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FULL PAPER

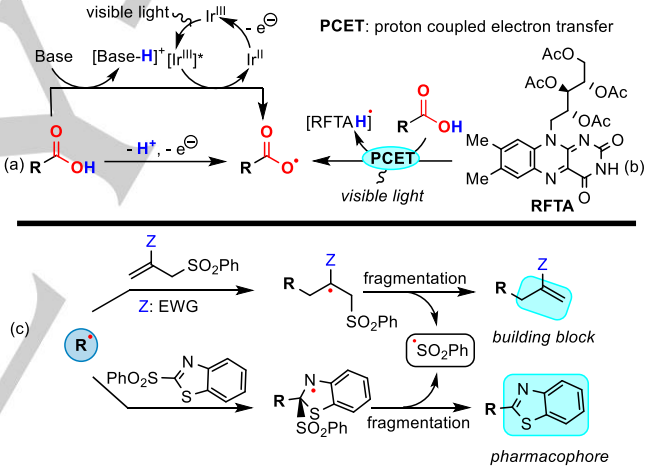
Direct decarboxylative allylation and arylation of aliphatic carboxylic acids using flavin mediated photoredox catalysis

Nieves P. Ramirez,[a] Teresa Lana-Villarreal,[b] and Jose C. Gonzalez-Gomez*[a]

Abstract: We describe herein a direct decarboxylative allylation of aliphatic carboxylic acids with allylsulfones using visible light and riboflavin tetraacetate (RFTA) as photocatalyst. The reaction proceeds at room temperature tolerating a wide range of functionalities, avoiding the use of external bases or additives. Mechanistic studies support that alkyl radicals are involved in the reaction, and that a true photocatalytic cycle is operating. It is proposed that the carboxylic acid is deprotonated by $[RFTA]^{\bullet-}$, and the corresponding carboxylate acts as reductive quencher of RFTA*, which after decarboxylation produces the alkyl radical. The methodology was adapted to prepare benzothiazoles substituted at C2, by reacting some carboxylic acids with 2-(phenylsulfonyl)benzothiazole. The number of carboxylic acids suitable for this arylation was lower than for the allylation and this different reactivity was briefly commented.

Introduction

In recent years, photoredox catalysis has made important progresses on the use of visible light energy to activate organic molecules and promote their reactivity under very mild and sustainable conditions.[1] In this context, the photocatalytic oxidation of aliphatic carboxylic acids is a very convenient approach to generate free radicals, after fast decarboxylation of the corresponding acyloxy radicals (k ~ 10^9 s^{-1} at 25 ºC).[2] Although other radical precursors have also been successfully exploited (*e.g.* alkyltrifluoroborates,[3] silicates,[4] dihydropyridines,[5] and Katritzky pyridinium salts[6]), carboxylic acids are ideal starting materials because they are abundant, inexpensive, stable and some of them are derived from biomass.[7] The vast majority of photocatalytic decarboxylative functionalizations of carboxylic acids use bases in stoichiometric amounts to facilitate the oxidation of the corresponding carboxylate. This is not surprising if we consider that the oxidation potential of the carboxylic acid (*e.g.* for phenylacetic acid $E_{1/2}(RCO_2H^{\bullet+}/RCO_2H)$ = +2.51 V *vs* SCE) is much higher than the one corresponding to the carboxylate (for tetrabutylammonium phenylacetate: $E_{1/2}(RCO_2^{\bullet}/RCO_2^{-})$ = +1.27 V *vs.* SCE).[8] Actually, functionalized carboxylic acids have been used in a variety of photocatalytic oxidative transformations of other functional groups, relying on the fact that the carboxyl group is not oxidizable itself.[9] In practice, the photocatalytic oxidation of carboxylic acids to acyloxy radicals usually involves a deprotonation by an external base, followed by a photoinduced electron transfer (PET) to strongly oxidizing photocatalysts (**Scheme 1a**). Although some iridium photocatalysts have very favorable redox potentials (*e.g.* for $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$: $E_{1/2}(*Ir^{III}/Ir^{II})$ = + 1.32 V *vs.* SCE)[10] for this transformation and convenient long excited state lifetimes, they are very rare and expensive, being organic dyes inexpensive and environmentally friendly alternatives.



Scheme 1. (a) Photocatalytic oxidation of carboxylic acids with Ir^{III}-derived photocatalyst. (b) RFTA acting as base and photocatalyst in the photooxidation of carboxylic acids. (c) Radical addition to allylsulfones or to 2-(phenylsulfonyl)benzothiazole, followed by elimination of phenyl sulfonyl radical.

Among different oxidizing organic photocatalysts, we were particularly attracted by riboflavin (RF),[11] a natural compound also known as vitamin B_2, which is very abundant and responsible for the redox activity of several flavo-enzymes.[12] Upon visible light irradiation (λ_{max} ~ 450 nm), RF is excited to its short-lived singlet state ($*S_1$, τ = 6.8 ns) and undergoes an efficient intersystem crossing (ϕ_{ISC} = 0.38) to obtain a long-lived triplet state ($*T_1$, τ = 15 µs), which is oxidant enough ($E_{1/2}$ ($^3RF*/RF^{\bullet-}$) = +1.50 V *vs* SCE) to oxidize carboxylates salts (+1.2 V ≤ $E_{1/2}$ ≤ +1.5 V *vs* SCE).[13] Notably, Gilmour's group reported that photoexcited RF is able to oxidize cinnamic acids and biaryl carboxylic acids, in the absence of any external base, to generate the corresponding carboxyl radical.[14] It was proposed that the

[a] M.Sc. N. P. Ramirez, Prof. J. C. Gonzalez-Gomez
Instituto de Síntesis Orgánica y Departamento de Química Orgánica
Universidad de Alicante
Apdo 99, E-03080 Alicante, Spain
E-mail: josecarlos.gonzalez@ua.es
http://iso.ua.es
[b] Prof. T. Lana-Villarreal
Instituto de Electroquímica y Departamento de Química Física
Universidad de Alicante

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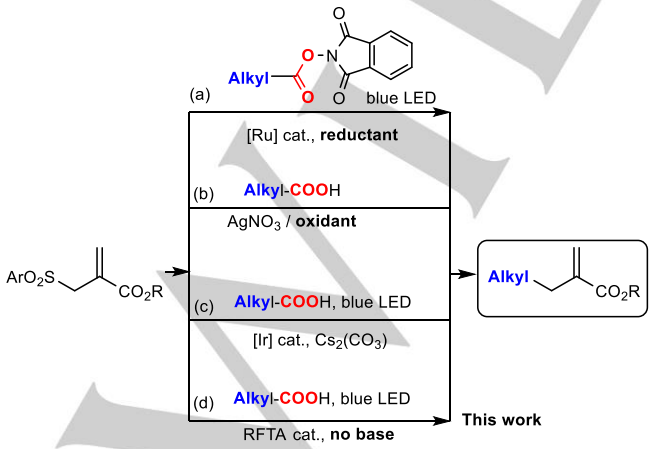
flavin moiety (pK_a of RFH$^{\bullet}$ = 8.3 in H_2O) can deprotonate the aliphatic carboxylic acid (pK_a ~ 5 in H_2O), before the PET, or in a formal proton-coupled electron transfer (PCET). In line with these results, MacMillan's group reported that riboflavin tetrabutyrate photocatalyzes the decarboxylative alkylation of peptides at the C-terminal carboxylic acid site more efficiently under mildly acidic conditions (pH 3.5).[15] Inspired by these findings, we have developed very recently a protocol in which a riboflavin tetraacetate (RFTA) acts as base and photocatalyst in the decarboxylative cyanation of aliphatic carboxylic acids, avoiding the use of stoichiometric bases.[16] Thus, we decided to extend the application of this economic, user-friendly and sustainable protocol to generate alkyl radicals (**Scheme 1b**) and explore other organic transformations. It is known that nucleophilic alkyl radicals are rapidly added to electron-deficient alkenes, generating stable radical intermediates, that can easily eliminate a sulfonyl radical from the β position (**Scheme 1c**).[17] In this context, we planned to examine the direct decarboxylative allylation of aliphatic carboxylic acids with allylsulfones using visible light and RFTA without any other additive. Our interest on this radical allylation stems from the fact that both substrates- carboxylic acids and allyl sulfones- are readily available, and the resulting alkene could serve as a versatile precursor by synthetic manipulations of the allyl moiety. Moreover, we also decided to examine 2-(phenylsulfonyl)benzothiazole as radical acceptor to obtain 2-alkyl benzothiazole derivatives,[18] an heterocyclic family with multiple bioactivities.[19]

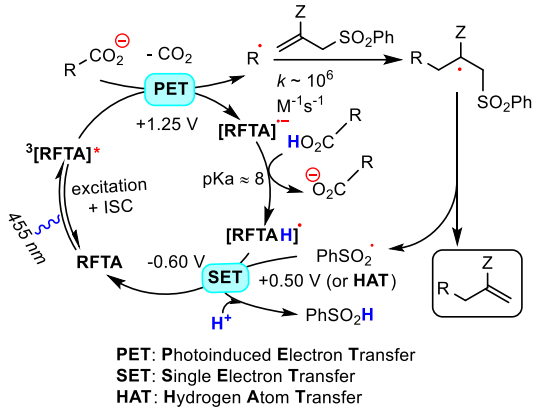
A fast and chemoselective photocatalytic decarboxylative allylation was recently developed (**Scheme 2a**), but using *N*-acyloxyphthalimides, $[Ru(bpy)_3](PF_6)_2$ as photocatalyst and stoichiometric amounts of reductants.[20] The silver catalyzed direct decarboxylative allylation of carboxylic acids (**Scheme 2b**) was also recently developed, showing broad substrate scope, but in this case $K_2S_2O_8$ was required in stoichiometric amounts to regenerate the Ag(II) catalyst.[21] The direct photocatalytic allylation of carboxylic acids *via* a redox-neutral process was not developed until very recently using $Ir(ppy)_2(bpy)PF_6$ as catalyst, and stoichiometric amounts of $Cs_2(CO_3)$, although it was limited to *N*-arylglycine derivatives (**Scheme 2c**).[22] Herein we report our results on the direct and redox-neutral photocatalytic allylation of carboxylic acids (**Scheme 2d**).



Scheme 2. Precedents in the photocatalytic decarboxylative allylation of carboxylic acids with allyl sulfones.

Results and Discussion

As in our previous communication, we have chosen RFTA [23] as the photocatalyst for this study because it shows better solubility in organic solvents, greater photostability and is less likely than RF to form aggregates through hydrogen bonding interactions.[24] A key feature in our redox-neutral visible light-promoted decarboxylative allylation of carboxylic acids with allylsulfones is the turnover of the RFTA catalyst with the phenyl sulfonyl radical ($PhSO_2^{\bullet}$). In our reaction design, (**Scheme 3**) a formal proton-coupled electron transfer between the photoexcited RFTA* and the carboxylic acid would explain the generation of alkyl radicals in the absence of base. Alternatively, it is plausible that a small fraction of *in situ* formed $[RFTA]^{\bullet-}$ deprotonates the carboxylic acid to give the corresponding carboxylate,[25] which in turn would be oxidized by the long-lived triplet-excited state of the flavin, generating the alkyl radical after rapid decarboxylation.[26] The addition of alkyl radicals to electron-deficient allylsulfones should be relatively fast (k ~ 10^6 $M^{-1}s^{-1}$),[20] and must be followed by a radical fragmentation to obtain the desired alkene. In the same event is produced the stabilized phenyl sulfonyl radical, which is easily reduced [$E_{1/2}(PhSO_2^{\bullet}/PhSO_2^{-})$ = +0.50 V *vs* SCE][27] by the hydroflavin radical [$E_{1/2}$(RFTA/RFTAH$^{\bullet}$) ≈ -0.60 V *vs* SCE],[28] thereby closing the catalytic cycle after proton transfer. According to the redox potentials involved, this electron transfer is highly exergonic ($\Delta G_{ET} \approx -25\ kcal/mol$). However, we can not rule out a hydrogen atom abstraction by phenyl sulfonyl radical from the hydroflavin radical to complete the photoredox neutral catalytic cycle.

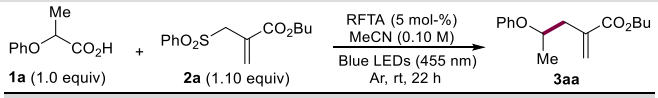


Scheme 3. Plausible mechanism for our photocatalytic decarboxylative allylation of carboxylic acids.

