Supporting Information

Regiodivergent Ring-Opening Cross-Coupling of Vinyl Aziridines with Phosphorus Nucleophiles: Access to Phosphorus-Containing Amino Acid Derivatives

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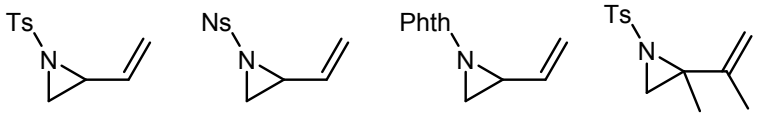
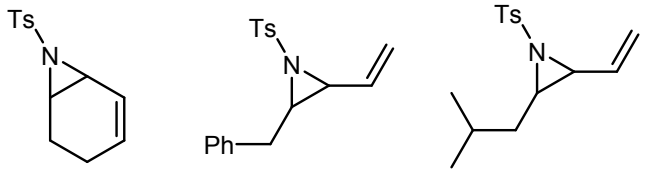
I. General Methods and Materials.

Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F^{254} plates and visualization on TLC was achieved by UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 or 600 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 or 150 MHz and was fully decoupled by broad band proton decoupling. Signals of ^{13}C spectra of carbon atom adjacent to phosphorus atom of organophosphorus compounds appeared as a doublet with varied coupling constants between C and P (J_{CP}). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$. ^{31}P NMR was recorded on 162 or 243 MHz and was fully decoupled by broad band proton decoupling. High-resolution mass spectra were obtained by using EI or FAB method from Korea Basic Science Institute (Daegu), and ESI method from KAIST Basic Science Institute. Commercial grade reagents and solvents were used without further purification except as indicated below.

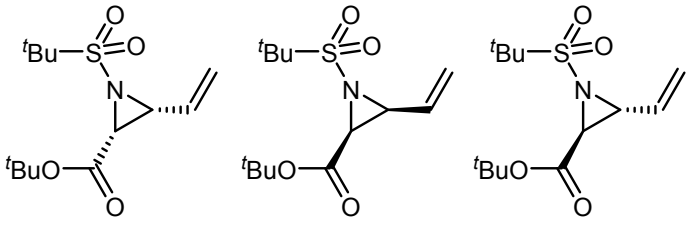
II. Synthesis of Vinyl Aziridines



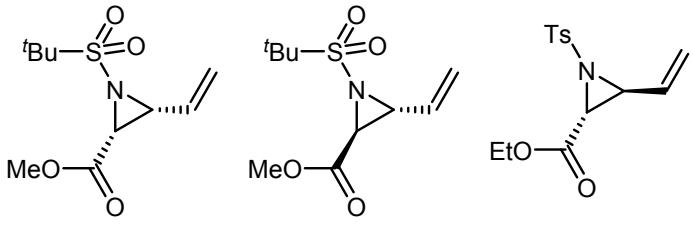
1a **1b** **1c** **1d**



1e **1f** **1g**



1h **1i** **1j**



1k **1l** **1m**

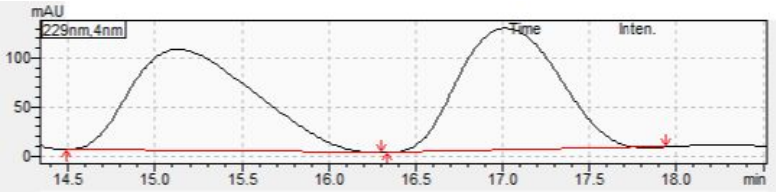
Vinyl aziridines were synthesized according to the literatures: **1a**[S1], **1b**[S2], **1c**[S3], **1d**[S4], **1e**[S5], **1f**[S6], **1g**[S7], and **1h-1m**[S8].

2-benzyl-1-tosyl-3-vinylaziridine (**1f**). White solid. mp 69-72 °C. ^{1}H NMR (300 MHz, Methanol-d_4) δ 7.67 – 7.56 (m, 2H), 7.31 – 7.22 (m, 2H), 7.17 – 7.07 (m, 3H), 7.10 – 6.99 (m, 2H), 5.83 (ddd, J = 17.2, 10.4, 6.9 Hz, 1H), 5.52 (ddd, J = 17.1, 1.7, 0.9 Hz, 1H), 5.38 (ddd, J = 10.4, 1.6, 0.8 Hz, 1H), 3.52 – 3.40 (m, 1H), 3.12 – 3.00 (m, 1H), 2.79 (dd, J = 14.5, 5.3 Hz, 1H), 2.62 (dd, J = 14.5, 8.1 Hz, 1H), 2.42 (s, 3H). HRMS (ESI+) m/z calcd. for $[C_{18}H_{19}NO_2S+Na]^+$: 336.1029, found: 336.1028.

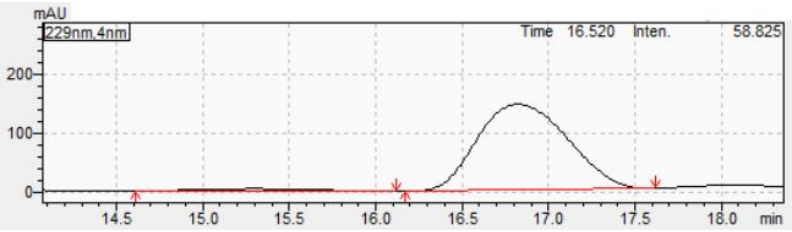
Chiral HPLC analysis of **1i-1k**.

HPLC conditions: OJ-H column, 5% iPrOH/Hx, 0.3 ml/min, R_t: 15.133 min (**1i**), 17.016 min (**1h**).

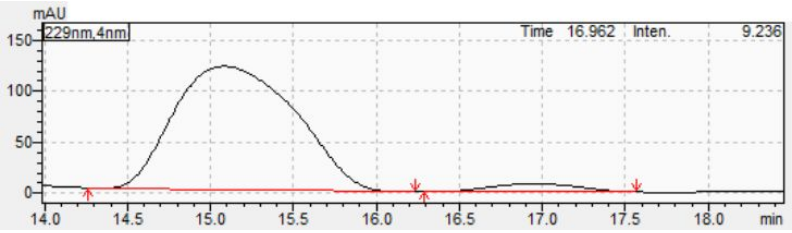
*Chiral HPLC-Chromatogram of the racemic mixture(**1h** and **1i**)*



*Chiral HPLC-Chromatogram of **1h (ee 92%)***

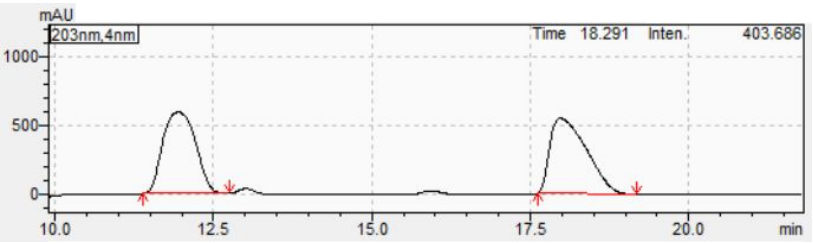


*Chiral HPLC-Chromatogram of **1i (ee 91%)***

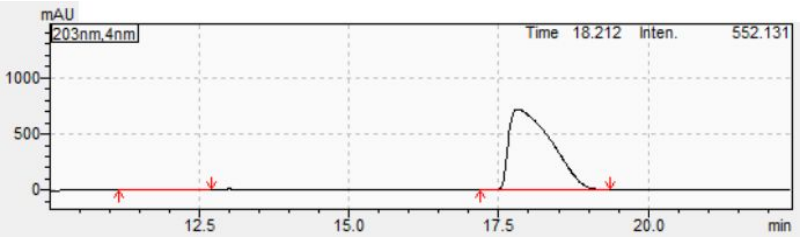


HPLC conditions: OJ-H column, 5% iPrOH/Hx, 0.5 ml/min, R_t: 11.945 min (enantiomer), 17.977 min (**1j**).

*Chiral HPLC-Chromatogram of the racemic mixture of **1j***



*Chiral HPLC-Chromatogram of **1j (ee >99%)***

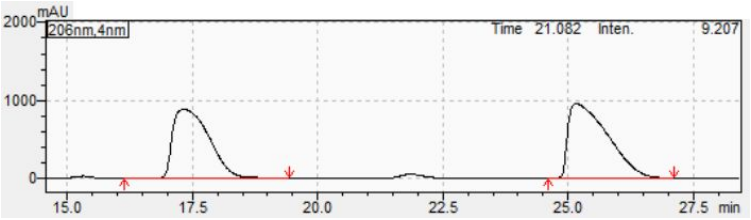


methyl (2R,3R)-1-(tert-butylsulfonyl)-3-vinylaziridine-2-carboxylate (**1k**). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddd, *J* = 17.3, 10.3, 8.0 Hz, 1H), 5.59 (dd, *J* = 17.4, 1.3 Hz, 1H), 5.43 (dd, *J* = 10.3, 1.3 Hz, 1H), 3.78 (s, 3H), 3.53 (d, *J* = 7.3 Hz, 1H), 3.44 (t, *J* = 7.7 Hz, 1H), 1.50 (s, 9H). HRMS (ESI+) m/z calcd. for $[C_{10}H_{17}NO_4S+Na]^+$: 270.0770, found: 270.0772.

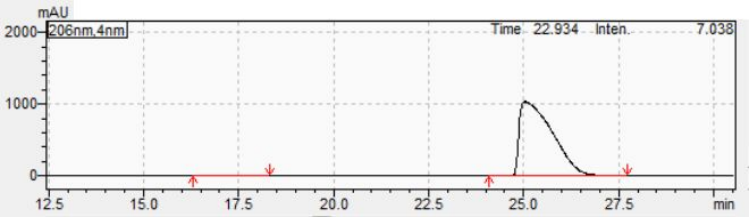
methyl (2S,3R)-1-(tert-butylsulfonyl)-3-vinylaziridine-2-carboxylate (**1l**). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (dt, *J* = 17.0, 9.9 Hz, 1H), 5.61 (dt, *J* = 16.9, 0.8 Hz, 1H), 5.45 (dt, *J* = 10.4, 0.6 Hz, 1H), 3.78 (s, 3H), 3.49 (dd, *J* = 9.5, 3.7 Hz, 1H), 3.42 (d, *J* = 3.7 Hz, 1H), 1.44 (s, 9H). HRMS (ESI+) m/z calcd. for $[C_{10}H_{17}NO_4S+Na]^+$: 270.0770, found: 270.0769.

HPLC conditions: OJ-H column, 5% iPrOH/Hx, 0.6 ml/min, R_t: 17.320 min (*enantiomer*), 25.158 min (**1l**).

Chiral HPLC-Chromatogram of the racemic mixture



*Chiral HPLC-Chromatogram of **1l (ee 99%)***



ethyl (2R,3S)-1-tosyl-3-vinylaziridine-2-carboxylate (**1m**). Transparent oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 6.20 – 6.07 (m, 1H), 5.63 (d, *J* = 17.0 Hz, 1H), 5.51 (d,

J = 10.2 Hz, 1H), 4.22 – 4.09 (m, 2H), 3.59 – 3.51 (m, 2H), 2.44 (s, 3H), 1.30 – 1.17 (m, 3H). HRMS (ESI+) m/z calcd. for $[C_{14}H_{17}NO_4S+Na]^+$: 318.0770, found: 318.0772.

III. Experimental Procedure

General Procedure for Phosphonation of Vinyl Aziridine (General Procedure A)

An oven-dried tube was charged with vinyl aziridine **1** (0.1 mmol), phosphorus reagent **2** (2.0 equiv) and $Cu(OAc)_2$ (20 mol %) dissolving in toluene (0.5 mL). The reaction mixture was stirred at room temperature. The reaction mixture was monitored by TLC using mixture of ethyl acetate and *n*-hexanes as the mobile phase. After the reaction completion, the resulting mixture was diluted with CH_2Cl_2, washed with aqueous NH_4Cl, and dried over $MgSO_4$. Upon filtration, the organic layer was concentrated and purified by flash chromatography on silica gel (ethyl acetate/*n*-hexanes) to give the desired product.

General Procedure for Phosphonation of Vinyl Aziridine using DBU (General Procedure B)

An oven-dried tube was charged with vinyl aziridine **1** (0.1 mmol), phosphorus reagent **2** (3.0 equiv), DBU (1.5 equiv) and $Cu(OAc)_2$ (20 mol %) dissolving in toluene (0.5 mL). The reaction mixture was stirred at room temperature. The reaction mixture was monitored by TLC using mixture of ethyl acetate and *n*-hexanes as the mobile phase. After the reaction completion, the resulting mixture was diluted with CH_2Cl_2, washed with aqueous NH_4Cl, and dried over $MgSO_4$. Upon filtration, the organic layer was concentrated and purified by flash chromatography on silica gel (ethyl acetate/*n*-hexanes or acetone/*n*-hexanes) to give the desired product.

General Procedure for Phosphonation for amino acid derivatives (General Procedure C)

An oven-dried tube was charged with vinyl aziridine **1** (0.1 mmol), phosphorus reagent **2** (3.0 equiv) and $AgNO_3$ (20 mol %) dissolving in MeCN (1.0 mL). The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was monitored by TLC using mixture of ethyl acetate and *n*-hexanes as the mobile phase. After the reaction completion, the resulting mixture was diluted with CH_2Cl_2, washed with aqueous NH_4Cl, and dried over $MgSO_4$. Upon filtration, the organic layer was concentrated and purified by flash chromatography on silica gel (ethyl acetate/*n*-hexanes) to give the desired product.

General Procedure for Aerobic Phosphatation of Vinylaziridines (General Procedure D)

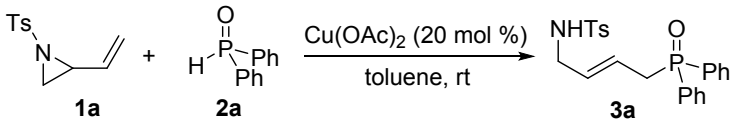
An oven-dried tube was charged with vinyl aziridine **1** (0.1 mmol), phosphorus reagent **2** (2.0 equiv) and $AgNO_3$ (20 mol %). Then, the tube was evacuated and backfilled with oxygen gas (repeated three times) and anhydrous toluene (1.0 mL) was added *via* syringe. The reaction mixture was stirred at 60 ^oC. The reaction mixture was monitored by TLC using mixture of ethyl acetate and hexanes as the mobile phase. After the reaction completion, the resulting mixture was diluted with CH_2Cl_2, washed with aqueous

$NaHCO_3$, and dried over $MgSO_4$. Upon filtration, the organic layer was concentrated and purified by flash chromatography on silica gel (ethyl acetate/*n*-hexanes) to give the desired product.

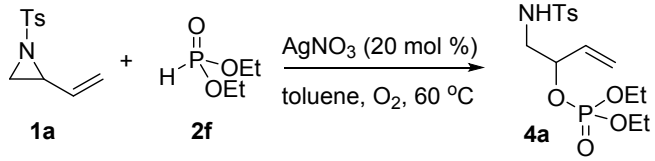
General Procedure for Aerobic Phosphatation of amino acid derivatives (General Procedure E)

An oven-dried tube was charged with vinyl aziridine **1** (0.1 mmol), phosphorus reagent **2** (3.0 equiv) and $AgNO_3$ (30 mol %). Then, the tube was evacuated and backfilled with oxygen gas (repeated three times) and anhydrous toluene (1.0 mL) was added *via* syringe. The reaction mixture was stirred at 60 °C for 17 h. The reaction mixture was monitored by TLC using mixture of ethyl acetate and hexanes as the mobile phase. After the reaction completion, the resulting mixture was filtered through a Celite pad. The organic layer was concentrated under reduced pressure and purified by flash chromatography on silica gel (ethyl acetate/*n*-hexanes) to give the desired product.

1 mmol scale Procedures



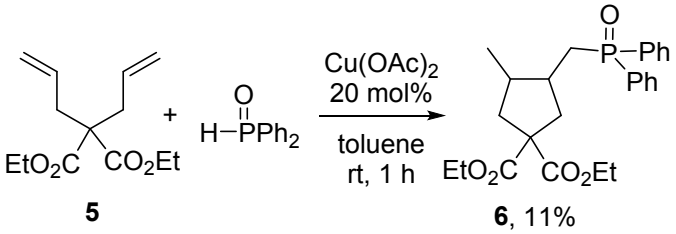
An oven-dried tube was charged with vinyl aziridine **1a** (223.1 mg, 1.0 mmol), **2a** (405.1 mg, 2.0 mmol) and $Cu(OAc)_2$ (36.4 mg, 0.2 mmol) dissolving in toluene (3 mL). The reaction mixture was stirred at room temperature. The reaction mixture was stirred for 2 h, and the resulting mixture was diluted with CH_2Cl_2, washed with aqueous NH_4Cl, and dried over $MgSO_4$. Upon filtration, the organic layer was concentrated and purified by flash chromatography on silica gel (ethyl acetate/*n*-hexanes = 3:1) to give the desired product **3a** (Yield 68%, 289.3 mg).



An oven-dried tube was charged with vinyl aziridine **1a** (222.8 mg, 1.0 mmol), **2f** (275.7 mg, 2.0 mmol) and $AgNO_3$ (33.7 mg, 0.2 mmol). Then, the tube was evacuated and backfilled with oxygen gas (repeated three times) in anhydrous toluene (5.0 mL) was added *via* syringe. The reaction mixture was stirred at 60 °C. The reaction mixture was stirred for 10 h, and the resulting mixture was diluted with CH_2Cl_2, washed

with aqueous NH_4Cl, and dried over $MgSO_4$. Upon filtration, the organic layer was concentrated and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:2) to give the desired product **4a** (Yield 75%, 284.4 mg).

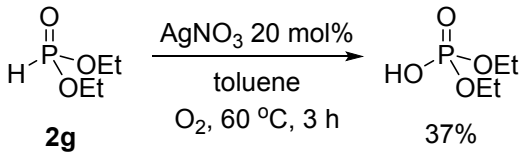
IV. Control Experiment



5 **6**, 11%

Radical capturing using diethyl 2,2-diallylmalonate (5)

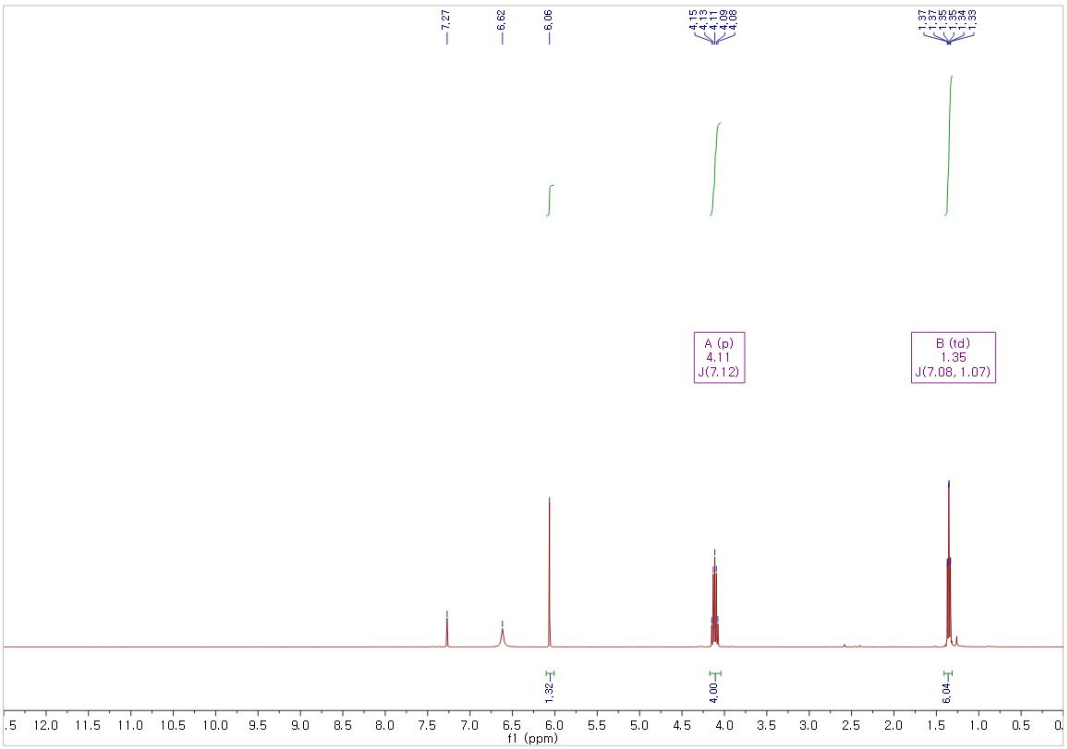
An oven-dried tube was charged with **5** (0.1 mmol), **2a** (2.0 equiv) and $Cu(OAc)_2$ (20 mol %) dissolving in toluene (0.5 mL). The reaction mixture was stirred at room temperature. After 1 h, the crude mixture was diluted with CH_2Cl_2 and washed with saturated ammonium chloride solution followed by brine. Then, the cyclized product **6** was isolated by pTLC (ethyl acetate/*n*-hexanes = 3:2). Yield 11% (4.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.70 (m, 4H), 7.57 – 7.40 (m, 6H), 4.20 – 4.02 (m, 4H), 2.48 – 2.29 (m, 4H), 2.28 – 2.15 (m, 2H), 2.16 – 2.05 (m, 1H), 1.97 (dd, *J* = 13.8, 5.1 Hz, 1H), 1.19 (dt, *J* = 13.6, 7.1 Hz, 6H), 0.88 (d, *J* = 7.1 Hz, 3H). The characterization data of **6** was full agreement with the reported literature.[S9]

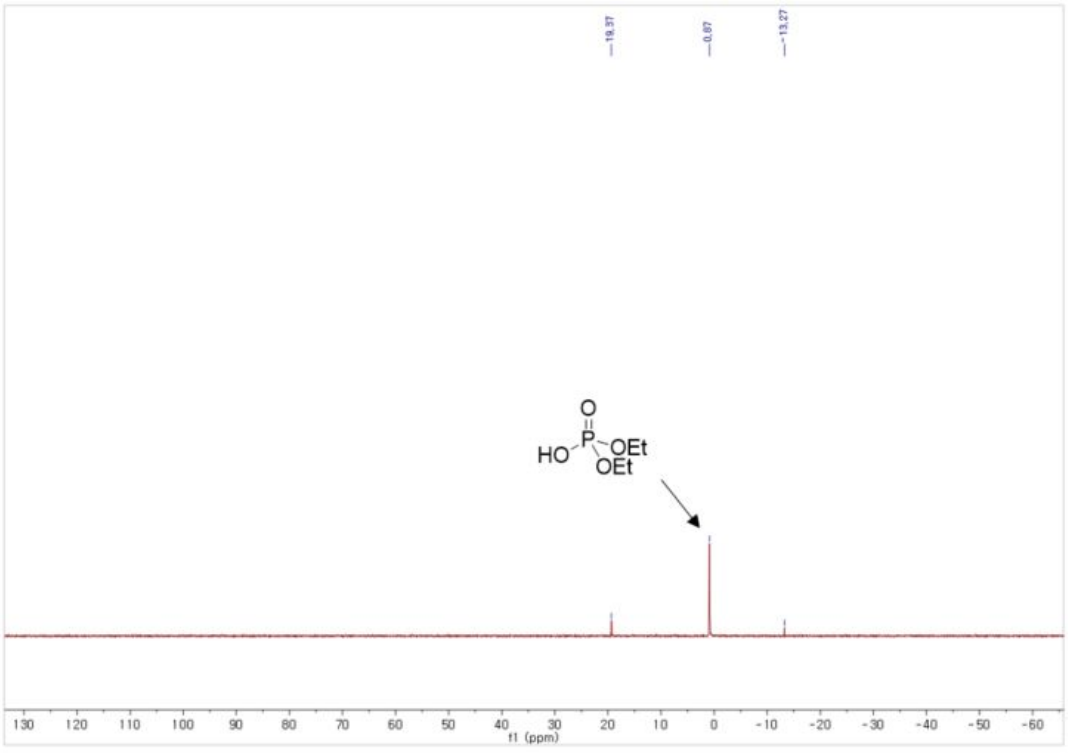


2g 37%

Formation of phosphate under Ag-catalyzed oxidation

An oven-dried tube was charged with **2g** (0.2 mmol) and $AgNO_3$ (20 mol %) dissolving in toluene (1.0 mL). The reaction mixture was stirred at 60 °C. After 1 h, the crude mixture was filtered through a Celite pad, washed with CH_2Cl_2, and concentrated under reduced pressure. Then, the mixture was analyzed by NMR spectroscopy using tetrabromoethane as an internal standard. ^{1}H and ^{31}P NMR spectrums were well matched with reported data.[S10]


7.27
6.62
6.06
4.15
4.13
4.11
4.09
4.08
1.37
1.37
1.35
1.34
1.33
A (p)
4.11
J(7.12)
B (td)
1.35
J(7.08, 1.07)
1.32
4.00
6.04
f1 (ppm)

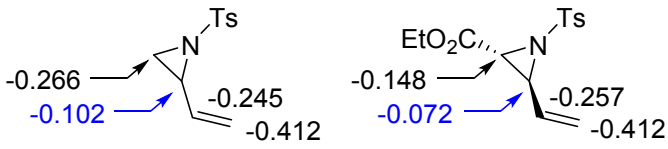

19.37
0.87
-13.27
HO
O
P
OEt
OEt
f1 (ppm)

V. Computational Study

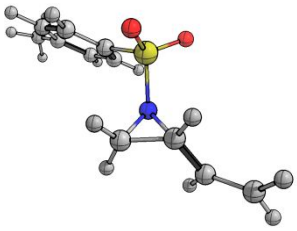
All geometry optimizations and energy calculations were performed at the B3LYP/6-31(d) level of theory using Gaussian 09.[S11]

- NBO charge analysis

Provided charges are NBO charges.[S12]



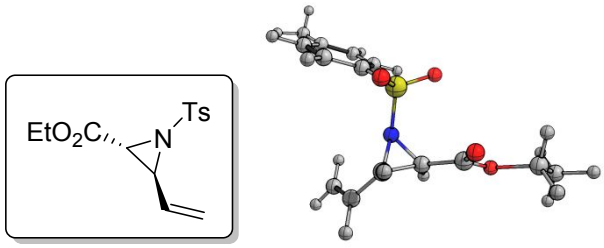
Cartesian coordinates (Å)



1a

C	-2.92690400	-0.20706200	-0.59143500
C	-1.86392700	-0.41616800	-1.61932900
H	-1.55011700	0.46200900	-2.17925500
N	-1.51359800	-0.48207400	-0.19288000
S	-0.65891400	0.84563600	0.48200000
O	-0.88820700	2.07338000	-0.30180700
O	-0.97079300	0.83435200	1.91512300
C	1.02725900	0.31233000	0.22734000
C	1.51552600	-0.78131700	0.94942100
C	1.83927300	1.00620500	-0.66866700
C	2.83367100	-1.18088600	0.75711000
H	0.87415400	-1.30796800	1.64842200
C	3.16019500	0.59298000	-0.84325700
H	1.44362100	1.85663200	-1.21331400
C	3.67757900	-0.50039900	-0.13682900
H	3.21854100	-2.03200800	1.31338500
H	3.79831900	1.13199100	-1.53874200
C	5.11470000	-0.92629000	-0.30657100
H	5.55248900	-0.51207000	-1.22023600
H	5.72707100	-0.58317700	0.53797700
H	5.20784000	-2.01738800	-0.34744300

H	-3.25865300	0.82442100	-0.48396900
H	-1.77381100	-1.36836200	-2.13626200
C	-3.91529900	-1.24482900	-0.22554700
H	-3.56341100	-2.27450000	-0.27199100
C	-5.17057600	-0.96970100	0.13268500
H	-5.53939000	0.05220100	0.19394200
H	-5.87583300	-1.75846800	0.37958800

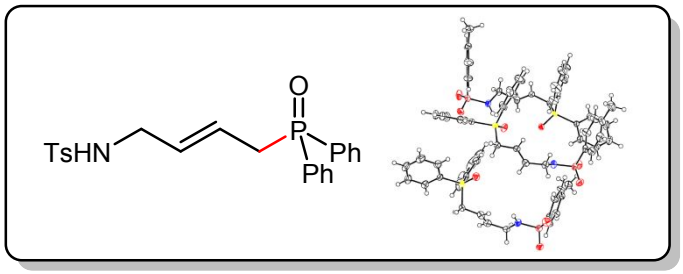


ethyl (2R,3S)-1-tosyl-3-vinylaziridine-2-carboxylate

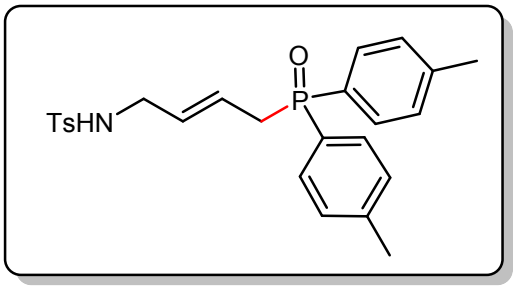
C	1.81235800	0.92951800	0.57266000
C	1.04389200	1.98251900	-0.19099200
H	1.99622500	1.06182500	1.63504000
H	1.30858800	2.00586300	-1.24854100
N	0.38240700	0.76515900	0.26460800
S	-0.19617200	-0.42698500	-0.84980400
O	-0.16951900	0.08913900	-2.22331000
O	0.47034000	-1.68459500	-0.48945100
C	-1.90601500	-0.51569300	-0.32652100
C	-2.24458300	-1.29791800	0.78099000
C	-2.87807100	0.18589400	-1.03851900
C	-3.57692200	-1.36750300	1.17518100
H	-1.47799000	-1.84716200	1.31745800
C	-4.20809800	0.10398800	-0.62686600
H	-2.59959400	0.77839200	-1.90329900
C	-4.57907500	-0.67034900	0.48017800
H	-3.84620300	-1.97638000	2.03478400
H	-4.96992800	0.64807200	-1.17927800
C	-6.02285600	-0.77950100	0.90391200
H	-6.63534000	0.00536800	0.44939300
H	-6.44845000	-1.74590900	0.60294300
H	-6.12847800	-0.70755100	1.99235700
C	0.63398500	3.27665300	0.41798400
H	1.24401500	4.12904100	0.12068200
C	-0.38490800	3.43538700	1.26268300
H	-1.01228200	2.59930300	1.56043300
H	-0.62533300	4.41095400	1.67625600
C	2.88381500	0.16631700	-0.16639100
O	2.99297800	0.10712800	-1.37252100

O	3.72554300	-0.40016300	0.70940600
C	4.81563100	-1.17251700	0.13677500
H	4.38606500	-1.96584100	-0.48217600
H	5.40307300	-0.51621600	-0.51290000
C	5.63710200	-1.72469900	1.28290300
H	5.03280900	-2.37407200	1.92498800
H	6.46862400	-2.31589600	0.88332400
H	6.05382800	-0.91878300	1.89629600

VI. Compound Characterizations

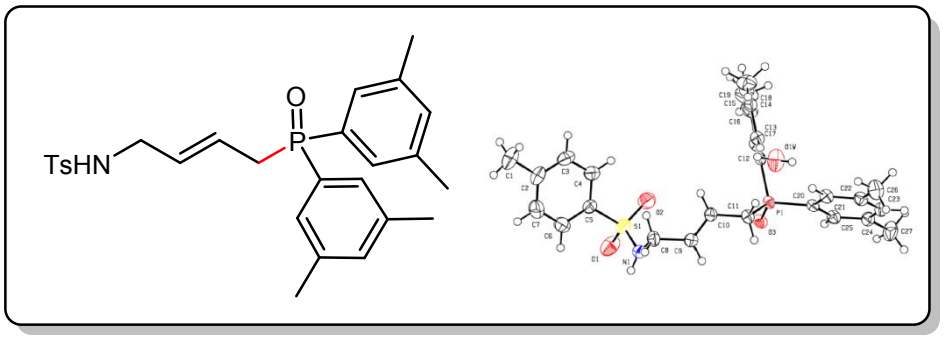


(E)-N-(4-(diphenylphosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3a). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:1). Yield 71% (30.0 mg). White solid. mp 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.64 (m, 6H), 7.57 – 7.43 (m, 6H), 7.26 (d, J = 8.3 Hz, 2H), 5.71 – 5.37 (m, 2H), 5.04 (t, J = 6.1 Hz, 1H), 3.44 (td, J = 6.0, 2.2 Hz, 2H), 3.15 – 2.94 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 137.0, 132.0 (d, J_{CP} = 2.9 Hz), 131.9 (d, J_{CP} = 99.6 Hz), 131.6 (d, J_{CP} = 11.5 Hz), 130.8 (d, J_{CP} = 9.3 Hz), 129.6, 128.7 (d, J_{CP} = 11.8 Hz), 127.0, 122.0 (d, J_{CP} = 9.3 Hz), 44.9 (d, J_{CP} = 2.0 Hz), 34.2 (d, J_{CP} = 68.3 Hz), 21.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 31.01. HRMS (ESI+) m/z calcd. for $[C_{23}H_{24}NNaO_3PS]^+$: 448.1107, found: 448.1089. X-ray crystallographic data of **3a** is provided in Appendix II.

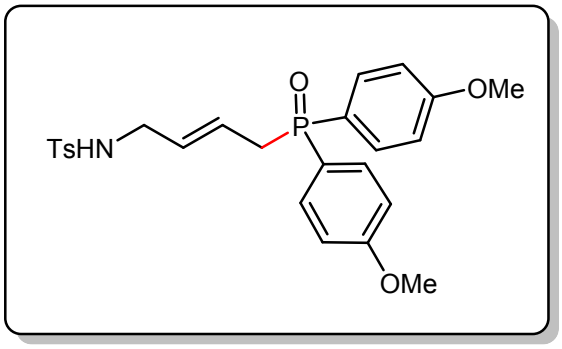


(E)-N-(4-(di-p-tolylphosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3b). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl

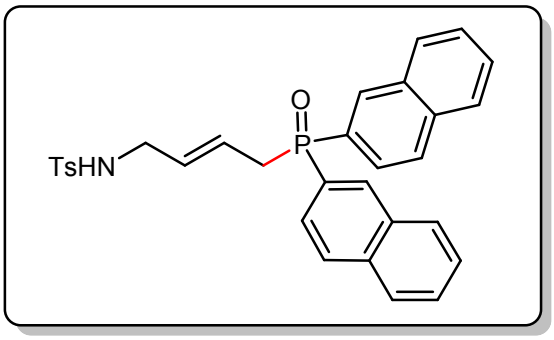
acetate/*n*-hexanes = 3:1). Yield 61% (27.5 mg). White solid. mp 58-62 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 8.2 Hz, 2H), 7.54 (dd, J = 11.3, 7.9 Hz, 4H), 7.32 – 7.18 (m, 6H), 5.60 – 5.50 (m, 1H), 5.49 – 5.39 (m, 1H), 5.14 (t, J = 6.1 Hz, 1H), 3.49 – 3.29 (m, 2H), 2.99 (dd, J = 14.0, 7.4 Hz, 2H), 2.39 (s, 3H), 2.38 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.2, 142.4 (d, J_{CP} = 2.7 Hz), 137.0, 131.2 (d, J_{CP} = 11.5 Hz), 130.9 (d, J_{CP} = 9.7 Hz), 129.6, 129.3 (d, J_{CP} = 12.0 Hz), 128.9 (d, J_{CP} = 102.1 Hz), 127.0, 122.6 (d, J_{CP} = 9.0 Hz), 44.9 (d, J_{CP} = 1.9 Hz), 34.5 (d, J_{CP} = 68.7 Hz), 21.5, 21.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.95. HRMS (ESI+) m/z calcd. for $[C_{25}H_{28}NO_3PS+Na]^+$: 476.1420, found: 476.1426.



(E)-N-(4-(bis(3,5-dimethylphenyl)phosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3c). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:1). Yield 73% (33.8 mg). White solid. mp 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 8.3 Hz, 2H), 7.34 – 7.21 (m, 6H), 7.14 (s, 2H), 5.63 – 5.38 (m, 2H), 4.96 (t, J = 6.0 Hz, 1H), 3.50 – 3.35 (m, 2H), 3.00 (dd, J = 13.7, 7.0 Hz, 2H), 2.40 (s, 3H), 2.33 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.1, 138.4 (d, J_{CP} = 6.3 Hz), 137.0, 133.6, 132.4 (d, J_{CP} = 99.3 Hz), 131.1, 129.5, 128.4, 127.1, 122.8, 45.0, 34.3 (d, J_{CP} = 66.6 Hz), 21.4, 21.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.15. HRMS (EI) calcd. for $C_{27}H_{32}NO_3PS$: [M] = 481.1841, found: 481.1843. X-ray crystallographic data of **3c** is provided in Appendix II.

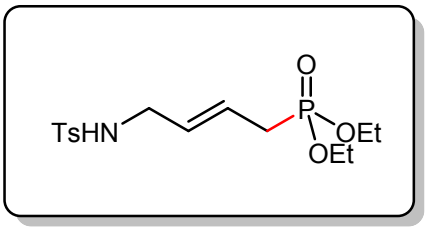


(E)-N-(4-(bis(4-methoxyphenyl)phosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (**3d**). The product was synthesized according to **General Procedure A** for 3 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 4:1 with addition of 2% of MeOH). Yield 75% (36.2 mg). White solid. mp 47-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.59 (dd, *J* = 11.0, 8.7 Hz, 4H), 7.28 (d, *J* = 8.1 Hz, 2H), 6.97 (dd, *J* = 8.8, 2.2 Hz, 4H), 5.62 – 5.49 (m, 1H), 5.49 – 5.37 (m, 1H), 4.72 (s, 1H), 3.85 (s, 6H), 3.44 (q, *J* = 5.8, 5.0 Hz, 2H), 2.98 (dd, *J* = 14.0, 7.3 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_{CP} = 2.8 Hz), 143.2, 136.9, 132.7 (d, J_{CP} = 10.7 Hz), 131.0 (d, J_{CP} = 11.6 Hz), 129.6, 127.1, 123.9, 122.9 (d, J_{CP} = 9.1 Hz), 114.2 (d, J_{CP}= 12.8 Hz), 55.3, 45.0 (d, J_{CP} = 2.2 Hz), 34.8 (d, J_{CP}= 69.1 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.83. HRMS (ESI+) m/z calcd. for $[C_{25}H_{28}NO_5PS+Na]^+$: 508.1318, found: 508.1321.

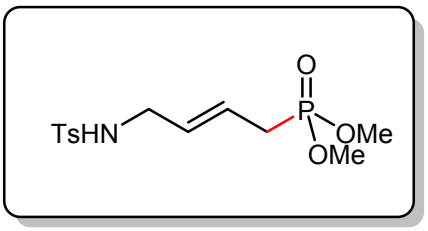


(E)-N-(4-(di(naphthalen-2-yl)phosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3e). The product was synthesized according to **General Procedure A** for 1.5 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:1). Yield 84% (44.2 mg). White solid. mp 59-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 13.3 Hz, 2H), 7.96 – 7.80 (m, 6H), 7.71 – 7.49 (m, 8H), 7.13 (d, *J* = 8.0 Hz, 2H), 5.74 – 5.60 (m, 1H), 5.60 – 5.42 (m, 2H), 3.51 – 3.37 (m, 2H), 3.18 (dd, *J* = 14.0, 7.2 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.0, 136.9, 134.6 (d, J_{CP} = 2.2 Hz), 133.0 (d, J_{CP} = 8.1 Hz), 132.4 (d, J_{CP} =

12.8 Hz), 131.6 (d, J_{CP} = 11.6 Hz), 129.5, 129.3 (d, J_{CP} = 99.4 Hz), 128.8, 128.5 (d, J_{CP} = 11.6 Hz), 128.2, 127.8, 127.0, 127.0, 125.6 (d, J_{CP} = 10.3 Hz), 122.2 (d, J_{CP} = 8.7 Hz), 44.9, 34.3 (d, J_{CP} = 68.8 Hz), 21.4. ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.22. HRMS (ESI+) m/z calcd. for $[C_{31}H_{28}NO_3PS+Na]^+$: 548.1420, found: 548.1423.

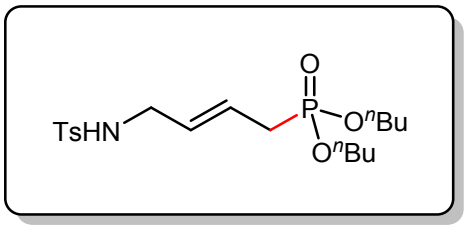


diethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3f). The product was synthesized according to **General Procedure B** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:1). Yield 70% (25.4 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 5.64 – 5.49 (m, 2H), 4.79 (t, *J* = 6.2 Hz, 1H), 4.06 (dqd, *J* = 8.0, 7.1, 1.2 Hz, 4H), 3.54 (q, *J* = 4.8 Hz, 2H), 2.57 – 2.44 (m, 2H), 2.42 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 130.1 (d, J_{CP} = 14.5 Hz), 129.7, 127.1, 123.1 (d, J_{CP} = 11.0 Hz), 62.0 (d, J_{CP} = 6.7 Hz), 45.0 (d, J_{CP} = 2.3 Hz), 30.1 (d, J_{CP} = 140.0 Hz), 21.5, 16.4 (d, J_{CP} = 6.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.23. HRMS (ESI+) m/z calcd. for $[C_{15}H_{24}NO_5PS+Na]^+$: 384.1005, found: 384.0996.

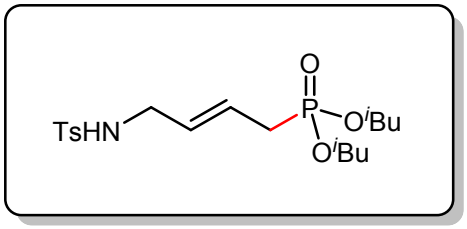


dimethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3g). The product was synthesized according to **General Procedure B** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:1). Yield 64% (21.1 mg). White solid. mp 98-100 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.66 – 5.48 (m, 2H), 5.04 (t, *J* = 6.4 Hz, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.56 – 3.50 (m, 2H), 2.57 – 2.48 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 136.9, 130.5 (d, J_{CP} = 14.6 Hz), 129.7, 127.1, 122.4 (d, J_{CP} = 11.1 Hz), 52.7 (d, J_{CP} = 6.8 Hz), 44.9 (d, J_{CP} = 2.1 Hz), 29.0 (d, J_{CP} = 140.3 Hz), 21.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.40. HRMS (EI) calcd.

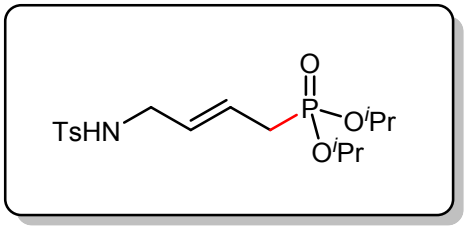
for $C_{13}H_{20}NO_5PS$: [M] = 330.0800, found: 333.0803.



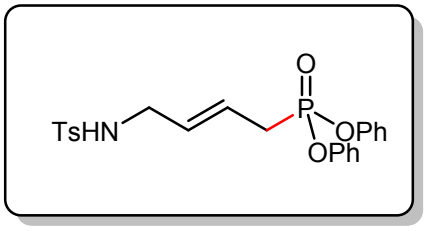
dibutyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3h). The product was synthesized according to **General Procedure B** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 55% (22.9 mg). Yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.62 – 5.47 (m, 2H), 4.98 – 4.84 (m, 1H), 4.04 – 3.93 (m, 4H), 3.61 – 3.45 (m, 2H), 2.60 – 2.44 (m, 2H), 2.42 (s, 3H), 1.70 – 1.52 (m, 4H), 1.44 – 1.29 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 130.1 (d, J_{CP} = 14.4 Hz), 129.7, 127.1, 123.2 (d, J_{CP} = 11.0 Hz), 65.7 (d, J_{CP} = 6.8 Hz), 45.0 (d, J_{CP} = 2.2 Hz), 32.5 (d, J_{CP} = 6.1 Hz), 29.9 (d, J_{CP} = 140.1 Hz), 21.5, 18.7, 13.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.16. HRMS (EI) calcd. for $C_{19}H_{32}NO_5PS$: [M] = 417.1739, found: 417.1741.



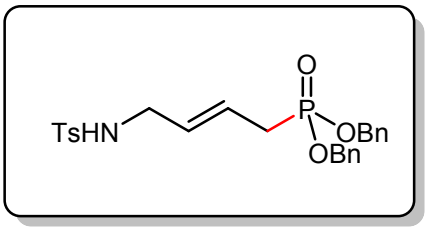
diisobutyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3i). The product was synthesized according to **General Procedure B** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 76% (31.5 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.72 – 5.45 (m, 2H), 4.85 (t, *J* = 6.2 Hz, 1H), 3.75 (q, *J* = 6.3 Hz, 4H), 3.58 – 3.46 (m, 2H), 2.58 – 2.45 (m, 2H), 2.41 (s, 3H), 1.88 (dp, *J* = 13.3, 6.7 Hz, 2H), 0.91 (s, 6H), 0.90 (d, *J* = 6.7 Hz, 13H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 130.1 (d, J_{CP} = 14.4 Hz), 129.7, 127.1, 123.1 (d, $_{CP}J$ = 11.1 Hz), 71.9 (d, J_{CP} = 7.1 Hz), 45.0 (d, J_{CP} = 2.3 Hz), 29.8 (d, J_{CP} = 140.5 Hz), 29.2 (d, J_{CP} = 6.3 Hz), 21.5, 18.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.90. HRMS (EI) calcd. for $C_{19}H_{32}NO_5PS$: [M] = 417.1739, found: 417.1741.



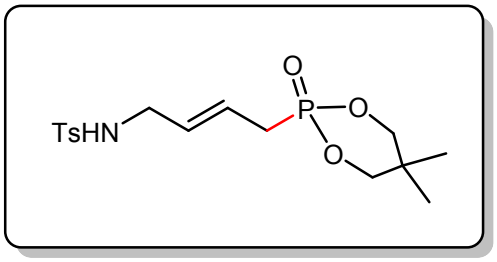
diisopropyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3j). The product was synthesized according to **General Procedure B** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 54% (18.0 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.9 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 5.61 – 5.46 (m, 2H), 4.75 (t, *J* = 6.2 Hz, 1H), 3.62 – 3.42 (m, 2H), 2.53 – 2.36 (m, 5H), 1.28 (dd, *J* = 8.9, 6.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 129.8, 129.7, 127.1, 123.7 (d, J_{CP} = 11.1 Hz), 70.4 (d, J_{CP} = 6.8 Hz), 45.0 (d, J_{CP} = 2.2 Hz), 31.3 (d, J_{CP} = 141.0 Hz), 24.0 (d, J_{CP} = 4.4 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.18. HRMS (EI) m/z calcd. for [$C_{17}H_{28}NO_5PS$]: [M] = 389.1426, found: 389.1427.



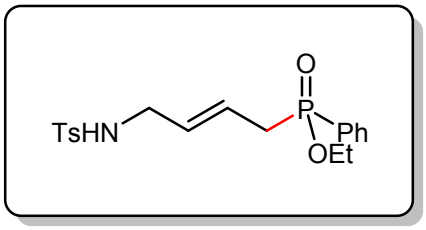
diphenyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3k). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 62% (28.1 mg). Transparent oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.40 – 7.24 (m, 6H), 7.19 – 7.11 (m, 6H), 5.77 – 5.53 (m, 2H), 4.80 – 4.61 (m, 1H), 3.53 (q, *J* = 5.6 Hz, 2H), 2.84 (dd, *J* = 21.9, 6.9 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.2 (d, J_{CP} = 8.9 Hz), 143.4, 136.9, 131.6 (d, J_{CP} = 15.3 Hz), 129.8, 129.7, 127.1, 125.3, 121.5 (d, J_{CP} = 11.5 Hz), 120.5 (d, J_{CP} = 4.5 Hz), 44.8 (d, J_{CP} = 2.2 Hz), 30.1 (d, J_{CP} = 140.0 Hz), 21.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 19.91. HRMS (ESI+) m/z calcd. for $[C_{23}H_{24}NO_5PS+Na]^+$: 480.1005, found: 480.1016.



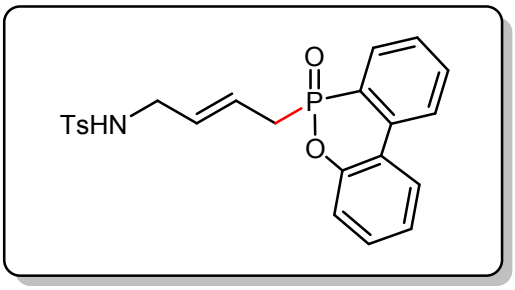
dibenzyl (E)-(4-((4-methylphenyl)sulfonamide)but-2-en-1yl)phosphonate (3l). The product was synthesized according to **General Procedure B** for 6 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 64% (31.0 mg). White liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.3 Hz, 2H), 7.40 – 7.28 (m, 10H), 7.28 (d, J = 8.0 Hz, 2H), 5.52 – 5.35 (m, 2H), 5.03 (dd, J = 11.9, 9.2 Hz, 2H), 4.93 (dd, J = 11.8, 8.6 Hz, 2H), 4.72 (t, J = 6.2 Hz, 1H), 3.48 – 3.41 (m, 2H), 2.53 – 2.49 (m, 1H), 2.46 (d, J = 6.7 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 136.1 (d, J_{CP} = 5.8 Hz), 130.5 (d, J_{CP} = 14.7 Hz), 129.7, 128.6, 128.5, 128.0, 127.1, 122.4 (d, J_{CP} = 11.2 Hz), 67.6 (d, J_{CP}= 6.7 Hz), 44.9, 30.4 (d, J_{CP} = 139.6 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.52. HRMS (ESI+) m/z calcd. For $[C_{25}H_{28}NO_5PS]^+$: 485.1426, found: 485.1429.



(E)-N-(4-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)but-2-en-1-yl)-4-methylbenzene sulfonamide (3m). The product was synthesized according to **General Procedure B** for 6 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 77% (28.5 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.67 – 5.51 (m, 2H), 5.27 – 5.19 (m, 1H), 4.17 (dd, J = 11.1, 8.2 Hz, 2H), 3.78 (dd, J = 14.3, 11.1 Hz, 2H), 3.51 (q, J = 5.0 Hz, 2H), 2.67 – 2.54 (m, 2H), 2.40 (s, 3H), 1.07 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.3, 137.0, 130.9 (d, J_{CP} = 14.5 Hz), 129.6, 127.1, 121.7 (d, J_{CP} = 11.4 Hz), 75.1 (d, J_{CP} = 6.2 Hz), 44.8 (d, J_{CP} = 2.2 Hz), 32.6 (d, J_{CP} = 5.8 Hz), 28.5 (d, J_{CP} = 137.0 Hz), 21.6, 21.4, 21.3. ^{31}P NMR (243 MHz, $CDCl_3$) δ 22.98. HRMS (EI) calcd. for $C_{16}H_{24}NO_5PS$: [M] = 373.1113, found: 373.1111.

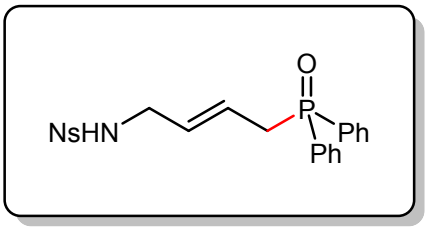


ethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)(phenyl)phosphinate (3n). The product was synthesized according to **General Procedure B** for 6 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 64% (25.2 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.67 (m, 4H), 7.59 – 7.53 (m, 1H), 7.50 – 7.43 (m, 2H), 7.28 (d, J = 7.7 Hz, 2H), 5.60 – 5.45 (m, 1H), 5.45 – 5.28 (m, 1H), 4.94 (t, J = 6.1 Hz, 1H), 4.13 – 3.98 (m, 1H), 3.94 – 3.81 (m, 1H), 3.53 – 3.39 (m, 2H), 2.80 – 2.54 (m, 2H), 2.41 (s, 3H), 1.27 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.9, 132.5 (d, J_{CP} = 2.8 Hz), 131.7 (d, J_{CP} = 9.7 Hz), 130.7 (d, J_{CP} = 12.9 Hz), 130.0 (d, J_{CP} = 125.6 Hz), 129.6, 128.6 (d, J_{CP} = 12.6 Hz), 127.1, 122.7 (d, J_{CP} = 9.2 Hz), 61.0 (d, J_{CP} = 6.6 Hz), 44.9 (d, J_{CP} = 2.2 Hz), 34.2 (d, J_{CP} = 97.6 Hz), 21.5, 16.4 (d, J_{CP} = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 41.02. HRMS (EI) calcd. for $C_{19}H_{24}NO_4PS$: [M] = 393.1164, found: 393.1165.

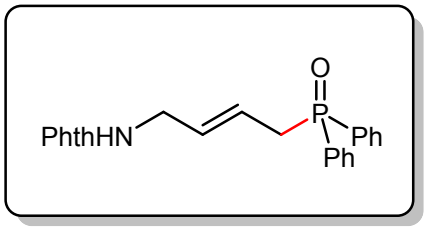


(E)-4-methyl-N-(4-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)but-2-en-1-yl)benzenesulfonamide (3o). The product was synthesized according to **General Procedure A** for 7 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 58% (25.4 mg). White solid. mp 59-61 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.2, 5.0 Hz, 1H), 7.89 (dd, J = 8.1, 1.6 Hz, 1H), 7.83 (ddd, J = 12.8, 7.6, 1.5 Hz, 1H), 7.72 – 7.64 (m, 3H), 7.50 (td, J = 7.5, 2.9 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.29 – 7.22 (m, 3H), 7.18 (d, J = 8.1 Hz, 1H), 5.51 – 5.32 (m, 2H), 4.54 (br, 1H), 3.36 (t, J = 5.1 Hz, 2H), 2.78 (dd, J = 17.6, 7.2 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4 (d, J_{CP} = 8.4 Hz), 143.4, 136.8, 135.8 (d, J_{CP} = 6.3 Hz), 133.5 (d, J_{CP} = 2.5 Hz), 131.5 (d, J_{CP} = 13.1 Hz), 130.7, 130.4 (d, J_{CP} = 10.3 Hz), 129.6, 128.5 (d, J_{CP} = 13.2 Hz), 127.0, 125.1, 124.7, 123.8 (d, J_{CP} = 120.1 Hz), 123.8 (d, J_{CP} = 9.7 Hz), 122.2 (d, J_{CP} = 10.6 Hz), 121.3 (d, J_{CP} = 10.2 Hz), 120.3 (d, J_{CP} = 6.3 Hz), 44.7 (d, J_{CP} = 2.4 Hz), 33.4 (d, J_{CP} = 93.3 Hz), 21.5.

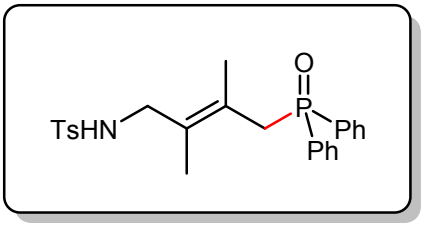
^{31}P NMR (162 MHz, $CDCl_3$) δ 34.32. HRMS (ESI+) m/z calcd. for $[C_{23}H_{22}NO_4PS+Na]^+$: 462.0899, found: 462.0909.



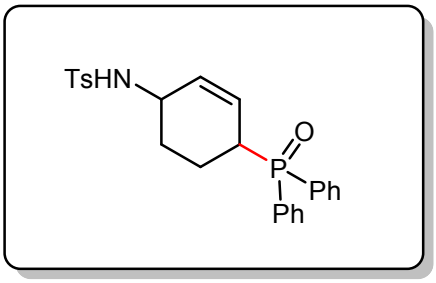
(E)-N-(4-(diphenylphosphoryl)but-2-en-1-yl)-4-nitrobenzenesulfonamide (3p). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:1). Yield 73% (33.5 mg). White solid. mp 49-51 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.8 Hz, 2H), 7.74 – 7.61 (m, 4H), 7.55 (td, *J* = 7.4, 1.5 Hz, 2H), 7.48 (td, *J* = 7.6, 3.0 Hz, 4H), 6.98 (t, *J* = 5.9 Hz, 1H), 5.69 – 5.58 (m, 1H), 5.58 – 5.48 (m, 1H), 3.52 (d, *J* = 5.0 Hz, 2H), 3.06 (dd, *J* = 13.7, 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 149.7, 146.4, 132.2 (d, J_{CP} = 2.7 Hz), 131.8 (d, J_{CP} = 113.1 Hz), 131.5, 130.9 (d, J_{CP} = 9.3 Hz), 128.8 (d, J_{CP} = 12.0 Hz), 128.2, 124.1, 121.9 (d, J_{CP} = 9.3 Hz), 44.8 (d, J_{CP} = 2.0 Hz), 34.0 (d, J_{CP} = 68.3 Hz). ^{31}P NMR (243 MHz, $CDCl_3$) δ 30.67. HRMS (ESI+) m/z calcd. for $[C_{22}H_{21}N_2O_5PS+Na]^+$: 479.0801, found: 479.0809.



(E)-2-((4-(diphenylphosphoryl)but-2-en-1-yl)amino)isoindoline-1,3-dione (**3q**). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl acetate/MeOH = 40:1). Yield 77% (32.1 mg). Yellow solid. mp 156-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.76 (m, 2H), 7.76 – 7.68 (m, 2H), 7.71 – 7.61 (m, 4H), 7.53 – 7.44 (m, 2H), 7.47 – 7.38 (m, 4H), 5.76 – 5.59 (m, 2H), 4.50 (t, *J* = 5.2 Hz, 1H), 3.61 – 3.53 (m, 2H), 3.10 (d, *J* = 6.0 Hz, 1H), 3.10 – 3.04 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 134.2, 132.6, 132.0, 131.8 (d, J_{CP}= 2.6 Hz), 131.3 (d, J_{CP} = 11.7 Hz), 130.9 (d, J_{CP} = 9.2 Hz), 130.1, 128.6 (d, J_{CP} = 11.7 Hz), 124.1 (d, J_{CP} = 9.0 Hz), 123.4, 53.1, 34.7 (d, J_{CP} = 68.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.46. HRMS (ESI+) m/z calcd. for $[C_{24}H_{21}N_2O_3P]^+$: 416.1290, found: 416.1287.



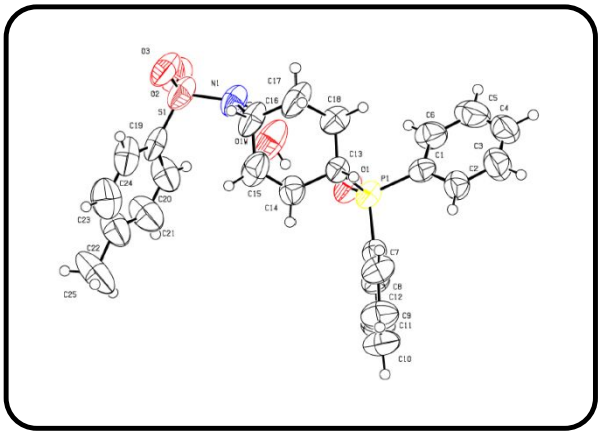
(E)-N-(4-(diphenylphosphoryl)-2,3-dimethylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3r). The product was synthesized according to **General Procedure A** for 1 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:3). Yield 74% (33.5 mg). White solid. mp 115-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 8.3 Hz, 2H), 7.77 – 7.66 (m, 4H), 7.62 – 7.53 (m, 2H), 7.54 – 7.45 (m, 4H), 7.11 (d, J = 8.0 Hz, 2H), 3.35 (s, 2H), 3.05 (d, J = 13.7 Hz, 2H), 2.36 (s, 3H), 1.78 (d, J = 5.4 Hz, 3H), 1.23 (d, J = 3.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.3, 137.3, 132.2 (d, J_{CP} = 98.6 Hz), 132.0 (d, J_{CP} = 2.4 Hz), 131.5 (d, J_{CP} = 10.1 Hz), 130.9 (d, J_{CP} = 9.4 Hz), 129.2, 128.6 (d, J_{CP} = 11.7 Hz), 127.3, 122.6 (d, J_{CP} = 10.7 Hz), 46.5 (d, J_{CP} = 2.9 Hz), 36.8 (d, J_{CP} = 65.9 Hz), 21.4, 21.2, 18.5 (d, J_{CP} = 3.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.58. HRMS (ESI+) m/z calcd. for $[C_{25}H_{28}NO_3PS+Na]^+$: 476.1420, found: 476.1420.



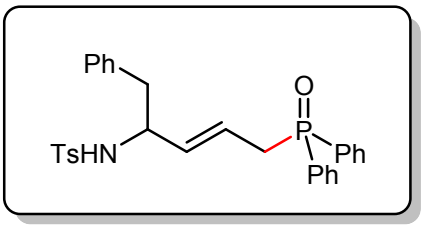
N-(4-(diphenylphosphoryl)cyclohex-2-en-1yl)-4-methylbenzenesulfonamide (**3s**). The product was synthesized according to **General Procedure A** (at 60 °C under N_2 atmosphere) for 3 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1 and CH_2Cl_2/MeOH = 30:1). Overall yield 77% (34.8 mg, trans:cis = 1:1.3).

***trans*-3s**, White solid. mp 179-181 °C. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.85 – 7.77 (m, 2H), 7.76 – 7.68 (m, 2H), 7.65 – 7.50 (m, 6H), 7.47 – 7.41 (m, 2H), 7.22 – 7.15 (m, 2H), 5.91 – 5.81 (m, 1H), 5.35 – 5.22 (m, 1H), 3.67 – 3.52 (m, 2H), 2.37 (s, 3H), 2.30 – 2.15 (m, 2H), 2.03 – 1.94 (m, 0H), 1.65 – 1.51 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.7, 138.2, 132.5, 132.4, 132.0 (d, J_{CP} = 2.7 Hz), 131.9 (d, J_{CP} = 2.6

Hz), 131.8 (d, J_{CP} = 8.6 Hz), 131.3 (d, J_{CP}= 23.8 Hz), 130.6 (d, J_{CP} = 9.1 Hz), 130.2, 129.4, 128.8 (d, J_{CP} = 11.6 Hz), 128.5 (d, J_{CP} = 11.7 Hz), 127.0, 119.3 (d, J_{CP} = 5.1 Hz), 50.8 (d, J_{CP} = 5.4 Hz), 39.5 (d, J_{CP} = 67.9 Hz), 27.5 (d, J_{CP} = 5.0 Hz), 23.4 (d, J_{CP} = 2.4 Hz), 21.5. HRMS (ESI+) m/z calcd. for $[C_{25}H_{26}NO_3PS+Na]^+$: 474.1263, found: 474.1265.

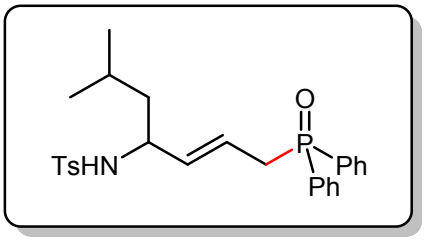


***cis*-3s**, White solid. mp 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.71 (m, 6H), 7.58 – 7.43 (m, 6H), 7.25 (d, *J* = 8.1 Hz, 3H), 6.04 (d, *J* = 9.1 Hz, 1H), 5.71 – 5.61 (m, 2H), 5.56 – 5.46 (m, 1H), 3.88 (s, 1H), 3.16 – 3.05 (m, 1H), 2.39 (s, 3H), 2.03 – 1.81 (m, 1H), 1.76 – 1.62 (m, 1H), 1.65 – 1.53 (m, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 142.9, 139.1, 132.1, 132.1 – 132.0 (m), 131.1 (d, J_{CP}= 8.6 Hz), 130.9 (d, J_{CP} = 8.6 Hz), 129.6, 128.8 (dd, J_{CP} = 11.4, 6.1 Hz), 126.9, 124.5 (d, J_{CP} = 6.8 Hz), 47.2, 35.5 (d, J_{CP} = 69.5 Hz), 28.0 (d, J_{CP} = 7.5 Hz), 21.5, 17.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.13. HRMS (ESI+) m/z calcd. for $[C_{25}H_{26}NO_3PS+Na]^+$: 474.1263, found: 474.1260. X-ray crystallographic data of ***cis*-3s** is provided in Appendix II.

