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One-Pot Synthesis of Diarylmethanones through Palladium-Catalyzed Sequential Coupling and Aerobic Oxidation of Aryl Bromides with Acetophenone as a Latent Carbonyl Donor

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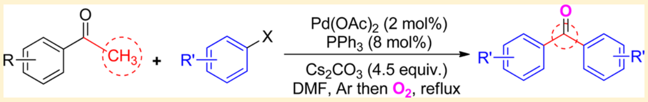
Supporting Information

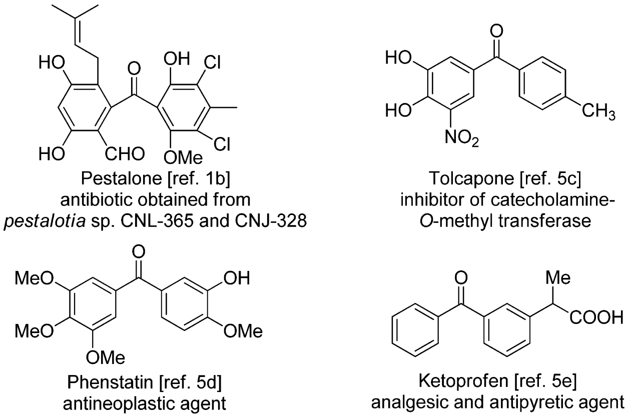
ABSTRACT: A one-pot palladium-catalyzed synthesis of symmetrical and unsymmetrical diarylmethanones using acetophenone and aryl bromides as raw materials has been developed. In this reaction, acetophenone acts as a latent carbonyl donor and two pathways of palladium-catalyzed sequential coupling and aerobic oxidation are identified. The reaction is applicable to a spectrum of substrates and delivers the products in moderate to good yields. This method can be used for the synthesis of ketoprofen, a nonsteroidal anti-inflammatory drug, in a two-step procedure and 45% overall yield.



INTRODUCTION

Diarylmethanones constitute a common structural motif that is found not only in natural products[1] but also in organic materials,[2] functional molecules,[3] and synthetic intermediates,[4] as well as compounds of biological and pharmaceutical importance[5] (a few examples are shown in Scheme 1).

Scheme 1. Bioactive Compounds with the Diarylmethanone Motif



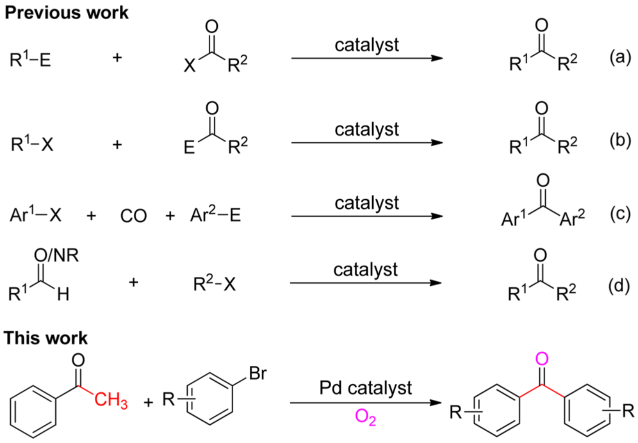
Pestalone [ref. 1b]
antibiotic obtained from
pestalotia sp. CNL-365 and CNJ-328

Tolcapone [ref. 5c]
inhibitor of catecholamine-*O*-methyl transferase

Phenstatin [ref. 5d]
antineoplastic agent

Ketoprofen [ref. 5e]
analgesic and antipyretic agent

Scheme 2. Catalyzed Couplings to Diarylmethanones and the Method Developed Herein



Developing various approaches to diarylmethanones is of great interest, and up to now numerous methods have been described (Scheme 2). Traditionally, diarylmethanones can be accessed by Friedel–Crafts acylation of aryl cycles with acid halide or acid anhydride[6] or by oxidizing the methylene group of diarylmethanes using oxidizing reagents, such as $KMnO_4$,[7] SeO_2,[8] CrO_3–SiO_2,[9] and *t*BuOOH.[10] Although these methods are efficient, they are not without their limitations. For example, the former tends to form highly toxic and corrosive waste in acylation and is limited by the narrow scope of substrates, whereas the latter needs harsh oxidation conditions and isolation of the products is usually difficult. In recent years, cross-coupling reactions using the catalysis of transition metals, especially palladium, have been developed, including direct C–C cross-coupling of organometallic reagents with electrophilic acid derivatives[11] (Scheme 2, reaction a) and polarity reversed acyl anion equivalents with electrophiles[12] (Scheme 2, reaction b), as well as the carbonylative cross-coupling reaction of aryl halides with organometallic reagents in the presence of carbon monoxide[13] (Scheme 2, reaction c). The problematic issues associated with these methods are the necessarily strict anhydrous conditions and the difficulty in the preparation of organometallic reagents in some cases. Therefore, some alternative approaches involving transition-metal-catalyzed reactions of aryl halide with aldehydes[14] or their derivatives

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such as *N*-pyrazyl aldimines[15] and *N-tert*-butyl hydrazones[16] (Scheme 2, reaction d) have been reported.

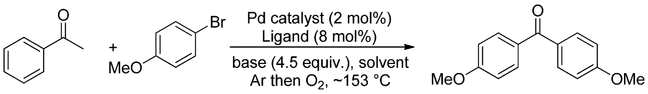
In our previous work, we reported a novel palladium-catalyzed coupling reaction of acetophenone with aryl halides to yield symmetric and unsymmetrical diarylmethanes, in which acetophenone acts as a formal methylene donor.[17] We envisioned that if the reaction was carried out in the presence of oxygen, diarylmethanones might be produced. Fortunately, we detected the generation of trace amounts of diarylmethanones in the synthesis of diarylmethanes in some cases, suggesting this possibility. This postulated method should be a straightforward approach to the synthesis of diarylmethanones with acetophenone as a latent carbonyl donor, and it has not been reported up to now to the best of our knowledge.

In this paper, we report this unprecedented one-pot synthesis of diarylmethanones using acetophenone as a latent carbonyl donor through palladium-catalyzed sequential coupling and aerobic oxidation. The investigation begins with screening for the optimal reaction conditions using the model reaction of acetophenone with 4-bromoanisole to give bis(4-methoxyphenyl)methanone, followed by substrate scope expansion. Under the optimal reaction conditions, access to ketoprofen, a nonsteroidal anti-inflammatory drug whose structure is shown in the lower right in Scheme 1, is performed in a two-step procedure. In addition, control reactions are provided for offering insight into the mechanism, which is illustrated to involve two pathways of palladium-catalyzed sequential coupling and aerobic oxidation.