Our studies began using 2-phenoxypropanoic acid (**1a**) and butyl 2-((phenylsulfonyl)methyl)acrylate (**2a**) as model substrates to screen different conditions for the decarboxylative allylation reaction (**Table 1**). When the reaction was performed using degassed MeCN (argon sparging over 10 min) and RFTA (5 mol-%) as photocatalyst, under irradiation with blue LEDs (λ_{max}

455 nm, 15 ± 2 mW/cm^2) at room temperature, the desired product **3aa** was obtained in 77% yield after 22 h (entry 1). Notably, using a higher load of RFTA (entry 2) did not provide any significant advantage over the previous conditions. Moreover, other solvent systems (entries 3 and 4) or the addition of an organic base (entry 5) in stoichiometric amount had a deleterious effect on the product yield. Incomplete conversion was observed when the reaction was run for only 8 h (entry 6). Furthermore, when the reaction was not degassed, product **3aa** was also obtained in a diminished yield (entry 7). Finally, control experiments revealed that both the light and the photocatalyst are required to the reaction takes place (entries 8 and 9). It is worth of note that although the allyl sulfone is frequently used in large excess (3 – 4 equiv) to minimize other competing reactions, we have optimized our reaction using an almost perfect stoichiometry.

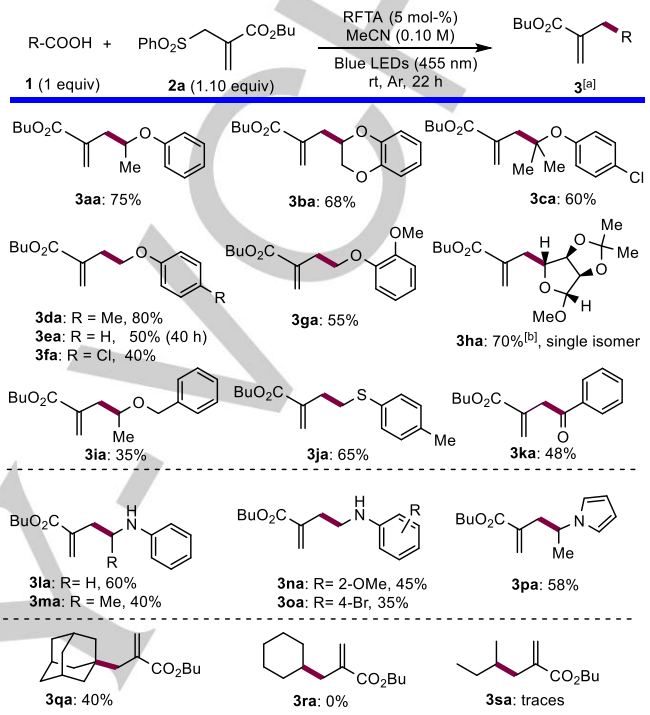
Table 1. Optimization of the decarboxylative allylation.



Entry	Modification from standard conditions	Yield (%)[a]
1	none	77
2	RFTA (10 mol-%)	78
3	In MeCN/H_2O (2:1)	41
4	In MeOH	33
5	DABCO (1 equiv)	27
6	8 h	46
7	No degassing	44
8	No photocatalyst	0
9	No light	0

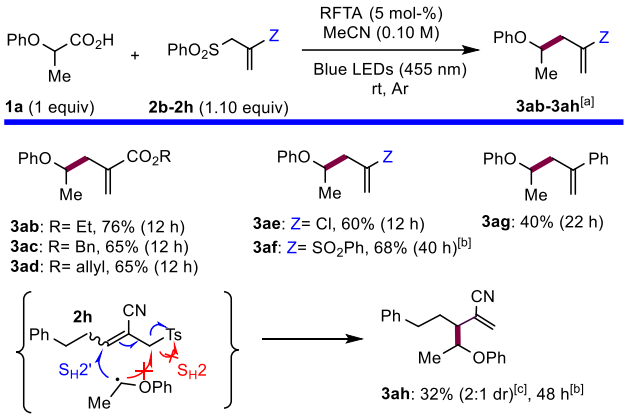
[a] Yield determined by GC using adamantane as internal standard.

Under our optimized reaction conditions, we examined different carboxylic acids with allylsulfone **2a** (**Scheme 4**). We were pleased to observe that different *α*-oxo carboxylic acids- including secondary, tertiary and even primary- were suitable substrates, giving the desired products (**3aa**–**3ia**) from moderate to good yields. Interestingly, the ribosic acid derivative afforded the desired product **3ha** in good yield as a single isomer with retention of the configuration,[29] although a longer time and two portions of 5 mol-% of photocatalyst were required. Moreover, an *α*-benzyloxy carboxylic acid was also tolerated with the catalytic protocol, although the corresponding product **3ia** was obtained in relatively low yield. Remarkably, an *α*-thio- carboxylic acid was also compatible under the reaction conditions, giving the desired product **3ja** in good yield, despite different possible parasitic reactions (*e.g.* overoxidation, homocoupling of intermediate radicals, hydrodecarboxylation, etc). In addition, an *α*-ketoacid was also a suitable substrate affording the desired ketone **3ka** in a moderate yield. *N*-arylglycine derivatives were also well tolerated under the optimized conditions and the corresponding products (**3la**-**3oa**) were obtained from moderate to good yields. Similarly, a pyrrole-derived carboxylic acid afforded the desired product **3pa** in good yield. Unfortunately, other common *N*-protecting groups, such as Boc and Cbz, were not suitable to transform the alanine derivatives in useful synthetic yields. We also explored a few non-activated *α-C* carboxylic acids, but only the tertiary adamantly carboxylic acid gave product **3qa** in moderate yield. The cyclohexyl- and *sec*-butyl carboxylic acids failed to give the desired products in significant amounts.



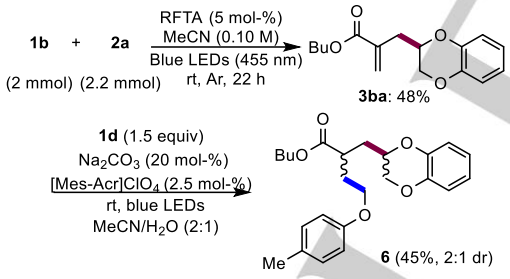
Scheme 4. Scope of carboxylic acids on the decarboxylative allylation. [a] Yields are reported for isolated pure products at 0.25 mmol scale. [b] After 24 h, another 5 mol-% of RFTA was added and the reaction was run over 12 h.

We also examined the scope of different allylsulfones under our optimized conditions, using 2-phenoxypropanoic acid as model substrate (**Scheme 5**). Terminal allylsulfones with different ester groups, including ethyl, benzyl, and allyl esters were compatible with this protocol, giving the corresponding products (**3ab**-**3ad**) in good yields. Other electron-withdrawing groups were also well tolerated in the terminal allylsulfones, such as chloro and phenylsulfone, giving the desired compounds **3ae** and **3af** in good yields. In addition, an electron-richer 2-phenylallylsulfone was also a suitable partner, likely by resonance stabilization of the benzylic radical intermediate, to provide product **3ag** in a moderate yield. Moreover, internal allyl sulfone **2h** was also tested, obtaining the terminal alkene **3ah** in low yield after a difficult purification, as a 2:1 mixture of diastereoisomers. This result supports a regioselective alkyl radical addition to the double bond of the allyl sulfone, followed by *β*-elimination of the sulfonyl radical (S_H2' pathway). Remarkably, the mild reaction conditions used were compatible with a broad range of functionalities, including: esters, ethers, phenyl rings, chloro substituents, ketals, thioethers, ketones, *N*-aryl amines, pyrroles, allyl groups, benzyl groups, sulfones and cyano groups.



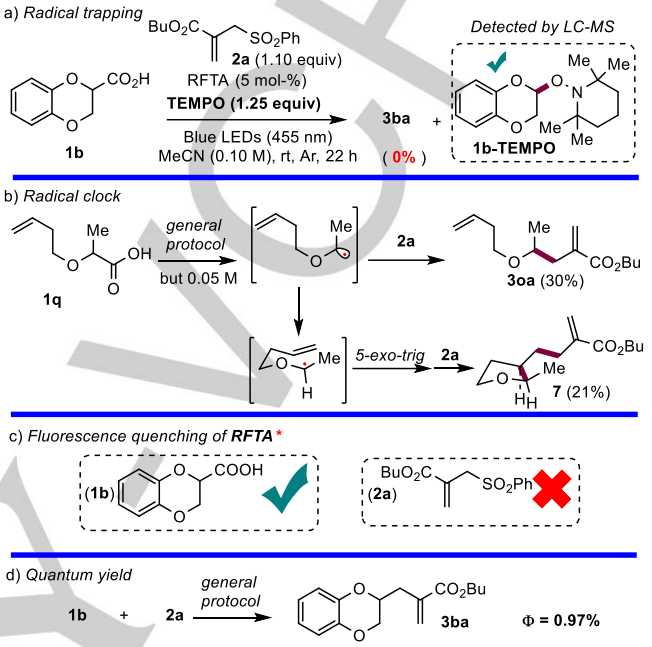
Scheme 5. Allyl sulfone scope with carboxylic acid **1a**. [a] Yields are reported for isolated pure products at 0.25 mmol scale. [b] 2 equiv of **1a** were used. [c] Determined by ^{1}H-NMR.

To examine the synthetic utility of our direct decarboxylative allylation, we carried out the preparation of compound **3ba** at 2 mmol scale under batch conditions (**Scheme 6**). Although the product was obtained in a synthetically useful yield (48%), a significant decreased was observed compared to the reaction at 0.25 mmol (68%).[30] Moreover, to show that the allyl moiety can also serve as a radical acceptor, we conducted the Giese decarboxylative alkylation using reaction conditions previously developed in our group.[31] Under these conditions, when carboxylic acid **1d** was employed, compound **6** was obtained in an unoptimized 45% yield.



Scheme 6. Preparation of **3ba** at 2 mmol scale and Giese decarboxylative alkylation with carboxylic acid **1d**.

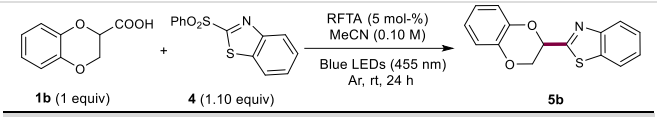
Evidence for the free radical involvement in these reactions follows from the observed inhibitory effect of TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl, **Scheme 7a**) on the allylation reaction. Eventually, the corresponding radical was trapped by TEMPO on this experiment to form adduct **1b-TEMPO**, which was detected by LC-MS. Additionally, when carboxylic acid **1q** was submitted to the allylation conditions with sulfone **2a**, the expected compound **3oa** was isolated, but also compound **7** from a fast *5-exo-trig* radical addition followed by the allylation reaction (**Scheme 7b**). In order to support the proposed mechanism, it was also checked that carboxylic acid **1b** was an efficient quencher of RFTA* luminescence's, while the emission intensity of the photoexcited catalyst was not altered in the presence of **2a** (**Scheme 7c**, details can be found in the supporting information). Finally, the quantum yield of the reaction of **1b** and **2a** resulted very low (**Scheme 7d**), supporting a closed photocatalytic cycle instead of a radical chain propagation.[32]



Scheme 7. Mechanistic studies.

We thus re-examined the reaction conditions to adapt our protocol for the decarboxylative arylation of aliphatic carboxylic acids, using **1b** and 2-(phenylsulfonyl)benzothiazole (**4**) as substrates (**Table 2**). Under the same allylation conditions the desired compound **5b** was obtained in moderate yield (entry 1). When 2 equivalents of the carboxylic acid were used, the reaction yield was slightly improved (entry 2). Different solvent systems were also examined to facilitate the solubility of the aryl sulfone at the beginning of the reaction, but none of them furnished the desired product in a better yield (entries 3-5). Finally, when the load of photocatalyst was increased to 10 mol-% and the reaction was run over 36 h, the best result was obtained (entry 6). Notably, this reaction is slower than the allylation, likely by a higher steric demand in the addition of the alkyl radical to the carbon atom next to the bulky sulfonyl group. It is worth saying that we recognized that a possible solution to this problem would be the C2-alkylation of unsubstituted benzothiazoles, thereby less sterically hindered and more easily available starting materials.[33] However, the reaction of **1b** with benzothiazole, using RFTA (10 mol-%) and air as terminal oxidant gave only traces of product **5b** (not shown).

Table 2. Re-examining reaction conditions for the decarboxylative arylation.

