

A Palladium Catalyzed Environmentally Benign Acylation

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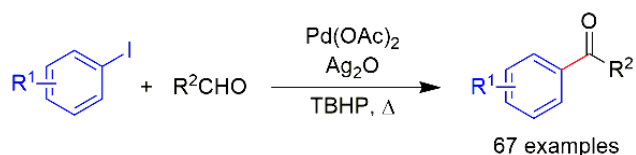
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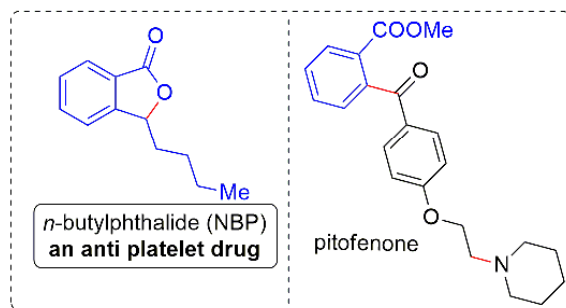
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- * environmentally benign and directing group free protocol
- * direct carbonylation; no need to activate the carbonyl group
- * eliminates the use toxic CO gas as carbonylating agent
- * simple iodo-arenes and aldehydes used as starting materials
- * broad substrate scope; synthesis of natural products



ABSTRACT:

Recent trends in research have gained an orientation towards developing efficient strategies using innocuous reagents. The earlier reported transition-metal catalyzed carbonylations involved either toxic carbon monoxide (CO) gas as carbonylating agent or functional group assisted *ortho* sp² C-H activation (i.e. *ortho* acylation) or carbonylation by the activation of carbonyl group (i.e. via the formation of enamines). Contradicting to these methods, here we describe an environmentally benign process, [Pd]-catalyzed direct carbonylation starting from simple and commercially available iodo arenes and aldehydes, for the synthesis of a wide variety of ketones. Moreover, this method comprises direct coupling of iodo-arenes with aldehydes without the activation of carbonyl and also without directing

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3 group assistance. Significantly, the strategy was successfully applied to the synthesis *n*-butylphthalide
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5 and pitofenone.
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10 11 **Introduction:**

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13 Aryl ketones are ubiquitous structural units that can be found in natural products, pharmaceuticals,
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15 agrochemicals, fragrances, dyes, and electronic materials.¹ Also; ketones have been recognized as crucial
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17 synthones in the realm of organic chemistry, as their electrophilic nature permits broad range of bond-
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19 forming transformations. Classical methods for their synthesis include: a) Friedel–Crafts acylation;² b)
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21 Grignard/Barbier reaction with aldehydes and followed by oxidation³ or Grignard reaction with nitriles^{3f}
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23 and c) organometallic 1,2-additions to Weinreb amides. Among these, the Friedel-Crafts acylation has
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25 drawbacks, as usually leads to isomeric mixtures and fails with electron-deficient arenes; latter one
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27 provides clean products, but involves a two-step process; while Weinreb amides afford pure products,
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29 however, the reaction works under strong nucleophilic conditions, therefore, might not be suitable to
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31 aromatic systems with sensitive functionalities (e.g., esters etc.). On the other hand, recently, transition-
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33 metal catalysis⁴ proved to be effective to furnish ketones such as: a) Nickel catalyzed coupling between
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35 iodoarenes and benzaldehydes;^{4a} b) Stille coupling of acyl chlorides with organostannanes;⁵ c) metal-
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37 mediated carbonylation between halo arenes and transmetalation reagents using toxic carbon
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39 monoxide (CO) gas as the carbonylating agent [(e.g., organostannanes, boronic acids etc.), Figure 1];⁶ d)
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41 metal-catalyzed direct acylations through activation of the carbonyl group of aldehydes via the
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43 formation of enamine (Figure 1);⁷ e) directing group assisting metal-catalyzed *ortho* acylations (Figure
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45 1)⁸ and f) alkene hydroacylations.⁹
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3 To the best of our knowledge, there are no reports on direct acylations of aldehydes without the
4 directing group assistance or without activating the carbonyl group of the aldehydes with secondary
5 amines, such as, pyrrolidine (in-situ enamine formation), under [Pd]-catalysis. With this background, we
6 intended the design and development of sustainable catalytic methods. Particularly, the development of
7 methods based on acylations becomes indispensable when the reaction can be executed: i) under
8 environmentally benign conditions; ii) without the use of toxic carbon monoxide (CO) gas; iii) using
9 direct carbonylation without the activation of carbonyl group of aldehydes; iv) without the assistance of
10 functional groups (so that enables the accomplishment of structurally diverse carbonyl compounds); v)
11 using simple, non-toxic, inexpensive and bench-top chemicals.
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28 In continuation of our research interests on transition-metal mediated efficient transformations,¹⁰
29 herein we disclose a novel and environmentally benign new one-pot method based on [Pd]-catalyzed
30 direct carbonylation reaction of iodo arenes with aldehydes (alkyl/aryl), leading to alkyl-aryl and aryl-aryl
31 ketones. This straightforward catalytic protocol does not require any directing group assistance or in-situ
32 enamine formation. Interestingly, this reaction made use of water present in the oxidizing agent
33 (aqueous TBHP) as the sole reaction medium. Notably, this process was successful by using simple and
34 commercially available bench-top iodo arenes and aldehydes as coupling partners. Unlike other earlier
35 reports on [Pd]-catalysis, which were applied to limited number of examples or either limited to
36 synthesis of benzophenone derivatives or restricted to the accomplishment of acetophenone
37 derivatives. This protocol was successfully applied for the synthesis of both benzophenones as well as
38 acetophenone derivatives. Thus, showed broad substrate scope and accomplished 67 examples. In
39 addition, significantly, the present strategy was extended to the synthesis of biologically important
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benzofuranones and also to the synthesis of the anti-platelet drug *n*-butylphthalide (NBP) and further applied to the synthesis of pitofenone, an antispasmodic which is used in Spasmalgon as combined drug.

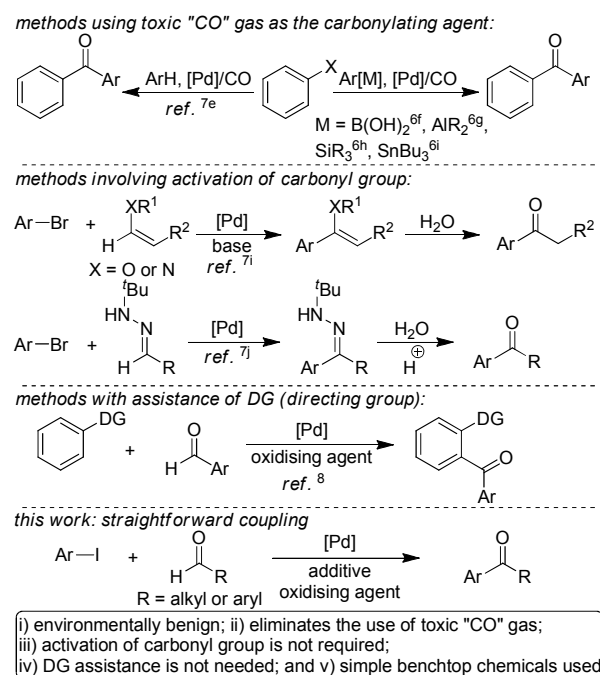


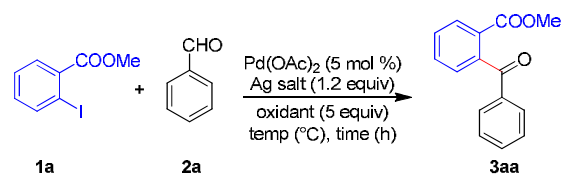
Figure 1: Reported approaches vs present method for the carbonyl compounds.

Results and Discussion:

Initially, we explored the reaction between 2-iodomethylbenzoate **1a** and benzaldehyde **2a**, in the presence of Pd(OAc)₂ (3 mol %)/Ag₂O (0.5 equiv) and aqueous TBHP in DCE at 80 °C for 18 h. As anticipated, the di-aryl ketone **3aa** was obtained, however, in poor yield (Table 1, entry 1). Increase of benzaldehyde **2a** and Pd(OAc)₂/Ag₂O improved the product **3aa** yield (Table 1, entries 2 to 4). Rather than using more amount of [Pd]-catalyst, further increase of aldehyde **2a** and aqueous TBHP, proved to be effective (Table 1, entries 5 to 7). To our delight, the reaction at elevated temperature (120 °C) without solvent DCE, furnished the product **3aa**, in good yield (Table 1, entry 8). Similarly, other solvents also proved to be inefficient (Table 1, entries 9 to 10). This may be due to further increase of dilution with solvents (Table 1, entries 1 to 5, 9 to 10 & 21). With PdCl₂ (5 mol %), the product **3aa** was obtained

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3 in moderate yield (Table 1, entry 11). While with AgOAc and Ag₂CO₃, the phenone **3aa** was formed in
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5 good and fair yields, respectively (Table 1, entries 12 to 13). Also, with TBHP in decane, the reaction
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7 furnished **3aa** in good yield (Table 1, entry 14). On the other hand, other oxidants were found to be
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9 inferior (Table 1, entries 15 to 17). Even TBAI (30 mol %) as additive does not show improvement (Table
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11 1, entry 18). The role of [Pd]-catalyst found vital, as no product **3aa** was formed without the catalyst
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13 (Table 1, entry 19). Also, the reaction without silver salt or the oxidant gave very poor yield of the
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15 product **3aa** (Table 1, entries 20 to 21). On the other hand, the reaction with other bases, such as, K₂CO₃
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17 and Cs₂CO₃, gave **3aa** in low yields, respectively (Table 1, entries, entries 22 to 23). The reaction in the
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19 presence of Pd(0)-catalyst with and without Ag₂O, furnished the product in fair and poor yields,
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21 respectively (Table 1, entries 24 to 25). Thus, the optimization studies revealed that the [Pd]-catalyst,
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23 silver salt and the oxidant TBHP are very much crucial to drive the reaction.
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29 **Table 1.** Optimization studies for the carbonylation product **3aa**.^a



Entry	Additives (equiv)	Oxidants (equiv)	Temp (°C)	Time (h)	Yield (%) ^b
1 ^{c,d,e}	Ag ₂ O (0.5)	TBHP in H ₂ O (3.0)	80	18	34
2 ^{d,f}	Ag ₂ O (0.5)	TBHP in H ₂ O (3.0)	80	18	47
3 ^{d,f,g}	Ag ₂ O (1.2)	TBHP in H ₂ O (3.0)	80	18	52
4 ^{d,f,h}	Ag ₂ O (1.2)	TBHP in H ₂ O (3.0)	80	18	50

5 ^d	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	80	18	67
6	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	100	16	70
7 ⁱ	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	100	16	69
8	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	120	12	74
9 ^j	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	80	18	40
10 ^k	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	120	12	37
11 ^l	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	120	13	54
12	AgOAc (1.2)	TBHP in H ₂ O (5.0)	120	12	71
13	Ag ₂ CO ₃ (1.2)	TBHP in H ₂ O (5.0)	120	12	59
14	Ag ₂ O (1.2)	TBHP in Decane (5.0)	120	12	71
15	Ag ₂ O (1.2)	DTBP (5.0)	120	12	16
16	Ag ₂ O (1.2)	H ₂ O ₂ (3.0)	120	14	26
17 ^d	Ag ₂ O (1.2)	<i>m</i> -CPBA (5.0)	80	16	10
18	Ag ₂ O (1.2) + TBAI (30 mol %)	TBHP in H ₂ O (5.0)	120	11	62
19 ^m	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	120	12	–
20	–	TBHP in H ₂ O (5.0)	120	12	15

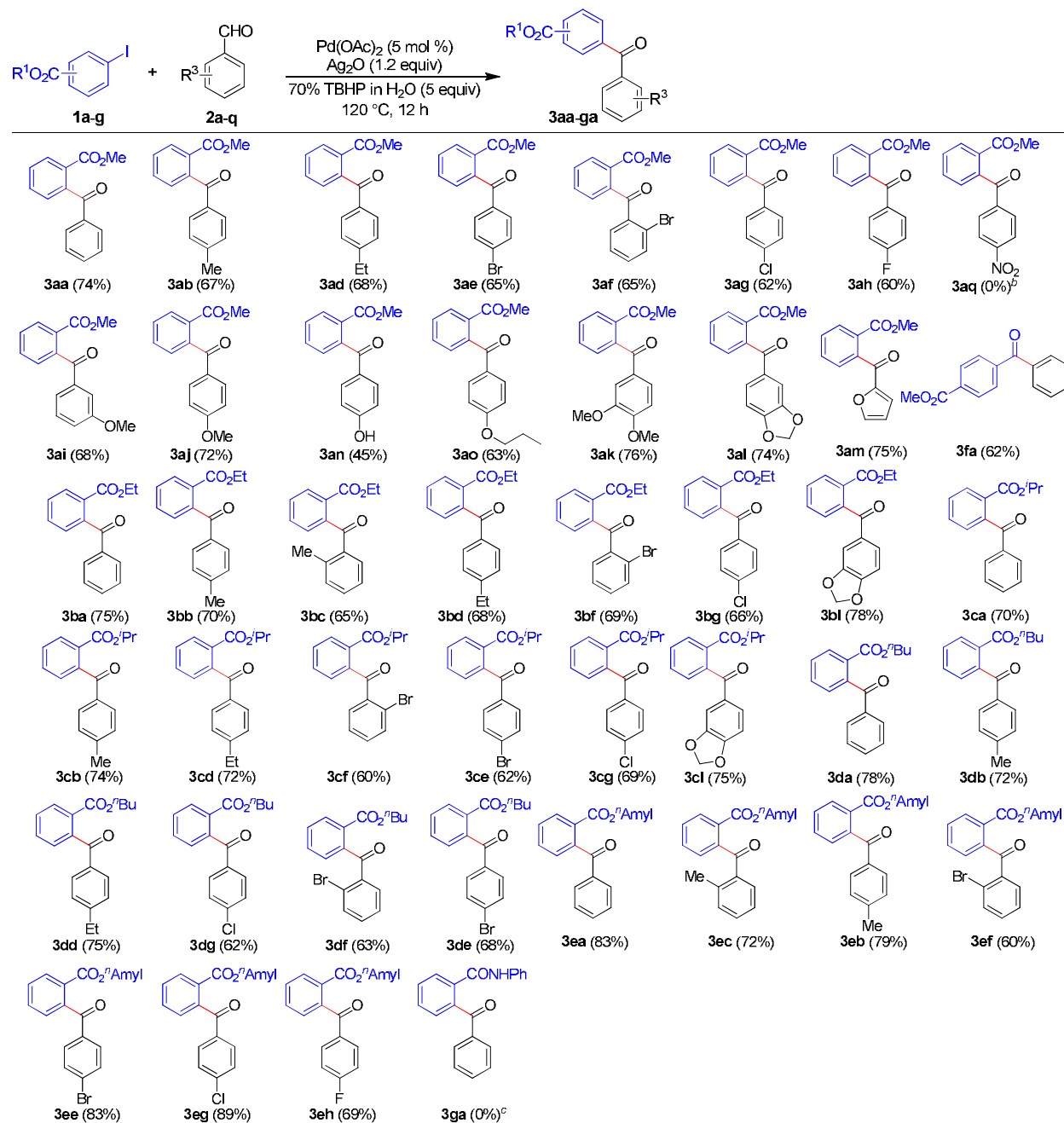
21 ^d	Ag ₂ O (1.2)	–	80	17	24
22	K ₂ CO ₃ (3.0)	TBHP in H ₂ O (5.0)	120	15	50
23	Cs ₂ CO ₃ (3.0)	TBHP in H ₂ O (5.0)	120	15	30
24 ⁿ	Ag ₂ O (1.2)	TBHP in H ₂ O (5.0)	120	14	69
25 ⁿ	–	TBHP in H ₂ O (5.0)	120	15	34

^aUnless otherwise mentioned, all the reactions were carried out by using 104.8 mg (0.40 mmol) of aryl iodide **1a**, 5 mol% of Pd(OAc)₂, 169.8 mg (1.6 mmol) of aldehyde **2a**, and TBHP in H₂O (5.0 equiv). ^bIsolated yields of chromatographically pure products. ^c1.5 equiv of aldehyde **2a** was used. ^d1.5 mL of DCE was used as solvent. ^e3 mol% of Pd(OAc)₂ was used. ^f2.0 equiv of aldehyde **2a** used. ^g10 mol% of Pd(OAc)₂ was used. ^h20 mol% of Pd(OAc)₂ was used. ⁱ6.0 equiv of aldehyde **2a** was used. ^jReaction was carried out in 1.5 mL of MeCN. ^kReaction was carried out in 1.5 mL of DMSO. ^l5 mol% of PdCl₂ was used. ^mReaction was performed without palladium catalyst. ⁿ5 mol% of Pd(PPh₃)₄ was used.

