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BF_3·OEt_2-mediated *syn*-selective Meyer–Schuster rearrangement of phenoxy propargyl alcohols for *Z*-β-aryl-α,β-unsaturated esters†

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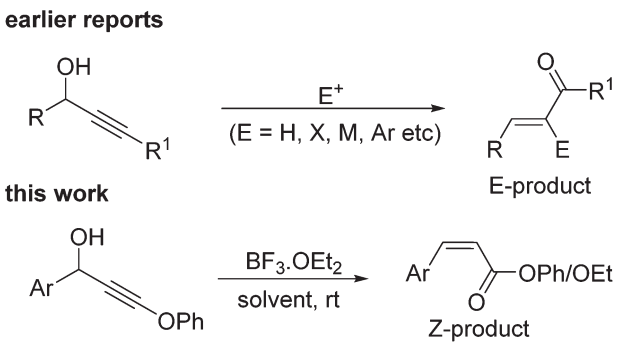
Synthesis of *Z*-β-aryl-α,β-unsaturated esters from readily available 1-aryl-3-phenoxy propargyl alcohols is achieved *via* a BF_3-mediated *syn*-selective Meyer–Schuster rearrangement under ambient conditions. The reaction mechanism is postulated to involve an electrophilic borylation of an allene intermediate as the key step to kinetically control the stereoselectivity.

Introduction

The Meyer–Schuster rearrangement (MSR)[1] has been evolved as a powerful tool for the synthesis of *trans*-α,β-unsaturated carbonyls, highly potential synthetic intermediates, from readily available propargyl alcohols *via* activation of hydroxyl and alkynyl moieties independently or cooperatively (Scheme 1). The reaction is well tuned for the entire spectrum of conjugated carbonyls *i.e.* conjugated-aldehydes,[1h] -ketones,[1i] -esters,[1j,k] -amides[1l] and even silylketones.[1m] Furthermore, halogenative,[1n–q] alkylative,[1r] allylative,[1s] arylative[1t] and trifluoromethylative[1u,v] versions of the reaction are reported for extra functionalization of the subunit in tandem. A long list of metal complexes based on Au, Ag, Cu, Ti, Re, V, Mo, W, and Ru are identified to execute this transformation. The only challenge yet to be addressed in this area of research is to achieve the *syn*-selective MSR averting the advantage of thermodynamic control for *trans*-products. As part of our on-going program[2] of uncovering the new activities of activated alkynes, we herein report a *syn*-selective MSR of phenoxy propargyl alcohols for *Z*-β-aryl-α,β-unsaturated esters.



Scheme 1 Meyer–Schuster rearrangements.

Results and discussion

Our synthetic efforts began with the optimization studies for the conversion of **1a**[2g] to **2a** (or **3a**) as shown in Table 1. The use of 0.5 equiv. of $AlCl_3$ in dioxane resulted in the formation of *trans*-ester **4a** almost exclusively (Table 1, entry 1). The substrate was found to be stable and no conversion was observed in the presence of other Lewis acids like $InCl_3$, $ZnCl_2$ and $MgCl_2$ (entries 2–4). Pleasingly, when we opted BF_3·OEt_2 for the conversion, the desired *cis*-ester **2a** was obtained in a reasonable ratio (**2a** : **4a** in 71 : 29) albeit in 35% yield (entry 5). An increase of BF_3·OEt_2 loading to 1 equivalent led to 55% yield of the product with no change of the ratio (entry 6).

A further increase of the dose of the acid incurred no change in the outcome (entry 7). The use of BF_3·THF (entry 8) instead of BF_3·OEt_2 was proved to be a bad choice (50% of **2a** : **4a** in 77 : 23). The change of the solvent to CH_3CN (entry 9) improved the ratio towards the *cis*-isomer (81 : 19) but still with a moderate yield (45%). Other solvents CH_2Cl_2, toluene, DMSO, DCE, DMF, DMA and THF all either produced an unacceptable ratio of the products or were found to be ineffective for the intended conversion (entries 10–16). Interestingly, EtOH as the solvent (entry 17) produced a better yield (69%) with an acceptable ratio of 77 : 23 (*Z*/*E* respectively) but with a concomitant trans-esterification yielding **3a**[3] instead of **2a**. Gratifyingly, the use of dioxane and EtOH as a 1 : 1 mixture (entry 18) of solvents improved both the yield (76%) and the

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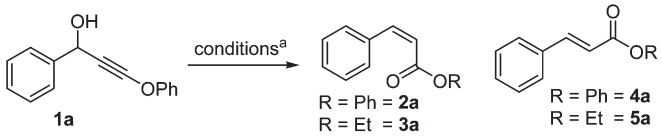
Table 1 Optimization studies

