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Utility of Bifunctional *N*-Heterocyclic Phosphine (NHP)-Thioureas for Metal-Free Carbon−Phosphorus Bond Construction toward Regio- and Stereoselective Formation of Vinylphosphonates

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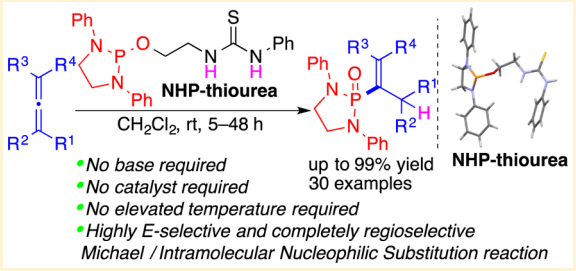
Supporting Information

ABSTRACT: An efficient and practical protocol for completely regioselective and highly stereoselective synthesis of vinyldiazaphosphonates from *N*-heterocyclic phosphine (NHP) and allenes via phospha-Michael/intramolecular nucleophilic substitution reaction has been developed. This transformation enabled the synthesis of valuable densely functionalized vinyldiazaphosphonates with a *β*-, *γ*-unsaturated ester moiety under mild reaction conditions. Synthetic utility of vinyldiazaphosphonates was demonstrated by a series of synthetic manipulations.



INTRODUCTION

Vinylphosphonates represent an exceedingly important class of organophosphorus compounds because of the wide range of applications in chemistry,[1] biology,[2] and materials science.[3] The functionalization of the vinylphosphonates under various reaction conditions provides access to versatile phosphorus-containing synthetic intermediates.[1] Such transformations include the Michael addition reactions (aza-,[4] sulfa-,[5] and oxa-Michael addition reactions[6]), Diels−Alder reaction,[7] epoxidations,[8] aminohydroxylation,[9] dihydroxylation,[10] aziridination,[11] Heck reaction,[12] ene reaction,[13] and cross-metathesis reactions.[14] In addition, vinylphosphonate derivatives have also shown significant biological activities: they have been extensively explored for anticancer,[2a,b] antiviral,[2c,d] and antibacterial applications.[15] Moreover, the synthetic utility of vinylphosphonate compounds expands to materials chemistry as copolymers,[16] additives,[3a−c] and fire retardants.[3e−g]

Since the pioneering early work by Kosolapoff and McCullough in 1951,[17] various synthetic methods for vinylphosphonate motifs have been developed over the past decades. The direct C−P bond forming approaches toward the synthesis of vinylphosphonates include transition-metal-catalyzed cross-coupling reactions of alkylphosphites with vinyl halides (Scheme 1, a),[18] metal-promoted hydrophosphorylation reactions of terminal alkynes with dialkylphosphites (Scheme 1, b),[19] and silver-mediated radical phosphonation reaction (Scheme 1, c).[20] Metalation of alkynylphosphonates via zirconation[21] or titanation,[22] yielding metallacycle intermediates, followed by hydrolysis of the intermediate, is an efficient route for the stereoselective synthesis of vinylphosphonates (Scheme 1, d). Nonetheless, many of the conventional methods generally suffer from harsh reaction conditions (elevated temperatures and strong base) or lack of regio- and stereoselectivity. Moreover, metal-mediated reactions frequently resulted in trace metal contamination in the desired products. This issue could prevent the vinylphosphonates from further broadening their application in pharmaceutically relevant fields. Alternatively, a metal-free direct addition of an alkylphosphite to an activated allene (phospha-Michael addition reaction)[23] was reported by Buono[24] and Metzger[25] to construct oxaphospholenes. Metzger and co-workers further demonstrated the conversion of oxaphospholene intermediates to the vinylphosphonates (Scheme 1, e); however, this method provided the desired product as an inseparable isomeric mixture (*E*/*Z* ratio = 1:1) with regard to the vinyl double bond.[25] Despite the great efforts devoted to the synthesis of vinylphosphonates, the regio- and stereoselective route for preparing vinylphosphonates under metal-free mild conditions is still highly desirable to address the limitations. Herein, we report a bifunctional *N*-heterocyclic phosphine (NHP)-mediated regio- and stereoselective C−P bond formation of vinyldiazaphosphonates with allenes via phospha-Michael/intramolecular nucleophilic substitution reaction (Scheme 1, f).

Conceptual description of a bifunctional NHP-promoted C−P bond forming reaction of vinyldiazaphosphonates with allene is presented in Scheme 2. Enhanced nucleophilicity at the phosphorus atom of the NHP by lone-pair electrons on the nitrogen atoms and the activation of allene electrophile through hydrogen bonding with Brønsted acid (thiourea motif) should serve as the driving forces for facilitating the Michael addition of the phosphorus nucleophile to the allene **A**, providing diazaphosphonium intermediate **B**. Proton transfer and subsequent intramolecular nucleophilic displacement[26] of the

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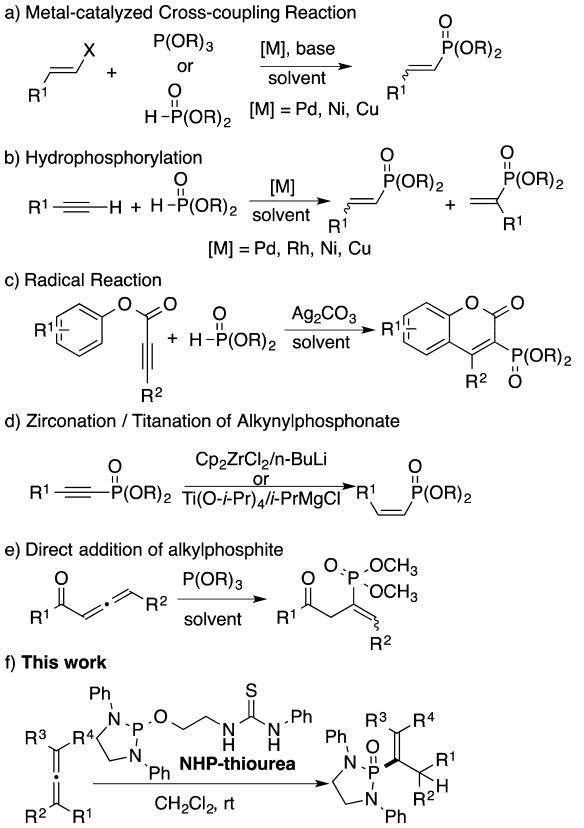
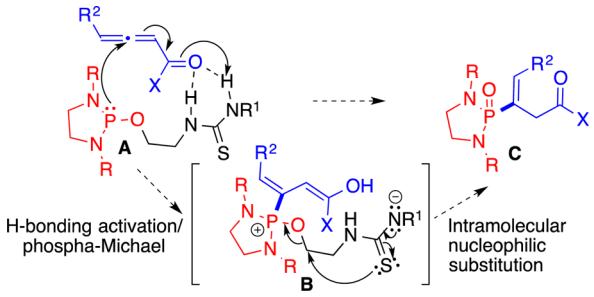
Scheme 1. Synthetic Methods of Vinylphosphonates



Scheme 2. Conceptual Design of Phospha-Michael/ Intramolecular Nucleophilic Substitution Reaction of Vinyldiazaphosphonates



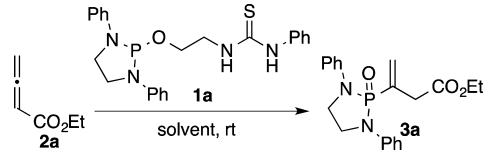
diazaphosphonium salt by anionic thiourea group accounts for the cleavage of the C−O bond and formation of the P═O bond of the vinyldiazaphosphonate. In this regard, the concept of bifunctional NHP is demonstrated by the dual role of hydrogen-bonding activation of the allene and a proton donor to an enolate intermediate. We envisioned that these features of the NHP could play a key role to achieve mild reaction conditions and high selectivity.

RESULTS AND DISCUSSION

To test our hypothesis, we began with the synthesis of bifunctional NHPs by treatment of NHP-Cl with 1-(2-hydroxyethyl)-3-phenylthiourea (see the Experimental Section). With NHPs in hand, we explored the optimization of reaction conditions for the synthesis of vinyldiazaphosphonates with NHPs and allene **2a**.

A solvent screening study provided DCM as the desired solvent for this transformation (Table 1, entry 7, >99%). An

Table 1. Solvent Screening Results

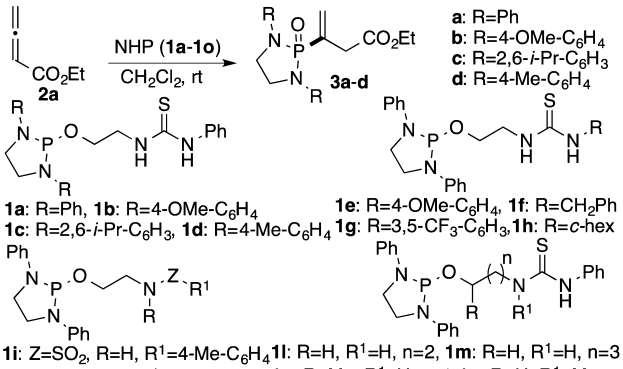


entry	NHP	solvent	time (h)	product/yield (%)[a,b]
1	**1a**	THF	5	**3a**/59
2	**1a**	toluene	5	**3a**/48
3	**1a**	$CHCl_3$	5	**3a**/80
4	**1a**	MeCN	5	**3a**/56
5	**1a**	Et_20	5	**3a**/65
6	**1a**	1,2-DCE	5	**3a**/50
7	**1a**	CH_2CI_2	5	**3a**/>99

[a]Reactions were performed using **2a** (0.30 mmol) and NHP (**1a**) (0.10 mmol) in solvent (0.15 mL) at rt for 5 h. [b]Isolated yield.

investigation on the steric and electronic effects of the NHPs revealed that a bulky substituent on the NHP motif significantly reduced the reaction efficiency (Table 2, entry 3), whereas the electronic effects of the NHP had a negligible influence on this reaction (Table 2, entries 1, 2, 4). Next, a systematic study of the effect of Brønsted acid on the reactivity of bifunctional

Table 2. Initial Screening Results[a]



entry	NHP	time (h)	product/yield (%)[b]
1	**1a**	5	**3a**/>99
2	**1b**	5	**3b**/97
3	**1c**	5	**3c**/trace
4	**1d**	5	**3d**/98
5	**1e**	5	**3a**/87
6	**1f**	5	**3a**/92
7	**1g**	5	**3a**/94
8	**1h**	5	**3a**/61
9	**1i**	5	**3a**/88
10	**1j**	5	**3a**/86
11	**1k**	5	**3a**/0
12	**1l**	5	**3a**/82
13	**1m**	5	**3a**/78
14	**1n**	5	**3a**/95
15	**1o**	5	**3a**/66

[a]Reactions were performed using **2a** (0.30 mmol) and NHP (**1a**−**1o**) (0.10 mmol) in CH_2CI_2 (0.15 mL) at rt for 5 h. [b]Isolated yield.

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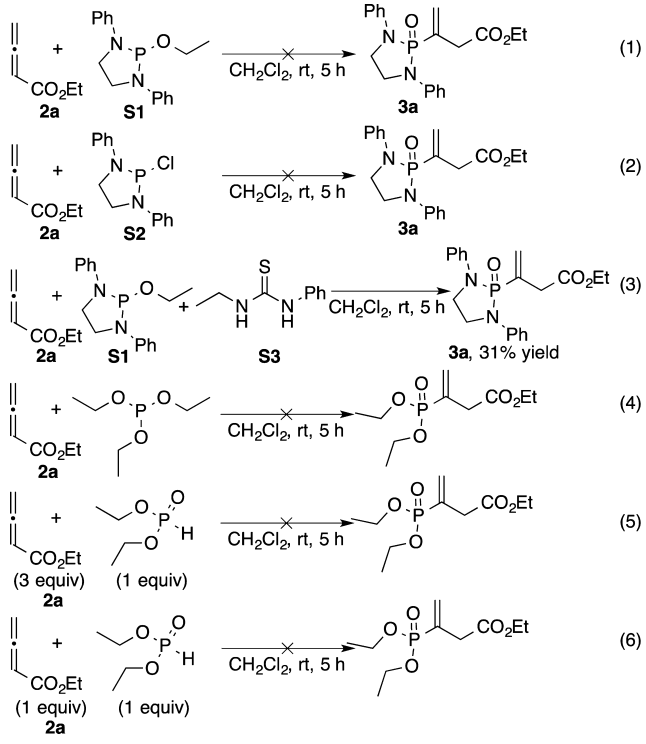
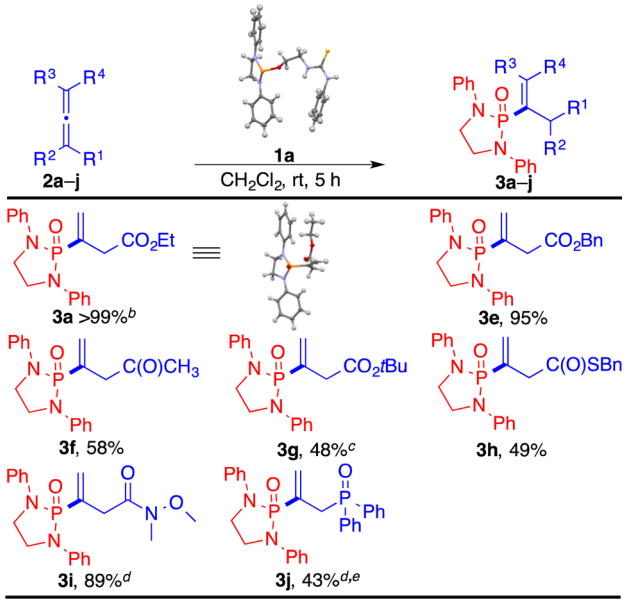
NHPs was conducted. This study disclosed that a Brønsted acid motif with a low pK_a value was required to afford the product in higher yield (entry 7 vs 8). Further optimization studies of the bifunctional NHP revealed that the length of the tether between the NHP motif and a Brønsted acid played a pivotal role in effective hydrogen-bonding activation of the allenoate. For example, NHPs with a longer tether provided lower product yields (entry 1 vs entries 12, 13). Finally, we investigated whether a Brønsted acid motif on the NHP scaffold is required for the reaction. NHP without a Brønsted acid moiety completely suppressed the reaction, demonstrating a critical role of the Brønsted acid as a hydrogen bond donor and proton source in the bifunctional NHP-mediated phospha-Michael addition reaction (entry 11). It is noteworthy that the Lewis base (NHP) and Brønsted acid (thiourea) functionalities must be present in the same molecule for a cooperative effect; otherwise, the reactivity of NHP was significantly reduced (Scheme 3, eq 3 (31% yield)). Notably, when triethylphosphite[25] or diethylphosphite,[27] which was widely used in the metal-mediated synthesis of vinylphosphonates (Scheme 1), was employed under the standard reaction conditions, formation of the desired product was not observed (Scheme 3, eqs 4–6).

