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A palladium catalyzed atom-efficient cross-coupling reactivity of triarylbismuths with α,β-unsaturated acyl chlorides

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ABSTRACT

An atom-efficient cross-coupling reactivity of triarylbismuths (1 equiv) was demonstrated by cross-coupling reaction with 3 equiv of α,β-unsaturated acyl chlorides under palladium catalysis in the synthesis of a series of functionalized α, β-unsaturated ketones in high isolated yields.

1. Introduction

The palladium catalyzed Suzuki-type cross-coupling reaction of acyl chlorides with organometallic reagents proceeds, in general, smoothly to furnish excellent yields of ketones [1]. Incidentally, the similar coupling reaction of α,β-unsaturated acyl chlorides with arylboronic acids has been reported to proceed only sluggishly leading to poor yields of α,β-unsaturated ketones, despite some reports showing the synthesis of one or two examples of chalcones as part of cross-coupling study involving acyl chlorides [1–3]. In fact, this poor reactivity of α,β-unsaturated acyl chlorides led to the change of strategy for the synthesis of chalcones by involving aroyl chlorides and stryrylboronic acids as electrophilic and nucleophilic coupling partners respectively in Suzuki-type cross-coupling reaction [2b]. Compounds containing chalcone functionality are well known for their important medicinal properties in addition to their utility for a variety of transformations in organic synthesis [4]. In principle, the direct cross-coupling of α,β-unsaturated acyl chlorides with organometallic reagent under metal catalysis is an ideal and a facile pathway to access chalcones, since α,β-unsaturated acyl chlorides are easily obtainable substrates [5,6]. Indeed, the traditional method of preparation of chalcones via Claisen–Schmidt reaction or Friedel–Crafts acylation protocols often produce unwanted side reactions in the presence of additional acid or base sensitive groups [4].

The organobismuths are important class of organometallic compounds [7] with low or non-toxicity and are easily available by known procedures. Although, use of these reagents for C–C bond formations under metal catalyzed conditions are limited at present [7–10], the applications of these reagents for C–N, C–O bond formations is well known in organic synthesis [7]. In our quest for developing atom-efficient organometallic reagents for C–C bond formations we recently uncovered a high reactivity of the triarylbismuths in cross-coupling reactions with a variety of electrophilic coupling partners under palladium catalysis [10]. In particular, we have disclosed the high atom-efficient cross-coupling reactivity of triarylbismuths with acid chlorides under palladium catalysis to give both diaryl and alkyl aryl ketones [10a]. Although we initially surmised the possibility of cross-coupling of α,β-unsaturated acyl chlorides with triarylbismuths in analogous manner, the reported poor reactivity of the former under Suzuki-type coupling conditions deterred us from exploring further. Our recent experience and the realization of relative facile reactivity of triarylbismuths with electrophilic coupling partners [10] spurred us return to this study involving α,β-unsaturated acyl chlorides with triarylbismuths under palladium catalysis. To our surprise, we discovered that the cross-coupling reaction of a variety of α,β-unsaturated acyl chlorides with triarylbismuths is very facile and more efficient under palladium catalyzed conditions. Herein, we report the first versatile reactivity of α,β-unsaturated acyl chlorides with

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triarylbismuths under palladium catalysis for the facile synthesis of diversely-substituted α,β-unsaturated ketones.

