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Pd-Catalyzed Threefold Arylation of Baylis–Hillman Bromides and Acetates with Triarylbismuth Reagents

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Dedicated to Professor Mariappan Periasamy on the occasion of his 60th birthday

Keywords: Bismuth / Palladium / Alkenes / Synthetic methods / C–C coupling

Functionalized alkyl 2-benzylacrylates and 2-benzylacrylonitriles were synthesized by means of atom-economic cross-couplings of Baylis–Hillman bromides or acetates with $BiAr_3$ under palladium-catalyzed conditions. These reactions, involving threefold aryl couplings using $BiAr_3$ reagents with bromides and acetates, are fast and are completed in 1–2 h with high product yields.

Introduction

Synthetic organic chemistry is profoundly enriched by Baylis–Hillman applications in a variety of synthetic transformations.[1] In particular, Baylis–Hillman adducts or their derivatives are extremely useful even under metal-catalyzed conditions.[2] Interestingly, Baylis–Hillman adduct derivatives such as 2-(halomethyl)acrylates, 2-(acetoxymethyl)-acrylates, or 2-(acetoxymethyl)acrylonitriles are important substrates in organic synthesis.[3] For example, 2-halomethylacrylates can be easily prepared through Baylis–Hillman/halogenation procedure[4] and are used in several reactions.[5] These substrates are employed (i) in the preparation of organotin[5a–5c] or organozinc[5d–5f] derivatives and are employed in metal-catalyzed reactions; (ii) in palladium-catalyzed cascade reactions[5g] to synthesize 3,3-disubstituted-2,3-dihydrobenzofurans; (iii) in couplings with arylzinc and heteroarylzinc,[5h] vinylzinc,[5i] and organomagnesium[5j] reagents, etc. Similarly, Baylis–Hillman acetates have also been frequently utilized in various metal-catalyzed[6] and other transformations.[7] The advantage of using these substrates is that they provide a onetime installation of multifunctional three-carbon skeleton of synthetic importance; for these reasons the search for new applications is continuing unabated.

Palladium-catalyzed cross-coupling reactions are prominently employed in organic synthesis for C–C bond formation with a variety of organometallic reagents.[8] Reactions such as the Suzuki, Negishi or similar couplings are usually limited to one C–C bond formation using the respective organoboron, zinc, or other reagents. Our sustained efforts in this area using triarylbismuths as atom-economic threefold arylating organometallic reagents led to the development of a new generation of coupling reactions with a variety of organic electrophiles under palladium catalysis.[9]

Allylic substrates are also important in cross-coupling reactions and considerable differences exist in the reactivity of these substrates under metal-catalyzed conditions.[2,5] Recently, we have demonstrated the novel cross-coupling reactivity of triarylbismuths with various allylic coupling partners under palladium-catalyzed conditions. For example, (*E*)-cinnamyl acetates,[9d] (*E*)-cinnamyl carbonates,[9e] and halide derivatives of Baylis–Hillman adducts[9f] reacted well in couplings with triarylbismuths under palladium-catalyzed thermal conditions. Therefore, it was of interest to further explore the coupling reactivity of Baylis–Hillman adducts derived from methyl 2-(bromomethyl)acrylate, methyl 2-(acetoxymethyl)acrylate, and 2-(acetoxymethyl)-acrylonitrile with triarylbismuth reagents. To our surprise, for example, alkyl 2-(bromomethyl)acrylates showed remarkable reactivity even at room temperature, whereas the corresponding acetates reacted under thermal conditions using palladium catalytic protocols. We report these studies herein.

Results and Discussion

Initially, we chose the combination of methyl 2-bromomethylacrylate (4 equiv.) and $BiPh_3$ (1 equiv.) to explore the coupling conditions, as summarized in Table 1. We began the coupling study with two different palladium catalysts and found that $[Pd(PPh_3)_4]$ was more effective, furnishing

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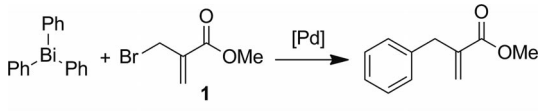
methyl 2-benzylacrylate in 73% yield (Table 1, entries 1–2). This demonstrated the facile reactivity of three equivalents of methyl 2-bromomethylacrylate with one equivalent of $BiPh_3$, resulting in threefold phenyl couplings with high product yield. We then proceeded to examine the reaction under different sets of conditions. For example, the reactions with a range of carbonate bases provided yields up to 61–70% (Table 1, entries 3–5). From this, it was pleasing to note that the couplings with K_3PO_4 base was more productive and gave relatively higher yield (Table 1, entry 2). The effect of temperature was then studied (Table 1, entries 6–8). Interestingly, the cross-coupling was facile even at room temperature, with 83% product yield being obtained (Table 1, entry 8). Encouragingly, coupling with 3.3 equivalents of methyl 2-bromomethylacrylate afforded the desired product in 91% yield (Table 1, entry 9). Hence, it was decided to use 3.3 equivalents of methyl 2-bromomethylacrylate for further screenings.

Table 1. Screening with Baylis–Hillman bromide.[a,b]



(1 equiv.) (4 or 3.3 equiv.) (3 equiv.)

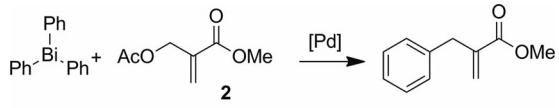
Entry	Catalyst/ ligand	**1** [equiv.]	Base	Solvent	*T* [°C]	Yield [%]
1	$Pd(OAc)_2$ /2PPh_3	4	K_3PO_4	DMF	90	65
2	$Pd(PPh_3)_4$	4	K_3PO_4	DMF	90	73
3	$Pd(PPh_3)_4$	4	Cs_2CO_3	DMF	90	70
4	$Pd(PPh_3)_4$	4	K_2CO_3	DMF	90	64
5	$Pd(PPh_3)_4$	4	Na_2CO_3	DMF	90	61
6	$Pd(PPh_3)_4$	4	K_3PO_4	DMF	60	88
7	$Pd(PPh_3)_4$	4	K_3PO_4	DMF	40	86
8	$Pd(PPh_3)_4$	4	K_3PO_4	DMF	25	83
9	$Pd(PPh_3)_4$	3.3	K_3PO_4	DMF	25	91
10	$Pd(PPh_3)_4$	3.3	K_3PO_4	NMP	25	75
11	$Pd(PPh_3)_4$	3.3	K_3PO_4	THF	25	72
12	$Pd(PPh_3)_4$	3.3	K_3PO_4	MeCN	25	70
13	$Pd(PPh_3)_4$	3.3	K_3PO_4	DMF	25	68[c]
14	$Pd(PPh_3)_4$	3.3	none	DMF	60	55[d]
15	none	3.3	K_3PO_4	DMF	60	–[e]

[a] Reaction conditions: $BiPh_3$ (0.25 mmol, 1.0 equiv.), Pd catalyst (0.0225 mmol, 0.09 equiv.), methyl 2-(bromomethyl)acrylate (1 mmol or 0.825 mmol, 4 or 3.3 equiv.), base (0.25 mmol, 1.0 equiv.), solvent (3 mL), 1 h. [b] Isolated yield. [c] With 1 mol-% catalyst. [d] Control without base. [e] Control without catalyst.

At this stage, a coupling study with a range of solvents such as acetonitrile, tetrahydrofuran, and *N*-methyl-2-pyrrolidinone (NMP), furnished 70–75% yield (Table 1, entries 10–12), whereas employing 1 mol-% catalyst afforded 68% yield of the desired product (Table 1, entry 13). Two independent control experiments without base and catalyst gave moderate or no coupling, respectively (Table 1, entries 14 and 15). During this screening, a biphenyl side product was formed in 10–15% yield, through a known homocoupling of triarylbismuths under palladium catalysis.[10] The present screening studies led us to the standardized conditions involving $[Pd(PPh_3)_4]$ catalyst with K_3PO_4 base in *N*,*N*-dimethylformamide (DMF) solvent at room temperature to obtain high yields of cross-coupling product (Table 1, entry 9). These conditions were used for further studies.

The high cross-coupling reactivity of $BiPh_3$ even at room temperature in threefold couplings with three equivalents of allylic substrate was pleasantly surprising and encouraged us to extend our study to the corresponding acetates under palladium-catalyzed conditions (Table 2). The cross-coupling of Baylis–Hillman acetate was initially carried out using the conditions established above (Table 2, entry 1). However, this attempt did not furnish the desired couplings with acetate at room temperature. Furthermore, the coupling reaction with $[Pd(PPh_3)_4]$ and K_3PO_4 base in DMF under thermal conditions at 60 °C furnished the product in only 61% yield (Table 2, entry 2).

Table 2. Screening with Baylis–Hillman acetate.[a,b]



(1 equiv.) (4 equiv.) (3 equiv.)

Entry	Catalyst	Base	Solvent	*T* [°C]	Yield [%]
1	$Pd(PPh_3)_4$	K_3PO_4	DMF	25	–[c]
2	$Pd(PPh_3)_4$	K_3PO_4	DMF	60	61
3	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	60	81
4	$PdCl_2(PPh_3)_2$	Cs_2CO_3	DMF	60	68
5	$PdCl_2(PPh_3)_2$	K_2CO_3	DMF	60	64
6	$PdCl_2(PPh_3)_2$	K_3PO_4	DMA	60	69
7	$PdCl_2(PPh_3)_2$	K_3PO_4	NMP	60	72
8	$PdCl_2(PPh_3)_2$	K_3PO_4	THF	60	–
9	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	40	73
10	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	90	63
11	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	60	76[d]
12	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	60	61[e]
13	$PdCl_2(PPh_3)_2$	K_3PO_4	DMF	60	69[f]
14	$PdCl_2(PPh_3)_2$	none	DMF	60	(34)[g]
15	none	K_3PO_4	DMF	60	–[h]

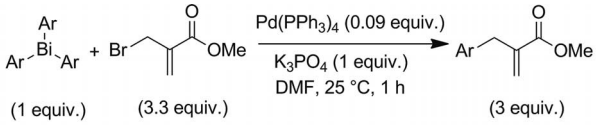
[a] Reaction conditions: Methyl 2-(acetoxymethyl)acrylate (1.0 mmol, 4.0 equiv.), $BiPh_3$ (0.25 mmol, 1.0 equiv.), Pd catalyst (0.0225 mmol, 0.09 equiv.), base (0.50 mmol, 2.0 equiv.), solvent (3 mL), 2 h. [b] Isolated yield of product. [c] Reaction with methyl 2-(acetoxymethyl)acrylate (0.825 mmol, 3.3 equiv.), base (0.25 mmol, 1 equiv.), 1 h. [d] Methyl 2-(acetoxymethyl)acrylate (0.825 mmol, 3.3 equiv.), 1 h. [e] With 3 mol-% catalyst. [f] With 1 equiv. K_3PO_4 base. [g] Control reaction without base, GC conversion shown in parentheses. [h] Control reaction without catalyst.

