# Support Information

# Selenium-catalyzed Allylic C-H Phosphoramidation of Alkenes

Chengjie Huang[1], Tao Yang[1], Jingyang Jia[1], Songsen Fu[1], Bang Hong[2], Fan Wu[1*] and Feng Ni[1,2*]

1, Institute of Drug Discovery Technology and Qian Xuesen Collaborative Research Center of Astrochemistry and Space Life Sciences, Ningbo University, Ningbo, Zhejiang 315211, China.

2, LeadArt Technologies Ltd., Ningbo, 315211, China.

E-mail: wufan@nbu.edu.cn (F. W.); nifeng@nbu.edu.cn (F. N.)

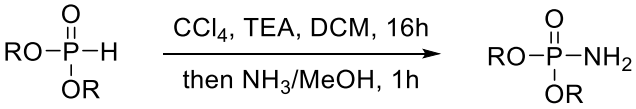
Content

## 1. General Information

Commercial reagents were purchased from Adamas, Aldrich, Bide, Energy Chemical, and J&K chemical, and were used as received. Chromatographic purification of products was accomplished using flash chromatography on 300-400 mesh silica gel. $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a Bruker instrument (500 MHz for $^{1}H$ NMR, 126 MHz for $^{13}C$ and 202 MHz for $^{31}P$) and are internally referenced to chemical shift of residual solvent (for $CDCl_3$, 7.26 and 77.16 ppm, respectively). Data for $^{1}H$ NMR are reported as follows: chemicals shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, coupling constant (Hz). $^{13}C$ spectra were recorded as chemical shifts in ppm and multiplicity where appropriate. $^{31}P$ NMR data were with complete proton decoupling and the chemical shifts were reported in ppm. High resolution mass spectroscopy (HR-MS) was performed on Thermo Q Exactive Plus (FTMS ESI) mass spectrometer and acetonitrile was used to dissolve the sample.

### 2. Synthesis of Phosphonamidates

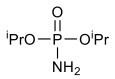
Phosphoramides used to synthesize products **4**, **7**, and **13** are commercially available and were used directly after being purchased from the aforementioned company. Phosphonamidates used to synthesize products **8-12** were synthesized following the method reported in the literature.[1] Phosphonamidates used to synthesize products **3**, **5**, **6** were synthesized using the following synthetic route.




**General Procedures:**

To a round bottom flask charged with magnetic stir bar was added DCM (10 mL), followed by TEA (2.8 mL, 20 mmol). Then the mixture of appropriate dialkyl phosphite (10 mmol) and $CCl_4$ (2 mL) was added dropwise at room temperature. After the addition, the reaction mixture was stirred at room temperature for 12 hours before adding $NH_3$ solution (50 mmol, 7mol/L in MeOH). The reaction mixture was then stirred at room temperature for another 12 hours. The reaction mixture was diluted with DCM (50 mL), and washed with *sat. aq.* $NaHCO_3$ (50 mL), brine (50 mL), dried over Na2SO4 and concentrated under reduced pressure to afford crude product. When the crude product was solid, it was triturated with petroleum ether for 1 hour, and then collected as white solid after vacuum filtration. When the crude product was oil, it was purified by column chromatography

to afford the pure compound.



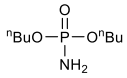
**Diisopropyl Phosphoramidate:** This compound was prepared according to the General Procedure, using diisopropylphosphite (10 mmol). The title compound was collected as a white solid (1.47 g, 81% yield).

$^{1}$H NMR (500 MHz, DMSO) δ 4.44 – 4.33 (m, 2H), 1.20 (d, $J$ = 6.3 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 68.9 (d, $J_{C\text{-}P}$ = 5.4 Hz), 23.7 (d, $J_{C\text{-}P}$ = 7.3 Hz), 23.6 (d, $J_{C\text{-}P}$ = 7.6 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 9.55.

HRMS (ESI) *m/z* calcd for $C_6H_{17}NO_3P^+$ [$(M+H)^+$] 182.0941, found 182.0943.



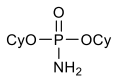
**Dibutyl Phosphoramidate:** This compound was prepared according to the General Procedure, using dibutylphosphite (10 mmol). The title compound was purified by column chromatography ($SiO_2$, 75% to 100% EtOAc in Hexanes) as a yellow oil (1.63 g, 78% yield).

$^{1}$H NMR (500 MHz, DMSO) δ 4.50 (d, $J$ = 5.8 Hz, 2H), 3.81 (q, $J$ = 6.7 Hz, 4H), 1.57 – 1.51 (m, 4H), 1.39 – 1.26 (m, 4H), 0.88 (t, $J$ = 7.4 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 64.6 (d, $J_{C\text{-}P}$ = 5.6 Hz), 32.0 (d, $J_{C\text{-}P}$ = 6.9 Hz), 18.4, 13.5.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 11.31.

HRMS (ESI) *m/z* calcd for $C_8H_{21}NO_3P^+$ [$(M+H)^+$] 210.1254, found 210.1252.



**Dicyclohexyl Phosphoramidate:** This compound was prepared according to the General Procedure, using dicyclohexylphosphite (10 mmol). The title compound was collected as a white solid (1.75 g, 67% yield).

$^{1}$H NMR (500 MHz, DMSO) δ 4.41 (d, $J$ = 5.3 Hz, 2H), 4.17 – 4.08 (m, 2H), 1.93 – 1.76 (m, 4H), 1.75 – 1.58 (m, 4H), 1.49 – 1.34 (m, 6H), 1.34 – 1.13 (m, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 73.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 33.1 (d, $J_{C\text{-}P}$ = 11.1 Hz), 33.0 (d, $J_{C\text{-}P}$ = 11.7 Hz), 24.9, 23.2.

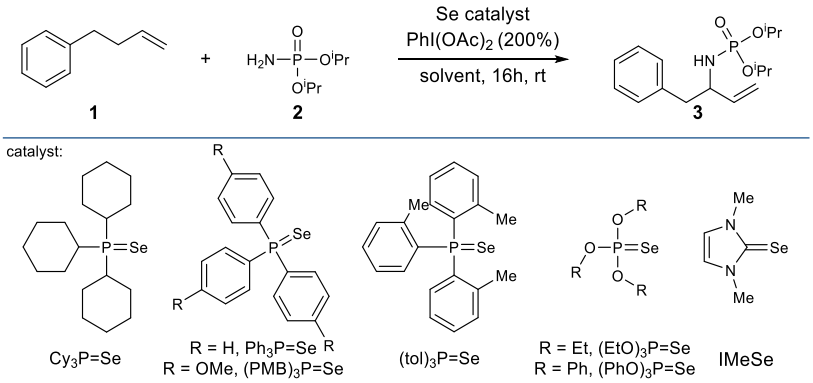
$^{31}$P NMR (202 MHz, $CDCl_3$) δ 9.73.

HRMS (ESI) *m/z* calcd for $C_{12}H_{25}NO_3P^+$ [$(M+H)^+$] 262.1567, found 262.1566.

## 3. Optimization of Reaction Conditions

### General Procedure and Result

To an oven-dried 8 mL vial equipped with a magnetic stir bar was added phosphoramide 2 (0.22-0.4 mmol, 1.1-2.0 equiv.), Se catalyst (0.01-0.04 mmol, 5-20 mol %), $PhI(OAc)_2$ (0.4 mmol, 2.0 equiv) and solvent (1 mL), followed by alkene 1 (0.2 mmol, 1.0 equiv.) *via* microsyringe. The reaction mixture was stirred at room temperature for 16 hours. Then the reaction mixture was diluted with EtOAc (5 mL) and then washed with 1M HCl (2 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 mL×2). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to afford the crude product. Then triethyl phosphate (18.2 mg, 0.1 mmol) was added as an internal standard and subjected to $^{31}P$ NMR. The NMR yield was calculated based on the integration ratio of products and internal standards.




| entry | Catalyst (mol%) | **2** (mol%) | solvent | yield (%)[b] |
|---|---|---|---|---|
| 1 | IMeSe (15) | 150 | $CH_3CN$ | 8 |
| 2 | $Cy_3p$=Se (15) | 150 | $CH_3CN$ | 80 |
| 3 | $Ph_3P$=Se (15) | 150 | $CH_3CN$ | 74 |
| 4 | $(PMB)_3P$=Se (15) | 150 | $CH_3CN$ | 6 |
| 5 | $(PhO)_3P$=Se (15) | 150 | $CH_3CN$ | 68 |
| 6 | $(OEt)_3P$=Se (15) | 150 | $CH_3CN$ | 46 |
| 7 | $(tol)_3P$=Se (15) | 150 | $CH_3CN$ | 83(78[c]) |
| 8 | $(tol)_3P$=Se (20) | 150 | $CH_3CN$ | 80 |
| 9 | $(tol)_3P$=Se (10) | 150 | $CH_3CN$ | 81 |
| 10 | $(tol)_3P$=Se (5) | 150 | $CH_3CN$ | 52 |
| 11 | $(tol)_3P$=Se (15) | 200 | $CH_3CN$ | 79 |
| 12 | $(tol)_3P$=Se (15) | 130 | $CH_3CN$ | 73 |
| 13 | $(tol)_3P$=Se (15) | 110 | $CH_3CN$ | 65 |
| 14 | $(tol)_3P$=Se (15) | 150 | DCM | 69 |
| 15 | $(tol)_3P$=Se (15) | 150 | toluene | 55 |
| 16 | $(tol)_3P$=Se (15) | 150 | DMF | 21 |
| 17 | $(tol)_3P$=Se (15) | 150 | THF | 68 |

| | | | | |
|---|---|---|---|---|
| 18[d] | $(tol)_3P$=Se (15) | 150 | $CH_3CN$ | 70 |
| 19[e] | $(tol)_3P$=Se (15) | 150 | $CH_3CN$ | -- |

[a]standard conditions: alkene **1** (0.2 mmol, 1.0 equiv.), Phosphoramide **2** (0.22-0.4 mmol, 1.1-2.0 equiv.), Se catalyst (0.01-0.04 mmol, 5-20 mol %), $PhI(OAc)_2$ (0.4 mmol, 2.0 equiv), solvent (1 mL), rt, 16 h [b], yields were determined by $^{31}P$ NMR using triethyl phosphate as the internal standard. [c] Isolated yield. [d]150 mol% $PhI(OAc)_2$ was used. [e] [Bis(trifluoroacetoxy)iodo]benzene was used instead of $PhI(OAc)_2$.

## 4. Allylic C-H Phosphoramidation Reaction

### 3.1 General Procedures

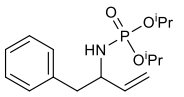
**General Procedure A-**for linear and exocyclic alkenes

To an oven-dried 8 mL vial equipped with a magnetic stir bar was added phosphoramide (0.3 mmol, 1.5 equiv.), $(tol)_3P$=Se (0.03 mmol, 15 mol %), $PhI(OAc)_2$ (0.4 mmol, 2.0 equiv) and $CH_3CN$ (1 mL), followed by the addition of alkene (0.2 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 24 hours, and then diluted with EtOAc (5 mL) and then washed with 1M HCl (2 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 mL×2). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography to afford desired product.

**General Procedure B-**for di- and tri-substituted cyclic alkenes （Products **27**, **28**, **31**, **34**）

To an oven-dried 8 mL vial equipped with a magnetic stir bar was added phosphoramide (0.3 mmol, 1.5 equiv.), IMeSe (0.03 mmol, 15 mol %), $PhI(OAc)_2$ (0.4 mmol, 2.0 equiv) and DCM (1 mL), followed by the addition of alkene (0.2 mmol, 1.0 equiv.). The reaction mixture was stirred at 40℃ for 16-24 hours, and then diluted with EtOAc (5 mL) and then washed with 1M HCl (2 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 mL×2). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography to afford desired product.

### 3.2 Synthesis and spectral Characterization of the Products




**Diisopropyl (1-phenylbut-3-en-2-yl)phosphoramidate (3):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol),

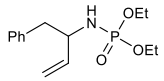
diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (48.6 mg, 78% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 5.83 – 5.73 (m, 1H), 5.18 – 5.00 (m, 2H), 4.57 – 4.43 (m, 2H), 3.99 – 3.90 (m, 1H), 2.90 (dd, $J$ = 13.3, 5.7 Hz, 1H), 2.80 (dd, $J$ = 13.4, 7.1 Hz, 1H), 2.54 (t, $J$ = 10.0 Hz, 1H), 1.33 – 1.24 (m, 9H), 1.22 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.5 (d, $J_{C\text{-}P}$ = 5.3 Hz), 137.4, 129.9, 128.4, 126.6, 114.6, 70.9 (d, $J_{C\text{-}P}$ = 5.9 Hz), 70.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 54.9, 43.5 (d, $J_{C\text{-}P}$ = 5.5 Hz), 24.0 (d, $J_{C\text{-}P}$ = 5.5 Hz), 23.9 (d, $J_{C\text{-}P}$ = 4.3 Hz), 23.89, 23.86, 23.84.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 5.94.

HRMS (ESI) *m/z* calcd for $C_{16}H_{27}NO_3P^+$ [$(M+H)^+$] 312.1723, found 312.1722.



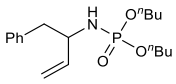

**diethyl (1-phenylbut-3-en-2-yl)phosphoramidate (4):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), diethyl phosphoramidate (45.9 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 50% to 75% EtOAc in Hexanes), the title compound was isolated as a colorless oil (47.1 mg, 83% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 5.86 – 5.77 (m, 1H), 5.24 – 4.99 (m, 2H), 4.05 – 3.83 (m, 4H), 3.83 – 3.67 (m, 1H), 2.89 – 2.65 (m, 3H), 1.24 (q, $J$ = 7.0 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 137.5, 129.9, 128.4, 126.6, 114.6, 62.3 (d, $J_{C\text{-}P}$ = 5.3 Hz), 62.2 (d, $J_{C\text{-}P}$ = 5.5 Hz), 55.2, 43.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 16.3 (d, $J_{C\text{-}P}$ = 7.3 Hz), 16.2 (d, $J_{C\text{-}P}$ = 7.3 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 7.64.

HRMS (ESI) *m/z* calcd for $C_{14}H_{23}NO_3P^+$ [$(M+H)^+$] 284.1410, found 284.1409.



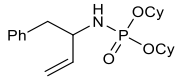

**dibutyl (1-phenylbut-3-en-2-yl)phosphoramidate (5):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), dibutyl phosphoramidate (62.8 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (55.0 mg, 81% yield).

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 2H), 7.24 – 7.15 (m, 3H), 5.86 – 5.77 (m, 1H), 5.21 – 5.00 (m, 2H), 3.96 – 3.78 (m, 4H), 3.75 – 3.65 (m, 1H), 2.88 – 2.74 (m, 2H), 2.69 (t, $J$ = 10.4 Hz, 1H), 1.65 – 1.50 (m, 4H), 1.40 – 1.30 (m, 4H), 0.94 – 0.88 (m, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, $J_{C\text{-}P}$ = 4.3 Hz), 137.5, 129.9, 128.4, 126.6, 114.6, 66.1 (d, $J_{C\text{-}P}$ = 5.7 Hz), 66.0 (d, $J_{C\text{-}P}$ = 5.8 Hz), 55.1, 43.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 32.5 (d, $J_{C\text{-}P}$ = 7.4 Hz), 32.4 (d, $J_{C\text{-}P}$ = 7.4 Hz), 18.8 (d, $J_{C\text{-}P}$ = 2.2 Hz), 13.7 (d, $J_{C\text{-}P}$ = 2.3 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 7.79.

HRMS (ESI) *m/z* calcd for $C_{18}H_{31}NO_3P^+$ [$(M+H)^+$] 340.2036, found 340.2036.



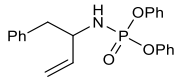

**dicyclohexyl (1-phenylbut-3-en-2-yl)phosphoramidate (6):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), dicyclohexyl phosphoramidate (78.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (57.9 mg, 74% yield).

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H), 7.24 – 7.15 (m, 3H), 5.83 – 5.73 (m, 1H), 5.18 – 4.98 (m, 2H), 4.32 – 4.17 (m, 2H), 4.02 – 3.88 (m, 1H), 2.90 (dd, $J$ = 13.4, 5.6 Hz, 1H), 2.81 (dd, $J$ = 13.2, 7.3 Hz, 1H), 2.54 (t, $J$ = 9.9 Hz, 1H), 2.03 – 1.60 (m, 8H), 1.60 – 1.15 (m, 12H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.6 (d, $J_{C\text{-}P}$ = 5.4 Hz), 137.4, 130.0, 128.4, 126.6, 114.6, 75.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 75.6 (d, $J_{C\text{-}P}$ = 5.9 Hz), 54.9, 43.5 (d, $J_{C\text{-}P}$ = 5.5 Hz), 33.7 (d, $J_{C\text{-}P}$ = 5.1 Hz), 33.60, 33.57, 33.54, 33.52, 25.4, 23.7, 23.6.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.14.

HRMS (ESI) *m/z* calcd for $C_{22}H_{35}NO_3P^+$ [$(M+H)^+$] 392.2349, found 392.2348.




**diphenyl (1-phenylbut-3-en-2-yl)phosphoramidate (7):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), diphenyl phosphoramidate (74.8 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 30% EtOAc in Hexanes), the title compound was isolated as a colorless oil (62.2 mg, 82% yield).

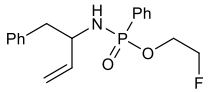
$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.06 (m, 15H), 5.83 – 5.71 (m, 1H), 5.13 – 4.99 (m, 2H), 4.20 – 4.12 (m, 1H), 3.88 (dd, $J$ = 12.6, 9.9 Hz, 1H), 2.87 (dd, $J$ = 13.5, 5.9 Hz, 1H), 2.77 (dd, $J$ = 13.6,

7.2 Hz, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 150.9 (d, $J_{C-P}$ = 7.1 Hz), 150.8 (d, $J_{C-P}$ = 7.0 Hz), 138.5 (d, $J_{C-P}$ = 4.5 Hz), 136.9, 129.8, 129.7, 129.6, 128.4, 126.7, 125.0, 120.3 (d, $J_{C-P}$ = 4.7 Hz), 120.2 (d, $J_{C-P}$ = 5.1 Hz), 115.4, 55.6, 43.3 (d, $J_{C-P}$ = 6.5 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ -1.88.

HRMS (ESI) *m/z* calcd for $C_{22}H_{23}NO_3P^+$ [$(M+H)^+$] 380.1410, found 380.1411.



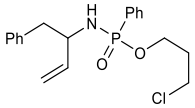

**2-fluoroethyl P-phenyl-N-(1-phenylbut-3-en-2-yl)phosphonamidate (8):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), 2-fluoroethyl P-phenylphosphonamidate (60.9 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 50% to 75% EtOAc in Hexanes), the title compound was isolated as a colorless oil (32.0 mg, 48% yield, ~1:1 mixture of two diastereomers).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.62 (m, 2H), 7.55 – 7.32 (m, 3H), 7.28 – 7.15 (m, 3H), 7.15 – 7.02 (m, 2H), 5.83 – 5.67 (m, 1H), 5.12 – 4.90 (m, 2H), 4.64 – 4.43 (m, 2H), 4.22 – 3.84 (m, 3H), 2.96 – 2.67 (m, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.6 (d, $J_{C-P}$ = 7.0 Hz), 139.4 (d, $J_{C-P}$ = 7.0 Hz), 137.5, 137.2, 132.05, 132.03, 132.00, 131.7, 131.6, 131.5, 129.85, 129.83, 128.6, 128.49, 128.46, 128.4, 126.7, 115.0, 114.9, 83.3 (dd, $J_{C-P,\ C-F}$ = 7.1, 4.3 Hz), 82.0 (dd, $J_{C-P,\ C-F}$ = 7.3, 4.5 Hz), 63.3 (dd, $J_{C-P,\ C-F}$ = 7.1, 5.4 Hz), 63.1 (dd, $J_{C-P,\ C-F}$ = 7.1, 5.3 Hz), 54.7, 54.6, 43.8 (d, $J_{C-P}$ = 5.6 Hz), 43.5 (d, $J_{C-P}$ = 5.4Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 22.07, 21.94.

HRMS (ESI) *m/z* calcd for $C_{18}H_{22}FNO_2P^+$ [$(M+H)^+$] 334.1367, found 334.1368.



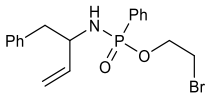

**3-chloropropyl P-phenyl-N-(1-phenylbut-3-en-2-yl)phosphonamidate (9):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), 3-chloropropyl P-phenylphosphonamidate (70.1 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a colorless oil (37.1 mg, 51% yield, ~1:1 mixture of two diastereomers).

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.58 (m, 2H), 7.54 – 7.31 (m, 3H), 7.31 – 7.16 (m, 3H), 7.16 – 6.99 (m, 2H), 5.84 – 5.64 (m, 1H), 5.13 – 4.88 (m, 2H), 4.17 – 3.82 (m, 3H), 3.67 – 3.55 (m, 2H), 2.95 – 2.63 (m, 3H), 2.13 – 1.97 (m, 2H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, $J_{C-P}$ = 3.3 Hz), 139.5 (d, $J_{C-P}$ = 3.4 Hz), 137.4, 137.1, 131.94, 131.92, 131.90, 131.6, 131.5, 131.45, 131.38, 130.2, 129.83, 129.78, 128.6, 128.48, 128.46, 128.45, 128.35, 126.69, 126.67, 114.9, 114.8, 61.2, 61.1, 54.7, 54.6, 43.8 (d, $J_{C-P}$ = 5.7 Hz), 43.5 (d, $J_{C-P}$ = 5.8 Hz), 41.2, 33.41 (d, $J_{C-P}$ = 5.2 Hz), 33.35 (d, $J_{C-P}$ = 5.3 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 21.44, 21.36.

HRMS (ESI) *m/z* calcd for $C_{19}H_{24}ClNO_2P^+$ [$(M+H)^+$] 364.1228, found 364.1227.



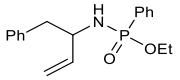

**2-bromoethyl P-phenyl-N-(1-phenylbut-3-en-2-yl)phosphonamidate (10):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), 2-bromoethyl P-phenylphosphonamidate (79.2 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a colorless oil (44.9 mg, 57% yield, ~1:1 mixture of two diastereomers).

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.64 (m, 2H), 7.54 – 7.34 (m, 3H), 7.30 – 7.18 (m, 3H), 7.16 – 7.04 (m, 2H), 5.85 – 5.64 (m, 1H), 5.15 – 4.91 (m, 2H), 4.29 – 3.84 (m, 3H), 3.48 (q, $J$ = 5.9 Hz, 2H), 3.00 – 2.63 (m, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, $J_{C-P}$ = 3.5 Hz), 139.4 (d, $J_{C-P}$ = 3.5 Hz), 137.4, 137.1, 132.11, 132.09, 132.07, 131.64, 131.56, 131.48, 129.85, 129.82, 128.60, 128.52, 128.48, 128.37, 126.74, 126.71, 115.0, 114.9, 63.7 (d, $J_{C-P}$ = 5.5 Hz), 63.6 (d, $J_{C-P}$ = 5.5 Hz), 54.8, 54.6, 43.8 (d, $J_{C-P}$ = 5.9 Hz), 43.4 (d, $J_{C-P}$ = 5.6 Hz), 30.9 (d, $J_{C-P}$ = 7.6 Hz), 30.8 (d, $J_{C-P}$ = 7.4 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 21.78, 21.67.

HRMS (ESI) *m/z* calcd for $C_{18}H_{22}BrNO_2P^+$ [$(M+H)^+$] 394.0566, found 394.0567.




**ethyl P-phenyl-N-(1-phenylbut-3-en-2-yl)phosphonamidate (11):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), ethyl P-phenylphosphonamidate (55.5 mg, 0.3 mmol). After purification by column chromatography

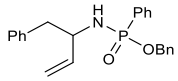
($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a colorless oil (44.1 mg, 70% yield, ~1:1 mixture of two diastereomers).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.62 (m, 2H), 7.51 – 7.31 (m, 3H), 7.26 – 7.16 (m, 3H), 7.13 – 7.00 (m, 2H), 5.82 – 5.65 (m, 1H), 5.09 – 4.89 (m, 2H), 4.10 – 3.81 (m, 3H), 2.88 – 2.76 (m, 2H), 2.71 (d, $J$ = 6.5 Hz, 1H), 1.28 (t, $J$ = 7.1, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.7 (d, $J_{C-P}$ = 3.7 Hz), 139.5 (d, $J_{C-P}$ = 3.6 Hz), 137.5, 137.2, 132.1, 131.71, 131.69, 131.67, 131.6, 131.5, 131.4, 130.71, 130.69, 129.80, 129.79, 128.43, 128.41, 128.38, 128.34, 128.32, 128.23, 126.60, 126.59, 114.8, 114.7, 60.6 (d, $J_{C-P}$ = 5.6 Hz), 60.5 (d, $J_{C-P}$ = 5.8 Hz), 54.6, 54.5, 43.8 (d, $J_{C-P}$ = 5.3 Hz), 43.5 (d, $J_{C-P}$ = 5.4 Hz), 16.5 (d, $J_{C-P}$ = 6.9 Hz), 16.4 (d, $J_{C-P}$ = 6.8 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 21.00, 20.85

HRMS (ESI) *m/z* calcd for $C_{18}H_{23}NO_2P^+$ [$(M+H)^+$] 316.1461, found 316.1462.



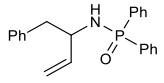

**benzyl P-phenyl-N-(1-phenylbut-3-en-2-yl)phosphonamidate (12):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), benzyl P-phenylphosphonamidate (74.2 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (52.1 mg, 69% yield, ~1:1 mixture of two diastereomers).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.63 (m, 2H), 7.50 – 7.42 (m, 1H), 7.42 – 7.27 (m, 7H), 7.27 – 7.14 (m, 3H), 7.10 – 7.00 (m, 2H), 5.81 – 5.64 (m, 1H), 5.11 – 4.78 (m, 4H), 4.04 – 3.85 (m, 1H), 2.99 – 2.85 (m, 1H), 2.77 (d, $J$ = 6.6 Hz, 1H), 2.72 (d, $J$ = 6.5 Hz, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.6 (d, $J_{C-P}$ = 3.6 Hz), 139.4 (d, $J_{C-P}$ = 3.6 Hz), 137.4, 137.2, 136.9 (d, $J_{C-P}$ = 7.3 Hz), 136.8 (d, $J_{C-P}$ = 7.5 Hz), 131.90, 131.88, 131.85, 131.68, 131.66, 131.59, 131.51, 130.3, 129.82, 129.80, 128.59, 128.56, 128.51, 128.45, 128.42, 128.40, 128.3, 128.17, 128.15, 127.71, 127.66, 126.6, 115.0, 114.8, 65.9 (d, $J_{C-P}$ = 5.3 Hz), 65.8 (d, $J_{C-P}$ = 5.3 Hz), 54.7, 54.6, 43.8 (d, $J_{C-P}$ = 5.8 Hz), 43.5 (d, $J_{C-P}$ = 5.7 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 21.77, 21.63

HRMS (ESI) *m/z* calcd for $C_{23}H_{25}NO_2P^+$ [$(M+H)^+$] 378.1617, found 378.1616.



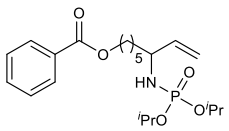
**P,P-diphenyl-N-(1-phenylbut-3-en-2-yl)phosphinic amide (13):** This compound was prepared according to the General Procedure A, using 4-phenyl-1-butene (26.4 mg, 30 μL, 0.2 mmol), P,P-diphenylphosphinic amide (65.2 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a colorless oil (20.8 mg, 30% yield, ~1:1 mixture of two diastereomers).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.79 (m, 2H), 7.73 – 7.63 (m, 2H), 7.52 – 7.32 (m, 6H), 7.31 – 7.23 (m, 3H), 7.17 (d, $J$ = 6.8, 2H), 5.94 – 5.82 (m, 1H), 5.23 – 5.02 (m, 2H), 3.94 – 3.83 (m, 1H), 3.01 – 2.89 (m, 2H), 2.86 (dd, $J$ = 10.9, 5.5 Hz, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.8 (d, $J_{C\text{-}P}$ = 5.5 Hz), 137.5, 133.3, 133.0, 132.4, 132.3, 132.2, 132.1, 131.99, 131.97, 131.9, 131.8, 130.2, 128.6 (d, $J_{C\text{-}P}$ = 4.3 Hz), 128.5 (d, $J_{C\text{-}P}$ = 4.7 Hz), 128.4, 126.7, 115.1, 54.9, 44.0 (d, $J_{C\text{-}P}$ = 5.2 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 22.38

HRMS (ESI) *m/z* calcd for $C_{22}H_{23}NOP^+$ $[(M+H)^+]$ 348.1512, found 348.1511.



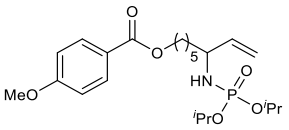

**6-((diisopropoxyphosphoryl)amino)oct-7-en-1-yl benzoate (14):** This compound was prepared according to the General Procedure A, using oct-7-en-1-yl benzoate (46.5 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (50.2 mg, 61% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.55 (t, $J$ = 7.4 Hz, 1H), 7.44 (t, $J$ = 7.6 Hz, 2H), 5.80 – 5.69 (m, 1H), 5.17 (d, $J$ = 17.2 Hz, 1H), 5.07 (d, $J$ = 10.3 Hz, 1H), 4.64 – 4.52 (m, 2H), 4.31 (t, $J$ = 6.6 Hz, 2H), 3.68 – 3.55 (m, 1H), 2.62 (t, $J$ = 10.0 Hz, 1H), 1.81 – 1.73 (m, 2H), 1.57 – 1.50 (m, 2H), 1.50 – 1.38 (m, 5H), 1.33 – 1.29 (m, 8H), 1.27 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.8, 140.4 (d, $J_{C\text{-}P}$ = 4.7 Hz), 132.9, 130.6, 129.6, 128.4, 114.4, 70.9 (d, $J_{C\text{-}P}$ = 5.8 Hz), 70.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 65.0, 54.1, 37.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 28.8, 26.1, 25.2, 24.03 (d, $J_{C\text{-}P}$ = 5.5 Hz), 23.95 (d, $J_{C\text{-}P}$ = 4.2 Hz), 23.94 (d, $J_{C\text{-}P}$ = 5.3 Hz), 23.90 (d, $J_{C\text{-}P}$ = 4.5 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.13.

HRMS (ESI) *m/z* calcd for $C_{21}H_{35}NO_5P^+$ $[(M+H)^+]$ 412.2247, found 412.2245.



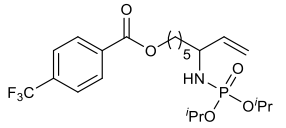
**6-((diisopropoxyphosphoryl)amino)oct-7-en-1-yl 4-methoxybenzoate (15):** This compound was prepared according to the General Procedure A, using oct-7-en-1-yl 4-methoxybenzoate (52.5 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (59.2 mg, 67% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 6.95 – 6.88 (m, 2H), 5.79 – 5.70 (m, 1H), 5.20 – 5.12 (m, 1H), 5.09 – 5.02 (m, 1H), 4.67 – 4.51 (m, 2H), 4.28 (t, $J$ = 6.6 Hz, 2H), 3.86 (d, $J$ = 1.8 Hz, 3H), 3.66 – 3.56 (m, 1H), 2.59 (t, $J$ = 10.0 Hz, 1H), 1.80 – 1.71 (m, 2H), 1.57 – 1.50 (m, 2H), 1.48 – 1.37 (m, 5H), 1.33 – 1.29 (m, 8H), 1.27 (d, $J$ = 6.1 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.5, 163.4, 140.4 (d, $J_{C-P}$ = 4.9 Hz), 131.6, 123.0, 114.4, 113.7, 70.9 (d, $J_{C-P}$ = 5.9 Hz), 70.8 (d, $J_{C-P}$ = 5.7 Hz), 64.7, 55.5, 54.1, 37.0 (d, $J_{C-P}$ = 5.7 Hz), 28.8, 26.0, 25.2 24.02 (d, $J_{C-P}$ = 5.4 Hz), 23.94 (d, $J_{C-P}$ = 4.2 Hz), 23.92 (d, $J_{C-P}$ = 5.5 Hz), 23.88 (d, $J_{C-P}$ = 4.2 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.12.

HRMS (ESI) *m/z* calcd for $C_{22}H_{37}NO_6P^+$ [$(M+H)^+$] 442.2353, found 442.2352.



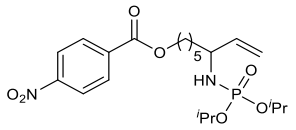
**6-((diisopropoxyphosphoryl)amino)oct-7-en-1-yl 4-(trifluoromethyl)benzoate (16):** This compound was prepared according to the General Procedure A, using oct-7-en-1-yl 4-(trifluoromethyl)benzoate (60.1 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (70.9 mg, 74% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, $J$ = 8.1 Hz, 2H), 7.71 (d, $J$ = 8.2 Hz, 2H), 5.80 – 5.69 (m, 1H), 5.21 – 5.13 (m, 1H), 5.10 – 5.01 (m, 1H), 4.63 – 4.51 (m, 2H), 4.35 (t, $J$ = 6.6 Hz, 2H), 3.67 – 3.58 (m, 1H), 2.56 (t, $J$ = 10.0 Hz, 1H), 1.82 – 1.75 (m, 2H), 1.59 – 1.51 (m, 2H), 1.50 – 1.37 (m, 4H), 1.33 – 1.29 (m, 9H), 1.27 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 165.6, 140.4 (d, $J_{C-P}$ = 4.7 Hz), 134.5 (d, $J_{C-F}$ = 32.7 Hz), 133.8, 130.1, 125.5 (d, $J_{C-F}$ = 3.8 Hz), 123.7 (d, $J_{C-F}$ = 272.9 Hz), 114.5, 71.0 (d, $J_{C-P}$ = 5.9 Hz), 70.9 (d, $J_{C-P}$ = 5.8 Hz), 65.6, 54.1, 37.0 (d, $J_{C-P}$ = 5.6 Hz), 28.7, 26.0, 25.2, 24.06 (d, $J_{C-P}$ = 5.3 Hz), 23.98 (d, $J_{C-P}$ = 4.2 Hz), 23.96 (d, $J_{C-P}$ = 5.6 Hz), 23.92 (d, $J_{C-P}$ = 4.6 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.11.

HRMS (ESI) *m/z* calcd for $C_{22}H_{34}F_3NO_5P^+$ [$(M+H)^+$] 480.2121, found 480.2123.



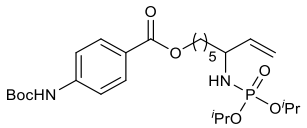
**6-((diisopropoxyphosphoryl)amino)oct-7-en-1-yl 4-nitrobenzoate (17):** This compound was prepared according to the General Procedure A, using oct-7-en-1-yl 4-nitrobenzoate (55.5 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (48.4 mg, 53% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 8.32 – 8.26 (m, 2H), 8.24 – 8.17 (m, 2H), 5.80 – 5.69 (m, 1H), 5.24 – 5.14 (m, 1H), 5.11 – 5.05 (m, 1H), 4.65 – 4.52 (m, 2H), 4.37 (t, *J* = 6.7 Hz, 2H), 3.68 – 3.58 (m, 1H), 2.57 (t, *J* = 10.0 Hz, 1H), 1.86 – 1.75 (m, 2H), 1.59 – 1.51 (m, 2H), 1.49 – 1.41 (m, 4H), 1.33 – 1.29 (m, 9H), 1.28 (d, *J* = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 164.9, 150.6, 140.4 (d, $J_{C-P}$ = 5.0 Hz), 135.9, 130.8, 123.7, 114.5, 71.0 (d, $J_{C-P}$ = 5.9 Hz), 70.9 (d, $J_{C-P}$ = 5.6 Hz), 66.0, 54.1, 37.0 (d, $J_{C-P}$ = 5.6 Hz), 28.7, 26.0, 25.2, 24.06 (d, $J_{C-P}$ = 5.4 Hz), 23.98 (d, $J_{C-P}$ = 4.0 Hz), 23.96 (d, $J_{C-P}$ = 5.8 Hz), 23.92 (d, $J_{C-P}$ = 4.6 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.12.

HRMS (ESI) *m/z* calcd for $C_{21}H_{34}N_2O_7P^+$ [$(M+H)^+$] 457.2098, found 457.2099.



**6-((diisopropoxyphosphoryl)amino)oct-7-en-1-yl 4-((tert-butoxycarbonyl)amino)benzoate (18):** This compound was prepared according to the General Procedure A, using oct-7-en-1-yl 4-((tert-butoxycarbonyl)amino)benzoate (69.5 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes),

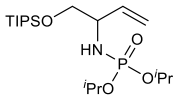
the title compound was isolated as a colorless oil (54.8 mg, 52% yield).

$^1$H NMR (500 MHz, CDCl3) δ 8.02 – 7.91 (m, 2H), 7.47 (d, $J$ = 8.5 Hz, 2H), 7.17 (s, 1H),5.80 – 5.69 (m, 1H), 5.21 – 5.12 (m, 1H), 5.09 – 5.03 (m, 1H), 4.65 – 4.53 (m, 2H), 4.28 (t, $J$ = 6.6 Hz, 2H), 3.66 – 3.56 (m, 1H), 2.60 (t, $J$ = 10.0 Hz, 1H), 1.80 – 1.70 (m, 2H), 1.59 – 1.49 (m, 11H), 1.46 – 1.40 (m, 3H), 1.34 – 1.29 (m, 9H), 1.27 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 166.4, 152.5, 143.0, 140.4 (d, $J_{C-P}$ = 5.8 Hz), 130.9, 124.6, 117.5, 114.4, 81.1, 70.9 (d, $J_{C-P}$ = 5.7 Hz), 70.8 (d, $J_{C-P}$ = 5.7 Hz), 64.8, 54.1, 37.0 (d, $J_{C-P}$ = 5.6 Hz), 28.8, 28.4, 26.0, 25.2, 24.02 (d, $J_{C-P}$ = 5.5 Hz), 23.94 (d, $J_{C-P}$ = 4.2 Hz), 23.92 (d, $J_{C-P}$ = 5.3 Hz), 23.88 (d, $J_{C-P}$ = 3.9 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.07.

HRMS (ESI) *m/z* calcd for $C_{26}H_{44}N_2O_7P^+$ [$(M+H)^+$] 527.2881, found 527.2880.



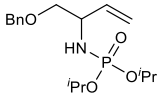

**diisopropyl (1-((triisopropylsilyl)oxy)but-3-en-2-yl)phosphoramidate (19):** This compound was prepared according to the General Procedure A, using (but-3-en-1-yloxy)triisopropylsilane (45.7 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 10% to 30% EtOAc in Hexanes), the title compound was isolated as a colorless oil (40.0 mg, 49% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.97 – 5.87 (m, 1H), 5.31 – 5.22 (m, 1H), 5.16 – 5.08 (m, 1H), 4.67 – 4.53 (m, 2H), 3.79 – 3.67 (m, 3H), 3.10 (t, $J$ = 9.6 Hz, 1H), 1.31 (t, $J$ = 5.9 Hz, 9H), 1.27 (d, $J$ = 6.3 Hz, 3H), 1.13 – 1.02 (m, 21H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.3 (d, $J_{C-P}$ = 5.2 Hz), 115.3, 70.9 (d, $J_{C-P}$ = 5.3 Hz), 70.8 (d, $J_{C-P}$ = 5.2 Hz), 67.2 (d, $J_{C-P}$ = 5.6 Hz), 55.6, 24.02 (d, $J_{C-P}$ = 5.5 Hz), 23.97 (d, $J_{C-P}$ = 4.2 Hz), 23.89 (d, $J_{C-P}$ = 5.6 Hz), 23.87 (d, $J_{C-P}$ = 4.2 Hz), 18.1, 12.0.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.59.

HRMS (ESI) *m/z* calcd for $C_{19}H_{43}NO_4PSi^+$ [$(M+H)^+$] 408.2693, found 408.2691.




**diisopropyl (1-(benzyloxy)but-3-en-2-yl)phosphoramidate (20):** This compound was prepared according to the General Procedure A, using ((but-3-en-1-yloxy)methyl)benzene (32.4 mg, 0.2

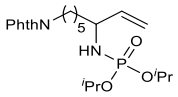
mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (20.5 mg, 30% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 5.94 – 5.84 (m, 1H), 5.33 – 5.25 (m, 1H), 5.18 – 5.12 (m, 1H), 4.61 – 4.54 (m, 2H), 4.53 (d, $J$ = 3.2 Hz, 2H), 3.89 – 3.79 (m, 1H), 3.57 – 3.45 (m, 2H), 3.01 (t, $J$ = 10.0 Hz, 1H), 1.31 – 1.23 (m, 12H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.1, 138.0 (d, $J_{C\text{-}P}$ = 5.1 Hz), 128.5, 127.83, 127.79, 115.7, 73.6 (d, $J_{C\text{-}P}$ = 5.3 Hz), 73.4, 71.0 (d, $J_{C\text{-}P}$ = 6.4 Hz), 70.9 (d, $J_{C\text{-}P}$ = 6.0 Hz), 53.8, 24.01 (d, $J_{C\text{-}P}$ = 5.0 Hz), 23.96 (d, $J_{C\text{-}P}$ = 5.6 Hz), 23.95 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.92 (d, $J_{C\text{-}P}$ = 4.0 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.26.

HRMS (ESI) *m/z* calcd for $C_{17}H_{29}NO_4P^+$ [$(M+H)^+$] 342.1829, found 342.1830.



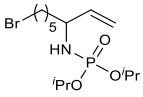

**diisopropyl (8-(1,3-dioxoisoindolin-2-yl)oct-1-en-3-yl)phosphoramidate (21):** This compound was prepared according to the General Procedure A, using 2-(oct-7-en-1-yl)isoindoline-1,3-dione (51.5mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a colorless oil (62.9 mg, 72% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.75 (m, 2H), 7.71 – 7.64 (m, 2H), 5.76 – 5.64 (m, 1H), 5.16 – 5.09 (m, 1H), 5.05 – 4.98 (m, 1H), 4.60 – 4.48 (m, 2H), 3.64 (t, $J$ = 7.3 Hz, 2H), 3.58 – 3.51 (m, 1H), 2.56 (t, $J$ = 10.0 Hz, 1H), 1.70 – 1.59 (m, 2H), 1.50 – 1.42 (m, 2H), 1.36 – 1.29 (m, 4H), 1.30 – 1.26 (m, 9H), 1.23 (d, $J$ = 6.3 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 168.5, 140.4 (d, $J_{C\text{-}P}$ = 4.7 Hz), 134.0, 132.2, 123.2, 114.3, 70.9 (d, $J_{C\text{-}P}$ = 5.9 Hz), 70.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 54.1, 38.0, 37.0 (d, $J_{C\text{-}P}$ = 5.9 Hz), 28.6, 26.8, 25.0, 24.00 (d, $J_{C\text{-}P}$ = 5.3 Hz), 23.92 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.90 (d, $J_{C\text{-}P}$ = 6.0 Hz), 23.87 (d, $J_{C\text{-}P}$ = 4.7 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.10.

HRMS (ESI) *m/z* calcd for $C_{22}H_{34}N_2O_5P^+$ [$(M+H)^+$] 437.2200, found 437.2201.




**diisopropyl (8-bromooct-1-en-3-yl)phosphoramidate (22):** This compound was prepared

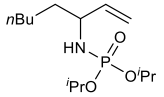
according to the General Procedure A, using 8-bromooct-1-ene (38.2 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (53.3 mg, 72% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.78 – 5.67 (m, 1H), 5.20 – 5.01 (m, 2H), 4.61 – 4.50 (m, 2H), 3.66 – 3.53 (m, 1H), 3.39 (t, $J$ = 6.8 Hz, 2H), 2.45 (t, $J$ = 9.9 Hz, 1H), 1.90 – 1.78 (m, 2H), 1.53 – 1.46 (m, 2H), 1.47 – 1.39 (m, 2H), 1.39 – 1.32 (m, 2H), 1.32 – 1.28 (m, 9H), 1.26 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 114.4, 70.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 70.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 54.1, 36.9 (d, $J_{C\text{-}P}$ = 5.5 Hz), 33.9, 32.8, 28.1, 24.6, 24.06 (d, $J_{C\text{-}P}$ = 5.4 Hz), 23.98 (d, $J_{C\text{-}P}$ = 4.2 Hz), 23.96 (d, $J_{C\text{-}P}$ = 5.6 Hz), 23.92 (d, $J_{C\text{-}P}$ = 4.7 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.08.

HRMS (ESI) *m/z* calcd for $C_{14}H_{30}BrNO_3P^+$ [$(M+H)^+$] 370.1141, found 370.1143.



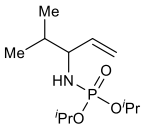

**diisopropyl oct-1-en-3-ylphosphoramidate (23):** This compound was prepared according to the General Procedure A, using 1-octene (22.4 mg, 31 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 15% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (39.0 mg, 67% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.78 – 5.66 (m, 1H), 5.13 (d, $J$ = 17.1 Hz, 1H), 5.03 (d, $J$ = 10.4 Hz, 1H), 4.61 – 4.49 (m, 2H), 3.63 – 3.49 (m, 1H), 2.69 – 2.55 (m, 1H), 1.51 – 1.43 (m, 2H), 1.34 – 1.26 (m, 12H), 1.25 (t, $J$ = 6.2 Hz, 6H), 0.85 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.6 (d, $J_{C\text{-}P}$ = 4.9 Hz), 114.1, 70.8 (d, $J_{C\text{-}P}$ = 5.8 Hz), 70.7 (d, $J_{C\text{-}P}$ = 5.5 Hz), 54.2, 37.1 (d, $J_{C\text{-}P}$ = 5.8 Hz), 31.7, 25.1, 24.01, 23.99 (d, $J_{C\text{-}P}$ = 5.4 Hz), 23.92 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.90 (d, $J_{C\text{-}P}$ = 5.4 Hz), 23.86 (d, $J_{C\text{-}P}$ = 4.2 Hz), 22.6, 14.1.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.19.

HRMS (ESI) *m/z* calcd for $C_{14}H_{31}NO_3P^+$ [$(M+H)^+$] 292.2036, found 292.2037.




**diisopropyl (4-methylpent-1-en-3-yl)phosphoramidate (24):** This compound was prepared according to the General Procedure A, using 4-methylpent-1-ene (16.8 mg, 25 μL, 0.2 mmol),

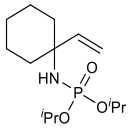
diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (39.5 mg, 75% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.79 – 5.67 (m, 1H), 5.23 – 5.08 (m, 2H), 4.65 – 4.50 (m, 2H), 3.54 – 3.42 (m, 1H), 2.60 (t, $J$ = 10.1 Hz, 1H), 1.87 – 1.72 (m, 1H), 1.35 – 1.29 (m, 9H), 1.27 (d, $J$ = 6.2 Hz, 3H), 0.89 (dd, $J$ = 6.9, 1.7 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.3 (d, $J_{C\text{-}P}$ = 4.1 Hz), 115.1, 70.7 (d, $J_{C\text{-}P}$ = 5.9 Hz), 70.6 (d, $J_{C\text{-}P}$ = 5.7 Hz), 59.4, 33.4 (d, $J_{C\text{-}P}$ = 5.9 Hz), 23.91 (d, $J_{C\text{-}P}$ = 5.5 Hz), 23.84 (d, $J_{C\text{-}P}$ = 4.0 Hz), 23.82 (d, $J_{C\text{-}P}$ = 5.9 Hz), 23.77 (d, $J_{C\text{-}P}$ = 4.3 Hz), 18.2, 17.9.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.47.

HRMS (ESI) *m/z* calcd for $C_{12}H_{27}NO_3P^+$ [$(M+H)^+$] 264.1723, found 264.1722.



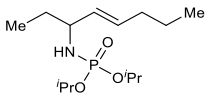

**diisopropyl (1-vinylcyclohexyl)phosphoramidate (25):** This compound was prepared according to the General Procedure A, using vinylcyclohexane (22.0 mg, 27 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (39.9 mg, 69% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 6.04 – 5.94 (m, 1H), 5.16 (d, $J$ = 17.6 Hz, 1H), 5.09 (d, $J$ = 10.8 Hz, 1H), 4.66 – 4.53 (m, 2H), 2.70 (d, $J$ = 7.0 Hz, 1H), 1.82 – 1.74 (m, 2H), 1.68 – 1.55 (m, 4H), 1.53 – 1.40 (m, 4H), 1.35 – 1.28 (m, 12H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 144.5, 113.1, 70.9 (d, $J_{C\text{-}P}$ = 5.9 Hz), 55.7, 37.0 (d, $J_{C\text{-}P}$ = 5.4 Hz), 25.7, 23.97, 23.93, 22.3.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 4.92.

HRMS (ESI) *m/z* calcd for $C_{14}H_{29}NO_3P^+$ [$(M+H)^+$] 290.1880, found 290.1879.




**diisopropyl (E)-oct-4-en-3-ylphosphoramidate (26):** This compound was prepared according to the General Procedure A, using (E)-Oct-4-ene (22.4 mg, 31 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20%

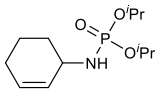
to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (36.1 mg, 62% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.78 – 5.66 (m, 1H), 5.13 (d, $J$ = 17.1 Hz, 1H), 5.03 (d, $J$ = 10.4 Hz, 1H), 4.61 – 4.49 (m, 2H), 3.63 – 3.49 (m, 1H), 2.69 – 2.55 (m, 1H), 1.51 – 1.43 (m, 2H), 1.34 – 1.26 (m, 12H), 1.25 (t, $J$ = 6.2 Hz, 6H), 0.85 (t, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 132.2 (d, $J_{C\text{-}P}$ = 5.0 Hz), 130.9, 70.7 (d, $J_{C\text{-}P}$ = 6.9 Hz), 70.6 (d, $J_{C\text{-}P}$ = 6.4 Hz), 55.1, 34.5, 30.4 (d, $J_{C\text{-}P}$ = 6.0 Hz), 24.06, 24.01, 23.98, 23.95, 23.93, 22.6, 13.8, 10.0.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.19.

HRMS (ESI) *m/z* calcd for $C_{14}H_{31}NO_3P^+$ [$(M+H)^+$] 292.2036, found 292.2035.



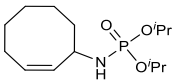

**diisopropyl cyclohex-2-en-1-ylphosphoramidate (27):** This compound was prepared according to the General Procedure A, using cyclohexene (16.4 mg, 20 µL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (30.9 mg, 59% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.75 – 5.70 (m, 1H), 5.65 – 5.60 (m, 1H), 4.62 – 4.63 (m, 2H), 3.69 – 3.54 (m, 1H), 2.58 (t, $J$ = 10.7 Hz, 1H), 1.98 – 1.85 (m, 3H), 1.71 – 1.44 (m, 3H), 1.30 (d, $J$ = 6.0 Hz, 6H), 1.29 (d, $J$ = 6.0 Hz, 6H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 130.3 (d, $J_{C\text{-}P}$ = 6.2 Hz), 129.7, 70.9 (d, $J_{C\text{-}P}$ = 6.2 Hz), 70.8 (d, $J_{C\text{-}P}$ = 6.1 Hz), 47.1, 32.0 (d, $J_{C\text{-}P}$ = 4.1 Hz), 24.8, 24.01, 23.99, 23.97, 23.95, 23.92, 20.0.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.49.

HRMS (ESI) *m/z* calcd for $C_{12}H_{25}NO_3P^+$ [$(M+H)^+$] 262.1567, found 262.1565.




**diisopropyl (Z)-cyclooct-2-en-1-ylphosphoramidate (28):** This compound was prepared according to the General Procedure A, using cis-Cyclooctene (22.0 mg, 26 µL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (41.1 mg, 71% yield).

