Tetrahedron 66 (2010) 3623–3632

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Pd(0)-catalyzed couplings using bromide and chloride derivatives of Baylis–Hillman adducts with triarylbismuths as atom-efficient multi-coupling nucleophiles

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ARTICLE INFO

Article history:
Received 2 February 2010
Received in revised form 28 February 2010
Accepted 5 March 2010
Available online 11 March 2010

Keywords:
Allylic bromides and chlorides
Baylis–Hillman adducts
Cross-coupling
Palladium
Triarylbismuths

ABSTRACT

Bromide and chloride derivatives of Baylis–Hillman adducts have been demonstrated to react efficiently with triarylbismuths affording allylic arylated products in high yields under palladium-catalyzed conditions. Triarylbismuths have been employed in sub-stoichiometric amounts as multi-coupling and atom-efficient nucleophiles in these reactions. The reactivity of both allylic bromides and chlorides was found to be facile and equally efficient in couplings with triarylbismuths.

1. Introduction

Bismuth compounds are environment friendly as they are non-toxic and have been used even in medicinal applications.[1] Bismuth reagents have also been utilized for many synthetic transformations in organic chemistry.[2] The chemistry of organobismuth compounds is of special interest as these are useful for carbon–carbon and carbon–heteroatom bond formations.[2a] There is a growing interest in the utilization of these compounds in several ways with promising novel reactivities.[3,4] Here, triarylbismuths needs a special mention as these compounds are useful as atom-efficient multi-coupling reagents in C–C coupling methods.[5–7] The multi-coupling ability of triarylbismuths reacting with three equivalents of organic electrophiles under metal catalyzed conditions is of interest to us, as this allows the development of atom-economic coupling reactions. Hence, we have been involved in the development of new atom-efficient or -economic C–C coupling reactions using triarylbismuths as multi-coupling organometallic nucleophiles.[6] Need for the development of multi-coupling organometallic reagents for C–C bonds formation is due to their importance in the chemical industry for pharmaceutical and material applications.[8]

The Baylis–Hillman reaction and its adducts provides a unique functional platform useful for a variety of synthetic transformations.[9] The pioneering work of Basavaiah et al.[10] and other groups have taken this reaction to a newer heights and is a testimony for its uniqueness to generate multi-functional skeletons in synthetic organic chemistry.[11,12] In the present context, Baylis–Hillman adducts have recently been involved in the coupling reactions with organometallic reagents such as organoboron, organosilicon and bimetallic reagents.[13] However, the reactivity using other derivatives of Baylis–Hillman adducts are less studied in coupling reactions. Although triarylbismuths coupling with allylic bromides[14] and acetates[6d] are known, the study of halide derivatives[15] of Baylis–Hillman adducts is of special importance from the view point of its reactivity and additional functional features. With this aim we have carried out the present study using bromide and chloride derivatives of Baylis–Hillman adducts with triarylbismuths under palladium-catalyzed conditions.

2. Results and discussion

The desired bromide and chloride derivatives of Baylis–Hillman adduct have been prepared according to known procedures[12] (Scheme 1).

These transformations afforded the corresponding bromide and chloride derivatives cleanly. So, with a view to study the reactivity of these substrates as organic electrophiles the following efforts

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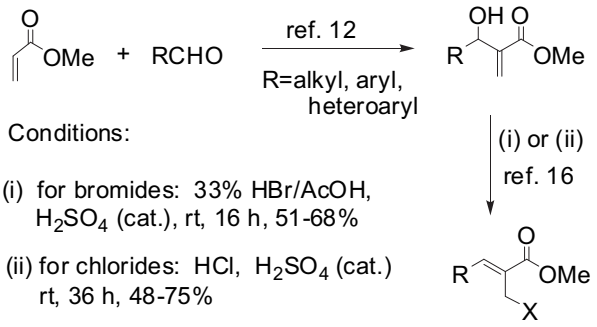
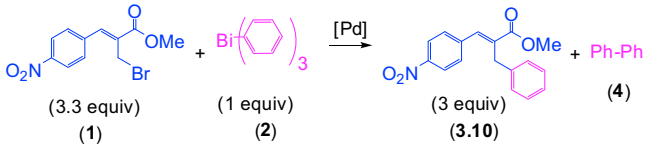
0040-4020/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2010.03.020



Scheme 1. Bromide and chloride derivatives of Baylis–Hillman adducts.

have been carried out under palladium catalysis. Firstly, the coupling study of bromide (**1**) derived from Baylis–Hillman adduct was employed with triphenylbismuth (**2**) under different catalytic conditions to check its efficacy to afford the arylated product **3.10** as summarized in Table 1.

Table 1
Screening conditions with bromide[a–c]

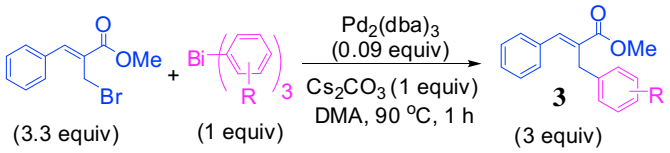


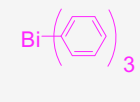
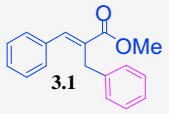
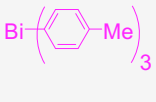
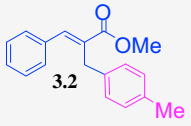
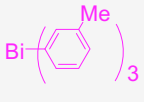
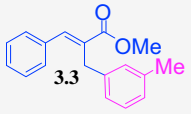
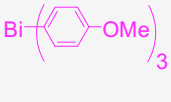
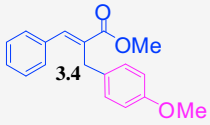
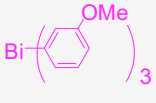
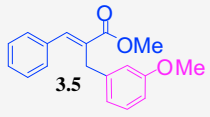
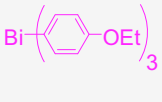
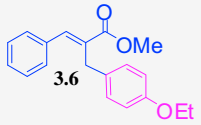
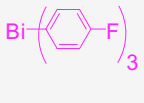
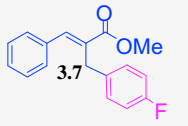
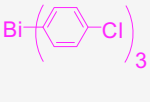
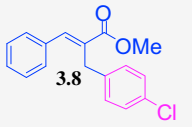
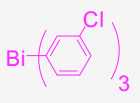
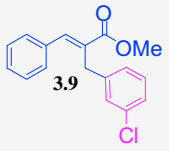
Entry	Catalyst & conditions	**3.10** (%)	**4** (%)
1	$Pd_2(dba)_3$, K_3PO_4 (1)/KI(2), DMF	39	34
2	$Pd(PPh_3)_4$, K_3PO_4 (1)/KI(2), DMF	20	55
3	$PdCl_2(PPh_3)_2$, K_3PO_4 (1)/KI(2), DMF	28	58
4	$Pd_2(dba)_3$, K_2CO_3(1), DMF	42	30
5	$Pd_2(dba)_3$, Na_2CO_3(1), DMF	54	21
6	$Pd_2(dba)_3$, Cs_2CO_3(1), DMF	57	13
7	$Pd_2(dba)_3$, Na_2CO_3(2), DMF	54	21
8	$Pd_2(dba)_3$, Cs_2CO_3(2), DMF	62	21
9	$Pd_2(dba)_3$, Cs_2CO_3(1), CH_3CN	29	53
10	$Pd_2(dba)_3$, Cs_2CO_3(1), DCE	29	15
11	$Pd_2(dba)_3$, Cs_2CO_3(1), DMA	79(75)	10
12	$Pd_2(dba)_3$, Cs_2CO_3(1), DMA	68[d]	14
13	$Pd_2(dba)_3$, Cs_2CO_3(1), DMA	50[e]	27
14	$Pd_2(dba)_3$, Cs_2CO_3(1), DMA	68[f]	9
15	$Pd_2(dba)_3$, Cs_2CO_3(1)/PPh_3, DMA	23[d]	70
16	$Pd_2(dba)_3$, No Base, DMA	55	16
17	No catalyst, Cs_2CO_3(1), DMA	4	8

[a] Conditions: $BiPh_3$ (1 equiv), bromide (3.3 equiv), base (1–2 equiv), additive (2 equiv), palladium catalyst (0.09 equiv), solvent (3 mL), 90 °C, 1 h.
[b] Conversions are based on GC analysis of the crude reaction mixture.
[c] Isolated yield is given in parenthesis.
[d] Reaction at 60 °C.
[e] Reaction at 40 °C.
[f] Reaction for 2 h.

