Metal-Free Hydrophosphanation of 1-Vinylimidazoles with Secondary Phosphanes: A Straightforward Atom-Economic Route to Tertiary Phosphanes with Imidazolyl Substituents

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Abstract: Free radical addition (UV irradiation, 2–7 h or AIBN, 65–70 °C, 6–7 h) of secondary phosphanes to 1-vinylimidazole, 2-methyl-1-vinylimidazole, and 1-vinylbenzimidazole proceeds regioselectively to give the corresponding anti-Markovnikov adducts in 88–98% yields.

Key words: nitrogen heterocycles, 1-vinylimidazoles, secondary phosphanes, radical reactions, phosphane addition

In recent years, the increasing interest is focused on the imidazolyl-substituted phosphanes as potent polydentate ligands for the design of metal complexes.[1] The latter ensure good performing catalysis in the hydroformylation of 1-octene,[1b] hydration,[1d] hydroamination,[1j] and hydrothiolation[1j] of terminal alkynes, palladium-catalyzed Suzuki[1e,g] and Sonogashira[1g] coupling of aryl halides, hydroxylation,[1i] and Buchwald–Hartwig amination[1e] of aryl chlorides. Such hybrid ligands are used as models to study the effects of phosphane and heterocyclic substituents on the coordination geometry of metal complexes and binding affinity of the soft P and hard N donors for specific metal.[1f–h]

Phosphorus-substituted imidazoles are prospective precursors in the synthesis of biologically active compounds, since the imidazole ring is a privileged structure of a wide range of natural products, including purines,[2] imidazole-based alkaloids, amino and nucleic acids, biotin, and vitamin B_{12}.[3]

Meanwhile, the known syntheses of imidazolyl phosphanes are multistep, laborious, and based commonly on the reactions of hazardous phosphorus halides with 2-lithiated imidazoles.[1] A less general approach to [2-(1-alkylimidazolyl)]phosphanes is a direct C-2 phosphanation of 1-alkylimidazoles by phosphane halides in pyridine/triethylamine.[4] This approach employing PCl_3 and 1-vinylimidazole allows tris[2-(1-vinylimidazolyl)]phosphane to be obtained in 29% yield only.[4c]

Therefore, the search for more straightforward and atom-economic (‘green’) route to tertiary phosphanes bearing imidazole and benzimidazole moieties remains a synthetic challenge. The addition of secondary phosphanes to 1-vinylimidazoles can be considered as a simple, single-step strategy for the synthesis of such imidazolyl phosphanes. However, there are only two papers[5] describing briefly the addition of H-phosphanes to 1-vinylimidazoles in a strongly basic catalytic systems. The process was performed in the presence of considerable amount (more than 40 mol% in total) of KO*t*-Bu and *n*-BuLi in THF and hexane as solvents.[5b] It took 85 hours to obtain the adduct in 69% yield.

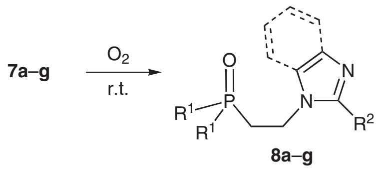
To the best of our knowledge, there are no explicit examples in the literature on the free-radical addition of secondary phosphanes to 1-vinylimidazoles. Noteworthy, such a process as atom-economic, metal-free, and wasteless fairly meets the requirements of green chemistry.

Herein we report a simple general and atom-economic synthesis of tertiary phosphanes bearing imidazolyl substituents by free radical addition of secondary phosphanes to available 1-vinylimidazoles. Readily accessible secondary phosphanes used in the work were mostly those, which are easily produced from red phosphorus and styrenes in one-pot procedure.[6]

The reaction proceeds under UV irradiation or in the presence of azaisobutyronitrile (AIBN) in dioxane at 65–70 °C to give the anti-Markovnikov adducts in near to quantitative yields (Table 1).[7]

Interestingly, secondary phosphine oxides do not add to vinylimidazoles under the above conditions (both under UV irradiation and in the presence of AIBN). This fact correlates well with the known data on the low reactivity of secondary phosphane oxides toward free radical initiation[8] due to a high P–H bond dissociation energy in the phosphoryl moiety.[9] Nevertheless, the strategy here elaborated opens an easy access to tertiary phosphine oxides **8a–g** via mild quantitative oxidation of the phosphanes **7a–g** (r.t., 12–24 h, acetone; Scheme 1).[10]

Actually, on demand, one can synthesize either tertiary phosphanes or corresponding phosphane oxides bearing imidazol substituents.



