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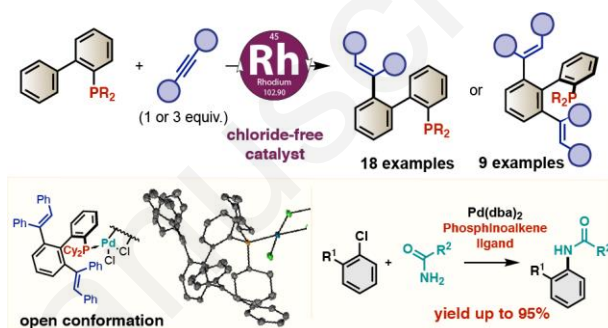
Late-Stage Diversification of Biarylphosphines through Rhodium(I)-Catalyzed C–H Bond Alkenylation with Internal Alkynes

Zhuan Zhang, Marie Cordier, Pierre H. Dixneuf, and Jean-François Soulé*

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Supporting Information Placeholder

ABSTRACT: We report herein P(III)-directed C–H bond alkenylation of (dialkyl)- and (diaryl)-biarylphosphines using internal alkynes. Chloride-free $[\text{Rh}(\text{COD})\text{OAc}]_2$ acts as a better catalyst than commercially available $[\text{RhCl}(\text{COD})]_2$. Conditions were developed to control the mono- and difunctionalization depending on the alkyne stoichiometry. One of these novel bis-alkenylated (dialkyl)biarylphosphine was employed for the preparation of a palladium(II) complex and some of these functionalized ligands have outperformed their corresponding unfunctionalized phosphines in Pd-catalyzed amidation with sterically hindered aryl chlorides.



Phosphine ligands play a significant role in catalysis, tuning the reactivity at the metal center through their modulable steric and electronic properties.¹ (Dialkyl)- or (diaryl)-biarylphosphines such as JohnPhos and XPhos ligands were widely employed in transition-metal catalysis (e.g., Pd or Au) owing their unique structural features displaying weak metal-arene interactions.² The presence of bulky substituents (*i.e.*, *i*Pr) at the both *ortho*-positions avoids the cyclometallation and lead to more active catalysts (Figure 1).

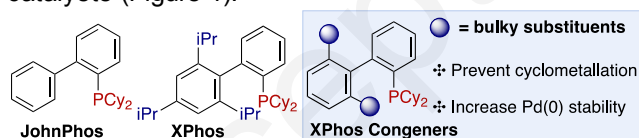


Figure 1. Relevant & Structural features of Biarylphosphines

However, the traditional synthetic approaches of biarylphosphines involve multistep synthesis with polar organometallic reagents making challenging the production of banks of multifunctional ligands to search for optimal catalytic activities. Recently, late-stage diversification—via C–H bond functionalization—was comfortably ensconced to optimize the design of pharmaceuticals,³ and organic materials;⁴ but it was barely employed for generation of ligand's bank.⁵ Since the discovery by Hartwig that regioselective C–H bond functionalization can be directed by P(III) atom,⁶ this strategy has been applied to quickly modify biaryl phosphines by C–H bond borylation;⁷ and by C–H bond

arylation,⁸ and C–H bond silylation.⁹ In 2019, our group reported *ortho*-C–H bond alkylation biarylphosphines allowing the preparation of 40 multifunctional phosphines with unique efficiency for catalytic carboxylation reaction. (Figure 1b).¹⁰ At the same time, Shi's group reported similar reactions, albeit using $[\text{RhCl}(\text{COD})]_2$.¹¹ They have also shown that terminal alkynes can be employed leading *ortho*-monoalkenylated biarylphosphines (Figure 1c).¹¹ In contrast to alkenes, with which *bis-ortho*-dialkylation easily occurs; with terminal alkynes, only the mono-alkenylation happened. As there was no example of mono- and di-alkenylation with internal alkynes, we investigate Rh(III) and Rh(I) catalytic system to reach this target (Figure 1d).

