

Carbonylative Suzuki–Miyaura Coupling of Arylboronic Acids with Aryl Iodides Catalyzed by the MCM-41-Supported Bidentate Phosphane Palladium(II) Complex

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The first heterogeneous carbonylative Suzuki–Miyaura cross-coupling reaction of arylboronic acids with aryl iodides under an atmospheric pressure of carbon monoxide has been achieved in anisole at 80 °C in the presence of a catalytic amount of an MCM-41-supported bidentate phosphane palladium(II) complex (MCM-41-2P-Pd^{II}), yielding unsymmetri-

cal biaryl ketones in good-to-high yields. This polymeric palladium catalyst exhibited higher activity and selectivity than [PdCl₂(PPh₃)₂] and can be reused at least 10 times without any decrease in activity.

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Introduction

Aryl ketones are important building blocks for a large number of natural products and pharmaceutical compounds, and many methods for their preparation have been reported.^[1] One general approach is the Friedel–Crafts acylation of substituted aromatic rings.^[2] The crucial disadvantage of traditional Friedel–Crafts acylation reactions is the use of more than a stoichiometric amount of aluminium trichloride, which is incompatible with many functional groups and generates a large amount of waste. Furthermore, the formation of *ortho* and *para* isomers with untunable regioselectivity results in separation problems and makes aryl ketones with *meta* substituents difficult to access. The transition-metal-catalyzed three-component cross-coupling reaction between arylmetal reagents, carbon monoxide, and aryl electrophiles has provided a straightforward and convenient route to the synthesis of unsymmetrical biaryl ketones. Various arylmetal reagents, including magnesium,^[3] aluminium,^[4] silicon,^[5] and tin compounds,^[6] have been reported to undergo carbonylative coupling, but the application of the protocol to aryl electrophiles with electron-withdrawing groups is severely limited due to a side-reaction that gives a direct coupling product without carbon monoxide insertion. Miyaura and co-workers reported the palladium-catalyzed carbonylative cross-coupling reaction of arylboronic acids with aryl halides, providing a new route to the synthesis of biaryl ketones.^[7] Zeni and co-workers reported the palladium-catalyzed carbonylative cross-coupling of 2-iodoselenophene and boronic acids.^[8]

Very recently, an *N*-heterocyclic carbene palladium complex catalyzed carbonylative Suzuki reaction has also been described.^[9] However, carbonylative Suzuki reactions generally proceed in the presence of a homogeneous palladium catalyst such as [PdCl₂(PPh₃)₂], [Pd(OAc)₂], and an *N*-heterocyclic carbene palladium complex, which makes the recovery of the metal tedious if not impossible and might result in unacceptable palladium contamination of the product. The high cost of transition-metal catalysts coupled with the toxic effects associated with many transition metals have led to increased interest in immobilizing catalysts onto a support. This class of supported reagents can facilitate both the isolation and recycling of the catalysts by simple filtration, thus providing an environmentally cleaner process.^[10] So far, polymer-supported palladium catalysts have successfully been used in, for example, the Heck reaction,^[11] the Suzuki reaction,^[12] the Sonogashira reaction,^[13] and the Stille reaction.^[14] However, to the best of our knowledge, there has been no general study of carbonylative Suzuki–Miyaura coupling reactions catalyzed by a polymer-supported palladium complex described to date.

Recent developments of the mesoporous material MCM-41 have provided a possible new candidate for a solid support for immobilization of homogeneous catalysts.^[15] MCM-41 has a regular pore diameter of around 5 nm and a specific surface area of >700 m² g⁻¹.^[16] Its large pore size allows passage of large molecules such as organic reactants and metal complexes through the pores to the surface of the channel.^[17] It is generally believed that a heterogeneous catalyst with a high surface area results in high catalytic activity. Considering the facts that the MCM-41 support has an extremely high surface area and the catalytic palladium species is anchored on the inner surface of the mesopore of the MCM-41 support, we expect that an MCM-41-

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supported palladium catalyst will exhibit high activity and good reusability. To date, only a few palladium complexes on a functionalized MCM-41 support have been prepared and successfully used in organic reactions.^[18] Recently, we reported the synthesis of the MCM-41-supported bidentate phosphane palladium(0) complex (abbreviated as MCM-41-2P-Pd⁰) and found that this complex is a highly active and recyclable catalyst for the Sonogashira reaction of aryl halides.^[13e] In this paper we wish to report that the carbonylative Suzuki–Miyaura cross-coupling reaction of arylboronic acids with aryl iodides under an atmospheric pressure of carbon monoxide can be easily achieved in the presence of a catalytic amount of MCM-41-supported bidentate phosphane palladium(II) complex (MCM-41-2P-Pd^{II}) to yield unsymmetrical biaryl ketones in good-to-high yields.

