Journal of Saudi Chemical Society (2021) **25**, 101178

King Saud University

**Journal of Saudi Chemical Society**

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ORIGINAL ARTICLE

# C-Ni bond functionalization in the reaction of binuclear cyclometallated Ni(II) complexes with chlorophosphines

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Received 20 October 2020; revised 6 December 2020; accepted 13 December 2020
Available online 28 December 2020

**KEYWORDS**

Functionalization;
Insertion;
Cyclonickellation;
Phosphinites

**Abstract** This manuscript reports successful C-H nickellation of the aryl phosphinites (i-$Pr_2$P(O-aryl) derived from un-substituted/substituted phenols: $C_6H_5OH$, 4-R-$C_6H_4OH$ (R = F, MeO). Nickellation was observed with the phosphinites at an ortho-C-H position to generate Br-bridged dimers [{$\kappa^P$,$\kappa^C$-(i-Pr)$_2$PO-aryl}cNi(μ-Br)]$_2$ (C1-C3). While conversion of monomeric complexes from dimeric cyclonickellated complexes, functionalization behaviour was studied under inert atmosphere by reacting synthesized complexes with $R_2PX$ in various solvents. In order to understand the feasibility of the reaction and to evaluate the properties of product of insertion, phosphinite-phosphine nickel complexes were also approached from a second side. Appearance of specific signals in NMR spectra of products, provided strong evidences of formation of the target products exhibiting fluxional behaviour.
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## 1. Introduction

Phenol and its derivatives are considered among the most common foundations of polymers, pharmaceuticals and biologically active natural products [1]. Due to their extensive applications in organic synthesis, functionalization of phenols has attracted great attention which is commonly observed at electron rich ortho/para positions of substituted phenols due to strong sigma donor ability of hydroxyl groups of phenols. To study C-H functionalization at meta position, indirect protocols like cyclo-addition or oxidation of cyclohexanones are needed [2] as direct meta-functionalization is still a great challenge [1]. Practically, most wanted feature of metal assisted functionalization processes is that they can be proceeded in one-pot way sidestepping the isolation of intermediate metallated moieties [3]. Intercepting the progress of catalytic reactions and probing the features of these key intermediates is advantageous for targeting and optimization of novel

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

https://doi.org/10.1016/j.jscs.2020.101178
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cyclometallated complexes for systematic metal assisted C-H functionalization study. Synthesis of expensive organic compounds has been carried out by C-H bond functionalization for few years and has become the main focus of organic researchers [4], particularly considerable efforts have been made recently for detailed mechanistic study of ortho C-H metallation [5]. Also meta C-H functionalization study has been carried out with a multiple directing groups [3].

Increasing trend towards the synthesis of cyclonickellated complexes for rational design of C-H functionalization study since past decade has revealed that easily synthesized nickel precursors can be advantageous substitutes of their extensively used Palladium counterparts [6–10]. Nickel-PCP and -POCP type pincer complexes synthesized from phenol based phosphinite ligands (Fig. 1. structures 1–7) have attracted the interest of researchers for their diverse applications as pre-catalysts in allylic additions, Suzuki couplings, Micheal additions, hydrosilylation of aldehydes, C-S couplings and reduction of $CO_2$ [11–13].

These developments and longstanding interest in cyclonickellated chemistry has attracted our attention to design this project. We prepared novel phenol derived cyclonickellated complexes and studied their functionalization behaviour under inert atmosphere to address the requisite of cost effective catalysts. To study the characteristic features of functionalized products, phosphine-phosphintie ligands were prepared to get target product.

## 2. Experimental

This research work involves C-H nickellation of the aryl phosphinites (i-$Pr_2$P(O-aryl) derived from three groups of un-substituted/substituted phenols: $C_6H_5OH$, 4-R-$C_6H_4OH$ (R = (a) F (b) MeO). Nickellation of phosphinites was observed at an ortho-C–H position to generate Br-bridged dimers [{$\kappa^P$, $\kappa^C$-(i-Pr)$_2$PO-aryl}Ni(μ-Br)]$_2$. After successful synthesis of dimeric nickel complexes, C-Ni bond functionalization study was carried out by reacting synthesized complexes with $ClPR_2$ in various solvents. As the products of insertion seemed difficult to identify and isolate, a different strategy was adopted to understand the feasibility of reaction and structural features of product formed during functionalization study which involved the synthesis of new type of phosphine-phosphinite ligands and their reaction with nickel precursor to get target monomeric complex. Detailed study of each reaction has been discussed under respective headings.

All operations were performed under inert atmosphere of nitrogen using standard Schlenk line techniques and an inert-atmosphere box. The solvents were dried by passage over a column of activated alumina, collected under nitrogen, and stored over 4 Å molecular sieves. Triethylamine was dried over $CaH_2$. Butyronitrile, liquid bromine, phenol, 4 fluoro phenol, 4 methoxy phenol, nickel, diisopropyl chlophosphine, diphenyl chlorophosphine and n-butyl Lithium were purchased from Sigma–Aldrich and were used without further purification. Solution transfers between the reaction vessels were done via cannula unless otherwise specified. All 1D NMR spectra were recorded at 400 MHz ($^1$H), 202.4 MHz ($^{31}$P) and 470.4 MHz ($^{19}$F). Chemical shift values are reported in ppm (δ) and referenced internally to the residual solvent signals ($^1$H 1.94 and $^{13}$C 118.26 ppm for $CHD_2CN$) or externally ($^{31}$P, $H_3PO_4$ in $D_2O$, $\delta = 0$; $^{19}$F, $CFCl_3$, $\delta = 0$). The values for coupling constants (J) are given in Hz.

### 2.1. Synthesis of nickel precursor

Synthesis of nickel precursor {(i-PrCN)$NiBr_2$}$_n$ was carried out by reported method [3]. To the weighed amount (3.5 g, 59.6 mmol) of nickel powder under reduced pressure (vacuum), butyronitrile (iPrCN) (15 mL) and precise amount of liquid bromine (3.52 mL, 68.6 mmol) were added carefully and dropwise in order to avoid vigorous reaction under nitrogen atmosphere and continuous stirring at 0 °C using ice bath. The colour of reaction mixture started changing to brownish-green due to the bromine. The reaction mixture was left to stir at room temperature overnight. Beige colour of reaction mixture indicated the completion of reaction. The product was washed with diethyl ether (3 × 5) to remove the unreacted materials and was dried under reduced pressure until rocky material was obtained which was then crushed to fine beige coloured powder.

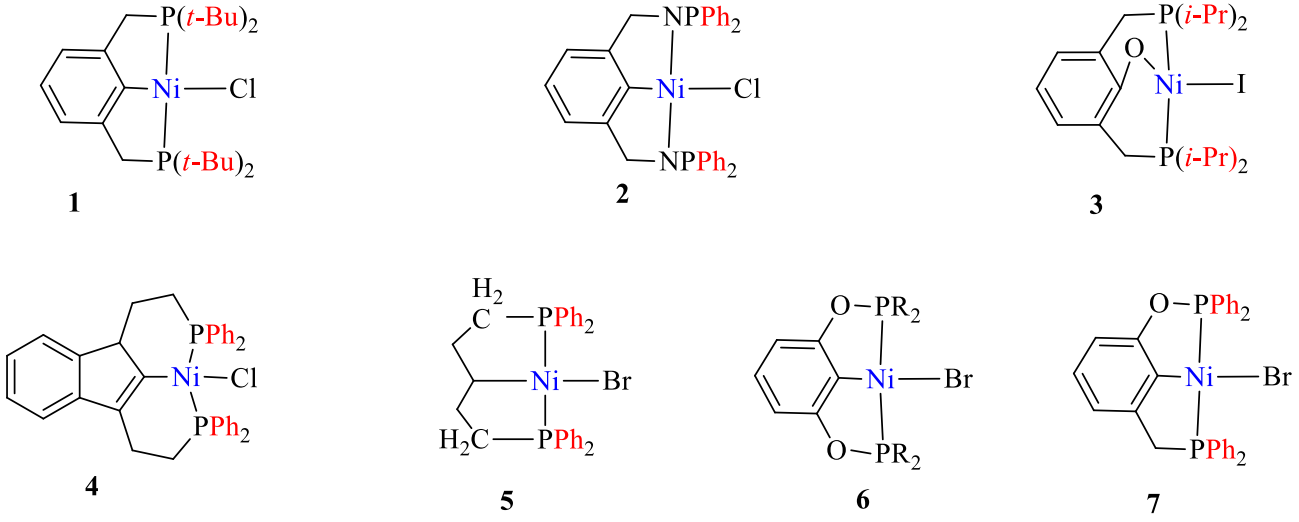



**Fig. 1** Synthesized -PCP and -POCOP type nickel complexes [14].

General procedure for the synthesis of phenol derived phosphinites ligands (L1-L6)

Synthesis of phenol derived phosphinites was carried out by reported method [3]. To a solution of phenol (R-aryl-OH) (2–5 mmol) in THF (20 mL) (dry), triethylamine ($Et_3N$) (1.1 eq.) and chlorophosphine ($ClPR_2$) (1.05 eq.) were added and allowed to stir at room temperature for 30–120 min until salt precipitated (as monitored by $^{31}P$ NMR). After removal of solvent under reduced pressure, the product was extracted with diethyl ether (3 × 15 mL) to yield a colourless or pale yellow oil (L1-L6) (detail has been given in supporting information).

