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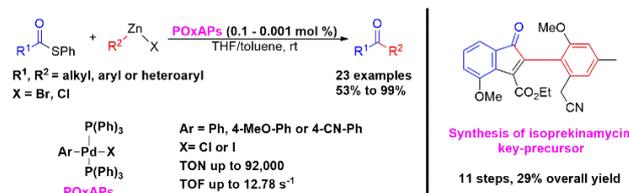
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# Fukuyama Cross-Coupling Approach to Isoprekinamycin: Discovery of the Highly Active and Bench Stable Palladium Precatalyst POxAP

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Supporting Information Placeholder



**ABSTRACT:** An efficient and user-friendly palladium(II) precatalyst, POxAP (Post-Oxidative-Addition Precatalyst), was identified for use in Fukuyama cross-coupling reactions. Suitable for storage under air, the POxAP precatalyst allowed the reaction between thioesters and organozinc reagents with turnover numbers of  $\approx 90,000$ . A series of 23 ketones were obtained with yields ranging from 53 to 99%. As proof of efficacy, an alternative approach was developed for the synthesis of a key-precursor of the natural product isoprekinamycin.

Benzo[a]fluorenes, including isoprekinamycin (IPK) and fluostatins A–Q, represent an interesting class of natural products.<sup>1</sup> IPK is particularly noteworthy as it bears a diazo group at the 5-position, which plays a crucial role in its cytotoxicity against cancer cell lines.<sup>2</sup> To date, only one total synthesis of IPK has been reported (Figure 1),<sup>2e</sup> where the key step involved formation of precursor **1** through a Suzuki-Miyaura cross-coupling reaction (CCR). While the transformation of **1** into IPK was efficiently achieved over 9 steps and in a 23% overall yield, the synthesis of **1** appeared less efficient, with 16 steps being required to give an overall yield of 3%. Thus, we herein propose an alternative approach based on the Fukuyama cross-coupling reaction,<sup>3</sup> where a palladium precatalyst POxAP, of generic formula PdX(Ar)(PPh<sub>3</sub>)<sub>2</sub> is employed to efficiently generate ketones.

