

Metal Catalyzed Synthetic Reactions via Aerobic Oxidation as a Key Step

Mitsuru Shindo and Kenji Matsumoto

Abstract New aerobic oxidative metal catalyzed synthetic reactions are described: The Cu(II) complex catalyzed the acylation of thioester in Wittig lactonization under neutral conditions and the dissymmetrization of symmetric dithiomalonates via selective monoacylation. The key step in this reaction was the formation of an acylketene, the stability of which would contribute to selectivity. The aerobic Rh/C-catalyzed oxidative homo- and cross-coupling of aryl amines was developed. The coupling reactions afforded symmetrical and nonsymmetrical biaryl amines in excellent yields. These reactions provide a mild, operationally simple, and efficient approach for the synthesis of biaryls which are important to pharmaceutical and materials chemistry.

Keywords Aerobic oxidation • Metal catalysts • Acylation • Coupling • Heterogeneous catalysts • Recyclable

1 Introduction

Metal-catalyzed reactions are one of the main topics in synthetic organic chemistry and process chemistry. Needless to say, numerous metal-catalyzed reactions have achieved highly efficient C–C, C–O, and C–heteroatom bond formations. Oxidative (or oxidation) reactions are frequently used in not only functional group transformation but also C–C or C–O bond formation along with C–H bond cleavage (oxidative coupling). In the oxidative metal-catalyzed reactions, if air or oxygen is an oxidant, usage of hazardous peroxides or toxic high valence metals can be

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avoided. In terms of green chemistry as well as practical synthesis, aerobic conditions would be favorable. Furthermore, reaction control would be more easily accomplished under aerobic conditions than inert gas atmosphere.

In this chapter, we describe our recent results on aerobic Cu(II) catalyzed acylation, in which catalyst deactivator is eliminated by oxidation, and aerobic metal catalyzed oxidative coupling reactions.

2 Aerobic Cu-Catalyzed Acylation-Wittig Reaction Under Neutral Conditions

2.1 Acylation-Wittig Reaction Under Neutral Conditions

During the course of our synthesis of xanthanolate sesquiterpenoids [1, 2], we found one-pot acylation-Wittig lactonization of acyloins (Fig. 1). A mixture of the acyloin **1** (α -hydroxy-cyclic hemiacetal as its equivalent) and excess amount of Wittig reagent **2** was heated in xylene at 150 °C to form a butenolide **3** in excellent yield. When the ester moiety was replaced to more acidic eliminating group like thiophenol, the reaction was fairly accelerated, albeit under harsh conditions (Fig. 2). These results indicated a reaction mechanism of the initial rate-determining acylation and the following intramolecular Wittig reaction.

2.2 Cu(II)-Catalyzed Acylation-Wittig Reaction [3]

In this successive lactonization, harsh conditions of an excess amount of the Wittig reagent and high temperatures were still required to complete the reaction. We then examined metal catalyzed reactions of this acylation-Wittig reaction under mild and neutral conditions [4, 5]. We focused on thioesters, which are easily handled, stable acylating agents of alcohols in organic syntheses and biological systems. Acylations with a thioester should be carried out under basic conditions for activation of the

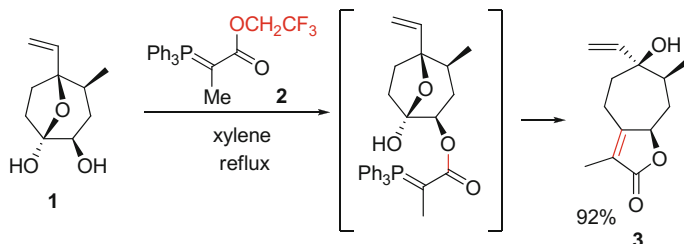


Fig. 1 One-pot acylation-Wittig lactonization of acyloins

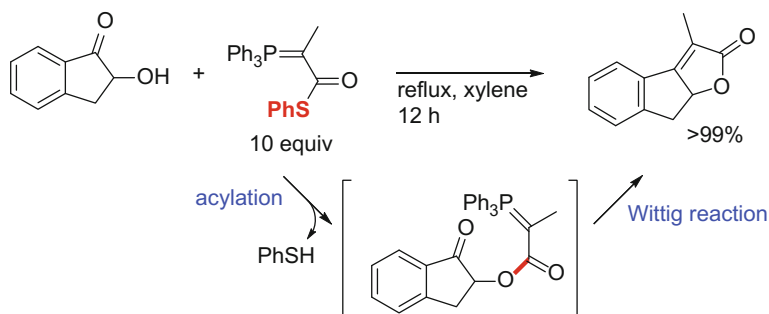
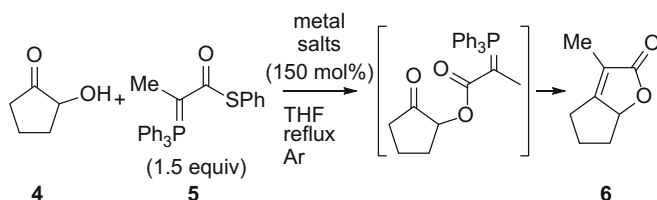


Fig. 2 One-pot lactonization using Wittig reagent with a thioester

Table 1 Acceleration of acylation by metal salts



Entry	Metal salt	Time (h)	Yield (%)
1	None	–	No reaction
2	Mg(OAc) ₂	3.5	Trace
3	Fe(OAc) ₂	3.5	11
4	Zn(OAc) ₂	3.5	61
5	Ag(OAc) ₂	3.5	51
6	Cu(OAc) ₂	0.5	80
7	CuCl ₂	–	No reaction
8	Cu(OTf) ₂	–	No reaction

alcohols. Although there have been several reports on *O*-acylations using thioesters accelerated by stoichiometric or substoichiometric amounts of soft metal salts, such as Hg(II), Ag(I), Cu(I), and Cu(II) [6–9], no catalytic reactions under neutral conditions were reported, because the thiolates eliminated by the acylation would deactivate the metal salts.