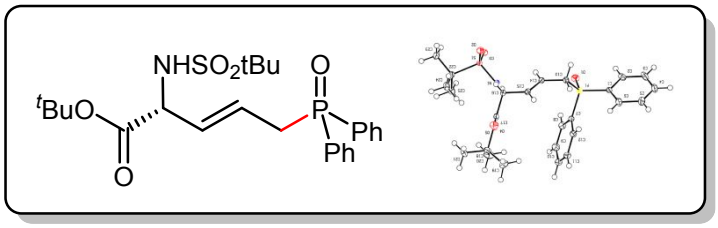


(E)-N-(5-(diphenylphosphoryl)-1-phenylpent-3-en-2-yl)-4-methylbenzenesulfonamide (3t). The product was synthesized according to **General Procedure A** for 3 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 60% (31.1 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74

– 7.62 (m, 4H), 7.58 – 7.48 (m, 2H), 7.52 – 7.41 (m, 6H), 7.21 – 7.09 (m, 5H), 6.92 – 6.79 (m, 2H), 5.61 – 5.46 (m, 1H), 5.45 – 5.32 (m, 1H), 4.53 (s, 1H), 3.90 – 3.74 (m, 1H), 3.00 (tq, J = 14.7, 6.7 Hz, 2H), 2.64 – 2.48 (m, 2H), 2.39 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.1, 137.3, 136.1, 135.6, 135.6, 132.4 (d, J_{CP} = 99.0 Hz), 132.2 (d, J_{CP} = 99.1 Hz), 131.9, 131.0 (d, J_{CP} = 7.7 Hz), 131.0 (d, J_{CP} = 7.6 Hz), 129.5, 129.4, 128.7 (d, J_{CP} = 4.2 Hz), 128.6 (d, J_{CP} = 4.4 Hz), 128.5, 127.1, 126.7, 120.9 (d, J_{CP} = 8.9 Hz), 56.3 (d, J_{CP} = 2.1 Hz), 41.8 (d, J_{CP} = 2.4 Hz), 34.4 (d, J = 68.4 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.84. HRMS (EI) calcd. for $C_{30}H_{30}NO_3PS$: [M] = 515.1684, found: 515.1688.



(E)-N-(1-(diphenylphosphoryl)-6-methylhept-2-en-4-yl)-4-methylbenzenesulfonamide (3u). The product was synthesized according to **General Procedure A** for 3 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 64% (30.9 mg). White solid. mp 146-149 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 – 7.61 (m, 6H), 7.51 (t, J = 7.5 Hz, 2H), 7.45 (dt, J = 7.9, 3.9 Hz, 4H), 7.22 (d, J = 7.9 Hz, 2H), 5.41 (dq, J = 14.1, 6.8 Hz, 1H), 5.18 (ddd, J = 15.4, 7.4, 4.5 Hz, 1H), 4.83 (d, J = 7.4 Hz, 1H), 3.60 (p, J = 7.3 Hz, 1H), 2.99 – 2.81 (m, 2H), 2.39 (s, 3H), 1.22 – 1.10 (m, 2H), 1.04 (dt, J = 13.6, 6.9 Hz, 1H), 0.64 (d, J = 4.0 Hz, 3H), 0.63 (d, J = 4.0 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.0, 138.1, 136.3 (d, J_{CP} = 11.7 Hz), 132.4 (d, J_{CP} = 99.4 Hz), 132.0 (d, J_{CP} = 97.7 Hz), 131.9 (d, J_{CP} = 2.9 Hz), 131.8 (d, J_{CP} = 3.4 Hz), 131.0 (d, J_{CP} = 9.1 Hz), 130.9 (d, J_{CP} = 9.1 Hz), 129.4, 128.6 (d, J_{CP} = 5.2 Hz), 128.5 (d, J_{CP} = 5.2 Hz), 127.2, 120.4 (d, J_{CP} = 8.8 Hz), 54.0 (d, J_{CP} = 2.1 Hz), 44.7, 34.5 (d, J_{CP} = 68.4 Hz), 24.0, 22.4, 21.9, 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.75. HRMS (EI) calcd. for $C_{27}H_{32}NO_3PS$: [M] = 481.1841, found: 481.1839.

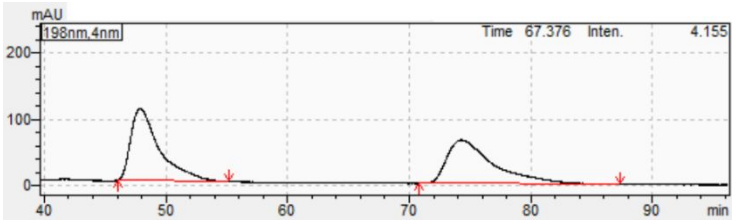


tert-butyl (R,E)-2-((1,1-dimethylethyl)sulfonamido)-5-(diphenylphosphoryl)pent-3-enoate (3v). The

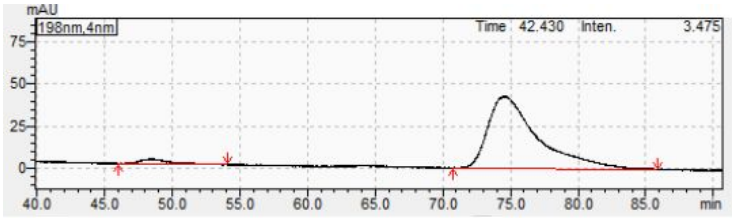
product was synthesized according to **General Procedure C** and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 72% (34.8 mg, ee 92%). White solid. mp 181-184 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.69 (m, 4H), 7.54 (t, J = 7.7 Hz, 2H), 7.49 (t, J = 3.7 Hz, 4H), 5.86 – 5.76 (m, 1H), 5.69 – 5.58 (m, 1H), 4.65 (d, J = 9.5 Hz, 1H), 4.45 (m, 1H), 3.24 – 3.07 (m, 2H), 1.39 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4 (d, J_{CP} = 2.4 Hz), 132.2 (d, J_{CP} = 98.5 Hz), 132.1 (d, J_{CP} = 99.1 Hz), 132.0 (d, J_{CP} = 3.2 Hz), 132.0 (d, J_{CP} = 3.2 Hz), 131.1 (d, J_{CP} = 12.9 Hz), 131.0 (d, J_{CP} = 9.0 Hz), 130.9 (d, J = 8.7 Hz), 128.7, 128.7, 122.7 (d, J_{CP} = 8.7 Hz), 83.1, 60.0, 58.9 (d, J_{CP} = 1.9 Hz), 34.6 (d, J_{CP} = 68.2 Hz), 27.8, 24.0. ^{31}P NMR (243 MHz, $CDCl_3$) δ 29.96. HRMS (ESI+) m/z calcd. for $[C_{25}H_{34}NO_5PS+Na]^+$: 514.1788, found: 514.1796. X-ray crystallographic data of **3v** is provided in Appendix II.

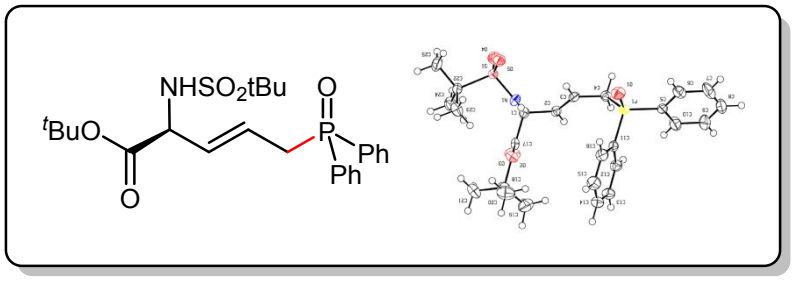
HPLC conditions: IC-3 column, 20% iPrOH/Hx, 1.0 ml/min, R_t: 48.417 min (**3w**), 74.555 min (**3v**).

Chiral HPLC-Chromatogram of the racemic mixture



*Chiral HPLC-Chromatogram of **3v*** (ee 92%)

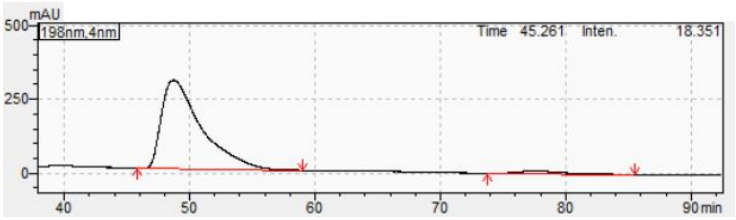




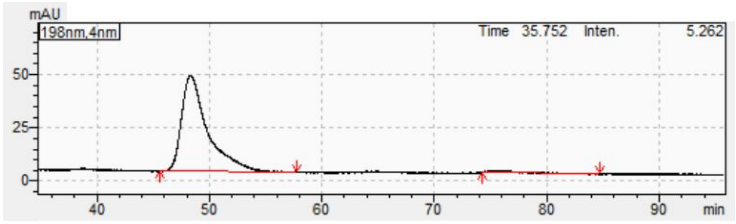
tert-butyl (S,E)-2-((1,1-dimethylethyl)sulfonamido)-5-(diphenylphosphoryl)pent-3-enoate (3w). The product was synthesized according to **General Procedure C** and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:1). Yield 67% (32.9 mg, ee 92%) from **1i**. Yield 70% (34.1 mg, ee 97%) from **1j**.

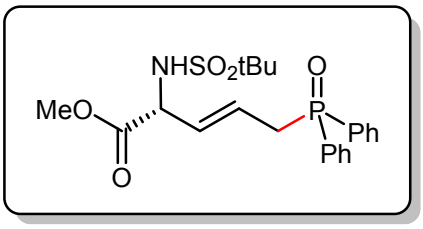
White solid. mp 181-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.65 (m, 4H), 7.57 – 7.40 (m, 6H), 5.88 – 5.74 (m, 1H), 5.69 – 5.57 (m, 1H), 4.71 (d, J = 9.5 Hz, 1H), 4.49 – 4.36 (m, 1H), 3.23 – 3.04 (m, 2H), 1.38 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.4 (d, J_{CP} = 2.5 Hz), 132.2 (d, J_{CP} = 99.2 Hz), 132.0 (d, J_{CP} = 3.6 Hz), 132.0 (d, J_{CP} = 99.5 Hz), 132.0 (d, J_{CP} = 3.7 Hz), 131.1 (d, J_{CP} = 11.7 Hz), 131.0 (d, J_{CP} = 9.3 Hz), 130.9 (d, J_{CP} = 9.3 Hz), 128.7 (d, J_{CP} = 1.5 Hz), 128.7 (d, J_{CP} = 1.5 Hz), 122.6 (d, J_{CP} = 9.0 Hz), 83.1, 60.0, 58.9 (d, J_{CP} = 2.2 Hz), 34.5 (d, J_{CP} = 68.1 Hz), 27.8, 24.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.06. HRMS (ESI+) m/z calcd. for $[C_{25}H_{34}NO_5PS+Na]^+$: 514.1788, found: 514.1790. X-ray crystallographic data of **3w** is provided in Appendix II.

*Chiral HPLC-Chromatogram of **3w from 1i*** (ee 92%)



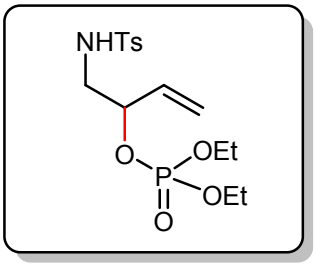
*Chiral HPLC-Chromatogram of **3w from 1j*** (ee 97%)



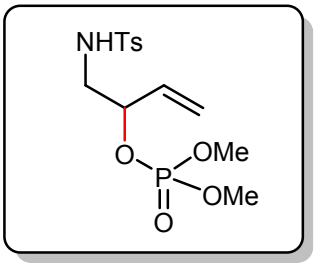


methyl (R,E)-2-((1,1-dimethylethyl)sulfonamido)-5-(diphenylphosphoryl)pent-3-enoate (3x). The product was synthesized according to **General Procedure C** and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2.5:1). Yield 70% (31.3 mg). Transparent oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 – 7.63 (m, 4H), 7.54 – 7.49 (m, 2H), 7.50 – 7.41 (m, 4H), 5.84 (dq, J = 14.1, 7.1 Hz, 1H), 5.58 (dt, J = 15.5, 5.2 Hz, 1H), 4.97 (d, J = 9.4 Hz, 1H), 4.55 (dt, J = 9.8, 4.6 Hz, 1H), 3.66 (s, 3H), 3.13 (dd, J = 14.6, 7.5 Hz, 2H), 1.28 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9 (d, J_{CP} = 2.7 Hz), 132.0 (d, J_{CP} = 99.7 Hz),

132.0 (d, J_{CP} = 2.9 Hz), 131.0 (d, J_{CP} = 3.4 Hz), 131.9 (d, J_{CP} = 2.5 Hz), 130.9 (d, J_{CP} = 3.4 Hz), 130.5 (d, J_{CP} = 11.6 Hz), 128.7 (d, J_{CP} = 3.3 Hz), 128.6 (d, J_{CP} = 3.3 Hz), 123.4 (d, J_{CP} = 8.9 Hz), 60.1, 58.2 (d, J_{CP} = 2.3 Hz), 52.8, 34.5 (d, J_{CP} = 67.7 Hz), 24.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.79. HRMS (EI) calcd. for $C_{22}H_{28}NO_5PS$: [M] = 449.1426, found: 449.1424.

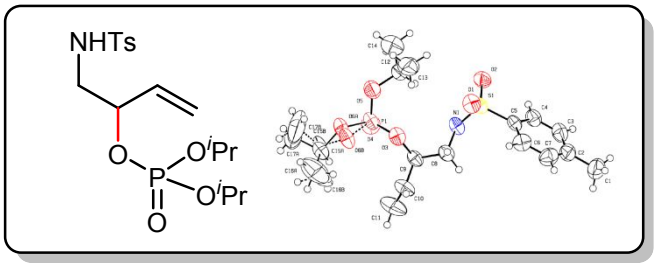


diethyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4a). The product was synthesized according to **General Procedure D** for 9 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:2). Yield 77% (29.2 mg). Light yellowish solid. mp 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.75 (ddd, *J* = 17.0, 10.5, 6.3 Hz, 1H), 5.59 (t, *J* = 6.0 Hz, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 4.75 (qd, *J* = 7.3, 3.5 Hz, 1H), 4.15 – 4.01 (m, 4H), 3.19 (ddd, *J* = 11.0, 7.1, 3.7 Hz, 1H), 3.09 (ddd, *J* = 13.2, 7.5, 5.1 Hz, 1H), 2.41 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 136.9, 133.3 (d, J_{CP} = 4.8 Hz), 129.7, 127.0, 119.1, 77.6 (d, J_{CP} = 5.5 Hz), 64.2 (d, J_{CP} = 5.9 Hz), 47.5 (d, J_{CP} = 5.0 Hz), 21.5, 16.0 (d, J_{CP} = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.41. HRMS (ESI+) m/z calcd. for $[C_{15}H_{25}NO_6PS]^+$: 378.1135, found: 378.1143.

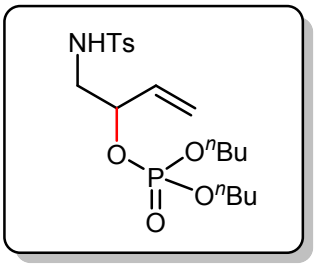


dimethyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4b). The product was synthesized according to **General Procedure D** for 7 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:2). Yield 76% (26.3 mg). White solid. mp 85-88 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 5.75 (ddd, *J* = 17.1, 10.6, 6.4 Hz, 1H), 5.50 – 5.43 (m, 1H), 5.36 (d, *J* = 17.1 Hz, 1H), 5.28 (d, *J* = 10.6 Hz, 1H), 4.81 – 4.72 (m, 1H), 3.75 (d, *J* = 4.4 Hz, 3H),

3.73 (d, J = 4.5 Hz, 3H), 3.23 – 3.16 (m, 1H), 3.11 (ddd, J = 13.3, 7.5, 5.5 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 137.0, 133.1 (d, J_{CP} = 4.3 Hz), 129.7, 127.1, 119.4, 77.9 (d, J_{CP} = 5.5 Hz), 54.6 (d, J_{CP} = 1.7 Hz), 54.6 (d, J_{CP} = 2.1 Hz), 47.5 (d, J_{CP} = 4.8 Hz), 21.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ 0.77. HRMS (ESI+) m/z calcd. for $[C_{13}H_{21}NO_6PS]^+$: 350.0822, found: 350.0824.

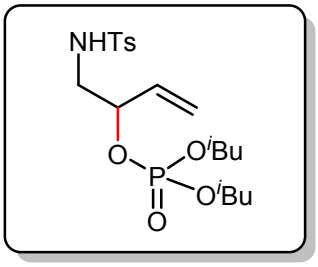


diisopropyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4c). The product was synthesized according to **General Procedure D** for 13 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 55% (22.3 mg). White solid. mp 62-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.9 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 5.75 (ddd, J = 17.0, 10.6, 6.1 Hz, 1H), 5.67 (dd, J = 7.4, 4.6 Hz, 1H), 5.33 (d, J = 17.2 Hz, 1H), 5.25 (d, J = 10.5 Hz, 1H), 4.79 – 4.68 (m, 1H), 4.68 – 4.53 (m, 2H), 3.21 (ddd, J = 13.4, 7.4, 3.4 Hz, 1H), 3.09 (ddd, J = 12.8, 7.7, 4.5 Hz, 1H), 2.42 (s, 3H), 1.32 (d, J = 5.8 Hz, 6H), 1.30 (d, J = 5.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.3, 136.9, 133.4 (d, J_{CP} = 5.3 Hz), 129.7, 127.0, 118.8, 77.3, 73.2 (d, J_{CP} = 5.6 Hz), 73.1 (d, J_{CP} = 5.7 Hz), 47.6 (d, J_{CP} = 4.4 Hz), 23.6 (d, J_{CP} = 3.4 Hz), 23.5 (d, J_{CP} = 2.9 Hz), 21.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.96. HRMS (ESI+) m/z calcd. for $[C_{17}H_{29}NO_6PS]^+$: 406.1448, found: 406.1456. X-ray crystallographic data of **4c** is provided in Appendix II.

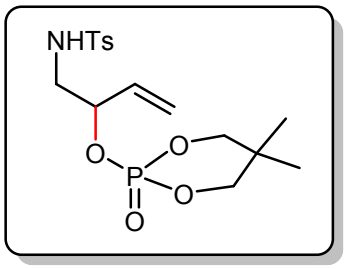


dibutyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4d). The product was synthesized according to **General Procedure D** for 48 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 50% (20.9 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 5.78 (ddd, J = 17.0, 10.5, 6.2 Hz, 1H), 5.54 (t, J = 6.1 Hz, 1H), 5.37 (d, J = 17.2 Hz,

1H), 5.29 (d, J = 10.5 Hz, 1H), 4.84 – 4.71 (m, 1H), 4.14 – 3.92 (m, 4H), 3.23 (dddd, J = 13.3, 7.2, 3.5, 1.3 Hz, 1H), 3.12 (ddd, J = 13.2, 7.5, 4.9 Hz, 1H), 2.44 (s, 3H), 1.72 – 1.58 (m, 4H), 1.40 (hd, J = 7.4, 1.4 Hz, 4H), 0.95 (td, J = 7.4, 1.5 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 137.0, 133.3 (d, J_{CP} = 4.8 Hz), 129.7, 127.1, 119.1, 77.6 (d, J_{CP} = 5.3 Hz), 68.0 (d, J_{CP} = 6.0 Hz), 47.5 (d, J_{CP} = 4.6 Hz), 32.2 (d, J_{CP} = 6.9 Hz), 21.5, 18.6, 13.5. ^{31}P NMR (243 MHz, $CDCl_3$) δ -1.29. HRMS (ESI+) m/z calcd. for $[C_{19}H_{33}NO_6PS]^+$: 434.1761, found: 434.1767.

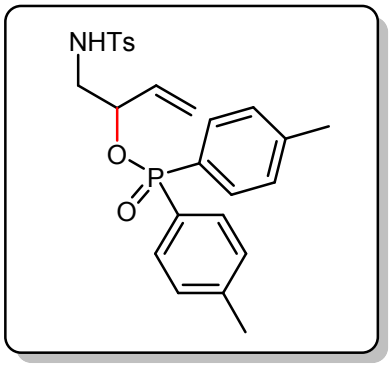


diisobutyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4e). The product was synthesized according to **General Procedure D** for 15 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:2). Yield 67% (29.1 mg). Dark yellowish solid. mp 51-55 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.75 (ddd, J = 16.9, 10.6, 6.2 Hz, 1H), 5.52 (t, J = 6.1 Hz, 1H), 5.34 (d, J = 17.2 Hz, 1H), 5.27 (d, J = 10.6 Hz, 1H), 4.75 (dt, J = 10.2, 6.7 Hz, 1H), 3.86 – 3.71 (m, 4H), 3.21 (ddd, J = 13.5, 7.1, 3.6 Hz, 1H), 3.10 (ddd, J = 13.1, 7.5, 5.0 Hz, 1H), 2.42 (s, 3H), 1.92 (dp, J = 13.3, 6.7 Hz, 2H), 0.92 (dd, J = 6.7, 1.6 Hz, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.4, 137.1, 133. (d, J_{CP} = 4.8 Hz), 129.7, 127.1, 119.1, 77.6 (d, J_{CP} = 5.5 Hz), 74.1 (d, J_{CP} = 6.4 Hz), 47.6 (d, J_{CP} = 4.7 Hz), 29.0 (d, J_{CP} = 7.3 Hz), 21.5, 18.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.17. HRMS (FAB) m/z calcd. for $[C_{25}H_{28}NO_3PS+H]^+$: 434.1766, found: 434.1769.

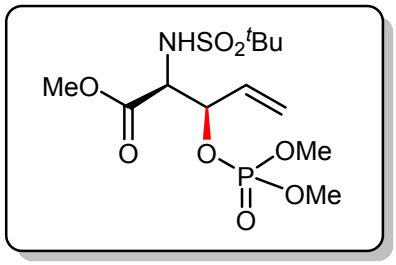


N-(2-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)oxy)but-3-en-1-yl)-4-methylbenzenesulfonamide (4f). The product was synthesized according to **General Procedure D** for 6

h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 55% (20.4 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.83 (ddd, *J* = 17.1, 10.5, 6.5 Hz, 1H), 5.61 – 5.51 (m, 1H), 5.39 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.6 Hz, 1H), 4.86 – 4.73 (m, 1H), 4.14 (dd, *J* = 10.9, 3.4 Hz, 1H), 4.03 (dd, *J* = 10.9, 3.6 Hz, 1H), 3.99 – 3.81 (m, 2H), 3.32 – 3.20 (m, 1H), 3.23 – 3.12 (m, 1H), 2.43 (s, 3H), 1.25 (s, 3H), 0.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.5, 137.0, 133.1 (d, J_{CP} = 4.9 Hz), 129.7, 127.1, 119.7, 78.2 (d, J_{CP} = 6.9 Hz), 77.8 (d, J_{CP} = 6.7 Hz), 77.5 (d, J_{CP} = 5.3 Hz), 47.5 (d, J_{CP} = 4.5 Hz), 32.1 (d, J_{CP} = 5.9 Hz), 21.6, 21.5, 20.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ -8.30. HRMS (ESI+) m/z calcd. for $[C_{16}H_{25}NO_6PS]^+$: 390.1135, found: 390.1137.



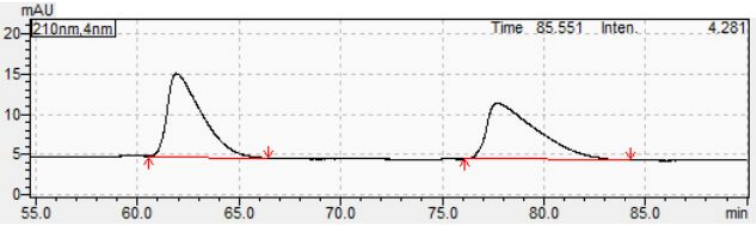
1-((4-methylphenyl)sulfonamido)but-3-en-2-yl di-p-tolylphosphinate (4g). The product was synthesized according to **General Procedure D** for 9 h and purified by flash chromatography (ethyl acetate/*n*-hexanes = 2:3). Yield 54% (25.5 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.69 – 7.55 (m, 3H), 7.30 – 7.21 (m, 4H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.93 (br, 1H), 5.76 (ddd, *J* = 16.7, 10.4, 5.7 Hz, 1H), 5.27 – 5.16 (m, 2H), 4.50 (q, *J* = 7.7, 7.3 Hz, 1H), 3.37 – 3.25 (m, 1H), 3.09 (dd, *J* = 13.7, 8.3 Hz, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2 (d, J_{CP} = 2.9 Hz), 142.9 (d, J_{CP} = 3.0 Hz), 142.8, 137.3, 133.7 (d, J_{CP} = 6.9 Hz), 132.1 (d, J_{CP} = 10.8 Hz), 131.2 (d, J_{CP} = 10.7 Hz), 129.5, 129.4 (d, J_{CP} = 10.8 Hz), 129.2 (d, J_{CP} = 11.2 Hz), 127.9 (d, J_{CP} = 146.7 Hz), 127.0, 125.7, 118.2, 76.4 (d, J_{CP} = 6.0 Hz), 48.0, 21.6, 21.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.84. HRMS (ESI+) m/z calcd. for $[C_{25}H_{29}NO_4PS]^+$: 470.1549, found: 470.1559.



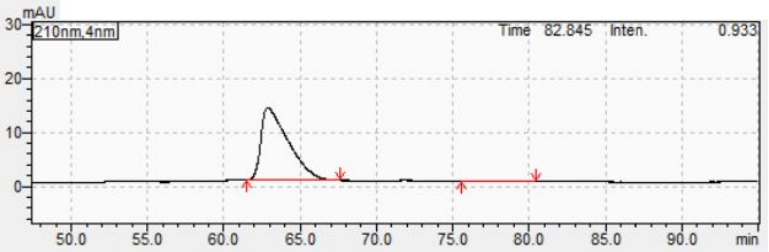
methyl (2R,3S)-3-((dimethoxyphosphoryl)oxy)-2-((1,1-dimethylethyl)sulfonamido)pent-4-enoate (4h). The product was synthesized according to **General Procedure E** and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 60% (22.6 mg, ee >99%). White solid. mp 97-100 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.91 – 5.81 (m, 1H), 5.47 (dd, J = 17.1, 1.2 Hz, 1H), 5.39 (dd, J = 10.6, 1.3 Hz, 1H), 5.13 – 5.08 (m, 1H), 5.07 (d, J = 10.0 Hz, 1H), 4.40 (dd, J = 10.1, 3.4 Hz, 1H), 3.80 (dd, J = 11.3, 1.2 Hz, 3H), 3.79 (s, 3H), 3.76 (dd, J = 11.3, 1.2 Hz, 3H), 1.39 (d, J = 1.2 Hz, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.1, 131.7 (d, J_{CP} = 4.0 Hz), 120.3, 79.2 (d, J_{CP} = 5.0 Hz), 60.7 (d, J_{CP} = 5.4 Hz), 60.4, 54.8 (d, J_{CP} = 6.1 Hz), 54.7 (d, J_{CP} = 6.2 Hz), 52.8, 24.1. ^{31}P NMR (243 MHz, $CDCl_3$) δ 0.58. HRMS (ESI+) m/z calcd. for $[C_{12}H_{24}NO_8PS+Na]^+$: 396.0852, found: 396.0851.

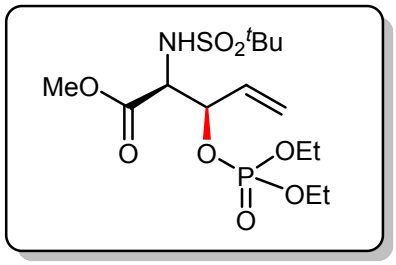
HPLC conditions: IA-3 column, 8% iPrOH/Hx, 0.7 ml/min, R_t: 61.916 min (**4h**), 77.716 min (minor).

Chiral HPLC-Chromatogram of the racemic mixture

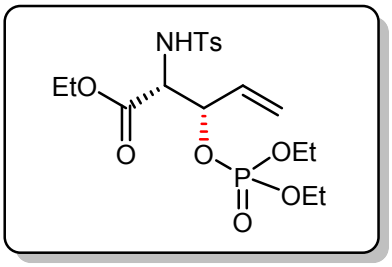


*Chiral HPLC-Chromatogram of **4h** (ee >99%)*





methyl (2S,3S)-3-((diethoxyphosphoryl)oxy)-2-((1,1-dimethylethyl)sulfonamido)pent-4-enoate (4i). The product was synthesized according to **General Procedure E** and purified by flash chromatography (ethyl acetate/*n*-hexanes = 3:2). Yield 52% (20.5 mg). Transparent oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 17.0, 10.6, 6.4 Hz, 1H), 5.46 (dt, *J* = 17.2, 1.3 Hz, 1H), 5.42 – 5.34 (m, 1H), 5.20 (d, *J* = 10.0 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.39 (dd, *J* = 10.0, 3.1 Hz, 1H), 4.22 – 4.03 (m, 4H), 3.80 (s, 3H), 1.40 (s, 9H), 1.39 – 1.28 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 131.9 (d, J_{CP} = 4.3 Hz), 119.9, 79.2 (d, J_{CP} = 5.2 Hz), 64.4 (d, J_{CP} = 4.5 Hz), 64.4 (d, J_{CP} = 4.5 Hz), 60.9 (d, J_{CP} = 5.3 Hz), 60.4, 52.8, 24.1, 16.1 (d, *J* = 1.4 Hz), 16.0 (d, *J* = 1.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ -1.70. HRMS (ESI+) m/z calcd. for $[C_{14}H_{29}NO_8PS]^+$: 402.1346, found: 402.1350.



ethyl (2R)-3-((diethoxyphosphoryl)oxy)-2-((4-methylphenyl)sulfonamido)pent-4-enoate (4j). The product was synthesized according to **General Procedure E** and purified by flash chromatography (ethyl acetate/*n*-hexanes = 1:1). Yield 41% (18.2 mg). Transparent oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 6.7 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 5.80 (dddd, *J* = 17.2, 10.6, 6.7, 1.5 Hz, 1H), 5.67 (d, *J* = 9.5 Hz, 1H), 5.37 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.32 (d, *J* = 10.0 Hz, 1H), 5.02 – 4.92 (m, 1H), 4.22 (ddd, *J* = 9.6, 3.6, 1.4 Hz, 1H), 4.17 – 4.08 (m, 2H), 4.05 (pd, *J* = 7.2, 1.5 Hz, 2H), 3.99 (qd, *J* = 7.1, 1.5 Hz, 2H), 2.40 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.7, 143.6, 137.1, 131.8 (d, J_{CP} = 4.3 Hz), 129.6, 127.2, 120.1, 78.6 (d, J_{CP} = 5.1 Hz), 64.4 (d, J_{CP} = 5.8 Hz), 64.2 (d, J_{CP} = 6.1 Hz), 62.1, 59.8 (d, J_{CP} = 5.8 Hz), 21.5, 16.1 (d, J_{CP} = 7.1 Hz), δ 16.0 (d, J_{CP} = 7.0 Hz), 13.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.03. HRMS (ESI+) m/z calcd. for $[C_{18}H_{28}NO_8PS+Na]^+$:

472.1165, found: 472.1164.

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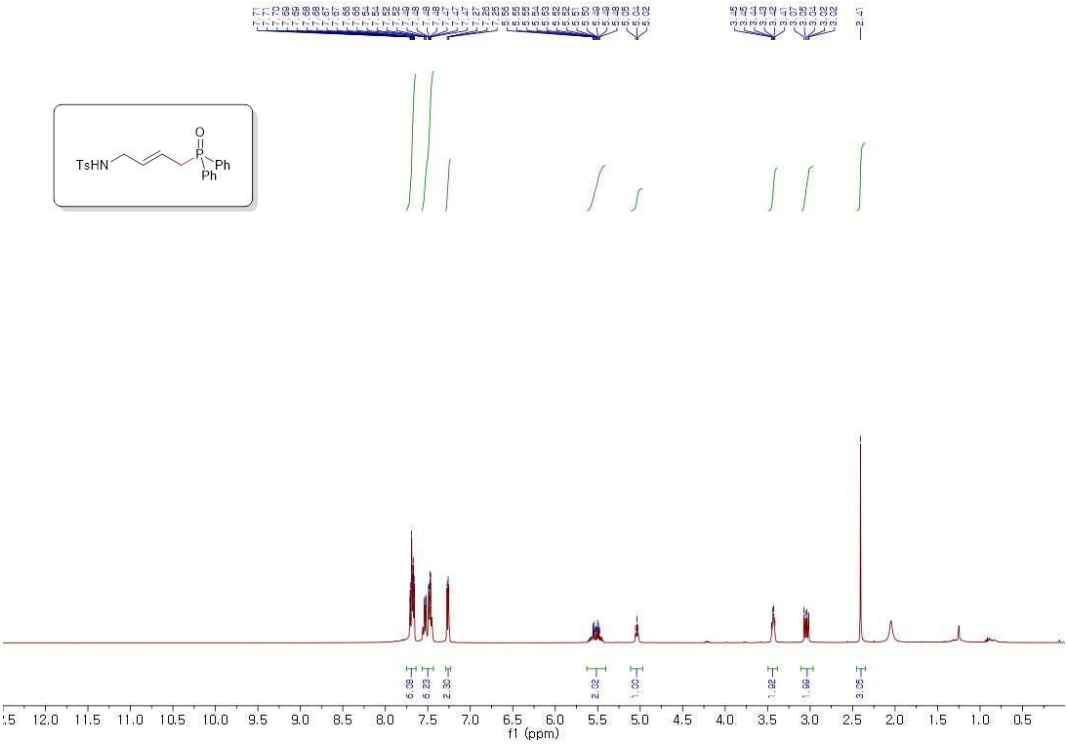
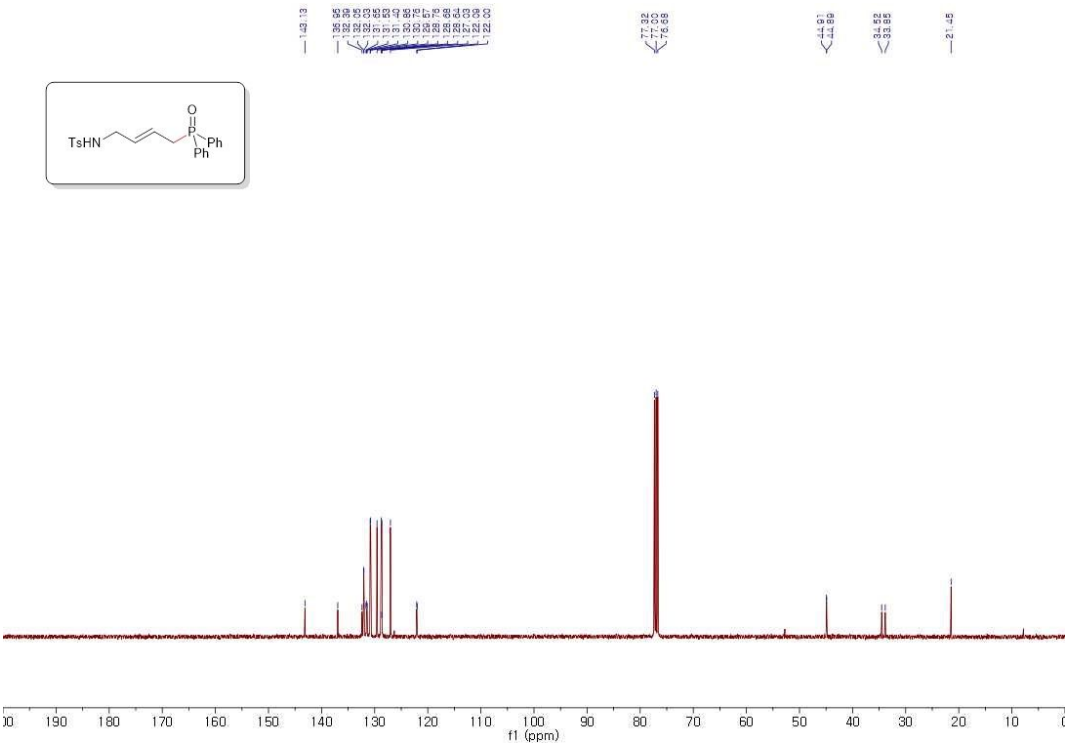
Appendix I

Spectral Copies of ^{1}H, ^{13}C and ^{31}P NMR Data Obtained in this Study

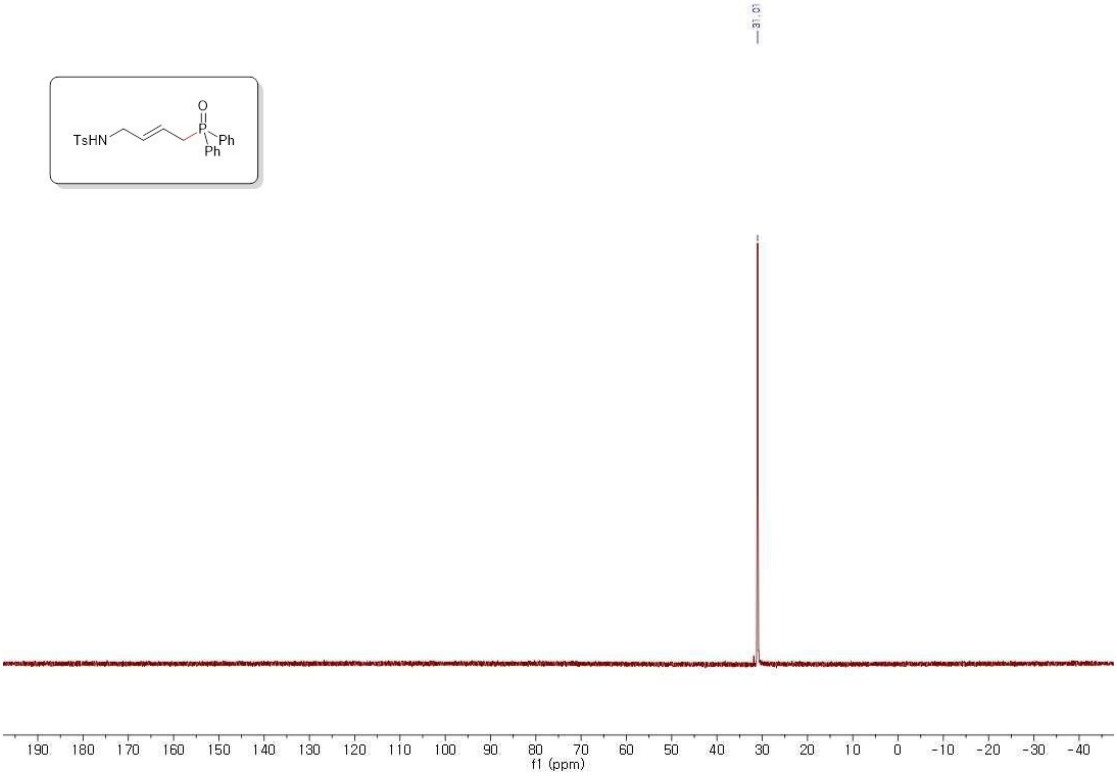
(E)-N-(4-(diphenylphosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3a)



400 MHz, ^{1}H NMR in $CDCl_3$

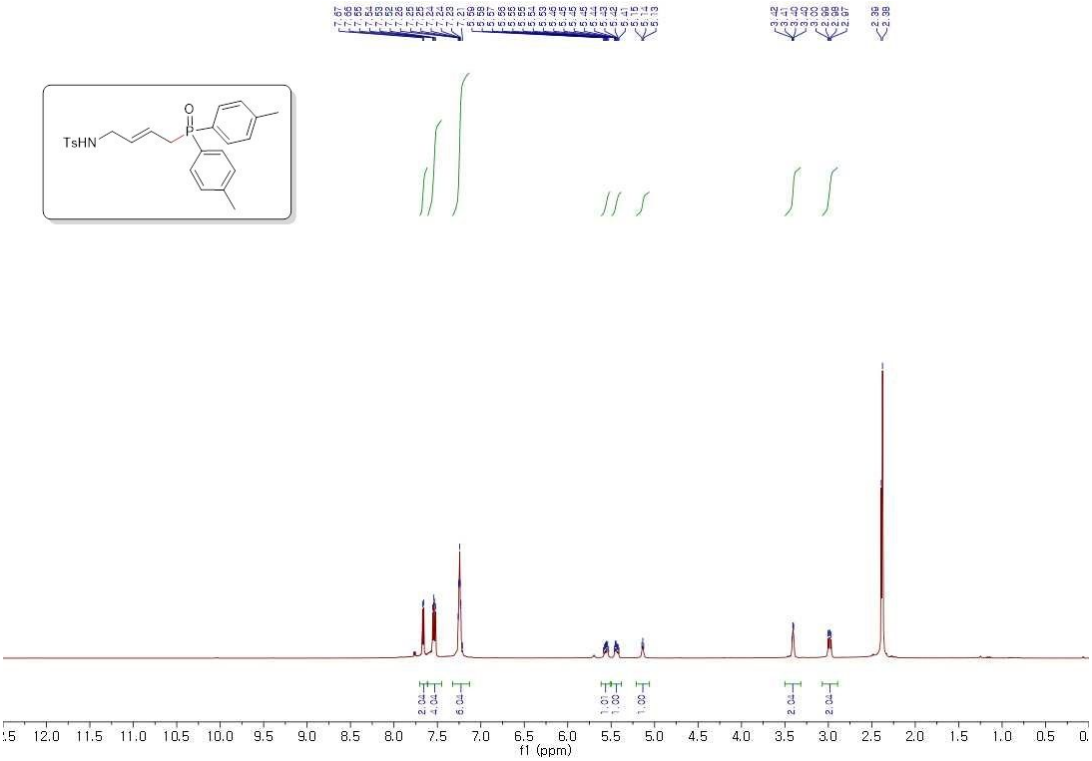


100 MHz, ^{13}C NMR in $CDCl_3$

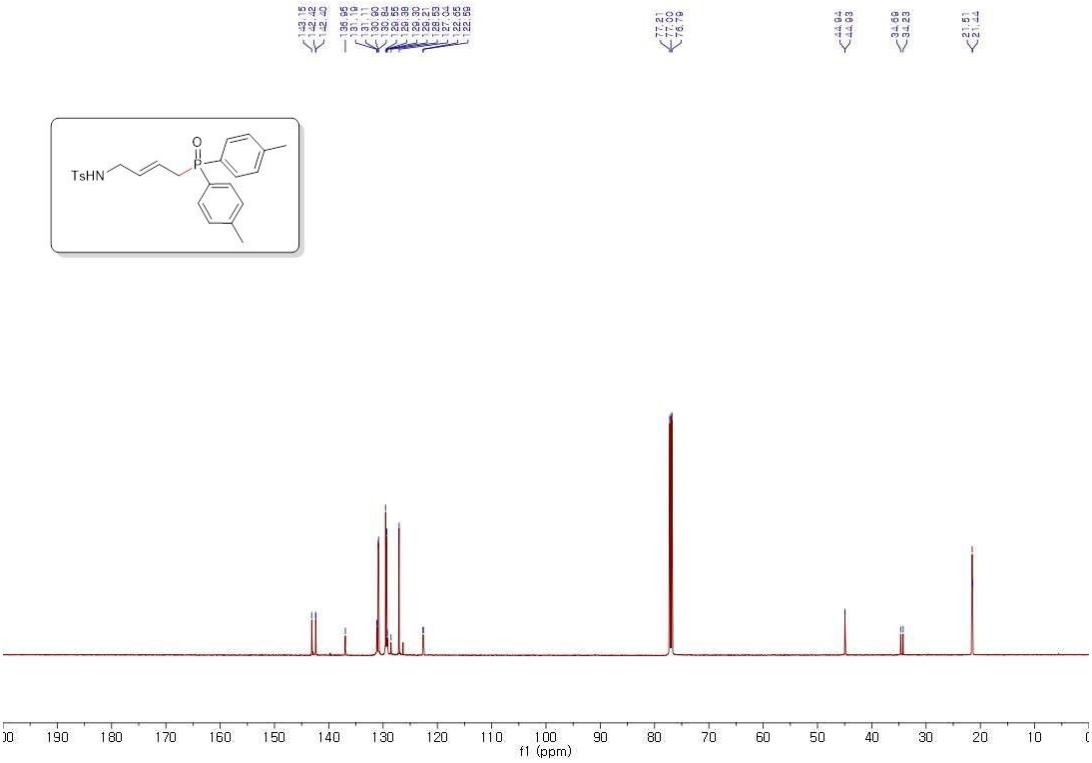


243 MHz, ^{31}P NMR in $CDCl_3$

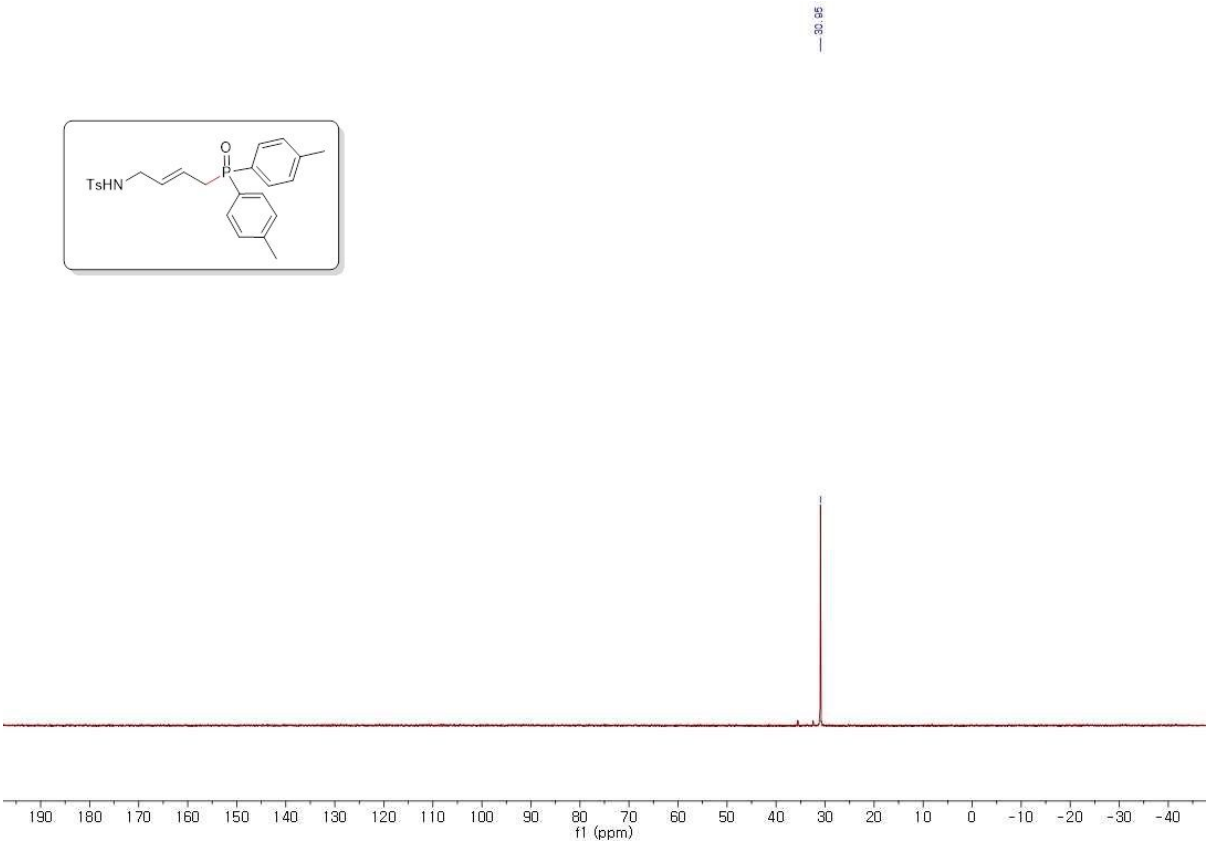
(E)-N-(4-(di-p-tolylphosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3b)



600 MHz, ^{1}H NMR in $CDCl_3$

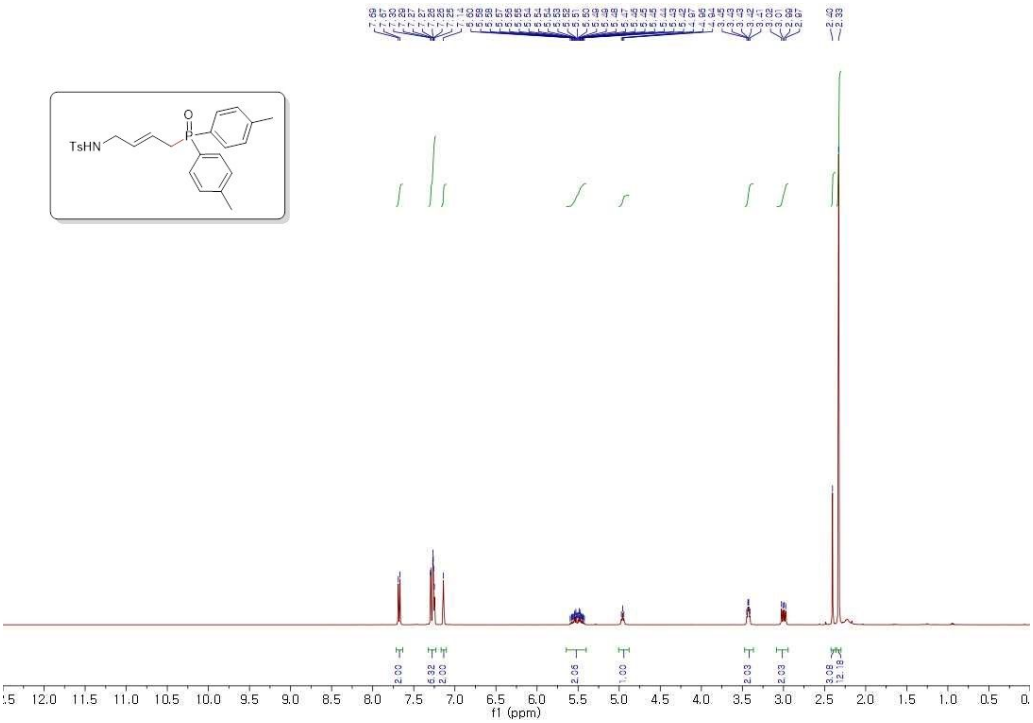


150 MHz, ^{13}C NMR in $CDCl_3$

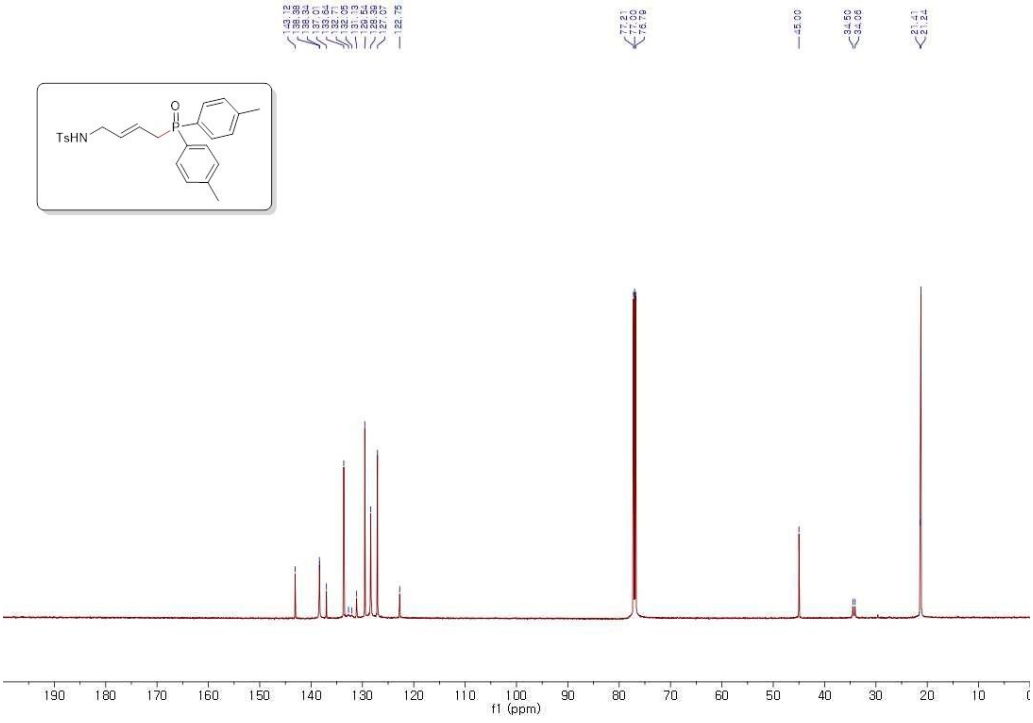


243 MHz, ^{31}P NMR in $CDCl_3$

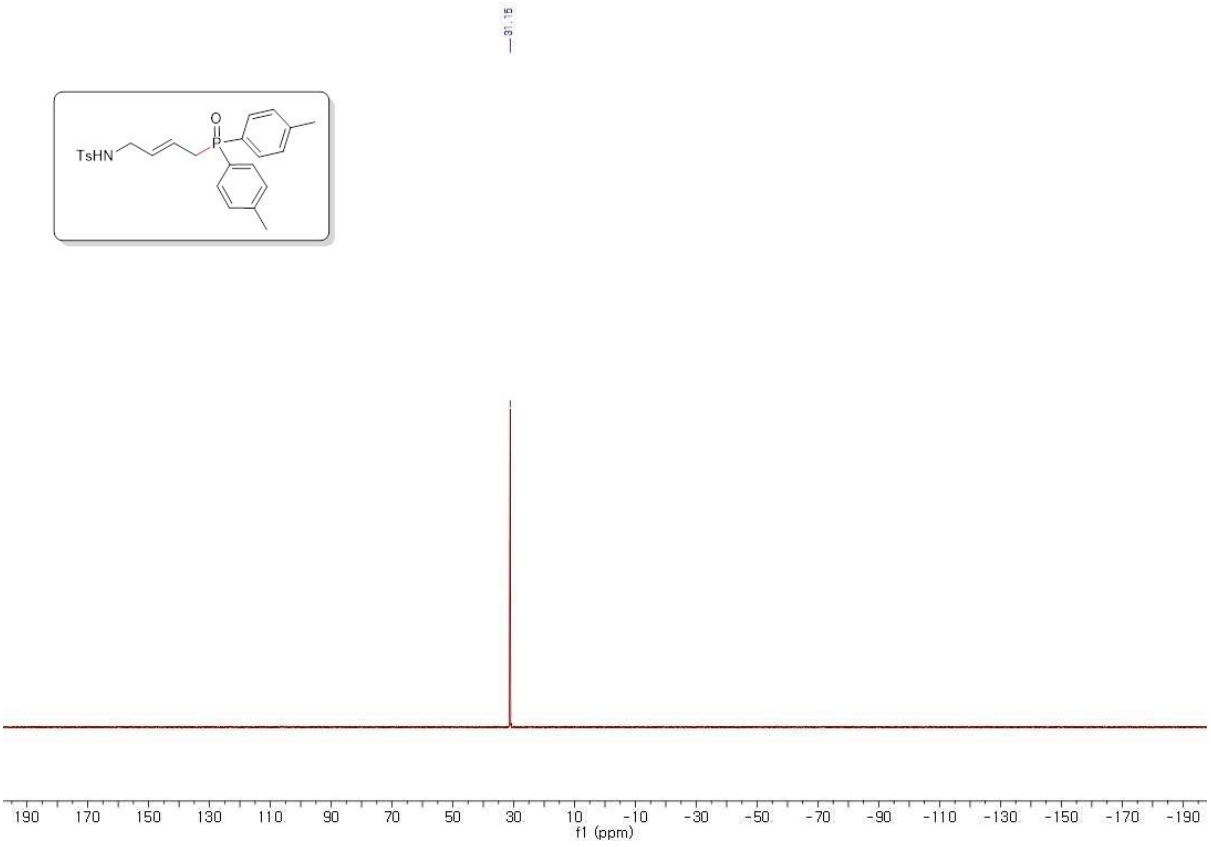
(E)-N-(4-(bis(3,5-dimethylphenyl)phosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3c)



600 MHz, ^{1}H NMR in $CDCl_3$

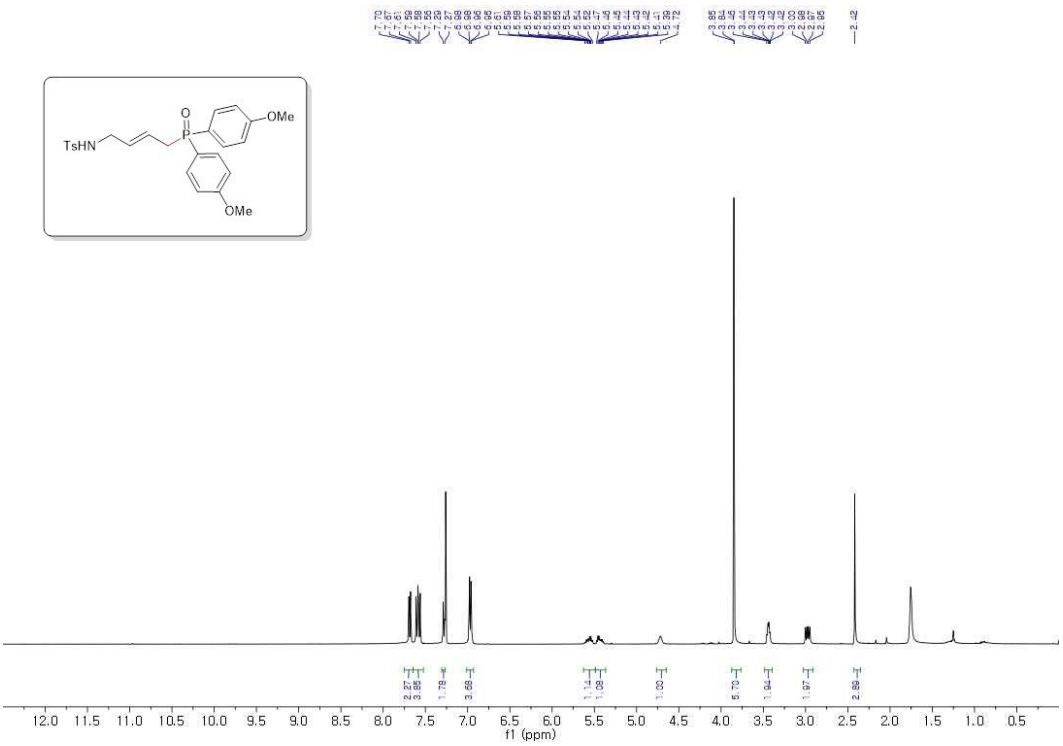


150 MHz, ^{13}C NMR in $CDCl_3$

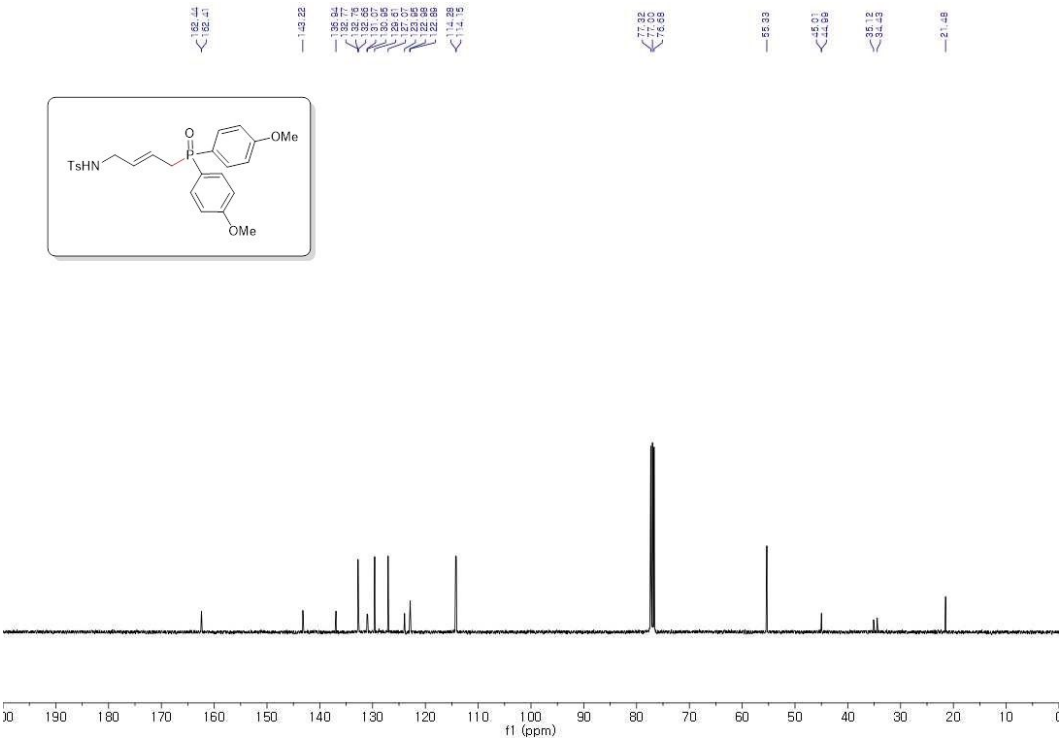


243 MHz, ^{31}P NMR in $CDCl_3$

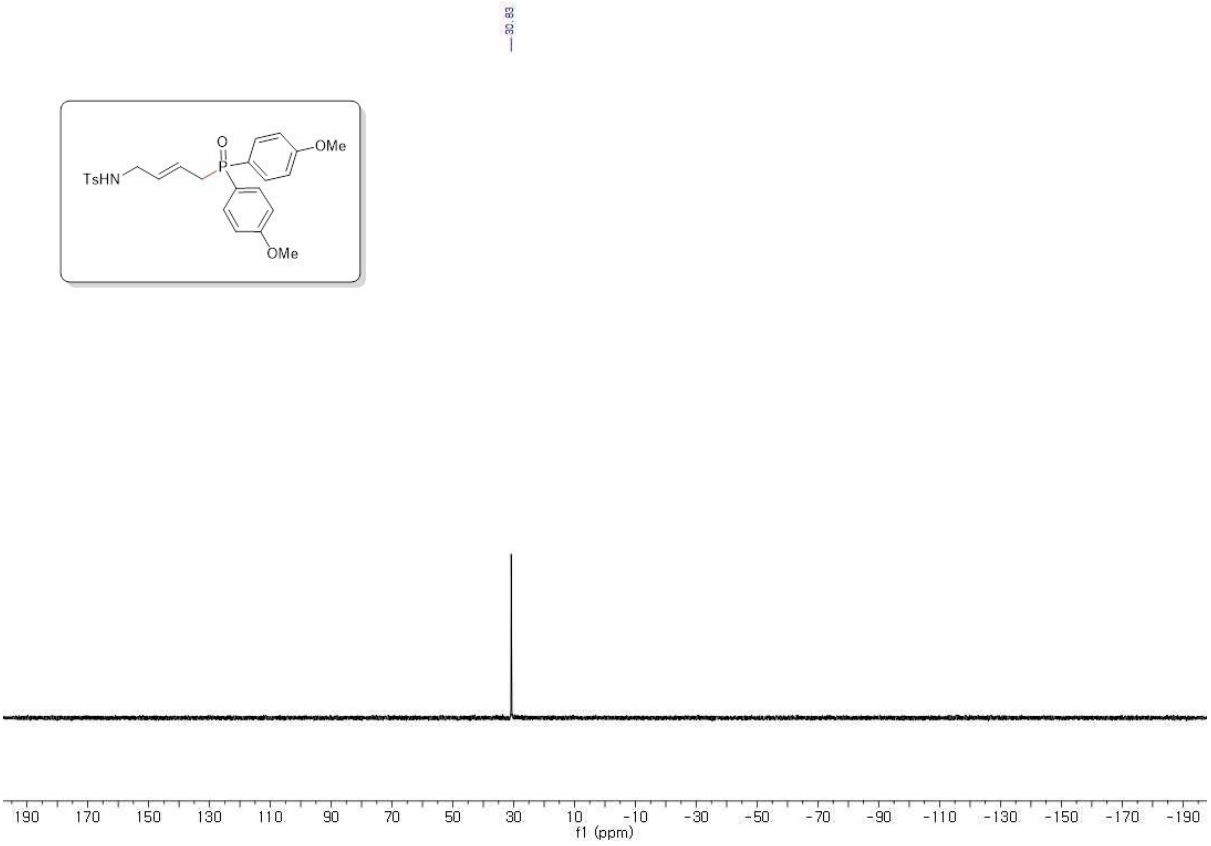
(E)-N-(4-(bis(4-methoxyphenyl)phosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3d)



