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Conversion of Carbonyl Compounds to Olefins via Enolate Intermediate

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Summary of main observation and conclusion A general and efficient protocol to synthesize substituted olefins from carbonyl compounds via nickel catalyzed C-O activation of enolates was developed. Besides ketones, aldehydes were also suitable substrates for the presented catalytic system to produce di- or tri- substituted olefins. It is worth noting that this approach exhibited good tolerance to highly reactive tertiary alcohols, which could not survive in other reported routes for converting carbonyl compounds to olefins. This method also showed good regio- and stereo-selectivity for olefin products. Preliminary mechanistic studies indicated that the reaction was accomplished through nickel catalyzed C-O activation of enolates, thus offering helpful contribution to current enol chemistry.

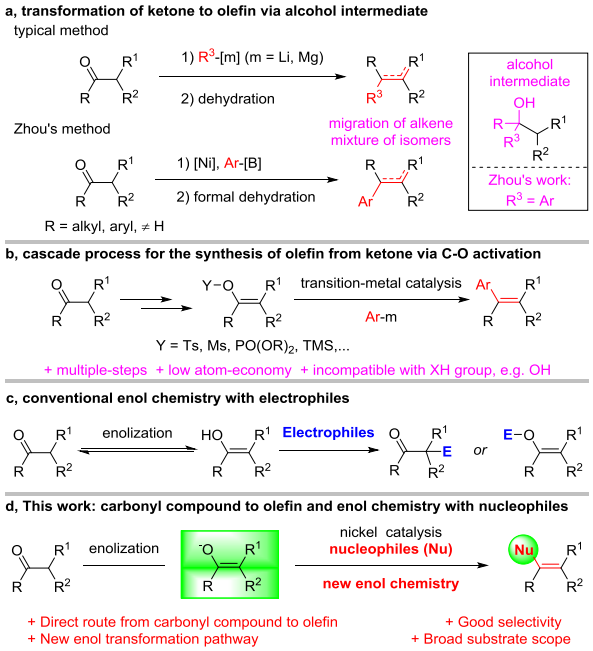
Background and Originality Content

Olefin is a mainstay in organic chemistry and broadly existed in π-conjugated materials, natural products and pharmaceuticals.[1] During the past decades, a myriad of methodologies have been developed to construct substituted olefins from existing alkenes,[2] such as cross-coupling of alkenyl halides,[3] Mizoroki-Heck reaction,[4] and olefin metathesis.[5] Although significant progresses which facilitate the efficient preparation of olefin structural motif have been achieved, these methods were generally based on alkene-type substrates and were majorly limited to the preparation of mono- and di-substituted olefins.[6] In comparison, the synthesis of tri- or tetra-substituted olefins lags far behind. Thus, new methods to synthesize olefins, especially multi-substituted olefins, from easily available building blocks are highly appealed.

Carbonyl compounds are ubiquitous in natural and synthetic worlds. As a category of abundant and relatively cheap organic chemicals, conversion of carbonyl compounds to olefins has drawn much attention in recent years. To date, three main strategies were developed to realize this goal. Carbonyl olefination, such as Wittig-type reaction, is a powerful tool to construct olefin motif, while the usage of stoichiometric amount of Wittig reagent limited its practical application.[7] Another strategy, which could be tracked back to early era, to prepare olefins from carbonyl compounds was achieved through the sequential transformations consisted of nucleophilic addition by active organometallic reagent and dehydration of produced alcohols in the presence of acid (**Scheme 1a**).[8] Recently, an update of this field was reported by Zhou and co-workers. They demonstrated an elegant example of preparation of alkenes from ketones via nickel catalysis.[9] Based on their intensive mechanism studies, tertiary alcohols was proved to be the key intermediate in this conversion, thus could not be tolerated in this transformation. This type of chemistry exhibited high efficiency and easy manipulations, while the regioselectivity of produced olefins remained challenging.

