Supporting Information

for

Microwave-assisted synthesis of $N,N$-bis(phosphinoylmethyl)amines and $N,N,N$-tris(phosphinoylmethyl)amines bearing different substituents on the phosphorus atoms

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Experimental procedures, characterization data, details of the NMR structural determination of all products and copies of $^{31}$P, $^1$H, and $^{13}$C NMR spectra for all compounds synthesized
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**General information**

The $^{31}$P, $^{13}$C, $^1$H NMR spectra were recorded in CDCl$_3$ solution on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 75.5 and 300 or 202.4, 125.7 and 500 MHz, respectively. Chemical shifts are reported downfield relative to 85% H$_3$PO$_4$ and TMS. The coupling constants are given in Hz. Mass spectrometric measurements were performed using a Q-TOF Premier mass spectrometer in positive electrospray mode and a Shimadzu LCMS-ITTOF mass spectrometer. The reactions were carried out in a 300 W CEM Discover microwave reactor (CEM Microwave Technology Ltd., Buckingham, UK) equipped with a pressure controller applying 30–80 W under isothermal conditions.

**General procedure for the synthesis of (aminomethyl)dibenzyl-, (aminomethyl)di(p-tolyl)- or (aminomethyl)diphenylphosphine oxides**

A mixture of 1.0 mmol amine (0.10 mL of butylamine, 0.12 mL of cyclohexylamine or 0.11 mL benzylamine), 1.0 mmol (0.03 g) of paraformaldehyde, and 1.0 mmol of the secondary phosphine oxide (0.24 g of di(p-tolyl)phosphine oxide, 0.24 g of dibenzylphosphine oxide or 0.20 g of diphenylphosphine oxide) and 1.5 mL of acetonitrile was heated at 100 °C in a closed vial in a CEM Discover microwave reactor equipped with a pressure controller for 1 h. Acetonitrile and the water formed during reaction were removed in vacuum. The crude product so obtained was passed through a 1 cm silica gel layer using ethyl acetate. After evaporating the solvent, the products 5a,b, 6a,b, 7a,b and 8 were obtained as crystals or oils. The following products were thus prepared:

**(Butylaminomethyl)di(p-tolyl)phosphine oxide (5a)**

Yield: 97% (0.31 g) of compound 5a as pale yellow oil; $^{31}$P NMR (CDCl$_3$) $\delta$ 42.1; $\delta[S1]$ (CDCl$_3$) 42.0; [M+H]$^+$ found = 316.1828, C$_{19}$H$_{27}$NOP requires 316.1825.
(Butylaminomethyl)dibenzyolphosphine oxide (5b)
Yield: 98% (0.31 g) of compound 5b as pale yellow crystals; $^{31}$P NMR (CDCl$_3$) δ 44.5; δ[S1] (CDCl$_3$) 44.6; [M+H]$^+$ found = 316.1832, C$_{19}$H$_{27}$NOP requires 316.1825.

(Cyclohexylaminomethyl)di(p-tolyl)phosphine oxide (6a)
Yield: 98% (0.33 g) of compound 6a as pale yellow oil; $^{31}$P NMR (CDCl$_3$) δ 29.5; δ[S1] (CDCl$_3$) 29.6; [M+H]$^+$ found = 342.1987, C$_{21}$H$_{29}$NOP requires 342.1981.

(Cyclohexylaminomethyl)dibenzylphosphine oxide (6b)
Yield: 96% (0.33 g) of compound 6b as white crystals; $^{31}$P NMR (CDCl$_3$) δ 44.2; δ[S1] (CDCl$_3$) 44.4; [M+H]$^+$ found = 342.1989, C$_{21}$H$_{29}$NOP requires 342.1981.

(Benzylaminomethyl)di(p-tolyl)phosphine oxide (7a)
Yield: 94% (0.33 g) of compound 7a as pale yellow crystals; $^{31}$P NMR (CDCl$_3$) δ 30.0; δ[S1] (CDCl$_3$) 29.9; [M+H]$^+$ found = 350.1669, C$_{22}$H$_{25}$NOP requires 350.1668.

(Benzylaminomethyl)dibenzylphosphine oxide (7b)
Yield: 97% (0.34 g) of compound 7b as white crystals; $^{31}$P NMR (CDCl$_3$) δ 43.6; δ[S1] (CDCl$_3$) 43.8; [M+H]$^+$ found = 350.1677, C$_{22}$H$_{25}$NOP requires 350.1668.