RESULTS AND DISCUSSION

Initially, we evaluated the feasibility of this reaction by using a model reaction of acetophenone with 4-bromoanisole in the presence of 2 mol % of $Pd(OAc)_2$, 8 mol % of PPh_3, and 2.5 equiv of Cs_2CO_3 in untreated DMF at 153 °C. The reaction was allowed to proceed for 1.5 h under argon and then changed to an oxygen atmosphere for another 3 h. To our delight, the desired product was obtained in 56% yield. Meanwhile, two byproducts, 4,4′-dimethoxybiphenyl and 4-methoxybenzophenone, were identified. The former is likely formed through homocoupling in the palladium-catalyzed system,[18] whereas the latter may be formed via a complex heterocoupling/oxidation process that needs further investigation. Interestingly, the formation of the latter compound could be suppressed by adjusting the time point for the change from an argon to an oxygen atmosphere. For example, when the reaction was allowed to proceed for 1, 3, or 5 h under argon and then the atmosphere was changed to oxygen, the yields of the byproduct 4-methoxybenzophenone were 13%, 3%, and 6%, respectively, whereas the yields of the target product bis(4-methoxyphenyl)methanone were 49%, 69%, and 42%, respectively (Supporting Information, Table S1).

Table 1. Optimization of the Conditions[a]



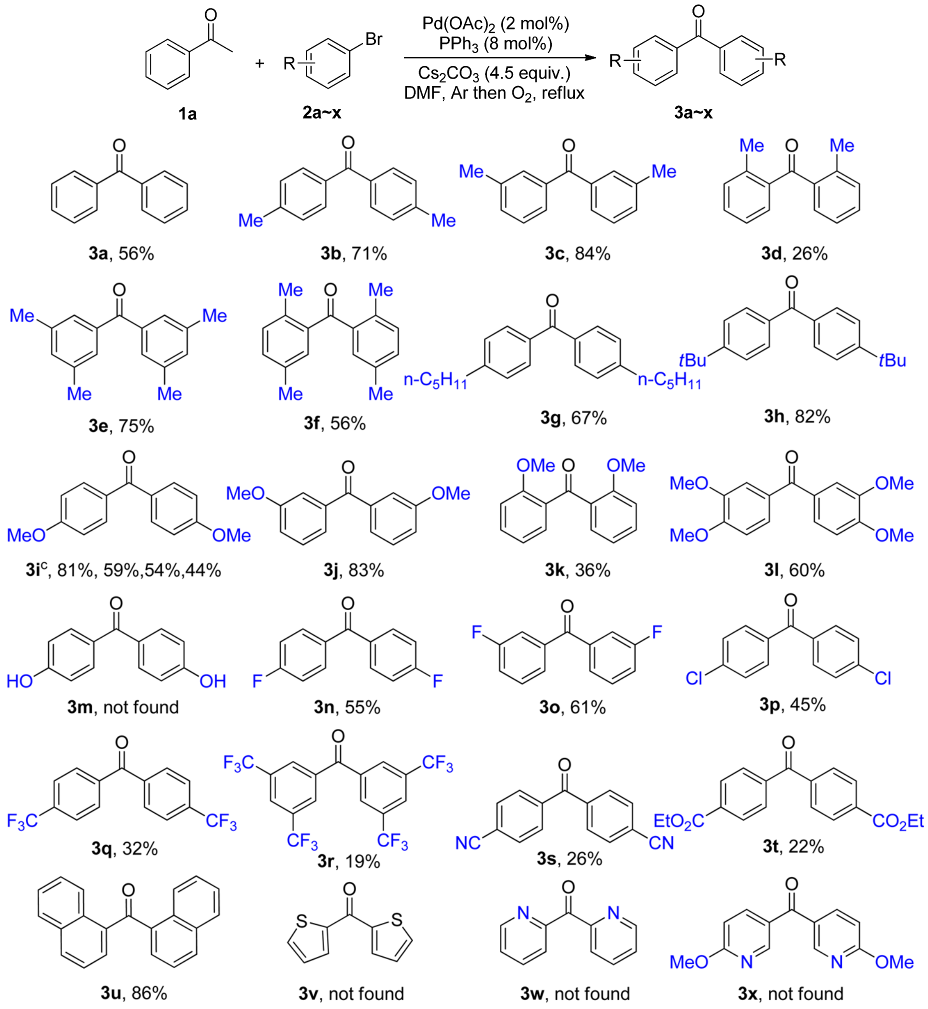
entry	catalyst	ligand	base[b]	solvent	yield (%)[c]
1	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	69
2	$PdCl_2$	PPh_3	Cs_2CO_3	DMF	36
3	$Pd(dba)_2$	PPh_3	Cs_2CO_3	DMF	33
4	$Pd_2(dba)_3$	PPh_3	Cs_2CO_3	DMF	22
5	BrettPhos palladacycle	PPh_3	Cs_2CO_3	DMF	47
6	RuPhos palladacycle	PPh_3	Cs_2CO_3	DMF	42
7	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	DMF	81 (47)[d]
8[e]	$Pd(OAc)_2$	L1	Cs_2CO_3	DMF	72
9	$Pd(OAc)_2$	Brettphos	Cs_2CO_3	DMF	50
10	$Pd(OAc)_2$	Xantphos	Cs_2CO_3	DMF	56
11	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	THF/DMSO/1,4-dioxane	0
12[f]	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	H_2O	0
13	$Pd(OAc)_2$	PPh_3	Cs_2CO_3	toluene	19
14	$Pd(OAc)_2$	PPh_3	K_2CO_3	DMF	56
15	$Pd(OAc)_2$	PPh_3	$K_3PO_4\cdot 3H_2O$	DMF	33
16	$Pd(OAc)_2$	PPh_3	KOH/KO*t*Bu	DMF	0

[a]Reactions were conducted with acetophenone (1.5 mmol) and 4-bromoanisole (3.0 mmol) in solvent (10 mL) at 153 °C under argon for 3 h, and then the atmosphere was changed to oxygen for another 3 h. [b]2.5 equiv of Cs_2CO_3 was used (entries 1−6). [c]Yield of isolated product. [d]Using anhydrous DMF as solvent. [e]Dicyclohexyl (2-mesityl-1*H*-inden-1-yl)phosphane was used as the ligand. [f]TBAB (5 mol %) was added.