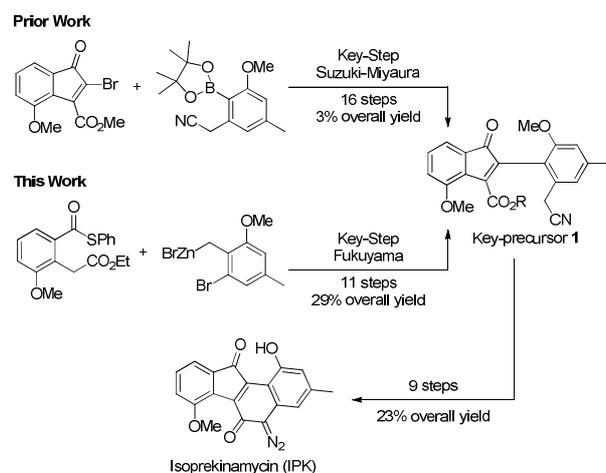


Figure 1. Synthetic strategies to the key IPK precursor

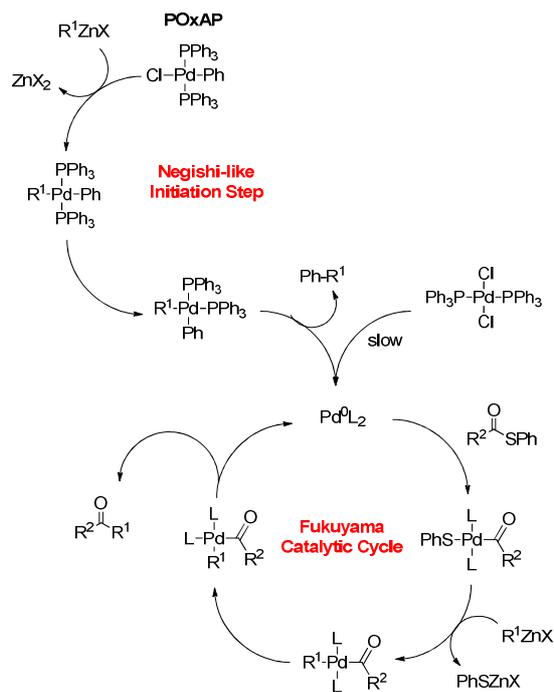
Table 1. Fukuyama CCR on a model system

entry <sup>a</sup>	cat.	temp (°C)	time (min)	yield (%) <sup>b</sup>	
				4a	5
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	25	15	9	27
2	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	50	15	8	62
3 <sup>c</sup>	Pd(dba) <sub>2</sub> /P(Fu) <sub>3</sub>	50	45	19	14
4 <sup>d</sup>	Pd <sub>2</sub> (dba) <sub>3</sub> /PCy <sub>3</sub> /ZnCl <sub>2</sub>	50	45	31	53
5 <sup>e</sup>	Ni(acac) <sub>2</sub>	50	45	0	0
6	NiCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	50	45	19	44
7	Cu(TMHD) <sub>2</sub>	50	45	27	41
8	Fe(acac) <sub>3</sub>	50	45	15	22
9	XPhos-Pd-G4	50	30	trace	0
10	PEPPSI-IPr	50	30	15	51
11 <sup>f</sup>	PdCl(Ph)(PPh <sub>3</sub> ) <sub>2</sub> [POxAP]	50	5	95	0

<sup>a</sup>Reaction conditions: Thioester **3a** (0.14 mmol), catalyst (1 mol %), BnZnBr (0.21 mmol, 0.82 M in THF), toluene (0.26 mL), rt. <sup>b</sup>Isolated yield. <sup>c</sup>1.4 mol % P(Fu)<sub>3</sub>. <sup>d</sup>2 mol % PCy<sub>3</sub> and 1 equiv ZnCl<sub>2</sub> were used. <sup>e</sup>10 mol % Ni(acac)<sub>2</sub>. <sup>f</sup>0.1 mol %

$\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$  (0.1 mL,  $1.4 \times 10^{-3}$  M in THF/toluene) was used.