Results and Discussion

The MCM-41-supported bidentate phosphane palladium(II) complex (MCM-41-2P-Pd^{II}) was prepared by following our previous procedure.^[13e] The phosphane and palladium contents were 1.12 and 0.51 mmol/g, respectively. Initially, to determine the optimum conditions, the carbonylative cross-coupling reaction of phenylboronic acid (1.1 equiv.) with 4-iodoacetophenone was examined under an atmospheric pressure of carbon monoxide. The results are summarized in Table 1. Of the temperatures evaluated (60, 80, and 100 °C), 80 °C gave the best result and no reaction occurred at 60 °C. The carbonylative coupling reaction worked well in less polar solvents such as anisole, dioxane, *o*-xylene, or toluene, with anisole proving the best choice, however, the carbonylative coupling product was obtained in low yield in polar solvents such as DMF, presumably due to another side-reaction leading to 4-acetylbenzoic acid (Table 1, entry 7).^[19] Bases affected the selectivity of the reaction. Cs₂CO₃ and K₃PO₄, which have been utilized in Suzuki–Miyaura coupling reactions of organoboron compounds,^[20] had a strong tendency to produce the direct coupling product, 4-acetylbiphenyl (21–23%; entries 9 and 10). K₂CO₃ (3 equiv.) suspended in anisole is the most efficient, yielding 4-acetylbenzophenone in 85% yield, which, however, was still accompanied by 4-acetylbiphenyl (8%; entry 2). Increasing the amount of palladium catalyst could shorten the reaction time, but did not increase the yield of 4-acetylbenzophenone (entry 11). Low palladium concentrations usually led to a longer reaction time, which is consistent with our experimental results (entry 12). Taken together, a good result was obtained when the carbonylative coupling reaction was carried out with 2 mol-% of MCM-41-2P-Pd^{II} with K₂CO₃ as the base in anisole at 80 °C (entry 2).

To examine the scope for this carbonylative cross-coupling reaction, various arylboronic acids were coupled with a variety of aryl iodides in anisole at 80 °C using K₂CO₃ as

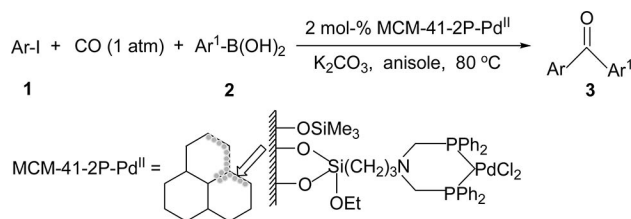
Table 1. Carbonylative coupling of phenylboronic acid with 4-iodoacetophenone under different conditions.^[a]

Entry	Solvent	Base	Catalyst amount [mol-%]	Temp. [°C], Time [h]	% Yield ^[b]	
					A	B
1	anisole	K ₂ CO ₃	2	60, 24	0	0
2	anisole	K ₂ CO ₃	2	80, 5	85	8
3	anisole	K ₂ CO ₃	2	100, 4	84	10
4	dioxane	K ₂ CO ₃	2	80, 5	83	10
5	<i>o</i> -xylene	K ₂ CO ₃	2	80, 5	80	11
6	toluene	K ₂ CO ₃	2	80, 5	65	14
7	DMF	K ₂ CO ₃	2	80, 24	16	0
8	anisole	Na ₂ CO ₃	2	80, 5	83	9
9	anisole	Cs ₂ CO ₃	2	80, 5	64	21
10	anisole	K ₃ PO ₄	2	80, 9	48	23
11	anisole	K ₂ CO ₃	4	80, 3	84	8
12	anisole	K ₂ CO ₃	1	80, 9	83	9

[a] Reaction conditions: phenylboronic acid (1.1 mmol), 4-iodoacetophenone (1.0 mmol), CO (1 atm), base (3 mmol), and solvent (6 mL). [b] Isolated yields.

the base in the presence of a catalytic amount of MCM-41-2P-Pd^{II} under an atmospheric pressure of carbon monoxide (Scheme 1). The experimental results are summarized in Table 2 and show that the carbonylative Suzuki–Miyaura cross-coupling reaction of phenylboronic acid with a variety of aryl iodides proceeded smoothly under mild conditions to give the corresponding carbonylative coupling products **3a–l** in good-to-high yields. The presence of a strong electron-withdrawing substituent such as NO₂ is known to promote the direct coupling reaction to produce the biaryl. For example, the carbonylative coupling reaction of triphenylalane with 4-iodonitrobenzene has been reported to provide a 41% yield of 4-nitrobenzophenone and a 55% yield of 4-nitrobiphenyl,^[4] and an analogous reaction with tributyltin hydride resulted in only a 9% yield of 4-nitrobenzaldehyde accompanied by an 84% yield of nitrobenzene.^[21] This polymeric palladium catalyst exhibits higher activity and selectivity than [PdCl₂(PPh₃)₂]. For example, the carbonylative coupling reaction of 4-iodonitrobenzene with phenylboronic acid in the presence of 2 mol-% of MCM-41-2P-Pd^{II} in anisole at 80 °C for 5 h gave an 88% yield of the carbonylative coupling product **3d** along with only a 9% yield of 4-nitrobiphenyl (entry 4). The same reaction in the presence of 3 mol-% of [PdCl₂(PPh₃)₂] in anisole at 80 °C for 5 h gave **3d** in 50% yield and 4-nitrobiphenyl in 35% yield.^[7b] The reactions of the sterically hindered 2-iodoanisole and 1-iodonaphthalene with phenylboronic acid also proceeded to afford the corresponding carbonylative coupling products **3e** and **3l** in good yields, respectively (entries 5 and 12). The carbonylative coupling of heteroaryl

