

## Supplementary data

### Exploiting steric control for the regioselective synthesis of *para*-substituted secondary anilines

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#### Electronic Supplementary Information

#### General considerations

All manipulations of air and/or water sensitive materials were performed under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove box (unless stated otherwise). Solvents were freshly distilled under nitrogen from sodium/benzophenone (tetrahydrofuran, diethyl ether, toluene, dme), from calcium hydride (dichloromethane), from sodium (hexane, pentane, 40-60 PE) or from P<sub>2</sub>O<sub>5</sub> (C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub>) and degassed prior to use. Elemental analyses were performed by S. Boyer at the University of North London and Mrs J. Dorstal of the analytical services of the Department of Chemistry, University of Durham. NMR were recorded on a Bruker AM 250, AMX 300 or AMX 400; chemical shifts were referenced to residual protio impurities in the deuterated solvent (<sup>1</sup>H), to the deuterated solvent (<sup>13</sup>C) or to external aqueous 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). All spectra were obtained at ambient probe temperatures unless stated otherwise. Infrared spectra were recorded (Nujol mulls [KBr windows], KBr discs, or in solution [KBr windows]) on a Perkin Elmer 1600 spectrophotometer; Nujol was dried over sodium wire. Mass spectra were recorded on a Kratos Concept 1H instrument and are reported in (*m/z*).

Aniline was dried and distilled prior to use and (Pr<sup>i</sup><sub>2</sub>N)<sub>2</sub>PCl prepared according to a literature procedure.<sup>i</sup> All other chemicals were obtained commercially and used as received.

GC-MS were performed using a Perkin-Elmer Turbomass spectrometer/ Perkin-Elmer Autosystem XL gas chromatograph.

## Syntheses

***N*-(1-Isopropyl-2-methylpropylidene)aniline, Pr<sup>i</sup><sub>2</sub>C(=NPh):** A xylene (200 mL) solution of 2,4-dimethyl-3-pentanone (70.8 mL, 0.5 mols), aniline (48 mL, 0.525 mols) and PTSA (0.25 g) was heated at reflux under Dean-Stark conditions for 4 days, after which time 8.1 mL of water had been evolved. Vacuum distillation removed xylene, aniline and ketone at < 40°C @ 0.4 mmHg and gave the product between 54-55°C @ 0.4 mmHg as a colourless oil (71.79 g, 76%); δ<sub>H</sub> (250.13 MHz; CDCl<sub>3</sub>) 7.18 (2H, m, *o*-C<sub>6</sub>H<sub>5</sub>), 6.90 (1H, m, *p*-C<sub>6</sub>H<sub>5</sub>), 6.55 (2H, m, *m*-C<sub>6</sub>H<sub>5</sub>), 2.70 (2H, sept, <sup>3</sup>J<sub>HH</sub> = 6.9, CH(CH<sub>3</sub>)<sub>2</sub>), 1.13 (6H, d, <sup>3</sup>J<sub>HH</sub> = 6.7, CH<sub>3</sub>), 0.95 (6H, d, <sup>3</sup>J<sub>HH</sub> = 6.9, CH<sub>3</sub>); δ<sub>C</sub>{<sup>1</sup>H} (62.90 MHz; CDCl<sub>3</sub>) 183.83 (s, C=N), 151.75 (s, *i*-C<sub>6</sub>H<sub>5</sub>), 128.97 (s, *o*-C<sub>6</sub>H<sub>5</sub>), 122.54 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 119.11 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 32.59 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 30.17 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 22.69 (s, CH<sub>3</sub>), 19.96 (s, CH<sub>3</sub>); EI 189 (M)<sup>+</sup>, 146 (M-Pr<sup>i</sup>)<sup>+</sup>.

***N*-(1-Isopropyl-2-methylpropyl)aniline, Pr<sup>i</sup><sub>2</sub>CH(N(H)Ph) (1).** This is a modification of the literature procedure.<sup>ii</sup> To a stirred, cooled (0°C) ethereal (200 mL) solution of Pr<sup>i</sup><sub>2</sub>C(=NPh) (18.53 g, 9.79×10<sup>-2</sup> mols) was added LiAlH<sub>4</sub> (1.0 M, diethyl ether, 117 mL, 5.85×10<sup>-2</sup> mols) and the mixture heated at reflux for 60 hours. After cooling (0°C), the mixture was cautiously hydrolysed with distilled water (150 mL). The organic fraction was separated and the aqueous fraction washed with Et<sub>2</sub>O (4 × 100 mL). The combined organic fractions were dried (MgSO<sub>4</sub>) and volatiles removed *in vacuo* to leave the product as a colourless oil, which is light sensitive, turning peach in colour unless kept in the dark (17.67 g, 94%), (Found: C, 81.76; H, 10.94; N, 7.43%. C<sub>13</sub>H<sub>21</sub>N requires: C, 81.62; H, 11.06; N, 7.32%); δ<sub>H</sub> (400.13 MHz, CDCl<sub>3</sub>) δ: 7.15 (2H, m, *o*-C<sub>6</sub>H<sub>5</sub>), 6.63 (3H, m, *p*-C<sub>6</sub>H<sub>5</sub> + *m*-C<sub>6</sub>H<sub>5</sub>), 3.41 (1H, br s, NH), 2.99 (1H, br t, <sup>3</sup>J<sub>HH</sub> = 6.0, CH(NHPh)(Pr<sup>i</sup>)<sub>2</sub>), 1.90 (2H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 0.98 (6H, d, <sup>3</sup>J<sub>HH</sub> = 6.8, CH<sub>3</sub>), 0.94 (6H, d, <sup>3</sup>J<sub>HH</sub> = 6.6, CH<sub>3</sub>); δ<sub>C</sub>{<sup>1</sup>H} (62.90 MHz, CDCl<sub>3</sub>) δ: 150.5 (s, *i*-C<sub>6</sub>H<sub>5</sub>), 129.4 (s, *o*-C<sub>6</sub>H<sub>5</sub>), 116.1 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 112.6 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 64.1 (s, CH(NHPh)(Pr<sup>i</sup>)<sub>2</sub>), 31.5 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 21.0 (s, CH<sub>3</sub>), 18.1 (s, CH<sub>3</sub>); EI: 191 (M)<sup>+</sup>, 148 (M-Pr<sup>i</sup>)<sup>+</sup>.