Therefore, the best optimized conditions were identified as **1a** (1.0 equiv), **2a** (4.0 equiv), Pd(OAc)₂ (5 mol %)/Ag₂O (1.2 equiv), aqueous TBHP (5.0 equiv) at 120 °C for 12 h to give **3aa** (Table 1, entry 8). With these optimized conditions in hand, to check the scope and generality of the method, we explored the reaction between electron deficient iodo arenes **1a-g** and benzaldehydes **2a-q**. Gratifyingly, the reaction was found amenable with various benzaldehydes **2a-q**, it showed broad substrate scope and afforded the corresponding aryl-aryl ketones **3aa-ga**, in moderate to very good yields (Table 2). Interestingly, the reaction was successful with benzaldehydes **2** having F, Cl, Br substituents. Notably, the reaction was also amenable with 2-furaldehyde **2m** (Table 2, **3am**). However, the reaction was unsuccessful with benzaldehyde having strong electron withdrawing nitro group (Table 2, **3aq**); even after many trials with varying amounts of the aldehydes and at different temperatures (i.e. neither the starting materials nor the products were isolated). In fact, these observations were in good agreement with that of reactions under such oxidative conditions. This may be probably due to the radical stabilizing effect of the

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3 electron withdrawing substituent.¹¹ Also; the reaction was unsuccessful with heterocyclic (pyridine and
4 thiophene) aldehydes. It was also observed that the reaction with bromo arene did not afford the
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6 ketone, which implies that the more reactive iodo arenes are essential for the success of the reaction.
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10 On the other hand, the reaction with the amide **1g** was unsuccessful to give **3ga** and furnished only the
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12 reductive de-iodinated by-product in 41% yield (Table 2).
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17 **Table 2:** Scope and generality of formation of aryl-aryl ketone **3aa-ga**.^a
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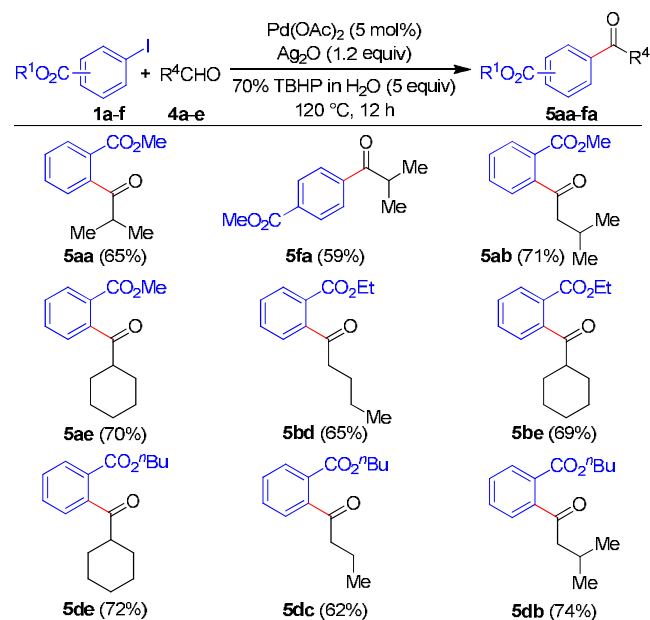


^aIsolated yields of chromatographically pure products **3aa-ga**. ^bNeither starting material nor product has isolated. ^cDe-iodinated by-product isolated with 41% yield.

To further check the scope and applicability of the strategy, the reaction was carried out between electron deficient iodo arenes **1a-f** and aliphatic aldehydes **4a-e**, under standard conditions. To our delight, the reaction was amenable with the aliphatic aldehydes **4a-e** as well, showed very good

substrate scope and furnished the corresponding alkyl-aryl ketones **5aa-fa**, in moderate to good yields, and thus reveals the importance of the present protocol (Table 3).

Table 3: Scope and generality of formation of alkyl-aryl ketone **5aa-fa**.^a



^aIsolated yields of chromatographically pure products **5aa-fa**.

In addition, to the spectroscopic data, the structure of aryl-aryl ketones **3** was further confirmed by the single crystal x-ray diffraction analysis of **3ah** (Figure 2), for details (CIF file) see; supporting information.

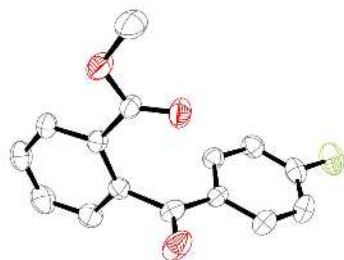
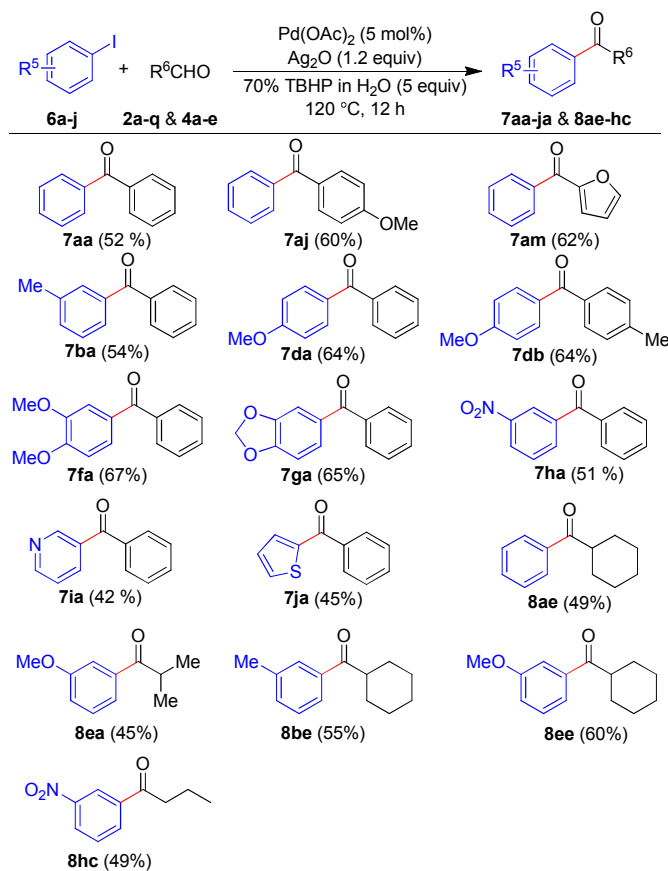


Figure 2: X-ray crystal structure of compound **3ah**. Ellipsoids are drawn at 50% probability level.

Furthermore, to show the applicability and significance of the present protocol, the reaction was also performed between simple to electron rich iodo arenes **6a-j** and aldehydes **2a-q** or **4a-e**, under established conditions. Gratifyingly, the reaction was quite successful and gave the corresponding di-aryl ketones **7aa-ja**, in moderate to good yields (Table 4). Notably, the reaction was compatible with strong electron withdrawing *meta*-nitroiodobenzene **6h** (Table 4, **7ha** & **8hc**). Also, found suitable with hetero-aryl iodides (Table 4, **7ia** & **7ja**). Significantly, the reaction was also amenable with the aliphatic aldehydes (**4c** & **4e**) and afforded the products **8ea-hc** in fair yields (Table 4).

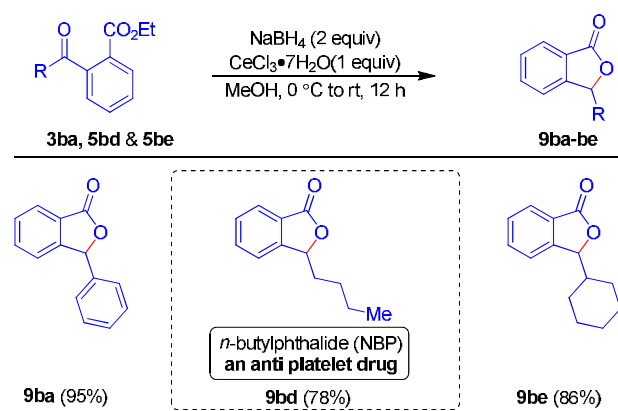
Table 4: Scope and generality of formation of aryl-aryl and aryl-alkyl ketone **7aa-ja** and **8ae-hc**.^a



^aIsolated yields of chromatographically pure products **7aa-ja** & **8ae-hc**.

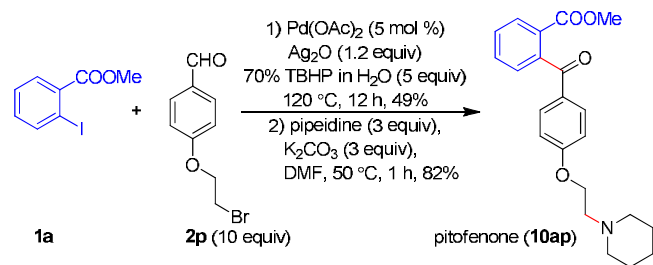
To further demonstrate the synthetic utility of the present strategy, it was extended to the synthesis of benzofuranones, the biologically important scaffolds. To our delight, as anticipated, selective reduction of the keto group of **3ba**, **5bd**, **3be** with NaBH₄ and in-situ intramolecular nucleophilic attack of the secondary hydroxyl group upon to ester moiety, afforded the benzofuranones **9ba-be** (Table 5). Significantly, this strategy was also successfully applied to the synthesis of *n*-butylphthalide (NBP)¹² **9bd**. The NBP is currently serving as an antiplatelet drug in the market for ischemia-cerebral apoplexy.

Table 5: Synthesis of benzofuranones **9ba-be**.^a



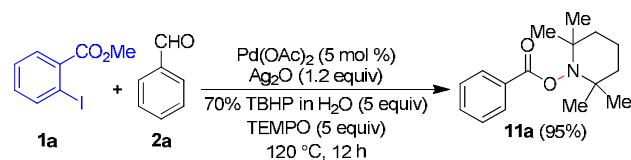
^aIsolated yields of chromatographically pure products **9ba-be**.

Most importantly, the strategy was further applied to the synthesis of the antispasmodic pitofenone, a combined drug in Spasmalgon. This drug helps in releasing pain and spasms of smooth muscles. Notably, the present protocol proved to be efficient as it enables the synthesis of pitofenone **10ap** in just two steps (Scheme 1).¹³



Scheme 1: Synthesis of pitofenone **10ap**.

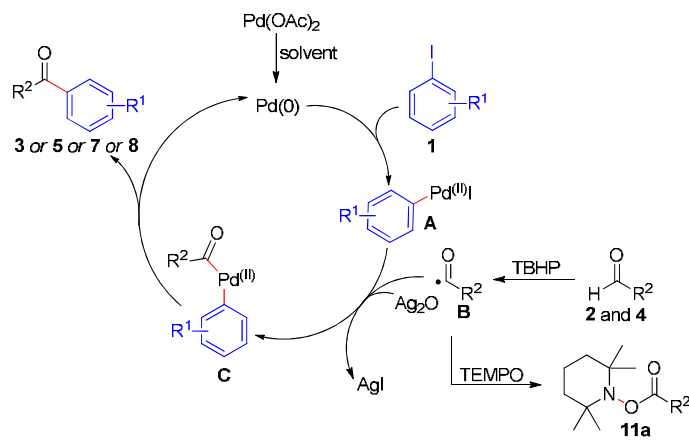
To further investigate the mechanism of the reaction, we assumed that the reaction may proceed via the formation of an acyl radical from the aldehydes (**2** & **4**) by TBHP. To prove the formation of radical, the reaction was performed in the presence of (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO), a free radical scavenger, under standard conditions. Gratifyingly, as predicted, the aldehyde radical trapped ester **11a** was formed in 95% yield with TEMPO (Scheme 2).¹⁴ On the other hand; the iodo ester **1a** was transformed into to the simple methyl benzoate in 15% yield via reductive de-iodination (Scheme 2).



Scheme 2: Synthesis of tempoester **11a**.

Though, the exact reaction mechanism is not clearly known, a plausible mechanism is depicted in Scheme 3. In this context, we presumed that the reaction might proceeds via Pd(0)/Pd(II) intermediates^{15,16,17} and Ag₂O could act as a base [as reaction is working in presence of K₂CO₃/Cs₂CO₃ (Table 1, entries 22 & 23)]. Pd(OAc)₂ could be reduced to Pd(0) by the solvent.^{15c} Thus, oxidative addition of Pd(0) onto the Ar-I bond leads to the formation of Pd(II)-intermediate **A**. In an independent path, the acyl radical **B** formed from aldehyde by the reaction of TBHP. Now, combination of **A** and **B** would furnish the Pd(II)-intermediate **C** which undergo reductive elimination and affords the ketones **3/5/7/8** along with the Pd(0)-catalyst and thus completes the catalytic cycle. However, the halophilic

nature of Ag^+ ions, it might be reasonable to form AgI while combining **B** with **A**. On the other hand, acceleration of the reaction in the presence of Ag_2O might also be due to salt effect on $[\text{Pd}]$ -catalysis.¹⁸



Scheme 3: Plausible reaction mechanism for the synthesis of ketones **3/5/7/8** from aldehydes **2** and **4**.

In summary, we have disclosed a simple $[\text{Pd}]$ -catalyzed direct acylation of iodo arenes with alkyl/aryl aldehydes, for the synthesis of wide variety of aryl-aryl and alkyl-aryl ketones with good substrate scope. Unlike some of the transition metal catalyzed reactions that made use of toxic carbon monoxide (CO) gas as carbonylating agent or activation of the carbonyl group or directing group assistance, the present protocol was successful under environmentally benign conditions, without the need to activate the carbonyl group and also without directing group assistance. Significantly, the strategy was extended to the synthesis of anti-platelet drug *n*-butylphthalide (NBP) and the antispasmodic drug pitofenone. Currently, the studies for the extension of this protocol to identify other substrates as aldehyde are under progress.

Experimental: General considerations:

IR spectra were recorded on a FTIR spectrophotometer. ^1H NMR spectra were recorded on 400 MHz spectrometer at 295 K in CDCl_3 ; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either internal standard tetramethylsilane (TMS) ($\delta_{\text{H}} = 0.00$ ppm) or

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3 CHCl_3 ($\delta_{\text{H}} = 7.25$ ppm). ^{13}C NMR spectra were recorded on 100 MHz spectrometer at RT in CDCl_3 ;
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5 chemical shifts (δ ppm) are reported relative to CHCl_3 [$\delta_{\text{C}} = 77.00$ ppm (central line of triplet)]. In the ^{13}C
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7 NMR, the nature of carbons (C, CH, CH_2 and CH_3) was determined by recording the DEPT-135 spectra. In
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9 the ^1H -NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q =
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11 quartet, qui = quintet, sept = septet, dd = doublet of doublet, m = multiplet and br. s = broad singlet.
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13 High-resolution mass spectra (HR-MS) were recorded on Q-TOF electron spray ionization (ESI) mode and
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15 atmospheric pressure chemical ionization (APCI) modes. Melting points were determined on an
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17 electrothermal melting point apparatus and are uncorrected. All small scale reactions were carried out
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19 using Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and
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21 ethyl acetate as eluents. Reactions were generally run under argon or a nitrogen atmosphere. Solvents
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23 were distilled prior to use; petroleum ether with a boiling range of 60 to 80 °C was used. Acme's silica-
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25 gel (60–120 mesh) was used for column chromatography (approximately 20 g per one gram of crude
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27 material).
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36 The compounds **1a-f**, **6a-j**, **2a-q** and **4a-e** which have been used are commercially available.
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40 **GP-1 [General Procedure for Preparation of Benzophenones and Acetophenones (3, 5, 7 & 8)]:**

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42 To an oven dried Schlenk tube, were added aryl iodide **1/6** (81.3-127.3 mg, 0.40 mmol), aldehyde **2/4**
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44 (169.8-366.5 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP (257.1
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46 mg, 2.0 mmol). The resulting reaction mixture was stirred at 120 °C for 12 h. The progress of the product
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48 **3/5/7/8** formation was monitored by TLC till the reaction was completed. The reaction mixture was
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50 allowed to cool to room temperature, diluted with aqueous NaHCO_3 solution and then extracted with
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52 ethyl acetate (3 × 15 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4)
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54 and filtered. Evaporation of the solvent under reduced pressure and purification of the crude material
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3 by silica-gel column chromatography (petroleum ether/ethyl acetate) furnished the products **3/ 5/7/8**
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5 (32.0-117.8 mg, 42-89%) as viscous liquid/solid.
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10 **GP-2 [General Procedure for Preparation of Benzofuranones (9)]:**