Scheme 1 Oxidation of phosphanes **7a–g**

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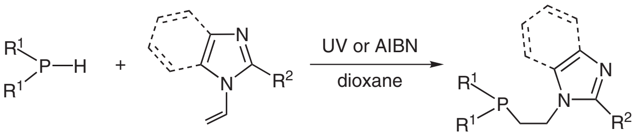
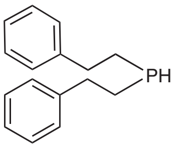
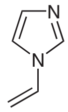
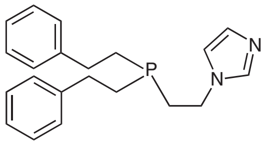
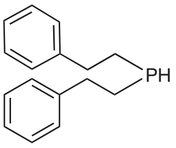
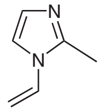
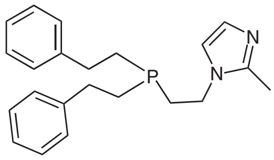
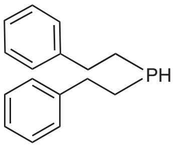
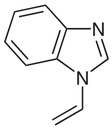
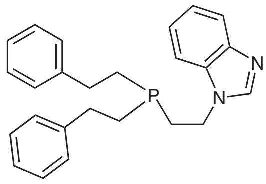
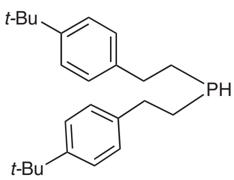
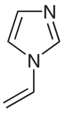
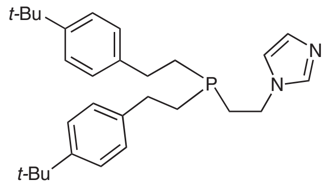
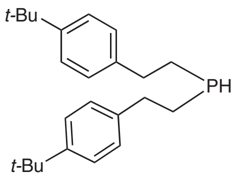
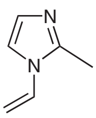
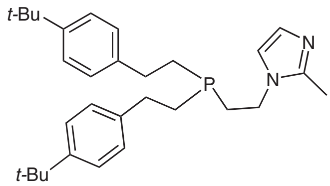
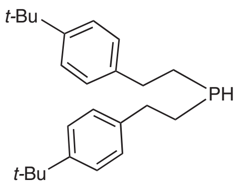
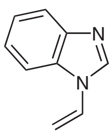
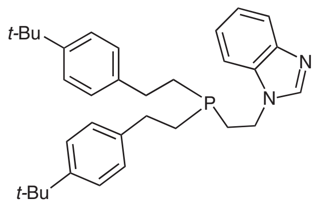
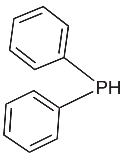
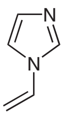
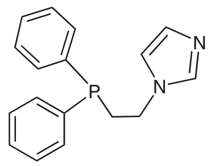
Table 1 Free-Radical Addition of Phosphanes **1–3** to 1-Vinylimidazoles **4–6**[a]



1–3 **4–6** **7a–g**

Phosphane	Imidazole	Product	Conditions	Yield (%)[b]
 **1**	 **4**	 **7a**	UV, 3 h AIBN, 6 h	96 98
 **1**	 **5**	 **7b**	UV, 3 h	96
 **1**	 **6**	 **7c**	UV, 7 h AIBN, 7 h	90 88
 **2**	 **4**	 **7d**	UV, 5 h	92
 **2**	 **5**	 **7e**	UV, 3 h	98
 **2**	 **6**	 **7f**	UV, 5 h	90
 **3**	 **4**	 **7g**	UV, 2 h	95

[a] The ratio of phosphane/imidazole was 1:1. All experiments were carried out under argon atmosphere.
[b] Isolated and pure compound.

