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Synthesis and characterisation of severely hindered P-OR compounds

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ABSTRACT

P-Cl substrates were converted into their P-OR analogues from hindered alcohols using an amine base. Where the system was severely hindered, more forcing conditions were required that necessitated the presence of a metal alkoxide nucleophile before successful reactions were observed. In some instances, the products were thermally unstable and reverted to alkenes by elimination reactions, while others were sensitive to moisture. Here, hydrolysis products prevailed if moisture was not rigorously excluded. Details are presented to obtain the P(III) and P(V) esters, diesters and half esters.

1. Introduction

Phosphines and their derivatives play significant roles in co-ordination chemistry and transition-metal catalysis.[1] Systems containing hindered P-OR moieties are useful in the Rh-catalysed hydroformylation reaction amongst others.[2] Alkyl-P(*O*)-OR and alkyl-P(*S*)-OR systems are implicated in some chemical warfare agents and the preparation of the hydrolysis products of such compounds is important in the detection of environmental degradation products of such materials where the manufacture or use of such weapons is suspected.[3] P(*O*) and P(*S*) compounds also have widespread industrial uses as ligands, pesticides, hydraulic fluids and flame retardants.[4]

The synthesis of P-OR compounds has typically been performed using triethylamine or similar amines as base.[5] Hindered phosphinites (R_2POR) have recently been prepared in high yield using some *tert*-alcohols with Ph_2PCl in the presence of DMAP as activator.[6] This approach, i.e., the use of an amine base, has its limitations when using severely hindered alcohols, especially when attempting to prepare phosphonites ($RP(OR)_2$).[7] However, cyclic phosphoramidites (of the MonoPhos™ variety) are readily available from, for example, BINOL by simple reaction thereof with $P(NMe_2)_3$, for example.[8] Such compounds have been used in a variety of impressive asymmetric syntheses.[9] The analogous but more hindered *tert*-alcohol TADDOL-derived phosphoramidites, which have been used in catalysed asymmetric reactions, are prepared via reaction of the TADDOL diol with PCl_3 in the presence of triethylamine,[10] conditions, which fail in non-cyclic instances to generate acyclic phosphite or phosphonite products. As a particular highlight to this problem of steric hindrance, it should be noted that $PhPCl_2$ reacts only once with *t*-BuMgCl, even when the Grignard reagent is present in excess.[11] This problem has not yet been dealt with adequately to allow the general preparation of such P(III) products, from which the P(*O*)-OR and P(*S*)-OR derivatives containing P(V) are available by oxidation techniques using hydrogen peroxide and elemental sulfur, respectively. Alternatively, the P(V)-containing P(*O*)-OR and P(*S*)-OR compounds are synthetically available by directly reacting the P(*O*)-Cl or P(*S*)-Cl precursors with the hindered alcohols,[12] but P(*X*)-Cl substrates are found to be less active than their P(III) counterparts,[13] and tend to promote elimination reactions leading to alkene by-products. Accordingly, there remains a call for attention to this persistent problem, which we investigated for several systems.

2. Results and discussion

2.1. Preparation of hindered P-OR mono- and diesters and their derivatives using an amine base

Reaction of chlorodiphenylphosphine **1** with 1 equiv of the hindered alcohols 2,2-dimethyl-1-propanol, 3-methyl-2-butanol, 3,3-dimethyl-2-butanol and 3-methyl-1-butanol, respectively, in the presence of triethylamine in dry benzene afforded the

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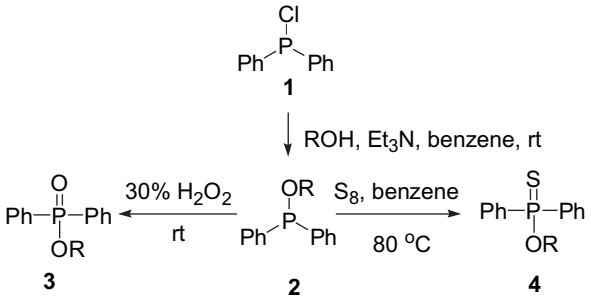
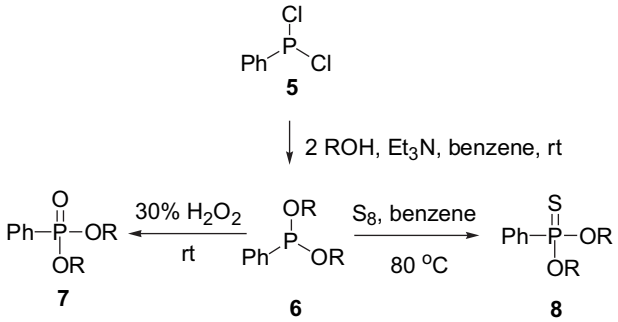
anticipated phosphorus ester products **2a**–**d** (Scheme 1). Typically, attempts of this nature making use of such sterically hindered nucleophiles have been met with degradation of the products to their corresponding alkenes by elimination reactions[14] but the work of Mukaiyama and others has improved on earlier protocols by making use of DMAP as an activator, for example.[6] In contrast, *t*-butylhydroperoxy analogues are well known, and are easily prepared presumably by virtue of the intervening oxygen atom, which somewhat removes the steric hindrance from the crowded P atom. Products **2** were readily converted into their P(V) derivatives upon reaction with hydrogen peroxide or elemental sulfur (Scheme 1).



Scheme 1. **2a** R: 2,2-dimethyl-1-propyl, 86%; **2b** R: 1,2-dimethyl-1-propyl, 76%; **2c** R: 1,2,2-trimethyl-1-propyl, 38%; **2d** R: 3-methyl-1-butyl, 84%; **3a** R: 2,2-dimethyl-1-propyl, 66%; **3b** R: 1,2-dimethyl-1-propyl, 84%; **3c** R: 1,2,2-trimethyl-1-propyl, 68%; **3d** R: 3-methyl-1-butyl, 76%; **4a** R: 2,2-dimethyl-1-propyl, 78%; **4b** R: 1,2-dimethyl-1-propyl, 76%; **4c** R: 1,2,2-trimethyl-1-propyl, 78%; **4d** R: 3-methyl-1-butyl, 72%.

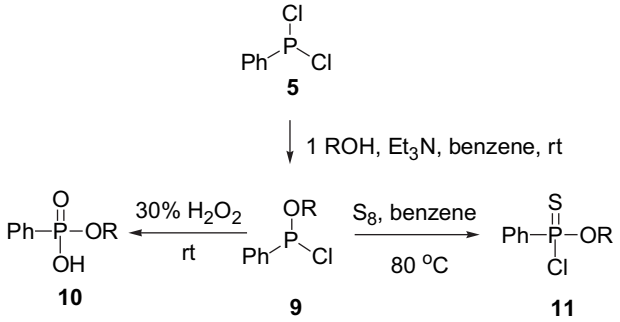
Dichlorophenylphosphine **5** was allowed to react with 2 equiv of the hindered alcohols 2,2-dimethyl-1-propanol, 3-methyl-2-butanol and 3,3-dimethyl-2-butanol, respectively, in the presence of triethylamine in dry benzene (Scheme 2). If the reaction mixture was treated with 30% aqueous hydrogen peroxide and elemental sulfur, respectively, the corresponding P*HP*(*O*)(OR)$_2$ or P*HP*(*S*)(OR)$_2$ products were isolated. These were readily characterised by standard analytical techniques.



Scheme 2. **6a** R: 2,2-dimethyl-1-propyl, 80%; **6b** R: 1,2-dimethyl-1-propyl, 40%; **6c** R: 1,2,2-trimethyl-1-propyl, 76%; **7a** R: 2,2-dimethyl-1-propyl, 46%; **7b** R: 1,2-dimethyl-1-propyl, 44%; **7c** R: 1,2,2-trimethyl-1-propyl, 50%; **8a** R: 2,2-dimethyl-1-propyl, 54%; **8b** R: 1,2-dimethyl-1-propyl, 41%; **8c** R: 1,2,2-trimethyl-1-propyl, 59%.

Interestingly, the ^{31}P NMR spectra and the gas chromatograms of **6b**, **7b** and **8b** each showed three signals. The mass spectra (GC–MS) of *each* of these three compounds for a given product gave the same fragmentation patterns and relative signal ratios of ions, which indicated the existence of stereoisomers. Since the starting alcohols are a racemic mixture of the *R* and *S* enantiomers and each of the products incorporates 2 equiv of these alcohols into their structures, two stereogenic centres are present in which four stereoisomers are possible.[15] These are (*R*,*R*), (*S*,*S*), (*R*,*S*) and (*S*,*R*). Of these, two [(*R*,*S*) and (*S*,*R*)] are different *meso* compounds while the (*R*,*R*) and (*S*,*S*) constitute a pair of enantiomers. In the *meso* products, the P centre is also stereogenic, implying that the *meso* isomers are diastereomeric.

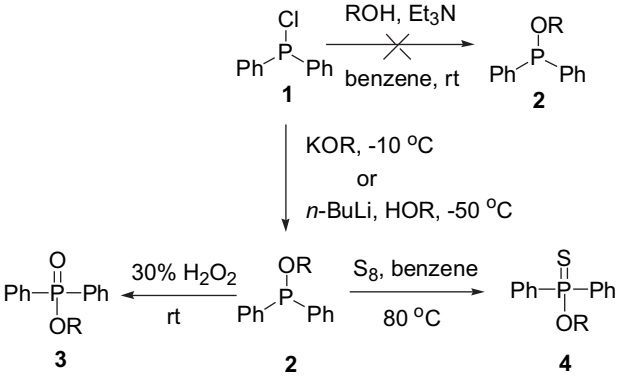
The half esters (**9**, **10** and **11**) of these compounds could also be prepared under conditions where the amount of the nucleophile present was restricted to only 1 equiv (Scheme 3). Isolation of the materials was performed by vacuum distillation in a system in which argon was continuously flushed around the bulb-to-bulb vacuum distillation apparatus to prevent ingression of air. Here, products **9b**, **10b** and **11b** also showed analytical data consistent with two distinct sets of isomers that are diastereomers of each other, indicative of the presence of a stereogenic centre on the alkyl side chain and one at the P atom.



Scheme 3. **9a** R: 2,2-dimethyl-1-propyl, 58%; **9b** R: 1,2-dimethyl-1-propyl, 66%; **9c** R: 1,2,2-trimethyl-1-propyl, 80%; **10a** R: 2,2-dimethyl-1-propyl, 70%; **10b** R: 1,2-dimethyl-1-propyl, 50%; **10c** R: 1,2,2-trimethyl-1-propyl, 82%; **11a** R: 2,2-dimethyl-1-propyl, 59%; **11b** R: 1,2-dimethyl-1-propyl, 47%; **11c** R: 1,2,2-trimethyl-1-propyl, 62%.

2.2. Preparation of severely hindered P-OR esters and their derivatives using improved nucleophiles

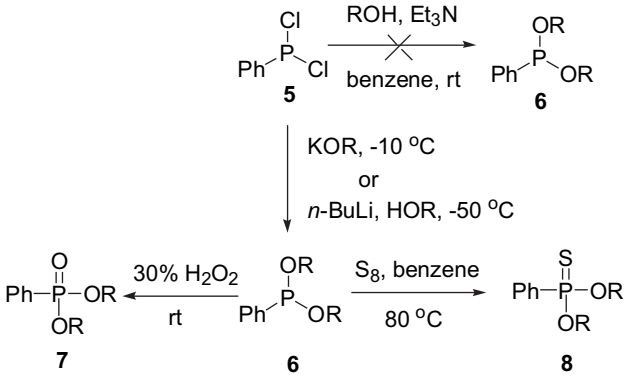
In the cases of the severely hindered alcohols *t*-butanol and 1,1-dimethyl-1-propanol, amine bases failed to facilitate the reaction in question with chlorodiphenylphosphine **1** (Scheme 4), which was successful only when reverting to the analogous lithium or potassium alkoxides. Here, freshly prepared lithium salts were readily available by reaction of the alcohol at −50 °C with *n*-BuLi in diethyl ether. Commercially available KO-*t*-Bu was useful only when freshly opened. Older commercial material consistently gave poor results, as did the use of lithium salts that were not freshly prepared. It is also clear from the yields that these reactions were more demanding than those of the less hindered alcohols. Importantly, it was a requirement for the reactions to be performed at low temperature otherwise little or no product was detected. The P(*O*) and P(*S*) derivatives **3** and **4** could also be isolated after oxidation of intermediates **2e** and **2f** with aqueous hydrogen peroxide or with elemental sulfur.



Scheme 4. **2e**: R: *t*-butyl, 48%; **2f** R: 1,1-dimethyl-1-propyl, 45%; **3e** R: *t*-butyl, 80%; **3f** R: 1,1-dimethyl-1-propyl, 66%; **4e** R: *t*-butyl, 81%; **4f** R: 1,1-dimethyl-1-propyl, 80%.

