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# Photocatalytic C(sp<sup>3</sup>)–H activation towards α-methylenation of ketones using MeOH as 1C source steering reagent

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Abstract. Unprecedented direct access to terminal enones via  $\alpha$ -methylenation of aryl ketones to form C=C bond is achieved under visible-light conditions using methanol as one carbon source substrate and solvent as well. The reaction involves Cu@g-C<sub>3</sub>N<sub>4</sub>-catalysed in situ oxidation of methanol into formaldehyde followed by dehydrative cross aldol type reaction. Various aryl ketones react efficiently with MeOH, producing  $\alpha,\beta$ unsaturated carbonyl compounds only in 4-8 h at room temperature in excellent yield (84-97%). Operational simplicity, wide substrate scope, ambient reaction conditions, visible-light photocatalysis and novel application of MeOH as methylene donor substrate are the salient features making the envisaged protocol mild, efficient and green alternative to the existing methods for synthesis of such fine chemicals.

**Keywords:** Visible-light; Terminal enone; Ketone; 1 C source; g-C<sub>3</sub>N<sub>4</sub>.

Visible light-induced photoredox catalysis has emerged as state-of-the-art alternative in modern organic synthesis for activation of organic molecules.<sup>[1,2]</sup> To design a photocatalyst with high selectivity and efficiency for accelerating the visible light-mediated organic transformations would advance the goal. The polymeric graphitic C<sub>3</sub>N<sub>4</sub> (g- $C_3N_4$ ) is one of the most charming materials<sup>[3]</sup> and is of particular interest as visible light photocatalyst,<sup>[4]</sup> although it has some limitations due to rapid charge recombination.<sup>[5]</sup> To overcome this problem, several strategies have been developed including doping of metal/non-metal in the cavity of  $g-C_3N_4^{[5-9]}$  as metaldoped g-C<sub>3</sub>N<sub>4</sub>, such as Cu/Co/Ni@g-C<sub>3</sub>N<sub>4</sub> shows extremely high catalytic activity for organic reactions along with its reusability.[10]

Direct functionalization of Csp<sup>3</sup>-H bond has received a great attention as it offers more efficient step and atom economical approach for synthesising complex organic framework.<sup>[11]</sup> Recently, synthesis of various  $\alpha,\beta$ -unstaurated carbonyl compounds has been reported *via* installation of terminal alkenes to aldehydes and ketones.<sup>[12-15]</sup> The strategy involves  $\alpha$ methylenation of carbonyl compounds with formaldehyde<sup>[12]</sup> (Scheme 1a) and paraformaldehyde<sup>[13a]</sup> (Scheme 1b) as one-carbon source through Eschenmoser's salt promoted Mannich-type reaction followed by elimination.<sup>[14,15]</sup> Thus, in spite of being highly reactive,<sup>[12,13]</sup> toxicity of HCHO has been the main limitation and led to search for new substrate scope for  $\alpha$ -methylenation of ketones. Accordingly, literature reports DMA,<sup>[16]</sup> DMF,<sup>[17]</sup> and DMSO<sup>[18]</sup> as alternative one carbon donating substrates for oxidative α-C-H-1c-e). However, poor methylenation (Scheme reactivity of these alternatives 1C-source<sup>[15-18]</sup> towards  $\alpha$ -methylenation essentially demand oxidising agents forcing refluxing temperature with slow and conversion rate.<sup>[15-18]</sup> Thus, search for efficient and mild one-carbon source for improved  $\alpha$ -methylenation of ketones is still crucial and highly demanding target in organic synthesis.

To fill this literature gap for  $\alpha$ -methylenation of ketones, we were fascinated to exploit the unparalleled high electrophilicity of HCHO for crossaldol type reaction with ketones having  $\alpha$ -hydrogen, but its toxicity and environmental impact was our



**Scheme 1.** Literature reports on  $\alpha$ - methylenation.

main concern. Alternatively, we anticipated to utilize methanol as 1C-source for in situ generation and utilization of HCHO for  $\alpha$ -Csp<sup>3</sup>-H methylenation. In of our continuation interest in organic transformations,<sup>[19]</sup> we report herein, the first visible light-induced  $\alpha$ -methylenation of ketones at room temperature using MeOH as 1-C source and Cu@g-C<sub>3</sub>N<sub>4</sub> as new and efficient photocatalyst without use of any oxidant, which is hitherto unreported and not accessible through any classical or modern approach reported till date for  $\alpha$ -methylenation of ketones (Scheme 1f).

