

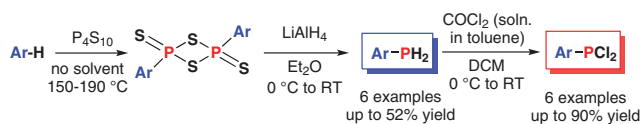
# Convenient and Scalable Synthesis of Aryldichlorophosphines and Primary Arylphosphines via Perthiophosphonic Anhydrides

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all steps scalable to multigram quantities  
 minimum purification required

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**Abstract** A scalable synthetic route to both primary arylphosphines ArPH<sub>2</sub> and aryldichlorophosphines ArPCl<sub>2</sub> is reported. The C–P bond formation was performed in a highly regioselective manner through electrophilic substitution of selected aromatic hydrocarbons (ArH) with phosphorus pentasulfide. The resultant perthiophosphonic anhydrides Ar<sub>2</sub>P<sub>2</sub>S<sub>4</sub> were then reacted with LiAlH<sub>4</sub> to give primary phosphines ArPH<sub>2</sub>. Subsequent reaction of ArPH<sub>2</sub> with phosgene solution gives dichlorophosphines ArPCl<sub>2</sub>. 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, <sup>31</sup>P NMR

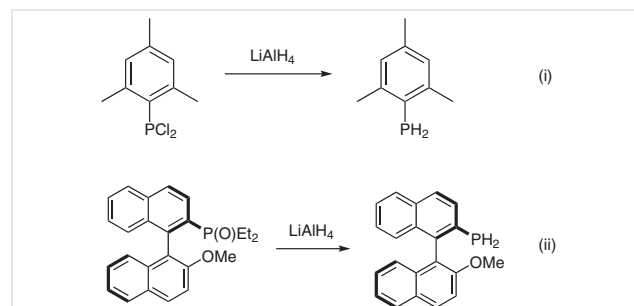
Both primary phosphines RPH<sub>2</sub> and dichlorophosphines RPCl<sub>2</sub> have a rich chemistry and are valuable reagents in reactions such as hydrophosphinations, dehydrocoupling and P–C bond formation.<sup>1–3</sup> This is facilitated by the reactive nature of P–H and P–Cl bonds, respectively.

However, this also means that primary phosphines, particularly those with a low molecular weight and minimal steric bulk protecting the –PH<sub>2</sub> 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.<sup>4–6</sup>

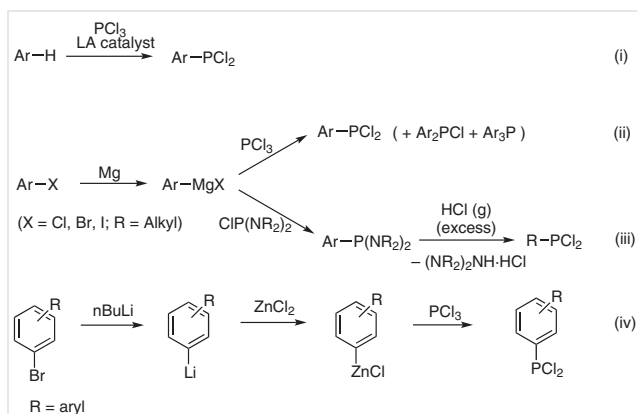
Dichlorophosphines appear to be ubiquitous within synthetic organophosphorus chemistry;<sup>7–12</sup> despite this,

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.

P–C bond formation is a crucial step in the synthesis of aryldichlorophosphines. Early examples involved reacting aromatic hydrocarbons or anisol derivatives with PCl<sub>3</sub> in the presence of a Lewis acid catalyst such as AlCl<sub>3</sub> or SnCl<sub>4</sub> (Scheme 2, route (i)).<sup>13,14</sup> Later examples used the reaction of PCl<sub>3</sub> with respective Grignard (or organolithium) reagent (Scheme 2, route (ii)) and this method is still routinely employed.<sup>15,16</sup> 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<sub>2</sub>PCl and Ar<sub>3</sub>P) are formed in significant amounts, impacting the yield of the dichlorophosphine. This synthetic route also suffers from poor functional group tolerance.



