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Pd/C: An Efficient, Heterogeneous and Reusable Catalyst for Phosphane-Free Carbonylative Suzuki Coupling Reactions of Aryl and Heteroaryl Iodides

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The carbonylative Suzuki coupling reaction of aryl boronic acid with different aryl and heteroaryl iodides was carried out to synthesize various unsymmetrical biaryl ketones by using Pd/C as an efficient, heterogeneous and reusable catalyst. The catalyst exhibits remarkable activity, and its reusability was tested up to four consecutive cycles. The reaction is applicable for various aryl and heteroaryl iodides having different steric and electronic properties. It provides good to excellent yield of the desired products. The developed protocol is advantageous with regard to the ease in handling the catalyst and the simple work-up procedure; it is also an environmentally benign process with effective catalyst recyclability.

Introduction

Synthesis of biaryl and heteroaryl carbonyl compounds has attracted considerable interest, as they are important building blocks for various natural products (e.g. Cotoin, Papaveraldine), biologically active compounds (e.g. Suprofen, Ketoprofen) and pharmaceutical compounds.[1] A common route for the synthesis of biaryl ketones involves Friedel–Crafts acylation of substituted aromatic ring compounds with acyl halides,[2] which is incompatible with many functional groups and requires over stoichiometric amounts of Lewis acid; furthermore, the regioselectivity is limited to the *para* position. Traditionally, biaryl ketones were synthesized by transition-metal-catalyzed, three-component, carbonylative cross-coupling reactions between organometallic reagents, carbon monoxide and aryl electrophiles, which is now considered as a useful tool for synthesis of a wide variety of carbonyl compounds. Various aryl metal reagents like magnesium,[3] silicon,[4] aluminium[5] and tin[6] have been reported. However, these carbonylative cross-coupling reactions have several limitations due to the formation of biaryl side products without carbon monoxide insertion, particularly with electron-deficient aryl halides.

In 1993, Suzuki et al. reported a facile protocol for the synthesis of biaryl ketones from carbon monoxide, aryl halide and aryl boronic acid by using palladium catalyst.[7] In principle, this reaction provides a versatile tool for organic synthesis, as boronic acids are generally nontoxic and stable to air and moisture. After the first report of Suzuki, several groups reported various protocols for the synthesis of such biaryl carbonyl compounds. Various palladium-based catalytic systems such as $PdCl_2(PPh_3)_2$,[8] $PdCl_2(PPh_3)_2$/$PdCl_2$(dppf),[9] $Pd(OAc)_2$-imidazolium salts,[10] $Pd(OAc)_2$/*N*,*N*-bis(2,6-diisopropylphenyl)dihydroimidazolium chloride,[11] an MCM-41-supported bidentate phosphane palladium complex,[12] $Pd(OAc)_2$/di-1-adamantyl-*n*-butylphosphane[13] and Pd/thiourea,[14] have been used for this transformation. However, despite their potential utility, the above methods suffer from one or more drawbacks such as the use of expensive, air/moisture sensitive phosphane-donating ligands and difficulties associated with the separation of catalyst and product, which limit their applications. Also, in many cases the catalysts used are homogeneous, and hence they are not recyclable. The loss of a palladium catalyst, even at ppm level, is not desirable because of its high cost and toxicity for pharmaceutical applications. Therefore, the search for a heterogeneous and reusable catalyst that could efficiently catalyze the carbonylative Suzuki coupling reaction without the aid of phosphane ligands is the subject of the present work. Moreover, a literature survey reveals that Pd/C was found to be an effective catalyst for the Suzuki–Miyaura reaction.[15] So, we chose Pd/C as the best alternative for the carbonylative Suzuki coupling reaction.