The reaction did not proceed in the absence of metal salts (Table 1, entry 1), and the hard metal salt such as magnesium acetate did not promote the reaction (entry 2). In contrast, 150 mol% of soft metal salts promoted the reaction to give the desired lactone **6** in good to moderate yields, (entries 3–6). And among the metals, Cu(OAc)₂ provided the best result (entry 6). The other Cu(II) salts did not almost accelerate the reaction (entries 7 and 8).

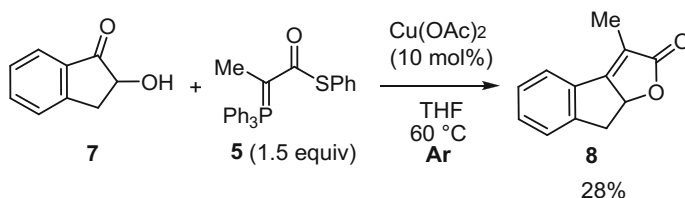
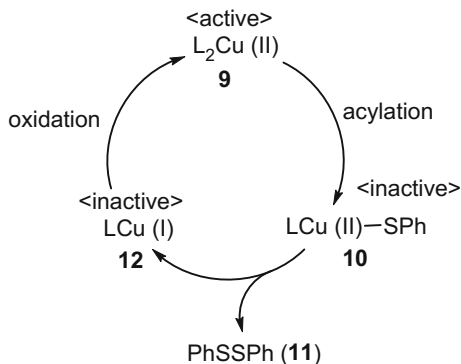


Fig. 3 Cu(II)-catalyzed acylation-Wittig reaction of acyloin **7**

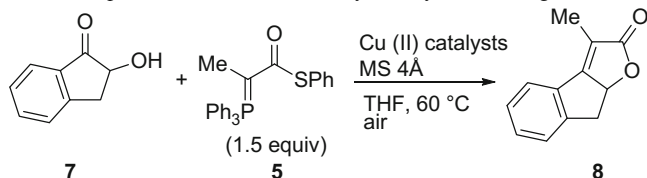
Fig. 4 Concept for catalytic cycle



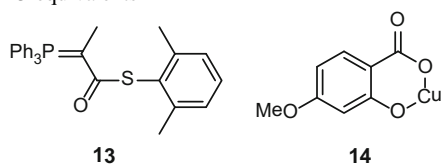
The next issue was how to develop the catalytic reaction. 10 mol% of Cu(OAc)_2 promoted the model reaction (Fig. 3) to yield the product **8** in only 28% *under argon*.

In the reaction cycle, thiophenol is eliminated. This byproduct forms an inactive thiophenol-Cu complex **10**. Therefore, the generation of this complex must be suppressed for the catalytic system. A small amount of diphenyl disulfide (**11**) was detected as a side product, which was formed by oxidation of the thiol along with reduction of the catalyst (Cu(II) to Cu(I)). We anticipated that in order to regenerate the active catalyst Cu(II) **9**, the thiolate should be oxidized to the disulfide **11**, possibly a poorer ligand for Cu(II), and the resulting Cu(I) **12** should be oxidized to Cu(II) (Fig. 4) [10].

Based on this concept, we attempted the Cu(II)-catalyzed Wittig lactonization of 2-hydroxyindanone (**7**) *under air* to achieve catalytic turnover using 10 mol% of Cu(OAc)_2 (Table 2, entry 1). After screening of ligands, the bidentate-type salicylate complex (**14**) provided **8** in higher yields (entry 2). Furthermore, OXONE[®] accelerated the catalytic reaction to provide **8** in 2 h in high yield (entry 3). Even when 2 mol% of the catalyst **14** was used, **8** was obtained in good yield (entry 4). These results suggested the rate determining step being re-oxidation of Cu(I) to Cu(II) in this catalytic system. Finally, the Wittig reagent **13** having 2,6-dimethylphenylthioester afforded **8** in excellent yield catalyzed by only 2 mol% of the copper complex **14**, probably because the sterically more hindered ArS-Cu(II) complex was more readily converted into disulfide and Cu(I).

Table 2 Optimization of Cu (II)-catalyzed acylation-Wittig lactonization

Entry	Catalyst	mol%	Wittig reagent	Oxidants	Time (h)	Yield (%)
1	Cu(OAc) ₂	10	5	Air	6	82
2	14	10	5	Air	5	97
3	14	10	5	OXONE ^{®a}	2	92
4	14	2	5	OXONE ^{®a}	5	76
5	14	2	13	OXONE ^{®a}	4	91

^a3 equivalents

Various kinds of acyloins were treated with **13** in the presence of the catalyst **14** in toluene, which was safer than THF under oxidative conditions, to provide the lactones in high yields (Fig. 5). Not only hydroxyketones (**15a–f**) but also a hydroxylactone **15g** could be employed to afford butenolides **16**. The hemiacetal **15h** was also transformed into the butenolide under much milder conditions than the original conditions. The sterically labile precursor **15i** of heritonin [**11**] was converted into the corresponding butenolide in high yield, without epimerization [**12**], because of mild and neutral conditions. Therefore, base or acid-labile substrates could be subjected to this acylation without decomposition or isomerization. This reaction was applied to synthesis of karrikinolide [**13**].