Scheme 3. Control Experiments



With the optimized reaction conditions established, we explored the scope of the reaction using various allene electrophiles and the NHP-thiourea **1a** (Tables 3 and 4). α- or γ-Substituted allenes with a wide range of electron-withdrawing substituents underwent clean reactions to afford the desired products in moderate to excellent yields (Tables 3 and 4, 31–99% yields). Moderately electron-withdrawing groups on allene (**2a**, **2e**) were necessary to achieve high yields (Table 3, **3a**: 99%, **3e**: 95%); strong electron-withdrawing groups (Table 3, **2f**, **2h–j**) or a bulky ester group on allene (**2g**) provided the desired products in moderate to good

Table 3. Substrate Scope of Allenes Bearing Different Electron-Withdrawing Groups for NHP-Mediated Vinyldiazaphosphonate Synthesis[a]



[a]Reactions were performed using **2** (0.30 mmol) and NHP **1a** (0.10 mmol) in CH_2Cl_2 (0.15 mL) at rt for 5–48 h. [b]Isolated yield. [c]Reaction run for 24 h. [d]Reaction run for 48 h. [e]Reaction was conducted with **2j** (0.92 equiv).

yields (**3f–j**: 43–89% yields). Next, we explored the effect of substituted allene on the reaction. In general, substituted allenes provided low product yields, presumably due to the steric encumbrance around the β-carbon of allene. Nonetheless, strong electron-withdrawing substituents on the α-carbon of allene (**2t**, **2u**) overcome the steric obstacles, providing excellent yields (Table 4, **3t**: 91%, **3u**: 90%). We attribute these high-yielding reactions to the increased reactivity of allenes activated by a strong electron-withdrawing group. To our delight, the vinyldiazaphosphonate structure **3a** was unambiguously determined by single-crystal X-ray analysis, providing the *s*-*cis* conformation (see the SI). In addition, we were pleased to find excellent *E* stereoselectivity with the allenes having γ-aryl or -branched substituents, providing only *E*-olefin products (Table 4, **3z**, **3aa**, **3ab**). This exclusive formation of *E*-olefin of vinylphosphonate compounds is a dramatic improvement of the stereoselectivity over the previous results provided with an inseparable 1:1 *E*/*Z* mixture.[25] Moreover, the tetrasubstituted alkenes, otherwise challenging to synthesize, were obtained in excellent yields (**3ac**: 91%, **3ad**: 94%). Gratifyingly, all allene electrophiles proceeded with complete regioselectivity to provide only the β-addition products.

We next turned our attention to the synthetic utility of vinyldiazaphosphonates, which were subjected to synthetic manipulations (Scheme 4). A reduction of diazaphosphono ester **3a** to alcohol **4a** was achieved with DIBAL-H. With the potential application of halogenated phosphorus-containing flame-retardants,[28] bromination of **3a** using NBS and benzoyl peroxide was performed to provide only aryl-brominated product **4b**. Additionally, the efficiency of the diazaphosphonate protecting group was demonstrated by the successful transformation of vinyldiazaphosphonate **3a** to vinylphosphonate **4c** in the presence of ethanolic HCl with excellent yield

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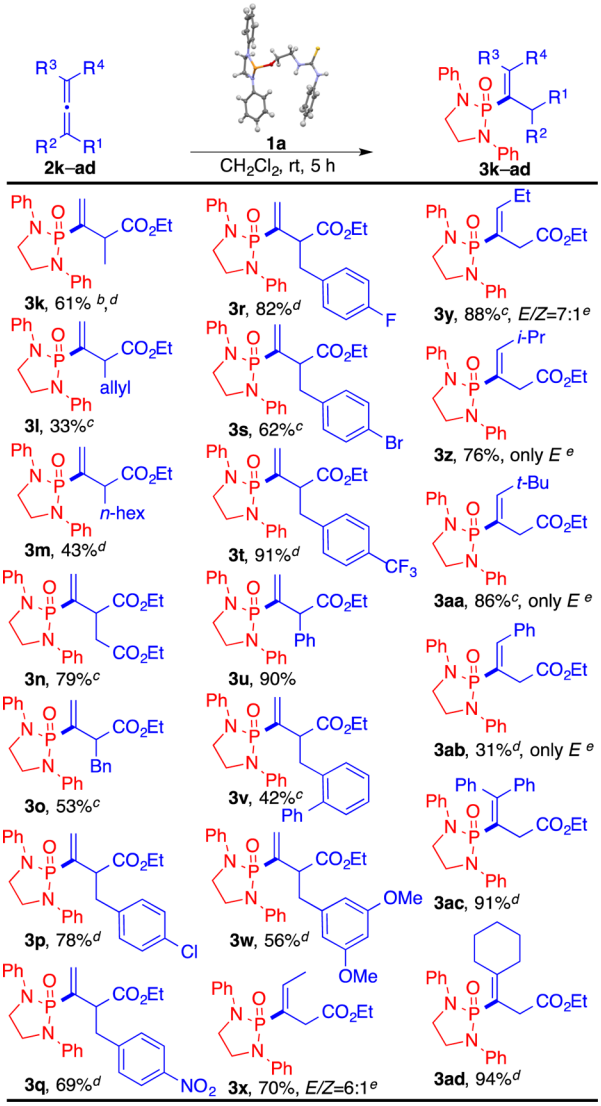
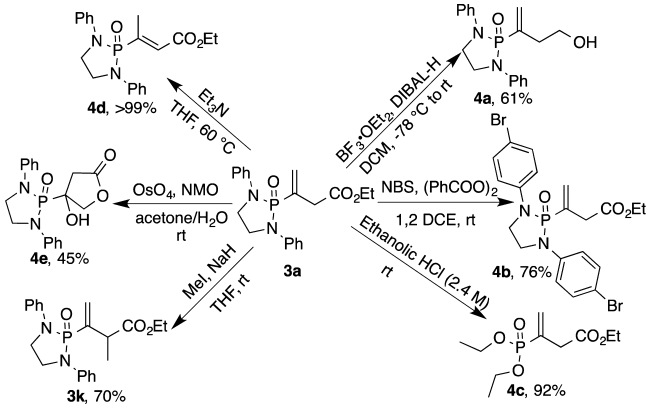
Table 4. Substrate Scope of Allenes Bearing α-, γ-Substituents[a]



[a]Reactions were performed using **2** (0.30 mmol) and NHP **1a** (0.10 mmol) in CH_2CI_2 (0.15 mL) at rt for 5–48 h. [b]Isolated yield. [c]Reaction run for 24 h. [d]Reaction run for 48 h. [e]E/Z ratio was determined by crude NMR spectrum.

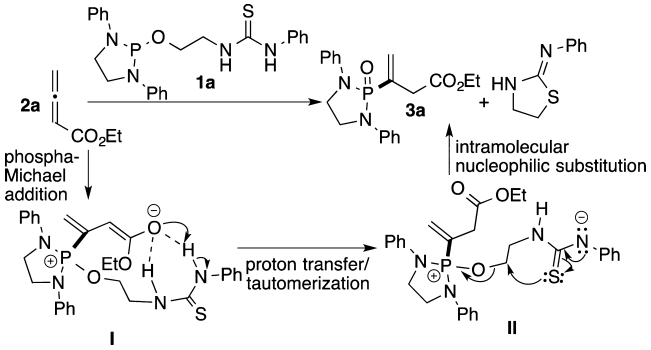
Scheme 4. Synthetic Manipulations of Vinyldiazaphosphonates



(92%). Moreover, the acidic proton on the vinyldiazaphosphonate led to the following useful transformations such as alkylation **3k** (70%) and isomerization **4d** (>99%). Finally, in an attempt to functionalize the vinyl group of **3a** to a diol derivative, we demonstrated a tandem dihydroxylation/lactonization[29] of **3a** to afford a diazaphosphono lactone **4e**.

On the basis of the results of our experiments, a preliminary proposed reaction pathway is illustrated in Scheme 5. The

Scheme 5. Proposed Reaction Sequence



Michael addition of bifunctional NHP **1a** to an allenoate **2a** activated through hydrogen bonding with Brønsted acid generates a diazaphosphonium intermediate **I**. The sequential proton transfer/tautomerization process corresponding to the formation of an anionic thiourea intermediate **II** induces the nucleophilic displacement of diazaphosphonium salt by the anionic thiourea group to generate vinyldiazaphosphonate **3a** and 1,3-thiazolidine. The thiazolidine byproduct was isolated, and the corresponding spectral data matched those reported in the literature.[30]

CONCLUSION

In conclusion, we have developed a novel *N*-heterocyclic phosphine-promoted phospha-Michael/intramolecular nucleophilic substitution reaction for the stereoselective construction of vinyldiazaphosphonates in moderate to excellent yields (31–99% yields). The vinyldiazaphosphonate product derived from the NHP-mediated transformation contains a versatile vinyl group and a *β*, *γ*-unsaturated ester motif. The Michael addition of the NHP to *α*-substituted or *γ*-substituted allenes proceeded with complete regioselectivity and showed good tolerance of various electron-withdrawing groups on the allenes. The potential synthetic utility of vinyldiazaphosphonate compounds was demonstrated by various synthetic manipulations. This work established the first general application of bifunctional NHP in organic synthesis to facilitate the rapid C–P bond forming approach to vinylphosphonate compounds under mild reaction conditions. This protocol will be a practical complement to those classical methods such as metal-promoted synthesis of vinylphosphonates.

EXPERIMENTAL SECTION

General Information. All reactions were carried out under an argon atmosphere in oven-dried glassware with a magnetic stirring bar. Dry solvents (THF, toluene, and DCM) were obtained by a solvent purification system under argon. All commercially available reagents were used as received without further purification. Purification of reaction products was carried out by flash column chromatography using silica gel 60 (230–400 mash). Analytical thin-layer chromatography was performed on 0.25 mm aluminum-backed silica gel 60-F

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plates. Visualization was accompanied by UV light and $KMnO_4$ solution. Concentration under reduced pressure refers to the removal of volatiles using a rotary evaporator attached to a dry diaphragm pump (10−15 mmHg), followed by pumping to a constant weight with an oil pump (<300 mTorr). Infrared (IR) spectra were recorded on an IR spectrometer with KBr wafers or a film on KBr plate. High-resolution mass spectra (HRMS) were recorded on an LCMS-IT-TOF mass spectrometer using ESI (electrospray ionization), MALDI (matrix-assisted laser desorption ionization), or APCI (atmospheric pressure chemical ionization). ^{1}H NMR spectra were recorded at 400 MHz using $CDCl_3$. The ^{1}H chemical shifts were referenced to residual solvent signals at δ 7.26 ($CHCl_3$) or δ 0.00 (TMS). ^{1}H NMR coupling constants (J) were reported in hertz (Hz), and multiplicities were indicated as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublet), dt (doublet of triplet). ^{13}C NMR spectra were recorded at 100.5 MHz using $CDCl_3$. The ^{13}C chemical shifts were referenced to residual solvent signals at δ 77.16 ($CHCl_3$). ^{31}P NMR spectra were recorded at 162 MHz using $CDCl_3$, and ^{31}P chemical shifts were reported relative to 85% H_3PO_4 as an external standard.

