Synthesis

Convenient and Scalable Synthesis of Aryldichlorophosphines and Primary Arylphosphines via Perthiophosphonic Anhydrides

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Abstract
A scalable synthetic route to both primary arylphosphines ArPH$_2$ and aryldichlorophosphines ArPCl$_2$ is reported. The C-P bond formation was performed in a highly regiospecific manner through electrophilic substitution of selected aromatic hydrocarbons (ArH) with phosphorus pentasulfide. The resultant perthiophosphonic anhydrides Ar$_2$P$_2$S$_4$ were then reacted with LiAlH$_4$ to give primary phosphines ArPH$_2$. Subsequent reaction of ArPH$_2$ with phosgene solution gives dichlorophosphines ArPCl$_2$. Each reaction step requires minimum purification and uses commercially available and economical precursors. The scope of the reaction was shown to include alkoxy and phenoxy substituted benzenes as well as naphthalene and fluorene as starting materials.

Key Words
Primary phosphine, Chlorophosphine, Organophosphorus synthesis, $^{31}$P NMR.

Introduction
Both primary phosphines RPH$_2$ and dichlorophosphines RPCl$_2$ have a rich chemistry and are valuable reagents in reactions such as hydrophosphinations, dehydrocoupling and P-C bond formation.$^{1-3}$ This is facilitated by the reactive nature of P-H and P-Cl bonds, respectively.

However, this also means that primary phosphines, particularly those with a low molecular weight and minimal steric bulk protecting the -PH$_2$ moiety, are extremely pyrophoric rendering them difficult
to synthesise and manipulate. Typically, primary phosphines are synthesised by the reaction between either alkyl/aryl dichlorophosphines (Scheme 1, route (i)) or phosphonates (Scheme 1, route (ii)) and a strong reducing agent.\textsuperscript{4-6}

\begin{center}
\begin{align*}
\text{Dichlorophosphines appear to be ubiquitous within synthetic organophosphorus chemistry,}^{7-12} \text{ despite this, the commercial availability of aryldichlorophosphines is limited and so laboratory scale syntheses have to be employed where access to a wider range of these compounds is required. A major challenge to overcome in these syntheses is the need for a highly selective formation of the desired species, which is crucial due to the limited options for post-synthetic purification, generally limited to fractional distillation (for sufficiently volatile species). Other options (in particular chromatography) are generally not accessible due to the very reactive nature of dichlorophosphines towards both oxygen and moisture.}

\text{P-C bond formation is a crucial step in the synthesis of aryldichlorophosphines. Early examples involved reacting aromatic hydrocarbons or anisol derivatives with } \text{PCl}_3 \text{ in the presence of a Lewis acid catalyst such as } \text{AlCl}_3 \text{ or } \text{SnCl}_4 \text{ (Scheme 2, route (i))}.^{13, 14} \text{ Later examples used reaction of } \text{PCl}_3 \text{ with respective Grignard (or organolithium) reagent (Scheme 2, route (ii)) and this method is still routinely employed}.^{15, 16} \text{ The disadvantage of this synthetic route is that due to the high reactivity of the Grignard (or organolithium) reagent often the products of multiple substitution (Ar}_2\text{PCl and Ar}_3\text{P) are formed in significant amounts, impacting the yield of the dichlorophosphine. This synthetic route also suffers from poor functional group tolerance.}
\end{align*}
\end{center}
To prevent the formation of byproducts due to multiple substitution, a protective group strategy was devised in which $\text{PCl}_3$ was replaced with $\text{ClP(NR}_2\text{)}_2$ (Scheme 2, route (iii)). Intermediate aminophosphinyl species $\text{ArP(NR}_2\text{)}_2$ is formed, which is isolated and then reacted with excess HCl gas to form the dichlorophosphine.\textsuperscript{4,17} While this synthetic route does prevent multiple substitution from occurring, a new challenge is presented through the use of HCl gas and separation of the dichlorophosphine from the co-formed dialkylammonium chloride.

More recently a systematic investigation of the synthesis of aryl- and heteroaryldichlorophosphines was reported by Karaghiosoff\textsuperscript{18} in which organozinc reagents were employed in the place of Grignard or organolithium reagents (Scheme 2, route (iv)). Lower polarity of C-Zn vs. C-Mg and C-Li bonds resulted in more controlled reactivity of organozinc species compare to Grignard reagents and organolithiums. Whilst this route presents improvement over the more conventional routes as it does avoid multiple substitution products and offers good functional group tolerance, it requires observing the right stoichiometry carefully, and distillation (or recrystallisation for solids) of the highly reactive product as a final purification step.

As outlined above the synthesis of dichlorophosphines is not straightforward, with multiple issues presented for each synthetic method. Our recent investigations required a synthesis of a series of
aryldichlorophosphines to allow for fine tuning of electronics of a target phosphorus containing molecule. This prompted synthesis of a series of aryldichlorophosphines, each in multigram quantities, with differing aryl groups. To synthesise these we have expanded on our previously reported “niche” synthetic route, originally used to form dichloroferrocenylphosphine $\text{FcPCl}_2$, via the perthiophosphonic anhydride, $\text{Fc}_2\text{P}_2\text{S}_4$ (Scheme 3).\(^{19}\)

![Scheme 3 Synthesis of $\text{FcPH}_2$ and $\text{FcPCl}_2$ reported previously by us.](image)

This unique method offers a route to a previously difficult to access dichlorophosphine $\text{FcPCl}_2$ in high yield, is easily scalable, uses economical commercially available precursors and does not require complex purification. The P-C bond forming step, in which perthiophosphonic anhydride $\text{Fc}_2\text{P}_2\text{S}_4$ is formed from ferrocene and $\text{P}_4\text{S}_{10}$, proceeds fully regioselectively with high yield (>80%).\(^{19}\)

Herein we report the expansion of this synthetic route to make a selection of primary and dichloroaryl phosphines.