The different palladium catalysts screened for the reaction showed poor coupling reactivity to furnish arylation product **3.10** under the conditions studied with K_3PO_4 base (entries 1–3). In the absence of effective cross-coupling, triphenylbismuth delivered homo-coupling biphenyl in higher amounts. This homo-coupling reactivity of triarylbismuths is well established using palladium catalysis.[7a] As $Pd_2(dba)_3$ catalyst demonstrated relative better performance among the catalysts studied, this has been further screened with different bases. These reactions provided moderate results with K_2CO_3, Na_2CO_3 and Cs_2CO_3 bases (entries 4–6). However, relative better performance was observed with Cs_2CO_3 as base both in terms of higher cross-coupling and lower homo-coupling conversion (entry 6). Further increase in base

Table 2
Couplings with different triarylbismuths[a–d]



Entry	$BiAr_3$	Product	Yield (%)
1			73
2			90
3			91
4			75
5			85
6			73
7			79
8			85
9			70

[a] Reaction conditions: methyl-(2-bromomethyl)-3-phenylacrylate (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), Cs_2CO_3 (0.25 mmol, 1 equiv), $Pd_2(dba)_3$ (0.0225 mmol, 0.09 equiv) and DMA (3 mL), 90 °C, 1 h.
[b] Isolated yields calculated considering all three aryl groups of triarylbismuths for coupling. Thus, 0.75 mmol of the product correspond to 100% yield.
[c] In general, homo-coupled bi-aryls from triarylbismuths formed in all the reactions and the amount varied with respect to the degree of the cross-coupling product.
[d] All products were characterized by ^1H NMR, ^{13}C NMR, IR and ESI-HRMS data and in comparison with literature data.

equivalents also did not improve the product conversion considerably (entries 7 and 8). Additionally, the influence of different solvents on the coupling was investigated with Cs_2CO_3 base (entries 9–11). During this study, *N*,*N*-dimethylacetamide (DMA) solvent was found to be more effective with increased coupling up to 75% yield of **3.10** (entry 11). The reaction was also studied at different temperature conditions. This has revealed that the coupling is not efficient under lower temperature conditions (entries 12 and 13). Additional time also did not improve the desired product formation (entry 14).

So, the coupling reaction carried out with 90 °C was found to be optimum temperature condition to obtain higher coupling yield (entry 11). Addition of triphenylphosphine as ligand resulted inferior conversion (entry 15). Further control reactions carried out without base and catalyst delivered poor results (entries16 and 17) indicating their effective role to furnish high coupling yield (entry 11).

With the above investigation it was found that the cross-coupling is more effective using $Pd_2(dba)_3$ catalyst and Cs_2CO_3 base in DMA solvent at 90 °C to furnish high yield of the product **3.10** in short reaction time. It is to be noted that the overall reaction involves the formation of three C–C bonds from triphenylbismuth in reaction with three equivalents of allylic bromide. This indicates the facile of reactivity of triphenylbismuth in the arylation of bromide derived from Baylis–Hillman adduct under the established protocol.

To expand the potential of this study, various triarylbismuths have been employed in the allylic arylation studies as given in Table 2. The electronically divergent triarylbismuths containing both electron-withdrawing and -donating groups performed efficiently giving high yields of arylated coupling products. Other way, this coupling reaction provided an opportunity for further functionalization of bromide derivative of Baylis–Hillman adduct with a variety of functionalized aryl substituents. Thus the coupling furnished various functionalized tri-substituted alkenes very efficiently.

To further explore the scope of this reaction, various other bromides derived from Baylis–Hillman adducts were subjected to cross-coupling with triarylbismuths under the established protocol. These results are summarized in Table 3. The couplings carried out with a variety of functionalized bromides underwent facile coupling to the corresponding arylated products. Overall, an efficient reactivity of divergent triarylbismuths was established with a variety of bromides in this study. In all these reactions each triarylbismuth was coupled with 3 equiv of bromides furnishing 3 equiv of the corresponding arylated products. Further, all the reactions were completed in short reaction time of 1 h despite the involvement of three couplings from triarylbismuths. This indicates the high reactivity of triarylbismuths as atom-efficient multi-coupling nucleophiles in these couplings.

It was fascinating to realize the facile reactivity of bromides derived from Baylis–Hillman adducts with triarylbismuths under the established palladium catalysis. This encouraged us to extend this study with chlorides of Baylis–Hillman adducts as these compounds are also promising and potential organic electrophiles (Table 4).

The coupling reaction of chloride derivative of Baylis–Hillman adduct (**5**) was carried out under the established protocol for bromide. This has provided only moderate conversion to product **3.10** (entry 1). As the optimized condition for bromide couplings found to be ineffective for corresponding chloride coupling, a brief screening has been carried out to find the right combination to improve the yield of arylation product **3.10**. As given in the Table 4, the reaction failed to provide better conversion to the desired product either with increase in reaction time or with additional amount of base (entries 2 and 3). However, when the amount of base was increased to three equivalents, the reaction provided arylated product up to 71% yield (entry 4). Then, it was decided to screen the reaction in different solvents and bases to affect further improvement in product yield. Reactions with different bases in DMA solvent were found to be ineffective to give high amount of the product (entries 7–9). Additional study with K_3PO_4 base in different solvents also did not furnish any further improvements (entries 10–13). A control reaction without base afforded poor conversion to cross-coupling product (entry 14). Another reaction without catalyst also furnished lower conversion (entry 15). From the above investigation, we found that the protocol with $Pd_2(dba)_3$ catalyst and in the presence of 3 equiv of Cs_2CO_3 in DMA solvent as an ideal combination to furnish high yield of coupling product **3.10** (entry 4).

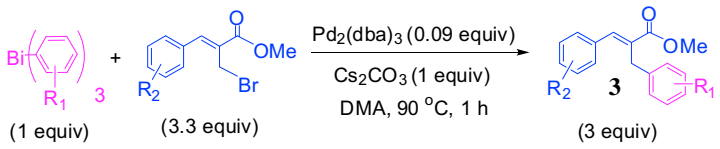
Hence, the coupling reactions of various Baylis–Hillman adducts derived chlorides have been studied with triarylbismuths under the optimized protocol. These results are given in Table 5. The reactivity of chloride derivatives was found to be equally efficient with different triarylbismuths giving high yields of the arylated products. These couplings of chlorides were almost comparable to that found with corresponding bromides in giving high yields of the products with triarylbismuths under the established conditions. Earlier couplings of allylic bromides with triarylbismuths involved longer reaction times even under refluxing conditions in the presence of palladium catalyst.[14b] Whereas, in this study bromide and chlorides derivatives of Baylis–Hillman adducts reacted very well in a facile manner and exhibited superior coupling reactivity with high yields in shorter reaction times. In addition, the coupling reactivity of these adducts is similar to that observed with allylic acetates under palladium-catalyzed conditions.[6d]

The mechanistic aspects of this reaction could be similar to the earlier known couplings as proposed in Scheme 2.[8a,13c] The oxidative addition of allylic halide (either bromide or chloride) would lead to the formation of π-allyl palladium intermediate. This in turn involves with $BiAr_3$ in transmetalation step to form arylallyl–palladium intermediate. Reductive elimination of this intermediate is expected to give the arylated product. As triarylbismuths are involved as multi-coupling nucleophiles in these couplings, participation of either Ar_2BiX or $ArBiX_2$ is essential in transmetalation step for the effective utilization of three aryl groups. Alternative regeneration of triarylbismuths via disproportion of arylbismuth halides in situ during the reaction is another possibility.[7a] The role of base in the reaction is expected to activate Bi–C bond of arylbismuths for facile transfer of aryl group during transmetalation step. Overall, the novel and efficient couplings of triarylbismuths with three equivalents of either bromide or chloride derivatives of Baylis–Hillman adducts were realized under the established conditions.

