**Supplementary Materials**

# Model study on photoinduced direct activation of cyclohexane for carbonylation reaction

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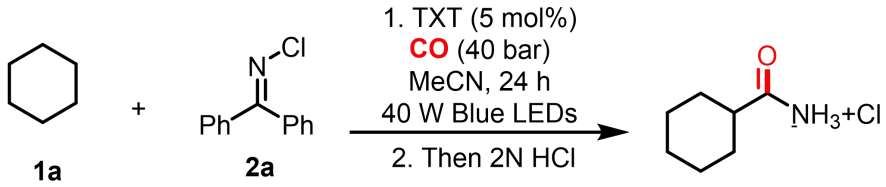
***Contents***

## 1. General Information.

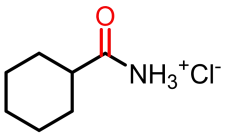
Unless otherwise noted, all reactions were carried out under carbon monoxide or nitrogen atmosphere. All reagents were from commercial sources (Sigma-Aldrich, Bidepharm, EnergyChemical) and used as received without further purification. All solvents were dried by standard techniques and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C), dichloromethane and ethyl acetate as eluent. All NMR spectra were recorded at ambient temperature using Bruker Avance III 400 MHz NMR ($^{1}$H, 400 MHz; $^{13}$C {1H}, 101 MHz, $^{19}$F 376 MHz). $^{1}$H NMR chemical shifts are reported relative to TMS and were referenced via residual proton resonances of the corresponding deuterated solvent ($CDCl_3$: 7.26 ppm) whereas $^{13}$C{1H} NMR spectra are reported relative to TMS via the carbon signals of the deuterated solvent ($CDCl_3$: 77.0 ppm. Data for $^{1}$H are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd (doublet of doublets), dt (doublet of triplets), qd (quartet of doublets), quint = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. All $^{13}$C NMR spectra were broad-band $^{1}$H decoupled. All reactions were monitored by GC-FID or NMR analysis. HRMS data was obtained with Micromass HPLC-Q-TOF mass spectrometer (ESI-TOF) or Agilent 6540 Accurate-MS spectrometer (Q-TOF). FT-ICR MS was obtained with Solarix FT-ICR MS (15 T, Bruker Daltonics GmbH, Bremen, Germany). Because of the high toxicity of carbon monoxide, all the reactions should be performed in an autoclave. The laboratory should be well-equipped with a CO detector and alarm system.

## 2. General Experimental Procedure and Characterization Data




**1a** **2a**

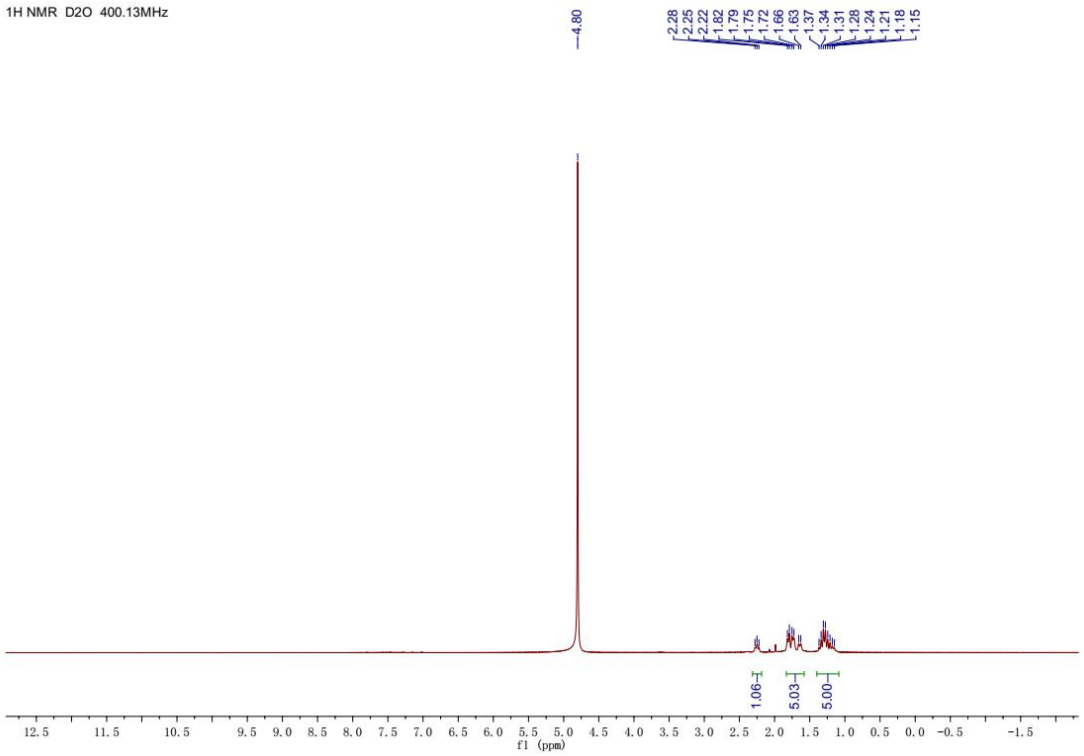
A 4 mL screw-cap vial was charged with **2a** (21 mg, 0.1 mmol), TXT (1.1mg, 5 mol%). After tightening the bottle cap, **1a** cyclohexane (108 μL, 10 equiv) and 2 mL of MeCN was added. the vial was moved to an alloy plate and put into an autoclave which are euphotic under argon atmosphere. At room temperature, the autoclave was charged with 40 atm of CO. The autoclave was placed on an environment equipped with a magnetic stirrer. The reaction mixture was stirred for 24 h under 40 W Blue LEDs (450-460nm). After the reaction was complete, the pressure in autoclave was released carefully. Then the HCl (2.0 equiv, 0.2 mL, 2 N) was added dropwise. The mixture was stirred for 3 hours at room temperature and monitored by TLC analysis. Then, the resulting mixture was extracted with water (3×3 mL). At last, the desired products were obtained by concentrating the aqueous phase.