On the basis of the above facts, we optimized the reaction conditions for the model reaction, and selected results are shown in Table 1. First, the ratios and loading amounts of $Pd(OAc)_2$ and PPh_3 were altered; the yield of the target product was significantly affected (Supporting Information, Table S2). It was found that the combination of 2 mol % of $Pd(OAc)_2$ and 8 mol % of PPh_3 could give bis(4-methoxyphenyl)methanone in 69% yield (Table 1, entry 1). However, a 1:2 molar ratio of $Pd(OAc)_2$ and PPh_3 promoted the formation of the homocoupling product 4,4′-dimethoxybiphenyl, likely via a peroxo complex $(\eta^2\text{-}O_2)Pd(PPh_3)_2$ intermediate as reported by Jutand.[19] In comparison to the $Pd(OAc)_2$ catalyst, other catalyst precursors, such as $PdCl_2$, $Pd_2(dba)_3$ (dba = dibenzylideneacetone), and palladacycles, gave the yields of the desired product down to 22−47% (Table 1, entries 2−6). When 4.5 equiv of Cs_2CO_3 was used, the yield was increased to 81% (Table 1, entry 7). Moreover, when PPh_3 was replaced with dicyclohexyl(2-mesityl-1*H*-inden-1-yl)phosphane (L1),[20] Brettphos, or Xantphos as the ligand, the yields were somewhat decreased (Table 1, entries 8−10). The choice of solvent for this reaction seems to be a critical factor. For example, if THF, DMSO, H_2O, or 1,4-dioxane was used, no product was observed (Table 1, entries 11 and 12), and toluene as the solvent resulted in a decreased yield of 19% (Table 1, entry 13). Interestingly, anhydrous DMF resulted in 47% yield, lower than the yield of 81% obtained in untreated DMF (Table 1, entry 7), suggesting the presence of trace water has an important role in this reaction. On the other hand, moderately strong bases, such as K_2CO_3 and $K_3PO_4\cdot 3H_2O$, resulted in moderate yields (Table 1, entries 14 and 15). However, strong bases, such as KOH and KO*t*Bu, shut down the reaction completely (Table 1, entry 16). Therefore, the optimal reaction conditions for the synthesis of diarylmethanones involves the use of untreated DMF as the solvent in the presence of $Pd(OAc)_2$ (2 mol %), PPh_3 (8 mol %), and Cs_2CO_3 (2.5 equiv) under reflux (ca. 153 °C) with argon protection for 3 h followed by a change to an oxygen atmosphere.

With the optimal conditions in hand, we continued to evaluate the substrate scope of this method for the synthesis of various symmetrical diarylmethanones. Different aryl bromides

Table 2. Substrate Scope for the Synthesis of Symmetrical Diarylmethanones[a,b]

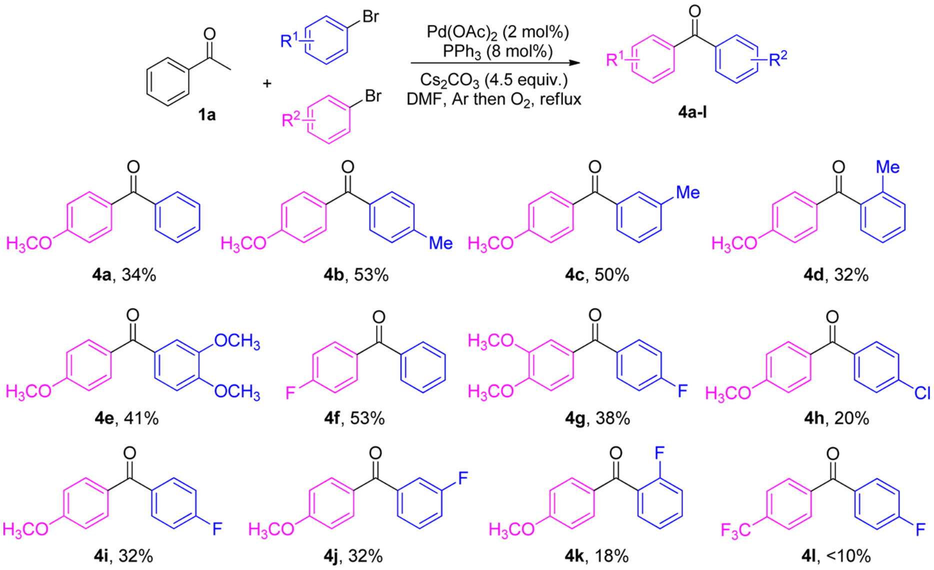


1a + **2a~x** → **3a~x**

3a, 56%
3b, 71%
3c, 84%
3d, 26%
3e, 75%
3f, 56%
3g, 67%
3h, 82%
3i[c], 81%, 59%,54%,44%
3j, 83%
3k, 36%
3l, 60%
3m, not found
3n, 55%
3o, 61%
3p, 45%
3q, 32%
3r, 19%
3s, 26%
3t, 22%
3u, 86%
3v, not found
3w, not found
3x, not found

[a] Conditions: acetophenone (1.5 mmol) and aryl bromide (3.0 mmol) under the optimal conditions except for **3n,o,q–t**, which were obtained by using 5 mol % of Pd(OAc)$_2$, 20 mol % of PPh$_3$ and 5.09 mmol of aryl bromide. [b] Yields of isolated products. [c] Yields in the cases of acetophenone, 4-fluoroacetophenone, 4-methoxyacetophenone, and 3-acetylpyridine used as the formal carbonyl donors, respectively.

Table 3. Cross-Coupling and Aerobic Oxidation for the Synthesis of Unsymmetrical Diarylmethanones[a]

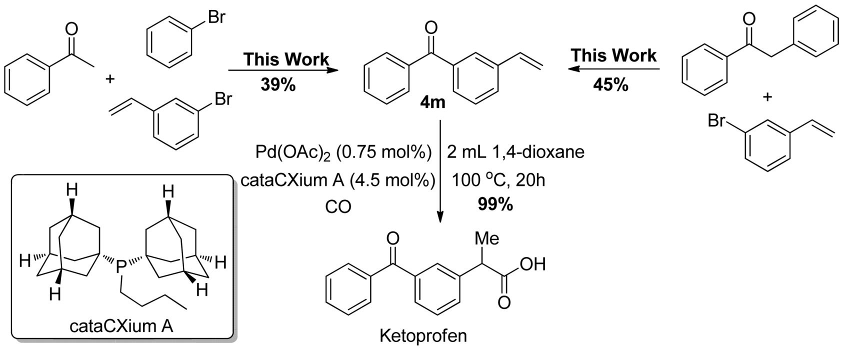


1a → **4a-l**

4a, 34%
4b, 53%
4c, 50%
4d, 32%
4e, 41%
4f, 53%
4g, 38%
4h, 20%
4i, 32%
4j, 32%
4k, 18%
4l, <10%

[a] Conditions: acetophenone (1.5 mmol) and aryl bromides (1.5 mmol) under the optimal conditions; Yields of isolated products.

Scheme 3. Synthetic Application of This Methodology to the Preparation of Ketoprofen



