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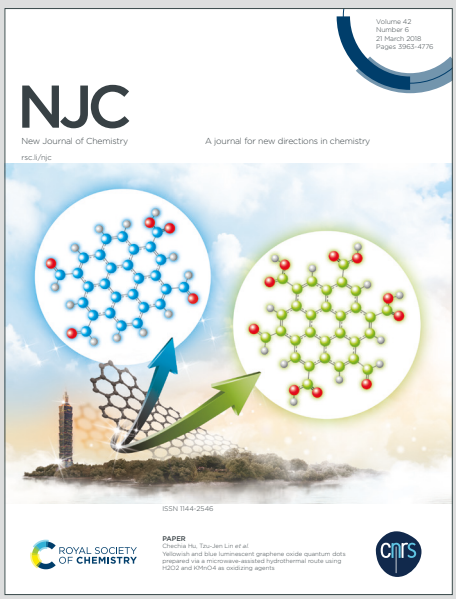

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DOI: 10.1039/D1NJ01348C

Novel *meta*-Benzothiazole and Benzimidazole Functionalised POCOP-Ni(II) Pincer Complexes as Efficient Catalysts in the Production of Diarylketones.

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ABSTRACT

The synthesis of four novel non-symmetric Ni(II)-POCOP pincer complexes *meta*-functionalized with either benzothiazole or benzimidazole at the central aryl ring is described. All complexes were fully characterised in solution by various analytical techniques and the molecular structures in the solid state of complexes ***1b***, ***2a*** and ***2b*** were unequivocally determined by single crystal X-ray diffraction analysis. In addition, the Ni(II)-POCOP pincer complexes were efficiently used as catalysts in the synthesis of diarylketones by cross-coupling reactions of functionalized benzaldehydes and boronic acid derivatives under relative mild conditions. An important aspect of this transformation is the dependence on the steric properties of the donor groups (OPR_2) of the pincer ligands, being more active the compounds having the phosphinitos bearing isopropyl groups (***1a*** and ***2a***) than those containing *tert*-butyl substituents (***1b*** and ***2b***).

1. Introduction

Pincer compounds represent an important facet of contemporary organometallic chemistry and homogenous catalysis.[1] Conferring thermal stability whilst permitting a broad range of metal-based reactivity. In particular, the application of *mer*-tridentate pincer ligands in different fields of science and catalysis has had a huge impact.[1b,2] The predictable and modular composition of pincer ligands enables the tunning of the steric and electronic properties of their metal derivatives through changes in the constituent donor groups (phosphines PR_2, amines NR_2, thioethers SR, selenoethers SeR and N-heterocyclic carbenes or a pair of donor groups among these functionalities), their substituents (R) or the backbone configuration itself.[1b,3] As a result, these adaptions have been extensively studied. However, despite much is already known about the chemistry of the most emblematic symmetric phosphine-based pincers with central pyridine or aryl donors,[4] the design of non-symmetric pincer architectures is still a highly developing topic, since these species can combine the properties of their symmetrical counterparts and disclose unique reactivities and non-typical features.[1c] In this sense, even though the non-symmetric pincer complexes are less common, mainly due to the difficulties in their preparation, in the last decade there has been a significant progress in this research field providing several examples of how the C_{2v} symmetry of aryl or pyridine-linked pincer ligand systems can be broken, generally, through one of the three ways shown in Figure 1.[1c,5]

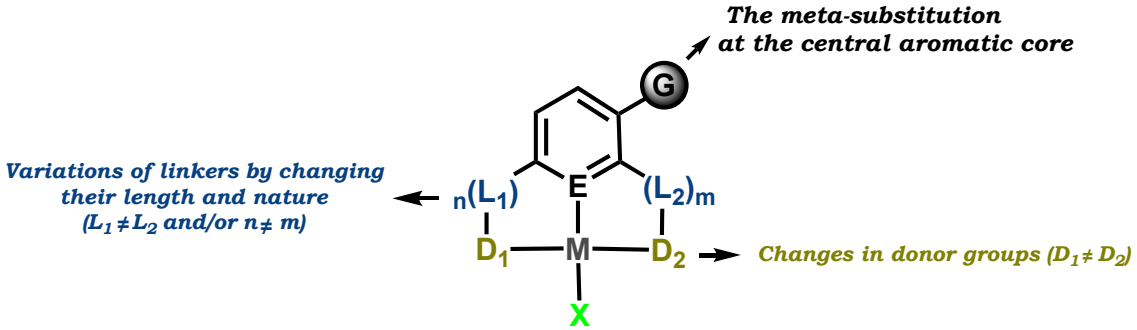

Figure 1. Modifiable sites on a pincer framework to produce non-symmetric pincer compounds.

The substitution on the main pincer backbone plays a more interesting role than the simple modification of the electronic character on the pincers, leading to the possibility of functionalization of the aromatic ring of the main framework with the introduction of potential molecular recognition sites or anchoring the metal pincer

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complex to supporting materials, dendrimers, polymers, etc.[6] On the other hand, within of the large family of phosphine-based pincer ligands, POCOP pincer ligands and their complexes are of special interest due to their relatively easy synthesis, turning them perfect templates to yield non-symmetric systems. In this respect, our group has been involved in the development of symmetric and non-symmetric functionalised POCOP pincer complexes and their application as colorimetric sensors of anions (CN^-, OH^-, F^-)[A][7] and catalysts [B, C][8] (Chart 1).

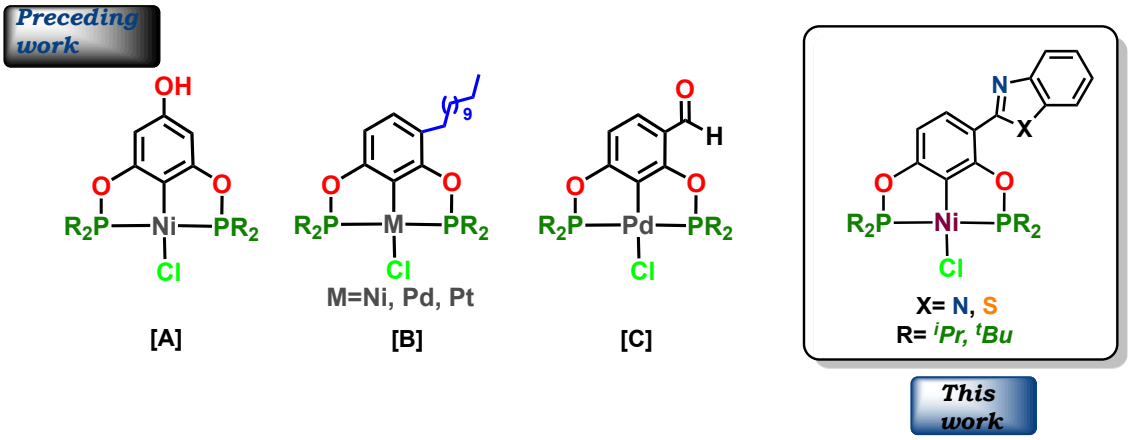
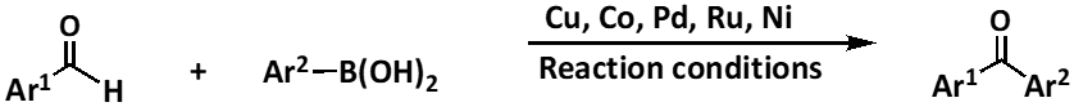


Chart 1

On the other side, diarylketone frameworks are an important motif in a wide array of pharmaceutical, organic materials, natural products and fine chemicals.[9] To date, the Friedel-Crafts reaction of substituted aromatic rings,[10] the cross-coupling reactions of boronic acid with either acyl chlorides or carboxylic anhydrides catalysed by palladium,[11] the Houben-Hoesch reaction of nitriles,[12] the acylation of organometallics with acyl electrophiles catalysed by transition metals and the nickel and palladium-catalysed Negishi cross-coupling of amides, among other procedures,[13] are some of the methods more used for the synthesis of diarylketones and their derivatives. However, these reactions still suffer some drawbacks, such as the highly basic or acidic conditions, use of expensive substrates, incompatibility with many functional groups and need for further functionalization steps that are time-consuming. Thus, the search of new routes to produce diarylketones through less expensive and practical procedures, using easily available substrates, is a challenging task for researches of worldwide. In this context, a very promising approach is the

synthesis of diarylketones by coupling reactions of aldehydes and arylboronic acids, which has been well documented with the assistance of homogeneous catalysts of palladium,[14] cobalt,[15] rhodium,[16] copper,[17] platinum,[18] ruthenium[19] and nickel[20] (Table 1). This process is particularly attractive because of the organoboron reagents are stable to air and moisture and have a good functional group tolerance, while the aldehydes are inexpensive and highly available. Then, the generation of diarylketones through more economical and cleaner processes by the use of stable compounds able to catalyse the coupling of aldehydes and arylboronic acids, without the requirement of any extra additive, using low catalyst loading under mild reaction conditions remains a topic of current relevance. In this context, the catalyst stability is a major concern, which enforces the usage of high catalyst loading (more than 5 mol%) in many reactions. And taking into account that, the pincer complexes have been widely used as catalysts in diverse coupling reactions[1b,2] offering excellent activities, largely, due to their high thermal stability, the assessment of pincer complexes as catalysts in the coupling of aldehydes and arylboronic acids to give diarylketones is relevant and pertinent. To the best of our knowledge, the synthesis of substituted benzophenones from aldehydes and arylboronic acids efficiently catalysed by Ni(II) pincer complexes has not been explored ever before.