**(para-bis(Diisopropylamino)phosphanyl-phenyl)-(1-isopropyl-2-methyl-propyl)-amine, Pr<sup>i</sup><sub>2</sub>CH[N(H)(para-{(Pr<sup>i</sup><sub>2</sub>N)<sub>2</sub>P}C<sub>6</sub>H<sub>4</sub>) (2a).** A Schlenk was charged with Pr<sup>i</sup><sub>2</sub>CH(N(H)Ph) (5.12 g, 2.68×10<sup>-2</sup> mols) which was degassed *in vacuo*. Et<sub>2</sub>O (40 mL) was added and the solution cooled (-78°C) and stirred as Bu<sup>n</sup>Li (1.6 M, hexanes, 17.6 mL, 2.81×10<sup>-2</sup> mols) was added dropwise. The peach coloured solution immediately turned blue-green, and was allowed to warm to RT with stirring over 1 hour to give a yellow solution. After re-cooling (-78°C), the solution was transferred *via* cannula onto a cooled (-78°C) suspension of (Pr<sup>i</sup><sub>2</sub>N)<sub>2</sub>PCl (7.15 g, 2.68×10<sup>-2</sup> mols) in Et<sub>2</sub>O (40 mL). The reaction vessel was left to warm to RT with stirring for 18 hours, yielding a yellow solution with white precipitate. Removal of volatiles *in vacuo* and extraction of product from LiCl with hexane gave a yellow solution. The hexane solution was concentrated and after prolonged cooling (-30°C), the product precipitated as white crystals (5.61 g, 96%), (Found: C, 71.14; H, 11.59; N, 9.95. C<sub>25</sub>H<sub>48</sub>N<sub>3</sub>P requires: C, 71.21; H, 11.47; N, 9.97%); δ<sub>H</sub> (250.13 MHz; CDCl<sub>3</sub>) 7.98 (2H, dd, <sup>3</sup>J<sub>HH</sub> 8.7, <sup>3</sup>J<sub>PH</sub> 6.7 Hz, *m*-C<sub>6</sub>H<sub>4</sub>), 6.53 (2H, dd, <sup>3</sup>J<sub>HH</sub> 8.7, <sup>4</sup>J<sub>PH</sub> 1.9 Hz, *o*-C<sub>6</sub>H<sub>4</sub>), 3.42 (4H, d sept, <sup>3</sup>J<sub>HH</sub> 6.7, <sup>3</sup>J<sub>PH</sub> 2.5, PNCH), 2.99 (1H, br d, <sup>3</sup>J<sub>HH</sub> 10.1, NH), 2.84 (1H, m, CNHCH), 1.58 (2H, overlapping sept, <sup>3</sup>J<sub>HH</sub> 6.4 Hz, CCH), 1.29 (12H, d, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, NCH(CH<sub>3</sub>)<sub>2</sub>), 1.27 (12H, d, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, NCH(CH<sub>3</sub>)<sub>2</sub>), 0.83 (6H, d, <sup>3</sup>J<sub>HH</sub> 6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>), 0.76 (6H, d, <sup>3</sup>J<sub>HH</sub> 6.7 Hz, CH(CH<sub>3</sub>)<sub>2</sub>); δ<sub>C</sub>{<sup>1</sup>H} (62.90 MHz; CDCl<sub>3</sub>) 150.1 (s, *ipso*-C<sub>6</sub>H<sub>4</sub>), 133.1 (d, <sup>1</sup>J<sub>PC</sub> 21.9 Hz, *ipso*-C<sub>6</sub>H<sub>4</sub>), 131.1 (s, C<sub>6</sub>H<sub>4</sub>), 112.9 (d, <sup>2</sup>J<sub>PC</sub> 5.6 Hz, C<sub>6</sub>H<sub>4</sub>), 64.4 (s, NCH), 48.2 (d, <sup>2</sup>J<sub>PC</sub> 11.7 Hz, NCH), 31.8 (s, CH), 25.1 (d, <sup>3</sup>J<sub>PC</sub> 7.6 Hz, NCH), 25.0 (d, <sup>3</sup>J<sub>PC</sub> 7.1 Hz, NCH), 21.3 (s, CH(CH<sub>3</sub>)<sub>2</sub>), 18.4 (s, CH(CH<sub>3</sub>)<sub>2</sub>); δ<sub>P</sub>{<sup>1</sup>H} (101.26 MHz; CDCl<sub>3</sub>) + 59.4 (s); EI: 421 (M<sup>+</sup>).

**(para-diphenylphosphanyl-phenyl)-(1-isopropyl-2-methyl-propyl)-amine, Pr<sup>i</sup><sub>2</sub>CH[N(H)(para-{Ph<sub>2</sub>P}C<sub>6</sub>H<sub>4</sub>) (2b).** A Schlenk was charged with **1** (1.04 g, 5.46×10<sup>-3</sup> mols) which was degassed *in vacuo*. Et<sub>2</sub>O (30 mL) was added and the solution cooled (-78°C) and stirred as Bu<sup>n</sup>Li (1.6 M, hexanes, 3.4 mL, 5.46×10<sup>-3</sup> mols) was added dropwise. The peach coloured solution immediately turned blue-green, and was allowed to warm to RT with stirring over 1 hour to give a yellow solution. After re-cooling (-78°C), Ph<sub>2</sub>PCl (1.0 mL, 5.46×10<sup>-3</sup> mols) was added slowly from a syringe. The reaction was allowed to warm to room temperature and stirred for a further 12h, resulting in the formation of a pale yellow/green solution and a white precipitate; δ<sub>P</sub>{<sup>1</sup>H} (121.94 MHz; CDCl<sub>3</sub>) +54.80 (s). Compound **2b** was converted directly to the corresponding sulphide **2e** (see below).

**(para-trimethylsilyl-phenyl)-(1-isopropyl-2-methyl-propyl)-amine, Pr<sup>i</sup><sub>2</sub>CH[N(H)(para-{Me<sub>3</sub>Si}C<sub>6</sub>H<sub>4</sub>)] (2c).** A Schlenk was charged with **1** (1.92 g, 0.01 mols) which was degassed *in vacuo*. Et<sub>2</sub>O (50 mL) was added and the solution cooled (-78°C) and stirred as Bu<sup>n</sup>Li (1.6 M, hexanes, 6.25 mL, 0.01 mols) was added dropwise. The peach coloured solution immediately turned blue-green, and was allowed to warm to RT with stirring over 1 hour to give a yellow solution. After re-cooling (-78°C), Me<sub>3</sub>SiCl (1.3 mL, 0.01 mols) was added slowly from a syringe. The reaction was allowed to warm to room temperature and stirred for a further 12h, resulting in the formation of a pale pink solution and white precipitate. All volatile components were removed *in vacuo* and the product extracted into CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL) and isolated by filtration. Removal of the solvent under vacuum afforded a red oil, which was distilled under reduced pressure (108-112°C, 0.2 mmHg; Kügelrohr) affording **2c** (2.42 g, 89%) as a clear yellow oil (Found: C, 73.02; H, 10.91; N, 5.29. C<sub>16</sub>H<sub>29</sub>NSi requires: C, 72.93; H, 11.09; N, 5.32%); δ<sub>H</sub> (250.13 MHz; CDCl<sub>3</sub>) 7.17 (2H, d, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, C<sub>6</sub>H<sub>4</sub>), 6.49 (2H, d, <sup>3</sup>J<sub>HH</sub> 7.8 Hz, C<sub>6</sub>H<sub>4</sub>), 3.37 (1H, br d, <sup>2</sup>J<sub>HH</sub> 10.0, NH), 2.90 (1H, m, CH(NHPh)(Pr<sup>i</sup>)<sub>2</sub>), 1.81 (2H, m, CH(CH<sub>3</sub>)<sub>2</sub>), 0.89 (6H, d, <sup>3</sup>J<sub>HH</sub> 6.1, CH<sub>3</sub>), 0.83 (6H, d, <sup>3</sup>J<sub>HH</sub> 6.1, CH<sub>3</sub>), 0.17 (9H, s, Me<sub>3</sub>Si); δ<sub>C</sub>{<sup>1</sup>H} (62.90 MHz; CDCl<sub>3</sub>) 150.9 (s, N-*ipso*-C<sub>6</sub>H<sub>4</sub>), 134.8 (s, N-*meta*-C<sub>6</sub>H<sub>4</sub>), 125.3 (s, Si-*ipso*-C<sub>6</sub>H<sub>4</sub>), 112.2 (s, N-*para*-C<sub>6</sub>H<sub>4</sub>), 63.7 (s, NCH), 31.4 (s, NCH), 21.1 (s, NCH), 18.2 (s, CH(CH<sub>3</sub>)<sub>2</sub>), -0.5 (s, (CH<sub>3</sub>)<sub>3</sub>Si); EI: 264 (MH<sup>+</sup>).