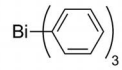
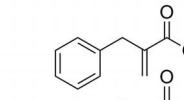
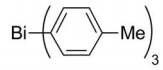
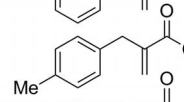
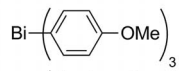
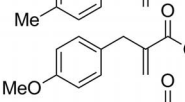
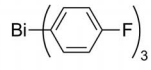
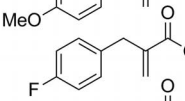
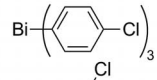
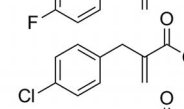
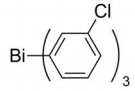
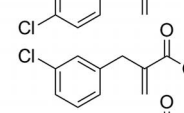
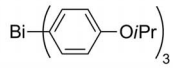
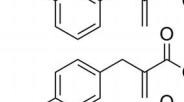
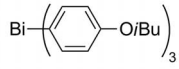
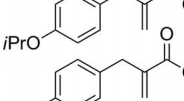
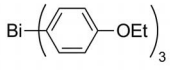
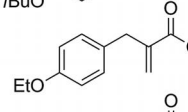
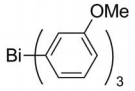
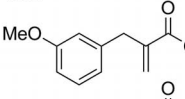
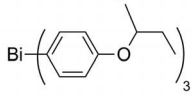
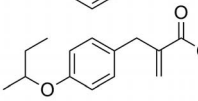
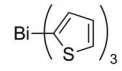
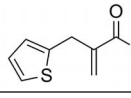
Additional investigations with $[PdCl_2(PPh_3)_2]$ as catalyst produced 81% yield (Table 2, entry 3). Different bases such as Cs_2CO_3 and K_2CO_3 afforded moderate yields (Table 2, entries 4 and 5), whereas the use of *N*,*N*-dimethylacetamide (DMA) or *N*-methyl-2-pyrrolidinone (NMP) as solvents gave 69 and 72% yield, respectively (Table 2, entries 6 and 7). Tetrahydrofuran (THF) solvent was found to be ineffective for this reaction (Table 2, entry 8). Conducting the coupling reactions either at 40 or 90 °C did not furnish high

yields (Table 2, entries 9 and 10) in comparison to the yield obtained at 60 °C (Table 2, entry 3). The reaction with 3.3 equivalents of acetate gave inferior coupling yield (Table 2, entry 11). Low catalyst loading and the use of 1 equivalent of base furnished moderate yields (Table 2, entries 12 and 13). Expectedly, performing the reaction without base or catalyst gave poor or no conversion, respectively (Table 2, entries 14 and 15). These efforts revealed that the conditions with $[PdCl_2(PPh_3)_2]$ as catalyst and K_3PO_4 (2 equiv.) as base in DMF solvent was high yielding for coupling reactions involving acetates (Table 2, entry 3). Biphenyl as a minor side product was formed in 10–15% yields in these reactions, and this amount was higher in reactions for which there was no cross-coupling reaction. From the above study, the Baylis–Hillman bromide was shown to be more reactive at room temperature than the corresponding acetate and, hence, demonstrated high reactivity under palladium catalytic conditions.

To evaluate the generality of the method, methyl 2-bromomethylacrylate was treated with a range of $BiAr_3$ reagents under the established room temperature conditions (Table 3). It is noteworthy that the coupling reaction of methyl 2-bromomethylacrylate showed high reactivity with electronically different $BiAr_3$ reagents. This evaluation

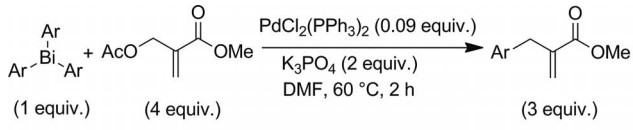
Table 3. Couplings of bromide with $BiAr_3$ reagents.[a]

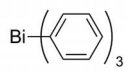
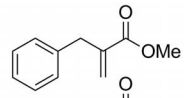
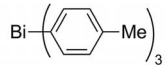
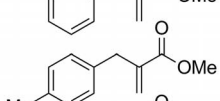
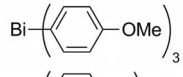
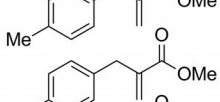
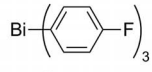
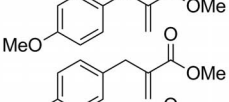
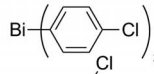
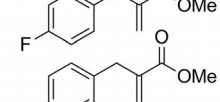
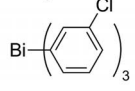
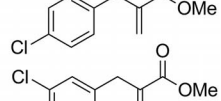
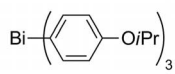
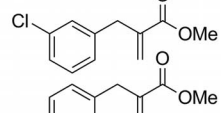


Entry	$BiAr_3$	Methyl 2-benzylacrylate		Yield [%][b]
1			**1a**	91
2			**2a**	85
3			**3a**	86
4			**4a**	90
5			**5a**	86
6			**6a**	87
7			**7a**	83
8			**8a**	82
9			**9a**	83
10			**10a**	94
11			**11a**	78
12			**12a**	74

[a] Reaction conditions: 2-(bromomethyl)acrylate (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), K_3PO_4 (0.25 mmol, 1 equiv.), $[Pd(PPh_3)_4]$ (0.0225 mmol, 0.09 equiv.), DMF (3 mL), 25 °C, 1 h. Biaryls as a minor homocoupling product was formed in all reactions. All products were identified by ^1H NMR, ^{13}C NMR, and IR spectroscopy and additionally by ESI-HRMS or EI-HRMS. [b] Isolated yield.

Table 4. Couplings of acetate with $BiAr_3$ reagents.[a]



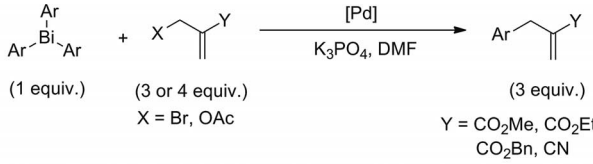
Entry	$BiAr_3$	Methyl 2-benzylacrylate		Yield [%][b]
1			**1a**	81
2			**2a**	78
3			**3a**	80
4			**4a**	61
5			**5a**	60
6			**6a**	47
7			**7a**	76
8			**8a**	71
9			**10a**	68
10			**13a**	61
11			**14a**	79
12			**15a**	77

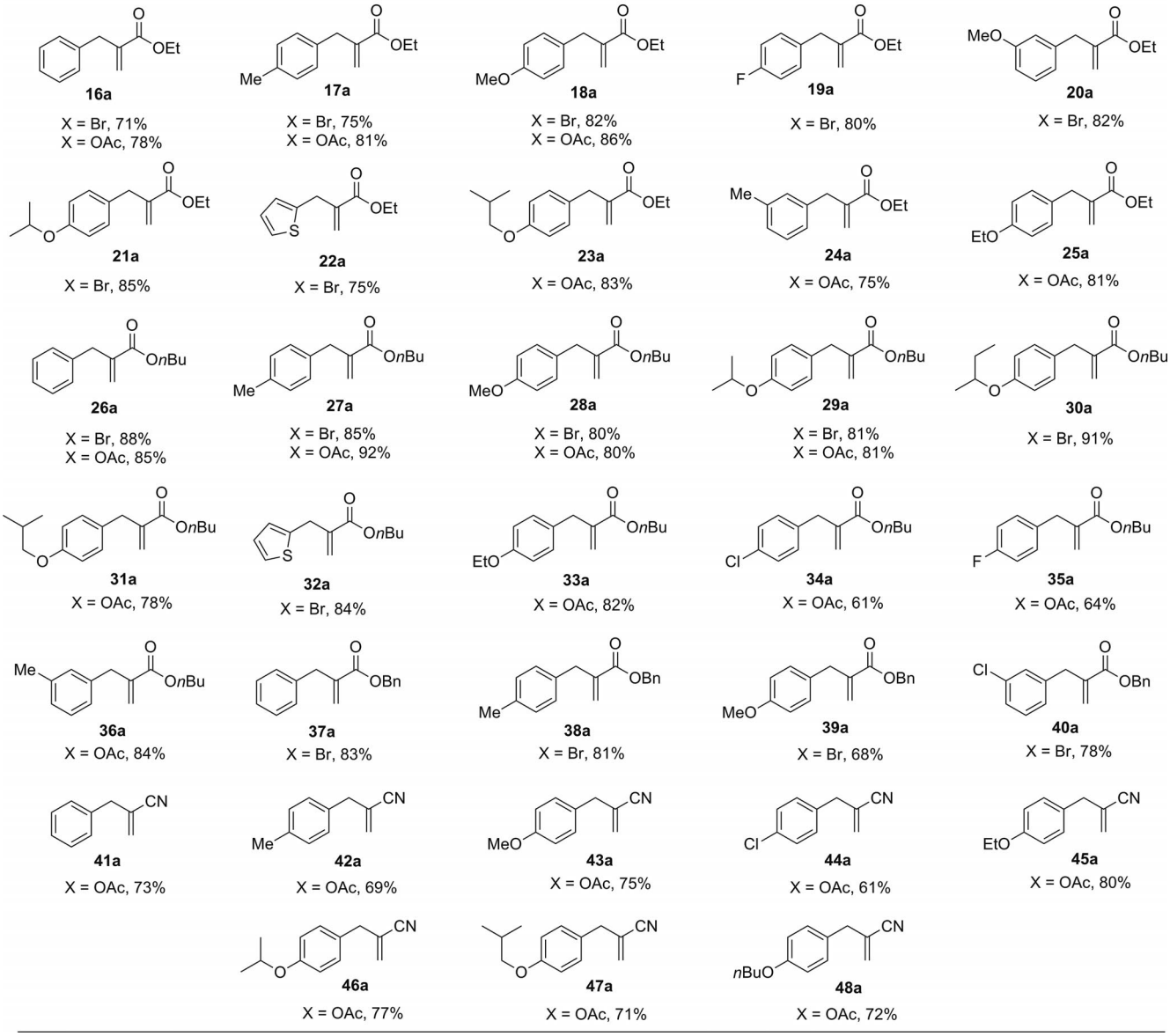
[a] Reaction conditions: methyl 2-(acetoxymethyl)acrylate (1 mmol, 4 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), K_3PO_4 (0.50 mmol, 2 equiv.), $[PdCl_2(PPh_3)_2]$ (0.0225 mmol, 0.09 equiv.), DMF (3 mL), 60 °C, 2 h. Biaryls as a minor side homocoupling product was formed in all reactions. All products were identified by ^1H NMR, ^{13}C NMR, and IR spectroscopy and additionally by ESI-HRMS or EI-HRMS. [b] Isolated yield.

