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A One-Pot Approach to 2-Substituted-2-(Dimethoxyphosphoryl)-Pyrrolidines from Substituted *tert*-Butyl 4-Oxobutylcarbamates and Trimethyl Phosphite

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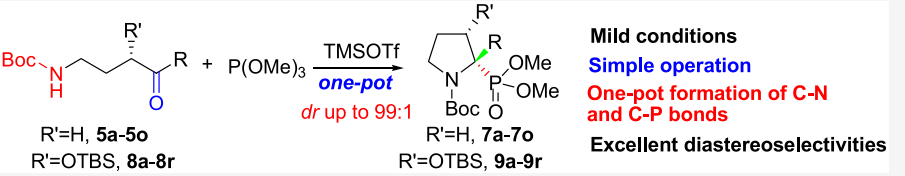

ABSTRACT: A novel approach to 2-substituted-2-(dimethoxyphosphoryl)-pyrrolidines **7a−7o** and **9a−9r** has been developed, which features a TMSOTf-mediated one-pot intramolecular cyclization and phosphonylation of substituted *tert*-butyl 4-oxobutylcarbamates. The major advantages of this method include simple operation under mild reaction conditions, the use of cheap Lewis acid, and good to excellent yields with high diastereoselectivities (*dr* up to 99:1).

INTRODUCTION

α-Aminophosphonic acids and their derivatives, classic isosteres of α-amino acids, have attracted great interest in organic and medicinal chemistry during the past few decades.[1] Such functional analogues of natural and unnatural α-amino acids have been widely used in agrochemicals[2] and medicines,[3] such as antibacterial agents,[4] antifungal agents,[2a,5] antiviral agents,[6] antibiotics,[7] enzyme inhibitors,[3a,8] and antitumor agents.[9] In addition to the usual application as important synthetic intermediates in organic synthesis,[10] they could also serve as probes in biology. Some typical examples include alafosfalin (an antibacterial agent) **1**,[11] K-26 (an ACE inhibitor) **2**,[12] MCR5 (a neuroprotective agent) **4**[13] and radical probe **3**[14] (Figure 1).

In the past few decades, tremendous efforts have been made to establish a new methodology for the syntheses of α-amino phosphonic acids and their derivatives.[15−20] One common approach was the three-component reaction of aldehydes (or ketones), primary amines, and phosphite (or phosphoric acid).[19] A direct transformation of amides to phosphonates was also achieved through a reductive process,[1b,20] which was further developed to prepare chiral α-amino phosphonates through asymmetric catalysis. In addition, Lewis acids[21] or transition metal complexes[22] could mediate the formation of acyliminium ions and its subsequent reaction with trimethyl phosphite to generate α-amino phosphonates (Figure 2, a). As for the preparation of piperidine α-tertiary amino phosphonates and their derivatives, two general approaches were often used, including the diethyl phosphite addition to readily available cyclic imines, and the Vilsmeier−Haack reaction of

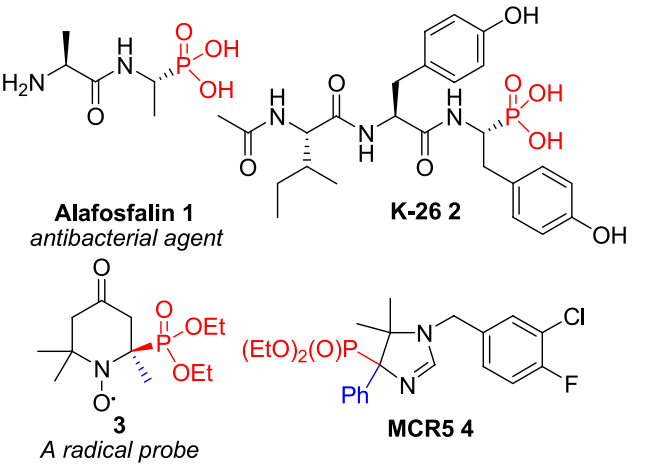

Figure 1. Several useful compounds containing α-aminophosphonic acid moiety.

lactams with triethyl phosphite prompted by phosphoryl chloride.[23] For example, a direct method to the heterocyclic α-tertiary amine phosphonates from the alkenyl ketones has

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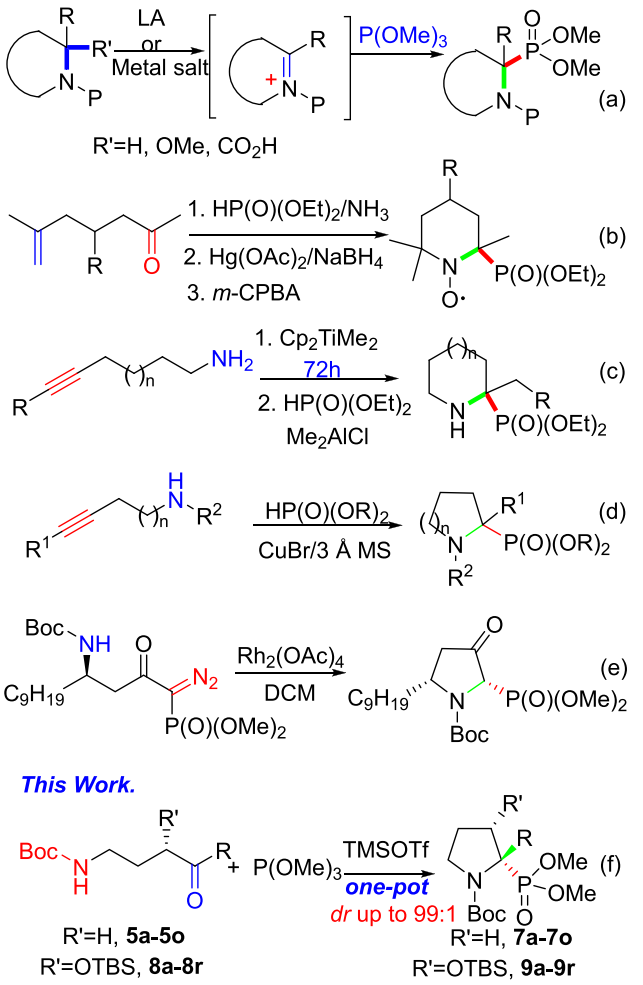


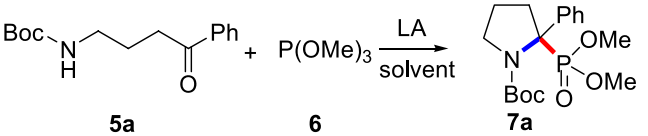
Figure 2. Our strategy to access 2-substituted-2-(dimethoxyphosphoryl)-pyrrolidines.

been also achieved; however, this transformation need three steps (Figure 2, b).[24] In addition, an amine containing alkynyl bond compound has been converted to piperidine α-tertiary amino phosphonates and their derivatives through the Cp_2TiMe_2 prompted intramolecular hydroamination and followed phosphorylation process, but the intramolecular hydroamination needs 72 h (Figure 2, c).[25] Similarly, the alkyne amination/phosphorylation catalyzed by copper converted the secondary aminoalkynes to various cyclic α-aminophosphonate derivatives (Figure 2, d).[26] δ-Amino α-diazo β-ketophosphonate has also been converted to 3-oxo pyrrolidine phosphonate via an intramolecular metal carbenoid N−H insertion (Figure 2, e).[27] On the basis of our continuous efforts in establishment of azaheterocyclic building blocks,[28] we envisioned that the addition-phosphates of the carbonyl containing amides could occur. Herein we present this effective approach to 2-substituted-2-(dimethoxyphosphoryl)-pyrrolidines through the intramolecular condensation and phosphatization process (Figure 2, f).

RESULTS AND DISCUSSION

Our investigation started with the reaction of trimethyl phosphite **6** with *tert*-butyl 4-oxo-4-phenylbutylcarbamate **5a**, which was prepared according to the known procedure (see the Supporting Information).[29] First, various metal salts including $Sc(OTf)_3$, $Yb(OTf)_3$, $In(OTf)_3$, $Cu(OTf)_2$, and $Cu(NTf_2)_2$ were examined, only trace amount of products were observed, and the starting material **5a** was almost intact (Table 1, entries 1−5). $CuBr_2$ could not promote this reaction

Table 1. Optimization of Reaction Conditions



5a **6** **7a**

entry[a]	Lewis acid (equiv)	solvent	T (°C)	yield (%)[b]
1	$Sc(OTf)_3$ (0.2)	DCM	−45 to rt	trace
2	$Yb(OTf)_3$ (0.2)	DCM	−45 to rt	trace
3	$In(OTf)_3$ (0.2)	DCM	−45 to rt	trace
4	$Cu(OTf)_2$ (0.2)	DCM	−45 to rt	trace
5	$Cu(NTf_2)_2$ (0.2)	DCM	−45 to rt	trace
6	$CuBr_2$ (0.2)	DCM	−45 to rt	0
7	$B(C_6F_5)_3$ (0.2)	DCM	−45	23
8	$B(C_6F_5)_3$ (0.5)	DCM	−45	35
9	TMSOTf (1.0)	DCM	−45	37
10	TMSOTf (1.5)	DCM	−45	64
11	TMSOTf (2.0)	DCM	−45	61
12	TMSOTf (1.5)	DCM	−45 to rt	53
13	TMSOTf (1.5)	DCM	−78	46
14	$BF_3{\cdot}Et_2O$ (1.5)	DCM	−45	51
15	$TiCl_4$ (1.5)	DCM	−45	47
16	TMSOTf (1.5)	THF	−45	44
17	TMSOTf (1.5)	PhMe	−45	38
18	TMSOTf (1.5)	DCE	−45	56

[a]The reactions were performed with **5a** (0.5 mmol), $P(OMe)_3$ **6** (0.6 mmol) and Lewis acid in dry solvent (2 mL) at assigned reaction temperature for 2 h. [b]Isolated yield.

at all, and no desired product was observed (Table 1, entry 6). When $B(C_6F_5)_3$ was used, the desired product **7a** was obtained in 23% yield (Table 1, entry 7). It should be noted that the yield of **7a** could be improved to 35% when 0.5 equiv of $B(C_6F_5)_3$ was used (Table 1, entry 8). Then, we turned to the application of stronger Lewis acids for this transformation, and TMSOTf proved to be a good choice. The experiments with different ratios of TMSOTf demonstrated the reaction and gave the best yield when 1.5 equiv of TMSOTf was used (Table 1, entries 9−11). In addition, neither higher temperature (−45 to rt) nor lower temperature (−78 °C) was beneficial for the yield of this one-pot process (Table 1, entries 12−13). Other Lewis acids, $BF_3{\cdot}Et_2O$ and $TiCl_4$, were also examined, but they did not perform as well as TMSOTf (Table 1, entries 14−15). Finally, different solvents, such as THF, PhMe, and DCE, were also screened, and all of them could afford the desired product, albeit with lower yields. (Table 1, entries 16−18).