iodides such as 2-iodothiophene with phenylboronic acid gave the corresponding heteroaryl ketone **3k** in 76% yield (entry 11).



Scheme 1. Synthesis of unsymmetrical biaryl ketones.

Table 2. Synthesis of unsymmetrical biaryl ketones.^[a]

Entry	Ar	Ar ¹	Product	% Yield ^[b]
1	4-CH ₃ COC ₆ H ₄	Ph	3a	85
2	4-CH ₃ OC ₆ H ₄	Ph	3b	86
3	4-CH ₃ C ₆ H ₄	Ph	3c	90
4	4-O ₂ NC ₆ H ₄	Ph	3d	88
5	2-CH ₃ OC ₆ H ₄	Ph	3e	67
6	3-CH ₃ C ₆ H ₄	Ph	3f	81
7	3-NCC ₆ H ₄	Ph	3g	84
8	4-H ₂ NC ₆ H ₄	Ph	3h	86
9	4-CH ₃ OCOC ₆ H ₄	Ph	3i	87
10	4-BrC ₆ H ₄	Ph	3j	86
11	2-thienyl	Ph	3k	76
12	1-naphthyl	Ph	3l	70
13	4-O ₂ NC ₆ H ₄	4-CH ₃ C ₆ H ₄	3m	85
14	4-CH ₃ OC ₆ H ₄	4-CH ₃ C ₆ H ₄	3n	83
15	4-CH ₃ COC ₆ H ₄	4-CH ₃ C ₆ H ₄	3o	87
16	4-BrC ₆ H ₄	4-CH ₃ C ₆ H ₄	3p	84
17	4-CH ₃ OCOC ₆ H ₄	4-CH ₃ C ₆ H ₄	3q	86
18	Ph	4-ClC ₆ H ₄	3r	84
19	4-CH ₃ OC ₆ H ₄	4-ClC ₆ H ₄	3s	86
20	4-CH ₃ C ₆ H ₄	4-ClC ₆ H ₄	3t	84
21	4-BrC ₆ H ₄	4-ClC ₆ H ₄	3u	79
22	4-CH ₃ OCOC ₆ H ₄	4-ClC ₆ H ₄	3v	85
23	2-thienyl	4-ClC ₆ H ₄	3w	80
24	1-naphthyl	4-ClC ₆ H ₄	3x	74
25	3-NCC ₆ H ₄	4-ClC ₆ H ₄	3y	82

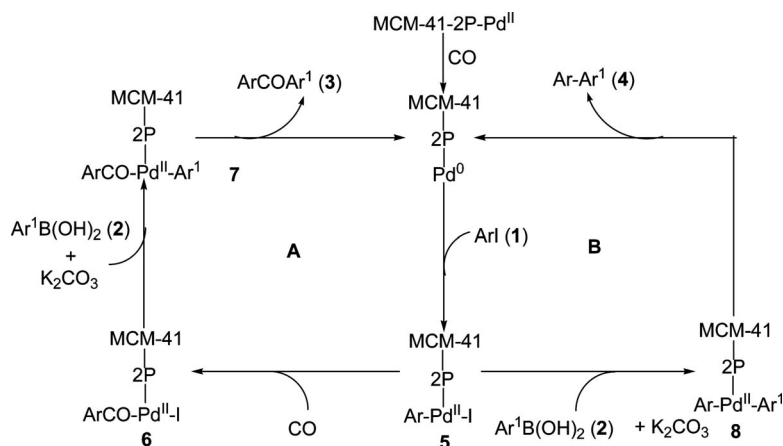
[a] The reaction was carried out with arylboronic acid (1.1 mmol), aryl iodide (1.0 mmol), CO (1 atm), K₂CO₃ (3 mmol), and palladium catalyst (2 mol-%) in anisole (6 mL) at 80 °C for 5 h. [b] Isolated yields.

