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Direct C–H Functionalization of Enamides and Enecarbamates by Using Visible-Light Photoredox Catalysis

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Abstract: Direct C–H functionalization of various enamides and enecarbamates was realized through visible-light photoredox catalyzed reactions. Under the optimized conditions using [Ir(ppy)$_2$(dtbbpy)PF$_6$] as photocatalyst in combination with Na_2HPO_4, enamides such as *N*-vinylpyrrolidinone could be easily functionalized by irradiation of the reaction mixture overnight in acetonitrile with visible light. The scope of the reaction with respect to enamide and enecarbamate substrates by using diethyl 2-bromomalonate for the alkylation reaction was explored, followed by an investigation of the scope of alkylating reagents used to react with the enamides and enecarbamates. The results indicated that reaction takes place with quite broad substrate scope, however, tertiary enamides with an internal C=C double bond in the *E* configuration could not be alkylated. Alkylation of *N*-vinyl tertiary enamides and enecarbamates gave monoalkylated products exclusively in the *E* configuration. Alkylation of *N*-vinyl secondary enamides gave doubly alkylated products. Double bond migration was observed in the reaction of electron-deficient bromides such as 3-bromoacetyl acetate with *N*-vinylpyrrolidinone. A mechanism is proposed for the reaction that is different from reported reactions of SOMOphiles with a nonfunctionalized C=C double bond. Further tests on the trifluoromethylation and arylation of enamides and enecarbamates under similar conditions showed that the reactions could serve as a mild, practical, and environmentally friendly approach to various functionalized enamides and enecarbamates.

Keywords: alkylation · C–H activation · iridium · photochemistry · redox chemistry

Introduction

Functionalized enamides, including enecarbamates,[1] are important structural motifs that are found in many biologically active natural products and pharmaceuticals such as TMC-95,[2] salicylihalamide A,[3] and related compounds.[4] They also serve as suitable substrates for enantioselective hydrogenation, leading to optically active amines or amino acid derivatives.[5] Furthermore, as electron-deficient counterparts of enamines, enamides can also be used as nucleophiles to undergo many important transformations.[6]

Common strategies used to prepare enamides are based on C–N bond formation, including the condensation of carbonyl compounds with amides[7] or Ullmann-type coupling between vinyl halides and amides.[8] These reported synthetic methods usually require harsh conditions or lead to mixture of *Z*/*E* isomers in parallel. Therefore, more efficient and selective protocols that can be applied under mild conditions to generate functionalized enamides as a single stereoisomer are still in high demand. Because a plethora of simple enamides are commercially available, direct functionalization of these readily available enamides represents a straightforward and flexible approach to various functionalized enamides. Due to their ground-state stability, ionic reactions of enamides have to be carried out under harsh conditions that typically have low functional group tolerance, and functionalized enamides cannot normally be regenerated.[1,9]

With our continuing efforts to use photoreactions as atom-economic synthetic approaches to various frameworks,[10] we are interested in developing green and efficient synthetic approaches to functionalized enamides by direct C–H functionalization of enamides through SOMOphilic pathways.[11–12] Inspired by the recent work of Masson on the generation of β-alkylated α-amido ethers from *N*-acyliminium cations, which were derived from enecarbamate-based SOMOphiles (Figure 1),[13] we envisaged that *N*-acyliminium **II**, generated upon visible-light catalysis, might be able to tautomerize and give a functionalized enamide with the absence of nucleophiles in the reaction system. The incorporation into the reaction of the generation of the primary radical and the oxidation of the amido radical in the same visi-

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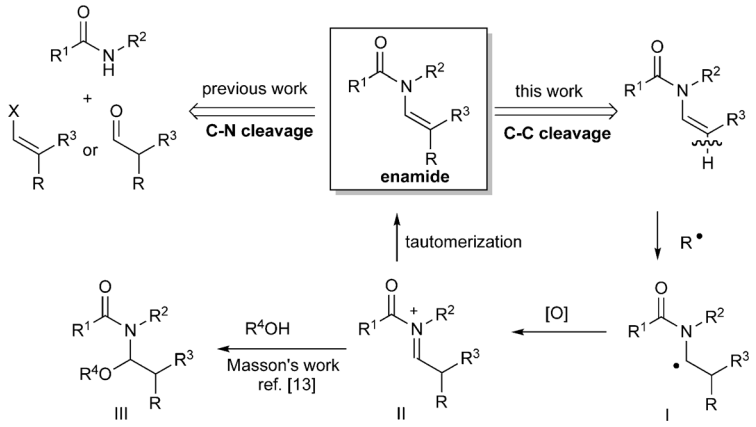


Figure 1. Rational design for direct C–H functionalization of enamides through a radical pathway.

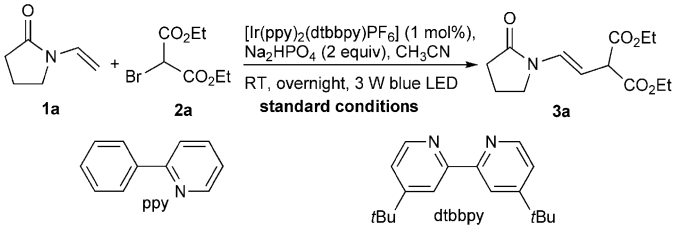
ble-light catalytic cycle could therefore avoid the use of toxic tin[12] or intense UV irradiation.[11]

Over the past five years, visible-light photoredox catalysis pioneered by MacMillan,[14] Yoon,[15] and Stephenson[16] has emerged as a powerful tool that can be used to promote useful single-electron-transfer redox transformations.[17,18] Stephenson and co-workers reported that alkyl radical species generated from electron-deficient bromides upon visible-light photoredox catalysis could react with alkenes, which ended with the formation of saturated halogenated compounds instead of any C–H functionalized alkenes.[16c] Courant and Masson demonstrated the generation of β-alkylated α-amido ethers from *N*-acyliminium cations that were derived from enecarbamate-based SOMOphiles.[13] To the best of our knowledge, there are no reported examples on the preparation of functionalized enamides through visible-light photoredox catalysis. Herein, we would like to report our efforts in direct C–H functionalization of enamides or enecarbamates mediated by visible-light photoredox catalysis using enamides as SOMOphiles.

Results and Discussion

When a solution of *N*-vinylpyrrolidinone (**1a**) and diethyl 2-bromomalonate (**2a**) in acetonitrile was irradiated overnight by visible-light in the presence of photocatalyst $[Ir(ppy)_2(dtbbpy)PF_6]$ and Na_2HPO_4, the alkylated configurationally pure *E*-enamide **3a** could be isolated in 91% yield (Table 1, entry 1). The reaction did not take place without the photocatalyst or base (Table 1, entries 2 and 3). Use of triethylamine (TEA) instead of Na_2HPO_4 led to the formation of the desired product in less than 5% yield due to decomposition of the starting material (Table 1, entry 4). When *N*,*N*-dimethylformamide (DMF) was used as solvent, the desired transformation was shut down (Table 1, entry 5). $[Ru(bpy)_3(PF_6)_2]$ was not a suitable catalyst in this reaction (Table 1, entry 6). When a household fluorescent bulb (26 W) was utilized as the source of visible light instead of 3 W blue LED, a comparable yield was obtained (Table 1, entry 7).

Table 1. Reaction optimization.[a]



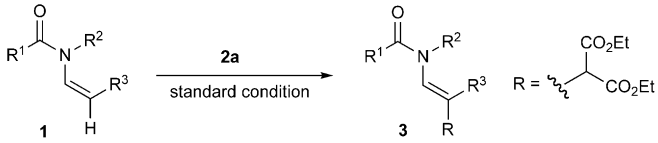
Entry	Conditions	Yield [%][b]
1	standard conditions	91
2	no $[Ir(ppy)_2(dtbbpy)PF_6]$	no reaction[c]
3	no Na_2HPO_4	no reaction[c]
4	TEA instead of Na_2HPO_4	<5[d]
5	DMF instead of CH_3CN	no reaction[c]
6	$[Ru(bpy)_3(PF_6)_2]$ instead of $[Ir(ppy)_2(dtbbpy)PF_6]$	no reaction[c]
7	26 W fluorescent bulb instead of blue LED[e]	90

[a] Reaction conditions: enamide **1a** (0.5 mmol), bromide **2a** (0.6 mmol), base (1.0 mmol), catalyst (0.005 mmol), CH_3CN (2.5 mL), 3 W blue LED, overnight. [b] Isolated yield. [c] The starting material **1a** was fully recovered. [d] The starting material decomposed. [e] Both the fluorescent bulb and the blue LED were purchased from a supermarket.

