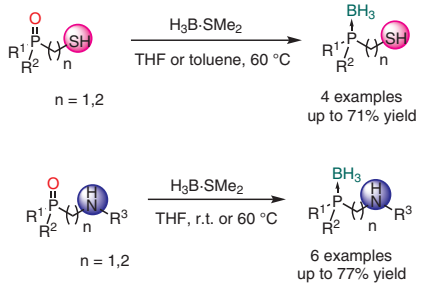
Synthesis S. Sowa et al. Paper

Reduction of Tertiary Phosphine Oxides by BH_3 Assisted by Neighboring Activating Groups

Sylwia Sowa
Marek Stankevič
Anna Flis
K. Michał Pietrusiewicz*

Department of Organic Chemistry, Faculty of Chemistry, Maria Curie Skłodowska University, Gliniana St. 33, Lublin 20-614, Poland
kazimierz.pietrusiewicz@poczta.umcs.lublin.pl



Received: 12.12.2017
Accepted after revision: 25.01.2018
Published online: 21.02.2018
DOI: 10.1055/s-0036-1591546; Art ID: ss-2017-z0812-op

Abstract Tertiary sulfanylphosphine and aminoalkylphosphine oxides can be easily converted into the corresponding tertiary sulfanylphosphine- and aminoalkylphosphine-boranes, respectively, through the facile P=O bond reduction by borane complexes. The easy reduction of the strong P=O bond by BH_3, a mild reducing agent, has been achieved through an intramolecular P=O -- B complexation directed by proximal SH or NH activating groups located at the α- or β-position to the P=O bond. A generalized reduction mechanism has been proposed.

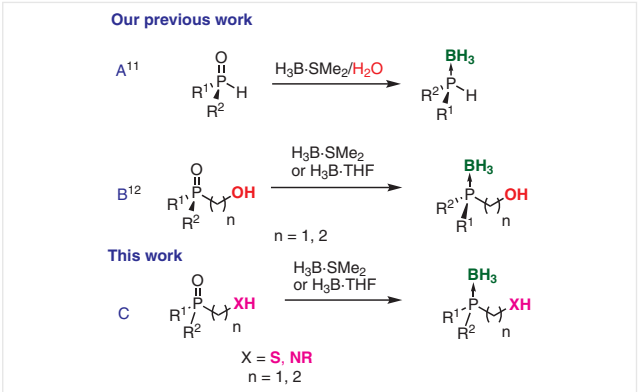
Key words phosphine-boranes, phosphine oxides, P=O bond reduction, reduction by borane, aminophosphines, sulfanylphosphines, neighboring group effects

The reduction of phosphine oxides to phosphines is one of the most useful and explored synthetic routes in organophosphorus chemistry.[1] Many different reducing agents have been employed but none of them resolve all problems. Metal hydrides, the reagents of first choice, are often used as reducing agents but they are incompatible with compounds possessing other reactive functionalities or chirality centers at the phosphorus atom.[2] To date, silanes are reducing agents of the greatest importance in organophosphorus chemistry. Among them $HSiCl_3$,[3] $PhSiH_3$,[4] and Si_2Cl_6[5] appear to be the most efficient and tolerant towards other functional groups. The reduction reactions usually occur in high yields and with high stereoselectivity. A range of modifications have also been developed, which include the addition of various additives to both silane[5a,6] and metal hydride reagents[7] for improving their activity or selectivity. The reduction of phosphine oxide is very often the limiting step in the synthetic sequence leading sometimes to the failure of the synthesis due to the huge loss of target phosphine during purification.[8] Therefore new, milder, simpler, and more selective methods for the reduction of strong P=O bond are in constant demand.

A rational approach to avoid dissipative phosphine isolation process would be a direct transformation of phosphine oxides into easily handled and storable phosphine-boranes. The development of new protocols for this type of transformations is one of the most attractive research topics in current organophosphorus chemistry.[9] Protocols, which can use BH_3 or its complexes as reducing agents are getting growing attention due to the mild reducing character of BH_3.[10]

Previously, we have shown that $H_3B{\cdot}SMe_2$ could be used for P=O bond reduction in secondary phosphine oxides directly providing the corresponding secondary phosphine-boranes. This reaction proceeded under mild reaction conditions and the addition of a small amount of water to the reaction mixture remarkably increased the yield of the products (Scheme 1A).[11] Recently, our group demonstrated that the same effect could be achieved for tertiary phosphine oxides possessing hydroxyl group in the carbon skeleton at the α- or β-carbon atom (Scheme 1B). The role of the hydroxyl group is to bind BH_3 and to facilitate its intramolecular coordination with phosphoryl oxygen, which in turn enables reduction of the P=O bond by another molecule of BH_3. Moreover, phosphine oxides possessing hydroxyalkyl group undergo the reduction of P=O bond in a highly stereoselective way.[12] Therefore, this approach could be recognized as a useful tool for the synthesis of new P-stereogenic phosphine-boranes as elegantly demonstrated by Buono and co-workers.[13]

Herein, we wish to present our results concerning the use of BH_3 for reduction of P=O bond in phosphine oxides possessing neighboring SH or NH activating groups (Scheme 1C). The success of this type of reductions opens a new route to the precursors of P,N-[14–16] and P,S-type[17]



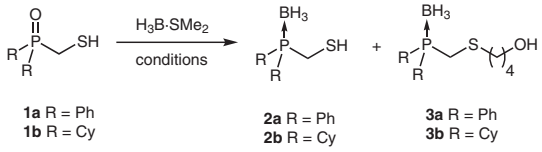
Scheme 1 Reduction of functionalized tertiary phosphine oxides with BH_3

ligands or reagents for Staudinger ligation.[18] Some precedents for NH-assisted reductions of phosphine oxides by BH_3 already exist[13a,14] but, to the best of our knowledge, there has been no evidence in the literature for the reduction of P=O bond in organophosphorus compounds possessing SH moiety as an activating group.

To probe the effect of an α-sulfanyl group on the facility of reduction of the P=O bond by BH_3, diphenyl(α-sulfanylmethyl)phosphine oxide (**1a**) and di-*c*-hexyl(α-sulfanylmethyl)phosphine oxide (**1b**) were chosen as substrates. In the preliminary experiment, phosphine oxide **1a** was treated with 3 equivalents of $H_3B{\cdot}SMe_2$ under conditions analogous to those developed by us for the reduction of α-hydroxyphosphine oxides.[12] It turned out that the activating effect of sulfur has been lower than oxygen still, however, this protocol enabled the complete conversion of phosphine oxide **1a**. We observed the formation of two phosphine-borane products **2a** and **3a** in a ratio of 0.56:1 (according to ^{31}P NMR spectrum) isolated in 29% and 31% yield, respectively (Table 1, entry 1). The phosphine oxide **1b** showed lower reactivity than **1a.** To complete the conversion of **1b** an increase in the amount of $H_3B{\cdot}SMe_2$ to 10 equivalents and prolongation of the reaction time to 24 hours were needed. That resulted in the formation of **3b** as the main product (according to ^{31}P NMR spectrum) isolated in 27% yield (entry 2).

The observed formation of phosphine-boranes **3** could be explained by the nucleophilic attack of an α-sulfanylphosphine-borane **2** on a BH_3-activated THF molecule resulting in the ring opening. To avoid this side reaction, THF was replaced with toluene. In this solvent, the complete conversion of an α-sulphanylphosphine oxide required the use of 6 equivalents of $H_3B{\cdot}SMe_2$and 16 hours reaction time in the case of **1a**, and 10 equivalents of $H_3B{\cdot}SMe_2$ and 24 hours reaction time in the case of **1b** (Table 1, entry 3 and 4, respectively). Quite surprisingly, despite the applied excess of borane a complete in situ complexation of the formed phosphines by BH_3 in toluene could not be achieved. In both

Table 1 Reactivity of α-Sulfanylphosphine Oxides Towards $H_3B{\cdot}SMe_2$

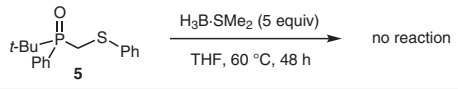


Entry	Compound	Conditions	Product	Yield (%)[a]
1	**1a**	$H_3B{\cdot}SMe_2$ (3 equiv), THF, 60 °C, 3 h	**2a** **3a**	29 (37)[b] 31 (63)[b]
2	**1a**	$H_3B{\cdot}SMe_2$ (10 equiv), THF, 60 °C, 24 h	**2b** **3b**	14 (25)[b] 27 (75)[b]
3	**1a**	$H_3B{\cdot}SMe_2$ (6 equiv), toluene, 60 °C, 16 h	**2a**	51 (60)[b,c,d]
4	**1b**[e]	$H_3B{\cdot}SMe_2$ (10 equiv), toluene, 60 °C, 24 h	**2b**	72 (77)[b,c,d]

[a] Isolated yields.
[b] Numbers in parentheses indicate yields according to ^{31}P NMR analysis.
[c] Isolated yield after additional boronation of the free phosphine formed under the reaction conditions (see Experimental Section).
[d] Partial oxidation took place before boranation.
[e] Compound **1b** has undergone partial dimerization forming bis-(di-*c*-hexylphosphorylmethyl) disulfide (**4**) while standing in $CHCl_3$ overnight (see Experimental Section).

cases a mixture of phosphine-borane **2** and the corresponding free phosphine in a ratio of 1:1.14 (for the reaction of **1a**) and 1:1 (for the reaction of **1b**) were observed in the crude reaction mixtures by ^{31}P NMR spectroscopy. However, evaporation of toluene, dissolution of the residue in ethyl acetate, and addition of extra $H_3B{\cdot}SMe_2$ (3 equiv) enabled the isolation of **2a** and **2b** as the only products in 51% and 72% yield, respectively (entries 3 and 4).

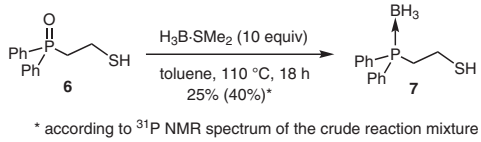
To confirm the activating effect of the α-sulfanyl group in the studied reductions, *tert*-butyl(phenylthiomethyl)phenylphosphine oxide (**5**) possessing protected sulfanyl group was submitted to the reaction under the studied conditions. As indicated in Scheme 2, no reaction was observed. This observation underscores the key role of the free SH group in the studied reduction process.



Scheme 2 Attempted reduction *tert*-butylphenyl(phenylthiomethyl)-phosphine oxide (**5**)

Next, we decided to check the reduction of diphenyl(2-sulfanylethyl)phosphine oxide (**6**) as a model for β-sulfanylphosphine oxides. Not unexpectedly, it turned out that placing the SH group in the β-position to phosphorus atom drastically decreased its activating effect. When the reaction was carried out at 60 °C, no conversion of the starting material was observed even after prolonged reaction time. Raising the reaction temperature to 110 °C for 18 hours led

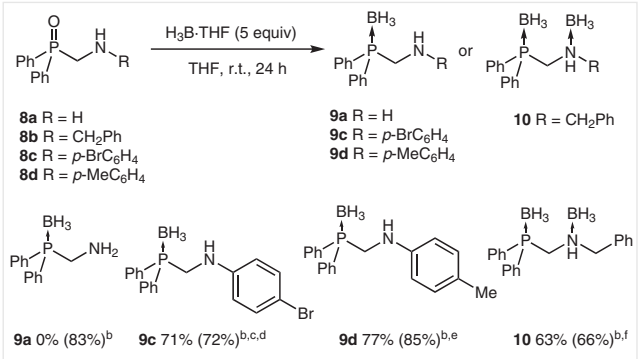
to the formation of the desired diphenyl(2-sulfanylethyl)phosphine-borane (**7**) albeit only in 25% yield (Scheme 3). However, under these conditions, starting phosphine oxide **6** appeared to be unstable, which might partially account for the observed low yield of **7**.



Scheme 3 Reduction of diphenyl(2-sulfanylethyl)phosphine oxide (**6**)

In extension of our study on BH_3 reduction of α-aminophosphine oxides, a short series of phosphine oxides **8** with varied substitution patterns were tested (Scheme 4). The activating effect of the α-amino group in these reactions was found to be higher than the one observed for α-sulfanylphosphine oxides. In nearly all cases the reactions proceeded to completion within 24 hours and at room temperature. It was also found that substituents at nitrogen atom remarkably improved stability of phosphine-boranes during their isolation. The formation of phosphine-borane **9a** with a primary amino group was observed only by ^{31}P NMR spectroscopy as this compound underwent decomposition during attempted purification. Interestingly, introduction of an aryl electron-withdrawing group at the nitrogen atom, like in **8c**, remarkably facilitated the reduction process. In this case, the formation of the desired aminophosphine-borane **9c** in 71% yield [along with 9% of secondary diphenylphosphine-borane (**11**) as the by-product] was observed already after 1 hour. By comparison, the analogous oxide **8b** possessing an electron-donating substituent was converted to the corresponding tertiary phosphine-borane with similar effectiveness but only after 24 hours and after using 10 equivalents of BH_3. In this case, however, the reaction afforded diborane **10**, apparently as a consequence of the higher electron density on alkyl-substituted nitrogen atom coinciding with a larger excess of used BH_3 enabling additional complexation at nitrogen atom.