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12 To a cold (0°C), magnetically stirred solution of keto ester **3ba/5bd/5be** (117.1-130.2 mg, 0.50 mmol) in
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14 MeOH (1 mL), were added sequentially CeCl₃·7H₂O (186.3 mg, 0.50 mmol) and NaBH₄ (38 mg, 1.0 mmol).
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17 The reaction mixture was stirred at 0 °C to room temperature for 12 to 24 h. The progress of the
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19 product **9ba/9bd/9be** formation was monitored by TLC. The reaction mixture was quenched with H₂O
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21 and then extracted with ethyl acetate (3 × 10 mL). Purification of the crude material by silica-gel column
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23 chromatography (petroleum ether/ethyl acetate) furnished the product **9ba/9bd/9be** (112.5-146.0 mg,
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25 78-95%) as a liquid/solid.
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31 **Ethyl-2-benzoylbenzoate (3aa):**^{19a} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40 mmol),
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33 aldehyde **2a** (169.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP
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35 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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37 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3aa** (71.1 mg, 74%) as a
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39 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.80, *R_f*(**3aa**)=0.30,
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41 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *ν*_{max}=2930, 17190, 1686, 1599, 1450, 1287, 1089, 934, 718
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43 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.03 (d, 1H, *J*=7.3), 7.73 (dd, 2H, *J*=8.5 and *J*=1.2 Hz), 7.65-7.61 (m,
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45 1H), 7.58-7.51 (m, 2H), 7.44-7.39 (m, 1H), 3.59 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ= 51.1 (CH₃),
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47 127.8 (CH), 128.5 (2×CH), 129.2 (2×CH), 129.6 (CH), 130.0 (CH), 131.4 (C_q), 132.4 (CH), 133.0 (CH), 137.2
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49 (C_q), 141.6 (C_q), 166.4 (C_q), 197.0(C_q) ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₅H₁₃O₃]⁺=[M+H]⁺: 241.0859;
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51 found 241.0868.
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3 **Methyl-2-(4-methylbenzoyl) benzoate (3ab):** GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
4 mmol), aldehyde **2b** (192.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
5 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
6 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3ab** (68.1 mg, 67%) as a
7 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.90, *R_f*(**3ab**)=0.30,
8 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2980, 1722, 1678, 1591, 1451, 1278, 1084, 953, 715
9 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.02 (dd, 1H, *J*=7.8 and *J*=0.9 Hz), 7.65-7.60 (m, 3H), 7.54 (td, 1H,
10 *J*=7.7 and *J*=1.2 Hz), 7.38 (dd, 1H, *J*=7.5 and *J*=1.2 Hz), 7.21 (d, 2H, *J*=7.8 Hz), 3.60 (s, 3H), 2.39 (s, 3H)
11 ppm. ¹³C NMR (CDCl₃, 100 MHz): δ= 21.7 (CH₃), 52.1 (CH₃), 127.5 (CH), 129.2 (2 × CH), 129.4 (2 × CH),
12 ¹³C NMR (CDCl₃, 100 MHz): δ= 21.7 (CH₃), 52.1 (CH₃), 127.5 (CH), 129.2 (2 × CH), 129.4 (2 × CH),
13 129.5 (CH), 130.1 (CH), 130.2 (C_q), 132.3 (CH), 134.7 (C_q), 141.9 (C_q), 143.9 (C_q), 166.5 (C_q), 196.7 (C_q)
14 ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₆H₁₅O₃]⁺=[M+H]⁺: 255.1016; found 255.1016.
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31 **Methyl-2-(4-ethylbenzoyl) benzoate (3ad):**^{19b} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
32 mmol), aldehyde **2d** (214.7 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
33 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
34 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3ad** (73.0 mg, 68%) as a
35 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.90, *R_f*(**3ad**)=0.30,
36 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2992, 1724, 1685, 1588, 1451, 1279, 1088, 9334, 712
37 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.03 (d, 1H, *J*=7.8 Hz), 7.66 (d, 2H, *J*=7.3 Hz), 7.61 (td, 1H, *J*=7.5 and
38 *J*=1.4 Hz), 7.54 (td, 1H, *J*=7.5 and *J*=1.4 Hz), 7.38 (dd, 1H, *J*=7.3 and *J*=0.9 Hz), 7.24 (d, 2H, *J*=7.8 Hz), 3.61
39 (s, 3H), 2.68 (q, 2H, *J*=7.6 Hz), 1.23 (t, 3H, *J*=7.6 Hz) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=15.1 (CH₃), 28.9
40 (t, ArCH₂CH₃), 52.2 (CH₃), 127.7 (CH), 128.0 (2×CH), 129.1 (C_q), 129.4 (CH), 129.5 (2×CH), 130.0 (CH),
41 132.3 (CH), 134.8 (C_q), 141.9 (C_q), 150.1 (C_q), 166.4 (C_q), 196.8 (C_q), ppm. HR-MS (ESI⁺) *m/z* calculated for
42 [C₁₇H₁₇O₃]⁺=[M+H]⁺: 269.1172; found 269.1178.
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6 **Methyl-2-(4-bromobenzoyl) benzoate (3ae):**^{19c} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
7 mmol), aldehyde **2e** (296.0 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
8 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
9 (petroleum ether/ethyl acetate, 97:03 to 96:04) furnished the product **3ae** (83.0 mg, 65%) as a
10 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.90, *R_f*(**3ae**)=0.40,
11 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2946, 1725, 1685, 1598, 1490, 1287, 1023, 999, 722
12 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.04 (d, 1H, *J*=7.8), 7.64 (ddd, 1H, *J*=7.8, *J*=5.8 and 1.4 Hz), 7.61-7.58
13 (m, 2H), 7.58-7.55 (m, 3H), 7.37 (dd, 1H, *J*=7.5 and 1.2 Hz), 3.64 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz):
14 δ=52.3 (CH₃), 127.6(CH), 128.3 (C_q), 129.0 (C_q), 129.8 (CH), 130.2 (CH), 130.6 (CH), 131.8 (2×CH), 132.6
15 (CH), 136.0 (C_q), 141.3 (C_q), 166.2 (C_q), 196.0 (C_q) ppm. HR-MS (ESI⁺) *m/z* calculated for
16 [C₁₅H₁₂BrO₃]⁺=[M+H]⁺: 318.9964; found 318.9951.
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33 **Methyl-2-(2-bromobenzoyl) benzoate (3af):** GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
34 mmol), aldehyde **2f** (296.0 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
35 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
36 (petroleum ether/ethyl acetate, 97:03 to 96:04) furnished the product **3af** (76.6 mg, 60%) as a colourless
37 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.90, *R_f*(**3af**)=0.40, UV
38 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2960, 1722, 1679, 1591, 1458, 1287, 1093, 943, 722 cm⁻¹.
39 ¹H NMR (CDCl₃, 400 MHz): δ=7.85 (dd, 1H, *J*=5.8 and *J*=2.9, Ar-H), 7.69-7.66 (m, 1H), 7.57 (dd, 2H, *J*=5.8
40 and 3.4 Hz), 7.47 (dd, 1H, *J*=5.8 and 2.9 Hz), 7.37-7.34 (m, 1H), 7.29-7.32 (m, 2H), 3.67 (s, 3H), ppm. ¹³C
41 NMR (CDCl₃, 100 MHz): δ=52.5 (CH₃), 121.3 (C_q), 127.0 (CH), 129.4 (CH), 129.8(CH), 131.0 (CH), 131.1
42 (C_q), 131.6 (CH), 132.5 (CH), 134.5 (CH), 138.2 (C_q), 139.9 (C_q), 167.4 (C_q), 195.3 (C_q) ppm. HR-MS (ESI⁺)
43 *m/z* calculated for [C₁₅H₁₂BrO₃]⁺=[M+H]⁺: 318.9964; found 318.9957.
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6 **Methyl-2-(4-chlorobenzoyl) benzoate (3ag):**^{19d} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
7 mmol), aldehyde **2g** (224.9 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
8 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
9 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3ag** (71.4 mg, 65%) as a
10 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.80, *R_f*(**3ag**)=0.30,
11 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2960, 1721, 1695, 1588, 1450, 1277, 1088, 943, 723
12 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.04 (d, 1H, *J*=7.3 Hz), 7.69-7.62 (m, 3H), 7.57 (ddd, 1H, *J*=7.3, 6.5 and
13 1.4 Hz), 7.41-7.36 (m, 3H), 3.64 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ= 52.3 (CH₃), 127.6 (CH), 128.9
14 (2×CH), 129.0 (C_q), 129.8 (CH), 130.2 (CH), 132.5 (2×CH), 135.6 (C_q), 139.5 (C_q), 141.3 (C_q), 166.2 (C_q),
15 195.8 (C_q) ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₅H₁₂ClO₃]⁺=[M+H]⁺: 275.0469; found 275.0476.
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31 **Methyl-2-(4-fluorobenzoyl) benzoate (3ah):**^{19e} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
32 mmol), aldehyde **2h** (198.6 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
33 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
34 (petroleum ether/ethyl acetate, 97:03 to 96:04) furnished the product **3ah** (64.0 mg, 62%) as a white
35 solid (m.p. 80-83 °C). [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1a**)=0.90, *R_f*(**3ah**)=0.40, UV
36 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2960, 1730, 1695, 1592, 1451, 1271, 1081, 932, 710 cm⁻¹.
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38 ¹H NMR (CDCl₃, 400 MHz): δ=8.04 (d, 1H, *J*=7.8 Hz), 7.76 (dd, 2H, *J*=8.8 and *J*=5.3 Hz), 7.63 (ddd, 1H,
39 *J*=7.3, *J*=5.3 and *J*=1.4 Hz), 7.58-7.54 (m, 1H), 7.37 (dd, 1H, *J*=7.5 and *J*=1.2 Hz), 7.08 (t, 2H, *J*=8.8 Hz), 3.64
40 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ= 52.3 (CH₃), 115.7 (2×CH), 127.6 (CH), 129.1 (C_q), 129.7 (CH),
41 130.2 (CH), 131.9 (2 × CH), 132.5 (CH), 133.7 (C_q), 141.5 (C_q), 166.3 (C_q), 166.9 (d, ¹*J*_{C-F} = 255.3 Hz),
42 195.5 (C_q) ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₅H₁₂FO₃]⁺=[M+H]⁺: 259.0765; found 259.0774.
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3 **Methyl-2-(3-methoxybenzoyl) benzoate (3ai):** GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
4 mmol), aldehyde **2i** (217.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
5 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
6 (petroleum ether/ethyl acetate, 93:07 to 88:12) furnished the product **3ai** (73.5 mg, 68%) as a colourless
7 viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f(\mathbf{1a})=0.90$, $R_f(\mathbf{3ai})=0.30$, UV
8 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2966, 1721, 1670, 1599, 1450, 1278, 1083, 933, 716$ cm⁻¹.
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10 ¹H NMR (CDCl₃, 400 MHz): $\delta=8.03$ (dd, 1H, $J=7.5$ and $J=1.2$ Hz), 7.62 (td, 1H, $J=7.4$ and $J=1.2$ Hz), 7.55 (td,
11 1H, $J=7.7$ and $J=1.2$ Hz), 7.41-7.39 (m, 2H), 7.29 (t, 1H, $J=7.8$ Hz), 7.18-7.16 (m, 1H), 7.08 (ddd, 1H, $J=8.0$,
12 $J=2.6$ and $J=0.9$ Hz), 3.83 (s, 3H), 3.62 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta= 52.2$ (CH₃), 55.4 (CH₃),
13 112.8 (CH), 119.8 (CH), 122.5 (CH), 127.8 (CH), 129.2 (C_q), 129.5 (2×CH), 129.6 (CH), 132.4 (CH), 138.5
14 (C_q), 141.7 (C_q), 159.8 (C_q), 166.4 (C_q), 196.8 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for
15 [C₁₆H₁₅O₄]⁺=[M+H]⁺: 271.0965; found 271.0968.
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33 **Methyl-2-(4-methoxybenzoyl) benzoate (3aj):** GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
34 mmol), aldehyde **2j** (217.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
35 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
36 (petroleum ether/ethyl acetate, 93:07 to 88:12) furnished the product **3aj** (77.8 mg, 72%) as a colourless
37 viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f(\mathbf{1a})=0.90$, $R_f(\mathbf{3aj})=0.30$, UV
38 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2950, 1721, 1675, 1578, 1451, 1282, 1084, 934, 719$ cm⁻¹.
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40 ¹H NMR (CDCl₃, 400 MHz): $\delta=8.02$ (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 7.71 (d, 2H, $J=8.8$ Hz), 7.61 (td, 1H, $J=7.5$
41 and $J=1.4$ Hz), 7.53 (td, 1H, $J=7.5$ and $J=1.4$ Hz), 7.37 (dd, 1H, $J=7.3$ and $J=0.9$ Hz), 6.89 (d, 1H, $J=8.8$ Hz),
42 3.84 (s, 3H), 3.62 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta= 52.2$ (CH₃), 55.4 (CH₃), 113.7 (2×CH),
43 127.7(CH), 129.1 (C_q), 129.3 (CH), 130.1 (CH), 130.2 (C_q), 131.6 (2×CH), 132.3 (CH), 142.0 (C_q), 163.5 (C_q),
44 166.5 (C_q), 195.8 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₆H₁₅O₄]⁺=[M+H]⁺: 271.0965; found
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271.0967.

Methyl-2-(3,4-dimethoxybenzoyl)benzoate (3ak):^{20b} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40 mmol), aldehyde **2k** (265.9 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 88:12 to 85:15) furnished the product **3ak** (91.3 mg, 76%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 85:15), *R_f*(**1a**)=0.95, *R_f*(**3ak**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2966, 1723, 1645, 1598, 1430, 1272, 1083, 936, 719 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.02 (dd, 1H, *J*=7.5 and *J*=1.2 Hz), 7.63-7.52 (m, 3H), 7.38 (dd, 1H, *J*=7.5 and *J*=1.2 Hz), 7.06 (dd, 1H, *J*=8.3 and *J*=1.9 Hz), 6.77 (d, 1H, *J*=8.8 Hz), 3.93 (s, 3H), 3.90 (s, 3H), 3.64 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=52.2 (CH₃), 55.9 (CH₃), 56.0 (CH₃), 109.8 (CH), 110.2 (CH), 125.1 (CH), 127.7 (CH), 129.1 (C_q), 129.4 (CH), 130.0 (CH), 130.4 (C_q), 132.2 (CH), 141.8 (C_q), 149.1 (C_q), 153.3 (C_q), 166.4 (C_q), 195.8 (C_q) ppm. HR-MS (ESI⁺) *m/z* calculated for [C₁₇H₁₇O₅]⁺=[M+H]⁺: 301.1071; found 301.1071.

Methyl-2-(benzo[d][1,3]dioxole-5-carbonyl)benzoate (3al): GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40 mmol), aldehyde **2l** (240.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 92:08) furnished the product **3al** (84.1 mg, 74%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), *R_f*(**1a**)=0.95, *R_f*(**3al**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2970, 1721, 1672, 1592, 1451, 1277, 1082, 933, 723 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.02 (d, 1H, *J*=7.3 Hz), 7.60 (td, 1H, *J*=7.5 and *J*=1.2 Hz), 7.53 (td, 1H, *J*=7.5 and *J*=1.4 Hz), 7.37-7.34 (m, 2H), 7.18-7.15 (m, 1H), 6.76 (d, 1H, *J*=8.3 Hz), 6.02 (s, 2H), 3.67 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=52.2 (CH₃), 101.9 (CH₂), 107.8 (CH), 108.5 (CH),