### *2.2. General procedure for the synthesis of cyclonickellated complexes (C1-C3)*

To the ligands (L1-L3), dry acetonitrile (MeCN) (20 mL), nickel precursor $\{(i\text{-PrCN})NiBr_2\}_n$ (1.2 eq.) and triethyl amine ($Et_3N$) (1.2 eq.) were added and stirred the greenish mixture at 80 °C until the reaction was complete (monitored by $^{31}P$ NMR by observing the disappearance of signal of starting material ca. 135 ppm). The solvent was evaporated under reduced pressure and the product was extracted with toluene which was later removed under reduced pressure. The orange powder or pasty product obtained was dissolved in diethyl ether, precipitated using hexane, filtered off and washed with hexane to completely remove impurities. The product thus obtained was dried under reduced pressure to yield an orange powder (C1-C3) (detail has been given in supporting information).

### *2.3. Functionalization study of C1 with $ClPPh_2$*

a. Added diphenyl chlorophosphine (0.11 mL, 0.6 mmol) to a stirring solution of C1 (0.71 g, 0.32 mmol) in dry THF (20 mL) at room temperature under inert atmosphere. Immediate colour change from greenish to brownish was observed (reaction was monitored by $^{31}P$ NMR). Left it to react for 24 h. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. Removed THF under reduced pressure. The product was extracted with diethyl ether (10 mL) leaving behind dusty coloured powder, the ether was removed from filtrate under vacuum which yielded dark brownish pasty material (A). $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal.

b. Added diphenyl chlorophosphine (0.11 mL, 0.6 mmol) to a stirring solution of C1 (0.71 g, 0.32 mmol) dry diethyl ether (10 mL) at room temperature under inert atmosphere. Initially, dimer was less soluble in ether, but addition of $ClPPh_2$ solubilized it and colour changed from orange to brownish (reaction was monitored by $^{31}P$ NMR). $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 189.2 (s). The product was extracted with ether and hexane leaving behind black residue, and after evaporation of hexane from filtrate, reddish brown pasty material (B) was obtained. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 148.3 (s), 150.3 (s), 180.5 (s), 182.5 (s), 189.3 (s).

### *2.4. Functionalization study of C2 with $ClPPh_2$*

a. Added diphenyl chlorophosphine (0.05 mL, 0.26 mmol) to a stirring solution of C2 (0.1 g, 0.13 mmol) in dry toluene (15 mL) at room temperature and monitored the reaction by $^{31}P$ NMR. Colour of solution turned to dark brown. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. Removed toluene under reduced pressure, added ether and hexane, product was not completely soluble, filtered it and obtained some blackish residue, dried it and stored. From orange coloured filtrate, removed solvent under reduced pressure. Dark brownish pasty material obtained. Again, added ether and hexane, removal of solvents yielded dark blackish residue (C) soluble in toluene. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal.

b. Added diphenyl chlorophosphine (0.05 mL, 0.26 mmol) to a stirring solution of C2 (0.1 g, 0.133 mmol) in dry THF (15 mL) at room temperature under inert atmosphere. Reaction was monitored by $^{31}P$ NMR. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 149.1 (s), 151.2 (s), 176.9 (s), 179.0 (s), 180.0 (s), 182.0 (s), 189.0 (s). Some material settled down, filtered off the settled material and dried it. Reddish brown powder poorly soluble in ether was obtained, tried its crystallization but failed. To the filtrate, added some hexane, some precipitates settled down, removal of hexane yielded brownish greasy product (D). $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal.

### *2.5. Functionalization study of C3 with $ClPPh_2$*

a. Added diphenyl chlorophosphine (0.05 mL, 0.26 mmol) to a stirring solution of C3 (0.1 g, 0.133 mmol) in dry toluene (20 mL) at room temperature under inert atmosphere. Colour of reaction mixture turned orange and remained same even after 1 h. Reaction was monitored by $^{31}P$ and $^{19}F$ NMR. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 188.9 (s). $^{19}F$ NMR (470.4 MHz, $CDCl_3$, δ ppm) −129.5 (s). Let the reaction run overnight at 80 °C. No progress of reaction was observed, removed the toluene under reduced pressure and extraction with ether and hexane (1:2) yielded brownish pasty material (E). $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 188.9 (s) (no shift of peak), $^{19}F$ NMR (470.4 MHz, $CDCl_3$, δ ppm) −129.5 (s) (no shift of peak).

b. Added diphenyl chlorophosphine (0.05 mL, 0.26 mmol) to a stirring solution of C3 (0.1 g, 0.133 mmol) in dry diethyl ether (20 mL) at room temperature under inert atmosphere. $^{1}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 188.85 (s), 184.95 (s). Removed the ether under reduced pressure and dissolved the product in THF. Left it to react overnight and monitored the reaction by $^{31}P$ NMR. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm). Reddish material (F) settled down, filtered off the settled material which was poorly soluble in ether. To the filtrate, added some hexane which started decomposing nickel complex as the appearance of green colour indicated. Crystallization attempts failed.

### *2.6. Functionalization study of C1 with $PPh_2OPh$ (L4)*

Added C1 (0.1 g, 0.14 mmol) to a stirring solution of $PPh_2OPh$ (L4) (0.08 g, 0.28 mmol) in dry diethylether (15 mL) at room temperature under inert atmosphere. Reaction was monitored by $^{31}P$ NMR. Evaporated ether and extracted the product with hexane, sticky brownish material (intermediate) (G) was obtained. $^{31}P$ NMR (202.4 MHz, $CDCl_3$, δ ppm) 120 (d), 186 (d). $^{1}H$ NMR (400 MHz, $CDCl_3$, δ ppm) 1.40 (6H, d.d, $CH_3$, $J$ = 6.37 Hz), 1.50 (6H, d.d, $CH_3$, $J$ = 7.24 Hz), 2.62 (2H, m, CH), 6.3 (1H, t, aryl-H, $J$ = 7.34 Hz), 6.64 (1H, d, aryl-H, $J$ = 8.11 Hz), 6.8 (1H, t, aryl-H, $J$ = 7.34 Hz), 6.98 (1H, t, aryl-H, $J$ = 7.24 Hz), 7.0 (1H, d, aryl-H, $J$ = 7.24 Hz), 7.18 (2H, t, aryl-H, $J$ = 8.11 Hz), 7.26 (3H, t,

aryl-H, $J$ = 8.11 Hz), 7.4 (5H, d, aryl-H, $J$ = 8.11 Hz), 7.88 (4H, m, aryl-H). Dissolved some of this intermediate product in ether to crystallize it and the other batch was dissolved in toluene and stirred at 80 °C to complete the reaction. Monitored the reaction by $^{31}$P NMR for 1.5 h. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) 120.2 (d), 150.3 (d), 180.5 (d), 186.4 (d). Evaporated toluene after 24 h and obtained brownish pasty material (H). $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) 120.2 (d), 150.3 (d), 180.5 (d), 186.4 (d), 80 (s). The reaction in toluene was incomplete, so evaporated toluene under reduced pressure and tried to see if reaction occurs in acetonitrile. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) 197 ppm. Heated (60 °C) the reaction mixture in order to see the effect of temperature, but no progress could be observed. Crystallization attempts failed.

### *2.7. General procedure for the synthesis of phosphine-phosphinite ligands (L7-L11)*

Phosphine-phosphinite ligands (L7-L11) were synthesized by new protocol which involved lithiation of preligands (L1, L4-L6) (phosphinite ligands) following the addition of another phosphine moiety to get target ligand. To the stirring solution of L1, L4-L6 in THF (20 mL), n-butyl lithium (1.2 eq) was added precisely at −80 °C under inert atmosphere and continuous stirring and then left it to react for 30 sec. Then a THF solution of diphenyl chlorophosphine ($ClPPh_2$) (1 eq.) was added to the reaction mixture at −30 °C and left it to react for 24 h·THF was removed under reduced pressure and extraction with ether (3 × 15 mL) (upon completion of reaction, as monitored by $^{31}$P NMR) yielded pale yellow oily product (L7-L11) (detail has been given in supporting information).

### *2.8. Cyclonickellation attempt on phosphine-phosphinite ligand L8*

Stirred a mixture of nickel precursor ($NiBr_2$iPrCN) (0.34 g, 0.9 mmol) and L8 (0.5 g, 1 mmol) in THF (20 mL) under inert atmosphere. Immediately, colour changed from greenish to dark brown. Monitored the reaction by $^{31}$P NMR and left it to react for 1 h. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. After 24 h, extracted the product with ether and hexane (1:2) and obtained reddish black pasty material (I) after evaporation of solvent. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. Dissolved I in toluene (15 mL) and tried precipitation with hexane, but no precipitates appeared. Removed the solvent under reduced pressure at 50 °C and again added hexane (30 mL), dark precipitates settled down with some sticky material on the walls of flask, transferred the precipitates and solvent to other flask using canula, filtered, dried the product under reduced pressure and obtained blackish powder (J). $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. All attempts to crystallize the product in various solvents failed.

