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Ruthenium-Catalyzed *ortho*-C−H Mono- and Di-imidation of Arenes with *N*-Tosyloxyphthalimide

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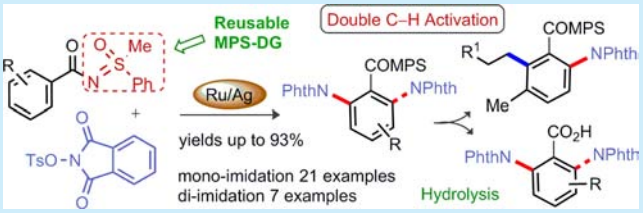
Supporting Information

ABSTRACT: The Ru(II)-catalyzed imidation of the *o*-C−H bond in arenes with *N*-tosyloxyphthalimide is realized with the assistance of a methyl phenylsulfoximine (MPS) directing group. This method is applicable to access the hitherto difficult *o*-C−H di-imidation products. The sequential C−N and C−C bond formation of *o*-C−H arenes creates peripherally decorated benzoic acid derivatives. The readily removable MPS-DG and easily modifiable phthaloyl moiety make this strategy synthetically viable for constructing highly functionalized C−N bearing arenes and heteroarenes.



Functionalization of an unactivated ubiquitous C−H bond is synthetically important, as its impact has strongly influenced the efficient construction of programmed complex molecular entities.[1] Thus, development of novel catalytic methods for the fabrication of C−C and C−heteroatom bonds through the activation of an inert C−H bond is always desirable. Among various bond forming processes, construction of a C−N bond in arenes is incredibly important; (hetero)aryl amines are widely found in natural products, pharmaceuticals, and agrochemicals (Figure 1A).[2]

The transition-metal catalyzed direct C−H amination of arenes is a potential alternative to the well-established Buchwald−Hartwig protocol for the construction of C−N bonds. The former method uses the ubiquitous C−H bonds, therefore giving access to a broad scope of substrates and producing minimum waste byproducts during the transformation.[3] Considerable effort has thus been made unraveling effective methods for the regioselective C−N bond formation of arenes; accordingly, a number of directing groups (DGs), aminating agents, and catalysts have been developed and successfully deployed.[4,5] In general, the nonmodifiable or modifiable DGs[6] effectively assist the formation of C(aryl)−N bonds.[3] Regrettably, their presence in the molecule limits wide synthetic applications; in contrast, the utilization of reusable-DG (RDG) could promote the synthetic viability of this protocol (Figure 1B).[4g] The relatively expensive and/or moisture sensitive Pd- and Rh-catalysts have extensively been used for the amination of C(arene)−H bonds in the presence of aminating agents, such as *N*-halo derivatives, NFSI, N−O bearing agents (*N*-hydroxy-carbamates, aryl or acyloxy amines), and aryl/alkyl sulfonyl azides (Figure 1B).[5,7]

Even though the use of an air-stable and cost-effective Ru-catalyst is beneficial, its implication for C(aryl)−N bond formation is rather less explored.[3f] For instance, a reusable methyl phenyl sulfoximine (**1′**; MPS), carbonyl, and/or heteroatom-bearing DG aided Ru-catalyzed *o*-C−H amidation of arenes has been performed with azides.[7] The fluoroaniline moiety exclusively assists enabling C−H amination of (hetero)-arenes with electrophilic aminating agent *O*-benzoyl hydroxylamine and a Ru(II)-catalyst.[8] The N-carbazolation of carbazoles is realized through the cross-dehydrogenative coupling between C−H and N−H bonds using a Ru-catalyst.[9] The importance of RDG and the use of air-stable Ru-catalysts in C−H activation prompted us to showcase a readily recoverable MPS-DG promoted regioselective *o*-C−H mono- and di-imidation of