To realize our idea, acetophenone 1a and methanol 2 was taken as model substrate to probe the feasibility of novel catalytic a-methylenation under visible light. The reaction mixture was stirred under the visible light at room temperature, and the results are summarized in Table 1. When, a mixture of acetophenone 1a (1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), PPh<sub>3</sub> (0.1 mmol) and MeOH (5 mL) was stirred for 8 h in the presence of  $g-C_3N_4$  (20 mg), and we were happy to isolate the desired product 2a albeit in very low yield (Table 1, entry 1). Then, we turned our attention to use metal-doped @g-C<sub>3</sub>N<sub>4</sub> as catalyst, and our strategy worked well as the product 2a was isolated in 6 h using Ni@g-C<sub>3</sub>N<sub>4</sub> (15 wt%, 20 mg) with improved yield of 2a (Table 1, entry 2). After screening different catalysts, Cu@g-C<sub>3</sub>N<sub>4</sub> (15 wt%, 20 mg) not only improved the yield up to 97% but it increased the conversion rate also and reaction got completed

**Table 1.** Optimization of reaction conditions for synthesis of terminal enone  $2a^{[a]}$ 

		OH Catalyst PPh <sub>3</sub> , Base rt., hv		Ph CH <sub>2</sub>
Ph				
Entry	Catalyst (mg)	Base	Time (h)	Yield (%) <sup>[b, c]</sup>
1	@g-C <sub>3</sub> N <sub>4</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	08	42
2	Ni@g-C <sub>3</sub> N <sub>4</sub> (20)	$K_2CO_3$	06	69
3	Co@g-C <sub>3</sub> N <sub>4</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	06	88
4	Fe@g-C <sub>3</sub> N <sub>4</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	06	81
5	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	$K_2CO_3$	04	97
6	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	Cs <sub>2</sub> CO <sub>3</sub>	04	86
7	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	CsOH	04	78
8	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	Cs <sub>2</sub> OAc	04	69
9	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	Na <sub>2</sub> CO <sub>3</sub>	04	79
10	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	Li <sub>2</sub> CO <sub>3</sub>	04	76
11	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	KOH	04	70
12	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	K <sub>3</sub> PO <sub>4</sub>	04	51
13	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	KO <sup>t</sup> Bu	04	55
14	Cu@g-C <sub>3</sub> N <sub>4</sub> (15)	K <sub>2</sub> CO <sub>3</sub>	04	92
15	Cu@g-C <sub>3</sub> N <sub>4</sub> (25)	K <sub>2</sub> CO <sub>3</sub>	04	97
16 <sup>[d]</sup>	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	K <sub>2</sub> CO <sub>3</sub>	04	-
17	Cu@g-C <sub>3</sub> N <sub>4</sub> (20)	-	04	-
18	-	K <sub>2</sub> CO <sub>3</sub>	04	-

<sup>[a]</sup>*Reaction conditions*: Acetophenone **1a** (1 mmol), MeOH (5 mL), PPh<sub>3</sub> (0.1 mmol), base (1 mmol), 7-volt LED light, r.t., in air. <sup>[b]</sup>Yield of isolated and purified product. <sup>[c]</sup>All compounds gave C, H and N analyses within  $\pm$  0.35%, and satisfactory spectral (<sup>1</sup>H NMR, <sup>13</sup>C NMR and EIMS) data. <sup>[d]</sup>Without PPh<sub>3</sub>.



Scheme 2. Control experiment for methylenation of ketone 1a.

only in 4h (Table 1, entries 2-5). The reason for increasing efficiency of the reaction by doping Cu may presumably be due to the presence of vacant dorbital, which polarizes carbonyl oxygen of formaldehyde for increasing its reactivity. Next, a variety of bases were screened (Table 1, entries 5-13) and  $K_2CO_3$  (1.0 mmol) was found the most efficient base in presence of PPh<sub>3</sub> (0.1 mmol) as additive for present transformation showing preeminent results with 97% yield in 4 h (Table 1, entry 5). The amount of catalyst was found 20 mg optimum; decreasing the catalyst loading from 20 to 15 mg, yield of the product 2a was also decreased (Table 1, entries 5 and 14), while there was no change in yield on increasing the catalytic amount (Table 1, entries 5 and 15). However, in the absence of either catalyst or additive or base, we could not isolate the any product 2a (Table 1, entries 16-18). Also, we performed the reaction under inert atmosphere. However, we did not isolate any product which confirms that oxygen from air is essential as oxidant for oxidation of MeOH into HCHO. Thus, the optimized condition for the present reaction was concluded as: Cu@g-C<sub>3</sub>N<sub>4</sub> (20 mg),  $PPh_3$  (0.1 mmol),  $K_2CO_3$  (1 mmol) with MeOH (5 mL) in presence of LED light at room temperature, and this outcome was applied as preeminent condition for construction of product 2a.

