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ARTICLE

Dual gold and photoredox catalysis: Visible light-mediated intermolecular atom transfer thiosulfonylation of alkenes

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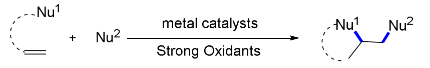
Regioselective difunctionalization of alkenes has attracted tremendous attentions from synthetic chemists, which has the advantage of introducing diverse functional groups onto vicinal carbons of common alkene moieties in a single operation. Herein, we report an unprecedented intermolecular atom transfer thiosulfonylation reaction of alkenes by combining gold catalysis and visible-light photoredox catalysis together. A trifluoromethylthio group (SCF_3) and other functionalized thio groups together with sulfonyl group were regioselectively introduced into alkenes in the most atom economic manner. A detailed mechanism study indicated that a synergistic combination of gold catalysis and photoredox catalysis is crucial for this reaction.

Introduction

Regioselective difunctionalization of alkenes has the advantage of introducing diverse functional groups onto vicinal carbons of common alkene moieties in a single operation and has attracted much attention from synthetic chemists.[1] Of the many catalytic processes that have been developed, a majority require stoichiometric amounts of an external strong oxidant, such as $PhI(OAc)_2$, Selectfluor (eqn (1))[2] and are typically initiated by a transition metal-catalyzed intramolecular addition. Fully intermolecular difunctionalization of alkenes is more challenging, because of the regiochemical issue (eqn (2)). Recently Stevenson developed elegant visible light-mediated atom transfer radical addition reactions converting haloalkanes and α-halocarbonyl compounds to alkenes.[3] Such neutral redox reactions are very attractive, because they are atom-economic and require no additional oxidants.



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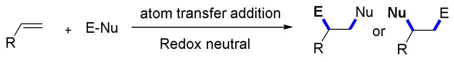

(2)

The trifluoromethylthio (SCF_3) group is a key structural unit in many pharmaceutical and agrochemical products, such as tiflorex, toltrazuril and vaniliprole.[4] It is well known that SCF_3 groups induce in a molecule even higher lipophilicity than trifluoromethyl substituents and consequently the incorporation of SCF_3 group into pharmaceuticals could greatly improve their ability to cross lipid membranes.[5] Because of this, the introduction of an SCF_3 group into small molecules has attracted much attention in synthetic chemistry.[6,7] Current methods for the construction of C-SCF_3 bond involve electrophilic trifluoromethylthio reagents[6] or the nucleophilic $AgSCF_3$ reagent[7]. Sulfonyl groups are similar in molecular size and charge distribution to carboxyl or phosphate groups, and the sulfonyl group has been introduced into bioactive molecules to improve their activity.[8] A sulfonyl group has two receptors for hydrogen bonds and this can enhance the binding affinities of drug molecules with target proteins. Sulfones can be easily transformed into other functional groups, such as alkenes, through Julia olefination.[9] We questioned whether both SCF_3 and sulfonyl groups could be introduced simultaneously into organic compounds in a single step. Such a transformation has not been described to date. This report describes a dual gold and photoredox catalytic approach to the intermolecular atom transfer thiosulfonylation of alkenes.

A combination of visible light-mediated photoredox catalysis[10] and transition-metal-catalysis is possible to bring two distinctive catalytic systems together and achieve unprecedented new reactions.[11] Recently, the use of gold(I) complexes in photoredox catalysis has gained considerable attention.[12, 13] This photoredox catalytic cycle triggers the conversion of Au(I) to Au(III) under mild conditions - a conversion which previously had only been achieved with stoichiometric quantities of strong oxidants.[14] In 2013, Glorius reported a first dual gold and photo-redox catalyzed reaction, which achieved intramolecular oxy- and aminoarylation of alkenes with aryldiazonium salts (Scheme 1A).[12b] Toste et al. took advantage of the visible light-mediated Au(I)/Au(III) cycle to produce arylative ring expansion reactions and carbon-phosphorus cross-coupling reactions (Scheme 1B).[12d,e] This

