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Palladium-Catalyzed Cross-Coupling Reactions of Organogold(I) Reagents with Organic Electrophiles

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Dedicated to Professor José Barluenga on the occasion of his 70th birthday

Abstract: The palladium-catalyzed cross-coupling reaction of organogold(I) reagents (alkyl, alkenyl, aryl, and alkynyl) with organic electrophiles, such as aryl and alkenyl halides, aryl triflates, benzyl bromide, and benzoyl chloride is reported. The reaction takes place, under palladium catalysis, at room temperature with short reaction times to give the corresponding cross-coupling products in high yields.

Keywords: cross-coupling • gold • homogeneous catalysis • palladium • synthetic methods

Introduction

In recent years, the chemistry of gold(I) complexes has attracted the attention of organic chemists due to their Lewis acid character and their ability to stabilize cationic reaction intermediates.[1] Nowadays, a significant number of synthetic transformations, such as nucleophilic additions to alkynes, alkenes, and allenes, propargylic Claisen rearrangements, cycloadditions and cycloisomerizations, and reduction and oxidation reactions can be performed through gold catalysis.[2] In these transformations, carbon–gold species are transient intermediates that can participate in further organic reactions.[2,3] On the other hand, organic reactions that involve the use of stoichiometric organogold(I) compounds are less developed, despite the important knowledge that can be gained for new synthetic transformations.[4]

The metal-catalyzed cross-coupling reaction of organometallic reagents with organic electrophiles is one of the most powerful reactions in organic synthesis.[5] A variety of metals have proven to be useful, with boron (Suzuki reaction), zinc (Negishi reaction) and tin (Stille reaction) as the most common organometallics used. Furthermore, in recent years we have found that organoindium compounds are also useful reagents in metal-catalyzed cross-coupling reactions.[6] Despite the significant number of metals that have been tested in these reactions,[7] the utility of gold organometallics has remained unexplored for decades. In a recent report, Blum and co-workers showed that vinyl-gold species, intermediates in a palladium-catalyzed carboauration of alkynes, can be used in cross-coupling reactions with organic electrophiles under palladium catalysis.[4a] Additionally, Hashmi et al. reported the cross-coupling reaction of organogold(I) reagents with aryl iodides.[4b] Nevertheless, important aspects about the reactivity organogold reagents, such as their versatility and the usefulness of alkylgold derivatives, still need to be developed. In this paper we report a general study about the reactivity of organogold(I) reagents in the palladium-catalyzed cross-coupling reaction with different organic electrophiles.

Results and Discussion

Gold organometallics (RAu, R_3Au) are usually unstable compounds that require phosphines or carbenes as stabilizing donor ligands.[8] Organogold(I) compounds can be prepared by transmetallation of organolithium or Grignard reagents and from boronic acids by using Au^I salts or cationic complexes.[9] For our study we were interested in preparing a variety of organogold(I) compounds (aryl, alkynyl, alkenyl, and alkyl) and we chose [Ph_3PAuCl] as the gold source, a commercially available complex soluble in the most common organic solvents currently used in gold-catalyzed

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reactions. Following a standard procedure,[10] the phenyl-, phenylethynyl-, butyl-, and (*E*)-1-heptenylgold phosphane reagents **1a**–**1d** were prepared in high yields by treatment of [Ph_3PAuCl] with the corresponding organolithium reagents in THF at −20 °C (Scheme 1). These compounds proved to be stable and could be stored at low temperature, with the exception of **1d**, which decomposed during the workup.[11]

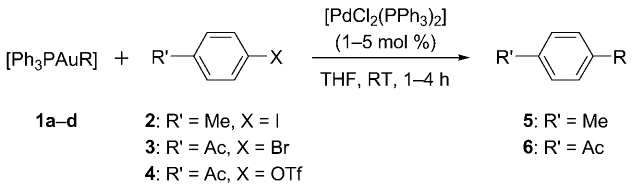
$$\mathrm{R{-}Li} \;+\; [\mathrm{Ph_3PAuCl}] \xrightarrow[-20\,^{\circ}\mathrm{C\ to\ RT}]{\mathrm{THF}} [\mathrm{Ph_3PAuR}]$$

1a: R = Ph, 92%
1b: R = PhC≡C, 99%
1c: R = *n*Bu, 83%
1d: R = (*E*)-1-heptenyl

Scheme 1. Preparation of organogold(I) reagents.