**Results and Discussion**

**Perthiophosphonic anhydrides synthesis**

The synthetic route towards primary and dichloroaryl phosphines (Scheme 4) begins with the synthesis of the perthiophosphonic anhydride compounds (1A – 1F). These six particular compounds were selected due to the ease at which they can be synthesised, this is achieved by a simple heating of $\text{P}_4\text{S}_{10}$ with the related hydrocarbon precursor - anisole, phenetole, 2-t-butylanisole, diphenyl ether, fluorene and naphthalene, respectively, at high temperature (150 – 190 °C, reaction time 1-5 hours). All of these compounds have previously been reported in the literature\(^{20-22}\) with the exception of fluorene derivative 1F. The arene reactants served also as solvents for the reaction, hence the molar ratio of reactants 1 : 2 to 1 : 2.5 was used (P : ArH). The reactions were performed under a gentle stream of nitrogen and the exhaust gasses were bubbled through aqueous NaOH solution to remove $\text{H}_2\text{S}$ formed as a by-product. The liquid mixtures obtained after heating were left
to cool to rt and the formed solid products were filtered off, washed with dichloromethane or diethyl ether and dried in vacuo. 1A – 1F form as yellow or white solids in yields in the range of 31-65% (see Table 1). They can be manipulated in air; however, they hydrolyse slowly hence long-term storage requires well-sealed vials.

While other routes exist for the synthesis of perthiophosphonic anhydrides, these are generally more complex and require several steps hence are less suitable to prepare starting materials for the synthetic sequence in this work.23, 24

An important point to make is that the arenes selected in this work contain no functional groups that will provide additional reactivity toward P₄S₁₀ such as ketones, esters and alcohols.25, 26 On the other hand, presence of electron donating groups (such as OMe) on the aromatic ring results in improved yields and shorter reaction times. Due to the inherent insolubility of perthiophosphonic anhydrides no NMR data could be collected for 1A – 1F. Nevertheless, the follow-on reactivity (see below) indicates the P-C bond formation is fully regiospecific in the reactions of P₄S₁₀ with both activated and non-activated arenes used in this study, with no other regioisomers detected by ³¹P{¹H} NMR in the phosphines 2A-F formed from 1A – 1F in the next step.

Scheme 4 Synthetic route used for the synthesis of primary phosphines 2A–2F and dichlorophosphines 3A–3F.
Reduction to Primary Phosphines

With the desired Ar$_2$P$_2$S$_4$ compounds in hand the next step was to reduce these with LiAlH$_4$ (4 eq. of LiAlH$_4$ per Ar$_2$P$_2$S$_4$ were used) to the corresponding primary phosphines ArPH$_2$ (2A – 2F). Both Ar$_2$P$_2$S$_4$ and LiAlH$_4$ were suspended in Et$_2$O, and the two suspensions added together slowly at 0 °C. The resulting suspension was filtered, degassed water was added, followed by a second filtration. In both filtrations, efficient washing of the solid on the filter was essential to achieve good yields. The filtrate and washings were collected, and the volatiles were removed in vacuo to yield the desired primary phosphines. No further purification was performed, the phosphines 2A-2D were obtained in good purity and reasonable yields (33-52%). The naphthalene species 2F was obtained in 8% yield only and small amount of naphthalene (formed in the reduction step rather than carried over from previous step) was present as shown by $^1$H NMR. Also, the reduction of 1E led to partial cleavage of the C-P bond as small amounts of fluorene were detected by $^1$H NMR alongside the major product 2E. Despite this, both 2E and 2F were of sufficient purity for further synthetic use and were used as obtained in the preparations of respective dichlorophosphines as described below.

Other reducing reagents (NaH and NaBH$_4$) were tested for the reduction of 2A-2F, however no phosphine was produced even at elevated temperatures in ethereal solvents.

Interestingly, of the six primary phosphine compounds synthesised in this work only two have been previously reported in the literature (2A and 2F),$^{27,28}$ demonstrating the ability of this synthetic route to provide access to a wider range of primary phosphines. Despite the lack of steric bulk protection, phosphines 2E and 2F showed remarkable stability in air in both the solid state and in solution with minimal oxidation observed. This enhanced stability to oxidation could be due to the conjugated aromatic system of naphthalene and fluorene, as the additional conjugation has been shown to stabilise primary phosphines against oxidation.$^{27,29}$ Analysis via $^{31}$P{$^1$H} NMR spectroscopy showed 2A-2F to display low frequency singlets within a very narrow shift range of -121.9 to -126.4 ppm (Table 1); these split to triplets of triplets in $^{31}$P NMR spectra with $^1$J$_{PH}$ of 199-202 Hz as expected. The purity of the products was further assessed by $^1$H and $^{13}$C{$^1$H} NMR. Apart from multinuclear NMR spectroscopy the novel compounds 2B, 2C, 2D and 2E were characterised by MS spectroscopy. The spectroscopic data obtained by us for the previously reported species (2A and 2F) were in agreement with the literature (see Experimental section).
Table 1 Isolated yields, purity and $^{31}$P{$_1^1$H} chemical shifts of synthesised perthiophosphonates 1A-F, primary phosphines 2A-F and dichlorophosphines 3A-F.