During the past decades, transition-metal catalysed cross-coupling reactions employed C-O electrophiles,[10] including alkenyl sulfonates,[11] phosphates,[12] carboxylates,[13] and silyl ethers,[14] have been developed as powerful and efficient tools to construct olefins. These protocols were featured by the easy preparation of substrates from ketones (**Scheme 1b**). Additionally, alkenyl methyl ethers were also suitable substrates in nickel catalysis, while the preparation of substrates was generally conducted through Wittig reaction.[15]

Scheme 1 Strategies for conversion of carbonyl compounds to olefins and design for new enol chemistry



Enol, the tautomer of carbonyl compound, has been well documented in textbooks.[16] Although the reactivity and selectivity of enol chemistry has been well developed, the transformation of enol/enolate was limited to the application in which enol was used as strong nucleophiles to react with various electrophiles (**Scheme 1c**).[2c, 16d, 17] Herein, by utilizing the enolization process, we demonstrated a direct and efficient protocol to prepare substituted olefins from carbonyl compounds via nickel catalyzed C-O activation of enolate (**Scheme 1d**). In this work, enol/enolate was used as electrophile to couple with nucleophiles in the presence of transition-metal catalysis, thus

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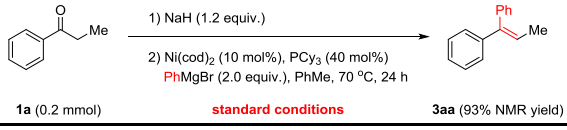
providing a new method to the direct transformation of enolates.

Results and Discussion

Propiophenone (**1a**) was selected as the model substrate to couple with PhMgBr (**2a**) (**Table 1**). After systematic screening of reaction conditions, we found that a cocktail containing $Ni(cod)_2$ (10 mol%) as the catalyst and PCy_3 (40 mol%) as the ligand in toluene at 70 °C promoted the coupling of **1a** with Grignard reagent (**2a**) in the presence of NaH (1.2 equiv.) as the base in 88% isolated yield (entry 1). Controlling experiments revealed the pivotal roles of nickel catalyst, ligand and base (entries 2-4). For example, the ketone **1a** was completely converted to tertiary alcohol in the absence of NaH and no desired olefin product **3aa** was observed. Other bases, such as LiH and KH, were also tested, while only a trace amount of product **3aa** was observed when LiH was used as the base (entries 4-5). The ligand effect was systematically investigated by using NaH as the base. Other ligands, including bidentate phosphine ligands, and NHC (N-heterocyclic carbene) ligands were applied to this transformation, while no better results were obtained (entries 7-11). Examination of solvent effect demonstrated that the coordinative solvents were not suitable for this reaction as they could poison the catalyst (entries 12-13). Furthermore, various iron catalysts were also used as alternatives to $Ni(cod)_2$, while no desired product **3aa** was obtained (entry 14). To our delight, the conversion also proceeded smoothly to furnish the desired product **3aa** in 87% NMR yield in the presence of 5 mol% nickel catalyst, which made it more practical (entry 15). The Knochel-type Grignard reagent was also tested, but lower yield was obtained (entry 16).

Table 1 Optimization Experiments [a]