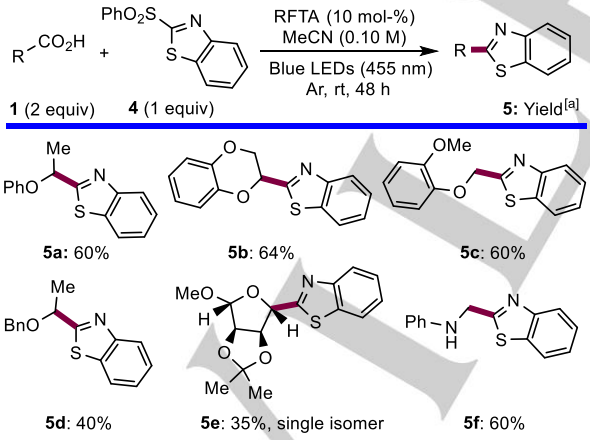


1b (1 equiv) **4** (1.10 equiv) **5b**

Entry	Modification from standard conditions	Yield (%)[a]
1	none	52
2	2 equiv of **1b** and 1 equiv of **4**	60
3	As in entry 2, but in 9:1 MeCN/EtOH	60
4	As in entry 2, but in EtOH	50
5	As in entry 2, but in acetone	52
6	entry 2, but 10 mol-% of RFTA and 36 h	**64** (95)[b]

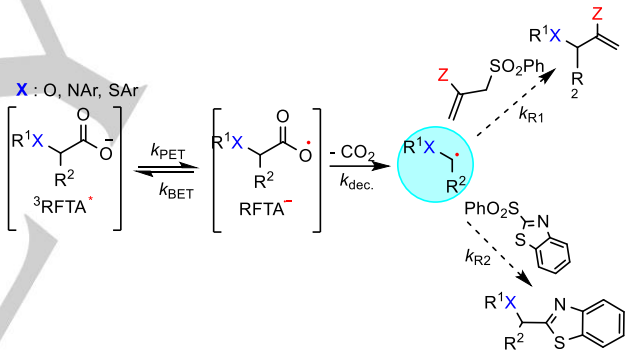
[a] Yields determined for isolated pure products. [b] Based on recovered compound **4**.

Having identified reasonably good reaction conditions, we screened some aliphatic carboxylic acids in the homolytic aromatic substitution (HAS) of 2-(phenylsulfonyl)benzothiazole (**Scheme 8**). As in the decarboxylative allylation, *α*-oxo carboxylic acids were suitable substrates in this transformation, obtaining the products **5a-5e** in yields from moderate to good. It is worth noting that during the formation of compound **5d** it was also observed the homocoupling of the corresponding radicals by GC-MS. In the case of compound **5e** the yield was also rather low, most likely due to a higher steric hindrance with the bulky radical involved in the transformation. Finally, the C2-*α*-aminomethylation of benzothiazole was accomplished using *N*-phenylglycine in our reaction conditions to obtain **5f** in good yield. Other carboxylic acids, such as: clofibric acid (1c), 2-(*p*-tolylthio)acetic acid (**1j**) and phenoxyacetic acid (**1e**) failed to give the desired benzothiazole, observing mainly the corresponding hydrodecarboxylation by GC-MS. Moreover, *N*-Boc phenylalanine gave only traces of the desired benzothiazole.



Scheme 8. Carboxylic acids scope in the HAS of **4**. [a] Yields are reported for isolated pure products at 0.25 mmol scale.

In our previous decarboxylative cyanation with TsCN, using RFTA as base and photocatalyst, the range of successful carboxylic acids was broader, being *α*-*N* carbamates and non-activated *α*-*C* carboxylic acids also suitable substrates.[16] In this work, we have observed that *α*-thio-, tertiary *α*-oxo- and *α*-keto carboxylic acids were successful in the decarboxylative allylation, but not in the arylation reaction. It is evident that most successful carboxylic acids in these reactions have an *α*-substituent that stabilizes the radical by resonance, thereby increasing the energy of the SOMO and their reactivity with electron-deficient radical acceptors. From Kochi's work it is known that decarboxylation (k_{dec}) of arylacetoxy radicals generated via PET in carboxylate ion pairs lies in the range of $\mathbf{10^9\ s^{-1}}$, competing with very fast back-electron transfer (k_{BET} $\sim\mathbf{10^{11}\ s^{-1}}$).[2] In this study was also concluded that decarboxylation of *α*-oxo benzylic carboxylic acids to provide stabilized benziloxy radicals is extremely fast (k_{dec} $\sim\mathbf{10^{11}\ s^{-1}}$). We thus reasoned that the success of these reactions depends on an extremely fast decarboxylation to override the back-electron transfer. It is also important the use of very electrophilic radical acceptors (with low steric demand) that rapidly trap the generated radical (in very low concentration), whereas the sulfonyl radical is produced to regenerate the RFTA and reset a new catalytic cycle. From the simplified picture depicted in **Scheme 9** it is also possible to anticipate that, if the reaction of the generated radical is not fast (k_{R1} or k_{R2}), the hydrogen atom abstraction from RFTAH• would be possible (hydrodecarboxylation) or even deactivation of the catalyst by radical-radical coupling.



Scheme 9. Different reactivity of carboxylic acids with the radical acceptors used.

Conclusions

In conclusion, we have demonstrated that the direct decarboxylative allylation of carboxylic acids with allylsulfones can be efficiently promoted at room temperature by visible light, using inexpensive RFTA as photocatalyst in the absence of base. The transformation is redox-neutral, avoiding the use of external additives and none of the reagents was used in large excess. Importantly, although the carboxylic acids required a heteroatom or a carbonyl group in the *α*-position, the mild reaction conditions used tolerate the presence of a wide range of functionalities. Moreover, some carboxylic acids were also successfully used under similar conditions in the decarboxylative homolytic aromatic substitution of 2-(phenylsulfonyl)benzothiazole, to obtain C2-substituted benzothiazoles in moderate to good yields.

Experimental Section

General Remarks: Reagents and solvents were purchased from different trading houses and were used without further purification, unless otherwise stated. Riboflavin Tetraacetate (RFTA) was prepared from commercial (-)-Riboflavin according to a reported procedure.[23] TLCs were performed on silica gel 60 F_{254}, using aluminium plates and visualized by exposure with UV or stain with PMA ($KMnO_4$.for compound **3qa**). Flash chromatographies (FC) were carried out on handpacked columns of silica gel 60 (230 – 400 mesh). Infrared (IR) analysis was performed with a JASCO FT/IR 4100 spectrophotometer equipped with an ATR component. LRMS were performed in an AGILENT 6890N mass spectrometer coupled with a gas chromatographer (GC); the mobile phase was helium (2 mL/min); HP-1 column of 12 m was used; temperature program starts at 80 ºC for 3 min, then up to 270 ºC with a rate of 15 ºC/min, and 10 min at 270 ºC, using the Electron Impact (EI) mode at 70 eV (unless otherwise indicated). HRMS analyses were carried out in an AGILENT 7200 using the Electron Impact (EI) mode at 70 eV by Q-TOF .^{1}H-NMR spectra were recorded at 300 or 400 MHz for ^{1}H-NMR and 75 or 101 MHz for ^{13}C NMR, using $CDCl_3$ as the solvent and referenced to $CDCl_3$ (unless otherwise indicated). ^{13}C NMR spectra were recorded with ^{1}H-decoupling at 100 MHz and referenced to $CDCl_3$ at 77.16 ppm. Reactions were irradiated in a PhotoRedOx Box Duo (Evoluchem™) equipped with two lamps LED CREE XPE 18W (450-455 nm).

General procedure for the decarboxylative allylation of carboxylic acids: The corresponding carboxylic acid (0.25 mmol) was added to a 2 dram vial, followed by RFTA (6.8 mg, 0.0125 mmol, 5 mol-%), and a solution of 2 (0.275 mmol, 1.1 equiv) in MeCN (2.5 mL). Then, the vial was sealed with a septum and the reaction mixture was degassed by sparging with Ar for 10 min. Finally, the vial was equipped with an Ar balloon and the yellow homogeneous solution was stirred at 25 ºC under blue LEDs irradiation (λ = 455 nm, 15 ± 2 mW/cm^2)[34] until full conversion or no progress of the reaction was observed by TLC or GC (generally 18 - 22 h). The solvent was removed under reduced pressure, affording a residue which was purified by FC.

Butyl 2-methylene-4-phenoxypentanoate (3aa): Compound **3aa** was prepared from 2-Phenoxypropanoic acid (**1a**) following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (51 mg, 0.19 mmol, 77%): TLC R_f 0.54 (95:5 Hexane/EtOAc); IR *v* 3014, 1712, 1639, 1591, 1489, 1237, 1214, 1157, 746 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30 - 7.23 (m, 2H), 6.95 - 6.89 (m, 3H), 6.24 (d, *J* = 1.5 Hz, 1H), 5.67 (dd, *J* = 2.5, 1.2 Hz, 1H), 4.61 (h, *J* = 6.2 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 2.83 (ddd, *J* = 13.9, 6.6, 1.0 Hz, 1H), 2.50 (ddd, *J* = 13.9, 6.3, 0.9 Hz, 1H), 1.71 - 1.61 (m, 2H), 1.46 - 1.34 (m, 2H), 1.31 (d, *J* = 6.1 Hz, 3H), 0.94 (t, *J* = 7.3 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.3 (C), 158.0 (C), 137.2 (C), 129.6 (2 x CH), 128.0 (CH_2), 120.7 (CH), 116.0 (2 x CH), 72.1 (CH), 64.9 (CH_2), 39.3 (CH_2), 19.8 (CH_3), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 11.15; LRMS (EI) *m/z* (%) = 262 (M$^+$, 2), 169 (34), 121 (18), 113 (100), 95 (33), 94 (39), 87 (12), 67 (19); HRMS (EI) *Calcd.* for $C_{16}H_{22}O_3$ - C_7H_9O 153.0916, found 153.0913.

Butyl 2-((2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)methyl)acrylate (3ba): Compound **3ba** was prepared from 1,4-Benzodioxane-2-carboxylic acid (**1b**) following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a pale-yellow oil (47 mg, 0.17 mmol, 68%): TLC R_f 0.57 (95:5 Hexane/EtOAc); IR *v* 2980, 2957, 2934, 1716, 1381, 1274, 1244, 1210, 1193, 1156, 1146, 1105, 1091, 1060, 960, 869, 755, 696 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.89 - 6.81 (m, 4H), 6.33 (d, *J* = 1.3 Hz, 1H), 5.73 (d, *J* = 1.2 Hz, 1H), 4.41 - 4.32 (m, 1H), 4.24 (dd, *J* = 11.3, 2.3 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.93 (dd, *J* = 11.3, 6.8 Hz, 1H), 2.72 (ddd, *J* = 14.3, 7.5, 0.8 Hz, 1H), 2.64 (ddd, *J* = 14.3, 5.8, 0.9 Hz, 1H), 1.72 - 1.62 (m, 2H), 1.47 - 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 166.9 (C), 143.3 (C), 143.1 (C), 135.6 (C), 128.5 (CH_2), 121.7 (CH), 121.4 (CH), 117.5 (CH), 117.2 (CH), 71.5 (CH), 67.4 (CH_2), 65.0 (CH_2), 33.8 (CH2), 30.8 (CH_2), 19.4 (CH_2), 13.6 (CH_3) ppm; GC R_T 12.44 min; LRMS (EI) *m/z* (%) = 276 (M$^+$, 28), 135 (100), 134 (10), 121 (12), 111 (16), 110 (11); HRMS (EI) *Calcd.* for $C_{16}H_{20}O_4$ 276.1362, found 276.1363.

Butyl 4-(4-chlorophenoxy)-4-methyl-2-methylenepentanoate (3ca): Compound **3ca** was prepared from 2-(4-Chlorophenoxy)-2-methylpropanoic acid *(Clofibric Acid)* (**1c**)[35] following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a pale-yellow oil (47 mg, 0.15 mmol, 60%): TLC R_f 0.65 (95:5 Hexane/EtOAc); IR *v* 2969, 2939, 2878, 1721, 1625, 1584, 1488, 1482, 1223, 1173, 1152, 1093, 949, 850, 814, 751 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.24 - 7.17 (m, 2H), 6.93 - 6.85 (m, 2H), 6.28 (d, *J* = 1.7 Hz, 1H), 5.71 - 5.66 (m, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 2.75 (s, 2H), 1.71 - 1.57 (m, 2H), 1.46 - 1.34 (m, 2H), 1.24 (s, 6H), 6.93 (t, *J* = 7.3 Hz, 3) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 168.1 (C), 153.9 (C), 137.6 (C), 129.0 (2 x CH), 128.7 (C), 128.2 (CH_2), 125.3 (2 x CH), 80.7 (C), 64.9 (CH_2), 43.4 (CH_2), 30.8 (CH_2), 26.2 (2 x CH_3), 19.3 (CH_2), 13.8 (CH_3) ppm; GC R_T 12.78 min; LRMS (EI) *m/z* (%) = 183 (M$^+$ - C_6H_4ClO, 13), 169 (11), 130 (29), 128 (88), 127 (40), 126 (100), 125 (15), 111 (32), 109 (32), 108 (27), 81 (100), 80 (31), 79 (40), 67 (11), 65 (23), 63 (10), 57 (11), 53 (15); HRMS (EI) *Calcd.* for $C_{17}H_{23}ClO_3$ 310.1336, found 310.1327.