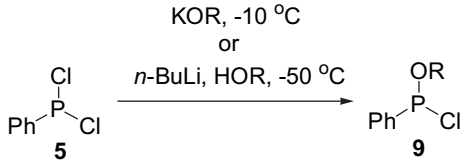
This was also found to be the case with dichlorophenylphosphine **5** as substrate, namely that the metal (Li or K) alkoxides were required before success was achieved (Scheme 5). Here, oxidation

products **7** and **8** underwent slow decomposition at ambient temperature while products **6** were stable under those conditions. Presumably, **7** and **8** underwent elimination reactions to produce the corresponding alkenes and the P(*X*)-OH by-products.[7a]



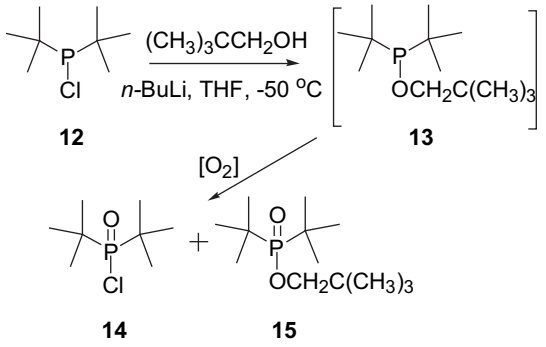
Scheme 5. **6e** R: *t*-butyl, 62%; **6f** R: 1,1-dimethyl-1-propyl, 60%; **7e** R: *t*-butyl, 61%; **7f** R: 1,1-dimethyl-1-propyl, 85%; **8e** R: *t*-butyl, 64%; **8f** R: 1,1-dimethyl-1-propyl, 82%.

The half esters could also be prepared by the same methodology using only 1 equiv of the nucleophile in question (Scheme 6). However, **9f** was so sensitive to hydrolysis and decomposition that it could not be isolated in a pure form but could be identified in the crude reaction mixture.



Scheme 6. **9e** R=*t*-butyl, 58%; **9f** R=1,1-dimethyl-1-propyl (no yield).

Not unexpectedly, di-*t*-butylchlorophosphine also failed to react with any hindered alcohols when simple amine bases were used. This substrate has been found to be particularly intractable by virtue of its steric crowding at the P atom, which precludes many nucleophiles from reacting there. Reaction of the lithium salt of 2,2-dimethylpropanol with this substrate allowed the isolation only of the oxidation product **14** and adduct **15** (Scheme 7). Surprisingly enough, P-Cl compound **14** was stable to hydrolysis and could be isolated by column chromatography, a testament to the severe hindrance about the P atom of that material. The desired compound **15** could be analysed spectroscopically but not isolated in pure form due to its instability.



Scheme 7.

Interestingly, when making use of *t*-butyldichlorophosphine as substrate, the diesters and their oxidation products (Scheme 8) could be obtained with the lithium salt of 2,2-dimethylpropanol (3 equiv) but not with the severely hindered lithium alkoxides of 3-methyl-2-butanol, 3,3-dimethyl-2-butanol, *t*-butanol and 2-methyl-2-butanol. In the latter instances, despite excess alkoxide reagents, the reaction was limited to the half esters **20**, which could be isolated in good yields (Scheme 9) despite heating to reflux temperatures. In the case of the less sterically encumbered lithium 2,2-dimethyl-1-propoxide, the half ester could be isolated if the amount of reagent present was limited to only 1.3 equiv (Scheme 8). With this substrate it appears as if more distal steric bulk allows the reaction to proceed to the diester (using 2,2-dimethylpropoxide) but more proximate bulk imposed even by an addition methyl group (using 3-methyl-2-butanoxide or 3,3-dimethyl-2-butoxide) limits the reaction to the half ester. This finding may be useful in the preparation of mixed esters, should this be called for.

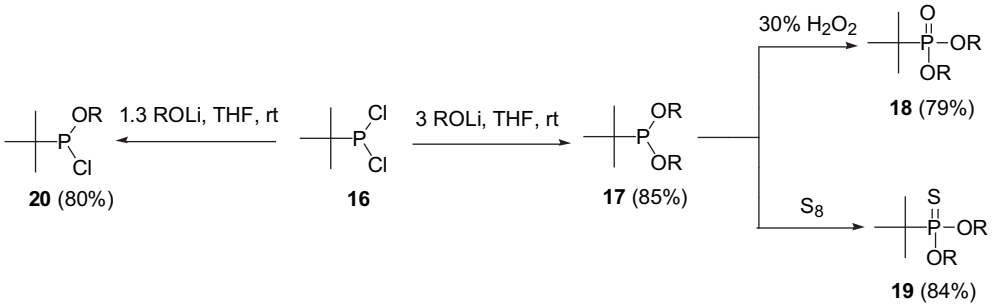
When investigating the mass spectra of the various classes of compound prepared here, several generalisations may be made. For Ph_2POR-type compounds **2**, the major fragmentation pathway involves C–O bond cleavage to afford ions of the type $[Ph_2POH]^+$. A similar dominant fragmentation to a stable ion occurs with the P(*O*) and P(*S*)-oxidised products **3** and **4**, in that a dominant base peak ion of the type $[Ph_2P(X)\text{-}OH]^+$ forms (X=O, S). With products of the $PhP(OR)_2$ **6** and $PhP(S)(OR)_2$ **8** variety a rapid loss of two alkyl groups to the $[PhP(OH)_2]^+$ or $[PhP(S)(OH)_2]^+$ ion ensues leading to weak intermediate ions, while in the case of $PhP(O)(OR)_2$ **7** the $[PhP(O)(OR)(OH)]^+$ ion manifests with medium relative intensity. Half ester intermediate products PhP(OR)Cl **9** were analysed and showed two dominant ions, namely $[PhPCl]^+$ and $[PhP(OH)Cl]^+$. The fragmentation tended to favour generation of the latter ion, which often presented as the base peak, presumably reflecting its stability *vis-à-vis* the former. The PhP(O)(OR)OH **10** and PhP(*S*)(OR)Cl **11** series of compounds also underwent a dominant C–O fragmentation pathway generally to afford $[PhP(O)(OH)_2]^+$ or $[PhP(S)(OH)Cl]^+$-type ions as dominant features of the mass spectra. Finally, *t*-butylphosphine derivatives **20** showed base peaks that dominated the spectra, the ions of which correlated with the stable *t*-butyl ion (*m*/*z* 57).

In conclusion, we have shown the hindered alcohols may sometimes be used as nucleophiles with P-Cl substrates in the presence of amine bases, while severely hindered alcohols require the use of the corresponding alkoxides as nucleophiles before a successful reaction is seen. With such systems, a dominant feature in most mass spectra is the cleavage of the C–O bond, often providing very stable ions that account for the base peaks in the respective spectra. For very hindered substrates, it is possible to isolate the half ester products despite the nucleophile being present in excess, possibly allowing ready access to mixed ester products.

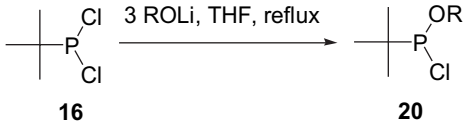
3. Experimental

3.1. General

All reactions were carried out in glassware dried by heating (hot air gun) under vacuum, under an atmosphere of nitrogen. Room temperature (rt) refers to 20–25 °C. All reagents were of synthetic grade and were used without further purification. Solvents were distilled from sodium/benzophenone prior to use. Triethylamine was distilled from sodium hydroxide and alcohols were distilled from magnesium filings prior to use. Melting points were determined on an electrothermal digital melting point apparatus. Nuclear magnetic resonance spectra were measured for $CDCl_3$ solutions on a Varian Gemini 2000 broadband NMR spectrometer at 300 MHz. All chemical shift values for ^1H and ^{13}C nuclei are reported as ppm δ-values downfield of Me_4Si. For ^{31}P NMR spectra, 85% phosphoric acid was used as external standard. The spectral coupling constant (*J* values) are reported in Hertz. Mass spectra were measured on an Agilent 5973 Network Mass Selective Detector running at an ionisation potential of 70 eV, connected to Agilent 6890N network GC system through a heated transfer line



Scheme 8. 17, **18**, **19**, **20a**: R=2,2-dimethyl-1-propyl.



Scheme 9. 20b R: 1,2-dimethyl-1-propyl, 78%; **20c** R 1,2,2-trimethyl-1-propyl, 84%; **20e** R: *t*-butyl, 65%; **20f** R: 1,1-dimethyl-1-propyl, 82%.

(280 °C) and are reported in *m*/*z*. IR Spectra were recorded on a Nicolet Series II Fourier Transform Infra-red Spectrometer at 15 scans per spectrum for neat liquids between potassium bromide disks. The course of the reactions was followed by ^{31}P NMR spectroscopic analysis of the reaction mixture.

3.2. General procedure for the preparation of alkyl diphenylphosphinites (2)

A mixture of the appropriate alcohol (11.0 mmol) and triethylamine (11.0 mmol) in dry benzene (20.0 mL) was added dropwise to chlorodiphenylphosphine (2.44 g, 11.0 mmol) in benzene (25.0 mL) at 0 °C. The ice bath was removed and the reaction mixture was stirred for 2 h at rt, after which petroleum ether (40.0 mL) was added. The precipitated triethylamine hydrochloride salt was filtered off using fine Celite on a sintered glass funnel under a nitrogen atmosphere. The filtrate was concentrated under reduced pressure followed by subjection to vacuum of 0.001 mmHg, to give a colourless oily product, which was analysed without further purification and found to be a pure product in all cases.

*3.2.1. 2,2-Dimethyl-1-propyl diphenylphosphinite (**2a**).* 2.60 g (86%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.60 (dd, 4H, J_{HH}=7.2 Hz, J_{HP}=1.7 Hz), 7.48–7.39 (m, 6H), 3.34 (d, 2H, H-1, J_{HP}=7.1 Hz), 0.95 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.3 (d, J_{CP}=17.2 Hz), 130.1 (d, J_{CP}=21.5 Hz), 129.1 (s), 128.2 (d, J_{CP}=6.9 Hz), 80.0 (d, J_{CP}=16.6 Hz), 33.1 (d, J_{CP}=8.3 Hz), 26.5 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 105.2; EIMS *m*/*z* 272 ([M]$^+$, 10%), 202 ([$C_{12}H_{11}OP$]$^+$, 100%); CI-HRMS $C_{17}H_{21}OP$ calcd 272.1330 found 272.1323; IR (ν_{max} cm^{-1}): 2978 (s, C–H), 1431 (s, *P*-phenyl), 934 (s, P–*O*–C).

*3.2.2. 1,2-Dimethyl-1-propyl diphenylphosphinite (**2b**).* 2.30 g (76%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.72–7.46 (m, 4H), 7.40–7.22 (m, 6H), 3.96–3.85 (m, 1H), 1.90 (dq, 1H, J_{HH}=6.9 Hz, J_{HH}=5.1 Hz), 1.24 (d, 3H, J_{HH}=6.3 Hz), 0.95 (d, 3H, J_{HH}=6.8 Hz), 0.94 (d, 3H, J_{HH}=6.8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.2 (d, J_{CP}=16.0 Hz), 142.5 (d, J_{CP}=14.9 Hz), 130.4 (d, J_{CP}=22.3 Hz), 129.9 (d, J_{CP}=21.5 Hz), 129.0 (s), 128.8 (s), 128.1 (d, J_{CP}=7.1 Hz), 82.2 (d, J_{CP}=18.9 Hz), 34.4 (d, J_{CP}=5.4 Hz), 18.5 (d, J_{CP}=4.9 Hz), 18.2 (s), 17.8 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 106.5; EIMS *m*/*z* 273 ([M+1]$^+$, 10%), 201 ([$C_{12}H_{10}OP$]$^+$, 100%); CI-HRMS $C_{17}H_{21}OP$ calcd 272.1330 found 272.1331; IR (ν_{max} cm^{-1}): 2942 (s, C–H), 1451 (s, *P*-phenyl), 971 (s, P–*O*–C).

