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Chiral multidentate oxazoline ligands based on cyclophosphazene cores: Synthesis, characterization and complexation studies

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Chiral oxazoline based bi and hexadentate ligands built on cyclophosphazene cores have been synthesized and characterized. $(NPPh_2)_2[NP(m\text{-}OC_6H_4C(O)OCH_3)_2]$ (**1**) was prepared by the reaction of *gem*-$(NPPh_2)_2(NPCl_2)$ with methyl-3-hydroxy benzoate in presence of Cs_2CO_3. Compound **1** was converted to the dicarboxylic acid $(NPPh_2)_2[NP(m\text{-}OC_6H_4C(O)OH)_2]$ (**2**) using base promoted hydrolysis with KO(t-Bu). The dicarboxylic acid **2** on reaction with oxalyl chloride followed by (*S*)-(+)-2-amino-3-methyl-1-butanol, triethylamine and mesyl chloride was converted to the C_2- symmetric phosphazene based chiral bisoxazoline ligand $(NPPh_2)_2[NP\{m\text{-}OC_6H_4(4\text{-}iPr\text{-}2\text{-}Ox)\}_2]$ **(3)** (Ox = oxazolinyl). A similar C_2-symmetric bisoxazoline derivative having oxazoline group attached to the para position of the phenyl ring was also synthesized starting from $(NPPh_2)_2[NP(p\text{-}OC_6H_4C(O)OCH_3)_2]$ (**4**) which was first converted to the dicarboxylic acid $(NPPh_2)_2[NP(p\text{-}OC_6H_4C(O)OH)_2]$ (**5**) and finally to $(NPPh_2)_2[NP\{p\text{-}OC_6H_4(4\text{-}iPr\text{-}2\text{-}Ox)\}_2]$ (**6**) and $(NPPh_2)_2[NP\{p\text{-}OC_6H_4(4\text{-}Ph\text{-}2\text{-}Ox)\}_2]$ (**7**) under similar reaction conditions. Reaction of **6** with $Pd(OAc)_2$ in acetic acid at room temperature and with $PdCl_2(C_6H_5CN)_2$ in

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†Electronic supplementary information (ESI) available: CCDC reference numbers 1007180-1007186. Selected bond distances and angles of compounds **1**, **2**, **4**, **5**, **7**, **14** and **18**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

refluxing benzene resulted in chiral palladium complexes $Pd(OAc)_2(NPPh_2)_2[NP\{p\text{-}OC_6H_4(4\text{-}iPr\text{-}2\text{-}Ox)\}_2]$ (**8**) and $PdCl_2(NPPh_2)_2[NP\{p\text{-}OC_6H_4(4\text{-}iPr\text{-}2\text{-}Ox)\}_2]$ **(9)**, respectively. The utility of these palladium complexes as chiral catalysts for the asymmetric rearrangement of trichloroacetimidates to trichloroacetamides has been explored. Hexa(methylbenzoate) derivative of cyclophosphazene $[PN(OC_6H_4COOCH_3)_2]_3$ (**10**) on treatment with KO(t-Bu) and H_2O gave the hexacarboxylic acid derivative $[PN(OC_6H_4COOH)_2]_3$ (**11**), which on treatment with oxalyl chloride followed by (*S*)-(+)-2-amino-3-methyl-1-butanol/(*S*)-(+)-2-phenylglycinol, triethylamine and mesyl chloride was converted to the C_3-symmetric cyclophosphazene based chiral hexaoxazoline ligands $[PN\{OC_6H_4(4\text{-}i\text{Pr-}2\text{-}Ox)\}_2]_3$ **(12)**, and $[PN\{OC_6H_4(4\text{-Ph-}2\text{-}Ox)\}_2]_3$ **(13**). Bis(Phebox) derivative of the cyclophosphazene was prepared starting from $(NPPh_2)_2[NP\{OC_6H_3(COOCH_3)_2\}_2]$ **(14)**, by the reaction of *gem*-$Ph_4P_3N_3Cl_2$ with dimethyl 5-hydroxyisophthalate in presence of Cs_2CO_3. Compound **14** was converted to the tetracarboxylic acid $(NPPh_2)_2[NP\{OC_6H_3(COOH)_2\}_2]$ (**15**) using base promoted hydrolysis with KO(t-Bu). The tetracarboxylic acid **15** on reaction with oxalyl chloride followed by (*S*)-(+)-2-amino-3-methyl-1-butanol/(*S*)-(+)-2-phenylglycinol, triethylamine and mesyl chloride was converted to the bis(Phebox) substituted tetraphenylcyclophosphazene derivatives $(NPPh_2)_2[NP\{OC_6H_3(4\text{-}iPr\text{-}2\text{-}Ox)_2\}_2]$ **(16)/** $(NPPh_2)_2[NP\{OC_6H_3(4\text{-Ph-}2\text{-}Ox)_2\}_2]$ **(17)**. A similar tetra(phebox) derivative was synthesized from $(NPPh_2)[NP\{OC_6H_3(COOCH_3)_2\}_2]_2$ **(18)** which was first converted to $(NPPh_2)[NP\{OC_6H_3(COOH)_2\}_2]_2$ **(19)** and further converted to the tetra(phebox) derivative $(NPPh_2)$ $[NP\{OC_6H_3(4\text{-Ph-}2\text{-}Ox)_2\}_2]_2$ **(20)**. All new compounds were characterized by IR, NMR [^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$] and HRMS studies. Compounds **1**, **2**, **4**, **5**, **7**, **14** and **18** have also been structurally characterized.

KEYWORDS: cyclophosphazenes, multidentate, oxazoline, chiral, palladium, Phebox.

Introduction

Six membered cyclophosphazene rings provide an elegant platform for building multidentate ligands having a stable core with or without the ring nitrogen's providing additional ligating sites.[1-3] The out of plane directionality of the cyclophosphazene ring substituents has also assisted in the design of a range of stable dendrimers[4] and multiporphyrin assemblies.[5] It is surprising to note that in spite of a wide range of possibilities, very few phosphazene based multidentate ligands are known in the field of asymmetric catalysis.[6,7] Various groups have tried to explore the chirality possible on the phosphazene ring by selective ring substitution studies focusing on the stereogenic property of tetracoordinated phosphorus atoms in cyclophosphazenes, following up the same by changes observed in the ^{31}P NMR spectra and by using HPLC techniques.[8] However, from an applied perspective, except a few which have multi-ligating sites and clearly display specific rotation of plane polarized light, most of these derivatives do not show promise as chiral ligands in asymmetric catalysis. In contrast, cyclophosphazene based dendrimers which contains chiral ferrocene based Josiphos units at the periphery have been found to be useful ligands in Rh-catalyzed asymmetric hydrogenation of dimethyl itaconate.[7]

Compounds containing chiral 2-oxazoline rings are widely used in asymmetric catalysis due to their ease of synthesis and effectiveness for diverse type of catalytic transformations.[9] Bis(oxazoline) ligands are among the most valuable class of oxazoline ligands from their ability to coordinate with a wide range of metals and due to the presence of C_2- axis in the resulting complexes, which is proven to be beneficial in controlling the enantioselectivity by reduction of possible transition states having square planar geometry.[10] Reports are available on trisoxazoline derived metal complexes being used as catalyst for Friedel-Crafts, Kinugasa 1,3-dipolar cycloaddition, cyclopropanation, Diels-Alder reaction and also for chiral recognition with good

selectivity.[11] It has been observed that in general, multi-oxazoline ligand bound metal complexes have advantages such as better catalyst stability, tunable chiral space and increased ligand diversity resulting in better enantifocal control, broader substrate scope, as well as better enantioselectivity under milder reaction conditions.[12] Although a few examples of mono, bis and hexa-oxazoline substituted cyclophosphazenes are known in the literature,[13] they are not suitable for asymmetric catalysis as most of them are achiral and those having chiral oxazoline groups are having the chiral centre adjacent to the oxygen atom of the oxazoline ring. It is known that oxazoline rings having chiral centre adjacent to its nitrogen atom are preferred in the asymmetric catalysis as the metal is held closer to the chiral centres strongly influencing the enantioselectivity.[9] Herein we report the first examples of chiral bis and hexa-oxazoline as well as multiphebox derivatives of cyclophosphazenes having the chiral center close to the nitrogen atom of the oxazoline ring. We have also explored the complexation behavior of few of these ligands with $Pd(OAc)_2$ and $PdCl_2(C_6H_5CN)_2$, and explored their possible utility in asymmetric catalysis. The new multi-oxazoline ligands having a cyclophosphazene core show promise for catalyzing many organic transformations and for chiral recognition.

Results and Discussion

Hexachlorocyclotriphosphazene contains both a C_3- axis (passing through the center of the P_3N_3 ring perpendicular to the ring plane) and three C_2- axes (passing through the ring phosphorus atom and its opposite ring nitrogen atom) (Figure 1). Therefore the ring can act as an excellent precursor for preparing multioxazoline ligands having C_2 and C_3 axis, which can play a critical role in determining the enantioselectivity of a catalytic reaction.

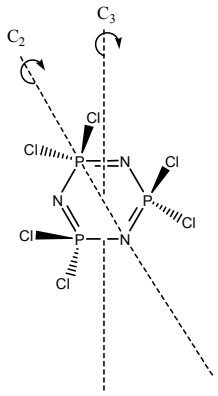
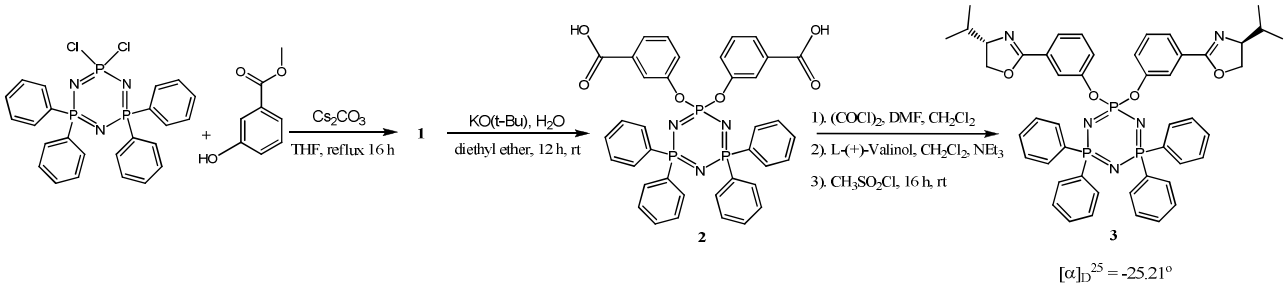


Fig. 1 C_3- and C_2- axis present in the cyclophosphazene ring.

Various ester derivatives of cyclophosphazenes ($P_3N_3Cl_6$, *gem*-$Ph_4P_3N_3Cl_2$ and *gem*-$Ph_2P_3N_3Cl_4$) were prepared by the reactions of their P-Cl bonds with methyl-3-hydroxy benzoate/methyl-4-hydroxy benzoate/dimethyl 5-hydroxyisophthalate in the presence of Cs_2CO_3 in the molar ratio 1:1:2. These multiester derivatives of cyclophosphazenes were converted to the corresponding carboxylic acid derivatives by using base promoted hydrolysis with KO(t-Bu) at room temperature.[14] Acid derivatives on treatment with oxalyl chloride followed by reaction with chiral 2-amino alcohols, trimethylamine and mesyl chloride were converted to the chiral oxazoline derivatives of the cyclophosphazenes. Using this approach, we have prepared chiral bisoxazoline derivatives of cyclophosphazenes having C_2 symmetry, hexaoxazoline derivatives of cyclophosphazene having C_3 axis and ligands having chiral multiphebox units substituted on the phosphazene scaffold.