Butyl 2-methylene-4-(*p*-tolyloxy)butanoate (3da): Compound **3da** was prepared from 2-(*p*-Tolyloxy)acetic acid (**1d**) following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (53 mg, 0.20 mmol, 80%): TLC R_f 0.41 (95:5 Hexane/EtOAc); IR *v* 2988, 2956, 2934, 2871, 1740, 1714, 1511, 1372, 1235, 1160, 1046, 1045, 817 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.07 (d, *J* = 9.2 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 6.28 (d, *J* = 1.3 Hz, 1H), 5.70 (dd, *J* = 2.5, 1.2 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.78 (td, *J* = 6.6, 0.8 Hz, 2H), 2.28 (s, 3H), 1.71 - 1.60 (m, 2H), 1.47 - 1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.1 (C), 156.7 (C), 137.1 (C), 130.1 (C), 130.0 (2 × CH), 127.2 (CH_2), 114.6 (2 × CH), 66.4 (CH_2), 64.9 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 20.6 (CH_3), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 11.82 min; LRMS (EI) *m/z* (%) = 262 (M$^+$, 2), 155 (17), 108 (21), 107 (13), 99 (100), 91 (14), 81 (11), 77 (10), 53 (11); HRMS (EI) *Calcd.* for $C_{16}H_{22}O_3$ 262.1569, found 262.1563.

Butyl 2-methylene-4-phenoxybutanoate (3ea): Compound **3ea** was prepared from 2-Phenoxyacetic acid (**1e**), following the general procedure, but in this case 40 h of reaction were required. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (32 mg, 0.13 mmol, 50%): TLC R_f 0.65 (95:5 Hexane/EtOAc); IR *v* 2824, 1713, 1598, 1498, 1471, 1294, 1241, 1208, 1160, 1020, 949, 815, 799, 753, 692 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.33 - 7.23 (m, 2H), 6.99 - 6.84 (m, 3H), 6.28 (d, *J* = 1.2 Hz, 1H), 5.72 (d, *J* = 1.2 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 2.80 (td, *J* = 6.6, 0.8 Hz, 2H), 1.76 - 1.62 (m, 2H), 1.41 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.1 (C), 158.8 (C), 137.1 (C), 129.6 (2 × CH), 127.3 (CH_2), 120.9 (CH), 114.7 (2 × CH), 66.3 (CH_2), 64.9 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 13.32 min; LRMS (EI) *m/z* (%) = 248 (M$^+$, 3), 155 (28), 99 (100), 94 (18), 81 (12), 77 (12); HRMS (EI) *Calcd.* for $C_{15}H_{20}O_3$ 248.1412, found 248.1402.

Butyl 4-(4-chlorophenoxy)-2-methylenebutanoate (3fa): Compound **3fa** was prepared from 2-(4-chlorophenoxy)acetic acid (**1f**) following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (28 mg, 0.10 mmol, 40%): TLC R_f 0.60 (95:5 Hexane/EtOAc); IR *v* 2958, 2934, 2871, 1713, 1631, 1596, 1579, 1493, 1471, 1281, 1241, 1210, 1159, 1033, 822 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.82 (d, *J* = 9.0 Hz, 2H), 6.28

(d, *J* = 1.2 Hz, 1H), 5.70 (d, *J* = 1.2 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.78 (td, *J* = 6.6, 0.8 Hz, 2H), 1.71 - 1.62 (m, 2H), 1.41 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *δ* 167.0 (C), 157.5 (C), 136.9 (C), 129.4 (2 × CH), 125.7 (C), 116.0 (2 × CH), 66.7 (CH_2), 64.9 (CH_2), 32.1 (CH_2), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 12.47 min; LRMS (EI) *m/z* (%) = 282 (M^+, 3), 155 (21), 128 (15), 99 (100), 81 (10); HRMS (EI) *Calcd.* for $C_{15}H_{19}ClO_3$ 282.1023, found 282.1000.

Butyl 4-(2-methoxyphenoxy)-2-methylenebutanoate (3ga): Compound **3ga** was prepared from 2-(2-methoxyphenoxy)acetic acid (**1g**) following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow oil (38 mg, 0.14 mmol, 55%): TLC R_f 0.38 (95:5 Hexane/EtOAc); IR *v* 2962, 1716, 1631, 1501, 1253, 1250, 1226, 1157, 1123, 1028, 742 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 6.98 - 6.85 (m, 4H), 6.29 (d, *J* = 1.3 Hz, 1H), 5.74 (dd, *J* = 2.4, 1.2 Hz, 1H), 4.18 (dd, *J* = 6.8, 2.2 Hz, 2H), 4.16 (dd, *J* = 6.8, 1.8 Hz, 2H), 3.86 (s, 3H), 2.85 (td, *J* = 7.0, 0.9 Hz, 2H), 1.71 - 1.61 (m, 2H), 1.41 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.94 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *δ* 167.1 (C), 149.7 (C), 148.4 (C), 137.0 (C), 127.5 (CH_2), 121.4 (CH), 121.1 (CH), 113.7 (CH), 112.2 (CH), 67.7 (CH_2), 64.9 (CH_2), 56.1 (CH_3), 32.1 (CH_2), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 14.34 min; LRMS (EI) *m/z* (%) = 278 (M^+, 1%), 155 (21), 124 (14), 109 (11), 99 (100), 81 (11); HRMS (EI) *Calcd.* for $C_{16}H_{22}O_4$ 278.1518, found 278.1521.

Butyl 2-((3a*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3-dioxol-4-yl)methyl)acrylate (3ha): Compound **3ha** was prepared from 2,3-*O*-isopropylidene-1-*O*-methyl-D-ribosic acid (**1h**) following the general procedure. In this case, after 24 h, another 5 mol-% of RFTA was added and the reaction was run for another 12 h. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a yellow oil (57 mg, 0.18 mmol, 70%, single diastereoisomer): TLC R_f 0.25 (94:5 Hexane/EtOAc); IR *v* 2976, 2961, 2939, 1715, 1379, 1266, 1244, 1208, 1187, 1154, 1144, 1105, 1090, 1058, 960, 871, 695 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 6.29 (d, *J* = 1.1 Hz, 1H), 5.67 (q, *J* = 1.2 Hz, 1H), 4.95 (s, 1H), 4.60 (dd, *J* = 14.0, 6.2 Hz, 2H), 4.44 (td, *J* = 7.6, 0.5 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 3.33 (s, 3H), 2.59 (d, *J* = 7.7 Hz, 2H), 1.73 - 1.60 (m, 2H), 1.47 (s, 3H), 1.44 - 1.37 (m, 2H), 1.30 (s, 3H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) *δ* 166.9 (C), 137.1 (C), 127.4 (CH_2), 112.5 (C), 109.9 (CH), 85.6 (CH), 85.5 (CH), 83.8 (CH), 64.9 (CH_2), 55.2 (CH_3), 37.4 (CH_2), 30.8 (CH_2), 26.6 (CH_3), 25.2 (CH_3), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 11.64 min; LRMS (EI) *m/z* (%) = 299 (M^+ - CH_3, 17), 211 (18), 196 (25), 174 (10), 173 (100), 171 (10), 169 (33), 141 (11), 140 (16), 139 (12), 123 (12), 122 (14), 119 (26), 117 (29), 116 (10), 115 (29), 97 (18), 95 (34), 94 (11), 87 (19), 85 (23), 59 (28), 58 (11), 57 (17), 55 (16); HRMS (EI) *Calcd.* for $C_{16}H_{26}O_6$ 314.1729, *found* 314.1727.

Butyl 4-(benzyloxy)-2-methylenepentanoate (3ia): Compound **3ia** was prepared from (*R*)-(+)-2-(Benzyloxy)propanoic acid (**1i**) following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (25 mg, 0.09 mmol, 35%): TLC R_f 0.40 (95:5 Hexane/EtOAc); IR *v* 2968, 2930, 2901, 1715, 1453, 1376, 1125, 1073, 909, 732, 697 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 7.38 - 7.27 (m, 5H), 6.22 (d, *J* = 1.7 Hz, 1H), 5.62 (dd, *J* = 2.6, 1.1 Hz, 1H), 4.53 (q, *J* = 11.8 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 2H), 3.73 (sext, *J* = 6.1 Hz, 1H), 2.66 (ddd, *J* = 13.8, 6.8, 0.9 Hz, 1H), 2.43 (ddd, *J* = 13.8, 6.0, 1.0 Hz, 1H), 1.68 - 1.58 (m, 2H), 1.39 (dq, *J* = 14.3, 7.3 Hz, 2H), 1.20 (d, *J* = 6.1 Hz, 3H), 0.94 (t, J = 7.3 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) *δ* 167.4 (C), 139.0 (C), 137.9 (C), 128.4 (2 × CH), 127.7 (2 × CH), 127.5 (CH_2), 127.3 (CH), 73.8 (CH), 70.7 (CH_2), 64.7 (CH_2), 39.6 (CH_2), 30.8 (CH_2), 19.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 13.74 min; HRMS (EI) *Calcd.* for $C_{17}H_{24}O_3$ 276.1725, found 276.1711.

Butyl 2-methylene-4-(*p*-tolylthio)butanoate (3ja): Compound **3ja** was prepared from 2-(*p*-Tolylthio)acetic acid (**1j**)[20] following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (45 mg, 0.16 mmol, 65%): TLC R_f 0.65 (95:5 Hexane/EtOAc); IR *v* 2962, 2936, 2874, 1710, 1634, 1489, 1177, 1173, 1124, 947, 803 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 7.27 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.21 (d, *J* = 1.2 Hz, 1H), 5.58 (d, *J* = 1.2 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 3.04 (t, *J* = 7.7 Hz, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.32 (s, 3H), 1.69 - 1.60 (m, 2H), 1.46 - 1.33 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *δ* 166.9 (C), 138.9 (C), 136.3 (C), 132.3 (C), 130.2 (2 × CH), 129.8 (2 × CH), 126.6 (CH_2), 64.8 (CH_2), 33.2 (CH_2), 32.4 (CH_2), 30.8 (CH_2), 21.1 (CH_3), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 12.85 min; LRMS (EI) *m/z* (%) = 278 (M^+, 35), 205 (10), 137 (100), 124 (10), 99 (82), 91 (18); HRMS (EI) *Calcd*. for $C_{16}H_{22}O_2S$ 278.1341, *found* 278.1350.

Butyl 2-methylene-4-oxo-4-phenylbutanoate (3ka): Compound **3ka** was prepared from 2-Oxo-2-phenylacetic acid (**1k**) following the general procedure. It was purified by FC (100% Hexane to 85:15 Hexane/EtOAc) and obtained as a pale-yellow oil (30 mg, 0.12 mmol, 48%): TLC R_f 0.32 (95:5 Hexane/EtOAc); IR *v* 2970, 1713, 1685, 1325, 1303, 1212, 1147, 910, 752, 730 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 8.01 - 7.95 (m, 2H), 7.63 - 7.53 (m, 1H), 7.51 - 7.43 (m, 2H), 6.40 (d, *J* = 1.0 Hz, 1H), 5.69 (d, *J* = 1.1 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 3.99 (d, *J* = 0.8 Hz, 2H), 1.68 - 1.54 (m, 2H), 1.35 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *δ* 197.0 (C), 166.6 (C), 136.7 (C), 135.0 (C), 133.4 (CH), 128.8 (2 × CH), 128.5 (CH_2), 128.4 (2 × CH), 65.0 (CH_2), 41.8 (CH_2), 30.7 (CH_2), 19.3 (CH_2), 13.8 (CH_3) ppm; GC R_T 13.71 min; LRMS (EI) *m/z* (%) = 173 (M^+ - C_4H_9O, 7), 172 (12), 106 (8), 105 (100), 77 (28); HRMS (EI) *Calcd.* for $C_{15}H_{18}O_3$ 246.1256, found 246.1245.