### *2.9. Cyclonickellation attempt on phosphine-phosphinite ligand L9*

a. Stirred a mixture of nickel precursor ($NiBr_2$iPrCN) (0.21 g, 0.7 mmol) and L9 (0.25 mL, 0.77 mmol) in dry THF (20 mL) under inert atmosphere. Immediately, colour changed from greenish to dark brown. Monitored the reaction by $^{31}$P NMR and left it to react for 1 h. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. After 24 h, extracted the product with ether and hexane (1:2). Some residual material settled down, filtered it and discarded the dusty coloured material produced in reaction flask. After the removal of solvent from filtrate, reddish black thick sticky material (K) left behind which was seen to be decomposed next day as indicated from appearance of green colour. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal.

b. Stirred a mixture of nickel precursor ($NiBr_2$iPrCN) (0.15 g, 0.55 mmol) and L9 (0.15 mL, 0.45 mmol) in dry diethylether under inert atmosphere. Initially, the colour of solution was light brown and turned dark brown after 5 h stirring with off white precipitates settled down. Filtered the solution and evaporated ether. Blackish thick sticky material (L) was obtained. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. Crystallization attempts remained unsuccessful.

### *2.10. Cyclonickellation attempt on phosphine-phosphinite ligand L10*

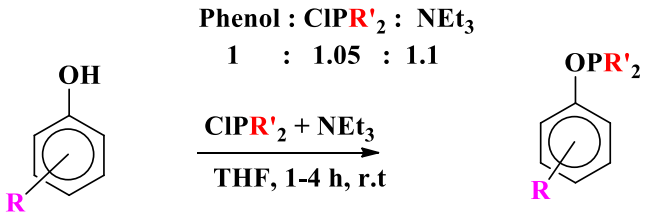
Stirred a mixture of nickel precursor ($NiBr_2$iPrCN) (0.34 g, 0.9 mmol) and L10 (0.4 g, 1 mmol) in dry THF (20 mL) under inert atmosphere. Immediately, colour changed from greenish to dark brown. Monitored the reaction by $^{31}$P NMR and left it to react for 1 h. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. After 24 h, extracted the product with ether and hexane (1:2) and washed with hexane. Some greenish material settled down each time hexane was added. After work up, dark reddish brown material was (M) was obtained. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) 64.3 (s), 134.5 (s), 149.4 (s), 151.4 (s), 180.7 (s), 182.7 (s).

### *2.11. Cyclonickellation attempt on phosphine-phosphinite ligand L11*

Stirred a mixture of nickel precursor ($NiBr_2$iPrCN) (0.13 g, 0.5 mmol) and L11 (0.29 mL, 0.5 mmol) in dry THF (20 mL) under inert atmosphere. Monitored the reaction by $^{31}$P and $^{19}$F NMR and left it to react for 48 h. $^{31}$P NMR (202.4 MHz, $CDCl_3$, δ ppm) no signal. $^{19}$F NMR (470.4 MHz, $CDCl_3$, δ ppm) −120.3 (s), −126.8 (s). Removed THF and extracted the product with ether. Reddish black thick sticky material (M) was obtained after evaporation of ether with some greenish material. Tried to precipitate it with ether and hexane mixture (1:3) but again green material settled down.

## 3. Results and discussion

The ligands $C_6H_5OP(iPr)_2$ (L1), 4MeO-$C_6H_4OP(iPr)_2$ (L2), 4F-$C_6H_4OP(iPr)_2$ (L3), $C_6H_5OPPh_2$ (L4), 4F-$C_6H_4OPPh_2$ (L5) and 2Br-$C_6H_4OPPh_2$ (L6) were successfully synthesized (Scheme 1). In THF (dry) solution (20 mL) of phenol (R-aryl-OH) (2–5 mmol), 1.10 equivalent triethylamine ($Et_3N$) and 2.10 equivalent chlorophosphine ($ClPR_2$) was added and allowed to stir at room temperature for 30–120 min until salt precipitated out (as monitored by $^{31}$P NMR). After workup, the pale yellow oil obtained. The appearance of single peak in $^{31}$P NMR spectra of L1-L6 at 147.4, 152.2, 150.96, 110.79, 113.13 and 114.11 ppm, respectively (Figs. S1–S6)




L1-L6

R= H, R'= *i*Pr (for L1)
R= 4MeO, R'= *i*Pr (for L2)
R= 4F, R'= *i*Pr (for L3)
R= H, R'= aryl (for L4)
R= 4F, R'= aryl (for L5)
R= 2Br, R'= aryl (for L6)

**Scheme 1** General synthetic route for the synthesis of aryl phosphinite ligands (L1-L6).

and at −123.7 and −121.38 ppm in $^{19}$F NMR spectra of L3 and L5, respectively (Figs. S7 and S8) and specific signals of protons in $^{1}$H NMR spectra of all ligands (Figs. S9–S14) supported the evidences of their successful syntheses. It was observed that electron withdrawing group i.e F and Br speed up the synthesis of ligands.

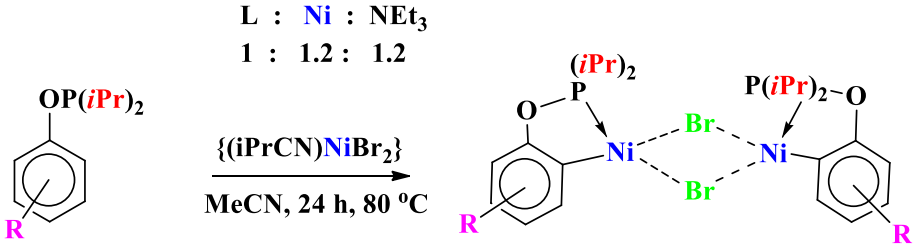
To facilitate the direct ortho-C–H nickellation of phosphinite ligands L1-L3, extensive heating of these ligands was carried out with Ni(II) precursor $\{(i\text{-PrCN})NiBr_2\}_n$ and triethylamine ($NEt_3$) in acetonitrile (MeCN) in 1: 1.2: 1.2 ratio which generated Br-bridged 5-membered cyclonickellated dimeric complexes $[\kappa^P,\kappa^C\text{-}(i\text{-Pr})_2PO\text{-}\ aryl\}Ni(\mu\text{-}Br)]_2$ (C1), $[\{\kappa^P,\ \kappa^C\text{-}(i\text{-Pr})_2P\text{-}(4MeO\text{-}O\text{-}aryl)\}Ni(\mu\text{-}Br)]_2$ (C2) and $[\{\kappa^P,\kappa^C\text{-}(i\text{-Pr})_2P\text{-}(4F\text{-}O\text{-}aryl)\}Ni(\mu\text{-}Br)]_2$ (C3), respectively after workup (Scheme 2). Vabre and co-workers investigated the effect of various solvents to improve the atom-efficiency of such reactions in order to favour the synthesis of dimeric complex [14,15]. Their findings inferred that employing acetonitrile as solvent lead cyclonickellation over a shorter reaction time at reduced temperatures, while using THF or ethyl acetate (as solvents) decreases the rate of reaction and cyclonickellation was incomplete even after 24 h. The feasibility of reaction in acetonitrile was attributed to its higher polarity having significant role in charge separation of reacting species [14]. This hypothesis was further supported by Mangin and co-worker [5]. They hypothesized that acetonitrile facilitates the cyclonikellation due to stronger nuclophilic character towards Ni(II) [5].

The reactions were monitored by the shifts of $^{31}$P signals of the starting ligands L1-L3 from ca. 147.4–152.2 ppm to 195.5–199.2 ppm, respectively which confirmed the synthesis of C1-C3 (Figs. S15–S17) and shift of $^{19}$F signal from −123 to −125.99 ppm for C3 (Fig. S18).

The synthesized complexes C1-C3 were further employed to study their C-Ni bond functionality to convert dimeric complexes into monomeric complexes. The attempts were made to insert $PR_2$ moiety in C-Ni bond in order to convert it to C-P bond by reacting C1-C3 with $XPR_2$ (R = $Ph_2$, X = Cl/O-aryl). The reactions were carried out in various solvents and heating effects were also probed to understand the chemistry of reactions (Scheme 3). Generally, immediate colour change and initial shifts of $^{31}$P NMR peaks during all reactions, indicated the insertion of $PR_2$ moiety.

During the C-Ni bond functionality study of C1 with $ClPPh_2$ in THF, dark brownish pasty product of insertion (A) (after workup with ether) was NMR silent. Incomplete functionalization was considered the result of using unsuitable solvent i.e THF, so further attempt was made with diethyl ether. Initially, dimer was less soluble in ether, but addition of $ClPPh_2$ solubilized it and colour changed from orange to brownish. Reddish brown pasty material (B) was obtained after work up. Initially, $^{31}$P NMR signal shift from 196.3 ppm to 189.2 ppm indicated the occurrence of reaction, however after work up, appearance of several peaks indicated the instability of product due to its decomposition during isolation (Fig. 2).

