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In Situ Generation of Palladium Nanoparticles: Ligand-Free Palladium Catalyzed Pivalic Acid Assisted Carbonylative Suzuki Reactions at Ambient Conditions

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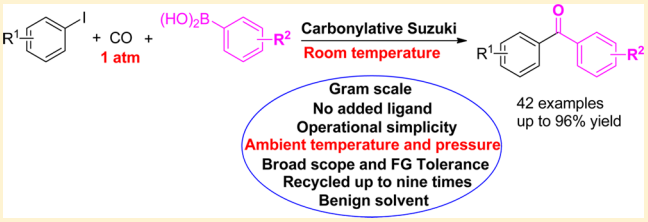
Supporting Information

ABSTRACT: Highly selective carbonylative Suzuki reactions of aryl iodides with arylboronic acids using an in situ generated nanopalladium system furnished products in high yields. The reactions were performed under ambient conditions and in the absence of an added ligand. The key to success is the addition of pivalic acid, which can effectively suppress undesired Suzuki coupling. The synthesis can be easily scaled up, and the catalytic system can be reused up to nine times. The nature of the active catalytic species are discussed.



Palladium-catalyzed carbonylative Suzuki reactions of aryl-X compounds with the C1 building block carbon monoxide are becoming a valuable tool in the synthesis of biaryl ketones that are important moieties in numerous natural products, pharmaceuticals, photosensitizers, and advanced organic materials.[1] Over the past decade, there have been great advances in the substrate scope, functional group tolerance, and range of various catalysts for promoting the transformation.[2] However, the vast majority of these methods require elevated temperatures (≥80 °C) and/or relatively high pressure (≥5 bar). Moreover, the cost of ligands are almost always necessary to achieve efficient catalysis.[2] All of these drawbacks impede the transfer of the advances to large-scale applications, particularly in complex organic syntheses. As carbon monoxide is relatively inert (bond energy, 257 kcal/mol) and can deactivate palladium,[3] the development of general room-temperature carbonylative Suzuki reactions of aryl-X compounds with arylboronic acids and carbon monoxide that proceed under atmospheric pressure without an extra ligand remains an important challenge for organic synthetic chemists.

Palladium nanoparticles usually show enhanced reactivity under mild conditions due to their large surface area[4] and have been widely used as catalysts in carbon−carbon bond-formation reactions.[5] Nevertheless, to the best of our knowledge, their applications as catalysts for carbonylative Suzuki reactions have not yet been reported.[6] This may be because palladium nanoparticles are known as excellent catalysts for Suzuki couplings[5d,e] and will contribute to problem of chemoselectivity when they are used for carbonylative Suzuki reactions.

We recently developed in situ generated metal nanoparticles-catalyzed cross-coupling reactions.[7] One of the attractive features of the in situ generated nanometal systems is to circumvent cumbersome processes for the preparation of metal nanoparticles.[5i,8] In addition, under mild conditions or even at room temperature the in situ nanocatalytic systems can achieve efficient catalysis.[7] Herein we report the first examples of an efficient nanopalladium catalytic system for carbonylative Suzuki reactions of aryl iodides without an additional ligand. Remarkably, this transformation proceeds smoothly at ambient temperature and pressure, which has also never been reported so far.

In our previous work, the in situ generated palladium nanoparticles effectively catalyzed the Suzuki coupling reactions of aryl chlorides with arylboronic acids at room temperature in PEG-400[9] (poly(ethylene glycol) with an average molecular weight of 400 Da).[7c] This work implies that the suppression of undesired Suzuki coupling reactions will be a daunting challenge when in situ generated palladium nanoparticles are used to catalyze carbonylative Suzuki reactions in PEG-400. It is well-known that a base plays an important role in palladium-catalyzed cross-coupling reactions. Hence, we initially investigated the effect of various bases on the model carbonylative Suzuki reaction of 4-iodonitrobenzene with phenylboronic acid at ambient temperature and pressure in PEG-400 (Table 1). The bases such as K_2CO_3, Cs_2CO_3, Na_2CO_3, KF, and TBAF·$2H_2O$ resulted in a significant amount of Suzuki coupling product **3a′a′** (Table 1, entries 1−5), whereas K_3PO_4 afforded desired carbonylative product **3aa** in a good yield, albeit with the concomitant generation of **3a′a′** in 13% yield (Table 1, entry 7).

Recently, Han and co-workers reported that pivalic acid can effectively suppress Suzuki reactions.[10] We assumed that the

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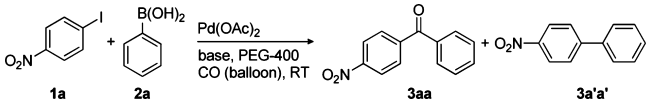
Table 1. $Pd(OAc)_2$-Catalyzed Carbonylative Suzuki Reaction of 1a with 2a[a]

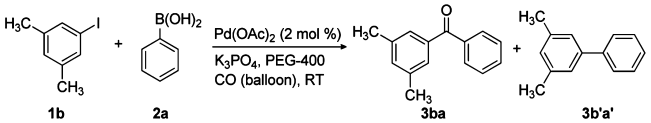


entry	base	time (h)	yield of **3aa** (%)	yield of **3a′a′** (%)
1	K_2CO_3	1	44	46
2	Cs_2CO_3	1	31	61
3	Na_2CO_3	3	59	32
4	KF	4	50	36
5	TBAF·$2H_2O$	9	30	31
6	$NH_3·H_2O$	9	trace	trace
7	K_3PO_4	1	83	13
8[c]	K_3PO_4, $tBuCO_2H$	2	84	10
9[b,c]	**K_3PO_4, $tBuCO_2H$**	**3**	**90**	**5**
10[b,c,d]	K_3PO_4, $tBuCO_2H$	4	85	5
11[b,c]	K_3PO_4, CH_3CO_2H	3	51	8
12[b,c]	K_3PO_4, CF_3CO_2H	3	74	5

[a]Reaction conditions (unless otherwise noted): **1a** (0.5 mmol), **2a** (0.75 mmol), CO (balloon), base (1.0 mmol), $Pd(OAc)_2$ (2 mol %), PEG-400 (2.0 g), rt. [b]With K_3PO_4 (0.75 mmol) for entries 9–12. [c]With acid (0.25 mmol) for entries 8–12. [d]The same conditions as above except with 1 mol % $Pd(OAc)_2$.

addition of the pivalic acid could suppress the formation of Suzuki coupling product in our case and may favor of the insertion of carbon monoxide from the gas phase. Gratifyingly, K_3PO_4/$tBuCO_2H$ as the base achieved an excellent yield of **3aa** in 90% with only 5% yield of the side product **3a′a′** at ambient temperature and pressure (Table 1, entry 9).[10] Other carboxylic acids such as CH_3COOH and CF_3COOH were tested (Table 1, entries 11 and 12). Although they also suppressed the Suzuki reaction, they gave lower yields of **3aa** under otherwise identical conditions. Furthermore, the role of the $tBuCO_2H$ to suppress the Suzuki coupling reaction and favor the carbonylative Suzuki coupling reaction was underlined by control experiments (Table 2).

