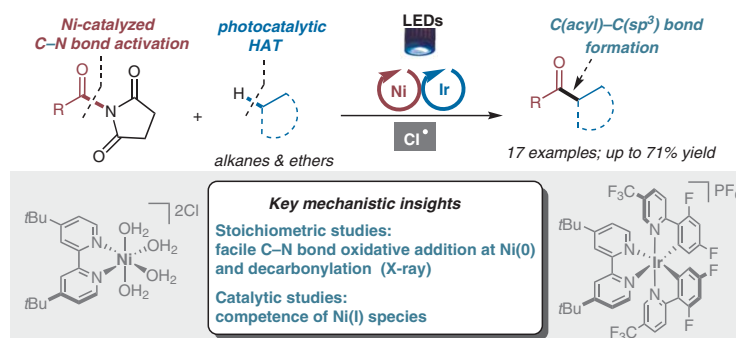


C(sp³)-H Bond Acylation with *N*-Acyl Imides under Photoredox/Nickel Dual Catalysis

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Synthetic development and mechanistic studies



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Abstract A novel Ni/photoredox-catalyzed acylation of aliphatic substrates, including simple alkanes and dialkyl ethers, has been developed. The method combines C-N bond activation of amides with a radical relay mechanism involving hydrogen-atom transfer. The protocol is operationally simple, employs bench-stable *N*-acyl imides as acyl-transfer reagents, and permits facile access to alkyl ketones under very mild conditions.

Key words nickel catalysis, photocatalysis, acylation, radical relay, C-N bond activation, ketones

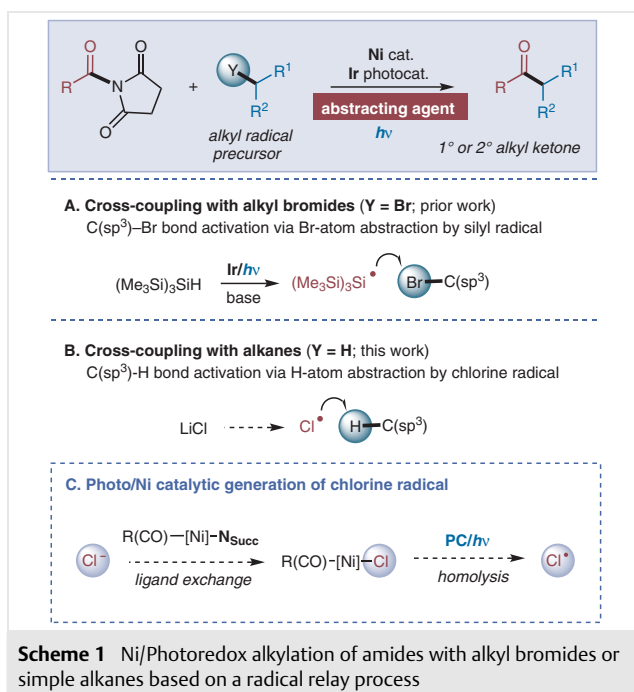
Ketones are ubiquitous chemical entities in everyday life. Found abundantly in nature, ketone groups are also present in numerous value-added pharmaceuticals and agrochemicals, as well as in fragrances, flavors, and fine chemicals. Alkyl ketones are extremely important scaffolds in multistep organic syntheses and offer multiple opportunities for late-stage derivatization of complex molecules.¹ The invention of new methods and strategies for the introduction of acyl functionalities into aliphatic backbones is therefore an ever-present challenge that has significant potential in various fields of chemistry.

Over the last decade, dual visible-light photoredox and nickel catalysis has emerged as a powerful but operationally simple strategy for achieving, under very mild reaction conditions, challenging C(sp²)-C(sp³) bond disconnections that are beyond the reach of classical cross-coupling approaches.^{2,3} Hence, this method brings prospects for innovation in the area of catalytic acylation reactions of C(sp³)-hybridized substrates,⁴ and thereby offers a new paradigm for the synthesis of structurally diverse and highly func-

tionalized alkyl ketones. Within this context, resonance-stabilized *N*-acyl imides stand amongst other carbonyl-type compounds as promising acyl electrophiles⁵ owing to their remarkable stability and their documented capability to engage in nickel-catalyzed cross-coupling reactions through C-N bond activation to forge C(acyl)-C(sp³) bonds.⁶ For instance, in 2017, Molander and co-workers⁷ reported the use of *N*-acylsuccinimides as suitable acyl-transfer reagents for photoredox nickel-catalyzed acylation of functionalized alkyl trifluoroborate nucleophiles.⁸ This provided a strong impetus to develop complementary methods that would exploit other readily available inexpensive aliphatic substrates.