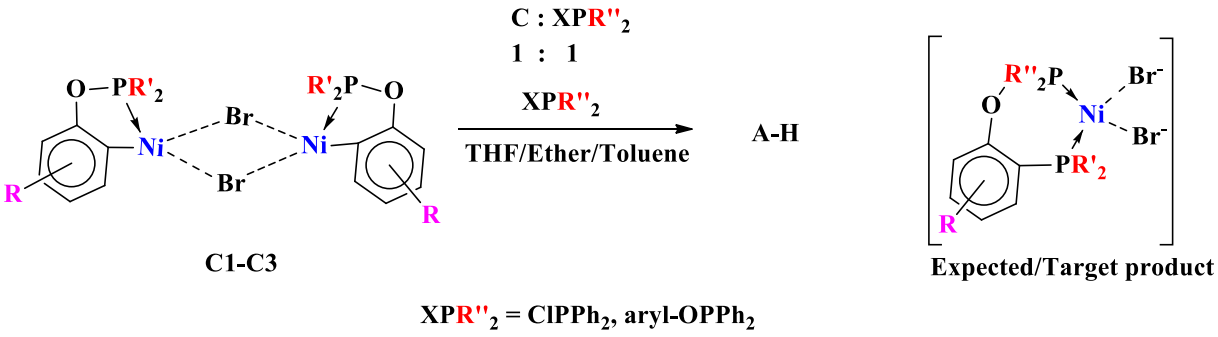
During the reaction of C2 with $ClPPh_2$ in toluene, initially, some weaker signals appeared in $^{13}$P NMR spectrum at ca.148–152 ppm in addition to strong signal at 189.0 ppm, but later they disappeared. After workup with diethyl ether and hexane, dark brownish residue (C) obtained was soluble in toluene but NMR silent. $^{31}$P NMR spectrum of same reaction in THF initially displayed some peaks at ca.175–182 and 150–152 ppm in addition to 189.0 ppm (Fig. 3), which disappeared later. Workup yielded reddish brown powder poorly




L1-L3 C1-C3

R= H, (for L1 and C1)
R= 4MeO (for L2 and C2)
R= 4F (for L3 and C3)

**Scheme 2** General synthetic route for the synthesis of cyclonickellated complexes (C1-C3) from aryl phosphinite ligands (L1-L3).




**Scheme 3** C-Ni bond functionality study of C1-C3.

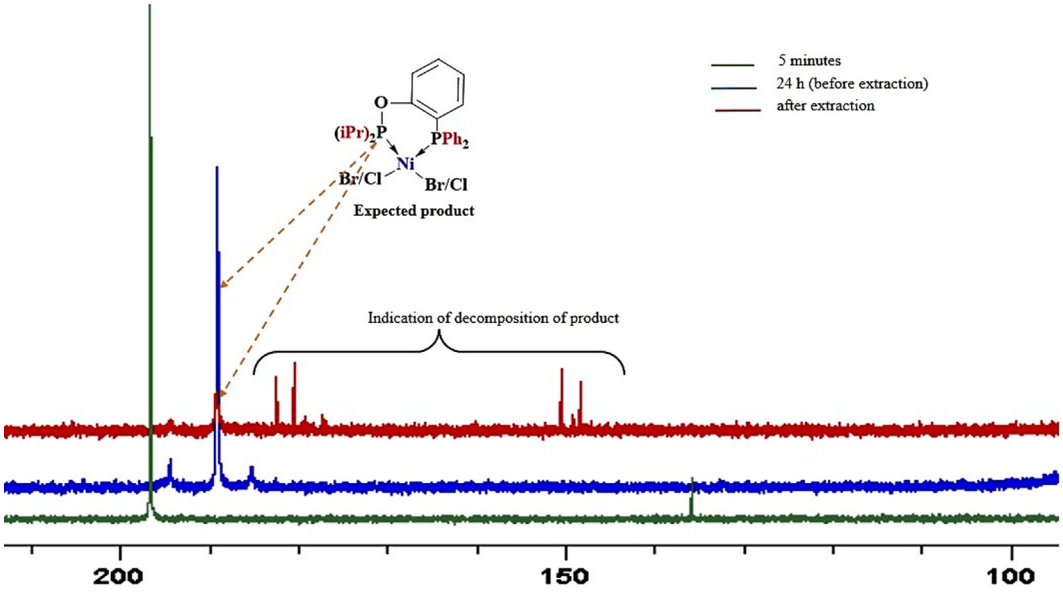



**Fig. 2** $^{31}$P NMR spectra of product of insertion of C1 in ether (before and after extraction).

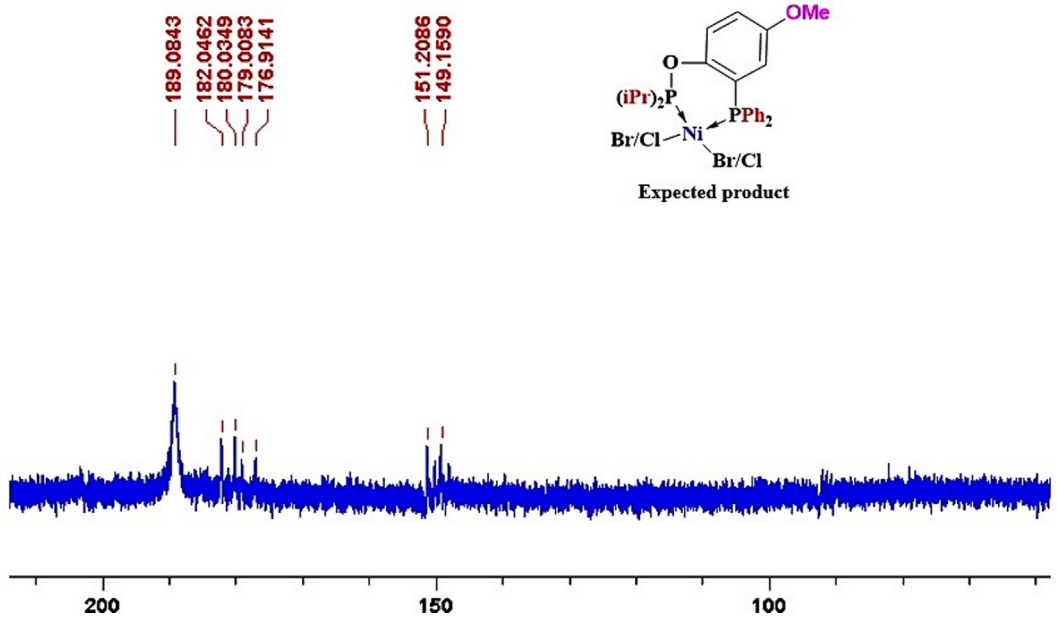


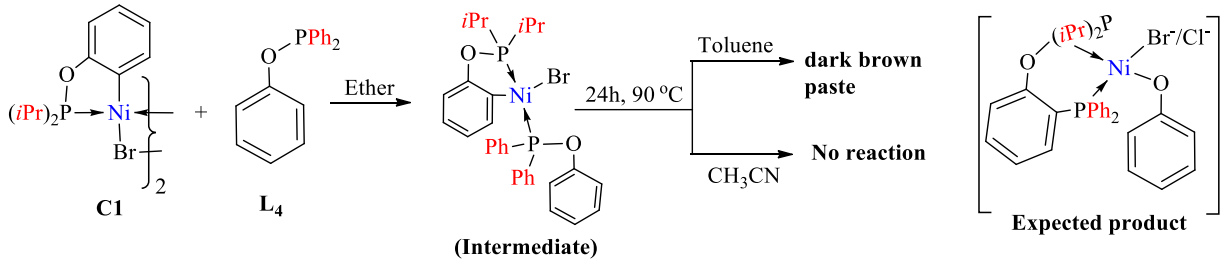

**Fig. 3** $^{31}$P NMR spectrum of product of insertion of C2 in THF.

soluble in diethyl ether and brownish greasy product (D) from filtrate but both of them were NMR silent (Scheme 4).

Monitoring the reaction of C3 with $ClPPh_2$ in dry toluene at ambient temperature, immediately displayed peak shift from 194.6 ppm to 188.9 ppm in $^{31}P$ NMR and −125.6 to −129.5 in $^{19}F$ NMR which indicated the incomplete reaction but later no change in peaks pattern was observed even after overnight heating at 80 °C (Figs. 4 and 5).

Same pattern of peaks was observed for brownish pasty material obtained (E) after workup but signals seemed to diminish with the passage of time. When the same reaction was carried out in diethyl ether at room temperature, immediate peak shift from 194.6 ppm to two signals at ca. 188.8 ppm and 184.9 ppm in $^{31}P$ NMR spectrum indicated the incomplete coordination of $P(iPr)_2$ moiety (Fig. 6) but some additional signals in $^{19}F$ NMR spectrum at −118.8, −120.6 and −123.3 ppm indicated decomposition of product (Fig. 7). This might be due to poor solubility in diethyl ether, so we tried the reaction in THF but the reddish material (F) obtained after workup was NMR silent.