400 MHz, ^{1}H NMR in $CDCl_3$

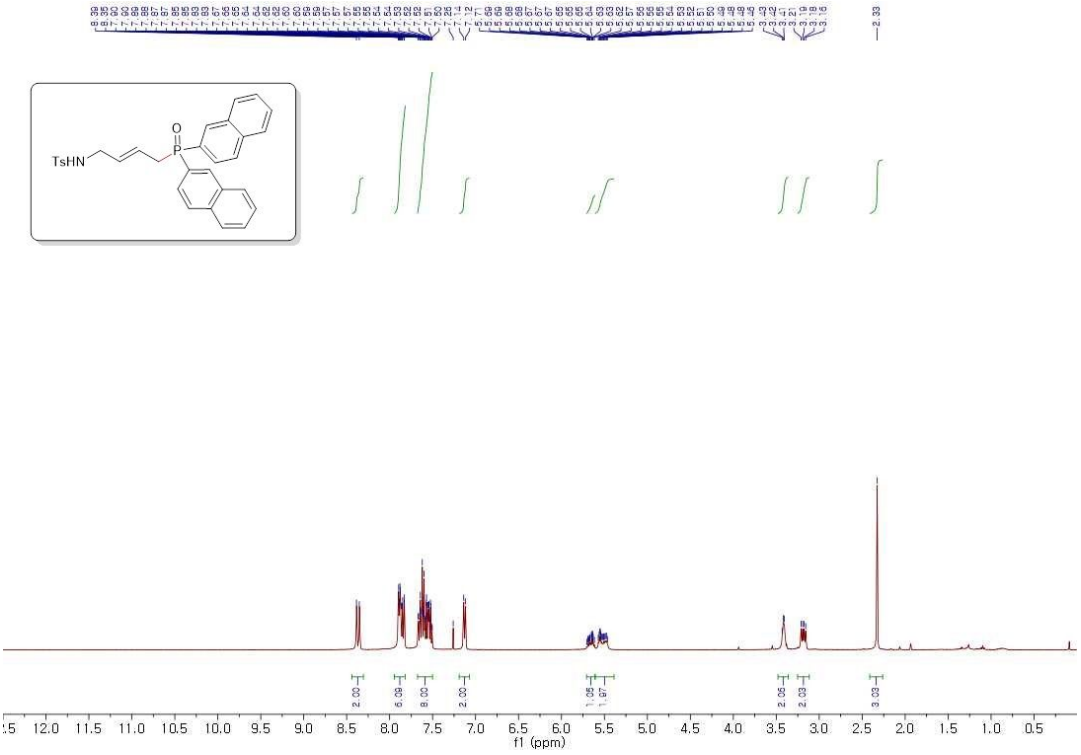


100 MHz, ^{13}C NMR in $CDCl_3$

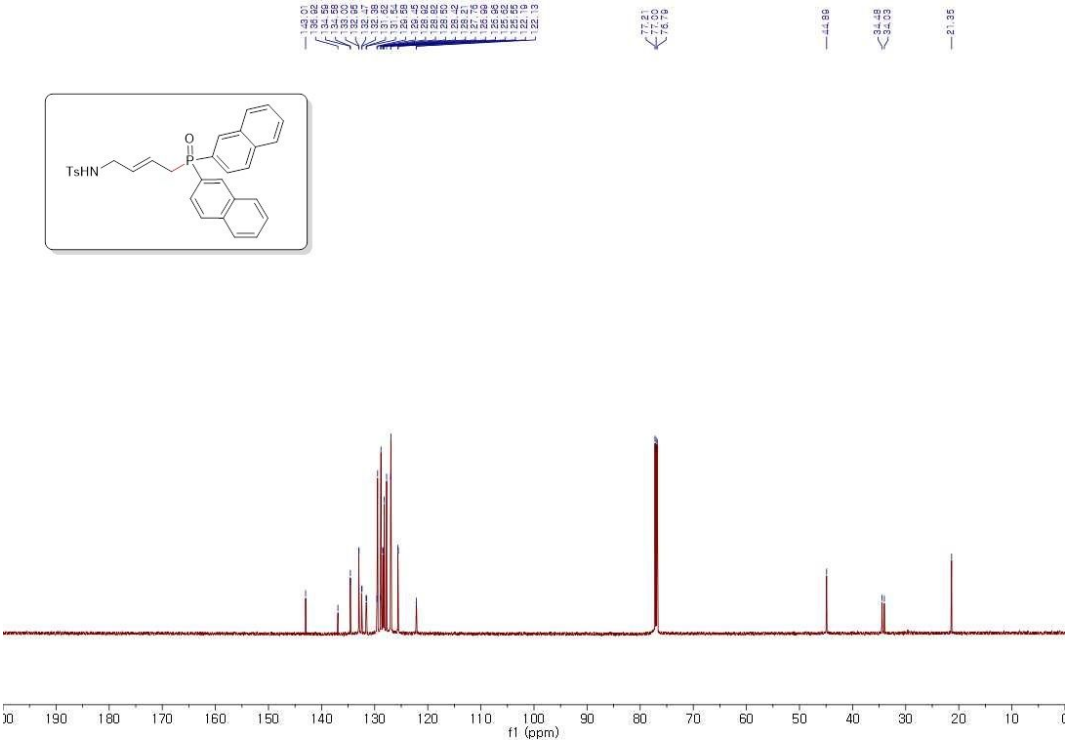


162 MHz, ^{31}P NMR in $CDCl_3$

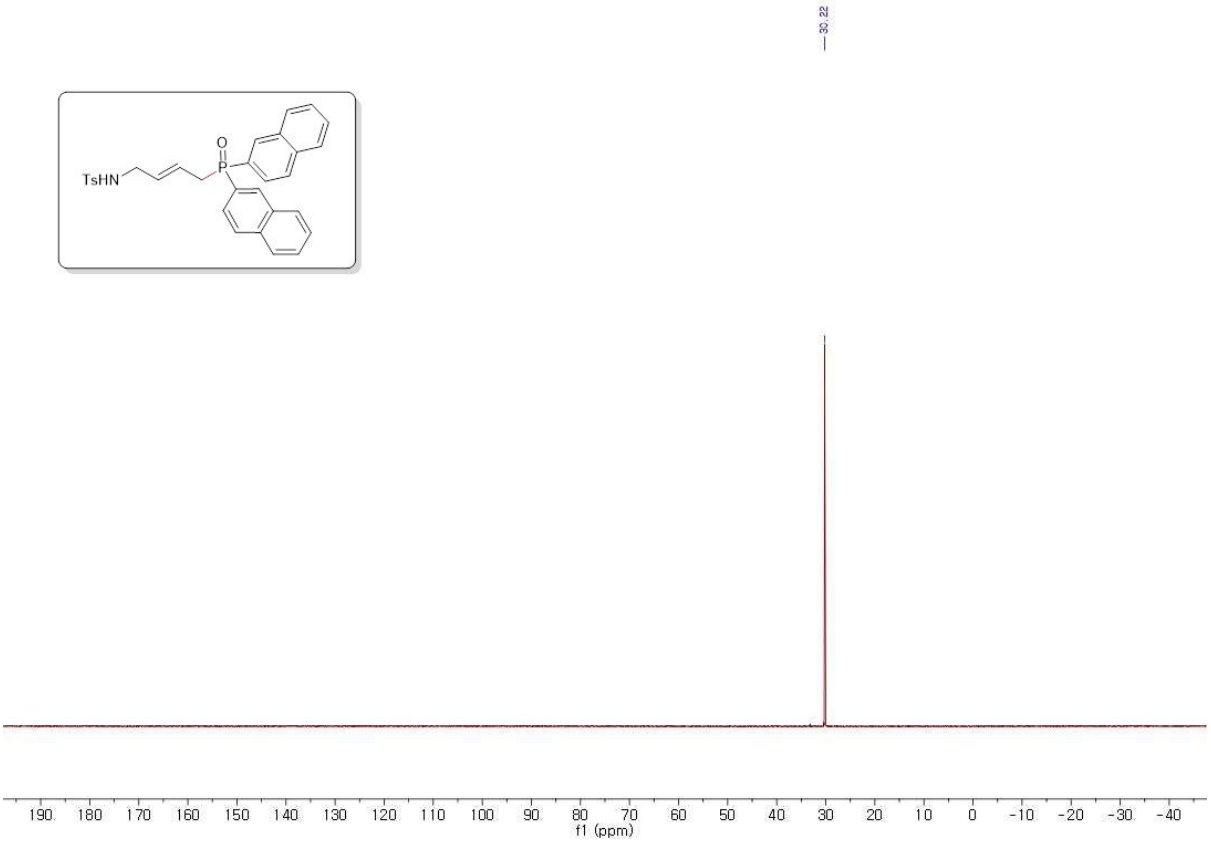
(E)-N-(4-(di(naphthalen-2-yl)phosphoryl)but-2-en-1-yl)-4-methylbenzenesulfonamide (3e)



400 MHz, ^{1}H NMR in $CDCl_3$

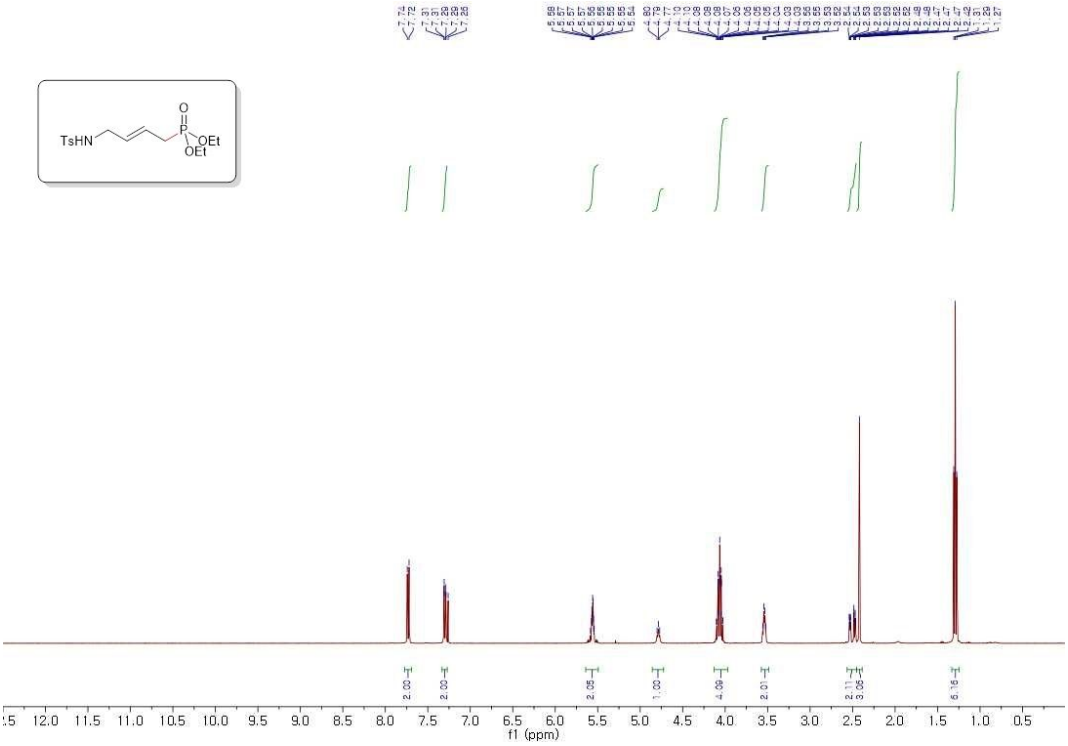


150 MHz, ^{13}C NMR in $CDCl_3$

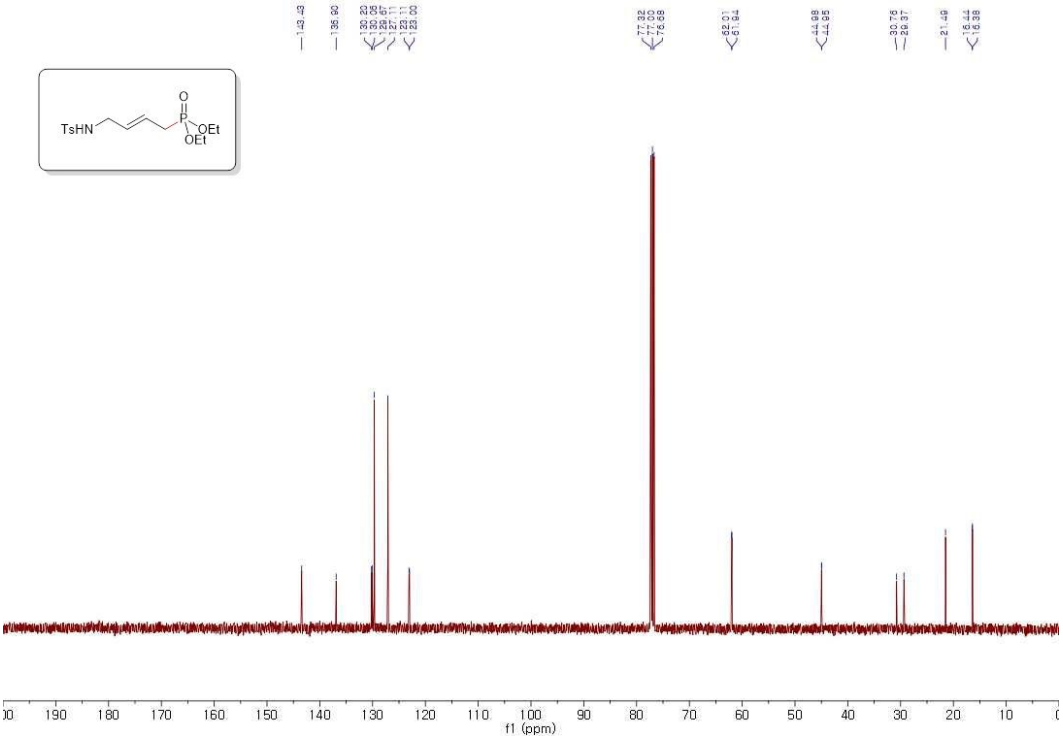


243 MHz, ^{31}P NMR in $CDCl_3$

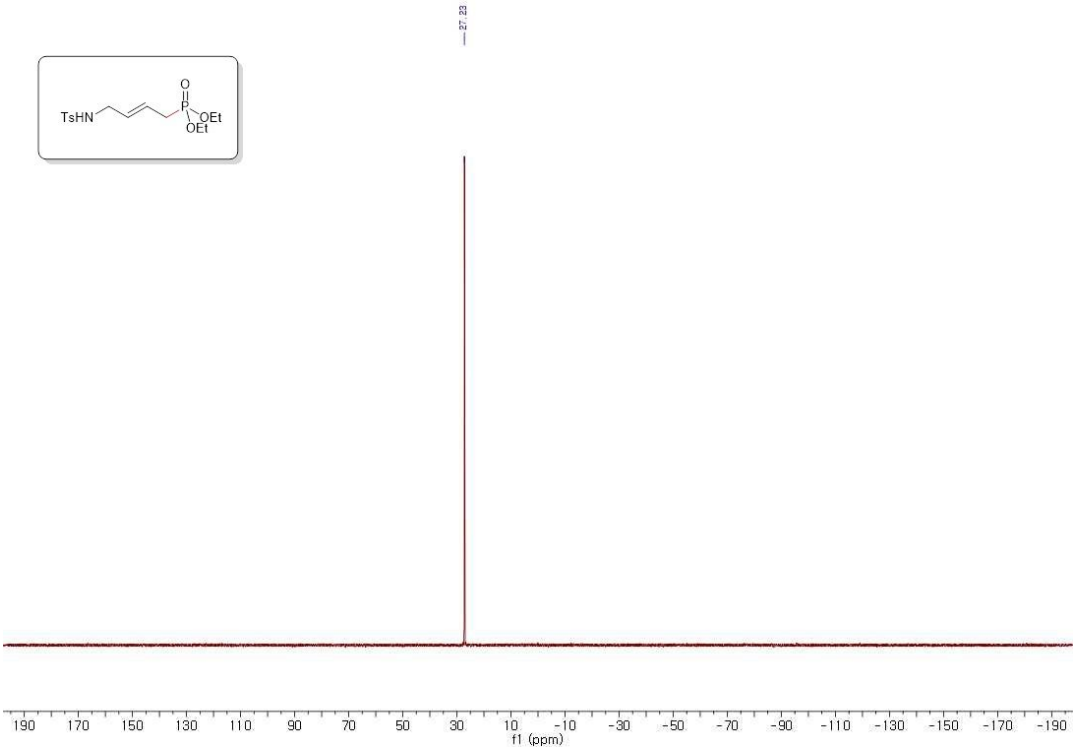
diethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3f)



400 MHz, ^{1}H NMR in $CDCl_3$

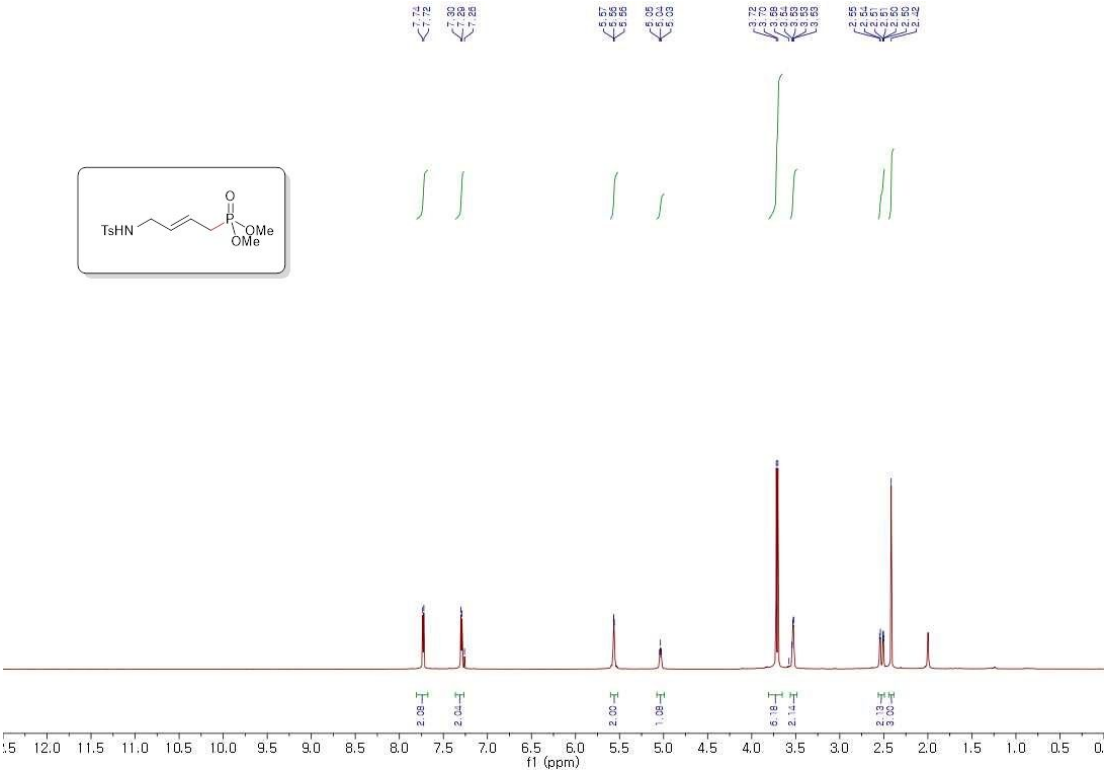


100 MHz, ^{13}C NMR in $CDCl_3$

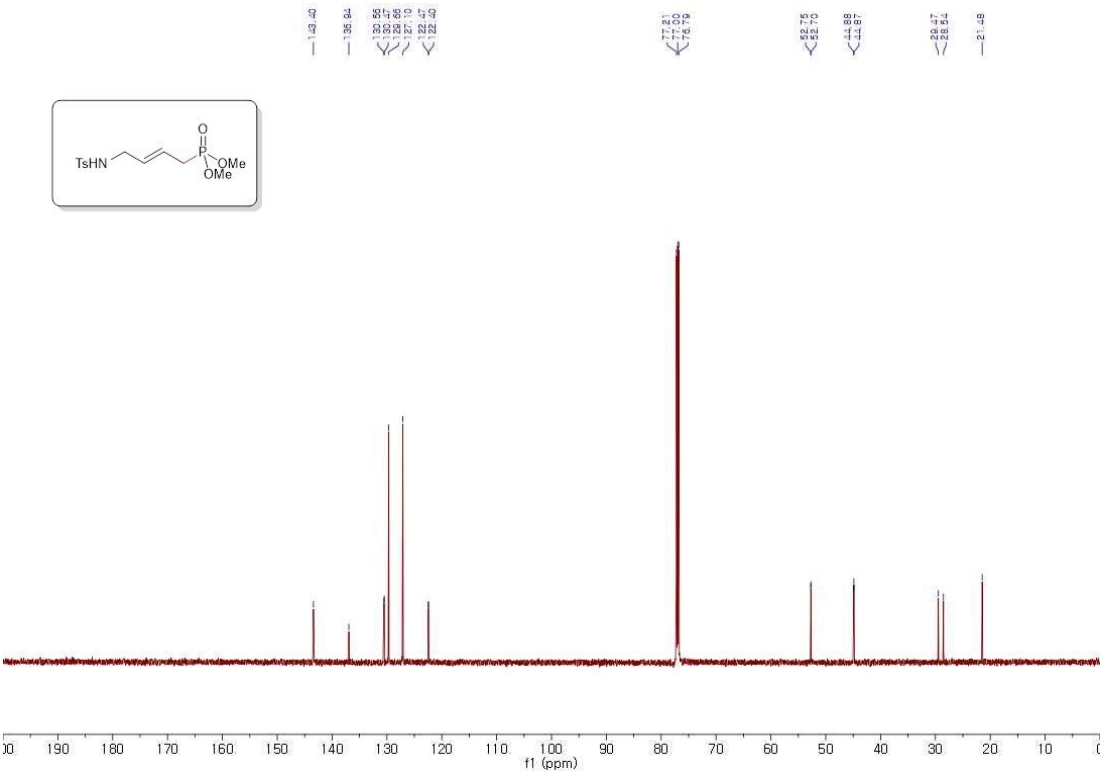


162 MHz, ^{31}P NMR in $CDCl_3$

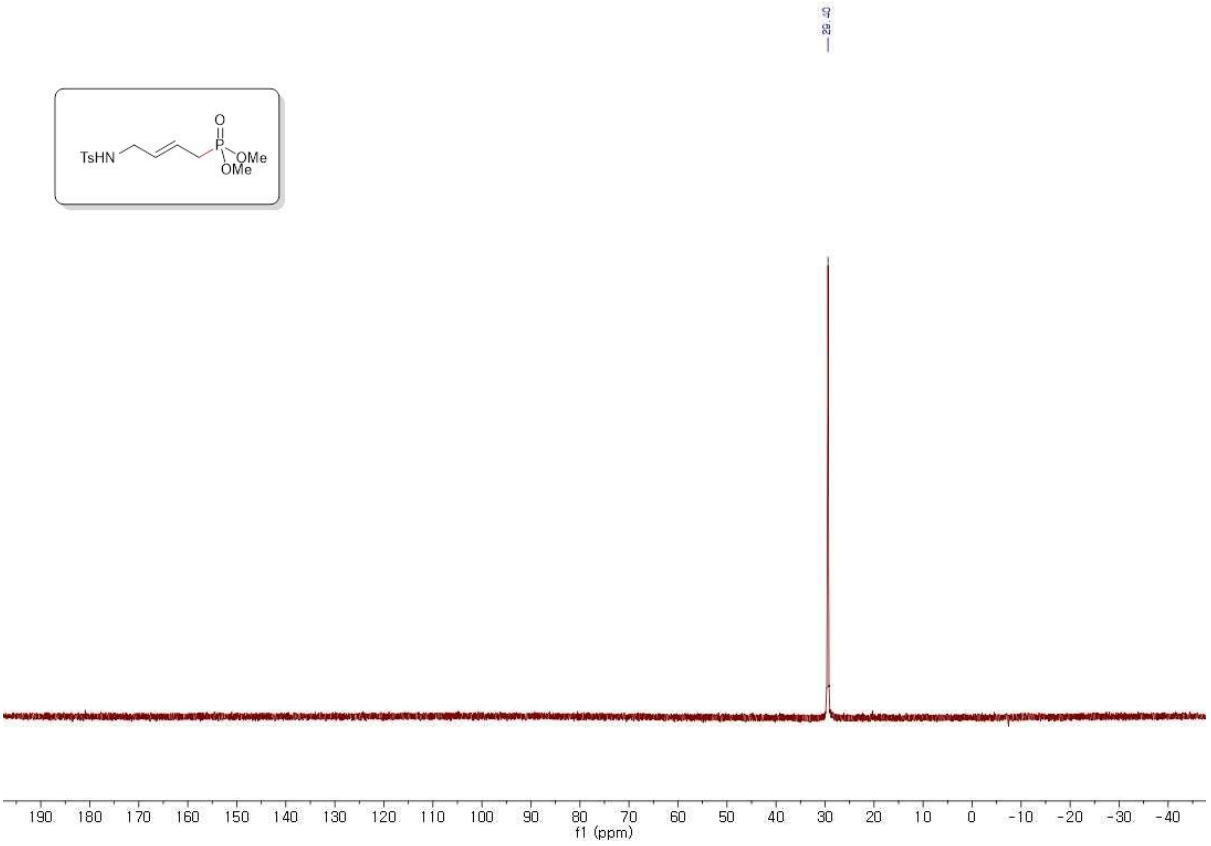
dimethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3g)



600 MHz, ^{1}H NMR in $CDCl_3$

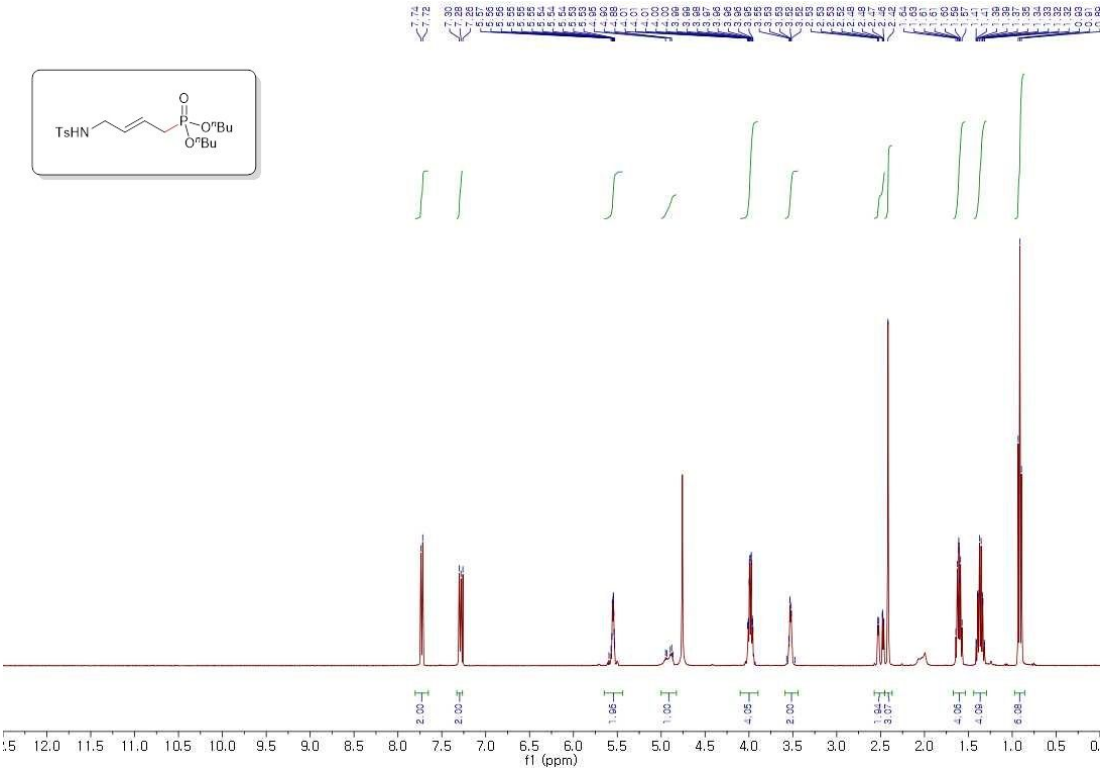


150 MHz, ^{13}C NMR in $CDCl_3$

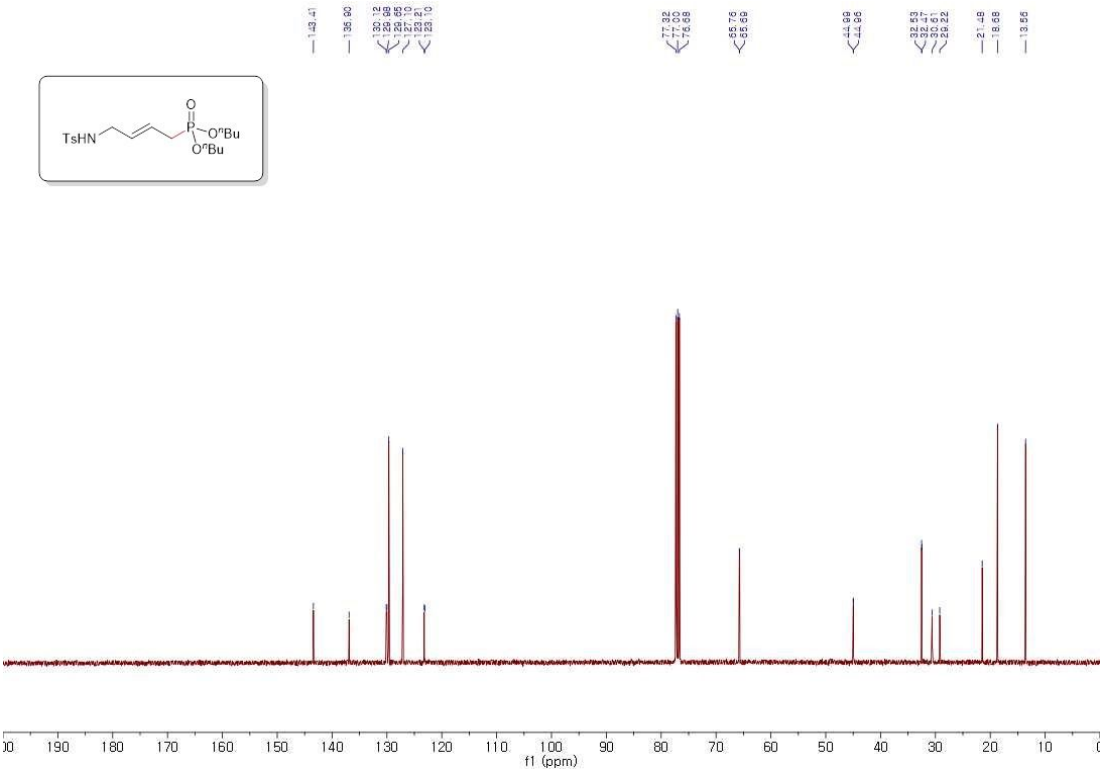


243 MHz, ^{31}P NMR in $CDCl_3$

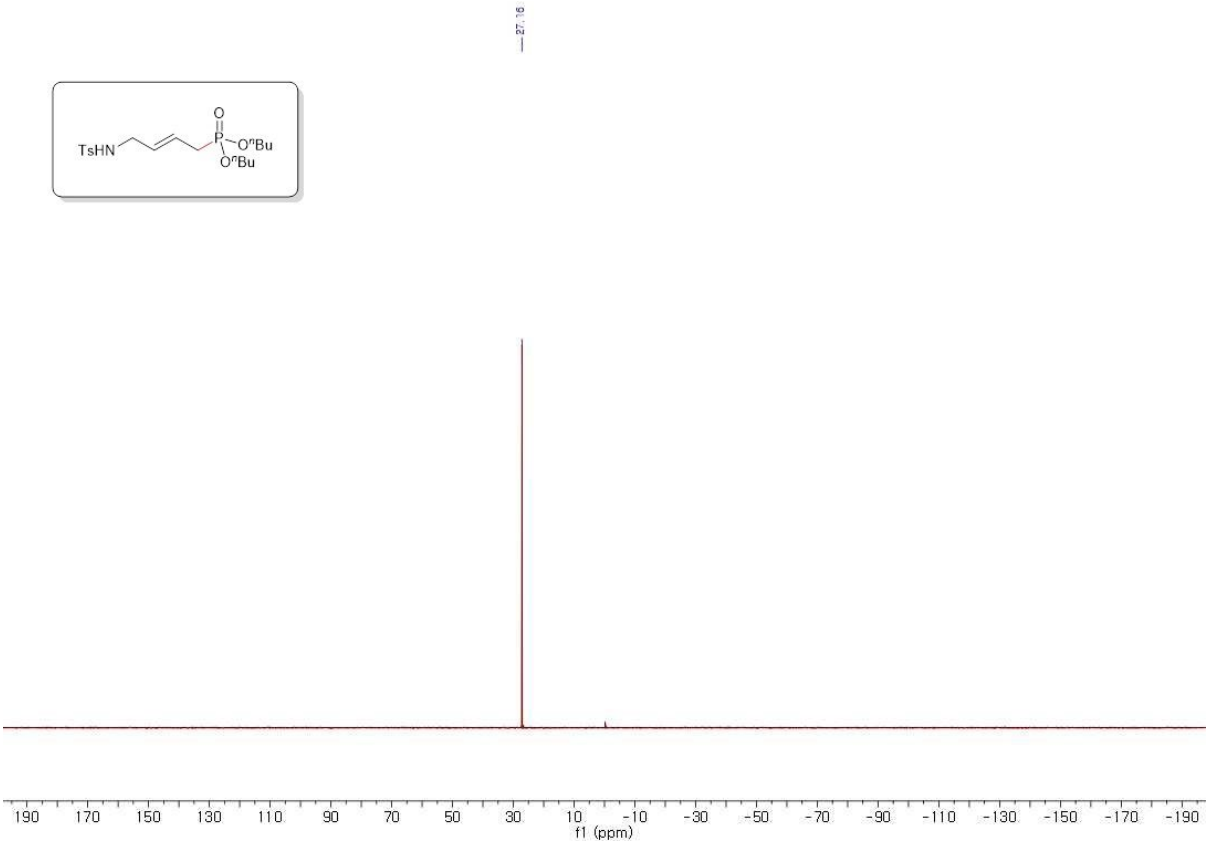
dibutyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3h)



400 MHz, ^{1}H NMR in $CDCl_3$

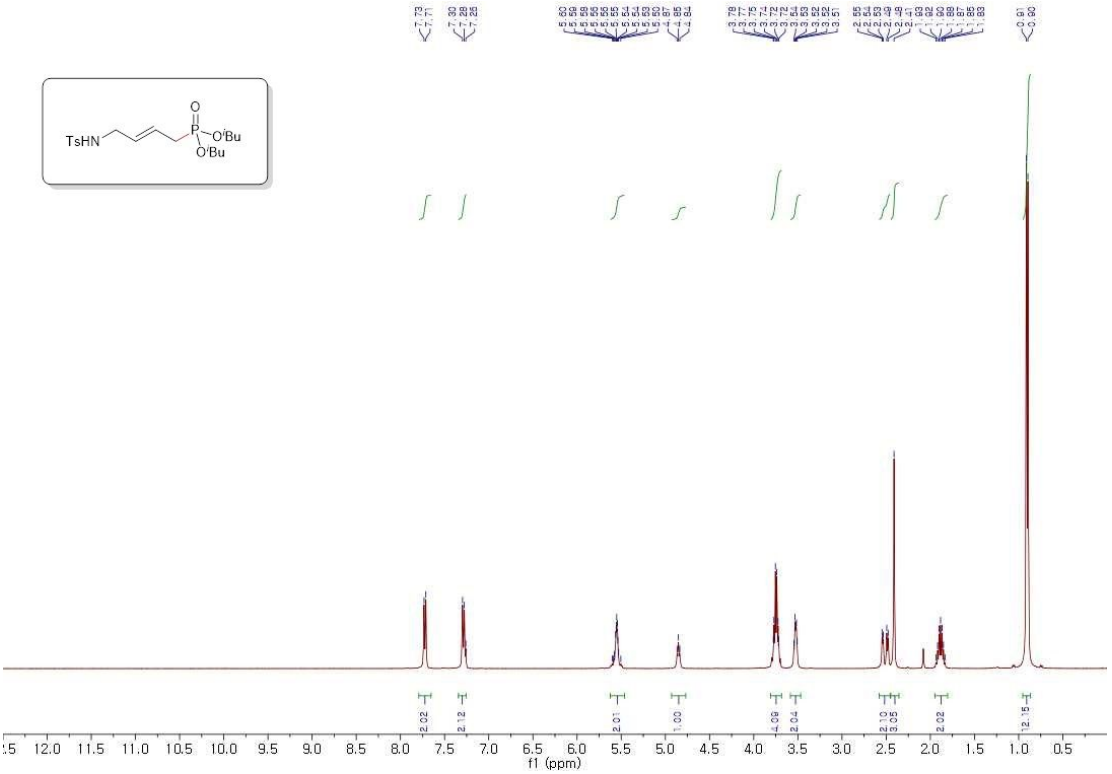


100 MHz, ^{13}C NMR in $CDCl_3$

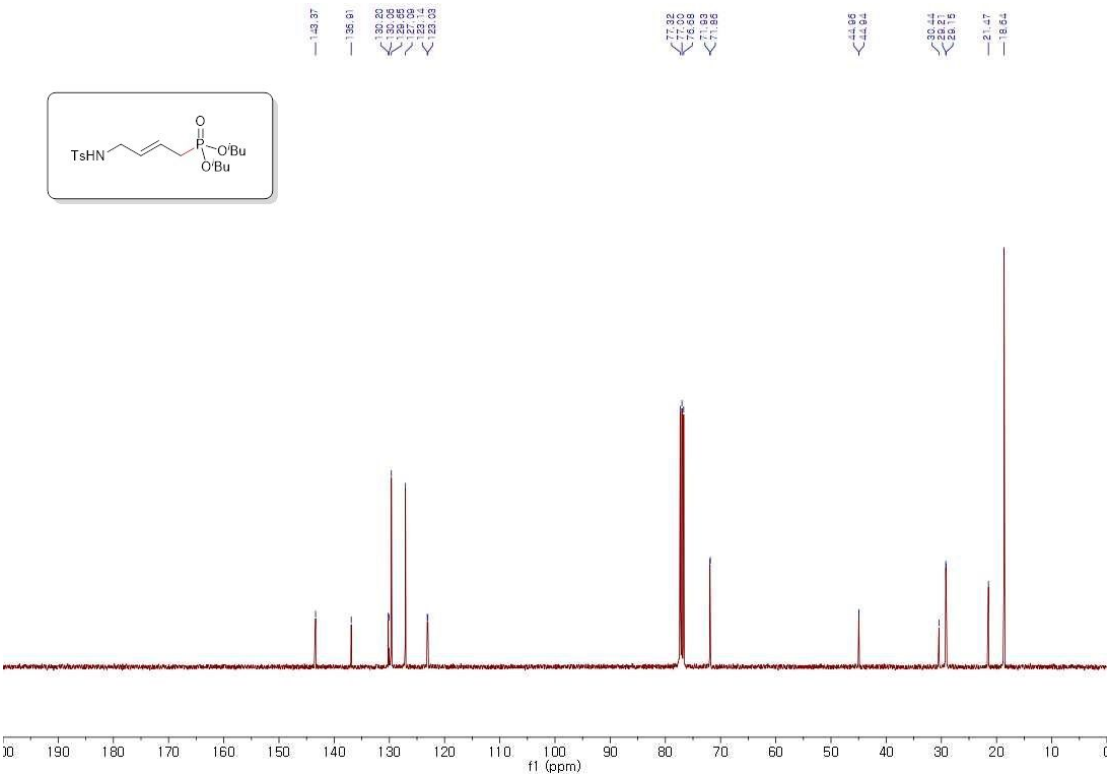


162 MHz, ^{31}P NMR in $CDCl_3$

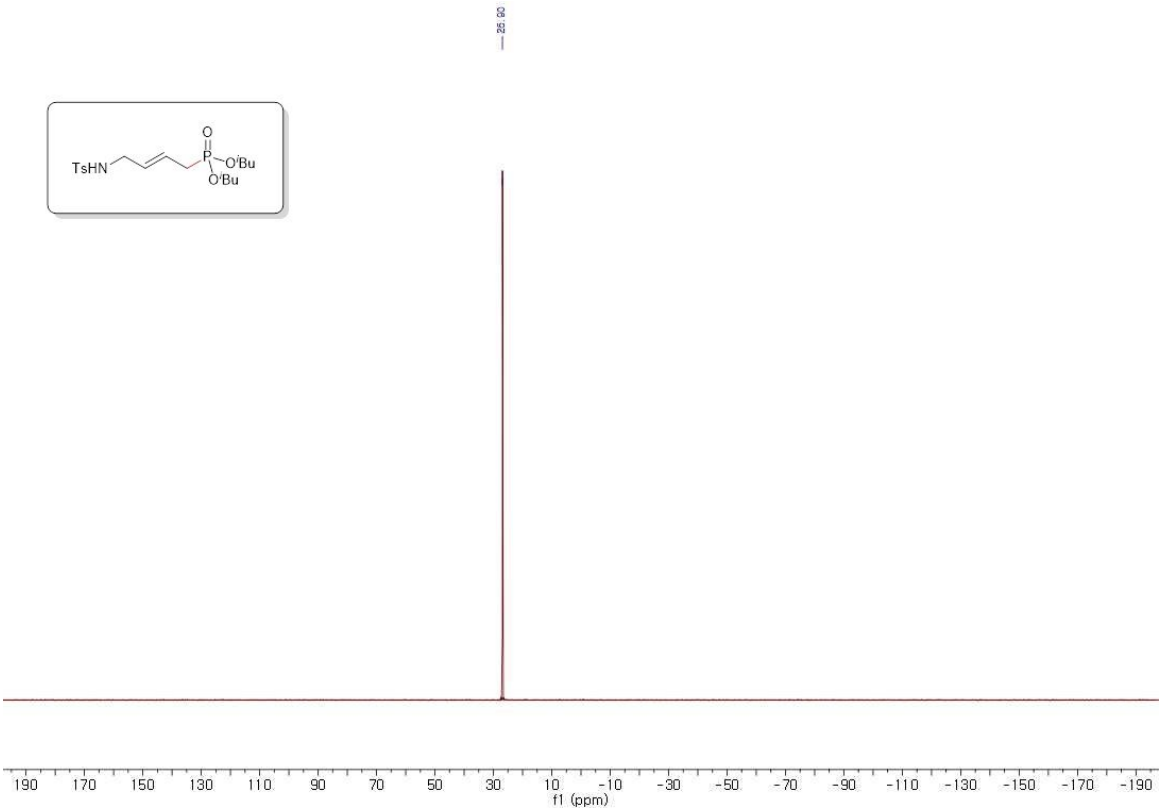
diisobutyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3i)



400 MHz, ^{1}H NMR in $CDCl_3$

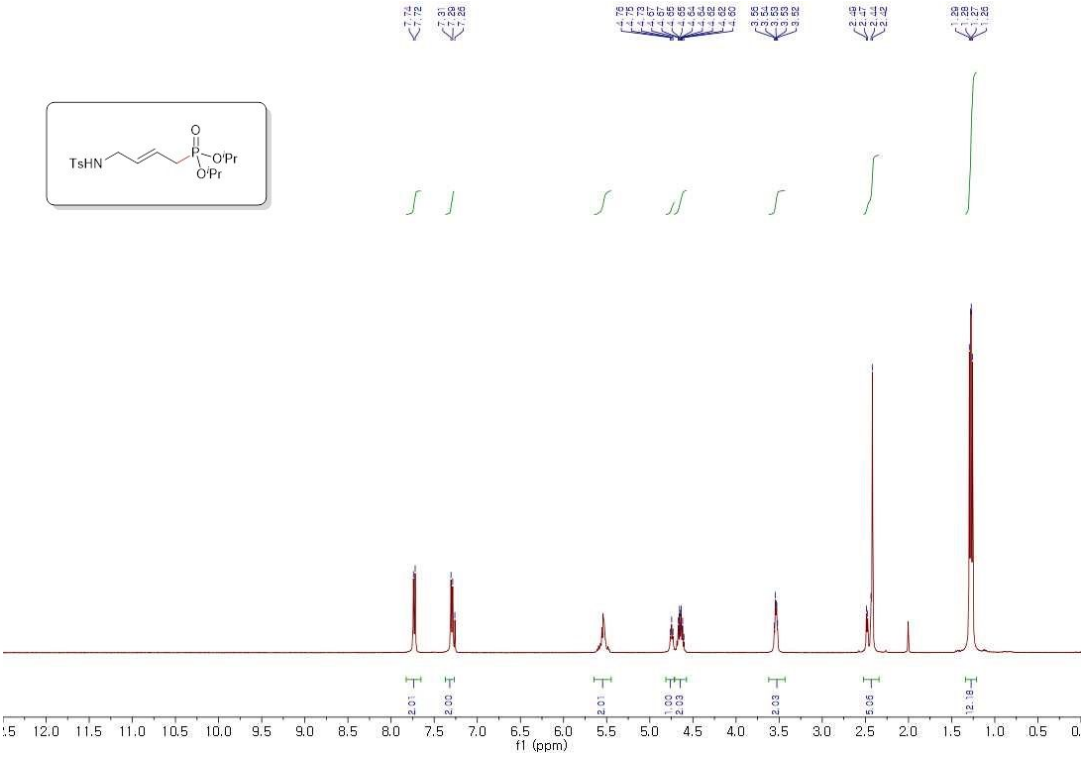


100 MHz, ^{13}C NMR in $CDCl_3$

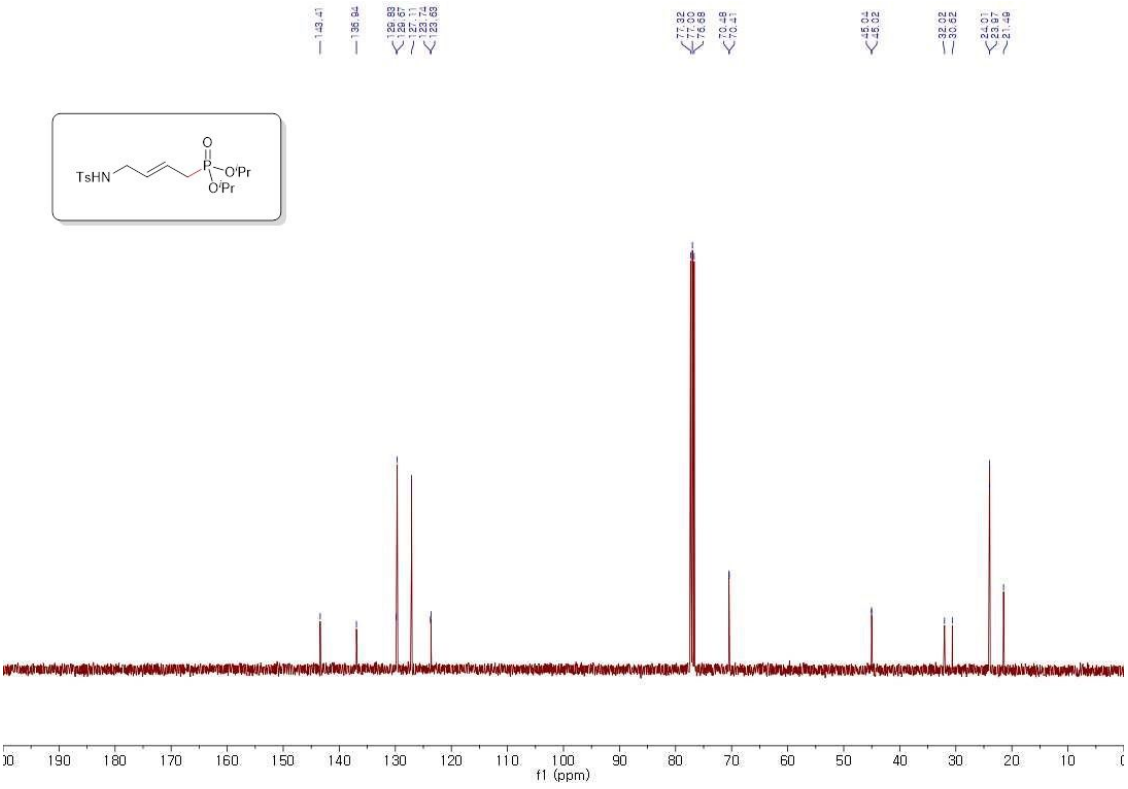


162 MHz, ^{31}P NMR in $CDCl_3$

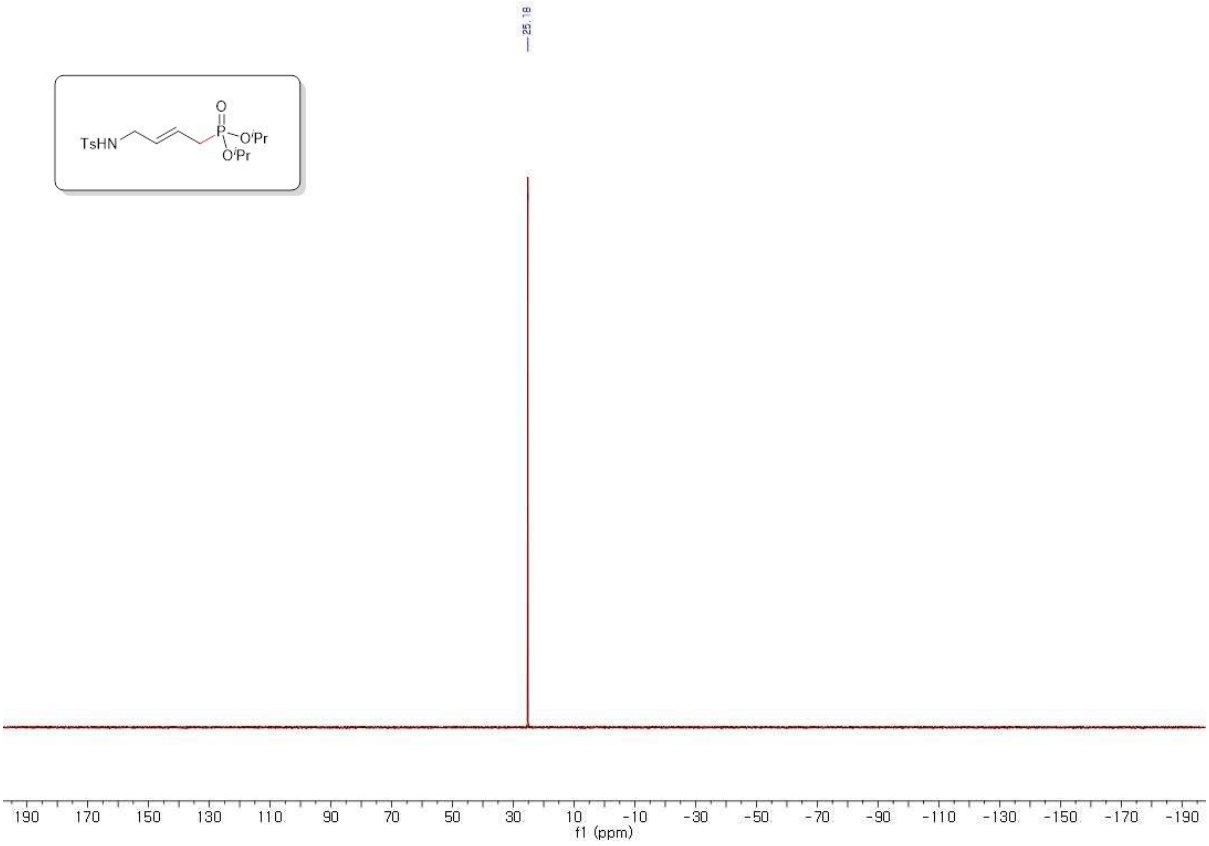
diisopropyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3j)



400 MHz, ^{1}H NMR in $CDCl_3$

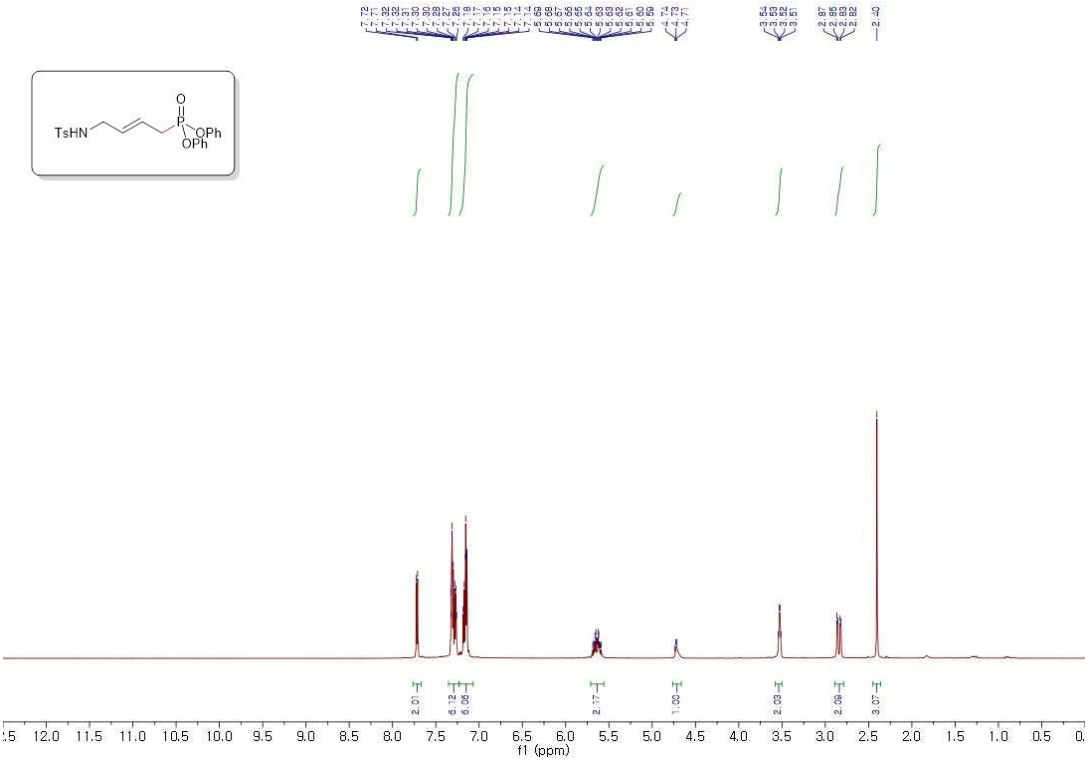


100 MHz, ^{13}C NMR in $CDCl_3$

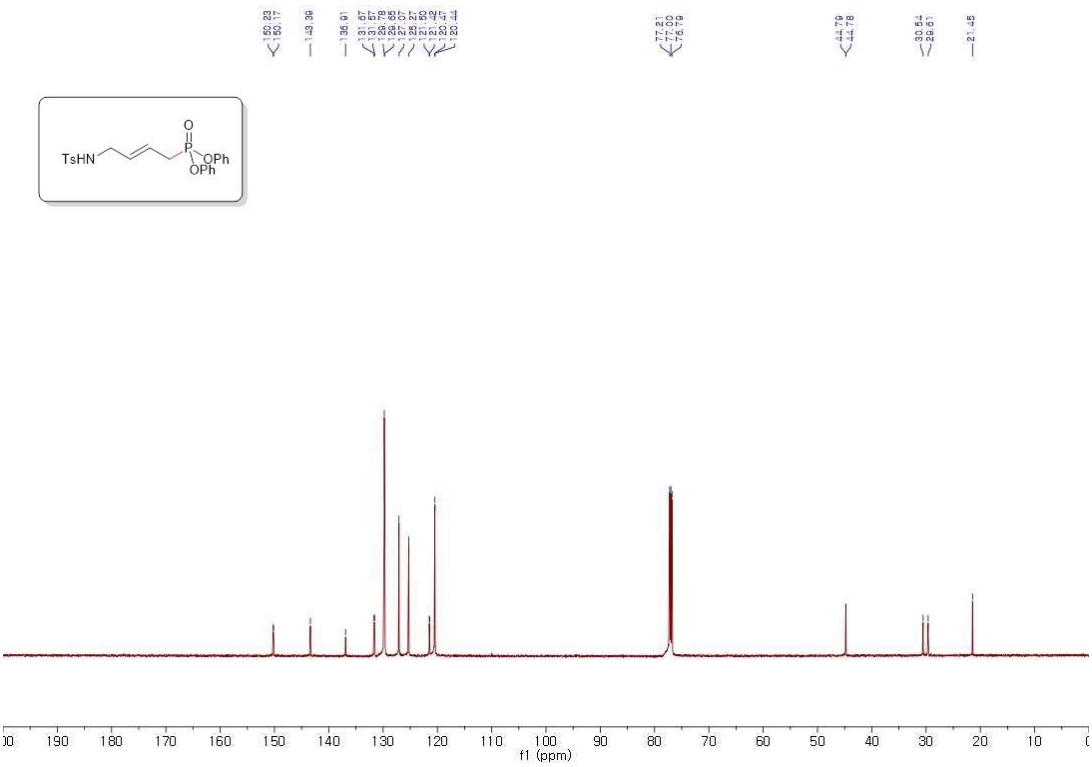


162 MHz, ^{31}P NMR in $CDCl_3$

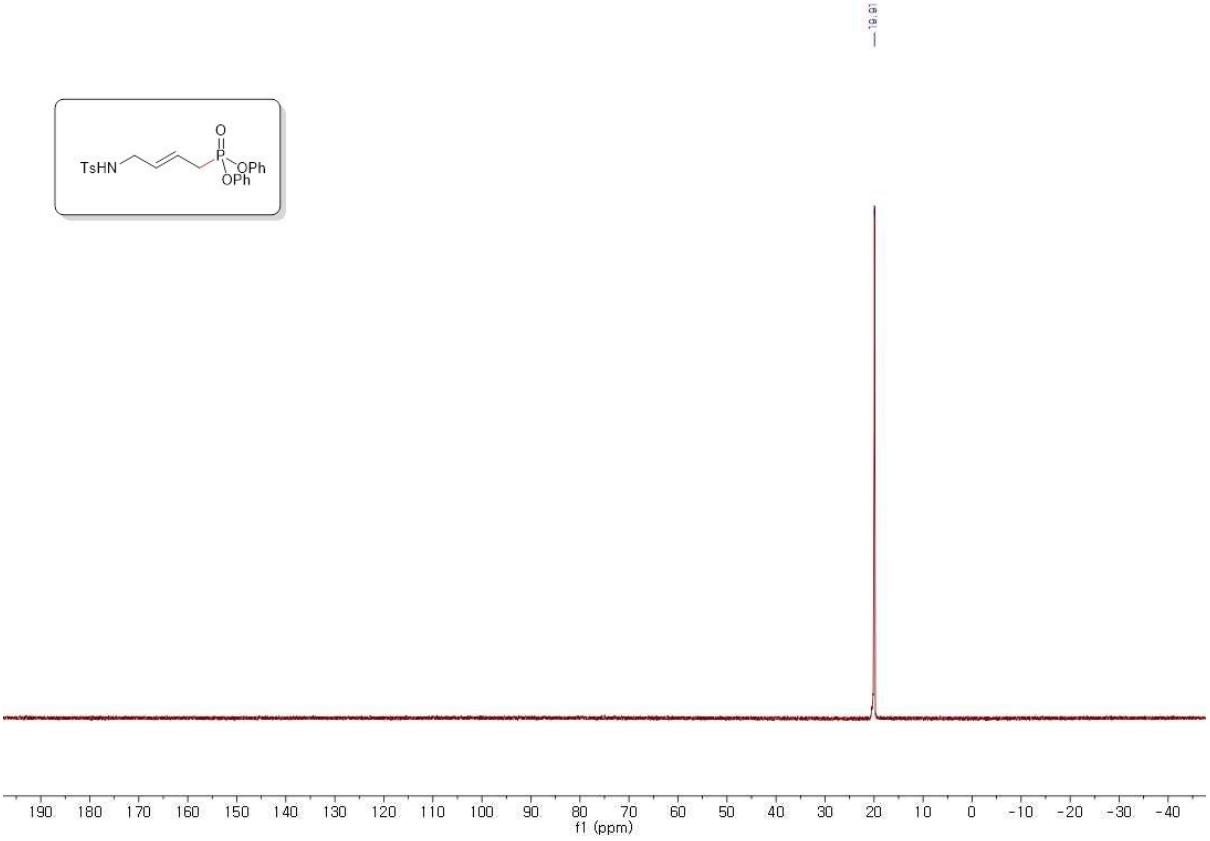
diphenyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)phosphonate (3k)



600 MHz, ^{1}H NMR in $CDCl_3$

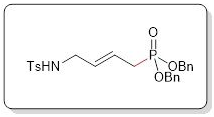


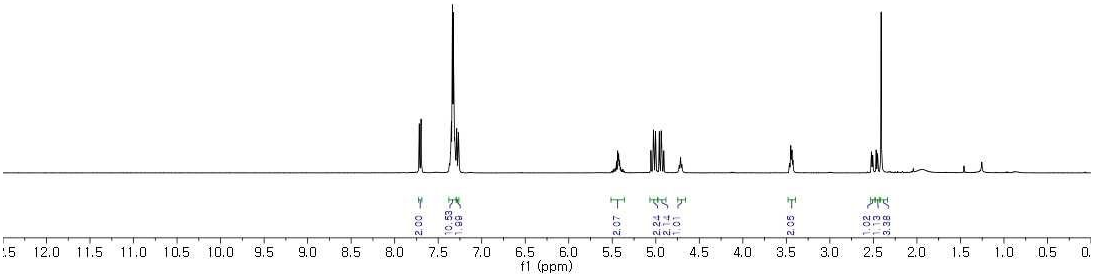
150 MHz, ^{13}C NMR in $CDCl_3$



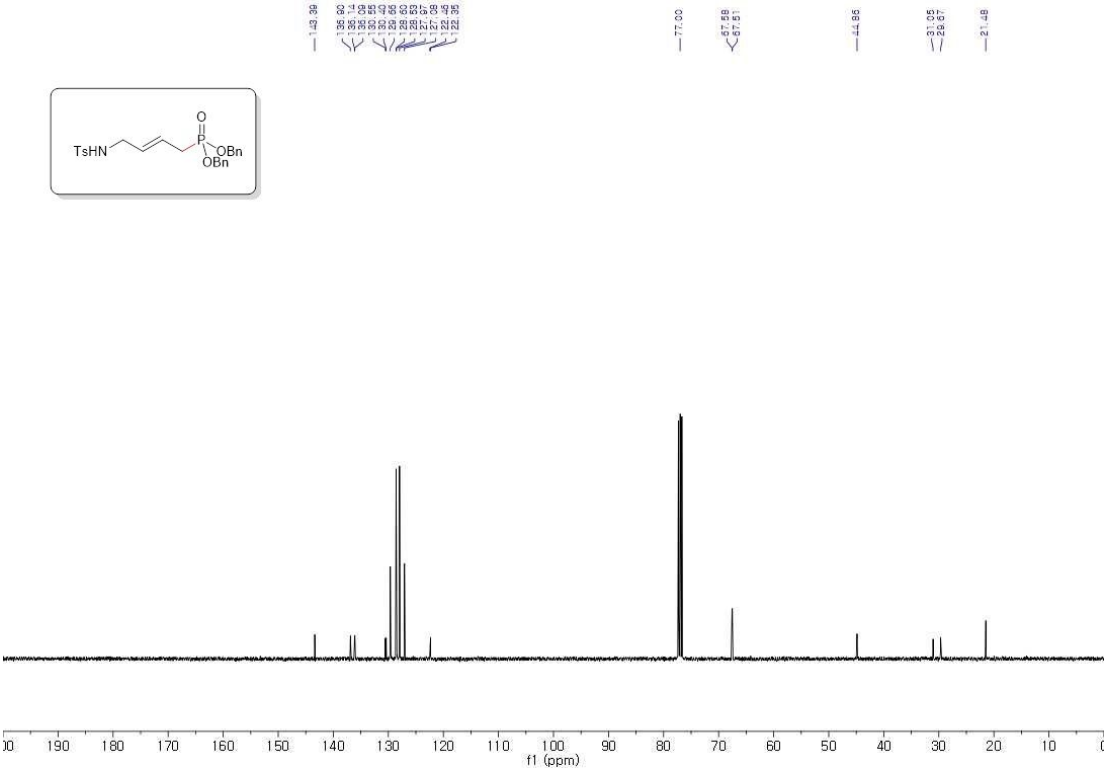
243 MHz, ^{31}P NMR in $CDCl_3$

Dibenzyl (E)-(4-((4-methylphenyl)sulfonamide)but-2-en-1yl)phosphonate (3l)