The carbonylative Suzuki–Miyaura cross-coupling reaction of substituted phenylboronic acids such as 4-methylphenylboronic acid and 4-chlorophenylboronic acid with a variety of aryl iodides also proceeded smoothly under the same conditions to give the corresponding unsymmetrical biaryl ketones in good-to-high yields (entries 13–25). The method provides a quite general route to the synthesis of unsymmetrical biaryl ketones with various functionalities. These results prompted us to investigate the reaction of aryl bromides, but the carbonylative coupling reaction did not occur under the conditions optimized for the iodides. Even though NaI or KI (3 equiv.) was used as the additive, as reported by Miyaura and co-workers,^[7b] the carbonylative

coupling reaction of aryl bromides with arylboronic acids in anisole at 80 or 100 °C afforded only traces of carbonylative coupling products after 24 h. On the other hand, the carbonylation of 4-bromiodobenzene selectively occurred at the C–I bond, that is, no diketones were formed (entries 10, 16, and 21).

To determine whether the catalysis was due to the MCM-41-2P-Pd^{II} complex or to a homogeneous palladium complex that comes off the support during the reaction and then returns to the support at the end, we performed the hot filtration test.^[22] We focused on the carbonylative coupling reaction of 4-iodonitrobenzene with phenylboronic acid. We filtered off the MCM-41-2P-Pd^{II} complex after a reaction time of 1 h and allowed the filtrate to react further. The catalyst filtration was performed at the reaction temperature (80 °C) to avoid possible re-coordination or precipitation of soluble palladium upon cooling. We found that no further reaction was observed after this hot filtration. This result suggests that the palladium catalyst remains on the support at elevated temperatures during the reaction. The heterogeneous carbonylative Suzuki–Miyaura cross-coupling of arylboronic acid with aryl iodide may proceed through a catalytic cycle analogous to that proposed for other metal reagents (cycle A in Scheme 2).^[3–6] Oxidative addition of ArI (**1**) to the MCM-41-2P-Pd⁰ complex provides the MCM-41-bound arylpalladium(II) complex (**5**), which is followed by migratory insertion of carbon monoxide to give the MCM-41-bound acylpalladium(II) complex (**6**). Subsequent transmetalation between **6** and arylboronic acid (**2**) with the aid of K₂CO₃ and reductive elimination of biaryl ketone (**3**) from intermediate **7** regenerates the MCM-41-2P-Pd⁰ complex. As **5** is a common intermediate for both the carbonylation (cycle A) and the direct coupling reaction, which gives biaryls (cycle B), large amounts of biaryls (**4**) are often formed when the insertion reaction of carbon monoxide into intermediate **5** is slower than the transmetalation reaction between **5** and arylboronic acid (**2**).

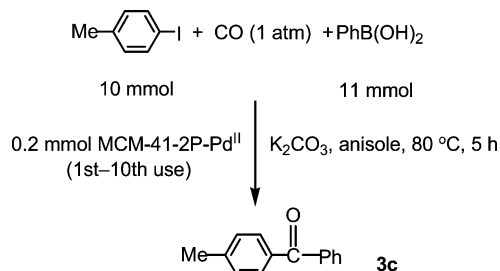
The MCM-41-2P-Pd^{II} catalyst can be easily recovered by simple filtration. We also investigated the possibility of reusing the catalyst through the carbonylative coupling reaction of 4-methyliodobenzene with phenylboronic acid. In general, continuous recycling of resin-supported palladium catalysts is difficult owing to leaching of the palladium species from the polymer supports, which often reduces their activity within five recycles. However, when the reaction of 4-methyliodobenzene with phenylboronic acid was performed even with 2 mol-% of MCM-41-2P-Pd^{II}, the catalyst could be recycled 10 times without any loss of activity. The reaction promoted by the catalyst on its tenth cycle gave **3c** in 88% yield (Table 3, entry 2). The average yield of **3c** from 10 consecutive reactions with the same catalyst was 89% (entry 3). The palladium content of the catalyst was determined to be 0.50 mmol/g after 10 consecutive runs, thus, only 2% of palladium had been lost from the MCM-41 support. The high stability and excellent reusability of the catalyst result from the chelating action of the bidentate phosphine ligand on palladium and the mesoporous structure



Scheme 2. Catalytic cycle.

of the MCM-41 support. The result is important from a practical point of view. The high catalytic activity, excellent reusability, and the easy accessibility of the MCM-41-2P-Pd^{II} catalyst make them a highly attractive supported palladium catalyst for the parallel solution-phase synthesis of diverse libraries of compounds.

Table 3. Carbonylative Suzuki–Miyaura coupling reaction of 4-methyliodobenzene with phenylboronic acid catalyzed by recycled catalyst.



Entry	Catalyst cycle	% Yield (isolated product)	TON
1	1st	90	45
2	10th	88	44
3	1st to 10th consecutive	av. 89	total of 445

Conclusions

We have described the first heterogeneous carbonylative Suzuki–Miyaura cross-coupling reaction catalyzed by an MCM-41-supported bidentate phosphane palladium(II) complex. This polymeric palladium catalyst exhibits higher activity and selectivity than [PdCl₂(PPh₃)₂] and can be reused 10 times without any decrease in activity. The carbonylative Suzuki–Miyaura coupling reaction of aryl iodides with arylboronic acids catalyzed by the MCM-41-2P-Pd^{II} complex under an atmospheric pressure of carbon monoxide provides a better and practical procedure for the synthesis of unsymmetrical biaryl ketones.