In turn, reduction of an α-Ph-substituted (aminomethyl)phosphine oxide **12**[19] provided the desired phosphine-borane **13**[20] in 37% yield along with a secondary amine **14** (32%), secondary *o*-anisylphenylphosphinous acid-borane (**15**,[11b] 26%), and *o*-anisylphenylphosphine-borane (**16**,[11a] 4%) (Scheme 5). The latter three products were most probably formed in a retro-Kabachnik–Fields process reverting phosphine oxide **12** to a secondary phosphine oxide and an imine, which both were further reacted with BH_3 under the reaction conditions to give the observed **16**,[11a] **15**,[11b] and amine **14**. It is worth noting that α-Ph-substituted (aminomethyl)phosphine oxide **12** was found to be thermally stable when heated without BH_3 at 60 °C for 24 hours. Most probably, in the studied reduction, BH_3 acted also as a Lewis acid facilitating the observed retro-Kabachnik–Fields reaction. The same explanation could be applied to the formation of secondary diphenylphosphine-borane (**11**) during the reduction of **8c** and **8d**.[21]



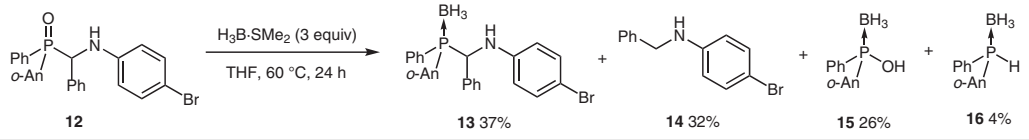
[a] Isolated yields of products are shown; [b] Numbers in parentheses indicate yields according to ^{31}P NMR analysis; [c] Reaction was carried out for 1 h; [d] Additionally 9% of diphenylphosphine-borane (**11**) and 20% of starting material **8d** were isolated; [e] Formation of diphenylphosphine-borane (**11**) was also observed; [f] Reaction was carried out with 10 equiv of $H_3B{\cdot}SMe_2$.

Scheme 4 Reactivity of α-aminophosphine oxides **8** towards BH_3 complexes.[a]

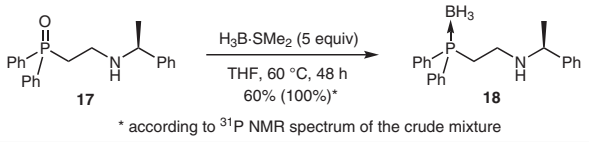
In accordance with the literature precedent,[14b] oxide **17** was found reactive enough to undergo reduction by $H_3B{\cdot}SMe_2$ and afforded the desired phosphine-borane product **18** in 60% yield. In this case, however, it was necessary to increase the reaction temperature to 60 °C to achieve the complete conversion of phosphine oxide **17**.

Finally, a singular β-aminophosphine oxide **17** was subjected to reduction with $H_3B{\cdot}SMe_2$ (Scheme 6).

In light of this and the previous work,[12,13a] we would like to propose a generalized reduction mechanism as depicted in Scheme 7. Initially, a reaction of BH_3 with an XH group of **I** affords intermediate **II** along with liberation of hydrogen gas. The formation of an intermediate of type **II** seems to be



Scheme 5 Reduction of α-Ph-substituted (aminomethyl)phosphine oxide **12** with $H_3B{\cdot}SMe_2$



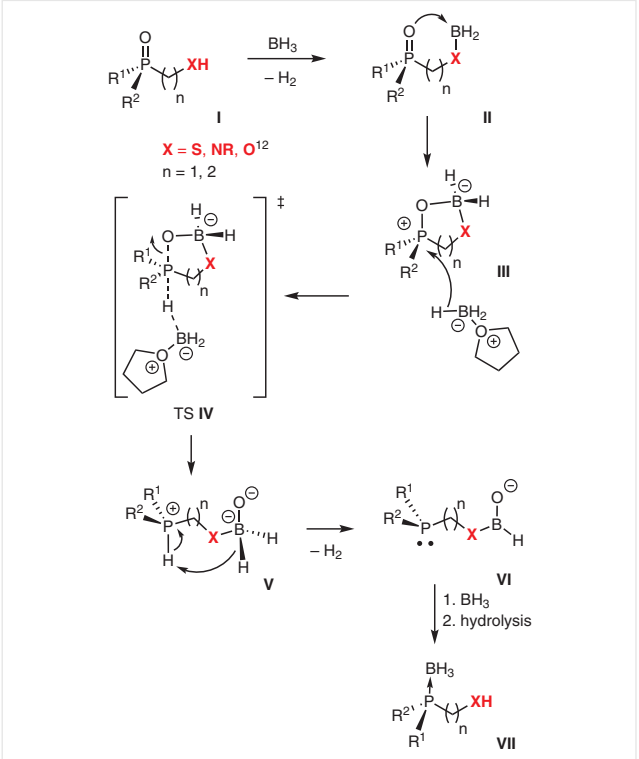
Scheme 6 Reduction of β-aminophosphine oxide (**17**)

prerequisite for the reduction process to occur. This would explain the observed lack of reactivity of S-protected thiolo phosphine oxide **6** towards BH_3, in analogy to inertness of an O-protected hydroxy phosphine oxide studied previously.[13a] In the next step, the intramolecular coordination of the resulting proximal boron functionality to phosphoryl oxygen leads to the formation of a cyclic zwitterionic intermediate **III**. Such intramolecular coordination process is effective only for phosphine oxides possessing an activating group at the α- or the β-position to phosphorus atom for which generation of the readily formed 5- or 6-membered ring intermediate **III** is possible.[12] In the next step, hydride transfer from external borane to phosphorus atom causes cleavage of the activated P–O bond in an S_N2-type process. In this step, the occurrence of a 5-membered ring in the trigonal bipyramidal transition state TS **IV** (n = 1) leads to lowering of its energy and facilitates the reduction process under mild conditions. As the experiments have confirmed, less effective stabilization of TS **IV** (n = 2) by a 6-memberd ring in the case of β-positioned activating groups necessitates typically elevation of reaction temperatures and application of longer reaction times.

Finally, the protonated phosphine **V** liberates another hydrogen molecule to give a free phosphine **VI**, which eventually undergoes complexation with BH_3 followed by hydrolytic deprotection of the activating group to give the final phosphine-borane **VII**.

The proposed mechanism seems to be general regardless of the type of activating group present in the phosphine oxide structure. It also implies that the inversion of configuration at phosphorus has to take place in the reduction step in each case. Reported observations that P-stereogenic hydroxymethylphosphinates, hydroxymethylphosphine oxides and β-aminophosphine oxides are reduced by BH_3 with inversion of configuration[10f,12,13a,14b] corroborate this statement fully.

In conclusion, a general and efficient method for the reduction of the P=O bond in tertiary phosphine oxides possessing activating group in proximity to phosphorus atom by commercially available BH_3 complexes has been further expanded. The key role of neighboring α or β activating group in the reduction process of phosphine oxide as well as the effect of the distance between the interacting centers were demonstrated. New convenient synthetic routes leading directly to aminophosphine-boranes and sulfanylphosphine-boranes have been developed.



Scheme 7 Plausible generalized mechanism of P=O bond reduction with BH_3

All reactions were performed under an argon atmosphere using Schlenk techniques. Only anhydrous solvents were used and all glassware were heated under vacuum prior to use. All chemicals were used as received, unless noted otherwise. Solvents for chromatography and crystallization were distilled once before use and the solvents for extraction were used as received. THF and toluene were distilled from sodium/benzophenone ketyl under argon. ^{1}H NMR, ^{31}P NMR, and ^{13}C NMR spectra were recorded on a Bruker Avance-500 spectrometer at ambient temperature in $CDCl_3$, unless otherwise noted. Chemical shifts (δ) are reported in ppm relative to residual solvent peak (7.26 ppm for ^{1}H and 77 ppm for ^{13}C). Mass spectra were recorded on Shimazu GC-MS QP2010S in electron ionization (EI) or fast atom bombardment (FAB) mode. IR spectra were recorded on Thermo Scientific Nicolet iS50 FT-IR ATR mode with diamond prism (4000–400 cm^{-1} window) as solids or thin films. In the IR spectra, only the strongest/structurally most important peaks (cm^{-1}) are listed. Melting points were determined on Büchi Melting Point M-560 in a capillary tube and are uncorrected. HPLC-HRMS analyses were performed on Shimazu HRMS ESI-IT-TOF using reverse phase stationary phase with H_2O/MeOH (80:20) as eluent, electrospray ionization (ESI), and IT-TOF detector. Optical rotations were measured on PerkinElmer 341LC spectrometer using a 1 mL cell with a 10 mm path length and are reported as follows: $[\alpha]_D^{25}$ (*c* g/100 mL, solvent). Elementary analyses were performed on a PerkinElmer CHN 2400 analyzer. TLC analyses were performed with precoated silica gel plates and visualized by UV light or $KMnO_4$ solution or I_2 on silica gel. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh).

The starting compounds: *tert*-butylphenylphosphine oxide,[22] *o*-anisylphenylphosphine oxide,[23] diphenylphosphine oxide,[2c] di-*c*-hexylphosphine oxide[24] were prepared according to reported methods. Optically active 2-[*N*-(1-methylbenzylamino)]ethyl(diphenyl)phosphine oxide[16] and diphenylvinylphosphine oxide[25] were available from another studies. The syntheses of starting sulfanylalkylphosphine oxides **1a**,**b**, **5**, **6** and aminoalkylphosphine oxides **8a–d** and **12** are detailed below.

α-Hydroxyphosphine Oxides; General Procedure

To a solution of respective secondary phosphine oxide (2.0 mmol) in anhyd THF was added DBU (29 µL, 0.2 mmol) followed by paraformaldehyde (180 mg, 6 mmol). The reaction mixture was heated at 60 °C for 24 h. The mixture was then evaporated to dryness and the residue was dissolved in CH_2Cl_2 (10 mL) and quenched with sat. aq NH_4Cl (5 mL). The resulting mixture was extracted with CH_2Cl_2 (5 × 30 mL), the combined organic phases were dried (anhyd Na_2SO_4), and evaporated. The residue was purified by column chromatography on silica gel using $CHCl_3$/EtOAc/MeOH (30:5:1, v/v/v) as eluent.

tert-Butyl(hydroxymethyl)phenylphosphine Oxide[12]

tert-Butylphenylphosphine oxide (0.364 g, 2.0 mmol) was reacted according to the general procedure to afford the title compound (0.33 g, 1.56 mmol, 78%) as a beige solid; mp 153.7–154.7 °C; R_f = 0.47 (EtOAc–MeOH 10:1).

IR (film, ATR): 3161, 2948, 2868, 1475, 1436, 1361, 1218, 1140, 1105, 1049, 839, 816, 753, 742, 694, 631, 507, 471, 439 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.66–7.69 (m, 2 H), 7.40–7.44 (m, 2 H), 7.48–7.50 (m, 1 H), 5.47 (br s, 1 H), 4.44 (dd, $J_{P,H}$ = 14.5 Hz, $J_{H,H}$ = 6.94 Hz, 1 H), 4.24 (dd, $J_{P,H}$ = 14.19 Hz, $J_{H,H}$ = 6.31 Hz, 1 H), 1.18 (d, $J_{H,P}$ = 14.19 Hz, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 131.6 (d, $J_{P,C}$ = 2.73 Hz), 131.5 (d, $J_{P,C}$ = 7.3 Hz), 128.7 (d, $J_{P,C}$ = 85.4 Hz), 128.2 (d, $J_{P,C}$ = 10.9 Hz), 57.4 (d, $J_{P,C}$ = 71.8 Hz), 32.5 (d, $J_{P,C}$ = 64.5 Hz), 24.6.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 46.39 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{17}O_2P$: 213.1039; found: 213.1039.

Anal. Calcd for $C_{11}H_{17}O_2P$: C, 62.25; H, 8.07. Found: C, 62.40; H, 8.11.

Diphenyl(hydroxymethyl)phosphine Oxide[26]

Diphenylphosphine oxide (0.404 g, 2 mmol) was reacted according to the general procedure to afford the title compound (0.371 g, 1.43 mmol, 73%) as a white solid; mp 135.4–135.9 °C; R_f = 0.27 ($CHCl_3$/MeOH 30:1).

IR (solid, ATR): 3201, 1436, 1214, 1151, 1122, 1097, 1052, 852, 740, 718, 691, 543, 489, 460, 435 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.78–7.75 (m, 3 H), 7.55–7.52 (m, 2 H), 7.48–7.45 (m, 3 H), 5.2 (br s, 1 H), 4.43 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.14 (s), 131.36 (d, $J_{P,C}$ = 9.08 Hz), 130.60 (d, $J_{P,C}$ = 86.29 Hz), 128.67 (d, $J_{P,C}$ = 10.90 Hz), 61.38 (d, $J_{P,C}$ = 81.74 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 30.90 (s).

HRMS (ESI-TOF): *m*/*z* [2 M + H]$^+$ calcd for $C_{13}H_{13}O_2P$: 465.1379; found: 465.1388.

Anal. Calcd for $C_{13}H_{13}O_2P$: C, 67.24; H, 5.64. Found: C, 67.09; H, 5.34.