using both electron-rich and electron-deficient $BiAr_3$ reagents gave the corresponding functionalized methyl 2-benzylacrylates products in excellent yields. It is particularly noteworthy to mention that tris-2-thiophenylbismuth also afforded the corresponding cross-coupled product methyl 2-(thiophen-2-yl)acrylate in high yield. Importantly, synthesis of this product through Heck couplings involving 2-bromothiophene and methyl acrylate was earlier reported to give a mixture of products and required a longer reaction time.[11]

Further elaboration of the coupling reactivity of Baylis–Hillman acetate was carried out with $BiAr_3$ reagents under the optimized conditions (Table 4). The couplings of different $BiAr_3$ reagents were facile and gave the corresponding arylated products in moderate to high yields in all cases.

Table 5. Couplings of different bromides and acetates with $BiAr_3$ reagents.[a,b]





[a] Reaction conditions for bromides: 2-(Bromomethyl)acrylate (0.825 mmol, 3.3 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), K_3PO_4 (0.25 mmol, 1 equiv.), $[Pd(PPh_3)_4]$ (0.0225 mmol, 0.09 equiv.), DMF (3 mL), 25 °C, 1 h. Reaction conditions for acetates: 2-(Acetoxymethyl)-acrylate (or) 2-(acetoxymethyl)acrylonitrile (1 mmol, 4 equiv.), $BiAr_3$ (0.25 mmol, 1 equiv.), K_3PO_4 (0.50 mmol, 2 equiv.), $[PdCl_2(PPh_3)_2]$ (0.0225 mmol, 0.09 equiv.), DMF (3 mL), 60 °C, 2 h. Biaryls as a minor side homocoupling product was formed in all reactions. All products were identified by ^1H NMR, ^{13}C NMR, and IR spectroscopy and additionally by ESI-HRMS or EI-HRMS. [b] Isolated yield.

The demonstrated novel and efficient coupling reactivity of both Baylis–Hillman bromide and acetate with a range of triarylbismuths under different conditions, prompted further studies with alkyl 2-(bromomethyl)acrylates, alkyl 2-(acetoxymethyl)acrylates, and 2-(acetoxymethyl)acrylonitrile, as summarized in Table 5. Ethyl and *n*-butyl derivatives of 2-bromomethylacrylates that were required for this study were synthesized by using literature procedures.[4] The corresponding benzyl derivative was also prepared by literature methods.[12a,12b] Alkyl 2-(acetoxymethyl)acrylates and 2-(acetoxymethyl)acrylonitriles were also obtained by using known methods.[12c] Thus, a series of coupling reactions conducted using alkyl 2-(bromomethyl)acrylates with ethyl, *n*-butyl and benzyl derivatives and different $BiAr_3$ reagents demonstrated promising reactivity under established palladium catalytic protocols. Encouragingly, $BiAr_3$ reagents in all cases provided three aryl groups for threefold couplings in reactions with bromides under room temperature conditions to give the corresponding 2-benzylacrylates in short reaction times. The corresponding reactivity of alkyl 2-(acetoxymethyl)acrylates is also noteworthy because these substrates reacted with a range of $BiAr_3$ reagents under thermal conditions with high yields. Further couplings with a different class of 2-(acetoxymethyl)acrylonitrile also demonstrated high reactivity with $BiAr_3$ reagents. Overall, these attempts demonstrated the atom-efficient multiple-coupling reaction of triarylbismuth reagents in threefold couplings with three equivalents of different allylic coupling partners in short reaction time in a palladium-catalyzed one-pot operation.

In this context, it should be mentioned that the previously known coupling reactions of allylic acetates,[9d] allylic carbonates,[9e] and halide derivatives of Baylis–Hillman adducts[9f] and allylic bromides[13] reacted under thermal conditions. Indeed, to the best of our knowledge, the present study is the first report on the room temperature coupling reactions of alkyl 2-bromomethylacrylates with $BiAr_3$ under palladium-catalyzed conditions. The reactivity of the corresponding acetates under thermal conditions was in accordance with earlier findings.

As noted above, the majority of products in this study were obtained in excellent yields. Known methods to synthesize some of these products are cumbersome in many ways,[14] whereas the present method is atom-economic, with threefold arylations effected by nontoxic $BiAr_3$ under straightforward coupling conditions. Most importantly, the coupling products obtained are highly sought-after as important building blocks for the synthesis of a variety of compounds that are useful in medicinal applications,[15] for hypoglycemic[15a] activity studies, human rennin inhibition[15b] studies, and HIV-1 protease inhibition[15c] studies. These products are also useful precursors for various other synthetic transformations.[16]

Conclusions

We have demonstrated novel cross-coupling reactions of various alkyl 2-(bromomethyl)acrylates, alkyl 2-(acetoxymethyl)acrylates, and 2-(acetoxymethyl)acrylonitrile in threefold couplings with $BiAr_3$ reagents under the established palladium-catalyzed coupling conditions for easy preparation of the functionalized alkyl 2-benzylacrylates and 2-benzylacrylonitriles in an atom-economic manner and in a one-pot operation. The reactions involving threefold aryl couplings using $BiAr_3$ reagents are fast (completed in 1–2 h) and high-yielding. This study demonstrated a general approach to the synthesis of various functionalized alkyl 2-benzylacrylates and 2-benzylacrylonitriles, which are useful for further applications in synthetic organic chemistry.

Experimental Section

General Methods: Triarylbismuth compounds were prepared either through aryllithium or Grignard reagents according to the literature procedures.[10b] All solvents employed were dried according to standard procedures. Analytical thin layer chromatography was performed on precoated aluminium plates with GF_{254} silica (Spectrochem, Mumbai). Products were isolated by column chromatography on 100–200 mesh silica gel by using a mixture of EtOAc and petroleum ether as eluent. GC analyses were performed with a Perkin Elmer (Clarus 500) gas chromatograph. ^1H NMR and ^{13}C NMR spectra were recorded with a JEOL-Delta (500 MHz) spectrometer by using $CDCl_3$ as solvent. Chemical shift values (δ) for protons and carbon atoms are expressed in parts per million (ppm) with respect to TMS. IR spectra were recorded with a Bruker Vector 22 FT-IR spectrometer. HR mass spectra were measured with a Waters HAB213 instrument by using the electrospray (ES) technique and with a CAB155 micromass spectrometer by using the electroionization (EI) technique.

Coupling of 2-(Bromomethyl)acrylates with $BiAr_3$ Reagents; Typical Procedure: To an oven-dried Schlenk tube, $BiPh_3$ (0.25 mmol, 110 mg, 1.0 equiv.), methyl 2-(bromomethyl)acrylate (0.825 mmol, 147.6 mg, 3.3 equiv.), K_3PO_4 (0.25 mmol, 53.0 mg, 1.0 equiv.), $[Pd(PPh_3)_4]$ (0.0225 mmol, 26.0 mg, 0.09 equiv.), and DMF (3 mL) were added under an N_2 atmosphere. The resulting mixture was stirred at 25 °C for 1 h, then extracted with ethyl acetate and submitted to usual workup procedures.[9a] The pure product **1a** was obtained as a colorless liquid (0.12 g, 91%). The isolated yield was calculated based on 3-phenyl couplings from $BiPh_3$ (thus, 0.75 mmol of the product corresponds to a 100% yield).

Coupling of 2-(Acetoxymethyl)acrylates with $BiAr_3$ Reagents; Typical Procedure: The above representative procedure given for the couplings of 2-(bromomethyl)acrylates was also followed for the coupling reactions of 2-(acetoxymethyl)acrylates with the following reaction conditions; $BiPh_3$ (0.25 mmol, 110 mg, 1.0 equiv.), methyl 2-(acetoxymethyl)acrylate (1 mmol, 158.0 mg, 4.0 equiv.), K_3PO_4 (0.50 mmol, 106.1 mg, 2.0 equiv.), $[PdCl_2(PPh_3)_2]$ (0.0225 mmol, 15.8 mg, 0.09 equiv.) and DMF (3 mL), 60 °C, 2 h.