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3 126.4 (CH), 127.6 (CH), 128.9 (C_q), 129.4 (CH), 130.1 (CH), 132.1 (C_q), 132.3 (CH), 141.9 (C_q), 148.2 (C_q),
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5 151.9(C_q), 166.3 (C_q), 195.3 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₆H₁₃O₅]⁺=[M+H]⁺: 285.0757;
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7 found 285.0766.
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12 **Methyl-2-(furan-2-carbonyl)benzoate (3am):**^{19e} GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
13 mmol), aldehyde **2m** (153.7 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
14 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
15 (petroleum ether/ethyl acetate, 92:08 to 88:12) furnished the product **3am** (69.5 mg, 75%) as a
16 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1a**)=0.90,
17 R_f(**3am**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2929, 1721, 1689, 1598, 1450, 1277,
18 1084, 938, 719 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.00 (dd, 1H, J=7.5 and J=1.2 Hz), 7.64-7.57 (m, 3H),
19 7.49 (dd, 1H, J=7.3 and J=1.4 Hz), 6.98 (d, 1H, J=3.4 Hz), 6.51 (dd, 1H, J=3.4 and J=1.4 Hz), 3.69 (s, 3H),
20 ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=52.4 (CH₃), 112.3 (CH), 119.0 (CH), 128.1 (CH), 129.7 (C_q), 130.0 (CH),
21 130.2 (CH), 132.2 (CH), 140.0 (C_q), 147.1 (CH), 152.7 (C_q), 166.6 (C_q), 184.2 (C_q) ppm. HR-MS (ESI⁺) m/z
22 calculated for [C₁₃H₁₁O₄]⁺=[M+H]⁺: 231.0652; found 231.0653.
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40 **Methyl-2-(4-hydroxybenzoyl) benzoate (3an):** GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
41 mmol), aldehyde **2n** (195.4 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
42 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
43 (petroleum ether/ethyl acetate, 93:07 to 90:10) furnished the product **3an** (46.0 mg, 45%) as a
44 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1a**)=0.90, R_f(**3an**)=0.30,
45 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}= 3421, 2951, 1722, 1670, 1592, 1451, 1272, 1088, 933,
46 712 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.00 (dd, 1H, J=7.5 and J=1.2 Hz), 7.82 (br.s, 1H), 7.63-7.59 (m,
47 3H), 7.53 (td, 1H, J=7.7 and J=1.2 Hz), 7.36 (dd, 1H, J=7.5 and J=1.2 Hz) 6.78-6.76 (m, 2H), 3.63 (s, 3H),
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3 ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=52.4$ (CH_3), 115.5 ($2\times\text{CH}$), 127.7(CH), 128.9 (C_q), 129.3 (C_q), 129.5
4
5 (CH), 130.1 (CH), 132.1 ($2\times\text{CH}$), 132.5 (CH), 141.7 (C_q), 161.4 (C_q), 166.9 (C_q), 196.9 (C_q) ppm. HR-MS
6
7
8 (ESI^+) m/z calculated for $[\text{C}_{16}\text{H}_{15}\text{O}_4]^+=[\text{M}+\text{H}]^+$: 271.0965; found 271.0969.
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12 **Methyl-2-(4-propoxybenzoyl) benzoate (3ao)**: GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40
13
14 mmol), aldehyde **2o** (262.7 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
15
16 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
17
18 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3ao** (75.2 mg, 63%) as a
19
20 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1a})=0.90$, $R_f(\mathbf{3ao})=0.40$,
21
22 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2932$, 1730, 1690, 1593, 1451, 1278, 1088, 934, 717
23
24 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) $\delta=8.02$ (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 7.71-7.62 (m, 2H), 7.60 (td, 1H, $J=7.4$
25
26 and $J=1.2$ Hz), 7.53 (td, 1H, $J=7.4$ and $J=1.2$ Hz), 7.36 (dd, 1H, $J=7.8$ and $J=0.9$ Hz) 6.89-6.87 (m, 2H), 3.95
27
28 (t, 2H, $J=6.6$ Hz) 3.63 (s, 3H), 1.85-1.76 (m, 2H), 1.02 (t, 3H, $J=7.5$ Hz) ppm. ^{13}C NMR (CDCl_3 , 100 MHz):
29
30 $\delta=10.4$ (CH_3), 22.4 (CH_2), 52.4 (CH_3), 69.7 (CH_2), 114.1 ($2\times\text{CH}$), 127.6(CH), 129.0 (C_q), 129.3 (CH), 129.9
31
32 (C_q), 130.0 (CH), 131.6 ($2\times\text{CH}$), 132.2 (CH), 142.0 (C_q), 163.1 (C_q), 166.4 (C_q), 195.8 (C_q) ppm. HR-MS (ESI^+)
33
34 m/z calculated for $[\text{C}_{18}\text{H}_{18}\text{NaO}_4]^+=[\text{M}+\text{Na}]^+$: 321.1097; found 321.1097.
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43 **Methyl-2-(4-(2-bromoethoxy)benzoyl)benzoate (3ap)**: GP-1 was carried out with aryl iodide **1a** (104.8
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45 mg, 0.40 mmol), aldehyde **2p** (916.6 mg, 4.0 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48
46
47 mmol) and TBHP (514.2 mg, 4.0 mmol). Purification of the crude material by silica-gel column
48
49 chromatography (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3ap** (72.0 mg,
50
51 49%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1a})=0.90$,
52
53 $R_f(\mathbf{3ap})=0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2966$, 1722, 1685, 1598, 1450, 1277,
54
55 1083, 933, 715 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz) $\delta=8.03$ (dd, 1H, $J=7.5$ and $J=1.2$ Hz), 7.74-7.71 (m, 2H),
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3 7.62 (td, 1H, $J=7.3$ and $J=1.4$ Hz), 7.54 (td, 1H, $J=7.3$ and $J=1.4$ Hz), 7.37 (dd, 1H, $J=7.5$ and $J=1.2$ Hz), 6.93-
4 6.89 (m, 2H), 4.36 (t, 2H, $J=6.3$ Hz) 3.64 (s, 3H), 3.64 (t, 2H, $J=6.3$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz):
5
6 $\delta=28.5$ (CH_2), 52.2 (CH_3), 67.8 (CH_2), 114.3 ($2\times\text{CH}$), 127.6(CH), 129.1 (C_q), 129.4 (CH), 130.1 (CH), 130.9
7
8 (C_q), 131.7 ($2\times\text{CH}$), 132.3 (CH), 141.9 (C_q), 161.9 (C_q), 166.4 (C_q), 195.7 (C_q) ppm. HR-MS (ESI^+) m/z
9
10 calculated for $[\text{C}_{17}\text{H}_{16}\text{BrO}_4]^+=[\text{M}+\text{H}]^+$: 365.0208; found 365.0206.
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17 **Methyl-4-benzoylbenzoate (3fa):**^{19f} GP-1 was carried out with aryl iodide **1f** (104.8 mg, 0.40 mmol),
18
19 aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
20
21 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
22
23 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3fa** (59.6 mg, 62%) as a colourless
24
25 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1f})=0.90$, $R_f(\mathbf{3fa})=0.30$, UV
26
27 detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=3000$, 1780, 1685, 1620, 1490, 1310, 1110, 988, 763 cm^{-1} .
28
29 ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.14$ (d, 2H, $J=8.8$ Hz), 7.80 (dd, 4H, $J=8.8$ and $J=7.5$ Hz), 7.61 (t, 1H, $J=7.5$
30
31 Hz), 7.49 (t, 2H, $J=7.5$ Hz), 3.95 (s, 3H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=52.4$ (CH_3), 128.4 ($2\times\text{CH}$),
32
33 129.5 ($2\times\text{CH}$), 129.7 ($2\times\text{CH}$), 130.1 ($2\times\text{CH}$), 132.9 (CH), 133.2 (C_q), 136.9 (C_q), 141.3 (C_q), 166.3 (C_q), 196.0
34
35 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{15}\text{H}_{13}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 241.0859; found 241.0869.
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43 **Ethyl-2-benzoylbenzoate (3ba):** GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40 mmol),
44
45 aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
46
47 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
48
49 (petroleum ether/ethyl acetate, 97:03 to 96:04) furnished the product **3ba** (76.3 mg, 75%) as a
50
51 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1b})=0.90$, $R_f(\mathbf{3ba})=0.30$,
52
53 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2919$, 2850, 1715, 1670, 1596, 1446, 1366, 1276,
54
55 1130, 1040, 931, 714 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.05$ (d, 1H, $J=7.3$), 7.74 (d, 2H, $J=6.5$ Hz), 7.64-
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3 7.52 (m, 3H), 7.40 (dd, 3H, $J=7.3$ and $J=6.5$ Hz), 4.05 (q, 2H, $J=7.3$ Hz), 1.04 (t, 2H, $J=7.3$ Hz) ppm. ^{13}C NMR
4
5 (CDCl₃, 100 MHz): $\delta=13.7$ (CH₃), 61.4 (CH₂), 127.6 (CH), 128.4 (2×CH), 129.3 (2×CH), 129.5 (CH), 130.1
6
7 (CH), 132.3 (CH), 133.0 (CH), 137.1 (C_q), 141.5 (C_q), 165.9 (C_q), 196.9 (C_q) ppm. HR-MS (ESI⁺) m/z
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9 calculated for [C₁₆H₁₅O₃]⁺=[M+H]⁺: 255.1016; found 255.1017.
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15 **Ethyl-2-(4-methylbenzoyl) benzoate (3bb)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40
16
17 mmol), aldehyde **2b** (192.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
18
19 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
20
21 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3bb** (75.3 mg, 70%) as a
22
23 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1b})=0.90$, $R_f(\mathbf{3bb})=0.30$,
24
25 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2921$, 2853, 1719, 1670, 1605, 1446, 1366, 1277,
26
27 1130, 1050, 981, 714 cm⁻¹. ^1H NMR (CDCl₃, 400 MHz): $\delta=8.04$ (d, 1H, $J=7.3$ Hz), 7.6 (d, 2H, $J=8.3$ Hz), 7.59
28
29 (dd, 1H, $J=7.3$ and $J=1.4$ Hz), 7.54 (ddd, 1H, $J=8.3$, $J=7.3$ and $J=1.4$ Hz), 7.36 (d, 1H, $J=7.8$ Hz), 7.20 (d, 2H,
30
31 $J=7.8$ Hz), 4.06 (q, 2H, $J=7.1$ Hz), 2.38 (s, 3H), 1.05 (t, 2H, $J=7.1$ Hz) ppm. ^{13}C NMR (CDCl₃, 100 MHz):
32
33 $\delta=13.6$ (CH₃), 21.6 (CH₃), 61.4 (CH₂), 129.1 (3×CH), 129.3 (CH), 129.5 (2×CH), 130.1 (C_q), 132.2 (CH), 134.7
34
35 (C_q), 141.8 (C_q), 143.9 (C_q), 166.0 (C_q), 196.6 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for
36
37 [C₁₇H₁₇O₃]⁺=[M+H]⁺: 269.1172; found 269.1172.
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46 **Ethyl-2-(2-methylbenzoyl) benzoate (3bc)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40
47
48 mmol), aldehyde **2c** (192.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
49
50 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
51
52 (petroleum ether/ethyl acetate, 95:05 to 94:06) furnished the product **3bc** (69.7 mg, 65%) as a
53
54 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1b})=0.90$, $R_f(\mathbf{3bc})=0.30$,
55
56 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2956$, 1720, 1675, 1598, 1450, 1277, 1083, 933, 713
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3 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =7.93 (d, 1H, J =8.8 Hz), 7.60-7.51 (m, 2H), 7.42-7.34 (m, 2H), 7.28 (d,
4
5 1H, J =7.8 Hz), 7.23 (d, 1H, J =7.8 Hz), 7.11 (t, 1H, J =7.8 Hz), 4.08 (q, 2H, J =7.3 Hz), 2.65 (s, 3H), 1.09 (t, 2H,
6
7 J =7.3 Hz) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =13.7 (CH_3), 21.6 (CH_3), 61.4 (CH_2), 125.3 (CH), 128.3 (CH),
8
9 129.8 (CH), 130.3 (C_q), 131.6 (CH), 131.8 (CH), 131.9 (CH), 136.5 (C_q), 140.0 (C_q), 142.5 (C_q), 166.5 (C_q),
10
11 198.6 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{17}\text{H}_{17}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 269.1172; found 269.1179.
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17 **Ethyl-2-(4-ethylbenzoyl) benzoate (3bd)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40
18
19 mmol), aldehyde **2d** (214.7 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
20
21 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
22
23 (petroleum ether/ethyl acetate, 97:03 to 96:04) furnished the product **3bd** (76.8 mg, 68%) as a
24
25 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1b})=0.90$, $R_f(\mathbf{3bd})=0.30$,
26
27 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2921$, 2853, 1719, 1671, 1607, 1453, 1363, 1277,
28
29 1130, 1050, 981, 814, 810, 713 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =8.07 (dd, 1H, J =7.5 and J =1.2 Hz), 7.69
30
31 (d, 2H, J =8.3 Hz), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 1H), 7.39 (dd, 1H, J =7.3 and J =0.9 Hz), 7.27 (d, 2H,
32
33 J =1.4 Hz), 4.09 (q, 2H, J =7.3 Hz), 2.71 (q, 2H, J =7.8 Hz), 1.25 (t, 2H, J =7.8 Hz), 1.07 (t, 2H, J =7.8 Hz) ppm.
34
35 ^{13}C NMR (CDCl_3 , 100 MHz): δ =13.6 (CH_3), 15.1 (CH_3), 28.9 (CH_2), 61.4 (CH_2), 127.6 (CH), 128.0 (2 \times CH),
36
37 129.4 (CH), 129.4 (C_q), 129.6 (2 \times CH), 130.1 (CH), 132.2 (CH), 135.0 (C_q), 141.9 (C_q), 150.1 (C_q), 166.0 (C_q),
38
39 196.7 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{18}\text{H}_{19}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 283.1329; found 283.1332.
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47 **Ethyl-2-(2-bromobenzoyl) benzoate (3bf)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40
48
49 mmol), aldehyde **2f** (296.0 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
50
51 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
52
53 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3bf** (87.9 mg, 66%) as a colourless
54
55 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1b})=0.90$, $R_f(\mathbf{3bf})=0.40$, UV
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3 detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} =2959, 2921, 2851, 1720, 1671, 1603, 1462, 1279, 1129,
4
5 1084, 1015, 933, 847, 751, 714 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =7.87-6.85 (m, 1H), 7.68-7.65 (m, 1H),
6
7 7.58-7.53 (m, 2H), 7.44-7.40 (m, 2H), 7.33-7.30 (m, 2H), 4.16 (q, 2H, J =7.0 Hz, OCH_2CH_3), 1.18 (t, 2H, J =7.0
8
9 Hz, CH_3) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =13.9 (CH_3), 61.6 (CH_2), 121.4(C_q), 127.0 (CH), 129.2 (CH),
10
11 129.7 (CH), 130.9 (CH), 131.4 (CH), 131.5 (C_q), 131.8 (CH), 132.5 (CH), 134.5 (CH), 138.2 (C_q), 140.0 (C_q),
12
13 167.0 (C_q), 195.4 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{16}\text{H}_{14}\text{BrO}_3]^+=[\text{M}+\text{H}]^+$: 333.0121; found
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15 333.0125.
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22 **Ethyl-2-(4-chlorobenzoyl) benzoate (3bg)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40
23
24 mmol), aldehyde **2g** (224.9 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
25
26 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
27
28 (petroleum ether/ethyl acetate, 97:03 to 96:04) furnished the product **3bg** (79.7 mg, 69%) as a
29
30 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1b})$ =0.90, $R_f(\mathbf{3bg})$ =0.35,
31
32 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} =2959, 2921, 2851, 1720, 1671, 1603, 1463, 1279,
33
34 1139, 1084, 1015, 935, 899, 857, 751, 710 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =8.06 (dd, 1H, J =7.5 and
35
36 J =1.2 Hz), 7.70-7.67 (m, 2H), 7.65-7.54 (m, 2H), 7.41-7.35 (m, 3H), 4.10 (q, 2H, J =7.3 Hz), 1.09 (t, 2H,
37
38 J =7.3 Hz) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =13.7(CH_3), 61.6 (CH_2), 127.5 (CH), 128.8 (2 \times CH), 129.3 (C_q),
39
40 129.7 (CH), 130.2 (CH), 130.7 (2 \times CH), 132.4 (CH), 135.6 (C_q), 139.5 (C_q), 141.2 (C_q), 165.7 (C_q), 195.8 (C_q)
41
42 ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{16}\text{H}_{14}\text{ClO}_3]^+=[\text{M}+\text{H}]^+$: 289.0626; found 289.0633.
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50 **Ethyl-2-(benzo[d][1,3]dioxole-5-carbonyl)benzoate (3bl)**: GP-1 was carried out with aryl iodide **1b**
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52 (110.4 mg, 0.40 mmol), aldehyde **2l** (240.2 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg,
53
54 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column
55
56 chromatography (petroleum ether/ethyl acetate, 95:05 to 92:08) furnished the product **3bl** (93.0 mg,
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3 78%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f(\mathbf{1b})=0.90$,
4
5 $R_f(\mathbf{3bl})=0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2925, 2857, 1718, 1668, 1598, 1456,$
6
7 1364, 1277, 1230, 1050, 983, 713 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta=8.03$ (d, 1H, $J=7.3$ Hz), 7.62–7.50 (m,
8
9 2H), 7.36–7.32 (m, 2H), 7.16 (dd, 1H, $J=8.0$ and $J=1.7$ Hz), 6.75 (d, 1H, $J=7.8$ Hz), 6.01 (s, 2H), 4.12 (q, 2H,
10
11 $J=6.8$ Hz), 1.11 (t, 2H, $J=6.8$ Hz) ppm. $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta=13.7$ (CH_3), 61.4 (CH_2), 101.8 (CH_2),
12
13 107.8 (CH), 108.5 (CH), 126.5 (CH), 127.5 (CH), 129.1 (C_q), 129.3 (CH), 130.1 (CH), 132.1 (C_q), 132.2 (CH),
14
15 141.8 (C_q), 148.1 (C_q), 151.8 (C_q), 165.8 (C_q), 195.3 (C_q) ppm. HR-MS (ESI^+) m/z calculated for
16
17 $[\text{C}_{17}\text{H}_{15}\text{O}_5]^+=[\text{M}+\text{H}]^+$: 299.0914; found 299.0919.
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26 **Isopropyl-2-benzoylbenzoate (3ca)**: GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40 mmol),
27
28 aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
29
30 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
31
32 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3ca** (75.1 mg, 70%) as a
33
34 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1c})=0.90$, $R_f(\mathbf{3ca})=0.40$,
35
36 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2980, 2924, 2853, 1716, 1673, 1594, 1451, 1347,$
37
38 1279 1081, 932, 709, 639 cm^{-1} . $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta=8.06$ (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 7.75 (dd,
39
40 2H, $J=8.3$ and $J=1.4$ Hz), 7.63–7.51 (m, 3H), 7.43–7.35 (m, 3H), 4.97 (sep, 1H, $J=6.3$ Hz), 1.00 (d, 6H, $J=6.3$
41
42 Hz), ppm. $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta=21.1$ ($2\times\text{CH}_3$), 69.4 (CH), 128.4 ($2\times\text{CH}$), 129.4 (CH), 129.5 ($2\times\text{CH}$),
43
44 129.5 (C_q), 130.1 (CH), 132.2 (CH), 133.1 (CH), 137.2 (C_q), 141.5 (C_q), 165.3 (C_q), 196.9 (C_q) ppm. HR-MS
45
46 (ESI^+) m/z calculated for $[\text{C}_{17}\text{H}_{17}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 269.1172; found 269.1165.
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54 **Isopropyl-2-(4-methylbenzoyl) benzoate (3cb)**: GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40
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56 mmol), aldehyde **2b** (192.2 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
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3 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
4
5 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3cb** (83.5 mg, 74%) as a
6
7 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1c})=0.90$, $R_f(\mathbf{3cb})=0.40$,
8
9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2981$, 2851, 1715, 1669, 1604, 1351, 1311, 1278,
10
11 1106, 1079, 932, 714 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.04$ (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 7.65 (d, 2H,
12
13 $J=8.3$ Hz), 7.58 (td, 1H, $J=7.3$ and $J=1.4$ Hz), 7.57-7.51 (m, 1H) 7.33 (dd, 1H, $J=7.5$ and $J=1.2$ Hz), 7.20 (d,
14
15 2H, $J=8.3$ Hz), 4.97 (sep, 1H, $J=6.3$ Hz), 2.38 (s, 3H), 1.01 (d, 6H, $J=6.3$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100
16
17 MHz): $\delta=21.2$ (2 $\times\text{CH}_3$), 21.6 (CH_3), 69.3 (CH), 127.5 (CH), 129.1 (2 $\times\text{CH}$), 129.2 (CH), 129.6 (C_q), 129.6
18
19 (2 $\times\text{CH}$), 130.1 (CH), 132.1 (CH), 134.8 (C_q), 141.7 (C_q), 143.9 (C_q), 165.3 (C_q), 196.5 (C_q) ppm. HR-MS (ESI $^+$)
20
21 m/z calculated for $[\text{C}_{18}\text{H}_{19}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 283.1329; found:283.1330.
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29 **Isopropyl-2-(4-ethylbenzoyl) benzoate (3cd)**: GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40
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31 mmol), aldehyde **2d** (214.7 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
32
33 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
34
35 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3cd** (85.3 mg, 72%) as a
36
37 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1c})=0.90$, $R_f(\mathbf{3cd})=0.40$,
38
39 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2971$, 2931, 2874, 1715, 1671, 1605, 1415, 1351,
40
41 1278, 1106, 1079, 933, 714, 579 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.04$ (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 7.67
42
43 (d, 2H, $J=8.3$ Hz), 7.59 (td, 1H, $J=7.3$ and $J=1.4$ Hz), 7.55-7.51 (m, 1H) 7.34 (dd, 1H, $J=7.3$ and $J=1.4$ Hz),
44
45 7.22 (d, 2H, $J=8.3$ Hz), 4.97 (sep, 1H, $J=6.3$ Hz), 2.67 (q, 2H, $J=7.3$ Hz), 7.67 (t, 3H, $J=7.3$ Hz), 1.01 (d, 6H,
46
47 $J=6.3$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=15.2$ (CH_3), 21.1 (2 $\times\text{CH}_3$), 28.9 (CH_2), 69.3(CH), 127.5 (CH),
48
49 127.9 (2 $\times\text{CH}$), 129.2 (CH), 129.6 (C_q), 129.7 (2 $\times\text{CH}$), 130.1 (CH), 132.1 (CH), 135.0 (C_q), 141.7 (C_q), 150.1
50
51 (C_q), 165.4 (C_q), 196.6 (C_q) ppm. HR-MS (ESI $^+$) m/z calculated for $[\text{C}_{19}\text{H}_{21}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 297.1485; found
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53 297.1496.
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6 **Isopropyl-2-(2-bromobenzoyl) benzoate (3cf):** GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40
7
8 mmol), aldehyde **2f** (296.0 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
9
10 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
11
12 (petroleum ether/ethyl acetate, 98:02 to 97:03) furnished the product **3cf** (83.3 mg, 60%) as a colourless
13
14 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1c})=0.90$, $R_f(\mathbf{3cf})=0.40$, UV
15
16 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2981, 2927, 1715, 1675, 1584, 1373, 1272, 1143, 1104,$
17
18 $1068, 929, 842, 396, 709, 645, 515$ cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=7.85$ (dd, 1H, $J=6.8$ and $J=1.9$ Hz),
19
20 7.66 (dd, 1H, $J=5.8$ and $J=3.4$ Hz), $7.55-7.53$ (m, 2H), $7.46-7.44$ (m, 1H), $7.40-7.38$ (m, 1H), 7.31 (dd, 1H,
21
22 $J=5.8$ and $J=3.4$ Hz), 5.07 (sep, 1H, $J=6.3$ Hz), 1.16 (d, 6H, $J=6.3$ Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz):
23
24 $\delta=21.4$ (2×CH₃), 69.4 (CH), 121.5 (C_q), 127.0 (CH), 129.0 (CH), 129.6 (CH), 130.7 (CH), 131.3 (CH), 132.0
25
26 (C_q), 132.0 (CH), 132.5 (CH), 134.5 (CH), 138.2 (C_q), 140.1 (C_q), 166.5 (C_q), 195.3 (C_q) ppm. HR-MS (ESI⁺)
27
28 m/z calculated for [C₁₇H₁₅BrNaO₃]⁺=[M+Na]⁺: 369.0097; found 369.0106.
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36 **Isopropyl-2-(4-bromobenzoyl) benzoate (3ce):** GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40
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38 mmol), aldehyde **2e** (396.0 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
39
40 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
41
42 (petroleum ether/ethyl acetate, 98:02 to 97:03) furnished the product **3ce** (86.1 mg, 62%) as a
43
44 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1c})=0.90$, $R_f(\mathbf{3ce})=0.40$,
45
46 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2980, 2925, 1712, 1674, 1584, 1467, 1373, 1272,$
47
48 $1133, 1104, 1068, 929, 842, 396, 709, 645, 515$ cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=8.06$ (dd, 1H, $J=7.8$ and
49
50 $J=0.9$ Hz), $7.64-7.60$ (m, 3H), $7.58-7.54$ (m, 3H), 7.33 (dd, 1H, $J=7.3$ and $J=0.9$ Hz), 4.99 (sep, 1H, $J=6.3$ Hz),
51
52 1.06 (d, 6H, $J=6.3$ Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=21.3$ (2×CH₃), 69.6 (CH), 127.4 (CH), 128.3 (C_q),
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54 129.5 (C_q), 129.6 (CH), 130.3 (CH), 130.9 (2×CH), 131.8 (2×CH), 132.4 (CH), 136.0 (C_q), 141.1 (C_q), 165.1
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(C_q), 196.0 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₇H₁₆BrO₃]⁺=[M+H]⁺: 347.0277; found 347.0268.

