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PAPER

Transformations of diphenylphosphinothioic acid tertiary amides mediated by directed *ortho* metallation†‡

Hajar el Hajjouji,[a] Eva Belmonte,[a] Jesús García-López,[a] Ignacio Fernández,[a] María José Iglesias,[a] Laura Roces,[b,c] Santiago García-Granda,[b] Anas El Laghdach[d] and Fernando López Ortiz*[a]

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ortho-Lithiation of *N*,*N*-diisopropyl-*P*,*P*-diphenylphosphinothioic amide using *n*-BuLi in the presence of TMEDA in diethyl ether followed by electrophilic trapping is described as an efficient method for the synthesis of *ortho*-functionalised derivatives in high yields. The structural modification of the phosphinothioic amide includes C–X (X = P, S, Si, Sn, I) and C–C bond forming reactions with a large variety of electrophiles. Additional applications based on functional group transformations are also reported. They include imine formation, desulfurization and Suzuki cross-coupling reactions on selected compounds.

1. Introduction

Directed *ortho* metallation (DoM) through an organolithium base followed by electrophilic quench is a well established method for the rational elaboration of aromatic rings.[1,2] The lithiation is promoted by a Directing Metallation Group (DMG). This is a polar functional group that determines the reaction conditions suitable for performing the deprotonation and the regioselectivity that can be achieved. In contrast to the extensively investigated applications of carbon-based DMGs, mainly tertiary carboxamide[3,2c,h] and oxazoline[4] groups, the structural modification of *P*-aryl rings *via* DoM reactions is less developed. The P═O group of phosphine oxides is perhaps the phosphorus-based DMG most studied.[5] DoM reactions of phosphine oxides in combination with aryl-coupling reactions represent a valuable method for synthesising chelating diphosphines containing an atropisomeric biaryl scaffold. These compounds have found widespread uses as chiral ligands in asymmetric catalysis.[6] Other *P*-based functional groups showing the ability of participating in DoM reactions of a *P*-phenyl ring are phosphine–borane complexes,[7] phosphorus ylides,[5a,8] phosphazenes,[9] phosphinic[10] and phosphinothioic amides,[11] phosphonates[12] and phosphonic[13] and thiophosphonic amides.[14] They are represented in Fig. 1, together with the most accepted mechanism of DoM reactions, the so called complex-induced proximity effect (CIPE).[15] In this model, the reactive groups are brought into proximity before the actual deprotonation takes place by forming a complex due to the coordination of the lithium ion of the base to the DMG of the substrate.

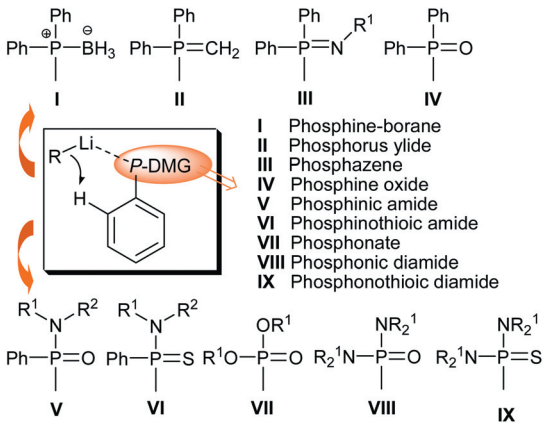
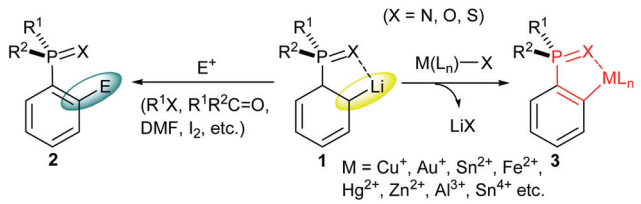


Fig. 1 *P*-Based DMGs.

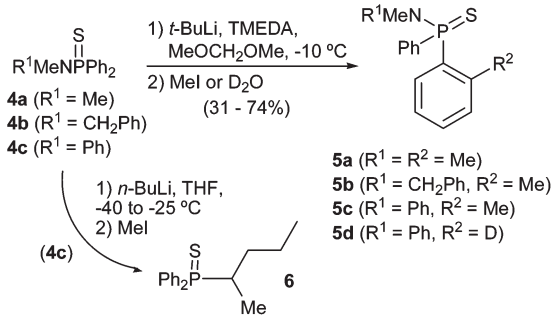
Besides the classical applications of *ortho* anions **1** in carbon–carbon and carbon–heteroatom bond-forming reactions *via* electrophilic quench to give derivatives **2** (Scheme 1), *ortho*-lithiated compounds bearing a P═X (X = N, O and S) group have been used as C,X chelating ligands. Lithium/metal transmetallation reactions of these anions with a variety of metal halides afford complexes **3** containing five-membered metallacycles in which

[a]*Área de Química Orgánica, Universidad de Almería, Carretera de Sacramento, 04120 Almería, Spain. E-mail: flortiz@ual.es; Fax: +34 950015481; Tel: +34 950015478*
[b]*Departamento de Química Física y Analítica, Universidad de Oviedo, Avda. Julián Clavería 8, 33006, Spain*
[c]*Servicios Científico Técnicos, Universidad de Oviedo, 33006 Oviedo, Spain*
[d]*Département de Chimie, Faculté des Sciences, Université Abdelmalek Essaâdi, BP. 2121, Mhannech II, 93002 Tétouan, Morocco*

† Dedicated to Prof. F. Palacios on occasion of his 60th birthday.
‡ Electronic supplementary information (ESI) available: ^{1}H, ^{13}C and ^{31}P NMR spectra of the new products and crystallographic data for **9** and **12**. CCDC 847136 (**9**), 847125 (**12**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ob25395j



Scheme 1 Synthetic applications of *ortho*-lithiated organophosphorus compounds.



Scheme 2 D*o*M of phosphinothioic amides under the conditions of Yoshifushi *et al.*[11].

the strength of the X···M bond can be tuned to the donor ability of the heteroatom present in the P═X moiety. Examples of this chemistry have been reported for almost all P═X derivatives mentioned above, the exceptions being phosphonic amides and phosphinothioic amides.

The previous description shows that efficient D*o*M processes have been established for the phosphorus-based DMGs included in Fig. 1 and the elaboration of the corresponding anions provided access to a great chemical diversity. The only exception is the phosphinothioic amide group. Yoshifuji *et al.*[11] achieved the *ortho*-lithiation of diphenylphosphinothioic amides **4** by treatment with an excess of *tert*-butyllithium in dimethoxymethane in the presence of one equivalent of TMEDA at −10 °C (Scheme 2). The site of lithiation was identified by quenching the anion with D_2O and MeI. In this way, compounds **5** were obtained in moderate to good yield. Using *s*-BuLi as base produced a decrease in the reaction yield (15% of **5b**). Most importantly, in the reaction of **4c** with *n*-BuLi (in THF) followed by quenching with MeI only the product of nucleophilic attack of the base to the phosphorus atom and subsequent PC_α-methylation **6** was observed.

To the best of our knowledge, no further uses of *ortho*-lithium phosphinothioic amides in organic and organometallic chemistry have been reported. However, some features of the N–P═S functional group make it attractive for synthetic applications with respect to the N–P═O analogues. Desulfurization[16] can be achieved under milder reaction conditions than deoxygenation of phosphinic amides to give P(III) derivatives[17] and the presence of the soft sulfur atom may enhance the selectivity for coordinating to soft metal ions.[18]

We have reported the use of *ortho*-lithiated phosphazenes[9g] and phosphinic amides[10d] as C–C–P–X pincer ligands (X = N, O). In order to explore the coordination properties of the analogous C–C–P–S system an efficient procedure for the D*o*M of phosphinothioic amides was required. Here, we describe a general method for the directed *ortho* lithiation of these organophosphorus compounds, the introduction into the N–P(═S)-phenyl framework of large structural diversity through reaction of the *ortho* anion with a variety of electrophiles (alkyl, tin, silicon, and phosphorus halides, sulfur, diiodoethane, benzaldehyde, benzophenone and DMF) and the conversion of *ortho*-functionalised products into more elaborated molecules *via* functional group transformation reactions (condensation, desulfurization and cross-coupling). Chiral phosphinothioic amides were also investigated. However, *ortho*-lithiation proceeded without diastereoselectivity.

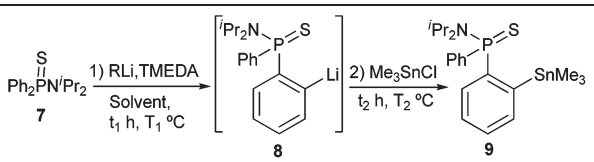
2. Results and discussion

Optimisation of the D*o*M reaction of 7

As the onset of our work we sought to replace the expensive and hazardous *t*-BuLi by the more convenient alkyllithium bases *s*-BuLi or *n*-BuLi. Decreasing the size of the base may favor the nucleophilic attack to the phosphorus leading to products of type **6**. In order to minimize this competing reaction we selected *N*,*N*-diisopropyl-*P*,*P*-diphenylphosphinothioic amide **7** as starting material. The bulky isopropyl groups would hinder the approach of the base to the electrophilic phosphorus center and the absence of *N*–Me or *N*–CH_2Ph groups (present in **4a** and **4b**) would preclude the possibility of lithiation at the *N*–C_α position.[19] Compound **7** was prepared in a yield of 55% by refluxing diisopropylamine and chlorodiphenylphosphine in toluene in the presence of triethylamine during 2 h followed by reaction with elemental sulfur overnight.[20]

The performance of the lithiation of **7** was established by quenching the anion with Me_3SnCl. It is a very good electrophile that proved to be very efficient for trapping *ortho*-lithiated phosphinic amides.[10g] The results of the optimisation of the D*o*M reaction of **7** are shown in Table 1. The first attempt of *ortho*-lithiation with *s*-BuLi in THF at 0 °C during 2 h was unsatisfactory. The desired product was formed in a conversion of 6%

Table 1 Optimisation of the *ortho*-lithiation-stannilation of phosphinothioic amide **7**



Entry	RLi	Solvent	t_1 (h)	T_1 (°C)	t_2 (h)	T_2 (°C)	**9**(%)[a]
1	*s*-BuLi	THF[b]	2	0	2	0	6
2	*n*-BuLi	Toluene	1	−90	0.5	−90	0
3	*n*-BuLi	Toluene	2	−90 → −15	0.5	−15	30
4	*n*-BuLi	Toluene	2	−15	2	−15	74
5	*n*-BuLi	Toluene	2	0	2	0	74
6	*n*-BuLi	Et_2O	2	−90 → 0	2	0	93
7	*n*-BuLi	Et_2O	2	0	2	0	96
8	*n*-BuLi	Et_2O[b]	2	0	2	0	71

[a] Conversion established on the basis of the $^{31}P\{^1H\}$-NMR spectrum of the crude reaction product. [b] TMEDA was not used.