After unsuccessful attempts to isolate product of insertion with $ClPPh_2$, nickel dimer (C1) was reacted with aryl-$OPPh_2$ (L4) in diethyl ether at room temperature. The appearance of two doublets at ca. 120 ppm and 186 ppm in $^{31}P$ NMR and specific signals in $^{1}H$ NMR spectra indicated that the ligand has broken the nickel dimer and produced an intermediate species (Figs. 8 and 9). Work up yielded sticky brownish material (G) (intermediate) which was heated in toluene at 80 °C to complete the reaction (Scheme 4). After 1.5 h, two additional doublets were observed at ca. 150 ppm and




**Scheme 4** C-Ni bond functionality study of C1 with aryl-$OPPh_2$.

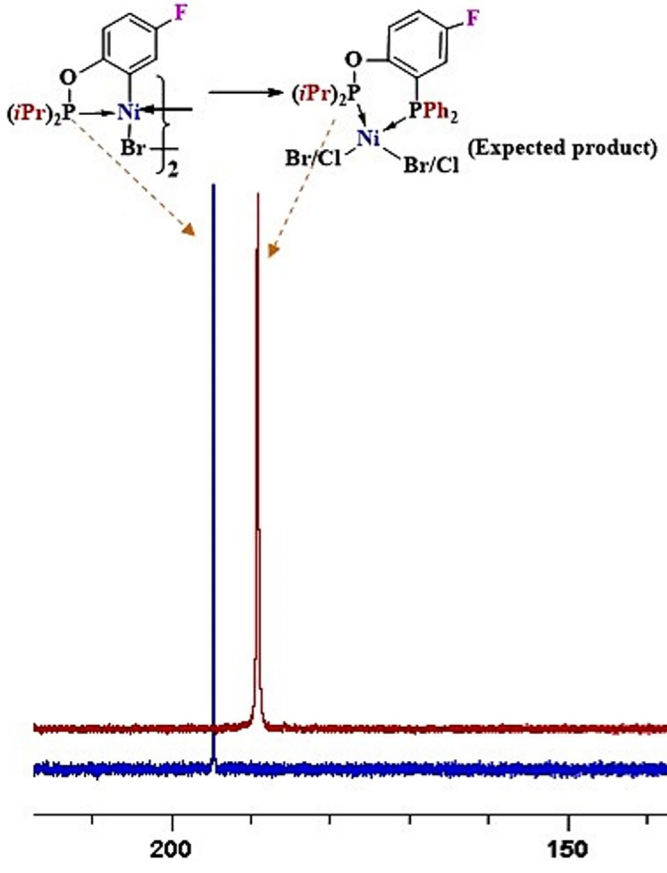



**Fig. 4** $^{31}P$ NMR spectra of product of insertion of C3 in toluene showing shift of peak during reaction.

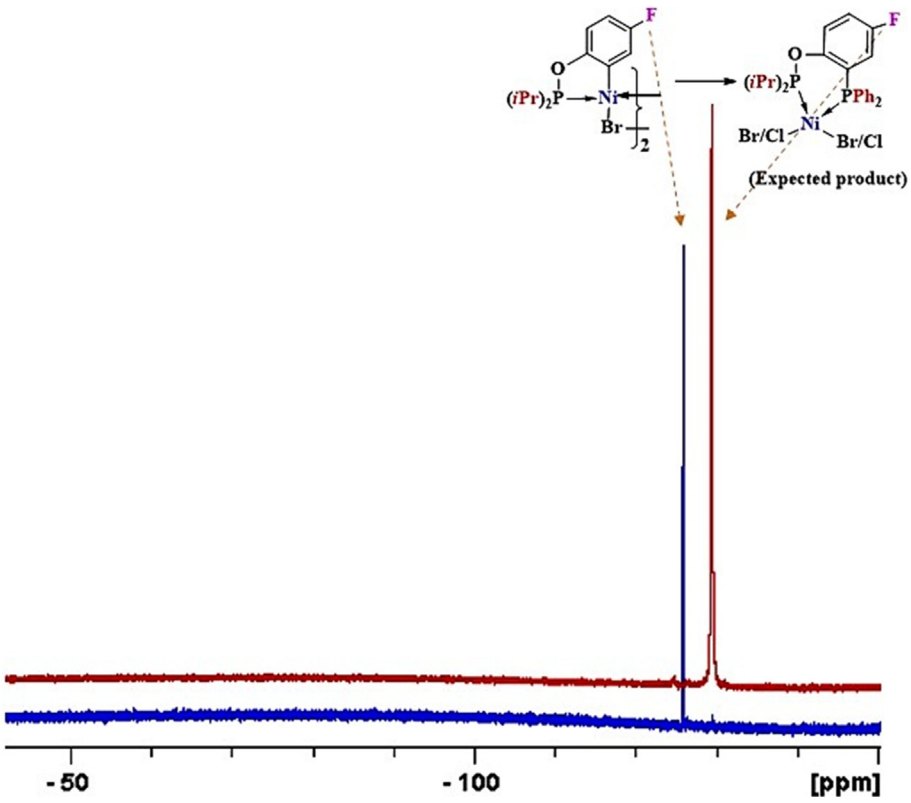



**Fig. 5** $^{19}F$ NMR spectrum of product of insertion of C3 in toluene showing shift of peak during reaction.

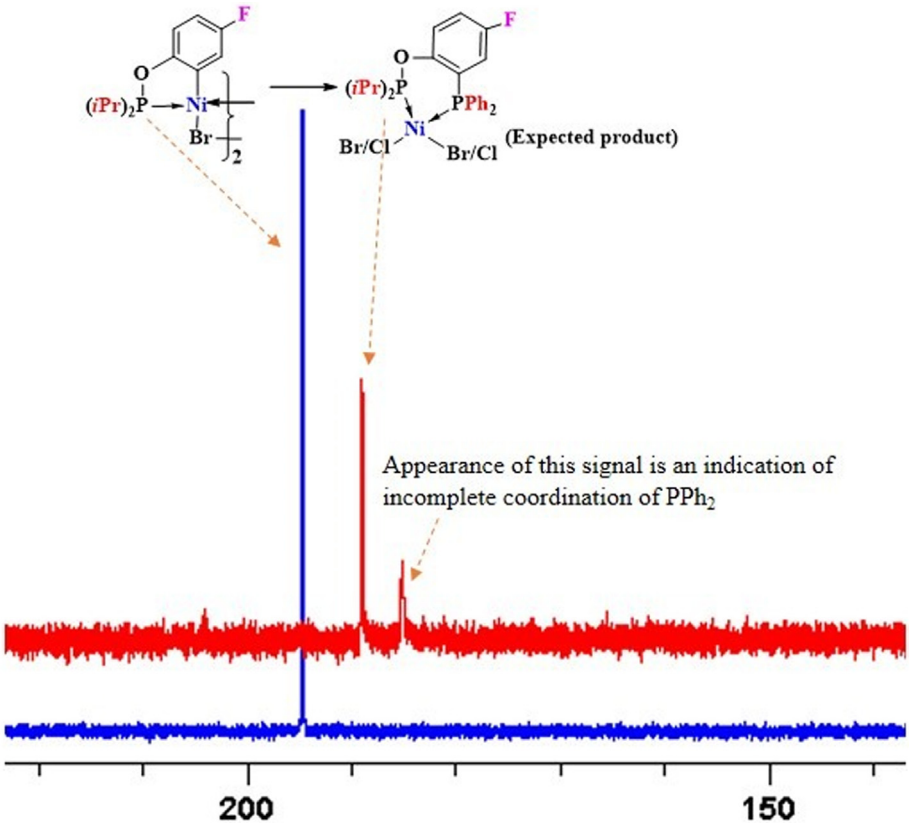



**Fig. 6** $^{31}P$ NMR spectra of product of insertion of C3 in diethyl ether indicating incomplete reaction.

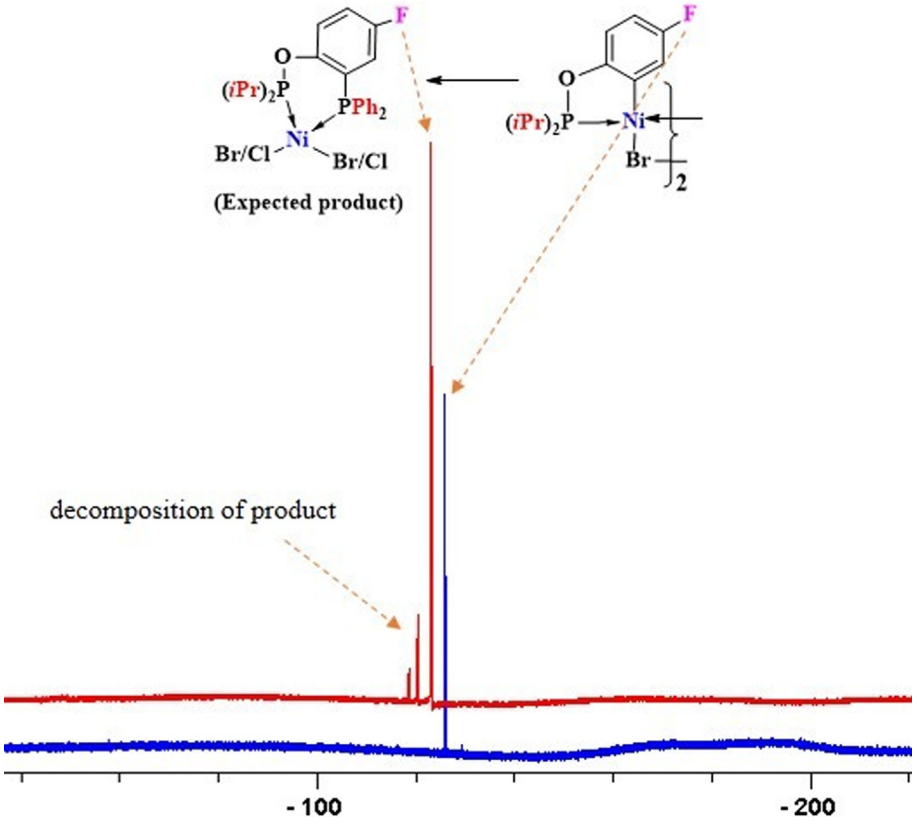



**Fig. 7** $^{19}F$ NMR spectrum of product of insertion of C3 in diethyl ether indicating the decomposition of product.

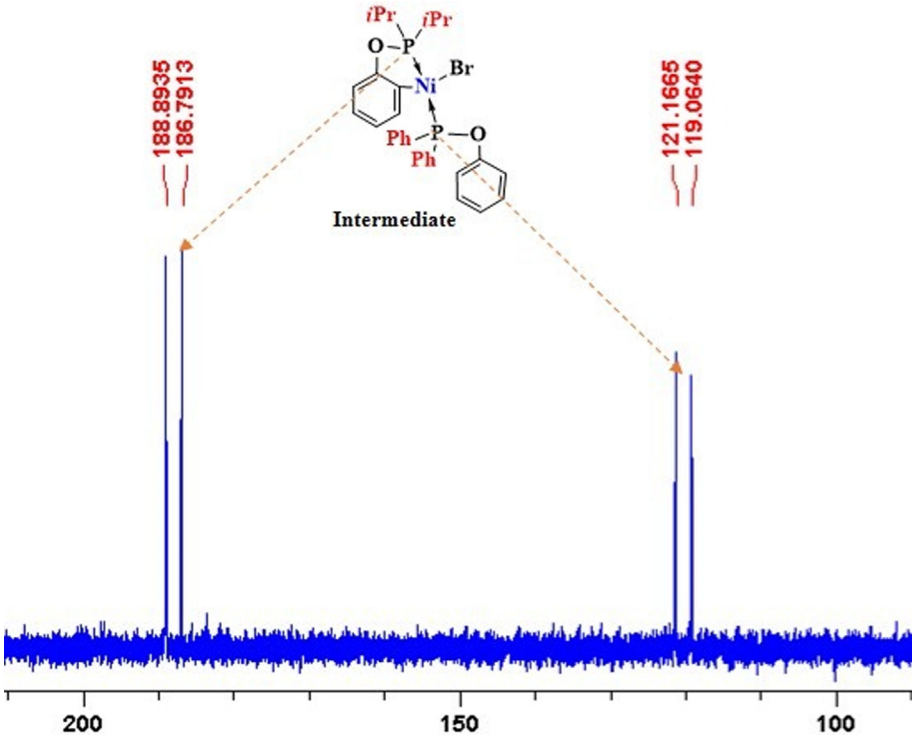



**Fig. 8** $^{31}P$ NMR spectrum of product of insertion of C1 in toluene with aryl-$OPPh_2$ intermediate.

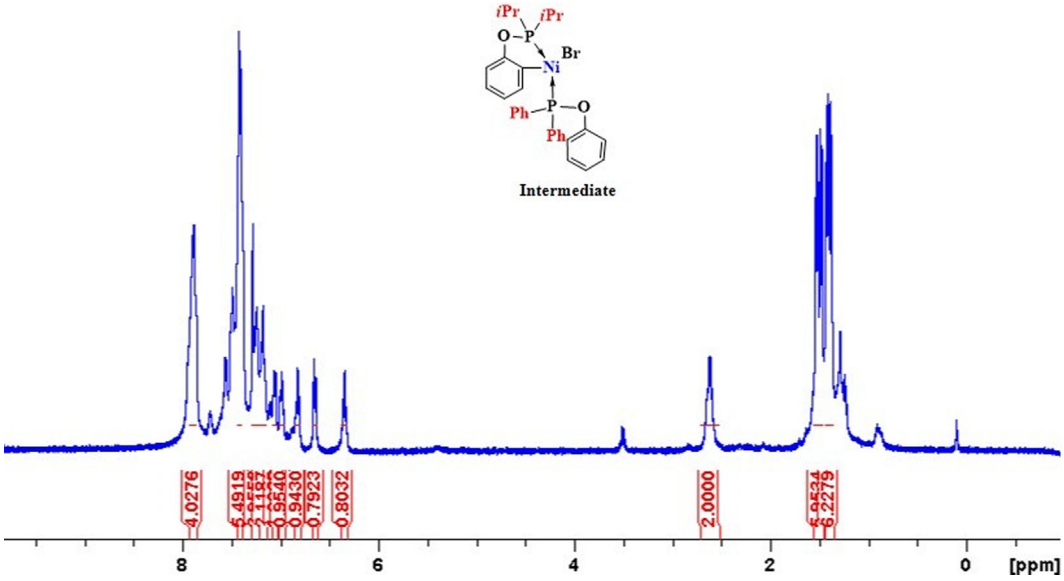