Taking inspiration from recent progress in cross-electrophile coupling reactions, i.e. the direct catalytic joining of two different electrophiles that avoids the need for pre-formed carbon nucleophiles,⁹ we developed a novel dual-catalytic acylation process using nonactivated alkyl bromides as electrophilic partners for *N*-acylsuccinimides. The process was designed to follow a radical relay pathway where a silyl radical is generated photocatalytically and serves as an abstracting agent to activate the alkyl bromide through homolytic C-Br bond cleavage (Scheme 1A).¹⁰ Another exciting challenge that we subsequently considered was the design of an alternative strategy that would rely on the selective C(sp³)-H bond activation of simple alkanes through a radical hydrogen-atom transfer (HAT) process.^{11,12}

The groups of Doyle and Molander independently demonstrated that organohalides could serve as both coupling partners and sources of halide radicals that act as potent H-abstrating agents in Ni/photoredox cross-coupling reactions with aliphatic substrates.¹³ Inspired by these sem-



inal reports, we questioned whether this strategy might be applicable to the coupling of amides with alkanes in the presence of an exogenous source of halide anions, e.g. lithium chloride (Scheme 1B).¹⁴ We hypothesized that oxidative addition of the amide to nickel and subsequent succinimide-to-chloride ligand exchange might readily generate an intermediate acyl–nickel chloride complex that could serve as source of chlorine radicals through Ni–Cl bond homolysis (Scheme 1C).^{12d,15}

In our initial exploratory studies,¹⁶ we used the coupling of *N*-benzoylsuccinimide (**1a**) with cyclohexane as a model system (Table 1). We found that the desired cross-coupling product **3a** was formed in optimal yields by using [Ni(dtbbpy)(H₂O)₄]Cl₂ (**I**; 4 mol%) (dtbbpy = 4,4'-di-*tert*-butyl-2,2'-bipyridine) and Ir{[dF(CF₃)ppy]₂(dtbbpy)}PF₆ (**II**; 0.5 mol%) [dF(CF₃)ppy = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine] complexes as a dual-catalytic system under irradiation by a 40 W blue LED lamp. Remarkably, solvent evaluation indicated that only benzene was suitable for delivering the desired ketone. Another critical feature for the success of the coupling reaction was the need for an external source of halogen atom. Lithium chloride was found to be the most effective source among the salts tested (LiCl, NaCl, KCl, TBAC, Et₃N⁺Bn Cl[−], NH₄Cl, and NaBr), and increasing the amount of this additive beyond one equivalent did not significantly increase the yield. Additionally, the reaction proceeded more efficiently by using a combination of tripotassium phosphate and sodium tungstate as a dual-base system (Table 1, entries 1–5).^{12d} Control experiments revealed that the dual-catalytic system and light irradiation were essential for this transformation (entries 6–8). *N*-Ben-

zoylglutarimide also proved to be a reactive substrate but gave **3a** in a lower yield (entry 9). Notably, by employing up to five equivalents of cyclohexane, ketone **3a** was isolated in a fair 53% yield after 24 hours of reaction. These conditions (entry 10) were therefore established as our standard conditions.¹⁷ Note that the use of cyclohexane as the solvent led essentially to no reaction, possibly due to the limited solubility of the catalyst and base in this reaction medium (entry 11).