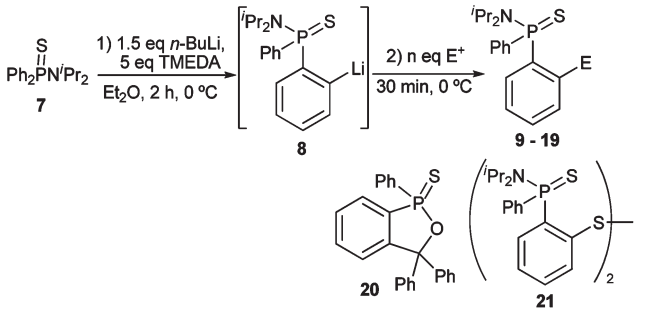
(entry 1). Next, we decided to apply D*o*M conditions similar to those successfully employed in the asymmetric *ortho*-deprotonation of phosphinic amides,[10g] *i.e.*, *n*-BuLi was used as base in toluene at −90 °C in the presence of 5 equiv of TMEDA as achiral surrogate of the chelating diamine (−)-sparteine (entry 2). After quenching the reaction at −90 °C unchanged **7** was fully retrieved. When the reaction was repeated and allowed to reach −15 °C *ortho*-stannylated **9** was obtained in a conversion of 30% (entry 3). Conversion increases to 74% when both the lithiation and quench steps are performed at −15 °C (entry 4). Raising the temperature of the process to 0 °C leads to the same conversion (entry 5). Significantly, at this rather high temperature for a lithiation reaction the phosphinothioic amide DMG resists attack by the base. Phosphine thioxides structurally similar to **6** are not observed. This suggests that TMEDA coordinates to the Li ion of the base to give a bulky complex [*n*-BuLi·TMEDA]$_n$ that cannot access the phosphorus atom blocked by the large N^{i}Pr$_2$ moiety.[21] Since *n*-BuLi exists as a bis-TMEDA-solvated dimer in Et$_2$O/TMEDA solutions,[22] we also assayed the D*o*M reaction of **7** with this combination of reagents and solvent. Phosphinothioic amide **7** and *n*-BuLi in Et$_2$O in the presence of 5 equiv of TMEDA were mixed at −90 °C and the temperature was allowed to rise to 0 °C during 2 h. The subsequent addition of Me$_3$SnCl furnished the desired product **9** in a conversion of 93% (entry 6). The precautionary use of low temperature is not necessary. When the reaction was performed at 0 °C under otherwise the same experimental conditions, compound **9** was obtained in a conversion of 96% (entry 7). Moreover, the process can be carried out in a 1 g scale with the same efficiency (conversion of 97%). The use of a relatively large amount of the complexing agent (5 equiv) seems to be necessary, since the conversion decreased to 71% when only 2 equiv of TMEDA were employed (entry 8).

The structure of **9** was assigned based on the mass spectrum and NMR data. Some key aspects are the ^{119}Sn satellites observed in the ^{31}P NMR spectrum ($^3J_{^{119}Sn^{31}P}$ = 37.9 Hz) and the presence of three H$_{ortho}$ (δ 7.91 ppm, 2H; δ 8.12 ppm, 1H), two pairs of diastereotopic methyl groups (δ 1.18 and 1.37 ppm) and the expected singlet for the SnMe$_3$ group (δ 0.16 ppm) in the ^{1}H NMR spectrum. The results above show that optimal *ortho*-lithiation of **7** requires a much higher temperature (0 °C) than the analogous phosphinic amide (−90 °C),[10g] which indicates that the N–P═S group is a less powerful DMG than the N–P═O moiety. This behavior can be explained based on the CIPE model. In contrast to the matched pair of hard centers represented by the combination oxygen/Li$^+$ in D*o*M of phosphinic amides, the soft sulfur atom of **7** will co-ordinate weakly to the hard Li$^+$. As a consequence, a loose complex will be formed between **7** and the base producing a rather small acidity increase of the *ortho* proton through the inductive effect.

ortho-Functionalisation of 7 using D*o*M methodology

Once experimental conditions were established for the high yield synthesis of *ortho*-stannyl diphenylphosphinothioic amide **9** *via* D*o*M of **7**, we investigated the scope of the method. With this aim, the *ortho*-lithiated species **8** was treated with a variety of electrophiles providing products **9–18** in moderate to high yields (Table 2).

Table 2 Products of *ortho*-lithiation-electrophilic trapping of phosphinothioic amide **7**



Entry	E$^+$	E	Comp.	Conv. (%)	Yield (%)
1	Me$_3$SnCl[a]	Me$_3$Sn	**9**	97	80
2	Me$_2$SnCl$_2$ [a,b]	Me$_2$SnCl	**10**	50	40
3	Me$_3$SiCl	Me$_3$Si	**11**	76	65
4	Ph$_2$PCl[c]	Ph$_2$P	**12**	70	64
5	ICH$_2$CH$_2$I	I	**13**	94	70
6	S$_8$	SH	**14**	71[d]	35 (**19**)[e]
7	S$_8$ + BnBr	SCH$_2$Ph	**15**	82	69
8	MeI	Me	**16**	100	82
9	EtI	Et	**17**	50	38
10	DMF[f]	CH═O	**18**	100	78
11	PhCH═O	PhCHOH	**19**	98[g]	52
12	Ph$_2$C═O[h]	Ph$_2$C–O	**20**	100	88

[a] Reaction time with the electrophile of 2 h. [b] 1.8 Equiv of electrophile were used. [c] Reaction time with the electrophile of 3 h. [d] 12% Of a mixture of *P*-epimeric disulfides **21** (*meso* : *rac*, ratio of 1 : 1) was also obtained. [e] Chromatographic purification produced the dimerization of thiol **14** to give disulfide **21**. [f] 3 Equiv of electrophile were used. [g] Mixture of diastereoisomers in a ratio 18 : 82. [h] 5 Equiv of electrophile were used.

The standard quenching conditions consisted of treating anion **8** with 1.5 equiv of electrophile during 30 min at 0 °C. In some cases, the amount of electrophile added and the time of contact with the anion were slightly varied to improve the performance of the synthesis. Purification of the desired compounds was achieved by flash column chromatography. Carbon–heteroatom bond forming reactions of **8** through halide displacement processes were extended to electrophiles such as Me$_2$SnCl$_2$, Me$_3$SiCl and Ph$_2$PCl (entries 2–4). In this way, the respective *ortho*-functionalised phosphinothioic amides **10**, **11** and **12** were obtained in good yields, except for the chlorostannyl derivative **10**. After some experimentation, we found that compound **10** could be isolated in an acceptable yield of 40% at best by using 1.8 equiv of electrophile. *ortho*-Iodination of **8** with 1,2-diiodoethane proceeded to give **13** which was isolated in a 70% yield after purification (entry 5).

The introduction of an SH group was accomplished by addition of sulfur to the toluene solution of **8**. The *ortho*-mercapto derivative **14** was formed in a 71% conversion (entry 6), together with 12% of the disulfide **21** (1 : 1 mixture of two diastereoisomers arising from the chirality of the phosphorus atoms). Isolation of **14** proved to be cumbersome. Column chromatography purification on silica gel promoted the conversion of thiol **14** into disulfides **21**. Disulfide formation could be avoided by *in situ* alkylation with benzyl bromide of the sulfide generated in the reaction of **8** with S$_8$. This "one-pot" reaction

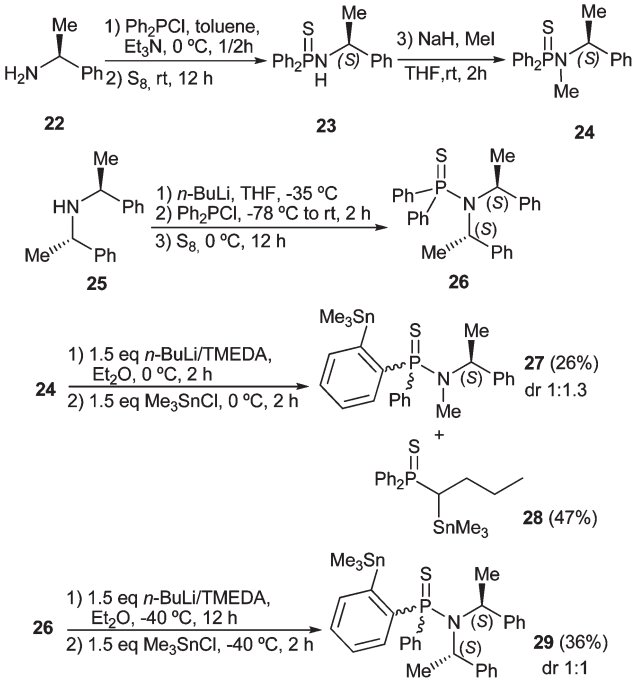
afforded the *S*-protected compound **15** in 69% isolated yield. Anion **8** participated also very efficiently in carbon–carbon bond construction by treatment with a series of *C*-based electrophiles. Methyl iodide, dimethylformamide and benzophenone reacted with **8** quantitatively leading after purification to the *ortho*-functionalised phosphinothioic amide derivatives **16**, **18** and **20**, respectively, in high yields (entries 8, 10 and 12). In the case of the ketone, the alkoxide generated in the addition of the *ortho* anion to the carbonyl group undergoes a cyclocondensation by attack on the phosphorus atom of the N–P═S moiety and subsequent elimination of the diisopropylamide group yielding the thiophosphalactone **20**. Quenching **8** with benzaldehyde provided a mixture of two diastereoisomeric hydroxy(phenyl)-methyl derivatives **19** (conversion of 98%) in a ratio 18 : 82 (entry 11). The major isomer was isolated after precipitation from diethyl ether in 52% yield. Using ethyl iodide as electrophile the reaction reached only 50% conversion (entry 9). The *ortho*-ethyl compound **17** was isolated through column chromatography in a 38% yield. All new compounds were characterized based on their spectroscopic data. Additionally, the crystal structures of **9** and **12** were determined through X-ray diffraction measurements (ESI‡).

The products in Table 2 demonstrate the usefulness of the new D*o*M methodology for accessing *ortho*-functionalised phosphinothioic amides showing wide structural diversity. Furthermore, these compounds can be considered as precursors for further manipulations *via* metal-mediated cross-coupling reactions[23] or functional group transformations for synthesising more complex molecules.

D*o*M reaction with chiral phosphinothioic amides 24 and 26

ortho-Lithiation of **7** implies the desymmetrization of the Ph_2P═S moiety. To augment the scope of the D*o*M process of phosphinothioic amides we decided to explore the introduction of asymmetry. We have previously shown that the *ortho*-lithiation of diphenylphosphinic amides can be carried out both in a diastereo-[10d] and enantioselective manner.[10g] The stereoselectivity observed ranged from low (dr 1 : 1 to 5 : 1) to moderate (ee 60%). The enantioselective D*o*M of phosphinic amides is achieved with [*n*-BuLi·(−)-sparteine] in toluene at −90 °C, *i.e.*, experimental conditions unsuited to the lithiation of **7** (Table 1, entry 2). Hence, we focused on the asymmetric D*o*M of chiral phosphinothioic amides **24** and **26** which contain easily accessible chiral auxiliaries. Compound **24** was synthesized in a two-steps process consisting of the reaction of (*S*)-1-phenylethanamine **22** with Ph_2PCl followed by treatment with S_8 to give (*S*)-*P*,*P*-diphenyl-*N*-(1-phenylethyl)phosphinothioic amide **23**. This compound was transformed into the *N*-methyl derivative **24** *via* deprotonation with NaH and subsequent addition of MeI (Scheme 3). The phosphinothioic amide **25** was prepared in 42% yield through a "one-pot" reaction involving deprotonation of the C_2-symmetric amine (*S*)-bis((*S*)-1-phenylethyl)amine **24** with *n*-BuLi in THF followed by reaction with chlorodiphenylphosphine and subsequent transformation into the P═S derivative by treatment with S_8 (Scheme 3).

As for compound **7**, Me_3SnCl was used as electrophile for establishing the site and extent of *ortho*-lithiation of **24** and **26**.