Butyl 2-methylene-4-(phenylamino)butanoate (3la): Compound **3la** was prepared from (*N*)-Phenylglycine (**1l**) following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (39 mg, 0.15 mmol, 60%): TLC R_f 0.29 (95:5 Hexane/EtOAc); IR *v* 2969, 2901, 1707, 1603, 1508, 1215, 1066, 908, 754, 731 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 7.23 - 7.14 (m, 2H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 2H), 6.25 (d, *J* = 1.3 Hz, 1H), 5.63 (d, *J* = 1.2 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.31 (t, *J* = 6.8 Hz, 2H), 2.64 (td, *J* = 6.8, 0.7 Hz, 2H), 1.77 - 1.59 (m, 2H), 1.43 - 1.40 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *δ* 167.2 (C), 147.5 (C), 138.3 (C), 129.4 (2 × CH), 126.9 (CH_2), 118.0 (CH), 113.5 (2 × CH), 65.0 (CH_2), 43.4 (CH_2), 32.0 (CH_2), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 11.99 min; LRMS (EI) *m/z* (%) = 247 (M^+, 14), 173 (24), 106 (100), 105 (15), 104 (11), 77 (21); HRMS (EI) *Calcd*. for $C_{15}H_{21}NO_2$ 247.1572, *found* 247.1565.

Butyl 2-methylene-4-(phenylamino)pentanoate (**3ma**): Compound **3ma** was prepared from (*N*)-Phenylalanine (**1m**)[36] following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a pale-yellow oil (26 mg, 0.10 mmol, 40%): TLC R_f 0.46 (95:5 Hexane/EtOAc); IR *v* 3398, 2961, 2929, 2870, 1710, 1602, 1500, 1317, 1255, 1215, 1161, 946, 744, 689 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *δ* 7.19 - 7.12 (m, 2H), 6.69 - 6.60 (m, 3H), 6.22 (d, *J* = 1.5 Hz, 1H), 5.59 (d, *J* = 1.3 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.71 (h, *J* = 6.4 Hz, 1H), 2.73 (ddd, *J* = 13.8, 6.4, 1.0 Hz, 1H), 2.32 (ddd, *J* = 13.8, 6.9, 0.8 Hz, 1H), 1.71 - 1.62 (m, 2H), 1.47 - 1.34 (m, 2H), 1.18 (d, *J* = 6.4 Hz, 3H), 0.94 (t, *J* = 7.3Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *δ* 167.6 (C), 147.4 (C), 138.3 (C), 129.4 (2 × CH), 127.3 (CH_2), 117.2 (CH), 113.3 (2 × CH), 64.9 (CH_2), 48.1 (CH), 39.4 (CH_2), 30.9 (CH_2), 20.7 (CH_3), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T = 13.98 min; LRMS (EI) *m/z* (%) = 261 (M^+, 4), 121 (11), 120 (100), 77 (11); HRMS (EI) *Calcd.* for $C_{16}H_{23}NO_2$ 261.1729, found 261.1735.

Butyl 4-((2-methoxyphenyl)amino)-2-methylenebutanoate (3na): Compound **3na** was prepared from (2-Methoxyphenyl)glycine (**1n**)[22]

following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a pale-yellow oil (31 mg, 0.11 mmol, 45%): TLC R_f 0.45 (95:5 Hexane/EtOAc); IR *v* 2960, 2901, 1713, 1602, 1512, 1244, 1222, 1156, 1124, 1028, 946 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.93 - 6.83 (m, 1H), 6.81 - 6.74 (m, 1H), 6.74 - 6.64 (m, 2H), 6.25 (d, *J* = 1.3 Hz, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.84 (s, 3H), 3.32 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 6.7 Hz, 2H), 1.75 - 1.60 (m, 2H), 1.42 (dq, *J* = 14.4, 7.3 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.2 (C), 147.2 (C), 138.3 (CH_2), 137.6 (C), 126.7 (CH), 121.5 (CH), 117.1 (C), 110.5 (CH), 109.7 (CH), 64.9 (CH_2), 55.6 (CH_3), 43.0 (CH_2), 32.0 (CH_2), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 15.0 min; LRMS (EI) *m/z* (%) = 277 (M^+, 16), 136 (100), 121 (14), 120 (17); HRMS (EI) *Calcd.* for $C_{16}H_{23}NO_3$ 277.1678, found 277.1678.

Butyl 4-((4-bromophenyl)amino)-2-methylenebutanoate (3oa): Compound **3oa** was prepared from (4-Bromophenyl)glycine (**1o**)[22] following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow oil (30 mg, 0.09 mmol, 35%): **TLC** R_f 0.44 (95:5 Hexane/EtOAc); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.27 - 7.21 (m, 2H), 6.53 - 6.48 (m, 2H), 6.24 (d, *J* = 1.3 Hz, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 3.26 (t, *J* = 6.8 Hz, 2H), 2.61 (td, *J* = 6.8, 0.7 Hz, 2H), 1.71 - 1.62 (m, 2H), 1.47 - 1.35 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.2 (C), 146.9 (C), 138.2 (C), 132.1 (2 × CH), 127.0 (CH), 114.7 (2 × CH), 109.2 (C), 65.0 (CH_2), 43.2 (CH_2), 31.9 (CH_2), 30.8 (CH_2), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 14.10 min; LRMS (EI) *m/z* (%) = 327 (M^+ ^{81}Br, 13), 325 (M^+ ^{79}Br, 14), 186 (95), 185 (11), 184 (100), 105 (11); HRMS (EI) *Calcd.* for $C_{15}H_{20}BrNO_2$ 325.0677, found 325.0650.

Butyl 2-methylene-4-(1*H*-pyrrol)-1-yl)pentanoate (3pa): Compound **3pa** was prepared from 2-(1*H*-Pyrrol-1-yl)propanoic acid (**1p**)[37] following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (35 mg, 0.15 mmol, 58%): TLC R_f 0.25 (95:5 Hexane/EtOAc); IR *v* 3023, 2955, 2928, 2871, 1707, 1631, 1487, 1220, 1165, 749 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.67 (t, *J* = 2.1 Hz, 2H), 6.11 (t, *J* = 2.0 Hz, 2H), 6.08 (d, *J* = 1.4 Hz, 1H), 5.31 (d, *J* = 1.2 Hz, 1H), 4.32 (dq, *J* = 13.4, 6.8 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 2.75 - 2.59 (m, 2H), 1.73 - 1.49 (m, 2H), 1.47 (t, *J* = 5.3 Hz, 2H), 1.45 - 1.35 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.0 (C), 136.9 (C), 127.8 (CH_2), 118.6 (2 × CH), 107.8 (2 × CH), 64.9 (CH_2), 54.4 (CH), 41.5 (CH_2), 30.8 (CH_2), 21.7 (CH_3), 19.4 (CH_2), 13.9 (CH_3) ppm; GC R_T 12.12 min; LRMS (EI) *m/z* (%) = 235 (M^+, 28), 178 (53), 163 (12), 134 (77), 133 (17), 132 (19), 118 (17), 117 (15), 94 (100); HRMS (EI) *Calcd*. for $C_{14}H_{21}NO_2$ 235.1572, *found* 235.1568.

Butyl 2-(((3r,5r,7r)-adamantan-1-yl)methyl)acrylate (3qa): It was prepared from adamantane-1-carboxylic acid (**1q**, 2 equiv) following the general procedure, but degasification was performed by three cycles of freeze-pump-thaw. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (27 mg, 0.10 mmol, 40%): TLC R_f 0.88 (90:10 Hexane/EtOAc); IR *v* 2903, 2847, 1718, 1176, 1132, 1059, 806 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) 6.19 (d, *J* = 1.9 Hz, 1H), 5.44 – 5.40 (m, 1H), 4.15 (t, *J* = 6.7 Hz, 2H), 2.17 (s, 2H), 1.95 (br s, 3H), 1.74 – 1.57 (m, 12H), 1.47 -1.46 (m, 4H), 0.97 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5 (C), 137.8 (C), 127.0 (CH_2), 64.67 (CH_2), 45.6 (CH_2), 42.2 (3 x CH_2), 37.1 (3 x CH_2), 33.4 (C), 30.8 (CH_2), 28.8 (3 x CH), 19.39 (CH_2), 13.88 (CH_3) ppm; GC R_T 12.33 min; LRMS (EI) *m/z* (%) = 276 (M^+, 1), 203 (2), 136 (11), 135 (100), 79 (10); HRMS (EI) *Calcd*. for $C_{18}H_{28}O_2$ 276.2089, *found* 276.2088.

Ethyl 2-methylene-4-phenoxypentanoate (3ab): Compound **3ab** was prepared from **2b** after 12 h, following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (45 mg, 0.19 mmol, 76%): TLC R_f 0.54 (98:2 Hexane/EtOAc); IR *v* 2985, 2976, 2901, 1712, 1599, 1586, 1491, 1406, 1394, 1381, 1241, 1231, 1174, 1157, 1076, 1066, 947, 891, 752, 692 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.31 - 7.22 (m, 2H), 6.95 - 6.92 (m, 3H), 6.25 (d, *J* = 1.5 Hz, 1H), 5.68 (d, *J* = 1.2 Hz, 1H), 4.61 (h, *J* = 6.2 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.83 (ddd, *J* = 13.9, 6.5, 0.9 Hz, 1H), 2.50 (ddd, *J* = 13.9, 6.4, 0.8 Hz, 1H), 1.31 (d, *J* = 6.2 Hz, 3H), 1.30 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.2 (C), 158.0 (C), 137.1 (C), 129.6 (2 × CH), 128.0 (CH_2), 120.7 (CH), 115.9 (2 × CH), 72.1 (CH), 61.0 (CH_2), 39.2 (CH_2), 19.8 (CH_3), 14.3 (CH_3) ppm; GC R_T 10.05 min; LRMS (EI) *m/z* (%) = 234 (M^+, 4), 189 (11), 141 (100), 121 (25), 113 (73), 95 (57), 94 (73), 87 (27), 68 (11), 67 (41), 66 (11), 65 (13); HRMS (EI) *Calcd*. for $C_{14}H_8O_3$ 234.1256, *found* 234.162.

Benzyl 2-methylene-4-phenoxypentanoate (3ac): Compound **3ac** was prepared from **2c** after 12 h, following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow oil (47 mg, 0.16 mmol, 65%): TLC R_f 0.47 (95:5 Hexane/EtOAc); IR *v* 3014, 1712, 1639, 1591, 1489, 1237, 1214, 1157, 746 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.40 - 7.32 (m, 5H), 7.25 - 7.19 (m, 2H), 6.95 - 6.84 (m, 3H), 6.31 (d, *J* = 1.4 Hz, 1H), 5.72 (d, *J* = 1.2 Hz, 1H), 5.21 (s, 2H), 4.61 (h, *J* = 6.2 Hz, 1H), 2.85 (ddd, *J* = 13.9, 6.7, 0.9 Hz, 1H), 2.53 (ddd, *J* = 13.9, 6.2, 0.8 Hz, 1H), 1.30 (d, *J* = 6.1 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.0 (C), 158.0 (C), 136.9 (C), 136.0 (C), 129.6 (2 × CH), 128.73 (2 × CH), 128.65 (CH), 128.4 (2 × CH), 128.3 (CH_2), 120.7 (CH), 115.9 (2 × CH), 72.0 (CH), 66.8 (CH_2), 39.3 (CH_2), 19.8 (CH_3) ppm; GC R_T 13.28 min; LRMS (EI) *m/z* (%) = 203 (M^+ - C_6H_5O, 19), 94 (11), 91 (100); HRMS (EI) *Calcd*. for $C_{19}H_{20}O_3$ 296.1412, *found* 296.1406.

Allyl 2-methylene-4-phenoxypentanoate (3ad): Compound **3ad** was prepared from **2d** after 12 h, following the general procedure. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (39 mg, 0.16 mmol, 65%): TLC R_f 0.49 (95:5 Hexane/EtOAc); IR *v* 1720, 1636, 1493, 1211, 1169, 908, 748 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.30 - 7.24 (m, 2H), 6.95 - 6.89 (m, 3H), 6.29 (d, *J* = 1.4 Hz, 1H), 5.95 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.71 (d, *J* = 1.2 Hz, 1H), 5.34 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.25 (ddd, *J* = 10.4, 2.6, 1.3 Hz, 1H), 4.67 (dt, *J* = 5.7, 1.4 Hz, 2H), 4.64 - 4.59 (m, 1H), 2.84 (ddd, *J* = 13.9, 6.6, 0.9 Hz, 1H), 2.52 (ddd, *J* = 13.9, 6.2, 0.9 Hz, 1H), 1.31 (d, *J* = 6.1 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 166.8 (C), 158.0 (C), 136.9 (C), 132.2 (CH), 129.6 (2 × CH), 128.5 (CH_2), 120.8 (CH), 118.4 (CH_2), 115.9 (2 × CH), 72.0 (CH), 65.6 (CH_2), 39.2 (CH_2), 19.8 (CH_3) ppm; GC R_T 10.45 min; LRMS (EI) *m/z* (%) = 246 (M^+, 5), 154 (10), 153 (100), 121 (25), 107 (15), 95 (25), 94 (54), 91(10), 67 (30), 65 (10); HRMS (EI) *Calcd*. for $C_{15}H_{18}O_3$ - C_6H_5O 153.0916, *found* 153.0916.