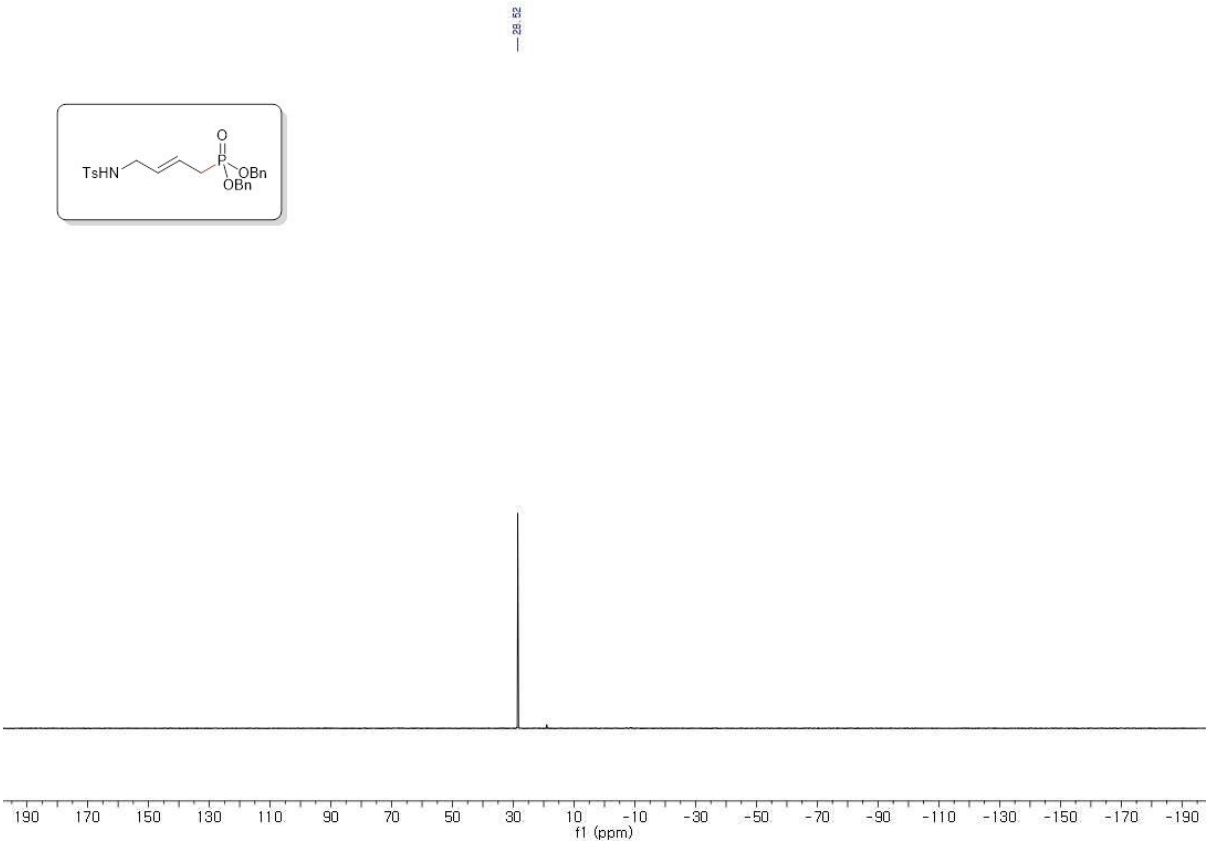




400 MHz, ^{1}H NMR in $CDCl_3$

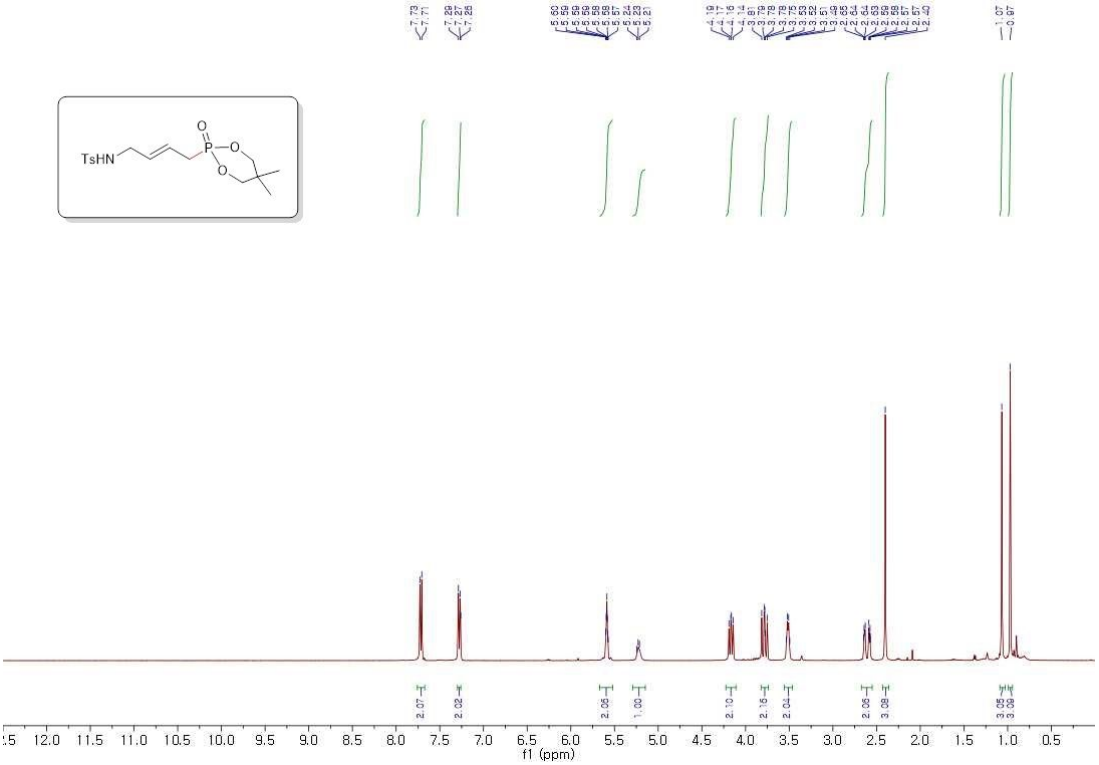


100 MHz, ^{13}C NMR in $CDCl_3$

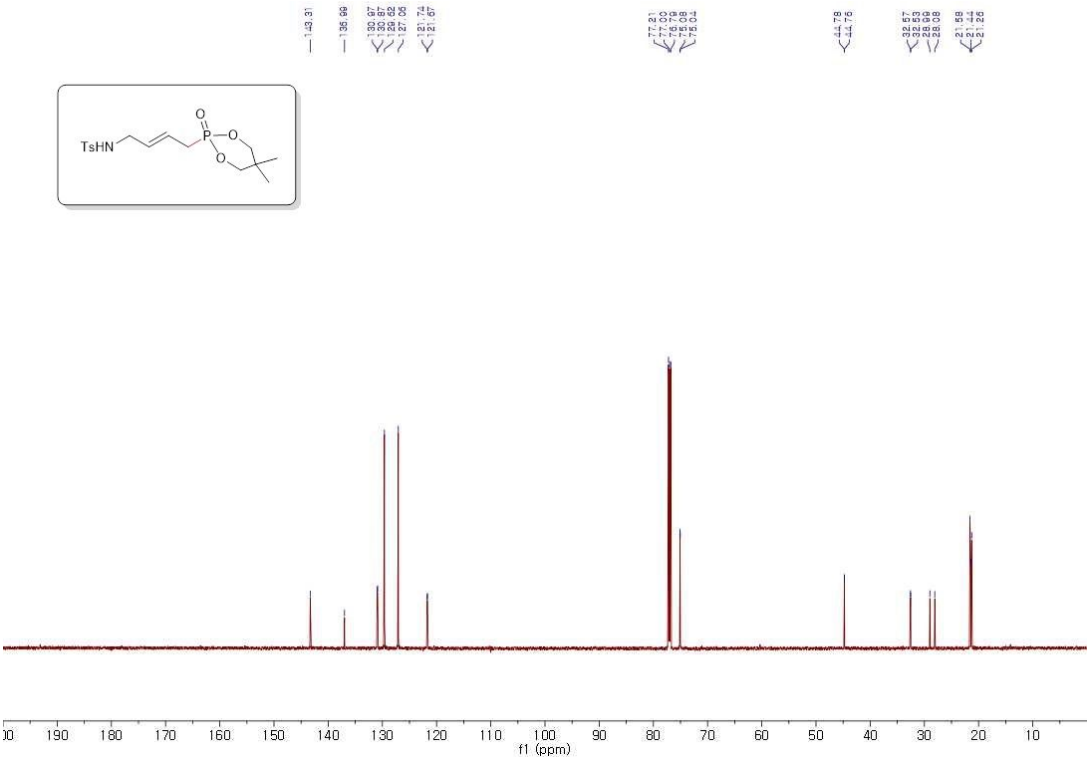


162 MHz, ^{31}P NMR in $CDCl_3$

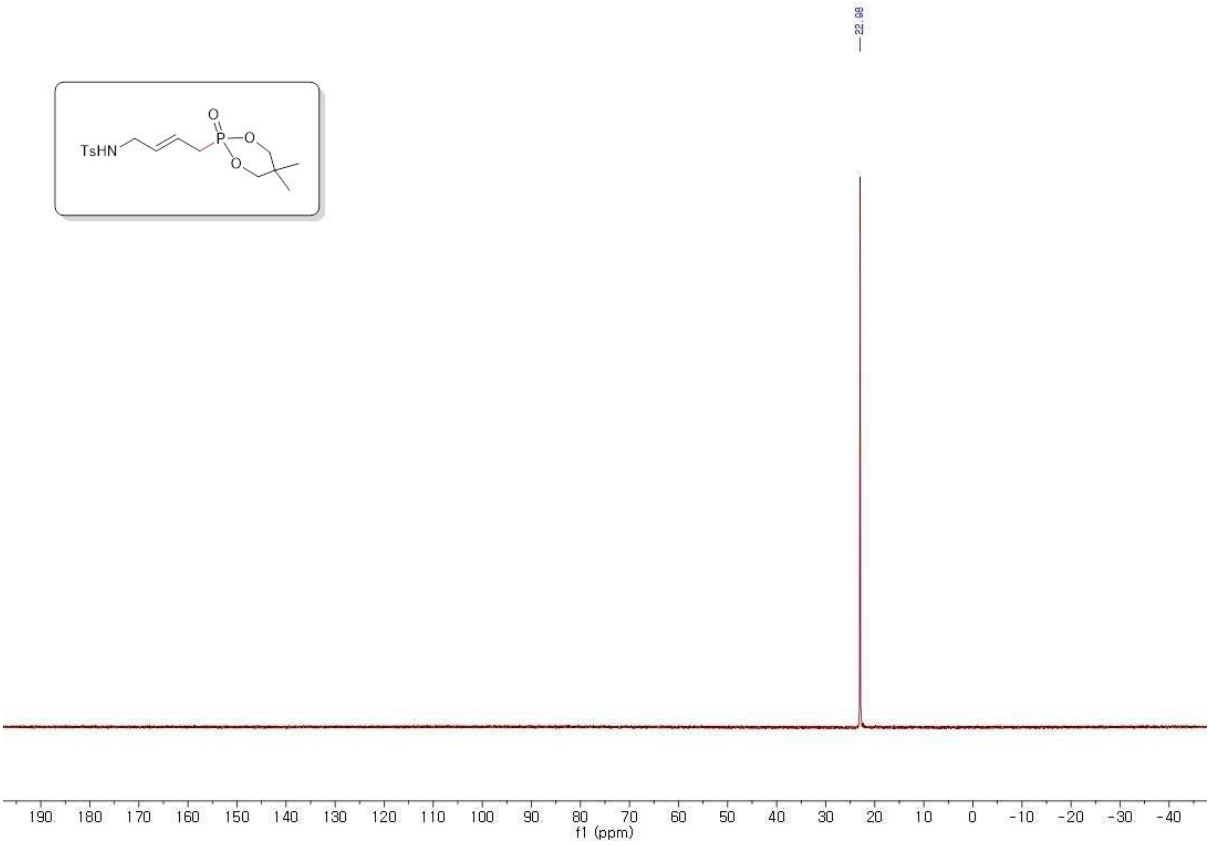
(E)-N-(4-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)but-2-en-1-yl)-4-methylbenzene sulfonamide (3m)



400 MHz, ^{1}H NMR in $CDCl_3$

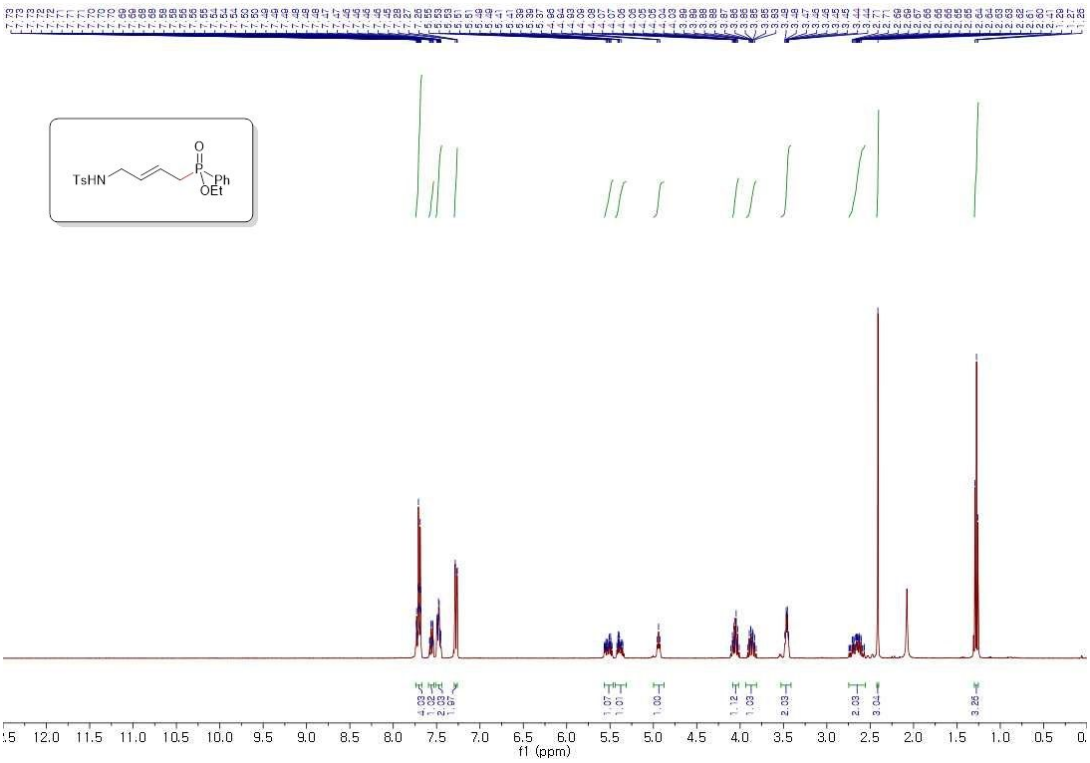


150 MHz, ^{13}C NMR in $CDCl_3$

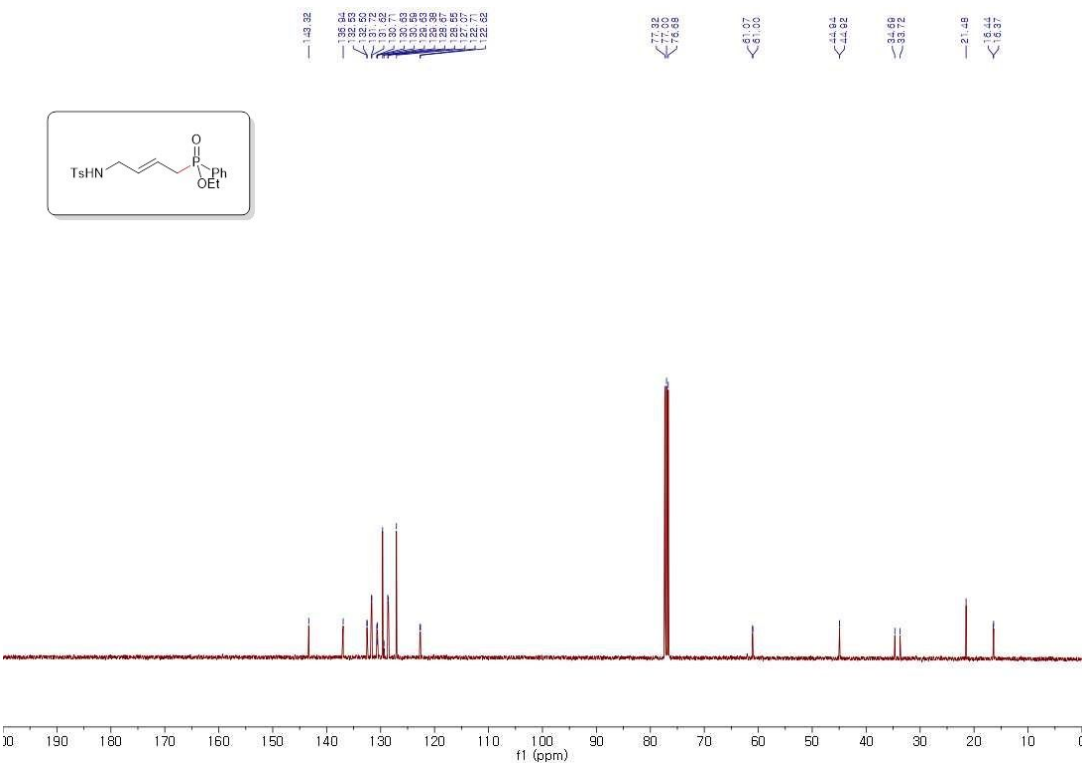


243 MHz, ^{31}P NMR in $CDCl_3$

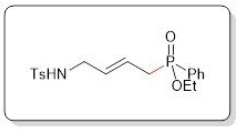
ethyl (E)-(4-((4-methylphenyl)sulfonamido)but-2-en-1-yl)(phenyl)phosphinate (3n)



400 MHz, ^{1}H NMR in $CDCl_3$

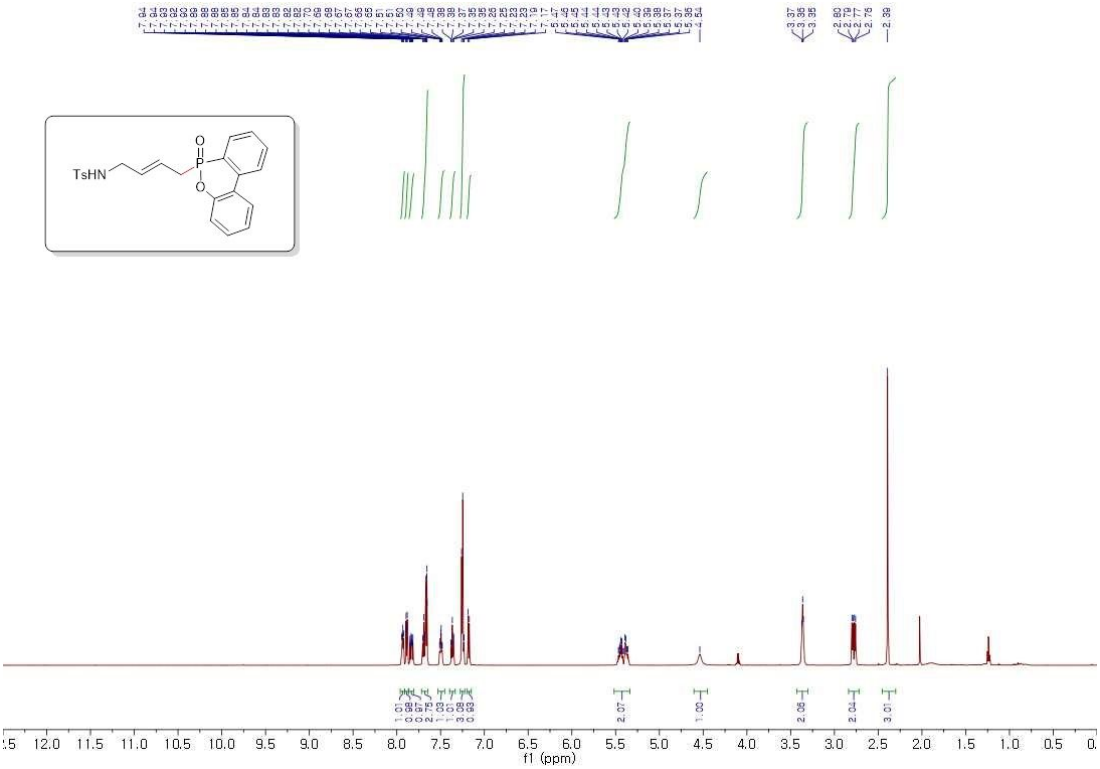


100 MHz, ^{13}C NMR in $CDCl_3$

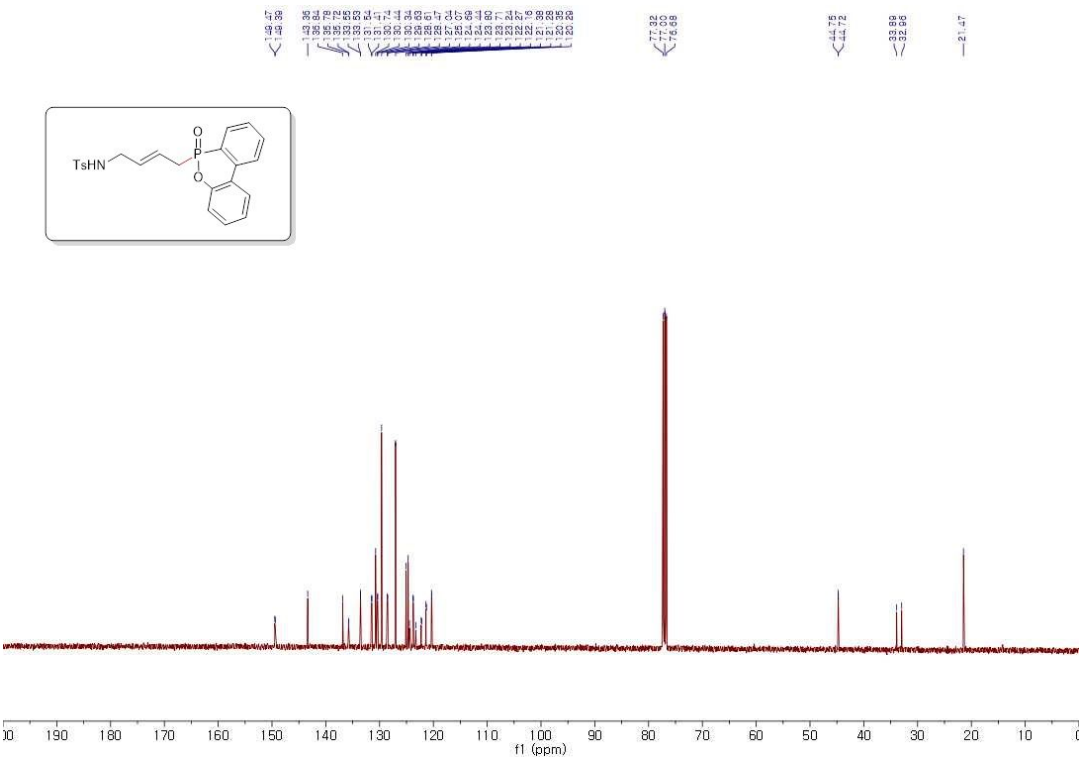


162 MHz, ^{31}P NMR in $CDCl_3$

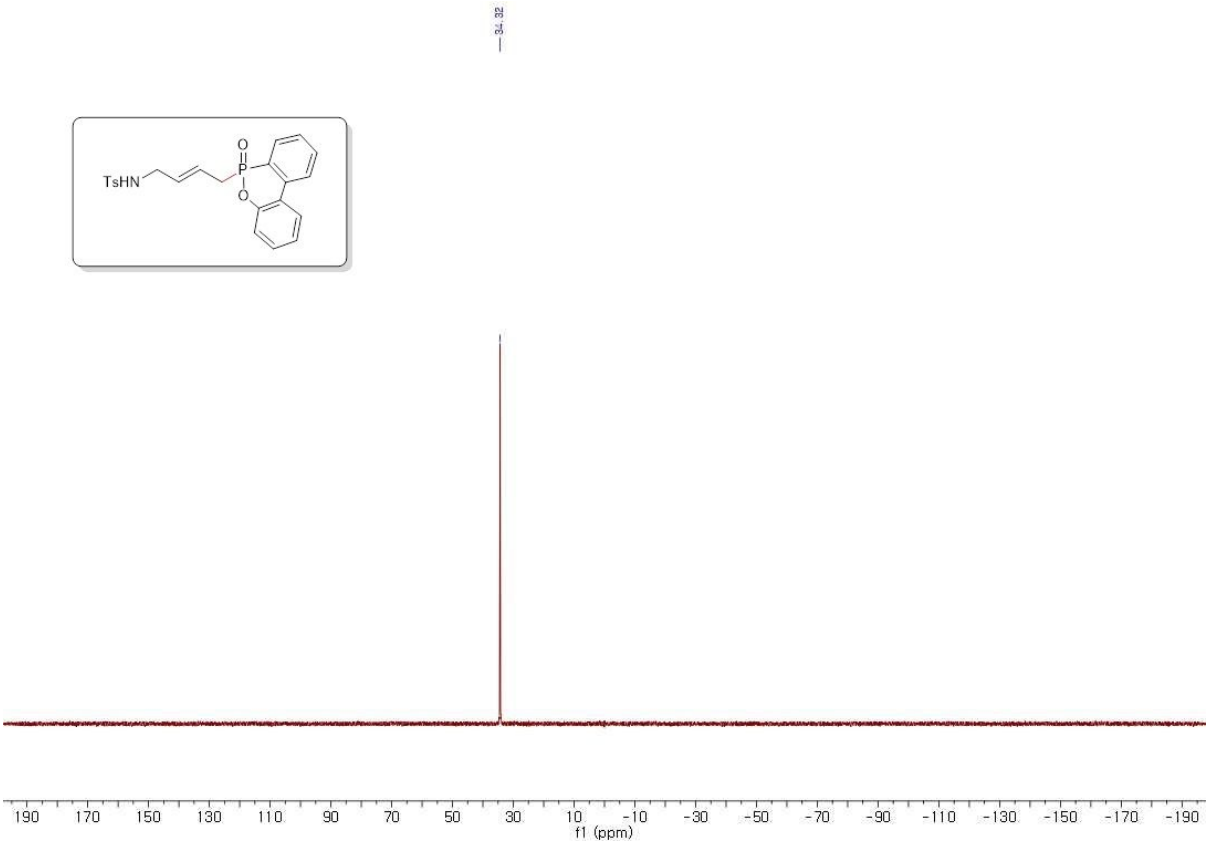
(E)-4-methyl-N-(4-(6-oxidodibenzo[c,e][1,2]oxaphosphinin-6-yl)but-2-en-1-yl)benzenesulfonamide (3o)



600 MHz, ^{1}H NMR in $CDCl_3$

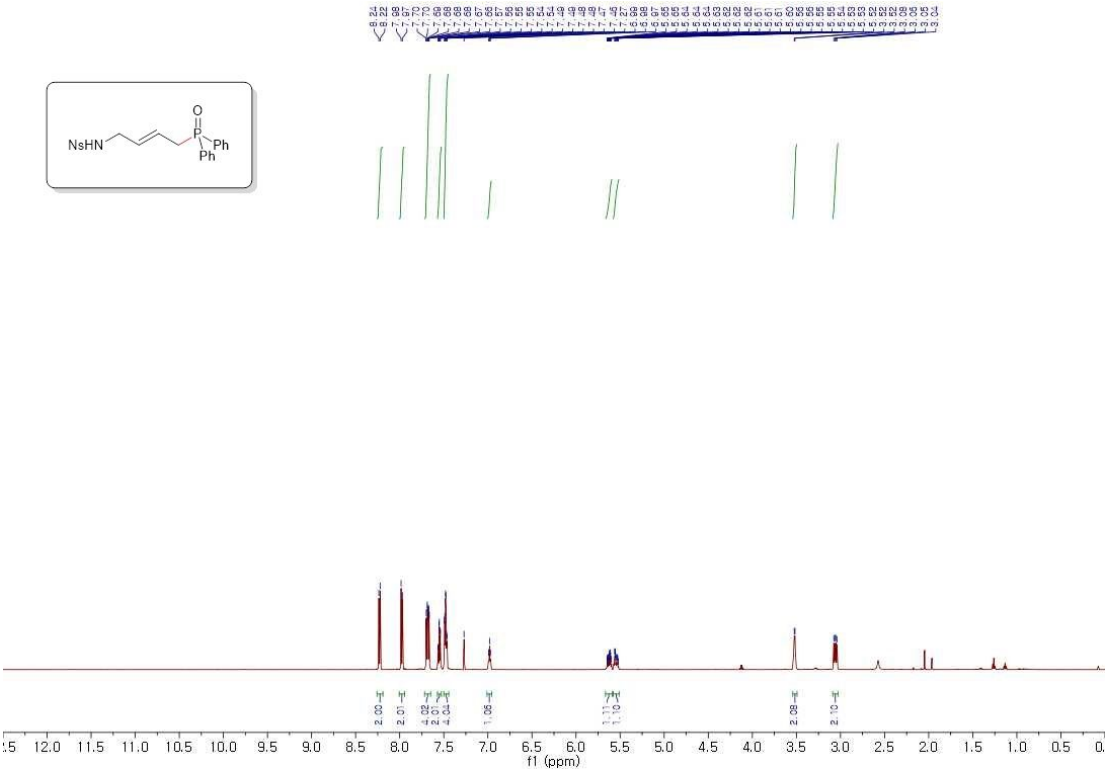


100 MHz, ^{13}C NMR in $CDCl_3$

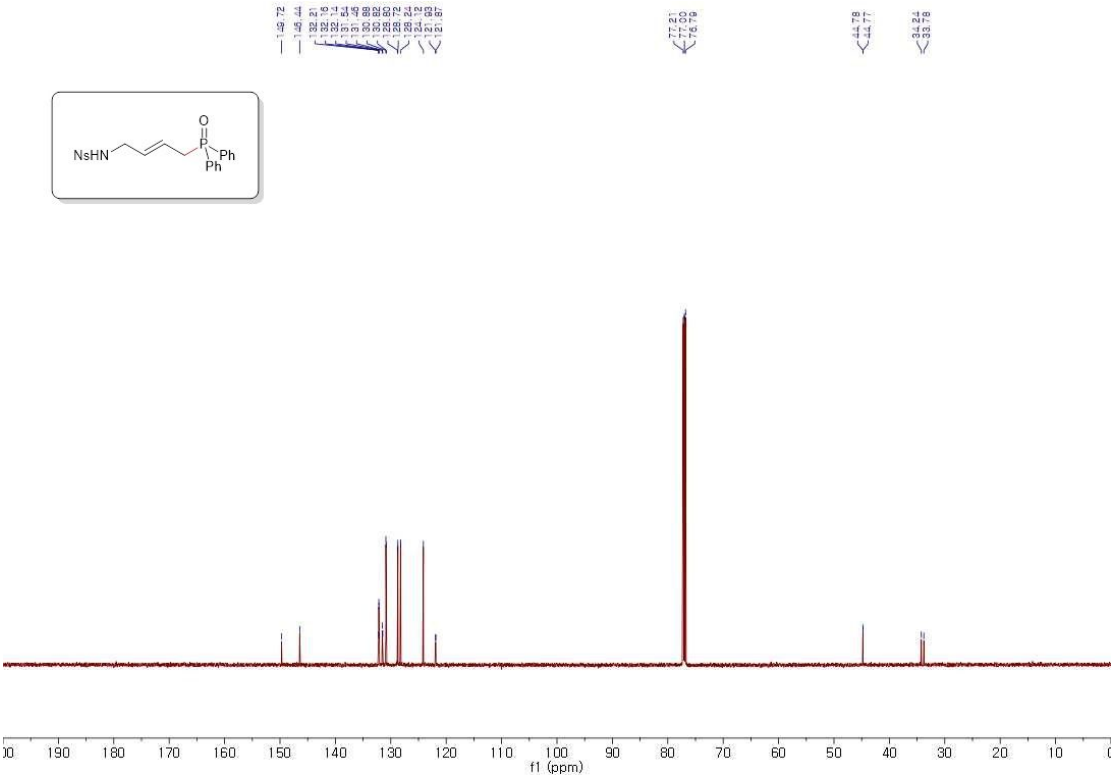


162 MHz, ^{31}P NMR in $CDCl_3$

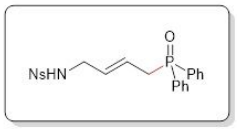
(E)-N-(4-(diphenylphosphoryl)but-2-en-1-yl)-4-nitrobenzenesulfonamide (3p)



600 MHz, ^{1}H NMR in $CDCl_3$

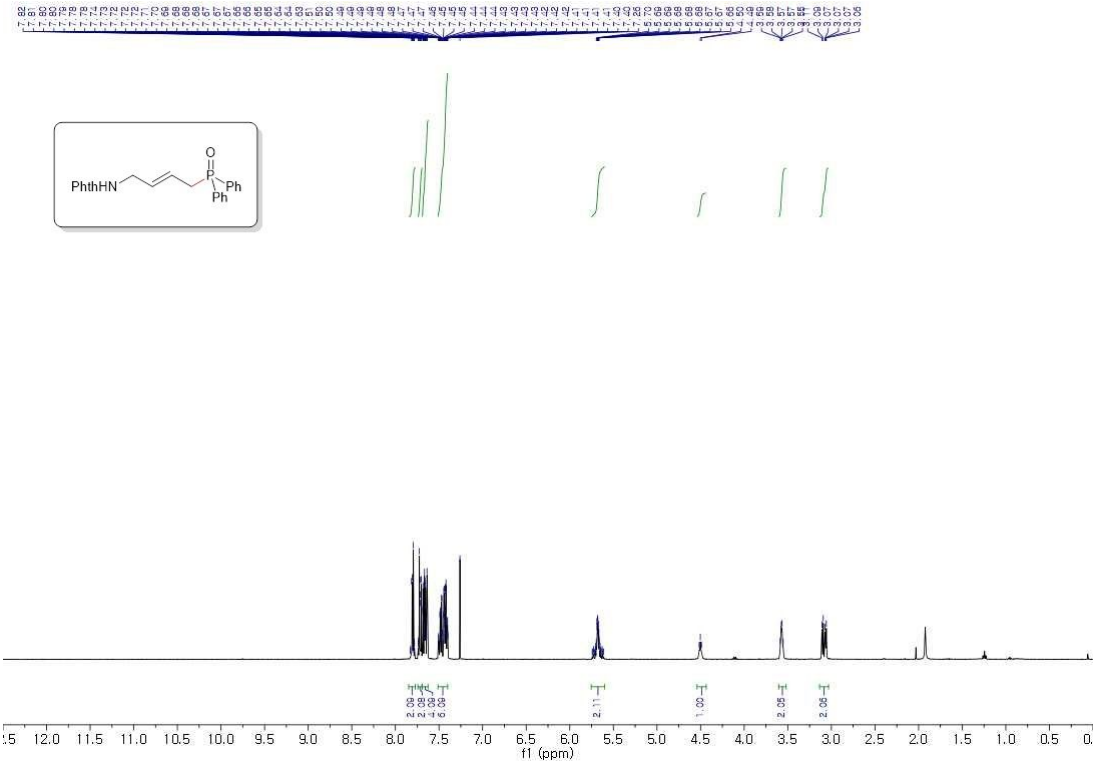


150 MHz, ^{13}C NMR in $CDCl_3$

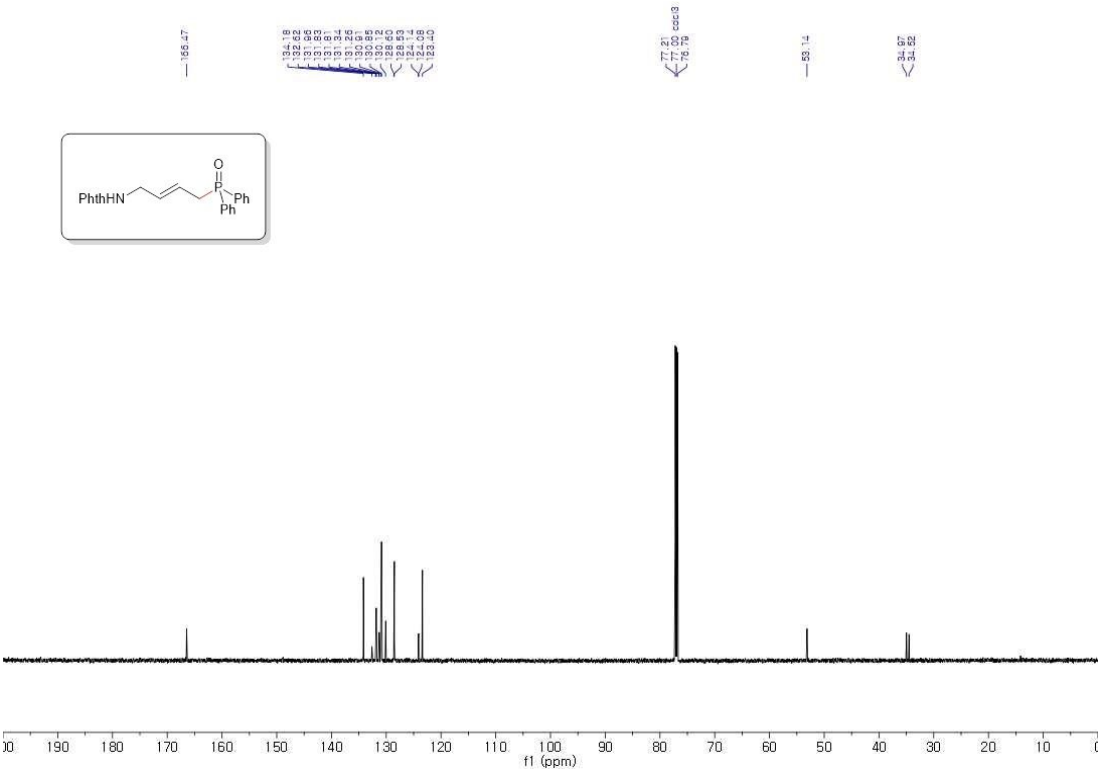


243 MHz, ^{31}P NMR in $CDCl_3$

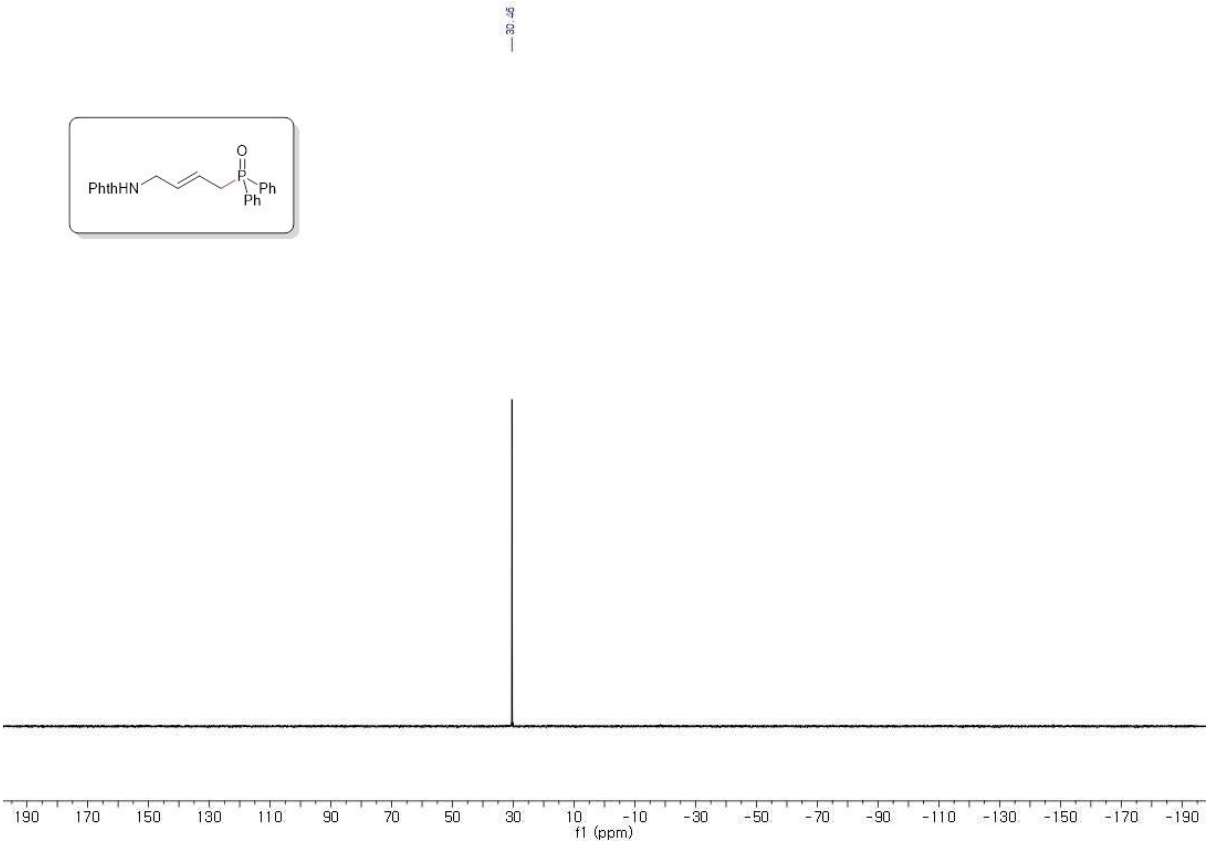
(E)-2-((4-(diphenylphosphoryl)but-2-en-1-yl)amino)isoindoline-1,3-dione (3q)



600 MHz, ^{1}H NMR in $CDCl_3$

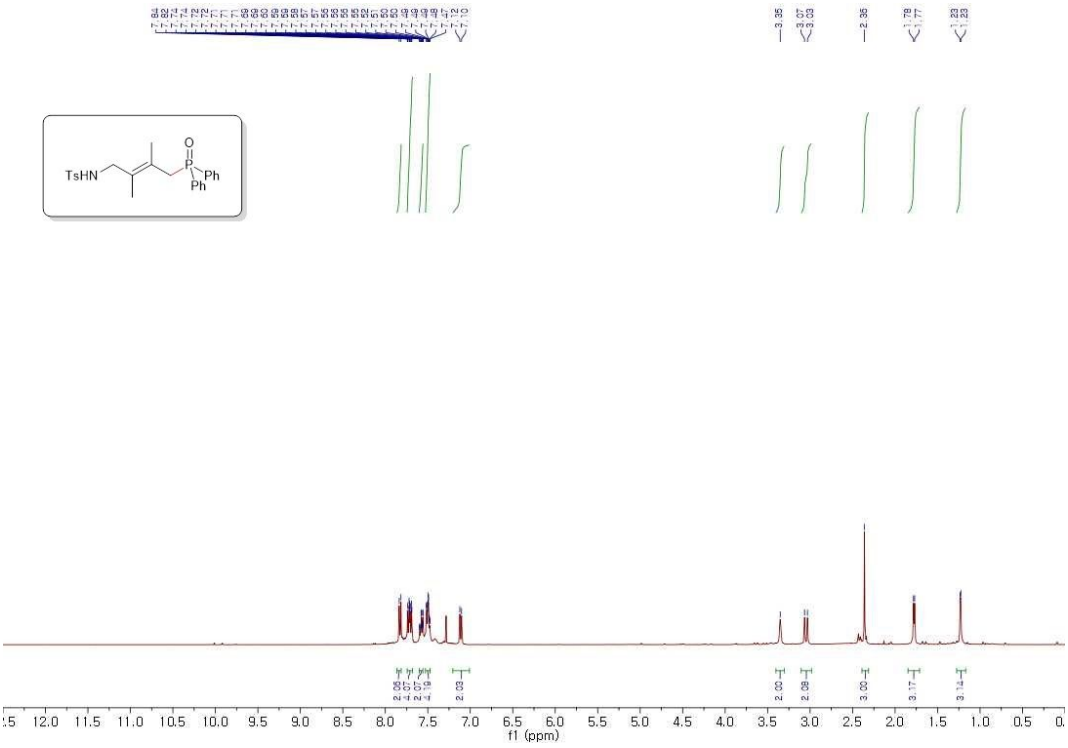


150 MHz, ^{13}C NMR in $CDCl_3$

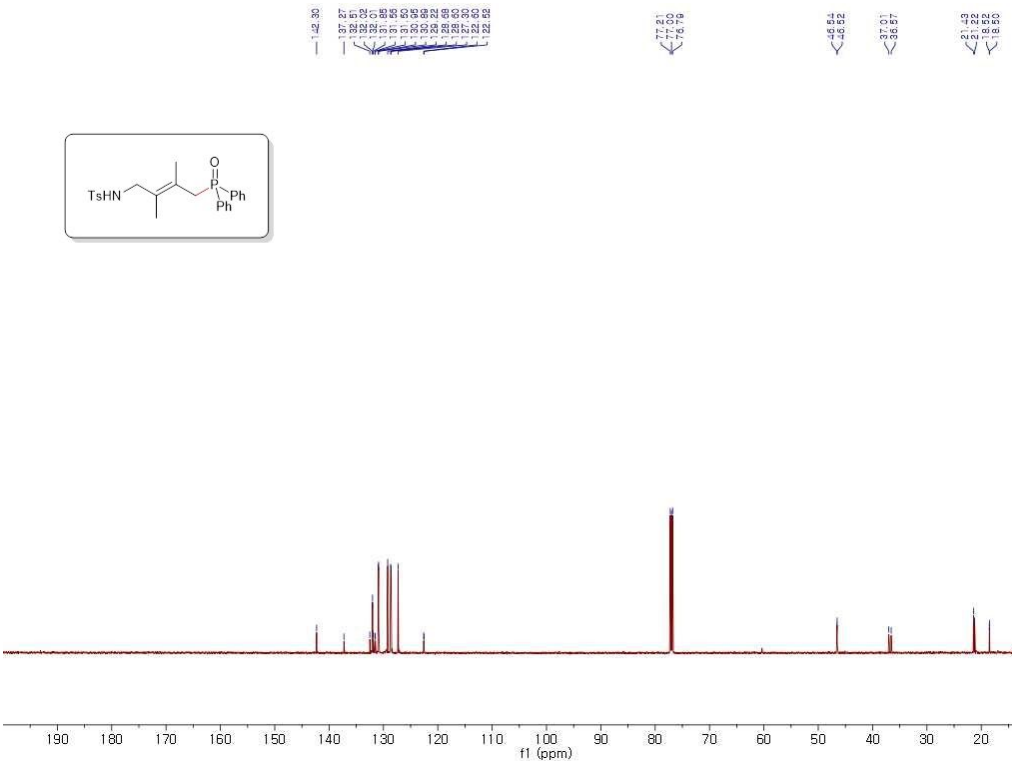


243 MHz, ^{31}P NMR in $CDCl_3$

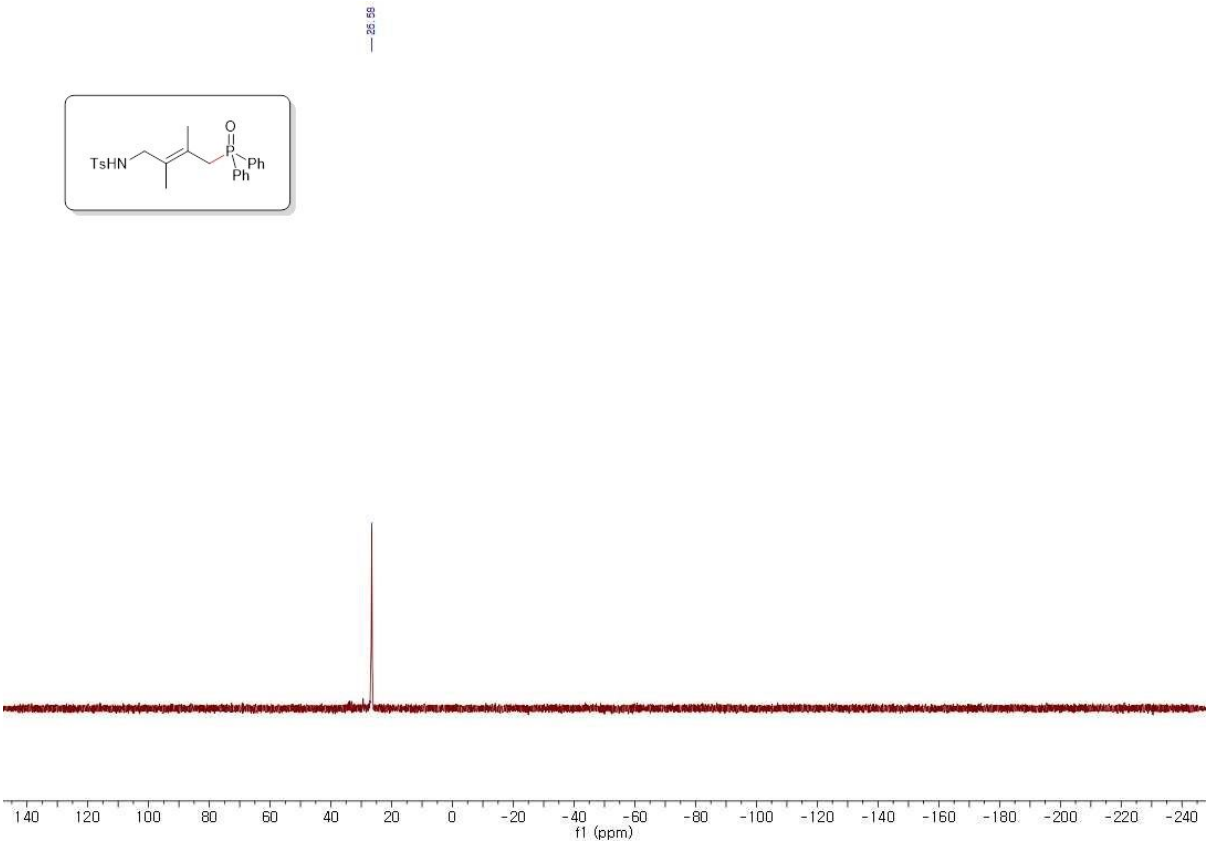
(E)-N-(4-(diphenylphosphoryl)-2,3-dimethylbut-2-en-1-yl)-4-methylbenzenesulfonamide (3r)



400 MHz, ^{1}H NMR in $CDCl_3$

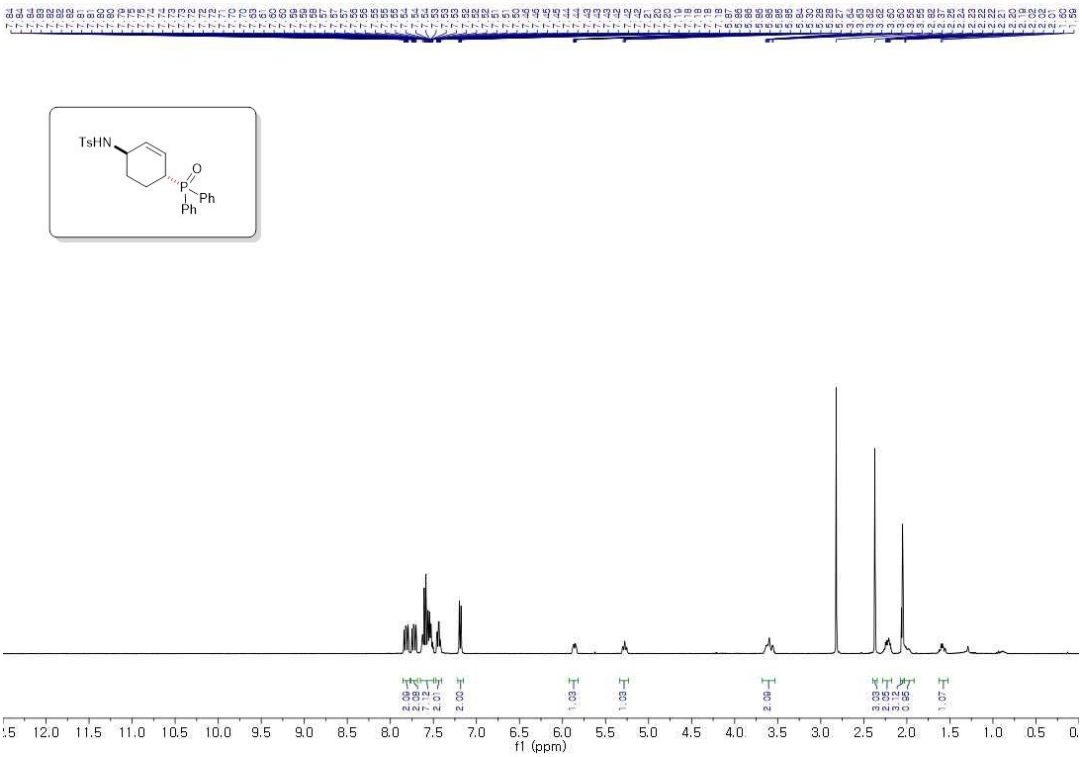


150 MHz, ^{13}C NMR in $CDCl_3$

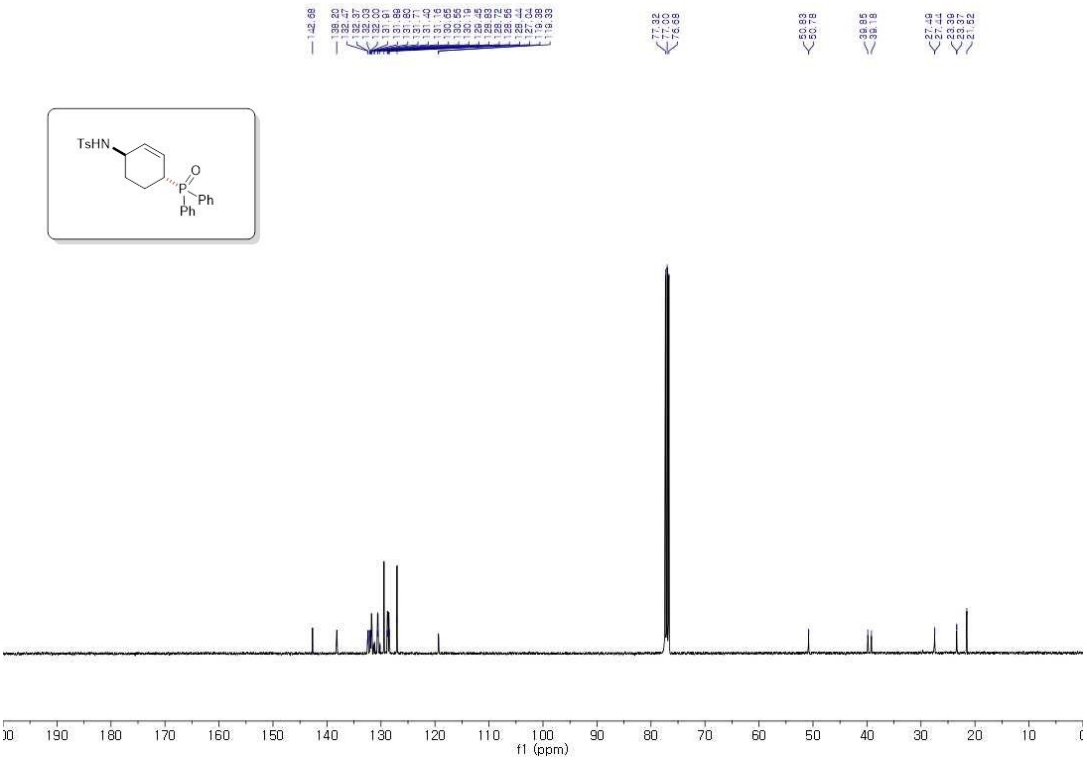


162 MHz, ^{31}P NMR in $CDCl_3$

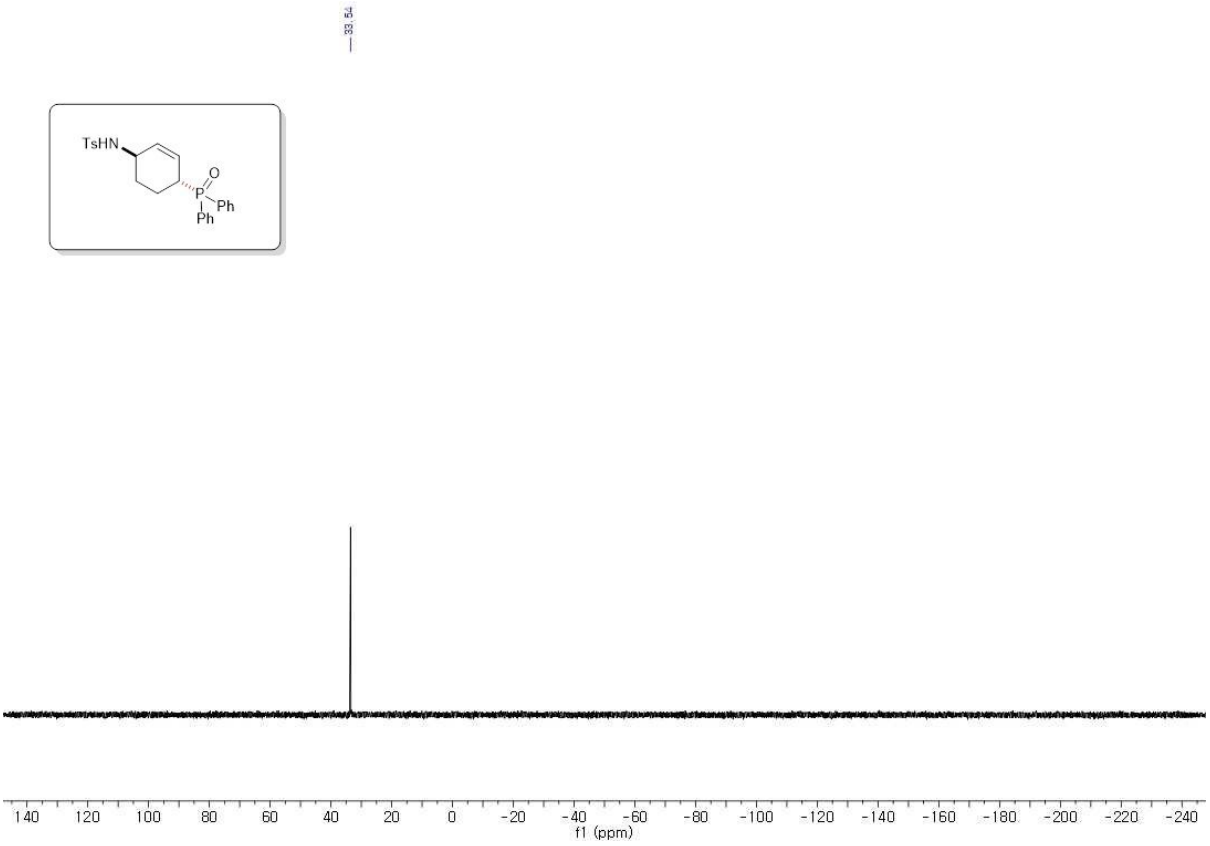
N-(4-(diphenylphosphoryl)cyclohex-2-en-1yl)-4-methylbenzenesulfonamide (*trans*-3s)



