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Trans-chelating ligands in palladium-catalyzed carbonylative coupling and methoxycarbonylation of aryl halides

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ABSTRACT

The manuscript describes the use of a *trans*-chelated palladium complex derived from 1,8-bis-(4-(diphenylphosphino)phenyl)anthracene (**1**) and *p*-TolPdI(TMEDA) as a precatalyst in carbonylative Suzuki coupling and methoxycarbonylation of aryl iodides and bromides. The catalyst is active in 0.01–1 mol% loading and demonstrates highly selective transformations. The selectivity is attributed to the unique structural features of the *trans*-chelating ligands.

1. Introduction

During the past few decades, enormous efforts have been devoted to the synthesis of transition-metal complexes as promoters for a variety of homogeneously catalyzed transformations. To a great extent, the recent progress in the development of efficient and selective catalysts is dependent on the synthesis of various ligands possessing unique electronic and steric properties. Although many different ligands' families have emerged in recent years, *cis*-chelating (having chelation angle below 100°) [1] and wide bite angle ones (with chelation angles ranging between 100° and 160°) [2,3] are the most commonly used, while *trans*-chelating ligands that coordinate metals at the angle of over 160° receive very little attention [4]. This is despite that several very interesting ligands belonging to this kind were studied in the context of their coordination chemistry and potential catalytic applications and demonstrated very unusual and fascinating properties [5].

As a part of our research program aiming the investigation of such compounds, we became interested in studying coordination chemistry and catalytic properties of the *trans*-chelating ligands based on 1,8-bis(*p*-(diphenylphosphino)phenyl)anthracene (**1**) (Fig. 1).

Recently we communicated on the synthesis and coordination properties of these ligands [6]. *Inter alia*, we found that the rigid all-aromatic scaffold ensures conformational stability of the resulting compounds and avoids multiple technical problems that are traditionally associated with the synthesis of *trans*-spanned species [7]. More importantly, the planar anthracene-based scaffold prefers a *trans*-chelation mode due to the adequately remote phosphine groups. On the other hand, while being *mainly trans*-chelating, some flexibility in coordination is allowed due to a limited rotation of the phosphine donors and phenyl rings around C–P and C–C bonds. The ability of a ligand to adapt different coordination geometries within a certain range is an important factor in catalysis, because it assists in stabilization of different intermediates (*e.g. cis*-chelated ones) that may form over the course of a catalytic cycle. For example, we demonstrated that $Pd(OAc)_2$/**1** is a highly reactive, mild and unusually selective catalyst for the palladium-catalyzed Mizoroki-Heck reaction of aryl bromides with cycloalkenes.

Herein we wish to report the continuation of our studies on the catalytic properties of palladium complexes bearing this *trans*-chelating ligand. In particular, we will discuss Pd-catalyzed carbonylation.

2. Results and discussion

Palladium-catalyzed carbonylative cross-coupling is a straightforward alternative to the classical Friedel–Crafts synthesis of diaryl ketones (Scheme 1) [8,9].

This transformation can be successfully realized through the three-component reaction of an aromatic electrophile (typically, aryl iodides, bromides, chlorides or triflates), carbon monoxide and an organometallic nucleophile from the standard arsenal of the cross-coupling reagents, such as organotin [10,11], organozinc

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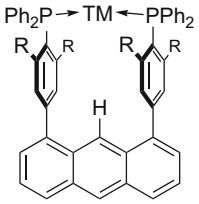
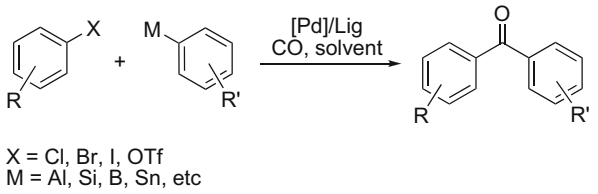


Fig. 1. 1,8-bis(*p*-(diphenylphosphino)phenyl)anthracene (**1**).



Scheme 1.

[12], organoaluminum [13,14], organosilicon [15,16] and organoboron [17–19]. Of course, the latter reagent is more attractive for the everyday use due to its great stability, availability and long shelf-life.