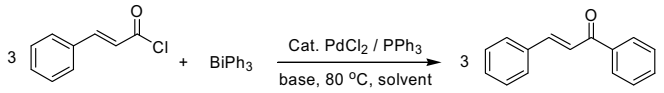
2. Results and discussion

As the reactivity of α,β-unsaturated acyl chlorides under Suzuki-type coupling conditions reported to be inefficient [2b], we were tempted to screen the reactivity of α,β-unsaturated acyl chlorides with triarylbismuths under similar conditions to our earlier palladium protocol for acyl chlorides [10a]. So, for the initial study we have carried out cross-coupling reaction of cinnamoyl chloride with triphenylbismuth in the presence of $PdCl_2/PPh_3$ catalytic system under different solvent, base conditions and the results are summarized in Table 1. From this study, it was found that the cross-coupling reaction produced moderate conversion in *N*,*N*-dimethylacetamide (DMA), 1,2-dimethoxyethane (DME), *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) solvents (entries 1–4). Under similar conditions, the conversion was good in acetonitrile and 1,4-dioxane solvents furnishing 69–71% of isolated yields of chalcone (entries 5–6). Additional screening in the presence of inorganic bases produced 69–79% (entries 7–10), while pyridine as a base produced 66% conversion under similar conditions (entry 11). As a result, triethylamine found to be more suitable and produced conversion up to 91% with 78% of the isolated yield of chalcone (entry 12). A control reaction carried out in the absence of palladium catalytic system but with triethylamine produced chalcone as cross-coupled product in 31% isolated yield (entry 13).

Another control reaction performed in the absence of both palladium catalyst and triethylamine produced 21% isolated yield of the product (entry 14). Further, it was found that triethylamine (1 equiv) is sufficient to obtain good cross-coupling conversion (entries 12, 15 and 16). Further, a control reaction carried out without triphenylphosphine furnished 46% of cross-coupled chalcone revealing that the ligand is necessary for coupling reaction to yield good conversion (entry 17). From this, it was emerged that the cross-coupling reaction of triphenylbismuth (1 equiv) with model substrate cinnamoyl chloride (4 equiv) was atom-efficient in 1,4-dioxane solvent with triethylamine (1 equiv) under palladium catalysis. This is very significant, as the corresponding reactivity of α,β-unsaturated acyl chloride was reported to be poor under Suzuki-type coupling conditions [2b]. Hence, it is remarkable that the present palladium catalyzed protocol is high yielding and atom-efficient as 1 equiv of triphenylbismuth could effectively cross-couple with 3 equiv of α,β-unsaturated acyl chlorides under easily obtainable conditions.

Hence, to further broaden the scope and versatility of this reaction, a variety of electronically divergent α,β-unsaturated acyl chlorides were employed for cross-coupling reaction with different triarylbismuths under standardized conditions (Table 2). The cross-coupling reaction of α,β-unsaturated acyl chlorides with different triarylbismuths proved to be efficient furnishing excellent yields of the corresponding functionalized α,β-unsaturated ketones. For example, the cross-coupling reaction of cinnamoyl chloride with three different triarylbismuths produced chalcones in 78–85% isolated yields (entries 1–3). Similarly, the other cinnamoyl chlorides with electron-rich substituents such as *p*-methyl, *p*-methoxy, *m*-methoxy groups delivered high yields of the corresponding chalcones (entries 4–12). Cinnamoyl chlorides having -chloro substituent in -*ortho*, -*meta* and -*para* positions furnished the corresponding chalcones in good to high yields (entries 13–21). Further, the cross-coupling reaction of *p*-bromo and *m*-bromo-cinnamoyl chlorides were found to be chemoselective giving the corresponding chalcones in good yields (entries 22–27). The reactivity of 3-furan-2-yl-acryloyl chloride was found to be excellent with different triarylbismuths furnishing the corresponding conjugated ketones in 79–86% yields (entries 28–30). The cross-coupling reaction of electron-deficient cinnamoyl chloride with -nitro substituent furnished the corresponding chalcone in 64% yield (entry 31). Overall, it was demonstrated that the reactivity of both electron-rich and -deficient cinnamoyl chlorides fared well in cross-coupling reaction with different triarylbismuths giving good to excellent yields of variety of functionalized α,β-unsaturated ketones.

Table 1
Screening conditions[a]



Entry	Solvent	Base (equiv)	t/h	Conv. (%)[b,c]
1	DMA	NEt_3 (1)	2	42
2	DMF	NEt_3 (1)	2	60
3	DME	NEt_3 (1)	2	47
4	THF	NEt_3 (1)	2	66
5	CH_3CN	NEt_3 (1)	2	84 (71)
6	1,4-Dioxane	NEt_3 (1)	2	85 (69)
7	1,4-Dioxane	K_3PO_4 (1)	4	79 (62)
8	1,4-Dioxane	Cs_2CO_3 (1)	4	71
9	1,4-Dioxane	K_2CO_3 (1)	4	69
10	1,4-Dioxane	Na_2CO_3 (1)	4	71
11	1,4-Dioxane	Pyridine (1)	4	66
12	1,4-Dioxane	NEt_3 (1)	4	91 (78)
13	1,4-Dioxane	NEt_3 (1)	4	(31)[d]
14	1,4-Dioxane	–	4	(21)[e]
15	1,4-Dioxane	–	4	73 (51)[f]
16	1,4-Dioxane	NEt_3 (3)	4	81 (76)
17	1,4-Dioxane	NEt_3 (1)	4	55 (46)[g]