**Fig. 9** $^{1}H$ NMR spectrum of product of insertion of C1 with aryl-$OPPh_2$ in toluene (intermediate).

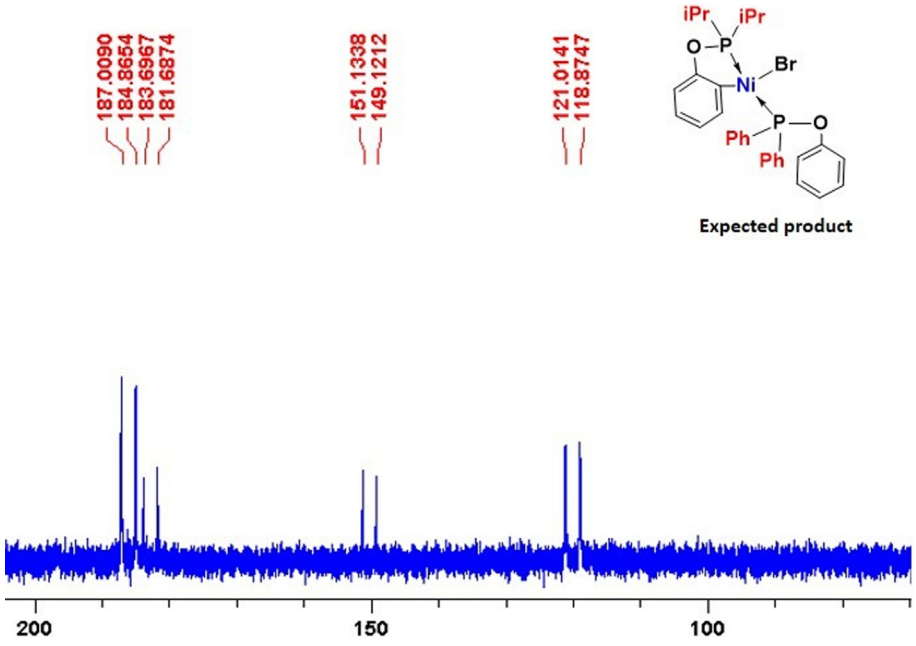



**Fig. 10** $^{31}P$ NMR spectrum of product of insertion of C1 with aryl-$OPPh_2$ in toluene (after 1.5 h).

180 ppm (Fig. 10). One more additional peak at ca. 80 ppm was observed after work up which generated brownish pasty product (H) (Fig. 11) indicating the incomplete reaction in toluene, so next reaction was tried in acetonitrile ($CH_3CN$), but the reaction did not occur in acetonitrile as indicated from appearance of a single peak at ca. 197 ppm corresponding to C1 (initial nickel dimer) and no progress of reaction was observed even after 24 h at high temperature (60 °C), so acetonitrile too was not suitable solvent for the reaction.

New type of phosphine-phosphinite ligands $BrC_6H_3(PPh_2)OP(iPr)_2$ (L7), $C_6H_4(PPh_2)OP(PPh)_2$ (L8), $C_6H_4P(iPr)_2OP(iPr)_2$ (L9), $C_6H_4P(iPr)_2OPPh_2$ (*L*10) and $FC_6H_3PPh_2OPPh_2$ (L11) were synthesized (to understand the potential of phosphine moiety to affect C-Ni bond functionality of dimeric nickel complexes) by derivatization of phenols by binding a $PR_2$ (R = $iPr_2$, aryl) moiety on the oxygen, and a second $PR_2$ moiety on the -ortho position. The second phosphine moiety was introduced by rearrangement of first phosphine moiety bound to oxygen of phenol by precise lithiation with n-butyl Lithium at −78 °C and subsequent reaction with $XPR_2$ to bind at ortho position (Scheme 5). The reactions were monitored by $^{31}P$, $^{1}H$ and $^{19}F$ NMR.

