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FULL PAPER

Direct Stereoselective β-Arylation of Enol Ethers by Decarboxylative Heck-type Reaction

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Abstract: Despite remarkable advances to promote regio- and stereoselective decarboxylative arylation of unactivated olefins with benzoic acid derivatives, methodologies involving hetero-substituted alkenes are still lacking. Herein, $Pd^{(II)}$-catalyzed decarboxylative Heck coupling of α-alkoxyacrylates with (hetero)aryl carboxylic acids for the stereocontrolled production of (*Z*)-β-heteroarylated vinyl ethers is reported. This methodology offers a rational and step-economical route to the synthesis of attractive β-arylated α-alkoxy α,β-unsaturated carboxylates family which emerged as a relevant class of building blocks with different applications. Mechanistically, whereas electron rich benzoic acids undergo a $Pd^{(II)}$-catalyzed decarboxylation, electron-deficient substrates proceed through silver(I)-mediated decarboxylation, explaining thus the formation of stereoisomers (*E*) and (*Z*) of β-arylated vinyl ethers in presence of these latter.

Introduction

Palladium-catalyzed Heck reaction of aryl halides with olefins has been regarded as one of the most powerful method for the formation of C-C bonds in organic synthesis.[1, 2] Its fundamental importance in synthetic organic chemistry has given a great impetus to the development of new versions of the Heck coupling, in which the electrophilic aryl halide is replaced by distinct substrates. Inexpensive, stable, easy to handle and to store, and readily available carboxylic acids are now identified as reliable masked organometallic building blocks in the development of innovative transition-metal catalyzed decarboxylative cross-coupling reactions for the construction of various $C(sp^2)$-C[3] and $C(sp^2)$-heteroatom bonds.[4-6] In 2002, Myers and co-workers have reported the first $Pd^{(II)}$-catalyzed decarboxylative Heck reaction of *ortho*-substituted arylcarboxylic acids with α,β-unsaturated carbonyls and styrenes.[7] While remarkable advances have been made to promote regio- and stereoselective decarboxylative arylation of unactivated olefins with aryl carboxylic acids,[8] few examples have been reported using hetero-substituted alkenes.[9]

Among classes of hetero-substituted alkenes, vinyl ethers represent one of the most reactive and valuable building blocks for the synthesis of complex organic molecules. These electron-rich alkenes are found in many natural products and biologically active molecules. Employed as masked-ketones and activated alkenes, vinyl ethers are involved in number of chemical transformations such as hydrolysis, reduction, cycloaddition reactions, Heck and related cross-coupling reactions to produce poly-functionalized ketones, alcohols, heterocycles and alkenes.[9-10] To date, Heck coupling of non-prefunctionalized vinyl ethers with halides is the most step-economical developed strategy (Eq 1, Figure 1),[11-12] but fraught with difficulties due to selectivity issues (α/β and *Z*/*E*).[12] In consequence, traditional cross-coupling reactions are preferred for a full control of the regio- and the stereochemistry when pre-metalated vinyl ethers are available (Eq 2).[10, 13]

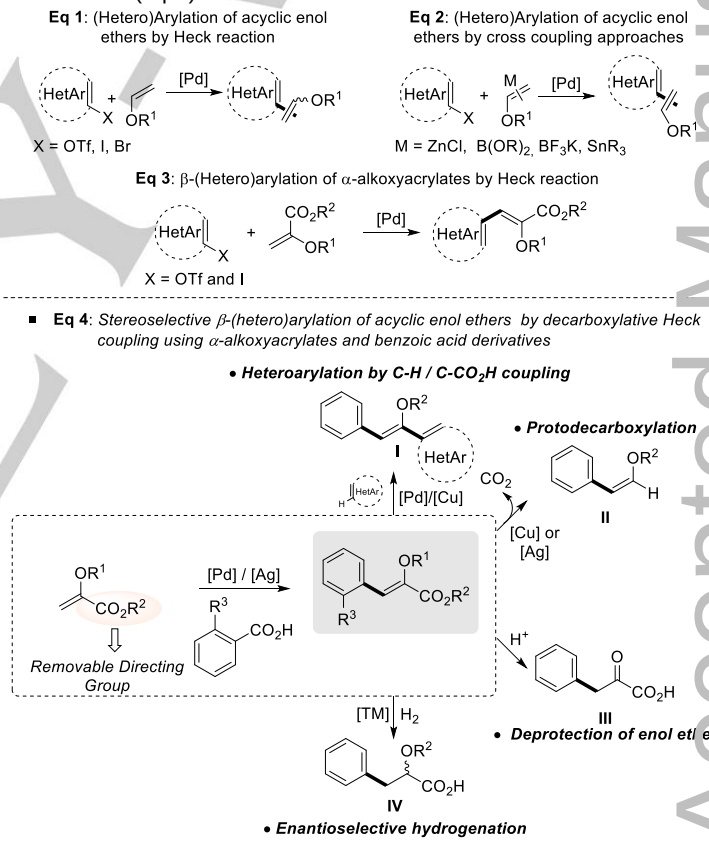


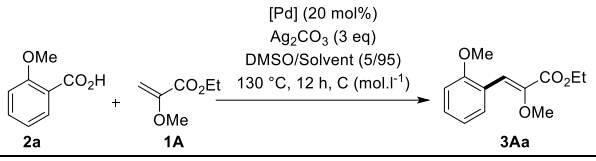
Figure 1: Pd-catalyzed arylation of enol ethers. [TM] = transition metal.

In this context, α-alkoxyacrylate derivatives have been selected as coupling partners of choice to address important challenges in the (hetero)arylation of enol ethers: (1) to control the selectivity in the Heck coupling (Eq 3),[14] and (2) to give access to several synthetically-challenging building blocks. Indeed, our group has recently reported the first regio- and stereocontrolled formation of α-heteroarylated enol ethers **I** by Pd-catalyzed decarboxylative C-H coupling of α-alkoxyacrylic acid derivatives, as well as the

synthesis of (*Z*)-β-arylated enol ethers **II** by copper mediated protodecarboxylation reactions.[15] Herein, Pd(II)-catalyzed decarboxylative Heck coupling of α-alkoxyacrylates with (hetero)aryl carboxylic acids for the stereocontrolled production of (*Z*)-β-heteroarylated vinyl ethers is reported (Figure 1, Eq 4). This methodology offers a rational and step-economical route to attractive β-arylated α-alkoxy α,β-unsaturated carboxylates. These latter are important precursors of α–keto esters **III**[16] and optically active α-oxo-functionalized carboxylic acids **IV** which are known to be valuable buildings blocks in pharmaceutical and agrochemical industries, as well as in total synthesis (Figure 1).[17]

Results and Discussion

Table 1. Optimization of the palladium-catalyzed decarboxylative Heck reaction with ethyl 2-methoxyacrylate **1A**

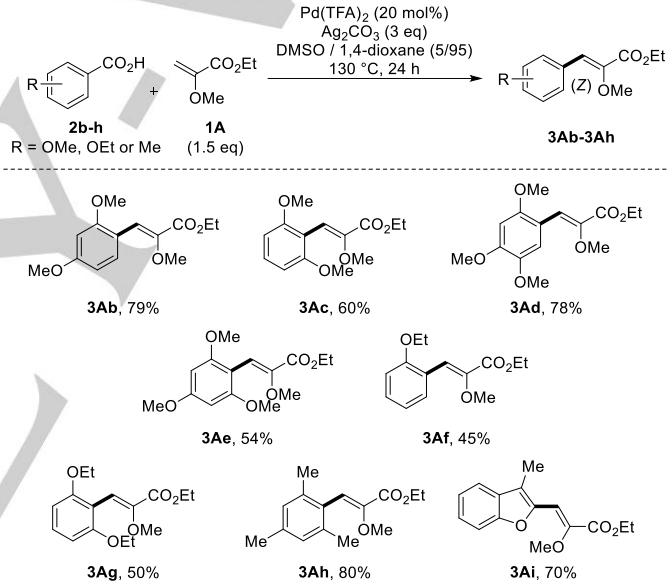


2a **1A** **3Aa**

Entry	[Pd]	Solvent	C (mol.L^{-1})	Yield (%)[b]
1	$Pd(TFA)_2$	DMF	0.2	23
2	$Pd(TFA)_2$	DMAc	0.2	10
3	$Pd(TFA)_2$	DMSO	0.2	21
4	$Pd(TFA)_2$	1,4-dioxane	0.2	49
5	$PdCl_2$	1,4-dioxane	0.2	42
6	$Pd(OAc)_2$	1,4-dioxane	0.2	35
7	$Pd(acac)_2$	1,4-dioxane	0.2	21
8[c]	$Pd(TFA)_2$	1,4-dioxane	0.2	27
9	$Pd(TFA)_2$	1,4-dioxane	0.4	40
10	$Pd(TFA)_2$	1,4-dioxane	0.08	61
11[d]	$Pd(TFA)_2$	1,4-dioxane	0.08	82

[a] Conditions: **2a** (1.0 equiv), **1A** (1.5 equiv), [Pd] (20 mol%), Ag_2CO_3 (3 equiv), Solvent, 130 °C, 12 h, C (mol.L^{-1}). [b] Yield of the isolated product. [c] Reaction carried out at 140 °C. [d] Reaction performed for 24 h.