With the organogold phosphanes in hand, we began our investigation into the palladium-catalyzed cross-coupling reaction of phenyl(triphenylphosphine)gold (**1a**) with aryl halides. In our first experiment, the reaction of isolated **1a** (1.1 equiv) with 4-iodotoluene (**2**, 1.0 equiv) in the presence of [$PdCl_2(PPh_3)_2$] (5 mol %) as the catalyst, in THF at room temperature, afforded the cross-coupling product **5a** in 99 % yield after 1 h (Table 1, entry 1). To our delight, the same yield was obtained when the cross-coupling reaction was performed without isolation of the organogold reagent. Additionally, the reaction with other palladium complexes ([$Pd(PPh_3)_4$], [$PdCl_2(dppf)$], [$Pd_2(dba)_3/PPh_3$]; dppf = 1,1′-bis(diphenylphosphino)ferrocene, dba = dibenzylideneacetone) or with lower catalyst loading (1 mol %) also provided the cross-coupling product in similar yields and reaction times. However, in the absence of the palladium catalyst we did not observe any reaction.

Table 1. Palladium-catalyzed cross-coupling reaction of organogold(I) reagents with aryl halides and triflates.



Entry	R	Electrophile	Product	Yield [%][a]
1	Ph **1a**	**2**	**5a**	99
2	PhC≡C **1b**		**5b**	98
3	*n*Bu **1c**		**5c**	–[b]
4	(*E*)-1-heptenyl **1d**		**5d**	85
5	Ph **1a**	**3**	**6a**	87
6	PhC≡C **1b**		**6b**	84
7	*n*Bu **1c**		**6c**	30 (98)[c]
8	(*E*)-1-heptenyl **1d**		**6d**	42 (95)[c]
9	Ph **1a**	**4**	**6a**	93
10	PhC≡C **1b**		**6b**	86
11	*n*Bu **1c**		**6c**	42 (84)[c]
12	(*E*)-1-heptenyl **1d**		**6d**	67 (95)[c]

[a] Yield of the isolated product. [b] 4,4′-Dimethylbiphenyl was isolated in 92 % yield. [c] In parentheses, the yields based on the recovered starting material (brsm). OTf = trifluoromethane sulfonate.

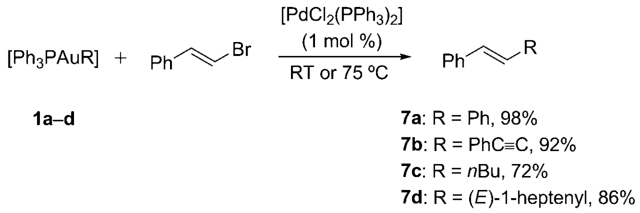
Encouraged by these results we tested the cross-coupling reaction of **1a** with other aryl halides, such as 4-bromoacetophenone (**3**) and the aryl triflate **4**. In both cases, the palladium-catalyzed reaction, carried out by using the previously developed reaction conditions, proceeded chemoselectively and the coupling product **6a** was obtained in 87 % and 93 % yield, respectively (Table 1, entries 5 and 9). These results confirm that aryl bromides and aryl triflates are suitable electrophiles for the cross-coupling reaction of organogold reagents.

Following our research, we studied the reactivity of alkynylgold reagents. The Pd-catalyzed alkynylation is one of the most general procedures for the synthesis of alkynes and a gold-catalyzed Sonogashira reaction was recently reported.[12] Gratifyingly, the cross-coupling reactions of phenylethynyl(triphenylphosphine)gold (**1b**) with the aryl halides **2** and **3**, and aryl triflate **4**, using [$PdCl_2(PPh_3)_2$] (1 mol %) as the catalyst, proceeded at room temperature in 1 h to afford the arylalkynes **5b** and **6b** in excellent yields (84–98 %, Table 1, entries 2, 6, and 10).