(Benzylaminomethyl)diphenylphosphine oxide (8)
Yield: 96% (0.32 g) of compound 8 as white crystals; $^{31}$P NMR (CDCl$_3$) δ 30.0; δ[S2] (CDCl$_3$) 29.7; [M+H]$^+$ found = 322.1316, C$_{20}$H$_{21}$NOP requires 322.1361.
Hydrogenation of (benzylaminomethyl)diphenylphosphine oxide
To 1.6 g (5.00 mmol) of (benzylaminomethyl)diphenylphosphine oxide (8) in 100 mL of methanol was added 0.50 g of 10% palladium on carbon (Selcat Q) and the suspension was then hydrogenated in a stainless steel autoclave at 12 bar and 75 °C for 3 h. The mixture was filtered, and the catalyst was washed with methanol. After evaporating the solvent and column chromatography 0.54 g (47%) of 9 was obtained as a white crystal.

(Aminomethyl)diphenylphosphine oxide (9)
Yield: 47% (0.54 g) of compound 9 as white crystals; $^{31}$P NMR (CDCl$_3$) δ 30.8; δ[S3] (CDCl$_3$) 30.4; [M+H]$^+$ found = 232.0891, C$_{13}$H$_{15}$NOP requires 232.0891.

General procedure for the synthesis of N,N-bis(phosphinoylmethyl)alkyl amines bearing different Y$_2$P=O groups
A mixture of 0.50 mmol (aminomethyl)phosphine oxides [(butylaminomethyl)di(p-tolyl)phosphine oxide: 0.16 g, (cyclohexylaminomethyl)di(p-tolyl)phosphine oxide: 0.17 g, (benzylaminomethyl)di(p-tolyl)phosphine oxide: 0.17 g, (butylaminomethyl)dibenzylphosphine oxide: 0.16 g, (cyclohexylaminomethyl)dibenzylphosphine oxide: 0.17 g, (benzylaminomethyl)dibenzylphosphine oxide: 0.17 g], 0.015 g (0.50 mmol) of paraformaldehyde, and 0.10 g (0.50 mmol) of diphenylphosphine oxide and 1.5 mL of acetonitrile was heated at 100 °C in a closed vial in a CEM Discover microwave reactor equipped with a pressure controller for 1 h. Acetonitrile and the water formed during reaction were removed under vacuum. The crude product so obtained was passed through a 1 cm silica gel layer using ethyl acetate. After evaporating the solvent, the products 10a,b, 11a,b and 12a,b were obtained as oils. The following products were thus prepared:
**N,N-(Di-p-tolylphosphinoylmethyl)(diphenylphosphinoylmethyl)butylamine (10a)**

Yield: 93% (0.25 g) of compound 10a as colorless oil. $^{31}$P NMR (CDCl$_3$) δ 29.3, 29.5; $^{13}$C NMR (CDCl$_3$) δ 14.0 (CH$_3$CH$_2$), 20.0 (CH$_3$CH$_2$), 21.5 (C$_4$CH$_3$), 28.6 (CH$_3$CH$_2$CH$_2$), 55.9 (dd, $^1$J$_{CP}$ = 85.3, $^3$J$_{CP}$ = 1.3, NCH$_2$PPh$_2$), 56.0 (dd, $^1$J$_{CP}$ = 85.2, $^3$J$_{CP}$ = 2.7, NCH$_2$P(p-tolyl)$_2$), 58.4 (t, $^3$J$_{CP}$ = 7.0, CH$_3$(CH$_2$)$_2$CH$_2$N), 128.3 (d, $^2$J$_{CP}$ = 11.7, C$_2$'), 129.10 (d, $^2$J$_{CP}$ = 11.9, C$_2$), 129.13 (d, $^1$J$_{CP}$ = 100.1, C$_1$), 131.17 (d, $^3$J$_{CP}$ = 9.2, C$_3$'), 131.21 (d, $^3$J$_{CP}$ = 8.6, C$_3$), 131.5 (d, $^1$J$_{CP}$ = 2.6, C$_4$'), 132.3 (d, $^1$J$_{CP}$ = 97.5, C$_1$'), 141.9 (d, $^1$J$_{CP}$ = 2.8, C$_4$); $^1$H NMR (CDCl$_3$) δ 0.73 (t, 3H, J$_{HH}$ = 7.3, CH$_3$CH$_2$), 0.95–1.06 (m, 2H, CH$_3$CH$_2$CH$_2$), 1.20–1.30 (m, 2H, CH$_3$CH$_2$CH$_2$), 2.35 (s, 6H, C$_4$CH$_3$), 2.95 (t, 2H, J$_{HH}$ = 7.1, CH$_3$CH$_2$CH$_2$CH$_2$N), 3.63 (d, 2H, $^1$J$_{HP}$ = 5.9, NCH$_2$P(p-tolyl)$_2$), 3.73 (d, 2H, $^1$J$_{HP}$ = 6.0, NCH$_2$PPh$_2$), 7.12–7.19 (m, 4H, C$_3$H), 7.22–7.39 (m, 4H, C$_3$H), 7.42–7.47 (m, 2H, C$_4$H), 7.58–7.65 (m, 4H, C$_2$H), 7.72–7.80 (m, 4H, C$_2$H); [M+H]$^+$ found = 530.2226, C$_{32}$H$_{38}$NO$_2$P$_2$ requires 530.2378.

