Letter

Enones from Acid Fluorides and Vinyl Triflates by Reductive Nickel Catalysis

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Supporting Information

ABSTRACT: A nickel-catalyzed reductive coupling between acid fluorides and vinyl triflates has been described. This method provides an efficient access to various enones and avoids the requirement for acyl or vinyl metallic reagents in the conventional approaches. The reaction proceeds with a broad range of acid fluorides and cyclic vinyl triflates, tolerating several functional groups. The utility of this synthetic method has been demonstrated by the late-stage modification of pharmaceuticals and biologically active natural compounds.

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E nones represent key structural motif in various pharmaceuticals and biologically active natural products, and they also constitute the foundation for various important reactions.¹ The synthesis of these valuable targets have traditionally been achieved through multistep synthesis, the aldol condensation, the Wittig olefination reactions, α,β -dehydrogenation of carbonyl compounds, and the Meyer–Schuster rearrangement, etc.² A potentially useful alternative strategy is the transitionmetal-catalyzed cross-coupling reaction between vinyl and acyl fragments.^{3,4} Over the past decades, this method has been significantly progressed by extensive studies on the reactions of acyl electrophiles with vinyl metallic reagents³ (Scheme 1, path

Scheme 1. Synthesis of Enones via Cross-Coupling of Vinyl and Acyl Fragments



a). There are also isolated examples that demonstrate the synthesis of enones via coupling of acyl metallic reagents with vinyl electrophiles⁴ (Scheme 1, path b). Construction of enones from vinyl and acyl electrophiles could be advantageous, with respect to the ready availability of reagents and cost effectivity, but remains unexplored (Scheme 1, path c).

The cross-electrophile reaction has recently emerged as a powerful alternative to conventional cross-couplings for C–C bond formation.⁵ The recently established reductive acylation

reactions enable facile access to ketones from readily available electrophiles.^{6–10} Progress in this field has led to various important methods for the acylation of aryl and alkyl electrophiles, with a broad spectrum of acyl electrophiles (e.g., activated amides,⁶ thioesters,⁷ pyridyloxyl esters,⁸ acid anhydrides,⁹ and acid chlorides^{7,10}) proven to be effective (Scheme 2a). However, to our knowledge, there has been no report describing the reductive acylation reaction of vinyl electrophiles to afford enones.



(a) Reductive acylation of aryl/alkyl electrophiles with acid derivatives



 $R^1 \xrightarrow{\text{TfO}} R^2 \xrightarrow{(\text{Ni})} R^1 \xrightarrow{\text{Reductant}} R^1 \xrightarrow{\text{Reductant}} R^2$

Acid fluorides are bench-stable and easily handled electrophiles, and they are readily available from carboxylic acids via many simple procedures.¹¹ These reagents have shown great stability toward nucleophiles, thus allowing for their isolation by organic extraction and flash chromatography on silica gel. Therefore, the use of acid fluorides as versatile acyl

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electrophiles in the cross-coupling reactions would provide an attractive synthetic route to ketone framework. In 2004, the Rovis group has reported the first cross-coupling reactions of acid fluorides with organometallic reagents using organozinc reagents.¹² Several recent studies have further demonstrated the potential of these reagents for the acylation of nucleophiles through Hiyama and Suzuki–Miyaura couplings.¹³ Encouraged by these findings and as part of our ongoing interest in cross-electrophile reaction,¹⁴ we wondered if acid fluoride could be employed in the coupling reactions with electrophiles. Herein, we report the first cross-electrophile reaction of acid fluorides, which enables the acylation of vinyl electrophiles (Scheme 2b). This method provides a convenient approach to enones, because the substrates are readily available from carboxylic acids and ketones.

We started our investigation by studying the reaction of benzoyl fluoride 1a with vinyl triflate 2a under the reductive conditions (see Tables S1–S7 in the Supporting Information for details). Finally, we found that the reaction with Ni(dppe)Cl₂ (10 mol%), L5 (12 mol%), and Mn (3.5 equiv) in DMA/toluene (3:2) at 70 °C gave the best result, affording 3a with 88% isolated yield (Table 1, entry 1). The

Table 1. Ni-Catalyzed Reductive Coupling of 1a with $2a^{a}$



"1a (0.15 mmol), 2a (0.1 mmol) was used; the yields were determined by GC analysis with dodecane as internal standard. ^b1a (0.3 mmol), 2a (0.2 mmol), isolated yield.