**Scheme 1** Examples of primary phosphine syntheses



**Scheme 2** Selected literature syntheses of dichlorophosphines

To prevent the formation of byproducts due to multiple substitution, a protective group strategy was devised in which  $\text{PCl}_3$  was replaced with  $\text{CIP}(\text{NR}_2)_2$  (Scheme 2, route (iii)). The intermediate aminophosphinyl species  $\text{ArP}(\text{NR}_2)_2$  is formed, which is isolated and then reacted with excess  $\text{HCl}$  gas to form the dichlorophosphine.<sup>4,17</sup> While this synthetic route does prevent multiple substitution from occurring, a new challenge is presented through the use of  $\text{HCl}$  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<sup>18</sup> in which organozinc reagents were employed in the place of Grignard or organolithium reagents (Scheme 2, route (iv)). Lower polarity of  $\text{C-Zn}$  vs.  $\text{C-Mg}$  and  $\text{C-Li}$  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 the 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).<sup>19</sup>

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  $\text{P-C}$

bond-forming step, in which the 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%).<sup>19</sup>

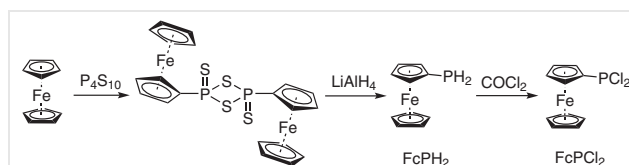
Herein, we report the expansion of this synthetic route to make a selection of primary and dichloroaryl phosphines.

## Perthiophosphonic Anhydrides Synthesis

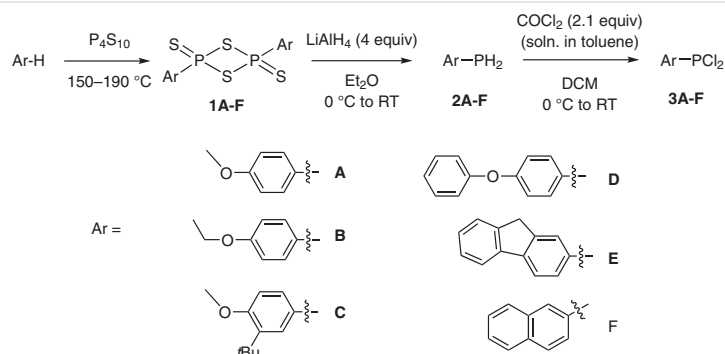
The synthetic route towards primary and dichloroaryl phosphines (Scheme 4) begins with the synthesis of the perthiophosphonic anhydride compounds **1A–F**. These six compounds were selected due to the ease with which they can be synthesised; this is achieved by a simple heating of  $\text{P}_4\text{S}_{10}$  with the related hydrocarbon precursor – anisole, phenetole, 2-*tert*-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,<sup>20–22</sup> with the exception of the 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 ( $\text{P}/\text{ArH}$ ). The reactions were performed under a gentle stream of nitrogen and the exhaust gasses were bubbled through an aqueous  $\text{NaOH}$  solution to remove  $\text{H}_2\text{S}$  formed as a by-product. The liquid mixtures obtained after heating were left to cool to room temperature and the formed solid products were filtered off, washed with dichloromethane or diethyl ether and dried in vacuo. Compounds **1A–F** 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.<sup>23,24</sup>

An important point to make is that the arenes selected in this work contain no functional groups that will provide additional reactivity toward  $\text{P}_4\text{S}_{10}$ , such as ketones, esters and alcohols.<sup>25,26</sup> On the other hand, the presence of electron-donating groups (such as  $\text{OMe}$ ) 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–F**. Nevertheless, the follow-on reactivity (see below) indicates the  $\text{P-C}$  bond formation is fully regioselective in the reactions of



**Scheme 3** Synthesis of  $\text{FcPH}_2$  and  $\text{FcPCl}_2$  reported previously by us



**Scheme 4** Synthetic route used for the synthesis of primary phosphines **2A–F** and dichlorophosphines **3A–F**

$P_4S_{10}$  with both activated and non-activated arenes used in this study, with no other regioisomers detected by  $^{31}P\{^1H\}$  NMR analysis in the phosphines **2A–F** formed from **1A–F** in the next step.