Methyl 2-Benzylacrylate (1a):[14g,17] Colorless liquid (0.12 g, 91%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.30 (m, 5 H, PhH), 6.22 (br. s, 1 H, C=CH_2), 5.45 (br. s, 1 H, C=CH_2), 3.73 (s, 3 H, OCH_3), 3.62 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.3, 140.0, 138.6, 129.0, 128.4, 126.3, 126.2, 51.8, 38.0 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1438, 1255, 1203, 1137, 948, 701 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{12}O_2$ $[M + H]^+$ 177.0916; found 177.0916.

Methyl 2-(4-Methylbenzyl)acrylate (2a):[17] Colorless liquid (0.121 g, 85%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.07–7.09 (m, 4

H, ArH), 6.21 (br. s, 1 H, C=CH_2), 5.45 (br. s, 1 H, C=CH_2), 3.73 (s, 3 H, OCH_3), 3.59 (s, 2 H, CH_2), 2.31 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 140.2, 135.8, 135.5, 129.0, 128.8, 126.0, 51.8, 37.5, 21.0 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1437, 1280, 1254, 1202, 1137, 947, 808 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}O_2$ [M + H]$^+$ 191.1072; found 191.1078.

Methyl 2-(4-Methoxybenzyl)acrylate (3a): Colorless liquid (0.133 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (d, J = 8.6 Hz, 2 H, ArH), 6.82 (d, J = 8.9 Hz, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.43 (br. s, 1 H, C=CH_2), 3.77 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.56 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.5, 158.1, 140.5, 130.7, 130.1, 126.1, 113.9, 55.3, 52.0, 37.2 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1437, 1258, 1203, 1136, 1050, 950, 785, 700 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}NaO_3$ [M + Na]$^+$ 229.0841; found 229.0844.

Methyl 2-(4-Fluorobenzyl)acrylate (4a): Colorless liquid (0.131 g, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13–7.15 (m, 2 H, ArH), 6.94–6.98 (m, 2 H, ArH), 6.21 (br. s, 1 H, C=CH_2), 5.45 (br. s, 1 H, C=CH_2), 3.72 (s, 3 H, OCH_3), 3.58 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.2, 161.5 (d, J = 243.2 Hz), 139.9, 134.2, 130.4 (d, J = 7.1 Hz), 126.3, 115.2 (d, J = 21.4 Hz), 51.9, 37.2 ppm. IR (film): $\tilde{\nu}$ = 1722, 1632, 1509, 1222, 1137, 841, 818 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{11}FO_2$ [M + H]$^+$ 195.0821; found 195.0826.

Methyl 2-(4-Chlorobenzyl)acrylate (5a):[17] Colorless liquid (0.136 g, 86%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.24–7.25 (m, 2 H, ArH), 7.11–7.13 (m, 2 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.47 (br. s, 1 H, C=CH_2), 3.72 (s, 3 H, OCH_3), 3.58 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 139.5, 137.1, 132.1, 130.3, 128.5, 126.5, 51.9, 37.4 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1491, 1437, 1203, 1137, 1090, 1016, 800 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{11}ClNaO_2$ [M + Na]$^+$ 233.0345; found 233.0346.

Methyl 2-(3-Chlorobenzyl)acrylate (6a): Colorless liquid (0.138 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.07–7.25 (m, 4 H, ArH), 6.25 (br. s, 1 H, C=CH_2), 5.49 (br. s, 1 H, C=CH_2), 3.72 (s, 3 H, OCH_3), 3.59 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 140.7, 139.3, 134.1, 129.6, 129.0, 127.1, 126.7, 126.5, 51.9, 37.7 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1436, 1202, 1139, 1078, 951, 725 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{11}ClO_2$ [M + H]$^+$ 211.0526; found 211.0529.

Methyl 2-(4-Isopropoxybenzyl)acrylate (7a): Colorless liquid (0.147 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06–7.08 (m, 2 H, ArH), 6.79–6.81 (m, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.43 (br. s, 1 H, C=CH_2), 4.46–4.53 (m, 1 H, OCH), 3.72 (s, 3 H, OCH_3), 3.54 (s, 2 H, CH_2), 1.31 [d, J = 6.1 Hz, 6 H, $C(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 156.4, 140.4, 130.4, 129.9, 125.8, 115.8, 69.8, 51.8, 37.1, 22.0 ppm. IR (film): $\tilde{\nu}$ = 1722, 1630, 1509, 1242, 1136, 953 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}O_3$ [M + H]$^+$ 235.1334; found 235.1339.

Methyl 2-(4-Isobutoxybenzyl)acrylate (8a): Colorless liquid (0.153 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.07–7.09 (m, 2 H, ArH), 6.80–6.83 (m, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.43 (br. s, 1 H, C=CH_2), 3.66–3.72 [m, 5 H, OCH_3 and OCH_2], 3.55 (s, 2 H, CH_2), 2.02–2.09 (m, 1 H, OCH), 1.00 [d, J = 6.5 Hz, 6 H, $C(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 157.8, 140.5, 130.3, 129.9, 125.8, 114.4, 74.4, 51.8, 37.1, 28.2, 19.2 ppm. IR (film): $\tilde{\nu}$ = 1723, 1631, 1512, 1245, 1135, 1035, 817 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}NaO_3$ [M + Na]$^+$ 271.1310; found 271.1314.

Methyl 2-(4-Ethoxybenzyl)acrylate (9a): Colorless liquid (0.138 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06–7.08 (m, 2 H, ArH), 6.79–6.81 (m, 2 H, ArH), 6.18 (br. s, 1 H, C=CH_2), 5.41 (br. s, 1 H, C=CH_2), 3.98 (q, J = 6.9 Hz, 2 H, OCH_2CH_3), 3.71 (s, 3 H, OCH_3), 3.54 (s, 2 H, CH_2), 1.38 (t, J = 6.9 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 157.4, 140.4, 130.5, 129.9, 125.9, 114.3, 63.3, 51.8, 37.1, 14.8 ppm. IR (film): $\tilde{\nu}$ = 1722, 1632, 1511, 1246, 1136, 1048, 776 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_3$ [M + Na]$^+$ 243.0997; found 243.0997.

Methyl 2-(3-Methoxybenzyl)acrylate (10a): Colorless liquid (0.145 g, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.24 (m, 1 H, ArH), 6.74–6.78 (m, 3 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.47 (br. s, 1 H, C=CH_2), 3.77 (s, 3 H, OCH_3), 3.72 (s, 3 H, OCH_3), 3.59 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.3, 159.6, 140.2, 139.8, 129.3, 126.4, 121.4, 114.7, 111.6, 55.1, 51.9, 38.0 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1437, 1258, 1203, 1136, 1050, 817, 785, 754, 700 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}NaO_3$ [M + Na]$^+$ 229.0841; found 229.0841.

Methyl 2-(4-*sec*-Butoxybenzyl)acrylate (11a): Colorless liquid (0.146 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06–7.08 (m, 2 H, ArH), 6.80–6.81 (m, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.44 (br. s, 1 H, C=CH_2), 4.21–4.27 (m, 1 H, OCH), 3.72 (s, 3 H, OCH_3), 3.55 (s, 2 H, CH_2), 1.68–1.76 (m, 1 H, CH), 1.55–1.63 (m, 1 H, CH), 1.27 (d, J = 6.3 Hz, 3 H, CH_3), 0.96 (t, J = 7.4 Hz, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 156.7, 140.4, 130.3, 129.9, 125.9, 115.8, 75.0, 51.8, 37.1, 29.1, 19.2, 9.8 ppm. IR (film): $\tilde{\nu}$ = 1721, 1615, 1508, 1241, 1133, 816 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}O_3$ [M + H]$^+$ 249.1491; found 249.1494.

Methyl 2-(Thiophen-2-ylmethyl)acrylate (12a): Brown liquid (0.101 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.14–7.15 (m, 1 H, ArH), 6.91–6.93 (m, 1 H, ArH), 6.82–6.83 (m, 1 H, ArH), 6.25 (br. s, 1 H, C=CH_2), 5.59 (br. s, 1 H, C=CH_2), 3.82 (s, 2 H, CH_2), 3.75 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 141.0, 139.4, 126.8, 126.4, 125.7, 124.0, 51.9, 32.0 ppm. IR (film): $\tilde{\nu}$ = 1722, 1632, 1438, 1203, 1151, 696 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}O_2S$ [M + H]$^+$ 183.0480; found 183.0487.

Methyl 2-(3-Fluorobenzyl)acrylate (13a): Colorless oil (0.0941 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.22–7.27 (m, 1 H, ArH), 6.89–6.98 (m, 3 H, ArH), 6.26 (br. s, 1 H, C=CH_2), 5.50–5.51 (m, 1 H, C=CH_2), 3.75 (s, 3 H, OCH_3), 3.62 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 162.8 (d, J = 244.4 Hz), 141.2 (d, J = 7.1 Hz), 139.3, 129.8 (d, J = 8.3 Hz), 126.7, 124.6, 115.8 (d, J = 20.2 Hz), 113.2 (d, J = 21.4 Hz), 51.9, 37.8 ppm. IR (film): $\tilde{\nu}$ = 1722, 1616, 1590, 1487, 1445, 1250, 1144, 954 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{11}FO_2$ [M + H]$^+$ 195.0821; found 195.0828.

Methyl 2-(3-Methylbenzyl)acrylate (14a): Colorless liquid (0.113 g, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17–7.20 (m, 1 H, ArH), 6.99–7.03 (m, 3 H, ArH), 6.23 (br. s, 1 H, C=CH_2), 5.46–5.47 (m, 1 H, C=CH_2), 3.73 (s, 3 H, OCH_3), 3.59 (s, 2 H, CH_2), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 140.1, 138.5, 137.9, 129.7, 128.2, 127.0, 126.2, 126.0, 51.8, 37.9, 21.3 ppm. IR (film): $\tilde{\nu}$ = 1722, 1631, 1437, 1201, 1135, 948 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{14}NaO_2$ [M + Na]$^+$ 213.0891; found 213.0892.