Figure 6 shows a proposed mechanism for this catalytic cycle. The Cu(II) catalyst **14** would activate the thioester **13** [**6**, **7**], which is converted into the phosphonium ketene intermediate **17** by double activation of the C–S and O–H bonds. The soft Lewis acidic Cu(II) specifically interacts with the thioester to accelerate elimination of the thiolate with the aid of electron-donating phosphorus ylide. Simultaneously, the alcohol **15** is deprotonated by salicylate to be converted into alkoxide **18**, which is acylated by **17**, followed by the intramolecular Wittig reaction, to furnish the lactone **16**. The resulting thiolate complex **19** would be homolytically cleaved into a thiyl radical **20** and the Cu(I) complex **21**. The former species would form the disulfide **22**, and the latter would be oxidized to regenerate the catalyst **14**. Molecular sieves could trap the water generated by oxidation. Accordingly, the Cu(II) catalyst would play a double role: activation of the thioester and oxidative removal of the thiolate.

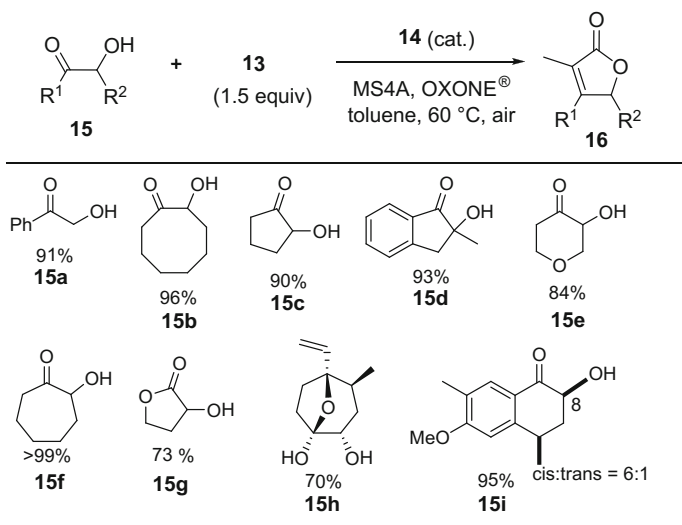


Fig. 5 Cu(II)-catalyzed one-pot lactonization

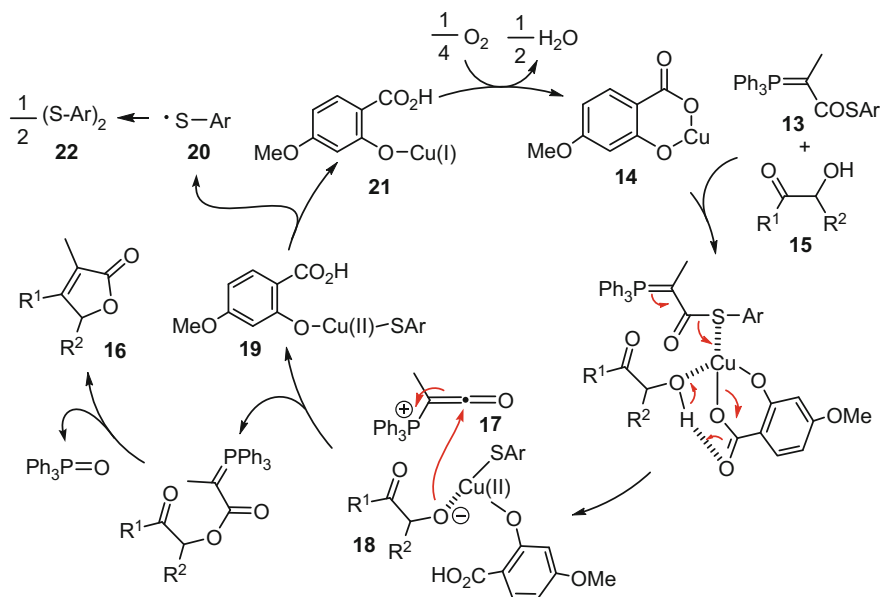


Fig. 6 Proposed mechanism for Cu(II)-catalyzed acylation

2.3 Cu(II) Catalyzed Dissymmetrization of Dithiomalonates [14]

Selective synthesis of dissymmetric malonates from the symmetric malonates is sometimes uncontrollable because esterification of malonic acid frequently produces the corresponding diester as well as the mono-ester, even if it is executed with an equimolar alcohol. Enzymatic methods are common for this conversion, but with the drawback of strong substrate specificity [15]. Nucleophilic ring-opening of Meldrum's acid have also been used [16, 17]; however, they are not always efficient due to facile decarboxylation. Niwayama's selective mono-hydrolysis of diesters including malonates successfully gives the dissymmetric half esters [18, 19]. A more efficient dissymmetrization of malonates that provides mono-esters (e.g. **24**) with an *activated acyl group* such as a thioester would be a valuable synthon directing to functionalized malonates **25** from inexpensive symmetrical malonates (Fig. 7) [20, 21].