Di-*c*-hexyl(hydroxymethyl)phosphine Oxide[12]

Di-*c*-hexylphosphine oxide (0.428 g, 2.0 mmol) was reacted according to the general procedure to afford the title compound (0.366 g, 1.5 mmol, 75%) as a yellowish solid; mp 154.1–155 °C; R_f = 0.21 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3231, 2931, 2917, 2851, 1739, 1446, 1141, 1116, 1042, 899, 857, 780, 657, 529, 491, 448, 426 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 4.47 (br s, 1 H), 3.95 (s, 2 H), 1.92–1.99 (m, 2 H), 1.79–1.91 (m, 8 H), 1.69–1.74 (m, 2 H), 1.40–1.54 (m, 4 H), 1.20–1.31 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 56.02 (d, $J_{P,C}$ = 72.66 Hz), 34.15 (d, $J_{P,C}$ = 61.67 Hz), 26.48 (d, $J_{P,C}$ = 11.81 Hz), 26.46 (d, $J_{P,C}$ = 11.81 Hz), 25.84, 25.33, 24.99.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 50.41 (s).

HRMS (ESI-TOF): *m*/*z* [2 M + H]$^+$ calcd for $C_{13}H_{25}O_2P$: 489.3257; found: 489.3244.

Anal. Calcd for $C_{13}H_{25}O_2P$: C, 63.91; H, 10.31. Found: C, 63.76; H, 10.63.

α-Chlorophosphine Oxides; General Procedure

In a two-necked round-bottom flask (50 mL) equipped with a magnetic stirrer and an argon inlet were placed the respective α-hydroxyphosphine oxide[12] (1.4 mmol) and PCl_5 (0.295 g, 1.41 mmol) in anhyd toluene/$CHCl_3$ mixture(5 mL/2 mL). The reaction mixture was heated at 60 °C for 24 h. Then, the solvent and $POCl_3$ were removed under reduced pressure. The residue was purified by column chromatography on silica gel using $CHCl_3$/EtOAc/MeOH (30:5:1 v/v/v) as eluent.

(Chloromethyl)diphenylphenylphosphine Oxide[27]

Diphenyl(hydroxymethyl)phosphine oxide (0.325 g, 1.4 mmol) was reacted according to the general procedure to afford the title compound (0.295 g, 1.18 mmol, 84%) as a white solid; mp 134.8–135.3 °C; R_f = 0.44 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 2974, 2924, 1441, 1404, 1194, 1127, 1106, 814, 756, 693, 671, 534, 491, 449, 417 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.79–7.84 (m, 4 H), 7.58–7.62 (m, 2 H), 7.50–7.54 (m, 4 H), 4.05 (d, J_{H-P} = 6.62 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.63 (d, $J_{P,C}$ = 3.63 Hz), 131.52 (d, $J_{C,P}$ = 9.08 Hz), 129.61 (d, $J_{C,P}$ = 130.54 Hz), 128.73 (d, $J_{C,P}$ = 12.72 Hz), 37.66 (d, $J_{C,P}$ = 71.75 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 28.32 (s).

MS (EI, 70 eV): *m*/*z* (%) = 251 (0.2), 250 (0.6, [M]), 249 (0.4), 201 (13), 201 (100), 183 (5), 152 (5), 108 (4), 91 (9), 77 (28), 51 (22).

HRMS (ESI-TOF): *m*/*z* [2 M + H]$^+$ calcd for $C_{13}H_{12}ClOP$: 501.0701; found: 501.0715.

Anal. Calcd for $C_{13}H_{12}ClOP$: C, 62.29; H, 4.83. Found: C, 61.99; H, 4.58.

Chloromethyl(di-*c*-hexyl)phosphine Oxide

Hydroxymethyl(di-*c*-hexyl)phosphine oxide (0.342 g, 1.4 mmol) was reacted according to the general procedure to afford the title compound (0.324 g, 1.23 mmol, 88%) as a white solid; mp 84.2–84.6 °C; R_f = 0.44 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 2972, 2917, 2846, 1739, 1445, 1215, 1169, 1143, 1003, 888.47, 856, 671, 533, 478, 420 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.58 (d, $J_{H,P}$ = 7.57 Hz, 2 H), 1.97–2.05 (m, 4 H), 1.81–1.90 (m, 6 H), 1.70–1.76 (m, 2 H), 1.46–1.64 (m, 4 H), 1.21–1.36 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 34.21 (d, $J_{C,P}$ = 58.1 Hz), 31.76 (d, $J_{C,P}$ = 57.22 Hz), 26.45 (d, $J_{C,P}$ = 12.73 Hz), 26.50 (d, $J_{C,P}$ = 11.81 Hz), 25.74, 25.39 (d, $J_{C,P}$ = 3.63 Hz), 24.90 (d, $J_{C,P}$ = 2.72 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 50.43 (s).

MS (EI, 70 eV): *m*/*z* (%) = 264 (1), 262 (3, [M]), 213 (9), 207 (6), 183 (7), 182 (12), 180 (32), 125 (12), 113 (12), 99 (23), 83 (66), 82 (31), 81(21), 79 (14), 67 (22), 55 (100), 54 (14), 53 (12).

HRMS (ESI-TOF): *m*/*z* [2 M + H]$^+$ calcd for $C_{13}H_{24}ClOP$: 525.2579; found: 525.2573.

Anal. Calcd for $C_{13}H_{24}ClOP$: C, 59.42; H, 9.21. Found: C, 59.05; H, 8.95.

α-Acetylthiophosphine Oxides; General Procedure

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet containing a solution of the respective α-chlorophosphine oxide (1 mmol) in anhyd DMF (2 mL) was added KSAc (2.5 mmol, 0.286 g). Then, the reaction mixture was stirred for 18 h at r.t. (25 °C) and evaporated to dryness. The residue was dissolved in CH_2Cl_2 (10 mL) and sat. aq NH_4Cl (5 mL) was added. The resulting mixture was extracted with CH_2Cl_2 (5 × 30 mL). The combined organic phases were dried (anhyd Na_2SO_4) and evaporated. The residue was purified by column chromatography on silica gel using $CHCl_3$/EtOAc/MeOH (30:5:1, v/v/v) or $CHCl_3$/MeOH (100:1, v/v) as eluent.

Acetylthiomethyl(diphenyl)phosphine Oxide[27]

Chloromethyl(diphenyl)phosphine oxide was reacted according to the general procedure (0.251 g, 1 mmol) to afford the title compound (0.232 g, 0.8 mmol, 80%) as a white solid; mp 94.7–96.3 °C; R_f = 0.40 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3053, 2948, 2896, 1694, 1438, 1188, 1123, 1102, 956, 752, 722, 692, 623, 533, 500, 418 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74–7.78 (m, 4 H), 7.52–7.56 (m, 2 H), 7.45–7.49 (m, 4 H), 3.76 (d, $J_{H,P}$ = 8.20 Hz, 2 H), 2.35 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.07 (d, $J_{P,C}$ = 4.54 Hz), 132.28 (d, $J_{P,C}$ = 2.72 Hz), 131.14 (d, $J_{P,C}$ = 103.54 Hz), 131.02 (d, $J_{P,C}$ = 9.99 Hz), 128.61 (d, $J_{P,C}$ = 11.81 Hz), 29.98, 27.23 (d, $J_{P,C}$ = 69.94 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.01 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{15}O_2PS$: 291.0595; found: 291.0603.

Anal. Calcd for $C_{15}H_{15}O_2PS$: C, 62.06; H, 5.21. Found: C, 61.91; H, 5.00.

Acetylthiomethyl(di-*c*-hexyl)phosphine Oxide

According to the general procedure, chloromethyl(di-*c*-hexyl)phosphine oxide (0.262 g, 1 mmol) was heated at 60 °C for 24 h to afford the title compound (0.299 g, 0.99 mmol, 99%) as a beige waxy solid; mp 94.7–96.3 °C; R_f = 0.40 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 2926, 2849, 1693, 1445, 1165, 1112, 956, 852, 825, 789, 626, 534, 453, 415 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.21 (d, $J_{H,P}$ = 8.20 Hz, 2 H), 2.38 (s, 3 H), 1.95–1.98 (m, 2 H), 1.78–1.89 (m, 8 H), 1.69–1.74 (m, 2 H), 1.37–1.49 (m, 4 H), 1.19–1.21 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.64 (d, $J_{P,C}$= 3.63 Hz, C), 35.98 (d, $J_{P,C}$= 65.39 Hz, CH), 30.19 (CH_3), 26.45 (d, $J_{C,P}$ = 12.73 Hz, CH_2), 26.38 (d, $J_{C,P}$ = 12.73 Hz, CH_2), 25.77 (CH_2), 25.65 (d, $J_{C,P}$ = 2.72 Hz, CH_2), 25.23 (d, $J_{C,P}$ = 3.63 Hz, CH_2).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 49.26 (s).

MS (EI, 70 eV): *m*/*z* (%) = 261 (5), 260 (29, [M]), 259 (16), 251 (11), 250 (8), 219 (6), 218 (6), 213 (8), 179 (22), 178 (100), 177 (7), 163 (5), 162 (14), 113 (12), 97 (29), 95 (14), 94 (13), 83 (27), 82 (8), 81 (33), 80 (5), 79 (14), 67 (10), 60 (25), 55 (71), 47 (6), 46 (7), 45 (39).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{27}O_2PS$: 303.1542; found: 303.1531.

Anal. Calcd for $C_{15}H_{27}O_2PS$: C, 59.57; H, 9.00. Found: C, 59.27; H, 8.69.

α-Sulfanylphosphine Oxides 1; General Procedure

Aq 3 M NaOH (0.7 mL, 2.1 mmol) was added to a solution of acetylthiomethylphosphine oxide (0.7 mmol) in anhyd MeOH (5 mL). The mixture was stirred at r.t. for 30 min. Then, the reaction mixture was acidified with aq 1 M HCl and extracted with $CHCl_3$ (5 × 20 mL). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and evaporated. The residue was purified by column chromatography using $CHCl_3$/EtOAc/MeOH (30:5:1, v/v/v) or $CHCl_3$/MeOH (100:1, v/v) as eluent.

Diphenyl(sulfanylmethyl)phosphine Oxide (1a)[18b]

Acetylthiomethyl(diphenyl)phosphine oxide (0.203 g, 0.7 mmol) was reacted according to the general procedure to afford **1a** as a white solid (0.132 g, 0.532 mmol, 76%); mp 121.4–122.1 °C; R_f = 0.29 ($CHCl_3$/MeOH 50:1).

IR (solid, ATR): 2944, 2898, 2360, 1435, 1182, 1120, 936, 776, 741, 720, 690, 529,506, 451, 416 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75–7.79 (m, 4 H), 7.56–7.74 (m, 6 H), 3.18–3.21 (m, 2 H), 1.99 (q, *J* = 7.88 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.20 (d, $J_{P,C}$ = 2.72 Hz), 131.16 (d, $J_{P,C}$ = 9.99 Hz), 131.10 (d, $J_{P,C}$ = 100.82 Hz), 128.72 (d, $J_{P,C}$ = 11.82 Hz), 22.42 (d, $J_{P,C}$ = 68.12 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.47 (s).

MS (EI, 70 eV): *m*/*z* (%) = 250 (3), 248 (16, [M]), 202 (45), 201 (71), 183 (10), 155 (24), 152 (11), 125 (15), 124 (17), 123 (18), 91 (13), 79 (6), 77 (100), 69 (6), 65 (9), 60 (37), 52 (11), 51 (76), 50 (21), 48 (55), 47 (78), 46 (72), 45 (87).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{13}OPS$: 249.0497; found: 249.0488.

Anal. Calcd for $C_{13}H_{13}OPS$: C, 62.89; H, 5.28. Found: C, 62.66; H, 5.33.

Di-*c*-hexyl(sulfanylmethyl)phosphine Oxide (1b)

Prepared according to the general procedure from acetylthiomethyl(di-*c*-hexyl)phosphine oxide (0.212 g, 0.7 mmol). The crude product was purified by column chromatography to give **1b** as an orange oil (0.129 g, 0.497 mmol, 71%); R_f = 0.45 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3420, 2922, 2850, 1640, 1447, 1158, 1116, 1005, 889, 854, 825, 770, 657, 531, 484, 420 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.69 (m, 2 H), 1.86–2.07 (m, 12 H), 1.70–1.77. (m, 2 H), 1.45–1.47 (m, 4 H), 1.20–1.33 (m, 5 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.56 (d, $J_{P,C}$ = 61.76 Hz, CH), 26.56 (d, $J_{P,C}$ = 12.72 Hz, CH_2), 26.52 (d, $J_{P,C}$ = 11.81 Hz, CH_2), 25.92 (d, $J_{P,C}$ = 1.82 Hz, CH_2), 25.86, 27.74 (d, $J_{P,C}$ = 1.82 Hz, CH_2), 15.93 (d, $J_{P,C}$ = 54.50 Hz, CH_2).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 49.29 (s).

MS (EI, 70 eV): *m*/*z* (%) = 261 (1), 260 (3, [M]), 179 (9), 133 (11), 132 (7), 97 (51), 96 (25), 95 (10), 83 (41), 82 (22), 81 (28), 79 (18), 77 (13), 67 (32), 64 (26), 63 (7), 60 (14), 55 (100), 54 (21), 53 (15), 48 (22), 47 (13), 46 (40), 45 (50).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{25}OPS$: 261.1436; found: 261.1426.