With the optimized conditions in hand, we examined the alkylation of various enamides with **2a** (Table 2). To our delight, all the monosubstituted tertiary enamides worked quite well (Table 2, entries 1–6). For example, cyclic enamides with a 5- or 6-membered ring (Table 2, entries 1–3) proceeded smoothly to give the desired alkylated enamides **3a** and **3b**, respectively. When the reaction of **1a** with **2a** was conducted on a gram scale with as low as 0.5% catalyst, **3a** could be isolated in comparable yield (Table 2, entry 2). Acyclic enamides **1c–e** were also suitable substrates for this kind of alkylation, and provided enamides **3c–e** in good yields (Table 2, entries 4–6). Interestingly, when monosubstituted secondary enamide **1f** was employed, the reaction did not stop at the monoalkylation stage. The reaction of **1f** with 2.5 equivalents of 2-bromomalonate (**2a**) resulted in the doubly alkylated product **3f** in good yield (Table 2, entry 7). The cyclic disubstituted enamide **1g** was also a good substrate in this reaction and gave the desired product **3g** in good yield (Table 2, entry 8). Whereas alkylation of the acyclic disubstituted *Z*-enamide **1h** gived the desired product **3h** in reasonable yield, the reaction of the *E*-enamide **1i** failed to provide any alkylation product (Table 2, entries 9 and 10).

The alkylation of a range of enecarbamates under the standard reaction conditions was then investigated; the results were shown in Table 3. *N*-Vinyloxazolidinones **1j–l**

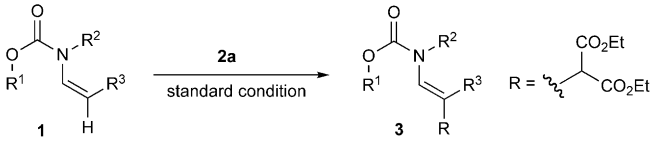
Table 2. Scope of enamides.[a]



Entry	Substrate	Product	Yield [%][b]
1	**1a** ($n=1$)	**3a**	91
2[c]	**1a** ($n=1$)	**3a**	85
3	**1b** ($n=2$)	**3b**	93
4	**1c** (R^1=Me, R^2=Me)	**3c**	81
5	**1d** (R^1=Me, R^2=Ph)	**3d**	75
6	**1e** (R^1=Ph, R^2=Ph)	**3e**	95
7[d]	**1f**	**3f**	57
8	**1g**	**3g**	81
9	**1h**	**3h**	68
10	**1i**	–	–[e]

[a] Reaction conditions: enamide **1** (0.5 mmol), bromide **2a** (0.6 mmol), Na_2HPO_4 (1.0 mmol), $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.005 mmol), CH_3CN (2.5 mL), 3 W blue LED, overnight. [b] Isolated yield. [c] The reaction carried out on 10 mmol scale in the presence of 0.5% $[Ir(ppy)_2(dtbbpy)PF_6]$. [d] 2.5 equiv of **2a** was used. [e] The starting material was fully recovered.

Table 3. Scope of enecarbamates.[a]



Entry	Substrate	Product	Yield [%][b]
1	**1j** (R^1=H)	**3j**	85
2	**1k** (R^1=Ph)	**3k**	83
3	**1l** (R^1=*i*Pr)	**3l**	72
4	**1m** (PG=Cbz)	**3m**	80
5	**1n** (PG=Boc)	**3n**	82

[a] Reaction conditions: enecarbamate **1** (0.5 mmol), bromide **2a** (0.6 mmol), Na_2HPO_4 (1.0 mmol), $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.005 mmol), CH_3CN (2.5 mL), 3 W blue LED, overnight. [b] Isolated yield.

could be alkylated through the reaction with 2-bromomalonate (**2a**) to give the alkylated products **3j–l** in moderate to good yields (Table 3, entries 1–3). Carbamate-protected tetrahydropyridines **1m–n** could also be functionalized under the standard conditions to give trisubstituted cyclic enecarbamates **3m** and **3n** in more than 80% yields (Table 3, entries 4 and 5).

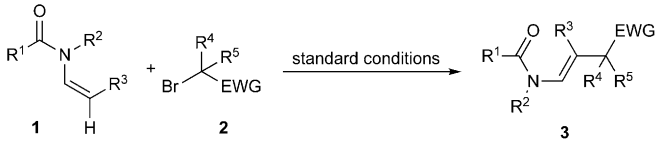
Next, we explored the scope of the alkylating reagents. Remarkably, a variety of electron-deficient bromides underwent this transformation successfully (Table 4). Ethyl 2-bromo-2,2-difluoroacetate (**2b**) reacted with different enamides or enecarbamates to give functionalized enamides **3o–q** in good yields (Table 4, entries 1–3). When 3-bromoacetoacetate (**2c**) was used to react with enecarbamate **1g**, the alkylation proceeded smoothly (Table 4, entry 4). Tertiary bromides (**2d** and **2e**) also worked quite well to give the alkylated products with a quaternary carbon (**3s** and **3t**) in good yields (Table 4, entries 5 and 6).

Interestingly, when more electron-deficient bromides were used as substrates to react with *N*-vinylpyrrolidinone (**1a**), the alkylation proceeded smoothly under the standard conditions, but was accompanied by double bond migration. As shown in Scheme 1, the reactions between *N*-vinylpyrrolidinone (**1a**) and **2c**, **2f–g** gave exclusively the double bond migrated products **3u–w**. When 2-bromo-1,3-diphenylpropane-1,3-dione (**2h**) was used to react with **1a**, both the desired alkylation product **3x** and the double bond migrated product **3y** were obtained. The two isomers **3x** and **3y** could be isolated by flash chromatography, but interconversion between the isomers was observed in solution, which could be monitored by NMR spectroscopic analysis.

It is noteworthy that all the products mentioned above were isolated in the *E* configuration exclusively without other stereoisomers. The *E* configuration of the disubstituted enamindes and enecarbamates was confirmed by the coupling constants observed in the NMR spectra, and the configuration of trisubstituted products (**3h**, **3u**, and **3w**) was confirmed by NOE effects (Figure 2).

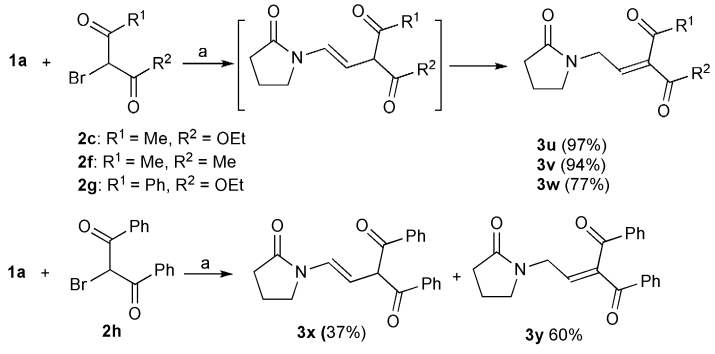
We next carried out control experiments to elucidate the reaction mechanism. The reaction could be totally terminated by the introduction of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), which indicated that this reaction proceeded through a one-electron transfer pathway. A mixture of *N*-vinylpyrrolidinone (**1a**) and 3-bromoacetyl acetate (**2c**) was irradiated under standard conditions until about 50% conversion was reached (2 h) and then the light source was removed. No further progress was observed after the reaction was stirred in the absence of light for 10 h. When the blue LED was reintroduced, the reaction went to comple-

Table 4. Scope of alkylating reagents.[a]



Entry	1	2	3	Yield [%][b]
1[c]	1a	2b	3o	78
2[c]	1b	2b	3p	85
3[c]	1d	2b	3q	75
4	1g	2c	3r	79
5	1a	2d	3s	81
6	1a	2e	3t	81

[a] Reaction conditions: enamide **1** (0.5 mmol), bromide **2** (0.6 mmol), Na_2HPO_4 (1.0 mmol), $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.005 mmol), CH_3CN (2.5 mL), 3 W blue LED, overnight. [b] Isolated yield. [c] $[Ir(dFCF_3ppy)_2(dtbbpy)PF_6]$ was used instead of $[Ir(ppy)_2(dtbbpy)PF_6]$. $dFCF_3ppy$ = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine.



Scheme 1. Alkylation with double bond migration.

tion in 5 h. These results indicated that external light was necessary for this transformation. When EtOH was introduced into the reaction mixture, the enamide was not regenerated under the standard conditions, and the iminium species was trapped by EtOH.[13]

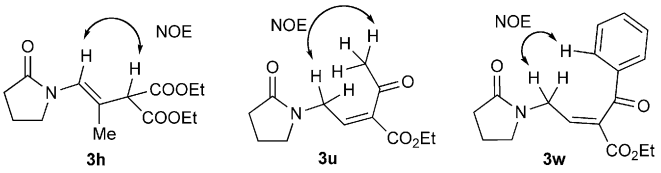


Figure 2. NOE effects of **3h**, **3u**, and **3w**.