400 MHz, ^{1}H NMR in Acetone-d_6

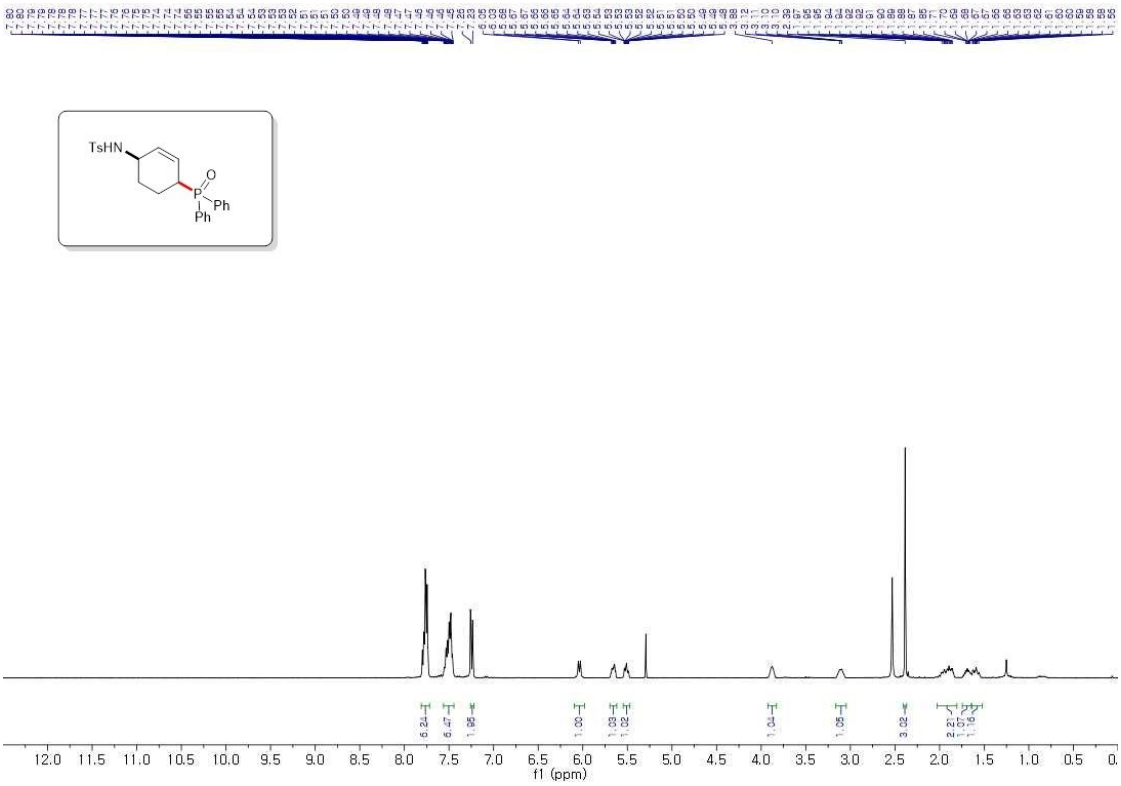


100 MHz, ^{13}C NMR in $CDCl_3$

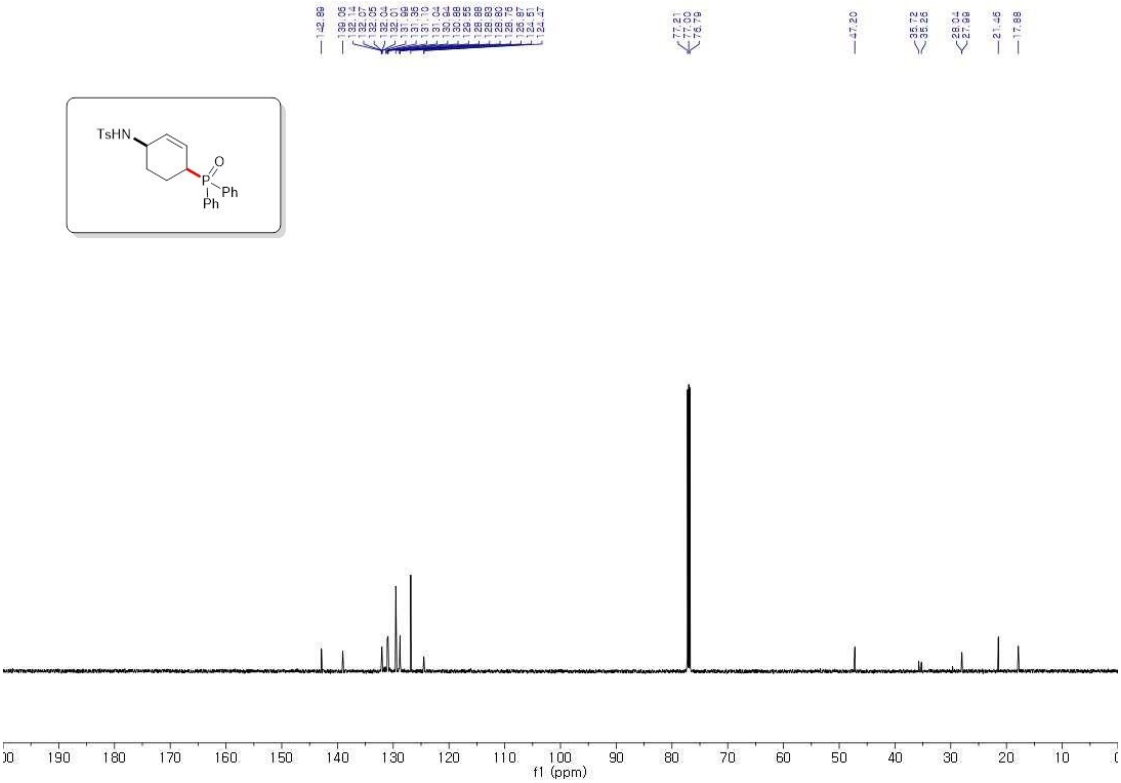


162 MHz, ^{31}P NMR in $CDCl_3$

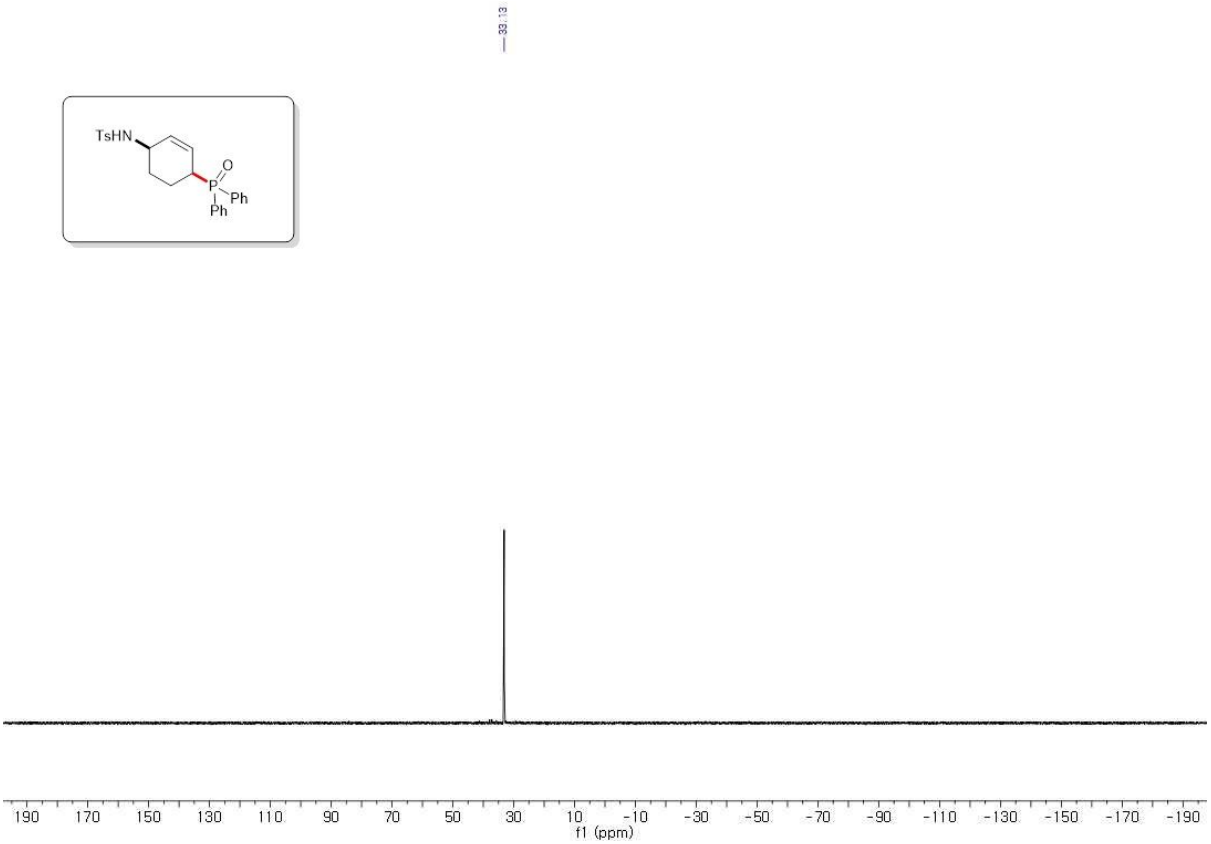
N-(4-(diphenylphosphoryl)cyclohex-2-en-1yl)-4-methylbenzenesulfonamide (*cis*-3s)



400 MHz, ^{1}H NMR in $CDCl_3$

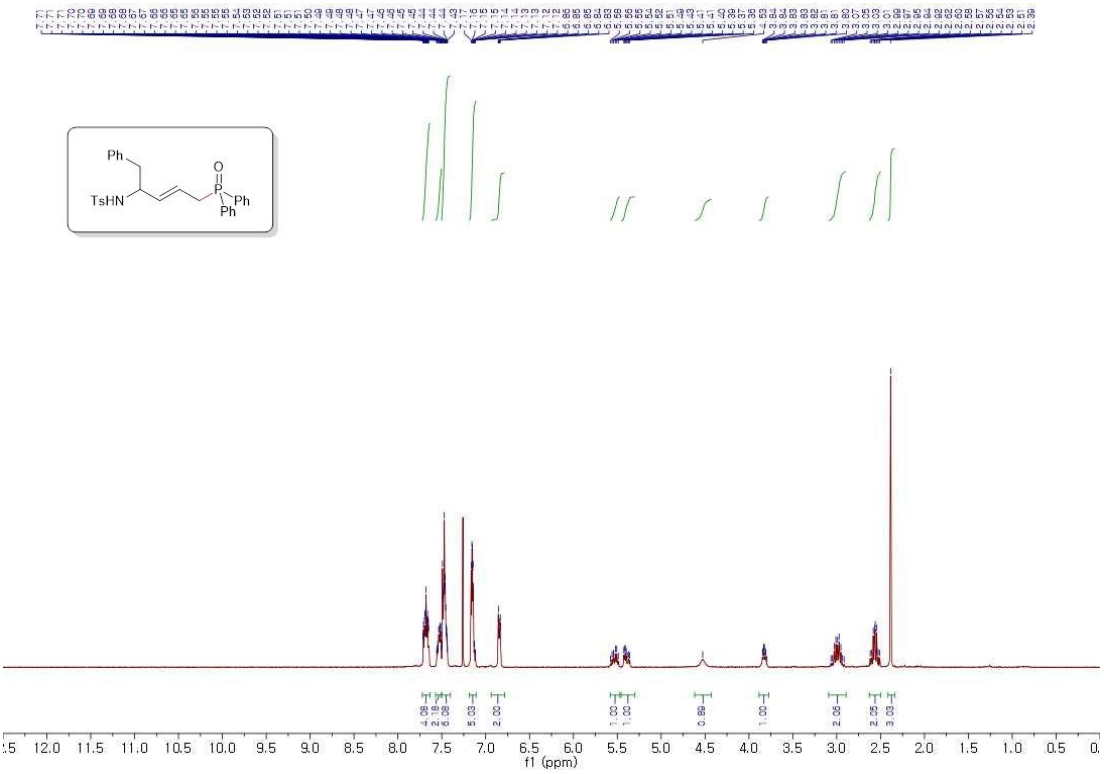


150 MHz, ^{13}C NMR in $CDCl_3$

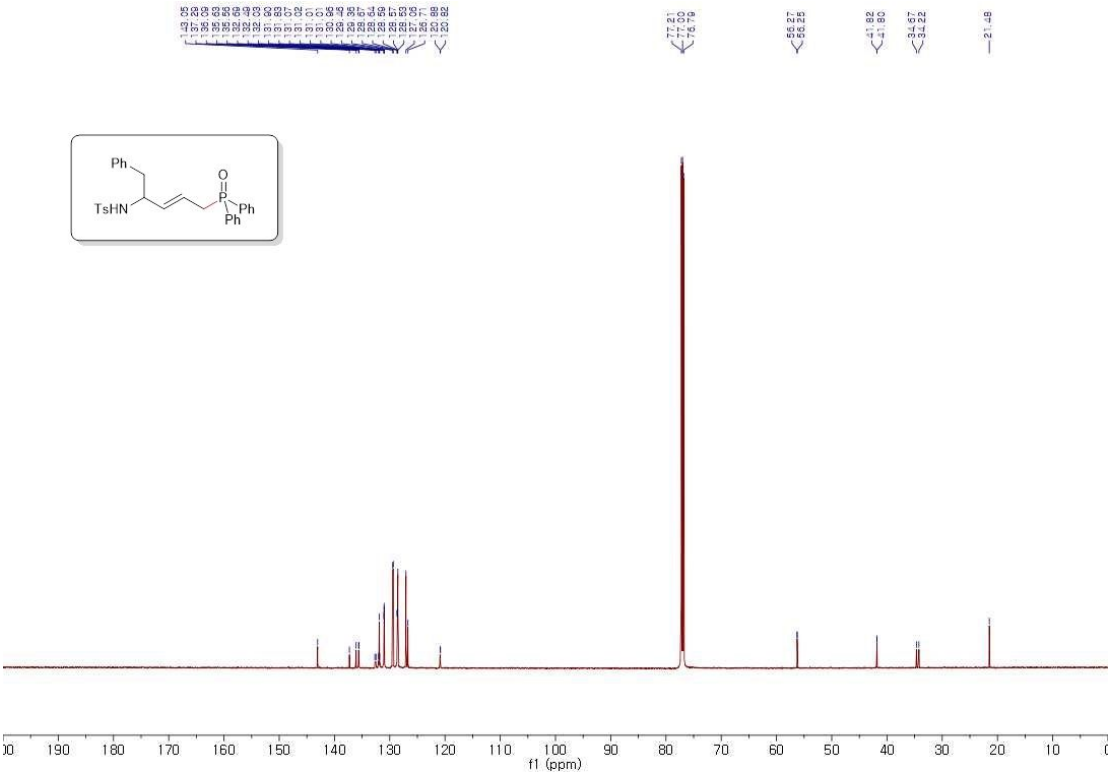


162 MHz, ^{31}P NMR in $CDCl_3$

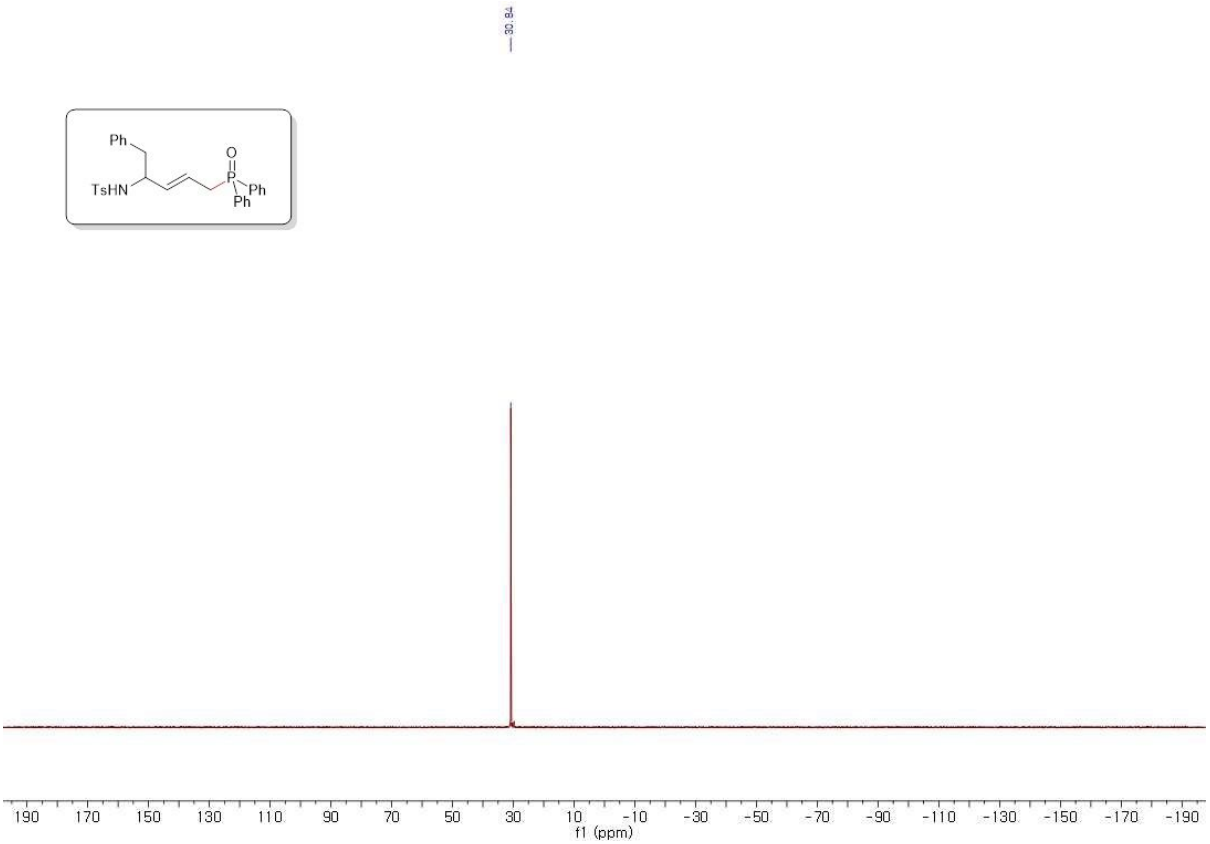
(E)-N-(5-(diphenylphosphoryl)-1-phenylpent-3-en-2-yl)-4-methylbenzenesulfonamide (3t)



400 MHz, ^{1}H NMR in $CDCl_3$

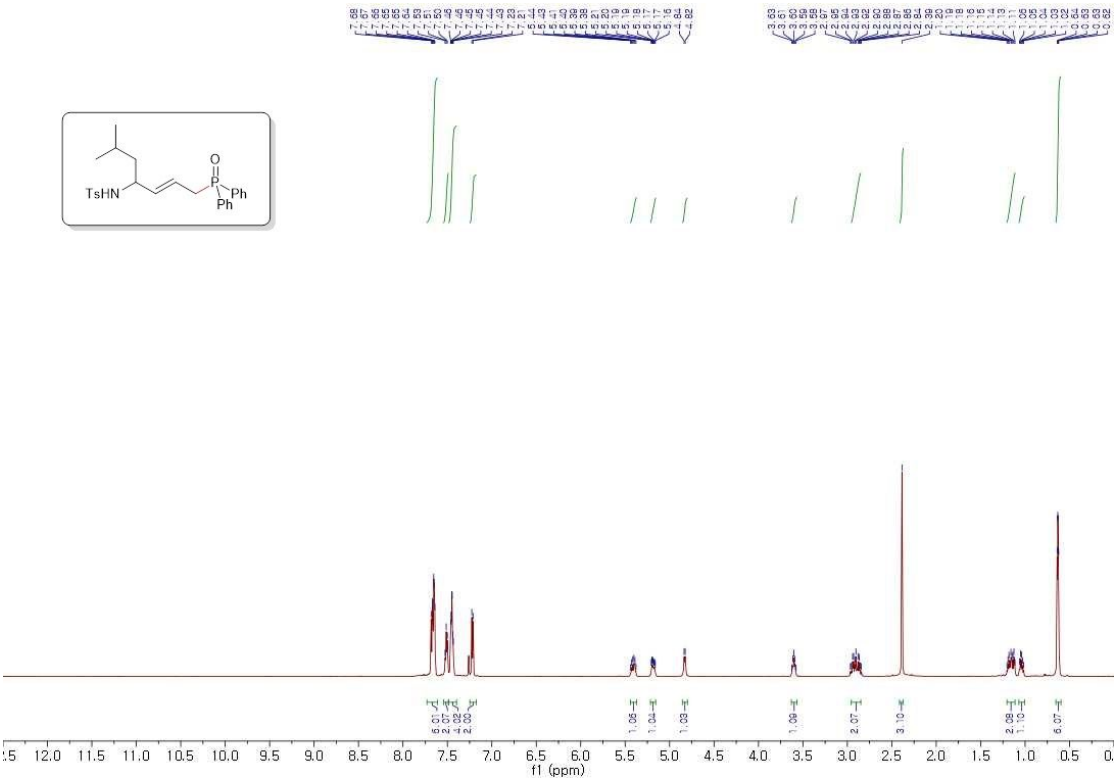


150 MHz, ^{13}C NMR in $CDCl_3$

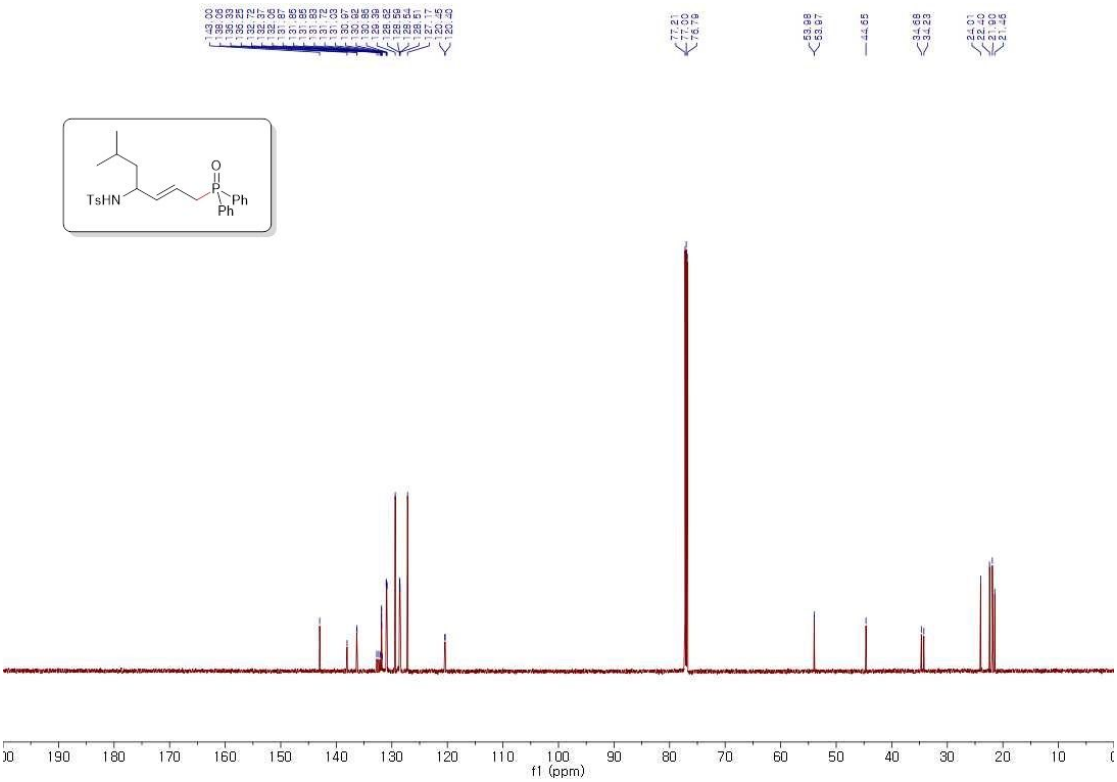


162 MHz, ^{31}P NMR in $CDCl_3$

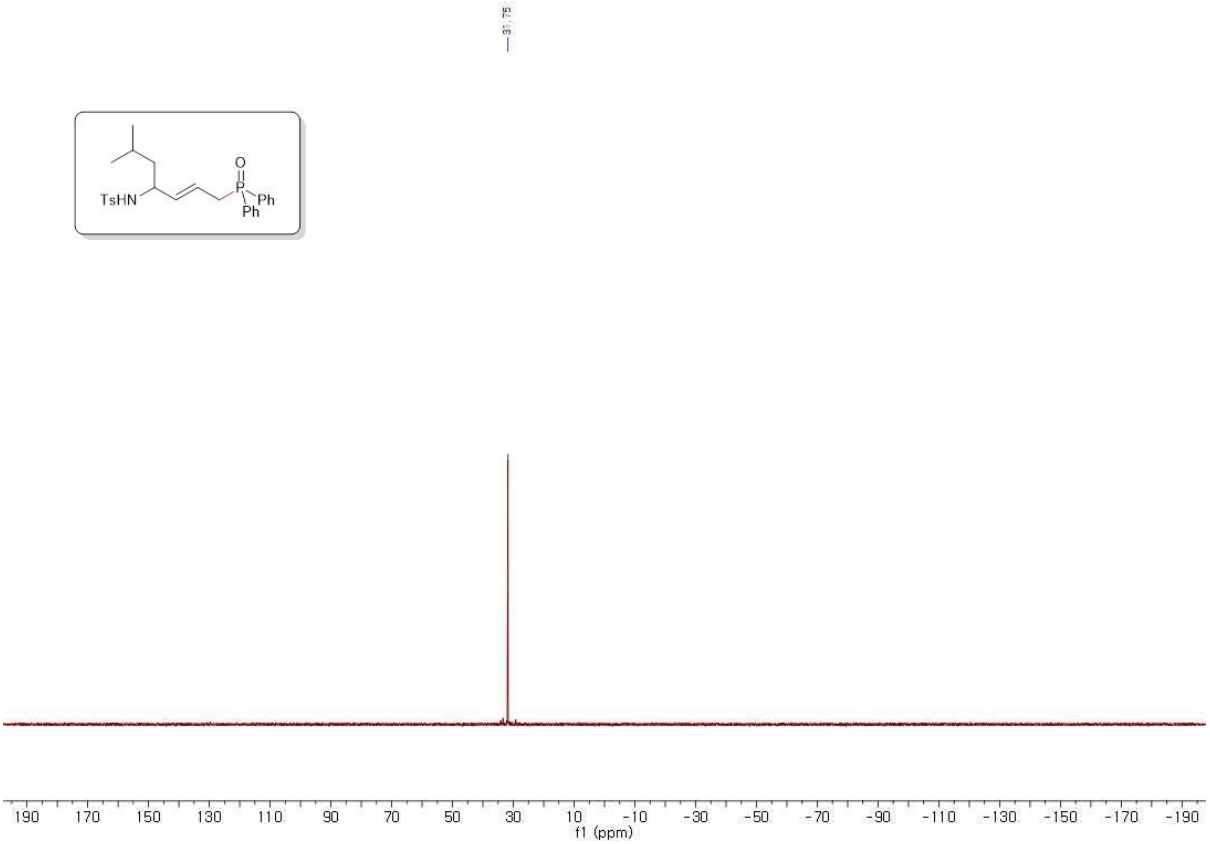
(E)-N-(1-(diphenylphosphoryl)-6-methylhept-2-en-4-yl)-4-methylbenzenesulfonamide (3u)



600 MHz, ^{1}H NMR in $CDCl_3$

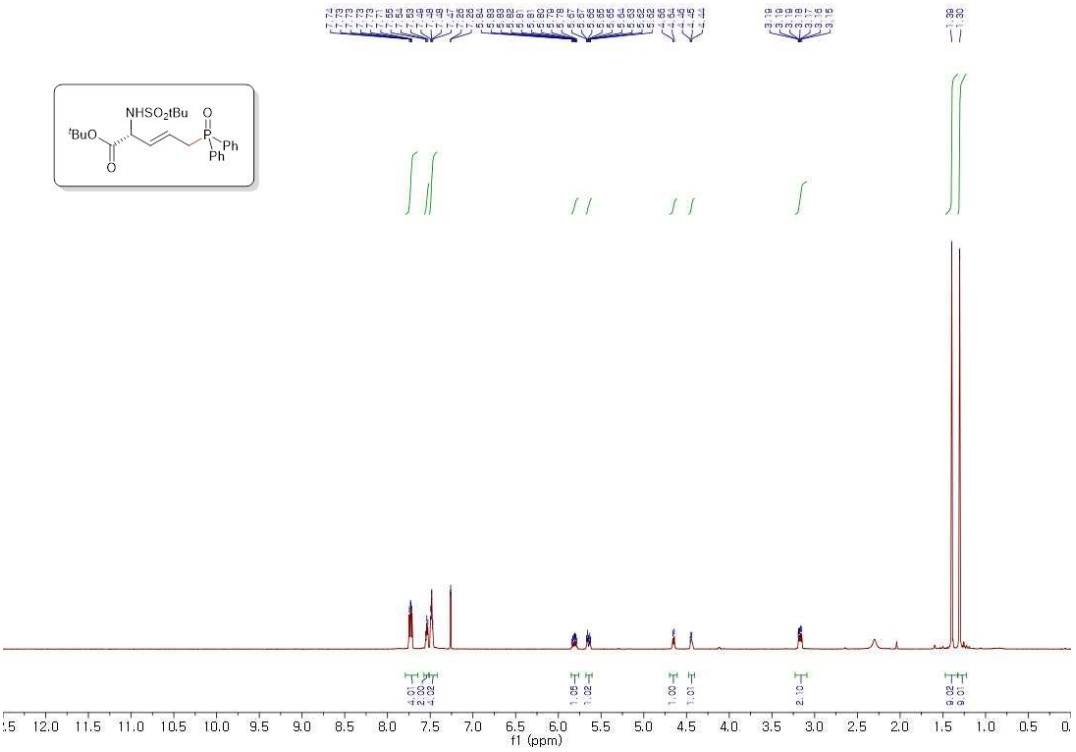


150 MHz, ^{13}C NMR in $CDCl_3$

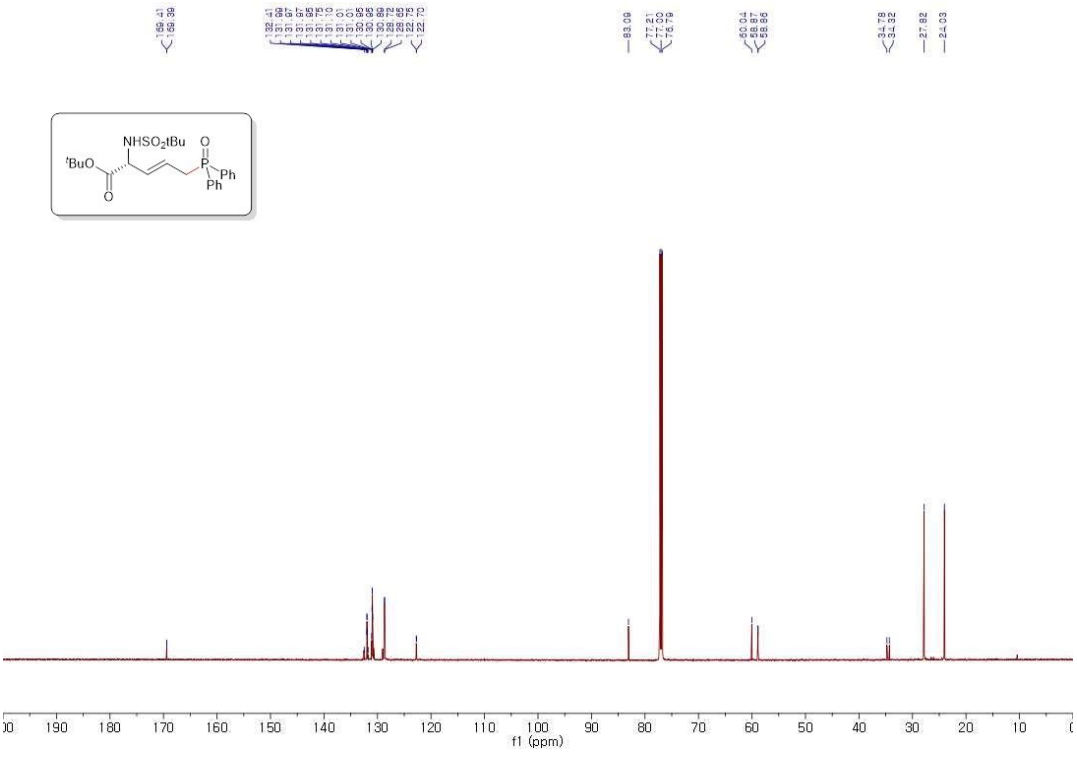


162 MHz, ^{31}P NMR in $CDCl_3$

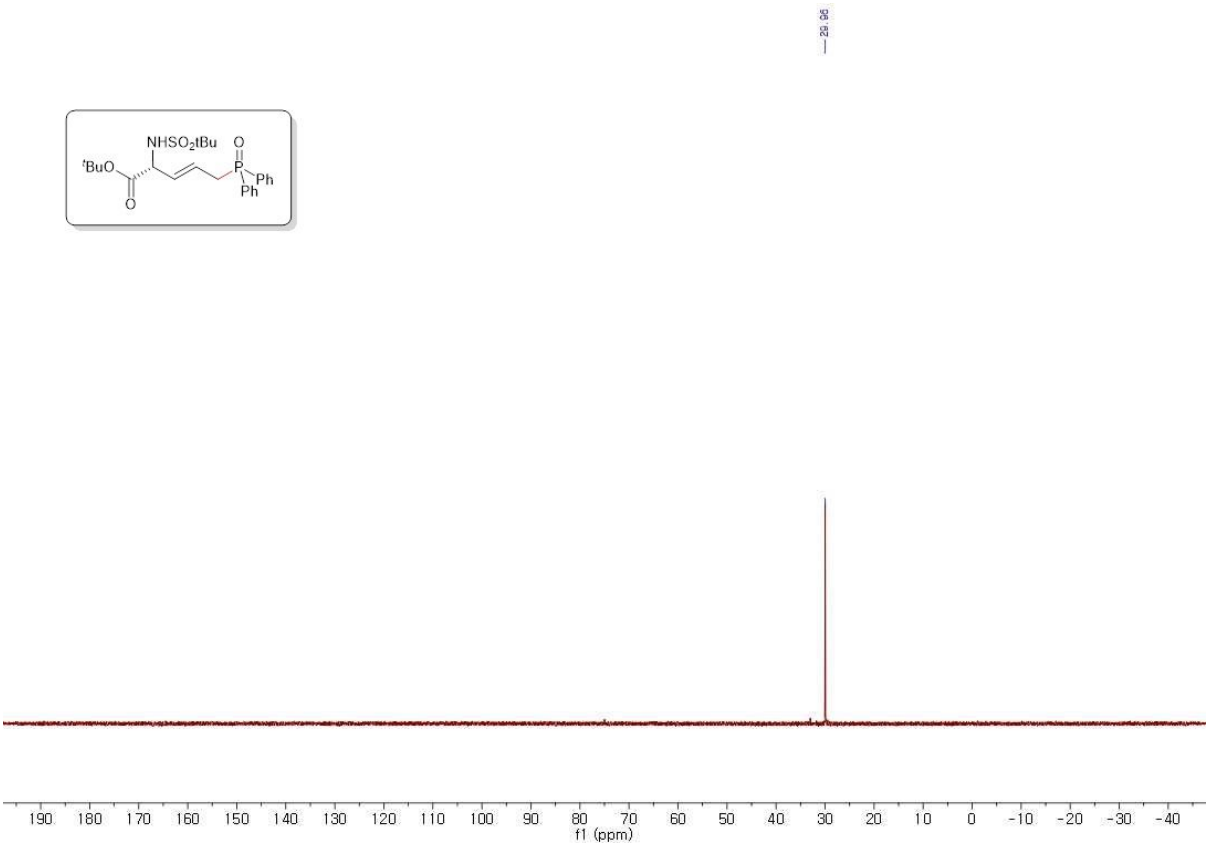
tert-butyl (R,E)-2-((1,1-dimethylethyl)sulfonamido)-5-(diphenylphosphoryl)pent-3-enoate (3v)



600 MHz, ^{1}H NMR in $CDCl_3$

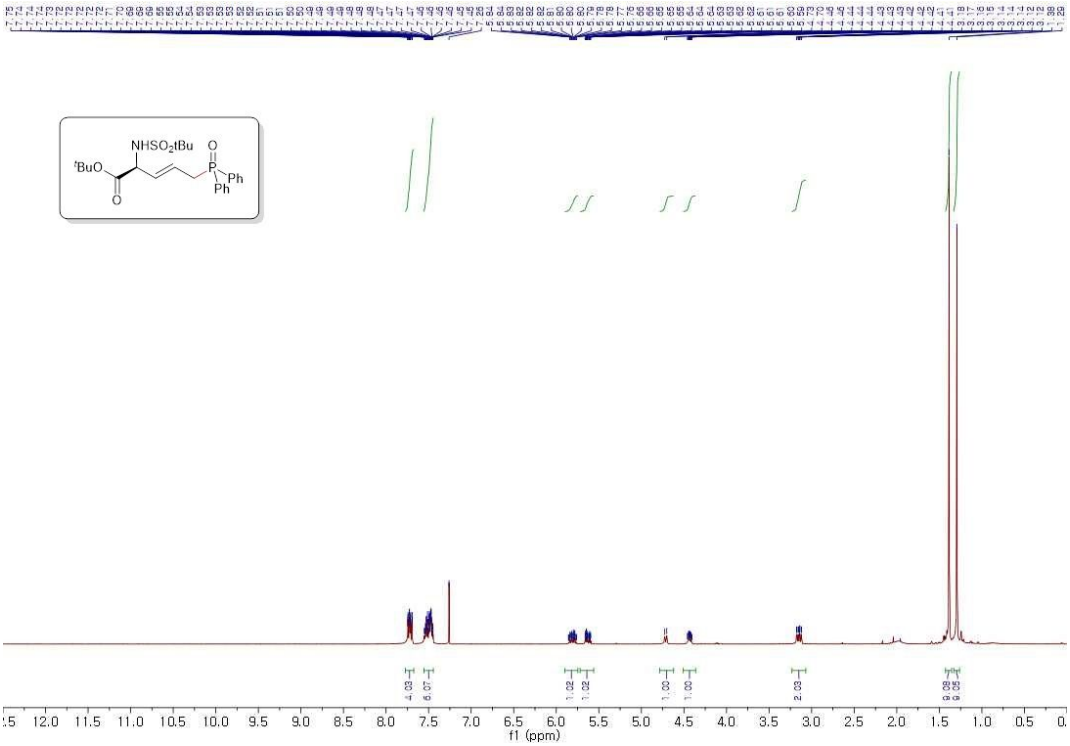


150 MHz, ^{13}C NMR in $CDCl_3$

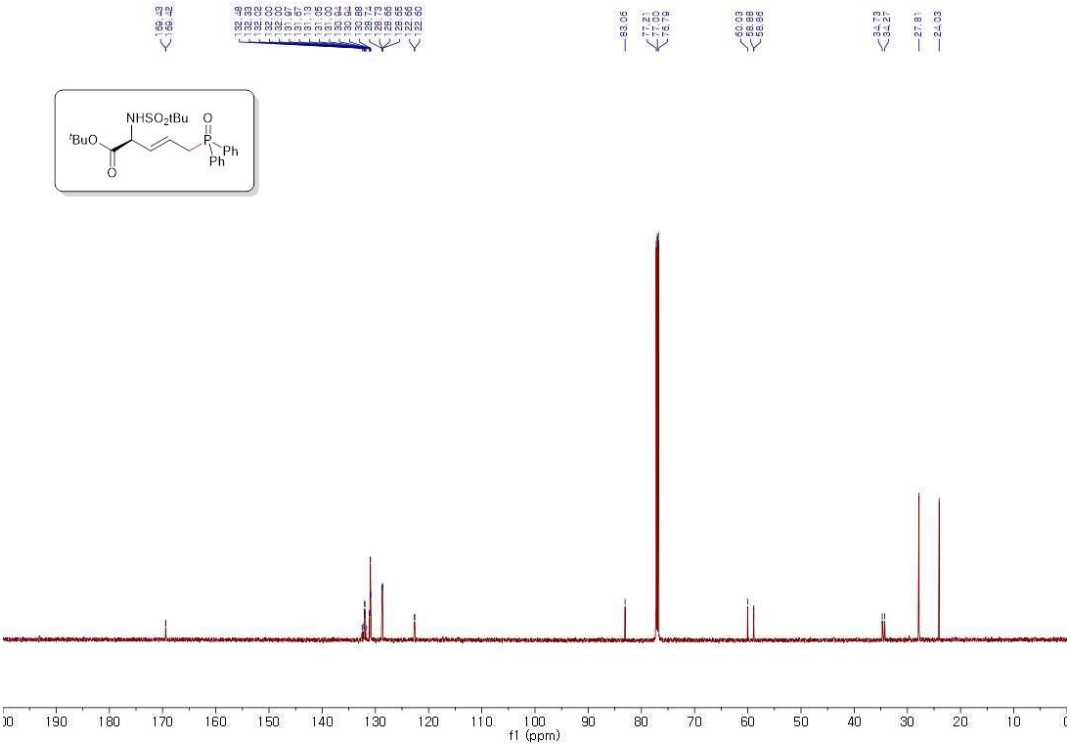


243 MHz, ^{31}P NMR in $CDCl_3$

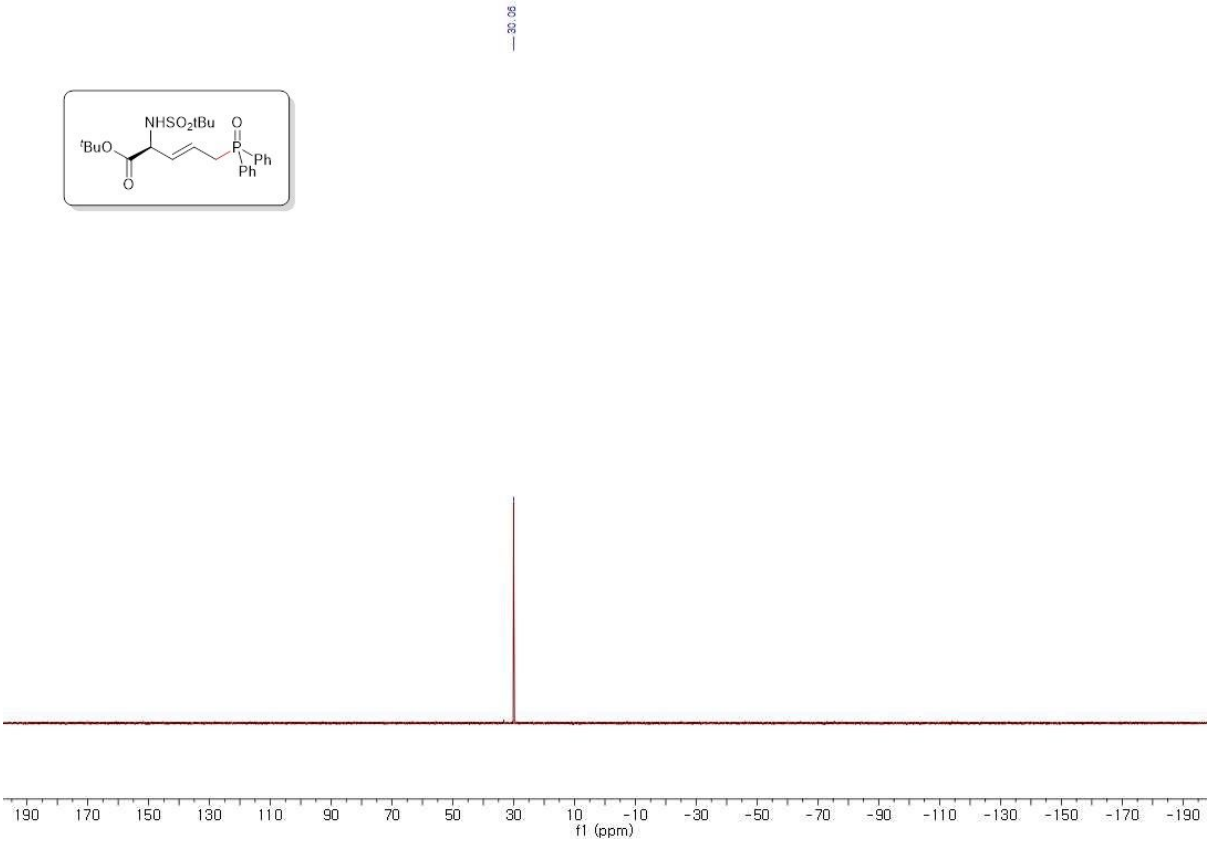
tert-butyl (S,E)-2-((1,1-dimethylethyl)sulfonamido)-5-(diphenylphosphoryl)pent-3-enoate (3w)



400 MHz, ^{1}H NMR in $CDCl_3$

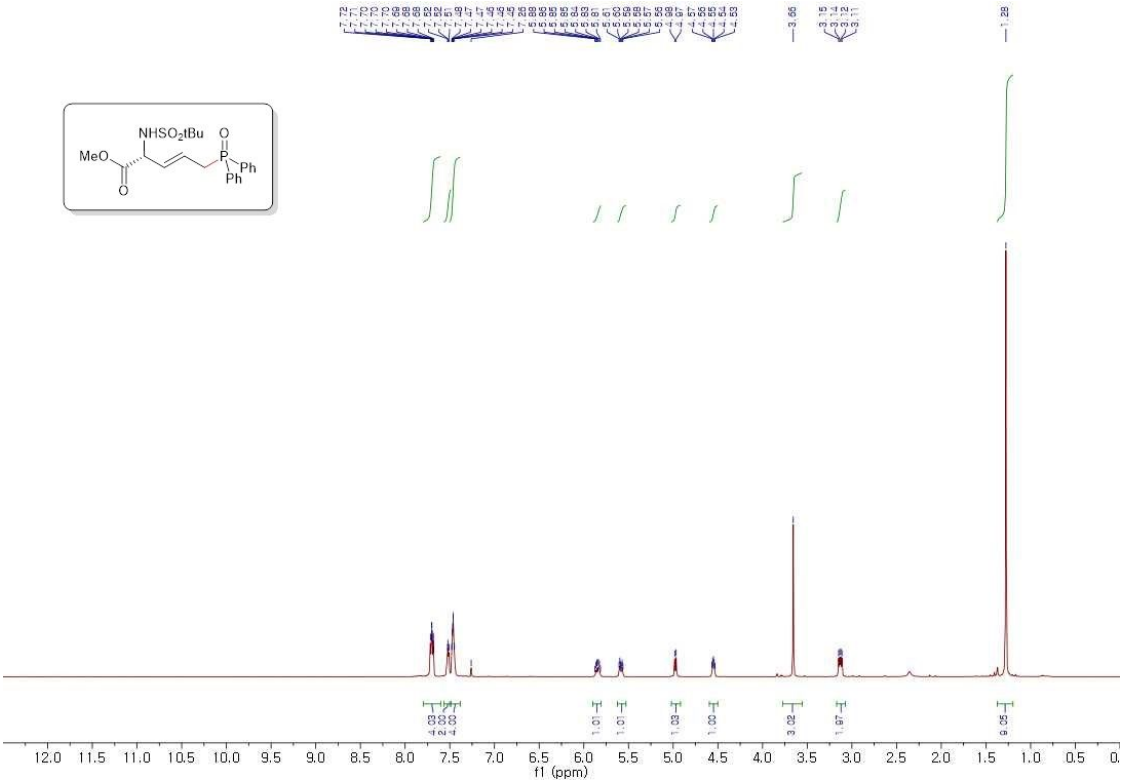


150 MHz, ^{13}C NMR in $CDCl_3$

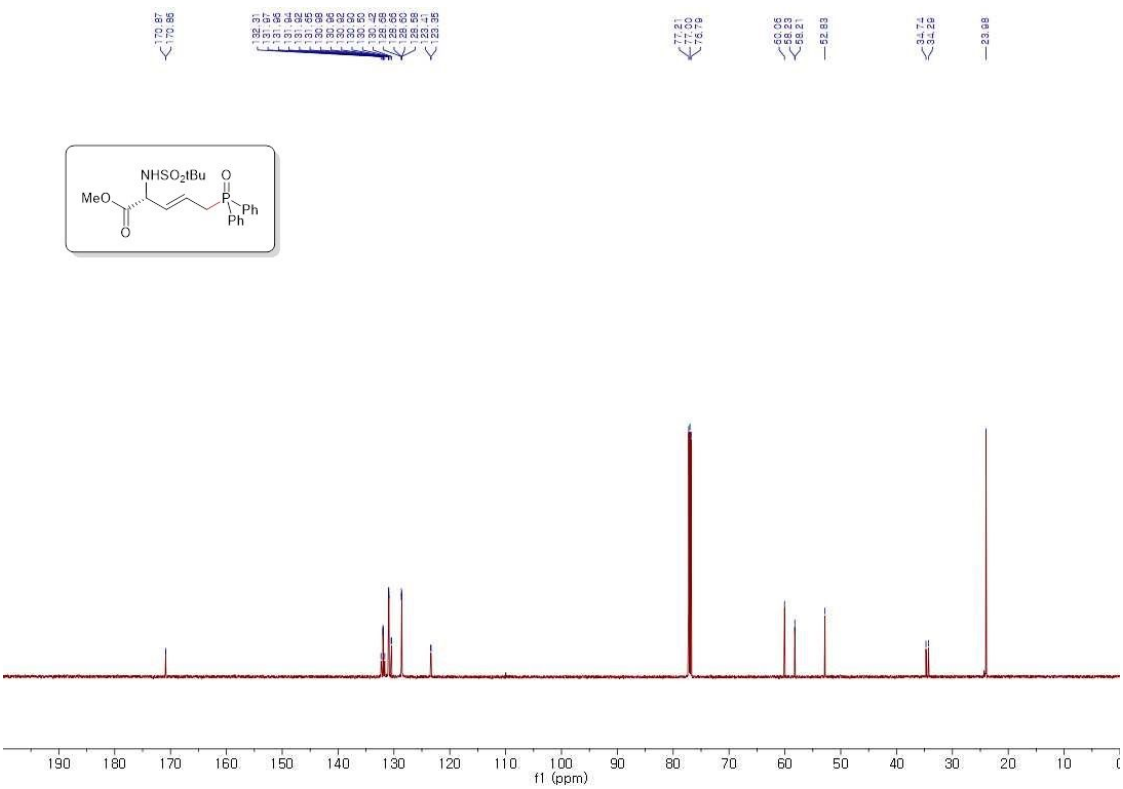


162 MHz, ^{31}P NMR in $CDCl_3$

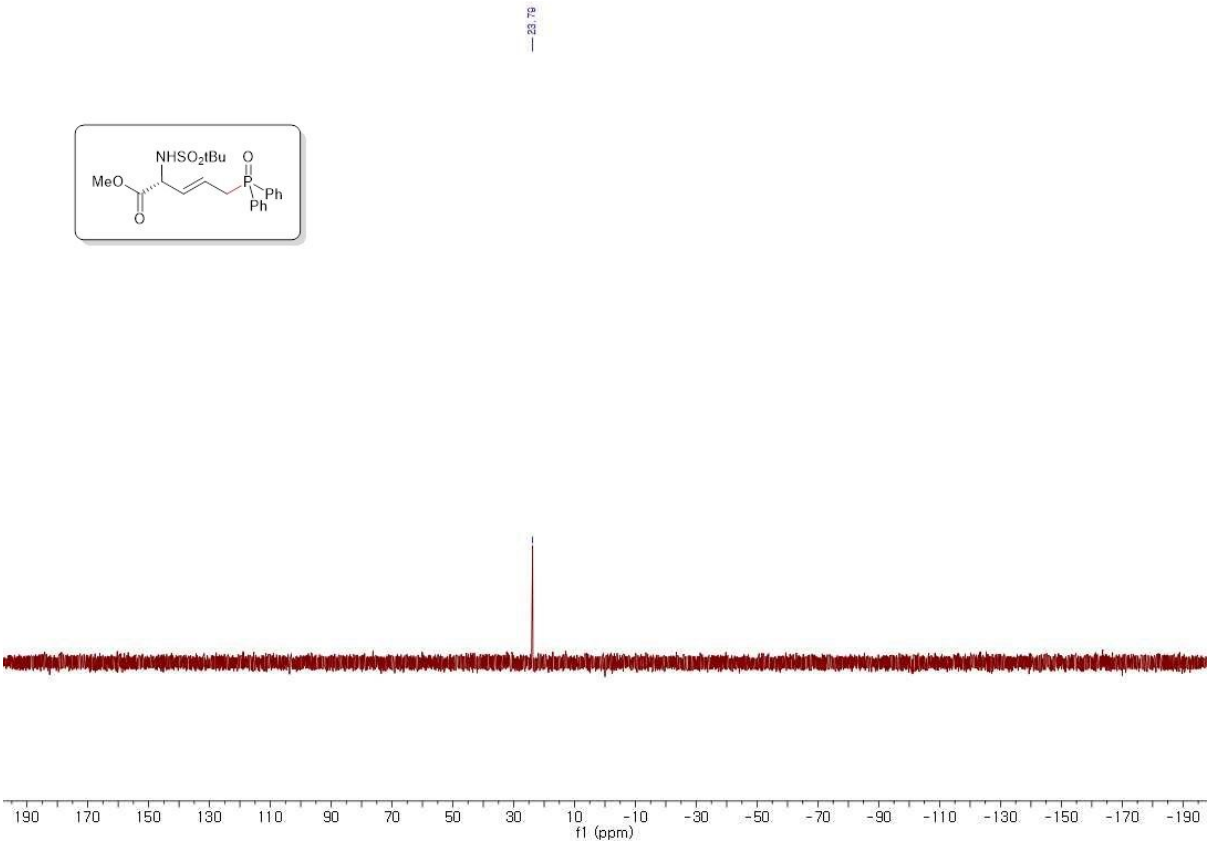
methyl (R,E)-2-((1,1-dimethylethyl)sulfonamido)-5-(diphenylphosphoryl)pent-3-enoate (3x)



600 MHz, ^{1}H NMR in $CDCl_3$

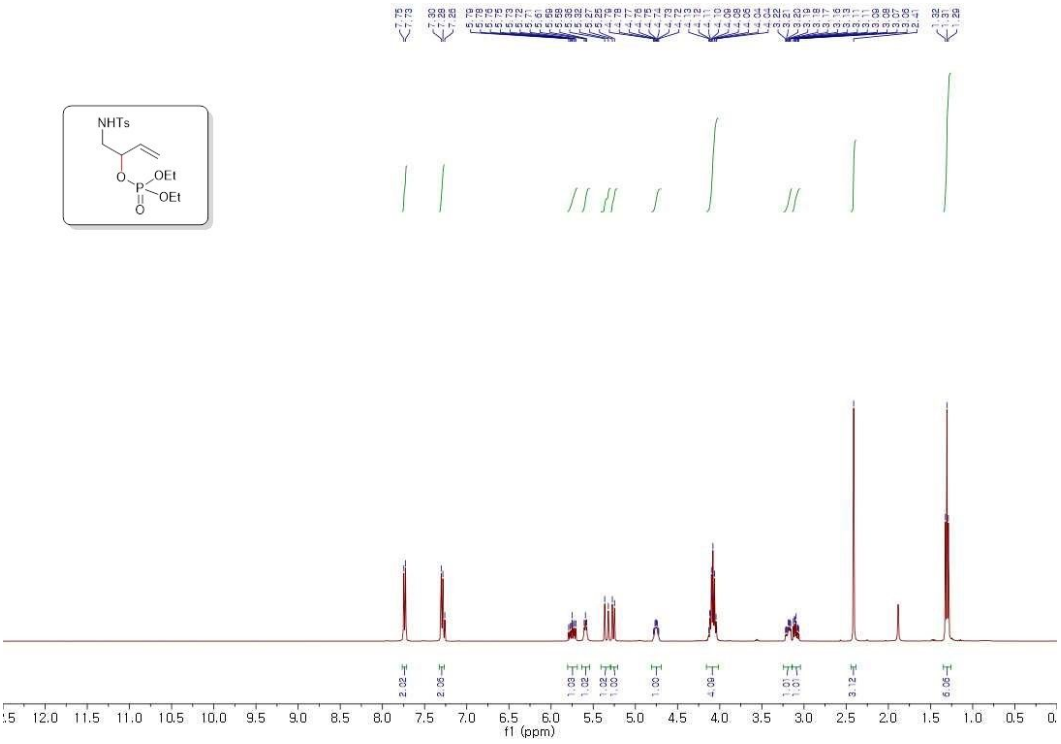


150 MHz, ^{13}C NMR in $CDCl_3$

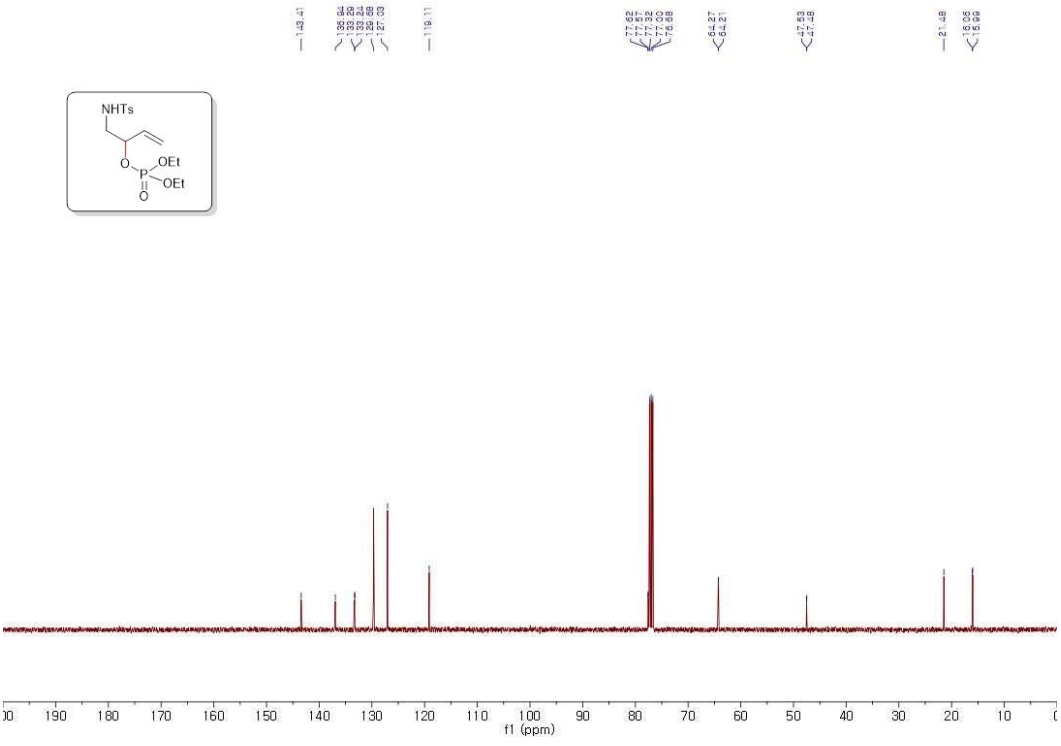


162 MHz, ^{31}P NMR in $CDCl_3$

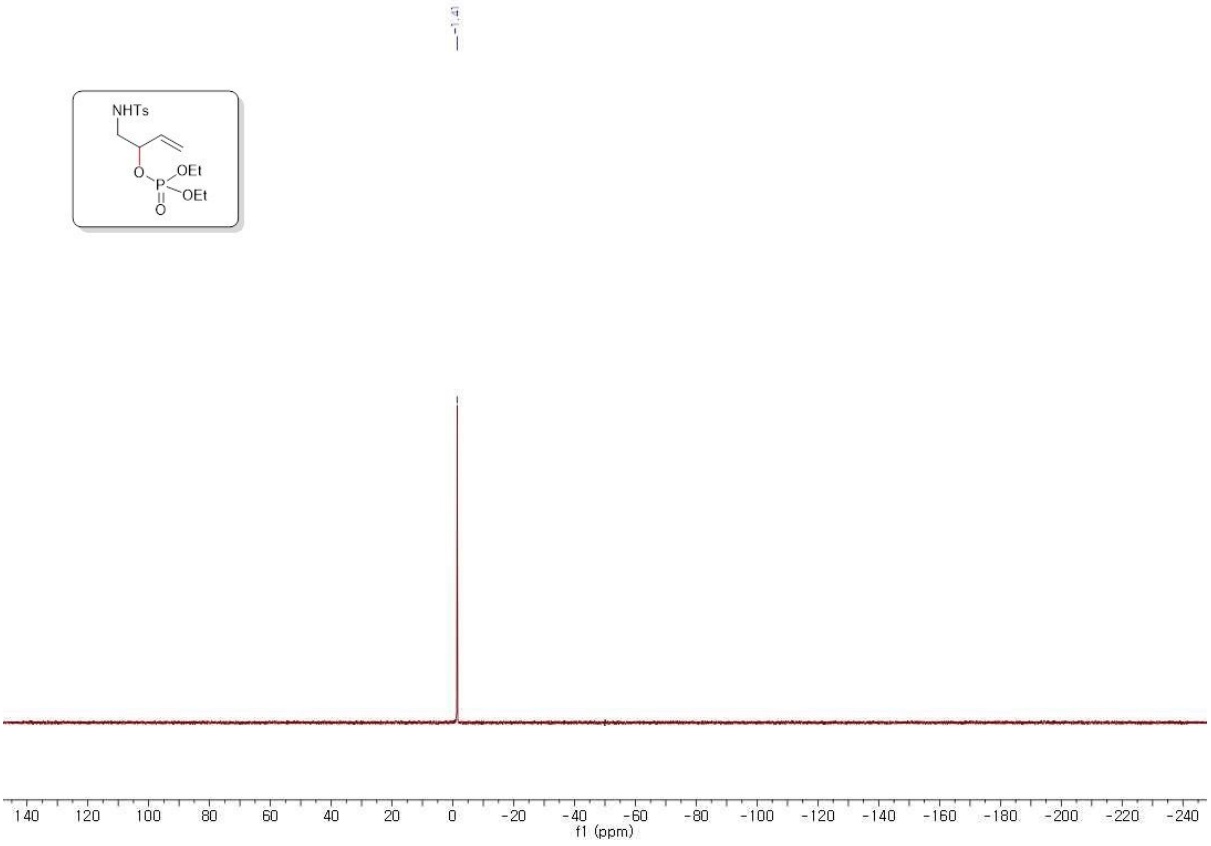
diethyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4a)



400 MHz, ^{1}H NMR in $CDCl_3$

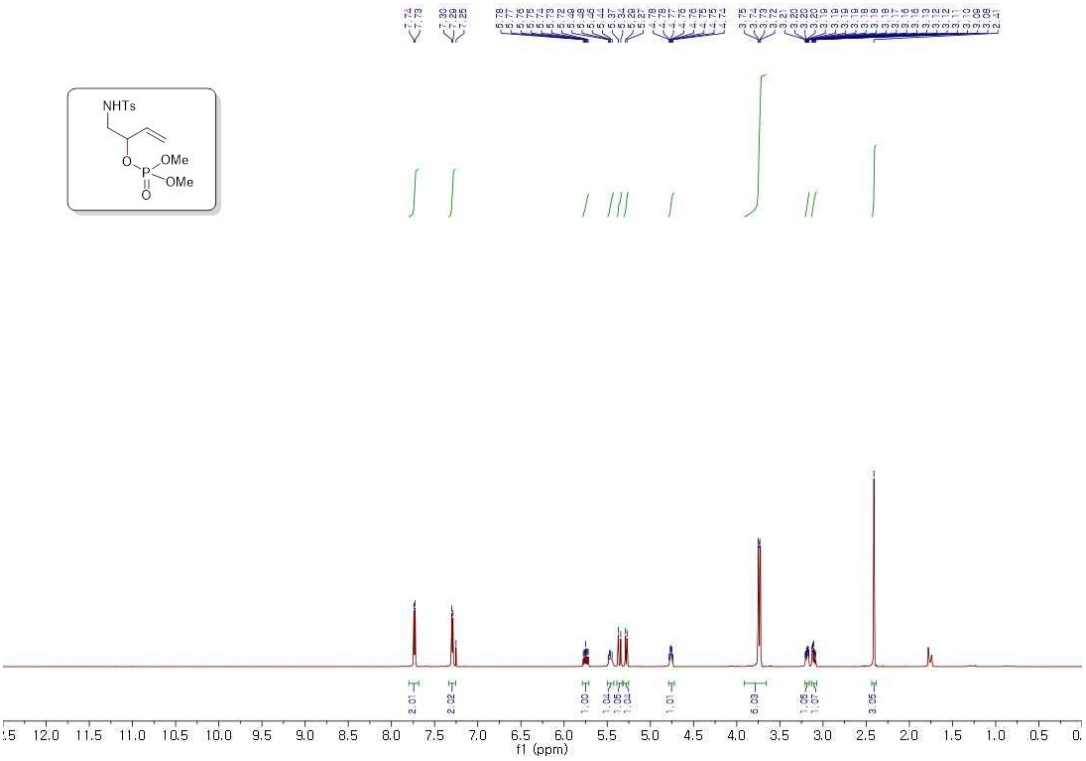


100 MHz, ^{13}C NMR in $CDCl_3$

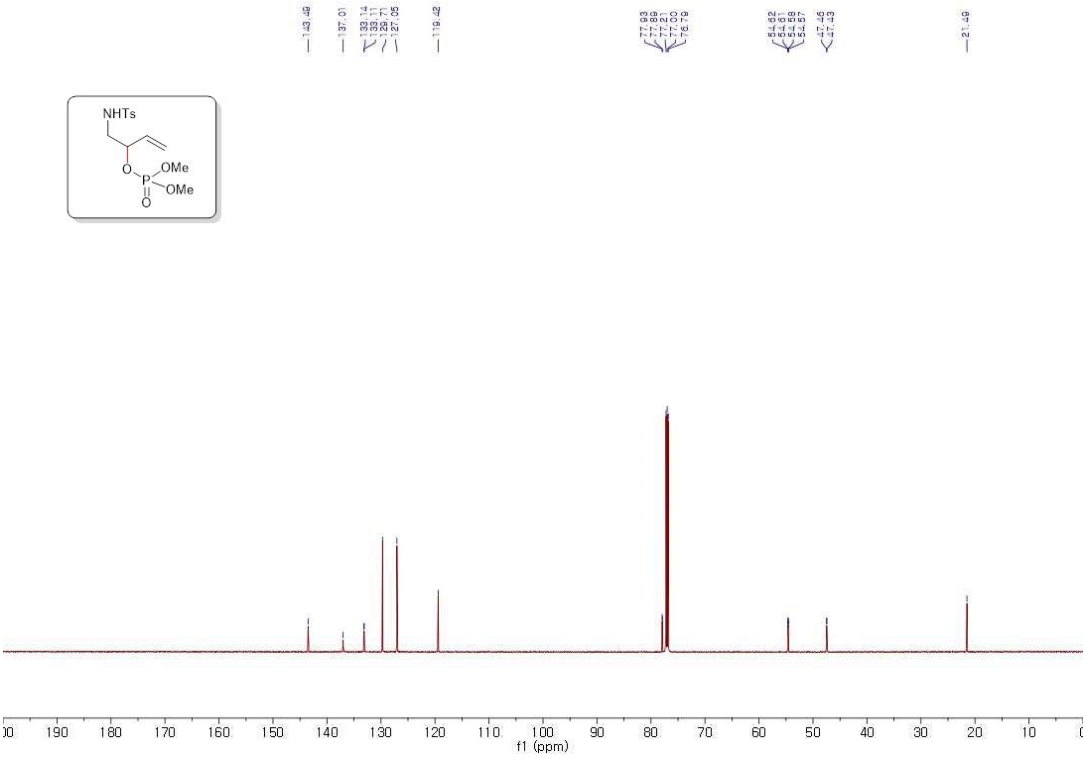


162 MHz, ^{13}C NMR in $CDCl_3$

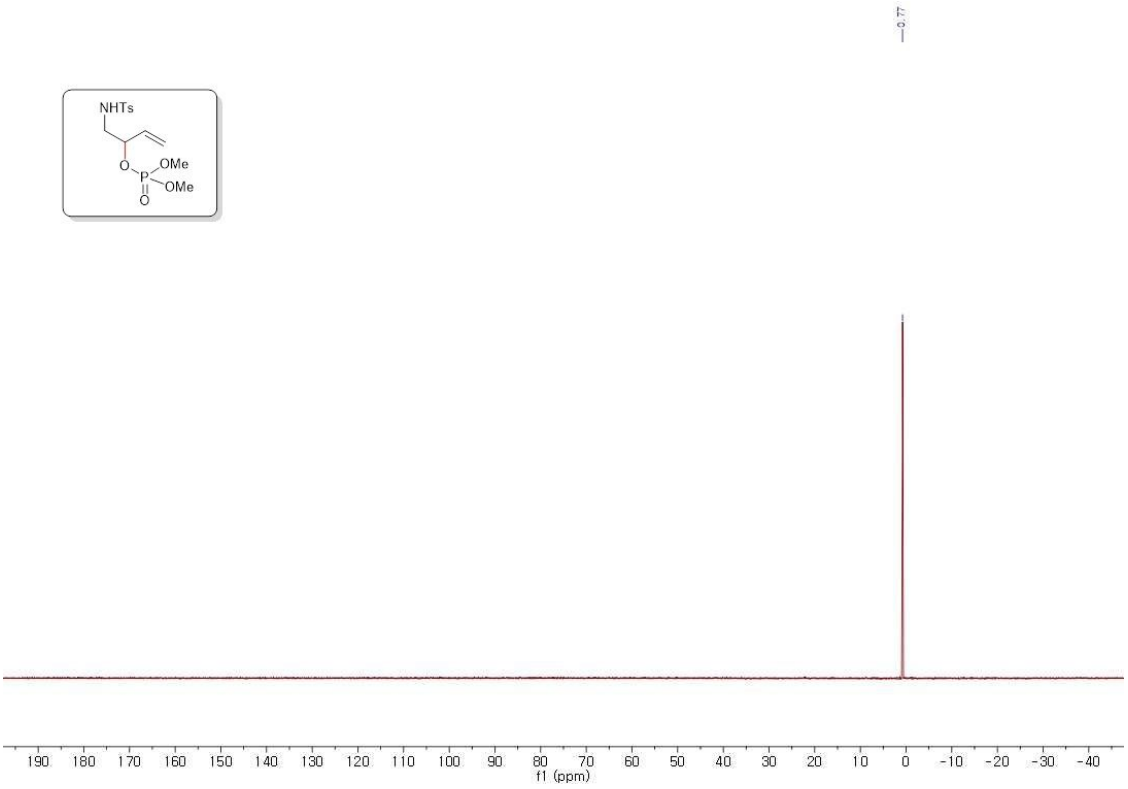
dimethyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4b).