In summary, a facile free-radical addition of secondary phosphanes to 1-vinylimidazoles has been accomplished. This simple, straightforward, and atom-economic method represents an advantageous alternative to the known multistep and laborious syntheses of tertiary phosphanes with imidazolyl substituents. Thus, the reaction developed paves a short and expedient way to a family of phosphanes bearing imidazolyl moieties, potent P,N donor ligands for the design of metal complex catalysts, and building blocks for organic synthesis. The results obtained contribute both to fundamental and synthetic chemistry of phosphorus and 1-vinylimidazoles.

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(7) **General Procedure for the Synthesis of Phosphanes 7a–g**
A solution of phosphane **1–3** (1 mmol) and imidazole **4–6** (1 mmol) in dioxane (0.5 mL) was irradiated (200 W Hg arc lamp) in a quartz ampoule (method A) or heated at 65–70 °C in the presence of AIBN (1 wt% of the total mass of reactants) in a sealed ampoule (method B; reaction times are given in Table 1). The reaction was monitored by ^{31}P NMR by disappearance of the signal of the starting phosphanes (δ = –69 to –70 ppm) and appearance of a new signal in the region of δ = –29 to –31 ppm, corresponding to tertiary phosphanes **7a–g**. Dioxane was then removed under reduced pressure and the residue was dissolved in hexane (3 mL). The solution was passed through a thin layer of Al_2O_3, and the solvent was evaporated in vacuo to give tertiary phosphanes **7a–g** of analytical purity. All manipulations were carried out under argon atmosphere.
Bis(2-phenethyl)-[2-(1*H*-imidazolyl)ethyl]phosphane (7a)
Anal. Calcd $C_{21}H_{25}N_2P$: C, 74.98; H, 7.49; N, 8.33; P, 9.21. Found: C, 74.70; H, 7.42; N, 8.13; P, 9.08. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.63–1.83 (m, 6 H, CH_2P), 2.68–2.75 (m, 4 H, CH_2Ph), 3.92–3.98 (m, 2 H, CH_2N), 6.84 and 7.03 (s, 2 H, $H^{4,5}$ in imidazole), 7.14–7.29 (m, 10 H, Ph), 7.41 (s, 1 H, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 29.0 (d, $^2J_{PC}$ = 13.7 Hz, CH_2Ph), 29.43 (d, $^1J_{PC}$ = 16.9 Hz, P*C*H_2CH_2N), 32.28 (d, $^1J_{PC}$ = 15.0 Hz, CH_2P), 44.70 (d, $^2J_{PC}$ = 22.8 Hz, CH_2N), 118.54 (C^4 in imidazole), 126.27 (*p*-C in Ph), 128.16 (*o*-C in Ph), 128.62 (*m*-C in Ph), 129.67 (C^5 in imidazole), 136.73 (C^2 in imidazole), 142.19 (d, $^3J_{PC}$ = 9.6 Hz, *ipso*-C in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –28.31 ppm.
Bis(2-phenethyl)[2-(2-methyl-1*H*-imidazolyl)ethyl]-phosphane (7b)
Anal. Calcd $C_{22}H_{27}N_2P$: C, 75.40; H, 7.77; N, 7.99; P, 8.84. Found: C, 75.65; H, 7.74; N, 7.93; P, 8.81. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.68–1.74 (m, 6 H, PCH_2), 2.32 (s, 3 H, Me), 2.69–2.71 (m, 4 H, CH_2Ph), 3.80–3.88 (m, 2 H, CH_2N), 6.74 and 6.85 (s, 2 H, $H^{4,5}$ in imidazole), 7.13–7.21 (m, 10 H, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 12.85 (Me), 28.75 (d, $^2J_{PC}$ = 14.1 Hz, CH_2Ph), 29.46 (d, $^1J_{PC}$ = 19.1 Hz, P*C*H_2CH_2N), 32.02 (d, $^1J_{PC}$ = 14.6 Hz, PCH_2), 43.52 (d, $^2J_{PC}$ = 21.8 Hz, CH_2N), 118.57 (C^4 in imidazole), 126.05 (*p*-C in Ph), 127.85 (*o*-C in Ph), 128.15 (C^5 in imidazole), 128.49 (*m*-C in Ph), 141.94 (d, $^3J_{PC}$ = 10.9 Hz, *ipso*-C in Ph), 143.76 (C^2 in imidazole) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.15 ppm.
Bis(2-phenethyl)[2-(1*H*-1,3-benzimidazolyl)ethyl]-phosphane (7c)
Anal. Calcd $C_{25}H_{27}N_2P$: C, 77.70; H, 7.04; N, 7.25; P, 8.01. Found: C, 77.68; H, 7.06; N, 7.21; P, 8.30. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.65–1.71 (m, 4 H, PCH_2), 1.86–1.89 (m, 2 H, P*CH_2*CH_2N), 2.65–2.66 (m, 4 H, CH_2Ph), 4.12–4.17 (m, 2 H, CH_2N), 7.08–7.29 (m, 12 H, Ph, $H^{5,6}$ in imidazole), 7.32, 7.81 and 7.83 (m, 3 H, $H^{4,7,2}$ in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.70 (d, $^1J_{PC}$ = 17.1 Hz, P*C*H_2CH_2N,), 28.76 (d, $^2J_{PC}$ = 13.9 Hz, CH_2Ph), 32.0 (d, $^1J_{PC}$ = 14.3 Hz, PH_2), 42.64 (d, $^2J_{PC}$ = 23.4 Hz, CH_2N), 109.40 (C^7 in imidazole), 120.36 (C^4 in imidazole), 122.02 (C^6 in imidazole), 122.76 (C^5 in imidazole), 126.06 (*p*-C in Ph), 127.97 (*o*-C in Ph), 128.60 (*m*-C in Ph), 133.24 (C^8 in imidazole), 141.96 (d, $^3J_{PC}$ = 10.9 Hz, *ipso*-C in Ph), 142.42 (C^2 in imidazole), 143.81 (C^9 in imidazole) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –30.96 ppm.
Bis[2-(4-*tert*-butylphen)ethyl][2-(1*H*-imidazolyl)ethyl]-phosphane (7d)
Anal. Calcd $C_{29}H_{41}N_2P$: C, 77.64; H, 9.21; N, 6.24; P, 6.90. Found: C, 77.66; H, 9.20; N, 6.21; P, 6.76. ^{1}H NMR (400.13

