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COMMUNICATION

Au(III)-catalyzed intermolecular amidation of benzylic C–H bonds†

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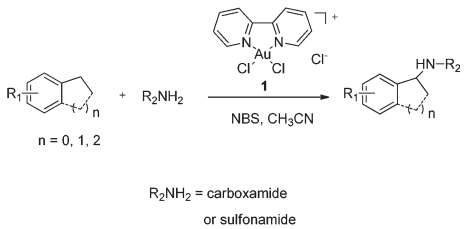
Au(III)-catalyzed intermolecular amidations of benzylic C–H bonds with sulfonamides and carboxamides are described. The protocol with the Au–bipy complex/*N*-bromosuccinimide system provides practical applications for synthesis of various amides *via* C–H activations. The reaction proceeds with high efficiency to give the corresponding amines, which are extremely useful synthetic intermediates.

Introduction

Transition metal catalyzed activations of C–H bonds, especially sp^3 C–H bonds, and subsequent C–C and C–N bond formations which avoid the use of prefunctionalized starting materials are valuable and straightforward synthetic strategies.[1] The direct C–N bond conversions of C–H bonds are of fundamental importance in organic synthesis, owing to the high prevalence of nitrogen-containing molecules in natural and pharmaceutical compounds.[2] The selective amidation among many different C–H bonds remains a challenge.[3] Considerable achievements have been made within the past several years in order to realize the intramolecular and intermolecular amidations *via* the activations of C–H bonds, particularly with regard to allylic and benzylic C–H bonds. Three factors must be considered in the amidations of C–H bonds: metal catalysts, oxidants and nitrogen sources. The reported metal catalysts include rhodium, ruthenium, silver, iron, copper and other metal complexes.[4–9] $PhI(OAc)_2$, *t*-BuOOAc, *t*-BuOOH and *N*-bromosuccinimide can be used in amidations of C–H bonds.[9] The C–H amidation methodologies reported usually proceed through transition metal–nitrene (imido) intermediates[4–7] and alternative nitrene derivatives such as chloramines-T,[10] bromamine-T,[11] and tosyloxycarbamates[12] have been used as the primary nitrogen sources.

Au catalysis has rapidly become a hot topic in chemistry in the past decade.[13] Au species are equally effective as heterogeneous or homogeneous catalysts,[14] which show excellent results in diversified reactions.[15] The use of powerful and environmentally benign Au(I) and Au(III) catalysts in functionalization of C–H bonds has highlighted their remarkable reactivity and leads to a significant increase in their utilisation.[16] He *et al.* achieved nitrene insertion into aromatic C–H bonds in a Au(III) catalyzed process for the formation of carbon–nitrogen bonds.[17] Insertion of PhI = NTs into a number of arenes was achieved at room temperature in the presence of 2 mol% $AuCl_3$. The authors commented that this procedure was only applicable to benzene rings possessing three or more substituents, which may be related to the higher nucleophilicities of these substrates. We have reported some Au–bipydine complex catalyzed formations of C–C, C–O and C–N bonds.[18] Oxidative α-cyanation of tertiary amines was catalyzed by Au complexes with trimethylsilyl cyanide to afford the corresponding α-aminonitriles in the presence of *tert*-butyl hydroperoxide in good to excellent yields under acid-free conditions at room temperature. Inspired by the previous good results, we are searching for a convenient, efficient, and general Au complex/oxidant system to achieve the selective amidation of C–H bonds. Fortunately, an excellent Au–bipy/*N*-bromosuccinimide system was developed for the amidation of sp^3 C–H bonds (Scheme 1).



Scheme 1 Gold-complex catalyzed amidation of benzylic C–H bonds.

