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Decarboxylative Elimination for the Synthesis of Olefins Via Photoredox/Cobalt Dual Catalysis

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DECARBOXYLATIVE ELIMINATION FOR THE SYSTHESIS OF
OLEFINS VIA PHOTOREDOX/COBALT DUAL CATALYSIS

by
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A THESIS

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DECARBOXYLATIVE ELIMINATION FOR THE SYSTHESIS OF OLEFINS VIA PHOTOREDOX/COBALT DUAL CATALYSIS

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University of Nebraska, 2017

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Carboxylic acids are abundant in nature, bench stable, cheap, and readily available and thus are ideal feedstocks for organic synthesis. Direct decarboxylation has been widely studied as an effective approach for different synthetic goals such as arylation, alkylation fluorination and vinylation. Decarboxylative elimination for the synthesis of useful olefin products is an under-developed transformation. In this thesis, we outlined the design of a dual catalytic system consisting of an organic photoredox catalyst and a cobaloxime hydrogen evolution catalyst to transform carboxylic acids to olefins via visible-light-promoted decarboxylative elimination under a mild and environmentally friendly condition. The use of the hydrogen evolution catalyst $\text{Co}(\text{dmgH})_2\text{PyCl}$ provides the advantage of avoiding using stoichiometric oxidants for the elimination step. With 2-phenylpropionic acid, a 90% yield of corresponding olefin was obtained. The catalytic system can be applied to other carboxylic acids with excellent yields.

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List of Abbreviations

HAT	hydrogen atom transfer
SET	single electron transfer
COPC	cobaloxime pyridine chloride
THF	tetrahydrofuran
EtOAc	ethyl acetate
DMF	<i>N,N</i> -dimethyl formamide
DMSO	dimethyl sulfoxide
equiv	equivalent
CsOAc	cesium acetate
NaOAc	sodium acetate
NMR	nuclear magnetic resonance
4CzIPN	2,4,5,6-tetra(carbazol-9-yl)isophthalonitrile
MeCN	acetonitrile
TBADT	tetra- <i>n</i> -butylammonium decatungstate
CFL	compact fluorescent lamp

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Chapter 1 Introduction

1.1 Functionalization of Carboxylic Acids via Decarboxylation Pathway

Easily accessible, bench stable, and cheap carboxylic acids have been commonly used as ideal and useful feedstocks for organic synthesis. Coupled with metal catalysts, such as Ni,¹⁻³ Cu,⁴⁻⁶ Rh,⁷⁻⁹ Ag,¹⁰⁻¹² and Pd,¹³⁻¹⁵ carboxylic acids can undergo decarboxylation to form various desired products. However, these metal-coupled decarboxylation pathways usually require high reaction temperature for the insertion of metal or the activation of intermediate, which increase the cost and hamper the large scale synthesis. Recently, a new strategy of using photoredox catalysts such as iridium complexes to perform the oxidative decarboxylation has emerged.¹⁶ By utilizing the energy from visible light, decarboxylation reactions can be conducted at room temperature. In the photocatalytic decarboxylation system, the carboxyl group is first deprotonated and then oxidized by the photocatalyst that has a high oxidation potential at the excited state. Followed by releasing the CO₂ molecule, an alkyl radical is formed (Figure 1-1). Different functionalization can then be performed such as alkylation, vinylation, arylation and fluorination depending on the choice of the radical trapping agent. Direct decarboxylation elimination to form olefins has not been reported until recently.¹⁷⁻¹⁹ Liu and co-workers utilized a metal-free, microwave-assisted method to afford olefins via the decarboxylative elimination.²⁰ The reaction conditions, however, require a stoichiometric hypervalent iodine reagent for the oxidization of the alkyl radical for elimination and microwave as the energy input, which is not an economical process for industrial applications.

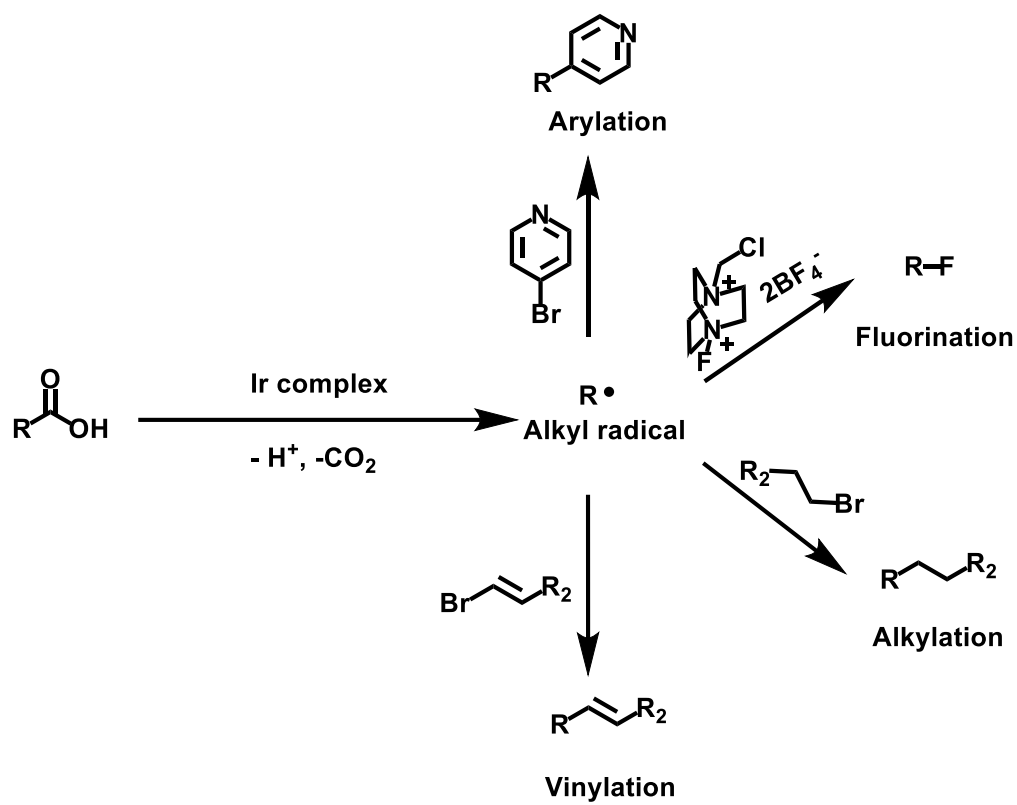
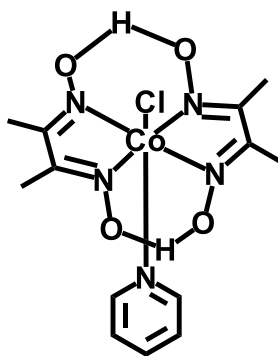


Figure 1-1. Oxidative decarboxylation via photoredox catalysis.

1.2 Hydrogen evolution catalyst cobaloxime and current study in organic synthesis

Cobalt complexes formed with nitrogen donor ligands, such as diglyoxime ligands, have been widely studied as hydrogen evolution catalysts for water splitting.²¹

Cobaloxime pyridine chloride (COPC) is one of the most commonly used cobaloxime complexes (Figure 1-2).



COPC
Cobaloxime pyridine chloride

Figure 1-2 Chemical structure of cobaloxime pyridine chloride COPC.

Recently, Sorensen and co-workers discovered an acceptorless dehydrogenation reaction through a cooperative base/metal catalysis,²² where COPC was used as a hydrogen atom transfer (HAT) catalyst that targets weak C-H bonds ($<50 \text{ kcal mol}^{-1}$). In their reaction design, alkanes were used as the substrates, which undergo a first dehydrogenation by a strong HAT catalyst, tetra-*n*-butylammonium decatungstate (TBADT), to lose one hydrogen atom and produce an alkyl radical. The alkyl radical activates the C-H bond at the β position and makes it possible for COPC to extract a second hydrogen atom and produce the final alkene products (Figure 1-3). Although COPC was called as a weak HAT catalyst in this work, the detailed mechanism was not

clear since the overall reaction could also be a stepwise electron transfer proton transfer process. In this case, instead of abstracting a hydrogen atom, the COPC catalyst acts as a base for deprotonation and an oxidant to accept one electron from the substrate. In general, this work revealed that the hydrogen at the β position to an alkyl radical could be extracted by COPC to generate the elimination product olefin.

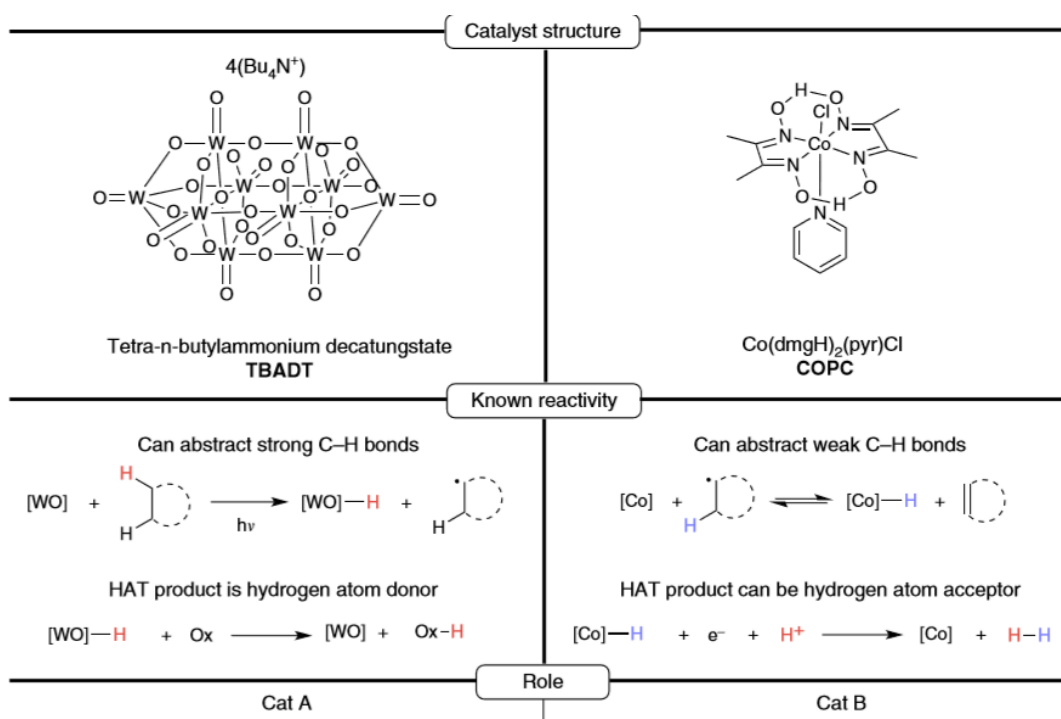


Figure 1-3 Cooperative HAT with TBADT and COPC catalysts.

Recently, several organic transformations have been developed where COPC was used as the catalyst, including the synthesis of indole,²³ site-specific functionalization of amino acid and its derivatives,²⁴ aromatic thiolation²⁵ and oxidation of β -alkyl styrene.²⁶ Although the individual reaction mechanisms vary, COPC was generally considered to remove one hydrogen atom via a similar stepwise electron transfer proton transfer process. It is known that the Co(III) complex of COPC can be reduced to generate a

Co(II) intermediate ($E_{1/2} = -0.68$ V vs SCE in MeCN)²⁷ in the presence of an electron donor and a photocatalyst upon light excitation. The Co(II) intermediate can be further reduced to generate a Co(I) species by interacting with the substrates (e.g. $E_{1/2} = -1.13$ V vs SCE in MeCN).²⁷ The Co(I) complex can then extract a proton to form Co(III)-H, which combines with one proton and releases a H₂ molecule, and Co(III)-complex was regenerated to complete the catalytic cycle. In other cases, the ground state photocatalyst reduces the Co(III)- to Co(II)-complex while the excited state generates the radical intermediate by oxidizing the substrate, and the single electron transfer step happens between the organic radical intermediate and Co(II) complex (Figure 1-4).

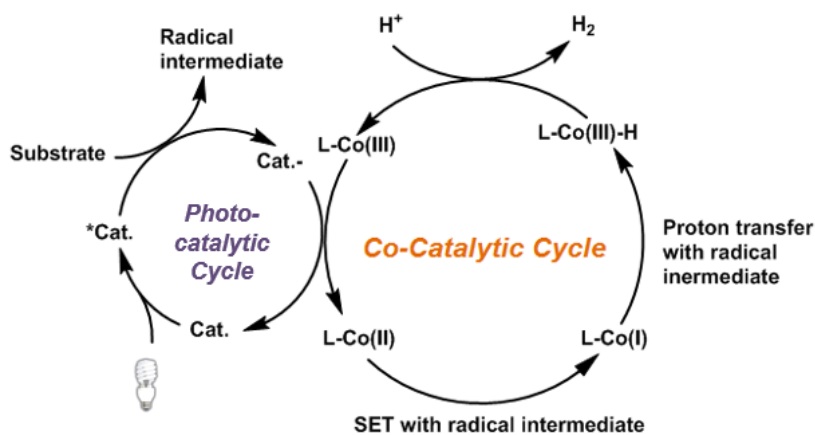
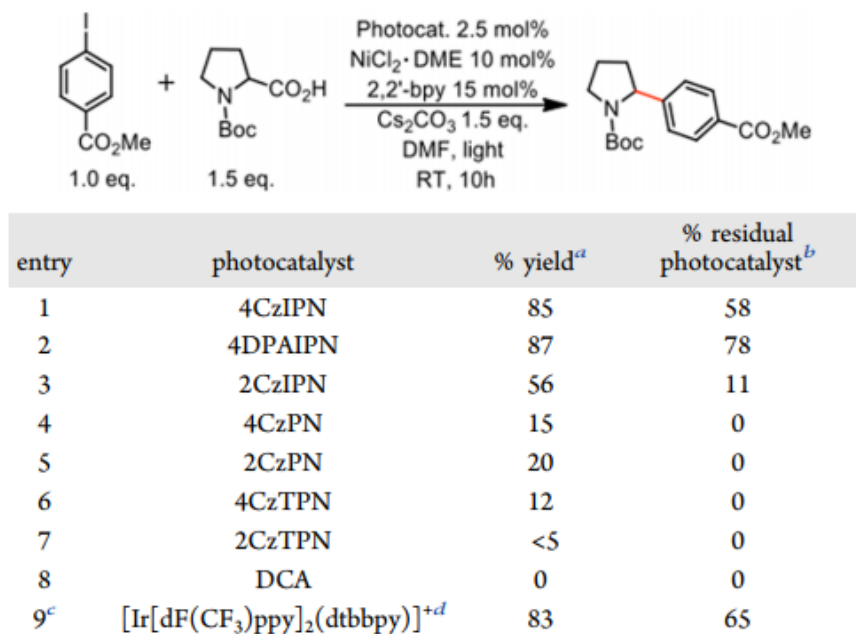


Figure 1-4 Reaction mechanism of photoredox/cobalt dual catalysis reaction.

1.3 Carbazolyl dicyanobenzene (CDCB)-based photocatalysts

Photoredox catalysis, as one of the most powerful synthetic approaches, has recently received wide attention. Our group has developed a series of metal-free photocatalysts on the basis of carbazolyl dicyanobenzene (CDCB) fluorophores.²⁸ By changing the number or position of the carbazolyl and cyano groups on the center phenyl ring, the photoredox potentials can be modified for different donor-acceptor (D-A) fluorophores. The structures of the photocatalysts are shown in Figure 1-5. The efficiencies of the CDCB fluorophores were evaluated by the photoredox/Ni-catalyzed decarboxylative cross coupling of α -amino acids and aryl halides. It was shown that using 4CZIPN (Table 1-1) as the photocatalyst, an excellent 85% yield of the cross-coupling product could be generated.

Table 1-1. Photoredox/Ni Catalyzed Decarboxylative Cross-Coupling.



^aIsolated yield. ^bMeasured by HPLC. ^c24 h to complete the reaction. ^d[dF(CF₃)ppy] = 2-(2,4-difluorophenyl)-5-trifluoromethyl-pyridine, dtbbpy = 4,4'-ditert-butyl-2,2'-bipyridine.

With four carbazolyl groups and two cyano groups on the *meta*-position of the center phenyl ring, 4CzIPN exhibits both good oxidation ability (+1.35 V vs SCE in MeCN) for excited state and good reduction ability (−1.21 V vs CSE in MeCN) for ground state (Table 1-2).