Furthermore, six sets of controlled experiments were performed to observe the catalytic effect of visible light in the present investigation by taking 1a  $(1.0 \text{ mmol}), \text{Cu@g-C}_3\text{N}_4 (20 \text{ mg}), \text{PPh}_3 (0.1 \text{ mmol})$ and K<sub>2</sub>CO<sub>3</sub> (1 mmol) (Scheme 2a-f). First experiment was performed using HCHO as 1-C source and water as solvent in presence of visible light and we isolated the desired product 2a in 6 h with satisfactory yield (Scheme 2a). Next, three separate experiments were run in without using visible light taking methanol as one carbon source as well as solvent, (i) in the dark condition (Scheme 2b), (ii) at room temperature (Scheme 2c) and at 80 ° C temperature (Scheme 2d). However, yield of the product 2a was lower in dark condition (35%) and good (73%) at room temperature as well as no change in yield at 80 ° C temperature. For the confirmation of radical formation, we have checked a set of experiment with 1 eq. of TEMPO (a stable free radical) and we observed that the very



Scheme 3. Substrate scope for the formation of terminal enones 2.

small amount (37%) of desired product 2a obtained (Scheme 2e). We also used the deuterated methanol and observed that the deuterated phenyl vinyl ketone (93%) obtained (Scheme 2f). Finally, model



Scheme 4. Tentative mechanism for formation of enone 2.

experiment (Table 1, entry 5) concluded that visible light not only improves the yield of product but also it increases the conversion rate showing co-operative effect with catalyst in the present reaction due to the higher triplet energy of acetophenone.<sup>[20]</sup>

With these optimized reaction conditions in hand, a variety of aromatic (1a-t) as well as heteroaromatic (1u-x) ketones were screened and the corresponding terminal enone 2a-x were isolated in good to excellent yield (Scheme 3). However, there was no specific effect of substituents on phenyl/heterocyclic ring was noticed and ketone 1 tolerated both electron withdrawing (F, Cl, Br, NO<sub>2</sub>, CN and CO<sub>2</sub>Me) as well as electron releasing (Me, OMe and OEt) groups to afford the corresponding enone 2 within 4-8 h under mild reaction conditions (Scheme 3). In case of aliphatic ketones, taking acetone as substrate, we did not isolate the corresponding product, presumably due to high volatility of acetone as the reaction was not performed in closed vessel instead in presence of light in open flask. But, using another aliphatic ketone, for example, heptanone, which is relatively less volatile (boiling point 151 ° C), corresponding enone was isolated albeit in low yield (31%) and hence we did not continue using other aliphatic ketones in the envisaged method. All the synthesized compounds were characterized by their <sup>1</sup>H and <sup>13</sup>C NMR spectra.

The formation of enone **2** from ketone **1** involves in situ conversion of MeOH into HCHO via initial formation of MeOK using K<sub>2</sub>CO<sub>3</sub> followed by PPh<sub>3</sub>/Cu@g-C<sub>3</sub>N<sub>4</sub>.<sup>[21]</sup> Catalysts such as Ir, Rh and Co having vacant *d*-orbital in combination with phosphine are reported to catalyze the oxidation of MeOH into HCHO through abstraction of Csp<sup>3</sup>-H proton of MeOH.<sup>[21,22]</sup> Optimization experiment reveals that neither Cu@gC<sub>3</sub>N<sub>4</sub> nor PPh<sub>3</sub> alone oxidizes the MeOH (Table 1, entry 16 and 18), which further concludes that  $PPh_3/Cu@g-C_3N_4$  binds with oxygen of MeOK and thus facilitating the oxidation of methanol (Scheme 4a). Tentative mechanism presumably proceeds through Cu@g-C<sub>3</sub>N<sub>4</sub> induced photocatalytic excitation of enolate 4 into corresponding radical 5, which further assist the carbon-carbon bond formation with electrophilic formaldehyde 3 producing corresponding alcohol 6, which finally underwent K<sub>2</sub>CO<sub>3</sub>-induced dehydration to afford the product 2a (Scheme 4). The reaction mechanism in the absence of light may be explained by simple base-catalyzed aldol reaction. The reaction presumably involves base-catalyzed activation of acetophenone to react with in situ generated HCHO, followed by dehydration of the aldol product.