Initially, we investigated the preparation of an unsubstituted version of the key precursor of IPK, as outlined in Table 1. Starting from commercially available 2-bromobenzoic acid, a copper-mediated acetylation was easily performed to obtain **2a** in 98% yield.<sup>4</sup> A coupling reaction with EDCI/HOBt led to thioester **3a**, a classical substrate of the Fukuyama reaction. Surprisingly, under standard conditions, the Fukuyama reaction between **3a** and benzylzinc bromide afforded the expected compound **4a** in a poor 8% yield (Table 1, entry 2), while naphthalenediol **5** was recovered as the main product (62% yield). A dropwise addition of benzylzinc bromide at 25 °C still gave a mixture of **4a** and **5** in yields of 9% and 27%, respectively (Table 1, entry 1). It was therefore considered that the Fukuyama reaction was relatively slow, thereby allowing any unreacted  $\text{BnZnBr}$  to act as a base toward ketone **4a**, speeding up the Dieckman condensation reaction and yielding compound **5**. Consequently, other catalytic conditions described previously in the literature were investigated for the Fukuyama CCR, with palladium, nickel, and iron-based catalysts being employed in the presence of various ligands or additives (Table 1, entries 3–8).<sup>5</sup> All conditions favored the formation of **5**, which we expect may be due to the slow formation of Pd(0) from Pd(II). Indeed, during the past decade, significant effort has been focused on the development of stable Pd(II) precatalysts, which can be easily transformed *in situ* into Pd(0).<sup>6</sup> In the Fukuyama CCR, 4<sup>th</sup> generation palladacycles from Buchwald's group led to traces of **4a**, while PEPPSI-IPr precatalyst from Organ's group afforded ketone **4a** in a 15% yield (Table 1, entries 9–10). It is important to highlight that these two precatalysts have been optimized for the Negishi CCR,<sup>7</sup> and may require different ligands for Fukuyama CCR. We then examined an alternative palladium precatalyst,  $\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$ , which we recently identified and referred to by a generic name, POxAP (i.e., a Post-Oxidative-Addition Precatalyst). Indeed,  $\text{PdX}(\text{Ar})(\text{PPh}_3)_2$  precatalysts respect the criteria of Pd-based OACs (oxidative addition complexes) recently described by Ingoglia and Buchwald.<sup>8</sup> This palladium complex is well-known in the literature, as it is formed through the first oxidative addition between  $\text{Pd}(0)\text{Ln}$  and  $\text{PhCl}$ , and is common in the majority of palladium-catalyzed CCRs.<sup>9</sup> While this complex has been extensively cited in various mechanistic studies, it has been scarcely described *per se* as a catalyst. We have only found three papers published in the seventies, at the very beginning of the palladium-catalyzed CCR era, in which  $\text{PdI}(\text{Ph})(\text{PPh}_3)_2$  was used in only one example of Heck CCR,<sup>10</sup> and Negishi CCR.<sup>11</sup> In 1976, Sekiya and Ishikawa reported that  $\text{PdI}(\text{Ph})(\text{PPh}_3)_2$  could be used as a catalyst in the Kumada CCR between  $\text{ArI}$  and  $\text{ArMgX}$ , with yields ranging from 32 to 82%.<sup>12</sup> Yet,  $\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$  complex is a bench stable Pd(II) complex, that can be both stored and manipulated under air, and is easily obtained from  $\text{Pd}(\text{PPh}_3)_4$ .<sup>13</sup> In the presence of an organozinc reagent  $\text{R}^1\text{ZnX}$ , this complex follows a Negishi-like initiation step, and provides  $\text{PhR}$  as well as a reactive Pd(0) entity, which is then available for a subsequent Fukuyama catalytic cycle (Figure 2).

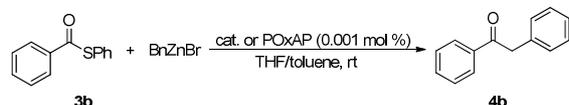


**Figure 2.** Comparison of the reaction mechanisms involved where  $\text{PdCl}_2(\text{PPh}_3)_2$  and the POxAP  $\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$  are employed

Thus, using Fleming's procedure,  $\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$  was obtained in a high yield, and was employed with a loading of 0.1 mol % in the Fukuyama CCR featured in Table 1. Pleasingly, ketone **4a** was obtained in a 95% yield after only 5 min, without any trace of naphthalenediol **5** being observed (Table 1, entry 11). To better determine the reactivity of this new precatalyst, we synthesized 3 derivatives, namely  $\text{PdCl}(4\text{-CN-Ph})(\text{PPh}_3)_2$ ,  $\text{PdCl}(4\text{-MeO-Ph})(\text{PPh}_3)_2$ , and  $\text{PdI}(4\text{-MeO-Ph})(\text{PPh}_3)_2$ , in which electron-donating or withdrawing groups were added to the phenyl ring, or where chlorine was substituted with iodine. These potential POxAPs were compared in a kinetic study based on the Fukuyama CCR, as shown in Table 2. Interestingly, with a loading of only 0.001 mol %,  $\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$  catalyzed the formation of ketone **4b** in a 92% yield with a turnover number (TON) of 92,000 (Table 2, entry 2). In comparison, classical  $\text{PdCl}_2(\text{PPh}_3)_2$  led to a poor yield of 12% (Table 2, entry 1), while other POxAPs gave similar yields and TONs to  $\text{PdCl}(\text{Ph})(\text{PPh}_3)_2$  (Table 2, entries 3–5). However, differences in reactivity appeared when measuring the turnover frequencies (TOF). Initial rates were determined for the first 30 min of the reaction, and it was found that the presence of an aryl moiety bearing an electron-withdrawing group (i.e., 4-CN-Ph, 2.22 vs 5.55  $\text{s}^{-1}$  for Ph) decreased the initial rate, while the presence of an electron-donating group (i.e., 4-OMe-Ph, 8.89 vs 5.55  $\text{s}^{-1}$  for Ph) increased this rate (Table 2, entries 3–5). This result is fully consistent with our proposed mechanism. Indeed, compared with electron-poor compounds, reductive elimination is favored by electron-rich compounds. Furthermore, the replacement of chlorine by iodine led also to an initial rate increase (i.e., 8.89 vs 12.8  $\text{s}^{-1}$ ) as iodine is more easily substituted by the organozinc reagent than chlorine (Table 2, entries 4–5). However, these differences in the initial rates disappeared