600 MHz, ^{1}H NMR in $CDCl_3$

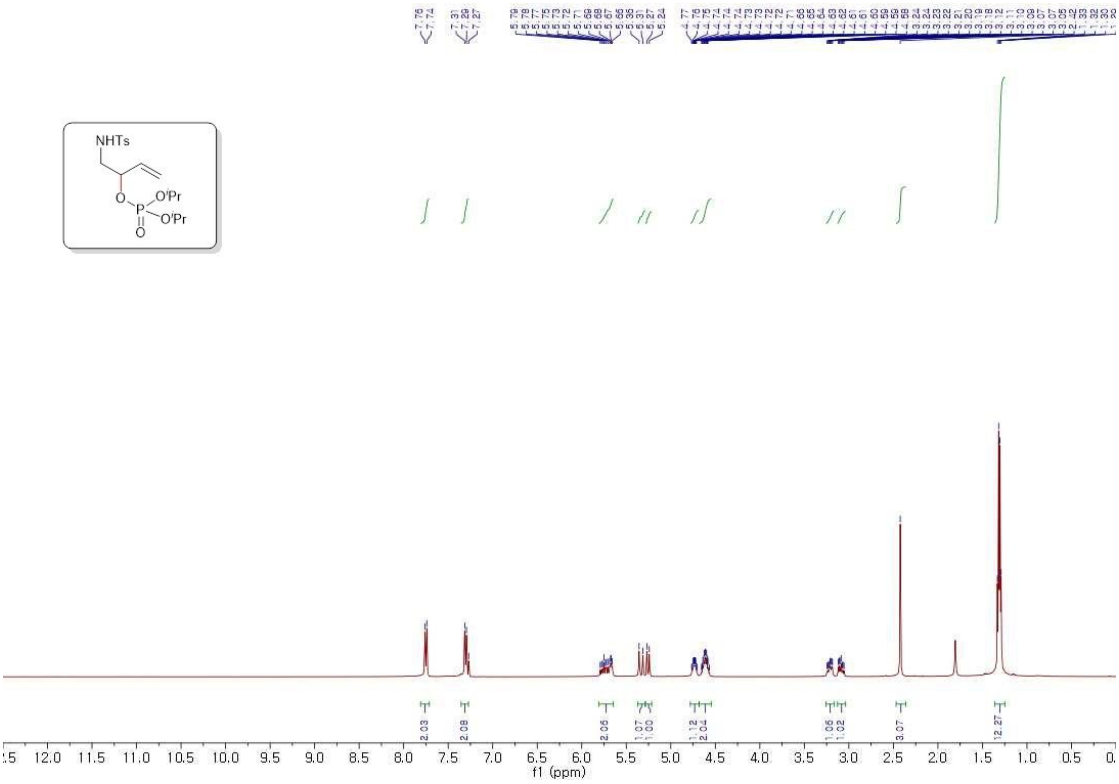


150 MHz, ^{13}C NMR in $CDCl_3$

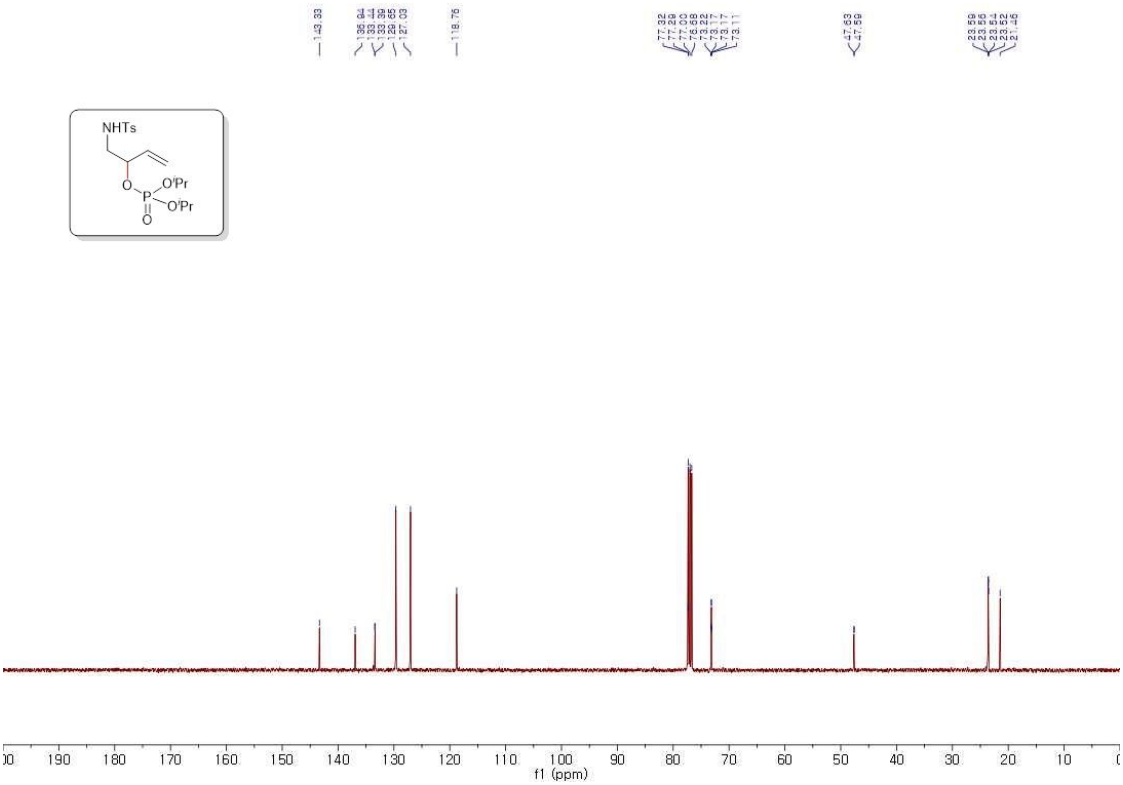


243 MHz, ^{31}P NMR in $CDCl_3$

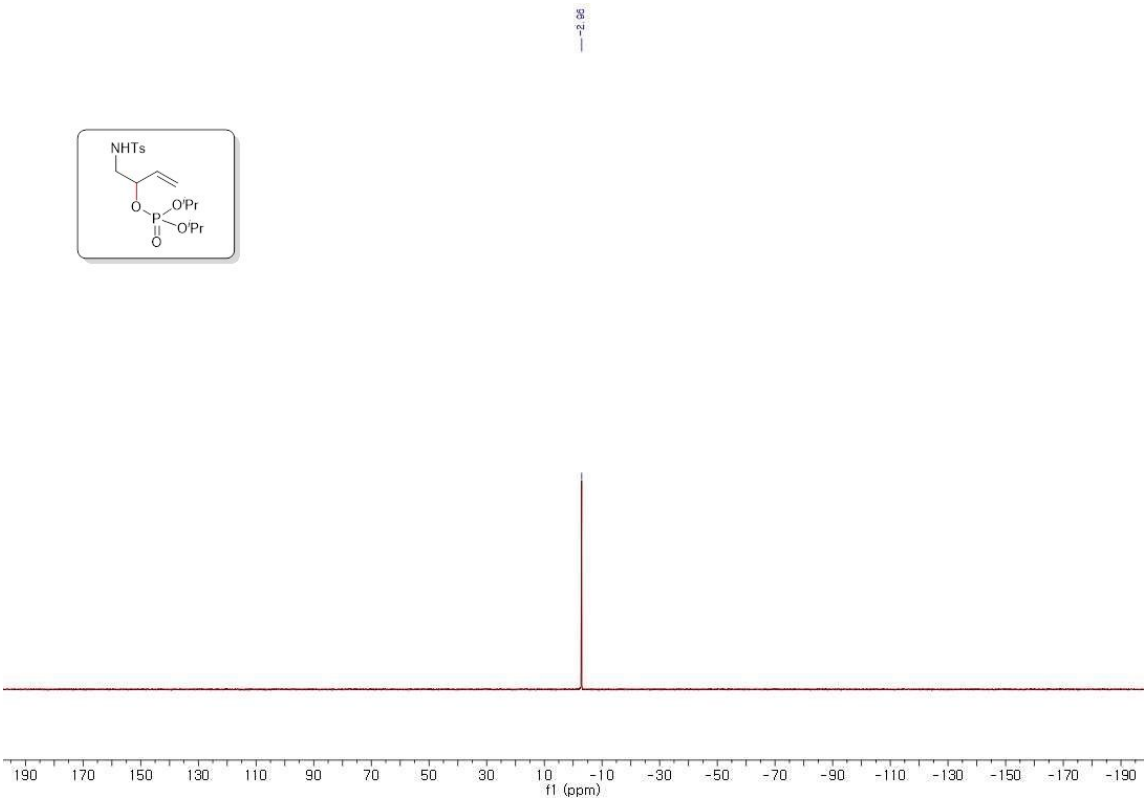
diisopropyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4c)



400 MHz, ^{1}H NMR in $CDCl_3$

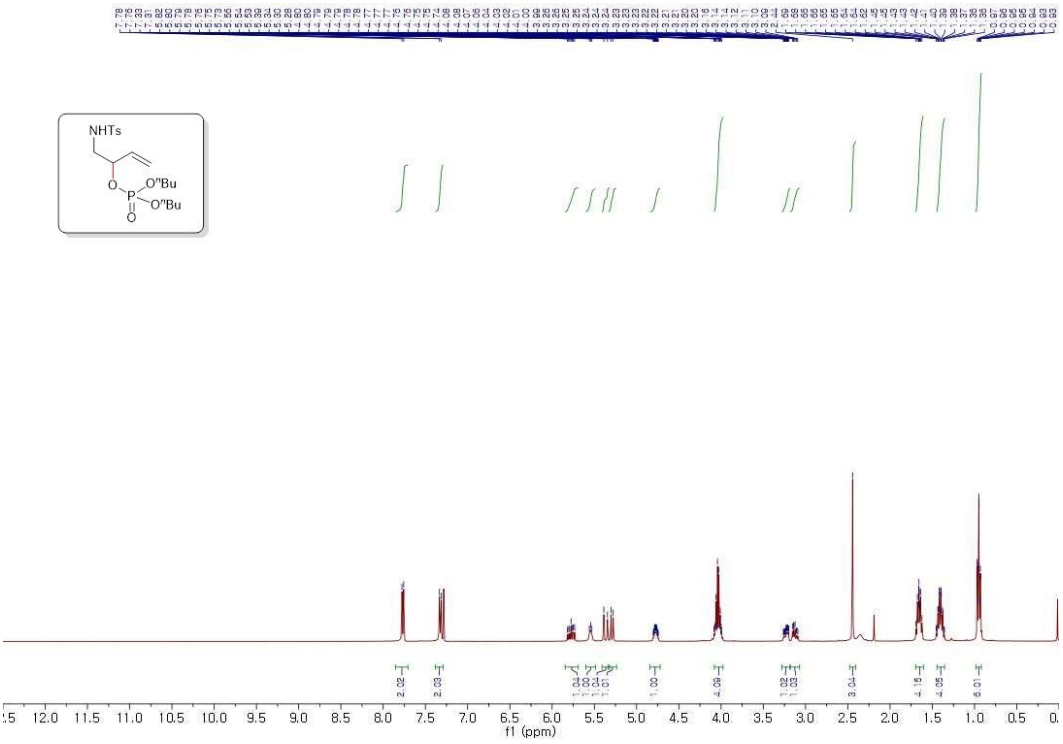


100 MHz, ^{13}C NMR in $CDCl_3$

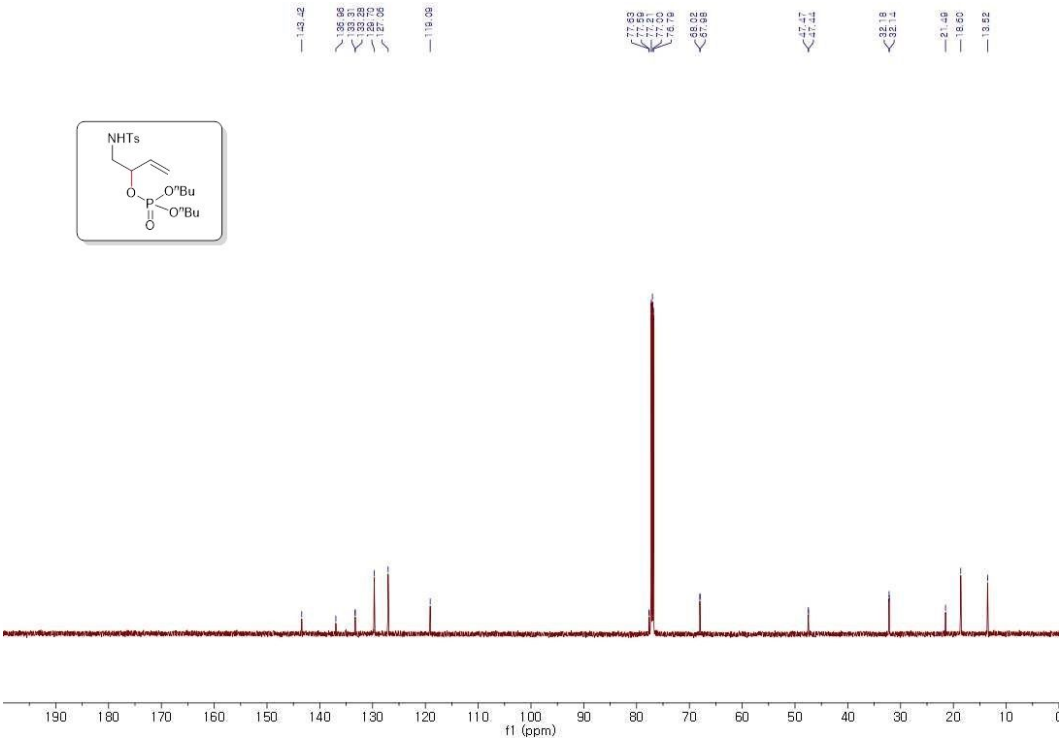


162 MHz, ^{31}P NMR in $CDCl_3$

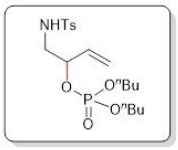
dibutyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4d)



400 MHz, ^{1}H NMR in $CDCl_3$

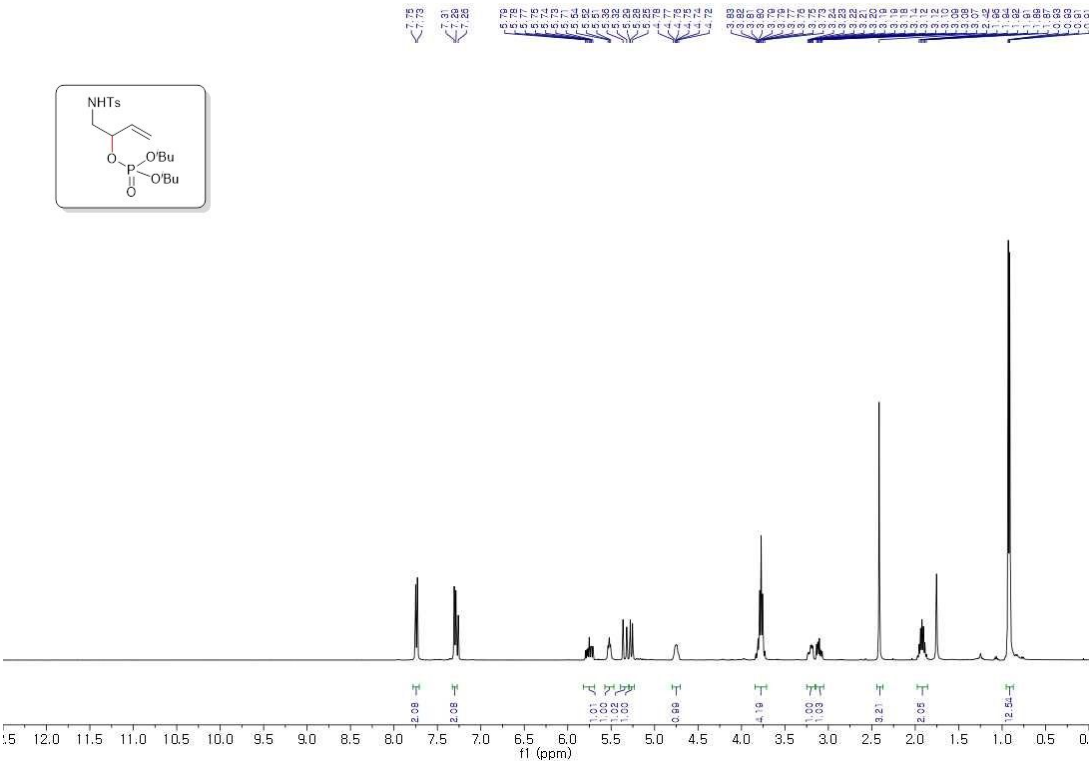


150 MHz, ^{13}C NMR in $CDCl_3$

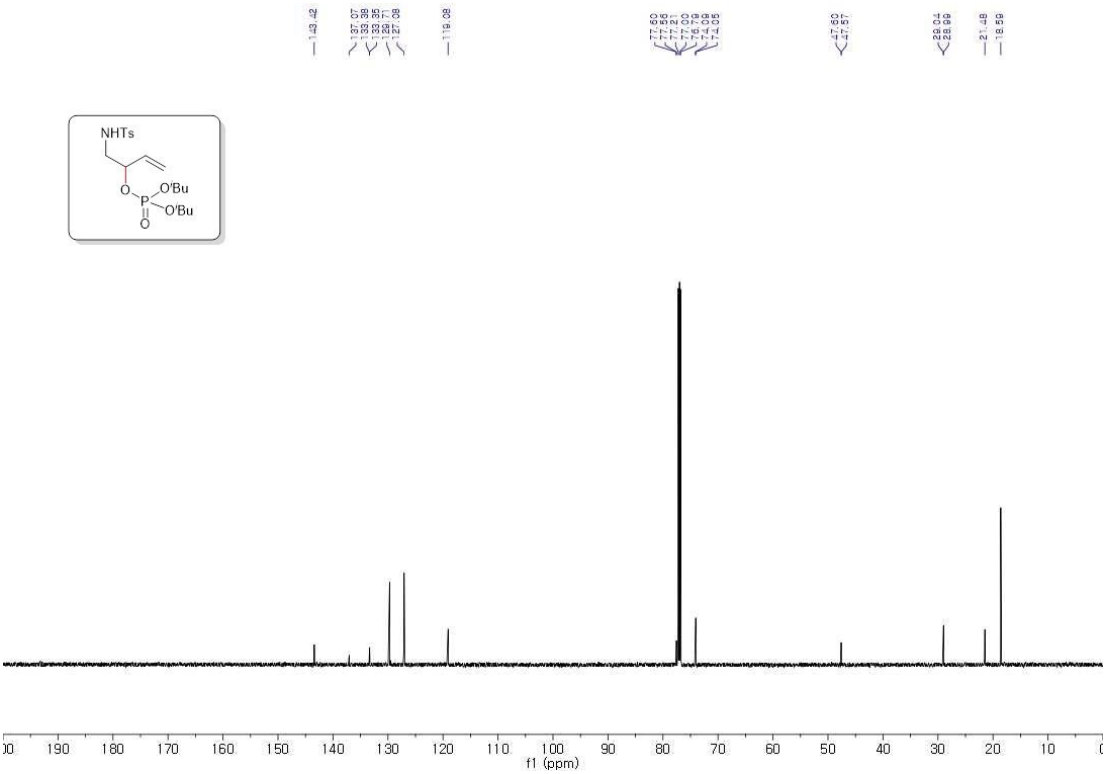


243 MHz, ^{31}P NMR in $CDCl_3$

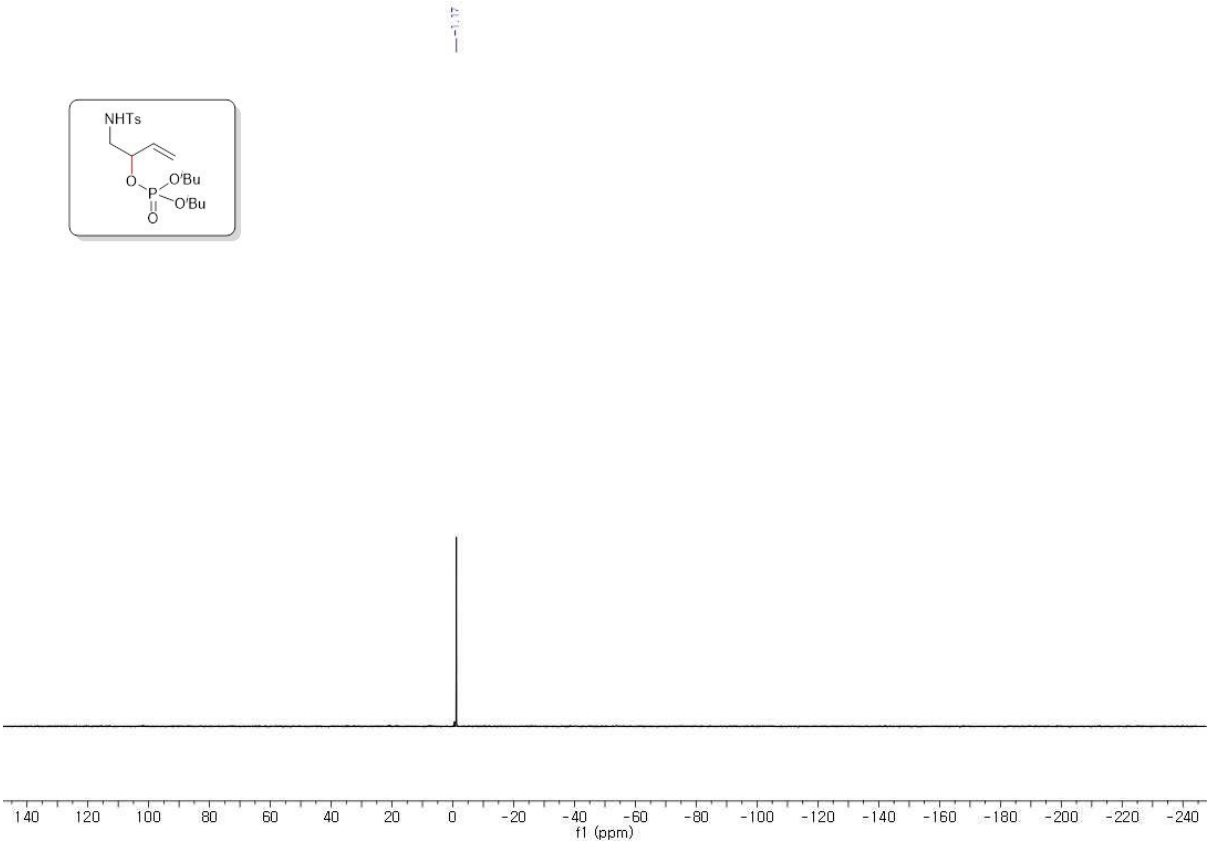
diisobutyl (1-((4-methylphenyl)sulfonamido)but-3-en-2-yl) phosphate (4e)



400 MHz, ^{1}H NMR in $CDCl_3$

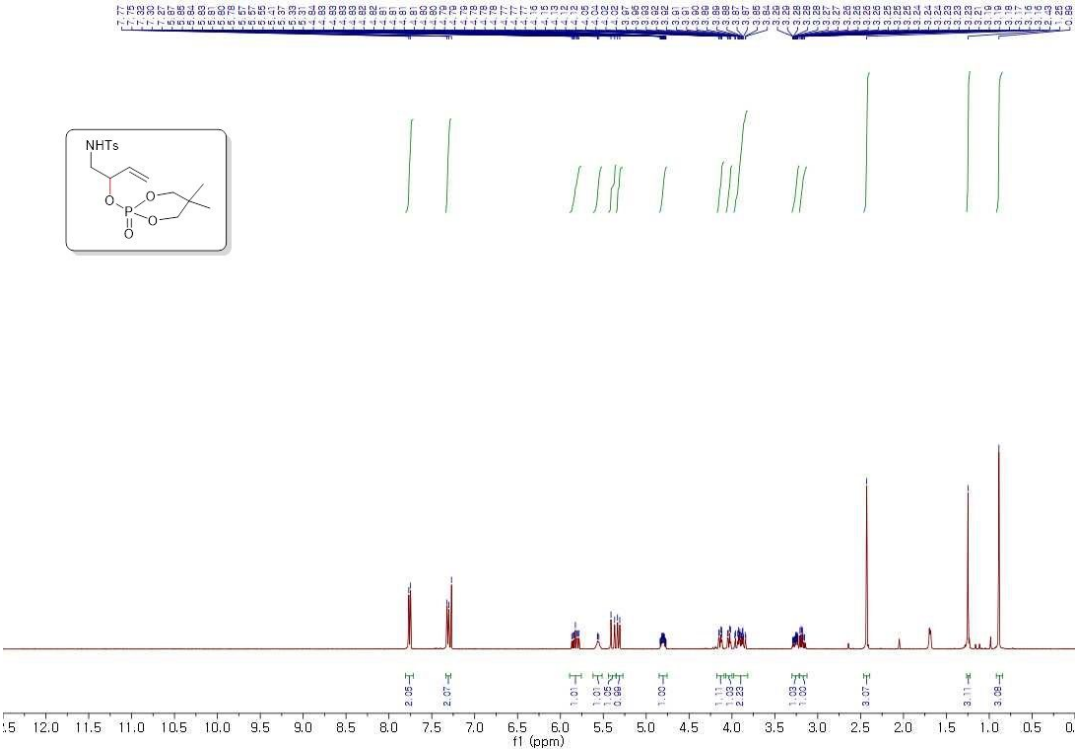


150 MHz, ^{13}C NMR in $CDCl_3$

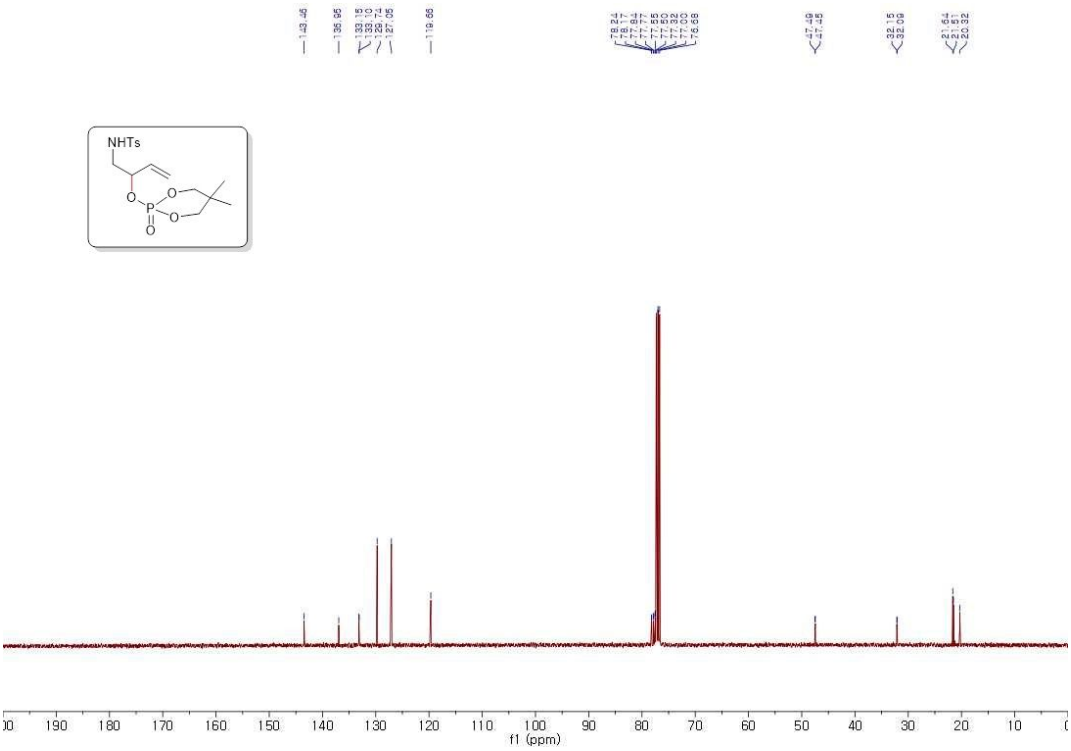


162 MHz, ^{31}P NMR in $CDCl_3$

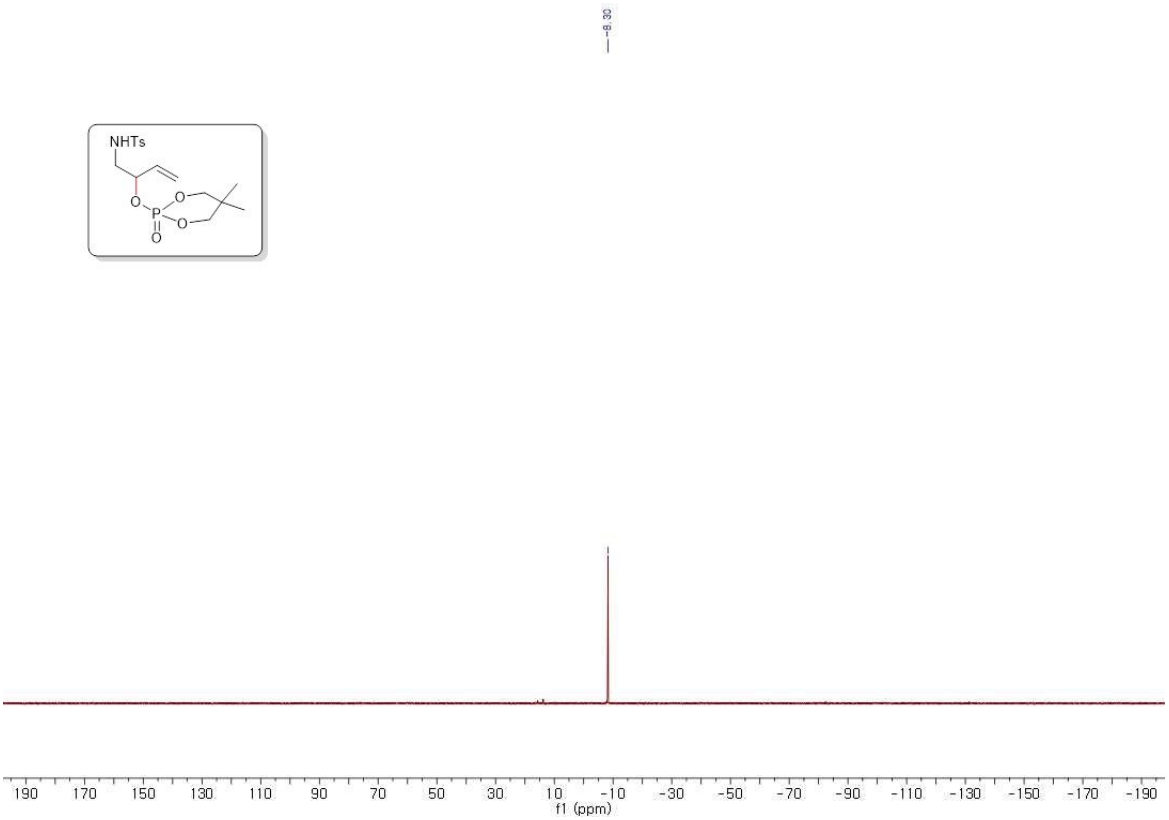
N-(2-((5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)oxy)but-3-en-1-yl)-4-methylbenzenesulfonamide (4f)



400 MHz, ^{1}H NMR in $CDCl_3$

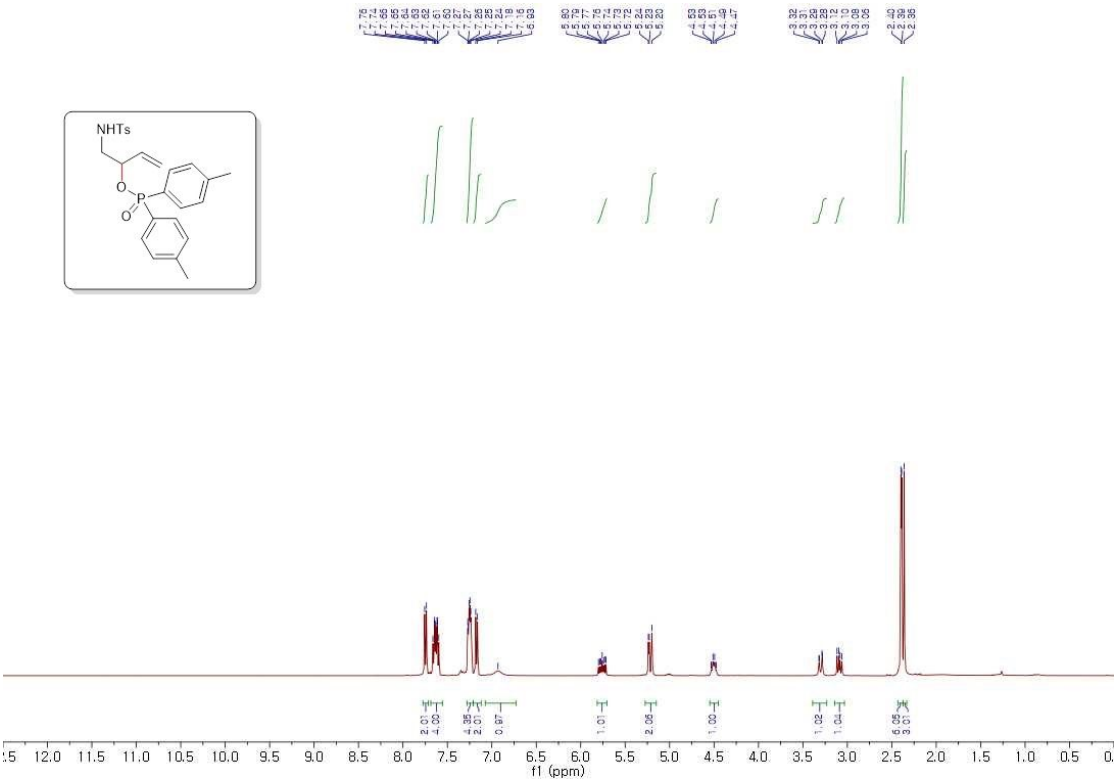


150 MHz, ^{13}C NMR in $CDCl_3$

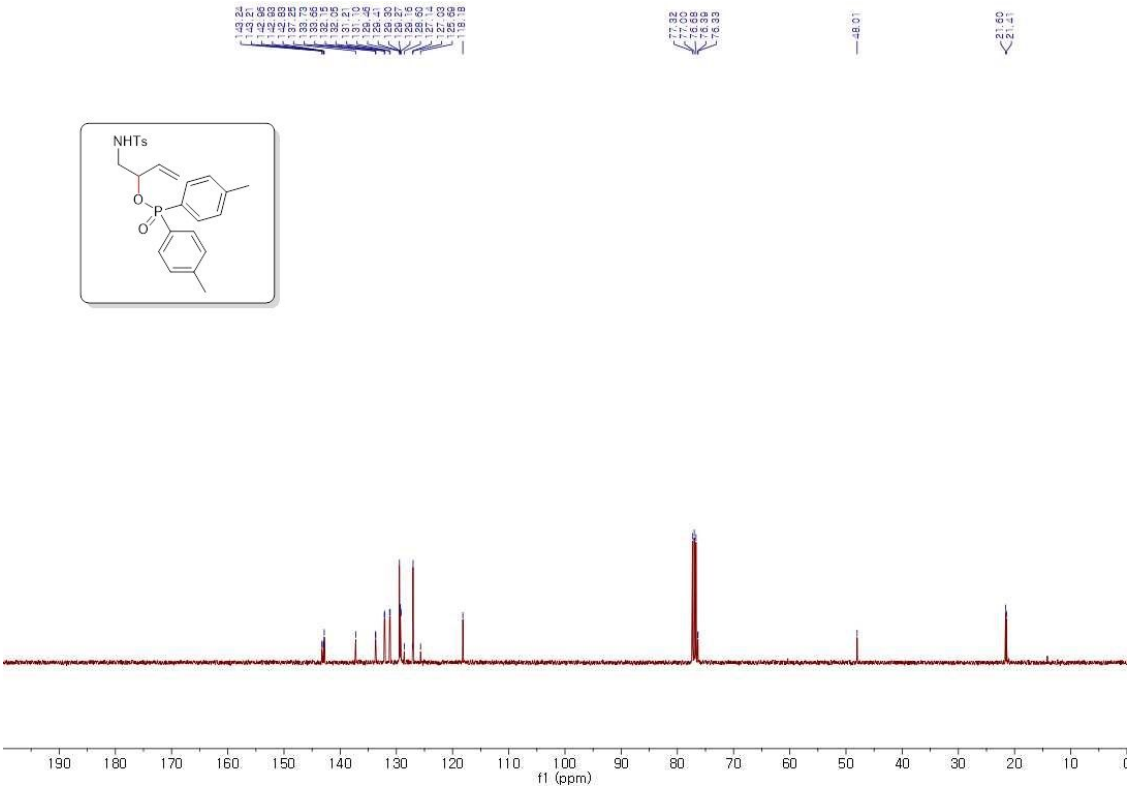


162 MHz, ^{31}P NMR in $CDCl_3$

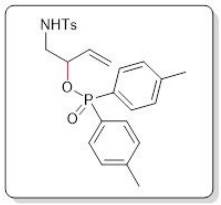
1-((4-methylphenyl)sulfonamido)but-3-en-2-yl di-p-tolylphosphinate (4g)



400 MHz, ^{1}H NMR in $CDCl_3$

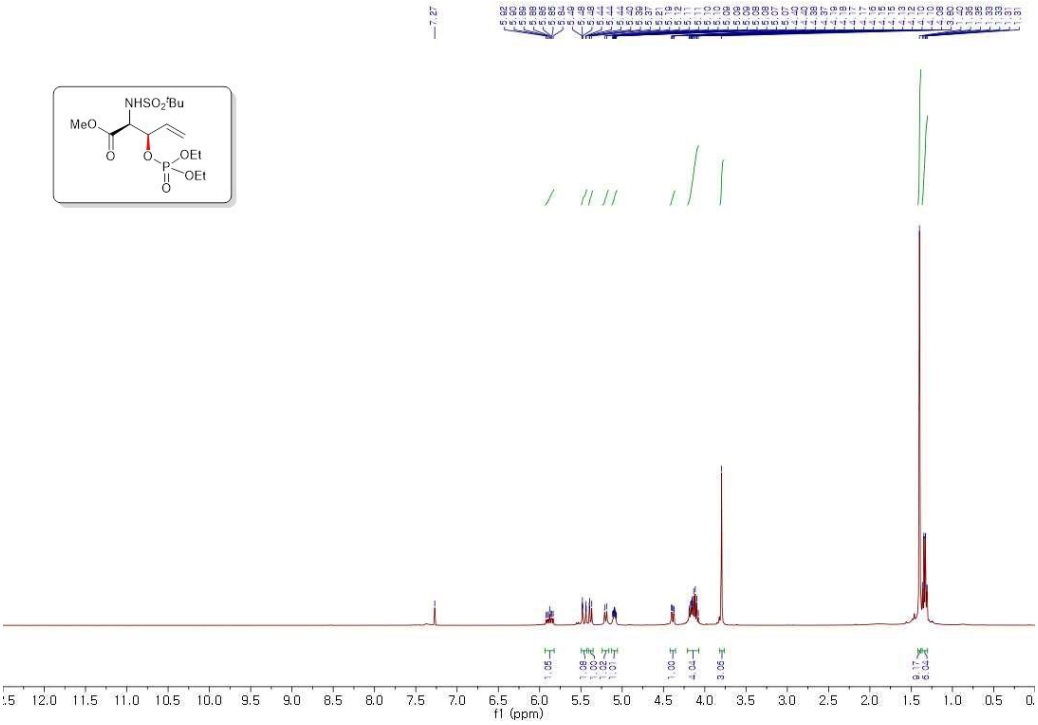


100 MHz, ^{13}C NMR in $CDCl_3$

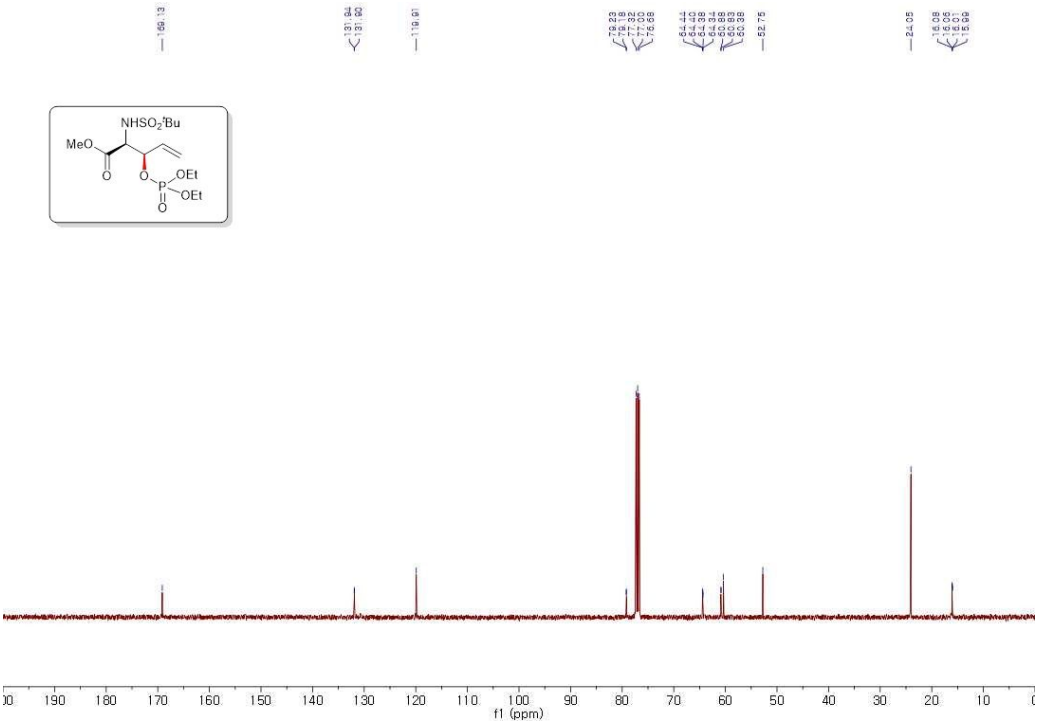


162 MHz, ^{31}P NMR in $CDCl_3$

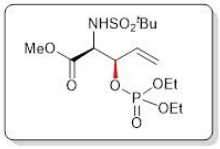
methyl (2S,3S)-3-((diethoxyphosphoryl)oxy)-2-((1,1-dimethylethyl)sulfonamido)pent-4-enoate (4h)



400 MHz, ^{1}H NMR in $CDCl_3$

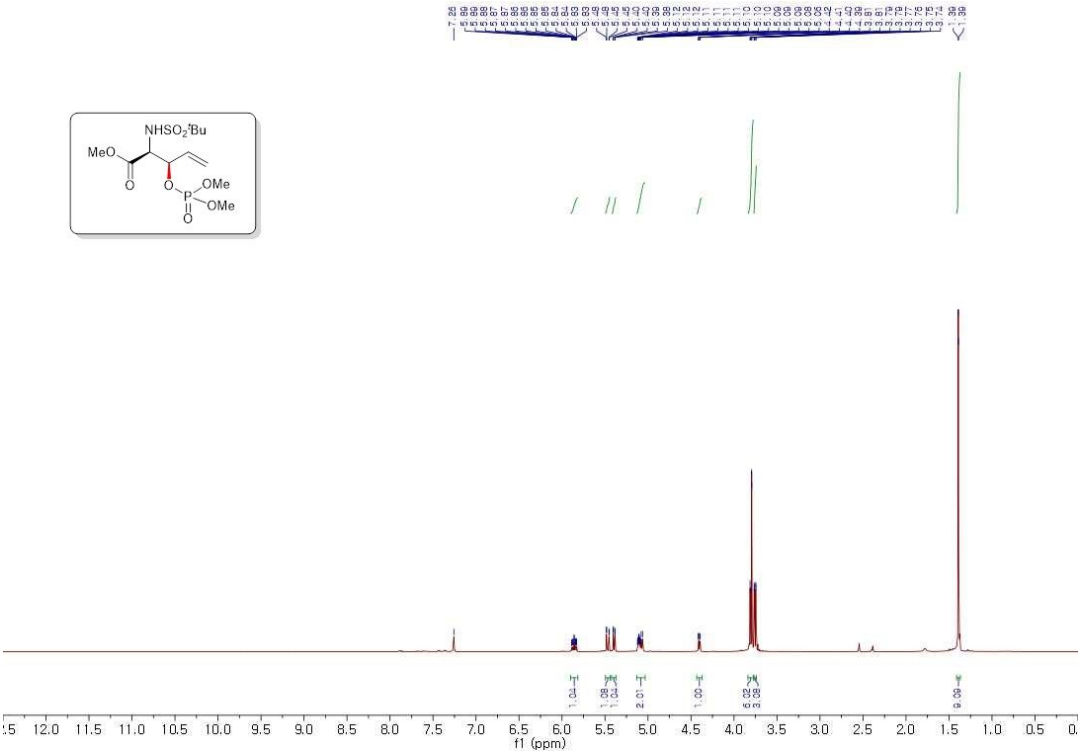


100 MHz, ^{13}C NMR in $CDCl_3$

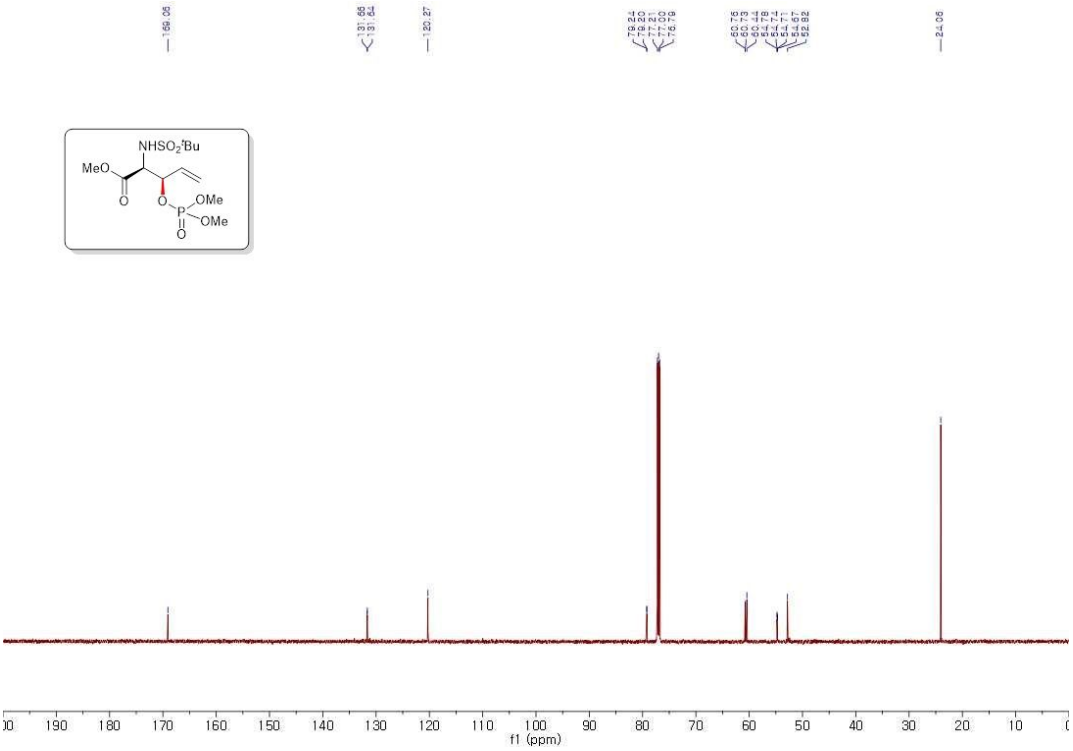


162 MHz, ^{31}P NMR in $CDCl_3$

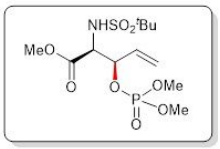
methyl (2R,3S)-3-((dimethoxyphosphoryl)oxy)-2-((1,1-dimethylethyl)sulfonamido)pent-4-enoate (4i)



400 MHz, ^{1}H NMR in $CDCl_3$

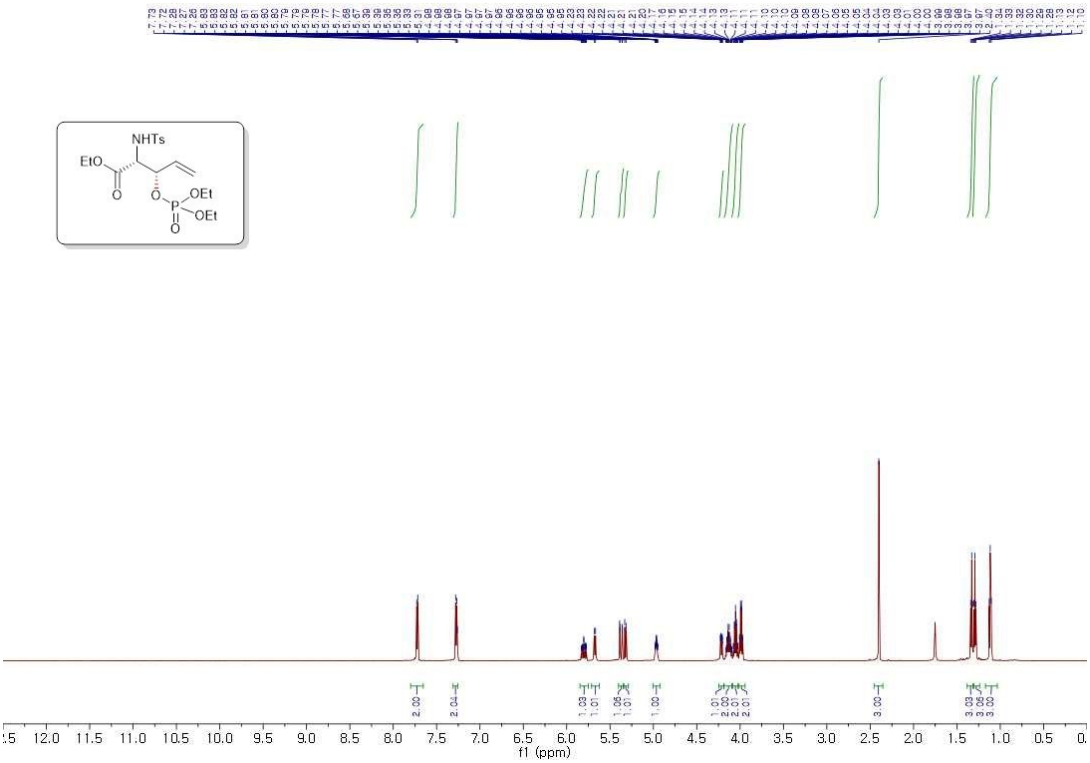


100 MHz, ^{13}C NMR in $CDCl_3$

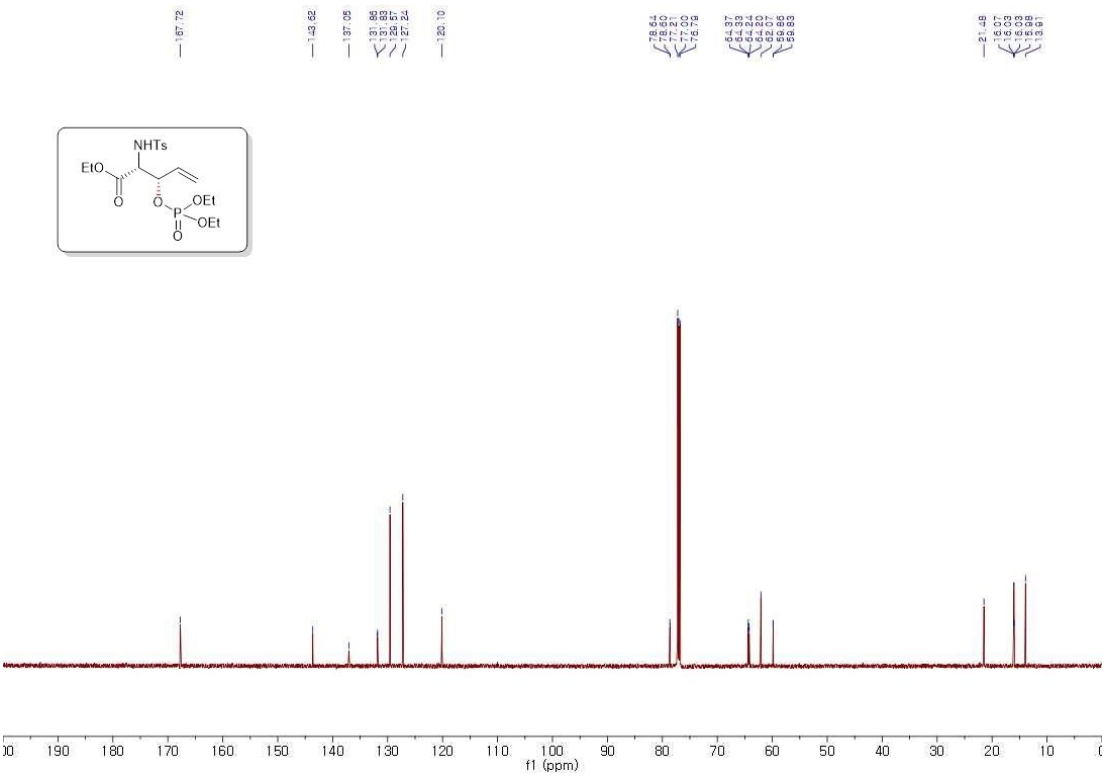


162 MHz, ^{31}P NMR in $CDCl_3$

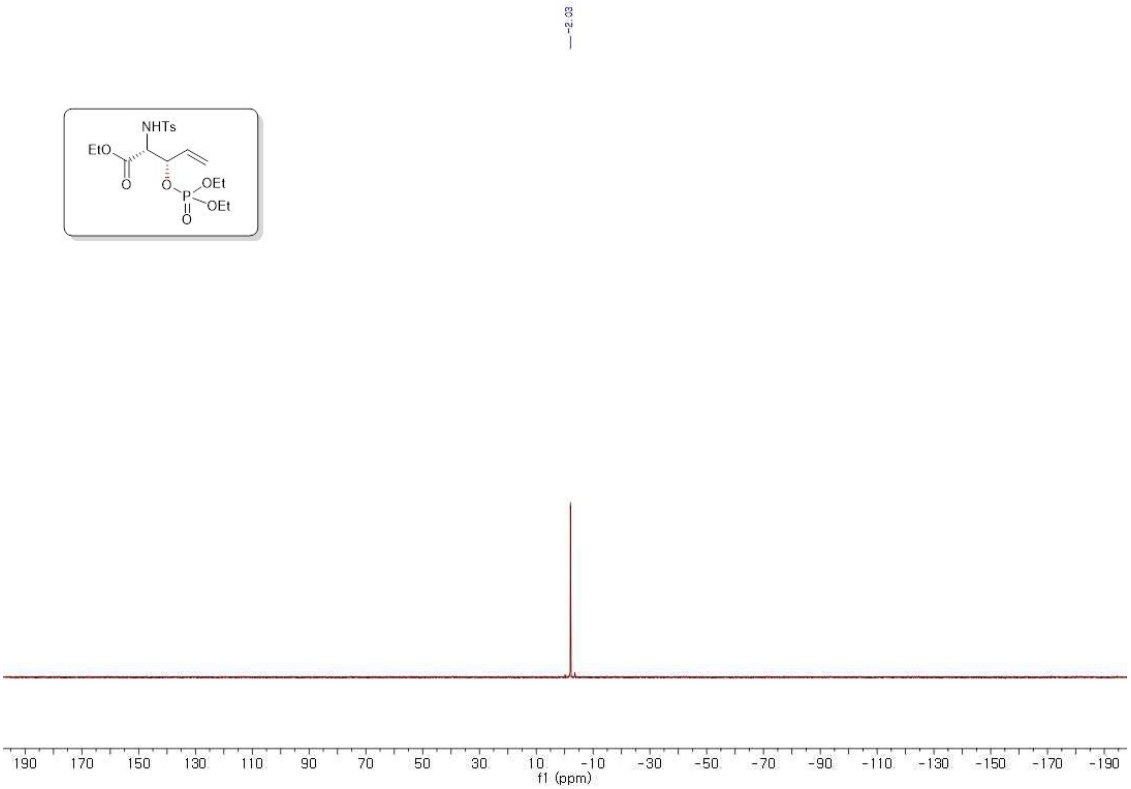
ethyl (2R)-3-((diethoxyphosphoryl)oxy)-2-((4-methylphenyl)sulfonamido)pent-4-enoate (4j)



600 MHz, ^{1}H NMR in $CDCl_3$



150 MHz, ^{13}C NMR in $CDCl_3$



162 MHz, ^{31}P NMR in $CDCl_3$

Appendix II

Crystallographic Data

Crystallographic Data for 3a (CCDC 1873505)

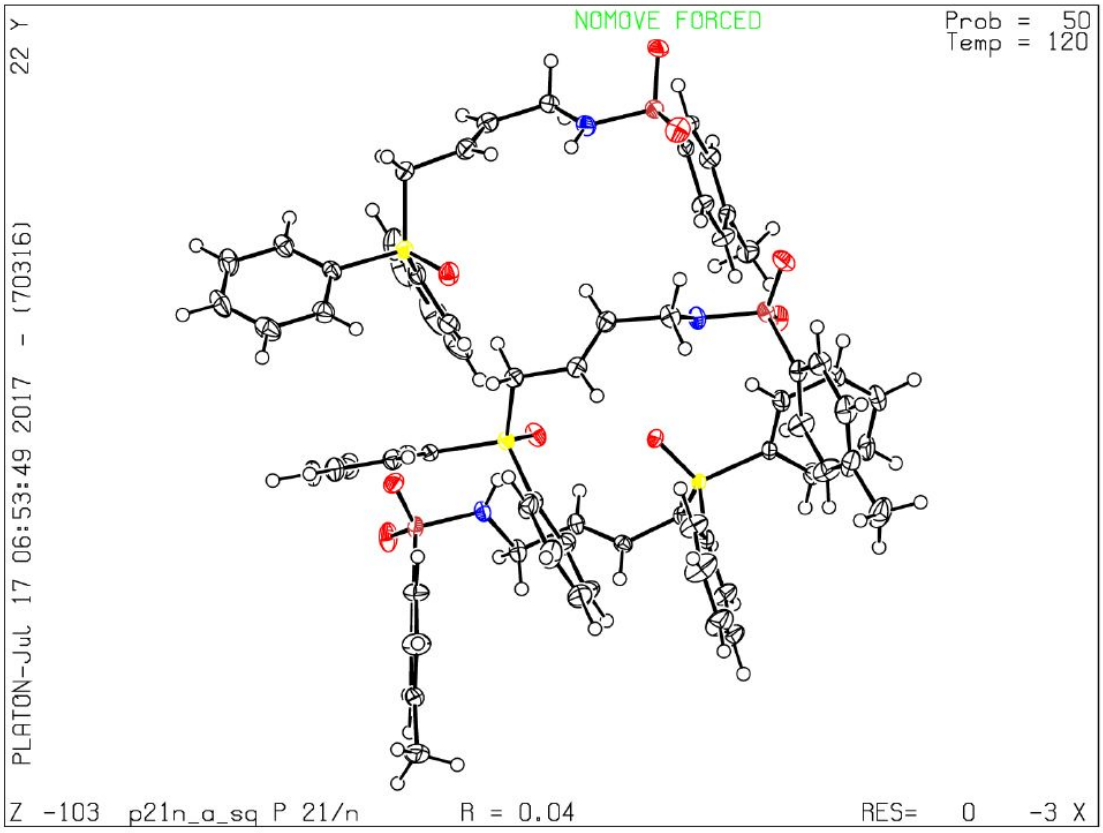


Table 1. Crystal data and structure refinement for p21n_a_sq.

