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Michael Addition of P-nucleophiles to Conjugated Nitrosoalkenes

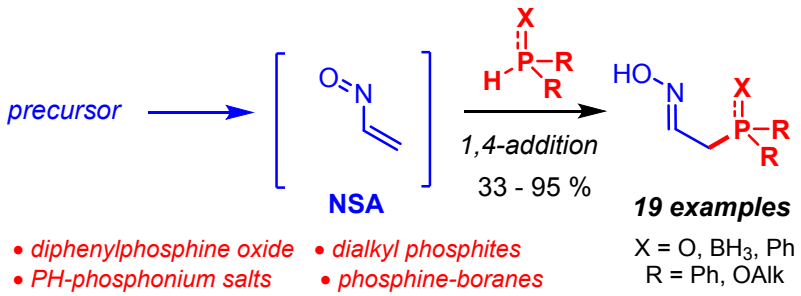
Yana A. Naumovich,[a] Sema L. Ioffe,[a] Alexey Yu. Sukhorukov,[a,b,c,*]

[a] N. D. Zelinsky Institute of Organic Chemistry, Leninsky prospect, 47, Moscow, Russia, 119991

[b] Higher Chemical College, D. Mendeleev University of Chemical Technology of Russia, Miusskaya sq., 9, Moscow, Russia, 125047

[c] Plekhanov Russian University of Economics, Stremyanny per. 36, Moscow, Russia, 117997

* sukhorukov@ioc.ac.ru



Abstract

A general approach to various α-phosphorus-substituted oximes (β-oximinoalkyl-substituted phosphonates, phosphine oxides, phosphine-borane complexes and phosphonium salts) was developed. The strategy exploits hitherto unknown Michael addition of PH-containing compounds (diphenylphosphine oxide, diisopropyl phosphite, phosphine-borane complexes and triphenylphosphonium bromide) to unstable conjugated nitrosoalkenes, which are generated *in situ* from corresponding nitrosoacetals. The resulting α-phosphorus-substituted oximes can be considered as useful P,N,O-ligands for catalysis and precursors to valuable β-aminophosphonates.

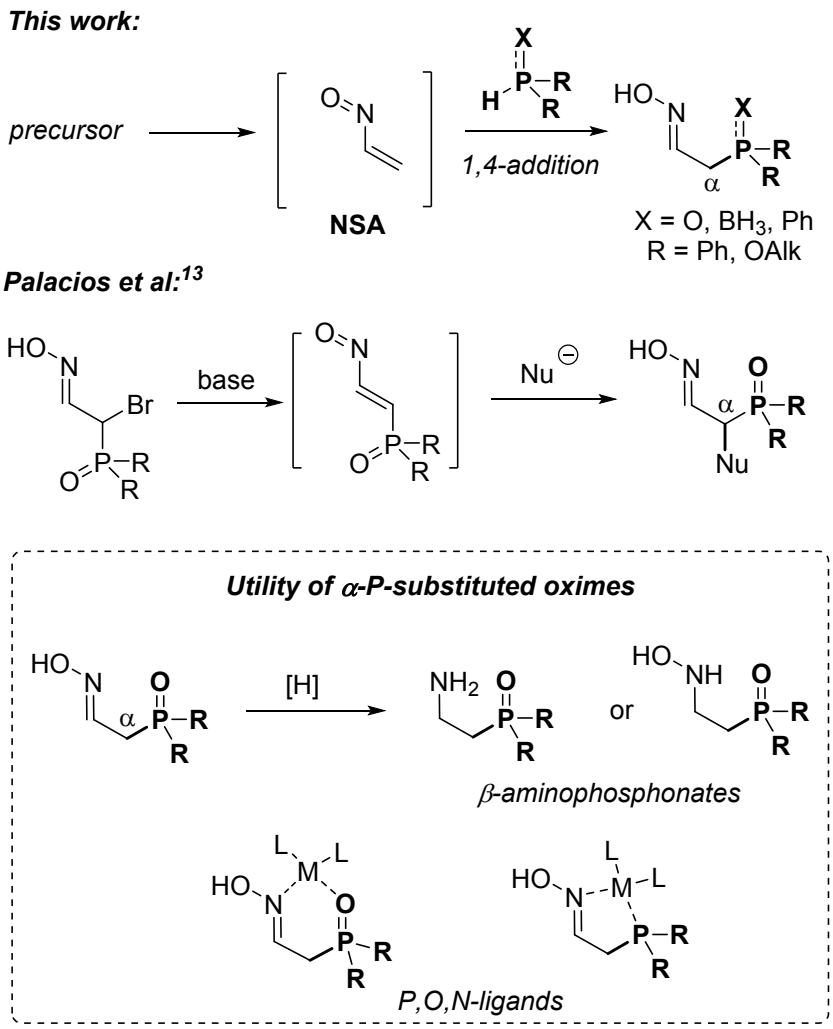
Introduction

Michael addition to conjugated nitrosoalkenes (**NSA**) is a promising approach to various α-substituted oximes, which are highly useful intermediates in organic synthesis.[1] This strategy is considered as an umpolung version of the conventional approach based on electrophilic addition to enolates followed by oximation.[1h,2] However, **NSA** are labile species, which tend toward polymerization and other side reactions.[1b] Successful coupling of nitrosoalkenes with nucleophiles is challenging and depends on many factors such as solvent, temperature, concentration and, especially, the nature of the **NSA** precursor.[1g] Nevertheless, much research has been done in the recent years to elaborate convenient methods for the Michael addition of various C-,[3] N-,[4] O-[5] and S-nucleophiles[2,6] to **NSA**.

On the other hand, the use of P-nucleophiles in this methodology was left unexplored to the best of our knowledge.[7] Addition of P-nucleophiles to **NSA** would lead to α-phosphorus-substituted oximes, which can be exploited as useful P,N,O-ligands[8] for catalysis[9] as well as precursors to molecules relevant to pharmaceutics and agrochemicals,[10] such as β-aminophosphonates[11] and β-hydroxylaminophosphonates[12] (Scheme 1). Therefore, in this paper, we describe our studies on the Michael addition of various P-nucleophiles to **NSA**, which led to the development of new methods for the synthesis of β-oximinoalkyl-substituted phosphonates (X = O), phosphine oxides and phosphites (X = O), phosphine-borane complexes (X = BH_3) and phosphonium salts (X = R). It is worthy of mention, that the synthesis of α-phosphorylated oximes via **NSA** have been described by Palacios et al,[13] however nitrosoalkenes already bearing a phosphorous-containing group were used in this strategy (Scheme 1). Other methods for the synthesis of α-P-substituted oximes exploit oximation of corresponding aldehydes/ketones,[14] addition of hydroxylamine to allenyl-substituted phosphine oxides,[15] S_N2 reactions of O-protected α-halooximes with tri-substituted phosphines,[16] dehydration of β-hydroxylamine-substituted phosphonium salts,[17] and addition of Wittig phosphine ylides to nitrile oxides.[7b] However, these approaches are not general and have been devised to access specific types of organophosphorous

derivatives of oximes. The method developed here allows the preparation of various classes of organophosphorous compounds exploiting a single precursor (an **NSA** derivative).

Scheme 1. Suggested approach to α-phosphorus-substituted oximes and their applications

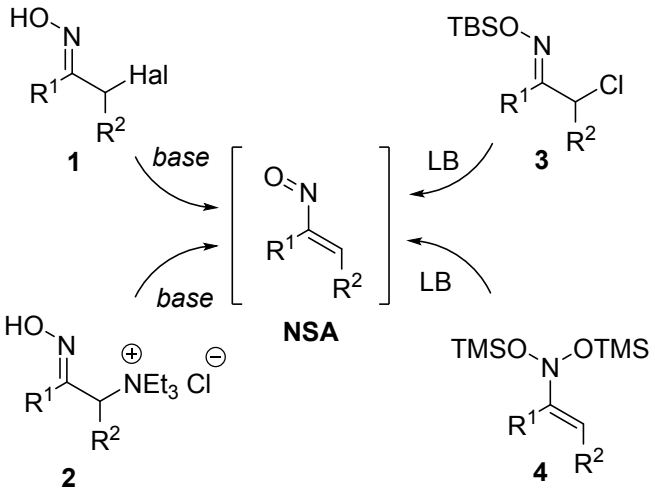


Results and discussion

The way how **NSA** are generated is essential for achieving a successful Michael addition and for prevention of side reactions. Conventional precursors of **NSA** are α-halooximes **1**,[1a,1b,18] which undergo deprotonation/elimination of the halide anion upon treatment with a Brønsted base (Scheme 2). However, under these conditions **NSA** are generated at high concentrations, thus facilitating side processes such as polymerization.[5b] More convenient **NSA** precursors are quaternary ammonium salts **2**,[19] silyl ethers of α-halooximes **3**,[3a,3b,18b] and nitrosoalkene acetals

4.[5b,6a,20] Silylated derivatives **3** and **4** liberate **NSA** upon the action of Lewis bases, which attack silicon atom enabling the subsequent elimination reaction. By changing the Lewis base, the rate of the formation of **NSA** can be affected. Compounds **1**-**3** are typically prepared from corresponding α-haloketones, while ene-nitrosoacetals **4** are accessed by double silylation of aliphatic nitro compounds.[20] In our studies aimed at achieving Michael addition of P-nucleophiles to **NSA**, all four types of nitrosoalkene precursors were examined.

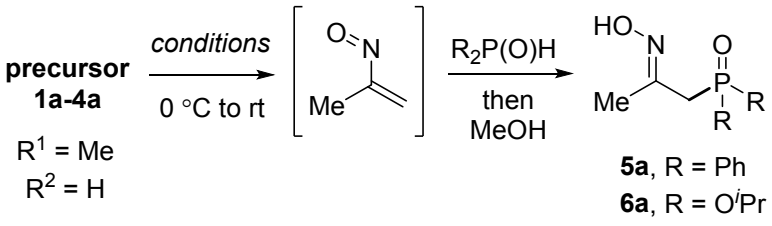
Scheme 2. Precursors of **NSA**



LB - Lewis base

Initially, we explored Michael addition of diphenylphosphine oxide (R = Ph) and diisopropyl phosphite (R = O^{i}Pr) with model precursors **1a-4a** in DMF under conditions used to generate **NSA**. Results are summarized in Table 1.