Experimental Section

General: All chemicals were of reagent grade and used as purchased. All solvents were dried and distilled before use. The products were purified by flash chromatography on silica gel. A mixture of EtOAc and hexane was generally used as the eluent. All carbonylative coupling products were characterized by comparison of their spectra and physical data with authentic samples. IR spectra were recorded with a Perkin–Elmer 683 instrument. ¹H and ¹³C NMR spectra were recorded with a Bruker AC-P400 (400 and 100 MHz, respectively) spectrometer in CDCl₃ as solvent. TMS was used as the internal standard. Melting points are uncorrected. Microanalyses were measured by using a Yanaco MT-3 CHN microelemental analyzer.

General Procedure for the Carbonylative Suzuki–Miyaura Cross-Coupling Reaction: A 50 mL round-bottomed flask equipped with a gas inlet tube, a reflux condenser, and a magnetic stirring bar was charged with MCM-41-2P-Pd^{II} (39 mg, 0.02 mmol Pd), aryl iodide (1.0 mmol), arylboronic acid (1.1 mmol), and K₂CO₃ (3 mmol). The flask was flushed with carbon monoxide and anisole (6 mL) was then added. After stirring at 80 °C for 5 h under CO (1 atm), the reaction mixture was cooled to room temperature and diluted with diethyl ether (50 mL). The palladium catalyst was separated from the mixture by filtration, washed with distilled water (3 × 10 mL), ethanol (2 × 10 mL), and ether (2 × 10 mL), and re-used in the next run. The ethereal solution was washed with water (3 × 20 mL) and dried with anhydrous magnesium sulfate and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 10:1).

4-Acetylbenzophenone (3a): Yield 0.191 g, 85%. White solid, m.p. 83–84 °C (ref.^[23] 83–84 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.07–8.05 (m, 2 H), 7.88–7.86 (m, 2 H), 7.82–7.80 (m, 2 H), 7.65–7.49 (m, 3 H), 2.68 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 197.57, 195.98, 141.31, 139.54, 136.89, 133.03, 130.12, 130.06, 128.50, 128.18, 26.94 ppm. IR (KBr): ν̄ = 1693, 1661, 1579, 931, 699 cm⁻¹. C₁₅H₁₂O₂ (224.26): calcd. C 80.34, H 5.39; found C 80.13, H 5.45.

4-Methoxybenzophenone (3b): Yield 0.182 g, 86%. White solid, m.p. 59–60 °C (ref.^[24] 61–62 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.85–7.82 (m, 2 H), 7.76–7.74 (m, 2 H), 7.58–7.45 (m, 3 H), 6.98–6.95 (m, 2 H), 3.88 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.64, 163.24, 138.27, 132.60, 131.94, 130.13, 129.76, 128.21, 113.57, 55.52 ppm. IR (KBr): ν̄ = 1651, 1599, 1508, 1172, 1029,

701 cm⁻¹. C₁₄H₁₂O₂ (212.25): calcd. C 79.22, H 5.70; found C 78.95, H 5.49.

4-Methylbenzophenone (3c): Yield 0.176 g, 90%. White solid, m.p. 56–57 °C (ref.^[24] 57–58 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.79–7.77 (m, 2 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.58–7.54 (m, 1 H), 7.48–7.44 (m, 2 H), 7.28–7.25 (m, 2 H), 2.43 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 196.52, 143.26, 137.96, 134.89, 132.19, 130.33, 129.95, 129.00, 128.23, 21.68 ppm. IR (KBr): ν̄ = 1657, 1606, 1578, 1277, 700 cm⁻¹. C₁₄H₁₂O (196.25): calcd. C 85.68, H 6.16; found C 85.43, H 5.89.

4-Nitrobenzophenone (3d): Yield 0.201 g, 88%. Yellow solid, m.p. 136–137 °C (ref.^[24] 138–139 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.35 (d, *J* = 8.8 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.82–7.80 (m, 2 H), 7.66–7.51 (m, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 194.84, 149.82, 142.88, 136.27, 133.51, 130.73, 130.12, 128.71, 123.57 ppm. IR (KBr): ν̄ = 1652, 1595, 1515, 1358, 707 cm⁻¹. C₁₃H₉NO₃ (227.22): calcd. C 68.72, H 3.99, N 6.16; found C 68.50, H 3.74, N 5.89.