Table 1. Comparison of Ni(II)-POCOP pincer complex, ***1a***, with other catalytic systems in the arylation of aldehydes with arylboronic acids to produce diaryl ketones. [a]Arylation of both aliphatic and aromatic aldehydes. NA= not applicable.



Entry	[M] (mol%)	Ligand (mol%)	Reaction conditions	Ref.
1	**$Cu(OTf)_2$ (10 mol%)**	Xantphos (15 mo%)	KF, Toluene, 24 h, 120 °C	[17]
2	**$CoCl_2$ (10 mol%)**	tmphen (15 mo%)	Cs_2CO_3, MeCN/Toluene 3:1, 12 h, 80 °C	[15]
3	**$Pd_2(dba)_3$ (2.5 mol %)**	NA	Cs_2CO_3, Toluene, 24 h, 120 °C	[14a]
4	**$Pd(PPh_3)_4$ (2 mol %)**	2-chloro-1,3-dimethyl imidazolidinium (1.2 eq)	K_3PO_4, Dioxane, 16 h, 90 °C	[14b]
5	**$[Pd(allyl)Cl]_2$ (0.5 - 1.5 mol%)**	Thioether-imidazolinium chloride (0.5-1.5 mol%),	CsF, Dioxane, 3 h, 80 °C	[14c]
6	**$RuHCl(CO)(PPh_3)_3$] (5 mol%)**	NA	Cs_2CO_3, H_2O, Toluene, 13 h, 110 °C.	[19a]

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7	[a]**[Ru(CO)$_3$Cl$_2$] (2.5 mol%)**	*t*-Bu$_3$P•HBF$_4$ (10 mo%)	K$_3$PO$_4$, *t*-BuCOMe (2 eq), H$_2$O, Toluene, 24 h, 100 °C	[19b]
8	**[Rh(CH$_2$CH$_2$)Cl]$_2$ (1.5 mol%)**	P(*t*-Bu)$_3$ (3 mol%)	K$_2$CO$_3$, Dioxane/Acetone 4:1, 4-8 h, 80 °C	[16]
9	[a]**[Ni(PPh$_3$)$_4$] (5 mol%)**	dcype (6 mol%)	Acetone, DMSO, 12h, 120 °C	[20]
10	**Ni(II)-POCOP, *1a*, (1 mol%)**	NA	Cs$_2$CO$_3$, Toluene/Acetone 4:1, 8 h, 80 °C	This work

Thus, motivated by the potential applications of functionalised POCOP-based pincers and the construction of non-symmetric pincer complexes by *meta*-substitution at the central aromatic core of the pincer, and as an extension to our related work with POCOP pincer ligands, we became interested in developing the chemistry of functionalized POCOP-based pincers with heterocyclic scaffolds. Specifically, benzimidazole and benzothiazole are important precursors due to their potential biological and pharmaceutical properties including anticancer, antimicrobial, antifungal, anticonvulsant, anti-inflammatory and antiviral activities.[21] Hence, the incorporation of biologically relevant fragments into the pincer backbone could be the start of a new type of potentially important bioorganometallic compounds with potential catalytic and biological applications. Furthermore, the inclusion of these heterocycles could lead to the coordination to a second transition metal such as Cu(II), Ag(I), Au(I), Pt(II), etc. to generate bimetallic complexes.[22] Thus, herein, we describe the synthesis and full characterization of a series of non-symmetric nickel pincer complexes based on *meta*-benzothiazole and *meta*-benzimidazole resorcinol derivatives and their catalytic evaluation in the synthesis of diarylketones from substituted benzaldehydes and phenylboronic acid.

2. Results and discussion.

2.1. Proligand synthesis.

The proligands ***P1*** and ***P2*** were prepared using an adapted procedure previously reported from commercially available 2,4-dihidroxybenzaldehyde, 2-aminothiophenol (***P1***) and 1,2-phenylendiamine (***P2***) outlined in Scheme 1. ***P1*** was synthetized in one step and isolated as a light-yellow solid with a yield of 62%, meanwhile ***P2*** was obtained in 77 % yield over two steps as a bright-white powder after its purification by flash chromatography. These compounds were further characterized by ^{1}H and ^{13}C{^{1}H}

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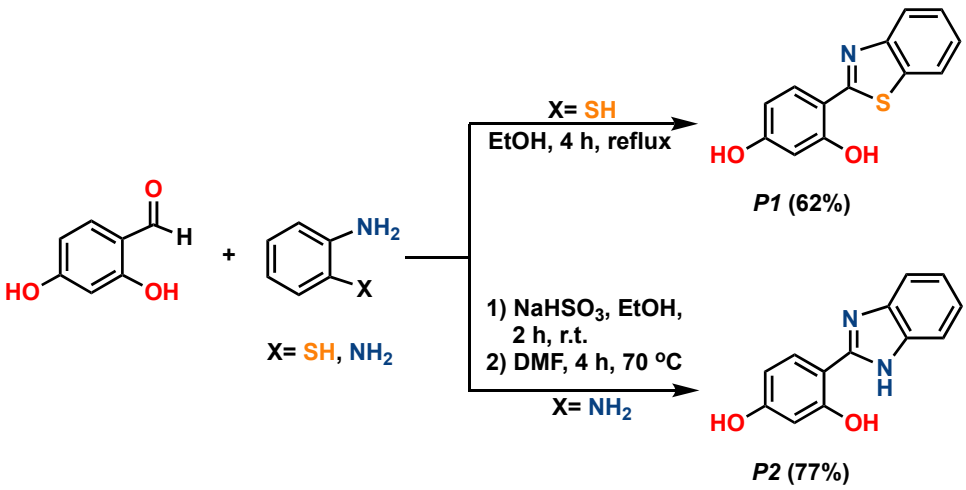
NMR and mass spectroscopy and structurally confirmed by direct comparison of previously reported data (full details are provided in the experimental section).[23]



Scheme 1. Synthesis of proligands ***P1*** and ***P2***

2.2. Ni-POCOP pincer complexes synthesis.

With the proligands in hand, the synthesis of nickel derivatives was targeted (Scheme 2). Using an adapted literature procedure[7b,8b,24], the non-symmetric nickel POCOP-pincer complexes were prepared by the *meta*-benzothiazole (***1a;*** *R=* ^{i}*Pr*, ***1b;*** *R=* ^{t}*Bu*) and *meta*-benzimidazole (***2a;*** *R=* ^{i}*Pr*, ***2b;*** *R=* ^{t}*Bu*) aryl backbone substitution and the products were obtained as analytically pure materials in moderate isolated yields (48-62%). POCOP-pincer ligands ***L1*** (benzothiazole) and ***L2*** (benzimidazole) were obtained through a procedure that involved the reaction of the proligands ***P1*** and ***P2*** with a base (Et_3N or DMAP) in THF at 40 °C for 1h. This was followed by treatment with the corresponding chlorophosphine at reflux temperature for 4h under nitrogen atmosphere. $^{31}P\{^{1}H\}$ NMR analysis of the ligands exhibited two singlets consistent with the non-symmetric nature of the pincer ligands[8a] ***L1a:*** δ 146.6(P^1) and 150.0(P^2) ppm, ***L1b:*** δ 146.5(P^1) and 153.5(P^2) ppm, ***L2a:*** δ 146.1(P^1) and 154.3(P^2) ppm, ***L2b:*** 147.2(P^1) and 155.0(P^2) ppm. These chemical shifts are similar to those reported for their non-symmetric POCOP free ligands analogous, and in general, as we have observed before, the signals at lower field correspond to the phosphorus nuclei (P^2) adjacent to the substituent at the 4 position, this assignation was established by direct comparison of their symmetric POCOP ligand counterparts.[8] Then, compounds ***L1a***, ***L1b***, ***L2a***, ***L2b***

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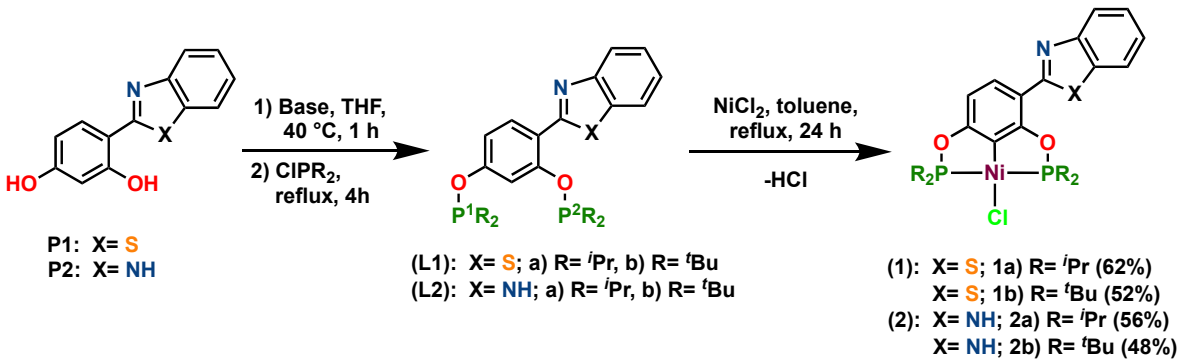
were used *in situ* without further purification for their direct metalation with $NiCl_2$ in refluxing toluene generating four air-stable non-symmetric Ni–POCOP pincer complexes.