Results and discussion

Initially, ethylbenzene (**5b**) and *p*-toluenesulfonamide (PTSA, **6a**) were chosen as the model substrates to optimize the catalysis conditions, including catalysts, oxidants and solvents. The results are listed in Table 1. Some Au catalysts, Au–bipy complex (**1**), Au–pyridine complex (**2**), Au–picolinic acid complex (**3**), Bu_4NAuCl_4, $AuCl_3$ and $AuClPPh_3$, were tested in CH_3CN (Fig. 1). Among the Au catalysts tested, Au–bipy complex (**1**) was found to be the most effective catalyst for the reaction (entry 5). No reaction was observed without using any catalyst (entry 1), $AuClPPh_3$ also showed no catalytic activity

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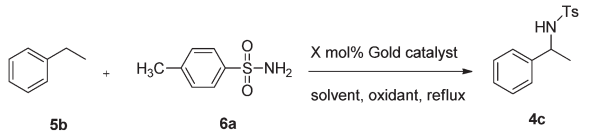
†Electronic supplementary information (ESI) available. See DOI: 10.1039/c2ob26857d

Table 1 Optimization of the gold-catalyzed amidation of ethylbenzene with *p*-toluenesulfonamide[a]



Entry	Catalyst (mol%)	Oxidant	Solvent	Time (h)	Yield[b] (%)
1	None	NBS	CH_3CN	10	Trace
2	$AuClPPh_3$ (10)	NBS	CH_3CN	10	Trace
3	$AuCl_3$ (10)	NBS	CH_3CN	10	21
4	Bu_4NAuCl_4 (10)	NBS	CH_3CN	8	55
5	**1** (10)	NBS	CH_3CN	8	68
6	**2** (10)	NBS	CH_3CN	12	51
7	**3** (10)	NBS	CH_3CN	13	42
8	**1** (10)	NBS	MeOH	8	60
9	**1** (10)	NBS	EtOH	8	62
10	**1** (10)	NBS	Toluene	8	75
11	**1** (10)	NCS	CH_3CN	8	70
12	**1** (10)	$PhI(OAc)_2$	CH_3CN	8	Trace
13	**1** (10)	*t*-BuOOH	CH_3CN	8	Trace
14	**1** (10)	*t*-BuOOAc	CH_3CN	8	Trace
15[c]	**1** (3)	NBS	CH_3CN	8	75
16[d]	**1** (3)	NBS	CH_3CN	3	78

[a] Reaction conditions: ethylbenzene (0.5 mmol), *p*-toluenesulfonamide (0.5 mmol), solvent (3 ml), oxidant (0.5 mmol) and gold catalyst (10 mol%). [b] Isolated yield. [c] 3 mol% gold complex **1**. [d] 1 mmol of ethylbenzene was used.

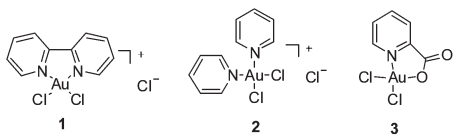
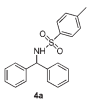
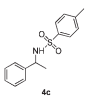
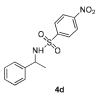
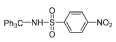
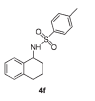
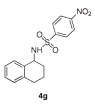
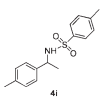
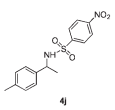
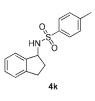
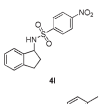
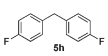
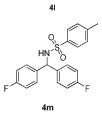
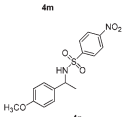
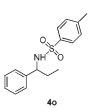
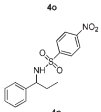


Fig. 1 Gold complexes **1**, **2** and **3**.

(entry 2). Although other gold complexes showed moderate catalytic activities, the reactions required relatively longer times to reach the reasonable yields (entries 4–7). $AuCl_3$, which was reported as the effective catalyst for the insertion of PhI = NTs into arenes,[17] showed a little catalytic activity for the reaction (entry 3). The effect of solvents (without any previous procedure for the commercially available solvents) was also investigated. Acetonitrile was the most effective solvent, although ethanol, methanol, and toluene could also be used (entries 7–9). A slightly lower yield was achieved when NCS replaced NBS as the oxidant (entry 11). No product was detected when other oxidants such as $PhI(OAc)_2$, *t*-BuOOAc, *t*-BuOOH and NCS were used (entries 12–14). The reaction also provided an excellent yield when the amount of Au–bipy complex (**1**) was reduced to 3 mol% (entry 15). The use of excess ethylbenzene (2 equiv.) shortened the reaction time to 2–3 h with a similar yield (entry 16). After the optimization of catalysts, oxidants and solvents, the following amidations were carried out under the standard conditions: 3 mol% Au–bipy as the catalyst, NBS as the oxidant, and acetonitrile as the solvent .