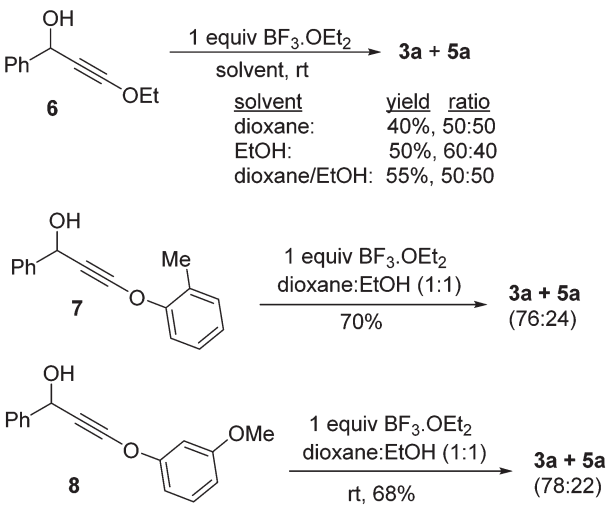


S. no.	Reagent	Equiv.	Solvent	Temp./time	Ratio of **2a : 3a : 4a : 5a**	Yield[b]
1	$AlCl_3$	0.5	Dioxane	rt/3 h	2 : 0 : 98 : 0	70%
2	$InCl_3$	0.5	Dioxane	rt/3 h	—[c]	—[c]
3	$ZnCl_2$	0.5	Dioxane	rt/3 h	—[c]	—[c]
4	$MgCl_2$	0.5	Dioxane	rt/3 h	—[c]	—[c]
5	$BF_3{\cdot}OEt_2$	0.5	Dioxane	rt/3 h	71 : 0 : 29 : 0	35%
6	$BF_3{\cdot}OEt_2$	1.0	Dioxane	rt/10 min	72 : 0 : 28 : 0	55%
7	$BF_3{\cdot}OEt_2$	2.0	Dioxane	rt/10 min	72 : 0 : 28 : 0	50%
8	$BF_3{\cdot}THF$	1.0	Dioxane	rt/1 h	77 : 0 : 23 : 0	50%
9	$BF_3{\cdot}OEt_2$	1.0	CH_3CN	rt/10 min	81 : 0 : 19 : 0	45%
10	$BF_3{\cdot}OEt_2$	1.0	CH_2Cl_2	rt/10 min	33 : 0 : 67 : 0	45%
11	$BF_3{\cdot}OEt_2$	1.0	Toluene	rt/10 min	50 : 0 : 50 : 0	40%
12	$BF_3{\cdot}OEt_2$	1.0	DMSO	rt/6 h	—[c]	—[c]
13	$BF_3{\cdot}OEt_2$	1.0	DCE	rt/6 h	—[c]	—[c]
14	$BF_3{\cdot}OEt_2$	1.0	DMF	rt/1 h	40 : 0 : 60 : 0	50%
15	$BF_3{\cdot}OEt_2$	1.0	DMA	rt/1 h	Decomposition	0%
16	$BF_3{\cdot}OEt_2$	1.0	THF	rt/1 h	—[c]	—[c]
17	$BF_3{\cdot}OEt_2$	1.0	Ethanol	rt/10 min	0 : 77 : 0 : 23	69%
18	**$BF_3{\cdot}OEt_2$**	**1.0**	**Dioxane : ethanol**	**rt/10 min**	**0 : 85 : 0 : 15**	**76%**
19	$BF_3{\cdot}OEt_2$	1.0	Dioxane : ethanol	0 °C/0.5 h	0 : 80 : 0 : 20	60%
20	$BF_3{\cdot}OEt_2$	1.0	Dioxane : ethanol[d]	rt/0.5 h	0 : 73 : 0 : 27	60%
21	$BF_3{\cdot}OEt_2$	1.0	Dioxane : ethanol[e]	rt/10 min	0 : 82 : 0 : 18	58%
22	$BF_3{\cdot}OEt_2$	1.0	Dioxane : CH_3OH	rt/10 min	0 : 80 : 0 : 20	70%
23	$BF_3{\cdot}OEt_2$	1.0	Dioxane : $(CH_3)_3COH$	rt/0.5 h	80 : 0 : 20 : 0	55%
24	$BF_3{\cdot}OEt_2$	1.0	Dioxane : $C_6H_5CH_2OH$	rt/6 h	—[c]	—[c]
25	TMSCI	1.0	Dioxane : ethanol	rt/6 h	—[c]	—[c]
26	$Ti(^iOPr)_4$	1.0	Dioxane : ethanol	rt/6 h	—[c]	—[c]
27	$Bi(OTf)_3$	1.0	Dioxane : ethanol	rt/6 h	0 : 73 : 0 : 27	50%
28	$Hg(OTf)_2$	1.0	Dioxane : ethanol	rt/6 h	—[c]	—[c]
29	$La(OTf)_3$	1.0	Dioxane : ethanol	rt/6 h	—[c]	—[c]
30	$FeCl_2$	1.0	Dioxane : ethanol	rt/6 h	—[c]	—[c]
31	AgOTf	1.0	Dioxane : ethanol	rt/6 h	0 : 84 : 0 : 16	40%
32	$Yb(OTf)_3$	1.0	Dioxane : ethanol	rt/6 h	0 : 86 : 0 : 14	35%
33	$Cu(OTf)_2$	1.0	Dioxane : ethanol	rt/6 h	0 : 50 : 0 : 50	40%
34	$Zn(OTf)_2$	1.0	Dioxane : ethanol	rt/6 h	—[c]	—[c]

[a] Reaction conditions: 1 mmol of **1a** in 4 mL of solvent was added to the reagent slowly at rt. [b] Isolated yields. [c] Most of the starting material was recovered. [d] Double concentration. [e] Half concentration.

ratio of the *syn* adduct (85 : 15). Attempts for further improvement by lowering the temperature or changing the reaction concentrations were all unsuccessful (entries 19–21). The use of MeOH (1 : 1 dioxane : MeOH) instead of EtOH afforded the methyl ester of the product in a similar yield and ratio (entry 22) whereas the reaction in *t*-BuOH afforded the phenyl ester (no trans-esterification) but in 55% yield (**2a : 3a** in 80 : 20).

The exchange of EtOH with benzyl alcohol completely halted the reaction. Other Lewis acids than $BF_3{\cdot}OEt_2$ like TMSCl, $Ti(iOPr)_4$, $Bi(OTf)_3$, $Hg(OTf)_2$, $La(OTf)_2$, $FeCl_2$, AgOTf, $Yb(OTf)_3$, $Cu(OTf)_2$ and $Zn(OTf)_2$ were either found to be less productive or completely ineffective (entries 25–34). We then verified whether we can avoid the unnecessary trans-esterification by directly choosing the ethoxypropargyl alcohol **6** (Scheme 2). Surprisingly, no selective rearrangement occurred, indicating that only a certain degree of electron richness (ethoxyacetylene is electronically rich compared to phenoxyace-



Scheme 2 Oxy terminal substitution effect on MSR.