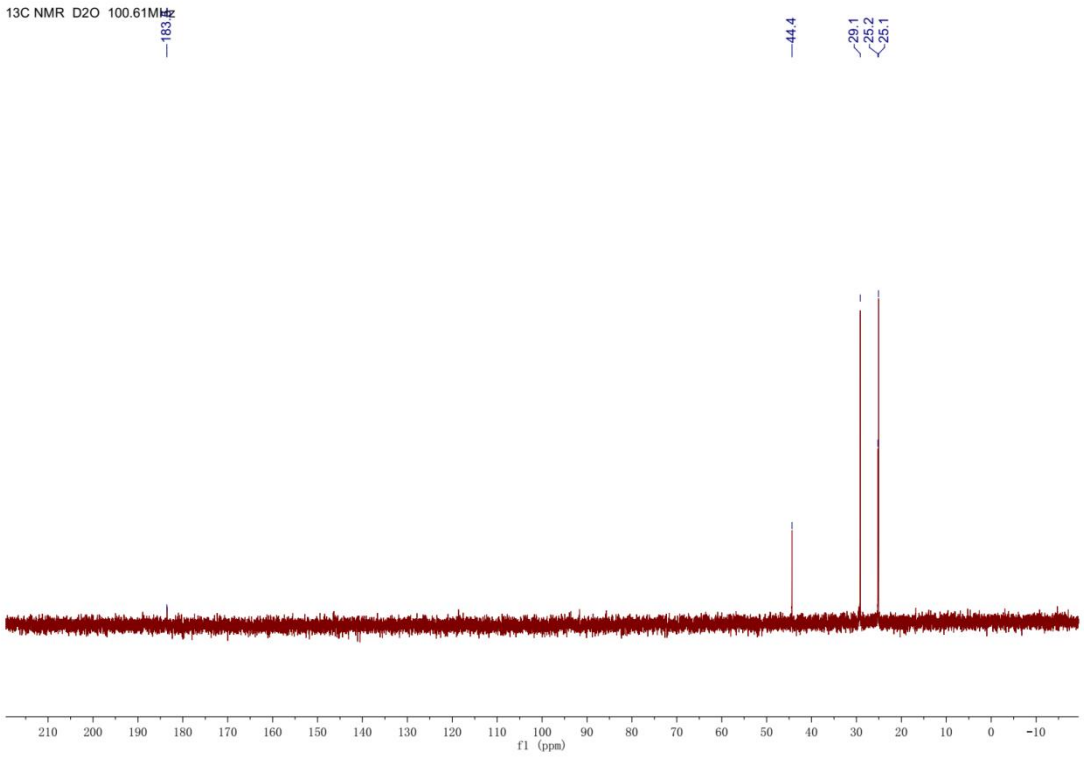



$^{1}$H NMR (400 MHz, $D_2O$) δ 2.25 (t, $J$ = 11.2 Hz, 1H), 1.90 – 1.55 (m, 5H), 1.47 – 1.02 (m, 5H).