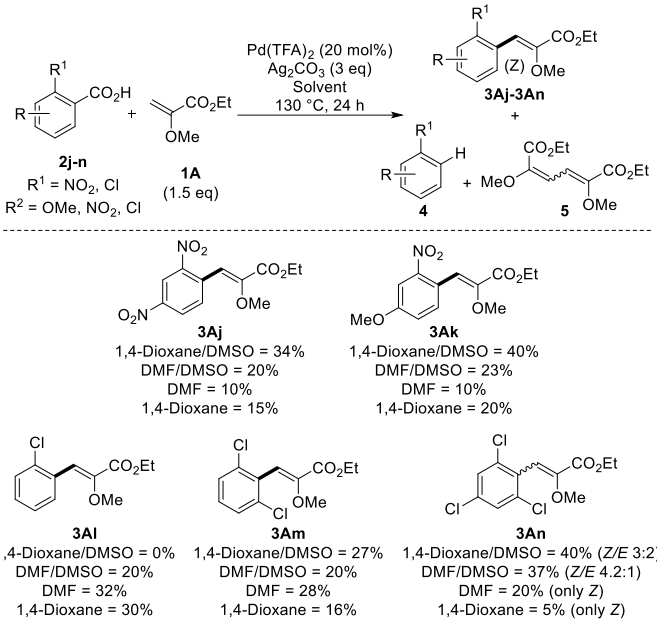
Our investigation about the β-arylation of ethyl 2-methoxyacrylate **1A**[18] by Pd-catalyzed decarboxylative Heck-type coupling was initiated with 2-methoxybenzoic acid **2a**. Choice of the coupling partner **2a** was driven by the steric hindrance and the electronic nature of the *ortho*-methoxy substituent, two factors which are known to facilitate the decarboxylative step.[19] Under the Myers's experimental conditions, the β-arylated 2-methoxyacrylate **3Aa** was immediately isolated in 23% yield in presence of $Pd(TFA)_2$ as catalyst and Ag_2CO_3 as additive in DMF (Table 1, Entry 1).[8a] In contrast to 1,4-dioxane/DMSO (95:5) system, the use of more polar solvents, such as DMF/DMSO, DMAc/DMSO or pure DMSO affected the efficiency of this coupling (Entries 2-4).[20] Other palladium sources such as $PdCl_2$, $Pd(OAc)_2$ and $Pd(acac)_2$ have been tested and gave lower yields, in accordance with previous Myers and Liu observations,[8b and 8d] highlighting the key role of $Pd(TFA)_2$ in the decarboxylative step (Entries 5-7). A further investigation of various oxidants revealed that Ag_2CO_3 remains the best for this transformation.[20] We also noticed that 3 equivalents of Ag_2CO_3 as well as sub-stoichiometric amounts (1.5 equivalents) of ethyl 2-methoxyacrylate **1A** are required to get an efficient $Pd^{(II)}$-catalyzed decarboxylative Heck reaction.[20] To get complete conversion of 2-methoxybenzoic acid **2a**, several parameters have been screened such as the temperature, the concentration and the reaction time (Entries 8-11). Although the increase of temperature and concentration of the media are deleterious (Entries 8-9), the decrease of this latter from 0.2 M to 0.08 M led to a better production of ethyl β-arylated 2-methoxyacrylate **3Aa** from 49% to 61% (Entry 9). Finally, extension of the reaction time from 12 h to 24 h allowed to reach a complete conversion of coupling partner **2a** with an excellent isolated yield of 82% in **3Aa** (Entry 11). Importantly, only the stereoisomer (Z) was observed and its configuration was confirmed by comparison with literature data.[17d].



Scheme 1. Substrate scope with electron-rich carboxylic acids.

With these optimized conditions in hands, the scope of the decarboxylative Heck coupling was undertaken on ethyl 2-methoxyacrylate **1A** with a panel of electron-rich benzoic acids. As shown in Scheme 1, a variety of substituted 2-alkoxybenzoic acids **2a, 2d** and **2f** displayed a good reactivity providing β-arylated 2-methoxyacrylates **3Ab, 3Ad** and **3Af** as pure (*Z*)-isomers in medium to good yields. Interestingly, β-arylated *o,o'*-dialkoxy-products **3Ac**, **3Ae** and **3Ag** were produced with slightly lower yields than the corresponding *ortho*-monosubstituted products. These results showed that the high steric hindrance associated with the high palladium-oxygen coordination reduce the effectiveness of the decarboxylative Heck coupling. In the same manner, the 2,4,6-trimethylbenzoic acid **2h** turned out to be a more effective substrate than the 2,4,6-trimethoxybenzoic acid, leading to the ethyl β-arylated 2-methoxyacrylate **3Ah** in 80% yield. To our delight, this methodology was also suitable when

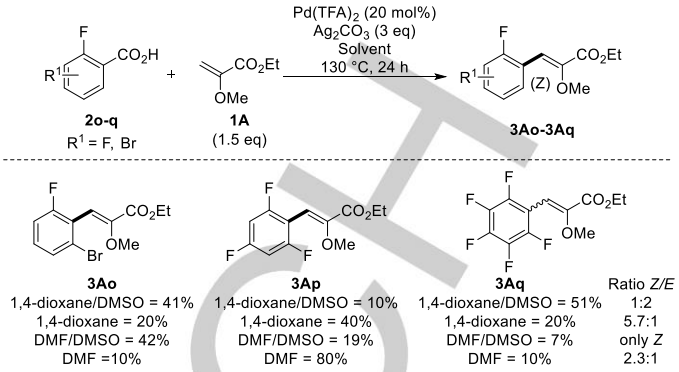
using 3-methyl benzofuran-2-carboxylic acid **2i** as coupling partner**,** giving the desired Heck coupling product **3Ai** in 70% yield.



Scheme 2. Substrate scope with electron-poor carboxylic acids.

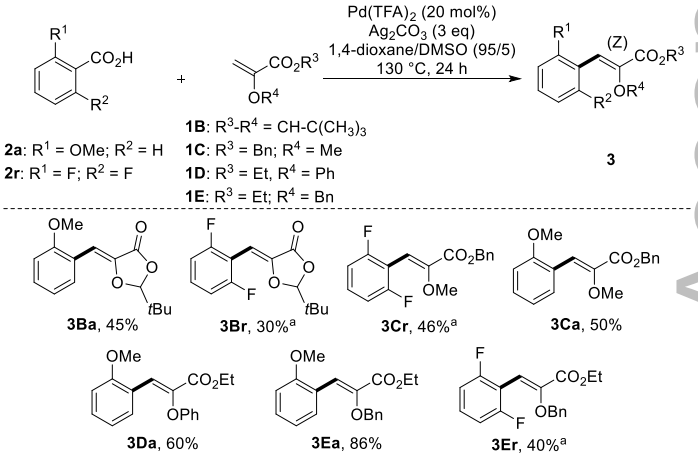
Next, we turned our attention to the evaluation of electron-poor nitrated and chlorinated benzoic acids **2j-n** as coupling partners under our optimized reaction conditions (Scheme 2). Globally, we first noticed significant lower yields (40-28%) compared with electron-rich benzoic acids, whatever the solvent mixture is (1,4-dioxane/DMSO, DMF/DMSO or in the absence of DMSO). This loss of efficiency results from the production of two side products **4** and **5** generated by silver mediated protodecarboxylation reaction and homocoupling reaction (Scheme 2). It is noteworthy that the use of 1,4-dioxane alone affected the performance of this process, thus pointing out the key role of highly polar solvent or co-solvent as DMF or DMSO for this transformation. [21] Moreover, all β-arylated 2-methoxyacrylates **3Aj-m** are obtained as pure (*Z*)-isomers, excepted for the coupling between 2,3,4-trichlorobenzoic acid **2n** and **1A.** Indeed**,** the ethyl β-arylated 2-methoxyacrylate **3An** is provided as a (*Z*/*E*)-isomers mixture (ratio 3:2) suggesting the involvement of a competitive mechanism. While a better ratio in favor of (Z)-isomer (ratio *Z*/*E* 4.2:1) was observed in DMSO/DMF mixture (5:95), the production of **3An** as pure (Z)-isomer was achieved in pure DMF albeit in 20% poor yield.