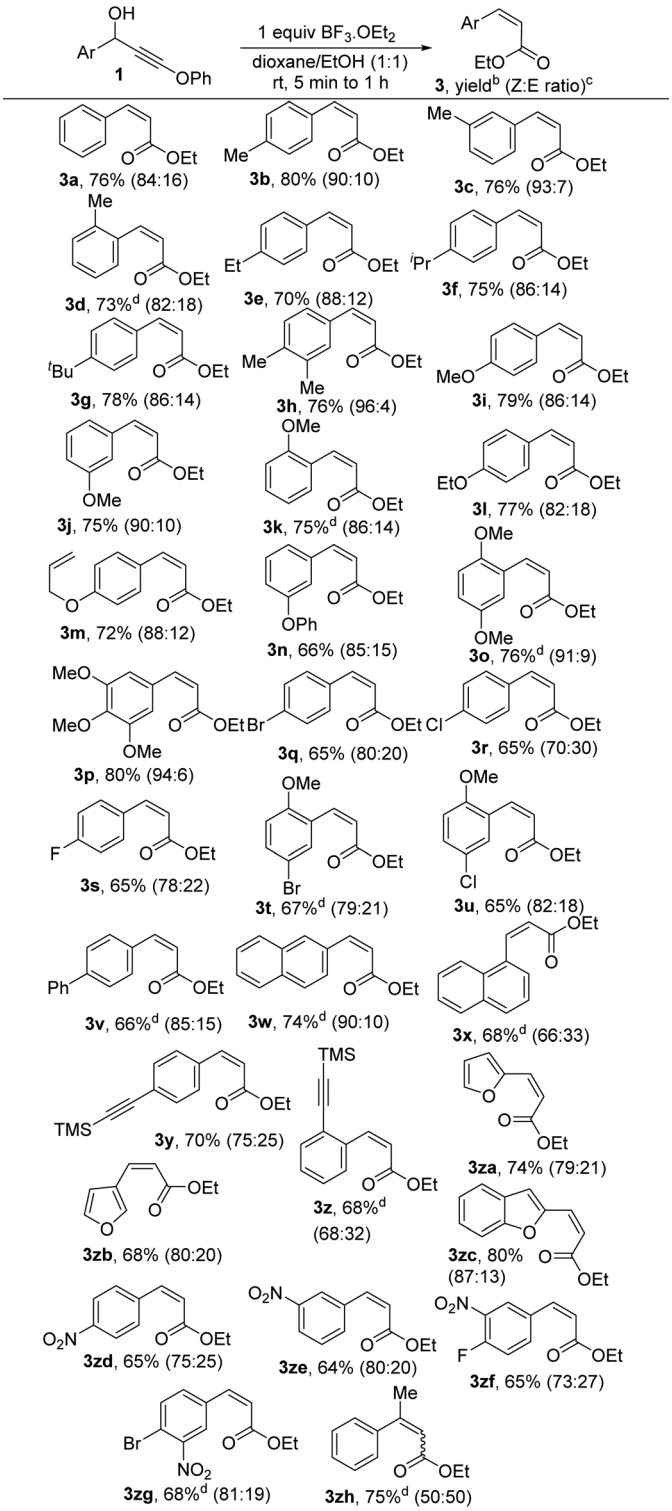
tylene) of the alkyne is key for kinetically controlled *cis*-selection in the product formation. Indeed, there were some reports in the literature which used ethoxypropargyl alcohols in MSR which often led to a *trans*-adduct or this kind of mixture of isomers. Furthermore, to unveil any role of steric and electronic factors exerted by the phenyl ring on oxy terminal, we synthesized the substrates **7** and **8** and screened them through the standard conditions. The yield and the ratio of the isomers were slightly varied but not in a favourable way. Synthesis of the substrates with an electron withdrawing group (–NO_2 or –F) attached to the phenoxy end seemed to be impractical (low yielding and non-reproducible) and hence could not be screened.

With these observations, we decided to go for generalization of *syn*-selective MSR with phenoxypropargyl alcohols as substrates using one equivalent of $BF_3{\cdot}OEt_2$ in the 1 : 1 dioxane/EtOH system. We then synthesized several 1-aryl-3-phenoxy propargyl alcohols and subjected to the standardized conditions (Table 2). Alkyl groups like Me, Et, iPr and *t*Bu on the phenyl ring were smoothly accommodated in the reaction irrespective of their position. Thus **1a–h** were converted to the corresponding *cis*-products **3a–h** in 70–80% yields with 82 : 18 to 96 : 4 ratios. Next, electron rich substrates with various alkoxy groups were tested.

o-, *m*- and *p*-Methoxy precursors (**1i–k**) conveniently reacted under the optimized conditions to afford the products (**3i–k**) in good yields and ratios. Other alkoxy groups like ethoxy, allyloxy and phenoxy groups (**1l–n**) were also equally tolerated in the reaction (**3l–n**). Similarly, di- and tri-methoxy adducts (**3o–p**) were successfully obtained in excellent yields (76–80%) and ratios (91 : 9 to 94 : 6) from the corresponding precursors (**1o–p**). Although the halo groups Br, Cl and F survived well in the reaction, their substitution (**1q–u**) was found to slightly discourage the reaction, thus producing the products (**3q–u**) in reduced yields (62–66%) and diminished ratios (70 : 30 to 82 : 18) of *cis*-adducts. Similarly, a *p*-phenyl substituted adduct (**1v**) was obtained in moderate yield but with comparably better selectivity (85 : 15). Furthermore, 2-naphthyl precursor **1w** smoothly underwent the transformation with an excellent yield (**3w**, 74%) and ratio (90 : 10) whereas its 1-naphthyl counterpart **1x** suffered the declined ratio of the *cis* adduct (66 : 33). This must have been due to steric constraints exerted by closely positioned C8-hydrogen. Next, as is evident from the conversion of **1y** and **1z** to **3y** and **3z**, respectively, alkynyl and trimethylsilyl groups were found unaffected under the optimised conditions but the alkyne group was found to be slightly detrimental for the ratio of the *cis*-adduct (75 : 25 to 68 : 32). Expanding the scope further, the heteroaryl adducts **3za–3zc** were obtained in good to excellent yields (68–80%) and ratios (79 : 21 to 87 : 13).

In the case of substrates with nitrophenyl substitution (**1zd–1zg**), the course of the reaction was found to be slightly different. Under the standard conditions, the *trans*-isomer was found to be the major adduct. When dioxane was used as the only solvent (instead of a 1 : 1 mixture of dioxane : ethanol) with 1 equivalent of $BF_3{\cdot}OEt_2$ (following alternate conditions

Table 2 *syn*-Selective MSR of phenoxypropargyl alcohols **1**[a]

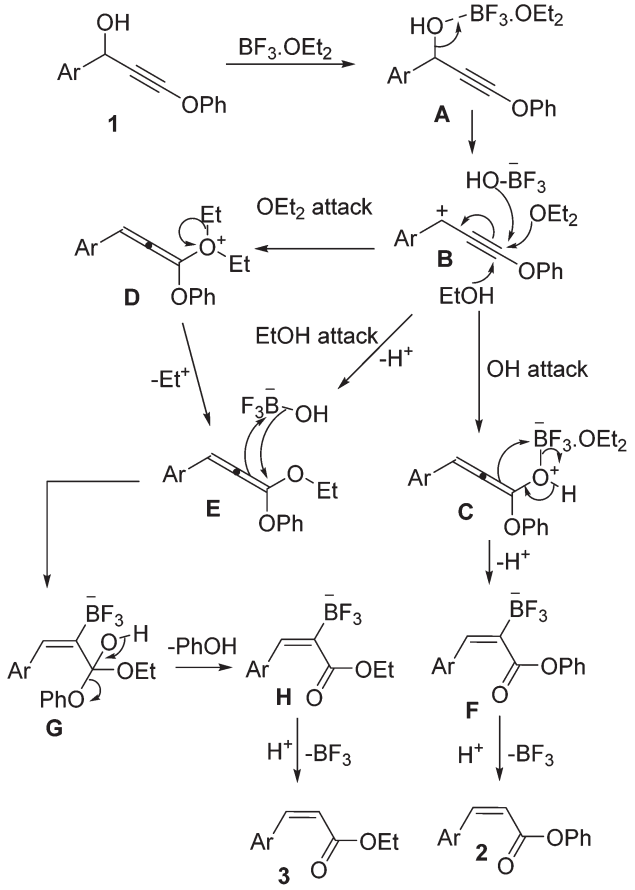


[a] Reaction conditions: 1 mmol of **1a** in 4 mL of solvent was added to the reagent slowly at rt. [b] Isolated yields of the *Z*-product. [c] The ratio was determined by ^{1}H NMR of the crude sample. [d] Yield of the mixture of *Z* & *E* isomers which were inseparable.