2-Methoxybenzophenone (3e):^[25] Yield 0.142 g, 67%. Oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.82–7.80 (m, 2 H), 7.56–7.52 (m, 1 H), 7.49–7.40 (m, 3 H), 7.37–7.35 (m, 1 H), 7.06–6.98 (m, 2 H), 3.71 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 196.50, 157.36, 137.81, 132.95, 131.91, 129.84, 129.59, 128.85, 128.24, 120.50, 111.47, 55.61 ppm. IR (neat): ν̄ = 1667, 1599, 1581, 1244, 1023, 702 cm⁻¹. C₁₄H₁₂O₂ (212.25): calcd. C 79.22, H 5.70; found C 79.35, H 5.88.

3-Methylbenzophenone (3f):^[26] Yield 0.159 g, 81%. Oil. ¹H NMR (400 MHz, CDCl₃): δ = 7.81–7.79 (m, 2 H), 7.63 (s, 1 H), 7.60–7.56 (m, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.41–7.33 (m, 2 H), 2.42 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 196.96, 138.14, 137.74, 137.61, 133.19, 132.33, 130.45, 130.03, 128.23, 128.08, 127.36, 21.36 ppm. IR (neat): ν̄ = 1660, 1598, 1281, 720 cm⁻¹. C₁₄H₁₂O (196.25): calcd. C 85.68, H 6.16; found C 85.50, H 6.32.

3-Cyanobenzophenone (3g): Yield 0.174 g, 84%. White solid, m.p. 91–92 °C (ref.^[27] 90–91 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.07 (s, 1 H), 8.06–8.04 (m, 1 H), 7.89–7.87 (m, 1 H), 7.79–7.77 (m, 2 H), 7.67–7.62 (m, 2 H), 7.53 (t, *J* = 7.8 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 194.44, 138.60, 136.31, 135.38, 133.88, 133.48, 133.32, 130.02, 129.43, 128.70, 117.98, 112.83 ppm. IR (KBr): ν̄ = 3076, 2232, 1663, 1597, 1280, 724 cm⁻¹. C₁₄H₉NO (207.23): calcd. C 81.14, H 4.38, N 6.76; found C 80.87, H 4.21, N 6.54.

4-Aminobenzophenone (3h): Yield 0.169 g, 86%. White solid, m.p. 120–121 °C (ref.^[24] 121–123 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.74–7.71 (m, 4 H), 7.56–7.43 (m, 3 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 4.17 (br., 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.36, 150.91, 138.86, 132.97, 131.43, 129.54, 128.08, 127.47, 113.65 ppm. IR (KBr): ν̄ = 3340, 3226, 1640, 1629, 1591, 1275, 687 cm⁻¹. C₁₃H₁₁NO (197.23): calcd. C 79.17, H 5.62, N 7.10; found C 78.95, H 5.44, N 6.92.

4-Methoxycarbonylbenzophenone (3i): Yield 0.209 g, 87%. White solid, m.p. 108–109 °C (ref.^[28] 106 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.14 (d, *J* = 8.4 Hz, 2 H), 7.83 (d, *J* = 8.4 Hz, 2 H), 7.80–7.78 (m, 2 H), 7.62–7.58 (m, 1 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 3.95 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.89, 166.21, 141.24, 136.88, 133.16, 132.94, 130.07, 129.75, 129.47, 128.45, 52.43 ppm. IR (KBr): ν̄ = 1717, 1647, 1596, 1276, 1107, 713 cm⁻¹. C₁₅H₁₂O₃ (240.26): calcd. C 74.99, H 5.03; found C 74.76, H 4.87.

4-Bromobenzophenone (3j): Yield 0.224 g, 86%. White solid, m.p. 78–79 °C (ref.^[29] 77–79 °C). ¹H NMR (400 MHz, CDCl₃): δ =

7.78–7.76 (m, 2 H), 7.69–7.67 (m, 2 H), 7.64–7.59 (m, 3 H), 7.49 (t, *J* = 7.6 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.67, 137.17, 136.31, 132.71, 131.63, 131.59, 129.96, 128.43, 127.54 ppm. IR (KBr): ν̄ = 1650, 1585, 1285, 725, 696 cm⁻¹. C₁₃H₉BrO (261.22): calcd. C 59.77, H 3.47; found C 59.49, H 3.28.

2-Benzoylthiophene (3k): Yield 0.143 g, 76%. White solid, m.p. 54–55 °C (ref.^[29] 56–57 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.89–7.85 (m, 2 H), 7.72–7.71 (m, 1 H), 7.64–7.63 (m, 1 H), 7.61–7.56 (m, 1 H), 7.51–7.47 (m, 2 H), 7.18–7.14 (m, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 188.28, 143.63, 138.14, 134.93, 134.29, 132.31, 129.19, 128.45, 128.03 ppm. IR (KBr): ν̄ = 1634, 1598, 1577, 1514, 1286, 842, 716 cm⁻¹. C₁₁H₈OS (188.25): calcd. C 70.18, H 4.28; found C 69.94, H 4.02.