Table 1. Reaction of **NSA** precursors **1a-4a** with diphenylphosphine oxide and diisopropyl phosphite



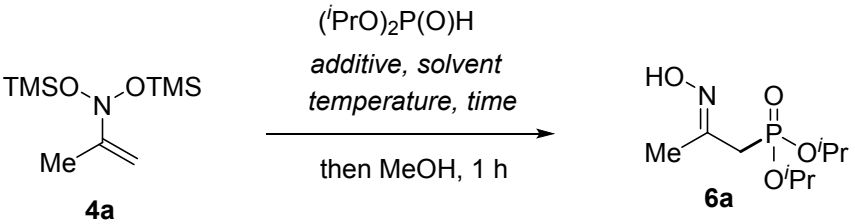
Entry	NSA precursor	Conditions	R	Yield, %[a]
1	**1a**	DMF, no additives	Ph	0 (**5a**)[b]
			O^{i}Pr	0 (**6a**)[c]
2	**1a**	DMF, Et_3N	Ph	traces (**5a**)[b]
			O^{i}Pr	0 (**6a**)[a]
3	**1a**	DMF, K_2CO_3	Ph	23 (**5a**)[b]
			O^{i}Pr	0 (**6a**)[c]
4	**2a**	DMF, no base	Ph	0 (**5a**)[b]
			O^{i}Pr	0 (**6a**)[c]
5	**2a**	DMF, Et_3N	Ph	0 (**5a**)[b]
			O^{i}Pr	0 (**6a**)[c]
6	**2a**	DMF, K_2CO_3	Ph	88 (**5a**)[b]
			O^{i}Pr	5 (**6a**)[c]
7	**3a**	DMF, no base	Ph	0 (**5a**)[b]
			O^{i}Pr	0 (**6a**)[c]
8	**3a**	DMF, Et_3N	Ph	0 (**5a**)[b]
			O^{i}Pr	0 (**6a**)[c]
9	**3a**	DMF, K_2CO_3	Ph	89 (**5a**)[b,d]
			O^{i}Pr	3 (**6a**)[c]
10	**3a**	DMF, TBAF	Ph	49 (**5a**)[b]
			O^{i}Pr	16 (**6a**)[c]
11	**4a**	DMF, no additives	Ph	81 (**5a**)[b]
			O^{i}Pr	38 (**6a**)[c]

Precursors **1a-4a**: R^1 = Me, R^2 = H, Hal = Cl. [a] Yield was determined by ^{1}H NMR with internal standard (trichloroethylene). [b] 2 equiv. of **NSA** precursor were used. [c] 1 equiv. of **NSA** precursor was used. [d] Mixture of **5a** with its TBS ether (ratio 1 : 1.5).

As can be seen from these data, the formation of Michael addition product could be achieved both with diphenylphosphine oxide and diisopropyl phosphate. However, the nature of **NSA** precursor proved to be crucial. No C,P-coupling products were obtained with chloroacetone oxime **1a** both with and without Et_3N additive (entries 1 and 2, Table 1). When K_2CO_3 was used as base, a small amount (23 %) of phosphine oxide **5a** was observed, yet no adduct with diisopropyl phosphite was detected (entry 3, Table 1). Less reactive quaternary salt **2a** afforded corresponding phosphine oxide **5a** in high yield in the presence of K_2CO_3, however, only 5 % of phosphonate **6a** were detected in a same reaction with diisopropyl phosphite (entry 6, Table 1). A similar result was observed when TBS ether of α-chloroacetone oxime **3a** was used as nitrosoalkene precursor in the presence of K_2CO_3 (entry 9, Table 1). Quaternary salt **2a** and TBS **3a** did not produce the desired C-P adducts with $Ph_2P(O)H$ or $(^iPrO)_2POH$ with Et_3N (entries 5 and 8, Table 1) or without a base (entries 4 and 7, Table 1). When TBAF was used to generate **NSA** from TBS ether **3a**, 16 % yield of phosphonate **6a** was obtained, however, the yield of phosphine oxide **5a** dropped to 49 % (entry 10, Table 1). Much better result was observed with ene-nitrosoacetal **4a**, which gave ca. 40 % of phosphonate **6a** and 81 % of phosphine oxide **5a** (entry 11, Table 1). It is noteworthy, that no additives were needed in this reaction (*vide infra*).

With these promising results in hand we turned our attention toward optimizing the reaction of diisopropyl phosphite with **NSA** precursor **4a** by screening reaction conditions and reagents ratio (Table 2).

Table 2. Reaction of **NSA** precursor **4a** with diisopropyl phosphite: an optimization study



Entry	Ratio 4a : (^{i}PrO)$_2$P(O)H	Additive	Solvent	Temperature, ° C	Reaction time, h	Yield of 6a, %[a,b]
1	1 : 1	no	DMF	0 °C to rt	24	38
2	1 : 1	no	DMSO	0 °C to rt	24	25
3	1 : 1	no	MeCN	0 °C to rt	24	18
4	1 : 1	no	THF	0 °C to rt	24	9
5	1 : 1	no	Et_2O	0 °C to rt	24	traces
6	1 : 1	no	MeOH	0 °C to rt	24	0
7	1 : 1	no	H_2O	0 °C to rt	24	0
8	1 : 1	no	urea/ChCl (2 : 1)	0 °C to rt	24	22
9	1 : 1	no	CH_2Cl_2/DMF (2 : 1)	0 °C to rt	24	20
10	1 : 1	no	no	0 °C to rt	24	11
11	1 : 1	DBU (10 mol%)	DMF	0 °C to rt	24	29
12	1 : 1	NaH (100 mol%)	THF	-78 °C	24	0
13	1 : 1	Ti(O^{i}Pr)$_4$ (10 mol%)	DMF	0 °C to rt	24	38
14	1 : 1	no	DMF	50 °C	3	39
15	1 : 1.5	no	DMF	0 °C to rt	24	56[b]
16	1.5 : 1	no	DMF	0 °C to rt	24	65[c]
17	1.5 : 1	no	DMF	-20 °C	24	68[c]

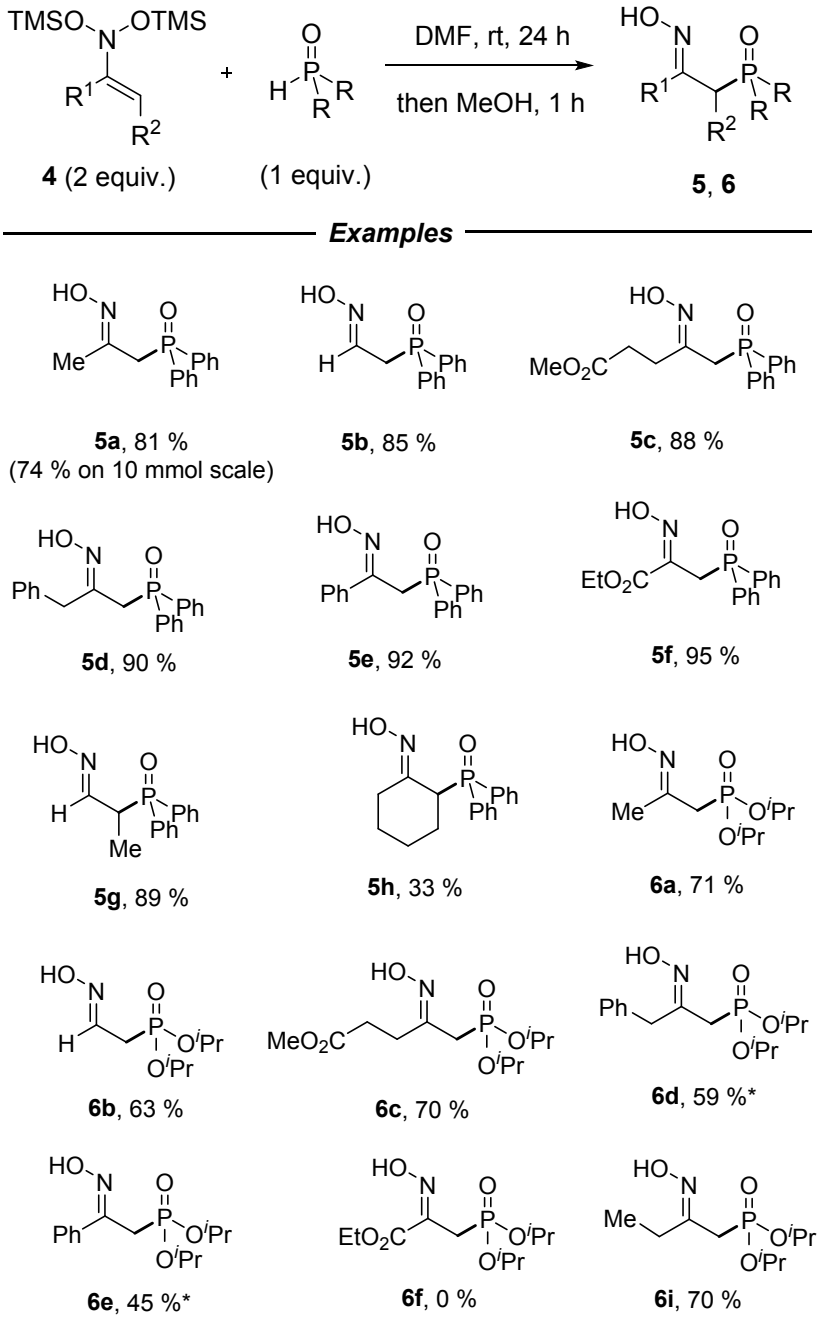
18	**2 : 1**	**no**	**DMF**	**0 °C to rt**	**24**	**74**[c]
19	4 : 1	no	DMF	0 °C to rt	24	82[c]
20	10 : 1	no	DMF	0 °C to rt	24	88[c]

[a] Yield was determined by ^{1}H NMR with internal standard (trichloroethylene). [b] Yield based on ene-nitrosoacetal **4a**. [b] Yield based on diisopropyl phosphite. ChCl – choline chloride.

Changing DMF to other solvents as well as conducting reaction under solvent-free conditions resulted in a considerable drop of the yield of Michael product **6a** (entries 1-10, Table 2, decomposition products of **4a** were detected). No product was obtained in protic solvents (water and methanol), which can themselves react with ene-nitrosoacetal **4a** (entries 6 and 7, Table 2). Deep eutectic solvent urea/ChCl, which was recently shown to be beneficial for reaction of **NSA** with S-nucleophiles,[6b] was also less efficient compared to DMF (entry 8, Table 2). Additives of bases to deprotonate $(^i\text{PrO})_2\text{POH}$ had no positive effect on the reaction outcome (entries 11 and 12, Table 2) as well as did not the addition of $\text{Ti}(\text{O}^i\text{Pr})_4$ (entry 13, Table 2), which is known to promote reactions with diisopropyl phosphite.[21] On the other hand, the yield of phosphonate **6a** substantially increased, when an excess of diisopropyl phosphite or **NSA** precursor **4a** was used (entries 15, 16 and 18-20, Table 2). Heating and cooling the reaction did not result in a noticeable increase of the yield of the product **6a** (entries 14 and 17, Table 2).

Based on these studies, ene-nitrosoacetals **4** were chosen as convenient **NSA** precursors to explore substrate scope of Michael addition of P-nucleophiles (Scheme 3). Using the optimized conditions (treatment of ene-nitrosoacetal **4** with a P-nucleophile in DMF), a series of ene-nitrosoacetals **4** were tested in reactions with diphenylphosphine oxide (R = Ph) and diisopropyl phosphite (R = O^{i}Pr). In most experiments, a 2-fold excess of ene-nitrosoacetals **4** was used to ensure full conversion of the P-nucleophile.