Anal. Calcd for $C_{13}H_{25}OPS$: C, 59.97; H, 9.68. Found: C, 59.67; H, 9.60.

Bis(di-*c*-hexylphosphorylmethyl) Disulfide (4)

It was observed by the way that compound **1b** underwent partial oxidative dimerization to bis-(di-*c*-hexylphosphorylmethyl) disulfide (**4**) while left in $CHCl_3$ at r.t. overnight. In order to complete oxidation of **1b**, the solution was left at r.t. for another 48 h. The resulting disulfide **4** was analyzed without further purification; brownish oil; R_f = 0.28 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (film, ATR): 2925, 2851, 2205, 1447, 1161, 1116, 890, 854, 770, 725, 641, 531, 484, 420 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ =3.32 (d, *J* = 6.94 Hz, 1 H), 1.69–2.03 (m, 24 H), 1.17–1.56 (m, 20 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.97 (d, $J_{P,C}$= 65.40 Hz, CH), 33.71 (d, $J_{P,C}$ = 46.32 Hz, CH_2), 26.48 (d, $J_{P,C}$ = 11.81 Hz, CH_2), 26.46 (CH_2), 26.40 (d, $J_{P,C}$ = 12.72 Hz, CH_2), 25.78 (d, $J_{P,C}$ = 3.76 Hz, CH_2), 25.36 (d, $J_{P,C}$ = 1.82 Hz, CH_2).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 49.02 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{48}O_2P_2S_2$: 519.2644; found: 519.2646.

[*tert*-Butyl(phenyl)phosphoryl]methyl Mesylate

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet, *t*-butylphenyl(hydroxymethyl)phosphine oxide[12] (0.331 g, 1.56 mmol) was dissolved in anhyd CH_2Cl_2(10 mL). Then, Et_3N (0.22 mL, 1.56 mmol) was added and the reaction mixture was cooled to 0 °C. MsCl (0.12 mL, 2.25 mmol) was added and the mixture was allowed to warm to r.t. and stirred overnight. The reaction mixture was acidified with aq 1 M HCl (5 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and evaporated. The residue was purified by column chromatography using EtOAc as eluent affording [*tert*-butyl(phenyl)phosphoryl]methyl mesylate as a white solid (0.425 g, 1.47 mmol, 94%); mp 121.5–122.5 °C; R_f = 0.24 (EtOAc).

IR (solid, ATR): 3303, 2971, 2929, 1436, 1365, 1352, 1339, 1167, 1114, 1004, 973, 819, 761, 736, 670, 632, 532, 501, 485, 466, 448 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.77 (m, 2 H), 7.56–7.62 (m, 1 H), 7.49–7.52 (m, 2 H), 4.83 (d, $J_{P,H}$ = 3.15 Hz, 2 H), 3.09 (s, 3 H), 1.20 (d, $J_{P,H}$ = 15.45 Hz, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.47 (d, $J_{P,C}$= 2.73 Hz), 131.63 (d, $J_{P,C}$= 8.17 Hz), 128.58 (d, $J_{P,C}$= 11.81 Hz), 127.36 (d, $J_{P,C}$= 90.83 Hz), 62.71 (d, $J_{P,C}$= 69.03 Hz), 37.83, 33.25 (d, $J_{P,C}$= 69.03 Hz), 24.41.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 41.44 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{19}O_4PS$: 291.0814; found: 291.0819.

Anal. Calcd for $C_{12}H_{19}O_4PS$: C, 49.65; H, 6.60. Found: C, 49.70; H, 6.70.

tert-Butylphenyl(phenylthiomethyl)phosphine Oxide (5)

In a two-necked round-bottom flask (50 mL) equipped with a magnetic stirrer and an argon inlet, thiophenol (0.107 mL, 1.04 mmol) was dissolved in anhyd THF (10 mL). The resulting mixture was cooled to –78 °C and *n*-BuLi (1.83 mL, 1.14 mmol, 1.6 M in hexanes) was added followed by [*tert*-butyl(phenyl)phosphoryl]methyl mesylate (0.3 g, 1.04 mmol). The resulting reaction mixture was allowed to warm to r.t. and stirred for 48 h. After that time, the residue was quenched with sat. aq NH_4Cl (5 mL) and extracted with $CHCl_3$ (3 × 15 mL). The combined organic phases were dried (anhyd Na_2SO_4), and concentrated. Column chromatography of the residue on silica gel using $CHCl_3$/EtOAc/MeOH (30:5:1, v/v/v) as eluent gave **5** as a yellowish solid (0.276 g, 0.906 mmol, 87%); mp 127.2–127.4 °C; R_f = 0.45 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 2949, 2905, 1576, 1473, 1437, 1404, 1171, 1113, 1026, 818, 740, 731, 693, 624, 506, 480, 472, 462 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75–7.71 (m, 2 H), 7.40–7.57 (m, 5 H), 7.17–7.29 (m, 3 H), 3.57 (m, 2 H), 1.20 (d, $J_{P,H}$ = 15.0 Hz, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ =136.28 (d, $J_{P,C}$= 5.45 Hz, C), 131.9 (d, $J_{P,C}$= 8.17 Hz, CH), 131.81 (d, $J_{P,C}$= 2.73 Hz, CH), 130.14 (CH), 129.11 (d, $J_{P,C}$= 90.83 Hz, C), 128.98 (CH), 128.2 (d, $J_{P,C}$= 10.90 Hz, CH), 126.82 (CH), 33.68 (d, $J_{P,C}$= 68.12 Hz, C), 28.76 (d, $J_{P,C}$= 58.13 Hz, CH_2), 24.69 (CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 45.68 (s).

MS (EI, 70 eV): *m*/*z* (%) = 305 (4), 304 (21, [M]), 259 (11), 248 (21), 247 (20), 202 (51), 201 (12), 182 (9), 157 (8), 155 (6), 154 (13), 139 (13), 126 (19), 125 (76), 124 (17), 123 (100), 121 (18), 109 (15), 92 (13), 91 (36), 79 (13), 77 (32), 65 (16), 57 (62), 47 (43), 45 (80).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{21}OPSNa$: 327.0943; found: 327.0935.

Anal. Calcd for $C_{17}H_{21}OPS$: C, 67.08; H, 6.95. Found: C, 66.88; H, 6.80.

Diphenylvinylphoshine Oxide[25]

This compound was available from our earlier studies.[25]

White solid; mp 115.0–115.8 °C; R_f = 0.64 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 2996, 1437, 1174, 1119, 1105, 971, 763, 734, 722, 693, 611, 532, 503, 471, 452 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74–7.68, 7.56–7.53 (m, 2 H), 7.51–7.46 (m, 4 H), 6.74–6.63 (m, 1 H), 6.39–6.24 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 134.82, 132.20 (dd, *J* = 2.72 Hz, $J_{C,P}$ = 148.72 Hz), 131.90 (d, $J_{P,C}$ = 2.72 Hz), 131.35 (d, $J_{P,C}$ = 9.99 Hz). 131.07 (dd, *J* = 2.72 Hz, $J_{P,C}$ = 432.31 Hz), 128.58 (d, $J_{P,C}$ = 11.88 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 23.93 (s).

MS (EI, 70 eV): *m*/*z* (%) = 229 (12), 228 (80, [M]), 227 (78), 202 (9), 201 (38), 200 (6), 199 (10), 185 (23), 183 (38), 152 (16), 149 (16), 134 (5), 133 (22), 121 (7), 10 (7), 107 (9), 105 (11), 104 (100), 95 (9), 91 (7), 78 (21), 77 (82), 76 (5), 51 (66), 50 (13), 47 (58).

Anal. Calcd for $C_{14}H_{13}OP$: C, 73.68; H, 5.74. Found: C, 73.63; H, 5.64.

Diphenyl(2-sulfanylethyl)phosphine Oxide (6)

In a two-necked round-bottom flask (100 mL) equipped with a magnetic stirrer and an argon inlet, diphenylvinylphosphine oxide[22] (0.228 g, 1 mmol) was dissolved in anhyd DMF (2 mL) and KSAc (0.343 g, 3 mmol) was added. The reaction mixture was stirred at 80 °C for 3 d, then evaporated to dryness, and the residue was partitioned between CH_2Cl_2 (20 mL) and H_2O (30 mL). The resulting mixture was extracted with CH_2Cl_2 (5 × 30 mL). The combined organic phases were dried (anhyd Na_2SO_4) and concentrated. The residue was purified by crystallization from EtOAc affording **6** as a beige solid (0.152 g, 0.58 mmol, 58%); mp 122.3–123.7 °C (EtOAc); R_f = 0.38 ($CHCl_3$/MeOH 15:1).

IR (solid, ATR): 3051, 1436, 1282, 1177, 1120, 1104, 1071, 784, 733, 690, 533, 505, 456, 420 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.78 (m, 4 H), 7.43–7.52 (m, 6 H), 2.71–2.76 (m, 2 H), 2.45–2.50 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.12 (d, $J_{P,C}$ = 99.9 Hz), 131.94 (d, $J_{P,C}$ = 2.73 Hz), 130.63 (d, $J_{P,C}$ = 9.99 Hz), 128.74 (d, $J_{P,C}$ = 11.81 Hz), 30.17 (d, $J_{P,C}$ = 67.21 Hz), 23.70 (d, $J_{P,C}$ = 1.82 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 30.27 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{15}OPS$: 263.0654; found: 263.0644.

Anal. Calcd for $C_{14}H_{15}OPS$: C, 64.10; H, 5.76. Found: C, 64.41; H, 5.60.

α-Aminophosphine Oxides 8 and 9; General Procedure

In a two-necked round-bottom flask (100 mL) equipped with a magnetic stirrer and an argon inlet were placed the respective secondary phosphine oxide (3 mmol), aldehyde (3 mmol), primary amine (3 mmol), and anhyd Na_2SO_4 (10 g) in anhyd toluene (20 mL). The reaction mixture was heated at 110 °C for 24 h. After completion, the reaction was allowed to cool to r.t., the solution was filtered, and evaporated. The residue was dissolved in $CHCl_3$(10 mL), then H_2O (10 mL) was added, and the mixture was extracted with $CHCl_3$ (3 × 30 mL). The combined organic phases were dried (anhyd Na_2SO_4), filtered, and toluene was evaporated. The residue was purified by column chromatography using $CHCl_3$/EtOAc/MeOH (30:5:1, v/v/v) as eluent.

N-Benzylaminomethyldiphenylphosphine Oxide (8b)[28]

Diphenylphosphine oxide (0.61 g, 3 mmol), paraformaldehyde (0.09 g, 3 mmol), and benzylamine (0.327 mL, 3 mmol) were reacted according to the general procedure to afford the title compound as a yellow solid (0.597 g, 1.86 mmol, 62%); mp 87.1–88.1 °C; R_f = 0.51 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3023, 2811, 1493, 1456, 1438, 1174, 1122, 1100, 1071, 1026, 805, 782, 753, 718, 691, 541, 509, 455, 448 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.74–7.78 (m, 4 H), 7.45–7.48 (m, 4 H), 7.52–7.55 (m, 2 H), 7.24–7.32 (m, 5 H), 3.88 (s, 2 H), 3.43 (d, $J_{P,H}$ = 7.88 Hz, 2 H), 2.16 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.94 (d, $J_{P,C}$ = 0.91 Hz), 131.92 (d, $J_{P,C}$ = 2.73 Hz), 131.81 (d, $J_{P,C}$ = 98.08 Hz), 131.12 (d, $J_{P,C}$= 9.08 Hz), 128.56 (d, $J_{P,C}$= 11.81 Hz), 128.36, 128.24, 127.18, 54.99 (d, $J_{P,C}$= 14.53 Hz), 48.02 (d, $J_{P,C}$= 81,47 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.45 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{20}NOP$: 322.1355; found: 322.1343.

Anal. Calcd for $C_{20}H_{20}NOP$: C, 74.75; H, 6.27, N, 4.35. Found: C, 74.72; H 6.44, N, 4.30.

(*N*-*p*-Bromophenylaminomethyl)diphenylphosphine Oxide (8c)

Diphenylphosphine oxide (0.61 g, 3 mmol), paraformaldehyde (0.09 g, 3 mmol), and *p*-bromophenylamine (0.516 g, 3 mmol) were reacted according to the general procedure to afford the title compound as a yellow solid (0.846 g, 2.19 mmol, 73%); mp 168.1–169.1 °C; R_f = 0.53 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3396, 3056, 1593, 1501, 1435, 1160, 1116, 1092, 1069, 998, 811, 748, 732, 691, 600, 567, 504, 482, 448, 406 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.75–7.79 (m, 4 H), 7.56–7.60 (m, 2 H), 7.23–7.25 (m, 2 H), 7.48–7.52 (m, 4 H), 6.54–6.56 (m, 2 H), 4.44 (br s, 1 H), 3.90 (d, $J_{H,P}$= 8.51 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.60 (d, $J_{P,C}$ = 9.99 Hz), 132.55 (d, $J_{P,C}$ = 2.73 Hz), 131.88, 131.55 (d, $J_{P,C}$ = 81.74 Hz), 131.06 (d, $J_{P,C}$ = 9.08 Hz), 128.89 (d, $J_{P,C}$ = 11.81 Hz), 121.45, 114.99, 110.33, 43.90 (d, $J_{P,C}$ = 78.11 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.14 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{19}H_{17}BrNOP$: 386.0304; found: 386.0300.