Scheme 2. Synthesis of non-symmetric Ni(II)-POCOP pincer complexes: ***1a***, ***1b***, ***2a*** and ***2b***.

Ni(II)-POCOP pincer complexes were characterised in solution, observing typical AB patterns of $^{31}P\{^1H\}$ resonances, displaying diagnostic *trans*-phosphinito couplings centred at δ 192.6 (d, P^1)/187.5(d, P^2) ($^2J_{P\text{-}P}$= 332 Hz), δ 197.5(d, P^1)/189.8(d, P^2) ($^2J_{P\text{-}P}$= 303 Hz), δ 193.6(d, P^1)/187.5(d, P^2) ($^2J_{P\text{-}P}$= 338 Hz), 196.2(d, P^1)/190.0(d, P^2) ($^2J_{P\text{-}P}$= 303 Hz) for ***1a***, ***1b***, ***2a***, ***2b*** respectively. As can be noticed, the phosphorus resonances in the nickel complexes are shifted to higher frequencies, *ca*. 50 ppm than those of the free pincer ligands (*vide supra*) due to the coordination to the metal center, thus confirming the formation of the desired non-symmetric pincer complexes. ^1H and $^{13}C\{^1H\}$ NMR spectra also provide further structural information. In all the cases, the C-H bond activation by the metalation process was evidenced by the disappearance of the *ortho*-protons resonances (R_2POC_{aryl}-C**H**$_{aryl}$-$C_{aryl}OPR_2$) of the complexes in the ^1H NMR spectra. Coordination of the pincer was also affirmed by $^{13}C\{^1H\}$ NMR displaying signals of the metallated C-Ni carbon as apparent triplets due to their coupling with, inequivalent, mutually *trans*-phosphorous nuclei at δ 124.8 (at, $^2J_{C\text{-}P}$= 19.4, 20.6 Hz) for ***1a***, 125.4 (at, $^2J_{C\text{-}P}$= 19.8, 22.1 Hz,) for ***1b***, 124.2 (at, $^2J_{C\text{-}P}$= 22.5, 22.8 Hz) for ***2a***, and 124.5 (at, $^2J_{C\text{-}P}$= 22.3, 22.5 Hz) for ***2b.*** The FT-IR spectra of all complexes exhibit key bands at *ca*. 1575 –1597cm^{-1}, *ca*. 1238 -1257 cm^{-1} and *ca*. 443-470 cm^{-1} assigned to *v*(P-0), *v*(C=N), and *v*(C-Ni), respectively. In the IR spectra of ***2a*** and ***2b***, the *v*(N-H) band is observed at *ca.* 3400 cm^{-1}. Mass spectra also confirmed the formation of the complexes. The resulting spectra exhibited the molecular ion $[M]^+$ at 568, 624, 551 and 607 m/z for complexes ***1a***, ***1b***, ***2a*** and ***2c*** respectively. Results obtained from elemental

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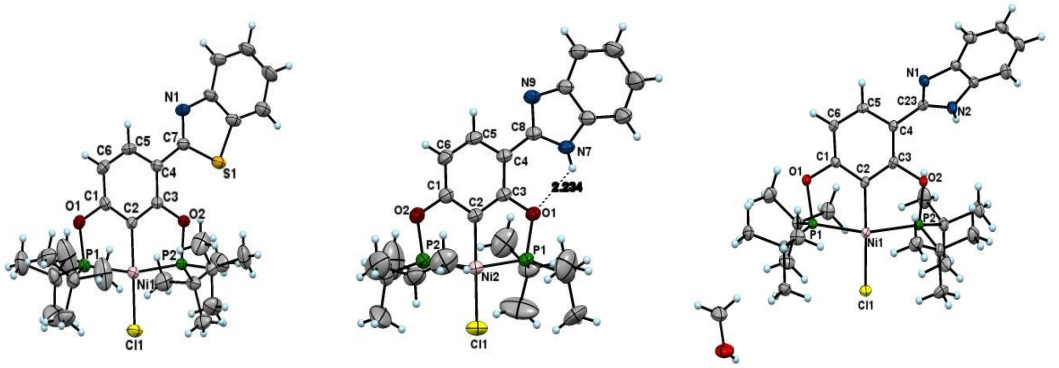
analysis of all compounds are also in agreement with the proposed structural formulations.

In addition, the molecular structures of complexes ***1b***, ***2a*** and ***2b*** were determined using single crystal X-ray diffraction analyses, fully confirming the structural formulations inferred from NMR spectroscopy and mass spectrometry. In all cases, crystals of the complexes suitable for their analysis were obtained by slow diffusion of methanol into saturated dichloromethane solutions of the complexes at room temperature (Figure 2).

Nickel pincer complexes crystallised in the monoclinic (***1b***, ***2a***) and triclinic (***2b***) systems exhibiting the adoption of distorted square planar metal coordination geometries. The coordination sphere in all complexes is constituted by one chloride and the corresponding pincer ligand, bonded in a tridentate manner through the two phosphorus atoms (P^1, P^2) and a sigma C-Ni bond with one carbon atom from the aryl backbone forming two five-membered metallocycles. The main distortion arises primarily from the bite angle of the POCOP ligand that results in a tightening of all C–Ni–P and P–Ni–P angles (*ca*.82° and *ca*.164°, respectively), whereas the C-Ni-Cl angles are fairly linear between 175-179°.

The Ni-C bond distances in all compounds are very similar *ca.*1.882 Å, while the Ni-Cl bonds distances are *ca*. 2.195Å (average), which are in agreement with other reported POCOP nickel complexes.[25] Also, complex ***2a*** displays an intramolecular hydrogen interaction N7-H---O2 providing a six-membered ring.



1b, [NiCl{C_6H_2-3-C_7H_4NS-2,6-{OP^tBu_2}$_2$}] *2a*, [NiCl{C_6H_2-3-$C_7H_5N_2$-2,6-{OP^iPr_2}$_2$}] *2b*, [NiCl{C_6H_2-3-$C_7H_5N_2$-2,6-{OP^tBu_2}$_2$}]•CH_3OH

Figure 2. Solid-state structures of ***1b***, ***2a*** and ***2b*** (thermal ellipsoids drawn at 30 % probability). *Selected bond lengths (Å):* ***1b*** Ni1-C2, 1.889(3), Ni1-P2 2.1685(11), Ni1-P1 2.1763(11), Ni1-Cl1 2.2051(10); ***2a*** Ni2-C2 1.883(2), Ni2-P1 2.1461(6), Ni2-P2

2.1480(7), Ni2-Cl1 2.1820(7); ***2b*** Ni1-C2 1.885(2), Ni1-P1 2.1862(6), Ni1-P2 2.1929(6), Ni1-Cl1 2.1971(6). *Selected angles (°):* ***1b*** C2-Ni1-P2 82.11(10), C2-Ni1-P1 82.19(11), P2-Ni1-P1 164.31(4), C2-Ni1-Cl1 179.43(11), P2-Ni1-Cl1 98.16(4), P1-Ni1-Cl1 97.53(4); ***2a*** C2-Ni2-P1 82.53(7), C2)-Ni2-P2 82.62(7), P1-Ni2-P2 164.41(3), C2-Ni2-Cl1 175.63(7), P1-Ni2-Cl1 99.11(3), P2-Ni2-Cl1 96.04(3); ***2b*** C2-Ni1-P1 82.59(7), C2-Ni1-P2 82.20(7), P1-Ni1-P2 164.48(3), C2-Ni1-Cl1 178.44(7), P1-Ni1-Cl1 95.97(2), P2-Ni1-Cl1 99.20(2).

Noteworthy, the fact that the twisting is minimum (θ= 0.06-2.93^0) in the metallacyles formed in the nickel 5,5-POCOP complexes (***1b***, ***2a*** and ***2b***), however the torsion in the metallacycle adjacent to the benzothiazole or benzimidazole groups is slightly larger than the other, probably, due to the steric effect of the substituent. Furthermore, the *meta*-substituents in the complexes ***1b*** and ***2a*** are slightly twisted out of the central aryl moiety plane, as indicated by the dihedral angle between the corresponding planes: ***1b*** 6.0°/6.0° for C5-C4-C7-N1/C3-C4-C6-S and ***2b*** 8.2°/11.4° for C5-C4-C8-N9/C3-C4-C8-N7), while the benzimidazole-substituent in the complex ***2b*** is twisted out by more than 35° (as measured by the C5-C4-C23-N1 and C3-C4-C23-N2 dihedrals of 36.4° and 41.5° respectively).

