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Domino-fluorination-protodefluorination enables decarboxylative cross-coupling of α-oxocarboxylic acids with styrene *via* photoredox catalysis

Muliang Zhang,† Junwei Xi,† Rehanguli Ruzi,† Nan Li,† Zhongkai Wu,† Weipeng Li,† Chengjian Zhu*†‡

† State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China

‡State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, China. E-mail: *cjzhu@nju.edu.cn*

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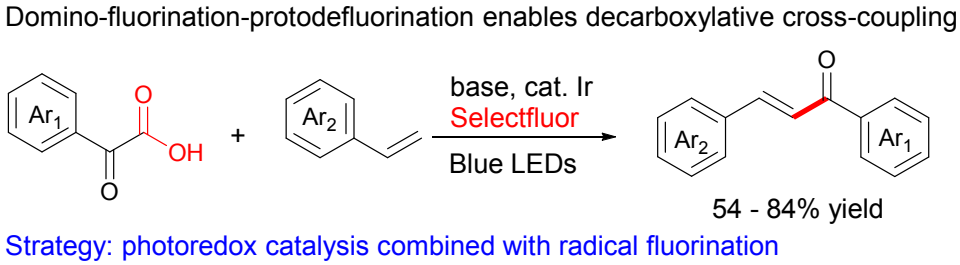
ABSTRACT

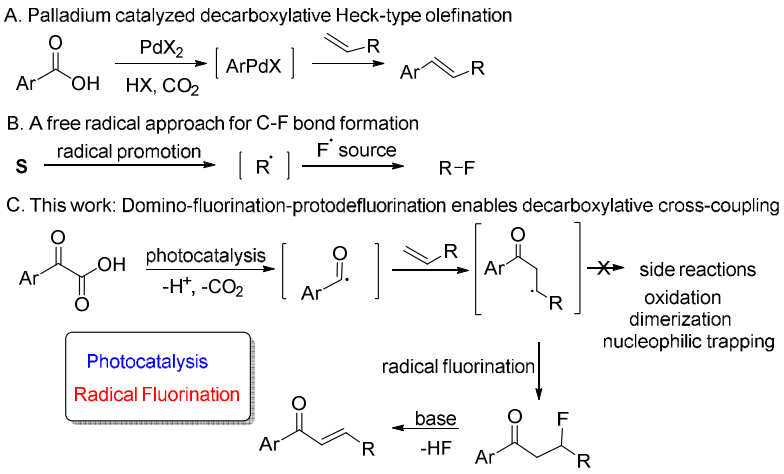


Domino-fluorination-protodefluorination decarboxylative cross-coupling of α-keto acids with styrene has been developed *via* photoredox catalysis. The critical part of this strategy is the formation of the carbon-fluorine (C-F) bond by the capture of a carbon-centered radical intermediate, which will overcome side reactions during the styrene radical functionalization process. Experimental studies have provided evidence indicating a domino-fluorination-protodefluorination pathway, with α-keto acid initiating the photoredox cycle. The present catalytic protocol also affords a novel approach for the construction of α,β-unsaturated ketones under mild conditions.

INTRODUCTION

Carboxylic acids are widely available in great structural diversity, and their conversion into valuable chemical products such as bioactive natural compounds and biofuels represents an important goal.[1] Accompanied by a latent and easily removable carboxylate group to direct reactivity,[2] carboxylic acids have been extensively developed to engage this kind of compounds in new catalytic organic transformations.[3] Since Myers first reported palladium catalyzed decar-

boxylative Heck-type olefination (Scheme 1 A),[4] transition-metal-catalyzed decarboxylative coupling reactions have been well-developed for modern organic synthesis.[5] While broadly used, most of the reactions still require high temperature, strong oxidant and harsh reaction conditions, which are often incompatible with many sensitive functional groups. Radical reactions are also widely used to construct carbon-carbon (C-C) or carbon-heteroatom (C-Het) bonds in organic synthesis.[6] In particular, electrophilic fluorine sources N-fluorobenzenesulfonimide (NFSI) and Selectfluor can effectively fluorinate alkyl radicals, compared to the traditional methods for fluorine incorporation,[7] and elegant solutions to introduce fluorine into a carbon skeleton structure using a free radical strategy have been reported (Scheme 1 B).[8] Meanwhile, visible-light mediated photoredox catalysis has emerged as a valuable platform for its unique ability to induce single electron transfer (SET) processes that allow the invention of many significant new chemical reactions.[9] The application of this strategy to radical decarboxylation functionalization has led to the discovery of novel reactivities and improved reaction conditions.[10]



Scheme 1. A) Palladium catalyzed decarboxylative Heck-type olefination. B) Free radical methods for fluorine incorporation. C) Our strategy for photoredox catalysis decarboxylative cross-coupling combined with radical fluorination.

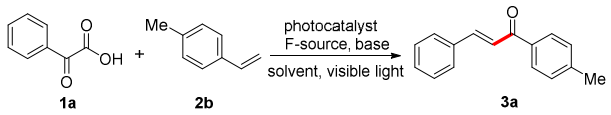
Prompted by the effectiveness of these two kinds of catalytic modes, we recognized that a novel decarboxylative cross-coupling strategy could be achieved *via* an alternative mechanistic pathway. We wondered whether attempts to combine photoredox catalysis with radical fluorination resulted in a direct and mild route to α,β-unsaturated ketones by decarboxylative coupling of simple α-keto acids and styrene, a transformation that to our knowledge has not yet been described (Scheme 1 C). The critical part of this strategy is the formation of a new C-F bond by the capture of a carbon-centered radical intermediate derived from radical addition and unique challenges with regard to unproductive oxidation,[11] dimerization[12] and nucleophilic trapping[13] during the styrene functionalization process are well addressed

by fluorine atom transfer from Selectfluor to the benzylic radical. In addition, decarboxylation of α-keto acids produces acyl radicals without the aid of other reagents.[14] Sequential elimination of hydrogen fluoride offers double-bond forming events because of the presence of a driving force to generate conjugated system. Moreover, a variety of naturally occurring and man-made compounds that show extraordinary biological and pharmacological activity (e.g., anticancer, antimicrobial, antioxidant, antiinflammatory) are in possess of α,β-unsaturated ketone core structures.[15] Based on our interest in photocatalytic research,[16] we herein detail the successful execution of this design principle, and present a new mechanism for the production of α,β-unsaturated ketones under mild reaction conditions.