Isopropyl-2-(4-chlorobenzoyl) benzoate (3cg): GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40 mmol), aldehyde **2g** (224.9 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 98:02 to 97:03) furnished the product **3cg** (83.5 mg, 69%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), R_f(**1c**)=0.90, R_f(**3cg**)=0.40, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2980, 2922, 2851, 1715, 1674, 1586, 1465, 1373, 1276, 1106, 1089, 931, 845, 746, 711, 515 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.05 (dd, 1H, J=7.8 and J=0.9 Hz), 7.69 (d, 2H, J=8.3 Hz), 7.63-7.53 (m, 2H), 7.39-7.32 (m, 3H), 4.99 (sep, 1H, J=6.3 Hz), 1.05 (d, 6H, J=6.3 Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=21.3 (2×CH₃), 69.5 (CH), 127.3 (CH), 128.7 (2×CH), 129.4 (C_q), 129.6 (CH), 130.2 (CH), 130.7 (2×CH), 132.3 (CH), 135.6 (C_q), 139.5 (C_q), 141.1 (C_q), 165.1 (C_q), 195.7 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₇H₁₆ClO₃]⁺=[M+H]⁺: 303.0782; found 303.0789.

Isopropyl-2-(benzo[d][1,3]dioxole-5-carbonyl)benzoate (3cl): GP-1 was carried out with aryl iodide **1c** (116.0 mg, 0.40 mmol), aldehyde **2l** (240.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 93:07 to 90:10) furnished the product **3cl** (93.7 mg, 75%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**1c**)=0.95, R_f(**3cl**)=0.30, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2982, 2851, 1713, 1665, 1605, 1351, 1313, 1278, 1106, 1079, 932, 714 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.02 (d, 1H, J=7.8 Hz), 7.59-7.48 (m, 2H), 7.35 (d, 1H, J=1.4 Hz), 7.30 (dd, 1H, J=7.5 and J=1.2 Hz), 7.16 (dd, 1H, J=8.3 and J=1.4 Hz), 6.74 (d, 1H, J=8.3 Hz), 6.00 (s, 2H), 5.01 (sep, 1H, J=6.3 Hz), 1.07 (d, 6H, J=6.3 Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=21.3 (2×CH₃), 69.3 (CH), 101.8 (CH₂), 107.8 (CH), 108.6 (CH), 126.5 (CH), 127.4 (CH), 129.2 (CH),

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3 129.5 (C_q), 130.1 (CH), 132.0 (CH), 132.2 (C_q), 141.7 (C_q), 148.1 (C_q), 151.8 (C_q), 165.2 (C_q), 195.1 (C_q)
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5 ppm. HR-MS (ESI⁺) m/z calculated for [C₁₈H₁₇O₅]⁺=[M+H]⁺: 313.1071; found 313.1077.
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10 **Butyl-2-benzoylbenzoate (3da)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40 mmol),
11 aldehyde **2a** (169.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP
12 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
13 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **3da** (88.1 mg, 78%) as a
14 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), R_f(**1d**)=0.90, R_f(**3da**)=0.40,
15 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2969, 1721, 1676, 1588, 1451, 1287, 1081, 934, 718
16 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.06 (dd, 1H, J=7.8 and 0.9 Hz), 7.75 (dd, 2H, J=8.3 and 0.9 Hz), 7.62
17 (td, 1H, J=7.4 and 1.2 Hz), 7.59-7.52 (m, 2H), 7.44-7.37 (m, 3H), 4.02 (t, 2H, J=6.6 Hz, OCH₂CH₂CH₂CH₃),
18 1.43-1.36 (m, 2H, OCH₂CH₂CH₂CH₃), 1.24-1.15 (m, 2H), 0.80 (t, 3H, J=7.3 Hz), ppm. ¹³C NMR (CDCl₃, 100
19 MHz): δ=13.6 (CH₃), 19.0 (CH₂), 30.2 (CH₂), 65.4 (CH₂), 127.6 (CH), 128.4 (2×CH), 129.4 (C_q), 129.4 (2×CH),
20 129.5 (CH), 130.2 (CH), 132.3 (CH), 133.1 (CH), 137.1 (C_q), 141.6 (C_q), 166.0 (C_q), 196.9 (C_q) ppm. HR-MS
21 (ESI⁺) m/z calculated for [C₁₈H₁₉O₃]⁺=[M+H]⁺: 283.1329; found 283.1336.
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40 **Butyl-2-(4-methylbenzoyl) benzoate (3db)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40
41 mmol), aldehyde **2b** (192.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
42 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
43 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3db** (85.4 mg, 72%) as a
44 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), R_f(**1d**)=0.90, R_f(**3db**)=0.35,
45 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}=2959, 1725, 1665, 1520, 1453, 1267, 1072, 936, 720
46 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.04 (dd, 1H, J=7.8 and 1.4 Hz), 7.64 (d, 2H, J=8.3 Hz), 7.60 (td, 1H,
47 J=7.8, and 1.4 Hz), 7.53 (td, 1H, J=7.5, and 1.2 Hz), 7.35 (dd, 1H, J=7.5 and 1.2 Hz), 7.20 (d, 2H, J=8.3 Hz),
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3 4.02 (t, 2H, $J=6.6$ Hz), 2.38 (s, 3H), 1.44-1.37 (m, 2H), 1.24-1.15 (m, 2H), 0.80 (t, 3H, $J=7.3$ Hz), ppm. ^{13}C
4
5 NMR (CDCl_3 , 100 MHz): $\delta=13.6$ (CH_3), 19.0 (CH_2), 21.6 (CH_3), 30.2 (CH_2), 65.3 (CH_2), 127.5 (CH), 129.1
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7 (2 \times CH), 129.3 (C_q), 129.3 (CH), 129.5 (2 \times CH), 130.1 (CH), 132.2 (CH), 134.6 (C_q), 141.8 (C_q), 143.9 (C_q),
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9 166.0 (C_q), 196.6 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{19}\text{H}_{21}\text{O}_3]^+ = [\text{M}+\text{H}]^+$: 297.1485; found
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11 297.1485.
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17 **Butyl-2-(4-ethylbenzoyl) benzoate (3dd)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40
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19 mmol), aldehyde **2d** (214.7 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
20
21 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
22
23 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3dd** (93.1 mg, 75%) as a
24
25 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1d})=0.90$, $R_f(\mathbf{3dd})=0.35$,
26
27 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2952$, 1722, 1673, 1596, 1452, 1274, 1086, 938, 719
28
29 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.04$ (dd, 1H, $J=7.5$ and 1.2 Hz), 7.67 (d, 2H, $J=8.3$ Hz), 7.63-7.52 (m,
30
31 2H), 7.35 (dd, 1H, $J=7.5$ and 1.2 Hz), 7.23 (d, 2H, $J=8.3$ Hz), 4.02 (t, 2H, $J=6.6$ Hz), 2.68 (q, 2H, $J=7.8$ Hz),
32
33 1.43-1.36 (m, 2H), 1.25-1.16 (m, 5H), 0.79 (t, 3H, $J=7.3$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.6$
34
35 (CH_3), 15.1 (CH_3), 19.0 (CH_2), 28.9 (CH_2), 30.2 (CH_2), 65.4 (CH_2), 127.5 (CH), 128.0 (2 \times CH), 129.3 (C_q),
36
37 129.3 (CH), 129.7 (2 \times CH), 130.1 (CH), 132.2 (CH), 134.8 (C_q), 141.8 (C_q), 150.1 (C_q), 166.1 (C_q), 196.7 (C_q)
38
39 ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{20}\text{H}_{23}\text{O}_3]^+ = [\text{M}+\text{H}]^+$: 311.1642; found 311.1649.
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47 **Butyl-2-(4-chlorobenzoyl) benzoate (3dg)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40
48
49 mmol), aldehyde **2g** (224.9 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
50
51 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
52
53 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3dg** (78.6 mg, 62%) as a
54
55 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1d})=0.90$, $R_f(\mathbf{3dg})=0.40$,
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3 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} =2966, 1721, 1675, 1590, 1450, 1257, 1083, 933, 714
4
5 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =8.05 (dd, 1H, J =7.8 and 0.9 Hz), 7.68 (d, 2H, J =8.8 Hz), 7.62 (td, 1H,
6
7 J =7.5, and 1.4 Hz), 7.55 (td, 1H, J =7.5, and 1.4 Hz), 7.39-7.34 (m, 3H), 4.04 (t, 2H, J =6.6 Hz), 1.47-1.40 (m,
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9 2H), 1.27-1.17 (m, 2H), 0.82 (t, 3H, J =7.3 Hz), 1 ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =13.6 (CH_3), 19.0 (CH_2),
10
11 30.2 (CH_2), 65.5 (CH_2), 127.4 (CH), 128.8 (2 \times CH), 129.2 (C_q), 129.6 (CH), 130.2 (CH), 130.7 (2 \times CH), 132.4
12
13 (CH), 135.5 (C_q), 139.5 (C_q), 141.1 (C_q), 165.8 (C_q), 195.8 (C_q) ppm. HR-MS (ESI^+) m/z calculated for
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15 $[\text{C}_{18}\text{H}_{18}\text{ClO}_3]^+=[\text{M}+\text{H}]^+$: 317.0939; found 317.0946.
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22 **Butyl-2-(2-bromobenzoyl) benzoate (3df)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40
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24 mmol), aldehyde **2f** (296.0 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
25
26 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
27
28 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3df** (91.0 mg, 63%) as a colourless
29
30 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1d})=0.90$, $R_f(\mathbf{3df})=0.40$, UV
31
32 detection]. IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} =2960, 1722, 1674, 1599, 1455, 1280, 1088, 939, 720 cm^{-1} .
33
34 ^1H NMR (CDCl_3 , 400 MHz): δ =7.87-7.85 (m, 1H), 7.68-7.65 (m, 1H), 7.59-7.51 (m, 2H), 7.44-7.41 (m, 2H),
35
36 7.34-7.29 (m, 1H), 4.12 (t, 2H, J =6.6 Hz), 1.58-1.51 (m, 2H), 1.33-1.24 (m, 2H), 0.84 (t, 3H, J =7.3 Hz),
37
38 ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =13.6 (CH_3), 19.0 (CH_2), 30.3 (CH_2), 65.5 (CH_2), 121.5 (C_q), 127.0 (CH),
39
40 129.1 (CH), 129.7 (CH), 130.8 (CH), 131.4 (CH), 131.6 (C_q), 131.9 (CH), 132.5 (CH), 134.5 (CH), 138.2 (C_q),
41
42 140.1 (C_q), 167.1 (C_q), 195.4 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{18}\text{H}_{18}\text{BrO}_3]^+=[\text{M}+\text{H}]^+$: 361.0434;
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47 found 361.0436.
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52 **Butyl-2-(4-bromobenzoyl) benzoate (3de)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40
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54 mmol), aldehyde **2e** (296.0 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
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56 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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(petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3de** (98.3 mg, 68%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1d})=0.90$, $R_f(\mathbf{3de})=0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2959$, 1720, 1675, 1598, 1450, 1277, 1083, 933, 713 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.05$ (dd, 1H, $J=7.8$ and 0.9 Hz), 7.65–7.53 (m, 6H), 7.34 (dd, 1H, $J=7.5$, and 1.2 Hz), 4.04 (t, 2H, $J=6.6$ Hz), 1.47–1.40 (m, 2H), 1.27–1.18 (m, 2H), 0.82 (t, 3H, $J=7.3$ Hz), 1 ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.6(\text{CH}_3)$, 19.0 (CH_2), 30.2 (CH_2), 65.5 (CH_2), 127.4 (CH), 128.3 (C_q), 129.2 (C_q), 129.7 (CH), 130.2 (CH), 130.8 (2 \times CH), 131.8 (2 \times CH), 132.4 (CH), 135.9 (C_q), 141.1 (C_q), 165.8 (C_q), 196.0 (C_q) ppm. HR-MS (ESI $^+$) m/z calculated for $[\text{C}_{18}\text{H}_{18}\text{BrO}_3]^+=[\text{M}+\text{H}]^+$: 361.0434; found 361.0434.