During the synthesis of L7 using ortho substituted phenol, appearance of two strong signals at ca −15.88 and 114.25 ppm

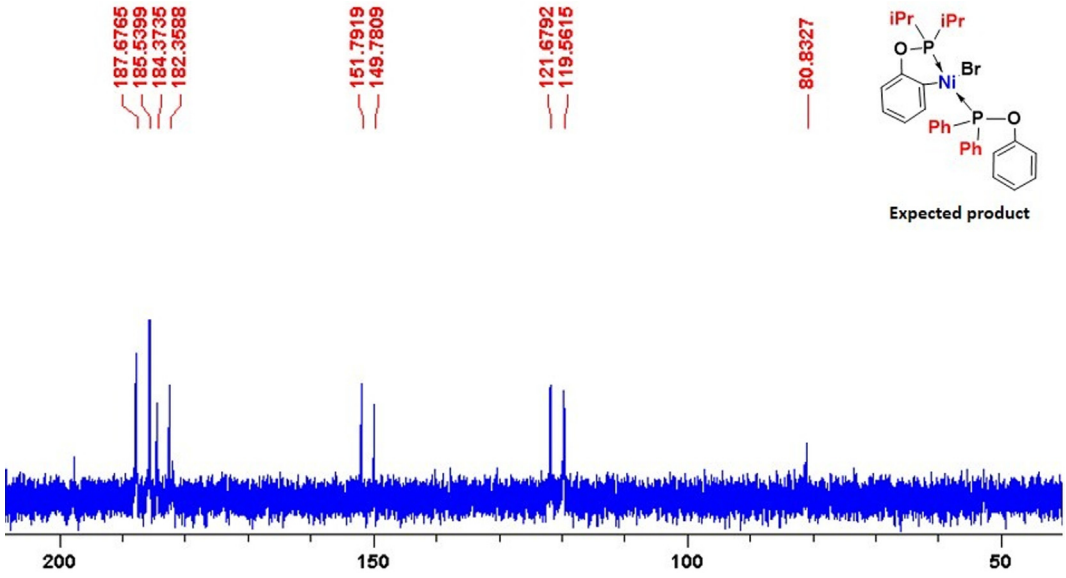
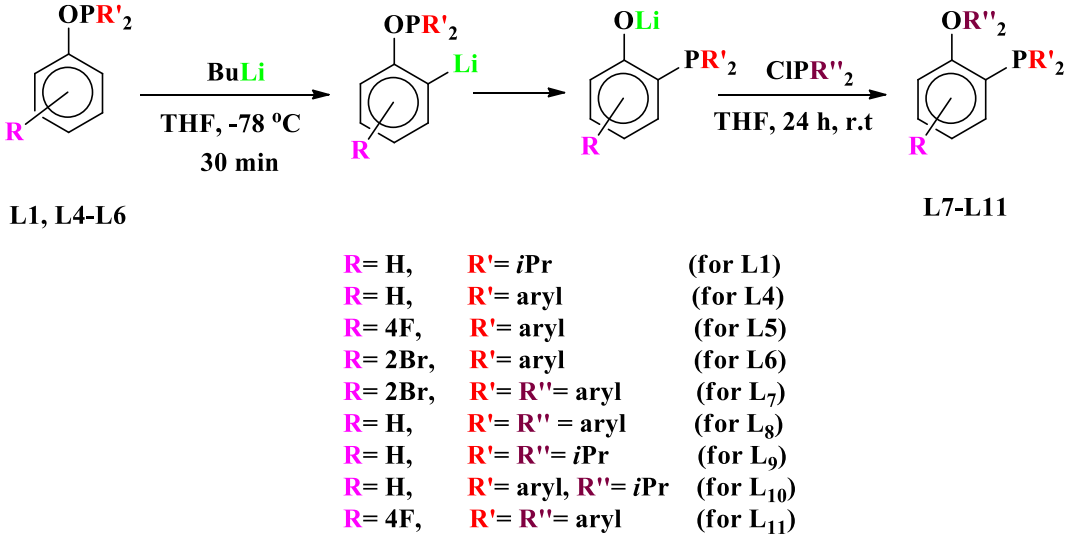



**Fig. 11** $^{31}$P NMR spectrum of product of insertion of C1 with aryl-OPPh$_2$ in toluene (after 24 h).



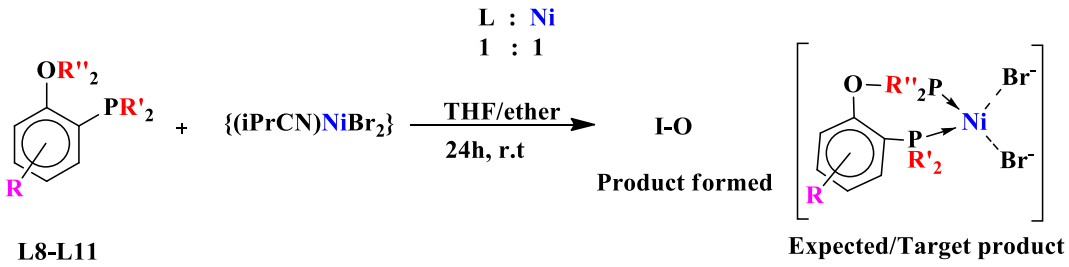

R= H, R'= *i*Pr (for L1)
R= H, R'= aryl (for L4)
R= 4F, R'= aryl (for L5)
R= 2Br, R'= aryl (for L6)
R= 2Br, R'= R''= aryl (for $L_7$)
R= H, R'= R'' = aryl (for $L_8$)
R= H, R'= R''= *i*Pr (for $L_9$)
R= H, R'= aryl, R''= *i*Pr (for $L_{10}$)
R= 4F, R'= R''= aryl (for $L_{11}$)

**Scheme 5** Synthesis of phosphine-phosphinite ligands (L7-L11).

in $^{31}$P NMR spectra indicated the formation of target ligand along with some unreacted material/by-product and it seemed that PPh$_2$ moiety has either replaced proton or bromide ion so there is equal possibility of formation of ligand both ways (Fig. S20). After workup with diethyl ether, the $^{1}$H NMR spectrum of oily product further indicated the presence of some by-product (Fig. S21). So, the attempts to synthesize pure ligands were made either with un-substituted or para substituted phenol as the results indicated that ortho substituition hinders the synthesis of target ligand. In this way, adopting the same protocol, yielded pure target ligands i.e L8,-L11 after workup as indicated from the appearance of two strong signals in their $^{31}$P NMR spectra. The peaks at −13.3, 3.18, −16.21, −15.8 ppm correspond to phosphorous bound to ortho carbon while signals at 113.3, 147.68, 147.53 and 113.6 ppm correspond to phosphorous bound to oxygen of phenol indicating successful synthesis of target phosphine-phosphinite ligands (Figs. S22–25).$^{1}$H and $^{19}$F NMR spectra further confirmed their successful synthesis (Figs. S26–S30).

In order to study the properties and chemical shift values of products of insertion of PR$_2$ moiety in previously synthesized dimeric cyclonickellated complexes C1-C3, attempts were made to synthesize target product by adopting an alternative approach by stirring mixtures of newly synthesized ligands L8-*L*11 and nickel precursor {(i-PrCN)NiBr$_2$}$_n$ in 1:1 ratio in THF or diethyl ether (Scheme 6).

Monitoring the reactions of L8 and L9 in THF by $^{31}$P NMR displayed no signals even after work up which yielded reddish black pasty materials (I, K) (NMR silent). Precipitation of (I) with hexane yielded black powder (J) highly soluble




**Scheme 6** Cyclonickellation of phosphine-phosphinite ligands (L8-L11).

in acetonitrile and toluene, moderately soluble in THF and poorly soluble in ether) but again NMR silent. The reaction of L9 in diethyl ether, yielded blackish thick sticky material (L) which was again NMR silent.

During the reactions of L10 and L11, the products appeared to be unstable and decomposed as indicated from appearance of greenish materials due to $Ni^{+2}/Ni^{o}$ reduction after workup, which were again $^{31}P$ NMR silent. Successive washing of product of L10 with hexane and filtration yielded dark reddish brown material (M) along with decomposed green material. Initially, appearance of two signals at ca. 64.3 ppm and 134.5 ppm indicated the formation of target product (Fig. 12), however after 24 h, some more signals at ca 149.4, 151.4, 180.7, 182.7 ppm in $^{31}P$ NMR spectrum indicated the decomposition of M (Fig. 13).