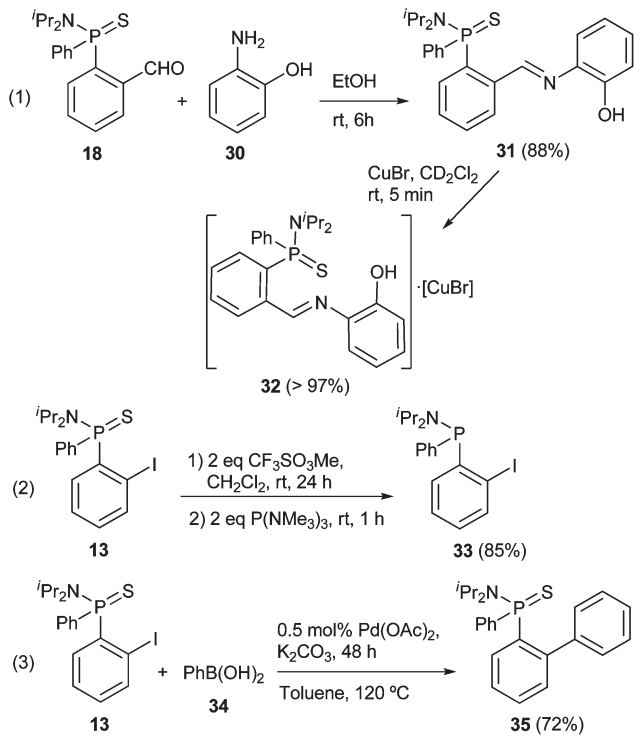
Scheme 3 Synthesis and D*o*M-stannylation of **24** and **26**.

ortho-Lithiation–stannylation of **24** using standard reaction conditions (Table 2) proceeded with a conversion of 73%. However, the major product formed **28** (47%) arise from the nucleophilic attack of the base to the phosphorus and subsequent PC_α-stannylation. The *ortho*-stannylphosphinothioic amides **27** were obtained in a disapointing conversion of 26% as a mixture of diastereoisomers in a ratio 1 : 1.3. The formation of **28** suggests that the phosphorus atom of **24** is more accessible than that of the diisopropyl derivative **7**. This side-reaction would be minimized using the chiral phosphinothioic amide **26** as starting material.

The D*o*M reaction of **26** proved to be challenging. Application of the experimental conditions optimised for **7** (Table 1, entry 7) afforded a complex mixture of products (conversion of 90%). The absence of ^{119}Sn satellites in the ^{31}P NMR spectrum of the crude reaction mixture indicated that neither *ortho*- nor NC_α-stannylation had taken place. After some trial and error experiments the best results were obtained by treating **26** with *n*-BuLi in diethyl ether in the presence of 5 equiv of TMEDA during 12 h at −40 °C followed by addition of Me_3SnCl at the same temperature. After reaction during 2 h, stannanes **29** were obtained in 36% conversion as a 1 : 1 mixture of diastereoisomers (Scheme 3). The same performance was observed when toluene was used as solvent (conversion of 31%, dr 1 : 1). The results obtained indicate that the efficient synthesis of chiral *ortho*-functionalised phosphinothioic amides requires a different approach. This topic is currently under investigation.

Applications of *ortho*-functionalised thiophosphinic amides

The D*o*M methodology developed with phosphinothioic amide **7** afforded compounds **9**–**20** containing functional groups that can be further elaborated to synthesize more complex molecules.



Scheme 4 Condensation, desulfurization and cross-coupling reactions on *ortho*-functionalised phosphinothioic amides **13** and **18**.

As representative examples of the transformations that can be performed, we describe here the application of carbaldehyde derivative **18** to the synthesis of an S,N,O tridentate ligand and two derivatization reactions of the *ortho*-iodophosphinothioic amide **13**, namely desulfurization and palladium-catalyzed Suzuki-coupling reactions (Scheme 4).

Condensation of aldehyde **18** with *o*-aminophenol in ethanol as solvent takes place quantitatively in 6 h. Elimination of the slight excess of aminophenol used *via* semipreparative HPLC gives the imine **31** in 88% isolated yield (eqn (1)). Compound **31** can be envisaged as a tridentate ligand having an S,N,O donor set.[24] Preliminary assays on the ability of **31** to coordinate to metal ions were performed in an NMR tube. The ^{1}H and ^{31}P NMR spectra of a 1 : 1 mixture of **31** and CuBr in CD_2Cl_2 solution showed the presence of a single species. All signals appeared broadened as compared with the free ligand and the chemical shifts were very similar to those of **31**. The high resolution mass spectrum of this species is characterized by an ion at *m*/*z* 499.1032 appropriate for the cation (MCu^{+}) of a 1 : 1 complex **32**.

Metal–ligand bonding was also supported by the IR and ^{13}C NMR spectra. The major changes are observed for the azomethine group: the IR absorption is shifted to lower wavenumbers in the complex ($\Delta\nu$(**31**–**32**) = 22 cm^{-1}) and the carbon signal could not be detected in the ^{13}C NMR spectrum (signal too broad). Small changes in the OH absorption band in the IR spectrum and the C_{ipso} linked to the oxygen in the ^{13}C NMR spectrum of **32** indicate that the oxygen atom is also coordinated to the metal. The OH signal could not be identified in the ^{1}H NMR spectrum. Most probably it was too wide to be detected. In contrast, the P═S group seems to be unaffected by the presence of the metal. The IR and ^{31}P NMR data of the phosphinothioic amide moiety of **31** and **32** are quite similar. These results suggest that in complex **32** the ligand is acting as a bidentate N,O donor.

Aminophosphines are important compounds with applications in diverse fields.[25] This type of products can be accessed *via* desulfurization of *ortho*-functionalised phosphinothioic amides. Desulfurization of **13** was achieved smoothly through *S*-methylation followed by treatment with HMPT (eqn (2)).[16f,26] The reaction proceeds quantitatively. Aminophosphine **33** was isolated in 85% yield after chromatographic purification. Finally, the participation of the *ortho*-iodo derivative **13** in a palladium-catalyzed Suzuki cross-coupling reaction was investigated.[27] The reaction of **13** with phenylboronic acid **34** in the presence of 5 mol% of palladium(II) acetate in toluene at reflux during 48 h affords the biphenylic compound **35** in a yield of 72%.

3. Conclusions

In conclusion, we have achieved the efficient *ortho*-lithiation of phosphinothioic amides through reaction with *n*-butyllithium in diethyl ether in the presence of an excess of TMEDA at 0 °C. Quenching the anion with a variety of carbon- and heteroatom-centered electrophiles afforded *ortho*-functionalised derivatives showing large structural diversity. The *ortho* substituents introduced in this way include Me_3Sn, Me_2SnCl, Me_3Si, Ph_2P, SH, SCH_2Ph, I, Me, Et, CHO, PhCHOH and Ph_2C–O. This methodology provides access to more complex molecules *via* additional manipulations. This statement has been demonstrated *via* imine formation followed by copper(I) complexation, desulfurization and cross-coupling reactions on selected substrates. In all cases, the new derivatives were obtained in high yield without affecting the thiophosphinic amide moiety. Further work in progress is aimed at developing alternative methods for accessing to chiral phosphinothioic amides *via* DoM reactions and to extend the applications of the *ortho*-lithiated species as pincer C,S ligands for the synthesis of metal complexes possessing activity as catalysts.

Experimental section

Reactions involving organolithium reagents were performed under an inert atmosphere of nitrogen using Schlenk techniques. Anhydrous solvents were obtained *via* elution through a solvent column drying system. Commercial reagents were distilled prior to their use, except organolithium bases. TLC was performed on Merck plates with aluminium backing and silica gel 60 F_{254}. Chromatographic separations were performed through semipreparative HPLC or column chromatography using silica gel 60 (40–63 μm). Melting points were recorded on a Büchi B-540 capillary melting point apparatus. Mass spectra were determined by atmospheric pressure chemical ionization (APCI). High resolution mass spectrometry (HRMS) spectra were measured using a LC/MSD-TOF Agilent Technologies instrument. ^{1}H (300.13 MHz), ^{13}C (75.47 MHz) and ^{31}P (121.47 MHz) NMR spectra were measured on a Bruker Avance DPX300 at room temperature using $CDCl_3$ or CD_2Cl_2 as solvent. Chemical shifts are referred to internal tetramethylsilane for ^{1}H and ^{13}C and to

external 85% H_3PO_4 for ^{31}P. IR spectra were run on a FTIR Mattson Genesis II spectrophotometer. Elemental analyses were performed in an Elementar Vario Micro analyser.

X-Ray crystallographic studies of 9 and 12

A suitable crystal of **9** and **12** was covered in Paratone-N and mounted onto a micromount. The crystal was transferred directly to the cold N_2 stream at 100 K of a CCD diffractometer with CuKα (λ = 1.54184 Å) (compound **9**) or MoKα (λ = 0.71073 Å) (compound **12**). The intensities were measured using the oscillation method. The crystal structures were solved by Direct Methods. The refinement was performed using full-matrix least squares on F^2. All non-H atoms were anisotropically refined. All H atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups).

Crystallographic calculations were carried out by the X-Ray Team, at the University of Oviedo, using the following programs: Bruker SMART[28] for data collection and cell refinement and Bruker SAINT[28] for data reduction for **12**; CrysAlis^{Pro} CCD and RES[29] for data collection, cell refinement, data reduction and empirical absorption correction for compound **9**; SIR-92[30] for structure solution; XABS2[31] for refined absorption correction for compound **12**; SHELXL-97[32] for structure refinement; WinGX[33] publication routines and enCIFer[34] for prepare materials for publication; PLATON[35] for the geometrical calculations; ORTEP-3[36] for windows for molecular graphics. Crystal data and structure refinement details for all complexes are outlined on Tables S1 and S2.‡ Crystallographic data (excluding structure factors) for the structures reported in this paper are available as ESI: CCDC: 847136 (**9**), CCDC: 847125 (**12**).‡

Synthesis of *N*,*N*-diisopropyl-*P*,*P*-diphenylphosphinothioic amide 7

Compound **7** has been prepared previously.[20] Spectroscopic data were not reported. We used a different method for synthesizing **7**. Under stirring, chlorodiphenylphosphine (6.48 mL, 35.4 mmol) was added to a solution of diisopropylamine (5 mL, 35.4 mmol) and triethylamine (12.33 mL, 88.5 mmol) in dry toluene (120 mL) at room temperature. The reaction was heated at 120 °C during 2 h and then was cooled down to 0 °C. Sulfur S_8 (1.26 g, 38.9 mmol of atomic S) was added slowly as a solid under a flow of nitrogen. The reaction mixture was stirred at room temperature during 12 h. Extraction with dichloromethane (3 × 20 mL) followed by solvent evaporation under vacuum afforded a crude product, which was purified by precipitation from diethyl ether.

Yield after precipitation 67%. White solid. Mp 147–148 °C. IR (KBr) 970, 755, 711, 671 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.24 (d, $^3J_{HH}$ 6.7 Hz, 12H), 3.58 (ds, $^3J_{PH}$ 16.3, $^3J_{HH}$ 6.7 Hz, 2H), 7.49–7.39 (m, 6HAr), 8.06–8.17 (m, 4HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.0 (d, $^3J_{PC}$ 3.3 Hz, CH_3), 48.7 (d, $^2J_{PC}$ 4.1 Hz, CH), 128.0 (d, $^3J_{PC}$ 12.8 Hz, CH), 131.2 (d, $^4J_{PC}$ 2.9 Hz, CH), 132.5 (d, $^2J_{PC}$ 10.7 Hz, CH), 135.00 (d, $^1J_{PC}$ 102.1 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 63.7 ppm. HRMS (ESI) calcd for $C_{18}H_{25}NPS$: 318.1445 (MH^+), found: 318.1430.