*3.2.3. 1,2,2-Trimethyl-1-propyl diphenylphosphinite (**2c**).* 1.20 g (38%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57–7.46 (m, 4H), 7.38–7.26 (m, 6H), 3.74 (dq, 1H, J_{HP}=8.8 Hz, J_{HH}=6.5 Hz), 1.18 (d, 3H, J_{HH}=6.5 Hz), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 144.0 (d, J_{CP}=18.0 Hz), 142.7 (d, J_{CP}=15.7 Hz), 130.5 (d, J_{CP}=22.3 Hz), 129.9 (d, J_{CP}=21.7 Hz), 129.0 (s), 128.8 (s), 128.1 (d, J_{CP}=7.4 Hz), 85.4 (d, J_{CP}=18.6 Hz), 35.6 (d, J_{CP}=6.3 Hz), 26.0 (s), 17.1 (d, J_{CP}=4.6 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 101.4; EIMS *m*/*z* 286 ([M]$^+$, 3%), 202 ([$C_{12}H_{11}OP$]$^+$, 100%); CI-HRMS $C_{18}H_{23}OP$ calcd 286.1487 found 286.1474; IR (ν_{max} cm^{-1}): 2989 (s, C–H), 1438 (s, *P*-phenyl), 944 (s, P–*O*–C).

*3.2.4. 3-Methyl-1-butyl diphenylphosphinite (**2d**).* 2.80 g (84%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.56–7.46 (m, 4H), 7.38–7.20 (d, 6H), 3.87 (dt, 2H, J_{HP}=9.0 Hz, J_{HH}=6.9 Hz), 1.75 (septet, 1H, J_{HH}=6.7 Hz), 1.58 (q, 2H, J_{HH}=6.8 Hz), 0.89 (d, 6H, J_{HH}=6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.2 (d, J_{CP}=17.6 Hz), 130.2 (d, J_{CP}=21.4 Hz) 129.1 (s), 128.2 (d, J_{CP}=6.8 Hz), 68.6 (d, J_{CP}=18.8 Hz), 40.2 (d, J_{CP}=7.7 Hz), 24.7 (s), 22.5 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 110.8; EIMS *m*/*z* 272 ([M]$^+$, 3%, 219 ([$C_{13}H_{16}OP$]$^+$, 3.4%), 203 ([$C_{12}H_{12}OP$]$^+$, 100%), 183 [$C_{12}H_8P$]$^+$, 14%); CI-HRMS $C_{17}H_{21}OP$ calcd 272.1330 found 272.1326; IR (ν_{max} cm^{-1}): 2955 (s, C–H), 1434 (s, *P*-phenyl), 939 (s, P–*O*–C).

*3.2.5. 1,1-Dimethyl-1-ethyl diphenylphosphinite (**2e**).* Potassium *tert*-butoxide (5.5 mL, 1.0 M in THF) was added dropwise to chlorodiphenylphosphine (1.0 mL, 1.22 g, 5.5 mmol) in benzene (25.0 mL) at 0 °C. After the addition, the cold bath was removed and stirring was continued at rt for 2 h. The reaction mixture was transferred to a sintered glass funnel containing fine Celite and filtered. The filtrate was concentrated on a rotary evaporator to give a crude product, which was distilled on a bulb-to-bulb distillation apparatus at 150 °C/60 millitorr give an oily substance (0.65 g, 45%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (dd, 4H, J_{HH}=7.7 Hz, J_{HP}=1.7 Hz), 7.54–7.32 (m, 6H), 1.55 (d, 9H, J_{HP}=0.8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.6 (d, J_{CP}=16.0 Hz), 129.9 (d, J_{CP}=22.0 Hz), 128.6 (s), 128.1 (d, J_{CP}=6.9 Hz), 76.7 (d, J_{CP}=12.3 Hz), 30.1 (d, J_{CP}=8.6 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 79.3; EIMS *m*/*z* 258 ([M]$^+$, 1%), 202 ([$C_{12}H_{11}OP$]$^+$, 100%); CI-HRMS $C_{16}H_{19}OP$ calcd 258.1174 found 258.1173; IR (ν_{max} cm^{-1}): 2975 (s, C–H), 1438 (s, *P*-phenyl), 938 (s, P–*O*–C).

*3.2.6. 1,1-Dimethyl-1-propyl diphenylphosphinite (**2f**).* Potassium 2-methyl-2-butoxide (5.5 mL, 1.0 M in THF) was added dropwise to chlorodiphenylphosphine (1.0 mL, 1.22 g, 5.5 mmol) in toluene (25.0 mL) at 0 °C. After the addition, the cold bath was removed and stirring was continued at rt for 2 h. The reaction mixture was transferred to a sintered glass funnel containing fine Celite and filtered. After removing the solvent, the crude product was distilled on

a bulb-to-bulb distillation set-up at 175 °C/80 millitorr to give an oily substance 0.72 g (48%).

^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58–7.50 (m, 4H), 7.39–7.26 (m, 6H), 1.76 (q, 2H, J_{HH}=7.4 Hz), 1.39 (s, 6H), 0.95 (t, 3H, J_{HH}=7.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 143.8 (d, J_{CP}=16.0 Hz), 130.1 (d, J_{CP}=20.1 Hz), 129.8 (d, J_{CP}=18.5 Hz), 128.6 (s), 128.1 (d, J_{CP}=6.9 Hz), 79.1 (d, J_{CP}=11.5 Hz), 35.6 (d, J_{CP}=6.0 Hz), 27.5 (d, J_{CP}=9.5 Hz), 27.3 (d, J_{CP}=9.5 Hz), 8.8 (d, J_{CP}=14.0 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 78.3; EIMS m/z 243 ($[C_{15}H_{16}OP]^+$, 21%), 203 ($[C_{12}H_{13}OP]^+$, 100%); CI-HRMS $C_{17}H_{21}OP$ calcd 272.1330 found 272.1344; IR (ν_{max} cm^{-1}): 2971 (s, C–H), 1434 (s, *P*-phenyl), 939 (s, P–*O*–C).

3.3. General procedure for the preparation of alkyl diphenylphosphinates (3)

A solution of 30% hydrogen peroxide (3.0 mL) was added to the relevant alkyl diphenylphosphinite in benzene (10.0 mL) and the resulting reaction mixture was stirred at rt for 1 h. Upon the completion of the reaction (^{31}P NMR monitored), water (10.0 mL) was added, followed by extraction with chloroform (3×10.0 mL). The combined organic phase was dried over anhydrous $MgSO_4$ and the solvent was removed on a rotary evaporator. The crude mixture was purified by column chromatography (silica gel, ethyl acetate/hexane 2:3) to give the product of as crystalline material.

*3.3.1. 2,2-Dimethyl-1-propyl diphenylphosphinate (**3a**).* Scale: 0.30 g (1 mmol), yield: 0.21 g (66%); mp 78–79 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89 (dd, 4H, J_{HH}=12.4 Hz, J_{HP}=1.6 Hz), 7.52–7.38 (m, 6H), 3.63 (d, 2H, J_{HP}=4.9 Hz), 1.05 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132.0 (d, J_{CP}=2.6 Hz), 131.6 (d, J_{CP}=136.4 Hz), 131.6 (d, J_{CP}=10.0 Hz), 128.5 (d, J_{CP}=13.1 Hz), 73.8 (d, J_{CP}=6.6 Hz), 32.2 (d, J_{CP}=7.4 Hz), 26.2 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 24.3; EIMS m/z 288 ($[M]^+$, 1%), 273 ($[C_{16}H_{18}O_2P]^+$, 7%), 231 ($[C_{13}H_{12}O_2P]^+$, 6%), 219 ($[C_{12}H_{12}O_2P]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 34%); CI-HRMS $C_{17}H_{21}O_2P$ calcd 288.1279 found 288.1273; IR (ν_{max} cm^{-1}): 2924 (s, C–H), 1439 (s, *P*-phenyl), 1222 (s, P═O), 1019 (s, P–*O*–C).

*3.3.2. 1,2-Dimethyl-1-propyl diphenylphosphinate (**3b**).* Scale: 0.40 g (1.5 mmol), yield: 0.27 g (84%); mp 79–82 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.95–7.72 (m, 4H), 7.69–7.40 (m, 6H), 4.43–4.32 (m, 1H), 2.00 (dq, 1H, J_{HH}=6.9 Hz, J_{HP}=1.8 Hz), 1.30 (d, 3H, J_{HH}=6.6 Hz), 1.01 (d, 3H, J_{HH}=6.9 Hz), 0.98 (d, 3H, J_{HH}=6.7 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132.4 (d, J_{CP}=122.2 Hz), 132.4 (d, J_{CP}=2.6 Hz), 132.1 (d, J_{CP}=123.9 Hz), 131.7 (s), 131.4 (d, J_{CP}=8.6 Hz), 131.3 (d, J_{CP}=9.7 Hz), 128.7 (d, J_{CP}=12.8 Hz), 128.1 (d, J_{CP}=13.4 Hz), 77.6 (d, J_{CP}=6.6 Hz), 33.7 (d, J_{CP}=5.2 Hz), 17.9 (s), 17.7 (s), 17.2 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 23.1; EIMS m/z 288 ($[M]^+$, 0.5%), 245 ($[C_{14}H_{14}O_2P]^+$, 10%), 219 ($[C_{12}H_{12}O_2P]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 79%); CI-HRMS $C_{17}H_{21}O_2P$ calcd 288.1279 found 288.1291; IR (ν_{max} cm^{-1}): 2966 (s, C–H), 1438 (s, *P*-phenyl), 1228 (s, P═O), 1129 (s, P–*O*–C).

*3.3.3. 1,2,2-Trimethyl-1-propyl diphenylphosphinate (**3c**).* Scale: 0.35 g (1.2 mmol); yield: 0.25 g (68%); mp 63–64 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.96–7.74 (m, 4H), 7.70–7.45 (m, 6H), 4.37 (dq, 1H, J_{HP}=8.0 Hz, J_{HH}=6.3 Hz), 1.28 (d, 3H, J_{HH}=6.3 Hz), 1.00 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 131.8 (d, J_{CP}=2.6 Hz), 131.8 (d, J_{CP}=2.9 Hz), 131.6 (d, J_{CP}=10.2 Hz), 131.5 (d, J_{CP}=10.3 Hz), 129.9 (d, J_{CP}=134.4 Hz), 129.7 (d, J_{CP}=135.8 Hz), 128.3 (d, J_{CP}=13.1 Hz), 80.8 (d, J_{CP}=7.2 Hz), 35.2 (d, J_{CP}=6.0 Hz), 25.8 (s), 17.1 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 22.7; EIMS m/z 302 ($[M]^+$, 1%), 245 ($[C_{14}H_{14}O_2P]^+$, 26%), 219 ($[C_{12}H_{12}O_2P]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 93%); CI-HRMS $C_{18}H_{23}OP$ calcd 302.1436 found 302.1423; IR (ν_{max} cm^{-1}): 2963 (s, C–H), 1438 (s, *P*-phenyl), 1223 (s, P═O), 958 (s, P–*O*–C).

*3.3.4. 3-Methyl-1-butyl diphenylphosphinate (**3d**).* Scale: 0.60 g, yield: 0.54 g (86%); mp 55–57 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.02 (dd, 4H, J_{HH}=12.0 Hz, J_{HP}=6.6 Hz), 7.80–7.60 (m, 6H), 4.25 (dt, 2H, J_{HP}=13.4 Hz, J_{HH}=6.7 Hz), 2.00 (septet, 1H, J_{HH}=6.7 Hz), 1.82 (q, 2H, J_{HH}=6.7 Hz), 1.10 (d, 6H, J_{HH}=6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132.0 (d, J_{CP}=2.6 Hz), 131.5 (d, J_{CP}=10.0 Hz), 131.5 (d, J_{CP}=136.3 Hz), 128.4 (d, J_{CP}=13.1 Hz), 63.3 (d, J_{CP}=6.0 Hz), 39.2 (d, J_{CP}=6.5 Hz), 24.6 (s), 22.3 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 30.1; EIMS m/z 288 ($[M]^+$, 0.2%), 245 ($[C_{14}H_{14}O_2P]^+$, 17%), 219 ($[C_{12}H_{12}O_2P]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 25%); CI-HRMS $C_{17}H_{21}O_2P$ calcd 288.1279 found 288.1284; IR (ν_{max} cm^{-1}): 2960 (s, C–H), 1439 (s, *P*-phenyl), 1223 (s, P═O), 1129 (s, P–*O*–C).

*3.3.5. 1,1-Dimethyl-1-ethyl diphenylphosphinate (**3e**).* Scale: 0.60 g (2.3 mmol); yield: 0.51 g (80%); mp 107–109 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (dd, 4H, J_{HH}=12.5 Hz, J_{HP}=1.7 Hz), 7.48–7.32 (m, 6H), 1.59 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 134.6 (d, J_{CP}=138.6 Hz), 131.4 (J_{CP}=2.9 Hz), 131.3 (d, J_{CP}=10.3 Hz), 128.2 (d, J_{CP}=13.2 Hz), 83.6 (d, J_{CP}=8.3 Hz), 30.9 (d, J_{CP}=3.7 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 19.4; EIMS m/z 259 ($[M\text{-}CH_3]^+$, 1%), 219 ($[C_{12}H_{12}O_2P]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 29%); CI-HRMS $C_{16}H_{19}O_2P$ calcd 274.1123 found 274.1123; IR (ν_{max} cm^{-1}): 2989 (s, C–H), 1438 (s, *P*-phenyl), 1224 (s, P═O), 1109 (s, P–*O*–C).