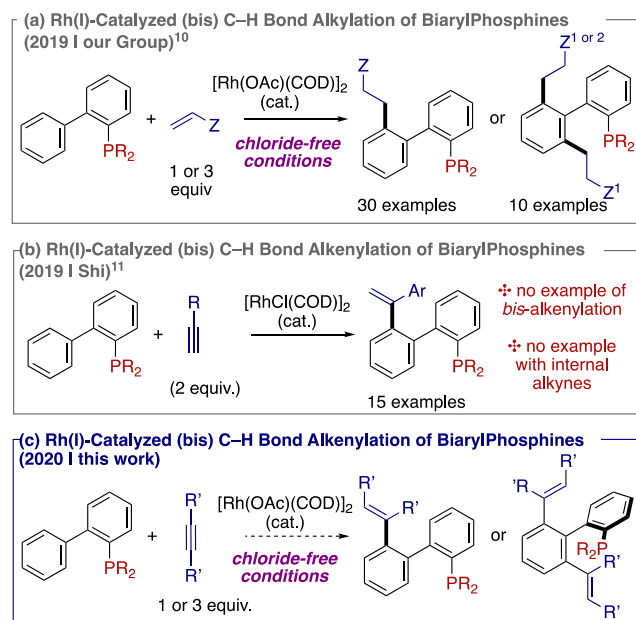
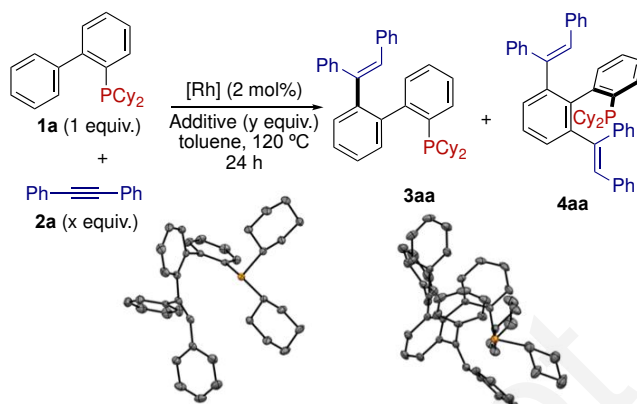


Figure 2. Late-stage Diversification of Biarylphosphines

We selected Cy-JohnPhos (**1a**) and diphenylacetylene (**2a**) as model substrates to investigate the C–H bond alkenylation directed by P(III) atom (Table 1). As the first attempt, we evaluated the conditions described by Fagnou for the hydroarylation of internal alkynes (namely, 2 mol% $\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2$ associated with PivOH in toluene)¹² but no reaction occurred (entry 1). The use of $[\text{Cp}^*\text{RhCl}_2]_2$ as catalyst also failed to deliver the functionalized phosphine **3aa** or **4aa**, likely due to strong P(III)–Rh(III) bonds (entry 2). We then evaluated Rh(I) catalyst, as we and others previously demonstrated their efficiency in P(III)-directed C–H bond activation/functionalization.^{7d, 8, 10–11} Moreover, Rh(I) catalysts have been also employed in alkenylation of arene $\text{C}(\text{sp}^2)\text{--H}$ bond with alkynes using a bidental directing group¹³ or nitrogen group.¹⁴ The Shi's conditions for alkenylation with terminal alkyne afforded **3aa** in only 23% yield (entry 3). The use of the Wilkinson catalyst $[\text{RhCl}(\text{PPh}_3)_3]$ gave a lower yield (entry 4). However, higher activity was observed using 2 mol% chloride-free $[\text{Rh}(\text{OAc})(\text{COD})]_2$ catalyst affording the mono-alkenylated phosphine **3aa** in 71% among with 21% of bis-alkenylated phosphine **4aa** (entry 5). Interestingly, in the presence of a base, the formation of the *bis-ortho'*-alkenylated phosphine **4aa** can be decreased, and the best result was obtained using 0.25 equivalent of KOAc affording **3aa** in 86% isolated yield (entries 6–10). To get the *bis-ortho'*-alkenylated phosphine **4aa** selectively, we increased the amount of diphenylacetylene (**2a**) (entries 11 and 12). In the presence of 3 equivalents of **2a** and 4 mol% of Rh catalyst, **4aa** was isolated in 75% yield (entry 13). Using 0.5 equiv. of KOAc, the isolated yield can rise up to 78% (entry 14).

