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Photoredox Mediated Nickel Catalyzed C(sp^3)–H Thiocarbonylation of Ethers

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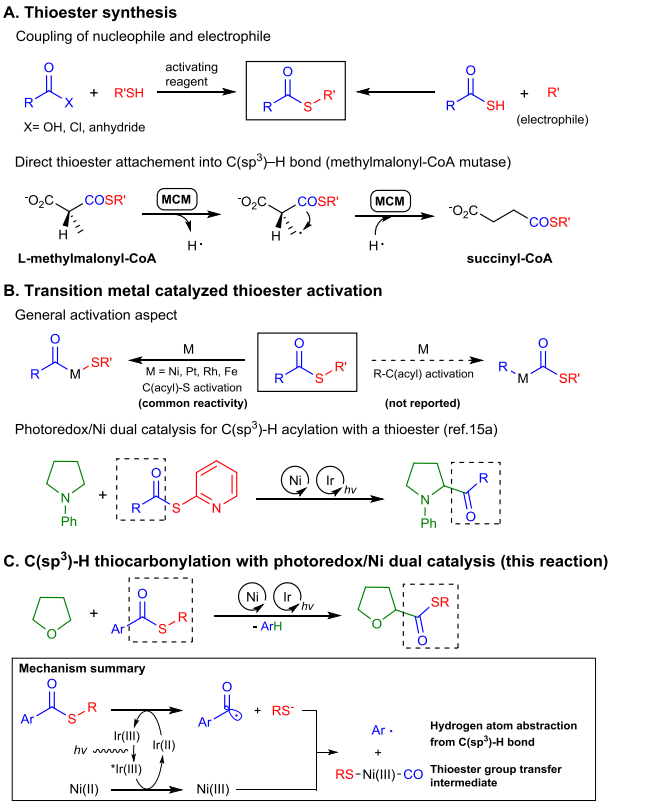
The first direct C(sp^3)–H thiocarbonylation reaction is achieved by visible light photoredox/Ni dual catalysis. Thioester group of thiobenzoate is transferred to α-oxy carbon of various cyclic/acyclic ethers, opposite to the commonly expected chemical reactivity involving acyl group transfer via the weaker C(acyl)–S activation. Through mechanistic studies, we proposed that the reaction is initiated by photocatalytic reduction and fragmentation of the thioester into acyl radical and thiolate. A nickel complex binds to the thiolate and induces decarbonylation of the acyl radical to form an aryl radical, which abstracts hydrogen from α-oxy carbon of ether. The resulting α-oxy C(sp^3) centered radical rebounds to (RS)(CO)Ni complex, which undergoes CO migratory insertion and reductive elimination to give the desired thioester product.

Introduction

Thioesters are versatile synthetic building blocks[1] and convenient protecting groups for thiols in organic synthesis.[2] As an activated analogue of alcohol-derived ester, it can be easily transformed into ester, amide, and ketone. In Nature, the thioester group plays critical role in metabolism[3] and cellular function regulation.[4] The thioester moiety also serves central role in Native Chemical Ligation (NCL)[5] and Expressed Protein Ligation (EPL)[6] in the biological sciences.

Due to its versatility, the direct and selective incorporation of a thioester group into the desired position of a molecule has high synthetic value. The most common method for thioester synthesis is a reaction between a thiol and an activated carboxylic acid, or the coupling of a thioacid and an electrophile (Scheme 1A).[7] However, the requirement of high oxidation state carbon-based reactants, harsh reaction conditions, and sensitivity of thiols towards oxidation limit the utility of the reactions. Several alternative synthetic methods have been developed including the oxidative thioesterification of aldehydes[8] and thiocarbonylation of alkenes[9] or organic halides[10] with carbon monoxide gas. Most of these methodologies still require a thiol and a suitable coupling partner as the reactants, sharing similar limitations of the classical syntheses.

Direct C–H thiocarbonylation can serve as an ideal approach for thioester synthesis. Indeed, Nature utilizes an inspiring C–H functionalization strategy for the synthesis of metabolically important thioesters. Methylmalonyl-CoA mutase (MCM) and coenzyme B_{12} catalyse L-methylmalonyl-CoA to succinyl-CoA isomerization by radical generation on an sp^3 hybridized carbon followed by intramolecular 1,2-migration of the thioester group (Scheme 1A).[11] However, to the best of our knowledge, a direct thioester group transfer reaction to a C–H bond has never been achieved in organic synthesis. To address the challenge, we envisioned an unprecedented C(sp^3)–H thiocarbonylation utilizing simple thioester molecules as the thioester group source.