The initial reactions were carried out on *gem*-$Ph_4N_3P_3Cl_2$ which unlike $N_3P_3Cl_6$, is a much simpler system with only two reactive P-Cl bonds available for substitution reactions and the rigidity provided by the PPh_2 moieties often help in realizing crystalline products. Also, it was felt that in asymmetric catalysis the steric interactions between the substrate and the tetraphenyl phosphazene unit is likely to favor the enantiomer leading to the major product similar to sterically bulky chiral

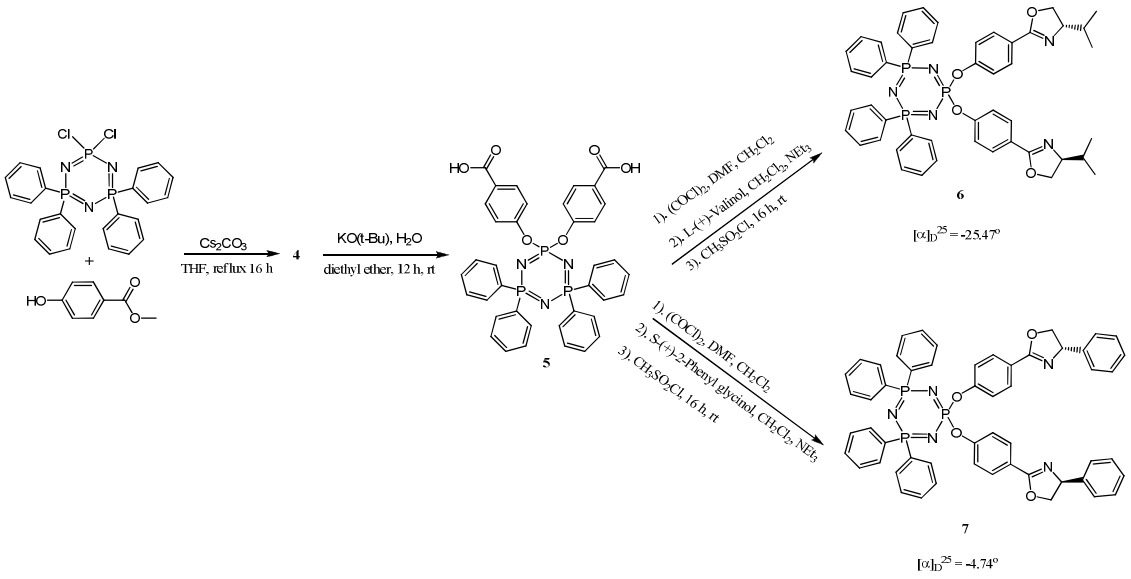
lignds based on sandwich compounds such as $CpFeC_5Ph_5$ and $CpCoC_4Ph_4$.[15] Diester **1** was prepared by condensation of methyl 3-hydroxy benzoate and *gem*-$Ph_4P_3N_3Cl_2$ in the presence of cesium carbonate. Compound **1** after conversion to the dicarboxylic acid **2** was reacted with oxalyl chloride, followed by (*S*)-(+)-2-amino-3-methyl-1-butanol [L-valinol], triethylamine and mesyl chloride to convert it to the novel phosphazene based bisoxazoline derived bidentate chiral ligand **3** ($[\alpha]_D^{25}$ = -25.21°) (Scheme 1). An attempted reaction of **3** with $Pd(OAc)_2$ in 1:1 molar ratio resulted in a highly viscous residue which could not be purified or characterized.



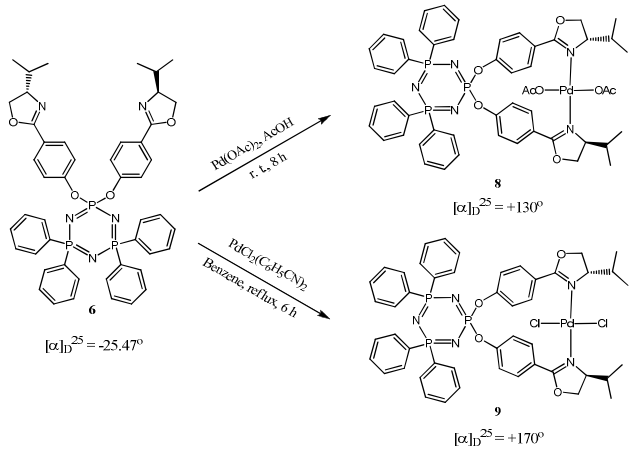
Scheme 1

Difficulty in obtaining a monomeric palladium complex of **3** prompted us to change the position of oxazoline group on the OPh group attached to phosphazene ring. Compound **6** having oxazoline groups attached to the para position of the phenyl group was prepared starting from methyl 4-hydroxybenzoate, using reaction conditions used for the synthesis of **3** (Scheme 2). Unlike **3**, compound **6** ($[\alpha]_D^{25}$ = -25.47°) when reacted with $Pd(OAc)_2$ at room temperature and with $PdCl_2(C_6H_5CN)_2$ under refluxing benzene conditions resulted in the formation of chiral palladium complexes **8** ($[\alpha]_D^{25}$ = +130°) and **9** ($[\alpha]_D^{25}$ = +170°) (Scheme 3). Compounds **8** and **9** were obtained as pale yellow colored solids whereas compound **6** was a colorless viscous liquid. Although attempts to crystallize compounds **8** and **9** were unsuccessful, their identity was conclusively proved by HRMS, CHN analysis, optical rotation and NMR studies. Another chiral

bis oxazoline ligand **7** ($[\alpha]_D^{25}$ = -4.74°), analogous to **6,** but having phenyl oxazoline ring instead of isopropyl oxazoline ring was prepared by replacing (*S*)-(+)-2-amino-3-methyl-1-butanol with (*S*)-(+)-2-phenylglycinol in the procedure used for the preparation of **6** (Scheme 2). Unlike **6**, compound **7** was obtained as a crystalline solid which was structurally characterized by X-ray diffraction studies and is the first example of a structurally characterized oxazoline derivative of cyclophosphazene. However, unlike **6**, an attempted reaction of **7** with $Pd(OAc)_2$ in 1:1 molar ratio resulted in an insoluble product.



Scheme 2

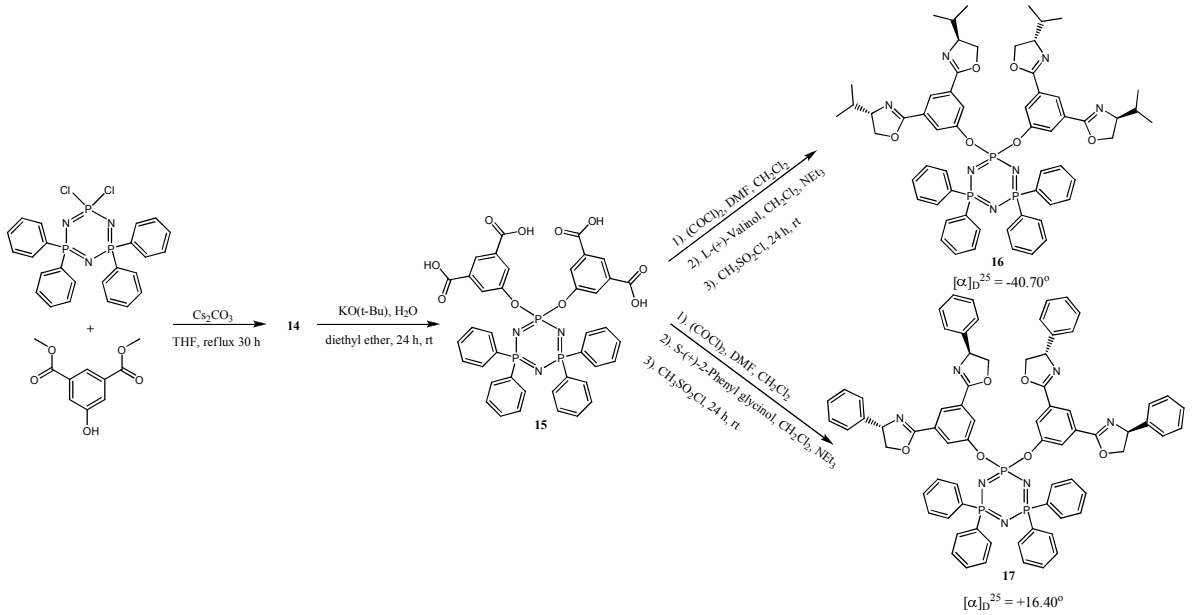


Scheme 3

After successfully characterizing the palladium complexes of **6**, we explored the possibility of preparing the hexa oxazoline derivatives of cyclophosphazenes. Starting from methyl 4-hydroxy benzoate and $N_3P_3Cl_6$ compound **10** was obtained, which was hydrolyzed to give the hexacarboxylic acid derivative **11**. Compound **11** was converted to the cyclophosphazene based hexaoxazoline ligands, **12** ($[\alpha]_D^{25}$ = -18.75°) and **13** ($[\alpha]_D^{25}$ = +4.30°) using reagents and reaction conditions similar to those used for compounds **6** and **7**, respectively (Scheme A, supplementary information). Trisoxazoline (having C_3 axis) appended on a benzene backbone have been investigated for molecular recognition and have shown promising selectivity for the recognition of ammonium, alkylammonium and sugar species, including examples of chiral recognition.[16] Our hexaoxazoline derivatives shows potential for similar type of molecular recognition.

Bis(oxazoline)phenyl (Phebox) are an important class of oxazoline ligands having two oxazoline rings attached to a phenyl ring and they are widely used as ligands in many asymmetric catalytic reactions.[17] We were interested in exploring the possibility of having multi(phebox) derivatives of cyclophosphazenes. Compounds **14** and **18** were prepared by reaction of dimethyl 5-hydroxyisophthalate with *gem*-$Ph_4P_3N_3Cl_2$ and *gem*-$Ph_2P_3N_3Cl_4$, respectively in the presence of Cs_2CO_3. These ester derivatives were converted to the tetra and octacarboxylic acid derivatives **15** and **19** by base promoted hydrolysis with KO(t-Bu) at room temperature. These carboxylic acid derivatives after reaction with oxalyl chloride, followed by (*S*)-(+)-2-amino-3-methyl-1-butanol/(*S*)-(+)-2-phenylglycinol, triethylamine and mesyl chloride were converted to the novel phosphazene based bis(phebox) compounds **16** ($[\alpha]_D^{25}$ = -40.70°) and **17** ($[\alpha]_D^{25}$ = +16.40°) (Scheme 4) and the tetrakis(phebox) derivative [compound **20** ($[\alpha]_D^{25}$

= +21.75°)] (Scheme B, supplementary information). Compounds **16**, **17** and **20** are the first examples of phebox derived cyclophosphazenes.



Scheme 4

Spectral Studies on compounds 1-20

Compounds **1-20** have been characterized by IR, NMR (^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$) and HRMS studies. ^{31}P NMR spectra of compounds **1 - 9** indicated a simple doublet for the PPh_2 moiety and a triplet for the $P(OPh)_2$ moiety. Signals corresponding to the PPh_2 moiety were observed in the range of 19.85- 21.00 ppm for compounds **1 – 9.** For the $P(OPh)_2$ moiety, they were observed in the range of 3.46-3.82 ppm for compounds **1 - 3** having meta substitution on the OPh ring, and in the range of 2.01- 2.77 ppm for the compounds **4 - 9** having para substitution on the OPh ring. ^{31}P NMR spectra of hexa substituted compounds **10 - 13** gave a singlet in the region 7.55 - 8.17 ppm as all three phosphorus atoms were in the same environment. ^{31}P NMR spectra of compounds **14-17**, which are derivatives of *gem*-$(NPPh_2)_2(NPR_2)$ gave a doublet corresponding to PPh_2 moiety in the range of 20.40 - 21.22 ppm and a triplet corresponding to $P(OPh)_2$ moiety

in the range of 3.34 - 4.22 ppm, whereas compounds **18** - **20**, which are derivatives of *gem*-$(NPPh_2)(NPR_2)_2$ gave a triplet corresponding to PPh_2 moiety in the range 22.60 - 22.88 ppm and a doublet corresponding to $P(OPh)_2$ moiety in the range of 7.15 - 7.89 ppm.

In the ^{1}H NMR of compounds **3**, **6** and **12**, having isopropyl derived oxazoline rings, signals corresponding to CH proton of oxazoline ring were observed in the range of 4.29 - 4.38 ppm, which were slightly deshielded compared to the same signal of compounds **7** and **13** (4.22 -4.28 ppm), having phenyl oxazoline rings. In contrast, signals corresponding to the CH_2 protons of oxazoline ring in compounds **3**, **6** and **12** were in the range 4.04 - 4.19 ppm, which were significantly deshielded compared to the same signals of compounds **7** and **13** (4.73 - 5.38 ppm). ^{13}C NMR δ values for the carbonyl group of ester derivatives were observed in the range of 164.92 - 166.44 ppm and for the carboxylic acid derivatives, they were in the range 165.50 - 167.66 ppm. Signal corresponding to the C=N unit of oxazoline, were observed at 161.97 - 163.00 ppm for isopropyl oxazoline compounds **3**, **6**, **12** and **16** and at 163.39 - 164.20 ppm for the phenyl oxazoline compounds **7**, **13**, **17** and **20**.