3. Conclusions

In summary, an efficient palladium-catalyzed conditions for the cross-coupling of triarylbismuths with bromide and chloride derivatives of Baylis–Hillman adducts have been developed. These protocols furnished high yields of arylated products in short reaction time. Involvement of triarylbismuths compounds in sub-stoichiometric amounts as multi-coupling organometallic nucleophiles is promising from the view point of atom-economic or atom-efficient couplings involving organometallic reagents. The study also disclosed the novel reactivity of both bromide and chloride derivatives of Baylis–Hillman adducts for C–C bond formations under palladium catalysis using triarylbismuth reagents.

Table 3
Couplings with different bromides and triarylbismuths[a–d]



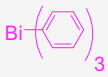
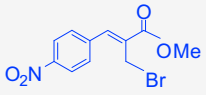
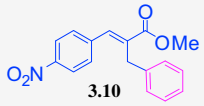
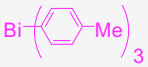
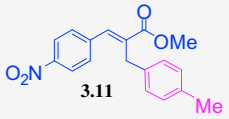
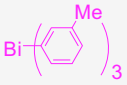
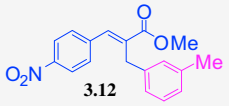
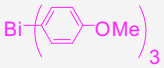
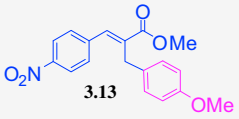
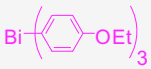
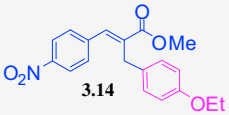
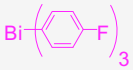
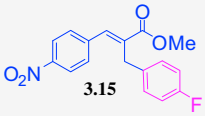
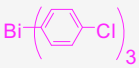
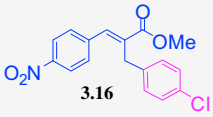
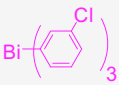
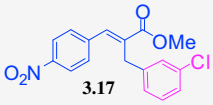
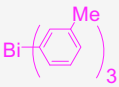
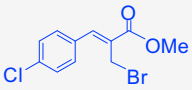
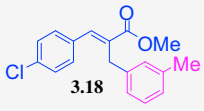
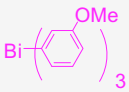
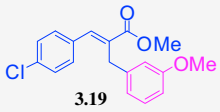
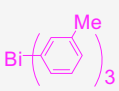
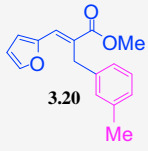
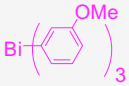
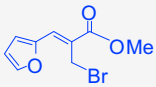
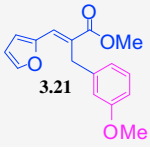
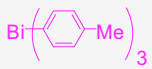
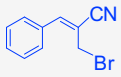
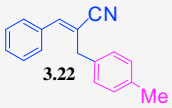
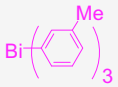
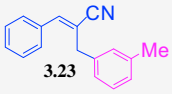
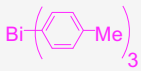
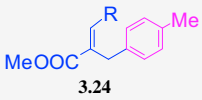
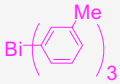
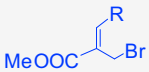
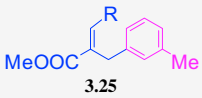
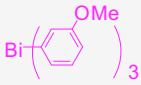
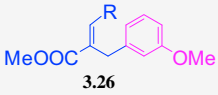
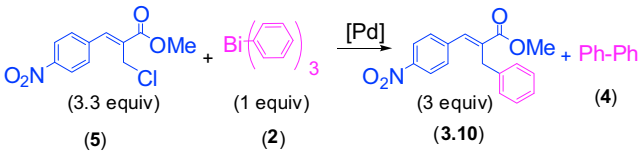
Entry	$BiAr_3$	Bromide	Product	Yield (%)
1			 **3.10**	75
2			 **3.11**	70
3			 **3.12**	80
4			 **3.13**	63
5			 **3.14**	60
6			 **3.15**	65
7			 **3.16**	60
8			 **3.17**	60
9			 **3.18**	80
10			 **3.19**	81
11			 **3.20**	78
12			 **3.21**	82

Table 3 (*continued*)

Entry	$BiAr_3$	Bromide	Product	Yield (%)
13			 **3.22**	75
14			 **3.23**	63
15			 **3.24**	72
16		 R = n-butyl	 **3.25**	74
17			 **3.26**	75

[a] Reaction conditions: bromide (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), Cs_2CO_3 (0.25 mmol, 1 equiv), $Pd_2(dba)_3$ (0.0225 mmol, 0.09 equiv) and DMA (3 mL), 90 °C, 1 h.
[b] Isolated yields calculated considering all three aryl groups from triarylbismuths for coupling. Thus, 0.75 mmol of the product correspond to 100% yield.
[c] In general, homo-coupled bi-aryls from triarylbismuths formed in all the reactions and the amount varied with respect to the degree of the cross-coupling product.
[d] All products were characterized by ^1H NMR, ^{13}C NMR, IR and ESI-HRMS data and in comparison with literature data.

Table 4
Screening conditions with chloride[a–c]



Entry	Catalyst & conditions	**3.10** (%)	**4** (%)
1	$Pd_2(dba)_3$, Cs_2CO_3(1), DMA	50	20
2	$Pd_2(dba)_3$, Cs_2CO_3(1), DMA	52[d]	20
3	$Pd_2(dba)_3$, Cs_2CO_3(2), DMA	55	20
4	$Pd_2(dba)_3$, Cs_2CO_3(3), DMA	74(71)	18
5	$Pd_2(dba)_3$, Cs_2CO_3(3), DMF	65(60)	23
6	$Pd_2(dba)_3$, Cs_2CO_3(3), NMP	66(58)	20
7	$Pd_2(dba)_3$, K_2CO_3(3), DMA	37	18
8	$Pd_2(dba)_3$, Na_2CO_3(3), DMA	42	13
9	$Pd_2(dba)_3$, K_3PO_4(3), DMA	55	19
10	$Pd_2(dba)_3$, K_3PO_4(3), DMF	11	19
11	$Pd_2(dba)_3$, K_3PO_4(3), NMP	46	14
12	$Pd_2(dba)_3$, K_3PO_4(3), DMF	57[d]	21
13	$Pd_2(dba)_3$, K_3PO_4(3), NMP	45[d]	20
14	$Pd_2(dba)_3$, No Base, DMA	42	24
15	No Catalyst, Cs_2CO_3 (3), DMA	4	10

[a] Conditions: $BiPh_3$ (1 equiv), chloride (3.3 equiv), base (1–3 equiv), palladium catalyst (0.09 equiv), solvent (3 mL), 90 °C, 1 h.
[b] Conversions are based on GC analysis of the crude reaction mixture with respect to triphenylbismuth.
[c] Isolated yield given in parenthesis.
[d] For 2 h.