### Reduction to Primary Phosphines

With the desired  $Ar_2P_2S_4$  compounds in hand, the next step was to reduce these with  $LiAlH_4$  (4 equiv of  $LiAlH_4$  per  $Ar_2P_2S_4$  were used) to the corresponding primary phosphines  $ArPH_2$  (**2A–F**). Both  $Ar_2P_2S_4$  and  $LiAlH_4$  were suspended in  $Et_2O$ , and the two suspensions were added together slowly at  $0\text{ }^\circ\text{C}$ . The resulting suspension was filtered, degassed water was added, and the mixture was filtered a second time. 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, and phosphines **2A–D** 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  $^1H$  NMR analysis. Also, the reduc-

tion of **1E** led to partial cleavage of the C–P bond, with small amounts of fluorene being detected by  $^1H$  NMR analysis 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–F**; 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**),<sup>27,28</sup> 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.<sup>27,29</sup> Analysis via  $^{31}P\{^1H\}$  NMR spectroscopy showed **2A–F** to display low-frequency singlets within a very narrow shift range of  $-121.9$  to  $-126.4$  ppm (Table 1); these split into triplets of triplets in the  $^{31}P$  NMR spectra with  $^1J_{PH}$

**Table 1** Isolated Yields, Purity and  $^{31}P\{^1H\}$  Chemical Shifts of Synthesised Perthiophosphonates **1A–F**, Primary Phosphines **2A–F** and Dichlorophosphines **3A–F**

Ar		<b>1</b> ( $Ar_2P_2S_4$ )	<b>2</b> ( $ArPH_2$ )		<b>3</b> ( $ArPCl_2$ )	
		Yield (%)	Yield [purity] <sup>a</sup> (%)	$\delta_p$ (ppm)	Yield [purity] <sup>a</sup> (%)	$\delta_p$ (ppm)
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	<b>A</b>	65	51 [97]	$-126.4$	74 [90]	162.0
<i>p</i> -EtOC <sub>6</sub> H <sub>4</sub>	<b>B</b>	57	52 [92]	$-125.9$	81 [92]	160.5
3- <i>t</i> Bu-4-MeOC <sub>6</sub> H <sub>3</sub>	<b>C</b>	60	33 [94]	$-125.3$	82 [92]	163.6
<i>p</i> -PhOC <sub>6</sub> H <sub>4</sub>	<b>D</b>	47	36 [87]	$-122.9$	90 [90]	162.7
2-Fluorenyl	<b>E</b>	94	33 [97]	$-121.9$	78 [93]	160.1
1-Naphthyl	<b>F</b>	31	8 [86]	$-126.1$	46 [92]	161.8

<sup>a</sup> Purity as assessed by  $^{31}P\{^1H\}$  NMR analysis.

of 199–202 Hz as expected. The purity of the products was further assessed by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR analysis. In addition to multinuclear NMR spectroscopy, the novel compounds **2B–E** were characterised by MS analysis. The spectroscopic data obtained by us for the previously reported species (**2A** and **2F**) were in agreement with the literature (see Experimental Section).

For **2B**, **2D** and **2F**, minor impurities were observed in the  $^{31}\text{P}\{^1\text{H}\}$  spectra as two singlets at approximately  $\delta_{\text{p}} -70$  ppm (2–4% of integral intensity). These were assigned as the respective diphosphines  $\text{ArP}(\text{H})\text{--P}(\text{H})\text{Ar}$ , which, due to the presence of two chiral P atoms, exist in two diastereomeric forms (*meso* and *rac*).<sup>30</sup> In the  $^{31}\text{P}$  NMR spectra, these minor signals split into symmetrical multiplets with pattern consistent with a  $\text{AA}'\text{XX}'$  spin system ( $\text{A}, \text{A}' = \text{P}, \text{X}, \text{X}' = \text{H}$ ). Spin system simulations were carried out to replicate the observed splitting pattern for selected examples (Figure 1).<sup>31</sup> These simulations yielded  $^1J_{\text{PP}} = 150$  Hz,  $^1J_{\text{PH}} = 150$  Hz and  $^2J_{\text{PH}} = 10$  Hz for one of the diastereomers of  $\text{ArP}(\text{H})\text{--P}(\text{H})\text{Ar}$  ( $\text{Ar} = p\text{-EtOC}_6\text{H}_4$ ), which is fully consistent with the suggested diphosphine 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.