MHz, $CDCl_3$): δ = 1.27 (s, 18 H, Me), 1.66–1.77 (m, 6 H, PCH_2), 2.66–2.68 (m, 4 H, $C\mathit{H}_2C_6H_4$), 3.94–3.97 (m, 2 H, CH_2N), 6.83 and 7.02 (s, 2 H, $H^{4,5}$ in imidazole), 7.08–7.10 and 7.29–7.31 (m, 8 H, C_6H_4), 7.43 (s, 1 H, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 28.90 (d, $^2J_{PC}$ = 12.7 Hz, $\mathit{C}H_2C_6H_4$), 29.43 (d, $^1J_{PC}$ = 19.4 Hz, $P\mathit{C}H_2CH_2N$), 31.47 (Me), 31.76 (d, $^1J_{PC}$ = 19.6 Hz, CH_2P), 34.50 (*C*-Me), 44.82 (d, $^2J_{PC}$ = 20.3 Hz, CH_2N), 118.62 (C^4 in imidazole), 125.59 (*o*-C in C_6H_4), 125.84 (C^5 in imidazole), 127.87 (*m*-C in C_6H_4), 136.69 (C^2 in imidazole), 139.18 (d, $^3J_{PC}$ = 10.9 Hz, *ipso*-C in C_6H_4), 149.15 (*p*-C in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –29.80 ppm.