General Procedure for the Synthesis of NHP-Thioureas (GP-1): 4-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)-*N*-phenylbutanethioamide (1a). To a solution of 2-chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (1.00 g, 3.62 mmol) in DCM (25 mL) were added 1-(2-hydroxyethyl)-3-phenylthiourea[32] (0.711 g, 3.62 mmol) and triethylamine (0.438 g, 4.34 mmol) at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 2 h. After stirring for 2 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (gradient eluent of Hexanes:EtOAc: 7/1 to 5/1) to give colorless crystalline solid **1a** (1.13 g, 2.58 mmol, 71%). R_f = 0.5 (Hexanes:EtOAc = 1:1); mp: 112−113 °C; IR (KBr, cm^{-1}): 3394, 3182, 3020, 2866, 1597, 1496, 1276, 1030; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (bs, 1H), 7.37 (app t, J = 7.2, Hz, 2H), 7.30−7.23 (m, 5H), 7.10−7.07 (m, 4H), 7.04 (d, J = 7.5 Hz, 2H), 6.91 (app t, J = 7.3, Hz, 2H), 6.26 (bs, 1H), 3.88−3.84 (m, 2H), 3.82−3.75 (m, 2H), 3.73−3.71 (m, 2H), 3.68−3.65 (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.4, 144.7 (d, J = 17.9 Hz), 136.0, 130.0, 129.4, 127.0, 124.9, 120.3, 115.3 (d, J = 14.2 Hz), 61.8, 47.4 (d, J = 9.7 Hz), 45.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.30 ppm; HRMS (APCI) calcd for $C_{23}H_{25}N_4OPS$ [M + Cl]$^-$: 471.1181; found: 471.1187.

*1-(2-((1,3-Bis(4-methoxyphenyl)-1,3,2-diazaphospholidin-2-yl)-oxy)ethyl)-3-phenylthiourea (**1b**).* 2-Chloro-1,3-bis(4-methoxyphenyl)-1,3,2-diazaphospholidine[33] (0.502 g, 1.48 mmol), 1-(2-hydroxyethyl)-3-phenylthiourea (0.291 g, 1.48 mmol), and triethylamine (0.165 g, 1.62 mmol) in DCM (15 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1b** (0.124 g, 0.249 mmol, 17%). R_f = 0.44 (Hexanes:EtOAc = 1:1); mp: 126−128 °C; IR (KBr, cm^{-1}): 3317, 2924, 2866, 1604, 1508, 1276, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (bs, 1H), 7.40−7.26 (m, 3H), 7.06−6.99 (m, 6H), 6.81 (d, J = 8.8 Hz, 2H), 6.29 (bs, 1H), 3.85−3.66 (m, 14H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.4, 153.8 (d, J = 1.5 Hz), 138.4, 138.3, 130.0, 126.9, 124.7, 116.6 (d, J = 12.7 Hz), 114.8, 61.5, 55.6 (d, J = 2.2 Hz), 48.1 (d, J = 9.7 Hz), 46.1; ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.11 ppm; HRMS (APCI): found [M + H]$^+$ values corresponding to 1-ethyl-3-phenylthiourea; calcd for $C_9H_{11}N_2S$ [M + H]$^+$: 179.0643; found: 179.0638.

*1-(2-((1,3-Bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-3-phenylthiourea (**1c**).* 2-Chloro-1,3-bis(2,6-diisopropylphenyl)-1,3,2-diazaphospholidine[33] (3.04 g, 6.86 mmol), 1-(2-hydroxyethyl)-3-phenylthiourea (1.64 g, 8.92 mmol), and triethylamine (0.900 g, 8.91 mmol) in toluene (36 mL) were subjected to the reaction conditions described in **GP-1**. Off-white solid **1c** (2.64 g, 4.35 mmol, 63%). R_f = 0.29 (Hexanes:EtOAc = 5:1); mp: 82−85 °C; IR (KBr, cm^{-1}): 3329, 2962, 2866, 1535, 1446, 1257, 1041; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (bs, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.29−7.13 (m, 9H), 6.44 (bs, 1H), 3.88−3.80 (m, 2H), 3.69−3.66 (m, 4H), 3.61−3.48 (m, 4H), 3.46 (quint, J = 4.5 Hz, 2H), 1.30−1.12 (m, 24H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.2, 149.4 (d, J = 2.9 Hz), 148.4 (d, J = 1.5 Hz), 137.7 (d, J = 14.2 Hz), 129.9, 127.3, 126.7, 124.3, 124.1, 54.3 (d, J = 6.7 Hz), 46.8 (d, J = 8.2 Hz), 28.3 (d, J = 74.0 Hz), 25.5 (d, J = 56.1 Hz), 24.2 9 d, J = 18.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 128.05 ppm; HRMS (APCI) calcd for $C_{35}H_{49}N_4OPS$ [M + Cl]$^-$: 639.3059; found: 639.3045.

*1-(2-((1,3-Di-p-tolyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-3-phenylthiourea (**1d**).* 2-Chloro-1,3-di-*p*-tolyl-1,3,2-diazaphospholidine[31] (0.250 g, 0.912 mmol), 1-(2-hydroxyethyl)-3-phenylthiourea (0.213 g, 1.09 mmol), and triethylamine (0.110 g, 1.09 mmol) in toluene (4.5 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1d** (0.163 g, 0.352 mmol, 39%). R_f = 0.49 (Hexanes:EtOAc = 1:1); mp: 136−139 °C; IR (KBr, cm^{-1}): 3367, 3190, 2866, 1616, 1512, 1269, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (bs, 1H), 7.40−7.27 (m, 3H), 7.06−6.97 (m, 10H), 6.26 (bs, 1H), 3.86−3.66 (m, 8H), 2.27 (s, 6H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.4, 142.2 (d, J = 17.9 Hz), 136.1, 129.9, 129.8, 129.5, 127.0, 124.8, 115.3 (d, J = 13.4 Hz), 61.7, 47.6 (d, J = 10.5 Hz), 46.0 (d, J = 2.9 Hz), 20.4 (d, J = 1.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.31 ppm; HRMS (ESI) calcd for $C_{25}H_{29}N_4OPS$ [M + H]$^+$: 464.1800; found: 464.1777.

*1-(2-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-3-(4-methoxyphenyl)thiourea (**1e**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.305 g, 1.08 mmol), 1-(2-hydroxyethyl)-3-(4-methoxyphenyl)thiourea[34] (0.245 g, 1.08 mmol), and triethylamine (0.131 g, 1.29 mmol) in DCM (10 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1e** (0.201 g, 0.431 mmol, 40%). R_f = 0.46 (Hexanes:EtOAc = 1:1); mp: 81−83 °C; IR (KBr, cm^{-1}): 3379, 3194, 3036, 2866, 1597, 1508, 1276, 1030; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.26 (m, 4H), 7.11−7.08 (m, 4H), 6.96−6.87 (m, 6H), 6.03 (bs, 1H), 3.90−3.86 (m, 2H), 3.84 (s, 3H), 3.81−3.76 (m, 2H), 3.74−3.64 (m, 4H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.9, 158.8, 144.7 (d, J = 17.9 Hz), 129.4, 129.0, 127.4, 120.3, 115.4, 115.2 (d, J = 9.7 Hz), 61.9, 55.5, 47.5 (d, J = 9.7 Hz), 45.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.07 ppm; HRMS (MALDI) calcd for $C_{24}H_{27}N_4O_2PS$ [M + H]$^+$: 467.1671; found: 467.1677.

*1-Benzyl-3-(2-((1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)-ethyl)thiourea (**1f**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.500 g, 1.80 mmol), 1-benzyl-3-(2-hydroxyethyl)urea[35] (0.387 g, 1.80 mmol), and triethylamine (0.224 g, 2.21 mmol) in DCM (15 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1f** (0.220 g, 0.489 mmol, 27%). R_f = 0.46 (Hexanes:EtOAc = 1:1); mp: 108−111 °C; IR (KBr, cm^{-1}): 3325, 3051, 2935, 1651, 1600, 1261, 1072; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.19 (m, 9H), 7.10 (d, J = 8.6 Hz, 4H), 6.84 (t, J = 8.6 Hz, 2H), 5.61 (bs, 1H), 4.35 (bs, 2H), 3.86−3.67 (m, 6H), 3.55 (bs, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 182.2, 144.7 (d, J = 17.2 Hz), 137.1, 129.5, 128.7, 127.9, 127.8, 120.3, 115.3 (d, J = 14.2 Hz), 62.8, 48.3, 47.3 (d, J = 9.7 Hz), 45.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.14 ppm; HRMS (APCI): found [M + H]$^+$ values corresponding to 1-benzyl-3-ethylthiourea ; calcd for $C_{10}H_{13}N_2S$ [M + H]$^+$: 193.0799; found 193.0792.

*1-(3,5-Bis(trifluoromethyl)phenyl)-3-(2-((1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)thiourea (**1g**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.506 g, 1.80 mmol), 1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-hydroxyethyl)thiourea[36] (0.661 g, 1.80 mmol), and triethylamine (0.219 g, 2.17 mmol) in DCM (15 mL) were subjected to the reaction conditions described in **GP-1**. Colorless crystalline solid **1g** (0.346 g, 0.604 mmol, 34%). R_f = 0.57 (Hexanes:EtOAc = 1:1); mp: 118−121 °C; IR (KBr, cm^{-1}): 3340, 3217, 3041, 2805, 1597, 1469, 1276, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (bs, 2H), 7.63 (s, 1H), 7.30 (t, J = 8.5 Hz, 4H), 7.16 (d, J = 7.2 Hz, 4H), 6.93 (app t, J = 7.3 Hz, 2H), 6.72 (bs, 1H), 6.08 (bs, 1H), 3.95−3.92 (m, 2H), 3.84−3.78 (m, 4H), 3.66 (bs, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.9, 144.6 (d, J = 17.9 Hz), 139.5, 132.3 (q, J = 34.4 Hz), 129.7, 124.3, 123.5, 120.5, 118.6, 116.2 (d, J = 14.2 Hz), 62.2, 47.3 (d, J = 9.7 Hz), 45.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.86 ppm; HRMS (APCI): found [M + H]$^+$ values corresponding to 1-(3,5-bis(trifluoromethyl)phenyl)-3-ethylthiourea; calcd for $C_{11}H_9F_6N_2S$ [M + H]$^+$: 315.0391; found 315.0376.

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*1-Cyclohexyl-3-(2-((1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)thiourea (**1h**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.420 g, 1.51 mmol), 1-cyclohexyl-3-(2-hydroxyethyl)urea[37] (0.308 g, 1.51 mmol), and triethylamine (0.181 g, 1.79 mmol) in DCM (18 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1h** (0.208 g, 0.470 mmol, 31%). R_f = 0.39 (Hexanes:EtOAc = 1:1); mp: 137−139 °C; IR (Neat, cm^{-1}): 3256, 3061, 2930, 2854, 1595, 1543, 1276, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (app t, J = 8.6 Hz, 4H), 7.17−7.14 (m, 4H), 6.95 (t, J = 7.2 Hz, 2H), 5.56 (bs, 2H), 3.93−3.86 (m, 2H), 3.84−3.78 (m, 2H), 3.72−3.68 (m, 2H), 3.57 (bs, 2H), 1.88 (d, J = 7.2 Hz, 2H), 1.71−1.58 (m, 4H), 1.37−1.26 (m, 2H), 1.19−0.99 (m, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.8, 144,7 (d, J = 17.9 Hz), 129.5, 120.4 (d, J = 1.5 Hz), 115.3 (d, J = 14.2 Hz), 62.8, 52.7, 47.4 (d, J = 10.5 Hz), 45.5, 32.7, 25.4, 24.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.73 ppm; HRMS (ESI) calcd for $C_{23}H_{31}N_4OPS$ $[M + H]^+$: 442.1956; found: 442.1926.

*N-(2-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-4-methylbenzenesulfonamide (**1i**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.501 g, 1.80 mmol), *N*-(2-hydroxyethyl)-4-methylbenzenesulfonamide[38] (0.388 g, 1.80 mmol), and triethylamine (0.219 g, 2.16 mmol) in DCM (15 mL) were subjected to the reaction conditions described in **GP-1**. Colorless crystalline solid **1i** (0.278 g, 0.610 mmol, 34%). R_f = 0.43 (Hexanes:EtOAc = 1:1); mp: 125−127 °C; IR (KBr, cm^{-1}): 3286, 3047, 2866, 1597, 1489, 1276, 1030; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dt, J = 8.3, 1.9 Hz, 2H), 7.32−7.27 (m, 4H), 7.17 (dd, J = 7.9, 0.6 Hz, 2H), 7.11−7.08 (m, 4H), 6.95 (app t, J = 7.3, Hz, 2H), 4.53 (t, J = 6.1 Hz, 1H), 3.86−3.81 (m, 2H), 3.80−3.75 (m, 2H), 3.56 (q, J = 5.2 Hz, 2H), 2.94 (q, J = 5.5 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 144.5 (d, J = 17.9 Hz), 143.2, 136.7, 129.6, 129.4, 126.9, 120.4, 115.3 (d, J = 14.2 Hz), 61.9, 47.3 (d, J = 9.7 Hz), 43.7 (d, J = 2.9 Hz), 21.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.95 ppm; HRMS (ESI) calcd for $C_{23}H_{26}N_3O_3PS$ $[M + H]^+$: 455.1432; found: 455.1428.

*N-(2-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-benzamide (**1j**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.308 g, 1.11 mmol), *N*-(2-hydroxyethyl)benzamide[39] (0.166 g, 1.11 mmol), and triethylamine (0.135 g, 1.33 mmol) in DCM (10 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1j** (0.165 g, 0.406 mmol, 37%). R_f = 0.26 (Hexanes:EtOAc = 1:1); mp: 124−126 °C. IR (KBr, cm^{-1}): 3360, 3059, 2870, 1643, 1597, 1496, 1276, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47−7.43 (m, 3H), 7.34 (app t, J = 7.6 Hz, 2H), 7.27−7.23 (m, 4H), 7.16−7.13 (m, 4H), 6.90 (app t, J = 7.3 Hz, 2H), 6.21 (s, 1H), 3.94−3.90 (m, 2H), 3.87−3.79 (m, 2H), 3.76−3.72 (m, 2H), 3.51 (q, J = 5.0 Hz, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 167.4, 144.7 (d, J = 17.2 Hz), 134.2, 131.2, 129.4, 128.4, 126.8, 120.3, 115.1 (d, J = 13.5 Hz), 62.4, 47.4 (d, J = 10.5 Hz), 40.5 (d, J = 3.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 104.10 ppm; HRMS (APCI): found $[M + H]^+$ values corresponding to *N*-ethylbenzamide; calcd for $C_9H_{10}NO$ $[M + H]^+$: 148.0762; found: 148.0761.