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

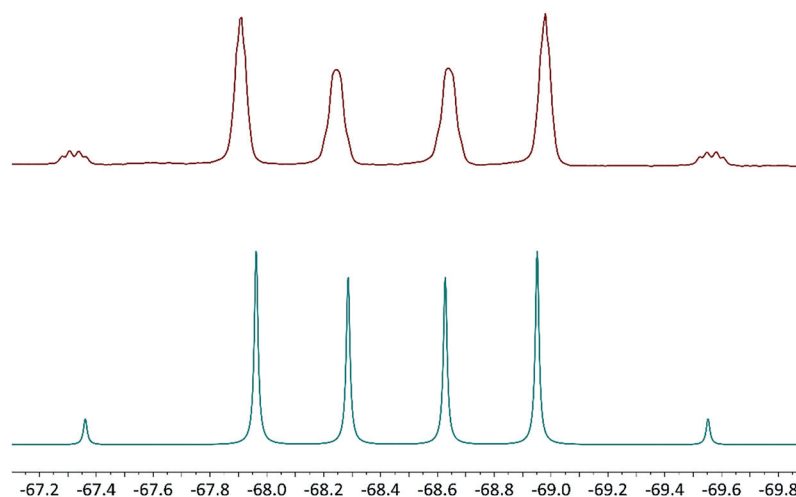
### Chlorination to Dichlorophosphines

In the last step of the synthetic sequence shown in Scheme 4, the primary phosphines **2A–F** were chlorinated

to the aryldichlorophosphines **3A–F**. A commercially available solution of phosgene in toluene (slight excess, 2.1 equiv) 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–F**. 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  $^{31}\text{P}\{^1\text{H}\}$  spectra of **3A–F** were as expected (singlets within a narrow range of  $\delta_{\text{p}}$  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  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR analysis, 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 on 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 room temperature for selected examples of primary phosphines, giving full conversion into the respective dichlorophosphines as judged by  $^{31}\text{P}\{^1\text{H}\}$  NMR analysis.

Syntheses of **3B–E** have not been reported previously. In addition to multinuclear NMR spectroscopy (as discussed above) the compounds were also characterised by MS analysis. The spectroscopic data obtained by us for previously reported species (**3A** and **3F**) agreed with the literature (see experimental section).

In summary, a multigram synthesis of a series of primary arylphosphines and aryldichlorophosphines has been reported. All steps use convenient, commercially available, and economical reagents. Each step requires minimum purification, which is of importance due to the highly reactive



**Figure 1** Top: Partial  $^{31}\text{P}$  NMR spectrum of diphosphine  $\text{ArP}(\text{H})\text{--P}(\text{H})\text{Ar}$  ( $\text{Ar} = p\text{-EtOC}_6\text{H}_4$ ) present as minor impurity in  $p\text{-EtOC}_6\text{H}_4\text{PH}_2$  (**2B**). Bottom: simulated  $^{31}\text{P}$  NMR spectrum.

nature of both compound types. The initial step (formation of perthiophosphonic anhydrides) proceeds highly regio-specifically, 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  $R_2P_2S_4$  compounds.

All manipulations (unless indicated otherwise) were performed under an atmosphere of nitrogen using standard Schlenk line techniques or under an atmosphere of argon in a Saffron glove box. Diethyl ether 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;<sup>32</sup> all other reagents were commercially available. All new compounds were characterised via  $^1H$ ,  $^{31}P\{^1H\}$  and  $^{13}C\{^1H\}$  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 with 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 with a Micromass LCT (electrospray ionisation) from solutions of the analyte in methanol.

#### Synthesis of Perthiophosphonic Anhydrides 1A–F

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  $H_2S$  formed as a by-product. The subsequent workup was performed in air (in a well ventilated fumehood).

#### Lawesson's Reagent, (4-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P<sub>2</sub>S<sub>4</sub> (1A)

**1A** was synthesised according to a reported literature procedure.<sup>20</sup> Anisole (48.7 g, 450 mmol) and  $P_4S_{10}$  (20.0 g, 45.0 mmol) were heated under reflux at 150 °C for 5 hours. The liquid mixture was allowed to cool to r.t. and a pale-yellow crystalline solid precipitated out, which was isolated by vacuum filtration. The solid was washed with ether (2 × 25 mL) and dried *in vacuo*.