<table>
<thead>
<tr>
<th>Ar</th>
<th>1 (Ar$_2$P$_2$S$_4$) Yield (%)</th>
<th>2 (ArPH$_2$) Yield [purity]$^1$ (%)</th>
<th>2 (ArPH$_2$) $\delta$$_P$ (ppm)</th>
<th>3 (ArPCl$_2$) Yield [purity]$^1$ (%)</th>
<th>3 (ArPCl$_2$) $\delta$$_P$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeOC$_6$H$_4$ A</td>
<td>65</td>
<td>51 [97]</td>
<td>-126.4</td>
<td>74 [90]</td>
<td>162.0</td>
</tr>
<tr>
<td>p-EtOC$_6$H$_4$ B</td>
<td>57</td>
<td>52 [92]</td>
<td>-125.9</td>
<td>81 [92]</td>
<td>160.5</td>
</tr>
<tr>
<td>3-tBu-4-MeOC$_6$H$_3$ C</td>
<td>60</td>
<td>33 [94]</td>
<td>-125.3</td>
<td>82 [92]</td>
<td>163.6</td>
</tr>
<tr>
<td>p-PhOC$_6$H$_4$ D</td>
<td>47</td>
<td>36 [87]</td>
<td>-122.9</td>
<td>90 [90]</td>
<td>162.7</td>
</tr>
<tr>
<td>2-Fluorenyl E</td>
<td>94</td>
<td>33 [97]</td>
<td>-121.9</td>
<td>78 [93]</td>
<td>160.1</td>
</tr>
<tr>
<td>1-Naphthyl F</td>
<td>31</td>
<td>8 [86]</td>
<td>-126.1</td>
<td>46 [92]</td>
<td>161.8</td>
</tr>
</tbody>
</table>

$^1$ Purity as assessed by $^{31}$P{$_1^1$H} NMR.

For 2B, 2D and 2F minor impurities were observed in the $^{31}$P{$_1^1$H} spectra as two singlets at approximately $\delta$$_P$ -70 ppm (2-4 % of integral intensity). These were assigned as the respective diphosphines ArP(H)-P(H)Ar, which due to the presence of two chiral P atoms exist in two diastereomeric forms (meso and rac). In the $^{31}$P NMR spectra these minor signals split to symmetrical multiplets with pattern consistent with AA'XX' spin system (A, A' = P, X, X' = H). Spin system simulations were carried out to replicate the observed splitting pattern for selected examples (Figure 1). These simulations yielded $^1$J$_{PP}$ =150 Hz, $^1$J$_{PH}$ = 150 Hz and $^2$J$_{PH}$ = 10 Hz for one of the diastereomers of ArP(H)-P(H)Ar (Ar = p-EtOC$_6$H$_4$), which is fully consistent with the suggested diphosphate structure. Note the contribution of the ortho protons from the aryl groups has been omitted from the simulated spectrum due to the extra complexity this presents.
Figure 1: Top: Partial $^{31}$P NMR spectrum of diphosphine ArP(H)-P(H)Ar (Ar = p-EtOC$_6$H$_4$) present as minor impurity in p-EtOC$_6$H$_4$PH$_2$ (2B). Bottom: simulated $^{31}$P NMR spectrum.

The diphosphine impurities presented no issues for the subsequent chlorination step as they were present in very small amounts and were converted to the same end product (ArPCl$_2$) on chlorination. Hence no attempt was made to remove these via further purification.

Chlorination to Dichlorophosphines

In the last step of the synthetic sequence shown in Scheme 4, the primary phosphines 2A-2F were chlorinated to the aryldichlorophosphines 3A-3F. A commercially available solution of phosgene in toluene (slight excess, 2.1 eq.) was added slowly, at -10 °C, to the solution of primary phosphine. The reaction mixture was left to stir overnight and subsequent removal of the volatiles in vacuo afforded 3A-3F. The dichlorophosphines were isolated in yields of 74-90 % and were obtained as oils except for 3F which was isolated in 46 % yield as an off-white solid. The $^{31}$P{$_1^H$} spectra of 3A-3F were as expected (singlets within a narrow range of δ$_P$ 160-164 ppm) and showed that all the primary phosphine starting material had been consumed during the chlorination step, with no other phosphorus containing species present. The purity of the products was further confirmed by $^1$H and $^{13}$C{$_1^H$} NMR, which indicated some fluorene was present in the sample of 3E, whilst the purity of the other samples was very good. This represents a marked improvement to previously reported methods, where vacuum distillation was required as a final purification step. Stoichiometric amount of
triphosgene was used as an alternative chlorinating reagent at rt for selected examples of primary phosphines, giving full conversion to respective dichlorophosphines as judged by $^{31}$P{^{1}H} NMR.

