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Supplemental Information

Electrophilic hydrophosphonylation of aldimines with alkylphosphonochloridates access to (*E*)-alk-1-enylphosphonamidates

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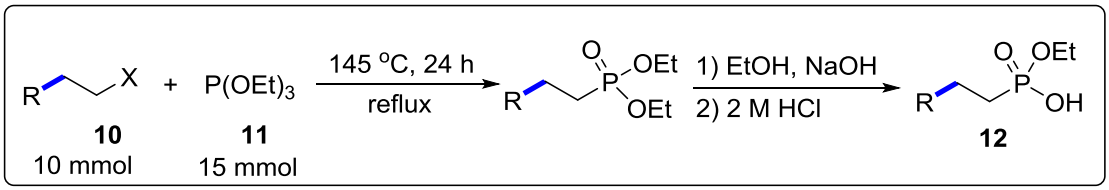
Table of Contents

1. General information

All reactions were carried out under anhydrous conditions employing standard techniques unless otherwise noted. Toluene was refluxed over sodium with diphenyl ketone as an indicator and freshly distilled prior to use. The products were purified on column chromatography with silica gel (200–300 mesh). Thin-layer chromatography (TLC) separations were performed on silica gel GF254 plates with a mixture of petroleum ether (PE) and ethyl acetate (EA) as eluent, and the plates were visualized with UV light. ^{1}H (400 MHz), ^{13}C (101 MHz), ^{19}F NMR (376 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker AMX 400 NMR spectrometer with TMS as an internal standard in $CDCl_3$ solution. Chemical shifts for ^{1}H NMR were reported in terms of chemical shift in reference to TMS at 0.00 ppm or residual $CHCl_3$ at 7.26 ppm (δ ppm). The following abbreviations were used to illustrate the diversities: δ = chemical shifts, *J* = coupling constant, s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, m = multiplet. Chemical shifts for ^{13}C NMR are reported in terms of chemical shift in reference to the $CDCl_3$ solvent signal (77.16 ppm, middle peak). Melting points were obtained on a Yanaco M500 melting point apparatus and are uncorrected. High resolution mass spectra were obtained via an Agilent LC/MSD TOF mass spectrometer.

Substituted dibenzo[*b*,*f*][1,4]oxazepines and dibenzo[*b*,*f*][1,4]thiazepines were synthesized by by cyclocondensations of *o*-aminophenols or *o*-aminothiophenols with *o*-halobenzaldehydes, *o*-fluoroacetophenone, and *o*-fluorobenzophenone with microwave-assisted one-pot method.[1] The phosphonochloridates were freshly synthesized prior to use by the reaction of ethyl hydrogen alkylphosphonates and thionyl chloride according to published procedures.[2] Others were commercially available and used as received, unless otherwise noted.

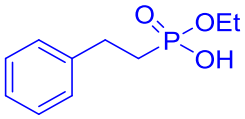
2. General procedure for the preparation of ethyl hydrogen alkylphosphonates 12



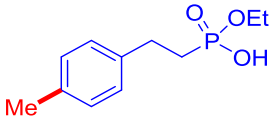
Alkyl halide **10** (10.0 mmol) and $P(OEt)_3$ **11** (15.0 mmol, 2.49 mL) were stirred and refluxed in a flask at 145 °C for 24 h. Diethyl alkylphosphonate was obtained in 140-190 °C fraction by reduced distillation under vacuum (< 2 mm Hg pressure). Then, 2 equivalents of sodium hydroxide and diethyl alkylphosphonate in 15 mL EtOH were stirred and refluxed at 85 °C for 12 h. After washing with brine (20 mL × 3), the aqueous phase was adjusted to acidity with HCl (2.0 mol/L), and sequentially extracted with dichloromethane (4 mL × 3). The combined organic layer was dried over anhydrous Na_2SO_4, and concentrated under vacuum to get the desired product **12**.

1. Lin, Y. C.; Li, N. C.; Cherng, Y. J. Microwave-Assisted Synthesis of Substituted Dibenzo[*b*,*f*][1,4]thiazepines, Dibenzo[*b*,*f*][1,4]oxazepines, Benzothiazoles, and Benzimidazoles. *J. Heterocycl. Chem*., **2014**, *51*, 808–814.
2. Xu, J. X.; Xia, C. F.; Yu, L.; Zhou, Q. Z. Synthesis of Phosphonopeptides Containing 1-Aminoalkylphosphonic acid. *Phosphorus Sulfur Silicon Relat. Elem.* **1999**, *152*, 35–44.

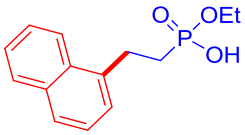
3. Characterization data of compounds 12a-12g



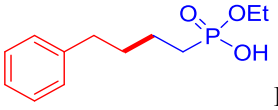
Ethyl hydrogen phenethylphosphonate (12a). Lit.[3] Brown oil (1.0 g, 48%). ^{1}H NMR (400 MHz, $CDCl_3$): 10.50 (1H, s), 7.27 (2H, t, J = 7.2 Hz), 7.19 (2H, t, J = 6.4 Hz), 7.17 (1H, d, J = 5.2 Hz), 4.09 (2H, dq, J = 7.1, 7.1 Hz), 3.01 – 2.84 (2H, m), 2.08 (1H, ddt, J = 3.6, 17.6, 18.0 Hz), 2.06 (1H, ddt, J = 3.6, 17.6, 18.0 Hz), 1.31 (3H, t, J = 7.0 Hz). ^{13}C NMR (101MHz, $CDCl_3$) 141.0 (d, J = 18.1 Hz), 128.6, 128.0, 126.3, 61.3 (d, J = 6.1 Hz), 28.5 (d, J = 2.9 Hz), 27.8 (d, J = 140.2 Hz), 16.3 (d, J = 5.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 32.46. HRMS (ESI) calcd. for $C_{10}H_{16}O_3P^+$ (M + H^+) *m/z* 215.0832, found 215.0833.



Ethyl hydrogen (4-methylphenethyl)phosphonate (12b). Brown oil (487 mg, 21%). ^{1}H NMR (400 MHz, $CDCl_3$): 12.16 (1H, s), 7.14 – 7.06 (4H, m), 4.09 (2H, dq, J = 7.2, 7.2 Hz), 2.95 – 2.80 (2H, m), 2.32 (3H, s), 2.05 (1H, ddt, J = 3.6, 18.0, 17.6 Hz). 2.04 (1H, ddt, J = 3.6, 18.0, 17.6 Hz). 1.32 (3H, t, J = 7.0 Hz). ^{13}C NMR (101MHz, $CDCl_3$) 138.4 (d, J = 18.9 Hz), 135.9, 129.3, 128.0, 61.2 (d, J = 6.6 Hz), 28.1 (d, J = 141.4 Hz), 28.1 (d, J = 4.1 Hz), 21.1, 16.5 (d, J = 6.4 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 32.84. HRMS (ESI) calcd. for $C_{11}H_{18}O_3P^+$ (M + H^+) *m/z* 229.0989, found 229.0997.



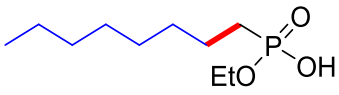
Ethyl hydrogen (2-(naphthalen-1-yl)ethyl)phosphonate (12c). Brown oil (60 mg，5%)**.** ^{1}H NMR (400 MHz, $CDCl_3$): 9.48 (1H, s), 8.03 (1H, d, J = 7.3 Hz), 7.85 (1H, d, J = 7.8 Hz), 7.73 (1H, d, J = 7.8 Hz), 7.54 – 7.44 (2H, m), 7.43 – 7.30 (2H, m), 4.31 – 3.99 (2H, m), 3.58 – 3.23 (2H, m), 2.36 – 2.11 (2H, m), 1.35 (3H, t, J = 6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): 137.1 (d, J = 2.4 Hz), 137.0 (d, J = 1.3 Hz), 134.0, 131.5, 129.0, 127.4, 126.3 (d, J = 4.0 Hz), 125.8, 125.7, 123.4, 61.6 (d, J = 4.8 Hz), 30.5 (d, J = 135.0 Hz), 25.8 (d, J = 5.4 HZ), 16.5 (d, J = 5.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 35.56. HRMS (ESI) calcd. for $C_{14}H_{18}O_3P^+$ (M + H^+) *m/z* 265.0989, found 265.0995.



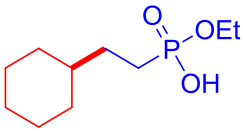
Ethyl hydrogen (4-phenylbutyl)phosphonate (12d). Yellow oil (223 mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$) 8.37 (1H, s), 7.30 – 7.24 (2H, m), 7.22 – 7.12 (3H, m), 4.11 –

3. Gobec, S.; Plantan, I.; Mravljak, J.; Švajger, U.; Wilson, R. A.; Besra, G. S.; Soares, S. L.; Appelberg, R.; Kikelj, D. Design, Synthesis, Biochemical Evaluation and Antimycobacterial Action of Phosphonate Inhibitors of Antigen 85C, A Crucial Enzyme Involved in Biosynthesis of the Mycobacterial Cell Wall. *Eur. J. Med. Chem*., **2007**, *42(1)*, 54–63.

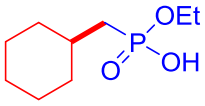
4.02 (2H, m), 2.66 – 2.58 (2H, m), 1.83 – 1.60 (6H, m), 1.31 (3H, t, J = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 142.0, 129.8, 128.4, 125.8, 61.5 (d, J = 6.5 Hz), 35.4 (d, J = 4.5 Hz), 32.3 (d, J = 17.1 Hz), 25.6 (d, J = 140.8 Hz), 22.1 (d, J = 4.9 Hz), 16.5 (d, J = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 33.94. HRMS (ESI) calcd. for $C_{12}H_{20}O_3P^+$ (M + H^+) *m/z* 243.1145, found 243.1153.



Ethyl hydrogen octylphosphonate (12e). Lit.[4] Yellow oil (750 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): 11.93 (s, 1H), 4.07 (dq, J = 7.2, 7.2 Hz, 2H), 1.78–1.53 (m, 4H), 1.41–1.22 (m, 13H), 0.87 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 61.0 (d, J = 6.8 Hz), 31.9, 30.7 (d, J = 17.2 Hz), 29.2 (d, J = 2.8 Hz), 26.7, 25.3, 22.8, 22.3 (d, J = 5.0 Hz), 16.5 (d, J = 6.4 Hz), 14.20. ^{31}P NMR (162 MHz, $CDCl_3$) 35.50. HRMS (ESI) calcd. for $C_{10}H_{23}O_3P$ (M + H^+) *m/z* 223.1458, found 223.1451.



Ethyl hydrogen (2-cyclohexylethyl)phosphonate (12f). Yellow oil (750 mg, 32%). ^{1}H NMR (400 MHz, $CDCl_3$): 10.72 (1H, s), 4.05 (2H, dq, J = 7.2, 7.2 Hz), 1.76 – 1.57 (7H, m), 1.53 – 1.41 (2H, m), 1.30 (3H, t, J = 7.0 Hz), 1.26 – 1.03 (4H, m), 0.95 – 0.79 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) 61.0 (d, J = 6.7 Hz), 38.4 (d, J = 17.1 Hz). 32.9, 29.5 (d, J = 4.6 Hz), 26.6, 26.3, 23.5 (d, J = 143.1 Hz), 16.5 (d, J = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 35.80. HRMS (ESI) calcd. for $C_{10}H_{22}O_3P^+$ (M + H^+) *m/z* 221.1302, found 221.1310.

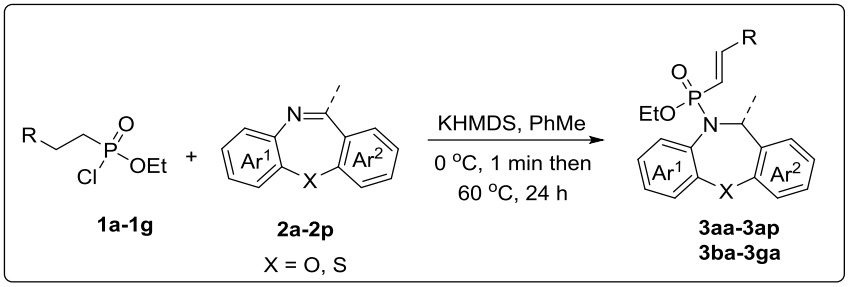


Ethyl hydrogen (cyclohexylmethyl)phosphonate (12g). Yellow oil (910 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) 11.8 (1H, s), 4.04 – 3.87 (2H, m), 1.72 – 1.46 (5H, m), 1.46 – 1.31 (2H, m), 1.20 (3H, td, J = 7.0, 4.6 Hz), 1.15 – 0.96 (4H, m), 0.80 – 0.73 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) 60.8 (d, J = 6.7 Hz), 34.6 (d, J = 10.8 Hz), 33.6 (d, J = 141.1 Hz), 32.7 (d, J = 3.5 Hz), 26.2 (d, J = 7.0 Hz), 26.1 (d, J = 76.2 Hz), 16.5 (d, J = 6.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 34.78. HRMS (ESI) calcd. for $C_9H_{20}O_3P^+$ (M + H^+) *m/z* 207.1145, found 207.1151.

4. General procedure for the synthesis of α,β-unsaturated phosphonamidates 3

General procedure A (for cyclic imines):

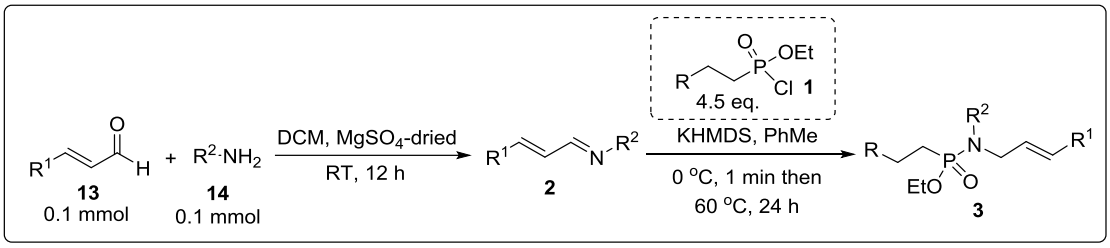
4. Fu, Z. C.; Sun, S. M.; Yang, A. J.; Sun, F.; Xu, J. X. Transition Metal-free Access to 3,4-Dihydro-1,2-oxaphosphinine-2-oxides from Phosphonochloridates and Chalcones Through Tandem Michael Addition and Nucleophilic Substitution. *Chem. Comm.*, **2019**, *55*, 13124–13127.



Ethyl hydrogen alkylphosphonate **12** (1.0 mmol) and thionyl chloride (1 mL) were added into a two-neck flask under an argon atmosphere. The mixture was refluxed at 80 °C for 12 h. After removal of HCl and residual $SOCl_2$ through addition of $CaCl_2$-dried, EtOH-free distilled chloroform and concentration, a 1.0 mmol/mL solution of the corresponding phosphonochloridate **1** in dry PhMe was prepared.

A solution of phosphonochloridate **1** (0.45 mmol, 0.45 mL) and dibenzo[*b*,*f*][1,4]oxazepine or dibenzo[*b*,*f*][1,4]thiazepine **2** (0.1 mmol) were added into an oven-dried tube and stirred at 0 °C for 1.0 min, followed by addition of 0.5 mol/L solution of KHMDS (0.45 mmol, 0.9 mL) in PhMe. Then, the resulting mixture was immediately stirred at 60 °C for 24 h. After quenching with saturated NH_4Cl, the mixture was extracted with dichloromethane (4 mL × 3). The combined organic layer was washed with brine (5 mL × 3), dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1, *v*/*v*) to afford the desired product **3 (3aa-3ap** and **3ba-3ga)**.

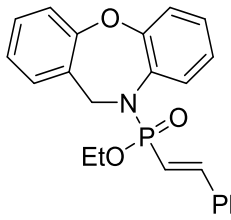
General procedure B (for in situ prepared imines):



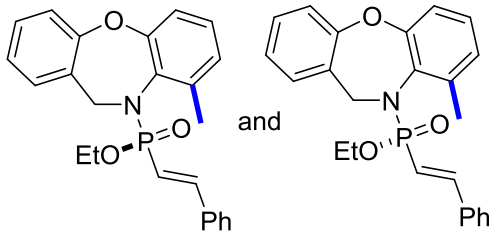
A tube was charged with unsaturated aldehyde **13** (0.1 mmol), amine **14** (0.1 mmol), and anhydrous $MgSO_4$ (0.2 mmol, 24 mg) in dried DCM. Then, the reaction mixture was stirred at room temperature for 12 h or more time to ensure that the raw materials were consumed as complete as possible. After filtration and removal of the solvent, the resulting linear imine **2** was prepared into 0.5 mL of dry PhMe solution to be used immediately in next step. The solid linear imines **2** were recrystallized from a mixture of PE and EA.

To a stirring solution of phosphonochloridate **1** (0.45 mmol, 0.45 mL) and imine **2** (0.1 mmol) in toluene (0.5 mL) in an oven-dried tube was added a 0.5 mol/L solution of KHMDS (0.45 mmol, 0.9 mL) at 0 °C and the mixture was stirred for 1.0 min. Then, the resulting mixture was further stirred at 60 °C for 24 h. After quenching with saturated NH_4Cl, the mixture was extracted with dichloromethane (4 mL × 3). The combined organic layer was washed with brine (5 mL × 3), dried over Na_2SO_4, and concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether/ethyl acetate = 2/1 to 1/1, *v*/*v*) to afford the desired product **3** (**3aA-3aO** and **3bC-3gC** and **3eP**).

5. Characterization data of compounds 3

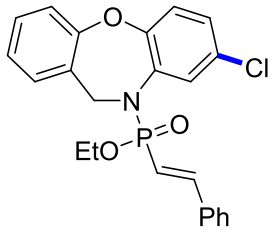


Ethyl (*E*)-dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl(styryl)phosphinate (3aa). Yellow oil, 37 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 (1H, d, J = 7.9 Hz), 7.32–7.30 (5H, m), 7.28 (1H, dd, J = 22.0, 17.4 Hz), 7.22 – 6.96 (7H, m), 6.17 (1H, dd, J = 19.3, 17.6 Hz), 4.78 (1H, dd, J = 16.3, 10.6 Hz), 4.71 (1H, dd, J = 16.3, 10.5 Hz), 4.22 – 4.09 (1H, m), 4.09 – 3.97 (1H, m), 1.27 (3H, t, J = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): 154.7, 153.9 (d, $J_{P\text{-}C}$ = 4.2 Hz), 147.1 (d, $J_{P\text{-}C}$ = 5.8 Hz), 135.3 (d, $J_{P\text{-}C}$ = 22.5 Hz)，134.1 (d, $J_{P\text{-}C}$ = 4.4 Hz), 129.9, 128.9, 128.8, 128.7 (d, $J_{P\text{-}C}$ = 1.4 Hz), 128.6, 127.9, 127.5 (d, $J_{P\text{-}C}$ = 0.6 Hz), 127.4, 124.20 (d, $J_{P\text{-}C}$ = 0.7 Hz), 123.1, 121.9, 120.7, 116.4 (, d, $J_{P\text{-}C}$ = 178.6 Hz), 60.9 (d, $J_{P\text{-}C}$ = 5.8 Hz), 51.0 (d, $J_{P\text{-}C}$ = 5.3 Hz), 16.3 (d, $J_{P\text{-}C}$ = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.0. HRMS (ESI) calcd. for $C_{23}H_{22}NO_3PNa^+$ (M + Na^+) *m/z* 414.1230, found 414.1222.

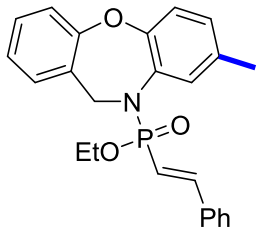


3ab **3ab'**

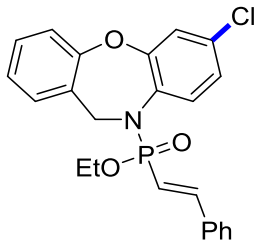
Ethyl *rel*-(*S,M,E*)-(9-methyldibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ab) and ethyl *rel*- (*R,M,E*)-(9-methyldibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ab'). Yellow oil, 25 mg, 62%, **3ab**:**3ab'** = 50:50. ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 (3H, dd, J = 6.7, 3.2 Hz), 7.37 – 7.33 (3H, m), 7.31 – 7.26 (3H, m), 7.23 – 7.18 (3H, m), 7.17 – 7.10 (5H, m), 7.10 – 6.91 (9H, m), 6.39 (1H, dd, J = 18.9, 17.6 Hz, **3ab**), 6.09 (1H, dd, J = 19.6, 17.5 Hz, **3ab'**), 4.90 (1H, dd, J = 17.2, 3.0 Hz), 4.89 (1H, dd, J = 17.6, 1.2 Hz), 4.39 (1H, dd, J = 26.5, 17.4 Hz, **3ab'**), 4.32 (1H, dd, J = 17.4, 7.7 Hz, **3ab**), 4.27 – 4.19 (1H, m), 4.19 – 4.10 (1H, m), 4.02 (2H, dq, J = 7.2, 7.2 Hz), 2.48 (6H, s), 1.33 (3H, t, J = 7.0 Hz), 1.11 (3H, t, J = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$): 163.3, 163.2, 157.2, 154.3, 154.2, 147.4 (d, J = 4.6 Hz), 146.73 (d, J = 4.7 Hz), 139.2, 139.0, 128.8, 128.7, 128.6, 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.1, 126.7, 126.5, 123.2 (d, J = 8.8 Hz), 121.2 (d, J = 6.2 Hz), 119.4 (d, J = 11.1 Hz), 116.5 (d, J = 174.7 Hz), 116.1 (d, J = 180.0 Hz), 61.2 (d, J = 5.1 Hz), 61.1 (d, J = 5.4 Hz), 50.3 (d, J = 4.2 Hz), 49.8 (d, J = 7.4 Hz), 18.7, 18.6, 16.5 (d, J = 6.7 Hz), 16.3 (d, J = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.17, 19.37. HRMS (ESI) calcd. for $C_{24}H_{24}NO_3PNa^+$ (M + Na^+) *m/z* 428.1386, found 428.1380.



Ethyl (*E*)-(8-chlorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ac). Colorless oil, 26 mg, 61%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.38 (1H, s), 7.34 – 7.27 (5H, m), 7.27 – 7.21 (1H, m), 7.20 – 7.16 (1H, m), 7.14 – 7.07 (4H, m), 7.01 (1H, t, *J* = 7.3 Hz), 6.11 (1H, dd, *J* = 19.7, 17.5 Hz), 4.78 (1H, dd, *J* = 16.1, 10.2 Hz), 4.66 (1H, dd, *J* = 16.1, 10.7 Hz), 4.23 – 4.10 (1H, m), 4.09 – 3.95 (1H, m), 1.30 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.5, 152.0 (d, *J* = 3.8 Hz), 147.6 (d, *J* = 5.7 Hz), 135.2 (d, *J* = 22.6 Hz), 135.0 (d, *J* = 3.9 Hz), 130.1, 129.0, 128.9 (d, *J* = 4.9 Hz), 128.6 (d, *J* = 6.4 Hz), 128.5, 128.4, 127.7, 127.4, 127.3, 123.4, 122.9, 120.5, 115.9 (d, *J* = 178.4 Hz), 61.1 (d, *J* = 5.8 Hz), 50.8 (d, *J* = 4.8 Hz), 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.76. HRMS (ESI) calcd. for $C_{23}H_{21}ClNO_3PNa^+$ (M + Na+) *m/z* 448.0840, found 448.0833.

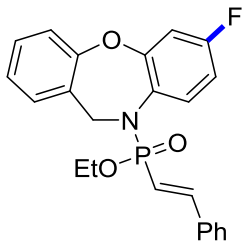


Ethyl (*E*)-(8-methyldibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ad). Colorless oil, 25 mg, 57%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.33 – 7.30 (6H, m), 7.29 (1H, dd, *J* = 22.1, 17.4 Hz), 7.20 – 7.14 (2H, m), 7.12 – 7.04 (3H, m), 6.99 – 6.95 (2H, m), 6.18 (1H, dd, *J* = 19.2, 17.6 Hz), 4.74 (1H, dd, *J* = 16.9, 11.2 Hz), 4.67 (1H, dd, *J* = 16.6, 10.8 Hz), 4.21 – 4.10 (1H, m), 4.09 – 3.97 (1H, m), 2.30 (3H, s), 1.27 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.7, 151.9 (d, *J* = 4.3 Hz), 147.0 (d, *J* = 5.6 Hz), 135.5, 135.3, 134.5, 134.0, 133.7 (d, *J* = 4.1 Hz), 131.0, 129.9, 129.2, 128.9, 128.8, 128.5, 128.2, 127.7, 127.2, 122.9, 121.5, 120.6, 116.6 (d, *J* = 178.4 Hz), 60.8 (d, *J* = 5.7 Hz), 51.1 (d, *J* = 5.3 Hz), 20.8, 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.89. HRMS (ESI) calcd. for $C_{24}H_{24}NO_3PNa^+$ (M + Na^+) *m/z* 428.1386, found 423.1383.

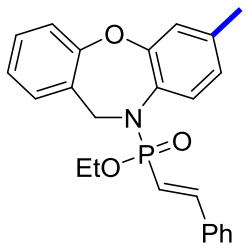


Ethyl (*E*)-(7-chlorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ae). Colorless oil, 23 mg, 54%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.34 – 7.27 (6H, m), 7.23 (1H, dd, *J* = 8.2, 3.0 Hz), 7.21 – 7.16 (2H, m), 7.14 – 7.08 (2H, m), 7.05 – 6.99 (2H, m), 6.10 (1H, dd, *J* = 18.8, 18.0 Hz), 4.75 (1H, dd, *J* = 16.0, 10.6 Hz), 4.67 (1H, dd, *J* = 15.9, 10.5 Hz), 4.20 – 4.09 (1H, m), 4.06 – 3.94 (1H, m), 1.28 (1H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.4, 153.7 (d, *J* = 4.3 Hz), 153.1 (d, *J* = 3.5 Hz), 147.6 (d, *J* = 3.5 Hz), 132.1, 130.1, 129.4, 129.0,

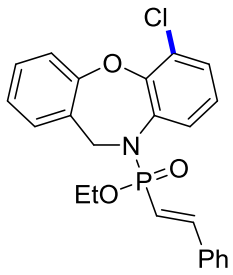
128.9 (d, *J* = 3.3 Hz), 127.7, 127.5, 124.1, 123.5, 121.4 (d, *J* = 154.5 Hz), 61.1 (d, *J* = 4.8 Hz), 50.9 (d, *J* = 4.5 Hz), 16.4 (d, *J* = 6.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.92. HRMS (ESI) calcd. for $C_{23}H_{21}ClO_3PNa^+$ (M + Na^+) *m/z* 448.0840, found 448.0834.



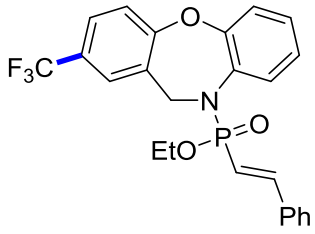
Ethyl (*E*)-(7-fluorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3af). Yellow oil, 12 mg, 29%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.35 – 7.24 (6H, m), 7.23 – 7.08 (5H, m), 7.02 (1H, t, *J* = 7.7 Hz), 6.85 (1H, td, *J* = 8.6, 2.9 Hz), 6.15 (1H, dd, *J* = 19.6, 17.5 Hz), 4.80 (1H, dd, *J* = 16.1, 10.1 Hz), 4.70 (1H, dd, *J* = 16.1, 10.4 Hz), 4.23 – 4.11 (1H, m), 4.09 – 3.96 (1H, m), 1.30 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.7, 149.7 (d, *J* = 3.1 Hz), 147.6 (d, *J* = 5.8 Hz), 135.2 (d, *J* = 23.0 Hz), 130.1, 129.6, 128.9, 128.8, 127.7, 127.6, 123.4, 122.6 (d, *J* = 9.3 Hz), 120.6, 115.9 (d, *J* = 179.1Hz), 114.9 (d, $J_{C\text{-}F}$ = 25.6 Hz), 113.8 (d, $J_{C\text{-}F}$ = 22.7 Hz), 61.1 (d, *J* = 5.6 Hz), 50.5 (d, *J* = 4.7 Hz), 16.4 (d, *J* = 6.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) -118.07. ^{31}P NMR (162 MHz, $CDCl_3$) 19.78. HRMS (ESI) calcd. for $C_{23}H_{21}FO_3PNa^+$ (M + Na^+) m/z 432.1135, found 432.1136.