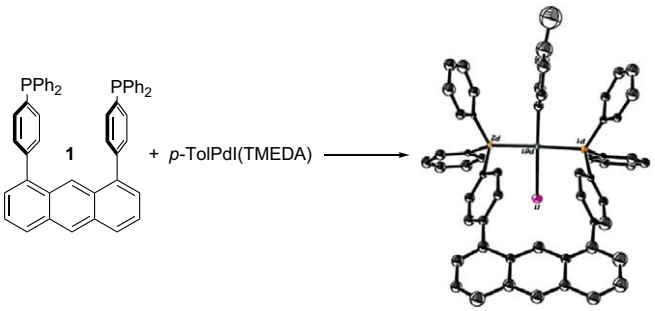
Unfortunately, two major problems often accompany the reaction: (a) relatively harsh reaction conditions and (b) relatively poor chemoselectivity on account of the homocoupling and dehalogenation. Paradoxically, both these problems are associated with the presence of carbon monoxide. On the one hand, the oxidative addition step of catalytically active 14-electron species across carbon–halogen bond (step a, Scheme 2) is difficult in the presence of CO [20], so reasonable TOFs require high temperature conditions. On the other hand, a slow, sterically troublesome CO insertion (step b, Scheme 2) [21] opens a shortcut to the formation of homocoupled and/or dehalogenated by-products [11,14,15,19].

There are several protocols which treat selectivity issues in these reactions. For example, $PdCl_2$/dppf/NaI system developed by Suzuki allows selective transformation of aryl triflates and bromides [18]. Additionally, $Pd(OAc)_2$/thiourea [22] and $PdCl_2/PCy_3$ catalysts [23] were found suitable for the carbonylative coupling of aryl iodides and heteroaryl bromides, respectively. Finally, Beller suggested the use of $Pd(OAc)_2$/diadmantanyl-*n*-butyl phosphine combination as a general catalyst for the efficient carbonylative Suzuki coupling [24]. His conditions are applicable even to electron-rich and sterically demanding aryl bromides. In this context, it would be interesting to test whether better selectivity may be achieved under *trans*-chelating ligand-assisted conditions.

Currently, our working hypothesis [6] is that unlike wide-bite ligands that are known to accelerate reductive elimination (product forming) step [3,25], mainly *trans*-chelating ligands such as **1** have an opposite effect of decelerating it [26,27]. If so, the CO-free channel might be shut down improving the selectivity of the reaction, possibly on account of lower TOFs, though.

The optimization of the reaction conditions initially focused the coupling of *p*-iodotoluene and phenylboronic acid and revealed that the best conversion and corresponding yield of the product (determined based on GC analysis versus internal standard) can be achieved when the reactants (in 1:1.5 ratio) are stirred at 90 °C under the CO atmosphere (5 bar) in the presence 1 mol% of $Pd(OAc)_2$/**1** and K_2CO_3 as a base in dioxane. Under these conditions we were able to obtain the product in ca. 90% conversion exclusively into the corresponding ketone. Lower CO pressure and other solvent/base combinations (DMF, toluene, Et_3N as a reaction medium, and $K_3PO_4{\cdot}H_2O$, K_3PO_4, Na_2CO_3, Cs_2CO_3, Et_3N as a base were tested) led to less satisfactory results.

However, the optimization series suffered from low reproducibility. Moreover, the reaction did not become more reproducible after exclusion of "the usual suspects" such as purity of the solvent, size and quality of the base and the stirring efficiency [28]. Then, we speculated, that inefficient conversion of $Pd(OAc)_2$/**1** into Pd(0)/**1** at the activation stage is responsible for the inconsistent results. This known issue is relatively sometimes seen in cross-coupling reactions [29,30] but maybe more pronounced in the case of *trans*-chelating ligands with large (>160°) chelation angle. Therefore, instead of the catalyst prepared *in situ* from $Pd(OAc)_2$ and **1**, we decided to employ a well-defined complex **2** (Eq. (1)) that is structurally related to the intermediates involved in the reaction (step a, Scheme 2) [31].



2

(1)

The complex was prepared by mixing together the *p*-TolPdI(TMEDA) [32] and **1** in chloroform. NMR measurements indicated the product form cleanly within 1–2 h – $^{31}P\{1H\}$ NMR spectrum of the reaction mixture displayed a sharp singlet with the resonance frequency of 20.4 ppm along with only minor impurities.

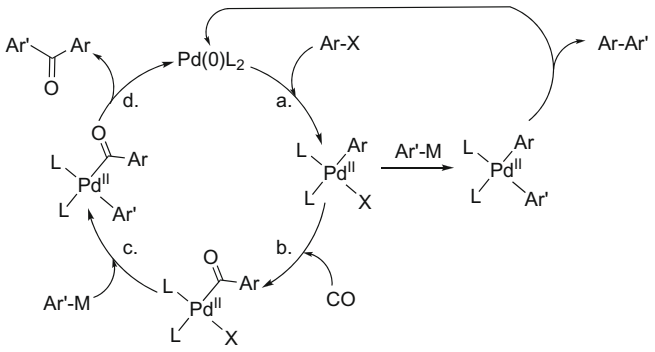
The solid state structure of the product was confirmed by the X-ray analysis [33]. As expected, complex **2** exists in almost perfect *trans*-spanned form (the ORTEP view is shown in Eq. (1)).