Fluorinated arenes are an important class of molecules that are widely used in pharmaceuticals, agrochemicals, functional materials such as liquid crystals (LCs), organic light-emitting diodes (OLED), and electron transport materials owing to the unique property of the fluoride group.[22] Therefore, efficient and selective methods for the facile introduction of fluorinated moiety into organic backbone have become a fascinating field of research in the last year,[8l] and transition metal catalysis has been successfully employed for this purpose.[23] However, the selective construction of mono- or polyfluoroarylated vinyl ethers remains unstudied to date.

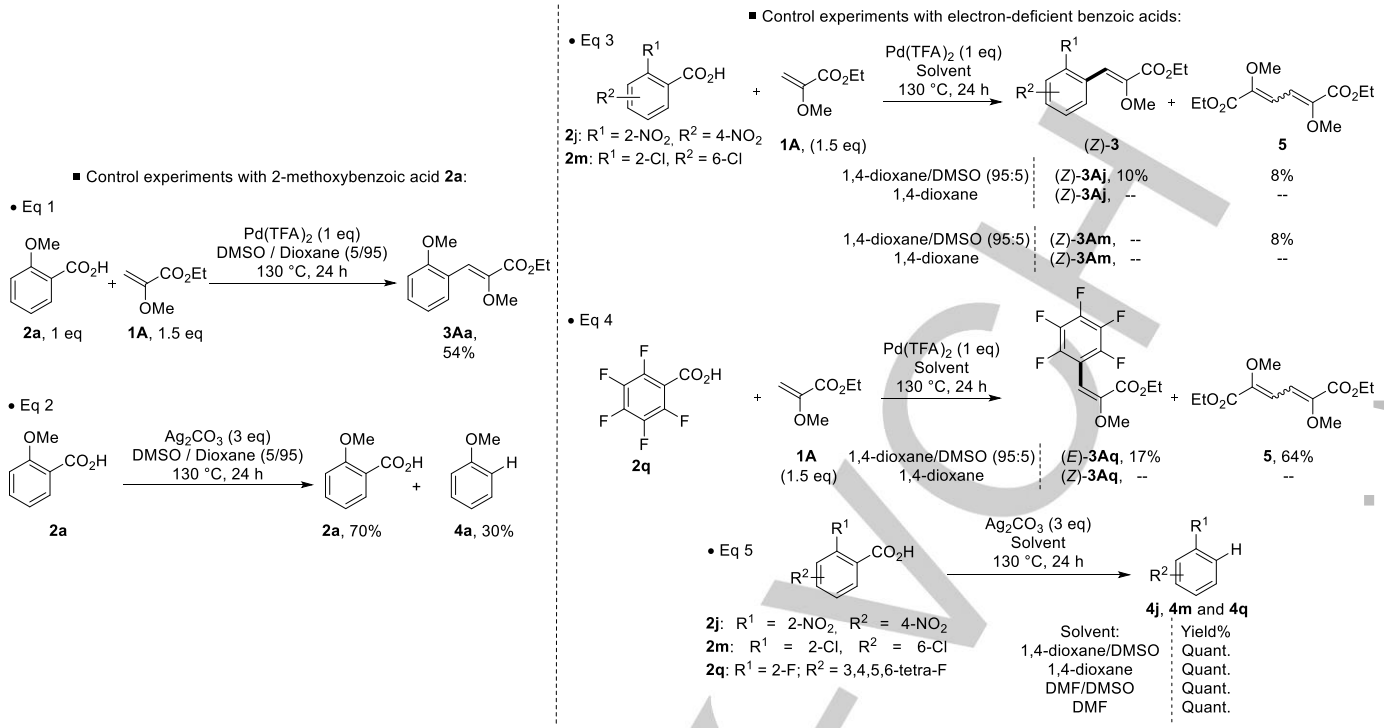


Scheme 3. Substrate scope with fluorinated benzoic acid derivatives.

In this context, the decarboxylative Heck-coupling of ethyl 2-methoxyacrylate **1A** with fluorinated benzoic acids **2o**-**q** was performed under the optimized reaction conditions (Scheme 3). 6-Bromo-2-fluorobenzoic acid **2o** was first employed and only isomer *Z*-**3Ao** was formed in 41% or 42% depending on the nature of the solvent mixture, 1,4-dioxane/DMSO or DMF/DMSO respectively. Unlike the result obtained with **2o**, DMSO as additive affected dramatically the coupling efficiency in presence of the more electron-deficient 2,4,6-trifluorobenzoic acid **2p.** Indeed, we observed that the reaction performed in pure 1,4-dioxane or DMF as solvent gave the isomer *Z*-**3Ap** in moderate 40% to good 80% yields respectively. The most electron-deficient pentafluorobenzoic acid **2q** was then engaged in the decarboxylative Heck-type coupling with **1A**. We were pleased to find that the ethyl pentafluoroarylated 2-methoxyacrylate **3Aq** was produced in 51% yield as a mixture of isomers *Z*-**3Aq** and *E*-**3Aq** with the (*E*)-isomer as the major one (ratio *Z*/*E* 1:2). It is noteworthy that the (Z)-**3Aq** isomer can be mainly produced in 1,4-dioxane as solvent (ratio *Z*/*E* 5.7:1) but with a dramatic fall of yield (20%). Finally, reactions performed in all others solvents proved to be ineffective.

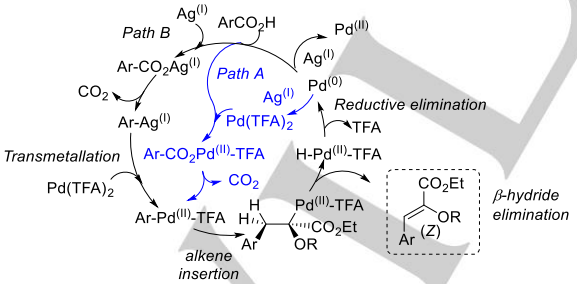


Scheme 4. Substrate scope with various α-alkoxyacrylates **1** and carboxylic acids **2a** and **2r**. [a]DMF/DMSO (95/5) was used.



Scheme 5. Control experiments with ethyl 2-methoxybenzoic acid and various electron-deficient benzoic acids.

To further examine the versatility of the methodology, the decarboxylative Heck-coupling of various α-alkoxy α,β-unsaturated carboxylates **1B-E** and *ortho*-substituted benzoic acids **2** was next achieved (Scheme 4). We were pleased to observe the stereocontrolled formation of desired (*Z*)-β-arylated products **3Ba** and **3Br** in moderate yields from 1,3-dioxolan-4-one **1B** with electron-rich and electron–deficient benzoic acids **2a** and **2r**. The benzyl α-methoxyacrylate **1C** as well as ethyl α-phenoxy- and α-benzyloxyacrylates **1D-E** have proved to be efficient coupling partners leading to a library of various (*Z*)-β-arylated acrylates **3Ca, 3Cn, 3Da, 3Ea** and **3En** in fair to good yields by using either electron-rich **2a** or electron-poor benzoic acid **2r**.

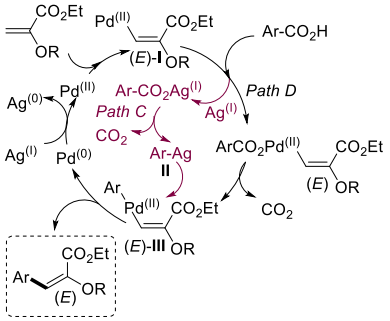


Scheme 6. Plausible mechanisms for the decarboxylative Heck-coupling of α-methoxyacrylates with electron-rich (path A) and electron-poor (path B) benzoic acids leading to (*Z*)-β-arylated α-alkoxyacrylates.