In continuation of our previous work on phosphane-free carbonylation reactions,[16] herein we report an efficient protocol for the carbonylative Suzuki coupling reaction of aryl boronic acid with various aryl and heteroaryl iodides with Pd/C as a heterogeneous and recyclable catalyst (Scheme 1). The catalyst showed remarkable activity, and the present system tolerates a wide variety of functional groups such as $–CH_3$, $–OCH_3$, $–NH_2$, $–COCH_3$, $–NO_2$

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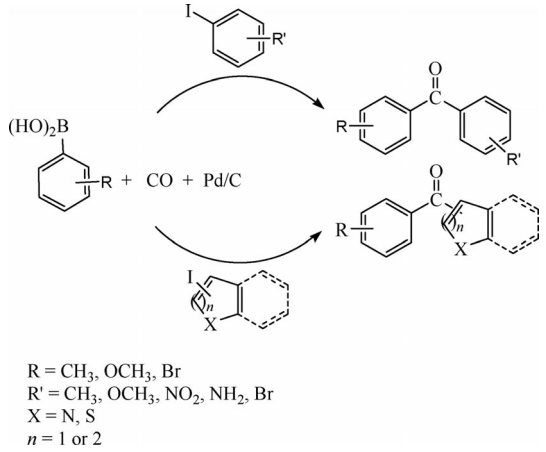
and –Br on both aryl boronic acid and aryl iodide. The catalyst was also found to be reusable for up to four consecutive cycles without any significant loss in activity.



Scheme 1. Carbonylative Suzuki coupling reaction of aryl and hetero aryl iodides with aryl boronic acid.

Results and Discussion

To optimize the reaction conditions, the carbonylative cross-coupling reaction of iodobenzene with phenyl boronic acid in the presence of Pd/C as a catalyst was chosen as a model system. The influence of various parameters such as solvent, base, temperature, CO pressure and time (Table 1) were examined on the model reaction. The influence of solvents on the carbonylative Suzuki coupling reaction was investigated (Table 1, Entries 1–6). Solvents like toluene (76%), *N*,*N*-dimethylformamide (10%), water (25%), diisopropyl ether (74%), acetonitrile (18%) and anisole (90%) were screened. It was observed that the reaction gave better results with ethereal solvents like diisopropyl ether and anisole. However, as the maximum yield of the desired product was obtained with anisole, it was used for further studies. It is well known that bases play a crucial role in coupling reactions; hence we attempted the reaction in the presence of various organic and inorganic bases (Table 1, Entries 6–12). Among the various bases screened, inorganic carbonates such as K_2CO_3 and Cs_2CO_3 were found to afford the desired product in good to excellent yields. The reaction using morpholine and piperidine yielded 75–85% of aminocarbonylated product instead of biaryl ketones. Thus, further reactions were carried out with K_2CO_3 as a base.

In order to examine the effect of temperature, reactions were carried out at different temperatures ranging from 80 to 120 °C (Table 1, Entries 6 and 13–14). It was observed that at 80 °C the yield of the desired product was low, whereas, on increasing the temperature up to 100 °C, 90% yield of the product was obtained within 8 h. With further increase in temperature, no profound increase in the yield of the product was observed. The influence of CO pressure and time were also studied, and the optimum pressure and time were used for further studies.

Table 1. Effect of reaction parameters on the carbonylative Suzuki coupling reaction of iodobenzene with phenyl boronic acid.[a]