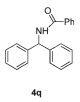
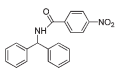
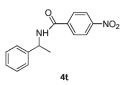
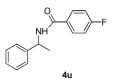
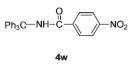
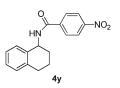
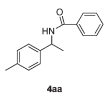
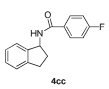
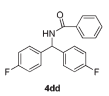
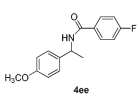
In order to explore the scopes of substrates for the amidations of benzylic sp^3 C–H bonds in the Au–bipy complex/NBS

Table 2 Gold–bipy/NBS catalyzed amidation of benzylic sp^3C–H bonds with sulphonamides[a]

Entry	5	6	Product 4	Yield[b] [%]
1				78
2	**5a**			73
3		**6a**		70
4	**5b**	**6b**		72
5		**6b**		81
6		**6a**		71
7	**5d**	**6b**		74
8		**6a**		70
9		**6a**		71
10	**5f**	**6b**		73
11		**6a**		72
12	**5g**	**6b**		69
13		**6a**		73
14		**6b**		71
15		**6a**		68
16	**5j**	**6b**		69

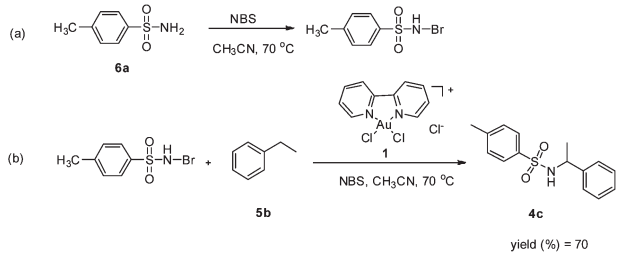
[a] Reaction conditions: benzylic reagent (1 mmol), amide (0.5 mmol), acetonitrile (3 ml), *N*-bromosuccinide (NBS) (0.5 mmol) and gold-complex **1** (3 mol%). [b] Isolated yield.

Table 3 Gold–bipy/NBS catalyzed amidation of benzylic sp^3C–H bonds with carboxamides[a]

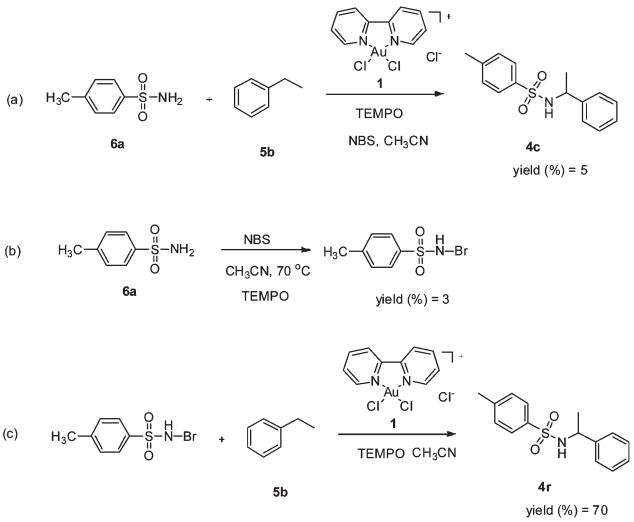
Entry	5	6	Product 4	Yield[b] (%)
1	**5a**			71
2	**5a**			73
3	**5b**	**6c**		70
4	**5b**	**6d**		70
5	**5b**			69
6	**5c**	**6c**		85
7	**5c**	**6d**		81
8	**5d**	**6c**		73
9	**5d**	**6d**		71
10	**5e**	**6c**		70
11	**5f**	**6c**		69
12	**5g**	**6c**		75
13	**5g**	**6e**		70
14	**5h**	**6c**		72
15	**5i**	**6e**		71

[a] Reaction conditions: benzylic reagent (1 mmol), amide (0.5 mmol), acetonitrile (3 ml), *N*-bromosuccinide (NBS) (0.5 mmol) and gold-complex **1** (3 mol%). [b] Isolated yield.

system, a series of benzylic substrates were investigated. As shown in Tables 2 and 3, all the substrates examined were selectively and efficiently converted into the corresponding amidation products in moderate yields. The activity order of benzylic reagents is triphenylmethane > diphenylmethane > ethylbenzene = tetrahydronaphthalene. The electron-donating or electron-withdrawing property of the substituents on benzene rings has no obvious effect on the reaction time and yield. For the carboxamides and sulfonamides, the electronic effects of the substrates are prime, the substrates containing the stronger electron-withdrawing groups show higher reactivity, and their order of activity is sulfonamides > benzamides.