To date, the respective role of $Pd(TFA)_2$ and Ag_2CO_3 in the Heck decarboxylative process with electron-rich benzoic acids has been experimentally and theoretically well investigated by Myers and Liu.[8b and 8d] Notably, it has been well established that the decarboxylation step occurs in the presence of palladium salt whereas Ag_2CO_3 acts as an oxidant for catalytic turnover. In order to confirm or invalidate this mechanism pathway for the β-arylation of ethyl 2-methoxyacrylate (**1a**) with electron-rich benzoic acids, control experiment with a stoichiometric amount of palladium in absence of Ag_2CO_3 has been performed (Scheme 5, eq 1). We noticed that stoichiometric amounts of $Pd(TFA)_2$ enabled the reaction of ethyl 2-methoxyacrylate **1a** with 2-methoxybenzoic acid **2a** in 1,4-dioxane/DMSO (95:5) mixture at 130 °C to generate the desired product **3Aa** in 54% yield. Additionally, a reaction was carried out with 2-methoxybenzoic acid **1a** using an excess of Ag_2CO_3 and in absence of $Pd(TFA)_2$ (Scheme 5, Eq 2). ^1H NMR analysis of the crude product showed a 7:3 ratio between the protonated product **4a** and the acid **1a**. Therefore, these results prove that the mechanistic hypothesis involving a palladium monocatalysis described by Myers[8b] is most likely happening in the presence of electron-rich benzoic acids (Scheme 6, path A).

However, based on works of Su[24] and Jana,[8l] a competitive process involving a Pd/Ag, bimetallic system can be envisaged with electron-deficient substrates for the formation of stereoisomers (*Z*), where the decarboxylation step is now mediated by silver(I) carbonate generating a arylpalladium species after transmetallation with $Pd(OAc)_2$ as depicted in path B, Scheme 6. Additional experimental controls using stoichiometric amount of $Pd(OAc)_2$ and silver(I)-mediated protodecarboxylation reactions were thus carried out from several electron-deficient benzoic acids (Scheme 5). The poor reactivity in absence of silver (I) salt as additive for decarboxylative Heck couplings (Eq 3 and 4), as well as the quantitative production of protonated arenes **4** from Ag(I)-mediated protodecarboxylation reactions, whatever the selected solvent is (Eq 5),[25] highlighted the predominant role of Ag_2CO_3 in the decarboxylation-metalation step. Therefore, all the above results converge to the mechanistic path B for which the $Pd(TFA)_2$-catalyzed decarboxylative step is

energetically higher than the Ag_2CO_3 mediated one due to the poor stabilization of the resulting positive charge produced during the *ipso*-decarboxylative transition state.



Scheme 7. Plausible mechanisms for the decarboxylative Heck-coupling of α-methoxy acrylates with electron-poor benzoic acids leading to (*E*)-β-arylated α-alkoxy acrylates.

By contrast, the production of β-arylated α-methoxyacrylates as (*E*)-isomer and enol ether homocoupling product **5** might be explained by a competitive mechanism to the Ag_2CO_3-mediated decarboxylative step. This competitive mechanism might involve an *ortho*-directed electrophilic palladation[26] of the enol ether in the presence of electron-poor benzoic acids. Two mechanistic pathways C and D can be considered for the formation of the intermediate (*E*)-**III** which provides the β-arylated (*E*)-isomer by reductive elimination (Scheme 7). Thus, the (*E*)-methoxyacrylate-palladium intermediate (**I**)[27] issued from the heteroatom-guided electrophilic palladation pathway[26] can undergo either (1) a transmetallation step with σ-arylsilver(I) species (**II**) arising from Ag_2CO_3-mediated decarboxylative-metalation step (Scheme 7, path C), or (2) a decarboxylation step to provide the intermediate (*E*)-**III** (Scheme 7, path D). This latter pathway can be envisaged because the stereoisomer (*E*)-**3Aq** is obtained during the decarboxylation/olefination coupling between the pentafluorobenzoic acid **2q** and the 2-methoxyacrylate **1A** in absence of Ag_2CO_3 but with stoichiometric amount of palladium. (Scheme 5, Eq 4).

Conclusion

In summary, we have developed the regio- and stereocontrolled synthesis of (*Z*)-β-(hetero)arylated vinyl ether *via* stereoselective decarboxylative Heck-type coupling of various 2-alkoxyacrylates under palladium catalysis using a variety of arene carboxylic acids as electrophiles. This methodology offers a rational and step-economical route to the synthesis of attractive β-arylated α-alkoxy α,β-unsaturated carboxylates family which emerged as a relevant class of building blocks with different applications. A noticeable difference has been observed between electron-rich and electron-deficient acids in terms of efficiency and stereochemistry. This substrate dependence is due to mechanistic divergences during the decarboxylation step. Whereas the mechanism pathway described by Myers is most likely happening with electron-rich benzoic acids (Scheme 7, Path A), the non-stabilization of the positive charge produced during the palladium-catalyzed *ipso*-decarboxylation transition state in presence of electron-deficient acids favors a competitive process involving an Ag_2CO_3-mediated decarboxylation. From this hypothesis, three mechanistic pathways have been speculated explaining the formation of stereoisomers (*E*) and (*Z*) in presence of electron-deficient benzoic acids (Schemes 6 and 7, Path B-D).

Experimental Section

General information: Solvents and reagents: All commercially available reagents were used as received, except otherwise specified. Palladium catalyst and phosphine ligands were stored in desiccators. Extra dry DMAc, 1,4-dioxane, DMF and DMSO were obtained from Accros Organic® in sealed bottles over 3Å or 4Å molecular sieves and stored under N_2. Purification: Chromatography columns were performed using silica gel (mesh size 60-80 mesh). TLC were performed using Merck® TLC silica gel 60 F_{254} and product revealed by UV irradiation (λ = 254 nm). Analysis: ^1H and ^{13}C NMR spectra were recorded at room temperature on a Brucker Advance spectrometer operating at 300 MHz and 75 MHz respectively. Chemical shifts (δ) are given as ppm relative to the residual solvent peak (7.26 for ^1H and 77.16 for ^{13}C in $CDCl_3$). Splitting patterns are indicating as fellow: br: broad; s: singulet; d: doublet; t: triplet; q: quartet; qt: quintuplet; sp: septuplet; dd: doublet of doublet; dt: doublet of triplet; tt: triplet of triplet; qt: quintuplet; m: multiplet. IR spectra recorded on Perkin Elmer Spectrum 100 FT IR spectrometers. Melting Point were measured on a Fisher Scientific hot stage melting point apparatus and are uncorrected. GC/MS analysis (EI, 70 Ev) were performed on the Agilent GC: 6850, MS: 5975 using HP-5MS column (30 m x 0.25 mm x 0.25 µm) with the following method: 50 °C (2 min) to 250 °C (15 min) with an increase of 25 °C.min^{-1}. Mass analysis (ESI) were performed on a LCQ Advantage. Ethyl 2-methoxyacrylate **1A**[18], 2-(1,1-dimethylethyl)-5-methylene-1,3-dioxolan-4-one **1B**[28] are synthetized according to the literature.

Synthesis of Cesium 2-methoxyacrylate 6, and 2-alkoxyacrylate derivatives 1C, 1D and 1E:

Cesium 2-methoxyacrylate 6: To a solution of cesium hydroxide monohydrate (16.8 mmol, 2.8 g,) in 11 mL of propan-2-ol and 15 mL of water was added in portion (very exothermic) ethyl 2-methoxyacrylate **1A** (15.3 mml, 2 g). The mixture was heated at reflux overnight and the solvent was evaporated to dryness under reduced pressure. The crude product was then triturated in cold propan-2-ol and filtered to give the cesium salt **6**. The solid was then washed with methanol and Et_2O to afford the product **6** (3.16 g, 13.5 mmol) in 80% yield as a white solid. mp = 155-157 °C (pentane). IR: 3445, 2972, 1728, 1156, 1094, 857 cm^{-1}. ^1H NMR (300 MHz, D_2O) δ 5.05 (d, *J* = 2.0 Hz, 1H), 4.53 (d, *J* = 1.9 Hz, 1H), 3.57 (s, 3H). ^{13}C NMR (75 MHz, D_2O) δ 170.77 (C), 156.07 (C), 90.31 (CH), 55.05 (CH_3). MS (ESI-TOF) *m/z* 101.02 [M-H$^+$].

Benzyl 2-methoxyacrylate 1C: To the solution of cesium salt **6** (1 eq, 4.29 mmol, 1 g) in 10 mL of anhydrous 1,4-dioxane was added HBTU (1.5 eq, 6.375 mmol, 2.4 g) and *N*,*N*-diisopropylethylamine (1.5 eq, 6.375 mmol, 1ml). The solution was then stirred for 5 min at r.t. To this mixture was added benzyl alcohol (1.1 eq, 4.675 mmol, 0.5 ml) and 4-dimethylaminopyridine (0.1 eq, 0.425 mmol, 52 mg), and the solution was then stirred at r.t. overnight. Solvents were removed under reduced pressure. The crude product was purified by flash chromatography (PE/Et_2O 8:2) to afford **1C** (500 mg, 2.635 mmol) in 62% as a yellow oil. IR: 3063, 2954, 2850, 1680, 1550, 1489, 1165, 750, 682 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (m, 5H), 5.39 (s, 1H), 5.26 (s, 2H), 4.65 (s, 1H), 3.66 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 145.5 (C), 136.1 (C), 128.7 (2xCH), 128.3 (2xCH), 118.0 (CH), 103,5 (2xCH), 66.8 (CH_2), 59.4 (CH_3). MS (ESI-TOF) m/z 193.07 [M+H$^+$]. HMRS (EI-TOF): calc. for $C_{11}H_{12}O_3$; 192.0786 found 192.0795.