Yield: 23.6 g (58.4 mmol, 65%).

#### (4-EtOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P<sub>2</sub>S<sub>4</sub> (1B)

**1B** was synthesised by adapting a reported literature procedure.<sup>20</sup> Phenetole (22.0 g, 180 mmol) and  $P_4S_{10}$  (10.0 g, 22.5 mmol) were heated under reflux to 165 °C for 2 hours. The liquid mixture was allowed to cool to r.t. Upon cooling, an off-white solid precipitated. The solid **1B** was filtered off, washed with ether (2 × 30 mL) and dried *in vacuo*.

Yield: 11.2 g (25.9 mmol, 57%).

#### (3-*t*Bu-4-MeOC<sub>6</sub>H<sub>3</sub>)<sub>2</sub>P<sub>2</sub>S<sub>4</sub> (1C)

**1C** was synthesised according to a reported literature procedure.<sup>22</sup> 2-*tert*-Butylanisole (27.0 g, 164 mmol) and  $P_4S_{10}$  (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 r.t. A crystalline pale-yellow solid precipitated out of solution, which was collected by vacuum filtration, washed with ether (50 mL) and dried *in vacuo*.

Yield: 13.9 g (26.9 mmol, 60%).

#### Belleau's Reagent (4-PhOC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>P<sub>2</sub>S<sub>4</sub> (1D)

**1D** was synthesised according to a reported literature procedure.<sup>21</sup> Diphenyl ether (57.4 g, 337 mmol) and  $P_4S_{10}$  (15.0 g, 33.7 mmol) were heated under reflux at 180 °C for 3 hours. The liquid mixture was cooled to r.t. to afford an off-white solid. The solid was isolated by filtration, washed with ether (3 × 50 mL) and dried *in vacuo*.

Yield: 16.6 g (31.4 mmol, 47%).

#### Flu<sub>2</sub>P<sub>2</sub>S<sub>4</sub>, Flu = 9H-fluorene-2-yl, (1E)

Fluorene (28.6 g, 172 mmol) and  $P_4S_{10}$  (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 r.t., 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 × 20 mL) and dried *in vacuo*.

Yield: 21.9 g (42 mmol, 94%); mp 232–234 °C

MS (EI+):  $m/z$  (%) = 259.98 (100) [M/2]<sup>+</sup>.

MS (CI+):  $m/z$  (%) = 261.0 (100) [M/2 + H]<sup>+</sup>, 520.98 (85) [M + H]<sup>+</sup>.

HRMS (CI+):  $m/z$  calcd for  $C_{26}H_{19}P_2S_4$  [M + H]<sup>+</sup> 520.9839; found: 520.9835

IR (KBr): 1610m (νC=C), 1446m (δC-H), 835m, 770m, 693s (νP=S)  $cm^{-1}$ .

Raman (sealed capillary): 3020w (νAr-H), 2906w (νC-H), 1606s (νC=C), 1480w (νC=C), 703m (νP=S)  $cm^{-1}$ .

#### Nap<sub>2</sub>P<sub>2</sub>S<sub>4</sub>, Nap = naphth-2-yl, (1F)

**1F** was synthesised by adapting a reported literature procedure.<sup>20</sup> Naphthalene (27.7 g, 216 mmol) and  $P_4S_{10}$  (12.0 g, 27 mmol) were heated to 190 °C under reflux for 3 hours. The liquid mixture was allowed to cool slowly to r.t., at which point a yellow solid began to precipitate. The solid **1F** was filtered off, washed with DCM (3 × 20 mL) and dried *in vacuo*.

Yield: 7.51 g (16.9 mmol, 31%).

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

The respective perthiophosphonic anhydride **1A–F** was suspended in diethyl ether (150 mL) and cooled to 0 °C. A suspension of  $LiAlH_4$  (4 equiv) 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 × 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 × 20 mL). The filtrate and washings were collected, and the volatiles were removed *in vacuo* to yield the desired primary phosphines **2A–F**.

#### 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 (400.1 MHz,  $C_6D_6$ ):  $\delta$  = 7.28–7.23 (2 H, m,  $H_2PCCH$ ), 6.62 (2 H, m,  $^3J_{HH} = 8.6$  Hz, OCCH), 3.90 (2 H, d,  $^1J_{HP} = 198.9$  Hz,  $PH_2$ ), 3.22 (3 H, s,  $CH_3$ ).