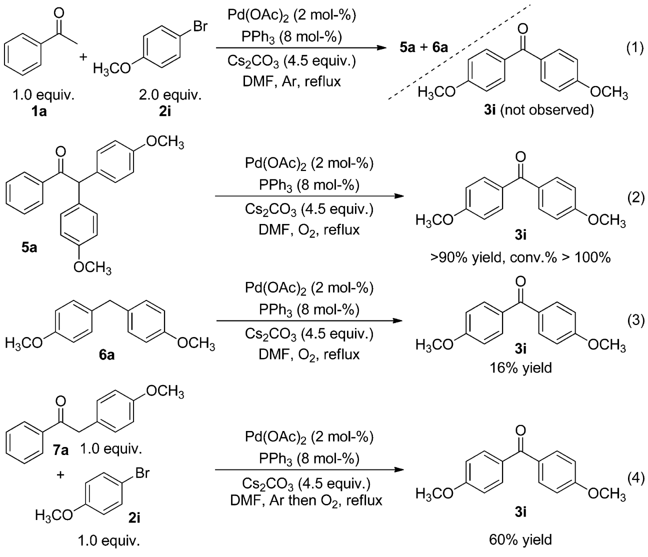
were subjected to react with acetophenone using the catalytic system, and the results are summarized in Table 2. The nature of the substituent of aryl halide has a pronounced influence on the yield, and generally the electron-donating substituents (**3b−l**) resulted in higher yields than the electron-withdrawing substituents (**3n−t**). This phenomenon can be attributed to the fact that aryl halides with electron-withdrawing groups are prone to undergo homocoupling to diaryl byproducts and decrease the rates of transmetalation and reductive elimination.[18b,21] For examples, aryl bromides bearing electron-withdrawing trifluoromethyl (**3q**), 3,5-bis(trifluoromethyl) (**3r**), cyano (**3s**), and ester groups (**3t**) led to low yields. Meanwhile, aryl bromides with hydroxyl (**3m**) and dimethylamino groups (data not shown) did not give any desired products, possibly due to the disturbance of the oxidative addition of aryl bromides to the palladium catalyst.[22] The presence of a meta or ortho substituent has little effect on the yields (**3c**,**d**,**f**,**j**,**k**,**o**). In addition, 1-bromonaphthalene produced bis(naphthalen-1-yl)methanone (**3u**) in 86% yield. It is worth noting that the reaction tolerates several functional groups, such as trifluoromethyl, cyano, and ester groups. However, the heteroaryl bromides could not deliver the desired bis(heteroaryl)methanones (**3v**,**w**,**x**), and instead, the homocoupled bis(heteroaryls) were obtained (Supporting Information, Scheme S1). Interestingly, other aryl methyl ketones, such as 4-fluoroacetophenone, 4-methoxyacetophenone, and 3-acetylpyridine, were also able to act as latent carbonyl donors in the coupling with 4-bromoanisole and gave the same desired bis(4-methoxyphenyl)methanone product in moderate yields (**3i**).

Further investigation of the efficiency of this method was performed for the synthesis of unsymmetrical diarylmethanones, and the results are shown in Table 3. Using acetophenone as the latent carbonyl donor, the reaction could be carried out for the cross couplings between various aryl bromides bearing a neutral, electron-donating, or electron-withdrawing group. For examples, the coupling between the pairs of bromobenzene and 4-bromoanisole (**4a**) or 4-fluorobromobenzene (**4f**), 4-bromoanisole and *p*-, *m*-, or *o*-bromotoluene (**4b−d**) or 3,4-dimethoxybromobenzene (**4e**), 4-bromoanisole and 4-chlorobromobenzene (**4h**) or *p*-, *m*- or *o*-fluorobromobenzene (**4i−k**), as well as the pair of 3,4-dimethoxybromobenzene and 4-fluorobromobenzene (**4g**), delivered the unsymmetrical diarylmethanones with good selectivity and moderate to low yields. Nevertheless, for the cross-coupling pair between aryl bromides that both bear an electron-withdrawing substituent, such as 4-fluorobromobenzene and 4-trifluoromethylbromobenzene, only a trace amount of the desired product was observed (**4l**). In these cross-coupling reactions, homocoupling products were also found. For example, acetophenone reacted with 4-bromoanisole and 4-fluorobromobenzene produced three products: bis(4-fluorophenyl)methanone (**3n**), (4-fluorophenyl)(4-methoxyphenyl)methanone (**4i**), and bis(4-methoxyphenyl)methanone (**3i**) in a ratio of 1:3.0:1.5 with the unsymmetrical product (**4i**) in 32% yield, showing some selectivity. Additionally, the three products from the cross-coupling synthesis of each of the desired compounds **4e**,**g**,**h** were also obtained, and their corresponding yield ratios are 2.1:3.2:1.0, 0.45:2.9:1.0, and 0.9:1.2:1.0, respectively. Detailed information is given in the Supporting Information (Scheme S2).

Ketoprofen, a potent nonsteroidal anti-inflammatory drug with the diarylmethanone motif, has been used as an analgesic and antipyretic agent as well as for the treatment of rheumatoid arthritis, osteoarthritis, and ankylosing spondylitis all over the world.[23] There are different routes for the industrial synthesis of ketoprofen that vary in the raw materials; generally at least four steps are involved.[5e,24] On the basis of the method developed in this work, the synthesis of ketoprofen was able to be accomplished by using two routes: one used acetophenone to couple with bromobenzene and 3-bromostyrene, followed by carbonylation[25] in 39% yield; the other used 1,2-diphenylethanone to couple with 3-bromostyrene, followed by the same carbonylation in 45% yield (Scheme 3). The second route will be discussed below. The two routes are convenient and possibly valuable because the syntheses can be performed in only two steps with readily available starting materials (cataCXium A in the second step is a commercial material having the structure shown in Scheme 3).

To gain insight into the reaction mechanism, a series of control experiments were carried out. As previously described, upon the treatment of acetophenone with 4-bromoanisole (**2i**) under the optimal conditions, the desired product bis(4-methoxyphenyl)methanone (**3i**) was obtained in 81% yield. However, if the reaction was carried out under an argon atmosphere for the entire time, no desired product but triarylethanone **5a** and diarylmethane **6a** were observed (Scheme 4, eq 1), indicating the necessity of oxygen for the reaction. **3i** was also obtained in high yield when the triarylethanone **5a** was subjected to the same conditions (Scheme 4, eq 2), even under conditions without the palladium catalyst, suggesting that **5a** was one possible intermediate. On the other hand, diarylmethane **6a** could be transformed to **3i** in only 16% yield (Scheme 4, eq 3). Interestingly, if the diarylethanone **7a** was used to couple with **2i** under the optimal conditions, **3i** was obtained in 60% yield (Scheme 4, eq

Scheme 4. Control Reactions for Exploring the Mechanism



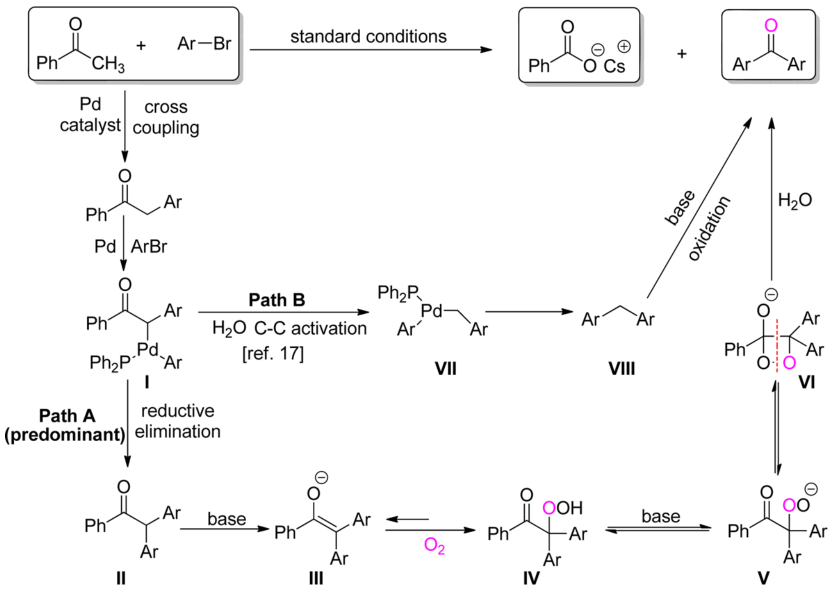
4). In particular, diarylethanones can be used for the synthesis of unsymmetrical diarylmethanones. For example, when 1,2-diphenylethanone was subjected to reaction with 4-bromoanisole or 4-fluorobromobenzene, the unsymmetrical diarylmethanone products (4-methoxyphenyl)phenylmethanone (**4a**) and (4-fluorophenyl)phenylmethanone (**4f**), were obtained in yields of 41% and 60%, respectively. Therefore, there are three possible intermediates involved in our developed method: triarylethanone **5a**, diarylmethane **6a**, and diarylethanone **7a**.