*N-(2-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-N-methylbenzamide (**1k**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.500 g, 1.80 mmol), 1-(2-hydroxyethyl)-1-methyl-3-phenylthiourea[26b] (0.320 g, 1.80 mmol), and triethylamine (0.219 g, 2.16 mmol) in DCM (15 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1k** (0.280 g, 0.668 mmol, 37%). R_f = 0.26 (Hexanes:EtOAc = 1:1); mp: 133−136 °C; IR (KBr, cm^{-1}): 3406, 3051, 2854, 1712, 1600, 1504, 1257, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.27 (m, 8H), 7.19−7.02 (m, 5H), 6.93 (tt, J = 7.4, 0.9 Hz, 2H), 3.94−3.77 (m, 6H), 3.54 (bs, 2H), 2.87−2.85 (m, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.4, 145.2 (d, J = 17.2 Hz), 136.3, 129.4, 129.2, 128.2, 126.7, 120.6, 115.2 (d, J = 14.2 Hz), 62.3, 48.8, 47.5 (d, J = 9.7 Hz), 39.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 102.60 ppm; HRMS (ESI): found $[M + H]^+$ values corresponding to *N*-ethyl-*N*-methyl benzamide; calcd for $C_{10}H_{12}NO$ $[M + H]^+$: 162.0919; found: 162.0923.

*1-(3-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)propyl)-3-phenylthiourea (**1l**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.400 g, 1.45 mmol), 1-(3-hydroxypropyl)-3-phenylthiourea[40] (0.304 g, 1.45 mmol), and triethylamine (0.175 g, 1.73 mmol) in DCM (10 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1l** (0.219 g, 0.488 mmol, 34%). R_f = 0.64 (Hexanes:EtOAc = 1:1); mp: 132−135 °C; IR (KBr, cm^{-1}): 3275, 3059, 2870, 1597, 1496, 1280, 1018; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.43 (t, J = 7.7 Hz, 2H), 7.31−7.18 (m, 8H), 7.02−6.99 (m, 4H), 6.90 (t, J = 7.3 Hz, 2H), 6.47 (s, 1H), 3.82−3.71 (m, 4H), 3.60−3.51 (m, 4H), 1.69−1.63 (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.3, 144.7 (d, J = 17.2 Hz), 136.2, 130.2, 129.4, 127.1, 125.1, 120.2 (d, J = 1.5 Hz), 115.1 (d, J = 13.5 Hz), 62.1, 47.4 (d, J = 9.7 Hz), 43.8, 29.4 (d, J = 2.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 103.18 ppm; HRMS (APCI) calcd for $C_{24}H_{27}N_4OPS$ $[M + Cl]^-$: 485.1337; found: 485.1328.

*1-(4-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)butyl)-3-phenylthiourea (**1m**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (1.70 g, 6.17 mmol), 1-(4-hydroxybutyl)-3-phenylthiourea[41] (2.00 g, 6.17 mmol), and triethylamine (0.747 g, 7.39 mmol) in DCM (18 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1m** (0.775 g, 1.67 mmol, 27%). R_f = 0.31 (Hexanes:EtOAc = 1:1); mp: 134−136 °C; IR (KBr, cm^{-1}): 3263, 3093, 2870, 1593, 1496, 1280, 1010; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (bs, 1H), 7.42 (t, J = 7.4 Hz, 2H), 7.32−7.21 (m, 7H), 7.15−7.09 (m, 4H), 6.85 (t, J = 7.2 Hz, 2H), 5.87 (bs, 1H), 3.88−3.81 (m, 2H), 3.78−3.73 (m, 2H), 3.58−3.53 (m, 2H), 3.39−3.37 (m, 2H), 1.42−1.39 (m, 4H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.1, 145.1 (d, J = 17.2 Hz), 136.1, 130.2, 129.3, 127.2, 125.1, 119.9, 115.3 (d, J = 14.2 Hz), 62.7, 47.4 (d, J = 10.5 Hz), 44.7, 27.7, 25.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 102.06 ppm; HRMS (ESI) calcd for $C_{25}H_{29}N_4OPS$ $[M - H]^-$: 463.1727; found: 463.1733.

*(R)-1-(2-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)propyl)-3-phenylthiourea (**1n**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.368 g, 1.32 mmol), (*R*)-1-(2-hydroxypropyl)-3-phenylurea[40] (0.280 g, 1.32 mmol), and triethylamine (0.159 g, 1.57 mmol) in DCM (15 mL) were subjected to the reaction conditions described in **GP-1**. Colorless crystalline solid **1n** (0.185 g, 0.408 mmol, 30%). R_f = 0.56 (Hexanes:EtOAc = 1:1) mp: 139−141 °C; IR (KBr, cm^{-1}): 3344, 3055, 3020, 2874, 1597, 1496, 1276, 1041; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36−7.21 (m, 8H), 7.11−7.01 (m, 6H), 6.94−6.87 (m, 2H), 6.01 (bs, 1H), 4.35−4.29 (m, 1H), 3.92−3.68 (m, 4H), 3.52 (t, J = 4.9, Hz, 2H), 1.01 (d, t, J = 6.5 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 180.9, 144.8 (dd, J = 17.9, 3.7 Hz), 136.5, 129.7, 129.4 (d, J = 9.7 Hz), 126.7, 124.7, 120.1, 115.42 (dd, J = 14.2, 11.2 Hz), 69.3, 51.2, 47.1 (d, J = 9.7 Hz), 19.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 106.33 ppm; HRMS (ESI) calcd for $C_{24}H_{27}N_4OPS$ $[M - H]^-$: 449.1570; found: 449.1590.

*1-(2-((1,3-Diphenyl-1,3,2-diazaphospholidin-2-yl)oxy)ethyl)-1-methyl-3-phenylthiourea (**1o**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (1.00 g, 3.62 mmol), 1-(2-hydroxyethyl)-1-methyl-3-phenylthiourea[42] (0.758 g, 3.62 mmol), and triethylamine (0.438 g, 4.34 mmol) in DCM (25 mL) were subjected to the reaction conditions described in **GP-1**. Colorless solid **1o** (0.460 g, 1.02 mmol, 29%). R_f = 0.39 (Hexanes:EtOAc = 1:1); mp: 119−121 °C; IR (KBr, cm^{-1}): 3302, 3032, 2870, 1597, 1492, 1273, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (bs, 1H), 7.32−7.25 (m, 8H), 7.13 (d, J = 7.8 Hz, 2H), 6.93 (app t, J = 7.3 Hz, 2H), 3.92−3.82 (m, 4H), 3.78 (quint, J = 3.7 Hz, 2H), 3.73 (bs, 2H), 3.04 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 182.9, 144.5 (d, J = 17.2 Hz), 139.9, 129.5, 128.6, 125.0, 124.5, 120.6, 115.4 (d, J = 14.2 Hz), 61.9, 54.4, 47.5 (d, J = 9.7 Hz), 39.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ 105.70 ppm; HRMS (MALDI) calcd for $C_{24}H_{27}N_4OPS$ $[M + H]^+$: 451.1721; found: 451.1727.

*2-Ethoxy-1,3-diphenyl-1,3,2-diazaphospholidine (**S1**).* 2-Chloro-1,3-diphenyl-1,3,2-diazaphospholidine[31] (0.600 g, 2.16 mmol), ethanol (0.110 g, 2.39 mmol), and triethylamine (0.261 g, 0.258 mmol) in DCM (10 mL) were subjected to the reaction conditions described in **GP-1**. White solid **S1** (0.208 g, 0.727 mmol, 34%). R_f = 0.72 (Hexanes:EtOAc = 1:1); mp: 88−89 °C; IR (KBr, cm^{-1}): 1595, 1500, 1273, 1026; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 8.4 Hz, 4H), 7.17−7.15 (m, 4H), 6.92 (t, J = 7.3 Hz, 2H), 3.89−3.77 (m, 4H), 3.64 (quint, J = 7.0 Hz, 2H), 1.05 (t, J = 6.9 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 145.2 (d, J = 17.2 Hz), 129.3, 119.9 (d, J = 1.5 Hz), 115.3 (d, J = 14.2 Hz), 59.2, 47.3 (d, J = 9.7 Hz), 16.6 (d, J = 2.9 Hz);

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^{31}P NMR (162 MHz, $CDCl_3$): δ 103.26 ppm; HRMS (APCI) calcd for $C_{16}H_{19}N_2OP$ $[M + H]^+$: 287.1308; found: 287.1301.

General Procedure for the Synthesis of Vinyldiazaphosphonates (GP-2): Ethyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (3a). To a solution of NHP-thiourea **1a** (45.0 mg, 0.103 mmol) in DCM (0.15 mL) was added allene[43] **2a** (34.6 mg, 0.309 mmol). The reaction mixture was stirred for 5 h at room temperature. After stirring for 5 h, the mixture was concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (gradient eluent of Hexanes:EtOAc: 5/1 to 3/1) to give off-white solid **3a** (37.9, 0.102 mmol, >99%). R_f = 0.26 (Hexanes:EtOAc = 1:1); mp: 107−109 °C; IR (Neat, cm^{-1}): 3059, 2982, 2901, 1732, 1601, 1504, 1269, 1126, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.27 (m, 4H), 7.21−7.19 (m, 4H), 7.00 (app t, J = 7.3 Hz, 2H), 6.74 (dd, J = 21.0, 1.5 Hz, 1H), 6.25 (dq, J = 44.2, 1.4 Hz, 1H), 3.92−3.86 (m, 4H), 3.52 (q, J = 7.1 Hz, 2H), 2.91 (dd, J = 16.0, 1.0 Hz, 2H), 0.88 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.2 (d, J = 4.5 Hz), 141.1 (d, J = 7.5 Hz), 138.9 (d, J = 8.9 Hz), 134.5 (d, J = 148.1 Hz), 129.2, 121.8, 116.3 (d, J = 5.2 Hz), 60.9, 43.3 (d, J = 8.9 Hz), 38.5 (d, J = 14.2 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.01 ppm; HRMS (APCI) calcd for $C_{20}H_{23}N_2O_3P$ $[M + H]^+$: 371.1519; found: 371.1508.

Ethyl 3-(1,3-Bis(4-methoxyphenyl)-2-oxido-1,3,2-diazaphospholidin-2-yl)but-3-enoate (3b). NHP-thiourea **1b** (49.6 mg, 0.100 mmol), allene **2a** (33.6 mg, 0.300 mmol), and DCM (0.30 mL) were subjected to the reaction conditions described in **GP-2** for 5 h. Off-white solid **3b** (41.7 mg, 0.097 mmol, 97%). R_f = 0.15 (Hexanes:EtOAc = 1:1); mp: 116−118 °C; IR (Neat, cm^{-1}): 3063, 2951, 2833, 1732, 1674, 1504, 1279, 1136, 1035; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 9.0 Hz, 4H), 6.85 (d, J = 9.0 Hz, 4H), 6.62 (dd, J = 20.9, 1.6 Hz, 1H), 6.17 (dd, J = 43.8, 1.2 Hz, 1H), 3.84−3.80 (m, 4H), 3.76 (s, 6H), 3.64 (q, J = 7.0 Hz, 2H), 2.92 (d, J = 15.4 Hz, 2H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.3 (d, J = 5.2 Hz), 154.9, 138.2 (d, J = 8.9 Hz), 134.6 (d, J = 148.8 Hz), 134.5 (d, J = 7.5 Hz), 118.1 (d, J = 4.5 Hz), 114.5, 60.8, 55.5, 44.1 (d, J = 8.2 Hz), 38.4 (d, J = 14.2 Hz), 13.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.11 ppm; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_5P$ $[M + H]^+$: 430.1658; found: 430.1679.

Ethyl 3-(2-Oxido-1,3-di-p-tolyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (3d). NHP-thiourea **1d** (46.4 mg, 0.100 mmol), allene **2a** (33.6 mg, 0.300 mmol), and DCM (0.30 mL) were subjected to the reaction conditions described in **GP-2** for 5 h. Off-white solid **3d** (39.2 mg, 0.0984 mmol, 98%). R_f = 0.37 (Hexanes:EtOAc = 1:1); mp: 137−139 °C; IR (Neat, cm^{-1}): 3061, 2957, 2862, 1732, 1614, 15145, 1269, 1136, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (s, 8H), 6.68 (dd, J = 20.9, 1.5 Hz, 1H), 6.20 (dd, J = 43.9, 1.4 Hz, 1H), 3.86−3.70 (m, 4H), 3.57 (q, J = 7.3 Hz, 2H), 2.89 (dd, J = 15.7, 0.97 Hz, 2H), 2.27 (s, 6H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.3 (d, J = 5.2 Hz), 138.6 (d, J = 8.2 Hz), 138.4 (d, J = 8.9 Hz), 134.6 (d, J = 148.1 Hz), 131.2, 129.7, 116.4 (d, J = 4.5 Hz), 60.8, 43.5 (d, J = 8.9 Hz), 38.5 (d, J = 13.5 Hz), 20.5, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.95 ppm; HRMS (APCI) calcd for $C_{22}H_{27}N_2O_3P$ $[M + H]^+$: 399.1832; found: 399.1824.