**N,N-(Dibenzylphosphinoylmethyl)(diphenylphosphinoylmethyl)butylamine (10b)**

Yield: 94% (0.25 g) of compound 10b as colorless oil. $^{31}$P NMR (CDCl$_3$) δ 29.3, 41.8; $^{13}$C NMR (CDCl$_3$) δ 14.0 (CH$_3$CH$_2$), 20.1 (CH$_3$CH$_2$), 28.4 (CH$_3$CH$_2$CH$_2$), 34.9 (d, $^1$J$_{CP}$ = 60.4, P(O)CH$_2$), 53.6 (dd, $^1$J$_{CP}$ = 81.5, $^3$J$_{CP}$ = 9.8, NCH$_2$PBn$_2$), 55.1 (dd, $^1$J$_{CP}$ = 86.5, $^3$J$_{CP}$ = 6.0, NCH$_2$PPh$_2$), 58.5 (dd, $^3$J$_{CP}$ = 7.8, 5.8, CH$_3$(CH$_2$)$_2$CH$_2$N), 126.7 (d, J$_{CP}$ = 2.7, C$_4$), 128.5 (d, $^2$J$_{CP}$ = 11.6, C$_2$'), 128.6 (d, J$_{CP}$ = 2.0, C$_3$), 129.8 (d, $^3$J$_{CP}$ = 5.2, C$_2$), 131.3 (d, $^3$J$_{CP}$ = 7.3, C$_3$'), 131.8 (d, $^3$J$_{CP}$ = 2.7, C$_4$'), 131.9 (d, $^2$J$_{CP}$ = 2.7, C$_1$), 132.1 (d, $^1$J$_{CP}$ = 97.6, C$_1$'); $^1$H NMR (CDCl$_3$) δ 0.83 (t, J$_{HH}$ = 7.2, 3H, CH$_3$), 1.06–1.36 (m, 4H, CH$_3$CH$_2$CH$_2$H), 2.72–3.08 (m, 8H, CH$_3$CH$_2$CH$_2$CH$_2$N, P(O)CH$_2$Ph, NCH$_2$PPh$_2$), 3.66 (d, $^3$J$_{HP}$ = 6.0, 2H, NCH$_2$PBn$_2$),
7.11–7.33 (m, 10H, C₂H, C₃H, C₄H), 7.40–7.52 (m, 6H, C₃'H, C₄'H), 7.82–7.95 (m, 4H, C₂'H); [M+H]^+<sub>found</sub> = 530.2167, C₃₂H₃₈NO₂P₂ requires 530.2378.

*N,N-(Di-p-tolylphosphinoylmethyl)(diphenylphosphinoylmethyl)cyclohexylamine (11a)*

Yield: 92% (0.26 g) of compound 11a as pale yellow oil. ³¹P NMR (CDCl₃) δ 29.9, 30.3; ¹³C NMR (CDCl₃) δ 21.6 (C₄CH₃), 25.7 (C₃), 26.2 (C₄), 27.8 (C₂), 51.7 (dd, ¹JC₄P = 87.2, ³JC₄P = 8.6, NCH₂PPh₂), 51.9 (dd, ¹JC₄P = 87.2, ³JC₄P = 7.4, NCH₂P(p-tolyl)₂), 61.8 (t, ³JC₄P = 5.9, C₁), 128.3 (d, ²JC₄P = 11.6, C₂a''), 129.06 (d, ²JC₄P = 11.9, C₂''), 129.07 (d, ¹JC₄P = 100.0, C₁''), 131.2 (d, ³JC₃P = 9.3, C₃a''), 131.3 (d, ³JC₃P = 9.0, C₃''), 131.4 (d, ⁴JC₃P = 2.6, C₄''), 132.2 (d, ¹JC₄P = 96.0, C₁'''), 141.8 (d, ⁴JC₃P = 2.7, C₄''); ¹H NMR (CDCl₃) δ 0.92–1.02 (m, 2H, C₂Hₐx), 1.22–1.34 (m, 3H, C₃Hₐx, C₄Hₐx), 1.54–1.71 (m, 5H, C₂Hₐq, C₃Hₐq, C₄Hₐq), 2.35 (s, 6H, C₄CH₃), 3.35–3.45 (m, 1H, C₁H), 3.67 (d, ¹JHP = 6.5, 2H, NCH₂P(p-tolyl)₂), 3.77 (d, ¹JHP = 6.6, 2H, NCH₂PPh₂), 7.12–7.20 (m, 4H, C₃''), 7.32–7.38 (m, 4H, C₃'H), 7.41–7.47 (m, 2H, C₄'') 7.58–7.66 (m, 4H, C₂H), 7.72–7.80 (m, 4H, C₂'H); [M+H]^+<sub>found</sub> = 556.2300, C₃₄H₄₀NO₂P₂ requires 556.2534.