1-Benzoylnaphthalene (3l):^[29] Yield 0.162 g, 70%. Oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.10–8.08 (m, 1 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 7.92–7.84 (m, 3 H), 7.59–7.42 (m, 7 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 198.06, 138.34, 136.37, 133.75, 133.28, 131.31, 130.99, 130.45, 128.49, 128.45, 127.82, 127.30, 126.50, 125.72, 124.38 ppm. IR (neat): ν̄ = 1659, 1596, 1578, 1282, 1249, 775, 697 cm⁻¹. C₁₇H₁₂O (232.28): calcd. C 87.91, H 5.21; found C 87.64, H 5.29.

4-Methyl-4'-nitrobenzophenone (3m): Yield 0.205 g, 85%. Yellow solid, m.p. 120–122 °C (ref.^[30] 120–121 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.34–8.32 (m, 2 H), 7.93–7.90 (m, 2 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 2.47 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 194.53, 149.67, 144.60, 143.33, 133.63, 130.57, 130.34, 129.40, 123.50, 21.77 ppm. IR (KBr): ν̄ = 1652, 1600, 1520, 1353, 1315, 732 cm⁻¹. C₁₄H₁₁NO₃ (241.24): calcd. C 69.70, H 4.60, N 5.80; found C 69.42, H 4.37, N 5.54.

4-Methoxy-4'-methylbenzophenone (3n): Yield 0.188 g, 83%. White solid, m.p. 88–89 °C (ref.^[29] 85–87 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.83–7.81 (m, 2 H), 7.69 (d, *J* = 8.0 Hz, 2 H), 7.28 (d, *J* = 8.4 Hz, 2 H), 6.98–6.96 (m, 2 H), 3.90 (s, 3 H), 2.45 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.39, 163.04, 142.63, 135.51, 132.45, 130.49, 130.02, 128.89, 113.49, 55.50, 21.64 ppm. IR (KBr): ν̄ = 1646, 1598, 1505, 1262, 1170, 849, 761 cm⁻¹. C₁₅H₁₄O₂ (226.28): calcd. C 79.62, H 6.24; found C 79.39, H 6.28.

4-Acetyl-4'-methylbenzophenone (3o): Yield 0.207 g, 87%. White solid, m.p. 109–111 °C (ref.^[31] 111–112 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.05 (d, *J* = 8.4 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H), 7.72 (d, *J* = 8.0 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 2.67 (s, 3 H), 2.45 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 197.59, 195.70, 143.98, 141.75, 139.37, 134.23, 130.34, 129.92, 129.19, 128.13, 26.91, 21.73 ppm. IR (KBr): ν̄ = 1689, 1651, 1604, 1286, 858, 757 cm⁻¹. C₁₆H₁₄O₂ (238.29): calcd. C 80.65, H 5.92; found C 80.38, H 5.71.

4-Bromo-4'-methylbenzophenone (3p): Yield 0.231 g, 84%. White solid, m.p. 139–140 °C (ref.^[29] 123–125 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.70–7.61 (m, 6 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 2.45 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.36, 143.57, 136.69, 134.49, 131.54, 131.46, 130.18, 129.11, 127.18, 21.67 ppm. IR (KBr): ν̄ = 1645, 1605, 1586, 1288, 748 cm⁻¹. C₁₄H₁₁BrO (275.24): calcd. C 61.09, H 4.03; found C 60.82, H 3.90.

4-Methoxycarbonyl-4'-methylbenzophenone (3q): Yield 0.218 g, 86%. White solid, m.p. 125–126 °C (ref.^[32] 127–128 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.16–8.13 (m, 2 H), 7.83–7.81 (m, 2 H), 7.72 (d, *J* = 8.4 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 3.97 (s, 3 H), 2.46 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.83, 166.40, 143.94, 141.73, 134.26, 132.99, 130.36, 129.68, 129.47, 129.18, 52.49, 21.74 ppm. IR (KBr): ν̄ = 1717, 1646, 1606, 1276,

1110, 736 cm⁻¹. C₁₆H₁₄O₃ (254.29): calcd. C 75.57, H 5.55; found C 75.32, H 5.40.

4-Chlorobenzophenone (3r): Yield 0.182 g, 84%. White solid, m.p. 73–74 °C (ref.^[29] 74–76 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.78–7.74 (m, 4 H), 7.62–7.58 (m, 1 H), 7.50–7.45 (m, 4 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.46, 138.90, 137.26, 135.89, 132.64, 131.46, 129.93, 128.64, 128.41 ppm. IR (KBr): ν̄ = 1651, 1597, 1586, 1285, 728, 696 cm⁻¹. C₁₃H₉ClO (216.71): calcd. C 72.05, H 4.19; found C 71.87, H 4.03.

4-Chloro-4'-methoxybenzophenone (3s): Yield 0.212 g, 86%. White solid, m.p. 125–126 °C (ref.^[29] 116–118 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.81–7.78 (m, 2 H), 7.71–7.69 (m, 2 H), 7.46–7.43 (m, 2 H), 6.98–6.95 (m, 2 H), 3.89 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 194.23, 163.40, 138.26, 136.58, 132.44, 131.15, 129.81, 128.52, 113.69, 55.52 ppm. IR (KBr): ν̄ = 1640, 1605, 1508, 1256, 1030, 853, 760 cm⁻¹. C₁₄H₁₁ClO₂ (246.74): calcd. C 68.15, H 4.49; found C 67.87, H 4.58.