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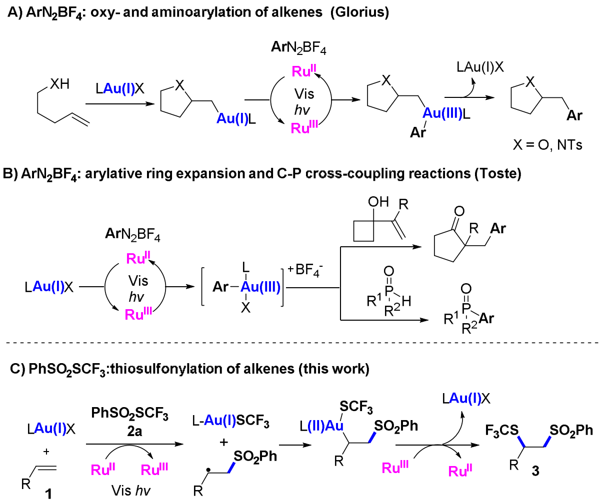
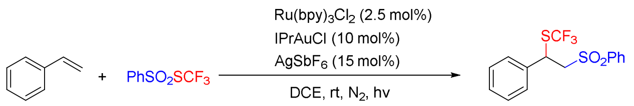
visible light-mediated single electron oxidative reaction has been utilized to access gold(III) complexes from gold(I) species.[12k] Recently Hashmi reported an aryldiazonium salts mediated Au(I) to Au (III) transformation upon irradiation with blue LED in the absence of a photosensitizer[12q]. In all these reactions,[12] the same aryldiazonium salts were used. The development of new gold/photoredox catalysis mode is highly desirable. To achieve the proposed trifluoromethylthiosulfonylation reaction in the most atom-economic manner, a difunctionalization reagent $PhSO_2SCF_3$ (**2a**) is required. This can be easily prepared from $PhSO_2Na$ and $AgSCF_3$ (For details, see supporting information (SI)). We envisioned that the reaction of $PhSO_2SCF_3$ with a cationic gold catalyst in the presence of a photocatalyst would generate an $LAuSCF_3$ species and a benzenesulfonyl radical, which can then add to the alkene forming a new alkyl radical.[3a] This radical may oxidize $LAuSCF_3$ to an Au(II) intermediate, which is further oxidized to an Au(III) derivative by the Ru^{III} catalyst. Subsequent reductive elimination forms the target difunctional product, regenerating the Au(I) catalyst (Scheme 1C). This reaction provided a new approach to introduce trifluoromethylthio (SCF_3) group at the α position of styrenes.



Scheme 1. Dual gold and photoredox catalytic reactions

Table 1. Optimization of reaction conditions[a]



1a **2a** **3a**

Entry	Variation from the "standard" conditions	Yield (%)[b]
1	None	94 (87)
2	AuCl instead of IPrAuCl	0.
3	PPh_3AuCl instead of IPrAuCl	56
4	IMesAuCl instead of IPrAuCl	72
5	PPh_3AuNTf_2 instead of IPrAuCl and $AgSbF_6$	67
6[b]	$IPrAuSbF_6$ instead of IPrAuCl and $AgSbF_6$	88
7	CH_3CN instead of DCE	5
8	CH_3OH instead of DCE	4
9	$Ru(phen)_3Cl_2$ instead of $Ru(bpy)_3Cl_2$	67
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	0
11	*fac*-$Ir(ppy)_3$ instead of $Ru(bpy)_3Cl_2$	0
12	IPrAuCl (5 mol%), $AgSbF_6$ (7.5 mol%), $Ru(bpy)_3Cl_2$ (1.2 mol%)	64

[a] Reaction conditions: a mixture of **1a** (0.4 mmol), **2a** (0.2 mmol), IPrAuCl (10 mol%), $AgSbF_6$ (15 mol%), $Ru(bpy)_3Cl_2$ (2.5 mol%), in DCE (1 mL) was stirred at rt under irradiation with a 100 w blue LED at N_2 atmosphere. [b] $Ru(bpy)_3(PF_6)_2$ instead of $Ru(bpy)_3Cl_2$. [C] Determined by ^{19}F NMR using (trifluoromethyl)benzene as the internal standard. The number in parentheses is the isolated yield. IPr = 1,3-bis(2,6-diisopropyl-phenyl)imidazol-2-ylidene, ppy = 2-phenylpyridine.

