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Nickel-Catalyzed Molybdenum-Promoted Carbonylative Synthesis of Benzophenones

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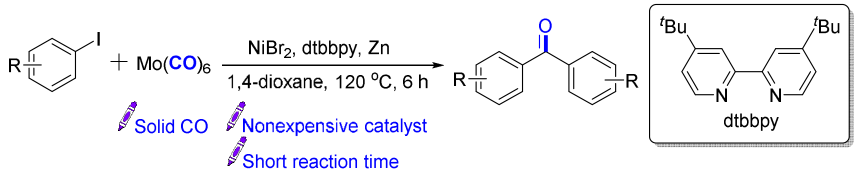
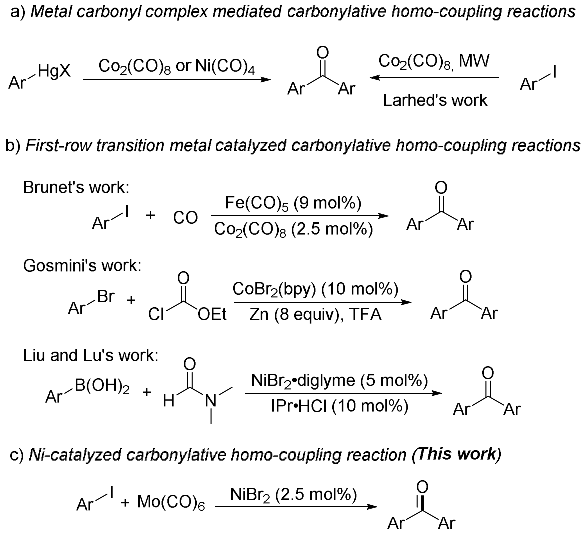


ABSTRACT: A nickel-catalyzed molybdenum-promoted carbonylative coupling reaction for the synthesis of benzophenones from aryl iodides has been developed. Various substituted diaryl ketones were synthesized in moderate to excellent yields under CO gas free conditions. A synergetic effect of both nickel and molybdenum has been observed, which is also responsible for the success of this transformation.

Benzophenones represent an important and versatile structure motif that is frequently present in natural products, materials, pharmaceuticals and other biologically active molecules.[1] Owing to their importance, various synthetic methodologies for the synthesis of diarylketones have been developed. Among them, transition metal catalyzed carbonylative coupling reactions have now emerged as one of the most powerful tools for the preparation of various functionalized ketones.[2] Many impressive improvements have been realized during the past decades since the pioneering works from Heck and co-workers.[3] However, most of the researches on carbonylative coupling reactions were based on palladium catalysts. Although palladium catalyst systems showed higher reactivity and efficiency, their high price and the demand of expensive phosphine ligands usage limited their wider applications, especially in large scales. In this aspect, non-noble metals, especially the first-row transition metals, turned out to be attractive alternatives.[4] Non-noble metals, such as nickel and cobalt, have already been reported to promote carbonylative coupling reactions (Scheme 1, a). Carbonylative homo-coupling of organomercuric halides RHgX with stoichiometric cobalt[5a,5b] and nickel carbonyls[5c] were reported in late 1960s. Knochel's group reported a cobalt mediated carbonylative homo-coupling of organozinc reagents in 1995.[6] In 2003, Larhed and colleagues developed a $Co_2(CO)_8$ mediated ultrafast carbonylative coupling of aryl halides under microwave irradiation.[7] Brunet and Taillefer developed a metal carbonyl-catalyzed carbonylation of aryl halides which lead to symmetric diaryl ketones production.[8] On the other hand, owing to the high toxicity of carbon monoxide, CO gas-free carbonylation reactions have been developed based on various CO surrogates.[9] Gosmini and co-workers developed a cobalt catalyzed carbonylative homo-coupling reaction for the synthesis of symmetrical diaryl ketones from aryl bromides and ethyl chloroformate.[10] Liu, Lu and their co-workers reported a nickel catalyzed carbonylation of arylboronic acids for the synthesis of symmetric diaryl ketones by employing DMF as an abundant and low-cost CO source (Scheme 1, b).[11] Our research group has been interested in developing new carbonylation reactions during the last few years. Recently, we developed a palladium catalyzed carbonylative homo-coupling of aryl iodides with formic acid as the CO source and sodium formate as the reductant.[12] In order to avoid the disadvantages from palladium catalysts, we become interested in developing a non-noble metal catalyzed carbonylation system.

