

## A New and Convenient Way for the Synthesis of Strong Non-ionic Bases

Marc Taillefer\*, Aurélien Hameau, Nicolas Rahier  
and Jean-Noël Volle\*

*Architectures moléculaires et matériaux nanostructurés, UMR CNRS 5076,  
Ecole Nationale Supérieure de Chimie de Montpellier  
8, Rue de l'Ecole Normale, 34296 Montpellier Cedex 5, France*

### General.

All reagents were obtained commercially, and were used with no further purification unless otherwise noted. Chlorodiphenylphosphine and dichlorophenylphosphine were purchased from Fluka, distilled in vacuum and stored under nitrogen atmosphere. Tetrahydrofuran was dried by distillation from over sodium and benzophenone. Dimethylsulfoxide was supplied by SDS Company with 99.5% purity and containing less 0.01% of water. Before using, dimethylsulfoxide was stored under nitrogen atmosphere and activated molecular sieves 4 Å for at least 48 hours. *n*-BuLi (1.6 M in Hexanes) was purchased from Aldrich and ammonia gaseous from Air Products with a purity of 99.9%. <sup>1</sup>H spectrums were done with a Bruker AC 200 MHz or DRX 250 MHz spectrometer. <sup>31</sup>P were performed with a Bruker AC-200 Mhz spectrometer operating at 81 Mhz and <sup>13</sup>C were recorded on a Bruker DRX 250 MHz or DRX 400 Mhz spectrometers with respectively frequencies of 63 MHz and 101 MHz. Elemental analysis FAB spectra were taken on a JEOL JMS-SX 102A spectrometer with *m*-nitrobenzyl alcohol (NBA) as matrix. Melting points were measured on Büchi B-540 apparatus and are uncorrected.

### Preparation of starting material.

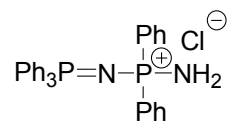
$\text{Ph}_3\text{P}^{\oplus}\text{Cl}^{\ominus}$  **Amino(triphenyl)phosphonium chloride (1b)**.<sup>1</sup> At room temperature and over 10 minutes, a solution of hexachloroethane (39.0 g, 0.165 mol) in tetrahydrofuran (150 mL) was added to a solution of triphenylphosphine (39.3 g, 0.15 mol) in tetrahydrofuran (150 mL). After 2 h of stirring, the mixture was cooling at -25 °C and ammonia gaseous was bubbled during 30 min. Then, the temperature was raised at 25 °C, the suspension was stirred again 2 h and tetrahydrofuran was removed by evaporation. The solid residue isolated was diluted with an aqueous solution of sodium chloride (250 mL, 10%) and extracted with chloroform (5 × 200 mL). The organic layers were combined, washed with an aqueous solution of sodium chloride (2 × 100 mL), dried with

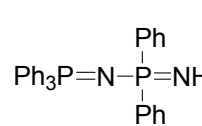
sodium sulfate, filtered and evaporated. Finally, the white solid recovered was dissolved in a dichloromethane/methanol mixture (150 mL, 7:3) and precipitated with diethyl ether (1 L). Upon filtration and rinsing with diethyl ether (200 mL) was obtained a white solid (39.8 g, 84%). M.p. 234 - 235 °C (lit.<sup>1</sup> 230 - 232 °C); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 7.7 – 7.4 (m, 9 H), 7.78 (dd, *J* = 13.5, 8.4 Hz, 6 H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>): δ = 134.4 (d, *J* = 2.8 Hz, 3 C), 133.7 (d, *J* = 11.8 Hz, 6 C), 129.8 (d, *J* = 13.2 Hz, 6 C), 124.4 (d, *J* = 103.5 Hz, 3 C); <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>): δ = 36.16 (s); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 190 (37) [<sup>37</sup>Cl<sup>-</sup>+NBA], 188 (100) [<sup>35</sup>Cl<sup>-</sup>+NBA], 37 (11) [<sup>37</sup>Cl<sup>-</sup>], 81 (34) [<sup>35</sup>Cl<sup>-</sup>]; MS [FAB<sup>+</sup> (NBA)]: *m/z* (%): 279 (22) [*M*<sup>+</sup>+1], 278 (100) [*M*<sup>+</sup>], 124 (9) [*M*<sup>+</sup>-2C<sub>6</sub>H<sub>5</sub>].

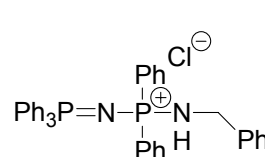
### Preparation of P<sub>2</sub>-H<sup>+</sup>

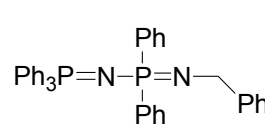
#### General procedure.