A dithiomalonate **26** was found to be selectively converted into a malonic acid *S*, *O*-ester **27** in excellent yield in the presence of the catalyst **14** (Fig. 8), although the Cu(II) catalyst did not activate simple thiol esters.

Interestingly, even in the absence of the Cu(II) catalyst **14**, the reaction was completed under the similar conditions to give the dissymmetric product **27** in excellent yield. This result suggested that the selective mono-alcoholysis was attributed to the intrinsic properties of dithiomalonates. Therefore, we started studies on this reaction under non-catalytic conditions.

The solvent effect was important because only polar solvents accelerated the reaction (Table 3). Finally, acetonitrile was the best solvent for mono-alcoholysis, giving the dissymmetric *S*,*O*-ester **27** quantitatively (entry 4).

The non-catalytic mono-alcoholysis of diphenyl dithiomalonates (**26**) with various alcohols provided the corresponding *S*,*O*-malonates **29** in 5–24 h in excellent

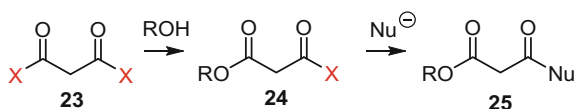


Fig. 7 Preparation of dissymmetric malonates

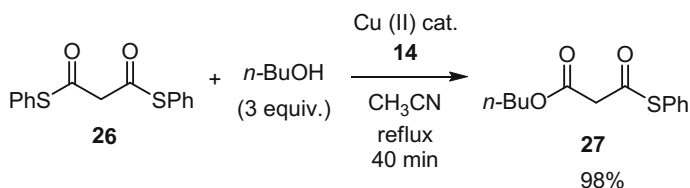
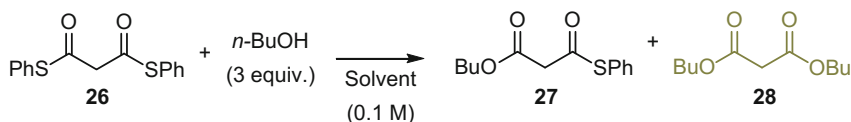


Fig. 8 Dissymmetrization of dithiomalonate **26**

Table 3 Screening of solvents

Entry	Solvent	Temperature (°C)	Time (h)	Ratio (27/28)	Yield (%)
1	Toluene	60	3.5		0
2	CH ₂ Cl ₂	40	3.5		0
3	THF	60	3.5		Trace
4	CH ₃ CN	60	2	>20:1	96
5	DMF	60	1.2	>20:1	83

Table 4 Dissymmetrization of diphenyl dithiomalonate (**26**)

Entry	Alcohol	Without 14		With 14 (1 mol%)	
		Time (h)	Yield (%)	Time (h)	Yield (%)
1	<i>n</i> -BuOH	2	96	0.6	91
2	<i>i</i> -PrOH	24	93	2	88
3	<i>t</i> -BuOH	24	70	1	82
4	HC≡CCH ₂ OH	24	0	4	71
5	CH ₂ =CHCH ₂ OH	24	0	2.5	82

yields with high selectivities except for propargyl and allyl alcohols (Table 4). The copper catalyst **14** significantly accelerated this mono-acylation with the aid of MS4A for trapping water, described section in Sect. 2.2. The reactions were completed within several hours, and even the less reactive allyl and propargyl alcohols gave the dissymmetric *S,O*-esters in excellent yields.

α -Alkyl-substituted dithiomalonates were also converted into dissymmetric *S,O*-malonates catalyzed by **14**, although the reaction was retarded (Fig. 9). The α -fluoromalonate showed much lower reactivity than α -alkylmalonate, even though its steric factor could be negligible. Neither α,α -dimethylmalonate **30** nor diphenyl dithiosuccinate (**31**) were inert to this reaction.

The thermal transesterification of ethyl acetoacetate has been known to proceed through an acylketene intermediate [22, 23]. In the alcoholysis of dithiomalonates, acylketenes would also be a key intermediate owing to the inertness of α,α -dimethylmalonate **30** and dithiosuccinate **31**. Rate constants of the reaction of **26** with *n*-butanol in acetonitrile were independent of the concentration of *n*-butanol. Therefore, the key intermediates in this alcoholysis were the ketenes **32**, and the ketene formation (**26** \rightarrow **32**) was the rate-determining step in the case of