Table 1 Reaction of *N*-Benzoylsuccinimide (**1a**) with Cyclohexane: Selected Experiments^a

Entry	Reaction conditions	Yield ^b (%) of 3a
1	as shown	50
2	no K ₃ PO ₄	27 ^c
3	no Na ₂ WO ₄ ·2H ₂ O	40 ^d
4	no K ₃ PO ₄ or Na ₂ WO ₄ ·2H ₂ O	18
5	no LiCl	3
6	no Ir photocatalyst	0
7	no light (darkness)	0
8	no Ni catalyst	0
9	<i>N</i> -benzoylglutarimide instead of 1a	42
10	cyclohexane (5 equiv), 24 h	61 (53) ^e
11	cyclohexane as solvent	1

^a Reactions were performed in benzene on a 0.6 mmol scale with irradiation by a 40 W blue LED Kessil lamp. See the Supporting Information for details of the lighting setup.

^b Determined by GC-MS with benzophenone as internal standard.

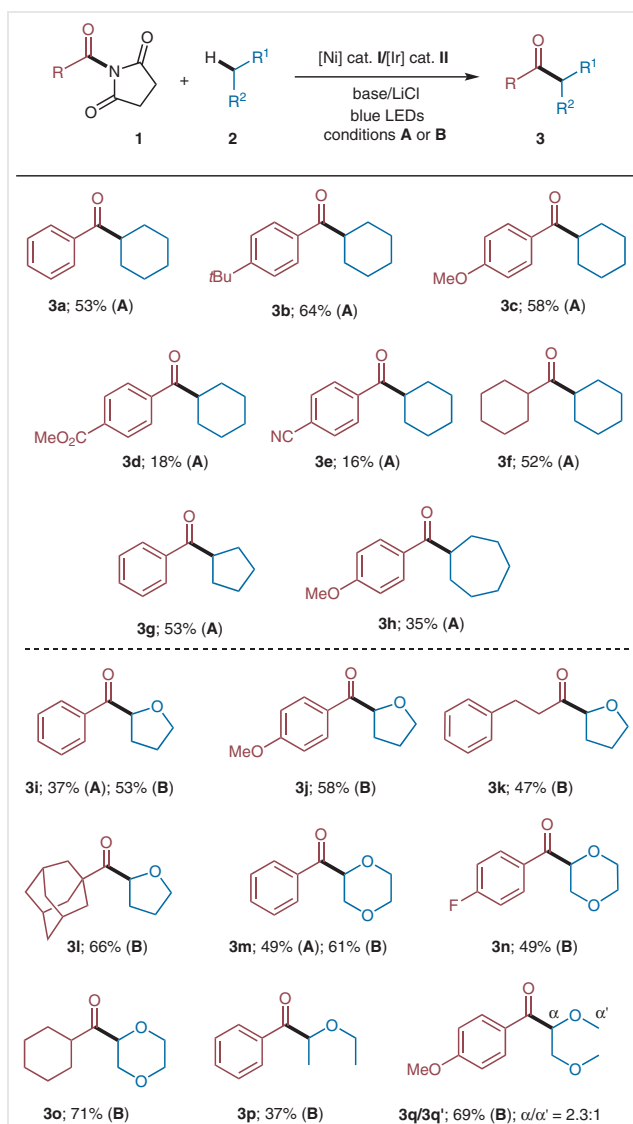
^c Na₂WO₄·2H₂O (3 equiv).

^d K₃PO₄ (3 equiv).

^e Isolated yield.

Having a reliable acylation protocol in hand (Conditions A), we explored the reactivity of various acyl succinimides and potential HAT substrates (Scheme 2). Various electron-rich and electron-neutral aroyl succinimides underwent coupling with cyclohexane in fair yields (**3a–c**), whereas electron-deficient derivatives were found to give significantly lower yields (**3d** and **3e**). The scope was expanded to acyl succinimides bearing alkyl groups, as illustrated by **3f**, thereby providing access to dialkyl ketones. Notably, other nonactivated cycloalkanes also participated in the coupling process (**3g** and **3h**). We also attempted the acylation of alkyl ethers to access the corresponding α-functionalized ketones. For instance, we examined the use of dialkyl ethers as both alkylating reagents and solvents, as safer alternatives to benzene. In our initial experimental observations on the coupling of **1a** with tetrahydrofuran,¹⁶ we found that

the new procedure (conditions B) required higher catalysts loadings (10 mol% of catalyst **I**; 2 mol% of catalyst **II**), but proceeded efficiently without the need for sodium tungstate as an additive.¹⁸ This is illustrated by the synthesis of a series of 2-acyltetrahydrofurans **3i–l** in moderate to good isolated yields. The same procedure successfully gave coupling products containing cyclic or linear aliphatic ethers such as 1,4-dioxane, diethyl ether, or 1,2-dimethoxyethane (**3m–q**). Notably, a separable 2.3:1 mixture of two regioisomeric products **3q** and **3q'** was generated by the acylation of DME.