[a] Equivalent ratios: $BiPh_3$ (1 equiv); $PdCl_2$ (9 mol%)/PPh_3 (18 mol%), cinnamoyl chloride (4.0 equiv), 80 °C.
[b] Based on GC analysis.
[c] Isolated yields are given in parentheses.
[d] Control without $PdCl_2/PPh_3$.
[e] Control without $PdCl_2/PPh_3$ and NEt_3.
[f] Control without NEt_3.
[g] Control without PPh_3.

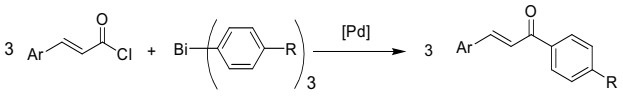
3. Conclusion

In conclusion, we have demonstrated the versatile atom-efficient reactivity of triarylbismuths with α,β-unsaturated acyl chloride under palladium catalyzed conditions. This study is very significant as the similar high reactivity was not known before with electronically divergent α,β-unsaturated acyl chlorides under Suzuki-type cross-coupling conditions. Additional advantage associated with the present method is that 1 equiv of triarylbismuth could be effectively cross-couple with 3 equiv of α,β-unsaturated acyl chloride. This will reduce the organometallic reagent loadings to 1/3 amount effectively in bulk scale operations in such coupling reactions. As triarylbismtuhs are readily accessible using standard procedures, the present palladium catalyzed protocol provides an easy access to a library of divergent α,β-unsaturated ketones in high yields. Hence, we believe that the first atom-efficient cross-coupling reaction of triarylbismuths with α,β-unsaturated acyl chloride reported here would further encourage the use of triarylbismuths as atom-efficient organometallic reagents for C–C bond formations in organic synthesis.

4. Experimental

General: All reactions were carried out in Schlenk tubes under nitrogen atmosphere using anhydrous organic solvents.

Table 2
Cross-coupling reaction of triarylbismuths with α,β-unsaturated acyl chlorides