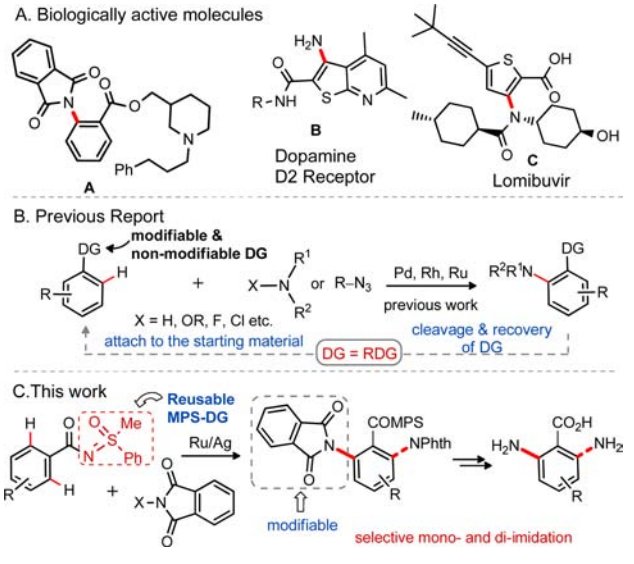


Figure 1. (A) Pharmaceutical important molecules. (B) Previous work on C−N bond formation of arenes. (C) The current work on Ru(II)-catalyzed imidation of arenes with the aid of reusable MPS-DG and modifiable *N*-tosyloxyphthalimide.

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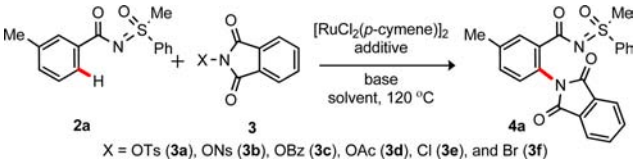
arenes with modifiable electrophilic iminating agent N-OTs-phthalimide under the combination of a Ru(II)-catalyst and Ag-salt (Figure 1C).

To begin, a reaction between *N*-(*m*-methylbenzoyl)MPS (**2a**) and *N*-OTs-phthalimide (**3a**) was commenced under different catalytic conditions comprising $[RuCl_2(p\text{-cymene})]_2$ and Ag-salts (Table 1). The desired *o*-C−H imidation product

Table 1. Optimization of *o*-C−H Imidation of *N*-Aroyl MPS[a]



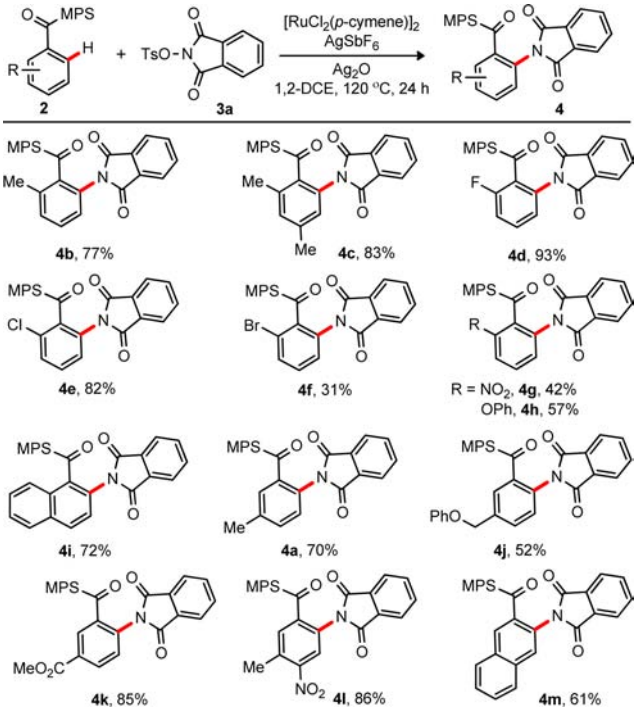
entry	3	additive (20 mol %)	base (0.1 mmol)	solvent (1.0 mL)	yield (%)[b]
1	**3a**	$AgSbF_6$	–	DCE	08
2	**3a**	$AgSbF_6$	$Cu(OAc)_2{\cdot}H_2O$	DCE	52
3	**3a**	$AgBF_4$	$Cu(OAc)_2{\cdot}H_2O$	DCE	32
4	**3a**	$NaBF_4$	$Cu(OAc)_2{\cdot}H_2O$	DCE	NR
5	**3a**	KPF_6	$Cu(OAc)_2{\cdot}H_2O$	DCE	07
6	**3a**	$AgSbF_6$	$Cu(OAc)_2$	DCE	47
7	**3a**	$AgSbF_6$	AgOAc	DCE	10
8	**3a**	$AgSbF_6$	NaOAc	DCE	21
9	**3a**	$AgSbF_6$	Ag_2O	DCE	72
10	**3a**	$AgSbF_6$	Ag_2O	DCE	85[c] (70)[c,d]
11	**3b**	$AgSbF_6$	Ag_2O	DCE	80
12	**3c**/**3d**	$AgSbF_6$	Ag_2O	DCE	35/5
13	**3e**/**3f**	$AgSbF_6$	Ag_2O	DCE	NR

[a]Reaction conditions: **2a** (0.1 mmol), **3** (0.15 mmol), $[RuCl_2(p\text{-cymene})]_2$ (5.0 mol %). [b]Conversion based on crude ^1H NMR of starting material. [c]$[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %). [d]**2a** (0.5 mmol), $ClCH_2CH_2Cl$ (2.0 mL), isolated yields. NR = no reaction.