Table 1-2 Redox Potentials of D-A Fluorophores and Common Visible Light Photocatalysts.^a

Photocatalyst	$E_{1/2}(P^+/*P)$	$E_{1/2>(*P/P^+)$	$E_{1/2}(P^+/P)$	$E_{1/2}(P/P^+)$	Excitation λ_{max}	Emission λ_{max}	E_{0-0}^b
2CzTPN ^c	-1.24	+1.34	+1.40	-1.30	430	511	2.64
4CzTPN ^c	-0.99	+1.41	+1.44	-1.02	463	556	2.43
2CzPN	-1.30	+1.32	+1.47	-1.45	365	530	2.77
4CzPN	-1.06	+1.40	+1.50	-1.16	435	535	2.56
2CzIPN	-1.41	+1.36	+1.46	-1.51	362	501	2.87
4CzIPN	-1.04	+1.35	+1.52	-1.21	435	535	2.56
4DPAIPN	-1.28	+1.10	+1.34	-1.52	425	523	2.62
[Ir(dF(CF ₃)ppy) ₂ (dtbbpy)] ^d	-0.89	+1.21	+1.69	-1.37	380	470	
[Ir(dF(CF ₃)ppy) ₂ (bpy)] ^d	-1.00 -0.87 ^e	+1.32 +1.46 ^e	+1.69 +1.81 ^e	-1.37 -1.23 ^e			
DCA	-0.83	+1.97/+2.06	+1.89 ^e	-0.97/-1.00 ^e			
Eosin Y	-1.11	+0.83	+0.78	-1.06			
Rose Bengal	-0.99	+0.66	+0.78	-1.11			
MB ^e		+1.48		+0.11			
Acr ⁺ -Mes		+2.06		-0.57			

^aAll potentials are given in volts versus the saturated calomel electrode (SCE). Measurements were performed in acetonitrile at room temperature unless otherwise noted. ^b E_{0-0} , the zero-zero vibrational state excitation energy, was estimated using the medium wavelengths between the lowest fluorescence excitation peak (excitation λ_{max}) and the fluorescence peak (emission λ_{max}) and was used to calculate $E_{1/2}(P^+/*P)$ ($=E_{1/2}(P^+/P) - E_{0-0}$) and $E_{1/2>(*P/P^+)$ ($=E_{0-0} + E_{1/2}(P/P^+)$). ^cIn CH₂Cl₂ solution. ^dCalculated according to the cyclic voltammetry data reported by Weaver et. al. ^ePrompt fluorescence.

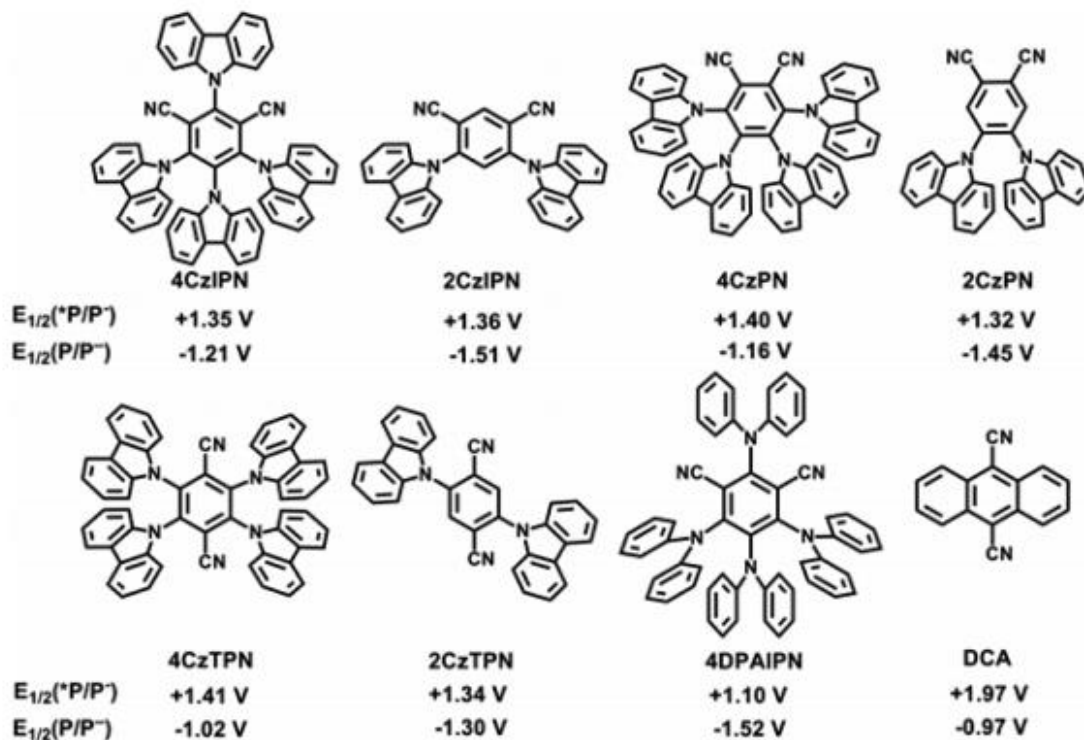


Figure 1-5. The structure of all photocatalysts.

1.4 General Goal of This Work

As previously discussed, carboxylic acids are inexpensive, bench stable, and readily available feedstocks. Decarboxylative elimination pathway is an interesting synthetic approach to utilize the carboxylic acid substrates, which has not been realized via mild photochemical pathways. The goal of this work is to build a new method for the synthesis of olefin by decarboxylative elimination from carboxylic acids via an efficient, economical, environmentally friendly photoredox/cobalt dual catalysis.

Chapter 2 Design Plan, Optimization, and Substrate Scope of Decarboxylative Elimination for Synthesis of Olefins

2.1 Design Plan

Inspired by the work of Macmillan and Sorensen, we envisioned it is possible to utilize a photoredox/cobalt dual catalytic system for synthesizing olefins from carboxylic acids. Upon visible light excitation, the SET process can proceed between the excited state of photocatalyst and the carboxylic acid. First, decarboxylation leads to the formation of an alkyl radical and the excited state of photocatalyst is reductively quenched. The Co(III)-complex can accept one electron from the photocatalyst radical anion to produce Co(II)-complex and regenerate the photocatalyst. The β C–H bond of the alkyl radical can be activated via the HAT pathway by Co(II) to generate the olefin product. Following this HAT process, one proton and one hydride from the Co(III)-H intermediate are combined to release a H₂ molecule and complete the turnover of the system (Figure 2-1).

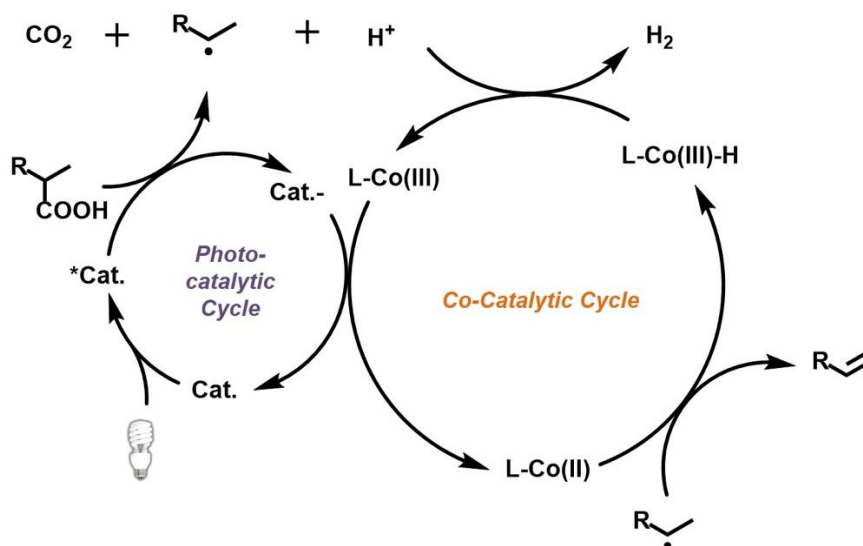


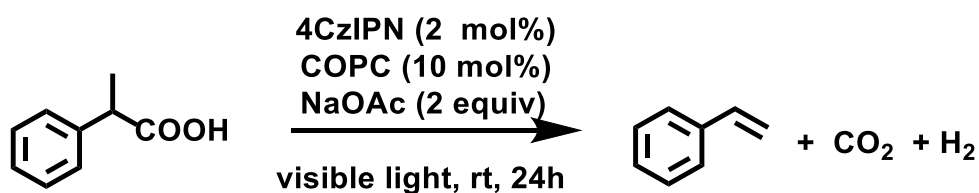
Figure 2-1 Proposed reaction mechanism.

2.2 Results and Discussion

2.2.1 Initial Investigation with 2-Phenylpropionic Acid

We first used 2-phenylpropionic acid as the substrate to test the proposed dual photoredox/cobalt HAT catalytic system. Several common organic solvents were used for screening (Table 2-1). 4CzIPN (2 mol%) was chosen as the photocatalyst, COPC (10 mol%) was used as the HAT catalyst, and sodium acetate was as the base in the decarboxylation process. The reaction was conducted at 0.05 mmol scale in 1 mL solvent and irradiated with compact fluorescent lamp (CFL) for 24 h at room temperature under argon.

The results showed that only DMSO or DMF can produce the desired olefin products in 33% and 15% yield, respectively. One possibility is that the reaction needs solvents with high polarity to stabilize the ionic species such as the conjugated base. It is not clear that MeCN is a poor solvent for this reaction, but it is likely due to the poor solubility of sodium acetate.

Table 2-1. Initial Study with 2-Phenylpropionic Acid^[a]

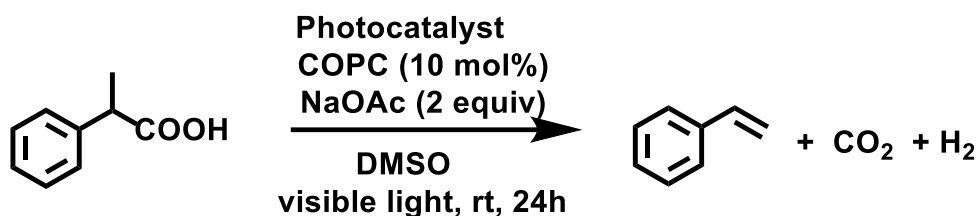
Solvents	Yield ^[b]
DMSO	33%
DMF	15%
Acetone	0%
DMAc	Trace
MeOH	0%
CH ₂ Cl ₂	0%
THF	0%
MeCN	0%
Toluene	0%

[a] Reaction conditions: 2-phenylpropionic acid (0.05 mmol), 4CzIPN (2 mol%), COPC (10 mol%), sodium acetate (0.1 mmol), CFL, 24 h at room temperature under Ar atmosphere. **[b]** Determined by NMR with dibromomethane as the internal reference.

2.2.2 Optimization of Photocatalysts

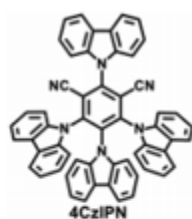
We next optimized the reaction conditions by screening different photocatalysts.

Four different photocatalysts were tested based on their photoredox potentials (Table 2-2).

Table 2-2. Optimization of Photocatalyst.^[a]

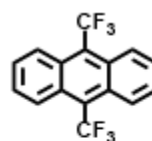
Photocatalyst	Yield ^[b]
4CzIPN	33%
DCA	trace
CF ₃ -Anthracene	0%
Mes-Acr-Ph	0%

[a] Reaction conditions: 2-phenylpropionic acid (0.05 mmol), COPC (10 mol%), different photocatalysts, sodium acetate (0.1 mmol) in 1 mL DMSO, irradiation with CFL light bulb for 24 h at room temperature under argon. **[b]** Determined by NMR with dibromomethane as the internal reference.



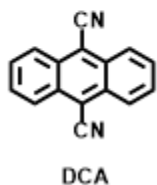
$$E_{1/2}(*P/P^-): +1.35V$$

$$E_{1/2}(P^-/P): -1.21V$$



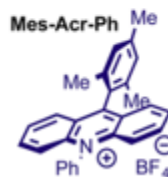
$$E_{1/2}(*P/P^-): +1.7V$$

$$E_{1/2}(P^-/P): -1.3V$$



$$E_{1/2}(*P/P^-): +1.97V$$

$$E_{1/2}(P^-/P): -0.97V$$



$$E_{1/2}(*P/P^-): +2.06V$$

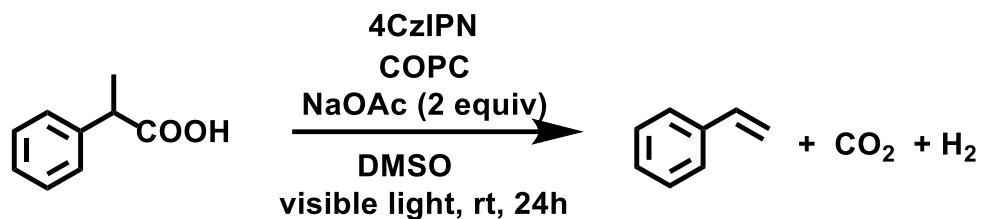
$$E_{1/2}(P^-/P): -0.57V$$

Only 4CzIPN produced desired product with a 33% yield. The low reduction potential ($-0.57V$) of Mes-Acr-Ph makes the reduction of Co(III) ($-0.68V$) an unlikely process. On the other hand, the high reduction potential ($-1.3V$) of CF₃-anthracene may

compete with the radical intermediate generated by the substrate to donate the electron to the Co(II) (-1.13V) complex and therefore inhibit the formation of the product. DCA only gave a trace amount of product, likely due to its poor photostability under the reaction condition.

2.2.3 Optimization of Catalyst Loading

We next optimized the loading of photocatalyst 4CzIPN and cobalt catalyst COPC. The amount of both 4CzIPN and COPC significantly affect the product yield and the best condition was 5 mol% 4CzIPN and 20 mol% COPC, which gave the highest yield (51%) of the alkene product. The high loadings of both catalysts suggest that a slow reaction rate especially for the elimination. Increasing the loading of COPC can accelerate the elimination process and give a higher reaction yield (up to 10 times increase). However, we did not test a higher loading of COPC than 20% due to the expense factor. We instead chose to screen for other conditions (*vide infra*).

Table 2-3. Optimization of Loadings of Photocatalyst and Cobalt Catalyst.^[a]

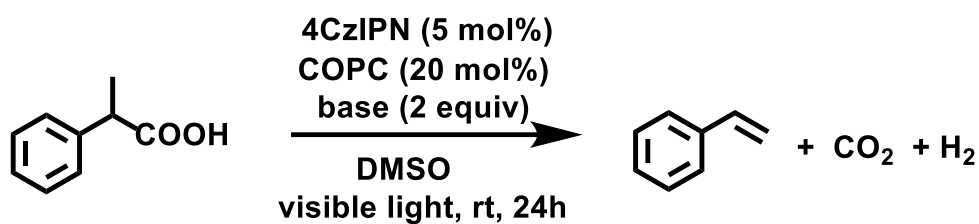
4CzIPN loading (mol %)	COPC loading (mol %)	Yield ^[b]
1	2	5%
1	5	13%
1	10	16%
1	20	39%
2	2	5%
2	5	16%
2	10	32%
2	20	43%
5	2	5%
5	5	22%
5	10	37%
5	20	51%

[a] Reaction conditions: 2-phenylpropionic acid (0.05 mmol), 4CzIPN and COPC with different catalyst loadings, sodium acetate (0.1 mmol) in 1 mL DMSO, irradiation with CFL light bulb for 24 h at room temperature under argon. **[b]** Determined by NMR with dibromomethane as the internal reference.

2.2.4 Optimization of Base

The strength of the basicity strongly affects the decarboxylation step. It should be strong enough to deprotonate the carboxylic acid, which allows for the oxidative decarboxylation. On the other hand, the base should not be too strong so that it can transfer the proton to the Co(III)-H complex for the hydrogen evolution step. We screened seven common inorganic bases to optimize the reaction. There was no clear relationship between the yield and the basicity. Weak base NaHCO_3 only gave a trace amount of product. Carbonates such as Na_2CO_3 , K_2CO_3 , and Cs_2CO_3 gave 46%, 53%, and 18% yield, respectively. Acetate bases performed generally better than carbonates, and CsOAc gave the best yield of 91% among all tested reactions. When a stronger base NaOH was used, the yield decreased to 33%.

Another factor which may cause the different performance for different bases is solubility. All inorganic bases tested here are only partially soluble in DMSO. The possible change of the solubility during the reaction could also affect the final yield.

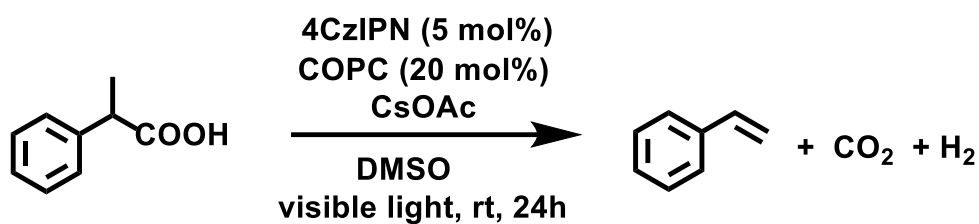
Table 2-4. Optimization of Inorganic Base.^[a]

Base	Yield ^[b]
Na ₂ CO ₃	46%
NaOAc	50%
Cs ₂ CO ₃	18%
CsOAc	91%
K ₂ CO ₃	53%
NaOH	33%
NaHCO ₃	trace

[a] Reaction conditions: 2-phenylpropionic acid (0.05 mmol), 4CzIPN (5 mol%), COPC (20 mol%), 2 equivalent different bases in 1 mL DMSO, irradiation with CFL for 24 h at room temperature under argon. **[b]** Determined by NMR with dibromomethane as the internal reference.