On the basis of the above experimental facts, a proposed mechanism involving a palladium-catalyzed sequential coupling and aerobic oxidation process can be outlined as shown in Scheme 5. First, the α-arylation of acetophenone **1a** with aryl bromide in the presence of palladium catalyst gives diarylethanone, which undergoes enolization and then reacts with the complex ArPd(PPh$_3$)$_2$Br to produce intermediate **I**, as elucidated in ref 26. Next, two possible competitive pathways may be present. In the first one (namely the triarylethanone pathway; Scheme 5, path A), intermediate **I** undergoes reductive elimination to form intermediate **II**, followed by enolization and then auto-oxidization to generate the α-ketohydroperoxide intermediate **IV**. The intermediate **IV** cyclizes with the neighboring carbonyl group to give the 1,2-dioxetane intermediate **VI** in the presence of base through the attack of the peroxide anion at the neighboing carbonyl group and then decomposes to give the desired diarylmethanone, concomitant with the production of cesium benzoate, which was separated and identified by ^{1}H NMR. The transformation from intermediate **II** to the target product diarylmethanone in this pathway has been well documented.[27] In the second pathway (namely the diarylmethane pathway; Scheme 5, path B), intermediate **I** may transform to intermediate **VII** via an α-cleavage reaction in the presence of trace H_2O in untreated DMF, followed by reductive elimination to afford intermediate **VIII**, which is oxidized to generate the final product via aerobic oxidation.[28] The transformation from intermediate **I** to **VIII** has been detailed in our previous work, and the presence of trace water is indispensable.[17] It is now clear that the change from an argon to an oxygen atmosphere is crucial and it should be carried out in the time after the sequential two-step coupling in path A as well as in path B. In addition, path A is dominant over path B because the intermediate **II** as the starting material gives diarylmethanone in high yield (Scheme 4, eq 2), whereas the intermediate **VIII** as the starting material affords diarylmethanone in low yield (Scheme 4, eq 3) in the control reactions.

■ CONCLUSIONS

In this work, we developed an unprecedented one-pot approach to the synthesis of a variety of symmetrical and unsymmetrical diarylmethanones from readily available aryl bromides. The synthesis can be performed through palladium-catalyzed sequential coupling and aerobic oxidation with molecular oxygen. In comparison to the reported methods, this protocol circumvents the need for the tedious preparation of organometallic reagents. One case of application in the synthesis of

Scheme 5. Proposed Reaction Mechanism



ketoprofen in a two-step fashion demonstrates the feasibility of this method. Control reactions using possible intermediates and the requirements of trace water and a change from an argon to an oxygen atmosphere as conditions form a firm base for us to outline the plausible reaction mechanism in detail, in which acetophenone acts as a latent carbonyl donor in the reaction. Therefore, the triarylethanone and diarylmethane pathways in the mechanism are identified, and the former is dominant.

■ EXPERIMENTAL SECTION

General Experimental Procedure for the Synthesis of Symmetrical and Unsymmetrical Diarylmethanones. DMF (10 mL) was added to a Schlenk tube charged with Cs_2CO_3 (2.20 g, 6.75 mmol), PPh_3 (31.44 mg, 0.12 mmol), $Pd(OAc)_2$ (6.73 mg, 0.03 mmol), ketone (1.5 mmol), and an aryl halide (3.0 mmol) at room temperature for the synthesis of symmetrical diarylmethanones, except for **3n**,**o**,**q**−**t**, which were obtained by using $Pd(OAc)_2$ (16.82 mg, 0.07 mmol), PPh_3 (78.59, 0.30 mmol), and aryl bromides (5.09 mmol). For the synthesis of unsymmetrical diarylmethanones, acetophenone (1.5 mmol) and two aryl halides (each was 1.5 mmol) or 1,2-diphenylethanone (1.5 mmol) and an aryl halide (1.5 mmol) were used. The resulting suspension was stirred and heated to 153 °C under argon for 3 h, and then the atmosphere was changed to O_2. The reaction progress was monitored by TLC. Upon completion of the reaction, the mixture was cooled and HCl (1.4 M in H_2O, 50 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL), and the organic extracts were combined, washed with saturated aqueous NH_4Cl (3 × 100 mL), dried with anhydrous sodium sulfate, and concentrated in vacuo to give a residue. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the product. All the as-synthesized diarylmethanones are shown in Tables 2 and 3.

*Diphenylmethanone (**3a**).*[29] Acetophenone (0.18 g, 1.5 mmol) and bromobenzene (0.47 g, 3.0 mmol) were used. The product was obtained as a pale yellow oil (0.15 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (d, J = 8.0 Hz, 4H), 7.57 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 6.0 Hz, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 196.6, 137.5, 132.3, 129.9, 128.2. MS: m/z 182 $[M]^+$. Anal. Calcd for $C_{13}H_{10}O$: C, 85.69; H, 5.53. Found: C, 85.49; H, 5.43.

*Di-p-tolylmethanone (**3b**).*[29] Acetophenone (0.18 g, 1.5 mmol) and 4-bromotoluene (0.51 g, 3.0 mmol) were used. The product was obtained as a white solid (0.22 g, 71%). Mp: 89.7−90.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70 (d, J = 8.0 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 2.43 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 196.2, 142.9, 135.1, 130.1, 128.9, 21.6. MS: m/z 210 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.54; H, 6.59.

*Di-m-tolylmethanone (**3c**).*[29] Acetophenone (0.18 g, 1.5 mmol) and 3-bromotoluene (0.51 g, 3.0 mmol) were used. The product was obtained as a yellow oil (0.26 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.62 (s, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.36 (dt, J_1 = 14.8, J_2 = 7.5 Hz, 4H), 2.41 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 197.1, 138.0, 137.7, 133.0, 130.3, 127.9, 127.3, 21.3. MS: m/z 210 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.49; H, 6.50.