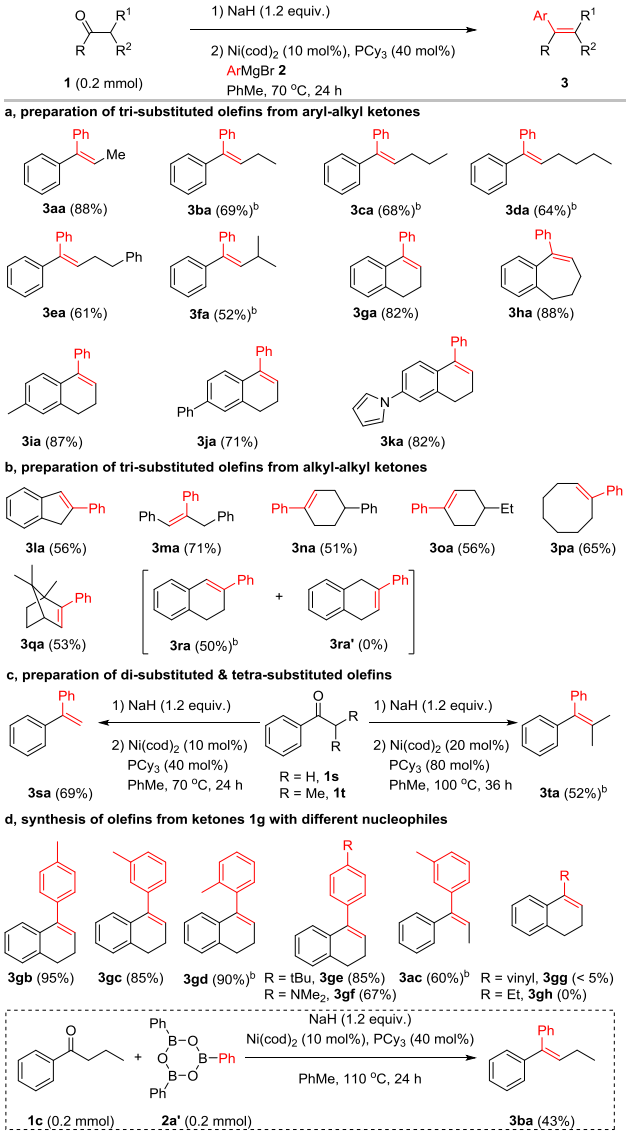


Entry	deviation from standard conditions	yield
1	none	93 (88)
2	without $Ni(cod)_2$	0
3	without PCy_3	17
4	without NaH	0
5	LiH instead of NaH	<5
6	KH instead of NaH	95
7	X-Phos instead of PCy_3	11
8	DCyPE instead of PCy_3	0
9	DCyPB instead of PCy_3	<5
10	IMes instead of PCy_3	45
11	IPr instead of PCy_3	62
12	THF instead of PhMe	0
13	2-Me-THF instead of PhMe	47
14	$FeBr_3$, $FeCl_3$, FeF_3 instead of $Ni(cod)_2$	0
15	$Ni(cod)_2$ (5 mol%), PCy_3 (20 mol%)	87
16	PhMgCl(LiCl) instead of PhMgBr	76%

[a] **1a** (0.2 mmol), NaH (0.24 mmol), $Ni(cod)_2$ (10 mol%), PCy_3 (40 mol%), and PhMgBr (0.4 mmol) in PhMe (0.6 mL) at 70 °C; [b] NMR yields were reported, isolated yield was presented in the parenthesis; [c] **1a** was transformed into alcohol completely.

Subsequently, the optimal conditions was applied to the preparation of various tri-substituted olefins from ketones (**Table 2**). Different aryl-alkyl ketones were subjected to the catalytic system and the desired olefins were obtained in moderate to good yields (**Table 2a**). However, with the increasing steric hindrance of alkyl group, the yields of corresponding olefins were dramatically decreased (cf: **3aa** and **3fa**). This catalytic system was also suitable for the conversion of benzo-fused cyclic ketones to furnish the targeted cyclic olefins. For example, the arylation of various substituted 1-tetralones were conducted and the desired products were obtained in good yields (**3ga**-**3ja**). It is worth noting that, the substrate containing aromatic C-N bond also proved suitable substrate in this catalytic system (**3ka**).[18]

Table 2 Substrate Scope



[a] Conditions: Ketones **1** (0.2 mmol), NaH (0.24 mol), PhMgBr (2.5 M in Et_2O) (0.4 mmol), catalyst $Ni(cod)_2$ (0.02 mmol), ligand PCy_3 (0.08 mmol) in PhMe (0.6 mL) at 70 °C for 24 h, isolated yields were reported; [b] NMR yields were reported.