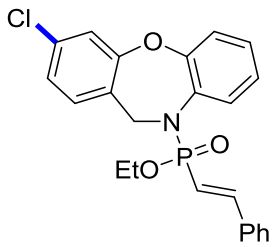
Ethyl (*E*)-(7-methyldibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ag). Colorless oil, 39 mg, 96%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.33 –7.31 (5H, m), 7.30 – 7.27 (1H, m), 7.27 – 7.15 (3H, m), 7.13 – 7.10 (2H, m), 7.04 – 6.97 (2H, m), 6.88 (1H, dd, *J* = 8.0, 1.5 Hz), 6.19 (1H, dd, *J* = 19.3, 17.5 Hz), 4.77 (1H, dd, *J* = 16.4, 10.7 Hz), 4.70 (1H, dd, *J* = 16.4, 10.6 Hz), 4.21 – 4.10 (1H, m), 4.09 – 3.98 (1H, m), 2.32 (3H, s), 1.29 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.6, 153.7 (d, *J* = 3.5 Hz), 146.9 (d, *J* = 5.7 Hz), 137.8, 135.4 (d, *J* = 22.6 Hz), 131.3 (d, *J* = 4.1 Hz), 129.9, 128.9, 128.8, 128.5, 128.4, 128.2, 127.7, 127.3, 126.4, 125.0, 123.0, 122.3, 120.7, 116.5 (d, *J* = 178.5 Hz), 60.8 (d, *J* = 5.6 Hz), 51.1 (d, *J* = 5.5 Hz), 21.0, 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.05. HRMS (ESI) calcd. for $C_{24}H_{24}NO_3PNa^+$ (M + Na^+) *m/z* 428.1386, found 428.1380.



Ethyl (*E*)-(6-chlorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ah). Colorless oil, 23 mg, 54%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 (1H, d, *J* = 7.8 Hz), 7.34 – 7.30 (6H, m), 7.29 – 7.24 (2H, m), 7.21 – 7.14 (1H, m), 7.10 – 7.03 (2H, m), 6.93 (1H, t, *J* = 7.8 Hz), 6.17 (1H, dd, *J* = 19.5, 17.5 Hz), 4.84 (1H, dd, *J* = 16.1, 10.0 Hz), 4.75 (1H, dd, *J* = 16.0, 10.7 Hz), 4.15 (1H, dq, *J* = 10.0, 7.2 Hz), 4.02 (1H, dq, *J* = 10.2, 7.2 Hz), 1.28 (1H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 152.8 (d, *J* = 4.1 Hz), 150.6, 147.5 (d, *J* = 5.5 Hz), 135.2 (d, *J* = 22.7 Hz), 134.1 (d, *J* = 4.0 Hz), 130.1, 129.5, 128.8, 127.8 (d, *J* = 17.3 Hz), 127.7, 127.3, 125.6, 124.7, 123.7, 122.4, 116.1 (d, *J* = 178.7 Hz), 61.1 (d, *J* = 5.7 Hz), 50.5 (d, *J* = 5.0 Hz), 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.07. HRMS (ESI) calcd. for $C_{23}H_{21}ClNO_3PNa^+$ (M + Na^+) *m/z* 448.0840, found 448.0832.

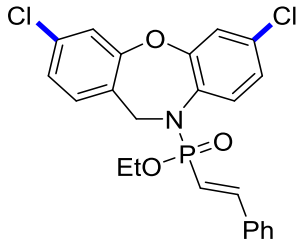


Ethyl (*E*)-styryl(2-(trifluoromethyl)dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)phosphinate (3ai). Colorless oil, 33 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 – 7.29 (3H, m), 7.28 – 7.18 (6H, m), 7.17 – 7.10 (3H, m), 7.07 – 7.01 (1H, m), 6.09 (1H, dd, *J* = 19.6, 17.5 Hz), 4.72 (1H, dd, *J* = 16.4, 10.3 Hz), 4.64 (1H, dd, *J* = 16.4, 10.5 Hz), 4.13 – 4.04 (1H, m), 4.01 – 3.90 (1H, m), 1.21 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 156.9, 153.3 (d, *J* = 3.8 Hz), 147.6 (d, *J* = 5.4 Hz), 135.1 (d, *J* = 22.6 Hz), 134.0 (d, *J* = 3.9 Hz), 130.2, 128.9 (d, *J* = 6.9 Hz), 128.1, 127.9, 127.7, 126.3 (q, $J_{F\text{-}C}$ = 274.1 Hz), 126.4, 125.8, 124.8, 121.9, 121.2, 116.0 (d, *J* = 178.5 Hz), 61.1 (d, *J* = 5.6 Hz), 51.2 (d, *J* = 5.1 Hz), 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.68. HRMS (ESI) calcd. for $C_{24}H_{21}F_3NO_3PNa^+$ (M + Na^+) *m/z* 482.1103, found 482.1095.

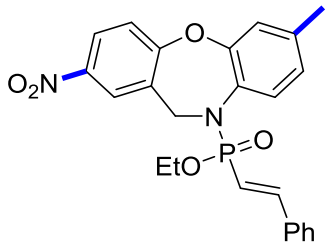


Ethyl (*E*)-(3-chlorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3aj). Colorless oil, 25 mg, 59%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 (1H, d, *J* = 7.8 Hz), 7.33 – 7.30 (6H, m), 7.29 – 7.23 (2H, m), 7.22 – 7.15 (1H, m), 7.10 – 7.02 (2H, m), 6.93 (1H, t, *J* = 7.8 Hz), 6.17 (1H, dd, *J* = 19.4, 17.6 Hz), 4.83 (1H, dd, *J* = 16.1, 10.0 Hz), 4.75 (1H, dd, *J* = 16.0, 10.7 Hz), 4.20 – 4.09 (1H, m), 4.07 – 3.97 (1H, m), 1.28 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 155.0, 153.4 (d, *J* = 4.1 Hz), 147.4 (d, *J* = 5.8 Hz), 135.3, 135.1, 133.9 (d, *J* =

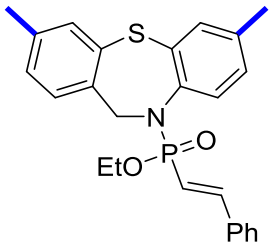
4.1 Hz), 133.6, 130.1, 129.9, 129.6, 128.9, 128.8 (d, *J* = 1.1 Hz), 127.7 (d, *J* = 4.2 Hz), 126.0, 124.6, 123.2, 121.8, 120.9, 116.2 (d, *J* = 178.3 Hz), 61.0 (d, *J* = 5.8 Hz), 50.7 (d, *J* = 5.4 Hz), 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.82. HRMS (ESI) calcd. for $C_{23}H_{21}ClNO_3PNa^+$ (M + Na^+) *m/z* 448.0840, found 428.0835.



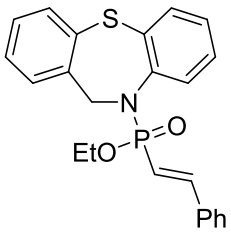
Ethyl (*E*)-(3,7-dichlorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3ak). Yellow oil, 28 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.29 – 7.20 (6H, m), 7.16 (1H, d, *J* = 3.9 Hz), 7.12 (1H, d, *J* = 2.2 Hz), 7.04 (1H, d, *J* = 1.8 Hz), 7.01 – 6.91 (3H, m), 6.02 (1H, dd, *J* = 18.4, 16.4 Hz), 4.65 (1H, dd, *J* = 15.5, 9.4 Hz), 4.55 (1H, dd, *J* = 15.3, 10.1 Hz), 4.12 – 4.02 (1H, m), 4.00 – 3.90 (1H, m), 1.23 (3H, t, *J* = 6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 153.7, 152.3 (d, *J* = 4.3 Hz), 146.8 (d, *J* = 5.8 Hz), 134.0 (d, *J* = 22.6 Hz), 132.9, 131.5 (d, *J* = 4.5 Hz), 131.4 (d, *J* = 1.3 Hz), 129.2, 128.9, 128.6, 127.9, 126.7, 125.1, 123.5, 122.6, 121.1, 119.9, 114.7 (d, *J* = 178.0 Hz), 60.2 (d, *J* = 5.8 Hz), 49.6 (d, *J* = 5.2 Hz), 15.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.76. HRMS (ESI) calcd. for $C_{23}H_{21}Cl_2NO_3P^+$ (M + H^+) *m/z* 460.0631, found 460.0631.



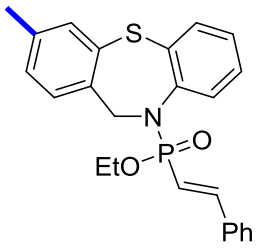
Ethyl (*E*)-(7-methyl-2-nitrodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(styryl)phosphinate (3al). Yellow oil, 12 mg, 26%. ^{1}H NMR (400 MHz, $CDCl_3$) 8.00 – 7.92 (2H, m), 7.30 – 7.23 (4H, m), 7.22 – 7.16 (3H, m), 7.11 – 7.07 (1H, m), 6.97 (1H, s), 6.89 – 6.85 (1H, m), 6.08 (1H, dd, *J* = 19.5, 17.5 Hz), 4.72 (1H, dd, *J* = 16.5, 10.3 Hz), 4.62 (1H, dd, *J* = 16.5, 10.6 Hz), 4.14 – 4.02 (1H, m), 4.02 – 3.91 (1H, m), 2.27 (3H, s), 1.22 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 159.3, 147.7 (d, *J* = 5.9 Hz), 142.5, 135.3 (d, *J* = 18.9 Hz), 130.3, 128.9, 128.8, 128.7 (d, J = 3.7 Hz), 127.8, 127.7, 126.42 (d, *J* = 3.1 Hz), 126.4, 126.0, 125.2, 124.4 (d, *J* = 14.6 Hz), 122.2, 121.5, 115.8 (d, *J* = 178.0 Hz), 61.2 (d, *J* = 5.6 Hz), 51.6 (d, *J* = 5.4 Hz), 21.0, 16.42 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.53. HRMS (ESI) calcd. for $C_{24}H_{23}N_2O_5PNa^+$ (M + Na^+) *m/z* 473.1237, found 473.1233.



Ethyl (*E*)-(3,7-dimethyldibenzo[*b,f*][1,4]thiazepin-10(11*H*)-yl)(styryl)phosphinate (3am). Yellow oil, 12mg, 25%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 – 7.30 (5H, m), 7.28 – 7.19 (2H, m), 7.02 – 6.98 (2H, m), 6.93 (1H, s), 6.87 (1H, dd, *J* = 8.0, 1.4 Hz), 6.81 (1H, d, *J* = 7.7 Hz), 6.16 (1H, dd, *J* = 19.2, 17.5 Hz), 4.73 (1H, dd, *J* = 16.1, 10.6 Hz), 4.66 (1H, dd, *J* = 16.1, 10.5 Hz), 4.18 (1H, dq, *J* = 10.0, 7.1 Hz), 4.06 (1H, dq, *J* = 10.1, 7.1 Hz), 2.33 (3H, s), 2.28 (3H, s), 1.30 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.4, 153.6 146.7, 138.6, 137.7, 135.6 (d, *J* = 20.8 Hz), 131.2, 129.7, 128.7, 128.5, 127.6, 124.8, 124.3, 123.7, 122.1, 121.0, 116.6 (d, *J* = 177.0 Hz), 60.8 (d, *J* = 8.7 Hz), 51.1 (d, *J* = 19.5 Hz), 21.0, 20.9, 16.4 (d, *J* = 8.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.06. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2SPNa^+$ (M + Na^+) *m/z* 458.1314, found 458.1315.

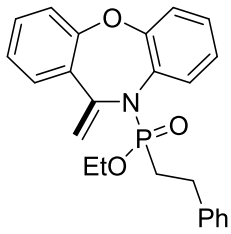


Ethyl (*E*)-dibenzo[*b,f*][1,4]thiazepin-10(11*H*)-yl(styryl)phosphinate (3an). Colorless oil, 30 mg 74%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.46 (2H, d, *J* = 8.0 Hz), 7.40 – 7.30 (6H, m), 7.30 – 7.09 (6H, m), 6.20 (1H, dd, *J* = 19.1, 17.6 Hz), 4.80 (1H, dd, *J* = 16.4, 10.5 Hz), 4.68 (1H, dd, *J* = 16.4, 10.4 Hz), 4.21 – 4.12 (1H, m), 4.12 – 4.01 (1H, m), 1.27 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 147.3 (d, *J* = 5.5 Hz), 144.8 (d, *J* = 5.3 Hz), 137.0, 135.4 (d, *J* = 22.5 Hz), 133.4 (d, *J* = 4.9 Hz), 132.9, 130.2, 129.9, 129.7, 128.8 (d, *J* = 7.4 Hz), 128.4, 128.2, 128.0, 127.7, 126.8, 126.1, 116.7 (d, *J* = 177.4 Hz), 61.1 (d, *J* = 5.5 Hz), 53.2 (d, *J* = 5.7 Hz), 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.90. HRMS (ESI) calcd. for $C_{23}H_{22}NO_2PSNa^+$ (M + Na^+) *m/z* 430.1001, found 430.0995.

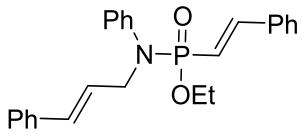


Ethyl (*E*)-(3-methyldibenzo[*b,f*][1,4]thiazepin-10(11*H*)-yl)(styryl)phosphinate (3ao). Yellow oil, 20 mg, 48%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.51 – 7.40 (2H, m), 7.37 – 7.29 (6H, m), 7.26 – 7.19 (1H, m), 7.18 – 7.11 (2H, m), 7.04 (1H, d, *J* = 7.7 Hz), 6.93 (1H, d, *J* = 7.7 Hz), 6.16 (1H, dd, *J* = 19.3, 17.5 Hz), 4.75 (1H, dd, *J* = 16.3, 10.7 Hz), 4.63 (1H, dd, *J* = 16.3, 10.4 Hz), 4.18 (1H, dq, *J* = 10.1, 7.2 Hz), 4.08 (1H, dq, *J* = 10.1, 7.2 Hz), 2.26 (3H, s), 1.28 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 147.1 (d, *J* = 5.5 Hz), 144.7 (d, *J* =

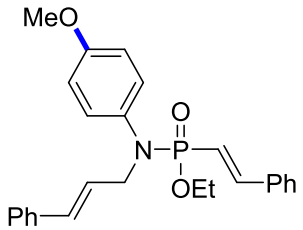
5.5 Hz), 137.6, 135.4 (d, *J* = 22.2 Hz), 134.1, 133.4 (d, *J* = 4.8 Hz), 132.7, 131.1, 130.1, 129.9, 129.6, 128.9, 128.7 (d, *J* = 6.3 Hz), 127.7 (d, *J* = 5.0 Hz), 126.8 (d, *J* = 19.5 Hz), 116.8 (d, *J* = 176.9 Hz), 61.1 (d, *J* = 5.6 Hz), 53.1 (d, *J* = 5.5 Hz), 20.9, 16.4 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.88. HRMS (ESI) calcd. for $C_{24}H_{24}NO_2PSNa^+$ (M + Na^+) *m/z* 444.1158, found 444.1153.



Ethyl (11-methylenedibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)(phenethyl)phosphinate (4). Yellow oil, 6 mg, 15%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.61 (1H, dd, *J* = 8.0, 1.5 Hz), 7.43 – 7.38 (1H, m), 7.34 – 7.26 (2H, m), 7.26 (7H, d, *J* = 2.2 Hz), 7.12 – 7.02 (2H, m), 5.62 (1H, d, *J* = 0.9 Hz), 5.45 (1H, d, *J* = 0.9 Hz), 4.36 – 4.23 (1H, m), 4.17 – 4.05 (1H, m), 3.07 – 2.79 (2H, m), 2.26 – 2.09 (2H, m), 1.28 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 133.7, 130.9, 130.4, 130.3, 128.9, 128.6, 128.5, 128.2, 128.1 (d, *J* = 4.3 Hz), 128.0, 126.1, 125.4, 125.3, 123.8, 121.3, 119.5, 118.3, 117.4, 109.8, 60.9 (d, *J* = 6.6 Hz), 28.4 (d, *J* = 128.3 Hz), 28.4 (d, *J* = 2.8 Hz), 16.3 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 29.46. HRMS (ESI) calcd. for $C_{24}H_{24}NO_3PNa^+$ (M + Na^+) *m/z* 428.1386, found 428.1386.

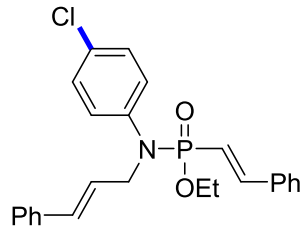


Ethyl *N*-cinnamyl-*N*-phenyl-*P*-((*E*)-styryl)phosphonamidate (3aA). Colorless oil, 16 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.43 – 7.31 (3H, m), 7.29 – 7.25 (3H, m), 7.24 – 7.19 (8H, m), 7.16 – 7.10 (1H, m), 7.08 – 7.02 (1H, m), 6.39 (1H, d, *J* = 15.9 Hz), 6.27 (1H, dd, *J* = 19.0, 17.5 Hz), 6.17 (1H, dt, *J* = 15.9, 6.3 Hz,), 4.39 – 4.32 (1H, m), 4.32 – 4.24 (1H, m), 4.18 – 4.08 (1H, m), 4.08 – 3.96 (1H, m), 1.25 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 147.1 (d, *J* = 5.7 Hz), 142.6 (d, *J* = 4.2 Hz), 135.4 (d, *J* = 22.3 Hz), 132.6, 130.0, 129.3, 128.9, 128.6, 127.7 (d, *J* = 5.6 Hz), 126.7, 126.5, 126.0 (d, *J* = 2.7 Hz), 125.2, 116.7 (d, *J* = 178.3 Hz), 60.9 (d, *J* = 5.8 Hz), 51.6 (d, *J* = 4.8 Hz), 16.5 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.21. HRMS (ESI) calcd. for $C_{25}H_{26}NO_2PNa^+$ (M + Na^+) *m/z* 426.1593, found 426.1583.

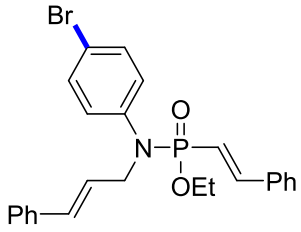


Ethyl *N*-cinnamyl-*N*-(4-methoxyphenyl)-*P*-((*E*)-styryl)phosphonamidate (3aB). Yellow oil, 20 mg, 46%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.38 – 7.30 (3H, m), 7.31 – 7.24 (3H, m), 7.23 – 7.22 (4H, m), 7.17 – 7.12 (2H, m), 7.08 – 7.02 (1H, m), 6.73 (1H, d, *J* = 8.7 Hz), 6.731 (1H, dd, *J* = 4.7, 4.7 Hz), 6.33 (1H, d, *J* = 13.6 Hz), 6.27 (1H, dd, *J* = 17.8, 16.4 Hz), 6.03 (1H, dt, *J* = 15.8, 6.4 Hz), 4.36 – 4.29 (1H, m), 4.29 – 4.21 (1H, m), 4.12 (1H,

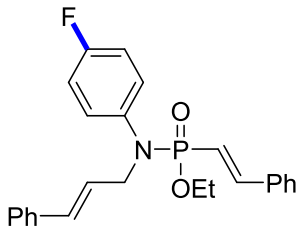
dq, *J* = 10.1, 7.1 Hz), 4.06 – 3.95 (1H, m), 3.72 (3H, s), 1.25 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 159.3, 147.1 (d, *J* = 5.6 Hz), 142.6 (d, *J* = 4.2 Hz), 135.4 (d, *J* = 22.5 Hz), 132.1, 130.0, 129.7, 129.2, 129.0, 128.9, 128.7, 128.6, 127.7 (d, *J* = 3.4 Hz), 126.1 (d, *J* = 3.1 Hz), 125.1, 124.4, 116.8 (d, *J* = 178.5 Hz), 114.1, 60.8 (d, *J* = 5.6 Hz), 55.4, 51.7 (d, *J* = 5.0 Hz), 16.5 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.20. HRMS (ESI) calcd. for $C_{26}H_{28}NO_3PNa^+$ (M + Na^+) *m/z* 456.1699, found 456.1693.



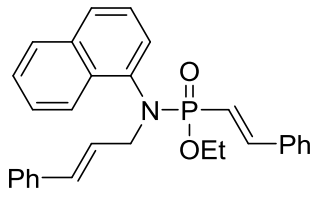
Ethyl *N*-(4-chlorophenyl)-*N*-cinnamyl-*P*-((*E*)-styryl)phosphonamidate (3aC). Yellow oil, 35 mg, 81%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.51 – 7.39 (3H, m), 7.37 – 7.26 (7H, m), 7.26 – 7.16 (5H, m), 6.45 (1H, d, *J* = 15.9 Hz), 6.32 (1H, dd, *J* = 19.1, 17.6 Hz), 6.20 (1H, dt, *J* = 15.8 Hz, *J* = 6.3 Hz), 4.39 (1H, dd, *J* = 14.9, 6.7 Hz), 4.32 (1H, dd, *J* = 15.3, 6.5 Hz), 4.20 (1H, dq, *J* = 9.8, 7.2 Hz), 4.14 – 4.02 (1H, m), 1.34 (3H, t, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.06. ^{13}C NMR (101 MHz, $CDCl_3$) 147.6 (d, *J* = 5.8 Hz), 141.1 (d, *J* = 4.5 Hz), 136.6, 135.1 (d, *J* = 22.3 Hz), 132.9, 130.5, 130.2, 129.3, 128.9, 128.7, 127.8 (d, *J* = 7.9 Hz), 127.1 (d, *J* = 3.5 Hz), 126.5, 126.1 (d, *J* = 2.2 Hz), 121.8, 116.1 (d, *J* = 178.2 Hz), 61.0 (d, *J* = 5.8 Hz), 51.5 (d, *J* = 5.1 Hz), 16.5 (d, *J* = 6.8 Hz). HRMS (ESI) calcd. for $C_{25}H_{26}ClNO_2P^+$ (M + H^+) m/z 438.1385, found 438.1377.



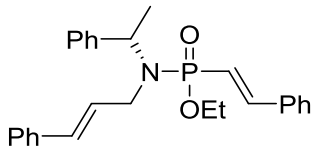
Ethyl *N*-(4-bromophenyl)-*N*-cinnamyl-*P*-((*E*)-styryl)phosphonamidate (3aD). Yellow oil, 1.7 g, 69% yield for 5 mmol scale. ^{1}H NMR (400 MHz, $CDCl_3$) 7.44 – 7.24 (m, 8H), 7.21– 7.07 (m, 6H), 6.38 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 19.4 Hz, *J* = 17.5 Hz, 1H), 6.12 (dt, *J* = 15.8 Hz, 6.2 Hz, 1H), 4.35-4.29 (m, 1H), 4.28 – 4.20 (m, 1H), 4.18 – 4.07 (m, 1H), 4.06 – 3.95 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$) 20.03. ^{13}C NMR (101 MHz, $CDCl_3$) 147.7 (d, *J* = 5.6 Hz), 141.7 (d, *J* = 4.7 Hz), 136.6, 135.1 (d, *J* = 22.2 Hz), 132.9, 132.2, 130.2, 128.9, 128.7, 127.8, 127.8, 127.3 (d, *J* = 3.2 Hz), 126.5, 126.1 (d, *J* = 1.1 Hz), 118.3, 116.0 (d, J = 178.3 Hz), 61.1 (d, *J* = 5.8 Hz), 51.3 (d, *J* = 4.9 Hz), 16.5 (d, *J* = 6.8 Hz). HRMS (ESI) calcd. for $C_{25}H_{26}BrNO_2P^+$ (M + H^+) m/z 482.0879, found 482.0884.



Ethyl *N*-cinnamyl-*N*-(4-fluorophenyl)-*P*-((*E*)-styryl)phosphonamidate (3aE). Colorless oil, 28 mg, 67%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.50 – 7.38 (3H, m), 7.38 – 7.32 (3H, m), 7.31 – 7.27 (4H, m), 7.25 – 7.17 (3H, m), 7.00 – 6.95 (2H, m), 6.41 (1H, d, *J* = 15.9 Hz), 6.29 (1H, dd, *J* = 18.9, 17.6 Hz), 6.20 (1H, dt, *J* = 15.8, 6.5 Hz), 4.38 – 4.30 (1H, m), 4.30 – 4.23 (1H, m), 4.23 – 4.14 (1H, m), 4.14 – 4.04 (1H, m), 1.33 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 161.8, 159.4, 147.4 (d, *J* = 5.7 Hz), 138.3, 136.7, 135.3 (d, *J* = 22.3 Hz), 133.0, 129.0 (d, *J* = 2.8 Hz), 128.9, 128.7, 127.8, 127.7, 126.5, 126.3, 116.3 (d, *J* = 178.2 Hz), 116.1, 115.9, 61.0 (d, *J* = 5.6 Hz), 52.2 (d, *J* = 4.9 Hz), 16.5 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.20. HRMS (ESI) calcd. for $C_{25}H_{25}FNO_2PNa^+$ (M + Na^+) *m/z* 444.1499, found 444.1494.

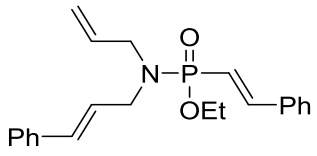


Ethyl *N*-cinnamyl-*N*-(naphthalen-1-yl)-*P*-((*E*)-styryl)phosphonamidate (3aF). Two stereoisomers exist in a ratio of 1:1 due to chiral P atom and axial hindrance between naphthalene-1yl and phosphonamidate groups. Yellow oil, 14 mg, 30%. ^{1}H NMR (400 MHz, $CDCl_3$) 8.21 (d, *J* = 7.7 Hz, 1H), 8.09 (d, *J* = 7.4 Hz, 1H), 7.78 (t, *J* = 5.5 Hz, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.23 (m, 17H), 7.19 – 7.04 (m, 14H), 6.29 (dd, *J* = 18.4 Hz, *J* = 18.8 Hz, 1H), 6.23 – 6.17 (m, 4H), 5.95 (t, *J* = 18.2 Hz, 1H), 4.68 – 4.56 (m, 1H), 4.55 – 4.47 (m, 1H), 4.16 – 3.83 (m, 8H), 1.26 (t, *J* = 6.8 Hz, 3H), 1.06 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 147.1, 138.1, 137.6, 136.9, 135.5 (d, *J* = 5.1 Hz), 135.3 (d, *J* = 8.7 Hz), 135.0, 133.1, 132.2 (d, *J* = 8.0 Hz), 129.8 (d, *J* = 9.7 Hz), 128.8 (d, *J* = 13.7 Hz), 128.6, 127.9 (d, *J* = 13.0 Hz), 127.6, 126.7, 126.5, 126.2, 125.6, 123.8 (d, *J* = 16.7 Hz), 117.2 (d, *J* = 176.1 Hz), 116.2 (d, *J* = 176.4 Hz),61.4 (d, *J* = 3.4 Hz), 61.3 (d, *J* = 3.4 Hz), 52.7 (d, *J* = 3.2 Hz), 52.3 (d, *J* = 3.2 Hz), 16.6 (d, *J* = 6.2 Hz), 16.4 (d, *J* = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.78, 20.20. HRMS (ESI) calcd. for $C_{29}H_{29}NO_2P^+$ (M + H^+) *m/z* 454.1930, found 454.1927.

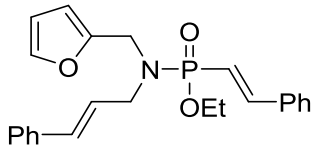


Ethyl *N*-cinnamyl-*N*-((*S*)-1-phenylethyl)-*P*-((*E*)-styryl)phosphonamidate (3aG). Colorless oil, 17 mg, 40%, dr = 50:50. ^{1}H NMR (400 MHz, $CDCl_3$) 7.41 – 7.32 (9H, m), 7.31 – 7.24 (11H, m), 7.22– 7.17 (6H, m), 7.16 – 7.10 (6H, m), 6.34 – 6.16 (4H, m), 5.90 – 5.79 (2H, m), 5.10 – 4.98 (2H, m), 4.15 – 4.03 (2H, m), 4.01 – 3.89 (2H, m), 3.70 – 3.59 (2H, m), 3.54 – 3.42 (2H, m), 1.57 (6H, dd, *J* = 11.5, 7.1 Hz), 1.27 (6H, q, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 23.48, 23.09. ^{13}C NMR (101 MHz, $CDCl_3$) 146.3 (d, *J* = 5.4 Hz), 146.0

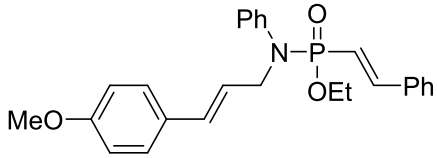
(d, *J* = 5.3 Hz), 142.1, 137.0, 135.6 (d, *J* = 24.1 Hz), 135.6 (d, *J* = 21.9 Hz), 131.4 (d, *J* = 3.3 Hz), 129.8, 129.2, 128.9, 128.6, 128.4, 128.1 (d, *J* = 0.9 Hz), 127.6, 127.6, 127.4 (d, *J* = 3.8 Hz), 126.4, 117.9 (d, *J* = 175.6 Hz), 117.7 (d, *J* = 176.1 Hz), 60.4 (t, *J* = 5.1 Hz), 53.8 (d, *J* = 5.0 Hz), 53.6 (d, *J* = 5.0 Hz), 45.0 (d, *J* = 5.2 Hz), 44.9 (d, *J* = 4.9 Hz), 19.6, 19.1, 16.58 (d, *J* = 2.3 Hz), 16.5 (d, *J* = 2.1 Hz). HRMS (ESI) calcd. for $C_{27}H_{31}NO_2P^+$ (M + H^+) *m/z* 432.2087, found 432.2094.