$^{31}P\{^1H\}$  NMR (162.0 MHz,  $C_6D_6$ ):  $\delta$  = –126.4 (s).

$^{31}P$  NMR (162.0 MHz,  $C_6D_6$ ):  $\delta$  = –126.4 (tt,  $^1J_{PH} = 199.0$  Hz,  $^4J_{PH} = 7.0$  Hz).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 160.2 (s, MeOC), 136.5 (d,  $^2J_{\text{CP}}$  = 17.4 Hz,  $\text{H}_2\text{PCCH}$ ), 118.1 (d,  $^1J_{\text{CP}}$  = 5.8 Hz,  $\text{H}_2\text{PC}$ ), 114.1 (d,  $^3J_{\text{CP}}$  = 6.9 Hz, OCCH), 54.1 (s,  $\text{H}_3\text{CO}$ ).

MS (ESI):  $m/z$  (%) = 335.06 (35)  $[(\text{CH}_3\text{OC}_6\text{H}_4\text{PH}_2\text{O})_2\text{Na}]^+$ , 179.02 (90)  $[(\text{CH}_3\text{OC}_6\text{H}_4\text{PH}_2\text{ONa})^+]$ , 157.04 (100)  $[(\text{CH}_3\text{OC}_6\text{H}_4\text{PH}_2\text{OH})^+]$ , 141.05 (5)  $[(\text{C}_7\text{H}_{10}\text{OP})^+]$ , (M + H) $^+$

Compound **2A** has been reported previously<sup>28</sup> 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%).

$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ): 7.30–7.24 (2 H, m, PCCH), 6.64 (2 H, m,  $^3J_{\text{HH}}$  = 7.8 Hz, OCCH), 3.89 (2 H, d,  $^1J_{\text{HP}}$  = 198.9 Hz,  $\text{PH}_2$ ), 3.53 (2 H, q,  $^3J_{\text{HH}}$  = 7.0 Hz,  $\text{CH}_2$ ), 1.09 (3 H, t,  $^3J_{\text{HH}}$  = 6.9 Hz,  $\text{CH}_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -126.1 (s).

$^{31}\text{P}$  NMR (162.0 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -126.1 (tt,  $^1J_{\text{PH}}$  = 198.8 Hz,  $^4J_{\text{PH}}$  = 6.8 Hz).

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

MS (ESI):  $m/z$  (%) = 363.09 (25)  $[(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{PH}_2\text{O})_2\text{Na}]^+$ , 193.04 (35)  $[(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{PH}_2\text{ONa})^+]$ , 171.06 (100)  $[(\text{C}_2\text{H}_5\text{OC}_6\text{H}_4\text{PH}_2\text{OH})^+]$ , 155.06 (5)  $[(\text{C}_8\text{H}_{12}\text{OP})^+]$ , (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 (2.00 g, 10.2 mmol, 33%).

$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.58–7.52 (1 H, m, Ar-H) 7.31–7.24 (1 H, m, Ar-H) 6.44–6.41 (1 H, m, Ar-H) 4.01 (2 H, d,  $^1J_{\text{HP}}$  = 198.0 Hz,  $\text{PH}_2$ ) 3.22 (3 H, s,  $\text{OCH}_3$ ) 1.41 (9 H, s,  $\text{C}(\text{CH}_3)_3$ ).

$^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -125.3 (s).

$^{31}\text{P}$  NMR (162.0 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = -125.3 (tt,  $^1J_{\text{PH}}$  = 198.6 Hz,  $^3J_{\text{PH}}$  = 7.7 Hz).

$^{13}\text{C}\{^1\text{H}\}$  NMR (125.8 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 159.1 (s,  $\text{H}_3\text{COC}$ ), 138.1 (d,  $^3J_{\text{CP}}$  = 6.3 Hz,  $\text{C-}t\text{Bu}$ ), 134.5 (d,  $^2J_{\text{CP}}$  = 18.2 Hz,  $\text{MeOCHCH}$ ), 133.8 (d,  $^2J_{\text{CP}}$  = 16.9 Hz,  $t\text{BuCCH}$ ), 117.8 (d,  $^1J_{\text{CP}}$  = 5.0 Hz,  $\text{H}_2\text{PC}$ ), 111.8 (d,  $^3J_{\text{CP}}$  = 7.8 Hz,  $\text{H}_3\text{COCCH}$ ), 54.2 (s,  $\text{H}_3\text{C-O}$ ), 34.7 (s,  $\text{C}(\text{CH}_3)_3$ ), 29.2 (s,  $\text{C}(\text{CH}_3)_3$ ).