Synthesis of (*S*)-*P*,*P*-diphenyl-*N*-(1-phenylethyl)phosphinothioic amide 23. The same procedure described for the synthesis of **7** was employed, except that the reaction was performed at 0 °C during 30 min using (*S*)-1-phenylethanamine **22** (1.54 mL, 6 mmol) as amine reagent. Yield after chromatography (ethyl acetate–hexane 1 : 1) 53%. Yellow oil. IR (KBr) 3261, 694 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.55 (d, $^3J_{HH}$ 6.7 Hz, 3H), 2.85 (dd, $^2J_{PH}$ 4.7, $^3J_{HH}$ 8.5 Hz, 1H), 4.6 (m, 1H), 7.2–7.54 (m, 11HAr), 7.9 (m, 2HAr), 8.06 (m, 2HAr) ppm. ^{13}C NMR (75.47 MHz) δ 25.4 (d, $^3J_{PC}$ 3.7 Hz, CH_3), 51.7 (CH), 126.3 (CH), 127.1 (CH), 128.2 (d, $^3J_{PC}$ 12.9 Hz, CH), 128.4 (d, $^3J_{PC}$ 12.9 Hz, CH), 128.5 (CH), 131.5 (d, $^4J_{PC}$ 2.9 Hz, CH), 131.6 (d, $^2J_{PC}$ 11.0 Hz, CH), 131.7 (d, $^4J_{PC}$ 3.1 Hz, CH), 131.8 (d, $^2J_{PC}$ 11.3 Hz, CH), 134.2 (d, $^1J_{PC}$ 102.5 Hz, C), 134.9 (d, $^1J_{PC}$ 102.1 Hz, C), 145.0 (d, $^3J_{PC}$ 6.9 Hz, C). ^{31}P NMR (121.47 MHz) δ 59.3 ppm.[37] HRMS (ESI) calcd for $C_{20}H_{21}NPS$: 338.1132 (MH^+), found: 338.1132.

Synthesis of (*S*)-*N*-methyl-*P*,*P*-diphenyl-*N*-(1-phenylethyl)-phosphinothioic amide 24. To a solution of **23** (0.3 g, 0.89 mmol) in THF (10 mL), 0.071 g of NaH (1.78 mmol) were added at 0 °C. The deprotonation was allowed to proceed during 1 h and then MeI (0.11 mL, 1.78 mmol) was added. The reaction was stirred during two additional hours. Then, methanol was added to quench the excess of NaH. The crude reaction mixture was poured into water, extracted with dichloromethane (3 × 20 mL) and the organic layers dried over anhydrous Na_2OS_4. Solvent evaporation under vacuum afforded a crude product, which was purified by column chromatography. Yield after chromatography (ethyl acetate–hexane 1 : 5) 53%. Colourless oil. IR (KBr) 718 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.61 (d, $^3J_{HH}$ 7.0 Hz, 3H), 2.38 (d, $^3J_{PH}$ 12.7 Hz, 3H), 4.97 (dq, $^3J_{PH}$ 10.9, $^3J_{HH}$ 7.0 Hz, 1H), 7.26–7.56 (m, 11HAr), 7.98 (m, 2HAr), 8.04 (m, 2HAr) ppm. ^{13}C NMR (75.47 MHz) δ 16.31 (d, $^3J_{PC}$ 1.5 Hz, CH_3), 28.6 (d, $^2J_{PC}$ 3.0 Hz, CH_3), 53.6 (d, $^2J_{PC}$ 4.2 Hz, CH), 127.0 (CH), 127.6 (CH), 128.2 (CH), 128.4 (d, $^3J_{PC}$ 13.0 Hz, CH), 131.4 (d, $^4J_{PC}$ 1.9 Hz, CH), 131.5 (d, $^4J_{PC}$ 2.0 Hz, CH), 132.1 (d, $^2J_{PC}$ 10.7 Hz, CH), 132.1 (d, $^2J_{PC}$ 10.7 Hz, CH), 133.3 (d, $^1J_{PC}$ 103.3 Hz, C), 133.6 (d, $^1J_{PC}$ 102.7 Hz, C), 141.6 (d, $^3J_{PC}$ 7.5 Hz, C). ^{31}P NMR (121.47 MHz) δ 69.6 ppm. HRMS (ESI) calcd for $C_{21}H_{23}NPS$: 352.1289 (MH^+), found: 352.1275.

Synthesis of *P*,*P*-diphenyl-*N*,*N*-bis((*S*)-1-phenylethyl)phosphinothioic amide 26. To a solution of (1*S*)-1-phenyl-*N*-[(1*S*)-1-phenylethyl]ethanamine **25** (1.14 g, 5.07 mmol) in THF (30 mL) at −35 °C, *n*-BuLi was added dropwise (3.8 mL, 6.08 mmol, 1.6 M in hexane). After 30 min, this solution was added dropwise into a solution of chlorodiphenylphosphine (1.11 mL, 6.08 mmol) in THF (30 mL) at −78 °C. The mixture was allowed to warm to room temperature during 2 h. Then, the reaction was cooled to 0 °C and sulfur S_8 (0.20 g, 6.08 mmol of atom S) was added slowly as a solid under a flow of nitrogen. The reaction mixture was stirred at room temperature during 12 h. Extraction with dichloromethane (3 × 20 mL) followed by solvent evaporation under vacuum afforded a crude product,

which was purified by flash column chromatography (eluent: ethyl acetate–hexane 1 : 10).

Yield after chromatography (ethyl acetate–hexane 1 : 10) 42%. White solid. Mp 82–83 °C. IR (KBr) 927, 752, 719, 697 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.86 (d, $^3J_{HH}$ 7.1 Hz, 6H), 4.87 (dc, $^3J_{PH}$ 17.7, $^3J_{HH}$ 7.1 Hz, 2H), 6.83–6.90 (m, 4HAr), 6.98–7.07 (m, 2HAr), 7.25–7.10 (m, 7HAr), 7.56–7.43 (m, 3HAr), 7.69 (ddd, $^3J_{PH}$ 13.6, $^3J_{HH}$ 8.5, $^4J_{HH}$ 1.3 Hz, 2HAr), 8.17 (ddd, $^3J_{PH}$ 9.6, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.8 Hz, 2HAr) ppm. ^{13}C NMR (75.47 MHz) δ 19.4 (d, $^3J_{PC}$ 2.7 Hz, CH_3), 54.9 (d, $^2J_{PC}$ 3.9 Hz, CH), 127.0 (s, CH), 127.1 (d, $^3J_{PC}$ 12.7 Hz, CH), 127.8 (s, CH), 127.9 (d, $^3J_{PC}$ 13.0 Hz, CH), 128.0 (s, CH), 130.6 (d, $^4J_{PC}$ 3.0 Hz, CH), 131.6 (d, $^4J_{PC}$ 3.0 Hz, CH), 131.9 (d, $^1J_{PC}$ 98.0 Hz, C), 133.4 (d, $^2J_{PC}$ 3.3 Hz, CH), 133.5 (d, $^2J_{PC}$ 2.9 Hz, CH), 134.1 (d, $^1J_{PC}$ 106.3 Hz, C), 142.7 (d, $^3J_{PC}$ 4.4 Hz, CH) ppm. ^{31}P NMR (121.47 MHz) δ 66.4 ppm. MS (API-ES), *m/z*: 442 (M + 1). Analysis: calculated (%) for $C_{28}H_{28}NPS$: C, 76.16; H, 6.39; N, 3.17; S, 7.26. Found: C, 75.85; H, 6.47; N, 2.99; S, 6.95.

General procedure for the synthesis of *ortho*-functionalised phosphinothioic amides 9–19, 21 and thiophosphalactone 20. Over a solution of *N*,*N*-diisopropyl-*P*,*P*-diphenylphosphinothioic amide **7** (300 mg, 0.946 mmol) and TMEDA (0.71 mL, 4.73 mmol) in dry diethyl ether (30 mL) at 0 °C was added a solution of *n*-BuLi (0.89 mL of a 1.6 M solution in hexane, 1.42 mmol). After 2 h of metallation at 0 °C was added 1.5 equiv (1.42 mmol) of the corresponding electrophile (for the reaction of lithiated **7** with dichlorodimethylstannane, *N*,*N*-dimethylformamide and benzophenone the number of equivalents were 1.8, 3 and 5, respectively). The reaction mixture was stirred at 0 °C during 30 min (for the reaction of lithiated **7** with chlorotrimethylstannane and dichlorodimethylstannane this time was increased to 2 h and 3 h, respectively) and then quenched with MeOH. The reaction mixture was poured into water and extracted with dichloromethane (2 × 15 mL). The organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. ^1H, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ NMR spectra of the crude reaction were always measured in order to determine the conversion of the process. The crude mixture was purified by flash column chromatography (silica gel), by semipreparative HPLC or by precipitation from diethyl ether.

***N*,*N*-Diisopropyl-*P*-phenyl-*P*-(2-(trimethylstannyl)phenyl)-phosphinothioic amide 9.** Yield after precipitation from diethyl ether 80%. White solid. Mp 106–107 °C. IR (KBr) 996, 755, 712, 693, 670 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.16 (s, 9H), 1.18 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.37 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.68 (dh, $^3J_{PH}$ 16.0, $^3J_{HH}$ 6.8 Hz, 2H), 7.49–7.35 (m, 5HAr), 7.82 (m, 1HAr), 7.91 (ddd, $^3J_{PH}$ 13.1, $^3J_{HH}$ 6.8, $^4J_{HH}$ 1.6 Hz, 4HAr), 8.12 (m, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 2.8 (CH_3), 23.2 (d, $^3J_{PC}$ 2.9 Hz, CH_3), 23.6 (d, $^3J_{PC}$ 2.9 Hz, CH_3), 48.7 (d, $^2J_{PC}$ 4.1 Hz, CH), 126.8 (d, $^3J_{PC}$ 11.2 Hz, CH), 127.7 (d, $^3J_{PC}$ 12.4 Hz, CH), 129.8 (d, $^4J_{PC}$ 3.3 Hz, CH), 131.1 (d, $^4J_{PC}$ 2.9 Hz, CH), 131.6 (d, $^2J_{PC}$ 11.2 Hz, CH), 133.3 (d, $^2J_{PC}$ 11.2 Hz, CH), 134.9 (d, $^1J_{PC}$ 95.7 Hz, C), 138.5 (d, $^3J_{PC}$ 19.9 Hz, CH), 141.0 (d, $^1J_{PC}$ 111.9 Hz, C), 150.4 (d, $^2J_{PC}$ 27.7 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 68.3 (d, $^3J^{119}_{Sn}{}^{31}_{P}$ 37.9 Hz) ppm. HRMS (ESI) calcd for $C_{21}H_{33}NPSSn$: 482.1093 (MH^+), found: 482.1077.