Next, we turned our attention to investigate the scope and limitation of this ring forming phosphorylation (Scheme 1). First, five *para*- or *meta* substituted phenyl ketones **5a**−**5e** were examined, and the *para* substituted substrates **7c** and **7d** showed slightly higher yields than *meta* substituted **7b** and **7e**. Aliphatic ketones **5f**−**5h** also worked well under the optimal reaction conditions, and the chain length of alkyl groups dramatically affected the yields of **7f**−**7h**. Notably, alkynyl ketones **5k**−**5n** could afford the desired products **7k**−**7n** in 72−84% yields. Pyridinyl substituent was tolerated in this reaction, and the alkynone substrate **5o** could lead to the

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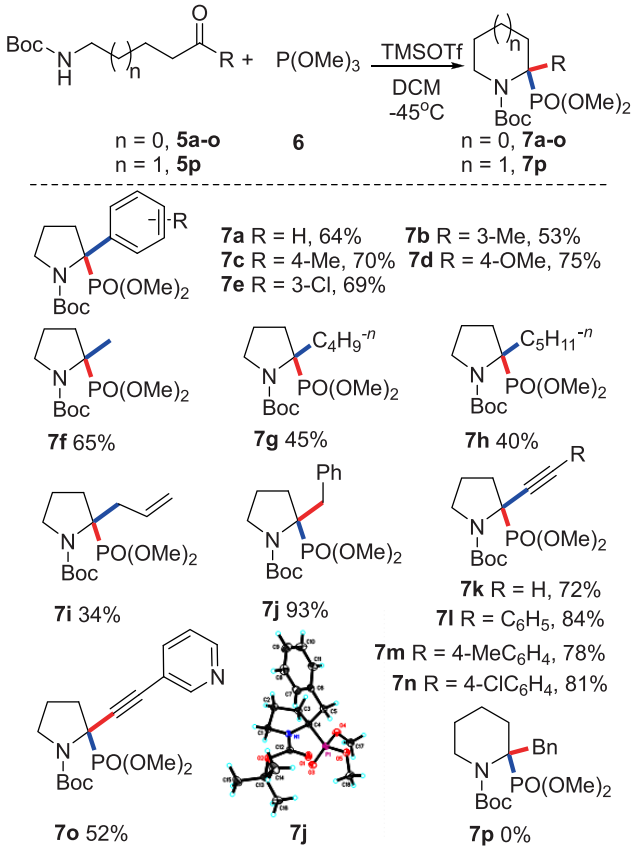
Scheme 1. Reactions of Substituted *tert*-Butyl 4-Oxobutylcarbamates with Trimethyl Phosphite[a,b]

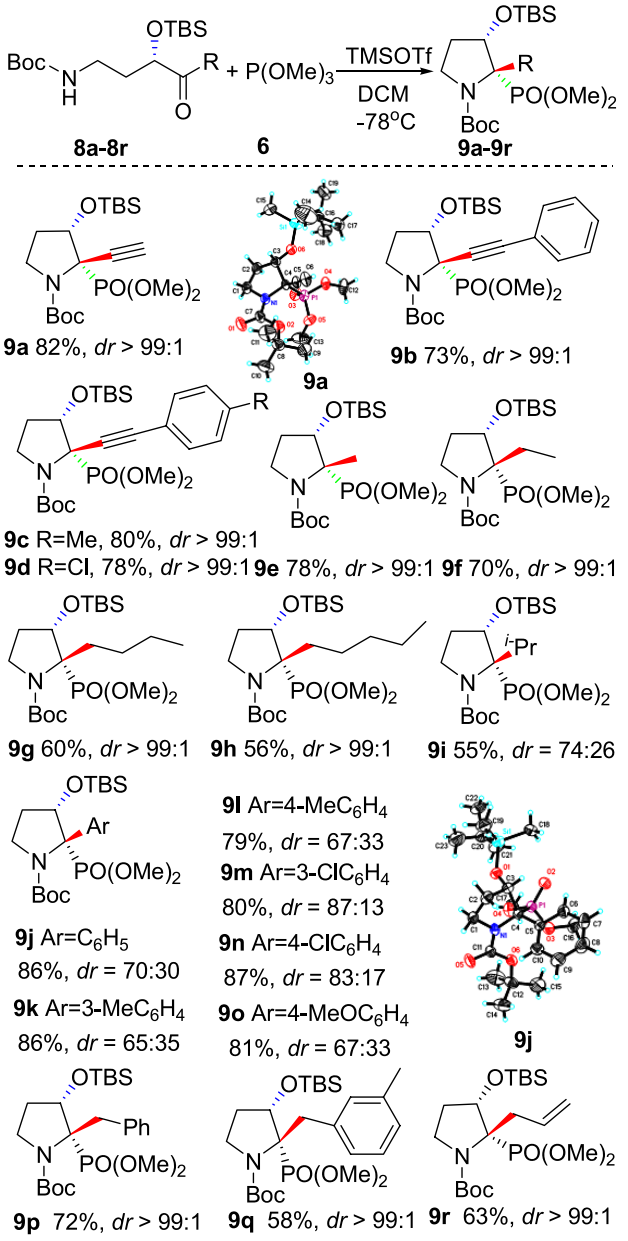


[a]The reactions were performed with carbamates **5a**−**5p** (0.5 mmol), $P(OMe)_3$ **6** (0.6 mmol), and TMSOTf (0.75 mmol) in dry DCM (2 mL) at −45 °C for 2 h. [b]Isolated yield.

desired **7o** in 52% yield. Although the allyl substituted ketone **5i** gave the corresponding product **7i** in 34% yield, the reaction of benzyl substituted ketone **5j** could produce the desired **7j** in 93% yield. To our disappointment, the efforts to prepare similar piperidin-2-yl phosphonate **7p** turned out to be fruitless. The chemical structures of **7a**−**7o** were unambiguously assigned according to X-ray crystallographic analysis of compound **7j** (see the Supporting Information).

Then, we extended the reaction to chiral ketone substrates **8a**−**8r**, which were prepared according to the known procedure (see the Supporting Information).[24] As shown in Scheme 2, all reactions proceeded well, and lower reaction temperature (−78 °C) was required for high diastereoselectivities (see the Supporting Information). First, when (*S*)-*tert*-butyl 3-(*tert*-butyldimethylsilyloxy)-4-oxohex-5-ynylcarbamate **8a** was examined, the desired **9a** was obtained in 82% yield with excellent diastereoselectivity (*dr* > 99:1). Other chiral alkynyl ketone substrates **8b**−**8d** also afforded the desired **9b**−**9d** in 73−80% yields with outstanding diastereoselectivities (*dr* > 99:1). Chiral aliphatic ketones **8e**−**8h** were also screened, and the desired **9e**−**9h** were generated in moderate yields with excellent diastereoselectivities (*dr* > 99:1). It is worth mentioning that isopropyl ketone substrate **8i** led to the desired **9i** in 55% yield with low diastereoselectivity (*dr* = 74:26). As a matter of fact, aryl ketone substrates **8j**−**8o** also resulted in the desired products **9j**−**9o** with low diastereoselectivities (*dr* from 65:35 to 87:13) despite the relatively

Scheme 2. Reactions of Chiral Substituted *tert*-Butyl 4-Oxobutylcarbamates with Trimethyl Phosphite[a,b]



[a]The reactions were performed with carbamates **8a**−**8r** (0.5 mmol) $P(OMe)_3$ **6** (0.6 mmol), and TMSOTf (0.75 mmol) in dry DCM (2 mL) at −78 °C for 2 h. [b]Isolated yield.

excellent yields (>79%). Although the benzyl and allyl ketone substrates **8p**−**8q** and **8r** gave the corresponding **9p**−**9q** and **9r** in moderate yields, excellent diastereoselectivities were achieved (*dr* > 99:1). The chemical structures and stereochemistry of the products **9a**−**9r** were unambiguously assigned by X-ray crystallographic analysis of compounds **9a** and **9j** (see the Supporting Information).

A possible mechanism for this one-pot approach to α-alkylated pyrrolidin-2-yl phosphonates is presented in Figure 3.[19i,22c,30,31] Under Lewis acid condition, the carbonyl group in **8a**−**8r** were activated to form Int-**1**, which experienced an intramolecular nucleophilic addition to give Int-**2**. Upon the cleavage of OTMS group, a key iminium intermediate Int-**3**

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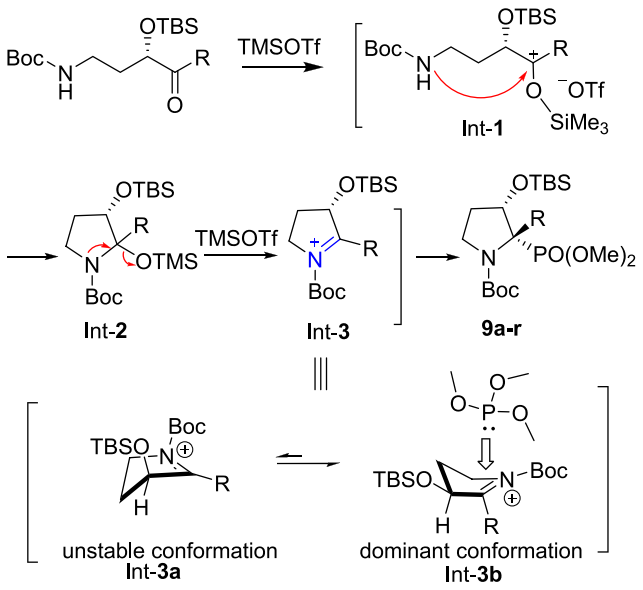

Figure 3. Possible mechanism of this approach.

was generated, which could subsequently react with trimethyl phosphite to give the desired phosphonates **9a−9r**. To explain the diastereoselectivities for this transformation, we speculate that the stable conformer Int-**3b** allowed the attack of trimethyl phosphite predominately from one side, forming the desired diastereomers **9a−9r**.

CONCLUSIONS

In summary, we have established a novel and practical approach for the preparation of α-alkylated pyrrolidin-2-yl phosphonates, through a one-pot intramolecular cyclization and phosphorylation process, from substituted *tert*-butyl 4-oxobutylcarbamates. A series of products **7a−7o** were conveniently prepared in moderate to good yields. On the basis of this efficient methodology, several chiral phosphonates **9a−9r** could be obtained with excellent diastereoselectivities (*dr* up to 99:1). Moreover, the operation of this one-pot transformation is very simple, using a cheap Lewis acid under mild reaction conditions. Further applications of this method in pharmaceutical chemistry are currently underway in our laboratory.

EXPERIMENTAL SECTION

General Considerations. DCM was distilled from phosphoric anhydride. Reactions were monitored by thin layer chromatography (TLC) on glass plates coated with silica gel with a fluorescent indicator. Flash chromatography was performed on silica gel (300−400) with petroleum/EtOAc as eluent. Optical rotations were measured on a polarimeter with a sodium lamp. HRMS were measured on a LCMS-IT-TOF or LTQ-Orbitrap-XL apparatus. IR spectra were recorded using film on a Fourier Transform Infrared Spectrometer. NMR spectra were recorded at 100, 162, or 400 MHz, and chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (77.16 ppm) for $^{13}C\{^1H\}$ NMR.

General Procedure for the Synthesis of 5a−5o and 8a−8r. To a stirred solution of *N*-Boc-2-pyrrolidinone[32] or (*S*)-*tert*-butyl 3-(*tert*-butyldimethylsilyloxy)-2-oxopyrrolidine-1-carboxylate[33] (2.0 mmol) in anhydrous THF (8 mL) was added Grignard reagent at −78 °C under argon atmosphere. After stirring for 2 h, the mixture was quenched with an aqueous solution of saturated NH_4Cl (5 mL), and extracted with EtOAc (15 mL × 3). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give **5a−5o** and **8a−8r**.

General Procedure for the Synthesis of 7a−7o. Carbamates **5a−5o** (0.5 mmol) were dissolved in dry DCM (2 mL) under argon atmosphere. $P(OMe)_3$ (0.6 mmol) and TMSOTf (0.75 mmol) were added at −45 °C subsequently. After stirring for 2 h at −45 °C, the mixture was quenched with an aqueous solution of saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **7a−7o**.

General Procedure for the Synthesis of 9a−9r. Carbamates **8a−8r** (0.5 mmol) were dissolved in dry DCM (2 mL) under argon atmosphere. $P(OMe)_3$ (0.6 mmol) and TMSOTf (0.75 mmol) were added at −78 °C subsequently. After stirring for 2 h at −78 °C, the mixture was quenched with an aqueous solution of saturated $NaHCO_3$ (5 mL), and extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine and dried over Na_2SO_4. Filtered and concentrated, the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 2:1) to give **9a−9r**.

*tert-Butyl 4-oxo-4-phenylbutylcarbamate (**5a**).*[34] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (432 mg, 82%). mp 85−86 °C [lit.[34] mp 80−82 °C]; IR (film) ν_{max} 3372, 1681, 1515, 1445, 1365, 1247, 1155, 739, 614 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02−7.93 (m, 2H), 7.63−7.40 (m, 3H), 4.70 (s, 1H), 3.32−3.15 (m, 2H), 3.09−3.00 (m, 2H), 2.03−1.87 (m, 2H), 1.44 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.9, 156.2, 136.9, 133.2, 128.7, 128.2, 79.3, 40.3, 35.9, 28.5, 24.7 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{15}H_{21}NO_3Na^+$ 286.1414, found 286.1413.

*tert-Butyl 4-oxo-4-m-tolylbutylcarbamate (**5b**).*[34] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (477 mg, 86%). mp 47−48 °C [lit.[34] mp 58−60 °C]; IR (film) ν_{max} 3361, 2975, 1682, 1517, 1366, 1249, 1164, 782 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 2H), 7.41−7.30 (m, 2H), 4.74 (s, 1H), 3.28−3.17 (m, 2H), 3.05−2.96 (m, 2H), 2.42 (s, 3H), 1.98−1.90 (m, 2H), 1.44 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.1, 156.2, 138.5, 137.0, 133.9, 128.7, 128.6, 125.4, 79.2, 40.3, 35.9, 28.5, 24.7, 21.4 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{16}H_{23}NO_3Na^+$ 300.1576, found 300.1561.