4a was noticed by ^1H NMR, when the reaction was conducted with $[RuCl_2(p\text{-cymene})]_2$ and $AgSbF_6$ in 1,2-dichloroethane (1,2-DCE) at 120 °C for 24 h (entry 1, Table 1). Surprisingly, addition of $Cu(OAc)_2{\cdot}H_2O$ improved the formation of **4a** (52%) (entry 2). The additives $AgBF_4$, $NaBF_4$, and KPF_6 instead of $AgSbF_6$ were not suitable (entries 3−5). The use of $Cu(OAc)_2$, AgOAc, or NaOAc resulted in poor yields (entries 6−8). To our delight, use of Ag_2O led to an enhanced yield of **4a** (72%) (entry 9). With a 10 mol % catalyst loading, **4a** was produced in 85% yield with complete consumption of **2a** (entry 10). The use of other solvents such as $CHCl_3$, toluene, CH_2Cl_2, and/or 1,4-dioxane resulted 13−82% of **4a**.[10] The Rh(III), Ir(III), and Pd(II) catalysts were unsuccessful.[10] Not surprisingly, the reaction did not produce **4a** in the absence of the Ru(II)-catalyst or silver salt.[10] Next, various electrophilic iminating reagents (N−X) were surveyed under the optimized conditions. The reaction between **2a** and the strong electron-withdrawing N-ONs phthalimide (**3b**) gave 80% of **4a** (entry 11). A poor yield for **4a** was observed when N-OBz/-OAc phthalimides (**3c** and **3d**) were employed (entry 12). The N−Cl and N−Br phthalimide (**3e** and **3f**) were turned futile (entry 13). It appears that N-OTs phthalimide (**3a**) is the best electrophilic iminating agent for the current imidation of benzoic acid derivatives (entry 10).

The optimized conditions shown in entry 10, Table 1 were examined by exploring the generality of *o*-C−H imidations of *N*-aroyl MPS derivatives **2** with **3a** (Scheme 1). In general, the steric bulkiness in the molecule retards reactivity and produces

Scheme 1. *o*-C−H Imidation of *N*-Aroyl MPS Derivatives[a,b]



[a]Reaction conditions: **2** (0.5 mmol), **3a** (0.75 mmol), $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %), Ag_2O (0.5 mmol), $ClCH_2CH_2Cl$ (2.0 mL) at 120 °C, 24 h. [b]Isolated yields.

poor product yield. Gratifyingly, the *o*-substituted compounds **2b−h** reacted comfortably with **3a** delivering the desired imidation products **4b−h** (Scheme 1). The *o*-methyl moiety did not hinder the reaction. The halo groups F, Cl, Br survived; the bulky functional groups −Br, $-NO_2$, and −OPh at the *o*-position in arenes imparted moderate reactivity furnishing **4f−h** in acceptable yields with decent recovery of the unreactive precursors.

The α-naphthyl compound furnished the *o*-C−H imidation product **4i** in 72% yield leaving the peri-C−H bond untouched. The regioselective imidation of *m*-substituted *N*-aroyl-MPS was next investigated. To our delight, the less hindered *o*-C−H bond of arenes exclusively underwent imidation to afford **4a** and **4j−l** (Scheme 1). The ester and $-NO_2$ functionalities did not affect the reaction outcome, delivering **4k** and **4l** in 85% and 86% yield, respectively. Imidation of β-naphthyl derivative **2m** gave **4m** in moderate yield.

In general, the heteroatom inherently binds to the metal and affects the reaction efficiency. We therefore envisaged examining the imidation of heteroarenes under the optimized conditions (Figure 2). The reaction of thienyl 2-carboxylic acid derivative **2n** with **3a** delivered **4n** in 90% yield (Figure 2). Imidation of 5-Me/Cl/Br thienyl 2-carboxylic acid derivatives produced the corresponding desired products **4o−q** in excellent yields, while the *o*-imidation of the benzofuran derivative furnished a poor amount of **4r**.