At this point, we were especially interested in exploring the reactivity of alkylgold reagents in cross-coupling reactions, since, to the best of our knowledge, no report in this area has been published to date. Surprisingly, the reaction of butyl(triphenylphosphine)gold (**1c**) with 4-iodotoluene using [$PdCl_2(PPh_3)_2$] (1 mol %) as catalyst, gave 4,4′-dimethylbiphenyl in 92 % yield at room temperature in 1 h. The reaction was only observed in the presence of the palladium complex, and the reductive homocoupling of 4-iodotoluene can be explained by the oxidative addition of the alkylgold(I) compound, although we were unable to find any precedence for this reactivity. On the other hand, the palladium-catalyzed cross-coupling reaction of **1c** with 4-bromoacetophenone (**3**) afforded the coupling compound **6c** as a single reaction product in a modest 30 % yield (98 % yield based on recovered starting material (brsm) **3**, Table 1, entry 7). Other reaction conditions with different palladium catalysts, such as [$Pd(PPh_3)_4$] or [$PdCl_2(dppf)$], at higher temperatures, or with a larger excess of the butylgold reagent **1c** did not improve the yield. In accordance with this result, the treatment of **1c** with aryl triflate **4** provided the coupling product **6c** in 42 % yield (84 % brsm, Table 1, entry 11). Notably, the butylgold phosphane **1c** remains in the reaction mixture, which suggests that the transmetallation is the rate-determining step in the cross-coupling reaction.

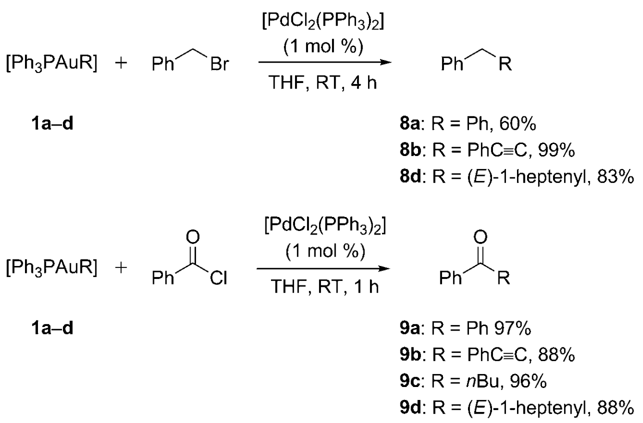
In a further step in the study of the reactivity of organogold reagents in cross-coupling reactions, we explored the reactivity of stereodefined alkenylgold reagents. For this purpose we used (*E*)-1-heptenyl(triphenylphosphine)gold (**1d**) prepared in situ from (*E*)-1-iodo-1-heptene (*E*/*Z* 82:18).[13] The palladium-catalyzed cross-coupling reaction of **1d** with 4-iodotoluene, under the previously developed reaction conditions, proceeded stereospecifically at room temperature affording the styrene **5d** in 85% yield (*E*/*Z* 81:19) after 2 h with retention of the double bond configuration (Table 1, entry 4).[14] The reaction using 4-bromoacetophenone (**3**) and aryl triflate **4** as electrophiles, also afforded the cross-coupling product **6d** (*E*/*Z* 79:21) chemoselectively in 42% and 67% yields (Table 1, entries 8 and 12). In these cases, some of the starting electrophile was recovered and the higher yields were obtained by using the aryl triflate **4** rather than 4-bromoacetophenone (**3**).

On the other hand, we also studied the cross-coupling reaction of the organogold reagents **1a**–**1d** with the stereodefined alkenyl halide β-bromostyrene (*E*/*Z* 90:10). The cross-coupling reaction of **1a**, using $[PdCl_2(PPh_3)_2]$ (1 mol%) as the catalyst at room temperature, resulted in a stereospecific reaction affording *trans*-stilbene (**7a**) in 98% yield after 4 h (Scheme 2). Analogously, the reaction of **1b** took place in excellent 92% yield affording the enyne **7b** without isomerization (*E*/*Z* 90:10), although in this case it was necessary to heat the reaction mixture at 75 °C for 2 h. In contrast to the previous examples using **1c**, the palladium-catalyzed cross-coupling reaction of **1c** with β-bromostyrene provided **7c** in 72% yield without isomerization of the double bond (*E*/*Z* 92:8). In the same way, the reaction of the (*E*)-1-heptenyl(triphenylphosphine)gold (**1d**) with β-bromostyrene gave the 1,3-diene **7d** (1*E*,3*E*/1*E*,3*Z* 85:15) in 86% yield with retention of the configuration in both reagents.