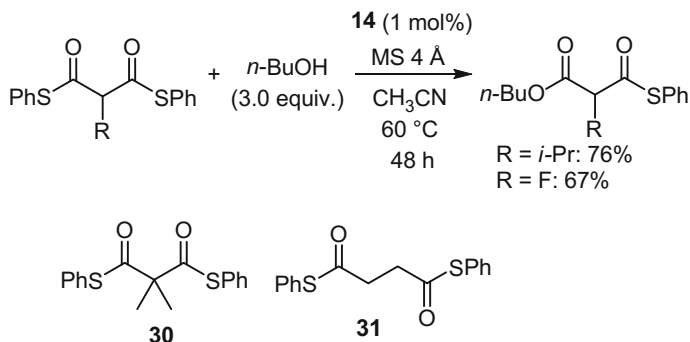


Fig. 9 Cu-catalyzed mono-butanalysis of α -substituted dithiomalonates

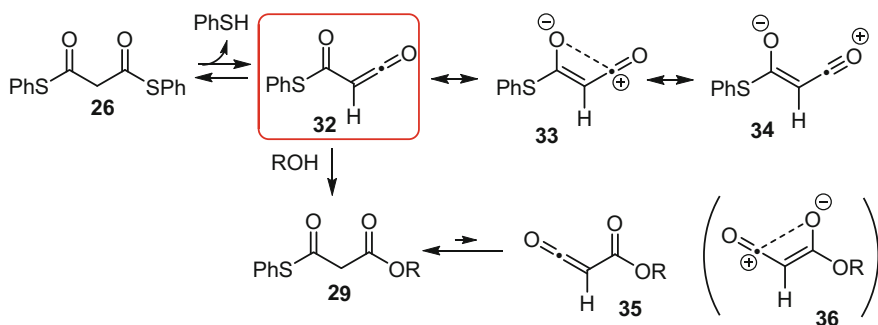


Fig. 10 Proposed mechanism for mono-alcoholysis of dithiomalonates

n-butanol (Fig. 10). The pronounced stability of **32** would be attributed to resonance structures (**33** and **34**) in addition to an intramolecular electrostatic interaction in **33**, according to the Tidwell's reports [24, 25]. The ketene **32** would be more stable than the oxocarbylketene **35**; therefore, zwitterionic stabilization in **36** was relatively ineffective. Consequently, the high selectivity of mono-alcoholysis could be attributed to the different stabilities of the acylketenes. The copper catalyst accelerated the conversion to **32** by activating the thioester. In the case of the less reactive alcohols and less reactive sterically hindered malonates, the rate-determining step may be shifted to acylation (**32** \rightarrow **29**).

In this section, aerobic Cu(II)-catalyzed acylations of Wittig lactonization and dissymmetrization of dithiomalonates were described. The Cu(II) complex-catalyzed reaction was the first catalytic acylation using thioesters under aerobic neutral conditions. Although this catalytic reaction is thus far limited to the Wittig reagent and dithiomalonates as thioesters, it may become a new principle for catalytic acylation. Further development of more efficient catalysts can be expected in the future. Since acylation is a conventional and fundamental method for C–C, C–O, and C–N bond formation, these aerobic catalytic methods will be valuable in synthetic organic chemistry and process chemistry.

3 Heterogeneous Metal-Catalyzed Aerobic Oxidative Biaryl Coupling

3.1 Aerobic Oxidative Homo-Coupling of Aryl Amines [26]

Biaryl compounds are privileged structural motifs found in many biologically important natural products, synthetic pharmaceuticals, and functional materials. In recent years, with the increasing pressure to develop environmentally friendly and sustainable methodologies, direct arylation, aryl–aryl bond formation through C–H bond activation, has captured growing attention as a very attractive methods for preparation of biaryls because the reactants do not have to be pre-functionalized, and because of the atom- and step-economy (Fig. 11) [27–33]. Among direct arylation methodologies, oxidative biaryl coupling is a simple and direct method for aryl–aryl bond formations. The oxidative coupling of naphthols and phenols leading to BINOL and biphenol derivatives has been well studied [34–37]. In strictly contrast, the oxidative coupling of aryl amines remains largely unexplored [38, 39], because aryl amines are easily oxidized, generating many side products. At the start of our study, catalytic processes are particularly limited and only an example of catalytic process was reported by Yang using catalytic amounts of FeCl_3 in combination with *m*CPBA [40]. Furthermore, the use of molecular oxygen as clean, safe, and inexpensive oxidant represents an important advance [41].

We anticipated that upon protonation of aryl amines under acidic conditions, the resulting ammonium salts may prevent side reactions induced by the high nucleophilicity or oxidation potential of aryl amines and undergo the desired oxidative coupling smoothly to yield homo-coupled products. The feasibility of this concept was confirmed by the oxidative coupling of 2-aminoanthracene (**37**) under heterogeneous aerobic conditions using 5% Rh/C catalyst (Table 5). To our delight, the use of methanesulfonic acid afforded the desired product **38**, but the yield was low (entry 1). Following this result, we examined various acidic solvents and found that trifluoroacetic acid (TFA) afforded the best result for obtaining dimer **38** in high yield (entry 2), whereas either difluoroacetic acid or acetic acid, the acidities of which are weaker than that of TFA, led to the reduced yields of **38** (entries 3 and 4). Interestingly, the reaction in hexafluoroisopropanol (HFIP) resulted in the exclusive formation of carbazole **39** in 76% yield (entry 5), but ethanol was unsuitable solvent (entry 6). The other aprotic solvents did not afford the coupling products (entries 7