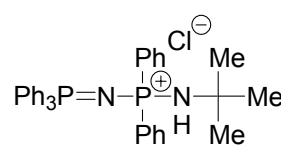
At -20 °C, a solution of butyllithium (30 mmol) in hexanes (19 mL) was added dropwise to a solution of amino(triphenyl)phosphonium chloride (**1b**, 4.7 g, 15 mmol) in tetrahydrofuran (130 mL). Upon addition, the mixture was stirred for half hour at -20 °C, chlorodiphenylphosphine (3.3 g, 4.0 mL, 18 mmol) and hexachloroethane (4.3 g, 18 mmol) were successively added. After 2 h at room temperature, the mixture was refluxed with an alkylamine (60 mmol) or stirred at 25 °C with ammonia for 2 h. The solvents were evaporated and a brine solution (100 mL, 10%) was poured. The aqueous mixture was extracted with chloroform (3 × 100 mL), organics layers were combined, dried with sodium sulfate and filtered. After evaporation, crystallization and finally a vacuum drying, salts **5a-c-H<sup>+</sup>** were obtained pure. The basic form **5a-c** have been studied by NMR spectroscopy after treatment of **5a-H<sup>+</sup>** (238 mg, 0.5 mmol), **5b-H<sup>+</sup>** (301 mg, 0.5 mmol) and **5c-H<sup>+</sup>** (285 mg, 0.5 mmol) with sodium hydride (12.0 mg, 0.5 mmol) in dimethylsulfoxide-d<sub>6</sub> (5 mL).

 **Compound (5a-H<sup>+</sup>)**.<sup>2</sup> From ammonia **5a-H<sup>+</sup>** was isolated as a white solid (6.7 g, 87%). M.p. 241 - 243 °C (lit.<sup>2</sup> 246 °C); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.8 – 7.3 (m, 25 H), 6.12 (s broad, 2 H); <sup>13</sup>C NMR (63 MHz, DMSO-d<sub>6</sub>): δ = 134.14 (d, *J* = 2.7 Hz, 3 C), 133.36 (d, *J* = 2.7 Hz, 2 C), 133.02 (d, *J* = 11.3 Hz, 6 C), 132.07 (d, *J* = 11.3 Hz, 4 C), 131.80 (dd, *J* = 132.7, 4.4 Hz, 2 C), 130.17 (d, *J* = 13.0 Hz, 6 C), 129.66 (d, *J* = 13.6 Hz, 4 C), 128.46 (dd, *J* = 106.4, 3.0 Hz, 3 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 20.82 (d, *J* = 4.2 Hz, 1 P), 18.30 (d, *J* = 4.2 Hz, 1 P); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 190 (29) [<sup>37</sup>Cl<sup>-</sup>+NBA], 188 (82) [<sup>35</sup>Cl<sup>-</sup>+NBA], 37 (33) [<sup>37</sup>Cl<sup>-</sup>], 35 (100) [<sup>35</sup>Cl<sup>-</sup>]; HR-MS [FAB<sup>+</sup> (NBA)]: *m/z*: calcd for C<sub>30</sub>H<sub>27</sub>N<sub>2</sub>P<sub>2</sub><sup>+</sup>: 477.1650; found 477.1648.

 **Compound (5a).** <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 8.0 – 7.4 (m); <sup>13</sup>C NMR (63 MHz, DMSO-d<sub>6</sub>): δ = 148.08 (dd, *J* = 121.9, 6.0 Hz, 2 C), 133.0 (d, *J* = 2.9 Hz, 3 C), 132.96 (d, *J* = 10.7 Hz, 6 C), 131.68 (d, *J* = 9.2 Hz, 4 C), 131.65 (dd, *J* = 103.7, 2.8 Hz, 3 C), 130.14 (d, *J* = 2.8 Hz, 2 C), 129.55 (d, *J* = 12.4 Hz, 6 C), 128.46 (d, *J* = 11.7 Hz, 4 C); <sup>31</sup>P NMR (81 MHz, THF/DMSO-d<sub>6</sub>): δ = 16.63 (d, *J* = 1.6 Hz, 1 P), 13.54 (d, *J* = 1.6 Hz, 1 P).