Reddish black thick sticky material (N) obtained after reaction of L11 was silent to $^{31}P$ NMR, however its $^{19}F$ NMR spectrum displayed a strong signal at ca. −126.8 ppm (Fig. 14) which was an indication of formation of product but later it decomposed and appeared $^{19}F$ NMR silent. All

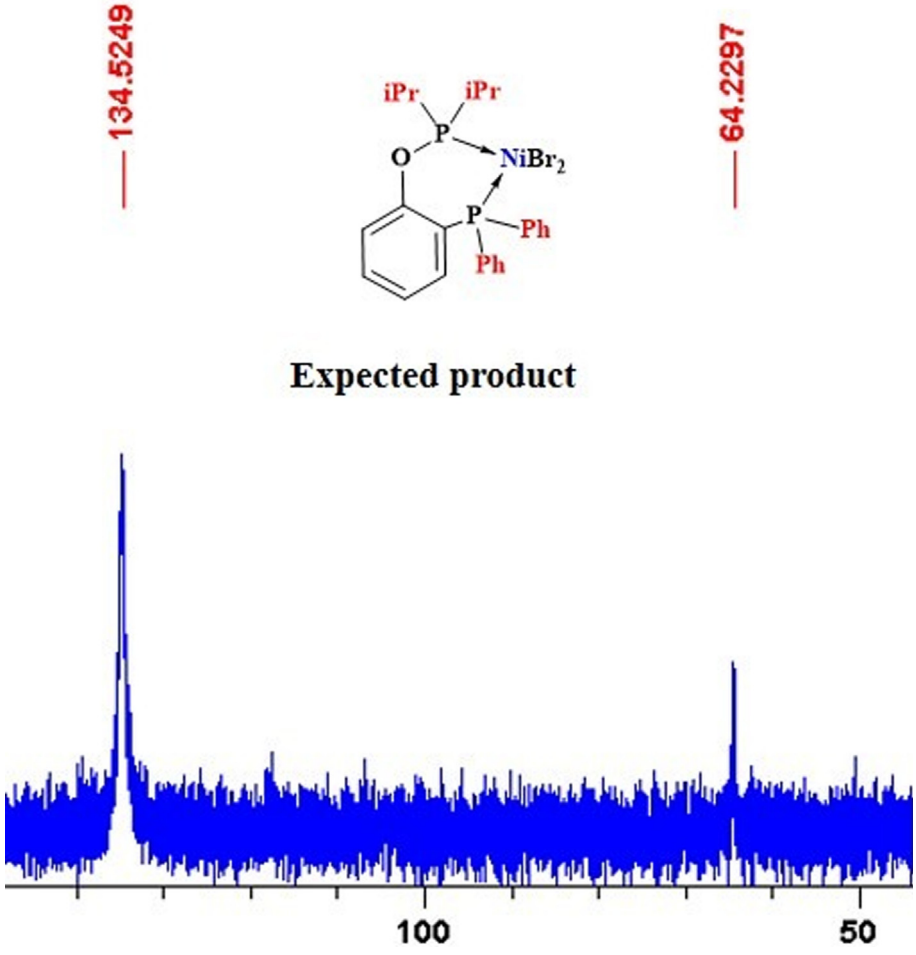



**Fig. 12** $^{31}P$ NMR spectrum of product of L10 (before extraction) showing successful synthesis of target complex.

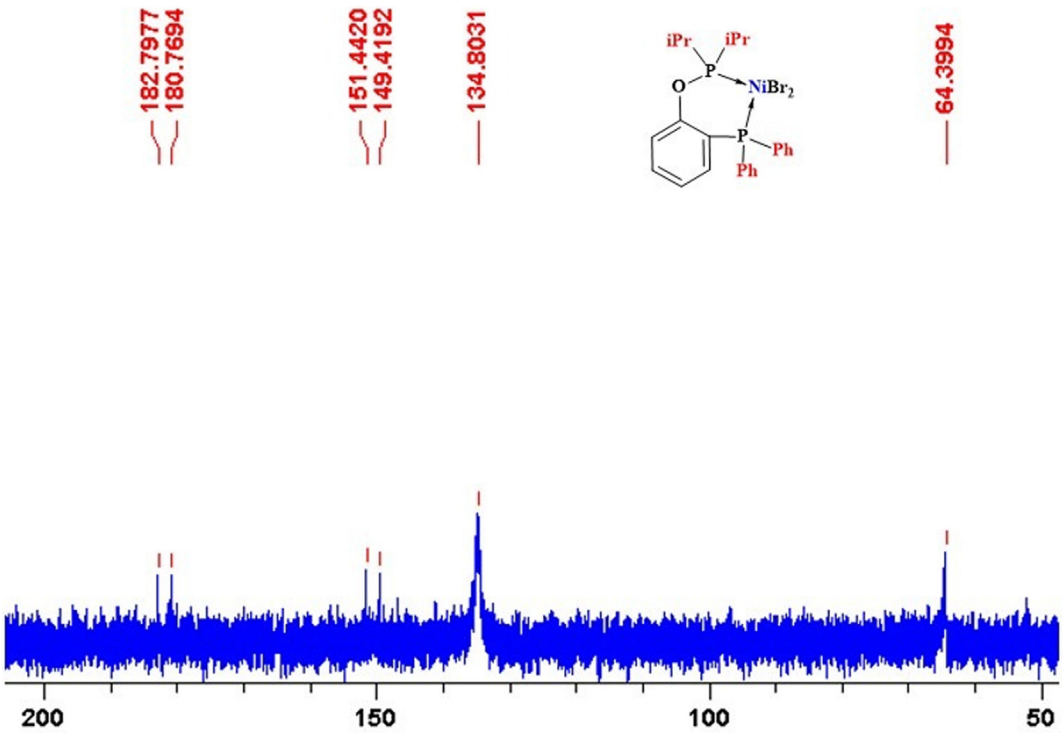



**Fig. 13** $^{31}$P NMR spectrum of product of L10 (after extraction) showing decomposition of complex.

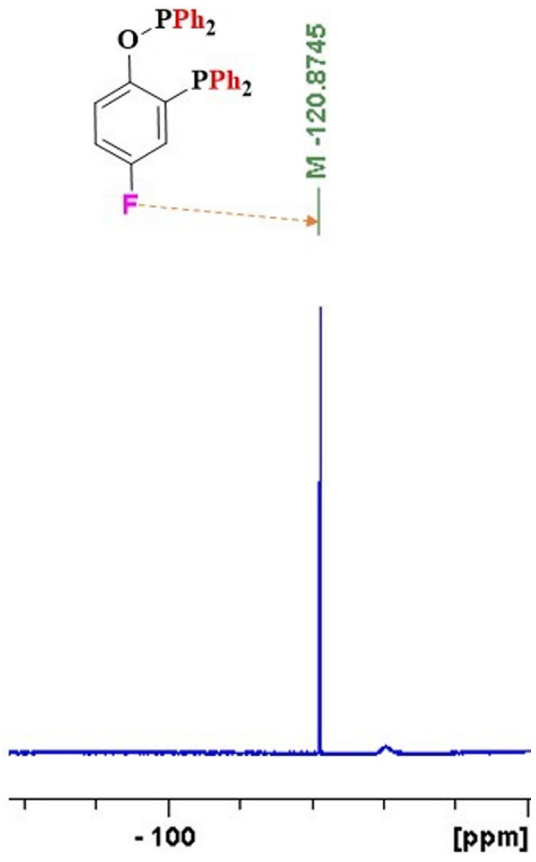



**Fig. 14** $^{19}$F NMR spectrum of product of L11 showing successful synthesis of expected nickel complex.

attempts to crystallize the products in various solvents remained unsuccessful.

## 4. Conclusion

Concludingly, ortho C-H nickellation of the aryl phosphinites i-$Pr_2$P(O-aryl) derived from three different phenols was carried out successfully to generate Br-bridged dimers [{$\kappa^P$, $\kappa^C$-(i-$Pr)_2$PO-aryl}Ni($\mu$-Br)]$_2$. While making attempts to functionalize these dimers by reacting with $R_2PX$, initial shifts of peaks indicated the coordination of $PR_2$ moiety. In order to understand the feasibility of the reaction and to evaluate the properties of final product of insertion, the target complexes were approached by phosphine-phosphinite ligands and then mixing them with nickel precursor to get target monomeric complex. Immediate colour change and appearance of strong signals in $^{31}$P NMR of products indicated the coordination. Due to high instability of product of insertion of cyclonickellated complexes, some new strategy is needed to synthesize target complexes.

## Authors' contributions

The research work discussed in the manuscript was carried out by Aqsa Habib under the supervision of Prof. Davit Zargarian and Dr. Loic Mangin in University de Montreal, Canada during International Research Support Initiative Program (IRSIP) sponsored by Higher Education Commission of Pakistan. The useful suggestions for the interpretation of the results were provided by Sharon Riaz, Ishaq Ahmad, Dure Najaf and Shagufta Kamal during preparation and revision of this manuscript

## Declaration of Competing Interest

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

## Acknowledgements

The authors are thankful to Higher Education Commission (HEC), Pakistan, for financial support in the frame of IRSIP grant for research Vide Letter No. 1-8/HEC/HRD/2017/6940 and NRPU grant Vide Letter No. 9512/Punjab/NRPU/R&D/HEC/2017 for the publication of this manuscript. Aqsa Habib also acknowledges the support and guidance of Prof. Davit Zargarian and Dr. Loic Mangin, University de Montreal, Canada, for facilitating in research work during IRSIP and sharing useful suggestions to compile the results and write this manuscript.

## Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jscs.2020.101178.

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