Applying **2** instead of the *in situ* formed $Pd(OAc)_2$/**1** indeed greatly improved the reproducibility, so that we were able to study the scope of the catalyst under the developed conditions. The results of the study are summarized in Table 1.

We were able to prepare a collection of differently substituted diaryl ketones starting from electron-rich, -neutral and -deficient aryl iodides and arylboronic acids in different combinations. It is worth noting that almost independently on the electronic properties of the staring materials the reactions go to completion and isolated yields reasonably match the GC-based conversions, while the formation of the homocoupled species *has never been* observed.

In a limited number of runs (*e.g.* **3e** and **3j**) we detected a significantly missing percentage. However, even in these cases, the difference between the GC-conversion and isolated yield originates from the conversion of the sterically hindered starting *o*-bromoiodobenzene to form 2-bromobenzoic acid in the presence of the trace water. Unfortunately, the virtue of *trans*-chelation is does not assist in suppression of this particular side reaction.

The reaction of aryl bromides under the same reaction conditions was slow so that higher reaction temperatures (130 °C) and longer reaction time (24 h) were required in order to drive the reactions to completion. For example, corresponding benzophenone derivatives were prepared from the electron-rich *p*-bromonitrobenzene and *p*-bromoacetophenone, as well as electron-neutral *p*-bromotoluene in good yield (entries **3m**–**o**, Table 1). Remarkably, the formation of only minor (less than 3%) CO-free biaryl by-product was detected in these runs stressing the fact that carbonylation reactions benefit from the use of the *trans*-spanned catalysts.



Scheme 2.

The formation of the by-produced 2-bromobenzoic acid in the entries **3e** and **3j** (Table 1) urged to test the applicability of the catalyst **2** to other carbonylation reactions, for example, methoxycarbonylation of aryl halides. Although the progress recently achieved in the field of alkoxycarbonylation of aryl halides is spectacular [9,34] and relatively simple catalysts efficiently promote the transformation of aryl iodides [35], bromides [36] and even chlorides [30,37] into carboxylic acid derivatives under relatively mild conditions, the quest after new catalytic systems is not over.