On the basis of these observations, a possible catalytic cycle was proposed as shown in Figure 3. The key steps include 1) visible-light excitation of Ir^{3+} complex to generate

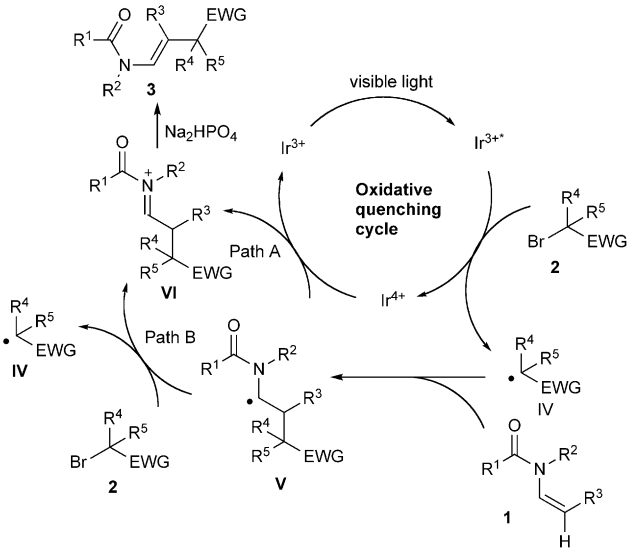
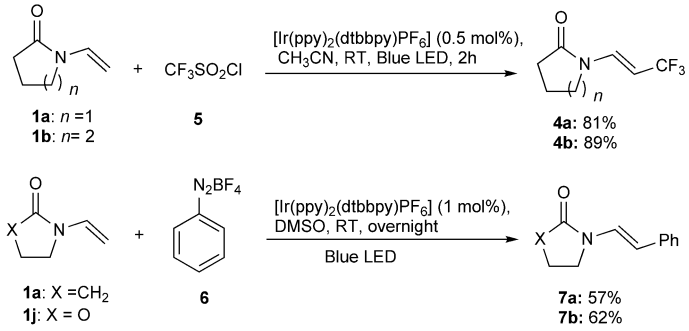


Figure 3. Proposed mechanism of enamides as SOMOphiles in the photoredox catalysis.

Ir^{3+*};[17] 2) oxidative quenching of Ir^{3+*} by electron-deficient bromide **2** to give Ir^{4+} and alkyl radical **IV** respectively;[16c] 3) radical addition of enamide **1** by alkyl radical **I** to provide amido radical **V**;[12h,13] 4) oxidation of amido radical **V** by Ir^{4+} to give *N*-acyliminium cation **VI** and regenaration of Ir^{3+} (Path A);[13] and finally 5) deprotonation and then tautomerization of *N*-acyliminium cation **VI** to produce functionalized enamide **3** assisted by base. At this stage, the radical propagation pathway could not be ruled out completely (Path B).

Given that radical species could be generated from trifluoromethanesulfonyl chloride[19] or aryl diazolium salt[20] under visible-light photoredox conditions, it is possible to realize trifluoromethylation and arylation based on our proposed mechasim (Scheme 2). Indeed, trifluoromethylation of enamides could be achieved under slightly modified standard conditions. *N*-Vinylpyrrolidinone (**1a**) and *N*-vinylpiperridinone (**1b**) could be trifluoromethylated with trifluoromethanesulfonyl chloride (**5**) in satisfactory yield with as low as 0.5% photocatalyst in the absence of base. Furthermore, arylation also worked quite well; *N*-vinylpyrrolidi-



Scheme 2. Trifluoromethylation and arylation of enamides and enecarbamates.

none (**1a**) and *N*-vinyloxazolidinone (**1j**) underwent arylation with phenyl diazolium salt (**6**) under our standard conditions to give aryl enamide **7a** and enecarbamate **7b**, respectively, in acceptable yields.

Conclusion

We have described a mild, practical, and environmentally friendly method for alkylation, trifluoromethylation, and arylation of enamides and enecarbamates through visible-light photoredox catalysis with as low as 0.5% photocatalyst. These reactions proceeded at room temperature in good to excellent chemical yields. Except for tertiary enamides with an internal C=C in the *E* configuration, which were not alkylated under the conditions described, the substrate scope for the reaction is broad and the reaction could be easily scaled up. Alkylation of *N*-vinyl secondary enamides gave doubly alkylated products. Double bond migration was observed in the reaction of electron-deficient bromides such as 3-bromoacetyl acetate with *N*-vinylpyrrolidinone. Alkylation of *N*-vinyl tertiary enamides and enecarbamates gave monoalkylated products exclusively in the *E* configuration. The stereoselective accessibility of functionalized enamides and enecarbamates, which are very important and useful motifs in natural products and chemical transformations, makes this protocol particularly attractive for the chemical community.

Experimental Section

General: CH_3CN and DMSO were dried according to standard procedures. Other reagents were used without further purification. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715) and visualized by fluorescence quenching under UV light and by staining with phosphomolybdic acid or potassium permanganate. Column chromatography was performed on EMD Silica Gel 60 (300–400 Mesh) using a forced flow of 0.5–1.0 bar. ^{1}H (400 MHz), ^{13}C (100 MHz), and ^{19}F (376 MHz) NMR spectra were measured with a Bruker Avance III-400 spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to the residual solvent peak; coupling constants are reported as Hertz (Hz), signal shapes and splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. IR spectra were recorded with a Nicolet 6700 spectrophotometer and are reported as wavenumbers (cm^{-1}). Enamides and enecarbamates **1a–i**,[21] **1m**,[21] **1n**,[21] **1j**,[22] **1k**,[23] **1l**,[24] α-bromine β-keto esters, and 1,3-diketones **2c–g**[25] were prepared according to published literature procedures.

General procedure A: Alkylation: A 10 mL round-bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **1a** (0.5 mmol, 1.0 equiv), **2a** (0.6 mmol, 1.2 equiv), $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.005 mmol, 0.01 equiv), and Na_2HPO_4 (1.0 mmol, 2 equiv). The flask was evacuated and backfilled with argon three times. CH_3CN (2.5 mL, 0.2 M) was added by using a syringe under argon. The mixture was then irradiated with a 3W blue LED strip overnight. When the reaction was complete (as judged by TLC analysis), the mixture was poured into a separating funnel containing H_2O (10 mL) and Et_2O (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2×10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc, 5:1 to 2:1) to afford the desired product.

(*E*)-Diethyl 2-[2-(2-oxopyrrolidin-1-yl)vinyl]malonate (3a): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3a** (112 mg, 91%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.07 (d, J=14.6 Hz, 1H), 5.16 (dd, J=9.5, 14.4 Hz, 1H), 4.26–4.15 (m, 4H), 4.02 (d, J=9.6 Hz, 1H), 3.57 (t, J=7.2 Hz, 2H), 2.49 (t, J=8.2 Hz, 2H), 2.17–2.09 (m, 2H), 1.28 ppm (t, J=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=173.3, 168.4 (2C), 127.9, 103.0, 61.7 (2C), 53.4, 45.0, 31.0, 17.4, 14.0 ppm (2C); IR (thin film): $\tilde{\nu}$=3449, 2986, 1723, 1698, 1662, 1413, 1323, 1303, 1242, 1303, 1242, 1171, 1145, 1094, 1027, 976, 856, 792 cm^{-1}; HRMS (ESI): m/z calcd for $C_{13}H_{20}NO_5$: 270.1336 $[M+H]^+$; found: 270.1337.

(*E*)-Diethyl 2-[2-(2-oxopiperidin-1-yl)vinyl]malonate (3b): According to general procedure A, **1b** (63 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3b** (132 mg, 93%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59 (d, J=14.7 Hz, 1H), 5.22 (dd, J=9.6, 14.6 Hz, 1H), 4.20 (q, J=7.1 Hz, 4H), 4.04 (d, J=9.6 Hz, 1H), 3.46 (t, J=6.0 Hz, 2H), 2.49 (t, J=6.5 Hz, 2H), 1.94–1.88 (m, 2H), 1.84–1.78 (m, 2H), 1.27 ppm (t, J=7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.6, 168.5 (2C), 131.1, 102.4, 61.7 (2C), 53.8, 45.2, 32.9, 22.5, 20.4, 14.0 ppm (2C); IR (thin film): $\tilde{\nu}$=3444, 2983, 2935, 1754, 1731, 1667, 1643, 1480, 1294, 1275, 1177, 1150, 1030, 962, 868 cm^{-1}; HRMS (ESI): m/z calcd for $C_{14}H_{22}NO_5$: 284.1492 $[M+H]^+$; found: 284.1497.

(*E*)-Diethyl 2-[2-(*N*-methylacetamido)vinyl]malonate (3c): According to general procedure A, **1c** (50 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3c** (104 mg, 81%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.52 and 6.86 (both d, J=14.6 and 13.8 Hz, 1H, rotamers), 5.19 (dd, J=9.6, 13.6 Hz, 1H), 4.25–4.18 (m, 4H), 4.03 and 3.99 (both d, J=9.5 and 9.4 Hz, 1H, rotamers), 3.15 and 3.10 (both s, 3H, rotamers), 2.23 and 2.21 (both s, 3H, rotamers), 1.30–1.26 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=169.2 and 169.1 (1C, rotamers), 168.6 and 168.4 (2C, rotamers), 133.2 and 131.2 (1C, rotamers), 102.3 and 101.9 (1C, rotamers), 61.8 and 61.7 (2C, rotamers), 53.6 and 53.5 (1C, rotamers), 33.0 and 29.3 (1C, rotamers), 22.5 and 21.8 (1C, rotamers), 14.0 ppm; IR (thin film): $\tilde{\nu}$=3463, 2982, 2937, 1732, 1681, 1649, 1467, 1391, 1368, 1273, 1178, 1148, 1019, 939, 862, 592 cm^{-1}; HRMS (ESI): m/z calcd for $C_{12}H_{20}NO_5$: 258.1336 $[M+H]^+$; found: 258.1339.