Bis[2-(4-*tert*-butylphen)ethyl][2-(2-methyl-1*H*-imidazolyl)ethyl]phosphane (7e)
Anal. Calcd $C_{30}H_{43}N_2P$: C, 77.88; H, 9.37; N, 6.06; P, 6.69. Found: C, 77.67; H, 9.34; N, 6.10; P, 6.63. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.28 (s, 18 H, MeC_6H_4), 1.67–1.75 (m, 6 H, PCH_2), 2.30 (s, 3 H, Me), 2.68–2.70 (m, 4 H, $C\mathit{H}_2C_6H_4$), 3.80–3.85 (m, 2 H, CH_2N), 6.75 and 6.80 (s, 2 H, $H^{4,5}$ in imidazole), 7.13–7.23 (m, 8 H, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 13.01 (Me), 28.76 (d, $^2J_{PC}$ = 14.3 Hz, $\mathit{C}H_2C_6H_4$), 29.49 (d, $^1J_{PC}$ = 18.8 Hz, $P\mathit{C}H_2CH_2N$), 31.47 (MeC_6H_4), 32.46 (d, $^1J_{PC}$ = 14.6 Hz, CH_2P), 34.50 (*C*-Me), 43.82 (d, $^2J_{PC}$ = 22.3 Hz, CH_2N), 118.52 (C^4 in imidazole), 126.09 (*o*-C in C_6H_4), 127.53 (C^5 in imidazole), 127.77 (*m*-C in C_6H_4), 141.95 (d, $^3J_{PC}$ = 10.7 Hz, *ipso*-C in C_6H_4), 143.76 (C^2 in imidazole), 144.15 (*p*-C in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.20 ppm.

Bis[2-(4-*tert*-butylphen)ethyl][2-(1*H*-1,3-benzimidazolyl)ethyl]phosphane (7f)
Anal. Calcd $C_{33}H_{43}N_2P$: C, 79.48; H, 8.69; N, 5.62; P, 6.21. Found: C, 79.40; H, 8.61; N, 5.58; P, 6.11. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.28 (s, 18 H, Me), 1.68–1.75 (m, 4 H, CH_2P), 1.93–1.98 (m, 2 H, $PC\mathit{H}_2CH_2N$), 2.64–2.71 (m, 4 H, $C\mathit{H}_2C_6H_4$), 4.19–4.25 (m, 2 H, CH_2N), 6.81 and 6.98 (m, 2 H, $H^{5,6}$ in imidazole), 7.03–7.07 and 7.28–7.31 (m, 9 H, C_6H_4, H^4 in imidazole), 7.79 and 7.85 (s, 2 H, $H^{7,2}$ in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.76 (d, $^1J_{PC}$ = 17.1 Hz, $\mathit{C}H_2CH_2N$), 28.70 (d, $^2J_{PC}$ = 13.9 Hz, $\mathit{C}H_2C_6H_4$), 31.27 (Me), 31.48 (d, $^1J_{PC}$ = 15.5 Hz, CH_2P), 34.26 (*C*Me), 42.72 (d, $^2J_{PC}$ = 23.1 Hz, CH_2N), 109.41 (C^7 in imidazole), 120.40 (C^4 in imidazole), 122.10 (C^6 in imidazole), 122.86 (C^5 in imidazole), 125.28 (*o*-C in C_6H_4), 127.72 (*m*-C in C_6H_4), 133.26 (C^8 in imidazole), 138.95 (d, $^3J_{PC}$ = 10.9 Hz, *ipso*-C in C_6H_4), 142.41 (C^2 in imidazole), 143.73 (C^9 in imidazole), 148.97 (*p*-C in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –31.15 ppm.