Scheme 3. Synthesis of phosphine oxides **5** and phosphonates **6** from ene-nitrosoacetals **4**



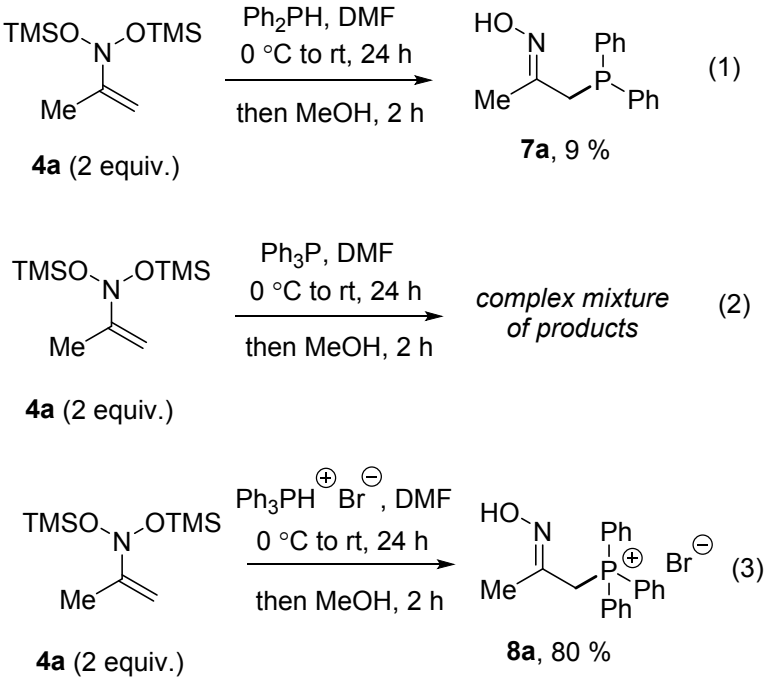
Yields are given based on P-nucleophile. * 3 equiv. of corresponding **NSA** precursor **4** were used.

Diphenylphosphine oxide (R = Ph) reacted smoothly under these conditions with various ene-nitrosoacetals **4a-h** affording corresponding phosphine oxide adducts **5a-h** in high yields (Scheme 3). Importantly, even enamine **4b** (R^1,R^2 = H), which is the precursor of highly unstable nitrosoethylene, delivered the Michael adduct **5b** in 85 % yield. Furthermore, the reaction could

be scaled up to 10 mmol of diphenylphosphine oxide without noticeable decrease in the yield as demonstrated by the synthesis of 2 grams of product **5a**. Reactions with diisopropyl phosphite proved to be more sensitive to the substitution in the **NSA** precursor. Enamines **4a-c**,**i** with R^1 = H, Alk provided corresponding phosphonates **6a-c**,**i** in good yields, while the phenyl substituted substrate **4e** gave adduct only in 28 % (the yield could be increased to 45 % with a 3-fold excess of **4e**). Also, we failed to achieve addition of diisopropyl phosphite to ene-nitrosoacetal **4f** bearing an electron withdrawing EtO_2C-group (product **6f** in Scheme 3). Most of oximes **5** and **6** were obtained as mixtures of *E*,*Z*-isomers, the ratio of which changes with time.[22]

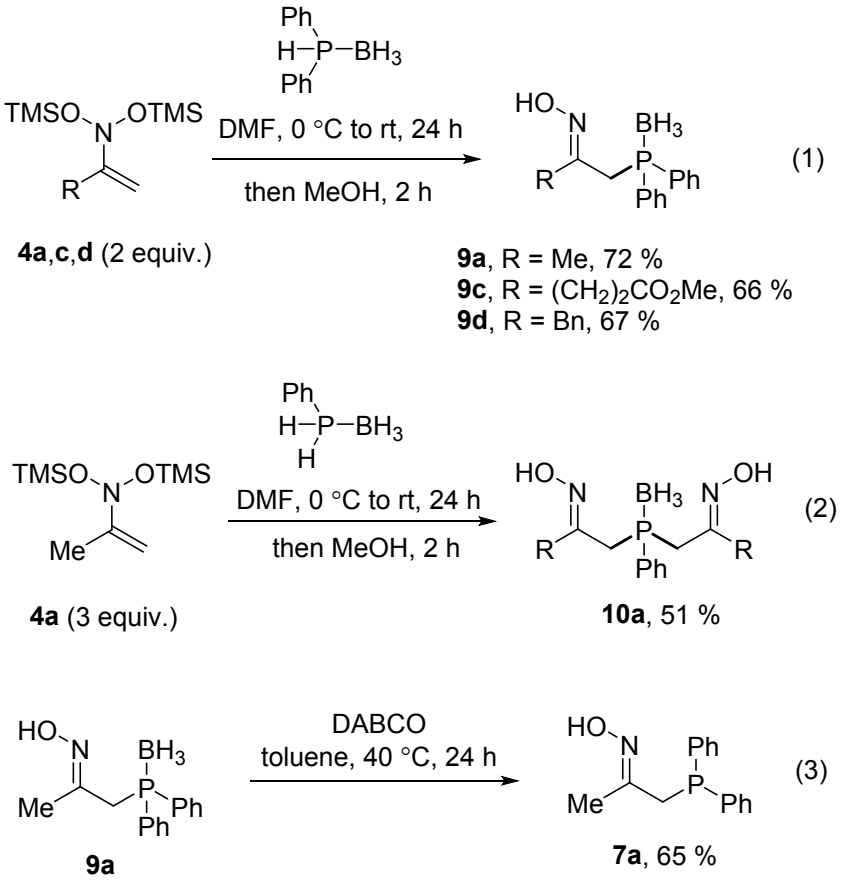
We then tested phoshines as nucleophiles in Michael addition to **NSA** nitrosoacetals **4** (Scheme 4). Our initial experiments with PH-phoshines were not successful. In reaction of model ene-nitrosoacetal **4a** with diphenyl phosphine only 9 % yield of corresponding adduct **7a** was formed (Scheme 4, eqn. (1)), and no Michael addition products were detected with $PhPH_2$. Reaction of ene-nitrosoacetal **4a** with PPh_3 afforded an indecipherable mixture of products (Scheme 4, eqn. (2)). Fortunately, when triphenylphosphonium bromide was employed instead of PPh_3, quaternary β-oximinoalkylphosphonium salt **8a** was obtained in 80 % isolated yield (Scheme 4, eqn. (3)).

Scheme 4. Reactions of ene-nitrosoacetal **4a** with Ph_2PH and $Ph_3PH^+Br^-$



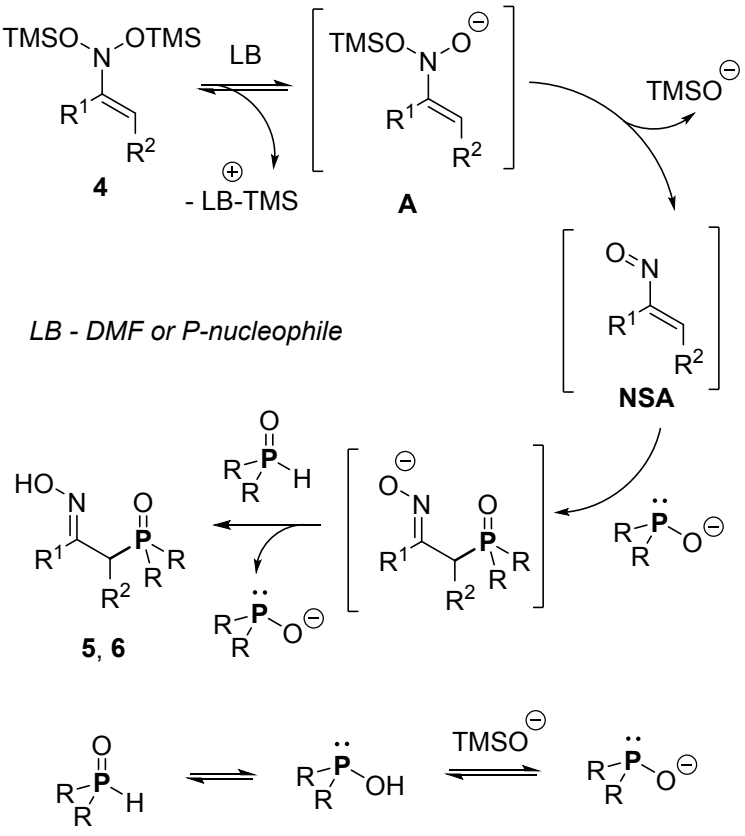
Having realized that quaternary phosphonium derivatives are more reactive towards **NSA**, we examined diphenylphosphine-borane complex[23] ($Ph_2PH{\bullet}BH_3$) as a nucleophile in reaction with ene-nitrosoacetals **4** Indeed, the desired tertiary phosphine-borane complexes **9a**,**c**,**d** were produced in this reaction in good yields and could be isolated by column chromatography (Scheme 5, eqn. (1)). Same reaction of **4a** with phenylphosphine-borane complex afforded bis(oxime)phophine derivative **10a** in moderate yield (Scheme 5, eqn. (2)). Phosphine-borane complexes **9** and **10** are remarkably stable at ambient conditions and do not suffer intramolecular reduction of oxime group. Given the possibility of removing BH_3 fragment using known procedures,[24] this transformation can be viewed as method for preparation of valuable tertiary β-oximinoalkylphosphines of type **7**. As a demonstration of this, borane **9a** was converted into free phosphine **7a** in 65 % yield upon the action of DABCO (Scheme 5, eqn. (3)).

Scheme 5. Addition of phosphine-borane complexes to ene-nitrosoacetals **4**



The plausible mechanism involved in the reaction of ene-nitrosoacetals **4** with P-H nucleophiles is depicted in Scheme 6. Blue color was observed in some reactions confirming the participation of **NSA** as intermediates. The later are generated from enamines **4** upon the attack of a Lewis base (LB) on the silicon atom followed by the fragmentation of heminitrosoacetal anion **A**. P-nucleophile or even DMF can act as a Lewis base (dissolution of **4a** in a pure DMF results in the appearance of blue color (λ_{max} = 738 nm) characteristic for **NSA)**.[5b,18a] Subsequent Michael addition of the deprotonated P-nucleophile to the transient **NSA** affords the corresponding α-P-substituted oxime.

Scheme 6. Plausible mechanism for coupling of ene-nitrosoacetals **4** with P-H nucleophiles



Conclusions

In conclusion, Michael addition of P-nucleophiles taken in H-form (diphenylphosphine oxide, diisopropyl phosphite, diphenylphosphine-borane complex and triphenylphosphonium bromide) to highly reactive conjugated nitrosoalkenes has been achieved. Among four types of **NSA** precursors tested, ene-nitrosoacetals **4** performed most efficient in these reactions. New methods for the synthesis of valuable β-oximinoalkyl-substituted phosphonates, phosphine oxides, phosphine-borane complexes and phosphonium salts have been developed.