RESULTS AND DISCUSSION

We first explored this domino-fluorination-protodefluorination decarboxylative cross-coupling reaction of benzoylformic acid **1a** with 4-methylstyrene **2b** in the presence of the photocatalyst *fac*-Ir(ppy)$_3$ (I), Selectfluor and Na_2HPO_4 at room temperature. To our delight, we observed the formation of the desired ketone product **3a** (Table 1, entry 1, 23% yield) in a 1:1 mixture of H_2O/CH_3CN (0.1 M) under irradiation with visible light from blue LEDs (5 W, λ_{max} = 455 nm). Encouraged by this promising result, we then screened a series of photocatalysts (I - IV) and found Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (IV) was designated as the suitable one with 54% yield (entries 2 - 4). Examination of a range of bases revealed that two equivalents of sodium acetate was superior (81% yield) with respect to reaction efficiency (entries 5-8). When we used other fluorine sources such as NFSI, no desired product could be observed (entry 9). The key role of water and acetonitrile as the solvent mixture was shown when either of these two solvents were used independently (entries 10 and 11). Finally, control experiments confirmed the requirement of a photocatalyst, and a light source in this new decarboxylative cross-coupling protocol (entries 12 and 13).

Table 1. Optimization studies.[a]



1a **2b** **3a**

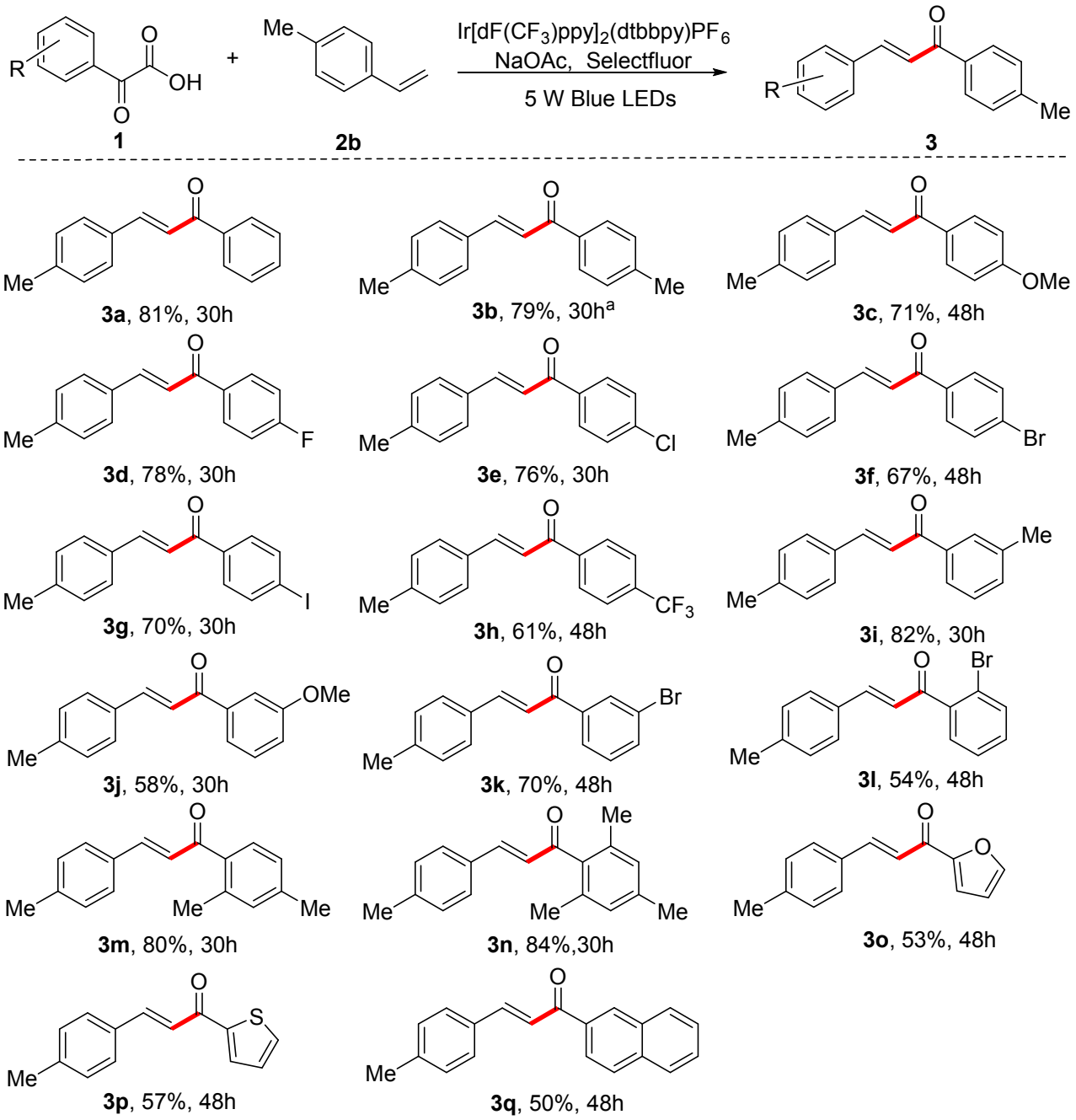
entry	photocat.	base	F source	solvent	yield[b]
1	I	Na_2HPO_4	Selectfluor	CH_3CN/H_2O	23
2	II	Na_2HPO_4	Selectfluor	CH_3CN/H_2O	34
3	III	Na_2HPO_4	Selectfluor	CH_3CN/H_2O	20
4	IV	Na_2HPO_4	Selectfluor	CH_3CN/H_2O	54
5	IV	$NaHCO_3$	Selectfluor	CH_3CN/H_2O	43
6	IV	Na_2CO_3	Selectfluor	CH_3CN/H_2O	18
7	IV	NaOAc	Selectfluor	CH_3CN/H_2O	81
8	IV	K_2HPO_4	Selectfluor	CH_3CN/H_2O	64
9	IV	NaOAc	NFSI	CH_3CN/H_2O	0