in entry 5, Table 1), the *cis*-adduct was obtained as the major product (more than 80 : 20) but surprisingly as a mixture of phenyl and ethyl esters. This current phenyl-to-ethyl trans-esterification occurred from an ether of $BF_3{\cdot}OEt_2$. The use of 2.5 equivalents of $BF_3{\cdot}OEt_2$ was necessary for the complete phenyl-to-ethyl transformation. But, the use of diethyl ether as a co-solvent to reduce the dose of $BF_3{\cdot}OEt_2$ did not work. Thus, **1zd–1zg** were converted to **3zd–3zg** in good yields (64–68%) and satisfactory ratios (81 : 19 to 73 : 27) using 2.5 equivalents of $BF_3{\cdot}OEt_2$ in dioxane at room temperature. Finally, setting a limitation, the reaction was not applicable to aliphatic substrates. Also, when an acetophenone (ketone) based substrate was used in the reaction, a 1 : 1 mixture of isomers was formed which again indicated that there existed a kinetic control based on the steric constraints of one of the intermediates which outshined the conjugation factor that should favour the *trans*-isomer. The ratio of the isomers was measured by ^{1}H NMR of the crude sample of the reaction after work-up. In 70% of the cases, the *E* and *Z* isomers were easily isolable and hence the data of the pure *Z* isomers are provided in the ESI† in those cases.

A mechanism is proposed in Scheme 3 rationalizing both the selective formation of *Z*-configured β-aryl-α,β-unsaturated esters and the trans-esterification. The reaction is initiated by the coordination of BF_3 to a free hydroxyl group (**A**). Thus the coordinated hydroxyl group gets easily cleaved (**B**) because of its benzylic nature which was further corroborated by an electron rich propargylic system. A concerted transfer of the hydroxyl group to the alkyne-terminal is disregarded because it fails to justify the formation of ethyl ester at the end. The subsequent C3-nucleophilic attack by hydroxyl oxygen (possible when done in only dioxane) or ethereal oxygen (in the case of nitrophenyl adducts **3zd–3zg**) or EtOH form **C** or **D** or **E**, respectively, which rationalizes the formation of both ethyl and/or phenyl esters at the end. Next, we presume that an electrophilic borylation of an allene intermediate, a key step which determines the stereoselective outcome of the reaction, led to **F–G** which has preferably hydrogen *cis* to the BF_3 fragment to minimize steric hindrance. The intermediate **G** after elimination of PhOH, due to the better leaving properties of the phenoxyl group over the ethoxyl group, formed **H**. The subsequent stereospecific boron–proton exchange in **F** and **H** led to the corresponding *cis*-products predominantly or exclusively. Our efforts to detect any intermediate by mass spectroscopy in the midway of the reaction all failed. To verify whether the phenyl ester **2a** was the initial product that thereafter underwent a tandem trans-esterification with EtOH, we treated the isolated **2a** with the optimized conditions (1 equiv. $BF_3{\cdot}OEt$, EtOH/dioxane). No trace of *trans*-esterified product **3a** was observed (**2a** was isolated as such), suggesting that the phenyl-to-ethyl exchange occurred during the reaction pathway (as we explained in Scheme 3) and not after the reaction. Finally, we at this stage are unable to explain why $BF_3{\cdot}OEt_2$ is required in a stoichiometric amount (1 equivalent) although it seems to act as a catalyst in the reaction.

In conclusion, we demonstrated the $BF_3{\cdot}OEt_2$ mediated synthesis of *Z*-β-aryl-α,β-unsaturated esters from readily available phenoxy propargyl alcohols *via* a hitherto formidable *syn* selective Meyer–Schuster rearrangement. The transformations proceed almost instantly (10 min) generating the products in excellent yields and with very high stereoselectivities. The mechanism appears to involve oxyborylation of an allene intermediate as the critical step for a kinetically controlled outcome of the reaction.



Scheme 3 Proposed mechanism for *syn*-selective MSR.

Experimental section

General information

All reagents and solvents were purchased from commercial sources and used without purification. NMR spectra were recorded with a 400 or 500 MHz spectrometer for ^{1}H NMR, 100 or 125 MHz for ^{13}C NMR spectroscopy. Chemical shifts are reported relative to the residual signals of tetramethylsilane in $CDCl_3$ or deuterated solvent $CDCl_3$ for ^{1}H and ^{13}C NMR spectroscopy. HRMS were recorded by using a Q-TOF mass spectrometer. Column chromatography was performed with silica gel (100–200 mesh) as the stationary phase. All reactions were monitored by using TLC.

General procedure A for synthesis of (*Z*)-α,β-unsaturated esters

1 equiv. (2.5 equiv. for **1zd–zg**) of BF_3 (in diethyl ether 48 w/v%) was added slowly to a solution of substrate **1** (1 mmol, 1 equiv.) in 4 mL of anhydrous 1 : 1 dioxane : ethanol (only dioxane in the case of **1zd–zg**) under a nitrogen atmosphere at room temperature. The resulting mixture was stirred at room temperature until the reaction was complete (10 min in general except **1zd** and **1ze** which took 1.5 h) as indicated by TLC. Then the ethanol was evaporated under reduced pressure and 10 ml water was added to the residue. The reaction was extracted with EtOAc (2 × 10 mL) and the combined organic layers were washed with brine, and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure the crude was purified by column chromatography with silica gel (100–200 mesh) using 1–5% EtOAc/hexanes to obtain the required product.

(*Z*)-Ethyl 3-phenylacrylate (3a). 0.128 g of **3a** was obtained from 0.224 g (1 mmol) of **1a** using general procedure A. Yield 73%; yellow oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.68–7.54 (m, 2H), 7.45–7.30 (m, 3H), 6.97 (d, *J* = 12.6 Hz, 1H), 5.97 (d, *J* = 12.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.2, 143.0, 134.9, 129.7, 129.0, 128.0, 119.9, 60.3, 14.1; IR (neat) ν 3399, 3019, 2927, 1637, 1403, 1216, 1157, 1068, 770, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{13}O_2$ $[M + H]^+$ 177.0916, found 177.0913.

(*Z*)-Ethyl 3-(*p*-tolyl)acrylate (3b). 0.152 g of **3b** was obtained from 0.238 g (1 mmol) of **1b** using general procedure A. Yield 80%; yellow oil; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.59–7.46 (m, 2H), 7.20–7.11 (m, 2H), 6.89 (d, *J* = 12.6 Hz, 1H), 5.89 (d, *J* = 12.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 1H) 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 166.4, 143.2, 139.3, 132.1, 130.0, 128.8, 118.9, 60.3, 21.4, 14.2; IR (neat) ν 3398, 3021, 1714, 1629, 1511, 1404, 1214, 1137, 1030, 762, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1072, found 191.1063.