**(para-trimethylstannyl-phenyl)-(1-isopropyl-2-methyl-propyl)-amine, Pr<sup>i</sup><sub>2</sub>CH[N(H)(para-{Me<sub>3</sub>Sn}C<sub>6</sub>H<sub>4</sub>)] (2d).** A Schlenk was charged with **1** (0.96 g, 5 mmols) which was degassed *in vacuo*. Et<sub>2</sub>O (50 mL) was added and the solution cooled (-78°C) and stirred as Bu<sup>n</sup>Li (1.6 M, hexanes, 3.1 mL, 5 mmols) was added dropwise. The peach coloured solution immediately turned blue-green, and was allowed to warm to RT with stirring over 1 hour to give a yellow solution. After re-cooling (-78°C), Me<sub>3</sub>SnCl (1.00 g, 5 mmols) was added slowly from a syringe. The reaction was allowed to warm to room temperature and stirred for a further 12h, resulting in the formation of a pale orange solution and white precipitate. All volatile components were removed *in vacuo* and the product extracted into CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 mL) and isolated by filtration. Removal of the solvent *in vacuo* afforded a dark red oil, which was distilled under reduced pressure (161-165°C, 0.2 mmHg; Kügelrohr)

affording **2d** (1.36 g, 77%) as a dark orange/brown oil (Found: C, 55.01; H, 8.43; N, 4.22.  $C_{16}H_{29}NSn$  requires: C, 54.27; H, 8.25; N, 3.96%);  $\delta_H$  (400.13 MHz;  $CDCl_3$ ) 7.02 (2H, d,  $^3J_{HH}$  7.8 Hz,  $C_6H_4$ ), 6.41 (2H, d,  $^3J_{HH}$  7.8 Hz,  $C_6H_4$ ), 3.66 (1H, br d,  $^2J_{HH}$  8.0, NH), 2.90 (1H, m,  $CH(NHPh)(Pr^i)_2$ ), 1.96 (2H, m,  $CH(CH_3)_2$ ), 0.91 (6H, d,  $^3J_{HH}$  6.1,  $CH_3$ ), 0.87 (6H, d,  $^3J_{HH}$  6.1,  $CH_3$ ), 0.20 (9H, s+satellites,  $^2J_{SnH}$  54.0 Hz,  $Me_3Sn$ );  $\delta_C\{^1H\}$  (100.62 MHz;  $CDCl_3$ ) 148.8 (s, N-*ipso*- $C_6H_4$ ), 142.0 (s+satellites,  $^1J_{SnC}$  470 Hz, Sn-*ipso*- $C_6H_4$ ), 134.3 (s, N-*meta*- $C_6H_4$ ), 112.2 (s, N-*para*- $C_6H_4$ ), 63.7 (s, NCH), 31.4 (s, NCH), 21.1 (s, NCH), 18.2 (s,  $CH(CH_3)_2$ ), -9.9 (s+satellites,  $^1J_{SnC}$  349 Hz,  $(CH_3)_3Sn$ ); ES+: 356 (MH<sup>+</sup>).

**(para-diphenylthiophosphanyl-phenyl)-(1-isopropyl-2-methyl-propyl)-amine,**

**Pr<sup>i</sup><sub>2</sub>CH[N(H)(para-{Ph<sub>2</sub>PS}C<sub>6</sub>H<sub>4</sub>) (2e).** To the reaction mixture obtained during the synthesis of **2b** was added excess elemental sulphur. After stirring at rt for 12h the solution was filtered through a plug of silica and all volatile components removed *in vacuo* to afford a beige solid. Recrystallisation from hexane/ $CH_2Cl_2$  at  $-30^\circ C$  gave **2e** (1.78 g, 80%) as colourless blocks suitable for a study by X-ray diffraction, (Found: C, 73.76; H, 7.41; N, 3.46.  $C_{25}H_{30}NPS$  requires: C, 73.71; H, 7.36; N, 3.44%);  $\delta_H$  (250.13 MHz;  $CDCl_3$ ) 7.63 (4H, m, arom.), 7.35 (8H, m, arom.), 6.47 (2H, dd,  $^3J_{HH}$  7.0 Hz,  $^4J_{HH}$  2.0 Hz,  $C_6H_4$ ), 3.77 (1H, br d,  $^2J_{HH}$  10.0, NH), 2.98 (1H, m,  $CH(NHPh)(Pr^i)_2$ ), 1.81 (2H, m,  $CH(CH_3)_2$ ), 0.93 (6H, d,  $^3J_{HH}$  6.0,  $CH_3$ ), 0.87 (6H, d,  $^3J_{HH}$  6.0,  $CH_3$ );  $\delta_C\{^1H\}$  (62.90 MHz;  $CDCl_3$ ) 152.9 (s, *ipso*- $C_6H_4$ ), 134.3 (d,  $^1J_{PC}$  85.3, *ipso*- $C_6H_5$ ), 134.2 (d,  $^3J_{PC}$  12.1 Hz,  $C_6H_4$ ), 132.4 (d,  $^2J_{PC}$  10.7 Hz, *o*- $C_6H_5$ ), 131.3 (d,  $^4J_{PC}$  2.8 Hz, *p*- $C_6H_5$ ), 128.5 (d,  $^3J_{PC}$  12.4 Hz, *m*- $C_6H_5$ ), 116.5 (d,  $^1J_{PC}$  96.4 Hz, *ipso*- $C_6H_4$ ), 112.1 (d,  $^2J_{PC}$  13.7 Hz,  $C_6H_4$ ), 63.7 (s, NCH), 31.3 (s, CH), 21.1 (s,  $CH(CH_3)_2$ ), 18.0 (s,  $CH(CH_3)_2$ );  $\delta_P\{^1H\}$  (121.94 MHz;  $CDCl_3$ ) + 42.2 (s); EI: 408 (MH<sup>+</sup>).