*N,N-(Dibenzylphosphinoylmethyl)(diphenylphosphinoylmethyl)cyclohexylamine (11b)*

Yield: 96% (0.27 g) of compound 11b as pale yellow oil. ³¹P NMR (CDCl₃) δ 30.1, 41.7; ¹³C NMR (CDCl₃) δ 25.6 (C₃), 26.1 (C₄), 27.9 (C₂), 34.8 (d, ¹JC₄P = 60.6, P(O)CH₂H₂), 49.5 (dd, ¹JC₄P = 83.5, ³JC₄P = 9.7, NCH₂PBN₂), 51.8 (dd, ¹JC₄P = 88.1, ³JC₄P = 6.2, NCH₂PPh₂), 61.8 (t, ³JC₄P = 5.3, C₁), 126.6 (d, ¹JC₄P = 2.6, C₄''), 128.5 (d, ²JC₄P = 11.7, C₂a''), 128.6 (d, ⁴JC₄P = 2.3, C₃''), 129.8 (d, ³JC₄P = 5.2, C₂''), 131.4 (d, ³JC₄P = 9.02 C₃aa''), 131.8 (d, ⁴JC₃P = 2.6, C₄aa''), 132.1 (d, ²JC₄P = 7.0, C₁'''), 131.9 (d, ¹JC₄P = 107.2, C₁aa''); ¹H NMR (CDCl₃) δ 0.80–1.26 (m, 5H, C₂Hₐx, C₃Hₐx, C₄Hₐx), 1.51–1.75 (m, 5H, C₂Hₐq, C₃Hₐq, C₄Hₐq), 2.70–3.32 (m, 7H, C₁H, P(O)CH₂Ph, NCH₂PPh₂), 3.69 (d, ¹JHP = 6.1, 2H, NCH₂PBN₂), 7.12–7.31 (m, 10H, C₂H, P(O)CH₂Ph, NCH₂PPh₂), 3.69 (d, ¹JHP = 6.1, 2H, NCH₂PBN₂), 7.12–7.31 (m, 10H, C₂H,
C₃H, C₄H), 7.40–7.53 (m, 6H, C₃-βH, C₄-βH), 7.83–7.96 (m, 4H, C₂-βH); 

[M+H]⁺ found = 566.2406, C₃₄H₆₀NO₂P₂ requires 556.2534.

N,N-(Di-p-tolylphosphinoylmethyl)(diphenylphosphinoylmethyl)benzylamine (12a)

Yield: 95% (0.27 g) of compound 12a as colorless oil. ³¹P NMR (CDCl₃) δ 29.8, 30.1; ¹³C NMR (CDCl₃) δ 21.6 (C₄CH₃), 55.1 (dd, ¹JCₚ = 85.1, ³JCₚ = 7.0, NCH₂P(Ph)₂), 55.2 (dd, ¹JCₚ = 85.0, ³JCₚ = 8.1, NCH₂P(2-tolyl)₂), 63.2 (t, ³JCₚ = 7.5, NCH₂Ph), 127.2 (C₄), 128.1 (C₂), 128.4 (d, ²JCₚ = 11.7, C₂-β'), 129.0 (d, ¹JCₚ = 94.9, C₁'), 129.1 (d, ²JCₚ = 12.0, C₂-β'), 129.9 (C₃), 131.1 (d, ³JCₚ = 9.1, C₃-β'), 131.2 (d, ³JCₚ = 9.2, C₃'), 131.5 (d, ¹JCₚ = 2.7, C₄-β'), 132.1 (d, ¹JCₚ = 98.2, C₁-β'), 137.7 (C₁), 141.9 (d, ¹JCₚ = 2.8, C₄'); ¹H NMR (CDCl₃) δ 2.34 (s, 6H, C₄CH₃), 3.66 (d, 2H, ¹JHP = 6.2, NCH₂P(p-tolyl)₂), 3.75 (d, 2H, ¹JHP = 6.2, NCH₂P(Ph)₂), 4.09 (s, 2H, CH₂N), 6.85 (d, 2H, JH₂ = 7.3, C₂H₂), 6.85 (d, JH₂ = 7.3, 2H, C₃H), 7.07–7.20 (m, 5H, C₃H, C₂H), 7.25–7.35 (m, 6H, C₃-βH, C₄-βH), 7.42 (d, JH₂ = 7.4, 2H, C₂H), 7.49 (dd, ²JH₂ = 11.1, JH₂ = 8.1, 4H, C₂-βH), 7.64 (dd, ²JH₂ = 11.0, JH₂ = 7.8, 4H, C₂-β'); [M+H]⁺ found = 564.2001, C₃₅H₆₈NO₂P₂ requires 564.2221.