Ethyl 2-phenoxyacrylate 1D: A suspension of ethyl 2-phenoxy-2-diethylphosphonoacetate[29] (200 mg, 0.632 mmol) and DBU (120 µL, 1.58

mmol) in anhydrous THF (6 mL) was stirred for 10 minutes at rt. To this mixture was added paraformaldehyde (28.46 mg, 0.95 mmol) and heated at reflux overnight. The solvent was then removed under reduced pressure, and the crude residue was dissolved in EtOAc. The organic layer was washed with saturated aqueous NH_4Cl solution, brine, dried over $MgSO_4$ and filtered. and washed with saturated aqueous NH_4Cl solution and brine. Solvents were removed under reduced pressure to give **1D** in quantitative yield as a colorless oil. IR: 2983, 1730, 1623, 1592, 1490, 1094 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 2H), 5.70 (d, *J* = 1.8 Hz, 1H), 4.90 (d, *J* = 1.8 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 155.3 (C) 150.6 (C), 129.6 (2xCH), 124.0 (CH), 119.0 (2xCH), 104.0 (2xCH), 61.7 (CH_2), 14.1 (CH_3). MS (ESI-TOF) *m/z* 193.15 [M+H$^+$]. HMRS (EI-TOF): calc. for $C_{11}H_{12}O_3$; 192.0786: found 192.0792.

Ethyl 2-(benzyloxy)acrylate 1E: A suspension of ethyl 2-benzyloxy-2-diethylphosphonoacetate[29-30] (200 mg, 0.6 mmol) and DBU (0.2 mL, 1.5 mmol) in THF (6 mL) was stirred for 10 minutes at rt. To this mixture was added paraformaldehyde (27 mg, 0.9 mmol) and heated at reflux overnight. The solvent was then removed under reduced pressure, and the crude residue was dissolved in EtOAc. The organic layer was washed with saturated aqueous NH_4Cl solution, brine, dried over $MgSO_4$ and filtered. Solvents were removed under reduced pressure to give **1E** in quantitative yield as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$) δ 7.4 (m, 5H), 5.35 (d, *J* = 2.0 Hz, 1H), 4.85 (s, 2H), 4.62 (d, *J* = 2 Hz, 1H), 4.23 (q, *J* = 7.1 Hz 2H), 1.32 (t, *J* = 7.1 Hz, 3H). Exhibited spectra data identical to previous reports.[31]

General procedure A for the decarboxylative Heck coupling: To an oven-dried sealed tube containing a magnetic stir bar were added α-alkoxyacrylates **1A–H** (1.5 eq), benzoic acid derivatives **2a–g** (1 eq), $PdTFA_2$ (20 mol%), and Ag_2CO_3 (3 eq). After purging the reaction vessel with nitrogen, anhydrous 1,4-dioxane (2.3 mL) and DMSO (0.1 mL) was added to the reaction mixture and the vessel was sealed with a screw cap. The reaction mixture was heated at 130 °C for 24 hours. After completion (as detected by TLC), the reaction mixture was poured into water (10 mL) and extracted with EtOAc (3x20 mL). The organic layer was dried over $MgSO_4$ and filtered over celite. Solvents were then removed under reduced pressure. The crude product was then purified by flash column chromatography.

(*Z*)-**ethyl 2-methoxy-3-(2-methoxyphenyl)acrylate 3Aa:** Compound **3Aa** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2-methoxy benzoic acid **2a** (30 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9/1) to afford **3Aa** (39 mg, 0.165 mmol) in 83% yield as a coloress oil. IR: 2990, 2841, 1715, 1620, 1580, 11474, 1113, 840, 752 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.44 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 8.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7 (C), 157.4 (C), 145.7 (C), 130.6 (CH), 130.3 (CH), 122.3 (C), 120.7 (CH), 117.3 (CH), 110.5 (CH), 61.2 (CH_2), 59.3 (CH_3), 55.6 (CH_3), 14.4 (CH_3). MS (ESI-TOF) *m/z* 237.12 [M+H$^+$]. HMRS (ESI-TOF): calc. for $C_{13}H_{17}O_4$; 237.1346: found 279.1345.

(*Z*)-**ethyl 3-(2,4-dimethoxyphenyl)-2-methoxyacrylate 3Ab**: Compound **3Ab** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,4-dimethoxybenzoic acid **2b** (37 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/AcOEt 95:5) to afford **3Ab** (43 mg, 0.158 mmol) in 79% yield as a yellow oil. IR: 2983, 2938, 1713, 1622, 1575, 1475, 862 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 1H), 7.41 (s, 1H), 6.52 (dd, *J* = 2.4 and 8.8 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (C), 161.6 (C), 158.9 (C), 144.1 (C), 131.7 (CH), 117.5 (CH), 115.3 (C), 105.0 (CH), 98.0 (CH), 61.0 (CH_2), 59.1 (CH_3), 55.6 (CH_3), 55.4 (CH_3), 14.5 (CH_3). MS (ESI-TOF) *m/z* 267.1 [M+H$^+$]. HMRS (EI+): calc. for $C_{14}H_{18}O_5$; 266.1154: found 266.1166.

(*Z*)-**ethyl 3-(2,6-dimethoxyphenyl)-2-methoxyacrylate 3Ac**: Compound **3Ac** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,6-dimethoxybenzoic acid **2c** (36 mg, 0.2 mmol) according to the general procedure A. The crude prodcut was purified by flash chromatography (PE/AcOEt 85:15) to afford **3Ac** (24 mg, 0.09 mmol) in 45% yield as a yellow oil. IR: 2989, 2941, 2834, 1714, 1582, 1471, 860 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.1 Hz, 1H), 6.89 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 6H), 3.59 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3 (C), 158.0 (2xC), 146.8 (C), 129.6 (CH), 112.9 (CH), 111.5 (C), 103.4 (2xCH), 61.2 (CH_2), 58.9 (CH_3), 55.8 (2xCH_3), 14.4 (CH_3). MS (ESI-TOF) *m/z* 267.1 [M+H$^+$]. HMRS (EI+): calc. for $C_{14}H_{18}O_5$; 266.1154: found 266.1147.

(*Z*)-**ethyl 2-methoxy-3-(2,4,5-trimethoxyphenyl)acrylate 3Ad:** Compound **3Ad** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,4,5-trimethoxybenzoic acid **2d** (43 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 75:25) to afford **3Ad** (46 mg, 0.15 mmol) in 78% yield a yellow oil. IR: 2954, 2845, 1720, 1607, 1550, 1450, 1211, 850 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) 7.83 (s, 1H), 7.44 (s, 1H), 6.49 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.85 (s, 6H), 3.74 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.9 (C), 153.0 (C), 149.4 (C), 143.9 (C), 143.4 (C), 117.7 (CH), 114.0 (C), 113.2 (CH), 96.5 (CH), 61.1 (CH_2), 59.3 (CH_3), 56.6 (CH_3), 56.3 (CH_3), 56.0 (CH_3), 14.5 (CH_3). MS (ESI-TOF) *m/z* 296.22 [M+H$^+$]. HMRS (ESI-TOF): calc. for $C_{15}H_{21}O_6$; 297.3190: found 297.3195.

(*Z*)-**ethyl 2-methoxy-3-(2,4,6-trimethoxyphenyl)acrylate 3Ae:** Compound **3Ae** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,4,6-trimethoxybenzoic acid **2e** (43 mg, 0.2 mmol) according to the general procedure A. The crude prodcut was purified by flash chromatography (PE/EtOAc 8:2) to afford **3Ae** (32 mg, 0.108 mmol) in 54% yield a yellow oil. IR: 2941, 2841, 1711, 1603, 1582, 1454, 1202, 809 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) 6.86 (s, 1H), 6.12 (s, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.59 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 161.7 (C), 158.9 (2xC), 146.1 (C), 113.1 (CH), 104.4 (C), 90.3 (2xCH), 61.1 (CH_2), 58.9 (CH_3), 55.8 (2xCH_3), 55.4 (CH_3), 14.4 (CH_3). MS (ESI-TOF) *m/z* 296.22 [M+H$^+$]. HMRS (ESI-TOF): calc. for $C_{15}H_{21}O_6$; 297.3190: found 297.3195.