2.2.5 Optimization of Amount of Base

The amount of CsOAc was further screened. Generally, a higher loading results in a higher yield. The best yield obtained was 91% when using 2 equivalent CsOAc was used. However, when amount of CsOAc was increased to 4 equivalents, the yield significantly decreased to 35%.

Table 2-5 Optimization of Amount of Base.^[a]

Base amount	Yield ^[b]
0.2 equiv	26%
0.4 equiv	35%
0.6 equiv	72%
0.8 equiv	73%
1 equiv	76%
2 equiv	91%
4 equiv	35%

[a] Reaction conditions: 2-phenylpropionic acid (0.05 mmol), 4CzIPN (5 mol%), COPC (20 mol%), CsOAc with different amount in 1 mL DMSO, irradiation with CFL for 24 h at room temperature under argon. **[b]** All the yields are determined by NMR with dibromomethane as the internal reference.

2.2.6 Summary of Reaction Optimization

After screening of photocatalyst, Co catalyst, and base, the highest yield of 91% was obtained when 5 mol% 4CzIPN, 20 mol% COPC, and 2 equivalent of CsOAc were used. First, the reaction is highly sensitive to the photoredox potentials of the photocatalyst. If the reduction potential is too low (e.g. Mes-Acr-Ph), the photocatalyst will not be able to reduce Co(III) to Co(II) and therefore the catalytic cycle does not proceed. If the

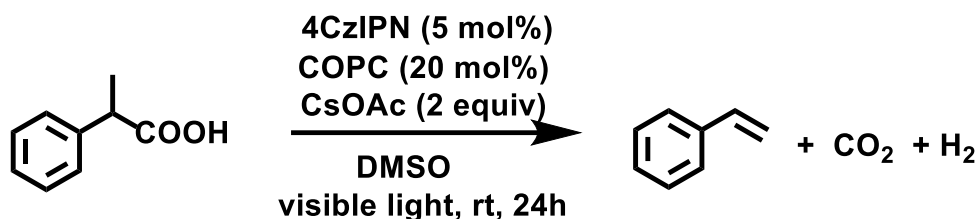
reduction potential is too high (e.g. CF₃-anthracene), the Co(II) complex will be reduced by the photocatalyst directly instead of by the substrate, which inhibits the elimination process.

The basicity of the reaction environment is also important since there are two proton transfer processes. First, the carboxylic acid needs to be deprotonated for the subsequent oxidization. If the base is not strong enough (e.g. NaHCO₃), the deprotonation will not proceed and thus inhibits the overall reaction. If the base is too strong (e.g. NaOH), the second proton transfer step during which the Co(III)-H complex produces the H₂ molecule is hindered since the proton prefers to bind with the base.

Since the basicity is an important factor to the reaction, the solvent choice is also limited. Different substrates have different pK_a values in different solvents and different bases have different solubility. Most solvents tested did not produce the desired olefin product. DMSO, which is an aprotic polar solvent, was finally chosen as the reaction solvent according to the optimization.

2.2.7 Control Experiment

Control experiments were conducted to support the proposed reaction mechanism. We removed each component in the reaction as the negative control to see if it is necessary in the reaction. The results showed the photocatalyst 4CzIPN, cobalt catalyst COPC, base, and light are all essential for this transformation (Table 2-6).

Table 2-6 Control experiments.^[a]

Conditions	Yield ^[b]
Standard Condition	91%
Without 4CzIPN	0%
Without COPC	0%
Without base	0%
Without light	0%

[a] Reaction conditions: 2-phenylpropionic acid (0.05 mmol), 4CzIPN (5 mol%), COPC (20 mol%), CsOAc (0.1 mmol) in 1 mL DMSO, irradiation with CFL for 24 h at room temperature under argon. **[b]** All the yields are determined by NMR with dibromomethane as the internal reference.

2.2.7 UV-vis Absorption Spectra

It is observed that the color of the reaction mixture changes from light brown to light violet after 24 hours. Upon the exposure to air, the color turned back to brown (Figure 2-1). The UV-vis absorption spectra of the reaction mixture were collected after 0 h, 20 h and 40 h (Figure 2-2a). A new peak around 650 nm appeared after reaction. It was previously reported that the absorption peak of Co(I)-complex is around 560 nm.²⁴ Thus the peak at 650 nm was attributed to the presence of the Co(I) complex with glyoxime as the ligand, which appears as the violet color. Upon exposure to air, the Co(I) complex can be oxidized immediately by oxygen and changes into the brown colored Co(III) complex.

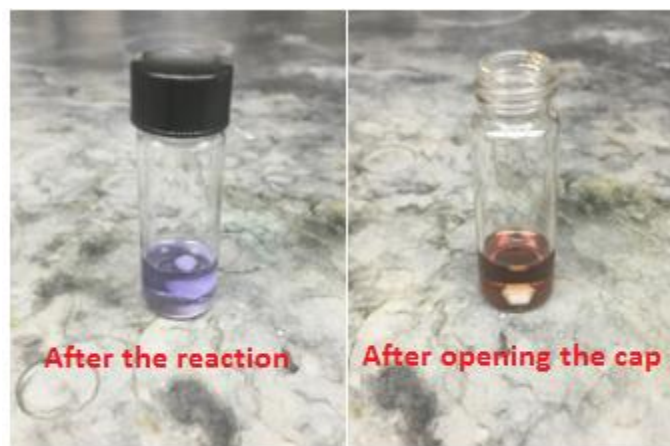


Figure 2-1 Color change after the reaction is finished and after exposure to air.

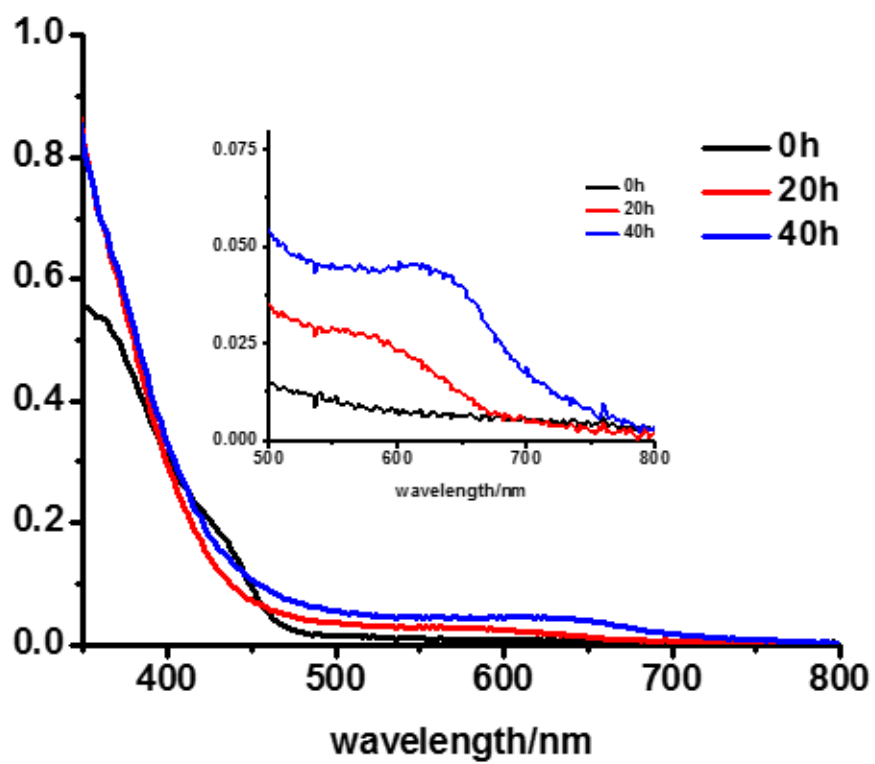
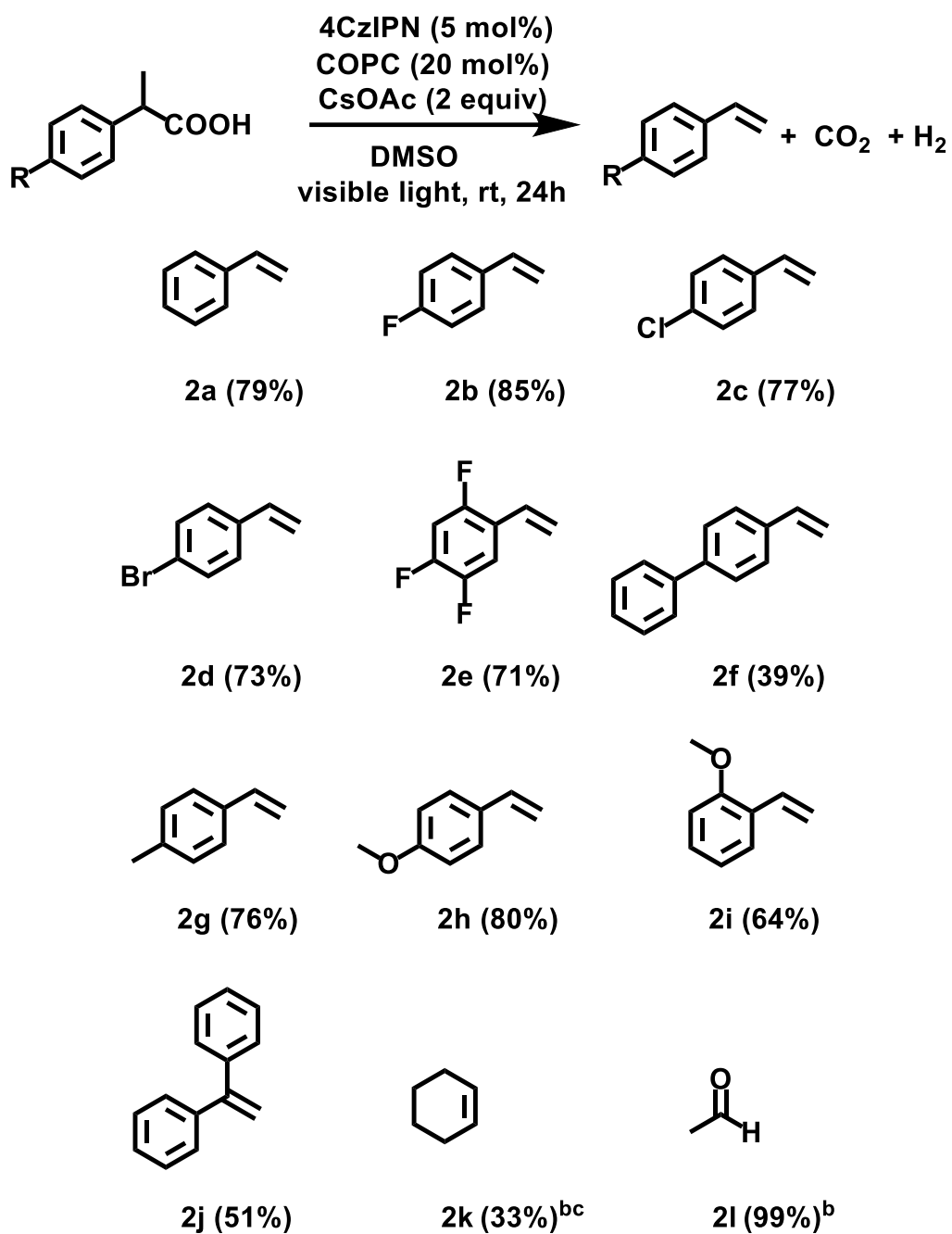


Figure 2-2. UV-vis absorption spectra of the reaction mixture after 0 h, 20 h and 40 h. The reaction was diluted to 0.005mol/L.2.2.8 Substrate Scope

The substrate scope was investigated by using 4CzIPN as a photocatalyst with COPC as a hydrogen evolution catalyst under the optimized reaction conditions (Table 2-7). Most of the substrates were derivatives of 2-phenylpropionic acid. Similar to 2-phenylpropionic acid, which produced 91% yield (79% isolated yield) olefin product, substrates with electron withdrawing groups (1b-1d) performed good to excellent yield.

Table 2-7. Substrate scope.^[a]

[a] Reaction conditions: 2-phenylpropionic acid derivatives (0.05 mmol), 4CzIPN (5 mol%), COPC (20 mol%), cesium acetate (0.1 mmol) in 1 mL DMSO, irradiation with CFL for 24 h at room temperature under argon. The yields shown are isolated yields. [b] yield determined from NMR. [c] d₆-DMSO was used as the solvent.

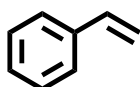
2.3 Experimental

2.3.1 General reagents, instrumentation, and procedures

All the feedstocks for syntheses of substrates and catalysts were purchased from commercial sources and used without further purification. ^1H NMR spectroscopy was performed on a Bruker FT-NMR spectrometer (300 MHz). All the products are known and compared with literature NMR.

General procedure for the catalytic reaction

The catalytic reaction was set up in a 3 mL vial, a mixture of 2-phenylpropionic acid (6.8 μL , 0.05 mmol), 4CzIPN (2 mg, 5 mol%), COPC (3.4 mg, 20 mol%), CsOAc (19.2 mg, 0.1 mmol) was dissolved in 1 mL DMSO. After degassing for 10 mins with Ar, the vial was set beside a CFL under a fan. The reaction was stirred for 24 h. Then the mixture was extracted with EtOAc for three times. The organic layer was collected and washed with brine, dried with anhydrous magnesium sulfate and concentrated in vacuo. Silica gel column chromatography (40:1-20:1) was used to purify the product.

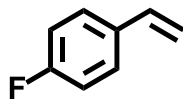


Styrene (2a)

Styrene was isolated as colorless liquid. Yield: 79%.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.32 (m, 5H), 6.78 (dd, $J = 8, 14$ Hz, 1H), 5.80 (d, $J = 14$ Hz, 1H), 5.31 (d, $J = 8$ Hz, 1H).

Literature²⁹: ^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.41-7.25 (m, 5H), 6.72 (dd, $J = 11, 17$ Hz, 1H), 5.76 (d, $J = 17$ Hz, 1H), 5.25 (d, $J = 11$ Hz, 1H).

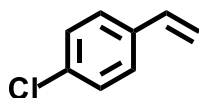


4-Fluorostyrene (2b)

4-Fluorostyrene was isolated as colorless liquid. Yield: 85%.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.41 (m, 2H), 7.05 (m, 2H), 6.72 (dd, $J = 8, 14$ Hz, 1H), 5.71 (d, $J = 14$ Hz, 1H), 5.26(d, $J = 8$ Hz, 1H).

Literature³⁰: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 5.21 (d, $J = 10.93$ Hz, 1H), 5.65 (d, $J = 17.54$ Hz, 1H), 6.66 (dd, $J = 10.88, 17.57$ Hz, 1H), 7.00 (t, $J = 8.66$ Hz, 2H), 7.36 (m, 2H).

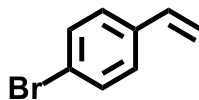


4-Chlorostyrene (2c)

4-Chlorostyrene was isolated as colorless liquid. Yield: 77%.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.34 (m, 4H), 6.70 (dd, $J = 8, 14$ Hz, 1H), 5.69 (d, $J = 14$ Hz, 1H), 5.31(d, $J = 8$ Hz, 1H).

Literature³⁰: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 5.24 (d, $J = 10.84$ Hz, 1H), 5.70 (d, $J = 17.59$ Hz, 1H), 6.65 (dd, $J = 10.89, 17.57$ Hz, 1H), 7.27 (m, 4H).

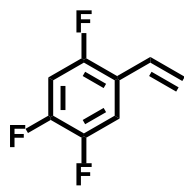


4-Bromostyrene (2d)

4-Bromostyrene was isolated as colorless liquid. Yield: 73%.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.48 (m, 2H), 7.31 (m, 2H), 6.69 (dd, $J = 8, 14$ Hz, 1H), 5.77 (d, $J = 14$ Hz, 1H), 5.31(d, $J = 8$ Hz, 1H).

Literature³¹: $^1\text{H NMR}$ (400 MHz, CDCl_3): 7.49 (d, $J = 8$ Hz, 2H), 7.31 (d, $J = 8$ Hz, 2H), 6.69 (dd, $J = 18, 11$ Hz, 1H), 5.78 (d, $J = 18$ Hz, 1H), 5.32 (d, $J = 11$ Hz, 1H).

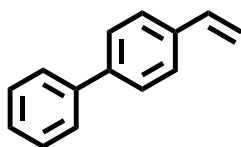


2,3,5-Tetrafluorostyrene (2e)

2,3,5-Tetrafluorostyrene was isolated as colorless liquid. Yield: 71%.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.66 (m, 1H), 7.42 (m, 1H), 6.72 (dd, $J = 8, 14$ Hz, 1H), 5.71 (d, $J = 14$ Hz, 1H), 5.26 (d, $J = 8$ Hz, 1H).