^{1}H and ^{13}C NMR of compound **6** showed interesting changes after complexation with palladium metal to give complexes **8** and **9**. Noticeable deshielding (from 1.90 ppm to ~ 3.02 ppm) in the ^{1}H NMR signals of the CH units of the oxazoline bound isopropyl groups were observed, when the ligand **6** was found to form complexes **8** and **9** with palladium (Figure A, supplementary information). Signals corresponding to CH and CH_2 units of the oxazoline ring were also found to be deshielded after complexation. On formation of the palladium complexes **8** and **9**, four of the phenyl protons were found to be significantly deshielded from 7.57 - 7.67 ppm in compound **6** to 8.26 - 8.34 ppm in compounds **8** and **9**, suggesting a possible C-H···Pd anagostic interaction between ortho phenyl protons and palladium atom.[18] ^{1}H NMR spectra of **8**

showed the presence of acetate group at δ value 1.70 ppm whose integration corresponds to that of six protons (Figure A, supplementary information). This sharp singlet for the acetate CH_3 proton at 1.70 ppm indicated complex **8** to be a *trans* palladium complex as a *cis* isomer is expected to give two signals for two acetate groups.[18a] ^{13}C NMR of **8** also showed the presence of acetate group at δ 176.48 (for C=O group) and 21.86 ppm (for OCH_3 group). ^{13}C NMR signal corresponding to oxazoline, C=N group was at 162.73 ppm in **6**, which get shifted downfield to 166.56 and 166.83 ppm for compounds **8** and **9**, respectively.

X-ray crystal structures of compounds 1, **2**, **4**, **5**, **7**, **14 and 18.**

The crystal structures of compounds **1**, **7** and **14** are given in Figures 2-4, and those of compounds **2**, **4**, **5** and **18** are given in the supplementary information. Crystallographic data and data collection parameters are given in Table 1 and bond lengths and bond angles are given in the supporting information. The phosphazene rings were found to be almost planar in compounds **4, 7** and **14** as the phosphorus atom and the opposite ring nitrogen atom were not found to deviate significantly from the mean plane defined by the other four atoms of the heterocycle. In contrast, the conformation of the P_3N_3 rings of **1** and **5** were more towards a half chair because in compound **1**, the P3 and N1 atoms were deviating from the mean plane defined by the other four atoms by 0.088(1) and 0.219(3) Å, respectively and in compound **5**, the P2 and N3 atoms were deviating from the mean plane defined by the other four atoms by 0.029(1) and 0.123(2) Å, respectively. In compound **2**, the phosphazene ring was found to be in a boat conformation because P1 and N2 atoms were deviating from the mean plane defined by other four atoms by -0.194(2) and -0.141(4) Å, respectively. P_3N_3 ring of compound **18** was also more like half chair

as P2 and N3 atoms were deviating from the mean plane defined by other four atoms by 0.243(1) and -0.067(2) Å, respectively.

In compounds **1**, **2**, **4**, **5** and **7**, the O-P-O angles were found to vary from 91.6(1) to 98.2(1)º and the P-O-C angles were found to be in the range of 117.7(5) to 125.7(2)º, indicating the flexibility of substitutents attached through the P-O bonds. In contrast, the C-P-C angles were found to be in the range of 103.8(4) to 107.3(2)º, confirming the more rigid nature of PPh_2 moieties. Angle between the mean plane through the P_3N_3 ring and the mean plane through the phenyl rings attached through the P-O bonds were found to be in the range of 13.8(1) to 89.3(6)º. P-O bond lengths were found to be in the range of 1.585(3) to 1.626(2) Å. Carbonyl group bond lenght (C=O) was found to be in the range of 1.184(5) - 1.208(3) Å, for the ester derivtives (compounds **1**, **4**, **14** and **18**) and 1.218(7) - 1.258(4) Å, for the acid derivatives (compounds **2** and **4**). In compound **7**, the oxazoline ring C=N bond length was in the range of 1.236(2) - 1.268(2) Å.

Dicarboxylic acids **2** and **5**, showed interesting intermolecular hydrogen bonding in their packing diagram. One of the carboxylic acid groups of **2** was involved in simple intermolecular hydrogen bonding with a carboxylic acid unit of another molecule resulting in linear chains, whereas carbonyl group of other carboxylic acid group was forming hydrogen bonding with the water molecule present in the crystal lattice and the hydroxyl group of same carboxylic acid was forming hydrogen bond with one of the phosphazene ring nitrogen atom, resulting in a two dimensional network (Figure 5). Unlike the hydrogen bonding in **2** which resulted in a two dimensional network, compound **5** was forming linear one dimensional hydrogen bonding network as both the carboxylic acid groups were involved in simple intermolecular hydrogen bonding with carboxylic acid groups of another molecule. Also, hydrogen bonding was

observed between the phosphazene ring nitrogen atom and hydroxyl group of methanol molecules present in the crystal lattice of **5** (Figure F, supplementary information).

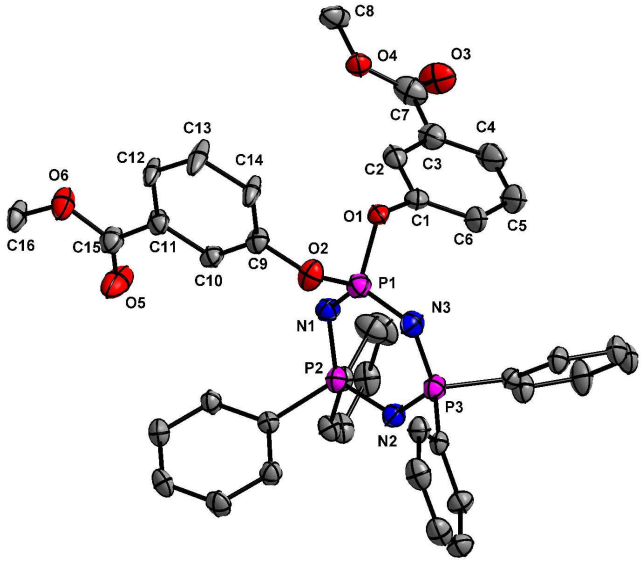


Fig. 2 ORTEP diagram of compound **1** with thermal ellipsoids at the 30% probability level (data was collected at 298 K).

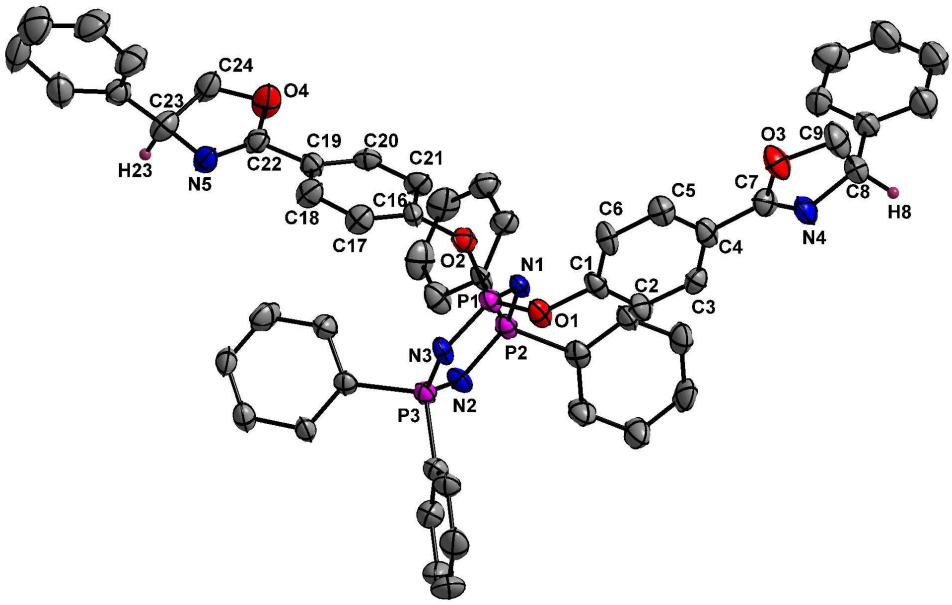


Fig. 3 ORTEP diagram of compound **7** with thermal ellipsoids at the 30% probability level (data was collected at 298 K).

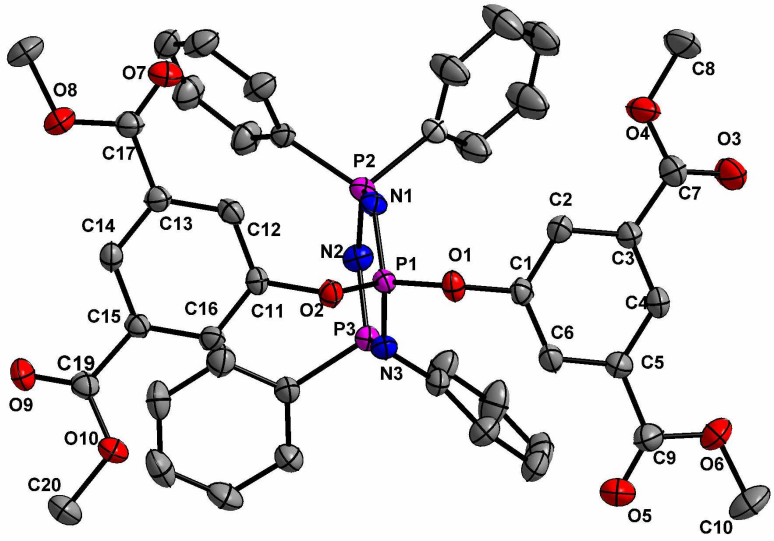


Fig. 4 ORTEP diagram of compound **14** with thermal ellipsoids at the 30% probability level (data was collected at 298 K).

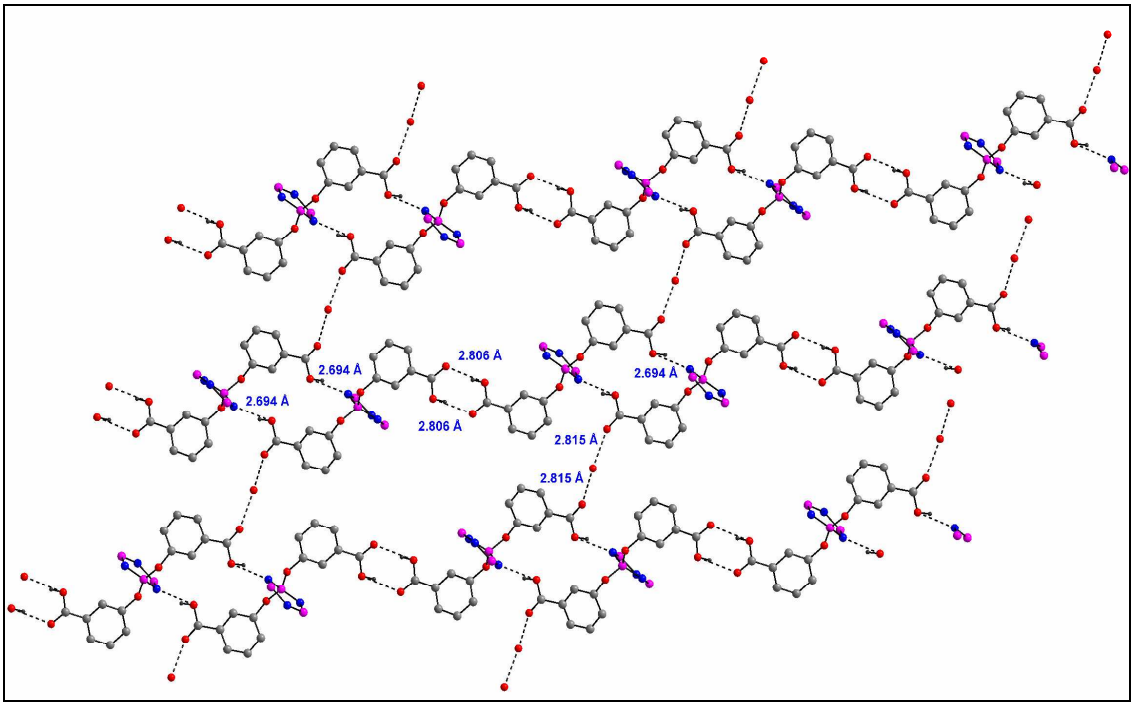


Fig. 5 Crystal structure of compound **2** showing intermolecular H-bonding (Phenyl groups of the PPh_2 moiety are omitted for clarity).