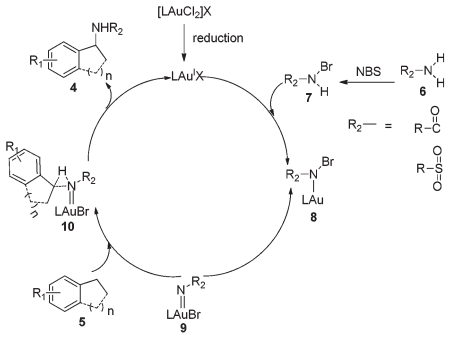
Scheme 2 (a) Conversion of sulfonamide to *N*-bromosulfonamide; (b) gold catalyzed reaction of ethylbenzene with *N*-bromosulfonamide.



Scheme 3 (a) Effect of a radical inhibitor on the gold catalyzed amidation; (b) effect of a radical inhibitor on the bromination of $TsNH_2$; (c) effect of a radical inhibitor on the reaction starting from the bromosulfonamide.

To gain insight into the gold-catalyzed amidation of benzylic C–H bonds, several control experiments were carried out to elucidate the mechanism. As shown in Scheme 2, reaction of sulfonylamide (**6a**) with NBS in acetonitrile produced *N*-bromo sulfonylamide, a similar product was obtained and identified by Sudalai.[19] Ethylbenzene (**5b**) and Au-complex (**1**) were added to the resulting solution, and the reaction provided 70% yield. Adding the radical inhibitor TEMPO (2,2,6,6-tetramethylpiperidinooxy) to the reaction of **5b** and **6a** dramatically decreased the reaction rate and yield (Scheme 3a). Two control experiments were carried out to elucidate which step the radical inhibitor had an effect on. As shown in Schemes 3b and 3c, the separate bromination step was stopped by the radical inhibitor, while the reaction starting from the bromo-amide still worked in the presence of TEMPO.

In light of our previous work on the Au-catalyzed oxidative C–C coupling, a plausible mechanism for the Au-catalyzed



Scheme 4 Plausible mechanism for the gold catalyzed amidation of benzylic bonds (L = 2,2′-bipyridine).

amidation of benzylic sp^3C–H bonds is shown in Scheme 4. Initially, Au^I species is generated *in situ* from the reduction of Au^{III} by the solvent or substrates.[18b,20] Reaction of carboxamide or sulfonylamide with NBS yields *N*-bromocarboxamide or *N*-bromosulfonamide **7**. Exchange of Au^I species with a proton in **7** gives intermediate complex **8**. Isomerization of **8** gives Au–nitrene complex **9**. **9** combines with the sp^3 C–H bond of the benzylic substrate to form the transition state **10**, and release of gold species in **10** gives the target product **4**.

Conclusions

In conclusion, we have demonstrated the novel Au-catalyzed amidation of benzylic C–H bonds *via* C–H activation. The reaction proceeds with high efficiency to give the corresponding amines which are extremely useful synthetic intermediates in the construction of biologically important compounds. Research is currently underway to elucidate the mechanism and to apply the principle to other catalytic systems.

Experimental section

General procedure for amidation of benzylic sp^3C–H bonds with amides

A 25 mL round-bottom flask equipped with a magnetic stirrer was charged with benzylic reagent (1 mmol), amide (0.5 mmol), acetonitrile (3 ml), *N*-bromosuccinide (NBS) (0.5 mmol) and gold-complex **1** (3 mol%). The resulting mixture was continuously stirred at 70 °C for 2–4 h. At the end of the reaction, the mixture was filtered and the filtrate was extracted with ethyl acetate (3–10 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel and the fraction was collected and concentrated to give the desired product.

Acknowledgements

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Notes and references

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