Scheme 1. Non-Noble Metal Promoted Carbonylative Homo-Coupling Reactions of Aryl Halides.



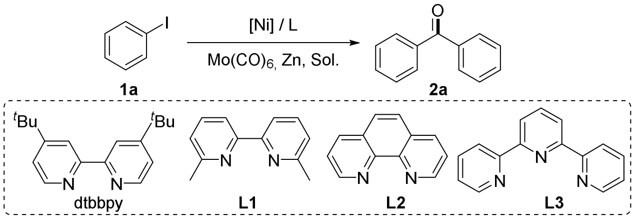
However, in general, one main issue for applying nickel catalyst in cabonylation reactions is the formation of $Ni(CO)_4$. $Ni(CO)_4$ is a highly toxic liquid (boiling point = 43 °C) and mainly applied in

Mond process for the purification of nickel metal. From catalyst point of view, $Ni(CO)_4$ is fully coordinated, due to the high affinity between CO and nickel, which limited the oxidative addition of C-X bond to nickel center and also the migratory insertion of CO. Hence, the choice of proper ligand and the right pressure of CO usually play an important role in the success of a nickel catalyzed carbonylation reaction. Herein, we report a new nickel-catalyzed carbonylative coupling of aryl iodides for the synthesis of benzophenones. With molybdenum carbonyl as the promoter and CO source, good yields of the desired benzophenones can be produced. Interestingly, the synergetic effect of both metals has found to be crucial.

Initially, iodobenzene was selected as the model substrate. To our delight, stirring a solution of iodobenzene, $Mo(CO)_6$ and zinc powder in the presence of $NiCl_2$ and dtbbpy (4,4'-di-*tert*-butyl-2,2'-bipyridine) in 1,4-dioxane at 120 °C, the carbonylative homo-coupling reaction proceeded successfully and the desired product diphenyl ketone was obtained in 64% yield (Table 1, entry 1). The yield was improved slightly to 70% when $NiBr_2$ was used as the catalyst (Table 1, entry 2). Other nickel catalysts, such as NiI_2, $Ni(cod)_2$ and $Ni(acac)_2$, resulted in decreased yields (Table 1, entries 3-5). The electronic and steric effect of the ligand played an important role on the reactivity. Generally, electron-rich ligands facilitate the oxidative addition of the metal to the C-X bonds. Thus, when less electron-rich ligands such as bipyridine and 1,10-phenanthroline was used, the desired ketone was obtained in 63% and 50% yields, respectively (Table 1, entries 6 and 8). Using 6,6'-dimethyl-2,2'-bipyridine **L1** as the ligand gave a moderate yield of 62%, which might be resulted from the steric hindrance effect (Table 1, entry 7). Notably, tridentate ligand **L3** gave similar reactivity to dtbbpy since the strong tridentate bonding of **L3** to nickel might prevent the bonding of multiple CO to the catalyst center (Table 1, entry 9).[13] However, considering the cost of **L3**, we decided choosing dtbbpy for further studies. The use of phosphine ligand turned out to be less effective (see details in SI). Screening of the solvents, such as THF and toluene failed to improve the yields (Table 1, entries 10 and 11, also see details in SI). The concentration of the substrates also affected the yields significantly. The yield was further improved to 74% when the reaction was performed at a higher concentration (Table 1, entry 12). Further screening of the reaction time revealed that prolonged reaction time would result decompose of the product (see details in SI). The best result was obtained when the reaction mixture was stirred at 120 ℃ for 6 hours and the diphenyl ketone was isolated in 86% yield (Table 1, entry 13). Furthermore, in addition to $Mo(CO)_6$, we tested other metal carbonyl complexes in this reaction. $Cr(CO)_6$ was also effective for this transformation, despite in a low yield (Table 1, entry 14). It should be noted that when the reaction was conducted without nickel catalyst, the desired product was obtained in 24% yield (Table 1, entry 15). However, when $Mo(CO)_6$ was replaced with 2 bar of CO gas, only trace amount of ketone was detected (Table 1, entry 16). These reactions indicate that $Mo(CO)_6$ not only acted as a CO surrogate, but also as a co-catalyst in this reaction. It's also important to mention that no reaction occurred in the absence of zinc or replace zinc by metallic manganese.