Anal. Calcd for $C_{19}H_{17}BrNOP$: C, 59.09; H, 4.44; N, 3.63. Found: C, 58.82; H, 4.30; N, 3.43.

Diphenyl(*N*-*p*-tolylaminomethyl)phosphine Oxide (8d)[29]

Diphenylphosphine oxide (0.61 g, 3 mmol), paraformaldehyde (3 mmol, 0.09 g), and *p*-tolylamine (0.321 g, 3 mmol) were reacted according to the general procedure to afford the title compound as a yellow solid (0.299 g, 0.93 mmol, 31%); mp 156.4–157.4 °C; R_f = 0.57 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3377, 3014, 1611, 1521, 1486, 1436, 1298, 1174, 1123, 1107, 806, 791, 741, 690, 555, 503, 414 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.77–7.82 (m, 4 H), 7.55–7.58 (m, 2 H), 7.47–7.51 (m, 4 H), 6.98–7.00 (m, 2 H), 6.59–6.61 (m, 2 H), 3.92 (d, $J_{P,H}$ = 8.83 Hz), 2.24 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.31 (d, $J_{P,C}$ = 11.81 Hz), 132.29 (d, $J_{P,C}$ = 2.73 Hz), 131.14 (d, $J_{P,C}$ = 99.91 Hz), 131.12 (d, $J_{P,C}$ = 9.08 Hz), 129.70, 128.77 (d, $J_{P,C}$ = 11.81 Hz), 127.95, 113.56, 44.21 (d, $J_{P,C}$ = 79.93 Hz), 20.35.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 29.61 (s).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{20}NOP$: 322.1355; found: 322.1360.

Anal. Calcd for $C_{20}H_{20}NOP$: C, 74.75; H, 6.27; N 4.36. Found: C, 74.55; H, 6.22; N, 4.43.

o-Anisylphenyl{1-phenyl-[*N*-(*p*-bromophenyl)amino]methyl}-phosphine Oxide (12)

o-Anisylphenylphosphine oxide (0.696 g, 3 mmol), benzaldehyde (0.305 mL, 3 mmol,) and *p*-bromophenylamine (0.516 g, 3 mmol) were reacted according to the general procedure to afford **12** as two diastereomers (dr = 1:0.9) isolated as a mixture (1.18 g, 2.4 mmol, 80%); R_f = 0.58 ($CHCl_3$/MeOH 30:1).

IR (solid, ATR): 3261, 3062, 1588, 1514, 1488, 1463, 1430, 1318, 1273, 1242, 1175, 1112, 1109, 1075, 1012, 828, 799, 765, 714, 690, 559, 522, 504, 478, 428 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.03–8.08 (m, 1 H, major), 7.82–7.86 (m, 2 H, minor), 7.72–7.77 (m, 1 H, minor), 7.52–7.56 (m, 1 H, major), 7.47–7.51 (m, 1 H, minor), 7.36–7.47 (m, 6 H), 7.19–7.31 (m, 7 H), 7.17–7.19 (m, 2 H, minor), 7.12–7.17 (m, 4 H), 7.11–7.12 (m, 2 H, major), 7.07–7.10 (m, 1 H), 7.05–7.07 (m, 1 H, major), 6.94–6.97 (m, 1 H, major), 6.91–6.94 (m, 1 H, minor), 6.76–6.78 (m, 1 H, minor), 6.55–6.58 (m, 2 H, minor), 6.44–6.49 (m, 2 H, major), 5.46–5.56 (m, 3 H), 5.25–5.31 (m, 1 H, major), 3.83 (s, 3 H, major), 3.77 (s, 3 H, minor).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 159.6 (d, $J_{P,C}$= 4.5 Hz, C), 158.9 (d, $J_{P,C}$= 4.5 Hz, C), 145.9 (d, $J_{P,C,N,C}$ = 11.8 Hz, C), 145.4 (d, $J_{P,C,N,C}$ = 12.7 Hz, C), 135.8 (CH), 135.5 (d, $J_{P,C}$ = 5.45 Hz, CH), 134.5 (d, $J_{P,C}$ = 4.5 Hz, CH), 134.2 (d, $J_{P,C}$ = 14.5 Hz, CH), 132.8 (d, $J_{P,C}$ = 100.0 Hz, C), 131.8 (CH), 131.7 (CH), 131.6 (d, $J_{P,C}$ = 2.7 Hz), 131.3 (d, $J_{P,C}$ = 10.0 Hz, CH), 130.9 (d, $J_{P,C}$ = 9.08 Hz, CH), 130.8 (d, $J_{P,C}$ = 103.5 Hz, C), 128.5 (d, $J_{P,C}$ = 4.5 Hz, CH), 128.2 (d, $J_{P,C}$ = 11.8 Hz, CH), 128.1 (CH), 128.0 (CH), 127.9 (d, $J_{P,C}$ = 5.5 Hz, CH), 127.8 (CH), 127.6 (d, $J_{P,C}$= 1.8 Hz, CH), 121.6 (d, $J_{P,C}$ = 10.9 Hz, CH), 121.1 (d, $J_{P,C}$ = 10.9 Hz, CH), 118.5 (d, $J_{P,C}$ = 95.4 Hz, C), 118.0 (d, $J_{P,C}$ = 101.7 Hz, C), 115.4 (CH), 115.2 (CH), 111.1 (d, $J_{P,C}$= 6.36 Hz, CH), 110.3 (d, $J_{P,C}$= 7.27 Hz, CH), 109.5 (d, $J_{P,C}$= 33.6 Hz, C), 58.0 (d, $J_{P,C}$ = 74.5 Hz, CH), 55.52 (CH_3), 55.50 (d, $J_{P,C}$ = 77.2 Hz, CH), 55.2 (CH_3).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 32.90 (s, minor), 33.20 (s, major).

Anal. Calcd for $C_{26}H_{23}BrNO_2P$: C, 63.43; H, 4.71; N, 2.84. Found: C, 63.77; H, 4.74; N, 2.65.

Aminomethyl(diphenyl)phosphine Oxide (8a)[30]

N-Benzylaminomethyl(diphenyl)phosphine oxide (**8b**; 0.307 g, 0.956 mmol) and Pd/C (61 mg) were placed in a freshly distilled MeOH (1 mL) in a Schlenk tube (25 mL), which was attached to a source of H_2 at atmospheric pressure (balloon). The mixture was carefully degassed by three freeze-pump-thaw cycles, refilled with H_2, and then warmed to r.t. The mixture was heated at 70 °C for 4 d. After completion of the reaction, the resulting mixture was filtered through a Celite pad, washed with MeOH (3 × 10 mL), and then MeOH was evaporated. The residue was purified by column chromatography using basic Al_2O_3 and $CHCl_3$/EtOAc/MeOH (30:5:1, v/v/v) as eluent affording **8a** as a colorless waxy solid; R_f = 0.38 ($CHCl_3$/EtOAc/MeOH 30:5:1).

IR (solid, ATR): 3392, 3053, 1671, 1543, 1436, 1160, 1120, 1036, 1014, 996, 889, 818, 717, 691, 544, 502 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.78 (m, 4 H), 7.52–7.55 (m, 2 H), 7.46–7.50 (m, 4 H), 3.51 (d, $J_{P,H}$ = 4.10 Hz, 2 H), 1.67 (br s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.06 (d, $J_{P,C}$ = 2.73 Hz), 128.75 (d, $J_{P,C}$ = 10.90 Hz), 131.01 (d, $J_{P,C}$ = 95.37 Hz), 131.04 (d, $J_{P,C}$ = 9.08 Hz), 41.90 (d, $J_{P,C}$ = 72.66 Hz).

^{31}P NMR (202 Hz, $CDCl_3$): δ = 30.41 (s).

HRMS (ESI-TOF): *m*/*z* calcld for $C_{13}H_{14}NOP$ $[M + H]^+$: 232.0886; found: 232.0872.

Anal. Calcd for $C_{13}H_{14}NOP$: C, 67.53; H, 6.10; N, 6.06. Found: C, 67.55; H, 6.00; N, 6.00.

2-[*N*-(1-Methylbenzylamino)]ethyl(diphenyl)phosphine Oxide (17)[16]

This compound was available from our earlier studies.[16]

White solid; mp 228.2–229.5 °C; R_f = 0.57 ($CHCl_3$/EtOAc/MeOH 30:5:1), $[\alpha]_D^{25}$ –26.33 (*c* 1, $CHCl_3$).

IR (solid, ATR): 2983, 2840, 2775, 2544, 2440, 1598, 1465, 1437, 1379, 1192, 1159, 1120, 1097, 1070, 924, 793, 752, 729, 704, 694, 566, 544, 511, 499, 467, 419 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.58–7.66 (m, 4 H), 7.47–7.51 (m, 4 H), 7.31–7.43 (m, 7 H), 4.17 (q, *J* = 6.62 Hz, 1 H), 3.08–3.21 (m, 2 H), 2.84–2.95 (m, 2 H), 2.05 (br s, 1 H), 1.70 (d, *J* = 6.94 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 135.53, 132.53 (d, $J_{P,C}$ = 2.73 Hz), 132.45 (d, $J_{P,C}$ = 2.73 Hz), 130.71 (d, $J_{P,C}$ = 83.56 Hz), 130.57 (d, $J_{P,C}$ = 9.99 Hz), 130.53 (d, $J_{P,C}$ = 9.99 Hz), 130.07 (d, $J_{P,C}$ = 81.74 Hz), 129.39, 129.37, 128.97 (d, $J_{P,C}$ = 11.81 Hz), 128.94 (d, $J_{P,C}$ = 11.81 Hz), 127.68, 59.02, 40.46, 25.95 (d, $J_{P,C}$ = 69.09 Hz), 20.43.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 33.68 (s).

HRMS (ESI-TOF): *m*/*z* $[M + H]^+$ calcd for $C_{22}H_{24}NOP$: 350.1668; found: 350.1668.

Anal. Calcd for $C_{22}H_{24}NOP$: C, 75.62; H, 6.92; N, 4.01. Found: C, 75.43; H, 6.61; N, 3.81.

Reduction of α-Sulfanylmethylphosphine Oxides 1 in THF; General Procedure

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet, α-sulfanylmethylphosphine oxide **1** (0.25 mmol) was dissolved in anhyd THF (2 mL). Then, $H_3B{\cdot}SMe_2$ (71 µL, 0.75 mmol or 237 µL, 2.5 mmol) was added via syringe over a period of 2 min to avoid uncontrolled bubbling. After the addition of BH_3 complex, the reaction mixture was heated at 60 °C for 3 or 24 h. Then, the mixture was evaporated to dryness and the residue was purified by column chromatography using hexane/EtOAc (6:1, v/v) and hexane/EtOAc (2:1, v/v) as eluent.

Diphenyl(sulfanylmethyl)phosphine-Borane (2a)[18b]

Phosphine oxide **1a** (0.062 g, 0.25 mmol) was reacted according to the general procedure to afford **2a**[18b] (0.0178 g, 0.0725 mmol, 29%) and [*S*-(4-hydroxybutyl)thiomethyl]diphenylphosphine-borane (**3a**) (0.0247 g, 0.078 mmol, 31%).

2a[18b]

Colorless oil; R_f = 0.57 (hexane/EtOAc 2:1).

IR (thin film, ATR): 3192, 3056, 2917, 2378, 2254, 1483, 1435, 1130, 1106, 1058, 999, 935, 778, 739, 692, 585, 493, 471, 436 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.73 (m, 4 H), 7.47–7.56 (m, 6 H), 3.20 (dd, *J* = 6.31, 8.20 Hz, 2 H), 1.90 (q, *J* = 8.20 Hz, 1 H), 0.7–1.31 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.51 (d, $J_{P,C}$= 9.09 Hz), 131.67 (d, $J_{P,C}$= 2.73 Hz), 128.93 (d, $J_{P,C}$= 9.99 Hz), 127.76 (d, $J_{P,C}$= 54.50 Hz), 19.69 (d, $J_{P,C}$= 32.70 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 21.99 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –39.39 (br m).

HRMS (ESI-TOF): *m*/*z* $[M]^+$ calcd for $C_{13}H_{16}BPS$: 245.0717; found: 245.0708.

Anal. Calcd for $C_{13}H_{16}BPS$: C, 63.44; H, 6.55. Found: C, 63.12; H, 6.30.

3a

Colorless oil; R_f = 0.13 (hexane/EtOAc 2:1).

IR (thin film, ATR): 3372, 3056, 2933, 2379, 1435, 1106, 1056, 1027, 999, 807, 739, 691, 608, 492, 470, 433 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.70–7.74 (m, 4 H), 7.45–7.54 (m, 6 H), 3.62 (t, *J* = 6.31 Hz, 2 H), 3.26 (d, *J* = 6.94 Hz, 2 H), 2.60 (t, *J* = 6.94 Hz, 2 H), 1.56–1.67 (m, 4 H), 1.56 (br s, 1 H), 0.70–1.36 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.51 (d, $J_{P,C}$= 9.09 Hz), 131.48 (d, $J_{P,C}$= 2.72 Hz), 128.77 (d, $J_{P,C}$= 9.99 Hz), 127.43 (d, $J_{P,C}$= 54.49 Hz), 62.22, 34.58 (d, $J_{P,C}$= 2.72 Hz), 31.48, 27.56 (d, $J_{P,C}$= 32.70 Hz), 25.26.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 18.46 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –39.01 (br m).