10	IV	NaOAc	Selectfluor	CH_3CN	34
11	IV	NaOAc	Selectfluor	H_2O	0
12	none	NaOAc	Selectfluor	CH_3CN/H_2O	12
13[c]	IV	NaOAc	Selectfluor	CH_3CN/H_2O	0

[a] The reactions were carried out with **1a** (0.2 mmol), **2b** (0.4 mmol, 2.0 equiv), base (0.4 mmol, 2.0 equiv), photocatalyst (0.002 mmol, 2 mol %), solvent (2 mL), Selectfluor (0.5 mmol, 2.5 equiv), at room temperature, 5 W blue LEDs, 36 h. [b] Isolated yields. [c] Reaction performed in the absence of light. [d] I = *fac*-$Ir(ppy)_3$, II = $Ir(ppy)_2(dtbbpy)PF_6$, III = $Ru(bpy)_3(PF_6)_2$, IV = $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$.

With the optimized reaction conditions shown above, we studied other substrates in this domino-fluorination-protodefluorination decarboxylative cross-coupling of α-keto acids and styrene. First, the scope of the α-oxocarboxylic acid substrate was investigated (Scheme 2). As for the effect of electronic properties of the substituents on the phenyl ring, benzoylformic acids bearing an electron-rich group (4-methyl or 4-methoxyl) yielded α,β-unsaturated ketones **3b** and **3c** smoothly, and electron-deficient (4-halogen substituents or 4-trifluoromethyl) acid derivatives yielded desired products (**3d**–**h**) in yields of 61 – 78%. The substrate with aryl iodide functional group sensitive to transition-metal catalysis remained intact in this reaction (**3g**), which provides the possibility for further functionalization. *Meta*-(methyl, methoxyl, bromo) substituted α-oxo acids were similarly found to be suitable substrates for this transformation and gave the desired ketones (**3i-k**) in good yield. For the *ortho*-substituted or sterically bulky substrate, the reaction delivered the corresponding products (**3m** and **3n**) with 80% and 84% yields, respectively, which may be due to radical reaction. Moreover, when heterocyclic 2-furanyl, 2-thienyl, and 2-naphthyl-substituted α-oxo acids were used, the unsaturated ketones (**3o-q**) were also obtained.