MS (ESI):  $m/z$  (%) = 431.21 (100)  $[(\text{MeO}(t\text{Bu})\text{C}_6\text{H}_3\text{P}(\text{HO})(t\text{Bu})\text{C}_6\text{H}_3\text{P}(\text{OH})_2+\text{Na})^+]$ , 251.14 (10)  $[(\text{MeO}(t\text{Bu})\text{C}_6\text{H}_3\text{P}(=\text{O})(\text{OH})\text{H}+\text{Na})^+]$ , 213.10 (20)  $[(\text{MeO}(t\text{Bu})\text{C}_6\text{H}_3\text{P}(=\text{O})\text{H}_2+\text{H})^+]$ .

#### 4-Phenoxyphenylphosphine (2D)

Starting from **1D** (8.00 g, 15.1 mmol), **2D** was isolated as a colourless oil (2.22 g, 11.0 mmol, 36%).

$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.19–7.11 (2 H, m, Ar-H), 7.08–6.98 (2 H, m, Ar-H), 6.97–6.65 (5 H, m, Ar-H), 4.02 (2 H, d,  $^1J_{\text{HP}}$  = 202.4 Hz,  $\text{PH}_2$ ).

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

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

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 157.9 (s, qC), 157.1 (s, qC), 136.6 (d,  $^3J_{\text{CP}}$  = 16.8 Hz, PCCHCH), 129.8 (s, CH), 123.4 (s, CH), 121.8 (d,  $^1J_{\text{CP}}$  = 8.1 Hz,  $\text{H}_2\text{PC}$ ), 119.1 (s, CH), 118.8 (d,  $^2J_{\text{CP}}$  = 6.7 Hz,  $\text{H}_2\text{PCCH}$ ).

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

#### 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%).

Mp 86–88 °C

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

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

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

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 143.4 (d,  $^3J_{\text{CP}}$  = 6.6 Hz, qC), 143.1 (s, qC), 141.9 (s, qC), 141.3 (s, qC), 133.2 (d,  $^2J_{\text{CP}}$  = 17.0 Hz,  $\text{H}_2\text{PCCH}$ ), 131.5 (d,  $^2J_{\text{CP}}$  = 15.8 Hz,  $\text{H}_2\text{PCCH}$ ), 126.9 (s, CH), 126.7 (s, CH), 126.1 (d,  $^1J_{\text{CP}}$  = 7.5 Hz,  $\text{H}_2\text{PC}$ ), 124.9 (s, CH), 120.0 (s, CH), 119.7 (d,  $^3J_{\text{CP}}$  = 7.0 Hz,  $\text{H}_2\text{PCCHCH}$ ), 36.3 (s,  $\text{CH}_2$ ).

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

#### 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%).

Mp 66–68 °C.

$^1\text{H}$  NMR (400.1 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.80–7.74 (1 H, m, Ar-H), 7.57–7.37 (3 H, m, Ar-H), 7.34–7.18 (3 H, m, Ar-H), 3.95 (2 H, d,  $^1J_{\text{HP}}$  = 202.4 Hz,  $\text{PH}_2$ ).

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

$^{31}\text{P}$  NMR (162.0 MHz,  $\text{CDCl}_3$ ):  $\delta$  = -121.9 (1 H, tt,  $^1J_{\text{PH}}$  = 202.3 Hz,  $^4J_{\text{PH}}$  = 7.1 Hz).

Values are in agreement with literature data.<sup>27</sup>

#### General Procedure for the Synthesis of Dichlorophosphines 3A–F

The respective primary phosphine (**2A–F**) was dissolved in DCM (150 mL) and cooled to -10 °C. A solution of phosgene (20% solution in toluene, 2.1 equiv) was added dropwise over 30 minutes. The resulting solution was allowed to warm to r.t. and stirred for a further 5 hours. The volatiles were removed *in vacuo* to yield the desired dichlorophosphine **3A–F**.