*tert-Butyl 4-oxo-4-p-tolylbutylcarbamate (**5c**).*[34] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (494 mg, 89%). mp 86−87 °C [lit.[34] mp 92−94 °C]; IR (film) ν_{max} 3394, 2983, 1706, 1669, 1512, 1292, 1167, 818, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87−7.82 (m, 2H), 7.28−7.22 (m, 2H), 4.72 (s, 1H), 3.25−3.14 (m, 2H), 3.02−2.97 (m, 2H), 2.41 (s, 3H), 1.96−1.87 (m, 2H), 1.42 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ 199.5, 156.2, 143.9, 134.5, 129.4, 128.3, 79.2, 40.3, 35.8, 28.5, 24.7, 21.7 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{16}H_{23}NO_3Na^+$ 300.1570, found 300.1568.

*tert-Butyl 4-(4-methoxyphenyl)-4-oxobutylcarbamate (**5d**).*[34] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (528 mg, 90%). mp 82−83 °C [lit.[34] mp 80−82 °C]; IR (film) ν_{max} 3357, 2971, 1675, 1594, 1509, 1362, 1252, 1160, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.92 (m, 2H), 6.97−6.91 (m, 2H), 4.74 (s, 1H), 3.88 (s, 3H), 3.29−3.17 (m, 2H), 3.02−2.91 (m, 2H), 1.97−1.86 (m, 2H), 1.44 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.5, 163.6, 156.2, 130.4, 130.0, 113.8, 79.2, 55.6, 40.3, 35.5, 28.5, 24.8 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{16}H_{23}NO_4Na^+$ 316.1519, found 316.1520.

*tert-Butyl 4-(3-chlorophenyl)-4-oxobutylcarbamate (**5e**).*[34] The title compound was purified by column chromatography (petroleum

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ether/ethyl acetate = 8:1, R_f = 0.3). White solid (476 mg, 80%). mp 73−74 °C [lit.[34] mp 80−82 °C]; IR (film) ν_{max} 3375, 2982, 1689, 1513, 1362, 1249, 1164, 782 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94−7.89 (m, 1H), 7.85−7.80 (m, 1H), 7.55−7.49 (m, 1H), 7.43−7.36 (m, 1H), 4.69 (s, 1H), 3.25−3.19 (m, 2H), 3.02−2.98 (m, 2H), 1.96−1.90 (m, 2H), 1.42 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 198.5, 156.2, 138.5, 135.1, 133.1, 130.1, 128.3, 126.3, 79.4, 40.1, 35.9, 285, 24.6 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{15}H_{20}ClNO_3Na^+$ 320.1024, found 320.1028.

*tert-Butyl 4-oxopentylcarbamate (**5f**).*[35] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Light yellow oil (298 mg, 74%). IR (film) ν_{max} 3368, 2968, 1708, 1520, 13628, 1245, 1164, 977 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.76 (s, 1H), 3.16−3.07 (m, 2H), 2.49−2.39 (m, 4H), 1.82−1.72 (m, 2H), 1.43 (s, 9H), 1.10−1.01 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 211.2, 156.1, 79.1, 39.4 (40.0), 36.0, 28.4, 24.2, 7.8 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{10}H_{19}NO_3Na^+$ 224.1257, found 224.1263.

*tert-Butyl 4-oxooctylcarbamate (**5g**).*[36] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Yellow oil (263 mg, 54%). IR (film) ν_{max} 3372, 2971, 1715, 1520, 1370, 1252, 1175, 1047 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.65 (s, 1H), 3.16−3.04 (m, 2H), 2.49−2.35 (m, 4H), 1.80−1.71 (m, 2H), 1.57−1.51 (m, 2H), 1.43 (s, 9H), 1.34−1.25 (m, 2H), 0.94−0.85 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 210.9, 156.2, 79.2, 42.7, 40.2, 39.9, 28.5, 26.0, 24.2, 22.4, 13.9 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{13}H_{25}NO_3Na^+$ 266.1727, found 266.1724.

*tert-Butyl 4-oxononylcarbamate (**5h**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (375 mg, 87%). mp 30−31 °C; IR (film) ν_{max} 3369, 2933, 1707, 1519, 1368, 1245, 1175, 781 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 1H), 3.19−3.00 (m, 2H), 2.50−2.37 (m, 4H), 1.82−1.69 (m, 2H), 1.63−1.50 (m, 2H), 1.44 (s, 9H), 1.35−1.21 (m, 4H), 0.92−0.81 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 211.0, 156.1, 79.2, 42.9, 40.1, 39.9, 31.5, 28.5, 24.1, 23.6, 22.5, 14.0 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{11}H_{21}NO_3Na^+$ 238.1414, found 238.1418.

*tert-Butyl 4-oxohept-6-enylcarbamate (**5i**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (291 mg, 64%). IR (film) ν_{max} 3364, 2975, 1708, 1520, 1362, 1249, 1171, 1039 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.01−5.82 (m, 1H), 5.24−5.08 (m, 2H), 4.71 (s, 1H), 3.21−3.15 (m, 2H), 3.14−3.06 (m, 2H), 2.52−2.47 (m, 2H), 1.79−1.71 (m, 2H), 1.44 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 208.4, 156.2, 130.6, 119.0, 79.3, 47.9, 40.0, 39.4, 28.4, 24.0 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{12}H_{21}NO_3Na^+$ 250.1414, found 250.1417.

*tert-Butyl 4-oxo-5-phenylpentylcarbamate (**5j**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (474 mg, 90%). mp 46−47 °C; IR (film) ν_{max} 3364, 2979, 1708, 1520, 1366, 1252, 1164, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39−7.16 (m, 5H), 4.57 (s, 1H), 3.71 (s, 2H), 3.16−3.00 (m, 2H), 1.78−1.72 (m, 2H), 1.45 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 208.0, 156.1, 134.3, 129.5, 128.9, 127.2, 79.3, 50.4, 40.0, 39.1, 28.5, 24.2 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{15}H_{21}NO_3Na^+$ 286.1414, found 286.1413.

*tert-Butyl 4-oxohex-5-ynylcarbamate (**5k**).*[37] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Yellow solid (262 mg, 62%). mp 65−66 °C [lit.[37] mp 68−70 °C]; IR (film) ν_{max} 3357, 2975, 2090, 1678, 1517, 1362, 1252, 1164 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.71 (s, 1H), 3.27 (s, 1H), 3.20−3.10 (m, 2H), 2.70−2.61 (m, 2H), 1.90−1.82 (m, 2H), 1.44 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.7, 156.1, 81.4, 79.4, 79.0, 42.8, 39.8, 28.5, 24.2 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{11}H_{17}NO_3Na^+$ 234.1101, found 234.1101.

*tert-Butyl 4-oxo-6-phenylhex-5-ynylcarbamate (**5l**).*[38] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (431 mg, 75%). mp 62−63 °C [lit.[38] mp 69.5−70.5 °C]; IR (film) ν_{max} 3368, 2975, 2204, 1671, 1513, 1362, 1249, 1171, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59−7.51 (m, 2H), 7.48−7.31 (m, 3H), 4.70 (s, 1H), 3.24−3.13 (m, 2H), 2.74−2.68 (m, 2H), 1.93−1.84 (m, 2H), 1.45 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 187.2, 156.1, 133.1, 130.8, 128.7, 119.9, 91.1, 87.8, 79.3, 42.8, 39.9, 28.5, 24.5 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{17}H_{21}NO_3Na^+$ 310.1414, found 310.1415.

*tert-Butyl 4-oxo-6-p-tolylhex-5-ynylcarbamate (**5m**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (428 mg, 71%). mp 75−77 °C; IR (film) ν_{max} 2975, 2193, 1667, 1509, 1362, 1168, 819 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.52−7.44 (m, 2H), 7.24−7.15 (m, 2H), 4.67 (s, 1H), 3.26−3.12 (m, 2H), 2.79−2.66 (m, 2H), 2.40 (s, 3H), 1.97−1.84 (m, 2H), 1.46 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 187.4, 156.2, 141.7, 133.3, 129.6, 116.9, 91.9, 87.8, 79.5, 42.9, 40.0, 28.5, 24.6, 21.9 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{18}H_{23}NO_3Na^+$ 324.1570, found 324.1567.

*tert-Butyl 6-(4-chlorophenyl)-4-oxohex-5-ynylcarbamate (**5n**).*[38] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (541 mg, 84%). mp 104−105 °C [lit.[38] mp 104.3−105 °C]; IR (film) ν_{max} 3350, 2982, 2200, 1678, 1517, 1362, 1252, 1164, 826 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.54−7.44 (m, 2H), 7.39−7.31 (m, 2H), 4.71 (s, 1H), 3.24−3.13 (m, 2H), 2.73−2.67 (m, 2H), 1.92−1.85 (m, 2H), 1.44 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 187.0, 156.1, 137.3, 134.3, 129.2, 118.5, 89.6, 88.5, 79.4, 42.8, 39.9, 28.5, 24.5 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{17}H_{20}ClNO_3Na^+$ 344.1024, found 344.1025.

*tert-Butyl 4-oxo-6-(pyridin-3-yl)hex-5-ynylcarbamate (**5o**).*[38] The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Light yellow solid (231 mg, 40%). mp 79−80 °C [lit.[38] mp 79.3−80 °C]; IR (film) ν_{max} 2982, 2204, 1678, 1517, 1366, 1274, 1168, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.82−8.76 (m, 1H), 8.70−8.63 (m, 1H), 7.91−7.80 (m, 1H), 7.39−7.30 (m, 1H), 4.71 (s, 1H), 3.24−3.15 (m, 2H), 2.79−2.72 (m, 2H), 1.96−1.88 (m, 2H), 1.45 (s, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 186.8, 156.1, 153.4, 150.9, 140.0, 123.4, 117.4, 90.3, 87.0, 79.4, 42.8, 39.9, 28.5, 24.5 ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{16}H_{20}N_2O_3Na^+$ 311.1372, found 311.1371.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-phenylpyrrolidine-1-carboxylate (**7a**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (114 mg, 64%). IR (film) ν_{max} 2913, 2850, 1700, 1384, 1252, 1164, 1028, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.44−7.20 (m, 5H), 3.89−3.70 (m, 6H), 3.70−3.52 (m, 2H), 2.95−2.66 (m, 1H), 2.31−2.18 (m, 1H), 1.92−1.73 (m, 1H), 1.69−1.55 (m, 1H), 1.53−1.20 (m, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.3, 140.0 (d, J = 7.3 Hz) (141.1), 128.2 (127.9), 127.9, 125.8 (125.9), 80.0 (80.6), 69.0 (d, J = 159.8 Hz) (68.9), 54.4 (d, J = 7.4 Hz) (54.3), 52.7 (d, J = 7.4 Hz) (52.5), 48.9 (d, J = 4.4 Hz) (49.4), 41.4 (43.3), 28.5 (28.1), 22.3 (d, J = 7.3 Hz) (21.5) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.0 (27.5) ppm; HRMS (ESI-Orbitrap) m/z $[M + Na]^+$ calcd for $C_{17}H_{26}NO_5PNa^+$ 378.1441, found 378.1436.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-m-tolylpyrrolidine-1-carboxylate (**7b**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (98 mg, 53%). IR (film) ν_{max} 2953, 1697, 1392, 1256, 1168, 1036, 756, 565 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.28−7.03 (m, 4H), 3.87−3.55 (m, 8H), 2.92−2.64 (m, 1H), 2.35 (s, 3H), 2.29−2.17 (m, 1H), 1.89−1.75 (m, 1H), 1.70−1.58 (m, 1H), 1.55−1.28 (m, 9H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.2 (154.5), 139.9 (d, J = 7.4 Hz) (140.9), 137.6 (137.4), 128.1, 127.8 (127.7), 126.5, 123.0 (d, J = 3.5 Hz), 80.0 (80.6), 69.0 (d, J = 159.9 Hz), 54.4 (d, J = 6.1 Hz), 52.9 (d, J = 7.4 Hz) (52.5), 49.0 (d, J = 3.3 Hz) (49.5), 41.4 (43.3), 28.6 (28.2), 22.3 (d, J = 8.8 Hz), 21.9 (21.7) ppm; ^{31}P NMR (162 MHz, $CDCl_3$,