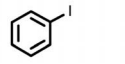
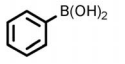
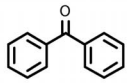
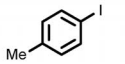
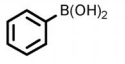
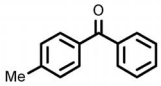
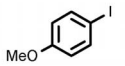
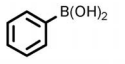
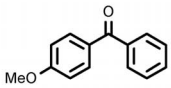
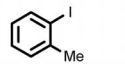
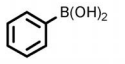
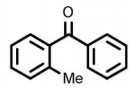
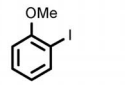
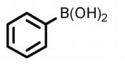
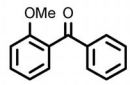
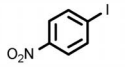
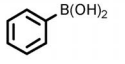
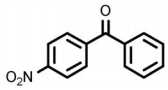
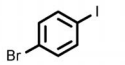
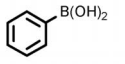
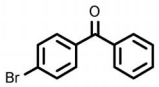
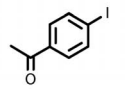
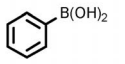
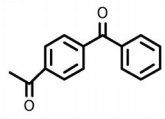
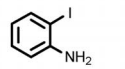
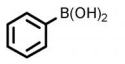
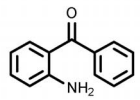
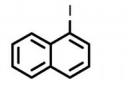
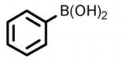
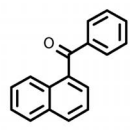
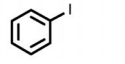
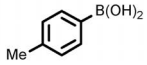
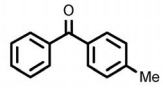
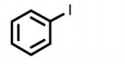
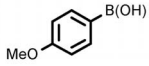
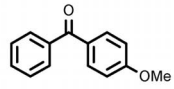
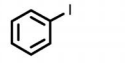
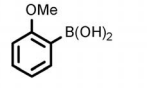
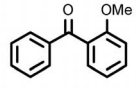
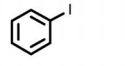
Entry	Solvent	Base	Temperature (°C)	Yield (%)[b]
Effect of solvent				
1	toluene	K_2CO_3	100	76
2	DMF	K_2CO_3	100	10
3	water	K_2CO_3	100	25
4	diisopropyl ether	K_2CO_3	100	74
5	acetonitrile	K_2CO_3	100	18
6	anisole	K_2CO_3	100	90
Effect of base				
7	anisole	Et_3N	100	25
8	anisole	Cs_2CO_3	100	70
9	anisole	K_3PO_4	100	40
10	anisole	morpholine	100	–
11	anisole	piperidine	100	–
12	anisole	DBU	100	–
Effect of temperature				
13	anisole	K_2CO_3	80	70
14	anisole	K_2CO_3	120	89
15[c]	anisole	K_2CO_3	100	75
16[d]	anisole	K_2CO_3	100	87

[a] Reaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), 10% Pd/C (2 mol-%), K_2CO_3 (3 mmol), solvent (10 mL), 8 h, CO pressure: 200 psi. [b] GC yield. [c] CO pressure: 100 psi. [d] Time: 6 h.

The optimized reaction conditions were iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), CO pressure (200 psi), 10% Pd/C (2 mol-%), K_2CO_3 (2 mmol) in anisole (10 mL) at 100 °C for 8 h. These conditions were applied to the coupling of a variety of phenyl boronic acids with a range of aryl and heteroaryl halides. Various electron-donating and electron-withdrawing groups like $–CH_3$, $–OCH_3$, $–NO_2$, –Br, $–COCH_3$, $–NH_2$ on both aryl iodide and boronic acid smoothly undergo carbonylative Suzuki coupling, providing the desired biaryl ketones (Table 2).

Iodobenzene reacts efficiently with phenyl boronic acid within 8 h, providing 90% yield of the desired product (Table 2, Entry 1). The carbonylative cross-coupling reaction of electron-donating substituents such as $–CH_3$ and $–OCH_3$ at the *para* and *ortho* positions with phenyl boronic acid went smoothly, providing good to excellent yields of the expected product (85–93%) (Table 2, Entries 2–5). The reaction of aryl iodides bearing electron-withdrawing groups such as $–NO_2$, –Br and $–COCH_3$ also permits the carbonylative coupling reaction with phenyl boronic acid, giving the required products in moderate to good yields under optimized reaction conditions (Table 2, Entries 6–8). The reaction of electron-rich *ortho*-iodoaniline with phenyl boronic acid yields *ortho*-aminobenzophenone in moderate amounts (83%, Table 2, Entry 9). The carbonylation of bulky 1-iodonaphthalene with phenyl boronic acid provided benzoyl naphthalene in 92% yield (Table 2, Entry 10). Next, we investigated the effect of substituents on phenyl boronic acid, both electron-donating and electron-withdrawing groups were well tolerated under optimized reaction conditions. Phenyl boronic acids substituted with electron-donat-