(*Z*)-**ethyl 3-(2-ethoxyphenyl)-2-methoxyacrylate 3Af**: Compound **3Af** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,6-diethoxybenzoic acid **2f** (33 mg, 30 µL, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford **3Af** (23 mg, 0.092 mmol) in 46% yield as a yellow oil. IR: 2998, 2941, 2842, 1706, 1604, 1574, 1500, 832, 770 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 1.3 and 7.8 Hz, 1H), 7.49 (s, 1H), 7.29 – 7.24 (m, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.11 (q, *J* = 7.0 Hz, 2H), 3.74 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (C), 156.9 (C), 145.6 (C), 130.6 (CH), 130.3 (CH), 122.5 (C), 120.6 (CH), 117.6 (CH), 111.7 (CH), 64.1 (CH_2), 61.2 (CH_2), 59.3 (CH_3), 14.9 (CH_3), 14.4 (CH_3) MS (ESI-TOF) *m/z* 251.13 [M+H$^+$].HMRS (ESI-TOF): calc. for $C_{14}H_{19}O_4$; 251.2940: found 251.2950.

(*Z*)-**ethyl 3-(2,6-diethoxyphenyl)-2-methoxyacrylate 3Ag:** Compound **3Ag** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,6-diethoxybenzoic acid **2g** (42 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Ag** (27 mg, 0.1 mmol) in 51% yield as coloress oil. IR: 2982, 2936, 1715, 1581, 1453, 842, 711 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (t, *J* = 8.3 Hz, 1H), 6.89 (s, 1H), 6.52 (d, *J* = 8.3 Hz, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 4H), 3.59 (s, 3H), 1.43 – 1.33 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 157.5 (2xC), 146.6 (C), 129.3 (CH), 112.8 (CH), 112.3 (C), 104.4 (2xCH), 64.1 (2xCH_2), 61.1 (CH_2), 58.9 (CH_3), 14.9 (2x CH_3), 14.4 (CH_3). MS (ESI-TOF) *m/z* 295.15 [M+H$^+$].HMRS (ESI-TOF): calc. for $C_{16}H_{23}O_5$; 295.3470: found 295.3480.

(*Z*)-**ethyl 3-mesityl-2-methoxyacrylate 3Ah**: Compound **3Ah** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 2,4,6-trimethylbenzoic acid **2h** (38 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford **3Ah** (40 mg, 0.16 mmol) in 80% yield as a colorless oil. IR: 2985, 2939, 2851, 1718, 1611, 1567, 1479, 852, 771 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 1H), 6.87 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.41 (s, 3H), 2.28 (s, 3H), 2.23 (s, 6H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (C) , 146.2 (C), 137.3 (C), 136.4 (2xC), 129.7 (C), 128.0 (2xCH), 119.8 (CH), 61.4 (CH_2), 59.4 (CH_3), 21.1 (CH_3), 20.54 (2xCH_3), 14.38 (CH_3). MS (ESI-TOF) *m/z* 249.20 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{15}H_{21}O_3$; 249.3220: found 249.3235.

(*Z*)-**ethyl 2-methoxy-3-(3-methylbenzofuran-2-yl)acrylate 3Ai**: Compound **3Ai** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol) and 3-methylbenzofuran-2-carboxylic acid **2i** (35 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford **3Ai** (37 mg, 0.142 mmol) in 71% yield as a yellow oil. IR: 2986, 2938, 2845,1711, 1613, 1570, 1016, 821 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 2H), 7.36 – 7.31 (m, 1H), 7.28 – 7.21 (m, 1H), 7.10 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 2.35 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 155.2 (C), 147.2 (C), 144.7 (C), 129.4 (C), 125.9 (CH), 122.7 (CH), 119.8 (CH), 119.5 (C), 111.5 (CH), 111.1 (CH), 61.5 (CH_2), 61.2 (CH_3), 14.5 (CH_3), 8.8 (CH_3). MS (ESI-TOF) *m/z* 261.11 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{15}H_{17}O_4$; 261.2890: found 261.2901.

(*Z*)-**ethyl 3-(2,4-dinitrophenyl)-2-methoxyacrylate 3Aj** : Compound **3Aj** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.300 mmol) and 2,4-dinitrobenzoic acid **2j** (42.4 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Aj** (20 mg, 0.068 mmol) in 34% yield as a yellow oil. IR: 2938, 2845, 1710, 1520, 1322, 1163, 1096, 886, 821 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.58 (dd, *J* = 2.0 and 8.2 Hz 1H), 7.82 (t, *J* = 8.2 Hz, 1H), 7.02 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (C), 161.7 (C), 158.9 (C), 144.1 (C), 131.7 (C), 117.5 (CH), 115.3 (CH), 105.1 (CH), 98.1 (CH), 61.1 (CH_2), 59.2 (CH_3), 14.5 (CH_3). MS (ESI-TOF) *m/z* 297.12 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{13}N_2O_7$; 297.2350: found 297.2420.

(*Z*)-**ethyl 2-methoxy-3-(4-methoxy-2-nitrophenyl)acrylate 3Ak**: Compound **(*Z*)-3Ak** was prepared for ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol), and 4-methoxy-2-nitro-benzoic acid **2k** (39.4 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Ak** (23 mg, 0.08 mmol) in 40% yield as a yellow oil. IR: 2938, 2845, 1690, 1520, 1330, 1163, 1096, 886, 821 cm^{-1}.^1H NMR (300 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 2.7 Hz, 1H), 7.31 (d, *J* = 9.2 Hz, 1H), 7.29 (s, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 3.78 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0 (C), 161.6 (C), 158.9 (C), 144.1 (C), 131.7 (CH), 117.5 (CH), 115.3 (C), 105.0 (CH), 98.0 (CH), 61.0 (CH_2), 55.6 (CH_3), 55.5 (CH_3), 14.5 (CH_3). MS (ESI-TOF) *m/z* 282.12 [M+H^+].HMRS (ESI-TOF): calc. for $C_{13}H_{16}NO_6$; 282.2640: found 282.2648.

(*Z*)-**ethyl 3-(2-chlorophenyl)-2-methoxyacrylate 3Al**: Compound **3Al** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol), and 2-chlorobenzoic acid **2l** (31 mg, 0.2 mmol) in DMF instead of 1.4-dioxane/DMSO according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Al** (23 mg, 0.096 mmol) in 32% yield as a yellow oil. IR: 2950, 2845, 1701, 1658, 1550, 1322, 1016, 753 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 2.0 and 5.7 Hz, 1H), 7.41 – 7.38 (m, 1H), 7.34 (s, 1H), 7.30 – 7.23 (m, 3H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.76 (d, *J* = 6.5 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (C), 147.1 (C), 134.3 (C), 131.6 (C), 131.1 (CH), 129.7 (CH), 129.6 (CH), 126.9 (CH), 118.6 (CH), 61.5 (CH_2), 59.6 (CH_3), 14.43 (CH_3). MS (ESI-TOF) *m/z* 241.12 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{14}ClO_3$; 241.6830: found 241.6920.

(*Z*)-**ethyl 3-(2,6-dichlorophenyl)-2-methoxyacrylate 3Am**: Compound **3Am** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol), and 2,6-dichlorobenzoic acid **2m** (38 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Am** (15 mg, 0.054 mmol) in 27% yield as a yellow oil. IR: 2983, 1723, 1644, 1580, 1428, 839, 777 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 2H), 7.21 – 7.15 (m, 1H), 6.82 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (C), 148.0 (C), 135.0 (2xC), 132.3 (C), 129.4 (CH), 127.8 (2xCH), 114.5 (CH), 61.8 (CH_2), 59.4 (CH_3), 14.3 (CH_3). MS (ESI-TOF) *m/z* 276.11 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{13}Cl_2O_3$; 276.1130: found 276.1210.