N,N-(Dibenzylphosphinoylmethyl)(diphenylphosphinoylmethyl)benzylamine (12b)

Yield: 97% (0.27 g) of compound 12b as colorless oil. ³¹P NMR (CDCl₃) δ ³¹P NMR (CDCl₃) δ 29.8, 41.2; ¹³C NMR (CDCl₃) δ 34.9 (d, ¹JCₚ = 60.6, P(O)CH₂), 52.7 (dd, ¹JCₚ = 81.2, ³JCₚ = 9.9, NCH₂PPh₂), 54.8 (dd, ¹JCₚ = 85.8, ³JCₚ = 5.7, NCH₂PPh₂), 61.2 (dd, ³JCₚ = 8.3, 6.0, CH₃CH₂CH₂N), 126.7 (d, JCP = 2.8, C₄'), 127.5 (C₄), 128.3 (C₃), 128.5 (d, JCP = 11.7, C₂-β'), 128.6 (d, JCP = 2.4, C₂-β'), 129.7 (d, ³JCₚ = 5.2, C₂-β'), 130.0 (C₂), 131.3 (d, ³JCₚ = 9.1, C₃-β'), 131.80 (d, ²JCₚ = 6.2, C₁'), 131.82 (d, JCP = 3.2, C₄'-β'), 131.85 (d, ¹JCₚ = 98.2, C₁-β'), 137.6 (C₁); ¹H NMR (CDCl₃) δ 2.66–2.89 (m, 4H, PCH₂Ph), 2.92 (d, 2H, ¹JHP = 5.2, NCH₂PPh₂), 3.70 (d, 2H, ¹JHP = 6.2, NCH₂PPh₂), 4.02 (s, 2H, NCH₂Ph), 7.01 (d, JH₂ = 7.5, 4H, C₃H), 7.05–
7.12 (m, 2H, C₃H), 7.16–7.30 (m, 9H, C₂H, C₂H, C₄H, C₄H), 7.39–7.51 (m, 6H, C₃''H, C₄''H), 7.81 (dd, J_HP = 11.1, J_HP = 7.1, 4H, C₂·H); [M+H]⁺ found = 564.1888, C₃₅H₃₆NO₂P₂ requires 564.2221.

**General procedure for the synthesis of N,N-bis(phosphinoylmethyl)amines containing different Y₂P=O groups**

A mixture of 0.12 g (0.50 mmol) of (aminomethyl)diphenylphosphine oxide (9), 0.015 g (0.5 mmol) of paraformaldehyde, and 0.10 g (0.50 mmol) of 0.5 mmol of the secondary phosphine oxide (0.10 g of diphenylphosphine oxide, 0.12 g of di(p-tolyl)phosphine oxide or 0.12 g of dibenzylphosphine oxide) and 1.5 mL of acetonitrile was heated at 100 °C in a closed vial in a CEM Discover microwave reactor equipped with a pressure controller for 40 min. Acetonitrile and the water formed during the reaction were removed in vacuum. The crude product so obtained was passed through a 1 cm silica gel layer using ethyl acetate. After evaporating the solvent, the products 13a–c were obtained as crystals or oils. The following products were thus prepared:

**N,N-Bis(diphenylphosphinoylmethyl)amine (13a)**

Yield: 96% (0.21 g) of compound 13a as colorless oil. $^{31}$P NMR (CDCl₃) δ 29.6; $^{13}$C NMR (CDCl₃) δ 55.1 (d, $^1J_{CP} = 81.5$, $^3J_{CP} = 10.7$, NCH₂PPh₂), 128.6 (d, $^2J_{CP} = 11.7$, C₂), 131.2 (d, $^3J_{CP} = 9.4$, C₃), 131.4 (d, $^1J_{CP} = 98.1$, C₁), 132.0 (d, $^3J_{CP} = 2.6$, C₄); $^1$H NMR (CDCl₃) δ 3.68 (d, $^1J_{HP} = 6.8$, 4H, NHCH₃P), 5.29 (s, 1H, NH), 7.38–7.45 (m, 8H, C₃H), 7.48–7.54 (m, 4H, C₄H₃), 7.67–7.74 (m, 8H, C₂H); [M+H]⁺ found = 446.1427, C₂₆H₃₆NO₂P₂ requires 446.1438.