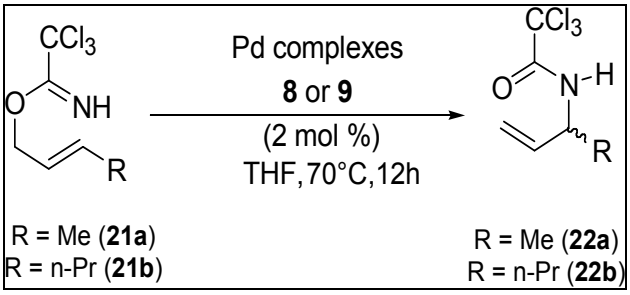
Table 1. X- ray crystal structure parameters of compounds **1**, **2**, **4**, **5**, **7**, **14** and **18**.

Parameters	**1**	**2**	**4**	**5**	**7**	**14**	**18**
Formula	$C_{40}H_{34}N_3O_6P_3$	$2(C_{38}H_{30}N_3O_6P_3)$, O	$C_{40}H_{34}N_3O_6P_3$	$C_{38}H_{30}N_3O_6P_3$, CH_4O	$C_{54}H_{44}N_5O_4P_3$	$C_{44}H_{38}N_3O_{10}P_3$	$C_{52}H_{46}N_3O_{20}P_3$
MW	745.61	1451.12	745.61	749.60	919.85	861.68	1125.83
cryst syst	triclinic	monoclinic	Orthorhombic	triclinic	monoclinic	triclinic	triclinic
Space group	$P\bar{1}$	C2/c	$P2_12_12_1$	$P\bar{1}$	$P2_1$	$P\bar{1}$	$P\bar{1}$
a /Å	9.767(3)	31.053(9)	10.755(1)	10.7692)	10.764(1)	10.233(3)	10.492(2)
b /Å	10.775(3)	13.909(4)	17.317(2)	11.159(2)	16.732(2)	10.856(3)	15.574(3)
c /Å	19.152(5)	20.169(6)	19.938(2)	15.827(2)	13.314(2)	23.310(6)	18.232(4)
α (°)	96.588(5)	90.00	90.00	96.595(3)	90.00	86.692(5)	101.573(4)
β (°)	104.136(5)	125.053(5)	90.00	102.633(3)	105.78(2)	82.415(5)	106.716(4)
γ (°)	104.661(5)	90.00	90.00	106.603(3)	90.00	67.156(4)	101.032(4)
V /Å^3	1857.1(9)	7131(4)	3713.4(7)	1746.1(4)	2308(5)	2365.5(11)	2695.0(9)
Z	2	4	4	2	2	2	2
T /K	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)	298(2)
λ /Å	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
ρ_c (g/cm3)	1.333	1.352	1.334	1.426	1.324	1.210	1.387
μ (mm-1)	0.212	0.219	0.212	0.227	0.183	0.181	0.190
Goodness of fit	1.018	1.030	1.219	1.025	1.018	0.932	1.018
θ range	1.12 - 25.00	1.60 - 25.00	1.56 - 25.00	1.34 - 25.00	3.93 - 25.00	1.76 - 25.00	1.21 - 25.00
Total reflections	18036	33798	35699	16884	2977	10261	26161
Unique reflections	6540	6281	6536	6145	2977	8324	9507
Observed data[$I > 2\sigma(I)$]	4065	3907	6300	5045	1983	4908	6475
R_{int}	0.0486	0.1001	0.0582	0.0391	0.0755	0.0275	0.0514
R_1, wR_2 [$(I > 2\sigma(I)$]	0.0566, 0.1403	0.0685, 0.1560	0.0487, 0.1024	0.0461, 0.1081	0.0541, 0.1259	0.0628, 0.1645	0.0548, 0.1272
R_1, wR_2 (all data)	0.0966, 0.1609	0.1183, 0.1766	0.0514, 0.1037	0.0586, 0.1138	0.0920, 0.1513	0.0915, 0.1790	0.0865, 0.1402

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\,(|F_o|^2 - |F_c|^2)^2]\}^{1/2}$

Catalytic studies using palladium complexes 8 and 9

The rearrangement of prochiral trichloro or trifluoroacetimidates to the corresponding chiral allylic trichloro or trifluoroacetamides is a method utilized to explore the catalytic activity of many catalysts.[19] To explore the catalytic activity of the palladium complexes **8** and **9**, we have carried out some preliminary studies using the aza-Claisen rearrangement of two selected trichloroacetimidates, $RCH{=}CHCH_2OC(NH)CCl_3$ (R = Me and n-Pr) with these complexes. Reactions were carried out in tetrahydrofuran over a period of 12 hours with a catalyst loading of 2 mol % as per the equation.



Scheme 5

The yields of the trichloroacetamides obtained after the aza-Claisen rearrangement were in the range of 78-88% and the ee's obtained ranged from 4-9%. Among the complexes, one having Pd-OAc bond was found to be better both in terms of yield and enantiomeric excess. The same reactions when carried out at room temperature resulted in very poor conversions even after stirring for 24 h. As four of the phenyl C-H protons are involved in a weak anagostic interaction as indicated by ^{1}H NMR, which increases the crowding around the active site and possibly is a reason for the relatively higher temperature required for the activation of the catalysts **8** and **9**. The reason behind low enantioselectivity of these catalysts may be the large distance of the

reaction center from the sterically hindered phosphazene unit and calls for further fine tuning of the catalyst with respect to size and nature of co-substituents. However, the high stability of these complexes **8** and **9** to air and moisture and good solubility in a variety of solvents facilitates easier and rougher handling of these complexes as catalysts and these compounds can act as model compounds for further fine tuning and use of cyclophosphazene based chiral ligands in asymmetric catalysis.

Circular dichroism (CD) spectra of chiral ligands

With a view to probe further the chirality of the new ligands synthesized in the present study, CD spectra of all the chiral ligands were recorded in the range 230 - 300 nm region by using ligand solutions ($c \sim 2.5$ - 4.0 X 10^{-4} M in dichloromethane) in 1 mm quartz cell with an averaging time of 5 s, and an average of 3 scans (see supporting information). Poor solubility of ligands in acetonitrile and methanol solvents prevented the scan in the far UV region (185- 230 nm) where the bands corresponding to π-π* transition of C=N chromophore present in oxazoline ring are expected.[20] However, bands corresponding to π-π* transition of phenyl chromophore has been observed in the CD spectra of all oxazoline derivatives. Bisoxazoline derivatives **3** and **6**, having isopropyl derived oxazoline rings gave broad intense negative bands at 253 and 249 nm, respectively, which was followed by another less intense negative band around 229 nm. In contrast, bisoxazoline derivative **7**, having phenyl derived oxazoline ring gave two broad intense negative bands of equal intensities at 255 and 266 nm. Hexaoxazoline derivative **12**, gave a strong negative band at 253 nm and two weak positive bands at 237 and 283 nm. In contrast, compound **13**, which is the phenyl analogue of **12**, gave two negative bands of equal intensities at 254 and 264 nm (similar to compound **7**). Compound **16**, which is having two isopropyl

phebox ligands gave two negative bands in the region of 232 and 258 nm, whereas compound **17**, having two phenyl phebox ligands gave a broad intense negative band around 255 nm. Compound **20**, having four phenyl phebox ligands gave a negative intense band at 256 nm and a weak positive band at 239 nm. As expected, the CD spectral measurement of the achiral starting material **4** gave no bands in the range of 230 - 300 nm.

Conclusions

First examples of a series of chiral bis-oxazoline derived bi and multidentate ligands centered on cyclophosphazenes having the chiral center close to the nitrogen atom of the oxazoline ring and having C_2 axis have been prepared and structurally characterized. These ligands have the potential to form a range of transition metal based chiral catalysts. Preliminary complexation studies with $Pd(OAc)_2$ and $PdCl_2(C_6H_5CN)_2$ indicate that monomeric chiral palladium complexes are isolable especially if oxazoline ring is substituted at the para position of the phenyl group attached to the phosphazene through P-O bonds. Hexa-oxazoline derivatives of cyclophosphazene were also prepared having C_3 rotational axis which have potential for chiral molecular recognition. First examples of multiphebox ligands substituted on the phosphazene core were also prepared and characterized. Metal complexes of multiphebox derivatives of cyclophosphazenes can catalyze the reactions characteristic of normal Phebox ligands. The study opens up new possibilities in the field of assymetric catalysis with multidentate cyclophosphazene based chiral ligands and we are currently exploring the utility of these chiral ligands in assymmetric catalysis and molecular recognition.

Experimental Section:

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under nitrogen atmosphere. All the solvents were freshly distilled using standard procedures and used. Isopropyl alcohol and n-hexane (HPLC grade, Merck) were used for the chiral HPLC studies. The compounds *gem*-diphenyltetrachlorocyclotriphosphazene[21] and *gem*-tetraphenyldichlorocyclotriphosphazene[21] were prepared according to literature procedures. $N_3P_3Cl_6$, mesyl chloride, L-valinol, (*S*)-(+)-2-phenylglycinol, $PdCl_2(C_6H_5CN)_2$ and $Pd(OAc)_2$ were procured from Aldrich and used as such. The purity of $N_3P_3Cl_6$ was confirmed by ^{31}P NMR studies with a single sharp peak at 19.8 ppm.

Instrumentation.

^{1}H, $^{13}C\{1H\}$ and $^{31}P\{^{1}H\}$ spectra were recorded on a Bruker Spectrospin DPX-300 NMR spectrometer at 300.13, 75.47 and 121.48 MHz respectively. IR spectra in the range 4000−250 cm^{-1} were recorded on a Nicolet Protége 460 FT-IR spectrometer as KBr pellets. Elemental analyses were carried out on a Carlo Erba CHNSO 1108 elemental analyzer. Mass spectra were recorded on a Bruker Micro-TOF QII quadrupole time-of-flight (Q-TOF) mass spectrometer. Optical rotations of the chiral compounds were measured on an Autopol V (Rudolph Research, Flanders, NJ) instrument. All the rotations were measured at 589 nm (sodium D line) using dichloromethane as solvent, and readings were cross-checked by taking measurements at two different concentrations. The enantiomeric excess was determined by a Shimadzu LC6AD HPLC instrument fitted with a Daicel OD-H chiral column. All HPLC analyses used to determine enantiomeric purity were calibrated with samples of the racemate. Circular dichroism (CD) spectra in the range 230 - 300 nm region were obtained by using AVIV circular dichroism spectrometer (Model 420SF, Lakewood, NJ, USA) at 20^{o} C. All the measurements were

performed using ligand solution (c = 2.5 - 4.0 X 10^{-4} M in dichloromethane) in 1 mm quartz cell, an averaging time of 5 s, and an average of 3 scans were recorded to generate the data.

X-ray Crystallography. Suitable crystals of compounds **1**, **2**, **4**, **5**, **7**, **14** and **18** were obtained by slow evaporation of their saturated solutions in ethyl acetate/hexane or chloroform/toluene solvent mixtures. Single-crystal diffraction studies were carried out on a Bruker SMART APEX CCD diffractometer with a Mo Kα (λ = 0.71073 Å) sealed tube. All crystal structures were solved by direct methods. The program *SAINT* (version 6.22) was used for integration of the intensity of reflections and scaling. The program *SADABS* was used for absorption correction. The crystal structures were solved and refined using the *SHELXTL* (version 6.12) package.[22] All hydrogen atoms were included in idealized positions, and a riding model was used. Non-hydrogen atoms were refined with anisotropic displacement parameters. The highly distorted solvent molecules in the crystals of **14** were omitted using the squeeze/platon algorithm in wingx suite. The resulting new data sets were generated, and the structures were refined to convergence.[23] Selected bond distances and angles for compounds **1**, **2**, **4**, **5**, **7**, **14** and **18** are given as supplementary data. Crystallographic data and data collection parameters for compounds are given in table 1.

Preparation of $(NPPh_2)_2[NP(m\text{-}OC_6H_4C(O)OCH_3)_2]$ (1).