Table 2. Crystallographic data for ***1b***, ***2a*** and ***2b***

Compound	***1b***	***2a***	***2b***
Formula	$C_{29}H_{42}ClNNiO_2P_2S$	$C_{25}H_{35}ClN_2NiO_2P_2$	$C_{29}H_{43}ClN_2NiO_2P_2$, CH_4O
Formula weight	624.79	551.65	639.79
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P21/c	P21/c	P-1
a (Å)	16.901(3)	17.1985(11)	7.9426(2)
b (Å)	11.935(2)	15.1991(9)	12.3331(3)
c (Å)	15.493(3)	10.8855(6)	17.1446(4)
α (°)	90	90	75.000(1)
β (°)	98.920(4)	104.680(2)	83.451(1)
γ (°)	90	90	84.215(1)
V (Å³)	3087.4(10)	2752.6(3)	1607.17(7)
Z	4	4	2
δ calc (g/cm³)	1.344	1.331	1.322
F(000)	1320	1160	680
T (K)	298	301	150
Crystal size / colour / shape	0.486 x 0.220 x 0.080 mm³ / yellow / prism	0.339 x 0.220 x 0.048 mm³ / yellow / hexanal-plate	0.397 x 0.183 x 0.091 mm³
θ range (°)	2.16 to 27.10	2.35 to 29.23	2.350 to 25.275
No. of rflns collected	28923	68831	13892
No. of indep rflns (R_{int}) (%)	6803 [$R_{(int)}$ = 10.5]	7454 [$R_{(int)}$ = 4.6]	5794 [$R_{(int)}$ = 6.37]
Completeness to theta= 25.242° (%)	99.9	99.9	99.3
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	6803 / 0 / 346	7454 / 0 / 309	5794 / 0 / 371
Goodness-of-fit on F²	1.044	1.024	0.949

Final R índices [I>2σ(I)] (%)	R = 5.87, R_w = 11.03	R = 4.23, R_w = 8.85	R = 3.45, R_w = 6.64
R indices (all data) (%)	R = 9.85, R_w = 12.66	R = 7.68, R_w = 10.37	R = 5.55, R_w = 7.34

DOI: 10.1039/D1NJ01348C

2.3. Catalytic activity

The catalytic activity of the synthesised complexes was evaluated in the synthesis of diarylketones by coupling of arylboronic acids and benzaldehyde derivatives. We started the investigation evaluating the activity of all the nickel complexes (***1a***, ***1b***, ***2a*** and ***2b***) in the cross-coupling reaction of phenylboronic acid and benzaldehyde (selected as a model reaction), using Cs_2CO_3 as base in either THF/acetone or toluene/acetone (Table 3). Among the screened complexes, ***1a*** and ***2a*** were, by far, the most efficient catalysts affording the benzophenone product in 98.5 and 96.3 % yields (Table 3, entries 1 and 5). By comparing the effect of the benzothiazole and benzimidazole substituents was observed that those do not have a significant influence in the coupling efficiency, but the yields are strongly related with the steric properties of the phosphine (entries 1, 3, 5 and 7). In this context, complexes bearing phosphinitos with isopropyl groups are better catalysts than those with *tert*-butyl substituents. Furthermore, a comparison between ***1a*** and its related symmetric Ni-POCOP pincer complex [NiCl{$C_6H_3(OP^iPr_2)_2$}], under the optimized reaction conditions, was made, resulting ***1a*** (98.5 % yield) better catalyst than its symmetric analogous (25.8 % yield) (Table 3, entries 1 and 14). These outcomes disclose the unique reactivity of the non-symmetric pincer complexes, however the true role of benzothiazole and benzimidazole substituents on the aryl ring is still unclear. However this behaviour may be related to electronic effects exerted by the heterocycle at the *meta*-position overall enhancing the reactivity of this species, although we cannot rule out potential steric effects or even discard the potential non innocent nature of the heterocycle during the catalytic reactions. All these hypotheses will require further theoretical and experimental (mechanistic) studies that will in turn allow us to shed further light on the real role of the *meta*-substituent. On the other hand, the efficiency of the reaction was found strongly dependent of the solvent nature, being the toluene/acetone mixture the most suitable giving better conversions than the THF/acetone system (Table 3, entries 1, 3, 5, 7, 11).

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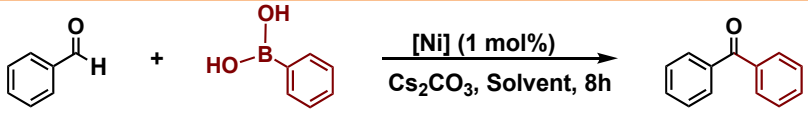
DOI: 10.1039/D1NJ01348C

Table 3. Cross-coupling reaction of phenylboric acid and benzaldehyde catalysed by nickel complexes ***1a***, ***1b***, ***2a*** and ***2b.***[a]

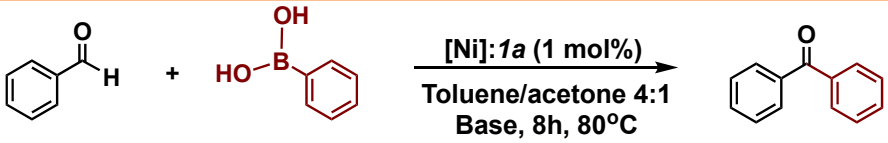


Entry	*[Ni]*	Solvent (4:1)	T(°C)	Yield (%)[b]
1	***1a***	Toluene/acetone	80	**98.5**
2		THF/acetone	65	75.8
3	***1b***	Toluene/acetone	80	67.6
4		THF/acetone	65	33.5
5	***2a***	Toluene/acetone	80	**96.3**
6		THF/acetone	65	70.8
7	***2b***	Toluene/acetone	80	78.3
8		THF/acetone	65	39.5
9	***1a***	Toluene/acetone	R.T.	ND
10		THF/acetone	R.T.	ND
11	***1a***	Toluene/acetone	50	43.3
12		THF/acetone	50	39.5
13*	***1a***	Toluene/acetone	80	52.6
14**	**[NiCl{$C_6H_3(OP^iPr_2)_2$}]**	Toluene/acetone	80	25.8

[a]Reaction conditions: phenylboronic acid (1.0 mmol), benzaldehyde (1.2 mmol), [Ni] (1 mol%), solvent (3.0 mL), Cs_2CO_3 (3.0 mmol) for 8 h. [b]Yields were determined by CG-MS/^{1}H NMR and are the average of two independent runs. ND = Not detected. R.T.= Room temperature.*Reaction carried out at 4h (entry 13). **Reaction catalysed by the symmetric pincer complex [NiCl{$C_6H_3(OP^iPr_2)_2$}].

As is well known, cross-coupling reactions are strongly related on the base used, thus, several bases were tested under the optimized reaction conditions using the best-found catalyst, ***1a*** (Table 3). The results obtained revealed that Cs_2CO_3 affords the best yield (Table 4, entry 6), nevertheless other bases such as $SrCO_3$ and Li_2CO_3 also showed good results (Table 4, entries 3 and 4).

Table 4. Cross-coupling reaction of phenylboric acid and benzaldehyde catalysed by nickel complexes ***1a*** using differnt bases.[a]



Entry	Base	Yield (%)[b]
1	K_2CO_3	77.7
2	Na_2CO_3	45.0

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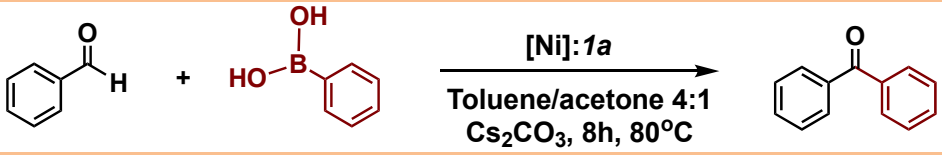
3	$SrCO_3$	93.6
4	Li_2CO_3	97.2
5	DMAP	50.0
6	Cs_2CO_3	98.5

[a]Reaction conditions: phenylboronic acid (1.0 mmol), benzaldehyde (1.2 mmol), [Ni] (1 mol%), toluene/acetone 4:1 (3.0 mL), base (3.0 mmol) for 8 h. [b]Yields were determined by CG-MS/^{1}H NMR and are the average of two independent runs.

In order to explore the effectiveness of complex ***1a***, the coupling reaction was also performed under the above reaction conditions with different catalyst loadings (Table 5). When 1 mol % of ***1a*** was used, benzophenone was obtained in ca. 98% yield after 8 h (entry 3). Reducing the amount of catalyst to 0.1 and 0.5 mol% (entries 1 and 2) the reaction produced low to moderate yields of the ketone in 8 h. Consequently, the catalyst loading of 1 mol % was used for further studies.

Table 5. Effect of catalyst ***1a*** loading.[a]



Entry	mol % of ***1a***	Yield (%)[b]	TOF (h^{-1})
1	0.1	43.2	54
2	0.5	66.2	16.6
3	1	98.5	12.3

[a]Reaction conditions: phenylboronic acid (1.0 mmol), benzaldehyde (1.2 mmol), [Ni] (0.1-1 mol%), toluene/acetone (3.0 mL), Cs_2CO_3 (3.0 mmol) for 8 h. [b]Yields were determined by CG-MS/^{1}H NMR and are the average of two independent runs.

Encouraged by these results, we turned our attention to extend the scope of this reaction to a series of substituted benzaldehydes to examine their electronic and steric effects (Table 6). Interestingly, variation of the electronic nature of the aromatic ring had little impact on the reaction efficiency and as a result, neutral **3a** along with electron-withdrawing and electron-donating substituents at *para*-positions provided the desired ketone products in moderate to excellent yields (3d, 3e, 3g-3i). On the other hand, *meta*-substituted benzaldehydes (entries 3c, 3f) coupled slightly less effectively than the corresponding *para*-substituted derivatives (3e, 3g). *Di*-substituted aldehydes are readily tolerated, and the desired product was obtained in good yields (3k).