Benzyl 3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-but-3-enoate (3e). NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[43] **2e** (53.8 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in GP-2 5 h. Off-white solid **3e** (42.3 mg, 0.0978 mmol, 95%). R_f = 0.24 (Hexanes:EtOAc = 1:1); mp: 155−157 °C; IR (Neat, cm^{-1}): 3063, 2947, 2885, 1732, 1597, 1501, 1273, 1130, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.19 (m, 11H), 7.08−7.05 (m, 2H), 6.99 (app t, J = 7.3 Hz, 2H), 6.74 (dd, J = 20.9, 1.5 Hz, 1H), 6.23 (dd, J = 44.1, 1.4 Hz, 1H), 4.48 (s, 2H), 3.86 (d, J = 6.9 Hz, 4H), 2.96 (d, J = 15.8 Hz, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 168.9 (d, J = 4.5 Hz), 141.0 (d, J = 7.5 Hz), 139.1 (d, J = 8.9 Hz), 135.3, 134.3 (d, J = 148.1 Hz), 129.2, 128.4, 128.2, 128.1, 121.9, 116.4 (d, J = 5.2 Hz), 66.4, 43.3 (d, J = 8.2 Hz), 38.4 (d, J = 14.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.90 ppm; HRMS (ESI) calcd for $C_{25}H_{25}N_2O_3P$ $[M + Na]^+$: 455.1495; found: 455.1489.

4-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)pent-4-en-2-one (3f). NHP-thiourea **1a** (30.0 mg, 0.0688 mmol), allene[44] **2f** (16.9 mg, 0.206 mmol), and DCM (0.18 mL) were subjected to the reaction conditions described in **GP-2** for 5 h. Yellow solid **3f** (13.6 mg, 0.0399 mmol, 58%). R_f = 0.31 (Hexanes:EtOAc = 1:1); mp: 112−115 °C; IR (Neat, cm^{-1}): 3063, 2947, 2877, 1709, 1597, 1501, 1269, 1122, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.27 (m, 4H), 7.23−7.20 (m, 4H), 7.00 (app t, J = 7.3 Hz, 2H), 6.74 (dd, J = 21.0, 1.5 Hz, 1H), 6.19 (dd, J = 44.4, 1.3 Hz, 1H), 3.90−3.80 (m, 4H), 2.98 (d, J = 16.1 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 204.6 (d, J = 3.7 Hz), 141.0 (d, J = 8.2 Hz), 138.6, 135.4 (d, J = 145.8 Hz), 129.3, 122.0, 116.4 (d, J = 5.2 Hz), 48.3 (d, J = 13.5 Hz), 43.1 (d, J = 8.9 Hz), 27.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.41 ppm; HRMS (ESI) calcd for $C_{19}H_{21}N_2O_2P$ $[M + H]^+$: 340.1341; found: 340.1324.

tert-Butyl 3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-but-3-enoate (3g). NHP-thiourea **1a** (20.0 mg, 0.0458 mmol), allene[45] **2g** (18.1 mg, 0.128 mmol), and DCM (0.20 mL) were subjected to the reaction conditions described **GP-2** for 24 h. Colorless solid **3g** (8.80 mg, 0.0220 mmol, 48%). R_f = 0.41 (Hexanes:EtOAc = 1:1); mp: 167−169 °C; IR (KBr, cm^{-1}): 2978, 1732, 1600, 1504, 1276, 1128, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 4H), 7.22−7.19 (m, 4H), 7.00 (app t, J = 7.3 Hz, 2H), 6.74 (d, J = 21.5 Hz, 1H), 6.25 (dd, J = 44.9, 1.4 Hz, 1H), 3.95−3.84 (m, 4H), 2.81 (d, J = 14.8 Hz, 2H), 1.14 (s, 9H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 168.6 (d, J = 6.7 Hz), 141.2 (d, J = 7.5 Hz), 137.9 (d, J = 8.9 Hz), 134.9 (d, J = 148.1 Hz), 129.2, 121.8, 116.4 (d, J = 5.2 Hz), 81.1, 43.5 (d, J = 8.2 Hz), 38.9 (d, J = 13.5 Hz), 27.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.82 ppm; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_3P$ $[M + H]^+$: 398.1759; found: 398.1767.

S-Benzyl 3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-but-3-enethioate (3h). NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[46] **2h** (59.8 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 5 h. Brown syrup **3h** (22.0 mg, 0.0490 mmol, 49%). R_f = 0.28 (Hexanes:EtOAc = 1:1); IR (Neat, cm^{-1}): 3063, 2924, 2874, 1685, 1597, 1501, 1269, 1122, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.18 (m, 11H), 7.06−6.99 (m, 4H), 6.75 (dd, J = 20.9, 13.2 Hz, 1H), 6.23 (dd, J = 44.1, 1.3 Hz, 1H), 3.86 (d, J = 7.0 Hz, 4H), 3.71 (s, 2H), 3.16 (dd, J = 15.6, 1.1 Hz, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 193.8 (d, J = 4.5 Hz), 141.1, 141.0, 136.5, 134.3 (d, J = 148.1 Hz), 129.2, 128.8, 128.5, 127.3, 122.0, 116.5, 46.6 (d, J = 13.5 Hz), 43.4 (d, J = 8.2 Hz), 33.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 16.74 ppm; HRMS (APCI) calcd for $C_{25}H_{25}N_2O_2PS$ $[M + H]^+$: 449.1453; found: 449.1490.

N-Methoxy-N-methyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enamide (3i). NHP-thiourea **1a** (40.0 mg, 0.0917 mmol), allene **2i** (34.9 mg, 0.275 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Off-white solid **3i** (31.4 mg, 0.0815 mmol, 89%). R_f = 0.06 (Hexanes:EtOAc = 1:1); mp 123−124 °C; IR (Neat, cm^{-1}): 3063, 2935, 1662, 1601, 1597, 1504, 1276, 1122, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.22 (m, 8H), 6.99 (app t, J = 7.2 Hz, 2H), 6.68 (dd, J = 21.3, 1.2 Hz, 1H), 6.12 (dq, J = 44.8, 1.6 Hz, 1H), 3.98−3.92 (m, 2H), 3.90−3.84 (m, 2H), 3.20 (s, 3H), 3.05 (d, J = 13.3 Hz, 2H), 2.81 (s, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.5, 141.3 (d, J = 8.2 Hz), 137.3 (d, J = 8.9 Hz), 135.1 (d, J = 146.6 Hz), 129.2, 121.8, 116.5 (d, J = 5.2 Hz), 60.7, 43.5 (d, J = 8.9 Hz), 36.7 (d, J = 13.5 Hz), 31.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.50 ppm; HRMS (ESI) calcd for $C_{20}H_{24}N_3O_3P$ $[M + H]^+$: 385.1555; found: 385.1568.

2-(3-(Diphenylphosphoryl)prop-1-en-2-yl)-1,3-diphenyl-1,3,2-diazaphospholidine 2-oxide (3j). NHP-thiourea **1a** (208 mg, 0.477 mmol), allene[47] **2j** (106 mg, 0.441 mmol), and DCM (0.80 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Colorless solid **3j** (0.102 g, 0.204 mmol, 43%). R_f = 0.13 (Hexanes:EtOAc = 1:1); mp: 80−81 °C; IR (Neat, cm^{-1}): 3055, 2939, 2875, 1599, 1504, 1267, 1120, 1035; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46−7.40 (m, 6H), 7.31−7.25 (m, 8H), 7.16−7.14 (m, 4H), 7.02 (app t, J = 7.4 Hz, 2H), 6.49 (dq, J = 10.4, 1.6 Hz, 1H), 6.41 (dq, J = 34.0, 1.7 Hz, 1H), 3.91−3.85 (m, 4H), 2.98−2.92 (m, 2H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 141.2 (d, J = 7.5 Hz), 137.9 (t, J = 8.2 Hz), 133.0 (d, J = 72.5 Hz), 131.9 (d, J = 6.7 Hz), 131.7 (d, J = 3.0

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Hz), 130.7 (d, J = 8.9 Hz), 129.4, 128.6 (d, J = 11.9 Hz), 122.1, 116.6 (d, J = 4.5 Hz), 43.6 (d, J = 8.2 Hz), 31.7 (dd, J = 67.3, 11.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 30.33 ppm (d, J = 30.07 Hz), 19.1 ppm (d, J = 29.74 Hz); HRMS (ESI) calcd for $C_{29}H_{28}N_2O_2P_2$ $[M + H]^+$: 498.1626; found: 498.1646.

*Ethyl 2-Methyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3k**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[47] **2k** (39.0 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** 48 h. Off-white solid **3k** (23.8 mg, 0.0619 mmol, 61%). R_f = 0.25 (Hexanes:EtOAc = 1:1); mp: 142−145 °C; IR (Neat, cm^{-1}): 3063, 2982, 2874, 1732, 1597, 1501, 1273, 1126, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.16 (m, 4H), 7.22−7.16 (m, 4H), 7.02−6.95 (m, 2H), 6.81 (d, J = 22.2 Hz, 1H), 6.32 (d, J = 45.6 Hz, 1H), 3.96−3.86 (m, 4H), 3.62−3.53 (m, 1H), 3.48−3.40 (m, 1H), 3.06−2.97 (m, 1H), 1.06 (d, J = 7.0 Hz, 3H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 172.7 (d, J = 5.2 Hz), 141.2 (dd, J = 8.2, 1.5 Hz), 140.5 (d, J = 128.6 Hz), 136.2, 129.1 (d, J = 26.9 Hz), 121.7 (d, J = 30.7 Hz), 116.3 (d, J = 5.2 Hz), 60.7, 43.4 (dd, J = 41.1, 7.5 Hz), 40.7 (d, J = 4.5 Hz), 17.4 (d, J = 5.9 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.73 ppm; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3P$ $[M + Na]^+$: 407.1495; found: 407.1490.

*Ethyl 2-(1-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-vinyl)pent-4-enoate (**3l**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2l** (47.1 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Off-white solid **3l** (13.9 mg, 0.0338 mmol, 33%). R_f = 0.22 (Hexanes:EtOAc = 1:1); mp: 151−153 °C; IR (Neat, cm^{-1}): 3059, 2982, 2854, 1732, 1601, 1504, 1284, 1126, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.15 (m, 8H), 7.03−7.94 (m, 2H), 6.85 (dd, J = 22.3, 0.8 Hz, 1H), 6.35 (d, J = 45.6 Hz, 1H), 5.39−5.28 (m, 1H), 4.81−4.75 (m, 2H), 3.97−3.89 (m, 4H), 3.58−3.44 (m, 2H), 2.95−2.88 (m, 1H), 2.42−2.34 (m, 1H), 2.00−1.94 (m,1H), 0.83 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.3 (d, J = 5.2 Hz), 141.1 (d, J = 8.2 Hz), 138.4 (d, J = 145.8 Hz), 137.0, 134.4, 129.2 (d, J = 26.2 Hz), 121.8 (d, J = 37.4 Hz), 117.2, 116.3 (dd, J = 8.2, 5.2 Hz), 60.7, 46.3 (d, J = 4.5 Hz), 43.4 (dd, J = 12.7, 8.2 Hz), 36.3 (d, J = 5.9 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.59 ppm; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_3P$ $[M + Na]^+$: 433.1652; found:433.1644.

*Ethyl 2-(1-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-vinyl)octanoate (**3m**).* NHP-thiourea **1a** (18.0 mg, 0.0412 mmol), allene **2m** (24.2 mg, 0.123 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** 48 h. Off-white solid **3m** (8.10 mg, 0.0178 mmol, 43%). R_f = 0.44 (Hexanes:EtOAc = 1:1); mp: 123−126 °C; IR (Neat, cm^{-1}): 3059, 2928, 2854, 1732, 1601, 1504, 1280, 1126, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.26 (m, 4H), 7.24−7.14 (m, 4H), 7.02−6.94 (m, 2H), 6.85 (dd, J = 22.4, 1.0 Hz, 1H), 6.35 (d, J = 45.9 Hz, 1H), 3.99−3.88 (m, 4H), 3.55−3.40 (m, 2H), 2.86−2.79 (m, 1H), 1.68−1.59 (m, 1H), 1.31−1.27 (m, 2H), 1.16−1.09 (m, 2H), 1.01−0.96 (m, 4H), 0.89−0.77 (m, 7H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 172.1 (d, J = 4.5 Hz), 141.1 (dd, J = 8.2, 5.8 Hz), 138.9 (d, J = 145.8 Hz), 136.8, 129.1 (d, J = 23.1 Hz), 121.7 (d, J = 33.6 Hz), 116.2 (d, J = 5.2 Hz), 60.6, 46.5 (d, J = 11.9 Hz), 43.4 (app d, J = 71.8 Hz), 32.2 (d, J = 5.9 Hz), 29.6, 28.6, 27.2, 22.4, 13.9, 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.97 ppm; HRMS (ESI) calcd for $C_{26}H_{35}N_2O_3P$ $[M + Na]^+$: 477.2278; found:477.2280.