*3.3.6. 1,1-Dimethyl-1-propyl diphenylphosphinate (**3f**).* Scale: 0.50 g (1.8 mmol); yield: 0.43 g (81%); mp 65–66 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (dd, 4H, J_{HH}=12.4 Hz, J_{HP}=1.6 Hz), 7.45–7.33 (m, 6H), 1.76 (q, 2H, J_{HH}=7.4 Hz), 1.42 (s, 6H), 0.94 (t, 3H, J_{HH}=7.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 134.6 (d, J_{CP}=139.1 Hz), 131.4 (s), 131.2 (d, J_{CP}=10.0 Hz), 128.2 (d, J_{CP}=13.2 Hz), 86.5 (d, J_{CP}=9.2 Hz), 36.5 (d, J_{CP}=5.2 Hz), 28.0 (d, J_{CP}=30.6 Hz, 2C), 8.70 (d, J_{CP}=14.0 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 19.3; EIMS m/z 273 ($[M\text{-}CH_3]^+$, 5%), 259 ($[C_{15}H_{16}O_2P]^+$, 19%), 219 ($[C_{12}H_{12}O_2P]^+$, 100%), 201 ($[C_{12}H_{11}OP]^+$, 82%); CI-HRMS $C_{17}H_{21}O_2P$ calcd 288.1279 found 288.1283; IR (ν_{max} cm^{-1}): 2978 (s, C–H), 1437 (s, *P*-phenyl), 1228 (s, P═O), 1124 (s, P–*O*–C).

3.4. General procedure for the preparation of alkyl diphenylphosphinothioates (4)

A mixture of alkyl diphenylphosphinite and 1.1 equiv of elemental sulfur dissolved in toluene was heated at reflux for 2 h. The progress of the conversion was monitored by ^{31}P NMR analysis. Upon completion of the reaction, the reaction mixture was cooled to room temperature. The excess sulfur was filtered off and the filtrate was concentrated on a rotary evaporator to give a solid crude product, which was further purified by column chromatography (silica gel, ethyl acetate/hexane 1:4).

*3.4.1. 2,2-Dimethyl-1-propyl diphenylphosphinothioate (**4a**).* Scale: 0.30 g (1.1 mmol); yield: 0.26 g (78%); mp 88–90 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.90 (dd, 4H, J_{HH}=12.8 Hz), 7.54–7.34 (m, 6H), 3.53 (d, 2H, J_{HP}=5.8 Hz), 0.87 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 134.4 (d, J_{CP}=110.5 Hz), 131.5 (d, J_{CP}=2.9 Hz), 130.9 (d, J_{CP}=11.5 Hz), 128.2 (d, J_{CP}=13.5 Hz), 73.6 (d, J_{CP}=6.6 Hz), 31.9 (d, J_{CP}=8.5 Hz), 26.3 (s); ^{31}P NMR ($CDCl_3$, 121.1 MHz): δ 74.1; EIMS m/z 304 ($[M]^+$ 40%), 235 ($[C_{12}H_{12}OPS]^+$, 36%), 218 ($[C_{12}H_{11}PS]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 21%); CI-HRMS $C_{17}H_{21}OPS$ calcd 304.1051 found 304.1046; IR (ν_{max} cm^{-1}): 2952 (s, C–H), 1436 (s, *P*-phenyl), 1111 (s, P–*O*–C), 730 (s, P═S).

*3.4.2. 1,2-Dimethyl-1-propyl diphenylphosphinothioate (**4b**).* Scale: 0.60 g (2.0 mmol); yield: 0.52 g (76%); mp 68–70 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.15–7.74 (m, 4H), 7.54–7.38 (m, 6H), 4.68 (dq, 1H, J_{HH}=6.3 Hz, J_{HP}=4.7 Hz), 1.88 (dq, 1H, J_{HH}=6.9 Hz), 1.12 (d, 3H, J_{HH}=6.3 Hz), 0.91 (d, 3H, J_{HH}=6.9 Hz), 0.88 (d, 3H, J_{HH}=6.8 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.9 (d, J_{CP}=109.1 Hz), 135.8 (d, J_{CP}=113.7 Hz), 131.5 (d, J_{CP}=2.9 Hz), 131.4 (d, J_{CP}=3.1 Hz), 131.2 (d,

J_{CP}=11.2 Hz), 130.9 (d, J_{CP}=11.5 Hz), 128.2 (d, J_{CP}=13.2 Hz), 77.9 (d, J_{CP}=5.4 Hz), 33.7 (d, J_{CP}=5.4 Hz), 18.0 (s), 17.7 (s), 17.4 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 72.2; EIMS *m/z* 235 ($[C_{12}H_{12}OPS]^+$, 100%), 217 ($[C_{12}H_{10}PS]^+$, 32%), 201 ($[C_{12}H_{10}OP]^+$, 29%); CI-HRMS $C_{17}H_{21}OPS$ calcd 304.1051 found 304.1044; IR (ν_{max} cm^{-1}): 2967 (s, C–H), 1435 (s, *P*-phenyl), 1116 (s, P–*O*–C), 726 (s, P=S).

*3.4.3. 1,2,2-Trimethyl-1-propyl diphenylphosphinothioate (**4c**).* Scale: 0.50 g (1.7 mmol); yield: 0.43 g (78%); mp 63–64 °C; ^{1}H NMR ($CDCl_3$): δ 8.04–7.86 (m, 4H), 7.60–7.44 (m, 6H), 4.70 (sextet, 1H, J_{HH}=6.6 Hz), 1.07 (d, 3H, J_{HH}=6.6 Hz), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 136.2 (d, J_{CP}=107.9 Hz), 135.9 (d, J_{CP}=115.7 Hz), 131.5 (d, J_{CP}=2.9 Hz), 131.3 (d, J_{CP}=3.1 Hz), 131.2 (d, J_{CP}=11.5 Hz), 130.7 (d, J_{CP}=11.2 Hz), 128.2 (d, J_{CP}=13.5 Hz), 128.2 (d, J_{CP}=13.4 Hz), 81.1 (d, J_{CP}=7.4 Hz), 35.1 (d, J_{CP}=6.6 Hz), 26.0 (s), 16.9 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 72.1; EIMS *m/z* 318 ([M]$^+$, 24%), 234 ($[C_{12}H_{11}OPS]^+$, 91%), 218 ($[C_{12}H_{12}PS]^+$, 100%), 201 ($[C_{12}H_{10}OP]^+$, 28%); CI-HRMS $C_{18}H_{23}OPS$ calcd 318.1207 found 318.1196; IR (ν_{max} cm^{-1}): 2965 (s, C–H), 1437 (s, *P*-phenyl), 1109 (s, P–*O*–C), 718 (s, P=S).

*3.4.4. 3-Methyl-1-butyl diphenylphosphinothioate (**4d**).* Scale: 1.00 g (3.6 mmol); yield: 0.80 g (73%); mp 77–79 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.92–7.86 (m, 4H), 7.54–7.34 (m, 6H), 4.02 (q, 2H, J_{HH}=6.8 Hz), 1.76 (septet, 1H, J_{HH}=6.7 Hz), 1.59 (q, J_{HH}=6.8 Hz), 0.88 (d, 6H, J_{HH}=6.3 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 134.5 (d, J_{CP}=109.6 Hz), 131.7 (d, J_{CP}=2.8 Hz), 131.0 (d, J_{CP}=11.3 Hz), 128.3 (d, J_{CP}=13.1 Hz), 63.3 (d, J_{CP}=5.9 Hz), 38.9 (d, J_{CP}=7.9 Hz), 24.6 (s), 22.4 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 80.4; EIMS *m/z* 304 ([M]$^+$, 5%), 235 ($[C_{12}H_{12}OPS]^+$, 100%), 217 ($[C_{12}H_{10}PS]^+$, 19%), 201 ($[C_{12}H_{10}OP]^+$, 33%), 183 ($[C_{10}H_{16}OP]^+$, 12%); CI-HRMS $C_{17}H_{21}OPS$ calcd 304.1051 found 304.1063; IR (ν_{max} cm^{-1}): 2956 (s, C–H), 1437 (s, *P*-phenyl), 1114 (s, P–*O*–C), 727 (s, P=S).

*3.4.5. 1,1-Dimethy-1-ethyl diphenylphosphinithioate (**4e**).* Scale: 0.45 g (1.7 mmol); yield: 0.33 g (66%); mp 79–80 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.98 (dd, 4H, J_{HH}=13.6 Hz, J_{HP}=1.8 Hz), 7.62–7.38 (m, 6H), 1.64 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.4 (d, J_{CP}=112.5 Hz), 131.1 (d, J_{CP}=2.9 Hz), 130.8 (d, J_{CP}=11.4 Hz), 128.1 (d, J_{CP}=13.5 Hz), 85.2 (d, J_{CP}=8.3 Hz), 30.6 (d, J_{CP}=3.7 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 63.9; EIMS *m/z* 290 ([M]$^+$, 3%), 234 ($[C_{12}H_{11}OPS]^+$, 100%), 217 [($C_{12}H_{10}PS]^+$, 11%), 201 ($[C_{12}H_8OP]^+$, 11%); CI-HRMS $C_{16}H_{19}OPS$ calcd 290.0894 found 290.0888; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1437 (s, *P*-phenyl), 1105 (s, P–*O*–C), 734 (s, P=S).

*3.4.6. 1,1-Dimethyl-1-propyl diphenylphosphinothioate (**4f**).* Scale: 0.50 g (1.8 mmol); yield: 0.44 g (80%); mp 65–66 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (dd, 4H, J_{HH}=13.8 Hz, J_{HP}=2.0 Hz), 7.45–7.35 (m, 6H), 1.85 (q, 2H, J_{HH}=7.4 Hz), 1.48 (s, 6H), 0.95 (t, 3H, J_{HH}=7.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.5 (d, J_{CP}=111.9 Hz), 131.1 (d, J_{CP}=2.9 Hz), 130.8 (d, J_{CP}=11.1 Hz), 128.1 (d, J_{CP}=13.4 Hz), 87.9 (d, J_{CP}=9.2 Hz), 36.5 (d, J_{CP}=4.6 Hz), 27.6 (s), 8.7 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 63.8; EIMS *m/z* 291 ($[C_{16}H_{20}OPS]^+$, 3%), 234 ($[C_{12}H_{11}OPS]^+$, 100%), 215 ($[C_{12}H_8PS]^+$, 11%), 199 ($[C_{12}H_{10}OP]^+$, 11%); CI-HRMS $C_{17}H_{21}OPS$ calcd 304.1051 found 304.1075; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1436 (s, *P*-phenyl), 1111 (s, P–*O*–C), 729 (s, P=S).

3.5. General procedure for the preparation of dialkyl phenylphosphonites (6a–c)

A mixture of appropriate anhydrous alcohol (30.0 mmol) and triethylamine (3.00 g, 29.7 mmol) in toluene 20.0 mL was added dropwise to dichlorophenylphosphine (2.60 g, 14.5 mmol) in toluene (25.0 mL) at 0 °C at such a rate that the temperature did not exceed 10 °C. The ice bath was removed and the reaction mixture was stirred for 2 h at rt, after which it was diluted with dry petroleum ether (40.0 mL). The precipitated triethylamine hydrochloride was filtered off using fine Celite and a sintered glass funnel under argon. The filtrate was concentrated on a rotary evaporator followed by followed by subjection to vacuum of 0.001 mmHg, to give a colourless oil product, which was analysed without further purification and found to be pure.

*3.5.1. Di-(2,2-dimethyl-1-propyl) phenylphosphonite (**6a**).* Yield: 3.20 g (80%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.63 (dd, 2H, J_{HH}=6.5 Hz, J_{HP}=2.0 Hz), 7.42–7.37 (m, 3H), 3.54 (dd, 2H, J_{HP}=9.6 Hz, J_{HH}=6.9 Hz), 3.40 (dd, 2H, J_{HP}=9.6 Hz, J_{HH}=5.1 Hz), 0.94 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.6 (d, J_{CP}=20.6 Hz), 130.4 (s), 130.0 (d, J_{CP}=7.1 Hz), 128.4 (d, J_{CP}=4.8 Hz), 76.2 (d, J_{CP}=7.1 Hz), 32.4 (d, J_{CP}=8.3 Hz), 26.4 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 147.1; EIMS *m/z* 282 ([M]$^+$, 6%), 212 ($[C_{11}H_{16}O_2P]^+$, 6%), 195 ($[C_{11}H_{16}OP]^+$, 5%), 142 ($[C_6H_7O_2P]^+$, 100%), 125 ($[C_6H_6OP]^+$, 20%); CI-HRMS $C_{14}H_{31}O_2P$ calcd 262.2062 found 262.2071; IR (ν_{max} cm^{-1}): 2962 (s, C–H), 1482 (s, *P*-phenyl), 1010 (s, P–*O*–C).