To check the reusability of catalyst, five sequential experiments were run (Fig. 1) using acetophenone **1** (1.0 mmol), PPh<sub>3</sub> (0.1 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol) in MeOH (5 mL), with Cu@g-C<sub>3</sub>N<sub>4</sub> (20 mg) under visible light condition at room temperature. After completion of each reaction, Cu@g-C<sub>3</sub>N<sub>4</sub> was recovered using centrifuge, washed with water and reused for the next reaction of fresh batch of acetophenone. The Cu@g-C<sub>3</sub>N<sub>4</sub> catalyst could be recycled and reused five times with good yield



**Fig. 1.** Recyclability of  $Cu@g-C_3N_4$  for the synthesis of 1-Phenylprop-2-en-1-one **2a**.

without any significant loss of its activity (Fig. 1). Furthermore, SEM (ESI, Fig. 2, S2) and XRD pattern (ESI, Fig. 3, S3) confirms that there was no substantial change in morphology and structure of catalyst after reused 5 times in consecutive reactions.

Thus, we disclose an original visible light induced mild and efficient method for methylenation of  $C(sp^3)$ -H in aryl alkyl ketones using MeOH with  $Cu@g-C_3N_4$  catalyst under ambient reaction conditions. Operational simplicity, wide substrate scope, excellent yield (84-97%) of enones, ambient reaction conditions and visible-light photocatalysis are the salient features of the envisaged protocols. Application of MeOH as new one carbon donor substrate for methylenation process as well as solvent for the reaction makes the envisaged method advantageous than earlier reported method for synthesis of such fine chemicals and would be the best alternative to be further exploited for academia and industries.

## **Experimental:**

#### Preparation of Cu@g-C<sub>3</sub>N<sub>4</sub>:

For preparation of photocatalyst, urea was calcinated at 500 °C temperature under air free condition in muffle furnace for 2 h, to get converted as yellowish graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) and then it was used as support for Cu-metal encapsulation.<sup>[23]</sup> The solution (sol) of  $g-C_3N_4$  (Sol A, 425 mg) and Cu(OAc)<sub>2</sub>.H<sub>2</sub>O (Sol B, 238 mg, 15 wt% of g-C<sub>3</sub>N<sub>4</sub>, Cu 75 mg) was prepared in aqueous methanol (50%) individually through sonication. Then, Sol B was added in Sol A and stirred for 6 h at room temperature (rt). Prepared nanoparticle was centrifuged and washed with water and methanol and dried under vacuum at 50 °C. The prepared Cu@g-C<sub>3</sub>N<sub>4</sub> catalyst was then characterized by FTIR, X-ray diffraction (XRD), photoluminescence (PL), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS).

#### Characterization of Cu@g-C<sub>3</sub>N<sub>4</sub>

SEM images exposed the two-dimensional arrangement and fine agglomeration in g-C<sub>3</sub>N<sub>4</sub> and Cu@g-C<sub>3</sub>N<sub>4</sub> (Fig. 2a and b).<sup>[23c]</sup> The Carbon and nitrogen in  $g-C_3N_4$  (Fig. 4a) and carbon, nitrogen and a small amount of Cu metal in Cu@g-C<sub>3</sub>N<sub>4</sub> were studied by EDX spectra (Fig. 4b). The X-ray diffraction (XRD) pattern has shown the graphiticlike phase of  $C_3N_4$  in g- $C_3N_4$  and  $Cu@g-C_3N_4$ . The strong peaks at 27.6° attributed to the typical characteristic (002) interlayer stacking peak and the weak diffraction (100) peak at 13.2° attributed to the in-plane repetitive units in the  $g-C_3N_4$  (JCPDS No. 85-1326) and confirmed the dissimilarity in  $g-C_3N_4$ and Cu@g-C<sub>3</sub>N<sub>4</sub> (Fig. 4c).<sup>[24]</sup> A transmission electron microscopy (TEM) image of g-C<sub>3</sub>N<sub>4</sub> and Cu@g-C<sub>3</sub>N<sub>4</sub> has also confirmed the graphitic- like structure and copper in Cu@g-C<sub>3</sub>N<sub>4</sub> and it also supported the XRD analysis very well (Fig. 2c and d).<sup>[23c]</sup> Blue luminescence was observed in photoluminescence spectra of g-C<sub>3</sub>N<sub>4</sub> and Cu@g-C<sub>3</sub>N<sub>4</sub> because of transition among lone pair (LP) states in the valence band and the  $\pi^*$  antibonding states in the conduction band. The PL spectrum of g-C<sub>3</sub>N<sub>4</sub> and Cu@g-C<sub>3</sub>N<sub>4</sub> (Fig. 4d) shows strong blue luminescence at  $\sim$ 465 nm and ~460 nm, respectively. The states consisting of the sp<sup>3</sup> C–N  $\sigma$  band, the sp<sup>2</sup> C–N  $\pi$  band, and the LP state of the bridge nitride atom are accountable for the luminescence from  $g-C_3N_4$ . The absorption in the visible region for g-C<sub>3</sub>N<sub>4</sub> helps in investigation of its visible light photocatalysis. The Fourier transform infrared (FTIR) spectrum exhibits evidently exposed broad bands in the  $3000-3500 \text{ cm}^{-1}$  region that could be recognized for O-H and N-H stretching. The absorption in the range of 1200-1700 cm<sup>-1</sup> is consigned to the characteristic stretching modes of g- $C_3N_4$  heterocycles. At ~806 cm<sup>-1</sup> absorption band is