Pentyl-2-benzoylbenzoate (3ea): GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40 mmol), aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3ea** (98.4 mg, 83%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1e})=0.90$, $R_f(\mathbf{3ea})=0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2960$, 1722, 1677, 1599, 1456, 1288, 1088, 944, 720 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=8.05$ (dd, 1H, $J=7.3$ and 1.4 Hz), 7.75 (dd, 2H, $J=8.5$ and 1.2 Hz), 7.64–7.51 (m, 3H), 7.44–7.36 (m, 3H), 4.00 (t, 2H, $J=6.6$ Hz), 1.45–1.37 (m, 2H), 1.24–1.11 (m, 4H), 0.81 (t, 3H, $J=7.0$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.8$ (CH_3), 22.2 (CH_2), 27.8 (CH_2), 27.9 (CH_2), 65.7 (CH_2), 127.5 (CH), 128.4 (2 \times CH), 129.4 (2 \times CH), 129.5 (CH), 129.6 (C_q), 130.1 (CH), 132.2 (CH), 133.0 (CH), 137.0 (C_q), 141.5 (C_q), 166.0 (C_q), 196.9 (C_q) ppm. HR-MS (ESI $^+$) m/z calculated for $[\text{C}_{19}\text{H}_{21}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 297.1485; found 297.1488.

Pentyl-2-(2-methylbenzoyl) benzoate (3ec): GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40 mmol), aldehyde **2c** (192.2 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and

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3 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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5 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3ec** (89.4 mg, 72%) as a
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7 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1e})=0.90$, $R_f(\mathbf{3ec})=0.30$,
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9 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2959$, 1722, 1685, 1568, 1462, 1255, 1088, 944, 730
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11 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.93$ (dd, 1H, , $J=7.3$ and 1.4 Hz), 7.59-7.51 (m, 2H), 7.41-7.35 (m, 2H),
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13 7.28 (d, 1H, $J=7.3$ Hz), 7.25-7.23 (m, 1H), 7.14-7.10 (m, 1H), 4.04 (t, 2H, $J=6.6$ Hz), 2.66 (s, 3H), 1.51-1.44
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15 (m, 2H), 1.24-1.15 (m, 4H), 0.81 (t, 3H, $J=7.0$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.8$ (CH_3),
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17 21.6(CH_3), 22.2 (CH_2), 27.9 (CH_2), 28.0 (CH_2), 65.6 (CH_2), 125.3 (CH), 128.2 (CH), 129.7 (CH), 129.8 (CH),
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19 130.3 (C_q), 131.7 (2 \times CH), 131.8 (CH), 131.9 (CH), 136.4 (C_q), 140.1 (C_q), 142.6 (C_q), 166.6 (C_q), 198.5 (C_q)
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21 ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{20}\text{H}_{23}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 311.1642; found 311.1644.
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29 **Pentyl-2-(4-methylbenzoyl) benzoate (3eb)**: GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40
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31 mmol), aldehyde **2b** (192.2 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
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33 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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35 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3eb** (98.1 mg, 79%) as a
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37 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1e})=0.90$, $R_f(\mathbf{3eb})=0.30$,
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39 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2967$, 1730, 1680, 1602, 1460, 1279, 1090, 940, 719
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41 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.93$ (dd, 1H, , $J=7.3$ and 1.4 Hz), 7.59-7.51 (m, 2H), 7.41-7.35 (m, 2H),
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43 7.28 (d, 1H, $J=7.3$ Hz), 7.25-7.23 (m, 1H), 7.14-7.10 (m, 1H), 4.03 (t, 2H, $J=6.6$ Hz), 2.66 (s, 3H), 1.51-1.44
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45 (m, 2H), 1.24-1.15 (m, 4H), 0.81 (t, 3H, $J=7.0$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.8$ (CH_3),
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47 21.6(CH_3), 22.2 (CH_2), 27.9 (CH_2), 27.9 (CH_2), 65.7 (CH_2), 127.5 (CH), 129.1 (2 \times CH), 129.3 (CH), 129.3 (C_q),
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49 129.6 (2 \times CH), 130.1 (CH), 132.1 (CH), 134.7 (C_q), 141.8 (C_q), 143.9 (C_q), 166.0 (C_q), 196.6 (C_q) ppm. HR-MS
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51 (ESI^+) m/z calculated for $[\text{C}_{20}\text{H}_{23}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 311.1642; found 311.1645.
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3 **Pentyl-2-(2-bromobenzoyl) benzoate (3ef):** GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40
4 mmol), aldehyde **2f** (296.0 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
5 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
6 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3ef** (86.1 mg, 60%) as a colourless
7 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1e})=0.90$, $R_f(\mathbf{3ef})=0.30$, UV
8 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2966$, 1730, 1685, 1588, 1460, 1287, 1093, 943, 723 cm⁻¹.
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10 ¹H NMR (CDCl₃, 400 MHz): $\delta=7.88$ -7.86 (m, 1H), 7.69-7.65 (m, 1H), 7.59-7.52 (m, 2H), 7.45-7.41 (m, 2H),
11 7.34-7.30 (m, 2H), 4.11 (t, 2H, $J=6.6$ Hz) 1.59-1.54 (m, 2H), 1.25-1.20 (m, 4H), 0.82 (t, 3H, $J=7.0$ Hz), ppm.
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13 ¹³C NMR (CDCl₃, 100 MHz): $\delta=13.9$ (CH₃), 22.2 (CH₂), 28.0 (2×CH₂), 65.9 (CH₂), 121.5 (C_q), 127.0 (CH),
14 129.1 (CH), 129.8 (CH), 130.8 (CH), 131.4 (CH), 131.6 (C_q), 132.0 (CH), 132.5 (CH), 134.5 (CH), 138.1 (C_q),
15 140.1 (C_q), 167.1 (C_q), 195.4 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₉H₂₀BrO₃]⁺=[M+H]⁺: 375.0590;
16 found 375.0592.
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33 **Pentyl-2-(4-bromobenzoyl) benzoate (3ee):** GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40
34 mmol), aldehyde **2e** (296.0 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
35 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
36 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3ee** (124.6 mg, 83%) as a
37 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1e})=0.90$, $R_f(\mathbf{3ee})=0.30$,
38 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2957$, 1699, 1680, 1600, 1460, 1282, 1085, 940, 720
39 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=8.06$ (dd, 1H, $J=7.8$ and 0.9 Hz), 7.65-7.54 (m, 6H), 7.34 (dd, 1H, $J=7.8$
40 and 0.9 Hz), 4.04 (t, 2H, $J=6.6$ Hz) 1.49-1.42 (m, 2H), 1.26-1.14 (m, 4H), 0.83 (t, 3H, $J=7.0$ Hz), ppm. ¹³C
41 NMR (CDCl₃, 100 MHz): $\delta=13.9$ (CH₃), 22.2 (CH₂), 27.9 (2×CH₂), 65.8 (CH₂), 127.4 (CH), 128.3 (C_q), 129.3
42 (C_q), 129.7 (CH), 130.3 (CH), 130.8 (2×CH), 131.8 (2×CH), 132.4 (CH), 135.9 (C_q), 141.1 (C_q), 165.8 (C_q),
43 195.9 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₉H₂₀BrO₃]⁺=[M+H]⁺: 375.0590; found 375.0600.
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6 **Pentyl-2-(4-chlorobenzoyl) benzoate (3eg):** GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40
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8 mmol), aldehyde **2g** (224.9 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
9
10 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
11
12 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3eg** (117.8 mg, 89%) as a
13
14 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1e**)=0.90, *R_f*(**3eg**)=0.30,
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16 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2950, 1721, 1676, 1599, 1451, 1278, 1084, 934, 714
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18 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.08-8.06 (m, 1H), 7.68 (d, 2H, *J*=8.8 Hz), , 7.62 (td, 1H, *J*=7.5 and 1.4
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20 Hz), 7.56 (td, 1H, *J*=7.5 and 1.4 Hz), 7.41-7.34 (m, 3H), 4.04 (t, 2H, *J*=6.6 Hz) 1.49-1.42 (m, 2H), 1.26-1.14
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22 (m, 4H), 0.83 (t, 3H, *J*=7.0 Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=13.8 (CH₃), 22.2 (CH₂), 27.9 (2×CH₂),
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24 65.8 (CH₂), 127.4 (CH), 128.8 (2×CH), 129.3 (C_q), 129.7 (CH), 130.3 (CH), 130.7 (2×CH), 132.4 (CH), 135.5
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26 (C_q), 139.5 (C_q), 141.2 (C_q), 165.8 (C_q), 195.7 (C_q) ppm. HR-MS (ESI⁺) *m/z* calculated for
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28 [C₁₉H₂₀ClO₃]⁺=[M+H]⁺: 331.1095; found 331.1091.
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36 **Pentyl-2-(4-fluorobenzoyl) benzoate (3eh):** GP-1 was carried out with aryl iodide **1e** (127.3 mg, 0.40
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38 mmol), aldehyde **2h** (198.6 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
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40 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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42 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **3eh** (86.8 mg, 69%) as a
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44 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1e**)=0.90, *R_f*(**3eh**)=0.30,
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46 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): *v*_{max}=2959, 1713, 1678, 1599, 1452, 1288, 1086, 934, 716
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48 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.06 (d, 1H, *J*=7.8 Hz), 7.77 (dd, 2H, *J*=8.8 and *J*=5.3 Hz), 7.64-7.54 (m,
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50 2H), 7.35 (dd, 1H, *J*=8.8 and *J*=5.3 Hz), 7.05(t, 2H, *J*=8.5 Hz), 4.04 (t, 2H, *J*=6.8 Hz) 1.49-1.42 (m, 2H), 1.26-
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52 1.12 (m, 4H), 0.83 (t, 3H, *J*=7.0 Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=13.8 (CH₃), 22.2 (CH₂), 27.9
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54 (2×CH₂), 65.8 (CH₂), 115.5 (CH), 115.7 (CH), 127.4 (CH), 129.3 (C_q), 129.6 (CH), 130.3 (CH), 132.0 (CH),
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56 139.5 (C_q), 141.2 (C_q), 165.8 (C_q), 195.7 (C_q) ppm.
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3 132.0 (CH), 132.3 (CH), 133.7 (C_q), 141.4 (C_q), 165.9 (C_q), 166.9 (d, ¹J_{C-F}=249.4 Hz), 195.4 (C_q) ppm HR-MS
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5 (ESI⁺) m/z calculated for [C₁₉H₂₀FO₃]⁺=[M+H]⁺: 315.1391; found 315.1399.
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10 **Methyl-2-isobutyrylbenzoate (5aa)**: GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40 mmol),
11 aldehyde **4a** (115.4 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP
12 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
13 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **5aa** (53.6 mg, 65%) as a
14 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), R_f(**1a**)=0.90, R_f(**5aa**)=0.30,
15 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}= 2933, 1720, 1625, 1488, 1480, 1395, 1313, 1098,
16 1018, 818, 739 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=7.91 (dd, 1H, J=7.8 and 0.9 Hz), 7.54 (td, 1H, J=7.4 and
17 1.2 Hz), 7.47 (td, 1H, J=7.8 and 1.2 Hz), 7.30 (dd, 1H, J=7.8, and 0.9 Hz), 3.86 (s, 3H), 3.04 (sep, 1H, J=6.8
18 Hz), 1.18 (d, H, J=6.8 Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=18.5 (2 × CH₃), 40.7 (CH), 52.5 (CH₃), 126.8
19 (CH), 128.3 (C_q), 129.4 (CH), 130.0 (CH), 132.1 (CH), 143.1 (C_q), 166.9 (C_q), 210.1 (C_q) ppm. HR-MS (ESI⁺)
20 m/z calculated for [C₁₂H₁₅O₃]⁺=[M+H]⁺: 207.1016; found 207.1018.
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38 **Methyl-4-isobutyrylbenzoate (5fa)**:^{20ch} GP-1 was carried out with aryl iodide **1f** (104.8 mg, 0.40 mmol),
39 aldehyde **4a** (115.4 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP
40 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
41 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **5fa** (48.7 mg, 59%) as a colourless
42 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), R_f(**1f**)=0.90, R_f(**5fa**)=0.40, UV
43 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max}= 2924, 1606, 1488, 1441, 1385, 1303, 1088, 1014, 814,
44 738 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ=8.11 (d, 2H, J=7.8 Hz), 7.98 (d, 2H, J=8.8 Hz), 3.94 (s, 3H), 3.54
45 (sep, 1H, J=6.8 Hz), 1.22 (d, H, J=6.8 Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): δ=19.0 (2 × CH₃), 35.8 (CH),
46 52.4 (CH₃), 128.2 (2×CH), 129.8 (2×CH), 133.6 (C_q), 139.6 (C_q), 166.3 (C_q), 204.0 (C_q) ppm. HR-MS (ESI⁺)
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m/z calculated for $[C_{12}H_{15}O_3]^+=[M+H]^+$: 207.1016; found 207.1013.

Methyl-2-(3-methylbutanoyl) benzoate (5ab): GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40 mmol), aldehyde **4b** (137.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **5ab** (62.5 mg, 71%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1a})=0.80$, $R_f(\mathbf{5ab})=0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2943, 1723, 1683, 1481, 1441, 1386, 1304, 1089, 1018, 815, 739$ cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=7.84$ (dd, 1H, $J=7.8$ and 0.9 Hz), 7.53 (td, 1H, $J=7.5$ and 1.4 Hz, Ar-H), 7.47 (td, 1H, $J=7.5$ and 1.4 Hz), 7.36 (dd, 1H, $J=7.8$, and 0.9 Hz, Ar-H), 3.87 (s, 3H, OCH₃), 2.70 (d, 2H, $J=6.8$ Hz), 2.25 (sep, 1H, $J=6.8$ Hz), 0.99 (d, 6H, $J=6.8$ Hz), ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=22.6$ (2 × CH₃), 24.5 (CH), 51.2 (CH₂), 52.5 (CH₃), 126.5 (CH), 128.9 (C_q), 129.8 (2×CH), 131.9 (CH), 143.0 (C_q), 167.4 (C_q), 204.8 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for $[C_{13}H_{17}O_3]^+=[M+H]^+$: 221.1172; found 221.1177.