**(1-Isopropyl-2-methyl-propyl)-bis(diisopropylamino)phosphanyl-(para-**

**bis(diisopropylamino)phosphanyl-phenyl)-amine (3a):** A Schlenk was charged with **2a** (1.00 g,  $2.37 \times 10^{-3}$  mols).  $Et_2O$  (10 mL) was added and the solution cooled ( $-78^\circ C$ ) and stirred as  $Bu^iLi$  (1.6 M, hexanes, 1.50 mL,  $2.37 \times 10^{-3}$  mols) was added dropwise. The colourless solution immediately turned red-brown, and was allowed to warm to RT with stirring over 1 hour to give a yellow solution. After re-cooling ( $-78^\circ C$ ), the solution was added to a cold ( $-78^\circ C$ ) suspension of  $(^iPr_2N)_2PCl$  (1.01 g,  $2.37 \times 10^{-3}$  mols) in  $Et_2O$  (10 mL). The reaction was

allowed to warm to room temperature and stirred for a further 12h, resulting in the formation of a pale yellow solution and white precipitate. The  $^{31}\text{P}$  NMR spectrum of the reaction mixture revealed only two resonances,  $\delta$  +61.3 (s) and 102.7 (s) ppm, consistent with the formation of **3a**. Volatile components were removed *in vacuo* to afford a yellow solid that was subsequently dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL). Excess elemental sulphur was added and stirred for 1h. The reaction mixture was filtered and the filtrate passed through a plug of silica. Removal of solvent under reduced pressure afforded **3a** as its disulphide (1.31 g, 77%). Crystals suitable for a study by X-ray crystallography were obtained by recrystallisation from  $\text{CH}_2\text{Cl}_2$ /hexane; (Found: C, 62.15; H, 10.56; N, 9.79.  $\text{C}_{37}\text{H}_{75}\text{N}_5\text{P}_2\text{S}_2$  requires: C, 62.06; H, 10.56; N, 9.78%);  $\delta_{\text{H}}$  (400.13 MHz; 323K;  $\text{CDCl}_3$ ) 8.04 (4H, br,  $\text{C}_6\text{H}_4$ ), 4.05 (4H, br sept.,  $^3J_{\text{HH}}$  7.0 Hz, PNCH), 3.82 (4H, sept.,  $^3J_{\text{HH}}$  7.0 Hz, PNCH), 3.64 (1H, t,  $^3J_{\text{HH}}$  5.9 Hz, NCH), 2.50 (2H, m, NCHCH), 1.36 (24H, d  $^3J_{\text{HH}}$  6.0 Hz, PNCHCH<sub>3</sub>), 1.22 (24H, d  $^3J_{\text{HH}}$  6.0 Hz, PNCHCH<sub>3</sub>), 1.12 (6H, d  $^3J_{\text{HH}}$  6.0 Hz, NCHCHCH<sub>3</sub>), 0.56 (6H, d  $^3J_{\text{HH}}$  6.0 Hz, NCHCHCH<sub>3</sub>);  $\delta_{\text{C}}$  (100.62 MHz; 323K;  $\text{CDCl}_3$ ) 146.4 (s, N-*ipso*- $\text{C}_6\text{H}_4$ ), 135.4 (d,  $^1J_{\text{PC}}$  120.0 Hz, P-*ipso*- $\text{C}_6\text{H}_4$ ), 132.8 (d,  $^2J_{\text{PC}}$  11.5 Hz,  $\text{C}_6\text{H}_4$ ), 129.9 (dd,  $^3J_{\text{PC}}$  6.0 Hz,  $^3J_{\text{PC}}$  12.9 Hz,  $\text{C}_6\text{H}_4$ ), 68.2 (s, NCH), 48.9 (d,  $^2J_{\text{PC}}$  5.2 Hz, PNCH), 47.8 (d,  $^2J_{\text{PC}}$  5.2 Hz, PNCH), 31.4 (d,  $^3J_{\text{PC}}$  3.1 Hz, NCHCH), 24.8 (d, 2.4 Hz, PNCHCH<sub>3</sub>), 24.7 (d, 2.4 Hz, PNCHCH<sub>3</sub>), 24.0 (d, 7.8 Hz, PNCHCH<sub>3</sub>), 23.9 (d, 7.8 Hz, PNCHCH<sub>3</sub>), 23.6 (s, NCHCHCH<sub>3</sub>), 19.6 (s, NCHCHCH<sub>3</sub>);  $\delta_{\text{P}}$  (161.99 MHz; 323K;  $\text{CDCl}_3$ ) +71.30 (s), +71.29 (s); EI: 716 (M+).

**One-pot preparation of 3a from 1:** A Schlenk was charged with  $\text{Pr}^i_2\text{CH}(\text{N}(\text{H})\text{Ph})$  (2.00 g, 0.010 mols) which was degassed *in vacuo*.  $\text{Et}_2\text{O}$  (40 mL) was added and the solution cooled ( $-78^\circ\text{C}$ ) and stirred as  $\text{Bu}^n\text{Li}$  (1.6 M, hexanes, 13.1 mL, 0.021 mols) was added dropwise. The peach coloured solution immediately turned dark blue-green, and was allowed to warm to RT with stirring over 1 hour to give a yellow/orange solution. After re-cooling ( $-78^\circ\text{C}$ ), the solution was transferred *via* cannula onto a cooled ( $-78^\circ\text{C}$ ) suspension of  $(\text{Pr}^i_2\text{N})_2\text{PCl}$  (5.59 g, 0.020 mols) in  $\text{Et}_2\text{O}$  (40 mL). The reaction vessel was left to warm to RT with stirring for 18 hours, yielding a dark yellow solution with white precipitate. Removal of volatiles *in vacuo* and extraction of product from  $\text{LiCl}$  with hexane gave a yellow solution. The hexane solution was removed under reduced pressure to afford **3a** as a white solid (5.80 g, 89%);  $\delta_{\text{P}}\{^1\text{H}\}$  (121.94 MHz;  $\text{CDCl}_3$ ) +102.7 (s), +60.2 (s).