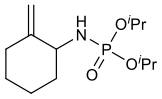
$^1$H NMR (500 MHz, $CDCl_3$) δ 5.65 – 5.57 (m, 1H), 5.33 – 5.24 (m, 1H), 4.64 – 4.47 (m, 2H), 4.05 – 3.93 (m, 1H), 2.64 (t, $J$ = 10.0 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.07 – 2.01 (m, 1H), 1.93 – 1.85 (m,

1H), 1.69 – 1.60 (m, 2H), 1.56 – 1.48 (m, 1H), 1.50 – 1.34 (m, 2H), 1.34 – 1.31 (m, 9H), 1.31 – 1.29 (m, 1H), 1.27 (d, $J$ = 6.2 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 134.2 (d, $J_{C-P}$ = 5.3 Hz), 128.7, 70.7 (d, $J_{C-P}$ = 5.4 Hz), 70.7 (d, $J_{C-P}$ = 5.3 Hz), 49.3, 38.9 (d, $J_{C-P}$ = 5.8 Hz), 29.3, 26.7, 26.6, 24.7, 24.04 (d, $J_{C-P}$ = 5.4 Hz), 23.97 (d, $J_{C-P}$ = 3.9 Hz), 23.95 (d, $J_{C-P}$ = 4.3 Hz), 23.86 (d, $J_{C-P}$ = 5.6 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.16.

HRMS (ESI) *m/z* calcd for $C_{14}H_{29}NO_3P^+$ [$(M+H)^+$] 290.1880, found 290.1880.



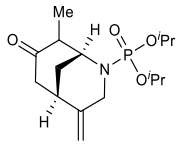

**diisopropyl (2-methylenecyclohexyl)phosphoramidate (29):** This compound was prepared according to the General Procedure A, using Methylenecyclohexane (19.2 mg, 24 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (34.1 mg, 62% yield).

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 4.91 (d, $J$ = 2.2 Hz, 1H), 4.74 (d, $J$ = 2.2 Hz, 1H), 4.67 – 4.52 (m, 2H), 3.59 – 3.45 (m, 1H), 2.77 (t, $J$ = 10.5 Hz, 1H), 2.43 – 2.35(m, 1H), 2.11 – 2.04 (m, 1H), 2.02 – 1.96 (m, 1H), 1.81 – 1.73 (m, 1H), 1.73 – 1.64 (m, 1H), 1.54 – 1.43 (m, 1H), 1.38 – 1.30 (m, 10H), 1.28 – 1.23 (m, 4H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 150.5 (d, $J_{C-P}$ = 6.0 Hz), 106.0, 70.9 (d, $J_{C-P}$ = 5.7 Hz), 70.8 (d, $J_{C-P}$ = 5.5 Hz), 54.5, 37.8 (d, $J_{C-P}$ = 3.4 Hz), 34.9, 27.8, 25.3, 24.1 (d, $J_{C-P}$ = 5.5 Hz), 24.0 (d, $J_{C-P}$ = 4.1 Hz), 23.9 (d, $J_{C-P}$ = 4.4 Hz), 23.8 (d, $J_{C-P}$ = 5.6 Hz).

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.46.

HRMS (ESI) *m/z* calcd for $C_{13}H_{27}NO_3P^+$ [$(M+H)^+$] 276.1723, found 276.1724.




**diisopropyl (8-methyl-4-methylene-7-oxo-2-azabicyclo[3.3.1]nonan-2-yl)phosphonate (30):** This compound was prepared according to the General Procedure A, using L(-)-Carvone (30.0 mg, 31 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a

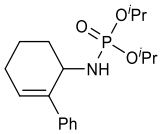
colorless oil (27.0 mg, 41% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 4.83 – 4.70 (m, 2H), 4.57 – 4.48 (m, 1H), 4.48 – 4.39 (m, 1H), 4.28 – 4.21 (m, 1H), 3.57 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.19 (dd, *J* = 16.0, 7.8 Hz, 1H), 3.07 – 3.01 (m, 1H), 2.63 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.52 – 2.41 (m, 2H), 2.11 – 2.04 (m, 2H), 1.31 – 1.20 (m, 15H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 212.0, 144.8 (d, $J_{C-P}$ = 4.1 Hz), 109.9, 71.0 (d, $J_{C-P}$ = 6.3 Hz), 70.5 (d, $J_{C-P}$ = 5.9 Hz), 54.5 (d, $J_{C-P}$ = 4.0 Hz), 49.4 (d, $J_{C-P}$ = 3.8 Hz), 47.7, 44.0 (d, $J_{C-P}$ = 2.8 Hz), 40.0, 35.5 (d, $J_{C-P}$ = 2.9 Hz), 23.97 (d, $J_{C-P}$ = 4.2 Hz), 23.94 (d, $J_{C-P}$ = 5.0 Hz), 23.89 (d, $J_{C-P}$ = 5.1 Hz), 23.81 (d, $J_{C-P}$ = 4.4 Hz), 11.7.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 5.71.

HRMS (ESI) *m/z* calcd for $C_{16}H_{29}NO_4P^+$ [$(M+H)^+$] 330.1829, found 330.1831.



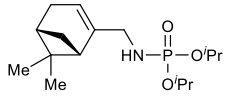

**diisopropyl (3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-yl)phosphoramidate (31):** This compound was prepared according to the General Procedure A, using 1-Phenyl-1-cyclohexene (31.6 mg, 32 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (49.3 mg, 73% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 2H), 7.32 – 7.25 (m, 2H), 7.25 – 7.17 (m, 1H), 6.07 (t, *J* = 4.0 Hz, 1H), 4.50 – 4.41(m, 1H), 4.41 – 4.33 (m, 1H), 4.33 – 4.25 (m, 1H), 2.39 (t, *J* = 9.5 Hz, 1H), 2.24 – 2.02 (m, 3H), 1.86 – 1.76 (m, 1H), 1.75 – 1.62 (m, 2H), 1.26 (d, *J* = 6.2 Hz, 4H), 1.21 (dd, *J* = 6.2 Hz, 6H), 1.20 (d, *J* = 6.2 Hz, 6H), 1.03 (d, *J* = 6.1 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.6, 139.3 (d, $J_{C-P}$ = 9.6 Hz), 128.8, 128.3, 127.0, 126.6, 70.7 (d, $J_{C-P}$ = 5.8 Hz), 47.5, 31.6, 25.9, 23.9 (d, $J_{C-P}$ = 5.0 Hz), 23.8 (d, $J_{C-P}$ = 4.5 Hz), 23.6 (d, $J_{C-P}$ = 5.4 Hz), 17.2.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 5.56.

HRMS (ESI) *m/z* calcd for $C_{18}H_{29}NO_3P^+$ [$(M+H)^+$] 338.1880, found 338.1879.




**diisopropyl (((1S,5R)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methyl)phosphoramidate (32):**

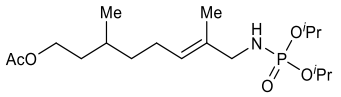
This compound was prepared according to the General Procedure A, using (1R)-(+)-alpha-pinene (27.2 mg, 32 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (33.4 mg, 52% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.41 – 5.36 (m, 1H), 4.63 – 4.51 (m, 2H), 3.39 – 3.31 (m, 2H), 2.49 – 2.39 (m, 1H), 2.39 – 2.32 (m, 1H), 2.32 – 2.14 (m, 2H), 2.11 – 2.04 (m, 2H), 1.35 – 1.21 (m, 15H), 1.12 (d, $J$ = 8.7 Hz, 1H), 0.80 (s, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 146.0 (d, $J_{C\text{-}P}$ = 8.3 Hz), 117.6, 70.8 (d, $J_{C\text{-}P}$ = 3.8 Hz), 70.7 (d, $J_{C\text{-}P}$ = 3.7 Hz), 46.3, 44.1, 41.0, 38.1, 31.7, 31.2, 26.3, 23.98, 23.94, 23.93, 21.2.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 7.03.

HRMS (ESI) *m/z* calcd for $C_{16}H_{31}NO_3P^+$ [$(M+H)^+$] 316.2036, found 316.2037.



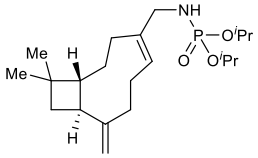

**(E)-8-((diisopropoxyphosphoryl)amino)-3,7-dimethyloct-6-en-1-yl acetate (33):** This compound was prepared according to the General Procedure A, using citronellyl acetate (39.7 mg, 45 μL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 40% to 60% EtOAc in Hexanes), the title compound was isolated as a colorless oil (37.0 mg, 49% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.34 – 5.28 (m, 1H), 4.65 – 4.50 (m, 2H), 4.16 – 3.97 (m, 2H), 3.36 (t, $J$ = 7.6 Hz, 2H), 2.53 – 2.42 (m, 1H), 2.07 – 1.93 (m, 5H), 1.70 – 1.59 (m, 4H), 1.58 – 1.48 (m, 1H), 1.47 – 1.39 (m, 1H), 1.39 – 1.23 (m, 13H), 1.22 – 1.12 (m, 1H), 0.90 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 171.3, 133.1 (d, $J_{C\text{-}P}$ = 7.3 Hz), 126.0, 70.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 63.1, 49.1, 36.8, 35.5, 29.6, 25.2, 24.0, 23.9 (d, $J_{C\text{-}P}$ = 1.4 Hz), 21.2, 19.5, 14.5.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.98.

HRMS (ESI) *m/z* calcd for $C_{18}H_{37}NO_5P^+$ [$(M+H)^+$] 378.2404, found 378.2403.




**diisopropyl ((1S,9R,Z)-6,10,10-trimethyl-2-methylenebicyclo[7.2.0]undec-5-en-3-yl)phosphor-amidate (34):** This compound was prepared according to the General Procedure B, using β-

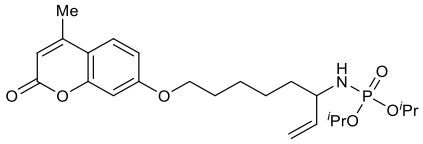
Caryophyllene (40.8 mg, 45 µL, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (26.8mg, 35% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.45 (t, $J$ = 8.1 Hz, 1H), 4.83 – 4.77 (m, 1H), 4.76 – 4.70 (m, 1H), 4.62 – 4.53 (m, 2H), 3.42 – 3.33 (m, 2H), 2.52 – 2.35 (m, 2H), 2.34 – 2.15 (m, 5H), 2.11 – 2.04 (m, 1H), 1.82 – 1.67 (m, 2H), 1.59 – 1.49 (m, 2H), 1.49 – 1.39 (m, 1H), 1.36 – 1.22 (m, 12H), 0.98 (s, 3H), 0.96 (s, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.6, 137.7 (d, $J_{C\text{-}P}$ = 7.8 Hz), 126.3, 110.7, 70.8 (d, $J_{C\text{-}P}$ = 5.6 Hz), 52.0, 46.9, 40.5, 40.2, 35.2, 33.3, 30.1, 27.4, 26.6, 25.7, 24.02, 24.00, 23.98, 23.95, 23.0.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.98.

HRMS (ESI) *m/z* calcd for $C_{21}H_{39}NO_3P^+$ [$(M+H)^+$] 384.2662, found 384.2663.



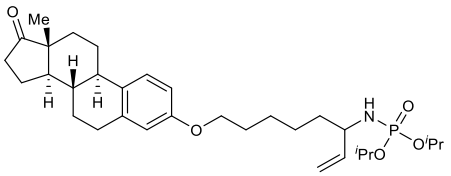

**diisopropyl (8-((4-methyl-2-oxo-2H-chromen-7-yl)oxy)oct-1-en-3-yl)phosphoramidate (35):** This compound was prepared according to the General Procedure A, using 4-methyl-7-(oct-7-en-1-yloxy)-2H-chromen-2-one (57.3 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (58.7 mg, 63% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.49 (d, $J$ = 8.8 Hz, 1H), 6.87 – 6.82 (m, 1H), 6.79 (d, $J$ = 2.5 Hz, 1H), 6.15 – 6.08 (m, 1H), 5.82 – 5.69 (m, 1H), 5.22 – 5.13 (m, 1H), 5.10 – 5.05 (m, 1H), 4.67 – 4.49 (m, 2H), 4.01 (t, $J$ = 6.5 Hz, 2H), 3.70 – 3.54 (m, 1H), 2.53 (t, $J$ = 10.0 Hz, 1H), 2.40 (d, $J$ = 1.2 Hz, 3H), 1.86 – 1.77 (m, 2H), 1.59 – 1.36 (m, 6H), 1.3 – 1.29 (m, 9H), 1.28 (d, $J$ = 6.1 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.3, 161.4, 155.4, 152.7, 140.5 (d, $J_{C\text{-}P}$ = 4.7 Hz), 125.6, 114.4, 113.5, 112.7, 111.9, 101.4, 70.9 (d, $J_{C\text{-}P}$ = 5.7 Hz), 70.8 (d, $J_{C\text{-}P}$ = 5.7 Hz), 68.5, 54.1, 37.0 (d, $J_{C\text{-}P}$ = 5.6 Hz), 29.0, 25.9, 25.2, 24.04 (d, $J_{C\text{-}P}$ = 5.3 Hz), 23.96 (d, $J_{C\text{-}P}$ = 4.2 Hz), 23.94 (d, $J_{C\text{-}P}$ = 5.5 Hz), 23.90 (d, $J_{C\text{-}P}$ = 4.5 Hz), 18.8.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.11.

HRMS (ESI) *m/z* calcd for $C_{24}H_{37}NO_6P^+$ [$(M+H)^+$] 466.2353, found 466.2355.



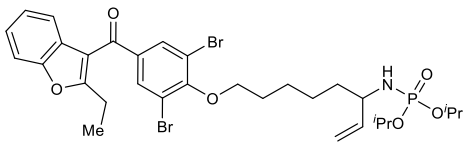
**diisopropyl (8-(((8S,9R,13R,14R)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)oxy)oct-1-en-3-yl)phosphoramidate (36):** This compound was prepared according to the General Procedure A, using (8S,9R,13R,14R)-13-methyl-3-(oct-7-en-1-yloxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (76.1 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 30% to 50% EtOAc in Hexanes), the title compound was isolated as a colorless oil (72.8 mg, 65% yield).

$^1$H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, $J$ = 8.5 Hz, 1H), 6.74 – 6.67 (m, 1H), 6.63 (d, $J$ = 2.7 Hz, 1H), 5.80 – 5.70(m, 1H), 5.21 – 5.12 (m, 1H), 5.10 – 5.02 (m, 1H), 4.64 – 4.51 (m, 2H), 3.92 (t, $J$ = 6.5 Hz, 2H), 3.68 – 3.57 (m, 1H), 2.95 – 2.79 (m, 2H), 2.59 – 2.46 (m, 2H), 2.42 – 2.35 (m, 1H), 2.28 – 2.20 (m, 1H), 2.18 – 2.09 (m, 1H), 2.08 – 2.03 (m, 1H), 2.03 – 1.97 (m, 1H), 1.97 – 1.92 (m, 1H), 1.80 – 1.72 (m, 2H), 1.63 – 1.38 (m, 12H), 1.33 – 1.29 (m, 9H), 1.27 (d, $J$ = 6.3 Hz, 3H), 0.91 (s, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 157.2, 140.5 (d, $J_{C\text{-}P}$ = 4.7 Hz), 137.8, 132.0, 126.4, 114.6, 114.3, 112.2, 70.8 (d, $J_{C\text{-}P}$ = 5.9 Hz), 70.7 (d, $J_{C\text{-}P}$ = 5.6 Hz), 67.8, 54.1, 50.5, 48.1, 44.1, 38.5, 37.1 (d, $J_{C\text{-}P}$ = 5.7 Hz), 36.0, 31.7, 29.7, 29.3, 26.7, 26.04, 26.01, 25.2, 24.03 (d, $J_{C\text{-}P}$ = 5.3 Hz), 23.95 (d, $J_{C\text{-}P}$ = 4.1 Hz), 23.93 (d, $J_{C\text{-}P}$ = 5.2 Hz), 23.89 (d, $J_{C\text{-}P}$ = 4.1Hz), 21.7, 13.9.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.13.

HRMS (ESI) *m/z* calcd for $C_{32}H_{51}NO_5P^+$ [$(M+H)^+$] 560.3499, found 560.3500.



**diisopropyl (8-(2,6-dibromo-4-(2-ethylbenzofuran-3-carbonyl)phenoxy)oct-1-en-3-yl)phosphoramidate (37):** This compound was prepared according to the General Procedure A, using (3,5-dibromo-4-(oct-7-en-1-yloxy)phenyl)(2-ethylbenzofuran-3-yl)methanone (106.9 mg, 0.2 mmol), diisopropyl phosphoramidate (54.4 mg, 0.3 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (72.8 mg,

51% yield).

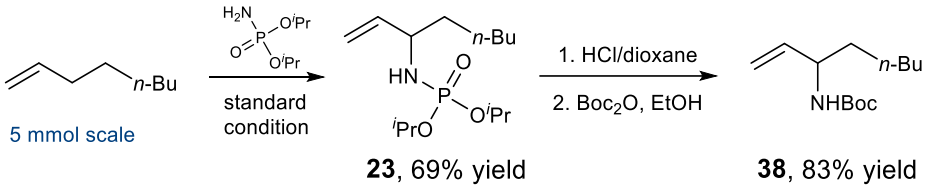
$^1$H NMR (500 MHz, $CDCl_3$) δ 7.97 (s, 2H), 7.50 – 7.47 (m, 1H), 7.43 – 7.38 (m, 1H), 7.32 – 7.27 (m, 1H), 7.5 – 7.20 (m, 1H), 5.80 – 5.72 (m, 1H), 5.20 – 5.15 (m, 1H), 5.09 – 5.04 (m, 1H), 4.65 – 4.52 (m, 2H), 4.09 (t, $J$ = 6.4 Hz, 2H), 3.70 – 3.57 (m, 1H), 2.88 (q, $J$ = 7.5 Hz, 2H), 2.65 (t, $J$ = 10.1 Hz, 1H), 2.03 (d, $J$ = 3.5 Hz, 1H), 1.94 – 1.86 (m, 2H), 1.62 – 1.53 (m, 4H), 1.49 – 1.40 (m, 2H), 1.35 (t, $J$ = 7.5 Hz, 3H), 1.32 – 1.29 (m, 9H), 1.27 (d, $J$ = 6.1 Hz, 3H), 1.26 – 1.22 (m, 1H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 188.2, 167.0, 157.2, 153.8, 140.5 (d, $J_{C-P}$ = 4.7 Hz), 137.1, 133.7, 126.5, 124.8, 124.0, 121.2, 118.8, 115.5, 114.4, 111.3, 73.9, 71.0 (d, $J_{C-P}$ = 5.8 Hz), 70.9 (d, $J_{C-P}$ = 5.6 Hz), 54.1, 37.1 (d, $J_{C-P}$ = 5.8 Hz), 30.1, 25.8, 25.3, 24.1 (d, $J_{C-P}$ = 5.2 Hz), 24.0 (d, $J_{C-P}$ = 5.5 Hz), 23.9 (d, $J_{C-P}$ = 5.7 Hz), 22.1, 12.3.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 6.16.

HRMS (ESI) *m/z* calcd for $C_{31}H_{41}Br_2NO_6P^+$ [$(M+H)^+$] 714.1012, found 714.1014

## 5. Synthetic Application-Scale up and Deprotection




**23**, 69% yield **38**, 83% yield

To an oven-dried 8 mL vial equipped with a magnetic stir bar was added diisopropyl phosphoramidate (1.36g, 7.5 mmol, 1.5 equiv.), $(tol)_3P$=Se (287 mg, 0.75 mmol, 15 mol %), $PhI(OAc)_2$ (3.22g, 10 mmol, 2.0 equiv) and $CH_3CN$ (25 mL), followed by the addition of alkene (0.56g, 0.78 mL, 5.0 mmol, 1.0 equiv.). The reaction mixture was stirred at room temperature for 24 hours, and then diluted with EtOAc (5 mL), washed with 1M HCl (2 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 mL×2). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes) to afford product **23** as white solid (1.0 g, 69% yield).

To a 8 mL vial equipped with magnetic stir bar was added compound **23** (145.7 mg, 0.5 mmol), followed by addition of HCl in dioxane (1 mL, 4 mol/L). The reaction mixture was stirred at room temperature for 16 hours when TLC checking suggested the completion of the reaction. The reaction

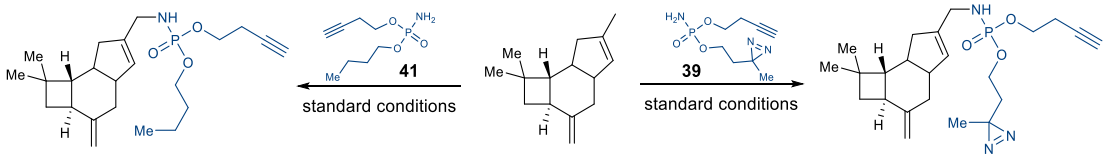
mixture was then concentrated under reduced pressure to afford crude products as yellow oil. The reaction mixture was then diluted with EtOH (2 mL), followed by the addition of TEA (208 uL, 1.5 mmol) and $Boc_2O$ (164 mg, 0.75 mmol). The reaction mixture was stirred at rt for 16 hours, and concentrated under reduced pressure to remove solvent. The reaction mixture was then diluted with EtOAc(10 mL), washed with 1M HCl (2 mL) and brine (2 mL), dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressure to afford crude product, which was purified by flash column chromatography ($SiO_2$, 10% to 20% EtOAc in Hexanes) to afford desired product as colorless oil (94.3 mg, 83% yield). The NMR spectra are consistent with the literature report.

$^1$H NMR (500 MHz, $CDCl_3$) δ 5.79 – 5.68 (m, 1H), 5.21 – 5.01 (m, 2H), 4.49 (br s, 1H), 4.08 (br s, 1H), 1.53 – 1.39 (s, 11H), 1.36 – 1.24 (m, 6H), 0.88 (t, $J$ = 6.79 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.5, 139.3, 114.3, 79.3, 52.9, 35.3, 31.7, 28.5, 25.5, 22.7, 14.1.

## 6. Biological Application

### 5.1 Probe Synthesis




**42**, 35% yield **40**, 37% yield

**but-3-yn-1-yl (2-(3-methyl-3H-diazirin-3-yl)ethyl) (((2aS,7bR)-1,1-dimethyl-3-methylene-2,2a,3,4,4a,7,7a,7b-octahydro-1H-cyclobuta[e]inden-6-yl)methyl)phosphoramidate (40)** To an oven-dried 8 mL vial equipped with a magnetic stir bar was added phosphoramidate **39** (35 mg, 0.15 mmol, 1.5 equiv.), IMeSe (3 mg, 0.03 mmol, 15 mol %), $PhI(OAc)_2$ (0.4 mmol, 2.0 equiv) and DCM (1 mL), followed by the addition of β-Caryophyllene (20.4 mg, 23 μL, 0.1 mmol). The reaction mixture was stirred at 40℃ for 24 hours, and then diluted with EtOAc (5 mL), washed with 1M HCl (2 mL). The organic layer was separated, and the aqueous layer was extracted with EtOAc (2 mL×2). The combined organic layers were dried over $Na_2SO_4$ and concentrated under reduced pressure to afford the crude product, which was purified by flash column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes) to afford desired product **40** as colorless oil (16.0 mg, 37% yield).

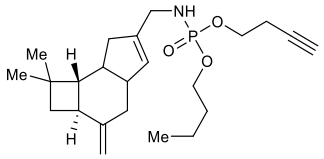
$^1$H NMR (500 MHz, $CDCl_3$) δ 5.46 (t, $J$ = 8.0 Hz, 1H), 4.81 (s, 1H), 4.73 (s, 1H), 4.17 – 4.02 (m, 3H), 4.02 – 3.87 (m, 2H), 3.44 (t, $J$ = 7.7 Hz, 2H), 2.71 – 2.53 (m, 1H), 2.61 – 2.55 (m, 2H), 2.48

(q, $J$ = 9.3 Hz, 1H), 2.31 – 2.18 (m, 4H), 2.00 (t, $J$ = 2.6 Hz, 1H), 1.76 – 1.57 (m, 6H), 1.07 (d, s, 3H), 0.99 (s, 3H), 0.96 (s, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.4, 137.5 (d, $J_{C-P}$ = 6.9 Hz), 126.8 (d, $J_{C-P}$ = 4.6 Hz), 110.8, 80.0, 70.3, 64.2 (d, $J_{C-P}$ = 4.5 Hz), 61.6 (d, $J_{C-P}$ = 5.6 Hz), 52.0, 46.8, 40.6 (d, $J_{C-P}$ = 4.5 Hz), 40.2, 35.6 (d, $J_{C-P}$ = 7.6 Hz), 35.2 (d, $J_{C-P}$ = 3.5 Hz), 33.4, 30.1, 27.3, 26.5 (d, $J_{C-P}$ = 2.7 Hz), 25.6 (d, $J_{C-P}$ = 2.1 Hz), 23.9, 23.0, 20.91, 20.9 (d, $J_{C-P}$ = 7.2 Hz), 20.0.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 8.70.

HRMS (ESI) *m/z* calcd for $C_{23}H_{35}N_3O_3P^+$ [$(M+H)^+$] 432.2411, found 432.2410.




**but-3-yn-1-yl butyl (((2aS,7bR)-1,1-dimethyl-3-methylene-2,2a,3,4,4a,7,7a,7b-octahydro-1H-cyclobuta[e]inden-6-yl)methyl)phosphoramidate** (**42**) Product **42** was prepared according to the above procedure, using β-Caryophyllene (20.4 mg, 23 μL, 0.1 mmol), phosphoramidate **41** (30.8 mg, 0.15 mmol). After purification by column chromatography ($SiO_2$, 20% to 40% EtOAc in Hexanes), the title compound was isolated as a colorless oil (14.3 mg, 35% yield).

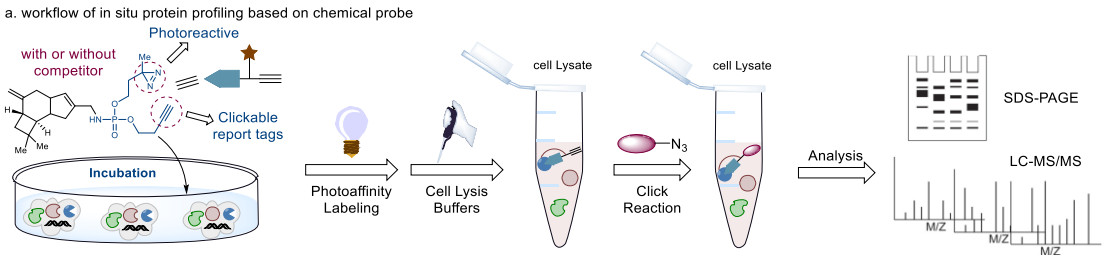
$^1$H NMR (500 MHz, $CDCl_3$) δ 5.45 (t, $J$ = 8.0 Hz, 1H), 4.81 (s, 1H), 4.73 (s, 1H), 4.14 – 3.95 (m, 4H), 3.41 (t, $J$ = 7.7 Hz, 2H), 2.63 – 2.43 (m, 4H), 2.32 – 2.18 (m, 4H), 2.14 – 2.06 (m, 1H), 2.00 (t, $J$ = 2.7 Hz, 1H), 1.73 – 1.61 (m, 5H), 1.45 – 1.36 (m, 3H), 0.99 (s, 3H), 0.96 (s, 3H), 0.93 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (126 MHz, $CDCl_3$) δ 155.5 (d, $J_{C-P}$ = 3.1 Hz), 137.6 (d, $J_{C-P}$ = 6.9 Hz), 126.7 (d, $J_{C-P}$ = 2.5 Hz), 110.8, 80.0, 70.2, 66.5 (d, $J_{C-P}$ = 5.6 Hz), 64.0 (d, $J_{C-P}$ = 5.4 Hz), 52.0 (d, $J_{C-P}$ = 3.5 Hz), 46.8, 40.6 (d, $J_{C-P}$ = 5.7 Hz), 40.2, 35.2 (d, $J_{C-P}$ = 5.0 Hz), 33.3 (d, $J_{C-P}$ = 1.7 Hz), 32.5 (d, $J_{C-P}$ = 7.1 Hz), 30.1, 27.4, 26.5 (d, $J_{C-P}$ = 4.1 Hz), 25.6 (d, $J_{C-P}$ = 2.9 Hz), 23.0 (d, $J_{C-P}$ = 1.9 Hz), 20.9 (d, $J_{C-P}$ = 7.3Hz), 18.9, 13.8.

$^{31}$P NMR (202 MHz, $CDCl_3$) δ 8.76.

HRMS (ESI) *m/z* calcd for $C_{23}H_{37}NO_3P^+$ [$(M+H)^+$] 406.2506, found 406.2504.

### 6.2 in-gel fluorescence scanning experiments




HeLa cells were seeded at a density of 5 × $10^5$ cells/well in a six well-plate and grown for 24 h before probe labeling. For concentration gradient experiment, the DMSO stock of probe (10mM) were diluted with serum-free media to the corresponding concentration and cells were treated with the probe-containing media at 37 °C for 1h under dark conditions. For the competition experiment, three different concentrations of competitor were used to co-treat cells with the probe (10μM), respectively. After probe labeling, cells were washed with cold PBS for 3 times and irradiated under UV light (365 nm) for 10 min on ice. The cells were scraped off and collected by centrifugation at 1,000 g for 3 mins at 4 °C.

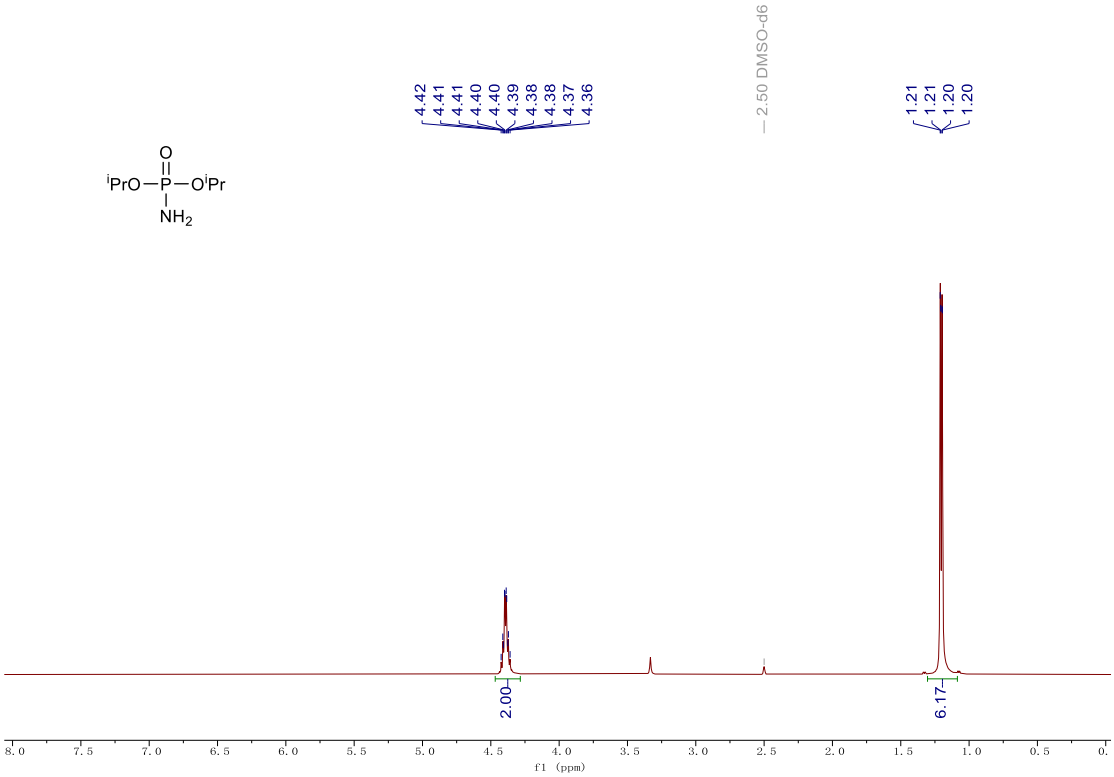
Cell pellets were resuspended in PBS with 0.1% Triton X-100 (Sigma-Aldrich) and lysed by sonication on ice. The proteome concentration was determined using the BCA protein assay (BCA Protein Assay Kit, Sangon Biotech) on a microplate reader (Thermo Fisher Scientific) and normalized to 2 mg/mL. To each sample (100 μL), 3 μL of a freshly prepared 'click' reagent mixture containing 0.05 mM TBTA (3.4 mM in DMSO), 1mM $CuSO_4$ (200mM in $H_2O$), 1mM TCEP (200mM in $H_2O$), and 50 μM TAMRA-azide (20 mM in DMSO) was added to conjugate the fluorophore to probe-labeled proteins. After each sample was immediately mixed by vortexing and gently rotated at room temperature for 2 h, 25 μL 5x SDS loading buffer were added and the sample heated for 5 min at 95℃. The samples were then separated by 10% SDS-PAGE, then visualized by in-gel fluorescence scanning (Bio-Rad ChenmiDoc TM MP) and Coomassie Brilliant Blue (CBB) staining.

References:

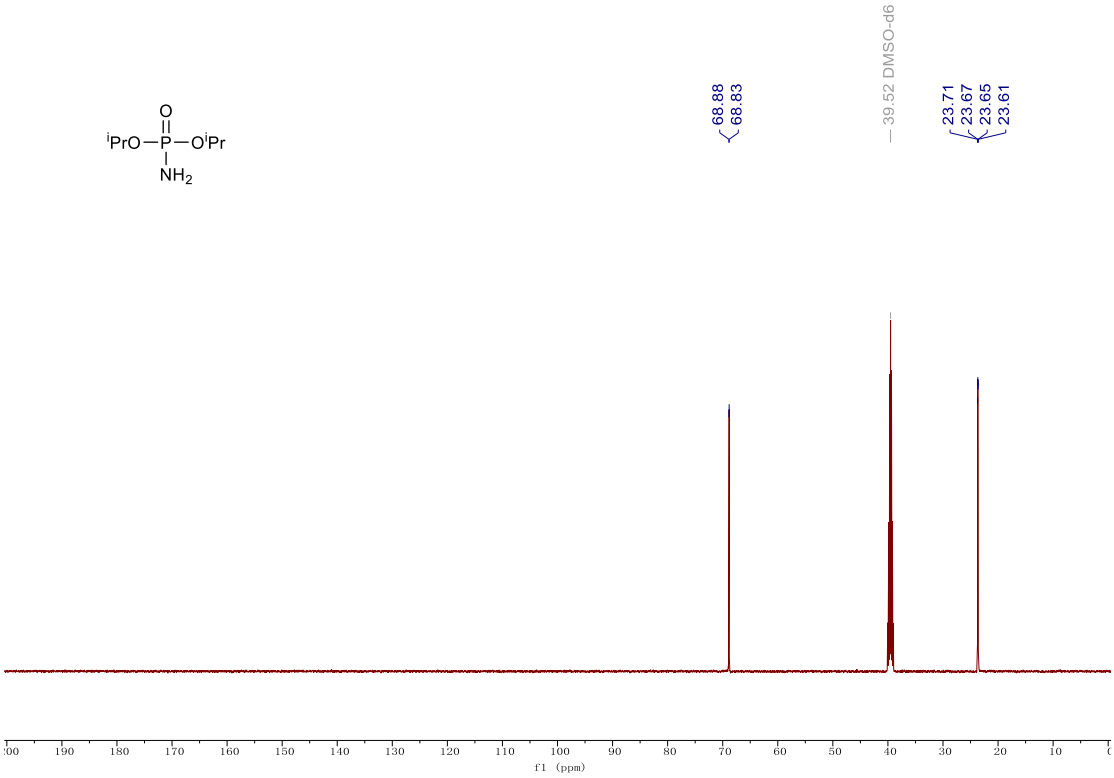
1. A. Nocentini, P. Gratteri, C. T. Supuran, *Chem. Eur. J.* **2019**, *25*, 1188 –1192.

## NMR Data

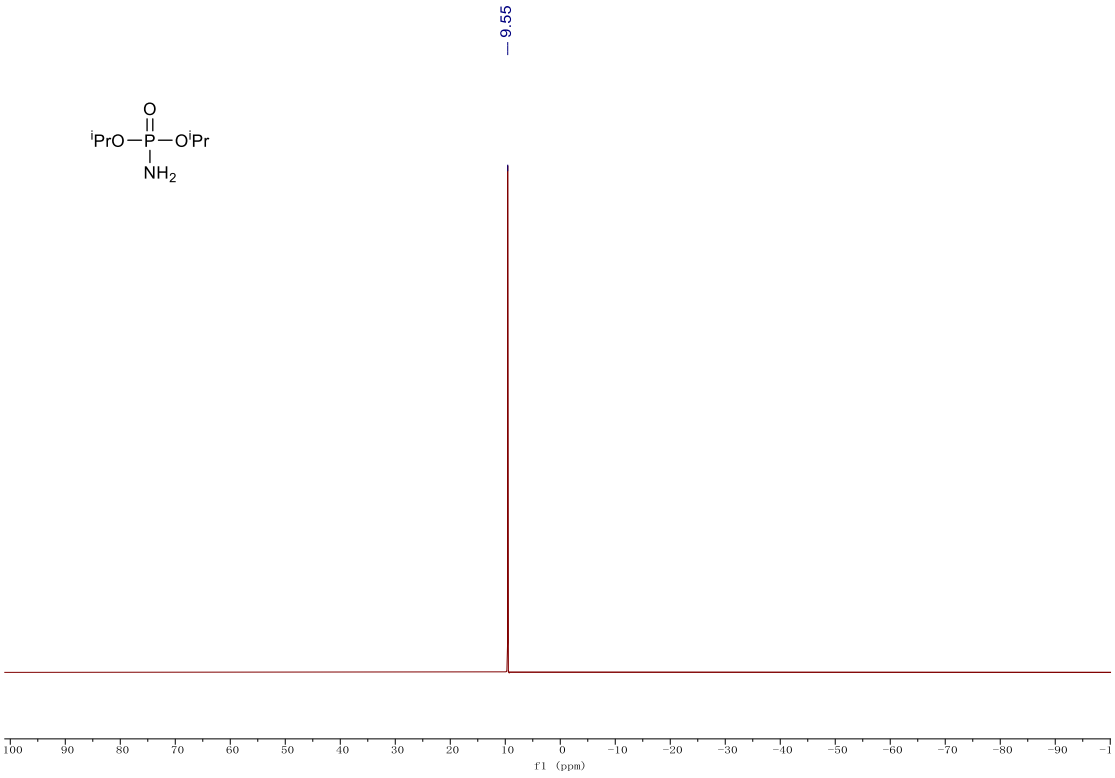
$^{1}$H NMR (500 MHz, $CDCl_3$)



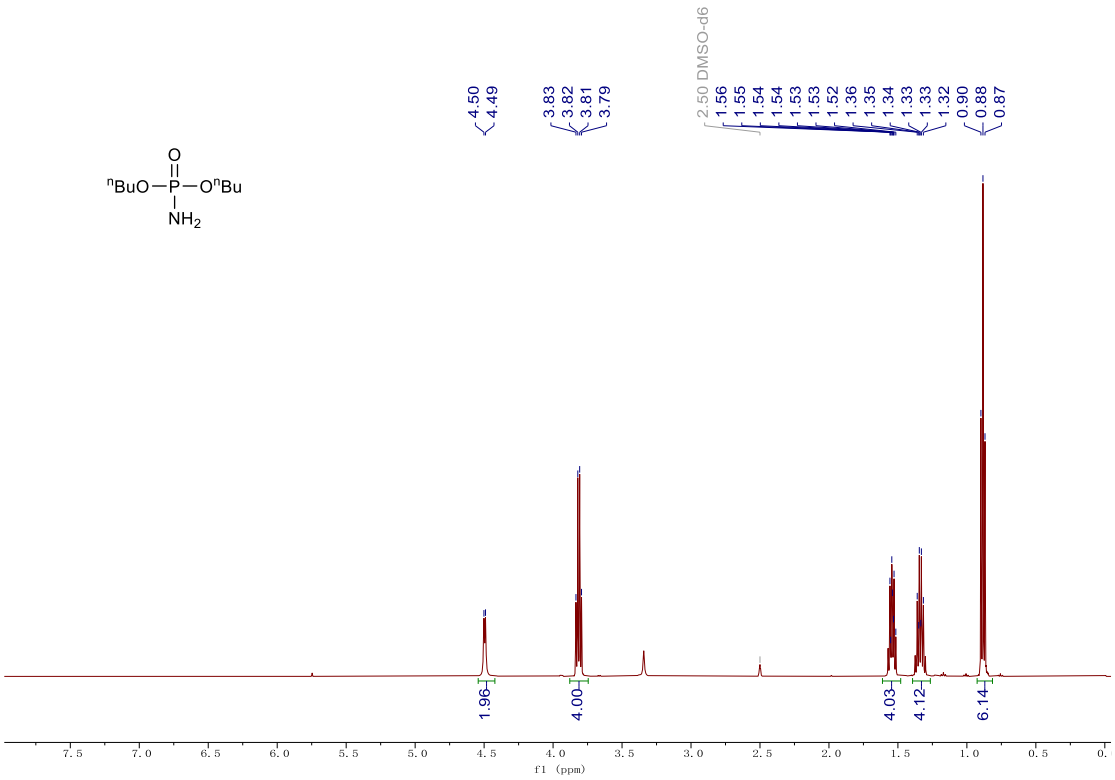

$^{13}$C NMR (126 MHz, $CDCl_3$)



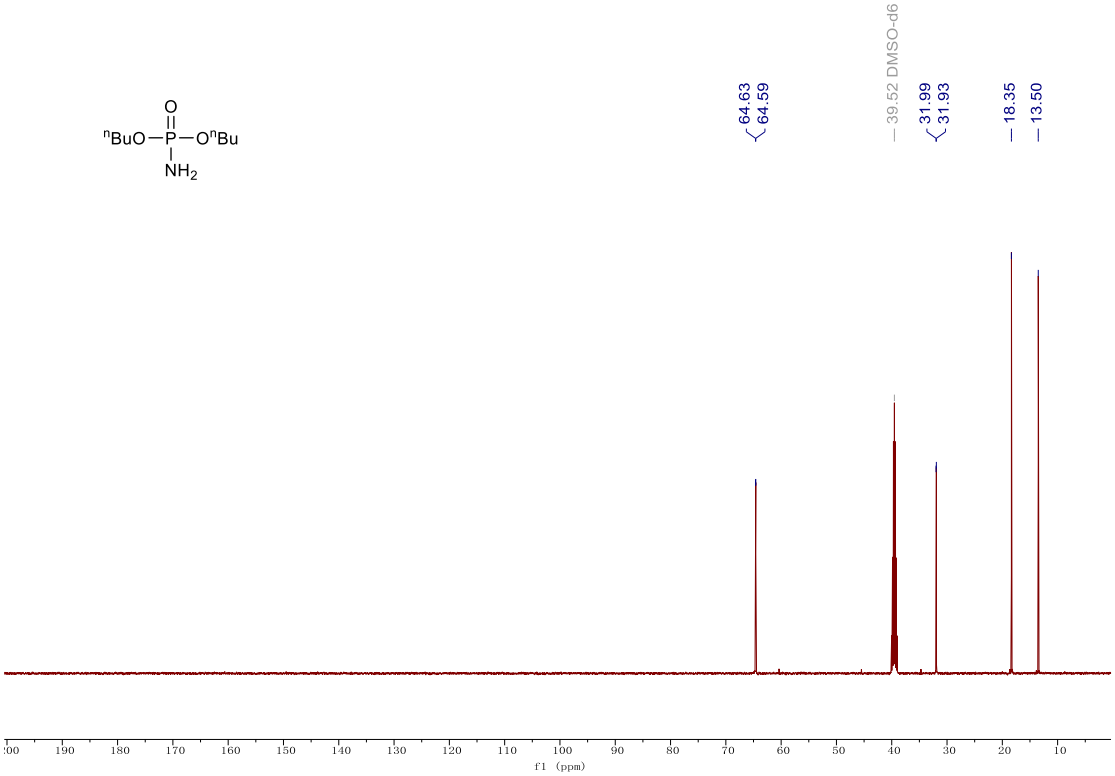
$^{31}P$ NMR (202 MHz, $CDCl_3$)



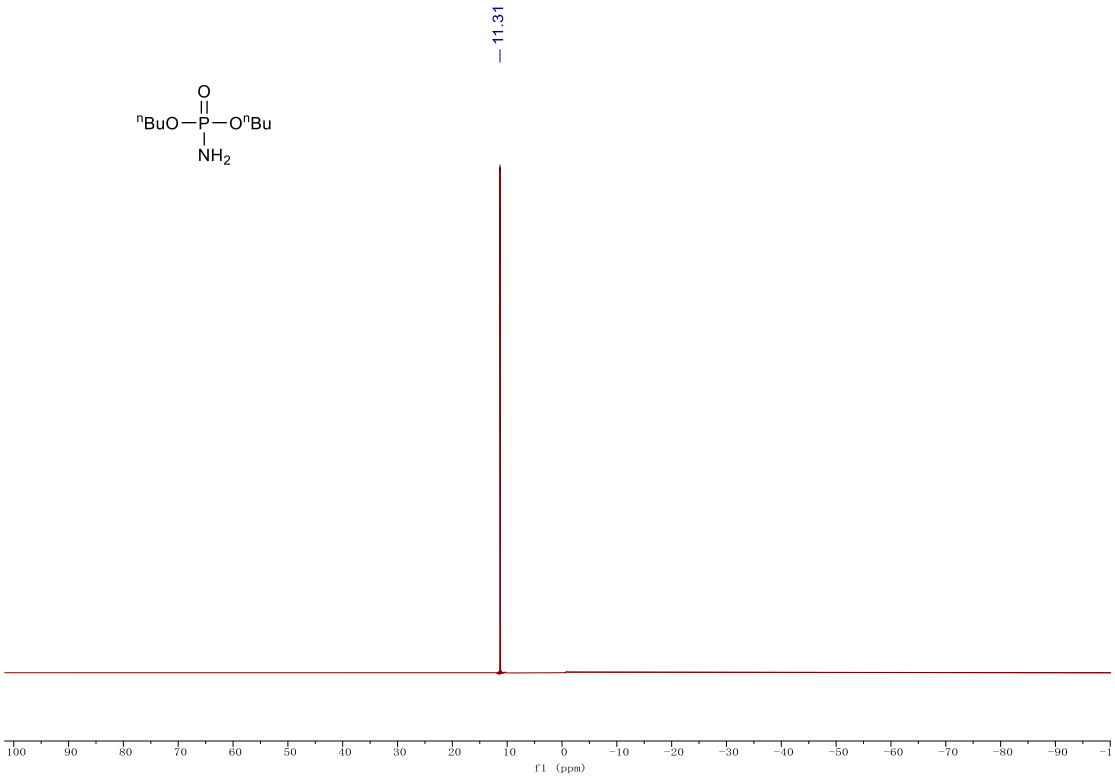

$^{1}H$ NMR (500 MHz, $CDCl_3$)



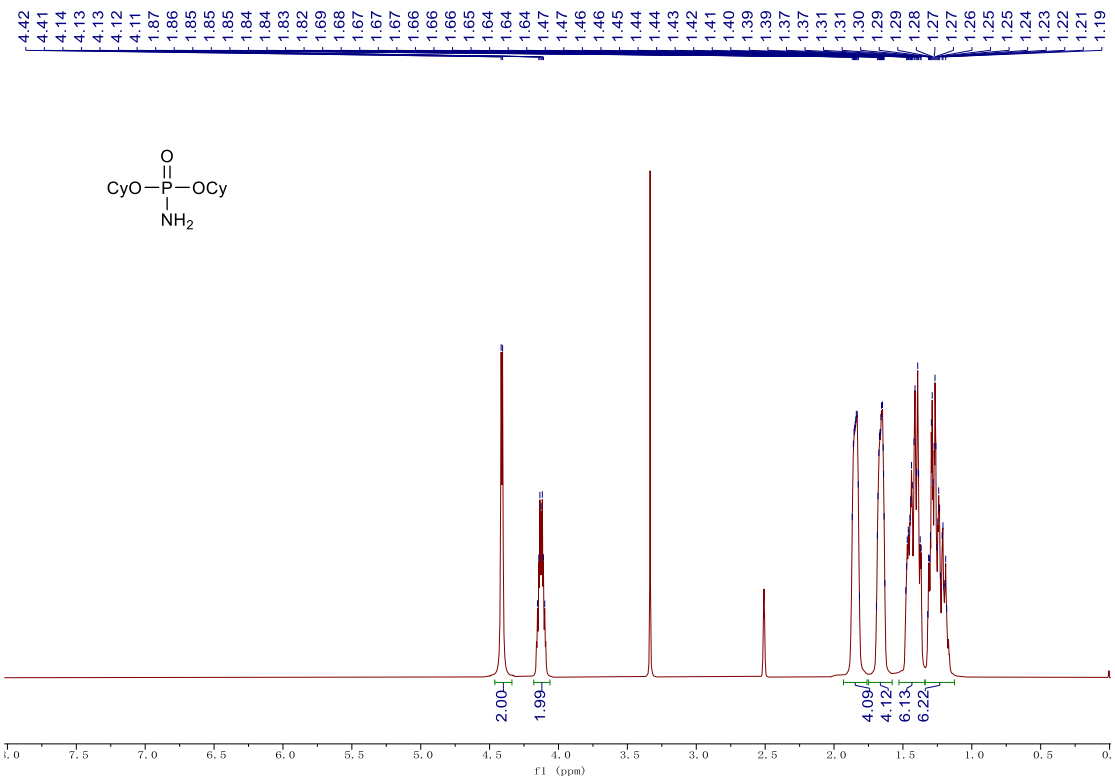
$^{13}C$ NMR (126 MHz, $CDCl_3$)



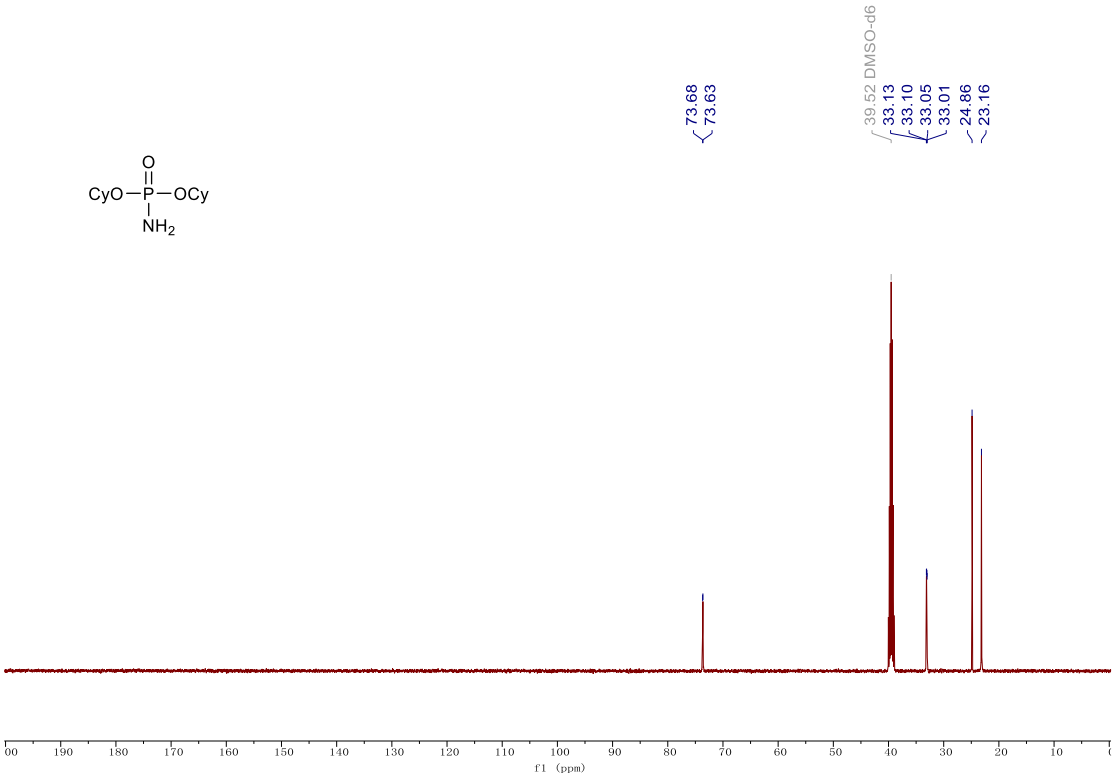

$^{31}P$ NMR (202 MHz, $CDCl_3$)