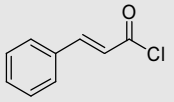
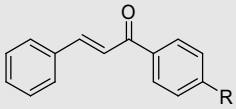
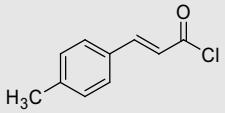
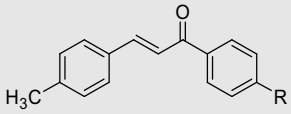
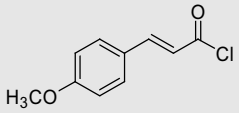
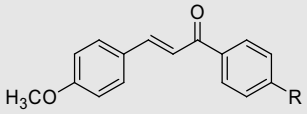
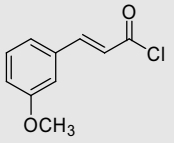
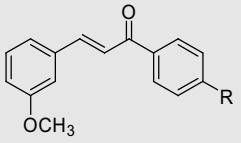
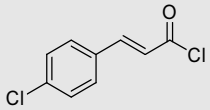
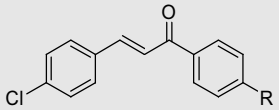
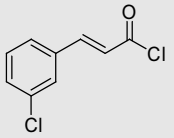
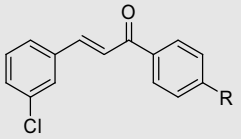
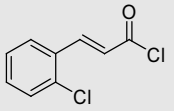
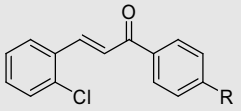
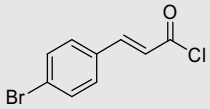
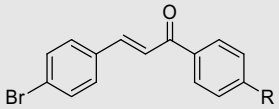
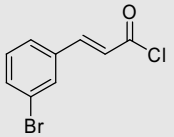
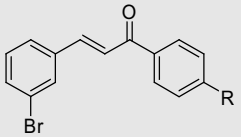
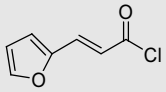
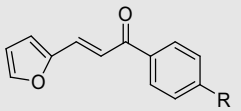
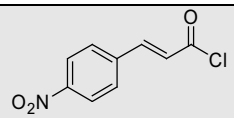
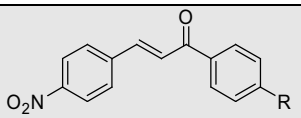
Entry	ArCH=CHCOCl	α,β-Unsaturated ketone		R	Yield (%)[a,b]	Ref.
1			**1a**	R = H	78	[11a]
2			**2a**	R = CH_3	85	[11a]
3			**3a**	R = OCH_3	81	[11a]
4			**4a**	R = H	83	[11a]
5			**5a**	R = CH_3	78	[11b]
6			**6a**	R = OCH_3	76	[11c]
7			**7a**	R = H	80	[11d]
8			**8a**	R = CH_3	87	[11e]
9			**9a**	R = OCH_3	90	[11f]
10			**10a**	R = H	84	[12a]
11			**11a**	R = CH_3	83	–
12			**12a**	R = OCH_3	85	[12b]
13			**13a**	R = H	91	[12c]
14			**14a**	R = CH_3	90	[12d]
15			**15a**	R = OCH_3	86	[11f]
16			**16a**	R = H	81	[12e]
17			**17a**	R = CH_3	79	[12f,13a]
18			**18a**	R = OCH_3	81	[12e,12f]
19			**19a**	R = H	71	[11e]
20			**20a**	R = CH_3	74	[11e]
21			**21a**	R = OCH_3	69	[13b]
22			**22a**	R = H	80	[13c]
23			**23a**	R = CH_3	75	–
24			**24a**	R = OCH_3	75	–
25			**25a**	R = H	72	[13d,13e]
26			**26a**	R = CH_3	71	[12e]
27			**27a**	R = OCH_3	78	[12e]
28			**28a**	R = H	79	[13d,13f,13g]
29			**29a**	R = CH_3	86	[13f,13g]
30			**30a**	R = OCH_3	84	[13f,13g]

Table 2 (*continued*)

31			**31a**	R = H	64 [13h]

[a] Condition: $BiAr_3$ (1 equiv), α,β-unsaturated acyl chloride (4 equiv), $PdCl_2$ (9 mol%)/PPh_3 (18 mol%), Et_3N (1 equiv), 1,4-dioxane (3 mL), 80 °C, 4 h.
[b] Isolated yields after column chromatography w.r.t $BiAr_3$.

1,4-Dioxane was freshly distilled over sodium-benzophenone ketyl prior to use and purged with nitrogen gas. All other solvents where ever used were purified by standard procedures.

Silica gel 60–120 (Acme, Mumbai) was used to perform column chromatography using ethyl acetate/petroleum ether as an eluent system. Aluminium sheets coated with silica gel 60 F_{254} (Merck) were used to perform thin layer chromatography (TLC) and were visualized under UV lamp. Melting points measured using JSGW melting point apparatus (Jain Scientific Glass Works, Ambala cantt, India) were uncorrected. The IR spectra were recorded on a Bruker vector 22 FT-IR spectrophotometer. The ^1H and ^{13}C NMR spectra were recorded on a JEOL-Lambda (400 MHz) spectrometer using $CDCl_3$ as a solvent. The chemical shifts (δ) are quoted in parts per million (ppm). The coupling constants (J) are reported in Hertz (Hz). α,β-Unsaturated acyl chlorides were prepared using the reported procedures [6]. Triarylbismuths were prepared using standard protocols [7]. GC analysis of the crude reaction mixtures was performed using Perkin–Elmer (Clarus 500) Gas Chromatograph. High resolution mass spectra were recorded using electrospray (ES) technique on Waters HAB213 Q-Tof Premier Micro mass spectrometer.