4-Chloro-4'-methylbenzophenone (3t): Yield 0.194 g, 84%. White solid, m.p. 127–129 °C (ref.^[29] 123–125 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.75 (d, *J* = 8.4 Hz, 2 H), 7.71 (d, *J* = 8.0 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.46 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 195.22, 143.53, 138.60, 136.25, 134.56, 131.34, 130.17, 129.10, 128.56, 21.66 ppm. IR (KBr): ν̄ = 1645, 1607, 1585, 1287, 1088, 853, 749 cm⁻¹. C₁₄H₁₁ClO (230.74): calcd. C 72.88, H 4.81; found C 72.63, H 4.70.

4-Bromo-4'-chlorobenzophenone (3u): Yield 0.233 g, 79%. White solid, m.p. 146–148 °C (ref.^[33] 147–148 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.73 (d, *J* = 8.4 Hz, 2 H), 7.64 (s, 4 H), 7.47 (d, *J* = 8.8 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 194.38, 139.21, 135.97, 135.46, 131.76, 131.41, 131.32, 128.79, 127.78 ppm. IR (KBr): ν̄ = 1646, 1586, 1289, 855, 753 cm⁻¹. C₁₃H₈BrClO (295.71): calcd. C 52.80, H 2.73; found C 52.54, H 2.61.

4-Chloro-4'-methoxycarbonylbenzophenone (3v):^[34] Yield 0.233 g, 85%. White solid, m.p. 168–169 °C. ¹H NMR (400 MHz, CDCl₃): δ = 8.15 (d, *J* = 8.4 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 2 H), 7.75 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 3.97 (s, 3 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 194.76, 166.19, 140.92, 139.51, 135.24, 133.45, 131.47, 129.64, 129.61, 128.84, 52.49 ppm. IR (KBr): ν̄ = 1732, 1651, 1588, 1283, 1111, 738 cm⁻¹. C₁₅H₁₁ClO₃ (274.75): calcd. C 65.57, H 4.04; found C 65.72, H 4.28.

2-(4-Chlorobenzoyl)thiophene (3w): Yield 0.178 g, 80%. White solid, m.p. 99–100 °C (ref.^[29] 93–95 °C). ¹H NMR (400 MHz, CDCl₃): δ = 7.83–7.80 (m, 2 H), 7.75–7.74 (m, 1 H), 7.63–7.62 (m, 1 H), 7.49–7.46 (m, 2 H), 7.18–7.16 (m, 1 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 186.97, 143.20, 138.71, 136.38, 134.85, 134.62, 130.62, 128.79, 128.13 ppm. IR (KBr): ν̄ = 1632, 1588, 1414, 1304, 853, 722 cm⁻¹. C₁₁H₇ClOS (222.74): calcd. C 59.32, H 3.17; found C 59.53, H 3.39.

1-(4-Chlorobenzoyl)naphthalene (3x):^[29] Yield 0.197 g, 74%. Oil. ¹H NMR (400 MHz, CDCl₃): δ = 8.12–7.91 (m, 3 H), 7.82–7.80 (m, 2 H), 7.57–7.41 (m, 6 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ = 196.62, 139.74, 136.71, 135.87, 133.79, 131.77, 131.58, 130.90, 128.84, 128.53, 127.82, 127.45, 126.63, 125.60, 124.39 ppm. IR (neat): ν̄ = 1661, 1586, 1508, 1284, 1251, 800, 778 cm⁻¹. C₁₇H₁₁ClO (266.77): calcd. C 76.54, H 4.16; found C 76.31, H 3.88.

4-Chloro-3'-cyanobenzophenone (3y): Yield 0.198 g, 82%. White solid, m.p. 139–140 °C (ref.^[35] 144–147 °C). ¹H NMR (400 MHz, CDCl₃): δ = 8.05 (s, 1 H), 8.00 (d, *J* = 7.6 Hz, 1 H), 7.88 (d, *J* = 7.6 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 2 H), 7.67–7.63 (m, 1 H), 7.51 (d, *J* = 8.0 Hz, 2 H) ppm. ¹³C NMR (100 MHz, CDCl₃): δ =

193.15, 139.92, 138.29, 135.54, 134.60, 133.68, 133.28, 131.37, 129.52, 129.08, 117.79, 113.05 ppm. IR (KBr): ν̄ = 2235, 1659, 1587, 1297, 1091, 850, 752 cm⁻¹. C₁₄H₈ClNO (241.72): calcd. C 69.57, H 3.34, N 5.79; found C 69.33, H 3.15, N 5.57.

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