Table 1. Optimization of the Reaction Conditions

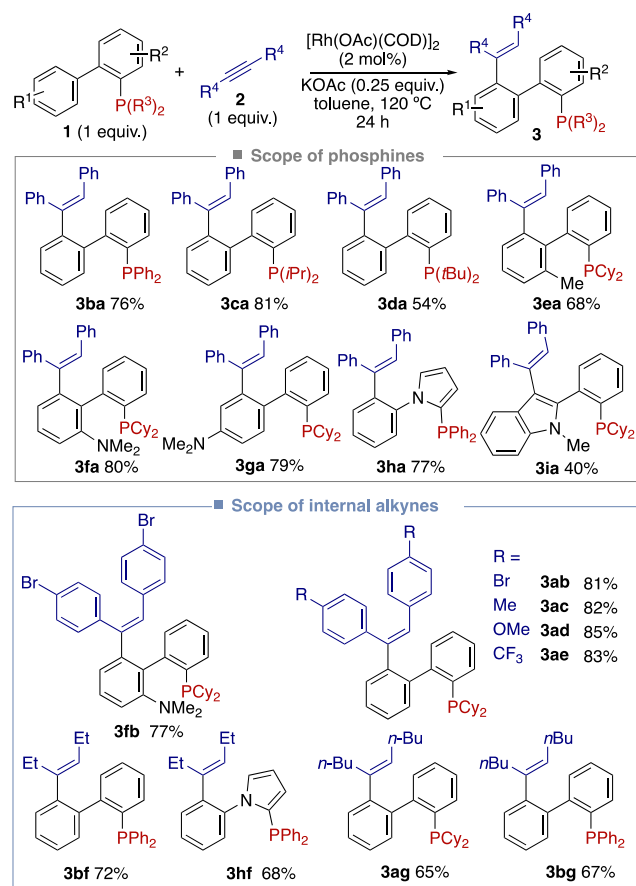


x-ray structure of 3aa		x-ray structure of 4aa	
[Rh]	Additive	3aa (%)	4aa (%)
1 $\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})_3(\text{SbF}_6)_2$	PivOH (5)	0	0
2 $[\text{Cp}^*\text{RhCl}_2]_2$	–	0	0
3 $[\text{RhCl}(\text{COD})]_2$	–	23	0
4 $\text{RhCl}(\text{PPh}_3)_3$	–	10	0
5 $[\text{Rh}(\text{OAc})](\text{COD})_2$	–	71	21
6 $[\text{Rh}(\text{OAc})](\text{COD})_2$	K_2CO_3 (0.25)	75	18
7 $[\text{Rh}(\text{OAc})](\text{COD})_2$	K_3PO_4 (0.25)	32	3
8 $[\text{Rh}(\text{OAc})](\text{COD})_2$	KOAc (0.25)	86	8
9 $[\text{Rh}(\text{OAc})](\text{COD})_2$	AcONa (0.25)	84	11
10 $[\text{Rh}(\text{OAc})](\text{COD})_2$	PivOK (0.25)	72	18
11 ^[a] $[\text{Rh}(\text{OAc})](\text{COD})_2$	KOAc (0.25)	55	43
12 ^[b] $[\text{Rh}(\text{OAc})](\text{COD})_2$	KOAc (0.25)	30	62
13 ^[b,c] $[\text{Rh}(\text{OAc})](\text{COD})_2$	KOAc (0.25)	15	75
14 ^[b,c] $[\text{Rh}(\text{OAc})](\text{COD})_2$	KOAc (0.5)	10	78