Results and discussion

To validate this concept, styrene (**1a**), and $PhSO_2SCF_3$ (**2a**) were selected as model substrates to test the feasibility of this hypothesis. After a detailed optimization of reaction conditions, the proposed alkene trifluoromethylthiosulfonylation product (**3a**) was achieved in 94% yield using the standard conditions: a mixture of IPrAuCl (10 mol%), $AgSbF_6$ (15 mol%), $Ru(bpy)_3Cl_2$ (2.5 mol%) in DCE (1mL) was stirred under irradiation for 1-3 hrs with 100 w blue LED in a N_2 atmosphere (Table 1, entry 1). The dual catalytic nature of this reaction was investigated by control experiments, which confirmed that the gold catalyst, the Ru(II) photosensitizer, and visible light irradiation are all necessary for the reaction (Table S2, entries 2-5). In the absence of silver salt, the reaction led to a dramatic decrease of yields (NMR yields < 5%), showing that the formation of a cationic gold species is highly important (Table S2, entry 4). Other gold catalysts such as AuCl, Ph_3PAuCl and Gagosz catalyst ($Ph_3PAuNTf_2$) are all less effective than IPrAuCl (entries 2-5). Silver free system using $IPrAuSbF_6$ and $Ru(bpy)_3(PF6)_2$ led to slightly lower 88% yield (entry 6), so silver is not necessary in this reaction. Reactions in other solvents such as acetonitrile and methanol led to only traces of products, and no solvent addition products, indicating that a carbocation mechanism is not involved (entries 7, 8). Other iridium photocatalysts including $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ and *fac*-$Ir(ppy)_3$ were also tested, no product was observed in the reaction system (entries 10-11). Trying to lower catalysts loading also led to a lower reaction yield (entry 12).

With these optimized conditions established, the scope of the dual gold and visible light-mediated alkene difunctionalization reaction was explored. As summarized in table 2, a wide range of styrene type alkenes were applicable and moderate to good isolated yields of product were achieved (**3a**-**3l**). Substrates bearing different electron-withdrawing or electron-donating groups at different positions in the aromatic ring were all compatible with this reaction. A series of functional groups such as ester, cyano, trifluoromethyl, halogen were all well tolerated under the reaction conditions. In particular, the alkene **1m**, containing an alkyne moiety, was also applicable to this reaction giving the corresponding alkene difunctionalized product (**3m**) in

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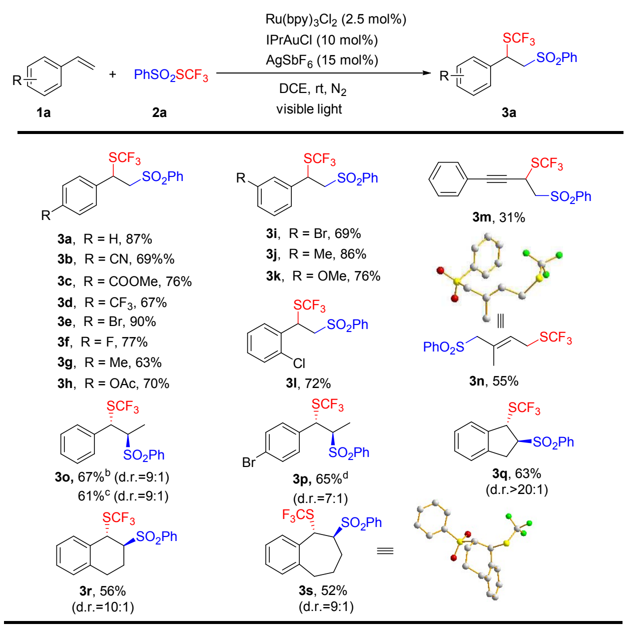
moderate yield. Notably, dienes such as isoprene were also amenable to this transformation, giving as the major product in 55% yield, the 1,4-addition product (**3n**), whose structure was confirmed by single X-ray analysis.