Fig. 2. (a) SEM image of  $g-C_3N_4$ , (b) SEM image of  $Cu@g-C_3N_4$ , (c) TEM image of  $g-C_3N_4$  and (d) TEM image of  $Cu@g-C_3N_4$ .



**Fig. 3.** XPS spectra of  $Cu@g-C_3N_4$ ; (a) Scan survey, (b) Cu 2p, (c) C 1s and (d) N 1s data.

considered to be the out-of-plane skeletal bending modes of triazine and the band at  $\sim 1640 \text{ cm}^{-1}$  is recognized to the C=N stretching vibration mode (ESI, Fig. 1, S2).<sup>[25]</sup>

Moreover, the X-ray photoelectron spectroscopy (XPS) measurements were performed to observe the chemical composition and chemical position of the constituent elements in the Cu@g-C<sub>3</sub>N<sub>4</sub> sample (Fig. 3). The XPS survey spectra depicts that C, N, and Cu elements were detected on the Cu@g-C<sub>3</sub>N<sub>4</sub> sample (Fig. 3a), indicating the loading of Cu on  $g-C_3N_4$ . The peaks of Cu  $2p_{3/2}$  and Cu  $2p_{1/2}$  were located at 932.8 and 946.5 eV, respectively, along with the presence of the two strong satellite peaks of copper at 938.3 and 962.3 eV, indicating the presence of Cu(II) in Cu@g- $C_3N_4$ , without the formation of any other oxidation state (Fig. 3b). The C 1s spectra peaks at 285.7 and 287.1 eV were assigned to the C=N coordination and sp<sup>2</sup>-hybridized carbon in N-containing aromatic rings (-N-C=N), respectively (Fig. 3c). The N 1s spectra



**Fig. 4.** EDX spectra of (a)  $g-C_3N_4$ , (b)  $Cu@g-C_3N_4$ , (c) XRD pattern of  $g-C_3N_4$ , and  $Cu@g-C_3N_4$  and (d) PL spectra of  $g-C_3N_4$ , and  $Cu@g-C_3N_4$ .

shown can be deconvoluted into four peaks. The peaks cantered at 398.1 and 398.7 eV are derived from the sp<sup>2</sup>-hybridized nitrogen atoms in -C=N-C groups and the amino function groups, respectively. The peak at around 400.2 eV was attributed to the charging effects or positive charge localization in heterocycles, while that at 399.4 eV is attributed to the tertiary nitrogen in N-C3 groups or in H-N-C2 (Fig. 3d).<sup>[23c]</sup>

#### General method for the synthesis of enones 2:

A flame-dried round bottom flask was charged with a mixture of acetophenone 1 (1.0 mmol), K<sub>2</sub>CO<sub>3</sub> (1.0 mmol), PPh<sub>3</sub> (0.1 mmol), Cu@g-C<sub>3</sub>N<sub>4</sub> (20 mg) in MeOH (5 mL) and stirred under the visible light condition at room temperature for 4-8 h. After completion of the reaction (as monitored by TLC), water was added to the reaction mixture and the catalyst was filtered and added EtOAc. Then, the organic layer was washed with brine  $(2 \times 10 \text{ mL})$  and water  $(2 \times 10 \text{ mL})$ , dried under vacuum evaporator to obtain the crude isolates, which were further purified by flash chromatography, EtOAc/n-hexane to obtain the analytically pure sample of product 2. data of Characterization all the synthesized compounds are given in ESI.

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## COMMUNICATION

Photocatalytic  $C(sp^3)$ –H activation towards  $\alpha$ -methylenation of ketones using MeOH as 1C source steering reagent

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