*3.5.2. Di-(1,2-dimethyl-1-propyl) phenylphosphonite (**6b**, three isomers).* Scale: 0.89 g, 5.0 mmol; yield 0.56 g (40%); bp 140 °C/60 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.70–7.50 (m, 2H), 7.45–7.30 (m, 3H), 4.10–3.72 (m, 2H), 1.95–1.45 (m, 2H), 1.21 (d, 6H, J_{HH}=6.3 Hz) 1.19 (d, 6H, J_{HH}=6.9 Hz), 0.94–086 (m, 12H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.8 (d, J_{CP}=14.8 Hz), 142.4 (d, J_{CP}=14.3 Hz), 129.9 (d, J_{CP}=21.3 Hz) 129.9 (s), 129.8 (d, J_{CP}=21.7 Hz), 129.7 (d, J_{CP}=21.6 Hz), 129.4 (s), 127.7 (d, J_{CP}=5.7 Hz), 80.2 (d, J_{CP}=16.6 Hz), 79.8 (d, J_{CP}=14.9 Hz), 79.0 (d, J_{CP}=12.6 Hz) 78.6 (d, J_{CP}=9.7 Hz), 34.5 (d, J_{CP}=4.9 Hz), 34.3 (d, J_{CP}=2.9 Hz), 18.8–18.2 (m, 3 isomers), 17.5 (d, J_{CP}=3.2 Hz), 17.4 (d, J_{CP}=4.6 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 157.2, 153.9 and 151.8 (three isomers); EIMS *m/z* 213 ($[C_{11}H_{17}O_2P]^+$, 9%), 195 ($[C_{11}H_{16}OP]^+$, 6%), 142 ($[C_6H_7O_2P]^+$, 100%), 125 ($[C_6H_6OP]^+$, 24%); CI-HRMS $C_{14}H_{31}O_2P$ calcd 262.2062 found 262.2069; IR (ν_{max} cm^{-1}): 2963 (s, C–H), 1435 (s, *P*-phenyl), 1026 (s, P–*O*–C).

*3.5.3. Di-(1,2,2-trimethyl-1-propyl) phenylphosphonite (**6c**, three isomers).* 2.30 g (76%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84–7.72 (m, 2H), 7.54–7.44 (m, 3H), 4.03–3.93 (m, 2H), 1.35 (d, 6H, J_{HH}=6.3 Hz), 0.97 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.3 (d, J_{CP}=15.1 Hz), 130.0 (d, J_{CP}=22.5 Hz), 129.3 (s), 127.8 (d, J_{CP}=6.0 Hz), 83.5 (d, J_{CP}=16.8 Hz), 35.5 (d, J_{CP}=5.7 Hz), 25.9 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 159.7, 150.7 and 146.9; EIMS *m/z* 183 ($[C_9H_{12}O_2P]^+$, 13%), 143 ($[C_6H_8O_2P]^+$, 100%), 125 ($[C_6H_7OP]^+$, 15%); CI-HRMS $C_{16}H_{35}O_2P$ calcd 290.2375 found 290.2386; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1459 (s, *P*-phenyl), 1078 (s, P–*O*–C).

3.6. General procedure for the preparation of dialkyl phenylphosphonites (6e–f)

The appropriate alcohol (60 mmol) in hexane (10.0 mL) was added dropwise to *n*-BuLi (20.0 mL of 2.5 M, 50 mmol) dissolved in hexane (50.0 mL) −50 °C. After the adding the alcohol, the mixture was stirred for 30 min at rt, after which it was cooled to −50 °C followed by addition of dichlorophenylphosphine (2.0 mL, 2.6 g, 14.5 mmol) dissolved in 5.0 mL hexane. Upon the completion of the reaction (^{31}P NMR monitored), the solvent was removed under reduced pressure. The product was isolated from the crude material by bulb-to-bulb vacuum distillation.

*3.6.1. Di-(1,1-dimethyl-1-ethyl) phenylphosphonite (**6e**).* Scale 2.60 g (14.5 mol); yield 2.3 g (62%); bp 110 °C/30 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.58 (dd, 2H, J_{HH}=6.6 Hz, J_{HP}=1.8 Hz), 7.41–7.31 (m, 3H), 1.43 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 145.7 (d, J_{CP}=12.2 Hz), 129.4 (s), 129.3 (d, J_{CP}=22.3 Hz), 127.9 (d, J_{CP}=5.9 Hz), 77.0 (d, J_{CP}=11.1 Hz), 30.9 (d, J_{CP}=8.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 132.2; EIMS *m/z* 183 ($[C_9H_{12}O_2P]^+$, 6%), 143 ($[C_6H_8O_2P]^+$, 100%), 125 ($[C_6H_7OP]^+$, 9%); CI-HRMS $C_{12}H_{27}O_2P$ calcd

234.1749 found 234.1755; IR (ν_{max} cm^{-1}): 2976 (s, C–H), 1366 (s, P-Ph), 1172 (s, P–*O*–C).

*3.6.2. Di-(1,1-dimethyl-1-propyl) phenylphosphonite (**6f**).* Scale: 2.60 g, 14.5 mol; yield 2.4 g (60%); bp 130 °C/30 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.66–7.58 (m, 2H), 7.42–7.31 (m, 3H), 1.68 (q, 4H, J_{HH}=7.4 Hz), 1.38 (d, 12H, J_{HP}=6.8 Hz), 0.91 (t, 6H, J_{HH}=7.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 145.9 (d, J_{CP}=13.1 Hz), 129.4 (d, J_{CP}=23.3 Hz), 129.0 (s), 127.8 (d, J_{CP}=6.2 Hz), 79.3 (d, J_{CP}=9.1 Hz), 36.5 (d, J_{CP}=5.4 Hz), 28.15 (d, J_{CP}=10.3 Hz), 27.9 (d, J_{CP}=9.5 Hz), 8.8 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 131.4; EIMS *m*/*z* 197 ([$C_{10}H_{14}O_2P$]$^+$, 6%), 183 ([$C_9H_{12}O_2P$]$^+$, 23%), 143 ([$C_6H_8O_2P$]$^+$, 100%), 125 ([C_6H_7OP]$^+$, 22%); CI-HRMS $C_{14}H_{31}O_2P$ calcd 262.2062 found 262.2077; IR (ν_{max} cm^{-1}): 2980 (s, C–H), 1462 (s, P–Ph), 1100 (s, P–*O*–C).

3.7. General procedure for the preparation of dialkyl phenylphosphonates (7)

A solution of 30% hydrogen peroxide (3.0 mL) was added dropwise to a solution of dialkyl phenylphosphonite in benzene (10.0 mL) and resulting reaction mixture was stirred at rt for an hour. Upon the completion of the reaction (^{31}P NMR monitored), water (10.0 mL) was added, followed by extraction with chloroform (3×10.0 mL). The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane 4:1) to give an oily-like product.

*3.7.1. Di-(2,2-dimethyl-1-propyl) phenylphosphonate (**7a**).* Scale: 1.00 g (3.5 mmol); yield: 0.48 g (46%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.87 (dd, 2H, J_{HH}=6.9 Hz, J_{HP}=1.5 Hz), 7.65–7.45 (m, 3H), 3.61 (dd, 2H, J_{HP}=9.3 Hz, J_{HH}=4.9 Hz), 3.71 (dd, 2H, J_{HP}=9.3 Hz, J_{HH}=4.9 Hz), 0.88 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132.3 (d, J_{CP}=3.1 Hz), 131.7 (d, J_{CP}=9.7 Hz), 128.3 (d, J_{CP}=14.9 Hz), 75.2 (d, J_{CP}=6.5 Hz), 32.1 (d, J_{CP}=7.2 Hz), 26.0 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 12.2; EIMS *m*/*z* 229 ([$C_{11}H_{18}O_3P$]$^+$, 25%), 213 ([$C_{11}H_{18}O_2P$]$^+$, 32%), 172 ([$C_7H_9O_3P$]$^+$, 37%), 159 ([$C_6H_8O_3P$]$^+$, 100%); CI-HRMS $C_{14}H_{31}O_3P$ calcd 278.2011 found 278.2028; IR (ν_{max} cm^{-1}): 2973 (s, C–H), 1388 (s, P–Ph), 1117 (s, P═O), 961 (s, P–*O*–C).

*3.7.2. Di-(1,2-dimethyl-1-propyl) phenylphosphonate (**7b**, three isomers).* Scale: 1.00 g (3.5 mmol); yield: 0.45 g (43%); The ^{1}H and ^{13}C NMR data refer to the major isomer; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.76 (dd, 2H, J_{HH}=13.5 Hz, J_{HP}=6.8 Hz), 7.50–7.33 (m, 3H), 4.40–4.24 (m, 2H), 1.83 (sextet, 2H, J_{HH}=6.3 Hz), 1.27 (d, 6H, J_{HH}=6.3 Hz), 0.77 (d, 6H, J_{HH}=6.9 Hz), 0.75 (d, 6H, J_{HH}=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 131.8 (s), 131.6 (d, J_{CP}=9.7 Hz), 128.1 (d, J_{CP}=14.8 Hz), 78.3 (d, J_{CP}=6.2 Hz), 33.7 (d, J_{CP}=5.7 Hz), 18.3 (d, J_{CP}=2.0 Hz), 17.8 (d, J_{CP}=1.4 Hz), 17.4 (d, J_{CP}=1.7 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 10.7, 10.3 and 9.8; EIMS *m*/*z* 229 ([$C_{11}H_{18}O_3P$]$^+$, 21%), 211 ([$C_{10}H_{12}O_3P$]$^+$, 45%), 185 ([$C_8H_{10}O_3P$]$^+$, 100%), 159 ([$C_6H_8O_3P$]$^+$, 100%), 141 ([$C_6H_7O_2P$]$^+$, 92%), 124 ([C_6H_5OP]$^+$, 16%); CI-HRMS $C_{14}H_{31}O_3P$ calcd 278.2011 found 278.1985; IR (ν_{max} cm^{-1}): 2975 (s, C–H), 1468 (s, P-Ph), 1267 (s, P═O), 1192 (s, P–*O*–C).

*3.7.3. Di-(1,2,2-trimethyl-1-propyl) phenylphosphonate (**7c**, three isomers).* Scale 1.00 g; yield: 0.52 g (50%) (three isomers); The ^{1}H and ^{13}C NMR data refer to that of the major isomer; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82–7.58 (m, 2H), 7.52–7.35 (m, 3H), 4.20–4.10 (m, 2H), 1.33 (d, 6H, J_{HH}=6.3 Hz), 0.93 (d, 9H, J_{HP}=1.2 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 131.7 (d, J_{CP}=4.3 Hz), 131.6 (s), 128.0 (d, J_{CP}=14.9 Hz), 81.1 (d, J_{CP}=7.1 Hz), 34.9 (d, J_{CP}=6.6 Hz), 17.5 (d, J_{CP}=17.9 Hz), 25.6 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 11.4, 10.6 and 9.7; EIMS *m*/*z* 269 ([$C_{14}H_{22}O_3P$]$^+$, 9%), 243 ([$C_{12}H_{20}O_3P$]$^+$, 9%), 227 ([$C_{12}H_{20}O_2P$]$^+$, 8%), 185 ([$C_8H_{10}O_3P$]$^+$, 100%), 159 ([$C_6H_8O_3P$]$^+$, 53%), 141 ([$C_6H_7O_2P$]$^+$, 12%); CI-HRMS $C_{16}H_{35}O_3P$ calcd 306.2324 found 306.2329; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1474 (s, P–Ph), 1261 (s, P═O), 1124 (s, P–*O*–C).

*3.7.4. Di-(1,1-dimethyl-1-ethyl) phenylphosphonate (**7e**).* Scale: 0.70 g (3.10 mmol); yield: 0.46 g (62%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (dd, 2H, J_{HH}=13.5 Hz, J_{HP}=1.2 Hz), 7.48–7.30 (m, 3H), 1.42 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 133.8 (d, J_{CP}=192.2 Hz), 131.4 (d, J_{CP}=9.7 Hz), 131.2 (d, J_{CP}=3.2 Hz), 127.9 (d, J_{CP}=15.1 Hz), 82.2 (d, J_{CP}=7.7 Hz), 30.4 (d, J_{CP}=4.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 3.6; EIMS *m*/*z* 199 ([$C_9H_{12}O_3P$]$^+$, 17%), 159 ([$C_6H_8O_3P$]$^+$, 100%), 141 ([$C_6H_7O_2P$]$^+$, 17%); CI-HRMS $C_{12}H_{27}O_3P$ calcd 250.1698 found 250.184; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1474 (s, P–Ph), 1261 (s, P═O), 1124 (s, P–*O*–C).