Table 2. Substrate scope of alkene trifluoromethylthiosulfonylation reactions[a]

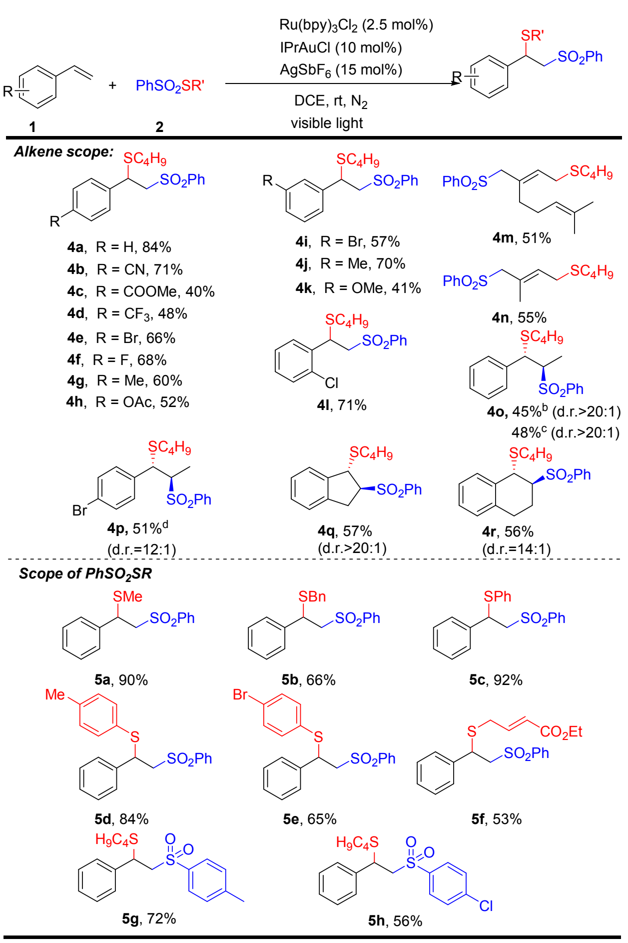


[a] Standard conditions were employed. Isolated yields were reported. Diastereoselectivities were determined by GC-Mass. [b] from (*E*)-alkene. [c] from (*Z*)-alkene. [d] from (*Z*)-alkene : (*E*)-alkene = 7 : 3.

Internal alkenes, including acyclic and cyclic alkenes were also suitable substrates. Most of the reactions exhibited excellent diastereoselectivities. Interestingly, *trans*-alkenes and *cis*-alkenes afforded the same major products (**4o**) in similar yields with similar diastereoselectivities，which is very important feature and also advantage of this reaction. The relative configuration of the seven-membered product **3s** was unambiguously characterized by single X-ray crystallography. However, the reactions of aliphatic alkenes were unsuccessful under the same conditions.

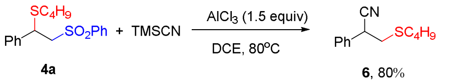
Organosulfur compounds are ubiquitous in the pharmaceutical industry, material science, and food chemistry.[15] The construction of C-S bonds is important but also challenging,[16] because a sulfur atom could coordinate with metal catalysts such as Au leading to catalyst inactivation. When we applied the above dual catalysis system to the general thiosulfonylation reaction of alkenes using PhSO$_2$SC$_4$H$_9$ (−1.64 V, vs SCE) as the reagent, which might be more challenging because of its lower oxidative potential comparing with PhSO$_2$SCF$_3$ (−1.11 V, vs SCE, Figure S5, SI), to our delight, the reactions were very successful (Table 3). Various alkenes including styrenes, internal alkenes and dienes all enter into this thiosulfonylation reaction giving the corresponding products in good yields (**4a**-**4r**). A large variety of alkyl and aromatic thio groups can be easily introduced into a styrene molecule, giving difunctional products generally in very good yields (**5a**-**5h**).

Table 3. Substrate scope of alkene thiosulfonylation reactions[a]



[a] Standard conditions were employed. Isolated yields were reported. Diastereoselectivities were determined by GC-Mass. [b] from (E)-alkene. [c] from (Z)-alkene. [d] from (Z)-alkene : (E)-alkene = 7 : 3.