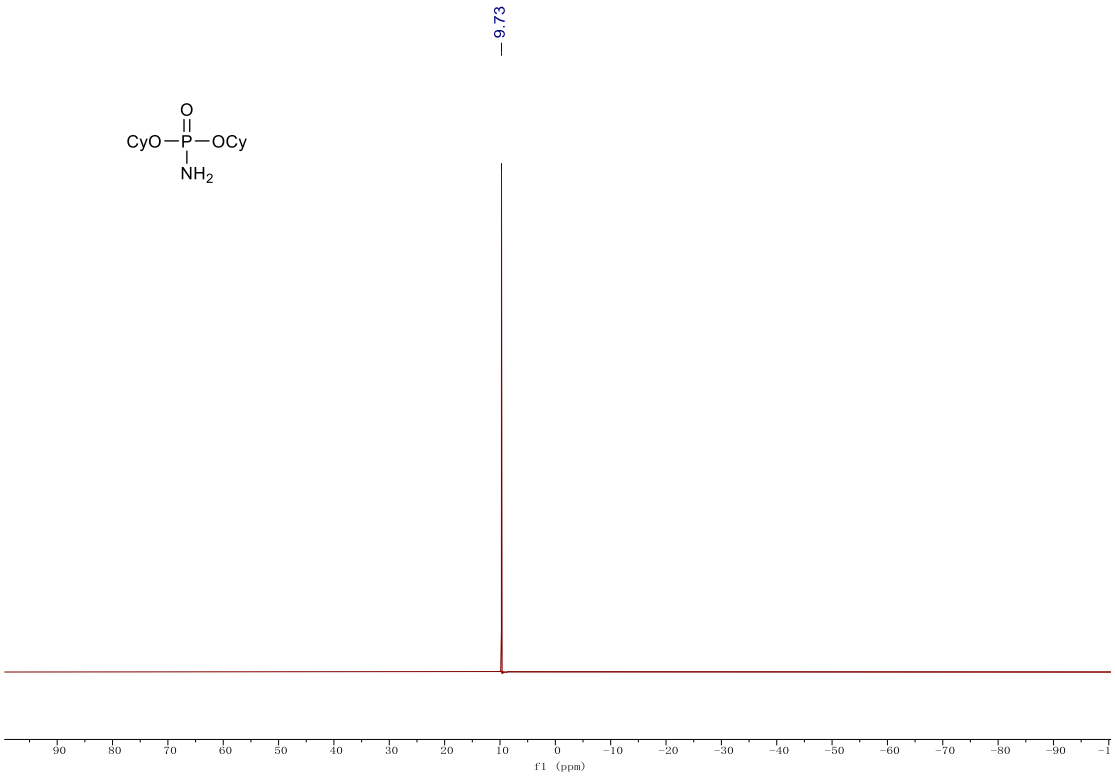
$^{1}$H NMR (500 MHz, $CDCl_3$)



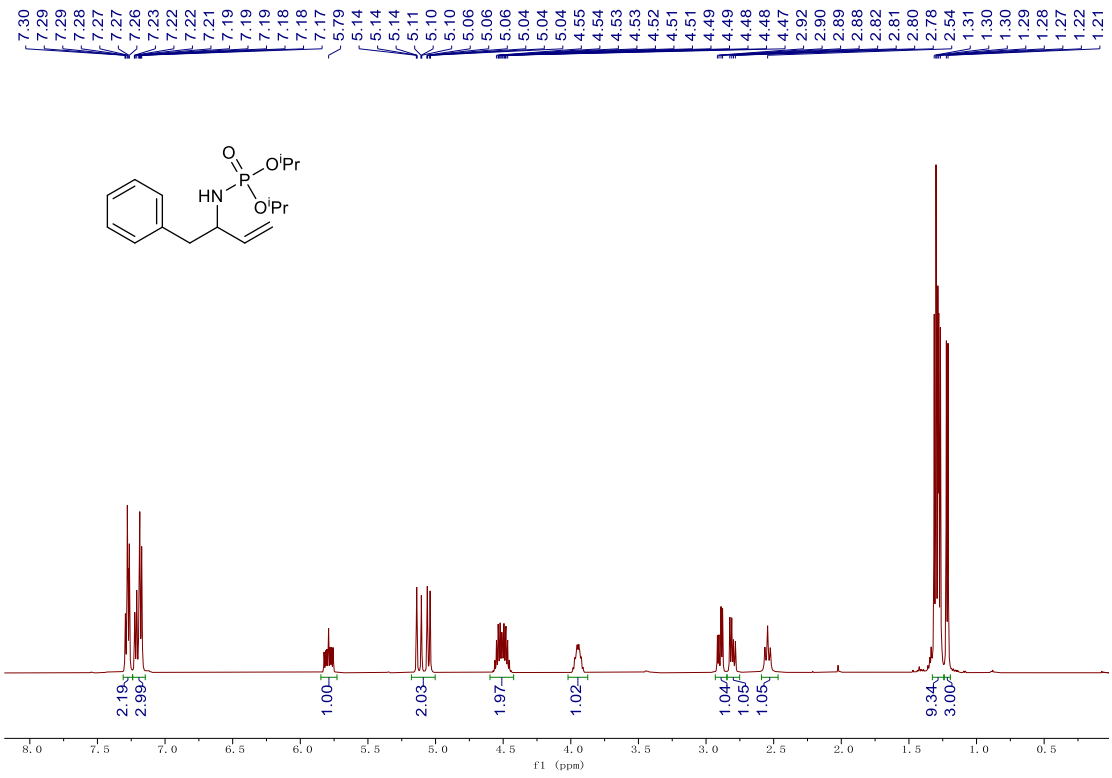

$^{13}$C NMR (126 MHz, $CDCl_3$)



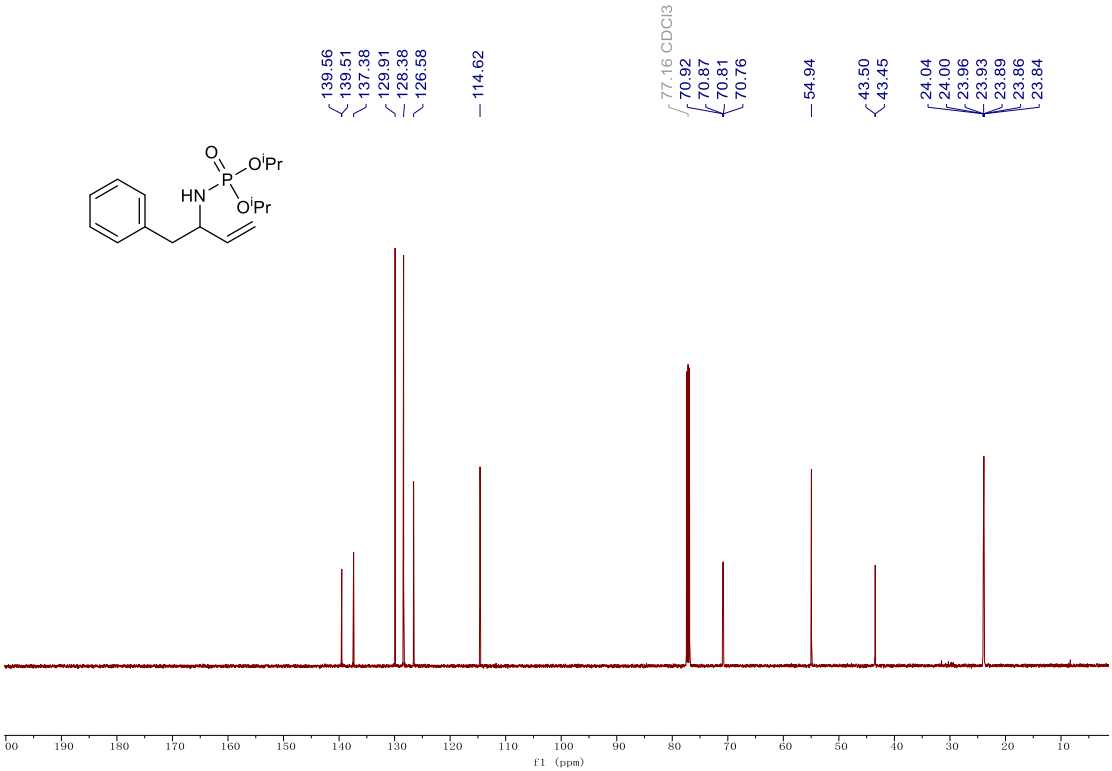
$^{31}$P NMR (202 MHz, $CDCl_3$)



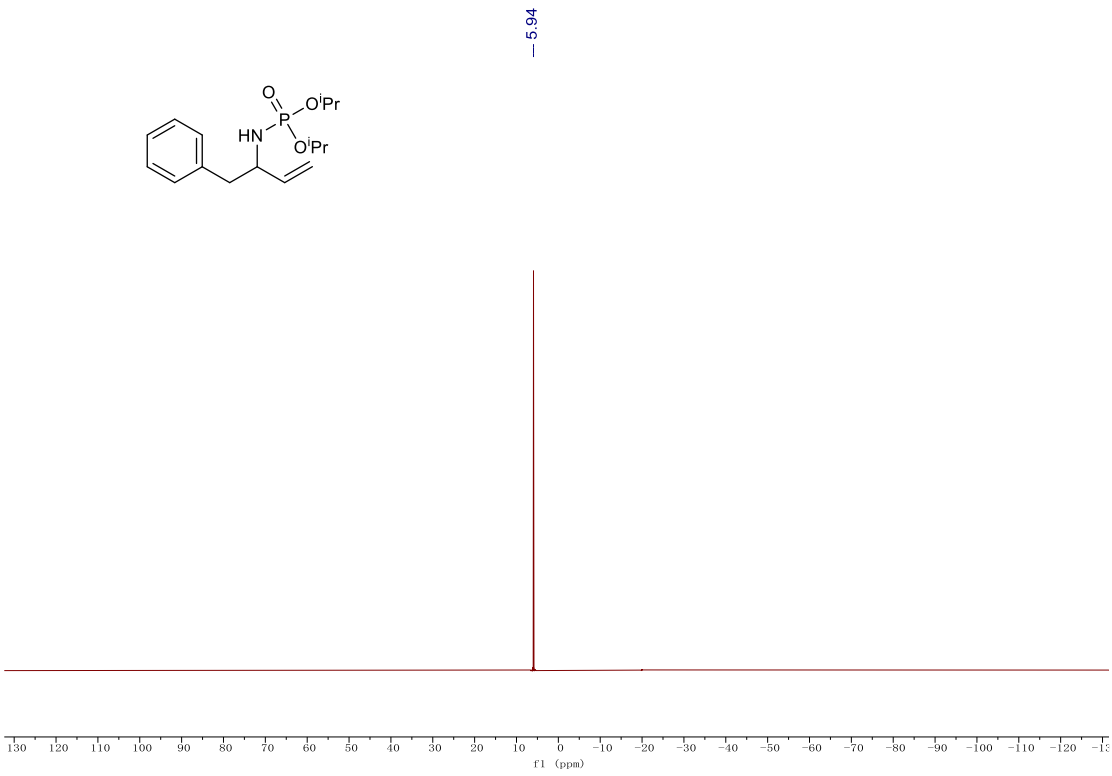

**3,** $^{1}$H NMR (500 MHz, $CDCl_3$)



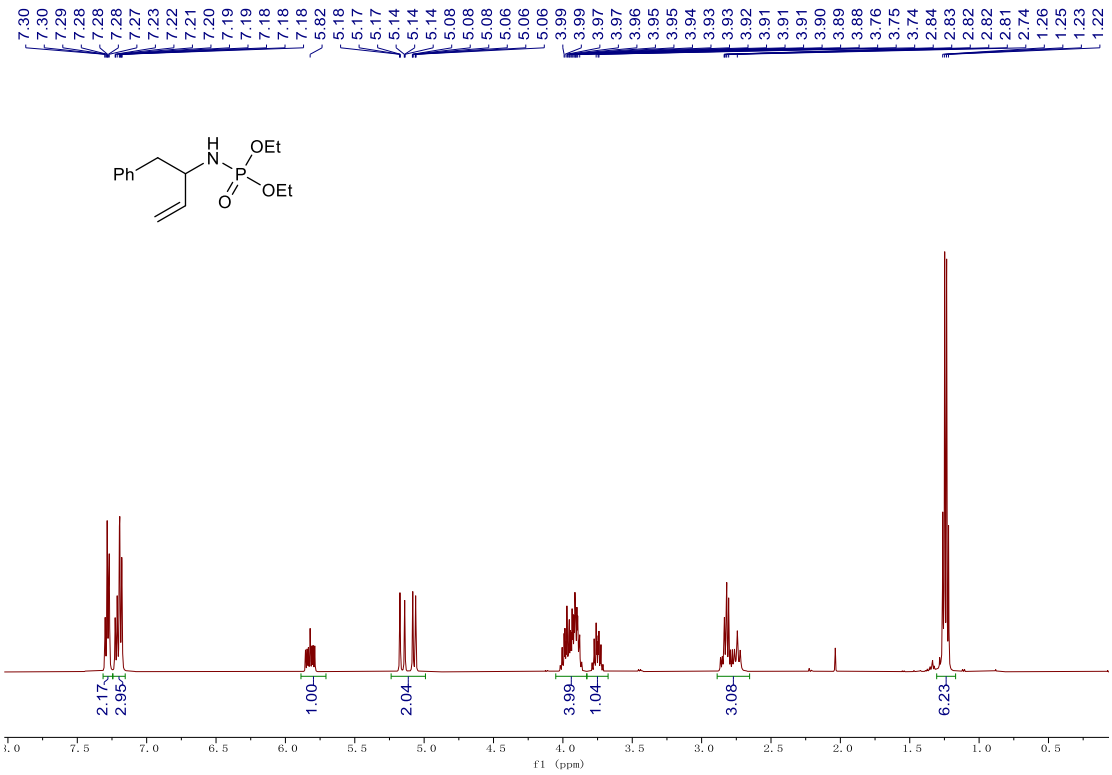
**3,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



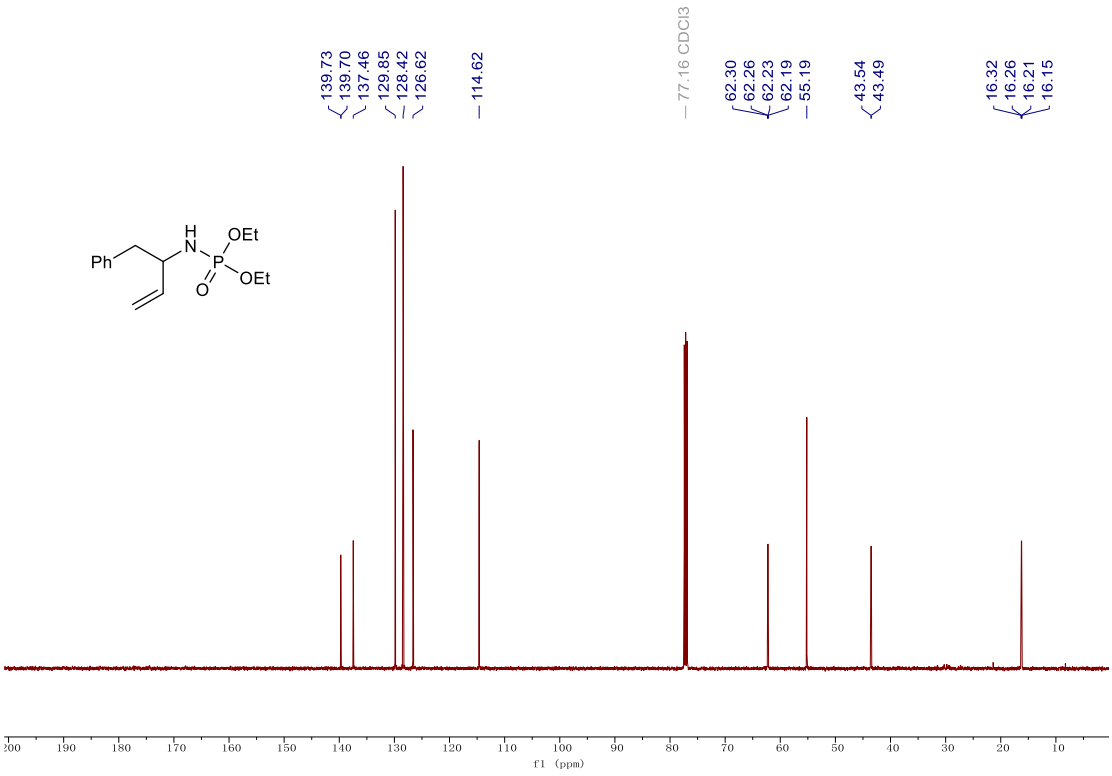

**3,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



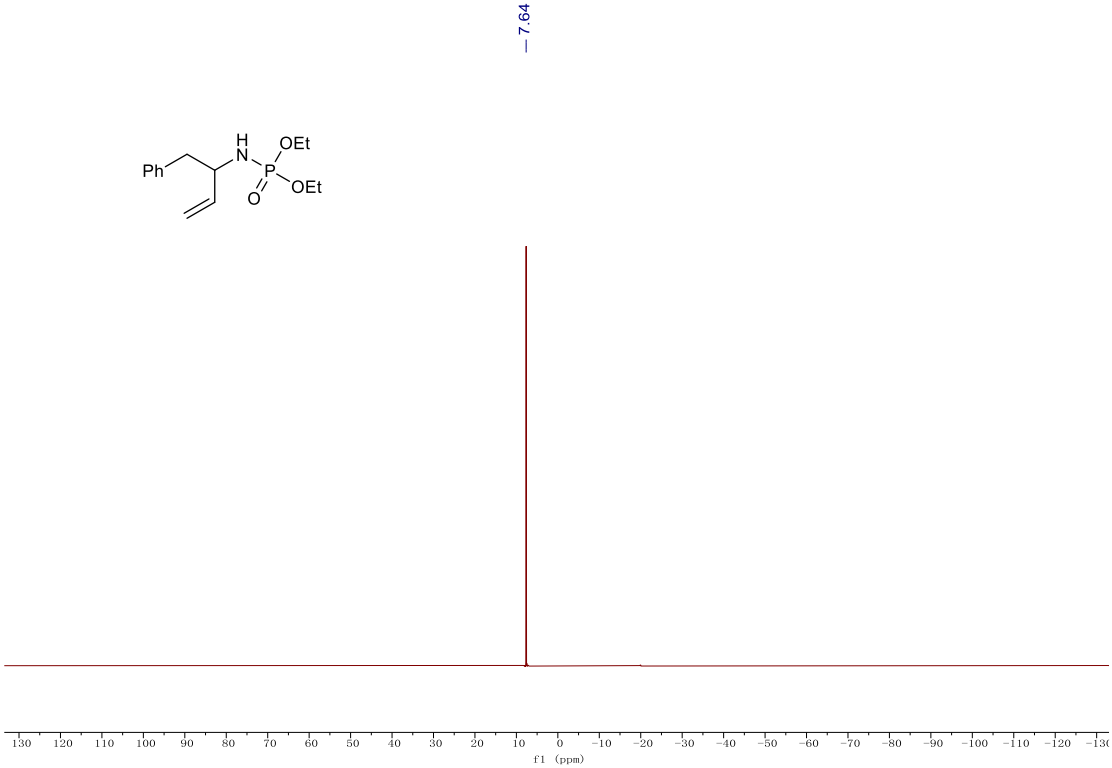
**4,** $^{1}$H NMR (500 MHz, $CDCl_3$)



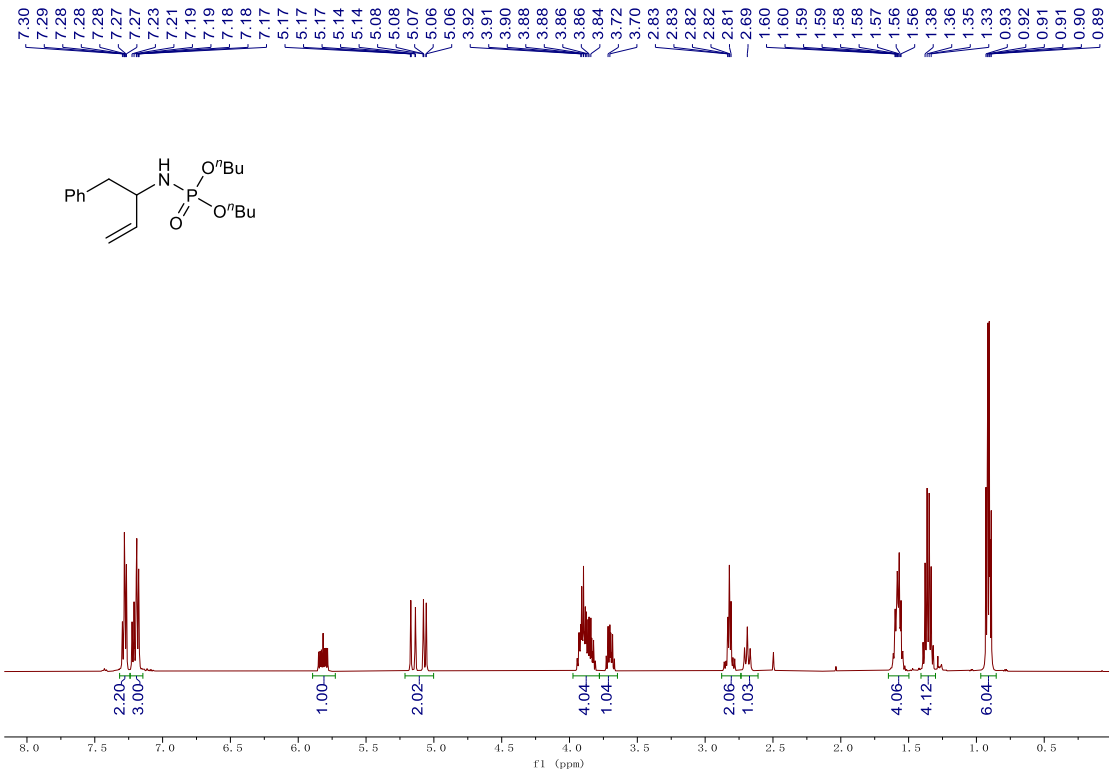

**4,** $^{13}$C NMR (126 MHz, $CDCl_3$)



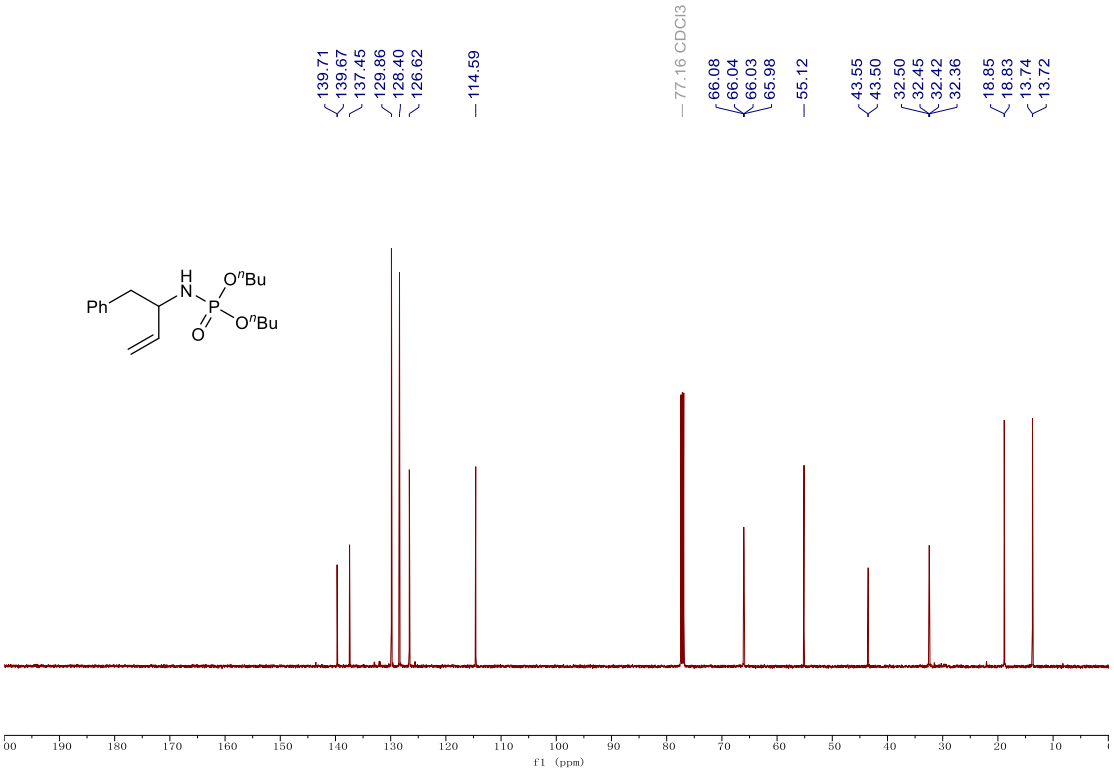
**4,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



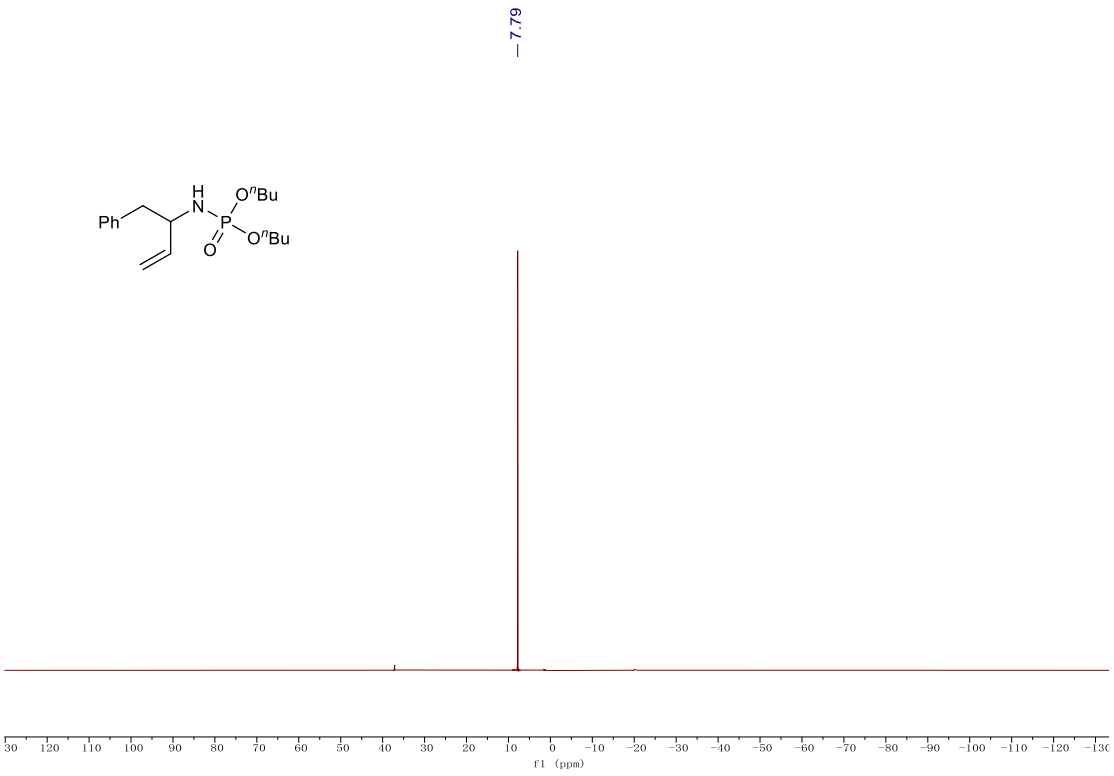

**5,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



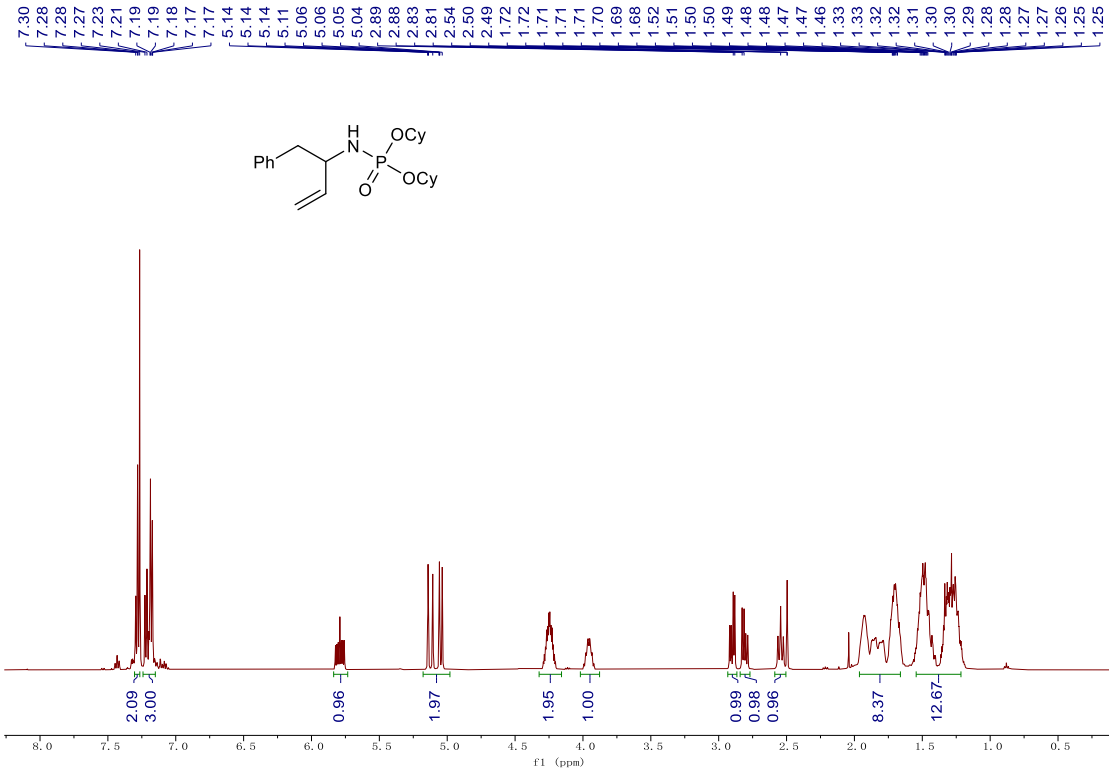
**5,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



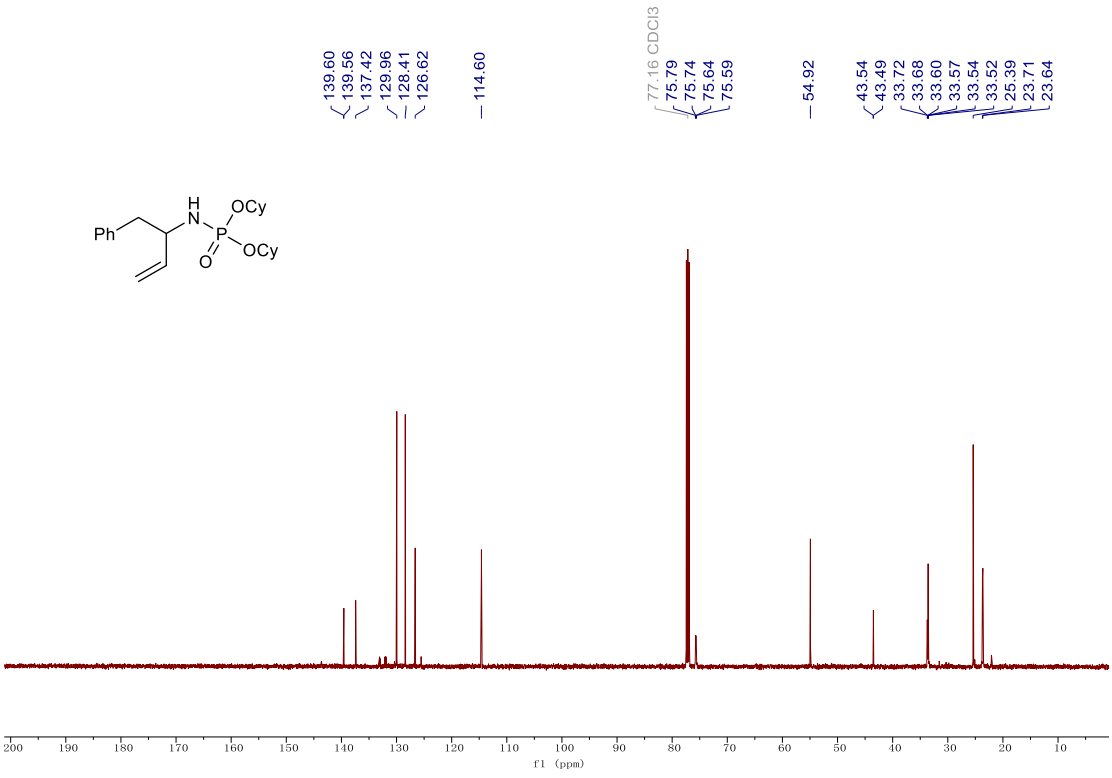

**5,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



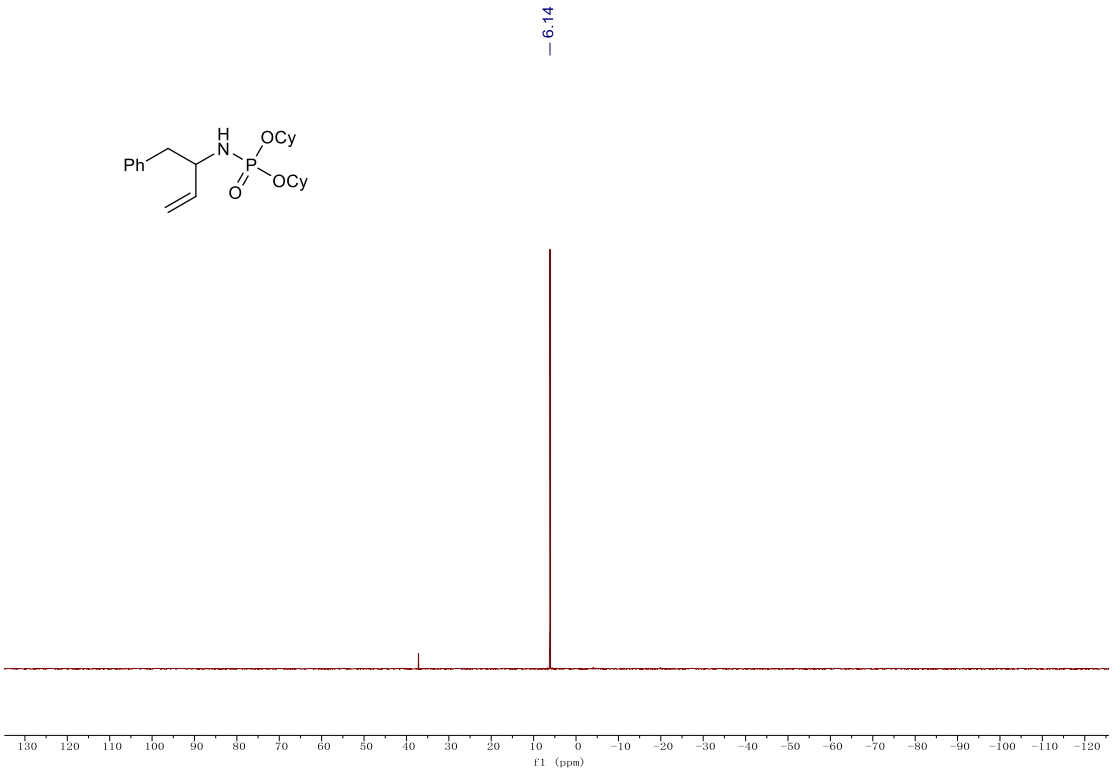
**6,** $^{1}$H NMR (500 MHz, $CDCl_3$)



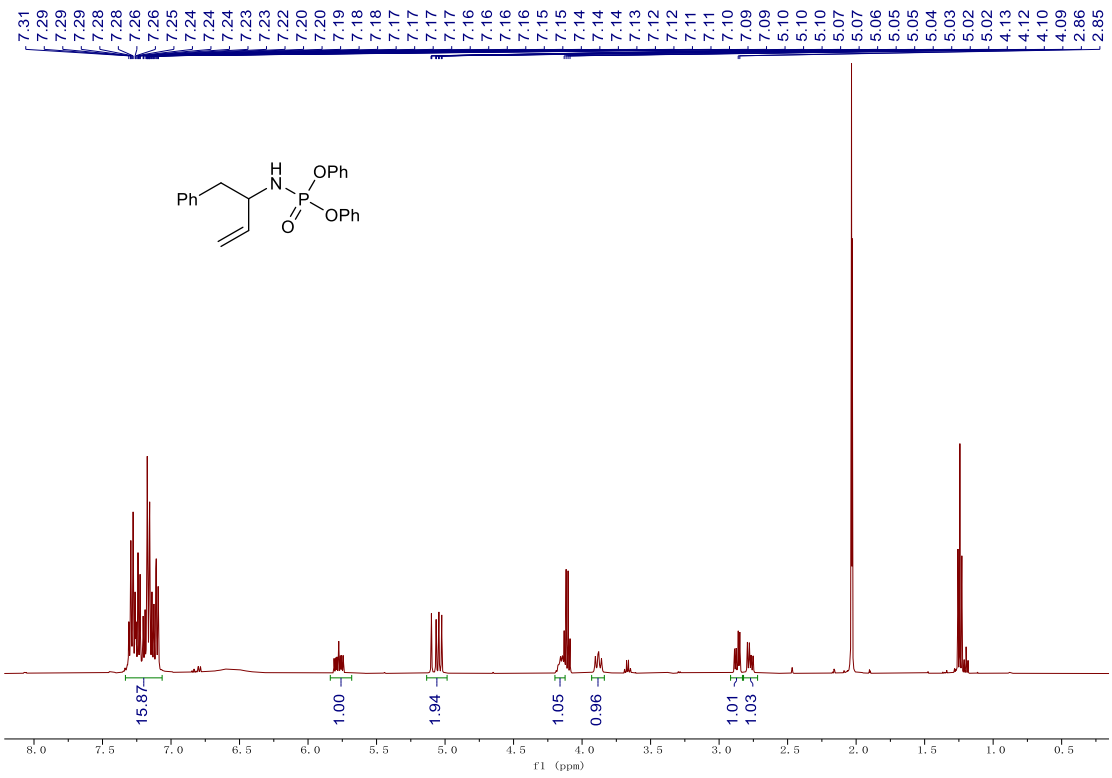

**6,** $^{13}$C NMR (126 MHz, $CDCl_3$)



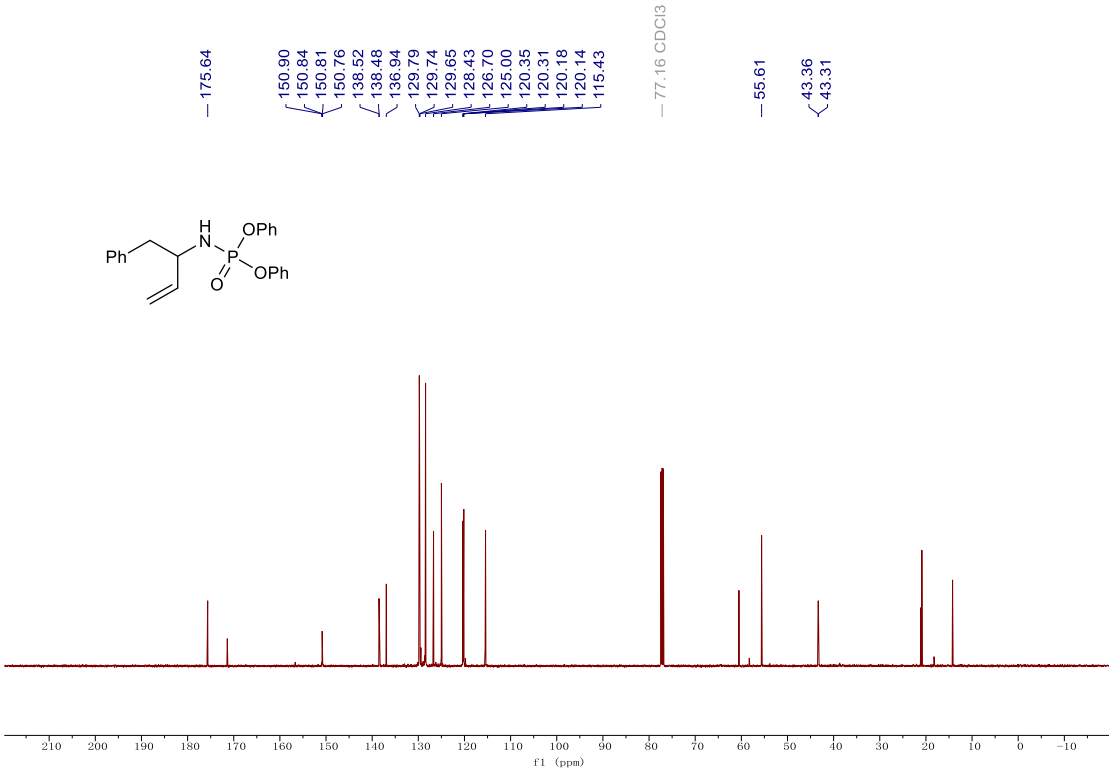
**6,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



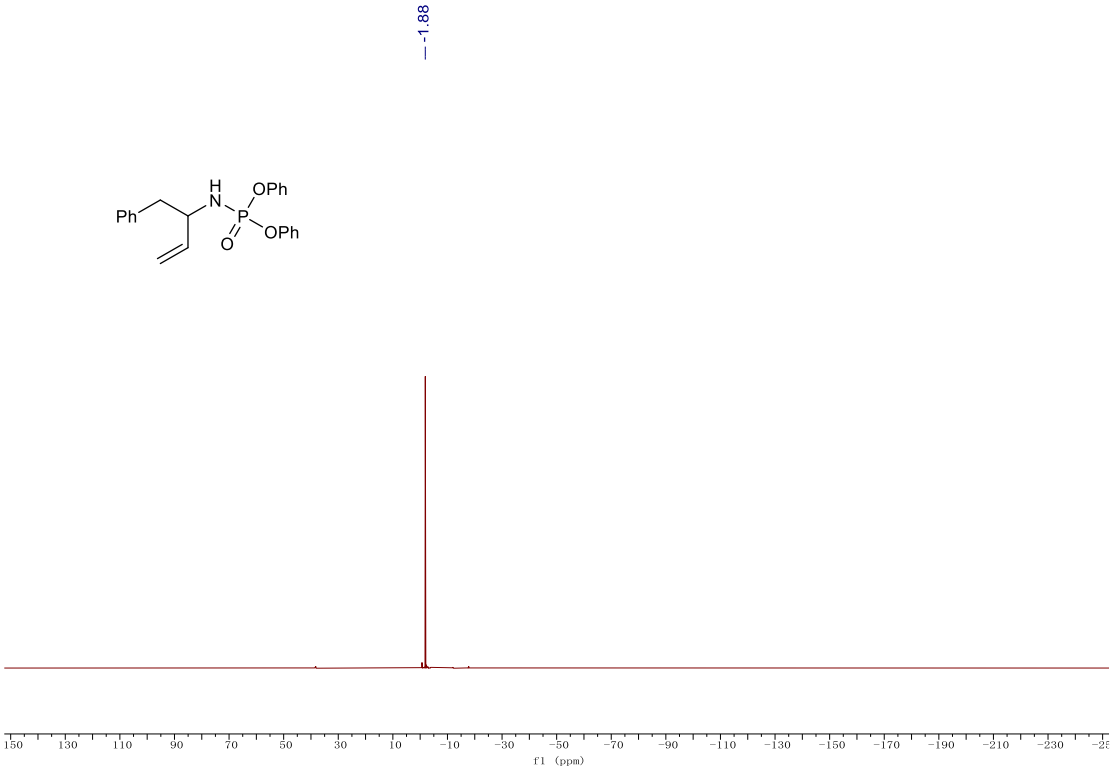

**7,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



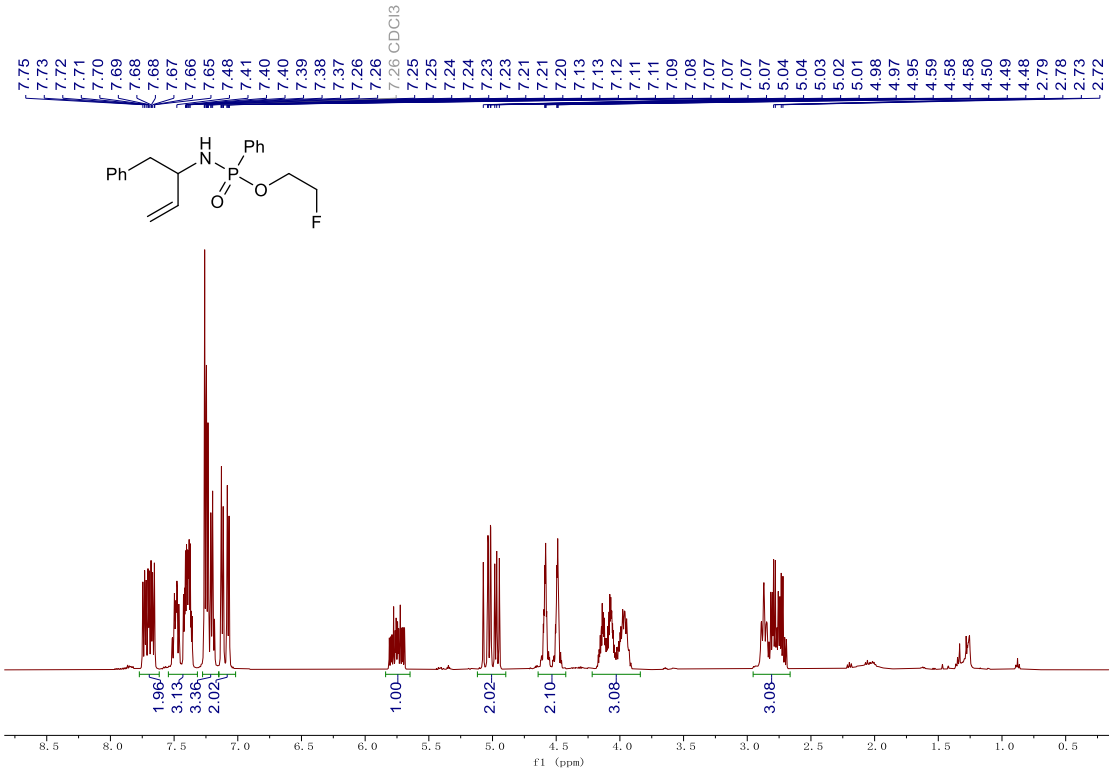
**7,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



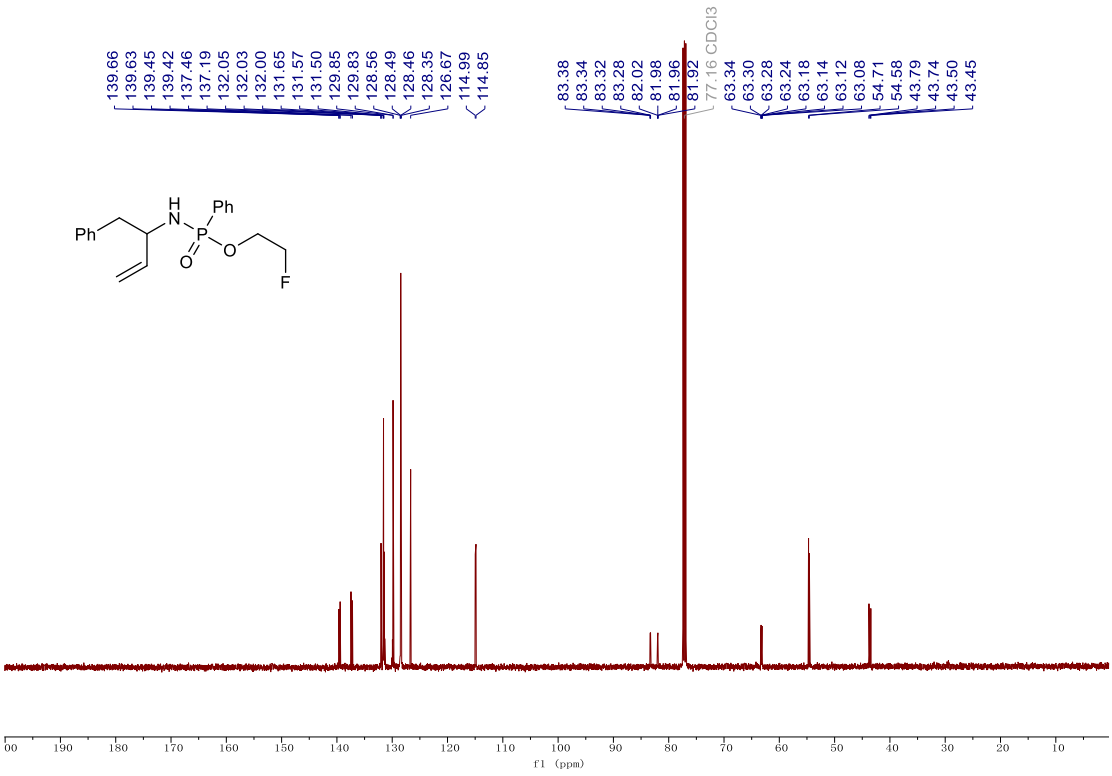

**7,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



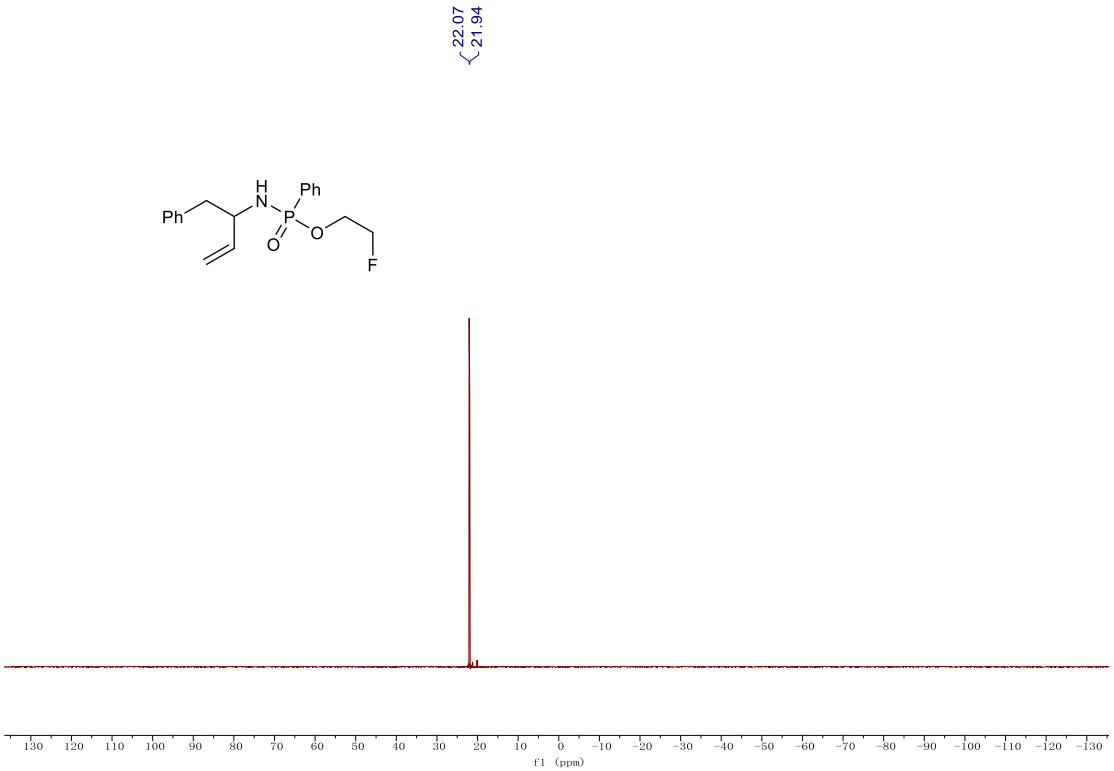
**8,** $^{1}$H NMR (500 MHz, $CDCl_3$)