 **Compound (5b-H<sup>+</sup>).** From benzylamine (3.2 g, 3.3 mL, 30 mmol) **5b-H<sup>+</sup>** was obtained as a white solid (6.9 g, 76%). M.p. 213 - 214 °C (ethanol/water); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.9 – 7.1 (m, 31 H), 3.86 (dd, *J* = 10.4 7.6 Hz, 2 H); <sup>13</sup>C NMR (63 MHz, DMSO-d<sub>6</sub>): δ = 139.92 (d, *J* = 7.3 Hz, 1 C), 134.30 (d, *J* = 2.3 Hz, 3 C), 133.80 (d, *J* = 2.3 Hz, 2 C), 132.90 (d, *J* = 11.5 Hz, 6 C), 132.56 (dd, *J* = 11.5 Hz, 4 C), 130.27 (d, *J* = 13.0 Hz, 6 C), 129.81 (d, *J* = 13.4 Hz, 4 C), 129.61 (dd, *J* = 131.1, 4.6 Hz, 2 C), 128.92 (s, 2 C), 128.24 (s, 2 C), 128.18 (dd, *J* = 106.6, 2.7 Hz, 3 C), 127.77 (s, 1 C), 44.41 (s, 1 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 23.08 (d, *J* = 6.0 Hz, 1 P), 18.61 (d, *J* = 6.0 Hz, 1 P); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 190 (36) [<sup>37</sup>Cl<sup>-</sup>+NBA], 188 (100) [<sup>35</sup>Cl<sup>-</sup>+NBA], 37 (32) [<sup>37</sup>Cl<sup>-</sup>], 35 (92) [<sup>35</sup>Cl<sup>-</sup>]; HR-MS [FAB<sup>+</sup> (NBA)]: *m/z*: calcd for C<sub>37</sub>H<sub>33</sub>N<sub>2</sub>P<sub>2</sub><sup>+</sup>: 567.2119; found 567.2137.

 **Compound (5b).** <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.9 – 7.0 (m, 30 H), 2.51 (d, *J* = 15.1 Hz, 2 H); <sup>13</sup>C NMR (63 MHz, DMSO-d<sub>6</sub>): δ = 147.12 (d, *J* = 21.5 Hz, 1 C), 138.22 (dd, *J* = 127.3, 4.2 Hz, 2 C), 133.13 (d, *J* = 2.7 Hz, 3 C), 132.95 (d, *J* = 10.7 Hz, 6 C), 132.37 (d, *J* = 9.2 Hz, 4 C), 131.39 (dd, *J* = 104.7, 1.9 Hz, 3 C), 130.65 (d, *J* = 1.5 Hz, 2 C), 129.62 (d, *J* = 12.3 Hz, 6 C), 128.69 (d, *J* = 11.9 Hz, 4 C), 128.30 (s, 2 C), 127.57 (s, 2 C), 125.93 (s, 1 C), 48.38 (s, 1 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 11.57 (d, *J* = 2.2 Hz, 1 P), 5.54 (d, *J* = 2.2 Hz, 1 P).

 **Compound (5c-H<sup>+</sup>).** From *tert*-butylamine (4.3 g, 6.3 mL, 60 mmol), **5c-H<sup>+</sup>** was recovered as a white solid (7.7 g, 90%). M.p. 273 - 274 °C (dec.); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.8 – 7.4 (m, 25 H), 6.12 (d, *J* = 13.1 Hz, 1 H), 1.15 (s, 9 H); <sup>13</sup>C NMR (63 MHz, DMSO-d<sub>6</sub>): δ = 134.35 (d, *J* = 2.3 Hz, 3 C), 133.61 (d, *J* = 2.3 Hz, 2 C), 132.93 (d, *J* = 11.1 Hz, 6 C), 132.59 (d, *J* = 11.5 Hz, 4 C), 131.23 (dd, *J* = 129.6, 4.6 Hz, 2 C), 130.33 (d, *J* = 13.0 Hz, 6 C), 129.69 (d, *J* = 13.4 Hz, 4 C), 128.20 (dd, *J* = 106.6, 2.3 Hz, 3 C), 54.33 (d, *J* = 3.8 Hz, 1 C), 32.11 (d, *J* = 4.2 Hz, 3 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 17.94 (d, *J* = 8.2 Hz, 1 P), 16.74 (d, *J* = 8.2 Hz, 1 P); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 190 (16) [<sup>37</sup>Cl<sup>-</sup>+NBA]; 188 (45) [<sup>35</sup>Cl<sup>-</sup>+NBA]; 37 (39) [<sup>37</sup>Cl<sup>-</sup>]; 35 (100) [<sup>35</sup>Cl<sup>-</sup>]; HR-MS [FAB<sup>+</sup> (NBA)]: *m/z*: calcd for C<sub>34</sub>H<sub>35</sub>N<sub>2</sub>P<sub>2</sub><sup>+</sup>: 533.2276; found 533.2293.