(*Z*)- **and** (*E*)-**ethyl 2-methoxy-3-(2,4,6-trichlorophenyl)acrylate** (*Z*)-**3An and** (*E*)-**3An**: Compound (*Z*)-**3An** and **(***E*)-**3An** were prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol), and 2,4,6-trichlorolbenzoic acid **2n** (45 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford (*Z*)-**3An** (24 mg, 0.048 mmol) in 24% yield as a colorless oil, and (*E*)-**3An** (10 mg, 0.032 mmol) in 16% yield as colorless oil. (*Z*)-**ethyl 2-methoxy-3-(2,4,6-trichlorophenyl)acrylate** (*Z*)-**3An**: IR: 2983, 2942, 1724, 1646, 1578, 1439, 848 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (s, 2H), 6.73 (s, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (C), 148.4 (C), 135.5 (2xC), 134.3 (C), 130.9 (C), 127.9 (2xCH), 113.7 (CH), 61.9 (CH_2), 59.4 (CH_3), 14.3 (CH_3). MS (ESI-TOF) *m/z* 308.97 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{12}Cl_3O_3$; 308.9874: found 308.9889. (*E*)-**ethyl 2-methoxy-3-(2,4,6-trichlorophenyl)acrylate** (*E*)-**3An**: IR: 2983, 2942, 1724, 1646, 1578, 1439, 848 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (s, 2H), 5.80 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (C), 149.4 (C), 135.5 (2xC), 133.3 (C), 132.8 (C), 127.7 (2xCH), 104.2 (CH), 61.6 (CH_2), 56.3 (CH_3), 13.8 (CH_3).

(*Z*)-**ethyl 3-(2-bromo-6-fluorophenyl)-2-methoxyacrylate 3Ao**: Compound **3Ao** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.300 mmol), and 6-bromo-2-fluorobenzoic acid **2o** (44 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Ao** (25 mg, 0.082 mmol) in 41% yield as a colorless oil. IR: 2938, 2845, 1706, 1650, 1601, 1450, 1096, 896, 830, 680 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$) δ -113.0 (d, *J* = 5.9 Hz, 1F). ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.8 Hz, 1H), 7.20 – 7.13 (m, 1H), 7.09 – 7.03 (m, 1H), 6.76 (s, 1H), 4.34 (q, *J* = 7.2 Hz, 2H), 3.70 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (C), 160.2 (d, $J_{C\text{-}F}$ = 251.3 Hz, C), 148.3 (C), 130.1 (d, $J_{C\text{-}F}$ = 5.8 Hz, CH), 128.2 (d, $J_{C\text{-}F}$ = 3.8 Hz, CH), 124.6 (d, $J_{C\text{-}F}$ = 4.0 Hz, C), 123.3 (d, $J_{C\text{-}F}$ = 18.8 Hz, C), 114, 8 (d, $J_{C\text{-}F}$ = 22.1 Hz, CH), 114.2 (CH), 61.7 (CH_2), 59.5 (CH_3), 14.3 (CH_3). MS (EI-TOF) *m/z* 303.10 [M+H^+]. HMRS (CI+): calc. for $C_{12}H_{13}BrFO_3$; 303.0032: found 303.0042.

(*Z*)-**ethyl 2-methoxy-3-(2,4,6-trifluorophenyl)acrylate 3Ap**: Compound **3Ap** was prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol), and 2,4,6-trifluorobenzoic acid **2p** (43 mg, 0.2 mmol) in DMF instead of 1,4-dioxane/DMSO according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford **3Ap** (42 mg, 0.16 mmol) in 80% yield as a yellow oil. IR: 2942, 2845, 1705, 1690, 1595, 1322, 1163, 1096, 893, 810, 680 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.33 (m, 2F), -107.80 (m, 1F). ^1H NMR (300 MHz, $CDCl_3$) δ 6.72 – 6.66 (m, 3H), 4.33 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (dt, $J_{C\text{-}F}$ = 15.0 and 249 Hz, C), 163.4 (C), 163.1 (C), 160.7 (ddd, $J_{C\text{-}F}$ = 10.1, 14.7 and 250 Hz, 2xC), 148.8 (C), 107.9 (CH), 100.5 (dd, $J_{C\text{-}F}$ = 3.1 and 25.5 Hz, CH), 100.1 (dd, $J_{C\text{-}F}$ = 2.1 and 24.6 Hz, CH), 61.6 (CH_2), 59.3 (CH_3), 14.2 (CH_3). MS (ESI-TOF) *m/z* 261.12 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{12}F_3O_3$; 261.2122: found 261.2210.

(*Z*)- **and** (*E*)-**ethyl 2-methoxy-3-(pentafluorophenyl)acrylates** (*Z*)-**3Aq and** (*E*)-**3Aq**: Compounds (*Z*)-**3Aq** and (*E*)-**3Aq** were prepared from ethyl 2-methoxyacrylate **1A** (39 mg, 0.3 mmol), and pentafluorobenzoic acid **2q**

(43 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford (*Z*)-**3Aq** (10 mg, 0.034 mmol) in 17% yield as a yellow oil, and (*E*)-**3Aq** (20 mg, 0.068 mmol) in 34% yield as a yellow oil. (*Z*)-**ethyl 2-methoxy-3-(pentafluorophenyl)acrylate** (*Z*)-**3Aq:** IR: 2880, 1705, 1672, 1598, 1322, 1163, 835 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$) δ -136.9 – 136.6 (m, 2F), -154.4 – -154.5 (t, *J* = 19.7 Hz, F), -162.4 – -162.5 (m, 2F). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.60 (bs, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.6 (C), 150.2 (C), 146.3 – 146.0 (m, C), 143.0 – 142.6 (m, C), 139, 6 – 139,0 (m, C), 136.3 – 135.9 (m, C), 108.9 (td, J_{C-F} = 4.1 and 18.1 Hz, C), 105.4 (d, J_{C-F} = 4.0 Hz, CH), 62.1 (CH_2), 59.5 (CH_3), 14.3 (CH_3). MS (ESI-TOF) *m/z* 297.15 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{10}F_5O_3$; 297.1930: found 297.1945. (*E*)-**ethyl 2-methoxy-3-(pentafluorophenyl)acrylate** (*E*)-**3Aq**: IR: 2880, 1705, 1672, 1598, 1322, 1163, 835 cm^{-1}. ^{19}F NMR (282 MHz, CDCl3) δ -139.9 (dd, *J* = 9.5 and 22.5 Hz, 2F),. -156.5 (t, *J* = 22.5 Hz, F), -163.3 (dd, *J* = 14.1 and 19.7 Hz, 2F). ^{1}H NMR (300 MHz, $CDCl_3$) 5.59 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.2 (C), 152.8 (C), 146.3 – 146.0 (m, C), 143.0 – 142.6 (m, C), 139.7 – 139.1 (m, C), 136.3 – 135.9 (m, C), 139.2 – 138.8 (m, C), 135.9 – 135.8 (m, C), 108.9 (td, J_{C-F} = 4.1 and 18.2 Hz), 105.3 (d, J_{C-F} = 2,1 Hz, CH), 61.9 (CH_2), 59.6 (CH_3), 14.3 (CH_3). HMRS (ESI-TOF): calc. for $C_{12}H_{10}F_5O_3$; 297.1930: found 297.1945.

(*Z*)-**2-(1,1-dimethylethyl)-5-(2-methoxybenzylidene)-1,3-dioxolan-4-one 3Ba**: Compound **3Ba** was prepared from **1B** (47 mg, 0.3 mmol), and 2-methoxybenzoic acid **1a** (35 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford 3**Ba** (21 mg, 0.08 mmol) in 40% yield as a yellow oil. IR: 2964, 1788, 1235, 753 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 1.6 and 7.8 Hz, 1H), 7.24 – 7.17 (m, 1H), 6.94 – 6.86 (m, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.51 (s, 1H), 3.78 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2 (C), 157.4 (C), 136.6 (C), 130.1 (CH), 129.9 (CH), 121.9 (C), 120.7 (CH), 110.6 (CH), 109.2 (CH), 101.7 (CH), 55.6 (CH_3), 36.1 (C), 23.0 (3xCH_3). MS (ESI-TOF) *m/z* 263.14 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{15}H_{19}O_4$; 263.3050: found 263.3122.

(Z)-**2-(1,1-dimethylethyl)-5-(2,6-difluorobenzylidene)-1,3-dioxolan-4-one 3Br**: Compound **3Br** was prepared from **1B** (47 mg, 0.3 mmol), and 2,6-difluorobenzoic acid **2r** (37 mg, 0.2 mmol) in DMF/DMSO instead of 1,4-dioxane/DMSO according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Br** (16 mg, 0.06 mmol) in 30% yield as a yellow oil. IR: 2964, 2850, 1788, 1680, 1235, 852, 753, 630 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$) δ -107.3 (t, *J* = 7.13 Hz, 2F). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 – 7.23 (m, 1H), 6.92 (t, *J* = 8.2 Hz, 2H), 6.40 (s, 1H), 5.55 (s, 1H), 1.02 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.09 (C), 160.7 (dd, J_{C-F} = 7.4 and 251 Hz, 2xC), 139.6 (C), 130.23 (t, J_{C-F} = 10.3 Hz, CH), 111.6 (d, J_{C-F} = 23.4 Hz, CH), 111.5 (d, J_{C-F} = 23.4 Hz, CH), 111.6 – 111.3 (m, C), 110.5 (CH), 93.7 (t, J_{C-F} = 2.3 Hz, CH), 36.3 (C), 23.0 (CH_3), 22.9 (2xCH_3). MS (ESI-TOF) *m/z* 269.12 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{14}H_{15}F_2O_3$; 269.2598: found 269.2630.