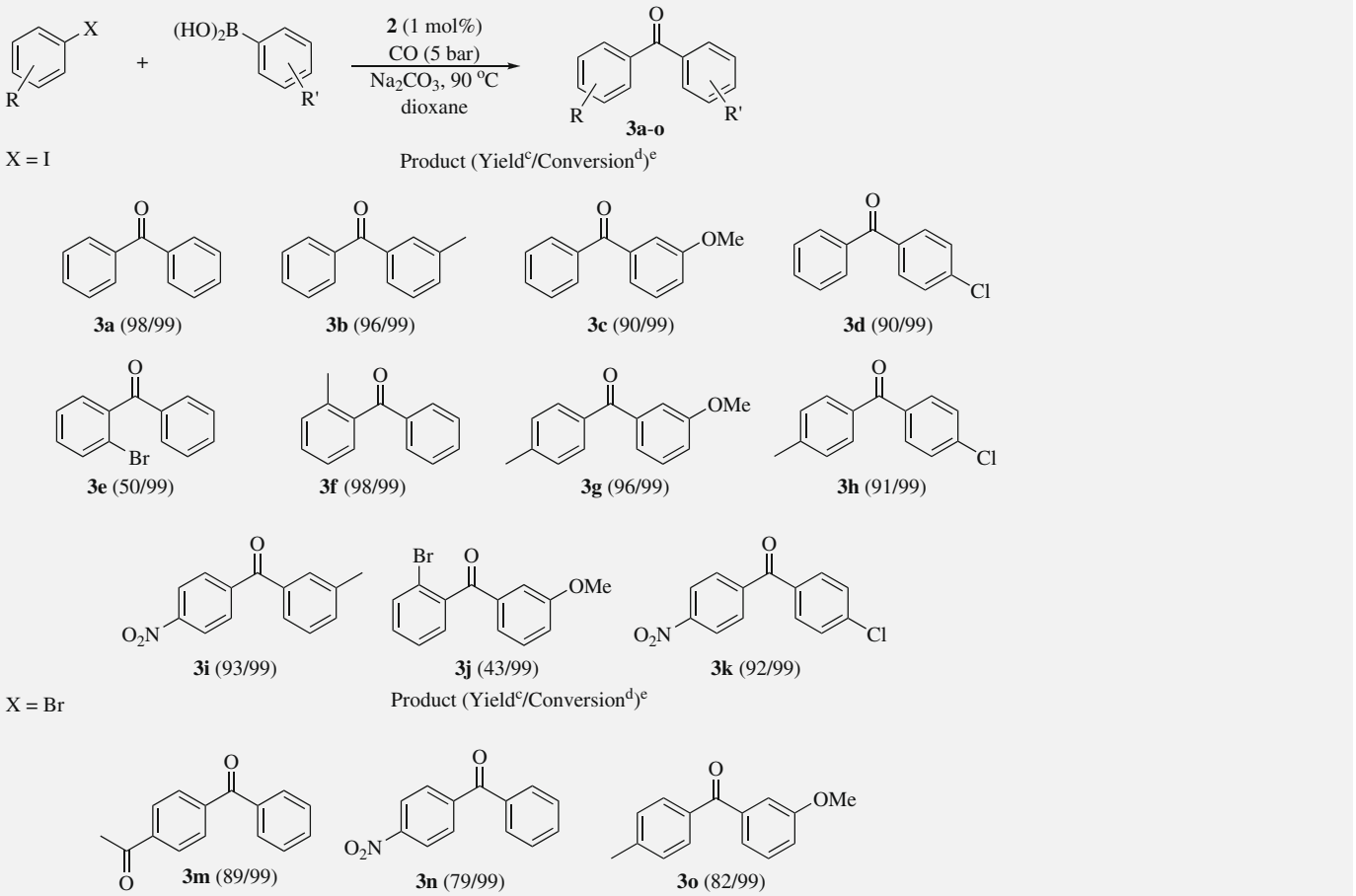
A brief experimentation helped us to determine optimal reaction conditions for this transformation. As we found, as little as 0.01–0.1 mol% of **2** in triethylamine in the presence of 10 equivalents of methanol under 5 bar of carbon monoxide is able to convert aryl iodides and bromides into the corresponding methyl esters. Aryl iodides are, naturally, more reactive and their reactions go to completion at 90 °C over 12 h, while complete conversion of aryl bromides is achieved after 24 h at 130 °C. No difference in selectivity of the transformation of aryl iodides and bromides has been observed (Table 2).

For example, electron-rich methyl- and methoxy-substituted iodides (**4a**, **4c** and **4e**, Table 2) and bromides (**4i**, **4j** and **4l**, Table 2) form the corresponding methyl esters in high yield. Similarly, electron-poor methyl esters bearing halo-, keto, cyano and nitro groups (**4b**, **4f**–**h** for aryl iodides; **4m** for aryl bromides) and heteroaryl esters (**4n**–**o**, from the corresponding heteroaryl bromides) were isolated in excellent yield as well. Remarkably, the reaction is less sensitive to the steric properties of the starting materials than the previously described carbonylative coupling. For example, 1,2-diiodobenzene to form dimethyl phthalate (**4d**) and 1-chloro-2-iodobenzene to form methyl 2-chlorobenzoate (**4f**) exhibited excellent conversions and isolated yields. Interestingly, unprotected 4-bromobenzyl alcohol (**4k**) can be suitable starting material, although the reaction of 4-bromoaniline suffered from the competitive self aminocarbonylation (**4p**, Table 2).

Aryl chlorides were found inert under the described reaction conditions.