4.1. Representative procedure

In a typical experiment, an oven-dried Schlenk tube under nitrogen atmosphere was charged with cinnamoyl chloride (0.166 g, 1 mmol), $BiPh_3$ (0.11 g, 0.25 mmol), $PdCl_2$ (0.004 g, 0.023 mmol), PPh_3 (0.012 g, 0.045 mmol) and Et_3N (0.025 g, 0.25 mmol) followed by the addition of anhydrous 1,4-dioxane (3 mL) and the contents were heated at 80 °C for 4 h. Then, the reaction mixture was cooled to room temperature and quenched with water and extracted with ethyl acetate (2 × 15 mL). The combined ethyl acetate extract was washed with dilute HCl (5 mL), saturated sodium bicarbonate solution (5 mL), brine (2 × 5 mL) and dried over $MgSO_4$. The crude product mixture thus obtained after removing the solvent was subjected to column chromatography and the pure chalcone was isolated in 78% yield with respect to triarylbismuth used. The product was characterized by ^1H NMR, ^{13}C NMR, IR and mass spectral analysis.

4.2. Spectral data

1,3-Bis(4-methoxyphenyl)-(2E)-2-propen-1-one, **9a**: m.p. 94–96 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.90–6.96 (m, 4H, CH_{ar}), 7.39–7.43 (d, 1H, J = 15.6 Hz, –CH=C*H*–C=O), 7.57–7.59 (d, 2H, J = 8.8 Hz, CH_{ar}), 7.74–7.78 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 8.00–8.02 (d, 2H, J = 8.8 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3, 55.4, 113.7, 114.3, 119.4, 127.7, 130.0, 130.3, 130.6, 131.2, 143.7, 161.4, 163.2, 188.7; IR ν_{max} (KBr, cm^{-1}): 1655; HRMS (ES^+) for (M+H) $C_{17}H_{17}O_3$ calcd: 269.1178; found: 269.1176.

3-(3-Methoxyphenyl)-1-phenyl-(2E)-2-propen-1-one, **10a**: m.p. 49–51 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.77 (s, 3H, OCH_3), 6.87–6.90 (m, 1H, CH_{ar}), 7.07–7.53 (m, 7H, CH_{ar} and –CH=C*H*–C=O), 7.67–7.71 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.93–7.95 (d, 2H, J = 8.6 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 113.3, 116.2, 121.0, 122.3, 128.4, 128.5, 129.9, 132.7, 136.2, 138.1, 144.7, 159.8, 190.4; IR ν_{max} (KBr, cm^{-1}): 1663; HRMS (ES^+) for (M+H) $C_{16}H_{15}O_2$ calcd: 239.1072; found: 239.1070.

3-(3-Methoxyphenyl)-1-(4-methylphenyl)-(2E)-2-propen-1-one, **11a**: m.p. 65–67 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 6.88-6.90 (m, 1H, CH_{ar}), 7.08 (s, 1H, CH_{ar}), 7.16–7.28 (m, 4H, CH_{ar}), 7.42–7.46 (d, 1H, J = 15.6 Hz, –CH=C*H*–C=O), 7.67–7.71 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.85–7.87 (d, 2H, J = 8.3 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 55.2, 113.3, 116.1, 120.9, 122.3, 128.6, 129.2, 129.8, 135.5, 136.3, 143.6, 144.2, 159.8, 189.9; IR ν_{max} (KBr, cm^{-1}): 1662; HRMS (ES^+) for (M+H) $C_{17}H_{17}O_2$ calcd: 253.1229; found: 253.1220.

3-(4-Chlorophenyl)-1-(4-methoxyphenyl)-(2E)-2-propen-1-one, **15a**: m.p. 129–131 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.89–6.92 (d, 2H, J = 8.8 Hz, CH_{ar}), 7.29–7.31 (d, 2H, J = 8.3 Hz, CH_{ar}), 7.42–7.46 (d, 1H, J = 15.6 Hz, –CH=C*H*–C=O), 7.48–7.50 (d, 2H, J = 8.3 Hz, CH_{ar}), 7.65–7.69 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.95–7.97 (d, 2H, J = 8.8 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 113.8, 122.2, 129.1, 129.4, 130.7, 130.8, 133.5, 136.1, 142.3, 163.5, 188.3; IR ν_{max} (KBr, cm^{-1}): 1653; HRMS (ES^+) for (M+H) $C_{16}H_{14}ClO_2$ calcd: 273.0682; found: 273.0687.