Experimental

All reactions were carried out in oven-dried (150°C) glassware. NMR spectra were recorded at room temperature with residual solvents peaks as an internal standard. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), m (multiplet), br (broad). HRMS were measured on electrospray ionization (ESI) instrument with a time-of-flight

(TOF) detector. Column chromatography was performed using silica gel 40-60 μm 60A with hexane/ethyl acetate mixtures as eluents. Analytical thin-layer chromatography was performed on silica gel plates with QF-254. Visualization was accomplished with UV light and or solution of anisaldehyde/H_2SO_4 in ethanol. CH_2Cl_2 and MeCN were distilled from CaH_2, DMF was distilled from CaH_2 under reduced pressure. THF and Et_2O were distilled from $LiAlH_4$. Hexane, petroleum ether, pentane, methanol and ethyl acetate were distilled without drying agents. Diphenylphosphine oxide, diisopropyl phosphite, diphenyl phosphine, triphenyl phosphine, phenyl phosphine (10 % soln in hexane) and BH_3-SMe_2 were commercial grade and were used as received. Triphenylphosphonium bromide,[25] quaternary triethylammonium salt **2a**[19] were prepared using previously described protocols. Previously described ene-nitrosoacetals **4a**,[26] **4b**,[26] **4c**,[27] **4d**,[28] **4e**,[29] **4f**,[27] **4g**[26] and **4h**[26] were prepared from corresponding aliphatic nitro compounds in accordance with literature procedures (for structures of **4** see Scheme S1 in the Supporting Information).

1-Chloropropan-2-one O-(*tert*-butyldimethylsilyl) oxime (3a). To a stirred solution of chloroacetone (0.73 mL, 0.85 g, 9.15 mmol) in $CHCl_3$ (27 mL) were added molecular sieves 4Å (1.7 g) followed by O-(*tert*-butyldimethylsilyl)hydroxylamine[30] (2.70 g, 18.4 mmol) at rt under argon atmosphere. The reaction was stirred for 24 h and additional portion of molecular sieves 4Å (1.7 g) was added and the mixture was kept for additional 120 h with occasional shaking. Then, the solution was filtered off, concentrated in vacuum (40 Torr, 40 °C), and the residue was subjected to flash chromatography on silica gel (eluent – petroleum ether) to give 0.706 g (35 % based on chloroacetone) of oxime ether **3a** as a colorless volatile liquid. R_f = 0.74 (EtOAc–hexane, 1:3). Mixture of *E*/*Z* isomers (ratio 6 : 1). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 4.12 (s, 2H), 2.00 (s, 3H), 0.95 (s, 9H), 0.19 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*, *E*-isomer) δ 157.7, 46.3, 26.1, 18.2, 12.2, -5.2. ^{1}H NMR (300 MHz, Chloroform-*d*, *Z*-isomer) δ 4.31 (s, 2H), 2.05 (s, 3H), 0.95 (s, 9H), 0.19 (s, 6H). HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_9H_{21}ClNOSi]^+$: 222.1075 and 224.1046; found: 222.1076 and 224.1047.

***N*-(But-1-en-2-yl)-O-(trimethylsilyl)-*N*-((trimethylsilyl)oxy)hydroxylamine (4i).** Prepared by silylation of 2-nitrobutane (1.9 g, 18.5 mmol) with TMSBr (5.4 mL, 40.6 mmol) and Et_3N (5.9 mL, 42.4 mmol) using a procedure analogous to the synthesis of enamine **4c**.[26] Yield: 3.77 g (82 %). Colorless liquid unstable at rt (stored in CH_2Cl_2 solution at -20 °C). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 5.01 (m, 1H), 4.55 (m, 1H), 2.31 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.19 (s, 18H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*) δ 161.5 (C), 101.4 (CH_2), 20.8 (CH_2), 12.4 (CH_3), 0.1 (6 CH_3). ^{29}Si{^{1}H} NMR (59 MHz, Chloroform-*d*): δ = 24.3. HRMS: *m*/*z* $[M+Na]^+$ calcd. for $[C_{10}H_{25}NO_2Si_2Na]^+$: 270.1316; found: 270.1316.

Procedure used for model experiments (Table 1, Table 2, entries 1, 11, 13): To a corresponding **NSA** precursor (**1a**, **2a**, **3a** or **4a**, 0.25 mmol for $(^i$PrO$)_2$POH, 0.5 mmol for Ph_2POH) were consequently added a solution of P-nucleophile (0.25 mmol) in DMF (0.4 mL) and additive (Et_3N – 1 equiv. per **NSA** precursor, K_2CO_3 – 0.5 equiv. per **NSA** precursor, TBAF – 1 equiv. per **NSA** precursor, DBU – 0.1 equiv. per **NSA** precursor, Ti(O^iPr)$_4$ – 0.1 equiv. per **NSA** precursor) at 0 °C under argon atmosphere with vigorous stirring. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 2 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was analyzed by ^{1}H NMR with internal standard (trichloroethylene). Results are summarized in Table 1.

Procedure used for model experiments (Table 2, entries 2-7, 10): To ene-nitrosoacetal **4a** (58 mg, 0.25 mmol) was added corresponding solvent (0.75 mL) followed by $(^i$PrO$)_2$POH at 0 °C under argon atmosphere with vigorous stirring. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 2 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was analyzed by ^{1}H NMR with internal standard (trichloroethylene). Results are summarized in Table 2.

Procedure used for model experiments (Table 2, entries 14-20): To a ene-nitrosoacetal **4a** (58 mg, 0.25 mmol) was added a solution of (^{i}PrO)$_2$POH (amount specified in Table 2) in DMF (0.4 mL for entries 14-18; 1 mL for entry 19; 2.5 mL for entry 20) at rt (for entry 14), 0 °C (for entries 15, 16, 18-20), -20 °C (for entry 17) under argon atmosphere with vigorous stirring. The reaction was kept at the temperature specified in Table 2 for the indicated period of time. Methanol (ca. 2 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was analyzed by ^{1}H NMR with internal standard (trichloroethylene). Results are summarized in Table 2.

General procedure for the addition of P-nucleophiles to ene-nitrosoacetals 4. A stock 1 M solution of ene-nitrosoacetal in CH_2Cl_2 (2 mL, 2 mmol) was placed in Schlenk tube and solvent was evaporated in vacuum. To the residue, a solution of a P-nucleophile (1 mmol, if not stated otherwise) in DMF (1.6 mL) was added at 0 °C under argon atmosphere with vigorous stirring. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 5 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was subjected to a column chromatography on silica gel (for compounds **5a-h**; **6a-e**,**i**) or crystallization (for compound **8a**) to give the desired product.

(2-(Hydroxyimino)propyl)diphenylphosphine oxide (5a). Prepared according to general procedure from 101 mg of diphenylphosphine oxide (0.5 mmol) and 233 mg of enamine **4a** (1.0 mmol). Yield: 111 mg (81 % based on Ph_2POH). White crystals. Mp 187 – 189 °C (pentane–Et_2O) (lit.[15c] 190 – 191 °C, lit.[14] 188 – 190 °C). R_f = 0.14 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 9 : 1, changes to ca. 1.5 : 1 upon standing). ^{1}H NMR (300 MHz, DMSO-d_6, *E*-isomer) δ 10.63 – 10.61 (br, 1H), 7.93 – 7.72 (m, 4H), 7.65 – 7.39 (m, 6H), 3.46 (d, J = 13.8 Hz, 2H), 1.79 (d, J = 2.4 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, DMSO-d_6, *E*-isomer) δ 149.0 (d, J = 8.7 Hz, C), 133.7 (d, J = 97.9 Hz, 2 C), 131.6 (d, J = 2.1 Hz, 2 CH), 130.6 (d, J = 9.4 Hz, 4 CH), 128.5 (d, J = 11.6 Hz, 4 CH), 36.7 (d, J = 67.1 Hz, CH_2), 15.2 (CH_3). ^{31}P{^{1}H} NMR (121

MHz, DMSO-d_6, *E*-isomer) δ 27.49. ^{1}H NMR (300 MHz, DMSO-d_6, *Z*-isomer, characteristic signals) δ 10.61 – 10.60 (br, 1H), 3.66 (d, *J* = 14.9 Hz, 2H), 1.82 (d, *J* = 2.3 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, DMSO-d_6, *Z*-isomer, characteristic signals) δ 130.4 (d, *J* = 10.2 Hz, 4 CH), 21.1 (CH_3). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6, *Z*-isomer) δ 26.60. FTIR (KBr): 3150 (s), 3059 (s), 2857 (s, sh), 1652 (w), 1589 (w), 1437 (s, sh), 1369 (m, sh), 1264 (m), 1173 (s), 1144 (s), 1120 (s), 1005 (m), 962 (s), 816 (m), 750 (s), 720 (s), 695 (s), 573 (m). HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{15}H_{17}NO_2P]^+$: 274.0991; found: 274.0986.

Scale-up synthesis of 5a. A stock 1 M solution of ene-nitrosoacetal **4a** in CH_2Cl_2 (20 mL, 20 mmol) was placed in Schlenk flask and solvent was evaporated in vacuum. To the residue, a cooled (0 – 5 °C) solution of diphenylphosphine oxide (10 mmol) in DMF (16 mL) was added dropwise at 0 °C under argon atmosphere with vigorous stirring. The mixture was slowly allowed to warm to rt and then kept overnight with occasional shaking. Methanol (ca. 30 mL) was added and the mixture was stirred for additional 1 h. Then, the solution was concentrated under reduced pressure to remove volatiles and DMF (40 – 50 °C) and dried in vacuum (0.2 Torr). The resulting white gummy solid was triturated with ethyl acetate several times, filtered and dried in vacuum until constant weight to give 1.81 g (66 %) of pure **5a**. Mother liquors were concentrated under reduced pressure and the residue was subjected to a column chromatography on silica gel to give additional 0.22 g (8 %) of **5a**. Overall yield: 2.03 g (74 %).

2-(Diphenylphosphoryl)acetaldehyde oxime (5b). Prepared according to general procedure from 152 mg of diphenylphosphine oxide (0.75 mmol) and 329 mg of enamine **4b** (1.5 mmol). Yield: 164 mg (85 % based on Ph_2POH). White crystals. Mp 158 – 161 °C (pentane–Et_2O). R_f = 0.17 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 9 : 1). ^{1}H NMR (300 MHz, DMSO-d_6, *E*-isomer) δ 10.88 (br s, 1H), 7.81 (dd, *J* = 10.9, 8.5 Hz, 4H), 7.62 – 7.47 (m, 6H), 7.23 (q, *J* = 6.5 Hz, 1H), 3.50 (dd, *J* = 14.2, 6.5 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, DMSO-d_6, *E*-isomer) δ 141.4 (dd, *J* = 8.3, 3.5 Hz, C), 133.2 (d, *J* = 98.4 Hz, 2 C-P), 131.8 (d, *J* = 2.8 Hz, 2 CH), 130.6 (d, *J* = 9.4 Hz, 4 CH), 128.7 (d, *J* = 11.7 Hz, 4 CH), 31.2 (d, *J* = 68.0 Hz, CH_2).