Methyl 2-[4-(Allyloxy)benzyl]acrylate (15a): Colorless oil (0.135 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, J = 8.5 Hz, 2 H, ArH), 6.84 (d, J = 8.8 Hz, 2 H, ArH), 6.20 (br. s, 1 H, C=CH_2), 6.01–6.08 (m, 1 H, C=CH_2), 5.38–5.44 (m, 2 H), 5.26–5.29 (m, 1 H), 4.50–4.52 (m, 2 H), 3.73 (s, 3 H, OCH_3), 3.56 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.4, 157.1, 140.4, 133.3, 130.8, 129.9, 125.9, 117.5, 114.6, 68.8, 51.8, 37.1 ppm. IR (film): $\tilde{\nu}$ = 1721, 1630, 1510, 1243, 1136, 1024, 997, 839 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{16}NaO_3$ [M + Na]$^+$ 255.0997; found 255.0998.

Ethyl 2-Benzylacrylate (16a):[18,14i] Colorless liquid (0.102 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.30 (m, 5 H, ArH), 6.22

(br. s, 1 H, C=CH_2), 5.44 (br. s, 1 H, C=CH_2), 4.18 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 3.62 (s, 2 H, CH_2), 1.25 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 140.3, 138.7, 129.0, 128.3, 126.2, 125.9, 60.7, 38.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1717, 1631, 1201, 1134, 1026, 747, 701 cm^{-1}. HRMS (EI): calcd. for $C_{12}H_{14}O_2$ [M – H]$^+$ 189.0916; found 189.0917.

Ethyl 2-(4-Methylbenzyl)acrylate (17a): Colorless liquid (0.115 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06–7.08 (m, 4 H, ArH), 6.20 (br. s, 1 H, C=CH_2), 5.43 (br. s, 1 H, C=CH_2), 4.17 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.58 (s, 2 H, CH_2), 2.31 (s, 3 H, CH_3), 1.26 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 140.5, 135.7, 135.6, 129.0, 128.9, 125.7, 60.6, 37.6, 21.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1718, 1632, 1514, 1278, 1195, 1134, 947, 806, 764 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_2$ [M + Na]$^+$ 227.1048; found 227.1048.

Ethyl 2-(4-Methoxybenzyl)acrylate (18a):[16b,19] Colorless liquid (0.135 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.11 (m, 2 H, ArH), 6.81–6.83 (m, 2 H, ArH), 6.18 (br. s, 1 H, C=CH_2), 5.41 (br. s, 1 H, C=CH_2), 4.17 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 3.77 (s, 3 H, OCH_3), 3.55 (s, 2 H, CH_2), 1.25 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 158.0, 140.7, 130.7, 130.0, 125.6, 113.7, 60.6, 55.2, 37.1, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1716, 1615, 1258, 1197, 1134, 949, 783 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_3$ [M + Na]$^+$ 243.0997; found 243.0992.

Ethyl 2-(4-Fluorobenzyl)acrylate (19a): Colorless liquid (0.125 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12–7.15 (m, 2 H, ArH), 6.94–6.97 (m, 2 H, ArH), 6.21 (br. s, 1 H, C=CH_2), 5.44 (br. s, 1 H, C=CH_2), 4.16 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.58 (s, 2 H, CH_2), 1.24 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 161.5 (d, J = 242.0 Hz), 140.2, 134.4, 130.4 (d, J = 8.3 Hz), 125.9, 115.1 (d, J = 21.4 Hz), 60.7, 37.3, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1716, 1632, 1510, 1223, 1136, 951 cm^{-1}. HRMS (ESI): [M – H]$^+$ calcd. for $C_{12}H_{13}FO_2$ 207.0822; found 207.0826.

Ethyl 2-(3-Methoxybenzyl)acrylate (20a): Colorless liquid (0.135 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.21 (m, 1 H, ArH), 6.74–6.79 (m, 3 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.46 (br. s, 1 H, C=CH_2), 4.18 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 3.78 (s, 3 H, OCH_3), 3.59 (s, 2 H, CH_2), 1.26 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 159.6, 140.3, 140.1, 129.3, 126.0, 121.4, 114.7, 111.6, 60.7, 55.1, 38.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1716, 1630, 1601, 1455, 1258, 1148, 1049, 784, 754, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_3$ [M + Na]$^+$ 243.0997; found 243.0995.

Ethyl 2-(4-Isopropoxybenzyl)acrylate (21a): Colorless liquid (0.158 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.07–7.08 (m, 2 H, ArH), 6.79–6.81 (m, 2 H, ArH), 6.18 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.47–4.52 (m, 1 H, OCH), 4.17 (q, J = 7.1 Hz, 2 H, OCH_2CH$_3$), 3.54 (s, 2 H, CH_2), 1.31 [d, J = 6.0 Hz, 6 H, C(CH$_3$)$_2$], 1.22–1.27 (m, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 156.3, 140.7, 130.5, 130.0, 125.5, 115.7, 69.8, 60.6, 37.1, 22.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1717, 1630, 1611, 1509, 1243, 1135, 955, 861, 844, 816 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}O_3$ [M + H]$^+$ 249.1491; found 249.1498.

Ethyl 2-(Thiophen-2-ylmethyl)acrylate (22a): Brown liquid (0.111 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13–7.14 (m, 1 H, ArH), 6.82–6.93 (m, 2 H, ArH), 6.24 (br. s, 1 H, C=CH_2), 5.57 (br. s, 1 H, C=CH_2), 4.20 (q, J = 7.1 Hz, 2 H, OCH_2CH$_3$), 3.82 (s, 2 H, CH_2), 1.28 (t, J = 7.1 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.5, 141.1, 139.7, 126.8, 126.1, 125.7, 124.0, 60.8, 32.0, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1718, 1633, 1199, 1157, 695 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{12}O_2S$ [M + H]$^+$ 197.0636; found 197.0637.

Ethyl 2-(4-Isobutoxybenzyl)acrylate (23a): Colorless oil (0.163 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, J = 8.2 Hz, 2 H, ArH), 6.82 (d, J = 8.5 Hz, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.17 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.68 [d, J = 6.4 Hz, 2 H, OCH_2CH(CH$_3$)$_2$], 3.55 (s, 2 H, CH_2), 2.01–2.11 [m, 1 H, OCH$_2$CH(CH$_3$)$_3$], 1.26 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3), 1.01 [d, J = 6.7 Hz, 6 H, C(CH$_3$)$_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 157.7, 140.8, 130.5, 129.9, 125.5, 114.4, 74.4, 60.6, 37.2, 28.2, 19.2, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1718, 1512, 1245, 1134, 1034, 785 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{22}O_3$ [M + H]$^+$ 263.1647; found 263.1649.

Ethyl 2-(3-Methylbenzyl)acrylate (24a): Colorless oil (0.116 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16–7.19 (m, 1 H, ArH), 6.99–7.03 (m, 3 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.45 (br. s, 1 H, C=CH_2), 4.17 (q, J = 7.1 Hz, 2 H, OCH_2CH$_3$), 3.59 (s, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 1.27 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 140.4, 138.6, 137.9, 129.8, 128.2, 127.0, 126.0, 125.9, 60.6, 37.9, 21.3, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1718, 1632, 1246, 1194, 1133, 752 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{16}NaO_2$ [M + Na]$^+$ 227.1048; found 227.1045.

Ethyl 2-(4-Ethoxybenzyl)acrylate (25a): Brown oil (0.142 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, J = 8.8 Hz, 2 H, ArH), 6.82 (d, J = 8.5 Hz, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.17 (q, J = 7.1 Hz, 2 H, OCH_2CH$_3$), 4.01 (q, J = 7.0 Hz, 2 H, OCH_2CH$_3$), 3.56 (s, 2 H, CH_2), 1.40 (t, J = 7.0 Hz, 3 H, OCH$_2$CH_3), 1.26 (t, J = 7.2 Hz, 3 H, OCH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 157.4, 140.7, 130.6, 130.0, 125.5, 114.3, 63.3, 60.6, 37.1, 14.8, 14.1 ppm. IR (film): $\tilde{\nu}$ = 1717, 1631, 1612, 1511, 1246, 1116, 1028 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}O_3$ [M + H]$^+$ 235.1334; found 235.1338.

***n*-Butyl 2-Benzylacrylate (26a):** Colorless liquid (0.144 g, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.29 (m, 5 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.44 (br. s, 1 H, C=CH_2), 4.11 (t, J = 6.5 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.62 (s, 2 H, CH_2), 1.57–1.63 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.31–1.35 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.90 (t, J = 7.3 Hz, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 140.4, 138.8, 129.1, 128.4, 126.3, 126.1, 64.7, 38.1, 30.6, 19.2, 13.8 ppm. IR (film): $\tilde{\nu}$ = 1718, 1632, 1195, 1135, 945, 701 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{18}NaO_2$ [M + Na]$^+$ 241.1204; found 241.1200.

***n*-Butyl 2-(4-Methylbenzyl)acrylate (27a):**[20] Colorless liquid (0.149 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06–7.10 (m, 4 H, ArH), 6.20 (br. s, 1 H, C=CH_2), 5.43 (br. s, 1 H, C=CH_2), 4.11 (t, J = 6.7 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.58 (s, 2 H, CH_2), 2.31 (s, 3 H, CH_3), 1.56–1.63 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.31–1.36 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.90 (t, J = 7.4 Hz, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 140.6, 135.8, 135.7, 129.1, 128.9, 125.9, 64.7, 37.7, 30.7, 21.1, 19.2, 13.8 ppm. IR (film): $\tilde{\nu}$ = 1718, 1633, 1514, 1191, 1135, 947, 815 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}O_2$ [M + H]$^+$ 233.1542; found 233.1545.

***n*-Butyl 2-(4-Methoxybenzyl)acrylate (28a):** Colorless liquid (0.149 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.11 (m, 2 H, ArH), 6.81–6.83 (m, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.41 (br. s, 1 H, C=CH_2), 4.11 (t, J = 6.7 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.77 (s, 3 H, OCH_3), 3.55 (s, 2 H, CH_2), 1.57–1.63 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.32–1.36 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.91 (t, J = 7.4 Hz, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 158.1, 140.8, 130.8, 130.0, 125.8,

113.8, 64.7, 55.3, 37.3, 30.7, 19.2, 13.8 ppm. IR (film): $\tilde{\nu}$ = 1717, 1631, 1512, 1248, 1133, 1036, 948, 817 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}O_3$ [M + H]$^+$ 249.1491; found 249.1491.

***n*-Butyl 2-(4-Isopropoxybenzyl)acrylate (29a):** Colorless liquid (0.167 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.07 (d, J = 8.4 Hz, 2 H, ArH), 6.80 (d, J = 8.7 Hz, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.47–4.52 (m, 1 H, OCH), 4.11 (t, J = 6.7 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.54 (s, 2 H, CH_2), 1.55–1.63 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.30–1.36 {m, 8 H, [OCH$_2$CH$_2$CH_2CH$_3$, C(CH$_3$)$_2$]}, 0.89–0.92 (m, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 156.3, 140.7, 130.6, 129.9, 125.6, 115.8, 69.8, 64.5, 37.2, 30.6, 22.0, 19.1, 13.6 ppm. IR (film): $\tilde{\nu}$ = 1718, 1631, 1509, 1243, 1135, 955, 843 cm^{-1}. HRMS (ESI): calcd. for $C_{17}H_{24}O_3$ [M + H]$^+$ 277.1804; found 277.1800.

***n*-Butyl 2-(4-*sec*-Butoxybenzyl)acrylate (30a):** Colorless liquid (0.198 g, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.06–7.08 (m, 2 H, ArH), 6.79–6.81 (m, 2 H, ArH), 6.18 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.21–4.26 (m, 1 H, OCH), 4.11 (t, J = 6.5 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.54 (s, 2 H, CH_2), 1.55–1.76 [m, 5 H, (CH_2, CH_3)], 1.26–1.41 [m, 4 H, (CH_2, CH_2)], 0.89–0.98 [m, 6 H, (CH_3, CH_3)] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.1, 156.7, 140.7, 130.5, 129.9, 125.6, 115.8, 75.0, 64.5, 37.2, 30.6, 29.1, 19.2, 19.1, 13.6, 9.8 ppm. IR (film): $\tilde{\nu}$ = 1718, 1631, 1509, 1243, 1132, 947, 817 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{26}O_3$ [M + H]$^+$ 291.1960; found 291.1963.

***n*-Butyl 2-(4-Isobutoxybenzyl)acrylate (31a):** Brown oil (0.171 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09 (d, J = 8.5 Hz, 2 H, ArH), 6.82 (d, J = 8.5 Hz, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.12 (t, J = 6.5 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.68 [d, J = 6.7 Hz, 2 H, OCH_2C(CH$_3$)$_2$], 3.56 (s, 2 H, CH_2), 2.03–2.09 (m, 1 H, CH), 1.59–1.64 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.31–1.39 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 1.01 [d, J = 6.7 Hz, 6 H, C(CH$_3$)$_2$], 0.91 (t, J = 7.4 Hz, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 157.7, 140.7, 130.5, 129.9, 125.6, 114.4, 64.5, 37.2, 30.6, 28.2, 19.2, 19.1, 13.7 ppm. IR (film): $\tilde{\nu}$ = 1718, 1631, 1512, 1245, 1006, 817 cm^{-1}. HRMS (ESI): calcd. for $C_{18}H_{26}O_3$ [M + H]$^+$ 291.1960; found 291.1964.

***n*-Butyl 2-(Thiophen-2-ylmethyl)acrylate (32a):** Brown liquid (0.141 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13–7.14 (m, 1 H, ArH), 6.91–6.92 (m, 1 H, ArH), 6.81–6.82 (m, 1 H, ArH), 6.24 (br. s, 1 H, C=CH_2), 5.57 (br. s, 1 H, C=CH_2), 4.13–4.17 (m, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.81 (s, 2 H, CH_2), 1.59–1.69 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.33–1.43 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.90–0.96 (m, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 141.1, 139.6, 126.8, 126.1, 125.6, 123.9, 64.7, 32.1, 30.5, 19.1, 13.6 ppm. IR (film): $\tilde{\nu}$ = 1719, 1632, 1198, 1156, 949, 850, 694 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{16}O_2S$ [M + H]$^+$ 225.0949; found 225.0947.

***n*-Butyl 2-(4-Ethoxybenzyl)acrylate (33a):** Colorless oil (0.161 g, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08–7.10 (m, 2 H, ArH), 6.80–6.83 (m, 2 H, ArH), 6.19 (br. s, 1 H, C=CH_2), 5.42 (br. s, 1 H, C=CH_2), 4.12 (t, J = 6.5 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.98–4.02 (m, 2 H, OCH_2CH$_3$), 3.55 (s, 2 H, CH_2), 1.58–1.64 (m, 2 H, OCH$_2$ CH_2CH$_2$CH$_3$), 1.31–1.41 [m, 5 H, (CH_2, CH_3)], 0.91 (t, J = 7.3 Hz, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 156.4, 140.7, 130.6, 129.9, 125.6, 114.3, 64.5, 63.3, 37.2, 30.6, 19.1, 14.8, 13.6 ppm. IR (film): $\tilde{\nu}$ = 1717, 1631, 1511, 1246, 1134, 1049, 817 cm^{-1}. HRMS (ESI): calcd. for $C_{16}H_{22}O_3$ [M + H]$^+$ 263.1647; found 263.1647.

***n*-Butyl 2-(4-Chlorobenzyl)acrylate (34a):** Colorless oil (0.116 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23–7.25 (m, 2 H, ArH), 7.12 (d, J = 8.2 Hz, 2 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.46 (br. s, 1 H, C=CH_2), 4.09–4.13 (m, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.58 (s, 2 H, CH_2), 1.56–1.66 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.24–1.35 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.89–0.92 (m, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 139.8, 137.2, 132.0, 130.2, 128.4, 126.2, 64.7, 37.5, 30.5, 19.1, 13.6 ppm. IR (film): $\tilde{\nu}$ = 1717, 1632, 1491, 1250, 1195, 815 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{17}ClO_2$ [M + H]$^+$ 253.0995; found 253.0993.

***n*-Butyl 2-(4-Fluorobenzyl)acrylate (35a):** Colorless oil (0.113 g, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.13–7.16 (m, 2 H, ArH), 6.95–6.98 (m, 2 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.45 (br. s, 1 H, C=CH_2), 4.12 (t, J = 6.7 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.59 (s, 2 H, CH_2), 1.57–1.63 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.30–1.37 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.91 (t, J = 7.3 Hz, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 161.5 (d, J = 242.0 Hz), 140.2, 134.3, 130.3 (d, J = 8.3 Hz), 126.0, 115.1 (d, J = 20.2 Hz), 64.6, 37.3, 30.5, 19.1, 13.6 ppm. IR (film): $\tilde{\nu}$ = 1718, 1632, 1510, 1222, 1136, 776 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{17}FO_2$ [M + H]$^+$ 237.1291; found 237.1299.

***n*-Butyl 2-(3-Methylbenzyl)acrylate (36a):** Colorless oil (0.146 g, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.16–7.19 (m, 1 H, ArH), 6.98–7.02 (m, 3 H, ArH), 6.22 (br. s, 1 H, C=CH_2), 5.45 (br. s, 1 H, C=CH_2), 4.12 (t, J = 6.5 Hz, 2 H, OCH_2CH$_2$CH$_2$CH$_3$), 3.59 (s, 2 H, CH_2), 2.32 (s, 3 H, CH_3), 1.58–1.64 (m, 2 H, OCH$_2$CH_2CH$_2$CH$_3$), 1.31–1.38 (m, 2 H, OCH$_2$CH$_2$CH_2CH$_3$), 0.89–0.96 (m, 3 H, OCH$_2$CH$_2$CH$_2$CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 140.3, 138.6, 137.9, 129.7, 128.2, 127.2, 126.9, 125.9, 64.6, 37.9, 30.5, 21.3, 19.1, 13.6 ppm. IR (film): $\tilde{\nu}$ = 1719, 1632, 1462, 1193, 1135, 948 cm^{-1}. HRMS (ESI): calcd. for $C_{15}H_{20}O_2$ [M + H]$^+$ 233.1542; found 233.1545.

Benzyl 2-Benzylacrylate (37a): Brown liquid (0.158 g, 83%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.18–7.35 (m, 10 H, ArH), 6.29 (br. s, 1 H, C=CH_2), 5.48–5.49 (m, 1 H, C=CH_2), 5.16 (s, 2 H, OCH_2), 3.65 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.6, 139.9, 138.5, 135.8, 129.0, 128.5, 128.4, 128.1, 128.0, 126.6, 126.3, 66.4, 38.0 ppm. IR (film): $\tilde{\nu}$ = 1718, 1631, 1495, 1453, 1248, 1193, 949, 746, 699 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{16}O_2$ [M]$^+$ 252.1150; found 252.1151.

Benzyl 2-(4-Methylbenzyl)acrylate (38a): Brown liquid (0.162 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.34 (m, 5 H, ArH), 7.06–7.10 (m, 4 H, ArH), 6.27 (br. s, 1 H, C=CH_2), 5.48–5.49 (m, 1 H, C=CH_2), 5.17 (s, 2 H, OCH_2), 3.61 (s, 2 H, CH_2), 2.32 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 140.1, 135.9, 135.8, 135.5, 129.0, 128.9, 128.4, 128.1, 128.0, 126.4, 66.4, 37.6, 21.0 ppm. IR (film): $\tilde{\nu}$ = 1718, 1631, 1189, 1130, 1025, 697 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{18}O_2$ [M]$^+$ 266.1307; found 266.1307.