Literature³²: ^1H NMR (400 MHz, CDCl_3): δ 7.26 (m, 1H), 6.89 (td, $J = 10.0, 6.4$ Hz, 1H), 6.75 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.72 (d, $J = 17.6$ Hz, 1H), 5.39 (d, $J = 11.2$ Hz, 1H).

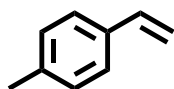


4-Phenylstyrene (2f)

4-Phenylstyrene was isolated as colorless liquid. Yield: 39%.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.68 (m, 4H), 7.42 (m, 5H), 6.68 (dd, $J = 8, 14$ Hz, 1H), 5.78 (d, $J = 14$ Hz, 1H), 5.31 (d, $J = 8$ Hz, 1H).

Literature³³: ^1H NMR (CDCl_3 , 500 MHz) δ 7.31-7.60 (m, 9H), 6.75 (dd, 1H, $J = 17.6$ Hz, 10.9 Hz), 5.78 (d, 1H, $J = 17.6$ Hz), 5.26 (d, 1H, $J = 10.9$ Hz).

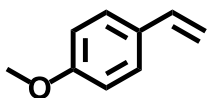


4-Methylstyrene (2g)

4-Methylstyrene was isolated as colorless liquid. Yield: 76%.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.36 (m, 2H), 7.19 (m, 2H), 6.75 (dd, $J = 8, 14$ Hz, 1H), 5.75 (d, $J = 14$ Hz, 1H), 5.24 (d, $J = 8$ Hz, 1H), 2.40 (s, 3H).

Literature³⁴: $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.35 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.0$ Hz, 2H), 6.73 (dd, $J = 17.6$ Hz; 10.9 Hz, 1H), 5.73 (dd, $J = 17.6$ Hz; 0.9 Hz, 1H), 5.22 (dd, $J = 10.9$ Hz; 0.9 Hz, 1H), 3.37 (s, 3H).

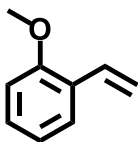


4-Methoxystyrene (2h)

4-Methoxystyrene was isolated as colorless liquid. Yield: 80%.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.41 (m, 2H), 6.91 (m, 2H), 6.72 (dd, $J = 8, 14$ Hz, 1H), 5.66 (d, $J = 14$ Hz, 1H), 5.18 (d, $J = 8$ Hz, 1H), 3.85 (s, 3H).

Literature: $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 3.82 (s, 3H), 5.16 (d, $J = 10.90$ Hz, 1H), 5.65 (d, $J = 17.59$ Hz, 1H), 6.70 (dd, $J = 10.65, 17.65$ Hz, 1H), 6.89 (d, $J = 8.56$ Hz, 2H), 7.38 (d, $J = 8.62$ Hz, 2H).

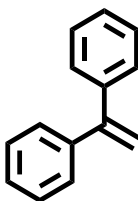


2-Methoxystyrene (2i)

2-Methoxystyrene was isolated as colorless liquid. Yield: 64%.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.51 (m, 1H), 7.30 (m, 1H), 7.08 (dd, $J = 8, 14$ Hz, 1H), 6.93 (m, 2H), 5.79 (d, $J = 14$ Hz, 1H), 5.31 (d, $J = 8$ Hz, 1H), 3.89 (s, 3H).

Literature³³: $^1\text{H NMR}$ (CDCl_3 , 500 MHz) δ 7.46 (d, 1H, $J = 7.5$ Hz), 7.21 (d, 1H, $J = 7.4$ Hz), 6.84-7.05 (m, 3H), 5.73 (d, 1H, $J = 17.7$ Hz), 5.25 (d, 1H, $J = 11.1$ Hz), 3.82 (s, 3H).



1,1-Diphenylethylene (2j)

1,1-Diphenylethylene was isolated as colorless liquid. Yield: 51%.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.39 (m, 10H), 5.52(s, 2H).

Literature³⁵: $^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ 7.37-7.32 (m, 10 H), 5.46 (s, 2 H).

2.3.2 Synthesis of Substrates

The 2-phenylpropionic substrates were synthesized according to the previous reported method.³⁶ The general procedure was shown below (Figure 2-3).

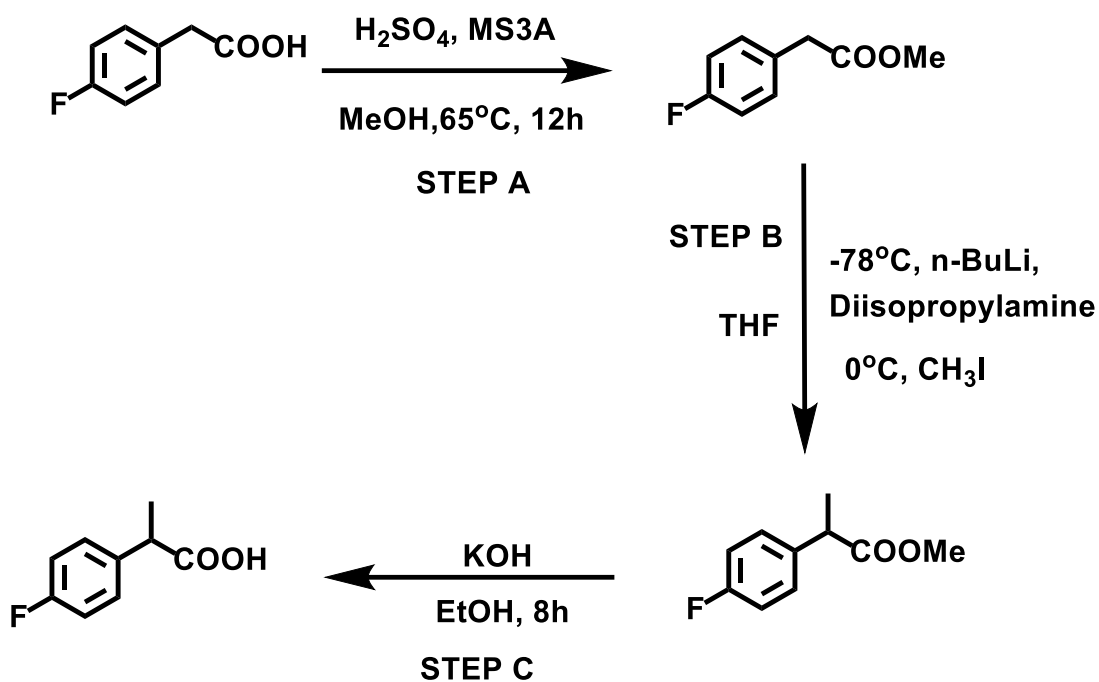


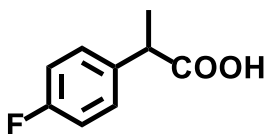
Figure 2-3. General synthetic procedure of 2-phenylpropionic substrates.

STEP A: 4-Fluorophenylacetic acid (8.3 mmol) was dissolved in MeOH (5 mL), concentrated sulfuric acid (catalytic amount) was added slowly to the solution. The mixture was heated under reflux (68°C) for 12 h. The mixture was then cooled down to

room temperature, neutralized by adding sodium hydrogen carbonate. Excess solvent MeOH was removed and the mixture was extracted with EtOAc for three times. The organic layer was collected and washed with brine, dried with anhydrous magnesium sulfate and concentrated in vacuo. Silica gel column chromatography (15:1) was used to purify the ester products.

STEP B: LDA solution was freshly made by slowly adding *n*-butyllithium (1.6 M in hexane, 2.3 mL) to diisopropylamine (0.5 mL, 3.6 mmol) solution in THF (4 mL) at -78°C under argon. The mixture was stirred for 30 min. Then a solution of methyl 4-fluorophenylacetate (3.0 mmol) in THF (5 mL) was added dropwise, and the mixture was stirred for 20 min before warming up to 0°C . Methyl iodide (0.3 mL, 4.8 mmol) was added to the mixture and stirred for 30 min. Hydrochloric acid (2.0 M) was used to acidify the mixture. Then the mixture was extracted with EtOAc for three times. The organic layer was collected and washed with brine, dried with anhydrous magnesium sulfate and concentrated in vacuo. Silica gel column chromatography (40:1-20:1) was used to purify the methylation products.

STEP C: A solution of methyl 2-(4-fluorophenyl) propanoate (1.4 mmol) in EtOH (3 mL) was added to a potassium hydroxide solution (0.5 g, 9.0 mmol in 3 mL water) at 0°C . The mixture was stirred for 8 h at the same temperature. Hydrochloric acid (2 M) was used to neutralize the mixture. Then the mixture was extracted with EtOAc for three times. The organic layer was collected and washed with brine, dried with anhydrous magnesium sulfate and concentrated in vacuo to get 2-phenylpropionic acid product.

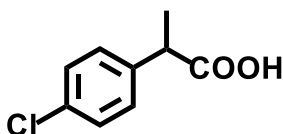


2-(4-fluorophenyl) propionic acid (1b)

Following the general procedure, 2-(4-fluorophenyl) propionic acid was isolated as white solid. Yield: 54%. MP: 168.16°C.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.32 (m, 2H), 7.06 (m, 2H), 3.74 (q, $J = 6$ Hz, 1H), 1.52 (d, $J = 6$ Hz, 3H).

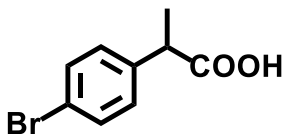
Literature³⁷: ^1H NMR (400 MHz, CDCl_3) δ 12.2-11.4 (br, 1 H), 7.31-7.24 (m, 2 H), 7.04-6.97 (m, 2 H), 3.72 (q, $J = 7.3$ Hz, 1 H), 1.49 (d, $J = 7.3$ Hz, 3 H).

**2-(4-chlorophenyl) propionic acid (1c)**

Following the general procedure, 2-(4-chlorophenyl) propionic acid was isolated as white solid. Yield: 75%. MP: 58-58.5°C.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.30 (m, 4H), 3.74 (q, $J = 6$ Hz, 1H), 1.52 (d, $J = 6$ Hz, 3H).

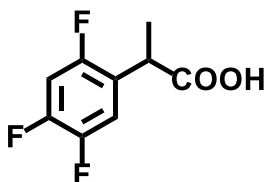
Literature³⁸: ^1H NMR (400 MHz; CDCl_3): 7.30 (2H, dt, J 8.8Hz, 2.2Hz), 7.25 (2H, dt, J 8.8Hz, 2.2Hz), 3.72 (1H, q, $J = 7.2$ Hz), 1.50 (3H, d, $J = 7.2$ Hz).

**2-(4-bromophenyl) propionic acid (1d)**

Following the general procedure, 2-(4-bromophenyl) propionic acid was isolated as white solid. Yield: 69%. MP: 72.5°C.

^1H NMR (CDCl_3 , 300 MHz, ppm): δ 7.48 (m, 2H), 7.22 (m, 2H), 3.72 (q, $J = 6$ Hz, 1H), 1.53 (d, $J = 6$ Hz, 3H).

Literature³⁸: ¹H NMR (CD₃COCD₃) δ 7.52 (2H, d), 7.35 (2H, d), 3.80 (1H, q), 1.45 (3H, d).

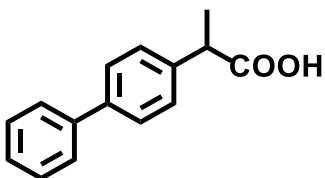


2-(2,3,5-trifluorophenyl) propionic acid (1e)

Following the general procedure, 2-(2,3,5-trifluorophenyl) propionic acid was isolated as white solid. Yield: 72%. MP: 121°C.

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.20 (m, 1H), 6.97 (m, 1H), 4.03 (q, J = 6 Hz, 1H), 1.54 (d, J = 6 Hz, 3H).

Literature³⁷: ¹H NMR (CDCl₃, 400 MHz, ppm): δ 7.22 (m, 1H), 7.01 (m, 1H), 4.05 (q, J = 9.2 Hz, 1H), 1.61 (d, J = 9.2 Hz, 3H).

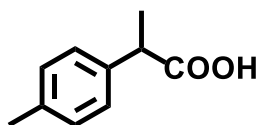


2-(4-phenylphenyl) propionic acid (1f)

Following the general procedure, 2-(4-phenylphenyl) propionic acid was isolated as white solid. Yield: 70%. MP: 168°C.

¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.60 (m, 4H), 7.44 (m, 5H), 3.82 (q J = 6 Hz, 1H), 1.59 (d, J = 6 Hz, 3H).

Literature³⁷: ¹H NMR (CDCl₃, 300 MHz, ppm): δ 7.81-7.35 (m, 5H), 3.80 (q J = 7 Hz, 1H), 1.61 (d, J = 7 Hz, 3H).

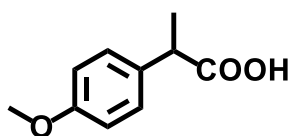


2-(4-methylphenyl) propionic acid (1g)

Following the general procedure, 2-(4-methylphenyl) propionic acid was isolated as white solid. Yield: 92%. MP:37-41°C.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.26 (m, 2H), 7.19 (m, 2H), 3.75 (q, $J = 6$ Hz, 1H), 2.38 (s, 3H), 1.55 (d, $J = 6$ Hz, 3H).

Literature³⁹: $^1\text{H NMR}$ (CDCl_3) δ 7.25–7.10 (m, 4H), 3.7 (q, 1H, $J=7.0$ Hz), 2.35 (s, 3H), 1.50 (d, 3H, $J=7.0$ Hz).

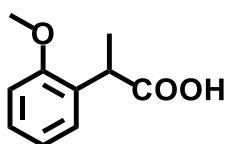


2-(4-methoxyphenyl) propionic acid (1h)

Following the general procedure, 2-(4-methoxyphenyl) propionic acid was isolated as white solid. Yield: 75%. MP: 35°C.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.29 (m, 2H), 6.91 (m, 2H), 3.88 (s, 3H), 3.73 (q, $J = 6$ Hz, 1H), 1.53 (d, $J = 6$ Hz, 3H).

Literature⁴⁰: $^1\text{H NMR}$ (CDCl_3): d 10.99 (br s, 1H, COOH), 7.17 (d, $J = 8.7$ Hz, 2H, Ar), 6.79 (d, $J = 8.7$ Hz, 2H, Ar), 3.72 (s, 3H, OMe), 3.61 (q, $J = 7.2$ Hz, 1H, 2-H), 1.42 (d, $J = 7.2$ Hz, 3H, 3-H).



2-(2-methoxyphenyl) propionic acid (1i)

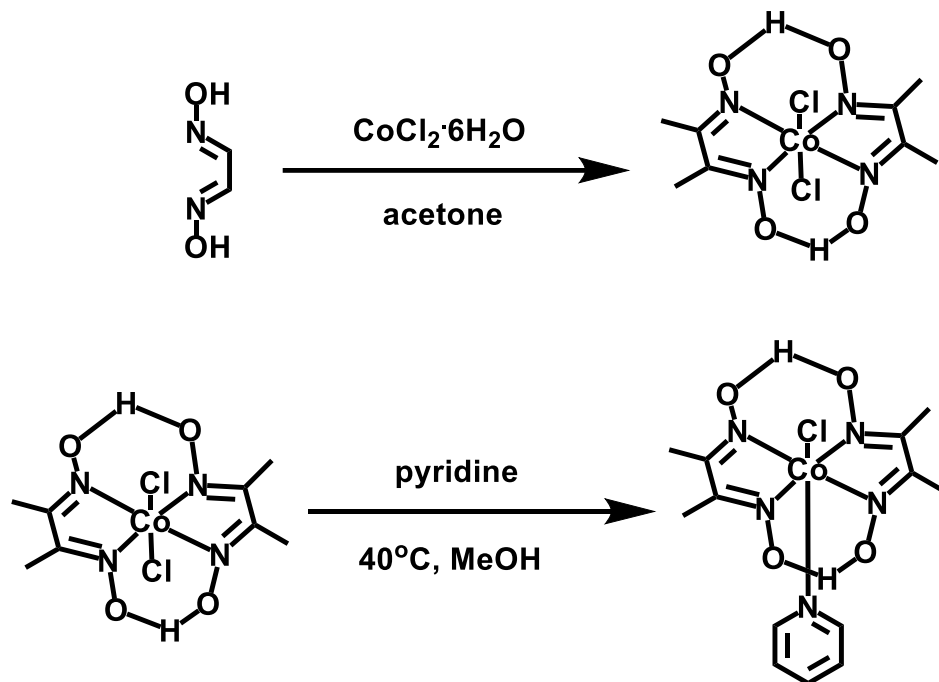
Following the general procedure, 2-(2-methoxyphenyl) propionic acid was isolated as white solid. Yield: 82%. MP: 100-101°C.