(*Z*)-Ethyl 3-(*m*-tolyl)acrylate (3c). 0.144 g of **3c** was obtained from 0.238 g, (1 mmol) of **1c** using general procedure A. Yield 76%; orange oil; R_f = 0.40 (SiO_2, 3% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.39 (d, *J* = 9.3 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 12.6 Hz, 1H), 5.93 (d, *J* = 12.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.36 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.2, 142.9, 137.4, 134.8, 130.3, 129.7, 127.9, 126.8, 119.7, 60.2, 21.3, 14.0; IR (neat) ν 3397, 3019, 1711, 1632, 1371, 1212, 1157, 1032, 759, 660; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1072, found 191.1063.

(*Z*)-Ethyl 3-(*o*-tolyl)acrylate (3d). 0.138 g of **3d** was obtained from 0.238 g, (1 mmol) of **1d** using general procedure A. Yield 73%; yellow oil; R_f = 0.50 (SiO_2, 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.36–7.15 (m, 4H), 7.12 (d, *J* = 12.1 Hz, 1H) 6.03 (d, *J* = 12.1 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.0, 143.0, 135.7, 135.1, 129.7, 128.8, 128.4, 125.2, 121.2, 60.2, 19.9, 14.0; IR (neat) ν 3398, 3019, 1709, 1635, 1385, 1216, 1159, 1030, 757, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1072, found 191.1068.

(*Z*)-Ethyl 3-(4-ethylphenyl)acrylate (3e). 0.142 g of **3e** was obtained from 0.252 g, (1 mmol) of **1e** using general procedure A. Yield 70%; orange oil; R_f = 0.50 (SiO_2, 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.64–7.56 (m, 2H), 7.29–7.17 (m, 2H), 6.93 (d, *J* = 12.6 Hz, 1H), 5.93 (d, *J* = 12.6 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.74–2.63 (m, 2H), 1.32–1.24 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.3, 143.2, 132.2, 130.1, 127.5, 126.6, 118.8, 60.1, 38.2, 15.3, 14.1; IR (neat) ν 3411, 3019, 2968, 1714, 1629, 1511, 1385, 1180, 757, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1229, found 205.1221.

(*Z*)-Ethyl 3-(4-isopropylphenyl)acrylate (3f). 0.163 g of **3f** was obtained from 0.266 g, (1 mmol) of **1f** using general procedure A. Yield 75%; orange oil; R_f = 0.60 (SiO_2, 3% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.60–7.53 (m, 2H), 7.24–7.18 (m, 2H), 6.90 (d, *J* = 12.7 Hz, 1H), 5.89 (d, *J* = 12.7 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.91 (sep, *J* = 6.9 Hz, 1H), 1.27–1.22 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.5, 150.3, 143.3, 132.4, 130.2, 126.2, 118.9, 60.3, 34.1, 29.9, 14.2; IR (neat) ν 3412, 2963, 1712, 1630, 1401, 1215, 1169, 1066, 762 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{19}O_2$ $[M + H]^+$ 219.1385, found 219.1382.

(*Z*)-Ethyl 3-(4-(*tert*-butyl)phenyl)acrylate (3g). 0.180 g of **3g** was obtained from 0.280 g, (1 mmol) of **1g** using general procedure A. Yield 78%; orange oil; R_f = 0.50 (SiO_2, 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.62–7.56 (m, 2H), 7.41–7.36 (m, 2H), 6.91 (d, *J* = 12.6 Hz, 1H), 5.90 (d, *J* = 12.6 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.33 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.3, 152.4, 143.2, 132.0, 129.9, 125.0, 118.9, 60.2, 34.8, 31.2, 14.2; IR (neat) ν 3410, 3019, 2968, 2400, 1710, 1629, 1511, 1402, 1385, 852, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{21}O_2$ $[M + H]^+$ 233.1542, found 233.1536.

(*Z*)-Ethyl 3-(3,4-dimethylphenyl)acrylate (3h). 0.155 g of **3h** was obtained from 0.252 g, (1 mmol) of **1h** using general procedure A. Yield 76%; orange oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.43–7.36 (m, 2H), 7.15–7.08 (m, 1H) 6.87 (d, *J* = 12.6 Hz, 1H), 5.88 (d, *J* = 12.6 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.27 (s, 6H), 1.27, (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.5, 143.2, 138.0, 136.1, 132.5, 131.2, 129.4, 127.5, 118.8, 60.3, 19.8, 19.8, 14.2; IR (neat) ν 3409, 3020, 1638, 1402, 1216, 1069, 769, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{17}O_2$ $[M + H]^+$ 205.1229, found 205.1221.

(*Z*)-Ethyl 3-(4-methoxyphenyl)acrylate (3i). 0.162 g of **3i** was obtained from 0.254 g, (1 mmol) of **1i** using general procedure A. Yield 79%; yellow oil; R_f = 0.60 (SiO_2, 4% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.78–7.65 (m, 2H), 6.98–6.79 (m, 3H) 5.84 (d, *J* = 12.7, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 166.4, 160.4, 143.1, 132.1, 127.4, 117.2,

113.4, 60.1, 55.2, 14.2; IR (neat) ν 3745, 3399, 3019, 1634, 1604, 1511, 1403, 1256, 1216, 1161, 1029, 769 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1021, found 207.1015.

(*Z*)-Ethyl 3-(3-methoxyphenyl)acrylate (3j). 0.154 g of **3j** was obtained from 0.254 g, (1 mmol) of **1j** using general procedure A. Yield 75%; yellow oil; R_f = 0.40 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.32–7.20 (m, 2H), 7.16–7.08 (m, 1H), 6.95–6.84 (m, 2H), 5.94 (d, J = 12.6 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.81 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.2, 159.3, 142.6, 136.2, 129.0, 122.4, 120.0, 115.0, 114.8, 60.3, 55.3, 14.1; IR (neat) ν 3399, 3019, 1637, 1403, 1215, 1156, 768, 669 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1021, found 207.1015.

(*Z*)-Ethyl 3-(2-methoxyphenyl)acrylate (3k). 0.154 g of **3k** was obtained from 0.254 g, (1 mmol) of **1k** using general procedure A. Yield 75%; yellow oil; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) 7.60–7.46 (m, 1H) 7.38–7.27 (m, 1H), 7.16 (d, J = 12.4 Hz, 1H), 6.99–6.82 (m, 2H), 5.97 (d, J = 12.4 Hz, 1H), 4.13 (q, J = 7.1 Hz, 1H), 3.83 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.3, 157.1, 138.9, 130.7, 130.3, 124.1, 120.0, 119.8, 110.2, 60.0, 55.4, 14.0; IR (neat) ν 3398, 3019, 1708, 1633, 1464, 1403, 1251, 1215, 1160, 1068, 1027, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_3$ $[M + H]^+$ 207.1021, found 207.1015.