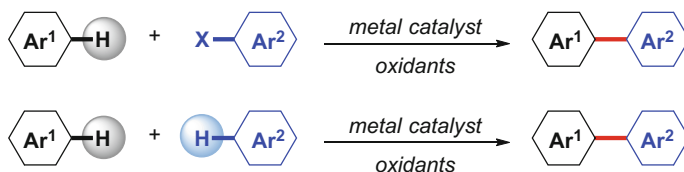
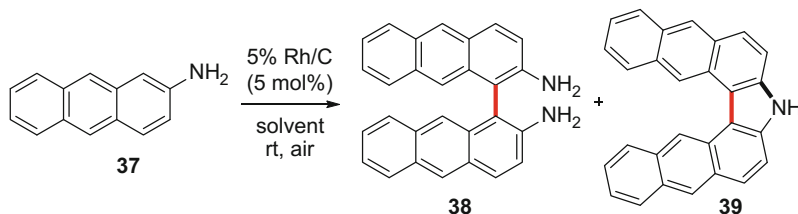
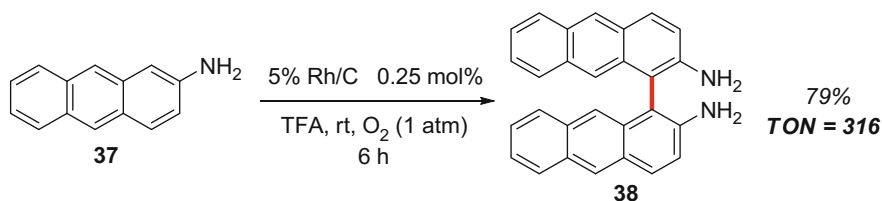


Fig. 11 Aryl–aryl bond formation via direct arylation

Table 5 Solvent effect for oxidative homo-coupling of aryl amines

Entry	Solvent	pKa	Time (h)	Yield (%)	
				38	39
1	CH ₃ SO ₃ H	-2.6	26	Low yield	
2	CF ₃ CO ₂ H	-0.2	0.8	90	2
3	CF ₂ HCO ₂ H	1.2	4	60	14
4	CH ₃ CO ₂ H	4.8	34	51	36
5	(CF ₃) ₂ CHOH	9.3	6	0	76
6	EtOH	15.5	24	15	6
7	THF	-	26	No reaction	
8	CH ₂ Cl ₂	-	26	No reaction	

**Fig. 12** Rh/C-catalyzed oxidative homo-coupling of 2-aminoanthracene

and 8). These results indicate that the acidic properties of solvents not only accelerate the reaction, but also control the product selectivity.

Besides Rh/C, other heterogeneous catalysts such as Rh/Al₂O₃, Ru/C, Pd/C, and PtO₂ also afforded **38** in high yields. Under 1 atm of oxygen, the reaction proceeded faster to give **38** in excellent yield. Furthermore, even using 0.25 mol% of 5% Rh/C, **38** was obtained in good yield and the turnover number (TON) reached up to 300 (Fig. 12). This is the first heterogeneously catalyzed aerobic oxidative coupling of aryl amines, which would provide the operationally simple and greener methodology for the efficient preparation of biaryl diamines.

With the optimized conditions in hand, the substrate scope was investigated with various aryl amines (Fig. 13). Using *N*-substituted-2-aminoanthracenes and

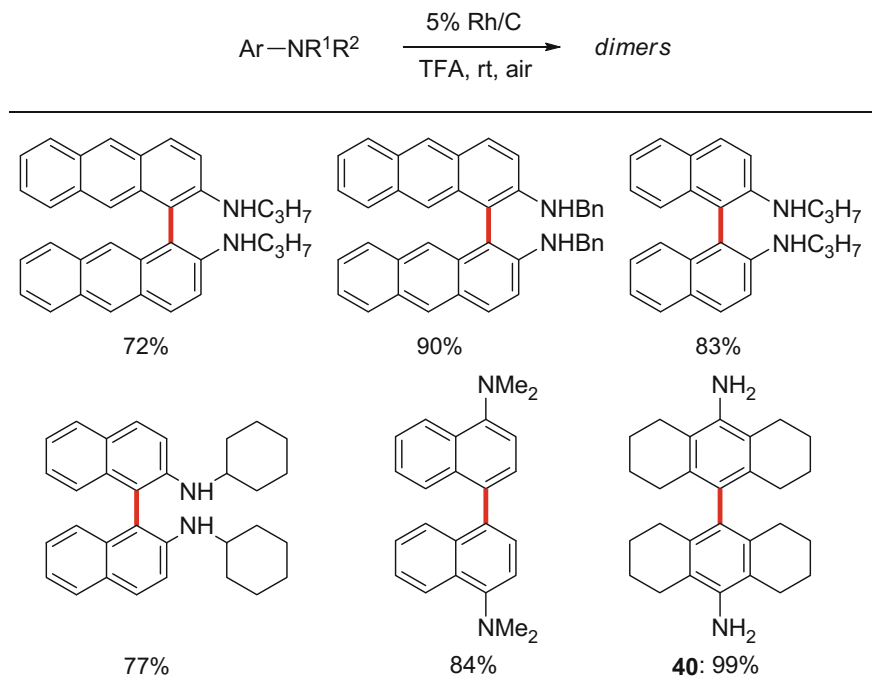


Fig. 13 Rh/C-catalyzed oxidative homo-coupling of aryl amines

2-aminonaphthalenes, dimers were obtained in good yields. Interestingly, 1-aminonaphthalenes underwent C–C bond formation at 4-position, generating dimers in excellent yields. The octahydroanthracene derivative, which is not a fused arene, also dimerized to afford the corresponding product **40** in quantitative yield. Thus, the anthracenes as well as naphthalene and aniline derivatives underwent oxidative coupling to afford the corresponding dimers in good yields, which show that this catalytic coupling reactions are highly versatile.