Scheme 2. Palladium-catalyzed cross-coupling reaction of organogold(I) reagents with β-bromostyrene.

At this stage, we were intrigued about the reactivity of organogold(I) reagents with other useful organic electrophiles in cross-coupling reactions, such as benzyl halides and acid chlorides. Benzyl halides are particularly interesting alkyl electrophiles in cross-coupling reactions since they readily undergo oxidative addition and do not suffer β-hydride elimination. The cross-coupling reaction of **1a** (1.1 equiv) with benzyl bromide and $[PdCl_2(PPh_3)_2]$ (1 mol%) as the catalyst afforded diphenylmethane (**8a**) in 60% yield, as a side product we observed the formation of biphenyl (Scheme 3). Alternatively, the reaction using **1b** afforded the coupling product **8b** in quantitative yield after 4 h at room temperature. This result is particularly interesting, since other organometallics have failed in the benzyl-alkynyl cross-coupling-type reaction.[15] Additionally, the reaction of the alkenylgold phosphane **1d** also provided the cross-coupling product **8d** (*E*/*Z* 80:20) in 83% yield without alkene isomerization. Overall, these novel results reveal organogold reagents to be promising reagents in the benzylic coupling.



Scheme 3. Palladium-catalyzed cross-coupling reaction of organogold(I) reagents with benzyl bromide and benzoyl chloride.

The palladium-catalyzed cross-coupling reaction of soft organometallics with acid chlorides is a mild synthetic procedure for the preparation of ketones.[16] For this reason we explored the reaction of phenyl-, phenylethynyl-, heptenyl-, and butylgold phosphanes (**1a**–**1d**) with benzoyl chloride. In all cases, the coupling reaction using only 1 mol% $[PdCl_2(PPh_3)_2]$ as catalyst took place efficiently at room temperature in 1 h, giving rise to the corresponding ketones **9a**–**9d** in high yields (88–97%, Scheme 3). Nevertheless, in the absence of a palladium catalyst the coupling reaction was not observed.

Conclusion

We have shown that aryl, alkynyl, alkenyl, and alkylgold(I) reagents participate in palladium-catalyzed cross-coupling reactions with different organic electrophiles, such as aryl and alkenyl halides, aryl triflates, benzoyl chloride, and benzyl bromide. The cross-coupling reaction can be performed under mild conditions, at room temperature and in short reaction times, by using the isolated or the preformed organogold reagent. The stability of the organogold phosphanes and their high versatility and efficiency with all the electrophiles tested is remarkable. These results show organogold(I) phosphanes as useful reagents in cross-coupling reactions and as valuable intermediates in organic synthesis.

Experimental Section

General: Unless otherwise is stated, all reactions were conducted in flame-dried glassware under a positive pressure of argon. Reaction temperatures refer to external bath temperatures. Anhydrous THF was obtained by distillation from the sodium/benzophenone. All other commercially available reagents were used as received. Organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated by using a rotary evaporator at aspirator pressure (20–30 mmHg). TLC was carried out on silica gel 60 F_{254} (layer thickness 0.2 mm) and components were located by observation under UV light and/or by treating the plates with a phosphomolybdic acid, or *p*-anisaldehyde reagent followed by heating. Column chromatography was performed on silica gel (230–400 mesh).[17] NMR spectra were performed in a Bruker Avance 300 spectrometer using the residual solvent signal as internal standard. DEPT spectroscopy was used to assign carbon types. The low resolution EIMS were measured on a Thermo Finnigan Trace MS spectrometer at 70 eV. The HRMS were measured on a Thermo Finnigan MAT 95XP spectrometer. IR spectra were taken with a Bruker Vector 22 and with ATR ("attenuated total reflectance").