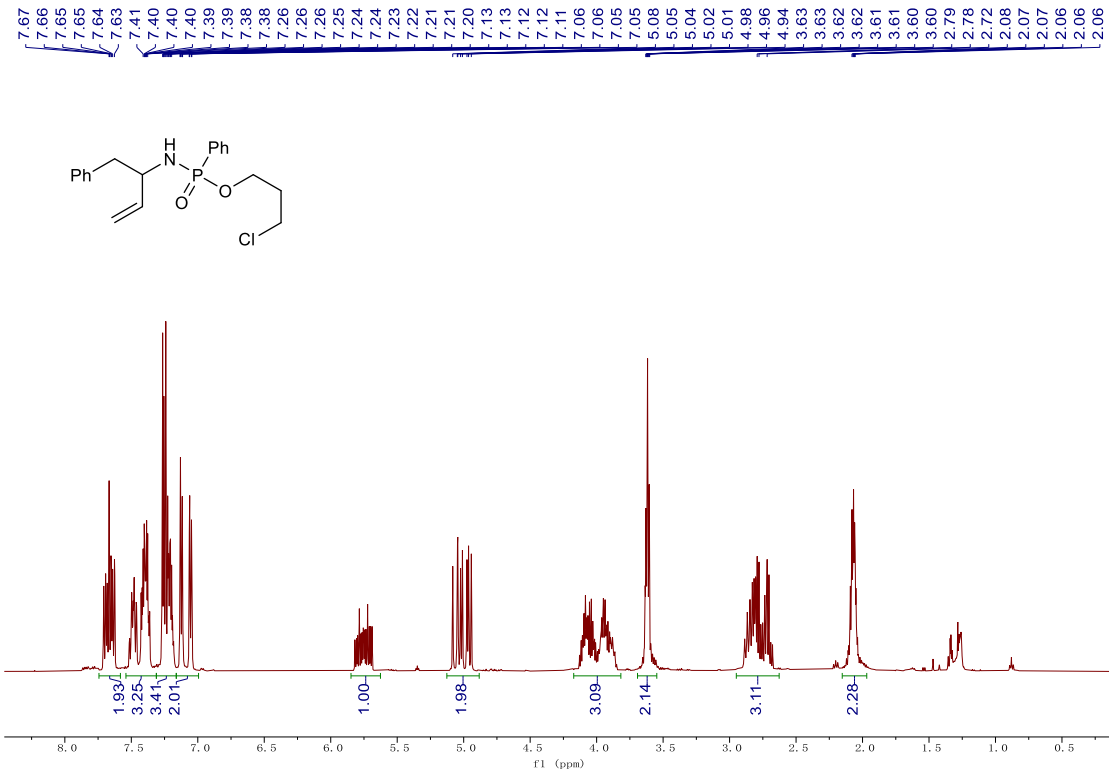

**8,** $^{13}$C NMR (126 MHz, $CDCl_3$)



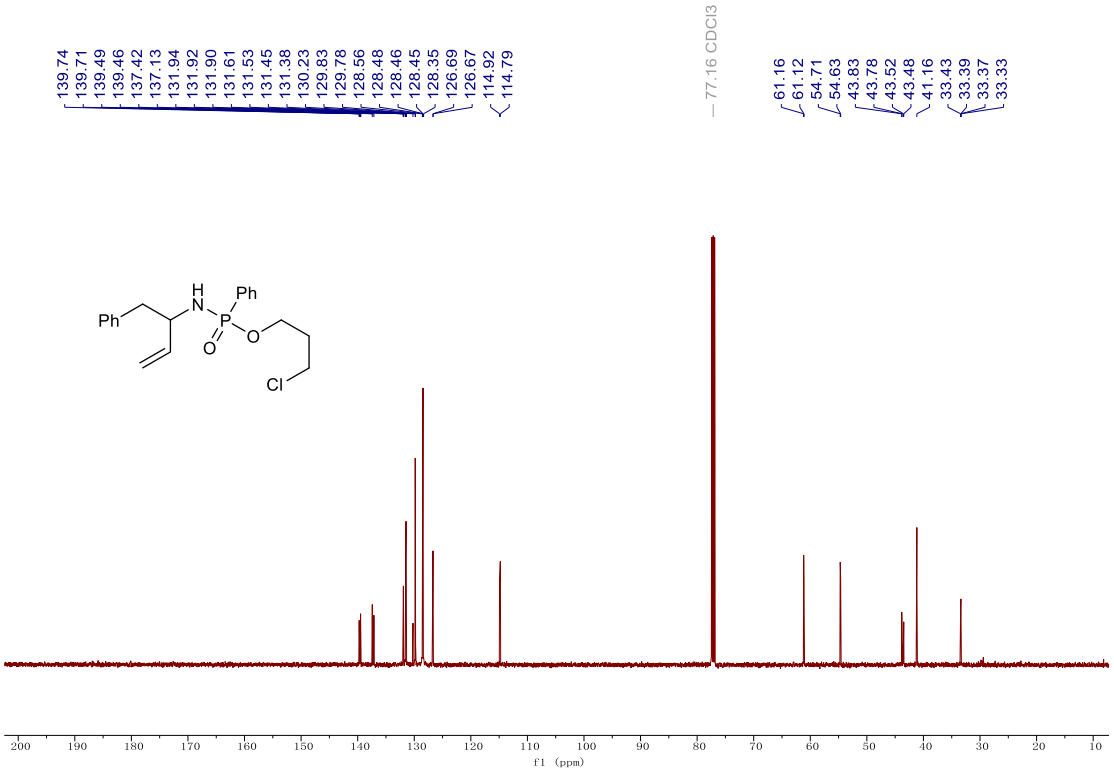
**8,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



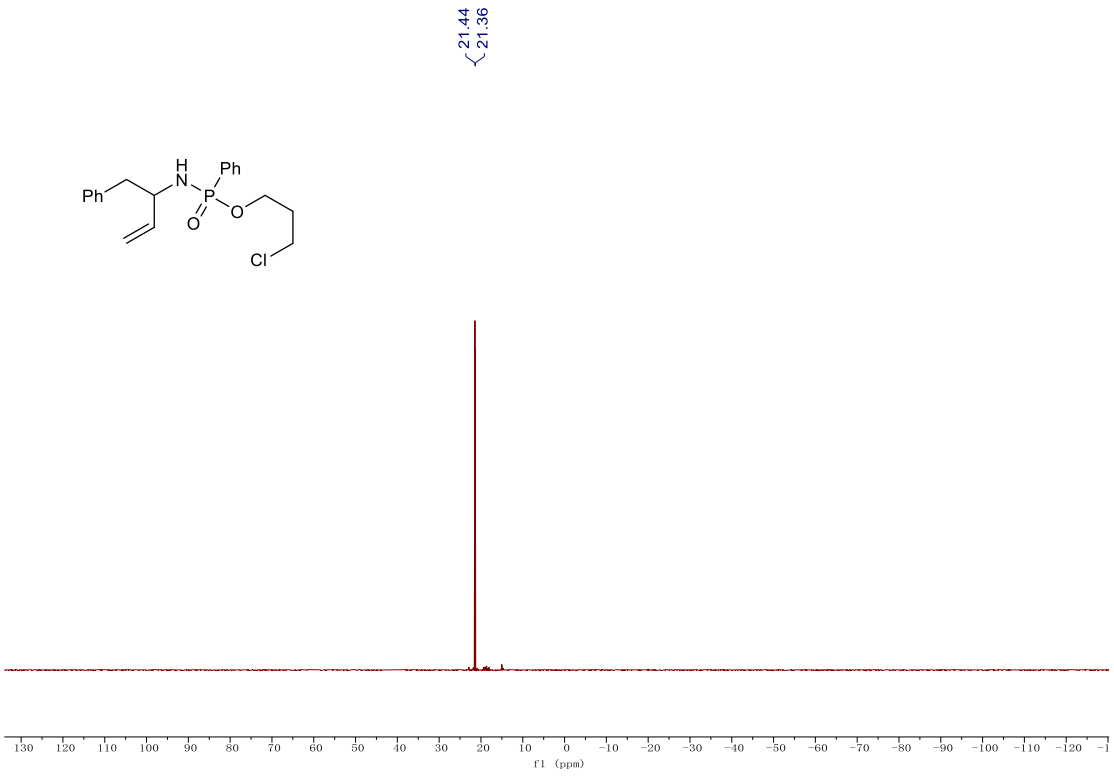

**9,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



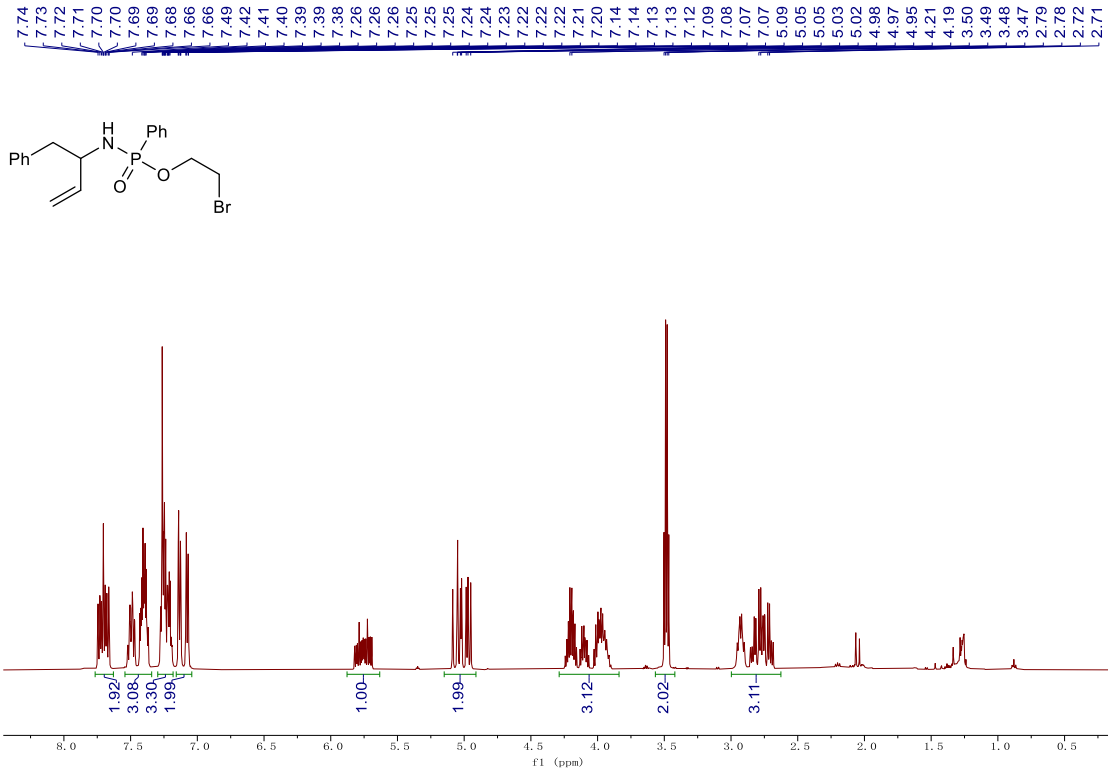
**9,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



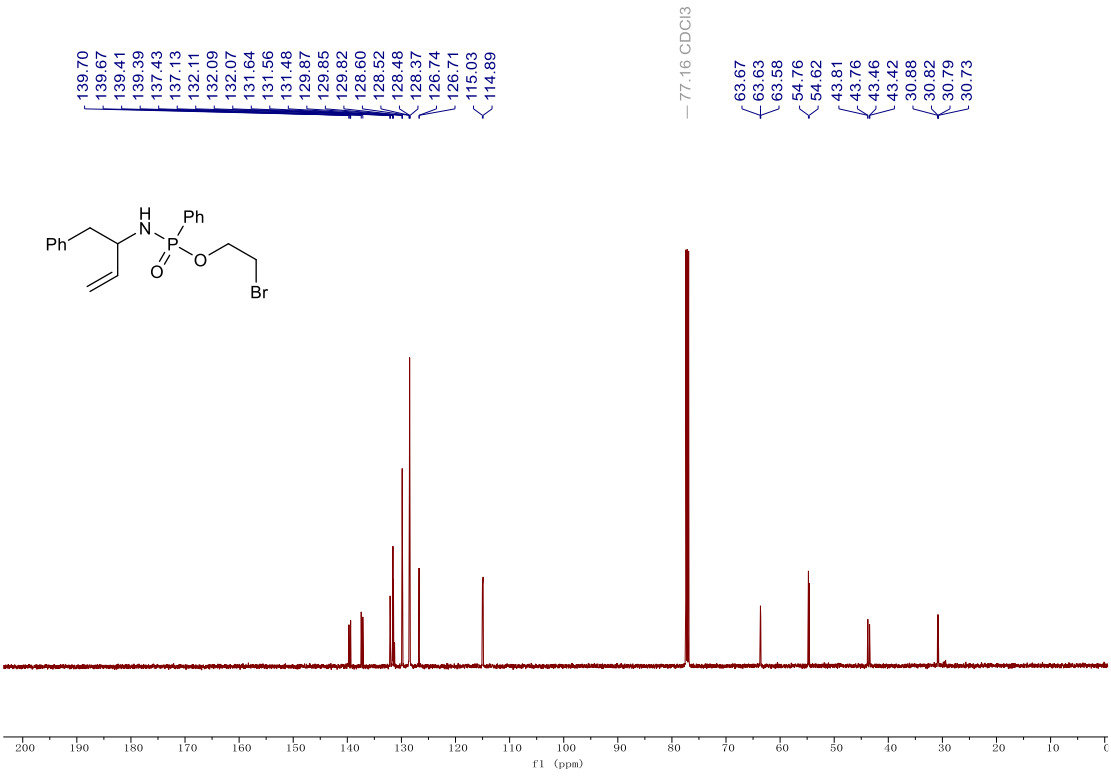

**9,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



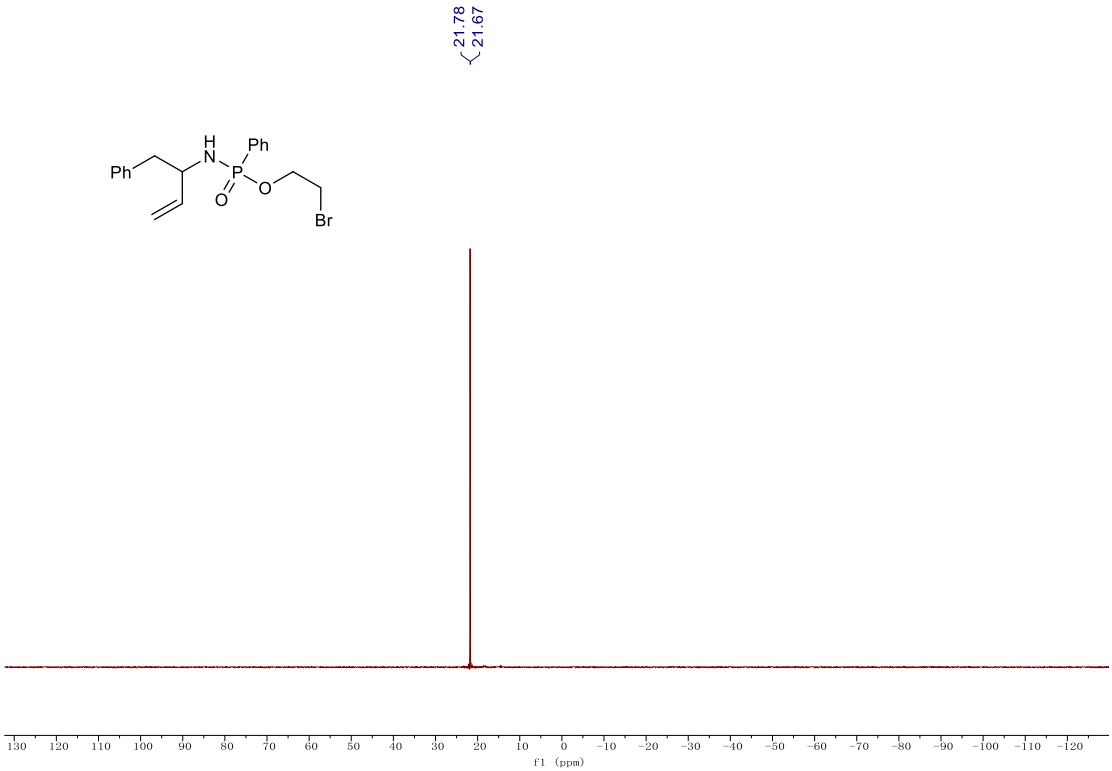
**10,** $^{1}$H NMR (500 MHz, $CDCl_3$)



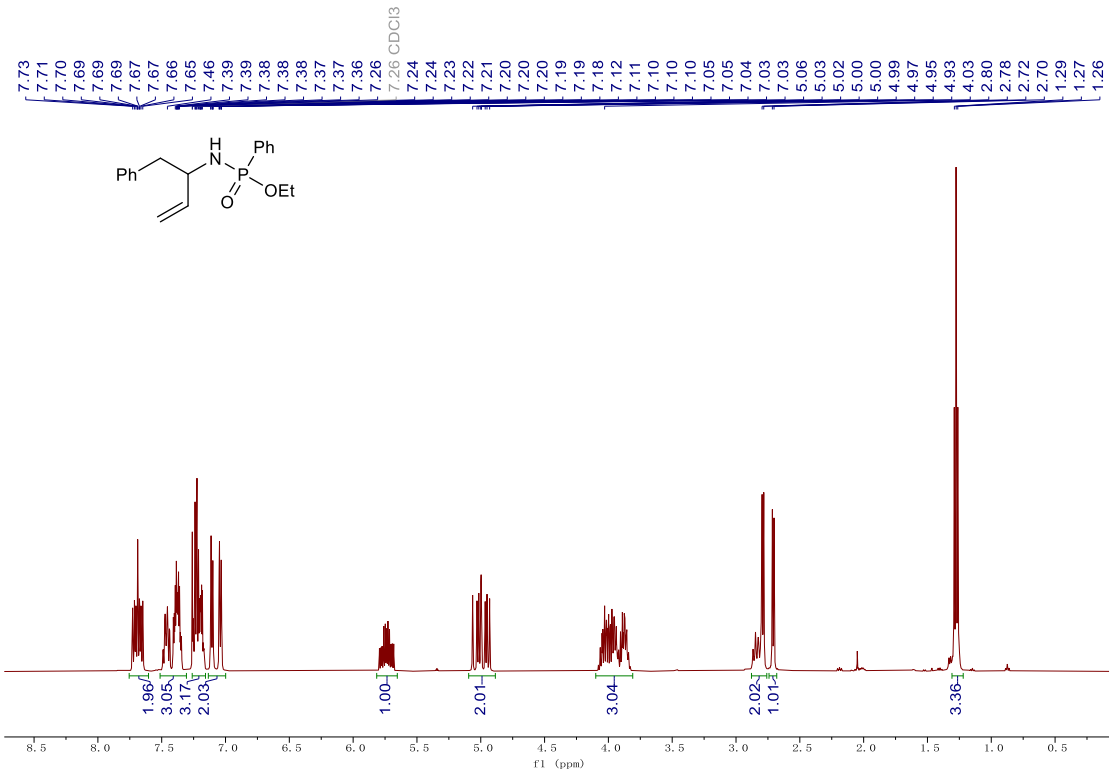

**10,** $^{13}$C NMR (126 MHz, $CDCl_3$)



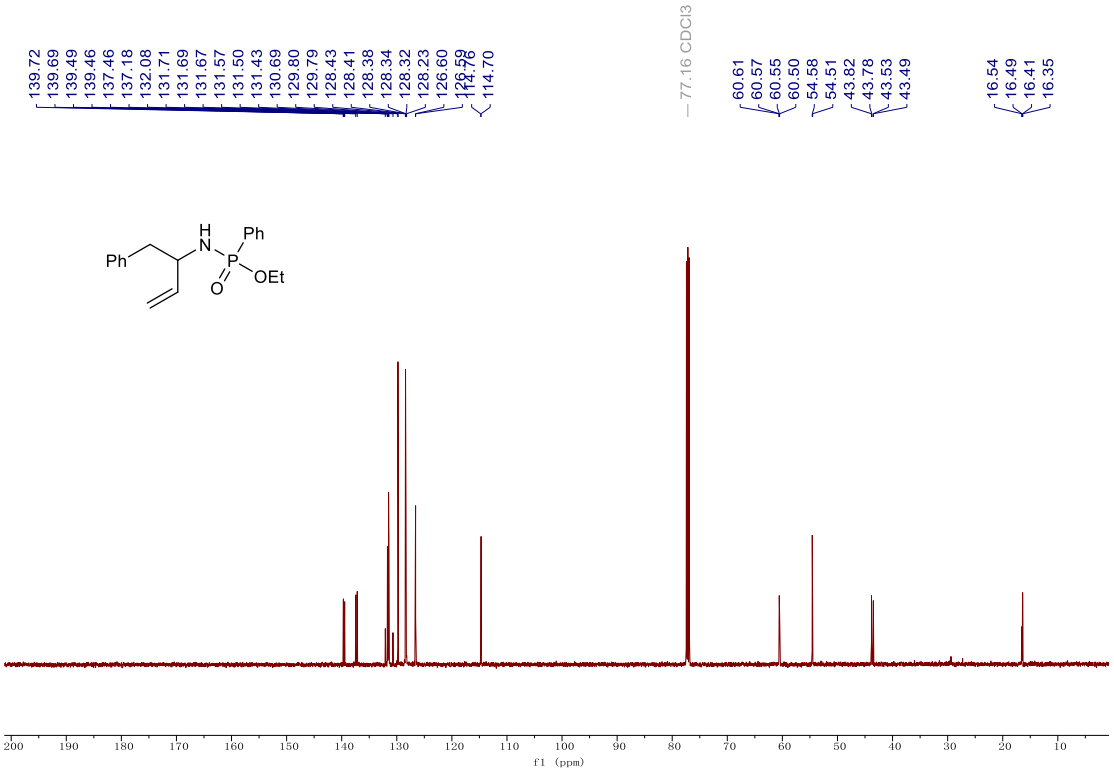
**10,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



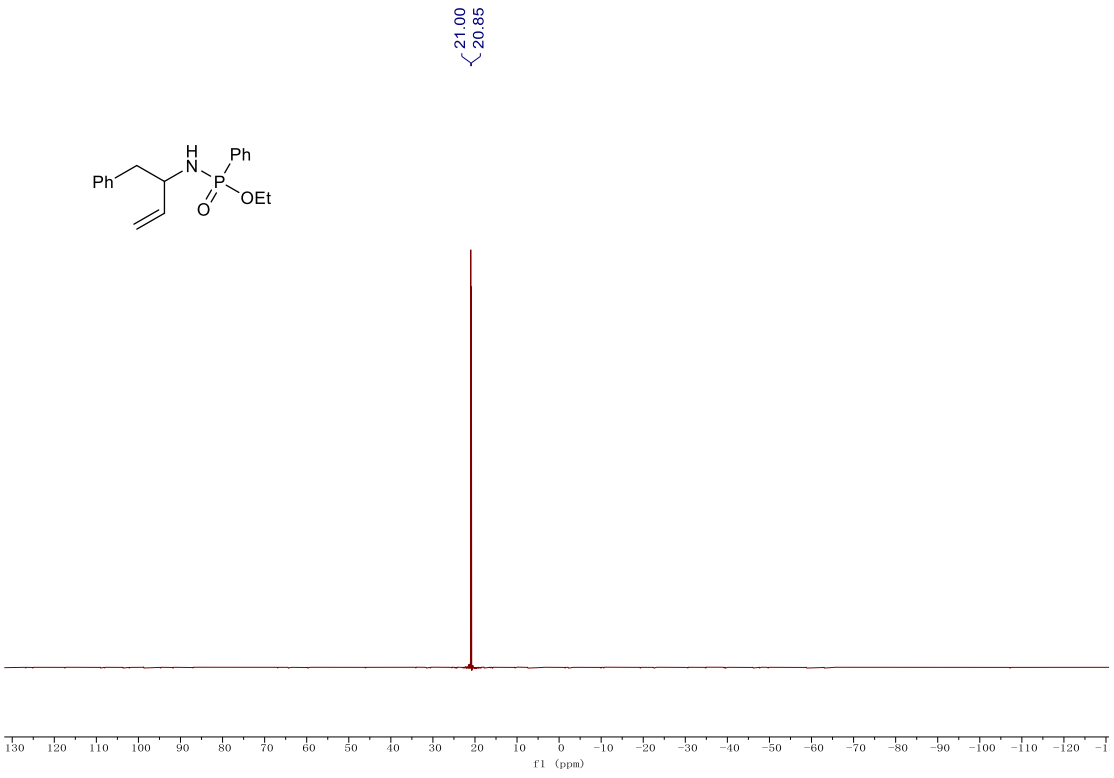

**11,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



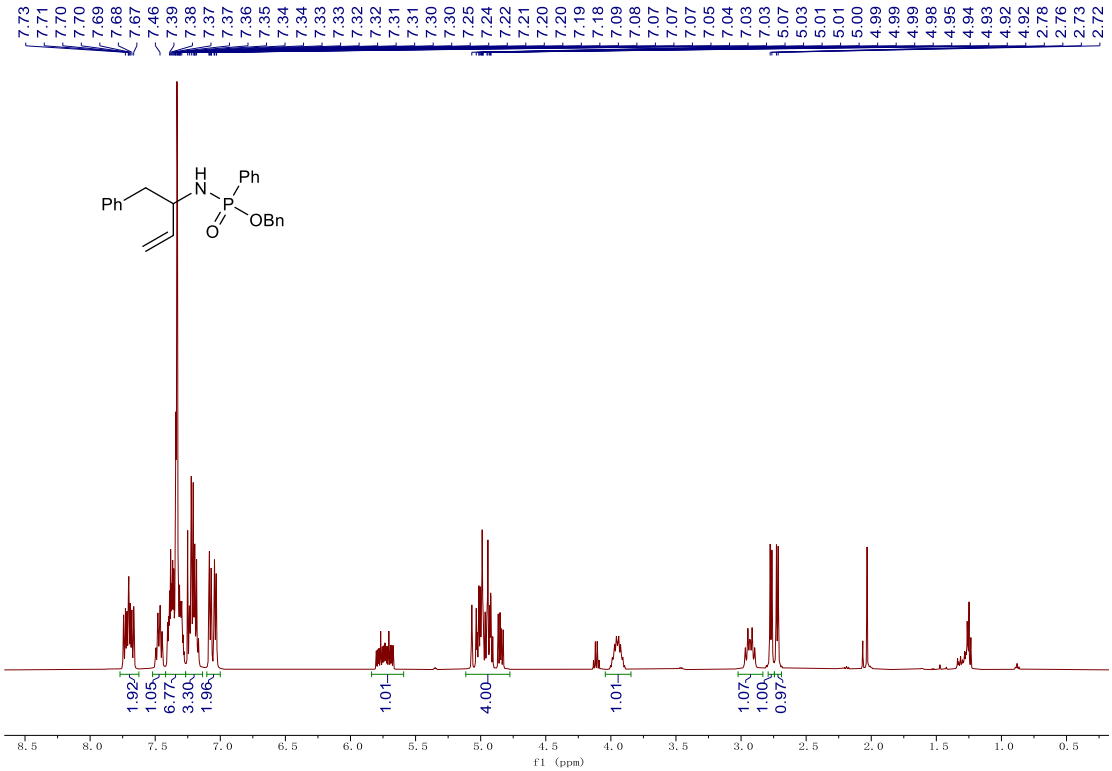
**11,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



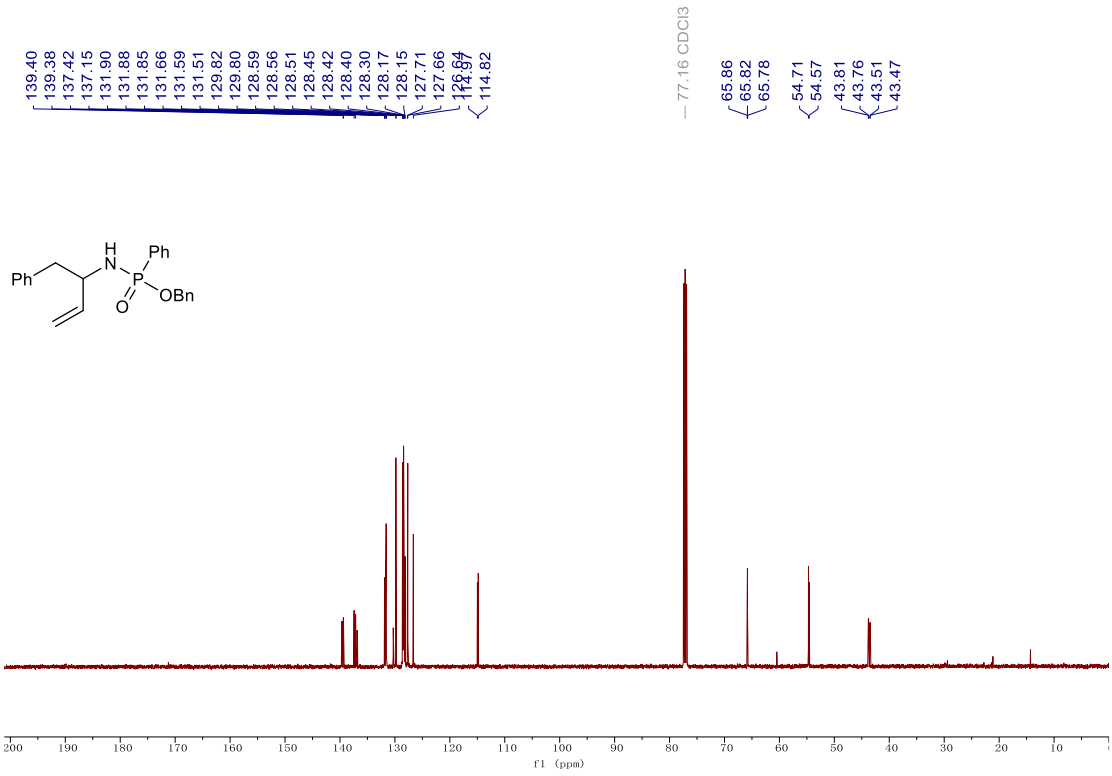

**11,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



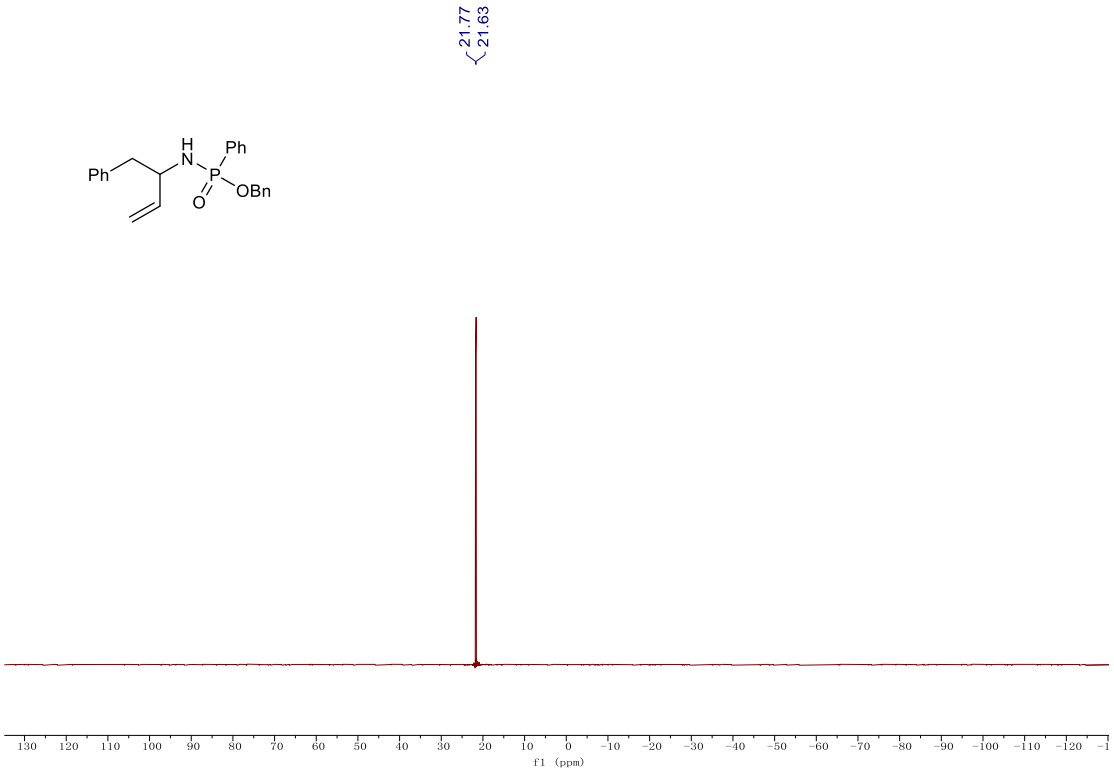
**12,** $^{1}$H NMR (500 MHz, $CDCl_3$)



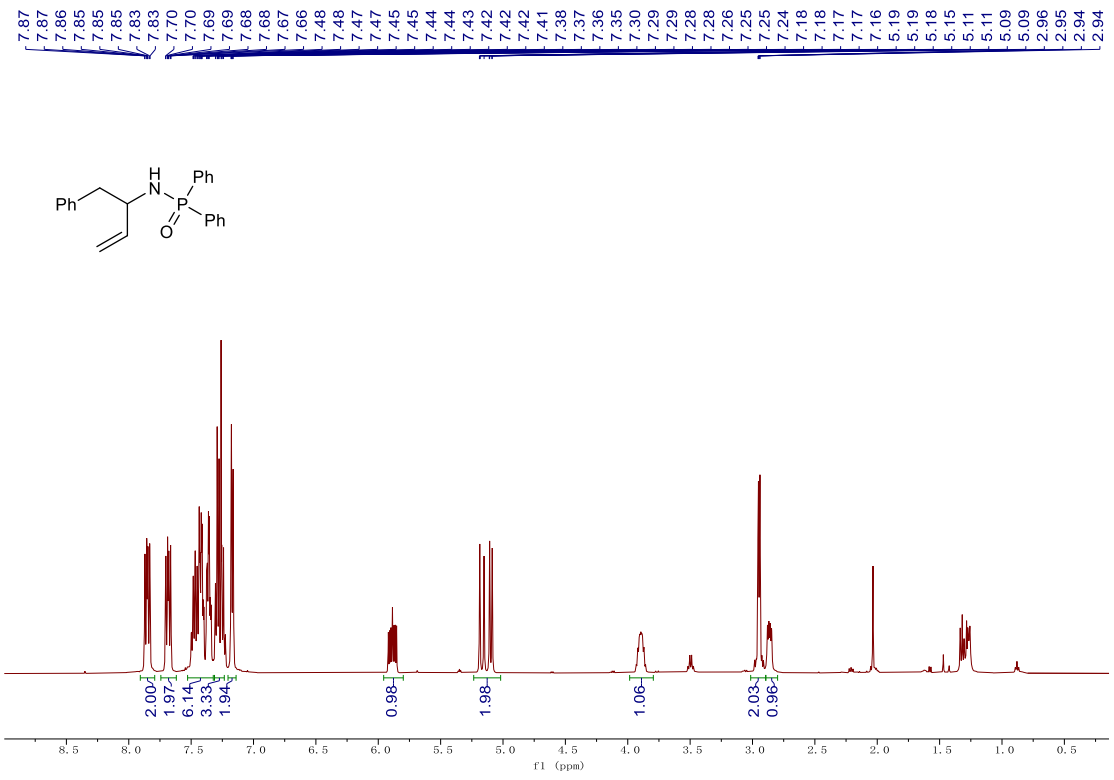

**12,** $^{13}$C NMR (126 MHz, $CDCl_3$)



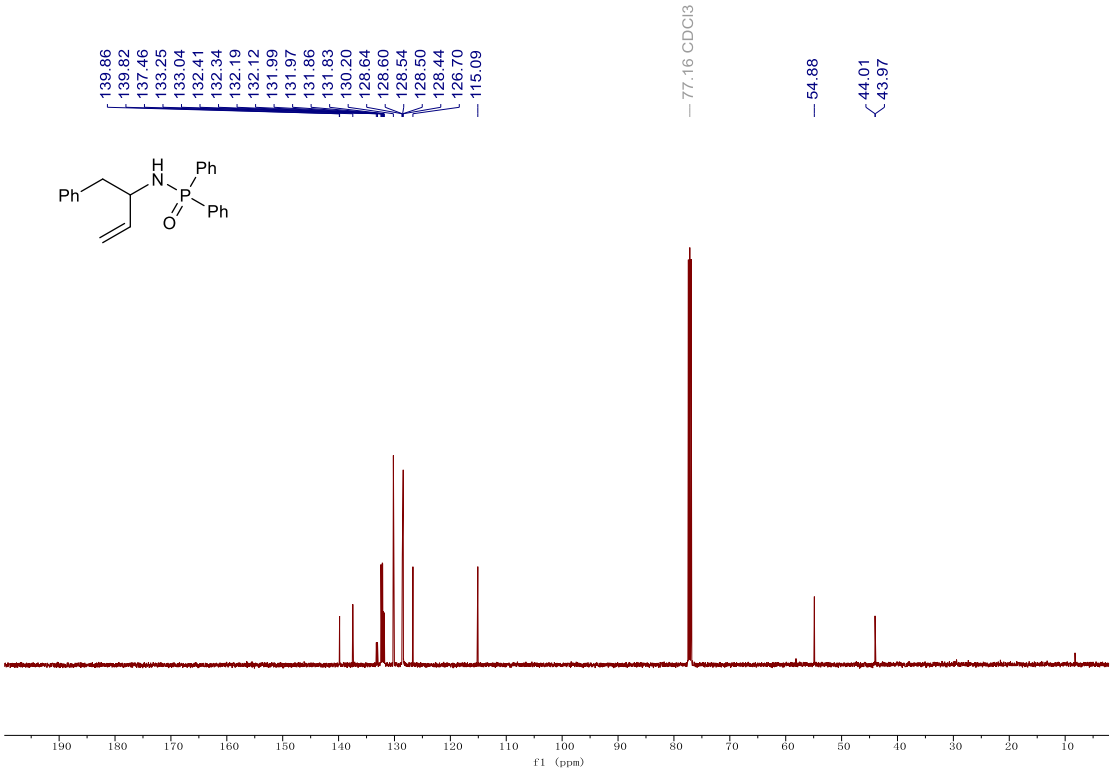
**12,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



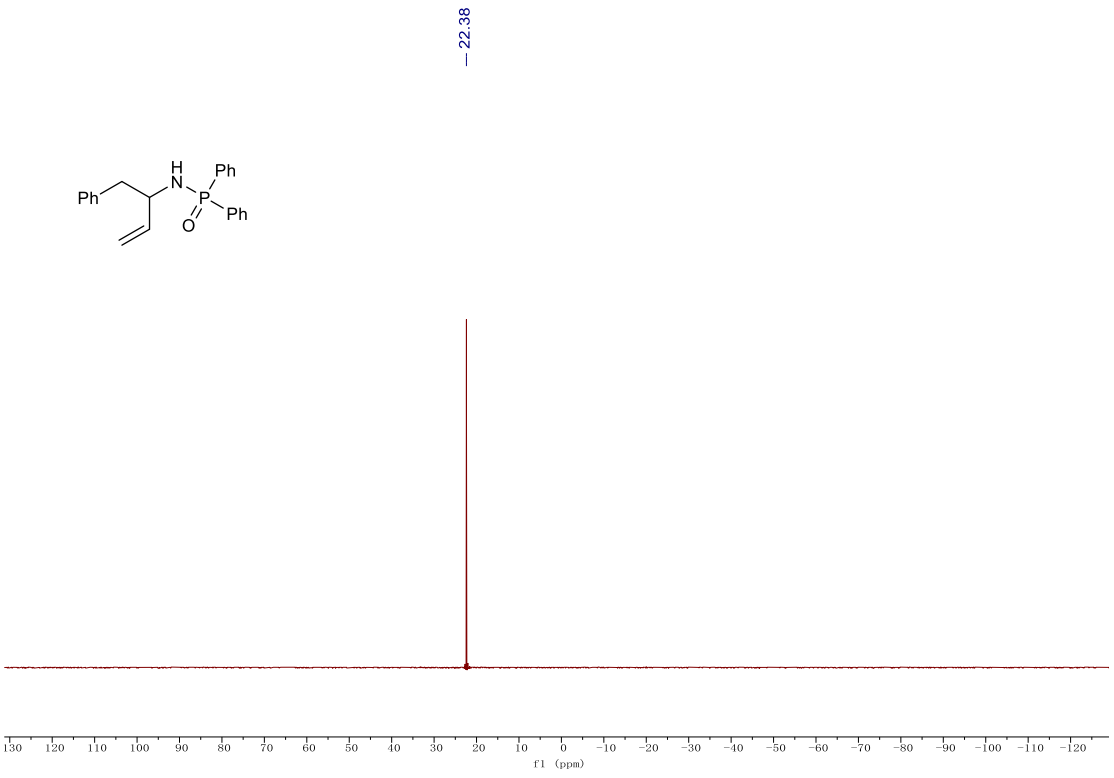

**13,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



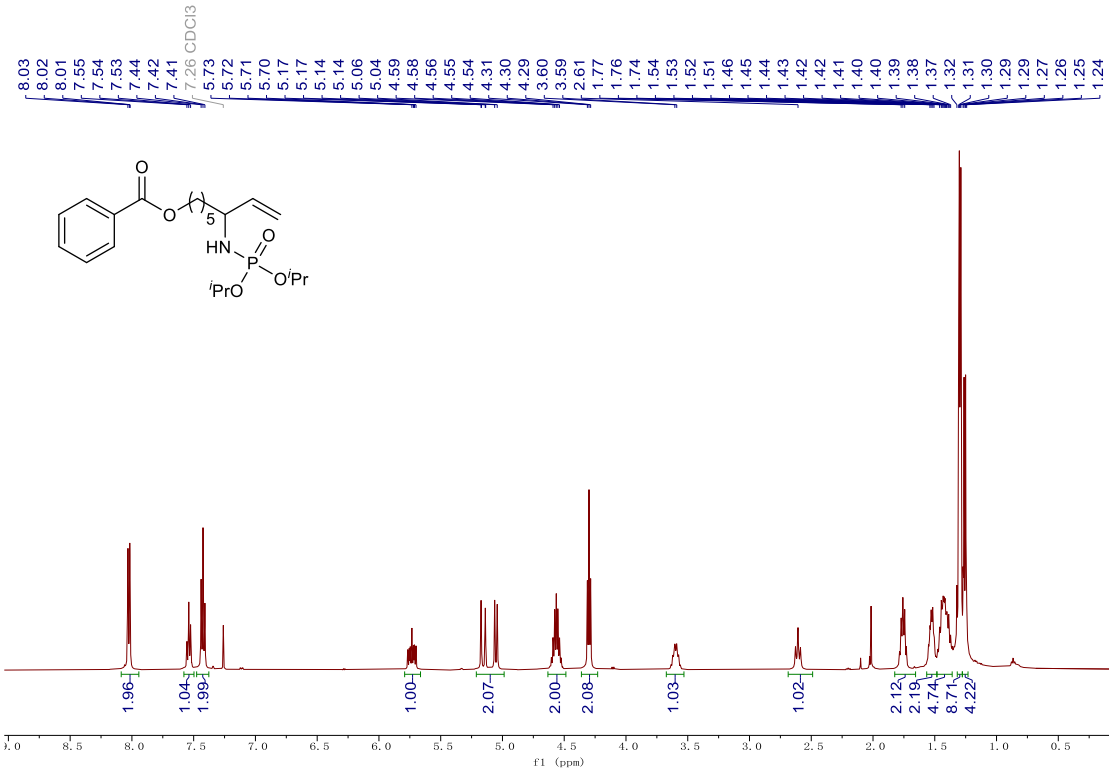
**13,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



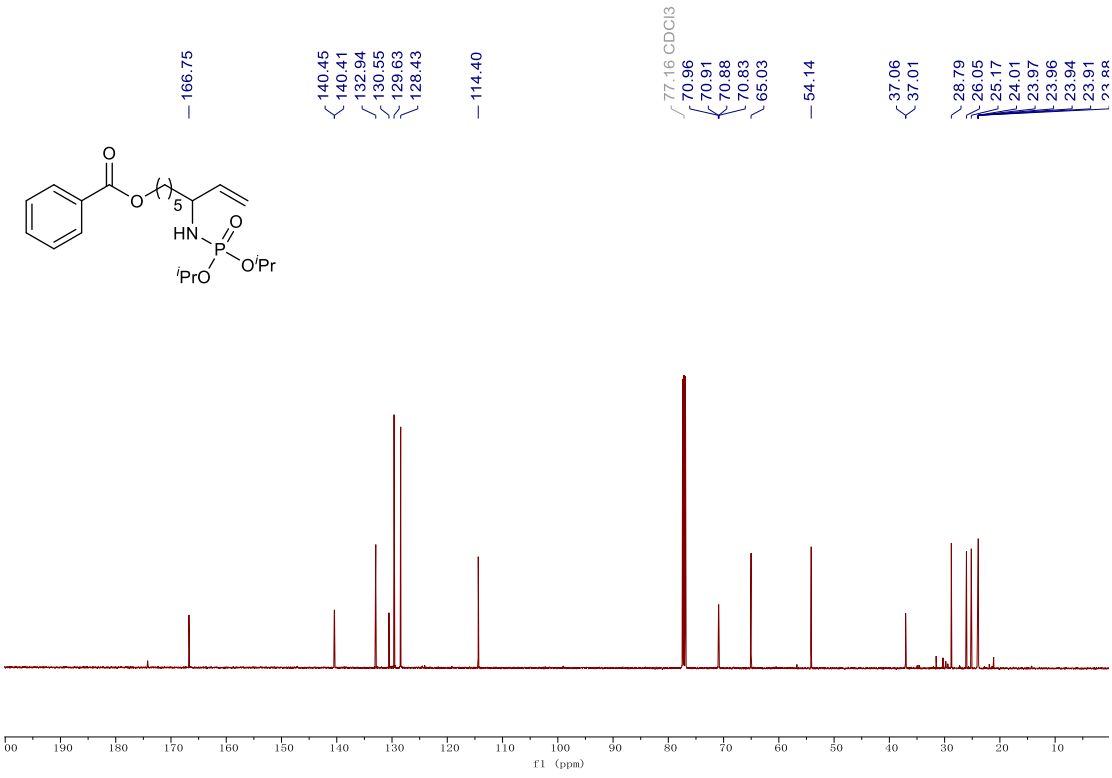

**13,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



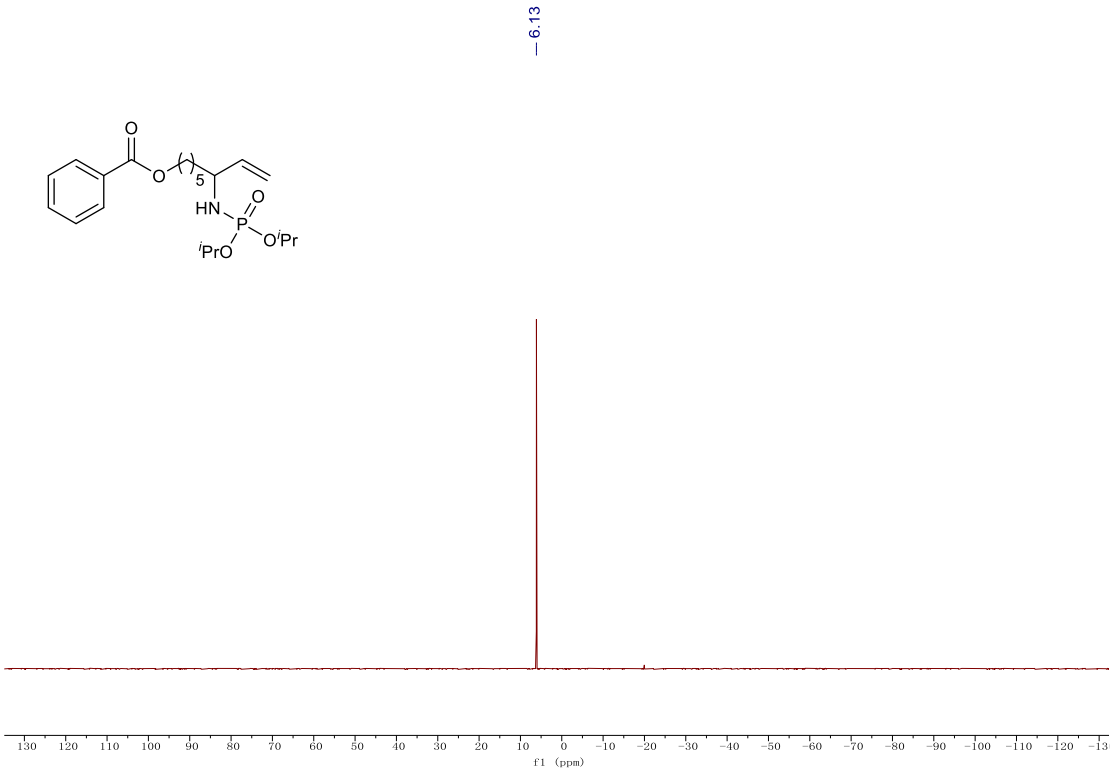
**14,** $^{1}$H NMR (500 MHz, $CDCl_3$)



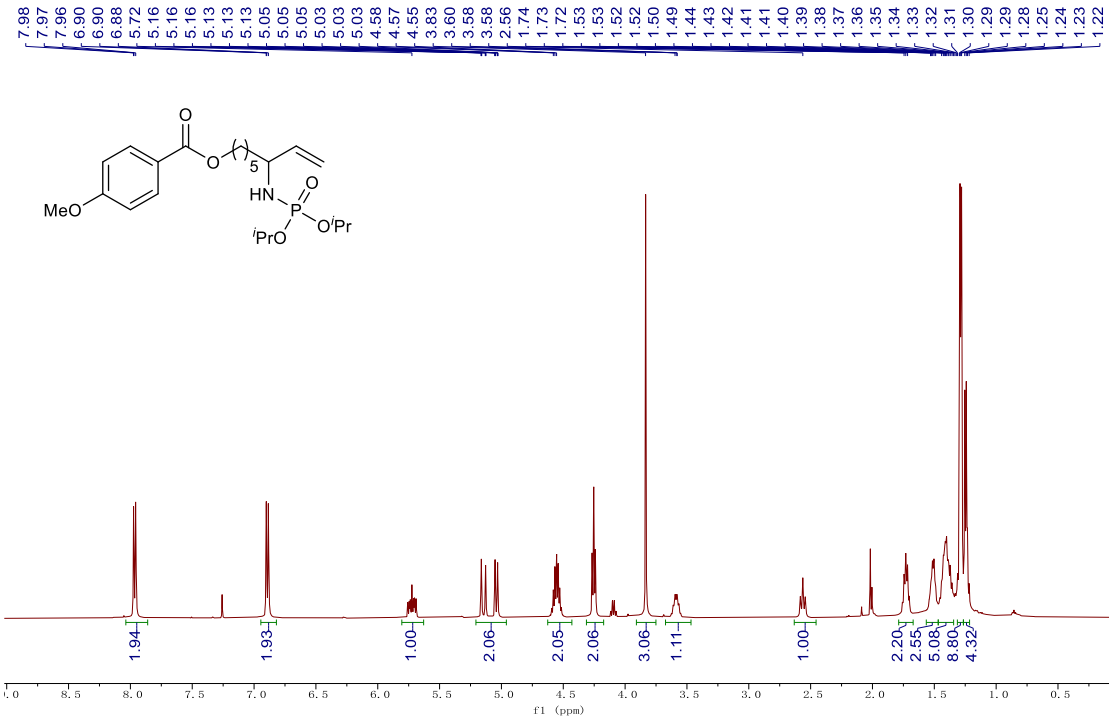

**14,** $^{13}$C NMR (126 MHz, $CDCl_3$)



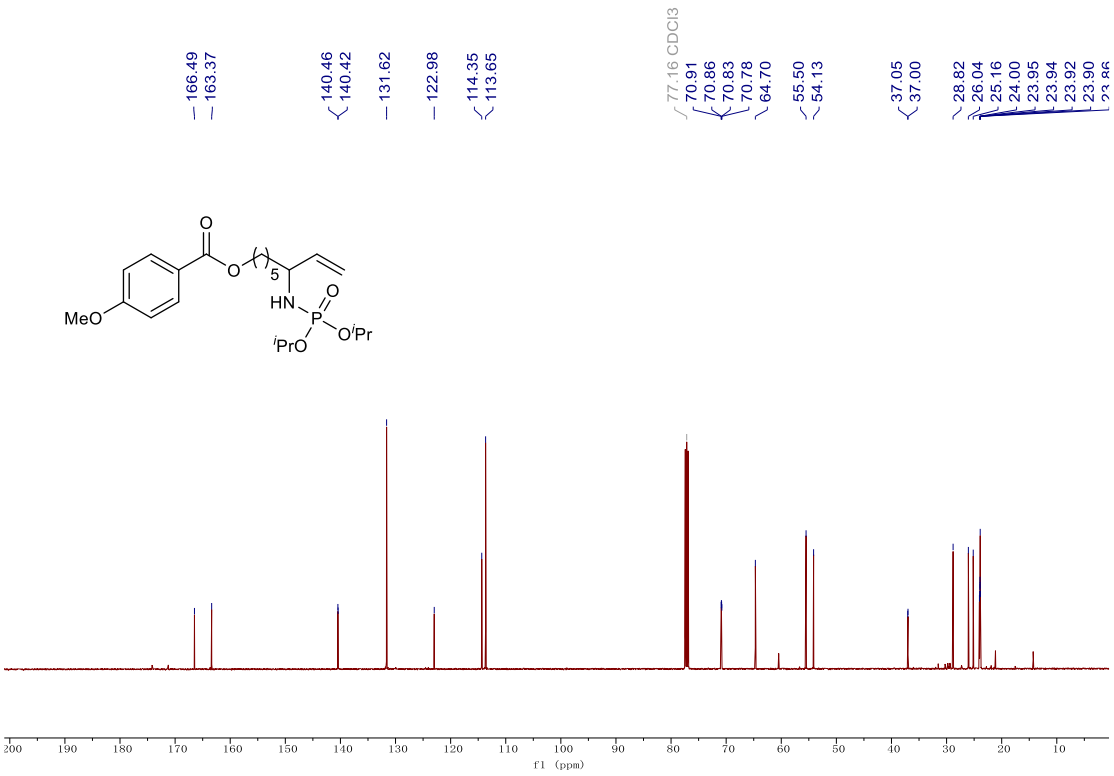
**14,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