Syntheses of 3B, 3C, 3D and 3E have not been reported previously. In addition to multinuclear NMR spectroscopy (as mentioned above) they were characterised also by MS spectroscopy. The spectroscopic data obtained by us for previously reported species (3A and 3F) agreed with the literature (see Experimental section).

**Conclusion**
A multigram synthesis of a series of primary arylphosphines and aryldichlorophosphines is reported. All steps use convenient, commercially available and economical reagents. Each step requires minimum purification, which is of importance due to the highly reactive nature of both compound types. The initial step (formation of perthiophosphonic anhydrides) proceeds highly regiospecifically and the nature of subsequent steps means multiple substitution is avoided, hence employing protection and subsequent deprotection strategies is not required. Future work will look to further extend the scope of this reaction to other $R_{2}P_{2}S_{4}$ compounds.

**Experimental Section**
**General Considerations**
All manipulations (unless indicated otherwise) were performed under an atmosphere of nitrogen using standard Schlenk line techniques or an atmosphere of argon in a Saffron glove box. Diethylether and dichloromethane (DCM) were collected from an MBraun solvent purification system and stored over activated 4Å molecular sieves. 2-tert-Butylanisole was prepared according to a literature method, all other reagents were commercially available. All new compounds were characterised via $^{1}$H, $^{31}$P{$^{1}$H} and $^{13}$C{$^{1}$H} NMR spectroscopy including the measurement of H-H COSY, H-C HSQC, H-C HMBC and H-P HMBC. $^{13}$C NMR spectra were recorded using the DEPT-Q pulse sequence. All spectra were recorded at 25°C using either a Bruker Avance III (500 MHz) spectrometer or a Bruker Avance II (400 MHz) spectrometer. In vacuo refers to pressure of ca 0.01-0.1 mbar. MS were acquired using a Micromass LCT (Electrospray Ionisation) from solutions of the analyte in methanol.

**Synthesis of perthiophosphonic anhydrides 1A-1F**
All syntheses in this section were performed under a gentle stream of nitrogen, and the exhaust gasses were bubbled through aqueous NaOH solution to remove H₂S formed as a by-product. The subsequent workup was performed in air (in a well ventilated fumehood).

**Lawesson’s Reagent, (4-MeO-C₆H₄)₂P₂S₄ (1A)**

1A was synthesised according to a previously reported literature procedure.²⁰ Anisole (48.7 g, 450 mmol) and P₄S₁₀ (20.0 g, 45.0 mmol) were heated under reflux at 150°C for 5 hours. The liquid mixture was allowed to cool to room temperature and a pale-yellow crystalline solid precipitated out which was isolated by vacuum filtration. The solid was washed with ether (2 x 25 ml) and dried *in vacuo* (23.6 g, 58.4 mmol, 65%).

**(4-EtOC₆H₄)₂P₂S₄ (1B)**

1B was synthesised by adapting a previously reported literature procedure.²⁰ Phenetole (22.0 g, 180 mmol) and P₄S₁₀ (10.0 g, 22.5 mmol) were heated under reflux to 165°C for 2 hours. The liquid mixture was allowed to cool to room temperature. Upon cooling an off-white solid precipitated. The solid 1B was filtered off, washed with ether (2 x 30 ml) and dried *in vacuo* (11.2 g, 25.9 mmol, 57%).

**(3-tBu-4-MeOC₆H₃)₂P₂S₄ (1C)**

1C was synthesised according to a previously reported literature procedure.²² 2-tert-butanisole (27.0 g, 164 mmol) and P₄S₁₀ (10.0 g, 22.5 mmol) were combined and heated to 180°C with stirring for 1 hour. The solution was then allowed to cool to room temperature. A crystalline pale-yellow solid precipitated out of solution which was collected by vacuum filtration, washed with ether (50 ml) and dried *in vacuo* (13.9 g, 26.9 mmol, 60%).

**Belleau’s Reagent (4-PhOC₆H₄)₂P₂S₄ (1D)**

1D was synthesised according to a previously reported literature procedure.²¹ Diphenyl ether (57.4 g, 337 mmol) and P₄S₁₀ (15.0 g, 33.7 mmol) were heated under reflux at 180°C for 3 hours. The liquid mixture was cooled to room temperature to afford an off-white solid. The solid was isolated by filtration, washed with ether (3 x 50 ml) and dried *in vacuo* (16.6 g, 31.4 mmol, 47%).

**Flu₂P₂S₄, Flu = 9H-fluoren-2-yl, (1E)**

Fluorene (28.6 g, 172 mmol) and P₄S₁₀ (10.0 g, 22.4 mmol) were heated under reflux at 190°C for 4 hours. The liquid mixture was then allowed to cool to room temperature, giving a solid clump. DCM
(30 ml) was added to form suspension after stirring. The pale-yellow solid 1E was filtered off, washed with DCM (2 x 20 ml) and dried in vacuo (21.9 g, 42 mmol, 94%).

M.p. 232-234°C

MS(EI+): m/z (%) 259.98 [½M⁺, 100];
MS (Cl+): m/z (%) 261.0 [(½(M+H)+, 100), 520.98 [(M+H)+, 85];
HRMS (Cl+): m/z (%) Found 520.9835, C₂₆H₁₉P₂S₄ [M+H]+ requires 520.9839;
IR νmax (KBr Disc, cm⁻¹): 1610m (νC=C), 1446m (δC-H), 835m, 770m, 693s (νP=S);
Raman (sealed capillary, cm⁻¹): 3020w (νAr–H), 2906w (νC–H), 1606s (νC=C), 1480w (νC=C), 703m (νP=S).