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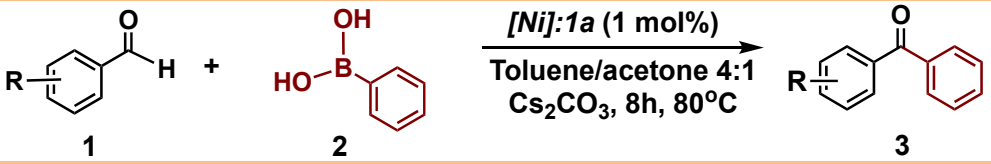
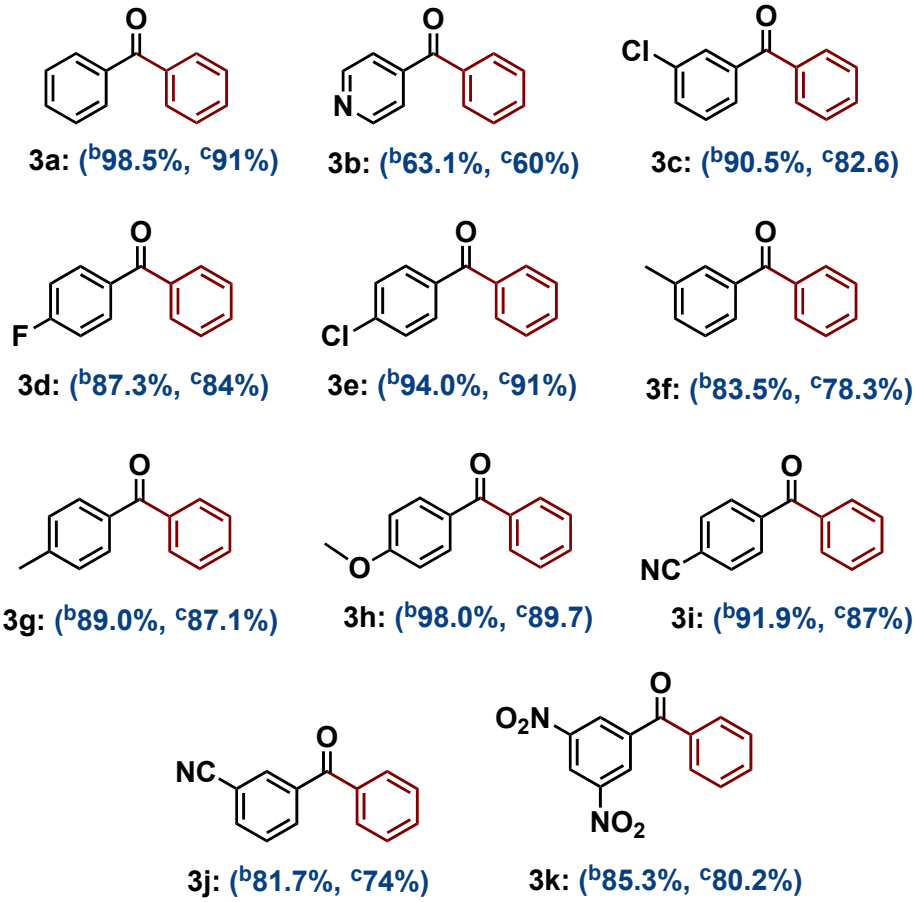
Table 6. Cross-coupling reactions of substituted aldehydes and phenylboronic acid catalysed by complex ***1a***.[a]



1 2 3



[a]Reaction conditions: phenylboronic acid (1.0 mmol), benzaldehyde derivatives (1.2 mmol), [Ni] (1-0.1 mol%), toluene/acetone (3.0 mL), Cs_2CO_3 (3.0 mmol) for 8 h. [b]Yields determined by CG-MS/^{1}H NMR and are the average of two independent runs. [c]Isolated Yields.

In addition, the scope of boronic acids was then investigated using benzaldehyde and 4-methoxybenzaldehyde as coupling partners, Table 7. These results indicate that hetero-aryl boronic acids, such as 3l and 3m, proceeded well and the desire coupling products were obtained, albeit the yields decreased to 64 %, which may be owing to the fact that heteroatom in the hetero-aryl boronic acid may deactivate the transition metal. On the other hand, we tried to extend this strategy on aliphatic aldehydes also. However, the results were not encouraging on these substrates.

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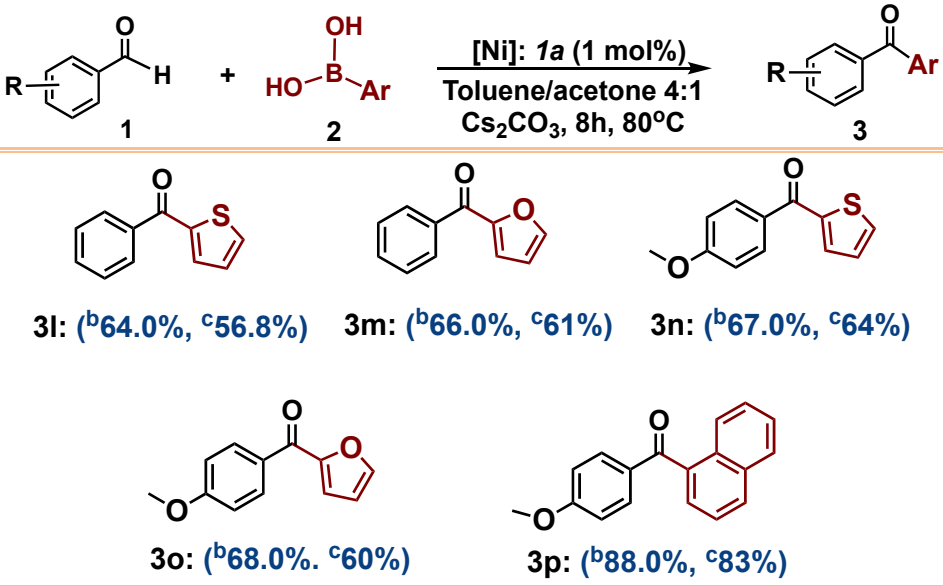
Table 7. Cross-coupling reactions of boronic acids with either benzaldehyde or 4-methoxybenzaldehyde catalysed by complex ***1a***.[a]



[a]Reaction conditions: boronic acid derivatives (1.0 mmol), benzaldehyde derivatives (1.2 mmol), [Ni] (1 mol%), toluene/acetone (3.0 mL), Cs_2CO_3 (3.0 mmol) for 8 h. [b]Yields determined by CG-MS/^{1}H NMR and are the average of two independent runs. [c]Isolated Yields.

It is worth noting that controlled experiments showed that in the absence of catalyst or base, no coupling reaction occurs. Furthermore, when the reactions were conducted in the absence of acetone, only traces of diarylketone were formed and reduction of benzaldehyde derivatives were also detected, which indicate that during the catalysis a nickel hydride species is likely produced, therefore the use of a hydride acceptor such as acetone was crucial to perform this reaction.

Finally, a mechanistic proposal for the synthesis of diarylketones catalysed by the Ni-POCOP complex (***1a***) is illustrated in the Scheme 3. This mechanism could involve a transmetalation step to yield (**I**), followed by the insertion of the aldehyde into the aryl-nickel bond furnished an alkoxo-nickel species (**II**). At this stage, two competitive mechanisms may be envisioned. The first one, include a β-hydrogen-elimination to release diarylketone (Heck-type mechanism) and a nickel hydride species (**III**). The later, reacted with acetone to afford and alkoxo-nickel (**IV**) complex, which is suitable for transmetalation with the boron reagent. In the second, the protonation of the alkoxo-nickel intermediate (**II**) with either water or boronic acid can led to the carbinol compound and the release of an active hydroxo-nickel species [Ni-X], followed by the deprotonation of carbinol and the consecutive regeneration of the alkoxo-nickel (**II**). At