Methyl-2-(cyclohexanecarbonyl) benzoate (5ae): GP-1 was carried out with aryl iodide **1a** (104.8 mg, 0.40 mmol), aldehyde **4e** (179.5 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 97:03 to 92:08) furnished the product **5ae** (68.9 mg, 70%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f(\mathbf{1a})=0.80$, $R_f(\mathbf{5ae})=0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2963, 1703, 1695, 1487, 1440, 1385, 1303, 1098, 1014, 818, 737$ cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=7.90$ (dd, 1H, $J=7.8$ and 0.9 Hz), 7.53 (td, 1H, $J=7.5$ and 1.4 Hz), 7.45 (td, 1H, $J=7.5$ and 0.9 Hz), 7.28 (dd, 1H, $J=7.5$, and 1.4 Hz), 3.86 (s, 3H), 2.78 (tt, 1H, $J=11.7$ and 3.4 Hz), 1.91 (d, 2H, $J=13.2$ Hz), 1.81–1.65 (m, 4H), 1.46–1.37 (m, 2H), 1.27–1.21 (m, 2H), ppm. ¹³C

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3 NMR (CDCl₃, 100 MHz): δ =25.8 (2 × CH₂), 25.9 (CH₂), 28.7 (2 × CH₂), 50.5 (CH), 52.5 (CH₃), 126.7 (CH),
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5 128.3 (C_q), 129.4 (CH), 130.0 (CH), 132.0 (CH), 143.1 (C_q), 167.0 (C_q), 209.3 (C_q) ppm. HR-MS (ESI⁺) m/z
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8 calculated for [C₁₅H₁₉O₃]⁺=[M+H]⁺: 247.1329; found 247.1336.
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12 **Ethyl-2-pentanoylbenzoate (5bd)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40 mmol),
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14 aldehyde **4d** (137.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP
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16 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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18 (petroleum ether/ethyl acetate, 96:04 to 92:08) furnished the product **5bd** (60.9 mg, 65%) as a
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20 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1b**)=0.85, *R_f*(**5bd**)=0.25,
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22 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} =2921, 2853, 1729, 1678, 1615, 1546, 1466, 1301,
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24 1130, 1050, 981, 951, 733 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.88 (dd, 1H, *J*=7.8 and 1.5 Hz), 7.53 (ddd,
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26 1H, *J*=7.8, 7.3 and 1.5 Hz), 7.46 (ddd, 1H, *J*=7.8, 7.3 and 1.5 Hz), 7.33 (dd, 1H, *J*=7.8 and 1.5 Hz), 4.33 (q,
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28 2H, *J*=7.3 Hz), 2.79 (t, 2H, *J*=7.3 Hz), 1.80–1.62 (m, 2H), 1.45–1.30 (m, 2H), 1.34 (t, 3H, *J*=7.3 Hz), 0.92 (t,
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30 3H, *J*=7.3 Hz) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ =13.9 (CH₃), 14.0 (CH₃), 22.3 (CH₂), 26.1 (CH₂), 42.6 (CH₂),
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32 61.6 (CH₂), 126.2 (CH), 128.8 (C_q), 129.6 (CH), 129.8 (CH), 131.9 (CH), 143.3 (C_q), 166.7 (C_q), 205.9 (C_q)
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34 ppm. HR-MS (ESI⁺) m/z calculated for [C₁₄H₁₉O₃]⁺=[M+H]⁺: 235.1329; found 235.1331.
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43 **Ethyl-2-(cyclohexanecarbonyl) benzoate (5be)**: GP-1 was carried out with aryl iodide **1b** (110.4 mg, 0.40
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45 mmol), aldehyde **4e** (179.5 mg, 1.6 mmol), Pd(OAc)₂ (5 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
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47 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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49 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **5be** (71.8 mg, 69%) as a
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51 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), *R_f*(**1b**)=0.80, *R_f*(**5be**)=0.30,
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53 UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): ν_{max} = 2923, 1720, 1685, 1487, 1440, 1385, 1300, 1087,
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55 1014, 894, 739 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ =7.93 (dd, 1H, *J*=7.8 and 1.0 Hz), 7.54 (ddd, 1H, *J*=7.8,
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3 7.3 and 1.0 Hz), 7.47 (ddd, 1H, $J=7.3$, 7.3 and 1.0 Hz), 7.30 (dd, 1H, $J=7.3$ and 1.0 Hz), 4.35 (q, 2H, $J=7.3$
4 Hz), 2.78 (tt, 1H, $J=11.7$ and 3.4 Hz), 2.00–1.90 (m, 2H), 1.86–1.75 (m, 2H), 1.55–1.40 (m, 2H), 1.36 (t, 3H,
5 $J=7.3$ Hz), 1.34–1.12 (m, 4H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=14.1$ (CH_3), 25.7 ($2 \times \text{CH}_2$), 25.8 (CH_2),
6 28.7 ($2 \times \text{CH}_2$), 50.3 (CH), 61.5 (CH_2), 126.7 (CH), 128.7 (C_q), 129.3 (CH), 129.9 (CH), 131.8 (CH), 142.9 (C_q),
7 166.5 (C_q), 209.2 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{16}\text{H}_{21}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 261.1485; found
8 261.1486.
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20 **Butyl-2-(cyclohexanecarbonyl) benzoate (5de)**: GP-1 was carried out with aryl iodide **1c** (121.6 mg, 0.40
21 mmol), aldehyde **4e** (179.5 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
22 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
23 (petroleum ether/ethyl acetate, 95:05 to 94:06) furnished the product **5de** (83.1 mg, 72%) as a
24 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1c})=0.85$, $R_f(\mathbf{5de})=0.30$,
25 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2953$, 1720, 1686, 1487, 1440, 1385, 1303, 1088,
26 1014, 814, 738 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.91$ (dd, 1H, $J=7.3$ and 0.9 Hz), 7.53 (td, 1H, $J=7.5$ and
27 1.4 Hz), 7.45 (td, 1H, $J=7.5$ and 1.4 Hz), 7.27 (dd, 1H, $J=7.3$ and 0.9 Hz), 4.28 (t, 2H, $J=6.8$ Hz), 2.76 (tt,
28 1H, $J=11.6$ and 3.3 Hz), 1.93 (d, 2H, $J=11.6$ Hz), 1.74–1.65 (m, 4H), 1.49–1.38 (m, 4H), 1.29–1.20 (m, 4H),
29 0.95 (t, 3H, $J=7.3$ Hz), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.7$ (CH_3), 19.2 (CH_2), 25.8 ($2 \times \text{CH}_2$), 25.9
30 (CH_2), 28.7 ($2 \times \text{CH}_2$), 30.6 (CH_2), 50.4 (CH), 61.5 (CH_2), 126.7 (CH), 128.8 (C_q), 129.3 (CH), 130.0 (CH),
31 131.9 (CH), 143.1 (C_q), 166.6 (C_q), 209.3 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{18}\text{H}_{25}\text{O}_3]^+=[\text{M}+\text{H}]^+$:
32 289.1798; found 289.1796.
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52 **Butyl-2-butyrylbenzoate (5dc)**: GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40 mmol),
53 aldehyde **4c** (115.4 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
54 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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(petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **5dc** (61.6 mg, 62%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{1d})=0.80$, $R_f(\mathbf{5dc})=0.30$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2963, 1780, 1680, 1482, 1441, 1386, 1304, 1058, 1054, 824, 748 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta=7.87$ (dd, 1H, $J=7.8$ and 0.9 Hz), 7.53 (td, 1H, $J=7.4$ and 1.2 Hz), 7.46 (td, 1H, $J=7.4$ and 1.2 Hz), 7.32 (dd, 1H, $J=7.8$, and 0.9 Hz), 4.27 (t, 2H), 2.75 (t, 2H, $J=7.8$ Hz), 1.78–1.66 (m, 4H), 1.46–1.37 (m, 2H), 1.00–0.92 (m, 6H), ppm. $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta=13.7$ (2 \times CH_3), 17.5 (CH_2), 19.1 (CH_2), 30.5 (CH_2), 44.8 (CH_2), 65.5 (CH_2), 126.2 (CH), 128.8 (C_q), 129.5 (CH), 129.8 (CH), 131.9 (CH), 143.3 (C_q), 166.8 (C_q), 205.8 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{15}\text{H}_{21}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 249.1485; found 249.1485.

Butyl-2-(3-methylbutanoyl) benzoate (5db): GP-1 was carried out with aryl iodide **1d** (121.6 mg, 0.40 mmol), aldehyde **4b** (137.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **5db** (77.6 mg, 74%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:5), $R_f(\mathbf{1d})=0.80$, $R_f(\mathbf{5db})=0.20$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2935, 1723, 1686, 1482, 1450, 1360, 1304, 1089, 1015, 811, 732 \text{ cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta=7.83$ (dd, 1H, $J=7.8$ and 0.9 Hz), 7.52 (td, 1H, $J=7.5$ and 1.4 Hz), 7.45 (td, 1H, $J=7.5$ and 1.4 Hz), 7.35 (dd, 1H, $J=7.8$, and 0.9 Hz), 4.28 (t, 2H), 2.70 (d, 2H, $J=6.8$ Hz), 2.24 (sep, 1H, $J=6.8$ Hz), 1.73–1.66 (m, 2H), 1.46–1.37 (m, 2H), 0.98 (d, 6H, $J=6.8$ Hz), 0.94 (t, 3H, $J=6.8$ Hz), ppm. $^{13}\text{C NMR}$ (CDCl_3 , 100 MHz): $\delta=13.7$ (CH_3), 19.1 (CH_2), 22.7 (2 \times CH_3), 24.6 (CH), 30.5 (CH_2), 51.3 (CH_2), 65.5 (CH_2), 126.5 (CH), 129.3 (C_q), 129.7 (CH), 129.7 (CH), 131.7 (CH), 143.0 (C_q), 167.0 (C_q), 204.9 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{16}\text{H}_{23}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 263.1642; found 263.1640.

Benzophenone (7aa):^{20a} GP-1 was carried out with aryl iodide **6a** (81.6 mg, 0.40 mmol), aldehyde **2a**

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3 (169.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0
4 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl
5 acetate, 97:03 to 95:05) furnished the product **7aa** (35.5 mg, 52%) as a colourless viscous liquid. [TLC
6 control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6a})=0.90$, $R_f(\mathbf{7aa})=0.40$, UV detection]. IR (MIR-ATR,
7 4000–600 cm⁻¹): $\nu_{max}=2960$, 1733, 1678, 1588, 1460, 1287, 1082, 934, 719 cm⁻¹. ¹H NMR (CDCl₃, 400
8 MHz): $\delta=7.81$ -7.79 (m, 4H), 7.60-7.56 (m, 2H), 7.50-7.46 (m, 4H), ppm. ¹³C NMR (CDCl₃, 100 MHz):
9 $\delta=128.3$ (3×CH), 130.0 (3×CH), 132.4 (2×CH), 137.6 (2C_q), 196.7 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for
10 [C₁₃H₁₁O]⁺=[M+H]⁺: 183.0804; found 183.0808.
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24 **(4-Methoxyphenyl)(phenyl) methanone (7aj)**: GP-1 was carried out with aryl iodide **6a** (81.6 mg, 0.40
25 mmol), aldehyde **2j** (217.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
26 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
27 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **7aj** (55.2 mg, 65%) as a colourless
28 viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6a})=0.90$, $R_f(\mathbf{7aj})=0.40$, UV
29 detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=2960$, 1730, 1672, 1588, 1452, 1278, 1081, 932, 716 cm⁻¹.
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31 ¹H NMR (CDCl₃, 400 MHz): $\delta=7.82$ (d, 2H, $J=8.8$ Hz), 7.74 (dd, 2H, $J=7.5$ and $J=1.2$ Hz), 7.58-7.53 (m, 1H),
32 7.46 (t, 2H, $J=7.5$ Hz), 6.95 (d, 2H, $J=8.8$ Hz), 3.88 (s, 3H), ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=55.5$ (CH₃),
33 113.5 (2×CH), 128.2 (2×CH), 129.7 (2×CH), 130.1 (C_q), 131.9 (CH), 132.5 (2×CH), 138.3 (C_q), 163.2 (C_q),
34 195.6 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for [C₁₄H₁₃O₂]⁺=[M+H]⁺: 213.0910; found 213.0912.
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49 **Furan-2-yl(phenyl)methanone (7am)**:^{20a} GP-1 was carried out with aryl iodide **6a** (81.6 mg, 0.40 mmol),
50 aldehyde **2m** (153.7 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and TBHP
51 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
52 (petroleum ether/ethyl acetate, 90:10 to 88:12) furnished the product **7am** (42.7 mg, 62%) as a
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3 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 85:15), $R_f(\mathbf{6a})=0.99$, $R_f(\mathbf{7am})=0.40$,
4 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{max}=2966$, 1723, 1676, 1599, 1451, 1278, 1084, 934, 714
5 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.95$ (dd, 2H, $J=8.3$ and $J=1.4$ Hz), 7.70 (d, 1H, $J=2.4$ Hz), 7.60-7.56 (m,
6 1H), 7.50-7.46 (m, 2H), 7.22 (d, 1H, $J=2.4$ Hz), 6.58 (dd, 1H, $J=3.6$ and $J=1.4$ Hz), ppm. ^{13}C NMR (CDCl_3 ,
7 100 MHz): $\delta=112.2$ (CH), 120.5 (CH), 128.4 (2 \times CH), 129.3 (2 \times CH), 132.5 (CH), 137.2 (C_q), 147.1 (CH),
8 152.3 (C_q), 182.5 (C_q) ppm. HR-MS (ESI $^+$) m/z calculated for $[\text{C}_{21}\text{H}_{14}\text{ClNNa}]^+=[\text{M}+\text{Na}]^+$: 338.0707; found
9 338.0708.
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22 **Phenyl (*m*-tolyl)methanone (7ba):** GP-1 was carried out with aryl iodide **6b** (87.2 mg, 0.40 mmol),
23 aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
24 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
25 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **7ba** (43.4 mg, 54%) as a
26 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6b})=0.80$, $R_f(\mathbf{7ba})=0.40$,
27 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{max}=2999$, 1730, 1680, 1600, 1480, 1290, 1063, 944, 744
28 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.79$ (dd, 2H, $J=8.3$ and $J=1.4$ Hz), 7.62-7.56 (m, 3H), 7.47 (t, 2H, $J=7.5$
29 Hz), 7.41-7.33 (m, 2H), 2.41 (s, 3H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=21.3$ (CH_3), 127.3 (CH), 128.1
30 (CH), 128.2 (2 \times CH), 130.0 (2 \times CH), 130.4 (CH), 132.3 (CH), 133.2 (CH), 137.6 (C_q), 137.7 (C_q), 138.1 (C_q),
31 196.9 (C_q) ppm. HR-MS (ESI $^+$) m/z calculated for $[\text{C}_{14}\text{H}_{12}\text{O}]^+=[\text{M}+\text{Na}]^+$: 219.0780; found 219.0776.
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50 **(4-Methoxyphenyl)(phenyl)methanone (7da):**^{20a} GP-1 was carried out with aryl iodide **6d** (93.6 mg, 0.40
51 mmol), aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and
52 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
53 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **7da** (50.9 mg, 60%) as a
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3 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6d})=0.80$, $R_f(\mathbf{7da})=0.40$,
4 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2988$, 1723, 1677, 1599, 1452, 1278, 1083, 935, 715
5 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.82$ (d, 2H, $J=8.8$ Hz), 7.74 (dd, 2H, $J=7.5$ and $J=1.2$ Hz), 7.58-7.53 (m,
6 1H), 7.46 (t, 2H, $J=7.5$ Hz), 6.95 (d, 2H, $J=8.8$ Hz), 3.88 (s, 3H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=55.5$
7 (CH₃), 113.5 (2×CH), 128.2 (2×CH), 129.7 (2×CH), 130.1 (C_q), 131.9 (CH), 132.5 (2×CH), 138.3 (C_q), 163.2
8 (C_q), 195.6 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for $[\text{C}_{14}\text{H}_{13}\text{O}_2]^+=[\text{M}+\text{H}]^+$: 213.0910; found 213.0912.
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19 **(4-Methoxyphenyl)(p-tolyl)methanone (7db)**: GP-1 was carried out with aryl iodide **6d** (93.6 mg, 0.40
20 mmol), aldehyde **2b** (192.2 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol) and
21 TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
22 (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **7db** (57.9 mg, 64%) as a
23 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 93:07), $R_f(\mathbf{6d})=0.80$, $R_f(\mathbf{7db})=0.30$,
24 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2960$, 1722, 1674, 1599, 1451, 1287, 1087, 934, 720
25 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.80$ (d, 2H, $J=8.8$ Hz), 7.67 (d, 2H, $J=7.8$ Hz), 7.26 (d, 2H, $J=7.8$ Hz),
26 6.95 (d, 2H, $J=8.8$ Hz), 3.88 (s, 3H), 2.43 (s, 3H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=21.6$ (CH₃), 55.5 (CH₃),
27 113.5 (2×CH), 128.9 (d, 2×CH), 130.0 (2×CH), 130.5 (C_q), 132.4 (2×CH), 135.5 (C_q), 142.6 (C_q), 163.0 (C_q),
28 195.4 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for $[\text{C}_{15}\text{H}_{15}\text{O}_2]^+=[\text{M}+\text{H}]^+$: 227.1067; found 227.1058.
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46 **(3,4-Dimethoxyphenyl)(phenyl)methanone (7fa)**: GP-1 was carried out with aryl iodide **6f** (105.6 mg,
47 0.40 mmol), aldehyde **2a** (169.8 mg, 1.6 mmol), Pd(OAc)₂ (5.0 mg, 5 mol %), Ag₂O (111.3 mg, 0.48 mmol)
48 and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
49 (petroleum ether/ethyl acetate, 90:10 to 88:12) furnished the product **7fa** (64.9 mg, 67%) as a white
50 solid (m.p. 81-83 °C). [TLC control (petroleum ether/ethyl acetate 85:15), $R_f(\mathbf{6f})=0.95$, $R_f(\mathbf{7fa})=0.40$, UV
51 detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2954$, 1730, 1685, 1599, 1451, 1278, 1084, 934, 719 cm^{-1} .
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3 ^1H NMR (CDCl_3 , 400 MHz): δ = 7.73 (d, 2H, J =6.8 Hz), 7.53 (t, 1H, J =6.8 Hz), 7.47-7.43 (m, 3H), 7.35 (dd,
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5 1H, J =8.3 and J =1.9 Hz), 6.86 (d, 1H, J =8.3 Hz), 3.93 (s, 3H), 3.91 (s, 3H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz):
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7 δ =55.9 (CH_3), 56.0 (CH_3), 109.6 (CH), 112.0 (CH), 125.4 (CH), 128.1 (2 \times CH), 129.6 (2 \times CH), 130.1 (C_q),
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9 131.8 (CH), 138.1 (C_q), 148.9 (C_q), 152.9 (C_q), 195.5 (C_q) ppm. HR-MS (ESI^+) m/z calculated for
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11 $[\text{C}_{15}\text{H}_{15}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 243.1016; found 243.1018.
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17 **Benzo[d][1,3]dioxol-5-yl(phenyl)methanone (7ga)**: GP-1 was carried out with aryl iodide **6g** (99.2 mg,
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19 0.40 mmol), aldehyde **2a** (169.8 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol)
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21 and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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23 (petroleum ether/ethyl acetate, 93:07 to 90:10) furnished the product **7ga** (58.8 mg, 65%) as a
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25 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f(\mathbf{6g})=0.95$, $R_f(\mathbf{7ga})=0.40$,
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27 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2957$, 1721, 1675, 1598, 1452, 1278, 1084, 934, 716
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29 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ = 7.73-7.71 (m, 2H), 7.54 (t, 1H, J =7.3 Hz), 7.44 (t, 2H, J =7.3 Hz), 7.33-
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31 7.36 (m, 2H), 6.83 (d, 2H, J =8.3 Hz), 6.03 (s, 2H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =101.8 (CH_2), 107.7
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33 (CH), 109.8 (CH), 126.8 (CH), 128.1 (2 \times CH), 129.6 (2 \times CH), 131.8 (C_q), 131.9 (CH), 138.0 (C_q), 147.8 (C_q),
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35 151.4 (C_q), 195.0 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{14}\text{H}_{11}\text{O}_3]^+=[\text{M}+\text{H}]^+$: 227.0703; found
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37 227.0702.
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45 **Cyclohexyl(phenyl)methanone (8ae)**:^{20a} GP-1 was carried out with aryl iodide **6a** (81.6 mg, 0.40 mmol),
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47 aldehyde **4e** (179.5 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
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49 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
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51 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **8ae** (36.9 mg, 49%) as a
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53 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6a})=0.90$, $R_f(\mathbf{8ae})=0.50$,
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55 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=3366$, 2993, 1666, 1497, 1450, 1389, 1383, 1028,
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3 1025, 830, 760 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =7.94-7.92 (m, 2H), 7.55-7.51 (m, 1H), 7.45 (t, 2H, J =7.5
4 Hz), 3.25 (tt, 1H, J =11.7 and 3.4 Hz), 1.90–1.41 (m, 4H), 1.72 (d, 1H, J =11.2 Hz), 1.54-1.47 (m, 1H), 1.44-
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7 1.36 (m, 2H), 1.34-1.24 (m, 2H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =21.4 (CH_3), 25.8 ($2 \times \text{CH}_2$), 25.9
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9 (CH_2), 29.4 ($2 \times \text{CH}_2$), 45.6 (CH), 128.2 ($2 \times \text{CH}$), 128.5 ($2 \times \text{CH}$), 132.7 (CH), 136.3 (C_q), 203.9 (C_q) ppm. HR-
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11 MS (ESI^+) m/z calculated for $[\text{C}_{13}\text{H}_{17}\text{O}]^+=[\text{M}+\text{H}]^+$: 189.1274; found 189.1275.
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17 **1-(3-Methoxyphenyl)-2-methylpropan-1-one (8ea)**:^{20c} GP-1 was carried out with aryl iodide **6e** (93.6
18 mg, 0.40 mmol), aldehyde **4a** (115.4 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48
19 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column
20 chromatography (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **8ea** (32.1 mg,
21 45%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 93:07), $R_f(\mathbf{6e})=0.90$,
22 $R_f(\mathbf{8ea})=0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2923, 1605, 1487, 1440, 1385, 1303,$
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24 1088, 1014, 814, 738 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =7.52 (d, 1H, J =7.8 Hz), 7.48-7.47 (m, 1H), 7.35 (t,
25 1H, J =8.0 Hz), 7.10-7.01 (m, 1H), 3.84 (s, 3H), 3.52 (sep, 1H, J =6.8 Hz), 1.20 (d, 6H, J =6.8 Hz), ppm. ^{13}C
26
27 NMR (CDCl_3 , 100 MHz): δ =19.2 ($2 \times \text{CH}_3$), 35.5 (CH), 55.4 (CH_3), 112.7 (CH), 119.1 (CH), 120.8 (CH), 129.5
28 (CH), 137.6 (C_q), 159.9 (C_q), 204.3 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{11}\text{H}_{15}\text{O}_2]^+=[\text{M}+\text{H}]^+$:
29 179.1067; found 179.1064.
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45 **Cyclohexyl(*m*-tolyl)methanone (8be)**:^{20d} GP-1 was carried out with aryl iodide **6b** (87.2 mg, 0.40 mmol),
46 aldehyde **4e** (179.5 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP
47 (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography
48 (petroleum ether/ethyl acetate, 97:03 to 95:05) furnished the product **8be** (44.5 mg, 55%) as a
49 colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6b})=0.90$, $R_f(\mathbf{8be})=0.50$,
50 UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2924, 1615, 1488, 1441, 1390, 1305, 1078, 1024, 818,$
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3 739 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): δ =7.74-7.72 (m, 2H, Ar-H), 7.34-7.32 (m, 2H), 3.24 (tt, 1H, J =11.7
4 and 3.4 Hz), 2.40 (s, 3H), 1.89–1.81 (m, 4H), 1.75-1.71 (m, 1H), 1.53-1.21 (m, 5H), ppm. ^{13}C NMR (CDCl_3 ,
5 100 MHz): δ =21.4 (CH_3), 25.8 ($2 \times \text{CH}_2$), 25.9 (CH_2), 29.4 ($2 \times \text{CH}_2$), 45.4 (CH), 125.4 (CH), 128.4 (CH),
6 128.7 (CH), 133.5 (CH), 136.4 (C_q), 138.3 (C_q), 204.2 (C_q) ppm. HR-MS (ESI^+) m/z calculated for
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$[\text{C}_{14}\text{H}_{19}\text{O}]^+=[\text{M}+\text{H}]^+$: 203.1430; found 203.1428.