[a] 2 equiv. of **2a**; [b] 3 equiv. of **2a**; [c] 4 mol% of Rh catalyst

Having determined the best reaction conditions for the mono- and di-alkenylation of biarylphosphine through P(III)-assisted C–H bond activation, we turned our attention to the scope of the reaction. Firstly, we investigated the mono-functionalization using 2 mol% of $[\text{Rh}(\text{OAc})(\text{COD})]_2$ associated with 25 mol% KOAc in toluene at 120 °C, and biarylphosphine/alkyne 1:1 ratio (Scheme 1). The reaction of biphenyl bearing (diphenylphosphino), or (di-*iso*-propylphosphino) with diphenylacetylene have afforded the corresponding phosphine-alkene ligands **3ba**, **3ca** in 76% and 81% yield, respectively. In contrast to the previous report on Rh(I)-catalyzed hydroarylation of terminal alkynes,¹¹ in which a sterically hindered *t*-Bu-JohnPhos (**1d**) is not reactive, the reaction with diphenylacetylene lead to the formation of mono-alkenylated phosphine **3da** in 54% yield. *Ortho'*-substituted biarylphosphines such as MePhos (**1e**) and DavePhos (**1f**) also underwent C–H bond alkenylation at *ortho'*-position affording the phosphines **3ea** and **3fa** in good yields. Rh(I)-catalyzed *ortho'*-C–H bond alkenylation of 2-dicyclohexylphosphino-4-(*N,N*-dimethylamino)-1,1'-biphenyl (**1g**) afford **3ga** in 79% yield. These reaction conditions are tolerant to heteroaromatic moieties. Indeed (cataCXium®P) with *N*-phenylpyrrole scaffold—developed by Beller's group for cross-couplings of aryl chlorides¹⁵ is alkenylated on the phenyl unit to provide the phosphino-alkene **3ha** in 77% yield. CM-Phos developed by Kwong for cross-coupling reactions with aryl mesylates,¹⁶ undergoes indolyl C3–H bond alkenylation to afford the **3ia** in moderate yields.

Scheme 1. Scope of Rhodium(I)-Catalyzed *Ortho'* C–H Bond Alkenylation of Biarylphosphines with Alkynes

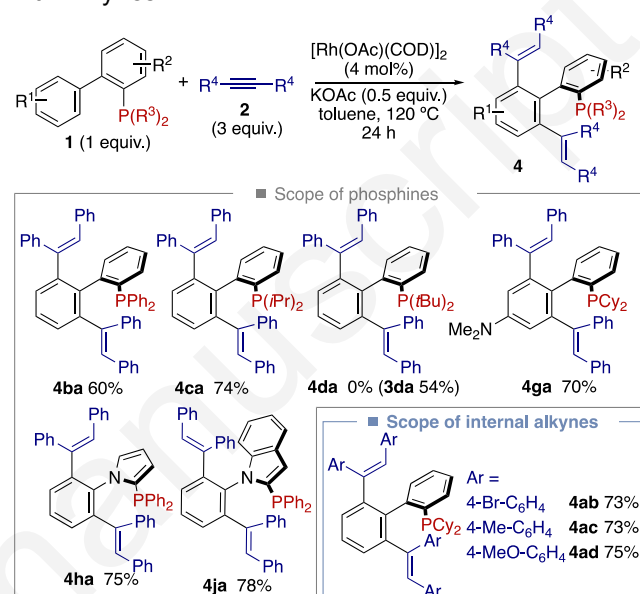


Then, we also investigated the reactivity of other internal alkynes. The functionalization of DavePhos (**1f**) with 1,2-bis(4-bromophenyl)ethyne afforded the phosphine **3fb** in 77% yield without the cleavage of C–Br bonds, which could be further employed to generate more diversity via cross-coupling reaction. Hydroarylation of 1,2-bis(4-bromophenyl)ethyne, 1,2-di-*p*-tolylethyne, 1,2-bis(4-methoxyphenyl)ethyne and 1,2-bis(4-(trifluoromethyl)phenyl)ethyne with JohnPhos (**1a**) efficiently occurred to produce **3ab–3ae** in good yields. Less reactive hex-3-yne (**2f**) and dec-5-yne (**2g**) were also suitable substrates in C–H bond alkenylation affording the novel phosphino-alkene ligands **3bf**, **3hf**, **3ag**, and **3bg** in good yields. However, the use of non-symmetrical alkynes (e.g., ethyl 3-phenylpropiolate or 1-phenyl-1-propyne) led to non-harvestable mixtures of isomers.