Nap₂P₂S₄, Nap = naphth-2-yl, (1F)

1F was synthesised by adapting a previously reported literature procedure.²⁰ Naphthalene (27.7 g, 216 mmol) and P₄S₁₀ (12.0 g, 27 mmol) were heated to 190°C under reflux for 3 hours. The liquid mixture was allowed to cool slowly to room temperature, at which point a yellow solid began to precipitate. The solid 1F was filtered off, washed with DCM (3 x 20 ml) and dried in vacuo (7.51 g, 16.9 mmol, 31%).

General Procedure for the Synthesis of Primary Phosphines (2A-2F)

The respective perthiophosphonic anhydride 1A-1F was suspended in diethyl ether (150 ml) and cooled to 0°C. A suspension of LiAlH₄ (4 eq.) in ether (50 ml) was added in small portions with vigorous stirring. The resulting mixture was stirred for 1 hour at 0°C. The mixture was then filtered to remove the insoluble solids which were washed with ether (2 x 10 ml). The filtrate and washings were collected, cooled to 0°C and degassed water (2 ml) was added cautiously dropwise. The resulting suspension was filtered again to remove the insoluble solids that had formed and the solid on the filter was washed with DCM (2 x 20 ml). The filtrate and washings were collected, and the volatiles were removed in vacuo to yield the desired primary phosphines 2A-2F.

4-Methoxyphenylphosphine (2A)

Starting from 1A (6.00 g, 14.8 mmol), 2A was isolated as a colourless oil (2.12 g, 15.1 mmol, 51%).

¹H NMR: δH (400.1 MHz, C₆D₆) 7.28-7.23 (2H, m, H₂PCC₇H), 6.62 (2H, m, ³JHH = 8.6 Hz, OCCH), 3.90 (2H, d, ³JHP = 198.9 Hz, PH₂), 3.22 (3H, s, CH₃).

³¹P{¹H} NMR: δP (162.0 MHz, C₆D₆) -126.4 (s)

³¹P NMR: δP (162.0 MHz, C₆D₆) -126.4 (tt, ³JPH = 199.0 Hz, ⁴JPH = 7.0 Hz)
Starting from 4-Phenoxyphenylphosphine (2D) has been reported previously but no characterisation data were provided.

4-Ethoxyphenylphosphine (2B)

Starting from 1B (8.00 g, 18.5 mmol), 2B was isolated as a clear colourless oil (1.77 g, 5.83 mmol, 52%).

3\textsuperscript{13}P\textsuperscript{(1)}H NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -126.1 (s)

3\textsuperscript{13}P NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -126.1 (tt, $^3$J$_{PP}$ = 198.0 Hz, $^4$J$_{PP}$ = 6.8 Hz)

3\textsuperscript{13}C\textsuperscript{(1)}H NMR: $\delta_c$ (100.6 MHz, C$_6$D$_6$) 159.6 (s, qC), 136.7 (d, $^2$J$_{CP}$ = 17.4 Hz, H$_3$PCCH), 117.9 (d, $^1$J$_{CP}$ = 5.5 Hz, qC), 114.7 (d, $^3$J$_{CP}$ = 6.9 Hz, OCCH), 62.8 (s, CH$_3$), 14.4 (s, H$_2$C)

MS (ESI): m/z (\%) 363.09 (25) [(C$_3$H$_5$OC$_6$H$_4$PH$_2$OH)Na$^+$], 193.04 (35) [(C$_3$H$_5$OC$_6$H$_4$PH$_2$ONa)$^-$], 171.06 (100) [(C$_3$H$_5$OC$_6$H$_4$PH$_2$OH)$^-$], 155.06 (5) [(C$_3$H$_5$OP)$^-$, (M+H)$^+$]

3-t-Butyl-4-methoxyphenylphosphine (2C)

Starting from 1C (8.00 g, 15.4 mmol), 2C was isolated as a clear colourless oil (2.22 g, 11.0 mmol, 36%).

3\textsuperscript{13}P\textsuperscript{(1)}H NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -125.3 (s)

3\textsuperscript{13}P NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -125.3 (tt, $^1$J$_{PH}$ = 198.6 Hz, $^3$J$_{PH}$ = 7.7 Hz)

3\textsuperscript{13}C\textsuperscript{(1)}H NMR: $\delta_c$ (125.8 MHz, C$_6$D$_6$) 159.1 (s, H$_2$CO), 138.1 (d, $^3$J$_{CP}$ = 6.3 Hz, C-tBu), 134.5 (d, $^2$J$_{CP}$ = 18.2 Hz, MeOCHCH), 133.8 (d, $^2$J$_{CP}$ = 16.9 Hz, tBuCCH), 117.8 (d, $^1$J$_{CP}$ = 5.0 Hz, H$_3$PC), 111.8 (d, $^3$J$_{CP}$ = 7.8 Hz, H$_2$OCOCCH), 54.2 (s, H$_3$C-O), 34.7 (s, C(CH$_3$)$_3$), 29.2 (s, C(CH$_3$)$_3$)