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rotamers) δ 29.1 (27.6) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{18}H_{28}NO_5PNa^+$ 392.1597, found 392.1591.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-p-tolylpyrrolidine-1-carboxylate (**7c**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow oil (129 mg, 70%). IR (film) ν_{max} 2957, 1708, 1392, 1256, 1164, 1036, 811, 749, 584 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.31−7.24 (m, 2H), 7.16−7.09 (m, 2H), 3.83−3.72 (m, 6H), 3.71−3.53 (m, 2H), 2.91−2.61 (m, 1H), 2.33 (s, 3H), 2.27−2.19 (m, 1H), 1.88−1.74 (m, 1H), 1.70−1.57 (m, 1H), 1.55−1.28 (m, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 154.3, 137.0 (d, *J* = 6.8 Hz) (137.9), 136.6, 128.9 (128.6), 125.8 (d, *J* = 4.3 Hz), 80.0 (80.7), 68.9 (d, *J* = 160.0 Hz), 54.5 (d, *J* = 5.5 Hz) (54.4), 52.7 (d, *J* = 6.1 Hz), 41.4 (43.4), 28.6 (28.2), 22.3 (d, *J* = 8.7 Hz) (21.5), 21.0 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 26.8 (25.2) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{18}H_{28}NO_5PNa^+$ 392.1597, found 392.1593.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-(4-methoxyphenyl)-pyrrolidine-1-carboxylate (**7d**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (145 mg, 75%). IR (film) ν_{max} 2953, 1700, 1509, 1392, 1252, 1179, 1036, 822 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.35−7.26 (m, 2H), 6.88−6.78 (m, 2H), 3.84−3.78 (m, 3H), 3.78−3.69 (m, 6H), 3.68−3.48 (m, 2H), 2.96−2.55 (m, 1H), 2.26−2.19 (m, 1H), 1.88−1.76 (m, 1H), 1.68−1.56 (m, 1H), 1.53−1.31 (m, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 158.5, 154.3, 131.8 (d, *J* = 5.5 Hz) (132.8), 127.1 (d, *J* = 4.4 Hz), 113.6 (113.2), 79.9 (80.7), 68.5 (d, *J* = 160.2 Hz), 54.5 (d, *J* = 6.6 Hz), 52.7 (d, *J* = 7.2 Hz), 48.9 (49.4), 41.3 (43.3), 28.6 (28.2), 22.2 (d, *J* = 8.9 Hz) (21.4) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.2 (27.5) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{18}H_{28}NO_6PNa^+$ 408.1547, found 408.1542.

*tert-Butyl 2-(3-chlorophenyl)-2-(dimethoxyphosphoryl)-pyrrolidine-1-carboxylate (**7e**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow oil (134 mg, 69%). IR (film) ν_{max} 3453, 2957, 1697, 1385, 1256, 1028, 760, 562 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.43−7.17 (m, 4H), 3.90−3.65 (m, 7H), 3.64−3.54 (m, 1H), 2.96−2.67 (m, 1H), 2.30−2.12 (m, 1H), 1.91−1.76 (m, 1H), 1.73−1.57 (m, 1H), 1.55−1.27 (m, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 154.2, 142.5 (d, *J* = 3.5 Hz) (143.3), 134.2, 129.5 (129.3), 127.3, 126.3, 124.2, 80.4 (81.0), 68.8 (d, *J* = 161.0 Hz) (68.6), 54.6 (d, *J* = 6.8 Hz), 52.8 (d, *J* = 7.2 Hz), 49.0 (49.5), 41.5 (43.3), 28.6 (28.2), 22.4 (d, *J* = 8.2 Hz) (21.7) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 28.4 (27.0) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{17}H_{25}ClNO_5PNa^+$ 412.1051, found 412.1052.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-methylpyrrolidine-1-carboxylate (**7f**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (95 mg, 65%). IR (film) ν_{max} 2969, 1698, 1387, 1244, 1156, 1111, 1031, 815 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 3.86−3.70 (m, 6H), 3.61−3.41 (m, 2H), 2.59−2.45 (m, 1H), 2.02−1.91 (m, 1H), 1.87−1.71 (m, 2H), 1.63−1.57 (d, *J* = 3.7 Hz, 3H), 1.47 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, Temp = 75 °C) δ 152.7, 78.5, 60.6 (d, *J* = 156.4 Hz), 52.3 (d, *J* = 7.0 Hz), 52.1 (d, *J* = 7.5 Hz), 48.3, 38.1, 27.8, 21.7 (d, *J* = 7.1 Hz) (20.9) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 31.0 (30.1) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{12}H_{24}NO_5PNa^+$ 316.1284, found 316.1279.

*tert-Butyl 2-butyl-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**7g**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (75 mg, 45%). IR (film) ν_{max} 2960, 1697, 1385, 1249, 1171, 1028, 819, 569 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 3.85−3.66 (m, 6H), 3.57−3.37 (m, 2H), 2.51−2.28 (m, 2H), 2.04−1.94 (m, 2H), 1.80−1.65 (m, 2H), 1.52−1.43 (m, 9H), 1.35−1.11 (m, 4H), 0.95−0.86 (m, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 153.6 (154.3), 79.3 (80.3), 64.9 (d, *J* = 154.1 Hz) (64.5), 53.5 (d, *J* = 5.7 Hz) (53.3), 52.4 (d, *J* = 6.2 Hz) (52.6), 49.4, 34.4 (35.6), 32.3 (33.0), 28.5, 25.3 (d, *J* = 8.9 Hz) (24.8), 22.9 (22.6), 21.9, 14.2 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 31.3 (30.3) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{15}H_{30}NO_5PNa^+$ 358.1754, found 358.1752.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-pentylpyrrolidine-1-carboxylate (**7h**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (70 mg, 40%). IR (film) ν_{max} 2951, 1697, 1382, 1247, 1170, 1032, 820, 565 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 3.86−3.66 (m, 6H), 3.58−3.30 (m, 2H), 2.49−2.29 (m, 2H), 2.02−1.90 (m, 2H), 1.78−1.67 (m, 2H), 1.53−1.42 (m, 9H), 1.33−1.10 (m, 6H), 0.94−0.78 (m, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 153.6 (154.3), 79.3 (80.3), 64.8 (d, *J* = 154.2 Hz) (64.6), 53.6 (d, *J* = 6.5 Hz) (53.4), 52.4 (d, *J* = 7.0 Hz) (52.6), 49.5 (d, *J* = 8.3 Hz), 35.6, 34.4, 32.4 (d, *J* = 6.2 Hz) (33.2), 32.0 (32.2), 28.5, 22.7 (d, *J* = 10.9 Hz) (22.3), 21.9, 14.1 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 31.3 (30.3) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{16}H_{32}NO_5PNa^+$ 372.1910, found 372.1906.

*tert-Butyl 2-allyl-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**7i**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (54 mg, 34%). IR (film) ν_{max} 2972, 1691, 1376, 1240, 1167, 1035, 822, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 5.74−5.58 (m, 1H), 5.21−5.09 (m, 2H), 3.87−3.68 (m, 6H), 3.52−3.13 (m, 3H), 2.47−2.34 (m, 2H), 2.01−1.82 (m, 2H), 1.78−1.67 (m, 1H), 1.53−1.43 (m, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 154.1 (153.6), 132.5 (d, *J* = 11.4 Hz) (132.1), 119.7 (119.5), 79.5 (80.6), 64.2 (d, *J* = 144.0 Hz) (63.9), 53.7 (d, *J* = 5.9 Hz) (53.4), 52.4 (d, *J* = 6.9 Hz) (52.7), 49.4, 36.6 (d, *J* = 6.7 Hz) (37.6), 34.0 (35.3), 28.5, 22.4 (21.6) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 30.4 (29.5) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{14}H_{26}NO_5PNa^+$ 342.1441, found 342.1442.

*tert-Butyl 2-benzyl-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**7j**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). White solid (172 mg, 93%). mp 108−109 °C; IR (film) ν_{max} 2975, 1693, 1392, 1249, 1160, 1058, 1024, 756 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.30−7.16 (m, 5H), 4.09−3.92 (m, 1H), 3.91−3.76 (m, 6H), 3.37−3.06 (m, 2H), 2.81−2.71 (m, 1H), 2.51−2.39 (m, 1H), 2.07−1.96 (m, 1H), 1.64−1.62 (m, 2H), 1.62−1.57 (m, 1H), 1.57−1.51 (m, 7H), 0.90−0.72 (m, 1H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 154.1 (154.4), 136.6 (d, *J* = 15.0 Hz) (136.3), 130.9 (130.6), 128.2 (128.5), 126.7 (126.9), 79.7 (81.2), 65.2 (d, *J* = 155.0 Hz) (65.1), 54.0 (d, *J* = 6.8 Hz) (53.8), 52.4 (d, *J* = 7.8 Hz) (52.6), 49.2 (d, *J* = 2.5 Hz) (49.5), 36.9 (d, *J* = 8.9 Hz) (38.2), 33.9 (35.2), 28.6, 22.1 (d, *J* = 4.0 Hz) (21.4) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 31.4 (30.0) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{18}H_{28}NO_5PNa^+$ 392.1597, found 392.1596.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-ethynylpyrrolidine-1-carboxylate (**7k**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow solid (109 mg, 72%). mp 73−74 °C; IR (film) ν_{max} 3221, 2957, 1693, 1392, 1252, 1168, 1021, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91−3.80 (m, 6H), 3.68−3.57 (m, 1H), 3.49−3.40 (m, 1H), 2.77−2.64 (m, 1H), 2.58−2.53 (d, *J* = 4.8 Hz, 1H), 2.42−2.29 (m, 1H), 2.06−1.91 (m, 2H), 1.49 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, Temp = 75 °C) δ 152.2, 81.1 (d, *J* = 4.4 Hz), 79.3, 75.2 (d, *J* = 9.3 Hz), 57.6, 55.9, 53.4, 53.5 (53.3), 47.7 (d, *J* = 2.5 Hz), 27.7, 22.0 (d, *J* = 3.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.0 (2.4) ppm; HRMS (ESI-Orbitrap) *m/z* [M + Na]$^+$ calcd for $C_{13}H_{22}NO_5PNa^+$ 326.1128, found 326.1127.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-(2-phenylethynyl)-pyrrolidine-1-carboxylate (**7l**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Light yellow oil (159 mg, 84%). IR (film) ν_{max} 2977, 1685, 1590, 1385, 1249, 1165, 1026, 762 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48−7.24 (m, 5H), 3.95−3.79 (m, 6H), 3.74−3.57 (m, 1H), 3.54−3.46 (m, 1H), 2.89−2.65 (m, 1H), 2.51−2.37 (m, 1H), 2.09−1.98 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ

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153.6, 131.8, 128.5, 128.4, 122.7, 86.6 (d, J = 2.7 Hz), 85.4 (d, J = 9.3 Hz), 80.5, 58.9, 57.2, 54.5, 48.6, 40.8, 28.5, 23.1 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.9 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{19}H_{26}NO_5PNa^+$ 402.1441, found 402.1437.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-(2-p-tolylethynyl)-pyrrolidine-1-carboxylate (**7m**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow oil (153 mg, 78%). IR (film) ν_{max} 3464, 2964, 1693, 1388, 1263, 1164, 1028, 808, 569 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32−7.25 (m, 2H), 7.13−7.00 (m, 2H), 3.95−3.74 (m, 6H), 3.70−3.53 (m, 1H), 3.50−3.37 (m, 1H), 2.84−2.64 (m, 1H), 2.47−2.36 (m, 1H), 2.29 (s, 3H), 2.05−1.85 (m, 2H), 1.46 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.4, 138.4, 131.5, 129.0, 119.5, 85.8 (d, J = 3.4 Hz), 85.3 (d, J = 9.3 Hz), 80.3, 58.8, 57.1, 54.3, 48.4, 40.6, 28.3, 22.8, 21.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.5 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{20}H_{28}NO_5PNa^+$ 416.4036, found 416.4032.

*tert-Butyl 2-(2-(4-chlorophenyl)ethynyl)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**7n**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (168 mg, 81%). IR (film) ν_{max} 2975, 1689, 1491, 1384, 1260, 1160, 1032, 837, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40−7.35 (m, 2H), 7.32−7.28 (m, 2H), 3.93−3.85 (m, 6H), 3.74−3.65 (m, 1H), 3.54−3.46 (m, 1H), 2.85−2.72 (m, 1H), 2.51−2.37 (m, 1H), 2.10−1.94 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.5, 134.6, 133.0, 128.7, 121.3, 87.7 (d, J = 3.5 Hz), 84.2 (d, J = 9.3 Hz), 80.5, 59.0, 57.2, 54.4, 48.6, 40.6, 28.5, 23.1 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 20.4 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{19}H_{25}ClNO_5PNa^+$ 436.1051, found 436.1054.