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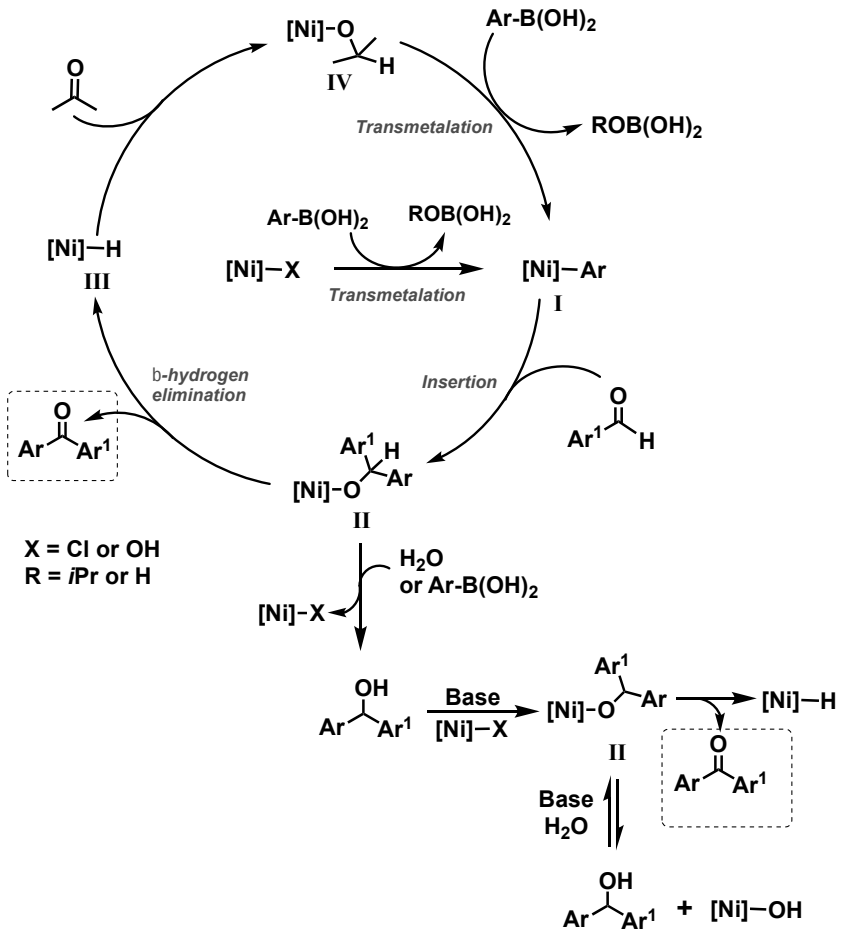
this stage, we believe that the base plays a key role in the catalytic cycle to regenerate the active alkoxo- and hydroxo-nickel species.

The presence of water in the reaction mechanism is proposed taking into account that boronic acids are prone to dehydratation, resulting in the formation of boroxine and water.[26] Furthermore, transmetallation of organoboron compounds to alkoxo or hydroxo complexes of palladium,[27] rhodium[16,28] or ruthenium[29] have been described, allowing regeneration of the aryl-metal species. However, the scope and mechanism of this catalytic reaction with Ni-POCOP complexes are still under investigation in our laboratory and the mechanistic proposal is base on some experimental results and literature reports.



Scheme 3. Mechanistic proposal for the synthesis of diarylketones catalysed by the Ni-POCOP complex.

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3. Conclusions

A series of new non-symmetric Ni(II)-POCOP pincer complexes have been synthetized in a facile manner in moderate to good yields (48-62%), where the main pincer backbone is *meta*-functionalized with heterocyclic scaffolds (benzothiazole or benzimidazole). All complexes were fully characterised and proved to be air, water and thermally stable. In addition, single crystal X-ray diffraction studies of complexes ***1b***, ***2a*** and ***2b*** unequivocally confirmed the tridentate coordination of the pincer ligands producing distorted square planar geometries around the Ni(II) center. The catalytic activity of these complexes was explored in the cross-coupling reactions of functionalized benzaldehydes and boronic acid derivatives to produce diarylketones in good to excellent yields, being the best catalysts those nickel complexes with less steric hindered donor groups *i.e.* R= ^{i}Pr. Noteworthy the fact that the benzothiazole and benzimidazole substituents doesn't seem to play any significant influence on the catalytic activity of the complexes.

This study represents the first synthesis of substituted benzophenones from aldehydes and arylboronic acids catalysed by Ni(II) pincer complexes. The successful use of these Ni(II) species suggest their potential in other transformations, and thus efforts to further explore their catalytic activity in other cross coupling reactions in currently under development in our laboratories, as well as the exploration of the potential biological activities of these species. These results will be disclosed in due time.

4. Experimental Section

4.1. General considerations

Unless otherwise noted, all experiments were carried out in nitrogen atmosphere. Solvents were purchased from Aldrich and dried under standard procedures. Solvents were dried (THF: Na^0/benzophenone, toluene: Na^0) and distilled under inert atmosphere. CH_2Cl_2 was dried over CaH_2. All other chemicals and filter aids were reagent grade and were used as received. Column chromatography was performed on silica gel (Merck, 230-700 mesh). Melting points were determined on a MEL-TEMP II in an open capillary tube. Elemental analyses were performed in a Thermo Scientific Flash 2000 elemental analyser. NMR experiments were recorded at 300 K on Bruker Avance 300 MHz and Varian Unity Inova 500 MHz spectrometers using TMS or residual

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proton solvents as internal standard; and H_3PO_4 as external standard. The deuterated solvent used was $CDCl_3$ and DMSO-d_6; chemical shifts (d) are quoted in ppm and coupling constants in Hz.; to indicate the multiplicity of the signals of ^{1}H NMR spectra, the following abbreviations have been used: (s) singlet, (d) doublet, (t) triplet, (at) apparent triplet, (m) multiplet, (dd) double doublet. Catalysis products were quantified with a GC-MS Agilent 6890N chromatograph equipped with a 30 m DB-1MS Agilent capillary column, coupled to an Agilent Technologies 5973 Mass Spectrometer equipped with an Inert Mass Selective Detector and ^{1}H NMR. Mass spectra were recorded on Jeol The AccuTOF JMS-T100LC and The MStationJMS-700 spectrometers, using $DART^+$ and FAB^+, respectively, as ionization techniques. Reagents for ligands preparation as well as reagents for POCOP ligands synthesis and solvents were purchased from Sigma-Aldrich. Flash chromatography was carried out using Silica gel 60, (Merck 230-400 mesh). Anhydrous $NiCl_2$ was prepared by heating $NiCl_2{\cdot}6H_2O$ (Sigma-Aldrich) at 120 °C for several hours. Ligands **P1** (4-(benzo[*d*]thiazol-2-yl)benzene-1,3-diol) and **P2** (4-(1*H*-benzo[*d*]imidazol-2-yl)benzene-1,3-diol) were prepared according to literature procedures using materials without further purification. Synthesis of POCOP-Ni(II) complexes was performed under N_2 atmosphere using standard Schlenk techniques. POCOP ligands were used *in situ* to lead the formation of respective nickel pincer complexes.

4.2. Synthesis of Proligands P1 and P2.

4.2.1. Synthesis of (4-(benzothiazol-2-yl)benzene-1,3-diol) (P1).

Ligand ***P1*** was obtained by reaction of 2,4-dihidroxybenzaldehyde (1.000 g, 7.24 mmol) and 2-aminothiophenol (0.776 mL, 7.24 mmol) in EtOH (25 mL) under reflux for 4 h. After heating, the reaction mixture was allowed to cool to room temperature, then concentrated *in vacuo* and purified by flash chromatography using silica gel and EtOAc/Hexanes (1:3) as eluent. The final product was isolated in 62% yield as a light-yellow solid (m.p.> 250 °C). ^{1}H NMR (300 MHz, DMSO-d_6): (δ) 11.80 (s, 1H, OH), 10.23 (s, 1H, OH), 8.06 (d, $^3J_{H\text{-}H}$= 9 Hz, $1H_{Bzt}$), 7.96 (d, $^3J_{H\text{-}H}$= 9 Hz, $1H_{Bzt}$), 7.91 (d, $^3J_{H\text{-}H}$= 9 Hz, $1H_{aryl}$), 7.48 (t, $^3J_{H\text{-}H}$= 9 Hz, $1H_{Bzt}$), 7.36 (t, $^3J_{H\text{-}H}$= 9 Hz, $1H_{Bzt}$), 6.52 (s, $1H_{aryl}$), 6.50 (d, $^3J_{H\text{-}H}$= 9 Hz, $1H_{aryl}$). $^{13}C\{^1H\}$ NMR (75.5 MHz, DMSO-d_6): (δ) 167.0 (Bzt), 162.5 (aryl), 158.0 (Aryl), 152.5 (Bzt), 133.5 (Bzt), 131.0 (aryl), 127.5 (Bzt), 125.0 (Bzt), 123.0 (Bzt), 122.0

(Bzt), 111.0 (Aryl), 109.0 (Aryl), 103.0 (Aryl). MS *m/z* DART$^+$: found, 244.0 $[(M+H)]^+$ (100%), calc. for $C_{13}H_9NO_2S$: 243.28. FT-IR (KBr, cm^{-1}): 3437, 1615, 1457, 1217, 956, 756, 459.