Scheme 1. Thioester synthesis

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† Electronic supplementary information (ESI) available: Experimental details and full characterization of substrates and products. Crystallographic data for compound **[Ni-II]**. **CCDC 1516709**. For ESI and crystallographic data in CIF or other electronic format see DOI:

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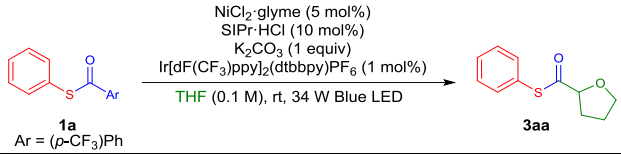
The biggest hurdle for the thioester group transfer reaction is relative weakness of C(acyl)–S bonds as compared to C(acyl)–C bond (Scheme 1B). Indeed, to the best of our knowledge, all literature examples concerning the oxidative addition of organometallic complex into thioesters show that the reaction preferably occurs in C(acyl)–S bond to give acyl–metal complex.[12] We could not find any example on selective C–C(acyl) bond activation in a thioester. Nevertheless, we initially postulated that selective activation of the C–C(acyl) bond could be achieved by controlling the electronic and steric character of the thioesters, motivated by the cases of selectivity control of C(aryl)–O vs C(acyl)–O bond activation in esters.[13] The theory was eventually proven incorrect.

Recently, visible light photoredox/transition metal dual catalysis[14] has been utilized for selective sp^3 C–H functionalization. The examples showed that even weakly reactive α-amino[15] and α-oxy[15d, 16] C(sp^3)–H bonds could be functionalized. We devised a strategy to merge photoredox driven C–H functionalization with transition metal mediated thioester activation. Specifically, we focused on the α-oxy C(sp^3)–H thiocarbonylation reaction, since α-oxy carboxylic acid derivatives are key functional groups in some pharmaceuticals such as selexipag or cetirizine. Herein, we report the first chemo-selective α-oxy C(sp^3)–H thiocarbonylation reaction with a newly proposed photoredox/Ni dual thioester activation strategy (Scheme 1C).

Results and Discussion

Recently, Doyle and co-workers succeeded in reacting an N-aryl amine with a 2-pyridylthioester under photoredox/Ni dual catalytic conditions (Scheme 1B).[15a] In this case, only the C–H acylation product via activation of the weaker C(acyl)–S bond was observed. To preferably activate the C(acyl)–C bond instead, we hypothesized that increasing the electron deficiency of the acyl group of the thioester could selectively weaken the C(acyl)–C bond. Indeed, an electron deficient thioester **1a** showed reasonably high reactivity toward the target reaction (Table 1, Table S1). After intensive optimizations (Table S2), an excellent yield (90%) of **3aa** was obtained using an N-heterocyclic carbene (NHC) based Ni(II) complex with Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 as a visible light photoredox catalyst in THF (**2a**) (Table 1, entry 1). The only detected side product was 4-trifluoromethyl diphenyl sulfide (**4a**), which was possibly formed by decarbonylation process.[17] It should be emphasized that the thioester product was solely formed without generation of α-oxy C–H acylation product.[15a] The reactivity highly depends on the electronic nature of thioesters. Among those tested, only thiobenzoate derivatives exhibited the desired activity (Table S1). A dramatic decrease in yield was observed when relatively electron rich acyl groups were used (Table 1, entries 2–3), while the pentafluorophenyl group gave a moderate yield (entry 4). Control experiments showed that Ni catalyst, NHC precursor, and photoredox catalyst are essential components of the reaction (entries 5–7). When the separately prepared N-heterocyclic carbene (NHC) SIPr was used as an additive, a moderate yield was obtained without the use of additional base, indicating the NHC bound nickel complex acted as the catalytically active species (entry 8). In addition, a good yield with full conversion was also obtained in a shortened reaction time of 4 h (entry 10).