*tert-Butyl 2-(dimethoxyphosphoryl)-2-(2-(pyridin-3-yl)ethynyl)-pyrrolidine-1-carboxylate (**7o**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow oil (99 mg, 52%). IR (film) ν_{max} 3464, 2953, 1686, 1388, 1252, 1164, 1024, 833, 576 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69−8.64 (m, 1H), 8.57−8.50 (m, 1H), 7.77−7.70 (m, 1H), 7.29−7.24 (m, 1H), 3.92−3.85 (m, 6H), 3.74−3.65 (m, 1H), 3.53−3.44 (m, 1H), 2.86−2.72 (m, 1H), 2.51−2.38 (m, 1H), 2.12−2.01 (m, 2H), 1.51 (s, 9H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.4, 152.4, 148.9, 138.7, 123.1, 120.0, 90.2 (d, J = 3.5 Hz), 82.0 (d, J = 9.4 Hz), 80.6, 58.9, 57.2, 54.4, 48.6, 40.5, 28.5, 23.2 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.7 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{18}H_{25}N_2O_5PNa^+$ 403.1393, found 403.1394.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxohex-5-ynylcarbamate (**8a**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Yellow oil (444 mg, 65%). $[\alpha]_D^{24}$ −4.1 (c 2.00, $CHCl_3$); IR (film) ν_{max} 3221, 2957, 1693, 1392, 1252, 1168, 1021, 573 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.80 (s, 1H), 4.28−4.23 (m, 1H), 3.37 (s, 1H), 3.29−3.14 (m, 2H), 2.06−1.90 (m, 2H), 1.47−1.40 (m, 9H), 0.92−0.90 (m, 9H), 0.12−0.04 (m, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 189.0, 155.9, 82.6, 79.9 (79.3), 77.7, 43.9, 37.0, 33.9, 28.5, 25.8, 18.3, −4.6, −5.2 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{17}H_{31}NO_4SiNa^+$ 364.1915, found 364.1916.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-6-phenylhex-5-ynylcarbamate (**8b**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Yellow oil (342 mg, 50%). $[\alpha]_D^{25}$ −39.2 (c 0.50, $CHCl_3$); IR (film) ν_{max} 2924, 2204, 1686, 1590, 1256, 1168, 833 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63−7.58 (m, 2H), 7.50−7.37 (m, 3H), 4.93 (s, 1H), 4.41−4.33 (m, 1H), 3.38−3.24 (m, 2H), 1.44 (s, 9H), 0.98 (s, 9H), 0.16 (s, 3H), 0.12 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.7, 155.9, 133.3, 131.0, 128.8, 120.0, 94.8, 86.6, 79.2, 77.9, 37.2, 34.3, 28.5, 25.9, 18.3, −4.5, −5.1 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{17}H_{31}NO_4SiNa^+$ 364.1915, found 364.1916.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-6-p-tolylhex-5-ynylcarbamate (**8c**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Yellow oil (665 mg, 77%). $[\alpha]_D^{26}$ −51.4 (c 1.00, $CHCl_3$); IR (film) ν_{max} 3357, 2931, 2193, 1671, 1502, 1256, 1160, 833, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54−7.47 (m, 2H), 7.25−7.17 (m, 2H), 4.94 (s, 1H), 4.41−4.29 (m, 1H), 3.39−3.24 (m, 2H), 2.41 (s, 3H), 2.15−1.99 (m, 2H), 1.44 (s, 9H), 0.98 (s, 9H), 0.16 (s, 3H), 0.12 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 189.9, 155.9, 141.9, 133.4, 129.6, 116.9, 95.7, 86.5, 79.2, 77.9, 37.2, 34.3, 28.5, 25.9, 21.9, 18.4, −4.5, −5.1 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{24}H_{37}NO_4SiNa^+$ 454.2384, found 454.2383.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-6-(4-chlorophenyl)-4-oxohex-5-ynylcarbamate (**8d**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Yellow oil (756 mg, 84%). $[\alpha]_D^{27}$ −28.2 (c 0.50, $CHCl_3$); IR (film) ν_{max} 3376, 2924, 2200, 1711, 1495, 1256, 1146, 837, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.58−7.48 (m, 2H), 7.42−7.35 (m, 2H), 4.89 (s, 1H), 4.36−4.30 (m, 1H), 3.36−3.25 (m, 2H), 2.12−1.96 (m, 2H), 1.55−1.54 (m, 3H), 1.44−1.43 (m, 6H), 0.97−0.92 (m, 9H), 0.15 (s, 3H), 0.12 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 189.6, 155.9, 137.5, 134.4, 129.3, 118.5, 93.2, 87.2, 83.2 (79.3), 77.8 (71.8), 41.9, 37.1 (34.3), 28.5 (28.2), 25.9, 18.3, −4.5, −5.1 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{23}H_{34}ClNO_4SiNa^+$ 474.1838, found 474.1837.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxopentylcarbamate (**8e**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (364 mg, 55%). $[\alpha]_D^{25}$ −8.6 (c 1.00, $CHCl_3$); IR (film) ν_{max} 3357, 2927, 2854, 1715, 1513, 1252, 1171, 841, 778 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.83 (s, 1H), 4.12−4.05 (m, 1H), 3.26−3.11 (m, 2H), 2.66−2.47 (m, 2H), 2.11 (s, 3H), 1.93−1.76 (m, 2H), 1.42 (s, 9H), 0.95−0.91 (m, 9H), 0.07 (s, 3H), 0.06 (s, 3H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, rotamers) δ 211.8, 155.8, 79.2, 37.0, 34.2, 28.6 (28.5), 25.8 (25.6), 18.1, −4.9, −5.0 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{16}H_{33}NO_4SiNa^+$ 354.2071, found 354.2080.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxohexylcarbamate (**8f**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (380 mg, 55%). $[\alpha]_D^{27}$ −18.1 (c 1.00, $CHCl_3$); IR (film) ν_{max} 3368, 2935, 2858, 1715, 1513, 1256, 1164, 841, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79 (s, 1H), 4.21−4.07 (m, 1H), 3.27−3.07 (m, 2H), 2.65−2.47 (m, 2H), 1.93−1.77 (m, 2H), 1.43 (s, 9H), 1.09−0.98 (m, 3H), 0.96−0.91 (m, 9H), 0.11−0.01 (m, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 214.2, 155.9, 79.2, 77.3, 37.1, 34.6, 31.1, 28.5, 25.9, 18.2, 7.4, −4.9 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{17}H_{35}NO_4SiNa^+$ 368.2228, found 368.2226.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxooctylcarbamate (**8g**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (635 mg, 85%). $[\alpha]_D^{24}$ −13.4 (c 1.00, $CHCl_3$); IR (film) ν_{max} 2960, 2854, 1711, 1590, 1260, 1175, 841, 775 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (s, 1H), 4.17−4.07 (m, 1H), 3.25−3.12 (m, 2H), 2.56−2.49 (m, 2H), 1.92−1.78 (m, 2H), 1.56−1.51 (m, 2H), 1.43 (s, 9H), 1.36−1.27 (m, 4H), 0.93 (s, 9H), 0.91−0.88 (m, 3H), 0.09−0.05 (m, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 213.6, 155.9, 79.2, 71.7, 37.5, 37.1, 34.3, 28.5 (28.1), 25.8, 25.3, 22.5, 18.1, 14.0, −4.9, −5.0 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{19}H_{39}NO_4SiNa^+$ 396.2541, found 396.2538.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxononylcarbamate (**8h**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (628 mg, 81%). $[\alpha]_D^{25}$ −10.2 (c 1.00, $CHCl_3$); IR (film) ν_{max} 2931, 1715, 1594, 1256, 1175, 1120, 837, 778 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82 (s, 1H), 4.17−4.07 (m, 1H), 3.27−3.14 (m, 2H), 2.59−2.48 (m, 2H), 1.92−1.78 (m, 2H), 1.60−1.51 (m, 2H), 1.43 (s, 9H), 1.35−1.24 (m, 4H), 0.94 (s, 9H), 0.92−0.88 (m, 3H), 0.10−0.04 (m, 6H) ppm; ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 213.6, 155.9, 79.2, 37.8, 37.2, 34.4, 31.6, 28.5, 25.9, 23.0, 22.6, 18.2, 14.0, −4.8, −5.0 ppm; HRMS (ESI-Orbitrap) m/z [M + Na]$^+$ calcd for $C_{20}H_{41}NO_4SiNa^+$ 410.2697, found 410.2696.

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*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-5-methyl-4-oxohexylcarbamate (**8i**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (503 mg, 70%). $[\alpha]_D^{25}$ +13.2 (*c* 1.00, $CHCl_3$); mp 53−54 °C; IR (film) ν_{max} 2971, 1711, 1590, 1249, 1175, 837, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.84 (s, 1H), 4.30−4.21 (m, 1H), 3.26−3.11 (m, 2H), 3.08−2.95 (m, 1H), 1.94−1.84 (m, 2H), 1.42 (s, 9H), 1.11−1.02 (m, 6H), 0.96−0.91 (m, 9H), 0.10−0.03 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (400 MHz, $CDCl_3$) δ 216.5, 155.9, 79.2, 76.5, 37.3, 35.4, 34.3, 28.5, 25.8, 19.3, 18.3, −4.8, −4.9 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{37}NO_4SiNa^+$ 382.2384, found 382.2380.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-4-phenylbutylcarbamate (**8j**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (614 mg, 78%). $[\alpha]_D^{25}$ −27.9 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2927, 2858, 1697, 1590, 1252, 1168, 833, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 8.16−8.08 (m, 2H), 7.73−7.65 (m, 1H), 7.61−7.49 (m, 2H), 5.17−4.96 (m, 2H), 3.50−3.25 (m, 2H), 2.21−2.06 (m, 2H), 1.54 (s, 9H), 1.08−0.97 (m, 9H), 0.19−0.12 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 201.0, 155.9, 134.8, 133.4, 129.0 (128.7), 128.0 (127.3), 79.2, 75.9, 37.6, 35.2, 28.4, 25.9, 18.3, −4.6, −5.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{35}NO_4SiNa^+$ 416.2228, found 416.2228.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-4-m-tolylbutylcarbamate (**8k**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Light yellow semisolid (701 mg, 86%). $[\alpha]_D^{27}$ −43.1 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 3383, 2927, 1697, 1513, 1249, 1171, 833, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.86−7.76 (m, 2H), 7.44−7.30 (m, 2H), 5.05−4.87 (m, 2H), 3.37−3.21 (m, 2H), 2.42 (s, 3H), 2.10−1.91 (m, 2H), 1.43 (s, 9H), 0.93 (s, 9H), 0.08 (s, 3H), 0.02 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 201.1, 156.0, 138.5, 134.9, 134.2, 129.5, 128.5, 126.2, 79.2, 75.9, 37.8, 35.3, 28.5, 25.9, 21.5, 18.3, −4.5, −5.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for$C_{22}H_{37}NO_4SiNa^+$ 430.2384, found 430.2390.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-4-p-tolylbutylcarbamate (**8l**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (759 mg, 93%). $[\alpha]_D^{26}$ −43.2 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 3383, 2927, 2854, 1715.07, 1252, 1146, 837, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.98−7.83 (m, 2H), 7.28−7.25 (m, 2H), 5.02−4.85 (m, 2H), 3.36−3.25 (m, 2H), 2.43 (s, 3H), 2.08−1.93 (m, 2H), 1.44 (s, 9H), 0.92 (s, 9H), 0.07 (s, 3H), 0.02 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 200.5, 155.9, 144.3, 132.2, 129.4, 129.2, 79.2, 75.9, 37.8, 35.4, 28.5, 25.9, 21.8, 18.4, −4.5, −5.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{37}NO_4SiNa^+$ 430.2384, found 430.2379.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-(3-chlorophenyl)-4-oxobutylcarbamate (**8m**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White semisolid (651 mg, 76%). $[\alpha]_D^{25}$ +12.7 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 3445, 2935, 1693, 1384, 1124, 837, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.44−7.38 (m, 1H), 7.31−7.22 (m, 3H), 4.26−3.92 (m, 2H), 3.82−3.74 (m, 1H), 3.65−3.49 (m, 1H), 2.17−1.93 (m, 2H), 1.55−1.29 (m, 4H), 1.15−1.09 (m, 5H), 0.91−0.84 (m, 9H), −0.08 (s, 3H), −0.19 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 199.9, 154.2, 147.3, 134.1 (133.3), 129.4, 127.3, 126.0, 123.7, 88.7 (83.2), 80.4 (81.2), 71.8, 44.0 (41.9), 30.0, 28.1 (28.5), 25.7 (25.9), 18.1, −5.0,-5.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{34}ClNO_4SiNa^+$ 450.1838, found 450.1834.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-(4-chlorophenyl)-4-oxobutylcarbamate (**8n**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (719 mg, 84%). $[\alpha]_D^{27}$ −28.8 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2927, 2861, 1704, 1587, 1252, 1175, 841, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04−7.89 (m, 2H), 7.46−7.41 (m, 2H), 4.93−4.74 (m, 2H), 3.39−3.23 (m, 2H), 2.07−1.96 (m, 2H), 1.43 (s, 9H), 0.91 (s, 9H), 0.08 (s, 3H), 0.01 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 199.9, 155.9, 139.9, 132.9, 130.8, 129.0 (128.6), 79.3, 76.4, 37.7, 35.5, 28.5, 25.9 (25.7), 18.3, −4.6, −5.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{21}H_{34}ClNO_4SiNa^+$ 450.1838, found 450.1839.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-(4-methoxyphenyl)-4-oxobutylcarbamate (**8o**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (466 mg, 55%). $[\alpha]_D^{24}$ −22.1 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 3361, 2927, 2865, 1697, 1598, 1509, 1260, 1175, 833, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10−7.99 (m, 2H), 6.97−6.90 (m, 2H), 4.98−4.81 (m, 2H), 3.89 (s, 3H), 3.37−3.24 (m, 2H), 2.10−1.92 (m, 2H), 1.44 (s, 9H), 0.92 (s, 9H), 0.07 (s, 3H), 0.01 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 199.4, 163.7, 155.9, 131.6, 127.6, 113.9, 79.2, 76.2, 55.6, 37.8, 35.6, 28.5, 25.9, 18.3, −4.6, −5.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{37}NO_5SiNa^+$ 446.2333, found 446.2332.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-5-phenylpentylcarbamate (**8p**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Light yellow oil (653 mg, 80%). $[\alpha]_D^{26}$ +2.6 (*c* 0.50, $CHCl_3$); IR (film) ν_{max} 2927, 1708, 1583, 1249, 1160, 833, 786 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.17 (m, 5H), 4.75 (s, 1H), 4.28−4.17 (m, 1H), 3.95−3.76 (m, 2H), 3.26−3.08 (m, 2H), 2.02−1.76 (m, 2H), 1.43 (s, 9H), 0.95 (s, 9H), 0.06 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 210.5, 155.9, 133.8, 129.8, 128.7, 127.1, 79.3, 44.6, 37.1, 34.5, 28.5, 25.9, 18.2, −4.8, −5.0 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{22}H_{37}NO_4SiNa^+$ 430.2384, found 430.2380.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxo-5-m-tolylpentylcarbamate (**8q**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). Colorless oil (371 mg, 44%). $[\alpha]_D^{25}$ −2.6 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 3376, 2931, 1715, 1256, 1171, 841, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29−7.21 (m, 1H), 7.12−7.07 (m, 1H), 7.03−6.97 (m, 2H), 4.80 (s, 1H), 4.32−4.23 (m, 1H), 3.93−3.76 (m, 2H), 3.28−3.14 (m, 2H), 2.36−2.32 (m, 3H), 2.03−1.79 (m, 2H), 1.46 (s, 9H), 0.98 (s, 9H), 0.09 (s, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 210.5, 155.9, 138.3, 133.7, 130.6, 128.6, 127.9, 126.8, 79.3, 77.5, 44.6, 37.1, 34.5, 28.5, 25.9, 21.5, 18.2, −4.8, −5.0 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{39}NO_4SiNa^+$ 444.2541, found 444.2540.