*Di-o-tolylmethanone (**3d**).*[12a] Acetophenone (0.18 g, 1.5 mmol) and 2-bromotoluene (0.51 g, 3.0 mmol) were used. The product was obtained as a yellow oil (0.08 g, 26%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (t, J = 8.0 Hz, 2H), 7.33−7.24 (m, 4H), 7.19 (t, J = 7.4 Hz, 2H), 2.44 (s, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 200.7, 138.9, 138.1, 131.4, 131.0, 130.3, 125.4, 20.7. MS: m/z 210 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.55; H, 6.56.

*Bis(3,5-dimethylphenyl)methanone (**3e**).* Acetophenone (0.18 g, 1.5 mmol) and 3,5-dimethylbromobenzene (0.56 g, 3.0 mmol) were used. The product was obtained as a white solid (0.27 g, 75%). Mp: 111.6−112.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.39 (s, 4H), 7.21 (s, 2H), 2.37 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 197.6, 138.0, 137.8, 133.9, 127.7, 21.2. MS: m/z 238 $[M]^+$. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.48; H, 7.47.

*Bis(2,5-dimethylphenyl)methanone (**3f**).*[6b] Acetophenone (0.18 g, 1.5 mmol) and 2,5-dimethylbromobenzene (0.56 g, 3.0 mmol) were used. The product was obtained as a yellow oil (0.20 g, 56%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.17 (dd, J_1 = 15.4, J_2 = 7.8 Hz, 4H), 7.11 (s, 2H), 2.37 (s, 6H), 2.28 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 201.1, 139.0, 134.9, 134.9, 131.7, 131.2, 130.5, 20.8, 20.1. MS: m/z 238 $[M]^+$. Anal. Calcd for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.52; H, 7.45.

*Bis(4-pentylphenyl)methanone (**3g**).* Acetophenone (0.18 g, 1.5 mmol) and 4-pentyl bromobenzene (0.68 g, 3.0 mmol) were used. The product was obtained as a yellow oil (0.32 g, 67%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.73 (d, J = 8.0 Hz, 4H), 7.27 (d, J = 8.0 Hz, 4H), 2.67 (t, J = 8.0 Hz, 4H), 1.65 (dt, J_1 = 14.9, J_2 = 7.4 Hz, 4H), 1.49−1.22 (m, 8H), 0.90 (t, J = 8.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 196.2, 147.8, 135.3, 130.2, 128.2, 35.9, 31.4, 30.9, 22.5, 14.0. MS: m/z 322 $[M]^+$. Anal. Calcd for $C_{23}H_{30}O$: C, 85.66; H, 9.38. Found: C, 85.47; H, 9.20.

*Bis(4-(tert-butyl)phenyl)methanone (**3h**).* Acetophenone (0.18 g, 1.5 mmol) and 4-*tert*-butylbromobenzene (0.64 g, 3.0 mmol) were used. The product was obtained as a white solid (0.36 g, 82%). Mp: 139.5−140.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.77 (d, J = 8.0 Hz, 4H), 7.49 (d, J = 8.0 Hz, 4H), 1.37 (s, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 196.1, 155.8, 135.1, 130.0, 125.1, 35.1, 31.1. MS: m/z 294 $[M]^+$. Anal. Calcd for $C_{21}H_{26}O$: C, 85.67; H, 8.90. Found: C, 85.50; H, 8.66.

*Bis(4-methoxyphenyl)methanone (**3i**).*[29] The ketone (1.5 mmol; acetophenone, 0.18 g; 4-fluoroacetophenone, 0.21 g; 4-methoxyacetophenone, 0.23 g; 3-acetylpyridine, 0.18 g) and 4-bromoanisole (0.56 g, 3.0 mmol) were used. The product was obtained as a white crystalline solid. The yields are indicated in Table 2 (0.29 g, 81%; 0.22 g, 59%; 0.20 g, 54%; 0.16 g, 44%). Mp: 151.9−152.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 8.0 Hz, 4H), 6.96 (d, J = 8.0 Hz, 4H), 3.88 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 194.4, 162.8, 132.2, 130.8, 113.4, 55.5. MS: m/z 242 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.19; H, 5.73.

*Bis(3-methoxyphenyl)methanone (**3j**).* Acetophenone (0.18 g, 1.5 mmol) and 3-bromoanisole (0.56 g, 3.0 mmol) were used. The product was obtained as a pale yellow oil (0.30 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.49−7.29 (m, 6H), 7.21−7.03 (m, 2H), 3.84 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 196.1, 159.4, 138.7, 129.1, 122.7, 118.7, 114.2, 55.3. MS: m/z 242 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.40; H, 5.70.

*Bis(2-methoxyphenyl)methanone (**3k**).* Acetophenone (0.18 g, 1.5 mmol) and 2-bromoanisole (0.56 g, 3.0 mmol) were used. The product was obtained as a white solid (0.13 g, 36%). Mp: 110.0−110.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.51 (d, J = 8.0 Hz, 2H), 7.43 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 2H), 6.91 (d, J = 8.0 Hz, 2H), 3.66 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 195.3, 158.2, 132.6, 130.4, 130.1, 120.3, 111.3, 55.6. MS: m/z 242 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.59; H, 6.09.

*Bis(3,4-dimethoxyphenyl)methanone (**3l**).* Acetophenone (0.18 g, 1.5 mmol) and 3,4-dimethoxybromobenzene (0.65 g, 3.0 mmol) were used. The product was obtained as a white solid (0.27 g, 60%). Mp: 152.0−152.7 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.44 (d, J = 1.8 Hz, 2H), 7.39 (dd, J_1 = 8.3, J_2 = 2.0 Hz, 1H), 6.91 (d, J = 8.3 Hz, 2H), 3.97 (s, 6H), 3.95 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 194.4, 152.5, 148.7, 130.6, 124.7, 112.1, 109.6, 56.0. MS: m/z 302 $[M]^+$. Anal. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00. Found: C, 67.72; H, 5.82.

*Bis(4-fluorophenyl)methanone (**3n**).* Acetophenone (0.18 g, 1.5 mmol) and 4-fluorobromobenzene (0.89 g, 5.09 mmol) were used. The product was obtained as a white solid (0.18 g, 55%). Mp: 106.8−107.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (dd, J_1 = 8.7, J_2 = 5.4 Hz, 4H), 7.18 (t, J = 8.6 Hz, 4H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 193.8, 166.6, 164.1, 133.6, 132.5, 132.4, 115.7, 115.4. MS: m/z 218 $[M]^+$. Anal. Calcd for $C_{13}H_8F_2O$: C, 71.56; H, 3.70. Found: C, 71.31; H, 3.82.

*Bis(3-fluorophenyl)methanone (**3o**).* Acetophenone (0.18 g, 1.5 mmol) and 3-fluorobromobenzene (0.89 g, 5.09 mmol) were used. The product was obtained as a white solid (0.20 g, 61%). Mp: 57.6−

58.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.57 (d, J = 8.0, 2H), 7.54−7.44 (m, 4H), 7.36−7.27 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 193.8, 163.7, 161.2, 139.0, 138.9, 132.7, 130.1, 128.4, 125.8, 125.7, 119.9, 119.7, 116.8, 116.5. MS: m/z 218 $[M]^+$. Anal. Calcd for $C_{13}H_8F_2O$: C, 71.56; H, 3.70. Found: C, 71.86; H, 3.94.