Table 1 Optimization of reaction conditions[a]



Entry	Reaction conditions	t (h)	Yield of (%)[b]
1	As shown	12	90[c]
2	Ar = Ph (**1u**)	12	7
3	Ar = (*p*-Me)Ph (**1v**)	12	2
4	Ar = C_6F_5 (**1w**)	12	49
5	No $NiCl_2$·glyme	12	0
6	No SIPr·HCl[d]	12	0
7	No Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6	12	0
8	SIPr instead of SIPr·HCl with no K_2CO_3	12	60
9	Ni(COD)$_2$ instead of $NiCl_2$·glyme	12	<1
10	As shown	4	89 (83[e])

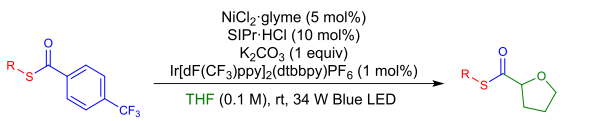
[a] Reaction conditions: thioester (0.25 mmol), $NiCl_2$·glyme (5 mol%), SIPr·HCl (10 mol%), K_2CO_3 (1 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1 mol%), and THF (2.5 mL) in 4 mL vial irradiated with a 34 W Blue LED. [b] GC yield using dodecane as internal standard. [c] α,α,α-Trifluorotoluene (75%) was observed. [d] SIPr·HCl = 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride. [e] Isolated yield.

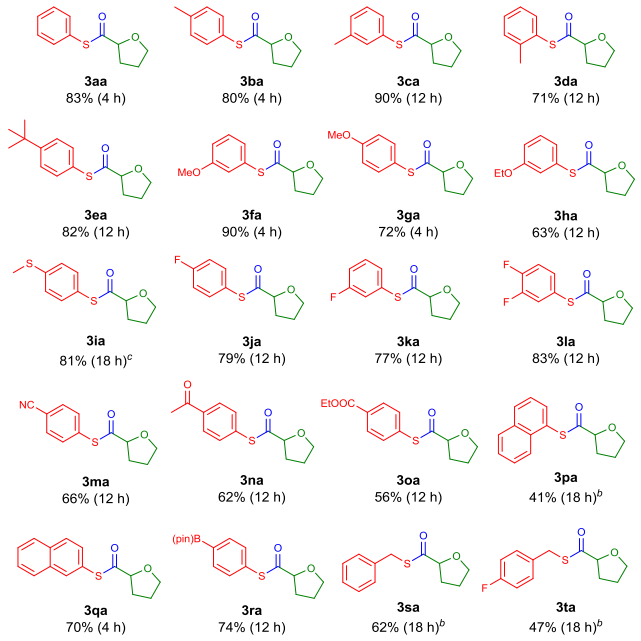
With the optimized conditions in hand, diverse aryl thioesters were applied for the thiocarbonylation reaction of THF (Table 2). A range of aryl thioesters with alkyl substituents in the *p*-, *m*- and *o*-positions gave good yields of the desired products (**3ba**–**3ea**). Alkoxy groups in the substrate did not mediate any side reactions, presumably due to the higher amount of the THF radical (**3fa**–**3ha**). A thioether group was also tolerated (**3ia**). Fluorine-containing thioesters showed excellent reactivity (**3ja**–**3la**). Encouragingly, C–N and C–O unsaturated bonds did not induce any side reactions or interfere with the catalytic reactivity (**3ma**–**3oa**). Naphthyl thioesters reacted smoothly, although 1-naphthylthioester gave a decreased yield (**3pa**, **3qa**). Notably, an aryl boronate, which can be further functionalized, was also tolerated under the reaction conditions (**3ra**). Finally, a benzyl thioester was successfully transferred to the α-oxy carbon of THF (**3sa**, **3ta**). However, aliphatic thioesters did not exhibit any reactivity under the described reaction conditions.

Next, the scope of ethers was investigated (Table 3). Selective and efficient reactions occurred in the α-oxy position of common cyclic ether solvents such as tetrahydropyran (**3ab**) and 1,4-dioxane (**3ac**). In the case of ethers in which the solubility of the Ni complex is poor, acetonitrile was adopted as a co-solvent. Diethylether (**2d**) underwent thiocarbonylation moderately (**3ad**). The use of anisole (**2e**) or *tert*-butyl methyl ether (MTBE, **2f**) gave the desired products in low yields (**3ae**, **3af**), possibly due to the relatively low stability of the primary alkyl radical compared to its secondary analogue. Other heterocycles such as thiophene and N-protected pyrrolidines (*N*-methyl, *N*-phenyl, and *N*-Boc) were tested as reactants using

acetonitrile or DMA as the co-solvent due to solubility issue, and no conversion was observed.