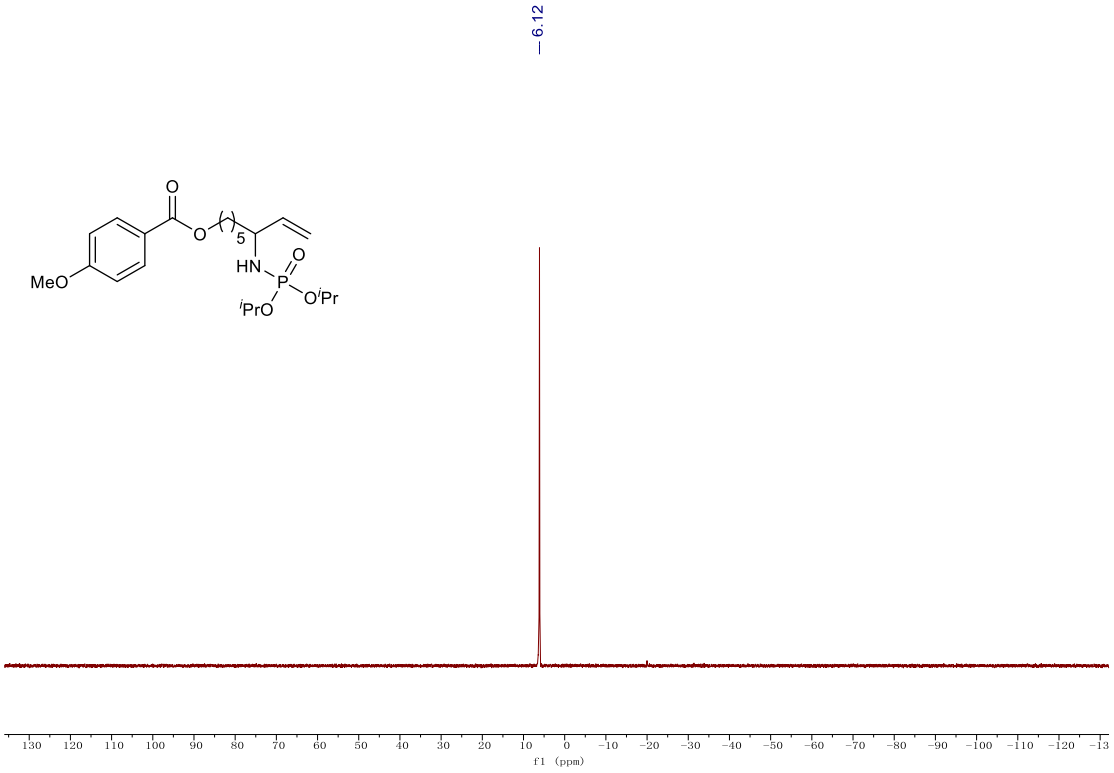

**15,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



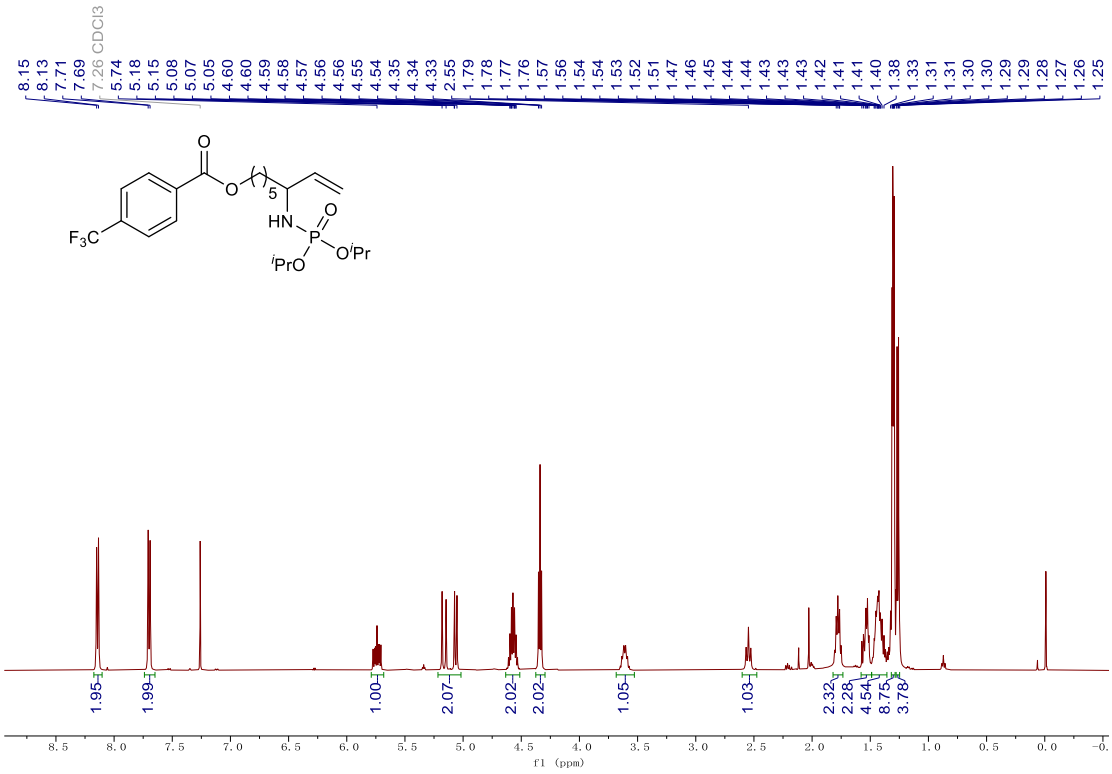

**15,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



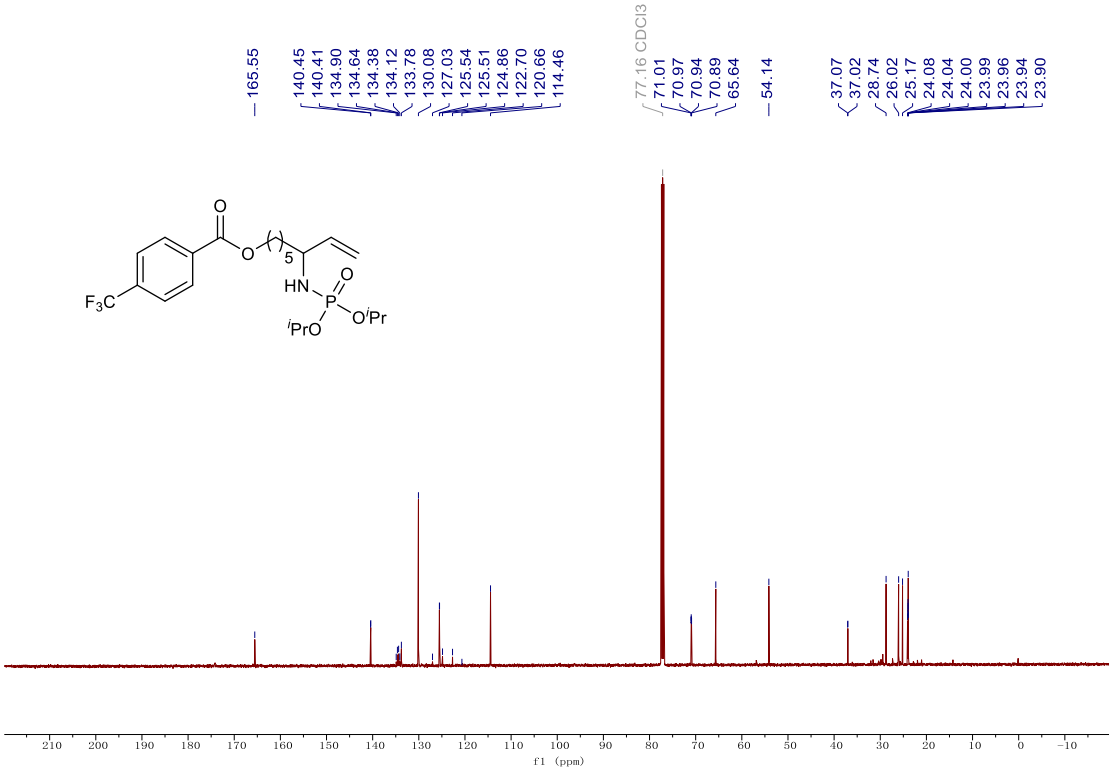

**15,** $^{31}$P NMR (202 MHz, $CDCl_3$)



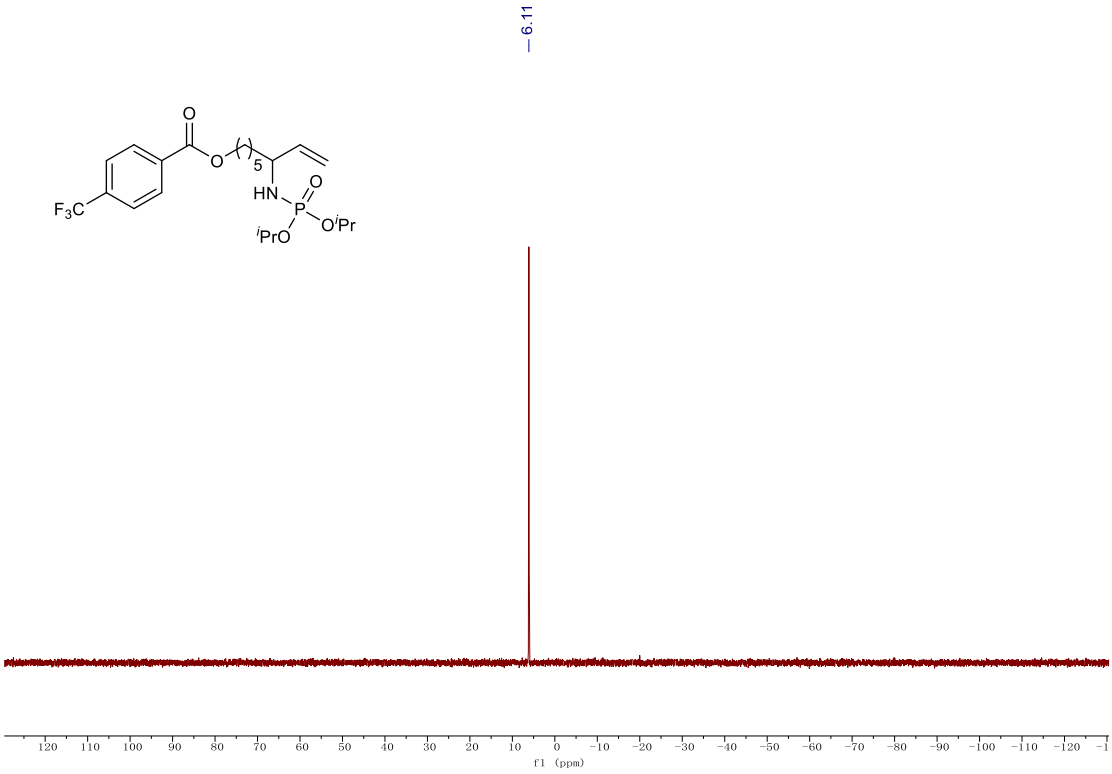

**16,** $^{1}$H NMR (500 MHz, $CDCl_3$)



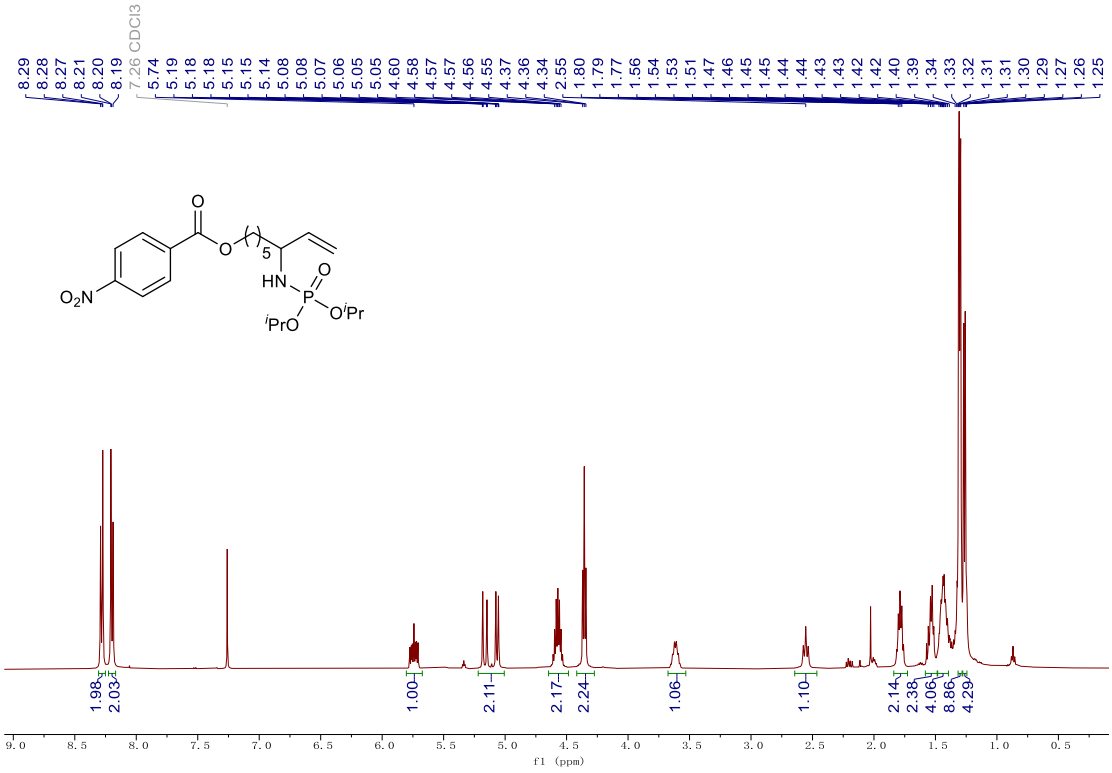

**16,** $^{13}$C NMR (126 MHz, $CDCl_3$)



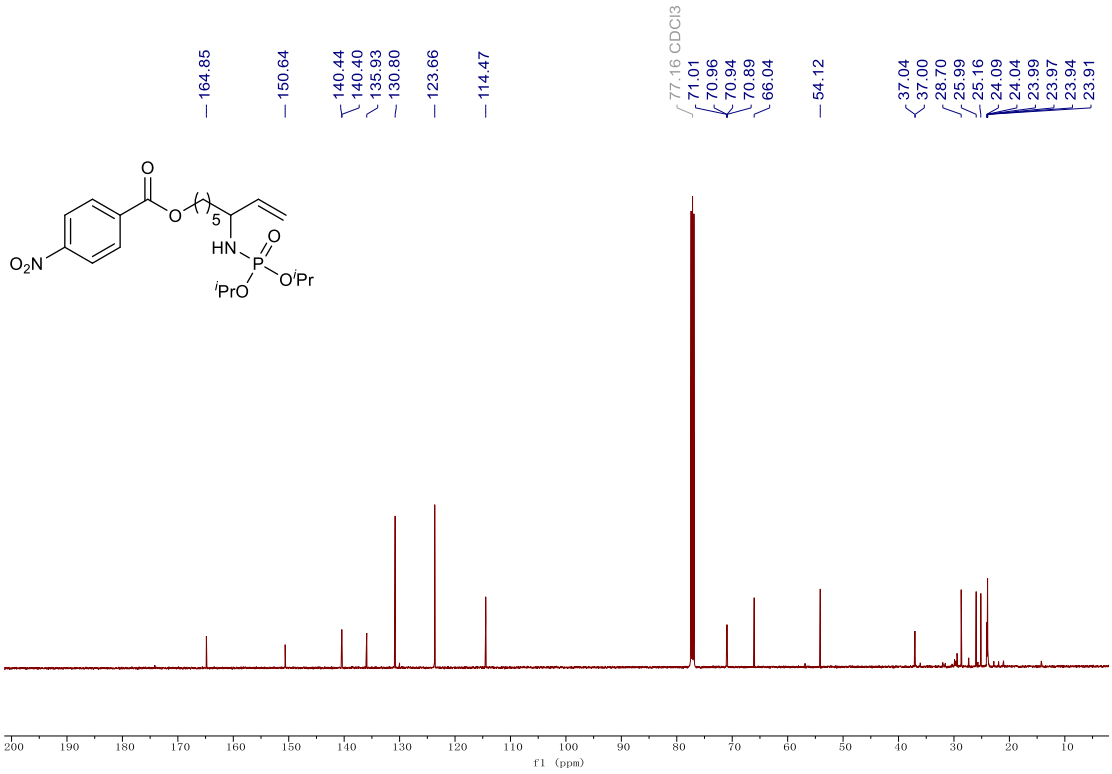

**16,** $^{31}$P NMR (202 MHz, $CDCl_3$)



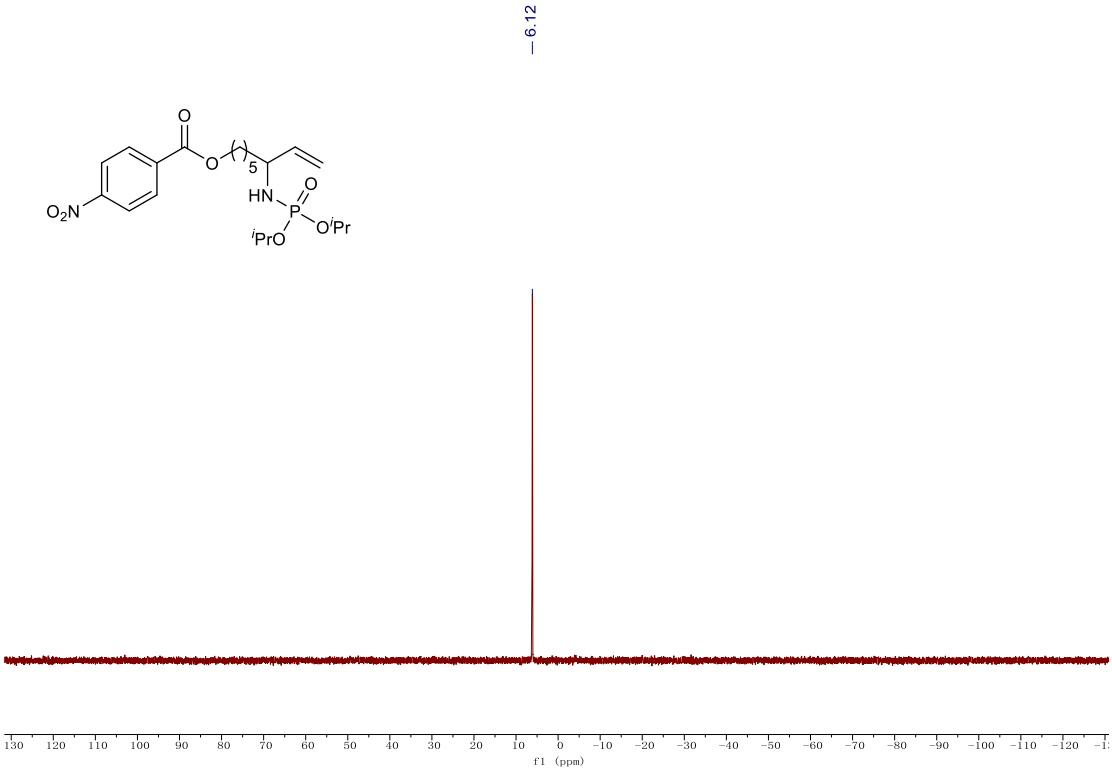

**17,** $^{1}$H NMR (500 MHz, $CDCl_3$)



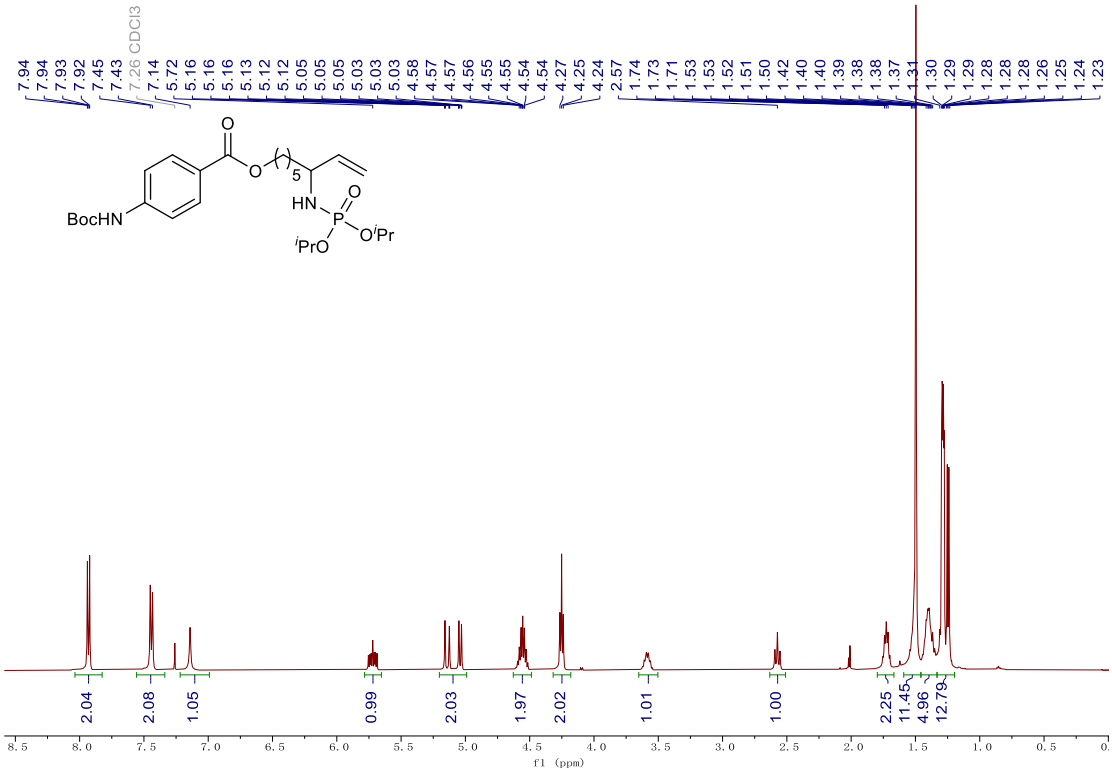

**17,** $^{13}$C NMR (126 MHz, $CDCl_3$)



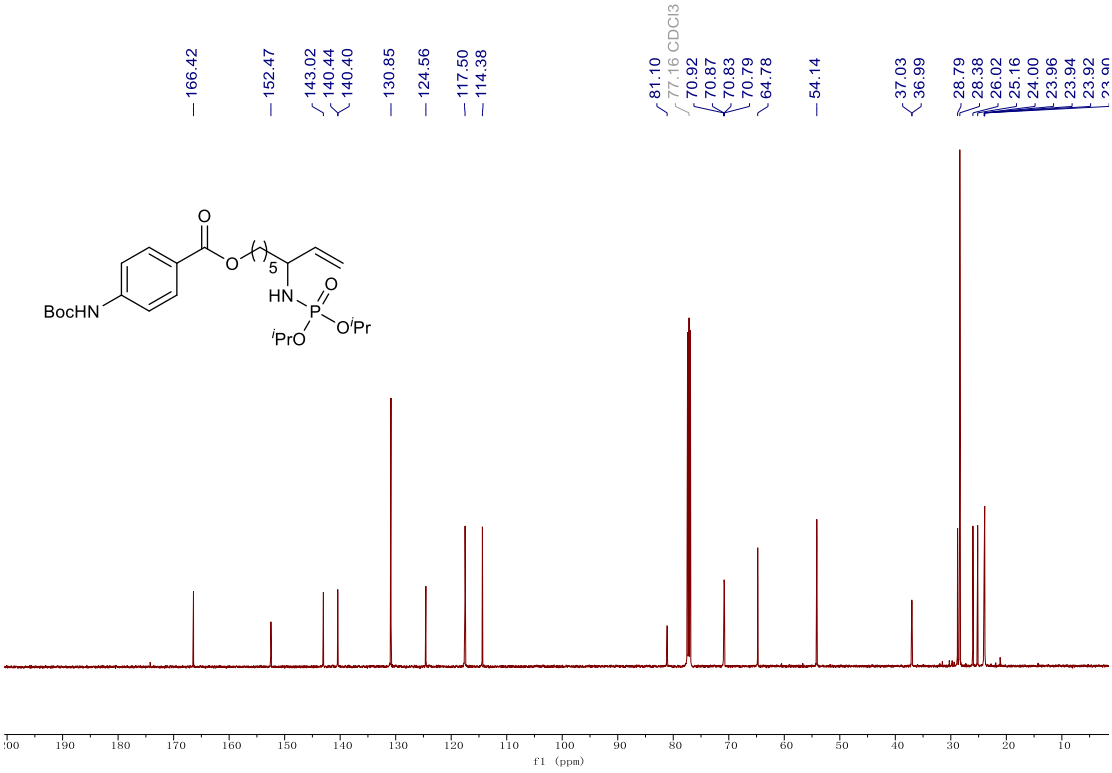

**17,** $^{31}$P NMR (202 MHz, $CDCl_3$)



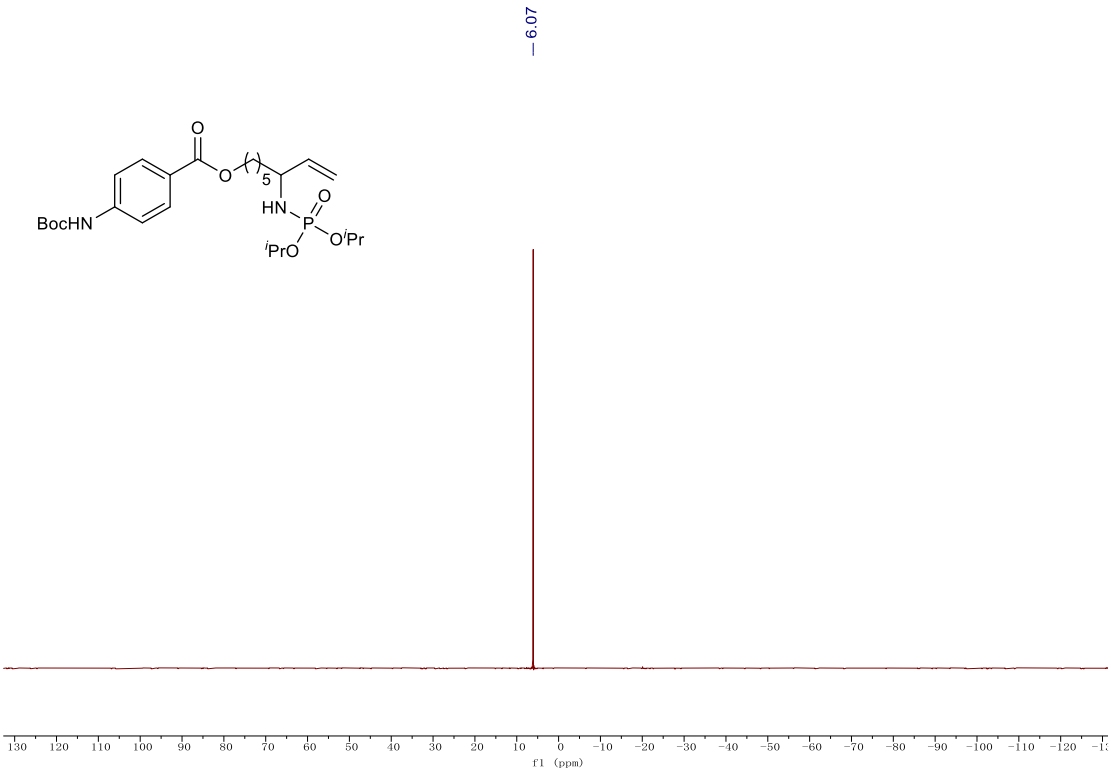

**18,** $^{1}$H NMR (500 MHz, $CDCl_3$)



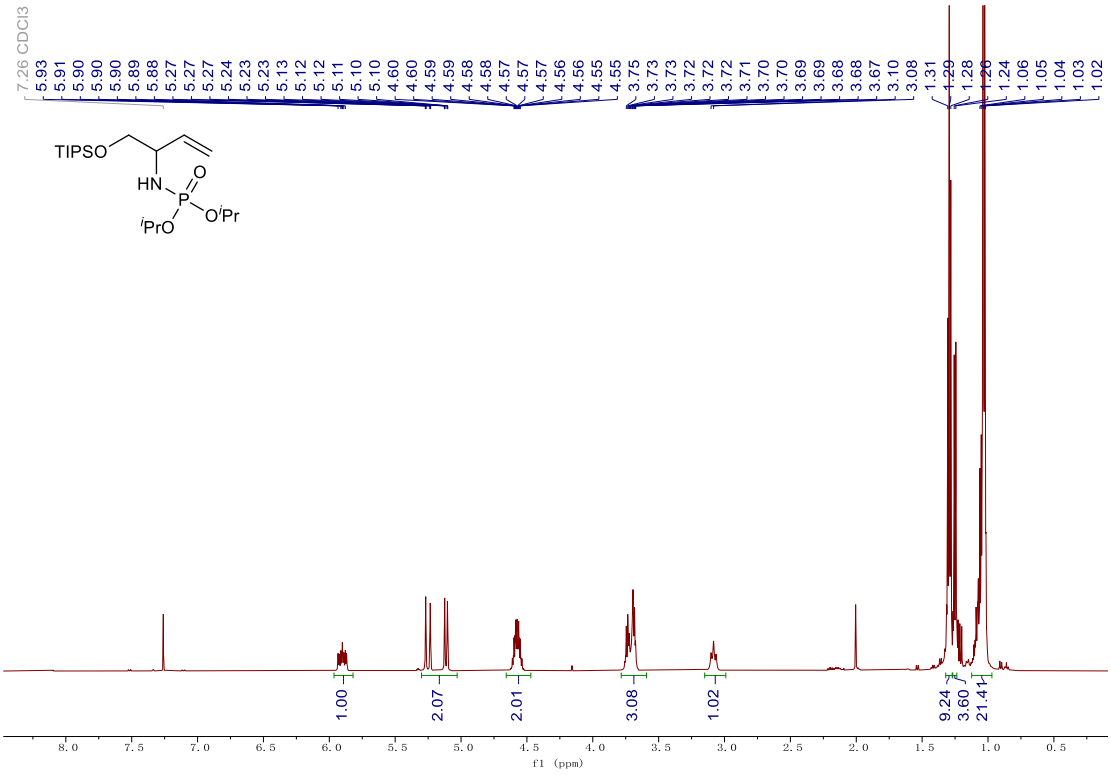

**18,** $^{13}$C NMR (126 MHz, $CDCl_3$)



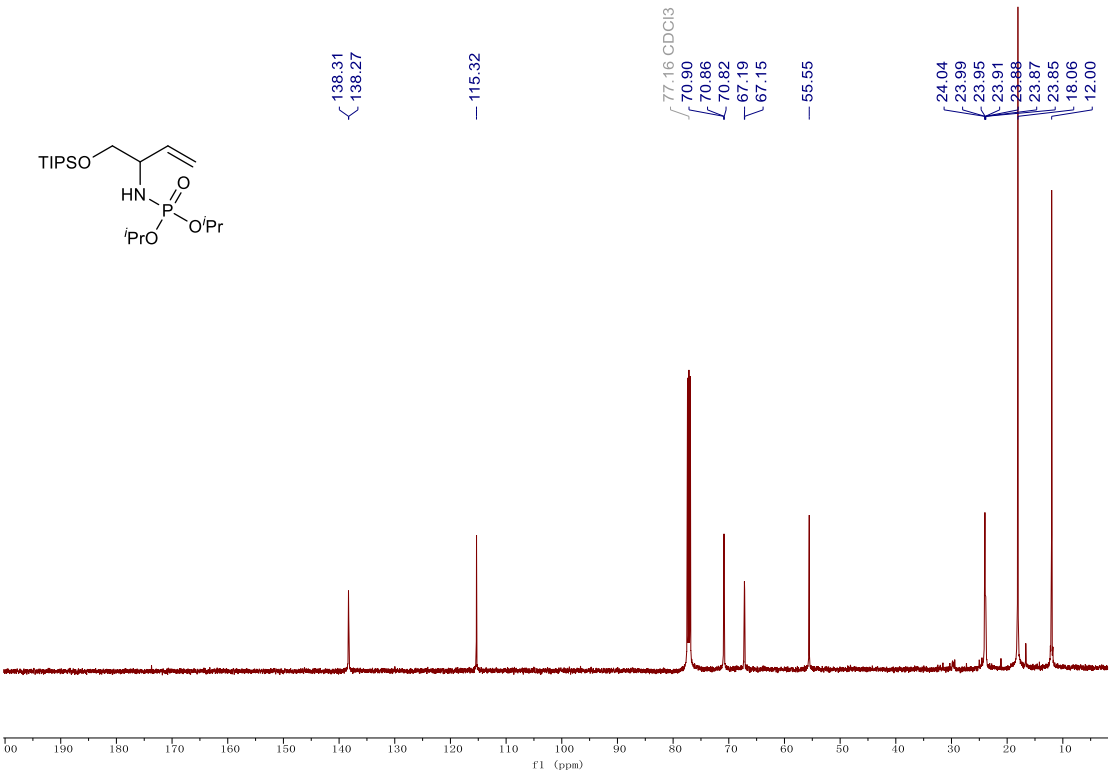

**18,** $^{31}$P NMR (202 MHz, $CDCl_3$)



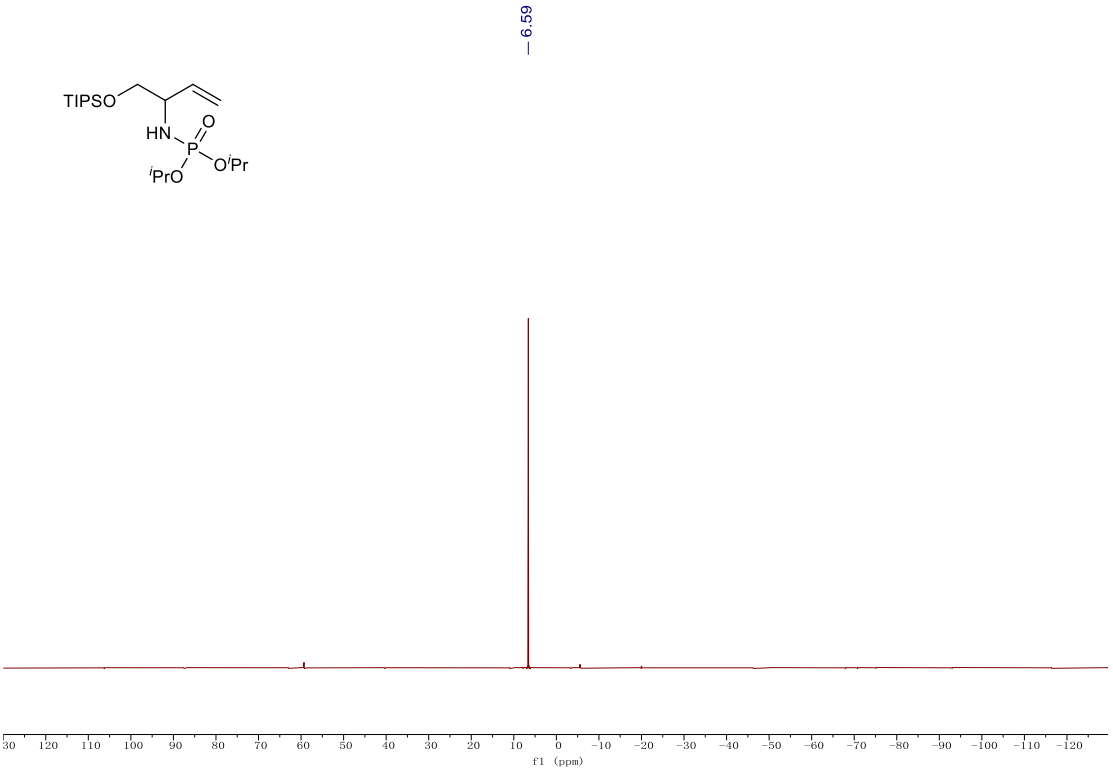

**19,** $^{1}$H NMR (500 MHz, $CDCl_3$)



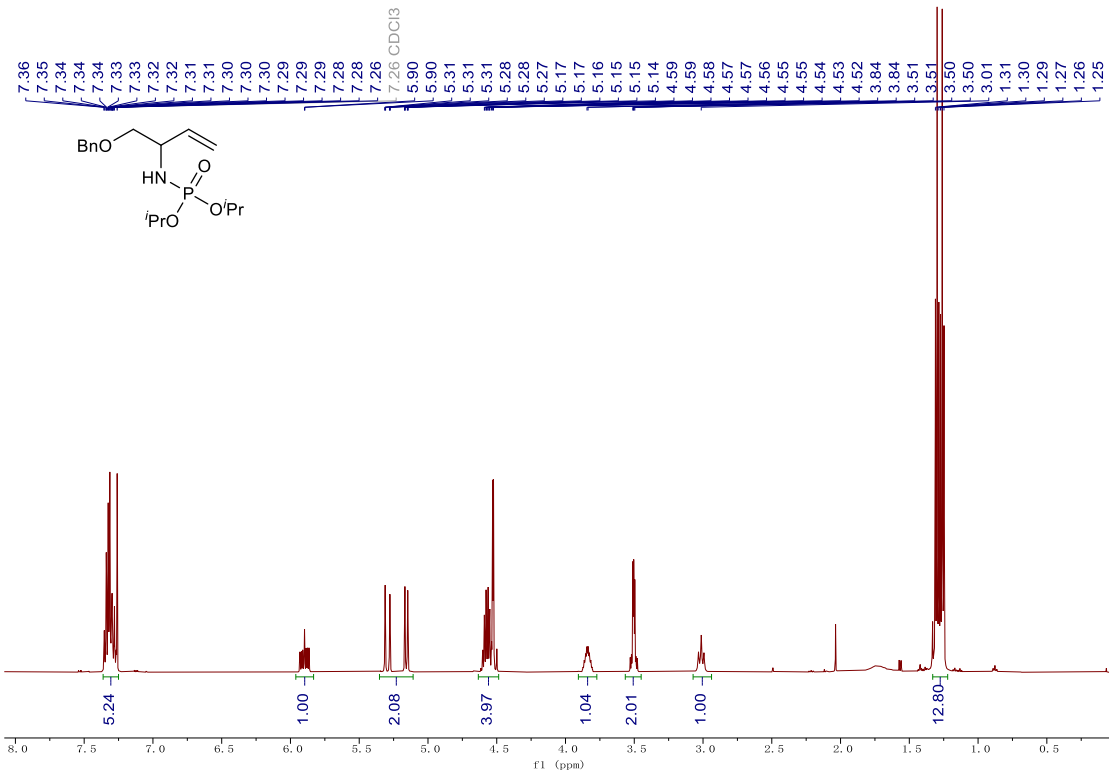

**19,** $^{13}$C NMR (126 MHz, $CDCl_3$)



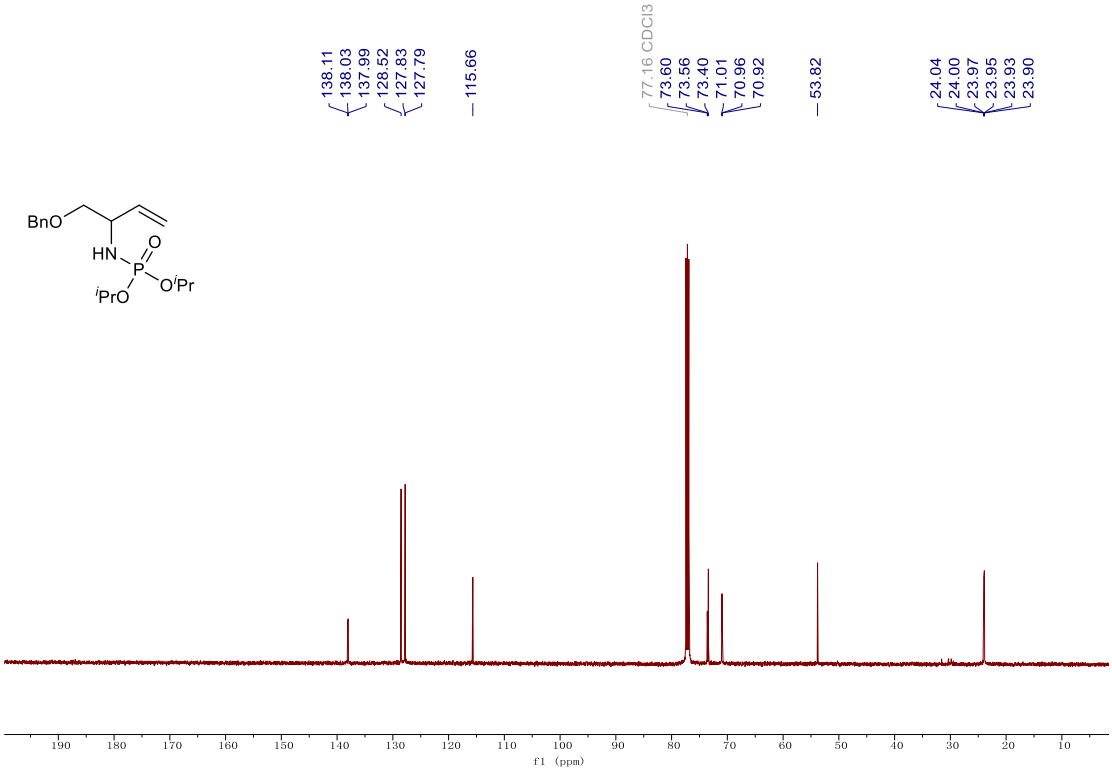

**19,** $^{31}$P NMR (202 MHz, $CDCl_3$)



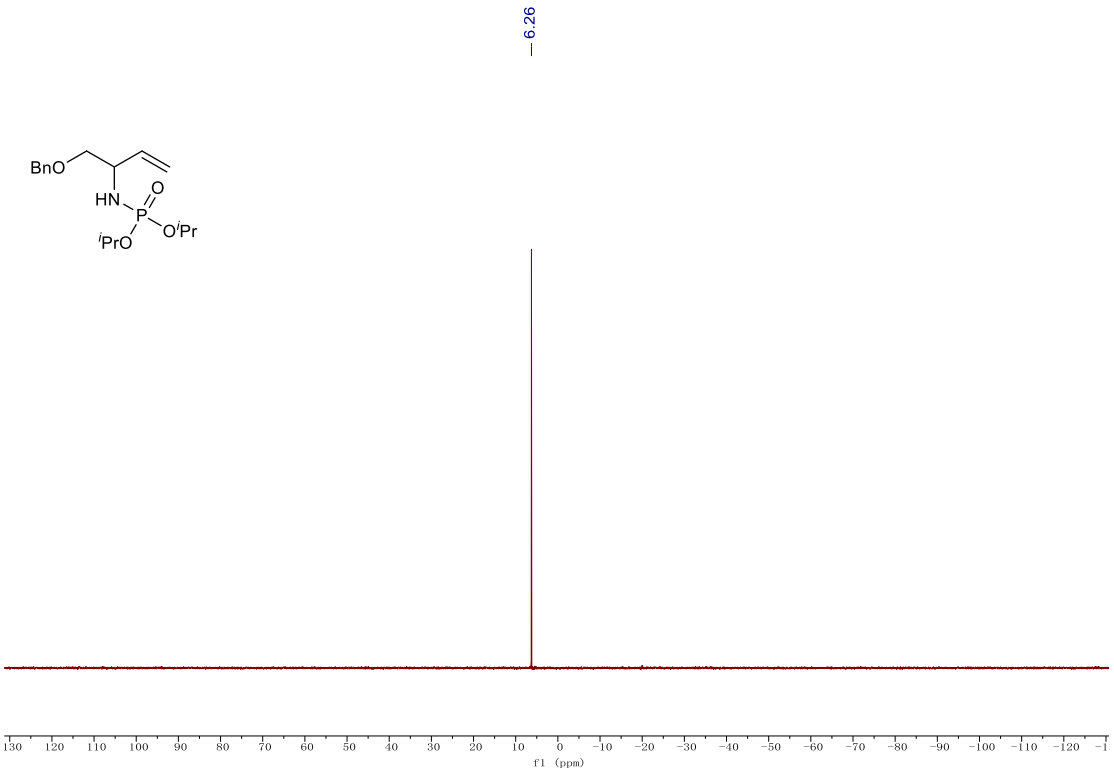

**20,** $^{1}$H NMR (500 MHz, $CDCl_3$)



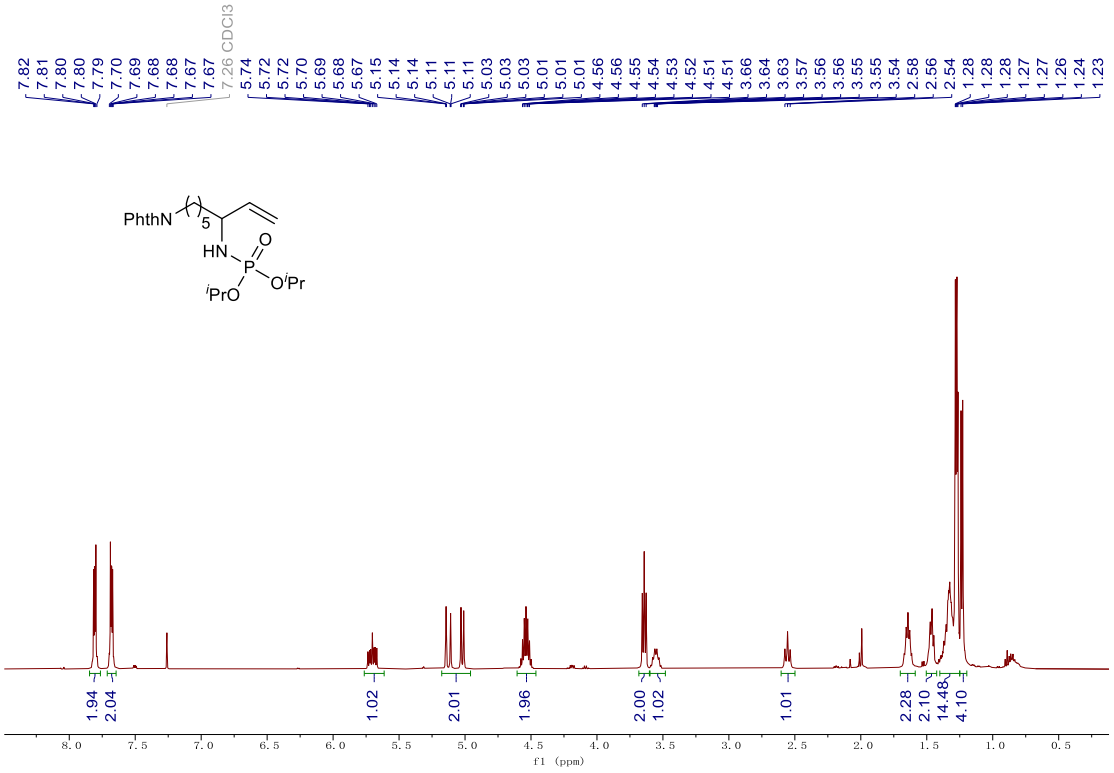

**20,** $^{13}$C NMR (126 MHz, $CDCl_3$)



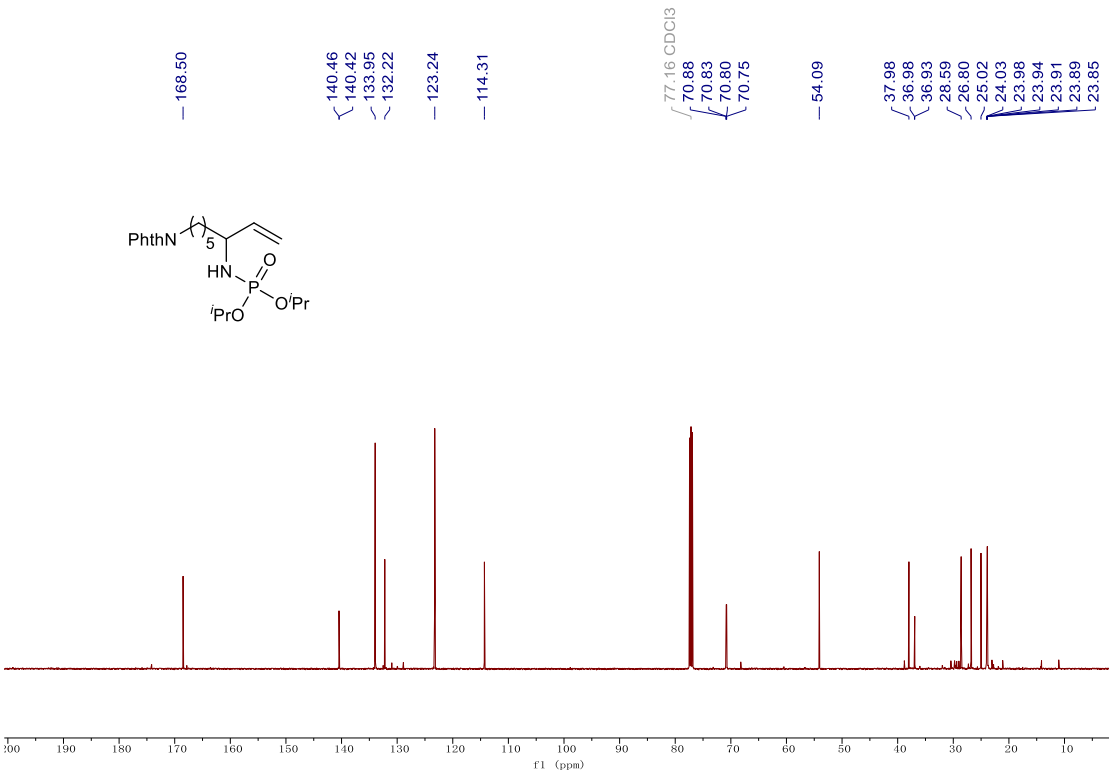

**20,** $^{31}$P NMR (202 MHz, $CDCl_3$)



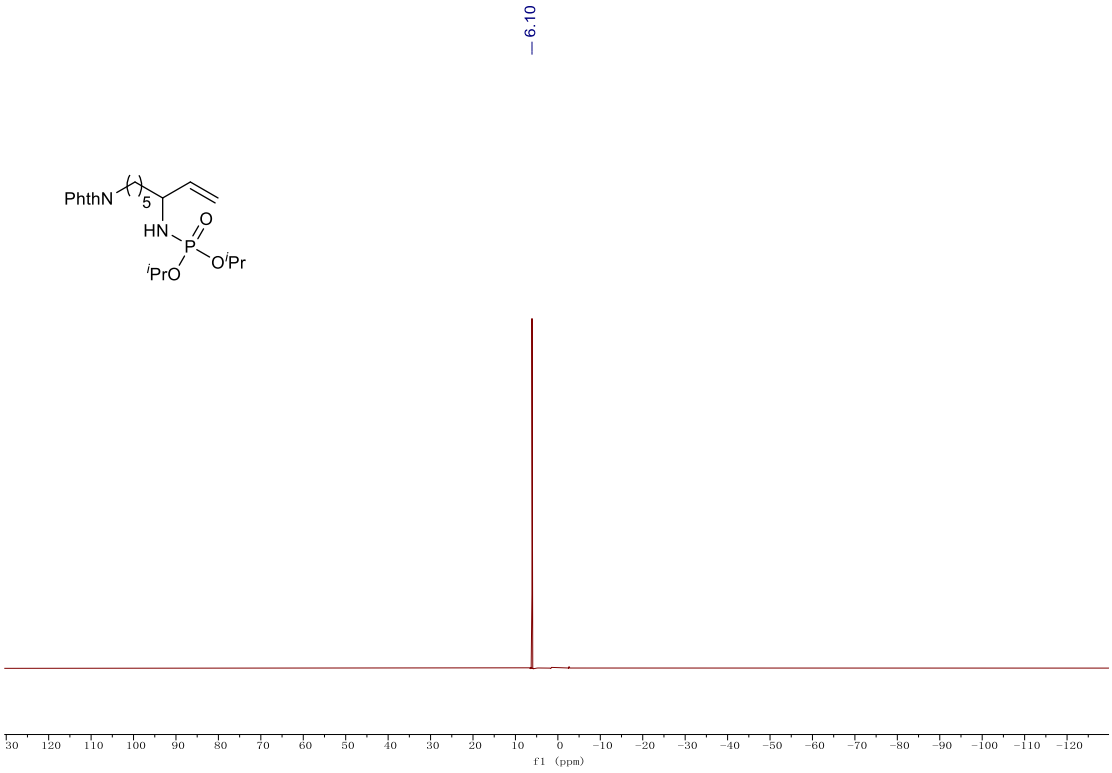