(*E*)-Diethyl 2-[2-(*N*-phenylacetamido)vinyl]malonate (3d): According to general procedure A, **1d** (80 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3d** (120 mg, 75%) as a colorless oil. IR (thin film): $\tilde{\nu}$=2979, 1735, 1682, 1662, 1495, 1373, 1312, 1270, 1224, 1183, 1117, 1029, 955, 703, 574, 521 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.68 (d, J=14.2 Hz, 1H), 7.51–7.48 (m, 2H), 7.45–7.41 (m, 1H), 7.21–7.19 (m, 2H), 4.64 (dd, J=9.6, 14.4 Hz, 1H), 4.20–4.09 (m, 4H), 4.01 (d, J=9.6 Hz, 1H), 1.86 (s, 3H), 1.22 ppm (t, J=7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=168.8, 168.3 (2C), 139.2, 132.3, 130.2

(2C), 128.9, 128.6 (2C), 105.2, 61.5 (2C), 53.4, 23.1, 13.9 ppm (2C); HRMS (ESI): *m/z* calcd for $C_{17}H_{22}NO_5$: 320.1492 $[M+H]^+$; found: 320.1496.

(*E*)-Diethyl 2-[2-(*N*-phenylbenzamido)vinyl]malonate (3e): According to general procedure A, **1e** (111 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3e** (181 mg, 95%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.62$ (d, $J=14.4$ Hz, 1H), 7.33–7.28 (m, 4H), 7.26–7.22 (m, 2H), 7.20–7.16 (m, 2H), 7.13–7.11 (m, 2H), 4.97 (dd, $J=9.6$, 14.4 Hz, 1H), 4.23–4.11 (m, 4H), 4.06 (d, $J=9.6$ Hz, 1H), 1.25 ppm (t, $J=7.1$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=$ 169.0, 168.3 (2C), 139.4, 135.0, 133.6, 130.1, 129.6 (2C), 129.0 (2C), 128.6 (2C), 128.1, 127.8 (2C), 106.7, 61.7 (2C), 53.5, 14.0 ppm (2C); IR (thin film): $\tilde{\nu}=3087$, 2980, 1735, 1664, 1596, 1494, 1448, 1375, 1326, 1309, 1215, 1180, 1116, 1025, 952, 733, 700, 657, 585, 517 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{22}H_{24}NO_5$: 382.1649 $[M+H]^+$; found: 382.1676.

Tetraethyl 2-(acetamidomethylene)propane-1,1,3,3-tetracarboxylate (3f): According to general procedure A, **1f** (43 mg, 0.5 mmol), **2a** (600 mg, 1.25 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3f** (114 mg, 57%) as a white solid powder. ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.85$ (d, $J=10.3$ Hz, 1H), 7.04 (d, $J=10.5$ Hz, 1H), 4.53 (s, 1H), 4.26–4.12 (m, 8H), 4.07 (s, 1H), 2.06 (s, 3H), 1.30–1.25 ppm (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.6$ (2C), 167.9, 167.8 (2C), 129.3, 105.4, 62.2 (2C), 61.8 (2C), 57.9, 51.7, 23.3, 13.9 ppm (4C); IR (thin film): $\tilde{\nu}=2984$, 1732, 1665, 1508, 1446, 1370, 1304, 1220, 1177, 1152, 1096, 1034 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{28}NO_9$: 402.1759 $[M+H]^+$; found: 402.1766.

Diethyl 2-(1-benzyl-6-oxo-1,4,5,6-tetrahydropyridin-3-yl)malonate (3g): According to general procedure A, **1g** (93 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3g** (140 mg, 81%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.33$–7.21 (m, 5H), 6.07 (s, 1H), 4.68 (s, 2H), 4.22–4.15 (m, 4H), 3.98 (s, 1H), 2.62 (t, $J=7.6$ Hz, 2H), 2.49 (t, $J=7.8$ Hz, 2H), 1.24 ppm (t, $J=7.2$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.1$, 167.7 (2C), 136.9, 129.5, 128.7 (2C), 127.6 (2C), 127.6, 112.3, 61.7 (2C), 55.8, 48.9, 31.2, 22.6, 14.0 ppm (2C); IR (thin film): $\tilde{\nu}=$ 2981, 2936, 1731, 1675, 1443, 1406, 1379, 1304, 1271, 1177, 1146, 1094, 1031, 730, 701, 499 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{19}H_{24}NO_5$: 346.1649 $[M+H]^+$; found: 346.1652.

(*E*)-Diethyl 2-[1-(2-oxopyrrolidin-1-yl)prop-1-en-2-yl]malonate (3h): According to general procedure A, **1h** (62 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3h** (96 mg, 68%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.48$ (s, 1H), 4.27–4.15 (m, 4H), 4.05 (s, 1H), 3.81 (t, $J=7.0$ Hz, 2H), 2.42 (t, $J=8.1$ Hz, 2H), 2.13–2.05 (m, 2H), 1.92 (d, $J=1.0$ Hz, 3H), 1.28 ppm (t, $J=7.1$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=174.9$, 168.2 (2C), 125.5, 116.8, 61.6 (2C), 59.2, 48.5, 30.3, 18.8, 14.6, 14.0 ppm (2C); IR (thin film): $\tilde{\nu}=2981$, 2929, 1731, 1701, 1462, 1408, 1385, 1368, 1302, 1264, 1208, 1149, 1095, 1032 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{22}NO_5$: 284.1492 $[M+H]^+$; found: 284.1497.

(*E*)-Diethyl 2-[2-(2-Oxooxazolidin-3-yl)vinyl]malonate (3j): According to general procedure A, **1j** (56 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3j** (115 mg, 85%) as a colorless oil. IR (thin film): $\tilde{\nu}=2984$, 1747, 1671, 1481, 1416, 1369, 1330, 1301, 1229, 1177, 1152, 1129, 1076, 1031, 948, 757 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.86$ (d, $J=14.3$ Hz, 1H), 5.06 (dd, $J=9.5$, 14.4 Hz, 1H), 4.50–4.46 (m, 2H), 4.26–4.17 (m, 4H), 4.04 (dd, $J=0.4$, 9.4 Hz, 1H), 3.78 (t, $J=8.3$ Hz, 2H), 1.28 ppm (t, $J=7.1$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.2$ (2C), 155.2, 128.3, 102.1, 62.4, 61.8 (2C), 53.0, 42.3, 13.9 ppm (2C); HRMS (ESI): *m/z* calcd for $C_{12}H_{18}NO_6$: 272.1129 $[M+H]^+$; found: 272.1130.

(*R,E*)-diethyl 2-[2-(2-oxo-4-phenyloxazolidin-3-yl)vinyl]malonate (3k): According to general procedure A, **1k** (94 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3k** (144 mg, 83%) as a colorless oil. $[\alpha]_D^{20}=-83.3$ ($c=2.77$, in CH_3CN); ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.41$–7.32 (m, 3H), 7.27–7.24 (m, 2H), 6.80 (d, $J=14.4$ Hz, 1H), 5.09 (dd, $J=5.1$, 9.0 Hz, 1H), 4.84 (dd, $J=9.5$, 14.6 Hz, 1H), 4.74 (t, $J=$ 8.9 Hz, 1H), 4.20–4.12 (m, 3H), 4.01–3.92 (m, 2H), 3.86 (dd, $J=0.4$, 9.6 Hz, 1H), 1.24 (t, $J=7.1$ Hz, 3H), 1.06 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.2$, 167.7, 155.5, 137.5, 129.3 (2C), 128.8, 127.0, 126.0 (2C), 104.6, 70.7, 61.8, 61.5, 58.3, 53.4, 14.0, 13.8 ppm; IR (thin film): $\tilde{\nu}=2983$, 1765, 1672, 1476, 1458, 1408, 1368, 1299, 1216, 1176, 1127, 1073, 1034, 947, 758, 701 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{22}NO_6$: 348.1442 $[M+H]^+$; found: 348.1444.

(*R,E*)-Diethyl 2-[2-(4-isopropyl-2-oxooxazolidin-3-yl)vinyl]malonate (3l): According to general procedure A, **1l** (77 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3l** (113 mg, 72%) as a colorless oil. $[\alpha]_D^{20}=-62.5$ ($c=0.40$, in CH_3CN); ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.76$ (d, $J=14.7$ Hz, 1H), 5.17 (dd, $J=9.6$, 14.7 Hz, 1H), 4.32–4.18 (m, 6H), 4.11–4.07 (m, 1H), 4.00 (d, $J=9.6$ Hz, 1H), 2.49–2.41 (m, 1H), 1.30–1.26 (m, 6H), 0.94 (d, $J=7.0$ Hz, 3H), 0.84 ppm (d, $J=6.9$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.4$, 168.3, 155.4, 127.2, 102.9, 63.2, 61.9, 61.8, 58.2, 53.4, 26.0, 17.8, 14.0, 13.9 ppm; IR (thin film): $\tilde{\nu}=2966$, 2936, 1750, 1672, 1466, 1415, 1394, 1369, 1316, 1217, 1178, 1151, 1123, 1031, 951, 863, 759, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{15}H_{24}NO_6$: 314.1598 $[M+H]^+$; found: 314.1603.