Bis(4-chlorophenyl)methanone (**3p**).[14a] Acetophenone (0.18 g, 1.5 mmol) and 4-chlorobromobenzene (0.58 g, 3.0 mmol) were used. The product was obtained as a white solid (0.17 g, 45%). Mp: 148.1−149.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.73 (d, J = 8.0 Hz, 4H), 7.47 (d, J = 8.0 Hz, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 194.2, 139.1, 135.4, 131.3, 128.7. MS: m/z 250 $[M]^+$. Anal. Calcd for $C_{13}H_8Cl_2O$: C, 62.18; H, 3.21. Found: C, 62.03; H, 3.44.

Bis(4-(trifluoromethyl)phenyl)methanone (**3q**).[15] Acetophenone (0.18 g, 1.5 mmol) and 4-(trifluoromethyl)bromobenzene (1.15 g, 5.09 mmol) were used. The product was obtained as a white solid (0.15 g, 32%). Mp: 103.9−104.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91 (d, J = 8.0 Hz, 4H), 7.86−7.73 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 194.4, 139.7, 134.5, 133.1, 130.2, 130.1, 128.5, 125.6, 125.6, 122.1. MS: m/z 318 $[M]^+$.

Bis(3,5-bis(trifluoromethyl)phenyl)methanone (**3r**). Acetophenone (0.18 g, 1.5 mmol) and 3,5-bis(trifluoromethyl)bromobenzene (1.49 g, 5.09 mmol) were used. The product was obtained as a white solid (0.13 g, 19%). Mp: 144.2−145.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.24 (s, 4H), 8.20 (s, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 190.8, 137.6, 133.3, 132.9, 132.6, 132.2, 129.8, 126.8, 124.0, 121.3, 118.6, 109.8. MS: m/z 454 $[M]^+$. Anal. Calcd for $C_{17}H_6F_{12}O$: C, 44.95; H, 1.33. Found: C, 44.76; H, 1.51.

Bis(4-cyanophenyl)methanone (**3s**).[29] Acetophenone (0.18 g, 1.5 mmol) and 4-bromobenzonitrile (0.93 g, 5.09 mmol) were used. The product was obtained as yellow solid (0.09 g, 26%). Mp: 163.6−164.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.86 (dd, J_1 = 19.1, J_2 = 8.2 Hz, 8H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 193.4, 139.7, 132.4, 130.2, 117.7, 116.5. MS: m/z 232 $[M]^+$. Anal. Calcd for $C_{15}H_8N_2O$: C, 77.58; H, 3.47; N, 12.06. Found: C, 77.44; H, 3.52; N, 12.25.

Bis(4-carbethoxyphenyl)methanone (**3t**).[29] Acetophenone (0.18 g, 1.5 mmol) and ethyl 4-bromobenzoate (1.16 g, 5.09 mmol) were used. The product was obtained as a white solid (0.11 g, 22%). Mp: 83.8−84.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.17 (d, J = 8.4 Hz, 4H), 7.84 (d, J = 8.3 Hz, 4H), 4.43 (q, J = 7.1 Hz, 4H), 1.43 (t, J = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 195.3, 165.6, 140.4, 134.0, 129.8, 129.5, 61.5, 14.2. MS: m/z 326 $[M]^+$.

Bis(naphthalen-1-yl)methanone (**3u**). Acetophenone (0.18 g, 1.5 mmol) and 1-bromonaphthalene (0.62 g, 3.0 mmol) were used. The product was obtained as a red oil (0.36 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.56 (dd, J_1 = 6.5, J_2 = 3.0 Hz, 2H), 8.00 (d, J = 8.1 Hz, 2H), 7.92 (dd, J_1 = 6.2, J_2 = 3.3 Hz, 2H), 7.57 (dt, J_1 = 5.8, J_2 = 4.4 Hz, 6H), 7.44−7.37 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 199.7, 137.0, 133.8, 132.5, 131.1, 130.4, 128.4, 127.8, 126.5, 125.8, 124.3. MS: m/z 282 $[M]^+$. Anal. Calcd for $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.24; H, 4.90.

(4-Methoxyphenyl)phenylmethanone (**4a**).[12a] Acetophenone (0.18 g, 1.5 mmol) and bromobenzene (0.24 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) or 1,2-diphenylethanone (0.29 4g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a pale yellow solid (0.11 g, 34%; 0.13, 41%). Mp: 65.6−66.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.85−7.81 (m, 2H), 7.78−7.72 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 195.5, 163.1, 138.1, 132.5, 131.8, 130.0, 129.6, 128.1, 113.4, 55.4. MS: m/z 212 $[M]^+$. Anal. Calcd for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70. Found: C, 79.02; H, 5.52.

(4-Methoxyphenyl)-p-tolylmethanone (**4b**).[14a] Acetophenone (0.18 g, 1.5 mmol) and 4-bromotoluene (0.26 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a white solid (0.18 g, 53%). Mp: 91.5−92.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.29−7.24 (m, 2H), 6.95 (d, J = 8.0 Hz, 2H), 3.87 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 195.3, 162.9, 142.6, 135.4, 132.4, 130.3, 130.0, 128.8, 113.4, 55.4, 21.6. MS: m/z 226 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.36; H, 6.16.

(4-Methoxyphenyl)-m-tolylmethanone (**4c**). Acetophenone (0.18 g, 1.5 mmol) and 3-bromotoluene (0.26 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a pale yellow oil (0.17 g, 50%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (d, J = 8.8 Hz, 2H), 7.57 (s, 1H), 7.53 (d, J = 6.8 Hz, 2H), 7.35 (d, J = 7.0 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 195.7, 163.1, 138.2, 138.0, 132.6, 132.5, 130.2, 130.1, 127.9, 126.9, 113.4, 55.4, 21.3. MS: m/z 226 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.38; H, 6.02.

(4-Methoxyphenyl)-o-tolylmethanone (**4d**).[12a] Acetophenone (0.18 g, 1.5 mmol) and 2-bromotoluene (0.26 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a pale yellow oil (0.11 g, 32%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 8.9 Hz, 2H), 7.40−7.33 (m, 1H), 7.31−7.20 (m, 3H), 6.93 (d, J = 8.9 Hz, 2H), 3.87 (s, 3H), 2.30 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, ppm): δ 197.3, 163.6, 139.1, 136.1, 132.5, 130.8, 130.4, 129.7, 127.9, 125.1, 113.6, 55.5, 19.8. MS: m/z 226 $[M]^+$. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.43; H, 6.01.