$^1\text{H NMR}$ (CDCl_3 , 300 MHz, ppm): δ 7.26 (m, 2H), 6.99 (m, 2H), 4.10 (q, $J = 6$ Hz, 1H), 3.86 (s, 3H), 1.51 (d, $J = 6$ Hz, 3H).

Literature⁴⁰: $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.31-6.92 (m, 4H), 4.11 (q, $J = 7.2$ Hz, 1H), 3.82 (s, 3H), 1.50 (d, $J = 7.2$ Hz, 3H).

2.3.3 Synthesis of COPC

The synthesis of COPC catalyst was based on the previously reported procedure.⁴¹



Synthesis of $[\text{CoCl}_2(\text{dmgH})(\text{dmgH}_2)]$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (5 g, 0.0210 mol) was dissolved in acetone (150 mL) and dimethylglyoxime (4.9 g, 0.0422 mol) was added. The reaction was stirred for 12 h. The green powder product was washed with acetone to give desired product. Yield: 5.9 g (79%).

Synthesis of COPC

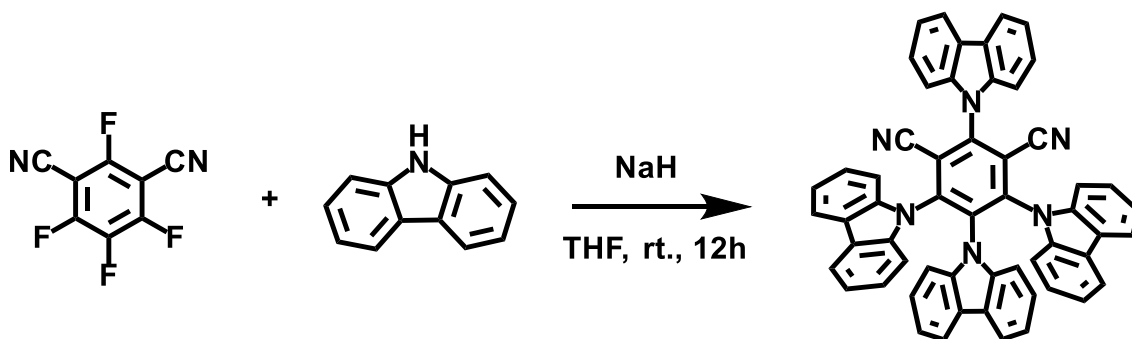
Et_3N (42 mL, 0.3 mmol) was added to the solution of $[\text{CoCl}_2(\text{dmgH})(\text{dmgH}_2)]$ (108 mg, 0.3 mmol) in MeOH (8 mL), resulting in a brown solution. Pyridine was added after five minutes and the reaction mixture was heated at 40°C for one hour. The solution was then cooled down to room temperature to precipitate the brown product, which was

filtered and washed with water (10 mL), ethanol (10 mL), and diethyl ether (10 mL) and dried under high vacuum.

^1H NMR (300 MHz, d_6 -DMSO, δ in ppm): 18.49 (br 2H), 8.03 (d, $J = 5.2$ Hz, 2H), 7.90 (m, 1H), 7.47 (m, 2H), 2.32 (s, 12H).

2.3.4 Synthesis of 4CzIPN

The synthesis of photocatalyst 4CzIPN was based on the previous work from our group.²⁸



NaH (60% in oil, 0.60 g, 15 mmol) was added slowly to a stirred solution of carbazole (1.67 g, 10.0 mmol) in dry THF (40 mL) under a nitrogen atmosphere at room temperature. After stirring for 30 min, tetrafluoroisophthalonitrile (0.40 g, 2.00 mmol) was added and stirred at room temperature for 12 h, 2 mL water was added to the reaction mixture. The resulting mixture was then concentrated under vacuo and washed by water and EtOH to yield the crude product, which was purified by recrystallization from hexane/ CH_2Cl_2 to give the final product (1.51 g, 96%).

^1H NMR (DMSO- d_6 , 400 MHz, ppm): δ 6.71 (t, $J = 8.0$ Hz, 2H), 6.82 (t, $J = 8.0$ Hz, 2H), 7.04~7.19 (m, 8H), 7.42~7.57 (m, 6H), 7.69~7.80 (m, 6H), 7.87 (d, $J = 4.0$ Hz, 4H), 8.21 (d, $J = 8.0$ Hz, 2H), 8.37 (d, $J = 8.0$ Hz, 2H).

2.3.5 NMR characterization and yield calculation

^1H NMR spectroscopy was performed on a Bruker FT-NMR spectrometer (300 MHz). For the screening process, the yields were determined directly from the NMR by calculating with internal standard. Dibromomethane was chosen as the internal standard, which has a singlet peak with chemical shift around 4.9 ppm on ^1H NMR spectrum. This peak will not be merged with the olefin products. Dibromomethane has low boiling point at 96-98 °C, which makes it easy to be removed by vacuo. The isolated yield of 2-phenylpropionic acid was similar but a little lower than the NMR yield. One possibility will be the product got lost during the work-up process since it is liquid and the boiling point is not high enough for prevention of evaporating.

2.4 Conclusion and Future Direction

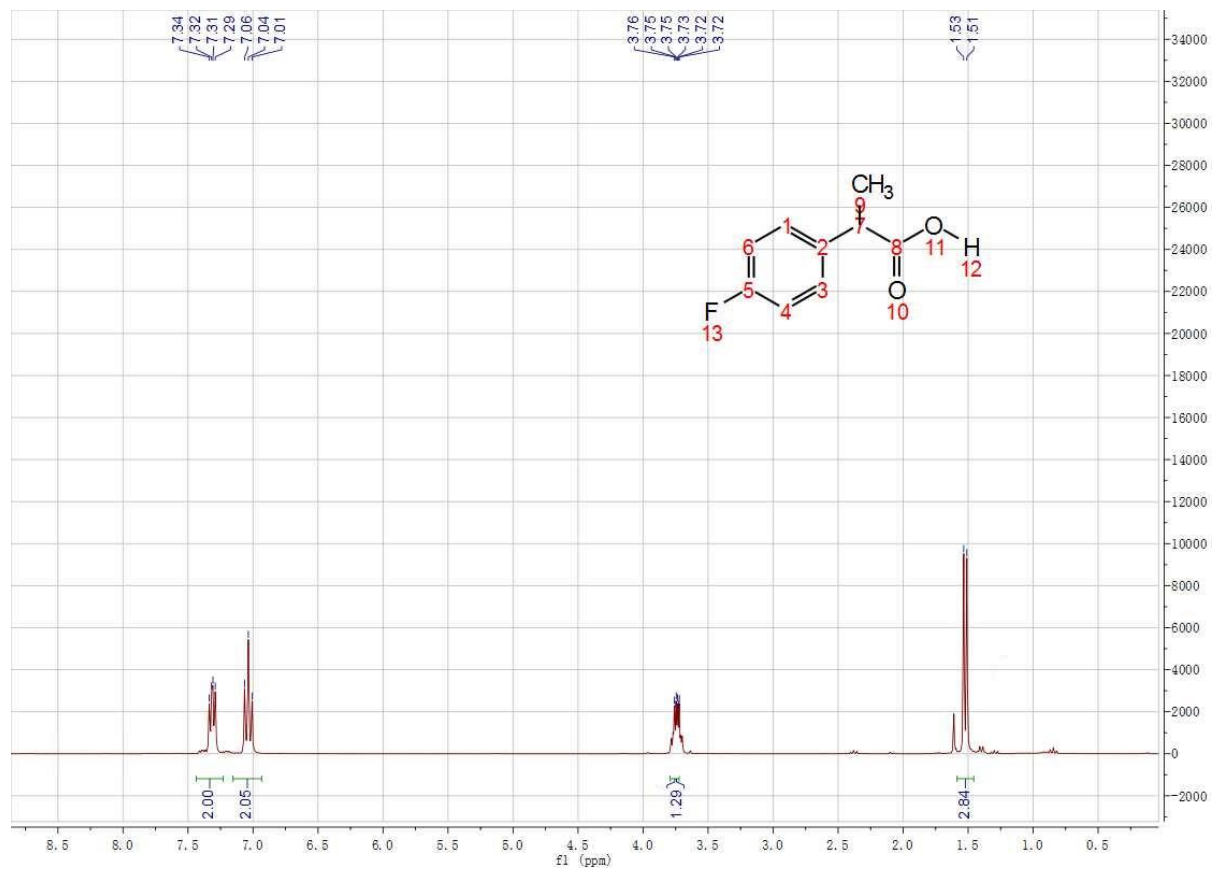
This work has focused on the design of a dual photoredox/Co metal catalytic system for the decarboxylative elimination and for synthesizing olefin products. Utilizing 4CzIPN as the phototacalyst and COPC as the hydrogen evolution catalyst, we did the optimization of the reaction conditions and got good to excellent yield for different kind of substrates. The overall reaction has been conducted under room temperature and a simple system only with some inorganic base as the additive. This work is the first example of decarboxylative elimination via photoredox catalysis method.

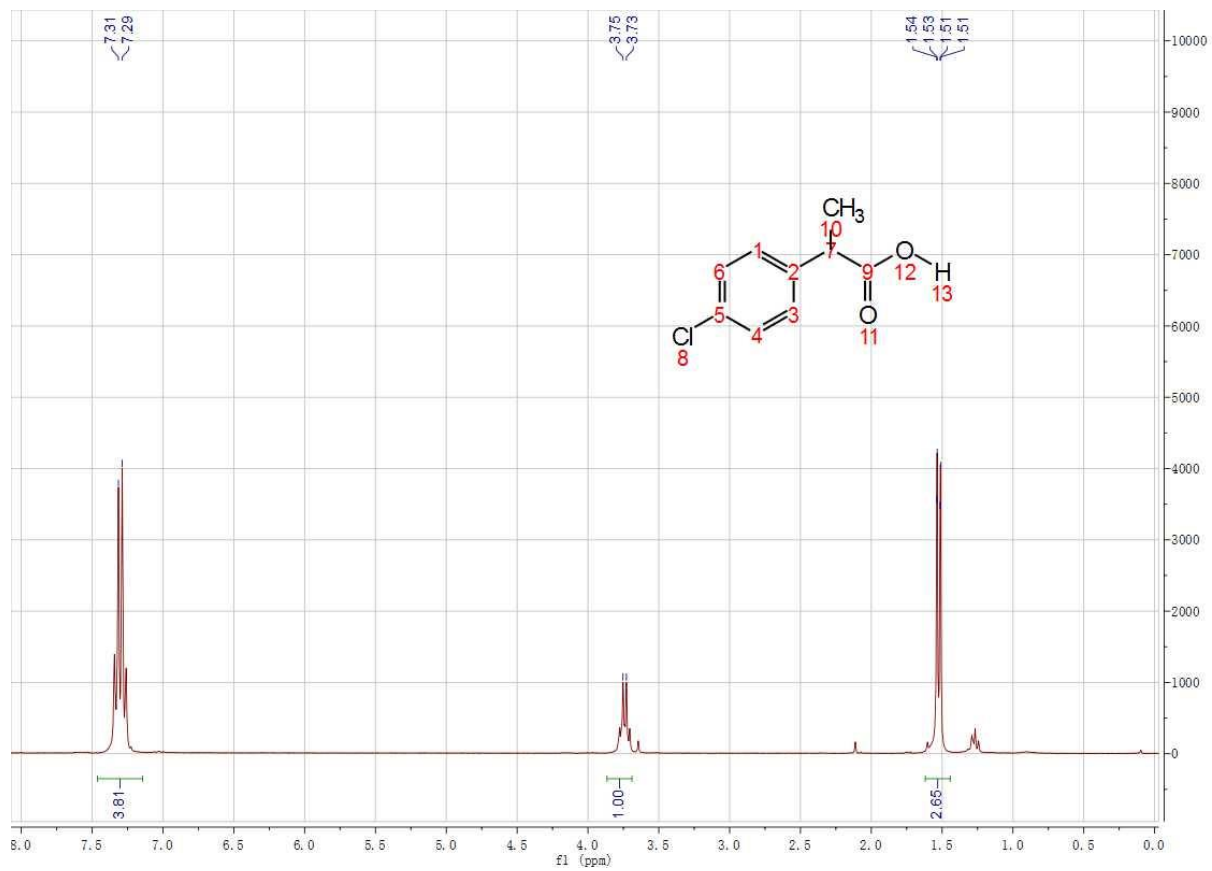
However, the substrate scope can be further explored. It should be noticed that most of the substrates are derivatives of 2-phenylpropionic acid, which could generate a stable benzyl radical as the intermediate. Changing the substrate to other fatty acid such as cyclohexyl carboxylic acid decreases the yield to about 30% and the solvent was limited to *d*₆-DMSO. We hypothesize that the unstable cyclohexane radical would undergo an HAT process and generate the hydrodecarboxylation product instead of elimination product. Further optimization can be tried to avoid the HAT process or to stabilize the alkyl radical. The goals of next step should be focused on bringing these valuable and novel transformation to saturated fatty acids, which are more abundant in nature.