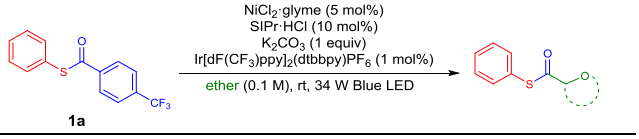
Table 2 Substrate scope of thioesters[a]

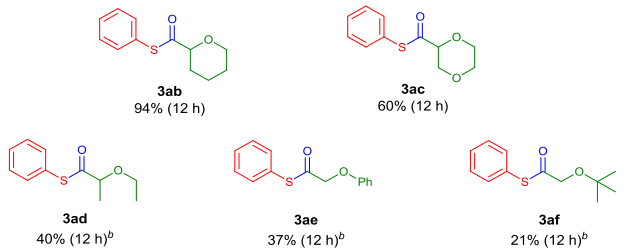




[a] Reaction conditions: thioester (0.25 mmol), $NiCl_2$·glyme (5 mol%), SIPr·HCl (10 mol%), K_2CO_3 (1 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1 mol%), and THF (2.5 mL) in 4 mL vial irradiated with a 34 W Blue LED. [b] 2 mol% of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 was used.

Table 3 Substrate scope of ethers[a]



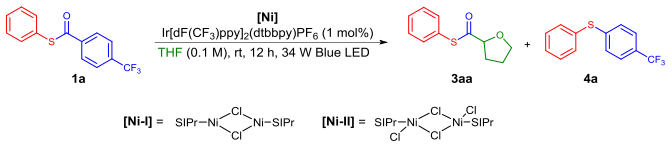


[a] Reaction conditions: **1a** (0.25 mmol), $NiCl_2$·glyme (5 mol%), SIPr·HCl (10 mol%), K_2CO_3 (1 equiv), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (1 mol%), and ether (2.5 mL) in 4 mL vial irradiated with a 34 W Blue LED. [b] Ether (2.5 mL) is mixed with CH_3CN (0.5 mL).

From mechanistic investigations, we realized that the initial hypothesis on preferable C–C(acyl) bond activation by Ni complex should be reconsidered. To obtain insight of relative bond strengths, we compared calculated bond dissociation energy (BDE) of C–C(acyl) bond with that of the C–S bonds as a preliminary tool like in the Ni catalyzed C(aryl)–O vs C(acyl)–O bond activation in ester.[13d] Differently from our expectation of significantly lowed BDE of C–C(acyl) bond in electron deficient thioester **1a**, the calculated BDE of the C–C(acyl) bond of thioester **1a** is still much higher than that of the C–S bonds (Table S3). Also, the BDE cannot explain the unique reactivity of **1a** among various thioesters since no significant difference among thioesters was found. In pursuit of an alternative pathway, a mechanism initiated by oxidative addition of Ni(0) into the C(acyl)–S bond was considered. Followed by decarbonylation and migratory insertion of CO into the Ni–S bond, it might generate a thiocarbonyl Ni intermediate. However, Holm and Tucci reported that CO migratory insertion preferably occurred to Ni–C bond over a Ni–S bond in [Ni(bpy)(R')(SR)] complexes.[18] Moreover, we found that $Ni(COD)_2$, a commonly used Ni(0) complex which has high oxidative addition activity, did not mediate the desired reaction. Instead, a significant amount of decarbonylation product **4a** was formed (Table 4). To identify active catalytic intermediates, syntheses of monomeric NHC-Ni(I) and Ni(II) complexes were attempted, but unsuccessful. Instead, catalytic activities of the reported NHC-Ni dimer complexes [(SIPr)NiCl]$_2$ (**[Ni-I]**)[19] and [(SIPr)NiCl]$_2$(μ-Cl)$_2$ (**[Ni-II]**)[20] were investigated to get insight on the oxidation state of Ni during the reaction (Table 4).[21] With **[Ni-I]**, the decarbonylation product **4a** was observed as the major product (29%) with 5% of **3aa**. On the contrary, well-defined NHC-Ni(II) dimer complex [(SIPr)NiCl]$_2$(μ-Cl)$_2$ (**[Ni-II]**) produced the C–H thiocarbonylation product **3aa** (11%) more than **4a** (8%).