4. Experimental section

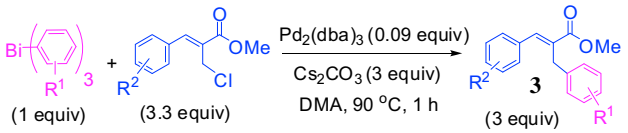
4.1. General

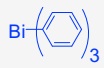
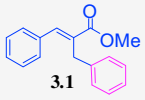
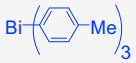
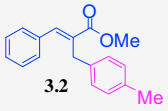
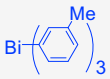
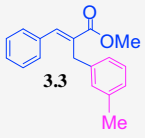
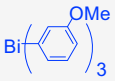
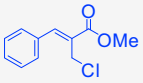
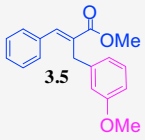
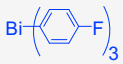
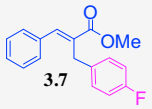
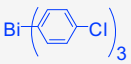
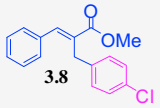
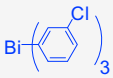
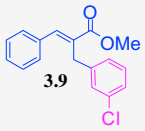
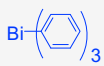
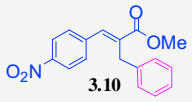
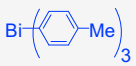
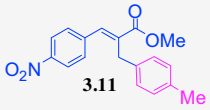
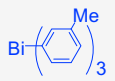
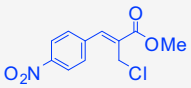
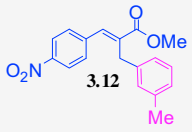
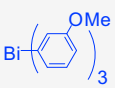
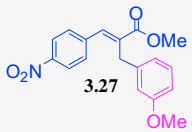
All Baylis–Hillman adducts and corresponding bromides/chlorides were prepared according to literature procedures.[16] Triarylbismuth compounds were prepared following known procedure.[2a] NMR spectra were recorded on JEOL–Lambda (400 MHz and 500 MHz) spectrometers with $CDCl_3$ solvent and TMS as an internal standard. HRMS was measured with Waters ESI-Q^{TOF} instrument. IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer. Analysis of crude reaction mixture and pure products were performed on Perkin Elmer (Clarus 500) Gas Chromatograph. Silica gel (100–200 mesh) for column chromatography and GF-254 silica gel (Merck) was used for TLC. All the solvents were distilled using standard drying methods prior to use. All the reactions were performed under nitrogen atmosphere in an oven dried Schlenk tubes and using dry solvents.

4.2. Representative procedure for cross-coupling of bromides of Baylis–Hillman adducts with triarylbismuths

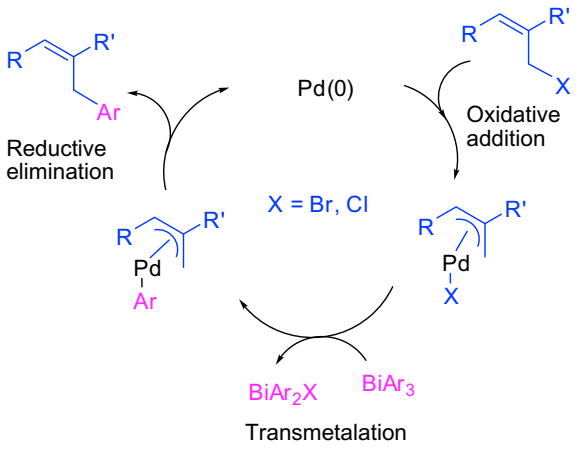
A hot-oven dried Schlenk tube was charged with methyl-(2-bromomethyl)-3-phenylacrylate (0.825 mmol, 0.210 g) followed by triphenylbismuth (0.25 mmol, 0.11 g), Cs_2CO_3 (0.25 mmol, 0.082 g), $Pd_2(dba)_3$ (0.0225 mmol, 0.0206 g) and DMA (3 mL) solvent under nitrogen atmosphere. Then the contents were stirred in an oil bath at 90 °C for 1 h. After the reaction time, contents were cooled, quenched with water (10 mL) and extracted with ethyl acetate (3×15 mL). The combined organic extract was washed with water (2×10 mL), brine (10 mL) and dried over anhydrous $MgSO_4$. The extract was concentrated under reduced pressure to obtain the crude product mixture. This was purified on silica gel by column chromatography (1% EtOAc/petroleum ether) to afford 2-benzyl-3-phenylacrylic acid methyl ester (**3.1**) as colourless oil (0.137 g, 73%). Isolated yield was calculated considering all three aryl groups for couplings from triphenylbismuth. Thus, 0.75 mmol of the product correspond to 100% yield. The product was identified by spectroscopic analysis and in comparison with the literature data.

Table 5
Couplings with different chlorides and triarylbismuths[a–d]



Entry	$BiAr_3$	Chloride	Product	Yield (%)
1			 3.1	76
2			 3.2	82
3			 3.3	82
4			 3.5	81
5			 3.7	80
6			 3.8	82
7			 3.9	80
8			 3.10	71
9			 3.11	73
10			 3.12	75
11			 3.27	75

[a] Reaction conditions: allylic chloride (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), Cs_2CO_3 (0.75 mmol, 3 equiv), $Pd_2(dba)_3$ (0.0225 mmol, 0.09 equiv) and DMA (3 mL), 90 °C, 1 h.
[b] Isolated yields calculated considering all three aryl groups from triarylbismuths for coupling. Thus, 0.75 mmol product correspond to 100% yield.
[c] In general, homo-coupled bi-aryls from triarylbismuths formed in all the reactions and the amount varied with respect to the degree of the cross-coupling product.
[d] All products were characterized by ^1H NMR, ^{13}C NMR, IR and ESI-HRMS data and in comparison with literature data.



Scheme 2. Proposed mechanistic cycle.

4.3. Representative procedure for cross-coupling of chlorides of Baylis–Hillman adduct with triarylbismuths

A hot-oven dried Schlenk tube was charged with methyl-(2-chloromethyl)-3-phenylacrylate (0.825 mmol, 0.174 g) followed by triphenylbismuth (0.25 mmol, 0.11 g), Cs_2CO_3 (0.75 mmol, 0.246 g), $Pd_2(dba)_3$ (0.0225 mmol, 0.0206 g) and DMA (3 mL) solvent under nitrogen atmosphere. The reaction mixture was stirred in an oil bath at 90 °C for 1 h. After the reaction time, contents were cooled, quenched with water (10 mL) and extracted with ethyl acetate (3×15 mL). The combined organic extract was washed with water (2×10 mL), brine (10 mL) and dried over anhydrous $MgSO_4$. The extract was concentrated under reduced pressure to obtain the crude product mixture. This was purified on silica gel by column chromatography (1% EtOAc/petroleum ether) to afford 2-benzyl-3-phenylacrylic acid methyl ester (**3.1**) as colourless oil (0.143 g, 76%). The product was identified by spectroscopic analysis and in comparison with the literature data.