Ethyl *N*-allyl-*N*-cinnamyl-*P*-((*E*)-styryl)phosphonamidate (3aH) Colorless oil, 11 mg, 30%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.51 – 7.47 (2H, m), 7.44 – 7.28 (10H, m), 6.52 (1H, d, *J* = 15.8 Hz), 6.37 (1H, dd, *J* = 20.6, 15.3 Hz), 6.15 (dt, *J* = 15.7, 6.6 Hz, 1H), 5.86 – 5.74 (m, 1H), 4.23 – 4.13 (1H, m), 4.12 – 4.01 (1H, m), 3.88 – 3.84 (2H, m), 3.73 (2H, dd, *J* = 9.0, 7.2 Hz), 1.39 (3H, t, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 23.01. ^{13}C NMR (101 MHz, $CDCl_3$) 152.0 (d, *J* = 2.7 Hz), 146.2 (d, *J* = 5.2 Hz), 142.3, 136.6, 133.4, 129.8, 128.8, 128.6, 127.7, 127.6, 126.4, 125.8 (d, *J* = 2.6 Hz), 116.8 (d, *J* = 178.5 Hz), 110.3, 108.7, 60.2 (d, *J* = 5.6 Hz), 47.0 (d, *J* = 4.9 Hz), 41.1 (d, *J* = 5.3 Hz), 16.4 (d, *J* = 6.9 Hz). HRMS (ESI) calcd. for $C_{22}H_{27}NO_2P^+$ (M + H^+) *m/z* 368.1774, found 368.1760.

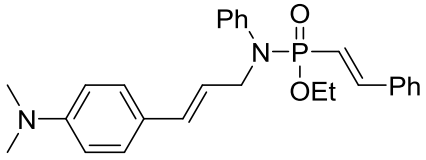


Ethyl *N*-cinnamyl-*N*-(furan-2-ylmethyl)-*P*-((*E*)-styryl)phosphonamidate (3aI). Colorless oil, 11 mg, 27%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.49 – 7.41 (m, 2H), 7.40 – 7.28 (m, 9H), 7.25 – 7.20 (m, 1H), 6.52 (d, *J* = 15.8 Hz, 1H), 6.36 (dd, *J* = 18.0 Hz, *J* = 18.0 Hz, 1H), 6.33 (dd, *J* = 1.6 Hz, *J* = 1.4 Hz, 1H), 6.25 (d, *J* = 3.1 Hz, 0H), 6.11 (dt, *J* = 15.8 Hz, *J* = 6.6 Hz, 1H), 4.31 (dd, *J* = 13.0 Hz, *J* = 7.1 Hz, 1H), 4.26 (dd, *J* = 9.5 Hz, *J* = 3.4 Hz, 1H), 4.24 – 4.12 (m, 1H), 4.11 – 4.01 (m, 1H), 3.79 (d, *J* = 6.9 Hz, 1H), 3.77 (d, *J* = 7.0 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 152.0 (d, *J* = 1.8 Hz), 146.2 (d, *J* = 5.3 Hz), 142.3, 136.7, 135.5 (d, *J* = 22.2 Hz), 133.4, 129.8, 128.8, 128.7, 127.8, 127.6, 126.5, 125.8, 116.9 (d, *J* = 178.6 Hz), 110.4, 108.8, 60.3 (d, *J* = 5.7 Hz), 47.1 (d, *J* = 4.7 Hz), 41.2 (d, *J* = 5.5 Hz), 16.5 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 23.05. HRMS (ESI) calcd. for $C_{24}H_{27}NO_3P^+$ (M + H^+) *m/z* 408.1724, found.408.1720.

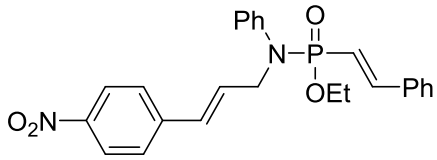


Ethyl *N*-((*E*)-3-(4-methoxyphenyl)allyl)-*N*-phenyl-*P*-((*E*)-styryl)phosphonamidate (3aJ). Yellow oil, 16 mg, 37%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.46 – 7.37 (3H, m), 7.38 – 7.30 (3H, m), 7.31 – 7.23 (5H, m), 7.23 – 7.13 (3H, m), 6.85 – 6.79 (2H, m), 6.35 (1H, dd, *J* = 34.5, 16.7 Hz), 6.22 (1H, dt, *J* = 15.9, 6.6 Hz), 4.36 – 4.23 (2H, m), 4.22 – 4.13 (1H, m), 4.13 – 4.03 (1H, m), 3.77 (3H, s), 1.32 (3H, t, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.43. ^{13}C NMR (101 MHz, $CDCl_3$) 157.7, 146.8 (d, *J* = 5.6 Hz), 137.0, 135.5 (d, *J* = 22.2 Hz),

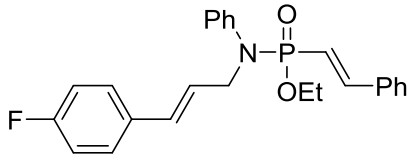
134.8 (d, *J* = 4.1 Hz), 132.7, 129.9, 129.3 (d, *J* = 2.4 Hz), 128.9, 128.6, 127.7 (d, *J* = 4.8 Hz), 126.8, 126.5, 116.8 (d, *J* = 177.8 Hz), 114.5, 60.8 (d, *J* = 5.9 Hz), 55.5, 52.4 (d, *J* = 5.7 Hz), 16.5 (d, *J* = 6.8 Hz). HRMS (ESI) calcd. for $C_{26}H_{28}NO_3PNa^+$ (M + Na^+) *m/z* 456.1699, found 456.1693.



Ethyl *N*-((*E*)-3-(4-(dimethylamino)phenyl)allyl)-*N*-phenyl-*P*-((*E*)-styryl)phosphonamidate(3aK). Yellow oil, 20 mg, 44%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.39 – 7.31(3H, m), 7.28 – 7.24 (3H, m), 7.23 – 7.15 (5H, m), 7.13 – 7.11 (2H, m), 7.06 – 7.01 (1H, m), 6.58 (1H, d, *J* = 5.5 Hz), 6.32 – 6.23 (2H, m), 5.96 (1H, dt, *J* = 15.7, 6.5 Hz), 4.35 – 4.19 (2H, m), 4.17 – 4.09(1H, m), 4.06 – 3.95 (1H, m), 2.86 (6H, s), 1.24 (3H, t, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.21. ^{13}C NMR (101 MHz, $CDCl_3$) 150.2, 146.9 (d, *J* = 5.4 Hz), 142.7 (d, *J* = 4.4 Hz), 135.5 (d, *J* = 22.5 Hz), 132.7, 129.9, 129.0 (d, *J* = 23.3 Hz), 128.9, 127.6 (d, *J* = 19.9 Hz), 127.5, 126.2 (d, *J* = 3.1 Hz), 125.0, 122.2, 117.0 (d, *J* = 178.5 Hz), 112.5, 60.8 (d, *J* = 5.7 Hz), 51.9 (d, *J* = 4.6 Hz), 40.6, 16.5 (d, *J* = 7.1 Hz). HRMS (ESI) calcd. for $C_{27}H_{31}N_2O_2PNa^+$ (M + Na^+) *m/z* 469.2015, found 469.2006.

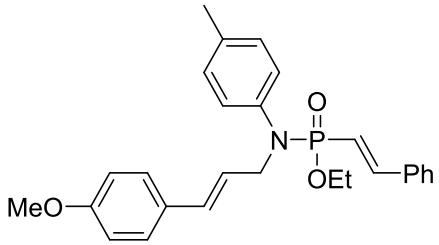


Ethyl *N*-((*E*)-3-(4-nitrophenyl)allyl)-*N*-phenyl-*P*-((*E*)-styryl)phosphonamidate (3aL). Yellow oil, 20 mg, 45%. ^{1}H NMR (400 MHz, $CDCl_3$) 8.11 (d, *J* = 8.8 Hz, 2H), 7.52 – 7.27 (m, 12H), 7.23 – 7.11 (m, 2H), 6.54 (d, *J* = 16.0 Hz, 1H), 6.43 (dt, *J* = 15.9, *J* = 5.8 Hz, 1H), 6.32 (dd, *J* = 19.2, *J* = 17.5 Hz, 1H), 4.45 (dd, *J* = 9.2, *J* = 5.9 Hz, 2H), 4.25 – 4.13 (m, 1H), 4.13 – 4.03 (m, 1H), 1.32 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 147.5 (d, *J* = 5.7 Hz), 147.0, 143.3, 142.4 (d, *J* = 4.2 Hz), 135.2 (d, *J* = 22.3 Hz), 132.0, 130.3 (d, *J* = 14.2 Hz,), 129.4, 128.9, 128.7, 128.2 (d, *J* = 7.4 Hz), 127.7, 127.0, 125.8 (d, *J* = 3.0 Hz), 125.4, 124.1, 116.2 (d, *J* = 178.2 Hz), 61.1 (d, *J* = 5.8 Hz), 51.3 (d, *J* = 5.1 Hz), 16.5 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.24. HRMS (ESI) calcd. for $C_{25}H_{25}N_2O_4PNa^+$ (M + Na^+) *m/z* 471.1444, found 471.1434.

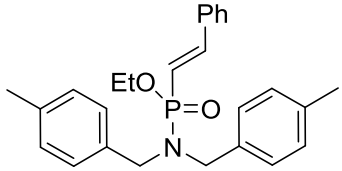


Ethyl *N*-((*E*)-3-(4-fluorophenyl)allyl)-*N*-phenyl-*P*-((*E*)-styryl)phosphonamidate (3aM). Colorless oil, 21 mg, 50%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.40 – 7.30 (3H, m), 7.30 – 7.25 (3H, m), 7.23 – 7.21 (3H, m), 7.20 – 7.13 (3H, m), 7.10 – 7.02 (1H, m), 6.91 – 6.84 (2H, m), 6.35 (1H, d, *J* = 15.9 Hz), 6.26 (1H, dd, *J* = 19.0, 17.5 Hz), 6.08 (1H, dt, *J* = 15.8, 6.3 Hz), 4.38 – 4.24 (2H, m), 4.17 – 4.07 (1H, m), 4.06 – 3.95 (1H, m), 1.25 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 161.2, 147.2 (d, *J* = 5.7 Hz), 142.6 (d, *J* = 4.3 Hz), 135.4 (d, *J* =

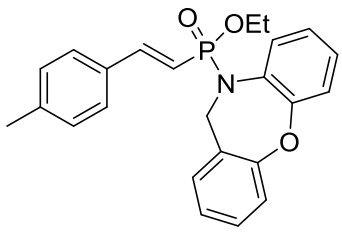
22.5 Hz), 133.0, 131.4, 130.1, 129.3, 128.9, 128.0 (d, *J* = 7.9 Hz), 127.7, 126.5, 126.0 (d, *J* = 3.1 Hz), 125.2, 116.6 (d, *J* = 178.5 Hz), 115.6, 115.4, 60.9 (d, *J* = 5.6 Hz), 51.5 (d, *J* = 5.0 Hz), 16.5 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.19. HRMS (ESI) calcd. for $C_{25}H_{25}FNO_2PNa^+$ (M + Na^+) *m/z* 444.1499, found 444.1492.



Ethyl *N*-((*E*)-3-(4-methoxyphenyl)allyl)-*P*-((*E*)-styryl)-*N*-(*p*-tolyl)phosphonamidate (3aN). Colorless oil, 19 mg, 43%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.45 – 7.37 (3H, m), 7.37 – 7.31 (3H, m), 7.25 – 7.19 (2H, m), 7.16 (2H, d, *J* = 7.9 Hz), 7.09 (2H, d, *J* = 8.3 Hz), 6.83 – 6.77 (2H, m), 6.38 (1H, d, *J* = 15.9 Hz), 6.33 (1H, dd, *J* = 18.7, 17.5 Hz), 6.09 (1H, dt, *J* = 15.8, 6.5 Hz), 4.40 – 4.24 (2H, m), 4.24 – 4.13 (1H, m), 4.13 – 4.02 (1H, m), 3.79 (3H, s), 2.30 (3H, s), 1.32 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 159.3, 146.8 (d, *J* = 5.7 Hz), 139.8 (d, *J* = 4.1 Hz), 135.3 (d, *J* = 49.8 Hz), 132.0, 129.9 (d, *J* = 5.2 Hz), 129.8, 128.9, 127.7 (d, *J* = 2.2 Hz), 126.7 (d, *J* = 2.7 Hz), 124.6, 116.9 (d, *J* = 178.3 Hz), 114.0, 60.7 (d, *J* = 5.7 Hz), 55.4, 52.0 (d, *J* = 5.1 Hz), 21.0, 16.5 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.27. HRMS (ESI) calcd. for $C_{27}H_{31}NO_3P^+$ (M + H^+) *m/z* 448.2037, found 448.2038.

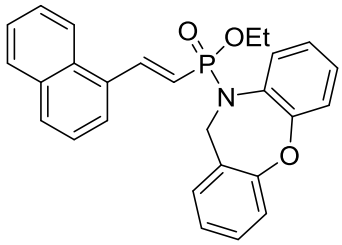


Ethyl (*E*)-*N*,*N*-bis(4-methylbenzyl)-*P*-styrylphosphonamidate (3aO). Colorless oil, 12 mg, 29%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.37 – 7.33 (2H, m), 7.40 – 7.34 (4H, m), 7.22 – 7.13 (2H, m), 7.10 (4H, d, *J* = 8.0 Hz), 7.05 (4H, d, *J* = 7.9 Hz), 6.25 (1H, dd, *J* = 17.9, 18.2 Hz), 4.12 – 4.05 (1H, m), 4.03 (2H, s), 4.01 (2H, s), 3.99 – 3.90 (1H, m), 2.27 (6H, s), 1.27 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 146.5 (d, *J* = 5.4 Hz), 137.1, 135.6 (d, *J* = 21.9 Hz), 134.6 (d, *J* = 2.5 Hz), 129.9, 129.3, 128.9, 128.8, 127.7, 126.6, 117.2 (d, *J* = 177.4 Hz), 60.7 (d, *J* = 5.5 Hz), 47.4 (d, *J* = 4.9 Hz), 21.3, 16.6 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 23.24. HRMS (ESI) calcd. for $C_{26}H_{31}NO_2P^+$ (M + H^+) *m/z* 420.2087, found 420.2092.

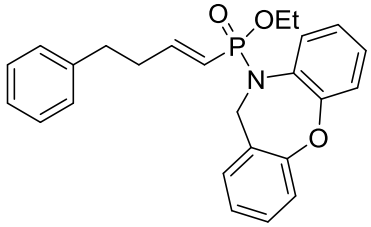


Ethyl (*E*)-dibenzo[*b*,*f*][1,4]oxazepin-10(11*H*)-yl(4-methylstyryl)phosphinate (3ba). Yellow oil, 18 mg, 45%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.30 (1H, d, *J* = 7.8 Hz), 7.20 – 7.07 (6H, m), 7.07 – 7.01 (4H, m), 6.95 (2H, dt, *J* = 14.6, 7.6 Hz), 6.04 (1H, dd, *J* = 19.5, 17.5 Hz), 4.70 (1H, dd, *J* = 16.0, 10.3 Hz), 4.63 (1H, dd, *J* = 16.0, 10.2 Hz), 4.12 –

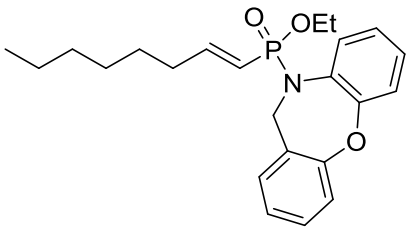
4.00 (1H, m), 4.00 – 3.87 (1H, m), 2.27 (3H, s), 1.18 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.7, 153.8 (d, *J* = 4.1 Hz), 147.15 (d, *J* = 5.8 Hz), 140.3, 134.2 (d, *J* = 4.7 Hz), 132.6 (d, *J* = 22.6 Hz), 129.5, 128.9 128.6, 127.7, 127.5, 127.4, 124.2, 123.1, 121.9, 120.7, 115.1 (d, *J* = 179.3 Hz), 60.8 (d, *J* = 5.6 Hz), 50.9 (d, *J* = 5.2 Hz), 21.5, 16.4 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.41. HRMS (ESI) calcd. for $C_{24}H_{25}NO_3P^+$ (M + H^+) *m/z* 406.1567, found 406.1574.



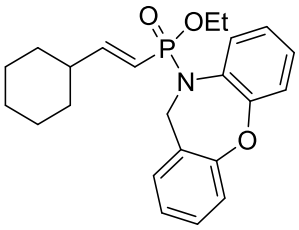
Ethyl (*E*)-dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl(2-(naphthalen-1-yl)vinyl)phosphinate (3ca). Brown oil, 6 mg, 15%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.97 (1H, dd, *J* = 22.0, 17.3 Hz), 7.83 – 7.69 (3H, m), 7.45 – 7.29 (5H, m), 7.16 – 6.91 (7H, m), 6.19 (1H, dd, *J* = 20.6, 17.5 Hz), 4.80 (1H, dd, *J* = 16.2, 10.1 Hz), 4.69 (1H, dd, *J* = 16.1, 10.7 Hz), 4.22 – 4.10 (1H, m), 4.10 – 3.99 (1H, m), 1.26 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.7, 154.0, 144.5 (d, *J* = 6.1 Hz), 134.2 (d, *J* = 4.1 Hz), 133.6, 133.2 (d, *J* = 22.3 Hz), 131.1, 130.1, 129.0, 128.8, 128.7, 127.6, 127.6, 126.7, 126.2, 125.5, 124.8, 124.4, 123.7, 123.3, 122.0, 120.8, 119.9 (d, *J* = 176.4 Hz), 61.0 (d, *J* = 5.6 Hz), 50.9 (d, *J* = 5.2 Hz), 16.5 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.38. HRMS (ESI) calcd. for $C_{27}H_{25}NO_3P^+$ (M + H^+) *m/z* 442.1567, found 442.1570.



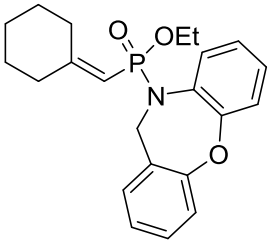
Ethyl (*E*)-dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl(4-phenylbut-1-en-1-yl)phosphinate (3da). Yellow oil, 20 mg, 49%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.19 – 7.16 (2H, m), , 7.15 – 7.05 (6H, m), 7.04 – 6.90 (6H, m), 5.54 (1H, dd, *J* = 21.8, 17.1 Hz), 4.62 (1H, dd, *J* = 16.1, 10.1 Hz), 4.54 (1H, dd, *J* = 16.2, 10.6 Hz), 4.03 – 3.92 (1H, m), 3.91 – 3.80 (1H, m), 2.52 (2H, t, *J* = 8.0 Hz), 2.30 (2H, dd, *J* = 14.5, 7.1 Hz), 1.14 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 153.5, 149.8 (d, *J* = 3.9 Hz), 133.3 (d, *J* = 22.6 Hz), 127.8, 127.5 (d, *J* = 1.3 Hz), 127.4, 127.4, 127.3, 127.3, 126.3 (d, *J* = 1.2 Hz), 126.2, 125.1, 123.0, 121.9, 120.7, 119.4, 118.5 (d, *J* = 175.2 Hz), 59.5 (d, *J* = 6.0 Hz), 49.6 (d, *J* = 5.3 Hz), 34.5, 33.0 (d, *J* = 1.3 Hz), 15.1 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.05. HRMS (ESI) calcd. for $C_{25}H_{27}NO_3P^+$ (M + H^+) *m/z* 420.1724, found 420.1725.



Ethyl (*E*)-dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl(oct-1-en-1-yl)phosphinate (3ea). Colorless oil, 16 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.25 (1H, d, *J* = 7.8 Hz), 7.16 – 7.04 (4H, m), 7.04 – 6.90 (3H, m), 6.46 (1H, ddt, *J* = 23.5, 17.0, 6.6 Hz), 5.49(1H, dd, *J* = 22.8, 17.1 Hz), 4.66 (1H, dd, *J* = 16.1, 10.0 Hz), 4.57 (1H, dd, *J* = 16.2, 10.4 Hz), 4.08 – 3.96 (1H, m), 3.95 – 3.80 (1H, m), 1.97 (1H, dd, *J* = 12.8, 6.2 Hz), 1.26 – 1.12 (12H, m), 0.80 (3H, t, *J* = 6.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 153.7, 152.8 (d, *J* = 4.3 Hz), 151.5 (d, *J* = 3.6 Hz), 133.4 (d, *J* = 4.4 Hz), 127.9, 127.5, 127.5 (d, *J* = 1.5 Hz), 126.6, 126.3 (d, *J* = 0.7 Hz), 123.1, 122.1, 120.8, 119.6, 117.8 (d, *J* = 175.5 Hz), 59.6 (d, *J* = 5.9 Hz), 49.7 (d, *J* = 5.3 Hz), 33.3, 33.1, 30.7, 27.8, 26.8, 21.7, 15.3 (d, *J* = 7.0 Hz), 13.2. ^{31}P NMR (162 MHz, $CDCl_3$) 19.54. HRMS (ESI) calcd. for $C_{23}H_{31}NO_3P^+$ (M + H^+) *m/z* 400.2037, found 400.2035.

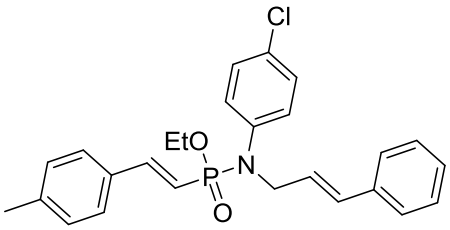


Ethyl (*E*)-(2-cyclohexylvinyl)(dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)phosphinate (3fa). Yellow oil, 26 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.31 (1H, d, *J* = 7.9 Hz), 7.23 – 7.11 (4H, m), 7.10 – 6.96 (3H, m), 6.47 (1H, ddd, *J* = 22.4, 17.3, 6.3 Hz), 5.50 (1H, ddd, *J* = 22.5, 17.3, 1.4 Hz), 4.72 (1H, dd, *J* = 16.2, 10.1 Hz), 4.63 (1H, dd, *J* = 16.2, 10.5 Hz), 4.15 – 4.03 (1H, m), 4.02 – 3.91 (1H, m), 1.99 – 1.89 (1H, m), 1.81 – 1.47 (6H, m), 1.23 (3H, t, *J* = 7.1 Hz), 1.19 – 1.06 (2H, m), 0.99 – 0.85 (2H, m). ^{13}C NMR (101 MHz, $CDCl_3$) 157.1 (d, *J* = 2.7 Hz), 154.7, 153.8 (d, *J* = 4.1 Hz), 134.4 (d, *J* = 4.2 Hz), 128.9, 128.6, 128.5, 127.5, 127.3, 124.1, 123.1, 121.8, 120.6, 116.2 (d, *J* = 175.4 Hz), 60.6 (d, *J* = 5.9 Hz), 50.7 (d, *J* = 5.1 Hz), 41.8 (d, *J* = 19.9 Hz), 31.4 (d, *J* = 5.4 Hz), 26.1, 25.7, 16.3 (d, *J* = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.40. HRMS (ESI) calcd. for $C_{23}H_{29}NO_3P^+$ (M + H^+) *m/z* 398.1880, found 398.1883.

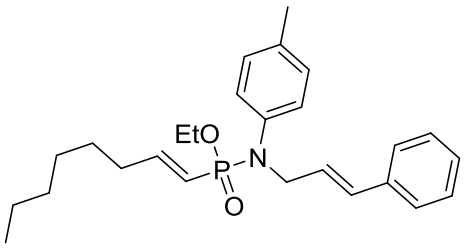


Ethyl (cyclohexylidenemethyl)(dibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)phosphinate (3ga). Yellow oil, 36 mg, 94%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.33 (1H, d, *J* = 7.9 Hz), 7.22 – 7.15 (2H, m), 7.15 – 7.09 (3H, m), 7.05 – 6.96 (2H, m), 5.25 (1H, d, *J* = 20.9 Hz), 4.79 (1H, dd, *J* = 15.9, 10.1 Hz), 4.66 (1H, dd, *J* = 15.9, 9.7 Hz), 4.08 (1H, dq, *J* = 10.1, 7.1 Hz), 3.93 (1H, dq, *J* = 10.1, 7.1 Hz), 2.39 – 2.30 (2H, m), 2.09 – 1.95 (2H, m), 1.54 –1.49 (1H, m), 1.47 – 1.35 (4H, m), 1.34 – 1.28 (1H, m), 1.25 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 165.8 (d,

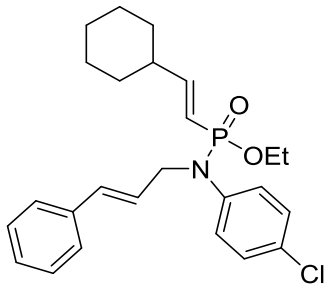
J = 6.2 Hz), 155.0, 152.9 (d, *J* = 4.7 Hz), 134.4 (d, *J* = 4.6 Hz), 129.0, 128.5, 128.1, 127.9, 126.7, 123.9, 123.0, 121.8, 120.4, 110.9 (d, *J* = 177.2 Hz), 59.9 (d, *J* = 5.8 Hz), 50.4 (d, *J* = 5.1 Hz), 39.1 (d, *J* = 22.8 Hz), 31.9 (d, *J* = 7.2 Hz), 28.3, 27.6, 25.9, 16.4 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 18.79. HRMS (ESI) calcd. for $C_{22}H_{27}NO_3P^+$ (M + H^+) *m/z* 384.1724, found 384.1731.



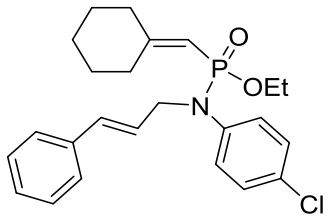
Ethyl *N*-(4-chlorophenyl)-*N*-cinnamyl-*P*-((*E*)-4-methylstyryl)phosphonamidate (3bC). Colorless oil, 16 mg, 36%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.36 (1H, dd, *J* = 21.9, 17.5 Hz), 7.26 (2H, d, *J* = 8.1 Hz), 7.22 – 7.18 (6H, m), 7.16 – 7.15 (4H, m), 7.09 (2H, d, *J* = 7.5 Hz), 6.38 (1H, d, *J* = 15.8 Hz), 6.24 – 6.07 (2H, m), 6.31 (1H, dd, *J* = 16.0, 8.4 Hz), 4.24 (1H, dd, *J* = 14.8, 7.4 Hz), 4.16 – 4.07 (1H, m), 4.04 – 3.96 (1H, m), 2.29 (3H, s), 1.26 (3H, t, *J* = 6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 147.6 (d, *J* = 5.7 Hz), 141.2 (d, *J* = 4.6 Hz), 140.6, 136.7, 132.9, 132.6 (d, *J* = 3.8 Hz), 132.4, 130.5, 129.7, 129.3, 129.2, 128.7, 128.5, 127.8, 127.8, 127.1 (d, *J* = 3.1 Hz), 126.5, 126.2 (d, *J* = 1.5 Hz), 114.8 (d, *J* = 178.9 Hz), 61.0 (d, *J* = 5.7 Hz), 51.5 (d, *J* = 4.8 Hz), 21.6, 16.5 (d, *J* = 6.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.53. HRMS (ESI) calcd. for $C_{26}H_{28}ClNO_2P^+$ (M + H^+) *m/z* 452.1541, found 452.1539.