**Compound (5c).** <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.9 – 7.3 (m, 20 H), 7.18 (s broad, 5 H); 0.97 (s, 9 H); <sup>13</sup>C NMR (63 MHz, DMSO-d<sub>6</sub>): δ = 142.39 (dd, *J* = 131.5, 7.7 Hz, 2 C), 133.06 (d, *J* = 10.7 Hz, 6 C), 132.83 (d, *J* = 2.7 Hz, 2 C), 132.77 (d, *J* = 2.7 Hz, 3 C), 132.29 (d, *J* = 9.2 Hz, 4 C), 130.19 (dd, *J* = 118.1, 1.5 Hz, 3 C), 129.35 (d, *J* = 12.7 Hz, 6 C), 127.93 (d, *J* = 11.9 Hz, 4 C), 51.63 (d, *J* = 5.4 Hz, 1 C), 36.27 (d, *J* = 12.3 Hz, 3 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 15.31 (d, *J* = 8.7 Hz, 1 P), 7.49 (d, *J* = 9.3 Hz, 1 P).

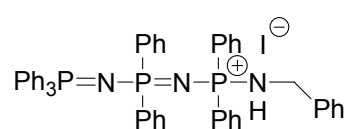
### Preparation of linear P<sub>3</sub>-H<sup>+</sup>

#### General procedure.

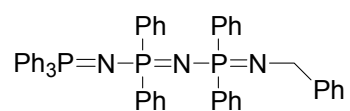
**8a-c-H<sup>+</sup>**, were prepared using a similar method to **5a-c-H<sup>+</sup>**, from pentaphenyldiphosphazanium chloride (**5a-H<sup>+</sup>**, 1.3 g, 2.5 mmol) and an aqueous solution of sodium iodide (5 %) instead of a aqueous solution of sodium chloride (10%). Basic forms **8a-c**, were prepared in situ respectively from **8a-H<sup>+</sup>** (402 mg, 0.5 mmol), **8b-H<sup>+</sup>** (441 mg, 0.5 mmol) and **8c-H<sup>+</sup>** (430 mg, 0.5 mmol) according to the methodology developed for **5a-c**.

**Compound 8a-H<sup>+</sup>**. From ammonia, **8a-H<sup>+</sup>** was obtained as a white solid (1.6 g, 79%). M.p. 165 - 167 °C (dec.); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.8 – 7.2 (m, 35 H), 5.77 (d broad, *J* = 2.7 Hz, 2 H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 135.27 (dd, *J* = 4.8, 3.5 Hz, 2 C), 133.45 (d, *J* = 2.7 Hz, 3 C), 132.49 (d, *J* = 11.1 Hz, 6 C), 132.49 (s, 2 C), 132.39 (dd, *J* = 131.2, 4.5 Hz, 2 C), 131.69 (s, 2 C), 131.54 (d, *J* = 11.2 Hz, 4 C), 131.29 (d, *J* = 11.6 Hz, 4 C), 129.60 (d, *J* = 12.8 Hz, 6 C), 128.93 (d, *J* = 13.4 Hz, 4 C), 128.90 (dd, *J* = 105.8, 3.1 Hz, 3 C), 128.74 (dd, *J* = 13.6 Hz, 4 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 15.55 (d, *J* = 1.6 Hz, 1 P), 14.13 (d, *J* = 6.5 Hz, 1 P), 6.97 (dd, *J* = 6.5, 1.6 Hz, 1 P); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 433 (16) [<sup>127</sup>I<sup>-</sup>+2NBA], 280 (100) [<sup>127</sup>I<sup>-</sup>+NBA], 127 (15) [<sup>127</sup>I<sup>-</sup>]; HR-MS [FAB<sup>+</sup> (NBA)]: calcd for C<sub>42</sub>H<sub>37</sub>N<sub>3</sub>P<sub>3</sub><sup>+</sup>: 676.2200; found 676.2241.

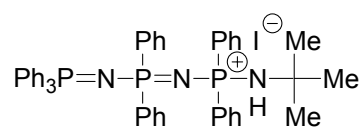
**Compound 8a.** <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.9 – 7.0 (m); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 142.24 (dd, *J* = 122.3, 5.8 Hz, 2 C), 138.53 (ddd, *J* = 131.8, 5.3, 2.7 Hz, 2 C), 132.89 (d, *J* = 2.7 Hz, 3 C), 132.61 (d, *J* = 11.0 Hz, 6 C), 131.36 (d, *J* = 12.1 Hz, 4 C), 131.34 (d, *J* = 8.7 Hz, 4 C), 130.52 (s, 2 C), 130.00 (dd, *J* = 105.5, 2.9 Hz, 3 C), 129.28 (s, 2 C), 129.22 (d, *J* = 12.7 Hz, 6 C), 128.16 (d, *J* = 13.0 Hz, 4 C), 127.66 (d, *J* = 11.6 Hz, 4 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 13.44 (s, 1 P), 12.65 (d, *J* = 4.4 Hz, 1 P), 3.69 (d, *J* = 4.4 Hz, 1 P).