3-(3-Chlorophenyl)-1-phenyl-(2E)-2-propen-1-one, **16a**: m.p. 68–70 °C [lit. 70 °C]; ^1H NMR (400 MHz, $CDCl_3$): δ 7.25–7.31 (m, 2H, CH_{ar}), 7.40–7.55 (m, 6H, CH_{ar} and –CH=C*H*–C=O), 7.63–7.67 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.93–7.95 (d, 2H, J = 7.8 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.2, 126.7, 127.8, 128.5, 128.6, 130.1, 130.2, 132.9, 134.9, 136.7, 137.8, 142.9, 190.0; IR ν_{max} (KBr, cm^{-1}): 1664; HRMS (ES^+) for (M+H) $C_{15}H_{12}ClO$ calcd: 243.0577; found: 243.0573.

3-(3-Chlorophenyl)-1-(4-methylphenyl)-(2E)-2-propen-1-one, **17a**: m.p. 73–75 °C [lit. 80 °C]; ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.22-7.24 (d, 2H, J = 8.0 Hz, CH_{ar}), 7.26–7.28 (d, 2H, J = 7.6 Hz, CH_{ar}), 7.40–7.47 (m, 2H, CH_{ar} and –CH=C*H*–C=O), 7.55 (s, 1H, CH_{ar}), 7.62–7.66 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.85–7.87 (d, 2H, J = 8.3 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 123.2, 126.7, 127.8, 128.6,129.3, 130.1, 130.1, 134.9, 135.3, 136.8, 142.5, 143.8, 189.4; IR ν_{max} (KBr, cm^{-1}): 1663; HRMS (ES^+) for (M+H) $C_{16}H_{14}ClO$ calcd: 257.0733, found: 257.0732.

3-(3-Chlorophenyl)-1-(4-methoxyphenyl)-(2E)-2-propen-1-one, **18a**: m.p. 102–104 °C [lit. 95 °C]; ^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 6.90-6.92 (d, 2H, J = 8.8 Hz, CH_{ar}), 7.25–7.27 (d, 2H, J = 7.8 Hz, CH_{ar}), 7.41–7.42 (m, 1H, CH_{ar}), 7.44–7.48 (d, 1H, J = 15.6 Hz, –CH=C*H*–C=O), 7.55 (s, 1H, CH_{ar}),7.63–7.66 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.95–7.98 (d, 2H, J = 8.8 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 113.8, 123.0, 126.7, 127.7, 130.0, 130.1, 130.7, 130.8, 134.8, 136.9, 142.1, 163.5, 188.1; IR ν_{max} (KBr, cm^{-1}): 1661; HRMS (ES^+) for (M+H) $C_{16}H_{14}ClO$ calcd: 273.0682; found: 273.0681.

3-(2-Chlorophenyl)-1-(4-methoxyphenyl)-(2E)-2-propen-1-one, **21a**: m.p. 74–76 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.89–6.92 (d, 2H, J = 8.8 Hz, CH_{ar}), 7.22–7.26 (m, 2H, CH_{ar}), 7.35–7.37 (m, 1H, CH_{ar}), 7.39–7.43 (d, 1H, J = 15.6 Hz, –CH=C*H*–C=O), 7.65–7.68 (m, 1H, CH_{ar}), 7.94-7.97 (d, 2H, J = 9.0 Hz, CH_{ar}), 8.06–8.10 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O); ^{13}C NMR (100 MHz,

$CDCl_3$): δ 55.4, 113.6, 113.8, 124.7, 127.0, 127.7, 130.2, 130.8, 130.9, 133.4, 135.3, 139.7, 163.5, 188.6; IR ν_{max} (KBr, cm^{-1}): 1660; HRMS (ES^+) for (M+H) $C_{16}H_{14}ClO_2$ calcd: 273.0682; found: 273.0681.