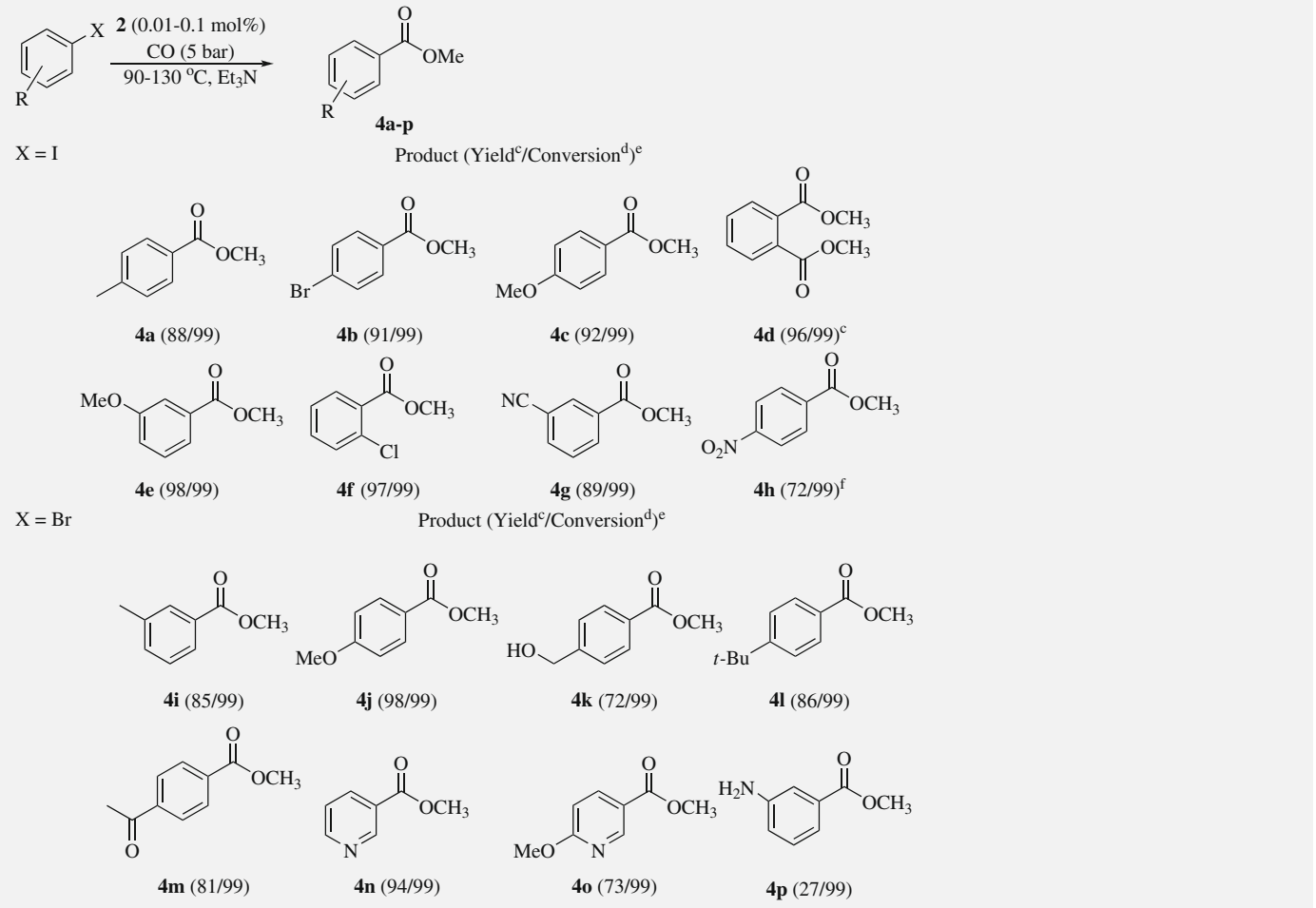
To conclude, we demonstrated that the structurally well defined complex of palladium **2** bearing the *trans*-chelating 1,8-

Table 1
Carbonylative Suzuki coupling of representative aryl iodides[a] and bromides[b] in the presence of **2** as a catalyst.



[a]Aryl iodide (1 mmol), **2** (0.01 mmol), dioxane (5 mL), CO (5 bar), K_2CO_3 (2 mmol), 90 °C for 12 h. [b]Aryl bromide (1 mmol), **2** (0.01 mmol), dioxane (5 mL), CO (5 bar), K_2CO_3 (2 mmol), 130 °C for 24 h. [c]Isolated yield of at least 95% pure compound. [d]Determined by GC. [e]Average of two runs.

Table 2
Methoxycarbonylation of representative aryl iodides[a] and bromides[b] in the presence of **2** as a catalyst.



[a]Aryl iodide (1 mmol), **2** (10^{-4} mmol), Et_3N (5 mL), methanol (10 mmol), CO (5 bar), 90 °C for 12 h. [b]Aryl bromide (1 mmol), **2** (10^{-3} mmol), Et_3N (5 mL), methanol (10 mmol), CO (5 bar), 130 °C for 24 h. [c]Isolated yield of at least 95% pure compound. [d]Determined by GC. [e]Average of two runs. [f]Contaminated with methyl *p*-aminobenzoate.

bis-(4-(diphenylphosphino)phenyl)anthracene (**1**) is a useful catalyst for the selective carbonylative Suzuki coupling and methoxycarbonylation of aryl iodides and bromides. The *trans*-coordination preference of **2** positively affects the selectivity of the reactions, although, on account of its reactivity – relatively harsh conditions required in order to achieve reasonable reaction rates for aryl bromides and the lack of reactivity of **2** toward aryl chlorides. The latter problem, however, can be at least partially overcome by modifying the ligand to possess more electron rich phosphines.