between 4 and 8 h (i.e., the cruising rate), where rates ranging from 1.46 to 1.6 s<sup>-1</sup> were recorded. Indeed, following our concept, all four POxAPs led to the same catalytic entity Pd(0)L<sub>n</sub>, which is consistent with observation of similar cruising rates following the initial stages of the reaction.

**Table 2. Kinetic study<sup>a</sup> into the Fukuyama CCR using various precatalysts of generic formula PdX(Ar)(PPh<sub>3</sub>)<sub>2</sub>**



entry	cat. or POxAP (0.001 mol %)	TON	TOF (s <sup>-1</sup> )		yield (%) <sup>d</sup>
			initial rate <sup>b</sup>	cruising rate <sup>c</sup>	
1	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	12,000	0.55	0.21	12
2	PdCl(Ph)(PPh <sub>3</sub> ) <sub>2</sub>	92,000	5.55	1.46	92
3	PdCl(4-CN-Ph)(PPh <sub>3</sub> ) <sub>2</sub>	83,000	2.22	1.53	83
4	PdCl(4-MeO-Ph)(PPh <sub>3</sub> ) <sub>2</sub>	89,000	8.89	1.60	89
5	PdI(4-MeO-Ph)(PPh <sub>3</sub> ) <sub>2</sub>	91,000	12.78	1.53	91

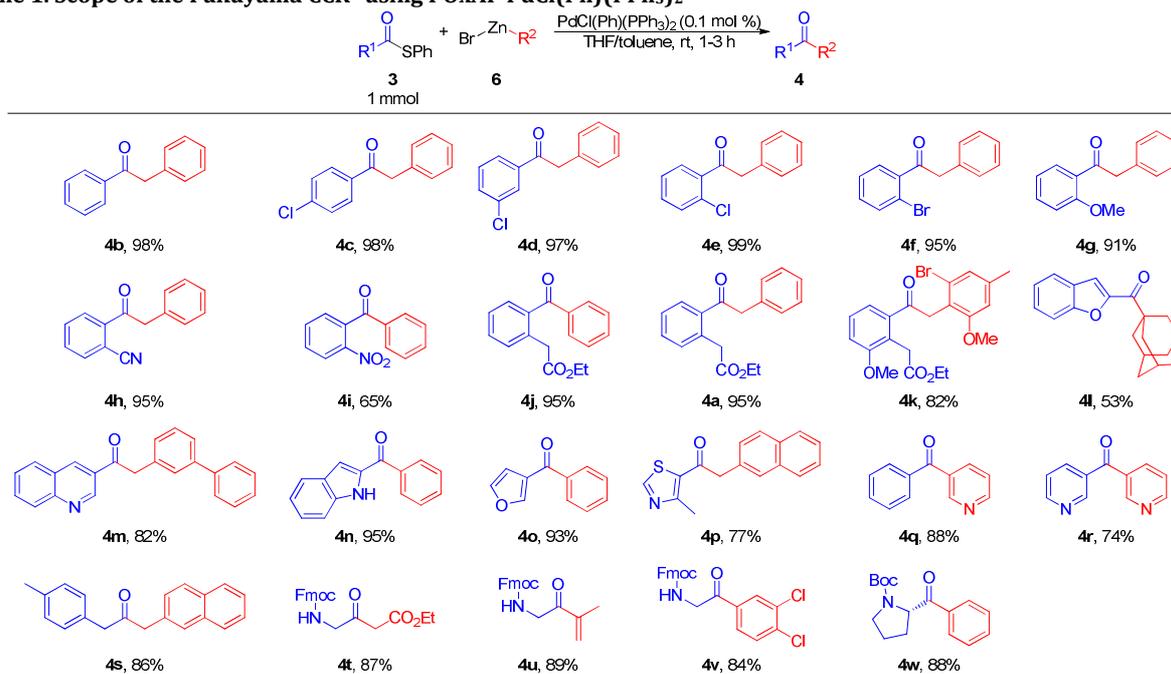
<sup>a</sup>Reaction conditions: Thioester **3b** (0.14 mmol), [Pd] (0.001 mol %), BnZnBr (0.21 mmol, 0.82 M in THF), toluene (0.26 mL), rt. <sup>b</sup>Initial rate was measured between 0 and 30 min. <sup>c</sup>Cruising rate was measured between 4 and 8 h. <sup>d</sup>Yield of **4b** was determined from the average of two independent experiments by HPLC/UV using caffeine as an internal standard.