*Diethyl 2-(1-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)vinyl)succinate (**3n**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2n** (52.3 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Off-white solid **3n** (37.1 mg, 0.0812 mmol, 79%). R_f = 0.15 (Hexanes:EtOAc = 1:1); mp: 103−105 °C; IR (Neat, cm^{-1}): 3063, 2982, 2874, 1732, 1597, 1504, 1288, 1157, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.26 (m, 4H), 7.21−7.18 (m, 4H), 7.03−6.96 (m, 2H), 6.79 (d, J = 21.6 Hz, 1H), 6.26 (d, J = 44.8 Hz, 1H), 4.02−3.88 (m, 6H), 3.73−3.65 (m, 1H), 3.59−3.51 (m, 1H), 3.47−3.39 (m, 1H), 2.69 (dd, J = 16.8, 10.9 Hz, 1H), 1.87 (dd, J = 16.9, 3.7 Hz, 1H), 1.13 (t, J = 7.1 Hz, 3H), 0.78 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.5 (d, J = 8.2 Hz), 171.1, 141.1 (dd, J = 14.9, 7.5 Hz), 138.8 (d, J = 148.1 Hz), 137.1 (d, J = 8.9 Hz), 129.2 (d, J = 28.4 Hz), 121.9 (d, J = 31.4 Hz), 116.4 (dd, J = 17.2, 5.2 Hz), 61.1, 60.7, 43.5 (dd, J = 19.4, 8.2 Hz), 41.8 (d, J = 13.4 Hz), 36.5 (d, J = 4.5 Hz), 13.9, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.01 ppm; HRMS (APCI) calcd for $C_{24}H_{29}N_2O_5P$ $[M + H]^+$: 457.1887; found: 457.1890.

*Ethyl 2-Benzyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3o**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2o** (62.5 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Pale yellow solid **3o** (25.2 mg, 0.0547 mmol, 53%). R_f = 0.27 (Hexanes:EtOAc = 1:1); mp: 153−155 °C; IR (Neat, cm^{-1}): 3063, 2978, 2870, 1732, 1597, 1501, 1276, 1153, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34−7.23 (m, 6H), 7.16−7.09 (m, 5H), 7.03 (app t, J = 7.3 Hz, 1H), 6.96 (app t, J = 7.3 Hz, 1H), 6.87 (dd, J = 22.3, 0.8 Hz, 1H), 6.81−6.79 (m, 2H), 6.46 (d, J = 45.5 Hz, 1H), 3.99−3.87 (m, 4H), 3.49−3.43 (m, 2H), 3.16−3.08 (m, 1H), 3.01−2.95 (m, 1H), 2.42 (dd, J = 13.2, 4.3 Hz, 1H), 0.72 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.4 (d, J = 5.2 Hz), 141.1 (d, J = 7.5 Hz), 139.0 (d, J = 145.8 Hz), 138.4, 137.2 (d, J = 8.9 Hz), 129.2 (d, J = 36.6 Hz), 128.5 (d, J = 20.9 Hz), 126.5, 121.9 (d, J = 35.1 Hz), 116.3 (d, J = 5.2 Hz), 116.2 (d, J = 5.2 Hz), 60.8, 48.4 (d, J = 12.7 Hz), 43.5 (dd, J = 47.1, 8.2 Hz), 38.5 (d, J = 5.2 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.63 ppm; HRMS (ESI) calcd for $C_{27}H_{29}N_2O_3P$ $[M + Na]^+$: 483.1808; found:483.1806.

*Ethyl 2-(4-Chlorobenzyl)-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3p**).* NHP-thiourea **1a** (43.0 mg, 0.0986 mmol), allene[48] **2p** (70.2 mg, 0.295 mmol), and DCM (0.3 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Off-white solid **3p** (38.1 mg, 0.0771 mmol, 78%). R_f = 0.23 (Hexanes:EtOAc = 1:1); mp: 152−153 °C; IR (Neat, cm^{-1}): 3061, 2980, 2875, 1732, 1599, 1494, 1271, 1153, 1035, 754; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.14 (m, 8H), 7.07−7.02 (m, 3H), 6.97 (app t, J = 7.2 Hz, 1H), 6.87 (d, J = 22.3 Hz, 1H), 6.71 (d, J = 8.4 Hz, 2H), 6.43 (d, J = 45.4 Hz, 1H), 3.96−3.86 (m, 4H), 3.55−3.43 (m, 2H), 3.11−3.04 (m, 1H), 2.97−2.91 (m, 1H), 2.41 (dd, J = 13.5, 4.7 Hz, 1H), 0.75 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.3 (d, J = 5.9 Hz), 141.1 (dd, J = 8.2, 2.2 Hz), 138.8 (d, J = 145.8 Hz), 137.2 (d, J = 8.2 Hz), 136.8, 132.3, 129.9, 129.2 (d, J = 34.4 Hz), 128.5, 121.9 (d, J = 29.2 Hz), 116.2 (dd, J = 27.6, 5.2 Hz), 60.9, 48.3 (d, J = 12.7 Hz), 43.5 (dd, J = 44.1, 8.2 Hz), 37.7 (d, J = 5.9 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.38 ppm; HRMS (ESI) calcd for $C_{27}H_{28}N_2O_3PCl$ $[M + H]^+$: 494.1526; found: 494.1538.

*Ethyl 2-(4-Nitrobenzyl)-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3q**).* NHP-thiourea **1a** (20.0 mg, 0.0458 mmol), allene[49] **2q** (34.1 mg, 0.137 mmol), and DCM (0.20 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Off-white solid **3q** (16.1 mg, 0.0318 mmol, 69%). R_f = 0.31 (Hexanes:EtOAc = 1:1); mp: 175−178 °C; IR (Neat, cm^{-1}): 3061, 2980, 2875, 1732, 1599, 1519, 1504, 1346, 1267, 1151, 1035; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, J = 8.6 Hz, 2H), 7.30−7.25 (m, 4H), 7.18−7.15 (m, 4H), 7.02−6.96 (m, 2H), 6.95−6.92 (m, 2H), 6.88 (d, J = 22.1 Hz, 1H), 6.48 (d, J = 45.2 Hz, 1H), 3.93−3.90 (m, 4H), 3.49 (q, J = 7.2 Hz, 2H), 3.18−3.05 (m, 2H), 2.58 (dd, J = 13.1, 4.9 Hz, 1H), 0.78 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.9 (d, J = 5.2 Hz), 146.6, 145.8, 140.9 (d, J = 8.2 Hz), 138.4 (d, J = 146.6 Hz), 137.3 (d, J = 8.2 Hz), 129.3 (d, J = 29.9 Hz), 123.5, 121.9 (d, J = 17.2 Hz), 116.3 (d, J = 4.5 Hz), 115.6 (d, J = 5.2 Hz), 61.2, 47.9 (d, J = 13.5 Hz), 43.4 (dd, J = 36.6, 8.2 Hz), 38.0 (d, J = 5.9 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.10 ppm; HRMS (ESI) calcd for $C_{27}H_{28}N_3O_5P$ $[M + H]^+$: 505.1767; found: 505.1792.

*Ethyl 2-(4-Fluorobenzyl)-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3r**).* NHP-thiourea **1a** (20.0 mg, 0.0458 mmol), allene[48] **2r** (30.3 mg, 0.137 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Colorless solid **3r** (18.1 mg, 0.0378 mmol, 82%). R_f = 0.29 (Hexanes:EtOAc = 1:1); mp: 164−166 °C; IR (Neat, cm^{-1}): 3066, 2985, 2877, 1732, 1601, 1504, 1346, 1280, 1157, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.14 (m, 8H), 7.03 (app t, J = 7.3 Hz, 1H), 6.96 (app t, J = 7.3 Hz, 1H), 6.87 (d, J = 22.3 Hz, 1H), 6.81−6.72 (m, 4H), 6.44 (d, J = 45.5 Hz, 1H), 3.97−3.87 (m, 4H), 3.47 (q, J = 7.2 Hz, 2H), 3.11−3.04 (m, 1H), 2.98−2.92 (m, 1H), 2.41 (dd, J = 13.6,

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4.6 Hz, 1H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.3 (d, J = 5.2 Hz), 161.5 (d, J = 244.5 Hz), 141.1 (d, J = 8.2 Hz), 138.8 (d, J = 145.8 Hz), 137.2 (app t, J = 4.5 Hz), 134.0 (d, J = 3.7 Hz), 130.0 (d, J = 8.2 Hz), 129.2 (d, J = 34.4 Hz), 121.9 (d, J = 29.2 Hz), 116.2 (dd, J = 23.9, 4.5 Hz), 115.1 (d, J = 20.9 Hz), 60.9, 48.5 (d, J = 12.7 Hz), 43.5 (dd, J = 45.6, 8.3 Hz), 37.6 (d, J = 5.2 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.46 ppm; HRMS (ESI) calcd for $C_{27}H_{28}N_2O_3FP$ $[M + H]^+$: 478.1822; found: 478.1844.

*Ethyl 2-(4-Bromobenzyl)-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3s**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2s** (86.0 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Off-white solid **3s** (34.1 mg, 0.0632 mmol, 62%). R_f = 0.22 (Hexanes:EtOAc = 1:1); mp: 152−155 °C; IR (Neat, cm^{-1}): 3063, 2978, 2870, 1732, 1597, 1504, 1265, 1153, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.14 (m, 10H), 7.03 (app t, J = 7.3 Hz, 1H), 6.96 (app t, J = 7.3 Hz, 1H), 6.86 (d, J = 22.2 Hz, 1H), 6.65 (d, J = 8.4 Hz, 2H), 6.42 (d, J = 45.6 Hz, 1H), 3.96−3.86 (m, 4H), 3.55−3.42 (m, 2H), 3.11−3.04 (m, 1H), 2.96−2.89 (m, 1H), 2.39 (dd, J = 13.6, 4.8 Hz, 1H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.2 (d, J = 5.2 Hz, 2H), 141.0 (dd, J = 8.2, 2.9 Hz), 138.7 (d, J = 146.6 Hz), 137.3, 131.4, 130.3, 129.2 (d, J = 34.4 Hz), 121.9 (d, J = 29.9 Hz), 120.4, 116.3 (d, J = 5.2 Hz), 116.0 (d, J = 5.2 Hz), 60.9, 48.2 (d, J = 12.7 Hz), 43.4 (dd, J = 43.4, 8.2 Hz), 37.8 (d, J = 5.9 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.39 ppm; HRMS (ESI) calcd for $C_{27}H_{28}BrN_2O_3P$ $[M + Na]^+$: 561.0913; found: 561.0931.

*Ethyl 3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-2-(4-(trifluoromethyl)benzyl)but-3-enoate (**3t**).* NHP-thiourea **1a** (20.0 mg, 0.0458 mmol), allene[50] **2t** (37.2 mg, 0.137 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Colorless solid **3t** (22.1 mg, 0.0418 mmol, 91%). R_f = 0.28 (Hexanes:EtOAc = 1:1); mp: 133−135 °C; IR (Neat, cm^{-1}): 3063, 2982, 2874, 1732, 1601, 1504, 1327, 1276, 1165, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35−7.15 (m, 10H), 7.03 (app t, J = 7.3 Hz, 1H), 6.97 (app t, J = 7.3 Hz, 1H), 6.95 (m, 2H), 6.90 (s, 2H), 6.87 (d, J = 13.7 Hz, 1H), 6.43 (d, J = 45.3 Hz, 1H), 3.97−3.87 (m, 4H), 3.54−3.43 (m, 2H), 3.16−3.01 (m, 2H), 2.49 (dd, J = 13.3, 4.5 Hz, 1H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.1 (d, J = 5.2 Hz), 142.4 (d, J = 1.5 Hz), 141.1 (d, J = 8.2 Hz), 138.7 (d, J = 146.6 Hz), 137.2 (t, J = 6.7 Hz), 129.2 (d, J = 35.5 Hz), 128.9, 125.3 (d, J = 3.7 Hz), 122.1, 121.8, 116.3 (d, J = 5.2 Hz), 116.0 (d, J = 5.2 Hz), 61.1, 48.1 (d, J = 12.7 Hz), 43.4 (dd, J = 42.6, 8.2 Hz), 38.1 (d, J = 5.9 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.26 ppm; HRMS (ESI) calcd for $C_{28}H_{28}N_2O_3F_3P$ $[M + H]^+$: 529.1863; found: 529.1888.

*Ethyl 3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-2-phenylbut-3-enoate (**3u**).* NHP-thiourea **1a** (34.4 mg, 0.0788 mmol), allene[51] **2u** (45.0 mg, 0.236 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 5 h. Off-white solid **3u** (31.6 mg, 0.0707 mmol, 90%). R_f = 0.30 (Hexanes:EtOAc = 1:1); mp: 162−165 °C; IR (Neat, cm^{-1}): 3057, 2985, 2904, 1732, 1601, 1504, 1272, 1127, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.20 (m, 6H), 7.14−7.07 (m, 5H), 7.01 (q, J = 7.5 Hz, 2H), 6.87 (dd, J = 21.9, 0.8 Hz, 1H), 6.77 (app d, J = 6.9 Hz, 2H), 6.10 (d, J = 45.0 Hz, 1H), 4.24 (d, J = 11.3 Hz, 1H), 3.94−3.75 (m, 4H), 3.71−3.63 (m, 1H), 3.60−3.52 (m, 1H), 0.98 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.0 (d, J = 6.7 Hz), 141.2 (d, J = 7.5 Hz), 140.8 (d, J = 8.2 Hz), 139.1 (d, J = 145.8 Hz), 135.3 (d, J = 6.7 Hz), 129.1, 128.5, 128.3, 127.4, 121.9 (d, J = 7.5 Hz), 116.3 (d, J = 4.5 Hz), 61.3, 53.0 (d, J = 16.5 Hz), 43.3 (d, J = 5.7 Hz), 13.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.03 ppm; HRMS (APCI) calcd for $C_{26}H_{27}N_2O_3P$ $[M + H]^+$: 447.1832; found: 447.1833.