MS (ESI): m/z (\%) 431.21 (100) [(MeO)(tBu)C$_6$H$_5$P](HO)(tBu)C$_6$H$_5$P(OH)$_2$Na$^+$], 251.14 (10) [(MeO)(tBu)C$_6$H$_5$P(OH)H$^+$Na$^+$], 213.10 (20) [(MeO)(tBu)C$_6$H$_5$P(OH)H$^+$]
$^1$H NMR: $\delta_H$ (400.1 MHz, C$_6$D$_6$) 7.19-7.11 (2H, m, Ar-H), 7.08-6.98 (2H, m, Ar-H), 6.97-6.65 (5H, m, Ar-H), 4.02 (2H, d, $^1J_{HP} = 202.4$ Hz, PH$_2$)

$^{31}$P$^1$H NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -125.9 (s)

$^{31}$P NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -125.8 (tt, $^1J_{PH} = 199.0$ Hz, $^4J_{PH} = 7.0$ Hz)

$^{13}$C$^1$H NMR: $\delta_C$ (100.6 MHz, C$_6$D$_6$) 157.9 (s, qC), 157.1 (s, qC), 136.6 (d, $^3J_{CP} = 16.8$ Hz, PCCH$_2$C), 129.8 (s, CH), 123.4 (s, CH), 121.8 (d, $^1J_{CP} = 8.1$ Hz, H$_2$PC), 119.1 (s, CH), 118.8 (d, $^1J_{CP} = 6.7$ Hz, H$_2$PCCH)

MS (ESI): m/z (%) 459.09 (58) [[(C$_6$H$_5$OC$_6$H$_4$PH$_2$O)$_2$Na]$^+$], 241.04 (74) [[(C$_6$H$_5$OC$_6$H$_4$PH$_2$ONa)$^+$], 219.06 (100) [(C$_6$H$_5$OC$_6$H$_4$PH$_2$OH)$^+$]

9H-Fluoren-2-ylphosphine (2E)

Starting from 1E (6.00 g, 11.5 mmol), 2E was isolated as a white solid (1.50 g, 7.56 mmol, 33%).

$^1$H NMR: $\delta_H$ (400.1 MHz, C$_6$D$_6$) 7.66-7.54 (1H, m, Ar-H), 7.49-7.10 (6H, m, Ar-H), 3.96 (2H, d, $^1J_{HP} = 198.7$ Hz, PH$_2$), 3.38 (2H, s, CH$_2$)

$^{31}$P$^1$H NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -122.9 (s)

$^{31}$P NMR: $\delta_p$ (162.0 MHz, C$_6$D$_6$) -122.9 (tt, $^1J_{PH} = 199.0$ Hz, $^4J_{PH} = 7.1$ Hz)

$^{13}$C$^1$H NMR: 143.4 (d, $^3J_{CP} = 6.6$ Hz, qC), 143.1 (s, qC), 141.9 (s, qC), 141.3 (s, qC), 133.2 (d, $^2J_{CP} = 17.0$ Hz, H$_2$PCCH), 131.5 (d, $^2J_{CP} = 15.8$ Hz, H$_2$PCCH), 126.9 (s, CH), 126.7 (s, CH), 126.1 (d, $^1J_{CP} = 7.5$ Hz, H$_2$PC), 124.9 (s, CH), 120.0 (s, CH), 119.7 (d, $^2J_{CP} = 7.0$ Hz, H$_2$PCCH$_2$C), 36.3 (s, CH$_2$)

M.p. 86-88°C

MS (ESI): m/z (%) 451.10 (44) [[(C$_6$H$_4$CH$_2$C$_6$H$_3$PH$_2$O)$_2$Na]$^+$], 237.04 (52) [(C$_6$H$_4$CH$_2$C$_6$H$_3$PH$_2$ONa)$^+$], 215.06 (100) [(C$_6$H$_4$CH$_2$C$_6$H$_3$PH$_2$OH)$^+$]

Naphthalen-2-ylphosphine (2F)

Starting from 1F (7.20 g, 16.2 mmol), 2F was isolated as an off-white solid (400 mg, 2.50 mmol, 8%)

$^1$H NMR: $\delta_H$ (400.1 MHz, CDCl$_3$) 7.80-7.74 (1H, m, Ar-H), 7.49-7.10 (6H, m, Ar-H), 3.96 (2H, d, $^1J_{HP} = 198.7$ Hz, PH$_2$)

$^{31}$P$^1$H NMR: $\delta_p$ (162.0 MHz, CDCl$_3$) -121.9 (s)

$^{31}$P NMR: $\delta_p$ (162.0 MHz, CDCl$_3$) -121.9 (1H, tt, $^1J_{PH} = 202.4$ Hz, PH$_2$)

M.p. 66-68°C
Values are in agreement with literature data.\textsuperscript{27}

**General Procedure for the Synthesis of Dichlorophosphines (3A-3F)**

The respective primary phosphine (2A-2F) was dissolved in DCM (150 ml) and cooled to -10°C. A solution of phosgene (20\% solution in toluene, 2.1 eq.) was added dropwise over 30 minutes. The resulting solution was allowed to warm to room temperature and stirred for a further 5 hours. The volatiles were removed \textit{in vacuo} to yield the desired dichlorophosphine 3A-3F.