To a stirred suspension of Cs_2CO_3 (17.10 g, 52.50 mmol) in 150 mL of dry THF was added a solution of methyl 3-hydroxy benzoate (3.91 g, 25.66 mmol) in 50 mL of THF and the resulting solution was stirred for 15 min at room temperature. $Ph_4P_3N_3Cl_2$ (6.00 g, 11.67 mmol) dissolved in 50 mL of THF was added dropwise to this solution and the resulting solution was refluxed under nitrogen atmosphere for 16 h. The reaction was monitored using thin layer

chromatography and ^{31}P NMR spectroscopy. Afterwards, the precipitated salt was filtered off and the resulting solution was evaporated off under reduced pressure and subjected to column chromatography on silica gel column using hexane/chloroform (1:1) as the eluent. $(NPPh_2)_2[NP(m\text{-}OC_6H_4C(O)OCH_3)_2]$ (**1**) was obtained as a white crystalline solid. Yield: 6.45 g, 74%. Mp: 109-111 $^{\circ}$C. Found: C, 63.96; H, 4.76; N, 5.44.Calcd. for $C_{40}H_{34}N_3O_6P_3$: C, 64.43; H, 4.60; N, 5.64. IR (ν, cm^{-1}): 3434br, 3075m, 3052m, 3006w, 2952m, 2360w, 1724vs, 1587s, 1482s, 1437s, 1296s, 1284s, 1267m, 1227vs, 1206vs, 1167vs, 1123s, 1098s, 989s, 935s. ^1H NMR ($CDCl_3$, ppm): δ 7.78 (m, 2H, Ph*H*), 7.69 - 7.58 (m, 10H, Ph*H*), 7.39 - 7.34 (m, 4H, Ph*H*), 7.29 - 7.23 (m, 10H, Ph*H*), 7.03 [t (J = 7.95), 2H, Ph*H*), 3.79 (s, 6H, C*H*$_3$). ^{13}C {^1H} NMR: 166.18 (*C*O), 150.80 [d (J= 6.64 Hz)], 136.56 [dm ($^1J_{P\text{-}C}$ = 134.12 Hz)], 131.23, 130.72, 130.58, 130.50, 130.43, 128.91, 128.00, 127.91, 127.81, 126.31 [d (J= 4.53 Hz)], 125.77, 122.95 [d (J= 4.75 Hz)] (Ph*C*), 52.02 (*C*H$_3$). $^{31}P\{^1H\}$ NMR: δ 20.87 [d (J =25.03 Hz), *P*$(C_6H_5)_2$], 3.82 [t (J =25.09 Hz), *P*$(OC_6H_4COOCH_3)_2$]. HRMS Calcd. for $C_{40}H_{34}N_3NaO_6P_3$ $[M+Na]^+$: 768.1553, Found: 768.1535.

Preparation of $(NPPh_2)_2[NP(m\text{-}OC_6H_4COOH)_2]$ (2).

To a stirred suspension of potassium *tert*-butoxide (4.82 g, 42.92 mmol) in 100 mL of dry ether, cooled to 0^{o}C was added (0.19 mL, 10.73 mmol) of water and the resulting slurry was stirred for 5 min. To this was added **1** (2.0 g, 2.68 mmol). The ice bath was removed and the reaction mixture was stirred at room temperature until the reaction was complete (~ 12 h). The reaction was quenched by adding ice water until two clear layers formed. The aqueous layer was separated and acidified to pH ~ 1-2 with dilute hydrochloric acid. The acididfied solution was extracted with ether, dried over anhydrous sodium sulphate and concentrated to give $(NPPh_2)_2[NP(m\text{-}OC_6H_4COOH)_2]$ (**2**) as a white crystalline solid. Yield: 1.75 g, 91%. Mp: 189 -

191 °C. Found: C, 62.53; H, 4.25; N, 5.34.Calcd. for $C_{38}H_{30}N_3O_6P_3$: C, 63.60; H, 4.21; N, 5.86. IR (ν, cm^{-1}): 3610w, 3522br, 3080m, 2362w, 1729s, 1689s, 1586s, 1485m, 1437s, 1392m, 1285s, 1208vs, 1171vs, 1121s, 1074m, 953vs. ^{1}H NMR (DMSO-d_6, ppm): δ 7.70- 7.65 (m, 4H, Ph*H*), 7.62 - 7.55 (m, 8H, Ph*H*), 7.46 - 7.42 (m, 4H, Ph*H*), 7.36 - 7.31(m, 8H, Ph*H*), 7.26 - 7.16 (m, 4H, Ph*H*). ^{13}C {^{1}H} NMR: 166.37 (*C*O), 150.32 [d (J= 6.87 Hz)], 136.32 [dm ($^1J_{P-C}$ = 133.14 Hz)], 132.36, 131.11, 129.92, 129.84, 129.77, 129.51, 128.29, 128.20, 128.11, 125.76, 125.50 [d (J= 4.38 Hz)], 122.18 [d (J= 4.53 Hz)] (Ph*C*). ^{31}P{^{1}H} NMR: δ 19.95 [d(J =26.12 Hz), *P*(C_6H_5)$_2$], 3.59 [t(J = 25.51 Hz), *P*(OC_6H_4COOH)$_2$]. HRMS Calcd. for $C_{38}H_{31}N_3O_6P_3$ $[M+H]^+$: 718.1420, Found: 718.1419.

Preparation of (NPPh$_2$)$_2$[NP{m-OC$_6$H$_4$(4-iPr-2-Ox)}$_2$] (3).

Acid **2** (0.50 g, 0.69 mmol) was dissolved in CH_2Cl_2 (50 mL). Oxalyl chloride (0.60 mL, 6.96 mmol) and DMF (1-2 drop) were added sequentially. Upon addition of the latter, gas evolution was observed. The resulting solution was stirred at room temperature. After 45 min, the solution was concentrated using a rotary evaporator to yield the acid chloride as a semisolid, which was used directly in the next step.

(*S*)-(+)-2-amino-3-methyl-1-butanol [L-valinol] (0.18 g, 1.74 mmol) was taken in a mixture of triethylamine (3 mL) and CH_2Cl_2 (20 mL). A solution of the crude acid chloride in 30 mL of CH_2Cl_2 was also transferred to this flask. The resulting solution was stirred at room temperature and after 2 hours, was cooled to 0 °C using an ice bath. Mesyl chloride (0.24 g, 2.09 mmol) was added and the resulting solution was allowed to warm to room temperature. After stirring for 16 h, the solution was washed with 100 mL of saturated aqueous sodium bicarbonate and 100 mL of brine using a separating funnel. The organic layer was dried over Na_2SO_4, filtered, and concentrated using a rotary evaporator. The residue was purified using a silica gel column with

hexane/ethyl acetate mixture as eluent. The bisoxazoline compound $(NPPh_2)_2[NP\{m\text{-}OC_6H_4(4\text{-}iPr\text{-}2\text{-}Ox)\}_2]$ (**3**) was obtained as semisolid while using 20% ethyl acetate/hexane mixture as the eluent. Yield: 0.48 g, 81%. $[\alpha]_D^{25}$ = –25.21° (c 0.20 in CH_2Cl_2). IR (ν, cm^{-1}): 3444br, 3056w, 2959m, 2926m, 2360w, 1723w, 1651m, 1606w, 1583m, 1486m, 1439m, 1358m, 1205vs, 1168vs, 1121m, 980m, 943m, 901m. ^{1}H NMR ($CDCl_3$, ppm): δ 7.70 - 7.60 (m, 12H, Ph*H*), 7.40 - 7.35 (m, 4H, Ph*H*), 7.30 - 7.24 (m, 8H, Ph*H*), 7.18 - 7.16 (m, 2H, Ph*H*), 7.00 [t(J = 7.80 Hz), 2H, Ph*H*], 4.38 - 4.29 (m, 2H, C*H*CH_2), 4.17 - 4.04 (m, 4H, CHC*H*$_2$), 1.88 [m, 2H, C*H*$(CH_3)_2$], 1.03 [d (J= 6.90 Hz), 6H, CHC*H*$_3$)], 0.93 [d (J= 6.90 Hz), 6H, CHC*H*$_3$)]. ^{13}C {^{1}H} NMR: 163.00 (*C*=N), 150.84 [d (J= 6.79 Hz)], 136.53 [dm ($^1J_{P\text{-}C}$ = 134.35 Hz)], 130.58, 130.52, 130.43, 128.85, 128.68, 127.93, 127.83, 127.74, 124.51, 121.71 [d (J = 5.28 Hz)] (Ph*C*), 72.10 (*C*HCH_2), 70.02 (CH*C*H_2), 32.61 [*C*H$(CH_3)_2$], 18.85 [CH(*C*$H_3)_2$], 17.91 [CH(*C*$H_3)_2$]. ^{31}P{^{1}H} NMR: δ 20.89 [d(J =24.15 Hz), *P*$(C_6H_5)_2$], 3.46 [t(J = 25.09 Hz), *P*$(OR)_2$]. HRMS Calcd. for $C_{48}H_{49}N_5O_4P_3$ $[M+H]^+$: 852.2992, Found: 852.3010.

Preparation of $(NPPh_2)_2[NP(p\text{-}OC_6H_4C(O)OCH_3)_2]$ (4).

The reaction of Cs_2CO_3 (17.11 g, 52.50 mmol), methyl 4-hydroxy benzoate (3.91 g, 25.66 mmol) and $Ph_4P_3N_3Cl_2$ (6.00 g, 11.67 mmol) was carried out and worked up in a manner similar to that of compound **1**. $(NPPh_2)_2[NP(p\text{-}OC_6H_4C(O)OCH_3)_2]$ (**4**) was obtained as white crystalline solid. Yield: 8.70 g, 87%. Mp: 157-159 °C. Found: C, 64.47; H, 4.56; N, 5.71.Calcd. for $C_{40}H_{34}N_3O_6P_3$: C, 64.43; H, 4.60; N, 5.64. IR (ν, cm^{-1}): 3413br, 3056w, 2925m, 1720s, 1600m, 1502m, 1436m, 1280s, 1211vs, 1180s, 1116s, 964m, 914s, 861m. ^{1}H NMR ($CDCl_3$, ppm): δ 7.64 - 7.03 (m, 28H, Ph*H*), 3.82 (s, 6H, -C*H*$_3$). ^{13}C {^{1}H} NMR: 166.44 (*C*O), 154.76 [d (J= 6.04 Hz)], 136.33 [dm ($^1J_{P\text{-}C}$ = 135.86 Hz)], 130.91, 130.55, 130.47, 130.40, 128.08, 127.99, 127.90, 126.32, 121.34 [d (J= 4.53 Hz)] (Ph*C*), 52.04 (*C*H$_3$). ^{31}P{^{1}H} NMR: δ 21.00 [d(J =24.18 Hz),

P(C_6H_5)$_2$], 2.65 [t(J =25.03 Hz), *P*($OC_6H_4COOCH_3$)$_2$]. HRMS Calcd. for $C_{40}H_{35}N_3O_6P_3$ $[M+H]^+$: 746.1733, Found: 746.1739.

Preparation of (NPPh$_2$)$_2$[NP(p-OC$_6$H$_4$COOH)$_2$] (5).

The reaction of potassium *tert*-butoxide (10.11 g, 90.12 mmol), water (0.40 mL, 22.53 mmol) and **4** (4.2 g, 5.63 mmol) was carried out and worked up in a manner similar to that of compound **2**. (NPPh$_2$)$_2$[NP(p-OC$_6$H$_4$COOH)$_2$] (**5**) was obtained as white crystalline solid. Yield: 3.62 g, 90%. Mp: 210 - 212 °C. Found: C, 63.47; H, 4.35; N, 5.54.Calcd. for $C_{38}H_{30}N_3O_6P_3$: C, 63.60; H, 4.21; N, 5.86. IR (ν, cm^{-1}): 3350br, 3058s, 2992, 2658m, 2535, 1687vs, 1599s, 1504s, 1427s, 1286s, 1211vs, 1121vs, 1024m, 967s, 910vs, 861s. ^{1}H NMR (DMSO-d$_6$, ppm): δ 7.65 - 7.53 (m, 12H, Ph*H*), 7.43 - 7.40 (m, 4H, Ph*H*), 7.34 - 7.32 (m, 8H, Ph*H*), 7.12 [d(J = 7.80 Hz), 4H, Ph*H*]. ^{13}C {^{1}H} NMR: 167.66 (*C*O), 154.96 [d (J= 6.04 Hz)], 137.29 [dm ($^1J_{P-C}$ = 134.35 Hz)], 132.32, 131.95, 131.04, 130.96, 130.88, 129.42, 129.33, 129.24, 128.39, 122.06 [d (J = 4.53 Hz)] (Ph*C*). ^{31}P{^{1}H} NMR: δ 19.85 [d(J =26.12 Hz), *P*(C_6H_5)$_2$], 2.66 [t(J = 25.33 Hz), *P*(OC_6H_4COOH)$_2$]. HRMS Calcd. for $C_{38}H_{31}N_3O_6P_3$ $[M+H]^+$: 718.1420, Found: 718.1420.

Preparation of (NPPh$_2$)$_2$[NP{p-OC$_6$H$_4$(4-iPr-2-Ox)}$_2$] (6).