(3,4-Dimethoxyphenyl)(4-methoxyphenyl)methanone (**4e**).[30] Acetophenone (0.18 g, 1.5 mmol) and 3,4-dimethoxybromobenzene (0.33 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a yellow solid (0.17 g, 41%). Mp: 90.0−91.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (d, J = 8.7 Hz, 2H), 7.44 (d, J = 1.7 Hz, 1H), 7.36 (dd, J = 8.3, 1.7 Hz, 1H), 6.96 (d, J = 8.7 Hz, 2H), 6.90 (d, J = 8.3 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H), 3.88 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 194.4, 162.7, 152.5, 148.8, 132.1, 130.7, 130.6, 124.7, 113.3, 112.1, 109.6, 55.9, 55.4. MS: m/z 272 $[M]^+$.

(4-Fluorophenyl)phenylmethanone (**4f**).[14c] Acetophenone (0.18 g, 1.5 mmol) and bromobenzene (0.24 g, 1.5 mmol) and 4-fluorobromobenzene (0.26 g, 1.5 mmol) or 1,2-diphenylethanone (0.294 g, 1.5 mmol) and 4-fluorobromobenzene (0.26 g, 1.5 mmol) were used. The product was obtained as a pale yellow oil (0.16 g, 53%; 0.18, 60%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.89−7.74 (m, 4H), 7.59 (ddd, J_1 = 7.2, J_2 = 2.7, J_3 = 1.1 Hz, 1H), 7.53−7.44 (m, 3H), 7.15 (t, J = 8.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 196.7, 166.6, 164.1, 137.5, 132.6, 132.4, 130.0, 129.8, 128.3, 128.2, 115.5, 115.3. MS: m/z 200 $[M]^+$. Anal. Calcd for $C_{13}H_9FO$: C, 77.99; H, 4.53. Found: C, 78.13; H, 4.42.

(3,4-Dimethoxyphenyl)(4-fluorophenyl)methanone (**4g**).[31] Acetophenone (0.18 g, 1.5 mmol) and 3,4-dimethoxybromobenzene (0.33 g, 1.5 mmol) and 4-fluorobromobenzene (0.26 g, 1.5 mmol) were used. The product was obtained as a yellow oil (0.15 g, 38%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83−7.78 (m, 2H), 7.48−7.45 (m, 1H), 7.34 (dd, J = 8.3, 1.8 Hz, 1H), 7.15 (t, J = 8.6 Hz, 2H), 6.90 (d, J = 8.3 Hz, 1H), 3.96 (s, 3H), 3.94 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 194.0, 166.2, 163.6, 152.9, 148.9, 134.3, 132.2, 132.1, 129.9, 129.8, 128.0, 125.1, 115.3, 115.1, 111.9, 109.7, 55.9. MS: m/z 260 $[M]^+$.

(4-Chlorophenyl)(4-methoxyphenyl)methanone (**4h**).[12a] Acetophenone (0.18 g, 1.5 mmol) and 4-chlorobromobenzene (0.29 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a white solid (0.07 g, 20%). Mp: 114.3−115.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 8.8 Hz, 2H), 7.70 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.7 Hz, 2H), 3.88 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 194.2, 163.3, 138.2, 136.5, 132.4, 131.1, 129.7, 128.5, 113.6, 55.5. MS: m/z 246$[M]^+$.

(4-Fluorophenyl)(4-methoxyphenyl)methanone (**4i**).[14a] Acetophenone (0.18 g, 1.5 mmol) and 4-fluorobromobenzene (0.26 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a white solid (0.11 g, 32%). Mp: 92.9−93.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (dt, J_1 = 8.8, J_2 = 2.7 Hz, 4H), 7.16 (t, J = 8.6 Hz, 2H), 7.03−6.89 (m, 2H), 3.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, ppm): δ 194.1, 166.2, 163.7, 163.2, 134.4, 132.5, 132.4, 132.3, 132.2, 129.9, 129.7, 128.1, 115.4, 115.2,

113.6, 113.5, 55.5. MS: m/z 230 [M]$^+$. Anal. Calcd for $C_{14}H_{11}FO_2$: C, 73.03; H, 4.82. Found: C, 73.30; H, 5.04.

*(3-Fluorophenyl)(4-methoxyphenyl)methanone **(4j)**.* Acetophenone (0.18 g, 1.5 mmol) and 3-fluorobromobenzene (0.26 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a white solid (0.11 g, 32%). Mp: 70.0−71.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83 (d, J = 8.0 Hz, 2H), 7.53 (d, J = 7.7 Hz, 1H), 7.46 (dd, J_1 = 7.8, J_2 = 5.1 Hz, 2H), 7.27 (d, J = 1.3 Hz, 1H), 6.98 (d, J = 8.0 Hz, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 194.0, 163.6, 163.4, 161.1, 140.3, 140.2, 132.5, 129.9, 129.8, 129.7, 129.5, 128.1, 125.4, 118.9, 118.7, 116.6, 116.4, 113.6, 113.5, 55.5. MS: m/z 230 [M]$^+$. Anal. Calcd for $C_{14}H_{11}FO_2$: C, 73.03; H, 4.82. Found: C, 72.88; H, 5.04.

*(2-Fluorophenyl)(4-methoxyphenyl)methanone **(4k)**.*[14a] Acetophenone (0.18 g, 1.5 mmol) and 2-fluorobromobenzene (0.26 g, 1.5 mmol) and 4-bromoanisole (0.28 g, 1.5 mmol) were used. The product was obtained as a pale yellow oil (0.06 g, 18%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.83 (d, J = 8.8 Hz, 2H), 7.80−7.71 (m, 1H), 7.56 (d, J = 7.4 Hz, 1H), 7.52−7.44 (m, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 195.6, 163.9, 163.1, 138.2, 132.5, 132.3, 131.9, 130.4, 130.0, 129.7, 128.4, 128.1, 124.2, 116.2, 116.0, 113.7, 113.5, 55.5. MS: m/z 230 [M]$^+$.

*Phenyl(3-vinylphenyl)methanone **(4m)**.*[25] Acetophenone (0.18 g, 1.5 mmol) and bromobenzene (0.24 g, 1.5 mmol) and 1-bromo-3-vinylbenzene (0.28 g, 1.5 mmol) or 1,2-diphenylethanone (0.294 g, 1.5 mmol) and 3-bromostyrene (0.28 g, 1.5 mmol) were used. The product was obtained as a pale yellow oil (0.12 g, 39%; 0.14, 45%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.81 (dd, J_1 = 11.4, J_2 = 4.8 Hz, 3H), 7.67−7.57 (m, 3H), 7.49−7.41 (m, 3H), 6.75 (dd, J_1 = 17.6, J_2 = 8.0 Hz, 1H), 5.81 (d, J = 17.6 Hz, 1H), 5.32 (d, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 196.6, 137.8, 137.7, 137.4, 135.9, 132.5, 132.4, 130.0, 129.9, 129.4, 128.4, 128.3, 128.2, 127.7, 115.2. MS: m/z 208 [M]$^+$. Anal. Calcd for $C_{15}H_{12}O$: C, 86.51; H, 5.81. Found: C, 86.13; H, 5.45.

ASSOCIATED CONTENT

Supporting Information

Text, tables, and figures giving additional data for the optimization of reaction conditions and ^{1}H NMR and ^{13}C{^{1}H} NMR spectra for all synthesized compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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