HRMS (ESI-TOF): *m*/*z* $[M]^+$ calcd for $C_{17}H_{24}BOPS$: 317.1292; found: 317.1282.

Anal. Calcd for $C_{17}H_{24}BOPS$: C, 64.16; H, 7.60. Found: C, 64.36; H. 7.80.

Di-*c*-hexyl(sulfanylmethyl)phosphine-borane (2b)

Di-*c*-hexyl(sulfanylmethyl)phosphine oxide (**1b**; 0.0651 g, 0.25 mmol) was reacted according to the general procedure to afford di-*c*-hexyl(sulfanylmethyl)phosphine-borane (**2b**) (0.009 g, 0.035 mmol, 14%) and di-*c*-hexyl[*S*-(4-hydroxybutyl)thiomethyl]phosphine-borane (**3b**) (0.022 g, 0.068 mmol, 27%).

2b

White solid; mp 73.5–74.5 °C; R_f = 0.66 (hexane/EtOAc 6:1).

IR (solid, ATR): 2928, 2848, 2549, 2381, 2271, 1739, 1453, 1446, 1261, 1134, 1063, 1048, 1003, 932, 888, 852, 794, 777, 752, 693, 670, 583, 516, 504, 450 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.69 (dd, *J* = 5.67, 7.57 Hz, 2 H), 1.81–1.98 (m, 11 H), 1.71–1.77 (m, 2 H), 1.39–1.52 (m, 4 H), 1.23–32 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 31.05 (d, $J_{P,C}$ = 30.88 Hz, CH), 26.99 (d, $J_{P,C}$ = 0.69 Hz, CH_2), 26.88 (d, $J_{P,C}$ = 0.72 Hz, CH_2), 26.82 (d, $J_{P,C}$ = 1.82 Hz, CH_2), 26.77 (d, $J_{P,C}$ = 8.17 Hz, CH_2), 25.87 (CH_2), 13.52 (d, $J_{P,C}$ = 25.43 Hz, CH_2).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 30.90 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$) δ = –43.47 (br m).

HRMS (ESI-TOF): *m*/*z* [(M – BH_3) + O + H]$^+$ calcd for $C_{13}H_{28}BPS$: 261.1436; found: 216.1443.

Anal. Calcd for $C_{13}H_{28}BPS$: C, 60.47; H, 10.93. Found: C, 60.17; H, 10.65.

3b

Colorless oil; R_f = 0.40 (hexane/EtOAc 2:1).

IR (thin film, ATR): 3366, 2927, 2852, 2378, 1448, 1060, 1004, 889, 854, 826, 792, 753, 600, 449, cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.68 (t, *J* = 5.67 Hz, 2 H), 2.72 (d, *J* = 7.25 Hz, 2 H), 2.64 (t, *J* = 6.94 Hz, 2 H), 2.54 (t, *J* = 6.94 Hz, 1 H), 2.11 (s, 1 H), 1.89–1.98 (m, 2 H), 1.77–1.89 (m, 6 H), 1.63–1.77 (m, 6 H), 1.37–1.58 (m, 5 H), 1.20–1.35 (m, 5 H), 0.01–0.66 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 62.36 (d, $J_{P,C}$ = 24.52 Hz, CH_2), 35.20 (d, $J_{P,C}$ = 3.63 Hz, CH_2), 34.01 (CH_2), 31.67 (d, $J_{P,C}$ = 22.71 Hz, CH_2), 30.78 (d, $J_{P,C}$ = 31.79 Hz, CH), 26.83 (d, $J_{P,C}$ = 11.81 Hz, CH_2), 26.71 (d, $J_{P,C}$ = 10.90 Hz, CH_2), 25.90 (CH_2), 25.34 (d, $J_{P,C}$ = 9.99 Hz, CH_2), 22.04 (d, $J_{P,C}$ = 25.43 Hz, CH_2).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 28.30 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –42.38 (br m).

HRMS (ESI-TOF): *m*/*z* [M]$^+$ calcd for $C_{17}H_{36}BOPS$: 329.2231; found: 329.2238.

Anal. Calcd for $C_{17}H_{36}BOPS$: C, 61.81, H, 10.99. Found: C, 62.11; H, 10.80.

Reduction of α-Sulfanylmethylphosphine Oxides 1 in Toluene; General Procedure

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet, α-sulfanylmethylphosphine oxide **1** (0.25 mmol) was dissolved in anhyd toluene (2 mL). Then, $H_3B{\cdot}SMe_2$ (142 µL, 1.5 mmol or 237 µL, 2.5 mmol) was added via syringe over a period of 2 min to avoid uncontrolled bubbling. After the addition of BH_3 complex, the reaction mixture was heated at 60 °C for 24 h. Then, the mixture was evaporated to dryness and controlled by NMR analysis. The residue was dissolved in anhyd EtOAc and $H_3B{\cdot}SMe_2$ (71 µL, 0.75 mmol) was added. When complexation of the phosphine was observed (10 min), the residue was quenched with sat. aq NH_4Cl (5 mL) and extracted with $CHCl_3$ (5 × 15 mL). The combined organic phases were dried (anhyd Na_2SO_4) and concentrated. The residue was purified by column chromatography on silica gel using hexane/EtOAc (6:1, v/v) as eluent.

Diphenyl(sulfanylmethyl)phosphine-Borane (2a)[18b]

Diphenyl(sulfanylmethyl)phosphine oxide (**1a**; 0.0621 g, 0.25 mmol) was reacted according to the general procedure to afford **2a** as a colorless oil (0.032 g, 0.128 mmol, 51%).

Di-*c*-hexyl(sulfanylmethyl)phosphine-Borane (2b)

Di-*c*-hexyl(sulfanylmethyl)phosphine oxide (**1b**; 0.0651 g, 0.25 mmol) was reacted according to the general procedure to afford **2b** as aa white solid (0.0465 g, 0.18 mmol, 72%).

Attempted Reduction of *tert*-Butylphenyl(phenylthiomethyl)phosphine Oxide (5)

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet, *tert*-butylphenyl(phenylthiomethyl)phosphine oxide (**5**; 0.1 g, 0.328 mmol) was dissolved in anhyd THF (2 mL). Then, $H_3B{\cdot}SMe_2$ (156 µL, 1.64 mmol) was added via syringe over a period of 2 min to avoid uncontrolled bubbling. After the addition of BH_3 complex, the reaction mixture was stirred for 48 h at 60 °C. Then, the reaction mixture was evaporated to dryness. The NMR analysis showed the presence of only the starting material.

Reduction of Diphenyl(2-sulfanylethyl)phosphine Oxide (6) to Diphenyl(2-sulfanylethyl)phosphine-Borane (7)

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet, diphenyl(2-sulfanylethyl)phosphine oxide (**6**; 0.0786 g, 0.3 mmol) was dissolved in anhyd toluene (2 mL). Then, $H_3B{\cdot}SMe_2$ (285 µL, 3 mmol) was added via syringe over a period of 2 min to avoid uncontrolled bubbling. After the addition of BH_3 complex, the reaction mixture was stirred for 18 h at 110 °C. Then, the mixture was evaporated to dryness and the residue was purified by column chromatography using hexane/acetone (4:1, v/v) as eluent affording **7** as a white solid (0.0195 g, 0.075 mmol, 25%); mp 153–154 °C (dec.); R_f = 0.38 (hexane/acetone 4:1).

IR (solid, ATR): 2922, 2852, 2378, 2250, 1435, 1109, 1061, 732, 690, 594, 492, 468, 444 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.78 (m, 4 H), 7.43–7.52 (m, 6 H), 2.71–2.76 (m, 2 H), 2.45–2.50 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.12 (d, $J_{P,C}$ = 99.9 Hz), 131.94 (d, $J_{P,C}$ = 2.73 Hz), 130.63 (d, $J_{P,C}$ = 9.99 Hz), 128.74 (d, $J_{P,C}$ = 11.81 Hz), 30.17 (d, $J_{P,C}$ = 67.21 Hz), 23.70 (d, $J_{P,C}$ = 1.82 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 15.03 (br m).

Anal. Calcd for $C_{14}H_{18}BPS$: C, 64.64; H, 6.97. Found: C, 64.70 H 7.01.

Reduction of α-Aminophosphine Oxides 8 and 12; General Procedure

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet, aminomethylphosphine oxide (0.3 mmol) was dissolved in anhyd THF (2 mL). Then, $H_3B{\cdot}THF$ (1.5 mL, 1.5 mmol, 1 M) was added via syringe over a period of 2 min to avoid uncontrolled bubbling. After the addition of BH_3 complex, the reaction mixture was stirred at r.t. for 24 h. Then, the mixture was evaporated to dryness and the residue was purified by column chromatography using hexane/EtOAc (4:1, v/v) or hexane/acetone (4:1, v/v) as eluent.

Aminomethyldiphenylphosphine-Borane (9a)

Aminomethyldiphenylphosphine oxide (**8a**; 0.0693 g, 0.3 mmol) was reacted according to the general procedure to afford the title compound with 83% yield according to ^{31}P NMR spectroscopy; R_f = 0.53 (hexane/EtOAc 4:1).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 14.42 (br m).

[*N*-(*p*-Bromophenyl)aminomethyl]diphenylphosphine-Borane (9c)

According to the general procedure, **8c** (0.116 g, 0.3 mmol) was reacted at r.t. for 1 h affording **9c** together with a small amount of diphenylphosphine-borane (**11**) as side-product.

9c

White solid (0.0817 g, 0.213 mmol, 71%); mp 99.7–100.7 °C; R_f = 0.41 (hexane/EtOAc 6:1).

IR (solid, ATR): 3406, 2393, 1591, 1497, 1435, 1312, 1236, 1108, 1073, 998, 899, 807, 749, 733, 688, 605, 493, 460, 427, 418 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.68–7.72 (m, 4 H), 7.52–7.55 (m, 2 H), 7.45–7.48 (m, 4 H), 7.22–7.25 (m, 2 H), 6.50–6.53 (m, 2 H), 4.10 (br s, 1 H), 3.91 (d, $J_{P,H}$= 5.67 Hz, 2 H), 0.69–1.41 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.39 (d, $J_{P,C,N,C}$ = 9.08 Hz), 134.34, 132.32, 131.91, 131.83 (d, $J_{P,C}$ = 2.72 Hz), 129.08 (d, $J_{P,C}$ = 9.99 Hz), 127.05 (d, $J_{P,C}$ = 55.40 Hz), 115.04, 110.47, 41.49 (d, $J_{P,C}$ = 42.69 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 16.13 (br m).

HRMS: *m*/*z* [M – H]$^+$ calcd for $C_{19}H_{20}BBrNP$: 382.0523; found: 382.0520.

Anal. Calcd for $C_{19}H_{20}BBrNP$: C, 59.42; H, 5.25; N, 3.65. Found: C, 59.28; H, 4.98; N 3.74.

11[31]

Colorless oil (0.0054 g, 0.027 mmol, 9%); R_f = 0.54 (hexane/EtOAc 6:1).

IR (thin film, ATR): 2384, 1437, 1056, 901, 699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.65–7.70 (m, 4 H), 7.44–7.54 (m, 6 H), 6.33 (dq, $J_{P,H}$ = 179.80 Hz, $J_{H,H}$ = 6.94 Hz, 1 H), 0.77–1.51 (br m, 3 H).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 1.51 (br m).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 132.92 (d, $J_{P,C}$ = 9.99 Hz), 131.62 (d, $J_{P,C}$ = 1.82 Hz), 129.04 (d, $J_{P,C}$ = 10.90 Hz), 126.11 (d, $J_{P,C}$ = 57.22 Hz).

MS (EI, 70 eV): *m*/*z* (%) = 186 (26, [M – BH_3]), 152 (4), 109 (9), 108 (100), 107 (44), 92 (5), 81 (5), 57 (5), 51 (10).

HRMS (ESI-TOF): *m*/*z* [M – BH_3 + H]$^+$ calcd for $C_{12}H_{14}BP$: 187.0671; found: 187.0667.

Anal. Calcd for $C_{12}H_{14}BP$: C, 72.06; H, 7.05. Found: C, 71.80; H, 6.99.

[*N*-(*p*-Tolyl)aminomethyl]diphenylphosphine-Borane (9d)

[*N*-(*p*-Tolyl)aminomethyl]diphenylphosphine oxide (**8d**; 0.096 g, 0.3 mmol) was reacted according to the general procedure to afford **9d** as a solid (0.0737 g, 0.231 mmol, 77%); mp 93.0–94.0 °C; R_f = 0.51 (hexane/EtOAc 4:1).

IR (solid, ATR): 3379, 3211, 3055, 2386, 1612, 1519, 1436, 1175, 1122, 1108, 1070, 944.53, 805, 739, 718, 689, 642, 550, 553, 495, 417 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.77 (m, 4 H), 7.51–7.53 (m, 2 H), 7.44–7.49 (m, 4 H), 6.98–7.01 (m, 2 H), 6.57–6.61 (m, 2 H), 3.94 (d, $J_{P,H}$= 5.99 Hz), 2.24 (s, 3 H), 0.71–1.43 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.16 (d, $J_{P,C,N,C}$ = 9.99 Hz), 132.46 (d, $J_{P,C}$ = 9.09 Hz), 131.64 (d, $J_{P,C}$ = 2.73 Hz), 129.70, 128.97 (d, $J_{P,C}$ = 9.99 Hz), 128.07, 127.39 (d, $J_{P,C}$ = 55.40 Hz), 113.63, 41.78 (d, $J_{P,C}$ = 42.69 Hz), 20.36.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 16.11 (br m).