Because the tested Ni complexes exhibited significantly lowered conversions, we retested the catalytic activity in presence of 1 mol% of $NiCl_2$·glyme (Table 4, entries 4–7). Under the conditions, difference in catalytic ability of Ni(0), Ni(I), and Ni(II) becomes more significant. While addition of 5 mol% of Ni(0) or Ni(I) does not facilitate the formation of **3aa**, presence of NHC-Ni(II) species gave meaningful improvements in reactivity, implying that Ni(II) could be the major catalytically active species.

Table 4 Catalytic activity of nickel complexes

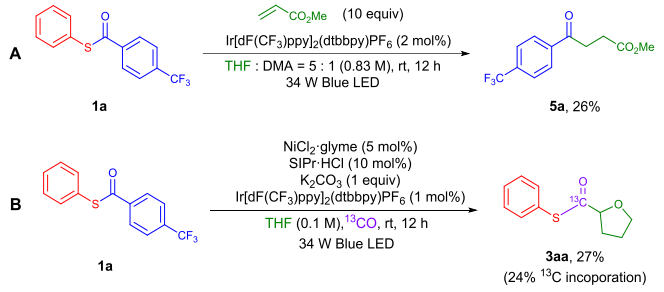


Entry	[Ni]	conversion	3aa	4a
1	$Ni(COD)_2$ (5 mol%) + SIPr (10 mol%)	11%	<1%	10%
2	**[Ni-I]** (2.5 mol%)	48%	5%	29%
3	**[Ni-II]** (2.5 mol%)	21%	11%	8%
4	$NiCl_2$·glyme (1 mol%)[a]	36%	21%	12%
5	$Ni(COD)_2$ (5 mol%) + $NiCl_2$·glyme (1 mol%)[a]	45%	18%	27%
6	**[Ni-I]** (2.5 mol%) + $NiCl_2$·glyme (1 mol%)[a]	52%	21%	28%
7	**[Ni-II]** (2.5 mol%) + $NiCl_2$·glyme (1 mol%)[a]	63%	42%	11%

[a] With SIPr·HCl (10 mol%) and K_2CO_3 (1 equiv).

The results indicate that oxidative addition type C–C(acyl) or C(acyl)–S bond activation by electron rich Ni(0) or Ni(I) did not lead to the formation of the desired product in our reaction.

Another possible thioester activation pathway is single electron reduction of the thioester. It is known that thioesters can be electrochemically reduced and fragmented into acyl radicals and thiolates.[22] The same process could be mediated by photoredox catalysis in our system. To check the validity of this hypothesis, cyclic voltammetry (CV) of **1a** was measured (Fig. S5). The results show an irreversible reduction peak [**1a**/**1a**$^{-}$] at E_P^{red} = –1.96 V vs Ag/AgNO$_3$ (0.01 M) electrode in CH$_3$CN (correlated to –1.65 V vs saturated calomel electrode (SCE) in CH$_3$CN). The significantly lower reduction potential of **1a** as compared to aliphatic thioesters and other relatively electron rich aryl thioesters could be the reason for the unique reactivity of **1a**.[23] Although the reduction potential [**1a**/**1a**$^{-}$] is higher than that of the possible reductant Ir(II) ($E_{1/2}^{red}$[Ir(III)/Ir(II)] = –1.37 V vs SCE in CH$_3$CN),[24] a small portion of reduction wave overlap may induce single electron transfer at a meaningful rate considering that an irreversible fragmentation may occur after reduction of the thioester. Also, it has been proposed that cationic character of photoredox catalyst may electrostatically stabilize the generated radical anion, facilitating reduction process.[25] Additionally, in the optimized reaction conditions, there is a chance that complexation of thioester and nickel complex can facilitate the thioester reduction process. To prove this hypothesis, a CV experiment of thioester was conducted in presence of stoichiometric amount of a Lewis acid. Mg(II) cation is utilized because it has redox-inactive character within scan range (E^{red} = -2.61 V vs SCE in H$_2$O) and has similar ionic radii (72 pm) compare to that of Ni(II) (69 pm).[26] Indeed, reduction peak shift from -1.65 V to -1.21 V (vs SCE) was observed (Fig. S6). To further validate this reduction process by capturing the *in situ* generated acyl radical, methyl acrylate was added to the system in absence of a Ni complex (Scheme 2A). The coupling product **5a** was isolated in 26% yield, confirming that the proposed photocatalytic fragmentation of the thioester can happen.