To gain insights into the reaction mechanism, the electron spin resonance (ESR) spectrum of the reaction using **37** and 5% Rh/Al₂O₃ under air was measured at room temperature, which indicated that the radical species are generated in the reaction mixture. Accordingly, the proposed mechanism is shown in Fig. 14. The catalytic cycle begins with a one-electron transfer from the ammonium salt **41** to the rhodium catalyst to produce the radical cation intermediate **42** and reduced rhodium, which is oxidized by molecular oxygen to regenerate the active rhodium metal. The radical cation **42** dimerizes to give the diiminium salt **43**, which tautomerizes to afford the coupled product **45** after work-up. Unlike the TFA system, in the presence of HFIP, the carbazole **39** is preferably produced. Probably owing to the higher p*K*_a value of HFIP, amino iminium intermediate **44** undergoes cyclization to produce **46**, which release ammonium to afford carbazole **47**.

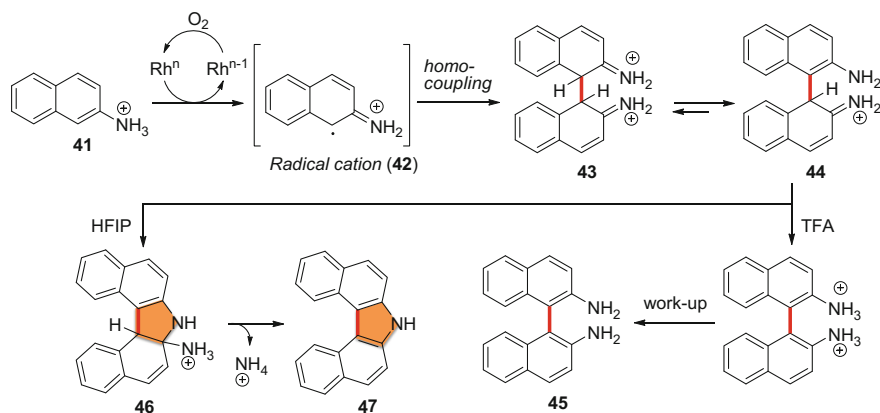


Fig. 14 Proposed mechanism for aerobic oxidative coupling of aryl amines

3.2 Aerobic C–H/C–H Cross-Coupling of Aryl Amines [42]

The C–H/C–H cross-coupling between two distinct aromatic compounds, also known as cross-dehydrogenative coupling (CDC), has recently attracted great attention as an efficient and promising strategy to synthesize a broad array of unsymmetrical biaryls [43–45]. In spite of significant development, the vast majority of C–H/C–H cross-coupling reactions are still limited by the high temperatures and stoichiometric amounts of strong oxidants that are required [46–49]. In particular, the oxidative C–H/C–H cross-coupling between two arenes with similar chemical and physical properties, such as phenol–phenol or aniline–aniline, are difficult to achieve due to the concomitant formation of homo-coupling products [50–53]. Kita and co-workers reported the metal-free oxidative cross-coupling of *N*-Ms protected aryl amines using hypervalent iodine reagents as the stoichiometric strong oxidant and developed the catalytic transformation in combination with *m*CPBA [54]. Waldvogel and co-workers have developed electrochemical oxidative phenol–aniline cross-coupling with high selectivity [55–57]. Despite these advances, since oxidative coupling of aryl amines are particularly difficult, there remains no general method for aniline–aniline cross-coupling [58].

We envisioned extending the above oxidative homo-coupling of aryl amines to CDC reaction. In comparison to homo-coupling, the control of selectivity for desired cross-coupling over homo-coupling represents a great challenge. Based on our previous results, we hypothesized that the homo-coupling could be suppressed if **48** had sterically hindered substituents on the amino group; the resulting radical cations **49** would preferentially react with sterically less hindered arenes **50** to provide cross-coupled biaryls **51** (Fig. 15).

Thus, we selected *N,N*-dimethylamino-2-naphthalene (**52**) as a substrate with a bulky amino group and optimized the cross-coupling of **52** with 3 equivalents of **53** in TFA under 1 atm of oxygen (Fig. 16). In the presence of 5% Rh/C (5 mol% of