		R_2 R_2 R_2 R_2	$R_1 = H, R_2 = H, L3$ $R_1 = {}^{t}Bu, R_2 = H, L4$
L1	L2	V N N	$R_1 = Bu, R_2 = Bu, L5$

use of other nickel precatalysts resulted in decreased yields (Table 1, entries 2–6). Tridentate nitrogen ligands proved to be more effective than bidentate nitrogen ligands, such as bipyridine L1 and phenanthroline L2 (Table 1, entries 1, 7–10). No reaction was observed when Zn was used as a reductant instead of Mn (Table 1, entry 11).¹⁵ The reaction

did not occur in the absence of Ni or Mn (Table 1, entry 12). Only a trace of product 3a was obtained when the reaction performed without ligand L5 (Table 1, entry 13). While the reaction in toluene gave a trace of 3a, an improved yield was obtained when the mixed solvent of DMA/toluene (3:2) was used (Table 1, entries 1, 14, and 15). The reaction of amide 4 and acyl chloride 5 with vinyl triflate gave no or low yield of the desired product. Inferior results were also obtained when other acyl electrophiles were employed (6-8).

With the optimized reaction conditions in hand, we then studied the scope of this reaction, with respect to vinyl triflates (Scheme 3). Cyclic vinyl triflates with five- to eight-membered

Scheme 3. Scope of Vinyl Triflates^a



^{*a*}**1a** (0.3 mmol), vinyl triflates (0.2 mmol) were used. Isolated yields. ^{*b*}**1a** (0.2 mmol), vinyl triflates (0.3 mmol) were used. 'Reaction at 100 °C. ^{*d*}**1a** (1.5 mmol), **2g** (1.0 mmol) were used. 'Reaction at 50 °C.

rings coupled with 1a to afford the acylated products with moderate to good yields (3a-3d). The reaction proved to be insensitive to steric hindrance, and the reactions of 3- and 6substituted vinyl triflates with 1a gave desired products with high yields (3e-3f). The presence of tertiary butyl (3g), phenyl (3h), gem dimethyl (3i), ester (3j), and ketal (3k)groups at the 4-position of vinyl triflates were tolerated. A moderate yield of 3l was obtained when 3,4-dihydronaphthalenyl triflate was used. The reactions of N-, O-, and Sheterocyclic vinyl triflates proceed smoothly to afford enones with synthetically useful yields (3m-3o). The reaction of 1a with fully substituted acyclic vinyl triflate afforded the product in 38% yield (3p). However, only a trace of products was obtained when 1,2-disubstituted (3q), 1-substituted (3r), or 2-substituted vinyl triflate (3s) was used. In these cases, the reactions typically gave vinyl-vinyl dimer,¹⁶ leaving acid fluoride 1a intact.

A broad range of acid fluorides coupled efficiently with vinyl triflate **2a** under the standard conditions (Scheme 4). Aromatic





^a2a (0.2 mmol), acid fluorides (0.3 mmol) were used. Isolated yields.
^b2a (0.3 mmol), acid fluorides (0.2 mmol) were used. ^cNiI₂ (10 mol
%) was used. ^d1i (1.5 mmol), 2a (1.0 mmol) was used. ^cL3 (15 mol
%) was used. ^f1-(4-^tBu-cyclohexenyl) triflate 2g was used.

acid fluorides with ortho-, meta-, and para-substituents reacted with 2a to afford products with high yields (3t-3v). Both electron-rich and electron-poor substituents at the aromatic rings were tolerated (3t-3x). The reactions were highly selective for the acylation of vinyl triflate, leaving Ar-Cl (3w), ester (3x), styrene (3y), amine (3z) intact. Acid fluorides derived from 2-naphthoic acid (3aa), ferrocenecarboxylic acid (3ab), and thianaphthene-2-carboxylic acid (3ac) were tolerated. Besides aromatic substrates, aliphatic acid fluorides also coupled with 2a efficiently, and afforded enones with good yields (3ad, 3ae). The coupling of vinyl acid fluoride with vinyl triflate gave dienone product with a moderate yield (3af).