The reaction of acid **5** (0.50 g, 0.69 mmol), oxalyl chloride (0.60 mL, 6.96 mmol), DMF (1-2 drop), (*S*)-(+)-2-amino-3-methyl-1-butanol [L-valinol] (0.18 g, 1.74 mmol), triethylamine (3 mL) and mesyl chloride (0.24 g, 2.09 mmol) was carried out and worked up in a manner similar to that of compound **3**. The bisoxazoline compound (NPPh$_2$)$_2$[NP{p-OC$_6$H$_4$(4-iPr-2-Ox)}$_2$] (**6**) was obtained as viscous liquid while using 20% ethyl acetate/hexane mixture as the eluent. Yield: 0.395 g, 67%. $[\alpha]_D^{25}$ = –25.47° (c 0.20 in CH_2Cl_2). IR (ν, cm^{-1}): 3438br, 3057w, 2959m, 2925m, 1650s, 1605m, 1505m,1356m, 1206vs, 1165s, 1123m, 1072m, 962m, 912s, 851m. ^{1}H NMR ($CDCl_3$, ppm): δ 7.67 - 7.57 (m, 12H, Ph*H*), 7.40 - 7.35 (m, 4H, Ph*H*), 7.30 - 7.26 (m, 8H, Ph*H*),

7.08 [d(J = 7.80 Hz), 4H, Ph*H*], 4.38 (m, 2H, C*H*CH_2), 4.19 - 4.09 (m, 4H, CHC*H_2*), 1.90 [m, 2H, C*H*$(CH_3)_2$], 1.03 [d (J= 6.60 Hz), 6H, CHC*H_3*)], 0.94 [d (J= 6.60 Hz), 6H, CHC*H_3*)]. ^{13}C {^{1}H} NMR: 162.73 (*C*=N), 153.44 [d (J= 6.79 Hz)], 136.43 [dm ($^1J_{P-C}$ = 136.61 Hz)], 130.81, 130.55, 130.48, 130.40, 129.36, 128.04, 127.95, 127.85, 124.11 [d (J = 1.51 Hz)], 121.30 [d (J = 4.53 Hz)] (Ph*C*), 72.39 (*C*HCH_2), 69.92 (CH*C*H_2), 32.70 [*C*H$(CH_3)_2$], 18.83 [CH(*C*$H_3)_2$], 17.90 [CH(*C*$H_3)_2$]. ^{31}P{^{1}H} NMR: δ 20.90 [d(J =24.54 Hz), *P*$(C_6H_5)_2$], 2.77 [t(J = 25.03 Hz), *P*$(OR)_2$]. HRMS Calcd. for $C_{48}H_{49}N_5O_4P_3$ $[M+H]^+$: 852.2992, Found: 852.2962.

Preparation of $(NPPh_2)_2$[NP{p-OC_6H_4(4-Ph-2-Ox)}$_2$] (7).

The reaction of acid **5** (1.00 g, 1.39 mmol), oxalyl chloride (1.20 mL, 13.93 mmol), DMF (1-2 drop), (*S*)-(+)-2-phenylglycinol (0.48 g, 3.48 mmol), triethylamine (6 mL) and mesyl chloride (0.48 g, 4.18 mmol) was carried out and worked up in a manner similar to that of compound **3**.

The bisoxazoline compound $(NPPh_2)_2$[NP{p-OC_6H_4(4-Ph-2-Ox)}$_2$] (**7**) was obtained as white solid while using 30% ethyl acetate/hexane mixture as the eluent. Yield: 0.80 g, 62%. Mp: 158-160 °C. $[\alpha]_D^{25}$ = - 4.74° (c 0.20 in CH_2Cl_2). Found: C, 70.57; H, 4.89; N, 7.50.Calcd. for $C_{54}H_{44}N_5O_4P_3$: C, 70.51; H, 4.82; N, 7.61. IR (ν, cm^{-1}): 3437br, 3056m, 3028w, 2922m, 2924m, 2898w, 2361w, 1646s, 1604m, 1504s, 1437m, 1357m, 1205vs, 1158vs, 1120s, 1072s, 951s, 909vs, 851s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.74 [d(J = 8.40 Hz), 4H, Ph*H*], 7.68 - 7.60 (m, 8H, Ph*H*), 7.41 - 7.26 (m, 22H, Ph*H*), 7.13 [d(J = 7.20 Hz), 4H, Ph*H*], 5.38 [dd(J = 9.90, 8.25), 2H, CHC*H_2*], 4.78 [t(J = 9.90, 8.40), 2H, CHC*H_2*], 4.28 [t(J = 8.25), 2H, C*H*CH_2]. ^{13}C {^{1}H} NMR: 164.20 (*C*=N), 153.80 [d (J= 6.94 Hz)], 142.36, 136.47 [dm ($^1J_{P-C}$ = 136.47Hz)], 130.85, 130.58, 130.50, 130.42, 129.68, 128.73, 128.06, 127.97, 127.88, 127.64, 126.67, 123.70, 121.47 [d (J= 4.91 Hz)], 74.88 (CH*C*H_2), 69.98 (*C*HCH_2). ^{31}P{^{1}H} NMR: δ 20.96 [d(J =24.54 Hz), *P*$(C_6H_5)_2$],

2.75 [t(J = 25.27 Hz), *P*(OR)$_2$]. HRMS Calcd. for $C_{54}H_{45}N_5O_4P_3$ $[M+H]^+$: 920.2679, Found: 920.2678.

Preparation of Pd(OAc)$_2$(NPPh$_2$)$_2$[NP{p-OC$_6$H$_4$(4-iPr-2-Ox)}$_2$] (8).

Palladium acetate (0.13 g, 0.59 mmol) was added to a solution of **6** (0.50 g, 0.59 mmol) in acetic acid (2.5 mL) and the mixture was stirred at room temperature for 8 h. The pale yellow precipitate formed was filtered, washed with acetic acid and dried under vacuum to get a pale yellow crystalline powder which was characterized as Pd(OAc)$_2$(NPPh$_2$)$_2$[NP{p-OC$_6$H$_4$(4-iPr-2-Ox)}$_2$] (**8**). Yield: 0.52 g, 82%. Mp: 121–124 °C (dec.). $[\alpha]_D^{25}$ = +130° (c 0.20 in $CHCl_3$). Found: C, 58.09; H, 5.08; N, 6.35. Calcd. for $C_{52}H_{54}N_5O_8P_3Pd$: C, 58.03; H, 5.06; N, 6.51. IR (ν, cm^{-1}): 3435br, 3055m, 2961m, 2925m, 1630s, 1508m, 1434m, 1373s, 1307s, 1254m, 1208vs, 1164vs, 1122s, 1020m, 956m, 915s, 852m. ^{1}H NMR ($CDCl_3$, ppm): δ 8.264 [d(J = 8.40 Hz), 4H, OPh*H*], 7.64 - 7.52 (m, 8H, Ph*H*), 7.33 - 7.21 (m, 8H, Ph*H*), 7.14- 7.05 (m, 8H, Ph*H*), 4.88 (m, 2H, C*H*CH$_2$), 4.43 - 4.37 (m, 4H, CHC*H*$_2$), 3.02 [m, 2H, C*H*(CH$_3$)$_2$], 1.70 (s, 6H, -COC*H*$_3$) 1.06 [d (J= 6.90 Hz), 6H, CHC*H*$_3$)], 0.72 [d (J= 6.60 Hz), 6H, CHC*H*$_3$)]. ^{13}C {^{1}H} NMR: 176.48 (*C*OCH$_3$), 166.56 (*C*=N), 153.31 [d (J= 5.41 Hz)], 135.63 [dm ($^1J_{P-C}$ = 147.93 Hz)], 130.42, 129.73, 129.53, 129.41, 129.05, 127.33, 127.08, 126.97, 126.71, 121.02 [d (J = 4.53 Hz)] (Ph*C*), 70.54 (*C*HCH$_2$), 66.91 (CH*C*H$_2$), 28.50 [*C*H(CH$_3$)$_2$], 21.86 (-CO*C*H$_3$), 17.94 [CH(*C*H$_3$)$_2$], 13.14 [CH(*C*H$_3$)$_2$]. ^{31}P{^{1}H} δ NMR: 20.69 [d(J = 25.88 Hz), *P*(C$_6$H$_5$)$_2$], 2.77 [t(J = 25.76 Hz), *P*(OR)$_2$]. HRMS Calcd. for $C_{52}H_{54}N_5NaO_8P_3Pd$ $[M+Na]^+$: 1098.2130, Found: 1098.2048.

Preparation of PdCl$_2$(NPPh$_2$)$_2$[NP{p-OC$_6$H$_4$(4-iPr-2-Ox)}$_2$] (9).

Compound **6** (80 mg, 0.09 mmol) was dissolved in 30 mL in dry benzene and PdCl$_2$(PhCN)$_2$ (36 mg, 0.09 mmol) was added with constant stirring and the mixture was refluxed for 6 h. Afterward, reaction mixture was filtered and evaporated off under reduced pressure to give crude

compound. $PdCl_2(NPPh_2)_2[NP\{p\text{-}OC_6H_4(4\text{-}iPr\text{-}2\text{-}Ox)\}_2]$ (**9**) was obtained as pale yellow solid after precipitating the crude compound solution in chloroform with hexane. Yield: 76 mg, 79%. Mp: 171–173 °C (dec.). $[\alpha]_D^{25}$ = +170° (c 0.20 in $CHCl_3$). Found: C, 56.19; H, 4.75; N, 6.75. Calcd. for $C_{48}H_{48}Cl_2N_5O_4P_3Pd$: C, 56.02; H, 4.70; N, 6.80. IR (ν, cm^{-1}): 3437br, 3053w, 2924s, 2856m, 2359w, 1633s, 1507m, 1375m, 1209vs, 1173vs, 1120m, 1020m, 916s. ^1H NMR ($CDCl_3$, ppm): δ 8.34 [d(J = 8.40 Hz), 4H, OPh*H*], 7.65 - 7.55 (m, 8H, Ph*H*), 7.32 - 7.21 (m, 12H, Ph*H*), 7.01 [d(J = 7.50 Hz), 4H, OPh*H*], 4.58 - 4.56 (m, 2H, C*H*CH_2), 4.49 [t(J = 9.30 Hz), 2H, CHC*H*$_2$], 4.43 - 4.38(m, 2H, CHC*H*$_2$), 3.05 [m, 2H, C*H*$(CH_3)_2$], 1.14 [d (J= 6.90 Hz), 6H, CHC*H*$_3$)], 1.05 [d (J= 6.60 Hz), 6H, CHC*H*$_3$)]. ^{13}C {^1H} NMR: 166.83 (*C*=N), 154.66 [d (J= 6.04 Hz)], 136.51 [dm ($^1J_{P\text{-}C}$ = 133.59 Hz)], 131.72, 130.93, 130.75, 130.59, 130.50, 130.43, 130.35, 128.09, 127.90, 121.78 [d (J = 5.28 Hz)] , 121.09 (Ph*C*), 72.01 (*C*HCH_2), 68.56 (CH*C*H_2), 30.09 [*C*$H(CH_3)_2$], 19.11 [CH(*C*$H_3)_2$], 15.24 [CH(*C*$H_3)_2$]. $^{31}P\{^1H\}$ NMR: δ 20.72 [d(J = 25.51 Hz), *P*$(C_6H_5)_2$], 2.01 [t(J = 26.12 Hz), *P*$(OR)_2$]. HRMS Calcd. for $C_{48}H_{48}Cl_2N_5O_4P_3Pd$ $[M]^+$: 1027.1336, Found: 1027.1271.

Preparation of $[PN(OC_6H_4C(O)OCH_3)_2]_3$ (10).

The reaction of Cs_2CO_3 (52.48 g, 161.08 mmol), methyl 4-hydroxy benzoate (11.38 g, 74.78 mmol) and $P_3N_3Cl_6$ (4.00 g, 11.51 mmol) was carried out (for 12 h) and worked up in a manner similar to that of compound **1**. The crude mixture was subjected to column chromatography on silica gel column using hexane/chloroform (1:2) as the eluent. $[PN(OC_6H_4COOCH_3)_2]_3$ (**10**) was obtained as white crystalline solid. Yield: 9.50 g, 79%. Mp: 152-153 °C. Found: C, 55.37; H, 4.16; N, 4.01.Calcd. for $C_{48}H_{42}N_3O_{18}P_3$: C, 55.34; H, 4.06; N, 4.03. IR (ν, cm^{-1}): 3428m, 2953m, 1926w, 1726vs, 1604vs, 1504vs, 1437vs, 1415m, 1284vs, 1208vs, 1184vs, 1163vs, 1113vs, 1016s, 962vs, 883s, 854s, 768s. ^1H NMR ($CDCl_3$, ppm): δ 7.86 [d(J = 8.70 Hz), 12H, Ph*H*],

6.99 [d(J = 8.70 Hz), 12H, Ph*H*], 3.93(s, 18H, -CH_3). ^{13}C {^{1}H} NMR: 165.90 (*C*O), 153.55, 131.27, 127.30, 120.50 (Ph*C*), 52.21 (*C*H_3). ^{31}P{^{1}H} NMR: δ 7.55 [s, *P*($OC_6H_4COOCH_3$)$_2$]. HRMS Calcd. for $C_{48}H_{42}N_3NaO_{18}P_3$ $[M+Na]^+$: 1064.1568, Found: 1064.1574.