**(1-Isopropyl-2-methyl-propyl)-diphenylphosphanyl-(*para*-trimethylsilanyl-phenyl)-**

**amine (3b):** A Schlenk was charged with  $\text{Pr}^i_2\text{CH}(\text{N}(\text{H})\text{Ph})$  (2.00 g, 0.010 mols) which was degassed *in vacuo*.  $\text{Et}_2\text{O}$  (20 mL) was added and the solution cooled ( $-78^\circ\text{C}$ ) and stirred as  $\text{Bu}^n\text{Li}$  (1.6 M, hexanes, 13.1 mL, 0.021 mols) was added dropwise. The peach coloured solution immediately turned dark blue-green, and was allowed to warm to RT with stirring over 2 hours to give a dark yellow solution. After re-cooling ( $-78^\circ\text{C}$ ), the solution was transferred *via* cannula onto a cooled ( $-78^\circ\text{C}$ ) solution of  $\text{Ph}_2\text{PCl}$  (10.5 mL, 0.010 mols) in  $\text{Et}_2\text{O}$  (20 mL).  $^{31}\text{P}$  NMR spectroscopy showed a single resonance at  $\delta -4.0$  (s) ppm. The reaction vessel was left to warm to RT with stirring for 18 hours, yielding a dark yellow solution with white precipitate. The reaction mixture was cooled ( $-78^\circ\text{C}$ ) and  $\text{Bu}^n\text{Li}$  (1.6 M, hexanes, 13.1 mL, 0.021 mols) was added dropwise, before allowing the Schlenk to warm to RT, affording a yellow/brown solution. After 1h at RT the mixture was re-cooled ( $-78^\circ\text{C}$ ) prior to slow addition of excess  $\text{Me}_3\text{SiCl}$  (2.5 mL, 0.020 mols) *via* syringe. The reaction was left stirring at RT for 12h to afford a dark yellow solution and a white precipitate. Volatiles were removed *in vacuo* and the product extracted from  $\text{LiCl}$  with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 10$  mL) by filtration under  $\text{N}_2$  and the solvent removed under reduced pressure to afford **3b** as a yellow/orange air sensitive waxy solid (3.39 g, 76%). Further attempts to purify **3b** lead to decomposition presumably as a result of the labile Si-N bond; (Found: C, 72.79; H, 7.91; N, 2.79.  $\text{C}_{28}\text{H}_{38}\text{NPSi}$  requires: C, 75.12; H, 8.56; N, 3.13%);  $\delta_{\text{H}}$  (250.13 MHz;  $\text{CDCl}_3$ ) 7.58 (4H, m,  $\text{C}_6\text{H}_5$ ), 7.24 (8H, m, arom.), 6.40 (2H, dd,  $^3J_{\text{HH}}$  6.9 Hz,  $^4J_{\text{HH}}$  1.8 Hz,  $\text{C}_6\text{H}_4$ ), 2.59 (1H, m,  $\text{CH}(\text{NHPH})(\text{Pr}^i)_2$ ), 2.06 (2H, m,  $\text{CH}(\text{CH}_3)_2$ ), 1.01 (6H, d,  $^3J_{\text{HH}}$  6.2,  $\text{CH}_3$ ), 0.91 (6H, d,  $^3J_{\text{HH}}$  6.2,  $\text{CH}_3$ ), 0.10 (9H, s,  $\text{Si}(\text{CH}_3)_3$ );  $\delta_{\text{C}}\{^1\text{H}\}$  (62.90 MHz;  $\text{CDCl}_3$ ) 144.9 (s, *ipso*- $\text{C}_6\text{H}_4$ ), 137.4 (d,  $^1J_{\text{PC}}$  15.8 Hz, *ipso*- $\text{C}_6\text{H}_5$ ), 133.8 (d,  $^2J_{\text{PC}}$  21.9 Hz, *o*- $\text{C}_6\text{H}_5$ ), 129.7 ( $^3J_{\text{PC}}$  10.9 Hz,  $\text{C}_6\text{H}_4$ ), 129.0 (s, *p*- $\text{C}_6\text{H}_5$ ), 128.8 (d,  $^3J_{\text{PC}}$  6.8 Hz, *m*- $\text{C}_6\text{H}_5$ ), 117.3 (d,  $^1J_{\text{PC}}$  26.4 Hz, *ipso*- $\text{C}_6\text{H}_4$ ), 112.9 (s,  $\text{C}_6\text{H}_4$ ), 67.5 (s, NCH), 30.6 (s, CH), 19.1 (s,  $\text{CH}(\text{CH}_3)_2$ ), 17.8 (s,  $\text{CH}(\text{CH}_3)_2$ ), -0.2 (s,  $\text{Si}(\text{CH}_3)_3$ );  $\delta_{\text{P}}\{^1\text{H}\}$  (121.94 MHz;  $\text{CDCl}_3$ ) -5.11 (s), EI: 448 (MH+).

***N*-lithium.tmeda-(1-isopropyl-2-methyl-propyl)-phenyl amide (4).** A Schlenk was charged with  $\text{Pr}^i_2\text{CH}(\text{N}(\text{H})\text{Ph})$  (2.08 g,  $1.09 \times 10^{-2}$  mols) which was degassed *in vacuo*.  $\text{Et}_2\text{O}$  (30 mL) was added and the solution cooled ( $-78^\circ\text{C}$ ) and stirred as  $\text{Bu}^n\text{Li}$  (1.6 M, hexanes, 5.5 mL,  $1.11 \times 10^{-2}$  mols) was added dropwise. The peach coloured solution immediately turned

blue-green before it was allowed to warm to RT with stirring over 1 hour to give a yellow solution. TMEDA (1.6 mL,  $1.09 \times 10^{-2}$  mols) was added dropwise inducing a slight lightening in colour. After stirring at RT for 1h, concentration of the solution *in vacuo* lead to the immediate precipitation of **4** as square yellow platelets, which were isolated by filtration (2.49 g, 73%), (Found: C, 71.35; H, 11.67; N, 9.76.  $C_{19}H_{36}N_3Li$  requires: C, 72.80; H, 11.58; N, 13.41%; reliable analyses could not be obtained presumably due to the sensitive nature of the compound);  $\delta_H$  (400.13 MHz; 300 K;  $C_6D_6$ ) 7.29 (2H, m,  $C_6H_4$ ), 6.45 (1H, br, NH), 6.40 (2H, m,  $C_6H_4$ ), 3.26 (1H, t,  $^3J_{HH}$  5.9 Hz, NCH), 1.81 (2H, sept,  $^3J_{HH}$  6.7 Hz, NCH(CH)), 1.75 (12H, s,  $NCH_3$ ), 1.59 (4H, s,  $NCH_2$ ), 1.18 (6H, d,  $^3J_{HH}$  6.7 Hz,  $NCH(CH_3)_2$ ), 1.02 (6H, d,  $^3J_{HH}$  6.7 Hz,  $NCH(CH_3)_2$ );  $\delta_C\{^1H\}$  (100.62 MHz;  $C_6D_6$ ) 164.5 (s, *Nipso*- $C_6H_4$ ), 130.4 (s br, *o*- $C_6H_4$ ), 112.8 (br  $\nu_{1/2}$  176 Hz, *Pipso*- $C_6H_4$ ), 105.9 (s, *m*- $C_6H_4$ ), 66.3 (s, NCH), 56.7 (s,  $NCH_2$ ), 45.7 (s,  $NCH_3$ ), 33.7 (s, NCH(CH)), 21.9 (s,  $CH(CH_3)_2$ ), 20.0 (s,  $CH(CH_3)_2$ ).