Diethyl 2-[1-(Benzyloxycarbonyl)-1,4,5,6-tetrahydropyridin-3-yl]malonate (3m): According to general procedure A, **1m** (110 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3m** (150 mg, 80%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.36$–7.28 (m, 5H), 6.97 and 6.86 (both s, 1H, rotamers), 5.17 (s, 2H), 4.21–4.16 (m, 4H), 4.02 and 3.95 (both s, 1H, rotamers), 3.62–3.58 (m, 2H), 2.20 (t, $J=5.8$ Hz, 2H), 1.87–1.82 (m, 2H), 1.28–1.2 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.2$ (2C), 153.5 and 152.9 (1C, rotamers), 136.2 and 136.1 (1C, rotamers), 128.5 (2C), 128.3 and 128.2 (1C, rotamers), 128.2, 128.0, 126.0 and 125.4 (1C, rotamers), 111.4 and 110.8 (1C, rotamers), 67.7 and 67.5 (1C, rotamers), 61.5, 61.4, 57.3, 42.1 and 41.0 (1C, rotamers), 23.4 and 22.9 (1C, rotamers), 21.4 and 21.2 (1C, rotamers), 14.0 ppm (2C); IR (thin film): $\tilde{\nu}=2981$, 1731, 1708, 1668, 1446, 1408, 1311, 1260, 1177, 1147, 1110, 1030, 989, 861, 761, 698, 602 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{20}H_{26}NO_6$: 376.1755 $[M+H]^+$; found: 376.1758.

Diethyl 2-[1-(*tert*-butoxycarbonyl)-1,4,5,6-tetrahydropyridin-3-yl]malonate (3n): According to general procedure A, **1n** (91 mg, 0.5 mmol), **2a** (143 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3n** (140 mg, 82%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.94$ and 6.78 (both s, 1H, rotamers), 4.23–4.19 (m, 4H), 4.00 and 3.97 (both s, 1H, rotamers), 3.56–3.49 (m, 2H), 2.18 (t, $J=5.6$ Hz, 2H), 1.88–1.80 (m, 2H), 1.48 (s, 9H), 1.32–1.24 ppm (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=168.3$ (2C), 152.6 and 151.9 (1C, rotamers), 126.1 and 126.0 (1C, rotamers), 110.0 and 109.3 (1C, rotamers), 80.9 and 80.7 (1C, rotamers), 61.4, 61.3, 57.5 and 57.4 (1C, rotamers), 42.2 and 41.2 (1C, rotamers), 28.2 (3C), 23.4 and 22.9 (1C, rotamers), 21.5 and 21.3 (1C, rotamers), 14.0 ppm (2C); IR (thin film): $\tilde{\nu}=2979$, 2936, 1733, 1703, 1665, 1394, 1367, 1306, 1255, 1156, 1033, 989, 855, 767 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{28}NO_6$: 342.1911 $[M+H]^+$; found: 342.1917.

(*E*)-Ethyl 2,2-difluoro-4-(2-oxopyrrolidin-1-yl)but-3-enoate (3o): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2b** (121 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(dFCF_3ppy)_2(dtbbpy)PF_6]$ (5.6 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3o** (91 mg, 78%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.56$ (dt, $J=14.5$, 2.2 Hz, 1H), 5.08 (dt, $J=14.5$, 11.0 Hz, 1H), 4.33 (q, $J=7.1$ Hz, 2H), 3.54 (t, $J=$ 7.3 Hz, 2H), 2.54 (t, $J=8.2$ Hz, 2H), 2.21–2.13 (m, 2H), 1.36 ppm (t, $J=$ 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=173.9$, 164.0 (t, $J=35.2$ Hz; 1C), 130.4 (t, $J=10.6$ Hz; 1C), 113.0 (t, $J=246.9$ Hz; 1C), 101.1 (t, $J=$ 26.2 Hz; 1C), 63.0, 44.8, 30.9, 17.4, 13.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-99.8$ ppm (2F); IR (thin film): $\tilde{\nu}=3448$, 2984, 1764, 1721, 1658, 1462, 1402, 1338, 1303, 1229, 1181, 1076, 1036, 966, 851 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{10}H_{14}F_2NO_3$: 234.0936 $[M+H]^+$; found: 234.0940.

(*E*)-Ethyl 2,2-difluoro-4-(2-oxooxazolidin-3-yl)but-3-enoate (3p): According to general procedure A, **1b** (56 mg, 0.5 mmol), **2b** (121 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(dFCF_3ppy)_2(dtbbpy)PF_6]$ (5.6 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3p** (109 mg, 85%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.37$ (d, $J=14.4$ Hz, 1H), 5.02 (dt, $J=14.4$, 11.0 Hz, 1H), 4.54–4.50 (m, 2H), 4.34 (q, $J=7.2$ Hz, 2H), 3.77 (t, $J=8.0$ Hz, 2H), 1.36 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=163.8$ (t, $J=35.2$ Hz; 1C), 154.8, 131.2 (t, $J=10.6$ Hz; 1C), 112.6 (t, $J=246.9$ Hz; 1C), 100.6 (t, $J=26.4$ Hz; 1C), 63.2, 62.4, 42.1, 13.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-99.9$ ppm (2F); IR (thin film): $\tilde{\nu}=2988$, 2923, 1763, 1669, 1480, 1418, 1373, 1343, 1302, 1202, 1070, 1033, 958, 757, 659 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_9H_{11}F_2NO_4Na$: 258.0548 $[M+Na]^+$; found: 258.0549.

(*E*)-Ethyl 2,2-difluoro-4-(*N*-phenylacetamido)but-3-enoate (3q): According to general procedure A, **1d** (80 mg, 0.5 mmol), **2b** (121 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(dFCF_3ppy)_2(dtbbpy)PF_6]$ (5.6 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3q** (114 mg, 75%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.16$ (d, $J=13.8$ Hz, 1H), 7.56–7.46 (m, 3H), 7.20–7.17 (m, 2H), 4.58–4.49 (m, 1H), 4.29 (q, $J=7.1$ Hz, 2H), 1.91 (s, 3H), 1.32 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.3$, 164.0 (t, $J=35.2$ Hz; 1C), 138.4, 134.9 (t, $J=10.1$ Hz; 1C), 130.5 (2C), 129.5, 128.5 (2C), 113.2 (t, $J=246.4$ Hz; 1C), 102.8 (t, $J=26.2$ Hz; 1C), 62.9, 23.2, 13.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-99.6$ ppm (2F); IR (thin film): $\tilde{\nu}=3095$, 2985, 1765, 1698, 1657, 1596, 1495, 1453, 1372, 1318, 1250, 1067, 970, 855, 776, 700, 594, 555 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{14}H_{15}F_2NO_3Na$: 306.0912 $[M+Na]^+$; found: 306.0932.

Ethyl 2-(1-benzyl-6-oxo-1,4,5,6-tetrahydropyridin-3-yl)-3-oxobutanoate (3r): According to general procedure A, **1g** (93 mg, 0.5 mmol), **2c** (125 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3r** (125 mg, 79%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.35$–7.25 (m, 5H), 5.64 (d, $J=9.3$ Hz, 1H), 5.38 (d, $J=14.9$ Hz, 1H), 4.23–4.11 (m, 2H), 4.06 (d, $J=15.1$ Hz, 1H), 3.46–3.43 (m, 1H), 2.43–2.40 (m, 2H), 2.20 (d, $J=1.4$ Hz, 3H), 2.19–2.13 (m, 1H), 1.96–1.83 (m, 1H), 1.27 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=172.7$, 168.1, 165.1, 136.7, 128.7 (2C), 128.2 (2C), 127.6, 103.7, 90.9, 59.7, 47.6, 39.5, 29.6, 22.9, 14.4, 14.2 ppm; IR (thin film): $\tilde{\nu}=2977$, 1686, 1645, 1465, 1453, 1383, 1333, 1260, 1229, 1136, 1098, 1072, 962, 937, 866, 769, 700 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{18}H_{22}NO_4$: 316.1543 $[M+H]^+$; found: 316.1547.