***P*-(2-(Chlorodimethylstannyl)phenyl)-*N*,*N*-diisopropyl-*P*-phenyl-phosphinothioic amide 10.** Yield after precipitation from diethyl ether 40%. White solid. Mp 178–182 °C (decomp). IR (KBr) 977, 759, 709, 664 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.63 (s, 3H), 1.07 (s, 3H), 1.16 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.30 (d, $^3J_{HH}$ 6.8 Hz, 6H′), 3.61 (ds, $^3J_{PH}$ 16.5, $^3J_{HH}$ 6.8 Hz, 2H), 7.68–7.41 (m, 5HAr), 7.96 (m, 2HAr), 8.05 (ddd, $^3J_{PH}$ 10.5, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz, 1HAr), 8.80 (ddd, $^3J_{PH}$ 4.2, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.4 Hz, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 7.2 (CH_3), 8.4 (d, $^4J_{PC}$ 3.0 Hz, CH_3), 22.7 (d, $^3J_{PC}$ 3.6 Hz, CH_3), 23.3 (d, $^3J_{PC}$ 3.6 Hz, CH_3), 49.2 (d, $^2J_{PC}$ 3.6 Hz, CH), 128.0 (d, $^3J_{PC}$ 11.4 Hz, CH), 128.3 (d, $^3J_{PC}$ 13.2 Hz, CH), 131.2 (d, $^3J_{PC}$ 10.8 Hz, CH), 131.6 (d, $^4J_{PC}$ 3.0 Hz, CH), 131.8 (d, $^1J_{PC}$ 101.5 Hz, C), 132.5 (d, $^4J_{PC}$ 3.0 Hz, CH), 133.4 (d, $^2J_{PC}$ 11.4 Hz, CH), 137.5 (d, $^1J_{PC}$ 112.3 Hz, C), 139.3 (d, $^2J_{PC}$ 19.2 Hz, CH), 149.4 (d, $^2J_{PC}$ 28.8 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 72.5 (d, $^3J^{119}_{Sn}{}^{31}_{P}$ 31.7 Hz) ppm. HRMS (ESI) calcd for $C_{20}H_{29}NPSSn$: 466.0780 ($M - Cl^+$), found: 466.0773.

***N*,*N*-Diisopropyl-*P*-phenyl-*P*-(2-(trimethylsilyl)phenyl)phosphinothioic amide 11.** Yield after purification through semipreparative HPLC using acetonitrile as eluent at a flow rate of 6 mL min^{-1} 65%. White solid. Mp 98–99 °C; IR (KBr) 1241, 962, 839, 752, 726, 693, 675 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 0.10 (s, 9H), 1.12 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.43 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.72 (ds, $^3J_{PH}$ 16.4, $^3J_{HH}$ 6.8 Hz, 2H), 7.35–7.51 (m, 5HAr), 7.77–7.91 (m, 3HAr), 7.99–8.13 (m, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 2.7 (CH_3), 23.4 (d, $^3J_{PC}$ 4.7 Hz, CH_3), 23.5 (d, $^3J_{PC}$ 3.7 Hz, CH_3), 48.7 (d, $^2J_{PC}$ 4.8 Hz, CH), 127.2 (d, $^3J_{PC}$ 12.0 Hz, CH), 127.8 (d, $^3J_{PC}$ 12.6 Hz, CH), 129.4 (d, $^4J_{PC}$ 3.3 Hz, CH), 130.9 (d, $^4J_{PC}$ 2.9 Hz, CH), 131.1 (d, $^2J_{PC}$ 11.5 Hz, CH), 132.7 (d, $^2J_{PC}$ 11.0 Hz, CH), 136.4 (d, $^1J_{PC}$ 94.6 Hz, C), 137.8 (d, $^3J_{PC}$ 17.4 Hz, CH), 141.39 (d, $^1J_{PC}$ 105.9 Hz, C), 146.0 (d, $^2J_{PC}$ 22.7 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 65.2 ppm. HRMS (ESI) calcd for $C_{21}H_{33}NPSSi$: 390.1841 (MH^+), found: 390.1842.

***P*-(2-(Diphenylphosphino)phenyl)-*N*,*N*-diisopropyl-*P*-phenyl-phosphinothioic amide 12.** Yield after chromatography (ethyl acetate–hexane 1 : 20) 64%. White solid. Mp 150–155 °C. IR (KBr) 970, 752, 720, 695, 670 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.14 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.47 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.86 (ds, $^3J_{PH}$ 16.6, $^3J_{HH}$ 6.8 Hz, 2H), 7.04–7.12 (m, 2HAr), 7.13–7.33 (m, 11HAr), 7.40–7.73 (m, 3HAr), 7.78–7.89 (m, 2HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.4 (d, $^3J_{PC}$ 1.7 Hz, CH_3), 23.7 (d, $^3J_{PC}$ 2.9 Hz, CH_3), 48.8 (d, $^2J_{PC}$ 4.6 Hz, CH), 127.5 (s, CH), 127.8 (d, $^3J_{PC}$ 12.9 Hz, CH), 127.8 (d, $^3J_{PC}$ 7.0 Hz, CH), 127.9 (d, $^3J_{PC}$ 7.3 Hz, CH), 128.0 (s, CH), 128.4 (dd, $^3J_{PC}$ 11.7 Hz, $^4J_{PC}$ 1.2 Hz, CH), 130.8 (dd, $^4J_{PC}$ 2.9 Hz, $^3J_{PC}$ 1.0 Hz, CH), 130.6 (d, $^4J_{PC}$ 3.0 Hz, CH), 130.8 (dd, $^2J_{PC}$ 10.2 Hz, $^3J_{PC}$ 7.7 Hz, CH), 131.5 (dd, $^2J_{PC}$ 11.1 Hz, $^5J_{PC}$ 3.2 Hz, CH), 132.9 (d, $^2J_{PC}$ 18.0 Hz, CH), 133.5 (d, $^2J_{PC}$ 20.0 Hz, CH), 137.1 (dd, $^1J_{PC}$ 98.2 Hz, $^4J_{PC}$ 2.2 Hz, C), 137.4 (d, $^1J_{PC}$ 16.5 Hz, C), 139.5 (d, $^1J_{PC}$ 16.2 Hz, C), 139.5 (dd, $^3J_{PC}$ 12.0 Hz, $^2J_{PC}$ 2.4 Hz, CH), 141.6 (dd, $^2J_{PC}$ 23.9 Hz, $^1J_{PC}$ 14.4 Hz, C), 142.8 (dd, $^1J_{PC}$ 103.4 Hz, $^2J_{PC}$ 29.4 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ −17.5 (d, $^3J_{PC}$ 25.1 Hz, P(III)), 63.3 (d, $^3J_{PC}$ 25.1 Hz, P═S) ppm. MS (API-ES), *m/z*: 502 (M + 1). Analysis: Calculated (%)

for $C_{30}H_{33}NP_2S$: C, 71.83; H, 6.63; N, 2.79; S, 6.39. Found: C, 72.02; H, 6.64; N, 2.79; S, 6.21.

***P*-(2-Iodophenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 13.** Yield after precipitation from diethyl ether 70%. White solid. Mp 133–134 °C; IR (KBr) 970, 752, 720, 694, 668 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.14 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.46 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.81 (ds, $^3J_{PH}$ 16.8, $^3J_{HH}$ 6.8 Hz, 2H), 7.12 (m, 1HAr), 7.54–7.40 (m, 4HAr), 7.88 (m, 2HAr), 8.01 (ddd, $^3J_{PH}$ 13.8, $^3J_{HH}$ 6.2, $^4J_{HH}$ 2.0 Hz, 1HAr), 8.07 (ddd, $^3J_{PH}$ 7.8, $^3J_{HH}$ 4.4, $^4J_{HH}$ 1.0 Hz, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.3 (d, $^3J_{PC}$ 1.5 Hz, CH_3), 23.5 (d, $^3J_{PC}$ 2.7 Hz, CH_3), 48.9 (d, $^2J_{PC}$ 4.7 Hz, CH), 100.5 (d, $^2J_{PC}$ 10.5 Hz, C), 127.5 (d, $^4J_{PC}$ 10.9 Hz, CH), 128.1 (d, $^3J_{PC}$ 13.0 Hz, CH), 130.9 (d, $^4J_{PC}$ 2.9 Hz, CH), 131.7 (d, $^3J_{PC}$ 2.9 Hz, CH), 132.0 (d, $^2J_{PC}$ 10.9 Hz, CH), 132.7 (d, $^3J_{PC}$ 9.7 Hz, CH), 134.2 (d, $^1J_{PC}$ 99.2 Hz, C), 137.1 (d, $^1J_{PC}$ 106.7 Hz, C), 143.6 (d, $^2J_{PC}$ 9.9 Hz, CH) ppn. ^{31}P NMR (121.47 MHz) δ 68.0 ppm. HRMS (ESI) calcd for $C_{18}H_{24}NPSI$: 444.0412 (MH^+), found: 444.0413.

***N*,*N*-Diisopropyl-*P*-(2-mercaptophenyl)-*P*-phenylphosphinothioic amide 14.** Conversion 71%. Identified from the crude reaction mixture. IR (KBr) 674 (P═S) 2318, 976, 751, 695, 672 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.23 (d, $^3J_{HH}$ 6.9 Hz, 6H), 1.42 (d, $^3J_{HH}$ 6.9 Hz, 6H), 3.79 (ds, $^3J_{PH}$ 16.7 Hz, $^3J_{HH}$ 6.9 Hz, 2H), 6.78 (d, $^4J_{PH}$ 0.8 Hz, 1HAr), 7.16–7.24 (m, 1HAr), 7.25–7.56 (m, 5HAr), 7.60 (ddd, $^3J_{PH}$ 14.5 Hz $^3J_{HH}$ 7.8 Hz, $^4J_{HH}$ 1.3 Hz, 1HAr), 7.89 (ddd, $^3J_{PH}$ 13.6 Hz, $^3J_{HH}$ 8.2 Hz, $^4J_{HH}$ 1.5 Hz, 2HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.6 (d, $^3J_{PC}$ 2.8 Hz, CH_3), 23.7 (d, $^3J_{PC}$ 2.2 Hz, CH_3), 49.0 (d, $^2J_{PC}$ 4.8 Hz, CH), 124.4 (d, $^3J_{PC}$ 11.7 Hz, CH), 128.1 (d, $^3J_{PC}$ 13.0 Hz, CH), 130.8 (d, $^1J_{PC}$ 99.0 Hz, C), 131.0 (d, $^4J_{PC}$ 2.6 Hz, CH), 131.2 (d, $^4J_{PC}$ 3.0 Hz, CH), 132.1 (d, $^2J_{PC}$ 11.1 Hz, CH), 132.60 (d, $^3J_{PC}$ 10.2 Hz, CH), 132.7 (d, $^2J_{PC}$ 9.5 Hz, CH), 134.7 (d, $^1J_{PC}$ 99.0 Hz, C), 138.9 (d, $^2J_{PC}$ 10.4 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 62.7 ppm.