General procedure for the preparation of organogold compounds: A 25 mL round-bottomed flask furnished with a stirrer bar was charged with [Ph_3PAuCl] (75 mg, 0.152 mmol) and a positive argon pressure was established. Dry THF (3 mL) was added and the resulting solution was cooled to −20 °C. A solution of RLi (1.0–2.3 M in hexanes, THF or Bu_2O, 0.182 mmol) was added dropwise, the mixture was stirred for 20 min, the cooling bath was removed, and the reaction mixture stirred for 1 h at RT. The solvent was evaporated under reduced pressure and benzene (5 mL) was added. The mixture was filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted with a minimum of benzene, filtered, washed with pentane and dried under high vacuum.

Phenyl(triphenylphosphine)gold (1a):[4c] Following the general procedure, **1a** was isolated as a white powder (74.8 mg, 0.139 mmol, 92 %). M.p. 160–161 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.88$–6.97 (m, 9H), 7.26 (t, ^3J (H,H) = 7.4 Hz, 1H), 7.37–7.44 (m, 6H), 7.52 (t, ^3J (H,H) = 7.5 Hz, 2H), 8.11 ppm (d, ^3J (H,H) = 7.0 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 125.9$ (s, CH), 127.5 (s, C), 127.7 (s, C), 127.7 (brs, CH), 128.7 (d, ^1J (C,P) = 10.5 Hz, CH), 130.6 (br s, CH), 134.2 (d, ^1J (C,P) = 13.9 Hz, CH), 140.0 ppm (s, CH); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): $\delta = 43.99$ ppm (s); IR (ATR): $\tilde{\nu} = 3051$, 3006, 2922, 2851, 1571, 1478, 1434 cm^{-1}; MS (70 eV): *m*/*z* (%): 536 (71) [M^+], 459 (100) [$M^+ - C_6H_5$]; HRMS (EI): *m*/*z*: calcd for $C_{24}H_{20}PAu$: 536.0963 [M^+]; found: 536.0944.

2-Phenylethynyl(triphenylphosphine)gold (1b):[18] Following the general procedure, a solution of phenylethynyllithium was prepared from phenylacetylene (20 μL, 0.182 mmol) and *n*BuLi (80 μL, 2.3 M in hexanes, 0.182 mmol) using a literature procedure.[6a] The product **1b** was isolated as a white powder (84.3 mg, 0.150 mmol, 99 %). M.p. 161–162 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 6.84$–6.98 (m, 9H), 7.02–7.08 (m, 3H), 7.19–7.26 (m, 6H), 7.84 ppm (d, $J = 7.9$ Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 126.1$ (s, CH), 127.5 (s, C), 127.8 (s, C), 128.1 (d, ^1J (C,P) = 12.2 Hz, CH), 128.8 (d, ^1J (C,P) = 11.2 Hz, CH), 129.9 (s, C), 130.6 (s, C), 130.8 (d, ^1J (C,P) = 2.2 Hz, CH), 132.4 (s, CH), 134.1 ppm (d, ^1J (C,P) = 13.9 Hz, CH); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): $\delta =$ 41.98 ppm (s); IR (ATR): $\tilde{\nu} = 3053$, 2923, 2357, 1595, 1483, 1435, 1331 cm^{-1}; MS (70 eV): *m*/*z* (%): 560 (18) [M^+], 459 (1) [$M^+ - C_8H_5$], 404 (100); HRMS (EI): *m*/*z* : calcd for $C_{26}H_{20}PAu$: 560.0963 [M^+]; found: 560.0985.

Butyl(triphenylphosphine)gold (1c):[19] Following the general procedure, **1c** was isolated as a colorless oil (64.7 mg, 0.125 mmol, 83 %). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): $\delta = 0.97$ (t, $J = 7.3$ Hz, 3H), 1.43–1.55 (m, 4H), 1.82–1.96 (m, 4H), 7.42–7.59 ppm (m, 15H); ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): $\delta = 14.3$ (s, CH_3), 29.5 (d, ^1J (C,P) = 5.3 Hz, CH_2), 30.8 (d, ^1J (C,P) = 94.9 Hz, CH_2), 34.1 (d, ^1J (C,P) = 3.8 Hz, CH_2), 128.9 (d, ^1J (C,P) = 10.3 Hz, CH), 130.7 (d, ^1J (C,P) = 2.1 Hz, CH), 131.8 (d, ^1J (C,P) = 45.1 Hz, C), 134.3 ppm (d, ^1J (C,P) = 13.7 Hz, CH); ^{31}P NMR (121.5 MHz, $CDCl_3$, 25 °C): $\delta = 46.37$ ppm (s); IR (ATR): $\tilde{\nu} = 3640$, 2952, 2914, 2867, 1479, 1434, 1381 cm^{-1}; MS (70 eV): *m*/*z* (%): 516 (7) [M^+], 487 (15) [$M^+ - C_2H_5$], 459 (100) [$M^+ - C_4H_9$]; HRMS (EI): *m*/*z*: calcd for $C_{22}H_{24}PAu$: 516.1276 [M^+]; found: 516.1251.