4.2.2. Synthesis of (4-(1*H*-benzoimidazol-2-yl)benzene-1,3-diol) (P2).

A mixture of 2,4-dihidroxybenzaldehyde (1.000 g, 7.24 mmol) and an equivalent of $NaHSO_3$ (0.760 g, 7.24 mmol) was dissolved in EtOH (25 ml) and stirred at room temperature for 2h. Then, a solution of 1,2-phenylendiamine (0.782 g, 7.24 mmol) in DMF (10 ml) was added to the mixture and refluxed for 4 h. Finally, the reaction mixture was poured in cold water to precipitate a white powder. Ligand **P2** was purified by flash chromatography (EtOAc/Hexanes, 1:3) and isolated in 77% yield as a bright-white powder (m.p.> 250 °C). ^{1}H NMR (300 MHz, DMSO-d_6): (δ) 13.12 (s, 1H, NH) 12.95 (s, 1H, OH), 10.00 (s, 1H, OH), 7.86 (d, $^3J_{H-H}$= 9 Hz, 1H_{aryl}), 7.57 (dd, $^3J_{H-H}$= 9 Hz, $^4J_{H-H}$= 3 Hz, 2H_{Bim}) 7.24(dd, $^3J_{H-H}$= 9 Hz, $^4J_{H-H}$= 3 Hz, 2H_{Bim},), 6.46 (dd, $^3J_{H-H}$= 9 Hz, $^4J_{H-H}$= 3 Hz, 1H_{aryl},), 6.41 (s, 1H_{aryl}). ^{13}C{^{1}H} NMR (75.5 MHz, DMSO-d_6): (δ) 161.1 (Aryl), 160.2 (Aryl), 152.8 (Bim), 141.4(Bim), 133.5 (Bim), 127.9 (Aryl), 122.9 (Bim), 117.9 (Bim), 111.62 (Bim), 108.0 (Aryl), 105.0 (Aryl), 103.0 (Aryl). MS *m/z* DART$^+$: found, 227.0 $[(M+H)]^+$ (100%), calc. for $C_{13}H_{11}N_2O_2$: 226.24. FT-IR (KBr, cm^{-1}): 3550, 3340, 1610, 1420, 1248, 828, 718, 518.

4.3. Synthesis of Ni-POCOP pincer complexes

4.3.1. Synthesis of [NiCl{C_6H_2-3-C_7H_4NS-2,6-(OP^iPr_2)$_2$}] (1a).

A 50 ml Schlenk flask provided with a magnetic stirring bar was charged with 100.0 mg (0.411 mmol) of proligand ***P1*** and dissolved in THF (20 mL). To this solution was added DMAP (110.4 mg, 0.904 mmol) and the resulting reaction mixture was heated at 40 °C for 1 h. Then, chlorodiisopropylphosphine (131.0 µL, 0.822 mmol) was aggregated dropwise to the stirring solution and refluxed for further 4 h. The resulting solution was filtrated and evaporated under reduced pressure and the residue redissolved in toluene (20 mL) and then $NiCl_2$ (53.03 mg, 0.411 mmol) was added. The resulting suspension was then set to reflux for 24 h. Finally, the reaction mixture was concentrated *in vacuo*, dissolved in dichloromethane (15 mL) and purified by flash chromatography on silica gel using dichloromethane/hexanes (1:1) as eluent. Complex

1a was isolated as a bright-yellow powder in 62% yield. ^{1}H NMR (500 MHz, $CDCl_3$): (δ) 8.19 (d, $^{3}J_{H-H}$= 9 Hz, 1H_{aryl}), 8.01 (d, $^{3}J_{H-H}$= 9 Hz, 1H_{Bzt}), 7.89 (d, $^{3}J_{H-H}$= 9 Hz, 1$H_{Bzt,}$), 7.45 (d,$^{3}J_{H-H}$= 6 Hz, 1H_{Bzt}), 7.33 (t, $^{3}J_{H-H}$= 6 Hz, 1$H_{Bzt,}$), 6.60 (d, $^{3}J_{H-H}$= 9 Hz, 1$H_{aryl,}$), 2.59 (m, 2H_{iPr}, CH), 2.46 (m, 2H_{iPr}, CH), 1.48 (td, $^{3}J_{H-H}$= 9 Hz, $^{3}J_{H-P}$= 6 Hz, 15H_{iPr}, CH_3), 1.37 (dd, $^{3}J_{H-H}$= 9 Hz, $^{3}J_{H-P}$= 6 Hz, 9H_{iPr}, CH_3). $^{13}C\{^{1}H\}$ NMR (126.6 MHz, $CDCl_3$): (δ) 169.5 (dd, $^{2}J_{C-P}$= 7.2 Hz, $^{3}J_{C-P}$= 13.0 Hz, Aryl), 164.6 (dd, $^{2}J_{C-P}$= 6.7 Hz, $^{3}J_{C-P}$= 14.2 Hz, Aryl), 162.9 (Bzt), 151.5 (Bzt), 134.3 (Bzt), 128.1 (Aryl), 124.9 (Bzt), 124.8 (at, $^{2}J_{C-P}$= 19.4, 20.6 Hz, Aryl), 123.2 (Bzt), 121.4 (Bzt), 120.0 (Bzt), 111.6 (d, $^{3}J_{C-P}$= 11.9 Hz, Aryl) 105.8 (d, $^{3}J_{C-P}$= 12.5 Hz, Aryl), 27.1(dd, J_{C-P}= 28.4, $^{3}J_{C-P}$= 17,) CH) 26.85 (dd, J_{C-P}= 28.4, $^{3}J_{C-P}$= 17), 16.5 (dd, $^{2}J_{C-P}$= 15.6, $^{4}J_{C-P}$ = 5.6 Hz, CH_3), 16.0 (br, CH_3), 15.7 (br, CH_3). $^{31}P\{^{1}H\}$ NMR (201.6 MHz, $CDCl_3$): (δ) 192.6 (d, P1, $^{2}J_{P-P}$= 332 Hz), 187.5 (d, P2, $^{2}J_{P-P}$= 332 Hz). MS *m/z* $DART^+$: found, 568.0 $[(M+H)]^+$ (30%), calc. for $C_{25}H_{34}ClNNiO_2P_2S$, 568.70. Anal. Calcd. for **1a,** $C_{25}H_{34}ClNNiO_2P_2S$: C, 52.80; H, 6.03; N, 2.46; S, 5.64. Found: C, 52.75; H, 6.08; N, 2.43; S, 5.61. FT-IR (KBr, cm^{-1}): 2921, 1596, 1241, 754, 460.

4.3.2. Synthesis of [NiCl{C_6H_2-3-C_7H_4NS-2,6-(OP^tBu_2)$_2$}] (1b).

An analogous procedure to that used for the synthesis of ***1a*** was employed for the preparation of ***1b***, using triethylamine (125.26 µL, 0.905 mmol) as base and di-terbutylchlorophosphine (155.78 µl, 0.823 mmol). The product was isolated in 52% yield as a yellow powder. X-Ray quality crystals were grown by slow diffusion of MeOH (6 mL) into a saturated CH_2Cl_2 solution (2 mL) of compound ***1b***. ^{1}H NMR (300 MHz, $CDCl_3$): (δ) 8.12 (d, $^{3}J_{H-H}$= 9 Hz, 1H_{aryl}), 7.94 (d, $^{3}J_{H-H}$= 6 Hz, 1H_{Bzt}), 7.81 (d, $^{3}J_{H-H}$= 6 Hz, 1H_{Bzt}), 7.37 (t, $^{3}J_{H-H}$= 6 Hz, 1H_{Bzt}), 7.25 (t, $^{3}J_{H-H}$= 6 Hz, 1H_{Bzt}), 6.51 (d, $^{3}J_{H-H}$= 9 Hz, 1H_{aryl}), 1.47 (dd, $^{3}J_{H-H}$= 15 Hz, $^{3}J_{H-P}$= 24 Hz, 36H_{tBu}, CH_3). $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$): (δ) 171.3 (dd, $^{2}J_{C-P}$= 8 Hz, $^{3}J_{C-P}$= 11 Hz, Aryl), 166.2 (dd, $^{2}J_{C-P}$= 6 Hz, $^{3}J_{C-P}$= 13 Hz, Aryl), 164.0 (Bzt), 152.6 (Bzt), 135.3 (Bzt), 128.9 (Aryl), 125.9 (Bzt), 125.4 (at, $^{2}J_{C-P}$= 19.8, 22.1 Hz, Aryl), 124.1 (Bzt), 122.4 (Bzt), 121.2 (Bzt), 112.3 (d, $^{3}J_{C-P}$= 11.9 Hz, Aryl), 106.6 (d, $^{3}J_{C-P}$= 12.6 Hz, Aryl), 39.8-39,4 (m, C_{tBu}), 28.3 (d, $^{3}J_{C-P}$= 5 Hz, CH_3), 28.0 (d, $^{3}J_{C-P}$= 5 Hz, CH_3). $^{31}P\{^{1}H\}$ NMR (121.6 MHz, $CDCl_3$): (δ) 197.5 (d, $^{2}J_{P-P}$= 300 Hz, P1), 189.8 (d, $^{2}J_{P-P}$= 300 Hz, P2). MS *m/z* FAB^+: found, 624.0 $[(M+H)]^+$ (60%), calc. for $C_{29}H_{42}ClNNiO_2P_2S$: 624.81. Anal. Calcd. for 1b, $C_{29}H_{42}ClNNiO_2P_2S$: C, 55.75; H, 6.78; N, 2.24; S, 5.13. Found: C, 55.71; H, 6.98; N, 2.19; S, 5.03. FT-IR (KBr, cm^{-1}): 2921, 1574, 1429, 1238, 827, 538.