Preparation of [PN(OC_6H_4COOH)$_2$]$_3$ (11).

To a stirred suspension of potassium *tert*-butoxide (14.48 g, 0.13 mol) in 300 mL of dry ether, cooled to 0^{o}C was added (0.58 mL, 32.25 mmol) of water and the resulting slurry was stirred for 5 min. To this was added **10** (2.8 g, 2.69 mmol). The ice bath was removed and the reaction mixture was stirred at room temperature until the reaction was complete (~ 24 h). The reaction was quenched by adding ice water until two clear layers formed. The aqueous layer was separated and acidified to pH ~ 1-2 with dilute hydrochloric acid. The product as a precipitate was obtained after stirring. The compound **11** was obtained after filteration, washing with water and drying. Yield: 2.12 g, 82%. Mp: > 275 $^{\circ}$C. Found: C, 52.47; H, 3.26; N, 4.31.Calcd. for $C_{48}H_{30}N_3O_{18}P_3$: C, 52.68; H, 3.16; N, 4.39. IR (ν, cm^{-1}): 3420br, 3080br, 1697vs, 1603vs, 1506s, 1425vs, 1279vs, 2110vs, 1162vs, 950vs. ^{1}H NMR (DMSO-d_6, ppm): δ 13.02 (s, 6H, -COO*H*), 7.84 [d(J = 8.70 Hz), 12H, Ph*H*], 7.01 [d(J = 8.70 Hz), 12H, Ph*H*]. ^{13}C {^{1}H} NMR: 166.29 (*C*O), 152.83, 131.30, 128.28, 120.57 (Ph*C*). ^{31}P{^{1}H} NMR: δ 8.01 [s, *P*(OC_6H_4COOH)$_2$]. HRMS Calcd. for $C_{42}H_{30}KN_3O_{18}P_3$ $[M+K]^+$: 996.0369, Found: 996.0329.

Preparation of [PN{OC_6H_4(4-*i*Pr-2-Ox)}$_2$]$_3$ (12).

The reaction of acid **11** (0.50 g, 0.52 mmol), oxalyl chloride (1.35 mL, 15.66 mmol), DMF (1-2 drop), (*S*)-(+)-2-amino-3-methyl-1-butanol [L-valinol] (0.40 g, 3.92 mmol), triethylamine (6.5 mL) and mesyl chloride (0.36 mL, 4.70 mmol) was carried out (for 2 days) and worked up in a manner similar to that of compound **3**. The hexaoxazoline compound [PN{OC_6H_4(4-*i*Pr-2-Ox)}$_2$]$_3$ (**12**) was obtained as white semisolid while using 50% ethyl acetate/hexane mixture as

the eluent. Yield: 0.38 g, 54%. $[\alpha]_D^{25}$ = –18.75° (c 0.20 in CH_2Cl_2). IR (ν, cm^{-1}): 3447br, 2960s, 2926m, 2361w, 1717w, 1652s, 1604m, 1505s, 1468w, 1414w, 1356s, 1269s, 1203vs, 1181vs, 1162vs, 1075s, 1017m, 948vs, 887s, 852s. ^{1}H NMR ($CDCl_3$, ppm): δ 7.73 [d(J = 7.80 Hz), 12H, Ph*H*], 6.85 [d(J = 7.80 Hz), 12H, Ph*H*], 4.33 (m, 6H, C*H*CH_2), 4.04 (m, 12H, CHC*H*$_2$), 1.78 [6H, m, C*H*$(CH_3)_2$], 0.93 [18H, d (J= 6Hz), CHC*H*$_3$)], 0.83 [18H, d (J= 6Hz), CHC*H*$_3$)]. ^{13}C {^{1}H} NMR: 162.54 (*C*=N), 152.39, 129.79, 124.82, 120.62 (Ph*C*), 72.23 (*C*HCH_2), 70.10 (CH*C*H$_2$), 32.59 [*C*H$(CH_3)_2$], 18.74 [CH(*C*H$_3)_2$], 17.89 [CH(*C*H$_3)_2$]. ^{31}P{^{1}H} NMR: δ 8.00 [s, *P*R$_2$]. HRMS Calcd. for $C_{72}H_{84}N_9NaO_{12}P_3$ $[M+Na]^+$: 1382.5344, Found: 1382.5311.

Preparation of [PN{OC$_6$H$_4$(4-Ph-2-Ox)}$_2$]$_3$ (13).

The reaction of acid **11** (0.50 g, 0.52 mmol), oxalyl chloride (1.35 mL, 15.66 mmol), DMF (1-2 drop), (*S*)-(+)-2-phenylglycinol (0.54 g, 3.92 mmol), triethylamine (6.5 mL) and mesyl chloride (0.36 mL, 4.70 mmol) was carried out (for 2 days) and worked up in a manner similar to that of compound **3**. The hexaoxazoline compound [PN{OC_6H_4(4-Ph-2-Ox)}$_2$]$_3$ (**13**) was obtained as white solid while using 50% ethyl acetate/hexane mixture as the eluent. Yield: 0.55 g, 61%. Mp: 58-60 °C. $[\alpha]_D^{25}$ = +4.30° (c 0.20 in CH_2Cl_2). Found: C, 69.17; H, 4.56; N, 8.01.Calcd. for $C_{90}H_{72}N_9O_{12}P_3$: C, 69.09; H, 4.64; N, 8.06. IR (ν, cm^{-1}): 3439br, 3292m, 2962m, 2924m, 2853w, 2359w, 1716w, 1648vs, 1604m, 1504s, 1358m, 1268s, 1204vs, 1180vs, 1161vs, 1074s, 949vs, 885m, 853m. ^{1}H NMR ($CDCl_3$, ppm): δ 7.94 [d(J = 8.71 Hz), 12H, -OPh*H*], 7.37-7.27 (m, 30H, Ph*H*), 7.04 [d(J = 8.40 Hz), 12H, -OPh*H*], 5.37 [t(J = 9.15), 6H, CHC*H*$_2$], 4.73 [t(J = 9.15), 6H, CHC*H*$_2$], 4.22 [t(J = 8.25), 6H, C*H*CH_2]. ^{13}C {^{1}H} NMR: 163.98 (*C*=N), 152.85, 142.35, 130.27, 128.87, 127.75, 126.86, 124.89, 121.01 (Ph*C*), 75.11 (CH*C*H$_2$), 70.21 (*C*HCH_2). ^{31}P{^{1}H} NMR: δ 8.17 [s, *P*R$_2$]. HRMS Calcd. for $C_{90}H_{73}N_9O_{12}P_3$ $[M+H]^+$: 1564.4586, Found: 1564.4611.

Preparation of $(NPPh_2)_2[NP\{OC_6H_3(C(O)OCH_3)_2\}_2]$ (14).

The reaction of Cs_2CO_3 (11.40 g, 35.00 mmol), dimethyl 5-hydroxyisophthalate (3.60 g, 17.11 mmol) and $Ph_4P_3N_3Cl_2$ (4.00 g, 7.77 mmol) was carried out (for 30 h) and worked up in a manner similar to that of compound **1**. $(NPPh_2)_2[NP\{OC_6H_3(C(O)OCH_3)_2\}_2]$ (**14**) was obtained as white crystalline solid. Yield: 4.56 g, 68 %. Mp: 117-119 °C. Found: C, 62.27; H, 4.46; N, 4.73.Calcd. for $C_{44}H_{38}N_3O_{10}P_3$: C, 61.33; H, 4.44; N, 4.88. IR (ν, cm^{-1}): 3440br, 3077w, 3055w, 2952m, 1730vs, 1592m, 1455m, 1434s, 1321s, 1252vs, 1205vs, 1172vs, 1122m, 1010s, 943m, 842m. ^1H NMR ($CDCl_3$, ppm): δ 8.34 (m, 2H, OPh*H*), 7.96 (m, 4H, OPh*H*), 7.67 - 7.61 (m, 8H, Ph*H*), 7.39 - 7.34 (m, 4H, Ph*H*), 7.29 - 7.23 (m, 8H, Ph*H*), 3.83 (s, 12H, -CH_3). ^{13}C {^1H} NMR: 165.36 (*C*O), 150.84 [d (J = 6.79 Hz)], 136.46 [dm ($^1J_{P-C}$ = 135.10 Hz)], 131.64 [d (J= 1.51 Hz)], 130.91, 130.57, 130.49, 130.42, 128.99, 127.19, 128.09, 128.00, 127.34 [d (J= 4.53 Hz)], 127.20 (Ph*C*), 52.41 (*C*H_3). ^{31}P {^1H} NMR: δ 21.22 [d(J =24.78 Hz), *P*$(C_6H_5)_2$], 4.22 [t(J =24.54 Hz), *P*$(OR)_2$]. HRMS Calcd. for $C_{44}H_{39}N_3O_{10}P_3$ $[M+H]^+$: 862.1843, Found: 862.1843.

Preparation of $(NPPh_2)_2[NP\{OC_6H_3(COOH)_2\}_2]$ (15).

The reaction of potassium *tert*-butoxide (12.50 g, 114.06 mmol), water (0.50 mL, 27.77 mmol) and **14** (3.0 g, 3.48 mmol) was carried out and worked up in a manner similar to that of compound **2**. $(NPPh_2)_2[NP\{OC_6H_3(COOH)_2\}_2]$ (**15**) was obtained as white solid. Yield: 2.60 g, 93 %. Mp: 233 - 235 °C. Found: C, 59.48; H, 3.68; N, 5.24.Calcd. for $C_{40}H_{30}N_3O_{10}P_3$: C, 59.64; H, 3.75; N, 5.22. IR (ν, cm^{-1}): 3439br, 3078w, 2973w, 2918w, 2617br, 1701s, 1593m, 1460m, 1438s, 1254s, 1202vs, 1173vs, 1120s, 1074m, 1008m, 977s, 916m, 840s. ^1H NMR (DMSO-d_6, ppm): δ 8.15 (s, 2H, OPh*H*), 7.82 (m, 4H, OPh*H*), 7.56 - 7.52 (m, 8H, Ph*H*), 7.46 - 7.41 (m, 4H, Ph*H*), 7.31 - 7.29 (m, 8H, Ph*H*). ^{13}C {^1H} NMR: 165.63 (*C*O), 150.21 [d (J= 6.87 Hz)], 136.08 [dm ($^1J_{P-C}$ = 136.68 Hz)], 132.77, 131.24, 129.84, 129.76, 129.69, 128.38, 128.28, 128.19,

126.58, 126.27 [d (J = 4.08 Hz)] (Ph*C*). $^{31}P\{^{1}H\}$ NMR: δ 20.40 [d(J =25.03 Hz), *P*(C_6H_5)$_2$], 4.21 [t(J = 25.09 Hz), *P*(OR)$_2$]. HRMS Calcd. for $C_{40}H_{31}N_3O_{10}P_3$ $[M+H]^+$: 806.1217, Found: 806.1216.

Preparation of (NPPh$_2$)$_2$[NP{OC$_6$H$_3$(4-iPr-2-Ox)$_2$}$_2$] (16).