Table 2. Effect of $tBuCO_2H$ on Products of the Reaction of 1-Iodo-3,5-dimethylbenzene (1b) with 2a[a]

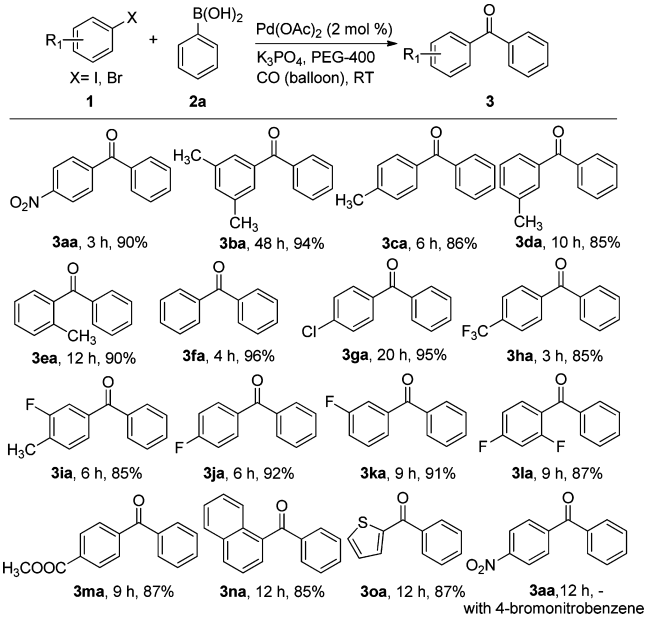


entry	$tBuCO_2H$	time (h)	yield of **3ba** (%)	yield of **3b′a′** (%)
1		6	48	50
2	**$tBuCO_2H$**	48	**94**	**trace**

[a]Reaction conditions (unless otherwise stated): **1b** (0.5 mmol), **2a** (0.75 mmol), CO (balloon), K_3PO_4 (0.75 mmol), $tBuCO_2H$ (0.25 mmol), $Pd(OAc)_2$ (2 mol %), PEG-400 (2.0 g), rt.

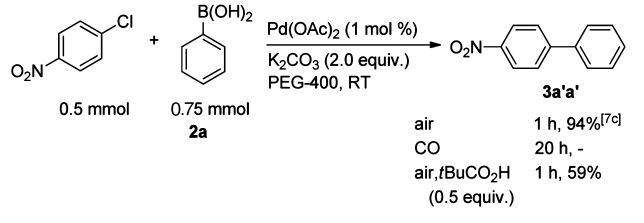
We next examined various aryl halides to couple with phenylboronic acid (**2a**) and CO (ambient pressure) by using K_3PO_4/$tBuCO_2H$ as the base and $Pd(OAc)_2$ as the catalyst in PEG-400 at room temperature (Scheme 1). The reactions worked smoothly with aryl iodides having *ortho*-, *meta*-, and *para*-substituents on the aryl ring to afford desired products **3aa**–**3oa** in 85–96% yields. A variety of functional groups such as methyl, trifluoromethyl, trifluoromethoxy, chloro, fluoro,

Scheme 1. Carbonylative Suzuki Reactions of Aryl Halides with 2a at Ambient Temperature and Pressure



methyl ester, and nitro on the aryl ring were well tolerated under the optimized reaction conditions. 1-Iodonaphthalene was found to be a good substrate for the transformation to furnish carbonylative product **3na** in 85% yield. Moreover, 2-iodothiophene as an example of a heterocyclic iodide gave 87% yield of desired coupling product **3oa**. Unfortunately, 4-bromonitrobenzene was unreactive. However, our previous report indicated that this catalytic system was efficient for the Suzuki reactions using aryl chlorides and bromides as substrates.[7c,d] To explain this observation, the control experiments were conducted: Suzuki reaction was completely inhibited (the desired product was not observed in 20 h) when the catalytic system of the previous report[7c] was performed in carbon monoxide atmosphere (ambient pressure), whereas this Suzuki reaction became quite slow (59% yield after1 h) when the pivalic acid was added to the original catalytic system (Scheme 2). These experiments suggest that the carbon monoxide plays a decisive role in deactivating or poisoning palladium catalyst.

Scheme 2. Effect of Various Conditions on the Suzuki Reaction of 4-Chloronitrobenzene and Phenylboronic Acid



Interestingly, double carbonylation of diiodobenzenes, including 1,2-diiodobenzene (**1q**), 1,3-diiodobenzene (**1r**), and 1,4-diiodobenzene (**1s**), provided diketones in 85%, 80%, and 95% yields, respectively (Scheme 3). The diketones are key intermediates for advanced functional materials.[1b,d]

Subsequently, the scope of the catalytic system for various arylboronic acids was evaluated (Scheme 4). Arylboronic acids

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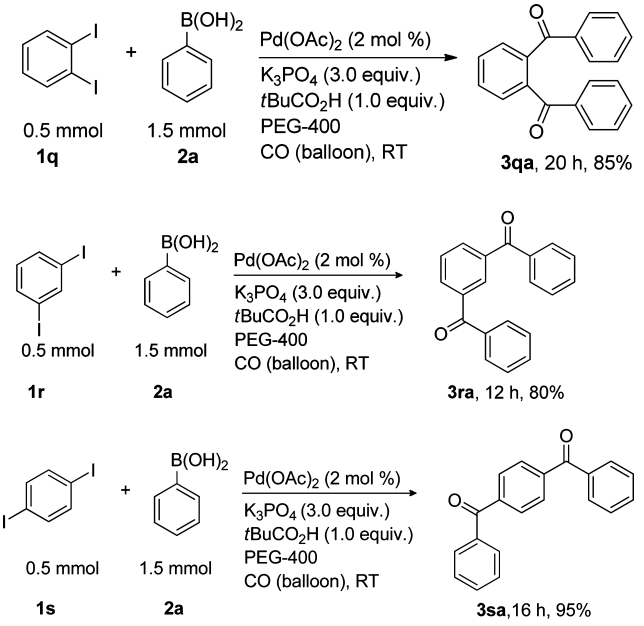
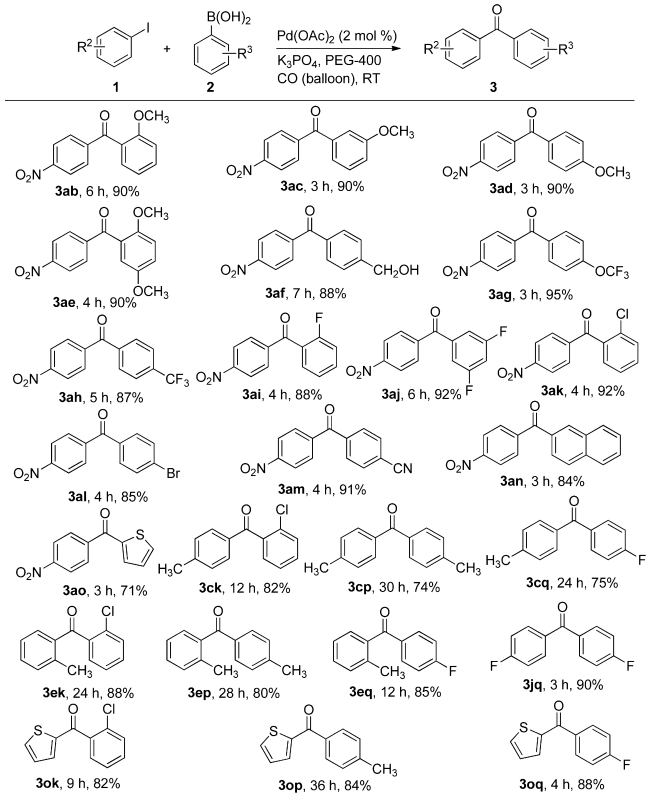
Scheme 3. Double Carbonylative Suzuki Reactions of Diiodobenzenes