We then explored the difunctionalization of biarylphosphine *ortho*, *ortho'*-C–H bonds using an excess amount of internal alkynes and 4 mol% of [Rh(OAc)(COD)]₂ associated with 50 mol% KOAc in toluene at 120 °C (Scheme 2). The steric factor of phosphorus substituent appears critical. The (diphenylphosphino), or (di-*iso*-propylphosphino) were efficient directing groups in the bis-*ortho*'-alkenylation affording **4ba** and **4ca** in 60% and 74% yield respectively. While the reaction with *t*Bu-JohnPhos (**1d**) failed to deliver the difunctionalized phosphine **4da** and we only observed the formation of monofunctionalized phosphine **3da** in 54% yield. The introduction of a strong electron-donating group, such as NMe₂, did not affect the reactivity as the dialkenylated product **4ga** was isolated in 70% yield. The

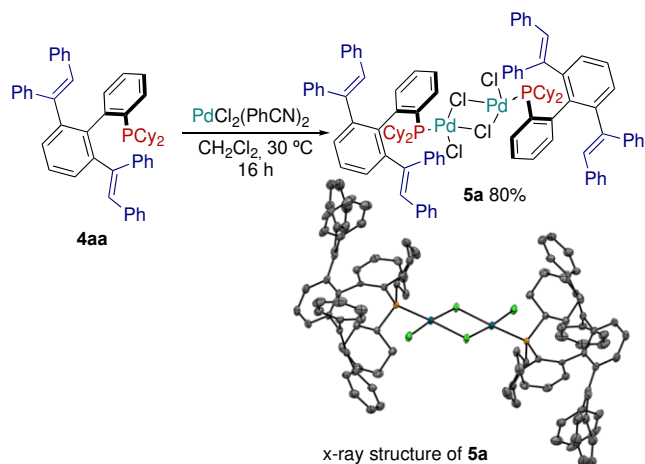
two-fold C–H bond activation/functionalization of cataCXum®P (**1h**) afford **4ha** in 75% yield. Bis-C–H bond alkenylation of **1a** were also carried out with other symmetrical *para*-substituted diarylacetylene (i.e., R = Br, Me, OMe) affording **4ab–4ad** in 73–75% yields. (CataCXum®P) with *N,N*-phenylindole scaffold **1j** was bis-alkenylated on the phenyl unit to provide the phosphine-bisalkene **4ja** in 78% yield.

Scheme 2. Scope of Rhodium(I)-Catalyzed Two-Fold *ortho*, *ortho'*-C–H Bonds Alkenylation of Biarylphosphines with Alkynes



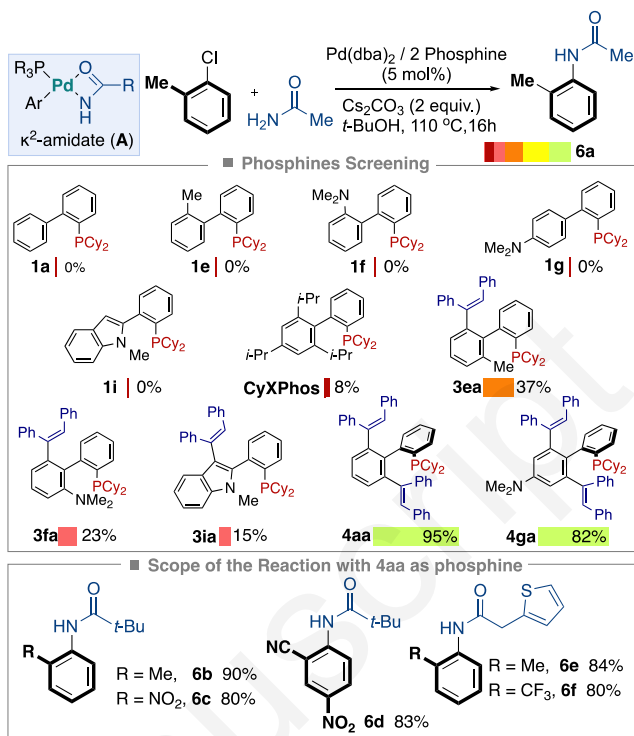
To estimate the coordination ability of phosphine **4aa**, we prepared the palladium(II) complex **5a** (Scheme 3). Mixing ligand **4a** and PdCl₂(PhCN)₂ in CH₂Cl₂ at room temperature led to the complete formation of complex **5a** as indicated by ³¹P{¹H} NMR with a downfield shift of the phosphorus atom from δ = –7.7 ppm in the free phosphine to δ = 67.0 ppm in the complex. In the X-ray crystallographic structure, complex **5a** was found to be a dimeric structure through a chloro-bridge unit with a distorted square planar coordination geometry. The Pd–Pd distance of 3.50 Å was somewhat longer than those of the corresponding SPhos compound (2.24 Å) and the Pd–P distance of 2.26 Å was similar to the SPhos–Palladium compound (2.25 Å). In contrast to JohnPhos and SPhos, which adopted a closed conformation,¹⁷ **5a** presents an open conformation, i.e., the orientation of the secondary aryl ring is pointing away from the metal center, avoiding a metal–arene interactions. This conformation switch might be due to the introduction of the very bulky 1,2-diphenylvinyl substituents.