Appendix

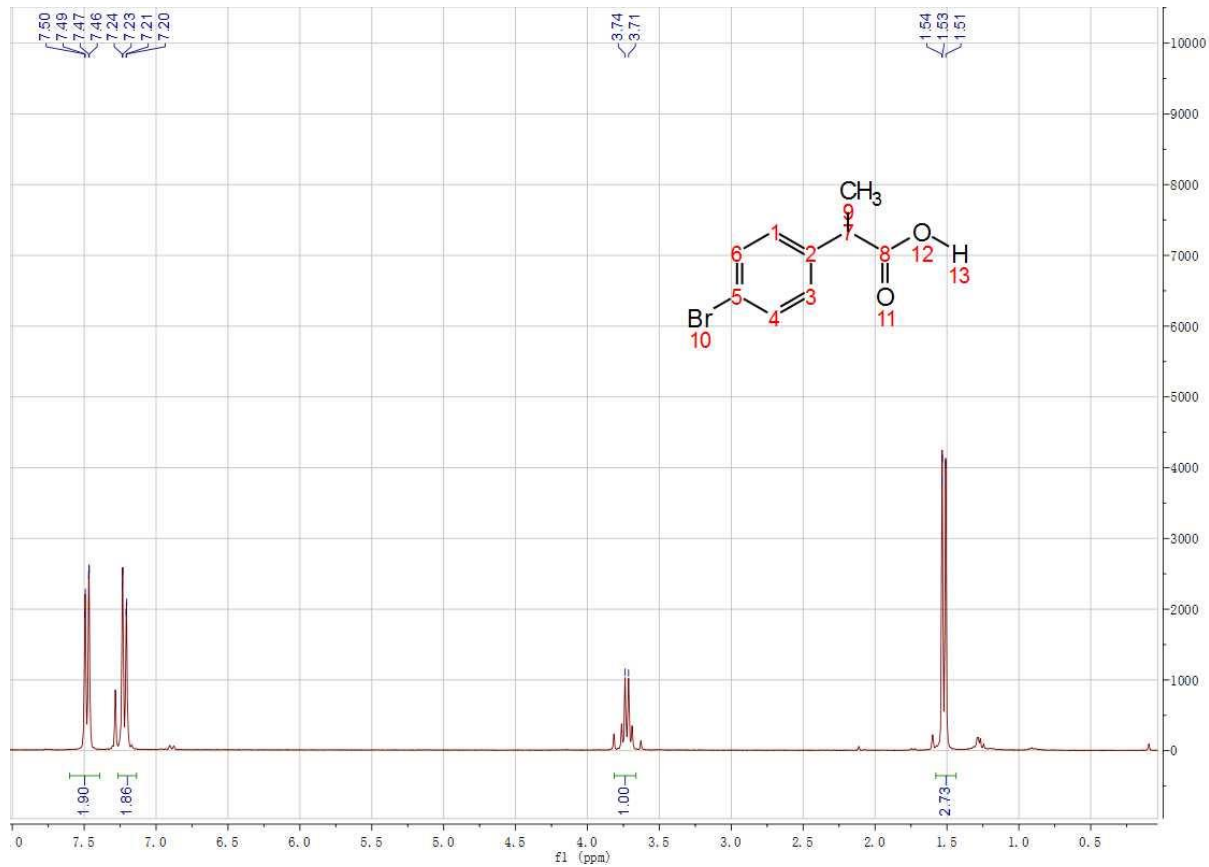
 $^1\text{H-NMR}$ spectra

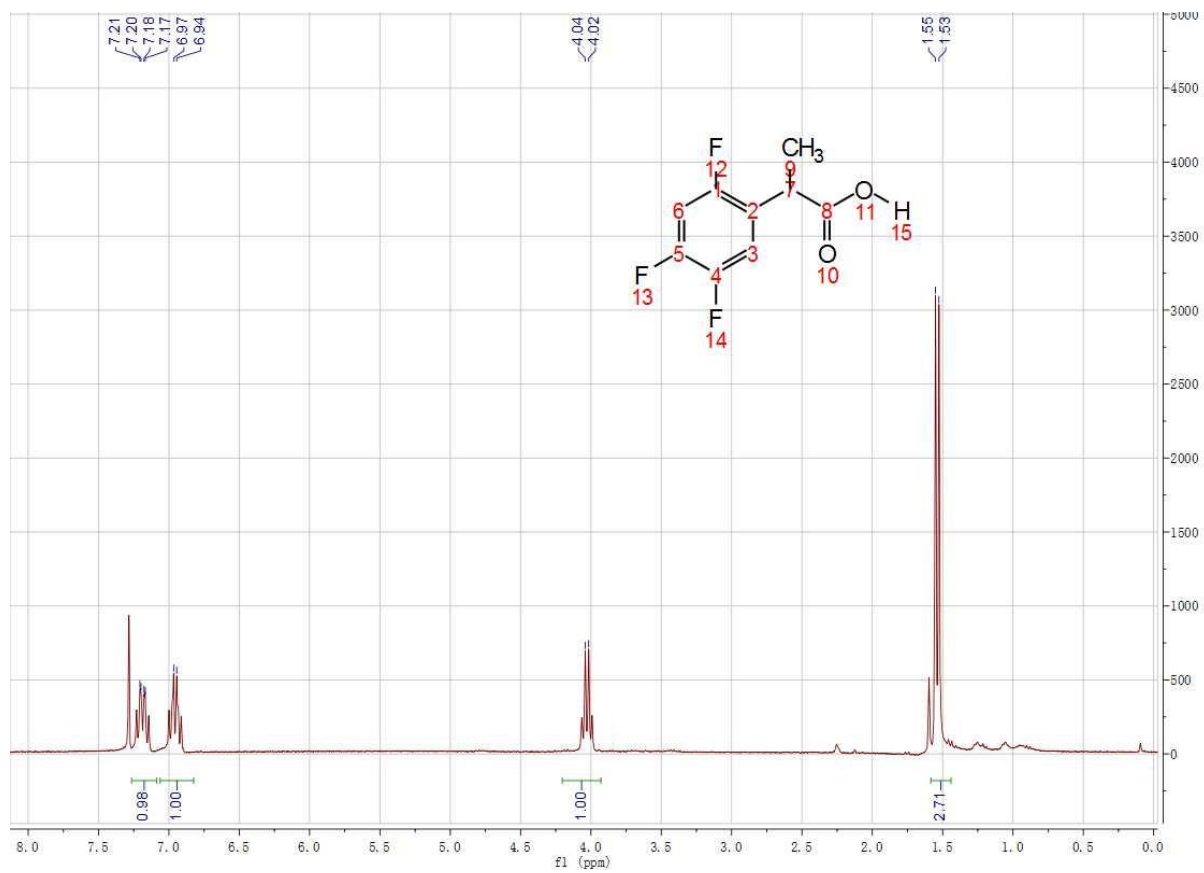
1b



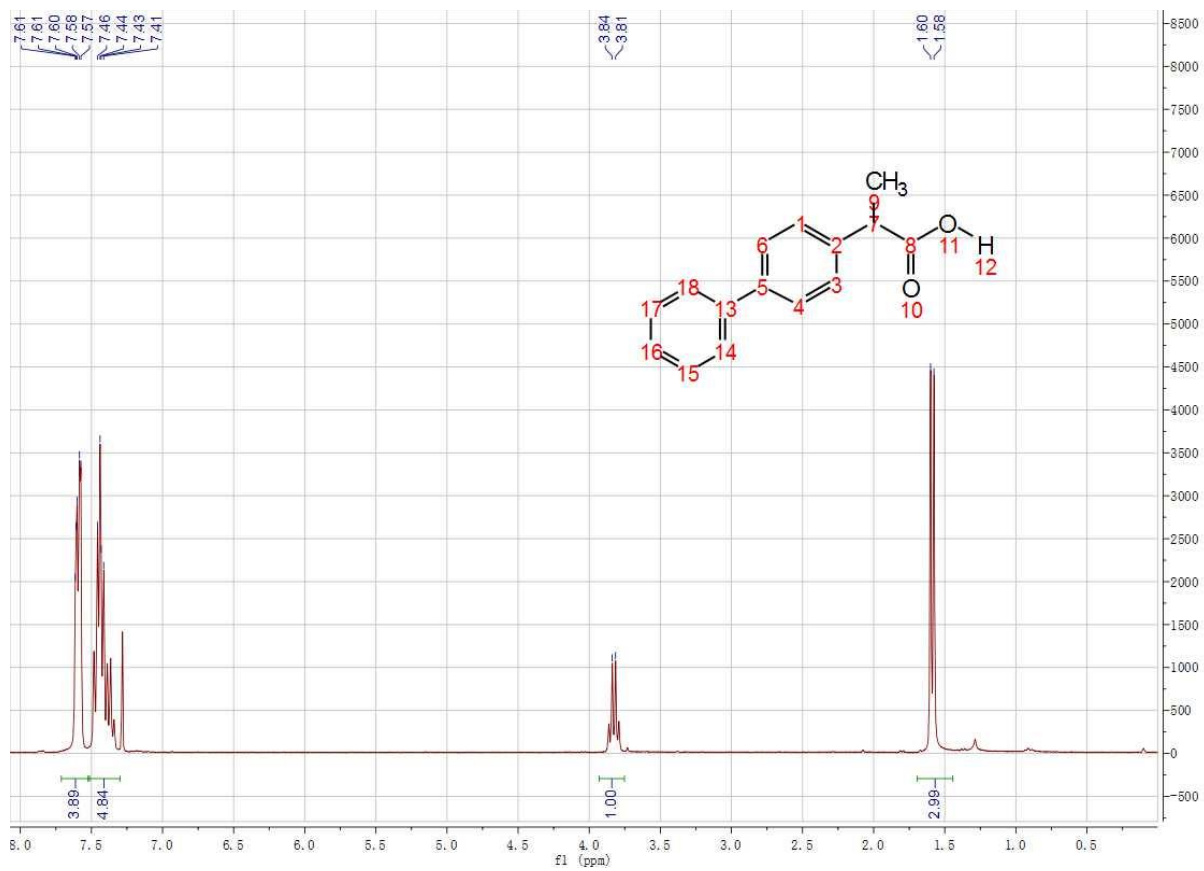
1c

1d

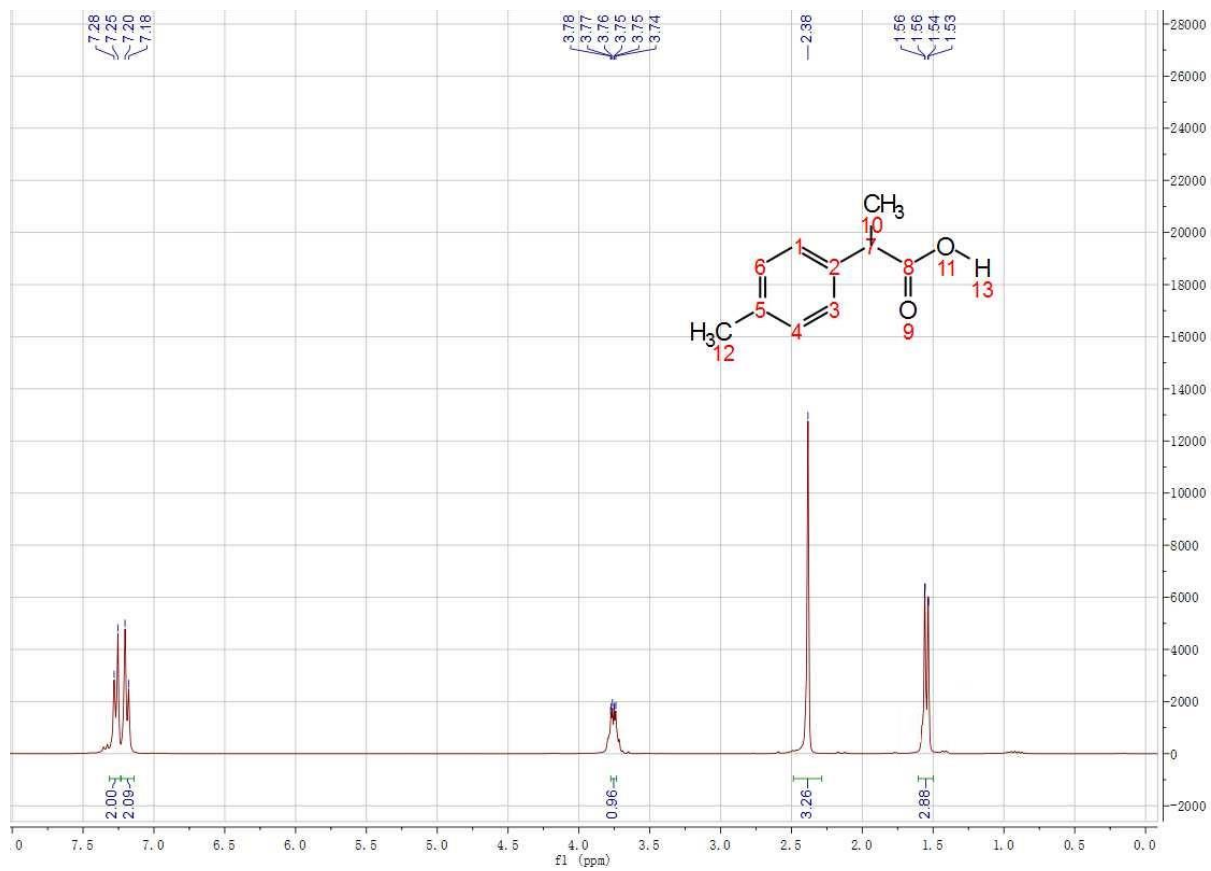


1e

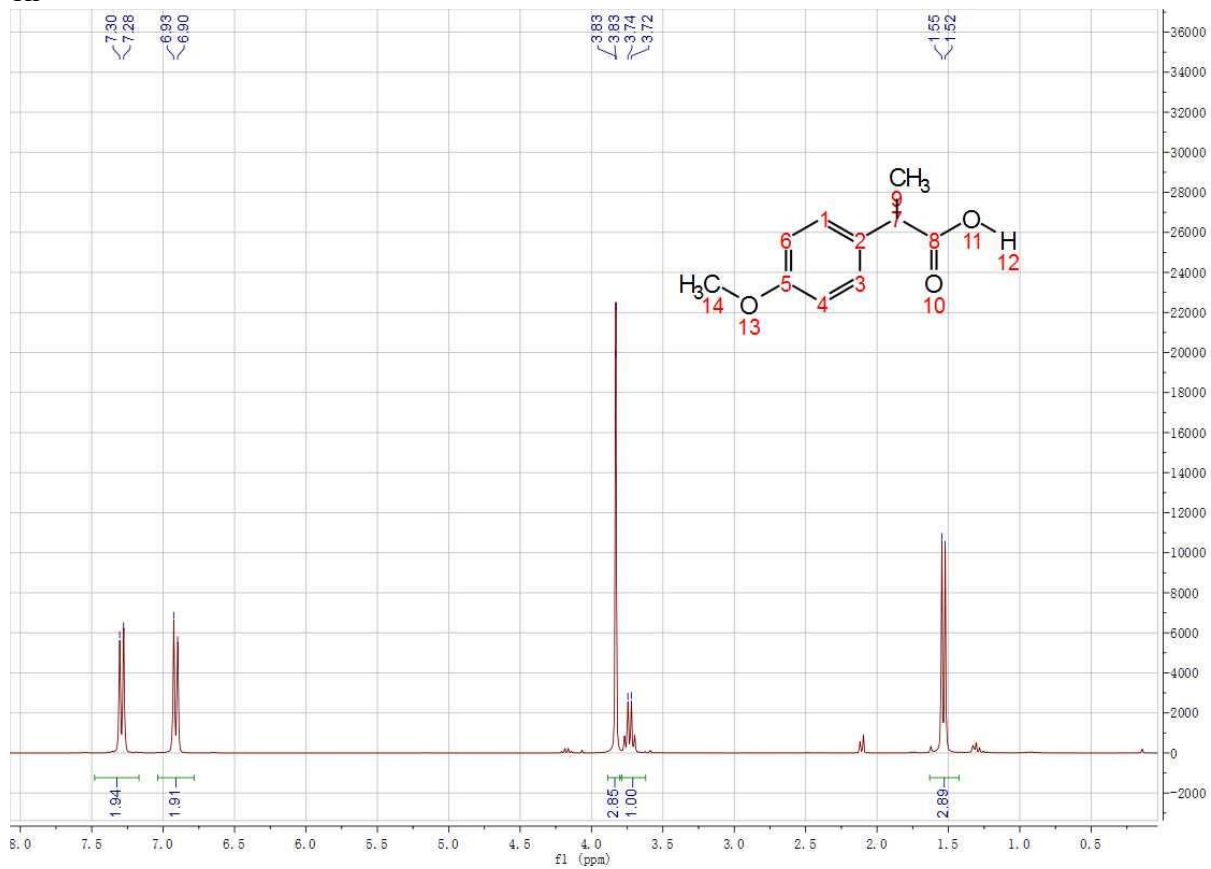
1f