Bis(phenhyl)-[2-(1*H*-imidazolyl)ethyl]phosphane (7g)
Anal. Calcd $C_{17}H_{17}N_2P$: C, 72.84; H, 6.11; N, 9.99; P, 11.05. Found: C, 72.80; H, 6.12; N, 9.93; P, 11.01. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 2.48–2.52 (m, 2 H, CH_2P), 3.96–4.01 (m, 2 H, CH_2N), 6.85 and 7.01 (m, 2 H, $H^{4,5}$ in imidazole), 7.31–7.71 (m, 10 H, Ph), 8.67 (s, 1 H, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 30.51 (d, $^1J_{PC}$ = 14.8 Hz, CH_2P), 44.13 (d, $^2J_{PC}$ = 23.5 Hz, CH_2N), 118.54 (C^4 in imidazole), 128.89 (d, $^3J_{PC}$ = 13.4 Hz, *m*-C in Ph), 129.16 (*p*-C in Ph), 129.57 (C^5 in imidazole), 130.69 (d, $^2J_{PC}$ = 11.4 Hz, *o*-C in Ph), 132.61 (d, $^1J_{PC}$ = 19.1 Hz, *ipso*-C in Ph), 136.77 (C^2 in imidazole) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = –20.84 ppm.

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(10) **General Procedure for the Preparation of the Phosphane Oxides 8a–g**
A solution of phosphane **7a**–**g** (1 mmol) in acetone was stirred at r.t. under air atmosphere. After reaction completion, as indicated by TLC, the solvent was removed under reduced pressure to afford phosphane oxide **8a**–**g**.

Bis(2-phenethyl)[2-(1*H*-imidazolyl)ethyl]phosphane Oxide (8a)
Yield 349 mg (99%), colorless crystalline solid, mp 99–102 °C (hexane). Anal. Calcd $C_{21}H_{25}N_2OP$: C, 71.57; H, 7.15; N, 7.95; P, 8.79. Found: C, 71.47; H, 7.12; N, 7.83; P, 8.71. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.91–2.08 (m, 6 H, CH_2P), 2.83–2.87 (m, 4 H, CH_2Ph), 4.16–4.23 (m, 2 H, CH_2N), 6.86 and 7.03 (s, 2 H, $H^{4,5}$ in imidazole), 7.16–7.28 (m, 10 H, Ph), 7.48 (s, 1 H, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.55 (d, $^2J_{PC}$ = 3.2 Hz, H_2Ph), 30.36 (d, $^1J_{PC}$ = 60.1 Hz, $P\mathit{C}H_2CH_2N$), 30.56 (d, $^1J_{PC}$ = 63.2 Hz, CH_2P), 40.14 (CH_2N), 118.64 (C^4 in imidazole), 126.68 (*p*-C in Ph), 128.0 (*o*-C in Ph), 128.75 (*m*-C in Ph), 129.60 (C^5 in imidazole), 136.91 (C^2 in imidazole), 140.13 (d, $^3J_{PC}$ = 11.0 Hz, *ipso*-C in Ph) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 43.56 ppm.

Bis(2-phenethyl)[2-(2-methyl-1*H*-imidazolyl)ethyl]-phosphane Oxide (8b)
Yield 359 mg (98%), light-yellow oil. Anal. Calcd $C_{22}H_{27}N_2OP$: C, 72.11; H, 7.43; N, 7.64; P, 8.45. Found: C, 72.15; H, 7.44; N, 7.63; P, 8.41. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.94–2.01 (m, 6 H, PCH_2), 2.36 (s, 3 H, Me), 2.83–2.87 (m, 4 H, CH_2Ph), 4.08–4.14 (m, 2 H, CH_2N), 6.78 and 6.87 (s, 2 H, $H^{4,5}$ in imidazole), 7.13–7.21 (m, 10 H, Ph) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 12.85 (Me), 27.51 (CH_2Ph), 29.62 (d, $^1J_{PC}$ = 60.2 Hz, $P\mathit{C}H_2CH_2N$), 30.49 (d, $^1J_{PC}$ = 63.5 Hz, CH_2P), 38.99 (CH_2N), 118.71 (C^4 in imidazole), 126.52 (*p*-C in Ph), 127.93 (*o*-C in Ph), 128.55 (C^5 in imidazole), 128.83 (*m*-C in Ph), 140.07 (d, $^3J_{PC}$ = 11.8 Hz, *ipso*-C in Ph), 144.12 (C^2 in imidazole) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 45.31 ppm.