4.4. Spectral data

*4.4.1. 2-Benzyl-3-phenylacrylic acid methyl ester (**3.1**)*[13a]. The crude product was purified by column chromatography using (1% ethyl acetate in petroleum ether) to give **3.1** as colourless oil (137 mg, 73%); R_f (2.5% ethyl acetate in petroleum ether) 0.45; IR (neat, cm^{-1}): 3026, 2949, 1712, 1629, 1435, 1264, 1202, 1089, 739; δ_H NMR (500 MHz, $CDCl_3$): 7.93 (s, 1H, C=CH), 7.18–7.36 (m, 10H, CH_{ar}), 3.95 (s, 2H, CH_2), 3.74 (s, 3H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$): 168.75, 141.09, 139.47, 135.41, 130.76, 129.74, 129.29, 128.67, 128.63, 128.00, 126.21, 52.22, 33.24.

*4.4.2. 2-(4-Methylbenzyl)-3-phenylacrylic acid methyl ester (**3.2**)*[13a]. The crude product was purified by column chromatography using (1% ethyl acetate in petroleum ether) to give **3.2** as colourless oil (180 mg, 90%); R_f (2.5% ethyl acetate in petroleum ether) 0.44; IR (neat, cm^{-1}): 3024, 2949, 1714, 1630, 1513, 1436, 1262, 1203, 1088, 779; δ_H NMR (500 MHz, $CDCl_3$): 7.91 (s, 1H, C=CH), 7.02–7.42 (m, 9H, CH_{ar}), 3.91 (s, 2H, CH_2), 3.74 (s, 3H, OCH_3), 2.31 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$): 168.67, 140.77, 136.20, 135.55, 135.34, 130.83, 129.22, 129.18, 128.69, 128.52, 127.74, 52.08, 32.70, 20.98; ESI(HRMS) (m/z) calcd for $C_{18}H_{19}O_2$, $(M+H)^+$ 267.1385, found 267.1381.

*4.4.3. 2-(3-Methylbenzyl)-3-phenylacrylic acid methyl ester (**3.3**)*. The crude product was purified by column chromatography using (1% ethyl acetate in petroleum ether) to give **3.3** as colourless oil (181 mg, 91%); R_f (2.5% ethyl acetate in petroleum ether) 0.44; IR (neat, cm^{-1}): 2949, 2855, 1714, 1606, 1436, 1236, 1033, 772; δ_H NMR (500 MHz, $CDCl_3$): 7.85 (s, 1H, C=CH), 7.21–7.30 (m, 5H, CH_{ar}), 7.10 (t, J=7.55, 8.25 Hz, 1H, CH_{ar}), 6.93 (t, J=8.60, 8.95 Hz, 3H, CH_{ar}), 3.84 (s, 2H, CH_2), 3.67 (s, 3H, OCH_3), 2.23 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$): 168.65, 140.91, 139.20, 138.07, 135.29, 130.61, 129.18, 128.61, 128.53, 126.88, 124.81, 52.10, 33.01, 21.45; ESI(HRMS) (m/z) calcd for $C_{18}H_{19}O_2$, $(M+H)^+$ 267.1385, found 267.1385.

*4.4.4. 2-(4-Methoxybenzyl)-3-phenylacrylic acid methyl ester (**3.4**)*[13a]. The crude product was purified by column chromatography using (2.5% ethyl acetate in petroleum ether) to give **3.4** as colourless oil (158 mg, 75%); R_f (5% ethyl acetate in petroleum ether) 0.55; IR (neat, cm^{-1}): 3000, 2950, 1714, 1511, 1439, 1247, 1033, 758; δ_H NMR (500 MHz, $CDCl_3$): 7.82 (s, 1H, C=CH), 7.23–7.34 (m, 5H, CH_{ar}), 7.03 (d, J=8.55 Hz, 2H, CH_{ar}), 6.75 (d, J=8.95 Hz, 2H, CH_{ar}), 3.81 (s, 2H, CH_2), 3.69 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$): 168.66, 157.92, 140.62, 135.30, 131.24, 130.98, 129.17, 128.81, 128.69, 128.53, 113.91, 55.18, 52.08, 32.20.

*4.4.5. 2-(3-Methoxybenzyl)-3-phenylacrylic acid methyl ester (**3.5**)*. The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.5** as colourless oil (179 mg, 85%); R_f (5% ethyl acetate in petroleum ether) 0.55; IR (neat, cm^{-1}): 2999, 2949, 2836, 1712, 1601, 1489, 1436, 1265, 1203, 982, 826; δ_H NMR (400 MHz, $CDCl_3$): 7.96 (s, 1H, C=CH), 7.21–7.45 (m, 6H, CH_{ar}), 6.77–6.84 (m, 3H, CH_{ar}), 3.96 (s, 2H, CH_2), 3.79 (s, 6H, OCH_3); δ_C NMR (100 MHz, $CDCl_3$): 168.54, 159.74, 141.02, 135.27, 129.43, 129.15, 128.72, 128.53, 120.24, 113.71, 111.37, 55.05, 52.08, 33.10; ESI(HRMS) (m/z) calcd for $C_{18}H_{19}NaO_3$ $(M+Na)^+$ 305.1154, found 305.1158.

*4.4.6. 2-(4-Ethoxybenzyl)-3-phenylacrylic acid methyl ester (**3.6**)*. The crude product was purified by column chromatography using (1.5% ethyl acetate in petroleum ether) to give **3.6** as colourless oil (162 mg, 73%); R_f (2.5% ethyl acetate in petroleum ether) 0.40; IR (neat, cm^{-1}): 3028, 2980, 1712, 1509, 1437, 1393, 1243, 1048, 806; δ_H NMR (400 MHz, $CDCl_3$): 7.92 (s, 1H, C=CH), 7.33–7.41 (m, 5H, CH_{ar}), 7.12 (d, J=8.32 Hz, 2H, CH_{ar}), 6.84 (d, J=8.28 Hz, 2H, CH_{ar}), 4.02 (q, J=7.08, 14.08 Hz, 2H, OCH_2CH_3), 3.90 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 1.42 (t, J=6.56 Hz, 3H, OCH_2CH_3); δ_C NMR (100 MHz, $CDCl_3$): 168.68, 157.35, 140.52, 135.39, 131.15, 129.19, 128.82, 128.66, 128.52, 114.55, 63.36, 52.05, 32.25, 14.87; ESI(HRMS) (m/z) calcd for $C_{19}H_{20}NaO_3$ $(M+Na)^+$ 319.1310, found 319.1311.

*4.4.7. 2-(4-Fluorobenzyl)-3-phenylacrylic acid methyl ester (**3.7**)*[13a]. The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.7** as light yellow oil (160 mg, 79%); R_f (2% ethyl acetate in petroleum ether) 0.40; IR (neat, cm^{-1}): 2951, 2845, 1713, 1631, 1508, 1437, 1261, 1092, 815; δ_H NMR (500 MHz, $CDCl_3$): 7.84 (s, 1H, C=CH), 7.24–7.27 (m, 5H, CH_{ar}), 7.04–7.07 (m, 2H, CH_{ar}), 6.86–6.91 (m, 2H, CH_{ar}), 3.83 (s, 2H, CH_2), 3.67 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$): 168.45, 161.38 (d, J_{CF}=241.25 Hz), 141.04, 134.90, 130.57, 129.30, 129.24, 129.08, 128.83, 128.60, 115.27 (d, J_{CF}=21.25 Hz), 52.12, 32.33.

*4.4.8. 2-(4-Chlorobenzyl)-3-phenylacrylic acid methyl ester (**3.8**)*[13a]. The crude product was purified by column chromatography using (1% ethyl acetate in petroleum ether) to give **3.8** as colourless oil, (182 mg, 85%); R_f (2% ethyl acetate in petroleum ether) 0.38; IR (neat, cm^{-1}): 2949, 1713, 1490, 1435, 1261, 1204, 1089, 833; δ_H NMR (400 MHz, $CDCl_3$): 7.95 (s, 1H, C=CH), 7.30–7.42 (m, 5H, CH_{ar}), 7.26 (d, J=8.52 Hz, 2H, CH_{ar}), 7.13 (d, J=8.28 Hz, 2H, CH_{ar}), 3.92 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3); δ_C NMR (100 MHz, $CDCl_3$): 168.35, 141.23, 137.93, 135.21, 131.93, 130.31, 129.61, 129.29, 129.07, 128.85, 128.63, 52.06, 32.58.