Ethyl *N*-cinnamyl-P-((*E*)-oct-1-en-1-yl)-*N*-(*p*-tolyl)phosphonamidate (3eP). Yellow oil, 18 mg, 43%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.24 – 7.17 (4H, m), 7.16 – 7.07 (1H, m), 7.06 – 6.99 (4H, m), 6.60 (1H, ddt, *J* = 21.3, 17.1, 6.7 Hz), 6.35 (1H, d, *J* = 15.9 Hz), 6.13 (1H, dt, *J* = 15.8, 6.3 Hz), 5.61 (1H, dd, *J* = 22.3, 17.1 Hz), 4.30 – 4.14 (2H, m), 4.11 – 3.99 (1H, m), 4.00 – 3.89 (1H, m), 2.22 (3H, s), 2.07 (2H, td, *J* = 14.2, 7.0 Hz), 1.38 – 1.26 (3H, m), 1.25 – 1.17 (9H, m), 0.80 (3H, t, *J* = 6.8 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 151.1 (d, *J* = 3.4 Hz), 138.9 (d, *J* = 4.5 Hz), 136.1, 133.7 (d, *J* = 0.7 Hz), 131.3, 128.8, 127.6, 126.6, 126.0 (d, *J* = 2.4 Hz), 125.5, 125.3 (d, *J* = 3.4 Hz), 118.2 (d, *J* = 175.3 Hz), 59.5 (d, *J* = 5.9 Hz), 50.5 (d, *J* = 5.1 Hz), 33.3 (d, *J* = 21.1 Hz)., 30.7, 27.9, 27.0, 21.7, 20.0, 15.5 (d, *J* = 7.0 Hz), 13.2. ^{31}P NMR (162 MHz, $CDCl_3$) 19.94. HRMS (ESI) calcd. for $C_{26}H_{37}NO_2P^+$ (M + H^+) *m/z* 426.2556, found 426.2565.



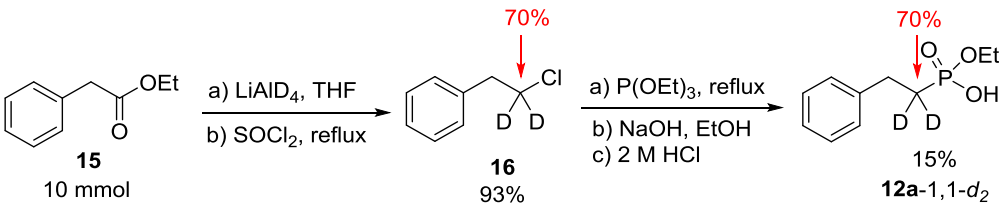
Ethyl *N*-(4-chlorophenyl)-*N*-cinnamyl-*P*-((*E*)-2-cyclohexylvinyl)phosphonamidate (3fC). Yellow oil, 22 mg, 49%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.22 – 7.21 (4H, m), 7.18 – 7.08 (5H, m), 6.64 – 6.49 (1H, m), 6.36 (1H, d, *J* = 15.9 Hz), 6.10 (1H, dt, *J* = 15.9, 6.3 Hz), 5.56 (1H, dd, *J* = 22.7, 17.2), 4.26 – 4.21 (2H, m), 4.11 – 4.01 (1H, m), 4.00 – 3.89 (1H, m), 1.37 – 1.18 (12H, m), 0.81 (3H, t, *J* = 6.7 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 157.7 (d, *J* = 2.2 Hz), 141.4 (d, *J* = 4.4 Hz), 136.7, 132.7, 130.2, 129.1, 128.7, 127.8, 126.8 (d, *J* = 3.2 Hz), 126.5, 126.3, 116.1 (d, *J* = 175.3 Hz), 60.8 (d, *J* = 5.9 Hz), 51.1 (d, *J* = 4.8 Hz), 42.1 (d, *J* = 19.7 Hz), 31.6, 26.8, 26.5 (d, *J* = 6.4 Hz)., 26.0, 25.7, 16.4 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.44. HRMS (ESI) calcd. for $C_{25}H_{32}ClNO_2P^+$ (M + H^+) *m/z* 444.1854, found 444.1855.



Ethyl *N*-(4-chlorophenyl)-*N*-cinnamyl-*P*-(cyclohexylidenemethyl)phosphonamidate (3gC). Yellow oil, 13 mg, 20%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.25 – 7.20 (4H, m), 7.18 – 7.10 (5H, m), 6.39 (1H, d, *J* = 15.9 Hz), 6.10 (1H, dt, *J* = 15.9, 6.2 Hz), 5.30 (1H, d, *J* = 21.2 Hz), 4.43 – 4.30 (1H, m), 4.30 – 4.18 (1H, m), 4.14 – 4.00 (1H, m), 3.99 – 3.86 (1H, m), 2.52 – 2.42 (2H, m), 2.18 – 2.02 (2H, m), 1.48 – 1.41 (3H, m), 1.31 – 1.23 (3H, m), 1.22 (3H, t, *J* = 7.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 136.8, 132.6, 129.1, 128.7, 127.8, 125.7 (d, *J* = 3.7 Hz), 117.3, 111.2 (d, *J* = 177.7 Hz), 60.1 (d, *J* = 3.2 Hz), 50.5 (d, *J* = 4.8 Hz), 39.1 (d, *J* = 22.7 Hz), 32.30 (d, *J* = 7.5 Hz), 28.5, 27.8 (d, *J* = 1.3 Hz), 25.9, 16.5 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 18.98. HRMS (ESI) calcd. for $C_{24}H_{30}ClNO_2P^+$ (M + H^+) *m/z* 430.1698, found 430.1689.

6. Isotope labeling experiments

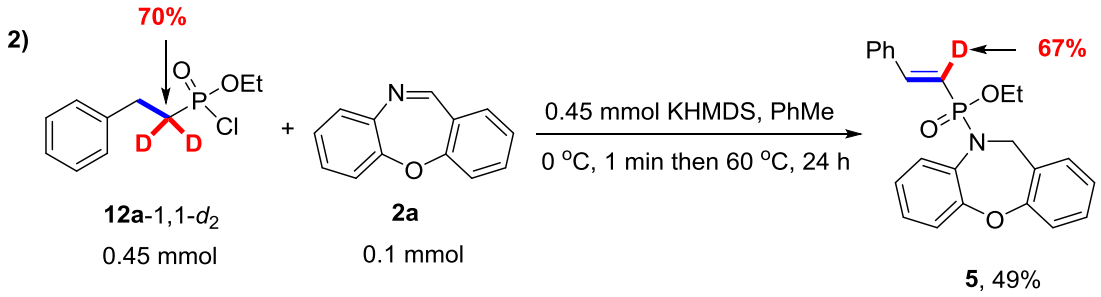
1)



To a stirring cold suspension of ethyl 2-phenylacetate **15** (1.64 g, 10 mmol) in dry THF (30 mL) in an ice bath was added $LiAlD_4$ powders (420 mg, 10 mmol) in three potions under N_2. The

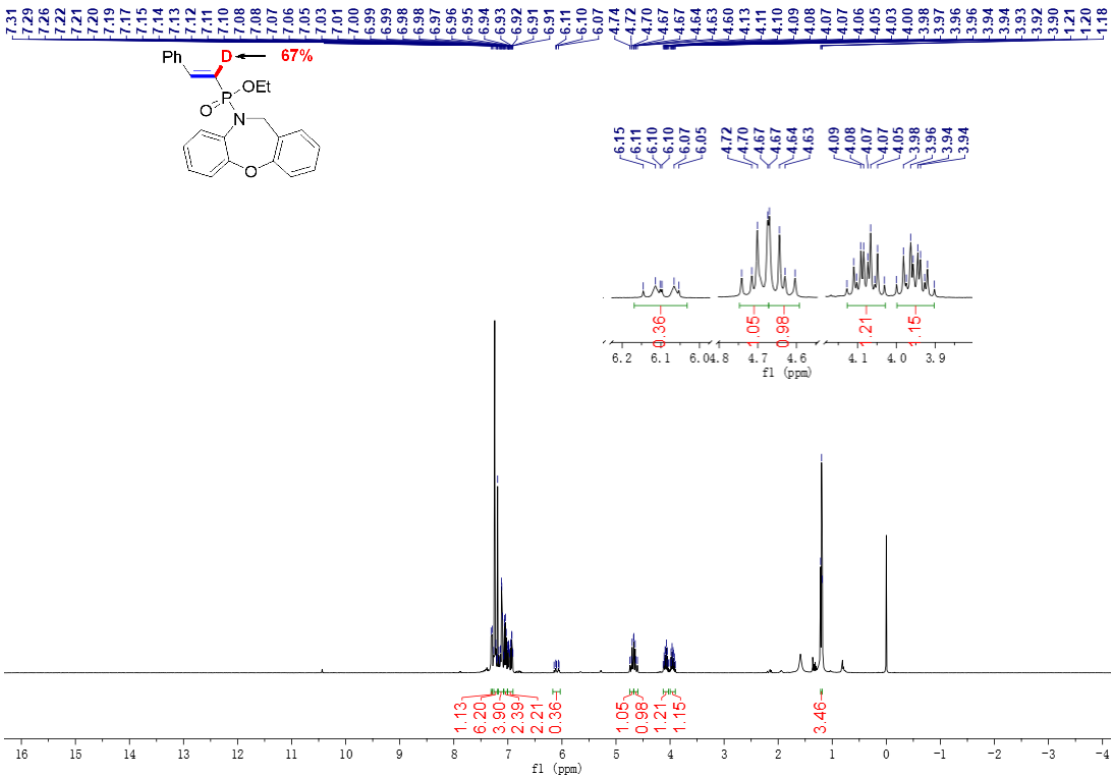
mixture was slowly warmed to the refluxing temperature for 4 h. The mixture was then cooled down to room temperature and quenched by addition of MeOH (1 mL) followed by addition of aq. solution of NaOH (10%, 15 mL). After the mixture was filtered through a pad of celite, THF was evaporated from the filtrate in vacuum. The resultant mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (2 × 15 mL) and dried over $NaSO_4$. After removal of the solvent in vacuum the residue was purified by flash chromatography (silica gel, 20% EtOAc in PE) to give 1.06 g (85%) of the desired product $PhCH_2CD_2OH$ with 70% deuteration as a colorless oil. [5] Next, $SOCl_2$ (2 mL) was added in it and the mixture was stirred at reflux temperature for 12 h. After concentration, the product (2-chloroethyl-2,2-d_2)benzene **16** was obtained.

According to the general procedure for the preparation of ethyl hydrogen alkylphosphonates **12**, the product **12a**-1,1-d_2 was obtained as a brown oil (350 mg, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) 11.21 (1H, s), 7.33 – 7.27 (2H, m), 7.25 – 7.18 (3H, m), 4.12 (2H, q, J = 7.2 Hz), 2.93 (2H, d, J = 9.5 Hz), 2.07 (0.6H, d, J = 18.3 Hz), 1.34 (3H, t, J = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 141.0 (d, J = 18.2 Hz), 128.7, 128.2, 126.5, 61.4 (d, J = 6.4 Hz), 28.3 (d, J = 3.3 Hz), 27.8 (d, J = 141.3 Hz), 16.5 (d, J = 6.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$): 33.62. HRMS (ESI) calcd. for $C_{10}H_{14}D_2O_3P^+$ (M + H^+) *m/z* 217.0958, found 217.0966.

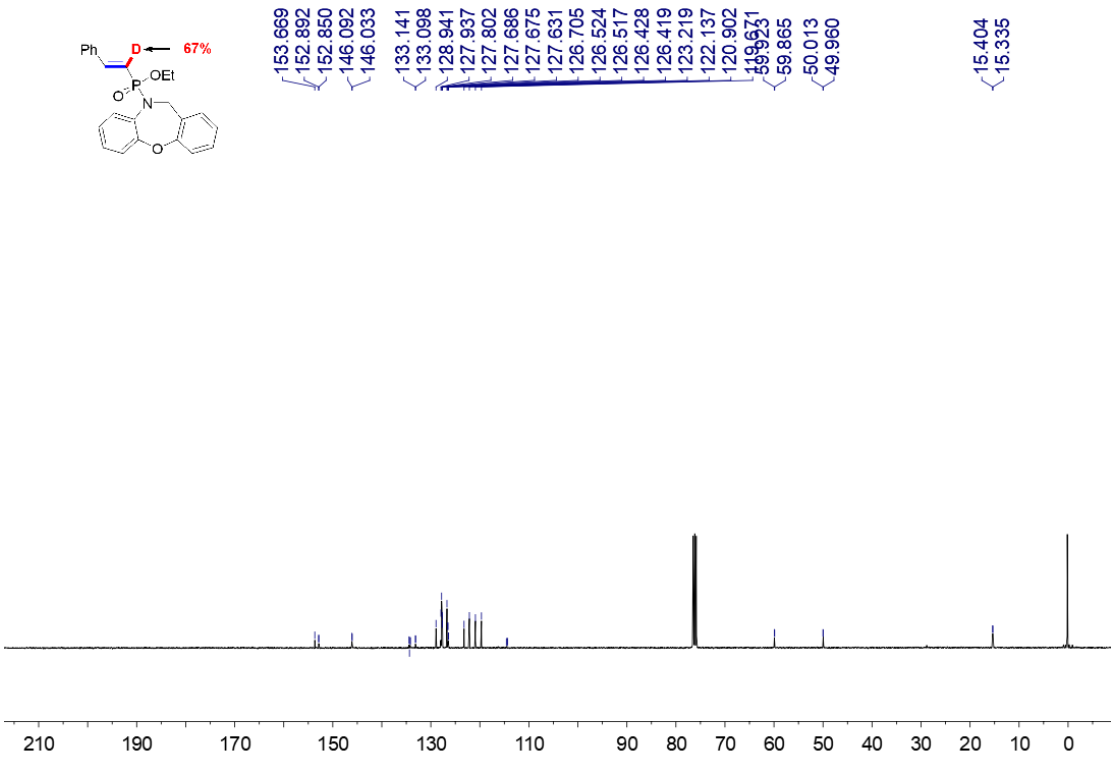


The reaction was performed following the **Conditions A**. The residue was purified by flash column chromatograph (PE:EA = 2:1, *v*/*v*) to give the product **5** with 67% deuteration as a yellow oil (19 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.30 (1H, d, J = 8.1 Hz), 7.27 – 7.18 (6H, m), 7.18 – 7.08 (4H, m), 7.08 – 7.01 (2H, m), 7.01 – 6.91 (2H, m), 6.10 (0.36H, dd, J = 19.3, 5.0 Hz), 4.71 (1H, dd, J = 16.3, 10.6 Hz), 4.64 (1H, dd, J = 16.2, 10.4 Hz), 4.08 (1H, dq, J = 10.1, 7.1 Hz), 3.95 (1H, dq, J = 10.1, 7.1 Hz), 1.20 (3H, t, J = 6.1 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 153.7, 152.9 (d, J = 4.2 Hz), 146.1 (d, J = 5.9 Hz), 134.5, 134.2 (d, J = 6.0 Hz), 133.1 (d, J = 4.3 Hz), 128.9, 127.9, 127.8, 127.7 (d, J = 1.2 Hz), 127.6, 126.7, 126.5 (d, J = 0.7 Hz), 126.4 (d, J = 0.9 Hz), 123.2, 122.1, 120.9, 119.7, 114.5 (t, $J_{D\text{-}C}$= 12.9 Hz), 59.9 (d, J = 5.9 Hz), 50.0 (d, J = 5.3 Hz), 15.4 (d, J = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 19.95. HRMS (ESI) calcd. for $C_{23}H_{22}DNO_3P^+$ (M + H^+) *m/z* 393.1473, found 393.1473.

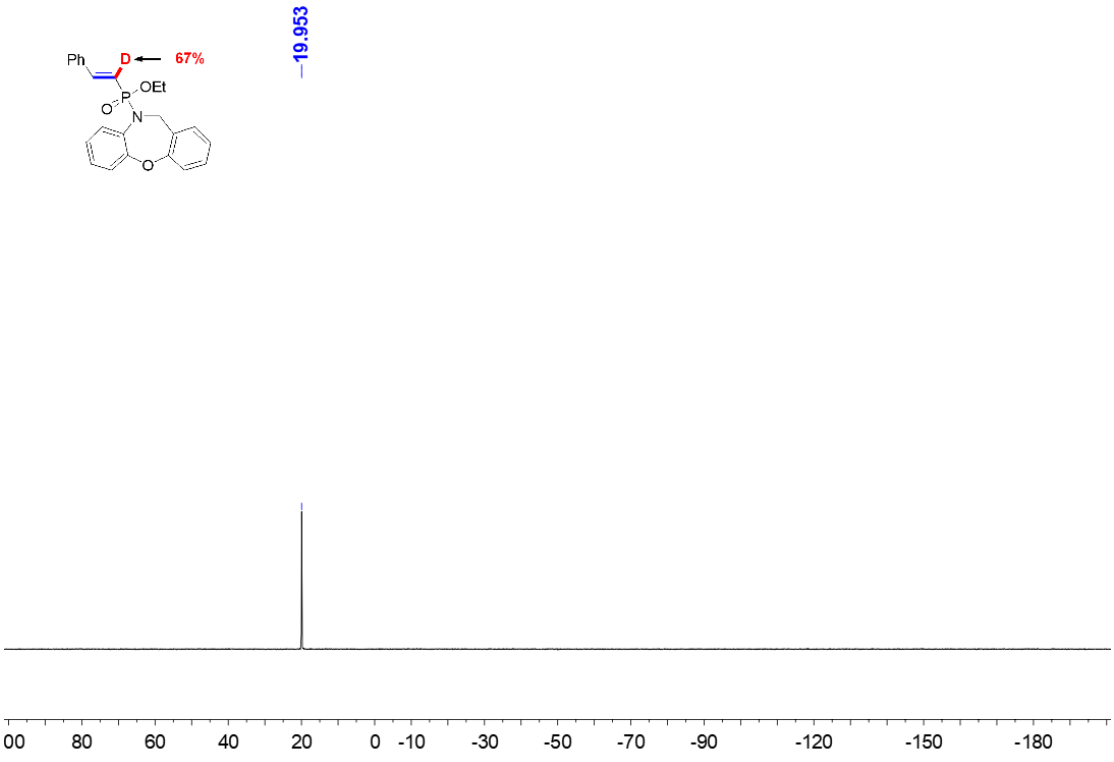
5. Lee, H.-I.; Dexter, A. F.; Fann, Y.-C.; Lakner, F. J.; Hager, L. P.; Hoffma, B. M.. *J. Am. Chem. Soc.*, **1997**, *119*, 4059–4069.



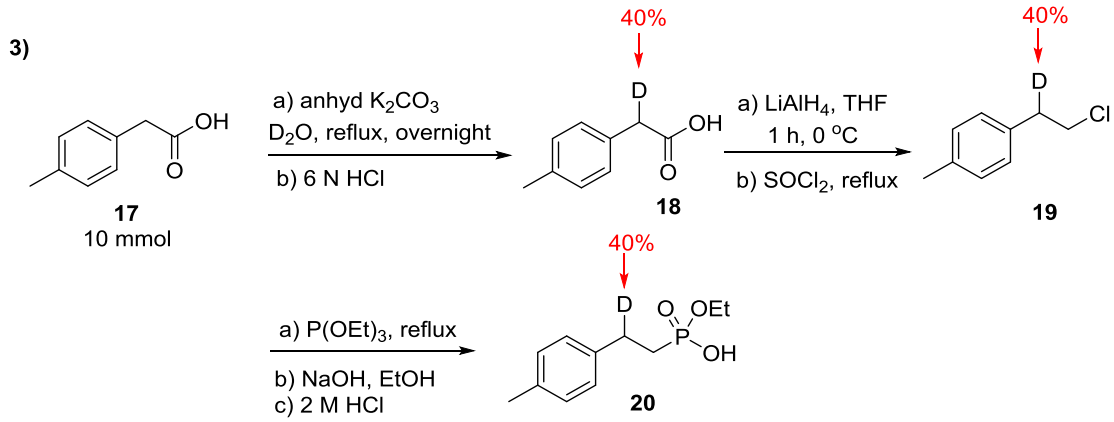
^{1}H NMR Spectrum of Compound **5**



^{13}C NMR Spectrum of Compound **5**



^{31}P NMR Spectrum of Compound **5**

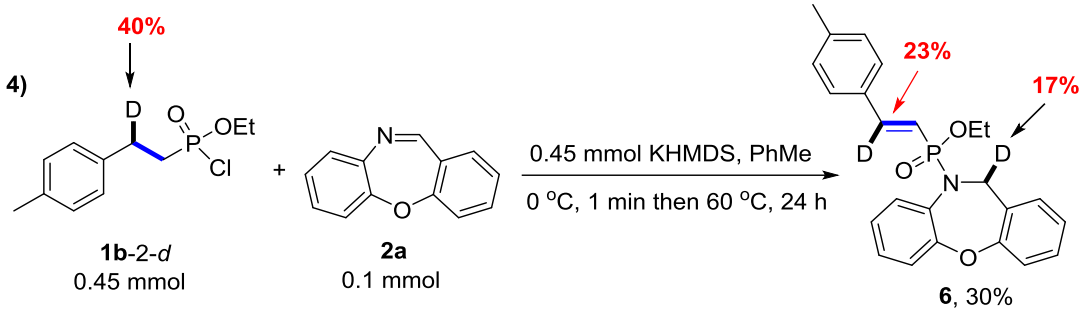


A mixture of 2-(*p*-tolyl)acetic acid **17** (1.50 g; 10 mmol), anhydrous potassium carbonate (10.30 g; 73.4 mmol), and deuterium oxide (15 mL) was refluxed overnight in a dried flask. After completion of reaction (as determined by GC-MS) the reaction mixture was cooled to about 0 °C, acidified to pH 2 with 6 N hydrochloric acid, and then extracted with diethyl ether (3 x 50 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated under reduced pressure to give 2-(*p*-tolyl)acetic-2-*d* acid **18** as a white solid with 40% deuteration in 96% yield. It was used without any purification in the next step. [6]

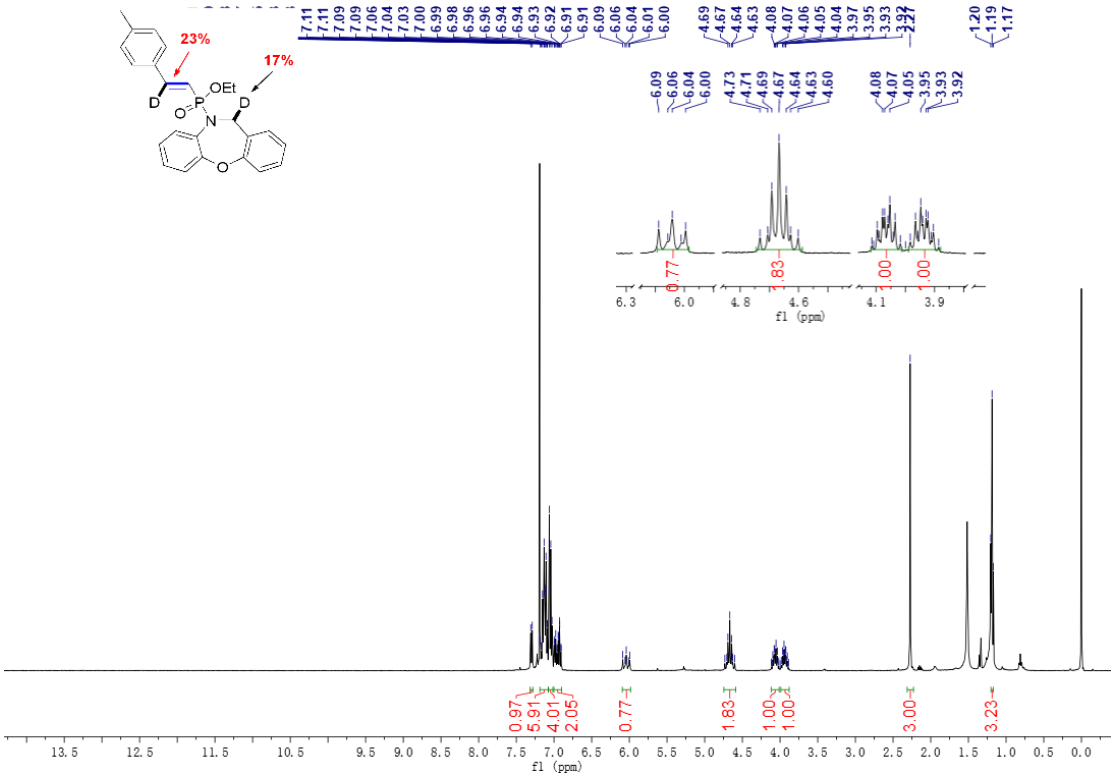
6. Singh, R.; Kolev, J. N.; Sutera, P. A.; Fasan, R. Enzymatic C(sp^3)-H Amination: P450-Catalyzed Conversion of Carbonazidates into Oxazolidinones. *ACS Catal*. **2015**, *5*, 1685−1691.

To a stirring solution of 2-(*p*-tolyl)acetic-2-*d* acid **18** (1.43 g, 9.5 mmol) in dry THF (30 mL) at 0 °C was added $LiAlH_4$ (399 mg, 9.5 mmol). The mixture was slowly warmed to the refluxing temperature for 4 h. The mixture was then cooled down to room temperature and quenched by addition of MeOH (1 mL) followed by addition of aq. solution of NaOH (10%, 15 mL). After the mixture was filtered through a pad of celite, THF was evaporated from the filtrate in vacuum. The resultant mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with brine (2 × 15 mL) and dried over $NaSO_4$. The solvent was removed in vacuum and the residue was purified by flash chromatography (silica gel, 20% EtOAc in PE) to give 1.35 g (98%) of the desired product 2-(*p*-tolyl)ethan-2-*d*-1-ol with 40% deuteration as a colorless oil. Next, $SOCl_2$ (4 mL) was added in it and the mixture was stirred at reflux temperature for 12 h. After concentration, the product 1-(2-chloroethyl-1-*d*)-4-methylbenzene **19** was obtained and was proceeded further in the next step without any purification.

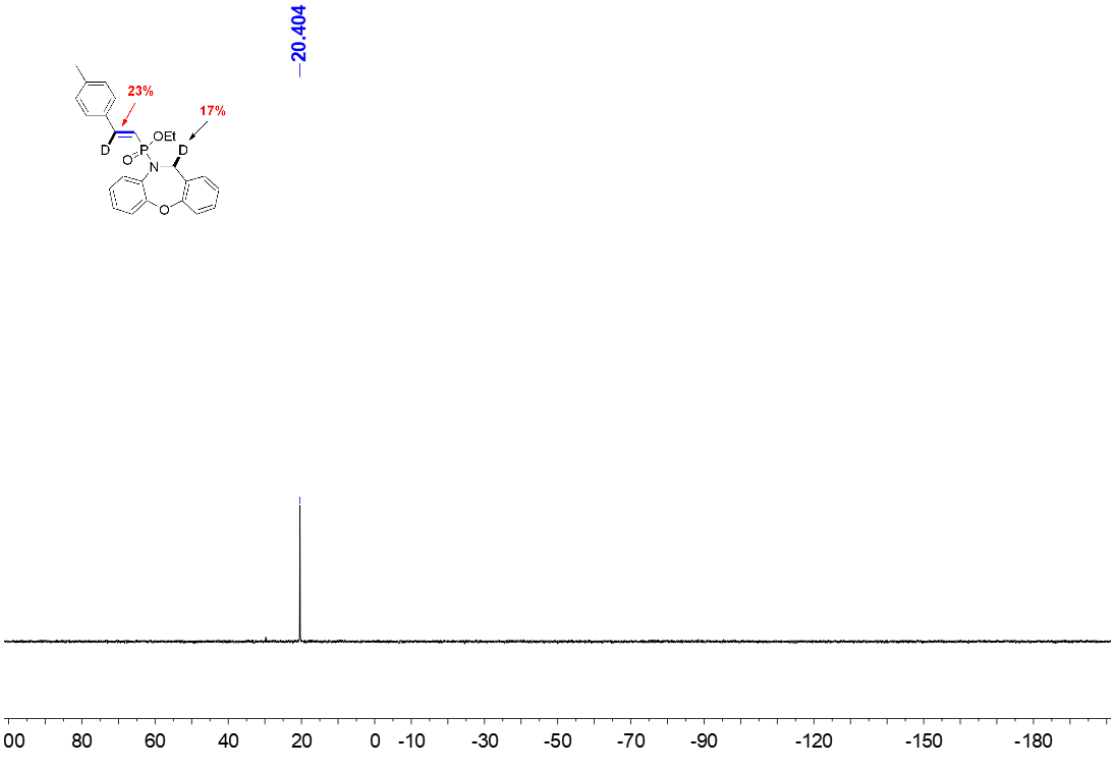
According to the general procedure for the preparation of ethyl hydrogen alkylphosphonates **10**, the product ethyl hydrogen (2-(*p*-tolyl)ethyl-2-*d*)phosphonate **20** was obtained as a brown oil (350 mg, 16%). ^{1}H NMR (400 MHz, $CDCl_3$) 12.45 (1H, s), 7.26 – 7.09 (4H, m), 4.23 – 4.10 (2H, m), 3.07 – 2.90 (1.6H, m), 2.39 (3H, s), 2.23 – 2.03 (2H, m), 1.39 (3H, t, *J* = 6.9 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 138.2 (d, *J* = 18.4 Hz), 135.8, 129.3, 128.0, 61.2 (d, *J* = 5.9 Hz), 28.1 (d, *J* = 136.8 Hz), 28.1 (dd, *J* = 12.1, 4.8 Hz), 21.1, 16.5 (d, *J* = 5.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 32.17. HRMS (ESI) calcd. for $C_{11}H_{17}DO_3P^+$ (M + H^+) *m/z* 230.1051, found 230.1059.