**21,** $^{1}$H NMR (500 MHz, $CDCl_3$)



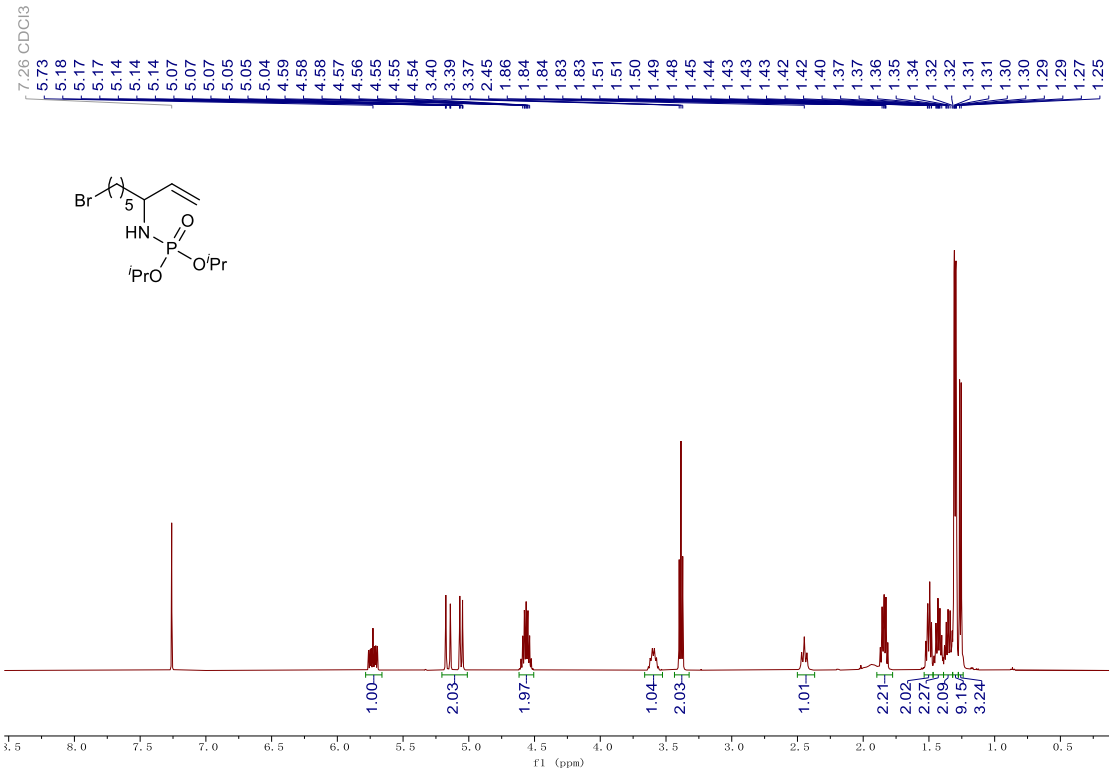

**21,** $^{13}$C NMR (126 MHz, $CDCl_3$)



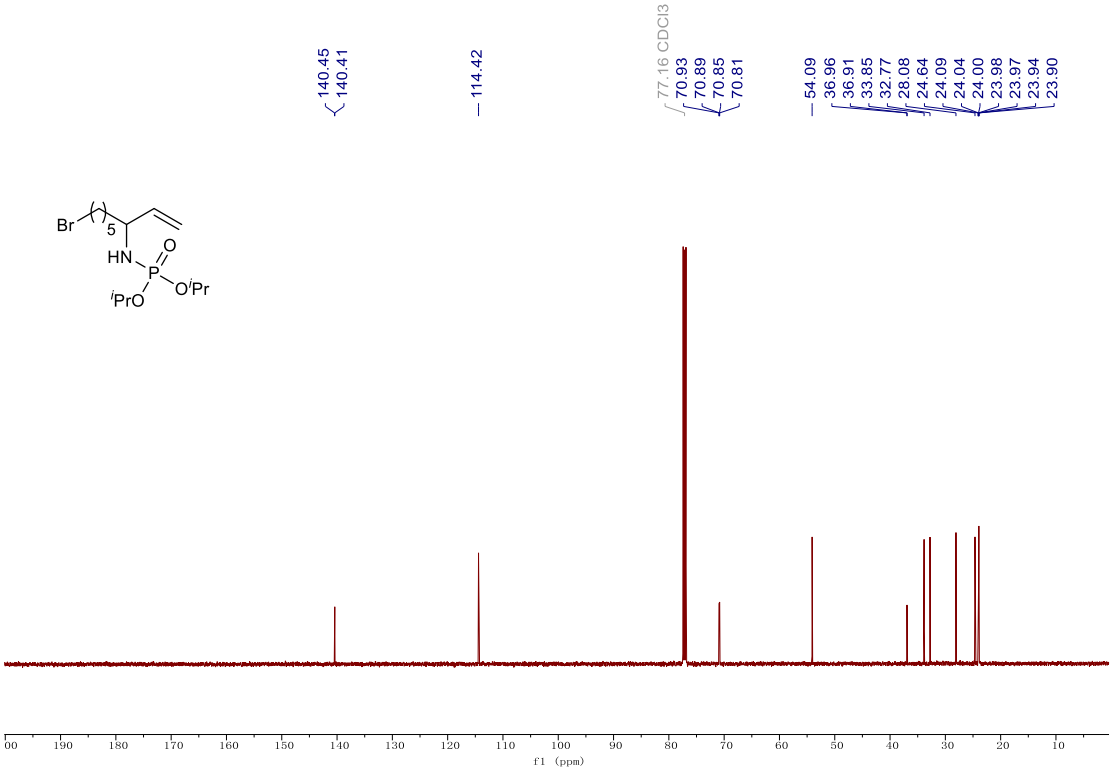

**21,** $^{31}$P NMR (202 MHz, $CDCl_3$)



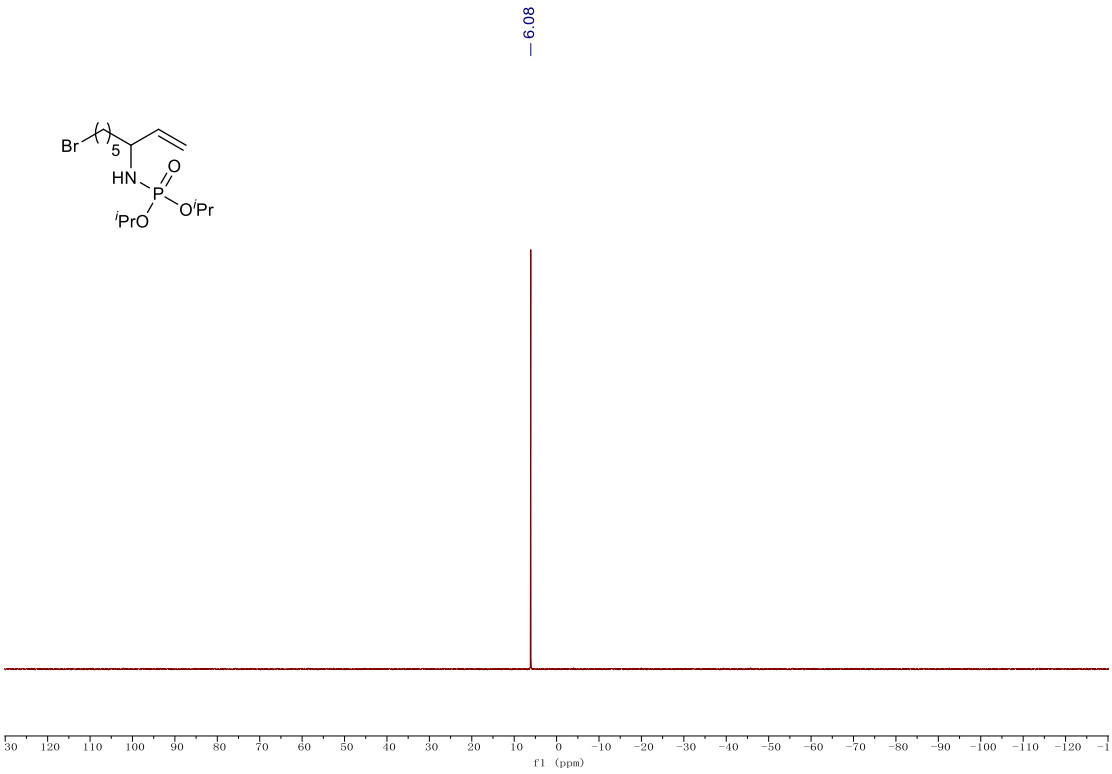

**22,** $^{1}$H NMR (500 MHz, $CDCl_3$)



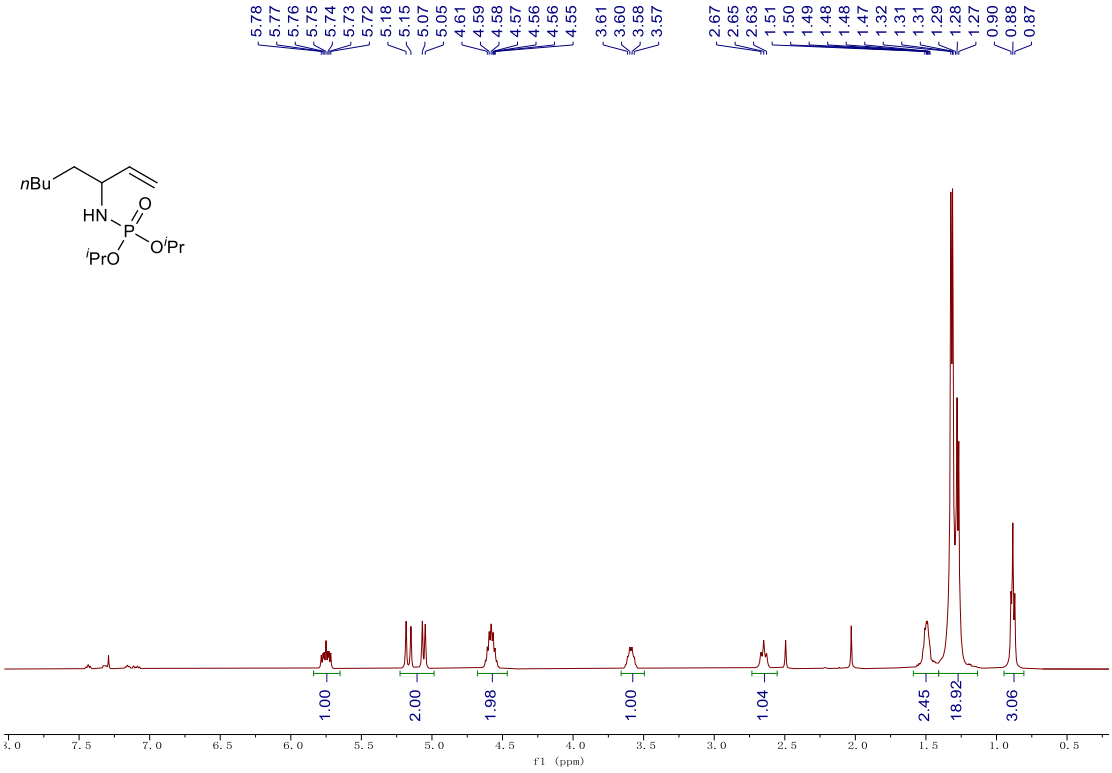

**22,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



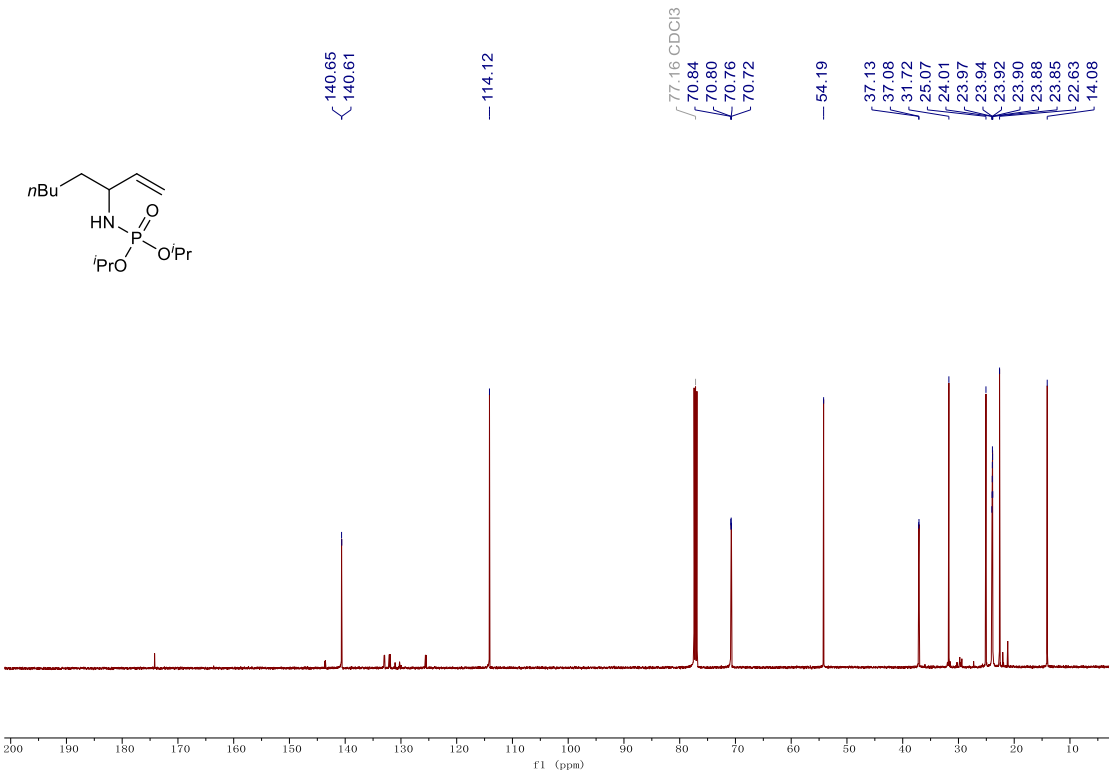

**22,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



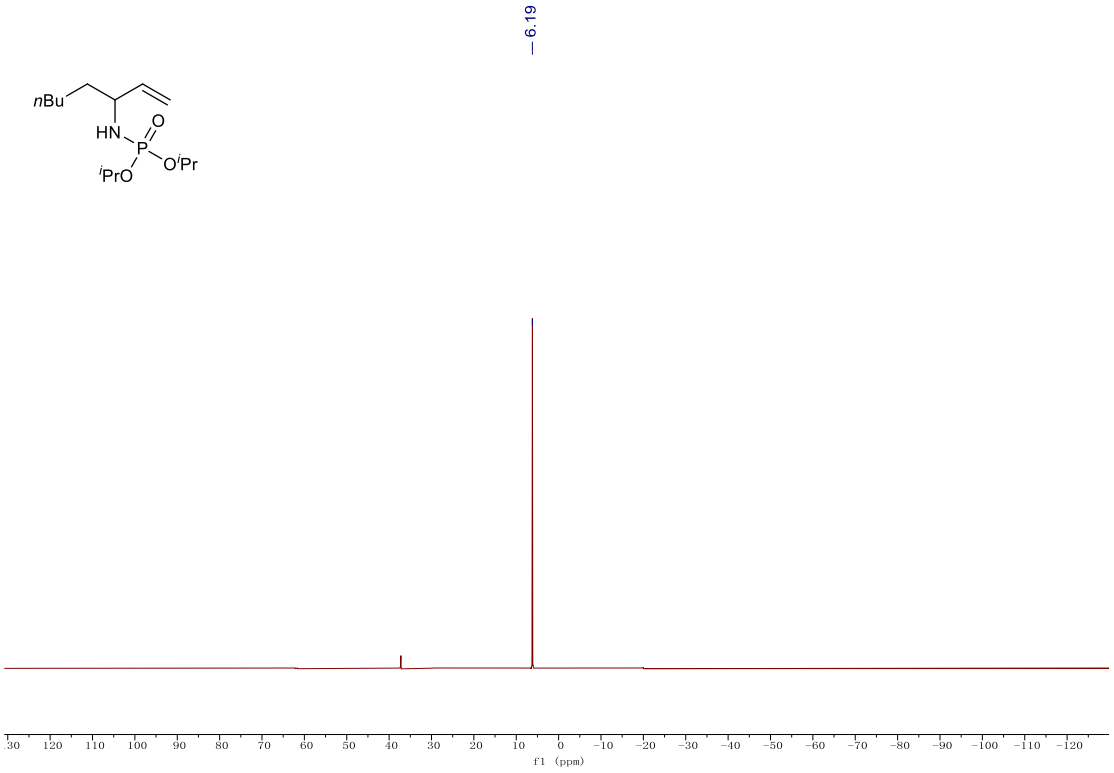

**23,** $^{1}$H NMR (500 MHz, $CDCl_3$)



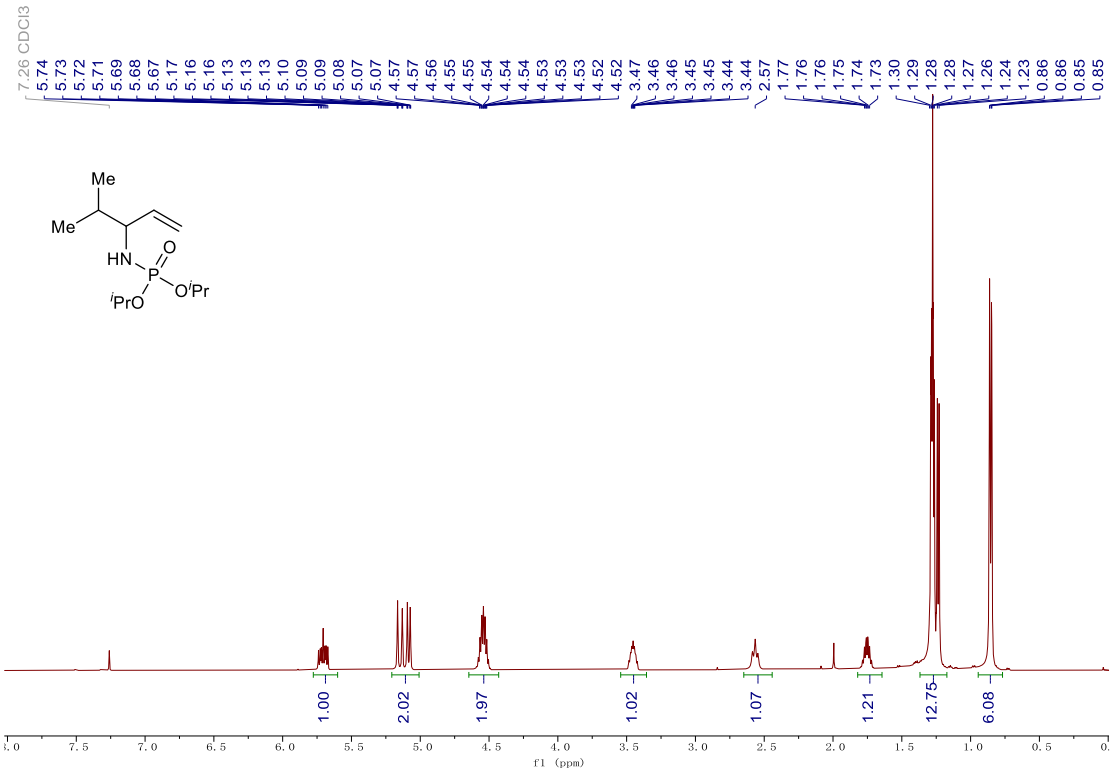

**23,** $^{13}$C NMR (126 MHz, $CDCl_3$)



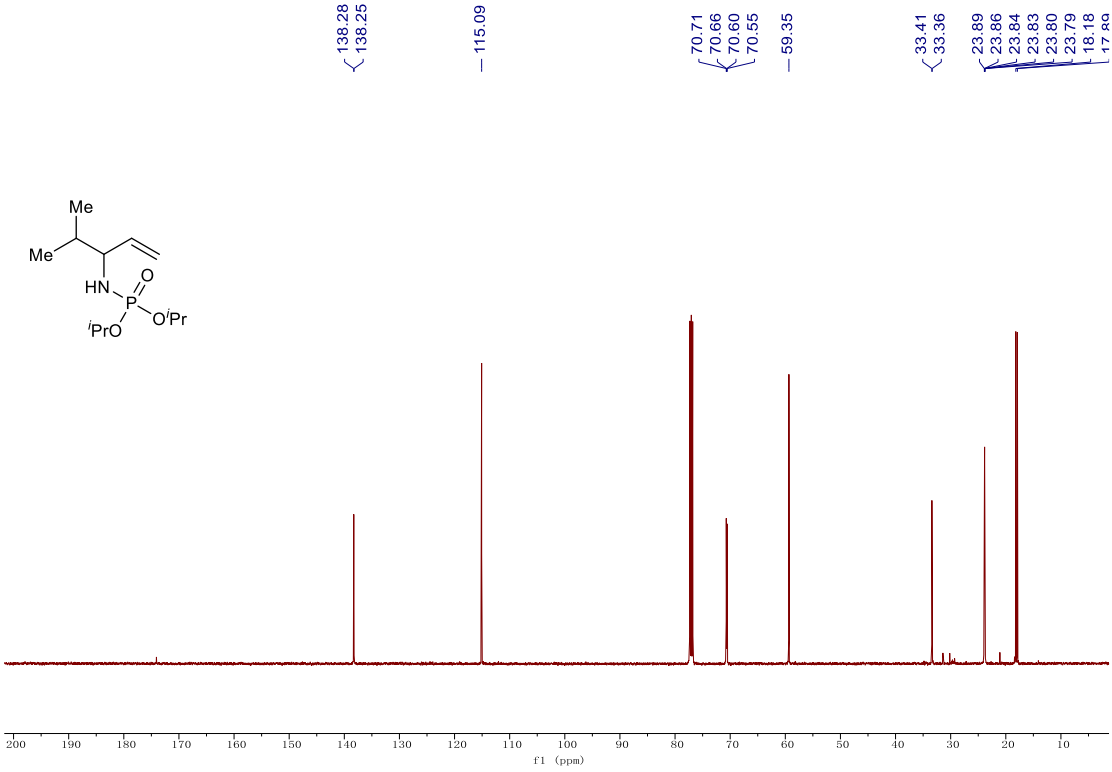

**23,** $^{31}$P NMR (202 MHz, $CDCl_3$)



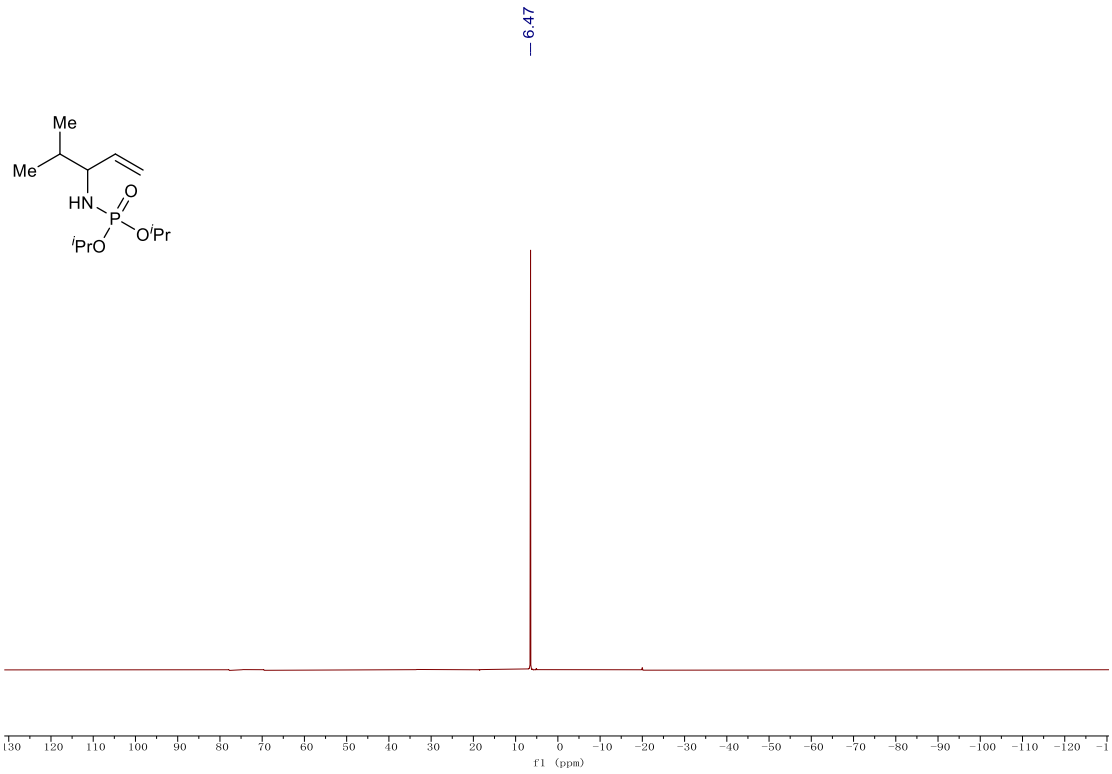

**24,** $^{1}$H NMR (500 MHz, $CDCl_3$)



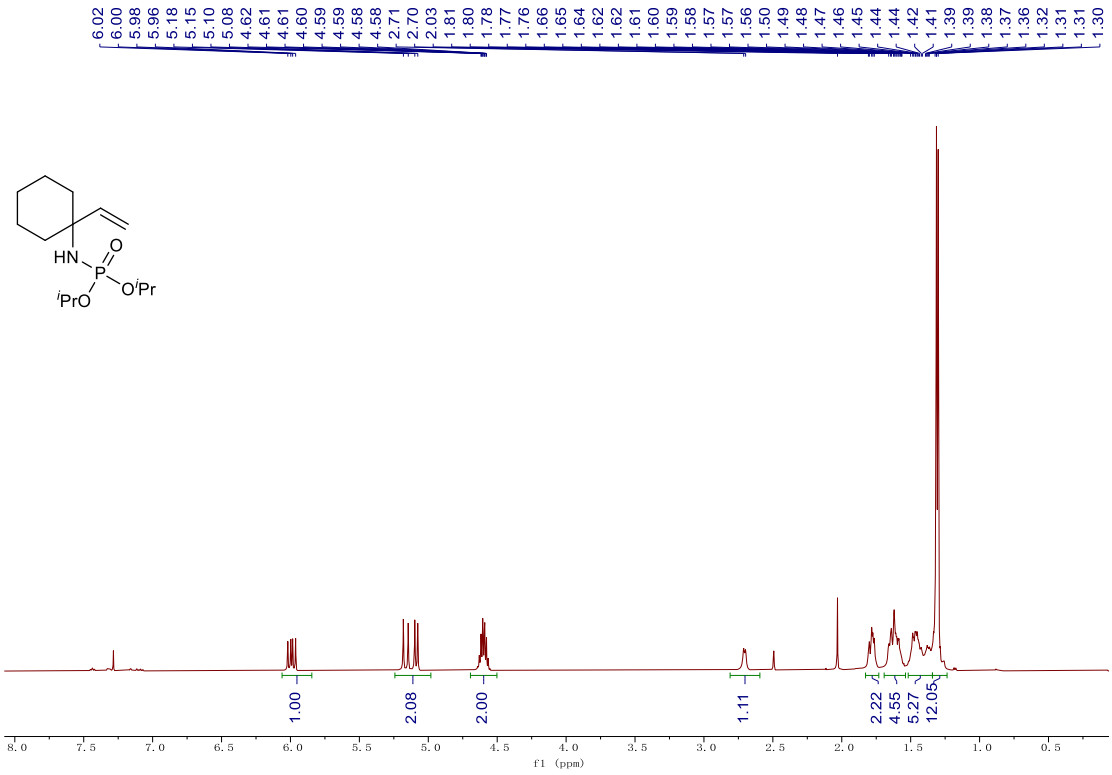

**24,** $^{13}$C NMR (126 MHz, $CDCl_3$)



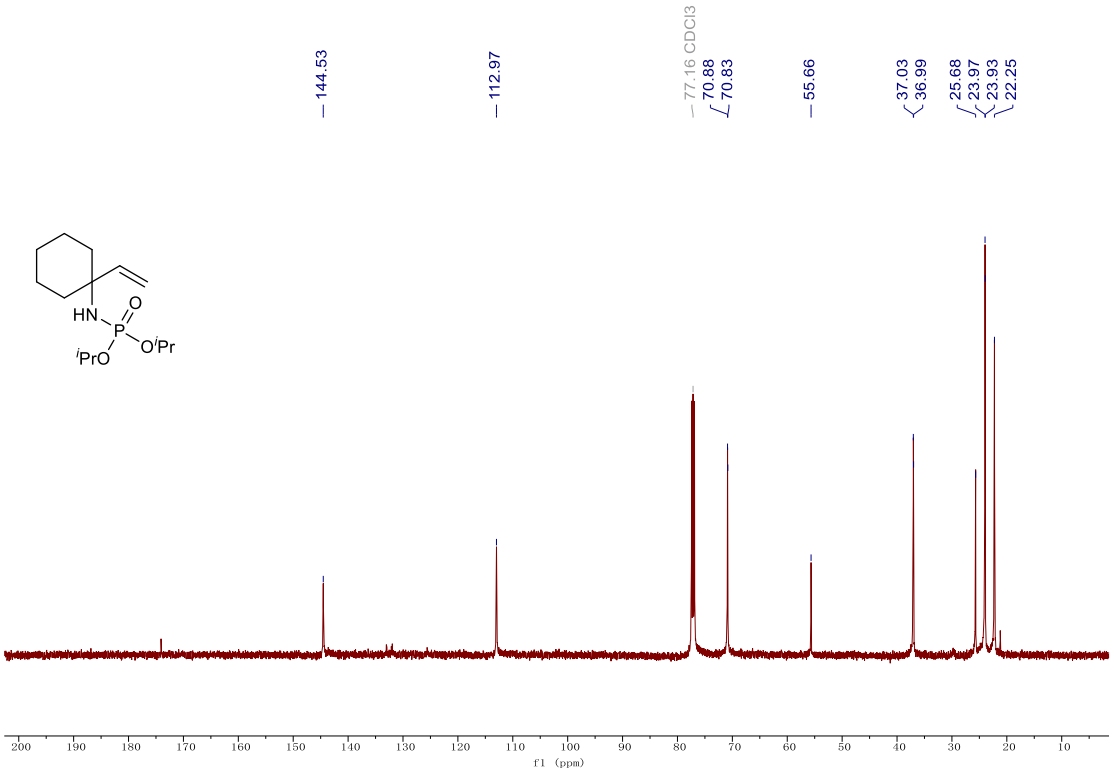

**24,** $^{31}$P NMR (202 MHz, $CDCl_3$)



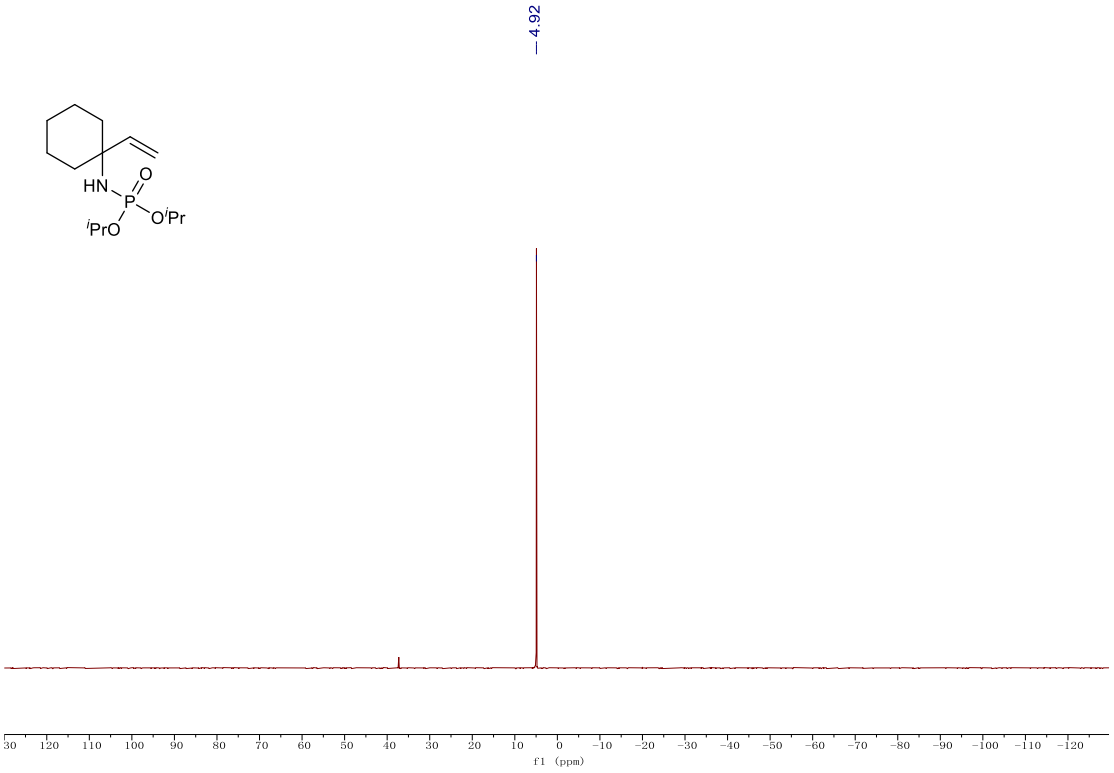

**25,** $^{1}$H NMR (500 MHz, $CDCl_3$)



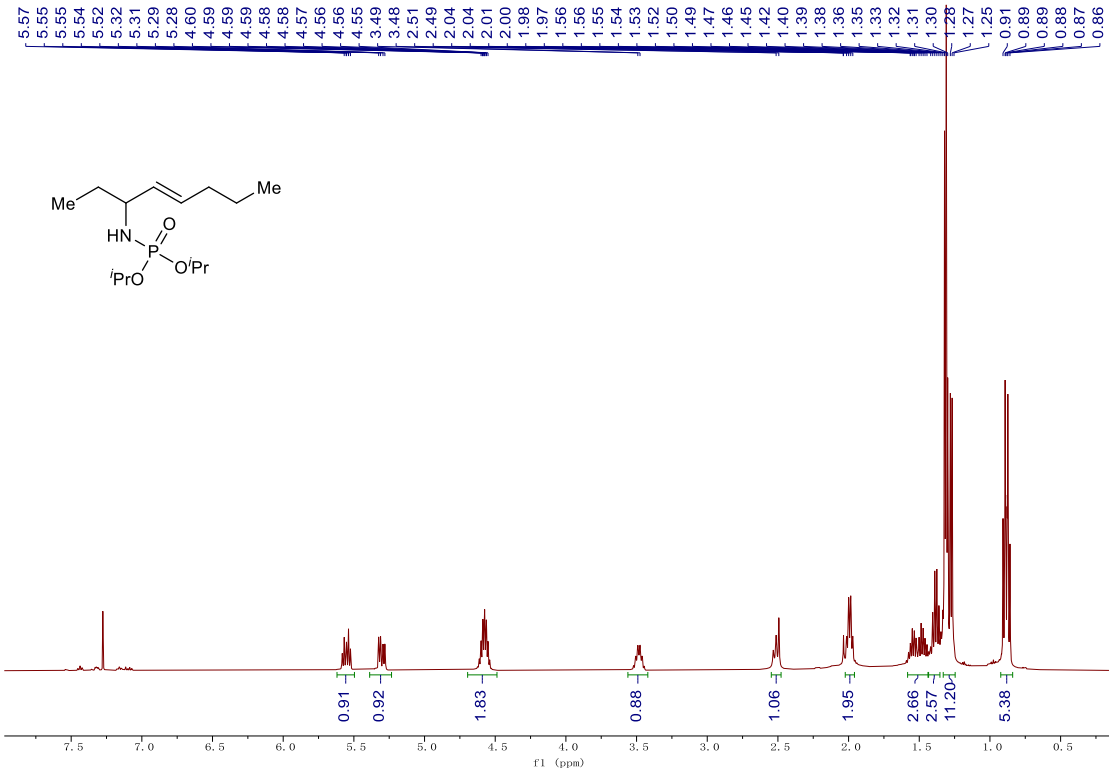

**25,** $^{13}$C NMR (126 MHz, $CDCl_3$)



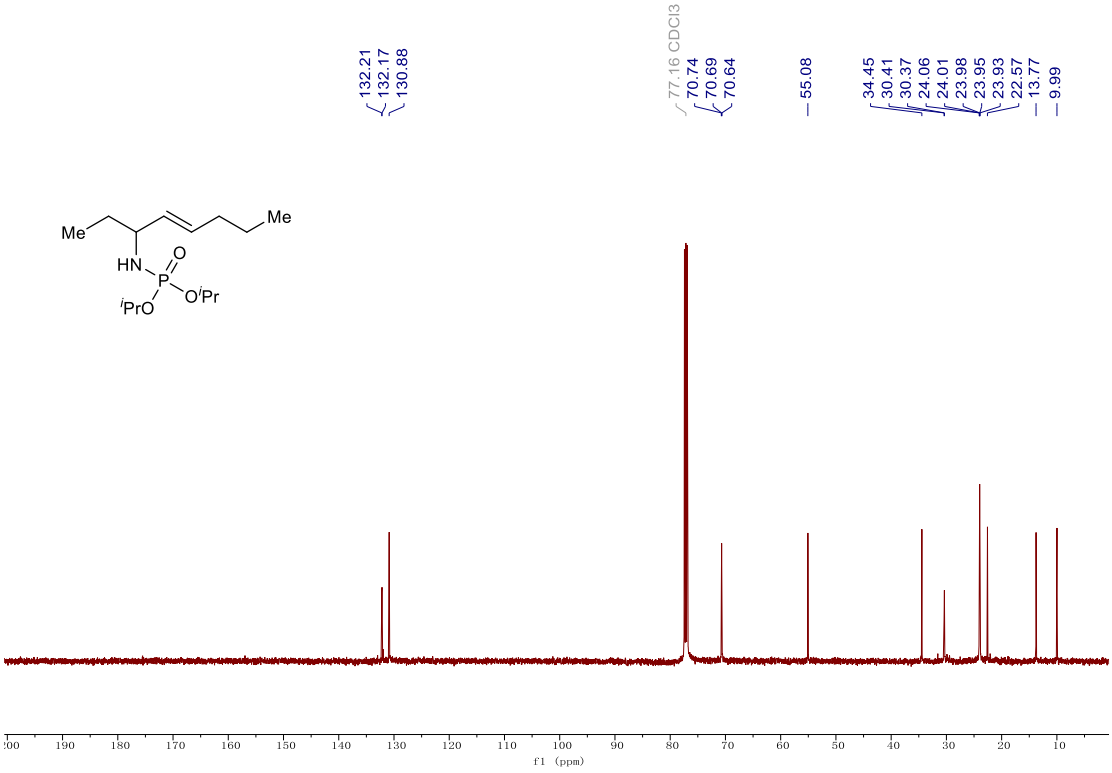

**25,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



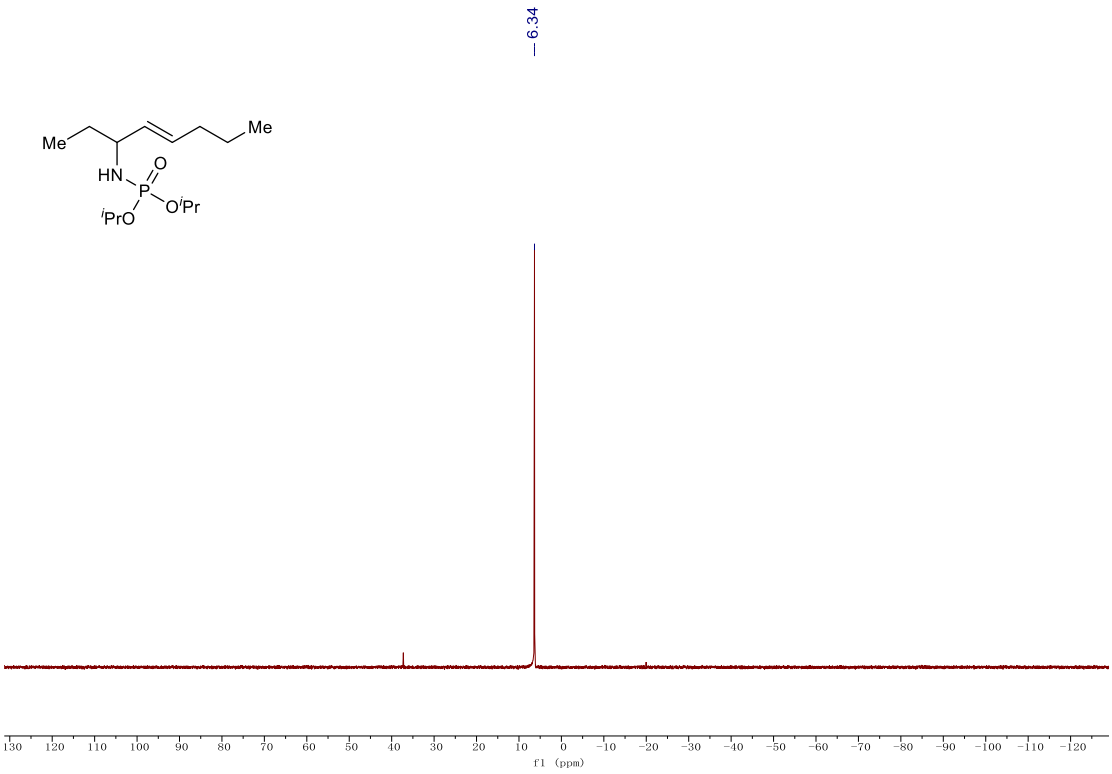

**26,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



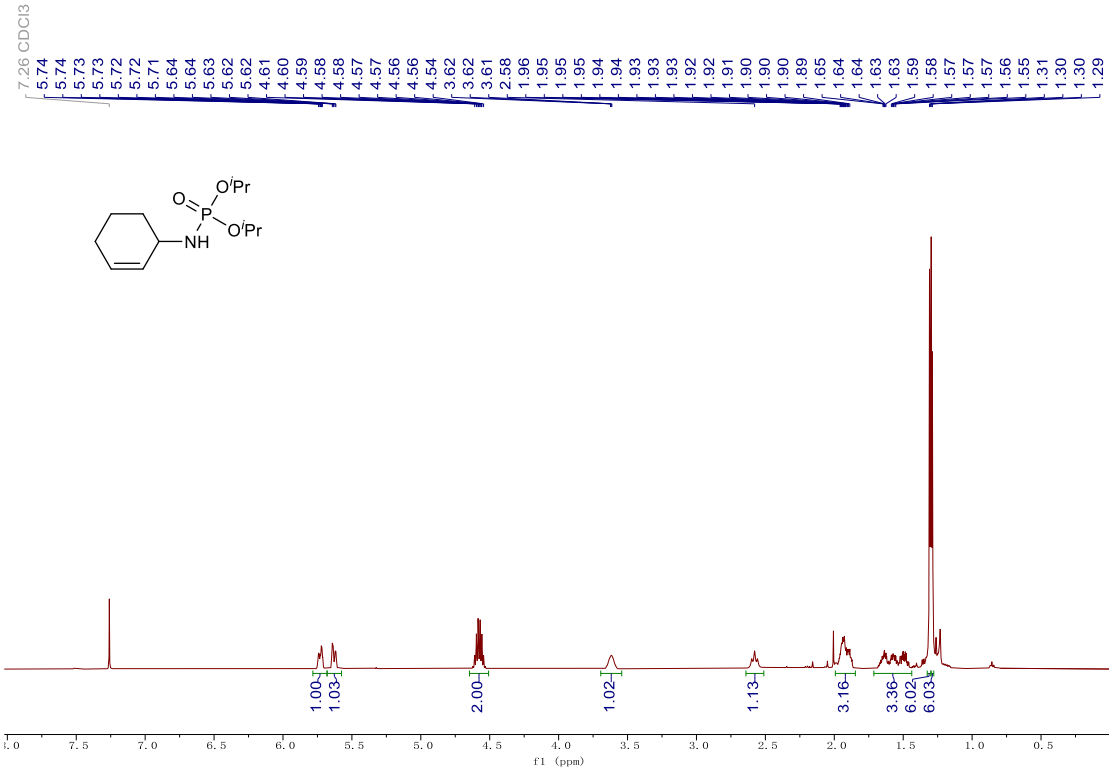

**26,** $^{13}$C NMR (126 MHz, $CDCl_3$)



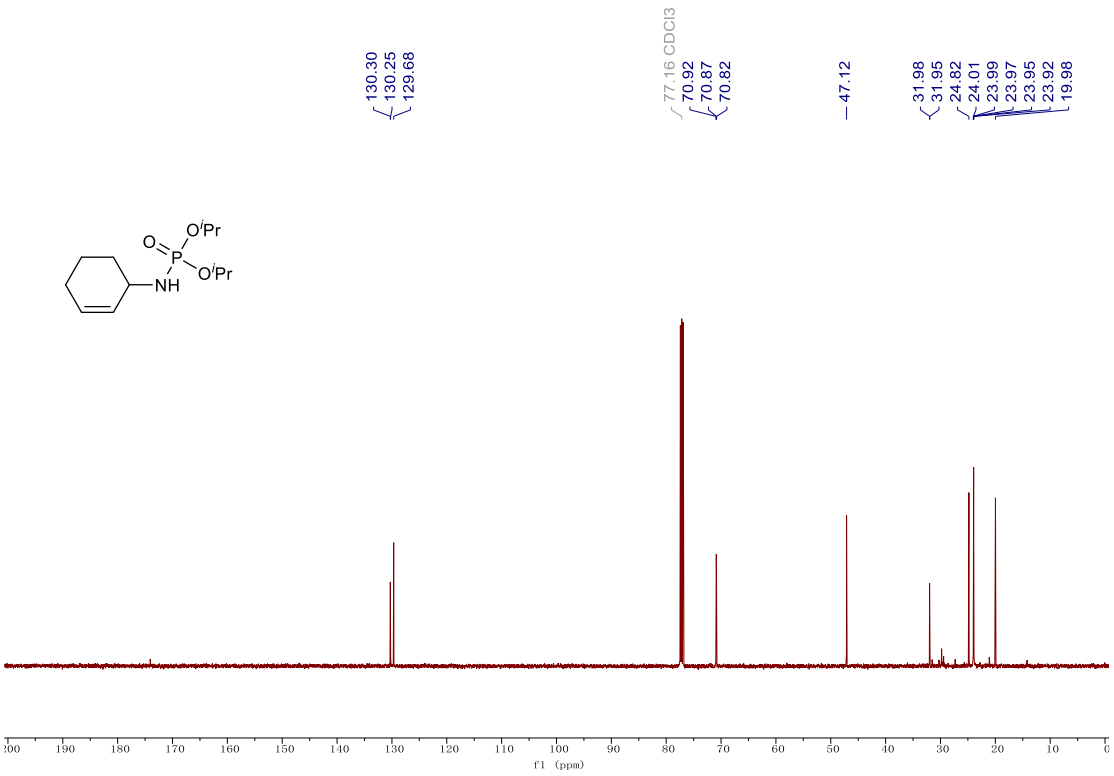

**26,** $^{31}$P NMR (202 MHz, $CDCl_3$)



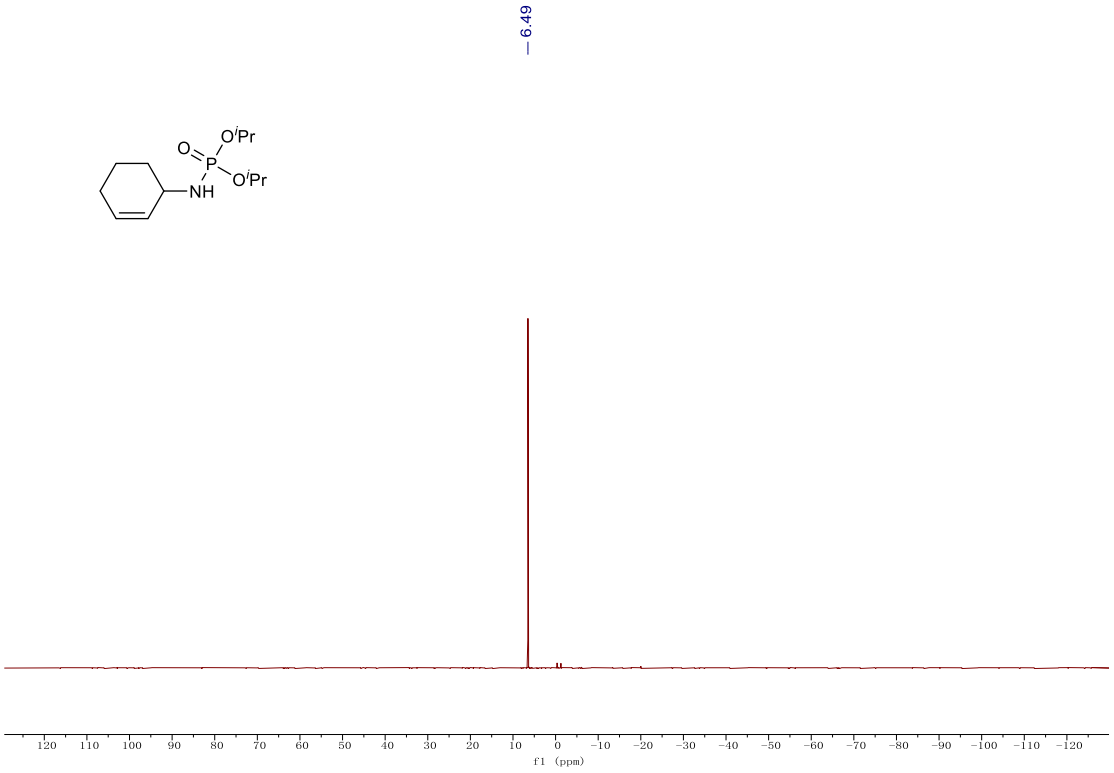

**27,** $^{1}$H NMR (500 MHz, $CDCl_3$)



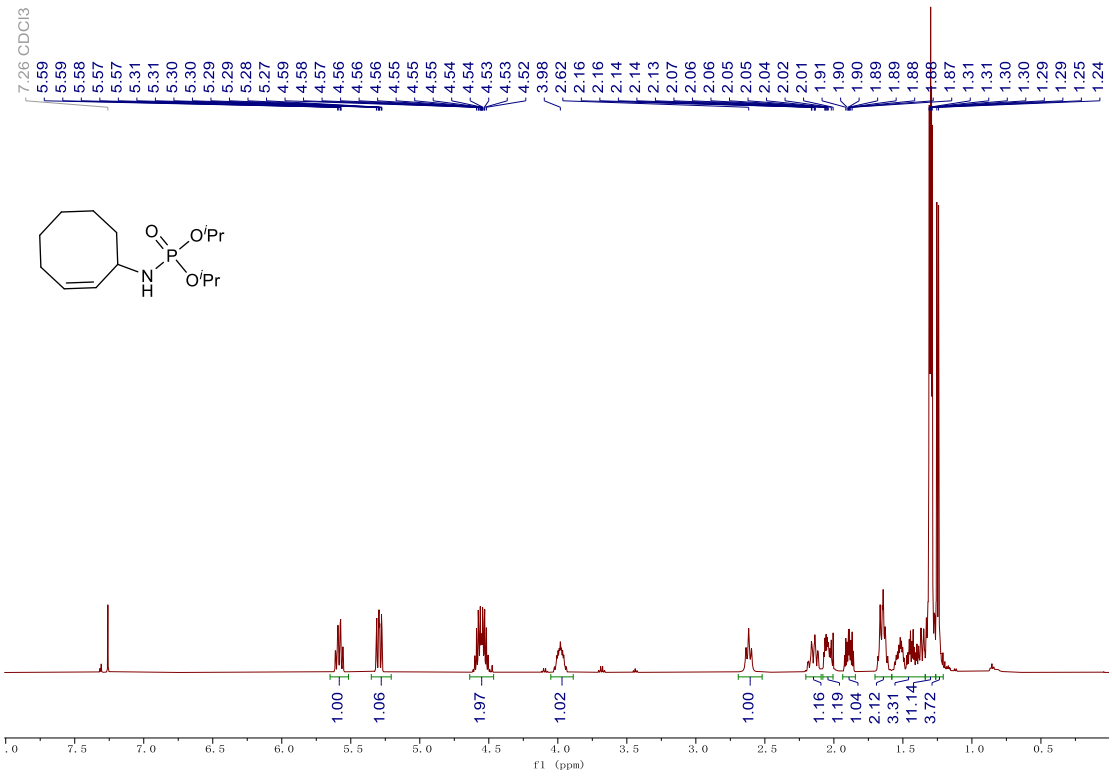