Safety note: Phosgene and carbon monoxide (evolved in the chlorination reaction) are highly toxic, use of well-ventilated fumehood is essential for this step.

**Dichloro(4-methoxyphenyl)phosphine (3A)**

Starting from 2A (2.00 g, 14.3 mmol), 3A was isolated as a yellow oil (2.22 g, 10.6 mmol, 74\%).

\textsuperscript{1}H NMR: $\delta$ (400.1 MHz, CD$_6$D$_6$) 7.54-7.49 (2H, m, Ar-H), 6.50 (2H, m, $^3$J$_{HH}$ = 8.7 Hz, Ar-H), 3.08 (3H, s, CH$_3$)

$^{31}$P($^1$H) NMR: $\delta$ (162.0 MHz, CD$_6$D$_6$) 162.0 (s)

All values are in agreement with literature data.\textsuperscript{13}

**Dichloro(4-ethoxyphenyl)phosphine (3B)**

Starting from 2B (1.50 g, 9.73 mmol), 3B was isolated as a pale-yellow oil (2.19 g, 3.68 mmol, 81\%).

\textsuperscript{1}H NMR: $\delta$ (400.1 MHz, CD$_6$D$_6$) 7.52 (2H, m, Ar-H), 6.54 (2H, d, $^3$J$_{HH}$ = 7.3 Hz, Ar-H), 3.39 (2H, q, $^3$J$_{HH}$ = 7.0 Hz, CH$_2$), 1.00 (3H, t, $^3$J$_{HH}$ = 7.0 Hz, CH$_3$)

$^{31}$P($^1$H) NMR: $\delta$ (162.0 MHz, CD$_6$D$_6$) 162.3 (s)

$^{13}$C($^1$H) NMR: $\delta$ (100.6 MHz, CD$_6$D$_6$) 162.7 (s, qC), 132.1 (d, $^2$J$_{CP}$ = 34.2 Hz, PCCH), 131.5 (d, $^2$J$_{CP}$ = 50.9 Hz, qC), 114.4 (d, $^3$J$_{CP}$ = 9.8 Hz, OCCH), 63.7 (s, CH$_2$), 14.1 (s, H$_3$C)

MS (ESI): m/z (%) 249.07 (100) [(C$_2$H$_5$OC$_6$H$_4$PCl(OMe)$_2$)$^+$], 201.07 (6) [(C$_2$H$_5$OC$_6$H$_4$POMeOH)$_2$]$^+$

**Dichloro(3-t-butyl-4-methoxyphenyl)phosphine (3C)**

Starting from 2C (2.00 g, 10.2 mmol), 3C was isolated as a pale-yellow oil (2.20 g, 8.30 mmol, 82\%)

\textsuperscript{1}H NMR: $\delta$ (400.1 MHz, CD$_6$D$_6$) 7.92-7.78 (2H, m, Ar-H), 7.05-7.00 (1H, m, Ar-H), 3.96 (3H, s, -CH$_3$), 1.47 (9H, s, C(CH$_3$)$_3$)

$^{31}$P($^1$H) NMR: $\delta$ (162.0 MHz, CD$_6$D$_6$) 163.6 (s)
$^{13}$C{$_1^1$}H NMR: $\delta$C (100.6 MHz, C$_6$D$_6$) 162.1 (s, H$_3$COC), 138.7 (d, $^3$J$_{CP}$ = 8.9 Hz, C-tBu), 131.3 (d, $^3$J$_{CP}$ = 50.6 Hz, Cl$_2$PC), 130.3 (d, $^2$J$_{CP}$ = 34.5 Hz, MeOCHCH), 128.8 (d, $^2$J$_{CP}$ = 35.0 Hz, tBuCCH), 111.6 (d, $^3$J$_{CP}$ = 10.1 Hz, H$_3$COCCH), 54.3 (s, H$_3$C), 35.2 (s, C(CH$_3$)$_3$), 28.9 (s, C(CH$_3$)$_3$)


Dichloro(4-phenoxyphenyl)phosphine (3D)

Starting from 2D (2.22 g, 11.0 mmol), 3D was isolated as a pale-yellow oil (2.67 g, 9.89 mmol, 90%).
$^1$H NMR: $\delta$H (400.1 MHz, C$_6$D$_6$) 7.51-7.38 (1H, m, Ar-H), 7.09-6.50 (8H, m, Ar-H)

$^{31}$P{$_1^1$}H NMR: $\delta$P (162.0 MHz, C$_6$D$_6$) 160.5 (s)

$^{13}$C{$_1^1$}H NMR: $\delta$C (100.6 MHz, C$_6$D$_6$) 161.6 (s, qC), 155.4 (s, qC), 133.7 (d, $^1$J$_{CP}$ = 51.8 Hz, PCC), 132.3 (d, $^2$J$_{CP}$ = 33.8 Hz, PCCH), 129.9 (s, CH), 124.4 (s, CH), 120.1 (s, CH), 117.7 (d, $^3$J$_{CP}$ = 9.1 Hz, OCCH)

MS (ESI): m/z (%) 401.13 (7) [(C$_6$H$_5$OC$_6$H$_3$P)$_2$H]+, 201.07 (100) [(C$_6$H$_5$OC$_6$H$_3$P)(OMe)]+

Dichloro(9H-fluoren-2-yl)phosphine (3E)