Benzyl 2-(4-Methoxybenzyl)acrylate (39a): Brown liquid (0.145 g, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.25–7.34 (m, 5 H, ArH), 7.08–7.10 (m, 2 H, ArH), 6.81–6.83 (m, 2 H, ArH), 6.25 (br. s, 1 H, C=CH_2), 5.46–5.47 (m, 1 H, C=CH_2), 5.16 (s, 2 H, OCH_2), 3.78 (s, 3 H, OCH_3), 3.58 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.7, 158.0, 140.3, 135.8, 130.5, 130.0, 128.4, 128.1, 128.0, 126.3, 113.7, 66.4, 55.2, 37.2 ppm. IR (film): $\tilde{\nu}$ = 1717, 1610, 1511, 1247, 1129, 950, 697 cm^{-1}. HRMS (EI): calcd. for $C_{18}H_{18}O_3$ [M]$^+$ 282.1256; found 282.1253.

Benzyl 2-(3-Chlorobenzyl)acrylate (40a): Brown liquid (0.168 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.17–7.34 (m, 9 H, ArH),

6.31 (br. s, 1 H, C=CH_2), 5.53 (br. s, 1 H, C=CH_2), 5.15 (s, 2 H, OCH_2), 3.61 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.3, 140.6, 139.2, 135.7, 134.1, 129.6, 129.0, 128.5, 128.1, 128.0, 127.2, 127.1, 126.5, 66.6, 37.7 ppm. IR (film): $\tilde{\nu}$ = 1718, 1632, 1431, 1192, 1133, 952, 729, 696 cm^{-1}. HRMS (EI): calcd. for $C_{17}H_{15}ClO_2$ $[M]^+$ 286.0761; found 286.0760.

2-Benzylacrylonitrile (41a):[17] Colorless oil (0.0781 g, 73%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20–7.36 (m, 5 H, ArH), 5.91 (br. s, 1 H, C=CH_2), 5.69 (br. s, 1 H, C=CH_2), 3.55 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.5, 131.0, 128.8, 127.3, 122.6, 118.4, 40.7 ppm. IR (film): $\tilde{\nu}$ = 2223, 1621, 1495, 1454, 943, 727, 699 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_9N$ $[M + H]^+$ 144.0813; found 144.0819.

2-(4-Methylbenzyl)acrylonitrile (42a):[17] Colorless oil (0.0812 g, 69%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.16 (m, 4 H, ArH), 5.90 (br. s, 1 H, C=CH_2), 5.68–5.69 (m, 1 H, C=CH_2), 3.51 (s, 2 H, CH_2), 2.34 (s, 3 H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.0, 132.4, 130.7, 129.5, 128.7, 122.8, 118.5, 40.2, 21.0 ppm. IR (film): $\tilde{\nu}$ = 2223, 1621, 1514, 1433, 942, 819, 760 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{11}N$ $[M + H]^+$ 158.0970; found 158.0979.

2-(4-Methoxybenzyl)acrylonitrile (43a): Colorless oil (0.0969 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11–7.13 (m, 2 H, ArH), 6.87–6.89 (m, 2 H, ArH), 5.88 (br. s, 1 H, C=CH_2), 5.67 (br. s, 1 H, C=CH_2), 3.80 (s, 3 H, CH_3), 3.49 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.8, 130.5, 129.9, 127.4, 123.1, 118.5, 114.2, 55.2, 39.9 ppm. IR (film): $\tilde{\nu}$ = 2223, 1611, 1512, 1248, 1178, 1033, 942 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{11}NO$ $[M + H]^+$ 174.0919; found 174.0914.

2-(4-Chlorobenzyl)acrylonitrile (44a):[17] Colorless oil (0.0814 g, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (d, J = 8.6 Hz, 2 H, ArH), 7.15 (d, J = 8.0 Hz, 2 H, ArH), 5.93 (br. s, 1 H, C=CH_2), 5.71 (br. s, 1 H, C=CH_2), 3.52 (s, 2 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.9, 133.3, 131.2, 130.2, 129.0, 122.2, 118.1, 40.0 ppm. IR (film): $\tilde{\nu}$ = 2224, 1622, 1491, 1406, 1089, 1016, 943 cm^{-1}. HRMS (EI): calcd. for $C_{10}H_8ClN$ $[M]^+$ 177.0345; found 177.0347.

2-(4-Ethoxybenzyl)acrylonitrile (45a): Brown oil (0.112 g, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10–7.11 (m, 2 H, ArH), 6.85–6.88 (m, 2 H, ArH), 5.88 (br. s, 1 H, C=CH_2), 5.67 (br. s, 1 H, C=CH_2), 4.02 (q, J = 7.0 Hz, 2 H, OCH_2CH_3), 3.48 (s, 2 H, CH_2), 1.41 (t, J = 7.0 Hz, 3 H, OCH_2CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.2, 130.5, 129.9, 127.3, 123.1, 118.5, 114.8, 63.4, 39.9, 14.8 ppm. IR (film): $\tilde{\nu}$ = 2223, 1612, 1512, 1247, 1178, 1115, 1047, 942 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{13}NNaO$ $[M + Na]^+$ 210.0895; found 210.0890.

2-(4-Isopropoxybenzyl)acrylonitrile (46a): Colorless oil (0.117 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.02–7.04 (m, 2 H, ArH), 6.78–6.80 (m, 2 H, ArH), 5.82 (br. s, 1 H, C=CH_2), 5.61 (br. s, 1 H, C=CH_2), 4.44–4.49 (m, 1 H, OCH), 3.42 (s, 2 H, CH_2), 1.27 [d, J = 6.3 Hz, 6 H, $OCH(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 157.1, 130.5, 129.9, 127.2, 123.1, 118.6, 116.1, 69.8, 39.9, 22.0 ppm. IR (film): $\tilde{\nu}$ = 2223, 1612, 1509, 1245, 1183, 1119, 953 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{15}NNaO$ $[M + Na]^+$ 224.1051; found 224.1055.

2-(4-Isobutoxybenzyl)acrylonitrile (47a): Colorless oil (0.113 g, 71%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.12 (m, 2 H, ArH), 6.85–6.88 (m, 2 H, ArH), 5.88 (br. s, 1 H, C=CH_2), 5.66–5.67 (m, 1 H, C=CH_2), 3.70 [d, J = 6.6 Hz, 2 H, $OCH_2CH(CH_3)_2$], 3.47 (s, 2 H, CH_2), 2.01–2.12 [m, 1 H, $OCH_2CH(CH_3)_2$], 1.02 [d, J = 6.8 Hz, 6 H, $OCH_2CH(CH_3)_2$] ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.5, 130.5, 129.9, 127.2, 123.1, 118.6, 114.8, 74.4, 39.9, 28.2, 19.2 ppm. IR (film): $\tilde{\nu}$ = 2223, 1612, 1512, 1470, 1246, 1175, 1033 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{17}NO$ $[M + H]^+$ 216.1388; found 216.1381.

2-(4-*n*-Butoxybenzyl)acrylonitrile (48a): Colorless oil (0.116 g, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.09–7.11 (m, 2 H, ArH), 6.85–6.87 (m, 2 H, ArH), 5.88 (br. s, 1 H, C=CH_2), 5.66–5.67 (m, 1 H, C=CH_2), 3.94 (t, J = 6.4 Hz, 2 H, $OCH_2CH_2CH_2CH_3$), 3.48 (s, 2 H, CH_2), 1.73–1.79 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 1.46–1.51 (m, 2 H, $OCH_2CH_2CH_2CH_3$), 0.97 (t, J = 7.4 Hz, 3 H, $OCH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 158.4, 130.5, 129.9, 127.2, 123.1, 118.5, 114.8, 67.6, 39.9, 31.3, 19.2, 13.8 ppm. IR (film): $\tilde{\nu}$ = 2223, 1612, 1512, 1247, 1177 cm^{-1}. HRMS (ESI): calcd. for $C_{14}H_{17}NO$ $[M + H]^+$ 216.1388; found 216.1382.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H NMR and ^{13}C NMR spectra of all important intermediates and final products.

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[1] a) D. Basavaiah, G. Veeraraghavaiah, *Chem. Soc. Rev.* **2012**, *41*, 68–78; b) D. Basavaiah, B. S. Reddy, S. S. Badsara, *Chem. Rev.* **2010**, *110*, 5447–5674; c) D. Basavaiah, K. V. Rao, R. J. Reddy, *Chem. Soc. Rev.* **2007**, *36*, 1581–1588; d) D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–891.

[2] S. Gowrisankar, H. S. Lee, S. H. Kim, K. Y. Lee, J. N. Kim, *Tetrahedron* **2009**, *65*, 8769–8780.

[3] Selected references: a) D. Basavaiah, S. Roy, *Org. Lett.* **2008**, *10*, 1819–1822; b) Q.-Q. Min, C.-Y. He, H. Zhou, X. Zhang, *Chem. Commun.* **2010**, *46*, 8029–8031; c) S. Zimdars, X. M. Jourdin, F. Crestey, T. Carell, P. Knochel, *Org. Lett.* **2011**, *13*, 792–795; d) M. P. Sibi, K. Patil, *Tetrahedron: Asymmetry* **2006**, *17*, 516–519; e) Y. J. Lee, A. Kubota, A. Ishiwata, Y. Ito, *Tetrahedron Lett.* **2011**, *52*, 418–421; f) H. Guthmann, D. Conole, E. Wright, K. Körber, D. Barker, M. A. Brimble, *Eur. J. Org. Chem.* **2009**, 1944–1960; g) Z.-H. Chen, Y.-Q. Zhang, Z.-M. Chen, Y.-Q. Tu, F.-M. Zhang, *Chem. Commun.* **2011**, *47*, 1836–1838.

[4] a) D. Basavaiah, M. Krishnamacharyulu, A. J. Rao, *Synth. Commun.* **2000**, *30*, 2061–2069; b) S. Brass, N.-S. Chan, C. Gerlach, T. Luksch, J. Böttcher, W. E. Diederich, *J. Organomet. Chem.* **2006**, *691*, 5406–5422.