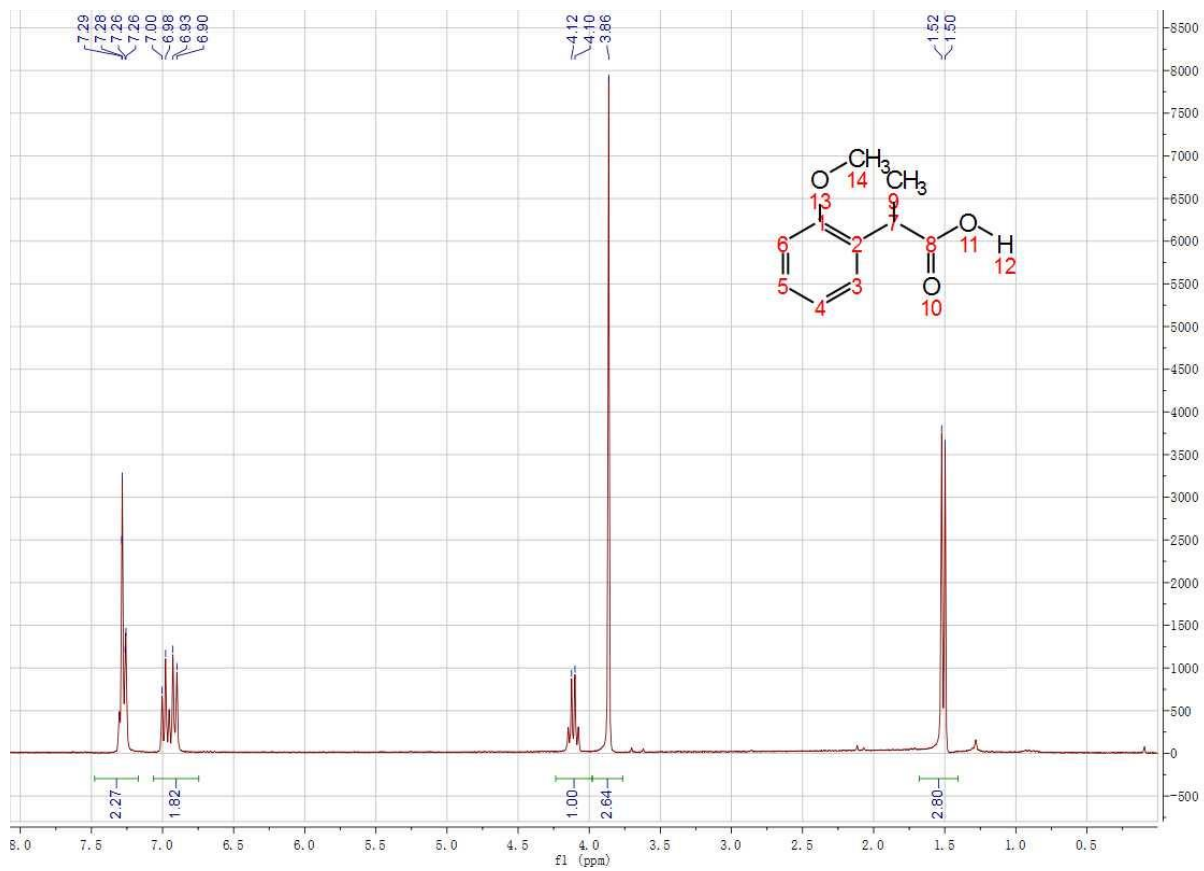
1g



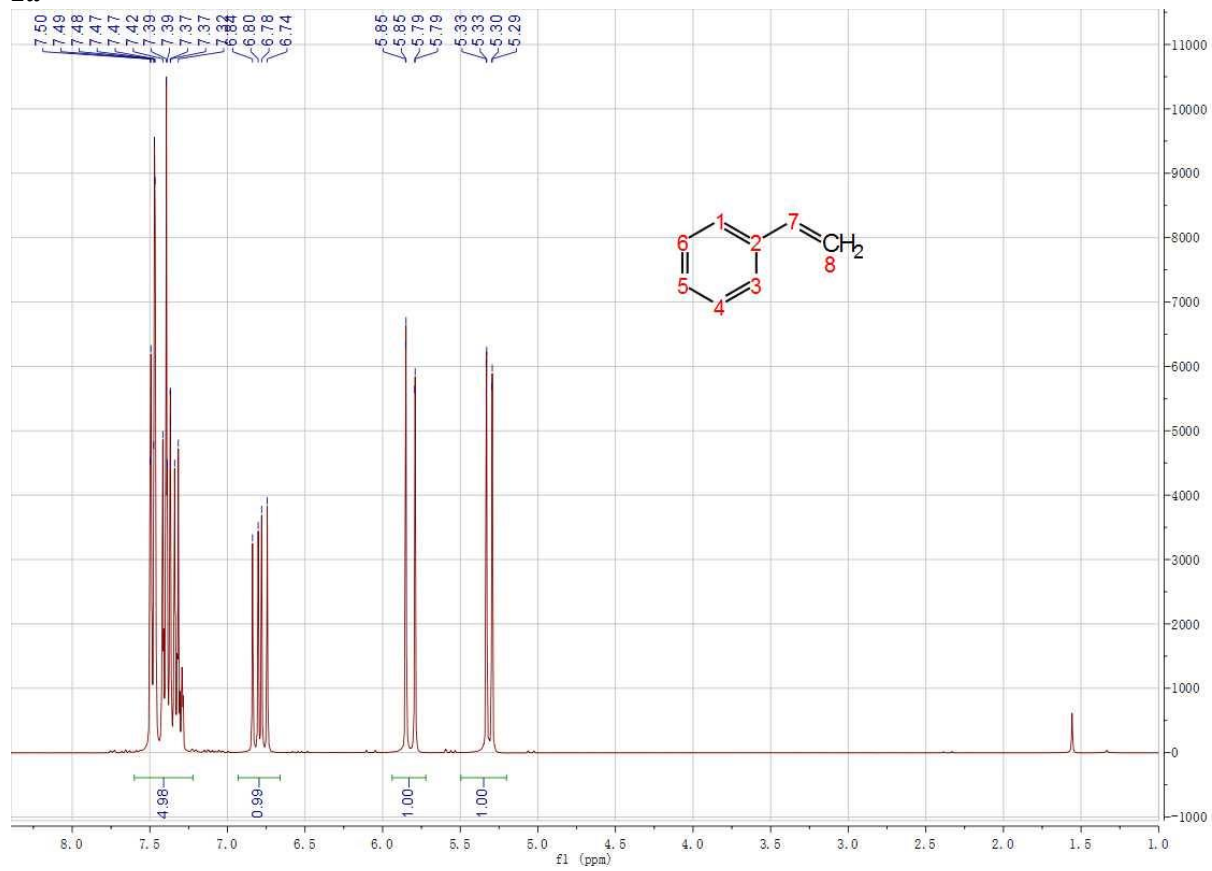
1h



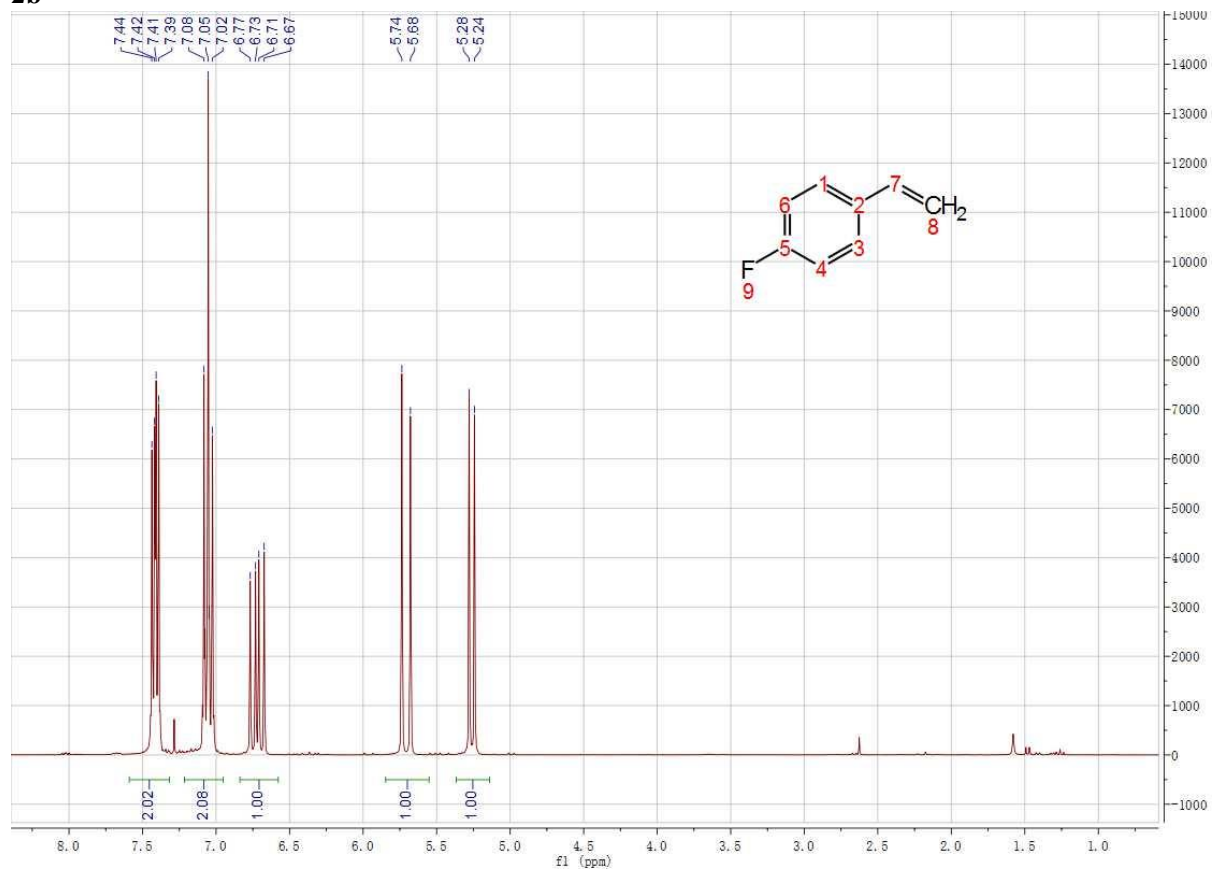
1i



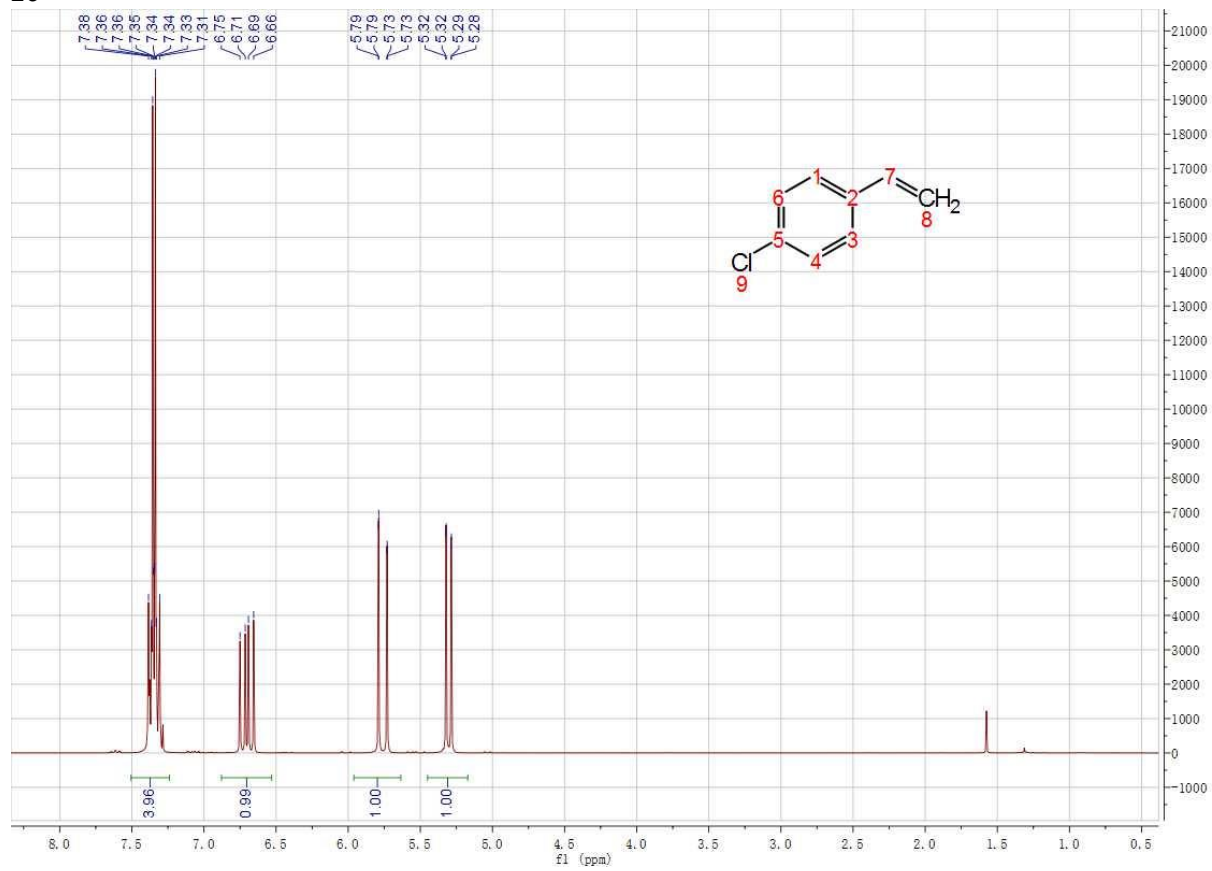
2a



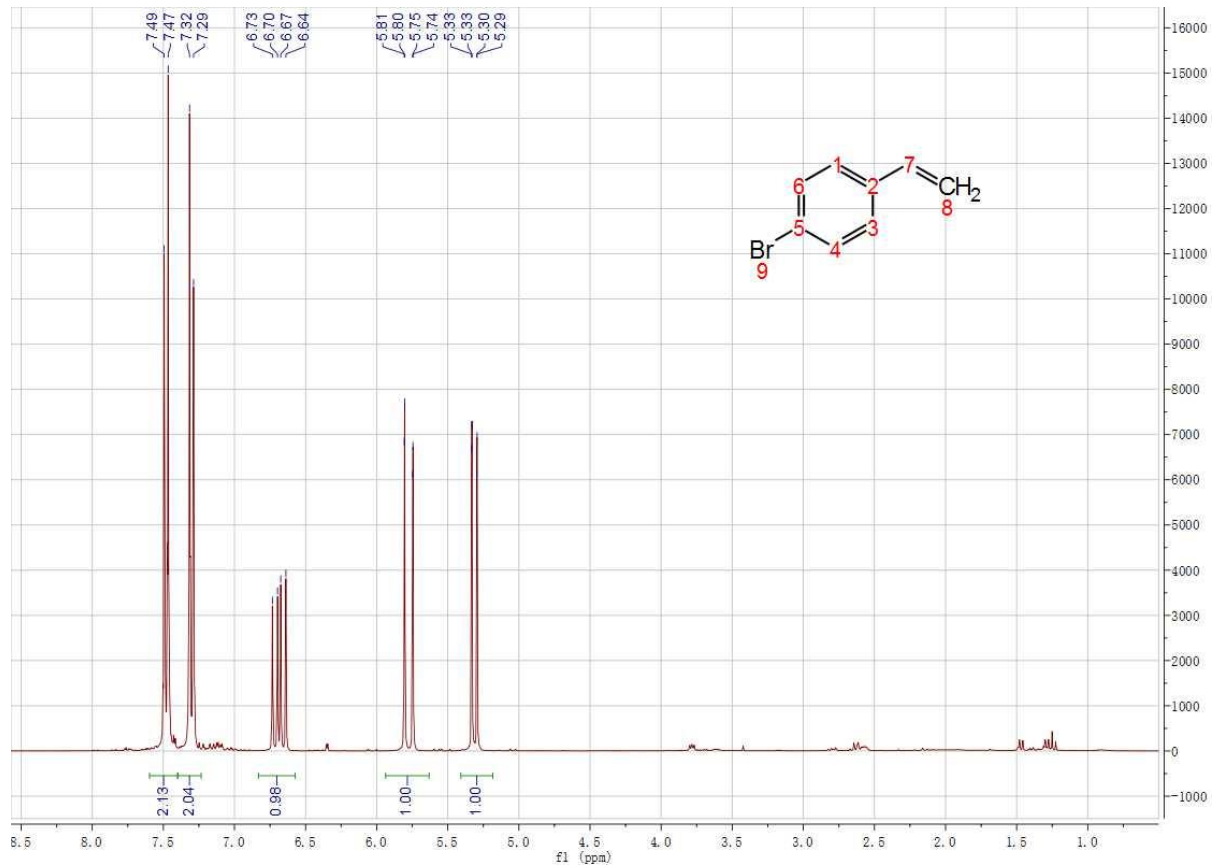
2b



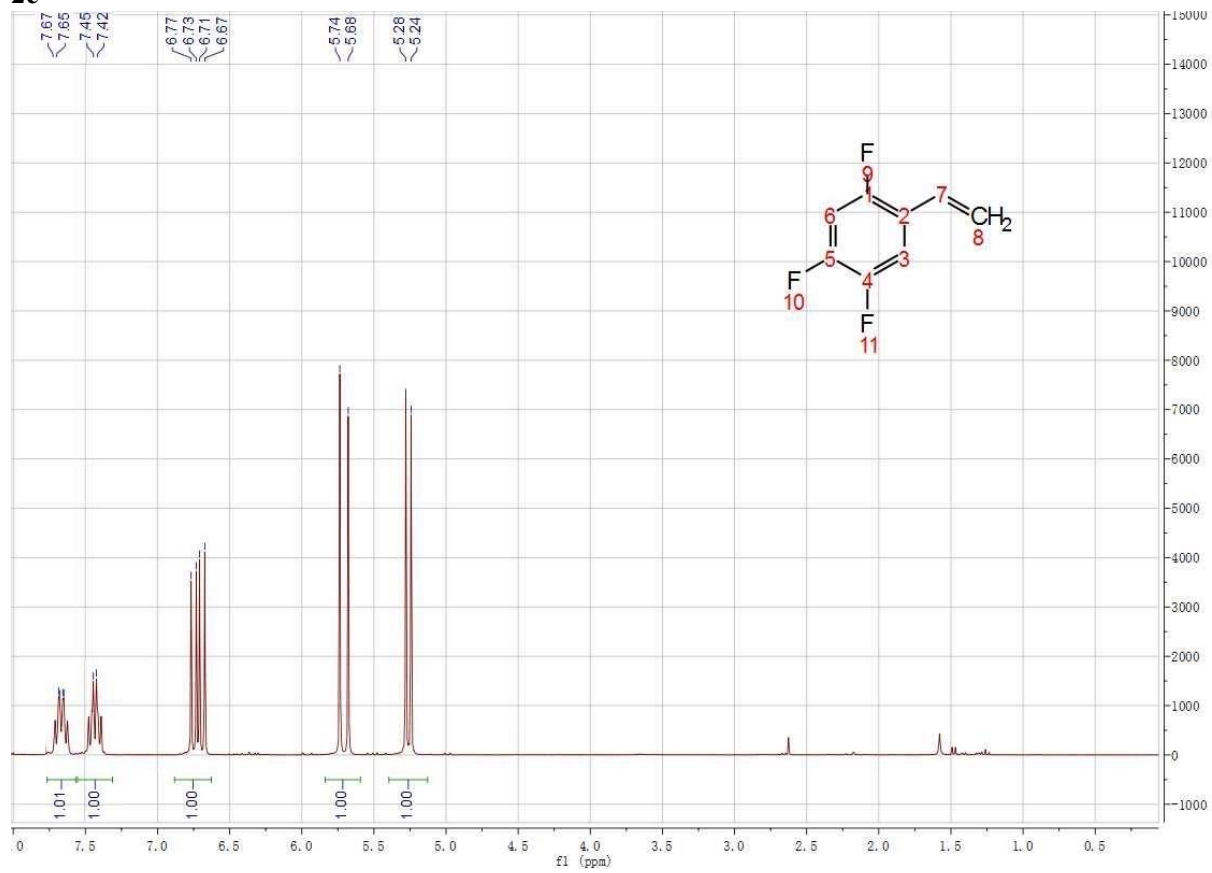
2c