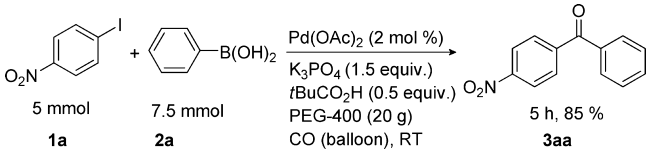
Scheme 4. Carbonylative Suzuki Reactions of Arylboronic Acids with Aryl Iodides at Ambient Temperature and Pressure



having either electron-donating or electron-withdrawing substituents worked well and delivered expected products in good to excellent yields. Remarkably, sensitive functional groups, such as hydroxyl, chloro, bromo, and nitrile, were well tolerated (i.e., **3af**, **3ak**, **3ck**, **3ek**, **3ok**, **3al**, and **3am**). Sterically hindered arylboronic acids also underwent the reaction smoothly and gave carbonylative Suzuki products up to 92% yield (i.e., **3ab**, **3ae**, **3ak**, **3ck**, **3ek**, and **3ok**). To our delight, a heterocyclic boronic acid, 2-thiopheneboronic acid (**2o**), was successfully transformed to desire product in a good yield (**3ao**) with a lower catalyst loading. Additionally, 4,4′-difluorobenzophenone (**3jq**), a key intermediate in the synthesis of denagliptin used for the treatment of type II diabetes, was produced in 90% yield under the applied reaction conditions.[11] However, 2,6-dimethylphenylboronic acid, 4-pyridinylboronic acid, and potassium phenyltrifluoroborate were found to be ineffective educts.

Encouraged by the results presented above, we subsequently carried out a carbonylative Suzuki reaction on a gram scale to demonstrate its utility. With 5 mmol of **1a**, **3aa** was produced in 85% yield under normal conditions (Scheme 5). Furthermore,

Scheme 5. Gram-Scale Synthesis of 3aa



the recyclability of the catalytic system was tested for the model reaction of 4-iodonitrobenzene with phenylboronic acid and carbon monoxide. The catalytic system maintained its high selectivity for nine consecutive cycles (Figure 1). After the nine-

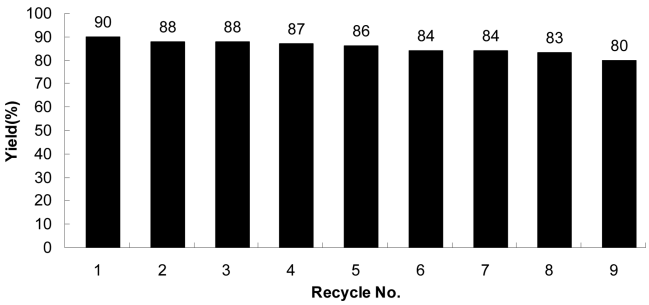


Figure 1. Catalyst reusability study.

run recycling uses, the total leaching of Pd to the combined diethyl ether extracts was found to be 4.2% (percentage of the Pd placed in the reaction) by ICP analysis.

In order to ascertain the real working catalyst, transmission electron microscopy (TEM) was used to examine the sample collected from the mixture of the model reaction under the standard conditions. The TEM result revealed palladium nanoparticles in situ generated and dispersed well in PEG-400 with an average particle size of 2.6 nm (Figure 2), consistent with our previous reports.[7] Additionally, ex situ generated palladium nanoparticles were prepared in PEG-400 according to our previously described method[7c] and then directly utilized to catalyze the model reaction under the standard conditions to furnish product **3aa** in 83%, comparable to the yield using the in situ generated palladium nanoparticles. Although the in situ generated palladium nanoparticles showed good activity, we still did not know whether the catalysis occurred on the cluster surface or by leached Pd species.[5g,12] Hence, control experiments were conducted to assess the homo/heterogeneous nature of the active nanocatalyst. A large excess of Hg(0) (relative to palladium) was added to the model

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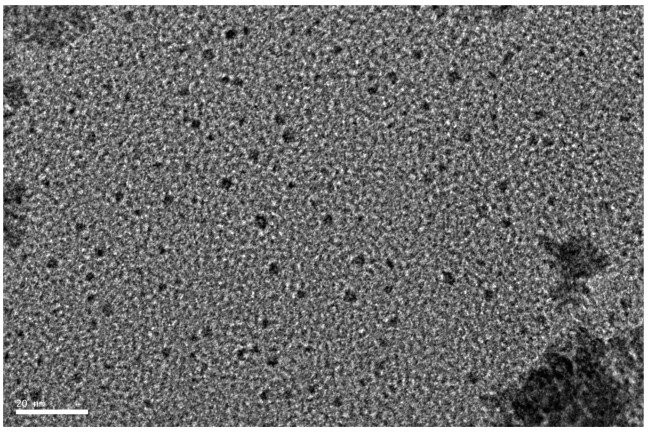
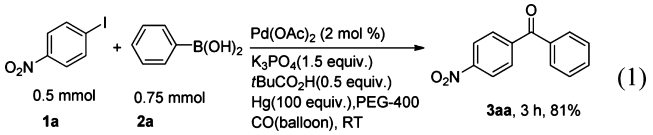


Figure 2. TEM image of the in situ generated palladium nanoparticles (scale bar = 20 nm).

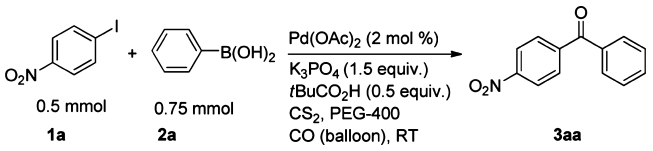
reaction under the standard conditions and had no significant effect on the catalytic activity (eq 1). Furthermore, the



(1)

introduction of quantitative CS_2 evaluated the presence of a homo/heterogeneous catalyst (Table 3). When 0.65 equiv of

Table 3. Quantitative CS_2 Poisoning Experiments



entry	CS_2 (equiv)	time (h)	yield (%)
1	0	3	90
2	0.65	3	85
3	1.0	3	<5
4	1.5	3	trace

CS_2 (relative to palladium) was added to the model reaction under the standard conditions, the reaction worked well to give **3aa** in 85% yield (Table 3, entry 2), whereas when the amount of CS_2 was increased to 1.0 and 1.5 equiv, the reactions were completely or almost completely inhibited (Table 3, entries 3 and 4). These poisoning experiments suggest that the active catalyst is very likely to be homogeneous in nature.[13]

In summary, we have described the first examples of a nanopalladium catalytic system for carbonylative Suzuki reactions of aryl iodides and have also successfully carried out the transformation under ambient temperature and pressure for the first time. Substrates with electron-donating or electron-withdrawing functionality, *ortho*-substitution, as well as active groups proceeded well and afforded the desired products in good to excellent yields. In addition, the double carbonylative functionalization of diiodobenzenes, which is rarely reported, is efficient in our catalytic system. Notably, the catalytic system is in situ generated, which can avoid cumbersome processes for the preparation of metal nanoparticles. In addition, the catalytic system can be recyclable. These features make the protocol attractive for broad applications. Our significant mechanistic studies suggest a typical heterogeneous reaction process is unlikely to be in operation.