*3.7.5. Di-(1,1-dimethyl-1-propyl) phenylphosphonate (**7f**).* Scale: 1.00 g (3.5 mmol); yield: 0.82 g (82%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.75 (dd, 2H, J_{HH}=13.5 Hz, J_{HP}=1.5 Hz), 7.48–7.30 (m, 3H), 1.73–1.59 (m, 4H), 1.38 (d, 12H, J_{HP}=32.7 Hz), 0.86 (t, 6H, J_{HH}=7.4 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 133.6 (d, J_{CP}=193.6 Hz), 131.3 (d, J_{CP}=9.9 Hz), 131.2 (d, J_{CP}=3.8 Hz), 128.0 (d, J_{CP}=15.1 Hz), 85.2 (d, J_{CP}=8.3 Hz), 36.1 (d, J_{CP}=5. 7 Hz), 27.6 (d, J_{CP}=2.8 Hz), 27.3 (d, J_{CP}=3.5 Hz), 8.5 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 3.4; EIMS *m*/*z*: 215 ([$C_{10}H_{16}O_3P$]$^+$ 30%), 197 ([$C_{10}H_{14}O_2P$]$^+$ 5%), 159 ([$C_6H_8O_3P$]$^+$ 100%), 141 ([$C_6H_7O_2P$]$^+$ 17%); CI-HRMS $C_{14}H_{31}O_3P$ calcd 278.2011 found 278.1998; IR (ν_{max} cm^{-1}): 2973 (s, C–H), 1388 (s, P–Ph), 1117 (s, P═O), 961 (s, P–*O*–C).

3.8. General procedure for the preparation di-(alkyl) phenylphosphonothioates (8)

A mixture of di-(alkyl) phenylphosphonite 1.0 g and equivalent amounts of elemental sulfur in toluene (20.0 mL) was heated under reflux for 3 h. Upon the completion of the reaction, ^{31}P NMR monitored, the reaction mixture was cooled to rt and the solvent was removed under reduced pressure. The crude product obtained was purified by column chromatography (silica gel, ethyl acetate/hexane, 2:3) to give a colourless oily product.

*3.8.1. Di-(2,2-dimethyl-1-propyl) phenylphosphonothioate (**8a**).* 0.60 g (54%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89 (dd, 2H, J_{HH}=14.1 Hz), 7.63–7.34 (m, 3H) 3.76–3.60 (m, 4H), 0.91 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 133.1 (d, J_{CP}=152.0 Hz), 131.9 (d, J_{CP}=3.2 Hz), 130.8 (d, J_{CP}=11.4 Hz), 128.0 (d, J_{CP}=14.9 Hz), 75.8 (d, J_{CP}=6.9 Hz), 32.0 (d, J_{CP}=8.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 79.5; EIMS *m*/*z* 314 ([M]$^+$, 18%), 245 ([$C_{11}H_{18}O_2PS$]$^+$, l6%), 229 ([$C_{11}H_{16}OPS$]$^+$, 9%), 175 ([$C_6H_8O_2PS$]$^+$, 100%), 157 ([C_6H_7OPS]$^+$, 20%); CI-HRMS $C_{14}H_{31}O_2PS$ calcd 294.1782 found 294.1789; IR (ν_{max} cm^{-1}): 2965 (s, C–H), 1481 (s, P–Ph), 1013 (s, P–*O*–C), 851 (s, P═S).

*3.8.2. Di-(1,2-dimethyl-1-propyl) phenylphosphonothioate (**8b**, three isomers).* 0.45 g (41%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.89 (dd, 2H, J_{HH}=14.4 Hz), 7.46–7.28 (m, 3H), 4.53 (octet, 2H, J_{HH}=6.0 Hz), 1.73 (sextet, 2H, J_{HH}=7.0 Hz), 1.05 (d, 6H, J_{HH}=6.3 Hz), 0.77 (d, 12H, J_{HH}=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.7 (d, J_{CP}=154.0 Hz), 132.0 (d, J_{CP}=3.4 Hz), 131.1 (d, J_{CP}=11.6 Hz), 128.3 (d, J_{CP}=15.0 Hz), 79.3 (d, J_{CP}=6.9 Hz), 33.5 (d, J_{CP}=5.4 Hz), 18.1 (m), 17.8 (m); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 77.9, 77.3 and 76.7; EIMS *m*/*z* 245 ([$C_{11}H_{18}O_2PS$]$^+$, 19%), 227 ([$C_{11}H_{16}OPS$]$^+$, 6%), 175 ([$C_6H_8O_2PS$]$^+$, 100%), 157 ([C_6H_7OPS]$^+$, 7%); CI-HRMS $C_{14}H_{31}O_2PS$ calcd 294.1782 found 294.1786; IR (ν_{max} cm^{-1}): 2973 (s, C–H), 1389 (s, P–Ph), 1117 (s, P–*O*–C), 731 (s, P═S).

*3.8.3. Di-(1,2,2-trimethyl-1-propyl) phenylphosphonothioate (**8c**, three isomers).* 0.65 g (59%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.91 (dd 2H, J_{HH}=14.4 Hz), 7.52–7.35 (m, 3H), 4.50–4.25 (m, 2H), 1.44 (d, 6H, J_{HH}=6.3 Hz), 0.76 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.5 (d,

J_{CP}=154.3 Hz), 131.5 (d, J_{CP}=3.2 Hz), 130.8 (d, J_{CP}=11.3 Hz), 127.8 (d, J_{CP}=15.1 Hz), 82.3 (d, J_{CP}=7.7 Hz), 34.9 (d, J_{CP}=7.4 Hz), 17.3 (d, J_{CP}=24.0 Hz), 25.8 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 78.8, 77.5 and 76.1; EIMS *m*/*z* 259 ($[C_{12}H_{19}O_2PS]^+$, 7%), 241 ($[C_{12}H_{18}OPS]^+$, 10%), 175 ($[C_6H_8O_2PS]^+$, 100%), 157 ($[C_6H_7OPS]^+$, 21%), 141 ($[C_6H_7PS]^+$, 7%); CI-HRMS $C_{16}H_{35}O_2PS$ calcd 322.2095 found 322.2105; IR (ν_{max} cm^{-1}): 2965 (s, C–H), 11,438 (s, P–Ph), 1120 (s, P–*O*–C), 811 (s, P═S), 739 (s, P═S).

*3.8.4. Di-(1,1-dimethyl-1-ethyl) phenylphosphonothioate (**8e**).* 0.68 g (61%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (dd, 2H, J_{HH}=14.4 Hz, J_{HP}=7.8 Hz), 7.62–7.26 (m, 3H), 1.48 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 138.3 (d, J_{CP}=152.3 Hz), 131.2 (d, J_{CP}=3.2 Hz), 130.8 (d, J_{CP}=11.9 Hz), 127.8 (d, J_{CP}=15.1 Hz), 84.0 (d, J_{CP}=9.2 Hz), 30.2 (d, J_{CP}=4.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 62.3; EIMS *m*/*z* 285 ([M-1]$^+$, 6%), 230 ($[C_{10}H_{15}O_2PS]^+$, 10%), 174 ($[C_6H_7O_2PS]^+$, 100%), 157 ($[C_6H_7OPS]^+$, 23%), 141 ($[C_6H_7PS]^+$, 30%); CI-HRMS $C_{12}H_{27}O_2PS$ calcd 266.1469 found 266.1468; IR (ν_{max} cm^{-1}): 2982 (s, C–H), 1438 (s, P–Ph), 1117 (s, P–*O*–C), 775 (s, P═S).

*3.8.5. Di-(1,1-dimethyl-1-propyl) phenylphosphonothioate (**8f**).* 0.94 g (85%); ^{1}H NMR ($CDCl_3$): δ 7.80–7.70 (m, 2H), 7.47–7.30 (m, 3H), 1.72 (q, J_{HH}=7 Hz), 1.47 (d, 12H, J_{HP}=34.9 Hz), 0.88 (t, 6H, J_{HH}=7.7 Hz); ^{13}C NMR ($CDCl_3$): δ 138.4 (d, J_{CP}=153.7 Hz), 131.1 (d, J_{CP}=3.1 Hz), 130.8 (d, J_{CP}=12.0 Hz), 127.8 (d, J_{CP}=14.9 Hz), 86.7 (d, J_{CP}=9.7 Hz), 36.4 (d, J_{CP}=5.4 Hz), 27.1 (d, J_{CP}=3.2 Hz), 8.6 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 61.9; EIMS *m*/*z* 231 ($[C_{10}H_{16}PS]^+$ 50%), 175 ($[C_6H_8O_2PS]^+$ 100%), 158 ($[C_6H_7OPS]^+$ 25%), 141 ($[C_6H_6PS]^+$ 30%); CI-HRMS $C_{14}H_{31}O_2PS$ calcd 294.1782 found 294.1771; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1436 (s, *P*-phenyl), 1111 (s, P–*O*–C), 729 (s, P═S).

3.9. General procedure for the preparation of alkyl phenylchlorophosphonites (9a–c)

A mixture of the appropriate alcohol (1.1 equiv), and triethylamine (1.1 equiv) in toluene (10.0 mL) was added dropwise to dichlorophenylphosphine (2.60 g, 14.6 mmol) in toluene (40.0 mL) at 0 °C at such a rate that the temperature did not exceed 5 °C. After the addition, the cold bath was removed and stirring continued at rt for 2 h. Upon the completion of the reaction, hexane (40.0 mL) was added and the precipitated triethylamine hydrochloride was filtered off using fine Celite and a sintered glass funnel under nitrogen. The filtrate was concentrated on a rotary evaporator to give a crude product as a colourless oily, which was purified on bulb-to-bulb distillation set-up.

*3.9.1. 2,2-Dimethyl-1-propyl phenylchlorophosphonite (**9a**).* 1.90 g (58%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.82–7.74 (m, 2H), 7.52–7.44 (m, 3H), 3.61 (d, 1H, J_{HH}=7.4 Hz), 3.58 (dd, 1H, J_{HH}=7.4 Hz), 0.95 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 141.1 (d, J_{CP}=37.4 Hz), 131.2 (s), 129.6 (d, J_{CP}=25.4 Hz) 128.4 (d, J_{CP}=6.2 Hz), 78.2 (d, J_{CP}=6.2 Hz), 32.3 (d, J_{CP}=6.0 Hz), 26.2 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 168.0; EIMS *m*/*z* 197 ($[C_{11}H_{18}OP]^+$, 15%), 143 ($[C_6H_5ClP]^+$, 100%), 126 ($[C_6H_7OP]^+$, 45%); CI-HRMS $C_{11}H_{16}ClOP$ calcd 230.0627 found 230.0616; IR (ν_{max} cm^{-1}): 2966 (s, C–H), 1481 (s, P–Ph), 1017 (s, P–*O*–C).

*3.9.2. 1,2-Dimethyl-1-propyl phenylchlorophosphonite (**9b**, two isomers).* 2.20 g (66%); Spectral data refer to the major isomer; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.85–7.72 (m, 2H), 7.50–7.35 (m, 3H), 4.20–3.98 (m, 1H), 1.85 (octet, 1H, J_{HH}=6.9 Hz), 1.31 (dd, 3H, J_{HH}=6.3 Hz, J_{HP}=0.9 Hz), 0.92 (d, 6H, J_{HH}=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.0 (d, J_{CP}=32.7 Hz), 131.1 (s), 129.5 (d, J_{CP}=25.9 Hz), 128.5 (d, J_{CP}=6.5 Hz), 83.2 (d, J_{CP}=13.4 Hz), 34.30 (d, J_{CP}=5.9 Hz), 18.6 (d, J_{CP}=2.6 Hz), 18.1 (s). 17.8 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 170.1 and 168.0 (two isomers); EIMS *m*/*z* 160 ($[C_6H_6ClOP]^+$, 100%), 143 ($[C_6H_5ClP]^+$, 38%), 125 ($[C_6H_6OP]^+$, 61%); CI-HRMS $C_{11}H_{16}ClOP$ calcd 230.0627 found 230.0631; IR (ν_{max} cm^{-1}): 2973 (s, C–H), 1474 (P–Ph), 953 (P–*O*–C).