Scheme 2. Mechanistic studies

Based on this rationale, a revised mechanism is proposed (Fig. 1). Initially the photo-activated Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$ complex ($E_{1/2}^{red}$ [*Ir(III)/Ir(II)] = +1.21 V vs SCE in CH$_3$CN)[24] oxidizes a model NHC-Ni(II) species (E_P^{red} [**[Ni-II]**$^{+}$/**[Ni-II]**] = +1.01 V vs SCE in CH$_3$CN) to Ni(III) (Fig. S7). The resulting Ir(II) complex reduces the thioester and returns to Ir(III). The reduced thioester is then fragmented into an aryl acyl radical excluding the thiolate, which can be immediately captured by Ni(III). The resulting aryl acyl radical is proposed to undergo Ni mediated decarbonylation to give the aryl radical. There have been a few reports that transition metal catalysts can mediate this process,[27] although formation of an aryl radical from an aryl acyl radical with CO exclusion would be difficult. To prove the generation of a Ni–CO intermediate during the reaction, we performed a reaction under a ^{13}CO atmosphere utilizing a two-chamber reactor developed by Skrydstrup et al. (Fig. S1).[29] A significant amount of ^{13}C incorporation in the acyl carbon of **3aa** was observed, indicating that a Ni–CO intermediate is formed during the course of the reaction (Scheme 2B). The aryl radical is highly reactive so that it can abstract a hydrogen from the relatively weak α-oxy carbon of THF as the next step.[16a] The role of aryl radial as hydrogen abstraction reagent was confirmed by generation of α,α,α-trifluorotoluene-*d* (**4a**-*d*) in case that the reaction was performed in THF-d_8 (Fig. S3). The resulting α-oxy alkyl radical adds to the Ni(III) complex to give Ni(IV). Migratory insertion of the CO ligand followed by reductive elimination can produce the desired thioester, regenerating the Ni(II) species. Although it is still difficult to rule out the possible more general Ni(I)-Ni(III) cycle, we prefer the proposed a Ni(II)-Ni(IV) cycle based on the experiments in Table 4.

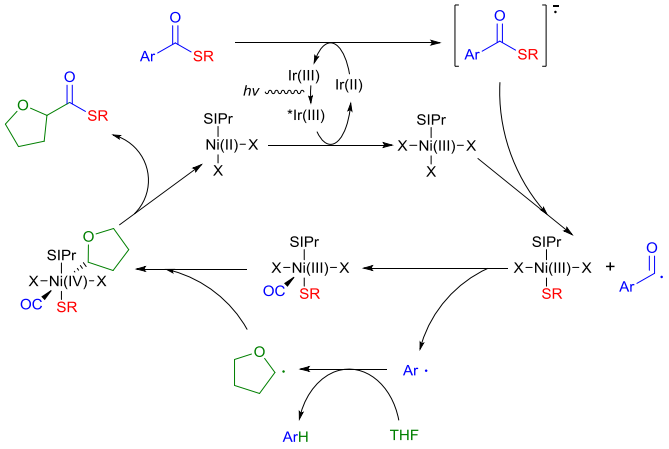


Fig. 1. Proposed mechanism.

Conclusions

The first selective C(sp^3)–H thiocarbonylation reaction is achieved. It is the first example of utilizing simple thioester molecules as the thioester group source in thiocarbonylation reaction, avoiding use of CO gas. Diverse aryl and benzyl thioesters could be synthesized in high yields. An iridium photoredox catalyst mediated electron transfer between a nickel complex and the thioester comprises the key step of the reaction. The developed direct C–H thiocarbonylation reaction will serve as a novel strategy to synthesize biologically and synthetically important thioesters under mild conditions.

Acknowledgements

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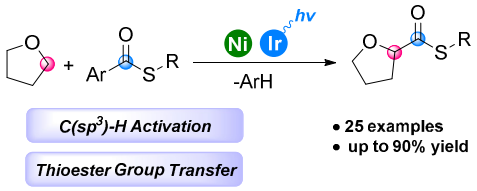

The first C(sp^3)–H thiocarbonylation is achieved by visible light photoredox/Ni dual catalysis using thiobenzoates as the thioester group source.