EXPERIMENT SECTION

General Procedure A: Preparation of (4-Nitrophenyl)-(phenyl)methanone. A 25-mL flask was charged with 4-iodonitrobenzene (0.5 mmol, 127.0 mg), phenylboronic acid (0.75 mmol, 92.4 mg), palladium acetate (0.01 mmol, 2.4 mg), K_3PO_4 (0.75 mmol, 164.2 mg), tBuCO$_2$H (0.25 mmol, 25.8 mg), and PEG-400 (2.0 g) before standard cycles of evacuation and backfilling with dry and pure carbon monoxide. The mixture was stirred under ambient temperature and pressure for the indicated time. At the end of the reaction, the reaction mixture was extracted with diethyl ether (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/diethyl ether = 25:1).

In the recycling experiment, the residue was subjected to a second run by charging it with the same substrates as mentioned above without further addition of $Pd(OAc)_2$ and PEG 400. In the third, sixth, and eighth runs, another 0.5 mL of PEG-400 was added to the reaction mixture.

General Procedure B: Preparation of 1,2-Phenylenebis-(phenylmethanone). A 25-mL flask was charged with 1,2-diiodobenzene (0.5 mmol, 171.2 mg), phenylboronic acid (1.5 mmol, 184.8 mg), palladium acetate (0.01 mmol, 2.4 mg), K_3PO_4 (1.5 mmol, 328.4 mg), tBuCO$_2$H (0.5 mmol, 51.6 mg), and PEG-400 (2.0 g) before standard cycles of evacuation and backfilling with dry and pure carbon monoxide. The mixture was stirred under ambient temperature and pressure for the indicated time. At the end of the reaction, the reaction mixture was extracted with diethyl ether (3 × 15 mL). The organic phases were combined, and the volatile components were evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate/triethylamine = 25:1:0.1).

(4-Nitrophenyl)(phenyl)methanone (3aa).[14] Following general procedure A, **3aa** was isolated as a light pink solid (102 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.8 Hz, 2 H), 7.92 (d, J = 8.8 Hz, 2 H), 7.79−7.77 (m, 2 H), 7.64 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.51 ppm (t, J = 7.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 149.8, 142.9, 136.3, 133.5, 130.7, 130.1, 128.7, 123.5 ppm; mp 136.8−137.2 °C.

3,5-Dimethylphenyl)(phenyl)methanone (3ba).[14] Following general procedure A, **3ba** was isolated as a light yellow solid (99 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 2 H), 7.56 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.46 (t, J = 7.8 Hz, 2 H), 7.38 (s, 2 H), 7.20 (s, 1 H), 2.36 ppm (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 137.88, 137.86, 137.7, 134.0, 132.2, 130.0, 128.2, 127.8, 21.20 ppm; mp 58.4−59.3 °C.

Phenyl(*p*-tolyl)methanone (3ca).[14] Following general procedure A, **3ca** was isolated as a white solid with low melting point (84 mg, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.75 (m, 2 H), 7.71 (d, J = 8.0 Hz, 2 H), 7.56 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.46 (t, J = 7.5 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 2.42 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 143.2, 137.9, 134.8, 132.1, 130.3, 129.9, 129.0, 128.2, 21.6 ppm.

Phenyl(*m*-tolyl)methanone (3da).[14] Following general procedure A, **3da** was isolated as light yellow oil (83 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 2H), 7.61 (s, 1 H), 7.60−7.54 (m, 2 H), 7.46 (m, 2 H), 7.39−7.32 (m, 2 H), 2.40 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 138.1, 137.7, 137.6, 133.2, 132.3, 130.4, 130.0, 128.2, 128.1, 127.4, 21.4 ppm.

Phenyl(*o*-tolyl)methanone (3ea).[14] Following general procedure A, **3ea** was isolated as a light yellow oil (88 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 2 H), 7.56 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 2 H), 7.38 (td, J = 7.4 Hz, J = 1.6 Hz, 1 H), 7.31−7.21 (m, 3 H), 2.31 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 138.6, 137.7, 136.7, 133.1, 131.0, 130.2, 130.1, 128.5, 128.4, 125.2, 20.0 ppm.

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Benzophenone (3fa).[14] Following general procedure A, **3fa** was isolated as a white solid with low melting point (87 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.78 (m, 4 H), 7.57 (tt, J = 7.4 Hz, J = 1.3 Hz, 2 H), 7.46 ppm (t, J = 7.6 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.0, 128.2 ppm.

(4-Chlorophenyl)(phenyl)methanone (3ga).[14] Following general procedure A, **3ga** was isolated as a white solid (103 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.72 (m, 4 H), 7.58 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.49−7.43 ppm (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 138.9, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.4 ppm; mp 74.3−74.7 °C.

Phenyl(4-(trifluoromethyl)phenyl)methanone (3ha).[14] Following general procedure A, **3ha** was isolated as a white solid (106 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.0 Hz, 2 H), 7.80−7.77 (m, 2 H), 7.73 (d, J = 8.0 Hz, 2 H), 7.61 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.49 ppm (t, J = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 140.7, 136.7, 133.7 (q, J = 32 Hz), 133.1, 130.11, 130.08, 128.5, 125.3 (q, J = 4 Hz), 123.6 ppm (q, J = 271 Hz); mp 116.4−116.9 °C.

(3-Fluoro-4-methylphenyl)(phenyl)methanone (3ia). Following general procedure A, **3ia** was isolated as a light yellow solid (91 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.75 (m, 2 H), 7.58 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.49−7.47 (m, 3 H), 7.45 (s, 1 H), 7.27 (t, J = 7.5 Hz, 1 H), 2.35 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2 (d, J = 2 Hz), 160.9 (d, J = 245 Hz), 137.4, 137.0 (d, J = 6 Hz), 132.5, 131.3 (d, J = 5 Hz), 130.2 (d, J = 17 Hz), 129.9, 128.3, 125.8 (d, J = 3 Hz), 116.5 (d, J = 23 Hz), 14.8 ppm (d, J = 4 Hz); HRMS (ESI) calcd for $C_{14}H_{12}FO$ [M + H] 215.08722, found 215.08641; IR ν_{max} (KBr)/cm^{-1} 3414, 3068, 2929, 2855, 1651, 1598, 1500, 1449, 1421, 1384, 1288, 899, 832, 723, 697; mp 43.7−44.5 °C.

(4-Fluorophenyl)(phenyl)methanone (3ja).[14] Following general procedure A, **3ja** was isolated as a light yellow oil (92 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.86 (m, 2 H), 7.74−7.76 (m, 2 H), 7.58 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.47 (t, J = 7.5 Hz, 2 H), 7.14 ppm (t, J = 8.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 165.4 (d, J = 253 Hz), 137.5, 133.8 (d, J = 3 Hz), 132.61, 132.58 (d, J = 15 Hz), 129.9, 128.4, 115.4 ppm (d, J = 22 Hz).