**Compound 8b-H<sup>+</sup>**. From benzylamine (0.65 g, 0.65 mL, 6 mmol), **8b-H<sup>+</sup>** was isolated as a slight yellow solid (1.5 g, 67%). M.p. 174 - 175 °C (CH<sub>2</sub>Cl<sub>2</sub>/methanol/hexanes); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.8 – 7.0 (m, 40 H), 6.5 – 6.3 (m, 1 H), 3.69 (t, *J* = 7.6 Hz, 2 H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 139.47 (d, *J* = 8.6 Hz, 1 C), 134.91 (dt, *J* = 135.7, 4.5 Hz, 2 C), 133.48 (d, *J* = 2.7 Hz, 3 C), 133.07 (d, *J* = 2.5 Hz, 2 C), 132.39 (d, *J* = 11.1 Hz, 6 C), 132.01 (d, *J* = 11.2 Hz, 4 C), 131.96 (s, 2 C), 131.22 (d, *J* = 11.6 Hz, 4 C), 130.22 (dd, *J* = 129.8, 4.0 Hz, 2 C), 129.59 (d, *J* = 12.8 Hz, 6 C), 129.23 (d, *J* = 13.2 Hz, 4 C), 128.73 (d, *J* = 13.7, 4 C), 128.66 (s, 2 C), 128.65 (dd, *J* = 106.1, 2.9 Hz, 3 C), 127.57 (s, 2 C), 127.45 (s, 1 C), 43.90 (s, 1 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 17.2 (d, *J* = 4.0 Hz, 1 P), 14.98 (d, *J* = 7.9 Hz, 1 P), 5.83 (dd, *J* = 7.9, 4.0 Hz, 1 P); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 433 (2) [<sup>127</sup>I<sup>-</sup>+2NBA], 280 (40) [<sup>127</sup>I<sup>-</sup>+NBA], 127 (100) [<sup>127</sup>I<sup>-</sup>]; HR-MS [FAB<sup>+</sup> (NBA)]: calcd for C<sub>49</sub>H<sub>43</sub>N<sub>3</sub>P<sub>3</sub><sup>+</sup>: 766.2670; found 766.2650.



**Compound 8b**. <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.8 – 6.9 (m, 40 H), 3.89 (d, *J* = 14.1 Hz); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 148.30 (d, *J* = 25.6 Hz, 1 C), 139.94 (dd, *J* = 126.8, 6.0 Hz, 2 C), 138.57 (ddd, *J* = 132.4, 52.5, 2.5 Hz, 2 C), 132.79 (d, *J* = 2.6 Hz, 3 C), 132.57 (d, *J* = 11.0 Hz, 6 C), 132.04 (d, *J* = 8.6 Hz, 4 C), 131.37 (d, *J* = 11.1 Hz, 4 C), 130.43 (d, *J* = 2.6 Hz, 2 C), 130.07 (dd, *J* = 105.5, 2.8 Hz, 3 C), 129.22 (s, 2 C), 129.16 (d, *J* = 12.7 Hz, 6 C), 128.08 (d, *J* = 13.2 Hz, 4 C), 127.75 (d, *J* = 11.4 Hz, 4 C), 127.73 (s, 2 C), 127.22 (s, 2 C), 125.13 (s, 1 C), 48.64 (d, *J* = 2.6 Hz, 1 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 12.32 (s, 1 P); 2.02 (s, 1 P); 1.06 (s, 1 P).