$^{31}P\{^{1}H\}$ NMR (121.49 MHz, DMSO-d_6, *E*-isomer) δ = 27.91. ^{1}H NMR (300 MHz, DMSO-d_6, *Z*-isomer, characteristic signals) δ 11.33 (br s, 1H), 6.70 (q, *J* = 5.8 Hz, 2H), 3.64 (dd, *J* = 14.4, 5.8 Hz, 4H). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, DMSO-d_6, *Z*-isomer) δ = 27.62. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{14}H_{15}NO_2P]^+$: 260.0835; found: 260.0832. Anal. Calcd. for $C_{14}H_{14}NO_2P$: C, 64.86 %; H, 5.44 %; N, 5.40 %. Found: C , 64.72 %; H, 5.47 %; N, 5.50 %.

Methyl 5-(diphenylphosphoryl)-4-(hydroxyimino)pentanoate (5c). Prepared according to general procedure from 101 mg of diphenylphosphine oxide (0.5 mmol) and 305 mg of enamine **4a** (1.0 mmol). Yield: 152 mg (88 % based on Ph_2POH). Oil which solidified upon standing. Mp 50 – 54 °C. R_f = 0.25 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 9 : 1). ^{1}H NMR (300 MHz, DMSO-d_6, *E*-isomer) δ 10.77 (s, 1H), 7.90 – 7.72 (m, 4H), 7.64 – 7.43 (m, 6H), 3.58 (s, 3H), 3.52 (d, *J* = 13.8 Hz, 2H), 2.55 (s, 4H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DEPT135, DMSO-d_6, *E*-isomer) δ 172.7 (C), 151.1 (C), 133.6 (d, *J* = 97.4 Hz, 2 C), 131.6 (d, *J* = 2.4 Hz, 2 CH), 130.6 (d, *J* = 9.4 Hz, 4 CH), 128.5 (d, *J* = 11.6 Hz, 4 CH), 51.3 (CH_3), 35.2 (d, *J* = 67.3 Hz, CH_2), 28.7 (CH_2), 24.4 (CH_2). $^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO-d_6, *E*-isomer) δ 27.91. ^{1}H NMR (300 MHz, DMSO-d_6, *Z*-isomer, characteristic signals) δ 10.91 (s, 1H), 3.67 (d, *J* = 15.1 Hz, 2H). $^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO-d_6, *Z*-isomer) δ 26.69. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{18}H_{21}NO_4P]^+$: 346.1203; found: 346.1193.

(2-(Hydroxyimino)-3-phenylpropyl)diphenylphosphine oxide (5d). Prepared according to general procedure from 51 mg of diphenylphosphine oxide (0.25 mmol) and 155 mg of enamine **4d** (0.5 mmol). Yield: 78 mg (90 % based on Ph_2POH). White crystals. Mp 128 – 131 °C (pentane–Et_2O). R_f = 0.36 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 1.4 : 1). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 10.1 – 8.3 (br, 1H), 7.77 – 7.68 (m, 4H), 7.55 – 7.33 (m, 6H), 7.29 – 7.18 (m, 5H), 3.87 (s, 2H), 3.20 (d, *J* = 13.6 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 152.0 (d, *J* = 8.8 Hz, C), 136.4 (C), 132.3 (d, *J* = 100.7 Hz, 2 C), 131.9 (d, *J* = 2.8 Hz, 2 CH), 131.0 (d, *J* = 9.4 Hz, 4 CH), 129.5 (2 CH), 128.7 (2 CH), 128.6 (d, *J* = 6.1 Hz, 4 CH), 126.5 (CH), 35.0 (d, *J* = 67.7 Hz, CH_2), 34.3 (CH_2). $^{31}P\{^{1}H\}$ NMR

(121 MHz, Chloroform-*d*) δ 30.42. ^{1}H NMR (300 MHz, Chloroform-*d*, *Z*-isomer) δ 10.1 – 8.3 (br, 1H), 7.88 – 7.78 (m, 4H), 7.55 – 7.33 (m, 6H), 7.29 – 7.18 (m, 5H), 3.66 (d, *J* = 1.9 Hz, 2H), 3.51 (d, *J* = 14.9 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 151.6 (d, *J* = 8.8 Hz, C), 136.8 (C), 130.9 (d, *J* = 9.0 Hz, 4 CH), 129.5 (2 CH), 126.6 (CH), 40.9 (CH_2), 29.2 (d, *J* = 65.2 Hz, CH_2). ^{31}P{^{1}H} NMR (121.49 MHz, Chloroform-*d*) δ = 29.92. FTIR (KBr): 3184 (m, br), 3060 (m, sh), 2879 (m, br), 1968 (w, sh), 1897 (w, sh), 1813 (w, sh), 1720 (w, sh), 1638 (w, sh), 1591 (w, sh), 1494 (m), 1453 (m), 1437 (s), 1390 (w), 1333 (w, sh), 1262 (m), 1184 (s), 1120 (s), 1100 (m), 1073 (w), 1029 (w), 976 (s), 836 (m), 734 (s, sh), 717 (s), 694 (s), 619 (w), 593 (m), 560 (m), 536 (s), 508 (s, sh), 412 (w, sh). HRMS: *m*/*z* [M+H]$^{+}$ calcd. for [$C_{21}H_{21}NO_2P$]$^{+}$: 350.1304; found: 350.1303.

(2-(Hydroxyimino)-2-phenylethyl)diphenylphosphine oxide (5e). Prepared according to general procedure from 101 mg of diphenylphosphine oxide (0.5 mmol) and 295 mg of enamine **4e** (1.0 mmol). Yield: 155 mg (92 % based on Ph_2POH). White crystals. Mp 155 –158 °C (pentane–Et_2O). R_f = 0.31 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 1.2 : 1). ^{1}H NMR (300 MHz, DMSO-d_6, *E*-isomer) δ 10.93 (br s, 1H), 7.83 – 7.69 (m, 4H), 7.55 – 7.38 (m, 6H), 7.25 (m, 5H), 3.83 (d, *J* = 13.6 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, DMSO-d_6, *E*-isomer, characteristic signals) δ 148.5 (d, *J* = 10.0 Hz, C), 133.9 (d, *J* = 98.4 Hz, 2 C), 131.4 (d, *J* = 1.9 Hz, 2 CH), 130.6 (d, *J* = 9.2 Hz, 4 CH), 36.4 (d, *J* = 67.3 Hz, CH_2). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6, *E*-isomer) δ 27.04. ^{1}H NMR (300 MHz, DMSO-d_6, *Z*-isomer) δ 11.49 (s, 1H), 7.83 – 7.69 (m, 4H), 7.67 – 7.58 (m, 2H), 7.55 – 7.38 (m, 6H), 7.25 (m, 3H), 4.11 (d, *J* = 15.4 Hz, 4H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, DMSO-d_6, *Z*-isomer, characteristic signals) δ 134.0 (d, *J* = 98.8 Hz, 2 C), 131.6 (d, *J* = 2.2 Hz, 2 CH), 130.5 (d, *J* = 9.5 Hz, 4 CH), 29.0 (d, *J* = 64.3 Hz, CH_2). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6, *Z*-isomer) δ 26.00. ^{13}C{^{1}H} NMR (75 MHz, DMSO-d_6, signals of both isomers): δ 135.8 (C), 133.8 (C), 128.6 (CH), 128.4 (d, *J* = 11.6 Hz, 4 CH), 128.3 (CH), 128.2 (2 CH), 127.9 (2 CH), 127.4 (2 CH), 126.4 (2 CH). HRMS: *m*/*z*

$[M+H]^+$ calcd. for $[C_{20}H_{19}NO_2P]^+$: 336.1148; found: 336.1148. Anal. Calcd. for $C_{20}H_{18}NO_2P$: C, 71.63 %; H, 5.41 %; N, 4.18 %. Found: C, 71.13 %; H, 5.06 %; N, 4.20 %.

Ethyl 3-(diphenylphosphoryl)-2-(hydroxyimino)propanoate (5f). Prepared according to general procedure from 76 mg of diphenylphosphine oxide (0.38 mmol) and 218 mg of enamine **4f** (0.75 mmol). Yield: 118 mg (89 % based on Ph_2POH). White solid. Mp 142 – 145 °C (pentane–Et_2O) (lit.[13b] 152 – 153 °C). R_f = 0.19 (EtOAc). Single isomer with *E*-configuration. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 12.91 (s, 1H), 7.90 – 7.78 (m, 4H), 7.57 – 7.37 (m, 6H), 4.06 (q, J = 7.1 Hz, 2H), 3.93 (d, J = 14.9 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*) δ 163.9 (C), 142.9 (d, J = 9.6 Hz, C), 132.1 (d, J = 2.5 Hz, 2 CH), 132.0 (d, J = 102.3 Hz, 2 C), 131.3 (d, J = 9.8 Hz, 4 CH), 128.6 (d, J = 12.3 Hz, 4 CH), 61.7 (CH_2), 28.7 (d, J = 64.7 Hz, CH_2), 14.1 (CH_3). ^{31}P{^{1}H} NMR (121.49 MHz, Chloroform-*d*) δ = 30.09. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{17}H_{19}NO_4P]^+$: 332.1046; found: 332.1049. NMR spectra are in agreement with literature data.[13b]

2-(Diphenylphosphoryl)propanal oxime (5g). Prepared according to general procedure from 101 mg of diphenylphosphine oxide (0.5 mmol) and 233 mg of enamine **4g** (1.0 mmol). Yield: 122 mg (89 % based on Ph_2POH). White crystals. Mp 157 – 159 °C (pentane–Et_2O). R_f = 0.22 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 1.1 : 1). ^{1}H NMR (300 MHz, COSY, HSQC, Chloroform-*d*, *E*-isomer) δ 11.01 – 9.47 (br, 1H, OH), 7.92 – 7.66 (m, 4H, *o*-C_6H_4), 7.56 – 7.28 (m, 7H, *m*,*p*-C_6H_5 and =CH), 3.58 – 3.37 (m, 1H, CH-P), 1.30 (dd, J = 15.6, 7.0 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, HSQC, Chloroform-*d*, *E*-isomer, characteristic signals) δ 147.4 (C), 36.3 (d, J = 69.1 Hz, CH_2), 11.4 (d, J = 3.8 Hz, CH_3). ^{1}H NMR (300 MHz, DMSO-d_6, *E*-isomer) δ 10.89 (br s, 1H, OH), 7.96 – 7.71 (m, 4H, *o*-C_6H_4), 7.69 – 7.38 (m, 6H, *m*,*p*-C_6H_5), 7.17 (dd, J = 6.7, 4.4 Hz, 1H, =CH), 4.00 – 3.75 (m, 1H, CH-P), 1.17 (dd, J = 15.3, 7.1 Hz, 3H, CH_3). ^{1}H NMR (300 MHz, COSY, HSQC, Chloroform-*d*, *Z*-isomer) δ 11.01 – 9.47 (br, 1H, OH), 7.92 – 7.66 (m, 4H, *o*-C_6H_4), 7.56 – 7.28 (m, 6H, *m*,*p*-C_6H_5), 6.84 (dd, J = 8.6, 4.6 Hz, 1H), 4.49 – 4.32 (m, 1H), 1.27 (dd, J = 15.9, 7.1 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, DEPT135,