(3-Fluorophenyl)(phenyl)methanone (3ka).[14] Following general procedure A, **3ka** was isolated as a light yellow oil (91 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80−7.77 (m, 2 H), 7.61−7.54 (m, 2 H), 7.50−7.42 (m, 4 H), 7.27 ppm (tdd, J = 8.3 Hz, J = 2.6 Hz, J = 1.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3 (d, J = 2 Hz), 162.5 (d, J = 247 Hz), 139.6 (d, J = 6 Hz), 137.0, 132.8, 130.0, 129.9, 128.4, 125.8 (d, J = 3 Hz), 119.4 (d, J = 21 Hz), 116.7 ppm (d, J = 22 Hz).

(2,4-Difluorophenyl)(phenyl)methanone (3la).[14] Following general procedure A, **3la** was isolated as light yellow oil (95 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 2 H), 7.61−7.55 (m, 2 H), 7.46 (t, J = 7.7 Hz, 2 H), 7.01−6.96 (m, 1 H), 6.89 (ddd, J = 10.5 Hz, J = 8.2 Hz, J = 2.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.3, 164.9 (dd, J = 253 Hz, J = 12 Hz), 160.9 (dd, J = 254 Hz, J = 12 Hz), 137.4, 133.4, 132.5 (dd, J = 10 Hz, J = 4 Hz), 129.7, 128.5, 123.3 (dd, J = 14 Hz, J = 4 Hz), 111.8 (dd, J = 21 Hz, J = 4 Hz), 104.7 ppm (t, J = 25 Hz).

Methyl 4-Benzoylbenzoate (3ma).[14] Following general procedure A, **3ma** was isolated as white solid (104 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 2 H), 7.82 (d, J = 8.6 Hz, 2 H), 7.79−7.77 (m, 2 H), 7.60 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.48 (t, J = 7.6 Hz, 2 H), 3.94 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 166.3, 141.3, 136.9, 133.2, 132.9, 130.1, 129.8, 129.5, 128.4, 52.4 ppm; mp 108.5−108.9 °C.

Naphthalen-1-yl(phenyl)methanone (3na).[14] Following general procedure A, **3na** was isolated as light white solid (99 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 9.0 Hz, 1 H), 7.99 (d, J = 8.1 Hz, 1 H), 7.91 (d, J = 7.5 Hz, 1 H), 7.86 (d, J = 8.4 Hz, 2 H), 7.60−7.56 (m, 2 H), 7.55−7.48 (m, 3 H), 7.45 ppm (t, J = 7.7 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 138.2, 136.3, 133.7, 133.2, 131.2, 130.9, 130.4, 128.4, 128.3, 127.7, 127.2, 126.4, 125.6, 124.3 ppm; mp 73.1−73.8 °C.

Phenyl(thiophen-2-yl)methanone (3oa).[14] Following general procedure A, **3oa** was isolated as a light yellow solid (82 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.83 (m, 2 H), 7.70 (dd, J = 4.9 Hz, J = 1.1 Hz, 1 H), 7.62 (dd, J = 3.8 Hz, J = 1.1 Hz, 1 H), 7.57 (tt, J = 7.4 Hz, J = 1.3 Hz, 1 H), 7.48 (t, J = 7.5 Hz, 2 H), 7.14 ppm (dd, J = 4.9 Hz, J = 3.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.2, 143.6, 138.1, 134.8, 134.2, 132.2, 129.1, 128.4, 127.9 ppm; mp 49.4−50.3 °C.

1,2-Phenylenebis(phenylmethanone) (3qa).[14] Following general procedure B, **3qa** was isolated as a white solid (122 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.67 (m, 4 H), 7.60 (s, 4 H), 7.50 (tt, J = 7.4 Hz, J = 1.3 Hz, 2 H), 7.35 ppm (t, J = 7.7 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 140.0, 137.2, 133.0, 130.3, 129.8, 129.7, 128.3 ppm; mp 145.8−146.4 °C.

1,3-Phenylenebis(phenylmethanone) (3ra).[14] Following general procedure B, **3ra** was isolated as a light yellow solid (114 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1 H), 8.00 (dd, J = 7.7 Hz, J = 1.7 Hz, 2 H), 7.82−7.79 (m, 4 H), 7.65−7.54 (m, 3 H), 7.47 ppm (t, J = 7.6 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 137.7, 136.9, 133.4, 132.8, 131.2, 130.0, 128.5, 128.4 ppm; mp 99.5−100.1 °C.

1,4-Phenylenebis(phenylmethanone) (3sa).[14] Following general procedure B, **3sa** was isolated as a light yellow solid (136 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 4 H), 7.83−7.81 (m, 4 H), 7.61 (tt, J = 7.4 Hz, J = 1.3 Hz, 2 H), 7.50 ppm (t, J = 7.6 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 140.6, 136.9, 133.0, 130.1, 129.7, 128.5 ppm; mp 164.1−164.6 °C.

(2-Methoxyphenyl)(4-nitrophenyl)methanone (3ab).[14] Following general procedure A, **3ab** was isolated as a light yellow solid (116 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.9 Hz, 2 H), 7.89 (d, J = 8.9 Hz, 2 H), 7.52 (ddd, J = 8.8 Hz, J = 7.0 Hz, J = 1.4 Hz, 1 H), 7.45 (dd, J = 7.5 Hz, J = 1.8 Hz, 1 H), 7.07 (td, J = 7.5 Hz, J = 0.9 Hz, 1 H), 6.98 (d, J = 8.3 Hz, 1 H), 3.66 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 157.6, 149.9, 143.1, 133.3, 130.2, 127.3, 123.4, 120.9, 111.5, 55.4 ppm; mp 117.8−118.2 °C.

(3-Methoxyphenyl)(4-nitrophenyl)methanone (3ac).[14] Following general procedure A, **3ac** was isolated as a yellow solid (116 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.9 Hz, 2 H), 7.91 (d, J = 8.9 Hz, 2 H), 7.39 (t, J = 7.9 Hz, 1 H), 7.34−7.33 (m, 1 H), 7.28 (dt, J = 8.0, 1.3 Hz, 1 H), 7.17 (ddd, J = 8.2, 2.7, 1.0 Hz, 1 H), 3.85 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.6, 159.8, 149.8, 142.9, 137.5, 130.6, 129.6, 123.5, 122.9, 119.9, 114.2, 55.5 ppm; mp 79.1−79.9 °C.

(4-Methoxyphenyl)(4-nitrophenyl)methanone (3ad).[14] Following general procedure A, **3ad** was isolated as a white solid (116 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2 H), 7.85 (d, J = 8.8 Hz, 2 H), 7.78 (d, J = 8.9 Hz, 2 H), 6.96 (d, J = 8.9 Hz, 2 H); 3.88 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.4, 164.0, 149.4, 143.7, 132.6, 130.3, 128.8, 123.4, 113.9, 55.6 ppm; mp 122.1−122.7 °C.