***P*-(2-(Benzylthio)phenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 15.** Yield after purification through semipreparative HPLC acetonitrile–water 95 : 5 as eluent at a flow rate of 8 mL min^{-1} 65%. Colourless oil; IR (KBr) 971, 748, 694, 671 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.17 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.43 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.79 (ds, $^3J_{PH}$ 16.5 Hz, $^3J_{HH}$ 6.8 Hz, 2H), 4.00 (d, $^2J_{HH}$ 12.9 Hz, 1H), 4.07 (d, $^2J_{HH}$ 12.9 Hz, 1H), 7.12–7.51 (m, 11HAr), 7.84–7.92 (m, 3HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.5 (d, $^3J_{PC}$ 1.9 Hz, CH_3), 23.6 (d, $^3J_{PC}$ 2.8 Hz, CH_3), 39.76 (s, CH_2), 48.80 (d, $^2J_{PC}$ 4.8 Hz, CH), 125.2 (d, $^3J_{PC}$ 11.9 Hz, CH), 126.97 (s, CH), 127.9 (d, $^3J_{PC}$ 13.0 Hz, CH), 128.2 (s, CH), 129.1 (s, CH), 130.5 (d, $^4J_{PC}$ 3.0 Hz, CH), 131.0 (d, $^4J_{PC}$ 2.7 Hz, CH), 131.4 (d, $^2J_{PC}$ 11.1 Hz, CH), 131.7 (d, $^2J_{PC}$ 9.6 Hz, CH), 132.1 (d, $^3J_{PC}$ 10.0 Hz, CH), 135.3 (d, $^1J_{PC}$ 105.7 Hz, C), 136.3 (d, $^1J_{PC}$ 100.4 Hz, C), 136.9 (s, C), 141.5 (d, $^2J_{PC}$ 10.28 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 61.7 ppm. HRMS (ESI) calcd for $C_{25}H_{31}NPS_2$: 440.1635 (MH^+), found: 440.1634.

***N*,*N*-Diisopropyl-*P*-phenyl-*P*-(*o*-tolyl)phosphinothioic amide 16.** Yield after precipitation from diethyl ether 82%. White solid. Mp 115–116 °C. IR (KBr) 974, 753, 691, 663 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$) δ 1.12 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.43 (d, $^3J_{HH}$ 6.8 Hz, 6H), 2.38 (s, 3H), 3.78 (ds, $^3J_{PH}$ 16.6, $^3J_{HH}$ 6.8 Hz, 2H), 7.27 (m, 2HAr), 7.51–7.37 (m, 4HAr), 7.79 (ddd, $^3J_{PH}$ 14.8, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.3 Hz, 2H), 7.89 (ddd, $^3J_{PH}$ 13.2, $^3J_{HH}$ 8.2, $^4J_{HH}$ 1.5 Hz, 2H) ppm. ^{13}C NMR (75.47 MHz) δ 22.5 (d, $^3J_{PC}$ 4.1 Hz, CH_3), 23.4 (d, $^3J_{PC}$ 1.8 Hz, CH_3), 23.6 (d, $^3J_{PC}$ 2.9 Hz, CH_3), 48.7 (d, $^2J_{PC}$ 4.7 Hz, CH), 125.2 (d, $^3J_{PC}$ 12.4 Hz, CH), 128.1 (d, $^3J_{PC}$ 12.6 Hz, CH), 130.8 (d, $^4J_{PC}$ 3.1 Hz, CH), 131.0 (d, $^4J_{PC}$ 2.9 Hz, CH), 131.1 (d, $^2J_{PC}$ 10.1 Hz, CH), 131.5 (d, $^2J_{PC}$ 11.2 Hz, CH), 132.7 (d, $^3J_{PC}$ 11.8 Hz, CH), 133.4 (d, $^1J_{PC}$ 102.9 Hz, C), 136.3 (d, $^1J_{PC}$ 95.3 Hz, C), 141.9 (d, $^2J_{PC}$ 12.0 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 62.0 ppm. HRMS (ESI) calcd for $C_{19}H_{27}NPS$: 332.1602 (MH^+), found: 332.1596.

***P*-(2-Ethylphenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 17.** Yield after chromatography (ethyl acetate–hexane 1 : 50) 38%. White solid. Mp 116–118 °C. IR (KBr) 664 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ 1.11 (t, $^3J_{HH}$ 7.4 Hz, 3H), 1.16 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.43 (d, $^3J_{HH}$ 6.8 Hz, 6H), 2.7 (m, 1H), 2.85 (m, 1H), 3.76 (ds, $^3J_{PH}$ 16.4, $^3J_{HH}$ 6.8 Hz, 2H), 7.2–7.54 (m, 6HAr), 7.79 (m, 1HAr), 7.89 (m, 2HAr) ppm. ^{13}C NMR (75.47 MHz) δ 14.7 (CH_3), 23.5 (d, $^3J_{PC}$ 1.7 Hz, CH_3), 23.6 (d, $^3J_{PC}$ 2.8 Hz, CH_3), 27.1 (d, $^3J_{PC}$ 4.8 Hz, CH_2), 48.8 (d, $^2J_{PC}$ 4.7 Hz, CH), 125.0 (d, $^3J_{PC}$ 12.5 Hz, CH), 128.0 (d, $^3J_{PC}$ 12.7 Hz, CH), 130.5 (d, $^3J_{PC}$ 11.6 Hz, CH), 130.7 (d, $^4J_{PC}$ 3.0 Hz, CH), 131.1 (d, $^2J_{PC}$ 10.6 Hz, CH), 131.2 (d, $^4J_{PC}$ 3.0 Hz, CH), 131.5 (d, $^2J_{PC}$ 11.0 Hz, CH), 133.0 (d, $^1J_{PC}$ 103.1 Hz, C), 137.1 (d, $^1J_{PC}$ 96.3 Hz, C), 148.1 (d, $^2J_{PC}$ 12.0 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 62.1 ppm. HRMS (ESI) calcd for $C_{20}H_{29}NPS$: 346.1758 (MH^+), found: 346.1745.

***P*-(2-Formylphenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 18.** Yield after precipitation from diethyl ether 78%. White solid. Mp 112–113 °C. IR (KBr) 2876, 2770, 1692, 976, 755, 719, 699, 671 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ 1.20 (d, $^3J_{HH}$ 6.6 Hz, 6H), 1.43 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.75 (ds, $^3J_{PH}$ 17.2, $^3J_{HH}$ 6.8 Hz, 2H), 7.55–7.42 (m, 3HAr), 7.65–7.59 (m, 2HAr), 7.81 (m, 1HAr), 7.94 (ddd, $^3J_{PH}$ 13.4, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.4 Hz, 2HAr), 8.06 (m, 1HAr), 10.74 (s, 1H) ppm. ^{13}C NMR (75.47 MHz) δ 23.2 (d, $^3J_{PC}$ 2.2 Hz, CH_3), 23.4 (d, $^3J_{PC}$ 2.5 Hz, CH_3), 49.1 (d, $^2J_{PC}$ 4.6 Hz, CH), 128.3 (d, $^3J_{PC}$ 12.7 Hz, CH), 129.2 (d, $^3J_{PC}$ 9.9 Hz, CH), 131.0 (d, $^2J_{PC}$ 8.5 Hz, CH), 131.4 (d, $^4J_{PC}$ 2.7 Hz, CH), 131.5 (d, $^3J_{PC}$ 3.0 Hz, CH), 131.8 (d, $^2J_{PC}$ 11.1 Hz, CH), 132.2 (d, $^4J_{PC}$ 11.8 Hz, CH), 136.3 (d, $^1J_{PC}$ 96.3 Hz, C), 138.3 (d, $^2J_{PC}$ 8.6 Hz, C), 138.4 (d, $^1J_{PC}$ 100.0 Hz, C), 191.0 (d, $^3J_{PC}$ 6.2 Hz, CH) ppm. ^{31}P NMR (121.47 MHz) δ 58.1 ppm. HRMS (ESI) calcd for $C_{19}H_{25}NOPS$: 346.1394 (MH^+), found: 346.1394.

***P*-(2-(Hydroxy(phenyl)methyl)phenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 19.** Yield after precipitation from diethyl ether 52%. White solid. Mp 181–183 °C. IR (KBr) 3360, 710 cm^{-1}. ^1H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ 1.20 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.48 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.85 (ds, $^3J_{PH}$ 16.8, $^3J_{HH}$ 6.8 Hz, 2H), 4.87 (bs, 1H), 6.18 (s, 1H), 7.03–7.29 (m, 6HAr), 7.37–7.59 (m, 5HAr), 7.94–8.09 (m, 3HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.4 (d, $^3J_{PC}$ 2.9 Hz, CH_3), 23.8 (d, $^3J_{PC}$ 1.8 Hz, CH_3), 49.1 (d, $^2J_{PC}$ 4.5 Hz, CH), 69.3 (d, $^3J_{PC}$ 5.8 Hz, CH), 126.3 (CH), 126.6 (CH), 126.7 (d, $^3J_{PC}$ 11.3 Hz, CH), 127.7 (CH), 128.2 (d, $^3J_{PC}$ 12.9 Hz, CH), 130.6 (d, $^2J_{PC}$ 8.4 Hz, CH), 131.6 (d, $^3J_{PC}$ 11.0 Hz, CH), 131.7 (d, $^4J_{PC}$ 2.9 Hz, CH),

132.0 (d, $^{4}J_{PC}$ 3.0 Hz, CH), 132.3 (d, $^{2}J_{PC}$ 11.4 Hz, CH), 134.2 (d, $^{1}J_{PC}$ 100.0 Hz, C), 135.8 (d, $^{1}J_{PC}$ 95.9 Hz, C), 142.0 (C), 148.6 (d, $^{2}J_{PC}$ 12.3 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 61.2 ppm. HRMS (ESI) calcd for $C_{25}H_{31}NOPS$: 424.1864 (MH^+), found: 424.1864.

1,3,3-Triphenyl-1,3-dihydrobenzo[*c*][1,2]oxaphosphole 1-sulfide 20. Yield after precipitation from diethyl ether 88%. Mp 93–94 °C. IR (KBr) 963, 861, 739, 700, 637 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 7.42–7.21 (m, 12HAr), 7.62–7.48 (m, 6HAr), 7.71 (dd, $^{3}J_{PH}$ 9.9, $^{3}J_{HH}$ 7.5 Hz, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 97.8 (d, $^{3}J_{PC}$ 4.9 Hz, C), 125.6 (d, $^{3}J_{PC}$ 11.9 Hz, CH), 127.4 (CH), 128.0 (CH), 128.1 (d, $^{3}J_{PC}$ 14.3 Hz, CH), 128.2 (CH), 128.2 (d, $^{2}J_{PC}$ 12.8 Hz, CH), 128.3 (CH), 128.4 (CH), 128.6 (CH), 129.7 (d, $^{3}J_{PC}$ 12.4 Hz, CH), 131.4 (d, $^{2}J_{PC}$ 13.2 Hz, CH), 131.9 (d, $^{4}J_{PC}$ 3.1 Hz, CH), 132.0 (d, $^{4}J_{PC}$ 2.9 Hz, CH), 132.8 (d, $^{1}J_{PC}$ 100.3 Hz, C), 134.3 (d, $^{1}J_{PC}$ 107.1 Hz, C), 142.2 (d, $^{3}J_{PC}$ 2.5 Hz, C), 144.1 (d, $^{3}J_{PC}$ 2.5 Hz, C), 147.1 (d, $^{2}J_{PC}$ 17.2 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 94.1 ppm. HRMS (ESI) calcd for $C_{25}H_{20}OPS$: 399.0973 (MH^+), found: 399.0968.