The sulfonyl group (-SO$_2$-) is a useful synthon for further transformations. For instance, the reaction of compound **4a** with TMSCN or allylsilane in the presence of aluminum chloride provided the sulfur migration substitution products **6** and **7** in good yields (eqn (3, 4)). This reaction might go through a neighboring group participating S$_N$1 type of reaction.



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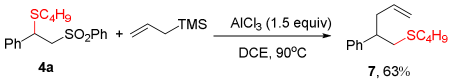

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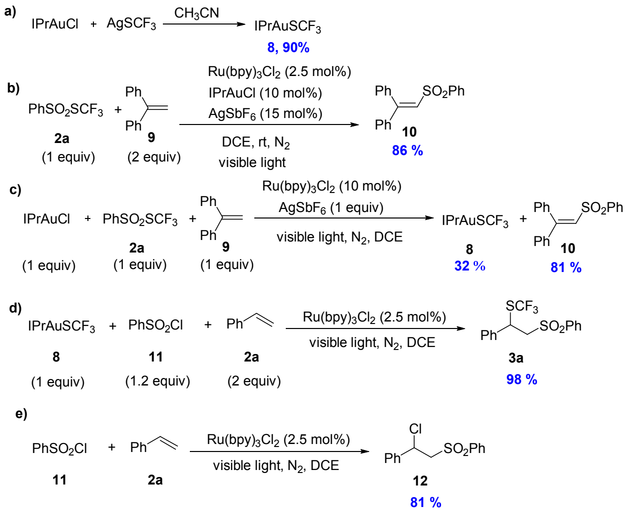
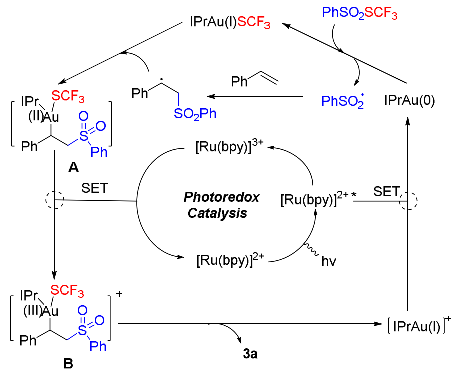
Control experiments were conducted to explore the mechanism of this reaction. The reaction of 1,1-diphenylethylene **9** under standard conditions, vinyl sulfone (**10**) was isolated in 86% isolated yield (scheme 2b). These results clearly indicate formation of the benzenesulfonyl radical in the reaction system. The ^{19}F NMR spectrum of the crude mixture from the reaction contained an additional signal at -26 ppm, which was later determined to be from IPrAuSCF$_3$ (**8**). This compound could be independently synthesized by the reaction of IPrAuCl and AgSCF$_3$, which is sufficiently stable to be isolated by column chromatography (Scheme 2a). A stoichiometric reaction between IPrAuCl, **2a** and the radical scavenger (**9**) afforded vinyl sulfone (**10**) in 81% isolated yield and **8** in 32% yield (Scheme 2c). This benzenesulfonyl radical could also be generated by PhSO$_2$Cl (**11**) in the presence of visible light,[3a] and the reaction between **8**, **11**, and **2a** afforded the target product (**3a**) in 98% yield (Scheme 2d). In contrast, without this gold intermediate, the direct atom transfer radical addition adduct **12** was obtained in 81% yield (Scheme 2e). This experiment demonstrated that IPrAuSCF$_3$ is the possible reaction intermediate.[17]