*3.9.3. 1,2,2-Trimethyl-1-propyl phenylchlorophosphonite (**9c**, two isomers).* 2.70 g (80%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.81–7.73 (m, 2H), 7.49–7.43 (m, 3H), 4.08–3.97 (m, 1H), 1.34 (d, 2H, J_{HH}=6.3 Hz), 0.91 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.2 (d, J_{CP}=31.7 Hz), 131.2 (s), 129.3 (d, J_{CP}=26.2 Hz), 128.5 (d, J_{CP}=6.5 Hz), 86.7 (d, J_{CP}=13.7 Hz), 35.5 (d, J_{CP}=6.8 Hz), 25.6 (s), 16.7 (d, J_{CP}=14.6 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 171.3 and 168.1; EIMS *m*/*z* 244 ([M]$^+$, 1%), 229 ($[C_{11}H_{15}ClOP]^+$, 10%), 187 ($C_8H_9ClOP]^+$, 9%), 160 ($[C_6H_6ClOP]^+$, 100%), 143 ($[C_6H_5ClP]^+$, 100%), 125 ($[C_6H_6OP]^+$, 86%); CI-HRMS $C_{12}H_{18}ClOP$ calcd 244.0784 found 244.0764; IR (ν_{max} cm^{-1}): 2973 (s, C–H), 1440 (s, P–Ph), 900 (s, P–*O*–C).

3.10. Preparation of 9e: 1,1-dimethyl-1-ethyl phenylchlorophosphonite

t-Butanol 1.50 g (20.0 mmol) in hexane (5 mL) was added dropwise to *n*-BuLi (6.0 mL, 2.5 M, 15.0 mmol) in hexane (25.0 mL) at −50 °C. The resulting reaction mixture was stirred for 30 min at rt after which it was again cooled to −50 °C followed by the addition of dichlorophenylphosphine (2.0 mL, 2.6 g, 14.5 mmol) dissolved in hexane (3.0 mL). The reaction mixture was stirred for 2 h at rt after which the solvent was removed under reduced pressure. The product was isolated from the crude material by bulb-to-bulb vacuum distillation.

1.80 g, (58%); bp 139 °C/40 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.84 (dt, 2H, J_{HH}=7.1 Hz, J_{HP}=2.9 Hz), 7.58–7.52 (m, 3H), 1.60 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 142.7 (d, J_{CP}=30.1 Hz), 130.9 (s), 129.2 (d, J_{CP}=26.0 Hz), 128.4 (d, J_{CP}=6.9 Hz), 80.7 (d, J_{CP}=9.1 Hz), 30.2 (d, J_{CP}=8.5 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 159.3; EIMS *m*/*z* 216 ([M]$^+$ 6%), 160 ($[C_6H_6ClOP]^+$, 100%), 143 ($[C_6H_5ClP]^+$, 16%), 125 ($[C_6H_6OP]^+$, 76%); CI-HRMS $C_{10}H_{14}ClOP$ calcd 216.0471 found 216.0468; IR (ν_{max} cm^{-1}): 2965 (s, C–H), 1481 (s, *P*-Phenyl), 1018 (s, P–*O*–C).

3.11. General procedure for the preparation of alkyl hydrogen phenylphosphonate (10a–c)

A solution of 30% hydrogen peroxide (3.0 mL) was added to a solution of alkyl phenylchlorophosphonite in benzene (10.0 mL) and resulting reaction mixture was stirred at Rt for an hour. Upon the completion of the reaction (^{31}P NMR monitored), water (10.0 mL) was added, followed by extraction with chloroform (3×10.0 mL). The combined organic phases were dried over anhydrous $MgSO_4$, and the solvent was removed on a rotary evaporator. The crude product obtained was analysed without further purification.

*3.11.1. 2,2-Dimethyl-1-propyl hydrogen phenylphosphonate (**10a**).* Scale: 1.00 g (4.3 mmol); yield: 0.70 g (70%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.5 (br s, 1H), 7.78 (dd, 2H, J_{HH}=13.8 Hz, J_{HP}=1.5 Hz), 7.56–7.36 (m, 3H), 3.65 (d, 2H, J_{HH}=5.4 Hz), 0.89 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 132.2 (d, J_{CP}=3.0 Hz), 131.3 (d, J_{CP}=10.0 Hz), 128.7 (d, J_{CP}=194.2 Hz), 128.3 (d, J_{CP}=15.1 Hz), 75.0 (d, J_{CP}=6.8 Hz), 32.0 (d, J_{CP}=7.4 Hz), 26.0 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 14.4; EIMS *m*/*z* 229 ($[C_{11}H_{18}O_3P]^+$, 22%), 213 ($[C_{10}H_{14}O_3P]^+$ 29%), 172 ($[C_7H_9O_3P]^+$ 41%), 159 ($[C_6H_8O_3P]^+$, 100%); CI-HRMS $C_{11}H_{17}O_3P$ calcd 228.0915 found 228.014; IR (ν_{max} cm^{-1}): 2961 (s, C–H), 1439 (s, P–Ph), 1221 (s, P═O), 986 (s, P–*O*–C).

*3.11.2. 1,2-Dimethyl-1-propyl hydrogen phenylphosphonate (**10b**).* Scale: 1.0 g (4.3 mmol), yield 0.65 g (65%); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.9 (br, 1H, OH), 7.79 (dd, 2H, J_{HH}=13.6 Hz, J_{HP}=1.5 Hz), 7.52–7.46 (m, 1H) 7.44–7.34 (m, 2H), 4.34 (dq, 1H, J_{HP}=12.8 Hz, J_{HH}=6.4 Hz), 1.80 (octet, 1H, J_{HH}=6.8 Hz), 1.22 (d, 3H, J_{HH}=6.0 Hz), 0.86 (s, 6H);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 132.0 (d, J_{CP} 3.0 Hz), 131.2 (d, J_{CP}=9.7 Hz), 130.0 (d, J_{CP} 195.1 Hz), 128.2 (d, J_{CP}=15.6 Hz), 78.8 (d, J_{CP}=6.7 Hz), 33.9 (d, J_{CP}=5.2 Hz), 18.3 (d, J_{CP}=2.3 Hz), 17.8 (s), 17.7 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.6 (s); EIMS *m/z*: 199 ($[C_9H_{12}O_3P]$ 50%), 173 ($[C_7H_{10}O_3P]^+$ 100%), 155 ($[C_{12}H_{12}OP]^+$ 100%), 141 ($[C_6H_6O_2P]^+$ 8%) (Diazomethane-treated); IR (ν_{max} cm^{-1}): 2949 (s, C–H), 1452 (s, P–Ph), 1226 (s, P═O), 991 (s, P–*O*–C).

*3.11.3. 1,2,2-Trimethyl-1-propyl hydrogen diphenylphosphonate (**10c**).* Scale: 0.80 g (3.3 mmol); yield 0.65 g (82%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 11.9 (br s, 1H), 7.78 (dd, 2H, J_{HH}=13.8 Hz, J_{HP}=1.5 Hz), 7.56–7.34 (m, 3H), 4.29–4.18 (m, 1H), 1.22 (d, 3H, J_{HH}=6.3 Hz), 0.86 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 131.9 (d, J_{CP}=3.2 Hz), 131.1 (d, J_{CP}=10.0 Hz), 129.7 (d, J_{CP}=196.1 Hz), 128.2 (d, J_{CP}=15.1 Hz), 81.6 (d, J_{CP}=7.4 Hz), 34.9 (d, J_{CP}=6.5 Hz), 25.6 (s), 16.7 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 13.1; EIMS *m/z* 199 ($[C_9H_{12}O_3P]^+$, 100%), 173 ($C_7H_{10}O_3P]^+$, 100%), 15 ($[C_7H_8O_2P]^+$, 100%), 141 ($C_6H_6O_2P]^+$, 30%), 141 ($C_6H_8O_3P]^+$, 100%); CI-HRMS $C_{12}H_{19}O_3P$ calcd 242.1072 found 242.1073; IR (ν_{max} cm^{-1}): 2968 (s, C–H), 1439 (s, P–Ph), 1216 (s, P═O), 991 (s, P–*O*–C).

3.12. General procedure for the preparation of alkyl phenylchlorophosphonothioates (11)

A mixture of *O*-alkyl phenylchlorophosphinoite (1.0 g) and 1.1 equiv of elemental sulfur in 10.0 mL of anhydrous toluene was heated under reflux for 30 min. The solvent was removed in vacuo and the crude product was subjected to high vacuum to remove less volatile materials, providing pure products.

*3.12.1. 2,2-Dimethyl-1-propyl phenylchloridophosphonothioate (**11a**).* 0.65 g (59%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.01 (dd, 2H, J_{HH}=16.5 Hz, J_{HP}=9.6 Hz), 7.62–7.45 (m, 3H), 4.07 (dd, 1H, J_{HH}=7.2 Hz), 3.87 (dd, 21, J_{HH}=8.2 Hz), 0.99 (d, 18H, J_{HP}=0.6 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 135.5 (d, J_{CP}=141.5 Hz), 133.0 (d, J_{CP}=3.5 Hz), 130.3 (d, J_{CP}=13.1 Hz), 128.5 (d, J_{CP}=16.5 Hz), 76.2 (d, J_{CP}=8.8 Hz), 31.91 (d, J_{CP}=9.1 Hz), 26.2 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 81.0; EIMS *m/z* 262 ($[M]^+$, 21%), 247 ($[C_{10}H_{13}ClOPS]^+$, 7%), 193 ($[C_6H_7ClOPS]^+$, 100%), 175 ($[C_6H_8O_2PS]^+$, 15%), 157 ($[C_6H_7OPS]^+$, 28%); CI-HRMS $C_{11}H_{16}ClOPS$ calcd 262.0348 found 262.0354; IR (ν_{max} cm^{-1}): 2968 (s, C–H), 1482 (s, P–Ph), 1017 (s, P–*O*–C), 743 (s, P═S) 857 (s, P═S).

*3.12.2. 1,2-Dimethyl-1-propyl phenylchlorophosphonothioate (**11b**, two isomers).* Scale: 1.00 g (4.3 mmol); yield: 0.52 g (47%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.99 (dd, 2H, J_{HH}=8.1 Hz, J_{HP}=8.1 Hz), 7.60–7.44 (m, 3H), 5.02–4.80 (m, 1H), 2.10–1.97 (m, 1H), 1.33 (d, 3H, J_{HH}=6.3 Hz), 1.02 (d, 3H, J_{HH}=6.3 Hz), 1.00 (d, 3H, J_{HH}=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 137.5 (d, J_{CP}=145.7 Hz), 132.8 (d, J_{CP}=3.8 Hz), 130.1 (d, J_{CP}=13.1 Hz), 128.4 (d, J_{CP}=16.2 Hz), 81.6 (d, J_{CP}=8.8 Hz), 33.8 (d, J_{CP}=7.4 Hz), 17.8 (s), 17.7 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 79.6 and 79.3; EIMS *m/z* 193 ($[C_6H_7ClOPS]^+$, 100%), 175 ($[C_6H_8O_2PS]^+$, 24%), 157 ($[C_6H_7OPS]^+$, 14%); CI-HRMS $C_{11}H_{16}ClOPS$ calcd 262.0348 found 262.0338; IR (ν_{max} cm^{-1}): 2973 (s, C–H), 1481 (s, P–Ph), 1110 (P–*O*–C), 806 (s, P═S), 740 (s, P═S).

*3.12.3. 1,2,2-Trimethyl-1-propyl phenylchorophosphonothioate (**11c**, two isomers).* 0.73 g (66%); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.05–7.93 (m, 2H), 7.62–7.44 (m, 3H), 4.92–4.76 (m, 1H), 1.46 (d, 3H, J_{HH}=6.3 Hz), 0.89 (d, 9H, J_{HP}=0.9 Hz); ^{13}C NMR ($CDCl_3$, 100.4 MHz): δ 137.1 (d, J_{CP}=143.1 Hz), 132.8 (d, J_{CP}=3.0 Hz), 130.0 (d, J_{CP}=14.9 Hz), 128.5 (d, J_{CP}=17.8 Hz), 84.6 (d, J_{CP}=9.8 Hz), 35.2 (d, J_{CP}=8.3 Hz), 25.8 (s), 16.2 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 79.7 and 79.3; EIMS *m/z* 239 ($[C_{12}H_{17}OPS]^+$, 2%), 193 ($[C_6H_7ClOPS]^+$, 26%), 175 ($[C_6H_8O_2PS]^+$, 14%), 157 ($[C_6H_7OPS]^+$, 7%), 84 ($[C_6H_{13}]^+$, 100%); CI-HRMS $C_{12}H_{18}ClOPS$ calcd 276.0504 found 276.0515; IR (ν_{max} cm^{-1}): 2970 (s, C–H), 1438 (s, P–Ph), 1004 (s, P–*O*–C), 804 (s, P═S), 740 (s, P═S).