**27,** $^{13}$C NMR (126 MHz, $CDCl_3$)




**27,** $^{31}$P NMR (202 MHz, $CDCl_3$)

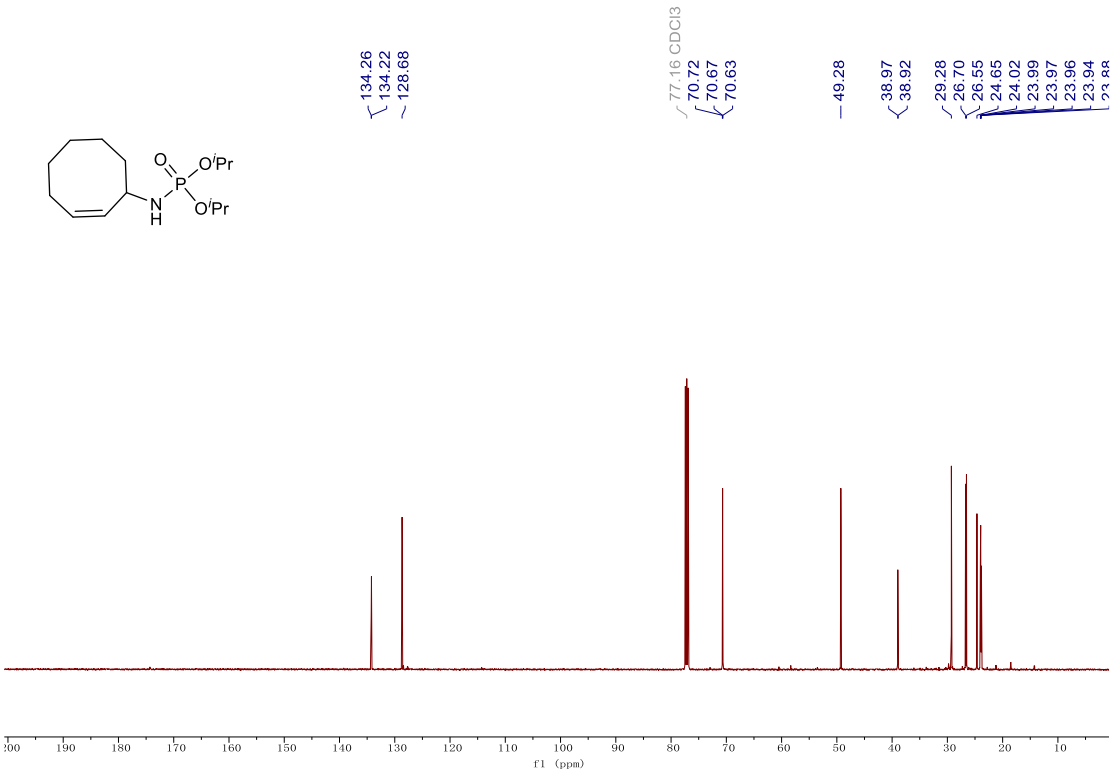



**28,** $^{1}$H NMR (500 MHz, $CDCl_3$)

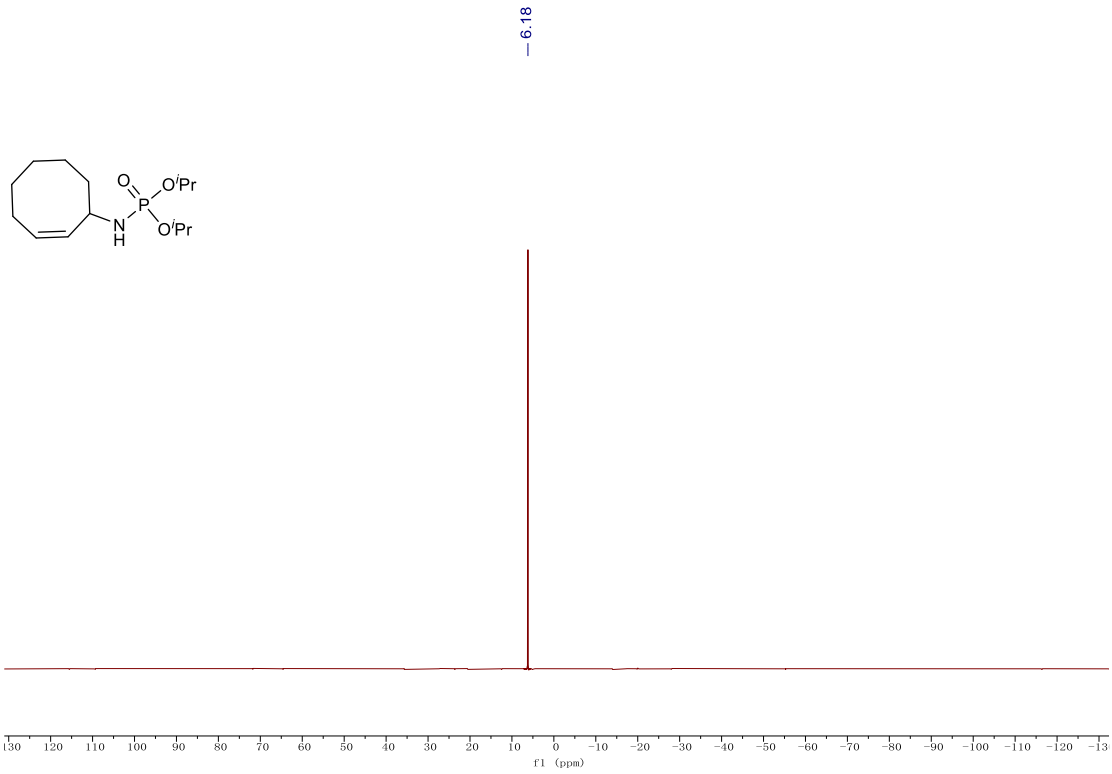



**28,** $^{13}$C NMR (126 MHz, $CDCl_3$)

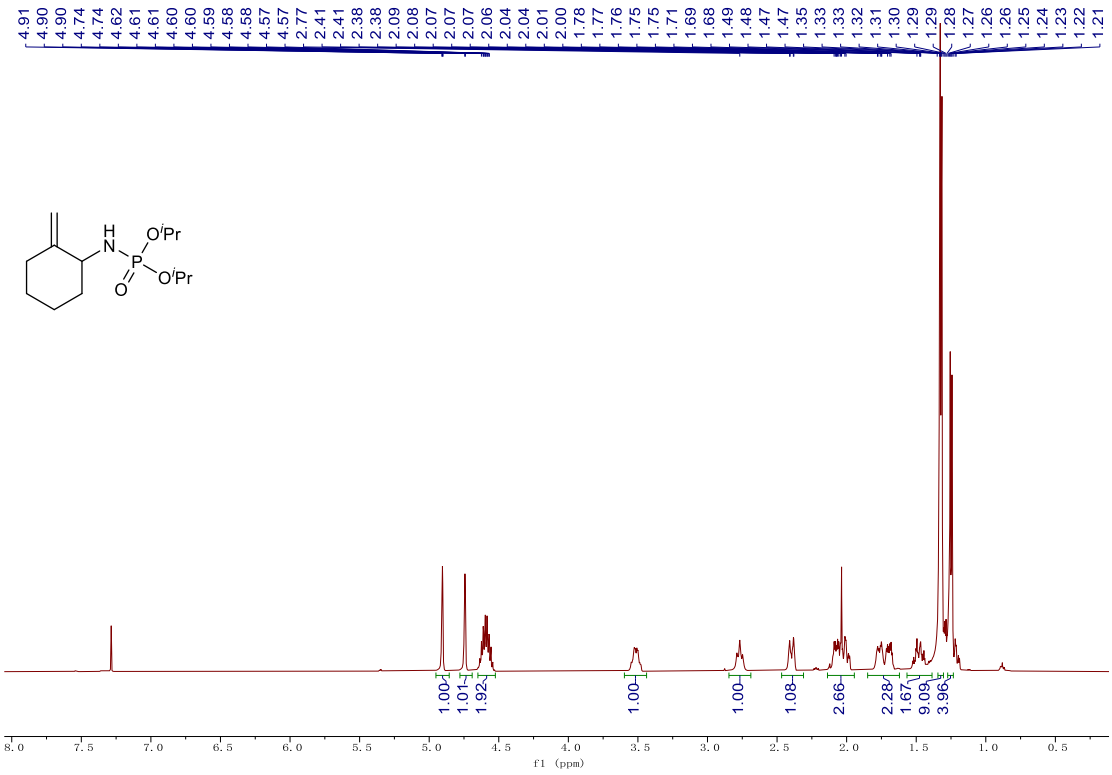
*



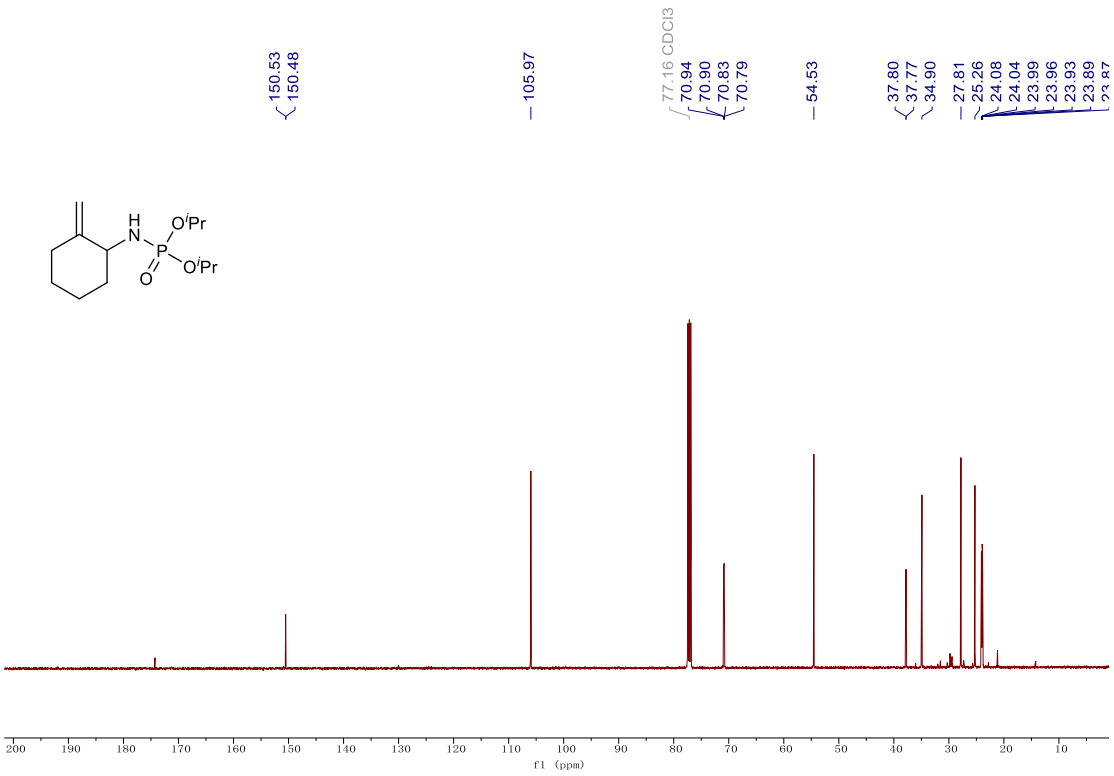

**28,** $^{31}$P NMR (202 MHz, $CDCl_3$)



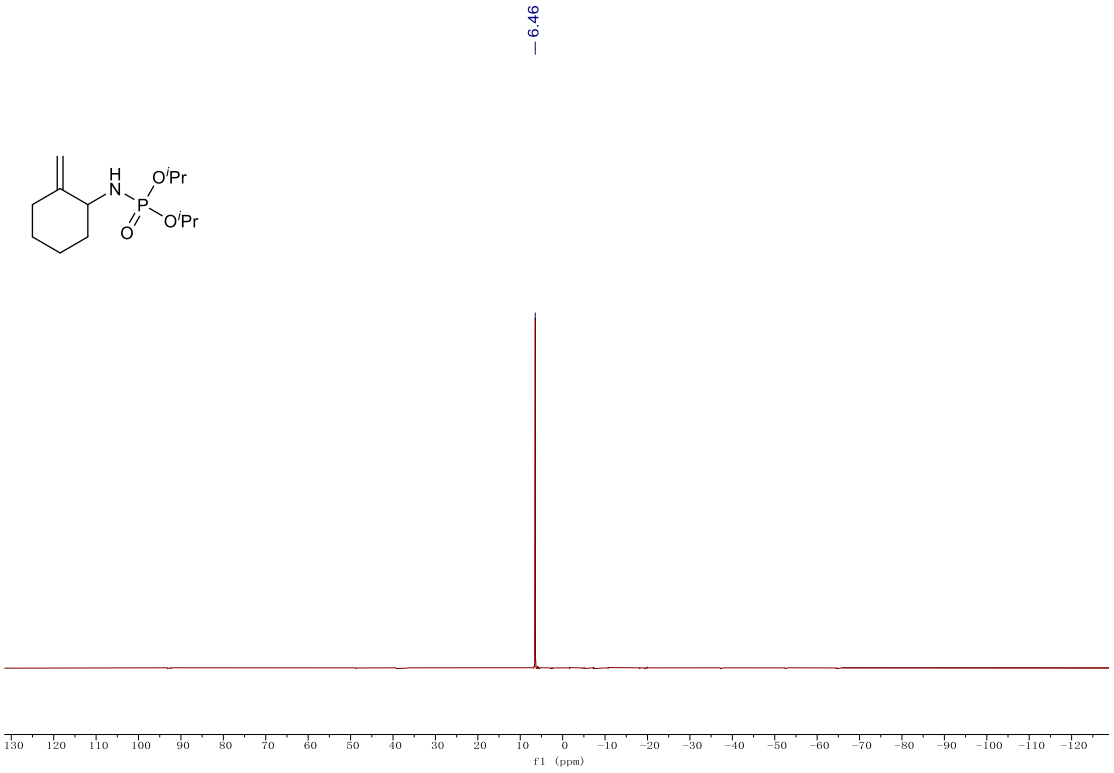

**29,** $^{1}$H NMR (500 MHz, $CDCl_3$)



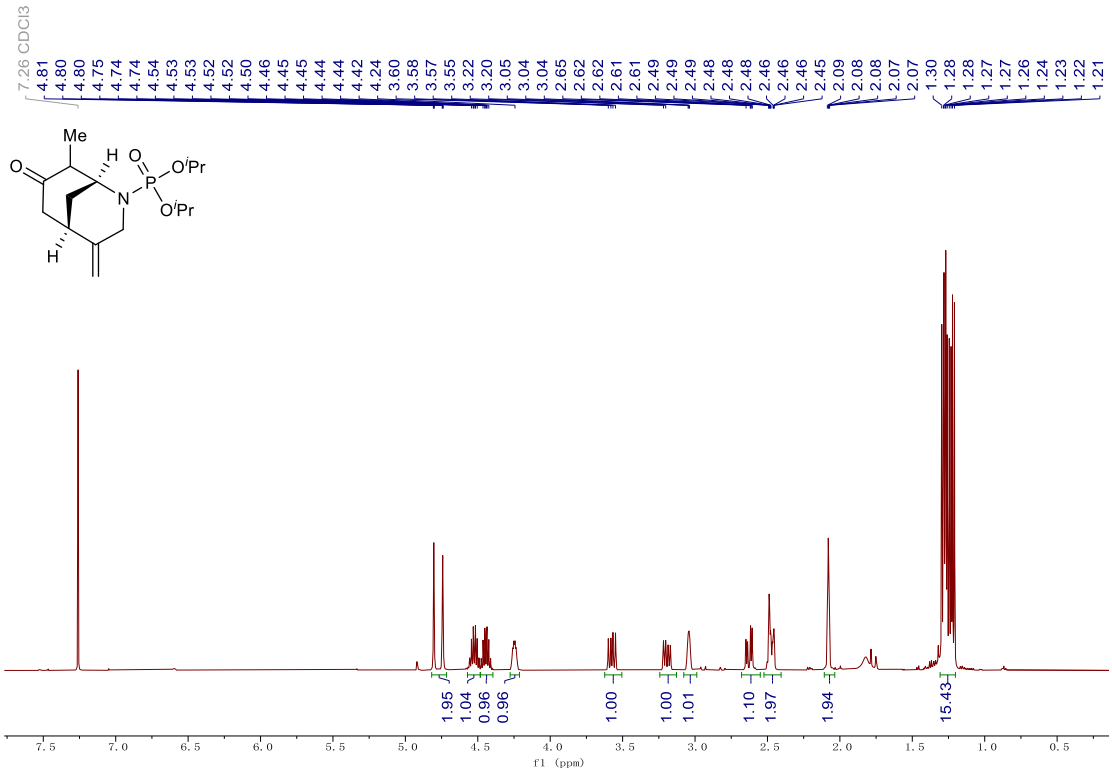

**29,** $^{13}$C NMR (126 MHz, $CDCl_3$)



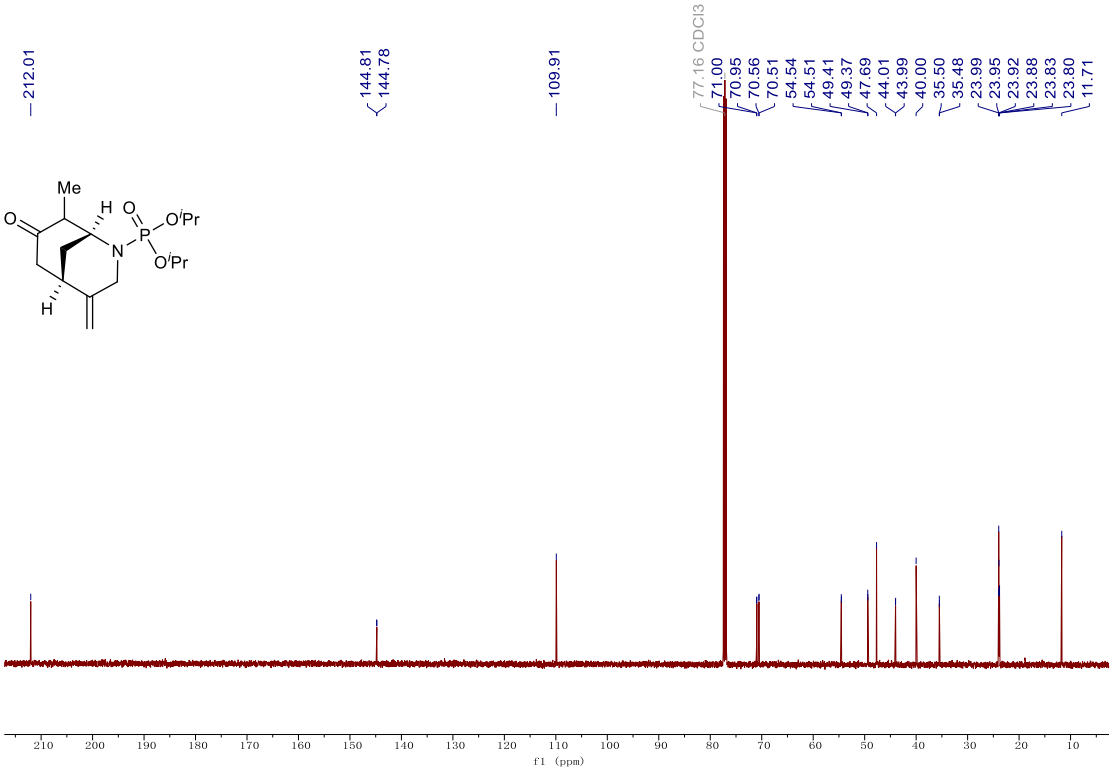

**29,** $^{31}$P NMR (202 MHz, $CDCl_3$)



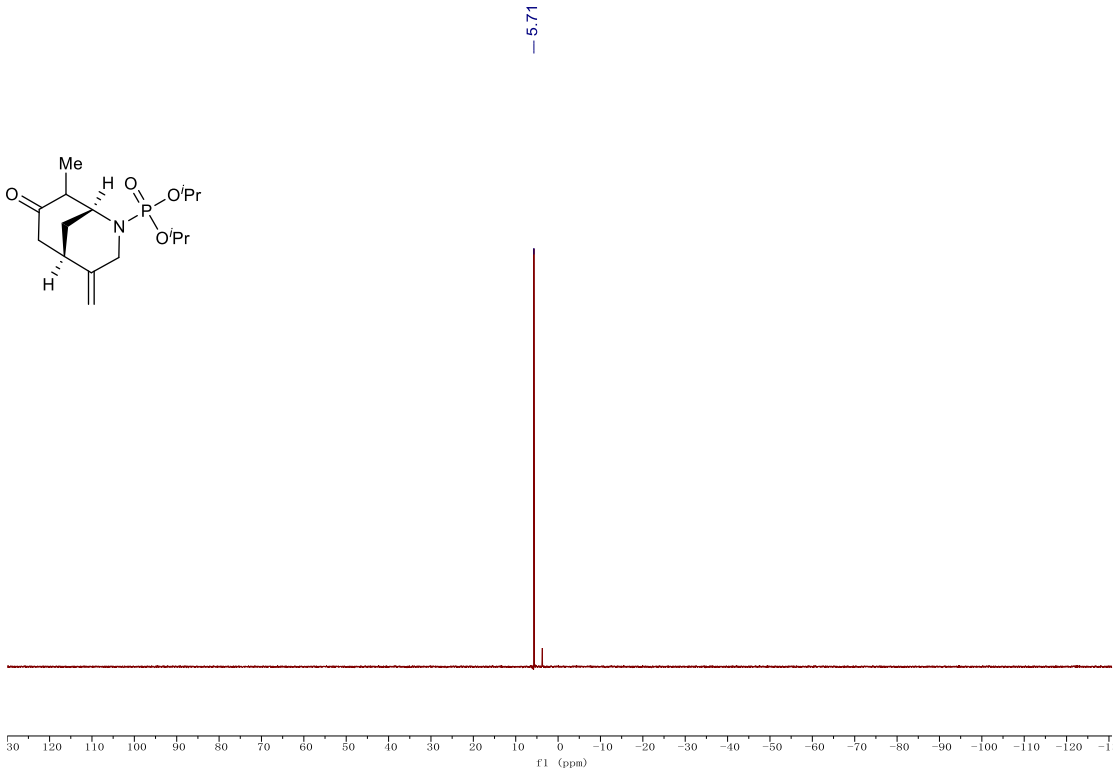

**30,** $^{1}$H NMR (500 MHz, $CDCl_3$)



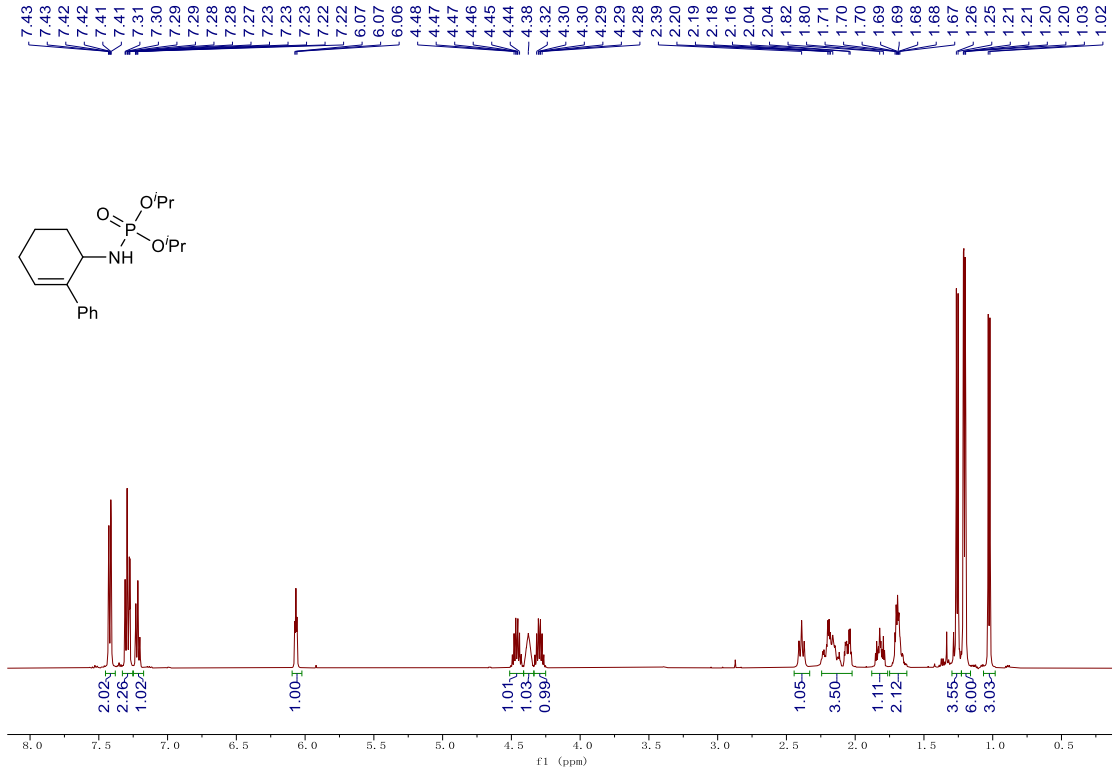

**30,** $^{13}$C NMR (126 MHz, $CDCl_3$)



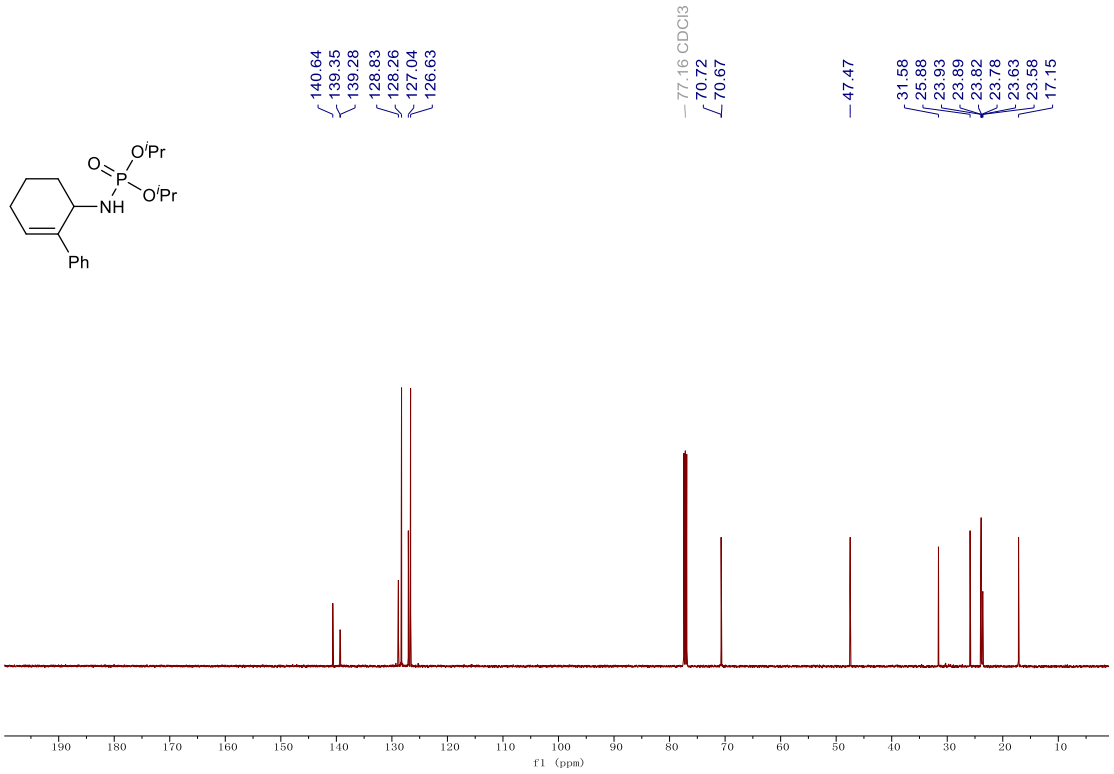

**30,** $^{31}$P NMR (202 MHz, $CDCl_3$)



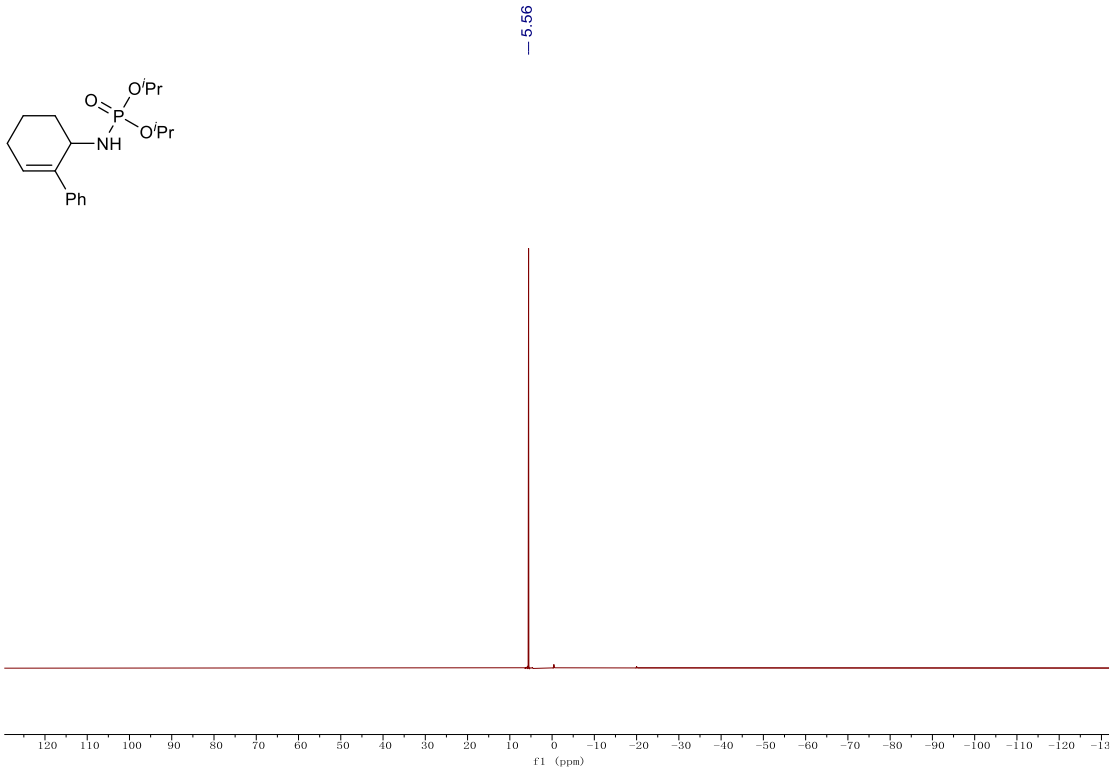

**31,** $^{1}$H NMR (500 MHz, $CDCl_3$)



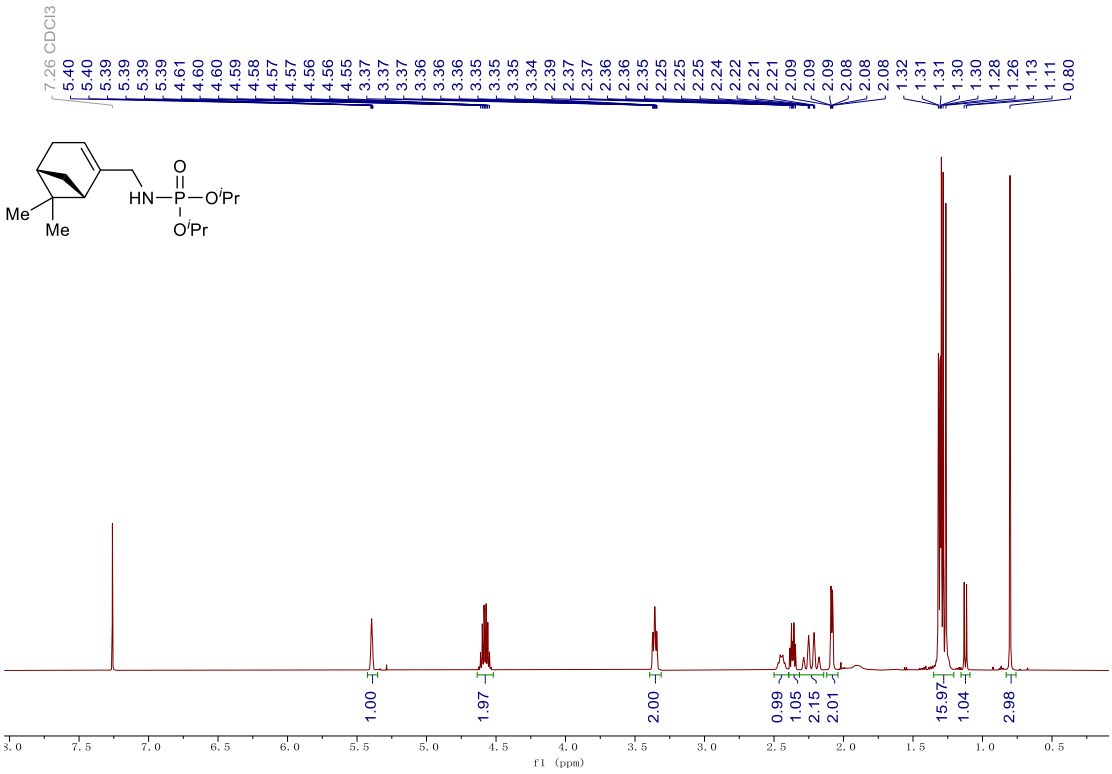

**31,** $^{13}$C NMR (126 MHz, $CDCl_3$)



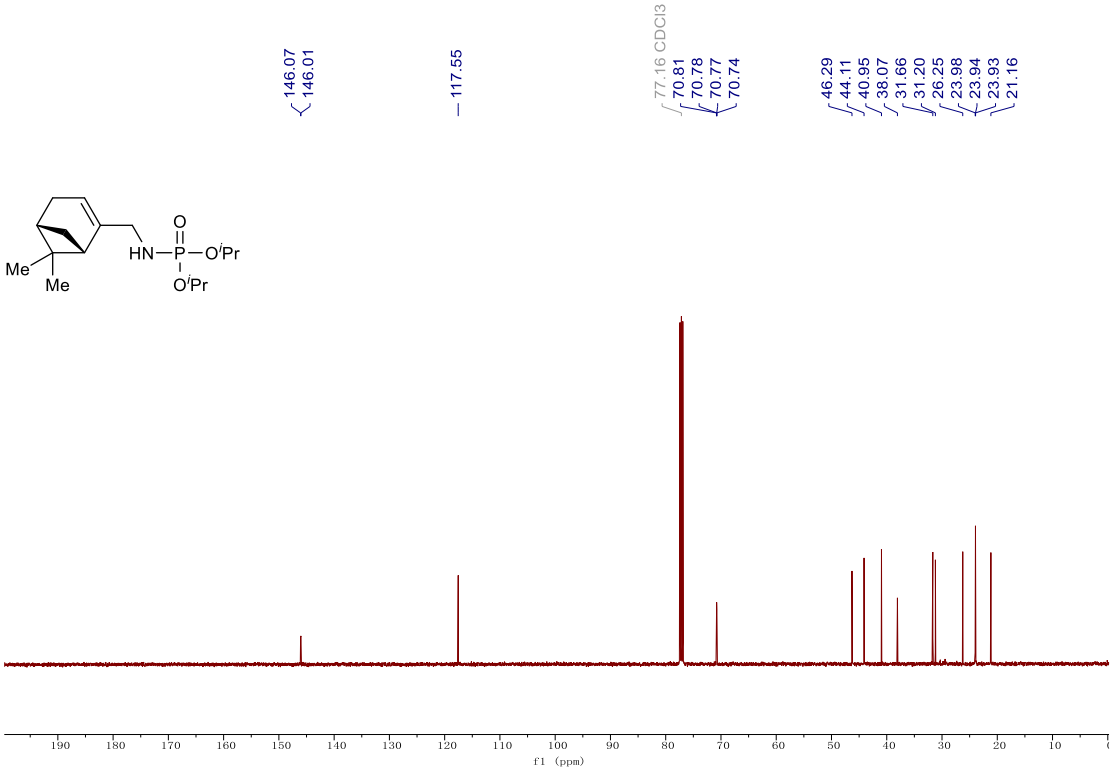

**31,** $^{31}$P NMR (202 MHz, $CDCl_3$)



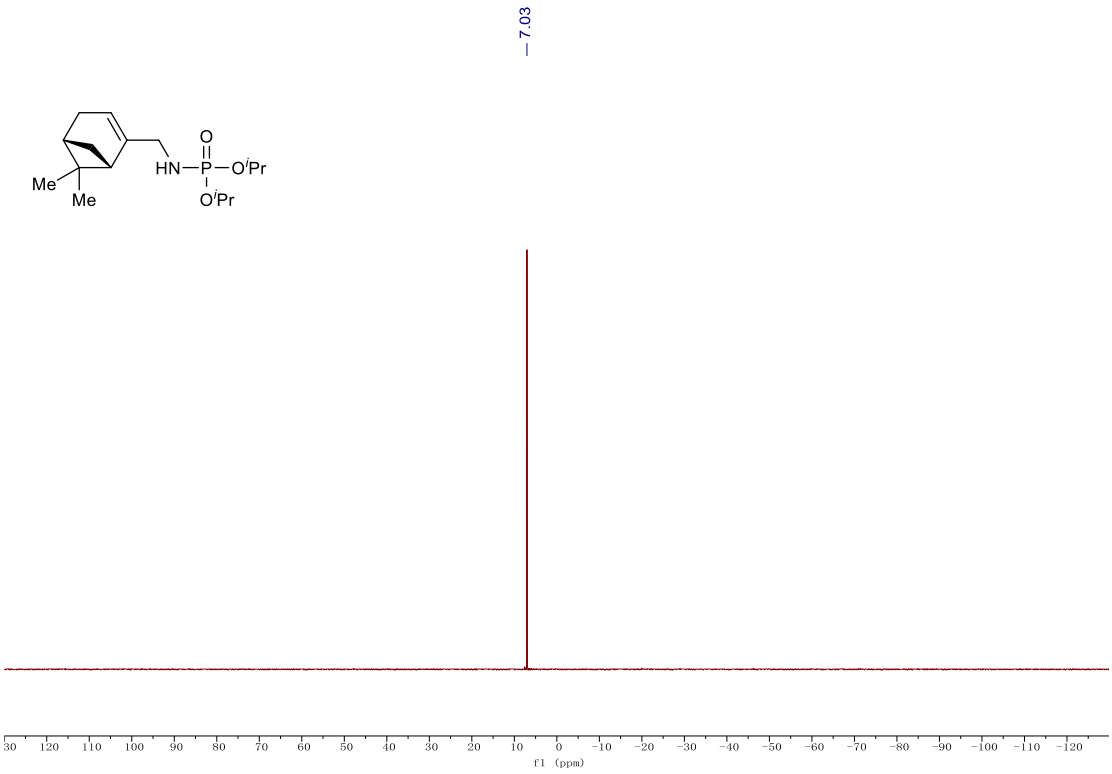

**32,** $^{1}$H NMR (500 MHz, $CDCl_3$)



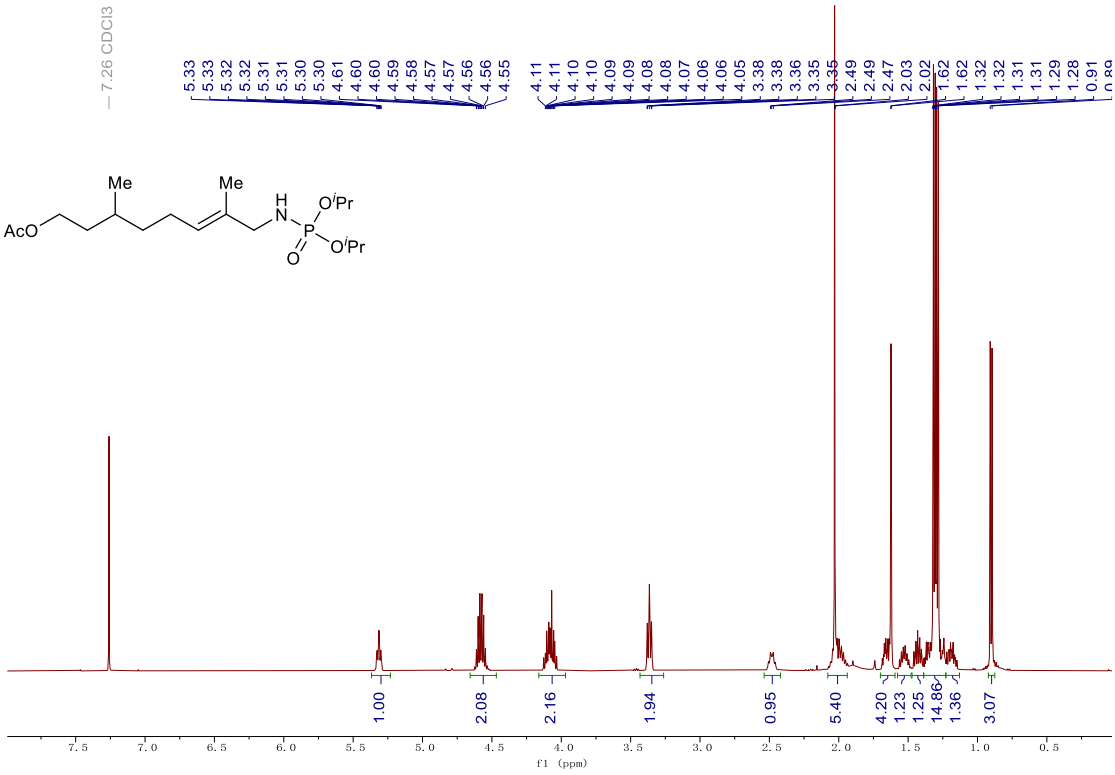

**32,** $^{13}$C NMR (126 MHz, $CDCl_3$)



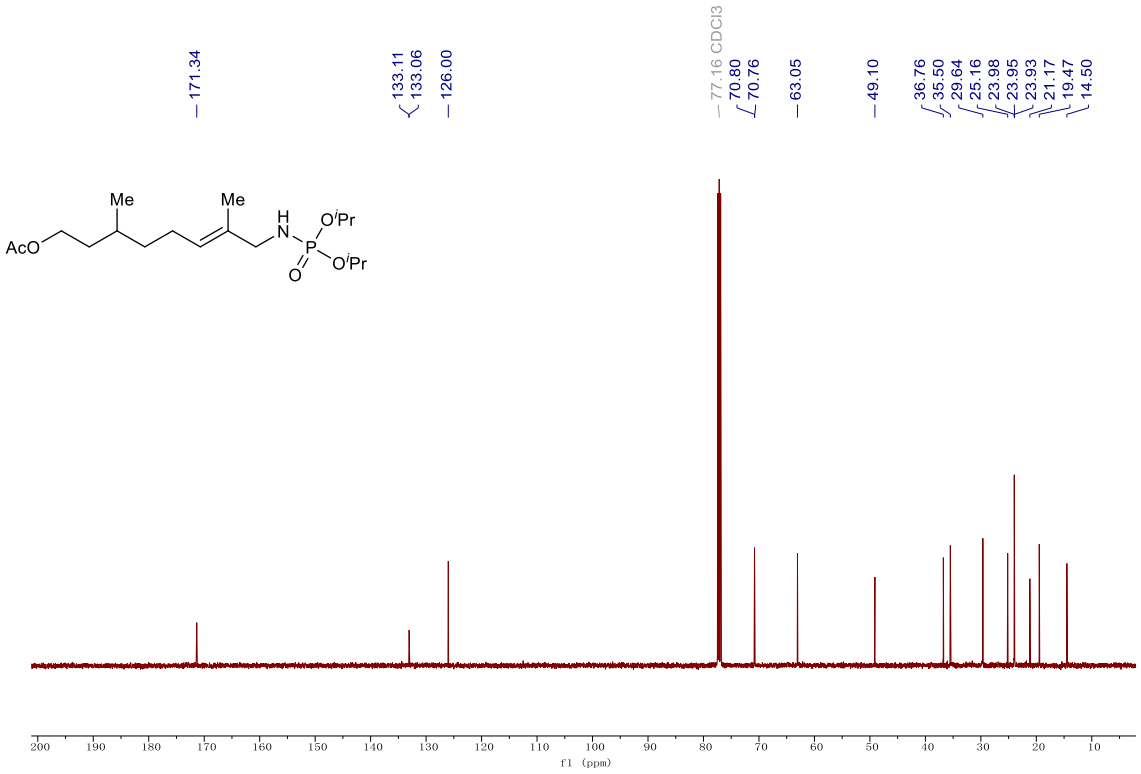

**32,** $^{31}$P NMR (202 MHz, $CDCl_3$)



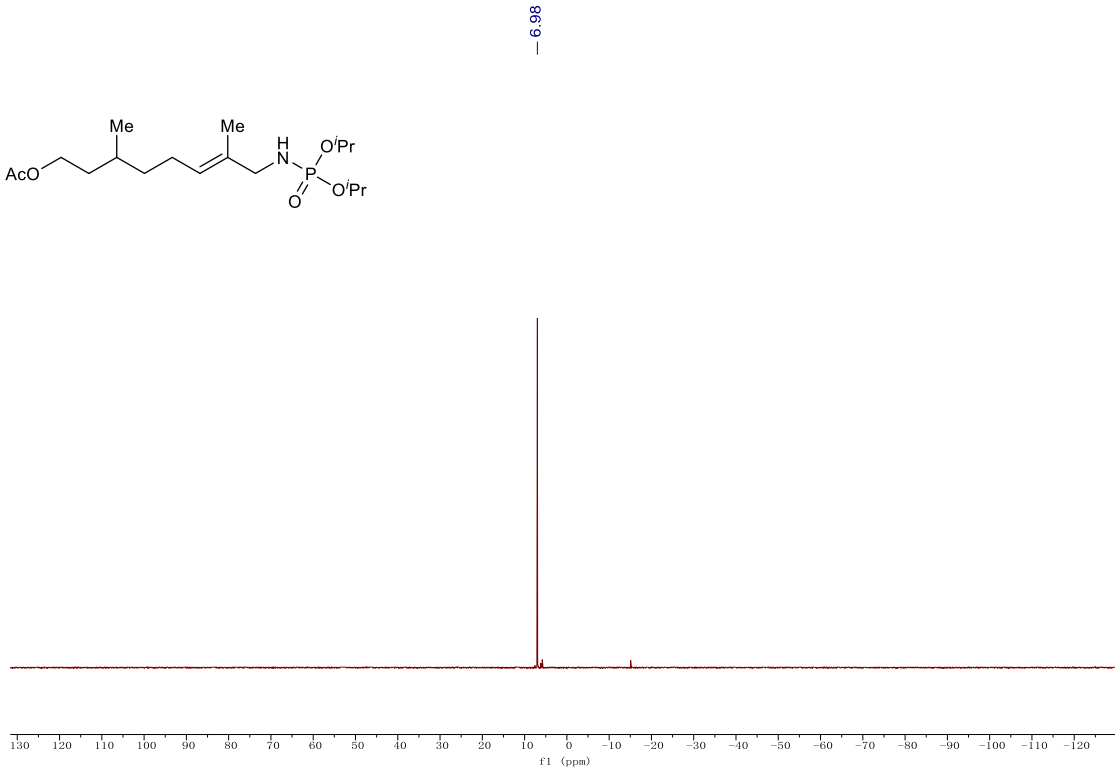

**33,** $^{1}$H NMR (500 MHz, $CDCl_3$)



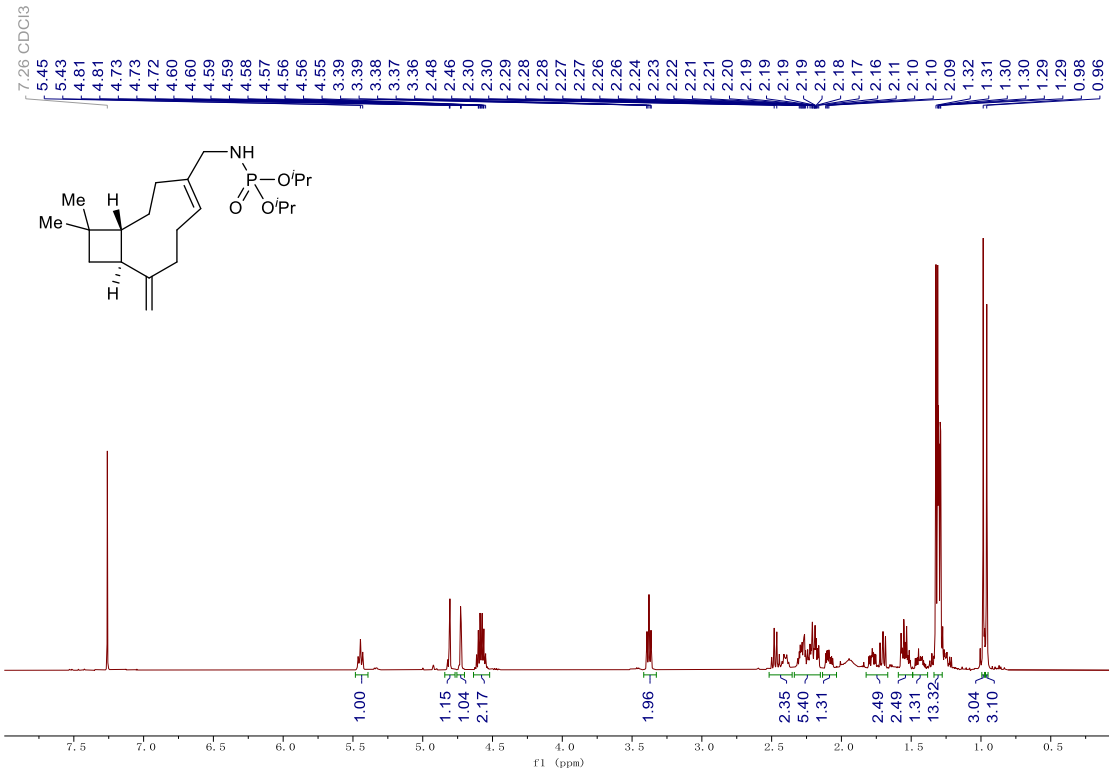

**33,** $^{13}$C NMR (126 MHz, $CDCl_3$)



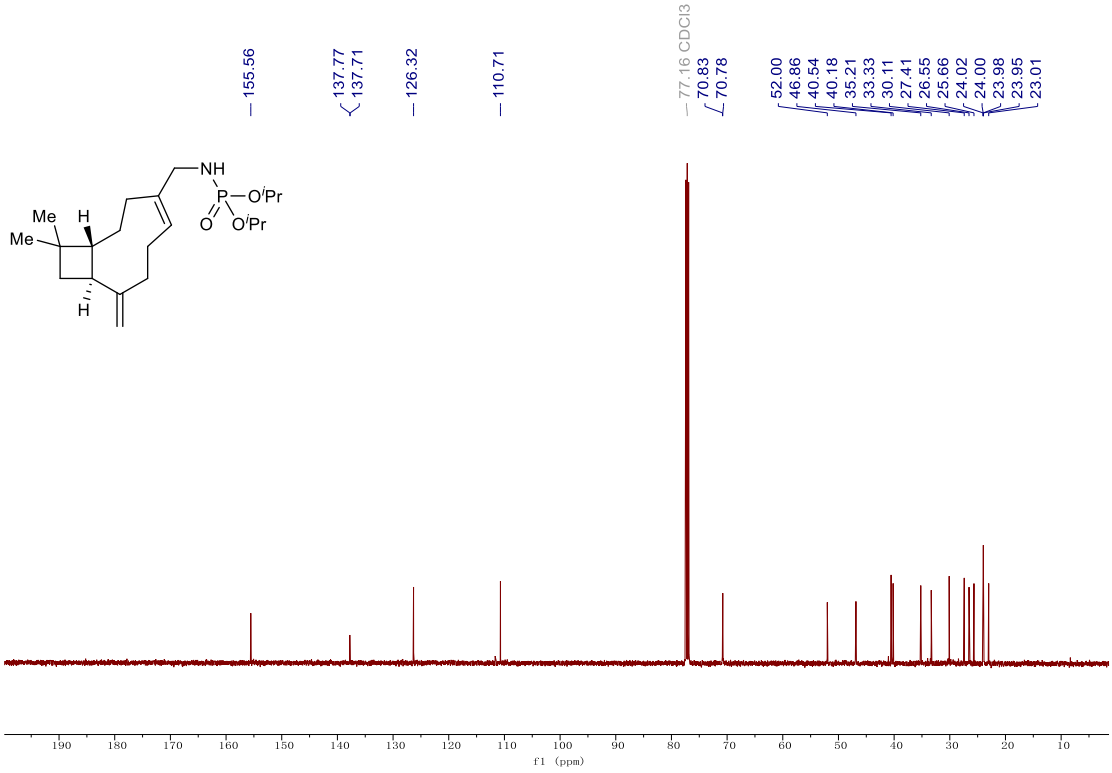