Scheme 2. Control experiments

Stern-Volmer fluorescence quenching experiments to gain insight into the photoredox catalytic cycle were performed (For details, see the supporting information (Figure S1-2, SI). The photoluminesecence of Ru (bpy)$_3^{2+}$ was quenched by IPrAuSbF$_6$ with a rate constant of 8.85 × 10^2 Lmol^{-1}. In contrast, PhSO$_2$SCF$_3$ (-1.11 V vs SCE) and styrene cannot serve as an emission quencher. The cyclic voltammogram of IPrAuSbF$_6$ contains a reversible reduction peak at -0.11 V vs SCE (Figure S5, SI), indicating that this cationic gold catalyst is easily reduced by the excited state of the photocatalyst Ru (bpy)$_3^{2+}$ ($E_{1/2}^{III/*II}$ = −0.81 V vs SCE).[10b] To characterize this electron transfer reaction further, a flash-photolysis study was carried out (Figure S3). Upon laser excitation by 355 nm light, the ground state absorption at ~450 nm was obviously bleached and a characteristic absorption band at ~360 nm was detected. This is ascribed to the reductive state of bipyridine in Ru(bpy)$_3$(SbF$_6$)$_2$ (Figure S4-a, SI).[18] When PhSO$_2$SCF$_3$ was introduced into a solution of Ru(bpy)$_3$(SbF$_6$)$_2$, the transient absorption spectra made almost no difference (Figure S4-b. SI). The lifetime of the excited state of Ru(bpy)$_3$(SbF$_6$)$_2$ slightly decreased from 493 to 473 ns from the kinetics probed at 450 nm. However, when IPrAuSbF$_6$ was added into a solution of Ru(bpy)$_3$(SbF$_6$)$_2$, a new absorption appeared at ~530 nm. This is characteristic of gold nanoparticles. At the same time, the lifetime of the excited state of Ru(bpy)$_3$(SbF$_6$)$_2$ decreased from 493 to 394 ns (Figure S4-c. SI). All these results suggested that the electron transfer between IPrAuSbF$_6$ and the excited ^{3}MLCT state of Ru(bpy)$_3$(SbF$_6$)$_2$ occurred, giving the active IPrAu(0) species which might aggregate to form gold nanoparticles[19]. The reductive IPrAu(0) catalyst formed *in situ* is highly reactive[20] and might react with PhSO$_2$SCF$_3$ providing IPrAuSCF$_3$ (**8**) and a benzenesulfonyl radical.



Scheme 3. Proposed mechanism

On the basis of the above results and previous reports,[12] a tentative proposed mechanism is shown in Scheme 3. Irradiation of Ru(bpy)$_3^{2+}$ generates a long-lived photoexcited state Ru (bpy)$_3^{2+*}$, which undergoes an single-electron transfer reaction with cationic IPrAu(I) to initiate the catalytic cycle and provide Ru(bpy)$_3^{3+}$ and the highly active IPrAu(0) which can reduce PhSO$_2$SCF$_3$ to form IPrAu(I)SCF$_3$ (**8**) and a benzenesulfonyl radical, which added to styrene affords an alkyl radical. This radical is able to oxidize **8** to the Au(II) intermediate **A**, which is further oxidized to the Au(III) intermediate (**B**) by Ru (bpy)$_3^{3+}$, generating Ru(bpy)$_3^{2+}$ thereby completing the photoredox catalytic cycle. Reductive elimination of the Au(III) intermediate **B** delivers the product and regenerates the Au(I) catalyst. This alkyl radical directly reacted with another equivalent of PhSO$_2$SCF$_3$ could also afford the target product in a radical chain mechanism. In our reaction, when the internal alkenes were employed as reaction substrates, excellent diastereoselectivities were observed and both *trans*- and *cis*-alkenes gave the same diastereomer, which

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is not common in pure radical reaction. The IPrAu(I)SCF$_3$ (**8**) approached the in situ formed alkyl radical from the less sterically hindered side, which might contribute to the excellent diastereoselectivity of this reaction. The proposed dual gold photoredox catalytic cycle maybe the major pathway, although the radical chain reaction couldn't be excluded. This gold catalytic cycle from Au(0) to Au(III) is similar to reported nickel participating photoredox catalytic cycles.

Conclusions

In summary, we have reported an intermolecular atom transfer thiosulfonylation reaction of alkenes. Both trifluoromethylthio group and other functionalized thio groups can be introduced into alkenes with excellent regioselectivity and diastereoselectivity. These reactions are promoted by a synergistic combination of gold catalysis and visible light photoredox catalysis. Detailed control experiments and reaction mechanism study indicate that the gold catalyst goes through four different valencies from Au(0) to Au(III), which is unprecedented in previously reported Au-catalyzed transformations. This new dual gold and photocatalysis mode holds potential for the applications to other important transformations.

Acknowledgements

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