(*Z*)-**benzyl 2-methoxy-3-(2,6-difluorophenyl)acrylate 3Cr**: Compound **3Cr** was prepared from **1C** (57 mg, 0.3 mmol), and 2,6-difluorobenzoic acid **2r** (37 mg, 0.2 mmol) in DMF/DMSO instead of 1,4-dioxane/DMSO according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 95:5) to afford **3Cr** (27 mg, 0.09 mmol) in 46% yield as a yellow oil. IR: 2992, 2850, 1720, 1625, 1590, 1501, 1016, 890, 821, 710 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.3 (t, *J* = 7.1 Hz, 2F). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.34 (m, 5H), 7.29 – 7.20 (m, 1H), 6.90 (t, *J* = 8.1 Hz, 2H), 6.84 (s, 1H), 5.31 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2 (C), 160.6 (dd, J_{C-F} = 7.3 and 249.9 Hz, 2xCH), 148.5 (C), 135.5 (C), 129.9 (t, J_{C-F} = 10.4 Hz, CH), 128.7 (2xCH), 128.5 (CH), 128.4 (2xCH), 111.4 (d, J_{C-F} = 23.7 Hz, CH), 111.3 (d, J_{C-F} = 23.8 Hz, CH), 111.4 – 110.9 (m, C), 109.4 (CH), 67.3 (CH_2), 59.5 (CH_3) . MS (ESI-TOF) *m/z* 305.13 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{17}H_{15}F_2O_3$; 305.2928: found 305.2935.

(*Z*)-**benzyl 2-methoxy-3-(2-methoxyphenyl)acrylate 3Ca**: Compound **3Ca** was prepared from **1C** (57 mg, 0.3 mmol), and 2-methoxybenzoic acid **1a** (30 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Ca** (30 mg, 0.1 mmol) in 50% yield as a yellow oil. IR: 2992, 2850, 1720, 1625, 1580, 11474, 1111, 830, 752 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 1.7 and 7.8 Hz, 1H), 7.51 (s, 1H), 7.47 – 7.27 (m, 5H), 7.01 – 6.94 (m, 1H), 6.88 (dd, *J* = 1.2 and 8.3 Hz, 1H), 5.31 (s, 2H), 3.85 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6 (C), 157.5 (C), 145.5 (C), 136.1 (C), 130.7 (CH), 130.4 (CH), 128.7 (2xCH), 128.3 (2xCH), 122.3 (C), 120.7 (CH), 118.0 (CH), 110.5 (CH), 66.8 (CH_2), 59.4 (CH_3), 55.7 (CH_3). MS (ESI-TOF) *m/z* 299.15 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{18}H_{19}O_4$; 299.3410: found 299.3425.

(*Z*)-**ethyl 3-(2-methoxyphenyl)-2-phenoxyacrylate 3Da**: Compound **3Da** was prepared from **1D** (58 mg, 0.300 mmol), and 2-methoxybenzoic acid **2a** (31 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Da** (36 mg, 0.12 mmol) in 60% yield as a yellow oil. IR: 2938, 2845, 1705, 1680, 1450, 1096, 1016, 821, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.78 (s, 1H), 7.25 – 7.11 (m, 3H), 6.99 – 6.93 (m, 3H), 6.85 – 6.79 (m, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (C), 157.7 (C), 156.9 (C), 140.0 (C), 130.9 (CH), 130.6 (CH), 129.7 (2xCH), 122.5 (CH), 121.6 (C), 120.9 (CH), 120.7 (CH), 115.7 (2xCH), 110.6 (CH), 61.4 (CH_2), 55.7 (CH_3), 14.2 (CH_3). MS (ESI-TOF) *m/z* 299.15 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{18}H_{19}O_4$; 299.3380: found 299.3395.

(*Z*)-**ethyl 2-benzyloxy-3-(2-methoxyphenyl)acrylate 3Ea**: Compound **3Ea** was prepared from **1E** (62 mg, 0.3 mmol), and 2-methoxybenzoic acid **1a** (31 mg, 0.2 mmol) according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Ea** (54 mg, 0.172 mmol) in 86% yield as a yellow oil. IR: 2940, 2845, 1710, 1670, 1550, 1100, 1016, 821, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 1.9 and 7.8 Hz, 1H), 7.53 (s, 1H), 7.45 – 7.36 (m, 2H), 7.34 – 7.27 (m, 4H), 6.96 – 6.88 (m, 2H), 4.93 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8 (C), 157.4 (C), 144.4 (C), 137.0 (C), 130.9 (CH), 130.3 (CH), 128.6 (CH), 128.5 (2xCH), 128.4 (CH), 128.1 (CH), 122.3 (C), 120.6 (CH), 118.3 (CH), 110.5 (CH), 73.6 (CH_2), 61.2 (CH_2), 55.6 (CH_3), 14.4 (CH_3). MS (ESI-TOF) *m/z* 313.15 [M+H^+]. HMRS (EI+): calc. for $C_{19}H_{20}O_4$; 312.1361: found 312.1353.

(*Z*)-**benzyl 2-benzyloxy-3-(2,6-difluorophenyl)acrylate 3Er**: Compound **3Er** was prepared for **1E** (62 mg, 0.3 mmol), and 2,6-difluorobenzoic acid **2r** (37 mg, 0.2 mmol) in DFM/DMSO instead of 1,4-dioxane/DMSO according to the general procedure A. The crude product was purified by flash chromatography (PE/EtOAc 9:1) to afford **3Er** (25 mg, 0.08 mmol) in 40% yield as a yellow oil. IR: 2850, 1720, 1625, 1590, 1501, 1016, 890, 821, 705 cm^{-1}. ^{19}F NMR (282 MHz, $CDCl_3$) δ -108.2 (t, *J* = 7.13 Hz, 2F). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 6H), 6.91 – 6.83 (m, 3H), 4.97 (s, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4 (C), 160.5 (dd, J_{C-F} = 7.3 and 249.9 Hz, 2C), 147.5 (C), 136.7 (C), 129.8 (t, *J* = 10.4 Hz, CH), 128.3 (2xCH), 128.2 (2xCH), 128.0 (CH), 111.6-111.3 (m, C), 111.3 (d, J_{C-F} = 23.8 Hz, CH), 111.2 (d, J_{C-F} = 23.8 Hz, CH), 110.9 (CH), 73.5 (CH_2), 61.7 (CH_2), 14.3 (CH_3). MS (ESI-TOF) *m/z* 319.12 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{18}H_{17}F_2O_3$; 319.3198: found 319.3205.

Diethyl 2,5-dimethoxyhexa-2,4-dienedioate 5: Compound **5** was obtained as a side product during the Myers coupling in presence of electron-deficient benzoic acids. Colorless oil. IR: 3453.5, 2986.1, 1718, 1248.4, 1093.6, 857.3 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3 (2xC), 148.4 (2xC), 116.7 (2xCH), 61.4 (2xCH_2), 60.7 (2xCH_3), 14.4 (2xCH_3). MS (ESI-TOF) *m/z* 259.15 [M+H^+]. HMRS (ESI-TOF): calc. for $C_{12}H_{19}O_6$; 259.2701: found 259.2720.

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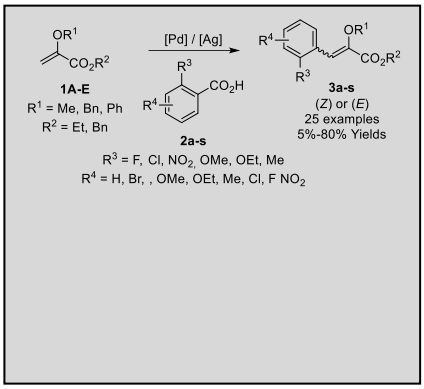
Arylation Enol Ethers.



Pd(II)-catalyzed decarboxylative Heck coupling of α-alkoxyacrylates with (hetero)aryl carboxylic acids for the stereocontrolled production of (*Z*)-β-heteroarylated vinyl ethers is reported. This methodology offers a rational and step-economical route to the synthesis of attractive β-arylated α-alkoxy α,β-unsaturated carboxylates family which emerged as a relevant class of building blocks with different applications.