3.13. 2,2-Dimethylpropyl di-*tert*-butylphosphinate (15)

2,2-Dimethyl-1-propanol (1.30 g, 13.6 mmol) was added dropwise to *n*-BuLi (12.5 mmol) in dry THF (40.0 mL) at −50 °C. The reaction mixture was stirred at rt for 1 h, after which it was cooled to −50 °C, followed by the addition of di-*tert*-butylchlorophosphine (0.5 mL; 2.6 mmol). The solution was heated under reflux for 2 h. The crude product obtained after removing the solvent consisted of unreacted di-*tert*-butylchlorophosphine, oxidised and hydrolysed starting material as well as the expected product. The product 2,2-dimethyl-1-propyl di-*tert*-butylphosphinate was purified by column chromatography (silica gel ethyl acetate/hexane 1: 9) to afford 0.31 g (46%) of the title compound.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.66 (d, 2H, J_{HP}=3.3 Hz), 1.21 (d, 18H, J_{HP}=14.1 Hz), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 76.0 (d, J_{CP}=8.0 Hz), 36.7 (d, J_{CP}=82.0 Hz), 32.5 (d, J_{CP}=6.8 Hz), 26.5 (s), 26.3 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 62.6; EIMS *m/z* 248 ($[M]^+$, 4%), 233 ($[C_{12}H_{26}O_2P]^+$, 10%), 192 ($[C_9H_{21}O_2P]^+$, 21%), 122 ($[C_4H_{11}O_2P]^+$, 100%); CI-HRMS $C_{13}H_{29}O_2P$ calcd 248.1905 found 248.1917; IR (ν_{max} cm^{-1}): 2958 (s, C–H), 1474 (s, C–P), 1230 (s, P═O), 1039 (s, P–*O*–C).

3.14. Di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonite (17)

To *n*-BuLi (5.0 mL of 2.5 M, 12.5 mmol) in dry diethyl ether (25.0 mL) was added 2,2-dimethylpropanol (1.10 g, 12.5 mmol) in 5.0 mL diethyl ether at −50 °C. The resulting reaction mixture was stirred at rt for an hour, after which it was cooled to −50 °C, followed by the addition of *tert*-butyldichlorophosphine (1.00 g, 6.30 mmol). The reaction mixture was heated under reflux for 2 h. The solvent was removed at in a rotary evaporator and the crude product obtained was purified by bulb-to-bulb vacuum distillation.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.69–3.65 (m, 4H), 1.18 (d, 9H, J_{HP}=16.8 Hz), 0.92 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 79.5 (d, J_{CP}=13.9 Hz), 34.3 (d, J_{CP}=117.2 Hz), 26.8 (s), 26.5 (d, J_{CP}=9.1 Hz), 24.3 (d, J_{CP}=15.7 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 191.183.8; EIMS *m/z* 262 ($[M]^+$, 6%), 193 ($[C_9H_{22}PO_2]^+$, 15%), 136 ($[C_5H_{13}PO_2]^+$, 78%), 123 ($[C_4H_{12}PO_2]^+$, 100%); CI-HRMS $C_{14}H_{31}O_2P$ calcd 262.2062 found 262.2076; IR (ν_{max} cm^{-1}): 2972 (s, C–H), 1466 (s, P–C$(CH_3)_3$), 1046 (s, P–*O*–C).

3.15. Di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonate (18)

A solution of 30% hydrogen peroxide (2.0 mL) was added to di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonite (0.40 g) dissolved in benzene (15.0 mL) at rt. The resulting mixture was stirred for 12 h; the solvent was removed under reduced pressure. Preparative column chromatography gave 0.33 g (79%) of di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonate.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.68 (d, 2H, J_{HH}=3.9 Hz), 3.67 (d, 2H, J_{HH}=3.9 Hz), 1.18 (d, 9H, J_{HP}=16.8 Hz), 0.92 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 75.1 (d, J_{CP}=8.0 Hz), 32.3 (d, J_{CP}=6.8 Hz), 31.9 (d, J_{CP}=142.9 Hz), 26.1 (s), 24.9 (d, J_{CP}=2.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 34.0; EIMS *m/z* 279 ($[M+1]^+$, 4%), 209 ($[C_9H_{22}PO_3]^+$, 14%), 193 ($[C_9H_{22}PO_2]^+$, 21%), 153 ($[C_5H_{14}PO_3]^+$, 78%), 139 ($[C_4H_{12}PO_3]^+$, 100%); CI-HRMS $C_{14}H_{31}O_3P$ calcd 278.2011 found 278.2014; IR (ν_{max} cm^{-1}): 2960 (s, C–H), 1480 (s, C–P), 1260 (s, P═O), 1023 (s, P–*O*–C).

3.16. Di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonothioate (19)

To di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonite (0.5 g) dissolved in toluene (20.0 mL) was added elemental sulfur, and the

resulting reaction mixture was heated under reflux for 4 h. The solvent was removed under reduce pressure and the crude product was purified by column chromatography ethyl acetate/hexane (2:5) to give 0.47 g (84%) of di-(2,2-dimethyl-1-propyl) *tert*-butylphosphonothioate.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.65 (dd, 4H, J_{HH}=6.0 Hz), 1.54 (d, 9H, J_{HP}=18.3 Hz), 0.92 (br s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 76.2 (d, J_{CP}=9.2 Hz), 37.3 (d, J_{CP}=110.7 Hz), 32.3 (d, J_{CP}=7.7 Hz), 26.3 (s), 24.8 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 104.0; EIMS *m*/*z* 294 ([M]$^+$, 20%), 238 ([$C_{10}H_{23}O_2PS$]$^+$, 5%), 209 ([$C_9H_{22}OPS$]$^+$, 15%), 155 ([$C_4H_{12}O_2PS$]$^+$, 100%); CI-HRMS $C_{14}H_{31}O_2PS$ calcd 294.1782 found 294.1806; IR (ν_{max} cm^{-1}): 2960 (s, C–H), 1474 (s, P–C(CH_3)$_3$), 1026 (s, P–*O*–C), 702 (s, P═S).

3.17. General procedure for the preparation of alkyl *tert*-butylphosphonochloridites (20)

One equivalent of the relevant alcohol in diethyl ether (10.0 mL) was added dropwise to *n*-BuLi (5.0 mL of 2.5 M, 12.5 mmol) in dry diethyl ether (25.0 mL) at −50 °C. The resulting reaction mixture was stirred at rt for 30 min, after which, it was cooled to −50 °C, followed by the addition of *tert*-butyldichlorophosphine 1.0 g (6.30 mmol). The reaction mixture was stirred for 2 h at rt. The solvent was removed under reduced pressure and the product purified by bulb-to-bulb vacuum distillation.

*3.17.1. 2,2-Dimethyl-1-propyl tert-butylphosphono-chloridite (**20a**).* Scale 0.50 g; yield 0.64 g (80%); bp 150 °C/80 millitorr.

^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.67 (dd, J_{HP}=5.7 Hz, J_{HH}=3.6 Hz), 1.18 (d, J_{HP}=12.3 Hz), 1.10 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 79.1 (d, J_{CP}=13.9 Hz), 34.6 (d, J_{CP}=6.5 Hz), 33.0 (d, J_{CP}=6.8 Hz), 26.4 (s), 23.8 (d, J_{CP}=15.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 183.7; EIMS *m*/*z* 210 ([M]$^+$ 5%), 195 ([$C_8H_{15}ClP$]$^+$, 2%), 141 ([$C_4H_{11}ClPO$]$^+$ 15%), 123, ([C_4H_9ClP]$^+$ 10%), 105 ([$C_4H_{10}PO$]$^+$, 11%), 57 ([C_4H_9]$^+$, 100%); CI-HRMS $C_9H_{20}ClOP$ calcd 210.0940 found 210.0945; IR (ν_{max} cm^{-1}): 2957 (s, C–H), 1478 (s, P–C(CH_3)$_3$), 1033 (s, P–*O*–C).

*3.17.2. 1,2-Dimethyl-1-propyl tert-butylphosphono-chloridite (**20b**, mixture of two isomers).* Scale 0.50 g; yield: 0.52 g (78%); bp 110 °C/30 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): 4.00–3.74 (m, 1H), 1.80–1.64 (m, 1H), 1.21 (d, 3H, J_{HH}=6.6 Hz), 1.81 (d, 3H, J_{HH}=6.6 Hz), 1.07 (d, 9H, J_{PH}=13.5 Hz), 1.06 (d, 9H, J_{PH}=13.5 Hz), 0.87 (d, 6H, J_{HH}=6.9 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): 82.6 (d, J_{CP}=11.4 Hz), 81.1 (d, J_{CP}=11.1 Hz), 36.8 (d, J_{CP}=27.6 Hz), 36.4 (d, J_{CP}=26.8 Hz), 34.2 (d, J_{CP}=5.9 Hz), 33.8 (d, J_{CP}=2.9 Hz), 23.6 (d, J_{CP}=9.1 Hz), 23.4 (d, J_{CP}=9.3 Hz), 17.8 (d, J_{CP}=2.3 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 207.5 and 204.6; EIMS *m*/*z* 210 ([$C_9H_{19}ClOP$]$^+$, 3%), 175 ([$C_9H_{19}OP$]$^+$, 42%), 167 ([$C_6H_{13}OP$]$^+$, 12%), 141 ([$C_4H_{11}ClOP$]$^+$, 35%), 123 ([C_4H_9ClP]$^+$, 33%), 57 ([C_4H_9]$^+$, 100%); CI-HRMS $C_9H_{20}ClOP$ calcd 210.0940 found 210.0957; IR (ν_{max} cm^{-1}): 2966 (s, C–H), 1474 (s, P–C(CH_3)$_3$).

*3.17.3. 1,2,2-Trimethyl-1-propyl tert-butylphosphonochloridite (**20c**).* Scale 0.50 g; yield: 0.56 g (84%); bp 110 °C/30 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.77 (dq, 1H, J_{HH}=6.6 Hz, J_{HP}=8.1 Hz), 3.67 (dq, 1H, J_{HP}=10.8 Hz, J_{HH}=6.6 Hz), 1.20 (d, 3H, J_{HH}=6.3 Hz), 1.74 (d, 3H, J_{HH}=6.6 Hz), 1.10 (d, 9H, J_{HP}=13.2 Hz), 1.06 (d, 9H, J_{HP}=13.5 Hz), 0.86 (s, 18H), 0.85 (s, 18H); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 85.6 (d, J_{CP}=10.0 Hz), 83.2 (d, J_{CP}=8.9 Hz), 37.1 (d, J_{CP}=28.1 Hz), 36.5 (d, J_{CP}=27.3 Hz), 35.6 (d, J_{CP}=6.5 Hz), 34.9 (d, J_{CP}=3.4 Hz), 25.8 (s), 25.7 (s), 23.8 (d, J_{CP}=14.0 Hz), 23.5 (d, J_{CP}=14.2 Hz); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 207.4 and 202.5; EIMS *m*/*z* 209 ([$C_9H_{19}ClOP$]$^+$, 6%), 189 ([$C_{10}H_{22}OP$]$^+$, 8%), 167 ([$C_6H_{13}OP$]$^+$, 42%), 123 ([C_4H_9ClP]$^+$, 33%), 84 ([C_6H_{12}]$^+$, 100%), 57 ([C_4H_9]$^+$, 100%); CI-HRMS $C_{10}H_{22}ClOP$ calcd 224.1097 found 224.1098; IR (ν_{max} cm^{-1}): 2958 (s, C–H), 1478 (s, C–P), 1194 (s, P–*O*–C).

*3.17.4. 1,1-Dimethyl-1-propyl tert-butylphosphonochloridite (**20f**).* 0.54 g (81%); bp 130 °C/40 millitorr; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.60 (q, 2H, J_{HH}=7.2 Hz), 1.33 (d, 9H, J_{HP}=9.9 Hz), 1.06 (s, 3H), 1.02 (s, 3H), 0.88 (t, 3H, J_{HH}=7.2 Hz); ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ 81.6 (d, J_{CP}=4.8 Hz), 36.2 (d, J_{CP}=27.0 Hz), 35.8 (d, J_{CP}=4.3 Hz), 27.3 (d, J_{CP}=9.1 Hz), 23.6 (s), 23.4 (s), 8.4 (s); ^{31}P NMR ($CDCl_3$, 121.5 MHz): δ 190.9; EIMS *m*/*z* 210 ([M]$^+$, 5%), 195 ([$C_8H_{15}ClP$]$^+$, 16%), 181 ([$C_7H_{15}ClP$]$^+$, 18%), 141 ([C_4H_1lOP]$^+$, 35%), 123 ([C_4H_9ClP]$^+$, 28%), 105 ([$C_4H_{10}OP$]$^+$, 21%), 57 ([C_4H_9]$^+$, 100%); CI-HRMS $C_9H_{20}ClOP$ calcd 210.0940 found 210.0943; IR (ν_{max} cm^{-1}): 2965 (s, C–H), 1480 (s, P–C(CH_3)$_3$), 1108 (s, P–*O*–C).

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Supplementary data

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