HSQC, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 146.7 (C), 30.2 (d, J = 69.6 Hz, CH_2), 11.0 (d, J = 4.9 Hz, CH_3). ^{1}H NMR (300 MHz, DMSO-d_6, *Z*-isomer) δ 11.30 (s, 1H, OH), 7.97 – 7.72 (m, 4H, *o*-C_6H_4), 7.67 – 7.41 (m, 6H, *m*,*p*-C_6H_5), 6.67 (dd, J = 8.5, 4.6 Hz, 1H, =CH), 4.47 – 4.30 (m, 1H, CH-P), 1.12 (dd, J = 14.8, 6.8 Hz, 3H, CH_3). ^{13}C{^{1}H} NMR (75 MHz, Chloroform-*d*, signals of both isomers): δ 132.4 – 131.9 (m, 2 *p*-C_6H_5), 131.2 (d, J = 99.8 Hz), 131.1 (d, J = 98.4 Hz), 131.0 (d, J = 98.2 Hz), 130.3 (d, J = 98.8 Hz) (2 C-P), 131.6 (d, J = 9.0 Hz), 131.3 (d, J = 9.2 Hz), 131.14 (d, J = 9.1 Hz), 131.10 (d, J = 9.4 Hz), 128.83 (d, J = 11.8 Hz), 128.78 (d, J = 11.7 Hz), 128.5 (d, J = 11.6 Hz) (8 *o*,*m*-C_6H_5). ^{31}P{^{1}H} NMR (121.49 MHz, Chloroform-*d*, both isomers) δ = 32.34 and 32.06. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{15}H_{17}NO_2P]^+$: 274.0991; found: 274.0993.

2-(Diphenylphosphoryl)cyclohexanone oxime (5h). Prepared according to general procedure from 202 mg of diphenylphosphine oxide (1 mmol) and 546 mg of enamine **4h** (2.0 mmol). Yield: 100 mg (32 % based on Ph_2POH). White crystals. Mp 79 – 83 °C (pentane–Et_2O). R_f = 0.35 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 1.1 : 1). ^{1}H NMR (300 MHz, HSQC, DMSO-d_6) δ 10.55 – 10.52 and 10.52 – 10.48 (2 br, 1H and 1H, OH, both isomers), 7.97 – 7.69 and 7.65 – 7.34 (2 m, 8H and 12 H, *o*,*m*,*p*-C_6H_5, both isomers), 4.60 – 4.47 (m, 1H, CH-P, *Z*-isomer), 3.79 – 3.65 (m, 1H, CH-P, *E*-isomer), 2.97 – 2.82 and 2.62 – 2.50 (2 m, 1 H and 1 H, both isomers), 2.38 – 1.10 (m, 14H). ^{13}C{^{1}H} NMR (75 MHz, HSQC, DMSO-d_6) δ 154.1 and 153.1 (2 m, 2 C=N, both isomers), 133.4 (d, J = 96.5 Hz), 133.2 (d, J = 93.2 Hz), 133.1 (d, J = 96.7 Hz) and 132.8 (d, J = 94.3 Hz) (4 C of C_6H_5, both isomers), 131.7 (d, J = 2.0 Hz), 131.5 (d, J = 2.5 Hz), 131.4 (d, J = 1.6 Hz) and 131.1 (d, J = 1.6 Hz) (4 CH of C_6H_5, both isomers), 130.9, 130.8, 130.7 and 130.6 (m, 8 CH of C_6H_5, both isomers), 128.8 (d, J = 11.0 Hz), 128.6 (d, J = 11.2 Hz), 128.2 (d, J = 11.0 Hz) and 127.9 (d, J = 11.6 Hz) (8 CH of C_6H_5, both isomers), 40.1 (CH-P, *E*-isomer, overlapped with DMSO-d_5), 33.7 (d, J = 65.5 Hz, CH-P, *Z*-isomer), 30.8, 27.0, 26.9, 26.6 (d, J = 3.8 Hz), 25.0, 23.4 and 22.6 (d, J = 3.2 Hz), 22.1 (8 CH_2, both isomers). ^{31}P{^{1}H} NMR (121 MHz, DMSO-d_6) δ 32.83 and 32.07 (both isomers). NMR spectra are in

agreement with literature data.[31] HRMS: *m/z* $[M+H]^+$ calcd. for $[C_{18}H_{21}NO_2P]^+$: 314.1304; found: 314.1302.

Diisopropyl (2-(hydroxyimino)propyl)phosphonate (6a). Prepared according to general procedure from 83 mg of diisopropyl phosphite (0.5 mmol) and 233 mg of enamine **4a** (1.0 mmol). Yield: 84 mg (71 % based on $(^iPrO)_2POH$). Oil. R_f = 0.24 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 9 : 1, changes to 1.5 : 1 upon standing). ^1H NMR (300 MHz, Chloroform-*d, E*-isomer) δ 9.8 – 8.9 (br s, 1H), 4.68 (m, 2H), 2.71 (d, *J* = 21.9 Hz, 2H), 1.96 (d, *J* = 2.1 Hz, 3H), 1.27 (m, 12H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d, E*-isomer) δ 150.8 (d, *J* = 9.2 Hz, C), 71.1 (d, *J* = 6.7 Hz, 2 CH), 35.1 (d, *J* = 140.4 Hz, CH_2), 24.1 (d, *J* = 3.9 Hz, 2 CH_3), 24.0 (d, *J* = 4.9 Hz, 2 CH_3), 14.6 (d, *J* = 1.4 Hz, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, *E*-isomer) δ 23.53. ^1H NMR (300 MHz, Chloroform-*d, Z*-isomer) δ 9.8 – 8.9 (br s, 1H), 4.68 (m, 2H), 3.01 (d, *J* = 23.5 Hz, 2H), 1.87 (s, 3H), 1.27 (m, 12H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d, Z*-isomer, characteristic signals) δ 28.25 (d, *J* = 138.1 Hz, CH_2), 20.84 (s, CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, *Z*-isomer) δ 22.36. NMR spectra are in accordance with literature data.[32] HRMS: *m/z* $[M+H]^+$ calcd. for $[C_9H_{21}NO_4P]^+$: 238.1204; found: 238.1203.

Diisopropyl (2-(hydroxyimino)ethyl)phosphonate (6b). Prepared according to general procedure from 166 mg of diisopropyl phosphite (1.0 mmol) and 438 mg of enamine **4a** (2.0 mmol). Yield: 141 mg (63 % based on $(^iPrO)_2POH$). Oil unstable at rt. R_f = 0.29 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 4 : 1). ^1H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 9.02 (br m, 1H), 7.38 (q, *J* = 6.4 Hz, 1H), 4.71 (m, 2H), 2.73 (dd, *J* = 21.7, 6.5 Hz, 2H), 1.30 (d, *J* = 6.0 Hz, 12H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 143.2 (d, *J* = 8.8 Hz, C), 71.4 (d, *J* = 6.6 Hz, 2 CH), 29.4 (d, *J* = 142.2 Hz, CH_2), 24.1 (d, *J* = 4.1 Hz, 2 CH_3), 24.1 (d, *J* = 4.1 Hz, 2 CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, *E*-isomer) δ 23.17 (d, *J* = 11.1 Hz). ^1H NMR (300 MHz, Chloroform-*d*, *Z*-isomer) δ 9.45 (br m, 1H), 6.78 (q, *J* = 5.8 Hz, 1H), 4.71 (m, 2H), 2.99 (dd, *J* = 21.6, 5.9 Hz, 2H), 1.30 (d, *J* = 6.0 Hz, 12H). $^{31}P\{^1H\}$ NMR (121

MHz, Chloroform-*d*, *Z*-isomer) δ 22.45 (d, J = 12.4 Hz). NMR spectra are in accordance with literature data.[33] HRMS: *m*/*z* $[M+Na]^+$ calcd. for $[C_8H_{18}NO_4PNa]^+$: 246.0872; found: 246.0866.

Methyl 5-(diisopropoxyphosphoryl)-4-(hydroxyimino)pentanoate (6c). Prepared according to general procedure from 165 mg of diisopropyl phosphite (1.0 mmol) and 610 mg of enamine **4c** (2.0 mmol). Yield: 216 mg (70 % based on $(^iPrO)_2POH$). Oil. R_f = 0.27 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 25 : 1). ^1H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 8.84 (br s, 1H), 4.82 – 4.65 (m, 2H), 3.68 (s, 3H), 2.81 (d, J = 21.9 Hz, 2H), 2.76 – 2.59 (m, 4H), 1.33 (d, J = 6.1 Hz, 6H), 1.31 (d, J = 6.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 173.2 (C), 152.8 (d, J = 9.9 Hz, C), 71.1 (d, J = 6.6 Hz, 2 CH), 51.7 (CH_3), 33.8 (d, J = 140.3 Hz, CH_2), 29.6 (CH_2), 24.1 (d, J = 1.5 Hz, CH_2), 24.0 (d, J = 3.9 Hz, 2 CH_3), 23.9 (d, J = 5.0 Hz, 2 CH_3). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, *E*-isomer) δ = 23.43. ^1H NMR (300 MHz, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 9.25 – 9.13 (br, 1H), 2.98 (d, J = 21.8 Hz, 2H). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, *Z*-isomer) δ 22.9. FTIR (thin layer): 3241 (s), 3093 (m), 2981 (s), 2935 (s), 1739 (s), 1439 (m), 1387 (m, sh), 1224 (s, sh), 1177 (s), 1105 (m), 993 (s), 892 (w), 758 (w), 610 (w). HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{12}H_{25}NO_6P]^+$: 310.1413; found: 310.1414.