(2,5-Dimethoxyphenyl)(4-nitrophenyl)methanone (3ae).[14] Following general procedure A, **3ae** was isolated as a yellow solid (129 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.9 Hz, 2 H), 7.89 (d, J = 8.9 Hz, 2 H), 7.06 (dd, J = 9.0 Hz, J = 3.1 Hz, 1 H), 6.99 (d, J = 3.1 Hz, 1 H), 6.92 (d, J = 9.0 Hz, 1 H), 3.79 (s, 3 H), 3.59 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 153.7, 151.8, 150.0, 143.0, 130.2, 127.7, 123.4, 119.1, 114.7, 113.0, 56.0, 55.9 ppm; mp 123.5−124.2 °C.

(4-(Hydroxymethyl)phenyl)(4-nitrophenyl)methanone (3af).[14] Following general procedure A, **3af** was isolated as a light yellow solid (113 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2 H), 7.90 (d, J = 8.9 Hz, 2 H), 7.78 (d, J = 8.3 Hz, 2 H), 7.50 (d, J = 8.3 Hz, 2 H), 4.81 (s, 2 H), 1.76 ppm (br s, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 149.8, 146.7, 142.9, 135.4, 130.6, 130.4, 126.7, 123.5, 64.5 ppm; mp 141.2−141.6 °C.

(4-Nitrophenyl)(4-(trifluoromethoxy)phenyl)methanone (3ag). Following general procedure A, **3ag** was isolated as a white solid (148 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.9 Hz, 2 H), 7.91 (d, J = 8.9 Hz, 2 H), 7.85 (d, J = 8.9 Hz, 2 H), 7.34 ppm (d, J = 8.9 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 152.9 (d, J = 2 Hz), 150.0, 142.3, 134.4, 132.1, 130.6, 123.7, 120.5 (q, J = 1 Hz), 120.3 ppm (q, J = 258 Hz); HRMS (ESI) calcd for $C_{14}H_9F_3NO_4$ [M + H] 312.04837, found 312.04850; IR ν_{max} (KBr)/

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cm^{-1} 3413, 3076, 1673, 1603, 1587, 1520, 1350, 1269, 1214, 852; mp 56.8−57.2 °C.

(4-Nitrophenyl)(4-(trifluoromethyl)phenyl)methanone (3ah).[14] Following general procedure A, **3ah** was isolated as a white solid (128 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.9 Hz, 2 H), 7.94 (d, J = 8.9 Hz, 2 H), 7.89 (d, J = 8.6 Hz, 2 H), 7.78 ppm (d, J = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 150.2, 141.8, 139.2, 134.7 (q, J = 32 Hz), 130.8, 130.2, 125.8 (q, J = 4 Hz), 123.8, 123.4 ppm (q, J = 273 Hz); mp 105.1−105.6 °C.

(2-Fluorophenyl)(4-nitrophenyl)methanone (3ai).[14] Following general procedure A, **3ai** was isolated as a white solid (108 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.9 Hz, 2 H), 7.94 (d, J = 8.9 Hz, 2 H), 7.64−7.56 (m, 2 H), 7.30 (td, J = 7.6 Hz, J = 1.0 Hz, 1 H), 7.19−7.14 ppm (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.7, 160.3 (d, J = 252 Hz), 150.2, 142.4, 134.4 (d, J = 9 Hz), 131.0 (d, J = 2 Hz), 130.4 (d, J = 1 Hz), 125.6 (d, J = 14 Hz), 124.7 (d, J = 4 Hz), 123.6, 116.5 ppm (d, J = 21 Hz); mp 116.3−116.8 °C.

(3,5-Difluorophenyl)(4-nitrophenyl)methanone (3aj). Following general procedure A, **3aj** was isolated as a white solid (121 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.9 Hz, 2 H), 7.92 (d, J = 8.9 Hz, 2 H), 7.31−7.28 (m, 2 H), 7.09 ppm (tt, J = 8.4 Hz, J = 2.3 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.1 (t, J = 3 Hz), 162.9 (dd, J = 251 Hz, J = 12 Hz), 150.2, 141.5, 139.1(t, J = 8 Hz), 130.7, 123.8, 113.0 (dd, J = 19 Hz, J = 8 Hz), 108.8 ppm (t, J = 25 Hz); HRMS (ESI) calcd for $C_{13}H_8F_2NO_3$ [M + H] 264.04722, found 264.04683; IR ν_{max} (KBr)/cm^{-1} 3416, 3080, 1669, 1594, 1523, 1442, 1330, 1239, 869, 815, 729; mp 122.6−123.0 °C.

(2-Chlorophenyl)(4-nitrophenyl)methanone (3ak).[14] Following general procedure A, **3ak** was isolated as a light yellow solid (120 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.9 Hz, 2 H), 7.93 (d, J = 8.9 Hz, 2 H), 7.51−7.45 (m, 2 H), 7.43−7.38 ppm (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 150.5, 141.2, 137.2, 132.1, 131.4, 130.7, 130.3, 129.5, 127.1, 123.8 ppm; mp 100.2−100.8 °C.

(4-Bromophenyl)(4-nitrophenyl)methanone (3al).[14] Following general procedure A, **3al** was isolated as a white solid (130 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.9 Hz, 2 H), 7.89 (d, J = 8.9 Hz, 2 H), 7.65 ppm (s, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 149.9, 142.3, 134.9, 132.0, 131.5, 130.6, 128.8, 123.6 ppm; mp 123.6−124.3 °C.

4-(4-Nitrobenzoyl)benzonitrile (3am).[14] Following general procedure A, **3am** was isolated as a light yellow solid (115 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.9 Hz, 2 H), 7.92 (d, J = 8.9 Hz, 2 H), 7.87 (d, J = 8.6 Hz, 2 H), 7.82 ppm (d, J = 8.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 150.3, 141.3, 139.7, 132.5, 130.8, 130.3, 123.8, 117.6, 116.7 ppm; mp 151.7−152.4 °C.

Naphthalen-2-yl(4-nitrophenyl)methanone (3an).[14] Following general procedure A, **3an** was isolated as a white solid (116 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.5 Hz, 2 H), 8.21 (s, 1 H), 7.97 (d, J = 8.5 Hz, 2 H), 7.95−7.87 (m, 4 H), 7.64 (t, J = 7.6 Hz, 1 H), 7.57 ppm (t, J = 7.5 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 149.8, 143.2, 135.6, 133.5, 132.4, 132.2, 130.7, 129.5, 129.0, 128.8, 127.9, 127.2, 125.2, 123.6 ppm; mp 145.8−146.3 °C.

(4-Nitrophenyl)(thiophen-2-yl)methanone (3ao).[14] Following general procedure A, **3ao** was isolated as light yellow solid (83 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.9 Hz, 2 H), 7.98 (d, J = 8.9 Hz, 2 H), 7.80 (dd, J = 4.9 Hz, J = 1.1 Hz, 1 H), 7.60 (dd, J = 3.8 Hz, J = 1.1 Hz, 1 H), 7.19 ppm (dd, J = 4.9 Hz, J = 3.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 149.8, 143.3, 142.6, 135.7, 135.5, 129.9, 128.4, 123.7 ppm; mp 173.8−174.3 °C.

(2-Chlorophenyl)(*p*-tolyl)methanone (3ck).[14] Following general procedure A, **3ck** was isolated as a light yellow solid (94 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.0 Hz, 2 H), 7.45−7.38 (m, 2 H), 7.35−7.33 (m, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 2.4 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.9, 144.7, 138.9, 134.0, 131.2, 130.9, 130.2, 130.0, 129.3, 129.0, 126.6, 21.7 ppm; mp 92.8−93.6 °C.

Di-*p*-tolylmethanone (3cp).[14] Following general procedure A, **3 cP** was isolated as a white solid (78 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.0 Hz, 4 H), 7.25 (d, J = 8.0 Hz, 4 H). 2.42 ppm (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 142.9, 135.2, 130.2, 128.9, 21.6 ppm; mp 76.0−76.6 °C.

(4-Fluorophenyl)(*p*-tolyl)methanone (3cq).[14] Following general procedure A, **3cq** was isolated as a white solid (80 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.0 Hz, J = 4.0 Hz, 2 H), 7.67 (d, J = 8.0 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.13 (t, J = 8.0 Hz, 2H), 2.42 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 165.2 (d, J = 252 Hz), 143.3, 134.8, 134.1 (d, J = 3 Hz), 132.5 (d, J = 9 Hz), 130.1, 129.0, 115.3 (d, J = 22 Hz), 21.6 ppm; mp 91.8−92.3 °C.

(2-Chlorophenyl)(*o*-tolyl)methanone (3ek).[14] Following general procedure A, **3ek** was isolated as a pale yellow liquid (101 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.35 (m, 4 H), 7.35−7.27 (m, 3 H), 7.20−7.15 (m, 1 H), 2.56 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 139.6, 139.5, 136.9, 132.0, 131.8, 131.4, 131.3, 130.3, 129.9, 126.7, 125.5, 21.1 ppm.

***o*-Tolyl(*p*-tolyl)methanone (3ep).**[14] Following general procedure A, **3ep** was isolated as pale yellow liquid (84 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 8.2, 2 H), 7.35 (dt, J = 7.1, 2.0, 1 H), 7.29−7.19 (m, 5 H), 2.40(s, 3 H), 2.30 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 144.0, 138.9, 136.4, 135.1, 130.8, 130.2, 129.9, 129.1, 128.2, 125.1, 21.6, 19.8 ppm.

(4-Fluorophenyl)(*o*-tolyl)methanone (3eq).[14] Following general procedure A, **3eq** was isolated as pale yellow liquid (91 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83−7.79(m, 2 H), 7.40−7.36(m, 1H), 7.28−7.24 (m, 3 H), 7.13−7.08 (m, 2 H), 2.30 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 165.8 (d, J = 254 Hz), 138.4, 136.6, 134.1 (d, J = 3 Hz), 132.7 (d, J = 9 Hz), 131.0, 130.3, 128.2, 125.3, 115.6 (d, J = 22 Hz), 19.9 ppm.

4,4′-Difluorobenzophenone (3jq).[14] Following general procedure A, **3jt** was isolated as a white solid (98 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81−7.76 (m, 4 H), 7.17−7.11 ppm (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 165.3 (d, J = 253 Hz), 133.6 (d, J = 3 Hz), 132.5 (d, J = 9 Hz), 115.5 ppm (d, J = 22 Hz); mp 106.7−107.2 °C.

(2-Chlorophenyl)(thiophen-2-yl)methanone (3ok).[14] Following general procedure A, **3ok** was isolated as a pale yellow liquid (91 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 4.9 Hz, J = 1.2 Hz, 1 H), 7.47−7.36 (m, 4 H), 7.35−7.31 (m, 1 H), 7.09 ppm (dd, J = 4.9 Hz, J = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.0, 143.6, 138.3, 135.9, 135.5, 131.2, 131.1, 130.2, 128.8, 128.3, 126.5 ppm.

Thiophen-2-yl(*p*-tolyl)methanone (3op).[14] Following general procedure A, **3op** was isolated as a white solid (85 mg, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, J = 8.0, 2 H), 7.67 (dd, J = 5.0 Hz, J = 1.1 Hz, 1 H), 7.62 (dd, J = 4.0 Hz, J = 1.1 Hz, 1 H), 7.27 (d, J = 7.9 Hz, 2 H), 7.13 (dd, J = 4.9 Hz, J = 3.8 Hz, 1 H), 2.41 ppm (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 187.8, 143.7, 142.9, 135.3, 134.4, 133.7, 129.3, 129.0, 127.8, 21.5 ppm; mp 67.8−68.3 °C.

(4-Fluorophenyl)(thiophen-2-yl)methanone (3oq).[14] Following general procedure A, **3oq** was isolated as a white solid (91 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90−7.86 (m, 2 H), 7.70 (dd, J = 5.0 Hz, J = 1.1 Hz, 1 H), 7.60 (dd, J = 3.8 Hz, J = 1.1 Hz, 1H), 7.17−7.13 ppm (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.6, 165.2(d, J = 252 Hz), 143.3, 134.6, 134.3 (d, J = 3 Hz), 134.2, 131.7 (d, J = 9 Hz), 128.0, 115.5 ppm (d, J = 22 Hz); mp 95.5−95.8 °C.

Hg(0) Poisoning Test. As general procedure A, a reaction of 4-iodonitrobenzene **1a** (0.5 mmol, 127.0 mg), phenylboronic acid **2a** (0.75 mmol, 92.4 mg), palladium acetate (0.01 mmol, 2.4 mg), K_3PO_4 (0.75 mmol, 164.2 mg), and tBuCO$_2$H (0.25 mmol, 25.8 mg) in PEG-400 (2.0 g), with the addition of elemental mercury (1 mmol, 100 equiv, 200.6 mg) (relative to palladium), was conducted. Following the reaction for 3 h under ambient temperature and pressure, the yield of the desired product **3aa** was 81%, suggesting that the reaction is not inhibited by the introduction of Hg(0) (eq 1).

CS_2 Poisoning Test. As per general procedure A, four reactions of 4-iodonitrobenzene **1a** (0.5 mmol, 127.0 mg), phenylboronic acid **2a** (0.75 mmol, 92.4 mg), palladium acetate (0.01 mmol, 2.4 mg), K_3PO_4 (0.75 mmol, 164.2 mg), and tBuCO$_2$H (0.25 mmol, 25.8 mg) in PEG-400 (2.0 g) were carried out, one as a control. Carbon disulfide, 0.65 equiv, 1.0 equiv, and 1.5 equiv (relative to palladium), respectively, was introduced to the reactions. All reaction mixtures were stirred under ambient temperature and pressure for 3 h. Subsequent analysis of the

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reactions suggests that the reactions are completely inhibited when employing ≥1.0 equiv of added CS_2.

■ ASSOCIATED CONTENT

Supporting Information

^1H NMR and ^{13}C NMR spectra for products. 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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■ REFERENCES

(1) (a) Maeyama, K.; Yamashita, K.; Saito, H.; Aikawa, S.; Yoshida, Y. *Polym. J.* **2012**, *44*, 315. (b) Chan, C. Y. K.; Zhao, Z. J.; Lam, J. W. Y.; Liu, J. Z.; Chen, S. M.; Lu, P.; Mahtab, F.; Chen, X. J.; Sung, H. H. Y.; Kwok, H. S.; Ma, Y. G.; Williams, I. D.; Wong, K. S.; Tang, B. Z. *Adv. Funct. Mater.* **2012**, *22*, 378. (c) Wen, A.; Wang, Z.; Hang, T.; Jia, Y.; Zhang, T.; Wu, Y.; Gao, X.; Yang, Z. *J. Chromatogr. B* **2007**, *856*, 348. (d) Zhao, W. L.; Carreira, E. M. *Org. Lett.* **2006**, *8*, 99. (e) Ong, A. L.; Kamaruddin, A. H.; Bhatia, S. *Process Biochem.* **2005**, *40*, 3526. (f) Furusawa, M.; Ido, Y.; Tanaka, T.; Ito, T.; Nakaya, K.; Ibrahim, I.; Ohyama, M.; Iinuma, M.; Shirataka, Y.; Takahashi, Y. *Helv. Chim. Acta* **2005**, *88*, 1048. (g) Bosca, F.; Miranda, M. A. *J. Photochem. Photobiol. B* **1998**, *43*, 1. (h) De Kimpe, N.; Keppens, M.; Froncg, G. *Chem. Commun.* **1996**, *5*, 635. (i) Dorman, G.; Prestwich, G. D. *Biochemistry* **1994**, *33*, 5661.

(2) For some recent reviews on Pd-catalyzed carbonylations of aryl halides, see: (a) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Rev.* **2013**, *113*, 1. (b) Wu, X.-F.; Neumann, H.; Beller, M. *Chem. Soc. Rev.* **2011**, *40*, 4986. (c) Grigg, R.; Mutton, S. P. *Tetrahedron* **2010**, *66*, 5515. (d) Brennführer, A.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 4114.

(3) (a) Barnard, C. F. J. *Organometallics* **2008**, *27*, 5402. (b) Barnard, C. F. J. *Org. Process Res. Dev.* **2008**, *12*, 566. (c) Chiusoli, G. P.; Maitlis, P. M. *Synthesis Based on Carbon Monoxide. Metal-Catalysis in Industrial Organic Processes*; RSC Publishing: Cambridge, 2006.

(4) (a) Serp, P.; Philippot, K. *Nanomaterials in Catalysis*; Wiley-VCH: Weinheim, 2013. (b) Astruc, D. *Nanoparticles and Catalysis*; Wiley-VCH: Weinheim, 2008; Vol. *1*.

(5) (a) Taladriz-Blanco, P.; Hervés, P.; Pérez-Juste, J. *Top. Catal.* **2013**, *56*, 1154. (b) Scholten, J. D.; Leal, B. C.; Dupont, J. *ACS Catal.* **2012**, *2*, 184. (c) Molnár, Á. *Chem. Rev.* **2011**, *111*, 2251. (d) Fihri, A.; Bouhrara, M.; Nekoueishahraki, B.; Basset, J.-M.; Polshettiwar, V. *Chem. Soc. Rev.* **2011**, *40*, 5181. (e) Balanta, A.; Godard, C.; Claver, C. *Chem. Soc. Rev.* **2011**, *40*, 4973. (f) Ranu, B. C.; Chattopadhyay, K.; Adak, L.; Saha, A.; Bhadra, S.; Dey, R.; Saha, D. *Pure Appl. Chem.* **2009**, *81*, 2337. (g) Astruc, D. *Inorg. Chem.* **2007**, *46*, 1884. (h) Phan, N. T. S.; van der Sluis, M.; Jones, C. J. *Adv. Synth. Catal.* **2006**, *348*, 609. (i) Astruc, D.; Lu, F.; Ruiz, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 7852. (j) Moreno-Mañas, M.; Pleixats, R. *Acc. Chem. Res.* **2003**, *36*, 638.

(6) (a) Dang, T. T.; Zhu, Y. H.; Ngiam, J. S. Y.; Ghosh, S. C.; Chen, A. Q.; Seayad, A. M. *ACS Catal.* **2013**, *3*, 1406. (b) Li, Z. L; Liu, J. H.; Huang, Z. W.; Yang, Y.; Xia, C. G.; Li, F. W. *ACS Catal.* **2013**, *3*, 839. (c) Prasad, A. S.; Satyanarayana, B. *J. Mol. Catal. A: Chem.* **2013**, *370*, 205. (d) Zhu, Y. H.; Li, C. Z.; Biying, A. O.; Sudarmadji, M.; Chen, A. Q.; Tuan, D. T.; Seayad, A. M. *Dalton Trans.* **2011**, *40*, 9320. (e) Liu, J. M.; Peng, X. G.; Sun, W.; Zhao, Y. W.; Xia, C. G. *Org. Lett.* **2008**, *10*, 3933. (f) Gniewek, A.; Trzeciak, A. M.; Ziółkowski, J. J.; Kępiński, L.; Wrzyszcz, J.; Tylus, W. *J. Catal.* **2005**, *229*, 332. (g) Grigg, R.; Zhang, L. X.; Collardb, S.; Keep, A. *Tetrahedron Lett.* **2003**, *44*, 6979.

(7) (a) Yao, L. F.; Zhou, Q.; Han, W.; Wei, S. H. *Eur. J. Org. Chem.* **2012**, 6856. (b) Han, W.; Liu, N.; Liu, C.; Jin, Z. L. *Chin. Chem. Lett.* **2010**, *21*, 1411. (c) Han, W.; Liu, C.; Jin, Z. L. *Adv. Synth. Catal.* **2008**, *350*, 501. (d) Han, W.; Liu, C.; Jin, Z. L. *Org. Lett.* **2007**, *9*, 4005.

(8) (a) Zahmakıran, M.; Özkar, S. *Nanoscale* **2011**, *3*, 3462. (b) Mohanty, A.; Garg, N.; Jin, R. C. *Angew. Chem., Int. Ed.* **2010**, *49*, 4962.

(9) (a) Colacino, E.; Martinez, J.; Lamaty, F.; Patrikeeva, L. S.; Khemchyan, L. L.; Ananikov, V. P.; Beletskaya, I. P. *Coord. Chem. Rev.* **2012**, *256*, 2893. (b) Chen, J.; Spear, S. K.; Huddleston, J. G.; Rogers, R. D. *Green Chem.* **2005**, *7*, 64.

(10) Liu, T.-P.; Xing, C.-H.; Hu, Q.-S. *Angew. Chem., Int. Ed.* **2010**, *49*, 2909.

(11) Appell, R. B.; Boulton, L. T.; Daugs, E. D.; Hansen, M.; Hanson, C. H.; Heinrich, J.; Kronig, C.; Lloyd, R. C.; Louks, D.; Nitz, M.; Praquin, C.; Ramsden, J. A.; Samuel, H.; Smit, M.; Willets, M. *Org. Process Res. Dev.* **2013**, *17*, 69.

(12) (a) Pachón, L. D.; Rothenberg, G. *Appl. Organomet. Chem.* **2008**, *22*, 288. (b) Thathagar, M. B.; Elshof, J. E.; Rothenberg, G. *Angew. Chem., Int. Ed.* **2006**, *45*, 2886. (c) Thathagar, M. B.; Beckers, J.; Rothenberg, G. *Adv. Synth. Catal.* **2003**, *345*, 979.

(13) Widegren, J . A.; Finke, R. G. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317.

(14) The structures of known compounds were confirmed by detailed NMR data comparison with those in the literatures.