*4.4.9. 2-(3-Chlorobenzyl)-3-phenylacrylic acid methyl ester (**3.9**)*. The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.9** as colourless

oil (150 mg, 70%); R_f (2% ethyl acetate in petroleum ether) 0.38; IR (neat, cm^{-1}): 2951, 1714, 1508, 1436, 1261, 1222, 1018, 924, 759; δ_H NMR (500 MHz, $CDCl_3$): 7.85 (s, 1H, C=CH), 7.02–7.34 (m, 9H, CH_{ar}), 3.80 (s, 2H, CH_2), 3.67 (s, 3H, OCH_3); δ_C NMR (100 MHz, $CDCl_3$): 168.28, 142.93, 141.50, 135.86, 135.13, 134.38, 129.71, 128.88, 128.64, 128.23, 126.38, 52.42, 32.87; ESI(HRMS) (m/z) calcd for $C_{17}H_{15}ClNaO_2$ $(M-2H+Na)^+$ 307.0513, found 307.0719.

*4.4.10. 2-Benzyl-3-(4-nitrophenyl) acrylic acid methyl ester (**3.10**)*[13a]. The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.10** as light yellow solid (166 mg, 75%); mp 96–98 °C; R_f (10% ethyl acetate in petroleum ether) 0.50; IR (neat, cm^{-1}): 3029, 2925, 2852, 1714, 1596, 1515, 1344, 1204, 1087, 927; δ_H NMR (500 MHz, $CDCl_3$) 8.12 (d, J=8.60 Hz, 2H, CH_{ar}), 7.85 (s, 1H, C=CH), 7.42 (d, J=8.60 Hz, 2H, CH_{ar}), 7.13–7.27 (m, 3H, CH_{ar}), 7.07 (d, J=7.20 Hz, 2H, CH_{ar}), 3.84 (s, 2H, CH_2), 3.71 (s, 3H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$) 167.81, 147.45, 141.77, 138.39, 138.18, 134.10, 129.79, 128.73, 127.71, 126.47, 123.77, 52.44, 33.11.

*4.4.11. 2-(4-Methylbenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.11**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.11** as light yellow solid (162 mg, 70%); mp 130–132 °C; R_f (10% ethyl acetate in petroleum ether) 0.48; IR (neat, cm^{-1}): 3111, 2956, 2925, 1713, 1514, 1436, 1344, 1258, 1203, 977; δ_H NMR (400 MHz, $CDCl_3$) 8.17(d, J=8.80 Hz, 2H, CH_{ar}), 7.88 (s, 1H, C=CH), 7.47 (d, J=8.56 Hz, 2H, CH_{ar}), 7.09 (d, J=8.04 Hz, 2H, CH_{ar}), 7.02 (d, J=8.04 Hz, 2H, CH_{ar}), 3.85 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); δ_C NMR (100 MHz, $CDCl_3$) 167.85, 147.46, 141.84, 137.94, 136.01, 135.27, 134.37, 129.81, 129.42, 127.58, 123.73, 52.39, 32.73, 20.96; ESI(HRMS) (m/z) calcd for $C_{18}H_{17}NNaO_4$ $(M+Na)^+$ 334.1055, found 334.0756.

*4.4.12. 2-(3-Methylbenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.12**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.12** as light yellow solid (180 mg, 80%); mp 112–114 °C; R_f (10% ethyl acetate in petroleum ether) 0.48; IR (neat, cm^{-1}): 3006, 2923, 1713, 1598, 1517, 1347, 1204, 980, 928; δ_H NMR (500 MHz, $CDCl_3$): 8.17 (d, J=8.60 Hz, 2H, CH_{ar}), 7.90 (s, 1H, C=CH), 7.47 (d, J=8.60 Hz, 2H, CH_{ar}), 7.17 (t, J=7.45 Hz, 1H, CH_{ar}), 6.92–7.01 (m, 3H, CH_{ar}), 3.86 (s, 2H, CH_2), 3.77 (s, 3H, OCH_3), 2.30 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$): 167.86, 147.45, 141.80, 138.12, 134.15, 129.82, 128.61, 128.47, 127.26, 124.64, 123.75, 52.43, 33.03, 21.44; ESI(HRMS) (m/z) calcd for $C_{18}H_{17}NO_4$ $(M+H)^+$ 312.1236, found 312.1239.

*4.4.13. 2-(4-Methoxybenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.13**).* The crude product was purified by column chromatography using (4% ethyl acetate in petroleum ether) to give **3.13** as pale yellow solid (153 mg, 63%); mp 107–109 °C; R_f (10% ethyl acetate in petroleum ether) 0.43; IR (neat, cm^{-1}): 3017, 2955, 1715, 1599, 1515, 1347, 1203, 1180, 1156, 928, 855; δ_H NMR (500 MHz, $CDCl_3$) 8.17 (d, J=8.60 Hz, 2H, CH_{ar}), 7.86 (s, 1H, C=CH), 7.47 (d, J=8.60 Hz, 2H, CH_{ar}), 7.03(d, J=9.20 Hz, 2H, CH_{ar}), 6.81 (d, J=8.60 Hz, 2H, CH_{ar}), 3.89 (s, 2H, CH_2), 3.76 (s, 6H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$) 167.86, 158.17, 147.44, 141.84, 139.78, 137.80, 134.51, 129.81, 128.70, 123.75, 114.12, 55.20, 52.41, 32.24; ESI(HRMS) (m/z) calcd for $C_{18}H_{17}NNaO_5$ $(M+Na)^+$ 350.1004, found 350.1006.

*4.4.14. 2-(4-Ethoxybenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.14**).* The crude product was purified by column chromatography using (4% ethyl acetate in petroleum ether) to give **3.14** as pale yellow solid (152 mg, 60%); mp 124–126 °C; R_f (10% ethyl acetate in petroleum ether) 0.45; IR (neat, cm^{-1}): 2927, 2852, 1717, 1598, 1515, 1346, 1204, 1156, 924, 820; δ_H NMR (500 MHz, $CDCl_3$) 8.18(d, J=8.55 Hz, 2H, CH_{ar}), 7.86 (s, 1H, C=CH), 7.47 (d, J=8.60 Hz, 2H, CH_{ar}), 7.02(d, J=8.05 Hz, 2H, CH_{ar}), 6.79 (d, J=8.60 Hz, 2H, CH_{ar}), 3.97 (q, J=7.45, 6.92 Hz, 2H, OCH_2CH_3), 3.82 (s, 2H, CH_2), 3.75 (s, 3H, OCH_3), 1.37 (t, J=7.45, 6.90 Hz, 3H, OCH_2CH_3); δ_C NMR (125 MHz, $CDCl_3$) 167.87, 157.53, 147.41, 141.85, 139.77, 137.75, 134.54, 129.81, 128.67, 123.72, 114.66, 63.35, 52.39, 32.24, 14.81; ESI(HRMS) (m/z) calcd for $C_{19}H_{19}NNaO_5$ $(M+Na)^+$ 364.1161, found 364.1164.