HRMS (ESI-TOF): *m*/*z* [M]$^+$ calcd for $C_{20}H_{23}BNP$: 318.1575; found: 318.1570

Anal. Calcd for $C_{20}H_{23}BNP$: C, 75.26; H, 7.26; N, 4.39. Found: C, 75.40; H, 7.35; N, 4.50.

***N*-Benzylaminomethyldiphenylphosphine Bisborane (10)**

N-Benzylaminomethyldiphenylphosphine oxide (**8b**; 0.0963 g, 0.3 mmol) was reacted with $H_3B{\cdot}SMe_2$ (285 µL, 3 mmol) according to the general procedure to afford **10** as a white solid (0.0629 g, 0.189 mmol, 63%); mp 121–122 °C (dec.); R_f = 0.64 (hexane/EtOAc 2:1).

IR (solid, ATR): 3219, 3060, 2930, 2381, 2317, 2277, 1483, 1435, 1407, 1172, 1161, 1103, 1069, 1059, 1015, 844, 746, 735, 688, 597, 497, 467, 417 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.84 (m, 2 H), 4.55 (br s, 1 H), 7.27–7.60 (m, 13 H), 3.98–4.02 (m, 1 H), 3.88–3.92 (m, 1 H), 3.80–3.84 (m, 1 H), 3.50–3.55 (m, 1 H), 0.68–1.84 (br m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 133.05, 132.62 (d, $J_{P,C}$ = 9.99 Hz), 129.26 (d, $J_{P,C}$ = 9.99 Hz), 130.06, 131.90 (d, $J_{P,C}$ = 9.99 Hz), 132.23 (d, $J_{P,C}$ = 2.72 Hz), 132.51, 129.22 (d, $J_{P,C}$ = 10.90 Hz), 129.02, 128.86, 127.72 (d, $J_{P,C}$ = 58.13 Hz), 125.68 (d, $J_{P,C}$ = 59.04 Hz), 61.36 (d, $J_{P,C}$ = 3.63 Hz), 50.80 (d, $^1J_{P,C}$ = 36.33 Hz).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 15.57 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –13.03 (br m), –41.08 (br m).

MS (FAB): *m*/*z* (%) = 333 (2, [M]), 198 (11), 183 (18), 129 (11), 120 (17), 108 (20), 91 (100), 77 (12), 65 (26), 50 (13).

Anal. Calcd for $C_{20}H_{26}B_2NP$: C, 72.13; H, 7.87; N, 4.21. Found: 71.77; H, 7.72; N, 4.35.

***o*-Anisyl-{1-[*N*-(*p*-bromophenyl)amino]-1-phenylmethyl}phenylphosphine-Borane (13)**

According to the general procedure, **12** (0.246 g, 0.5 mmol) was reacted with $H_3B{\cdot}SMe_2$ (142 µL, 1.5 mmol) at 60 °C for 24 h to afford **13**; benzyl-*p*-bromophenylamine (**14**)[32]; *o*-anisylphenylphosphinous acid borane (**15**)[11b]; and *o*-anisylphenylphosphine-borane (**16**).[11a]

13

White solid, two diastereomers (dr = 1:0.4, ^{31}P NMR) isolated as a mixture (0.091 g, 0.185 mmol, 37%); dr = 1:0.55; R_f = 0.38 (hexane/EtOAc 6:1).

IR (thin film, ATR): 3384, 3027, 2940, 2377, 1735, 1590, 1493, 1475, 1461, 1428, 1309, 1276, 1247, 1175, 1065, 1017, 802, 759, 740, 699, 689, 600, 591, 550, 496, 459, 436 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.97 (m, 1 H, minor), 7.64–7.67 (m, 3 H), 7.54–7.57 (m, 1 H, minor), 7.33–7.46 (m, 5 H), 7.20–7.32 (m, 8 H), 7.07–7.20 (m, 7 H), 6.97–6.99 (m, 1 H, minor), 6.86–6.81 (m, 1 H, major), 6.82–6.85 (m, 1 H, major), 6.56–6.57 (m, 2 H, major), 6.38–6.40 (m, 2 H, minor), 5.85 (d, $J_{H,P}$ = 17.65 Hz, major), 5.82 (d, $J_{H,P}$ = 16.08 Hz, minor), 5.34 (br s, 2 H), 3.78 (s, 3 H, minor), 3.69 (s, 3 H, major), 0.73–1.24 (br m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.2 (d, $J_{P,C}$= 1.5 Hz, minor, C), 160.8 (d, $J_{P,C}$= 1.82 Hz, major, C), 145.7 (d, $J_{P,C,N,C}$ = 9.1 Hz, minor, C), 145.1 (d, $J_{P,C,N,C}$ = 11.8 Hz, major, C), 137.1 (d, $J_{P,C}$= 13.63 Hz, minor, CH), 137.0 (d, $J_{P,C}$= 14.5 Hz, major, CH), 135.7 (d, $J_{P,C}$= 3.6 Hz, major, C), 135.6 (d, $J_{P,C}$= 3.6 Hz, minor, C), 134.3 (d, $J_{P,C}$ = 1.8 Hz, major, CH), 134.1 (d, $J_{P,C}$= 1.8 Hz, minor, CH), 132.7 (d, $J_{P,C}$ = 8.2 Hz, minor, CH), 131.9 (s, major, CH), 131.8 (s, minor, CH), 131.3 (d, $J_{P,C}$ = 9.1 Hz, major, CH), 130.97 (d, $J_{P,C}$ = 2.72 Hz, minor, CH), 130.4 (d, $J_{P,C}$ = 2.7 Hz, major, CH), 129.8 (d, $J_{P,C}$ = 57.2 Hz, C), 128.5 (d, $J_{P,C}$ = 3.6 Hz, CH), 128.3 (d, $J_{P,C}$ = 10.0 Hz, major, CH), 128.0 (d, $J_{P,C}$ = 10.0 Hz, minor, CH), 127.8 (d, $J_{P,C}$ = 1.9 Hz, major, CH), 128.71, 127.9 (d, $J_{P,C}$ = 3.6 Hz, minor), 127.2 (d, $J_{P,C}$ = 57.2 Hz, C), 121.7 (d, $J_{P,C}$ = 11.8 Hz, minor, CH), 121.3 (d, $J_{P,C}$ = 12.7 Hz, major, CH), 115.4 (s, major, CH), 115.2 (s, minor, CH), 114.5 (d, $J_{P,C}$ = 57.2 Hz, major, C), 114.5 (d, $J_{P,C}$ = 51.8 Hz, minor, C), 111.5 (d, $J_{P,C}$ = 4.5 Hz, minor, CH), 111.1 (d, $J_{P,C}$ = 3.6 Hz, major, CH), 109.9 (s, major, CH), 109.6 (s, minor, CH), 55.6 (s, minor, CH_3), 55.4 (s, major, CH_3), 54.8 (d, $J_{P,C}$ = 38.2 Hz, minor, CH), 51.8 (d, $J_{P,C}$ = 43.6 Hz, major, CH).

^{31}P NMR (202 MHz, $CDCl_3$): δ = 27.64 (br m, minor), 25.19 (br m, major).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –41.47 (br m).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{26}H_{26}BBrNOP$: 490.1098; found: 490.1101.

Anal. Calcd for $C_{26}H_{26}BBrNOP$: C, 63.71; H, 5.35; N, 2.86. Found: C, 63.34; H, 5.30; N, 2.70.

14[32]

White solid (0.0419 g, 0.16 mmol, 32%); R_f = 0.63 (hexane/EtOAc 6:1).

IR (solid, ATR): 3192, 2259, 1593, 1492, 1451, 1398, 1321, 1294, 1262, 1190, 1178, 1068, 883, 809, 730, 696, 641, 546, 502, 456 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34–7.36 (m, 4 H), 7.30–7.32 (m, 1 H), 7.24–7.25 (m, 2 H), 6.51–6.52 (m, 2 H), 4.31 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.01, 109.09, 114.39, 127.36, 128.67, 131.90, 138.82, 41.28.

MS (EI, 70 eV): *m*/*z* (%) = 263 (13, [M + 1]), 261 (13), 91 (100), 65 (13).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{12}BrN$: 262.0226; found: 262.0227.

Anal. Calcd for $C_{13}H_{12}BrN$: C, 59.56; H, 4.61; N, 5.34. Found: C, 59.62; H, 4.65; N, 5.37.

15[11b]

White solid (0.0312 g, 0.13 mmol, 26%); mp 94.0–94.2 °C; R_f = 0.25 (hexane/EtOAc 2:1).

IR (solid, ATR): 3406, 2386, 2292, 1591, 1573, 1470, 1458, 1433, 1277, 1249, 1163, 1155, 1138, 1114, 1089, 1071, 1014, 888, 799, 759, 706, 689, 628, 489, 471, 434 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ =7.86–7.90 (m, 1 H), 7.62–7.66 (m, 2 H), 7.54–7.58 (m, 1 H), 7.40–7.49 (m, 3 H), 7.13–7.18 (m, 1 H), 6.96–6.98 (m, 1 H), 5.29 (br s, 1 H), 3.79 (s, 3 H), 0.67–1.39 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.62, 134.31 (d, $J_{P,C}$ = 16.35 Hz), 133.85 (d, $J_{P,C}$ = 61.76 Hz), 131.24, 130.18 (d, $J_{P,C}$ = 11.81 Hz), 128.34 (d, $J_{P,C}$ = 10.90 Hz), 121.74 (d, $J_{P,C}$ = 12.72 Hz), 119.81 (d, $J_{P,C}$ = 57.22 Hz), 111.38, 56.0.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 97.13 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –38.17 (br m).

HRMS (ESI-TOF): *m*/*z* [M]$^+$ calcd for $C_{13}H_{16}BO_2P$: 245.0894; found: 245.0887.

Anal. Calcd for $C_{13}H_{16}BO_2P$: C, 63.46; H, 6.55. Found: C, 63.70; H, 6.88.

16[11a]

White solid (0.0046 g, 0.02 mmol, 4%); mp 92.0–92.6 °C; R_f = 0.45 (hexane/EtOAc 6:1).

IR (solid, ATR): 2380, 2256, 1587, 1576, 1477, 1455, 1432, 1295, 1247, 1133, 1060, 1023, 912, 898, 767, 739, 694, 591, 486, 442, 419 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73–7.78 (m, 1 H), 7.60–7.72 (m, 2 H), 7.49–7.54 (m, 1 H), 7.44–7.49 (m, 1 H), 7.38–7.43 (m, 2 H), 7.05–7.10 (m, 1 H), 6.91–6.96 (m, 1 H), 6.58 (dq, $J_{P,H}$= 392.36 Hz, 1 H), 3.85 (s, 3 H), 0,67–1.34 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.51, 134.90 (d, $J_{P,C}$ = 13.62 Hz), 133.81 (d, $J_{P,C}$ = 1.82 Hz), 132.78 (d, $J_{P,C}$ = 9.08 Hz), 131.04 (d, $J_{P,C}$ = 1.81 Hz), 126.84 (d, $J_{P,C}$ = 9.99 Hz), 126.79 (d, $J_{P,C}$ = 59.04 Hz), 121.33 (d, $J_{P,C}$ = 11.81 Hz), 110.72 (d, $J_{P,C}$ = 3.63 Hz), 55.72.

^{31}P NMR (202 MHz, $CDCl_3$): δ = –16.44 (br m).

^{11}B NMR (160.5 MHz, $CDCl_3$): δ = –40.38 (br m).

MS (EI, 70 eV): *m*/*z* (%) = 218 (8), 216 (58) [M], 183 (24), 138 (55), 137 (62), 123 (7), 109 (21), 108 (66), 107 (45), 95 (8), 94 (12), 92 (11), 91 (100), 81 (6), 78 (16), 77 (16), 68 (10), 65 (13), 63 (7), 57 (6), 51 (19).

HRMS (ESI-TOF): *m*/*z* [M]$^+$ calcd for $C_{13}H_{16}BOP$: 229.0945; found: 229.0944.

Anal. Calcd for $C_{13}H_{16}BOP$: C, 67.87; H, 7.01. Found: C, 67.58, H, 6.70.

Reduction of β-Aminophosphine Oxide 17 by H_3B·SMe_2 to 2-[*N*-(1-Methylbenzylamino)]ethyl(diphenyl)phosphine-Borane (18)

In a two-necked round-bottom flask (25 mL) equipped with a magnetic stirrer and an argon inlet β-aminophosphine oxide **17** (0.105 g, 0.3 mmol) was dissolved in anhyd THF (5 mL). Then, H_3B·SMe_2(142 µL, 1.5 mmol) was added via syringe over a period of 2 min to avoid uncontrolled bubbling. After the addition of BH_3 complex, the reaction mixture was heated at 60 °C for 48 h. Then, the mixture was evaporated to dryness and the residue was purified by column chromatography using basic Al_2O_3 and hexane/EtOAc (4:1, v/v) as eluent affording **18** as a colorless oil (0.0625 g, 0.18 mmol, 60%); R_f = 0.57 (hexane/EtOAc 4:1); $[\alpha]_D^{25}$ –35 (*c* 0.70, $CHCl_3$).