((4-chloropent-4-en-2-yl)oxy)benzene (3ae): Compound **3ae** was prepared from **2e** after 12 h, following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (30 mg, 0.15 mmol, 60%): TLC R_f 0.67 (98:2 Hexane/EtOAc); IR *v* 3025, 2943, 1718, 1635, 1597, 1587, 1494, 1380, 1240, 1220, 1081, 1016, 754 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.32 - 7.25 (m, 2H), 6.97 - 6.90 (m, 3H), 5.25 (s, 2H), 4.70 (h, *J* = 6.2 Hz, 1H), 2.85 (dd, *J* = 14.5, 6.3 Hz, 1H), 2.50 (dd, *J* = 14.4, 6.5 Hz, 1H), 1.35 (d, *J* = 6.1 Hz, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 157.8 (C), 138.9 (C), 129.7 (2 × CH), 121.1 (CH), 116.2 (2 × CH), 115.0 (CH_2), 71.2 (CH_2), 46.1 (CH), 19.5 (CH_3) ppm; GC R_T 8.18 min; LRMS (EI) *m/z* (%) = 196 (M^+, 11), 121 (41), 94 (100), 77 (16); HRMS (EI) *Calcd*. for $C_{11}H_{13}ClO$ 196.0655, *found* 196.0658.

((4-phenoxypent-1-en-2-yl)sulfonyl)benzene (3af): Compound **3af** was prepared from **2f**, following the general procedure. In this case the reaction was run during 40 h employing 2 equiv of **1a** and 1 equiv of **2f**. It was purified by FC (100% Hexane to 75:25 Hexane/EtOAc) and obtained as a white solid (31 mg, 0.10 mmol, 68%): TLC R_f 0.11 (95:5 Hexane/EtOAc); IR *v* 3063, 2980, 2930, 1598, 1586, 1491, 1446, 1304, 1292, 1237, 1173,

1139, 1081, 952, 689 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.92 - 7.82 (m, 2H), 7.65 - 7.57 (m, 1H), 7.55 - 7.45 (m, 2H), 7.30 - 7.20 (m, 2H), 6.98 - 6.88 (m, 1H), 6.84 - 6.76 (m, 2H), 6.44 (br s, 1H), 5.93 (br s, 1H), 4.60 - 4.50 (m, 1H), 2.66 (ddd, J = 15.4, 7.4, 0.8 Hz, 1H), 2.49 (ddd, J = 15.4, 5.2, 1.0 Hz, 1H), 1.26 (d, J = 6.1 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.4 (C), 146.7 (C), 138.7 (C), 133.7 (CH), 129.7 (2 × CH), 129.4 (2 × CH), 128.3 (2 × CH), 127.0 (CH_2), 121.2 (CH), 115.9 (2 × CH), 71.5 (CH), 36.7 (CH_2), 19.7 (CH_3) ppm; GC R_T 16.85 min; LRMS (EI) *m/z* (%) = 302 (M^+, 9), 210 (13), 209 (100), 143 (93), 125 (35), 121 (21), 94 (47), 77 (34), 67 (26), 65 (11); HRMS (EI) *Calcd*. for $C_{17}H_{18}O_3S$ 302.0977, *found* 302.0985.

(4-phenoxypent-1-en-2-yl)benzene (3ag): Compound **3ag** was prepared from **2g** after 16 h, following the general procedure. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (24 mg, 0.10 mmol, 40%): TLC R_f 0.77 (95:5 Hexane/EtOAc); IR *v* 2972, 2949, 2930, 2911, 1598, 1493, 1375, 1231, 1174, 1081, 1067, 1054, 912, 781, 750, 713, 692 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.45 - 7.16 (m, 7H), 6.94 - 6.85 (m, 1H), 6.84 - 6.74 (m, 2H), 5.33 (d, J = 1.4 Hz, 1H), 5.18 (d, J = 1.1 Hz, 1H), 4.45 - 4.38 (m, 1H), 3.08 (ddd, J = 14.1, 5.8, 0.9 Hz, 1H), 2.65 (ddd, J = 14.1, 7.4, 0.9 Hz, 1H), 1.28 (d, J = 6.1 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 157.9 (C), 145.3 (C), 141.2 (C), 129.5 (2 × CH), 128.5 (2 × CH), 127.7 (CH), 126.4 (2 × CH), 120.8 (CH), 116.2 (2 × CH), 115.5 (CH), 72.5 (CH), 42.7 (CH_2), 19.7 (CH_3) ppm; GC R_T 11.33 min; LRMS (EI) *m/z* (%) = 238 (M^+, 25), 146 (12), 145 (100), 144 (30), 143 (18), 130 (17), 129 (84), 128 (21), 121 (54), 117 (21), 115 (18), 103 (33), 94 (17), 91 (22), 77 (34), 65 (10); HRMS (EI) *Calcd*. for $C_{17}H_{18}O$ 238.1358, *found* 238.1361.

2-methylene-3-phenethyl-4-phenoxypentanenitrile (3ah): Compound **2ah** was prepared from **2h** after 48 h, following the general procedure. In this case 2 equiv of **1a** and 1 equiv of **2h** were used. It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a colorless oil (26 mg, 0.09 mmol, 32% in a 3:2 *dr* according to GC): TLC R_f 0.30 (95:5 Hexane/EtOAc); IR *v* 2950, 2925, 2166, 2036, 1598, 1492, 1238, 1078, 944, 752, 694 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *(mixture of diastereoisomers)* δ 7.35 - 7.13 (m, 9H), 7.00 - 6.84 (m, 3H), 6.10 (d, J = 0.6 Hz, 0.47H), 6.08 (d, J = 0.5 Hz, 0.44 H), 5.84 (brs, 0.47H), 5.82 (brs, 0.47H), 4.45 - 4.33 (m, 1H), 2.84 - 2.68 (m, 1H), 2.61 - 2.36 (m, 2H), 2.28 – 2.12 (m, 1H), 2.08 - 1.80 (m, 2H), 1.30 (d, J = 0.7 Hz, 1.5H), 1.28 (d, J = 0.6 Hz, 1.5H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) (*mixture of diastereoisomers)* δ 157.7, 157.6, 141.08, 141.05, 133.9, 133.7, 129.8, 129.7, 128.67, 128.65, 128.5, 126.3, 126.28, 121.4, 121.3, 116.3, 116.0, 75.1, 75.0, 50.31, 50.26, 33.31, 33.3, 30.9, 17.5, 17.4 ppm; GC *Diastereoisomer A:* R_T 15.90 min; *Diastereoisomer B:* R_T 16.00 min; LRMS (EI) *Diastereoisomer A: m/z* (%) = 291 (M^+, 15), 121 (83), 105 (15), 94 (68), 92 (11), 91 (100), 77 (25), 65 (13); *Diastereoisomer B: m/z* (%) = 291 (M^+, 14), 121 (81), 105 (16), 94 (73), 91 (100), 77 (23), 65 (14); HRMS (EI) *Calcd*. for $C_{20}H_{21}NO$ 291.1623, *found* 291.1623.

General procedure for the decarboxylative arylation of carboxylic acids: 2-(phenylsulfonyl)benzo[*d*]thiazole (**4**, 68.8 mg, 0.25 mmol, 1 equiv) was added to a 2 dram vial equipped with a stirring magnetic bar, followed by RFTA (13.6 mg, 0.025 mmol, 10 mol-%), the corresponding carboxylic acid (0.50 mmol, 2 equiv) and MeCN (2.5 mL). The vial was sealed with a septum and the reaction mixture submitted to three cycles of freeze-pump-thaw. Finally, the vial was equipped with an Ar balloon and the yellow mixture[38] was stirred at 25 °C under blue LEDs irradiation (λ = 455 nm, 15 ± 2 mW/cm^2)[34] until no progress was observed by TLC or GC (generally 36 h). The solvent was removed under reduced pressure, affording a residue which was purified by FC**.**

2-(1-phenoxyethyl)benzo[*d*]thiazole (5a): Compound **5a** was prepared from 2-Phenoxypropanoic acid (**1a**) following the *general procedure for the decarboxylative arylation.* It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a white solid (38 mg, 0.15 mmol, 60%): TLC R_f 0.47 (95:5 Hexane/EtOAc); IR *v* 2987, 2901, 1597, 1493, 1261, 1217, 1065, 907, 753, 728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.53 - 7.45 (m, 1H), 7.42 - 7.35 (m, 1H), 7.29 - 7.22 (m, 2H), 7.03 - 6.98 (m, 2H), 6.98 - 6.93 (m, 1H), 5.77 (q, J = 6.5 Hz, 1H), 1.85 (d, J = 6.5 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) 175.1 (C), 157.4 (C), 152.9 (C), 134.9 (C), 129.7 (2 × CH), 126.3 (CH), 125.3 (CH), 123.1 (CH), 122.1 (CH), 121.9 (CH), 115.9 (2 × CH), 74.7 (CH), 23.0 (CH_3) ppm; GC R_T 14.96 min; LRMS (EI) *m/z* (%) = 255 (M^+, 3), 163 (11), 162 (100), 109 (14); HRMS (EI) *Calcd.* for $C_{15}H_{13}NOS$ 255.0718, found 255.0706.

2-(2,3-dihydrobenzo[*b*][1,4]dioxin-2-yl)benzo[*d*]thiazole (5b): Compound **5b** was prepared from 1,4-Benzodioxane-2-carboxylic acid (**1b**) following the *general procedure for the decarboxylative arylation.* It was purified by FC (100% Hexane to 95:5 Hexane/EtOAc) and obtained as a white solid (43 mg, 0.16 mmol, 64%): TLC R_f 0.31 (95:5 Hexane/EtOAc); IR *v* 2987, 2901, 1494, 1263, 1215, 1074, 1053, 907, 748, 729 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.55 - 7.90 (m, 1H), 7.45 - 7.39 (m, 1H), 7.12 - 7.04 (m, 1H), 6.99 - 6.89 (m, 3H), 5.65 (dd, J = 6.9, 2.7 Hz, 1H), 4.72 (dd, J = 11.4, 2.7 Hz, 1H), 4.43 (dd, J = 11.4, 6.9 Hz, 1H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.8 (C), 153.1 (C), 143.2 (C), 142.4 (C), 135.0 (C), 126.5 (CH), 125.6 (CH), 123.4 (CH), 122.4 (CH), 122.2 (CH), 122.0 (CH), 117.7 (CH), 117.6 (CH), 73.6 (CH), 67.2 (CH_2) ppm; GC R_T 16.66 min; LRMS (EI) *m/z* (%) = 270 (M^+ + 1, 11), 269 (63), 241 (11), 226 (11), 224 (36), 207 (11), 162 (12), 161 (100), 160 (37), 135 (26), 108 (12), 69 (11). Characterization data matched that reported in the literature.[39]

2-((2-methoxyphenoxy)methyl)benzo[*d*]thiazole (5c): Compound **5c** was prepared from 2-(2-Methoxyphenoxy)acetic acid (**1g**) following the *general procedure for the decarboxylative arylation.* It was purified by FC (100% Hexane to 85:15 Hexane/EtOAc) and obtained as a yellow oil (41 mg, 0.15 mmol, 60%): TLC R_f 0.16 (95:5 Hexane/EtOAc); IR *v* 2971, 2901, 1501, 1254, 1045, 1028, 905, 760, 724 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 8.6 Hz, 1H), 7.53 - 7.45 (m, 1H), 7.44 - 7.36 (m, 1H), 7.06 - 7.00 (m, 1H), 6.98 - 6.92 (m, 2H), 6.91 - 6.83 (m, 1H), 5.56 (s, 2H), 3.92 (s, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 150.1 (C), 147.4 (C), 126.6 (C), 125.7 (C), 123.2 (CH), 122.9 (CH), 122.1 (CH), 121.1 (2 × CH), 115.6 (C), 112.5 (2 × CH), 69.3 (CH_2), 56.2 (CH_3) ppm; GC R_T 16.44 min; LRMS (EI) *m/z* (%) = 271 (M^+, 22), 149 (13), 148 (100); HRMS (EI) *Calcd.* for $C_{15}H_{13}NO_2S$ 271.0667, found 271.0667.