Scheme 2 Scope of *N*-acylsuccinimides and alkanes. *Reagents and conditions A*: 0.6 mmol scale; Ni cat **I** (4 mol%), Ir cat **II** (0.5 mol%), K_3PO_4 (2 equiv), $Na_2WO_4 \cdot 2H_2O$ (1 equiv), LiCl (1 equiv), alkane (5 equiv), benzene (0.1 M), 40 W blue LED Kessil lamp (455 nm), 24–48 h. *Reagents and conditions B*: 0.4 mmol scale Ni cat **I** (10 mol%), Ir cat **II** (2 mol%), K_3PO_4 (1.5 equiv); LiCl (1 equiv), alkane as solvent (0.125 M), 30 W blue LED lamp (450 nm), 24–48 h. Isolated yields are reported.

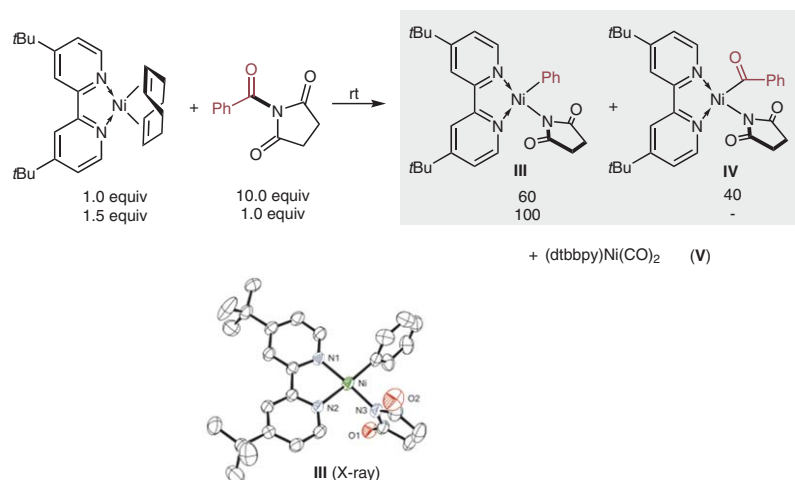
Interestingly, the byproducts regularly obtained from the reaction of *N*-acylsuccinimides with alkanes were the symmetrical dialkyl ketones deriving from homocoupling of the alkane, together with the corresponding $C(Ar)-C(sp^3)$ bond-formation products. A series of experiments were carried out to gain information on the reaction pathway and the origin of these products (Scheme 3). As a prototypical example, the coupling of *N*-benzoylsuccinimide (**1a**) with cyclohexane afforded the desired cross-coupling product (**3a**), along with small amount of cyclohexylbenzene (**4a**; $\leq 10\%$) and dicyclohexylmethanone (**3f**; $\leq 20\%$), suggesting the occurrence of a decarbonylative pathway.^{5g,9d} Accordingly, an excess of **1a** (10 equiv) was found to react spontaneously with (dtbbpy)Ni(COD) (1 equiv) to afford a mixture of complexes assigned to the corresponding Ni(II)-aryl complex **III** and the Ni(II)-acyl complex (**IV**) in a 3:2 ratio (1H NMR), together with the dicarbonyl complex (dtbbpy)Ni(CO)₂ (**V**) (Scheme 3A).¹⁶ By adjusting the stoichiometry of (dtbbpy)Ni(COD) (1.5 equiv) and **1a** (1 equiv), the Ni(II)-aryl complex **III** could be obtained selectively and isolated for full characterization, including single-crystal X-ray diffraction analysis (Scheme 3A).¹⁹ The molecular structure of **III** displays a square-planar geometry of the nickel center, and represents a unique example of structural characterization of a Ni(II)- N_{succ} complex formed by a C–N bond oxidative addition–decarbonylation sequence of amides with Ni(0).²⁰ All attempts to generate the acyl complex **IV** selectively or to isolate it from the reaction mixture were unsuccessful. This result indicates that *N*-acylsuccinimides undergo spontaneous oxidative addition to Ni(0) followed by facile decarbonylation, providing a plausible pathway to the symmetrical dialkyl ketones²¹ and the decarbonylative products.²² Comparatively, the reaction of benzoyl chloride with (dtbbpy)Ni(COD) led exclusively to the corresponding acyl-Ni(II) chloride complex **VI**.^{16,12b}