(*Z*)-Ethyl 3-(4-ethoxyphenyl)acrylate (3l). 0.169 g of **3l** was obtained from 0.268 g, (1 mmol) of **1l** using general procedure A. Yield 77%; yellow oil; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.74–7.61 (m, 2H), 6.92–6.73 (m, 3H), 5.81 (d, J = 12.7, 1H), 4.91 (q, J = 7.1 Hz, 2H), 4.05 (q, J = 7.0, 2H), 1.41 (t, J = 7.0 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.6, 159.9, 143.3, 132.3, 127.3, 117.2, 114.0, 63.5, 60.2, 14.8, 14.3; IR (neat) ν 3396, 3021, 1710, 1604, 1510, 1396, 1216, 1044, 765, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{17}O_3$ $[M + H]^+$ 221.1178, found 221.1164.

(*Z*)-Ethyl 3-(4-(allyloxy)phenyl)acrylate (3m). 0.167 g of **3m** was obtained from 0.280 g, (1 mmol) of **1m** using general procedure A. Yield 72%; yellow oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.75–7.64 (m, 2H), 6.93–6.86 (m, 2H), 6.82 (d, J = 12.7 Hz, 1H), 6.13–5.97 (m, 1H), 5.82 (d, J = 12.7 Hz 1H), 5.46–5.36 (m, 1H), 5.34–5.23 (m, 1H), 4.60–4.50 (m, 2H), 4.19 (q, J = 7.1 Hz, 2H), 1.27 (t, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.4, 159.4, 143.1, 133.0, 132.2, 127.5, 117.8, 117.3, 114.2, 68.7, 60.1, 14.2; IR (neat) ν 3411, 3019, 2968, 1714, 1629, 1402, 1215, 852, 757 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{17}O_3$ $[M + H]^+$ 233.1178, found 233.1177.

(*Z*)-Ethyl 3-(3-phenoxyphenyl)acrylate (3n). 0.176 g of **3n** was obtained from 0.316 g, (1 mmol) of **1n** using general procedure A. Yield 66%; orange oil; R_f = 0.60 (SiO_2, 4% EtOAc/hexanes); ^{1}HNMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.35–7.29 (m, 4H), 7.20 (s, 1H), 7.10 (t, J = 7.3 Hz, 1H), 7.03–6.96 (m, 3H), 6.88 (d, J = 12.6 Hz, 1H), 5.94 (d, J = 12.6 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.1, 157.1, 157.0, 141.9, 136.7, 129.8, 129.4, 124.6, 123.4, 120.7, 119.9, 119.4, 119.0, 60.5, 14.1; IR (neat) ν 3391, 3021, 2401, 1521, 1414, 1215, 1026, 761, 670 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{17}O_3$ $[M + H]^+$ 269.1178, found 269.1181.

(*Z*)-Ethyl 3-(2,5-dimethoxyphenyl)acrylate (3o). 0.179 g of **3o** was obtained from 0.284 g, (1 mmol) of **1o** using general procedure A. Yield 76%; yellow oil; R_f = 0.60 (SiO_2, 5% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.25–7.19 (m, 1H), 7.12 (d, J = 12.5 Hz, 1H) 6.91–6.74 (m, 2H), 5.96 (d, J = 12.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 3.76 (s, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.3, 152.9, 151.7, 138.4, 124.8, 120.3, 116.1, 115.7, 111.4, 60.2, 56.1, 55.8, 14.1; IR (neat) ν 3848, 3398, 3019, 2927, 1702, 1632, 1496, 1215, 1046, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{17}O_4$ $[M + H]^+$ 237.1127, found 237.1120.

(*Z*)-Ethyl 3-(3,4,5-trimethoxyphenyl)acrylate (3p). 0.212 g of **3p** was obtained from 0.314 g, (1 mmol) of **1p** using general procedure A. Yield 80%; yellow solid; R_f = 0.60 (SiO_2, 10% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.02 (s, 2H), 6.77 (d, J = 12.8, 1H) 5.86 (d, J = 12.8, 1H), 4.16 (q, J = 7.1, 2H), 3.84 (s, 9H), 1.24 (t, J = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 166.1, 152.5, 142.9, 139.0, 130.0, 118.7, 107.8, 60.6, 60.1, 55.9, 14.0; IR (neat) ν 3399, 3022, 1732, 1637, 1403, 1246, 1218, 770, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{14}H_{19}O_5$ $[M + H]^+$ 267.1232, found 267.1224.

Ethyl (*Z*)-3-(4-bromophenyl)acrylate (3q). 0.164 g of **3q** was obtained from 0.301 g (1 mmol) of **1q** using general procedure A. Yield 65%; orange oil; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.64–7.60 (m, 2H), 7.02 (t, J = 8.6 Hz, 2H), 6.87 (d, J = 12.6 Hz, 1H), 5.92 (d, J = 12.6 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 166.0, 142.0, 132.1, 132.0, 119.5, 115.0, 114.8, 60.3, 14.0; IR (neat) ν 3390, 3019, 2399, 1637, 1522, 1215, 831, 757 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{12}BrO_2$ $[M + H]^+$ 255.0021, found 255.0020.

Ethyl (*Z*)-3-(4-chlorophenyl)acrylate (3r). 0.136 g of **3r** was obtained from 0.258 g, (1 mmol) of **1r** using general procedure A. Yield 65%; orange oil; R_f = 0.60 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.54 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 12.7 Hz, 1H), 5.95 (d, J = 12.7 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 165.9, 141.8, 134.9, 133.3, 131.2, 128.2, 120.4, 60.4, 14.1; IR (neat) ν 3391, 3019, 2400, 1633, 1402, 1215, 929, 831 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{12}ClO_2$ $[M + H]^+$ 211.0526, found 211.0522.

Ethyl (*Z*)-3-(4-fluorophenyl)acrylate (3s). 0.126 g of **3s** was obtained from 0.242 g, (1 mmol) of **1s** using general procedure A. Yield 65%; orange oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.65–7.61 (m, 2H), 7.05–7.00 (m, 2H), 6.87 (d, J = 12.7 Hz, 1H), 5.92 (d, J = 12.7 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 165.9, 162.9 (d, J = 249.4 Hz), 142.0, 132.0 (d, J = 8.4 Hz), 130.9 (d, J = 3.2 Hz), 119.4 (d, J = 1.1 Hz), 114.9 (d, J = 21.5 Hz), 60.2, 14.0; IR (neat) ν 3684,

3022, 2401, 1713, 1631, 1511, 1421, 1215, 928, 846, 762 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{12}FO_2$ $[M + H]^+$ 195.0821, found 195.0821.