***N*,*N*′-(Disulfanediylbis(2,1-phenylene))bis(*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide) 21.** Yield after chromatography (ethyl acetate–hexane 1 : 9) 35% (mixture 1 : 1 of diastereoisomers). White solid. Mp 100–107 °C (decomp). IR (KBr) 974, 745, 719, 694, 672 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ 1.20 (m, 12H), 1.39 (m, 12H), 3.79 (m, 4H), 7.17–7.23 (m, 2HAr), 7.23–7.32 (m, 2HAr), 7.38–7.52 (m, 6HAr), 7.64–7.75 (m, 4HAr), 7.84–7.93 (m, 4HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.6 (d, $^{3}J_{PC}$ 2.9 Hz, CH_3), 23.6 (d, $^{3}J_{PC}$ 2.9 Hz, CH_3), 23.6 (d, $^{3}J_{PC}$ 2.5 Hz, CH_3), 23.7 (d, $^{3}J_{PC}$ 2.5 Hz, CH_3), 48.9 (d, $^{2}J_{PC}$ 4.7 Hz, CH), 49.0 (d, $^{2}J_{PC}$ 4.7 Hz, CH), 125.0 (d, $^{3}J_{PC}$ 11.6 Hz, CH), 125.1 (d,$^{3}J_{PC}$ 11.4 Hz, CH), 128.0 (d, $^{3}J_{PC}$ 13.0 Hz, CH), 128.4 (d, $^{3}J_{PC}$ 15.7 Hz, CH), 128.6 (d, $^{3}J_{PC}$ 15.7 Hz, CH), 131.1 (d, $^{4}J_{PC}$ 3.1 Hz, CH), 131.1 (d, $^{4}J_{PC}$ 2.9 Hz, CH), 131.5 (d, $^{4}J_{PC}$ 2.7 Hz, CH), 131.5 (d, $^{4}J_{PC}$ 2.7 Hz, CH), 131.8 (d, $^{2}J_{PC}$ 9.3 Hz, CH), 131.8 (d, $^{2}J_{PC}$ 9.5 Hz, CH), 132.1 (d, $^{3}J_{PC}$ 11.2 Hz, CH), 132.1 (d, $^{3}J_{PC}$ 11.2 Hz, CH), 133.7 (d, $^{1}J_{PC}$ 104.8 Hz, C), 133.9 (d, $^{1}J_{PC}$ 104.6 Hz, C), 134.9 (d, $^{1}J_{PC}$ 99.0 Hz, C11), 135.1 (d, $^{1}J_{PC}$ 99.2 Hz, C11), 141.7 (d, $^{2}J_{PC}$ 10.1 Hz, C6), 141.8 (d, $^{2}J_{PC}$ 10.1 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 60.6, 60.4 ppm. HRMS (ESI) calcd for $C_{36}H_{47}N_2P_2S_4$: 697.2097 (MH^+), found: 697.2072.

Procedure for the synthesis of *o*-stannylphosphinothioic amide 27. The general method described above for the synthesis of compounds **9–21** was applied to the preparation of **27** using phosphinothioic amide **24** (0.26 g 0.75 mmol) as starting material. Yield after chromatography (CH_2Cl_2–hexane 30 : 70) 20% (mixture 1 : 1.3 of diastereoisomers). Oil. IR (KBr) 720 cm^{-1}. ^{1}H NMR (300.13 MHz, $CDCl_3$, 25 °C) δ δ 0.16 (s, 9H), 0.17 (s, 9H), 1.61 (d, $^{3}J_{HH}$ 7.0 Hz, 3H), 1.62 (d, $^{3}J_{HH}$ 7.0 Hz, 3H), 2.34 (d, $^{3}J_{PH}$ 11.6 Hz, 3H), 2.36 (d, $^{3}J_{PH}$ 11.0 Hz, 3H), 4.98 (dq, $^{3}J_{PH}$ 10.2, $^{3}J_{HH}$ 7.0 Hz, 1H), 5.08 (dq, $^{3}J_{PH}$ 12.0, $^{3}J_{HH}$ 7.0 Hz, 1H), 7.24–7.22 (m, 2 × 10HAr), 7.59–7.93 (m, 2 × 4HAr) ppm. ^{13}C NMR (75.47 MHz) δ −3.7 (CH_3), −3.6 (CH_3), 16.0 (CH_3), 17.1 (d, $^{2}J_{PC}$ 2.1 Hz, CH_3), 29.1 (d, $^{3}J_{PC}$ 3.2 Hz, CH_3), 29.2 (d, $^{3}J_{PC}$ 3.8 Hz, CH_3), 53.2 (d, $^{2}J_{PC}$ 4.2 Hz, CH), 53.9 (d, $^{2}J_{PC}$ 4.3 Hz, CH), 127.0 (CH), 127.1 (CH), 127.2 (d, $^{3}J_{PC}$ 11.6 Hz, CH), 127.3 (d, $^{3}J_{PC}$ 11.5 Hz, CH), 127.8 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (d, $^{3}J_{PC}$ 12.6 Hz, CH), 128.4 (d, $^{3}J_{PC}$ 12.8 Hz, CH), 129.9 (d, $^{4}J_{PC}$ 3.3 Hz, CH), 130.0 (d, $^{4}J_{PC}$ 3.1 Hz, CH), 131.3 (d, $^{2}J_{PC}$ 11.7 Hz, CH), 131.3 (d, $^{2}J_{PC}$ 11.3 Hz, CH), 131.3 (d, $^{4}J_{PC}$ 3.1 Hz, CH), 131.4 (d, $^{4}J_{PC}$ 3.1 Hz, CH), 132.0 (d, $^{2}J_{PC}$ 10.8 Hz, CH), 132.2 (d, $^{2}J_{PC}$ 10.6 Hz, CH), 133.7 (d, $^{1}J_{PC}$ 98.3 Hz, C), 134.3 (d, $^{1}J_{PC}$ 97.9 Hz, C), 138.3 (d, $^{3}J_{PC}$ 19.6 Hz, CH), 138.5 (d, $^{3}J_{PC}$ 19.8 Hz, CH), 139.4 (d, $^{1}J_{PC}$ 110.7 Hz, C), 139.8 (d, $^{1}J_{PC}$ 110.5 Hz, C), 141.5 (d, $^{3}J_{PC}$ 4.7 Hz, C), 141.7 (d, $^{3}J_{PC}$ 7.1 Hz, C), 150.6 (d, $^{2}J_{PC}$ 26.9 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 72.6 (major), 73.1 (minor) ppm. HRMS (ESI) calcd for $C_{24}H_{31}NPSSn$: 516.0943 (MH^+), found: 516.0943.

Procedure for the synthesis of *o*-stannylphosphinothioic amide 29. Over a solution of **26** (30 mg, 0.068 mmol) and TMEDA (0.20 mL, 0.340 mmol) in dry diethyl ether (5 mL) at −40 °C, was added a solution of *n*-BuLi (0.06 mL of a 1.6 M solution in hexane, 0.102 mmol). After 12 h of metallation at −40 °C was added 20 mg (0.102 mmol) of chlorotrimethylstannane. The reaction mixture was stirred at −40 °C during 2 h and then quenched with MeOH. The reaction mixture was poured into water and extracted with dichloromethane (2 × 15 mL). The organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR spectra of the crude reaction were always measured in order to determine the conversion of the process. The crude mixture was purified by flash column chromatography on silica gel. The best results were obtained using ethyl acetate–hexane 1 : 10 as eluent. This procedure yielded a mixture containing **29** (1 : 1 ratio of diastereoisomers) as the major component.

Conversion 36% (mixture 1 : 1 of diastereoisomers). ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 0.17 (s, 9H), 0.18 (s, 9H), 1.65 (d, $^{3}J_{HH}$ 7.1 Hz, 6H), 1.89 (d, $^{3}J_{HH}$ 7.1 Hz, 6H), 4.92 (dq, $^{3}J_{PH}$ 15.6, $^{3}J_{HH}$ 7.1 Hz, 2H), 5.00 (dq, $^{3}J_{PH}$ 16.4, $^{3}J_{HH}$ 7.1 Hz, 2H), 6.81–6.89 (m, 4HAr), 6.89–6.98 (m, 2HAr), 7.04–7.61 (m, 34HAr), 7.64–8.23 (m, 8HAr). ^{13}C NMR (75.47 MHz) δ −2.6 (d, $^{4}J_{PC}$ 0.8 Hz, CH_3), −2.3 (d, $^{4}J_{PC}$ 0.6 Hz, CH_3), 19.7 (d, $^{3}J_{PC}$ 2.9 Hz, CH_3), 20.5 (d, $^{3}J_{PC}$ 1.7 Hz, CH_3), 55.3 (d, $^{2}J_{PC}$ 3.8 Hz, CH), 55.3 (d, $^{2}J_{PC}$ 4.2 Hz, CH), 126.2 (d, $^{3}J_{PC}$ 11.8 Hz, CH), 126.5 (d, $^{3}J_{PC}$ 11.2 Hz, CH), 126.8 (s, CH), 126.9 (d, $^{3}J_{PC}$ 12.7 Hz, CH), 126.9 (s, CH), 127.7 (s, CH), 127.8 (d, $^{3}J_{PC}$ 12.8 Hz, CH), 127.9 (s, CH), 127.9 (s, CH), 128.5 (s, CH), 129.5 (d, $^{4}J_{PC}$ 3.5 Hz, CH), 130.1 (d, $^{4}J_{PC}$ 3.7 Hz, CH), 130.5 (d, $^{4}J_{PC}$ 2.9 Hz, CH), 131.0 (d, $^{4}J_{PC}$ 2.8 Hz, CH), 132.8 (d, $^{1}J_{PC}$ 101.3 Hz, C), 133.1 (d, $^{2}J_{PC}$ 10.9 Hz, CH), 133.2 (d, $^{2}J_{PC}$ 12.5 Hz, CH), 133.7 (d, $^{2}J_{PC}$ 10.6 Hz, CH), 133.9 (d, $^{2}J_{PC}$ 11.5 Hz, CH), 134.3 (d, $^{1}J_{PC}$ 98.4 Hz, C), 138.1 (d, $^{3}J_{PC}$ 20.1 Hz, CH), 138.5 (d, $^{3}J_{PC}$ 20.3 Hz, CH), 139.7 (d, $^{1}J_{PC}$ 108.3 Hz, C), 139.9 (d, $^{1}J_{PC}$ 113.9 Hz, C), 142.4 (d, $^{3}J_{PC}$ 4.4 Hz, C), 142.8 (d, $^{3}J_{PC}$ 4.1 Hz, C), 150.2 (d, $^{2}J_{PC}$ 27.7 Hz, C), 150.4 (d, $^{2}J_{PC}$ 29.0 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 70.7, 72.6 ppm.

Procedure for the synthesis of imine 31. Over a solution of **18** (100 mg, 0.29 mmol) in ethanol (5 mL) at room temperature, was added 2-aminophenol **30** (35 mg, 0.32 mmol). The reaction was stirred during 6 h. Then, EtOH was removed under reduced pressure. ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR spectra of the crude reaction were measured in order to determine the conversion of

the process. The crude mixture was purified by semipreparative HPLC to give 92 mg of imine **31**.