**Compound 8c-H<sup>+</sup>**. From *tert*-butylamine (1.1 g, 1.6 mL, 15 mmol), **8c-H<sup>+</sup>** was isolated as a white solid (1.7 g, 79%). M.p. 237 - 238 °C (dec.); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.9 – 7.1 (m, 25 H), 5.45 (d, *J* = 13.9 Hz, 1 H), 1.07 (s, 9 H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 134.80 (dt, *J* = 135.7, 4.2 Hz, 2 C), 133.49 (d, *J* = 2.2 Hz, 3 C), 132.74 (s, 2 C), 132.36 (d, *J* = 11.1 Hz, 6 C), 132.12 (dd, *J* = 128.5, 3.8 Hz, 2 C), 132.09 (d, *J* = 11.3, 4 C), 131.95 (s, 2 C), 131.21 (d, *J* = 11.7, Hz, 4 C), 129.59 (d, *J* = 12.8 Hz, 6 C), 129.0 (d, *J* = 13.4 Hz, 4 C), 128.78 (d, *J* = 13.6, 4 C), 128.74 (dd, *J* = 106.4, 2.4 Hz, 3 C), 53.27 (d, *J* = 3.5 Hz, 1 C), 31.68 (d, *J* = 3.9 Hz, 3 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 13.62 (d, *J* = 7.1 Hz, 1 P), 11.09 (d, *J* = 10.9 Hz, 1 P), 3.88 (dd, *J* = 10.9, 7.6 Hz, 1 P); MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 433 (15) [<sup>127</sup>I<sup>-</sup>+2NBA], 280 (100) [<sup>127</sup>I<sup>-</sup>+NBA], 127 (24) [<sup>127</sup>I<sup>-</sup>]; HR-MS [FAB<sup>+</sup> (NBA)]: calcd for C<sub>46</sub>H<sub>45</sub>N<sub>3</sub>P<sub>3</sub><sup>+</sup>: 732.2826; found 732.2838.

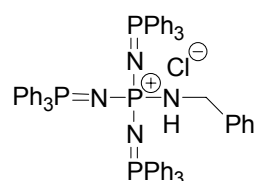
**Compound 8c.**  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 7.8 - 7.0$  (m, 35 H), 0.95 (s, 9 H);  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ ):  $\delta = 143.42$  (dd,  $J = 129.4, 6.6$  Hz, 2 C), 138.55 (ddd,  $J = 132.9, 5.0, 2.4$  Hz, 2 C), 132.74 (d,  $J = 2.7$  Hz, 3 C), 132.56 (d,  $J = 11.1$  Hz, 6 C), 132.08 (dd,  $J = 9.2$  Hz, 4 C), 131.48 (d,  $J = 11.2$  Hz, 4 C), 130.28 (dd,  $J = 105$  Hz, 3 C), 130.21 (d,  $J = 2.7$  Hz, 2 C), 129.14 (d,  $J = 12.7$  Hz, 6 C), 128.39 (d,  $J = 2.3$  Hz, 2 C), 127.84 (d,  $J = 13.1$  Hz, 4 C), 127.15 (d,  $J = 11.7$  Hz, 4 C), 51.08 (d,  $J = 4.6$  Hz, 1 C), 35.95 (d,  $J = 11.9$  Hz, 3 C);  $^{31}\text{P}$  NMR (81 MHz, DMSO- $d_6$ ):  $\delta = 10.42$  (d,  $J = 2.2$  Hz, 1 P), -3.23 (dd,  $J = 3.8, 2.2$  Hz, 1 P), -17.99 (d,  $J = 3.8$  Hz, 1 P).

### Preparation of cross $\text{P}_3\text{-H}^+$

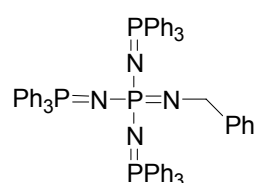
**Compound 10- $\text{H}^+$ .** According to the method of preparation of **5c- $\text{H}^+$** , using amino(triphenyl)phosphonium chloride (**1b**, 4.7 g, 15 mmol), chloro(diphenyl)phosphine (1.0 g, 1.3 mL, 7.5 mmol), hexachloroethane (1.9 g, 8 mmol) and an aqueous solution of sodium iodide (5%), **10- $\text{H}^+$**  was obtained as a white solid (5.3 g, 81%). m.p. 214 - 216 °C (methanol/water);  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 7.8 - 7.1$  (m, 35 H), 4.52 (d,  $J = 4.9$  Hz, 1 H), 0.96 (s, 9H);  $^{13}\text{C}$  NMR (63 MHz, DMSO- $d_6$ ):  $\delta = 138.22$  (dt,  $J = 165.2, 4.6$  Hz, 1 C), 133.73 (d,  $J = 1.9$  Hz, 6 C), 133.02 (d,  $J = 11.1$  Hz, 12 C), 131.95 (d,  $J = 2.3$  Hz, 1 C), 131.65 (d,  $J = 11.1$  Hz, 2 C), 129.86 (d,  $J = 12.7$  Hz, 12 C), 129.73 (dd,  $J = 106.6, 3.1$  Hz, 6 C), 129.07 (d,  $J = 8.8$  Hz, 2 C), 52.01 (d,  $J = 1.5$  Hz, 1 C), 31.80 (d,  $J = 4.6$  Hz, 3 C);  $^{31}\text{P}$  NMR (81 MHz, DMSO- $d_6$ ):  $\delta = 12.06$  (d,  $J = 5.5$  Hz, 1 P), 5.15 (t,  $J = 5.5$  Hz, 1 P); MS [FAB $^-$  (NBA)]:  $m/z$  (%): 433 (15) [ $^{127}\text{I}^- + 2\text{NBA}$ ]; 280 (100) [ $^{127}\text{I}^- + \text{NBA}$ ]; 127 (24) [ $^{127}\text{I}^-$ ]; HR-MS [FAB $^+$  (NBA)]: calcd for  $\text{C}_{46}\text{H}_{45}\text{N}_3\text{P}_3^+$ : 732.2826; found: 732.2805.