(*Z*)-Ethyl 3-(5-bromo-2-methoxyphenyl)acrylate (3t). 0.190 g of **3t** was obtained from 0.332 g, (1 mmol) of **1t** using general procedure A. Yield 67%; yellow oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.67–7.57 (m, 1H), 7.46–7.32 (m, 1H) 7.04 (d, *J* = 12.4 Hz, 1H), 6.83–6.68 (m, 1H), 5.98 (d, *J* = 12.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.1, 156.3, 137.2, 133.3, 132.7, 126.2, 121.4, 113.0, 112.0, 60.4, 55.8, 14.1; IR (neat) ν 3398, 3019, 2926, 1635, 1404, 1215, 1068, 768, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{14}BrO_3$ $[M + H]^+$ 285.0126, found 285.0125.

(*Z*)-Ethyl 3-(5-chloro-2-methoxyphenyl)acrylate (3u). 0.156 g of **3u** was obtained from 0.288 g, (1 mmol) of **1u** using general procedure A. Yield 65%; yellow oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.53–7.48 (m, 1H), 7.30–7.19 (m, 1H), 7.04 (d, *J* = 12.4 Hz, 1H), 6.89–6.74 (m, 1H), 5.98 (d, *J* = 12.4 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.0, 155.8, 137.3, 130.4, 129.7, 125.7, 124.9, 121.3, 115.5, 60.4, 55.8, 14.1; IR (neat) ν 3399, 3019, 2925, 1712, 1635, 1484, 1407, 1253, 1215, 1159, 769 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{14}ClO_3$ $[M + H]^+$ 241.0631, found 241.0630.

(*Z*)-Ethyl 3-([1,1′-biphenyl]-4-yl)acrylate (3v). 0.166 g of **3v** was obtained from 0.300 g, (1 mmol) of **1v** using general procedure A. Yield 66%; orange gum; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.77–7.69 (m, 2H), 7.67–7.56 (m, 4H), 7.50–7.43 (m, 2H), 7.41–7.34 (m, 1H), 6.98 (d, *J* = 12.7 Hz, 1H), 5.99 (d, *J* = 12.7 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.1, 142.6, 141.7, 140.4, 133.7, 130.5, 128.7, 127.5, 127.0, 126.5, 119.6, 60.2, 14.1; IR (neat) ν 3399, 3021, 1711, 1631, 1485, 1215, 1181, 1031, 854, 761 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{17}H_{17}O_2$ $[M + H]^+$ 253.1229, found 253.1226.

(*Z*)-Ethyl 3-(naphthalen-2-yl)acrylate (3w). 0.167 g of **3w** was obtained from 0.274 g, (1 mmol) of **1w** using general procedure A. Yield 74%; yellow gum; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 8.05 (s, 1H), 7.91–7.68 (m, 4H), 7.56–7.42 (m, 2H), 7.10 (d, *J* = 12.6, 1H), 6.04 (d, *J* = 12.6, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.30–1.23 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.4, 143.0, 133.5, 133.0, 132.5, 129.9, 128.5, 127.7, 127.5, 127.1, 126.8, 126.3, 120.1, 60.4, 14.2; IR (neat) ν 3408, 2932, 1630, 1397, 1068, 768, 703 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1072, found 227.1071.

(*Z*)-Ethyl 3-(naphthalen-1-yl)acrylate (3x). 0.153 g of **3x** was obtained from 0.274 g, (1 mmol) of **1x** using general procedure A. Yield 68%; orange oil; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 15.5 Hz, 0.5H), 8.26–8.18 (m, 0.5H), 7.98–7.79 (m, 4H), 7.79–7.72 (m, 0.5H), 7.65–7.40 (m, 6H), 6.55 (d, *J* = 15.7 Hz, 0.5H), 6.26 (d, *J* = 12.1 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 1.5H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 166.0, 141.9, 141.7, 133.7, 133.3, 133.1, 131.9, 131.5, 131.1, 130.5, 128.7, 128.6, 126.9, 126.6, 126.3, 125.9, 125.5, 125.0, 124.5, 123.5, 122.9, 121.0, 60.6, 60.2, 14.4, 13.9; IR (neat) ν 3399, 3019, 2928, 2349, 1634, 1584, 1403, 1215, 1155, 1068 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{15}H_{15}O_2$ $[M + H]^+$ 227.1072, found 227.1071.

Ethyl (*Z*)-3-(4-((trimethylsilyl)ethynyl)phenyl)acrylate (3y). 0.190 g of **3y** was obtained from 0.320 g, (1 mmol) of **1y** using general procedure A. Yield 70%; orange oil; R_f = 0.6 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.47–7.41 (m, 2H), 6.88 (d, *J* = 12.4 Hz, 1H), 5.95 (d, *J* = 12.4 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.0, 142.0, 134.9, 131.5, 129.7, 123.7, 120.5, 104.9, 95.6, 60.4, 14.1, 0.02; IR (neat) ν 3019, 2399, 1602, 1522, 1476, 1215, 1024, 758 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{21}O_2Si$ $[M + H]^+$ 273.1311, found 273.1285.

(*Z*)-Ethyl 3-(2-((trimethylsilyl)ethynyl)phenyl)acrylate (3z). 0.184 g of **3z** was obtained from 0.320 g, (1 mmol) of **1z** using general procedure A. Yield 68%; yellow oil; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, *Z*/*E* mixture) δ 7.68–7.57 (m, 1.4H), 7.55–7.46 (m, 1.6H), 7.38–7.21 (m, 4.4 Hz), 6.06 (d, *J* = 12.4, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*/*E* mixture) δ 166.8, 166.0, 142.3, 141.6, 137.5, 136.2, 133.0, 132.2, 129.5, 129.3, 128.8, 128.3, 127.8, 126.2, 123.8, 122.8, 121.5, 121.2, 120.0, 103.2, 102.6, 101.1, 99.8, 60.5, 60.3, 14.3, 14.0, 0.02, 0.05; IR (neat) ν 3021, 2272, 1730, 1593, 1487, 1216, 1085, 766 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{16}H_{21}O_2Si$ $[M + H]^+$ 273.1311, found 273.1285.

(*Z*)-Ethyl 3-(furan-2-yl)acrylate (3za). 0.116 g of **3za** was obtained from 0.214 g, (1 mmol) of **1za** using general procedure A. Yield 70%; orange gum; R_f = 0.50 (SiO_2, 3% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 7.71–7.62 (m, 1H), 7.50–7.43 (m, 1H), 6.77 (d, *J* = 12.9 Hz, 1H), 6.51–6.46 (m, 1H), 5.73 (d, *J* = 12.9 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 166.2, 151.0, 144.0, 130.5, 117.1, 114.6, 112.7, 60.3, 14.4; IR (neat) ν 3400, 3019, 1638, 1403, 1216, 1069, 769, 669 cm^{-1}; HRMS (ESI-TOF) calcd for $C_9H_{11}O_3$ $[M + H]^+$ 167.0708, found 167.0716.