Cyclohexyl(3-methoxyphenyl)methanone (8ee):^{20e} GP-1 was carried out with aryl iodide **6e** (93.6 mg, 0.40 mmol), aldehyde **4e** (179.5 mg, 1.6 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg, 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 95:05 to 93:07) furnished the product **8ee** (52.3 mg, 60%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 95:05), $R_f(\mathbf{6e})=0.90$, $R_f(\mathbf{8ee})=0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2933, 1689, 1482, 1443, 1388, 1301, 1080, 1013, 818, 737 \text{ cm}^{-1}$. ^1H NMR (CDCl_3 , 400 MHz): δ =7.74-7.72 (m, 2H), 7.34-7.32 (m, 2H), 3.24 (tt, 1H, J =11.7 and 3.4 Hz), 2.40 (s, 3H), 1.89–1.81 (m, 4H), 1.75-1.71 (m, 1H), 1.53-1.21 (m, 5H) ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ =21.4 (CH_3), 25.8 ($2 \times \text{CH}_2$), 25.9 (CH_2), 29.4 ($2 \times \text{CH}_2$), 45.4 (CH), 125.4 (CH), 128.4 (CH), 128.7 (CH), 133.5 (CH), 136.4 (C_q), 138.3 (C_q), 204.2 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{14}\text{H}_{19}\text{O}]^+=[\text{M}+\text{H}]^+$: 203.1430; found 203.1428.

7ha^{20h}, **7ia**^{20f}, **7ja**^{20e}, **8hc**^{20g} reported in literature.

3-Phenylisobenzofuran-1(3H)-one (9ba):^{20f} GP-2 was carried out with keto ester **3ba** (127.1 mg, 0.50 mmol), NaBH_4 (38 mg, 1.0 mmol), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (186.3 mg, 0.50 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 85:15 to 80:20) furnished the product **9ba** (146.0 mg, 95%) as a white coloured solid (m.p: 107-109 $^\circ\text{C}$). [TLC control (petroleum ether/ethyl acetate 80:20), $R_f(\mathbf{3ba})=0.90$, $R_f(\mathbf{9ba})=0.40$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2960, 1730, 1685, 1599, 1460, 1287, 1093, 943, 716 \text{ cm}^{-1}$. ^1H NMR (CDCl_3 , 400 MHz): δ =7.97 (d, 1H,

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$J=7.3$ Hz), 7.65 (t, 1H, $J=7.5$ Hz), 7.55 (t, 1H, $J=7.5$ Hz), 7.39-7.36 (m, 3H), 7.34 (d, 1H, $J=6.8$ Hz), 7.27 (dd, 2H, $J=6.8$ and $J=2.9$ Hz), 6.41 (s, 1H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=83.0$ (CH), 123.1 (CH), 125.8 (C_q), 125.9 (CH), 127.3 (2 \times CH), 129.3 (2 \times CH), 129.6 (CH), 129.6 (CH), 134.6 (CH), 136.7 (C_q), 150.0 (C_q), 170.8 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{14}\text{H}_{11}\text{O}_2]^+=[\text{M}+\text{H}]^+$: 211.0754; found 211.0760.

3-Butylisobenzofuran-1(3H)-one (9bd): GP-2 was carried out with keto ester **5bd** (117.1 mg, 0.50 mmol), NaBH_4 (38 mg, 1.0 mmol), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (186.3 mg, 0.50 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10 to 85:15) furnished the product **9bd** (112.5 mg, 78%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f(\mathbf{5bd})=0.90$, $R_f(\mathbf{9bd})=0.35$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2970$, 1740, 1685, 1602, 1460, 1287, 1093, 946, 752 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.87$ (d, 1H, $J=7.8$ Hz), 7.65 (td, 1H, $J=7.5$ and $J=0.9$ Hz), 7.50 (t, 1H, $J=7.5$ Hz), 7.43-7.41 (m, 1H), 5.46 (dd, 1H, $J=7.8$ and $J=3.9$ Hz), 2.07-1.99 (m, 1H), 1.78-1.70 (m, 1H), 1.50-1.32 (m, 4H), 0.89 (t, 1H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): $\delta=13.8$ (CH_3), 22.4 (CH_2), 26.8 (CH_2), 34.4 (CH_2), 81.4 (CH), 121.7 (CH), 125.7 (CH), 126.1 (C_q), 129.0 (CH), 133.9 (CH), 150.1 (C_q), 170.7 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{12}\text{H}_{15}\text{O}_2]^+=[\text{M}+\text{H}]^+$: 191.1067; found 191.1073.

3-Cyclohexylisobenzofuran-1(3H)-one (9be): GP-2 was carried out with keto ester **5be** (130.2 mg, 0.50 mmol), NaBH_4 (38 mg, 1.0 mmol), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (186.3 mg, 0.50 mmol). Purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 90:10 to 85:15) furnished the product **9be** (134.8 mg, 86%) as a colourless viscous liquid. [TLC control (petroleum ether/ethyl acetate 90:10), $R_f(\mathbf{5be})=0.90$, $R_f(\mathbf{9be})=0.35$, UV detection]. IR (MIR-ATR, 4000–600 cm^{-1}): $\nu_{\text{max}}=2957$, 1735, 1695, 1588, 1440, 1227, 1083, 953, 723 cm^{-1} . ^1H NMR (CDCl_3 , 400 MHz): $\delta=7.85$ (d, 1H, $J=7.3$ Hz), 7.65-7.65 (m, 1H), 7.48 (t, 1H, $J=7.5$ Hz), 7.42 (d, 1H, $J=8.3$ Hz), 5.30 (d, 1H, $J=3.9$ Hz), 1.93-1.75 (m, 3H), 1.68-1.62 (m,

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3 2H), 1.04-1.31 (m, 6H), ppm. ^{13}C NMR (CDCl_3 , 100 MHz): δ = 25.7 (CH_2), 25.9 (CH_2), 25.9 (CH_2), 26.1 (CH_2),
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5 29.1 (CH_2), 42.0 (CH), 85.3 (CH), 122.1 (CH), 125.5 (CH), 126.5 (C_q), 128.9 (CH), 133.7 (CH), 148.7 (C_q),
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7 170.7 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{14}\text{H}_{17}\text{O}_2]^+=[\text{M}+\text{H}]^+$: 217.1223; found 217.1223.
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12 **Pitofenone (10ap)**:¹³ To an oven dried Schlenk tube, were added keto ester **3ap** (30.0 mg, 0.08 mmol),
13 piperidine (21.1 mg, 0.24 mmol) and K_2CO_3 (33.8 mg, 0.24 mmol) in DMF. The resulting reaction mixture
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15 was stirred 50 °C for 1 h. The reaction mixture was allowed to cool to room temperature, diluted with
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17 H_2O and then extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated
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19 NaCl solution, dried (Na_2SO_4) and filtered. Evaporation of the solvent under reduced pressure and
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21 purification of the crude material by silica-gel column chromatography (petroleum ether/ethyl acetate,
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23 30:70 to 20:80) furnished the product **10ap** (25.0 mg, 82%) as a colourless viscous liquid. [TLC control
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25 (petroleum ether/ethyl acetate 00:100), $R_f(\mathbf{3ap})=0.99$, $R_f(\mathbf{10ap})=0.20$, UV detection]. IR (MIR-ATR, 4000–
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27 600 cm^{-1}): $\nu_{\text{max}}=2960$, 2912, 1722, 1685, 1566, 1455, 1255, 1060, 944, 718 cm^{-1} . ^1H NMR (CDCl_3 , 400
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29 MHz=8.02 (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 7.69 (d, 2H, , $J=9.2$ Hz), 7.60 (td, 1H, $J=7.3$ and $J=1.4$ Hz), 7.53 (td,
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31 1H, $J=7.3$ and $J=1.4$ Hz), 7.36 (dd, 1H, $J=7.8$ and $J=0.9$ Hz), 6.89 (d, 2H, , $J=9.2$ Hz), 4.13 (t, 2H, $J=6.1$ Hz),
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33 3.62 (s, 1H), 2.76 (t, 2H, $J=6.1$ Hz), 2.49 (brs, 4H), 1.61-1.56 (m, 4H), 1.45-1.41 (m, 2H) ppm. ^{13}C NMR
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35 (CDCl_3 , 100 MHz): δ =24.1 (CH_2), 25.9 (2× CH_2), 52.2 (CH_3), 55.0 (2× CH_2), 57.7 (CH_2), 66.2 (CH_2), 114.3
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37 (2×CH), 127.6(CH), 129.0 (C_q), 129.3 (CH), 130.1 (CH), 130.2 (C_q), 131.6 (2×CH), 132.3 (CH), 142.0 (C_q),
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39 162.8 (C_q), 166.4 (C_q), 195.8 (C_q) ppm. HR-MS (ESI^+) m/z calculated for $[\text{C}_{22}\text{H}_{26}\text{NO}_4]^+=[\text{M}+\text{H}]^+$: 368.1856;
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41 found 368.1861.
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52 **2,2,6,6-Tetramethylpiperidin-1-yl benzoate (11a)**:^{14b} To an oven dried Schlenk tube, were added **1a**
53 (100 mg, 1.0 mmol), aldehyde **2a** (169.8 mg, 1.6 mmol), TEMPO (312.5 mg, 2.0 mmol), $\text{Pd}(\text{OAc})_2$ (5.0 mg,
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55 5 mol %), Ag_2O (111.3 mg, 0.48 mmol) and TBHP (257.1 mg, 2.0 mmol). The resulting reaction mixture
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3 was stirred at 120 °C for 12 h. Progress of the reaction was monitored by TLC till the reaction was
4 completed. The reaction mixture was quenched by the addition of aqueous NaHCO₃ solution and then
5 extracted with ethyl acetate (3 × 15 mL). The organic layers were washed with saturated NaCl solution,
6 dried (Na₂SO₄) and filtered. Evaporation of the solvent under reduced pressure and purification of the
7 crude material by silica-gel column chromatography (petroleum ether/ethyl acetate, 55:45 to 50:50)
8 first furnished the simple de-iodinated ester (8.3 mg, 15%) as colourless viscous liquid and then gave the
9 product **11a** (397.1 mg, 95 %) as white solid. [TLC control (petroleum ether/ethyl acetate 50:50),
10 $R_f(\mathbf{2a})=0.99$, $R_f(\mathbf{11a})=0.50$, UV detection]. IR (MIR-ATR, 4000–600 cm⁻¹): $\nu_{max}=3422$, 2943, 1635, 1497,
11 1450, 1395, 1373, 1098, 1024, 824, 748 cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): $\delta=8.10$ (d, 2H, $J=7.3$ Hz), 7.59 (d,
12 1H, $J=7.0$ Hz), 7.48 (t, 2H, $J=7.3$ Hz), 1.84–1.59 (m, 5H), 1.44–1.50 (m, 1H), 1.30 (s, 3H), 1.14 (s, 3H),
13 ppm. ¹³C NMR (CDCl₃, 100 MHz): $\delta=16.3$ (CH₂), 21.0 (2 × CH₃), 31.3 (2 × CH₃), 38.4 (2 × CH₂), 59.7 (2C_q),
14 127.8 (2×CH), 128.9 (2×CH), 129.0 (C_q), 132.2 (CH), 165.7 (C_q) ppm. HR-MS (ESI⁺) m/z calculated for
15 [C₁₆H₂₃NNaO₂]⁺=[M+Na]⁺: 284.1621; found 284.1624.
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33 ASSOCIATED CONTENT

34 Supporting Information

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39 Copies of ¹H-NMR and ¹³C-NMR spectra of all compounds and CIF file for **3ah** are provided. This
40 material is available free of charge via the Internet at <http://pubs.acs.org>.
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