We then compared the catalytic activity of complex **I** with that of other potent nickel catalytic intermediates (Scheme 3B). Surprisingly, the use of Ni(COD)₂ with dtbbpy as an exogenous ligand instead of complex **I** resulted in a very low 8% reaction yield. Furthermore, no reaction was observed with the Ni(II)-aryl intermediate **III**. On the other hand, the nickel(II)-acyl chloride complex **VI** was found to be catalytically competent, affording very similar results to those with complex **I**. Notably, only trace amounts of the desired product were observed in the absence of LiCl, confirming its key role in the reaction, probably through succinimide-to-chloride exchange at nickel. At this stage, the involvement in the catalytic cycle of active paramagnetic species generated in situ from nickel(II) complexes was envisioned. Indeed, as recently demonstrated by the group of Hazari,²³ paramagnetic Ni(I) species with bipyridine ligands can participate as key intermediates in nickel-catalyzed $C(sp^2)-C(sp^3)$ bond-forming reactions. We decided to examine this possibility, and we prepared the [(dtbbpy)Ni(Cl)]₂ dimer **VII** by the reported procedure.¹⁶ Remark-

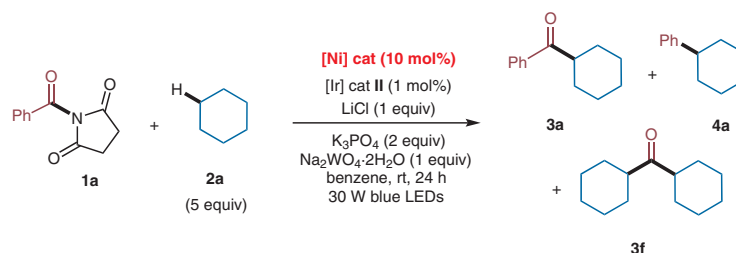
ably, the paramagnetic nickel species **VII** was found to be catalytically active and performed more efficiently than the nickel(II)-dichloro complex **I**.

These preliminary experiments suggest that the nickel-catalyzed acylation of C(sp³)-H bonds with *N*-acylsuccinimides does not follow the same pathway as that proposed.

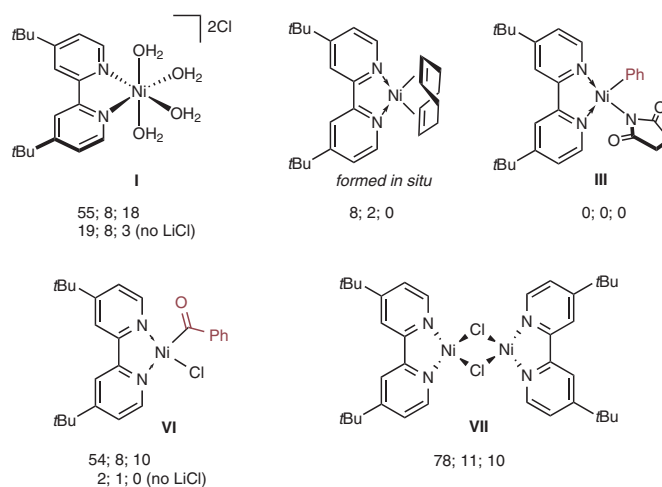
A. Evidence for nickel-promoted spontaneous decarbonylative pathway of *N*-acylsuccinimides