*Ethyl 2-([1,1′-Biphenyl]-2-ylmethyl)-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3v**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene **2v** (86.0 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Off-white solid **3v** (23.1 mg, 0.0430 mmol, 42%). R_f = 0.22 (Hexanes:EtOAc = 1:1); mp: 175−176 °C; IR (Neat, cm^{-1}): 3059, 2978, 2870, 1732, 1597, 1504, 1276, 1149, 1037; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28−7.19 (m, 7H), 7.16−7.09 (m, 3H), 7.07−6.98 (m, 7H), 6.93−6.89 (m, 2H), 6.81 (dd, J = 22.3, 0.9 Hz, 1H), 6.29 (d, J = 45.5 Hz, 1H), 3.85−3.72 (m, 2H), 3.70−3.57 (m, 2H), 3.20 (q, J = 7.0 Hz, 2H), 3.11−3.04 (m, 1H), 3.00−2.94 (m, 1H), 2.87−2.82 (m, 1H), 0.65 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.8 (d, J = 4.5 Hz), 141.9, 141.3, 141.1 (dd, J = 11.9, 8.2 Hz), 138.5 (d, J = 145.8 Hz), 137.7 (d, J = 8.9 Hz), 134.9, 130.3, 129.6, 129.2, 128.9 (d, J = 4.5 Hz), 128.1, 127.2, 126.9, 126.6, 121.6 (d, J = 30.7 Hz), 116.2 (dd, J = 36.6, 4.5 Hz), 60.5, 46.7 (d, J = 12.7 Hz), 43.1 (d, J = 8.2 Hz), 35.8 (d, J = 5.9 Hz), 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.27 ppm; HRMS (APCI) calcd for $C_{33}H_{33}N_2O_3P$ $[M + H]^+$: 537.2302 ; found: 537.2302.

*Ethyl 2-(3,5-Dimethoxybenzyl)-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3w**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[52] **2w** (73.0 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Pale yellow solid **3w** (30.4 mg, 0.0578 mmol, 56%). R_f = 0.25 (Hexanes:EtOAc = 1:1); mp: 137−139 °C; IR (Neat, cm^{-1}): 3063, 2935, 2839, 1732, 1597, 1504, 1273, 1153, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.14 (m, 8H), 7.01 (app t, J = 7.3 Hz, 1H), 6.96 (app t, J = 7.3 Hz, 1H), 6.87 (d, J = 22.2 Hz, 1H), 6.48 (d, J = 45.5 Hz, 1H), 6.21 (t, J = 2.3 Hz, 1H), 5.99 (d, J = 2.3 Hz, 2H), 3.97−3.87 (m, 4H), 3.67 (s, 6H), 3.56−3.44 (m, 2H), 3.12−3.04 (m, 1H), 2.97−2.91 (m, 1H), 2.30 (dd, J = 13.2, 3.8 Hz, 1H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 171.4 (d, J = 5.9 Hz), 160.6, 141.1 (dd, J = 8.2, 2.2 Hz), 140.8, 139.1 (d, J = 145.8 Hz), 137.1 (d, J = 8.2 Hz), 129.2 (d, J = 32.9 Hz), 121.8 (d, J = 12.7 Hz), 116.2 (dd, J = 27.6, 5.2 Hz), 106.6, 98.5, 60.8, 55.1 (d, J = 2.2 Hz), 48.3 (d, J = 13.5 Hz), 43.5 (d, J = 37.4, 8.2 Hz), 38.9 (d, J = 5.2 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.48 ppm; HRMS (APCI) calcd for $C_{29}H_{33}N_2O_5P$ $[M + H]^+$: 521.2200; found: 521.2202.

NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[43] **2x** (33.6 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described **GP-2** for 5 h. Off-white solid **3xa** (23.3 mg, 0.0606 mmol, 59%) and **3xb** (4.40 mg, 0.0114 mmol, 11%).

*Ethyl (E)-3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-pent-3-enoate (**3xa**).* Off-white solid (23.3 mg, 0.0606 mmol, 59%). R_f = 0.21 (Hexanes:EtOAc = 1:1); mp: 147−149 °C. IR (Neat, cm^{-1}): 3059, 2978, 2897, 1728, 1597, 1501, 1280, 1130, 1041; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (dq, J = 22.1, 7.0 Hz, 1H), 7.29−7.25 (m, 4H), 7.18−7.16 (m, 4H), 6.97 (app t, J = 7.3 Hz, 2H), 3.95−3.83 (m, 4H), 3.41 (q, J = 7.1 Hz, 2H), 2.94 (d, J = 18.6 Hz, 2H), 1.92 (dd, J = 7.0, 3.3 Hz, 3H), 0.83 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.3 (d, J = 2.2 Hz), 150.4 (d, J = 10.4 Hz), 141.3 (d, J = 8.2 Hz), 129.1, 125.5 (d, J = 154.8 Hz), 121.5, 116.2 (d, J = 5.2 Hz), 60.7, 43.2 (d, J = 8.2 Hz), 32.8 (d, J = 14.1 Hz), 15.7 (d, J = 17.9 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.22 ppm; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3P$ $[M + Na]^+$: 407.1495; found: 407.1497.

*Ethyl (Z)-3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-pent-3-enoate (**3xb**).* Off-white solid (4.40 mg, 0.0114 mmol, 11%). R_f = 0.27 (Hexanes:EtOAc = 1:1); mp: 141−143 °C. IR (Neat, cm^{-1}): 3065, 2984, 2889, 1724, 1599, 1498, 1271, 1128, 1035; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32−7.27 (m, 4H), 7.17−7.14 (m, 4H), 6.98 (app t, J = 7.2 Hz, 2H), 7.39 (dq, J = 47.7, 7.2 Hz, 1H), 3.91−3.87 (m, 4H), 3.45 (q, J = 7.0 Hz, 2H), 2.79 (d, J = 15.8 Hz, 2H), 2.46 (dd, J = 7.4, 3.5 Hz, 3H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.2 (d, J = 2.9 Hz), 153.3 (d, J = 11.9 Hz), 141.3 (d, J = 8.2 Hz), 129.1, 124.1 (d, J = 148.8 Hz), 121.6, 116.0 (d, J = 5.2 Hz), 60.6, 43.4 (d, J = 8.2 Hz), 40.9 (d, J = 15.7 Hz), 16.5 (d, J = 5.2 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.87 ppm; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_3P$ $[M + Na]^+$: 407.1495; found: 407.1497.

NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2y** (43.3 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Off-white solid **3ya** (31.2 mg, 0.0783 mmol, 76%) and **3yb** (5.10 mg, 0.0128 mmol, 12%).

*Ethyl (E)-3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-hex-3-enoate (**3ya**).* Off-white solid (31.2 mg, 0.0783 mmol, 76%). R_f = 0.29 (Hexanes:EtOAc = 1:1); mp: 139−140 °C; IR (Neat, cm^{-1}): 3059, 2970, 2877, 1739, 1601, 1504, 1273, 1130, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33−7.24 (m, 5H), 7.19−7.17 (m, 4H), 6.97 (app t, J = 7.3 Hz, 2H), 3.94−3.83 (m, 4H), 3.38 (q, J = 7.1 Hz, 2H), 2.91 (d,

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J = 18.8 Hz, 2H), 2.33−2.25 (m, 2H), 1.09 (t, J = 7.5 Hz, 3H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.3 (d, J = 2.2 Hz), 157.2, 141.3 (d, J = 8.2 Hz), 129.1, 123.4 (d, J = 153.3 Hz), 121.5, 116.1 (d, J = 4.5 Hz), 60.7, 43.2 (d, J = 7.5 Hz), 33.0 (d, J = 3.9 Hz), 23.4 (d, J = 17.2 Hz), 13.5, 12.8; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.45 ppm; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_3P$ [M + Na]$^+$: 421.1652; found: 421.1647.

*Ethyl (Z)-3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-hex-3-enoate (**3yb**).* Off-white solid (5.10 mg, 0.0128 mmol, 12%). R_f = 0.26 (Hexanes:EtOAc = 1:1); mp: 111−113 °C; IR (Neat, cm^{-1}): 3061, 2962, 2874, 1728, 1599, 1500, 1271, 1128, 1035; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31−7.26 (m, 4H), 7.18−7.16 (m, 4H), 6.99 (td, J = 7.2, 0.8 Hz, 2H), 6.57 (dt, J = 47.7, 7.8 Hz, 1H) 3.94−3.84 (m, 4H), 3.45 (q, J = 6.5 Hz, 2H), 3.08−2.98 (m, 2H), 2.79 (d, J = 15.8 Hz, 2H), 1.14 (t, J = 7.6 Hz, 3H), 0.86 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.2, 160.3 (d, J = 12.7 Hz), 141.3 (d, J = 7.5 Hz), 129.1, 122.4 (d, J = 149.6 Hz), 121.6, 116.1 (d, J = 5.2 Hz), 60.6, 43.4 (d, J = 8.2 Hz), 40.9 (d, J = 15.7 Hz), 23.2 (d, J = 4.5 Hz), 13.6, 13.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.74 ppm; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_3P$ [M + Na]$^+$: 421.1652; found: 421.1647.

*Ethyl (E)-5-Methyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)hex-3-enoate (**3z**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2z** (47.6 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 5 h. Off-white solid **3z** (32.5 mg, 0.0789 mmol, 76%). R_f = 0.21 (Hexanes:EtOAc = 1:1); mp: 126−129 °C; IR (Neat, cm^{-1}): 3063, 2962, 2870, 1724, 1597, 1504, 1276, 1126, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.23 (m, 4H), 7.18−7.16 (m, 4H), 7.13−7.07 (m, 1H), 6.97 (app t, J = 7.3 Hz, 2H), 3.92−3.82 (m, 4H), 3.36 (q, J = 6.6 Hz, 2H), 3.08 (d, J = 16.0 Hz, 2H), 1.20 (s, 9H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.2 (d, J = 2.2 Hz), 162.1 (d, J = 8.2 Hz), 141.2 (d, J = 8.2 Hz), 129.0, 121.4, 120.5, 116.1 (d, J = 4.5 Hz), 60.7, 43.2 (d, J = 8.2 Hz), 33.2 (d, J = 14.2 Hz), 29.4 (d, J = 16.5 Hz), 21.5, 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.80 ppm; HRMS (ESI) calcd for $C_{23}H_{29}N_2O_3P$ [M + Na]$^+$: 435.1808; found: 435.1801.

*Ethyl (E)-5,5-Dimethyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)hex-3-enoate (**3aa**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[48] **2aa** (52.0 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 24 h. Off-white solid **3aa** (38.2 mg, 0.0895 mmol, 86%). R_f = 0.26 (Hexanes:EtOAc = 1:1); mp: 115−117 °C; IR (Neat, cm^{-1}): 3063, 2958, 2870, 1728, 1601, 1501, 1280, 1126, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30−7.23 (m, 4H), 7.18−7.16 (m, 4H), 6.97 (app t, J = 7.3 Hz, 2H), 3.92−3.82 (m, 4H), 3.36 (q, J = 6.6 Hz, 2H), 3.08 (d, J = 16.0 Hz, 2H), 1.20 (s, 9H), 0.82 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.4, 163.2 (d, J = 8.2 Hz), 141.2 (d, J = 7.5 Hz), 128.9, 121.4, 121.2 (d, J = 148.8 Hz), 116.0 (d, J = 5.2 Hz), 60.7, 43.2 (d, J = 8.2 Hz), 36.1 (d, J = 18.7 Hz), 32.9 (d, J = 13.5 Hz), 29.8 (d, J = 2.2 Hz), 13.5; ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.56 ppm; HRMS (ESI) calcd for $C_{24}H_{31}N_2O_3P$ [M + Na]$^+$: 449.1965; found: 449.1960.

*Ethyl (E)-3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-4-phenylbut-3-enoate (**3ab**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[53] **2ab** (43.3 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** 48 h. Off-white solid **3ab** (14.1 mg, 0.0315 mmol, 31%). R_f = 0.23 (Hexanes:EtOAc = 1:1); mp: 155−158 °C; IR (Neat, cm^{-1}): 3059, 2924, 2854, 1736, 1601, 1501, 1130, 1269, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, J = 23.3 Hz, 1H), 7.52 (app d, J = 8.2 Hz, 2H), 7.39−7.34 (m, 3H), 7.29−7.24 (m, 8H), 6.98 (app t, J = 6.9 Hz, 2H), 3.98−3.88 (m, 4H), 3.46 (q, J = 7.1 Hz, 2H), 3.11 (d, J = 19.9 Hz, 2H), 0.85 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 169.6, 151.0 (d, J = 11.2 Hz), 142.8, 141.1 (d, J = 8.2 Hz), 135.3 (d, J = 20.9 Hz), 129.2, 128.8, 128.5, 125.7 (d, J = 151.1 Hz), 121.7, 116.2 (d, J = 5.9 Hz), 61.1, 43.3 (d, J = 8.2 Hz), 34.3 (d, J = 12.7 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.81 ppm; HRMS (ESI) calcd for $C_{26}H_{27}N_2O_3P$ [M + Na]$^+$: 469.1652; found: 469.1660.