3-(4-Bromophenyl)-1-(4-methylphenyl)-(2E)-2-propen-1-one, **23a**: m.p. 149–151 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.21–7.23 (d, 2H, J = 8.0 Hz, CH_{ar}), 7.41–7.53 (m, 5H, CH_{ar} and –CH=C*H*–C=O), 7.63–7.67 (d, 1H, J = 15.6 Hz, –*CH*=CH–C=O), 7.84–7.86 (d, 2H, J = 8.3 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 122.5, 124.6, 128.6, 129.3, 129.7, 132.1, 133.9, 135.4, 142.8, 143.8, 189.6; IR ν_{max} (KBr, cm^{-1}): 1657; HRMS (ES^+) for (M+H) $C_{16}H_{14}BrO$ calcd: 301.0228; found: 301.0224 and (M+2+H) $C_{16}H_{14}BrO$ calcd: 303.0228; found: 303.0202.

3-(4-Bromophenyl)-1-(4-methoxyphenyl)-(2E)-2-propen-1-one, **24a**: m.p. 137–139 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.89–6.91 (d, 2H, J = 8.6 Hz, CH_{ar}), 7.41–7.53 (m, 5H, CH_{ar} and –CH=C*H*–C=O), 7.63–7.67 (d, 1H, J = 15.6 Hz, –*CH*=CH–C=O), 7.94–7.96 (d, 2H, J = 8.3 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.4, 113.8, 122.3, 124.4, 129.6, 130.7, 132.1, 133.9, 142.4, 163.5, 188.3; IR ν_{max} (KBr, cm^{-1}): 1656; HRMS (ES^+) for (M+H) $C_{16}H_{14}BrO_2$ calcd: 317.0177; found: 317.0175 and (M+2+H) $C_{16}H_{14}BrO_2$ calcd: 319.0177; found: 319.0165.

3-(3-Bromophenyl)-1-(4-methylphenyl)-(2E)-2-propen-1-one, **26a**: m.p. 100–102 °C [lit. 80 °C]; ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 7.18–7.24 (m, 3H, CH_{ar}), 7.42–7.47 (m, 3H, CH_{ar} and –CH=C*H*–C=O), 7.61–7.65 (d, 1H, J = 15.6 Hz, –*CH*=CH–C=O), 7.71 (s, 1H, CH_{ar}), 7.85–7.87 (d, 2H, J = 8.3 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 123.0, 123.2, 127.2, 128.6, 129.3, 130.4, 130.7, 133.0, 135.2, 137.0, 142.4, 143.9, 189.4; IR ν_{max} (KBr, cm^{-1}): 1664; HRMS (ES^+) for (M+H) $C_{16}H_{14}BrO$ calcd: 301.0228; found: 301.0226 and (M+2+H) $C_{16}H_{14}BrO$ calcd: 303.0228; found: 303.0211.

3-(3-Bromophenyl)-1-(4-methoxyphenyl)-(2E)-2-propen-1-one, **27a**: m.p. 106–108 °C [lit. 108 °C]; ^1H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H, OCH_3), 6.90–6.92 (d, 2H, J = 8.8 Hz, CH_{ar}), 7.19–7.23 (m, 1H, CH_{ar}), 7.43–7.47 (m, 3H, CH_{ar} and CH=C*H*–C=O), 7.61–7.65 (d, 1H, J = 15.6 Hz, –C*H*=CH–C=O), 7.71 (s, 1H, CH_{ar}), 7.95–7.97 (d, 2H, J = 8.8 Hz, CH_{ar}); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 113.8, 123.0, 123.0, 127.1, 130.3, 130.6, 130.7, 130.8, 132.9, 137.2, 142.0, 163.5, 188.1; IR ν_{max} (KBr, cm^{-1}): 1660; HRMS (ES^+) for (M+H) $C_{16}H_{14}BrO_2$ calcd: 317.0177; found: 317.0170 and (M+2+H) $C_{16}H_{14}BrO_2$ calcd: 319.0177; found: 319.0153.

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