We next examined the imidations of *para*- and unsubstituted *N*-aroyl-MPS derivatives (Scheme 2). To our surprise, reaction of *p*-methyl substituted **2s** with **3a** under the optimized conditions produced *o*-mono- (40%) and *o*-di-imidation (21%)

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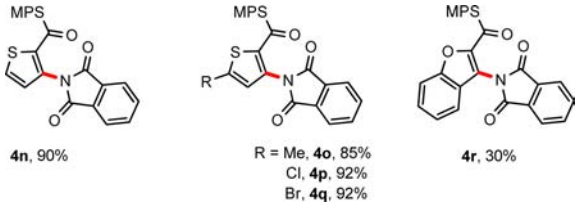
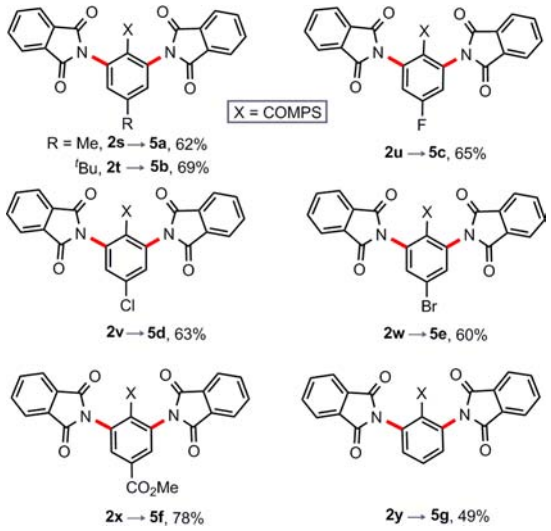


Figure 2. *o*-C−H imidation of *N*-heteroaroyl MPS derivatives.

Scheme 2. *o*-C−H Di-imidation of *p*- and Unsubstituted *N*-Aroyl MPS Derivatives[a,b]



[a]Reaction conditions: **2** (0.5 mmol), **3** (1.5 mmol), $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgSbF_6$ (40 mol %), Ag_2O (0.5 mmol), $ClCH_2CH_2Cl$ (3.0 mL) at 120 °C, 48 h. [b]Isolated yields.

products. The direct introduction of two C−N bonds adjacent to the DG in benzoic acid derivatives is difficult; in addition, the *o*-di-iminated benzoic acids are useful scaffolds.[8] Gratifyingly, some variation of the reaction conditions consisting of an increased amount of **3a** (3.0 equiv) led to better delivery of the *o*-di-imidation compound in 48 h.[10] The *p*-Me/*t*-Bu/F/Cl/Br/CO_2Me bearing *N*-aroyl-MPS smoothly furnished the desired di-imidation products **5a−f** in good yields (Scheme 2); the halo and ester groups in arenes did not affect reaction efficiency. Whereas reaction of unsubstituted *N*-benzoyl-MPS **2y** with **3a** produced **5g** in 49% isolated yield.

The use of bulkier diphenylsulfoximine (DPS) instead of MPS for the imidation of *N*-[4-methylbenzoyl]-diphenylsulfoximine (**2z**) led to the corresponding *o*-mono (40%) and *o*-di-imidation (17%) products with the recovery of unreacted **2z** (32%) in 24 h, a consequence of poor reactivity under the assistance of bulkier DPS-DG.[10]

The steric and electronic effect of sulfoximine derivatives to the *o*-C−H imidation of arenes was analyzed next (Figure 3). The *S*,*S*-dimethyl-sulfoximine and cyclic *S*,*S*-tetramethylene-sulfoximine moieties moderately assist the imidation affording **6a** and **6b** in 70% and 63% yield, respectively, while the sterically demanding *S*,*S*-diphenyl-sulfoximine DG did not facilitate effective C(aryl)−H imidation. Based on these results, the MPS was determined to be a potential DG for the *o*-C−H imidation of arenes with N-OTs phthalimide.