(*E*)-Ethyl 2-acetyl-2-methyl-4-(2-oxopyrrolidin-1-yl)but-3-enoate (3s): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2d** (134 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3s** (103 mg, 81%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.01$ (d, $J=14.9$ Hz, 1H), 5.41(d, J=14.9 Hz, 1H), 4.22 (q, $J=7.1$ Hz, 2H), 3.57 (t, $J=7.2$ Hz, 2H), 2.50 (t, $J=8.1$ Hz, 2H), 2.17 (s, 3H), 2.16–2.09 (m, 2H), 1.55 (s, 3H), 1.27 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=203.5$, 173.3, 171.9, 125.8, 109.4, 61.7, 60.3, 45.1, 31.1, 26.0, 19.4, 17.4, 14.0 ppm; IR (thin film): $\tilde{\nu}=2983$, 1713, 1654, 1461, 1402, 1355, 1338, 1297, 1230, 1107, 1021, 959 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{13}H_{20}NO_4$: 254.1387 $[M+H]^+$; found: 254.1389.

(*E*)-3-Methyl-3-[2-(2-oxopyrrolidin-1-yl)vinyl]pentane-2,4-dione (3t): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2e** (116 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3t** (91 mg, 81%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.99$ (d, $J=14.9$ Hz, 1H), 5.48 (d, $J=15.0$ Hz, 1H), 3.58 (t, $J=7.2$ Hz, 2H), 2.51 (t, $J=8.2$ Hz, 2H), 2.18–2.10 (m, 2H), 2.15 (s, 6H), 1.54 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=205.5$ (2C), 173.4, 126.1, 109.1, 66.8, 45.2, 31.1, 26.6 (2C), 18.5, 17.4 ppm; IR (thin film): $\tilde{\nu}=3448$, 2924, 2358, 1698, 1652, 1461, 1402, 1355, 1297, 1250, 1203, 1090, 1016, 962 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}NO_3$: 224.1281 $[M+H]^+$; found: 224.1284.

(*E*)-Ethyl 2-acetyl-4-(2-oxopyrrolidin-1-yl)but-2-enoate (3u): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2c** (125 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3u** (116 mg, 97%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.46$ (dd, $J=4.9$, 10.0 Hz, 1H), 4.18 (q, $J=7.1$ Hz, 2H), 3.42–3.36 (m, 1H), 3.31–3.25 (m, 1H), 3.15–3.08 (m, 1H), 2.72 (dd, $J=3.5$, 15.8 Hz, 1H), 2.43 (t, $J=8.2$ Hz, 2H), 2.22 (s, 3H), 2.12–1.99 (m, 2H), 1.29 ppm (t, $J=7.1$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=175.4$, 166.7, 165.3, 100.9, 82.4, 59.6, 41.1, 32.0, 31.0, 17.7, 14.3, 13.5 ppm; IR (thin film): $\tilde{\nu}=2980$, 1701, 1650, 1462, 1418, 1384, 1324, 1287, 1261, 1219, 1149, 1084, 1022, 957, 893, 764 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{12}H_{18}NO_4$: 240.1230 $[M+H]^+$; found: 240.1229.

3-[2-(2-oxopyrrolidin-1-yl)ethylidene]pentane-2,4-dione (3v): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2f** (107 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3v** (99 mg, 94%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): $\delta=6.47$ (dd, $J=5.0$, 10.0 Hz, 1H), 3.41–3.35 (m, 1H), 3.30–3.24 (m, 1H), 3.21–3.13 (m, 1H), 2.82–2.76 (m, 1H), 2.45–2.41 (m, 2H), 2.26 (t, $J=1.6$ Hz, 3H), 2.24 (s, 3H), 2.11–2.04 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=193.8$, 175.5, 166.4, 111.5, 82.5, 41.2, 32.7, 31.0, 29.5, 17.8, 14.6 ppm; IR (thin film): $\tilde{\nu}=3343$, 3004, 2981, 2912, 1683, 1604, 1424, 1384, 1363, 1283, 1269, 1213, 1155, 1130, 981, 926, 905, 784, 627 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{11}H_{16}NO_3$: 210.1125 $[M+H]^+$; found: 210.1127.

(*E*)-Ethyl 2-benzoyl-4-(2-oxopyrrolidin-1-yl)but-2-enoate (3w): According to general procedure A, **1a** (56 mg, 0.5 mmol), **2g** (163 mg, 0.6 mmol), Na_2HPO_4 (142 mg, 1 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in CH_3CN (2.5 mL) afforded **3w** (125 mg, 77%) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.81$–7.79 (m, 2H), 7.44–7.35 (m, 3H), 6.60 (dd, $J=4.9$, 10.1 Hz, 1H), 4.18–4.13 (m, 2H), 3.50–3.44 (m, 1H), 3.41–3.34 (m, 2H), 2.95 (dd, $J=4.9$, 16.5 Hz, 1H), 2.43 (t, $J=8.2$ Hz, 2H), 2.13–1.98 (m, 2H), 1.22 ppm (t, $J=7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=175.5$, 164.6, 163.9, 130.7, 129.3 (2C), 129.1, 127.7 (2C), 101.2, 81.8, 60.0, 41.3, 34.1, 31.1, 17.9, 14.2 ppm; IR (thin film): $\tilde{\nu}=$ 2980, 1702, 1630, 1493, 1447, 1415, 1242, 1154, 1085, 1068, 1022, 888, 759, 695 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_{17}H_{19}NO_4$ Na: 324.1206 $[M+Na]^+$; found: 324.1273.

General procedure B: Trifluoromethylation: A 10 mL round-bottom flask was equipped with a rubber septum and magnetic stir bar and was charged with **1a** (0.5 mmol, 1.0 equiv), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.0025 mmol, 0.005 equiv). The flask was evacuated and backfilled with argon three times. Compound **5** (1 mmol, 2 equiv) and CH_3CN (2.5 mL, 0.2 M) was added by using a syringe under argon. The mixture was then irradiated with a 3 W blue LED strip for 2 h. When the reaction was complete (as judged by TLC analysis), the mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (hexane/EtOAc, 5:1 to 2:1) to afford the desired product.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)pyrrolidin-2-one (4a): According to general procedure B, **1a** (56 mg, 0.5 mmol), **5** (106 μL, 1.0 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (2.5 mg, 0.0025 mmol) in CH_3CN (2.5 mL) afforded **4a** (82 mg, 81%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): $\delta=7.63$ (dd, $J=1.8$, 14.4 Hz, 1H), 5.05–4.96 (m, 1H), 3.54 (t, $J=7.2$ Hz, 2H), 2.55 (t, $J=8.1$ Hz, 2H), 2.22–2.15 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=174.1$, 131.1 (q, $J=7.3$ Hz; 1C), 124.3 (q, $J=266.5$ Hz; 1C), 98.4 (q, $J=34.8$ Hz; 1C), 44.7, 30.8, 17.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=-60.4$ ppm (3F); IR (thin film): $\tilde{\nu}=3098$, 3071, 2974, 1720, 1667, 1484, 1419, 1338, 1239, 1117, 1042, 979, 832, 777, 658, 625, 526 cm^{-1}; HRMS (ESI): *m/z* calcd for $C_7H_8F_3NONa$: 202.0450 $[M+Na]^+$; found: 202.0448.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)piperidin-2-one (4b): According to general procedure B, **1b** (63 mg, 0.5 mmol), **5** (106 μL, 1.0 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (2.5 mg, 0.0025 mmol) in CH_3CN (2.5 mL) afforded **4b** (96 mg, 89%) as a white solid. IR (thin film): $\tilde{\nu}=3093$, 2947, 1691, 1649, 1474, 1414, 1331, 1272, 1168, 1089, 982, 876, 748, 648 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): $\delta=8.17$ (dd, $J=1.9$, 14.7 Hz, 1H), 5.09–5.01 (m, 1H), 3.41 (t, $J=6.2$ Hz, 2H), 2.55 (t, $J=6.6$ Hz, 2H), 1.99–1.91 (m, 2H), 1.89–1.82 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=169.2$, 134.3 (q, $J=7.2$ Hz; 1C), 124.6 (q, $J=265.9$ Hz; 1C), 97.7 (q, $J=34.3$ Hz; 1C), 45.3, 33.0, 22.3, 20.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta=$ −60.0 ppm (3F); HRMS (ESI): *m/z* calcd for $C_8H_{10}F_3NONa$: 216.0607 $[M+Na]^+$; found: 216.0606.

General procedure C: Arylation: A 10 mL round-bottom flask was equipped with a rubber septum and magnetic stir bar and charged with **6**

(0.5 mmol, 1 equiv), **1a** (1 mmol, 2 equiv), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (0.005 mmol, 0.01 equiv). The flask was evacuated and backfilled with argon three times. DMSO (2.5 mL, 0.2 M) was added by using a syringe under argon. The mixture was then irradiated with a 3 W blue LED strip overnight. When the reaction was complete (as judged by TLC analysis), the mixture was poured into a separating funnel containing H_2O (10 mL) and Et_2O (15 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2×10 mL). The combined organic layers were dried with Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc, 8:1 to 5:1) to afford the desired product.