*(S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-4-oxohept-6-enylcarbamate (**8r**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 8:1, R_f = 0.3). White solid (315 mg, 44%). $[\alpha]_D^{23}$ −7.4 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 3361, 2931, 1711, 1509, 1252, 1164, 837, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 5.99−5.86 (m, 1H), 5.22−5.11 (m, 2H), 4.79 (s, 1H), 4.20−4.14 (m, 1H), 3.41−3.31 (m, 2H), 3.24−3.19 (m, 2H), 1.95−1.83 (m, 2H), 1.43 (s, 9H), 0.96−0.93 (m, 9H), 0.09 (s, 3H), 0.07 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 211.3, 155.8, 130.4, 118.9, 79.3, 77.8, 42.5, 37.0, 34.4, 28.5, 25.9, 18.2, −4.9, −5.0 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{18}H_{35}NO_4SiNa^+$ 380.2228, found 380.2231.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-ethynylpyrrolidine-1-carboxylate (**9a**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow solid (178 mg, 82%). $[\alpha]_D^{25}$ +15.2 (*c* 0.50, $CHCl_3$); mp 93−95 °C; IR (film) ν_{max} 2927, 1590, 1388, 1124, 1043, 837, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.54 (ddd, *J* = 17.6, 7.6, 6.8 Hz, 1H), 3.88−3.80 (m, 6H), 3.63−3.51 (m, 2H), 2.68−2.54 (m, 1H), 2.33−2.22 (m, 1H), 2.12−2.01 (m, 1H), 1.48 (s, 9H), 0.93 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, Temp = 75 °C) δ 152.2, 81.9 (d, *J* = 4.6 Hz), 80.1 (d, *J* = 2.6 Hz), 79.2, 77.0 (d, *J* = 8.9 Hz), 61.2 (d, *J* = 168.8 Hz), 53.1 (d, *J* = 7.2 Hz), 52.8 (d, *J* = 7.4 Hz), 44.5, 29.8, 27.7, 25.3, 17.4, −5.0, −5.3 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 18.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{19}H_{36}NO_6PSiNa^+$ 456.1942, found 456.1941.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-(2-phenylethynyl)pyrrolidine-1-carboxylate (**9b**).* The title compound was purified by column chromatography

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(petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow oil (186 mg, 73%). $[\alpha]_D^{25}$ +13.8 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2920, 1594, 1381, 1252, 1124, 1032, 837, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.45−7.42 (m, 2H), 7.34−7.29 (m, 3H), 4.62 (ddd, *J* = 16.8, 7.2, 6.4 Hz, 1H), 3.89−3.82 (m, 6H), 3.64−3.58 (m, 2H), 2.39−2.23 (m, 1H), 2.14−2.03 (m, 1H), 1.49 (s, 9H), 0.93 (m, 9H), 0.17 (s, 3H), 0.14 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, Temp = 75 °C) δ 152.3, 130.7 (d, *J* = 2.2 Hz), 128.3, 122.1 (d, *J* = 2.6 Hz), 86.4 (d, *J* = 2.1 Hz), 85.7 (d, *J* = 9.0 Hz), 81.9 (d, *J* = 4.3 Hz), 79.1, 61.6 (d, *J* = 167.4 Hz), 53.2 (d, *J* = 7.3 Hz), 53.0 (d, *J* = 7.5 Hz), 44.4, 29.7, 27.7, 25.3, 17.4, −5.1, −5.3 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{40}NO_6PSiNa^+$ 532.2255, found 532.2259.

*(2S,3S)-tert-Butyl 3-((tert-butyldimethylsilyl)oxy)-2-(dimethoxyphosphoryl)-2-(p-tolylethynyl)pyrrolidine-1-carboxylate (**9c**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (209 mg, 80%). $[\alpha]_D^{23}$ +29.3 (*c* 3.00, $CHCl_3$); IR (film) ν_{max} 3372, 2971, 1715, 1520, 1370, 1252, 1175, 1047 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.34−7.29 (m, 2H), 7.14−7.05 (m, 2H), 4.60 (ddd, *J* = 18.0, 7.2, 6.4 Hz, 1H), 3.88−3.79 (m, 6H), 3.66−3.54 (m, 2H), 2.33 (s, 3H), 2.14−2.04 (m, 1H), 1.48 (s, 9H), 0.92 (s, 9H), 0.16 (s, 3H), 0.13 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.7, 138.5, 131.5, 129.1, 119.7, 87.0 (d, *J* = 8.6 Hz), 85.2, 82.6, 80.2, 62.7 (d, *J* = 170.4 Hz), 54.1 (d, *J* = 7.5 Hz), 53.9, 45.3, 30.8, 28.4, 25.7, 21.5, 18.2, −4.5, −4.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.3 ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{42}NO_6PSiNa^+$ 546.2411, found 546.2409.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(2-(4-chlorophenyl)ethynyl)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9d**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (212 mg, 78%). $[\alpha]_D^{24}$ +34.3 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2957, 2854, 1689, 1388, 1256, 1124, 1043, 830, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40−7.34 (m, 2H), 7.31−7.26 (m, 2H), 4.60 (ddd, *J* = 18.8, 7.2, 6.4 Hz, 1H), 3.89−3.79 (m, 6H), 3.66−3.53 (m, 2H), 2.41−2.29 (m, 1H), 2.15−2.05 (m, 1H), 1.49 (s, 9H), 0.93 (s, 9H), 0.17 (s, 3H), 0.14 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.6, 134.5, 132.9, 128.7, 121.4, 87.1, 85.8 (d, *J* = 8.3 Hz), 82.6, 80.4, 63.4, 62.5 (d, *J* = 170.4 Hz), 54.0 (d, *J* = 7.3 Hz), 45.3, 30.9, 28.5, 25.8, 18.3, −4.5, −4.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.2 ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{25}H_{39}ClNO_6PSiNa^+$566.1865, found 566.1869.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-methylpyrrolidine-1-carboxylate (**9e**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Light yellow solid (165 mg, 78%). $[\alpha]_D^{27}$ +49.3 (*c* 1.00, $CHCl_3$); mp 68−69 °C; IR (film) ν_{max} 2949, 1711, 1366, 1252, 1157, 1039, 837, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.00−3.86 (m, 1H), 3.81−3.69 (m, 6H), 3.59−3.51 (m, 1H), 3.50−3.37 (m, 1H), 2.40−2.25(m, 1H), 1.99−1.93 (m, 1H), 1.76−1.60 (m, 3H), 1.46 (s, 9H), 0.93 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, Temp = 75 °C) δ 152.6, 81.5, 78.5, 64.2 (d, *J* = 160.0 Hz), 52.0 (d, *J* = 7.0 Hz), 51.4 (d, *J* = 7.5 Hz), 44.4, 28.5, 27.8, 25.2, 20.7 (d, *J* = 5.8 Hz), 17.3, −5.0, −5.3 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.8 ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{38}NO_6PSiNa^+$ 446.2098, found 446.2097.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-ethylpyrrolidine-1-carboxylate (**9f**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (153 mg, 70%). $[\alpha]_D^{26}$ +18.2 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2957, 1711, 1373, 1252, 1149, 1032, 833, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.30−4.14 (m, 1H), 3.80−3.70 (m, 6H), 3.63−3.55 (m, 1H), 3.42−3.28 (m, 1H), 2.68−2.35(m, 2H), 2.01−1.88 (m, 2H), 1.05−1.44 (m, 9H), 0.94 (s, 9H), 0.87−0.79 (m, 3H), 0.16−0.06 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.5 (153.1), 80.2 (79.3), 74.7 (74.2), 69.2 (d, *J* = 154.7 Hz), 53.1 (d, *J* = 6.6 Hz), 52.3 (d, *J* = 7.0 Hz), 45.7 (45.3), 29.5, 28.5 (28.7), 25.8, 22.7 (d, *J* = 5.6 Hz), 18.2, 6.8 (7.0, 6.7), −4.4, −4.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 26.8 (25.9) ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{40}NO_6PSiNa^+$ 460.2255, found 460.2258.