Scheme 2. Scope of α-keto acid in this decarboxylative cross-coupling reaction

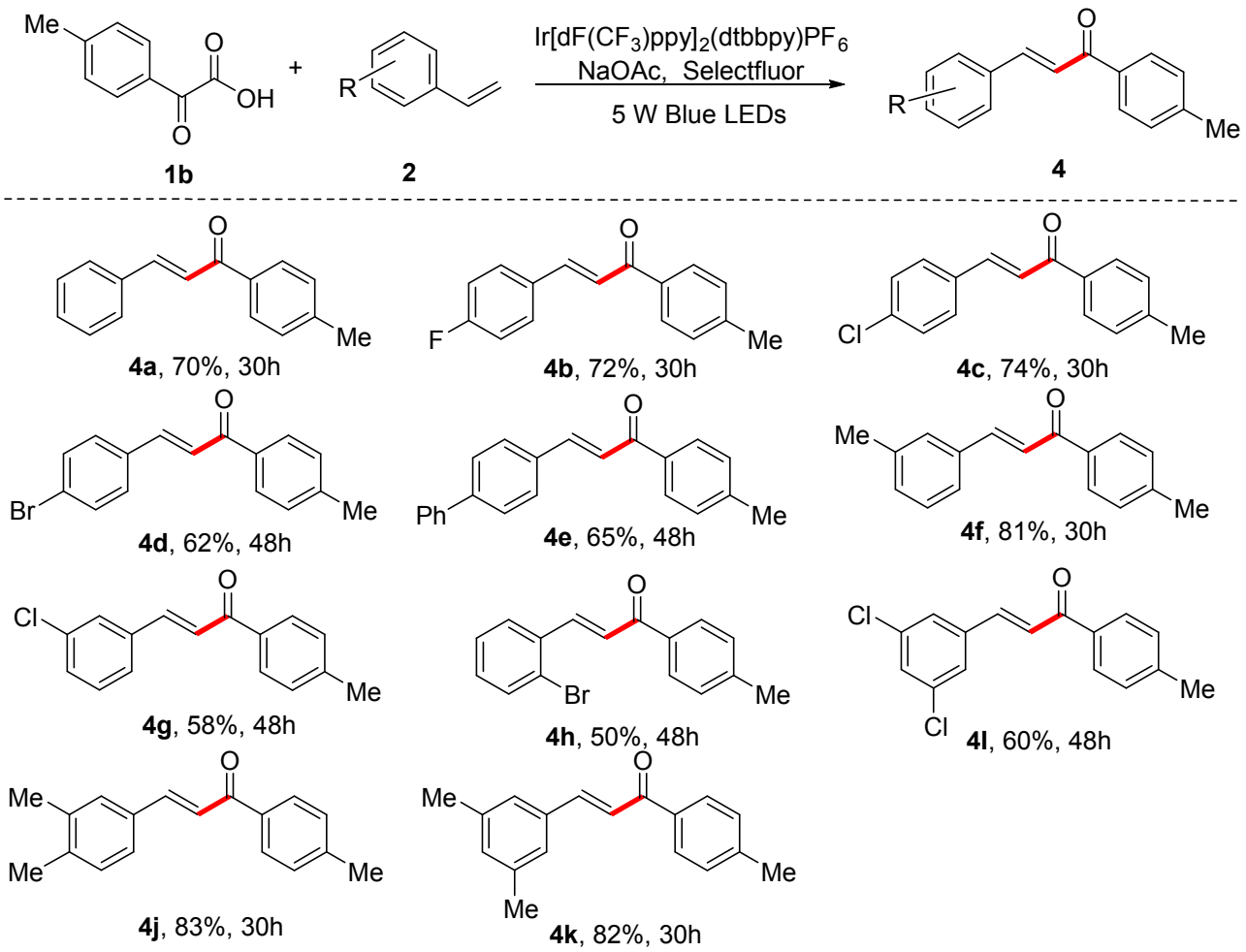


Reaction conditions: **1** (0.2 mmol), **2b** (0.4 mmol, 2.0 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol, 2 mol %), NaOAc (0.4 mmol, 2.0 equiv), CH_3CN/H_2O (V/V = 1:1, 2 mL), Selectfluor (0.5 mmol, 2.5 equiv), at room temperature, 5 W blue LEDs, 30 - 48 h. [a]Reaction carried out on 5 mmol scale.

Encouraged by the above promising results obtained, we further applied the optimized reaction conditions to investigate the substrate scope of alkenes, and the results are summarized in Scheme 3. A series of styrenes, with various substituents on the aromatic ring, were found to be suitable candidates to offer the desired ketones in good

yields. Styrenes having halogen substituents such as fluoro, chloro and bromo groups afforded the corresponding products (**4b-d**). *Para*-phenylstyrene also reacted with α-oxocarboxylic acid under the standard reaction conditions to afford the coupling product (**4e**) in 65% yield. Notably, a *meta*-chloro (**4g**) or *ortho*-bromo (**4h**) substituent on the phenyl ring of styrenes could also be well tolerated. The styrenes with more substituents (methyl, chloro) on the phenyl ring were used, they all underwent the decarboxylative cross-coupling with α-oxocarboxylic acids, yielding α,β-unsaturated ketone products (**4l-k**) in 60 – 83% yields.

Scheme 3. Scope of styrene in this decarboxylative cross-coupling reaction.

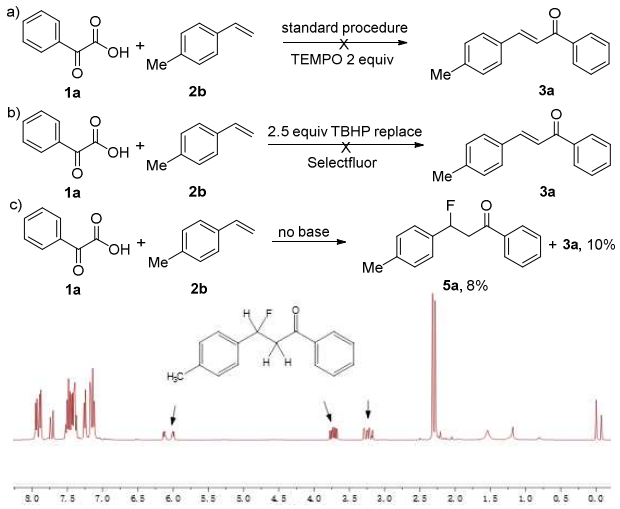


Reaction conditions: **1b** (0.2 mmol), **2** (0.4 mmol, 2.0 equiv), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol, 2 mol %), NaOAc (0.4 mmol, 2.0 equiv), CH_3CN/H_2O (V/V = 1:1, 2 mL), Selectfluor (0.5 mmol, 2.5 equiv), at room temperature, 5 W blue LEDs, 30 - 48 h.

To gain mechanistic insight into the visible-light-mediated photoredox catalysis for domino-fluorination-protodefluorination decarboxylative cross-coupling, the radical scavenger TEMPO (2, 2, 6, 6-tetramethyl-1-

piperidinyloxy) was introduced into the photochemical system, and the reaction was completely restrained under optimized reaction conditions, indicating that a SET radical process is operating (Scheme 4 a). To test if the benzylic radical derived from radical addition of acyl radical to styrene undergo the direct oxidation and deprotonation to release the final product, we used TBHP to replace Selectfluor and observed no ketone product (Scheme 4 b).[17] These experimental results suggested Selectfluor was not simply an oxidant for participating in the photocatalytic cycle, but might contribute to decarboxylative cross-coupling process. In the absence of base, we monitored the acylfluorinated product of styrenes in the reaction mixture by NMR spectrum although only a small amount. (Scheme 4 c), which implied that **5a** may be the reaction intermediate and unstable to eliminate hydrogen fluoride in the presence of base.[18] Finally, we performed fluorescence quenching experiments with the $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as photocatalyst (See: Supporting Information). The results of a series of Stern−Volmer quenching studies revealed the initiation point of the photoredox catalytic cycle likely began with the oxidation of α-keto acids.