**Preparation of phenyl-triisopropylsilanyl-amine (5).** Compound **5** was prepared according to a slight modification of the literature procedure.<sup>iii</sup> To a cold ( $-78^\circ C$ ) solution of aniline (2.4 mL, 25.9 mmol) in  $Et_2O$  (20 mL) was added  $Bu^iLi$  (1.6M hexanes, 16.3 mL, 25.9 mmol), which on warming afforded an orange solution. After a period of 30 mins at RT, the solution was cooled ( $-78^\circ C$ ) and a cold ( $-78^\circ C$ ) solution of TIPSCl (5.6 mL, 25.9 mmol) added. On warming to RT the solution became dark red and a white precipitate formed. After stirring at RT for 16h, all volatile components were removed *in vacuo* to afford a dark brown oil. Extraction with  $CH_2Cl_2$  ( $2 \times 10$  mL) followed distillation under reduced pressure ( $80-85^\circ C$ , 0.2 mmHg; Kugelrohr) affording **5** (3.88 g, 60%) as a dark brown oil;  $\delta_H$  (400.13 MHz;  $CDCl_3$ ) 7.24 (2H, m, *ortho*- $C_6H_4$ ), 6.87 (1H, td,  $^3J_{HH}$  6.4,  $^4J_{HH}$  0.8 Hz, *para*- $C_6H_4$ ), 6.74 (2H, td,  $^3J_{HH}$  6.4,  $^4J_{HH}$  0.8 Hz, *meta*- $C_6H_4$ ), 3.20 (1H, br,  $\nu_{1/2}$  11 Hz, NH), 1.22 (m, SiCH),<sup>†</sup> 1.16 (s, SiCH( $CH_3$ ))<sup>‡</sup>;  $\delta_C\{^1H\}$  (100.62 MHz;  $CDCl_3$ ) 148.2 (s, *Nipso*- $C_6H_4$ ), 129.5 (s, *o*- $C_6H_4$ ), 118.2 (s, *p*- $C_6H_4$ ), 117.1 (s, *m*- $C_6H_4$ ), 18.6 (s, SiCH( $CH_3$ )<sub>2</sub>), 12.5 (s, SiCH); GC 8.69 (100%) minutes.

<sup>†</sup> Overlapping signals: combined integration = 21H.

<sup>‡</sup> The appearance of the isopropyl methyl resonance as a singlet is in accord with that reported previously.<sup>iii</sup>

Solutions of **5** in dry  $CDCl_3$  slowly hydrolyse under air, hydrolysis being complete after *ca.* 48 h. Samples of **5** remain unchanged for months if kept under dry, oxygen-free conditions.

**Reaction of 5 with Bu<sup>n</sup>Li and (Pr<sup>i</sup><sub>2</sub>N)<sub>2</sub>PCl.** A Schlenk was charged with **5** (0.45 g, 1.80 mmols) which was degassed *in vacuo*. Et<sub>2</sub>O (30 mL) was added and the solution cooled (-78°C) and stirred as Bu<sup>n</sup>Li (1.6 M, hexanes, 1.1 mL, 1.80×10<sup>-3</sup> mols) was added dropwise. The solution was re-cooled (-78°C) and added to a cold (-78°C) suspension of (Pr<sup>i</sup><sub>2</sub>N)<sub>2</sub>PCl (0.48 g, 1.80 mmols). This gave a pale yellow solution, which on warming to RT became a green-yellow and formed a white precipitate. The reaction was left stirring at RT for 18h after which time volatiles were removed *in vacuo* and the product extracted from LiCl with CH<sub>2</sub>Cl<sub>2</sub> (2×10 mL) by filtration under N<sub>2</sub> and the solvent removed under reduced pressure to afford a brown sticky oil; δ<sub>P</sub>{<sup>1</sup>H} (161.98 MHz; CH<sub>2</sub>Cl<sub>2</sub>) + 110.4 (s, 1P, **7**), +58.3 (s, 3P, **6**). Further attempts to purify the mixture lead to decomposition; hence, HCl (1.0 M, Et<sub>2</sub>O, 10.8 mL, 108.00 mmols) was added slowly to a solution (Et<sub>2</sub>O, 15 mL) of the brown oil at RT. The reaction mixture was then stirred at RT for 18h, affording an orange oil and an off-white precipitate. Removal of volatile components *in vacuo* followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (2×10 mL) gave a dark orange-brown solution: δ<sub>P</sub>{<sup>1</sup>H} (161.98 MHz; CH<sub>2</sub>Cl<sub>2</sub>) +215 (s, PCl<sub>3</sub>), + 160 (s, **8**); GC 8.29 (TIPSCl) minutes. The presence of Pr<sup>i</sup><sub>2</sub>NH<sub>2</sub>Cl and C<sub>6</sub>H<sub>5</sub>NH<sub>3</sub>Cl were confirmed by <sup>1</sup>H spectroscopy and EI mass spectrometry.

**bis(diisopropylamino)phosphanyl-(para-bis(diisopropylamino)phosphanyl-phenyl)-triisopropylsilanyl-amine (9):** A Schlenk was charged with **5** (0.45 g, 1.80×10<sup>-3</sup> mols) which was degassed *in vacuo*. Et<sub>2</sub>O (30 mL) was added and the solution cooled (-78°C) and stirred as Bu<sup>n</sup>Li (1.6 M, hexanes, 2.2 mL, 3.60×10<sup>-3</sup> mols) was added dropwise. The solution was re-cooled (-78°C) and added to a cold (-78°C) suspension of (Pr<sup>i</sup><sub>2</sub>N)<sub>2</sub>PCl (0.96 g, 3.60×10<sup>-3</sup> mols). This gave a dark orange solution, which on warming to RT became dark brown and formed a white precipitate. The reaction was left stirring at RT for 18h after which time volatiles were removed *in vacuo* and the product extracted from LiCl with CH<sub>2</sub>Cl<sub>2</sub> (2×10 mL) by filtration under N<sub>2</sub> and the solvent removed under reduced pressure to afford **9** as a waxy tan solid [0.88 g, 69%; δ<sub>P</sub> (161.98 MHz; CDCl<sub>3</sub>) +111.0 (s), +58.9 (s)]. Following addition of CH<sub>2</sub>Cl<sub>2</sub> (10 mL) and excess elemental sulphur to **9**, the reaction mixture was stirred at RT for 18h. The reaction mixture was filtered and the filtrate passed through a plug of silica. Removal of solvent under reduced pressure afforded **9** as its disulphide following