$^{13}$C NMR (101 MHz, $D_2O$) δ 183.6, 44.4, 29.1, 25.2, 25.1.

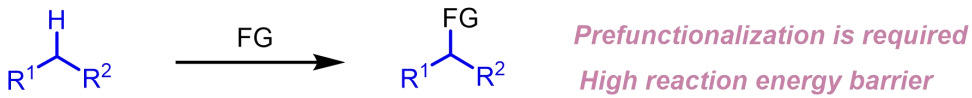
## 3. Copies of $^{1}H$, $^{13}C$.



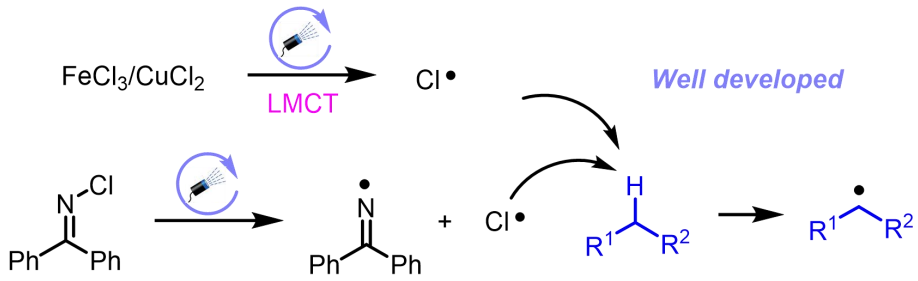



## 4. General scheme and proposed mechanism

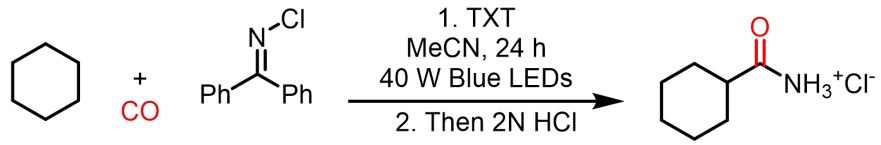
**A: The activation of $C_{sp3}$-H bond**



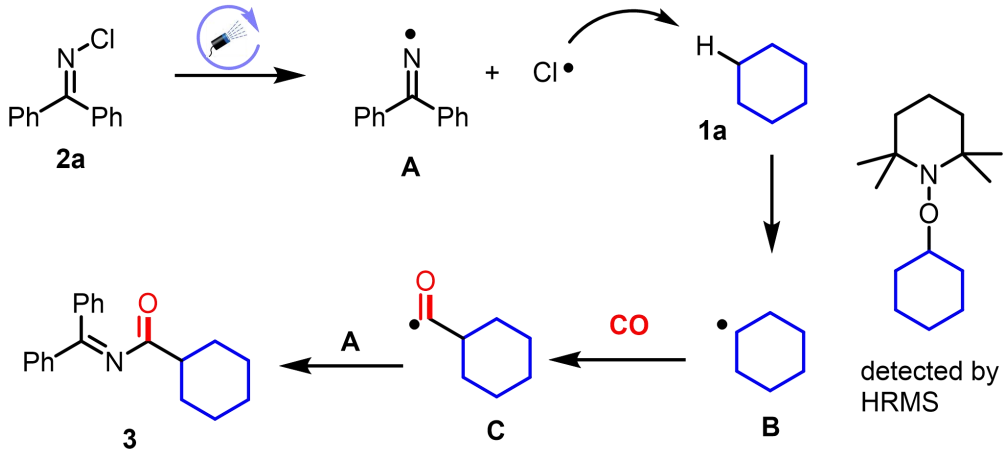

**B: Hydrogen extraction strategy by chlorine radical**




**C: This work: Photoinduced C-H bond activation carbonylation reaction of cyclohexane**




**Supplementary Scheme 1.** Activation carbonylation of C-H bonds.




**Supplementary Scheme 2**. Proposed Reaction Mechanism.