The reaction of acid **15** (1.00 g, 1.24 mmol), oxalyl chloride (2.20 mL, 24.84 mmol), DMF (1-2 drop), (*S*)-(+)-2-amino-3-methyl-1-butanol [L-valinol] (0.64 g, 6.21 mmol), triethylamine (10 mL) and mesyl chloride (0.85 g, 7.45 mmol) was carried out (for 24 h) and worked up in a manner similar to that of compound **3**. (NPPh$_2$)$_2$[NP{OC$_6$H$_3$(4-iPr-2-Ox)$_2$}$_2$] (**16**) was obtained as solid while using 30% ethyl acetate/hexane mixture as the eluent. Yield: 0.83 g, 62 %. $[\alpha]_D^{25}$ = –40.70° (c 0.20 in CH_2Cl_2). Found: C, 66.78; H, 6.25; N, 9.15. Calcd. for $C_{60}H_{66}N_7O_6P_3$: C, 67.09; H, 6.19; N, 9.13. IR (ν, cm^{-1}): 3438br, 3056w, 2959s, 2926m, 2359w, 1723w, 1654s, 1589s, 1459m, 1438m, 1370m, 1206vs, 1167vs, 1121s, 984s, 884m. ^{1}H NMR ($CDCl_3$, ppm): δ 8.18 (s, 2H, OPh*H*), 7.71 (s, 4H, OPh*H*), 7.60 - 7.51 (m, 8H, Ph*H*), 7.21 - 7.19 (m, 4H, Ph*H*), 7.13 (m, 8H, Ph*H*), 4.22 - 4.14 (m, 4H, C*H*CH$_2$), 4.03 - 3.87 (m, 8H, CHC*H*$_2$), 1.71 [m, 4H, C*H*(CH$_3$)$_2$], 0.91 [d (J= 6.60 Hz), 12H, CHC*H*$_3$)], 0.80 [d (J= 6.60 Hz), 12H, CHC*H*$_3$)]. ^{13}C $\{^{1}H\}$ NMR: 161.97 (*C*=N), 150.76 [d (J= 6.79 Hz)], 136.56 [dm ($^{1}J_{P-C}$ = 136.53 Hz)], 130.54, 130.48, 130.39, 130.32, 129.15, 127.92, 127.82, 127.73, 124.52, 124.06 [d (J = 4.53 Hz)] (Ph*C*), 72.65 (*C*HCH$_2$), 70.13 (CH*C*H$_2$), 32.78 [*C*H(CH$_3$)$_2$], 18.89 [CH(*C*H$_3$)$_2$], 18.16 [CH(*C*H$_3$)$_2$]. $^{31}P\{^{1}H\}$ NMR: δ 21.01 [d(J = 25.27 Hz), *P*(C_6H_5)$_2$], 3.34 [t(J = 25.21 Hz), *P*(OR)$_2$]. HRMS Calcd. for $C_{60}H_{67}N_7O_6P_3$ $[M+H]^+$: 1074.4360, Found: 1074.4361.

Preparation of (NPPh$_2$)$_2$[NP{OC$_6$H$_3$(4-Ph-2-Ox)$_2$}$_2$] (17).

The reaction of acid **15** (0.50 g, 0.62 mmol), oxalyl chloride (1.10 mL, 12.41 mmol), DMF (1-2 drop), (*S*)-(+)-2-phenylglycinol (0.43 g, 3.10 mmol), triethylamine (5.6 mL) and mesyl chloride

(0.43 g, 3.72 mmol) was carried out (for 24 h) and worked up in a manner similar to that of compound **3**. $(NPPh_2)_2[NP\{OC_6H_3(4\text{-}Ph\text{-}2\text{-}Ox)_2\}_2]$ (**17**) was obtained as white solid while using 40% ethyl acetate/hexane mixture as the eluent. Yield: 0.60 g, 80%. Mp: 70 - 72 °C. $[\alpha]_D^{25}$ = + 16.40° (c 0.20 in CH_2Cl_2). Found: C, 71.57; H, 4.89; N, 8.15.Calcd. for $C_{72}H_{58}N_7O_6P_3$: C, 71.46; H, 4.83; N, 8.10. IR (ν, cm^{-1}): 3442br, 3058w, 2963w, 2923w, 1715w, 1650s, 1587s, 1455m, 1438m, 1371m, 1269m, 1206vs, 1167vs, 1122m, 985s, 884m. ^1H NMR ($CDCl_3$, ppm): δ 8.44 (s, 2H, OPh*H*), 7.93 (s, 4H, OPh*H*), 7.73 - 7.61 (m, 8H, Ph*H*), 7.37 - 7.19 (m, 32H, Ph*H*), 5.34 [t(J = 9.30), 4H, CHC*H*$_2$], 4.68 [t(J = 9.30), 4H, CHC*H*$_2$], 4.15 [t(J = 8.40), 4H, C*H*CH$_2$]. ^{13}C {^1H} NMR: 163.50 (*C*=N), 151.13 [d (J= 6.79 Hz)], 142.34, 136.64 [dm ($^1J_{P\text{-}C}$ = 132.84 Hz)], 130.74, 130.66, 130.59, 130.50, 129.10, 128.84, 128.16, 127.97, 127.73, 126.87, 125.19, 124.79 [d (J= 4.45 Hz)], 75.00 (CH*C*H$_2$), 70.21 (*C*HCH$_2$). $^{31}P\{^1H\}$ NMR: δ 21.10 [d(J =24.91 Hz), *P*(C_6H_5)$_2$], 3.49 [t(J = 25.09 Hz), *P*(OR)$_2$]. HRMS Calcd. for $C_{72}H_{59}N_7O_6P_3$ $[M+H]^+$: 1210.3734, Found: 1210.3779.

Preparation of $(NPPh_2)[NP\{OC_6H_3(C(O)OCH_3)_2\}_2]_2$ (18).

The reaction of Cs_2CO_3 (3.02 g, 9.28 mmol), dimethyl 5-hydroxyisophthalate (0.98 g, 4.64 mmol) and $Ph_2P_3N_3Cl_4$ (0.50 g, 1.16 mmol) was carried out (for 8 h) and worked up in a manner similar to that of compound **1**. $(NPPh_2)[NP\{OC_6H_3(C(O)OCH_3)_2\}_2]_2$ (**18**) was obtained as white crystalline solid. Yield: 1.04 g, 80 %. Mp: 122-125 °C. Found: C, 55.57; H, 4.16; N, 3.59.Calcd. for $C_{52}H_{46}N_3O_{20}P_3$: C, 55.47; H, 4.12; N, 3.73. IR (ν, cm^{-1}): 3434br, 2955m, 1731vs, 1594s, 1435s, 1320s, 1254vs, 1108s, 1011vs, 946s, 903m, 852m. ^1H NMR ($CDCl_3$, ppm): δ 8.42 (s, 4H, OPh*H*), 7.98 (s, 8H, OPh*H*), 7.45 - 7.32 (m, 6H, Ph*H*), 7.22 - 7.15 (m, 4H, Ph*H*), 3.87 (s, 24H, -C*H*$_3$). ^{13}C {^1H} NMR: 164.92 (*C*O), 150.47 [t (J = 3.77 Hz)], 134.09 [dm ($^1J_{P\text{-}C}$ = 136.09 Hz)], 131.77, 131.05, 130.00, 129.85, 128.04, 127.86, 127.20, 126.32 (Ph*C*), 52.28 (*C*H$_3$). $^{31}P\{^1H\}$

NMR: δ 22.87 [t(J = 33.41 Hz), $P(C_6H_5)_2$], 7.62 [d(J = 33.41 Hz), $P(OR)_2$]. HRMS Calcd. for $C_{52}H_{47}N_3O_{20}P_3$ $[M+H]^+$: 1126.1960, Found: 1126.1802.

Preparation of $(NPPh_2)$ $[NP\{OC_6H_3(COOH)_2\}_2]_2$ (19).

The reaction of potassium *tert*-butoxide (1.28 g, 11.37 mmol), water (0.05 mL, 2.84 mmol) and **18** (0.20 g, 0.18 mmol) was carried out and worked up in a manner similar to that of compound **2**. $(NPPh_2)$ $[NP\{OC_6H_3(COOH)_2\}_2]_2$ (**19**) was obtained as white solid. Yield: 0.17 g, 94 %. Mp: 248 - 250 °C. Found: C, 51.74; H, 2.88; N, 4.05.Calcd. for $C_{44}H_{30}N_3O_{20}P_3$: C, 52.14; H, 2.98; N, 4.15. IR (ν, cm^{-1}): 3427br, 3086br, 2926m, 1709vs, 1597m, 1463m, 1419m, 1302s, 1220s, 1186s, 1118s, 1015s, 987s, 909m, 855s. ^1H NMR (DMSO-d_6, ppm): δ 8.23 (s, 4H, OPh*H*), 7.86 (s, 8H, OPh*H*), 7.40 - 7.17 (m, 10H, Ph*H*). ^{13}C $\{^1H\}$ NMR: 165.50 (*C*O), 150.01, 134.08 [dm ($^1J_{P\text{-}C}$ = 136.08 Hz)], 133.06, 131.62, 129.53, 129.39, 128.33, 128.15, 126.92, 125.49 (Ph*C*). $^{31}P\{^1H\}$ NMR: δ 22.88 [t(J = 33.32 Hz), $P(C_6H_5)_2$], 7.89 [d(J = 32.32 Hz), $P(OR)_2$]. HRMS Calcd. for $C_{44}H_{31}N_3O_{20}P_3$ $[M+H]^+$: 1014.0708, Found: 1014.0647.

Preparation of $(NPPh_2)$ $[NP\{OC_6H_3(4\text{-}Ph\text{-}2\text{-}Ox)_2\}_2]_2$ (20).

The reaction of acid **19** (0.30 g, 0.30 mmol), oxalyl chloride (1.10 mL, 11.84 mmol), DMF (1-2 drop), (*S*)-(+)-2-phenylglycinol (0.41 g, 2.96 mmol), triethylamine (6 mL) and mesyl chloride (0.43 g, 3.72 mmol) was carried out (for 24 h) and worked up in a manner similar to that of compound **3**. $(NPPh_2)$ $[NP\{OC_6H_3(4\text{-}Ph\text{-}2\text{-}Ox)_2\}_2]_2$ (**20)** was obtained as white solid while using 50% ethyl acetate/hexane mixture as the eluent. Yield: 0.24 g, 44 %. Mp: 84 - 86 °C. $[\alpha]_D^{25}$ = +21.75° (c 0.20 in CH_2Cl_2). Found: C, 70.78; H, 4.85; N, 8.19. Calcd. for $C_{108}H_{86}N_{11}O_{12}P_3$: C, 71.16; H, 4.76; N, 8.45. IR (ν, cm^{-1}): 3424br, 3061w, 3029w, 2958m, 2924s, 2853m, 2360m, 1728m, 1650vs, 1587s, 1535m, 1455s, 1372s, 1269m, 1229vs, 1175vs, 1124w, 1093w, 1010m, 986vs, 896s. ^1H NMR ($CDCl_3$, ppm): δ 8.53 (s, 4H, OPh*H*), 8.03 (s, 8H, OPh*H*), 7.51 - 7.06 (m,

50H, Ph*H*), 5.40 - 5.26 (m, 8H, CHCH_2), 4.69 - 4.64 (m, 8H, CHCH_2), 4.17 - 4.10 (m, 8H, C*H*CH$_2$). ^{13}C {^{1}H} NMR: 163.39 (*C*=N), 142.31 [d (J= 3.70 Hz)], 139.43, 130.47, 130.32, 129.45, 129.32, 128.84, 128.21, 128.03, 127.71, 126.86, 125.47, 124.34, 124.16 (Ph*C*), 75.04 (CH*C*H$_2$), 70.26 (*C*HCH$_2$). ^{31}P{^{1}H} NMR: δ 22.60 [d(J = 32.50 Hz), *P*(C$_6$H$_5$)$_2$], 7.15 [t(J = 32.68 Hz), *P*(OR)$_2$]. HRMS Calcd. for $C_{108}H_{87}N_{11}O_{12}P_3$ $[M+H]^+$: 1822.5749, Found: 1822.5685.

General procedure for rearrangement of allylic trichloroacetimidates catalyzed by palladacycle 8 and 9: (Table 2). A solution of catalysts 8 or **9** (0.02 mmol) and THF (0.5 mL) was added to trichloroacetimidates **21a-b** (1 mmol) in an oven-dried, 2 mL reaction vial. The vial was capped and then maintained at 70°C. After 12 h, the solution was concentrated. Purification by silica gel column chromatography using 1% EtOAc/hexane provided allylic trichloroacetamides **22a-b**. Chiral HPLC analysis (Shimazdu, Diacel OD-H column, 0.5-2% IPA/*n*-hexane, 0.8 mL/min) was used to determine the enantiomeric excess of **22a-b**.

Yield of **22a** : 88% (when complex **8** was used) and 82% (when complex **9** was used)

Yield of **22b** : 85% (when complex **8** was used) and 78% (when complex **9** was used)

ee of **22a**: : 9% (when complex **8** was used) and 8% (when complex **9** was used)

ee of **22b**: : 5% (when complex **8** was used) and 4% (when complex **9** was used)

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Chiral multidentate oxazoline ligands based on cyclophosphazene cores: Synthesis, characterization and complexation studies

Dheeraj Kumar, Jatinder Singh and Anil J. Elias *

Chiral oxazoline derivatives of cyclophosphazenes were prepared and their complexation and catalytic studies for the asymmetric rearrangement of trichloroacetimidates to trichloroacetamides has been evaluated.