Bis(2-phenethyl)[2-(1*H*-1,3-benzimidazolyl)ethyl]-phosphane Oxide (8c)
Yield 398 mg (99%), colorless crystalline solid, mp 190–200 °C (hexane). Anal. Calcd $C_{25}H_{27}N_2OP$: C, 74.61; H, 6.76; N, 6.96; P, 7.70. Found: C, 74.67; H, 6.56; N, 6.87; P, 7.75. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.85–1.92 (m, 4 H, PCH_2), 2.11–2.17 (m, 2 H, $PC\mathit{H}_2CH_2N$), 2.74–2.79 (m, 4 H, CH_2Ph), 4.41–4.48 (m, 2 H, CH_2N), 7.03–7.27 (m, 12 H, Ph, $H^{5,6}$ in imidazole), 7.35 (s, 1 H, H^4 in imidazole), 7.76 and 7.92 (m, 2 H, $H^{7,2}$ in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.55 (CH_2Ph), 28.36 (d, $^2J_{PC}$ = 60.0 Hz, $P\mathit{C}H_2CH_2N$), 30.67 (d, $^1J_{PC}$ = 62.0 Hz, CH_2P), 38.26 (CH_2N), 109.41 (C^7 in imidazole), 120.52 (C^4 in imidazole), 122.48 (C^6 in imidazole), 123.27 (C^5 in imidazole), 126.64 (*p*-C in Ph), 127.96 (*o*-C in Ph), 128.72 (*m*-C in Ph), 132.99 (C^8 in imidazole), 140.04 (d, $^3J_{PC}$ = 12.5 Hz, *ipso*-C in Ph), 142.93 and 143.65 ($C^{2,9}$ in imidazole) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 43.95 ppm.

Bis[2-(4-*tert*-butylphen)ethyl][2-(1*H*-imidazolyl)ethyl]-phosphane Oxide (8d)
Yield 455 mg (98%), colorless crystalline solid, mp 140–141 °C (hexane). Anal. Calcd $C_{29}H_{41}N_2OP$: C, 74.97; H, 8.89; N, 6.03; P, 6.67. Found: C, 74.86; H, 8.95; N, 6.21; P, 6.76. ^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.29 (s, 18 H, Me), 1.95–2.06 (m, 6 H, PCH_2), 2.71–2.83 (m, 4 H, CH_2Ph), 4.20–4.22 (m, 2 H, CH_2N), 6.84 (s, 1 H, H^4 in imidazole), 7.04–7.32 (m, 9 H, C_6H_4, H^5 in imidazole), 7.46 (s, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.11

(CH_2Ph), 30.47 (d, $^1J_{PC}$ = 60.7 Hz, PCH_2CH_2N), 30.54 (d, $^1J_{PC}$ = 62.7 Hz, CH_2P), 31.29 (Me), 34.40 (*C*Me), 40.26 (CH_2N), 118.69 (C^4 in imidazole), 125.67 (*o*-C in C_6H_4), 127.73 (*m*-C in C_6H_4), 129.66 (C^5 in imidazole), 136.93 (d, $^3J_{PC}$ = 12.6 Hz, *ipso*-C in Ph), 149.23 and 149.82 (C^2 in imidazole and *p*-C in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 44.86 ppm.

Bis[2-(4-*tert*-butylphen)ethyl][2-(2-methyl-1*H*-imidazolyl)ethyl]phosphane Oxide (8e)