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DOI: 10.1039/D1NJ01348C

4.3.3. Synthesis of [NiCl{C_6H_2-3-$C_7H_5N_2$-2,6-(OP^iPr_2)$_2$}] (2a).

A 50 ml Schlenk flask provided with a magnetic stirring bar was charged with 100.0 mg (0.442 mmol) of proligand ***P2*** and dissolved in THF (20 ml). To the resulting solution DMAP (118.6, 0.973 mmol) was added and the mixture heated to 40°C for 1h. After this time, chlorodiisopropylphosphine (140.1 µl, 0.884 mmol) was added dropwise under stirring and further refluxed for 4h. The resulting solution was filtrated and evaporated under reduced pressure and the residue redissolved in toluene (20 ml) and then $NiCl_2$ (57.27 mg, 0.442 mmol) added. The resulting suspension was set to reflux for 24h. After the prescribed reaction time, the reaction mixture is concentrated *in vacuo* and purified by flash chromatography using silica gel and dichloromethane/hexanes (1:1) as eluent. The product was isolated in 56% yield as a light-yellow powder. X-Ray quality crystals were grown by slow diffusion of MeOH (6 mL) into a saturated CH_2Cl_2 solution (2 mL) of the pincer complex **2a**. ^{1}H NMR (300 MHz, $CDCl_3$): (δ) 12.0 (s, NH), 8.40 (d, $^3J_{H-H}$= 9 Hz, 1H$_{aryl}$), 7.90 (m, 2H$_{Bim}$), 7.20 (m, 2H$_{Bim}$), 6.50 (d, $^3J_{H-H}$= 9 Hz, 1H$_{aryl}$), 3.0 (m, 2H$_{iPr}$, CH), 2.40 (m, 2H$_{iPr}$, CH), 1.35 (tdd, $^3J_{H-H}$= 23.2, 13.5 Hz, $^3J_{H-P}$= 7.1 Hz, 24H$_{iPr}$, CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): (δ) 169.3 (dd, $^2J_{C-P}$= 11.2 Hz, $^3J_{C-P}$= 9.7 Hz, Aryl), 163.8 (dd, $^2J_{C-P}$= 11.2 Hz, $^3J_{C-P}$= 9.7 Hz, Aryl), 148.6 (Bim), 136.8 (s, C8), 127.9 (Bim), 127.0 (Aryl), 124.8 (Bim), 124.2 (at, $^2J_{C-P}$= 22.5, 22.8 Hz, Aryl), 122.0 (2C, Bim), 107.0 (d, $^3J_{C-P}$= 10.5 Hz, Aryl), 106.3 (s, $^3J_{C-P}$= 11.2 Hz, Aryl), 27.15 (dd, J_{C-P}= 24 Hz, $^3J_{C-P}$= 4 Hz, CH$_{iPr}$), 26.9(dd, J_{C-P}= 24 Hz, $^3J_{C-P}$= 4.5 Hz, CH$_{iPr}$), 16.45 (dd, $^2J_{C-P}$= 7.5, $^4J_{C-P}$= 5.5 Hz, CH_3), 16.0 (br, CH_3), 15.6 (br, CH_3). ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$): (δ) 193.6 (d, $^2J_{P-P}$= 338.0 Hz, P1), 187.5 (d, P2, $^2J_{P-P}$= 338.0 Hz, P2). MS *m/z* FAB$^+$: found, 551.0 [(M+H)]$^+$ (100%), calc. for $C_{25}H_{35}ClN_2NiO_2P_2$: 551.6. Anal. Calcd. for 2a, $C_{25}H_{35}ClN_2NiO_2P_2$: C, 54.43; H, 6.40; N, 5.08. Found: C, 54.12; H, 6.28; N, 5.15. FT-IR (KBr, cm^{-1}): 3389, 2920, 1583, 1257, 829, 656.

4.3.4. Synthesis of [NiCl{C_6H_2-3-$C_7H_5N_2$-2,6-(OP^tBu_2)$_2$}], 2b.

A similar procedure to that of complex **2a** was employed for the synthesis of complex ***1b*** using triethylamine (134.68 µl, 0.973 mmol) as base and chloroditertbutylphosphine (167.2 µl, 0.884 mmol). The product was isolated in 48% yield as a yellow powder. X-Ray quality crystals were grown by slow diffusion of MeOH

(6 ml) into a saturated CH_2Cl_2 solution (2 ml) of ***2b***. ^{1}H NMR (300 MHz, $CDCl_3$): (δ) 12.0(s, NH), 8.77 (d, $^3J_{H-H}$= 9 Hz, 1H_{aryl}), 7.85 (m, 2H_{Bim}), 7.50 (m, 2H_{Bim}), 6.8 (d, $^3J_{H-H}$= 9 Hz, 1H_{aryl},), 1.58 (dd, $^3J_{H-H}$= 15 Hz, $^3J_{H-P}$= 24 Hz, 27H_{tBu}, CH_3), 1.42 (dd, $^3J_{H-H}$= 9 Hz, $^3J_{H-P}$= 6 Hz, 9H_{tBu}, CH_3). ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$): (δ) 170.0 (m, 2C, Aryl), 164.4 (dd, $^2J_{C-P}$= 6 Hz, $^3J_{C-P}$= 13 Hz, Aryl), 148.9 (Bim), 128.3 (Bim), 127.9 (Bim), 127.18 (Bim), 124.5 (at, $^2J_{C-P}$= 22.3, 22.5 Hz, Aryl), 124.3 (Bim), 121.3 (2C, Bim), 107.0 (d, $^3J_{C-P}$= 11.3 Hz, Aryl), 106.1 (d, $^3J_{C-P}$= 11.3 Hz, Aryl), 38.6-38.3 (m, C_{tBu}), 27.1 (d, $^3J_{C-P}$= 5 Hz, CH_3), 26.9 (d, $^3J_{C-P}$= 4.5 Hz, CH_3). ^{31}P{^{1}H} NMR (121.6 MHz, $CDCl_3$): (δ) 196.2 (d, P1, $^2J_{P-P}$= 302 Hz), 190.0 (d, P2, $^2J_{P-P}$= 302.8 Hz). MS *m/z* FAB$^+$: found, 607.0 [(M+H)]$^+$ (100%), calc. for $C_{29}H_{43}ClN_2NiO_2P_2$: 607.7. Anal. Calcd. for **2b**, $C_{29}H_{43}ClN_2NiO_2P_2$: C, 57.31; H, 7.13; N, 4.61. Found: C, 57.19; H, 7.08; N, 4.71. FT-IR (KBr, cm^{-1}): 3389, 2920, 1583, 1257, 829, 656.

4.4. Catalytic experiments.

The reactions were performed in 10 mL reaction tubes equipped with J. Young valves and an inner magnetic stirring bar containing a mixture of the corresponding Ni-cat. (0.01 mmol), phenylboronic acid (1 mmol), benzaldehyde derivative (1.2 mmol), base (3 mmol) and 3 mL of solvent (toluene/acetone or THF/acetone, 4:1). The reaction mixture was stirred and heated in an oil bath at 80°C or 65 °C for 8h. After the prescrived reaction times the resulting mixtures were cooled to room temperature, evaporated to dryness followed by extraction with CH_2Cl_2 (3 X 3 mL) and dried with anhydrous Na_2SO_4, filtered through celite, and analysed by GC-MS and ^{1}H NMR. The crude products were purified by silica gel column chromatography using ethyl acetate/hexanes as eluent.

4.5 Crystallographic details

Yellow prisms of complexes **1b** (CCDC 2062553), **2a** (CCDC 2062554) and **2b** (CCDC 2062552), were grown independently from CH_2Cl_2/CH_3OH solvent systems and mounted on glass fibers, and then placed on a Bruker Smart Apex II diffractometer with a Mo-target X-ray source (λ = 0.71073Å). Complex **1b** and **2a** were collected at 298 K and complex **2b** at 150 K. The detector was placed at a distance of 5.0 cm from the crystals, frames were collected with a scan width of 0.5 in ω and an exposure time

of 10 s/frame. Frames were integrated with the Bruker SAINT software package[30] using a narrow-frame integration algorithm. Non-systematic absences and intensity statistics were used in monoclinic P2(1)/c space group for **1b** and **2a** and triclinic space group for **2b**. The structures were solved using Patterson methods using SHELXS-2014/7 program.[31] The remaining atoms were located via a few cycles of least squares refinements and difference Fourier maps. Hydrogen atoms were input at calculated positions and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a Ueq = 1.2 Å and a Ueq = 1.5 Å for methyl groups to precedent atom in all cases. For all complexes, the final cycle of refinement was carried out on all non-zero data using SHELXL-2014/7.[31] Absorption correction was applied using SADABS program.[32]

5. Supplementary information

Supplementary data for compounds **1b** (CCDC 2062553), **2a** (CCDC 2062554) and **2b** (CCDC 2062552) was deposited at the Cambridge Crystallographic Data Centre. Copies of this information are available free of charge on request from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk) quoting the deposition numbers 2062552-2062554.

6. Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationship that could have appeared to influence the work reported in this paper.

7. Acknowledgments

We would like to thank Dr. Francisco Javier Pérez Flores, Q. Eréndira García Ríos, M.Sc. Lucia del Carmen Márquez Alonso, M.Sc. Lucero Ríos Ruiz, M.Sc. Alejandra Núñez Pineda (CCIQS), Q. María de la Paz Orta Pérez, Q. Roció Patiño-Maya and Ph.D. Nuria Esturau Escofet for technical assistance. A. A. C-G. would like to thank CONACYT (No. de becario: 583187) for Ph.D. scholarship. The financial support of this research by PAPIIT-DGAPA-UNAM (PAPIIT IN210520) and CONACYT A1-S-33933 is gratefully acknowledged.

View Article Online
DOI: 10.1039/D1NJ01348C

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