2-(1-(benzyloxy)ethyl)benzo[*d*]thiazole (5d): Compound **5d** was prepared from (*R*)-(+)-2-(Benzyloxy)propanoic acid (**1i**) following the *general procedure for the decarboxylative arylation.* It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a pale-yellow oil (27 mg, 0.10 mmol, 40%): TLC R_f 0.31 (95:5 Hexane/EtOAc); IR *v* 2987, 2901, 1508, 1395, 1215, 1066, 1056, 907, 747, 725 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, J = 8.1, 0.5 Hz, 1H), 7.92 (dd, J = 7.9, 0.7 Hz, 1H), 7.54 - 7.28 (m, 8H), 5.01 (q, J = 6.5 Hz, 1H), 4.69 (d, J = 11.6 Hz, 1H), 4.60 (d, J = 11.6 Hz, 1H), 1.70 (d, J = 6.5 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 176.5 (C), 152.8 (C), 137.6 (C), 134.9 (C), 128.6 (2 × CH), 128.1 (2 × CH), 128.0 (2 × CH), 126.2 (CH), 125.3 (CH), 123.0 (CH), 122.1 (CH), 75.7 (CH), 71.8 (CH_2), 22.7 (CH_3) ppm; GC R_T 15.58 min; LRMS (EI) *m/z* (%) = 224 (10), 164 (12), 163 (100), 162 (M^+- OBn, 46), 91 (33); HRMS (EI) *Calcd.* for C_9H_9NS 163.0456, found 163.0451.

2-((3a*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4*d*][1,3]dioxol-4-yl)benzo[*d*]thiazole (5e): Compound **5e** was prepared from 2,3-*O*-isopropylidene-1-*O*-methyl-D-ribosic acid (**1h**) following the *general procedure for the decarboxylative arylation.* It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (28 mg, 0.09 mmol, 35%): TLC R_f 0.23 (95:5 Hexane/EtOAc); IR *v* 2986,

2934, 1598, 1493, 1446, 1375, 1306, 1239, 1141, 1084, 907, 867, 728, 689 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 8.2 Hz, 1H), 7.88 (dd, J = 7.9, 0.7 Hz, 1H), 7.52 - 7.44 (m, 1H), 7.43 - 7.35 (m, 1H), 5.60 (dd, J = 5.9, 1.1 Hz, 1H), 5.54 (br s, 1H), 5.17 (s, 1H), 4.69 (d, J = 5.9 Hz, 1H), 3.39 (s, 3H), 1.57 (s, 3H), 1.57 (s, 3H) ppm; ^{13}C-NMR (75 MHz, $CDCl_3$) δ 170.2 (C), 152.9 (C), 135.4 (C), 126.3 (CH), 125.4 (CH), 123.3 (CH), 121.8 (CH), 113.1 (C), 111.1 (CH), 86.4 (CH), 85.4 (CH), 84.2 (CH), 56.2 (CH_3), 26.7 (CH_3), 25.3 (CH_3) ppm; GC R_T 15.48 min; LRMS (EI) m/z (%) = 292 (M^+ - CH_3, 10), 218 (11), 208 (11), 207 (92), 190 (25), 189 (23), 165 (14), 164 (39), 163 (30), 162 (17), 161 (100), 160 (22), 135 (25), 108 (12), 85 (15), 58 (14); HRMS (EI) *Calcd.* for $C_{15}H_{17}NO_4S$ 307.0878, found 307.0883.

***N*-(benzo[*d*]thiazol-2-ylmethyl)aniline (5f):** Compound **5f** was prepared from (*N*)-Phenylglycine (**1l**) following the *general procedure for the decarboxylative arylation.* It was purified by FC (100% Hexane to 80:20 Hexane/EtOAc) and then treated with ^{i}PrOH/Hexanes to filtered out the starting sulfone and obtain **5f** as a colorless oil (36 mg, 0.15 mmol, 60%): TLC R_f 0.13 (95:5 Hexane/EtOAc); IR v 2987, 2901, 1216, 1066, 1056, 906, 754, 727, 671 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 8.01 (d, J = 7.9 Hz, 1H), 7.83 (dd, J = 8.0, 0.6 Hz, 1H), 7.51 - 7.45 (m, 1H), 7.39 - 7.34 (m, 1H), 7.23 - 7.15 (m, 2H), 6.84 - 6.67 (m, 3H), 4.78 (s, 2H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 173.2 (C), 153.6 (C), 147.0 (C), 129.5 (2 × CH), 126.1 (CH), 125.0 (CH), 122.9 (CH), 121.9 (CH), 118.9 (C), 113.4 (2 × CH), 47.2 (CH_2) ppm; GC R_T 16.29 min; LRMS (EI) m/z (%) = 241 (M^+ + 1, 18), 240 (100), 239 (27), 238 (24), 237 (27), 210 (13), 149 (10), 148 (36), 136 (23), 135 (11), 108 (10), 106 (76), 105 (13), 104 (12), 77 (30); HRMS (EI) *Calcd.* for $C_{14}H_{12}N_2S$ 240.0721, found 240.0718.

General procedure for the synthesis of 3qa and 7: 2-(but-3-en-1-yloxy)propanoic acid[40] **(1q)** (28.8 mg, 0.2 mmol, 1 equiv) was added to a 2 dram vial equipped with a stirring magnetic bar, followed by RFTA (5.44 mg, 0.01 mmol, 5 mol-%), and a solution of **2a** (0.22 mmol, 56.4 mg, 1.1 equiv) in MeCN (4 mL). The vial was sealed with a septum and the reaction mixture submitted to three cycles of freeze-pump-thaw. Finally, the vial was equipped with an Ar balloon and the yellow mixture was stirred at 25 ºC under blue LEDs irradiation (λ = 455 nm, 15 ± 2 mW/cm^2) until no progress was observed by TLC or GC (24 h). The solvent was removed under reduced pressure and pure compounds **3qa** and **7** was obtained after purification by flash column chromatography.

Butyl 4-(but-3-en-1-yloxy)-2-methylenepentanoate (3qa): Compound **3qa** was prepared from 2-(but-3-en-1-yloxy)propanoic acid (**1q**) following the procedure above described. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (15 mg, 0.06 mmol, 30%): TLC R_f 0.75 (90:10 Hexane/EtOAc); IR v 2960, 2930, 2873, 1716, 1631, 1458, 1326, 1219, 1125, 912, 735 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.19 (d, J = 1.7 Hz, 1H), 5.81 (ddt, J = 17.0, 10.2, 6.7 Hz, 1H), 5.60 (dd, J = 2.7, 1.1 Hz, 1H), 5.12 - 4.97 (m, 2H), 4.15 (t, J = 6.6 Hz, 2H), 3.64 - 3.39 (m, 3H), 2.59 (ddd, J = 13.8, 6.7, 1.0 Hz, 1H), 2.35 (ddd, J = 13.8, 6.7, 1.0 Hz, 1H), 2.32 -2.25 (m, 2H), 1.72 – 1.59 (m, 2H), 1.50 – 1.35 (m, 2H), 1.14 (d, J = 6.2 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.5 (C), 137.9 (C), 135.6 (CH), 127.2 (CH_2), 116.3 (CH_2), 74.3 (CH), 68.2 (CH_2), 64.7 (CH_2), 39.4 (CH_2), 34.7 (CH_2), 30.8 (CH_2), 19.8 (CH_2), 19.4 (CH_3), 13.9 (CH_3) ppm; GC R_T 11.23 min; LRMS (EI) m/z (%) = 155 (M^+ - C_5H_9O, 11), 113 (45), 111 (11), 99 (54), 95 (18), 81 (31), 69 (18), 67 (14), 55 (100); HRMS (EI) *Calcd.* for $C_{14}H_{24}O_3$ – $C_9H_5O_2$ 155.1072, found 155.1066.

Butyl 2-methylene-4-[(2*R*,3*S*)-2-methyltetrahydrofuran-3-yl)butanoate (7): Compound **7** was prepared from 2-(but-3-en-1-yloxy)propanoic (**1q**) following the procedure above described. It was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) and obtained as a colorless oil (10 mg, 0.04 mmol, 21%): TLC R_f 0.44 (90:10 Hexane/EtOAc); IR v 2959, 2929, 2872, 1718, 1457, 1186, 1155, 1069, 941, 735 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 6.15 (d, J = 1.4 Hz, 1H), 5.54 (dd, J = 2.7, 1.3 Hz, 1H), 4.16 (t, J = 6.6 Hz, 2H), 4.07 (p, J = 6.5 Hz, 1H), 3.93 (td, J = 8.4, 3.7 Hz, 1H), 3.69 (dd, J = 15.6, 8.3 Hz, 1H), 2.45 - 2.20 (m, 2H), 2.19 - 1.95 (m, 2H), 1.75 - 1.57 (m, 5H), 1.47 - 1.36 (m, 2H), 1.08 (d, J = 6.5 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) δ 167.4, 141.0, 124.7, 66.5, 64.7, 41.8, 31.11, 31.08, 30.8, 28.9, 19.4, 16.2, 13.9 ppm; GC R_T 12.61 min; LRMS (EI) m/z (%) = 167 (M^+, 25), 166 (84), 151 (48), 140 (18), 139 (10), 138 (20), 125 (20), 124 (16), 123 (39), 122 (20), 121 (26), 112 (16), 111 (54), 110 (17), 109 (11), 108 (11), 107 (11), 105 (10), 99 (11), 98 (28), 97 (66), 96 (25), 95 (100), 94 (40), 93 (30); HRMS (EI) *Calcd.* for $C_{14}H_{24}O_3$ – $C_4H_{10}O_2$ 166.0994, found 166.099.

Butyl 2-((2,3-dihydrobenzo[b][1,4]dioxin-2-yl)methyl)-4-(*p*-tolyloxy)butanoate (6): Compound **1d** (57 mg, 0.3 mmol, 1.5 equiv.) was added to a 2 dram vial equipped with a stirring magnetic bar, followed by a solution of **3ba** (49.8 mg, 0.2 mmol, 1 equiv.) in MeCN (0.7 mL), Na_2CO_3 (4.24 mg, 0.04 mmol, 20 mol-%) and [Mes-Acr]ClO_4 (2.08 mg, 2.5 mol-%). Finally, H_2O (0.3 mL) was added and the vial was sealed with a cap. The yellow solution was irradiated using blue LED's and stirred at room temperature, without any inert atmosphere, until complete conversion was observed (monitored by TLC and/or GC, 22 h). The reaction mixture was concentrated under reduced pressure and the residue was purified by FC (100% Hexane to 90:10 Hexane/EtOAc) to obtain **6** as a colorless oil (36 mg, 0.09 mmol, 45%): (~2:1 dr according to GC-MS); TLC R_f 0.47(90:10 Hexane/EtOAc); IR v 2965, 2926, 1729, 1510, 1494, 1264, 1241, 1175, 1045, 817, 746 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) *(mixture of diastereoisomers)* δ 7.07 (d, J = 8.2 Hz, 2H), 6.85 - 6.82 (m, 4H), 6.78 - 6.76 (m, 2H), 4.25 - 3.87 (m, 6H), 3.11 - 2.85 (m, 1H), 2.28 (s, 3H), 2.21 - 1.93 (m, 2H), 1.88 - 1.74 (m, 1H), 1.60 - 1.55 (m, 2H), 1.41 - 1.30 (m, 2H), 0.94 – 0.77 (m, 3H) ppm; ^{13}C-NMR (101 MHz, $CDCl_3$) *(mixture of diastereoisomers)* δ 175.3, 156.7, 143.24, 143.15, 143.12, 130.20, 130.19, 130.0, 121.7, 121.6, 121.48, 117.52, 117.51, 117.2, 114.53, 114.50, 71.3, 68.1, 67.8, 65.7, 65.6, 64.84, 64.81, 39.0, 38.6, 33.4, 33.2, 32.5, 31.7, 30.7, 20.6, 19.29, 19.28, 13.83,13.80 ppm; GC R_T *Diastereoisomer A:* 24.07 min; *Diastereoisomer B:* 24.50 min LRMS (EI) m/z (%) = *Diastereoisomer A:* 398 (M^+, 10), 325 (13), 291 (30), 236 (15), 235 (100), 149 (12), 147 (10), 135 (26), 125 (10), 121 (17), 108 (10), 107 (11), 101 (10); *Diastereoisomer B:* 398 (M^+, 11), 325 (13), 291 (27), 236 (14), 235 (100), 149 (11), 135 (22), 121 (15); HRMS (EI) *Calcd.* for $C_{24}H_{30}O_5$ 398.2093, found 398.2081.

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[1] For recent reviews, see: a) N. A. Romero, D. A. Nicewicz, *Chem. Rev.*, **2016**, *116*, 10075-10166; b) D. Staveness, I. Bosque; C. R. J. Stephenson, *Acc. Chem. Res.*, **2016**, *49*, 2295–2306; c) J. K. Matsui, S. B. Lang, D. R. Heitz, G. A. Molander, *ACS Catal.* **2017**, *7*, 2563−2575; d) L. M. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* **2018**, *57*, 10034–10072; e) C. R. J. Stephenson, T. P. Yoon, D. W. C. Macmillan, Visible Light Photocatalysis in Organic Chemistry; Wiley: Weinheim, Germany, **2018**.