[5] Selected references: a) A. Zakarian, A. Batch, R. A. Holton, *J. Am. Chem. Soc.* **2003**, *125*, 7822–7824; b) Y. Nakao, J. Satoh, E. Shirakawa, T. Hiyama, *Angew. Chem.* **2006**, *118*, 2329; *Angew. Chem. Int. Ed.* **2006**, *45*, 2271–2274; c) B. Leroy, *Tetrahedron Lett.* **2005**, *46*, 7563–7566; d) A. Metzger, M. A. Schade, P. Knochel, *Org. Lett.* **2008**, *10*, 1107–1110; e) C.-Y. Liu, P. Knochel, *Synlett* **2007**, 2081–2085; f) T. Stüdemann, P. Knochel, *Angew. Chem.* **1997**, *109*, 132; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 93–95; g) M. Szlosek-Pinaud, P. Diaz, J. Martinez, F. Lamaty, *Tetrahedron Lett.* **2003**, *44*, 8657–8659; h) A. Krasovskiy, V. Malakhov, A. Gavryushin, P. Knochel, *Angew. Chem.* **2006**, *118*, 6186; *Angew. Chem. Int. Ed.* **2006**, *45*, 6040–6044; i) T. Stüdemann, M. Ibrahim-Ouali, P. Knochel, *Tetrahedron* **1998**, *54*, 1299–1316; j) O. Baron, P. Knochel, *Angew. Chem.* ***2005****, 117*, 3193; *Angew. Chem. Int. Ed.* **2005**, *44*, 3133–3155.

[6] a) P.-A. R. Breuil, F. W. Patureau, J. N. H. Reek, *Angew. Chem.* **2009**, *121*, 2196; *Angew. Chem. Int. Ed.* **2009**, *48*, 2162–2165; b) O. Roy, A. Riahi, F. Hénin, J. Muzart, *Tetrahedron* **2000**, *56*, 8133–8140; c) S. Ma, S. Yu, Z. Peng, H. Guo, *J. Org. Chem.*

2006, *71*, 9865–9868; d) B. Mariampillai, C. Herse, M. Lautens, *Org. Lett.* **2005**, *7*, 4745–4747; e) S. Ma, S. Yu, *Tetrahedron Lett.* **2004**, *45*, 8419–8422; f) M. Takagi, K. Yamamoto, *Chem. Lett.* **1989**, 2123–2124.

[7] a) Z. Zhuang, F. Pan, J.-G. Fu, J.-M. Chen, W.-W. Liao, *Org. Lett.* **2011**, *13*, 6164–6167; b) R. Takagi, T. Nerio, Y. Miwa, S. Matsumura, K. Ohkata, *Tetrahedron Lett.* **2004**, *45*, 7401–7405; c) J. Qi, J. A. Porco Jr., *J. Am. Chem. Soc.* **2007**, *129*, 12682–12683; d) S. K. Mandal, M. Paira, S. C. Roy, *J. Org. Chem.* **2008**, *73*, 3823–3827; e) Y. Du, J. Feng, X. Lu, *Org. Lett.* **2005**, *7*, 1987–1989; f) Y. Du, X. Lu, C. Zhang, *Angew. Chem.* **2003**, *115*, 1065; *Angew. Chem. Int. Ed.* **2003**, *42*, 1035–1037; g) J. Feng, X. Lu, A. Kong, X. Han, *Tetrahedron* **2007**, *63*, 6035–6041.

[8] a) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; b) R. Jana, T. P. Pathak, M. S. Sigman, *Chem. Rev.* **2011**, *111*, 1417–1492; c) A. B. Dounay, L. E. Overman, *Chem. Rev.* **2003**, *103*, 2945–2963.

[9] a) M. L. N. Rao, D. N. Jadhav, P. Dasgupta, *Org. Lett.* **2010**, *12*, 2048–2051 and references cited therein; b) M. L. N. Rao, V. Venkatesh, D. Banerjee, *Synfacts* **2008**, *4*, 406–406; c) M. L. N. Rao, D. Banerjee, R. J. Dhanorkar, *Synfacts* **2010**, *8*, 928–928; d) M. L. N. Rao, D. Banerjee, S. Giri, *Tetrahedron Lett.* **2009**, *50*, 5757–5761; e) M. L. N. Rao, D. Banerjee, S. Giri, *J. Organomet. Chem.* **2010**, *695*, 1518–1525; f) M. L. N. Rao, D. Banerjee, R. J. Dhanorkar, *Tetrahedron* **2010**, *66*, 3623–3632.

[10] a) D. H. R. Barton, N. Ozbalik, M. Ramesh, *Tetrahedron* **1988**, *44*, 5661–5668; b) H. Suzuki, Y. Matano (Eds.), *Organobismuth Chemistry*, Elsevier, Amsterdam, **2001**.

[11] I. Kondolff, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2003**, *44*, 8487–8491.

[12] a) Y. Makhynya, Z. Hussain, T. Bauschlicher, P. Schwinte, F. Siebert, W. Gärtner, *Eur. J. Org. Chem.* **2007**, 1287–1293; b) B. M. O'Leary, T. Szabo, N. Svenstrup, C. A. Schalley, A. Lützen, M. Schäfer, J. Rebek Jr., *J. Am. Chem. Soc.* **2001**, *123*, 11519–11533; c) J. Wassenaar, M. Kuil, J. N. H. Reek, *Adv. Synth. Catal.* **2008**, *350*, 1610–1614.

[13] a) M. Wada, H. Ohki, *J. Synth. Org. Chem. Jpn.* **1989**, *47*, 425–435; b) X. Huang, J. L. Wu, *Chin. Chem. Lett.* **1997**, *8*, 759–762.

[14] a) H. Amri, M. R. J. Villieras, *J. Organomet. Chem.* **1986**, *308*, C27–C32; b) D. Basavaiah, N. Kumaragurubaran, *Tetrahedron Lett.* **2001**, *42*, 477–479; c) T. Stüdemann, V. Gupta, L. Engman, P. Knochel, *Tetrahedron Lett.* **1997**, *38*, 1005–1008; d) Y. Nakao, Y. Hirata, S. Ishihara, S. Oda, T. Yukawa, E. Shirakawa, T. Hiyama, *J. Am. Chem. Soc.* **2004**, *126*, 15650–15651; e) J.-B. Baudin, S. A. Julia, *Tetrahedron Lett.* **1988**, *29*, 3255–3258; f) N. El Alami, C. B. J. Villieras, *J. Organomet. Chem.* **1988**, *353*, 157–168; g) C. Nájera, B. Mancheno, M. Yus, *Tetrahedron Lett.* **1989**, *30*, 3837–3840; h) H.-S. Lee, J.-S. Park, B. M. Kim, S. H. Gellman, *J. Org. Chem.* **2003**, *68*, 1575–1578; i) H. Amri, M. R. J. Villieras, *J. Organomet. Chem.* **1990**, *384*, 1–11.

[15] a) K. Eistetter, H. P. O. Wolf, *J. Med. Chem.* **1982**, *25*, 109–113; b) P. Bühlmayer, A. Caselli, W. Fuhrer, R. Göschke, V. Rasetti, H. Rüeger, J. L. Stanton, L. Criscione, J. M. Wood, *J. Med. Chem.* **1988**, *31*, 1839–1846; c) D. Lu, R. Vince, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5614–5619.

[16] a) X. Han, Y. Wang, F. Zhong, Y. Lu, *J. Am. Chem. Soc.* **2011**, *133*, 1726–1729; b) O. Tamura, T. Shiro, M. Ogasawara, A. Toyao, H. Ishibashi, *J. Org. Chem.* **2005**, *70*, 4569–4577; c) C. L. Friend, N. S. Simpkins, M. Anson, M. E. C. Polywka, *Tetrahedron* **1998**, *54*, 2801–2808; d) C.-G. Huang, B.-R. Chang, N.-C. Chang, *Tetrahedron Lett.* **2002**, *43*, 2721–2723; e) K. Nishide, S. Ohsugi, H. Shiraki, H. Tamakita, M. Node, *Org. Lett.* **2001**, *3*, 3121–3124; f) X. Liu, X. E. Hu, X. Tian, A. Mazur, F. H. Ebetino, *J. Organomet. Chem.* **2002**, *646*, 212–222.

[17] D. Basavaiah, K. R. Reddy, N. Kumaragurubaran, *Nat. Protoc.* **2007**, *2*, 2665–2676.

[18] a) R. Queignec, B. Kirschleger, F. Lambert, M. Aboutaj, *Synth. Commun.* **1988**, *18*, 1213–1223; b) B. Kirschleger, R. Queignec, *Synthesis* **1986**, 926–928; c) N. S. Mani, C. M. Mapes, J. Wu, X. Deng, T. K. Jones, *J. Org. Chem.* **2006**, *71*, 5039–5042; d) J. E. Beddow, S. G. Davies, K. B. Ling, P. M. Roberts, A. J. Russell, A. D. Smith, J. E. Thomson, *Org. Biomol. Chem.* **2007**, *5*, 2812–2825.

[19] M. R. Heinrich, O. Blank, D. Ullrich, M. Kirschstein, *J. Org. Chem.* **2007**, *72*, 9609–9616.

[20] a) P.-A. Enquist, J. Lindh, P. Nilsson, M. Larhed, *Green Chem.* **2006**, *8*, 338–343; b) J. Lindh, P.-A. Enquist, A. Pilotti, P. Nilsson, M. Larhed, *J. Org. Chem.* **2007**, *72*, 7957–7962.

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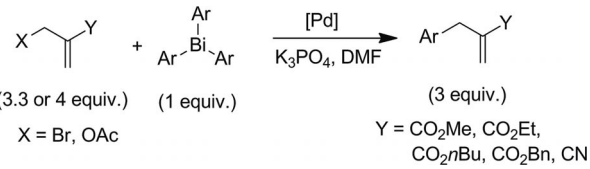
Cross-Coupling



Functionalized alkyl 2-benzylacrylates and 2-benzylacrylonitriles were synthesized by cross-coupling of Baylis–Hillman bromides or acetates with $BiAr_3$ under palladium-catalyzed conditions. These reactions involve threefold aryl couplings using $BiAr_3$ reagents with bromides and acetates, are fast, and provide high product yields.

Keywords: Bismuth / Palladium / Alkenes / Synthetic methods / C–C coupling