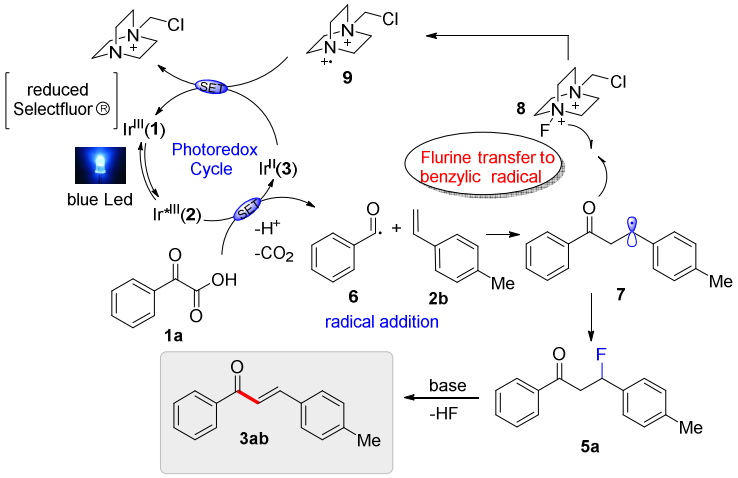
Scheme 4. Mechanistic investigation of the decarboxylative cross-coupling reaction.



On the basis of the experimental results and literature reported,[19] a possible mechanism is shown in Scheme 5. Under visible-light irradiation, the photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (**1**) leads to the formation of a long-lived excited state Ir^{*III} (**2**), undergoing a metal to ligand charge-transfer (MLCT) process. Ir^{*III} (**2**) can serve as an efficient oxidizing agent to oxide α-keto acid by a SET process with the reduced Ir^{II} (**3**) species. The corresponding carboxyl radical species would quickly extrude CO_2 to give the acyl radical species **6**. The radical addition of **6** to styrene **2b** delivers the critical benzylic radical **7**. At this stage, direct fluorine atom transfer from Selectfluor to the benzylic radical **7** is proposed to construct the C-F bond with concomitant generation of the corresponding Selectfluor radical cation

9. Subsequently, radical cation **9** would act as an oxidant to complete the photoredox cycle as a suitable electron acceptor in the conversion of reduced state Ir^{II} (**3**) to the ground state Ir^{III} (**1**) species. The acylfluorinated product **5a** is unstable to eliminate hydrogen fluoride in the presence of base, delivering the final α,β-unsaturated ketone product **3a**.

Scheme 5. Possible reaction mechanism



In conclusion, we have developed a visible-light-mediated photoredox catalysis protocol for domino-fluorination-protodefluorination decarboxylative cross-coupling of α-keto acids with styrene. Challenges associated with styrene functionalization process were efficiently overcome by rapid fluorine atom transfer from Selectfluor to the benzylic radical combined with photoredox catalysis. This domino-fluorination-protodefluorination catalytic strategy provides a novel pathway for the construction of α,β-unsaturated ketones, with a variety of functional groups tolerated on both α-keto acids and styrene. Extending this method to other challenging reaction systems is currently being explored in our laboratory.

EXPERIMENTAL SECTION

General Information: All regents were AR regents commercial available. Phenylglyoxylic acid **1a** was purchased from Sigma-Aldrich. Other keto acids **1** were prepared from the corresponding methyl ketones according to the reported procedure.[20] Styrenes **2** were purchased from TCI, Alfa or Acros. All of other commercially available compounds were used without further purification. Thin Layer Chromatography (TLC) was used to detect the progress of reactions and to separate products. HRMS data were recorded by a TOF LC/MS. Melting points (mp) were determined with a digital electrothermal apparatus without further correction. ^{1}H NMR, ^{13}C NMR and ^{19}F NMF spectra were recorded using 400 MHz spectrometer at room temperature, with TMS as internal standard. Chemical shifts (δ) are determined

in ppm downfield from tetramethylsilane. Abbreviations for signal couplings are: s, singlet; d, doublet; t, triplet; m, multiplet.

General procedure for the decarboxylative cross coupling of α-keto acids with styrene: A 10 mL oven-dried Schlenk-tube was charged with photocatalyst $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.004 mmol, 0.02 equiv), the corresponding keto acid (1, 0.2 mmol), Selectfluor (0.5 mmol, 2.5 equiv.), and NaOAc (0.4 mmol, 2.0 equiv). The tube was evacuated and backfilled with Ar (three times), Styrenes (2, 0.4 mmol, 2.0 equiv.) in CH_3CN/H_2O (1:1, 2 mL) were added by syringe under Ar. The tube was then sealed and was placed at a distance (app. 5 cm) from 5W blue LEDs lamb, and the mixture was stirred for 30 - 48 h at room temperature. The resulting mixture was diluted with EtOAc (15 mL). The organic layers were washed with H_2O and brine, dried over anhydrous Na_2SO_4 and the solvent was then removed under vacuo. The residue was purified with chromatography column on silica gel (gradient eluent of EtOAc/petroleum ether: 1/200 to 1/100) to give the corresponding products **3** or **4**.

(E)-1-phenyl-3-(p-tolyl)prop-2-en-1-one (**3a**) (36.0 mg, 81% yield). White solid; mp: 113-114 ^oC; ^1H NMR (400 MHz, Chloroform-d) δ 8.05 - 7.97 (m, 2H), 7.79 (d, J = 15.7 Hz, 1H), 7.61 - 7.44 (m, 6H), 7.22 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.7, 145.0, 141.1, 138.4, 132.7, 132.2, 129.7, 128.6, 128.5, 128.5, 21.6. HRMS (ESI) Calcd for $C_{16}H_{15}O$ $[M+H]^+$: 223.1177, found: 223.1178.

(E)-1,3-di-p-tolylprop-2-en-1-one (**3b**): (912 mg, 79% yield). White solid; mp: 128-130 ^oC; ^1H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 6.4 Hz, 2H), 7.78 (d, J = 15.7 Hz, 1H), 7.56 - 7.43 (m, 3H), 7. 30 -7.20 (m, 4H), 2.42 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.1, 144.5, 143.5, 141.0, 135.8, 132.3, 129.7, 129.3, 128.6, 128.5, 121.1, 21.7, 21.6. HRMS (ESI) Calcd for C17H17O $[M+H]^+$: 237.1274, found: 237.1276.