IR (thin film, ATR): 3056, 2961, 2916, 2849, 2379, 1436, 1107, 1060, 1027, 734, 692, 592, 544, 472, 428 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.63 (m, 4 H), 7.38–7.47 (m, 6 H), 7.19–7.18 (m, 5 H), 3.71 (q, *J* = 6.31 Hz, 1 H), 2.70–2.78 (m, 2 H), 2.37–2.42 (m, 2 H), 1.60 (br s, 1 H), 1.27 (d, *J* = 6.62 Hz, 3 H), 0.53–1.19 (br m, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 145.08, 132.01 (d, $J_{P,C}$ = 9.99 Hz), 131.99 (d, $J_{P,C}$ = 9.09 Hz), 131.12 (d, $J_{P,C}$ = 2.73 Hz), 129.35 (d, $J_{P,C}$ = 55.40 Hz), 128.76 (d, $J_{P,C}$ = 9.99 Hz), 128.38, 126.92, 126.49, 57.78, 41.63 (d, $J_{P,C}$ = 2.73 Hz), 26.32 (d, $J_{P,C}$ = 36.33 Hz), 24.10.

^{31}P NMR (202 MHz, $CDCl_3$): δ = 13.80 (br m).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{27}BNP$: 348.2044; found: 348.2040.

Anal. Calcd for $C_{22}H_{27}BNP$: C, 76.10, H, 7.84, N, 4.03. Found: C, 76.20, H, 7.90, N, 4.00.

Funding Information

This work was financially supported by the Polish Ministry of Science and Higher Education through the grant (N N204 111 035).

Acknowledgment

We acknowledge the synthetic assistance of M. Sc. Anna Szmigielska (Department of Organic Chemistry, Faculty of Chemistry, Maria Curie Sklodowska University).

References

(1) Quin, L. D. *A Guide to Organophosphorus Chemistry*; Wiley-Interscience: New York, **2000**.

(2) (a) Hiney, R. M.; Higham, L. J.; Müller-Bunz, H.; Gilheany, D. G. *Angew. Chem. Int. Ed.* **2006**, *45*, 7248. (b) Byrne, P. A.; Rajendran, K. V.; Muldoon, J.; Gilheany, D. G. *Org. Biomol. Chem.* **2012**, *10*, 3531. (c) Busacca, C. A.; Lorenz, J. C.; Grinberg, N.; Haddad, N.; Hrapchak, M.; Latli, B.; Lee, H.; Sabila, P.; Saha, A.; Sarvestani, M.; Shen, Sh.; Varsolona, R.; Wei, X.; Senanayake, C. H. *Org. Lett.* **2005**, *7*, 4277. (d) Busacca, C. A.; Raju, R.; Grinberg, N.; Haddad,

N.; James-Jones, P.; Lee, H.; Lorenz, J. C.; Saha, A.; Senanayake, C. H. *J. Org. Chem.* **2008**, *73*, 1524. (e) Ghosh, A. K.; Nicponski, D. R.; Kass, J. *Tetrahedron Lett.* **2012**, *53*, 3699.

(3) (a) Ros, A.; Estepa, B.; Bermejo, A.; Álvarez, E.; Fernández, R.; Lassaletta, J. M. *J. Org. Chem.* **2012**, *77*, 4740. (b) Chen, Z.; Huang, Z.; Li, Y.; Lim, L. H.; Zhou, J.; Su, H.; Zhou, F. *Angew. Chem. Int. Ed.* **2013**, *52*, 4906.

(4) (a) Ebner, C.; Müller, C. A.; Markert, C.; Pfaltz, A. *J. Am. Chem. Soc.* **2011**, *133*, 4710. (b) Nigra, M. M.; Yeh, A. J.; Okrut, A.; DiPasquale, A. G.; Yeh, S. W.; Solovyov, A.; Katz, A. *Dalton Trans.* **2013**, *42*, 12762.

(5) (a) Naumann, K.; Zon, G.; Mislow, K. *J. Am. Chem. Soc.* **1969**, *91*, 7012. (b) Valentine, D. Jr.; Blount, J. F.; Toth, K. *J. Org. Chem.* **1980**, *45*, 3691.

(6) (a) Coumbe, T.; Lawrence, N. J.; Muhammad, F. *Tetrahedron Lett.* **1994**, *35*, 625. (b) Wu, H.-C.; Yu, J.-Q.; Spencer, J. B. *Org. Lett.* **2004**, *6*, 4675. (c) Berthod, M.; Favre-Réguillon, A.; Mohamad, J.; Mignani, G.; Docherty, G.; Lemaire, M. *Synlett* **2007**, 1545. (d) Li, Y.; Das, S.; Zhou, S.; Junge, K.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 9727. (e) Li, Y.; Lu, L.-Q.; Das, S.; Pisiewicz, S.; Junge, K.; Beller, M. *J. Am. Chem. Soc.* **2012**, *134*, 18325.

(7) Imamoto, T.; Kikuchi, S.-I.; Miura, T.; Wada, Y. *Org. Lett.* **2001**, *3*, 87.

(8) (a) Gladiali, S.; Dore, A.; Fabbri, D.; Medici, S.; Pirri, G.; Pulacchini, S. *Eur. J. Org. Chem.* **2000**, 2861. (b) Higham, L. J.; Clarke, E. F.; Müller-Bunz, H.; Gilheany, D. G. *J. Organomet. Chem.* **2005**, *690*, 211.

(9) For a related direct conversion of phosphine oxides to phosphine-boranes by $(COCl)_2/NaBH_4$ or $(Et_3O)BF_4/NaBH_4$, see: (a) Rajendran, K. V.; Gilheany, D. G. *Chem. Commun.* **2012**, *48*, 817. (b) Kenny, N. P.; Rajendran, K. V.; Jennings, E. V.; Gilheany, D. G. *Chem. Eur. J.* **2013**, *19*, 14210.

(10) For a direct conversion of phosphine oxides to phosphine-boranes by BH_3complexes, see: (a) Köster, R.; Morita, Y. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 593. (b) Köster, R.; Schüßler, W.; Synoradzki, L. *Chem. Ber.* **1987**, *120*, 1105. (c) Keglevich, G.; Fekete, M.; Chuluunbaatar, T.; Dobó, A.; Harmat, V.; Tőke, L. *J. Chem. Soc., Perkin Trans. 1* **2000**, 4451. (d) Keglevich, G.; Chuluunbaatar, T.; Ludányi, K.; Tőke, L. *Tetrahedron* **2000**, *56*, 1. (e) Kiełbasiński, P.; Albrycht, M.; Żurawinski, R.; Mikołajczyk, M. *J. Mol. Catal. B: Enzym.* **2006**, *39*, 45. (f) Kwiatkowska, M.; Krasiński, G.; Cypryk, M.; Cierpiał, T.; Kiełbasiński, P. *Tetrahedron: Asymmetry* **2011**, *22*, 1581.

(11) (a) Stankevič, M.; Pietrusiewicz, K. M. *Synlett* **2003**, 1012. (b) Stankevič, M.; Andrijewski, G.; Pietrusiewicz, K. M. *Synlett* **2004**, 311.

(12) Sowa, S.; Stankevič, M.; Szmigielska, A.; Małuszyńska, H.; Kozioł, A. E.; Pietrusiewicz, K. M. *J. Org. Chem.* **2015**, *80*, 1672.

(13) (a) Lemouzy, S.; Nguyen, D. H.; Camy, V.; Jean, M.; Gatineau, D.; Giordano, L.; Naubron, J.-V.; Vanthuyne, N.; Hérault, D.; Buono, G. *Chem. Eur. J.* **2015**, *21*, 15607. (b) Lemouzy, S.; Jean, M.; Hérault, D.; Buono, G. *Org. Lett.* **2016**, *18*, 140. (c) Getineau, D.; Nguyen, D. H.; Hérault, D.; Vanthuyne, N.; Leclaire, J.; Giordano, L.; Buono, G. *J. Org. Chem.* **2015**, *80*, 4132.

(14) (a) Yan, Y.; Zhang, X. *J. Am. Chem. Soc.* **2006**, *128*, 7189. (b) Su, H. Y.; Taylor, M. S. *J. Org. Chem.* **2017**, *82*, 3173.

(15) (a) Bálint, E.; Tripolszky, A.; Jablonkai, E.; Karaghiosoff, K.; Czugler, M.; Mucsi, Z.; Kollár, L.; Pongrácz, P.; Keglevich, G. *J. Organomet. Chem.* **2016**, *801*, 111. (b) Keglevich, G.; Szekrényi, A.; Szöllősy, Á.; Drahos, L. *Synth. Commun.* **2011**, *41*, 2265. (c) Balint, E.; Fazekas, E.; Pinter, G.; Szöllősy, A.; Holczbauer, T.; Czugler, M.; Drahos, L.; Kortve, T.; Keglevich, G. *Curr. Org. Chem.* **2012**, *16*, 547. (d) Bálint, E.; Fazekas, E.; Pongrácz, P.; Kollár, L.; Drahos, L.; Holczbauer, T.; Czugler, M.; Keglevich, G. *J. Organomet. Chem.* **2012**, *717*, 75. (e) Bálint, E.; Tajti, Á.; Kalocsai, D.; Mátravölgyi, B.; Karaghiosoff, K.; Czugler, M.; Keglevich, G. *Tetrahedron* **2017**, *73*, 5659.

(16) Maj, A. M.; Pietrusiewicz, K. M.; Suisse, I.; Agbossou, F.; Mortreux, A. *J. Organomet. Chem.* **2001**, *626*, 157.

(17) Sugama, H.; Saito, H.; Danjo, H.; Imamoto, T. *Synthesis* **2001**, 2348.

(18) (a) Nilsson, B. L.; Kiessling, L. L.; Raines, R. T. *Org. Lett.* **2001**, *3*, 9. (b) Mühlberg, M.; Jaradat, D. M. M.; Kleineweischede, R.; Papp, I.; Dechtrirat, D.; Muth, S.; Broncel, M.; Hackenberger, C. P. R. *Bioorg. Med. Chem.* **2010**, *18*, 3679. (c) Sowa, S.; Mühlberg, M.; Pietrusiewicz, K. M.; Hackenberger, C. P. R. *Bioorg. Med. Chem.* **2013**, *21*, 3465.

(19) Compound **12** was used in the form of a 1:0.9 diastereoisomeric mixture.

(20) Compound **13** was isolated in the form of a 1:0.4 diastereoisomeric mixture while the crude reaction mixture indicated dr = 1:0.55.

(21) The product of retro-Kabachnik–Fields reaction of **8c** and **8d** in the presence of BH_3 was diphenylphosphine oxide, which underwent reduction with BH_3 leading to the formation of diphenylphosphine-borane (**11**), similar to the reaction of **12** with $H_3B{\cdot}SMe_2$ where phosphinous acid-borane **15** and secondary phosphine-borane **16** were present as products of complexation and reduction, respectively. For more details, see references 11a,b.

(22) Holt, J.; Maj, A. M.; Schudde, E. P.; Pietrusiewicz, K. M.; Sieroń, L.; Wieczorek, W.; Jerphagnon, T.; Arends, I. W. C. E.; Hanefeld, U.; Minnaard, A. J. *Synthesis* **2009**, 2061.

(23) Wife, R. L.; van Oort, A. B.; van Doorn, J. A.; van Leeuwen, P. W. N. M. *Synthesis* **1983**, 71.

(24) Achard, T.; Giordano, L.; Tenaglia, A.; Buono, G.; Gimbert, Y. *Organometallics* **2010**, *29*, 3936.

(25) (a) Xu, Y.; Xia, J.; Guo, H. *Synthesis* **1986**, 691. (b) Caudrado, P.; Gonzalez-Nogal, A. M.; Sarmentero, M. A. *Chem. Eur. J.* **2004**, *10*, 4491.

(26) Komarnicka, U. K.; Starosta, R.; Kyzioł, A.; Jezowska-Bojczuk, M. *Dalton Trans.* **2015**, *44*, 12688.

(27) Wang, Z. A.; Kurra, Y.; Wang, X.; Zeng, Y.; Lee, Y.-J.; Sharma, V.; Lin, H.; Dai, S. Y.; Liu, W. R. *Angew. Chem. Int. Ed.* **2017**, *56*, 1643.

(28) Couture, A.; Deniau, E.; Grandclaudon, P.; Woisel, P. *Tetrahedron Lett.* **1996**, *52*, 4433.

(29) Lach, J.; Guo, C.-Y.; Kindermann, M. K.; Jones, P. G.; Heinicke, J. *Eur. J. Org. Chem.* **2010**, *6*, 1176.

(30) Van Es, J. J. G. S.; Jaarsveld, K.; Van der Ger, A. *J. Org. Chem.* **1990**, *55*, 4063.

(31) Baccolini, G.; Boga, C.; Mazzacurati, M.; Sangirardi, F. *Org. Lett.* **2006**, *8*, 1677.

(32) Yang, C.-T.; Fu, Y.; Huang, Y.-B.; Yi, J.; Liu, Q.-X.; Guo, L. *Angew. Chem. Int. Ed.* **2009**, *48*, 7398.