3. Experimental

All chemicals were purchased from elsewhere and used without further purification. 1,8-bis-(4-(diphenylphosphino)phenyl) anthracene (**1**) prepared following published procedure [6]. NMR spectra were recorded on a Bruker instrument operating at 400 MHz for proton, 100 MHz for carbons and 161 MHz for phosphorus. Gas chromatography analyses were performed on a Hewlett–Packard 5890 instrument with a FID detector and a Hewlett–Packard 25 m × 0.2 mm i.d. Supelcowax-10 capillary column. Yields refer to isolated yields of compounds greater than 95% purity as determined proton Nuclear Magnetic Resonance spectroscopy (^{1}H NMR) analysis. Yields reported in Tables 1 and 2 are an average of two runs. The CAS numbers of the known compound were listed. Spectroscopy data of the known compounds matches with the data reported in the corresponding references.

3.1. Synthesis of *2*

1,8-Bis((4-diphenylphosphino)phenyl)anthracene (21 mg, 0.03 mmol) and (TMEDA)Pd(4-$CH_3C_6H_4$)I (13.2 mg, 0.03 mmol) in chloroform (2 ml) was stirred for 10 min at room temperature under dry nitrogen. All volatiles were evaporated under reduced pressure. The residue was rinsed with diethyl ether and dried *in vacuo*, affording **2** as a yellow powder. ^{1}H NMR ($CDCl_3$) δ, ppm: 8.59 (s, 1H), 8.52 (s, 1H), 8.12 (m, 6H), 8.02 (d, J_{H-H} = 7.4 Hz, 2H), 7.73 (d, J_{H-H} = 9.2 Hz, 2H), 7.59 (m, 18H), 7.09 (m, 2H), 6.93 (m, 8H), 2.03 (s, 3H). ^{31}P NMR, δ, ppm: 21.4. Elemental *Anal.* Calc. for $C_{57}H_{43}IP_2Pd$: C, 66.91; H, 4.24. Found: C, 67.09; H, 4.38%.

3.2. General procedure for the Pd-catalyzed carbonylative Suzuki coupling

The 50 ml stainless steel high pressure Parr reactor was charged with **2** (0.01 mmol), K_2CO_3 (2 mmol), aryl halide (1 mmol), boronic acid (1.5 mmol), and 3 mL of dioxane. The reactor was sealed, purged with CO three times and pressurized to 5 bar. The resulting mixture was stirred at the indicated temperature for indicated time before being cooled to ambient temperature. The reaction

mixture was diluted with CH_2Cl_2 and washed with water three times. The organic layer was dried over $MgSO_4$, then filtered and concentrated *in vacuo*. The product was purified by the column chromatography on silica.

3.2.1. ***3a*** *[CAS 119-61-9]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.87 (d, J_{H-H} = 7.6 Hz, 4H), 7.62 (t, J_{H-H} = 7.2 Hz, 2H), 7.51 (d, J_{H-H} = 7.6 Hz, 4H). ^{13}C NMR δ 196.8, 137.5, 132.5, 130.3, 127.9.

3.2.2. ***3b*** *[CAS 643-65-2]*

^{1}H NMR ($CDCl_3$) δ, ppm: 7.83 (d, J = 8 Hz, 2H), 7.66 (s, 1H), 7.61 (d, J_{H-H} = 8 Hz, 2H), 7.51 (t, J = 7.6 Hz, 2H), 7.42 (m, 2H), 2.43 (s, 3H). ^{13}C NMR δ, ppm: 196.9, 138.1, 137.7, 137.6, 133.2, 132.3, 130.4, 130.0, 129.7, 128.1, 127.3, 21.3.

3.2.3. ***3c*** *[CAS 6136-67-0]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.83 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.6 Hz, 1H), 7.51 (t, J = 8.4 Hz, 4H), 7.39 (m, 2H), 7.15 (dd, J = 7.8 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR, δ, ppm: 196.5, 159.6, 138.9, 137.6, 132.4, 130.0, 129.2, 128.2, 122.8, 118.8, 114.3, 55.4.

3.2.4. ***3d*** *[CAS 134-85-0]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.80 (t, J = 7.2 Hz, 4H), 7.63 (t, J = 7.8 Hz, 1H), 7.52 (m, 4H). ^{13}C NMR, δ, ppm: 195.5, 138.9, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.4.