**N,N-(Diphenylphosphinoylmethyl)(di-p-tolylphosphinoylmethyl)amine (13b)**

Yield: 95% (0.22 g) of compound 13b as colorless oil. $^{31}$P NMR (CDCl₃) δ 29.4, 29.8; $^{13}$C NMR (CDCl₃) δ 21.6 (C₄CH₃), 50.5 (d, $^1J_{CP} = 81.5$, $^3J_{CP} = 10.4$, NCH₂PPh₂), 50.7 (dd,
$^1J_{CP} = 81.0$, $^3J_{CP} = 10.9$, NCH$_2$P(p-tolyl)$_2$, 128.2 (d, $^1J_{CP} = 100.4$, C$_1$), 128.5 (d, $^2J_{CP} = 11.6$, C$_2$), 129.3 (d, $^2J_{CP} = 12.0$, C$_2'$), 131.1 (d, $^3J_{CP} = 2.3$, C$_3$), 131.2 (d, $^3J_{CP} = 1.9$, C$_3'$), 131.4 (d, $^1J_{CP} = 98.2$, C$_1$), 131.9 (d, $^2J_{CP} = 2.7$, C$_4$), 142.4 (d, $^2J_{CP} = 2.8$, C$_4'$); $^1$H NMR (CDCl$_3$) $\delta$ 2.38 (s, 6H, C$_4$CH$_3$), 3.62 (d, 2H, $^1J_{HP} = 7.0$, NCH$_2$P(p-tolyl)$_2$), 3.67 (d, 2H, $^1J_{HP} = 7.1$, NCH$_2$PPh$_2$), 5.29 (s, 1H, NH), 7.17–7.21 (m, 4H, C$_3'$H), 7.36–7.46 (m, 4H, C$_3$H), 7.47–7.63 (m, 6H, C$_2'$H, C$_4$H), 7.65–7.76 (m, 4H, C$_2$H); [M+H]$^+$ found = 474.1752, C$_{28}$H$_{30}$NO$_2$P$_2$ requires 474.1751.

$N,N$-(Diphenylphosphinoylmethyl)(dibenzylphosphinoylmethyl)amine (13c)

Yield: 97% (0.23 g) of compound 13c as white crystals. Mp: 149–153 °C. $^{31}$P NMR (CDCl$_3$) $\delta$ 29.5, 43.8; $^{13}$C NMR (CDCl$_3$) $\delta$ 34.2 (d, $^1J_{CP} = 60.0$, P(O)CH$_2$), 46.5 (dd, $^1J_{CP} = 79.2$, C$_4$), 50.3 (dd, $^1J_{CP} = 80.7$, $^3J_{CP} = 9.4$, NCH$_2$PPh$_2$), 126.9 (d, $^1J_{CP} = 2.9$, C$_4$), 128.6 (d, $^2J_{CP} = 11.7$, C$_2$), 128.8 (d, $^1J_{CP} = 2.4$, C$_3'$), 129.6 (d, $^3J_{CP} = 5.1$, C$_2'$), 131.1 (d, $^3J_{CP} = 9.3$, C$_3$), 131.4 (d, $^1J_{CP} = 99.8$, C$_1$), 131.5 (d, $^2J_{CP} = 7.1$, C$_1'$), 132.1 (d, $^1J_{CP} = 2.8$, C$_4$); $^1$H NMR (CDCl$_3$) $\delta$ 2.89 (d, $^1J_{HP} = 6.6$, 2H, NCH$_2$PPh$_2$), 2.94–3.13 (m, 4H, P(O)CH$_2$Ph) 3.58 (d, $^1J_{HP} = 7.0$, 2H, NCH$_2$PBN$_2$), 5.29 (s, 1H, NH), 7.09–7.18 (m, 4H, C$_3'$H), 7.19–7.33 (m, 6H, C$_2'$H, C$_4'$H), 7.43–7.59 (m, 6H, C$_3$H, C$_4$H), 7.73–7.85 (m, 4H, C$_2$H); [M+H]$^+$ found = 474.1743, C$_{28}$H$_{30}$NO$_2$P$_2$ requires 474.1751.

General procedure for the synthesis of $N,N,N$-tris(phosphinoylmethyl)amines

A mixture of 0.50 mmol of $N,N$-bis(phosphinoylmethyl)amines (0.22 g of $N,N$-bis(diphenylphosphinoylmethyl)amine or 0.24 g of $N,N$-(diphenylphosphinoylmethyl)(di-p-tolylphosphinoylmethyl)amine), 0.015 g (0.50 mmol) of paraformaldehyde, and 0.50 mmol of the secondary phosphine oxide (0.12 g of dibenzylphosphine oxide, 0.12 g of di(p-tolyl)phosphine oxide or 0.10 g of diphenylphosphine oxide) and 1.5 mL of acetonitrile was heated at 100 °C in a closed vial in a CEM Discover microwave reactor equipped with a pressure controller for 2 h. Acetonitrile and the water formed during the reaction were
removed in vacuum. The crude product so obtained was passed through a 1 cm silica gel layer using ethyl acetate. After column chromatography, the products 14–17 were obtained as crystals. The following products were thus prepared:

**N,N,N-Tris(diphenylphosphinoylmethyl)amine (14)**

Yield: 27% (0.09 g) of compound 14 as white crystals. Mp: 71–74 °C. $^{31}\text{P}$ NMR (CDCl$_3$) δ 30.3; $^{13}\text{C}$ NMR (CDCl$_3$) δ 58.1 (dt, $^1J_{CP} = 83.5$, $^3J_{CP} = 7.6$, NCH$_2$PPh$_2$), 128.3 (d, $^2J_{CP} = 11.9$, C$_2$), 131.1 (d, $^3J_{CP} = 9.4$, C$_3$), 131.54 (d, $J_{CP} = 2.6$, C$_4$). 131.54 (d, $^1J_{CP} = 99.7$, C$_1$); $^1\text{H}$ NMR (CDCl$_3$) δ 4.21 (d, 6H, $^1J_{HP} = 6.6$, NCH$_2$PPh$_2$), 7.19–7.29 (m, 12H, C$_3$H), 7.33–7.41 (m, 6H, C$_4$H$_2$), 7.75 (dd, 12H, $^2J_{HP} = 11.1$, $J_{HP} = 7.8$, C$_2$H$_2$); [M+H]$^+$ found = 660.1972, C$_{39}$H$_{37}$NO$_3$P$_3$ requires 660.1986.

**N,N,N-[Bis(diphenylphosphinoylmethyl)(di-p-tolylphosphinoylmethyl)]amine (15)**

Yield: 77% (0.26 g) of compound 15 as white crystals. Mp: 76–79 °C. $^{31}\text{P}$ NMR (CDCl$_3$) δ 28.0, 28.3; $^{13}\text{C}$ NMR (CDCl$_3$) δ 21.5 (C$_4$CH$_3$), 58.1 (dd, $^1J_{CP} = 84.0$, $^3J_{CP} = 7.8$, NCH$_2$PPh$_2$), 58.3 (dd, $^1J_{CP} = 83.8$, $^3J_{CP} = 7.6$, NCH$_2$P(p-tolyl)$_2$), 128.5 (d, $^1J_{CP} = 102.1$, C$_1$), 128.4 (d, $^2J_{CP} = 11.9$, C$_2$), 129.1 (d, $^2J_{CP} = 12.2$, C$_2'$), 131.1 (d, $^3J_{CP} = 9.8$, C$_3'$), 131.2 (d, $^3J_{CP} = 9.4$, C$_3$), 131.5 (d, $J_{CP} = 2.7$, C$_4$), 131.7 (d, $^1J_{CP} = 99.5$, C$_1$), 141.8 (d, $J_{CP} = 2.8$, C$_4'$); $^1\text{H}$ NMR (CDCl$_3$) δ 2.30 (s, 6H, C$_4$CH$_3$), 4.14 (d, 2H, $^1J_{HP} = 6.3$, NCH$_2$P(p-tolyl)$_2$), 4.19 (d, 4H, $^1J_{HP} = 6.4$, NCH$_2$PPh$_2$), 7.03 (d, 4H, $^3J_{HP} = 6.0$, C$_3$H), 7.21–7.29 (m, 8H, C$_3$H), 7.38 (t, 4H, $J_{HP} = 67.2$, C$_4$H), 7.61 (dd, 4H, $^2J_{HP} = 11.2$, $J_{HP} = 8.0$, C$_2$H), 7.74 (dd, 8H, $^2J_{HP} = 11.2$, $J_{HP} = 7.60$, C$_2$H); [M+H]$^+$ found = 688.2281, C$_{41}$H$_{41}$NO$_2$P$_2$ requires 688.2299.
N,N,N-[Bis(diphenylphosphinoymethyl)(dibenzylphosphinoymethyl)]amine

(16)