Table 2. Carbonylative Suzuki coupling reaction of aryl iodides with various boronic acids.[a]

No.	Aryl iodide	Aryl boronic acid	Product	Yield (%)[b]
1				90
2				93
3				90
4				85
5				89
6				70
7				72
8				85
9				83
10				92
11				86
12				81
13				60
14				70

[a] Reaction conditions: aryl iodide (1 mmol), aryl boronic acid (1.2 mmol), CO (200 psi), 10% Pd/C (2 mol-%), K_2CO_3 (3 mmol), anisole (10 mL), 100 °C, 8 h. [b] Isolated yield.

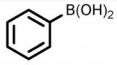
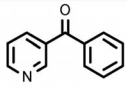
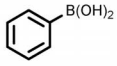
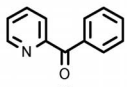
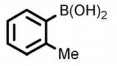
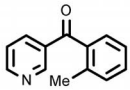
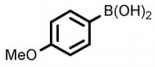
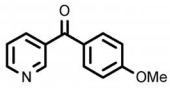
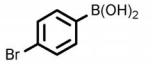
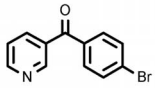
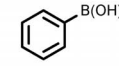
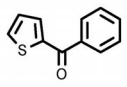
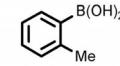
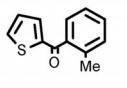
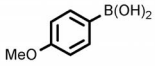
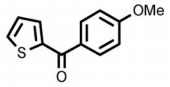
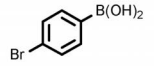
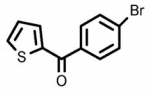
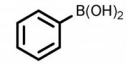
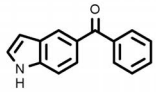
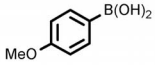
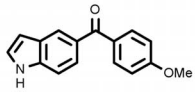
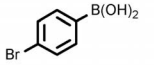
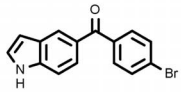
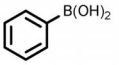
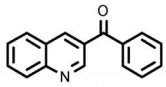
ing groups like $–CH_3$ and $–OCH_3$ at the *para* or even *ortho* positions gave the desired products in moderate to high yields (Table 2, Entries 11–13). However, the reaction of iodobenzene with *p*-bromophenyl boronic acid gave 70% yield of the desired product under the optimized reaction conditions (Table 2, Entry 14). Several groups such as Sasson and co-workers and Thathagar and co-workers have replaced expensive aryl iodide by aryl bromides or chlorides in various C–C coupling reactions;[17–18] however, these protocols do not provide satisfactory yields in our case.

For generality, we extended our protocol to heteroaryl iodides such as 2-iodopyridine, 3-iodopyridine, 2-iodothiophene, 5-iodoindole and 3-iodoquinoline (Table 3, Entries 1–14). The reaction of various heteroaryl iodides with different phenyl boronic acids gave good to excellent yields of the desired carbonylated products in 10–12 h. The carbonylative Suzuki coupling reaction of 2-iodopyridine and 3-iodopyridine with phenyl boronic acid using Pd/C as a catalyst provides 83% and 87% yield, respectively, of the desired products (Table 3, Entries 1–2). The reaction of 3-iodopyridine with electron-rich aryl boronic acids such as 2-methylphenyl boronic acid and 4-methoxyphenyl boronic acid offer products in admirable yield (86–83%) (Table 3, Entries 3–4). The reaction of 3-iodopyridine with *para*-bromophenyl boronic acid gave a moderate yield (70%) of the desired product (Table 3, Entry 5). To our delight, the Pd/C catalyzed the carbonylative Suzuki coupling reaction of 2-iodothiophene with a variety of phenyl boronic acids to provide good yields (73–86%) of the desired products (Table 3, Entries 6–9).

Encouraged by these results, we used Pd/C in the carbonylative Suzuki coupling reactions of 5-iodoindole and 3-iodoquinoline with different aryl boronic acids. To the best of our knowledge, there is no general method reported for the synthesis of sterically hindered heteroaryl ketones from iodoindole and iodoquinoline through carbonylative Suzuki cross-coupling. 5-Iodoindole smoothly underwent carbonylative coupling with phenyl boronic acid, providing 83% yield of the carbonylative Suzuki product (Table 3, Entry 10). The reaction of 5-iodoindole with phenyl boronic acids bearing electron-donating and electron-withdrawing groups such as $–OCH_3$ and –Br provided the desired carbonylated products with good yields (Table 3, Entries 11–12). Remarkably, the reaction of 3-iodoquinoline with phenyl boronic acid afforded the desired product in 84% yield (Table 3, Entry 13). The reaction of 3-methyl phenyl boronic acid with 3-iodoquinoline went smoothly, producing 79% yield of the anticipated product (Table 3, Entry 14).

It is well known that supported palladium leaches out into the solvent at high temperature, and the reaction is catalyzed mainly by this dissolved palladium species.[16b] So, after completion of the reaction, leaching of palladium in the solution was checked by using ICP-AES analysis, which showed only 0.24 ppm of palladium in solution. We can conclude that no significant leaching of palladium occurred. The reusability of the catalyst was also examined for the standard reaction of iodobenzene with phenyl boronic acid. After completion of the reaction, the reaction mixture was filtered, the catalyst was washed with distilled water and kept at 200 °C in a furnace for 12 h for activation prior to the next reaction cycle. The Pd/C was found to

Table 3. Carbonylative Suzuki coupling reaction of heteroaryl iodides with various aryl boronic acids.[a]

No.	Het-aryl iodide	Boronic acid	Product	Yield (%)[b]
1				87
2				83
3				86
4				83
5				70
6				86
7				85
8				81
9				73
10[c]				83
11[c]				83
12[c]				77
13[c]				84
14[c]				79

[a] Reaction conditions: heteroaryl iodide (1 mmol), aryl boronic acid (1.2 mmol), CO (200 psi), 10% Pd/C (2.5 mol-%), K_2CO_3 (3 mmol), toluene (10 mL), Time = 10 h, T = 100 °C. [b] Isolated yields. [c] Reaction time 12 h.

maintain its high activity and selectivity for four consecutive cycles (Figure 1). There was no significant decrease in yield during the first three cycles; however, the yield decreased by up to 80% for the fourth cycle. This decrease in yield was mainly due to workup loss or handling loss of the catalyst during the successive recycles. When the catalyst that was lost during the first four recycles was compensated, we observed 88% yield of the product (see Figure 1, IV*). It should be noted that the compensated catalyst was taken from parallel sets of recycling experiments after the 3rd recycle. Thus, the catalyst was successfully recycled, and the reusability procedure was tested up to four times with consistent results.

Figure 1. Catalyst reusability study. Reaction conditions: iodobenzene (1 mmol), phenyl boronic acid (1.2 mmol), CO (200 psi), 10% Pd/C (2 mol-%), K_2CO_3 (3 mmol), anisole (10 mL), 100 °C, 8 h, GC yield.

Conclusions

We have developed an efficient, heterogeneous and reusable catalytic system for the carbonylative Suzuki coupling reaction of aryl and heteroaryl iodides. The reaction was optimized with respect to various parameters and could be used for the carbonylative Suzuki coupling reaction of different aryl boronic acids with a variety of aryl and heteroaryl iodides, affording good to excellent yields of the desired products, demonstrating the broad application of the methodology. Catalyst reusability and Pd leaching were also examined, and Pd/C was found to be effectively recyclable for four consecutive cycles without any significant loss in catalytic activity.

Experimental Section

All the chemicals were obtained from Lancaster (Alfa-Aesar) and used without further treatment. Amorphous Pd/C (10 wt.-%) was used for all studies. Optimized yields were based on GC analysis with a Perkin–Elmer chromatograph (30 m × 0.32 mm 1D-0.25 μm BP-10). All the products were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (Varian Mercury 300 NMR Spectrometer) and GC–MS analysis (Shimadzu QP 2010).

General Experimental Procedure for the Carbonylative Suzuki Reaction of Aryl Iodide: To a 100 mL autoclave were added aryl iodide (1.0 mmol), aryl boronic acid (1.2 mmol), 10% Pd/C (2 mol-%), anisole (10 mL) and K_2CO_3 (3 mmol). The mixture was first stirred for 10 min and then flushed with CO; then 200 psi of CO was taken, and the reaction mixture was heated at 100 °C for 8 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The catalyst was filtered, and the residue obtained was purified by column chromatography (silica gel, 60–

120 mesh; petroleum ether/ethyl acetate, 60:80) to afford the desired carbonylated product. The identity of the products was confirmed by GC–MS, ^{1}H NMR, ^{13}C NMR and IR spectroscopic techniques. The purity of the compounds was determined by GC–MS analysis.

General Experimental Procedure for the Carbonylative Suzuki Reaction of Heteroaryl Iodide: To a 100 mL autoclave were added heteroaryl iodide (1.0 mmol), aryl boronic acid (1.2 mmol), 10% Pd/C (2.5 mol-%), toluene (10 mL) and K_2CO_3 (3 mmol). The mixture was first stirred for 10 min and then flushed with CO; then 200 psi of CO was taken, and the reaction mixture was heated at 100 °C for 10–12 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The catalyst was filtered, and the residue obtained was purified by column chromatography (silica gel, 60–120 mesh; petroleum ether/ethyl acetate, 60:80) to afford the desired carbonylated product. The identity of the products was confirmed by GC–MS, ^{1}H NMR, ^{13}C NMR and IR spectroscopic techniques. The purity of the compounds was determined by GC–MS analysis.

Procedure for Catalyst Recycling: The catalyst obtained after filtration was washed with distilled water (10 mL × 3) and then with methanol (5 mL × 3) to remove any organic material present. The catalyst was then dried in an oven at 200 °C for 12 h and then used for the next cycle.

Characterization of Selected Compounds

4-Acetylbenzophenone: Table 2, Entry 8. Yield: 190 mg (85%); solid. IR (KBr): $\tilde{\nu}$ = 2920, 2852, 1689, 1657, 1593, 1445, 1402, 1358, 1277, 1072, 963, 931, 845, 795, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.66 (s, 3 H), 7.52–7.47 (t, J = 7.5 Hz, 2 H), 7.65–7.59 (t, J = 8.8 Hz, 1 H), 7.82–7.79 (d, J = 8.4 Hz, 2 H), 7.88–7.87 (d, J = 8.4 Hz, 2 H), 8.07–8.04 (d, J = 8.8 Hz 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 22.71 (CH_3), 128.18 (2CH), 128.49 (2CH), 130.05 (2CH), 130.11 (2CH), 132.99 (CH), 136.97 (C), 139.62 (C), 141.36 (C), 195.89 (CO), 197.47 (CO) ppm. MS (70 eV): m/z (%) = 224 (53), 209 (100), 181 (10), 147 (35), 105 (80), 77 (78), 43 (35).

2-Aminobenzophenone: Table 2, Entry 9. Yield: 163 mg (83%); solid. IR (KBr): $\tilde{\nu}$ = 3436, 3318, 3054, 2934, 1626, 1589, 1553, 1479, 1449, 1328, 1303, 1250, 1151, 1025, 938, 912, 745, 703, 645 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.1 (br., 2 H), 6.61–6.55 (t, J = 7.9 Hz, 1 H), 6.73–6.7 (d, J = 8 Hz, 1 H), 7.3–7.24 (m, 2 H), 7.46–7.42 (t, J = 5.9 Hz, 1 H), 7.51–7.49 (d, J = 7.3 Hz, 2 H), 7.64–7.61 (d, J = 8.1 Hz, 2 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 115.53 (CH), 117.04 (CH), 118 (CH), 128.1 (2CH), 129.13 (2CH), 131.04 (CH), 134.24 (CH), 134.59 (CH), 140.16 (C), 150.99 (C), 199.09 (CO) ppm. MS (70 eV): m/z (%) = 197 (100), 120 (41), 105 (16), 92 (31), 77 (44), 65 (36), 51 (19).

Pyridin-3-yl-*o*-tolylmethanone: Table 3, Entry 3. Yield: 171 mg (86%); solid. IR (KBr): $\tilde{\nu}$ = 2925, 2851, 1729, 1670, 1584, 1463, 1292, 1270, 1190, 1081, 1025, 966, 925, 796, 737, 650 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.38 (s, 3 H), 7.46–7.26 (m, 5 H), 8.16–8.14 (d, J = 8.1 Hz, 1 H), 8.81–8.79 (d, J = 6.2 Hz, 1 H), 8.93 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 14.14 (CH_3), 119 (CH), 123.59 (CH), 125.47 (CH), 129.01 (CH), 131.13 (CH), 131.48 (C), 133.4 (C), 137.28 (CH), 147.11 (C), 151.31 (CH), 153.12 (CH), 196.81 (CO) ppm. MS (70 eV): m/z (%) = 196 (100), 197 (45), 182 (5), 168 (34), 141 (5), 119 (51), 106 (11), 91 (75), 89 (22), 78 (30), 65 (41), 51 (31), 45 (34).

(1*H*-Indol-5-yl)phenylmethanone: Table 3, Entry 10. Yield: 182 mg (83%); solid. IR (KBr): $\tilde{\nu}$ = 3292, 2923, 2851, 1621, 1607, 1572, 1431, 1322, 1116, 1092, 957, 880, 734 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.62 (d, J = 2.2 Hz, 1 H), 7.27–7.26 (dd, J = 2.56, 2.93 Hz, 1 H), 7.45–7.44 (m, 3 H), 7.5–7.47 (d, J = 8.06 Hz, 1 H), 7.57–7.55 (d, $J_{H,H}$ = 7.3 Hz, 1 H), 7.83–7.77 (dd, J = 6.96, 8.8 Hz, 2 H), 8.13 (s, 1 H), 8.93 (br., 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 104.14 (CH), 111.21 (CH), 124.15 (CH), 125.41 (CH), 125.99 (CH), 127.19 (C), 128.17 (2CH), 129.57 (C), 129.98 (2CH), 131.76 (CH), 138.45 (C), 139.01 (C), 197 (CO) ppm. MS (ESI+): calcd. for [M + 1] 222.08; found 222.1.

(1*H*-Indol-5-yl)(4-methoxyphenyl)methanone: Table 3, Entry 11. Yield: 207 mg (83%); solid. IR (KBr): $\tilde{\nu}$ = 3262, 2929, 2840, 1624, 1508, 1420, 1308, 1252, 1175, 1116, 1093, 1029, 964, 885, 849, 823, 760, 731, 614, 576 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.88 (s, 3 H), 6.6 (d, J = 2.2 Hz, 1 H), 6.98–6.95 (d, J = 8.8 Hz, 2 H), 7.26–7.25 (d, J = 2.6 Hz, 1 H), 7.42–7.4 (d, J = 8.4 Hz, 1 H), 7.73–7.7 (d, J = 7 Hz, 1 H), 7.86–7.83 (d, J = 8.8 Hz, 2 H), 8.1 (s, 1 H), 8.9 (br., 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 55.5 (CH_3), 104.15 (CH), 111.07 (CH), 113.35 (CH), 113.59 (CH), 124.07 (CH), 124.86 (CH), 125.94 (CH), 127.16 (C), 130.19 (C), 131.44 (C), 132.56 (2CH), 138.2 (C), 162.77 (C), 196.67 (CO) ppm. MS (ESI+): calcd. for [M + 1] 252.09; found 252.1.