The assistance of a single reusable DG for the regioselective induction of different functionalities on *o*-C−H bonds of arenes

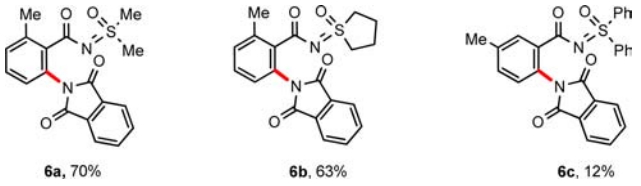
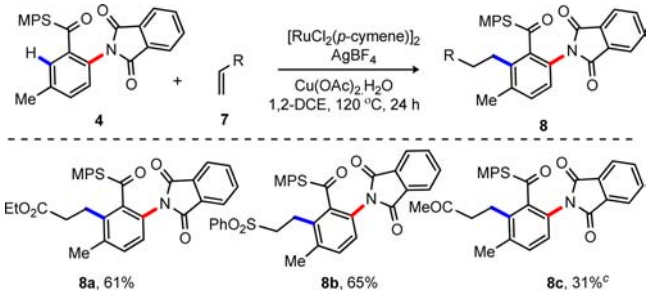


Figure 3. *o*-C−N bond formation of arenes with various sulfoximine derivatives.

is always admirable, as this method creates peripherally decorated hetero(arenes) through sequential functionalization of C−H bonds. We therefore envisaged exposing *o*-imidation compound **4a** to the recently developed Ru-catalyzed C−C bond forming conditions.[11] Interestingly, reaction of **4a** with ethyl acrylate (**7a**) under Ru-catalysis produced inseparable alkenylation and alkylation products, which on hydrogenation led to alkylation compound **8a** in 61% yield (Scheme 3).

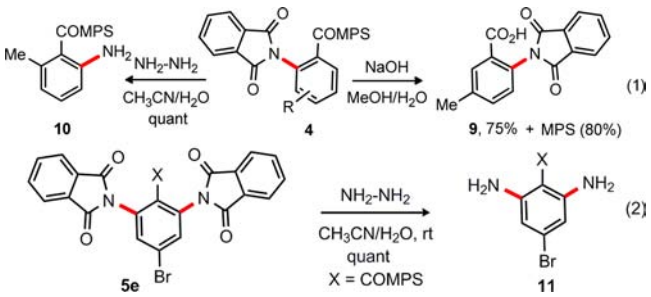
Scheme 3. Sequential *o*-C−H Functionalization[a,b]



[a]Reaction conditions: (i) **4** (0.3 mmol), **7** (0.6 mmol), $[RuCl_2(p\text{-cymene})]_2$ (10 mol %), $AgBF_4$ (20 mol %), $Cu(OAc)_2{\cdot}H_2O$ (0.3 mmol), $ClCH_2CH_2Cl$ (2.0 mL) at 120 °C, 24 h, (ii) Pd/C, H_2 balloon in MeOH. [b]Isolated yields. [c]Hydroarylation product

Following this method, **8b** was readily accessed from **2a** involving an imidation, alkenylation, and hydrogenation sequence. In contrast, the hydroarylation product **8c** was directly obtained during the C−C bond formation from **4a**.[11] The current method is suitable for introducing consecutive C−N and C−C bonds on arene carboxylic acid derivatives with the aid of an MPS-DG, which to the best of our knowledge is unprecedented.

As shown previously,[7a,11a] hydrolysis of **4a** with aqueous NaOH in MeOH readily cleaved the MPS-DG at 60 °C in 6 h. The *o*-phthalimido benzoic acid **9** was isolated in 75% yield along with the recovery of MPS-DG (80%) (eq 1).



Furthermore, the reductive cleavage of the *N*-phthaloyl moiety of mono- and di-imidation products with $NH_2{-}NH_2$ in CH_3CN/H_2O led to anilines **10** and **11** in quantitative yields (eq 1 and 2).[12] With the easy recovery of MPS-DG, and the

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ready modifiable nature of the *N*-phthalimide moiety, we believe the current method is synthetically viable.

In summary, we have shown a Ru(II)-catalyzed MPS-RDG enabled *o*-C−H imidation of benzoic acid derivatives with *N*-tosyloxyphthalimide. The current method exhibits major outcomes: the participation of a broad substrate scope including heteroarenes and tolerance of a wide array of functional groups, the facile reactivity of *o*-substituted compounds for the efficient production of the *o*-C−N bond, the occurrence of challenging *o*-di-imidations, the realization of sequential *o*-C−N and *o*-C−C bonds, the easy recovery of the MPS group from the products, and the ready modification of the phthalimide moiety leading to anilines. With these benefits, we believe this method will find broad synthetic application.

■ ASSOCIATED CONTENT

Supporting Information

Detailed experimental procedures and spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

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Notes

The authors declare no competing financial interest.

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