(E)-1-(4-methoxyphenyl)-3-(p-tolyl)prop-2-en-1-one (**3c**): (35.8mg, 71% yield). White solid; mp: 156-158 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.12 - 7.96 (m, 2H), 7.78 (d, *J* = 15.6 Hz, 1H), 7.60 - 7.44 (m, 3H), 7.21 (d, *J* = 7.9 Hz, 2H), 7.04 - 6.89 (m, 2H), 3.87 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.8, 163.4, 144.1, 140.8, 132.4, 131.2, 130. 8, 129.7, 128.4, 120.8, 113.8, 55.5, 21.5. HRMS (ESI) Calcd for $C_{17}H_{16}O_2$ $[M+H]^+$: 252.1150, found: 252.1154.

(E)-1-(4-fluorophenyl)-3-(p-tolyl)prop-2-en-1-one (**3d**): (37.4mg, 78% yield). White solid; mp: 124-126 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 - 7.89 (m, 2H), 7.70 (d, *J* = 15.6 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 15.6 Hz, 1H), 7.22 - 6.99 (m, 4H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.9, 165.5(d, *J* = 254.2 Hz),

145.2, 141.2, 134.7, 132.1, 131.1 (d, J = 9.2 Hz), 129.8, 128.5, 120.6, 115.7 (d, J = 21.8 Hz), 21.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.73. HRMS (ESI) Calcd for $C_{16}H_{14}FO$ $[M+H]^+$: 241.1023, found: 241.1025.

(E)-1-(4-chlorophenyl)-3-(p-tolyl)prop-2-en-1-one (**3e**): (38.9 mg, 76% yield). White solid; mp: 158-160 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 - 7.90 (m, 2H), 7.79 (d, J = 15.7 Hz, 1H), 7.54 (d, J = 8.1 Hz, 2H), 7.49 - 7.39 (m, 3H), 7.24 (t, J = 8.4 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.3, 145.5, 141.4, 139.1, 136.7, 132.0, 129.9, 129.7, 128.9, 128.6, 120.5, 21.6. HRMS (ESI) Calcd for $C_{16}H_{14}ClO$ $[M+H]^+$: 257.0728, found: 257.0728.

(E)-1-(4-bromophenyl)-3-(p-tolyl)prop-2-en-1-one (**3f**): (40.2 mg, 67% yield). White solid; mp:160-163 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 - 7.83 (m, 2H), 7.79 (d, J = 15.7 Hz, 1H), 7.67 - 7.61 (m, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 15.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.5, 145.5, 141.4, 137.1, 132.0, 131.9, 130.1, 129.8, 128.6, 127.7, 120.5, 21.6. HRMS (ESI) Calcd for $C_{16}H_{14}BrO$ $[M+H]^+$: 301.0223, found: 301.0227.

(E)-1-(4-iodophenyl)-3-(p-tolyl)prop-2-en-1-one (**3g**): (48.7mg, 70% yield). White solid; mp:156-158 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, J = 8.4 Hz, 2H), 7.79 (d, J = 15.7 Hz, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 15.7 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189. 8, 145.6, 141.4, 137.9, 137.6, 132.0, 129.9, 129.8, 128.6, 120.4, 100.5, 21.6. HRMS (ESI) Calcd for $C_{16}H_{14}IO$ $[M+H]^+$: 349.0084, found: 349.0086.

(E)-3-(p-tolyl)-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**3h**): (35.4mg, 61% yield). White solid; mp: 145-147 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, J = 8.1 Hz, 2H), 7.76 - 7.60 (m, 3H), 7.46 (d, J = 8.1 Hz, 2H), 7.35 (d, J = 15.7 Hz, 1H), 7.15 (d, J = 8.0 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.7, 146.2, 141.7, 141.2, 133.9 (q, J = 32.6 Hz), 131.8, 129.8, 128.7, 128.6, 125.6 (q, J = 3.7 Hz), 123.7 (q, J = 272.7 Hz), 120.6, 21.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.96. HRMS (ESI) Calcd for $C_{17}H_{14}F_3O$ $[M+H]^+$: 291.0991, found: 291.0994.

(E)-1-(m-tolyl)-3-(p-tolyl)prop-2-en-1-one (**3i**): (38.7 mg, 82% yield). White solid; mp: 68-70^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 - 7.69 (m, 3H), 7.53 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 15.7 Hz, 1H), 7.37 (d, J = 5.2 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.43 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.8, 144.8, 141.1, 138.4, 133.5, 132.2, 129.0, 128.5, 128.5, 125.7, 121.3, 21. 6, 21.4. HRMS (ESI) Calcd for $C_{17}H_{17}O$ $[M+H]^+$: 237.1274, found: 237.1276.

(E)-1-(3-methoxyphenyl)-3-(p-tolyl)prop-2-en-1-one (**3j**): (29.2 mg, 58% yield). White solid; mp: 48-50 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 15.7 Hz, 1H), 7.62 - 7.51 (m, 4H), 7.47 (d, *J* = 15.7 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.17 - 7.09 (m, 1H), 3.88 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.4, 159.9, 145.0, 141.1, 139.8, 132.2, 129.7, 129.6, 128.5, 121.2, 121.0, 119.2, 112.7, 55.5, 21.6. HRMS (ESI) Calcd for $C_{17}H_{16}O_2$ $[M+H]^+$: 252.1150, found: 252.1154.