*4.4.15. 2-(4-Fluorobenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.15**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.15** as light yellow solid (153 mg, 65%); mp 97–99 °C; R_f (10% ethyl acetate in petroleum ether) 0.48; IR (neat, cm^{-1}): 2925, 2852, 1726, 1434, 1257, 1098, 757; δ_H NMR (400 MHz, $CDCl_3$) 8.13(d, J=8.76 Hz, 2H, CH_{ar}), 7.83 (s, 1H, C=CH), 7.40 (d, J=8.52 Hz, 2H, CH_{ar}), 6.88–7.04 (m, 4H, CH_{ar}), 3.79 (s, 2H, CH_2), 3.71 (s, 3H, OCH_3); δ_C NMR (100 MHz, $CDCl_3$) 167.62, 161.54 (d, J_{CF}=243.00 Hz), 147.56, 141.67, 138.20, 134.10, 129.72, 129.24, 129.16, 123.81, 115.53 (d, J_{CF}=22.00 Hz), 52.42, 32.36; ESI(HRMS) (m/z) calcd for $C_{17}H_{14}FNNaO_4$ $(M+Na)^+$ 338.0805, found 338.0808.

*4.4.16. 2-(4-Chlorobenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.16**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.16** as pale yellow solid (149 mg, 60%); mp 103–105 °C; R_f (10% ethyl acetate in petroleum ether) 0.48; IR (neat, cm^{-1}): 3108, 2953, 2850, 1713, 1633, 1599, 1343, 1257, 1207, 927, 821; δ_H NMR (500 MHz, $CDCl_3$): 8.19(d, J=9.15 Hz, 2H, CH_{ar}), 7.91 (s, 1H, C=CH), 7.45 (d, J=8.60 Hz, 2H, CH_{ar}), 7.23–7.26(m, 2H, CH_{ar}), 7.06 (d, J=8.60 Hz, 2H, CH_{ar}), 3.85 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$): 167.53, 147.54, 141.57, 138.49, 136.91, 133.64, 132.30, 129.70, 129.09, 128.84, 123.84, 52.48, 32.54; ESI(HRMS) (m/z) calcd for $C_{17}H_{14}ClNNaO_4$ $(M+Na)^+$ 354.0509, found 354.0507.

*4.4.17. 2-(3-Chlorobenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.17**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.17** as pale yellow solid (149 mg, 60%); mp 99–101 °C; R_f (10% ethyl acetate in petroleum ether) 0.47; IR (neat, cm^{-1}): 3108, 2928, 2851, 1717, 1633, 1596, 1345, 1204, 1092, 977, 854; δ_H NMR (500 MHz, $CDCl_3$): 8.21(d, J=9.15 Hz, 2H, CH_{ar}), 7.94 (s, 1H, C=CH), 7.46 (d, J=8.05 Hz, 2H, CH_{ar}), 7.01–7.25 (m, 4H, CH_{ar}), 3.87 (s, 2H, CH_2), 3.78 (s, 3H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$): 167.48, 147.58, 141.52, 138.77, 134.57, 133.29, 129.95, 127.88, 126.77, 125.93, 123.87, 52.53, 32.81; ESI (HRMS) (m/z) calcd for $C_{17}H_{14}ClNNaO_4$ $(M+Na)^+$ 354.0509, found 354.0508.

*4.4.18. 2-(3-Methylbenzyl)-3-(4-chlorophenyl) acrylic acid methyl ester (**3.18**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.18** as light yellow oil (180 mg, 80%); R_f (2.5% ethyl acetate in petroleum ether) 0.44; IR (neat, cm^{-1}): 2950, 2923, 1714, 1490, 1436, 1279, 1202, 836, 771; δ_H NMR (400 MHz, $CDCl_3$) 7.89(s, 1H, C=CH), 7.18–7.36 (m, 5H, CH_{ar}), 6.98–7.10 (m, 3H, CH_{ar}), 3.91 (s, 2H, CH_2), 3.78 (s, 3H, OCH_3), 2.34 (s, 3H, CH_3); δ_C NMR (100 MHz, $CDCl_3$): 168.42, 139.54, 138.85, 138.19, 133.72, 131.23, 130.49, 128.79, 128.54, 127.01, 124.73, 52.18, 32.98, 21.45; ESI(HRMS) (m/z) calcd for $C_{18}H_{17}ClNaO_2$ $(M+Na)^+$ 323.0815, found 323.0819.

*4.4.19. 2-(3-Methoxybenzyl)-3-(4-chlorophenyl) acrylic acid methyl ester (**3.19**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.19** as light yellow oil (191 mg, 81%); R_f (2.5% ethyl acetate in petroleum ether) 0.39; IR (neat, cm^{-1}): 2949, 2837, 1713, 1598, 1489, 1308, 1263, 1203, 1089, 1013, 774; δ_H NMR (500 MHz, $CDCl_3$) 7.86(s, 1H, C=CH), 7.15–7.31 (m, 5H, CH_{ar}), 6.64–6.83 (m, 3H, CH_{ar}), 3.89 (s, 2H,

CH_2), 3.76 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$) 168.48, 159.92, 139.87, 134.88, 133.77, 130.61, 129.70, 128.93, 120.24, 113.84, 111.50, 55.21, 52.35, 33.17; ESI(HRMS) (m/z) calcd for $C_{18}H_{17}ClNaO_3$ $(M+Na)^+$ 339.0764, found 339.0765.

*4.4.20. 2-(3-Methylbenzyl)-3-(furan-2-yl) acrylic acid methyl ester (**3.20**).* The crude product was purified by column chromatography using (2% ethyl acetate in petroleum ether) to give **3.20** as brown oil (151 mg, 78%); R_f (2.5% ethyl acetate in petroleum ether) 0.43; IR (neat, cm^{-1}): 2952, 1710, 1632, 1437, 1205, 1093, 1020, 778; δ_H NMR (500 MHz, $CDCl_3$): 7.39 (s, 1H, C=CH), 6.90–7.17 (m, 5H, CH_{ar}), 6.44 (d, J=3.45 Hz, 1H, CH_{ar}), 6.30 (d, J=3.60 Hz, 1H, CH_{ar}), 3.95 (s, 2H, CH_2), 3.68 (s, 3H, OCH_3), 2.22 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$):168.44, 153.07, 138.95, 137.86, 129.10, 128.22, 126.82, 125.66, 125.23, 117.57, 113.97, 52.22, 33.25, 21.42; ESI(HRMS) (m/z) calcd for $C_{16}H_{16}NaO_3$ $(M+Na)^+$ 279.0997, found 279.0990.

*4.4.21. 2-(3-Methoxybenzyl)-3-(furan-2-yl) acrylic acid methyl ester (**3.21**).* The crude product was purified by column chromatography using (2.5% ethyl acetate in petroleum ether) to give **3.21** as brown oil (167 mg, 82%); R_f (2.5% ethyl acetate in petroleum ether) 0.39; IR (neat, cm^{-1}): 2951, 1709, 1627, 1437, 1256, 1205, 1047, 775; δ_H NMR (500 MHz, $CDCl_3$): 7.39(s, 1H, C=CH), 7.10 (t, J=7.90 Hz, 1H, CH_{ar}), 6.72–6.79 (m, 3H, CH_{ar}), 6.65 (dd, J=2.05, 8.25 Hz, 1H, CH_{ar}), 6.45 (d, J=3.40 Hz, 1H, CH_{ar}), 6.31 (d, J=3.45 Hz, 1H, CH_{ar}), 3.98 (s, 2H, CH_2), 3.69 (s, 6H, OCH_3); δ_C NMR (125 MHz, $CDCl_3$): 168.34, 159.56, 153.03, 140.67, 129.27, 127.75, 125.71, 120.72, 117.72, 114.05, 111.36, 55.09, 52.20, 33.32; ESI(HRMS) (m/z) calcd for $C_{16}H_{16}NaO_4$ $(M+Na)^+$ 295.0944, found 295.0944.