**Compound 10. 10- $\text{H}^+$**  (430 mg, 0.5 mmol) is dissolved in DMSO- $d_6$  (5 mL) and sodium hydride was added (12 mg, 0.5 mmol). The mixture was stirred under vacuum (30 mmHg) for 1 h, **10** was prepared quantitatively.  $^1\text{H}$  NMR (200 MHz, DMSO- $d_6$ ):  $\delta = 7.8 - 7.2$  (m, 32 H), 7.1 - 6.8 (m, 3 H), 0.99 (s, 9 H);  $^{13}\text{C}$  NMR (63 MHz, DMSO- $D_6$ ):  $\delta = 148.71$  (d,  $J = 146.5$  Hz, 1 C), 133.53 (d,  $J = 10.7$  Hz, 12 C), 133.47 (d,  $J = 102.4$  Hz, 6 C), 132.03 (s, 6 C), 131.23 (d,  $J = 9.6$  Hz, 2 C), 128.79 (d,  $J = 12.3$  Hz, 12 C), 127.46 (s, 1 C), 127.15 (d,  $J = 12.3$  Hz, 2 C), 51.48 (d,  $J = 4.2$  Hz, 1 C), 35.99 (d,  $J = 12.3$  Hz, 3 C);  $^{31}\text{P}$  NMR (81 MHz, DMSO- $d_6$ ):  $\delta = 2.24$  (d,  $J = 17.4$  Hz), -10.45 (t,  $J = 17.4$  Hz).

### Preparation of cross $P_4-H^+$ .



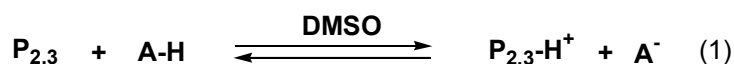
**Compound 12-H<sup>+</sup>.** At -20 °C, a solution of butyllithium (40 mmol) in hexanes (25 mL) was added dropwise to a solution of amino(triphenyl)phosphonium chloride (**1b**, 6.3 g, 20 mmol) in tetrahydrofuran (175 mL). Upon half hour at -20 °C, the temperature was down at -65 °C and phosphorus pentachloride (1.1 g, 5 mmol) was added. After 1 h at -65 °C, the temperature was raised at 25°C and the mixture stirred for 12 h. The precipitate was filtered and washed successively with tetrahydrofuran (30 mL), diethyl ether (2 × 25 mL) and pentanes (25 mL). The white powder obtained was mixed with benzylamine (5 mL) and heated at 100 °C for 4 h. After addition of diethyl ether (25 mL), the precipitate formed was filtered and washed with chloroform (25 mL). The filtrate was recovered, precipitated with diethyl ether (50 mL), filtered and recrystallized with a mixture of methanol and water. A white powder was obtained (2.9 g, 58%). M.p. 232 – 233 °C (methanol/water); <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.8 – 6.8 (m, 50 H), 3.84 (dd, *J* = 10.3, 6.9 Hz, 2 H), 2.00 (q, *J* = 7.4 Hz, 1 H); <sup>1</sup>H NMR (250 MHz, CDCl<sub>3</sub>): δ = 7.70 – 7.45 (m, 18 H), 7.45 – 7.20 (m, 27 H), 7.15 – 7.05 (m, 3 H), 6.80 – 6.95 (m, 2 H), 3.8 – 3.3 (m, 3H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 141.28 (d, *J* = 8.8 Hz, 1 C), 133.49 (s, 9 C), 133.43 (d, *J* = 11.0 Hz, 18 C), 130.06 (dd, *J* = 104.6, 4.0 Hz, 9 C), 128.82 (d, *J* = 12.3 Hz, 18 C), 127.94 (s, 2 C), 127.11 (s, 2 C), 126.38 (s, 1 C), 44.99 (s, 1 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 7.36 (d, *J* = 8.2 Hz, 3 P), 0.84 (q, *J* = 8.2 Hz, 1 P); MS [FAB<sup>+</sup> (NBA)]: *m/z* (%): 965 (100) [*M*<sup>+</sup>], 688 (10) [*M*<sup>+</sup>-Ph<sub>3</sub>PN], 583 (41) [688-NHCH<sub>2</sub>Ph]; MS [FAB<sup>-</sup> (NBA)]: *m/z* (%): 343 (10) [<sup>37</sup>Cl<sup>-</sup>+2NBA]; 341 (28) [<sup>35</sup>Cl<sup>-</sup>+2NBA]; 190 (34) [<sup>37</sup>Cl<sup>-</sup>], 188 (100) [<sup>35</sup>Cl<sup>-</sup>]. Elemental analysis: calcd. (%) for C<sub>61</sub>H<sub>53</sub>N<sub>4</sub>P<sub>4</sub>Cl.0.5H<sub>2</sub>O (1010.47): calcd C 72.50, H 5.39, N 5.55; found C 72.68, H 5.33, N 5.67.



**Compound 12. 12-H<sup>+</sup>** (200 mg, 0.2 mmol) was dissolved in DMSO-d<sub>6</sub> (10 mL) and treated by sodium amide (7.5 mg, 0.3 mmol). The solution was vigorously stirring for half hour, **12** was quantitatively obtained. <sup>1</sup>H NMR (200 MHz, DMSO-d<sub>6</sub>): δ = 7.80 – 6.8 (m, 50 H), 4.15 (d, *J* = 18.1 Hz, 2 H); <sup>13</sup>C NMR (101 MHz, DMSO-d<sub>6</sub>): δ = 150.53 (d, *J* = 26.3 Hz, 1 C), 133.91 (dd, *J* = 102.1, 3.2 Hz, 9 C), 133.16 (d, *J* = 10.3 Hz, 18 C), 131.12 (s, 9 C), 128.15 (d, *J* = 12.1 Hz, 18 C), 127.79 (s, 2 C), 127.01 (s, 2 C), 124.10 (s, 1 C), 51.50 (d, *J* = 4.4 Hz, 1 C); <sup>31</sup>P NMR (81 MHz, DMSO-d<sub>6</sub>): δ = 3.34 (q, *J* = 7.1 Hz, 1 P), 2.07 (d, *J* = 7.1 Hz, 3 P).

### Determination of the $pK_b$ values of bases $P_2$ -*t*-Bu (**5a**), $P_3$ -*t*-Bu (**8c**, **10**).

Bases **5a**, **8c** and **10** were prepared in situ according to previously described method, by dissolving the acid salt **5a-H<sup>+</sup>**, **8c-H<sup>+</sup>** or **10-H<sup>+</sup>** (0.5 mmol), in dry dimethylsulfoxide (5 mL) and treating with sodium hydride (1 eq.). A standard compound (A-H, 1 eq.) was introduced, phenol with **5a**, pyrazole with **8c** and benzylamine with **10**. After 15 minutes of a vigorous stirring, an aliquot was charged in a NMR tube under nitrogen atmosphere and analyzed in <sup>31</sup>P NMR. The ratio basic  $P_{2,3}$  and acid  $P_{2,3}$ -H<sup>+</sup> forms were determined to help of the signal of phosphorus bearing three phenyls, which shift between its initial value (form basic) to final value (acid form). The signal displacement observed of P<sup>V</sup> is a linear relationship to ratio  $P_{2,3}/P_{2,3}$ -H<sup>+</sup>, affording the determination of their molar ratios in solution. Thus, the <sup>DMSO</sup> $k_a$  value was calculated from eq 2 and  $pK_a$  by eq 3 (Scheme 1).



$$K_a = 10^{-pK_{AH}} \times \frac{[AH] [P_{2,3,4}]}{[A] [P_{2,3,4}-H^+]} = 10^{-pK_{AH}} \times \frac{[P_{2,3,4}]^2}{[P_{2,3,4}-H^+]^2} \quad (2)$$

$$pK_a = -\log K_a \quad (3)$$

#### Scheme 1.

#### References

- (1) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, N. L. Smith, *J. Am. Chem. Soc.*, **1959**, *81*, 2982 - 2985.
- (2) M. Biddlestone, R. A. Shaw., *J. Chem. Soc. Dalton Trans.*, **1975**, 2527 – 2530.