Further proof of the proposed mechanism shown in Figure 2 is the fact that 3-phenylpyridine (Ph-R<sup>1</sup>) was detected by mass spectroscopy, which resulted from the Negishi-like initiation step in the presence of pyridin-3-ylzinc bromide. All POxAPs were bench-stable for several weeks, and could be both manipulated and stored under air.

Metal-catalyzed formation of ketones is still a very prolific area of scientific investigation,<sup>14</sup> as ketone-containing products are numerous in many fields of chemistry.

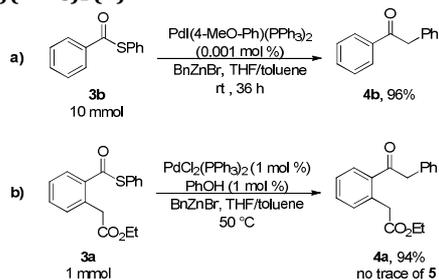
Using PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub>, we then investigated the scope of the Fukuyama CCR at the 1 mmol scale, synthesizing 23 ketones in yields ranging from 53 to 99% (Scheme 1). As shown, aryl, heteroaryl, and alkyl thioesters were easily coupled to aryl or alkyl organozinc reagents in high yields. Even bulky ketone **4k** was obtained in 82% yield despite the steric hindrance on both the thioester and the organozinc reagent. In addition, the use of 0.1 mol % PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub> produced a range of ketones over 1–3 h at room temperature. Furthermore, with a 0.001 mol % loading of PdI(4-MeO-Ph)(PPh<sub>3</sub>)<sub>2</sub>, an extended reaction time of 36 h transformed 10 mmol of thioester **3b** into the corresponding ketone **4b** in 96% yield (Scheme 2a).

**Scheme 1. Scope of the Fukuyama CCR<sup>a</sup> using POxAP PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub>**



<sup>a</sup>Reaction conditions: Thioester **3** (1 mmol), PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub> (0.1 mol %), R<sup>2</sup>ZnBr **6** (1.5 mmol in THF), toluene (2.5 mL), rt, 1–3 h.