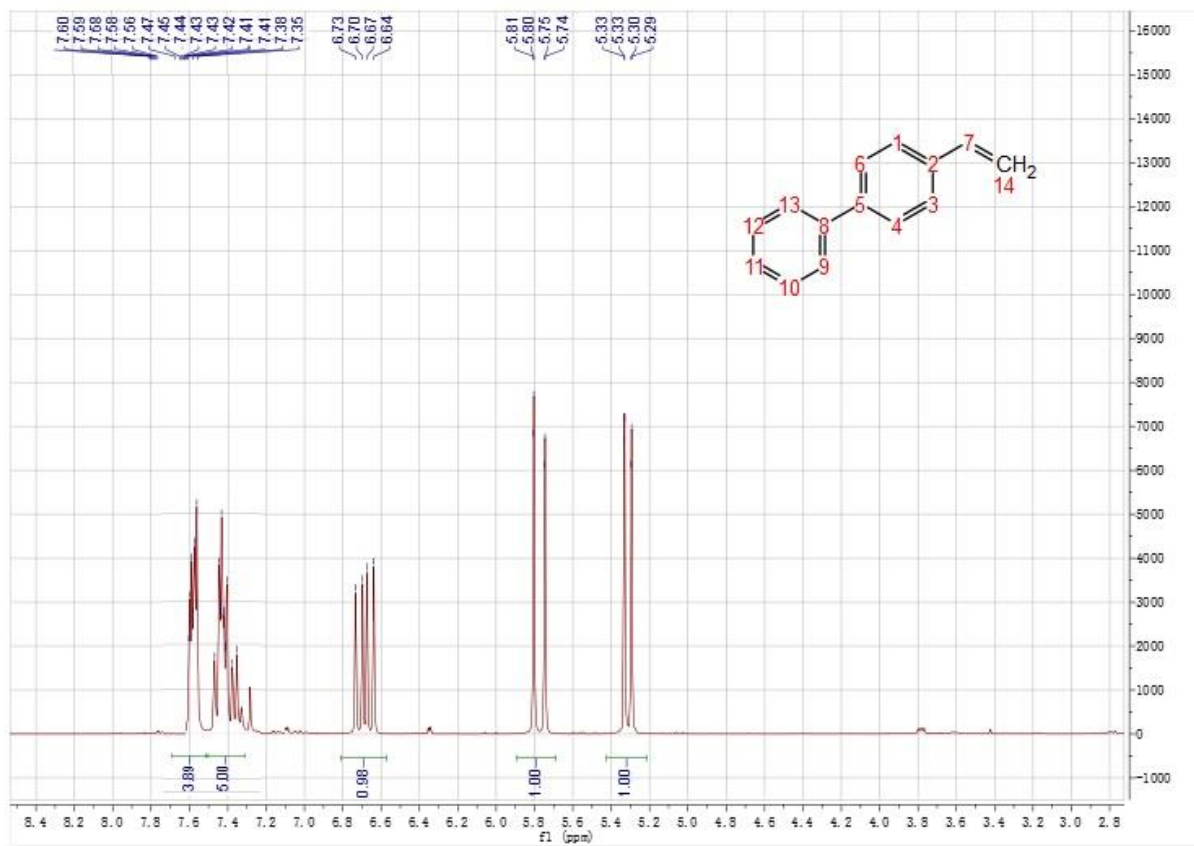
2d



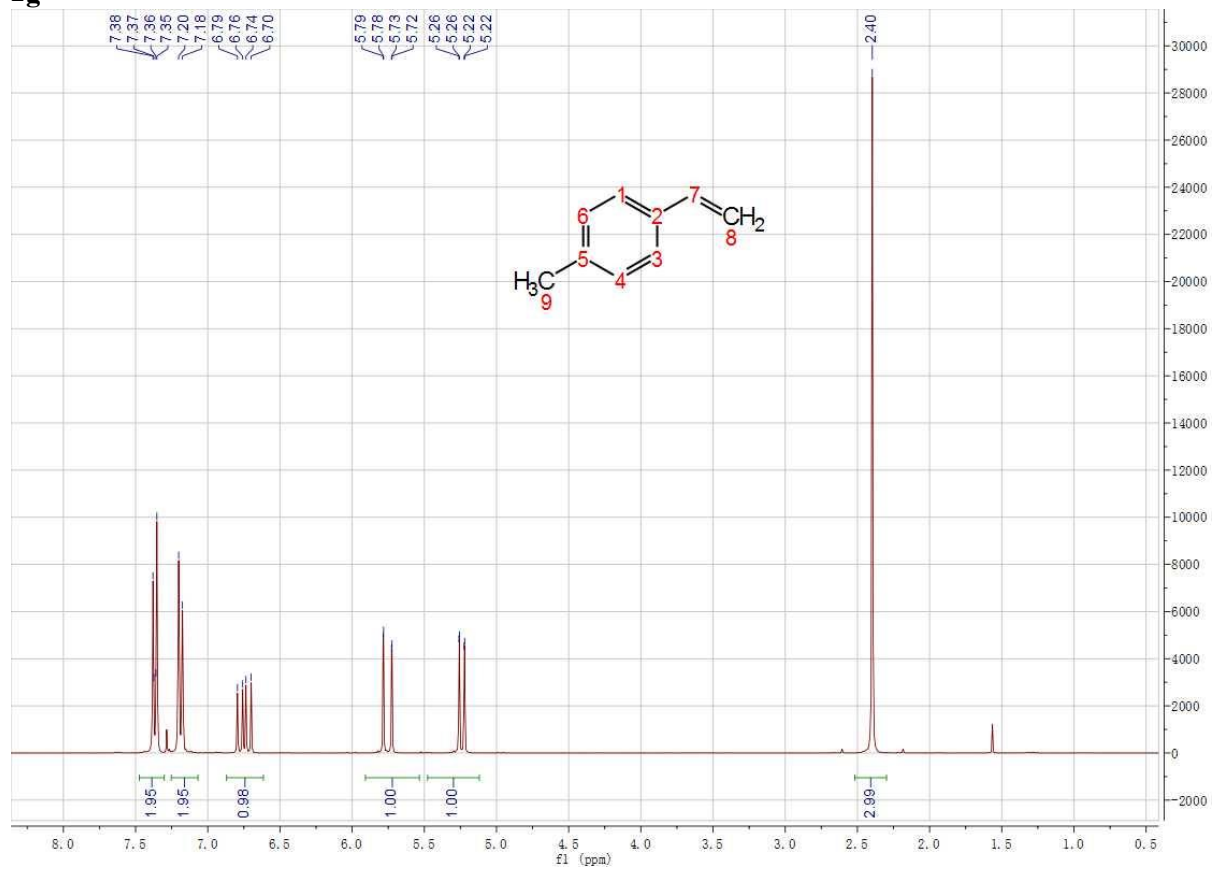
2e



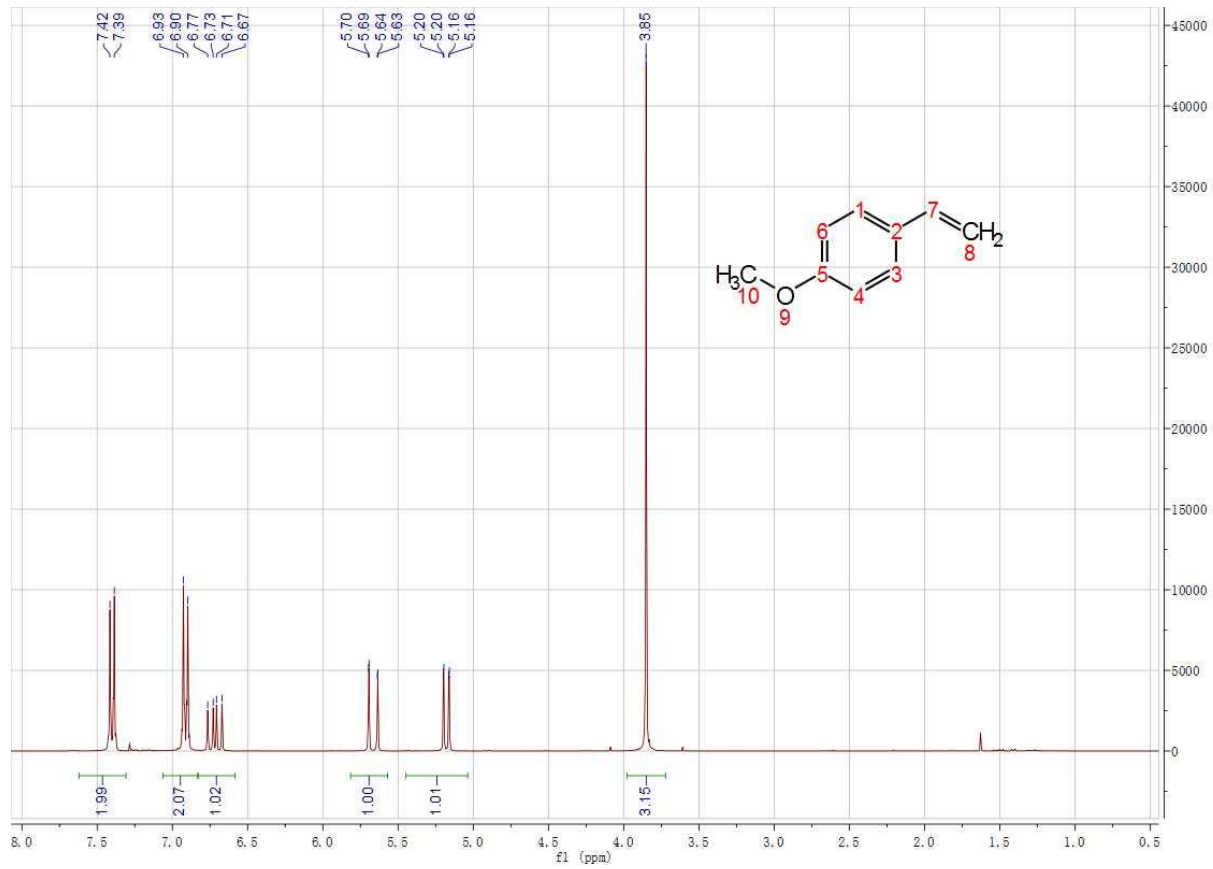
2f



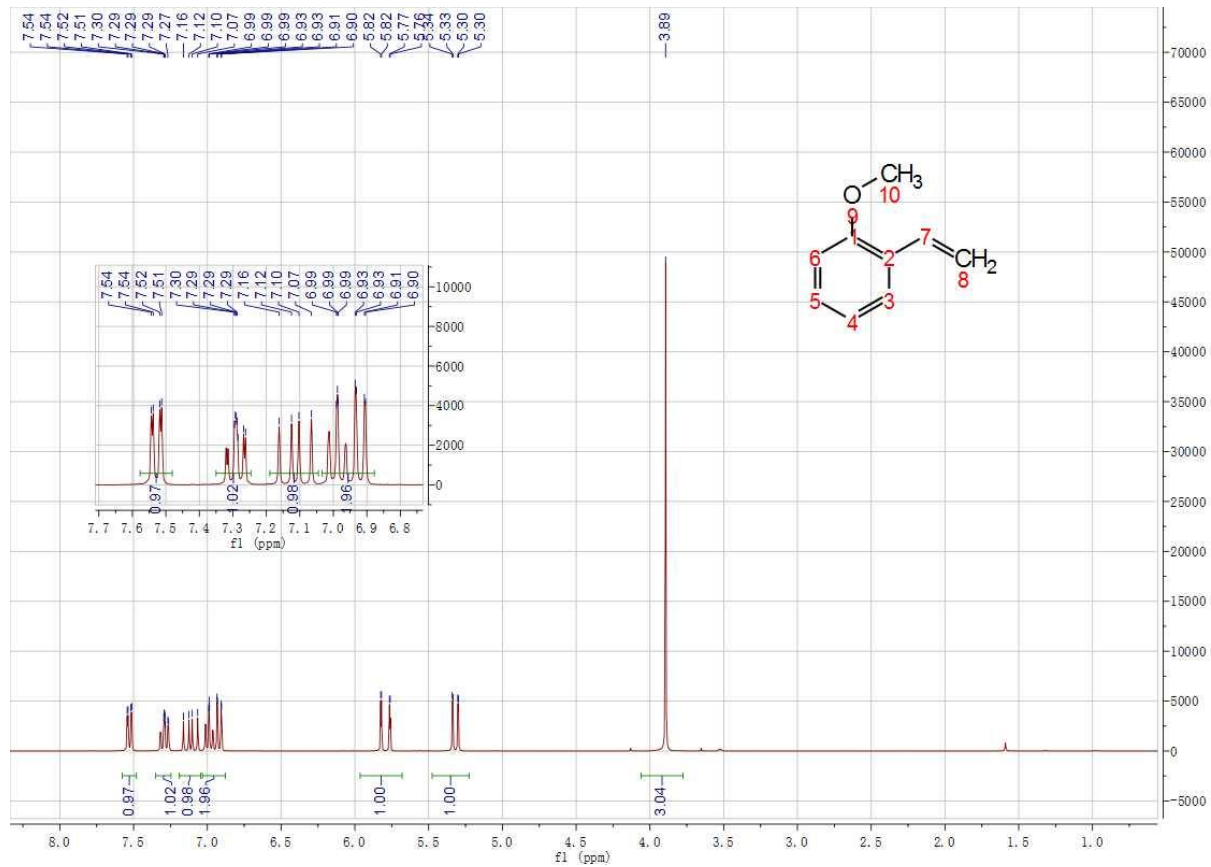
2g



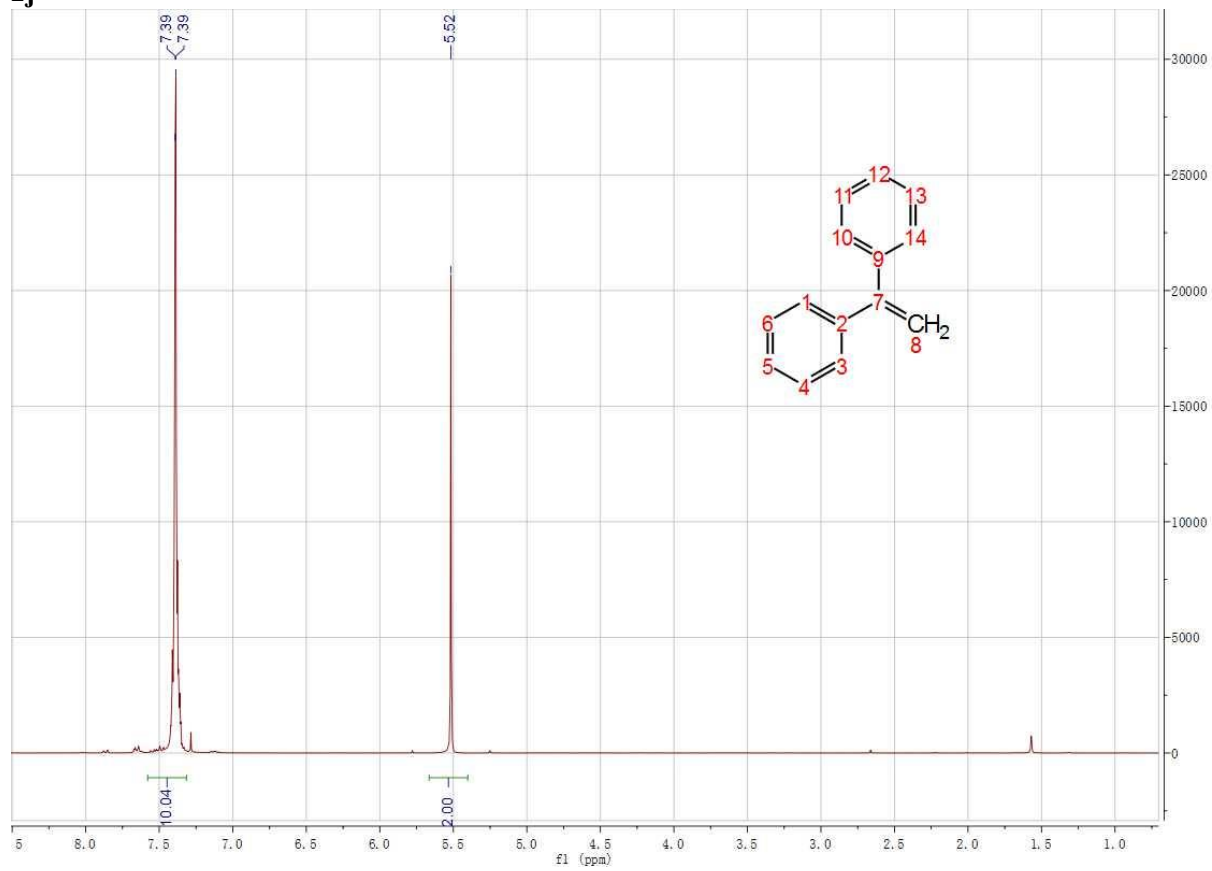
2h



2i



2j



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