Identification code	p21n_a_sq	
Empirical formula	C23 H24 N O3 P S	
Formula weight	425.46	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 14.4540(11) Å	α= 90°.
	b = 14.7931(11) Å	β= 102.836(3)°.
	c = 32.417(3) Å	γ = 90°.
Volume	6758.3(9) $Å^3$	
Z	12	
Density (calculated)	1.308 Mg/m^3	

Absorption coefficient	0.244 mm^{-1}
F(000)	2808
Crystal size	0.250 x 0.210 x 0.180 mm^3
Theta range for data collection	2.923 to 26.000°.
Index ranges	-17<=h<=17, -17<=k<=18, -39<=l<=39
Reflections collected	321407
Independent reflections	13210 [R(int) = 0.0582]
Completeness to theta = 25.242°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6804 and 0.6188
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13210 / 0 / 787
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0443, wR2 = 0.1149
R indices (all data)	R1 = 0.0527, wR2 = 0.1214
Extinction coefficient	n/a
Largest diff. peak and hole	0.955 and -0.733 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	7168(1)	4277(1)	5571(1)	17(1)
C(2)	6961(2)	4082(2)	5142(1)	21(1)
C(3)	6041(2)	3864(2)	4942(1)	23(1)
C(4)	5321(2)	3838(1)	5163(1)	20(1)
C(5)	4315(2)	3621(2)	4944(1)	26(1)
C(6)	5548(2)	4029(2)	5594(1)	23(1)
C(7)	6462(2)	4250(2)	5800(1)	22(1)
C(8)	8242(2)	6180(2)	5386(1)	23(1)
C(9)	8225(2)	7190(2)	5411(1)	26(1)
C(10)	8362(2)	7656(2)	5761(1)	26(1)
C(11)	8286(2)	8673(2)	5784(1)	26(1)
C(12)	6217(2)	8829(1)	5559(1)	22(1)
C(13)	6231(2)	9016(2)	5137(1)	36(1)
C(14)	5414(3)	8905(2)	4827(1)	53(1)
C(15)	4592(2)	8615(2)	4932(1)	63(1)
C(16)	4568(2)	8431(2)	5351(1)	54(1)
C(17)	5387(2)	8538(2)	5665(1)	33(1)
C(18)	7353(1)	10182(1)	6082(1)	20(1)
C(19)	7562(2)	10785(2)	5785(1)	24(1)
C(20)	7650(2)	11704(2)	5876(1)	30(1)
C(21)	7523(2)	12022(2)	6260(1)	32(1)
C(22)	7304(2)	11431(2)	6556(1)	32(1)
C(23)	7224(2)	10509(2)	6468(1)	26(1)
C(24)	5392(2)	3593(1)	7344(1)	20(1)
C(25)	5942(2)	3283(2)	7723(1)	27(1)
C(26)	5515(2)	3093(2)	8056(1)	32(1)
C(27)	4551(2)	3212(2)	8019(1)	32(1)
C(28)	4097(3)	2984(2)	8383(1)	47(1)

C(29)	4019(2)	3544(2)	7640(1)	36(1)
C(30)	4426(2)	3730(2)	7301(1)	29(1)
C(31)	6742(2)	5338(2)	7263(1)	23(1)
C(32)	6786(2)	6320(2)	7158(1)	22(1)
C(33)	6425(2)	6958(2)	7357(1)	20(1)
C(34)	6352(1)	7938(1)	7233(1)	19(1)
C(35)	3685(2)	7804(2)	7466(1)	31(1)
C(36)	4619(2)	8109(1)	7532(1)	21(1)
C(37)	3770(2)	7846(2)	8214(1)	42(1)
C(38)	3265(2)	7672(2)	7808(1)	41(1)
C(39)	4693(2)	8148(2)	8283(1)	39(1)
C(40)	5123(2)	8275(2)	7944(1)	29(1)
C(41)	5101(1)	9456(1)	6964(1)	18(1)
C(42)	4608(2)	9758(2)	6569(1)	23(1)
C(43)	4561(2)	10676(2)	6479(1)	31(1)
C(44)	5008(2)	11293(2)	6776(1)	34(1)
C(45)	5512(2)	10996(2)	7170(1)	29(1)
C(46)	5555(2)	10083(2)	7263(1)	23(1)
C(47)	1364(2)	10067(1)	5891(1)	18(1)
C(48)	407(2)	10279(2)	5819(1)	24(1)
C(49)	20(2)	10505(2)	6161(1)	28(1)
C(50)	562(2)	10512(2)	6572(1)	27(1)
C(51)	104(2)	10727(2)	6934(1)	39(1)
C(52)	1517(2)	10303(2)	6633(1)	31(1)
C(53)	1923(2)	10078(2)	6298(1)	25(1)
C(54)	823(2)	8251(1)	5310(1)	22(1)
C(55)	941(2)	7255(1)	5251(1)	19(1)
C(56)	776(1)	6647(1)	5521(1)	17(1)
C(57)	961(1)	5651(1)	5496(1)	16(1)
C(58)	2134(2)	4118(1)	5835(1)	16(1)
C(59)	1375(2)	3528(2)	5702(1)	24(1)
C(60)	1545(2)	2610(2)	5674(1)	29(1)
C(61)	2460(2)	2278(2)	5776(1)	29(1)

C(62)	3213(2)	2858(2)	5911(1)	29(1)
C(63)	3055(2)	3777(2)	5941(1)	24(1)
C(64)	786(2)	5394(2)	6468(1)	26(1)
C(65)	1703(2)	5473(1)	6404(1)	17(1)
C(66)	2442(2)	5662(2)	6747(1)	30(1)
C(67)	2264(2)	5757(2)	7146(1)	41(1)
C(68)	1351(2)	5680(2)	7207(1)	38(1)
C(69)	615(2)	5504(2)	6867(1)	34(1)
N(1)	8287(1)	5752(1)	5802(1)	23(1)
N(2)	6107(1)	4889(1)	6904(1)	20(1)
N(3)	1778(1)	8661(1)	5416(1)	19(1)
O(1)	7172(1)	8447(1)	6361(1)	26(1)
O(2)	4587(1)	7743(1)	6703(1)	23(1)
O(3)	2875(1)	5823(1)	5873(1)	17(1)
O(4)	8977(1)	4347(1)	5591(1)	25(1)
O(5)	8450(1)	4426(1)	6266(1)	30(1)
O(6)	6832(1)	3376(1)	7008(1)	26(1)
O(7)	5245(1)	3605(1)	6533(1)	25(1)
O(8)	2871(1)	9938(1)	5589(1)	26(1)
O(9)	1313(1)	10151(1)	5090(1)	30(1)
P(1)	7242(1)	8983(1)	5978(1)	18(1)
P(2)	5122(1)	8262(1)	7075(1)	16(1)
P(3)	1990(1)	5316(1)	5896(1)	14(1)
S(1)	8303(1)	4652(1)	5828(1)	20(1)
S(2)	5925(1)	3818(1)	6915(1)	18(1)
S(3)	1874(1)	9746(1)	5467(1)	19(1)

Table 3. Bond lengths [Å] and angles [°] for **3a**.

C(1)-C(2)	1.387(3)
C(1)-C(7)	1.389(3)
C(1)-S(1)	1.757(2)
C(2)-C(3)	1.383(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.389(3)
C(3)-H(3)	0.9500
C(4)-C(6)	1.390(3)
C(4)-C(5)	1.505(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-C(7)	1.381(3)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-N(1)	1.476(3)
C(8)-C(9)	1.497(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.305(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.512(3)
C(10)-H(10)	0.9500
C(11)-P(1)	1.819(2)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(17)	1.390(3)
C(12)-C(13)	1.398(3)
C(12)-P(1)	1.789(2)
C(13)-C(14)	1.379(4)
C(13)-H(13)	0.9500

C(14)-C(15)	1.375(6)
C(14)-H(14)	0.9500
C(15)-C(16)	1.391(6)
C(15)-H(15)	0.9500
C(16)-C(17)	1.389(4)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(23)	1.391(3)
C(18)-C(19)	1.393(3)
C(18)-P(1)	1.806(2)
C(19)-C(20)	1.390(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.381(4)
C(20)-H(20)	0.9500
C(21)-C(22)	1.387(4)
C(21)-H(21)	0.9500
C(22)-C(23)	1.393(3)
C(22)-H(22)	0.9500
C(23)-H(23)	0.9500
C(24)-C(30)	1.387(3)
C(24)-C(25)	1.385(3)
C(24)-S(2)	1.764(2)
C(25)-C(26)	1.385(3)
C(25)-H(25)	0.9500
C(26)-C(27)	1.382(4)
C(26)-H(26)	0.9500
C(27)-C(29)	1.385(4)
C(27)-C(28)	1.511(3)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-C(30)	1.384(3)
C(29)-H(29)	0.9500

C(30)-H(30)	0.9500
C(31)-N(2)	1.471(3)
C(31)-C(32)	1.497(3)
C(31)-H(31A)	0.9900
C(31)-H(31B)	0.9900
C(32)-C(33)	1.314(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.502(3)
C(33)-H(33)	0.9500
C(34)-P(2)	1.803(2)
C(34)-H(34A)	0.9900
C(34)-H(34B)	0.9900
C(35)-C(38)	1.389(4)
C(35)-C(36)	1.395(3)
C(35)-H(35)	0.9500
C(36)-C(40)	1.394(3)
C(36)-P(2)	1.803(2)
C(37)-C(39)	1.377(4)
C(37)-C(38)	1.380(4)
C(37)-H(37)	0.9500
C(38)-H(38)	0.9500
C(39)-C(40)	1.388(3)
C(39)-H(39)	0.9500
C(40)-H(40)	0.9500
C(41)-C(42)	1.393(3)
C(41)-C(46)	1.395(3)
C(41)-P(2)	1.801(2)
C(42)-C(43)	1.389(3)
C(42)-H(42)	0.9500
C(43)-C(44)	1.377(4)
C(43)-H(43)	0.9500
C(44)-C(45)	1.394(4)
C(44)-H(44)	0.9500

C(45)-C(46)	1.383(3)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(47)-C(53)	1.385(3)
C(47)-C(48)	1.388(3)
C(47)-S(3)	1.763(2)
C(48)-C(49)	1.387(3)
C(48)-H(48)	0.9500
C(49)-C(50)	1.388(4)
C(49)-H(49)	0.9500
C(50)-C(52)	1.386(3)
C(50)-C(51)	1.503(3)
C(51)-H(51A)	0.9800
C(51)-H(51B)	0.9800
C(51)-H(51C)	0.9800
C(52)-C(53)	1.385(3)
C(52)-H(52)	0.9500
C(53)-H(53)	0.9500
C(54)-N(3)	1.476(3)
C(54)-C(55)	1.500(3)
C(54)-H(54A)	0.9900
C(54)-H(54B)	0.9900
C(55)-C(56)	1.313(3)
C(55)-H(55)	0.9500
C(56)-C(57)	1.502(3)
C(56)-H(56)	0.9500
C(57)-P(3)	1.813(2)
C(57)-H(57A)	0.9900
C(57)-H(57B)	0.9900
C(58)-C(59)	1.392(3)
C(58)-C(63)	1.393(3)
C(58)-P(3)	1.801(2)
C(59)-C(60)	1.387(3)

C(59)-H(59)	0.9500
C(60)-C(61)	1.381(4)
C(60)-H(60)	0.9500
C(61)-C(62)	1.379(3)
C(61)-H(61)	0.9500
C(62)-C(63)	1.385(3)
C(62)-H(62)	0.9500
C(63)-H(63)	0.9500
C(64)-C(69)	1.379(3)
C(64)-C(65)	1.391(3)
C(64)-H(64)	0.9500
C(65)-C(66)	1.389(3)
C(65)-P(3)	1.799(2)
C(66)-C(67)	1.381(3)
C(66)-H(66)	0.9500
C(67)-C(68)	1.381(4)
C(67)-H(67)	0.9500
C(68)-C(69)	1.378(4)
C(68)-H(68)	0.9500
C(69)-H(69)	0.9500
N(1)-S(1)	1.6287(19)
N(1)-H(1)	0.8800
N(2)-S(2)	1.6081(18)
N(2)-H(2A)	0.8800
N(3)-S(3)	1.6167(18)
N(3)-H(3A)	0.8800
O(1)-P(1)	1.4941(16)
O(2)-P(2)	1.4926(15)
O(3)-P(3)	1.4983(14)
O(4)-S(1)	1.4430(16)
O(5)-S(1)	1.4281(17)
O(6)-S(2)	1.4354(16)
O(7)-S(2)	1.4342(16)

O(8)-S(3)	1.4349(17)
O(9)-S(3)	1.4396(17)

C(2)-C(1)-C(7)	120.70(19)
C(2)-C(1)-S(1)	120.74(16)
C(7)-C(1)-S(1)	118.37(16)
C(3)-C(2)-C(1)	119.33(19)
C(3)-C(2)-H(2)	120.3
C(1)-C(2)-H(2)	120.3
C(2)-C(3)-C(4)	121.1(2)
C(2)-C(3)-H(3)	119.5
C(4)-C(3)-H(3)	119.5
C(3)-C(4)-C(6)	118.45(19)
C(3)-C(4)-C(5)	121.1(2)
C(6)-C(4)-C(5)	120.4(2)
C(4)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(4)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(7)-C(6)-C(4)	121.5(2)
C(7)-C(6)-H(6)	119.3
C(4)-C(6)-H(6)	119.3
C(6)-C(7)-C(1)	118.9(2)
C(6)-C(7)-H(7)	120.5
C(1)-C(7)-H(7)	120.5
N(1)-C(8)-C(9)	112.17(18)
N(1)-C(8)-H(8A)	109.2
C(9)-C(8)-H(8A)	109.2
N(1)-C(8)-H(8B)	109.2
C(9)-C(8)-H(8B)	109.2
H(8A)-C(8)-H(8B)	107.9

C(10)-C(9)-C(8)	125.0(2)
C(10)-C(9)-H(9)	117.5
C(8)-C(9)-H(9)	117.5
C(9)-C(10)-C(11)	124.7(2)
C(9)-C(10)-H(10)	117.7
C(11)-C(10)-H(10)	117.7
C(10)-C(11)-P(1)	109.98(15)
C(10)-C(11)-H(11A)	109.7
P(1)-C(11)-H(11A)	109.7
C(10)-C(11)-H(11B)	109.7
P(1)-C(11)-H(11B)	109.7
H(11A)-C(11)-H(11B)	108.2
C(17)-C(12)-C(13)	120.3(2)
C(17)-C(12)-P(1)	117.75(19)
C(13)-C(12)-P(1)	121.93(19)
C(14)-C(13)-C(12)	119.5(3)
C(14)-C(13)-H(13)	120.2
C(12)-C(13)-H(13)	120.2
C(15)-C(14)-C(13)	120.2(3)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	120.9(3)
C(14)-C(15)-H(15)	119.6
C(16)-C(15)-H(15)	119.6
C(17)-C(16)-C(15)	119.4(3)
C(17)-C(16)-H(16)	120.3
C(15)-C(16)-H(16)	120.3
C(16)-C(17)-C(12)	119.7(3)
C(16)-C(17)-H(17)	120.2
C(12)-C(17)-H(17)	120.2
C(23)-C(18)-C(19)	119.4(2)
C(23)-C(18)-P(1)	118.97(17)
C(19)-C(18)-P(1)	121.59(17)

C(20)-C(19)-C(18)	120.2(2)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(21)-C(20)-C(19)	120.0(2)
C(21)-C(20)-H(20)	120.0
C(19)-C(20)-H(20)	120.0
C(20)-C(21)-C(22)	120.4(2)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(21)-C(22)-C(23)	119.8(2)
C(21)-C(22)-H(22)	120.1
C(23)-C(22)-H(22)	120.1
C(18)-C(23)-C(22)	120.2(2)
C(18)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(30)-C(24)-C(25)	120.2(2)
C(30)-C(24)-S(2)	120.02(17)
C(25)-C(24)-S(2)	119.79(18)
C(26)-C(25)-C(24)	119.4(2)
C(26)-C(25)-H(25)	120.3
C(24)-C(25)-H(25)	120.3
C(27)-C(26)-C(25)	121.4(2)
C(27)-C(26)-H(26)	119.3
C(25)-C(26)-H(26)	119.3
C(26)-C(27)-C(29)	118.2(2)
C(26)-C(27)-C(28)	120.5(3)
C(29)-C(27)-C(28)	121.3(3)
C(27)-C(28)-H(28A)	109.5
C(27)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(27)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5

C(30)-C(29)-C(27)	121.5(2)
C(30)-C(29)-H(29)	119.2
C(27)-C(29)-H(29)	119.2
C(29)-C(30)-C(24)	119.2(2)
C(29)-C(30)-H(30)	120.4
C(24)-C(30)-H(30)	120.4
N(2)-C(31)-C(32)	108.01(17)
N(2)-C(31)-H(31A)	110.1
C(32)-C(31)-H(31A)	110.1
N(2)-C(31)-H(31B)	110.1
C(32)-C(31)-H(31B)	110.1
H(31A)-C(31)-H(31B)	108.4
C(33)-C(32)-C(31)	122.9(2)
C(33)-C(32)-H(32)	118.5
C(31)-C(32)-H(32)	118.5
C(32)-C(33)-C(34)	125.0(2)
C(32)-C(33)-H(33)	117.5
C(34)-C(33)-H(33)	117.5
C(33)-C(34)-P(2)	109.86(14)
C(33)-C(34)-H(34A)	109.7
P(2)-C(34)-H(34A)	109.7
C(33)-C(34)-H(34B)	109.7
P(2)-C(34)-H(34B)	109.7
H(34A)-C(34)-H(34B)	108.2
C(38)-C(35)-C(36)	120.2(2)
C(38)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(40)-C(36)-C(35)	119.0(2)
C(40)-C(36)-P(2)	123.07(17)
C(35)-C(36)-P(2)	117.91(18)
C(39)-C(37)-C(38)	120.3(2)
C(39)-C(37)-H(37)	119.9
C(38)-C(37)-H(37)	119.9

C(37)-C(38)-C(35)	120.1(3)
C(37)-C(38)-H(38)	120.0
C(35)-C(38)-H(38)	120.0
C(37)-C(39)-C(40)	120.2(3)
C(37)-C(39)-H(39)	119.9
C(40)-C(39)-H(39)	119.9
C(39)-C(40)-C(36)	120.2(2)
C(39)-C(40)-H(40)	119.9
C(36)-C(40)-H(40)	119.9
C(42)-C(41)-C(46)	119.4(2)
C(42)-C(41)-P(2)	118.70(16)
C(46)-C(41)-P(2)	121.89(17)
C(43)-C(42)-C(41)	119.8(2)
C(43)-C(42)-H(42)	120.1
C(41)-C(42)-H(42)	120.1
C(44)-C(43)-C(42)	120.5(2)
C(44)-C(43)-H(43)	119.7
C(42)-C(43)-H(43)	119.7
C(43)-C(44)-C(45)	120.1(2)
C(43)-C(44)-H(44)	120.0
C(45)-C(44)-H(44)	120.0
C(46)-C(45)-C(44)	119.8(2)
C(46)-C(45)-H(45)	120.1
C(44)-C(45)-H(45)	120.1
C(45)-C(46)-C(41)	120.4(2)
C(45)-C(46)-H(46)	119.8
C(41)-C(46)-H(46)	119.8
C(53)-C(47)-C(48)	120.4(2)
C(53)-C(47)-S(3)	119.31(16)
C(48)-C(47)-S(3)	120.26(17)
C(49)-C(48)-C(47)	119.0(2)
C(49)-C(48)-H(48)	120.5
C(47)-C(48)-H(48)	120.5

C(48)-C(49)-C(50)	121.8(2)
C(48)-C(49)-H(49)	119.1
C(50)-C(49)-H(49)	119.1
C(52)-C(50)-C(49)	117.9(2)
C(52)-C(50)-C(51)	122.2(2)
C(49)-C(50)-C(51)	119.9(2)
C(50)-C(51)-H(51A)	109.5
C(50)-C(51)-H(51B)	109.5
H(51A)-C(51)-H(51B)	109.5
C(50)-C(51)-H(51C)	109.5
H(51A)-C(51)-H(51C)	109.5
H(51B)-C(51)-H(51C)	109.5
C(50)-C(52)-C(53)	121.5(2)
C(50)-C(52)-H(52)	119.3
C(53)-C(52)-H(52)	119.3
C(47)-C(53)-C(52)	119.4(2)
C(47)-C(53)-H(53)	120.3
C(52)-C(53)-H(53)	120.3
N(3)-C(54)-C(55)	107.84(17)
N(3)-C(54)-H(54A)	110.1
C(55)-C(54)-H(54A)	110.1
N(3)-C(54)-H(54B)	110.1
C(55)-C(54)-H(54B)	110.1
H(54A)-C(54)-H(54B)	108.5
C(56)-C(55)-C(54)	123.0(2)
C(56)-C(55)-H(55)	118.5
C(54)-C(55)-H(55)	118.5
C(55)-C(56)-C(57)	125.17(19)
C(55)-C(56)-H(56)	117.4
C(57)-C(56)-H(56)	117.4
C(56)-C(57)-P(3)	110.89(14)
C(56)-C(57)-H(57A)	109.5
P(3)-C(57)-H(57A)	109.5

C(56)-C(57)-H(57B)	109.5
P(3)-C(57)-H(57B)	109.5
H(57A)-C(57)-H(57B)	108.0
C(59)-C(58)-C(63)	119.57(19)
C(59)-C(58)-P(3)	123.24(16)
C(63)-C(58)-P(3)	117.15(16)
C(60)-C(59)-C(58)	119.7(2)
C(60)-C(59)-H(59)	120.2
C(58)-C(59)-H(59)	120.2
C(61)-C(60)-C(59)	120.4(2)
C(61)-C(60)-H(60)	119.8
C(59)-C(60)-H(60)	119.8
C(62)-C(61)-C(60)	120.0(2)
C(62)-C(61)-H(61)	120.0
C(60)-C(61)-H(61)	120.0
C(61)-C(62)-C(63)	120.2(2)
C(61)-C(62)-H(62)	119.9
C(63)-C(62)-H(62)	119.9
C(62)-C(63)-C(58)	120.1(2)
C(62)-C(63)-H(63)	120.0
C(58)-C(63)-H(63)	120.0
C(69)-C(64)-C(65)	120.4(2)
C(69)-C(64)-H(64)	119.8
C(65)-C(64)-H(64)	119.8
C(66)-C(65)-C(64)	119.0(2)
C(66)-C(65)-P(3)	117.83(17)
C(64)-C(65)-P(3)	123.11(16)
C(67)-C(66)-C(65)	120.1(2)
C(67)-C(66)-H(66)	119.9
C(65)-C(66)-H(66)	119.9
C(66)-C(67)-C(68)	120.5(2)
C(66)-C(67)-H(67)	119.7
C(68)-C(67)-H(67)	119.7

C(69)-C(68)-C(67)	119.6(2)
C(69)-C(68)-H(68)	120.2
C(67)-C(68)-H(68)	120.2
C(64)-C(69)-C(68)	120.4(2)
C(64)-C(69)-H(69)	119.8
C(68)-C(69)-H(69)	119.8
C(8)-N(1)-S(1)	118.31(15)
C(8)-N(1)-H(1)	120.8
S(1)-N(1)-H(1)	120.8
C(31)-N(2)-S(2)	120.23(14)
C(31)-N(2)-H(2A)	119.9
S(2)-N(2)-H(2A)	119.9
C(54)-N(3)-S(3)	119.07(14)
C(54)-N(3)-H(3A)	120.5
S(3)-N(3)-H(3A)	120.5
O(1)-P(1)-C(12)	111.46(10)
O(1)-P(1)-C(18)	112.74(10)
C(12)-P(1)-C(18)	106.91(10)
O(1)-P(1)-C(11)	111.63(10)
C(12)-P(1)-C(11)	108.35(11)
C(18)-P(1)-C(11)	105.42(10)
O(2)-P(2)-C(41)	111.11(9)
O(2)-P(2)-C(34)	113.11(9)
C(41)-P(2)-C(34)	106.83(10)
O(2)-P(2)-C(36)	111.65(10)
C(41)-P(2)-C(36)	107.21(10)
C(34)-P(2)-C(36)	106.58(10)
O(3)-P(3)-C(65)	110.72(9)
O(3)-P(3)-C(58)	111.50(9)
C(65)-P(3)-C(58)	106.54(9)
O(3)-P(3)-C(57)	113.64(9)
C(65)-P(3)-C(57)	107.46(10)
C(58)-P(3)-C(57)	106.61(9)

O(5)-S(1)-O(4)	119.27(10)
O(5)-S(1)-N(1)	106.53(10)
O(4)-S(1)-N(1)	106.69(10)
O(5)-S(1)-C(1)	108.33(10)
O(4)-S(1)-C(1)	108.57(10)
N(1)-S(1)-C(1)	106.81(10)
O(7)-S(2)-O(6)	119.99(10)
O(7)-S(2)-N(2)	106.32(9)
O(6)-S(2)-N(2)	107.89(10)
O(7)-S(2)-C(24)	107.64(10)
O(6)-S(2)-C(24)	106.67(10)
N(2)-S(2)-C(24)	107.84(10)
O(8)-S(3)-O(9)	119.44(10)
O(8)-S(3)-N(3)	106.39(10)
O(9)-S(3)-N(3)	107.92(10)
O(8)-S(3)-C(47)	107.51(10)
O(9)-S(3)-C(47)	107.28(10)
N(3)-S(3)-C(47)	107.82(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for p21n_a_sq. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	13(1)	14(1)	23(1)	0(1)	3(1)	-1(1)
C(2)	19(1)	21(1)	24(1)	-3(1)	9(1)	-3(1)
C(3)	25(1)	25(1)	18(1)	-4(1)	5(1)	-4(1)
C(4)	18(1)	16(1)	23(1)	2(1)	2(1)	-2(1)
C(5)	19(1)	29(1)	30(1)	0(1)	0(1)	-3(1)
C(6)	18(1)	31(1)	23(1)	2(1)	8(1)	-2(1)
C(7)	21(1)	28(1)	16(1)	-1(1)	4(1)	-3(1)
C(8)	20(1)	21(1)	31(1)	-3(1)	9(1)	0(1)
C(9)	26(1)	27(1)	29(1)	3(1)	11(1)	1(1)
C(10)	23(1)	26(1)	30(1)	3(1)	7(1)	-2(1)
C(11)	24(1)	19(1)	37(1)	-2(1)	14(1)	-4(1)
C(12)	25(1)	15(1)	25(1)	-4(1)	3(1)	-1(1)
C(13)	52(2)	26(1)	26(1)	0(1)	-1(1)	-7(1)
C(14)	72(2)	32(2)	38(2)	-2(1)	-24(2)	1(2)
C(15)	49(2)	37(2)	77(3)	-16(2)	-40(2)	16(2)
C(16)	20(1)	33(2)	104(3)	-21(2)	-2(2)	4(1)
C(17)	24(1)	24(1)	53(2)	-9(1)	11(1)	1(1)
C(18)	16(1)	17(1)	24(1)	-4(1)	1(1)	1(1)
C(19)	23(1)	22(1)	26(1)	-2(1)	0(1)	3(1)
C(20)	27(1)	21(1)	38(1)	4(1)	-4(1)	0(1)
C(21)	28(1)	19(1)	44(2)	-9(1)	-5(1)	3(1)
C(22)	30(1)	31(1)	34(1)	-15(1)	2(1)	2(1)
C(23)	25(1)	25(1)	28(1)	-6(1)	4(1)	-1(1)
C(24)	26(1)	17(1)	15(1)	0(1)	2(1)	-2(1)
C(25)	29(1)	29(1)	21(1)	4(1)	2(1)	2(1)
C(26)	47(2)	30(1)	18(1)	6(1)	5(1)	-1(1)
C(27)	48(2)	24(1)	26(1)	-3(1)	16(1)	-13(1)
C(28)	74(2)	37(2)	40(2)	-2(1)	33(2)	-16(1)

C(29)	28(1)	46(2)	35(1)	-5(1)	11(1)	-10(1)
C(30)	25(1)	39(1)	23(1)	1(1)	2(1)	-2(1)
C(31)	22(1)	22(1)	22(1)	-1(1)	-2(1)	1(1)
C(32)	19(1)	23(1)	22(1)	0(1)	2(1)	-3(1)
C(33)	17(1)	23(1)	18(1)	2(1)	0(1)	-1(1)
C(34)	16(1)	20(1)	19(1)	-2(1)	1(1)	-2(1)
C(35)	22(1)	34(1)	37(1)	9(1)	6(1)	0(1)
C(36)	22(1)	15(1)	25(1)	1(1)	7(1)	0(1)
C(37)	58(2)	33(1)	47(2)	1(1)	36(2)	-1(1)
C(38)	26(1)	44(2)	57(2)	14(1)	21(1)	2(1)
C(39)	62(2)	32(1)	28(1)	-7(1)	20(1)	-13(1)
C(40)	37(1)	24(1)	27(1)	-5(1)	10(1)	-10(1)
C(41)	16(1)	16(1)	23(1)	-1(1)	7(1)	-1(1)
C(42)	20(1)	21(1)	26(1)	1(1)	3(1)	0(1)
C(43)	30(1)	26(1)	37(1)	9(1)	3(1)	1(1)
C(44)	34(1)	17(1)	51(2)	5(1)	12(1)	-1(1)
C(45)	32(1)	19(1)	38(1)	-7(1)	10(1)	-7(1)
C(46)	24(1)	21(1)	25(1)	-3(1)	7(1)	-3(1)
C(47)	20(1)	12(1)	22(1)	-1(1)	4(1)	-2(1)
C(48)	22(1)	18(1)	30(1)	2(1)	0(1)	-1(1)
C(49)	18(1)	20(1)	48(2)	-1(1)	9(1)	2(1)
C(50)	27(1)	18(1)	39(1)	-8(1)	16(1)	-3(1)
C(51)	40(2)	33(1)	52(2)	-12(1)	29(1)	-3(1)
C(52)	26(1)	44(2)	23(1)	-10(1)	5(1)	-3(1)
C(53)	17(1)	35(1)	24(1)	-5(1)	5(1)	2(1)
C(54)	22(1)	16(1)	25(1)	1(1)	-2(1)	-1(1)
C(55)	21(1)	16(1)	17(1)	-2(1)	1(1)	-1(1)
C(56)	15(1)	17(1)	18(1)	-2(1)	2(1)	1(1)
C(57)	15(1)	15(1)	16(1)	0(1)	1(1)	-1(1)
C(58)	21(1)	13(1)	16(1)	0(1)	5(1)	-1(1)
C(59)	21(1)	19(1)	31(1)	-1(1)	3(1)	-2(1)
C(60)	33(1)	16(1)	36(1)	-3(1)	4(1)	-7(1)
C(61)	39(1)	14(1)	32(1)	0(1)	7(1)	2(1)

C(62)	27(1)	20(1)	40(1)	3(1)	6(1)	7(1)
C(63)	21(1)	17(1)	32(1)	-1(1)	5(1)	-1(1)
C(64)	23(1)	33(1)	23(1)	-2(1)	6(1)	-9(1)
C(65)	21(1)	13(1)	18(1)	0(1)	5(1)	-2(1)
C(66)	23(1)	45(2)	20(1)	0(1)	3(1)	-6(1)
C(67)	38(2)	66(2)	17(1)	0(1)	2(1)	-14(1)
C(68)	50(2)	48(2)	21(1)	-3(1)	18(1)	-13(1)
C(69)	33(1)	43(2)	31(1)	-1(1)	17(1)	-10(1)
N(1)	23(1)	18(1)	28(1)	-9(1)	5(1)	-4(1)
N(2)	24(1)	16(1)	18(1)	3(1)	-1(1)	1(1)
N(3)	22(1)	13(1)	23(1)	-1(1)	4(1)	0(1)
O(1)	34(1)	23(1)	21(1)	1(1)	8(1)	-2(1)
O(2)	22(1)	19(1)	23(1)	-5(1)	-5(1)	0(1)
O(3)	16(1)	16(1)	20(1)	-1(1)	4(1)	-4(1)
O(4)	15(1)	22(1)	40(1)	-5(1)	7(1)	1(1)
O(5)	23(1)	35(1)	27(1)	2(1)	-3(1)	-2(1)
O(6)	29(1)	24(1)	27(1)	1(1)	7(1)	9(1)
O(7)	35(1)	24(1)	15(1)	-1(1)	1(1)	-4(1)
O(8)	27(1)	23(1)	31(1)	-5(1)	14(1)	-8(1)
O(9)	48(1)	20(1)	19(1)	7(1)	4(1)	-2(1)
P(1)	20(1)	15(1)	19(1)	-2(1)	7(1)	-2(1)
P(2)	15(1)	14(1)	17(1)	-2(1)	1(1)	-1(1)
P(3)	14(1)	11(1)	15(1)	0(1)	3(1)	-2(1)
S(1)	14(1)	18(1)	26(1)	-2(1)	2(1)	-1(1)
S(2)	23(1)	16(1)	15(1)	0(1)	2(1)	1(1)
S(3)	26(1)	14(1)	17(1)	1(1)	6(1)	-3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3a**.

	x	y	z	U(eq)
H(2)	7448	4098	4988	25
H(3)	5898	3730	4648	27
H(5A)	4016	4159	4796	40
H(5B)	3961	3428	5153	40
H(5C)	4315	3133	4739	40
H(6)	5064	4007	5749	28
H(7)	6606	4381	6095	26
H(8A)	7664	5969	5184	28
H(8B)	8799	5988	5277	28
H(9)	8106	7516	5152	32
H(10)	8521	7333	6021	31
H(11A)	8241	8936	5499	31
H(11B)	8862	8919	5975	31
H(13)	6799	9217	5065	43
H(14)	5420	9029	4540	64
H(15)	4034	8540	4717	75
H(16)	3996	8234	5421	65
H(17)	5379	8413	5952	40
H(19)	7646	10567	5520	29
H(20)	7797	12112	5673	36
H(21)	7586	12650	6321	39
H(22)	7210	11654	6819	39
H(23)	7081	10102	6672	32
H(25)	6606	3202	7755	32
H(26)	5892	2875	8315	39
H(28A)	4190	2340	8452	71
H(28B)	3417	3116	8303	71

H(28C)	4390	3347	8630	71
H(29)	3359	3647	7613	43
H(30)	4048	3949	7043	35
H(31A)	7384	5068	7313	28
H(31B)	6497	5263	7523	28
H(32)	7089	6490	6938	26
H(33)	6193	6786	7598	24
H(34A)	6669	8039	6995	23
H(34B)	6675	8314	7475	23
H(35)	3334	7685	7187	37
H(37)	3480	7759	8446	51
H(38)	2629	7461	7762	49
H(39)	5037	8268	8563	47
H(40)	5762	8477	7994	34
H(42)	4304	9336	6362	27
H(43)	4219	10882	6210	37
H(44)	4972	11920	6711	40
H(45)	5825	11420	7374	35
H(46)	5896	9881	7532	28
H(48)	22	10270	5541	29
H(49)	-633	10660	6112	34
H(51A)	-100	10165	7047	58
H(51B)	-447	11118	6834	58
H(51C)	562	11038	7157	58
H(52)	1903	10315	6912	37
H(53)	2578	9933	6347	30
H(54A)	445	8522	5047	26
H(54B)	489	8359	5541	26
H(55)	1144	7056	5007	22
H(56)	520	6853	5750	20
H(57A)	1066	5502	5212	19
H(57B)	398	5309	5536	19
H(59)	745	3754	5631	29

H(60)	1028	2207	5583	35
H(61)	2571	1649	5752	34
H(62)	3841	2627	5984	35
H(63)	3575	4175	6035	28
H(64)	275	5265	6235	32
H(66)	3070	5727	6708	36
H(67)	2774	5875	7381	49
H(68)	1232	5750	7482	45
H(69)	-15	5456	6907	41
H(1)	8305	6082	6029	27
H(2A)	5826	5208	6682	24
H(3A)	2288	8319	5452	23

Table 6. Torsion angles [°] for **3a**.

C(7)-C(1)-C(2)-C(3)	0.4(3)
S(1)-C(1)-C(2)-C(3)	-174.44(17)
C(1)-C(2)-C(3)-C(4)	0.0(3)
C(2)-C(3)-C(4)-C(6)	-0.6(3)
C(2)-C(3)-C(4)-C(5)	178.7(2)
C(3)-C(4)-C(6)-C(7)	0.7(3)
C(5)-C(4)-C(6)-C(7)	-178.6(2)
C(4)-C(6)-C(7)-C(1)	-0.3(3)
C(2)-C(1)-C(7)-C(6)	-0.3(3)
S(1)-C(1)-C(7)-C(6)	174.67(17)
N(1)-C(8)-C(9)-C(10)	8.7(3)
C(8)-C(9)-C(10)-C(11)	-176.1(2)
C(9)-C(10)-C(11)-P(1)	109.9(2)
C(17)-C(12)-C(13)-C(14)	-0.3(4)
P(1)-C(12)-C(13)-C(14)	-178.5(2)
C(12)-C(13)-C(14)-C(15)	0.2(4)
C(13)-C(14)-C(15)-C(16)	0.1(5)
C(14)-C(15)-C(16)-C(17)	-0.3(4)
C(15)-C(16)-C(17)-C(12)	0.2(4)
C(13)-C(12)-C(17)-C(16)	0.1(4)
P(1)-C(12)-C(17)-C(16)	178.41(19)
C(23)-C(18)-C(19)-C(20)	0.5(3)
P(1)-C(18)-C(19)-C(20)	-179.54(17)
C(18)-C(19)-C(20)-C(21)	-0.4(3)
C(19)-C(20)-C(21)-C(22)	-0.3(4)
C(20)-C(21)-C(22)-C(23)	0.8(4)
C(19)-C(18)-C(23)-C(22)	0.0(3)
P(1)-C(18)-C(23)-C(22)	-179.95(18)
C(21)-C(22)-C(23)-C(18)	-0.6(4)
C(30)-C(24)-C(25)-C(26)	1.5(4)
S(2)-C(24)-C(25)-C(26)	-178.86(19)

C(24)-C(25)-C(26)-C(27)	-0.6(4)
C(25)-C(26)-C(27)-C(29)	-1.0(4)
C(25)-C(26)-C(27)-C(28)	178.8(2)
C(26)-C(27)-C(29)-C(30)	1.8(4)
C(28)-C(27)-C(29)-C(30)	-178.1(3)
C(27)-C(29)-C(30)-C(24)	-0.9(4)
C(25)-C(24)-C(30)-C(29)	-0.8(4)
S(2)-C(24)-C(30)-C(29)	179.6(2)
N(2)-C(31)-C(32)-C(33)	111.9(2)
C(31)-C(32)-C(33)-C(34)	-172.67(19)
C(32)-C(33)-C(34)-P(2)	115.5(2)
C(38)-C(35)-C(36)-C(40)	0.3(4)
C(38)-C(35)-C(36)-P(2)	179.8(2)
C(39)-C(37)-C(38)-C(35)	-0.3(4)
C(36)-C(35)-C(38)-C(37)	0.3(4)
C(38)-C(37)-C(39)-C(40)	-0.1(4)
C(37)-C(39)-C(40)-C(36)	0.7(4)
C(35)-C(36)-C(40)-C(39)	-0.7(4)
P(2)-C(36)-C(40)-C(39)	179.7(2)
C(46)-C(41)-C(42)-C(43)	-0.9(3)
P(2)-C(41)-C(42)-C(43)	178.44(18)
C(41)-C(42)-C(43)-C(44)	0.7(4)
C(42)-C(43)-C(44)-C(45)	0.1(4)
C(43)-C(44)-C(45)-C(46)	-0.6(4)
C(44)-C(45)-C(46)-C(41)	0.3(4)
C(42)-C(41)-C(46)-C(45)	0.4(3)
P(2)-C(41)-C(46)-C(45)	-178.92(18)
C(53)-C(47)-C(48)-C(49)	0.2(3)
S(3)-C(47)-C(48)-C(49)	178.24(17)
C(47)-C(48)-C(49)-C(50)	-1.0(3)
C(48)-C(49)-C(50)-C(52)	1.4(4)
C(48)-C(49)-C(50)-C(51)	-177.7(2)
C(49)-C(50)-C(52)-C(53)	-1.2(4)

C(51)-C(50)-C(52)-C(53)	177.9(2)
C(48)-C(47)-C(53)-C(52)	0.1(4)
S(3)-C(47)-C(53)-C(52)	-178.00(19)
C(50)-C(52)-C(53)-C(47)	0.4(4)
N(3)-C(54)-C(55)-C(56)	108.8(2)
C(54)-C(55)-C(56)-C(57)	-174.58(19)
C(55)-C(56)-C(57)-P(3)	106.5(2)
C(63)-C(58)-C(59)-C(60)	-0.6(3)
P(3)-C(58)-C(59)-C(60)	-178.23(18)
C(58)-C(59)-C(60)-C(61)	0.0(4)
C(59)-C(60)-C(61)-C(62)	0.7(4)
C(60)-C(61)-C(62)-C(63)	-0.7(4)
C(61)-C(62)-C(63)-C(58)	0.0(4)
C(59)-C(58)-C(63)-C(62)	0.7(3)
P(3)-C(58)-C(63)-C(62)	178.38(18)
C(69)-C(64)-C(65)-C(66)	0.0(4)
C(69)-C(64)-C(65)-P(3)	178.58(19)
C(64)-C(65)-C(66)-C(67)	0.9(4)
P(3)-C(65)-C(66)-C(67)	-177.7(2)
C(65)-C(66)-C(67)-C(68)	-1.2(4)
C(66)-C(67)-C(68)-C(69)	0.4(5)
C(65)-C(64)-C(69)-C(68)	-0.8(4)
C(67)-C(68)-C(69)-C(64)	0.6(4)
C(9)-C(8)-N(1)-S(1)	179.62(15)
C(32)-C(31)-N(2)-S(2)	178.86(15)
C(55)-C(54)-N(3)-S(3)	175.85(14)
C(17)-C(12)-P(1)-O(1)	22.1(2)
C(13)-C(12)-P(1)-O(1)	-159.58(19)
C(17)-C(12)-P(1)-C(18)	-101.47(19)
C(13)-C(12)-P(1)-C(18)	76.8(2)
C(17)-C(12)-P(1)-C(11)	145.35(18)
C(13)-C(12)-P(1)-C(11)	-36.4(2)
C(23)-C(18)-P(1)-O(1)	-9.4(2)

C(19)-C(18)-P(1)-O(1)	170.71(17)
C(23)-C(18)-P(1)-C(12)	113.45(18)
C(19)-C(18)-P(1)-C(12)	-66.5(2)
C(23)-C(18)-P(1)-C(11)	-131.39(18)
C(19)-C(18)-P(1)-C(11)	48.7(2)
C(10)-C(11)-P(1)-O(1)	47.0(2)
C(10)-C(11)-P(1)-C(12)	-76.11(19)
C(10)-C(11)-P(1)-C(18)	169.72(16)
C(42)-C(41)-P(2)-O(2)	0.9(2)
C(46)-C(41)-P(2)-O(2)	-179.78(17)
C(42)-C(41)-P(2)-C(34)	124.67(17)
C(46)-C(41)-P(2)-C(34)	-56.0(2)
C(42)-C(41)-P(2)-C(36)	-121.38(18)
C(46)-C(41)-P(2)-C(36)	58.0(2)
C(33)-C(34)-P(2)-O(2)	-60.95(17)
C(33)-C(34)-P(2)-C(41)	176.49(14)
C(33)-C(34)-P(2)-C(36)	62.11(17)
C(40)-C(36)-P(2)-O(2)	159.65(18)
C(35)-C(36)-P(2)-O(2)	-19.9(2)
C(40)-C(36)-P(2)-C(41)	-78.4(2)
C(35)-C(36)-P(2)-C(41)	102.03(19)
C(40)-C(36)-P(2)-C(34)	35.7(2)
C(35)-C(36)-P(2)-C(34)	-143.85(18)
C(66)-C(65)-P(3)-O(3)	-26.8(2)
C(64)-C(65)-P(3)-O(3)	154.60(18)
C(66)-C(65)-P(3)-C(58)	94.56(19)
C(64)-C(65)-P(3)-C(58)	-84.0(2)
C(66)-C(65)-P(3)-C(57)	-151.49(18)
C(64)-C(65)-P(3)-C(57)	30.0(2)
C(59)-C(58)-P(3)-O(3)	-157.61(17)
C(63)-C(58)-P(3)-O(3)	24.75(19)
C(59)-C(58)-P(3)-C(65)	81.5(2)
C(63)-C(58)-P(3)-C(65)	-96.15(18)

C(59)-C(58)-P(3)-C(57)	-33.1(2)
C(63)-C(58)-P(3)-C(57)	149.31(17)
C(56)-C(57)-P(3)-O(3)	-56.84(16)
C(56)-C(57)-P(3)-C(65)	66.02(16)
C(56)-C(57)-P(3)-C(58)	179.93(14)
C(8)-N(1)-S(1)-O(5)	173.91(15)
C(8)-N(1)-S(1)-O(4)	45.49(18)
C(8)-N(1)-S(1)-C(1)	-70.48(18)
C(2)-C(1)-S(1)-O(5)	-154.98(18)
C(7)-C(1)-S(1)-O(5)	30.1(2)
C(2)-C(1)-S(1)-O(4)	-24.1(2)
C(7)-C(1)-S(1)-O(4)	160.96(17)
C(2)-C(1)-S(1)-N(1)	90.62(19)
C(7)-C(1)-S(1)-N(1)	-84.34(19)
C(31)-N(2)-S(2)-O(7)	177.09(16)
C(31)-N(2)-S(2)-O(6)	-52.99(19)
C(31)-N(2)-S(2)-C(24)	61.88(19)
C(30)-C(24)-S(2)-O(7)	-33.7(2)
C(25)-C(24)-S(2)-O(7)	146.69(18)
C(30)-C(24)-S(2)-O(6)	-163.65(19)
C(25)-C(24)-S(2)-O(6)	16.7(2)
C(30)-C(24)-S(2)-N(2)	80.7(2)
C(25)-C(24)-S(2)-N(2)	-98.98(19)
C(54)-N(3)-S(3)-O(8)	177.41(15)
C(54)-N(3)-S(3)-O(9)	-53.27(18)
C(54)-N(3)-S(3)-C(47)	62.32(18)
C(53)-C(47)-S(3)-O(8)	-25.9(2)
C(48)-C(47)-S(3)-O(8)	156.07(17)
C(53)-C(47)-S(3)-O(9)	-155.51(18)
C(48)-C(47)-S(3)-O(9)	26.4(2)
C(53)-C(47)-S(3)-N(3)	88.48(19)
C(48)-C(47)-S(3)-N(3)	-89.58(19)

Symmetry transformations used to generate equivalent atoms:

Crystallographic Data for 3c (CCDC 1872886)

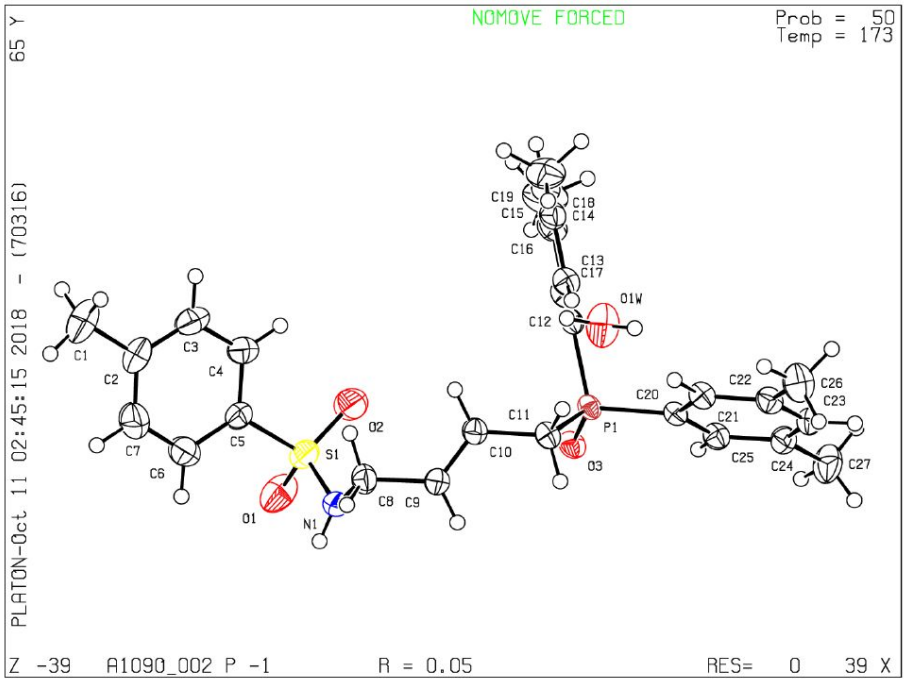


Table 1. Crystal data and structure refinement for **3c**.

Empirical formula	$C_{27}H_{34}NO_4PS$	
Formula weight	499.58	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 8.159(2) Å	α = 116.598(8)°
	b = 13.097(4) Å	β = 92.096(8)°
	c = 14.363(4) Å	γ = 102.099(8)°
Volume	1326.9(6) $Å^3$	
Z	2	
Density (calculated)	1.250 Mg/m^3	
Absorption coefficient	0.215 mm^{-1}	
F(000)	532	
Crystal size	0.332 x 0.325 x 0.198 mm^3	

Theta range for data collection	2.914 to 29.187°.
Index ranges	–11<=h<=11, –17<=k<=17, –19<=l<=19
Reflections collected	44926
Independent reflections	7043 [R(int) = 0.0577]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7458 and 0.7005
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7043 / 2 / 322
Goodness-of-fit on F^2	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0483, wR2 = 0.1160
R indices (all data)	R1 = 0.0727, wR2 = 0.1355
Extinction coefficient	0.0123(17)
Largest diff. peak and hole	0.433 and –0.385 $e \cdot Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	3888(4)	11344(2)	11111(2)	66(1)
C(2)	2899(3)	10389(2)	10062(2)	45(1)
C(3)	3164(3)	10475(2)	9158(2)	52(1)
C(4)	2262(3)	9619(2)	8181(2)	48(1)
C(5)	1086(3)	8648(2)	8111(2)	35(1)
C(6)	802(3)	8537(2)	9007(2)	47(1)
C(7)	1708(3)	9410(2)	9971(2)	54(1)
S(1)	-12(1)	7529(1)	6870(1)	38(1)
O(1)	-1773(2)	7220(2)	6949(2)	58(1)
O(2)	483(3)	7932(2)	6119(1)	56(1)
N(1)	673(2)	6390(2)	6628(1)	36(1)
C(8)	2484(3)	6445(2)	6549(2)	36(1)
C(9)	2799(2)	5762(2)	5443(1)	32(1)
C(10)	3843(2)	6207(2)	4967(1)	31(1)
C(11)	4226(2)	5493(2)	3882(1)	30(1)
P(1)	3121(1)	5683(1)	2877(1)	25(1)
O(3)	1227(2)	5336(1)	2788(1)	31(1)
C(12)	3909(2)	7205(2)	3165(1)	26(1)
C(13)	5610(2)	7793(2)	3574(1)	31(1)
C(14)	6222(2)	8965(2)	3793(2)	34(1)
C(15)	5110(3)	9535(2)	3584(2)	36(1)
C(16)	3418(3)	8962(2)	3156(2)	37(1)
C(17)	2820(2)	7791(2)	2956(2)	33(1)
C(18)	8049(3)	9596(2)	4249(2)	52(1)
C(19)	2263(3)	9608(3)	2924(3)	62(1)
C(20)	3810(2)	4798(2)	1658(1)	25(1)
C(21)	5504(2)	4759(2)	1590(1)	29(1)
C(22)	5981(2)	4077(2)	621(2)	32(1)

C(23)	4755(2)	3475(2)	-270(2)	33(1)
C(24)	3069(2)	3498(2)	-218(2)	33(1)
C(25)	2604(2)	4160(2)	755(1)	30(1)
C(26)	7797(3)	3999(2)	543(2)	48(1)
C(27)	1757(3)	2820(2)	-1195(2)	51(1)
O(1W)	8841(2)	6543(2)	3849(1)	56(1)

Table 3. Bond lengths [Å] and angles [°] for **3c**.

C(1)-C(2)	1.512(3)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(3)	1.374(3)
C(2)-C(7)	1.387(4)
C(3)-C(4)	1.391(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.383(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.381(3)
C(5)-S(1)	1.767(2)
C(6)-C(7)	1.387(3)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
S(1)-O(1)	1.4324(18)
S(1)-O(2)	1.4345(17)
S(1)-N(1)	1.5991(18)
N(1)-C(8)	1.475(3)
N(1)-H(1N)	0.83(3)
C(8)-C(9)	1.498(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.314(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.501(2)
C(10)-H(10)	0.9500
C(11)-P(1)	1.8105(18)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
P(1)-O(3)	1.4999(13)

P(1)-C(20)	1.8043(18)
P(1)-C(12)	1.8067(19)
C(12)-C(17)	1.394(2)
C(12)-C(13)	1.397(2)
C(13)-C(14)	1.392(3)
C(13)-H(13)	0.9500
C(14)-C(15)	1.391(3)
C(14)-C(18)	1.504(3)
C(15)-C(16)	1.391(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.398(3)
C(16)-C(19)	1.510(3)
C(17)-H(17)	0.9500
C(18)-H(18A)	0.9800
C(18)-H(18B)	0.9800
C(18)-H(18C)	0.9800
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-C(25)	1.393(2)
C(20)-C(21)	1.399(2)
C(21)-C(22)	1.400(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.390(3)
C(22)-C(26)	1.510(3)
C(23)-C(24)	1.386(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.393(3)
C(24)-C(27)	1.510(3)
C(25)-H(25)	0.9500
C(26)-H(26A)	0.9800
C(26)-H(26B)	0.9800
C(26)-H(26C)	0.9800

C(27)-H(27A)	0.9800
C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800
O(1W)-H(1W)	0.896(10)
O(1W)-H(2W)	0.896(10)

C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(3)-C(2)-C(7)	117.8(2)
C(3)-C(2)-C(1)	120.0(2)
C(7)-C(2)-C(1)	122.2(2)
C(2)-C(3)-C(4)	121.5(2)
C(2)-C(3)-H(3)	119.2
C(4)-C(3)-H(3)	119.2
C(5)-C(4)-C(3)	119.6(2)
C(5)-C(4)-H(4)	120.2
C(3)-C(4)-H(4)	120.2
C(6)-C(5)-C(4)	120.1(2)
C(6)-C(5)-S(1)	119.91(16)
C(4)-C(5)-S(1)	119.99(17)
C(5)-C(6)-C(7)	119.1(2)
C(5)-C(6)-H(6)	120.5
C(7)-C(6)-H(6)	120.5
C(2)-C(7)-C(6)	122.0(2)
C(2)-C(7)-H(7)	119.0
C(6)-C(7)-H(7)	119.0
O(1)-S(1)-O(2)	119.28(12)
O(1)-S(1)-N(1)	106.40(10)
O(2)-S(1)-N(1)	108.65(10)

O(1)-S(1)-C(5)	108.93(10)
O(2)-S(1)-C(5)	106.42(10)
N(1)-S(1)-C(5)	106.53(10)
C(8)-N(1)-S(1)	119.67(14)
C(8)-N(1)-H(1N)	119.1(19)
S(1)-N(1)-H(1N)	114.2(19)
N(1)-C(8)-C(9)	112.93(16)
N(1)-C(8)-H(8A)	109.0
C(9)-C(8)-H(8A)	109.0
N(1)-C(8)-H(8B)	109.0
C(9)-C(8)-H(8B)	109.0
H(8A)-C(8)-H(8B)	107.8
C(10)-C(9)-C(8)	124.28(18)
C(10)-C(9)-H(9)	117.9
C(8)-C(9)-H(9)	117.9
C(9)-C(10)-C(11)	123.60(17)
C(9)-C(10)-H(10)	118.2
C(11)-C(10)-H(10)	118.2
C(10)-C(11)-P(1)	113.31(13)
C(10)-C(11)-H(11A)	108.9
P(1)-C(11)-H(11A)	108.9
C(10)-C(11)-H(11B)	108.9
P(1)-C(11)-H(11B)	108.9
H(11A)-C(11)-H(11B)	107.7
O(3)-P(1)-C(20)	110.77(8)
O(3)-P(1)-C(12)	112.08(8)
C(20)-P(1)-C(12)	106.75(8)
O(3)-P(1)-C(11)	113.79(8)
C(20)-P(1)-C(11)	106.07(8)
C(12)-P(1)-C(11)	106.94(8)
C(17)-C(12)-C(13)	119.57(17)
C(17)-C(12)-P(1)	119.78(13)
C(13)-C(12)-P(1)	120.63(14)

C(14)-C(13)-C(12)	120.80(17)
C(14)-C(13)-H(13)	119.6
C(12)-C(13)-H(13)	119.6
C(15)-C(14)-C(13)	118.61(17)
C(15)-C(14)-C(18)	121.01(19)
C(13)-C(14)-C(18)	120.38(19)
C(16)-C(15)-C(14)	121.80(18)
C(16)-C(15)-H(15)	119.1
C(14)-C(15)-H(15)	119.1
C(15)-C(16)-C(17)	118.76(18)
C(15)-C(16)-C(19)	120.0(2)
C(17)-C(16)-C(19)	121.2(2)
C(12)-C(17)-C(16)	120.44(17)
C(12)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(14)-C(18)-H(18A)	109.5
C(14)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(14)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(16)-C(19)-H(19A)	109.5
C(16)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(16)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(25)-C(20)-C(21)	119.65(16)
C(25)-C(20)-P(1)	118.03(13)
C(21)-C(20)-P(1)	122.30(13)
C(20)-C(21)-C(22)	120.15(17)
C(20)-C(21)-H(21)	119.9
C(22)-C(21)-H(21)	119.9

C(23)-C(22)-C(21)	118.75(17)
C(23)-C(22)-C(26)	120.61(18)
C(21)-C(22)-C(26)	120.65(18)
C(24)-C(23)-C(22)	121.94(17)
C(24)-C(23)-H(23)	119.0
C(22)-C(23)-H(23)	119.0
C(23)-C(24)-C(25)	118.71(17)
C(23)-C(24)-C(27)	120.87(18)
C(25)-C(24)-C(27)	120.42(18)
C(20)-C(25)-C(24)	120.75(17)
C(20)-C(25)-H(25)	119.6
C(24)-C(25)-H(25)	119.6
C(22)-C(26)-H(26A)	109.5
C(22)-C(26)-H(26B)	109.5
H(26A)-C(26)-H(26B)	109.5
C(22)-C(26)-H(26C)	109.5
H(26A)-C(26)-H(26C)	109.5
H(26B)-C(26)-H(26C)	109.5
C(24)-C(27)-H(27A)	109.5
C(24)-C(27)-H(27B)	109.5
H(27A)-C(27)-H(27B)	109.5
C(24)-C(27)-H(27C)	109.5
H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5
H(1W)-O(1W)-H(2W)	105(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	70(2)	55(2)	45(1)	-1(1)	-1(1)	18(1)
C(2)	49(1)	39(1)	38(1)	6(1)	3(1)	18(1)
C(3)	63(2)	30(1)	50(1)	13(1)	2(1)	0(1)
C(4)	65(2)	34(1)	41(1)	18(1)	6(1)	2(1)
C(5)	42(1)	27(1)	34(1)	12(1)	7(1)	11(1)
C(6)	51(1)	47(1)	42(1)	24(1)	6(1)	2(1)
C(7)	63(2)	60(2)	38(1)	23(1)	8(1)	11(1)
S(1)	42(1)	31(1)	37(1)	12(1)	2(1)	7(1)
O(1)	40(1)	47(1)	66(1)	8(1)	3(1)	11(1)
O(2)	86(1)	43(1)	39(1)	22(1)	-2(1)	9(1)
N(1)	40(1)	28(1)	38(1)	14(1)	15(1)	6(1)
C(8)	38(1)	40(1)	26(1)	14(1)	6(1)	8(1)
C(9)	35(1)	30(1)	27(1)	12(1)	4(1)	6(1)
C(10)	34(1)	32(1)	25(1)	13(1)	3(1)	5(1)
C(11)	30(1)	35(1)	27(1)	16(1)	5(1)	9(1)
P(1)	21(1)	30(1)	25(1)	14(1)	6(1)	5(1)
O(3)	21(1)	38(1)	36(1)	18(1)	9(1)	6(1)
C(12)	22(1)	32(1)	25(1)	14(1)	6(1)	7(1)
C(13)	24(1)	38(1)	32(1)	17(1)	4(1)	7(1)
C(14)	29(1)	37(1)	30(1)	14(1)	4(1)	1(1)
C(15)	41(1)	33(1)	37(1)	19(1)	9(1)	6(1)
C(16)	38(1)	41(1)	40(1)	25(1)	9(1)	13(1)
C(17)	25(1)	42(1)	35(1)	22(1)	4(1)	8(1)
C(18)	34(1)	51(1)	61(2)	26(1)	-5(1)	-7(1)
C(19)	56(2)	65(2)	88(2)	53(2)	6(1)	22(1)
C(20)	24(1)	28(1)	26(1)	15(1)	6(1)	6(1)
C(21)	24(1)	35(1)	31(1)	17(1)	4(1)	8(1)
C(22)	29(1)	35(1)	37(1)	19(1)	10(1)	12(1)

C(23)	39(1)	31(1)	31(1)	14(1)	12(1)	12(1)
C(24)	34(1)	32(1)	28(1)	12(1)	3(1)	5(1)
C(25)	24(1)	34(1)	31(1)	16(1)	3(1)	5(1)
C(26)	35(1)	64(2)	52(1)	26(1)	17(1)	26(1)
C(27)	45(1)	56(1)	32(1)	7(1)	-3(1)	5(1)
O(1W)	40(1)	74(1)	49(1)	20(1)	5(1)	26(1)

Table 5. Hydrogen bonds for **3c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(3)#1	0.83(3)	2.10(3)	2.923(2)	173(3)
O(1W)-H(1W)...O(2)#2	0.896(10)	2.118(11)	3.013(3)	176(3)
O(1W)-H(2W)...O(3)#2	0.896(10)	1.925(10)	2.821(2)	178(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z+1 #2 x+1,y,z

Crystallographic Data for *cis*-3s (CCDC 1872730)

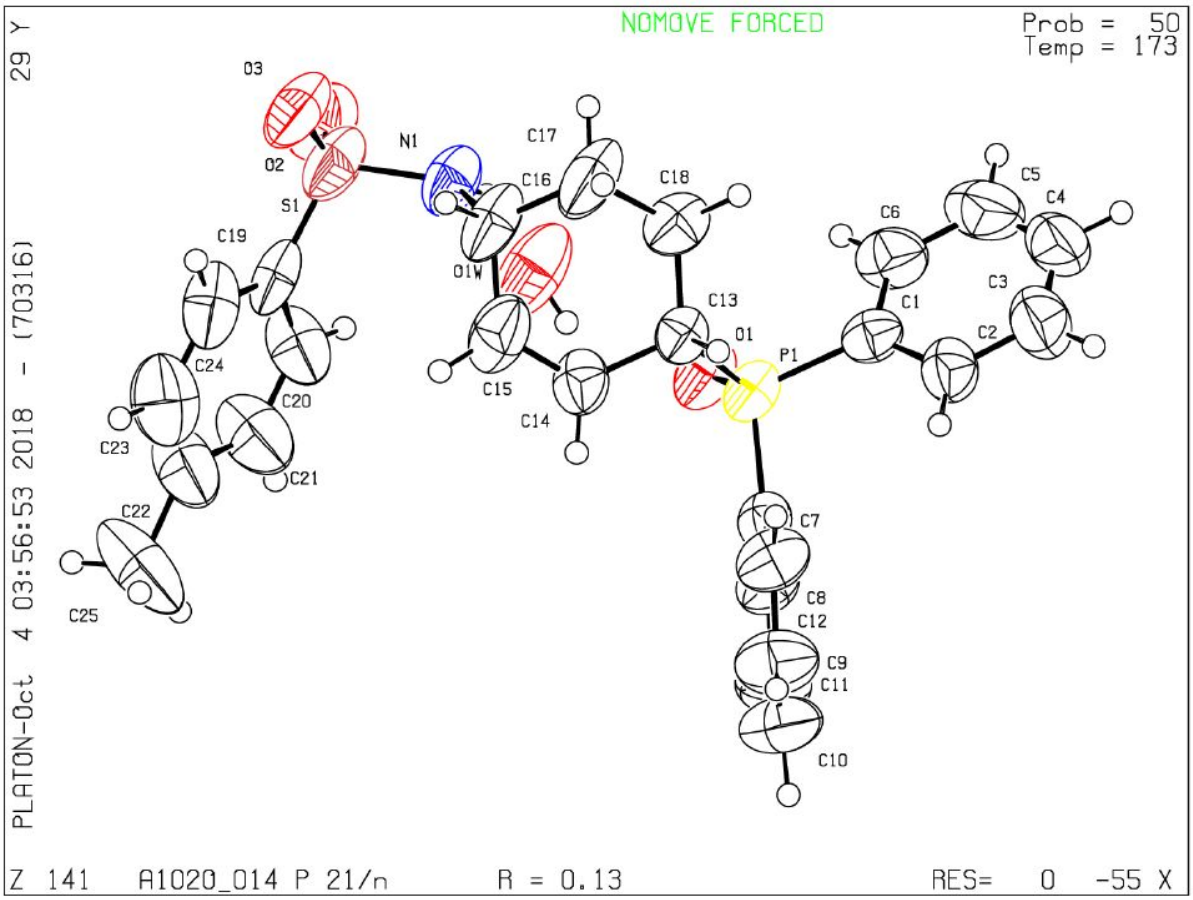


Table 1. Crystal data and structure refinement for ***cis*-3s**.