*4.4.22. 2-(4-Methylbenzyl)-3-phenylacrylonitrile (**3.22**)[13b].* The crude product was purified by column chromatography using (1% ethyl acetate in petroleum ether) to give **3.22** as colourless oil (131 mg, 75%); R_f (2.5% ethyl acetate in petroleum ether) 0.58; IR (neat, cm^{-1}): 2919, 2851, 2211, 1624, 1513, 1448, 1215, 738; δ_H NMR (500 MHz, $CDCl_3$): 7.71(d, J=6.90 Hz, 2H, CH_{ar}), 7.38–7.41 (m, 3H, CH_{ar}), 7.13–7.20 (m, 4H, CH_{ar}), 6.94 (s, 1H, C=CH), 3.66 (s, 2H, CH_2), 2.34 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$): 143.77, 136.96, 133.56, 133.30, 130.02, 129.54, 128.75, 128.63, 118.72, 111.02, 41.76, 21.05.

*4.4.23. 2-(3-Methylbenzyl)-3-phenylacrylonitrile (**3.23**).* The crude product was purified by column chromatography using (2.5% ethyl acetate in petroleum ether) to give **3.23** as colourless oil (110 mg, 63%); R_f (2.5% ethyl acetate in petroleum ether) 0.58; IR (neat, cm^{-1}): 3029, 2919, 2210, 1585, 1448, 1213, 1036, 771; δ_H NMR (500 MHz, $CDCl_3$): 7.41–7.72(m, 2H, CH_{ar}), 7.14–7.40 (m, 7H, CH_{ar}), 6.94 (s, 1H, C=CH), 3.66 (s, 2H, CH_2), 2.34 (s, 3H, CH_3); δ_C NMR (125 MHz, $CDCl_3$): 144.08, 139.82, 138.22, 134.68, 130.40, 129.75, 128.60, 128.22, 126.05, 118.85, 110.95, 42.25, 21.63; ESI(HRMS) (m/z) calcd for $C_{17}H_{14}N$ $(M-H)^+$ 232.1132 found, 232.1135.

*4.4.24. 3-Butyl-2-(4-methylbenzyl) acrylic acid methyl ester (**3.24**).* The crude product was purified by column chromatography using (0.5% ethyl acetate in petroleum ether) to give **3.24** as colourless oil (133 mg, 72%); R_f (0.5% ethyl acetate in petroleum ether) 0.45; IR (neat, cm^{-1}): 2955, 2928, 1714, 1513, 1436, 1270, 1139, 777; δ_H NMR (400 MHz, $CDCl_3$): 6.89–7.08 (m, 5H, CH_{ar}), 3.67 (s, 3H, OCH_3), 3.63 (s, 2H, CH_2), 2.23–2.31 (m, 5H, CH_3, $-CH_2-$), 1.24–1.51 (m, 4H, $-CH_2-CH_2-$), 0.84–0.94 (m, 3H, $-CH_3$); δ_C NMR (100 MHz, $CDCl_3$) 168.18, 144.18, 136.65, 135.34, 130.86, 128.97, 128.01, 51.65, 31.87, 30.82, 28.61, 22.44, 20.94, 13.84; ESI(HRMS) (m/z) calcd for $C_{16}H_{22}NaO_2$ $(M+Na)^+$ 269.1517, found 269.1510.

*4.4.25. 3-Butyl-2-(3-methylbenzyl)acrylic acid methyl ester (**3.25**).* The crude product was purified by column chromatography using (0.5% ethyl acetate in petroleum ether) to give **3.25** as colourless oil (138 mg, 74%); R_f (0.5% ethyl acetate in petroleum ether) 0.45; IR (neat, cm^{-1}): 2955, 2928, 1714, 1436, 1268, 1201, 766, 699; δ_H NMR (400 MHz, $CDCl_3$) 6.90–7.16 (m, 5H, CH_{ar}), 3.68 (s, 3H, OCH_3), 3.66 (s, 2H, CH_2), 2.22–2.31(m, 5H, CH_3, $-CH_2-$), 1.29–1.47 (m, 4H, $-CH_2-CH_2-$), 0.82–0.94 (m, 3H, $-CH_3$); δ_C NMR (100 MHz, $CDCl_3$) 168.18, 144.39, 139.62, 137.79, 130.69, 128.91, 128.16, 126.67, 125.13, 51.67, 32.18, 30.78, 28.63, 22.43, 21.40, 13.83; ESI(HRMS) (m/z) calcd for $C_{16}H_{22}NaO_2$ $(M+Na)^+$ 269.1517, found 269.1512.

*4.4.26. 3-Butyl-2-(3-methoxybenzyl) acrylic acid methyl ester (**3.26**).* The crude product was purified by column chromatography using (0.5% ethyl acetate in petroleum ether) to give **3.26** as colourless oil (147 mg, 75%); R_f (0.5% ethyl acetate in petroleum ether) 0.43; IR (neat, cm^{-1}): 2928, 2857, 1713, 1600, 1435, 1261, 1144, 1048, 769; δ_H NMR (400 MHz, $CDCl_3$): 7.15 (t, J=7.56 Hz, 1H, CH_{ar}), 6.93 (t, J=7.56 Hz, 1H, CH_{ar}), 6.69–6.76 (m, 3H, CH_{ar}), 3.75 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.65 (s, 2H, CH_2), 2.25 (q, J=7.32, 7.56 Hz, 2H, $-CH_2-$), 1.24–1.46 (m, 4H, $-CH_2-CH_2-$), 0.88–0.90 (m, 3H, $-CH_3$); δ_C NMR (100 MHz, $CDCl_3$): 168.11, 159.59, 144.55, 141.35, 130.48, 129.19, 120.57, 113.98, 111.17, 55.05, 51.70, 32.28, 30.79, 28.64, 22.44, 13.83; ESI(HRMS) (m/z) calcd for $C_{16}H_{22}O_3$ $(M+H)^+$ 263.1647, found 263.1646.

*4.4.27. 2-(3-Methoxybenzyl)-3-(4-nitrophenyl) acrylic acid methyl ester (**3.27**).* The crude product was purified by column chromatography using (4% ethyl acetate in petroleum ether) to give **3.27** as pale yellow solid (182 mg, 75%); mp 108–110 °C; R_f (10% ethyl acetate in petroleum ether) 0.45; IR (neat, cm^{-1}): 3016, 2930, 2836, 1713, 1603, 1518, 1347, 1315, 1293, 1049, 896; δ_H NMR (400 MHz, $CDCl_3$): 8.21(d, J=8.52 Hz, 2H, CH_{ar}), 7.94 (s, 1H, C=CH), 7.51 (d, J=9.04 Hz, 2H, CH_{ar}), 7.22–7.28 (m, 1H, CH_{ar}), 6.66–6.81 (m, 3H, CH_{ar}), 3.91 (s, 2H, CH_2), 3.81 (s, 3H, CH_3), 3.79 (s, 3H, CH_3); δ_C NMR (100 MHz, $CDCl_3$): 167.74, 159.85, 147.46, 141.72, 140.00, 138.25, 133.91, 129.80, 123.73, 119.99, 113.79, 111.43, 55.08, 52.41, 33.07; ESI(HRMS) (m/z) calcd for $C_{18}H_{17}NNaO_5$ $(M+Na)^+$ 350.1004, found 350.1004.

Acknowledgements

We thank the Department of Science and Technology (DST), New Delhi for supporting this work under green chemistry program (SR/S5/GC-11/2008). D.B. and R.J.D. thank IIT Kanpur and CSIR, New Delhi for research fellowships respectively.

Supplementary data

Supplementary data containing ^1H and ^{13}C NMR spectra of all the products can be found in the online version. Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.03.020.

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