B. Evaluation of catalytic activity of nickel complexes for the acylation of cyclohexane with *N*-acylsuccinimide



Catalysts and associated yields (%)^a of **3a**; **4a**; **3f**



^a Yields determined by GC-MS with benzophenone as an internal standard

Scheme 3 (A) Reaction of **1a** with (dtbbpy)Ni(COD) and (B) the catalytic behavior of several nickel species

for other acyl substrates. In related coupling processes involving chloroformates and acyl chlorides as substrates reported by the groups of Doyle^{12d} and Shibasaki,^{12b} the oxidative addition of the acyl substrate proceeds at Ni(0) species. With *N*-acylsuccinimides, although oxidative addition of the C–N bond to Ni(0) readily occurs, our experiments suggest that the C–N bond-activation step proceeds at Ni(I) during the catalysis. Further mechanistic studies are clearly necessary to confirm the specific behavior of these acyl substrates, which might be exploited to design complementary mechanistic sequences.²⁴

In summary, we have described a new acylation reaction of C(sp³)–H bonds by using bench-stable *N*-acyl imide substrates. The dual-catalytic process combines nickel-catalyzed C–N bond activation with photocatalytic HAT, and provides operationally simple access to valuable alkyl ketones. Notably, *N*-acylsuccinimides were shown to undergo ready C–N bond oxidative addition to Ni(0), followed by decarbonylation, under mild conditions. Identification of by-products of the acylation reaction suggested that the development of decarbonylative cross-coupling pathways under mild conditions by using photoredox/Ni catalysis can be envisioned. Further investigations are underway to achieve a better understanding of the reaction mechanism.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0040-1707301>.

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- (16) See the Supporting Information for more details.
- (17) **Cyclohexyl(phenyl)methanone (3a); Typical Procedure A**
In an argon-filled glovebox, a 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with Ir{[dF(CF₃)ppy]₂(dtbbpy)}PF₆ (0.003 mmol, 3.2 mg), [Ni(dtbbpy)(H₂O)₄]Cl₂ (0.024 mmol, 11.2 mg), K₃PO₄ (1.2 mmol, 254 mg), Na₂WO₄·2 H₂O (0.6 mmol, 200 mg), LiCl (0.6 mmol, 25 mg), N-benzoylsuccinimide (0.6 mmol, 122 mg), cyclohexane (3.0 mmol, 325 µL), and anhyd benzene (6 mL). The sealed vessel was taken out of the glovebox, and the stirred mixture was irradiated by a 40 W blue LED Kessil lamp (455 nm) for 24 hours at RT. To remove solid residues, the mixture was filtered through a short pad of Celite with CH₂Cl₂ as the eluent. The volatiles were removed under vacuum and the crude residue was purified by column chromatography [silica gel, cyclohexane–EtOAc (10:1)] to give a colorless oil; yield: 60 mg (53%). The ¹H NMR and ¹³C NMR spectra were consistent with values reported in the literature.^{8b}
- (18) **Phenyl(tetrahydrofuran-2-yl)methanone (3i); Typical Procedure B**
On the bench top, an 8 mL scintillation vial equipped with a magnetic stirrer bar was charged with Ir{[dF(CF₃)ppy]₂(dtbbpy)}PF₆ (0.008 mmol, 9 mg), [Ni(dtbbpy)(H₂O)₄]Cl₂ (0.04 mmol, 18.7 mg), K₃PO₄ (0.6 mmol, 127 mg), LiCl (0.4 mmol, 17 mg), N-benzoylsuccinimide (0.4 mmol, 81.3 mg), and anhyd THF (3.2 mL, 0.125 M). The vial was sparged with argon then sealed, and the stirred mixture was irradiated by a 30 W blue LED lamp (450 nm; EvoluChem PhotoRedOx Box device) for 24 h at RT. To remove solid residues, the mixture was filtered through a short pad of Celite with CH₂Cl₂ as eluent. The volatiles were removed under vacuum and the crude residue was purified by column chromatography [silica gel cyclohexane–EtOAc (10:1)] to give a colorless oil; yield: 37.5 mg (53%). The ¹H NMR and ¹³C NMR spectra were consistent with the values reported in the literature.^{12b}
- (19) CCDC 2018793 contains the supplementary crystallographic data for complex **III**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.
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