*(2S,3S)-tert-Butyl 2-butyl-3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9g**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (140 mg, 60%). $[\alpha]_D^{25}$ +15.4 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2953, 1711, 1377, 1249, 1149, 1028, 841, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.33−4.16 (m, 1H), 3.79−3.66 (m, 6H), 3.64−3.55 (m, 1H), 3.40−3.25 (m, 1H), 2.59−2.27(m, 2H), 1.79−1.83 (m, 2H), 1.51−1.43 (m, 9H), 1.41−1.29 (m, 2H), 1.22−1.07 (m, 2H), 0.93 (s, 9H), 0.93−0.86 (m, 3H), 0.14−0.07 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.5 (153.0), 80.2 (79.3), 75.5 (75.0), 68.3 (d, *J* = 164.4 Hz), 53.2 (d, *J* = 6.7 Hz) (53.0), 52.3 (d, *J* = 7.1 Hz) (52.2), 45.7 (45.3), 30.1 (d, *J* = 5.2 Hz), 29.5 (d, *J* = 4.9 Hz), 28.4 (28.8), 25.7, 24.9 (d, *J* = 10.8 Hz) (24.6), 22.9 (d, *J* = 18.1 Hz), 18.1, 14.5, −4.4, −4.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 26.7 (25.8) ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{44}NO_6PSiNa^+$ 488.2568, found 488.2569.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-pentylpyrrolidine-1-carboxylate (**9h**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). White solid (134 mg, 56%). $[\alpha]_D^{25}$ +17.4 (*c* 1.00, $CHCl_3$); mp 69−70 °C; IR (film) ν_{max} 2953, 1711, 1594, 1373, 1252, 1039, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.35−4.15 (m, 1H), 3.75−3.68 (m, 6H), 3.61−3.53 (m, 1H), 3.39−3.23 (m, 1H), 2.58−2.29 (m, 2H), 1.95−1.80 (m, 2H), 1.49−1.43 (m, 9H), 1.36−1.26 (m, 4H), 1.23−1.09 (m, 2H), 0.92 (s, 9H), 0.91−0.85 (m, 3H), 0.11−0.07 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.5 (153.0), 80.1 (79.2), 75.5 (74.9), 68.3 (d, *J* = 154.5 Hz), 53.1 (d, *J* = 6.6 Hz) (53.0), 52.3 (d, *J* = 7.1 Hz) (52.1), 45.7 (45.3), 32.1 (31.9), 30.3 (d, *J* = 5.2 Hz), 29.5, 28.4 (28.8), 25.8, 22.9 (d, *J* = 15.7 Hz), 22.1 (d, *J* = 10.1 Hz), 18.1, 14.1 (d, *J* = 13.6 Hz), −4.4, −4.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 26.7 (25.8) ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{46}NO_6PSiNa^+$ 502.2724, found 502.2726.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-isopropylpyrrolidine-1-carboxylate (**9i**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (93 mg, 41%). $[\alpha]_D^{25}$ +14.9 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2949, 1711, 1366, 1244.90, 1036, 833, 775, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.47−4.29 (m, 1H), 3.82−3.65 (m, 6H), 3.64−3.55 (m, 1H), 3.43−3.26 (m, 1H), 3.19−2.98 (m, 1H), 2.28−2.02 (m, 1H), 1.99−1.88 (m, 1H), 1.54−1.39 (m, 9H), 1.26−1.16 (m, 3H), 0.92 (s, 9H), 0.84 (d, *J* = 6.8 Hz, 3H), 0.16−0.08 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.7 (153.3), 80.5 (79.3), 74.7 (73.9), 73.2 (d, *J* = 152.3 Hz), 52.5 (d, *J* = 7.1 Hz), 46.4 (d, *J* = 13.7 Hz), 31.5 (31.4), 29.7 (d, *J* = 7.8 Hz), 29.3 (d, *J* = 8.2 Hz), 28.5, 25.9, 18.9 (19.2), 18.1 (17.9), −3.6, −4.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 27.3 (26.8) ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{42}NO_6PSiNa^+$ 474.2411, found 474.2411.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-isopropylpyrrolidine-1-carboxylate (**9i-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (32 mg, 14%). $[\alpha]_D^{24}$ +2.6 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2954, 1701, 1385, 1249.06, 1022, 831, 770, 560 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 4.95−4.84 (m, 1H), 3.82−3.70 (m, 6H), 3.66−3.47 (m, 2H), 3.08−2.95 (m, 1H), 2.09−1.96 (m, 1H), 1.79−1.66 (m, 1H), 1.51−1.46 (m, 9H), 1.28 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H), 0.91 (s, 9H), 0.16−0.08 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.9 (154.5), 80.5 (79.6), 77.7 (d, *J* = 7.9 Hz) (78.7), 73.1 (d, *J* = 138.4 Hz) (73.7), 53.7 (d, *J* = 7.0 Hz), 52.1 (d, *J* = 7.2 Hz), 46.8 (46.3), 33.1 (32.2), 29.7 (d, *J* = 5.8 Hz) (30.1), 28.6 (28.5), 26.1, 18.9 (d, *J* = 12.6 Hz) (18.5), 18.1 (17.9), −4.2, −4.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 33.7 (31.1) ppm; HRMS (ESI-Orbitrap) *m*/*z* [M + Na]$^+$ calcd for $C_{20}H_{42}NO_6PSiNa^+$ 474.2411, found 474.2408.

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*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-phenylpyrrolidine-1-carboxylate (**9j**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Pink solid (146 mg, 60%). $[\alpha]_D^{25}$ +10.3 (*c* 1.00, $CHCl_3$); mp 116−117 °C; IR (film) ν_{max} 2953, 2854, 1689, 1388, 1245, 1108.98, 1054, 837 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.52−7.26 (m, 5H), 4.66−4.56 (m, 1H), 3.91−3.61 (m, 5H), 3.59−3.40 (m, 3H), 1.74−1.66 (m, 2H), 1.59−1.50 (m, 5H), 1.47−1.32 (m, 4H), 1.00−0.88 (m, 9H), 0.21−0.02 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.9 (154.3), 138.7 (138.3), 128.5 (128.2), 127.4, 126.6 (126.3), 85.0 (82.8), 80.5 (79.8), 75.5 (d, *J* = 162.9 Hz), 53.4 (d, *J* = 4.7 Hz) (53.9), 51.9 (d, *J* = 5.2 Hz), 47.4 (47.0), 30.7 (d, *J* = 7.6 Hz) (29.9), 28.6 (28.4), 26.9, 18.2, −4.7, −5.0 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 23.2 (22.8) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{40}NO_6PSiNa^+$ 508.2255, found 508.2257.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-phenylpyrrolidine-1-carboxylate (**9j-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (63 mg, 26%). $[\alpha]_D^{24}$ +29.5 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2953, 2850, 1700, 1384, 1249, 1054, 1024, 830 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.34−7.17 (m, 5H), 4.91−4.78 (m, 1H), 3.85−3.68 (m, 8H), 2.28−2.16 (m, 1H), 1.81−1.68 (m, 1H), 1.51−1.45 (m, 5H), 1.22−1.19 (m, 4H), 0.64−0.58 (m, 9H), −0.10 (s, 3H), −0.31 to −0.42 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.7 (154.4), 135.6 (d, *J* = 6.5 Hz) (136.5), 127.6 (d, *J* = 5.2 Hz) (127.8), 127.2 (126.9), 126.8 (126.6), 80.5 (80.0), 77.8 (d, *J* = 5.7 Hz) (79.2), 74.7 (d, *J* = 151.0 Hz) (75.2), 54.2 (d, *J* = 7.2 Hz) (54.4), 52.6 (d, *J* = 8.0 Hz) (52.4), 46.4 (46.6), 32.4 (32.0), 28.6 (28.0), 25.5 (25.4), 17.7 (d, *J* = 5.9 Hz), −4.8 (−5.0), −5.4 (−5.5) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.5 (27.4) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{40}NO_6PSiNa^+$ 508.2255, found 508.2258.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-m-tolylpyrrolidine-1-carboxylate (**9k**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow solid (140 mg, 56%). $[\alpha]_D^{27}$ +9.4 (*c* 1.00, $CHCl_3$); mp 137−138 °C; IR (film) ν_{max} 2953, 1693, 1392, 1245, 1113, 1061, 834, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.36−7.15 (m, 3H), 7.10−7.02 (m, 1H), 4.64−4.52 (m, 1H), 3.87−3.58 (m, 5H), 3.56−3.33 (m, 3H), 2.34(s, 3H), 1.78−1.51 (m, 2H), 1.57−1.31 (m, 9H), 1.00−0.85 (m, 9H), 0.22−0.01 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.2 (155.0), 138.1 (138.4), 137.8 (137.7), 128.3, 128.1 (128.0), 127.0 (127.1), 123.5 (123.7), 82.8 (84.8), 79.7 (80.5), 75.4 (d, *J* = 162.8 Hz) (75.2), 53.5 (d, *J* = 6.3 Hz) (53.2, 53.9), 51.8 (d, *J* = 6.9 Hz), 47.0 (d, *J* = 3.3 Hz) (47.4), 30.7 (d, *J* = 7.4 Hz) (29.8), 28.6 (28.4), 26.0, 21.9 (21.7), 18.2, −4.5, −4.9 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 23.2 (22.7) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{43}NO_6PSi^+$ 500.2592, found 500.2595.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-m-tolylpyrrolidine-1-carboxylate (**9k-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Pink oil (75 mg, 30%). $[\alpha]_D^{23}$ +41.3 (*c* 3.00, $CHCl_3$); IR (film) ν_{max} 2953, 1697, 1396, 1252, 1058, 1028, 833, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.18−6.93 (m, 4H), 4.92−4.72 (m, 1H), 3.83−3.65 (m, 8H), 2.30 (d, *J* = 4.4 Hz, 3H), 2.23−2.13 (m, 1H), 1.79−1.65 (m, 1H), 1.50−1.20 (m, 9H), 0.64−0.59 (m, 9H), −0.10 (m, 3H), −0.31 to −0.45 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.7 (154.3), 136.2 (136.0), 135.3 (135.2), 128.4 (d, *J* = 5.5 Hz, 128.6), 127.5 (127.1), 127.2 (126.8), 124.5, 124.5 (124.6), 80.3 (79.9), 77.8 (d, *J* = 6.3 Hz) (79.2), 74.6 (d, *J* = 150.5 Hz) (75.3), 54.1 (d, *J* = 7.2 Hz) (54.4), 52.7 (d, *J* = 8.0 Hz) (52.3), 46.6 (46.3), 32.1 (d, *J* = 2.7 Hz) (32.5), 28.5 (28.0), 25.5 (d, *J* = 5.3 Hz), 21.7 (21.5), 17.7 (17.6), −4.9 (−5.0), −5.5 (−5.6) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.5 (27.3) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{42}NO_6PSiNa^+$ 522.2411, found 522.2415.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-p-tolylpyrrolidine-1-carboxylate (**9l**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (132 mg, 53%). $[\alpha]_D^{25}$ +10.9 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2953, 2854, 1686, 1392, 1252, 1061, 841, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.38−7.10 (m, 4H), 4.64−4.54 (m, 1H), 3.87−3.60 (m, 5H), 3.58−3.36 (m, 3H), 2.33 (s, 3H), 1.75−1.58 (m, 2H), 1.56−1.34 (m, 9H), 0.98−0.90 (m, 9H), 0.19 (s, 3H), 0.13−0.05 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.2 (155.0), 137.0, 135.3, 129.1 (128.8), 126.2 (126.4), 82.7 (84.8), 79.7 (80.5), 75.3 (d, *J* = 163.3 Hz) (75.1), 53.2 (d, *J* = 6.6 Hz) (53.4, 53.9), 51.8, 47.0 (47.4), 30.7 (d, *J* = 6.8 Hz) (29.7), 28.6 (28.4), 26.0, 21.0, 18.2, −4.5, −4.9 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 23.4 (22.8) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{42}NO_6PSiNa^+$ 522.2411, found 522.2418.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-p-tolylpyrrolidine-1-carboxylate (**9l-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (65 mg, 26%). $[\alpha]_D^{23}$ +22.7 (*c* 3.00, $CHCl_3$); IR (film) ν_{max} 2953, 2850, 1689, 1384, 1245, 1054, 833, 775, 558 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.23−7.12 (m, 2H), 7.08−7.03 (m, 2H), 4.90−4.75 (m, 1H), 3.85−3.68 (m, 8H), 2.30 (d, *J* = 10.8 Hz, 3H), 2.24−2.14 (m, 1H), 1.78−1.63 (m, 1H), 1.51−1.22 (m, 9H), 0.66−0.69 (m, 9H), −0.09 (s, 3H), −0.27 to −0.43(m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.4 (154.7), 136.1 (d, *J* = 7.4 Hz), 132.3 (d, *J* = 6.5 Hz) (133.2), 127.9, 127.5, 79.9 (80.4), 77.7 (d, *J* = 6.0 Hz) (79.1), 74.4 (d, *J* = 151.0 Hz) (75.0), 54.2 (d, *J* = 7.2 Hz) (54.4), 52.4, 52.5 (52.2), 46.3 (46.5), 32.5 (d, *J* = 3.3 Hz) (32.1), 28.6 (28.1), 25.5 (d, *J* = 5.8 Hz), 21.0, 17.8 (17.7), −4.8 (−4.9), −5.4 (−5.5) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.7 (27.5) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{42}NO_6PSiNa^+$ 522.2411, found 522.2419.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(3-chlorophenyl)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9m**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). White solid (182 mg, 70%). $[\alpha]_D^{25}$ +5.8 (*c* 2.00, $CHCl_3$); mp 156−156 °C; IR (film) ν_{max} 2953, 1708, 1396, 1249, 1058, 833, 775, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.51−7.19 (m, 4H), 4.60−4.48 (m, 1H), 3.89−3.43 (m, 8H), 1.86−1.59 (m, 2H), 1.58−1.26 (m, 9H), 1.01−0.85 (m, 9H), 0.21−0.02 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.1 (154.6), 141.1 (140.7), 134.3, 129.6 (129.4), 127.6, 126.7 (126.9), 124.6 (124.9), 82.9 (85.1), 80.1 (80.8), 74.9 (d, *J* = 163.4 Hz) (74.4), 53.3 (d, *J* = 6.3 Hz) (53.5, 53.9), 52.1 (d, *J* = 6.5 Hz), 46.8 (47.1), 30.7 (29.9), 28.6 (28.3), 25.9, 18.2, −4.6, −4.9 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 22.8 (22.4) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{39}ClNO_6PSiNa^+$ 542.1865, found 542.1866.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(3-chlorophenyl)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9m-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (26 mg, 10%). $[\alpha]_D^{25}$ +24.4 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2953, 1700, 1377, 1249, 1050, 1028, 830, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.29−7.16 (m, 4H), 4.91−4.72 (m, 1H), 3.85−3.69 (m, 8H), 2.26−2.15 (m, 1H), 1.82−1.67 (m, 1H), 1.50 (brs, 5H), 1.51−1.23 (m, 9H), 0.68−0.59 (m, 9H), −0.08 (s, 3H), −0.23 to −0.38 (m, 2H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.3, 138.9 (d, *J* = 7.6 Hz), 138.0 (d, *J* = 6.4 Hz), 133.3 (133.1), 128.4 (d, *J* = 6.9 Hz) (128.1), 127.0 (126.8), 125.6, 125.8 (125.7), 80.4 (80.8), 77.8 (d, *J* = 5.4 Hz) (79.3), 74.3 (d, *J* = 151.9 Hz) (74.8), 54.4 (d, *J* = 7.2 Hz) (54.5), 52.6, 52.7 (52.4), 46.6 (46.3), 32.6 (32.2), 28.6 (28.1), 25.5 (d, *J* = 4.5 Hz), 17.8 (17.7), −4.8 (−4.9), −5.4 (−5.7) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 28.7 (26.6) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{39}ClNO_6PSiNa^+$ 542.1865, found 542.1871.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(4-chlorophenyl)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9n**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). White solid (187 mg, 72%).