(*Z*)-Ethyl 3-(furan-3-yl)acrylate (3zb). 0.112 g of **3zb** was obtained from 0.214 g, (1 mmol) of **1zb** using general procedure A. Yield 68%; brown gum; R_f = 0.40 (SiO_2, 2% EtOAc/hexanes); ^1H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 8.11 (s, 1H), 7.42–7.36 (m, 1H), 6.95–6.90 (m, 1H), 6.69 (d, *J* = 12.5 Hz, 1H), 5.79 (d, *J* = 12.5 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 1H 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 166.3, 147.0, 142.9 133.6, 121.3, 116.8, 112.3, 60.1, 14.3; HRMS (ESI-TOF) calcd for $C_9H_{11}O_3$ $[M + H]^+$ 167.0708, found 167.0718.

(*Z*)-Ethyl 3-(benzofuran-2-yl)acrylate (3zc). 0.151 g of **3zc** was obtained from 0.264 g, (1 mol) of **1zc** using general procedure A. Yield 70%; yellow gum; R_f = 0.50 (SiO_2, 4% EtOAc/hexanes);

^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 7.95 (s, 1H), 7.66–7.59 (m, 1H), 7.48–7.42 (m, 1H), 7.38–7.30 (m, 1H), 7.27–7.19 (m, 1H), 6.88 (d, J = 12.9 Hz, 1H), 5.96 (d, J = 12.9 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 165.9, 154.9, 151.7, 130.3, 128.9, 126.2, 123.2, 122.3, 118.7, 112.6, 111.3, 60.5, 14.3; IR (neat) ν 3399, 3021, 1709, 1633, 1425, 1215, 1021, 761, 669 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{13}H_{13}O_3$ $[M + H]^+$ 217.0865, found 217.0852.

(*Z*)-Ethyl 3-(4-nitrophenyl)acrylate (3zd). 0.143 g of **3zd** was obtained from 0.269 g, (1 mmol) of **1zd** using general procedure A. Yield 65%; yellow solid; R_f = 0.6 (SiO_2, 5% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 8.32–8.10 (m, 2H), 7.76–7.59 (m, 2H), 7.00 (d, J = 12.5 Hz, 1H), 6.12 (d, J = 12.5 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 165.4, 147.6, 141.6, 140.6, 130.3, 123.4, 123.2, 60.8, 14.1; IR (neat) ν 3401, 3020, 1594, 1514, 1402, 1385, 1258, 1067, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{12}NO_4$ $[M + H]^+$ 222.0766, found 222.0774.

(*Z*)-Ethyl 3-(3-nitrophenyl)acrylate (3ze). 0.141 g of **3ze** was obtained from 0.269 g, (1 mmol) of **1ze** using general procedure A. Yield 64%; orange gum; R_f = 0.7 (SiO_2, 5% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 8.43 (s, 1H), 8.24–8.12 (m, 1H) 7.92–7.81 (m, 1H), 7.59–7.48 (m, 1H), 6.99 (d, J = 12.5 Hz, 1H), 6.11 (d, J = 12.5 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 165.5, 140.5, 136.5, 135.5, 129.0, 124.5, 123.5, 122.8, 115.3, 60.8, 14.1; IR (neat) ν 3408, 3020, 1590, 1402, 1385, 1215, 1154, 1068, 757 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{12}NO_4$ $[M + H]^+$ 222.0766, found 222.0772.

Ethyl (*Z*)-3-(4-fluoro-3-nitrophenyl)acrylate (3zf). 0.155 g of **3zf** was obtained from 0.287 g, (1 mmol) of **1zf** using general procedure A. Yield 65%; orange oil; R_f = 0.60 (SiO_2, 5% Ehexanes); ^{1}H NMR (400 MHz, $CDCl_3$, *Z* isomer) δ 8.34 (dd, J = 7.1, 2.2 Hz, 1H), 7.86–7.90 (m, 1H), 7.26 (dd, J = 10.4, 8.7 Hz, 1H), 6.89 (d, J = 12.5 Hz, 1H), 6.08 (d, J = 12.5 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z* isomer) δ 165.4, 15.5 (d, J = 262.7 Hz), 139.6, 136.9 (d, J = 8.6), 131.8 (d, J = 4.3 Hz), 127.5, 122.6, 118.0 (d, J = 21.0 Hz), 60.9, 14.1; IR (neat) ν 3407, 3020, 1630, 1531, 1400, 1379, 1261, 1066, 770, 666 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{11}FNO_2$ $[M + H]^+$ 240.0672, found 240.0670.

(*Z*)-Ethyl 3-(4-bromo-3-nitrophenyl)acrylate (3zg). 0.202 g of **3zg** was obtained from 0.346 g, (1 mmol) of **1zg** using general procedure A. Yield 68%; yellow gum; R_f = 0.50 (SiO_2, 5% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, major *Z* isomer) δ 8.13–8.07 (m, 1H), 7.77–7.47 (m, 2H), 6.92–6.74 (m, 2H), 6.09 (d, J = 12.5 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, major *Z* isomer) δ 165.3, 139.4, 135.4, 134.6, 134.2, 129.5, 126.6, 123.0, 115.3, 60.9, 14.0; IR (neat) ν 3409, 3020, 1638, 1537, 1402, 1385, 1216, 1069, 769, 668 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{11}H_{11}BrNO_4$ $[M + H]^+$ 299.9871, found 299.9865.

Ethyl 3-phenylbut-2-enoate (3zh). 0.142 g of **3zh** was obtained from 0.238 g (1 mmol) of **1zh** using general procedure A. Yield 75%; yellow oil; R_f = 0.4 (SiO_2, 2% EtOAc/hexanes); ^{1}H NMR (400 MHz, $CDCl_3$, *Z*/*E* mixture) δ 7.53–7.43 (m, 2H), 7.41–7.28 (m, 6H), 7.25–7.16 (m, 2H), 6.14 (d, J = 1.2 Hz, 1H), 5.91 (d, J = 1.4 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 4.00 (q, J = 7.1 Hz, 2H), 2.58 (d, J = 1.2 Hz, 3H), 2.18 (d, J = 1.4 Hz, 3H), 1.32 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, *Z*/*E* mixture) δ 166.9, 165.9, 155.5, 155.3, 142.3, 140.9, 129.0, 128.5, 127.9, 127.7, 126.9, 126.3, 117.8, 117.2, 59.8, 59.8, 27.1, 18.0, 14.4, 14.0; IR (neat) ν 3400, 3020, 2981, 2927, 1708, 1630, 1488, 1444, 1273, 1165, 1045, 855, 697 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{12}H_{15}O_2$ $[M + H]^+$ 191.1072, found 191.1068.

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