Yield 464 mg (97%), colorless crystalline solid, mp 134–136 °C (hexane). Anal. Calcd $C_{30}H_{43}N_2OP$: C, 75.28; H, 8.05; N, 5.85; P, 6.47. Found: C, 75.36; H, 8.25; N, 6.01; P, 6.56. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.28 (s, 18 H, Me), 1.94–2.05 (m, 6 H, CH_2P), 2.41 (s, 3 H, Me in imidazole), 2.82–2.84 (m, 4 H, C$H_2C_6H_4$), 4.11–4.18 (m, 2 H, CH_2N), 6.76 and 6.91 (s, 2 H, $H^{4,5}$ in imidazole), 7.07–7.10 and 7.25–7.32 (m, 8 H, C_6H_4) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 12.95 (Me in imidazole), 27.25 (d, $^2J_{PC}$ = 3.0 Hz, $CH_2C_6H_4$), 29.82 (d, $^1J_{PC}$ = 61.9 Hz, PCH_2CH_2N), 30.62 (d, $^1J_{PC}$ = 64.1 Hz, CH_2P), 31.44 (Me), 34.53 (*C*Me), 39.45 (CH_2N), 118.89 (C^4 in imidazole), 125.85 (*o*-C in C_6H_4), 127.22 (C^5 in imidazole), 127.80 (*m*-C in C_6H_4), 137.13 (d, $^3J_{PC}$ = 12.8 Hz, *ipso*-C in C_6H_4), 144,38 (C^2 in imidazole), 149.80 (*p*-C in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 44.74 ppm.

Bis[2-(4-*tert*-butylphen)ethyl][2-(1*H*-1,3-benzimidazolyl)-ethyl]phosphane Oxide (8f)

Yield 509 mg (99%); light-yellow oil. Anal. Calcd $C_{33}H_{43}N_2OP$: C, 77.01; H, 8.42; N, 5.44; P, 6.02. Found: C, 77.17; H, 8.50; N, 5.73; P, 6.11. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.25 (s, 18 H, Me), 1.88–2.03 (m, 4 H, CH_2P), 2.14–2.18 (m, 2 H, PCH_2CH_2N), 2.76–2.78 (m, 4 H, CH_2Ph), 4.45–4.51 (m, 2 H, CH_2N), 6.98 and 7.01 (s, 2 H, $H^{5,6}$ in imidazole), 7.24–7.34 (m, 8 H, C_6H_4), 7.39 (s, 1 H, H^4 in imidazole), 7.78 (s, 1 H, H^7 in imidazole), 7.91 (s, 1 H, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 27.13 (CH_2Ph), 28.54 (d, $^1J_{PC}$ = 60.0 Hz, PCH_2CH_2N), 30.65 (d, $^1J_{PC}$ = 62.6 Hz, CH_2P), 31.26 (Me), 34.33 (*C*Me), 38.30 (CH_2N), 109.35 (C^7 in imidazole), 120.60 (C^4 in imidazole), 122.49 (C^6 in imidazole), 123.29 (C^5 in imidazole), 125.61 (*o*-C in C_6H_4), 127.63 (*m*-C in C_6H_4), 134.91 (C^8 in imidazole), 136.94 (d, $^3J_{PC}$ = 11.4 Hz, *ipso*-C in C_6H_4), 142.83 (C^2 in imidazole), 143.72 (C^9 in imidazole), 149.61 (*p*-C in C_6H_4) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 44.83 ppm.

Bis(phenyl)-[2-(1*H*-imidazolyl)ethyl]phosphane Oxide (8g)

Yield 287 mg (97%), colorless crystalline solid, mp 38–39 °C (hexane). Anal. Calcd $C_{17}H_{17}N_2OP$: C, 68.91; H, 5.78; N, 9.45; P, 10.45. Found: C, 68.89; H, 5.77; N, 9.43; P, 10.41. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.77–2.78 (m, 2 H, CH_2P), 4.28–4.30 (m, 2 H, CH_2N), 6.88 and 6.93 (s, 2 H, $H^{4,5}$ in imidazole), 7.27–7.70 (m, 10 H, Ph), 8.04 (s, 1 H, H^2 in imidazole) ppm. ^{13}C NMR (100.62 MHz, $CDCl_3$): δ = 32.15 (d, $^1J_{PC}$ = 67.7 Hz, CH_2P), 40.43 (CH_2N), 118.69 (C^4 in imidazole), 128.91 (d, $^3J_{PC}$ = 12.3 Hz, *m*-C in Ph), 129.96 (C^5 in imidazole), 130.47 (d, $^2J_{PC}$ = 9.5 Hz, *o*-C in Ph), 131.56 (d, $^1J_{PC}$ = 100.3 Hz, *ipso*-C in Ph), 136.77 (C^2 in imidazole) ppm. ^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 29.46 ppm.