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$[\alpha]_D^{25}$ +6.8 (*c* 1.00, $CHCl_3$); mp 132−133 °C; IR (film) ν_{max} 2916, 2850, 1711, 1384, 1249, 1054, 833, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.48−7.27 (m, 4H), 4.55−4.47 (m, 1H), 3.90−3.61 (m, 5H), 3.60−3.40 (m, 3H), 1.85−1.76 (m, 0.36H), 1.73−1.67 (m, 0.64H), 1.66−1.56 (m, 1H), 1.55−1.26 (m, 9H), 0.97−0.86 (m, 9H), 0.19−0.10 (m, 3H), 0.09−0.01 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.7 (154.2), 137.6 (137.1), 133.3, 128.6 (128.3), 127.9 (128.1), 82.9 (85.1), 80.1 (80.8), 74.9 (d, *J* = 163.4 Hz) (79.5), 53.3 (d, *J* = 6.9 Hz) (53.6, 53.9), 52.1 (d, *J* = 5.8 Hz), 46.9 (47.3), 30.7 (d, *J* = 5.9 Hz) (29.8), 28.6 (28.4), 25.9, 18.2, −4.5 (−4.6), −4.9 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 23.0 (22.6) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{39}ClNO_6PSiNa^+$ 542.1865, found 542.1868.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(4-chlorophenyl)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9n-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (39 mg, 15%). $[\alpha]_D^{24}$ +20.3 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2953, 2854, 1693, 1388, 1249, 1054, 1021, 833, 778 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.30−7.20 (m, 4H), 4.90−4.76 (m, 1H), 3.86−3.69 (m, 8H), 2.28−2.13 (m, 1H), 1.79−1.65 (m, 1H), 1.50−1.22 (m, 9H), 0.67−0.60 (m, 9H), −0.26 to −0.36 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 154.5, 134.4 (d, *J* = 6.9 Hz) (135.4), 132.6 (132.4), 129.1 (d, *J* = 5.0 Hz) (129.2), 127.3 (127.0), 80.3 (80.8), 77.7 (d, *J* = 5.3 Hz) (79.1), 74.2 (d, *J* = 5.4 Hz) (74.6), 54.4, 54.3 (54.7), 52.5 (d, *J* = 8.0 Hz), 46.3 (46.51), 32.5 (32.1), 28.6 (28.1), 25.5 (d, *J* = 5.0 Hz), 17.8 (17.7), −4.8 (−4.9), −5.3 (−5.4) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.0 (26.9, 25.1) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{23}H_{39}ClNO_6PSiNa^+$ 542.1865, found 542.1868.

*(2S,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (**9o**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (139 mg, 54%). $[\alpha]_D^{23}$ +4.6 (*c* 3.00, $CHCl_3$); IR (film) ν_{max} 2953, 1711, 1506, 1396, 1249, 1054, 833, 551 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.46−7.29 (m, 2H), 6.94−6.80 (m, 2H), 4.61−4.50 (m, 1H), 3.95−3.82 (m, 1H), 3.80 (s, 3H), 3.75−3.69 (m, 3H), 3.69−3.56 (m, 1H), 3.56−3.33 (m, 3H), 1.75−1.59 (m, 2H), 1.55−1.35 (m, 9H), 0.98−0.89 (m, 9H), 0.21−0.13 (m, 3H), 0.12−0.06 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 158.8, 154.2 (154.9), 131.1 (130.2), 127.5 (127.7), 126.1, 113.8, 113.4 (114.2), 82.6 (84.7), 79.7 (80.5), 74.9 (d, *J* = 163.6 Hz) (74.6), 55.3 (55.7), 53.3 (53.8), 51.8, 46.9 (47.4), 30.6 (d, *J* = 6.4 Hz) (29.7), 28.6, 28.5 (28.4), 25.9, 18.2, −4.6, −4.9 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 23.5 (22.8) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + H]^+$ calcd for $C_{24}H_{43}NO_7PSi^+$ 516.2541, found 516.2549.

*(2R,3S)-tert-Butyl 3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)-2-(4-methoxyphenyl)pyrrolidine-1-carboxylate (**9o-2**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (70 mg, 27%). $[\alpha]_D^{24}$ +14.6 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2953, 1697, 1506, 1381, 1256, 1058, 834, 558 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.27−7.16 (m, 2H), 6.84−6.74 (m, 2H), 4.87−4.73 (m, 1H), 3.81−3.74 (m, 7H), 3.74−368 (m, 4H), 2.24−2.12 (m, 1H), 1.89−1.59 (m, 2H), 1.51−1.48 (m, 5H), 1.26−1.21 (m, 4H), 0.68−0.60 (m, 9H), −0.09 (m, 3H), −0.25 to −0.38 (m, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 158.4, 154.4 (154.7), 128.7 (d, *J* = 5.3 Hz) (128.9), 127.6 (d, *J* = 6.0 Hz), 112.8 (112.4), 80.0 (80.4), 79.0 (d, *J* = 7.3 Hz), 74.0 (d, *J* = 151.6 Hz) (74.5), 55.4 (55.5), 54.3, 54.2 (54.4), 52.4 (d, *J* = 7.9 Hz), 46.2 (46.5), 32.4 (d, *J* = 3.6 Hz) (32.0), 28.6 (28.1), 25.6 (d, *J* = 5.0 Hz) (26.0), 17.8 (d, *J* = 6.5 Hz), −4.8 (−4.9), −5.3 (−5.4) ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 29.8 (27.5) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{42}NO_7PSiNa^+$ 538.2360, found 538.2364.

*(2S,3S)-tert-Butyl 2-benzyl-3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9p**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Colorless oil (180 mg, 72%). $[\alpha]_D^{24}$ −26.4 (*c* 2.00, $CHCl_3$); IR (film) ν_{max} 2949, 1704, 1373, 1252, 1124, 1032, 833, 771 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.33−7.17 (m, 5H), 4.27−4.00 (m, 2H), 3.85−3.73 (m, 6H), 3.66−3.48 (m, 1H), 3.32−2.99 (m, 2H), 2.29−2.04 (m, 1H), 1.53 (s, 9H), 1.49−1.44 (m, 1H), 1.01−0.91 (m, 9H), 0.13−0.00 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 153.6 (154.6), 136.3 (136.2), 131.1, 130.0 (128.5), 128.2, 126.7 (126.8), 79.6 (81.0), 75.9 (d, *J* = 108.7 Hz) (74.9), 70.3 (d, *J* = 8.7 Hz) (68.7), 53.3 (d, *J* = 7.7 Hz) (52.8), 52.3 (d, *J* = 8.3 Hz) (52.7), 45.9, 34.4 (d, *J* = 7.8 Hz) (35.3), 29.5 (29.2), 28.6 (28.5), 25.8, 18.1, −3.8 (−4.2), −4.6 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 26.3 (25.5) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{24}H_{42}NO_6PSiNa^+$ 522.2411, found 522.2415.

*(2S,3S)-tert-Butyl 2-(p-methylbenzene)-3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9q**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). White semisolid (149 mg, 58%). $[\alpha]_D^{25}$ −33.2 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2927, 1708, 1377, 1252, 1127, 1036, 775 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 7.19−7.02 (m, 4H), 4.26−4.05 (m, 2H), 3.88−3.74 (m, 6H), 3.63−3.49 (m, 1H), 3.25−2.99 (m, 2H), 2.34−2.30 (m, 3H), 1.77 (brs, 1H), 1.57−1.53 (m, 9H), 1.47−1.45 (m, 1H), 1.02−0.90 (m, 9H), 0.13−0.00 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, rotamers) δ 153.6 (154.7), 137.6, 136.1 (136.4), 132.0 (131.2), 128.2 (128.0), 127.4 (127.6), 79.6 (81.0), 75.8 (d, *J* = 105.7 Hz) (74.8), 70.3 (d, *J* = 14.1 Hz) (68.7), 53.4 (d, *J* = 7.2 Hz) (52.8), 52.3 (d, *J* = 7.7 Hz) (52.8), 46.0 (44.9), 34.2 (d, *J* = 7.8 Hz) (35.2), 29.4 (29.2), 28.6 (d, *J* = 8.0 Hz), 25.9, 21.4, 18.1, −3.7 (−4.1), −4.6 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 26.4 (25.6) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{25}H_{44}NO_6PSiNa^+$ 536.25677, found 536.2570.

*(2S,3S)-tert-Butyl 2-allyl-3-(tert-butyldimethylsilyloxy)-2-(dimethoxyphosphoryl)pyrrolidine-1-carboxylate (**9r**).* The title compound was purified by column chromatography (petroleum ether/ethyl acetate = 2:1, R_f = 0.3). Yellow oil (142 mg, 63%). $[\alpha]_D^{25}$ −17.5 (*c* 1.00, $CHCl_3$); IR (film) ν_{max} 2953, 1704, 1377, 1249, 1149, 1036, 837, 767 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, rotamers) δ 5.63−5.52 (m, 1H), 5.23−5.14 (m, 2H), 4.25−4.13 (m, 1H), 3.79−3.71 (m, 6H), 3.62−3.53 (m, 1H), 3.52−3.24 (m, 2H), 2.63−2.52 (m, 1H), 2.45−2.30 (m, 1H), 1.95−1.86 (m, 1H), 1.50−1.44 (m, 9H), 0.93 (s, 9H), 0.10 (s, 3H), 0.08 (s, 3H) ppm; $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, Temp = 75 °C) δ 152.3, 132.4, 118.7, 75.0, 67.5, 66.0, 52.1 (d, *J* = 7.1 Hz), 51.5 (d, *J* = 7.3 Hz), 44.8, 33.7 (d, *J* = 6.7 Hz), 28.2, 27.7, 25.2, 17.2, −4.9, −5.2 ppm; ^{31}P NMR (162 MHz, $CDCl_3$, rotamers) δ 25.9 (25.0) ppm; HRMS (ESI-Orbitrap) *m*/*z* $[M + Na]^+$ calcd for $C_{20}H_{40}NO_6PSiNa^+$ 472.2255, found 472.2257.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.1c00935.

Copies of ^1H, $^{13}C\{^1H\}$, ^{31}P NMR spectra, HPLC data, and X-ray structural data (PDF)

Accession Codes

CCDC 2071721−2071723 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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