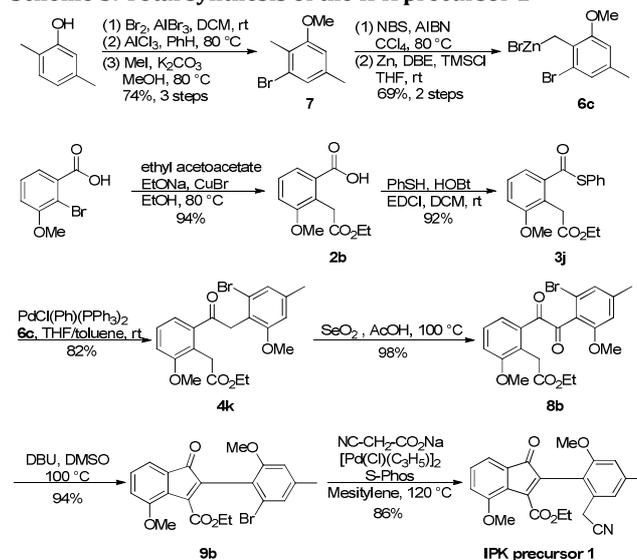
**Scheme 2. Scale-Up (a) and *in situ* generation of PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub> (b)**



Interestingly, POxAP can also be generated *in situ* starting from PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>. Indeed, in 2006, Yasuda et al. reported that PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> reacts with phenolate to afford PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub> in a low yield (≈10%).<sup>15</sup> Moreover, through the use of equimolar amounts of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> and PhOH in the presence of organozinc reagents, the POxAP PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub> was generated *in situ*, as confirmed by NMR spectroscopy (see SI), and compound **4a** was obtained in 94% yield (Scheme 2b), without any trace of naphthalenediol **5**.

With the efficient precatalyst POxAP in hand, we attempted to complete the synthesis of the IPK precursor (Scheme 3) following the strategy proposed in Figure 1. Starting from 2,5-dimethylphenol, the perbromination of positions 3, 4, and 6, followed by the debromination of positions 4 and 6 by AlCl<sub>3</sub>, led to the desired 3-bromo-2,5-dimethylphenol. Following a subsequent O-methylation step, **7** was obtained in a 74% overall yield (3 steps). Radical bromination of the methyl group at position 2 then gave organozinc **6c**, which was stored in THF. Subsequently, 2-bromo-3-methoxybenzoic acid was coupled to ethyl acetoacetate in the presence of a catalytic amount of copper

**Scheme 3. Total synthesis of the IPK precursor 1**



bromide. While sodium ethanolate is required for the copper-mediated coupling reaction, it also promoted an *in situ* deacetylation to afford **2b** in a 94% yield. Following formation of the thioester **3j** under standard conditions, a Fukuyama CCR was performed with organozinc **6c** using POxAP PdCl(Ph)(PPh<sub>3</sub>)<sub>2</sub> to give **4k** in 82% yield, which was oxidized by SeO<sub>2</sub> in AcOH.<sup>16</sup> Several conditions were then attempted for the subsequent cyclization. While TEA in hot ethanol produced **9a** (Table 1), the unsubstituted analog of **9b**, the steric hindrance imparted by both aromatic rings of **8b** prevented the formation of **9b** itself. Several conditions were examined (see SI), but only the use of DBU in hot DMSO led to indanone **9b** in an excellent yield. Finally, a palladium-catalyzed cyanation reaction led to the desired

IPK precursor **1**. This compound was synthesized over 11 steps and in an overall yield of 29%. This compares to a 3% overall yield from 16 steps as reported previously.<sup>2e</sup>

In conclusion, we demonstrated that the POxAPs of generic formula PdX(Ar)(PPh<sub>3</sub>)<sub>2</sub>, prepared from the oxidative addition of Pd(0) with ArX, constituted efficient Pd(II) precatalysts. Indeed, these bench stable POxAPs could be employed in particularly low quantities (0.001 mol %) to perform Fukuyama CCRs and generate a large diversity of ketones. This efficacy was demonstrated through the development of a convenient route to IPK. The use of these POxAP are not limited to the Fukuyama CCR, and their efficacies in other palladium-catalyzed CCRs are currently under investigation.

## ASSOCIATED CONTENT

### Supporting Information

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

Full experimental details; <sup>1</sup>H and <sup>13</sup>C NMR spectra (doc)

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### Author Contributions

The manuscript was written through contributions of all authors.

### Notes

The authors declare no competing financial interest.

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