[2] J. K. Kochi, T. M. Bockman, S. M. Hubig, *J. Org. Chem.* **1997**, *62*, 2210-2221.

[3] Potassium alkyltrifluoroborates have relatively low oxidation potentials and have been employed as radical precursors in many photocatalyst-mediated transformations. For some relevant examples, see: a) Y. Yasu, T. Koike, M. Akita, *Adv. Synth. Catal.* **2012**, *354*, 3414-3420; b) K. Miyazawa, Y. Yasu, T. Koike, M. Akita, *Chem. Commun.* **2013**, *49*, 7249-7251; c) J. C. Tellis, D. N. Primer, G. A. Molander, *Science* **2014**, *345*, 433-436; d) G. A. Molander, *J. Org. Chem.* **2015**, *80*, 7837-7848; e) D. N. Primer, I. Karakaya, J. C. Tellis, G. A. Molander, *J. Am. Chem. Soc.* **2015**, *137*, 2195-2198.

[4] Light-mediated oxidation of alkyl bis(catecholato)-silicates can be carried out using mildly oxidizing photocatalysts to generate alkyl radicals ($E_{1/2}$ = +0.3 to +0.9 V *vs.* SCE). For relevant references, see: a) D. Matsuoka, Y. Nishigaichi, *Chem. Lett.* **2015**, *44*, 163−165; b) V. Corcé, L. M. Chamoreau, E. Derat, J.-P. Goddard, C. Ollivier, L. Fensterbank, *Angew. Chem., Int. Ed.* **2015**, *54*, 11414−11418; c) K. Lin, C. B. Kelly, M. Jouffroy, G. A. Molander, *Org. Synth.* **2017**, *94*, 16-33.

[5] DHPs might undergo photocatalyst-mediated oxidative fragmentation ($E_{1/2}$ = +1.10 V *vs.* SCE), generating alkyl radicals and pyridinium salts. See: J.-P. Cheng, Y. Lu, X.-Q. Zhu, Y. Sun, F. Bi, J. He, *J. Org. Chem.* **2000**, *65*, 3853−3857.

[6] Single-electron reduction of Katritzky pyridinium salts ($E_{1/2}$ = −0.93 V *vs.* SCE) has recently been employed for the generation of alkyl radicals. See: F. J. R. Klauck, M. J. James, F. Glorius, *Angew. Chem., Int. Ed.*, **2017**, *56*, 12336-12339.

[7] For recent reviews, see: a) A. J. J. Straathof, *Chem. Rev.* **2014**, *114*, 1871-1908; b) H. Fu, Y. Jin, *Asian J. Org. Chem*. **2017**, *6*, 368 - 385.

[8] L. Capaldo, L. Buzzetti, D. Merli, M. Fagnoni, D. Ravelli, *J. Org. Chem.* **2016**, *81*, 7102−7109.

[9] For some relevant examples, see: a) D. S. Hamilton, D. A. Nicewicz, *J. Am. Chem. Soc.* **2012**, *134*, 18577−18580; b) A. J. Perkowski, D. A. Nicewicz, *J. Am. Chem. Soc.* **2013**, *135*, 10334−10337; c) M. A. Zeller, M. Riener, D. A. Nicewicz, *Org. Lett.* **2014**, *16*, 4810−4813.

[10] a) D. Hanss, J. C. Freys, G. Bernardinelli, O. S. Wenger, *Eur. J. Inorg. Chem.* **2009**, 4850-4859; b)This photocatalyst can be purchased from Sigma-Aldrich (Product number: 804215) at ≈ 1360 €/ mmol.

[11] Riboflavin can be purchased from TCI-Europe (Product number: R0020) at ≈ 0.27 €/ mmol.

[12] K. S. Conrad, C. C. Manahan, B. R. Crane, *Nat. Chem. Bio.* **2014**, *10*, 801-809.

[13] a) For photophysical properties of riboflavin, see: B. König, S. Kümmel, R. Cibulka, Flavin photocatalysis. In Chemical Photocatalysis: B. König, Ed. De Gruyter: Regensburg, **2013**, p 45-66, and references therein; b) For standard redox potentials of carboxylic acids, see: H. G. Roth, N. A. Romero, D. A. Nicewicz, *Synlett* **2016**, *27*, 714−723.

[14] a) J. B. Metternich, R. Gilmour, *J. Am. Chem. Soc.* **2016**, *138*, 1040−1045; b) T. Morack, J. B. Metternich, R. Gilmour, *Org. Lett.* **2018**, *20*, 1316-1319.

[15] S. Bloom, C. Liu, D. K. Kölmel, J. X. Qiao, Y. Zhang, M. A. Poss, W. R. Ewing, D. W. C. MacMillan, *Nat. Chem.* **2018**, *10*, 205-211.

[16] N. P. Ramirez, B. König, J. C. Gonzalez-Gomez, *Org. Lett*, **2019**, *21*, 1368-1373.

[17] a) G. A. Russell, P. Ngoviwatchai, H. Tashtoush, A. Pla-Dalmau, R. K. Khanna, *J. Am. Chem. Soc.* **1988**, *110*, 3530-3538; b) Y. Amaoka, M. Nagatomo, M. Watanabe, K. Tao, S. Kamijo, M. Inoue, *Chem. Sci.* **2014**, *5*, 4339-4345; c) A. Noble, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2014**, *136*, 11602-11605; d) Reference 4b.

[18] For precedents in the radical addition to 2-(phenylsulfonyl)benzothiazole, see: a) D. B. Jacobson, B. S. Freiser, *J. Am. Chem. Soc.* **1984**, *106*, 4623-4624; b) Y. Ikeda, R. Ueno, Y. Akai, E. Shirakawa, *Chem.Commun.*, **2018**, *54*, 10471-10474.

[19] For a recent review: A. Rouf, C. Tanyeli, *Eur. J. Med. Chem*. **2015**, *97*, 911-927.

[20] C. Hu, Y. Chen, *Org. Chem. Front.*, **2015**, *2*, 1352-1355.

[21] L. Cui, H. Chen, C. Liu, C. Li, *Org. Lett*., **2016**, *18*, 2188-2191.

[22] Y. Duan, M. Zhang, R. Ruzi, Z. Wu, C. Zhu, *Org. Chem. Front.*, **2017**, *4*, 525-528. This photocatalyst can be purchased from Strem Chemicals (Product number: 77-0465) at ≈ 582€/ mmol. The reaction is limited to *N*-arylglycine most likely due to the poor oxidation power of this photocatalyst [$E_{1/2}$ ($^*Ir^{III}/Ir^{II}$) = +0.81 V *vs* SCE].

[23] RFTA was obtained in one step by acetylation of RF, according to a reported procedure: R. A. Larson, P.L. Stackhouse, T.O. Crowley, *Environ. Sci. Technol.* **1992**, *26*, 1792-1798.

[24] C. K. Remucal, K. McNeill, *Environ. Sci. Technol.* **2011**, *45*, 5230–5237.

[25] It is reported that electron transfer between ^{3}RFTA* and its ground state can generate the corresponding oxidized and reduced radicals (D-D reaction); see: P. F. Heelis, *Chem. Soc. Rev.* **1982**, *11*, 15-39. We acknowledge to one of the reviewers for this suggestion. The [RFTA]$^{\bullet-}$ is also regenerated after the PET between the ^{3}RFTA* and the carboxylate.

[26] a) For the pKa value of RFlH/RFl$^{\bullet}$, see: A. Enrenberg, F. Müller, P. Hemmerich, *Eur. J. Biochem.*, **1967**, *2*, 286-293; b) For a recent characterization of RFTA where deprotonation of carboxylic acids is proposed by the corresponding radical anion, see: M. März, M. Kohout, T. Neveselý, J. Chudoba, D. Prukata, S. Nizinski, M. Sikorski, G. Burdzinski, R. Cibulka, *Org. Biomol. Chem.,* **2018**, *16*, 6809-6817.

[27] B. Persson, *Acta Chem. Scand.* **1977**, *31B*, 88-89.

[28] Values from –0.80 V to –0.45 V have been reported, to be dependent on the solvents. See: R. Martinez-Haya, M. A. Miranda, M. L. Marin, *Eur. J. Org. Chem.* **2017**, 2164–2169, and references therein.

[29] The radical generated is stabilized by orbital interactions with both axial ring oxygen lone pair and adjacent σ* C-O bond (anomeric effect), and reacts from the less hindered convex face. For precedents, see: a) S. Ventre, F. R. Petronijevic, D. W. C. MacMillan, *J. Am. Chem. Soc.* **2015**, *137*, 5654−5657; b) X. Zhou, P. Wang, L. Zhang, P. Chen, M. Ma, N. Song, S. Ren, M. Li, *J. Org. Chem.* **2018**, *83*, 588−603.

[30] Since the reaction mixture is homogeneous during all the process, a possible solution to scale up the reaction would be to use a flow reactor, where the illuminated area-to-reaction volume ratio is maximized. For some recent examples, see: a) J. W. Beatty, J. J. Douglas, R. Miller, R. C. McAtee, K. P. Cole, C. R. J. Stephenson, *Chem.* **2016**, *1*, 456–472; b) H. Seo, M. H. Katcher, T. F. Jamison, *Nat. Chem.* **2017**, *9*, 453-456; c) F. Lima, L. Grunenberg, H. B. A. Rahman, R. Labes, J. Sedelmeierb, S. V. Ley, *Chem. Commun.*, **2018**, *54*, 5606-5609; d) J. C. Gonzalez-Gomez, N. P. Ramirez, T. Lana-Villarreal, P. Bonete, *Org. Biomol. Chem.* **2017**, *15*, 9680-9684.

[31] N. P. Ramirez, J. C. Gonzalez-Gomez, *Eur. J. Org. Chem.* **2017**, 2154-2163.

[32] Details can be found in the supporting information file. For a comprehensive discussion of this issue, see: M. A. Cismesia, T. P. Yoon, *Chem. Sci*. **2015**, *6*, 5426-5434.

[33] For a recent photocatalytic procedure for the decarboxylative C2-alkylation of benzothiazoles with carboxylic acids, see: B. Wang, P. Li, T. Miao, L. Zou, L. Wang, *Org. Biomol. Chem.* **2019**, *17*, 115-122.

[34] The incident light intensity on the reactor was measured using an optical power meter (Thorlabs PM100D) equipped with a thermopile sensor (Thorlabs model S310C).

[35] Prepared according: E. J. Corey, S. Barcza, G. Klotmann, *J. Am. Chem. Soc.* **1969**, *91*, 4782 - 4786.

[36] Prepared according to: Sharma, K. K.; Sharma, S.; Kudwal, A.; Jain, R. *Org. Biomol. Chem.* **2015**, *13*, 4637 – 4641.

[37] N. N. Bhuvan Kumar, O. A. Mukhina, A. G. Kutateladze, *J. Am. Chem. Soc.* **2013**, *135*, 9608 – 9611.

[38] The aryl sulfone was only dissolved after few minutes of irradiation.

[39] W. - M. Zao, X. -L. Chen, J. - W. Yuan, L. - B. Qu, L. - K. Duan, Y. - F. Zhao, *Chem. Commun.* **2014**, *50*, 2018 - 2020.

[40] M. Eh, *Synthesis* **2003**, *3*, 365 - 370.

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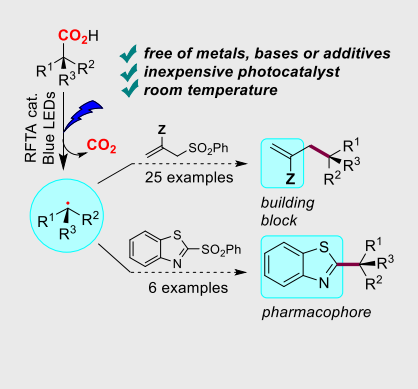
Entry for the Table of Contents

FULL PAPER

The direct decarboxylative allylation of carboxylic acids with allylsulfones can be efficiently promoted at room temperature by visible light using inexpensive RFTA as photocatalyst in the absence of base. Under similar conditions, some carboxylic acids can be successfully used in the decarboxylative homolytic aromatic substitution of 2-(phenylsulfonyl)benzothiazole.



*Riboflavin photocatalysis

Synthetic Methods*

Nieves P. Ramirez, Teresa Lana-Villarreal, Jose C. Gonzalez-Gomez

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Direct decarboxylative allylation and arylation of aliphatic carboxylic acids using flavin mediated photoredox catalysis