(*E*)-*P*-(2-(((2-Hydroxyphenyl)imino)methyl)phenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 31. Yield after semipreparative HPLC (acetonitrile as eluent, flow rate of 8 mL min^{-1}) 73%. Yellow oil. IR (KBr) 3414, 1619, 975, 751, 707, 669 cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.22 (d, $^3J_{HH}$ 6.9 Hz, 6H), 1.46 (d, $^3J_{HH}$ 6.9 Hz, 6H), 3.79 (ds, $^3J_{PH}$ 17.5 Hz, $^3J_{HH}$ 6.9 Hz, 2H), 6.64 (dd, $^3J_{HH}$ 8.1 Hz, $^4J_{HH}$ 1.5 Hz, 1HAr), 6.76 (ddd, $^3J_{HH}$ 8.1 Hz, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.3 Hz, 1HAr), 6.93 (dd, $^3J_{HH}$ 8.1 Hz, $^4J_{HH}$ 1.3 Hz, 1HAr), 7.14 (ddd, $^3J_{HH}$ 8.1 Hz, $^3J_{HH}$ 7.4 Hz, $^4J_{HH}$ 1.5 Hz, 1HAr), 7.43–7.56 (m, 3HAr), 7.60 (tdd, $^3J_{HH}$ 7.5 Hz, $^4J_{PH}$ 2.0 Hz, $^4J_{HH}$ 1.5 Hz, 1HAr), 7.67 (ttd, $^3J_{HH}$ 7.5 Hz, $^4J_{HH}$ = $^5J_{PH}$ 1.5 Hz, $^5J_{HH}$ 0.6 Hz, 1HAr), 7.84 (ddd, $^3J_{PH}$ 14.6 Hz, $^3J_{HH}$ 7.5 Hz, $^4J_{HH}$ 1.5 Hz, 1HAr), 7.93–8.05 (m, 2HAr), 8.40 (ddd, $^3J_{HH}$ 7.5 Hz, $^4J_{PH}$ 5.0 Hz, $^4J_{HH}$ 1.5 Hz, 1HAr), 9.48 (s, 1H) ppm. ^{13}C NMR (75.47 MHz) δ 23.0 (d, $^3J_{PC}$ 1.8 Hz, CH_3), 23.3 (d, $^3J_{PC}$ 2.4 Hz, CH_3), 49.0 (d, $^2J_{PC}$ 4.5 Hz, CH), 114.6 (CH), 116.6 (CH), 120.0 (CH), 128.2 (d, $^3J_{PC}$ 12.6 Hz, CH), 128.6 (d, $^3J_{PC}$ 10.2 Hz, CH), 128.8 (CH), 130.1 (d, $^3J_{PC}$ 12.1 Hz, CH), 131.1 (d, $^2J_{PC}$ 8.7 Hz, CH), 131.2 (d, $^4J_{PC}$ 3.0 Hz, 2 × CH), 131.9 (d, $^2J_{PC}$ 11.1 Hz, CH), 135.5 (C), 136.4 (d, $^1J_{PC}$ 99.1 Hz, C), 136.7 (d, $^1J_{PC}$ 96.1 Hz, C), 138.0 (d, $^2J_{PC}$ 8.7 Hz, C), 153.4 (C), 156.5 (d, $^3J_{PC}$ 6.6 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 59.4 ppm. HRMS (ESI) calcd for $C_{25}H_{30}N_2OPS$: 437.1816 (MH^+), found: 437.1820.

Procedure for the synthesis of complex 32. Over a solution of **31** (40 mg, 0.09 mmol) in CD_2Cl_2 (0.5 mL) at 25 °C was added copper(I) bromide (13 mg, 0.09 mmol). The mixture was stirred for 1 min and the brown solution formed was analyzed by NMR spectroscopy. Then, the solvent was removed under reduced pressure affording 50 mg of complex **32**. Yield 94%. Brown solid. Mp 103 °C. IR (KBr) 3417, 1597, 976, 751, 706, 668 cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.21 (d, $^3J_{HH}$ 6.4 Hz, 6H), 1.45 (d, $^3J_{HH}$ 6.4 Hz, 6H), 3.78 (ds, $^3J_{PH}$ 23.3 Hz, $^3J_{HH}$ 6.4 Hz, 2H), 6.58 (d, $^3J_{HH}$ 7.4 Hz, 1HAr), 6.77 (t, $^3J_{HH}$ 7.4 Hz, 1HAr), 6.93 (d, $^3J_{HH}$ 7.4 Hz, 1HAr), 7.12 (t, $^3J_{HH}$ 7.4 Hz, 1HAr), 7.45–7.59 (m, 3HAr), 7.63 (t, $^3J_{HH}$ 7.5 Hz, 1HAr), 7.70 (t, $^3J_{HH}$ 7.3 Hz, 1HAr), 7.89 (dd, $^3J_{PH}$ 14.4 Hz, $^3J_{HH}$ 7.4 Hz, 1HAr), 7.99 (dd, $^3J_{PH}$ 13.0 Hz, $^3J_{HH}$ 6.8 Hz, 2HAr), 8.32 (t, $^3J_{HH}$ = $^4J_{PH}$ 7.3 Hz, 1HAr), 9.26 (s, 1H) ppm. ^{13}C NMR (75.47 MHz) δ 23.0 (d, $^3J_{PC}$ 1.8 Hz, CH_3), 23.3 (d, $^3J_{PC}$ 2.4 Hz, CH_3), 49.0 (d, $^2J_{PC}$ 4.5 Hz, CH), 114.6 (CH), 116.6 (CH), 120.0 (CH), 128.2 (d, $^3J_{PC}$ 12.6 Hz, CH), 128.6 (d, $^3J_{PC}$ 10.2 Hz, CH), 128.8 (CH), 130.1 (d, $^3J_{PC}$ 12.1 Hz, CH), 131.1 (d, $^2J_{PC}$ 8.7 Hz, CH), 131.2 (d, $^4J_{PC}$ 3.0 Hz, 2 × CH), 131.9 (d, $^2J_{PC}$ 11.1 Hz, CH), 135.5 (C), 136.4 (d, $^1J_{PC}$ 99.1 Hz, C), 136.7 (d, $^1J_{PC}$ 96.1 Hz, C), 138.0 (d, $^2J_{PC}$ 8.7 Hz, C), 153.4 (C), 156.5 (d, $^3J_{PC}$ 6.6 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 59.4 ppm. HRMS (ESI) calcd for $C_{25}H_{29}N_2OPSCu$: 499.1034 (MCu^+), found: 499.1032.

Procedure for the synthesis of 1-(2-iodophenyl)-*N*,*N*-diisopropyl-1-phenylphosphinamine 33. To a solution of **13** (100 mg, 0.226 mmol) in dry dichloromethane (20 mL) was added methyl triflate (51 µL, 0.452 mmol) under an inert atmosphere. The resulting solution was stirred at room temperature during 24 h. Then tris(dimethylamino)phosphine (HMPT) was added (82 µL, 0.452 mmol) and the reaction mixture was stirred at 25 °C during 1 h. Afterward, solvent was removed under reduced pressure to yield an oil that was purified by column flash chromatography over silica gel. In this way, 78 mg of aminophosphine **33** were obtained.

Yield after chromatography (dichloromethane) 85%. Mp 118–119 °C. IR (KBr) 1120, 964, 746, 696, 510 cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2, 25 °C) δ 1.03 (d, $^3J_{HH}$ 6.5 Hz, 6H), 1.26 (d, $^3J_{HH}$ 6.5 Hz, 6H), 3.63 (ds, $^3J_{PH}$ 10.6 Hz, $^3J_{HH}$ 6.5 Hz, 2H), 7.03 (dt, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ 1.8 Hz, 1HAr), 7.29–7.41 (m, 5HAr), 7.45 (tt, $^3J_{HH}$ 7.6 Hz, $^4J_{HH}$ = $^4J_{PH}$ 1.0 Hz, 1HAr), 7.67 (ddd, $^3J_{HH}$ 7.6 Hz, $^3J_{PH}$ 2.3 Hz, $^4J_{HH}$ 1.8 Hz, 1HAr), 7.85 (ddd, $^3J_{HH}$ 7.6 Hz, $^4J_{PH}$ 3.2 Hz, $^4J_{HH}$ 1.0 Hz, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 23.6 (d, $^3J_{PC}$ 7.7 Hz, CH_3), 24.4 (d, $^3J_{PC}$ 5.2 Hz, CH_3), 47.6 (d, $^2J_{PC}$ 10.3 Hz, CH), 102.3 (d, $^2J_{PC}$ 40.5 Hz, C), 127.7 (CH), 128.1 (d, $^3J_{PC}$ 7.0 Hz, CH), 128.3 (CH), 129.4 (CH), 132.7 (d, $^2J_{PC}$ 4.1 Hz, CH), 133.2 (d, $^2J_{PC}$ 20.9 Hz, CH), 139.1 (d, $^1J_{PC}$ 8.1 Hz, C), 140.0 (d, $^3J_{PC}$ 2.7 Hz, CH), 144.3 (d, $^1J_{PC}$ 16.3 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 48.3 ppm. HRMS (ESI) calcd for $C_{18}H_{24}NPI$: 412.0691 (MH^+), found: 412.0686.

Procedure for the synthesis of *P*-(biphenyl-2-yl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide 35. To a solution of $Pd(OAc)_2$ (2.6 mg, 5% mol, 11.3 µmol) in dry toluene (10 mL) were added K_2CO_3 (62 mg, 0.452 mmol), *P*-(2-iodophenyl)-*N*,*N*-diisopropyl-*P*-phenylphosphinothioic amide **13** (100 mg, 0.226 mmol) and $PhB(OH)_2$ **34** (41 mg, 0.339 mmol). The reaction mixture was stirred at 120 °C for 48 h and then was cooled to room temperature. A ^{31}P-NMR spectrum of an aliquot was measured in $CDCl_3$ to determine the conversion of the process. Solvent evaporation under reduced pressure provided a yellow solid that was purified by column chromatography on silica gel furnishing 64 mg of biphenyl **35**.

Yield after chromatography (ethyl acetate–hexane, 1 : 3) 72%. Colourless oil. IR (KBr) 970, 750, 692, 661 cm^{-1}. ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.04 (d, $^3J_{HH}$ 6.8 Hz, 6H), 1.44 (d, $^3J_{HH}$ 6.8 Hz, 6H), 3.63 (ds, $^3J_{PH}$ 17.2 Hz, $^3J_{HH}$ 6.8 Hz, 2H), 6.95–7.01 (m, 3HAr) 7.04–7.14 (m, 2HAr), 7.15–7.23 (m, 1HAr), 7.28–7.35 (m, 1HAr), 7.36–7.44 (m, 2HAr), 7.50–7.59 (m, 2HAr), 7.62–7.74 (m, 2HAr), 8.27–8.40 (m, 1HAr) ppm. ^{13}C NMR (75.47 MHz) δ 22.7 (d, $^3J_{PC}$ 2.1 Hz, CH_3), 23.3 (d, $^3J_{PC}$ 2.5 Hz, CH_3), 48.8 (d, $^2J_{PC}$ 4.5 Hz, CH), 126.8 (CH), 126.9 (d, $^3J_{PC}$ 12.0 Hz, CH), 127.2 (CH), 127.0 (s, CH), 127.2 (d, $^3J_{PC}$ 12.8 Hz, CH), 129.9 (d, $^4J_{PC}$ 2.9 Hz, CH), 130.1 (d, $^4J_{PC}$ 0.6 Hz, CH), 130.7 (d, $^4J_{PC}$ 2.9 Hz, CH), 131.6 (d, $^2J_{PC}$ 11.2 Hz, CH), 132.2 (d, $^2J_{PC}$ 9.9 Hz, CH), 133.0 (d, $^3J_{PC}$ 11.2 Hz, CH), 134.1 (d, $^1J_{PC}$ 103.5 Hz, C), 134.4 (d, $^1J_{PC}$ 95.1 Hz, C), 141.3 (d, $^3J_{PC}$ 3.3, C), 145.2 (d, $^2J_{PC}$ 11.2 Hz, C) ppm. ^{31}P NMR (121.47 MHz) δ 62.0 ppm. HRMS (ESI) calcd for $C_{24}H_{29}NPS$: 394.1758 (MH^+), found: 394.1746.

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