(E)-1-(3-bromophenyl)-3-(p-tolyl)prop-2-en-1-one (3k): (42.0 mg, 70% yield). white solid; mp:132-134 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.13 (t, *J* = 1.7 Hz, 1H), 7.92 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.73 - 7.64 (m, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.46 - 7.33 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.1, 145.8, 141.5, 140.2, 135.5, 131.9, 131.5, 130.2, 129.8, 128.6, 127.0, 122.9, 120.4, 21.6. HRMS (ESI) Calcd for $C_{16}H_{14}BrO$ $[M+H]^+$: 301.0223, found: 301.0224.

(E)-1-(2-bromophenyl)-3-(p-tolyl)prop-2-en-1-one (**3l**): (32.4 mg, 54% yield). White solid; mp: 135-138 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.2 Hz, 1H), 7.48 - 7.35 (m, 5H), 7.34 - 7.28 (m, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 16.1 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 194.7, 146.9, 141.6, 141.3, 133.4, 131.7, 131.3, 129.8, 129.2, 128.7, 127.3, 125.2, 119.5, 21.6. HRMS (ESI) Calcd for $C_{16}H_{14}BrO$ $[M+H]^+$: 301.0223, found: 301.0226.

(E)-1-(2,4-dimethylphenyl)-3-(p-tolyl)prop-2-en-1-one (**3m**): (40.0 mg, 80% yield). White solid; mp: 100-104 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 - 7.41 (m, *J* = 7.7 Hz, 4H), 7.30 - 6.94 (m, 5H), 2.43 (s, 3H), 2.37 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.08, 145.4, 141.0, 140.8, 137.4, 136.3, 132.2, 132.1, 129.7, 128.6, 128.4, 126.1, 125.8, 21.5, 21.4, 20.4. HRMS (ESI) Calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found: 251.1432.

(E)-1-mesityl-3-(p-tolyl)prop-2-en-1-one (**3n**): (44.4 mg, 84% yield). White solid; mp: 56-58 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 8.1 Hz, 2H), 7.21 - 7.07 (m, 3H), 6.94 - 6.80 (m, 3H), 2.37 (s, 3H), 2.32 (s, 3H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.6, 146.9, 141.4, 138.3, 137.2, 134.1, 131.7, 129.7, 128.5, 128.4, 127.5, 21.6, 21.2, 19.4. HRMS (ESI) Calcd for $C_{19}H_{21}O$ $[M+H]^+$: 265.1587, found: 265.1589.

(E)-1-(furan-2-yl)-3-(p-tolyl)prop-2-en-1-one (3o): (22.5 mg, 53% yield). White solid; mp: 96-98 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 15.8 Hz, 1H), 7.64 (d, *J* = 2.3 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 15.8 Hz, 1H), 7.32 (d, *J* = 3.6 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.58 (dd, *J* = 3.6, 1.7 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100

MHz, Chloroform-*d*) δ 178.1, 153.8, 146.4, 144.1, 141.2, 132.1, 129.7, 128.6, 120.2, 117.3, 112.5, 21.6. HRMS (ESI) Calcd for $C_{14}H_{13}O_2$ $[M+H]^+$: 213.0910, found: 213.0912.

(E)-1-(thiophen-2-yl)-3-(p-tolyl)prop-2-en-1-one (**3p**): (26.0 mg, 57% yield).White solid; mp:112-114 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 - 7.76 (m, 2H), 7.66 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 15.6 Hz, 1H), 7.24 - 7.13 (m, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 182.1, 145.7, 144.2, 141.2, 133.7, 132.0, 131.7, 129.7, 128.5, 128.2, 120.6, 21.6. HRMS (ESI) Calcd for $C_{14}H_{13}OS$ $[M+H]^+$: 229.0682, found: 229.0685.

(E)-1-(naphthalen-2-yl)-3-(p-tolyl)prop-2-en-1-one (**3q**): (27.2 mg, 50% yield). White solid; mp: 141-143 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.10 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.02 - 7.81 (m, 4H), 7.72 - 7.49 (m, 5H), 7.24 (d, *J* = 7.3 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.4, 144.9, 141.1, 135.7, 135.5, 132.6, 132.3, 129.7, 129.8, 129.5, 128.6, 128.3, 127.8, 126.8, 124.6, 121.1, 21.6. HRMS (ESI) Calcd for $C_{20}H_{16}O$ $[M+H]^+$: 272.1201, found: 272.1204.

(E)-3-phenyl-1-(p-tolyl)prop-2-en-1-one (**4a**): (31.1 mg, 70% yield). White solid; mp: 48-50 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 15.7 Hz, 1H), 7.65 - 7.62 (m, 2H), 7.53 (d, *J* = 15.7 Hz, 1H), 7.42 – 7.39 (m, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 190.0, 144.4, 143.7, 135.6, 135.0, 130.4, 129.4, 128.9, 128.7, 128.4, 122.1, 21.7. HRMS (ESI) Calcd for $C_{16}H_{15}O$ $[M+H]^+$: 223.1177, found: 223.1179.

(E)-3-(4-fluorophenyl)-1-(p-tolyl)prop-2-en-1-one (**4b**): (34.6 mg, 72% yield). White solid; mp:152-154 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 6.7 Hz, 2H), 7.77 (d, *J* = 15.7 Hz, 1H), 7.67 - 7.58 (m, 2H), 7.47 (d, *J* = 15.7 Hz, 1H), 7.30 (d, *J* = 7.3 Hz, 2H), 7.16 - 7.05 (m, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 164.0 (d, *J* = 251.6 Hz), 143.7, 143.1, 135.5, 131.3 (d, *J* = 2.8 Hz), 130.3 (d, *J* = 8.5 Hz), 129.4, 128.6, 121.8, 116.1 (d, *J* = 21.9 Hz), 21.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.25. HRMS (ESI) Calcd for $C_{16}H_{14}FO$ $[M+H]^+$: 241.1023, found: 241.1025.