**33,** $^{31}$P NMR (202 MHz, $CDCl_3$)



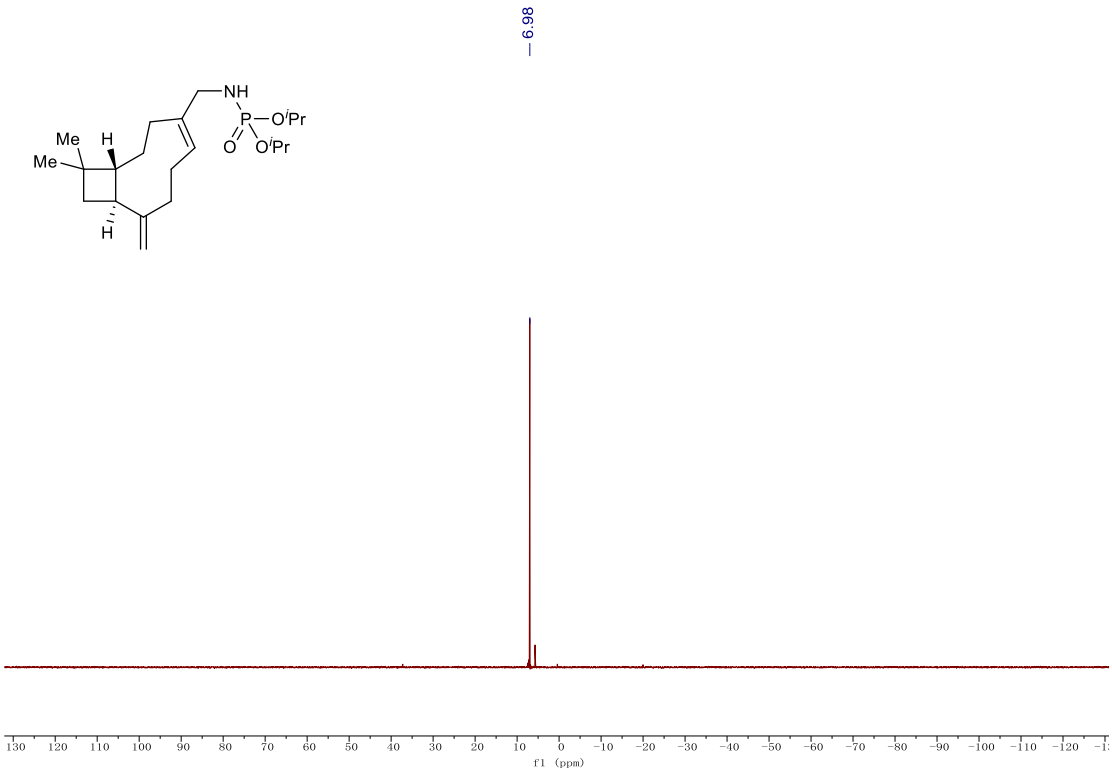

**34,** $^{1}$H NMR (500 MHz, $CDCl_3$)



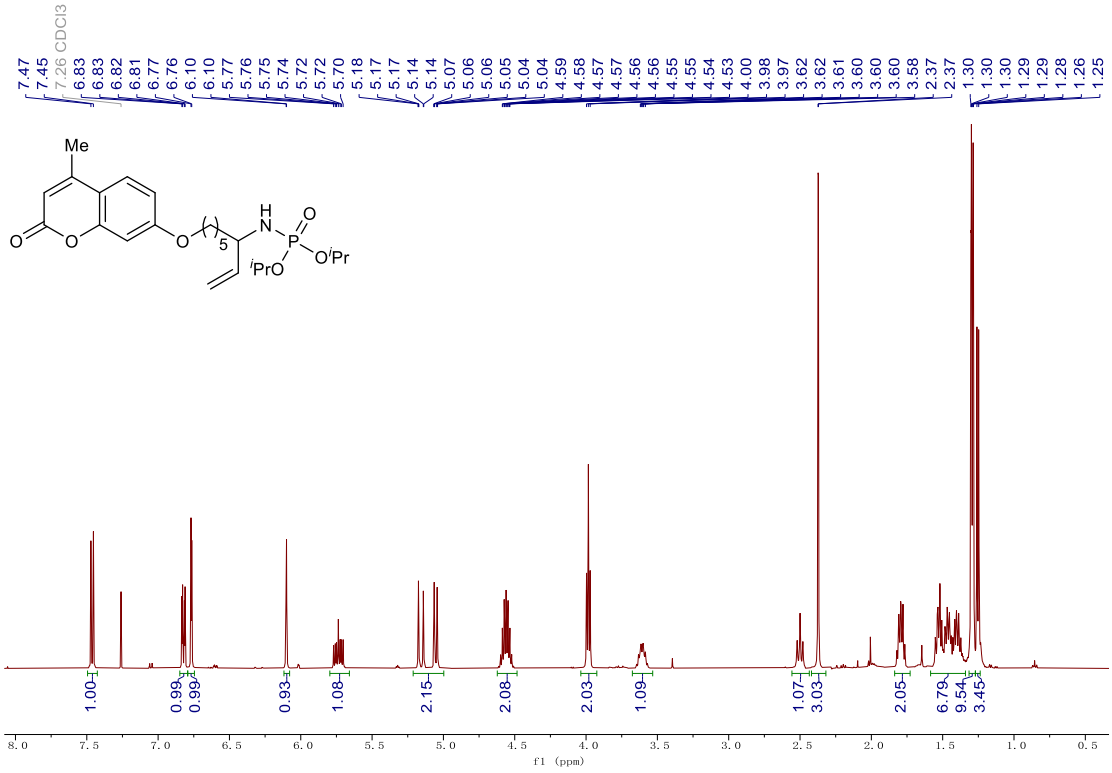

**34** $^{13}$C NMR (126 MHz, $CDCl_3$)



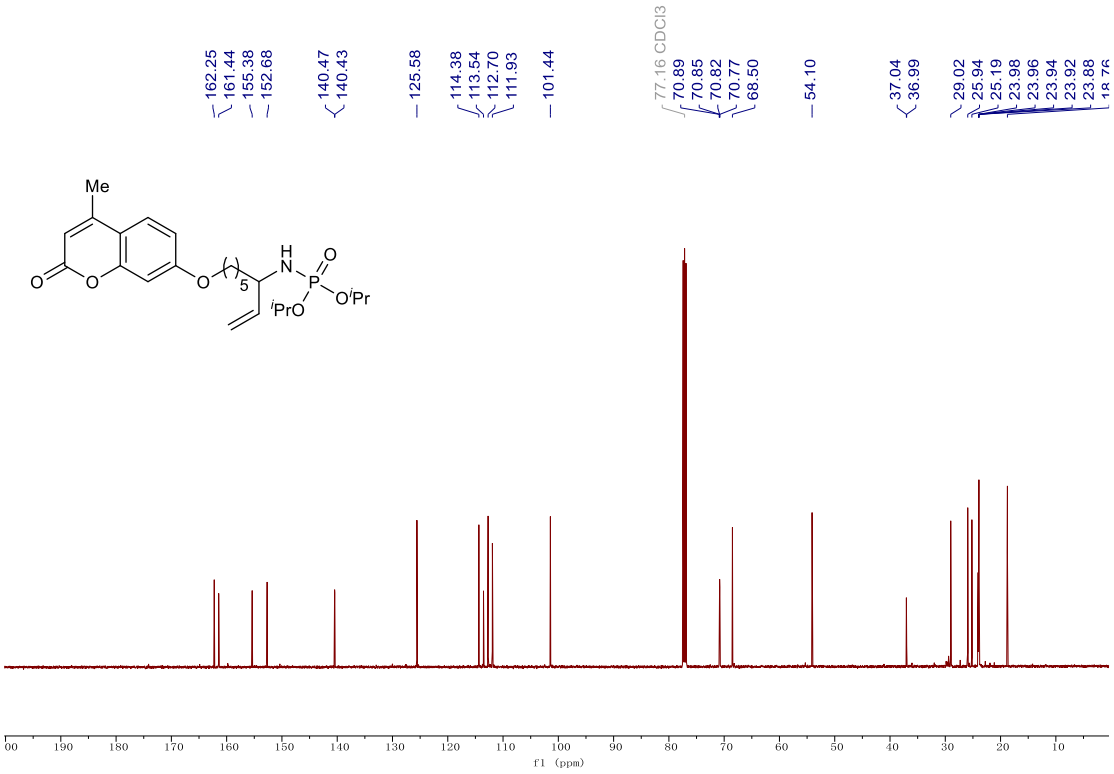

**34,** $^{31}$P NMR (202 MHz, $CDCl_3$)



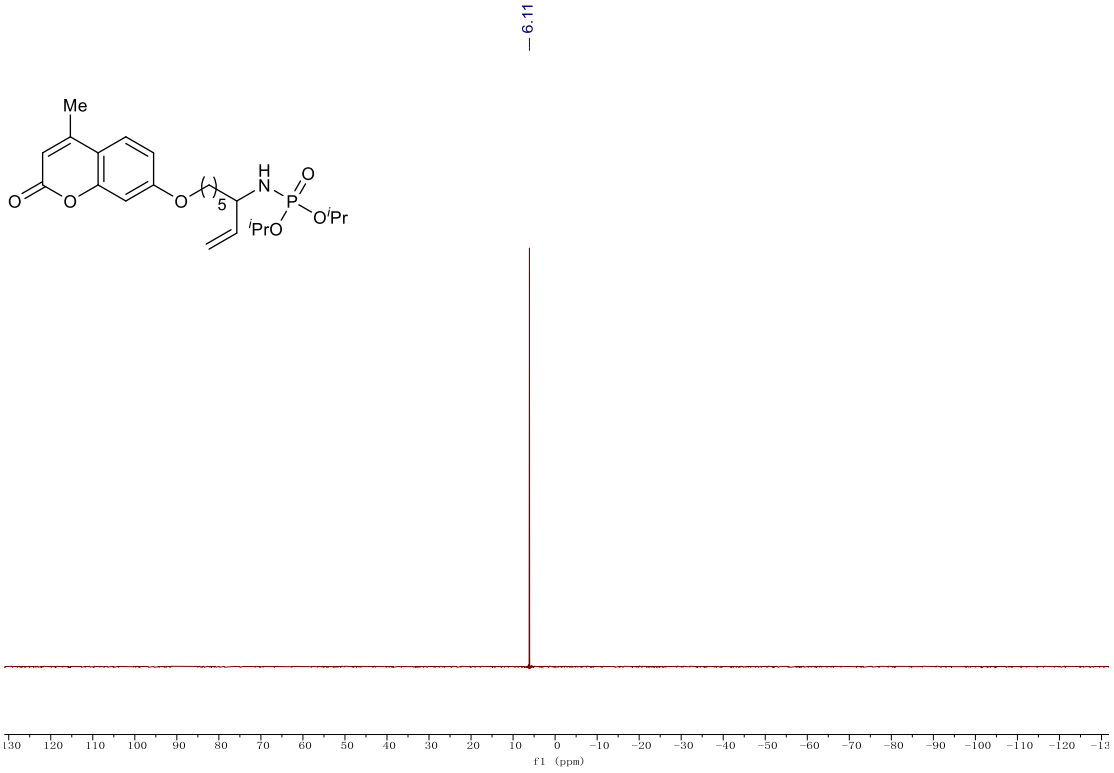

**35,** $^{1}$H NMR (500 MHz, $CDCl_3$)



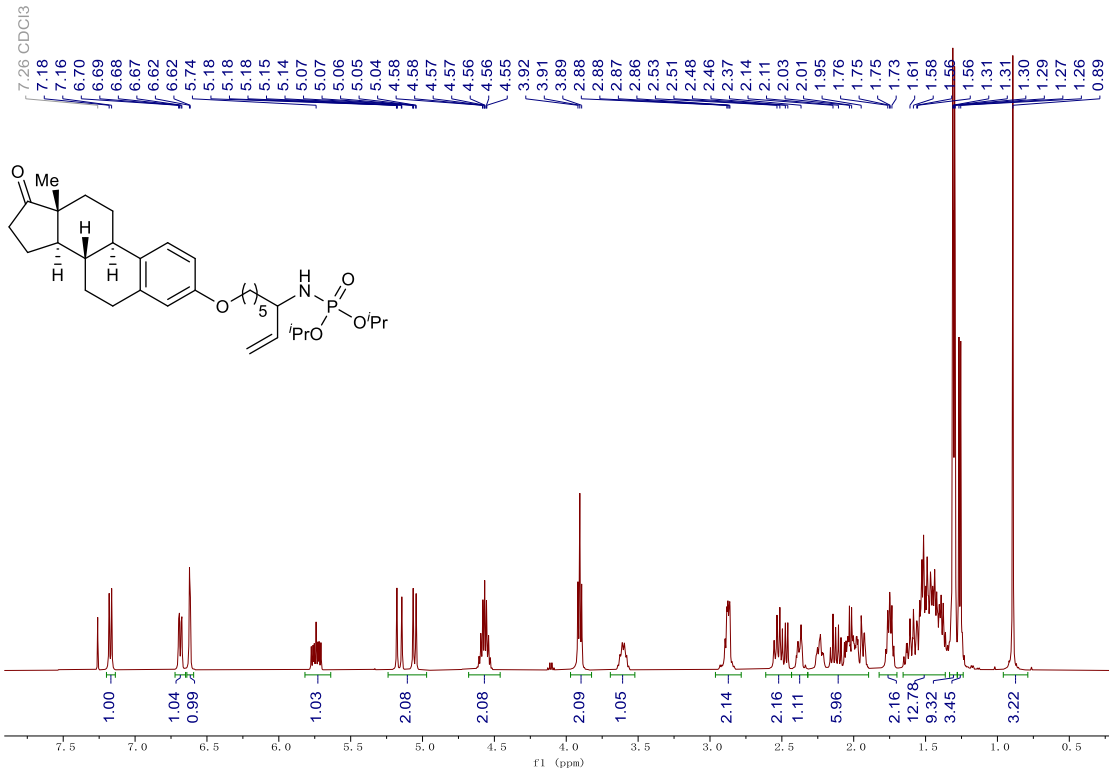

**35,** $^{13}$C NMR (126 MHz, $CDCl_3$)



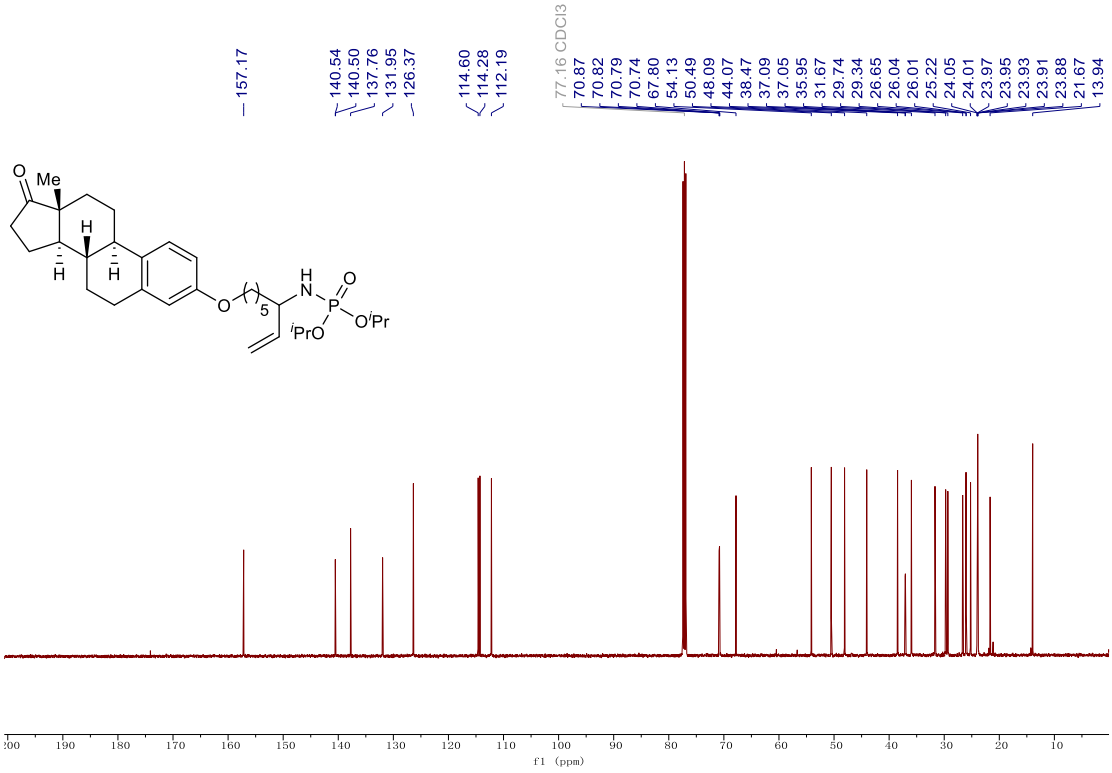

**35,** $^{31}$P NMR (202 MHz, $CDCl_3$)



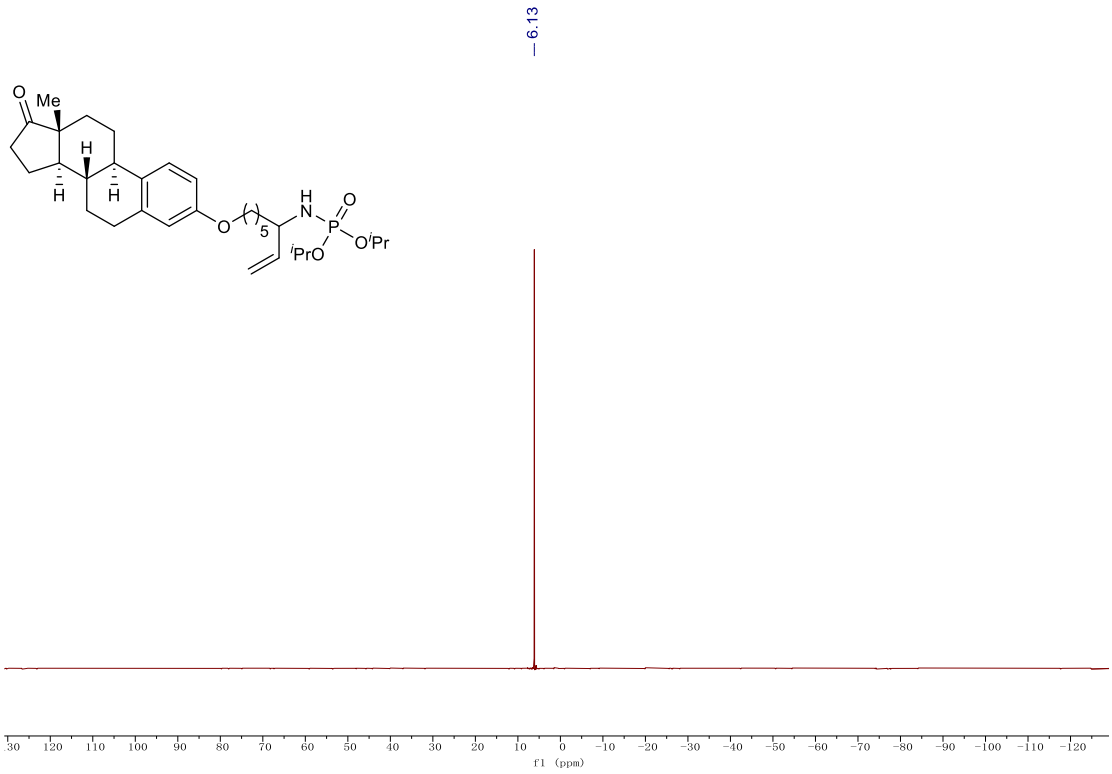

**36,** $^{1}$H NMR (500 MHz, $CDCl_3$)



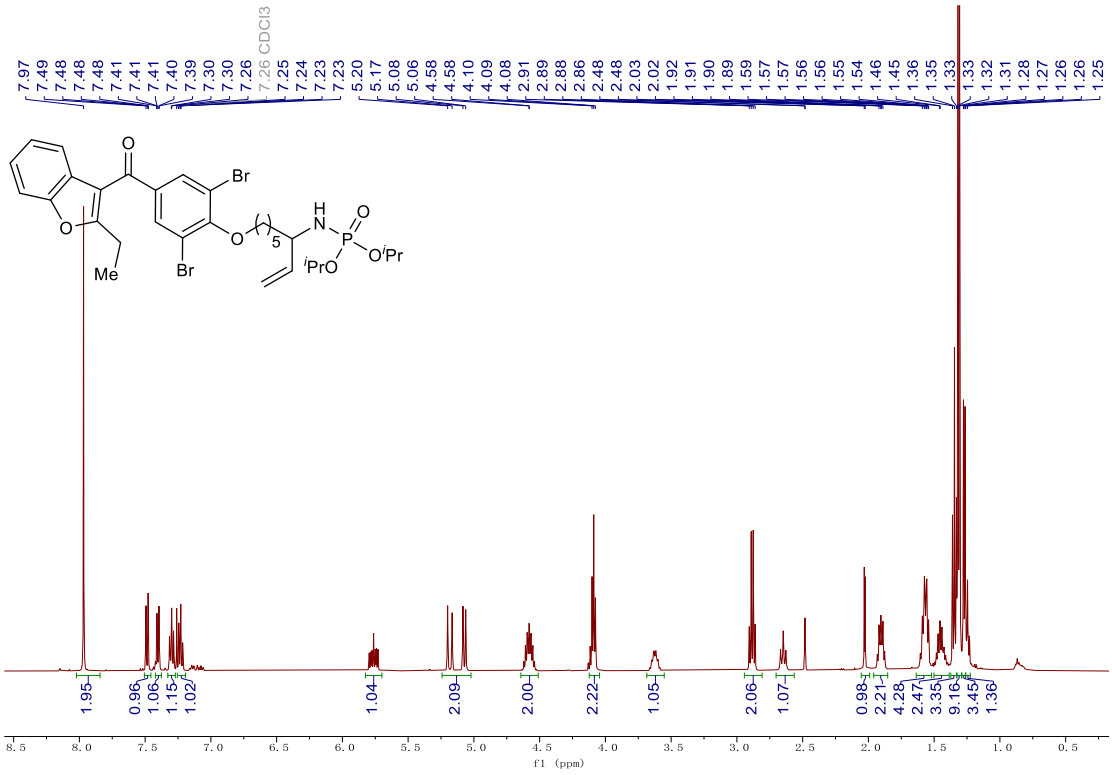
**36,** $^{13}C$ NMR (126 MHz, $CDCl_3$)



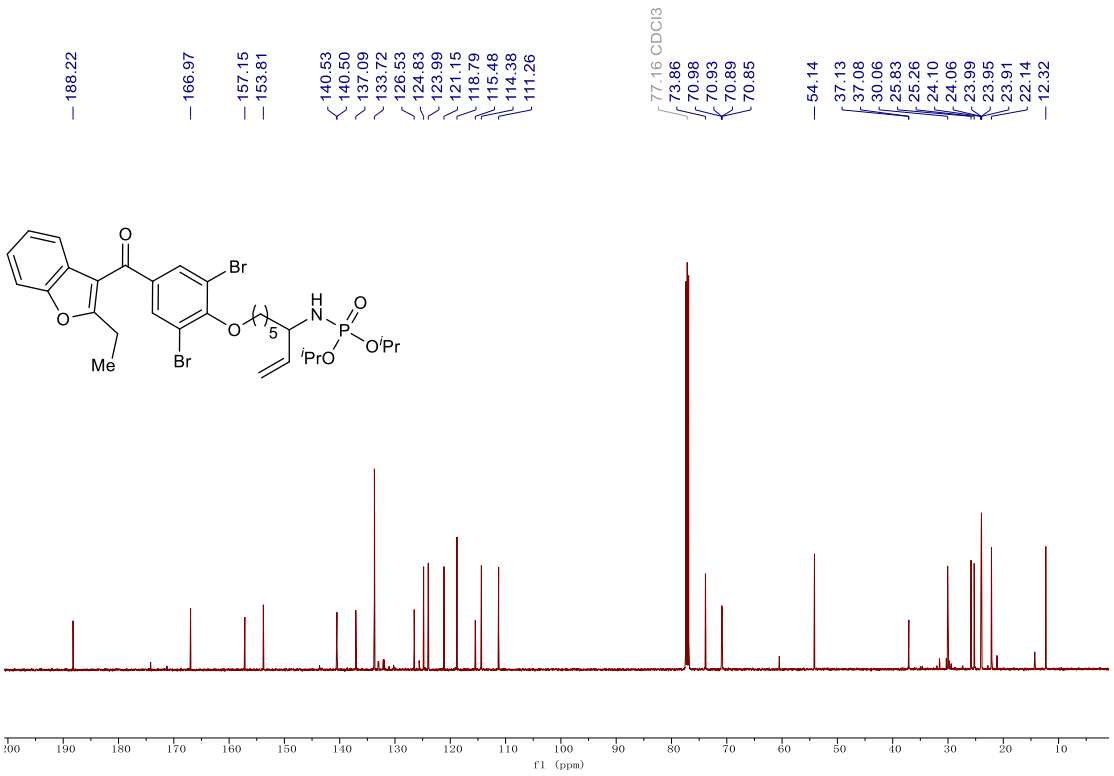
**36,** $^{31}P$ NMR (202 MHz, $CDCl_3$)



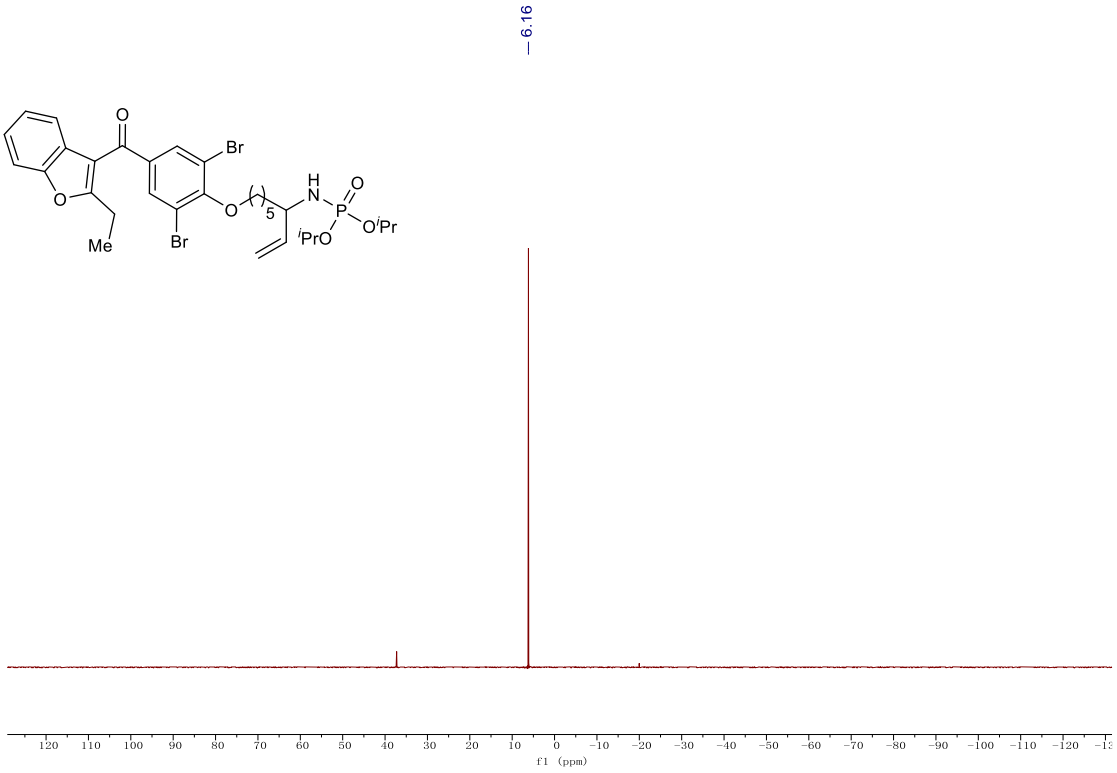

**37,** $^{1}$H NMR (500 MHz, $CDCl_3$)



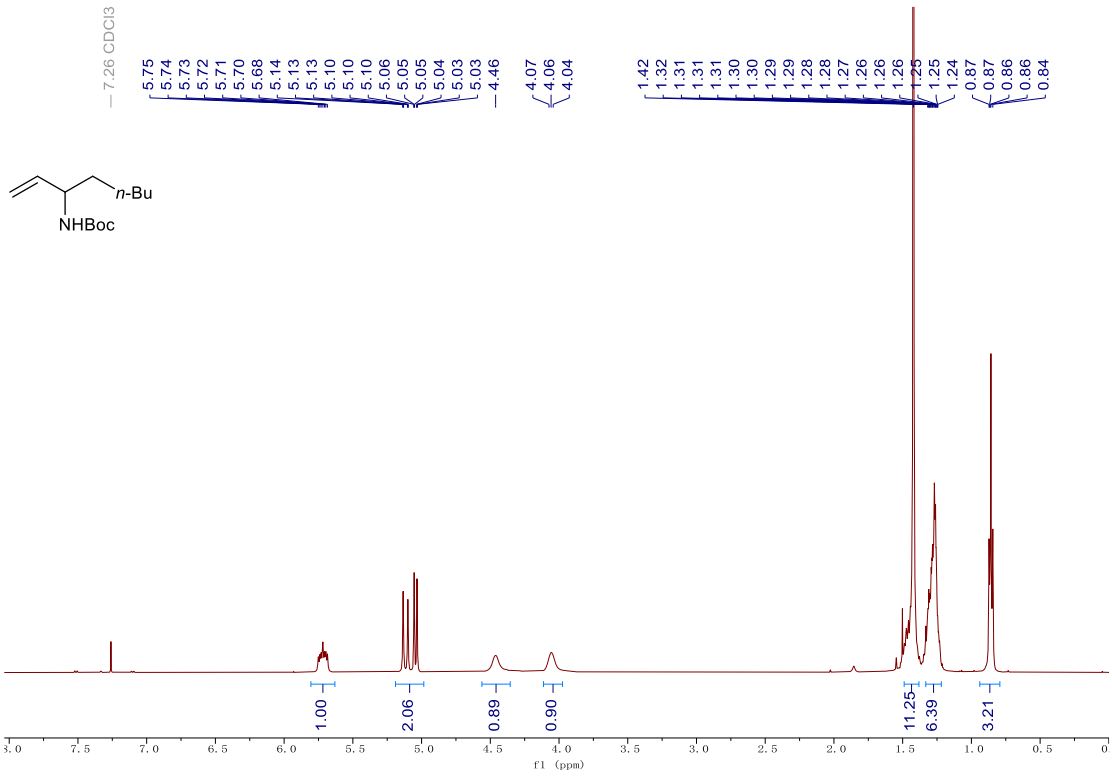

**37,** $^{13}$C NMR (126 MHz, $CDCl_3$)



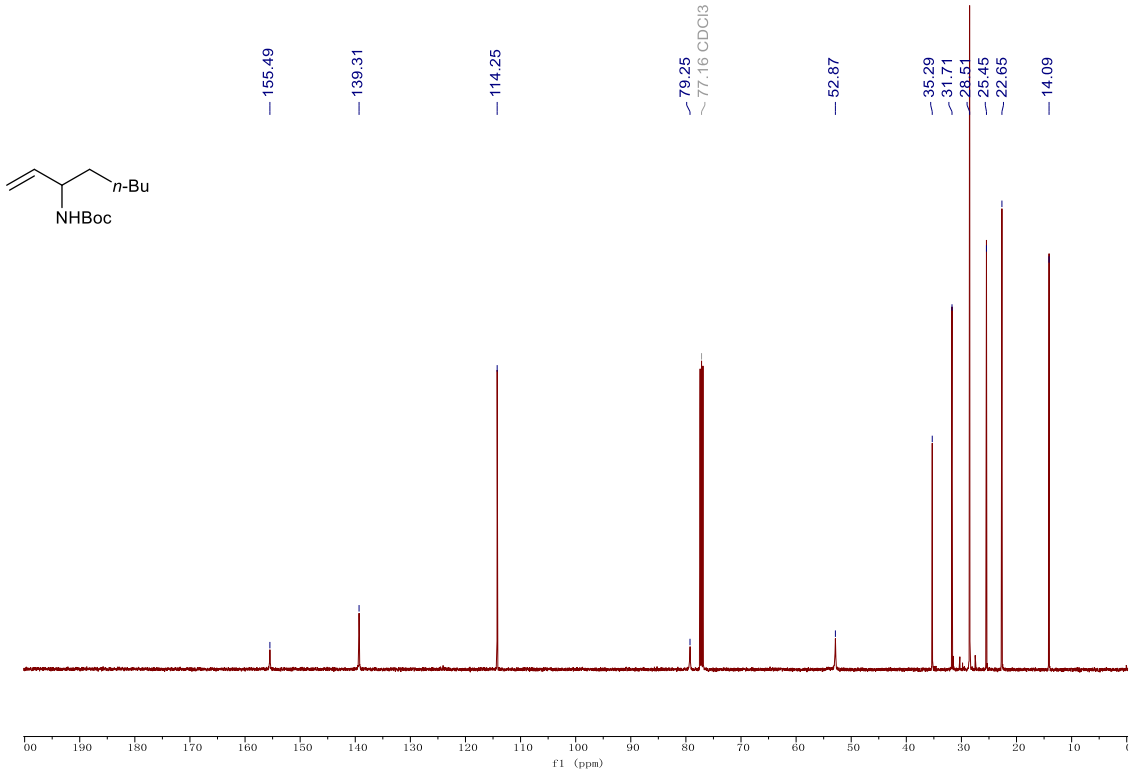

**37,** $^{31}$P NMR (202 MHz, $CDCl_3$)



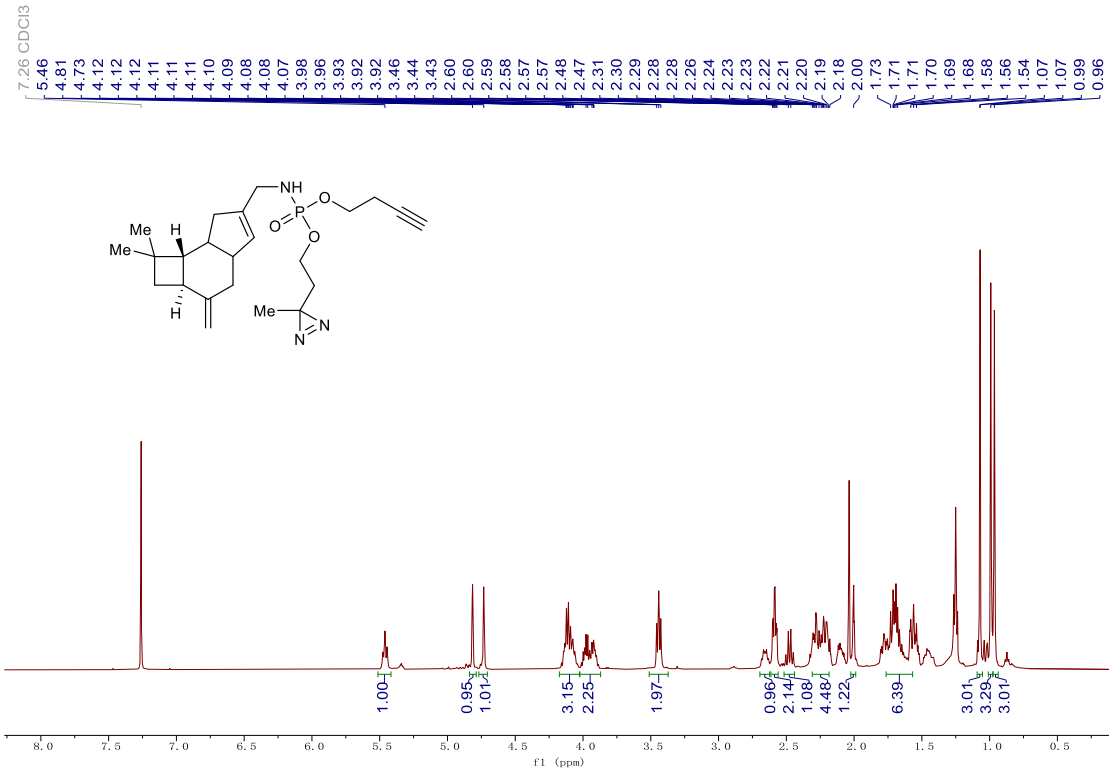

**38,** $^{1}$H NMR (500 MHz, $CDCl_3$)



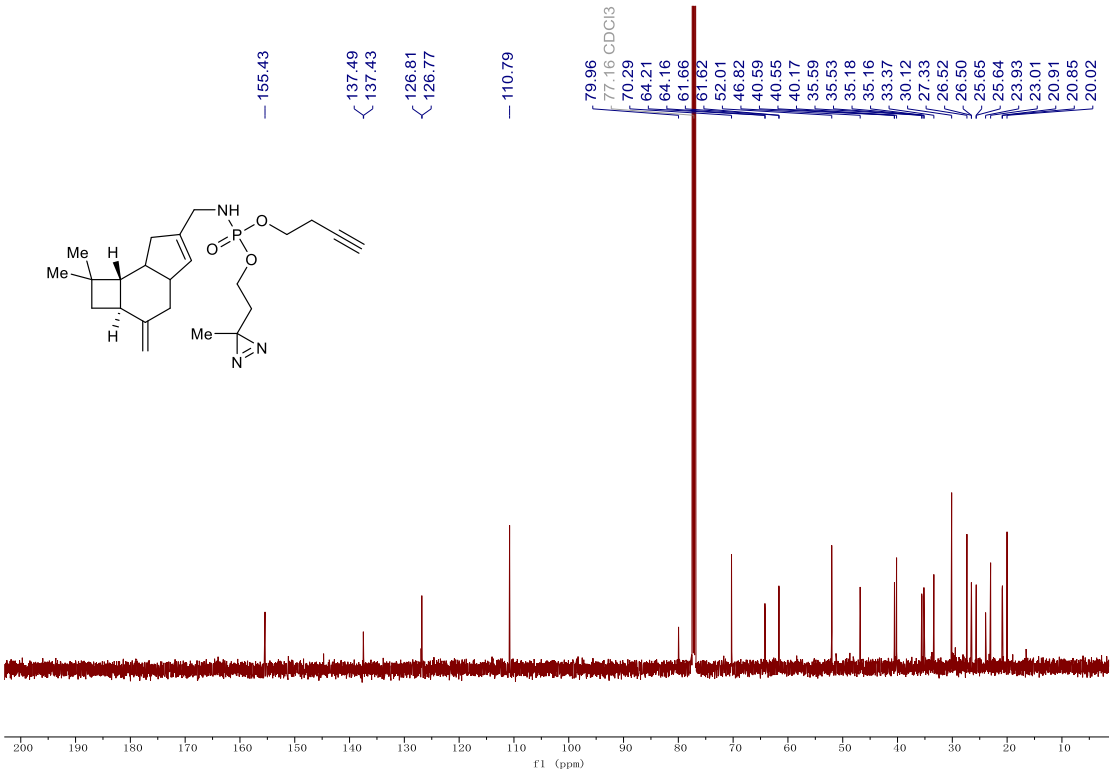

**38,** $^{13}$C NMR (126 MHz, $CDCl_3$)



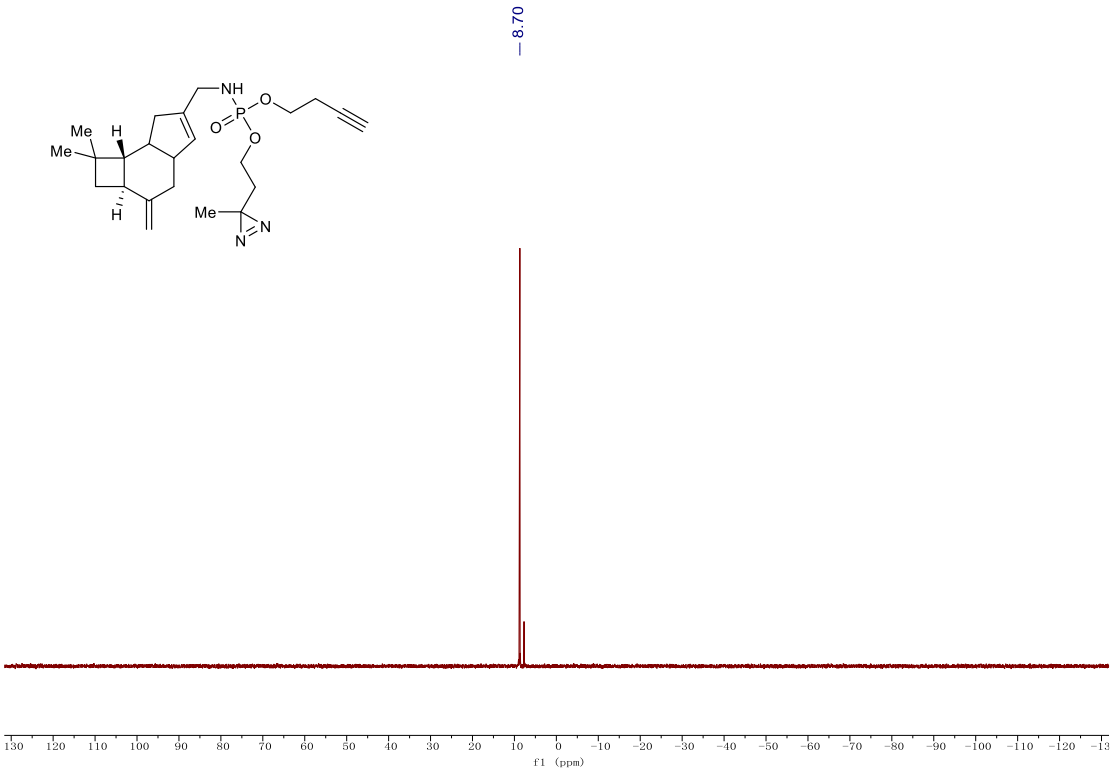
**40,** $^{1}$H NMR (500 MHz, $CDCl_3$)



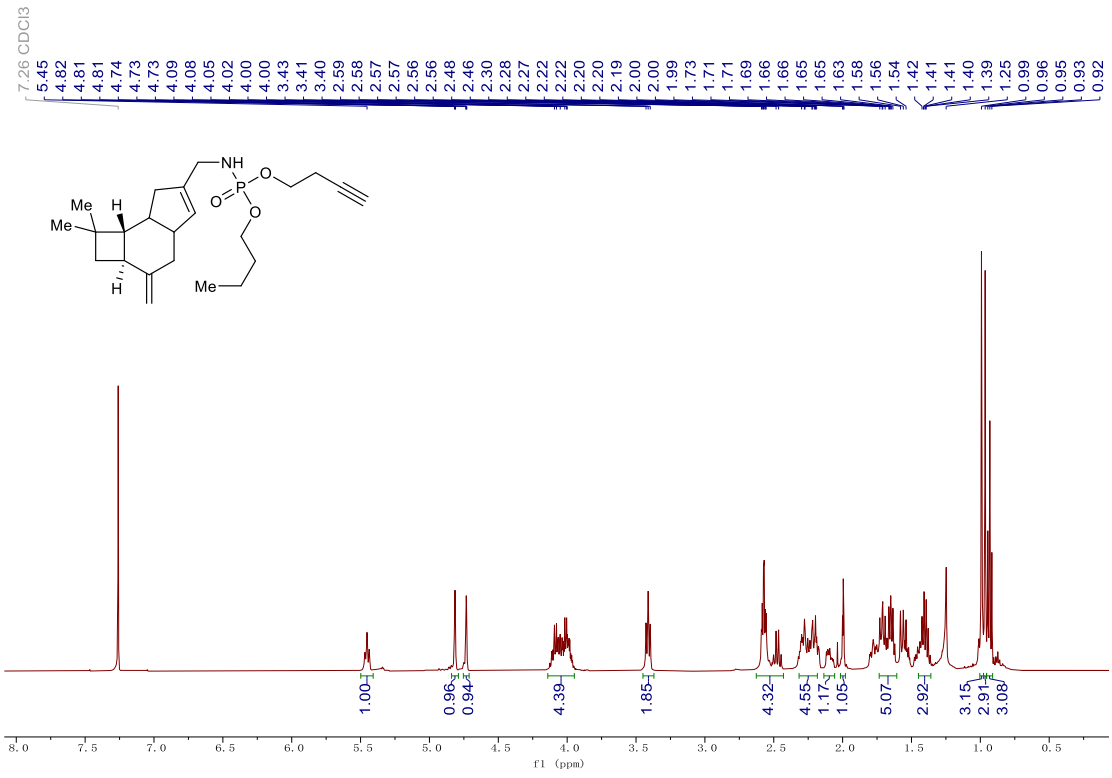

**40,** $^{13}$C NMR (126 MHz, $CDCl_3$)



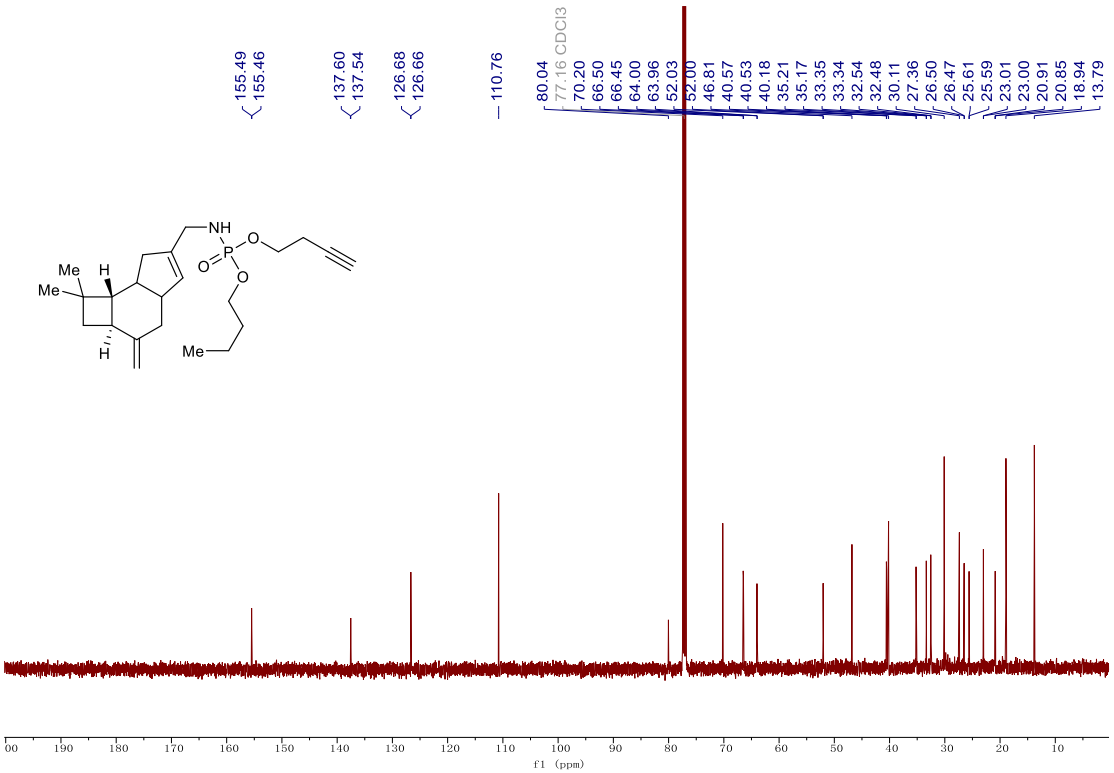
**40,** $^{31}P$ NMR (202 MHz, $CDCl_3$)




**42,** $^{1}H$ NMR (500 MHz, $CDCl_3$)



**42,** $^{13}C$ NMR (126 MHz, $CDCl_3$)




**42,** $^{31}P$ NMR (202 MHz, $CDCl_3$)