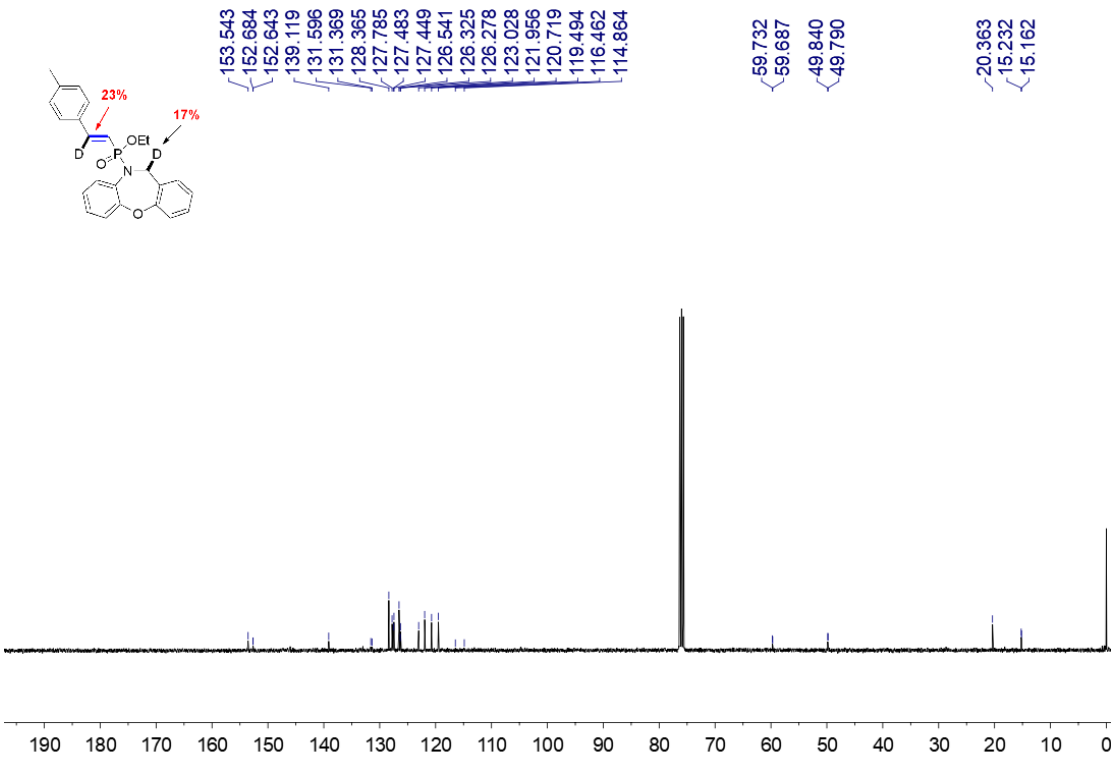
The reaction was performed following the **Conditions A**. The residue was purified by flash column chromatograph (PE:EA = 2:1, *v*/*v*) to give the product **6** with 17% deuteration as a yellow oil (12 mg, 30%). ^{1}H NMR (400 MHz, $CDCl_3$) 7.30 (1H, d, *J* = 8.0 Hz), 7.18 – 7.07 (6H, m), 7.08 – 7.01 (4H, m), 7.00 – 6.90 (2H, m), 6.04 (0.77H, dd, *J* = 19.2, 17.7 Hz), 4.70 (0.9H, dd, *J* = 16.0, 10.3 Hz), 4.63 (0.8H, dd, *J* = 15.9, 10.1 Hz), 4.12 – 4.00 (1H, m), 4.00 – 3.88 (1H, m), 2.27 (3H, s), 1.19 (3H, t, *J* = 7.0 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) 154.7, 153.8 (d, *J* = 4.1 Hz), 140.3, 132.7 (d, *J* = 22.9 Hz), 129.5, 128.9, 128.7, 128.6, 127.7, 127.5, 127.4 124.2, 123.1, 121.9, 120.7, 116.8 (d, *J* = 160.8 Hz), 60.9 (d, *J* = 4.5 Hz), 50.9 (d, *J* = 5.0 Hz), 21.5, 16.4 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 20.40. HRMS (ESI) calcd. for $C_{24}H_{24}DNO_3P^+$ (M + H^+) m/z 407.1630 found 407.1620.



^{1}H NMR Spectrum of Compound **6**



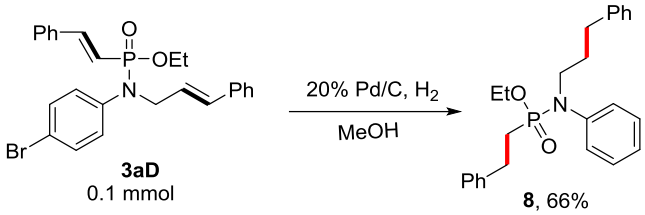
^{31}P NMR Spectrum of Compound **6**



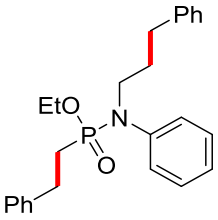
^{13}C NMR **Spectrum of Compound** 6

7. Application experiments

Procedure for the hydrogenation of compound 3aD

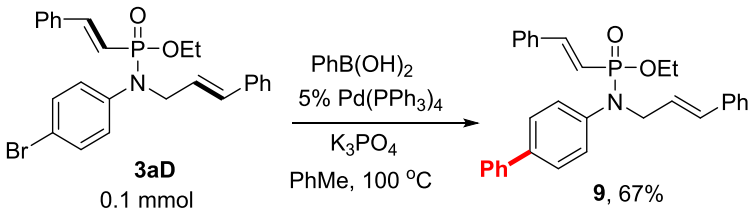


To a dired tube charged with a solution of **3aD** (48 mg, 0.1 mmol) in methanol (3 mL) was added dried 10% Pd/C (21 mg, 0.02 mmol of Pd, 20 mol%) under N_2 atmosphere. The tube was charged with a hydrogen balloon. The reaction mixture was stirred at room temperature for 12 h. After the mixture was filtered through a pad of celite, MeOH was evaporated from the filtrate in vacuum. The resultant mixture was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL) and dried over $NaSO_4$. After removal of the solvent in vacuum the residue was purified by flash silica gel chromatography with EtOAc and PE (1:5, *v*/*v*) as eluent to give product **8** (27 mg, 66% yield).

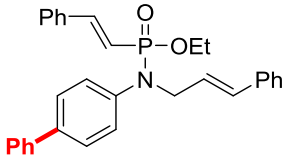


Ethyl *P*-phenethyl-*N*-phenyl-*N*-(3-phenylpropyl)phosphonamidate (8). Yellow oil, 27 mg, 66%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.32 (t, *J* = 7.8 Hz, 2H), 7.28 – 7.04 (m, 13H), 4.20 (dp, *J* = 10.1 Hz, *J* = 7.1 Hz, 1H), 4.03 (dp, *J* = 10.0 Hz, *J* = 7.1 Hz, 1H), 3.76 (dq, *J* = 14.0 Hz, *J* = 7.6 Hz, 1H), 3.63 – 3.49 (m, 1H), 2.86 (dd, *J* = 17.3, *J* = 8.7 Hz, 2H), 2.68 – 2.54 (m, 2H), 2.10 – 1.88 (m, 2H), 1.86 – 1.75 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 142.2 (d, *J* = 4.4 Hz), 141.7, 141.5, 141.3, 129.5, 128.6, 128.5, 128.4, 128.2, 126.3, 126.2, 126.2, 126.0, 125.5, 60.2 (d, *J* = 6.7 Hz), 48.6 (d, *J* = 3.5 Hz), 32.3 (d, *J* = 185.7 Hz), 29.5 (d, *J* = 69.2 Hz), 28.5 (d, *J* = 3.1 Hz), 27.9, 16.5 (d, *J* = 6.7 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 31.85. HRMS (ESI) calcd. for $C_{25}H_{31}NO_2P^+$ (M + H^+) *m/z* 408.2087 found 408.2088.

Procedure for the Suzuki coupling reaction of compound 3aD



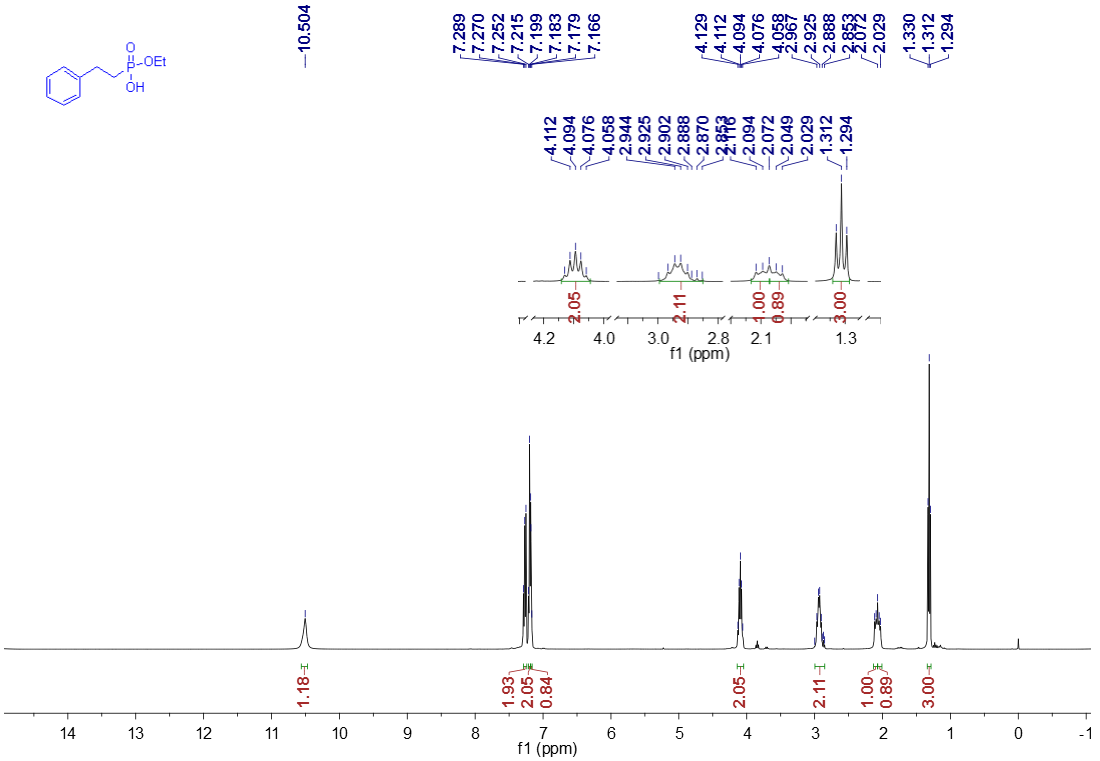
Compound **3aD** (48 mg, 0.1 mmol), $PhB(OH)_2$ (19.8 mg, 0.15 mmol), $Pd(PPh_3)_4$ (7.8 mg, 0.005 mmol, 5 mol%), and K_3PO_4 (43 mg, 0.2 mmol) were added into a 8 mL reaction tube. The tube was charged with N_2 and added 1.5 mL of dry PhMe. Then the resultant mixture was stirred in a classic oil bath at 100 °C for 18 h. After cooling to room temperature, water (5 mL) was added into the reaction mixture. The resulting mixture was extracted with ethyl acetate (10 mL x 3). The combined organic phase was dried over anhydrous Na_2SO_4. After removal of solvent the residue was subjected to flash column chromatography (PE:EA = 5:1 to 3:1, *v*/*v*) to afford product **9** (32 mg, 67% yield).



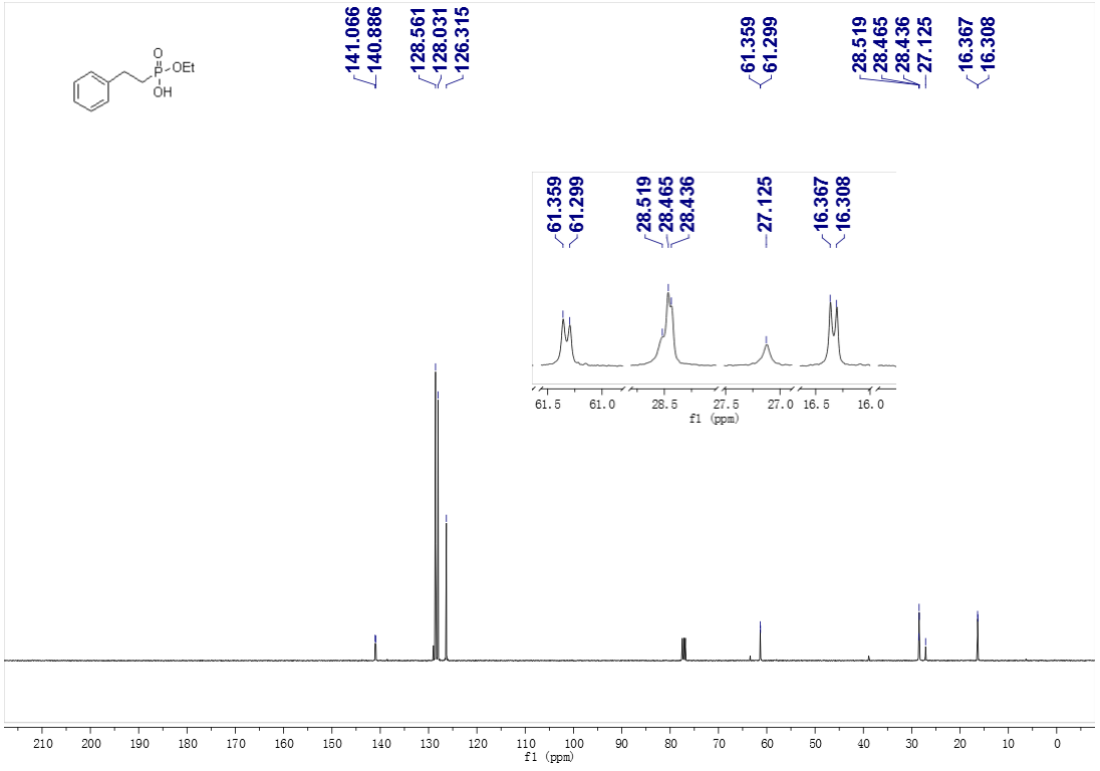
Ethyl *N*-([1,1'-biphenyl]-4-yl)-N-cinnamyl-P-((*E*)-styryl)phosphonamidate (9). Yellow oil, 32 mg, 67%. ^{1}H NMR (400 MHz, $CDCl_3$) 7.59 – 7.48 (m, 5H), 7.47 – 7.41 (m, 4H), 7.41 – 7.37 (m, 2H), 7.37 – 7.27 (m, 8H), 7.24 – 7.19 (m, 1H), 6.53 (d, *J* = 16.1 Hz, 1H), 6.41 (dd, *J* = 19.2, *J*= 17.5 Hz, 1H), 6.29 (dt, *J* = 15.9, *J* = 6.2 Hz, 1H), 4.52 – 4.38 (m, 2H), 4.31 – 4.19 (m, 1H), 4.19 – 4.07 (m, 1H), 1.37 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 147.4 (d, *J* = 5.9 Hz), 141.9 (d, *J* = 4.5 Hz), 140.6, 137.8, 136.9, 135.4 (d, *J* = 22.3 Hz), 132.8, 130.2, 129.0 (d, *J* = 3.6 Hz), 128.7, 127.9, 127.9, 127.8, 127.4, 127.1, 126.7 (d, *J* = 2.1 Hz), 126.6, 125.9 (d, *J* = 3.5 Hz), 116.6 (d, *J* = 178.5 Hz), 61.1 (d, *J* = 6.0 Hz), 51.5 (d, *J* = 5.1 Hz), 16.6 (d, *J* = 7.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) 17.76. HRMS (ESI) calcd. for $C_{31}H_{31}NO_2P^+$ ($M + H^+$) *m/z* 480.2087 found 480.2087.

8. Copies of NMR spectra of compounds 12, 3, 4, 8, and 9

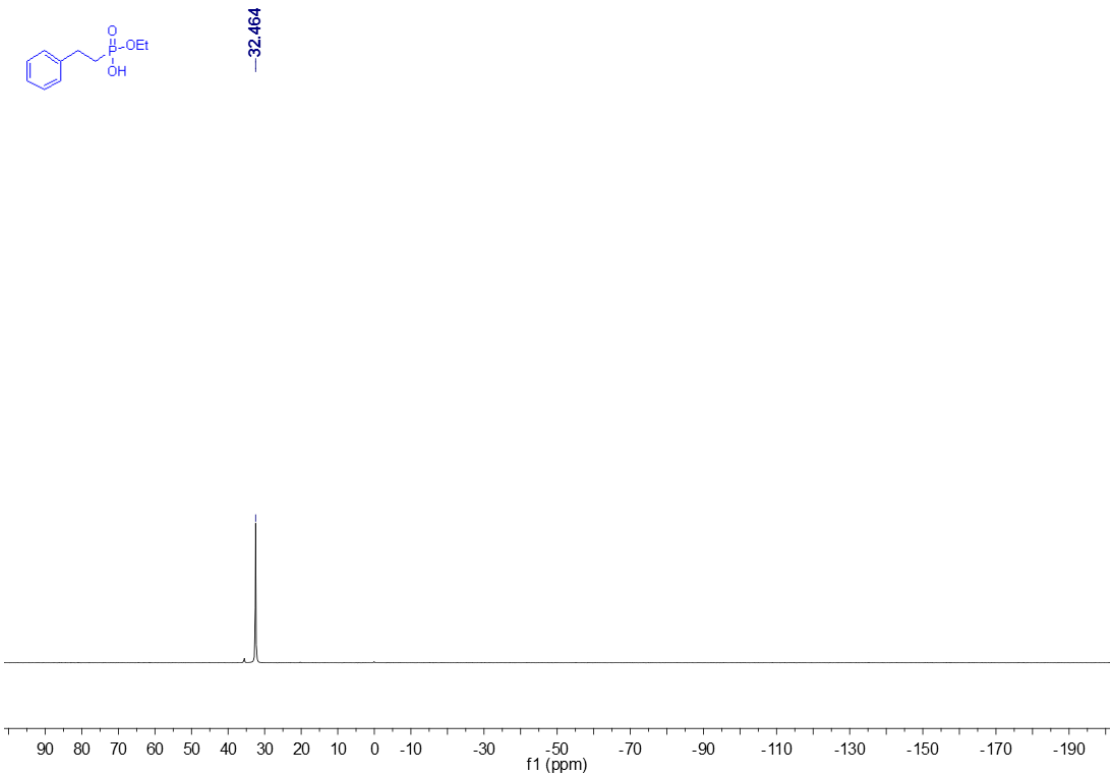
Copies of ^{1}H (400 MHz), ^{31}P (377 MHz) and ^{13}C (101 MHz) spectra of products **12a-12g** in $CDCl_3$