(*E*)-1-Hepten-1-yl(triphenylphosphine)gold (1d): Following the general procedure, a solution of (*E*)-1-heptenyllithium, prepared from (*E*)-1-iodo-1-heptene (40.8 mg, 0.182 mmol, *E*/*Z* 82:18) and *t*BuLi (0.215 mL, 1.7 M in pentane, 0.364 mmol), was added to a solution of [Ph_3PAuCl] (90 mg, 0.182 mmol) in THF (3 mL) and the resulting organogold phosphane **1d** was used directly in the palladium-catalyzed cross-coupling reaction. Alternatively, **1d** can be prepared from (*E*)-1-heptenylboronic acid: Cs_2CO_3 (105.4 mg, 0.323 mmol) and [Ph_3PAuCl] (80 mg, 0.161 mmol) were added successively to a solution of (*E*)-1-heptenylboronic acid (45.9 mg, 0.323 mmol) in dry isopropyl alcohol (5 mL). The resultant white suspension was stirred at 50 °C for 24 h and taken to dryness by rotary evaporation. The solid was extracted with benzene, filtered through Celite, concentrated in vacuo to dryness, washed with pentane and dried. The solid was re-extracted with a minimum of benzene, filtered, washed with pentane and dried under high vacuum, to give organogold phosphane **1d** as a pale brown solid (80.7 mg, 0.145 mmol, 90 %). M.p. 91–93 °C; ^{1}H NMR (300 MHz, C_6D_6, 25 °C): $\delta = 0.87$ (t, ^3J (H,H) = 7.2 Hz, 3H), 1.26–1.49 (m, 4H), 1.61–1.71 (m, 2H), 2.56 (q, ^3J (H,H) = 6.9 Hz, 2H), 6.43–6.56 (m, 1H), 6.85–6.97 (m, 9H), 7.35–7.43 (m, 6H), 7.53 ppm (dd, ^3J (H,H) = 18.4, 5.1 Hz, 1H); ^{13}C NMR (75 MHz, C_6D_6, 25 °C): $\delta = 14.0$ (CH_3), 22.8 ($2 \times CH_2$), 30.2 (CH_2), 31.7 (CH_2), 128.7 (d, ^1J (C,P) = 10.5 Hz, CH), 130.5 (CH), 131.7 (d, ^1J (C,P) = 47.2 Hz, C), 134.2 (d, ^1J (C,P) = 13.8 Hz, CH), 144.4 (CH), 146.4 ppm (CH); ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): $\delta = 45.41$ ppm (s). IR (ATR): $\tilde{\nu} = 3053$, 2952, 2916, 2849, 1583, 1479 cm^{-1}.

General procedure for the palladium-catalyzed cross-coupling reaction: A solution of [Ph_3PAuR] (1.1 equiv), freshly prepared in situ by reaction of RLi (1.1 equiv) with [Ph_3PAuCl] (1.1 equiv) at −20 °C and warming to RT for 1 h, was added to a mixture of the electrophile (1.0 equiv) and palladium catalyst (1 mol %) in dry THF (4 mL). The resulting mixture was stirred at RT under argon until the starting material had been consumed (TLC). The reaction mixture was concentrated under reduced pressure and Et_2O (20 mL) was added. The ethereal phase was washed with aqueous HCl (5 %, 10 mL), brine (10 mL), dried with $MgSO_4$, filtered, and concentrated to a reduced volume under vacuum. The residue was purified by flash chromatography to afford, after concentration and high-vacuum drying, the corresponding cross-coupling product.

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