Empirical formula	$C_{25}H_{28}NO_4PS$	
Formula weight	469.51	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 9.766(2) Å	α = 90°
	b = 16.136(4) Å	β = 99.178(5)°
	c = 15.584(4) Å	γ = 90°
Volume	2424.3(10) Å^3	

Z	4
Density (calculated)	1.286 Mg/m^3
Absorption coefficient	0.230 mm^{-1}
F(000)	992
Crystal size	0.265 x 0.202 x 0.089 mm^3
Theta range for data collection	2.934 to 24.150°.
Index ranges	–11<=h<=11, –18<=k<=18, –17<=l<=17
Reflections collected	38563
Independent reflections	3862 [R(int) = 0.2497]
Completeness to theta = 24.150°	99.7 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3862 / 289 / 299
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	R1 = 0.1293, wR2 = 0.2287
R indices (all data)	R1 = 0.2742, wR2 = 0.3253
Largest diff. peak and hole	0.632 and –0.344 $e \cdot Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for ***cis*-3s**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
P(1)	4614(3)	7192(2)	5299(2)	58(1)
O(1)	4215(8)	6315(4)	5117(5)	70(2)
C(1)	3107(12)	7783(7)	5377(6)	58(2)
C(2)	3016(13)	8643(7)	5201(8)	71(3)
C(3)	1802(16)	9046(10)	5276(9)	98(4)
C(4)	721(17)	8663(13)	5526(9)	110(5)
C(5)	769(16)	7834(13)	5693(9)	109(5)
C(6)	1983(13)	7404(9)	5607(8)	84(4)
C(7)	5444(11)	7630(7)	4472(7)	58(3)
C(8)	6321(14)	8298(8)	4578(8)	80(4)
C(9)	6983(15)	8565(10)	3906(10)	98(4)
C(10)	6678(16)	8204(10)	3105(9)	103(5)
C(11)	5779(15)	7532(9)	2999(9)	90(4)
C(12)	5159(13)	7267(7)	3666(7)	69(3)
C(13)	5780(11)	7323(6)	6321(6)	54(2)
C(14)	7109(12)	6878(7)	6289(8)	68(3)
C(15)	7769(14)	6443(9)	6916(9)	94(4)
C(16)	7199(15)	6232(7)	7722(7)	82(4)
C(17)	6139(17)	6842(8)	7866(8)	108(5)
C(18)	5126(13)	7068(7)	7084(7)	72(3)
N(1)	6628(12)	5377(6)	7715(6)	76(3)
S(1)	7595(5)	4616(2)	8089(2)	89(1)
O(2)	6729(11)	3902(5)	8004(7)	109(3)
O(3)	8296(11)	4822(5)	8924(5)	103(3)
C(19)	8836(15)	4470(7)	7443(8)	73(3)
C(20)	8421(15)	4253(9)	6579(9)	91(4)
C(21)	9367(17)	4155(11)	6066(12)	117(5)
C(22)	10742(18)	4203(11)	6303(13)	117(5)

C(23)	11169(18)	4451(11)	7165(13)	123(5)
C(24)	10181(16)	4574(8)	7719(10)	97(4)
C(25)	11773(19)	4112(14)	5718(14)	179(9)
O(1W)	4975(15)	4924(6)	6105(7)	119(4)

Table 3. Bond lengths [Å] and angles [°] for ***cis*-3s**.

P(1)-O(1)	1.483(7)
P(1)-C(1)	1.774(12)
P(1)-C(7)	1.775(11)
P(1)-C(13)	1.816(10)
C(1)-C(6)	1.354(15)
C(1)-C(2)	1.414(15)
C(2)-C(3)	1.374(17)
C(2)-H(2)	0.9500
C(3)-C(4)	1.33(2)
C(3)-H(3)	0.9500
C(4)-C(5)	1.36(2)
C(4)-H(4)	0.9500
C(5)-C(6)	1.399(19)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.370(15)
C(7)-C(12)	1.374(14)
C(8)-C(9)	1.385(17)
C(8)-H(8)	0.9500
C(9)-C(10)	1.366(18)
C(9)-H(9)	0.9500
C(10)-C(11)	1.389(18)
C(10)-H(10)	0.9500
C(11)-C(12)	1.352(16)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.491(15)
C(13)-C(18)	1.495(15)
C(13)-H(13)	1.0000
C(14)-C(15)	1.291(15)
C(14)-H(14)	0.9500

C(15)-C(16)	1.492(18)
C(15)-H(15)	0.9500
C(16)-C(17)	1.470(17)
C(16)-N(1)	1.488(15)
C(16)-H(16)	1.0000
C(17)-C(18)	1.487(16)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
N(1)-S(1)	1.601(10)
N(1)-H(1N)	0.93(13)
S(1)-O(3)	1.410(9)
S(1)-O(2)	1.423(10)
S(1)-C(19)	1.710(15)
C(19)-C(24)	1.325(17)
C(19)-C(20)	1.388(16)
C(20)-C(21)	1.323(18)
C(20)-H(20)	0.9500
C(21)-C(22)	1.34(2)
C(21)-H(21)	0.9500
C(22)-C(23)	1.40(2)
C(22)-C(25)	1.47(2)
C(23)-C(24)	1.41(2)
C(23)-H(23)	0.9500
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
O(1W)-H(1W1)	0.831(10)
O(1W)-H(2W1)	0.831(10)

O(1)-P(1)-C(1)	109.3(5)

O(1)-P(1)-C(7)	112.1(5)
C(1)-P(1)-C(7)	108.4(5)
O(1)-P(1)-C(13)	112.9(5)
C(1)-P(1)-C(13)	106.7(5)
C(7)-P(1)-C(13)	107.2(5)
C(6)-C(1)-C(2)	117.8(12)
C(6)-C(1)-P(1)	119.4(10)
C(2)-C(1)-P(1)	122.8(10)
C(3)-C(2)-C(1)	118.4(13)
C(3)-C(2)-H(2)	120.8
C(1)-C(2)-H(2)	120.8
C(4)-C(3)-C(2)	122.7(16)
C(4)-C(3)-H(3)	118.7
C(2)-C(3)-H(3)	118.7
C(3)-C(4)-C(5)	120.4(17)
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-C(6)	118.3(16)
C(4)-C(5)-H(5)	120.9
C(6)-C(5)-H(5)	120.9
C(1)-C(6)-C(5)	122.4(15)
C(1)-C(6)-H(6)	118.8
C(5)-C(6)-H(6)	118.8
C(8)-C(7)-C(12)	118.5(11)
C(8)-C(7)-P(1)	125.0(9)
C(12)-C(7)-P(1)	116.5(9)
C(7)-C(8)-C(9)	120.8(12)
C(7)-C(8)-H(8)	119.6
C(9)-C(8)-H(8)	119.6
C(10)-C(9)-C(8)	119.9(14)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(9)-C(10)-C(11)	118.9(14)

C(9)-C(10)-H(10)	120.5
C(11)-C(10)-H(10)	120.5
C(12)-C(11)-C(10)	120.5(13)
C(12)-C(11)-H(11)	119.8
C(10)-C(11)-H(11)	119.8
C(11)-C(12)-C(7)	121.2(12)
C(11)-C(12)-H(12)	119.4
C(7)-C(12)-H(12)	119.4
C(14)-C(13)-C(18)	112.3(10)
C(14)-C(13)-P(1)	110.0(7)
C(18)-C(13)-P(1)	112.2(8)
C(14)-C(13)-H(13)	107.4
C(18)-C(13)-H(13)	107.4
P(1)-C(13)-H(13)	107.4
C(15)-C(14)-C(13)	124.7(13)
C(15)-C(14)-H(14)	117.6
C(13)-C(14)-H(14)	117.6
C(14)-C(15)-C(16)	123.6(14)
C(14)-C(15)-H(15)	118.2
C(16)-C(15)-H(15)	118.2
C(17)-C(16)-N(1)	110.4(13)
C(17)-C(16)-C(15)	110.0(11)
N(1)-C(16)-C(15)	113.3(10)
C(17)-C(16)-H(16)	107.6
N(1)-C(16)-H(16)	107.6
C(15)-C(16)-H(16)	107.6
C(16)-C(17)-C(18)	115.6(11)
C(16)-C(17)-H(17A)	108.4
C(18)-C(17)-H(17A)	108.4
C(16)-C(17)-H(17B)	108.4
C(18)-C(17)-H(17B)	108.4
H(17A)-C(17)-H(17B)	107.4
C(17)-C(18)-C(13)	114.0(12)

C(17)-C(18)-H(18A)	108.8
C(13)-C(18)-H(18A)	108.8
C(17)-C(18)-H(18B)	108.8
C(13)-C(18)-H(18B)	108.8
H(18A)-C(18)-H(18B)	107.6
C(16)-N(1)-S(1)	120.7(9)
C(16)-N(1)-H(1N)	117(8)
S(1)-N(1)-H(1N)	116(8)
O(3)-S(1)-O(2)	118.1(6)
O(3)-S(1)-N(1)	109.0(5)
O(2)-S(1)-N(1)	106.2(6)
O(3)-S(1)-C(19)	106.9(7)
O(2)-S(1)-C(19)	107.4(6)
N(1)-S(1)-C(19)	109.0(6)
C(24)-C(19)-C(20)	117.9(15)
C(24)-C(19)-S(1)	123.3(12)
C(20)-C(19)-S(1)	118.7(11)
C(21)-C(20)-C(19)	119.4(15)
C(21)-C(20)-H(20)	120.3
C(19)-C(20)-H(20)	120.3
C(20)-C(21)-C(22)	126.5(18)
C(20)-C(21)-H(21)	116.8
C(22)-C(21)-H(21)	116.8
C(21)-C(22)-C(23)	114.4(17)
C(21)-C(22)-C(25)	125.6(19)
C(23)-C(22)-C(25)	119.7(18)
C(22)-C(23)-C(24)	120.1(17)
C(22)-C(23)-H(23)	120.0
C(24)-C(23)-H(23)	120.0
C(19)-C(24)-C(23)	121.5(16)
C(19)-C(24)-H(24)	119.2
C(23)-C(24)-H(24)	119.2
C(22)-C(25)-H(25A)	109.5

C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
H(1W1)-O(1W)-H(2W1)	106(10)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for ***cis*-3s**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	77(2)	43(2)	49(2)	-3(1)	-5(2)	-4(2)
O(1)	94(6)	42(4)	66(5)	-4(3)	-11(4)	-11(4)
C(1)	62(5)	67(5)	43(6)	-1(5)	0(4)	-10(5)
C(2)	73(7)	66(6)	72(8)	-4(6)	8(6)	10(6)
C(3)	93(10)	111(10)	90(10)	-9(8)	15(9)	34(7)
C(4)	76(9)	184(13)	70(9)	13(11)	16(8)	45(10)
C(5)	68(8)	182(13)	78(9)	10(11)	19(8)	-4(9)
C(6)	63(7)	112(9)	75(8)	9(8)	7(7)	-19(6)
C(7)	60(7)	63(6)	47(5)	-3(5)	-1(5)	4(5)
C(8)	95(10)	80(8)	61(7)	-3(6)	3(6)	-18(6)
C(9)	100(11)	111(11)	85(8)	0(7)	19(8)	-31(8)
C(10)	114(12)	130(12)	69(7)	15(8)	27(8)	-16(8)
C(11)	115(11)	96(10)	66(7)	-10(7)	31(7)	-1(7)
C(12)	86(9)	64(7)	53(6)	-3(5)	4(6)	-3(6)
C(13)	68(6)	42(6)	50(5)	-7(4)	3(4)	2(5)
C(14)	68(7)	75(8)	57(6)	-8(5)	-7(5)	10(6)
C(15)	75(9)	95(9)	101(9)	29(7)	-17(6)	-3(6)
C(16)	136(10)	47(5)	50(6)	-8(5)	-26(6)	11(6)
C(17)	189(14)	67(7)	62(7)	8(7)	-3(7)	44(9)
C(18)	99(8)	60(7)	55(5)	-8(6)	4(5)	-6(6)
N(1)	106(8)	49(4)	67(7)	2(5)	-4(5)	7(5)
S(1)	134(3)	51(2)	74(2)	12(2)	-2(2)	11(2)
O(2)	147(9)	56(5)	127(8)	19(5)	28(6)	1(5)
O(3)	168(9)	73(6)	59(5)	13(4)	-3(5)	30(6)
C(19)	94(6)	44(6)	69(6)	10(5)	-22(5)	10(6)
C(20)	70(8)	102(10)	98(8)	-32(8)	0(6)	13(8)
C(21)	86(8)	146(13)	121(10)	-27(11)	22(7)	11(11)
C(22)	82(8)	132(13)	140(11)	-11(11)	23(8)	30(10)

C(23)	90(9)	122(13)	148(11)	-3(12)	-3(7)	14(10)
C(24)	101(7)	76(9)	101(9)	-6(8)	-23(6)	22(9)
C(25)	106(13)	220(20)	225(18)	-33(18)	75(13)	47(15)
O(1W)	184(11)	60(6)	93(7)	3(5)	-37(8)	-6(7)

Table 5. Hydrogen bonds for ***cis*-3s** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1W)	0.93(13)	1.97(13)	2.854(14)	159(12)
O(1W)-H(1W1)...O(1)	0.831(10)	2.10(13)	2.756(12)	136(17)
O(1W)-H(2W1)...O(1)#1	0.831(10)	2.56(18)	2.954(14)	110(16)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Crystallographic Data for 3v (CCDC 1872880)

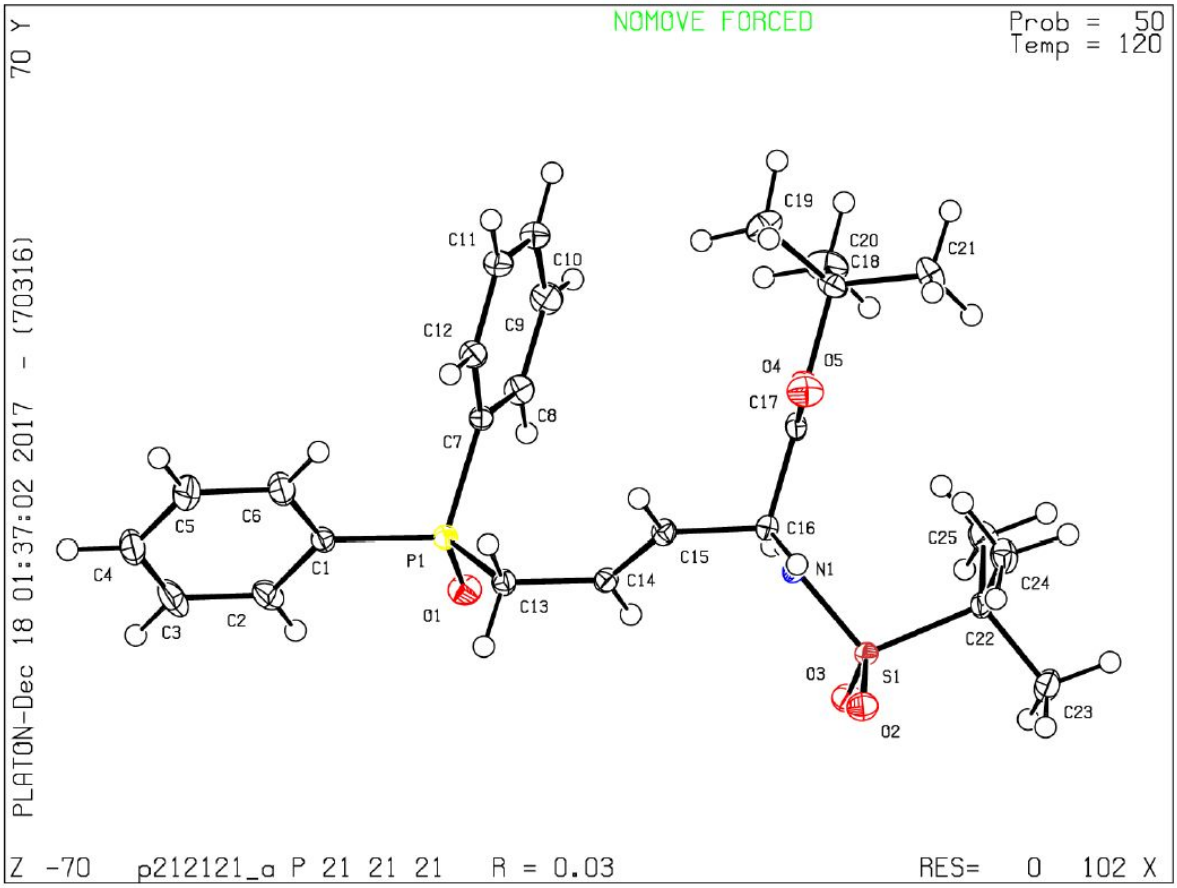


Table 1. Crystal data and structure refinement for **3v**.

Identification code	p212121_a	
Empirical formula	C25 H34 N O5 P S	
Formula weight	491.56	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.8707(2) Å	α= 90°.
	b = 17.4003(8) Å	β= 90°.
	c = 24.7047(12) Å	γ = 90°.

Volume	2523.63(19) $Å^3$
Z	4
Density (calculated)	1.294 Mg/m^3
Absorption coefficient	0.227 mm^{-1}
F(000)	1048
Crystal size	0.260 x 0.210 x 0.150 mm^3
Theta range for data collection	3.299 to 33.390°.
Index ranges	-8<=h<=9, -26<=k<=26, -38<=l<=38
Reflections collected	107206
Independent reflections	9681 [R(int) = 0.0454]
Completeness to theta = 25.242°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6804 and 0.6188
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9681 / 0 / 304
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0768
R indices (all data)	R1 = 0.0446, wR2 = 0.0815
Absolute structure parameter	0.008(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.295 and -0.381 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **3v**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4387(3)	5350(1)	4553(1)	14(1)
C(2)	2480(3)	4912(1)	4685(1)	21(1)
C(3)	2496(4)	4452(1)	5147(1)	28(1)
C(4)	4398(4)	4418(1)	5474(1)	26(1)
C(5)	6310(4)	4845(1)	5343(1)	27(1)
C(6)	6310(3)	5308(1)	4882(1)	22(1)
C(7)	5021(3)	6918(1)	4140(1)	13(1)
C(8)	3417(3)	7501(1)	4070(1)	18(1)
C(9)	3957(3)	8253(1)	4215(1)	22(1)
C(10)	6073(3)	8421(1)	4433(1)	22(1)
C(11)	7689(3)	7845(1)	4496(1)	20(1)
C(12)	7185(3)	7097(1)	4342(1)	16(1)
C(13)	6298(3)	5622(1)	3484(1)	14(1)
C(14)	6249(3)	6113(1)	2984(1)	14(1)
C(15)	8022(3)	6524(1)	2817(1)	14(1)
C(16)	8013(3)	7030(1)	2318(1)	12(1)
C(17)	9176(3)	7789(1)	2473(1)	14(1)
C(18)	8418(3)	9120(1)	2755(1)	18(1)
C(19)	9904(3)	9074(1)	3256(1)	25(1)
C(20)	6166(3)	9511(1)	2884(1)	28(1)
C(21)	9612(4)	9500(1)	2280(1)	28(1)
C(22)	5585(3)	7724(1)	1054(1)	14(1)
C(23)	4749(3)	7515(1)	489(1)	24(1)
C(24)	8140(3)	7889(1)	1051(1)	20(1)
C(25)	4258(3)	8409(1)	1283(1)	21(1)
N(1)	5740(2)	7126(1)	2092(1)	14(1)
O(1)	1801(2)	5934(1)	3737(1)	20(1)
O(2)	6557(2)	6289(1)	1306(1)	20(1)

O(3)	2634(2)	6760(1)	1482(1)	19(1)
O(4)	11230(2)	7844(1)	2502(1)	21(1)
O(5)	7672(2)	8337(1)	2587(1)	16(1)
P(1)	4162(1)	5956(1)	3957(1)	12(1)
S(1)	5055(1)	6892(1)	1481(1)	12(1)

Table 3. Bond lengths [Å] and angles [°] for **3v**.

C(1)-C(6)	1.393(2)
C(1)-C(2)	1.393(2)
C(1)-P(1)	1.8144(16)
C(2)-C(3)	1.396(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.379(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.384(3)
C(4)-H(4)	0.9500
C(5)-C(6)	1.395(3)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.395(2)
C(7)-C(12)	1.400(2)
C(7)-P(1)	1.8061(16)
C(8)-C(9)	1.394(3)
C(8)-H(8)	0.9500
C(9)-C(10)	1.386(3)
C(9)-H(9)	0.9500
C(10)-C(11)	1.388(3)
C(10)-H(10)	0.9500
C(11)-C(12)	1.388(2)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.502(2)
C(13)-P(1)	1.8095(16)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.329(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.514(2)

C(15)-H(15)	0.9500
C(16)-N(1)	1.4558(19)
C(16)-C(17)	1.536(2)
C(16)-H(16)	1.0000
C(17)-O(4)	1.212(2)
C(17)-O(5)	1.329(2)
C(18)-O(5)	1.491(2)
C(18)-C(21)	1.518(3)
C(18)-C(19)	1.518(3)
C(18)-C(20)	1.521(3)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-C(23)	1.524(2)
C(22)-C(24)	1.527(2)
C(22)-C(25)	1.533(2)
C(22)-S(1)	1.8172(16)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
N(1)-S(1)	1.6147(13)

N(1)-H(1)	0.8800
O(1)-P(1)	1.4898(12)
O(2)-S(1)	1.4387(13)
O(3)-S(1)	1.4399(12)

C(6)-C(1)-C(2)	119.10(15)
C(6)-C(1)-P(1)	124.27(12)
C(2)-C(1)-P(1)	116.63(13)
C(1)-C(2)-C(3)	120.01(18)
C(1)-C(2)-H(2)	120.0
C(3)-C(2)-H(2)	120.0
C(4)-C(3)-C(2)	120.57(18)
C(4)-C(3)-H(3)	119.7
C(2)-C(3)-H(3)	119.7
C(3)-C(4)-C(5)	119.81(17)
C(3)-C(4)-H(4)	120.1
C(5)-C(4)-H(4)	120.1
C(4)-C(5)-C(6)	120.08(19)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(1)-C(6)-C(5)	120.42(17)
C(1)-C(6)-H(6)	119.8
C(5)-C(6)-H(6)	119.8
C(8)-C(7)-C(12)	119.67(15)
C(8)-C(7)-P(1)	117.02(13)
C(12)-C(7)-P(1)	123.31(12)
C(9)-C(8)-C(7)	119.82(16)
C(9)-C(8)-H(8)	120.1
C(7)-C(8)-H(8)	120.1
C(10)-C(9)-C(8)	120.16(16)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
C(9)-C(10)-C(11)	120.24(16)

C(9)-C(10)-H(10)	119.9
C(11)-C(10)-H(10)	119.9
C(10)-C(11)-C(12)	120.04(16)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(7)	120.00(16)
C(11)-C(12)-H(12)	120.0
C(7)-C(12)-H(12)	120.0
C(14)-C(13)-P(1)	109.57(11)
C(14)-C(13)-H(13A)	109.8
P(1)-C(13)-H(13A)	109.8
C(14)-C(13)-H(13B)	109.8
P(1)-C(13)-H(13B)	109.8
H(13A)-C(13)-H(13B)	108.2
C(15)-C(14)-C(13)	123.19(14)
C(15)-C(14)-H(14)	118.4
C(13)-C(14)-H(14)	118.4
C(14)-C(15)-C(16)	124.31(14)
C(14)-C(15)-H(15)	117.8
C(16)-C(15)-H(15)	117.8
N(1)-C(16)-C(15)	112.42(12)
N(1)-C(16)-C(17)	113.87(13)
C(15)-C(16)-C(17)	107.20(12)
N(1)-C(16)-H(16)	107.7
C(15)-C(16)-H(16)	107.7
C(17)-C(16)-H(16)	107.7
O(4)-C(17)-O(5)	126.37(16)
O(4)-C(17)-C(16)	121.60(15)
O(5)-C(17)-C(16)	111.97(13)
O(5)-C(18)-C(21)	108.56(14)
O(5)-C(18)-C(19)	110.36(14)
C(21)-C(18)-C(19)	112.87(16)
O(5)-C(18)-C(20)	102.26(14)

C(21)-C(18)-C(20)	111.71(16)
C(19)-C(18)-C(20)	110.55(16)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(23)-C(22)-C(24)	110.91(14)
C(23)-C(22)-C(25)	111.08(14)
C(24)-C(22)-C(25)	110.78(14)
C(23)-C(22)-S(1)	106.72(11)
C(24)-C(22)-S(1)	108.70(11)
C(25)-C(22)-S(1)	108.50(11)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5

C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
C(16)-N(1)-S(1)	123.89(11)
C(16)-N(1)-H(1)	118.1
S(1)-N(1)-H(1)	118.1
C(17)-O(5)-C(18)	121.28(13)
O(1)-P(1)-C(7)	111.99(8)
O(1)-P(1)-C(13)	113.63(8)
C(7)-P(1)-C(13)	105.39(7)
O(1)-P(1)-C(1)	110.48(8)
C(7)-P(1)-C(1)	108.33(7)
C(13)-P(1)-C(1)	106.69(7)
O(2)-S(1)-O(3)	119.30(8)
O(2)-S(1)-N(1)	108.22(8)
O(3)-S(1)-N(1)	106.48(7)
O(2)-S(1)-C(22)	107.52(8)
O(3)-S(1)-C(22)	107.30(7)
N(1)-S(1)-C(22)	107.50(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **3v**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	15(1)	12(1)	14(1)	0(1)	2(1)	-1(1)
C(2)	19(1)	18(1)	25(1)	1(1)	4(1)	-4(1)
C(3)	32(1)	18(1)	33(1)	6(1)	12(1)	-5(1)
C(4)	41(1)	18(1)	20(1)	5(1)	8(1)	1(1)
C(5)	34(1)	26(1)	20(1)	6(1)	-6(1)	-2(1)
C(6)	22(1)	23(1)	21(1)	7(1)	-3(1)	-5(1)
C(7)	14(1)	13(1)	12(1)	1(1)	0(1)	0(1)
C(8)	17(1)	17(1)	20(1)	0(1)	-1(1)	4(1)
C(9)	27(1)	17(1)	23(1)	-1(1)	0(1)	6(1)
C(10)	31(1)	16(1)	19(1)	-2(1)	1(1)	-3(1)
C(11)	21(1)	20(1)	18(1)	-1(1)	-1(1)	-5(1)
C(12)	15(1)	16(1)	18(1)	1(1)	-2(1)	-1(1)
C(13)	16(1)	13(1)	13(1)	1(1)	1(1)	1(1)
C(14)	16(1)	13(1)	12(1)	0(1)	-1(1)	1(1)
C(15)	14(1)	14(1)	13(1)	1(1)	-2(1)	2(1)
C(16)	12(1)	14(1)	11(1)	1(1)	0(1)	1(1)
C(17)	14(1)	15(1)	12(1)	4(1)	0(1)	-1(1)
C(18)	19(1)	13(1)	22(1)	0(1)	-1(1)	-3(1)
C(19)	24(1)	32(1)	20(1)	-6(1)	-3(1)	-2(1)
C(20)	25(1)	21(1)	40(1)	-6(1)	-2(1)	6(1)
C(21)	38(1)	21(1)	26(1)	7(1)	3(1)	-9(1)
C(22)	13(1)	15(1)	12(1)	2(1)	0(1)	-2(1)
C(23)	27(1)	30(1)	14(1)	4(1)	-2(1)	-7(1)
C(24)	14(1)	26(1)	21(1)	6(1)	1(1)	-4(1)
C(25)	21(1)	16(1)	25(1)	3(1)	2(1)	2(1)
N(1)	11(1)	19(1)	11(1)	0(1)	0(1)	2(1)
O(1)	13(1)	23(1)	24(1)	0(1)	-5(1)	-1(1)
O(2)	26(1)	16(1)	19(1)	-4(1)	3(1)	4(1)

O(3)	15(1)	23(1)	19(1)	-1(1)	-1(1)	-7(1)
O(4)	12(1)	24(1)	27(1)	-4(1)	1(1)	-1(1)
O(5)	13(1)	13(1)	21(1)	0(1)	-1(1)	-1(1)
P(1)	11(1)	13(1)	13(1)	1(1)	-1(1)	-1(1)
S(1)	13(1)	13(1)	11(1)	0(1)	0(1)	-2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **3v**.

	x	y	z	U(eq)
H(2)	1168	4928	4460	25
H(3)	1186	4158	5237	33
H(4)	4396	4104	5788	31
H(5)	7624	4821	5566	32
H(6)	7630	5598	4793	26
H(8)	1960	7385	3923	22
H(9)	2872	8651	4164	27
H(10)	6420	8932	4541	26
H(11)	9140	7963	4644	23
H(12)	8310	6707	4373	20
H(13A)	7823	5649	3654	17
H(13B)	5993	5080	3386	17
H(14)	4884	6131	2778	16
H(15)	9386	6498	3023	16
H(16)	8977	6775	2037	15
H(19A)	9121	8773	3535	38
H(19B)	10199	9593	3393	38
H(19C)	11351	8825	3165	38
H(20A)	5196	9511	2562	43
H(20B)	6452	10042	2998	43
H(20C)	5400	9232	3177	43
H(21A)	10990	9209	2189	42
H(21B)	10030	10027	2377	42
H(21C)	8588	9508	1967	42
H(23A)	3138	7369	506	35
H(23B)	5643	7083	349	35
H(23C)	4928	7959	248	35
H(24A)	8465	8305	795	30

H(24B)	8967	7425	941	30
H(24C)	8627	8042	1415	30
H(25A)	4453	8854	1045	31
H(25B)	4834	8533	1645	31
H(25C)	2638	8277	1306	31
H(1)	4676	7322	2302	17

Table 6. Torsion angles [°] for **3v**.

C(6)-C(1)-C(2)-C(3)	1.3(3)
P(1)-C(1)-C(2)-C(3)	-177.95(14)
C(1)-C(2)-C(3)-C(4)	-0.7(3)
C(2)-C(3)-C(4)-C(5)	-0.1(3)
C(3)-C(4)-C(5)-C(6)	0.3(3)
C(2)-C(1)-C(6)-C(5)	-1.1(3)
P(1)-C(1)-C(6)-C(5)	178.03(15)
C(4)-C(5)-C(6)-C(1)	0.4(3)
C(12)-C(7)-C(8)-C(9)	-1.8(2)
P(1)-C(7)-C(8)-C(9)	178.55(14)
C(7)-C(8)-C(9)-C(10)	-0.6(3)
C(8)-C(9)-C(10)-C(11)	1.7(3)
C(9)-C(10)-C(11)-C(12)	-0.3(3)
C(10)-C(11)-C(12)-C(7)	-2.2(3)
C(8)-C(7)-C(12)-C(11)	3.3(2)
P(1)-C(7)-C(12)-C(11)	-177.17(13)
P(1)-C(13)-C(14)-C(15)	119.54(15)
C(13)-C(14)-C(15)-C(16)	-179.32(14)
C(14)-C(15)-C(16)-N(1)	10.0(2)
C(14)-C(15)-C(16)-C(17)	135.82(16)
N(1)-C(16)-C(17)-O(4)	-156.35(15)
C(15)-C(16)-C(17)-O(4)	78.65(19)
N(1)-C(16)-C(17)-O(5)	26.03(18)
C(15)-C(16)-C(17)-O(5)	-98.97(15)
C(15)-C(16)-N(1)-S(1)	-121.66(13)
C(17)-C(16)-N(1)-S(1)	116.17(14)
O(4)-C(17)-O(5)-C(18)	1.7(3)
C(16)-C(17)-O(5)-C(18)	179.17(13)
C(21)-C(18)-O(5)-C(17)	66.54(19)
C(19)-C(18)-O(5)-C(17)	-57.6(2)
C(20)-C(18)-O(5)-C(17)	-175.28(15)

C(8)-C(7)-P(1)-O(1)	1.58(15)
C(12)-C(7)-P(1)-O(1)	-178.01(13)
C(8)-C(7)-P(1)-C(13)	125.60(13)
C(12)-C(7)-P(1)-C(13)	-53.99(15)
C(8)-C(7)-P(1)-C(1)	-120.51(13)
C(12)-C(7)-P(1)-C(1)	59.90(15)
C(14)-C(13)-P(1)-O(1)	59.48(13)
C(14)-C(13)-P(1)-C(7)	-63.49(12)
C(14)-C(13)-P(1)-C(1)	-178.52(11)
C(6)-C(1)-P(1)-O(1)	-173.34(15)
C(2)-C(1)-P(1)-O(1)	5.84(15)
C(6)-C(1)-P(1)-C(7)	-50.34(17)
C(2)-C(1)-P(1)-C(7)	128.85(13)
C(6)-C(1)-P(1)-C(13)	62.69(16)
C(2)-C(1)-P(1)-C(13)	-118.12(13)
C(16)-N(1)-S(1)-O(2)	26.67(15)
C(16)-N(1)-S(1)-O(3)	156.07(12)
C(16)-N(1)-S(1)-C(22)	-89.19(14)
C(23)-C(22)-S(1)-O(2)	68.22(13)
C(24)-C(22)-S(1)-O(2)	-51.46(14)
C(25)-C(22)-S(1)-O(2)	-172.01(12)
C(23)-C(22)-S(1)-O(3)	-61.27(13)
C(24)-C(22)-S(1)-O(3)	179.05(12)
C(25)-C(22)-S(1)-O(3)	58.51(13)
C(23)-C(22)-S(1)-N(1)	-175.47(11)
C(24)-C(22)-S(1)-N(1)	64.85(13)
C(25)-C(22)-S(1)-N(1)	-55.69(13)

Crystallographic Data for 3w (CCDC 1872887)

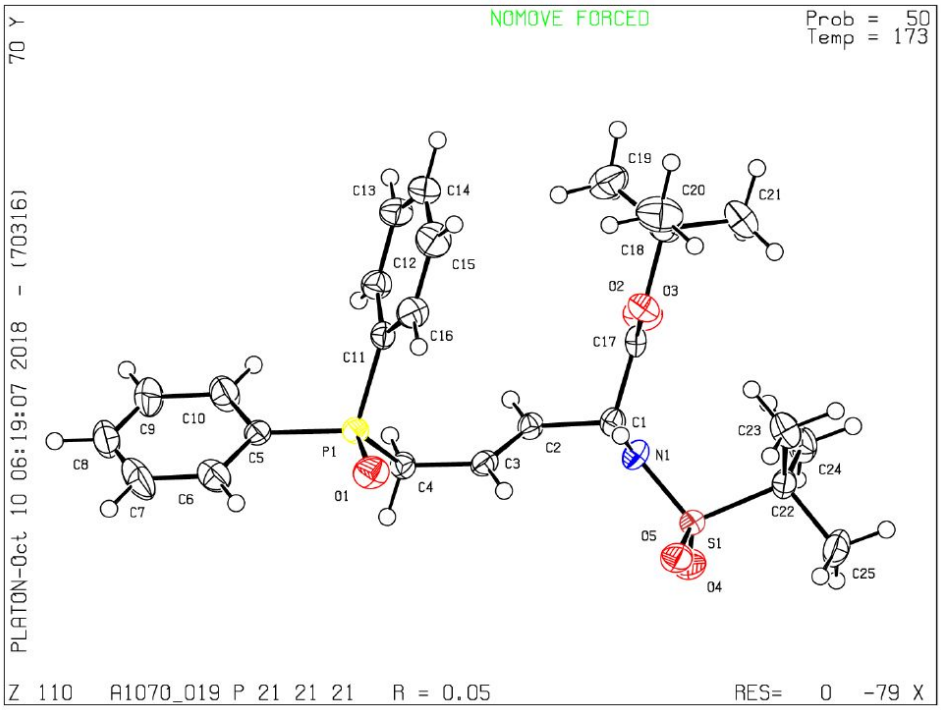


Table 1. Crystal data and structure refinement for **3w**.

Empirical formula	$C_{25}H_{34}NO_5PS$	
Formula weight	491.56	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.9129(4) Å	α = 90°
	b = 17.4156(13) Å	β = 90°
	c = 24.861(2) Å	γ = 90°
Volume	2560.1(3) $Å^3$	
Z	4	
Density (calculated)	1.275 Mg/m^3	
Absorption coefficient	0.224 mm^{-1}	
F(000)	1048	

Crystal size	0.725 x 0.075 x 0.058 mm^3
Theta range for data collection	2.339 to 27.930°.
Index ranges	–7<=h<=7, –22<=k<=22, –32<=l<=32
Reflections collected	39795
Independent reflections	6078 [R(int) = 0.1036]
Completeness to theta = 25.242°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6823
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6078 / 0 / 308
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0549, wR2 = 0.0781
R indices (all data)	R1 = 0.1027, wR2 = 0.0871
Absolute structure parameter	0.00(4)
Extinction coefficient	0.0047(7)
Largest diff. peak and hole	0.358 and –0.311 $e \cdot Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **3w**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	1977(5)	7027(2)	2325(1)	24(1)
C(2)	1991(5)	6523(2)	2818(1)	24(1)
C(3)	3716(6)	6118(2)	2988(1)	25(1)
C(4)	3693(5)	5631(2)	3484(1)	25(1)
P(1)	5824(1)	5956(1)	3952(1)	24(1)
O(1)	8147(4)	5929(1)	3731(1)	37(1)
C(5)	5599(5)	5351(2)	4546(1)	25(1)
C(6)	7481(7)	4926(2)	4679(2)	38(1)
C(7)	7479(8)	4466(2)	5135(2)	52(1)
C(8)	5597(8)	4431(2)	5457(2)	47(1)
C(9)	3733(8)	4844(2)	5326(2)	50(1)
C(10)	3708(7)	5302(2)	4870(2)	40(1)
C(11)	4994(6)	6916(2)	4138(1)	24(1)
C(12)	2859(6)	7099(2)	4339(1)	30(1)
C(13)	2381(6)	7843(2)	4493(2)	37(1)
C(14)	3970(8)	8408(2)	4432(1)	41(1)
C(15)	6040(7)	8240(2)	4217(2)	42(1)
C(16)	6570(6)	7494(2)	4070(1)	34(1)
C(17)	817(6)	7783(2)	2477(1)	26(1)
O(2)	2310(4)	8332(1)	2585(1)	29(1)
O(3)	-1204(4)	7838(1)	2506(1)	39(1)
C(18)	1584(6)	9113(2)	2756(2)	33(1)
C(19)	140(7)	9064(2)	3257(2)	49(1)
C(20)	3817(7)	9496(2)	2878(2)	54(1)
C(21)	378(8)	9491(2)	2292(2)	55(1)
N(1)	4218(5)	7119(2)	2094(1)	25(1)
S(1)	4901(1)	6881(1)	1489(1)	24(1)
O(4)	3409(4)	6283(1)	1321(1)	38(1)

O(5)	7288(4)	6746(1)	1491(1)	35(1)
C(22)	4388(5)	7709(2)	1063(1)	27(1)
C(23)	5713(6)	8388(2)	1285(2)	38(1)
C(24)	1865(5)	7875(2)	1059(2)	38(1)
C(25)	5210(6)	7493(2)	500(1)	44(1)

Table 3. Bond lengths [Å] and angles [°] for **3w**.

C(1)-N(1)	1.453(4)
C(1)-C(2)	1.509(4)
C(1)-C(17)	1.532(5)
C(1)-H(1)	1.0000
C(2)-C(3)	1.310(4)
C(2)-H(2)	0.9500
C(3)-C(4)	1.497(4)
C(3)-H(3)	0.9500
C(4)-P(1)	1.804(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
P(1)-O(1)	1.480(2)
P(1)-C(11)	1.803(3)
P(1)-C(5)	1.819(3)
C(5)-C(6)	1.377(5)
C(5)-C(10)	1.381(5)
C(6)-C(7)	1.388(6)
C(6)-H(6)	0.9500
C(7)-C(8)	1.372(6)
C(7)-H(7)	0.9500
C(8)-C(9)	1.356(5)
C(8)-H(8)	0.9500
C(9)-C(10)	1.387(5)
C(9)-H(9)	0.9500
C(10)-H(10)	0.9500
C(11)-C(16)	1.382(5)
C(11)-C(12)	1.395(5)
C(12)-C(13)	1.380(5)
C(12)-H(12)	0.9500
C(13)-C(14)	1.369(5)
C(13)-H(13)	0.9500

C(14)-C(15)	1.368(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.384(5)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-O(3)	1.201(4)
C(17)-O(2)	1.328(4)
O(2)-C(18)	1.488(4)
C(18)-C(21)	1.507(5)
C(18)-C(20)	1.510(5)
C(18)-C(19)	1.514(5)
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
N(1)-S(1)	1.611(3)
N(1)-H(1N)	0.82(3)
S(1)-O(4)	1.428(2)
S(1)-O(5)	1.431(2)
S(1)-C(22)	1.815(3)
C(22)-C(24)	1.519(4)
C(22)-C(23)	1.523(5)
C(22)-C(25)	1.528(5)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800

C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800

N(1)-C(1)-C(2)	112.4(3)
N(1)-C(1)-C(17)	114.2(3)
C(2)-C(1)-C(17)	107.5(3)
N(1)-C(1)-H(1)	107.5
C(2)-C(1)-H(1)	107.5
C(17)-C(1)-H(1)	107.5
C(3)-C(2)-C(1)	125.4(3)
C(3)-C(2)-H(2)	117.3
C(1)-C(2)-H(2)	117.3
C(2)-C(3)-C(4)	124.3(3)
C(2)-C(3)-H(3)	117.9
C(4)-C(3)-H(3)	117.9
C(3)-C(4)-P(1)	110.3(2)
C(3)-C(4)-H(4A)	109.6
P(1)-C(4)-H(4A)	109.6
C(3)-C(4)-H(4B)	109.6
P(1)-C(4)-H(4B)	109.6
H(4A)-C(4)-H(4B)	108.1
O(1)-P(1)-C(11)	112.13(15)
O(1)-P(1)-C(4)	113.53(15)
C(11)-P(1)-C(4)	105.42(15)
O(1)-P(1)-C(5)	110.55(15)
C(11)-P(1)-C(5)	107.98(14)
C(4)-P(1)-C(5)	106.88(14)
C(6)-C(5)-C(10)	118.7(3)
C(6)-C(5)-P(1)	116.6(3)
C(10)-C(5)-P(1)	124.7(3)
C(5)-C(6)-C(7)	120.5(4)

C(5)-C(6)-H(6)	119.8
C(7)-C(6)-H(6)	119.8
C(8)-C(7)-C(6)	120.1(4)
C(8)-C(7)-H(7)	119.9
C(6)-C(7)-H(7)	119.9
C(9)-C(8)-C(7)	119.7(4)
C(9)-C(8)-H(8)	120.2
C(7)-C(8)-H(8)	120.2
C(8)-C(9)-C(10)	120.7(4)
C(8)-C(9)-H(9)	119.7
C(10)-C(9)-H(9)	119.7
C(5)-C(10)-C(9)	120.3(4)
C(5)-C(10)-H(10)	119.9
C(9)-C(10)-H(10)	119.9
C(16)-C(11)-C(12)	119.1(3)
C(16)-C(11)-P(1)	117.5(3)
C(12)-C(11)-P(1)	123.4(2)
C(13)-C(12)-C(11)	120.0(3)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(14)-C(13)-C(12)	120.2(3)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(15)-C(14)-C(13)	120.2(3)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	120.4(3)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(11)-C(16)-C(15)	119.9(3)
C(11)-C(16)-H(16)	120.0
C(15)-C(16)-H(16)	120.0
O(3)-C(17)-O(2)	126.3(3)

O(3)-C(17)-C(1)	121.9(3)
O(2)-C(17)-C(1)	111.8(3)
C(17)-O(2)-C(18)	121.6(3)
O(2)-C(18)-C(21)	108.6(3)
O(2)-C(18)-C(20)	102.1(3)
C(21)-C(18)-C(20)	112.0(3)
O(2)-C(18)-C(19)	110.3(3)
C(21)-C(18)-C(19)	112.8(3)
C(20)-C(18)-C(19)	110.6(3)
C(18)-C(19)-H(19A)	109.5
C(18)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
C(18)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
C(18)-C(20)-H(20A)	109.5
C(18)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
C(18)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(1)-N(1)-S(1)	124.7(2)
C(1)-N(1)-H(1N)	118(2)
S(1)-N(1)-H(1N)	117(2)
O(4)-S(1)-O(5)	119.35(16)
O(4)-S(1)-N(1)	107.83(15)
O(5)-S(1)-N(1)	106.68(15)

O(4)-S(1)-C(22)	107.79(15)
O(5)-S(1)-C(22)	107.28(14)
N(1)-S(1)-C(22)	107.38(15)
C(24)-C(22)-C(23)	111.1(3)
C(24)-C(22)-C(25)	110.7(3)
C(23)-C(22)-C(25)	111.2(3)
C(24)-C(22)-S(1)	108.6(2)
C(23)-C(22)-S(1)	108.6(2)
C(25)-C(22)-S(1)	106.6(2)
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(22)-C(25)-H(25A)	109.5
C(22)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
C(22)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **3w**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	22(2)	28(2)	22(2)	1(2)	-4(1)	0(2)
C(2)	25(2)	24(2)	22(2)	1(2)	4(2)	-4(2)
C(3)	29(2)	25(2)	22(2)	-2(1)	4(2)	-2(2)
C(4)	28(2)	23(2)	23(2)	1(1)	-1(2)	-2(1)
P(1)	22(1)	24(1)	24(1)	1(1)	3(1)	1(1)
O(1)	27(1)	43(2)	42(2)	-1(1)	10(1)	2(1)
C(5)	30(2)	23(2)	22(2)	-4(1)	-6(2)	1(2)
C(6)	38(2)	32(2)	44(2)	1(2)	-5(2)	4(2)
C(7)	59(3)	34(2)	62(3)	12(2)	-29(2)	5(2)
C(8)	77(3)	29(2)	34(2)	7(2)	-17(2)	-3(2)
C(9)	68(3)	44(2)	38(2)	16(2)	12(2)	4(2)
C(10)	38(2)	40(2)	42(2)	12(2)	6(2)	9(2)
C(11)	26(2)	24(2)	21(2)	2(1)	-2(1)	-1(2)
C(12)	30(2)	30(2)	31(2)	0(2)	4(2)	-1(2)
C(13)	36(2)	38(2)	36(2)	-3(2)	4(2)	10(2)
C(14)	61(3)	26(2)	35(2)	-4(2)	-2(2)	4(2)
C(15)	51(2)	32(2)	44(2)	0(2)	1(2)	-13(2)
C(16)	34(2)	33(2)	34(2)	-1(2)	2(2)	-3(2)
C(17)	28(2)	30(2)	19(2)	8(1)	-2(2)	0(2)
O(2)	26(1)	23(1)	38(2)	1(1)	1(1)	1(1)
O(3)	21(2)	45(2)	50(2)	-7(1)	0(1)	2(1)
C(18)	37(2)	24(2)	39(2)	0(2)	5(2)	5(2)
C(19)	51(2)	57(3)	40(2)	-9(2)	7(2)	5(3)
C(20)	50(3)	41(2)	72(3)	-12(2)	4(2)	-9(2)
C(21)	74(3)	36(2)	55(3)	11(2)	-4(2)	17(2)
N(1)	24(2)	32(2)	19(2)	-2(1)	0(1)	-5(1)
S(1)	29(1)	24(1)	21(1)	-1(1)	0(1)	3(1)
O(4)	49(2)	30(1)	34(2)	-7(1)	-5(1)	-6(1)

O(5)	31(1)	43(2)	32(1)	-1(1)	2(1)	15(1)
C(22)	28(2)	32(2)	21(2)	5(2)	0(2)	2(1)
C(23)	41(2)	31(2)	43(2)	9(2)	-1(2)	-1(2)
C(24)	31(2)	46(2)	36(2)	9(2)	-1(2)	9(2)
C(25)	51(3)	58(2)	24(2)	9(2)	7(2)	11(2)

Table 5. Hydrogen bonds for **3w** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(3)#1	0.82(3)	2.38(3)	3.153(4)	158(3)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z

Crystallographic Data for 4c (CCDC 1872732)

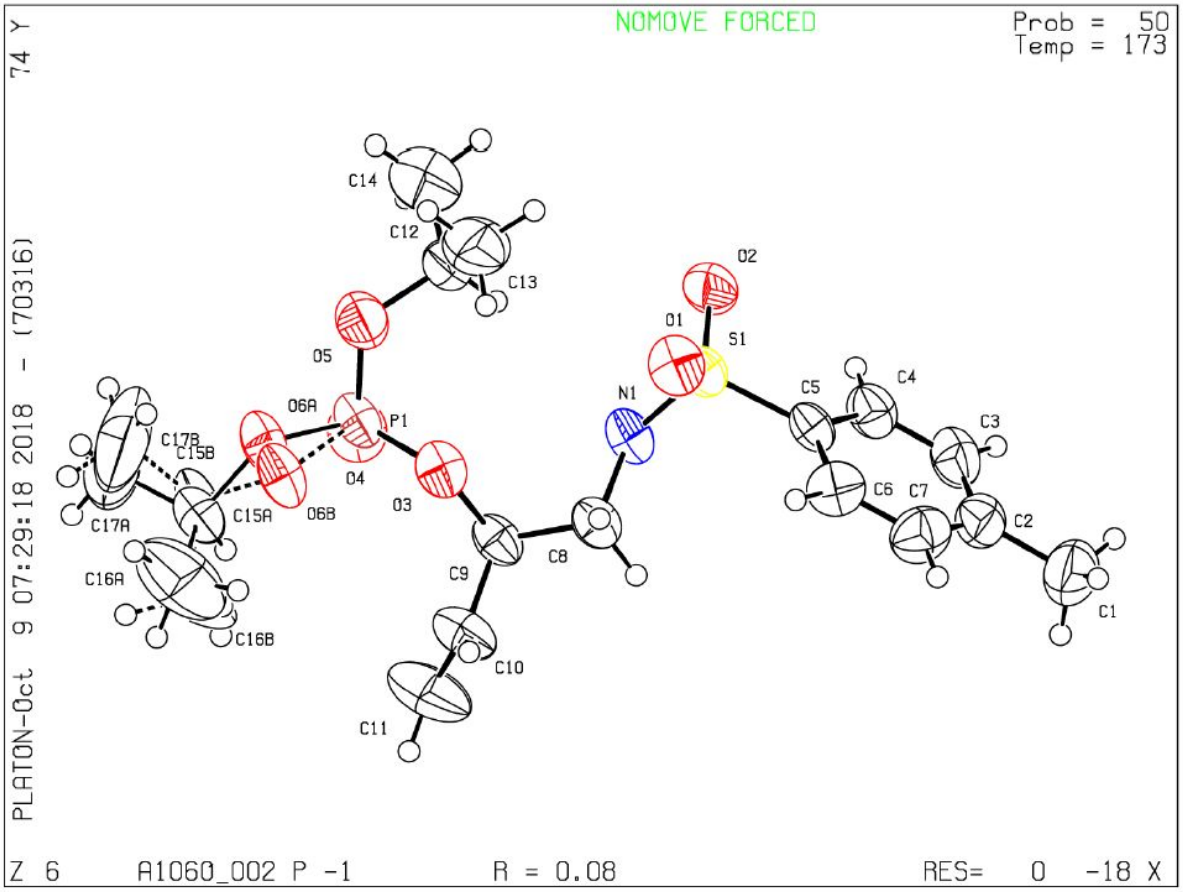


Table 1. Crystal data and structure refinement for **4c**.

Empirical formula	$C_{17}H_{28}NO_6PS$	
Formula weight	405.43	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	*P*-1	
Unit cell dimensions	a = 10.3053(17) Å	α = 103.730(5)°
	b = 10.8278(19) Å	β = 110.849(5)°
	c = 11.6058(19) Å	γ = 104.371(5)°
Volume	1093.9(3) Å^3	

Z	2
Density (calculated)	1.231 Mg/m^3
Absorption coefficient	0.250 mm^{-1}
F(000)	432
Crystal size	0.345 x 0.185 x 0.112 mm^3
Theta range for data collection	3.011 to 26.543°.
Index ranges	–12<=h<=12, –13<=k<=13, –14<=l<=13
Reflections collected	33600
Independent reflections	4519 [R(int) = 0.0860]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7454 and 0.6683
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4519 / 315 / 282
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0763, wR2 = 0.2365
R indices (all data)	R1 = 0.1250, wR2 = 0.2857
Largest diff. peak and hole	0.690 and –0.511 $e \cdot Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **4c**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5523(9)	-176(7)	-1770(7)	99(2)
C(2)	6005(6)	1165(5)	-675(5)	66(1)
C(3)	5134(6)	1961(6)	-777(5)	69(1)
C(4)	5574(5)	3178(5)	231(5)	59(1)
C(5)	6895(4)	3619(5)	1362(4)	46(1)
C(6)	7790(5)	2853(5)	1481(5)	62(1)
C(7)	7332(7)	1633(6)	453(6)	74(1)
S(1)	7413(1)	5134(1)	2679(1)	51(1)
O(1)	9000(3)	5659(4)	3391(3)	64(1)
O(2)	6675(4)	5967(4)	2139(4)	69(1)
N(1)	6745(4)	4749(4)	3653(4)	50(1)
C(8)	7364(5)	4031(5)	4507(5)	52(1)
C(9)	7198(5)	4483(5)	5768(4)	52(1)
C(10)	7577(6)	3640(6)	6580(6)	74(2)
C(11)	6657(8)	3022(8)	6985(8)	110(3)
O(3)	8201(3)	5899(3)	6498(3)	54(1)
P(1)	7803(1)	7004(1)	7292(1)	53(1)
O(4)	6224(4)	6617(4)	6945(4)	69(1)
O(5)	8551(4)	8315(4)	7101(4)	77(1)
C(12)	8242(8)	8344(6)	5763(6)	81(2)
C(13)	9724(10)	8617(7)	5704(8)	106(2)
C(14)	7606(11)	9417(9)	5612(9)	116(3)
O(6A)	8839(15)	7564(13)	8805(9)	65(3)
C(15A)	8490(40)	7070(30)	9770(30)	66(4)
C(16A)	9640(20)	6620(30)	10490(20)	147(7)
C(17A)	8430(20)	8220(15)	10703(13)	108(5)
O(6B)	8860(30)	7040(30)	8690(20)	57(4)
C(15B)	8320(70)	7240(60)	9700(50)	62(6)
C(16B)	8600(70)	6150(40)	10160(40)	173(17)
C(17B)	9350(60)	8660(40)	10690(40)	178(15)

Table 3. Bond lengths [Å] and angles [°] for **4c**.

C(1)-C(2)	1.512(8)
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(2)-C(7)	1.381(8)
C(2)-C(3)	1.386(8)
C(3)-C(4)	1.380(7)
C(3)-H(3)	0.9500
C(4)-C(5)	1.383(6)
C(4)-H(4)	0.9500
C(5)-C(6)	1.379(6)
C(5)-S(1)	1.762(5)
C(6)-C(7)	1.390(8)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
S(1)-O(1)	1.427(3)
S(1)-O(2)	1.433(3)
S(1)-N(1)	1.600(4)
N(1)-C(8)	1.468(6)
N(1)-H(1N)	0.875(19)
C(8)-C(9)	1.514(6)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-O(3)	1.453(5)
C(9)-C(10)	1.483(7)
C(9)-H(9)	1.0000
C(10)-C(11)	1.310(8)
C(10)-H(10)	0.9500
C(11)-H(11A)	0.9500
C(11)-H(11B)	0.9500
O(3)-P(1)	1.562(3)

P(1)-O(4)	1.449(3)
P(1)-O(5)	1.545(4)
P(1)-O(6A)	1.559(10)
P(1)-O(6B)	1.59(2)
O(5)-C(12)	1.479(6)
C(12)-C(14)	1.485(10)
C(12)-C(13)	1.512(10)
C(12)-H(12)	1.0000
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
O(6A)-C(15A)	1.46(3)
C(15A)-C(16A)	1.45(3)
C(15A)-C(17A)	1.47(3)
C(15A)-H(15A)	1.0000
C(16A)-H(16D)	0.9800
C(16A)-H(16E)	0.9800
C(16A)-H(16F)	0.9800
C(17A)-H(17D)	0.9800
C(17A)-H(17E)	0.9800
C(17A)-H(17F)	0.9800
O(6B)-C(15B)	1.46(6)
C(15B)-C(16B)	1.46(5)
C(15B)-C(17B)	1.52(7)
C(15B)-H(15B)	1.0000
C(16B)-H(16A)	0.9800
C(16B)-H(16B)	0.9800
C(16B)-H(16C)	0.9800
C(17B)-H(17A)	0.9800
C(17B)-H(17B)	0.9800

C(17B)-H(17C)	0.9800
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(7)-C(2)-C(3)	118.2(5)
C(7)-C(2)-C(1)	120.8(6)
C(3)-C(2)-C(1)	121.0(6)
C(4)-C(3)-C(2)	120.7(5)
C(4)-C(3)-H(3)	119.6
C(2)-C(3)-H(3)	119.6
C(3)-C(4)-C(5)	120.3(5)
C(3)-C(4)-H(4)	119.9
C(5)-C(4)-H(4)	119.9
C(6)-C(5)-C(4)	120.1(4)
C(6)-C(5)-S(1)	119.7(4)
C(4)-C(5)-S(1)	120.1(3)
C(5)-C(6)-C(7)	118.8(5)
C(5)-C(6)-H(6)	120.6
C(7)-C(6)-H(6)	120.6
C(2)-C(7)-C(6)	121.9(5)
C(2)-C(7)-H(7)	119.0
C(6)-C(7)-H(7)	119.0
O(1)-S(1)-O(2)	119.6(2)
O(1)-S(1)-N(1)	107.6(2)
O(2)-S(1)-N(1)	106.1(2)
O(1)-S(1)-C(5)	107.4(2)
O(2)-S(1)-C(5)	107.4(2)
N(1)-S(1)-C(5)	108.2(2)
C(8)-N(1)-S(1)	121.6(3)

C(8)-N(1)-H(1N)	108(4)
S(1)-N(1)-H(1N)	120(4)
N(1)-C(8)-C(9)	109.2(4)
N(1)-C(8)-H(8A)	109.8
C(9)-C(8)-H(8A)	109.8
N(1)-C(8)-H(8B)	109.8
C(9)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.3
O(3)-C(9)-C(10)	109.9(4)
O(3)-C(9)-C(8)	106.8(3)
C(10)-C(9)-C(8)	112.0(4)
O(3)-C(9)-H(9)	109.3
C(10)-C(9)-H(9)	109.3
C(8)-C(9)-H(9)	109.3
C(11)-C(10)-C(9)	122.3(6)
C(11)-C(10)-H(10)	118.9
C(9)-C(10)-H(10)	118.9
C(10)-C(11)-H(11A)	120.0
C(10)-C(11)-H(11B)	120.0
H(11A)-C(11)-H(11B)	120.0
C(9)-O(3)-P(1)	123.4(3)
O(4)-P(1)-O(5)	116.9(2)
O(4)-P(1)-O(6A)	114.6(5)
O(5)-P(1)-O(6A)	93.7(5)
O(4)-P(1)-O(3)	113.9(2)
O(5)-P(1)-O(3)	103.4(2)
O(6A)-P(1)-O(3)	112.3(6)
O(4)-P(1)-O(6B)	117.3(8)
O(5)-P(1)-O(6B)	108.0(10)
O(3)-P(1)-O(6B)	94.3(8)
C(12)-O(5)-P(1)	120.9(3)
O(5)-C(12)-C(14)	107.6(5)
O(5)-C(12)-C(13)	105.2(6)

C(14)-C(12)-C(13)	114.4(6)
O(5)-C(12)-H(12)	109.8
C(14)-C(12)-H(12)	109.8
C(13)-C(12)-H(12)	109.8
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(14)-H(14A)	109.5
C(12)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(12)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
C(15A)-O(6A)-P(1)	125.2(15)
C(16A)-C(15A)-O(6A)	111(2)
C(16A)-C(15A)-C(17A)	109(2)
O(6A)-C(15A)-C(17A)	107.7(17)
C(16A)-C(15A)-H(15A)	109.7
O(6A)-C(15A)-H(15A)	109.7
C(17A)-C(15A)-H(15A)	109.7
C(15A)-C(16A)-H(16D)	109.5
C(15A)-C(16A)-H(16E)	109.5
H(16D)-C(16A)-H(16E)	109.5
C(15A)-C(16A)-H(16F)	109.5
H(16D)-C(16A)-H(16F)	109.5
H(16E)-C(16A)-H(16F)	109.5
C(15A)-C(17A)-H(17D)	109.5
C(15A)-C(17A)-H(17E)	109.5
H(17D)-C(17A)-H(17E)	109.5
C(15A)-C(17A)-H(17F)	109.5

H(17D)-C(17A)-H(17F)	109.5
H(17E)-C(17A)-H(17F)	109.5
C(15B)-O(6B)-P(1)	116(3)
O(6B)-C(15B)-C(16B)	99(4)
O(6B)-C(15B)-C(17B)	104(4)
C(16B)-C(15B)-C(17B)	113(4)
O(6B)-C(15B)-H(15B)	113.2
C(16B)-C(15B)-H(15B)	113.2
C(17B)-C(15B)-H(15B)	113.2
C(15B)-C(16B)-H(16A)	109.5
C(15B)-C(16B)-H(16B)	109.5
H(16A)-C(16B)-H(16B)	109.5
C(15B)-C(16B)-H(16C)	109.5
H(16A)-C(16B)-H(16C)	109.5
H(16B)-C(16B)-H(16C)	109.5
C(15B)-C(17B)-H(17A)	109.5
C(15B)-C(17B)-H(17B)	109.5
H(17A)-C(17B)-H(17B)	109.5
C(15B)-C(17B)-H(17C)	109.5
H(17A)-C(17B)-H(17C)	109.5
H(17B)-C(17B)-H(17C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$ x 10^3) for **4c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	133(6)	75(4)	90(4)	16(3)	69(4)	24(4)
C(2)	77(3)	61(3)	64(3)	20(2)	44(3)	15(2)
C(3)	65(3)	80(3)	47(3)	19(2)	19(2)	18(3)
C(4)	57(3)	73(3)	51(2)	26(2)	23(2)	30(2)
C(5)	40(2)	63(2)	42(2)	25(2)	22(2)	20(2)
C(6)	46(2)	68(3)	73(3)	27(2)	24(2)	26(2)
C(7)	75(3)	70(3)	90(4)	29(3)	44(3)	37(3)
S(1)	45(1)	62(1)	47(1)	24(1)	19(1)	22(1)
O(1)	41(2)	76(2)	64(2)	21(2)	20(2)	11(2)
O(2)	87(3)	73(2)	61(2)	34(2)	30(2)	45(2)
N(1)	35(2)	78(3)	43(2)	27(2)	16(2)	27(2)
C(8)	47(2)	66(3)	52(2)	27(2)	25(2)	24(2)
C(9)	40(2)	68(3)	48(2)	28(2)	20(2)	13(2)
C(10)	67(3)	90(4)	70(3)	51(3)	25(3)	25(3)
C(11)	92(5)	137(6)	125(6)	95(5)	51(5)	29(4)
O(3)	34(1)	71(2)	55(2)	22(2)	23(1)	12(1)
P(1)	43(1)	72(1)	41(1)	23(1)	17(1)	13(1)
O(4)	44(2)	83(2)	73(2)	25(2)	21(2)	22(2)
O(5)	85(3)	67(2)	56(2)	18(2)	26(2)	0(2)
C(12)	120(5)	58(3)	56(3)	22(2)	40(3)	14(3)
C(13)	148(6)	87(4)	121(6)	52(4)	93(6)	40(4)
C(14)	143(7)	115(6)	107(6)	59(5)	54(5)	57(5)
O(6A)	56(4)	88(6)	39(3)	20(4)	16(3)	15(4)
C(15A)	68(10)	82(8)	51(5)	32(5)	27(6)	22(5)
C(16A)	131(13)	234(19)	141(14)	129(14)	62(11)	111(14)
C(17A)	110(10)	100(8)	91(8)	2(6)	58(7)	14(7)
O(6B)	38(6)	103(12)	49(5)	33(7)	29(5)	36(9)
C(15B)	59(11)	100(13)	39(8)	30(9)	27(8)	33(10)
C(16B)	210(30)	171(19)	120(20)	118(18)	40(20)	50(20)
C(17B)	190(30)	130(15)	130(20)	-45(15)	90(20)	0(20)

Table 5. Hydrogen bonds for **4c** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(4)#1	0.875(19)	1.95(3)	2.790(5)	162(5)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1