Diisopropyl (2-(hydroxyimino)-3-phenylpropyl)phosphonate (6d). Prepared according to general procedure from 83 mg of diisopropyl phosphite (0.5 mmol) and 464 mg of enamine **4d** (1.5 mmol). Yield: 92 mg (59 % based on $(^iPrO)_2POH$). Oil. R_f = 0.46 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 15 : 1). ^1H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 9.86 – 9.44 (br m, 1H), 7.40 – 7.11 (m, 5H), 4.84 – 4.67 (m, 2H), 3.96 (s, 2H), 2.67 (d, J = 21.7 Hz, 2H), 1.34 (d, J = 6.1 Hz, 6H), 1.32 (d, J = 6.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 152.1 (d, J = 9.6 Hz, C), 136.4 (C), 129.4 (2 CH), 128.7 (2 CH), 126.6 (CH), 71.1 (d, J = 6.9 Hz, 2 CH), 33.6 (d, J = 1.9 Hz, CH_2), 32.3 (d, J = 141.2 Hz, CH_2), 24.1 (d, J = 3.8 Hz, 2 CH_3), 24.0 (d, J = 4.9 Hz, 2 CH_3). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, *E*-isomer) δ 23.70. ^1H NMR (300 MHz, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 3.72

(d, J = 2.4 Hz, 2H), 2.96 (d, J = 23.7 Hz, 2H). $^{31}P\{^{1}H\}$ NMR (121 MHz, Chloroform-*d*, *Z*-isomer) δ 22.4. FTIR (KBr): 3239 (s, br), 3065 (s, sh), 2980 (s), 2930 (s), 2246 (w), 1726 (m), 1650 (m), 1602 (m), 1495 (m), 1454 (m), 1376 (m), 1237 (s, sh), 1144 (m), 1104 (m), 993 (s, br), 911 (m), 861 (w), 734 (s), 702 (m), 647 (w), 601 (w), 550 (w), 479 (w). HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{15}H_{25}NO_4P]^+$: 314.1516; found: 314.1518.

Diisopropyl (2-(hydroxyimino)-2-phenylethyl)phosphonate (6e). Prepared according to general procedure from 83 mg of diisopropyl phosphite (0.5 mmol) and 443 mg of enamine **4e** (1.5 mmol). Yield: 67 mg (45 % based on $(^{i}PrO)_2POH$). Oil. R_f = 0.22 and 0.34 (2 isomers, EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 22 : 1, changes to 3 : 1 upon standing). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 9.55 – 9.35 (br s, 1H), 7.52 (d, J = 6.5 Hz, 2H), 7.42 – 7.28 (m, 3H), 4.63 (m, 2H), 3.10 (d, J = 21.5 Hz, 2H), 1.20 (d, J = 6.2 Hz, 6H), 1.14 (d, J = 6.2 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 150.0 (d, J = 10.0 Hz, C), 133.3 (C), 129.0 (CH), 128.5 (2 CH), 128.0 (2 CH), 71.0 (d, J = 6.9 Hz, 2 CH), 34.7 (d, J = 141.7 Hz, CH_2), 24.1 (d, J = 3.7 Hz, 2 CH_3), 23.8 (d, J = 5.2 Hz, 2 CH_3). $^{31}P\{^{1}H\}$ NMR (121 MHz, Chloroform-*d*, *E*-isomer) δ 23.35. ^{1}H NMR (300 MHz, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 3.50 (d, J = 23.5 Hz, 1H). $^{31}P\{^{1}H\}$ NMR (121 MHz, Chloroform-*d*, *Z*-isomer) δ 22.1. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{14}H_{23}NO_4P]^+$: 300.1359; found: 300.1358.

Diisopropyl (2-(hydroxyimino)butyl)phosphonate (6i). Prepared according to general procedure from 165 mg of diisopropyl phosphite (1.0 mmol) and 494 mg of enamine **4i** (2.0 mmol). Yield: 216 mg (70 % based on $(^{i}PrO)_2POH$). Oil. R_f = 0.29 (EtOAc). Dynamic mixture of *E*/*Z* isomers (ratio 15 : 1, changes to ca. 1 : 1 upon standing). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 9.95 – 8.86 (br, 1H), 4.76 – 4.60 (m, 2H), 2.69 (d, J = 21.9 Hz, 2H), 2.47 (q, J = 7.0 Hz, 2H), 1.27 (s, 12H), 1.05 (t, J = 7.0 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 155.2 (d, J = 6.9 Hz, C), 71.0 (d, J = 6.8 Hz, 2 CH), 32.7 (d, J = 141.3 Hz, CH_2), 24.1 (d, J = 3.8 Hz, 2 CH_3), 24.0 (d, J = 5.0 Hz, 2 CH_3), 21.5 (d, J = 1.7 Hz, CH_2), 9.9 (CH_3). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, Chloroform-*d*, *E*-isomer) δ = 23.68. ^{1}H NMR

(300 MHz, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 3.01 (d, *J* = 23.6 Hz, 2H), 2.41 – 2.33 (m, 2H). $^{31}P\{^{1}H\}$ NMR (121 MHz, Chloroform-*d*, *Z*-isomer) δ 22.49. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{10}H_{23}NO_4P]^+$: 252.1359; found: 252.1363.

1-(Diphenylphosphino)propan-2-one oxime (7a). In a Schlenk tube was placed 1 mL of 1 M solution of ene-nitrosoacetal **4a** (233 mg, 1 mmol) in CH_2Cl_2 and solvent was evaporated in vacuum. To the residue, a solution of diphenyl phosphine (0.26 mL, 1.5 mmol) in DMF (1.6 mL) was added at 0 °C under argon atmosphere. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 5 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was subjected to a column chromatography on silica gel to give 22 mg (9 % based on **4a**) of phosphine **7a** as white crystals. Mp 97 – 101 °C. R_f = 0.38 (EtOAc–hexane, 1:1). Dynamic mixture of *E*/*Z* isomers (ratio 20 : 1). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 8.65 – 7.55 (br, 1H), 7.47 – 7.39 (m, 4H), 7.36 – 7.29 (m, 6H), 3.00 (d, *J* = 1.4 Hz, 2H), 1.97 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 155.6 (d, *J* = 8.3 Hz, C), 137.9 (d, *J* = 13.7 Hz, 2 C-P), 132.9 (d, *J* = 19.2 Hz, 4 CH), 129.0 (2 CH), 128.6 (d, *J* = 6.9 Hz, 4 CH), 36.8 (d, *J* = 16.0 Hz, CH_2), 14.9 (d, *J* = 6.2 Hz, CH_3). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, Chloroform-*d*, *E*-isomer) δ = -19.63. ^{1}H NMR (300 MHz, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 3.22 (d, *J* = 2.0 Hz, 2H), 1.73 (s, 3H). $^{31}P\{^{1}H\}$ NMR (121.49 MHz, Chloroform-*d*, *Z*-isomer) δ = -16.18. HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{15}H_{17}NOP]^+$: 258.1048; found: 258.1071.

(2-(Hydroxyimino)propyl)triphenylphosphonium bromide (8a). In a Schlenk tube was placed 1 mL of 1 M solution of ene-nitrosoacetal **4a** (233 mg, 1 mmol) in CH_2Cl_2 and solvent was evaporated in vacuum. To the residue, a solution of triphenylphosphonium bromide (214 mg, 80 % purity, 0.5 mmol) in DMF (0.8 mL) was added at 0 °C under argon atmosphere. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 5 mL) was added and the mixture was stirred for additional 1 h and then

concentrated under reduced pressure (40 – 50 °C). The residue was treated with water (ca. 3 mL), the precipitate was filtered off, washed with diethyl ether and dried to give 91 mg of salt **8a**. Second crystallization from mother liquor gave addition 74 mg of **8a**. Yield: 165 mg (80 % based on triphenylphosphonium bromide). White crystals. Mp 195 – 199 °C (H_2O). Single isomer with unknown configuration. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.02 (s, 1H), 7.94 – 7.62 (m, 15H), 4.94 (d, J = 14.4 Hz, 2H), 1.82 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, DMSO-d_6) δ 147.6 (d, J = 9.1 Hz, C), 134.4 (d, J = 3.1 Hz, 3 CH), 133.7 (d, J = 10.4 Hz, 6 CH), 129.8 (d, J = 12.7 Hz, 6 CH), 119.7 (d, J = 88.0 Hz, 3 C-P), 28.4 (d, J = 54.6 Hz, CH_2), 15.1 (d, J = 8.0 Hz, CH_3). ^{31}P{^{1}H} NMR (121.49 MHz, DMSO-d_6) δ = 22.32. FTIR (KBr): 3490 (m), 3422 (w), 3134 (s, br), 3060 (s), 2901 (m), 2866 (m), 2207 (w), 2034 (w), 1727 (w, sh), 1663 (w, sh), 1586 (m), 1482 (m), 1436 (s), 1369 (m), 1340 (m), 1315 (m, sh), 1183 (w, sh), 1107 (s), 997 (m, sh), 971 (m), 846 (w), 814 (m), 776 (w), 750 (s), 715 (s), 687 (s), 615 (w), 511 (s, sh), 491 (s), 442 (m). HRMS: m/z [M-Br]$^+$ calcd. for [$C_{21}H_{21}NOP$]$^+$: 334.1355; found: 334.1359.

General procedure for the addition of Ph_2PH•BH_3 complex to *N*,*N*-bis(oxy)enamines 4. *Preparation of diphenylphosphine-borane complex*:[34] in a Schlenk tube with anhydrous THF (3.5 mL) was added Ph_2PH (304 μL, 1.75 mmol) followed by Me_2S•BH_3 (166 μL, 1.75 mmol) complex at 0 °C under argon atmosphere. The mixture was stirred for 1 h to give a 0.5 M solution of Ph_2PH•BH_3 complex in THF (^{1}H NMR spectrum matched with literature data[35]). *Reaction with enamines **4***: 1.5 mL of the obtained 0.5 M solution of Ph_2PH•BH_3 in THF was mixed with DMF (1.2 mL). The resulting solution was added to ene-nitrosoacetal **4** (1.5 mmol) at 0 °C under argon atmosphere. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 5 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was subjected to column chromatography on silica gel to give Michael adduct **9**.

1-(Diphenylphosphino)propan-2-one oxime borane complex (9a). Prepared according to general procedure from 1.5 mL of 0.5 M solution of Ph_2PH•BH_3 (0.75 mmol) in THF and 350

mg of enamine **4a** (1.5 mmol). Yield: 146 mg (72 % based on phosphine complex). Oil. R_f = 0.5 (EtOAc–hexane, 1:1). Dynamic mixture of *E*/*Z* isomers (ratio 1.7 : 1). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 8.62 – 8.08 (br, 1H), 7.84 – 7.65 (m, 4H), 7.56 – 7.39 (m, 6H), 3.25 (d, *J* = 12.5 Hz, 2H), 1.90 (d, *J* = 2.3 Hz, 3H), 1.67 – 0.50 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 152.4 (d, *J* = 4.4 Hz, C), 132.4 (d, *J* = 9.4 Hz, 4 CH), 131.5 (2 CH), 128.9 (d, *J* = 9.9 Hz, 4 CH), 128.4 (d, *J* = 66.9 Hz, 2 C), 34.2 (d, *J* = 33.0 Hz, CH_2), 15.8 (CH_3). ^{1}H NMR (300 MHz, Chloroform-*d*, *Z*-isomer) δ 8.62 – 8.08 (br, 1H), 7.84 – 7.65 (m, 4H), 7.56 – 7.39 (m, 6H), 3.51 (d, *J* = 13.4 Hz, 2H), 1.89 (d, *J* = 1.9 Hz, 3H), 1.67 – 0.50 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*, *Z*-isomer) δ 151.2 (d, *J* = 4.1 Hz, C), 132.4 (d, *J* = 9.8 Hz, 4 CH), 131.5 (2 CH), 129.0 (d, *J* = 54.6 Hz, 2 C), 128.8 (d, *J* = 9.8 Hz, 4 CH), 27.2 (d, *J* = 31.9 Hz, CH_2), 21.5 (CH_3). ^{31}P{^{1}H} NMR (121 MHz, Chloroform-*d*, both isomers) δ 15.05 (br m). ^{11}B{^{1}H} NMR (96 MHz, Chloroform-*d*, both isomers) δ -36.38 – -40.64 (br m). HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{15}H_{20}BNOP]^+$: 272.1373; found: 272.1369; *m*/*z* $[M-H]^+$ calcd. for $[C_{15}H_{18}BNOP]^+$: 270.1216; found: 270.1213.