The broad existence of ketone and carboxylic acid in pharmaceuticals and biologically active natural compounds makes the late-stage modification of such functional groups particularly attractive. Under our conditions, vinyl triflates derived from biologically active molecules such as (+)-nootkatone and testosterone were efficiently acylated (**3ag**, **3ah**). We then investigated the vinylation reactions of several biologically active carboxylic acid compounds. Acid fluorides derived from roflumilast intermediate (**3ai**), probenecid (**3aj**), adapalene (**3ak**), and lithocholic acid (**3al**) could be vinylated smoothly, and afforded the modified products with yields of 56-83% (see Scheme 5).

Scheme 5. Late-Stage Modification of Complex Molecules^a



^aSee conditions in Table 1, entry 1. Acid fluorides (0.3 mmol) and vinyl triflates (0.2 mmol) were used. Isolated yields. ^bL3 (15 mol%) was used. ^cAcid fluoride (0.2 mmol), 2a (0.3 mmol) were used.

Both acid fluorides and vinyl triflates will undergo oxidative addition to Ni(0) to form PhCO–Ni(II)–F and vinyl–Ni(II)–X intermediates.^{12,17} In order to determine which intermediate is formed first, we studied the relative reactivity of **1a** and **2a** toward nickel catalyst under the modified standard conditions (Scheme 6).¹⁸ While most of substrate **1a** was

Scheme 6. Experiments To Reveal the Relative Reactivity of 1a and 2a toward Nickel Catalyst



recovered after 15 h, all of **2a** was consumed to afford **11** and **12** with yields of 10% and 78%, respectively. Moreover, only decarbonylative products such as Ph–H (5% yield) and Ph–Ph (trace) were observed from the reaction of **1a**.¹⁷ These results suggest that the reaction might start with the formation of vinyl–Ni(II)–X rather than PhCO–Ni(II)–F intermediate.

Although a detailed mechanism for this reaction is yet to be established, based on the results described above and previous reports, 5,14a we tentatively proposed a catalytic cycle as shown in Scheme 7. The oxidative addition of vinyl triflate to Ni(0) would give vinylnickel(II) intermediate **A**, which could be reduced to vinylnickel(I) **B** by reductant.¹⁹ The oxidative addition of substrate **1** to intermediate **B**, followed by reductive elimination process would afford the desired product **3** and recycle the catalyst with Mn.²⁰ Presently, we cannot rule out a radical mechanism as shown in many reductive Csp³– Csp² couplings.²¹

In summary, we have developed a Ni-catalyzed reductive coupling between acid fluorides and vinyl triflates. This reaction represents the first cross-electrophile reaction of acid fluorides, and the first reductive acylation of vinyl electrophiles. The method has provided an efficient approach to enones,

Scheme 7. Proposed Mechanism



which are key structural motifs in a variety of biologically active compounds and the foundation for various important reactions. The reaction proceeds with a broad range of acid fluorides (e.g., aryl, vinyl, and alkyl acid fluorides) and cyclic vinyl triflates. The broad existence of ketone and carboxylic acid in pharmaceuticals and biologically active natural compounds makes the method particularly attractive for latestage modification of these molecules.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or-glett.9b01164.

Detailed optimization of reaction conditions, parts of the mechanistic studies, detailed experimental procedures, characterization data, and copies of ¹H and ¹³C NMR spectra for new compounds (PDF)

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The authors declare no competing financial interest.

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(21) The presence of a radical scavenger such as BHT (butylated hydroxytoluene) or 1,1-diphenylethylene showed no effects on the reaction of 1a and 2a (see Table S8 in the Supporting Information). However, the reaction was totally inhibited when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 1.5 equiv) was used, but no radical trapping product was observed. This might be due to the presence of a single-electron process capable of reducing oxidized Ni catalyst. Nevertheless, we currently cannot rule out a radical activation of the substrate. For related mechanism, see: Biswas, S.; Weix, D. J. Mechanism and Selectivity in Nickel-Catalyzed Cross-Electrophile Coupling of Aryl Halides with Alkyl Halides. J. Am. Chem. Soc. 2013, 135, 16192 (also see ref 5c).