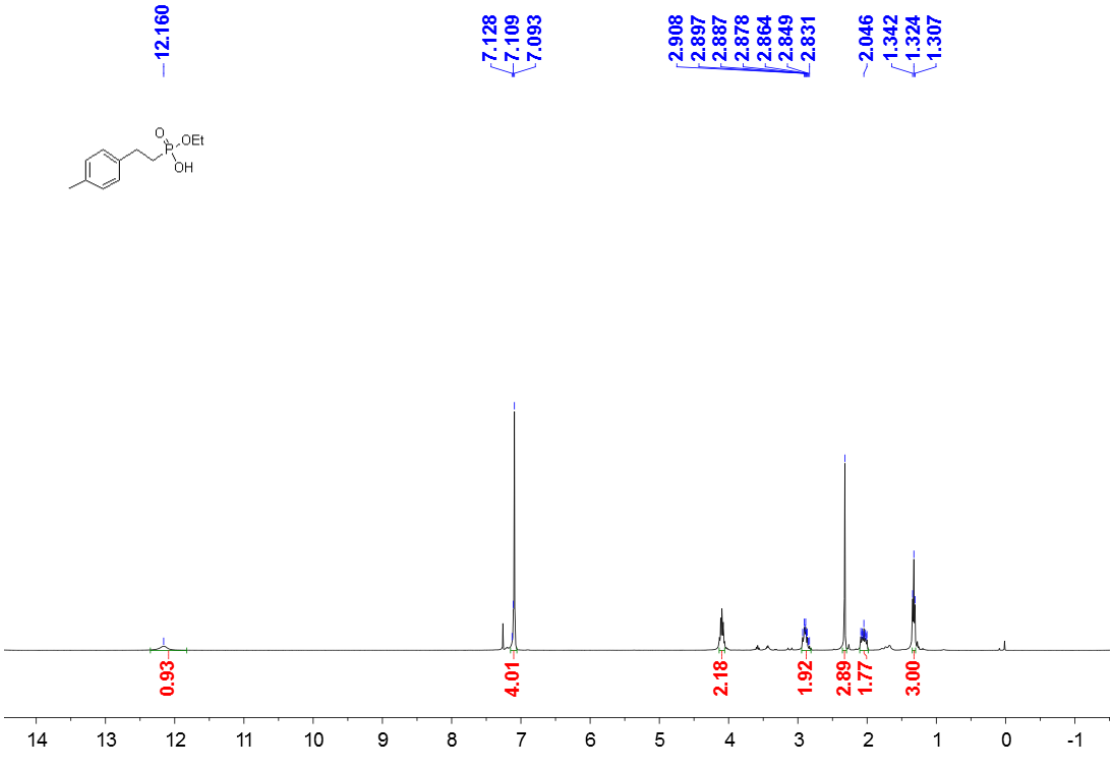
^{1}H NMR Spectrum of Compound **12a**



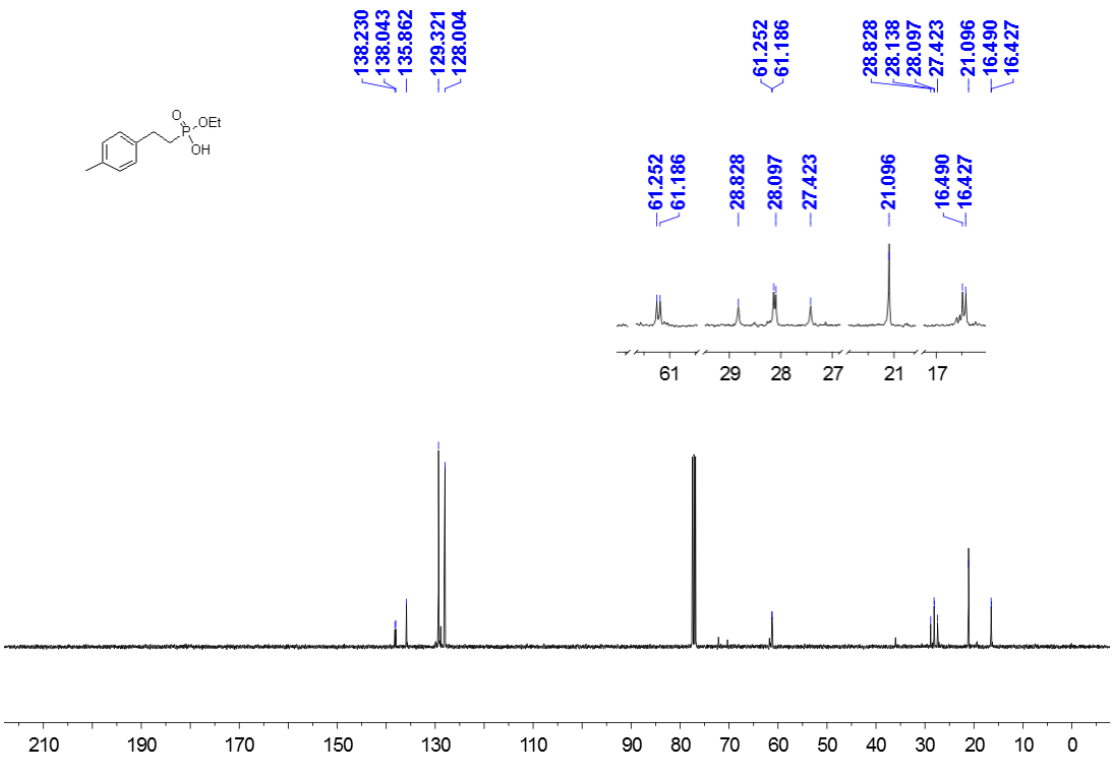
^{13}C NMR Spectrum of Compound **12a**



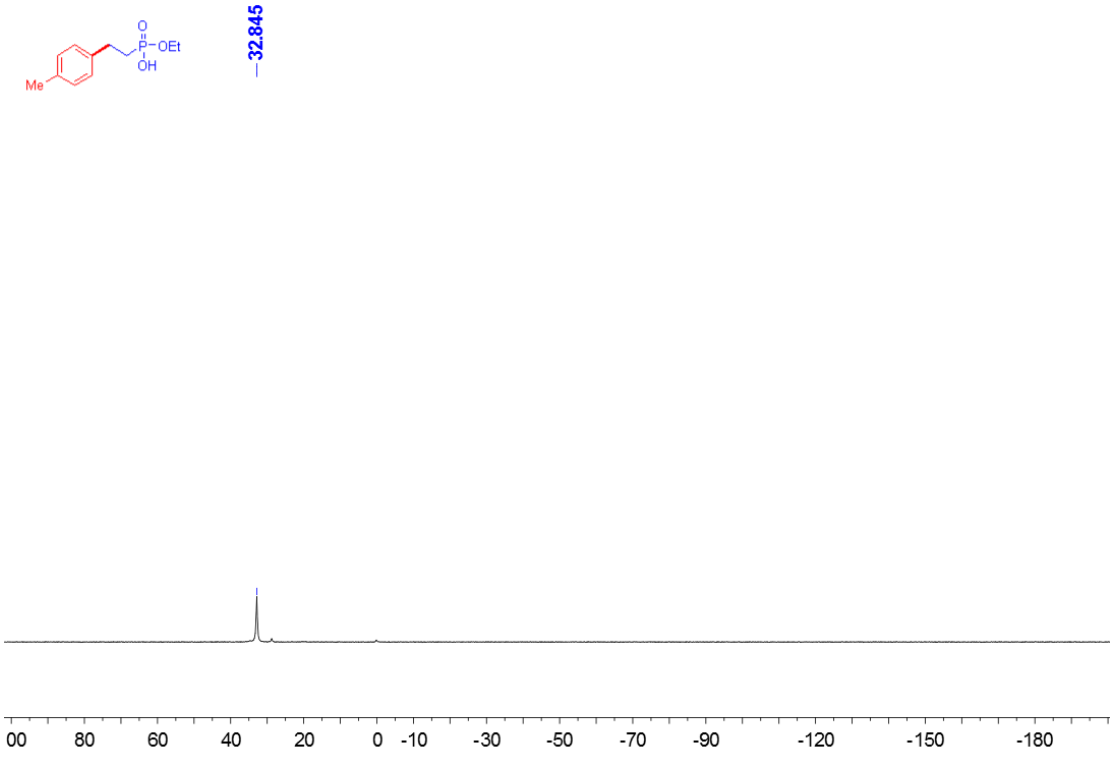
^{31}P NMR Spectrum of Compound **12a**



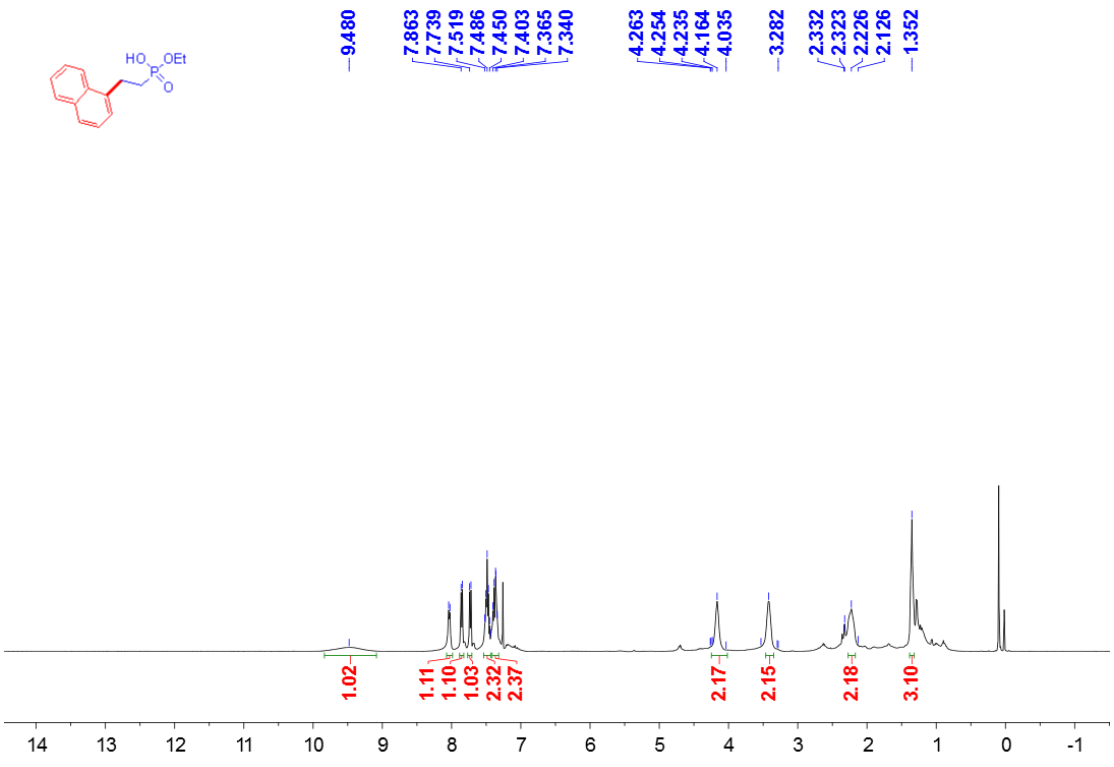
^{1}H NMR Spectrum of Compound **12b**



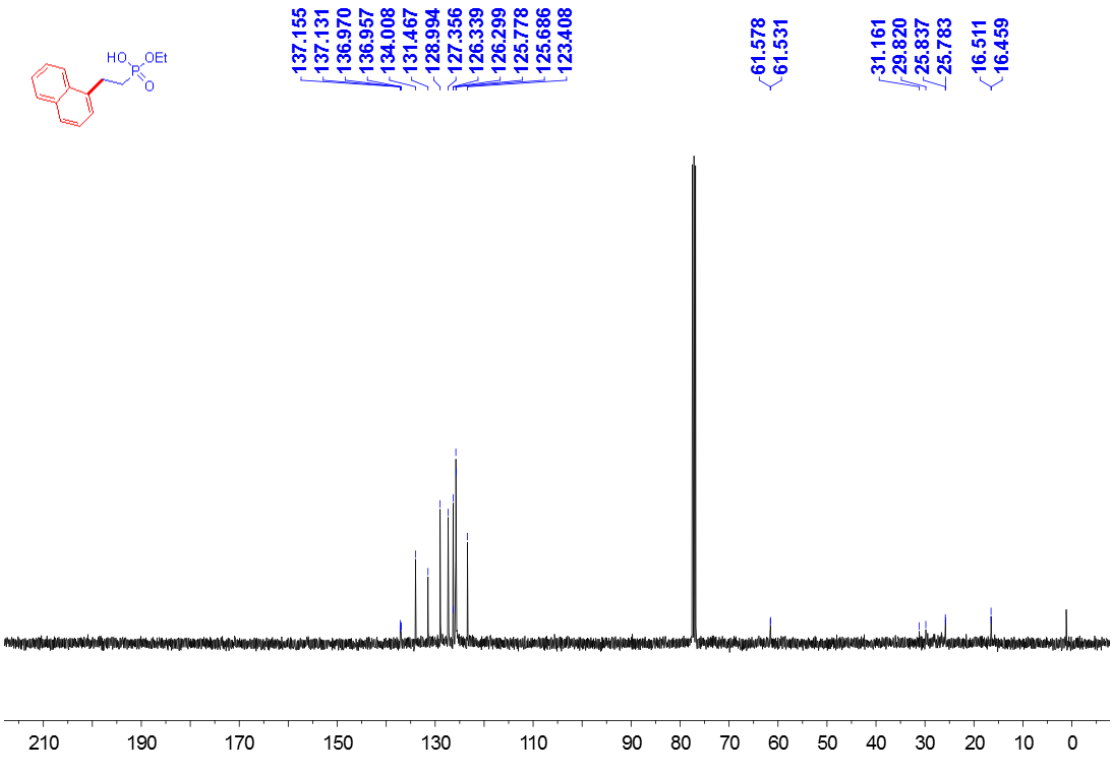
^{13}C NMR Spectrum of Compound **12b**



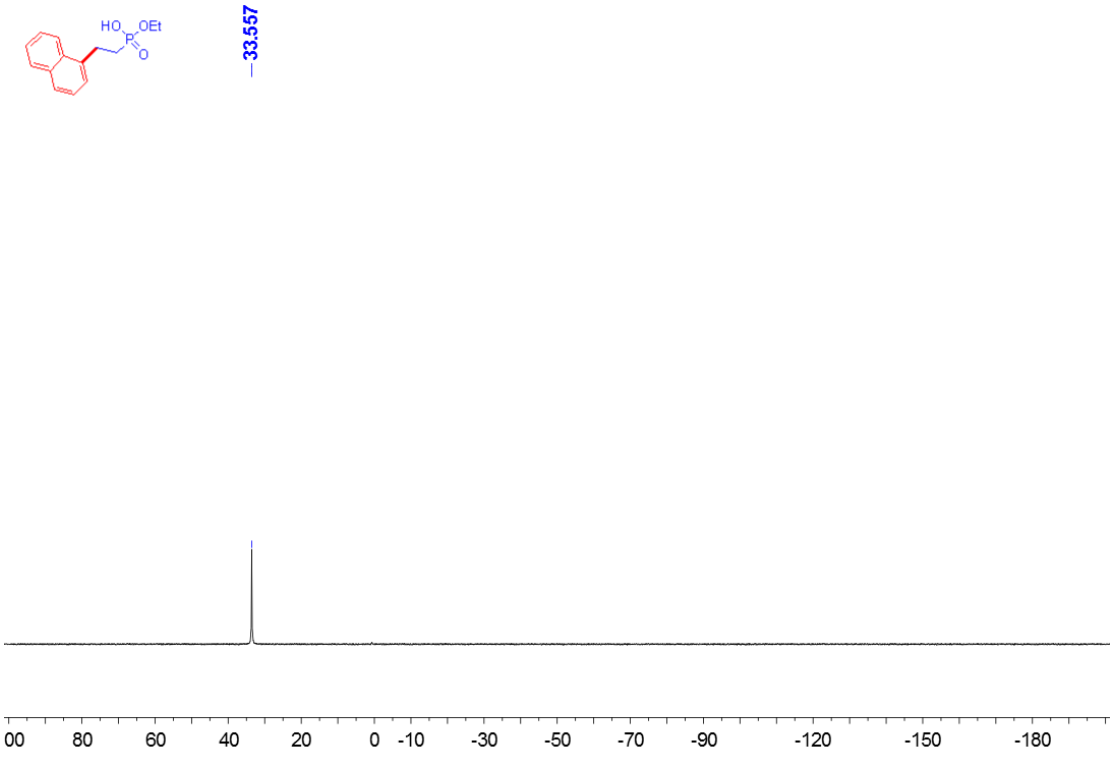
^{31}P NMR Spectrum of Compound **12b**



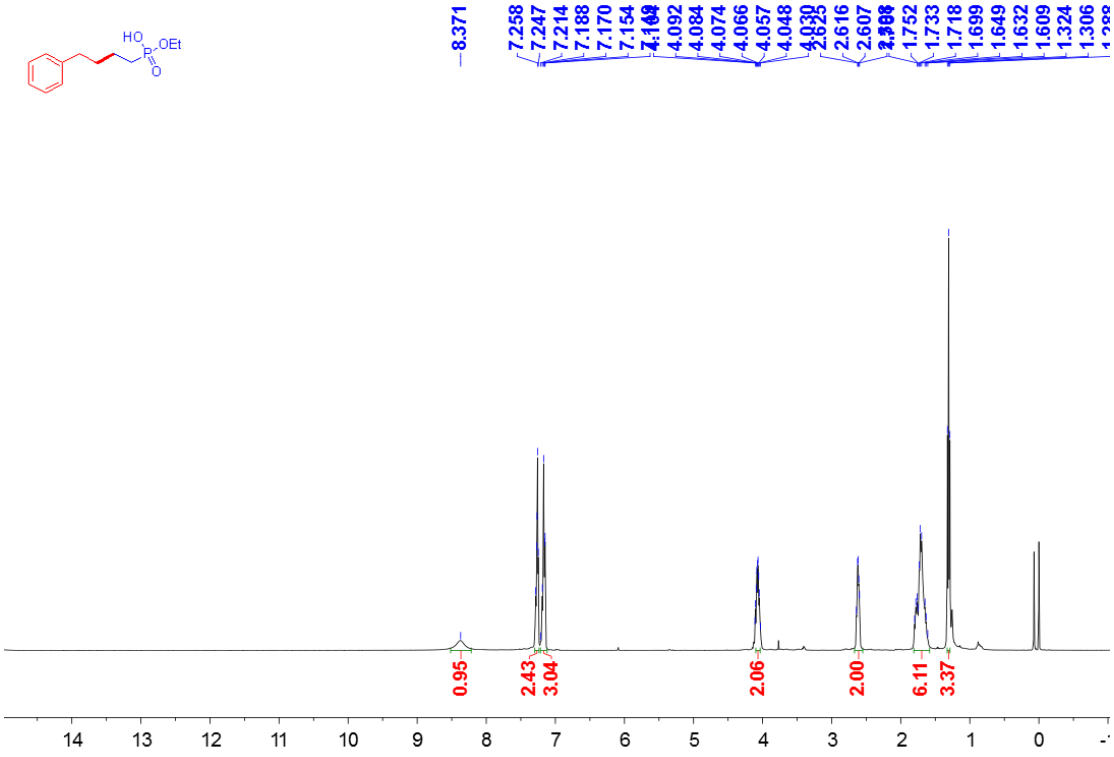
^{1}H NMR Spectrum of Compound **12c**



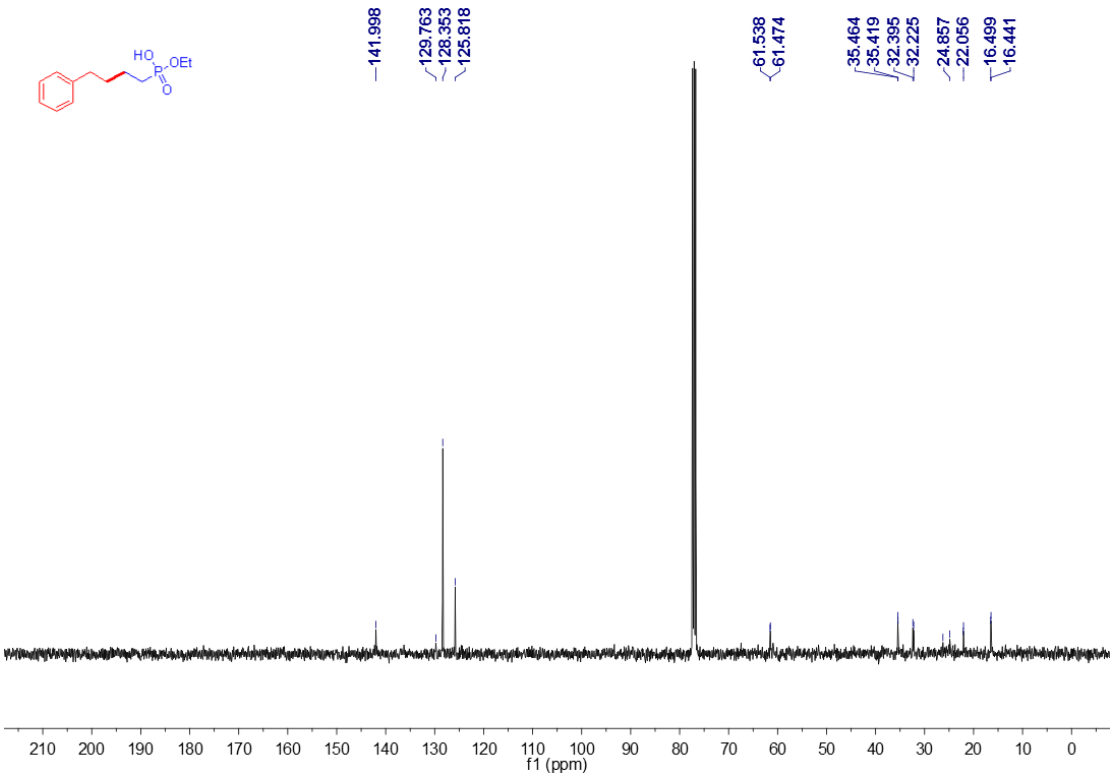
^{13}C NMR Spectrum of Compound **12c**



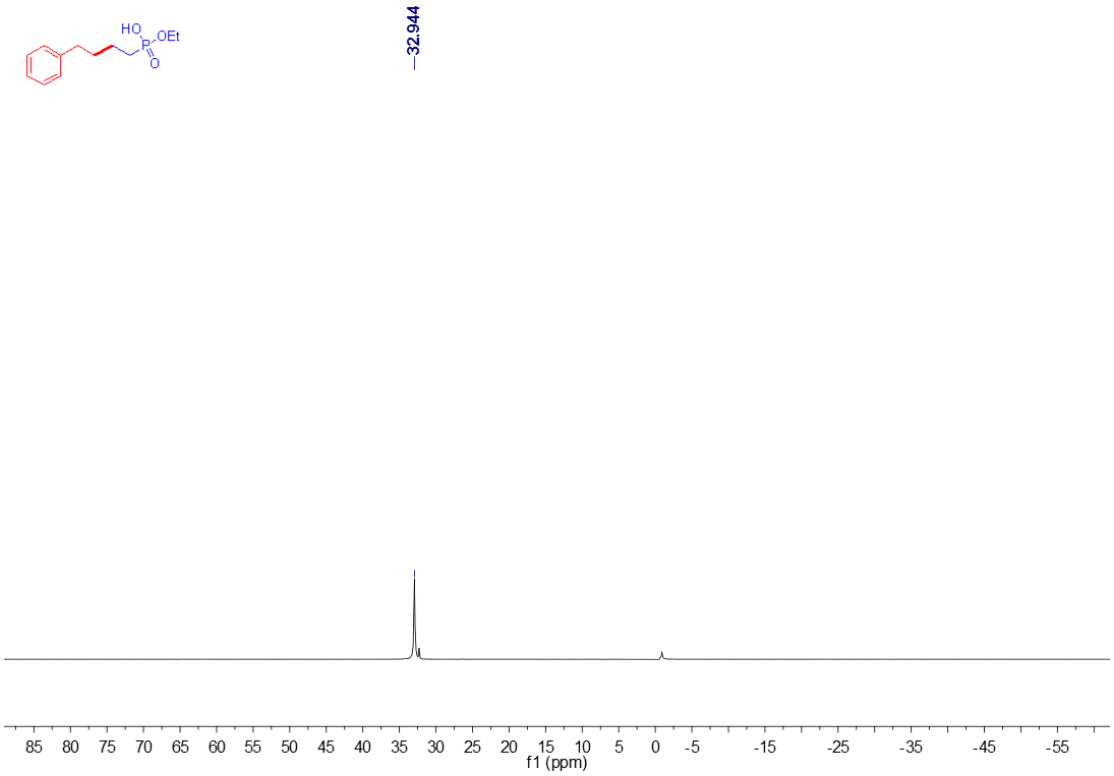
^{31}P NMR Spectrum of Compound **12c**



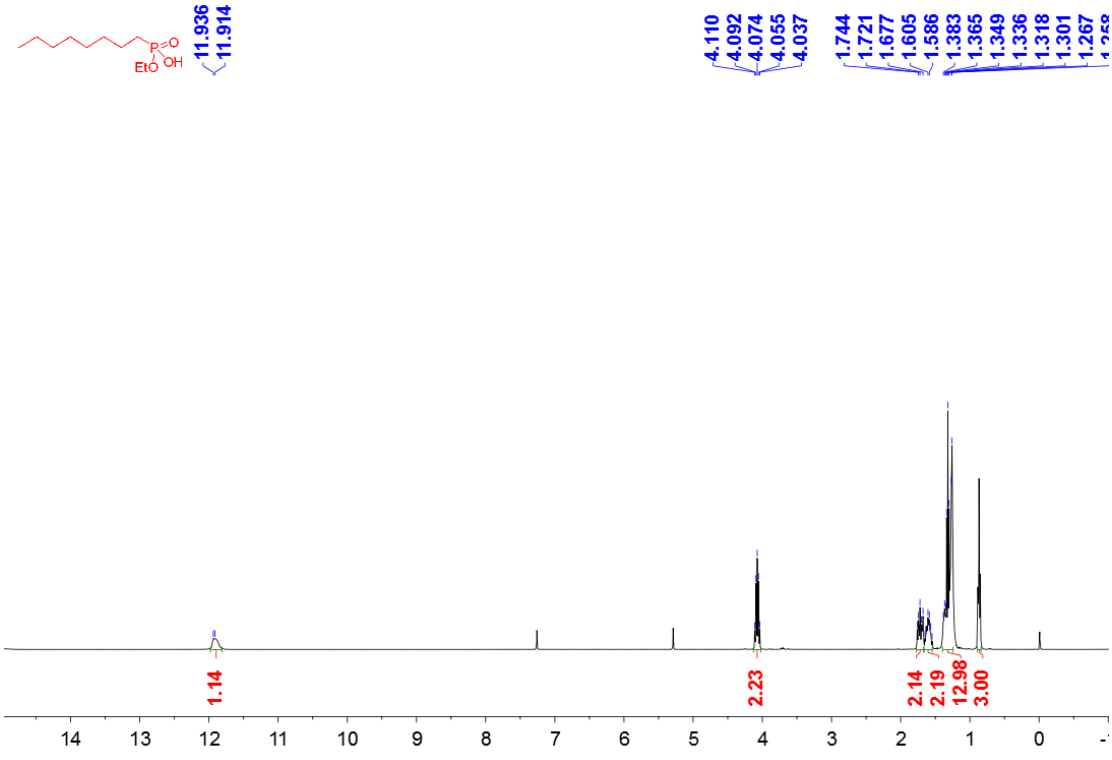
^{1}H NMR Spectrum of Compound **12d**



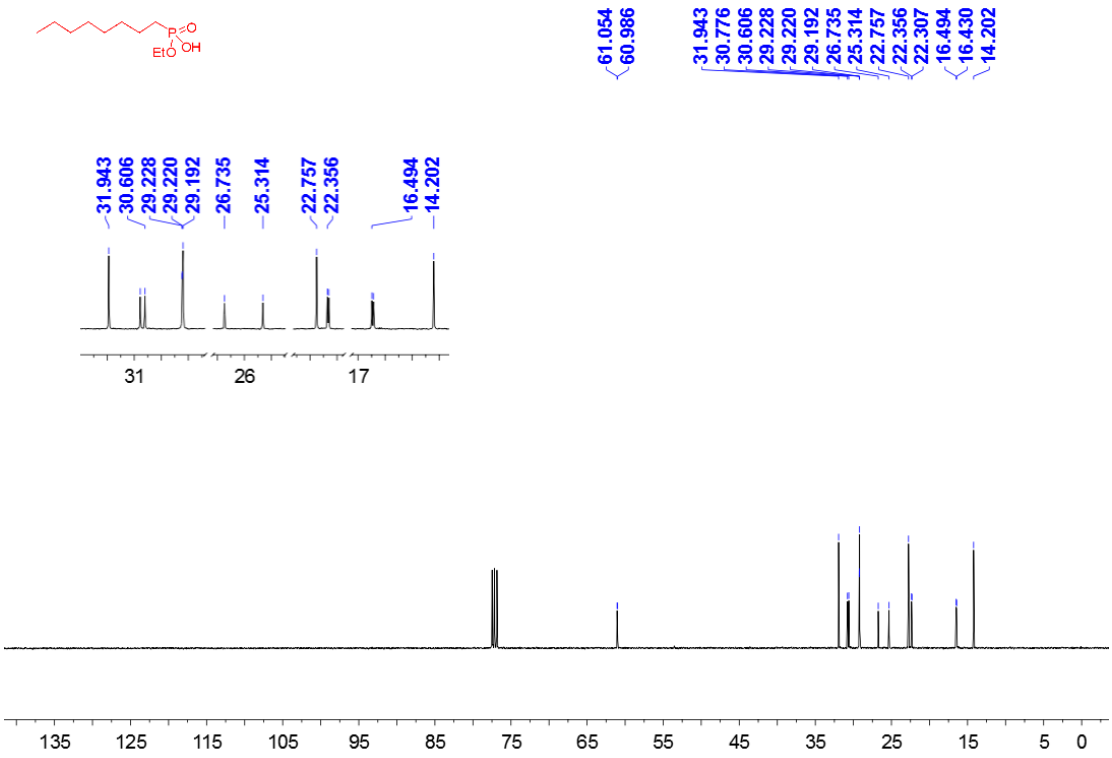
^{31}C NMR Spectrum of Compound **12d**



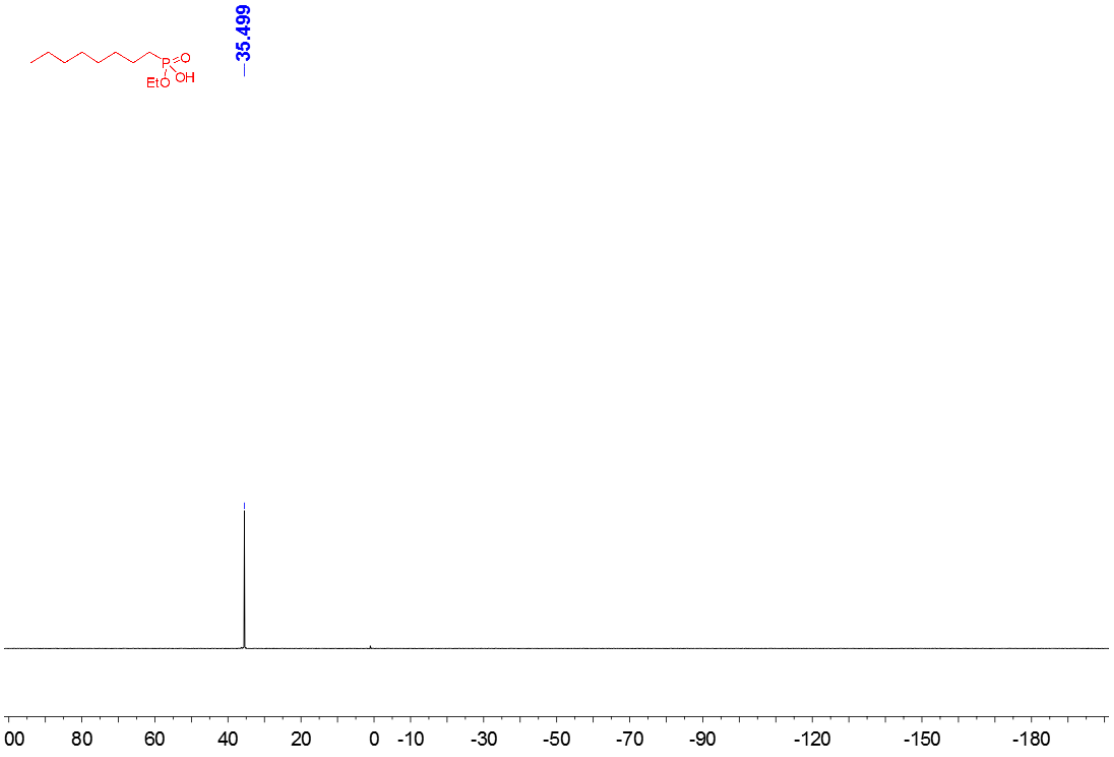
^{31}P NMR Spectrum of Compound **12d**



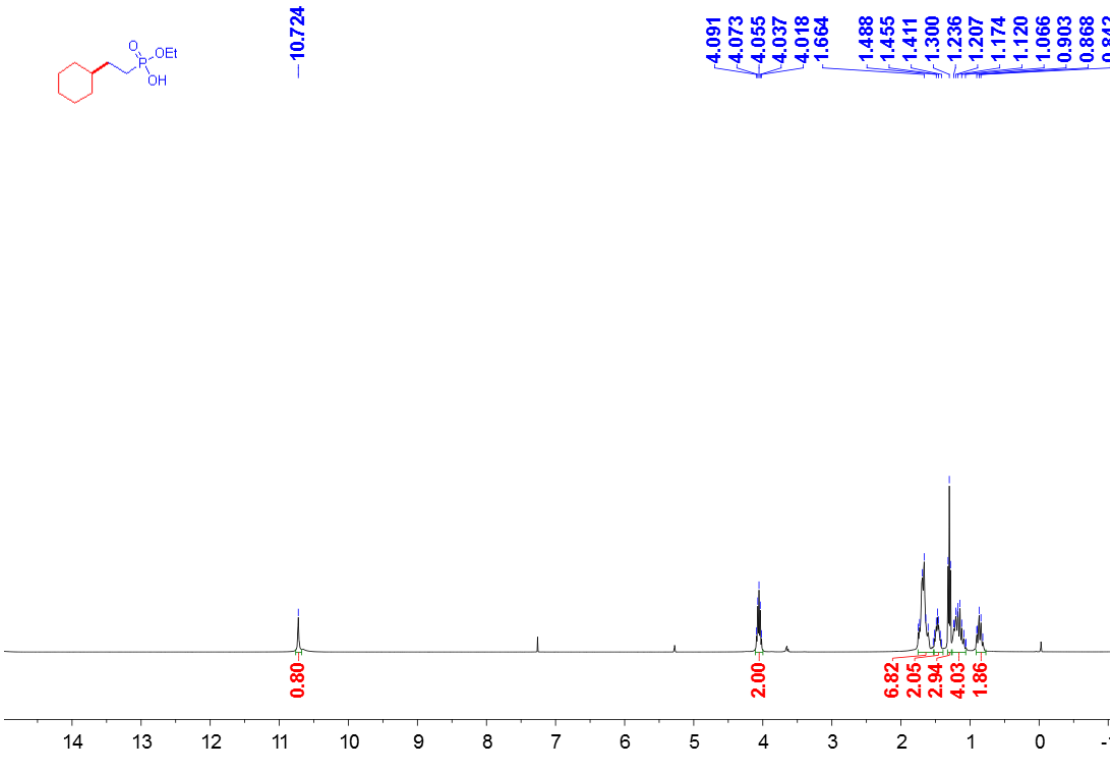