recrystallisation from CH<sub>2</sub>Cl<sub>2</sub>/hexane (0.75 g, 54%); (Found: C, 59.10; H, 10.11; N, 9.00. C<sub>37</sub>H<sub>75</sub>N<sub>5</sub>P<sub>2</sub>S<sub>2</sub> requires: C, 60.50; H, 10.54; N, 9.05%); δ<sub>H</sub> (400.13 MHz; CDCl<sub>3</sub>) 7.90 (4H, br, C<sub>6</sub>H<sub>4</sub>), 3.95 (4H, br sept., <sup>3</sup>J<sub>HH</sub> 6.9 Hz, PNCH), 3.65 (4H, sept., <sup>3</sup>J<sub>HH</sub> 6.9 Hz, PNCH), 1.24 (27H, m, SiCH and PNCHCH<sub>3</sub>), 1.12 (s, 18H, SiCH(CH<sub>3</sub>)); δ<sub>C</sub>{<sup>1</sup>H} (100.62 MHz; CDCl<sub>3</sub>) 147.0 (s, *Nipso*-C<sub>6</sub>H<sub>4</sub>), 134.5 (d, <sup>1</sup>J<sub>PC</sub> 115.0 Hz, *P-ipso*-C<sub>6</sub>H<sub>4</sub>), 130.1 (d, <sup>2</sup>J<sub>PC</sub> 9.0 Hz, C<sub>6</sub>H<sub>4</sub>), 128.3 (dd, <sup>3</sup>J<sub>PC</sub> 6.9 Hz, <sup>3</sup>J<sub>PC</sub> 11.0 Hz, C<sub>6</sub>H<sub>4</sub>), 18.4 (s, SiCH(CH<sub>3</sub>)<sub>2</sub>), 12.5 (d, <sup>3</sup>J<sub>PC</sub> 1.1 Hz, SiCH); δ<sub>P</sub> (161.98 MHz; CDCl<sub>3</sub>) +74.9 (s), +68.3 (s).

**(1-Isopropyl-2-methyl-propyl)-methyl-phenyl-amine (10).** This compound was prepared by reductive methylation using a modification of a literature procedure.<sup>iv</sup> An acetonitrile solution (125 mL) of (1-isopropyl-2-methyl-propyl)-phenyl-amine (**1**) (4.0g, 0.02 mols) was treated with aqueous formaldehyde (37%, 25.2 mL, 0.03 mol) and NaBH<sub>3</sub>CN (5.94 g, 0.09 mol). Glacial acetic acid (3.2 mL) was added drop-wise over a period of 10 minutes, inducing an exothermic reaction, during which time the reaction mixture darkened considerably. After stirring at r.t. for 2 h, a second portion of glacial acetic acid (3.2 mL) was added drop-wise over a period of 10 minutes before leaving the mixture to stir at r.t. for 30 minutes. The reaction mixture was poured into Et<sub>2</sub>O (300 mL), washed with 1.0M KOH solution (3 × 100 mL) and saturated brine (100 mL). Finally the orange ether solution was separated and dried over K<sub>2</sub>CO<sub>3</sub>. Removal of all volatile components under reduced pressure afforded **10** as an analytically pure orange oil (2.90 g, 67%), (Found: C, 81.92; H, 11.25; N, 6.74. C<sub>14</sub>H<sub>23</sub>N requires: C, 81.89; H, 11.29; N, 6.82%); δ<sub>H</sub> (301.24 MHz; CDCl<sub>3</sub>) 7.22 (2H, m, *m*-C<sub>6</sub>H<sub>5</sub>), 6.79 (2H, d, <sup>3</sup>J<sub>HH</sub> 8.2 Hz, *m*-C<sub>6</sub>H<sub>5</sub>), 6.64 (1H, t, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, *p*-C<sub>6</sub>H<sub>5</sub>), 3.44 (1H, t, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, CH), 2.83 (3H, s, NMe), 2.16 (2H, overlapping sept, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, CH), 0.99 (6H, d, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, CH<sub>3</sub>), 0.92 (6H, d, <sup>3</sup>J<sub>HH</sub> 7.0 Hz, CH<sub>3</sub>); δ<sub>C</sub>{<sup>1</sup>H} (75.76 MHz; CDCl<sub>3</sub>) 159.5 (s, *ipso*-C<sub>6</sub>H<sub>5</sub>), 136.6 (s, *m*-C<sub>6</sub>H<sub>5</sub>), 122.6 (s, *p*-C<sub>6</sub>H<sub>5</sub>), 119.2 (s, *o*-C<sub>6</sub>H<sub>5</sub>), 75.0 (s, CH), 41.2 (s, NMe), 37.8 (s, CH), 28.7 (s, CH<sub>3</sub>), 27.3 (s, CH<sub>3</sub>); GC-MS: 15.7 minutes; EI: 206 (MH<sup>+</sup>, 1%), 205 (MH<sup>+</sup>, 15%), 162 (100%).

**(1-Isopropyl-2-methyl-propylidene)-*p*-tolyl-amine:** A xylene (200 mL) solution of 2,4-dimethyl-3-pentanone (51.95 g, 0.44 mols), toluidine (49.90 g, 0.46 mols) and PTSA (0.25 g) was heated at reflux under Dean-Stark conditions for 4 days, after which time 7.0 mL of water

had been evolved. Vacuum distillation removed xylene, aniline and ketone at  $< 50^{\circ}\text{C}$  @ 0.2 mmHg and gave the product between  $170\text{-}172^{\circ}\text{C}$  @ 0.2 mmHg as an orange/brown oil (52.78 g, 59%);  $\delta_{\text{H}}$  (250.13 MHz;  $\text{CDCl}_3$ ) 7.05 (2H, d,  $^3J_{\text{HH}}$  9.0 Hz, *o*- $\text{C}_6\text{H}_4$ ), 6.50 (2H, d,  $^3J_{\text{HH}}$  9.0 Hz, *p*- $\text{C}_6\text{H}_5$ ), 2.80 (2H, m,  $\text{CH}(\text{CH}_3)_2$ ), 2.30 (3H, s, *p*- $\text{CH}_3$ ), 1.18 (6H, d,  $^3J_{\text{HH}} = 6.9$ ,  $\text{CH}_3$ ), 1.00 (6H, d,  $^3J_{\text{HH}} = 6.9$ ,  $\text{CH}_3$ );  $\delta_{\text{C}}\{\text{H}\}$  (62.90 MHz;  $\text{CDCl}_3$ ) 183.6 (s,  $\text{C}=\text{N}$ ), 149.0 (s, *i*- $\text{C}_6\text{H}_4$ ), 144.1 (s, *i*- $\text{C}_6\text{H}_4$ ), 129.4 (s,  $\text{C}_6\text{H}_5$ ), 118.9 (s,  $\text{C}_6\text{H}_5$ ), 32.2 (s,  $\text{CH}(\text{CH}_3)_2$ ), 30.0 (s,  $\text{CH}(\text{CH}_3)_2$ ), 22.6 (s,  $\text{CHCH}_3$ ), 20.8 (s, *p*- $\text{CH}_3$ ), 19.8 (s,  $\text{CHCH}_3$ ); EI: 204 (MH)<sup>+</sup>; IR KBr, neat)  $1653\text{cm}^{-1}$  ( $\text{C}=\text{N}$ ).