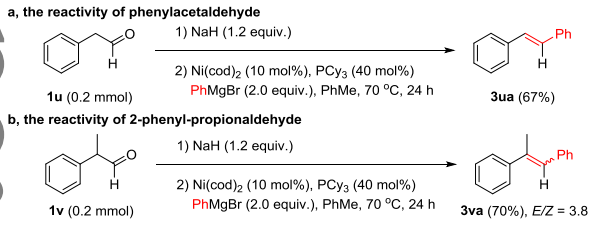
Furthermore, we examined the reactivity of alkyl-alkyl ketones under the standard conditions (**Table 2b**). Besides dibenzyl ketones (**3la** and **3ma**), other aliphatic ketones were also transformed to the corresponding alkenes in moderate to good yields (**3na**-**3pa**). Ketones with a rigid skeleton, such as Camphor, were also transformed to the desired product in an acceptable yield (**3qa**). It is noteworthy that, 2-tetralone, with two different

alpha-Hs, offered the single product **3ra** in 50% yield.

Inspired by the successful preparation of tri-substituted olefins, we further applied this method to synthesize di-substituted and tetra-substituted olefins (**Table 2c**). As we anticipated, the desired di-substituted olefin **3sa** was furnished in 69% isolated yield under standard conditions. Due to the steric effect of substrate, the tetra-substituted olefin product **3ta** was obtained in a much lower yield with iso-butyrophenone **1t** as the substrate under standard conditions. Fortunately, the desired product **3ta** could be obtained in moderate yield under modified conditions.

With 1-tetralone (**1g**) as the model substrate, we investigated the reactivity of different Grignard reagents (**Table 2d**). Various aryl Grignard reagents were submitted to the catalytic system and the corresponding products were obtained in good yields (**3ga**-**3gf**). It is worthy to note that the steric hindrance of nucleophiles did not affect the efficiency. The cross-coupling of ketone **1a** with Grignard **2c** was also conducted, and the desired product was obtained in moderate yield (**3ac**). Alkenyl Grignard reagent was also submitted to this conversion, while present low efficiency (**3gg**). Unfortunately, we failed observing the desired product when EtMgBr was used as the nucleophile (**3gh**). Moreover, phenylboroxine (**2a'**) could also be used as the nucleophile in this transformation, and the desired product was obtained in a moderate yield (43%), indicated the potential to apply weaker nucleophilic reagents to this conversion system (**3ba**).

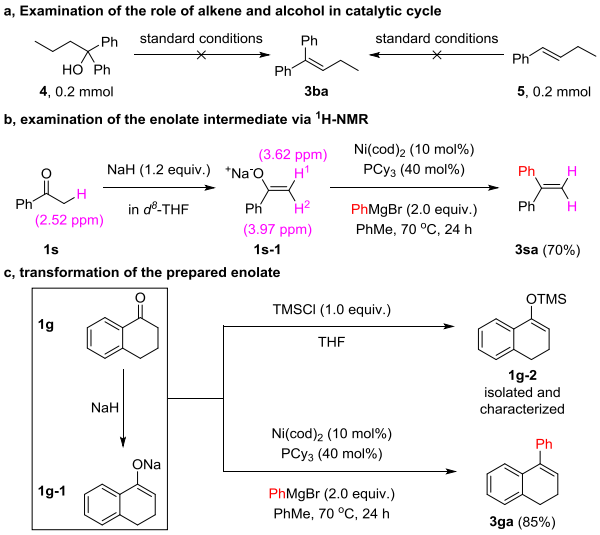
Scheme 2, Investigation of the reactivity of aldehydes



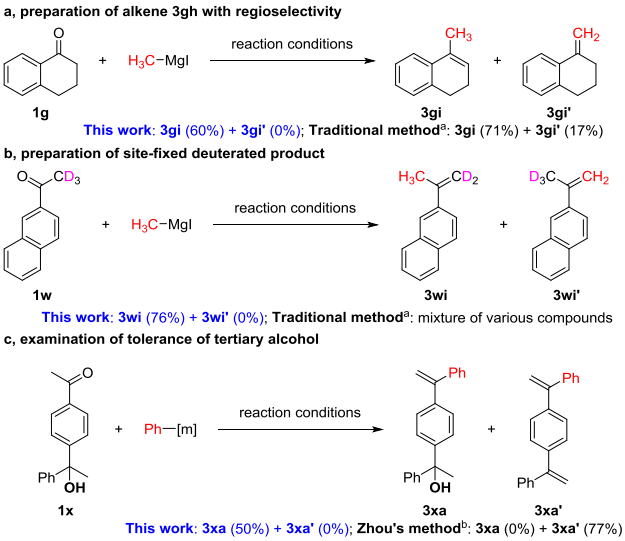
In order to extend the substrate scope, we investigated the performance of aldehydes in this catalytic system. To our delight, when aldehyde **1u** was used, trans-stilbene 3ua was obtained as the single isomer in 67% isolated yield (**Scheme 2a**), and the aldol condensation product was not observed by checking the crude reaction mixture using the ^{1}H NMR and GC-MS analysis. Furthermore, the conversion of more steric hindered aldehyde **1v** to tri-substituted olefin was also investigated and the desired product **3va** was isolated in 70% yield with two different isomers (**Scheme 2b**).

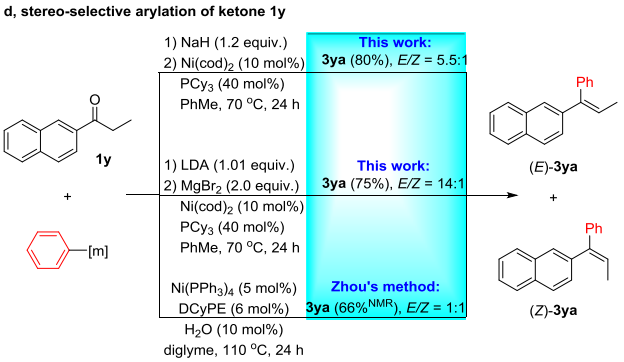
To gain insights into the mechanism, we prepared compounds **4** and **5**. However, no desired product 3ba was observed for **4** and **5** under the standard conditions (**Scheme 3a**). These results excluded the possibility that tertiary alcohols or alkenes were the key intermediates in the catalytic cycle. We further monitored the reaction of ketone **1s** with NaH by ^{1}H NMR, and found that the chemical shifts of α-protons were changed, which indicated the formation of enolate **1s-1** (**Scheme 3b**). This enolate was submitted to the catalytic system and the desired product **3sa** was obtained in 70% isolated yield, thus supporting the formation of enolate intermediate in the catalytic cycle. To further demonstrate this enolate intermediate in this transformation, we prepared the enolate **1g-1** as a yellow solid, and then submitted it into the reaction with TMSCl and obtained the product **1g-2**, this enolate was also submitted to the standard conditions, and forged the corresponding product **3ga** in 85% NMR yield (**Scheme 3c**). This result further indicated that the transformation was furnished via an enolate intermediate.

Scheme 3, Preliminary mechanistic study of nickel catalyzed conversion of carbonyl compounds to olefins



Scheme 4. Application of the nickel catalyzed conversion of carbonyl compounds to olefins and comparison with other method. [a] Me-MgI, THF, r.t., then working-up with HCl (aq.); [b] $Ni(PPh_3)_4$ (10 mol%), DCyPE (12 mol%), H_2O (10 mol%), $(PhBO)_3$ (1.0 equiv.), diglyme, 110 °C, 24 h





Based on the aforementioned researches, olefins could be prepared with predictable regioselectivity using the presenting method. Indeed, when MeMgI (**2i**) was used as an alternative nucleophile in this catalytic system, the desired product **3gi** was obtained as the single product in 60% isolated yield (**Scheme 4a**). In comparison, the traditional method, constituted by the nucleophilic addition of MeMgI to 1-tetralone (**1g**) and

dehydration with aqueous HCl, led to the formation of the mixture of **3gi** and product **3gi'**.[2c] Furthermore, the methylation of the deuterium labelled substrate 1w was also conducted, and the desired product **3wi** was obtained as the single product in 76% yield, while relatively poor regioselectivity was observed when using traditional method (**Scheme 4b**).[2c] Therefore, the current method could be a promising candidate for preparing the site-fixed deuterated product.

As that enolate was demonstrated as the key intermediate, acid-sensitive functional groups, such as tertiary alcohol, should be tolerated in this catalytic system. As we expected, the desired product **3xa** was obtained exclusively in 50% isolated yield using the presented catalytic system (**Scheme 4c**). The conversion of **1x** was also conducted using Zhou's conditions, and only a di-olefinated product **3xa'** was observed in a good yield.[9] Under the standard conditions, we also conducted the phenylation of ketone **1y**, and yielded the compound **1yg** in 80% yield with moderate Z/E selectivity (E/Z = 5.5). If LDA was used as the base instead of NaH, product 1yg could be obtained in 75% yield with high Z/E ratio (E/Z = 14). In comparison, Zhou's method was also applied to the conversion of **1y** while only low selectivity was observed for the products (**Scheme 4d**).[9]

Conclusions

In summary, we demonstrated a general and direct protocol to convert carbonyl compounds to substituted olefins via enolate intermediate. Besides ketones, aldehydes were proved to be suitable for this method. The conversion of ketones to alkenes with methyl magnesium iodide was also conducted with good yield and ideal regioselectivity. Acid-sensitive functional groups, such as tertiary alcohol, could be tolerated. Preliminary mechanism studies ruled out the participation of alcohol and olefin as key intermediates. Therefore, this research could be a helpful update for the enol chemistry. Now we are still working on expanding the substrate scope and the detailed reaction mechanism.

Experimental

General method for the conversion of carbonyl compound **1a** to olefin **3aa**: In a nitrogen-filled glove-box, a 25 mL oven-dried seal-tube equipped with a magnetic stir bar was charged with ketone **1a** (0.2 mmol, 26.9 mg), NaH (0.24 mmol, in mineral oil), then THF (1 mL) was added via syringe. The mixture was stirred for 1 hours, and then the solvent THF was removed with a cold trap under reduced pressure. Catalyst $Ni(cod)_2$ (0.01 mmol, 5.6 mg), ligand PCy_3 (0.04 mmol, 22.4 mg), and PhMe (0.6 mL) were added. Next, Grignard reagent **2a** (0.4 mmol in Et_2O) was added via syringe. The reaction was removed from the glove-box and maintained at 70 ^{o}C for 24 h in an oil-bath. Then, the reaction was quenched by EtOH (1.5 mL). The desired products were purified by flash chromatography on silica gel (petroleum ether), and **3aa** obtained as colourless oil in 88% yield (34.2 mg).Analytical data for **3aa**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.14 (m, 7H), 6.16 (q, *J* = 7.0 Hz, 1H), 1.75 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.94, 142.43, 140.00, 130.03, 128.12, 128.03, 127.17, 126.80, 126.69, 124.10, 15.68; MS (EI): 198 (M^+).

Supporting Information

The supporting information for this article is available on the WWW under https://doi.org/10.1002/cjoc.2018xxxxx.

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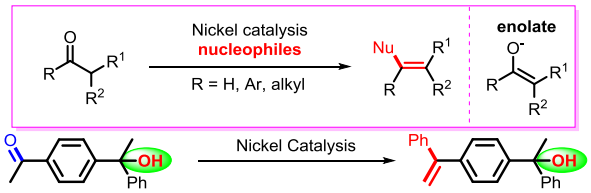

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