^{1}H NMR Spectrum of Compound **12e**



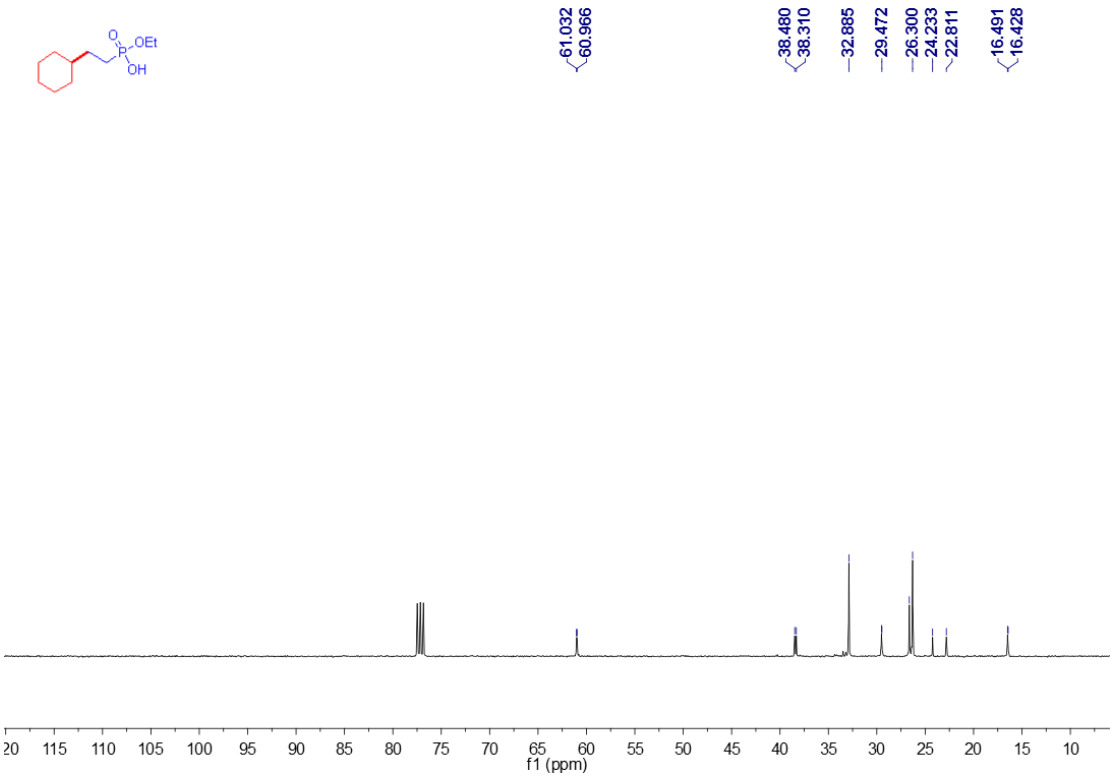
^{13}C NMR Spectrum of Compound **12e**



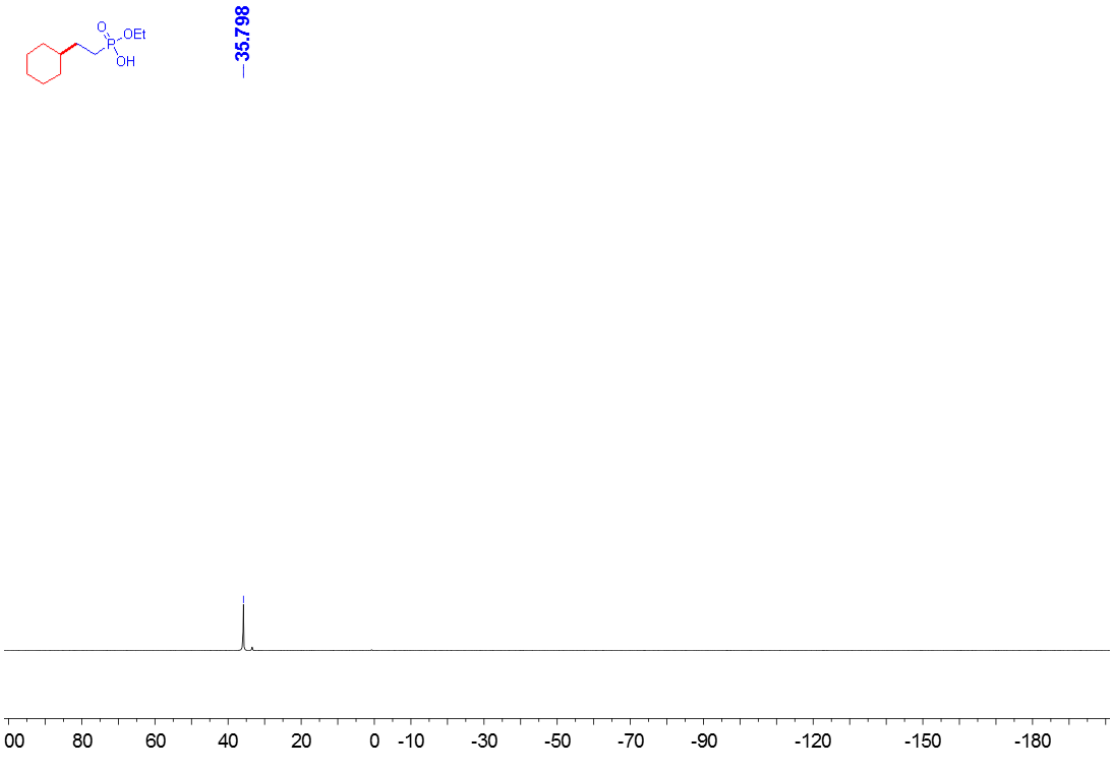
^{31}P NMR Spectrum of Compound **12e**



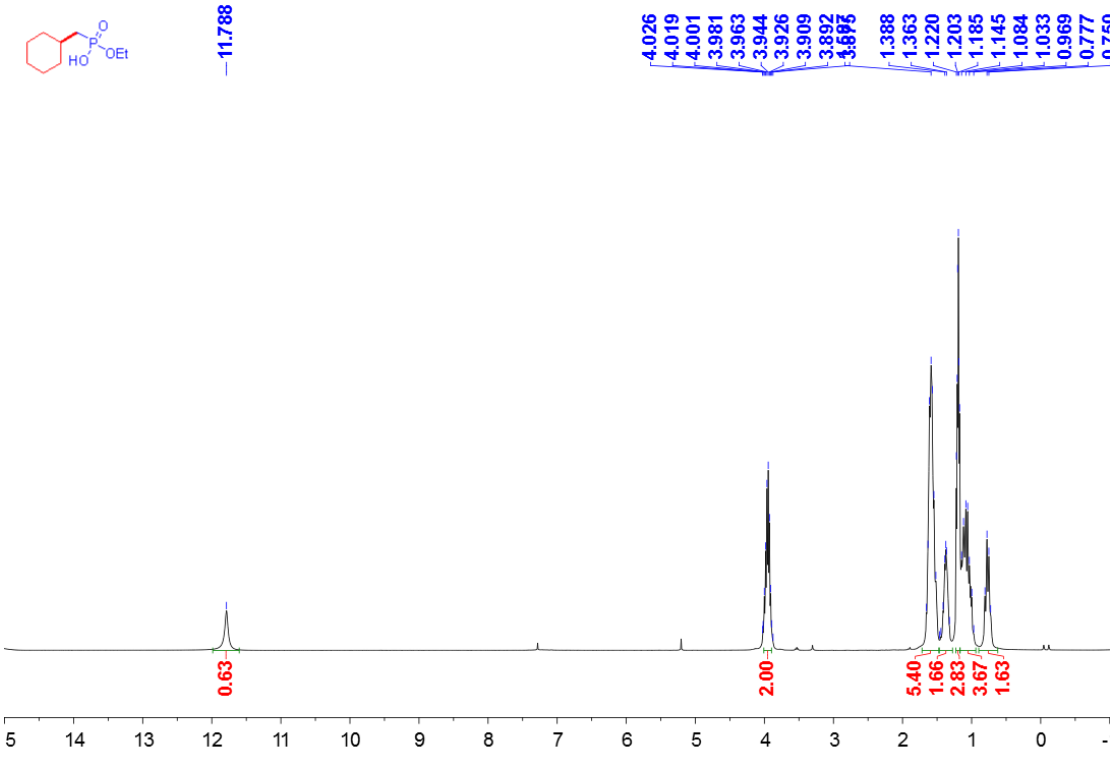
^{1}H NMR Spectrum of Compound **12f**



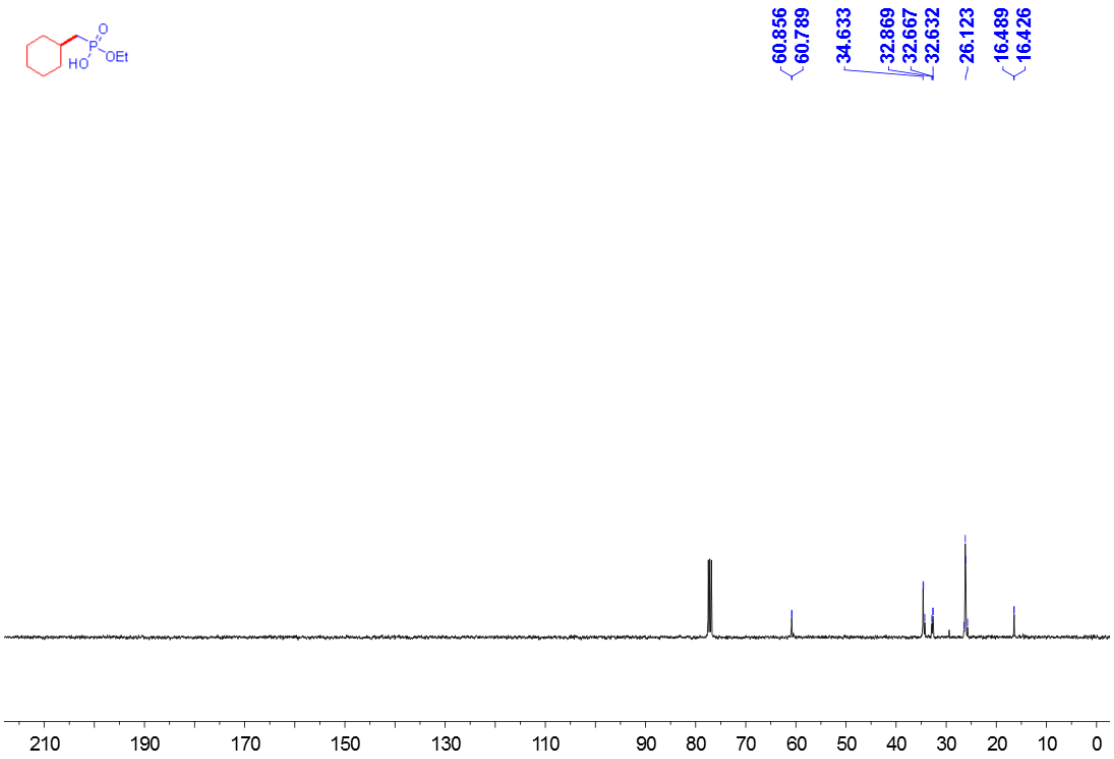
^{13}C NMR Spectrum of Compound **12f**



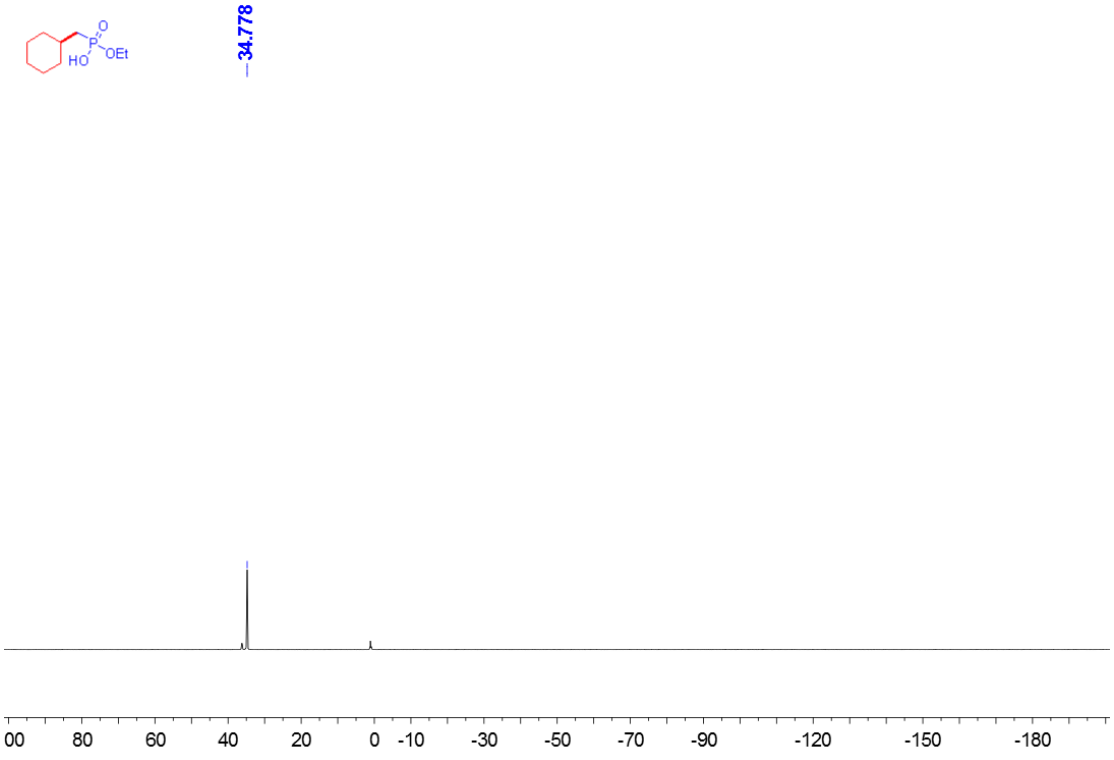
^{31}P NMR Spectrum of Compound **12f**



^{1}H NMR Spectrum of Compound **12g**

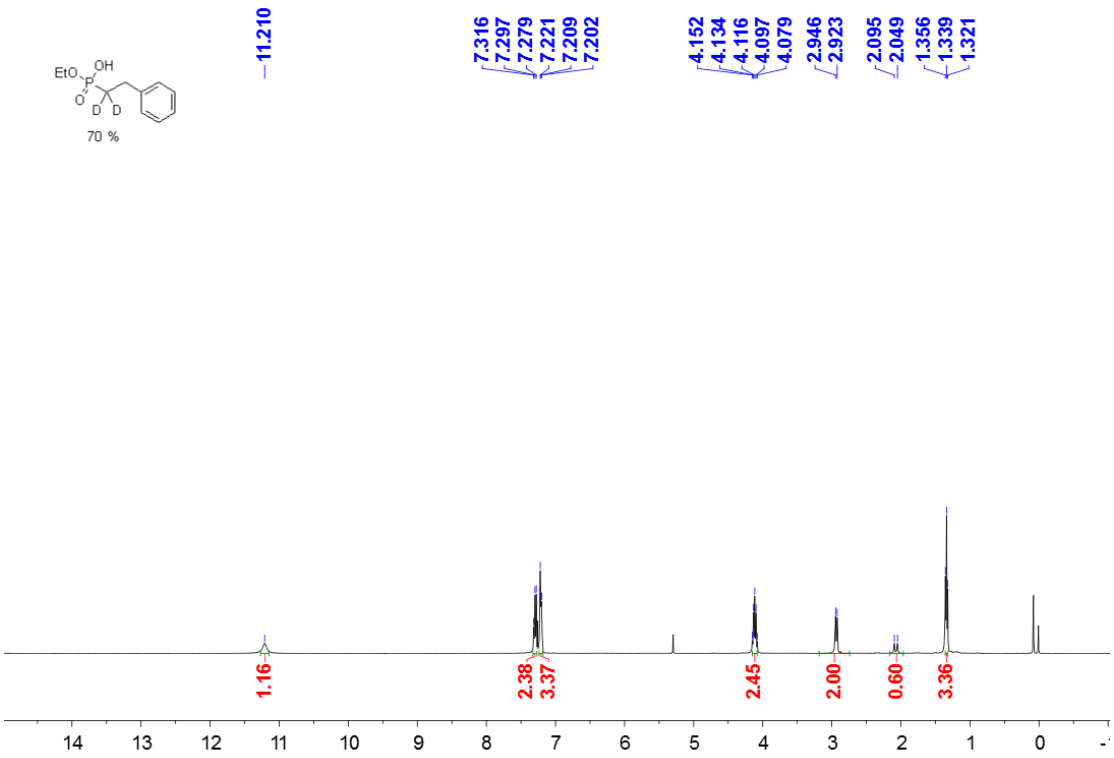


^{13}C NMR Spectrum of Compound **12g**

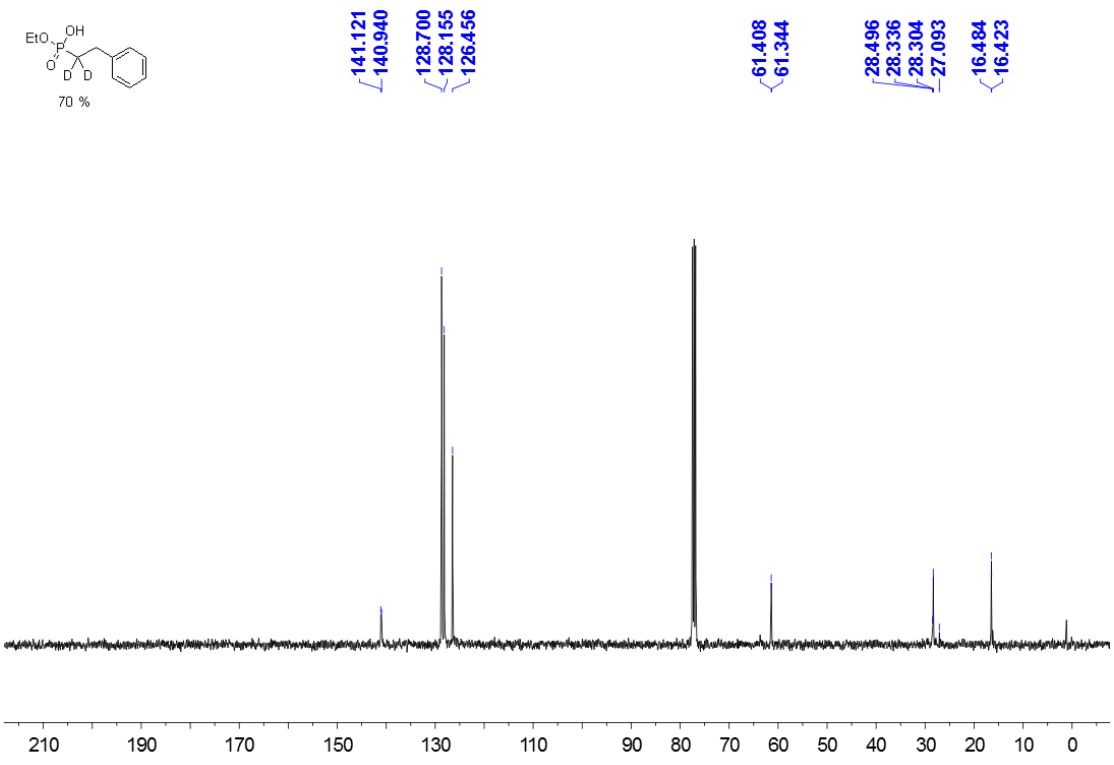


^{31}P NMR Spectrum of Compound **12g**

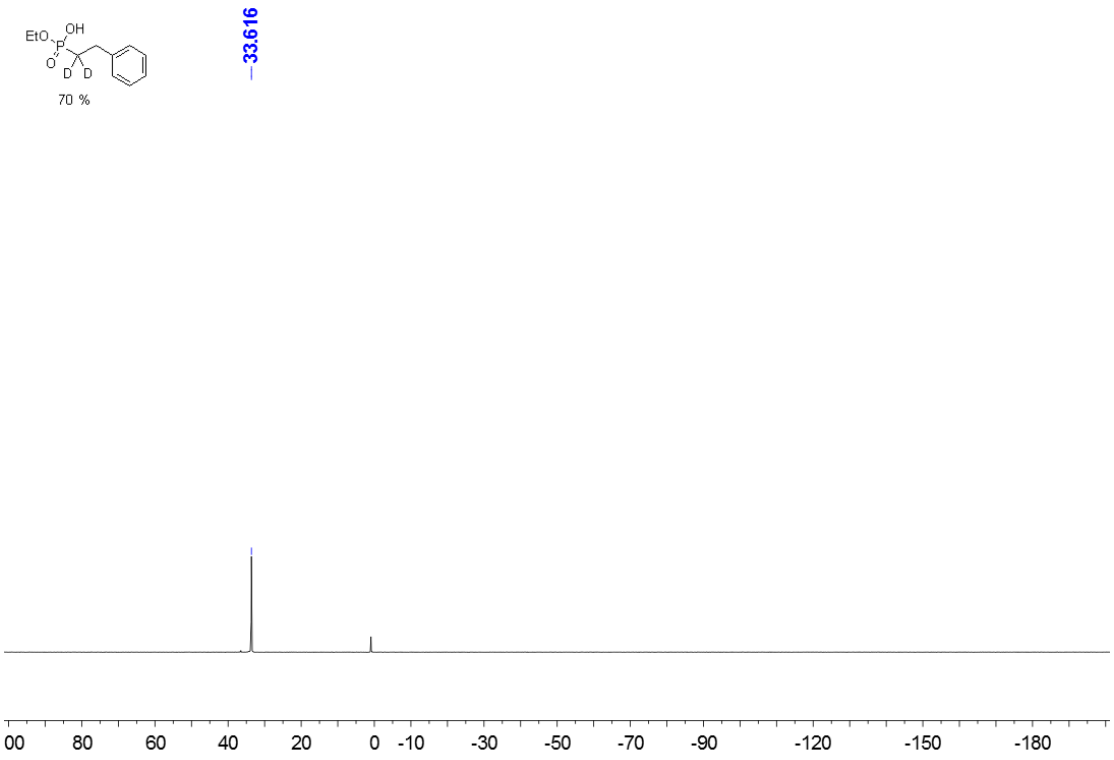
Copies of ^{1}H, ^{31}P and ^{13}C spectra of products **12a-1,1-*d*$_2$** and **20**



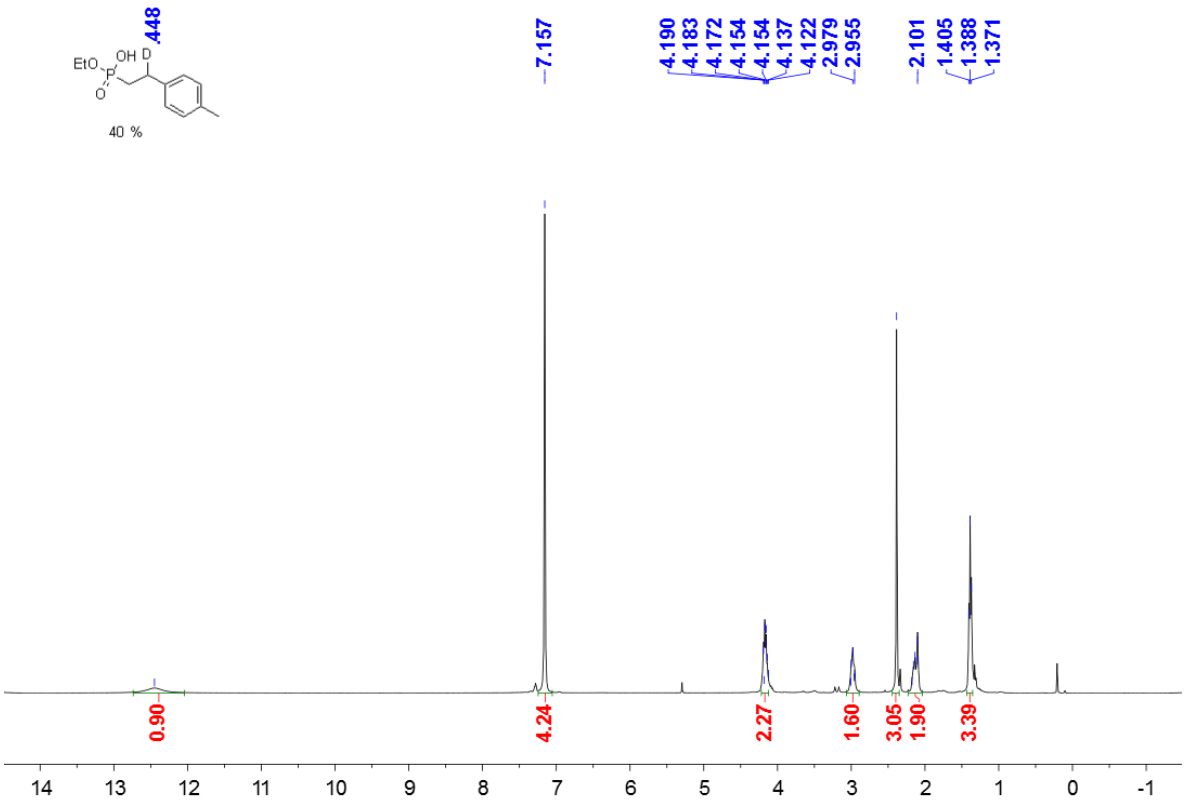
^{1}H NMR Spectrum of Compound **12a-1,1-*d*$_2$**



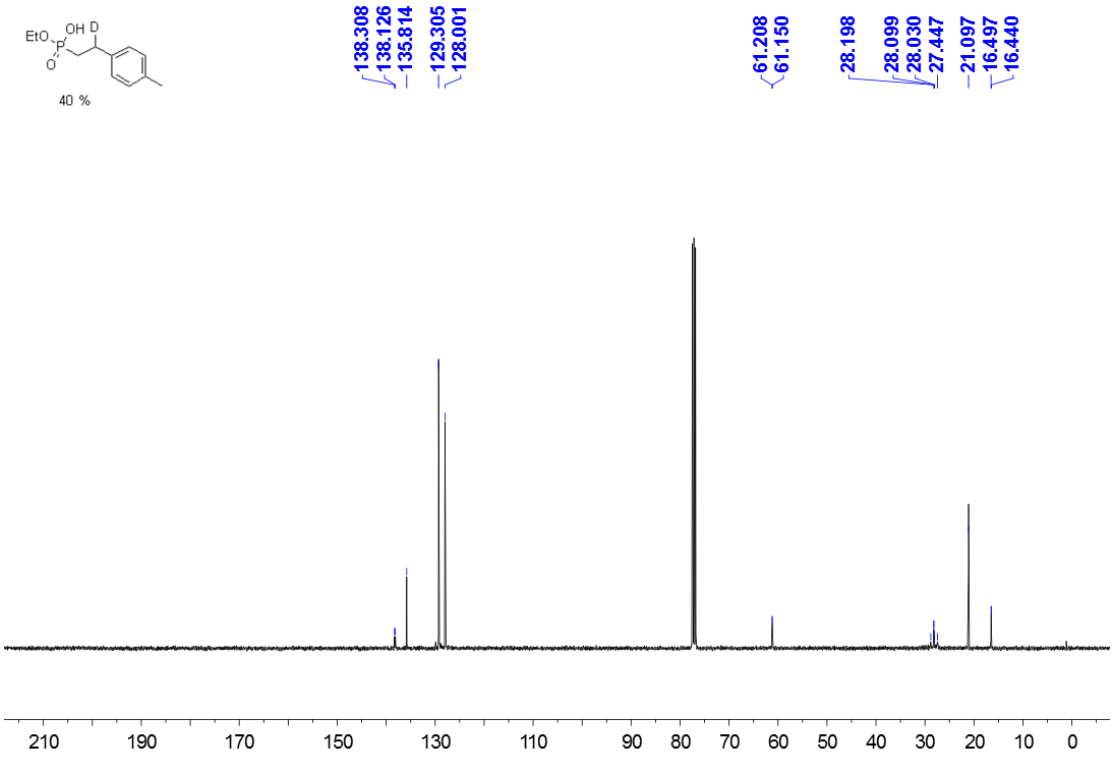
^{13}C NMR Spectrum of Compound **12a-1,1-*d*$_2$**



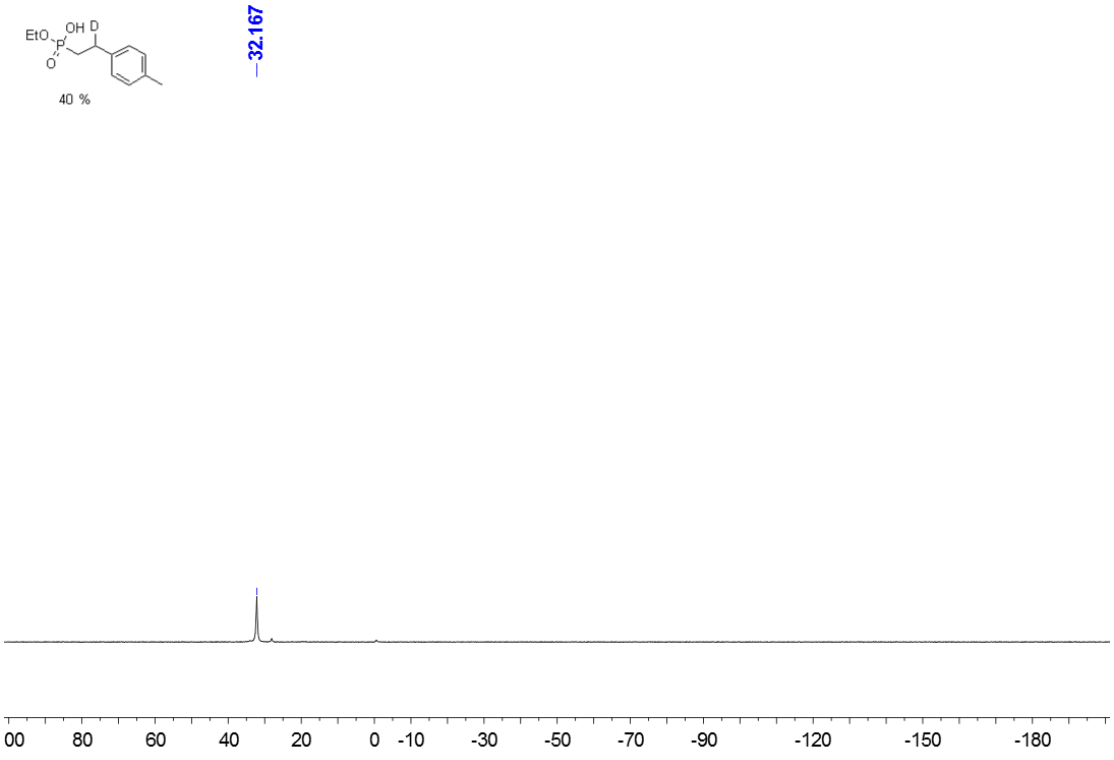
^{31}P NMR Spectrum of Compound **12a-1,1-*d*$_2$**