Yield: 48% (0.16 g) of compound 16 as white crystals. Mp: 72–75 °C. $^{31}$P NMR (CDCl$_3$) δ 30.5, 40.8; $^{13}$C NMR (CDCl$_3$) δ 33.8 (d, $^1J_{CP} = 61.6$, P(O)CH$_2$), 55.6 (dd, $^1J_{CP} = 80.5$, $^3J_{CP} = 7.1$, NCH$_2$PBn$_2$), 56.6 (dd, $^1J_{CP} = 84.1$, $^3J_{CP} = 7.6$, NCH$_2$PPh$_2$), 125.7 (d, $J_{CP} = 2.7$, C$_4$), 127.5 (d, $^2J_{CP} = 11.7$, C$_2$), 127.6 (d, $J_{CP} = 2.4$, C$_3$), 128.7 (d, $^3J_{CP} = 5.3$, C$_2$), 130.1 (d, $^3J_{CP} = 9.4$, C$_3$), 130.3 (d, $^1J_{CP} = 99.4$, C$_1$), 130.7 (d, $^2J_{CP} = 7.8$, C$_1$), 130.9 (d, $J_{CP} = 2.8$, C$_4$); $^1$H NMR (CDCl$_3$) δ 2.63 (d, $^1J_{HP} = 13.2$, 4H, NCH$_2$PPh$_2$), 3.48 (dd, $^1J_{HP} = 59.9$, $^3J_{HP} = 4.7$, 4H, P(O)CH$_2$Ph), 3.96 (d, $^1J_{HP} = 6.5$, 2H, NCH$_2$PBn$_2$), 7.03 (d, $^3J_{HP} = 7.1$, 4H, C$_3$), 7.09–7.22 (m, 6H, C$_2$H, C$_4$H), 7.23–7.39 (m, 12H, C$_3$H, C$_4$H), 7.73–7.85 (m, 8H, C$_2$H); [M+H]$^+$ found = 688.2276, C$_{41}$H$_{41}$NO$_3$P$_3$ requires 688.2299.

N,N,N-[(Diphenylphosphinoymethyl)(di-$p$-tolylphosphinoymethyl) (dibenzylphosphinoymethyl)]amine (17)

Yield: 59% (0.21 g) of compound 17 as white crystals. Mp: 69–72 °C. $^{31}$P NMR (CDCl$_3$) δ 30.2, 30.4, 40.52, $^{13}$C NMR (CDCl$_3$) δ 21.5 (C$_4$H$_3$), 34.8 (d, $^1J_{CP} = 61.4$, P(O)CH$_2$Ph), 56.7 (dd, $^1J_{CP} = 78.8$, $^3J_{CP} = 7.5$, NCH$_2$PBn$_2$), 57.7 (dd, $^1J_{CP} = 83.8$, $^3J_{CP} = 7.6$, NCH$_2$PPh$_2$), 57.8 (dd, $^1J_{CP} = 85.7$, $^3J_{CP} = 8.4$, NCH$_2$P($p$-tolyl)$_2$), 126.9 (d, $J_{CP} = 2.9$, C$_v$), 128.3 (d, $^1J_{CP} = 101.8$, C$_1$), 128.5 (d, $^2J_{CP} = 11.8$, C$_2$), 128.6 (d, $J_{CP} = 1.9$, C$_3$), 129.3 (d, $^2J_{CP} = 12.1$, C$_2$), 129.7 (d, $^3J_{CP} = 5.2$, C$_2$), 131.16 (d, $^3J_{CP} = 9.2$, C$_3$), 131.23 (d, $^3J_{CP} = 8.5$, C$_4$), 131.5 (d, $^1J_{CP} = 99.3$, C$_3$), 131.7 (d, $J_{CP} = 2.7$, C$_4$), 131.8 (d, $^2J_{CP} = 9.7$, C$_1$), 142.1 (d, $J_{CP} = 2.7$, C$_v$); $^1$H NMR (CDCl$_3$) δ 2.31 (s, 6H, C$_6$H$_3$), 2.73 (d, 4H, $^1J_{HP} = 13.2$, PCH$_2$Ph), 3.47 (d, 2H, $^1J_{HP} = 6.4$, NCH$_2$PBn$_2$), 3.99 (d, 2H, $^1J_{HP} = 6.4$, NCH$_2$P($p$-tolyl)$_2$), 4.03 (d, 2H, $^1J_{HP} = 6.2$, NCH$_2$PPh$_2$), 7.12 (d, 4H, $^3J_{HP} = 7.3$, C$_3$H), 7.14–7.17 (m, 4H, C$_3$H), 7.24–7.30 (m, 6H, C$_3$H, C$_4$H), 7.35–7.41 (m, 4H, C$_2$H), 7.42–7.46 (m, 2H, C$_2$H), 7.73 (dd, 4H, $^2J_{HP} = 11.2$, $J_{HP} = 8.0$, C$_2$H), 7.88 (dd, 8H, $^2J_{HP} = 11.4$, $J_{HP} = 7.17$, C$_2$H); [M+H]$^+$ found = 716.2584, C$_{41}$H$_{41}$NO$_3$P$_3$ requires 716.2612.
$^{13}$C NMR (CDCl$_3$)

$^{31}$P NMR (CDCl$_3$)
$^{31}$P NMR (CDCl$_3$)

$^{1}H$ NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^{31}$P NMR (CDCl$_3$)

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