Scheme 3. Stabilization of Pd(II) with the Bulky Phosphine ligand **4aa**



Finally, we would like to demonstrate the positive effect of the introduction of alkenyl group on biarylphosphines by comparing the catalytic activity of a couple of these novel (bis)-alkenylated (dialkyl)biarylphosphines with their parent phosphine often used in Pd-catalyzed cross-coupling reaction. Aryl chlorides are much less reactive substrates in Pd-catalyzed cross-coupling reactions, albeit they are more abundant and less expensive than bromide or iodide equivalents. Their cross-coupling with amides remains challenging as specific phosphine ligands have to be designed to promote the oxidative addition to aryl chlorides and reductive elimination of an amidate ligand from Pd(II) centers which can generate κ^2 -amidate palladium intermediate complexes (**A**, Scheme 4) resulting in the inhibition of reductive elimination and by the way catalytic efficiencies.¹⁸ We selected electron-rich and sterically hindered 2-chlorotoluene and acetamide as model substrates to evaluate the potential of our bifunctional biarylphosphines in Pd-catalyzed amidation (Scheme 4). In the presence of 2.5 mol% Pd(dba)₂/2phosphine and 2 equivalents of Cs₂CO₃ in *t*-BuOH, the commercially available (dicyclohexyl)biarylphosphines [JohnPhos (**1a**), MePhos (**1e**), DavePhos (**1f**), DavePhos analogue (**1g**), cataCXium®Pin (**1i**) and XPhos] were almost inactive. Interestingly, the use of phosphinoalkene hybrid ligands **3ea**, **3fa**, or **3ia** gave the desired *N*-arylamide **6a** in 15–37% yields. Surprisingly higher yields were observed using the phosphines bearing two alkenyl units **4aa** and **4ga** leading to the formation of **6a** in 95% and 82% yield, respectively. This positive rise of activity is expected to arise from the presence of the very bulky alkenyl group at both *ortho*-positions which might stabilize Pd intermediates by noncovalent interactions¹⁹ or/and may avoid the formation of κ^2 -amidate palladium intermediate complexes (**A**). Using the most active bifunctional phosphine **4aa**, we confirmed that cross C–N bond-coupling nicely occurred affording the aryl amide **6b–6f** in high yields (Scheme 4, bottom).

Scheme 4. Application of Bis-Alkenylated (Dialkyl)biarylphosphine in the Pd-Catalyzed Amidation of Aryl Chlorides.



In summary, we report the first example of C–H bond alkenylation of aromatic C–H bonds of biarylphosphines with internal alkynes through P(III)-directed C–H bond cleavage with Rh(I)(OAc) catalysts. The use of KOAc associated with chloride-free Rh(I) catalyst allowed the mono-functionalization or the difunctionalization depending on the stoichiometry of reaction. A new class of phosphino-alkene(s) ligands with different steric and electronic properties are obtained in good yields. The introduction of these very bulky vinyl substituents induces a conformation switch of palladium complex from closed to open form. A significant consequence for the catalytic performance is that monophosphines that have typically been ineffective in the amidation of aryl chlorides were morphed into ligands that create highly active palladium catalysts in amidation of *ortho*-substituted aryl chlorides. Applications of the developed ligand libraries and more detailed coordination studies are currently ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

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

Crystallographic information file (CIF) for CCDC 968419 (**3aa**)

Crystallographic information file (CIF) for CCDC 1968421 (**4aa**)

Crystallographic information file (CIF) for CCDC 1982983 (**5a**)

Additional procedures and data including characterizations, crystal structures, and NMR results (PDF)

AUTHOR INFORMATION

Corresponding Author

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