(E)-3-(4-chlorophenyl)-1-(p-tolyl)prop-2-en-1-one (**4c**): (37.9 mg, 74% yield). White solid; mp: 147-149 ^oC; ^1H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 8.2 Hz, 2H), 7.75 (d, J = 15.7 Hz, 1H), 7.60 - 7.47 (m, 3H), 7.39 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 189.7, 143.9, 142.9, 136.3,

135.5, 133.5, 129.6, 129.4, 129.2, 128.7, 122.5, 21.7. HRMS (ESI) Calcd for C16H14ClO [M+H]+: 257.0728, found: 257.0728.

(E)-3-(4-bromophenyl)-1-(p-tolyl)prop-2-en-1-one (**4d**): (37.3 mg, 62% yield). White solid; mp: 132-134 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.93 (d, J = 8.2 Hz, 2H), 7.73 (d, J = 15.7 Hz, 1H), 7.61 - 7.45 (m, 5H), 7.31 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 189.7, 143.8, 142.9, 135.5, 133.9, 132.2, 129.8, 129.4, 128.7, 124.6, 122.6, 21.7. HRMS (ESI) Calcd for C16H14BrO [M+H]+: 301.0223, found: 301.0227.

(E)-3-([1,1'-biphenyl]-4-yl)-1-(p-tolyl)prop-2-en-1-one (**4e**): (38.7 mg, 65% yield). White solid; mp:112-114 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.66 - 7.60 (m, 4H), 7.57 (d, *J* = 15.7 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.9, 143.9, 143.7, 143.2, 140.2, 135.7, 133.9, 129.4, 128.9, 128.7, 127.9, 127.6, 127.1, 121.9, 21.7. HRMS (ESI) Calcd for $C_{22}H_{18}O$ $[M+H]^{+}$: 298.1358, found: 298.1359.

(E)-3-(m-tolyl)-1-(p-tolyl)prop-2-en-1-one (**4f**): (38.2 mg, 81% yield). White solid; mp: 83-84 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.52 (d, *J* = 15.7 Hz, 1H), 7.45 (d, *J* = 6.6 Hz, 2H), 7.34 - 7.27 (m, 3H), 7.22 (d, *J* = 7.5 Hz, 1H), 2.44 (s, 3H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 144.6, 143.6, 138.6, 135.7, 134.9, 131.3, 129.3, 129.1, 128.8, 128.7, 125.7, 121.9, 21.7, 21.4.

(E)-3-(3-chlorophenyl)-1-(p-tolyl)prop-2-en-1-one (**4g**): (29.7 mg, 58% yield). White solid; mp: 71-73 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 15.7 Hz, 1H), 7.64 (s, 1H), 7.56 - 7.46 (m, 2H), 7.39 - 7.21 (m, 4H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.6, 143.9, 142.6, 136.9, 135.4, 134.9, 130.2, 130.2, 129.4, 128.7, 127.8, 126.8, 123.3, 21.7. HRMS (ESI) Calcd for $C_{16}H_{14}ClO$ $[M+H]^{+}$: 257.0728, found: 257.0729.

(E)-3-(2-bromophenyl)-1-(p-tolyl)prop-2-en-1-one (**4h**): (30.0 mg, 50% yield). White solid; mp: 44-46 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 15.7 Hz, 1H), 7.93 - 7.91 (m, 2H), 7.71 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 (d, *J* = 9.1 Hz, 1H), 7.41 (d, *J* = 15.7 Hz, 1H), 7.36 - 7.15 (m, 4H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 143.9, 142.7, 135.3, 135.1, 133.5, 131.3, 129.4, 128.8, 127.9, 127.7, 125.9, 125.1, 21.7. HRMS (ESI) Calcd for $C_{16}H_{14}BrO$ $[M+H]^{+}$: 301.0223, found: 301.0227.

(E)-3-(3,5-dichlorophenyl)-1-(p-tolyl)prop-2-en-1-one (**4i**): (34.8 mg, 60% yield). White solid; mp: 148-150 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.07 (d, J = 15.7 Hz, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.67 (d, J = 8.5 Hz, 1H), 7.51 -

7.40 (m, 2H), 7.32 - 7.24 (m, 3H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-d) δ 189.5, 144.1, 138.8, 136.3, 136.0, 135.2, 131.9, 130.1, 129.4, 128.8, 128.5, 127.5, 124.9, 21.7. HRMS (ESI) Calcd for C16H13Cl2O [M+H]+: 291.0338, found: 291.0339.

(E)-3-(3,4-dimethylphenyl)-1-(p-tolyl)prop-2-en-1-one (**4j**): (41.5 mg, 83% yield). White solid; mp:118-120 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 15.7 Hz, 1H), 7.48 (d, *J* = 15.7 Hz, 1H), 7.43 - 7.34 (m, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 1H), 2.42 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 144.7, 143.5, 139.8, 137.2, 135.8, 132.7, 130.3, 129.6, 129.3, 128.6, 126.1, 21.7, 19.9, 19.8. HRMS (ESI) Calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found: 251.1432.

(E)-3-(3,5-dimethylphenyl)-1-(p-tolyl)prop-2-en-1-one (**4k**): (41.0 mg, 82% yield). White solid; mp: 115-117 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 15.7 Hz, 1H), 7.51 (d, *J* = 15.7 Hz, 1H), 7.33 - 7.22 (m, 4H), 7.04 (s, 1H), 2.43 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.1, 144.8, 143.5, 138.5, 135.7, 134.9, 132.3, 129.3, 128.7, 126.3, 121.9, 21.7, 21.2. HRMS (ESI) Calcd for $C_{18}H_{19}O$ $[M+H]^+$: 251.1430, found: 251.1431.

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Supporting Information:

^{1}H and ^{13}C NMR spectra of compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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