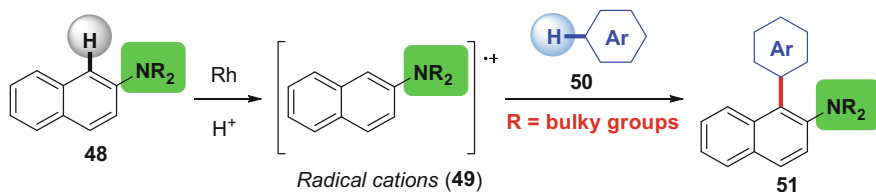


Fig. 15 Working hypothesis for C-H/C-H cross-coupling of aryl amines

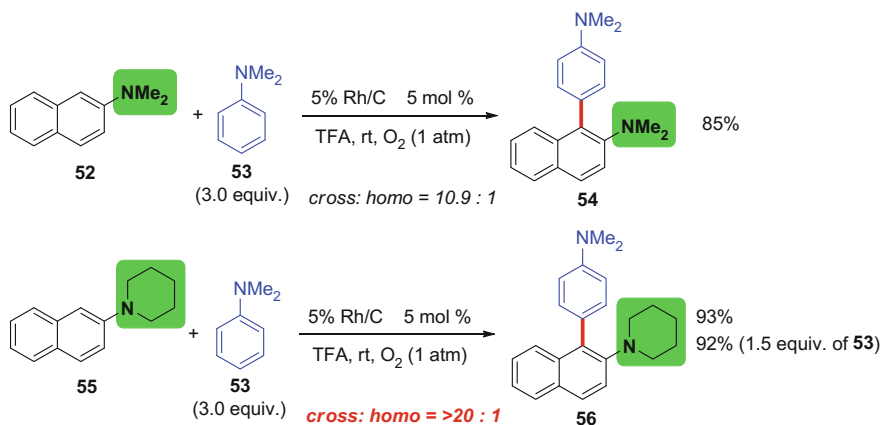


Fig. 16 Oxidative C-H/C-H cross-coupling of aryl amines

rhodium), the desired cross-coupled product **54** was obtained in 85% along with a small amount of the dehydridimer of **52**. Following this result, we investigated the cross-coupling using various 2-naphthyl amines and found that amino substituents played important role on the selectivity of the reaction. When piperidino analog **55** was employed, the homo-coupling product was not observed and desired product **56** was obtained in 93% yield. Furthermore, even using a small amount of **53**, the reaction of **55** provided **56** in excellent yield.

Since high selectivity was obtained with **55**, the substrate scope was investigated with various aryl amines (Fig. 17). Several kinds of anilines, phenols and anisoles were reacted with **55** to give unsymmetrical biaryls in excellent yields and selectivities. *N,N*-Dibenzylamino-2-naphthalene also reacted with aniline to give **57** efficiently. Furthermore, even using 0.27 mol% of 5% Rh/C, **57** was obtained in good yield and the turnover number (TON) reached up to 280 [59].

To demonstrate the potential applications of the present cross-coupling, the preparation of versatile 1,1'-binaphthyl-based ligands was examined (Fig. 18). Cross-coupling of **52** with an excess of 2-naphthol proceeded to give NOBIN analog **58** in 62%. NOBIN is used not only in asymmetric catalysis, but is also used as a source of various 1,1'-binaphthyl-based ligands [60]. Additionally, since the amino groups can be used for further transformations, our methodology provides efficient access to a variety of biaryls with interesting functions and biological activities.

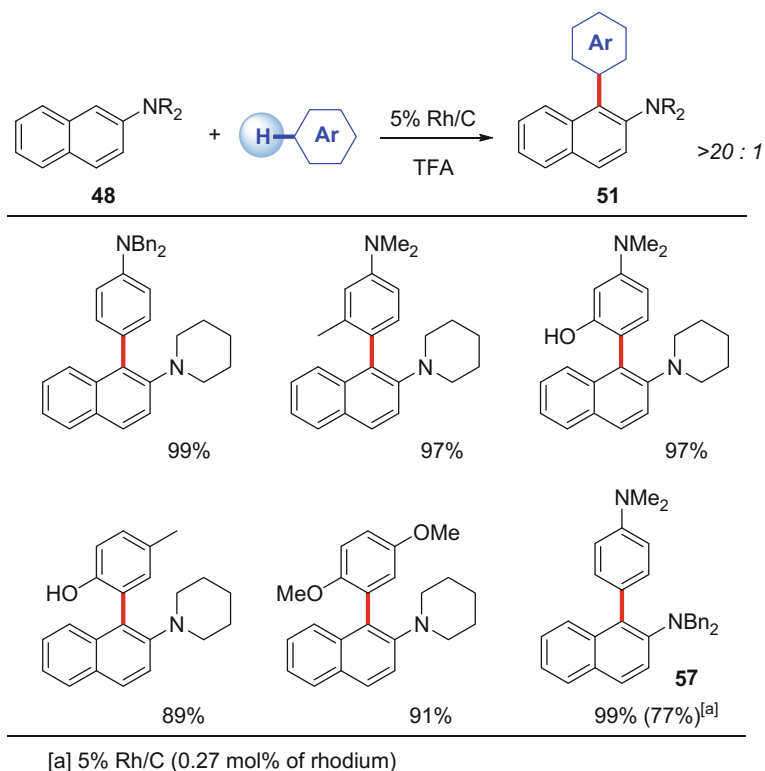


Fig. 17 Oxidative C–H/C–H cross-coupling of aryl amines

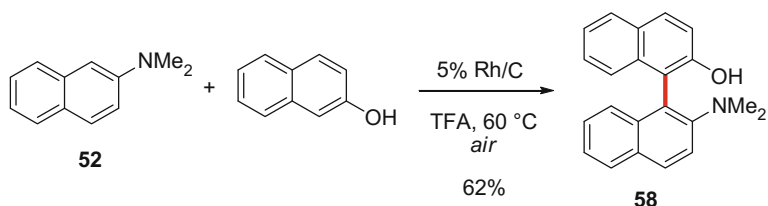


Fig. 18 Synthetic utility of the cross-coupling reaction

4 Conclusion

We demonstrated two kinds of aerobic oxidative metal catalyzed synthetic reactions that we recently developed. The homogeneous Cu(II) complex catalyzed acylations present new synthetic strategies of one-pot lactonization and dissymmetrization of malonate. These reactions can be carried out under mild and neutral conditions, which are compatible with acid- or base-labile functionality, especially for synthesis

of complex molecules. The aerobic oxidative metal catalyzed coupling reactions provide not only homo-coupled biaryl products but also cross coupled ones, which are highly useful for materials and medicinal chemistry. Furthermore, the reaction has special features including dehydrogenative direct C–C coupling, recyclable heterogeneous catalysts used, and oxygen as an oxidant. The current catalytic reactions will provide benign and scalable processes in synthetic organic chemistry.

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