(4-Bromophenyl)(1*H*-indol-5-yl)methanone: Table 3, Entry 12. Yield: 231 mg (77%); solid. IR (KBr): $\tilde{\nu}$ = 3269, 1644, 1595, 1429, 1329, 1284, 1203, 1330, 1284, 1203, 1100, 1067, 1011, 977, 878, 841, 773, 754, 729 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.65 (d, J = 2.2 Hz, 1 H), 7.3–7.26 (d, J = 12.46 Hz, 1 H), 7.47–7.44 (d, J = 8.8 Hz, 2 H), 7.7–7.67 (d, J = 8.4 Hz, 2 H), 7.77–7.73 (d, J = 9.9 Hz, 2 H), 8.09 (s, 1 H), 8.6 (br., 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 104.4 (CH), 111.21 (CH), 124.18 (CH), 125.22 (CH), 125.95 (CH), 126.61 (C), 127.3 (C), 129.46 (C), 131.55 (2CH), 131.47 (2CH), 137.82 (C), 138.46 (C), 196.29 (CO) ppm. MS (ESI+): calcd. for [M + 1] 299.99; found 300.0.

Phenylquinolin-3-ylmethanone: Table 3, Entry 13. Yield: 206 mg (84%); solid. IR (KBr): $\tilde{\nu}$ = 3052, 2924, 2853, 1649, 1598, 1572, 1493, 1445, 1367, 1290, 1245, 1178, 1122, 935, 911, 860, 759, 726, 698 595 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 7.55 (m, 3 H), 7.67–7.5 (dd, J = 7.7, 8.1 Hz, 1 H), 7.87–7.8 (m, 2 H), 7.92–7.89 (d, J = 8.1 Hz, 2 H), 8.2–8.18 (d, J = 8.43 Hz, 1 H), 8.53 (s, 1 H), 9.33 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 126.55 (CH), 127.57 (CH), 128.63 (3CH), 129.15 (C), 129.4 (C), 130.01 (2CH), 131.85 (CH), 133.06 (CH), 136.95 (C), 138.83 (CH), 149.37 (C), 150.29 (CH), 194.81 (CO) ppm. MS (70 eV): m/z (%) = 233 (100), 204 (12), 176 (3), 156 (29), 128 (50), 105 (66), 77 (78), 45 (89).

Quinolin-3-yl-*m*-tolylmethanone: Table 3, Entry 14. Yield: 195 mg (79%); solid. IR (KBr): $\tilde{\nu}$ = 3057, 2917, 1656, 1617, 1596, 1495, 1415, 1368, 1292, 1189, 1039, 788, 758, 588 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.42 (s, 3 H), 7.45–7.38 (m, 2 H), 7.67–7.6 (dd, J = 7.3, 7.0 Hz, 1 H), 7.95–7.81 (m, 4 H), 8.23–8.2 (d, J = 8.8 Hz, 1 H), 8.56 (s, 1 H), 9.31 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75.43 MHz): δ = 21.14 (CH_3), 126.45 (CH), 127.5 (CH),128.3 (CH),129.05 (CH), 130.01 (C), 130.18 (CH), 130.93 (C), 131.8 (CH), 133.76 (CH), 134.61 (C), 138.72 (CH), 138.43 (CH), 138.88 (C), 148.85 (C), 149.94 (CH), 194.82 (CO) ppm. MS (70 eV): m/z (%) = 247 (100), 232 (81), 218 (7), 204 (6), 156 (30), 128 (57), 119 (78), 101 (40), 91 (75), 75 (19), 65 (34), 51 (14), 45 (27).

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