3.2.5. ***3e*** *[CAS 13047-06-8]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.85 (d, J = 8 Hz, 2H), 7.68 (m, 2H), 7.50 (t, J = 7.4 Hz 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.39 (t, J = 6.4 Hz 2H). ^{13}C NMR, δ, ppm: 195.8, 140.7, 136.1, 133.7, 133.2, 131.1, 130.2, 129.0, 128.6, 127.2, 119.5.

3.2.6. ***3f*** *[CAS 131-58-8]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.81 (d, J = 8 Hz, 2H), 7.76 (d, J = 8 Hz, 2H), 7.61 (t, J = 7 Hz, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 2.46 (s, 3 H). ^{13}C NMR, δ, ppm: 196.4, 143.2, 137.9, 134.9, 133.5, 132.3, 131.2, 130.3, 129.9, 128.9, 128.2, 21.6.

3.2.7. ***3g*** *and* ***3o*** *[CAS 85520-37-4]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.76 (d, J = 8 Hz, 2H), 7.40 (m, 3H), 7.30 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 6.8 Hz, 1H), 3.86 (s, 3H), 2.45 (s, 3H). ^{13}C NMR, δ, ppm: 196.2, 159.5, 143.2, 139.2, 134.9, 130.2, 129.1, 128.9, 122.6, 118.5, 114.3, 55.4, 21.64.

3.2.8. ***3h*** *[CAS 5395-79-9]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.76 (m, 4H), 7.47 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR, δ, ppm: 195.1, 143.5, 138.5, 139.2, 134.5, 131.3, 130.1, 129.1, 128.5, 21.6.

3.2.9. ***3i*** *[CAS 131822-45-2]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.33 (d, J = 7.6 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H), 7.63 (s, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.48 (d, J = 7 Hz, 1H), 7.433 (t, J = 7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR, δ, ppm: 194.9, 149.7, 143.0, 138.6, 136.3, 134.2, 130.6, 130.4, 128.4, 127.4, 123.50, 21.3.

3.2.10. ***3j*** *[CAS 890098-06-3]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.67 (d, J = 7.6 Hz, 1H), 7.47 (m, 2H), 7.38 (t, J = 7.6 Hz, 3H), 7.31 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR, δ, ppm: 195.6, 159.8, 140.7, 137.4, 133.19, 131.1, 129.5, 128.9, 127.1, 123.5, 120.4, 119.5, 113.6, 55.4.

3.2.11. ***3k*** *[CAS 7497-60-1]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.38 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H). ^{13}C NMR, δ, ppm: 193.5, 149.9, 142.4, 140.1, 134.5, 131.4, 130.5, 129.0, 123.6.

3.2.12. ***3m*** *[CAS 53689-84-2]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.38 (d, J = 8.2 Hz, 2H), 7.94 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.2 Hz, 2H), 7.54 (d, J = 8.2 Hz, 2H). ^{13}C NMR, δ, ppm: 193.5, 149.9, 142.4, 140.1, 134.5, 131.4, 130.5, 129.0, 123.6.

3.2.13. ***3n*** *[CAS 1144-74-7]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.36–8.34 (m, 2H), 7.95–7.93 (m, 2H), 7.80 (t, J = 4.0 Hz, 2H), 7.65 (d, J = 8 Hz, 1H), 7.53 (t, J = 8 Hz, 2H). ^{13}C NMR, δ, ppm: 194.7, 149.8, 142.9, 136.3, 133.5, 130.4, 130.1, 128.6, 123.1.

3.3. General procedure for Pd-catalyzed methoxycarbonylation

The 50 ml stainless steel high pressure Parr reactor was charged with **2** (10^{-3}–10^{-4} mmol), aryl iodide or bromide (1 mmol), methanol (10 mmol), and thriethylamine (2 mL). The reactor was sealed and pressurized with CO(g) to 5 bar. The autoclave was sealed, purged with CO three times and pressurized to 5 bar. The resulting mixture was stirred at the indicated temperature for indicated time before being cooled to ambient temperature. The reaction mixture was ediluted with CH_2Cl_2 and washed with sodium bicarbonate three times. The organic layer was dried over $MgSO_4$, then filtered and concentrated *in vacuo*. The product was purified by the column chromatography on silica if necessary.

3.3.1. ***4a*** *[CAS 99-75-2]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.00, (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 3.91 (s, 3H), 2.41 (s, 3H). ^{13}C NMR, δ, ppm: 167.2, 143.5, 129.6, 129.0, 127.4, 51.9, 21.6.

3.3.2. ***4b*** *[CAS 619-42-1]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.93 (d, J = 8.9 Hz, 2H), 7.61 (d, J = 8.9 Hz, 2H), 3.93 (s, 3H). ^{13}C NMR, δ, ppm: 166.35, 131.7, 131.1, 129.0, 128.0, 51.9.