*Ethyl 3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-4,4-diphenylbut-3-enoate (**3ac**).* NHP-thiourea **1a** (202 mg, 0.463 mmol), allene[54] **2ac** (363 mg, 1.38 mmol), and DCM (1.00 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Off-white solid **3ac** (0.221 g, 0.423 mmol, 91%). R_f = 0.33 (Hexanes:EtOAc = 1:1); mp: 159−161 °C; IR (Neat, cm^{-1}): 3059, 2982, 2870, 1732, 1593, 1504, 1276, 1126, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (t, J = 7.8 Hz, 4H), 7.25−7.12 (m, 10H), 7.05 (t, J = 7.2 Hz, 2H), 6.93−6.91 (m, 2H), 6.77−6.75 (m, 2H), 3.92 (q, J = 7.0 Hz, 2H), 3.79 (d, J = 14.8 Hz, 2H), 3.46−3.41 (m, 2H), 2.61−2.56 (m, 2H), 1.10 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.9 (d, J = 4.5 Hz), 160.8 (d, J = 9.7 Hz), 142.1 (d, J = 18.7 Hz), 141.3 (t, J = 7.5 Hz),129.1, 128.3, 127.7 (t, J = 3.7 Hz), 127.2, 124.5 (d, J = 151.1 Hz), 121.7, 116.9 (d, J = 4.5 Hz), 60.6, 42.7 (d, J = 9.7 Hz), 39.1 (d, J = 12.7 Hz), 14.0; ^{31}P NMR (162 MHz, $CDCl_3$): δ 18.30 ppm; HRMS (APCI) calcd for $C_{32}H_{31}N_2O_3P$ [M + H]$^+$: 523.2145; found: 523.2156.

*Ethyl 3-Cyclohexylidene-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)propanoate (**3ad**).* NHP-thiourea **1a** (45.0 mg, 0.103 mmol), allene[55] **2ad** (56.1 mg, 0.309 mmol), and DCM (0.15 mL) were subjected to the reaction conditions described in **GP-2** for 48 h. Off-white solid **3ad** (42.7 mg, 0.0973 mmol, 94%). R_f = 0.33 (Hexanes:EtOAc = 1:1); mp: 124−126 °C; IR (Neat, cm^{-1}): 3063, 2931, 2854, 1732, 1597, 1504, 1280, 1126, 1033; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29−7.25 (m, 4H), 7.17−7.15 (m, 4H), 6.96 (app t, J = 7.3 Hz, 2H), 3.91−3.85 (m, 4H), 3.43 (q, J = 7.1 Hz, 2H), 3.15−3.31 (m, 2H), 2.98 (d, J = 17.5 Hz, 2H), 2.29 (bs, 2H), 1.78 (bs, 2H), 1.63 (bs, 4H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 170.0 (d, J = 2.9 Hz), 167.9 (d, J = 11.9 Hz), 141.5 (d, J = 8.2 Hz), 128.9, 121.3, 116.1 (d, J = 5.2 Hz), 114.3 (d, J = 154.1 Hz), 60.5, 43.4 (d, J = 7.5 Hz), 34.7 (dd, J = 16.4, 12.7 Hz), 31.7 (d, J = 5.2 Hz), 28.2 (d, J = 3.0 Hz), 26.4, 13.7; ^{31}P NMR (162 MHz, $CDCl_3$): δ 22.18 ppm; HRMS (APCI) calcd for $C_{25}H_{31}N_2O_3P$ [M + H]$^+$: 439.2145; found: 439.2159.

*2-(4-Hydroxybut-1-en-2-yl)-1,3-diphenyl-1,3,2-diazaphospholidine 2-oxide (**4a**).* To a solution of **3a** (0.170 g, 0.458 mmol) in DCM (1.5 mL) was slowly added BF_3·OEt_2 (0.075 mL, 0.597 mmol) at −78 °C under argon. After stirring for 30 min at −78 °C, DIBAL-H (1 M in hexanes) (1.30 mL, 1.37 mmol) was added and stirred for 2 h. After stirring for 2 h at −78 °C, the reaction mixture was warmed up to room temperature and stirred for 1 h. After stirring for 1 h at room temperature, the reaction mixture was cooled down to −78 °C, and it was slowly quenched with methanol. Volatiles were removed under reduced pressure. The residue was dissolved in DCM and was washed with water and brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography (Hexanes:EtOAc = 2:8) on silica gel to give white solid **4a** (91.5 mg, 0.278 mmol, 61%). R_f = 0.14 (Hexanes:EtOAc = 1:1); mp: 186−188 °C; IR (Neat, cm^{-1}): 3321 (br), 2945, 2860, 1599, 1494, 1269, 1122, 1051; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (t, J = 8.5 Hz, 4H), 7.18 (d, J = 7.8 Hz, 4H), 7.00 (t, J = 7.3 Hz, 2H), 6.45 (d, J = 22.7 Hz, 1H), 5.99 (dd, J = 47.2, 1.4 Hz, 1H), 3.89−3.77 (m, 4H), 3.50 (t, J = 6.5 Hz, 2H), 2.23−2.17 (m, 2H), 1.96 (bs, 1H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 141.2 (d, J = 8.2 Hz), 138.5 (d, J = 142.1 Hz), 134.9, 129.3, 122.0, 116.5 (d, J = 4.5 Hz), 60.8 (d, J = 5.2 Hz), 43.6 (d, J = 8.2 Hz), 34.9 (d, J = 11.9 Hz), ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.94 ppm; HRMS (APCI) calcd for $C_{21}H_{25}N_2O_3P$ [M + H]$^+$: 385.1676; found: 385.1688.

*Ethyl 3-(1,3-Bis(4-bromophenyl)-2-oxido-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**4b**).* To a solution of **3a** (50.0 mg, 0.134 mmol) in 1,2-dichloroethane (1.5 mL) were added benzoyl peroxide (4.0 mg, 0.016 mmol) and *N*-bromosuccinimide (60.8 mg, 0.341 mmol) at room temperature. After stirring for 4 h, volatiles were removed under reduced pressure. The residue was subjected to column chromatography (Hexanes:EtOAc = 7:3) on silica gel to give off-white solid **4b** (54.0 mg, 0.102 mmol, 76%). R_f = 0.37 (Hexanes:EtOAc = 1:1); mp: 163−165 °C; IR (Neat, cm^{-1}): 3041, 2985, 2891, 1732, 1589, 1494, 1280, 1132, 1033, 619; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, J = 8.6 Hz, 4H), 7.07 (d, J = 9.1 Hz, 4H), 6.72 (dd, J = 21.1, 1.3 Hz, 1H), 6.27 (dd, J = 44.6, 1.3 Hz, 1H), 3.87−3.81 (m, 4H), 3.58 (q, J = 7.1 Hz, 2H), 2.89 (dd, J = 16.4, 0.9 Hz, 2H), 0.93 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 168.9 (d, J = 3.7 Hz), 139.9 (d, J = 8.2 Hz), 139.7, 133.8 (d, J = 147.3 Hz), 132.1,

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117.9 (d, J = 5.2 Hz), 114.8, 61.1, 43.3 (d, J = 8.2 Hz), 38.5 (d, J = 14.2 Hz), 13.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ 17.07 ppm; HRMS (APCI) calcd for $C_{20}H_{21}Br_2N_2O_3P$ $[M + H]^+$: 528.9714; found: 528.9703.

*Ethyl 3-(Diethoxyphosphoryl)but-3-enoate (**4c**).* A solution of **3a** (40.0 mg, 0.107 mmol) in 2.4 M ethanolic HCl (1 mL) was stirred for 18 h at room temperature. After stirring for 18 h, volatiles were removed under reduced pressure. The residue was dissolved in EtOAc, filtered, dried over Na_2SO_4, and concentrated under reduced pressure to give brown liquid **4c** (24.6 mg, 0.0983 mmol, 92%). R_f = 0.12 (EtOAc); IR (Neat, cm^{-1}): 2984, 1737, 1257, 1157, 1026; ^{1}H NMR (400 MHz, CD_3OD): δ 6.16 (d, J = 22.1 Hz, 1H), 6.04 (dd, J = 47.3, 1.2 Hz, 1H), 4.13 (q, J = 7.0 Hz, 2H), 4.09−4.01 (m, 4H), 3.25 (d, J = 14.9 Hz, 2H), 1.31−1.22 (m, 9H); ^{13}C NMR (100.5 MHz, CD_3OD): δ 171.7 (d, J = 5.2 Hz), 135.2 (d, J = 8.9 Hz), 133.6 (d, J = 181.0 Hz), 63.9 (d, J = 5.9 Hz), 62.3, 38.7 (d, J = 11.9 Hz), 16.7 (d, J = 6.7 Hz), 14.6; ^{31}P NMR (162 MHz, CD_3OD): δ 18.17 ppm; HRMS (ESI) calcd for $C_{10}H_{19}O_5P$ $[M + H]^+$: 250.0970; found: 250.0956.

*Ethyl (E)-3-(2-Oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)-but-2-enoate (**4d**).* To a solution of **3a** (10.0 mg, 0.026 mmol) in THF (0.2 mL) was added triethylamine (8.0 mg, 0.08 mmol) at room temperature, and the resulting mixture was stirred for 24 h at 60 °C. After stirring for 24 h, volatiles were removed under reduced pressure. The residue was subjected to column chromatography (Hexanes:EtOAc = 2:1) on silica gel to give off-white solid **4d** (9.9 mg, 0.026 mmol, >99%). R_f = 0.49 (Hexanes:EtOAc = 1:1); mp: 208−210 °C; IR (Neat, cm^{-1}): 2976, 2926, 1718, 1599, 1504, 1334, 1275, 1120, 1039; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 8.6 Hz, 4H), 7.19 (d, J = 8.6 Hz, 4H), 7.11−7.01 (m, 3H), 4.17 (q, J = 7.1 Hz, 2H), 3.98−3.85 (m, 4H), 2.00 (dd, J = 16.8, 1.7 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ 164.9 (d, J = 29.2 Hz), 146.8 (d, J = 138.4 Hz), 140.9 (d, J = 7.5 Hz), 134.3 (d, J = 11.9 Hz), 129.4, 122.3, 116.5 (d, J = 4.5 Hz), 60.6, 44.1 (d, J = 8.2 Hz), 29.6, 14.1 (t, J = 5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 19.22 ppm; HRMS (ESI) calcd for $C_{20}H_{23}N_2O_3P$ $[M + Na]^+$: 393.1339; found: 393.1331.

*4-Hydroxy-4-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)dihydrofuran-2(3H)-one (**4e**).* To a solution of **3a** (100 mg, 0.271 mmol) in acetone (3 mL) and water (0.3 mL) were added OsO_4 (2.5% wt t-BuOH, 0.28 mL, 0.0271 mmol) and N-methylmorpholine N-oxide (34.1 mg, 0.292 mmol) at room temperature, and the resulting mixture was stirred for 60 h at room temperature. After stirring for 60 h, volatiles were removed under reduced pressure. The residue was subjected to column chromatography (Hexanes:EtOAc = 1:1) on silica gel to give white solid **4e** (44.2 mg, 0.123 mmol, 45%). R_f = 0.21 (Hexanes:EtOAc = 1:1); mp 207−209 °C; IR (Neat, cm^{-1}): 3394 (bs), 2850, 1768, 1597, 1490, 1265, 1124, 1033; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40−7.33 (m, 8H), 7.05 (bs, 2H), 6.33 (bs, 1H), 4.46 (d, J = 9.6 Hz, 1H), 3.95 (bs, 2H), 3.72 (d, J = 9.4 Hz, 3H), 3.03 (dd, J = 16.8, 6.8 Hz, 1H), 1.98 (d, J = 16.8 Hz, 1H); ^{13}C NMR (100.5 MHz, DMSO-d_6): δ 174.0 (d, J = 19.4 Hz), 141.7 (dd, J = 9.7, 8.3 Hz), 129.2 (d, J = 7.5 Hz), 122.2 (d, J = 2.9 Hz), 117.7 (d, J = 24.6, 3.7 Hz), 78.3, 76.9, 75.2 (d, J = 16.4 Hz), 43.4 (dd, J = 11.9, 7.5 Hz); ^{31}P NMR (162 MHz, DMSO-d_6): δ 21.45 ppm; HRMS (ESI) calcd for $C_{18}H_{19}N_2O_4P$ $[M + H]^+$: 358.1082; found: 358.1065.

*Ethyl 2-Methyl-3-(2-oxido-1,3-diphenyl-1,3,2-diazaphospholidin-2-yl)but-3-enoate (**3k**).* To a solution of **3a** (14 mg, 0.037 mmol) in THF (0.5 mL) was added NaH (60% dispersion in mineral oil, 1.6 mg, 0.041 mmol) portionwise at 0 °C. The reaction mixture was warmed up to room temperature and stirred for 30 min. After stirring for 30 min at room temperature, the reaction mixture was cooled down to 0 °C, followed by addition of methyl iodide (27.0 mg, 0.19 mmol). After stirring for 15 h at room temperature, the reaction was quenched by slow addition of ice water at 0 °C and volatiles were removed under reduced pressure. The residue was dissolved in DCM and was washed with water and brine. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel to give off-white solid **3k** (10 mg, 0.026 mmol, 70%).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02184.

^{1}H and ^{13}C NMR spectra of new compounds, thermal ellipsoid plot for **1a** and **3a** (PDF)

X-ray crystallographic data for **1a** (CIF)

X-ray crystallographic data for **3a** (CIF)

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Notes

The authors declare the following competing financial interest(s): A patent application has been submitted.

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