Safety note: Phosgene and carbon monoxide (evolved in the chlorination reaction) are highly toxic, use of a 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%).

$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.54–7.49 (2 H, m, Ar-H), 6.50 (2 H, m,  $^3J_{\text{HH}}$  = 8.7 Hz, Ar-H), 3.08 (3 H, s,  $\text{CH}_3$ ).

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

All values are in agreement with literature data.<sup>13</sup>

#### 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%).

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

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

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

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

#### Dichloro(3-tert-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%).

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

$^{31}\text{P}\{^1\text{H}\}$  NMR (162.0 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 163.6 (s).

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 162.1 (s,  $\text{H}_3\text{COC}$ ), 138.7 (d,  $^3J_{\text{CP}}$  = 8.9 Hz, *C*-tBu), 131.3 (d,  $^1J_{\text{CP}}$  = 50.6 Hz,  $\text{Cl}_2\text{PC}$ ), 130.3 (d,  $^2J_{\text{CP}}$  = 34.5 Hz, MeOCHCH), 128.8 (d,  $^2J_{\text{CP}}$  = 35.0 Hz, tBuCCH), 111.6 (d,  $^3J_{\text{CP}}$  = 10.1 Hz,  $\text{H}_3\text{COCCH}$ ), 54.3 (s,  $\text{H}_3\text{CO}$ ), 35.2 (s,  $\text{C}(\text{CH}_3)_3$ ), 28.9 (s,  $\text{C}(\text{CH}_3)_3$ ).

MS (ESI):  $m/z$  (%) = 273.13 (14)  $[(\text{MeO})(\text{tBu})\text{C}_6\text{H}_3\text{P}(\text{O})(\text{OMe})_2+\text{H}^+]$ , 257.13 (32)  $[(\text{MeO})(\text{tBu})\text{C}_6\text{H}_3\text{P}(\text{OMe})_2+\text{H}^+]$ , 243.11 (100)  $[(\text{MeO})(\text{tBu})\text{C}_6\text{H}_3\text{P}(\text{OH})(\text{OMe})+\text{H}^+]$ .

#### 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%).

$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.51–7.38 (1 H, m, Ar-H), 7.09–6.50 (8 H, m, Ar-H).

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

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

MS (ESI):  $m/z$  (%) = 401.13 (7)  $[(\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{P})_2\text{H}^+]$ , 201.07 (100)  $[(\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{PH})^+]$ .

#### 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%).

Mp 66–68 °C.

$^1\text{H}$  NMR (400.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.75–7.57 (2 H, m, Ar-H), 7.53–7.33 (2 H, m, Ar-H), 7.30–7.08 (3 H, m, Ar-H), 3.27 (2 H, s,  $\text{CH}_2$ ).

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

$^{13}\text{C}\{^1\text{H}\}$  NMR (100.6 MHz,  $\text{CDCl}_3$ ) 146.5 (s, qC), 143.8 (d,  $^3J_{\text{CP}}$  = 8.2 Hz, qC), 143.2 (s, qC), 141.7 (s, qC), 138.2 (d,  $^1J_{\text{CP}}$  = 52.0 Hz,  $\text{Cl}_2\text{PC}$ ), 129.3 (d,  $^2J_{\text{CP}}$  = 37.9 Hz,  $\text{Cl}_2\text{PCCH}$ ), 128.3 (s, CH), 127.1 (s, CH), 126.7 (d,  $^2J_{\text{CP}}$  = 28.4 Hz,  $\text{Cl}_2\text{PCCH}$ ), 125.3 (s, CH), 120.9 (s, CH), 120.0 (d,  $^3J_{\text{CP}}$  = 10.1 Hz,  $\text{Cl}_2\text{PCCHCH}$ ), 36.9 (s,  $\text{CH}_2$ ).

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

#### 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%).

$^1\text{H}$  NMR (300.1 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 7.95–7.70 (1 H, m, Ar-H) 7.56–6.89 (6 H, m, Ar-H).

$^{31}\text{P}\{^1\text{H}\}$  NMR (121.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  = 160.1 (s).

All values are in agreement with literature data.<sup>12</sup>

#### Conflict of Interest

The authors declare no conflict of interest.

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#### Supporting Information

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