With the optimized reaction conditions in hand (Table 1, entry 13), we began to investigate the substrates scope of the reaction with various substituted aryl iodides. As summarized in Table 2, a series of substituted aryl iodides were successfully applied to the carbonylative homo-coupling reaction. Both electron-donating group (Table 2, **2a**-**2h**) and electron-withdrawing group (Table 2, **2i**, **2j**, **2l**, **2m**) substituted iodobenzenes were well tolerated and delivered the corresponding diaryl ketones in 57-93% yields. It should be mentioned that fluoro- and chloro-substituted iodobenzenes were well tolerated in this transformation (Table 2, **2i**, **2j** and **2m**). However, when 4-bromo-iodobenzene was used in this reaction, only trace amount of desired product could be detected from the reaction mixture (Table 2, **2k**). Moreover, heteroaryl iodides such as 3-iodothiophene was also subjected to the carbonylative homo-coupling reaction, and the corresponding ketone was conveniently generated in 61% yield (Table 2, **2n**). Besides, 1-iodonaphthalene was tolerated and the corresponding product was produced in 73% yield (Table 2, **2o**).

Table 1. Optimization of the reaction conditions.[a]



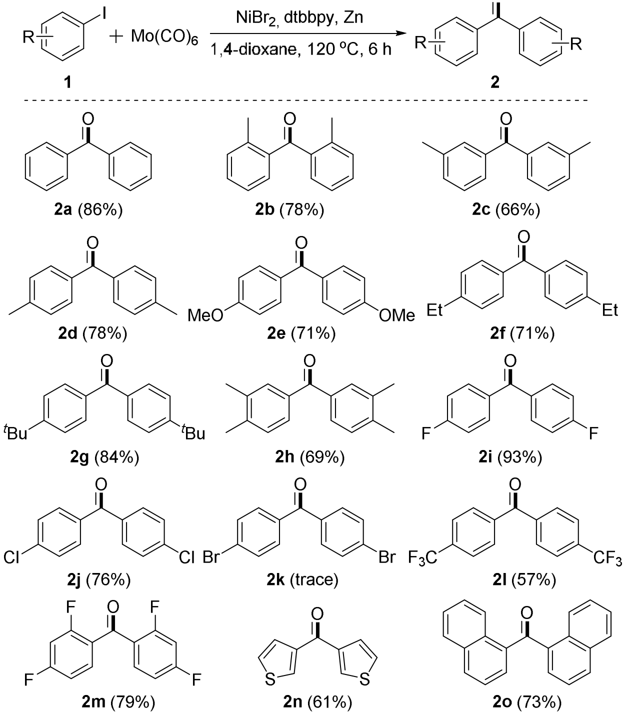
entry	[Ni] (mol%)	ligand (mol%)	solvent	yield[b]
1	$NiCl_2$ (5)	dtbbpy (5)	dioxane	64
2	$NiBr_2$ (5)	dtbbpy (5)	dioxane	70
3	NiI_2 (5)	dtbbpy (5)	dioxane	69
4	$Ni(cod)_2$ (5)	dtbbpy (5)	dioxane	21
5	$Ni(acac)_2$ (5)	dtbbpy (5)	dioxane	57
6	$NiBr_2$ (5)	bpy (5)	dioxane	63
7	$NiBr_2$ (5)	L1 (5)	dioxane	62
8	$NiBr_2$ (5)	L2 (5)	dioxane	50
9	$NiBr_2$ (5)	L3 (5)	dioxane	70
10	$NiBr_2$ (5)	dtbbpy (5)	THF	17
11	$NiBr_2$ (5)	dtbbpy (5)	toluene	17
12[c]	$NiBr_2$ (2.5)	dtbbpy (2.5)	dioxane	74
13[c,d]	**$NiBr_2$ (2.5)**	**dtbbpy (2.5)**	**dioxane**	**90 (86[e])**
14[c,d,f]	$NiBr_2$ (2.5)	dtbbpy (2.5)	dioxane	35
15[c,d]			dioxane	24
16[c,d,g]	$NiBr_2$ (2.5)	dtbbpy (2.5)	dioxane	0

[a] Reaction condition: iodobenzene (0.5 mmol), catalyst, ligand, $Mo(CO)_6$ (1 equiv), Zn (3 equiv), solvent (2 mL), 120 °C, 16 h. [b] GC yield, with dodecane as the internal standard. [c] iodobenzene (1 mmol), $Mo(CO)_6$ (0.5 equiv), Zn (1.5 equiv). [d] 6 h. [e] Isolated yield. [f] $Cr(CO)_6$ was used instead of $Mo(CO)_6$. [g] 2 bar of gaseous CO was used instead of $Mo(CO)_6$.

Then, we turned our attention to test this procedure for the carbonylative cross-coupling reaction. When a mixed substrates (0.5 mmol 1-fluoro-4-iodobenzene **1i** and 0.5 mmol 1-iodo-4-methoxybenzene **1e**) were subjected to the optimized conditions,

2i, cross-coupling products **2ei** and **2e** were obtained in 1.4 : 2.5 : 1 selectivity (Table 3, entry 1). This is different from the previous work,[12] where the homo-coupling product was the major product. In addition, no matter **1i** or **1e** was used excessively, the amount of cross-coupling product **2ei** was somehow larger than that of homo-coupling products **2i** and **2e**, despite with poor selectivity (Table 3, entries 2 and 3). A TEMPO testing was performed as well, and 74% yield of the desired benzophenone can be produced in the presence of 2 equivalents of TEMPO under our standard conditions (Scheme 2). This result can exclude the involvement of radical intermediates in this transformation.

Table 2. Ni-catalyzed carbonylative benzophenones synthesis.[a]

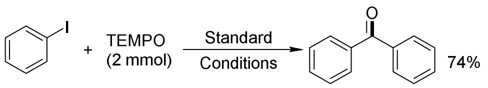


[a]Reaction condition: aryl iodides (1 mmol), NiBr$_2$ (0.025 mmol), dtbbpy (0.025 mmol), Mo(CO)$_6$ (0.5 mmol), Zn (1.5 mmol), 1,4-dioxane (2 mL), 120 °C, 6 h, isolated yield.

Table 3. Carbonylative cross-coupling testings.

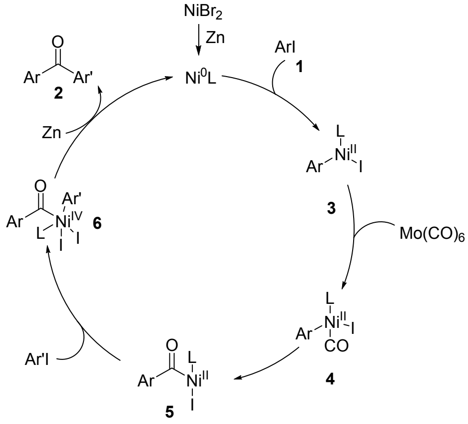
entry	1i (mmol)	1e (mmol)	2i (mmol)	2ei (mmol)	2e (mmol)
1	0.5	0.5	0.13	0.23	0.09
2	0.5	1.0	0.07	0.32	0.24
3	1.0	0.5	0.31	0.37	0.06

Scheme 2. Control experiment with TEMPO.



Concerning the reaction mechanism, Yamane and Ren reported a palladium-catalyzed carbamoylation of aryl halides by tungsten carbonyl amine complex,[14] where they proposed an alternative possible mechanism for palladium-catalyzed amide formation involving transmetalation between carbamoylmetal complex and arylpalladium(II) intermediate. Mo(CO)$_6$ was also reported to promote the aminocarbonylation reaction of aryl halides.[15] Although the direct oxidative addition of molybdenum to carbon-halogen bond has been reported,[16] high reaction temperature was usually needed (120–160 °C). Although the detailed mechanism is still not clear at this stage, based on our results and the previous literatures,[4,13-17] a possible reaction mechanism is proposed in Scheme 3. First, oxidative addition of Ni^0 with the aryl iodide to give the aryl nickel complex **3**, which underwent a CO transmission with Mo(CO)$_6$ to give an aryl nickel-carbonyl complex **4**. Then, insertion of a carbonyl ligand of **4** would generate an acyl nickel complex **5**. After oxidative addition with another molecular of substrate, complex **6** will be produced as the key intermediate which can produce the final ketone product after reductive elimination and Ni^0 been regenerated with zinc as the reducing reagent. In this catalytic system, the generated acyl nickel complex **5** is very electron deficient and more tend to coordinate with electron rich substrates via π-coordination model. This can also explain why carbonylative cross-coupling product is always the main product as shown in Table 3, which also makes it different from palladium chemistry.[12]

Scheme 3. Plausible Reaction Mechanism.



In conclusion, we have developed a nickel-catalyzed molybdenum-promoted carbonylative coupling reaction of aryl iodides for the synthesis of benzophenones. A series of substituted diaryl ketones were synthesized in moderate to excellent yields. A synergetic effect of both nickel and molybdenum had been observed which proven crucial for the success of this transformation.

EXPERIMENTAL SECTION

General information: All reactions were carried out under a nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. All solvents were dried by standard techniques, and distilled prior to use. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (bp. 60~90 °C) and ethyl acetate as eluent. ^{1}H and ^{13}C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard and CDCl$_3$ (^{1}H NMR δ 7.26, ^{13}C NMR δ 77.0) as solvent. All coupling constants (J) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quatriplet, m = multiplet, br = broad. Gas chromatography (GC) analyses were performed on a Shimadzu GC-2014C chromatograph equipped with a FID detector. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV.

General procedure: $NiBr_2$ (5.5 mg, 0.025 mmol), dtbbpy (6.7 mg, 0.025 mmol), $Mo(CO)_6$ (132 mg, 0.5 mmol) and zinc power (98 mg, 1.5 mmol) were transferred into an 15 mL tube which was filled with nitrogen. 1,4-Dioxane (2 mL) and iodobenzene (114 uL, 1.0 mmol) were added to the reaction tube. Then the tube was sealed and the mixture was stirred at 120 °C for 6 h. After the reaction was completed, the reaction mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the corresponding product.

Spectroscopic Data of the Products

Benzophenone (**2a**) Prepared from iodobenzene (114 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a yellow oil (78.4 mg, 86%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 7.2 Hz, 4H), 7.63 (t, J = 7.4 Hz, 2H), 7.52 (t, J = 7.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 137.6, 132.4, 130.1, 128.3.

Di-*o*-tolylmethanone (**2b**) Prepared from 1-iodo-2-methylbenzene (128 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a yellow oil (82.2 mg, 78%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (td, J = 7.5, 1.1 Hz, 1H), 7.30 (dd, J = 12.9, 7.3 Hz, 2H), 7.21 (t, J = 7.4 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.8, 139.0, 138.2, 131.4, 131.1, 130.3, 125.4, 20.7.

Di-*m*-tolylmethanone (**2c**) Prepared from 1-iodo-3-methylbenzene (130 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a yellow solid (69.2 mg, 66%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.57 (d, J = 7.3 Hz, 1H), 7.37 (dt, J = 14.9, 7.5 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 138.1, 137.8, 133.1, 130.4, 128.0, 127.4, 21.4.

Di-*p*-tolylmethanone (**2d**) Prepared from 1-iodo-4-methylbenzene (222.5 mg, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a white solid (82.3 mg, 78%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 2H), 7.24 – 7.18 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 142.9, 135.2, 130.2, 128.9, 21.6.

Bis(4-methoxyphenyl)methanone (**2e**) Prepared from 1-iodo-4-methoxylbenzene (234.0 mg, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 20:1, Rf = 0.3) the desired compound was isolated as a yellow solid (85.2 mg, 71%).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.8 Hz, 2H), 6.96 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.4, 162.8, 132.2, 130.8, 113.5, 55.5.

Bis(4-ethylphenyl)methanone (**2f**) Prepared from 1-ethyl-4-iodobenzene (145 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a yellow solid (84.8 mg, 71%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 2.74 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 149.1, 135.5, 130.3, 127.7, 28.9, 15.3.

Bis(4-(*tert*-butyl)phenyl)methanone (**2g**) Prepared from 1-(*tert*-butyl)-4-iodobenzene (181 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a yellow solid (123.5 mg, 84%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 4H), 7.49 (d, J = 8.3 Hz, 4H), 1.37 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2, 155.9, 135.2, 130.0, 125.2, 35.1, 31.2.

Bis(3,4-dimethylphenyl)methanone (**2h**) Prepared from 4-iodo-1,2-dimethylbenzene (232.1 mg, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a yellow solid (82.2 mg, 69%).[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 2H), 7.52 (d, J = 7.7 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 2.34 (d, J = 8.4 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 141.6, 136.6, 135.8, 131.1, 129.3, 127.9, 19.9, 19.7.

Bis(4-fluorophenyl)methanone (**2i**) Prepared from 1-fluoro-4-iodobenzene (118 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a white solid (101.3 mg, 93%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.77 (m, 4H), 7.16 (t, J = 8.6 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.7, 166.3 (d, J = 52.5 Hz), 133.6, 132.5 (d, J = 9.0 Hz), 115.5 (d, J = 22.2 Hz).

Bis(4-chlorophenyl)methanone (**2j**) Prepared from 1-chloro-4-iodobenzene (238.5 mg, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a light yellow solid (94.7 mg, 76%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 139.1, 135.5, 131.3, 128.7.

Bis(4-(trifluoromethyl)phenyl)methanone (**2l**) Prepared from 1-iodo-4-(trifluoromethyl)benzene (150 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a white solid (90.4 mg, 57%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 4H), 7.78 (d, J = 8.2 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.3, 139.7, 134.3 (q) , 130.2, 125.6 (d, 3 Hz), 122.2.

Bis(2,4-difluorophenyl)methanone (**2m**) Prepared from 2,4-difluoro-1-iodobenzene (123 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.20) the desired compound was isolated as a white solid (100.4 mg, 79%).[11] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 14.9, 8.2 Hz, 1H), 7.03 – 6.96 (m, 1H), 6.89 – 6.80 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 166.9 (d, J = 12 Hz), 164.4 (d, J = 12 Hz), 163.1 (d, J = 12 Hz), 160.5 (d, J = 12 Hz), 132.6 (d, J = 10 Hz), 123.9 (dd, J = 13 Hz, 3 Hz) 115.7 (d, J = 22 Hz) 112.1 (d, J = 22 Hz), 104.5 (t).

Di(thiophen-3-yl)methanone (**2n**) Prepared from 3-iodothiophene (106 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.25) the desired compound was isolated as a brown solid (59.2 mg, 61%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 2.8, 1.1 Hz, 1H), 7.60 (dd, J = 5.0, 1.0 Hz, 1H), 7.38 (dd, J = 5.0, 2.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3, 142.0, 132.7, 128.3, 126.3.

Di(naphthalen-1-yl)methanone (**2o**) Prepared from 1-iodonaphthalene (150 uL, 1.0 mmol). After purification by column chromatography (petroleum ether / EtOAc = 50:1, Rf = 0.20) the desired compound was isolated as a red-brown solid (102.2 mg, 73%).[7] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 – 8.49 (m, 1H), 8.04 (d, J = 8.2 Hz, 1H), 7.98 – 7.93 (m, 1H), 7.64 – 7.57 (m, 3H), 7.44 (t, J = 7.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 137.2, 133.9, 132.5, 131.2, 130.5, 128.5, 127.8, 126.6, 125.9, 124.4.

(4-Fluorophenyl)(4-methoxyphenyl)methanone (**2ei**) Prepared from 1-fluoro-4-iodobenzene (59 uL, 0.5 mmol) and 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol). After purification by column chromatography (petroleum ether / EtOAc = 30:1, Rf = 0.25) the desired compound was isolated as a white solid (51.5 mg, 45%).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 4H), 7.19 (t, J = 8.6 Hz, 2H), 7.01 (d, J = 8.7 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.1, 165.0 (d, J = 253 Hz), 163.3, 134.4, 132.39, 132.3 (d, J = 9.1 Hz), 130.0, 115.3 (d, J = 22.2 Hz), 113.6, 55.5.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Optimization detail and NMR spectrums (PDF)

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Notes

The authors declare no competing financial interest.

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