Methyl 5-(diphenylphosphanyl)-4-(hydroxyimino)pentanoate borane complex (9c). Prepared according to general procedure from 2 mL of 0.5 M solution of $Ph_2PH{\bullet}BH_3$ (1 mmol) in THF and 610 mg of enamine **4c** (2 mmol). Yield: 226 mg (66 % based on phosphine complex). Oil. R_f = 0.45 (EtOAc–hexane, 1:1). Dynamic mixture of *E*/*Z* isomers (ratio 2.6 : 1). ^{1}H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 8.66 – 7.93 (br, 1H), 7.83 – 7.64 (m, 4H), 7.57 – 7.37 (m, 6H), 3.66 (s, 3H), 3.35 (d, *J* = 12.5 Hz, 2H), 2.65 – 2.52 (m, 4H), 1.70 – 0.46 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 173.3 (C), 154.2 (d, *J* = 4.4 Hz, C), 132.4 (d, *J* = 9.4 Hz, 4 CH), 131.5 (d, *J* = 2.8 Hz, 2 CH), 128.9 (d, *J* = 9.9 Hz, 4 CH), 128.6 (d, *J* = 55 Hz, 2 C), 51.8 (CH_3), 32.8 (d, *J* = 33.0 Hz, CH_2), 29.8 (CH_2), 25.1 (CH_2). ^{1}H NMR (300 MHz, Chloroform-*d*, *Z*-isomer) δ 8.66 – 7.93 (br, 1H), 7.83 – 7.64 (m, 4H), 7.57 – 7.37 (m, 6H), 3.61 (s, 3H), 3.50 (d, *J* = 13.3 Hz, 2H), 2.65 – 2.52 (m, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 1.70 – 0.46 (m, 3H). ^{13}C{^{1}H} NMR (75 MHz, DEPT135, Chloroform-*d*, *Z*-isomer) δ 173.1 (C), 152.2

(d, J = 4.8 Hz, C), 132.4 (d, J = 9.4 Hz, 4 CH), 131.5 (d, J = 2.8 Hz, 2 CH), 129.0 (d, J = 55 Hz, 2 C), 128.7 (d, J = 9.4 Hz, 4 CH), 51.7 (CH_3), 30.2 (CH_2), 30.1 (CH_2), 26.5 (d, J = 31.9 Hz, CH_2). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, both isomers) δ 16.46 – 14.28 (m). $^{11}B\{^1H\}$ NMR (96 MHz, Chloroform-*d*) δ -35.16 – -41.17 (m). FTIR (KBr): 3418 (br, s), 3060 (s, sh), 2952 (s, sh), 2388 (s, sh), 2260 (m), 1644 (m), 1485 (m), 1437 (s), 1361 (m), 1311 (s), 1258 (s, sh), 1200 (s), 1173 (s), 1108 (s), 1062 (s), 1028 (m), 965 (s), 906 (m, sh), 839 (m), 738 (s), 694 (s), 593 (m), 497 (m), 471 (m), 434 (m). HRMS: *m*/*z* $[M+Na]^+$ calcd. for $[C_{18}H_{23}BNO_3PNa]^+$: 366.1406; found: 366.1404; *m*/*z* $[M-H]^+$ calcd. for $[C_{18}H_{22}BNO_3P]^+$: 342.1430; found: 342.1437.

1-(Diphenylphosphanyl)-3-phenylpropan-2-one oxime borane complex (9d). Prepared according to general procedure from 1.5 mL of 0.5 M solution of $Ph_2PH{\bullet}BH_3$ (0.75 mmol) in THF and 464 mg of enamine **4d** (1.5 mmol). Yield: 174 mg (67 % based on phosphine complex). Oil. R_f = 0.63 (EtOAc–hexane, 1:1). *E*-isomer, which isomerizes upon standing in solution to give 2.3 : 1 mixture of *E*/*Z* isomers. ^1H NMR (300 MHz, Chloroform-*d*, *E*-isomer) δ 7.85 – 7.62 (m, 4H), 7.59 – 7.38 (m, 6H), 7.37 – 7.09 (m, 6H), 3.85 (s, 2H), 3.15 (d, J = 12.4 Hz, 2H), 1.84 – 0.48 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, *E*-isomer) δ 153.8 (d, J = 3.9 Hz, C), 136.0 (C), 132.4 (d, J = 9.4 Hz, 4 CH), 131.5 (d, J = 2.2 Hz, 2 C), 129.3 (2 CH), 128.9 (d, J = 9.9 Hz, 4 CH), 128.7 (2 CH), 128.6 (d, J = 55.2 Hz, 2 C), 126.7 (CH), 34.2 (CH_2), 31.0 (d, J = 32.5 Hz, CH_2). ^1H NMR (300 MHz, Chloroform-*d*, *Z*-isomer, characteristic signals) δ 3.62 (s, 2H), 3.38 (d, J = 13.4 Hz, 2H). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, both isomers) δ 15.41 (br m). $^{11}B\{^1H\}$ NMR (96 MHz, Chloroform-*d*, both isomers) δ -35.74 – -40.90 (br m). HRMS: *m*/*z* $[M+Na]^+$ calcd. for $[C_{21}H_{23}BNOPNa]^+$: 370.1506; found: 370.1502; *m*/*z* $[M-H]^+$ calcd. for $[C_{21}H_{22}BNOP]^+$: 346.1530; found: 346.1525.

1,1'-(Phenylphosphanediyl)bis(propan-2-one) dioxime borane complex (10a). *Preparation of phenylphosphine-borane complex*: in a Schlenk tube with anhydrous THF (2 mL) was added a solution of $PhPH_2$ in hexane (1.6 mL, 1.0 mmol) followed by $Me_2S{\bullet}BH_3$ (0.095 mL, 1.0 mmol) complex at 0 °C under argon atmosphere. The mixture was stirred for 1 h to give a solution of

$PhPH_2 \bullet BH_3$ complex (^1H NMR spectrum matched with literature data[35]). *Reaction with enamine **4a***: 2.8 mL of the obtained solution of $PhPH_2 \bullet BH_3$ (0.75 mmol) was mixed with DMF (1.2 mL). The resulting solution was added to ene-nitrosoacetal **4a** (699 mg, 3.0 mmol) at 0 °C under argon atmosphere. Then, cooling bath was removed and the resulting solution was allowed to stand for 24 h at rt with occasional shaking. Methanol (ca. 5 mL) was added and the mixture was stirred for additional 1 h and then concentrated under reduced pressure (40 – 50 °C). The residue was subjected to column chromatography on silica gel to give 102 mg (51 % based on phosphine complex) of Michael adduct **10a** as colorless oil. R_f = 0.38 (EtOAc–hexane, 1:1). Dynamic mixture of isomers. ^1H NMR (300 MHz, Chloroform-*d*, all isomers) δ 8.98 – 8.07 (br, 2H, 2 OH), 7.94 – 7.70 (m, 2H), 7.60 – 7.40 (m, 3H), 3.41 – 2.89 (m, 4H), 1.84 (s, 6H), 1.49 – 0.41 (m, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, signals of *E*-fragments) δ 152.7 (d, J = 5.0 Hz, 2 C), 152.5 (d, J = 5.7 Hz, 2 C), 34.0 (d, J = 31.4 Hz, 2 CH_2), 33.1 (d, J = 31.4 Hz, 2 CH_2), 16.0 (2 CH_3), 15.8 (2 CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, DEPT135, Chloroform-*d*, signals of *Z*-fragments) δ 151.5 (d, J = 6.0 Hz, 2 C), 151.4 (d, J = 5.3 Hz, 2C), 27.8 (d, J = 30.0 Hz, 2 CH_2), 27.5 (d, J = 30.3 Hz, 2 CH_2), 21.6 (2 CH_3), 21.5 (2 CH_3). Other signals: 132.5 (d, J = 9.4 Hz, 2 CH), 132.1 (CH), 128.94 (d, J = 9.8 Hz) and 128.88 (d, J = 10.1 Hz) (2 CH), 127.1 (d, J = 50.6 Hz, C), 126.6 (d, J = 51.4 Hz, C). $^{31}P\{^1H\}$ NMR (121 MHz, Chloroform-*d*, all isomers) δ 16.21 – 12.13 (br m). $^{11}B\{^1H\}$ NMR (96 MHz, Chloroform-*d*, all isomers) δ -36.09 – -42.11 (br m). FTIR (KBr): 3241 (s br, OH), 2920 (m), 2400 (s), 1654 (m), 1438 (m), 1400 (m), 1373 (m), 1275 (s), 1112 (s), 1020 (m), 820 (s), 882 (m), 749 (s), 610 (s). HRMS: *m*/*z* $[M+H]^+$ calcd. for $[C_{12}H_{21}BN_2O_2P]^+$: 267.1430; found: 267.1433; *m*/*z* $[M-H]^+$ $[C_{12}H_{19}BN_2O_2P]^+$: 265.1274; found: 265.1277.

Conversion of borane complex 9a into free phosphine 7a. To a solution of phosphine-borane complex **9a** (113 mg, 0.42 mmol) in toluene (0.5 mL) was added DABCO (50 mg, 0.45 mmol) under argon atmosphere. The mixture was stirred at 40 °C for 24 h (within 3 days), and then concentrated in vacuum. The residue was subjected to a column chromatography on silica gel

under gentle argon pressure (eluent: hexane/ethyl acetate 10 : 1 → 5 : 1 → 3 : 1) to give 70 mg (65 %) of phosphine **7a** in two fractions one containing predominantly *E*-isomer and the second one containing mostly *Z*-isomer. R_f = 0.38 and 0.29 (EtOAc–hexane, 1:1), respectively.

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Supporting information:

Copies of NMR and FT-IR spectra, structures of initial enamines **4**.

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