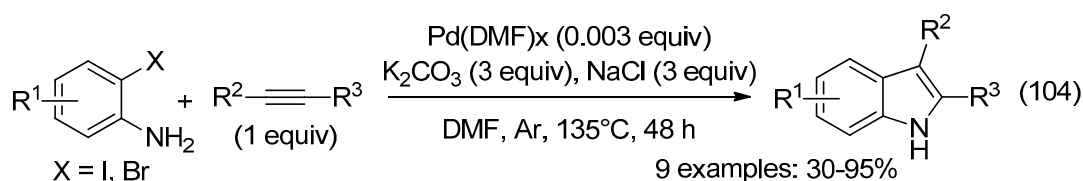


In addition, DMF can act as stabilizing agent of metal colloids to afford effective and recyclable catalysts, based for examples:

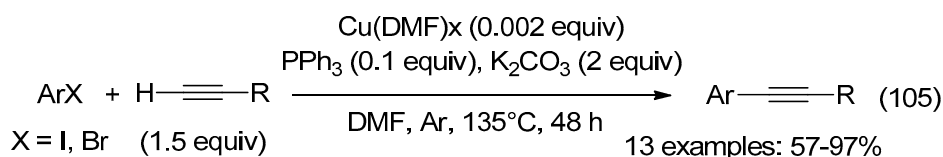
- on iron for the hydrosilylation of alkenes (Equation (103)) [109],



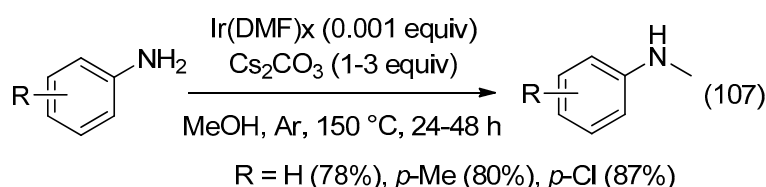
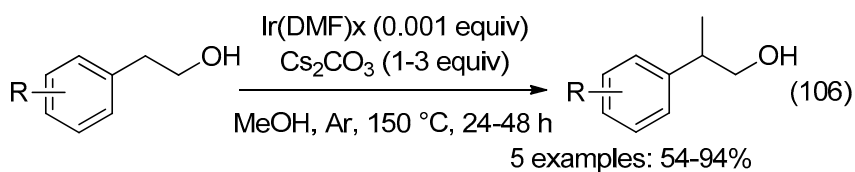
- on palladium for the synthesis of 2,3-disubstituted indoles from 2-haloanilines and alkynes (Equation (104)) [110],



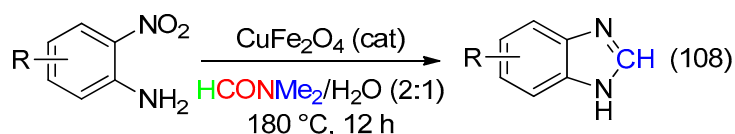
- on copper for Sonogashira–Hagihara cross-coupling reactions (Equation (105)) [111],



- on iridium for methylation of alcohols (Equation (106)) and amines (Equation (107)), using methanol as the C1 source [112].



Thermal decomposition of DMF leads to CO, which reacts with water under CuFe_2O_4 catalysis to produce hydrogen [113]. In the presence of 2-nitroanilines, this water gas shift reaction was part of a domino reaction involving the reduction of the nitro group followed by cyclisation into benzimidazoles using a CH from the NMe_2 of DMF (Equation (108)) [113]. Such cyclisation is above documented under different experimental conditions (Equation (18)) [50].



25. Conclusions

This minireview highlights recent uses of DMF and DMAc as sources of building blocks in various reactions of the organic synthesis. We assume that new uses of these multipurpose reagents will be reported.

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Conflicts of Interest: The authors declare no conflicts of interest.

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