3.3.3. ***4c*** *and* ***4j*** *[CAS 121-98-2]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.00 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 3.88 (s, 3H), 3.85 (s, 3H). ^{13}C NMR, δ, ppm: 166.7, 131.5, 128.1, 122.4, 113.5, 55.2, 51.7.

3.3.4. ***4d*** *[CAS 131-11-3]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.71 (m, 2H), 7.53 (m, 2H), 3.88 (s, 3H). ^{13}C NMR, δ, ppm: 167.9, 131.8, 131.0, 128.7, 52.5.

3.3.5. ***4e*** *[CAS 5368-81-0]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.64 (d, J = 7.1 Hz, 1H), 7.56 (s, 1H), 7.35 (t, J = 7.1 Hz, 1H), 7.11 (d, J = 8 Hz, 1H) 3.91 (s, 3H), 3.84 (s, 3H). ^{13}C NMR, δ, ppm: 166.9, 159.5, 131.4, 129.3, 121.9, 119.4, 113.9, 55.3, 52.1.

3.3.6. ***4f*** *[CAS 610-96-8]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.80 (d, J = 7.7 Hz, 1H), 7.43 (m, 2H), 7.29 (t, J = 7.7 Hz, 1H), 3.90 (s, 3H). ^{13}C NMR, δ, ppm: 166.0, 133.6, 132.5, 131.3, 131.0, 130.0, 126.5, 52.3.

3.3.7. ***4g*** *[CAS 13531-48-1]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.33 (s, 1H), 8.28 (d, J = 7.2 Hz, 1H), 7.86 (d, J = 8 Hz, 1H), 7.62 (d, J = 8 Hz, 1H) 3.97 (s, 3H). ^{13}C NMR, δ, ppm: 164.9, 135.8, 133.5, 133.1, 131.4, 129.4, 117.7, 112.9, 52.5.

3.3.8. ***4h*** *[CAS 619-50-1]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.26 (m, 4H), 3.96 (s, 3H). ^{13}C NMR, δ, ppm: 165.1, 150.6, 135.5, 130.7, 123.5, 52.8.

3.3.9. ***4i*** *[CAS 99-36-5]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.02 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.2 Hz, 2H), 4.76 (s, 2H), 3.92 (s, 3H). ^{13}C NMR, δ, ppm: 167.2, 138.1, 133.6, 133.4, 130.1, 128.2, 126.7, 52.0, 21.2.

3.3.10. ***4k*** *[CAS 6908-41-4]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.87 (m, 2H), 7.38 (m, 2H), 3.91 (s, 3H), 2.41 (s, 1H). ^{13}C NMR, δ, ppm: 167.1, 146.4, 129.6, 128.9, 126.4, 64.2, 52.1.

3.3.11. ***4l*** *[CAS 26537-19-9]*

^{1}H NMR ($CDCl_3$) 8.00 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 9H). ^{13}C NMR, δ, ppm: 167.1, 156.5, 129.4, 127.3, 125.3, 51.9, 35.0, 31.1.

3.3.12. ***4m*** *[CAS 3609-53-8]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.12 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8.4 Hz, 2H), 3.94 (s, 3H), 2.63 (s, 3H). ^{13}C NMR, δ, ppm: 197.5, 166.2, 140.2, 133.88, 129.8, 128.1, 52.4, 26.8.

3.3.13. ***4n*** *[CAS 93-60-7]*

^{1}H NMR ($CDCl_3$), δ, ppm: 9.17 (s, 1H), 8.73 (d, J = 4.5 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR, δ, ppm: 165.6, 153.3, 150.8, 136.9, 125.9, 123.2, 52.3.

3.3.14. ***4o*** *[CAS 26218-80-4]*

^{1}H NMR ($CDCl_3$), δ, ppm: 8.80 (s, 1H), 8.12 (d, J = 8.1 Hz, 1H), 6.74 (d, J = 9.3 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H). ^{13}C NMR, δ, ppm: 166.8, 165.5, 149.9, 139.4, 119.5, 110.5, 53.9, 51.9.

3.3.15. ***4p*** *[CAS 4818-10-9]*

^{1}H NMR ($CDCl_3$), δ, ppm: 7.35 (m, 2H), 7.19 (d, J = 8 Hz, 1H), 6.84 (m, 1H), 3.87 (s, 3H). ^{13}C NMR, δ, ppm: 167.4, 146.9, 131.0, 129.2, 119.4, 115.7, 52.0.

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