Starting from 2E (2.20 g, 11.1 mmol), 3E was isolated as an off-white solid (2.32 g, 8.68 mmol, 78%).
$^1$H NMR: $\delta$H (400.1 MHz, C$_6$D$_6$) 7.75-7.57 (2H, m, Ar-H), 7.53-7.33 (2H, m, Ar-H), 7.30-7.08 (3H, m, Ar-H), 3.27 (2H, s, CH$_2$

$^{31}$P{$_1^1$}H NMR: $\delta$P (162.0 MHz, C$_6$D$_6$) 162.7 (s)

$^{13}$C{$_1^1$}H NMR: $\delta$C (100.6 MHz, CDCl$_3$) 146.5 (s, qC), 143.8 (d, $^3$J$_{CP}$ = 8.2 Hz, qC), 143.2 (d, $^3$J$_{CP}$ = 52.0 Hz, Cl$_2$PC), 129.3 (d, $^2$J$_{CP}$ = 37.9 Hz, Cl$_2$PCCH), 128.3 (s, CH), 127.1 (s, CH), 126.7 (d, $^2$J$_{CP}$ = 28.4 Hz, Cl$_2$PCCH), 125.3 (s, CH), 120.9 (s, CH), 120.0 (d, $^3$J$_{CP}$ = 10.1 Hz, Cl$_2$PCCH), 36.9 (s, CH$_3$)

M.p. 66-68°C

MS (ESI): m/z (%) 281.07 (36) [(C$_6$H$_4$CH$_2$C$_6$H$_3$P(OMe)$_2$Na]$^+$, 259.09 (58) [(C$_6$H$_4$CH$_2$C$_6$H$_3$P(OMe)$_2$H]$^+$, 245.07 (100) [(C$_6$H$_4$CH$_2$C$_6$H$_3$P(OMe)OH]$^+$

Dichloro(naphthalene-2-yl)phosphine (3F)

Starting from 2F (383 mg, 2.39 mmol), 3F was isolated as a pale-yellow solid (250 mg, 1.09 mmol, 46%).
$^1$H NMR: $\delta$H (300.1 MHz, C$_6$D$_6$) 7.95-7.70 (1H, m, Ar-H) 7.56-7.33 (2H, m, Ar-H), 7.53-7.33 (2H, m, Ar-H), 7.30-7.08 (3H, m, Ar-H), 3.27 (2H, s, CH$_2$)

$^{31}$P{$_1^1$}H NMR: $\delta$P (162.0 MHz, C$_6$D$_6$) 162.7 (s)

$^{13}$C{$_1^1$}H NMR: $\delta$C (100.6 MHz, CDCl$_3$) 146.5 (s, qC), 143.8 (d, $^3$J$_{CP}$ = 8.2 Hz, qC), 143.2 (d, $^3$J$_{CP}$ = 52.0 Hz, Cl$_2$PC), 129.3 (d, $^2$J$_{CP}$ = 37.9 Hz, Cl$_2$PCCH), 128.3 (s, CH), 127.1 (s, CH), 126.7 (d, $^2$J$_{CP}$ = 28.4 Hz, Cl$_2$PCCH), 125.3 (s, CH), 120.9 (s, CH), 120.0 (d, $^3$J$_{CP}$ = 10.1 Hz, Cl$_2$PCCH), 36.9 (s, CH$_3$)

M.p. 66-68°C

MS (ESI): m/z (%) 281.07 (36) [(C$_6$H$_4$CH$_2$C$_6$H$_3$P(OMe)$_2$Na]$^+$, 259.09 (58) [(C$_6$H$_4$CH$_2$C$_6$H$_3$P(OMe)$_2$H]$^+$, 245.07 (100) [(C$_6$H$_4$CH$_2$C$_6$H$_3$P(OMe)OH]$^+$

Dichloro(naphthalene-2-yl)phosphine (3F)
$^{31}$P$^1$H NMR: $\delta$P (121.5 MHz, C$_6$D$_6$) 160.1 (s)

All values are in agreement with literature data.\(^{12}\)

Conflict of Interest

The authors declare no conflict of interest.

Supporting Information

Supporting information for this article is available online at https://doi.org/XXX.

Data Availability Statement

The research data underpinning this publication can be accessed at https://doi.org/XXX

Graphical Abstract

![Graphical Abstract](image)

All steps scalable to multigram quantities, minimum purification required

References


NMR Spectra of Products

2A:

$^1\text{H}$:
$^31$P$^1$H:

$^31$P:

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$^{13}\text{C}[^1\text{H}]$

$^{1}\text{H}$
$^{31}\text{P}[^1\text{H}]$:
$^{13}$C($^1$H):

$^1$H:

2C:
$^{31}$P($^1$H):

$^{31}$P:
$^{13}\text{C}[^1\text{H}]:$

$^1\text{H}:$
$^{13}$C($^1$H):

2F:

$^1$H:
$^{3}B$: $^{1}H$: 

$^{31}P^{(1)H}$:
$^{13}$C($^1$H):

$^{1}$H:

$^{3}$C:
$^{13}$C($^1$H):

$^1$H:

3E:

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$^{3}F$: 

$^{1}H$: 

$^{31}P(^{1}H)$: