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J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.6b00872 • Publication Date (Web): 08 Jul 2016 Downloaded from http://pubs.acs.org on July 10, 2016

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The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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# Experimental Basicities of Superbasic Phosphonium Ylides and Phosphazenes

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## Abstract

Experimental basicities of some of the strongest superbases ever measured (phosphonium ylides) are reported and by employing these compounds the experimental self-consistent basicity scale of superbases in THF, reaching  $pK_{\alpha}$  (estimate of  $pK_a$ ) 35 and spanning more than 30  $pK_a$  units, has been compiled. Basicities of altogether 47 compounds (around half of which are newly synthesized) are included. The solution basicity of the well-known *t*-Bu-N=P<sub>4</sub>(dma)<sub>9</sub> phosphazene superbase is now rigorously linked to the scale. The compiled scale is a useful tool for further basicity studies in THF as well as in other solvents, in particular in acetonitrile. A good correlation between basicities in THF and acetonitrile spanning 25 orders of magnitude gives access to experimentally supported very high ( $pK_a$  over 40) basicities in acetonitrile, which cannot be directly measured. Analysis of structure-basicity trends is presented.

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# Introduction

Significant effort has been made in research of strongly basic compounds in recent decades and base strength has always been one of the key considerations. Although the strongest known bases are mostly ionic compounds<sup>1,2</sup> (alkali metal alkyls, amides and hydrides), nonionic bases are preferred in many applications as they usually offer milder reaction conditions, "cleaner" deprotonation and less side-products.<sup>3–6</sup> The most basic non-ionic compounds that have been systematically experimentally studied are different substituted phosphazenes. Initially synthesized and described by the Schwesinger group,<sup>7,8</sup> they have been modified by others,<sup>9–11</sup> studied in different solvents<sup>11–13</sup> and applied in numerous synthetic transformations.<sup>3–5,14–18</sup>

The increasing interest in strong non-ionic bases – for use as catalysts<sup>3,5,14,15</sup> and auxiliary reagents in synthesis<sup>3</sup> – has motivated the creation of a variety of novel (potentially) superbasic compound families, for example phosphatranes and their derivatives,<sup>19</sup> BIG bases,<sup>20</sup> cyclopropenimine superbases,<sup>9,21</sup> bisphosphazene proton sponges<sup>10,22</sup>. Progress has also been made in computational estimation of solution-phase basicities and new exciting families of bases have been proposed on the basis of computations:<sup>23</sup> polycyclic proton sponges,<sup>24</sup> calixa-pyridines,<sup>25</sup> etc.<sup>26</sup>

Basicity is a core characteristic of any basic molecule, and practical application as well as systematic development of new superbases require reliable basicity data of the existing molecules and understanding of the factors governing basicity.<sup>11,26,27</sup> Other desired properties of new compounds, besides high basicity, are high stability in non-inert media (of both neutral and protonated forms), low nucleophilicity, not too high molar mass, sufficient thermal stability, non-toxicity and low cost.

Basicities of strong bases have been measured in different solvents,<sup>8,12,13,20</sup> but in contrast to development of new bases, progress in basicity measurement has been less pronounced. Although very strong experimental basicity values have been recently reported (BIG bases,<sup>20</sup> imidazolidine ylidene amines,<sup>28</sup> higher order cyclopropeneimine bases<sup>9</sup>), the most recent rigorous extension of the self-consistent basicity scale in THF dates back to  $2005^{11}$  and reaches p $K_{\alpha}$  value 28. p $K_{\alpha}$  values are estimates of free ion p $K_a$  values that have been obtained from measurements of ion-pair equilibria with correction for ion pairing, see below. The self-consistent basicity scale in acetonitrile (MeCN) currently reaches p $K_a$  value 32. Basicity measurements of new superstrong bases are essentially comparisons with reference bases<sup>13,20</sup> and can be reliably carried out when basicity differences do not exceed 1.5 (preferably 1.0) p $K_a$  units and the role of self-consistent scales is providing reliable basicity values for such reference bases. Thus, researchers are currently without a convenient tool for experimental determination of basicities of the strongest bases.

The experimental studies of superbasicity in solution can be conveniently carried out in a rather limited number of solvents. The solvent is required to be sufficiently differentiating (i.e. to have very low acidity), stable in the presence of highly basic compounds, available at high degree of purity and have adequate dissolving ability and optical properties suiting the chosen measurement method. The best known solvents that meet these requirements are ethers (incl. THF), dimethyl sulfoxide, to some extent acetonitrile and some others. Occasionally good correlations have been found between basicity values in different solvents.<sup>8,13</sup> This enables estimation of basicities in practically problematic cases by correlation analysis from the experimental data in another solvent. A good example is prediction of  $pK_a$  values of strong bases in acetonitrile from data obtained in THF.<sup>8,20</sup> The

validity of such approach in the case of phosphazene bases has been recently indirectly supported by computations.<sup>27</sup> In view of the above, THF is an obvious choice for superbasicity measurements. Its low acidity and high stability enable measuring very high basicity values and a remarkable amount of basicity data is already available in THF.

The main aim of this work, was to significantly extend the existing self-consistent basicity scale in THF, published in different papers,<sup>11,12,20,29</sup> towards stronger bases, reaching  $pK_{\alpha}$  around 35 and bringing its full span to 30 orders of magnitude. The resulting scale is envisaged as a useful tool for future studies of very strong bases and will open up the possibility of estimating (using correlation analysis) the  $pK_a$  values of the strongest bases in other solvents, importantly in acetonitrile, which is widely used for acid-base studies but where direct experimental  $pK_a$  measurements at this high basicity level are not possible.

It is preferable to conduct measurements of acid-base equilibria in highly diluted solutions to minimize the impact of various association reactions on the results. Of the many methods that have been used for superbasicity studies (NMR,<sup>9,29,30</sup>, potentiometry,<sup>7,8,31,32</sup> conductometry,<sup>33</sup> UV-Vis spectrophotometry<sup>12,13,20</sup>) the UV-Vis spectrophotometric method has proven to yield the most reliable results, as it is possible to work at low concentrations of compounds and easily detect problems, such as side reactions and non-reversibility of deprotonation.

In order to obtain reliable basicity values with the UV-Vis spectrophotometric method, compounds are needed that besides very high basicity also have suitable spectral properties – i.e. the neutral and protonated forms of the compound have to have different spectra. The key compound family for extending the scale, which satisfies both requirements, is a series of newly synthesized phosphonium ylide superbases (Scheme 1). The higher basicities of

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phosphonium ylides compared to the corresponding phosphazenes with similar molar weight<sup>27</sup> give them practical importance in organic synthesis<sup>34,35</sup> and because of that their basicities are also interesting by themselves. Only few members of this superbase family have experimental basicity values available.<sup>31,32,34</sup>

The simple form of dissociation equation of a cationic acid  $HB^+$  (protonated base B) (Equation 1) adequately represents the proton transfer process in polar media, but does not hold in low-polarity solvents, such as THF, where ion aggregation takes place because of insufficient screening of charged particles (relative permittivity 7.6<sup>36</sup>).

$$HB^+ + S \quad \overleftarrow{K_a} \quad B + HS^+$$
 (1)

$$K_{a} = \frac{a(B) \cdot a(HS^{+})}{a(HB^{+})}$$
(2)

As most ions in THF exist in the form of contact or solvent-separated ion pairs and direct measurement of solvated proton activity  $a(HS^+)$  in THF is very difficult, direct computation of  $K_a$  according to Equation 2 is impractical. To overcome these difficulties, relative (instead of absolute) basicity of two bases is measured and furthermore, equilibrium between ion pairs (Equation 3) is often studied in low-polarity solvents, instead of equilibrium between free solvated ions.<sup>12</sup>

$$\mathbf{B}_{2} + \mathbf{H}\mathbf{B}_{1}^{+}\mathbf{A}^{-} \xleftarrow{K_{d}^{+}\mathbf{H}\mathbf{B}_{1}^{+}\mathbf{A}^{-}} \mathbf{B}_{2} + \mathbf{H}\mathbf{B}_{1}^{+} + \mathbf{A}^{-} \xleftarrow{K} \mathbf{H}\mathbf{B}_{2}^{+} + \mathbf{B}_{1} + \mathbf{A}^{-} \xleftarrow{1/K_{d}^{+}\mathbf{H}\mathbf{B}_{2}^{+}\mathbf{A}^{-}} \mathbf{H}\mathbf{B}_{2}^{+}\mathbf{A}^{-} + \mathbf{B}_{1}$$
(3)

Protonated bases  $B_1$  and  $B_2$  form ion pairs with a counter-ion A<sup>-</sup>.  $K_d$  denotes the dissociation constant of the respective ion pair. The value directly measured in titration experiments is the difference of ion-pair basicities  $pK_{ip}$  of the bases, the so-called relative ion-pair basicity, denoted as  $\Delta pK_{ip}$  and can be found from eq 4:

$$\Delta p K_{ip} = p K_{ip} (HB_2^+A^-) - p K_{ip} (HB_1^+A^-) = \log \frac{K \cdot K_d^{HB_1^+A^-}}{K_d^{HB_2^+A^-}} = \log \frac{a (HB_2^+A^-) \cdot a(B_1)}{a (HB_1^+A^-) \cdot a(B_2)}$$
(4)

Ion pair dissociation constants  $K_d$  are estimated using the Fuoss equation<sup>37</sup> and  $\Delta p K_{\alpha}$  (the estimate of  $p K_a$  difference of bases B<sub>1</sub> and B<sub>2</sub>) is calculated according to Equation 5:

$$\Delta p K_{\alpha} = p K_{\alpha} (HB_2^+) - p K_{\alpha} (HB_1^+) = \Delta p K_{ip} - \log \frac{K_d^{HB_1^+A^-}}{K_d^{HB_2^+A^-}}$$
(5)



<sup>*a*</sup> See Table 1 for the substituent configurations of specific ylides.

# Results

The p $K_{ip}$  measurements were carried out with 47 bases using altogether 87 overlapping  $\Delta pK_{ip}$ measurements (see Table 1). This way the p $K_{ip}$  range of 23 to 34 (p $K_{\alpha}$  range of 23 to 35) in THF is now covered by rigorous multiply overlapping self-consistent basicity measurements. Both ion-pair (p $K_{ip}$ ) values and values corrected for ion pairing (p $K_a$  estimates, denoted as p $K_a$ ) are given in Table 1. Together with the earlier data there is now continuous selfconsistent basicity scale available in THF solution ranging from p $K_a$  3 to 35.0, i.e. spanning more than 30 orders of magnitude, see Table 1.

Table 1. Self-consistent basicity scale in THF solution.

| No | Compound <sup>a</sup>   | Δp <i>K</i> <sub>ip</sub> | рК <sub>ір</sub><br>(THF) | р <i>К</i> α<br>(ТНF) | р <i>К</i> а <sup>b</sup><br>(месм) |  |
|----|---|---------------------------|---------------------------|-----------------------|-------------------------------------|--|
| 1  | t-Bu-N=P <sub>4</sub> (pyrr) <sub>9</sub>   | <b>•</b> •                | 34.2                      | 35.3                  | 44.0 <sup>c</sup>                   |  |
| 2  | t-Bu-N=P₄(dma)₀   |                           | 33.0                      | 33.9                  | 42.7 <sup>c</sup>                   |  |
| 3  | H <sub>2</sub> C=P(2,4,6-(MeO) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> ) <sub>2</sub> Ph                                  |                           | 32.9                      | 33.5                  | 42.1                                |  |
| 4  | Ph(CH <sub>3</sub> )CH-N=P <sub>4</sub> (pyrr) <sub>9</sub>   |                           | 32.9                      | 33.9                  | 42.6                                |  |
| 5  | Ph(CH <sub>3</sub> )C=P(2,4,6-(MeO) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> ) <sub>3</sub>                                |                           | 32.1                      | 33.0                  | 41.6                                |  |
| 6  | (CH <sub>3</sub> ) <sub>2</sub> C=P(2,4,6-(MeO) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> )Ph <sub>2</sub>                  |                           | 31.8                      | 32.4                  | 40.9                                |  |
| 7  | Ph(CH <sub>3</sub> )CH-N=P <sub>4</sub> (dma) <sub>9</sub>  |                           | 31.7                      | 32.7                  | 41.2                                |  |
| 8  | MeO-CH=P(4-MeO-C <sub>e</sub> H <sub>4</sub> ) <sub>3</sub>   | 0.8 1.1                   | 30.9                      | 31.7                  | 40.0                                |  |
| 9  | (CH₃)₂C=P(4-MeO-C₅H₄)₃  |                           | 30.8                      | 31.5                  | 39.9                                |  |
| 10 | Ph(CH <sub>3</sub> )C=P(2.6-(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> ) <sub>3</sub>                                  |                           | 30.8                      | 31.6                  | 40.0                                |  |
| 11 | CH <sub>2</sub> -CH=P(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> Ph  | 0.4                       | 30.3                      | 30.8                  | 39.0                                |  |
| 12 | Et-N=P <sub>1</sub> (imme) <sub>3</sub>   |                           | 30.2                      | 30.9                  | 39.2                                |  |
| 13 | (CH3)2C=P(3.5-(MeO)2-CeH3)3   |                           | 29.9                      | 30.7                  | 38.9                                |  |
| 14 | HaC=P(2.4.6-(MeO)a-CaHa)Pha   |                           | 29.8                      | 30.4                  | 38.6                                |  |
| 15 | CH=-CH=P(C++)Ph=  |                           | 29.8                      | 30.2                  | 38.4                                |  |
| 16 | Et-N=P.(tmg).   |                           | 29.7                      | 30.4                  | 38.7                                |  |
| 17 | MeQ-CH=P(C-H)Ph-  |                           | 29.7                      | 30.4                  | 38.3                                | <sup><i>a</i></sup> Colors are used according to       |
| 18 | (CH_)-C=P(dma)-   |                           | 29.5                      | 29.6                  | 37.7                                | g  |
| 10 |   |                           | 20.4                      | 20.0                  | 20.0                                | protonation center: carbon -                           |
| 19 | $P_{2}C - P(C_{6}P_{11})_{2}P(i)$   |                           | 29.4                      | 29.9                  | 20.0                                |  |
| 20 |   | 2.0 1.0                   | 29.0                      | 29.7                  | 30.0                                | black, nitrogen – blue,                                |
| 21 |   | 0.3 1.8 1.1               | 20.0                      | 29.4                  | 37.0                                | $phosphorus - green^{b}$ If not                        |
| 22 | $Pn(CH_3)CH-N=P_4(Pn)_9$  |                           | 20.0                      | 30.0                  | 30.2                                | phosphorus green. If not                               |
| 23 | $(CH_3)_2 C = PPH_3$  |                           | 20.7                      | 20.9                  | 30.9                                | stated otherwise, $pK_a$ values                        |
| 24 | r-Bu-N=P <sub>1</sub> (tmg) <sub>3</sub>  |                           | 28.4                      | 29.1                  | 37.3                                |  |
| 25 | $t - Bu - N = P_3(Oma)_6 N = t_2$   | 1.2                       | 28.3                      | 29.4                  | 37.6                                | in MeCN were estimated                                 |
| 26 | $H-N=P_1(tmg)_3$  | 1.3 1.0                   | 28.1                      | 29.0                  | 37.2                                | from the data in THE using                             |
| 27 | 4-MeO-C <sub>6</sub> H <sub>4</sub> -N=P <sub>4</sub> (pyrr) <sub>9</sub>   | 0.8 0.6                   | 27.8                      | 28.9                  | 37.1                                | from the data in TTT using                             |
| 28 | $H_2C=P(4-MeO-C_6H_4)_3$  |                           | 27.8                      | 28.5                  | 36.5                                | linear regression. $pK_a$ values                       |
| 29 | CH <sub>3</sub> -CH=PPn <sub>3</sub>  |                           | 27.5                      | 27.9                  | 35.9                                |  |
| 30 | Ph-N=P <sub>4</sub> (pyrr) <sub>9</sub>   |                           | 27.4                      | 28.5                  | 36.6                                | of phosphazenes were                                   |
| 31 | CH <sub>3</sub> -CH=P(1-Napht)Ph <sub>2</sub>   |                           | 27.3                      | 27.8                  | 35.8                                | coloulated by $\Sigma_{2}$ 0 and $\pi V$               |
| 32 | <i>t</i> -Bu-N=P <sub>3</sub> (dma) <sub>6</sub> N( <i>i</i> -Pr) <sub>2</sub>  |                           | 27.1                      | 28.2                  | 36.4                                | calculated by Eq 9 and $pK_a$                          |
| 33 | Ph-CH=P(pyrr)₂tmg   |                           | 27.1                      | 27.7                  | 35.6                                | values of phosphonium vlides                           |
| 34 | H <sub>2</sub> C=P(3,5-(MeO) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> ) <sub>3</sub>                                       |                           | 26.7                      | 27.5                  | 35.3                                | ·  |
| 35 | H <sub>2</sub> C=P(3-MeO-C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub>   |                           | 26.6                      | 27.1                  | 34.9                                | by Eq 10. <sup>c</sup> Literature values. <sup>8</sup> |
| 36 | Ph-CH=P(dma) <sub>2</sub> tmg   |                           | 26.6                      | 27.1                  | 34.9                                | <i>d</i>   |
| 37 | H <sub>2</sub> C=PPh <sub>3</sub>   |                           | 26.2                      | 26.6                  | 34.4                                | " Anchor compounds of the                              |
| 38 | (CH <sub>3</sub> ) <sub>3</sub> C-CH=PPh <sub>3</sub>   |                           | 26.1                      | 26.7                  | 34.5                                | THE scale Values in THE                                |
| 39 | t-Bu-N=P <sub>3</sub> (Ph) <sub>7</sub>   |                           | 25.6                      | 26.7                  | 34.7                                | THI Seale. Values in THI                               |
| 40 | Ph-CH=P(-NMe-CH <sub>2</sub> -CH <sub>2</sub> -) <sub>3</sub> N   | 1.6                       | 25.4                      | 26.1                  | 33.18°                              | from ref. <sup>11</sup> . <sup>e</sup> Experimental    |
| 41 | H <sub>2</sub> C=P(2,4,6-(Me) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> ) <sub>3</sub>                                      |                           | 25.2                      | 25.6                  | 33.3                                | -  |
| 42 | Et-N=P <sub>2</sub> (dma) <sub>5</sub> <sup>d</sup>   |                           | 24.9                      | 25.3                  | 32.94 <sup>c</sup>                  | values from this work. <sup>7</sup>                    |
| 43 | t-Bu-N=P <sub>2</sub> (dma) <sub>5</sub>  |                           | 24.4                      | 25.0                  | 33.13°                              | Experimental value from ref                            |
| 44 | Ph-CH=P(pyrr) <sub>3</sub>  |                           | 23.8                      | 24.3                  | 32.46 <sup>e</sup>                  | Experimental value from fel.                           |
| 45 | P(-NMe-CH <sub>2</sub> -CH <sub>2</sub> -) <sub>3</sub> N   |                           | 23.8                      | 24.1                  | 32.90 <sup>f</sup>                  | <sup>38</sup> . Prediction by Eq 8 gives               |
| 46 | 4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CH=P(2,4,6-(MeO) <sub>3</sub> -C <sub>6</sub> H <sub>2</sub> ) <sub>3</sub> | -1.4 <b>*</b>             | 23.4                      | 24.5                  | 30.72 <sup>e</sup>                  | 510  |
| 47 | Ph-CH=P(dma) <sub>3</sub>   | <u>+ '+'</u>              | 22.3                      | 22.7                  | 31.26°                              | 31.7.  |

The multiple overlapping measurements ensure the reliability of the obtained values and help to estimate their self-consistency. The entire basicity range covered involves at least two independent pathways of measurements and the relative basicity between any two bases can be obtained by combining at least two independent sets of measurements. Reversibility of protonation/deprotonation process was checked with all bases.

The absolute basicities were obtained by anchoring the scale to the  $pK_{ip}$  and  $pK_{\alpha}$  values of three compounds for which basicity values are known: *t*-Bu-N=P<sub>1</sub>(tmg)<sub>3</sub>, 4-MeO-C<sub>6</sub>H<sub>4</sub>-N=P<sub>4</sub>(pyrr)<sub>9</sub> and Et-N=P<sub>2</sub>(dma)<sub>5</sub> (their  $pK_{ip}$  and  $pK_{\alpha}$  values in Table 1 are from ref. <sup>11</sup>). The  $pK_{ip}$  and  $pK_{\alpha}$  values for individual bases were found similarly to previous works.<sup>12,13</sup> The essence of the approach is minimizing the sum of squares (*SS*) of differences between directly measured relative  $\Delta pK_{ip}$  (or  $\Delta pK_{\alpha}$ ) values and the assigned absolute  $pK_{ip}$  (or  $pK_{\alpha}$ ) values by allowing the absolute values to change, except those of the anchor compounds. *SS* is calculated according to eq 6 (presented here for  $pK_{\alpha}$ ):

$$SS = \sum_{i=1}^{n_m} \left\{ \Delta p K_{\alpha}^i - \left[ p K_{\alpha} (HB_2^+) - p K_{\alpha} (HB_1^+) \right] \right\}^2$$
(6)

The sum is taken over all the measurements (altogether  $n_{\rm m}$  measurements) whereby  $\Delta p K_{\alpha}^{i}$  is the result of a relative basicity measurement of bases B<sub>1</sub> and B<sub>2</sub> (expressed as acidities of the conjugate acids HB<sub>1</sub><sup>+</sup> and HB<sub>2</sub><sup>+</sup>). B<sub>2</sub> is the base with higher basicity.  $p K_{\alpha}$ (HB<sub>1</sub><sup>+</sup>) and  $p K_{\alpha}$ (HB<sub>2</sub><sup>+</sup>) are the absolute  $p K_{\alpha}$  values for the two bases as found by the least squares procedure. The precision and consistency of the results can be assessed using the consistency standard deviation as defined by eq 7:<sup>13</sup>

$$s = \sqrt{\frac{SS}{n_m - n_c}} \tag{7}$$

The overall number of derived  $pK_{\alpha}$  values is denoted by  $n_c$ . The consistency standard deviation of the scale in Table 1 is 0.13, indicating good consistency for these highly demanding measurements. In the highest basicity region of this scale it became gradually more difficult to deprotonate the protonated bases with any of the common very strong deprotonating agents, so that eventually only KH and metallic K worked. Indirect evidence also points towards increasing influence of deprotonation of THF molecules in the high basicity range. Given these increasing difficulties it is not expected that the self-consistent THF basicity scale can be extended much upwards from the present highest  $pK_{\alpha}$  value 35.3. Similarly it is not expected that  $pK_a$  values much higher than 33-34 can be directly measured in MeCN.

In addition to the compounds in Table 1 the basicities of four weaker bases were measured in THF: 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(dma)<sub>3</sub> (**53**) ( $pK_{ip} = 17.3$ ,  $pK_{\alpha} = 17.6$ ), 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(pyrr)<sub>3</sub> (**52**) ( $pK_{ip} = 18.2$ ,  $pK_{\alpha} = 18.7$ ), *t*-Bu-N=P<sub>2</sub>(Ph)<sub>5</sub> (**56**) ( $pK_{ip} = 19.6$ ,  $pK_{\alpha} = 20.4$ ) and 3-Cl-C<sub>6</sub>H<sub>4</sub>-CH=P(dma)<sub>3</sub> (**49**) ( $pK_{ip} = 20.1$ ,  $pK_{\alpha} = 20.4$ ); and the basicities of some of the weaker bases were measured in MeCN. Details of these additional measurements are in the Supporting Information.

## Discussion

#### **Basicities of compounds in THF and MeCN**

Basicities in MeCN are known to correlate well with basicities in THF,<sup>13,20</sup> especially in the groups of structurally similar compounds.  $pK_a$  values of some phosphazenes in MeCN have been estimated from the experimental data in THF,<sup>8,20</sup> but this has not yet been attempted with phosphonium vlides. In this work the correlation from ref.<sup>20</sup>, built upon a set of compounds with sterically crowded nitrogen protonation sites (but otherwise belonging to different families – amidines, guanidines, phosphazenes), was extended towards higher basicities by including three alkylimino phosphazenes<sup>8</sup> – t-Bu-N=P<sub>4</sub>(pyrr)<sub>9</sub> (1), t-Bu-N=P<sub>4</sub>(dma)<sub>9</sub> (2) and Et-N= $P_2(dma)_6$  (42) – and supplemented with six phosphonium ylides studied both in THF and MeCN: Ph-CH=P(-NMe-CH<sub>2</sub>-CH<sub>2</sub>-)<sub>3</sub>N (40), t-Bu-N=P<sub>2</sub>(dma)<sub>5</sub> (43), Ph-CH=P(pyrr)<sub>3</sub> (44), Ph-CH=P(dma)<sub>3</sub> (47), 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>3</sub> (46), 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(pyrr)<sub>3</sub> (52) and 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(dma)<sub>3</sub> (53). The acetonitrile  $pK_a$  values of the highest phosphazene homologues – t-Bu-N=P<sub>4</sub>(dma)<sub>9</sub> and t-Bu-N=P<sub>4</sub>(pyrr)<sub>9</sub> – have previously been derived by extrapolation from data measured in THF, benzene or fluorobenzene,<sup>8</sup> but almost no experimental details are presented.<sup>8</sup> Therefore, because (1) the extrapolation procedure was very different from the correlation procedure used in this work, (2) three different solvents were used<sup>8</sup> and (3) the validity of the acetonitrile  $pK_a$  values of these two bases has been recently indirectly supported by computations,<sup>27</sup> we have decided to include them in the overall correlation equation of this work. Figure 1 demonstrates that the new additions fit very well into the correlation, even though phosphonium ylides have wider scatter of data points than the other compounds. This good correlation confirms that the  $pK_a$ 

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values of strong bases in MeCN may be estimated from THF data of the compounds from different families.

Correlation equations have been built upon the composite set of all bases for which experimental MeCN  $pK_a$  values are available, namely MTBD, DBU, PhTMG, DMAN, 2-NO<sub>2</sub>-4-CF<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>-N=P<sub>1</sub>(pyrr)<sub>3</sub>, 2,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-N=P<sub>1</sub>(pyrr)<sub>3</sub>, 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-N=P<sub>3</sub>(pyrr)<sub>7</sub>, Ph-N=P<sub>3</sub>(dma)<sub>7</sub>, Me-N=P<sub>1</sub>(dma)<sub>3</sub>, Ph-N=P<sub>1</sub>(pyrr)<sub>3</sub>, *t*-Bu-N=P<sub>1</sub>(pyrr)<sub>3</sub>, **1**, **2**, **40**, **42**, **44**, **46**, **47**, **52** and **53** (Equation 8), as well as subsets of 10 phosphazenes, namely 2-NO<sub>2</sub>-4-CF<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>-N=P<sub>1</sub>(pyrr)<sub>3</sub>, 2,5-Cl<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>-N=P<sub>1</sub>(pyrr)<sub>3</sub>, 4-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-N=P<sub>3</sub>(pyrr)<sub>7</sub>, Ph-N=P<sub>3</sub>(dma)<sub>7</sub>, Me-N=P<sub>1</sub>(dma)<sub>3</sub>, Ph-N=P<sub>1</sub>(pyrr)<sub>3</sub>, **4**-CF<sub>3</sub>-C<sub>6</sub>H<sub>4</sub>-N=P<sub>3</sub>(pyrr)<sub>7</sub>, Ph-N=P<sub>3</sub>(dma)<sub>7</sub>, Me-N=P<sub>1</sub>(dma)<sub>3</sub>, Ph-N=P<sub>1</sub>(pyrr)<sub>3</sub>, *t*-Bu-N=P<sub>1</sub>(pyrr)<sub>3</sub>, **1**, **2** and **42** (Equation 9) and 6 phosphonium ylides, namely **40**, **44**, **46**, **47**, **52** and **53** (Equation 10). Equations 8 (all bases) and 9 (phosphazenes) are almost identical, while equation 10 is somewhat different and considerably less accurate.

All bases:  

$$pK_{\alpha}(\text{THF}) = (0.92 \pm 0.02) \cdot pK_{a}(\text{MeCN}) - (5.15 \pm 0.51) \quad (8)$$

$$n = 20, R^{2} = 0.9936, S = 0.6$$
Phosphazenes:  

$$pK_{\alpha}(\text{THF}) = (0.92 \pm 0.02) \cdot pK_{a}(\text{MeCN}) - (5.11 \pm 0.52) \quad (9)$$

$$n = 10, R^{2} = 0.9973, S = 0.5$$
Phosphonium ylides:  

$$pK_{\alpha}(\text{THF}) = (0.90 \pm 0.11) \cdot pK_{a}(\text{MeCN}) - (4.20 \pm 3.25) \quad (10)$$

$$n = 6, R^{2} = 0.9441, S = 0.9$$

The  $pK_a$  (MeCN) values of phosphazenes studied in this work were estimated using Equation 9 and the  $pK_a$  (MeCN) values of phosphonium ylides using Equation 10. The standard uncertainties of the predicted  $pK_a$  values of phosphazenes and ylides are estimated equal to 0.5 and 1.5  $pK_a$  units, respectively. In the case of phosphazenes this corresponds to the overall

standard deviation S of the corresponding regression. In the case of phosphorus ylides the uncertainty has been estimated higher than S because of the extrapolation involved in predictions.

A p $K_a$ (MeCN) estimate of the phosphane P(-NMe-CH<sub>2</sub>-CH<sub>2</sub>-)<sub>3</sub>N found using Equation 8 is 31.7, while the corresponding experimental value is 32.90.<sup>38</sup> The quality of the prediction is good, considering that neither phosphanes nor any other bases with basicity center on phosphorus atom are represented in the correlation.

Figure 1. Correlation between  $pK_a$  values of different bases in acetonitrile and  $pK_{\alpha}$  values in THF.<sup>*a*</sup>



<sup>*a*</sup> Compound classes:  $\bigcirc$  Phosphazenes,  $\square$  amidines and guanidines,  $\triangle$  phosphonium ylides,  $\diamondsuit$  1,8dimethylaminonaphthalene.

# Effect of structure on basicity

The largest group of bases investigated in this work are phosphonium ylides. Their P=C bond behaves rather as a zwitterionic P<sup>+</sup>-C<sup>-</sup> bond and thus the ylidic carbon in many ways behaves as a carbanionic center.<sup>39,40</sup> This feature is responsible for the main usage of ylides in today's organic chemistry for forming C-C bonds. The partly carbanionic nature of the ylidic carbon causes the very high basicity of ylides,<sup>27</sup> which is also typical to carbanions. Some of the investigated ylides have structure and substitution pattern similar to phosphazenes with known experimental basicities, so that the basicities can be directly compared. The ylide Ph-CH=P(dma)<sub>2</sub>tmg is by 8 orders of magnitude more basic than the phosphazene Ph-N=P(dma)<sub>2</sub>tmg (p $K_{ip} = 18.1$ ).<sup>11</sup> The compound 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(pyrr)<sub>3</sub> is by almost 5 orders of magnitude more basic than 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-N=P<sub>1</sub>(pyrr)<sub>3</sub> (p $K_{\alpha} = 13.3$ ).<sup>11</sup> Thus the present results confirm that phosphonium ylides are by orders of magnitude more basic than phosphazenes (phosphorus imines) with the same substitution pattern.

The set of bases used for investigation of structure-basicity relation contains 16 ylides of the general structure  $R^1R^2C=P(R^3)_2R^4$  where  $R^1$  and  $R^2$  are either H or CH<sub>3</sub> and  $R^3$  and  $R^4$  are either phenyl rings with different number (from 0 to 3) of methoxy groups or cyclohexyl groups (compounds 3, 5, 6, 9, 10, 11, 13, 14, 15, 18, 23, 28, 29, 33, 34, 36). It was found that the basicity of this set of compounds, ranging for close to 7 orders of magnitude, can be well described by the following equation:

$$pK_{a} = (26.7 \pm 0.2) + (1.33 \pm 0.12)n_{CH3} + (-5.0 \pm 0.6)n_{Ph} + (1.40 \pm 0.10)n_{2,6-MeO} + (0.64 \pm 0.09)n_{4-MeO} + (0.18 \pm 0.06)n_{3,5-MeO} + (1.58 \pm 0.17)n_{C-Hexvl}$$
(11)

$$(n = 16, R^2 = 0.98, S = 0.38)$$

where  $n_{\text{CH3}}$  is the number of CH<sub>3</sub> groups among R<sup>1</sup> and R<sup>2</sup>;  $n_{\text{Ph}}$  is the number of phenyl groups among R<sup>1</sup> and R<sup>2</sup>;  $n_{2,6\text{-MeO}}$  is the number of methoxy groups in 2 and/or 6 positions of phenyl rings of R<sup>3</sup> and R<sup>4</sup>;  $n_{4\text{-MeO}}$  is the number of methoxy groups in 4 position of phenyl rings of R<sup>3</sup> and R<sup>4</sup>;  $n_{3,5\text{-MeO}}$  is the number of methoxy groups in 3 and/or 5 positions of phenyl rings of R<sup>3</sup> and R<sup>4</sup>;  $n_{C\text{-Hexyl}}$  is the number of cyclohexyl rings among R<sup>3</sup> and R<sup>4</sup>. The intercept 26.7 ± 0.2 is formally expected to be equal to the p $K_{\alpha}$  value of H<sub>2</sub>C=P(Ph)<sub>3</sub> and is in excellent agreement with the experimental value 26.6 of this compound.

The good fit of Equation 11 with the experimental data shows that the influence of structural features on basicity is to a very good approximation additive, and indirectly serves as a piece of evidence for the good quality of the experimental data.

Examining the coefficient values in Equation 11 reveals that the most efficient way of increasing basicity of this compound family is adding MeO substituents to the aromatic ring: 2,4,6-trisubstitution of one ring leads to 3.2-3.5  $pK_a$  units of basicity increase. 3 and 5 substitution is significantly less efficient. Methylation of the ylidic carbon leads to more than 1  $pK_a$  units of basicity increase, while introducing a phenyl substituent to the ylidic carbon leads to dramatic – by more than 5  $pK_a$  units – basicity decrease. This extreme sensitivity of the basicity center to phenyl substitution gives additional evidence that the P=C bond in ylides should rather be viewed as P<sup>+</sup>-C<sup>-</sup>, i.e. zwitterionic. In the case of phenyl substitution the negative charge on ylidic carbon will be efficiently delocalized in the aromatic ring and protonation becomes significantly less favorable, as the aromatic ring stabilizes the neutral ylide but does not offer any stabilization to its protonated form. The strong basicity redusing effect of the 4-NO<sub>2</sub> substituent is an additional piece of evidence.

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Among the compounds measured in this work is  $(CH_3)_2C=P(dma)_3$  (18), which has earlier been reported to be by only an order of magnitude less basic than the P<sub>4</sub> phosphazene *t*-Bu-N=P<sub>4</sub>(dma)<sub>9</sub>.<sup>34</sup> The current results place this compound at p $K_{\alpha}$  28.7, which is more than six orders of magnitude weaker than the *t*-Bu-N=P<sub>4</sub>(dma)<sub>9</sub> phosphazene. This serves as a good demonstration of the need for reliable basicity scales in studies of strong bases.

Phosphonium ylides of the structure  $R^1R^2C=P(Ar^3)_2Ar^4$  are the key family of compounds in the present study. These compounds are useful for basicity studies, because they (in salt form) are relatively easy to synthesize, have strong UV absorbance, and a very wide basicity range is achievable with different substituents. Within the range of structural variations used for compiling Equation 11 the basicity of the ylides can be easily predicted using the equation. Already the ylides with just one phosphorus atom can have basicities comparable to P<sub>4</sub> phosphazenes, which enabled linking P<sub>4</sub> phosphazenes to the scale. Equation 11 enables estimating the pK<sub>a</sub> value of the strongest ylide that is possible to construct with the above listed substituents: (CH<sub>3</sub>)<sub>2</sub>C=P(2,4,6-(MeO)<sub>3</sub>-C6H<sub>2</sub>)<sub>3</sub>. The estimate of pK<sub>a</sub> in THF is 39.6 and pK<sub>a</sub> in MeCN (using eq 10) is 49. Both values are truly impressive for a P<sub>1</sub> base.

The available data enable direct comparison of the effects pyrrolidino, dimethylamino and phenyl substituents on basicity. The basicity increases in the row Ph(CH<sub>3</sub>)CH-N=P<sub>4</sub>(Ph)<sub>9</sub>  $\rightarrow$ Ph(CH<sub>3</sub>)CH-N=P<sub>4</sub>(dma)<sub>9</sub>  $\rightarrow$  Ph(CH<sub>3</sub>)CH-N=P<sub>4</sub>(pyrr)<sub>9</sub> as follows: 30.0  $\rightarrow$  32.7  $\rightarrow$  33.9 (p $K_{\alpha}$ values). It can be seen that unsubstituted phenyl rings are weaker basicity enhancers than dma or pyrr groups: replacing one Ph by dma would lead to roughly 0.9 p $K_a$  units of basicity increase. Similar conclusion is reached by comparing *t*-Bu-N=P<sub>2</sub>(dma)<sub>5</sub> and *t*-Bu-N=P<sub>2</sub>(Ph)<sub>5</sub>: the former is by close to 5 orders of magnitude more basic.

At the same time, as demonstrated above, introducing methoxy groups into 2, 4 and 6 positions of a phenyl ring leads to basicity increase of more than 3 orders of magnitude. This means that methoxylated phenyl rings connected to phosphorus are more efficient basicity enhancers than dma or pyrr fragments. In the current scale this is demonstrated e.g. by comparison of basicities of  $(CH_3)_2C=P(2,4,6-(MeO)_3-C_6H_2)Ph_2$  and  $(CH_3)_2C=P(dma)_3$ : with just one of the rings methoxylated, the former is by more than 2 orders of magnitude more basic than the latter.

## Conclusions

With the help of a series of substituted phosphonium ylides with widely tunable basicities (more than 10 orders of magnitude) the span of the self-consistent basicity scale in THF is now wider than 30 orders of magnitude and its highest basicity limit is at  $pK_{\alpha}$  35. The excellent correlation ( $R^2 = 0.996$ ) between basicities in THF and acetonitrile covering a basicity range of more than 25 orders of magnitude renders this scale a useful tool for further basicity studies besides THF also in acetonitrile. In addition, since THF can be viewed as a model low-polarity solvent and the basicity trends found in THF are expected to be well applicable to other low-polarity solvents, as well as the gas phase, its potential usage is expected to be even wider.

### Experimental

#### **Chemicals and consumables**

Romil SpS tetrahydrofuran was used for basicity measurements after additional purification with careful sodium/benzophenone treatment. Distillation of the 24 h stirred and 2 h refluxed mixture yielded solvent with water content below 1 ppm (according to Karl-Fisher titration with Mettler Toledo DL32 Coulometer). Romil SpS acetonitrile was used after drying over molecular sieves (3Å) for at least 24 h to achieve water content below 5 ppm. Potassium hydride (KH, 30% suspension in mineral oil) was applied for liberation of bases in stock solutions. The oil was washed out with THF and KH was dried under vacuum in the glovebox. In THF, methanesulfonic acid (>99%) solution was used as acidic titrant, and *t*-Bu-N=P<sub>4</sub>(dma)<sub>9</sub> (Initially 0.8M in hexane) solution as basic titrant. In MeCN the corresponding solutions were made from trifluoromethanesulfonic acid (99+%) and Et-N=P<sub>2</sub>(dma)<sub>5</sub> (98%) or Et-N=P<sub>2</sub>(pyrr)<sub>5</sub> (see details of synthesis in SI).

# Synthesis, Purification, and Characterization of Compounds

## General

The Kirsanov<sup>41</sup> reaction between PCl<sub>5</sub> and suitable amine/imine compounds was used to synthesize phosphazene salts. Free phosphazene bases may be liberated from their salts by means of *t*-BuOK in dimethoxyethane (DME) as described in ref. <sup>11</sup>. Triflate salts of phosphazenes, if needed, were synthesized from free bases or by reaction from their HBF<sub>4</sub> or HBPh<sub>4</sub> salts. Tris-substituted phosphines are available commercially or were synthesized according to literature procedures. The reaction between lithiated or Zn-catalyzed aryls or Grignard reagents of halogen aryls with phosphorus halogenides was used. The following phosphines were prepared: P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>7</sub>,<sup>36,37</sup> P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>Ph,<sup>42,43</sup> P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>7</sub>,<sup>42,43</sup> P(3,5-

 $(MeO)_2-C_6H_3)_3$ ,<sup>47,48</sup>  $P(dma)_3$ ,<sup>49</sup>  $P(pyrr)_3$ ,<sup>49</sup>  $P(C_6H_{11})_2Ph$ ,<sup>50</sup>  $P(C_6H_{11})Ph_2$ ,<sup>50</sup>  $P(Napht)Ph_2$ ,<sup>51</sup>  $P(dma)_2Cl$ ,<sup>52</sup>  $P(pyrr)_2Cl$ .<sup>52</sup>

In the reaction between  $P(pyrr)_2Cl$  or  $P(dma)_2Cl$  and TMG and also between  $P(pyrr)Cl_2$  or  $P(dma)Cl_2$  and TMG the same products, i.e.  $P(pyrr)_2tmg$  and  $P(dma)_2tmg$  were obtained, respectively. It seems to be due to the disproportionation of already formed compounds on the reaction and/or distillation.<sup>53,54</sup>

Phosphonium salts were synthesized according to eq 12:41,55

$$R_{3}P + R'X \xrightarrow{(X=CI, Br, I)} R_{3}P^{+} - R' + X^{-} \xrightarrow{CF_{3}SO_{3}Na} R_{3}P^{+} - R' + CF_{3}SO_{3}^{-}$$
(12)

The reactions were carried out sometimes as a neat mixture of reagents or in benzene, toluene, DME, EtOH, *i*-PrOH or nitromethane solution under reflux. Benzene or alcohols as solvents sometimes give strongly solvated phosphonium halogenides. To destroy these adducts recrystallization from THF/MeOH may be recommended following crushing the crystal mass with dichloromethane and concentrating the extracts in high vacuum. Dry solvents and argon atmosphere were used for all syntheses except for metathesis reactions. To make phosphonium salts more soluble in THF and to unify anions of compounds for acid-base measurements the halogenide anions were exchanged for triflate anion by metathesis reaction with sodium triflate in water or in water/alcohol mixture.

The following compounds were synthesized as described in literature:  $1,^{8}$   $16,^{11}$   $24 - 27,^{11}$   $30,^{11}$   $32,^{8}$   $37,^{56,57}$   $39,^{58}$   $43,^{8}$   $45,^{59}$   $56.^{58}$  Compounds 2 (0.8 M solution in hexane, hexane was evaporated before use) and 42 (98%) have commercial origin and were used without purification.

The structure and purity of synthesized compounds were checked by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectrometric analyses on, a 200 MHz, 400 MHz or 700 MHz NMR spectrometer. Chemical

shifts are given relative to TMS as internal standard for <sup>1</sup>H NMR spectra, relative to the solvent residual peak<sup>60</sup> or to TMS for <sup>13</sup>C NMR spectra, and relative to 85% H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P NMR spectra. High resolution ESI mass spectra were obtained on a hybrid FT-ICR-MS system. Melting points are uncorrected. Sometimes in the course of melting of phosphonium salts they slowly decompose. The synthesis of phosphonium salts and phosphazenes was not optimized.

## Typical examples of starting compounds synthesis

# P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>Ph and P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)Ph<sub>2</sub><sup>42</sup>

The mixture of 1,3,5-trimethoxybenzene, phenyldichlorophosphine and  $ZnCl_2$  in ratio 30:10:30 mmol (or 1,3,5-trimethoxybenzene, diphenylclorophosphine and  $ZnCl_2$  in relation 10:10:30 mmol respectively) was heated at 65 °C for 6-8 hours and left overnight at room temperature. Benzene (30 mL) and ~12% NH<sub>4</sub>OH solution (30 mL) were added to the sticky mass, an extra stirrer bar was added to the reaction flask, and the mixture was stirred until all mass was dissolved. The organic layer was separated, washed with water and brine, and dried over MgSO<sub>4</sub>. The benzene was evaporated in vacuum to get a crystalline mass, which may be recrystallized from ethanol.

P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>Ph: yield 40%, mp 152-153°C, <sup>31</sup>P NMR (CDCl<sub>3</sub>, 81 MHz) δ -46.3. P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)Ph<sub>2</sub>: yield 30%, mp 103-104°C, 31P NMR (CD<sub>3</sub>Cl, 81 MHz) δ -26.4.

The <sup>1</sup>H NMR spectra were in accordance with literature data.<sup>43</sup>

# 1,3-Dimethyl-2-imidazolidinimine (immeH)

2-Chloro-1,3-dimethylimidazolium chloride<sup>61</sup> (65 g, 0.38 mol) was dissolved in 70 ml of  $CH_2Cl_2$  and treated at 0 °C with threefold excess of NH<sub>3</sub> (19 g, 1.1 mol). The precipitate (1:1

mixture of **immeH**·HCl and NH<sub>4</sub>Cl ) was filtered, washed with some CH<sub>2</sub>Cl<sub>2</sub>, dried and dissolved in 180 ml of 26% NaOH. Ammonia was removed under reduced pressure on rotary evaporator and the obtained precipitate was filtered off. The upper organic layer was separated and distilled in vacuum at 46-48 °C/0.3 Torr to give 24 g (58%) of colorless liquid, **immeH**. Synthesis of ImmeH has also been reported in literature.<sup>62</sup>

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 4.04 (s, 1H), δ 3.16 (s, 4H), δ 2.73 (s, 6H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 163.2, 47.3, 33.0.

## Synthesis of bases

# H<sub>2</sub>C=P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>2</sub>Ph·CF<sub>3</sub>SO<sub>3</sub>H (3·CF<sub>3</sub>SO<sub>3</sub>H)

Bis(2,4,6-trimethoxyphenyl)phenylphosphine (0.30 g, 0.68 mmol) and 1.0 ml of CH<sub>3</sub>I were mixed and stirred with glass stick at 50  $^{\circ}$ C for 15 min. The formed thick paste was diluted with diethyl ether and filtered to give 0.39 g (0.66 mmol, 97%) of **3**·HI as yellowish fine crystals, mp 192.8-193.7  $^{\circ}$ C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.68 – 7.40 (m, 5H), 6.24 (d, *J*=4.7 Hz, 4H), 3.84 (s, 6H), 3.51 (s, 12H), 2.52 (d, *J*<sub>P-H</sub>=14.6 Hz, 3H).<sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 167.3 (d, *J*=1.4 Hz), 164.1 (d, *J*=1.6 Hz), 132.2 (d, *J*=3.2 Hz), 130.8 (d, *J*=11.3 Hz), 128.7 (d, *J*=13.4 Hz), 126.7 (d, *J*<sub>P-C</sub>=96.3 Hz), 92.0 (d, *J*=7.0 Hz), 89.4, 87.3, 56.5 (d, *J*<sub>P-C</sub>=1.9 Hz), 16.5 (d, *J*<sub>P-C</sub>=64.4 Hz). <sup>31</sup>P NMR (81MHz, CD<sub>3</sub>CN) δ 6.7. HRMS (ESI+): calc for C<sub>25</sub>H<sub>30</sub>O<sub>6</sub>P<sup>+</sup>, 457.17745; found, 457.17745.

The triflate was prepared by mixing  $3 \cdot \text{HI}$  (0.22 g, 0.40 mmol) and sodium triflate (72 mg, 0.42 mmol) in warm solvent mixture (20 ml of water and 3.0 ml of ethanol). The solvent was decanted and the glassy drops on the flask walls were treated with ethanol. The ethanolic

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solution was evaporated to dryness to give 0.13 g (0.21 mmol, 53%) of somewhat foamy solid  $3 \cdot CF_3SO_3H$ , which melts at 60-70  $^{0}C$ .

# Ph(CH<sub>3</sub>)CH-N=P<sub>4</sub>(pyrr)<sub>9</sub>·HBPh<sub>4</sub> (4·HBPh<sub>4</sub>)

Solution of Ph(CH<sub>3</sub>)CH-N=PCl<sub>3</sub><sup>63</sup> (2.2 g, 8.5 mmol, synthesized as described for compound 7·HBF<sub>4</sub>) in 3.0 ml of THF was added to the solution of free phosphazene base H-N=P<sub>1</sub>(pyrr)<sub>3</sub><sup>8</sup> (15.4 g, 60 mmol) in 12 ml of THF at -70 <sup>o</sup>C. The mixture was allowed to warm to room temperature, the solvent was removed and the residue was heated at 110 <sup>o</sup>C for 18 h. To the cooled mixture 30 ml of toluene and 2 ml of 1,1,2-trichloroethane was added, and the mixture was set aside for a night. The mixture was filtered and the solution was evaporated to dryness. The residue, raw 4·HCl (11 g), was dissolved in 40 ml of 70% aqueous ethylamine solution and 1.1 g of NaBF<sub>4</sub> dissolved in 10 ml of water was added. Extra 8 ml of water was added to the warm solution to generate a persistent turbidity, and then the mixture was set aside for a day. The mixture was filtered to get 5.9 g (5.8 mmol, 69%) of raw 4·HBF<sub>4</sub> salt. It was recrystallized from 1:3 mixture of Hex/EtOAc to get 2.6 g off-white crystal of 4·HBF<sub>4</sub>, mp 170-180 <sup>o</sup>C (dec).

From the mother liquid 2.5 g (2.5 mmol) of  $4 \cdot \text{HBF}_4$  salt was recovered. It was dissolved in 8 ml of MeOH and transferred to  $4 \cdot \text{HBPh}_4$  salt by means of NaBPh<sub>4</sub> (0.9 g, 2.6 mmol) dissolved in 3 ml of MeOH. The white crystals were filtered off, recrystallized from 30 ml of 3:1 mixture of MeOH/MeCN to get 2.6 g (2.1 mmol, 84 %) of  $4 \cdot \text{HBPh}_4$ , mp 200-220 <sup>0</sup>C (dec).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.61 – 6.70 (m, 10H), 4.37 (dp,  $J_{P-H}$ =13.0 Hz, J=6.1 Hz, 1H), 3.28 – 2.82 (m, 27H), 2.31 (t, J=6.3 Hz, 1H), 1.91 – 1.54 (m, 27H), 1.40 (d, J=6.6 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 165.4 (d,  $J_{P-C}$ =49.3 Hz), 163.5 (d,  $J_{P-C}$ =49.3 Hz), 147.5 (d,

J=7.5 Hz), 136.4 (dd, J=2.9 Hz, J=1.4 Hz), 128.3, 126.6, 125.9, 125.3 (dd, J=5.5 Hz, J=2.7 Hz), 121.4 , 51.9 (d, J=2.2 Hz), 46.6 (d, J=4.8 Hz), 26.3 (d, J=8.9 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  -0.23 (d,  $J_{P-C}=43.7$  Hz), -19.8 (q,  $J_{P-C}=46.9$  Hz,  $J_{P-C}=45.3$  Hz). HRMS (ESI+): calc for C<sub>44</sub>H<sub>82</sub>N<sub>13</sub>P<sub>4</sub><sup>+</sup>, 916.57611; found, 916.57607.

## Ph(CH<sub>3</sub>)C=P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (5·CF<sub>3</sub>SO<sub>3</sub>H)

Tris(2,4,6-trimethoxyphenyl)phosphine (0.53 g, 1.0 mmol) was dissolved in 1.7 ml of hot toluene and (1-bromoethyl)benzene (0.19 g, 1.0 mmol) was added. The mixture was heated at 100 °C for 1 h and then cooled down. The formed crystals were filtered off, washed with toluene and dried in vacuum. The **5**·HBr (0.60 g, 0.84 mmol, 84%) was obtained as colorless crystals, mp 205.3-206.4 °C (dec).

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.11 (s, 5H), 6.15 (d, *J*=4.4 Hz, 6H), 5.93 (dd, *J*<sub>P-H</sub>=20.4 Hz, *J*=7.2 Hz, 1H), 3.85 (s, 9H), 3.54 (s, 18H), 1.57 (dd, *J*<sub>P-H</sub>=21.5 Hz, *J*=7.2 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  166.4 (d, *J*=2.0 Hz), 164.6, 139.4 (d, *J*=5.1 Hz), 129.4 (d, *J*=5.8 Hz), 128.6 (d, *J*=3.6 Hz), 127.9 (d, *J*=4.2 Hz), 93.6 (d, *J*<sub>P-C</sub>=99.0 Hz), 91.7 (d, *J*=7.1 Hz), 56.6, 56.4, 39.5 (d, *J*<sub>P-C</sub>=48.1 Hz), 15.7.

HRMS (ESI+): calc for  $C_{35}H_{42}O_9P^+$ , 637.25610; found, 637.25592.

The triflate salt was prepared by mixing  $5 \cdot$ HBr (0.10 g, 0.14 mmol) and CF<sub>3</sub>SO<sub>3</sub>Na (25 mg, 0.145 mmol) in hot water (3 ml). The crystals were washed with water and dried in vacuum to give 80 mg (0.10 mmol, 72%) of  $5 \cdot$ CF<sub>3</sub>SO<sub>3</sub>H, mp 201.3-202.3 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.22 – 7.03 (m, 6H), 6.14 (m, 5H), 5.93 (dq,  $J_{P-H}$ =20.5 Hz, *J*=6.9 Hz, 1H), 3.85 (d, *J*=6.0 Hz, 9H), 3.54 (s, 18H), 1.57 (dd,  $J_{P-H}$ =21.4 Hz, *J*=7.1 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 163.4, 138.9 (d, *J*=4.9 Hz), 136.0, 136.0, 129.4 (d, *J*=5.9 Hz),

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128.7 (d, *J*=3.7 Hz), 128.2 (d, *J*=4.4 Hz), 105.0 (d, *J*=6.8 Hz), 101.6 (d, *J*<sub>P-C</sub>=91.5 Hz), 56.3, 39.4 (d, *J*<sub>P-C</sub>=44.8 Hz), 15.84. <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 19.9.

# (CH<sub>3</sub>)<sub>2</sub>C=P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)Ph<sub>2</sub>·CF<sub>3</sub>SO<sub>3</sub>H (6·CF<sub>3</sub>SO<sub>3</sub>H)

*i*-Propyl(2,4,6-trimethoxyphenyl)diphenylphosphonium iodide ( $\mathbf{6}$ ·HI)<sup>64</sup> (0.10 g, 0.19 mmol) was dissolved in 1.5 ml warm ethanol and CF<sub>3</sub>SO<sub>3</sub>Na solution (36 mg, 0.20 mmol) in 0.5 ml of ethanol was added. For precipitation of the product 4.0 ml of water was added and the mixture was stored for a day. The collected colorless crystals of  $\mathbf{6}$ ·CF<sub>3</sub>SO<sub>3</sub>H were filtered off and dried. Yield 80 mg (0.147 mmol, 77%), mp 155.0-155.6 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.90 – 7.52 (m, 10H), 6.32 (d, *J*=4.4 Hz, 2H), 4.16 – 3.91 (m, 1H), 3.89 (s, 3H), 3.64 (s, 6H), 1.10 (dd, *J*<sub>P-H</sub>=19.2 Hz, *J*=6.9 Hz, 6H). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 26.7

## Ph(CH<sub>3</sub>)CH-N=P<sub>4</sub>(dma)<sub>9</sub>·HBF<sub>4</sub> (7·HBF<sub>4</sub>)

Ph(CH<sub>3</sub>)CH-N=PCl<sub>3</sub> was synthesized by the Kirsanov method<sup>63</sup> from 11 g (96 mmol) of phenyl-ethylamine and 20.5 g (96 mmol) of PCl<sub>5</sub> in 130 ml of CCl<sub>4</sub>. The mixture was stirred and heated until the evolution of HCl gas stopped. The solution was filtered, the solvent was removed and the residual oil was distilled at 70-75  $^{0}$ C/0.3 Torr. Yield 15 g (60 mmol, 62%). H-N=P<sub>1</sub>(dma)<sub>3</sub><sup>8</sup> (10.5 g, 58.9 mmol) was dissolved in 12 ml of THF and the solution of Ph(CH<sub>3</sub>)CH-N=PCl<sub>3</sub> (2.2 g, 8.5 mmol) in 3 ml of THF was added at -70 °C with a syringe. The mixture was allowed to warm to room temperature, the solvent was removed and the residue was heated at 110 °C for 24 h. To the cool mixture of 23 ml of THF and 2 ml of 1,1,2-trichloroethane was added and the H-N=P<sub>1</sub>(dma)<sub>3</sub>·HCl was filtered off. The filtrate was concentrated and the solvent was completely removed under high vacuum. The raw product 7·HCl, brownish oil, was dissolved in 25 ml of 70% EtNH<sub>2</sub> aqueous solution and 1.0 g (9.1

mmol) of NaBF<sub>4</sub> dissolved in 3 ml of water was added. The clear mixture was slightly warmed and water was added up to persistent turbidity (about 15 ml). A soft waxy precipitate formed. The solvent was decanted and the residue was once more treated with 70 % EtNH<sub>2</sub> solution (40 ml) and water (42 ml) and set aside for 2 days. Colorless crystals were filtered off, washed with 30% EtNH<sub>2</sub> aqueous solution and dried in vacuum. Yield 2.6 g (3.5 mmol, 41%) of 7·HBF<sub>4</sub>, mp 201-205 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.44 – 7.09 (m, 5H), 4.38 (dp, *J*=14.1 Hz, *J*=6.8 Hz, 1H), 2.90 – 2.43 (m, 54H), 2.41 – 2.21 (m, 1H), 1.41 (d, *J*=6.7 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  147.2 (d, *J*=6.2 Hz), 128.2, 126.4, 125.8, 51.6 (d, *J*=1.7 Hz), 37.1 (d, *J*=4.5 Hz), 26.6 (d, *J*=5.3 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  14.6 (d, *J*<sub>P-C</sub>=47.8 Hz), -19.6 (q, *J*<sub>P-C</sub>=49.6 Hz, *J*<sub>P-C</sub>=47.8 Hz). HRMS (ESI+): calc for C<sub>26</sub>H<sub>64</sub>N<sub>13</sub>P<sub>4</sub><sup>+</sup>, 682.43526; found, 682.43526.

## MeO-CH=P(4-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (8·CF<sub>3</sub>SO<sub>3</sub>H)

P(4-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (0.25 g, 0.71 mmol) and excess of MeOCH<sub>2</sub>Cl (0.57 g, 7.0 mmol) were mixed in 1.0 ml of DME at 40 °C and stirred for 2 h. Colorless crystals were filtered off, washed with DME and dried in vacuum to give 0.27 g, (0.62 mmol, 87%) of **8**·HCl, mp 194-195 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 7.76 – 7.56 (m, 6H), 7.29 – 7.16 (m, 6H), 5.28 (d, *J*=4.7 Hz, 2H), 3.91 (s, 9H), 3.53 (d, *J*=0.8 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ 166.0 (d, *J*=3.0 Hz), 136.97 (d, *J*=11.6 Hz), 116.88 (d, *J*=13.8 Hz), 108.6 (d, *J*<sub>P-C</sub>=94.5 Hz), 67.1(d, *J*<sub>P-C</sub>=71.1 Hz), 62.65 (d, *J*=13.3 Hz), 56.77. <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN) δ 15.5.

HRMS (ESI+): calc for  $C_{23}H_{26}O_4P^+$ , 397.15632; found, 397.15644.

The triflate was prepared by mixing  $\mathbf{8}$ ·HCl (0.20 g, 0.46 mmol) and CF<sub>3</sub>SO<sub>3</sub>Na (80 mg, 0.46 mmol) in 5.0 ml of water. An oil separated which was washed with water and then dissolved in ethanol. Ethanolic solution was concentrated to give colorless oil of  $\mathbf{8}$ ·CF<sub>3</sub>SO<sub>3</sub>H (0.16g, 0.29 mmol, 63%,) which did not crystallize even at -15 °C.

## $(CH_3)_2C=P(4-MeO-C_6H_4)_3$ ·CF<sub>3</sub>SO<sub>3</sub>H (9·CF<sub>3</sub>SO<sub>3</sub>H)

The mixture of P(4-MeO-C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> (0.52 g, 1.47 mmol), isopropyl iodide (0.36 g, 2.1 mmol) and 6.0 ml of nitromethane was stirred at 100 °C for 2 h. The solvent was evaporated at reduced pressure and the residue, a glassy mass, was triturated with glass stick with 3.0 ml of benzene to wash off the starting phosphine. The solid was filtered off and dried under high vacuum at 60 °C for 2 h. <sup>1</sup>H NMR showed the compound to be 1:1 adduct of **9**·HI and benzene (0.53 g, 0.88 mmol, 60%), and it does not have an exact melting point.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.80 – 7.62 (m, 6H), 7.37 (s, C<sub>6</sub>H<sub>6</sub>), 7.21 (dd, *J*=9.0 Hz, *J*=2.6 Hz, 6H), 4.01 – 3.77 (m, 10H), 1.26 (dd, *J*<sub>P-H</sub>=18.4 Hz, *J*=7.0 Hz, 6H). <sup>31</sup>P NMR (81MHz, CD<sub>3</sub>CN) δ 28.6

The triflate salt was prepared by mixing  $9 \cdot \text{HI}$  (0.23 g, 0.38 mmol) and CF<sub>3</sub>SO<sub>3</sub>Na (76 mg,0.44 mmol) in 3.0 ml of warm isopropanol. The solvent was removed at 60 °C/0.05 Torr. The residue, a sticky mass, was treated with CH<sub>2</sub>Cl<sub>2</sub>, filtered and solution was evaporated to dryness to give 80 mg (0.147 mmol, 38%) of colorless glassy mass,  $9 \cdot \text{CF}_3\text{SO}_3\text{H}$ , mp 61-63 °C (dec).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 8.00 – 7.63 (m, 6H), 7.28 – 7.04 (m, 6H), 4.67 (qd, *J*=6.9 Hz, *J*=3.7 Hz, 1H), 3.92 (d, *J*=7.1 Hz, 9H), 1.30 (dd, *J*<sub>P-H</sub>=18.6 Hz, *J*=6.9 Hz, 6H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 164.5 (d, *J*=2.9 Hz), 135.8 (d, *J*=10.7 Hz), 116.3 (d, *J*=13.2 Hz), 108.4 (d, *J*<sub>P-C</sub>=91.1 Hz), 56.1, 22.7 (d, *J*<sub>P-C</sub>=50.4 Hz), 16.6 (d, *J*=2.1 Hz).

HRMS (ESI+): calc for  $C_{24}H_{28}O_3P^+$ , 395.17706; found, 395.17700.

## Ph(CH<sub>3</sub>)C=P(2,6-(MeO)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (10·CF<sub>3</sub>SO<sub>3</sub>H)

P(2,6-(MeO)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub> (0.50 g, 1.13 mmol) was dissolved in 25 ml of warm toluene and (1bromoethyl)benzene (0.22 g, 1.18 mmol) was added. The mixture was heated at 80 °C for 1 h, cooled and the formed precipitate was filtered off, washed with toluene and dried in vacuum. The **10**·HBr was obtained (0.52 g, 0.75 mmol, 73.3%) as a white powder, mp 217-218 °C (dec).

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.50 (t, *J*=8.4 Hz, 3H), 7.26 – 7.00 (m, 5H), 6.73 – 6.52 (m, 6H), 6.16 (dd,  $J_{P-H}=20.8$  Hz, *J*=7.2 Hz, 1H), 3.55 (s, 18H), 1.62 (dd,  $J_{P-H}=21.8$  Hz, *J*=7.2 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 165.4, 165.4, 163.6, 138.4 (d, *J*=5.1 Hz), 128.4 (d, *J*=5.8 Hz), 127.6 (d, *J*=3.6 Hz), 126.9 (d, *J*=4.2 Hz), 117.2 , 92.6 (d, *J*<sub>P-C</sub>=99.0 Hz), 90.7 (d, *J*=7.1 Hz), 55.5, 55.3, 38.5 (d, *J*<sub>P-C</sub>=48.1 Hz), 14.7. <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ = 22.7.

HRMS (ESI+): calc for  $C_{32}H_{36}O_6P^+$ , 547.22440; found, 547.22437.

The triflate was prepared by reaction mixing the bromide salt 10·HBr (0.33 g, 0.60 mmol) and CF<sub>3</sub>SO<sub>3</sub>Na (0.11 g, 0.60 mmol) in warm 1:1 mixture of *i*-PrOH/H<sub>2</sub>O to give 0.31 g (0.50 mmol, 83%) of 10·CF<sub>3</sub>SO<sub>3</sub>H, mp 300.0-301.5 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.63 – 7.25 (m, 3H), 7.28 – 6.83 (m, 5H), 6.77 – 6.33 (m, 6H), 6.32 – 5.96 (m, 1H), 3.53 (s, 18H), 1.63 (dd, *J*=21.8 Hz, *J*=7.2 Hz, 3H).<sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  163.4, 138.9 (d, *J*=4.9 Hz), 136.0 (d, *J*=1.2 Hz), 129.4 (d, *J*=5.9 Hz), 128.7 (d, *J*=3.7 Hz), 128.2 (d, *J*=4.4 Hz), 105.0 (d, *J*=6.8 Hz), 101.6 (d, *J*<sub>P-C</sub>=91.5 Hz), 56.3, 39.4 (d, *J*<sub>P-C</sub>=44.8 Hz), 15.8.

#### $CH_3$ - $CH=P(C_6H_{11})_2Ph$ · $CF_3SO_3H$ (11· $CF_3SO_3H$ )

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The salt 11·HBr<sup>50</sup> (0.10 g, 0.26 mmol) was converted into triflate by reaction with CF<sub>3</sub>SO<sub>3</sub>Na (50 mg, 0.29 mmol) in 1.0 ml of water at room temperature. The crystals were recrystallized from 4:1 mixture of AcOEt/EtOH to give 60 mg (51%) of pure product (11·CF<sub>3</sub>SO<sub>3</sub>H), mp 161.4-162.5 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.92 – 7.61 (m, 5H), 2.91 – 2.57 (m, 2H), 2.24 – 0.96 (m, 23H). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) δ 32.9.

#### Et-N=P<sub>1</sub>(imme)<sub>3</sub>·HBF<sub>4</sub> (12·HBF<sub>4</sub>)

In 25 ml of CH<sub>2</sub>Cl<sub>2</sub> 2.05 g (9.86 mmol) of PCl<sub>5</sub> was suspended at -40 °C and 6.7 g (59 mmol) of **immeH** (*vide supra*) was slowly added. The mixture was stirred and allowed to warm up to room temperature and additionally stirred for another 1 h. Then the mixture was cooled again to -30 °C and a cold mixture of 0.68 g (15 mmol) ethylamine and 1.7 ml of triethylamine was added with a syringe. The mixture was stirred until the ambient temperature was achieved and then set aside for one day. The crystal mass that formed was filtered off and the filtrate was concentrated in vacuum to yield 4.8 g of **12**·HCl. This salt was dissolved in 30 ml of water and a solution of 1.13 g (10.2 mmol) NaBF<sub>4</sub> in 2 ml of water was added. The formed **12**·HBF<sub>4</sub> was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> layer was separated and dried with MgSO<sub>4</sub>. The solvent was removed under reduced pressure to give 2.0 g of soft colorless crystals. Recrystallization from 1:2 mixture of MeOH/AcOEt gave 1.90 g (4.0 mmol, 38%) of **12**·HBF<sub>4</sub>, mp 142-144 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 1.14 (dt, *J*=0.90 Hz, *J* =7.16 Hz, 3H), 2.47 (br, 2H), 2.90 (s, 18H), 3.44 (s, 12H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 156.7 (d, *J*=7.5), 47.1, 36.2 (d, *J*=1.5), 33.7, 17.1 (d, *J*=8.5). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) -11.06.

Anal. Calc for C<sub>17</sub>H<sub>36</sub>F<sub>4</sub>BN<sub>10</sub>P: C, 40.97; H, 7.28; N, 28.11. Found: C, 40.99; H, 7.30; N, 28.26.

# $(CH_3)_2C=P(3,5-(MeO)_2-C_6H_3)_3\cdot CF_3SO_3H (13\cdot CF_3SO_3H)$

Tris(3,5-dimethoxyphenyl)phosphine<sup>47,48</sup> (0.35 g, 0.79 mmol), excess of isopropyl iodide (1.12 g, 6.6 mmol) and 4.5 ml of dry toluene were heated in stoppered test tube at 110 °C for 5 h and cooled down. The formed fine precipitate was filtered off and washed with benzene to give 0.13 g of **13**·HI (mp 223-225 °C), which was then dissolved in 9.0 ml 2:1 solution of H<sub>2</sub>O/EtOH at 70 °C. Sodium triflate (50 mg, 0.29 mmol) in 0.2 ml of water was added and the solution was let to stand overnight. The formed crystals were filtered off to get 0.11 g (0.14 mmol, 18% overall) of **13**·CF<sub>3</sub>SO<sub>3</sub>H, mp 187-189 °C.

<sup>1</sup>H NMR (700 MHz, CD<sub>3</sub>CN) δ 6.90 (m, 3H), 6.86 (dd, *J*=2.2 Hz, *J*=13.2 Hz, 6H), 3.90 (m, 1H), 3.81 (s, 18H), 1.32 (dd, *J*=6.8 Hz, *J*<sub>P-H</sub>=18.7 Hz, 6H). <sup>13</sup>C NMR (176 MHz, CD<sub>3</sub>CN) δ 163.1 (d, *J*=18.6 Hz), 122.2 (q, *J*<sub>F-C</sub>=318 Hz), 112 (d, *J*=10.6 Hz), 107.0 (d, *J*=2.3 Hz), 57.0, 22.1 (d, *J*<sub>P-C</sub>=48.6), 16.9 (d, *J*=1.9 Hz). <sup>31</sup>P NMR (81MHz, CD<sub>3</sub>CN) δ 35.3. <sup>19</sup>F NMR (658 MHz, CD<sub>3</sub>CN) δ -79.3.

HRMS (ESI+): calc for  $C_{27}H_{34}O_6P^+$ , 485.20875; found, 485.20883.

## H<sub>2</sub>C=P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)Ph<sub>2</sub>·CF<sub>3</sub>SO<sub>3</sub>H (14·CF<sub>3</sub>SO<sub>3</sub>H)

To  $14 \cdot HI^{43}$  (0.22 g, 0.44 mmol) CF<sub>3</sub>SO<sub>3</sub>Na (80 mg, 0.45 mmol) was added in ethanolic solution (2 ml) at 60 °C. The solvent was removed, the residue was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered, and the solution was evaporated to dryness. The hard glassy foam ( $14 \cdot CF_3SO_3H$ ) was obtained (0.19 g, 3.6 mmol, 83%). It does not have a sharp melting point.<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.96 – 7.47 (m, 10H), 6.34 (d, *J*=4.7 Hz, 2H), 3.91 (s, 3H), 3.56 (s, 6H), 2.63 (d, *J*=14.1 Hz, 3H). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  15.2.

## $CH_3$ - $CH=P(C_6H_{11})Ph_2$ · $CF_3SO_3H$ (15· $CF_3SO_3H$ )

 The salt **15**·HBr<sup>50</sup> (0.16 g, 0.42 mmol) was dissolved in 5.0 ml of warm water and the solution of CF<sub>3</sub>SO<sub>3</sub>Na (90 mg, 0.52 mmol) in 0.5 ml of water was added. The oily drops separated at once and solidified soon. Water was decanted off and formed solid (**15**·CF<sub>3</sub>SO<sub>3</sub>H) was dried at reduce pressure on P<sub>2</sub>O<sub>5</sub>. Yield 0.14 g (0.31 mmol, 74%), mp 98.0-99.8 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 – 7.56 (m, 10H), 2.95 (dd,  $J_{P-H}$ =11.8 Hz, J=7.5 Hz, 2H), 2.23 – 0.80 (m, 13H). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  33.3.

# MeO-CH=P(C<sub>6</sub>H<sub>11</sub>)Ph<sub>2</sub>·CF<sub>3</sub>SO<sub>3</sub>H (17·CF<sub>3</sub>SO<sub>3</sub>H)

Cyclohexyldiphenylphosphine<sup>50</sup> (0.21 g, 1.0 mmol) and MeOCH<sub>2</sub>Cl (0.20 g, 2.5 mmol) were heated together at 80 °C for 3 days. The volatile compounds were removed at reduced pressure to give 0.28 g of 17·HCl as a glassy mass. The salt was dissolved in 4 ml of water and a solution of CF<sub>3</sub>SO<sub>3</sub>Na (0.15 g, 0.88 mmol) in 1.0 ml of water was added at room temperature. The mixture was stirred for an hour and filtered. The crystals (17·CF<sub>3</sub>SO<sub>3</sub>H) on the filter were washed with cold ethanol, dried and recrystallized from ethyl acetate. Yield 0.19 g (0.41 mmol, 46%), mp 122.8-123.8 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 – 7.58 (m, 10H), 5.04 (s, 2H), 3.49 (s, 3H), 2.24 – 0.94 (m, 10H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  134.9 (d, *J*=3.0 Hz), 133.7 (d, *J*=8.7 Hz), 130.2 (d, *J*=12.0 Hz), 114.9 (d, *J*<sub>P-C</sub>=80.3 Hz), 63.6 (d, *J*<sub>P-C</sub>=66.1 Hz), 62.3 (d, *J*=12.8 Hz), 30.7 (d, *J*<sub>P-C</sub>=43.6 Hz), 25.8 (d), 25.5 (d, *J*=13.7 Hz), 25.1 (d, *J*=1.4 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  24.8. HRMS (ESI+): calc for C<sub>20</sub>H<sub>26</sub>OP<sup>+</sup>, 313.17158; found, 313.17162.

# (CH<sub>3</sub>)<sub>2</sub>C=P(dma)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (18·CF<sub>3</sub>SO<sub>3</sub>H)

*i*-Propyltris(dimethylamino)phosphonium iodide  $18 \cdot HI^{34}$  (0.40 g, 1.2 mmol) was dissolved in 5.0 ml of water at 60 °C and CF<sub>3</sub>SO<sub>3</sub>Na solution (0.22 g, 1.2 mmol) in warm water was added

.The white precipitate was filtered off, washed with water and dried in vacuum to give 0.36 g (1.0 mmol, 83%) of **18**·CF<sub>3</sub>SO<sub>3</sub>H as white crystals, mp 364-365 °C. <sup>1</sup>H NMR (CD<sub>3</sub>CN, 400 MHz)  $\delta$  3.00 – 2.87 (m, 1H), 2.74 (d, *J*=9.6 Hz, 18H), 1.26 (dd,

*J*<sub>P-H</sub>=18.2 Hz, *J*=7.1 Hz, 6H). <sup>31</sup>P NMR (CD<sub>3</sub>CN, 162 MHz) δ 65.6.

## $H_2C=P(C_6H_{11})_2Ph \cdot CF_3SO_3H (19 \cdot CF_3SO_3H)$

Methyl-bis(cyclohexyl)phenylphosphonium iodide  $19 \cdot HI^{50,65}$  (83 mg, 0.2 mmol) was converted into triflate salt by reaction with CF<sub>3</sub>SO<sub>3</sub>Na (50 mg, 0.29 mmol) in 4.5 ml of hot water. The solvent was decanted from formed oily mass and the residue was dissolved in 0.5 ml of warm ethanol. Water was added drop by drop to precipitate the triflate crystals. Yield 40 mg (0.09 mmol, 45%) of  $19 \cdot CF_3SO_3H$  as white crystals, mp 127-128 °C.

<sup>1</sup>H NMR (200 MHz, CDCl3)  $\delta$  7.94 – 7.55 (m, 5H), 3.07 – 2.58 (m, 2H), 2.18 (d, *J*=12.4, 3H), 2.08 – 0.95 (m, 20H). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  33.3.

## R-(+)-Ph(CH<sub>3</sub>)CH-N=P<sub>1</sub>(imme)<sub>3</sub>·HBF<sub>4</sub> (20·HBF<sub>4</sub>)

A three-necked flask, equipped with a mechanical stirrer and a gas outlet (HCl gas evolves) was charged with 150 ml of CCl<sub>4</sub> and 20.8 g (0.10 mol) of phosphorus pentachloride. R-(+)-1-Phenyl-ethylamine 12.1 g (0.10 ml) was added at room temperature and the mixture was heated at 70 °C for 5 h and left for the night under a weak flow of argon. Next day the solvent was removed at reduced pressure and the residue was distilled in vacuum to give 15.6 g (61 mmol, 61%) of R-(+)-Ph(CH<sub>3</sub>)CH-N=PCl<sub>3</sub> as a colorless liquid, bp 72-74 °C/0.30 Torr.

Then, a 50 ml two-neck flask equipped with mechanical stirrer and a gas outlet with bubble counter was charged with 12.3 g (0.108 mmol) of **immeH** (*vide supra*) and 13 ml of

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chlorobenzene. The reaction was carried out under argon atmosphere. The solution was cooled to -50 °C and a solution of 4.1 g (16.0 mmol) of R-(+)-Ph(CH<sub>3</sub>)CH-N=PCl<sub>3</sub> in 4 ml of chlorobenzene was slowly added. The mixture was allowed to warm to room temperature and was set aside for a night. Precipitated **immeH**·HCl was filtered off and the solvent and the excess of **immeH** were removed in vacuum. The residue, brownish **20**·HCl salt was dissolved in 40 ml of water, the solution of 1.5 g (14.0 mmol) of NaBF<sub>4</sub> in 5 ml of water was added and the settled oil was triturated with glass stick to give 5.4 g of raw HBF<sub>4</sub> salt as a solid. It was recrystallized from 1:7 mixture of CHCl<sub>3</sub>/AcOEt, yielding 4.3 g (7.3 mmol, 49.3%) of colorless crystals, mp 107.0-107.9 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.10-7.40 (m, 5H), 4.38 (q, *J*=6.9, 1H), 3.34 (s, 12H), 2.86 (s, 18H), 1.45 (d, *J*=6.9, 3H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 156.5 (d, *J*=7.8), 146.5 (d, *J*=3.7), 128.1, 126.7, 126.2, 51.9, 47.1, 33, 25.7 (d, *J*=7.0 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) δ -11.7 Anal. Calc for C<sub>23</sub>H<sub>40</sub>BF<sub>4</sub>N<sub>10</sub>P: C, 48.09; H, 7.02; N, 24.38. Found: C, 48.13; H, 7.09; N, 24.40.

## H-N=P<sub>1</sub>(imme)<sub>3</sub>·HBPh<sub>4</sub> (21·HBPh<sub>4</sub>)

The solution of 11 g (97 mmol) of **immeH** in 10 ml of  $CH_2Cl_2$  was added dropwise to the suspension of 3.2 g (16 mmol) phosphorus pentachloride in 50 ml of  $CH_2Cl_2$  at -40 °C under mechanical stirring. The resulting slurry was kept at -40 °C for 1 h, allowed to warm up to ambient temperature, and stirred for another 3 h. The mixture was then cooled again to -30 °C and an excess of  $NH_3$  (8 g, 16 mmol) was passed into the mixture under vigorous stirring. The mixture was allowed to warm up to room temperature and then set aside for a night. The solid (**immeH**·HCl and ammonium chloride) was filtered off and washed with  $CH_2Cl_2$ . The filtrate was evaporated to dryness to give 5.2 g of  $H-N=P_1(imme)_3$ ·HCl as a thick colorless paste. The paste was dissolved in 10 ml water and a solution of 1.66 g (15 mmol) of NaBF<sub>4</sub> was added.

Tetrafluoroborate salt of the product was extracted with CH<sub>2</sub>Cl<sub>2</sub>, organic layer was dried with MgSO<sub>4</sub>. Later on, MgSO<sub>4</sub> was filtered and the solvent was removed in vacuum to give 3.6 g (45%) of colorless solid, mp 132-133 °C. For analysis **21**·HBPh<sub>4</sub> salt was prepared by reaction with NaBPh<sub>4</sub> in methanolic solution, obtained colorless needles, mp 139-141 °C. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.46 (m 8H), 7.09 (t, *J*=7.1 Hz, 8H) , 6.93 (t, *J*=7.0 Hz, 4H), 3.23 (s, 12H), 2.84 (s, 18H), 2.60 (br, 2H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  164,3 (q, *J*<sub>P-C</sub>=49,4 Hz), 156.4 (d, *J*=7.3 Hz), 136.3 (d, *J*=1.2 Hz), 125,5 (q, *J*=2.6 Hz), 121.5, 47.1, 33.8. <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  -10.8. Anal. Calc for C<sub>39</sub>H<sub>52</sub>BN<sub>10</sub>P: C, 66.66; H, 7.46; N, 19.93. Found: C, 66.71; H, 7.48; N, 19.85.

## $R-(+)-Ph(CH_3)CH-N=P_4(Ph)_9 \cdot HBF_4$ (22·HBF<sub>4</sub>)

Following the procedure described in literature<sup>58</sup> and starting from 3.14 g (10 mmol) of H-N=P<sub>1</sub>(Ph)<sub>3</sub>·HCl and 20 mmol of BuLi in THF solution (85 ml) the intermediate (Ph<sub>3</sub>P=N-)<sub>3</sub>PCl<sub>2</sub> was synthesized (1.57 g, 1.67 mmol). It was mixed with excess of *R*-(+)phenyletylamine (1.9 g, 15 mmol) and heated at 90 °C for 4 h. The mixture was cooled down and 12 ml of diethyl ether was added. Additional 12 ml of diethyl ether was added to the precipitated sticky mass. Solvent was then removed and the soft precipitate was treated with 10 ml of chloroform and the mixture was filtered. The filtrate was concentrated, dissolved in 8 ml of chloroform and 45 ml of diethyl ether was added. The formed precipitate was filtered off and twice recrystallized from 3:2 mixture of H<sub>2</sub>O/MeOH and once from EtOH to give 0.3 g (0.29 mmol, 17.7%) of desired phosphazene salt **22**·HCl. The chloride was converted into tetrafluoroborate salt by means of sodium tetrafluoroborate in water solution (5 ml) and extracted with CH<sub>2</sub>Cl<sub>2</sub>. CH<sub>2</sub>Cl<sub>2</sub> layer was separated, dried with MgSO<sub>4</sub> and the solvent was removed in vacuum to give 0.26 g (0.24 mmol, 83%) of **22**·HBF<sub>4</sub>, mp 290-299 °C.

The triflate salt was prepared from 60 mg (0.06 mmol) of **22**·HCl and 20 mg (0.12 mmol) of CF<sub>3</sub>SO<sub>3</sub>Na in methanolic solution (1.5 ml) at room temperature. The solvent was evaporated to give 58 mg (0.051 mmol, 85%) of **22**·CF<sub>3</sub>SO<sub>3</sub>H as a white powder, mp 230-240 °C (dec). <sup>1</sup>H NMR (700 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 – 7.52 (m, 9H), 7.33 – 7.21 (m, 36H), 7.15 (t, *J*=7.3 Hz, 1H), 7.08 (t, *J*=7.5 Hz, 2H), 6.75 (d, *J*=7.6 Hz, 2H), 4.30 (dt, *J*<sub>P-H</sub>=12.1 Hz, 7.1 Hz, 1H), 1.00 (d, *J*=6.8 Hz, 3H). <sup>13</sup>C NMR (176 MHz, CDCl<sub>3</sub>)  $\delta$  132.6 (d, *J*=10.8 Hz), 132.4 (d, *J*=2.6 Hz), 130.2 (d, *J*=4.1 Hz), 129.6 (d, *J*=4.1 Hz), 128.6 (d, *J*=12.8 Hz), 128.3, 126.6, 125.8, 51.7 (d, *J*=2.1 Hz), 26.0 (d, *J*=7.3 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  8.5 (d, *J*=7.4 Hz), -1.4. HRMS (ESI+): calc for C<sub>62</sub>H<sub>55</sub>N<sub>4</sub>P<sub>4</sub><sup>+</sup>, 979.33717; found, 979.33791.

# (CH<sub>3</sub>)<sub>2</sub>C=PPh<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (23·CF<sub>3</sub>SO<sub>3</sub>H)

Isopropyl(triphenyl)phosphonium iodide  $(23 \cdot \text{HI})^{66}$  (0.27 g, 0.62 mmol) converted into triflate by reaction with CF<sub>3</sub>SO<sub>3</sub>Na (0.12 g, 6.8 mmol) in 3:1 mixture of H<sub>2</sub>O/EtOH at 60 °C. The formed pale yellowish crystals were filtered off to give 0.26 g (5.7 mmol, 92%) of desired salt (23·CF<sub>3</sub>SO<sub>3</sub>H), mp 141-142 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN) δ 7.96 – 7.81 (m, 6H), 7.80 – 7.66 (m, 9H), 2.91 (dt,  $J_{P-H}$ =13.9 Hz, J=0.8 Hz, 6H), 1.95 (p, J=2.5 Hz, 1H). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ 136.0 (d, J=3.1 Hz), 134.2 (d, J=10.8 Hz), 131.1 (d, J=12.9 Hz), 120.3 (d,  $J_{P-C}$ =88.9 Hz), 118.2, 9.8 (d,  $J_P$ . c=57.7 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 21.7.

# $H_2C=P(4-MeO-C_6H_4)_3 \cdot CF_3SO_3H (28 \cdot CF_3SO_3H)$

The mixture of tris-(4-methoxyphenyl)phosphine (0.15 g, 0.43 mmol) and excess of methyl iodide (1 ml) was stirred for 0.5 h at room temperature. The excess of methyl iodide was removed to give  $28 \cdot \text{HI}^{67}$  (0.20 g, 0.40 mmol). The salt was dissolved in 5 ml of water and CF<sub>3</sub>SO<sub>3</sub>Na (76 mg, 0.44 mmol) dissolved in 0.5 ml of water was added. The colorless oily

substance precipitated, which solidified soon. It was filtered off, washed with water and dried in vacuum, yielding 0.16 g (3.1 mmol, 77.5%) of **28**·CF<sub>3</sub>SO<sub>3</sub>H, mp 140-160 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.70 – 7.45 (m, 6H), 7.31 – 7.12 (m, 6H), 3.90 (s, 9H), 2.68 (d,  $J_{P-H}$ =13.8 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  165.8 (d, J=2.9 Hz), 136.2 (d, J=12.3 Hz), 116.8 (d, J=14.0 Hz), 111.6 (d,  $J_{P-C}$ =96.9 Hz), 56.8, 10.5 (d,  $J_{P-C}$ =60.4 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  21.0 – 19.9 (m).

HRMS (ESI+): calc for  $C_{22}H_{24}O_3P^+$ , 367.14576; found, 367.14603.

# CH<sub>3</sub>-CH=PPh<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (29·CF<sub>3</sub>SO<sub>3</sub>H)

Ethyl-triphenylphosphonium bromide<sup>68</sup> (0.41 g, 1.1 mmol) was dissolved in 2.0 ml of warm water and CF<sub>3</sub>SO<sub>3</sub>Na solution (0.20 g, 1.16 mmol) in 0.5 ml of water was added. From the cold solution the white powder was precipitated, filtered off, washed with water and dried in vacuum to give 0.42 g (0.97 mmol, 88%) of **29**·CF<sub>3</sub>SO<sub>3</sub>H, mp 125-126.7 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 8.01 – 7.51 (m, 15H), 3.40 (dq, *J*=12.7 Hz, *J*=7.5 Hz, 2H), 1.37 (dt, *J*<sub>P-H</sub>=19.9 Hz, *J*=7.4 Hz, 3H). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) δ 25.9.

# CH<sub>3</sub>-CH=P(1-Napht)Ph<sub>2</sub>·CF<sub>3</sub>SO<sub>3</sub>H (31·CF<sub>3</sub>SO<sub>3</sub>H)

1-Naphtyldiphenylphosphine<sup>51</sup> (0.50 g, 1.60 mmol) was dissolved in 2.0 ml of toluene. An excess of ethyl bromide (0.5 g) was added and the mixture was stirred at 70 °C for one day. The mixture was cooled down, the formed precipitate was filtered off, washed with toluene and dried in vacuum to give 0.37 g (0.88 mmol, 55%) of **31**·HBr as a white powder, mp 244-245 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.45 – 7.37 (m, 7H), 3.95 (dq, *J*=11.9 Hz, *J*=7.4 Hz, 2H), 1.37 (dtd, *J*<sub>P-H</sub>=20.2 Hz, *J*=7.5 Hz, *J*=1.2 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  136.9 (d, *J*=10.1 Hz), 136.2 , 134.2 (d, *J*=2.9 Hz), 133.3 (d, *J*=9.6 Hz), 132.3 (d, *J*=9.9 Hz), 131.5 (d, *J*=8.4

Hz), 129.8 (d, J=12.5 Hz), 129.6, 128.2, 126.9, 125.0 (d, J=14.1 Hz), 124.0 (d, J=6.5 Hz), 118.7, 117.0, 17.4 (d,  $J_{P-C}=53.0$  Hz), 6.7 (d, J=5.3 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  26.6. To prepare the triflate salt, **31**·HBr (0.23 g, 0.55 mmol) was dissolved in 2.0 ml of warm ethanol and CF<sub>3</sub>SO<sub>3</sub>Na (0.11 g, 0.64 mmol) was added. Warm water was added to the warm ethanolic solution up to turbidity (5.8 ml) and the mixture was set aside for a night. The colorless crystals were filtered off and dried to give 0.19 g (0.38 mmol, 70%) of **31**·CF<sub>3</sub>SO<sub>3</sub>H, mp 138.5-139.2 °C.

HRMS (ESI+): calc for C<sub>24</sub>H<sub>22</sub>P<sup>+</sup>, 341.14536; found, 341.14555.

### Ph-CH=P(pyrr)<sub>2</sub>tmg·CF<sub>3</sub>SO<sub>3</sub>H (33·CF<sub>3</sub>SO<sub>3</sub>H)

TMG (3.0 g, 26 mmol) was dissolved in 30 ml of hexane and a solution of  $P(pyrr)_2Cl^{52}$  (2.37 g, 11.5 mmol) in 30 ml of hexane was added at -20 °C. The mixture was allowed to warm to room temperature and stirred at 50 °C for 3 h. The TMG·HCl was filtered off and filtrate was concentrated. The residue as colorless oil was distilled at 124-126 °C/0.07-0.1 Torr to give 2.4 g of distillate. According to the <sup>31</sup>P NMR analysis the residue contains 71% of P(pyrr)<sub>2</sub>tmg ( $\delta$  104, 87.6, 86.4 in relation of 1:5:1).

A solution of benzyl bromide (1.0 g, 5.8 mmol) in 4 ml DMF was added to the solution of 2.4 g of phosphines (~ 6 mmol of bis(pyrrolidine)tetramethylguanidinephosphine) in 8.0 ml of DMF at -30 °C and the mixture was stirred at 50 °C for 3 h. The solvent was evaporated while the temperature was raised to 100-150 °C. The solid residue (2.0 g) was washed with diethyl ether and **33**·HBr was obtained. It was dissolved in water and sodium tetrafluoroborate solution (0.6 g, 5.6 mmol) in 1.0 ml of water was added, the precipitate was filtered off and recrystallized from 3:1 mixture of EtOAc/MeOH. Yield 0.9 g (1.9 mmol, 33%) of **33**·HBF<sub>4</sub> as a colorless crystals, mp 142-143 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.53 – 7.26 (m, 3H), 7.25 – 6.99 (m, 2H), 3.51 (d, *J*=14.9 Hz, 2H), 3.38 – 3.15 (m, 4H), 3.13 – 2.93 (m, 4H), 2.77 (s, 12H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 132.1 (d, *J*=8.2 Hz), 131.0 (d, *J*=5.6 Hz), 129.9 (d, *J*=3.1 Hz), 128.4 (d, *J*=3.6 Hz), 47.9 (d, *J*=4.5 Hz), 40.8, 33.5 (d, *J*<sub>P-C</sub>=91.3 Hz), 27.1 (d, *J*=8.4 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 16.9.

Triflate salt  $33 \cdot CF_3SO_3H$  was prepared by mixing 0.1 g (0.22 mmol) of  $33 \cdot HBF_4$  and 40 mg (0.23 mmol) of  $CF_3SO_3Na$  in 2.0 ml of 1:1 mixture of MeCN/EtOH at room temperature. The mixture was stirred 0.5 h and then cooled down. Water (0.45 ml) was added to crystallize out  $33 \cdot CF_3SO_3H$  as white crystals, yield 62 mg (1.2 mmol, 53%), mp 145-146 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.51 – 7.23 (m, 5H), 3.50 (d, *J*=14.9 Hz, 2H), 3.35 – 3.15 (m, 4H), 3.14 – 2.94 (m, 4H), 2.77 (s, 12H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 132.1 (d, *J*=8.2 Hz), 131.0 (d, *J*=5.7 Hz), 129.9 (d, *J*=3.1 Hz), 128.4 (d, *J*=3.6 Hz), 47.9 (d, *J*=4.4 Hz), 40.8, 33.5 (d, *J*<sub>P-C</sub>=90.9 Hz), 27.1 (d, *J*=8.4 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 16.9. HRMS (ESI+): calc for C<sub>20</sub>H<sub>35</sub>N<sub>5</sub>P<sup>+</sup>, 376.26246; found, 376.26240.

# H<sub>2</sub>C=P(3,5-(MeO)<sub>2</sub>-C<sub>6</sub>H<sub>3</sub>)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (34·CF<sub>3</sub>SO<sub>3</sub>H)

Tris-(3,5-dimethoxyphenyl)phosphine (0.40 g, 0.94 mmol) and an excess of methyl iodide (1 ml) were mixed and stirred for 15 min. The precipitate was filtered off and washed with diethyl ether. Pale yellow crystals were dried to give 0.51 g (0.87 mmol, 93%) of **34**·HI, mp 224.5-225.0 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 6.93 – 6.86 (m, 3H), 6.82 – 6.75 (m, 3H), 6.74 – 6.68 (m, 3H), 3.82 (s, 18H), 2.86 (d,  $J_{P-H}$ =14.1 Hz, 3H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 163.05 (d, J=19.5 Hz), 122.97, 121.19, 112.16 (d, J=12.2 Hz), 107.22 (d, J=2.5 Hz), 56.98. <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 24.9.

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HRMS (ESI+): calc for  $C_{25}H_{30}O_6P^+$ , 457.17745; found 457.17730.

The triflate salt was prepared by mixing 34·HI (0.43 g, 0.74 mmol) and CF<sub>3</sub>SO<sub>3</sub>Na (0.15 g, 0.87 mmol) in 15 ml of 1:1 solution of H<sub>2</sub>O/EtOH at 65 °C. From the cold solution the formed precipitate was filtered off, washed with water and dried to give 0.40 g (0.66 mmol, 62%) of 34·CF<sub>3</sub>SO<sub>3</sub>H, mp 157.0-159.5 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 6.93 – 6.86 (m, 3H), 6.76 (d, *J*=2.2 Hz, 3H), 6.69 (d, *J*=2.2 Hz, 3H), 3.81 (s, 18H), 2.77 (d, *J*<sub>P-H</sub>=14.0 Hz, 3H). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 26.2 (dq,  $J_{P-C}=29.1$  Hz,  $J_{P-C}=14.4$  Hz).

## $H_2C=P(3-MeO-C_6H_4)_3 \cdot CF_3SO_3H$ (35·CF<sub>3</sub>SO<sub>3</sub>H)

Tris-(3-methoxyphenyl)phosphine (0.30 g, 0.85 mmol) and an excess of methyl iodide (0.8 ml) were mixed and stirred at room temperature. The excess of methyl iodide was then removed, to the remaining solid additional 3 ml of diethyl ether was added and the mixture was triturated with glass stick. The yellowish powder was filtered off and dried after washing with diethyl ether and benzene/diethyl ether mixture resulting **35**·HI (0.24 g, 0.49 mmol, 57%) was obtained, mp 161-163 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.59 (m, 3H), 7.38 – 7.10 (m, 9H), 3.90 (s, 9H), 3.23 (d,  $J_{P-H}=13.4$  Hz, 3H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>)  $\delta$  160.7 (d, J=16.3 Hz), 131.8 (d, J=15.3 Hz), 125.3 (d, J=10.4 Hz), 121.8 – 120.3 (m), 119.2, 118.3 (d, J=12.3 Hz), 56.5, 11.8 (d,  $J_{P-C}=56.8$  Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>)  $\delta$  36.8.

HRMS (ESI+): calc for  $C_{22}H_{24}O_3P^+$ , 367.14576; found, 367.14583.

The triflate salt was prepared by dissolving **35**·HI (0.12 g, 0.24 mmol) in 5 ml of water at 70 °C and adding CF<sub>3</sub>SO<sub>3</sub>Na solution (60 mg, 0.34 mmol) in 0.2 ml of water giving glassy drops

of precipitated  $35 \cdot CF_3SO_3H$  onto the flask walls. Water was decanted off, the substance was washed with water and dried in high vacuum to get 70 mg (0.14 mmol, 56%) of  $35 \cdot CF_3SO_3H$  as a colorless sticky mass.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 7.75 – 7.51 (m, 3H), 7.51 – 7.31 (m, 3H), 7.31 – 7.04 (m, 6H), 3.83 (s, 9H), 2.84 (d,  $J_{P-H}$ =13.9 Hz, 3H). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 22.6.

## Ph-CH=P(dma)<sub>2</sub>tmg·CF<sub>3</sub>SO<sub>3</sub>H (36·CF<sub>3</sub>SO<sub>3</sub>H)

Following the procedure described in ref.<sup>69</sup> for synthesis of bis(diethylamino)tetramethylguanidinophosphine, to the TMG solution (4.6 g, 40 mmol) in 45 ml of hexane was added a solution of P(dma)<sub>2</sub>Cl (3.09 g, 20 mmol) in 25 ml of hexane at -20 °C and the mixture was heated at 50 °C for 3 h. The TMG·HCl salt was filtered off, filtrate was concentrated and °C/1.5 distilled Torr 2.4 (10.3)mmol. 51%) of at to give g bis(dimethylamino)tetramethylguanidinophosphine.

A solution of benzylbromide (0.96 g, 5.5 mmol) in 4.0 ml of DMF was added to the solution of  $P(dma)_2$ tmg (1.3 g, 5.5 mmol) in 4 ml of DMF at -20 °C and the mixture was stirred and heated at 50 °C for 1 h. The solvent was evaporated, the residue - white mass - was washed with diethyl ether and recrystallized from 1:1 mixture of CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O to give 0.6 g (1.5 mmol, 27%) of **36**·HBr.

The triflate salt was prepared by mixing 0.5 g (1.23 mmol) of **36**·HBr and 0.22 g (1.24 mmol) of CF<sub>3</sub>SO<sub>3</sub>Na in 2.5 ml of water. White crystals that formed were filtered off, washed with water and dried in vacuum to give 0.52 g (1.1 mmol, 89%) **36**·CF<sub>3</sub>SO<sub>3</sub>H, mp 147.2-148.2 °C. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.53 – 7.24 (m, 3H), 7.20 – 7.00 (m, 2H), 3.53 (d, *J*<sub>P-H</sub>=15.3 Hz, 2H), 2.77 (s, 12H), 2.67 (d, *J*=9.4 Hz, 12H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  162.8, 132.0

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(d, J=8.0 Hz), 131.1 (d, J=5.7 Hz), 129.9 (d, J=3.1 Hz), 128.5 (d, J=3.6 Hz), 40.9, 37.1 (d, J=4.2 Hz), 32.8 (d,  $J_{P-C}=95.5$  Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  26.8. HRMS (ESI+): calc for C<sub>16</sub>H<sub>31</sub>N<sub>5</sub>P<sup>+</sup>, 324.23116; found, 324.23118.

# (CH<sub>3</sub>)<sub>3</sub>C-CH=PPh<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (38·CF<sub>3</sub>SO<sub>3</sub>H)

Neopentyl(triphenyl)phosphonium iodide  $(38 \cdot HI)^{70}$  (0.42 g, 0.91 mmol) was dissolved in 1.5 ml of hot ethanol and a solution of CF<sub>3</sub>SO<sub>3</sub>Na (0.17 g, 0.99 mmol) in 0.5 ml of water was added. About 5 ml of warm water had to be added to precipitate crystals of  $38 \cdot CF_3SO_3H$  from cooled solution. Yield 0.30 g (6.2 mmol, 68%), mp 190.0-191.4 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 8.12 – 7.56 (m, 15H), 3.55 (d,  $J_{P-H}$ =13.0, 2H), 0.97 (s, 9H). <sup>31</sup>P NMR (81MHz, CDCl<sub>3</sub>) δ 19.0.

HRMS (ESI+): calc for  $C_{27}H_{34}O_6P^+$ , 485.20875; found, 485.20883.

#### $Ph-CH=P(-NMe-CH_2-CH_2-)_3N\cdot CF_3SO_3H (40\cdot CF_3SO_3H)$

The starting phosphonium bromide **40**·HBr was synthesized as described in ref. <sup>71</sup> The triflate salt was prepared by mixing 0.31 g (0.8 mmol) of **40**·HBr and 0.14 g (0.8 mmol) of CF<sub>3</sub>SO<sub>3</sub>Na in aqueous solution. The precipitate was filtered, washed with water and dried in vacuum over P<sub>2</sub>O<sub>5</sub> yielding 0.22 g (0.48 mmol, 60%) of desired product **40**·CF<sub>3</sub>SO<sub>3</sub>H, mp 137.6-138.6 °C.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.33 (s, 5H), 3.59 (d,  $J_{P-H}$ =17.2 Hz, 2H), 2.99 – 2.55 (m, 21H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 131.0 (d, J=8.3 Hz), 130.1 (d, J=6.0 Hz), 129.3 (d, J=2.8 Hz), 127.9 (d, J=3.4 Hz), 121.1 (d,  $J_{F-C}$ =321.1 Hz, CF<sub>3</sub>SO<sub>3</sub>H), 51.1, 49.1 (d, J=2.6 Hz), 35.9 (d, J=2.5 Hz), 32.9 (d,  $J_{P-C}$ =121.8 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) δ 50.0. HRMS (ESI+): calc for C<sub>16</sub>H<sub>28</sub>N<sub>4</sub>P<sup>+</sup>, 307.20461; found, 307.20465.

The methyl-tris-mesitylphosphonium iodide **41**·HI<sup>44,72,73</sup> (0.24 g,0.45 mmol) was dissolved in 2.6 ml of ethanol and CF<sub>3</sub>SO<sub>3</sub>Na solution in 0.5 ml of water was added . The mixture was stirred for 15 min and more water was added (about 6 ml) to precipitate **41**·CF<sub>3</sub>SO<sub>3</sub>H. It was dried in vacuum to give 0.23 g (0.42 mmol, 92%) of desired product, mp 259.3-260.6 °C. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.37 – 6.97 (m, 6H), 2.79 (d, *J*=12.0 Hz, 3H), 2.31 (d, *J*<sub>P</sub>. H=18.0 Hz, 18H), 1.91 (s, 9H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  146.1 (d, *J*=3.1 Hz), 145.0 (d, *J*=10.6 Hz), 144.7 (d, *J*=10.6 Hz), 134.2 – 133.4 (m), 121.2 (d, *J*<sub>P-C</sub>=79.8 Hz), 24.1 (t, *J*=4.7 Hz), 21.2 (d, *J*=1.5 Hz).<sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  7.7. HRMS (ESI+): calc for C<sub>28</sub>H<sub>36</sub>P<sup>+</sup>, 403.25491; found, 403.25431.

# 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(2,4,6-(MeO)<sub>3</sub>-C<sub>6</sub>H<sub>2</sub>)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (46·CF<sub>3</sub>SO<sub>3</sub>H)

Tris(2,4,6-trimethoxyphenyl)phosphine (0.53 g, 1.0 mmol) was dissolved in 5.5 ml of benzene and a solution of 4-nitrobenzylbromide (0.22 g, 1.0 mmol) in 2 ml of benzene was added at room temperature. The mixture was stored for a night. The solvent was then decanted off and precipitate dried in vacuum. This solid mass (0.7 g) was dissolved in 14 ml of 1:1 mixture of MeOH/H<sub>2</sub>O and 0.13 g (0.4 mmol) of sodium tetrafluoroborate dissolved in 1 ml of water was added. The solvent was removed and the residue was recrystallized from 14 ml of MeOH. Colorless crystals were filtered off and dried to give 0.48 g (0.63 mmol, overall yield 63%) of **46**·HBF<sub>4</sub>, mp 254.7-255.8 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  8.01 – 7.84 (m, 2H), 7.31 (m, 2H), 6.15 (d, *J*=4.8 Hz, 6H), 4.83 (d, *J*<sub>P-H</sub>=17.7 Hz, 2H), 3.82 (d, *J*=1.7 Hz, 9H), 3.61 (d, *J*=1.8 Hz, 18H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  167.2 (d, *J*=1.7 Hz), 164.8 (d, *J*=1.4 Hz), 147.8 (d, *J*=3.4 Hz), 143.3 (d, *J*=6.7 Hz), 131.8 (d, *J*=8.6 Hz), 123.8 (d, *J*=1.9 Hz), 94.4 (d, *J*=1.3 Hz), 92.3 (d, *J*=7.4 Hz), 56.8, 56.7, 36.8 (d, *J*<sub>P-C</sub>=58.4 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  6.1.

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HRMS (ESI+): calc for  $C_{34}H_{39}O_{11}NP^+$ , 668.22552; found, 668.22590.

The triflate salt was prepared by mixing a solution of  $46 \cdot \text{HBF}_4$  (60 mg, 0.08 mmol) in warm 1:1 mixture of MeCN/MeOH (4.5 ml) and a solution of CF<sub>3</sub>SO<sub>3</sub>Na (14 mg 0.08 mmol) in 0.5 ml of water. The additional quantity of water was added to form turbidity. An hour later fine colorless needles were formed, these were filtered off and dried to give 58 mg (0.07 mmol, 87%) of  $46 \cdot \text{CF}_3\text{SO}_3\text{H}$ , mp 139-140 °C.

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 8.02 – 7.78 (m, 2H), 7.42 – 7.23 (m, 2H), 6.15 (d, *J*=4.8 Hz, 6H), 4.83 (d, *J*<sub>P-H</sub>=17.8 Hz, 2H), 3.81 (d, *J*=2.1 Hz, 9H), 3.60 (s, 18H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 167.1 (d, *J*=1.7 Hz), 164.8 (d, *J*=1.4 Hz), 147.8 (d, *J*=3.3 Hz), 143.3 (d, *J*=6.7 Hz), 131.8 (d, *J*=8.6 Hz), 123.8 (d, *J*=2.0 Hz), 94.4 (d, *J*=1.3 Hz), 92.3 (d, *J*=7.1 Hz), 56.8, 56.7, 36.8 (d, *J*<sub>P-C</sub>=58.6 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 6.1.

## Synthesis of some benzyl substituted amino phosphonium salts

The following general procedure<sup>74,75</sup> was used for the synthesis benzyl substituted amino phosphonium salts of **44**, **47**, **49**, **52**, **53**. A solution of benzylbromide in DMF (0.1 mol, 40 ml) was added to a phosphine compound solution in DMF (0.1 mol, 40 ml) at 0 °C. The mixture was stirred at 50 °C for 0.5 h, then it was cooled down and the formed crystals were filtered off, washed with DMF and dried in vacuum at 60 °C.

## Ph-CH=P(pyrr)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (44·CF<sub>3</sub>SO<sub>3</sub>H)

From benzylbromide solution (1.7 g, 10 mmol) in 1.5 ml of DMF and tris(pyrrolidine)phosphine<sup>52</sup> solution (2.4 g, 10 mmol) in 5 ml of DMF 2.3 g (5.6 mmol, 56%)

of raw **44**·HBr was obtained. It was recrystallized from 2:1 mixture of CHCl<sub>3</sub>/THF, mp 220-225 °C (dec).

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.71 – 7.12 (m, 5H), 4.17 (d,  $J_{P-H}$ =15.8 Hz, 2H), 3.50 – 3.08 (m, 12H), 2.20 – 1.61 (m, 12H). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>) δ 130.1 (d, J=6.1 Hz), 128.9 (d, J=8.7 Hz), 128.7 (d, J=3.2 Hz), 127.7 (d, J=3.8 Hz), 47.8 (d, J=3.2 Hz), 31.4 (d,  $J_{P-C}$ =100.1 Hz), 26.0 (d, J=7.3 Hz). <sup>31</sup>P NMR (81 MHz, CDCl<sub>3</sub>) δ 41.5. HRMS (ESI+): calc for C<sub>19</sub>H<sub>31</sub>N<sub>3</sub>P<sup>+</sup>, 332.22501; found, 332.22510.

The salt  $44 \cdot CF_3SO_3H$  was prepared by mixing 0.79 g (1.9 mmol) of the  $44 \cdot HBr$  and 0.33 g (1.9 mmol) of  $CF_3SO_3Na$  in 3 ml of water. The salt  $44 \cdot CF_3SO_3H$  was collected as colorless crystals (0.82 g, 1.7 mmol, 89%), mp 153.3-154.2 °C.

## Ph-CH=P(dma)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (47·CF<sub>3</sub>SO<sub>3</sub>H)

From tris(dimethylamino)phosphine<sup>74,75</sup> solution (4.1 g, 25 mmol) in 10.0 ml of DMF and a solution of benzyl bromide (5.4 g, 25 mmol) in 10 ml of DMF 4.0 g (11.9 mmol, 48%) of **47**·HBr was obtained, mp 232.4-233.8 °C (lit mp 229 °C). The triflate salt was prepared by mixing 0.80 g (2.4 mmol) of **47**·HBr and 0.42 g (2.4 mmol) of CF<sub>3</sub>SO<sub>3</sub>Na in 2.0 ml of water to get 0.56 g (1.39 mmol, 58%) of **47**·CF<sub>3</sub>SO<sub>3</sub>H, mp 189-190 °C. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  7.47 – 7.28 (m, 5H), 3.81 (d, *J*<sub>P-H</sub>=16.2 Hz, 2H), 2.65 (d,

*J*=9.8 Hz, 18H). <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN) δ 56.1.

#### $3-Cl-C_6H_4-CH=P(dma)_3\cdot CF_3SO_3H(49\cdot CF_3SO_3H)$

From 3-chlorobenzylbromide (5.14 g, 25 mmol) in 10.0 ml of DMF and tris(dimethylamino)phosphine (4.1 g, 25 mmol) in 10.0 ml of DMF **49**·HBr was obtained as white crystals, yield 7.2 g (19.5 mmol, 78%), mp 212.4-213.5 °C.

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<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  7.54 – 7.18 (m, 4H), 3.87 (d, *J*<sub>P-H</sub>=16.5 Hz, 2H), 2.67 (d, *J*=9.9 Hz, 18H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  135.2 (d, *J*=3.5 Hz), 132.8 (d, *J*=8.4 Hz), 131.8 (d, *J*=3.1 Hz), 131.1 (d, *J*=6.1 Hz), 129.9 (d, *J*=5.9 Hz), 129.1 (d, *J*=3.7 Hz), 37.8 (d, *J*=3.1 Hz), 30.2 (d, *J*<sub>P-C</sub>=107.1 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  = 56.5.

The triflate salt  $49 \cdot CF_3SO_3H$  was prepared from 0.5 g (1.36 mmol) of the bromide and 0.24 g (1.4 mmol) of  $CF_3SO_3Na$  in 2.0 ml of water to give 0.52 g (1.2 mmol, 85%) of  $49 \cdot CF_3SO_3H$  as white crystals, mp 101.7-102.5 °C.

<sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN)  $\delta$  7.39 (d, *J*=1.1 Hz, 4H), 3.82 (d, *J*<sub>P-H</sub>=16.7 Hz, 2H), 2.66 (d, *J*=9.9 Hz, 18H). <sup>31</sup>P NMR (162 MHz, CD<sub>3</sub>CN)  $\delta$  55.6. HRMS (ESI+): calc for C<sub>13</sub>H<sub>24</sub>N<sub>3</sub>ClP<sup>+</sup>, 288.13909; found, 288.13899.

# 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(pyrr)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (52·CF<sub>3</sub>SO<sub>3</sub>H)

From 4-nitrobenzylbromide solution (2.2 g, 10 mmol) in 5 ml of DMF and tris(pyrrolidino)phosphine<sup>52</sup> solution (2.4 g, 10 mmol) in 5 ml of DMF 2.0 g (4.3 mmol, 43%) yellowish crystals of **52**·HBr was obtained, mp 230 °C (dec).

<sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN) δ 8.31 – 8.11 (m, 2H), 7.86 – 7.66 (m, 2H), 4.25 (d,  $J_{P-H}$ =17.1, 2H), 3.34 – 3.07 (m, 12H), 2.07 – 1.77 (m, 12H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN) δ 148.6, 138.9 (d, J=8.7 Hz), 132.6 (d, J=5.9 Hz), 124.8 (d, J=3.1 Hz), 48.7 (d, J=3.4 Hz), 32.3 (d, J=101.2 Hz), 26.9 (d, J=7.4 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN) δ 40.1. HRMS (ESI+): calc for C<sub>19</sub>H<sub>30</sub>O<sub>2</sub>N<sub>4</sub>P<sup>+</sup>, 377.21009; found, 377.21005.

The salt **52**·CF<sub>3</sub>SO<sub>3</sub>H was prepared by mixing 0.6 g (1.4 mmol) of **52**·HBr and 0.25 g (1.45 mmol) of CF<sub>3</sub>SO<sub>3</sub>Na in 4.0 ml of hot water. 0.63 g (1.12 mmol) of **52**·CF<sub>3</sub>SO<sub>3</sub>H as colorless crystals was obtained, mp 210-212 °C (dec).

## 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-CH=P(dma)<sub>3</sub>·CF<sub>3</sub>SO<sub>3</sub>H (53·CF<sub>3</sub>SO<sub>3</sub>H)

From 4-nitrobenzylbromide (5.40 g, 25 mmol) and tris(dimethylamino)phosphine (4.1 g, 25 mmol) DMF solution of **53**·HBr was obtained. To precipitate **53**·HBr 30 ml of diethyl ether was added to the DMF solution. The obtained crystals were filtered off and washed with diethyl ether and acetone. Yield 2.9 g (7.6 mmol, 38%) of yellowish crystals, mp 219-222 °C. <sup>1</sup>H NMR (200 MHz, CD<sub>3</sub>CN)  $\delta$  8.38 – 8.11 (m, 2H), 7.70 (dt, *J*<sub>P-H</sub>=8.9 Hz, *J*=2.5 Hz, 2H), 4.32 (d, *J*<sub>P-H</sub>=17.3 Hz, 2H), 2.70 (d, *J*=9.9 Hz, 18H). <sup>13</sup>C NMR (50 MHz, CD<sub>3</sub>CN)  $\delta$  138.8 (d, *J*=8.4 Hz), 132.8 (d, *J*=6.0 Hz), 124.9 (d, *J*=3.1 Hz), 38.0 (d, *J*=3.3 Hz), 30.9 (d, *J*<sub>P-C</sub>=105.8 Hz). <sup>31</sup>P NMR (81 MHz, CD<sub>3</sub>CN)  $\delta$  56.2.

The triflate salt was prepared by mixing 0.7 g (1.85 mmol) of **53**·HBr and 0.32 g (1.86 mmol) of CF<sub>3</sub>SO<sub>3</sub>Na in 1.5 ml of water. The oil settled down, to solidify the oil it was triturated with glass stick. Yield 0.5 g (1.1 mmol, 60%) of **53**·CF<sub>3</sub>SO<sub>3</sub>H as a white crystals, 114.4-115.0 °C. HRMS (ESI+): calc for  $C_{13}H_{24}O_2N_4P^+$ , 299.16314; found, 299.16343.

Methods of  $pK_{ip}$  and  $pK_{\alpha}$  determination in THF and  $pK_a$  determination in MeCN. The UV-Vis spectrophotometric titration method used in this work was mainly the same as described earlier:<sup>11,12,20</sup> simultaneous spectrophotometric titration of two free bases of comparable basicity was carried out in THF or MeCN solution. Solutions were prepared and titration experiments were carried out in a glovebox under argon (5.0) atmosphere.

UV-Vis spectra were recorded using Perkin Elmer spectrophotometers Lambda 12, Lambda 40 or Lambda 45 with external cell compartment in MBraun gloveboxes with argon atmosphere. The cell compartment was connected to the UV-Vis spectrophotometer with two quartz fiber optic cables. Because of the higher reactivity of phosphonium ylides as compared to phosphazenes, the experimental conditions in this work (chiefly purity of the solvent, also the oxygen level in the glove box) had to be more rigorously controlled than in analogous

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measurements in our previous works.<sup>12</sup> The residual concentrations of water vapor and oxygen in the glovebox were constantly monitored and kept below 0.1 ppm. Ylides react fiercely with traces of water and dissolved oxygen in the solvent. Since in all measurements one of the bases competing for a proton was an ylide it is safe to assume that during measurements the solutions were essentially free of water and oxygen. Obviously, as a result, part of ylide is lost from solution and the respective phosphine oxide is formed. However, because of the nature of the  $p_{K_{ip}}$  measurement and calculation method this does not result in measurement error. Knowing the exact concentrations of the measured compounds is not essential, and the required relative concentrations are found from spectra. Furthermore, the formed phosphine oxide is a much weaker base than ylide and will not participate in the solution. It also absorbs at much shorter wavelength than ylides and will thus not interfere with spectrophotometry if sufficiently long wavelength is used.

Stock solutions of bases as well as titrants were prepared fresh daily in a glovebox. However, in THF slightly different approach had to be used for phosphonium ylides. In order to minimize the side reactions, free bases were liberated in stock solutions (stored at  $-10^{\circ}$ C) immediately before spectrophotometric titration with KH. The obtained solution was transferred into the spectrophotometric cell and titrated. The concentration of the bases under investigation was always below 0.2 mM and concentration of titrants in the range of 0.5 to 5.0 mM. The reversibility of all equilibria was verified by titration with *t*-Bu-N=P<sub>4</sub>(dma)<sub>9</sub> solution or, in the case of the most basic compounds, by applying the potassium rod as deprotonating agent (the rod was dipped directly into the cell).

The  $\Delta p K_{ip}$  values were calculated from the titration spectra as described in ref.<sup>12</sup>.  $\Delta p K_{\alpha}$  values were obtained from the  $\Delta p K_{ip}$  values by correcting them for ion-pairing using the Fuoss equation<sup>37</sup> as described previously.<sup>12</sup>

**Supporting Information.** NMR spectra, ionic radii used for estimating  $pK_{\alpha}$  values and details of basicity measurements of some of the weaker bases (not included in Scheme 1).

### Acknowledgements

This research was supported by the EU through the European Regional Development Fund (TK141 "Advanced materials and high-technology devices for energy recuperation systems"), by the Estonian National R & D infrastructure development program of Measure 2.3 'Promotion of development activities and innovation' (Regulation No. 34) funded by the Enterprise Estonia foundation, and by Ministry of Education and Science of Estonia (the institutional research grant No. IUT20-14).

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**Graphical abstract:** 