(*E*)-1-Styrylpyrrolidin-2-one (7a): According to general procedure C, **1a** (112 mg, 1 mmol), **6** (100 mg, 0.5 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in DMSO (2.5 mL) afforded **7a** (54 mg, 57%) as a white solid. IR (thin film): $\tilde{\nu}$=2969, 2934, 2896, 1688, 1641, 1481, 1449, 1407, 1339, 1288, 1240, 959, 751, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=7.62 (d, J=14.8 Hz, 1H), 7.36–7.34 (m, 2H), 7.30–7.26 (m, 2H), 7.19–7.15 (m, 1H), 5.87 (d, J=14.9 Hz, 1H), 3.63 (t, J=7.2 Hz, 2H), 2.53 (t, J=8.1 Hz, 2H), 2.18–2.09 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=173.4, 136.4, 128.7 (2C), 126.6, 125.7 (2C), 123.6, 111.8, 45.3, 31.3, 17.5 ppm; HRMS (ESI): m/z calcd for $C_{12}H_{14}NO$: 188.1070 $[M+H]^+$; found: 188.1070.

(*E*)-3-Styryloxazolidin-2-one (7b): According to general procedure C, **1j** (113 mg, 1 mmol), **6** (100 mg, 0.5 mmol), and $[Ir(ppy)_2(dtbbpy)PF_6]$ (5 mg, 0.005 mmol) in DMSO (2.5 mL) afforded **7b** (66 mg, 62%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$): δ=7.38 (d, J=14.7 Hz, 1H), 7.34–7.26 (m, 4H), 7.20–7.16 (m, 1H), 5.77 (d, J=14.7 Hz, 1H), 4.51–4.47 (m, 2H), 3.86–3.82 ppm (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.4, 135.9, 128.8 (2C), 126.7, 125.5 (2C), 124.0, 111.1, 62.3, 42.5 ppm; IR (thin film): $\tilde{\nu}$=2921, 1747, 1655, 1596, 1481, 1450, 1417, 1340, 1285, 1230, 1178, 1083, 1035, 977, 933, 823, 749, 692, 612; HRMS (ESI): m/z calcd for $C_{11}H_{11}NO_2Na$: 212.0682 $[M+Na]^+$; found: 212.0718.

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[1] a) D. R. Carbery, *Org. Biomol. Chem.* **2008**, *6*, 3455; b) G. R. Dake, *Synlett* **2012**, *23*, 814.
[2] J. Kohno, Y. Koguchi, M. Nisshio, K. Nakao, M. Kuroda, R. Shimizu, T. Ohnuki, S. J. Komatsubara, *J. Org. Chem.* **2000**, *65*, 990.
[3] K. L. Erickson, J. A. Beutler, J. H. Cardellina, II, M. R. Boyd, *J. Org. Chem.* **1997**, *62*, 8188.
[4] L. Yet, *Chem. Rev.* **2003**, *103*, 4283.
[5] For recent reviews, see: a) K. Gopalaiah, H. B. Kagan, *Chem. Rev.* **2011**, *111*, 4599; b) T. C. Nugent, M. El-Shazly, *Adv. Synth. Catal.* **2010**, *352*, 753.
[6] R. Matsubara, S. Kobayashi, *Acc. Chem. Res.* **2008**, *41*, 292.
[7] For selected examples of condensation of amides and carbonyl compounds, see: a) C. A. Zezza, M. B. Smith, *Synth. Commun.* **1987**, *17*, 729; b) M. J. Kiefel, J. Maddock, G. Pattenden, *Tetrahedron Lett.* **1992**, *33*, 3227; c) W. Adam, S. G. Bosio, N. J. Turro, B. T. Wolff, *J. Org. Chem.* **2004**, *69*, 1704.
[8] For recent selected examples, see: a) R. C. Shen, J. A. Porco, Jr., *Org. Lett.* **2000**, *2*, 1333; b) R. Shen, C. T. Lin, J. A. Porco, Jr., *J. Am. Chem. Soc.* **2002**, *124*, 5650; c) L. Jiang, G. E. Job, A. Klapars, S. L. Buchwald, *Org. Lett.* **2003**, *5*, 3667; d) X. Pan, Q. Cai, D. Ma, *Org. Lett.* **2004**, *6*, 1809; e) C. Han, R. Shen, S. Su, J. A. Porco Jr., *Org. Lett.* **2004**, *6*, 27; f) R. S. Coleman, P.-H. Liu, *Org. Lett.* **2004**, *6*, 577; g) L. Shen, R. P. Hsung, Y. Zhang, J. E. Antoline, X. Zhang, *Org. Lett.* **2005**, *7*, 3081; h) T. Hu, C. Li, *Org. Lett.* **2005**, *7*, 2035; i) M. C. Willis, G. N. Brace, I. P. Homes, *Synthesis* **2005**, 3229; j) C. Sun, J. E. Camp, S. M. Weinreb, *Org. Lett.* **2006**, *8*, 1779; k) Y. Bolshan, R. A. Batey, *Angew. Chem.* **2008**, *120*, 2139; *Angew. Chem. Int. Ed.* **2008**, *47*, 2109. l) For a general review of the synthesis of enamides and related compounds by cross-coupling reactions, see: J. R. Dehli, J. L. Legross, C. Bolm, *Chem. Commun.* **2005**, 973.
[9] For recent selected examples, see: a) R. Matsubara, P. Vital, Y. Nakamura, H. Kiyohara, S. Kobayashi, *Tetrahedron* **2004**, *60*, 9769; b) R. Matsubara, Y. Nakamura, S. Kobayashi, *Angew. Chem.* **2004**, *116*, 1711; *Angew. Chem. Int. Ed.* **2004**, *43*, 1679; c) R. Matsubara, Y. Nakamura, S. Kobayashi, *Angew. Chem.* **2004**, *116*, 3320; *Angew. Chem. Int. Ed.* **2004**, *43*, 3258; d) H. Kiyohara, R. Matsubara, S. Kobayashi, *Org. Lett.* **2006**, *8*, 5333; e) R. Matsubara, S. Kobayashi, *Angew. Chem.* **2006**, *118*, 8161; *Angew. Chem. Int. Ed.* **2006**, *45*, 7993; f) M. C. Jones, S. P. Marsden, D. M. M. Subtil, *Org. Lett.* **2006**, *8*, 5509; g) F. Berthiol, R. Matsubara, N. Kawai, S. Kobayashi, *Angew. Chem.* **2007**, *119*, 7949; *Angew. Chem. Int. Ed.* **2007**, *46*, 7803; h) M. Terada, K. Machioka, K. Sorimachi, *J. Am. Chem. Soc.* **2007**, *129*, 10336; i) M. Terada, K. Sorimachi, *J. Am. Chem. Soc.* **2007**, *129*, 292; j) Y.-X. Jia, J. Zhong, S.-F. Zhu, C.-M. Zhang, Q.-L. Zhou, *Angew. Chem.* **2007**, *119*, 5661; *Angew. Chem. Int. Ed.* **2007**, *46*, 5565; k) P. A. Alexander, S. P. Marsden, D. M. M. Subtil, J. C. Reader, *Org. Lett.* **2005**, *7*, 5433; l) M. Terada, K. Soga, N. Momiyama, *Angew. Chem.* **2008**, *120*, 4190; *Angew. Chem. Int. Ed.* **2008**, *47*, 4122; m) G. J. Brizgys, H. H. Jung, P. E. Floreancig, *Chem. Sci.* **2012**, *3*, 438.
[10] For selected publications on photochemistry from our group, see: a) D. D. Wu, L. Wang, K. Xu, J. Song, H. K. Fun, J. Xu, Y. Zhang, *Chem. Commun.* **2012**, *48*, 1168; b) D. Wu, M. He, Q. Liu, W. Wang, J. Zhou, L. Wang, H.-K. Fun, J. Xu, Y. Zhang, *Org. Biomol. Chem.* **2012**, *10*, 3626; c) X. Chen, C. Huang, W. Zhang, Y. Wu, X. Chen, C. Zhang, Y. Zhang, *Chem. Commun.* **2012**, *48*, 6432–6434; d) L. Wang, Y. Huang, Y. Liu, H. K. Fun, Y. Zhang, *J. Org. Chem.* **2010**, *75*, 7757; e) H. Yu, J. Li, Z. Kou, X. Du, Y. Wei, H. K. Fun, J. Xu, Y. Zhang, *J. Org. Chem.* **2010**, *75*, 2989.
[11] a) V. Florian, J. Kai, S. Juergen, B. Thorsten, *Synthesis* **2009**, 4268; b) B. Thorsten, B. Hermann, H. Klaus, *J. Am. Chem. Soc.* **1999**, *121*, 10650; c) B. Thorsten, *Angew. Chem.* **1996**, *108*, 976; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 884; d) For a general review about photochemistry of enamides, see: G. R. Lens, *Synthesis* **1978**, 489.
[12] For selected transformations of enamides involving radical species, see: a) D. P. Curran, E. Eichenberger, M. Collis, M. G. Roepel, G. Thoma, *J. Am. Chem. Soc.* **1994**, *116*, 4279; b) M. A. Guerrero, R. Cruz-Almanza, L. D. Miranda, *Tetrahedron* **2003**, *59*, 4953; c) T. Okitsu, M. Saito, O. Tamura, H. Ishibashi, *Tetrahedron* **2005**, *61*, 9180; d) T. Taniguchi, A. Ishita, M. Uchiyama, O. Tamura, O. Muraoka, G. Tanabe, H. Ishibashi, *J. Org. Chem.* **2005**, *70*, 1922; e) T. Taniguchi, H. Ishibashi, *Tetrahedron* **2008**, *64*, 8773; f) T. Taniguchi, H. Zaimoku, H. Ishibashi, *Heterocycles* **2009**, *77*, 575; g) A. J. Clark, D. P. Curran, J. V. Geden, N. James, P. Wilson, *J. Org. Chem.* **2011**, *76*, 4546; h) G. K. Friestad, Y. Wu, *Org. Lett.* **2009**, *11*, 819.
[13] T. Courant, G. Masson, *Chem. Eur. J.* **2012**, *18*, 423.
[14] a) D. A. Nagib, D. W. C. MacMillan, *Nature* **2011**, *480*, 224; b) P. V. Pham, D. A. Nagib, D. W. C. MacMillan, *Angew. Chem.* **2011**, *123*, 6243; *Angew. Chem. Int. Ed.* **2011**, *50*, 6119; c) H.-W. Shih, M. N. Van der Wal, R. L. Grange, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2010**, *132*, 13600; d) D. A. Nagib, M. E. Scott, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2009**, *131*, 10875; e) D. A. Nicewicz, D. W. C. MacMillan, *Science* **2008**, *322*, 77.
[15] a) J. D. Parrish, M. A. Ischay, Z. Lu, S. Guo, N. R. Peters, T. P. Yoon, *Org. Lett.* **2012**, *14*, 1640; <lit b> E. L. Tyson, E. P. Farney, T. P. Yoon, *Org. Lett.* **2012**, *14*, 1110; <lit c> Z. Lu, M. Shen, T. P. Yoon, *J. Am. Chem. Soc.* **2011**, *133*, 1162; d) M. A. Ischay, Z. Lu, T. P. Yoon, *J. Am. Chem. Soc.* **2010**, *132*, 8572; e) J. Du, T. P. Yoon, *J. Am. Chem. Soc.* **2009**, *131*, 14604; f) M. A. Ischay, M. E. Anzovino, J. Du, T. P. Yoon, *J. Am. Chem. Soc.* **2008**, *130*, 12886.
[16] a) L. Furst, J. M. R. Narayanam, C. R. J. Stephenson, *Angew. Chem.* **2011**, *123*, 9829; *Angew. Chem. Int. Ed.* **2011**, *50*, 9655; b) J. W.

Tucker, J. M. R. Narayanam, P. S. Shah, C. R. J. Stephenson, *Chem. Commun.* **2011**, *47*, 5040; c) J. D. Nguyen, J. W. Tucker, M. D. Konieczynska, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2011**, *133*, 4160; d) C. Dai, J. M. R. Narayanam, C. R. J. Stephenson, *Nat. Chem.* **2011**, *3*, 140; e) J. W. Tucker, J. D. Nguyen, J. M. R. Narayanam, S. W. Krabbe, C. R. J. Stephenson, *Chem. Commun.* **2010**, *46*, 4985; f) J. W. Tucker, J. M. R. Narayanam, S. W. Krabbe, C. R. J. Stephenson, *Org. Lett.* **2010**, *12*, 368; g) L. Furst, B. S. Matsuura, J. M. R. Narayanam, J. W. Tucker, C. R. J. Stephenson, *Org. Lett.* **2010**, *12*, 3104; h) A. G. Condie, J. C. Gonzelez-Gomez, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2010**, *132*, 1464; i) J. M. R. Narayanam, J. W. Tucker, C. R. J. Stephenson, *J. Am. Chem. Soc.* **2009**, *131*, 8756.

[17] For recent reviews about visible-light photocatalysis, see: a) J. W. Tucker, C. R. J. Stephenson, *J. Org. Chem.* **2012**, *77*, 1617; b) J. M. R. Narayanam, C. R. J. Stephenson, *Chem. Lett. Chem. Soc., Rev.* **2011**, *40*, 102; c) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* **2010**, *2*, 527; d) K. Zeitler, *Angew. Chem.* **2009**, *121*, 9969; *Angew. Chem. Int. Ed.* **2009**, *48*, 9785.

[18] For recent selected examples of visible-light photocatalysis, see: a) Y.-Q. Zou, L.-Q. Lu, L. Fu, N.-J. Chang, J. Rong, J.-R. Chen, W.-J. Xiao, *Angew. Chem.* **2011**, *123*, 7309; *Angew. Chem. Int. Ed.* **2011**, *50*, 7171; b) M.-H. Larraufie, R. Pellet, L. Fensterbank, J.-P. Goddard, E. Lacote, M. Malacria, C. Ollivier, *Angew. Chem.* **2011**, *123*, 4555; *Angew. Chem. Int. Ed.* **2011**, *50*, 4463; c) S. R. Andrews, J. J. Becker, M. R. Gagne, *Org. Lett.* **2011**, *13*, 2406; d) M. Rueping, C. Vila, R. M. Koenigs, K. Poscharny, D. C. Fabry, *Chem. Commun.* **2011**, *47*, 2360; e) J. Xuan, Y. Cheng, J. An, L.-Q. Lu, X-.X. Zhang, W.-J. Xiao, *Chem. Commun.* **2011**, *47*, 8337; f) M. Neumann, S. Fuldner, B. Kçnig, K. Zeitler, *Angew. Chem.* **2011**, *123*, 981; *Angew. Chem. Int. Ed.* **2011**, *50*, 951; g) D. P. Hari, B. Konig, *Org. Lett.* **2011**, *13*, 3852; h) Y.-Q. Zou, J.-R. Chen, X.-P. Liu, L.-Q. Lu, R. L. Davis, K. A. Jorgensen, W.-J. Xiao, *Angew. Chem. Int. Ed.* **2012**, *51*, 784; i) Y. Miyake, K. Nakajima, Y. Nishibayashi, *J. Am. Chem. Soc.* **2012**, *134*, 3338; j) Y. Cheng, J. Yang, Y. Qu, P. Li, *Org. Lett.* **2012**, *14*, 98; k) M. Zlotorzynska, G. M. Sammis, *Org. Lett.* **2011**, *13*, 6264; l) J. B. Edson, L. P. Spencer, J. M. Boncella, *Org. Lett.* **2011**, *13*, 6156; m) S. Maity, M. Zhu, R. S. Shinabery, N. Zheng, *Angew. Chem. Int. Ed.* **2012**, *51*, 222; n) M. Rueping, S. Zhu, R. M. Koenigs, *Chem. Commun.* **2011**, *47*, 12709; o) Y. Su, L. Zhang, N. Jiao, *Org. Lett.* **2011**, *13*, 2168.

[19] For visible-light photoredox catalyzed trifluoromethylation, see: N. Iqbal, S. K. Chai, E. Ko, E. J. Cho, *Tetrahedron Lett.* **2012**, *53*, 2005. See also refs.[14a,14d]

[20] For recent examples of arylation mediated by visible-light photoredox catalysis, see: a) D. P. Hari, P. Schroll, B. König, *J. Am. Chem. Soc.* **2012**, *134*, 2958; b) Kalyani, K. B. McMurtrey, S. R. Neufeldt, M. S. Sanford, *J. Am. Chem. Soc.* **2011**, *133*, 18566.

[21] J. B. Feltenberger, R. Hayashi, Y. Tang, E. S. C. Babiash, R. P. Hsung, *Org. Lett.* **2009**, *11*, 3666; see also reference [8c].

[22] O. Okitsu, R. Suzuki, S. Kobayashi, *J. Org. Chem.* **2001**, *66*, 809.

[23] C. Yu, L. Hu, *Tetrahedron Lett.* **2001**, *42*, 5167.

[24] I. S. Villar, A. Gradillas, J. P. Castells, *Eur. J. Org. Chem.* **2010**, 5850.

[25] A. T. Khan, M. A. Ali, P. Goswami, L. H. Choudhury, *J. Org. Chem.* **2006**, *71*, 8961.

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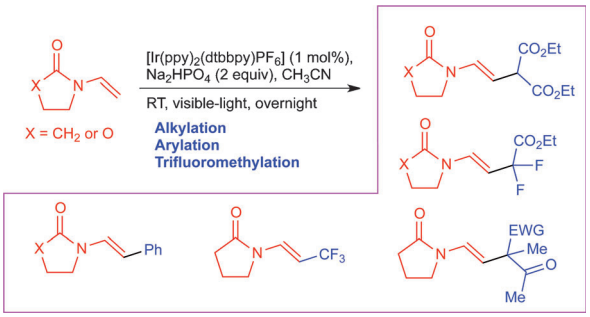

Lighting the way! A mild, practical, and environmentally friendly strategy for alkylation, trifluoromethylation, and arylation of enamides and enecarbamates with a broad substrate scope by using visible-light photoredox-catalyzed direct C–H functionalization is described (see scheme).

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