**(1-Isopropyl-2-methyl-propyl)-*p*-tolyl-amine (11):** To a stirred, cooled ( $0^{\circ}\text{C}$ ) ethereal (200 mL) solution of  $\text{Pr}^i_2\text{C}(\text{=N}^i\text{-CH}_3\text{-C}_6\text{H}_4)$  (20.30 g,  $99.9 \times 10^{-3}$  mols) was added  $\text{LiAlH}_4$  (1.0 M, diethyl ether, 120 mL, 0.12 mols) and the mixture heated at reflux for 60 hours. After cooling ( $0^{\circ}\text{C}$ ), the mixture was cautiously hydrolysed with distilled water (150 mL). The organic fraction was separated and the aqueous fraction washed with  $\text{Et}_2\text{O}$  ( $4 \times 100$  mL). The combined organic fractions were dried ( $\text{MgSO}_4$ ) and volatiles removed *in vacuo* to leave the product as an orange oil, which is light sensitive, turning red/brown in colour unless kept in the dark (18.24 g, 89%); since GC-MS analysis ( $>96\%$ ) revealed the purity of **11** to be high, no further purification was undertaken; (Found: C, 81.84; H, 10.89; N, 7.00%.  $\text{C}_{14}\text{H}_{23}\text{N}$  requires: C, 81.89; H, 11.29; N, 6.82%);  $\delta_{\text{H}}$  (301.24 MHz,  $\text{CDCl}_3$ )  $\delta$ : 6.90 (2H, d,  $^3J_{\text{HH}}$  8.0 Hz,  $\text{C}_6\text{H}_4$ ), 6.50 (2H,  $^3J_{\text{HH}}$  8.0 Hz,  $\text{C}_6\text{H}_4$ ), 3.28 (1H, br s, NH), 2.93 (1H, br  $\nu_{1/2}$  17 Hz, NCH), 2.20 (2H, s, *p*- $\text{CH}_3$ ), 1.82 (2H, m,  $\text{CH}(\text{CH}_3)_2$ ), 0.97 (6H, d,  $^3J_{\text{HH}} = 5.7$ ,  $\text{CH}_3$ ), 0.91 (6H, d,  $^3J_{\text{HH}} = 5.7$ ,  $\text{CH}_3$ );  $\delta_{\text{C}}\{\text{H}\}$  (75.76 MHz,  $\text{CDCl}_3$ )  $\delta$ : 141.5 (s, *i*- $\text{C}_6\text{H}_5$ ), 130.2 (s,  $\text{C}_6\text{H}_4$ ), 126.1 (s, *p*- $\text{CH}_3\text{-C}$ ), 116.1 (s, *p*- $\text{C}_6\text{H}_5$ ), 112.5 (s,  $\text{C}_6\text{H}_4$ ), 70.4 (s, NCH), 31.0 (s,  $\text{CH}(\text{CH}_3)_2$ ), 20.9 (s, *p*- $\text{CH}_3$ ), 20.1 (s,  $\text{CH}_3$ ), 19.2 (s,  $\text{CH}_3$ ); EI: 205 (M)<sup>+</sup>.

**Diphenylphosphino-methyl-phenyl-amine (12)<sup>v</sup>:**  $^n\text{BuLi}$  (1.6M, 3.10 mL,  $4.87 \times 10^{-3}$  mols), To a cooled ( $-78^{\circ}\text{C}$ ) Schlenk charged with **10** (1.00 g,  $4.87 \times 10^{-3}$  mols) and  $\text{Et}_2\text{O}$  (20 mL) was added  $\text{Bu}^n\text{Li}$  (1.6M, 3.10 mL,  $4.87 \times 10^{-3}$  mols) *via* a syringe. The solution was stirred and allowed to warm to rt to afford a red/brown solution. After 1 h at rt the reaction mixture was cooled ( $-78^{\circ}\text{C}$ ) and added to a cooled ( $-78^{\circ}\text{C}$ ) solution of  $\text{Ph}_2\text{PCl}$  (1.12 mL,  $4.87 \times 10^{-3}$  mols) in  $\text{Et}_2\text{O}$  (10 mL). On warming to rt a brown solution and a white precipitate were obtained.

Removal of volatile components *in vacuo* followed by extraction with CH<sub>2</sub>Cl<sub>2</sub> (2×10 mL) afforded **12** as a brown oil (1.36 g, 96% yield) that was pure according to <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy. The spectroscopic data were consistent with those reported in the literature; δ<sub>P</sub>{<sup>1</sup>H} (161.98 MHz; CH<sub>2</sub>Cl<sub>2</sub>) +56.8 (s).

**Reaction of 10 with Bu<sup>n</sup>Li and (<sup>i</sup>Pr<sub>2</sub>N)<sub>2</sub>PCl:** To a cooled (-78°C) Schlenk charged with **10** (1.30 g, 6.34×10<sup>-3</sup> mols) and Et<sub>2</sub>O (20 mL) was added Bu<sup>n</sup>Li (1.6M, 4.00 mL, 6.34×10<sup>-3</sup> mols) *via* a syringe. The solution was stirred and allowed to warm to rt to afford a red/brown solution. After 1 h at rt the reaction mixture was cooled (-78°C) and added to a cooled (-78°C) suspension of (<sup>i</sup>Pr<sub>2</sub>N)<sub>2</sub>PCl (1.69 g, 6.34×10<sup>-3</sup> mols) in Et<sub>2</sub>O (20 mL). On warming to rt a brown solution and a white precipitate were obtained. The <sup>31</sup>P NMR spectrum of the reaction mixture displayed a sharp resonance at δ + 105.2 ppm and overlapping signals at *ca.* δ + 56-61 ppm, which correspond to the formation of **13** and **14**, in <16% and 72%, respectively. This assignment was further confirmed by addition of excess elemental sulphur to the reaction mixture, stirring at rt for 12h, followed by filtration and removal of volatile components *in vacuo* to afford a waxy brown solid; GC-MS analysis : 20.2 (371 {MH<sup>+</sup>}, 16%, **13**), 24.5 (371 {MH<sup>+</sup>}, 72%, **14**). Attempts at the separation of **13** from **14** proved unsuccessful.

**Reaction of 11 with <sup>n</sup>BuLi and Ph<sub>2</sub>PCl:** To a cooled (-78°C) Schlenk charged with **11** (1.00 g, 4.87×10<sup>-3</sup> mols) and Et<sub>2</sub>O (20 mL) was added <sup>n</sup>BuLi (1.6M, 3.10 mL, 4.87×10<sup>-3</sup> mols) *via* a syringe. The solution was stirred and allowed to warm to rt to afford a dark blue solution. After 1 h at rt the reaction mixture was cooled (-78°C) and a solution of Ph<sub>2</sub>PCl (0.90 mL, 4.87×10<sup>-3</sup> mols) added directly *via* syringe. On warming to rt a dark brown solution and a white precipitate were obtained. The <sup>31</sup>P NMR spectrum of the reaction mixture displayed a multitude of resonances, which included a sharp resonance at δ - 4.8 ppm (consistent with the formation of **15**), confirming complete consumption of Ph<sub>2</sub>PCl. Following addition of excess elemental sulphur to the reaction mixture, stirring at rt for 12h, filtration and removal of volatile components *in vacuo*, all attempts to further purify the reaction mixture were unsuccessful; GC-MS analysis : 25.9 (423 {MH<sup>+</sup>}, 30%, **15**).

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