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Photoredox-Catalyzed Oxidation of Anions for the Atom-Economical Hydro-, Amido-, and Dialkylation of Alkenes

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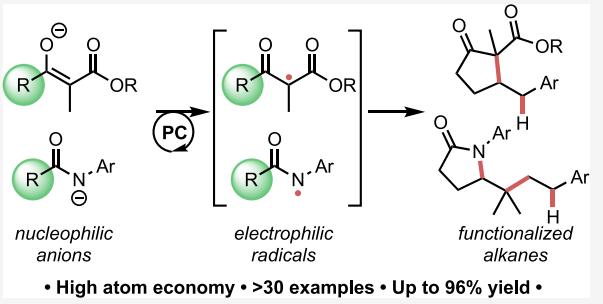
ABSTRACT: Photoredox catalysis has become a powerful method to generate free radical intermediates in organic synthesis. This report describes the use of photoredox catalysis to directly oxidize common nucleophilic anions to access electrophilic 1,3-dicarbonyl and amidyl radical intermediates. First, conjugate bases of 1,3-dicarbonyls were oxidized to neutral radical species for intramolecular hydro- and dialkylation of alkenes. This overall redox-neutral process provided cyclopentanone products in excellent yields (up to 96%). The scope included a variety of styrene radical acceptors and products with newly formed vicinal quaternary carbons. This process was then extended to the synthesis of pyrrolidinones by alkene amidoalkylation that proceeded via *N*-aryl amidyl radical intermediates in good yield (up to 85%). These reactions were characterized by their mild conditions, high atom economy, and the absence of stoichiometric byproducts. Mechanistic and computational studies supported a stepwise proton-coupled electron transfer mechanism, where an "electron borrowing" photocatalyst oxidizes an anion and reduces a benzylic radical after bond formation.



INTRODUCTION

Carbon−carbon bond formation using photoredox catalysis has become a powerful and widespread subfield of synthetic organic chemistry in recent years.[1−6] By harnessing the energy of visible light, transition metal and organic photosensitizers can perform single-electron transfer (SET) reactions with organic substrates to generate carbon-centered radicals. For instance, photoredox and acid or base cocatalysis enables proton-coupled electron transfer (PCET)[7,8] to generate ketyl[9−11] and amidyl radical intermediates.[12−16] In this way, photoredox-catalyzed SET has afforded umpolung species that are key constituents of many new C−C bond-forming processes. The generation of useful free radical intermediates by single-electron transfer processes therefore remains a fruitful and important area of study.

Stable organic anions such as carboxylates,[17−19] borates,[20−23] silicates,[24−29] and sulfinates[30] have been shown to undergo photoredox-catalyzed oxidation, followed by fragmentation to generate carbon-centered radical intermediates that participate in a wide variety of interesting transformations.[2,31,32] We envisioned that anion oxidation could be expanded to low-pK_a organic molecules that form stable anions such as 1,3-dicarbonyls and amides. The inherently electron-rich nature of these anions, coupled with the SET capabilities of photoredox catalysts, should facilitate productive oxidation events if the resulting radical species are thermodynamically stable enough to favor a forward reaction. These resulting electrophilic radicals would therefore provide direct reactive umpolungs of their nucleophilic precursors. The proposed processes further benefit from ready availability of starting materials as well as the typically mild nature of photoredox catalysis.

In the case of 1,3-dicarbonyls, removal of a single electron converts malonate-type nucleophiles into electron-poor, resonance-stabilized radicals that can react at carbon. These radicals have demonstrated utility in the generation of challenging substructures such as all-carbon quaternary centers, polycyclic species by cascade additions, and regioselective carbofunctionalization of alkenes (Figure 1a).[33] Although the generation of these radicals has been extensively reported using manganese(III),[33−36] cerium(IV),[37,38] and iron(III)[39] reagents, these metal-mediated conditions require superstoichiometric amounts of metal salts and strong terminal oxidants. One recent report by Baran has improved the efficiency of this reaction by regenerating the active Mn(III) catalyst electrochemically, but the application was only reported for a single substrate.[40] Photoredox catalysis presents an opportunity to

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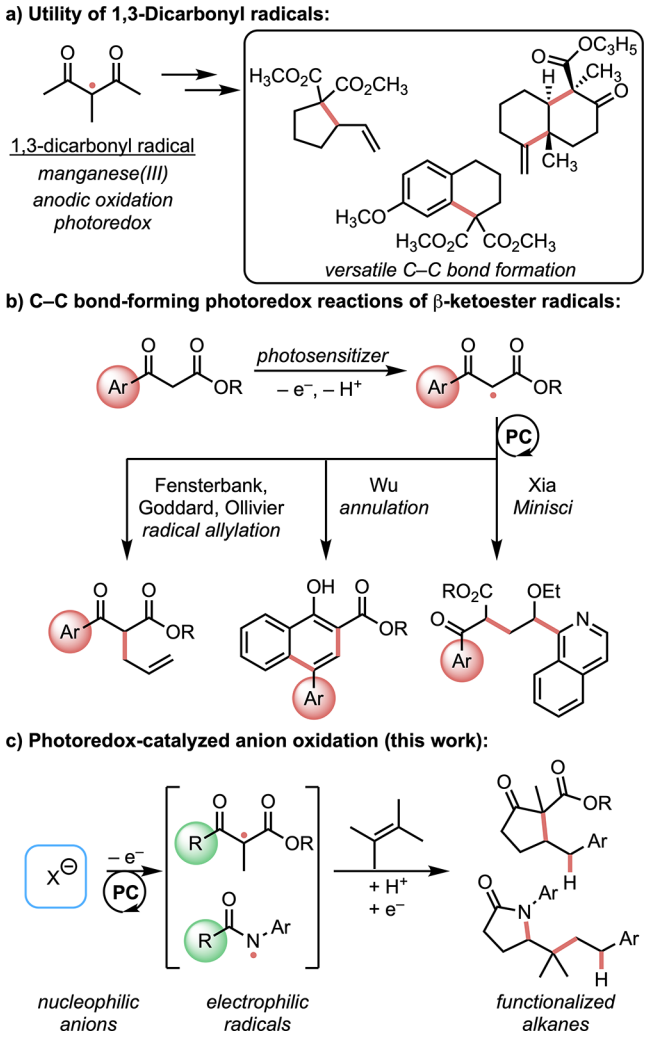


Figure 1. 1,3-Dicarbonyl radicals and proposed utility of photoredox-catalyzed anion oxidation.

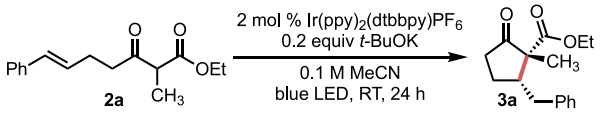
drastically reduce the amount of transition metal used in this class of oxidation reactions. To date, only a handful of examples of photo-generated 1,3-dicarbonyl radicals have been reported (Figure 1b).[41] For example, Fensterbank, Goddard, and Ollivier have reported the oxidative chemistry of aromatic β-ketoesters in radical allylations and oxidative dimerizations.[42] Wu and Xia have reported the use of 1,3-dicarbonyl radicals in cascade reactions.[43−45]

Reported methods of photocatalytic generation of 1,3-dicarbonyl radicals are only effective with aromatic benzoylacetate-derived starting materials, which have materially different redox properties to alkyl β-ketoesters and other 1,3-dicarbonyls. DFT calculations have found that aromatic β-ketoesters have positive electron affinities and are more easily reduced, while alkyl β-ketoesters have negative electron affinities.[46] Furthermore, alkyl β-ketoesters have lower equilibrium concentrations of the more easily oxidized enol tautomer.[47] Catalytic access to alkyl 1,3-dicarbonyl radicals would increase synthetic versatility of these intermediates, providing access to a wider variety of functionalized products. Herein, we describe the successful implementation of a photoredox-catalyzed anion oxidation strategy in the synthesis of 1,3-dicarbonyl and amidyl radicals and their applications in alkene addition reactions (Figure 1c).

RESULTS AND DISCUSSION

Discovery and Optimization. The conversion of styrene-derived substrate **2a** to cyclopentanone **3a** was chosen for discovery and optimization (Table 1). 5-Exo-trig cyclization of a 1,3-dicarbonyl radical generated from **2a** would produce a benzylic radical intermediate. The stability of this intermediate would simultaneously favor cyclization and the subsequent electron transfer to a stabilized anion. Indeed, our initial optimization studies found that the benzylic radical could be directly reduced under these conditions (see the Supporting Information for details on reaction discovery).[48] In the presence of the catalyst $[Ir(dtbbpy)(ppy)_2]PF_6$ (**1**) and cocatalytic potassium *tert*-butoxide, β-ketoester **2a** was transformed into cyclopentanone **3a** in excellent yield with no stoichiometric byproducts (Table 1, entry 1). Potassium *tert*-butoxide was chosen as the optimal base because of its low cost and ease of use although cesium carbonate and DBU were also productive bases (entries 2−3). Acetonitrile was identified as a uniquely effective solvent (entry 4). The photoredox catalyst $[Ir(dtbbpy)(ppy)_2]PF_6$ (**1**) was the most effective, likely due to the larger potentials for both the Ir(III)* to Ir(II) reduction (−0.66 V vs SCE) and the Ir(II) to Ir(III) oxidation (+1.51 V vs SCE)[1] when compared to other transition metal-based photocatalysts (entries 5 and 6). This Ir(II) to Ir(III) potential was particularly important for this reaction because it enables the direct reduction of a benzylic radical (−1.10 V vs SCE;[49] vide infra). These redox potentials also allow these reactions to occur without the need for thiol H-atom donors. Curious about the low levels of diastereoselectivity observed, we hypothesized that the addition of coordinating Lewis acids could improve the selectivity by potentially rigidifying the β-ketoester enolate. Although marginal improvements in diastereoselectivity could be observed by the addition of magnesium bromide diethyl etherate, yields suffered signifi-

Table 1. Discovery and Optimization of Alkene Hydroalkylation



entry	deviation from standard conditions[a]	yield **3a** (%)[b]	d.r.[c]
1	none	96	1.8:1
2	Cs_2CO_3 *instead of* *t*-BuOK	87	1.6:1
3	DBU *instead of* *t*-BuOK	56	1.7:1
4	CH_2Cl_2 or THF *instead of* MeCN	<5	Nd
5	$[Ru(bpy)_3](PF_6)_2$ and Cs_2CO_3 *instead of* **1** and *t*-BuOK	15	Nd
6	$Ir(ppy)_3$ and Cs_2CO_3 *instead of* **1** and *t*-BuOK	39	Nd
7	Addition of 2 equiv $MgBr_2{\cdot}OEt_2$	29	3.4:1
8	no **1**	<5	Nd
9	no light	<5	Nd
10	no *t*-BuOK	<5	Nd
11	1 mmol scale	93	1.3:1
12	48 h reaction time	98	1.8:1

[a]Standard conditions: 0.2 mmol **2a**, 0.2 equiv *t*-BuOK, 2 mol % **1**, CH_3CN (0.1 M). [b]Combined yield of **3a** diastereomers, determined after purification by silica gel chromatography. [c]Major diastereomer, shown, determined by NOESY analysis. D.r. determined by ^1H NMR analysis of unpurified reaction mixtures.

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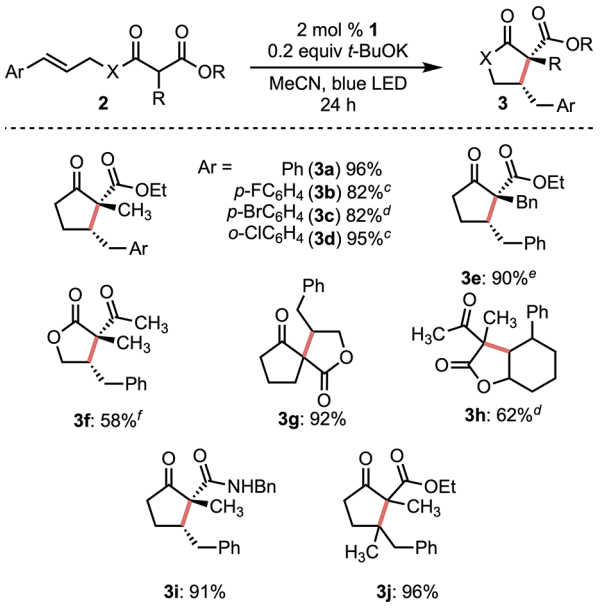
cantly (entry 7). Control experiments demonstrated that no reaction was observed in the absence of iridium catalyst **1**, light, or base (entries 8−10). Gratifyingly, the reaction could be scaled to 1 mmol of **2a** without a significant reduction in yield (entry 11), and reaction times could be similarly extended (entry 12). It is important, however, to control the temperature of this reaction, as elevated temperatures led to the formation of an unidentified byproduct that was challenging to separate from cyclopentanones **3**.[50]

Scope of Hydroalkylation. The optimized conditions were used to explore the scope of this hydroalkylation reaction (Table 2). Halogen-substituted styrenes were well-tolerated

Table 2. Hydroalkylation Substrate Scope[a,b]

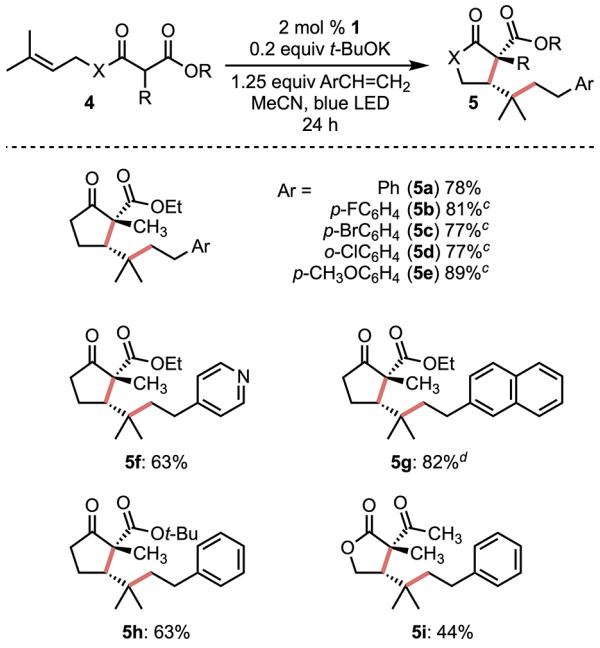


[a]Reaction conditions: 0.2 mmol **2**, 2 mol % **1**, 0.2 equiv *t*-BuOK, 1 mL CH_3CN, blue LED, 24 h. [b]d.r. for all reaction between 1.6 and 2:1 unless otherwise noted (see the Experimental Section and the Supporting Information). Yields reported as the sum of both diastereomers after purification. Major diastereomer of **3a** shown as determined by NOESY analysis, others assigned by analogy. [c]72 h reaction time. [d]48 h reaction time. [e]d.r. = 3:1. [f]d.r. = 1:1.

(**3b−d**). Benzyl substitution of the 2-position (**3e**) resulted in comparable yields and mild improvements in diastereoselectivity. Lactones could also be produced (**3f−h**) albeit in reduced yields. This photoredox reaction also provided *β*-ketoamide **3i** in excellent yield. In this case, the secondary amide was necessary because the $A^{1,3}$-strain produced in the enolization restricted the use of tertiary amide substrates. Cyclopentanone **3j** demonstrates the capability of this reaction to produce vicinal all-carbon quaternary centers. Furthermore, cyclized products **3** typically did not need extensive purification, and in most cases, a pure material was obtained by an aqueous workup and simple silica gel filtration that removed the base and iridium catalysts. Although the diastereoselectivity of this reaction was modest, the diastereomers of most cyclopentanone products could be separated by standard chromatographic methods. One primary limitation was that only pendant styrenes were productive substrates for this addition. This is likely due to the inability of the reduced state of the photocatalyst (**1**) to reduce non-benzylic alkyl radicals. Attempts to employ H-atom transfer reagents to expand this hydroalkylation to substrates such as **4a** were unsuccessful.[16,51] Another well-known limitation of the oxidative formation of 1,3-dicarbonyl radicals is overoxidation of substrates without 2-substitution, and these substrates similarly provided only trace amounts of cyclized products under photoredox conditions.[33]

Alkene Dialkylation. During our investigations into the alkene hydroalkylation by 1,3-dicarbonyl radicals, we discovered that catalyst **1** was not a strong enough reducing agent to transfer an electron to unstabilized alkyl radicals. This was evident by the reduced yield of hydroalkylation of alkene **4a**. This observation, however, led us to envision a dialkylation reaction with exogenous styrene. In line with our hypothesis, a slight excess of styrene added to the same reaction conditions with trisubstituted alkenes such as **4** provided alkene dialkylation products (**5**) in excellent yields (Table 3). The

Table 3. Dialkylation Substrate Scope[a,b]



[a]Reaction conditions: 0.2 mmol **4**, 2 mol % **1**, 0.2 equiv *t*-BuOK, 1.25 equiv $ArCHCH_2$, 1 mL CH_3CN, blue LED, 24 h. [b]d.r. for all reactions between 1.2 and 3:1 (see the Experimental Section and the Supporting Information). Yields reported as the sum of both diastereomers after purification. Major diastereomer assigned by analogy to **3a**. [c]48 h reaction time. [d]72 h reaction time.

scope of the reaction was comparable to that of the hydroalkylation reaction. Dialkylation was successful with a wide variety of styrene partners. Halogenated (**5a−d**) and electron-rich (**5e**) styrenes were well-tolerated, including *o*-substitution (**5d**). Electron-poor vinylpyridine (**5f**) was also a suitable substrate for this dialkylation reaction. The identity of the ester also had a minimal effect on the reaction. *tert*-Butyl *β*-ketoester product **5h** and lactone **5i** were both produced in good yields. As in the case of the hydroalkylation reaction, the syntheses of lactones (**5i**) by this process suffered somewhat in yield. Interestingly, no intermolecular alkylation of the 2-position by styrene was observed. Our attempts to conduct a direct intermolecular reaction (e.g., between ethyl 2-oxocyclopentane-1-carboxylate and styrene) provided only the recovered starting material.

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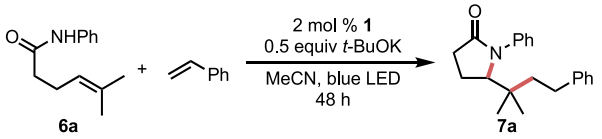
Alkene Amidoalkylation. In an extension of our hypothesis that the oxidation of anionic conjugate bases could lead to useful radical intermediates, we investigated *N*-aryl amides (**6**) as acidic precursors to amidyl radicals.[52,53] Although similar photoredox-catalyzed amidoalkylation reactions have been reported by Knowles and others,[13,14,54] the concerted PCET mechanism described in these earlier reports was only capable of effecting Giese-type additions to electron-poor alkenes. We were therefore interested in understanding any differential reactivity of amidyl radicals generated from anion oxidation.

Some additional optimization from the dialkylation conditions was required for this amidoalkylation reaction (Table 4, see the Supporting Information). The reduced basicity of amide **6a** compared to 1,3-dicarbonyls required higher concentrations of the base (entry 1), but potassium *tert*-butoxide remained the optimal base (entry 2). Acetonitrile was again found to be the optimal medium, but unlike the reactions of **2** and **4**, reactivity was observed in other solvents (entry 3). Amidoalkylation of **6a** was generally slower than the hydro- and dialkylation reactions, and optimal yields were obtained at 48 to 72 h (entry 5). Control reactions confirmed the necessity of a base, a photocatalyst, and light activation (entries 6–8). As with the hydro- and dialkylation reactions, these transformations were clean, with no stoichiometric byproducts.

Table 4. Discovery and Optimization of Alkene Amidoalkylation

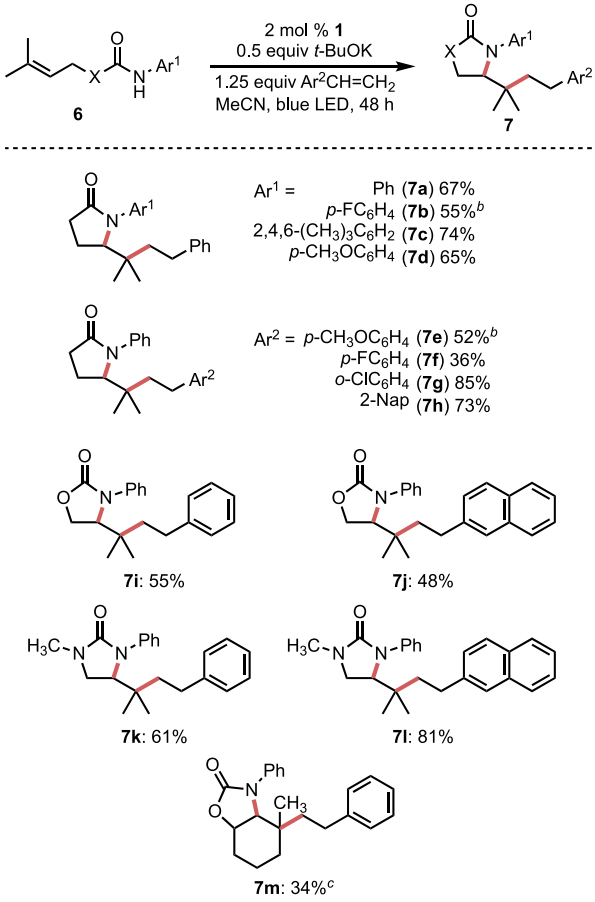


entry	deviation from standard conditions[a]	yield **7a** (%)
1	none	67
2	K_2CO_3 *instead of* *t*-BuOK	46
3	DMF *instead of* MeCN	23
4	$[Ru(bpy)_3](PF_6)_2$ *instead of* **1**	<5
5	24 h reaction time	50
6	no **1**	<5
7	no light	<5
8	no base	<5

[a]Standard conditions: 0.2 mmol **6a**, 0.5 equiv *t*-BuOK, 2 mol % **1**, 1.25 equiv styrene, 0.3 M CH_3CN, blue LED, 48 h.

The scope of photoredox-catalyzed oxidation of amide ions for amidoalkylation was broad both in scope of the amide (**6**) and styrene components (Table 5). Although only anilide derivatives were successful substrates in this reaction, a variety of aromatic substituents were tolerated, including electron-poor (**7b**) and electron-rich (**7d**) functional groups as well as sterically demanding ortho-substituents (**7c**). A similar trend was observed for the styrene component, and a variety of substitutions of the aromatic ring provided pyrrolidinone products in good yields including electron-rich (**7e**), halogenated (**7f–g**), and naphthyl (**7h**) styrenes. *N*-aryl carbamates and ureas were also suitable substrates, providing the corresponding substituted oxazolidinones (**7i**, **7j**) and imidazolidinone (**7k**, **7l**) products in good yields. The fused ring oxazolidinone **7m** was also formed in modest yield. The incorporation of electron-rich alkenes in this example confirms that stepwise PCET via amidyl anion oxidation is a complementary method to other reactions with amidyl intermediates.

Table 5. Amidoalkylation Substrate Scope[a]



[a]Reaction conditions: 0.2 mmol **6**, 2 mol % **1**, 0.5 equiv *t*-BuOK, 1.25 equiv Ar^2CHCH_2, 0.7 mL CH_3CN, blue LED, 48 h. [b]72 h reaction time. [c]1:1 d.r. Yield reported as the sum of both diastereomers after purification.

Mechanistic Investigations. Our discovery of this new approach to the synthesis of 1,3-dicarbonyl and amidyl radicals motivated experimental studies on the mechanism of the hydroalkylation reaction. Our initial mechanistic proposal involved direct single-electron oxidation of the *β*-ketoester enolate **8** by the photoexcited state of iridium catalyst **1** (Scheme 1). The resulting free radical **9** would undergo 5-*exo*-trig cyclization to provide benzylic radical **10**. Single-electron reduction of **10** by the reduced form of catalyst **1** would then provide anion **11**. This step would regenerate the ground state of catalyst **1**. Additionally, anion **11** would be protonated by available acid in solution (i.e., *tert*-butanol, unreacted **2**, or acetonitrile solvent), supporting the need for only a catalytic amount of base. A key feature of this mechanism is essentially "electron borrowing," where catalyst **1** both removes and replaces an electron from the substrate in an overall redox-neutral process.

Fluorescence quenching was used to understand the nature of the catalyst–substrate interactions. Quenching of photoexcited catalyst **1** ($[Ir]^{III}*$) was not observed in the presence of ethyl 2-methylacetylacetate (**12**), styrene, or potassium *tert*-butoxide alone (Figure 2a). The absence of quenching in the presence of styrene rules out the possibility of reactivity driven

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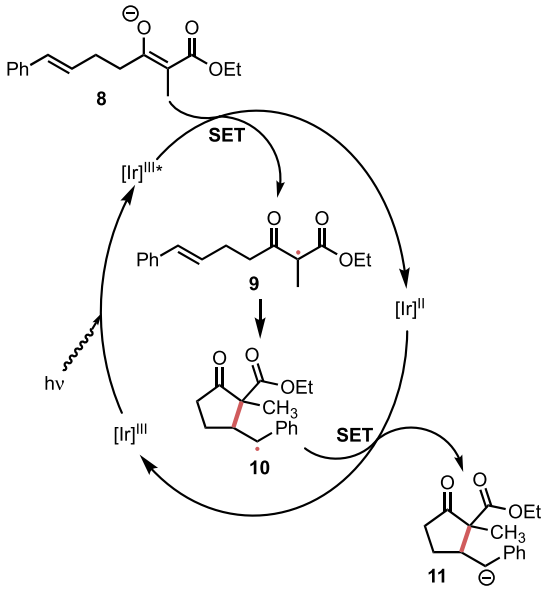
Scheme 1. Proposed Mechanism of the Hydroalkylation Reaction ($[Ir]^{III}$ = 1)



by the radical cation of the styrene moiety.[48] Fluorescence quenching of **1** was only observed in the presence of both **12** and potassium *tert*-butoxide. This observation held true both when a 1:1 mixture of **12** and *t*-BuOK was used as the titrant, or when a constant concentration of **12** was titrated with *t*-BuOK. In both cases, quenching was non-linear; however, no significant shifts in the UV−vis spectrum were observed for mixtures of **1** and *t*-BuOK or **12** that might indicate precomplexation. These fluorescence quenching experiments support the proposed mechanisms in which photoexcited iridium complex **1** directly oxidizes the *β*-ketoester enolate **8**. Although a concerted proton-coupled electron transfer (PCET) event cannot be completely ruled out by these observations, the strong thermodynamic preference for deprotonation of **2** by potassium *tert*-butoxide (ΔpK_a(DMSO) ~15) combined with the observed fluorescence quenching of photoexcited **1** when titrated with a premixed solution of 1:1 substrate/base are consistent with a stepwise PCET pathway, where deprotonation of substrate precedes oxidative SET by the excited state of **1**.[8] This is also supported by the observation that a variety of bases composed of different functional groups and pK_a values are capable of adequately catalyzing the reaction.

A free radical mechanism was also supported by the observation of TEMPO-trapped product **13** (Figure 2b). Isolation of cyclopentanone **13** supports the intermediacy of radical **10** formed by 5-*exo*-trig cyclization in the proposed mechanism. We were unable to observe radical-trapping products directly from **9** or of the *β*-ketoester itself under our conditions, though oxyamination of 1,3-dicarbonyls has been observed in other photoredox-catalyzed reactions, where the 1,3-dicarbonyl radical is a proposed intermediate.[46]

Computational studies uncovered the fundamentals of the reaction and the diastereoselectivity of the radical addition. Radical intermediates **9** and **10** as well as the diastereomeric transition states (*R*,*R*)-**TS-1** and (*R*,*S*)-**TS-2** in the conversion of **9** to **10** were investigated. Geometries were optimized at the UB3LYP/6-311+G(2d,p) level of theory with a CPCM solvation model for acetonitrile. The optimized geometries

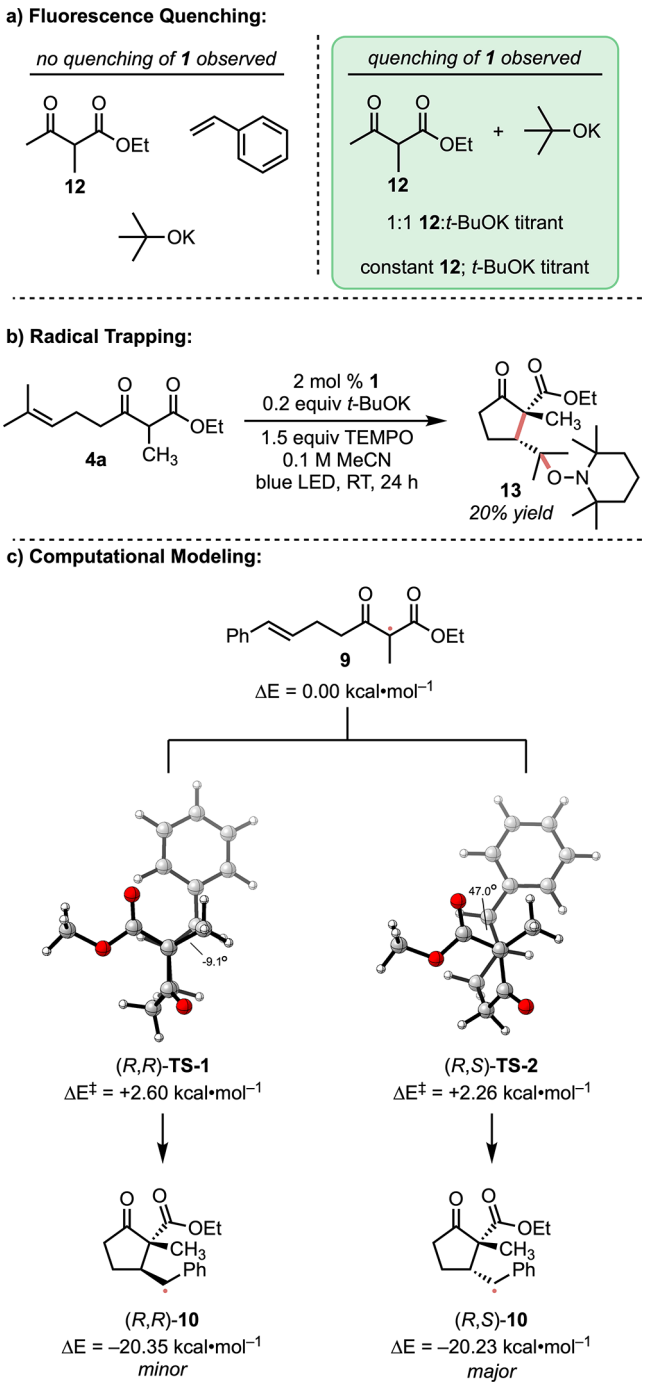


Figure 2. Mechanistic investigations into 1,3-dicarbonyl radical reactivity.[55]

were then calculated using the compound method CBS-QB3 with the same solvation model, which is considered more accurate for radical species.[56,57] These studies found that intramolecular cyclization of **9** to **10** is facile, requiring only 2.3 kcal·mol^{-1} for the lowest energy diastereomeric transition state ((*R*,*S*)-**TS-2**). Overall, this step is exergonic by approximately 20 kcal·mol^{-1}. When taken in conjunction with the observation that only radical intermediate **10** was trapped by TEMPO, these results indicate that radical fragmentation (i.e., **10** to **9**) is relatively slow. The small difference between diastereomeric transition states **TS-1** and **TS-2** of 0.3 kcal·mol^{-1} is in line with the low diastereoselectivity generally observed in hydro-

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alkylation and dialkylation reactions (Figure 2c). Although the energy difference is small, calculations correctly predicted the major diastereomer. Close inspection of the transition states revealed more significant eclipsing interactions along the forming bond in the higher-energy **TS-1**. These interactions likely explain why increasing the steric size of the 2-substituent increases the diastereoselectivity (i.e., **3e**, 3:1 dr), but increasing the size of the more remote ester group has a minimal effect (i.e., **5h**, 1.7:1 dr). This is also supported by the generally increased diastereoselectivity of the dialkylation reaction, which increases the steric demand at the alkene.

Taken together, the mechanistic information collected on these alkene addition reactions supports the direct oxidation of anionic intermediates by a photoexcited iridium catalyst (**1**) as described in Scheme 1.

CONCLUSIONS

In summary, we have developed a method for the photoredox-catalyzed oxidation of stable organic ions derived from the deprotonation of acidic groups to reactive radical intermediates. The utility of these 1,3-dicarbonyl and amidyl radical intermediates was demonstrated in hydro-, di-, and amidoalkylation reactions of alkenes in high yields. The direct oxidation of an anion enabled the expansion of photoredox-generated 1,3-dicarbonyl radicals to include the more challenging and synthetically versatile alkyl β-ketoester substrates. Mechanistic studies support a free radical "electron borrowing" mechanism that involves initial oxidation of the β-ketoester enolate by the iridium photoredox catalyst, followed by a later reduction of a cyclized radical intermediate. Investigations into the further application of these key intermediates are ongoing.

EXPERIMENTAL SECTION

General Experimental Procedures. All reactions were carried out in dry glassware under an argon atmosphere using standard Schlenck techniques unless otherwise specified. Acetonitrile, THF, and dichloromethane solvents were purified by passage through solvent purification columns. Light-promoted reactions were conducted in borosilicate vials 3 cm from a Kessil A150W lamp (30 W, peak intensity ~ 460 nm). Ambient temperature was maintained in the reactor using a small desk fan to circulate the air around the reaction vessel. **2a**,[58] **2f**, **2g**,[59] **4i**,[60] **6a−d**, **6i**, **6k**,[14] and **6m**[13] were prepared according to the literature procedures. Other commercially available reagents, solvents, and silica gel were used as received unless otherwise specified. Computational results were obtained using the Schrödinger suite of programs for conformational analysis and Gaussian 16 Rev. C.01 for quantum mechanical calculations (for details, see the Supporting Information).

The ^{1}H NMR spectra were acquired at 300 or 400 MHz, the ^{13}C{^{1}H} NMR spectra at 75 or 100 MHz, and the ^{19}F NMR spectra at 376 MHz as $CDCl_3$ solutions at 298 K unless otherwise noted. Residual $CHCl_3$ solvent peaks were referenced to 7.26 and 77.16 ppm for ^{1}H and ^{13}C{^{1}H} NMR, respectively. The ^{19}F NMR spectra were referenced to added α,α,α-trifluorotoluene at −62.61 ppm. The high-resolution mass spectra (HRMS) were provided by the University of California, Irvine Mass Spectrometry Facility. All HRMS were obtained in positive-ion CI or ESI mode.

General Procedure for the Alkene Hydroalkylation. *Ethyl 2-Benzyl-1-methyl-5-oxocyclopenate-1-carboxylate (**3a**).* Potassium *tert*-butoxide (4.7 mg, 0.04 mmol, 0.2 equiv) and $[Ir(ppy)_2(dtbbpy)]PF_6$ (**1**, 3.6 mg, 0.004 mmol, 0.02 equiv) were added to an oven-dried vial with a stir bar. The vial was then covered with a septum and evacuated/backfilled with Argon three times. **2a** (52 mg, 0.20 mmol, 1 equiv) dissolved in degassed acetonitrile (2.0 mL, 0.1 M) was then injected through septum, which was swapped for a screw cap and sealed with Teflon tape. The mixture was then stirred under blue LED irradiation with air cooling for 24 h. The reaction mixture was then diluted with ethyl acetate (1 mL) and quenched with saturated aqueous NH_4Cl (2 mL). The phases were separated, and the aqueous phase was extracted with additional ethyl acetate (2 × 2 mL). The combined organic layers were then washed with saturated aqueous NaCl (2 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by automated column chromatography (SiO_2, 0−50% ethyl acetate in the hexane gradient) provided 50 mg (96%) of **3a** as a colorless oil in a 1.8:1 mixture of diastereomers. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz; $CDCl_3$): δ ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−7.25 (m, 3H), 7.24−7.11 (m, 2H), 4.03 (qd, J = 7.2, 2.9 Hz, 2H), 3.00 (ddt, J = 11.9, 9.1, 6.2 Hz, 1H), 2.79 (dd, J = 13.5, 6.1 Hz, 1H), 2.56 (dd, J = 13.5, 9.2 Hz, 1H), 2.49−2.28 (m, 2H), 2.13−1.97 (m, 1H), 1.68−1.51 (m, 3H), 1.26 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 215.7, 172.3, 139.4, 129.0, 128.6, 126.5, 61.4, 59.7, 47.0, 37.6, 36.5, 25.7, 14.2, 13.5; FTIR (thin film, cm^{-1}): 2979, 2935, 1750, 1729; HRMS (ESI-TOF) m/z: calcd for $C_{16}H_{20}O_3Na$ $(M + Na)^+$, 283.1310; found, 283.1315.

1 mmol Scale Reaction. Potassium *tert*-butoxide (22 mg, 0.02 mmol, 0.2 equiv) and $[Ir(ppy)_2(dtbbpy)]PF_6$ (**1**, 18 mg, 0.02 mmol, 0.02 equiv) were added to an oven-dried borosilicate test tube (13 × 100 mm) with a stir bar. The tube was sealed with a septum and copper wire, and the atmosphere was purged by argon flow for 5 min **2a** (260 mg, 1.0 mmol, 1 equiv) dissolved in degassed acetonitrile (10 mL, 0.1 M) was then injected through septum. The mixture was then stirred under blue LED irradiation with air cooling for 24 h. The reaction mixture was then diluted with ethyl acetate (10 mL) and quenched with saturated aqueous NH_4Cl (10 mL). The phases were separated, and the aqueous phase was extracted with additional ethyl acetate (2 × 10 mL). The combined organic layers were then washed with saturated aqueous NaCl (10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. Purification by automated column chromatography (SiO_2, 0−50% ethyl acetate in hexanes gradient) provided 242 mg (93%) of **3a** as a colorless oil as a 1.3:1 mixture of diastereomers.

*Ethyl 2-(4-Fluorobenzyl)-1-methyl-5-oxocyclopentane-1-carboxylate (**3b**).* Following the general procedure, 46 mg (82%; 1.9:1 dr) of **3b** was produced as a colorless oil from styrene **2b** (56 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 72 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17−7.08 (m, 2H), 7.03−6.88 (m, 2H), 4.04 (qd, J = 7.1, 1.4 Hz, 2H), 2.97 (ddt, J = 12.0, 8.9, 6.2 Hz, 1H), 2.76 (dd, J = 13.7, 6.3 Hz, 1H), 2.54 (dd, J = 13.7, 9.0 Hz, 1H), 2.50−2.29 (m, 2H), 2.02 (dddd, J = 12.8, 8.6, 6.2, 2.5 Hz, 1H), 1.65−1.53 (m, 1H), 1.25 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 215.5, 172.2, 161.7 (d, J = 242 Hz), 135.0 (d, J = 3 Hz), 130.4 (d, J = 6 Hz), 115.4 (d, J = 22 Hz), 61.5, 59.6, 47.0, 37.5, 35.7, 25.6, 14.2, 13.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ −116.7 (m); FTIR (thin film, cm^{-1}): 2980, 2857, 1750, 1729, 1530; HRMS (CI-TOF) m/z: calcd for $C_{16}H_{19}FO_3$ $(M)^+$, 278.1318; found, 278.1316.

*Ethyl 2-(4-Bromobenzyl)-1-methyl-5-oxocyclopentane-1-carboxylate (**3c**).* Following the general procedure, 56 mg (82%; 1.4:1 dr) of **3c** was produced as a colorless oil from styrene **2c** (68 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 48 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42 (d, J = 8.3 Hz, 2H), 7.05 (d, J = 8.3 Hz, 2H), 4.33−4.05 (m, 2H), 2.91 (dd, J = 13.4, 4.5 Hz, 1H), 2.58 (ddd, J = 19.2, 7.4, 2.6 Hz, 1H), 2.37 (dd, J = 13.4, 10.3 Hz, 1H), 2.27−2.04 (m, 2H), 1.88 (ddd, J = 11.5, 6.1, 3.5 Hz, 2H), 1.38−1.21 (m, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 216.0, 170.7, 138.6, 131.7, 130.7, 120.3, 61.4, 59.3, 51.1, 37.6, 36.9, 26.1, 18.8, 14.4; FTIR (thin film, cm^{-1}): 2978, 2936, 1750, 1729, 1709, 1489; HRMS (CI-TOF) m/z: calcd for $C_{16}H_{19}{}^{79}BrO_3$ $(M)^+$, 338.0518; found, 338.0504.

*Ethyl 2-(2-Chlorobenzyl)-1-methyl-5-oxocyclopentane-1-carboxylate (**3d**).* Following the general procedure, 56 mg (95%; 1.7:1

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dr) of **3d** was produced as a colorless oil from styrene **2d** (59 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 72 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.44−7.32 (m, 1H), 7.24−7.15 (m, 3H), 4.34−4.11 (m, 2H), 3.14 (dd, J = 13.2, 4.0 Hz, 1H), 2.68−2.43 (m, 2H), 2.41−2.25 (m, 1H), 2.18 (ddd, J = 19.3, 10.8, 9.3 Hz, 1H), 2.09−1.79 (m, 2H), 1.34 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 216.2, 170.8, 137.2, 134.1, 131.3, 129.9, 128.1, 126.9, 61.4, 59.4, 49.1, 37.7, 35.0, 25.9, 18.5, 14.4; FTIR (thin film, cm^{-1}): 2979, 2934, 1730, 1706, 1476; HRMS (CI-TOF) m/z: calcd for $C_{16}H_{19}ClO_3$ $(M)^+$, 294.1023; found, 294.1032.

*Ethyl 1,2-Dibenzyl-5-oxocyclopentane-1-carboxylate (**3e**).* Following the general procedure, 60 mg (90%; 3:1 dr) of **3e** was produced as a colorless oil from styrene **2e** (67 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.16 (m, 6H), 7.14−7.03 (m, 4H), 4.27 (ddq, J = 39.1, 10.8, 7.1 Hz, 2H), 3.45 (d, J = 14.1 Hz, 1H), 3.16 (d, J = 14.1 Hz, 1H), 3.03 (dd, J = 12.4, 3.2 Hz, 1H), 2.51−2.22 (m, 3H), 1.88−1.63 (m, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 216.2, 170.8, 139.6, 136.8, 130.9, 129.0, 128.6, 128.6, 127.0, 126.5, 64.4, 61.6, 44.3, 39.1, 37.2, 36.4, 26.0, 14.5; FTIR (thin film, cm^{-1}): 2955, 2920, 2850, 1750, 1730, 1706, 1454; HRMS (CI-TOF) m/z: calcd for $C_{22}H_{24}O_3$ $(M)^+$, 336.1725; found, 336.1731.

*3-Acetyl-4-benzyl-3-methyldihydrofuran-2(3H)-one (**3f**).* Following the general procedure, 33 mg (58%; 1:1 dr) of **3f** was produced as a colorless oil from styrene **2f** (46 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36−7.21 (m, 3H), 7.19−7.14 (m, 2H), 4.17 (dd, J = 9.2, 7.3 Hz, 1H), 3.95 (dd, J = 9.2, 8.0 Hz, 1H), 3.29 (dtd, J = 11.2, 7.6, 4.8 Hz, 1H), 2.85 (dd, J = 13.6, 4.8 Hz, 1H), 2.47 (dd, J = 13.6, 11.2 Hz, 1H), 2.32 (s, 3H), 1.49 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 203.9, 176.8, 137.9, 129.0, 128.8, 127.1, 70.2, 59.0, 42.8, 33.7, 26.2, 14.9; FTIR (thin film, cm^{-1}): 2997, 2918, 1768, 1710, 1496; HRMS (CI-TOF) m/z: calcd for $C_{14}H_{16}O_3H$ $(M + H)^+$, 233.1178; found, 233.1178.

*4-Benzyl-2-oxaspiro[4.4]nonane-1,6-dione (**3g**).* Following the general procedure, 45 mg (92%; 2:1 dr) of **3g** was produced as a colorless oil from styrene **2g** (49 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35−7.23 (m, 3H), 7.17−7.11 (m, 2H), 4.43 (dd, J = 9.0, 6.8 Hz, 1H), 3.99 (dd, J = 9.0, 5.5 Hz, 1H), 3.08 (ddt, J = 11.0, 6.8, 5.5 Hz, 1H), 2.80 (dd, J = 13.8, 5.4 Hz, 1H), 2.59−2.45 (m, 2H), 2.43−2.29 (m, 2H), 2.29−2.12 (m, 2H), 1.99 (tdd, J = 11.6, 6.4, 3.3 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 213.6, 175.3, 137.5, 129.0, 128.9, 127.1, 70.5, 60.6, 43.1, 37.5, 34.7, 28.7, 19.4; FTIR (thin film, cm^{-1}): 2964, 2920, 2853, 1768, 1733, 1464; HRMS (CI-TOF) m/z: calcd for $C_{15}H_{16}O_3H$ $(M + H)^+$, 245.1178; found, 245.1183.

*3-Acetyl-3-methyl-4-phenylhexahydrobenzofuran-2(3H)-one (**3h**).* Following the general procedure, 33 mg (62%; 6.7:1.4:1 dr) of **3h** was produced as a colorless oil from styrene **2h** (54 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 72 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48−7.38 (m, 2H), 7.35−7.28 (m, 3H), 4.89 (dt, J = 10.6, 6.7 Hz, 1H), 3.17 (dd, J = 12.0, 6.8 Hz, 1H), 2.66 (dq, J = 11.9, 6.9 Hz, 1H), 2.10 (tdd, J = 10.2, 7.2, 3.3 Hz, 3H), 1.79 (s, 3H), 1.64−1.46 (m, 1H), 1.43−1.23 (m, 1H), 1.21 (d, J = 7.0 Hz, 3H), 0.88 (tddd, J = 13.7, 10.2, 6.2, 3.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 208.7, 178.5, 140.3, 129.7, 127.8, 127.1, 75.4, 58.7, 45.9, 35.3, 29.6, 28.1, 28.0, 17.8, 15.3; FTIR (thin film, cm^{-1}): 2944, 2870, 1774, 1705; HRMS (CI-TOF) m/z: calcd for $C_{17}H_{20}O_3H$ $(M + H)^+$, 273.1491; found, 273.1504.

*N,2-dibenzyl-1-methyl-5-oxocyclopenaten-1-carboxamide (**3i**).* Following the general procedure, 58 mg (91%; 1.9:1 dr) of **3i** was produced as a colorless oil from styrene **3i** (64 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.32 (m, 2H), 7.31−7.27 (m, 5H), 7.23−7.18 (m, 1H), 7.17−7.13 (m, 2H), 6.96 (s, 1H), 4.48 (d, J = 5.7 Hz, 2H), 3.11−2.96 (m, 1H), 2.63−2.18 (m, 4H), 1.93 (dtd, J = 8.8, 6.5, 4.2 Hz, 2H), 1.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 219.7, 170.5, 140.2, 138.2, 129.2, 128.9, 128.6, 127.9, 127.7, 126.4, 59.6, 49.4, 43.4, 36.4, 36.1, 23.1, 21.5; FTIR (thin film, cm^{-1}): 3305, 3028, 2925, 1729, 1645, 1540; HRMS (CI-TOF) m/z: calcd for $C_{21}H_{23}NO_2$ $(M)^+$, 321.1729; found, 321.1731.

*Ethyl 2-Benzyl-1,2-dimethyl-5-oxocyclopentane-1-carboxylate (**3j**).* Following the general procedure, 52 mg (96%; 1.3:1 dr) of **3j** was produced as a colorless oil from styrene **2j** (54 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.37−7.12 (m, 5H), 4.36−4.09 (m, 2H), 2.73 (d, J = 13.1 Hz, 1H), 2.67−2.53 (m, 2H), 2.45−2.12 (m, 2H), 1.67−1.57 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.21 (s, 3H), 0.76 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 216.7, 171.7, 137.5, 130.5, 128.2, 126.6, 63.9, 61.3, 46.7, 43.9, 35.8, 32.4, 21.5, 14.3, 14.1; FTIR (thin film, cm^{-1}): 2978, 2932, 1749, 1726, 1709, 1453; HRMS (CI-TOF) m/z: calcd for $C_{17}H_{22}O_3$ $(M)^+$, 274.1569; found, 274.1565.

General Procedure for the Alkene Dialkylation. *Ethyl 1-Methyl-2-(2-methyl-4-phenylbutan-2-yl)-5-oxocyclopentane-1-carboxylate (**5a**).* To a flame-dried vial charged with a magnetic stirring bar were added ketoester **4a** (42 mg, 0.2 mmol, 1.0 equiv), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol, 2 mol %), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol, 0.2 equiv). The vial was evacuated and backfilled three times with argon, after which acetonitrile (2 mL, 0.1 M) and styrene (29 μL, 0.25 mmol, 1.25 equiv; inhibitors removed by filtration through basic alumina immediately before use) were added. The reaction mixture was then vigorously degassed with bubbling argon. The vial was then capped and sealed with Teflon tape. The mixture was then stirred under blue LED irradiation with air cooling for 24 h. The reaction mixture was quenched with saturated aqueous ammonium chloride (2 mL) and extracted with ethyl acetate (3 × 2 mL). The combined organic phases were washed with brine (3 mL) and dried over anhydrous sodium sulfate, filtered, and concentrated. The crude reaction mixture was purified by automated column chromatography (SiO_2, 5−100% ethyl acetate in hexanes gradient) to afford 49 mg (78%) of **5a** as a colorless oil as a 3.1:1 mixture of diastereomers. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.33−7.24 (m, 2H), 7.18 (td, J = 5.8, 1.7 Hz, 3H), 4.19−3.94 (m, 2H), 2.71−2.48 (m, 3H), 2.32−1.94 (m, 3H), 1.78−1.49 (m, 3H), 1.45 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 1.09 (s, 3H), 0.98 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 216.9, 172.0, 142.9, 128.6, 128.4, 125.9, 61.2, 58.9, 58.2, 44.2, 37.4, 36.3, 30.5, 25.2, 25.0, 22.2, 21.9, 13.9; FTIR (thin film, cm^{-1}): 2963, 2935, 1750, 1729, 1454; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{28}O_3Na$ $(M + Na)^+$, 339.1936; found, 339.1941.

*Ethyl 2-(4-(4-Fluorophenyl)-2-methylbutan-2-yl)-1-methyl-5-oxocyclopentane-1-carboxylate (**5b**).* Following the general procedure, 54 mg (81%; 2.4:1 dr) of **5b** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and 4-fluorostyrene (30 mg, 0.25 mmol) in acetonitrile (2 mL) with a 48 h reaction time. A single diastereomer could be isolated for characterization purposes: ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.12 (dd, J = 8.4, 5.7 Hz, 2H), 6.96 (t, J = 8.7 Hz, 2H), 4.15 (q, J = 6.9 Hz, 2H), 2.81 (dd, J = 13.2, 5.7 Hz, 1H), 2.55 (t, J = 8.4 Hz, 2H), 2.50−2.30 (m, 2H), 2.08 (dddd, J = 14.0, 7.9, 5.8, 1.7 Hz, 1H), 1.87−1.72 (m, 1H),

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1.57 (q, J = 7.2 Hz, 2H), 1.30 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H), 1.03 (d, J = 5.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ 216.5, 173.8, 161.5 (d, J = 243 Hz), 138.7 (d, J = 3.8 Hz), 129.9 (d, J = 7.5 Hz), 115.5 (d, J = 21 Hz), 61.7, 61.0, 54.0, 37.6, 36.1, 29.9, 26.0, 25.0, 23.0, 21.5, 15.7, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.7 (m); FTIR (thin film, cm^{-1}): 2967, 2876, 1750, 1729, 1510; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{27}FO_3Na$ $(M + Na)^+$, 357.1842; found, 357.1841.

*Ethyl 2-(4-(4-Bromophenyl)-2-methylbutan-2-yl)-1-methyl-5-oxocyclopentane-1-carboxylate (**5c**).* Following the general procedure, 61 mg (77%; 2:1 dr) of **5c** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and 4-bromostyrene (46 mg, 0.25 mmol) in acetonitrile (2 mL) with a 48 h reaction time. A single diastereomer could be isolated for characterization purposes: ^1H NMR (300 MHz; $CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 2H), 7.05 (d, J = 8.4 Hz, 2H), 4.15 (q, J = 6.9 Hz, 2H), 2.81 (dd, J = 13.2, 7.2 Hz, 1H), 2.53 (t, J = 8.1 Hz, 2H), 2.53−2.25 (m, 2H), 2.16−1.99 (m, 1H), 1.79 (tdd, J = 12.8, 11.4, 8.6 Hz, 1H), 1.68−1.43 (m, 2H), 1.30 (s, 3H), 1.26−1.16 (t, J = 7.2 Hz, 3H), 1.03 (d, J = 5.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 216.2, 173.6, 141.9, 131.6, 130.2, 119.6, 61.5, 60.8, 53.7, 44.2, 37.4, 36.0, 29.9, 25.8, 24.8, 21.3, 15.5, 14.1; FTIR (thin film, cm^{-1}): 2966, 2941, 1751, 1727, 1488; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{27}{}^{79}BrO_3Na$ $(M + Na)^+$, 417.1041; found, 417.1058.

*Ethyl 2-(4-(2-Chlorophenyl)-2-methylbutan-2-yl)-1-methyl-5-oxocyclopentane-1-carboxylate (**5d**).* Following the general procedure, 54 mg (77%; 1.6:1 dr) of **5d** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and 2-chlorostyrene (35 mg, 0.25 mmol) in acetonitrile (2 mL) with a 48 h reaction time. A single diastereomer could be isolated for characterization purposes: ^1H NMR (300 MHz; $CDCl_3$): δ 7.33 (d, J = 6.9 Hz, 1H), 7.20−7.12 (m, 3H), 4.15 (qd, J = 7.2, 1.8 Hz, 2H), 2.85 (dd, J = 13.2, 5.7 Hz, 1H), 2.79−2.62 (m, 2H), 2.53−2.31 (m, 2H), 2.18−2.09 (m, 1H), 1.88−1.72 (m, 1H), 1.67−1.45 (m, 2H), 1.31 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H), 1.06 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ 216.4, 173.6, 140.5, 133.9, 130.4, 129.7, 127.4, 127.1, 61.5, 60.8, 53.8, 42.3, 37.4, 36.0, 28.6, 25.6, 24.6, 21.3, 15.5, 14.1; FTIR (thin film, cm^{-1}): 2966, 2943, 1750, 1728; HRMS (ESI-TOF) m/z: calcd for $C_{20}H_{27}ClO_3Na$ $(M + Na)^+$, 373.1546; found, 373.1528.

*Ethyl 2-(4-(4-Methoxyphenyl)-2-methylbutan-2-yl)-1-methyl-5-oxocyclopentane-1-carboxylate (**5e**).* Following the general procedure, 62 mg (89%; 2.1:1 dr) of **5e** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and 4-methoxystyrene (33 mg, 0.25 mmol) in acetonitrile (2 mL) with a 48 h reaction time. A single diastereomer could be isolated for characterization purposes: ^1H NMR (300 MHz; $CDCl_3$): δ 7.09 (d, J = 8.4 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.15−3.98 (m, 2H), 3.80 (s, 3H), 2.65 (dd, J = 18.6, 8.1 Hz, 1H), 2.56−2.49 (m, 2H), 2.31−2.09 (m, 1H), 2.06−1.97 (m, 2H), 1.73−1.54 (m, 3H), 1.46 (s, 3H), 1.26 (t, J = 7.1, 3H), 1.03 (d, J = 31.8 Hz, 6H); $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ 216.9, 172.0, 157.9, 134.9, 129.2, 114.0, 61.2, 58.9, 58.2, 55.4, 44.4, 37.4, 36.2, 29.5, 25.2, 25.0, 22.2, 21.9, 13.9; FTIR (thin film, cm^{-1}): 2959, 2935, 1750, 1726; HRMS (ESI-TOF) m/z: calcd for $C_{21}H_{31}O_4Na$ $(M + Na)^+$, 369.2042; found, 369.2058.

*Ethyl 1-Methyl-2-(2-methyl-4-(pyridin-4-yl)butan-2-yl)-5-oxocyclopentane-1-carboxylate (**5f**).* Following the general procedure, 40 mg (63%; 1.2:1 dr) of **5f** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and 4-vinylpyridine (26 mg, 0.25 mmol) in acetonitrile (2 mL) with a 24 h reaction time. Diastereomers could not be separated in this case, and some key spectroscopic features are listed, see the printed spectra for details: ^1H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 2H), 7.12 (d, J = 4.9 Hz, 2H), 4.22−3.86 (m, 1H), 2.86−1.91 (m, 5H), 1.88−1.47 (m, 1H), 1.44 (s, 3H), 1.29 (s, 1H), 1.19 (td, J = 7.1, 2.6 Hz, 3H), 1.06 (s, 3H), 0.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 216.3, 215.8, 173.5, 171.9, 153.8, 148.4, 148.3, 124.4, 61.6, 61.3, 60.7, 59.1, 58.1, 53.6, 42.9, 42.6, 37.3, 37.3, 36.4, 36.1, 30.2, 30.2, 25.9, 25.2, 24.9, 24.7, 22.3, 21.9, 21.3, 15.5, 14.2, 13.9; FTIR (thin film, cm^{-1}): 2967, 2939, 1750, 1735, 1601; HRMS (ESI-TOF) m/z: calcd for $C_{19}H_{27}NO_3Na$ $(M + Na)^+$, 340.1889; found, 340.1838.

*Ethyl 1-Methyl-2-(2-methyl-4-(naphthalen-2-yl)butan-2-yl)-5-oxocyclopentane-1-carboxylate (**5g**).* Following the general procedure, 60 mg (82%; 1.2:1 dr) of **5g** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and 2-vinylnaphthalene (39 mg, 0.25 mmol) in acetonitrile (2 mL) with a 72 h reaction time. A single diastereomer could be isolated for characterization purposes: ^1H NMR (300 MHz; $CDCl_3$): δ 7.80, (t, J = 8.7 Hz, 3H), 7.62 (s, 1H), 7.49−7.42 (m, 2H), 7.33 (dd, J = 8.4, 1.5 Hz, 1H), 4.15−3.99 (m, 2H), 2.78−2.68 (m, 2H), 2.63 (d, J = 6.9 Hz, 1H), 2.30−2.17 (m, 2H), 2.13−2.05 (m, 2H), 1.82−1.48 (m, 2H), 1.49 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H), 1.09 (d, J = 33.3 Hz, 6H); $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ 216.9, 172.0, 140.4, 133.8, 132.1, 128.1, 127.7, 127.5, 127.4, 126.3, 126.1, 125.3, 61.2, 59.0, 58.2, 44.0, 37.4, 36.3, 30.6, 30.5, 25.3, 25.0, 22.3, 21.9, 13.9; FTIR (thin film, cm^{-1}): 2969, 2871, 1750, 1725; HRMS (ESI-TOF) m/z: calcd for $C_{24}H_{30}O_3Na$ $(M + Na)^+$, 389.2093; found, 389.2097.

*tert-Butyl 1-Methyl-2-(2-methyl-4-(naphthalen-2-yl)butan-2-yl)-5-oxocyclopentane-1-carboxylate (**5h**).* Following the general procedure, 43 mg (63%; 1.7:1 dr) of **5h** was produced as a colorless oil from ketoester **4h** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^1H NMR (400 MHz; $CDCl_3$): δ 7.32−7.28 (m, 2H), 7.21−7.18 (m, 3H), 2.66−2.56 (m, 3H), 2.28−2.10 (m, 2H), 2.07−1.96 (m, 2H), 1.71−1.57 (m, 2H), 1.43 (s, 3H), 1.38 (s, 9H), 1.13 (s, 3H), 1.05 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 217.0, 171.1, 143.0, 128.5, 128.5, 125.9, 82.5, 59.4, 59.0, 44.3, 37.4, 36.4, 30.6, 27.9, 25.7, 25.5, 22.3, 21.9; FTIR (thin film, cm^{-1}): 2973, 2936, 1749, 1723; HRMS (ESI-TOF) m/z: calcd for $C_{22}H_{32}O_3Na$ $(M + Na)^+$, 367.2249; found, 367.2247.

*Ethyl 3-Methyl-4-(2-methyl-4-phenylbutan-2-yl)-2-oxotetrahydrofuran-3-carboxylate (**5i**).* Following the general procedure, 26 mg (44%; 2.3:1 dr) of **5i** was produced as a colorless oil from ketoester **4i** (37 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (4.7 mg, 0.04 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (2 mL) with a 24 h reaction time. A single diastereomer could be isolated for characterization purposes: ^1H NMR (400 MHz, $CDCl_3$): δ 7.34−7.09 (m, 5H), 4.43 (dd, J = 9.1, 7.8 Hz, 1H), 4.23 (dd, J = 10.6, 9.0 Hz, 1H), 3.18 (dd, J = 10.5, 7.7 Hz, 1H), 2.63−2.48 (m, 2H), 2.33 (s, 3H), 1.60−1.49 (m, 7H), 1.06 (s, 3H), 0.99 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 204.7, 177.3, 142.1, 128.7, 128.7, 126.2, 67.8, 59.7, 50.2, 44.4, 35.4, 30.3, 26.6, 25.7, 25.2, 16.0; FTIR (thin film, cm^{-1}): 2967, 2939, 1767, 1714; HRMS (CI-TOF) m/z: calcd for $C_{18}H_{24}O_3H$ $(M + H)^+$, 289.1804; found, 289.1794.

General Procedure for the Alkene Amidoalkylation. *5-(2-Methyl-4-phenylbutan-2-yl)-1-phenylpyrrolidin-2-one (**7a**).* To a flame-dried vial charged with a magnetic stirring bar were added amide **6a** (41 mg, 0.2 mmol, 1.0 equiv), $[Ir(dtbbpy)(ppy)_2](PF_6)$ (3.6 mg, 4.0 μmol, 2 mol %), and potassium *tert*-butoxide (11 mg, 0.1 mmol, 0.5 equiv). The vial was evacuated and backfilled three times with argon, after which acetonitrile (0.7 mL, 0.3 M) and styrene (29 μL, 0.25 mmol, 1.25 equiv; inhibitors removed by filtration through basic alumina immediately before use) were added. The vial was then capped and sealed with Teflon tape. The mixture was then stirred under blue LED irradiation with air cooling for 48 h. The reaction mixture was then diluted with saturated aqueous ammonium chloride (2 mL) and extracted with ethyl acetate (3 × 2 mL). The combined organic phases were washed with saturated sodium chloride (3 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude reaction mixture was purified by column chromatography (SiO_2, 40% ethyl acetate in hexanes) to afford 41 mg (67%) of **7a** as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$): δ 7.44−7.29 (m, 4H), 7.25−7.19 (m, 3H), 7.18−7.11 (m, 1H), 7.00−6.93 (m, 2H), 4.25

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(dd, J = 9.1, 2.6 Hz, 1H), 2.64 (dt, J = 17.3, 9.8 Hz, 1H), 2.53−2.42 (m, 3H), 2.36−2.20 (m, 1H), 2.16−2.06 (m, 1H), 1.56−1.38 (m, 2H), 0.89 (s, 3H), 0.84 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.6, 142.6, 140.4, 129.1, 128.5, 128.3, 126.5, 126.0, 125.9, 68.0, 41.7, 39.8, 31.6, 30.3, 25.0, 24.0, 20.9; FTIR (thin film cm^{-1}): 2962, 2931, 1686, 1684; HRMS (ESI-TOF) m/z: calcd for $C_{21}H_{25}NONa$ $(M + Na)^+$, 330.1834; found, 330.1835.

*1-(4-Fluorophenyl)-5-(2-methyl-4-phenylbutan-2-yl)pyrrolidin-2-one (**7b**).* Following the general procedure, 36 mg (55%) of **7b** was produced as a colorless oil from amide **6b** (44 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 72 h reaction time. ^1H NMR (400 MHz, $CDCl_3$): δ 7.38−7.21 (m, 4H), 7.26−7.12 (m, 1H), 7.18−7.04 (m, 2H), 7.04−6.96 (m, 2H), 4.20 (dd, J = 9.0, 2.7 Hz, 1H), 2.64 (dt, J = 17.3, 9.7 Hz, 1H), 2.59−2.39 (m, 3H), 2.39−2.18 (m, 1H), 2.11 (ddt, J = 13.2, 9.7, 3.3 Hz, 1H), 1.60−1.36 (m, 2H), 0.89 (s, 3H), 0.83 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.7, 160.8 (d, J = 247 Hz), 142.5, 136.3 (d, J = 3.5 Hz), 128.6, 128.2, 127.6 (d, J = 10 Hz), 126.0, 115.9 (d, J = 24 Hz), 68.3, 41.6, 39.7, 31.4, 30.2, 25.0, 24.0, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.4 (m); FTIR (thin film, cm^{-1}): 3026, 2964, 2874, 1700, 1603; HRMS (CI-TOF) m/z: calcd for $C_{21}H_{24}FNOH$ $(M + H)^+$, 326.1920; found, 326.1918.

*1-Mesityl-5-(2-methyl-4-phenylbutan-2-yl)pyrrolidin-2-one (**7c**).* Following the general procedure, 52 mg (74%) of **7c** was produced as a colorless oil from amide **6c** (49 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz, $CDCl_3$): δ 7.23−7.09 (m, 5H), 6.91 (d, J = 7.8 Hz, 1H), 6.83−6.78 (m, 1H), 3.97 (dd, J = 8.8, 2.6 Hz, 1H), 2.63 (dt, J = 16.3, 9.7 Hz, 1H), 2.51−2.34 (m, 2H), 2.31 (s, 3H), 2.29 (s, 3H), 2.28−2.02 (m, 6H), 1.55 (td, J = 13.2, 4.9 Hz, 1H), 1.35 (td, J = 13.3, 4.7 Hz, 1H), 0.96 (s, 3H), 0.95 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 176.1, 142.6, 137.3, 136.9, 135.6, 133.8, 130.1, 129.9, 128.4, 128.3, 125.8, 67.4, 41.9, 39.2, 30.8, 30.3, 24.4, 23.9, 21.7, 21.0, 19.8, 18.9; FTIR (thin film, cm^{-1}): 3025, 2960, 2877, 1751, 1607; HRMS (CI-TOF) m/z: calcd for $C_{24}H_{31}NO$ $(M)^+$, 349.2406; found, 349.2393.

*1-(4-Methoxyphenyl)-5-(2-methyl-4-phenylbutan-2-yl)-pyrrolidin-2-one (**7d**).* Following the general procedure, 44 mg (65%) of **7d** was produced as a colorless oil from amide **6d** (47 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz; $CDCl_3$): δ 7.33−7.10 (m, 5H), 6.95 (m, 7.00−6.91, 4H), 4.17 (dd, J = 8.9, 3.0 Hz, 1H), 3.82 (s, 3H), 2.62 (dt, J = 17.2, 9.6 Hz, 1H), 2.58−2.36 (m, 3H), 2.36−2.16 (m, 1H), 2.09 (ddt, J = 13.3, 9.7, 3.5 Hz, 1H), 1.48 (qdd, J = 13.7, 10.6, 6.3 Hz, 2H), 0.90 (s, 3H), 0.85 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz; $CDCl_3$): δ 175.9, 158.0, 142.6, 133.1, 128.5, 128.3, 127.2, 125.9, 114.4, 68.1, 55.6, 41.6, 39.4, 31.3, 30.2, 24.9, 24.1, 20.8; FTIR (thin film, cm^{-1}): 2961, 1705, 1608l 1510; HRMS (ESI-TOF) m/z: calcd for $C_{22}H_{27}NO_2Na$ $(M + Na)^+$, 360.1939; found, 360.1943.

*5-(2-Methyl-4-(p-tolyl)butan-2-yl)-1-phenylpyrrolidin-2-one (**7e**).* Following the general procedure, 35 mg (52%) of **7e** was produced as a colorless oil from amide **6a** (41 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and 4-methoxystyrene (34 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 72 h reaction time. ^1H NMR (300 MHz, $CDCl_3$): δ 7.52−7.30 (m, 4H), 7.33−7.16 (m, 1H), 6.98−6.86 (m, 2H), 6.86−6.73 (m, 2H), 4.26 (dd, J = 9.0, 2.6 Hz, 1H), 3.79 (s, 3H), 2.81−2.00 (m, 6H), 1.57−1.32 (m, 2H), 0.90 (s, 3H), 0.84 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 175.6, 157.8, 140.3, 134.5, 129.1, 126.4, 126.2, 125.9, 113.8, 67.8, 55.3, 41.9, 39.6, 31.5, 29.2, 24.9, 24.0, 20.8; FTIR (thin film, cm^{-1}): 2960, 2934, 1695, 1512; HRMS (CI-TOF) m/z: calcd for $C_{22}H_{27}NO_2H$ $(M + H)^+$, 338.2120; found, 338.2113.

*5-(4-(4-Fluorophenyl)-2-methylbutan-2-yl)-1-phenylpyrrolidin-2-one (**7f**).* Following the general procedure, 24 mg (36%) of **7f** was produced as a colorless oil from amide **6a** (41 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and 4-fluorostyrene (37 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz; $CDCl_3$): δ 7.34−7.17 (m, 4H), 7.17−7.04 (m, 1H), 6.83−6.67 (m, 4H), 4.11 (dd, J = 9.0, 2.6 Hz, 1H), 2.51 (dt, J = 17.1, 9.7 Hz, 1H), 2.44−2.04 (m, 4H), 2.04−1.85 (m, 1H), 1.41−1.07 (m, 2H), 0.89 (s, 3H), 0.84 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 175.6, 161.2 (d, J = 244 Hz), 140.3, 138.1 (d, J = 3 Hz), 129.5 (d, J = 7.6 Hz), 129.1, 126.5, 125.9, 115.2 (d, J = 21 Hz), 67.8, 41.8, 39.7, 31.5, 29.4, 24.7, 24.0, 20.8; ^{19}F NMR (376 MHz, $CDCl_3$): δ −117.7 (m); FTIR (thin film, cm^{-1}): 2963, 2939, 1700, 1597; HRMS (CI-TOF) m/z: calcd for $C_{21}H_{23}FNOH$ $(M + H)^+$, 326.1920; found, 326.1920.

*5-(4-(2-chlorophenyl)-2-methylbutan-2-yl)-1-phenylpyrrolidin-2-one (**7g**).* Following the general procedure, 58 mg (85%) of **7g** was produced as a colorless oil from amide **6a** (41 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and 2-chlorostyrene (42 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz, $CDCl_3$): δ 7.45−7.19 (m, 6H), 7.16−7.07 (m, 2H), 6.95−6.90 (m, 1H), 4.26 (dd, J = 9.0, 2.6 Hz, 1H), 2.77−2.40 (m, 4H), 2.37−2.19 (m, 1H), 2.12 (ddt, J = 13.1, 9.8, 3.0 Hz, 1H), 1.46 (tt, J = 11.1, 7.6 Hz, 2H), 0.90 (s, 3H), 0.85 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 175.5, 140.3, 140.0, 133.7, 130.1, 129.5, 129.0, 127.4, 126.9, 126.4, 125.9, 68.1, 39.7, 39.5, 31.5, 28.1, 24.9, 23.7, 20.7; FTIR (thin film, cm^{-1}): 3063, 2964, 1703, 1674, 1596; HRMS (CI-TOF) m/z: calcd for $C_{21}H_{24}ClNOH$ $(M + H)^+$, 342.1625; found, 342.1632.

*5-(2-Methyl-4-(naphthalen-2-yl)butan-2-yl)-1-phenylpyrrolidin-2-one (**7h**).* Following the general procedure, 52 mg (73%) of **7h** was produced as a colorless oil from amide **6a** (41 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and 2-vinylnaphthalene (39 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (400 MHz, $CDCl_3$): δ 7.83−7.67 (m, 3H), 7.48−7.31 (m, 6H), 7.30−7.23 (m, 2H), 7.08 (dd, J = 8.4, 1.8 Hz, 1H), 4.29 (dd, J = 9.1, 2.5 Hz, 1H), 2.72−2.56 (m, 3H), 2.49 (ddd, J = 17.3, 10.5, 3.2 Hz, 1H), 2.30 (dddd, J = 13.4, 10.5, 9.8, 9.0 Hz, 1H), 2.18−2.08 (m, 1H), 1.55 (qdd, J = 13.7, 11.0, 6.1 Hz, 2H), 0.95 (s, 3H), 0.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 175.6, 140.5, 140.0, 133.7, 132.1, 129.2, 128.0, 127.7, 127.4, 127.2, 126.5, 126.1, 126.1, 126.0, 125.3, 67.9, 41.6, 39.8, 31.6, 30.4, 24.8, 24.1, 20.9; FTIR (thin film, cm^{-1}): 3055, 2964, 2873, 1693, 1597; HRMS (CI-TOF) m/z: calcd for $C_{25}H_{27}NOH$ $(M + H)^+$, 358.2171; found, 358.2171.

*4-(2-Methyl-4-phenylbutan-2-yl)-3-phenyloxazolidin-2-one (**7i**).* Following the general procedure, 34 mg (55%) of **7i** was produced as a colorless oil from carbamate **6i** (41 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49−7.34 (m, 3H), 7.29−7.20 (m, 3H), 7.20−7.12 (m, 1H), 7.04−6.87 (m, 2H), 4.51−4.29 (m, 3H), 2.48 (dd, J = 9.6, 7.7 Hz, 2H), 1.55−1.39 (m, 2H), 0.94 (s, 3H), 0.89 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 157.2, 142.1, 139.1, 129.4, 128.6, 128.2, 126.5, 126.1, 125.0, 64.3, 64.2, 40.6, 38.7, 30.1, 23.8, 22.9; FTIR (thin film, cm^{-1}): 3026, 2965, 2874, 1750, 1598; HRMS (CI-TOF) m/z: calcd for $C_{20}H_{23}NO_2H$ $(M + H)^+$, 310.1807; found, 310.1808.

*4-(2-Methyl-4-(naphthalen-2-yl)butan-2-yl)-3-phenyloxazolidin-2-one (**7j**).* Following the general procedure, 35 mg (48%) of **7j** was produced as a colorless oil from carbamate **6i** (41 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and 2-vinylnaphthalene (39 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84−7.66 (m, 3H), 7.50−7.38 (m, 6H), 7.34 (d, J = 1.7 Hz, 1H), 7.33−7.24 (m, 1H), 7.07 (dd, J = 8.4, 1.8 Hz, 1H), 4.51−4.32 (m, 3H), 2.63 (dd, J = 9.6, 7.7 Hz, 2H), 1.58−1.48 (m, 2H), 0.97 (s, 3H), 0.94 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 157.2, 139.5, 139.1, 133.7, 132.1, 129.4, 128.1, 127.7, 127.4, 127.1, 126.5, 126.1, 125.4, 125.0, 64.3, 64.1, 40.5, 38.8, 30.2, 23.6, 22.9; FTIR (thin film, cm^{-1}): 2963, 2862, 1751, 1735, 1598; HRMS (CI-TOF) m/z: calcd for $C_{24}H_{25}NO_2H$ $(M + H)^+$, 360.1964; found, 360.1965.

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*1-Methyl-4-(2-methyl-4-phenylbutan-2-yl)-3-phenylimidazolidin-2-one (**7k**).* Following the general procedure, 39 mg (61%) of **7k** was produced as a colorless oil from urea **6k** (44 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and styrene (26 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40−7.29 (m, 3H), 7.27−7.11 (m, 5H), 7.00−6.94 (m, 2H), 4.23 (dd, J = 9.6, 4.6 Hz, 1H), 3.51 (t, J = 9.4 Hz, 1H), 3.32 (dd, J = 9.3, 4.7 Hz, 1H), 2.84 (s, 3H), 2.55−2.40 (m, 2H), 1.57−1.37 (m, 2H), 0.89 (s, 3H), 0.85 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 159.8, 142.6, 141.5, 129.0, 128.5, 128.3, 125.9, 125.3, 61.3, 47.2, 40.8, 38.9, 31.0, 30.3, 24.2, 23.2; FTIR (thin film, cm^{-1}): 3025, 2964, 2873, 1695, 1597; HRMS (CI-TOF) m/z: calcd for $C_{21}H_{26}N_2OH$ $(M + H)^+$, 323.2123; found, 323.2130.

*1-Methyl-4-(2-methyl-4-(naphthalen-2-yl)butan-2-yl)-3-phenylimidazolidin-2-one (**7l**).* Following the general procedure, 60 mg (81%) of **7l** was produced as a colorless oil from urea **6k** (44 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and 2-vinylnaphthalene (39 mg, 0.25 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.1 Hz, 1H), 7.71 (dd, J = 8.2, 4.2 Hz, 2H), 7.50−7.33 (m, 6H), 7.20 (tt, J = 6.4, 2.1 Hz, 2H), 7.09 (dd, J = 8.4, 1.8 Hz, 1H), 4.27 (dd, J = 9.6, 4.6 Hz, 1H), 3.54 (t, J = 9.5 Hz, 1H), 3.35 (dd, J = 9.3, 4.7 Hz, 1H), 2.85 (s, 3H), 2.65 (dd, J = 9.8, 7.5 Hz, 2H), 1.66−1.42 (m, 2H), 0.94 (s, 3H), 0.90 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 159.8, 141.5, 140.0, 133.7, 132.0, 129.0, 128.0, 127.7, 127.4, 127.2, 126.1, 126.0, 125.4, 125.3, 121.2, 61.2, 47.2, 40.8, 39.0, 31.0, 30.4, 24.0, 23.1; FTIR (thin film, cm^{-1}): 2961, 2927, 1703, 1684, 1472; HRMS (CI-TOF) m/z: calcd for $C_{25}H_{28}N_2O$ $(M)^+$, 372.2202; found, 372.2198.

*4-Methyl-4-phenethyl-3-phenylhexahydrobenzo[d]oxazol-2(3H)-one (**7m**).* Following the general procedure, 23 mg (34%, 1:1 dr) of **7m** was produced as a colorless oil from carbamate **6m** (46 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), potassium *tert*-butoxide (11 mg, 0.1 mmol), and styrene (31 mg, 0.3 mmol) in acetonitrile (0.7 mL) with a 48 h reaction time. ^1H NMR (300 MHz, $CDCl_3$): δ 7.61−7.51 (m, 2H), 7.38 (dd, J = 8.7, 7.2 Hz, 2H), 7.23−7.06 (m, 4H), 6.91−6.84 (m, 2H), 4.76 (td, J = 4.4, 2.2 Hz, 1H), 4.21 (d, J = 6.3 Hz, 1H), 2.44 (t, J = 8.7 Hz, 2H), 2.35−2.26 (m, 1H), 1.83−1.67 (m, 2H), 1.61−1.50 (m, 2H), 1.43−1.20 (m, 3H), 1.08 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 156.7, 142.1, 138.8, 129.2, 128.4, 128.2, 125.9, 125.6, 123.4, 75.2, 62.3, 45.0, 38.9, 34.0, 29.5, 26.8, 21.3, 15.9; FTIR (thin film, cm^{-1}): 2940, 1703, 1599, 1501; HRMS (CI-TOF) m/z: calcd for $C_{22}H_{25}NO_2$ $(M)^+$, 335.1885; found, 335.1887.

*Ethyl 1-Methyl-2-oxo-5-(2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propan-2-yl)cyclopentane-1-carboxylate (**13**).* Following the general procedure, 15 mg (20%) of **13** was produced as a colorless oil from ketoester **4a** (42 mg, 0.20 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (3.6 mg, 0.004 mmol), 2,2,6,6-tetramethylpiperidin-1-oxyl (47 mg, 0.3 mmol), and potassium *tert*-butoxide (4.7 mg, 0.04 mmol) in acetonitrile (2 mL) with a 24 h reaction time. ^1H NMR (300 MHz; $CDCl_3$): δ 4.14−4.09 (m, 2H), 2.71−2.52 (m, 2H), 2.31−2.06 (m, 3H), 1.48 (s, 7H), 1.35 (s, 4H), 1.28−1.23 (m, 7H), 1.13−1.11 (m, 12H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 216.4, 171.6, 80.9, 61.1, 60.4, 59.5, 59.3, 58.2, 41.1, 41.1, 37.2, 35.8, 35.4, 25.1, 24.3, 22.3, 21.4, 21.1, 21.0, 17.1, 13.8; FTIR (thin film, cm^{-1}): 2976, 2934, 2872, 1753, 1732, 1709; HRMS (ESI-TOF) m/z: calcd for $C_{21}H_{37}NO_4Na$ $(M + Na)^+$, 390.2620; found, 390.2606.

General Procedures for the Synthesis of β-Ketoester Substrates 2 and 4. *Ethyl (E)-7-(4-Fluorophenyl)-2-methyl-3-oxohept-6-enoate (**2b**).* To an oven-dried flask charged with a magnetic stir bar was added NaH (60% dispersion in mineral oil; 511 mg, 12.8 mmol, 1.2 equiv). The flask was evacuated and backfilled three times with argon, after which THF (53 mL, 0.2 M) was added. The reaction mixture was cooled to 0 °C, and ethyl 2-methylacetoacetate (1.5 mL, 10.7 mmol, 1.0 equiv) was added dropwise. After 30 min, *n*-BuLi (1.8 M in hexane; 6.5 mL, 11.7 mmol, 1.1 equiv) was added dropwise and left to stir for 20 min at 0 °C. *p*-Fluorocinnamyl chloride (2.0 g, 11.7 mmol, 1.1 equiv) was dissolved in THF (2 mL) and added dropwise to the 2-methylacetoacetate solution. The reaction mixture was allowed to warm to room temperature for 17 h. At completion (TLC), the reaction was diluted with saturated aqueous ammonium chloride (50 mL). The mixture was then extracted with ethyl acetate (3 × 25 mL). The combined organic phases were washed with brine (25 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by automated column chromatography (SiO_2, 0−50% gradient of ethyl acetate in hexanes) to provide 750 mg (25% yield) of **2b** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.32−7.24 (m, 2H), 6.97 (t, J = 8.7 Hz, 2H), 6.37 (d, J = 15.8 Hz, 1H), 6.09 (dt, J = 15.8, 6.8 Hz, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.53 (q, J = 7.2 Hz, 1H), 2.84−2.58 (m, 2H), 2.49 (dt, J = 7.8, 6.5 Hz, 2H), 1.35 (d, J = 7.2 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 205.1, 170.6, 162.1 (d, J = 245 Hz), 133.7, 129.9, 128.4, 127.6 (d, J = 8 Hz), 115.5 (d, J = 22 Hz), 61.5, 53.1, 41.0, 27.0, 14.2, 12.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ −115.2 (m): FTIR (thin film, cm^{-1}): 2984, 2940, 1749, 1602; HRMS (ESI-TOF) m/z: calcd for $C_{16}H_{19}FO_3Na$ $(M + Na)^+$, 301.1216; found, 301.1204.

*Ethyl (E)-7-(4-Bromophenyl)-2-methyl-3-oxohept-6-enoate (**2c**).* Following the general procedure, 940 mg (29%) of **2c** was produced as a colorless oil from NaH (60% dispersion in mineral oil; 452 mg, 11.3 mmol) ethyl 2-methylacetoacetate (1.4 g, 9.4 mmol), *n*-butyllithium (2.0 M in hexane; 5.2 mL, 10.4 mmol), and *p*-bromocinnamyl chloride (2.4 g, 10.4 mmol), in THF (47 mL). ^1H NMR (300 MHz, $CDCl_3$): δ 7.45−7.35 (m, 2H), 7.22−7.13 (m, 2H), 6.34 (d, J = 15.9 Hz, 1H), 6.17 (dt, J = 15.8, 6.7 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.53 (q, J = 7.2 Hz, 1H), 2.86−2.58 (m, 2H), 2.49 (dt, J = 7.7, 6.6 Hz, 2H), 1.38−1.33 (m, 3H), 1.28−1.21 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 205.0, 170.6, 136.4, 131.7, 130.0, 129.6, 127.7, 120.9, 61.6, 53.1, 40.9, 27.0, 14.2, 12.9; FTIR (thin film, cm^{-1}): 2925, 1738, 1733; HRMS (ESI-TOF) m/z: calcd for $C_{16}H_{19}BrO_3Na$ $(M + Na)^+$, 361.0415; found, 361.0418.

*Ethyl (E)-7-(2-Chlorophenyl)-2-methyl-3-oxohept-6-enoate (**2d**).* Following the general procedure, 246 mg (24%) of **2d** was produced as a colorless oil from NaH (60% dispersion in mineral oil; 174 mg, 4.0 mmol) ethyl 2-methylacetoacetate (523 mg, 3.6 mmol), *n*-butyllithium (1.8 M in hexane; 2.2 mL, 4.0 mmol), and *o*-chlorocinnamyl chloride (747 mg, 4.0 mmol), in THF (18 mL). ^1H NMR (300 MHz, $CDCl_3$): δ 7.47 (dd, J = 7.5, 2.0 Hz, 1H), 7.32 (dd, J = 7.6, 1.8 Hz, 1H), 7.24−7.09 (m, 2H), 6.78 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 6.8 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.55 (q, J = 7.1 Hz, 1H), 2.90−2.61 (m, 2H), 2.56 (q, J = 6.8 Hz, 2H), 1.36 (d, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 204.9, 170.5, 135.4, 132.6, 131.6, 129.6, 128.2, 127.1, 126.8, 126.7, 61.4, 52.9, 40.8, 27.0, 14.1, 12.7; FTIR (thin film, cm^{-1}): 2984, 2940, 1743, 1714; HRMS (CI-TOF) m/z: calcd for $C_{16}H_{19}ClO_3$ $(M)^+$, 294.1023; found, 294.1019.

*Ethyl (E)-2,6-Dimethyl-3-oxo-7-phenylhept-6-enoate (**2j**).* Following the general procedure, 225 mg (30%, inconsequential mixture of *cis*/*trans* isomers) of **2j** was produced as a colorless oil from NaH (60% dispersion in mineral oil; 162 mg, 4.1 mmol) ethyl 2-methylacetoacetate (389 mg, 2.7 mmol), *n*-butyllithium (1.6 M in hexane; 2.5 mL, 4.1 mmol), and 2-methylcinnamyl chloride (495 mg, 2.7 mmol), in THF (14 mL). Mixture of alkene diastereomers. Major diastereomer: ^1H NMR (300 MHz, $CDCl_3$): δ 7.37−7.13 (m, 5H), 6.27 (s, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.56 (q, J = 7.1 Hz, 1H), 2.90−2.63 (m, 2H), 2.51−2.42 (m, 2H), 1.86 (t, J = 1.8 Hz, 3H), 1.36 (d, J = 7.2 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 205.5, 170.7, 138.2, 137.3, 128.9, 128.2, 126.2, 125.7, 61.5, 53.1, 40.2, 34.3, 18.0, 14.3, 12.9; FTIR (thin film, cm^{-1}): 2982, 2940, 1739, 1714; HRMS (CI-TOF) m/z: calcd for $C_{17}H_{22}O_3$ $(M)^+$, 274.1569; found, 274.1573.

*Ethyl 2,7-Dimethyl-3-oxooct-6-enoate (**4a**).* Following the general procedure, 554 mg (38%) of **4a** was produced as a colorless oil from NaH (60% dispersion in mineral oil; 333 mg, 8.3 mmol), ethyl 2-methylacetoacetate (1 g, 6.94 mmol), *n*-butyllithium (2.2 M in hexane; 3.5 mL, 7.63 mmol), and 1-bromo-3-methylbut-2-ene (1.1 g, 7.63 mmol), in THF (32 mL). ^1H NMR (300 MHz, $CDCl_3$): δ 5.04

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(td, J = 7.2, 1.6 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.49 (q, J = 7.1 Hz, 1H), 2.68−2.42 (m, 2H), 2.32−2.08 (m, 2H), 1.66 (s, 3H), 1.60 (s, 3H), 1.31 (d, J = 7.1 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 205.8, 170.7, 133.1, 122.6, 61.4, 53.1, 41.5, 25.8, 22.4, 17.8, 14.2, 12.8; FTIR (thin film, cm^{-1}): 2983, 2938, 2916, 1739, 1717; HRMS (CI-TOF) m/z: calcd for $C_{12}H_{20}O_3$ $(M)^+$, 212.1413; found, 212.1421.

*Ethyl 2,7-Dimethyl-3-oxooct-6-enoate (**4h**).* To a flame-dried round-bottom flask equipped with a stir bar was added sodium hydride (60% dispersion in mineral oil, 178 mg, 4.45 mmol). The flask was evacuated and refilled with argon three times before THF (7.2 mL, 0.65 M) was added, and the mixture was cooled to 0 °C with stirring. *tert*-Butyl 7-methyl-3-oxooct-6-enoate (1.0 g, 4.68 mmol) dissolved in THF (1 mL) was added dropwise, followed by iodomethane (0.28 mL, 4.45 mmol). The reaction mixture was stirred at 0 °C for 2 h before it was transferred to a separatory funnel with ethyl acetate (10 mL) and saturated aqueous ammonium chloride (10 mL). The layers were separated, and the aqueous phase was washed with additional ethyl acetate (2 × 10 mL). The combined organic phases were washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by automated column chromatography (0−50% gradient of ethyl acetate in hexanes) to provide 295 mg (26%) of **4h** as a colorless oil. ^1H NMR (300 MHz; $CDCl_3$): δ 5.05 (tt, J = 7.1, 1.4 Hz, 1H), 3.41 (q, J = 7.1 Hz, 1H), 2.70−2.42 (m, 2H), 2.27 (q, J = 7.3 Hz, 2H), 1.67 (s, 3H), 1.61 (s, 3H), 1.45 (s, 9H), 1.27 (d, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 206.1, 169.9, 133.0, 122.7, 81.8, 54.1, 41.5, 28.1, 25.8, 22.5, 17.8, 12.8; FTIR (thin film, cm^{-1}):2979, 2933, 1739, 1714, 1455; HRMS (CI-TOF) m/z: calcd for $C_{14}H_{24}O_3H$ $(M + H)^+$, 241.1804; found, 241.1815.

*Ethyl (E)-2-Benzyl-3-oxo-7-phenylhept-6-enoate (**2e**).* To a flame-dried round-bottom flask equipped with a stir bar was added sodium hydride (60% dispersion in mineral oil, 147 mg, 3.67 mmol). The flask was evacuated and refilled with argon three times before THF (15 mL, 0.25 M) was added, and the mixture was cooled to 0 °C with stirring. Ethyl (*E*)-3-oxo-7-phenylhept-6-enoate (905 mg, 3.67 mmol) dissolved in THF (1 mL) was added dropwise, followed by benzyl bromide (0.46 mL, 3.86 mmol). The reaction mixture was stirred at 0 °C for 2 h before it was transferred to a separatory funnel with ethyl acetate (10 mL) and saturated aqueous ammonium chloride (10 mL). The layers were separated, and the aqueous phase was washed with additional ethyl acetate (2 × 10 mL). The combined organic phases were washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by automated column chromatography (0−50% gradient of ethyl acetate in hexanes) to provide 659 mg (53%) of **2e** as a colorless oil. ^1H NMR (300 MHz; $CDCl_3$): δ 7.41−6.95 (m, 10H), 6.32 (dt, J = 15.8, 1.3 Hz, 1H), 6.07 (dt, J = 15.8, 6.7 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.78 (t, J = 7.6 Hz, 1H), 3.15(dd, J = 7.6, 1.9 Hz, 2H), 2.79−2.61 (m, 1H), 2.56−2.39 (m, 2H), 2.42−2.34 (m, 1H), 1.16 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 204.0, 169.2, 138.3, 137.5, 131.1, 129.0, 128.7, 128.6, 128.5, 127.3, 126.8, 126.1, 61.6, 60.8, 42.5, 34.2, 26.8, 14.2; FTIR (thin film, cm^{-1}): 3027, 2980, 2926, 1739, 1714; HRMS (ESI-TOF) m/z: calcd for $C_{22}H_{24}O_3H$ $(M + H)^+$, 359.1623; found, 359.1624.

*3,4,5,6-Tetrahydro-[1,1′-biphenyl]-3-yl 2-Methyl-3-oxobutanoate (**2h**).* To a flame-dried round-bottom flask equipped with a stir bar was added sodium hydride (60% dispersion in mineral oil, 153 mg, 3.83 mmol). The flask was evacuated and refilled with argon three times before THF (5.3 mL, 0.8 M) was added, and the mixture was cooled to 0 °C with stirring. 3,4,5,6-Tetrahydro-[1,1′-biphenyl]-3-yl 3-oxobutanoate (1.1 g, 4.26 mmol) dissolved in THF (0.5 mL) was added dropwise, followed by iodomethane (0.27 mL, 4.26 mmol). The reaction mixture was stirred at 0 °C for 2 h before it was transferred to a separatory funnel with ethyl acetate (10 mL) and saturated aqueous ammonium chloride (10 mL). The layers were separated, and the aqueous phase was washed with additional ethyl acetate (2 × 10 mL). The combined organic phases were washed with saturated aqueous sodium chloride, dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by automated column chromatography (0−50% gradient of ethyl acetate in hexanes) to provide 602 mg (52%) of **2h** as a colorless oil as an inconsequential mixture of diastereomers: ^1H NMR (400 MHz, $CDCl_3$): δ 7.50−7.19 (m, 5H), 6.07 (s, 1H), 5.51 (s, 1H), 3.51 (qd, J = 7.2, 1.9 Hz, 1H), 2.63−2.47 (m, 1H), 2.45−2.31 (m, 1H), 2.25 (d, J = 2.8 Hz, 3H), 1.99−1.75 (m, 2H), 1.36 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 203.8, 170.5, 143.1, 141.1, 128.5, 127.9, 125.6, 121.6, 121.5, 70.2, 54.0, 54.0, 28.7, 28.6, 28.0, 27.9, 27.5, 19.4, 12.9; FTIR (thin film, cm^{-1}): 2940, 1729, 1699; HRMS (CI-TOF) m/z: calcd for $C_{17}H_{20}O_3$ $(M)^+$, 272.1407; found, 272.1413.

*(E)-N-Benzyl-2-methyl-3-oxo-7-phenylhept-6-enamide (**2i**).* Benzylamine (0.21 mL, 1.92 mmol, 1 equiv), ketoester 2a (500 mg, 1.92 mmol, 1 equiv), and DMAP (469 mg, 3.84 mmol, 2 equiv) were dissolved in toluene, and the solution was heated to reflux under an argon atmosphere for 24 h. The reaction mixture was then transferred to a separatory funnel and washed with water (10 mL). The layers were separated, and the aqueous phase was extracted with ethyl acetate (3 × 25 mL). The combined organic phases were then washed with saturated aqueous ammonium chloride (10 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The residue was purified by automated column chromatography (SiO_2, 0−100% gradient of ethyl acetate in hexanes) to provide 182 mg (29%) of **2i** as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ 7.36−7.15 (m, 10H), 6.52 (s, 1H), 6.40 (d, J = 15.8 Hz, 1H), 6.15 (dt, J = 15.8, 6.8 Hz, 1H), 4.50−4.31 (m, 2H), 3.49 (q, J = 7.2 Hz, 1H), 2.87−2.63 (m, 2H), 2.48 (q, J = 6.7 Hz, 2H), 1.42 (d, J = 7.2 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 209.0, 169.3, 138.0, 137.4, 131.2, 128.9, 128.7, 128.4, 127.8, 127.7, 127.3, 126.2, 54.6, 43.8, 41.2, 26.9, 15.2; FTIR (thin film, cm^{-1}): 3287, 3029, 2935, 1721, 1642; HRMS (CI-TOF) m/z: calcd for $C_{21}H_{23}NO_2$ $(M)^+$, 321.1729; found, 321.1736.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c03055.

Reaction optimization details; fluorescence-quenching studies; ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra of novel compounds; and computational data (PDF)

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Notes

The authors declare no competing financial interest.

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