^{1}H NMR Spectrum of Compound **20**

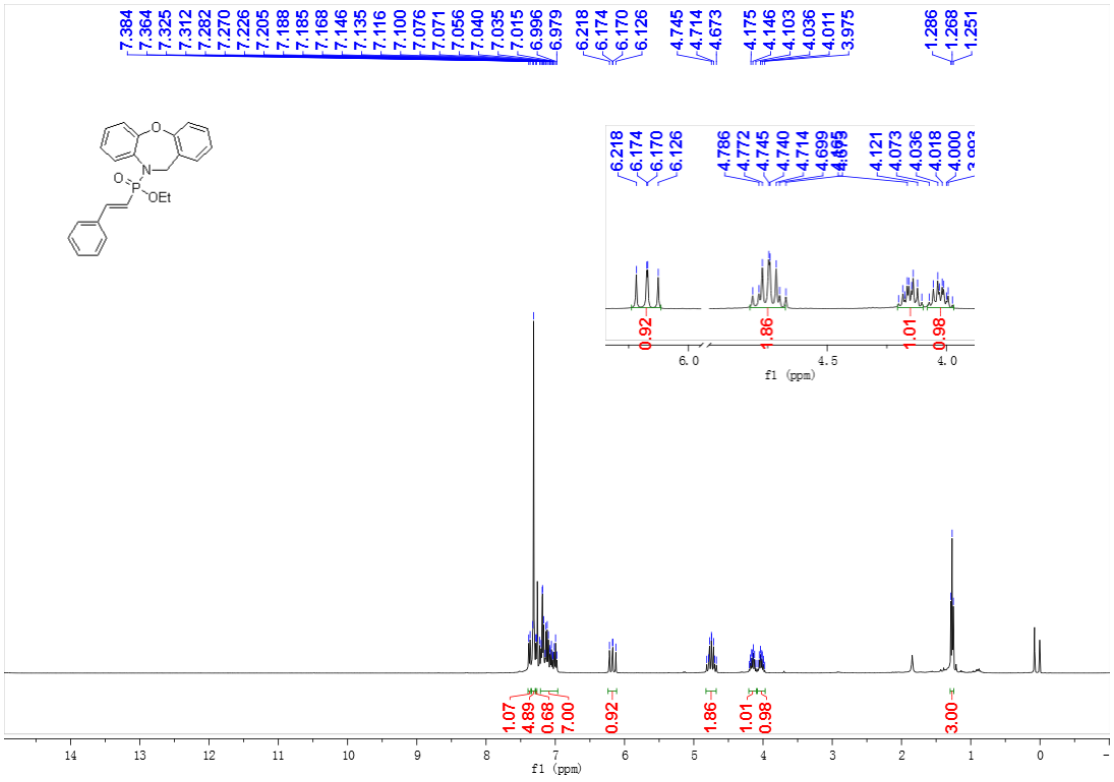


^{13}C NMR Spectrum of Compound **20**

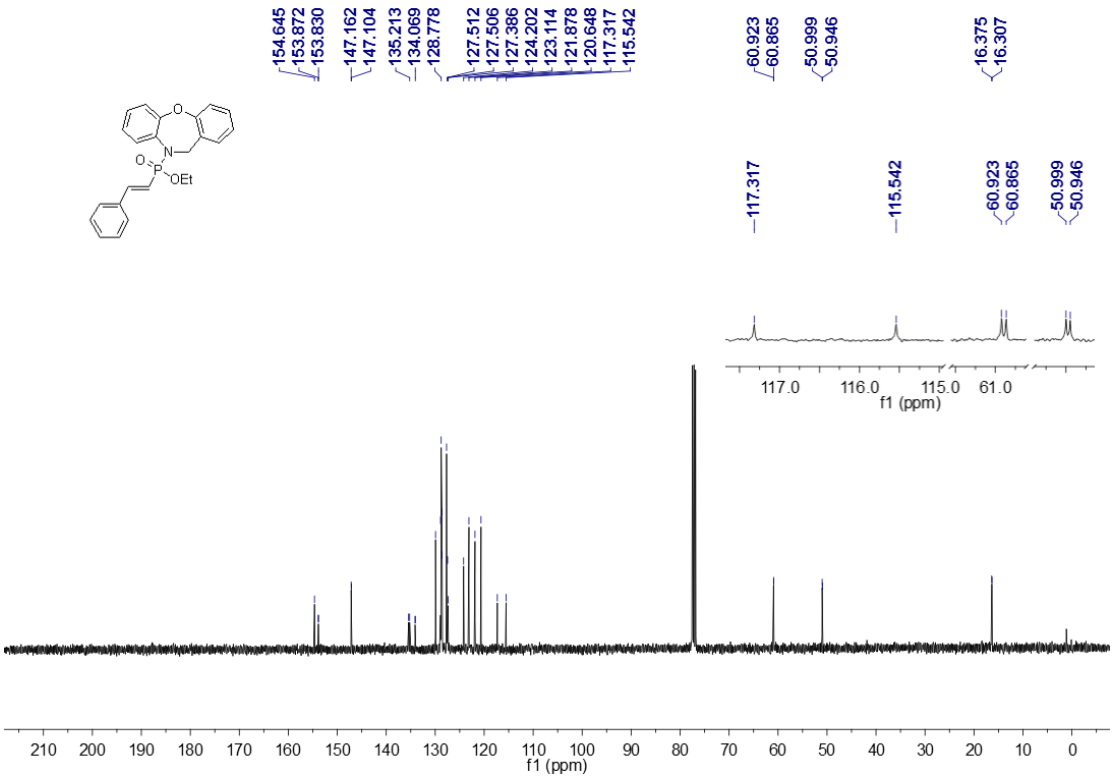


^{31}P NMR Spectrum of Compound **20**

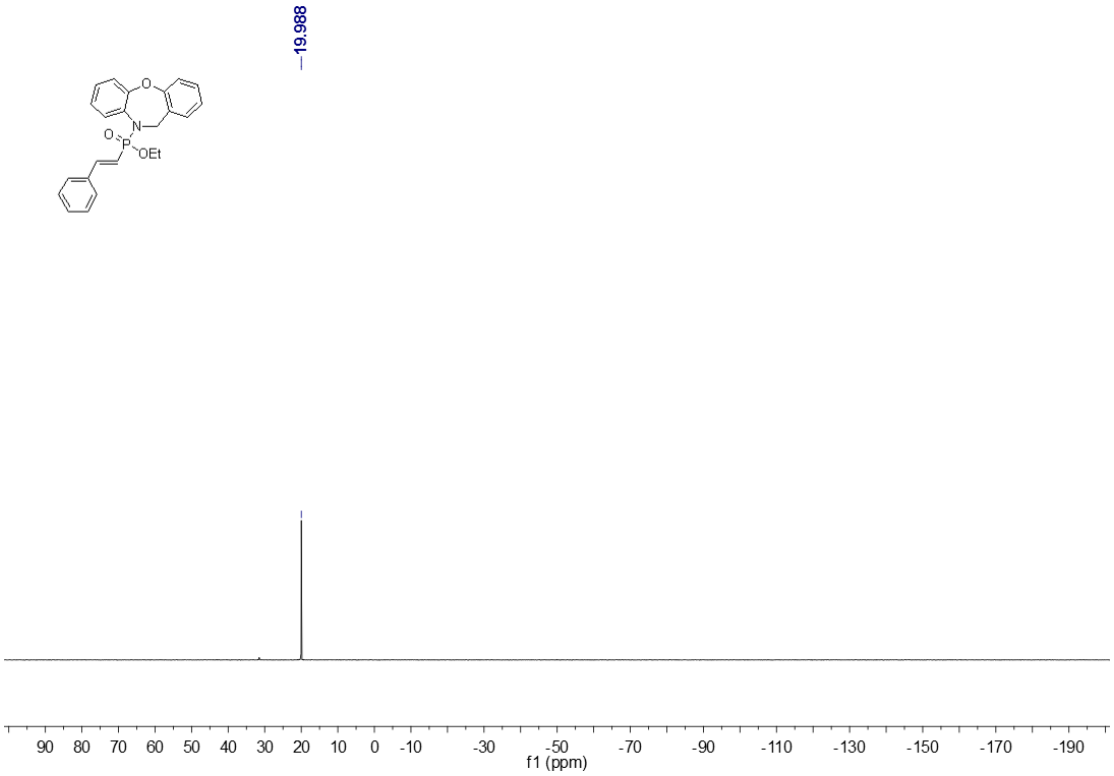
Copies of ^{1}H, ^{19}F, ^{31}P, and ^{13}C spectra of products **3aa-3ao，4** and **3Aa-3gC**



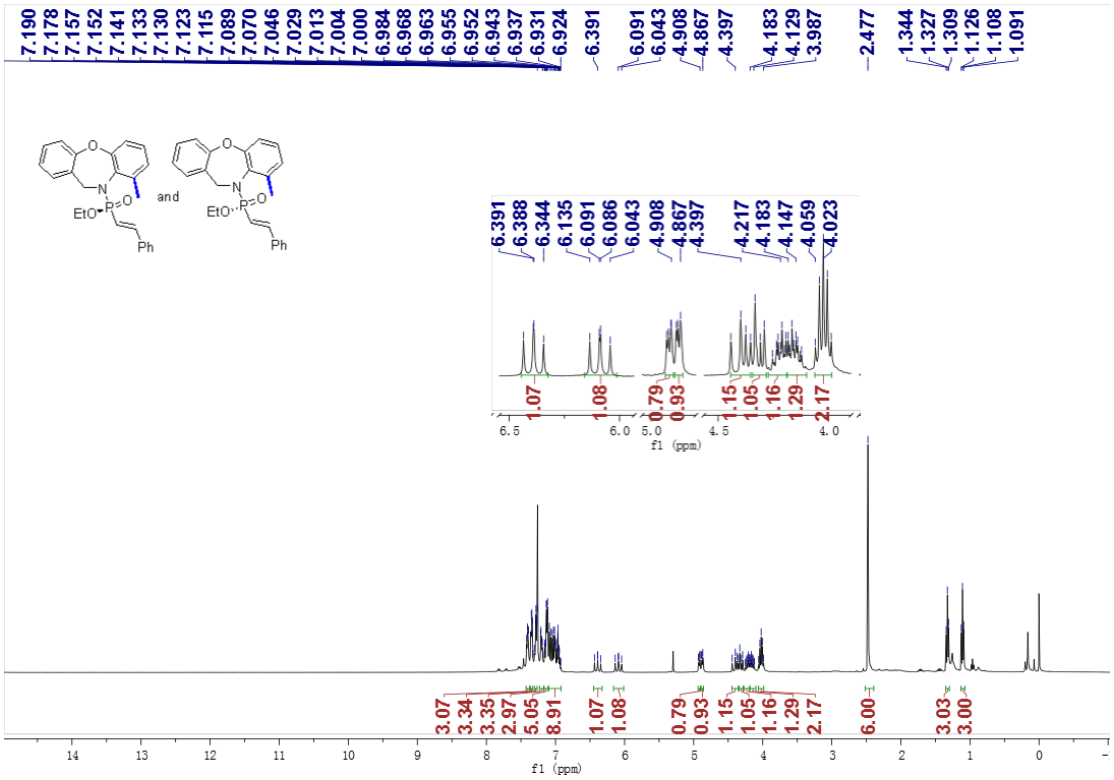
^{1}H NMR Spectrum of Compound **3aa**



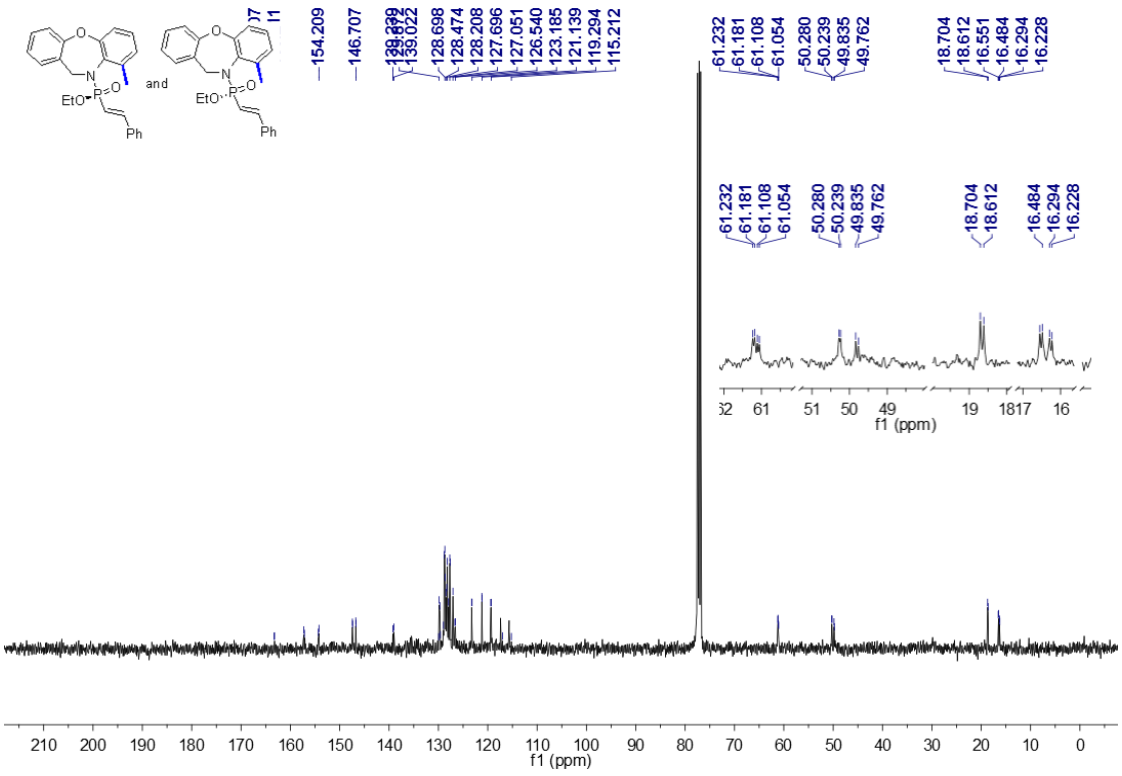
^{13}C NMR Spectrum of Compound **3aa**



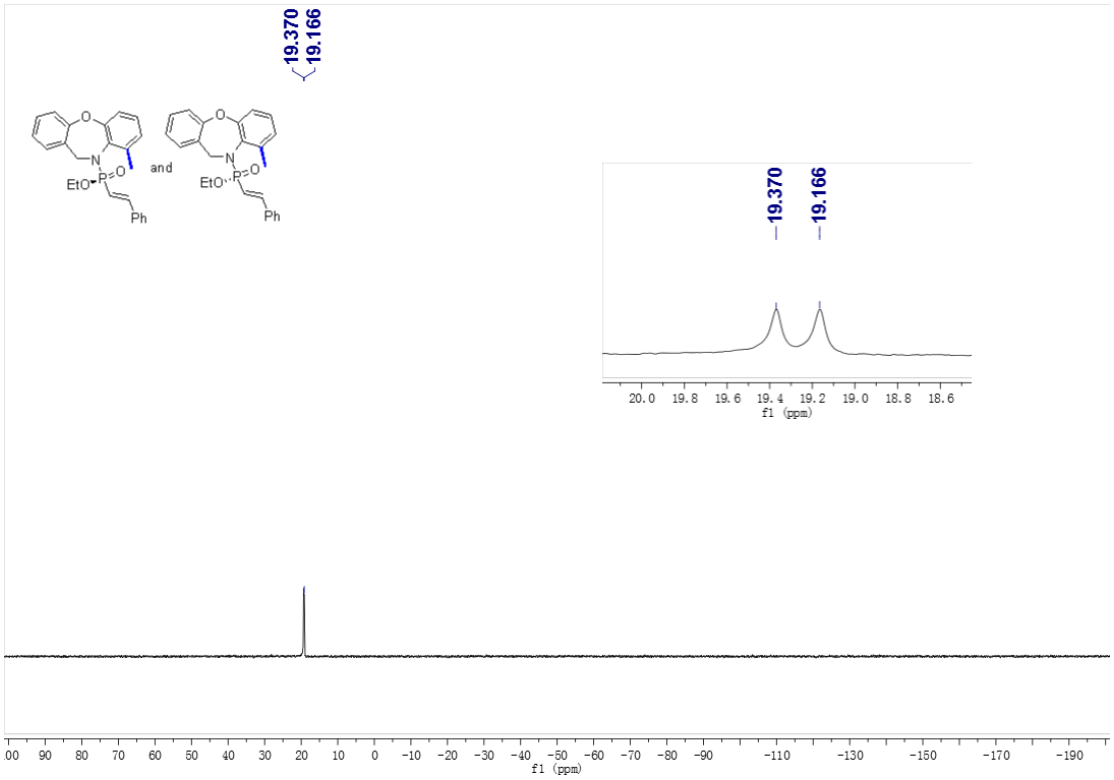
^{31}P NMR Spectrum of Compound **3aa**



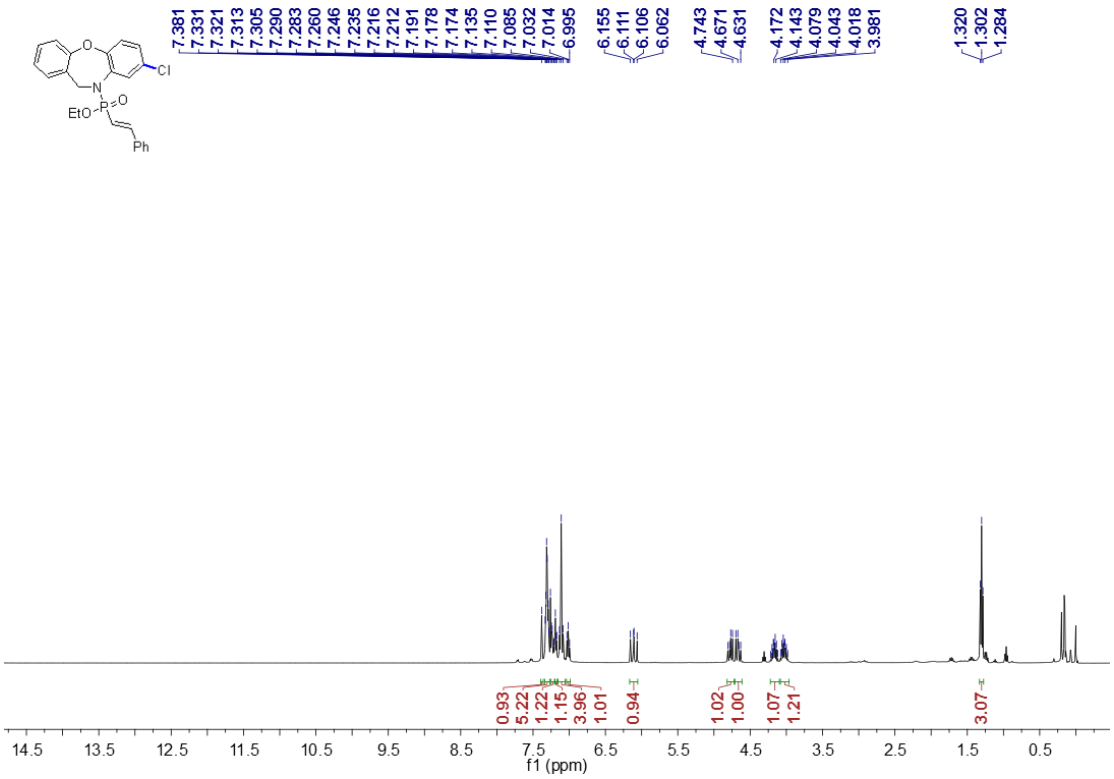
^{1}H NMR Spectrum of Compound **3ab**



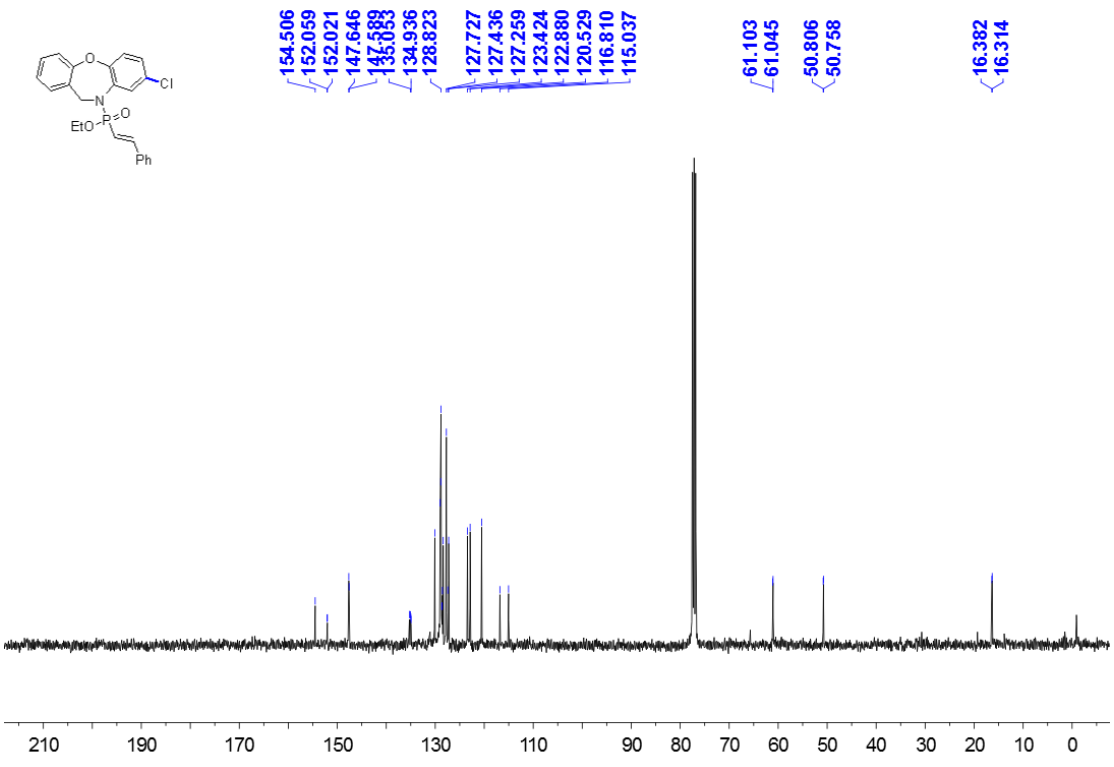
^{13}C NMR Spectrum of Compound **3ab**



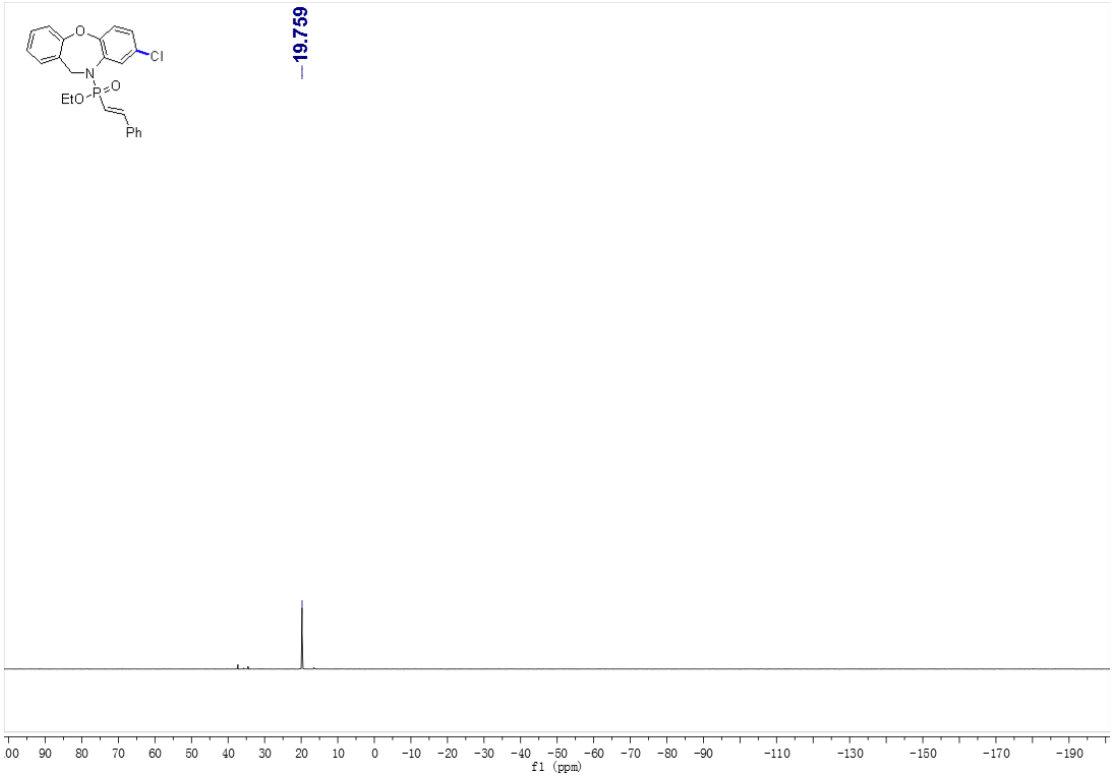
^{31}P NMR Spectrum of Compound **3ab**



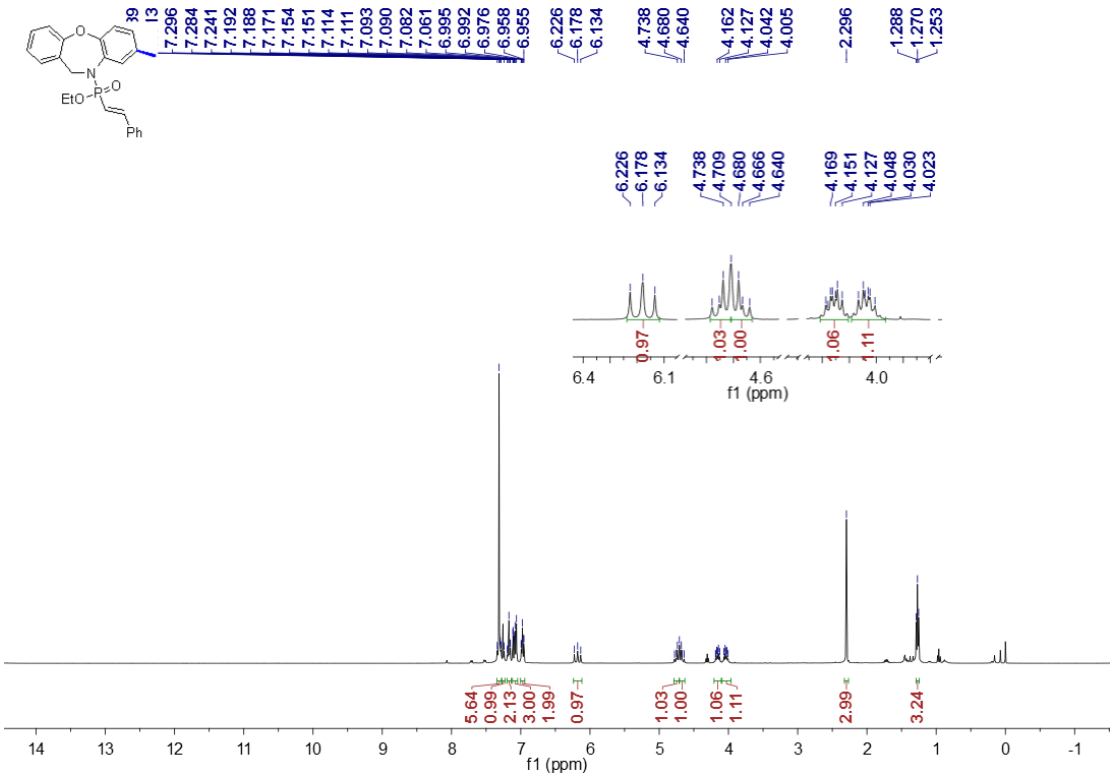
^{1}H NMR Spectrum of Compound **3ac**



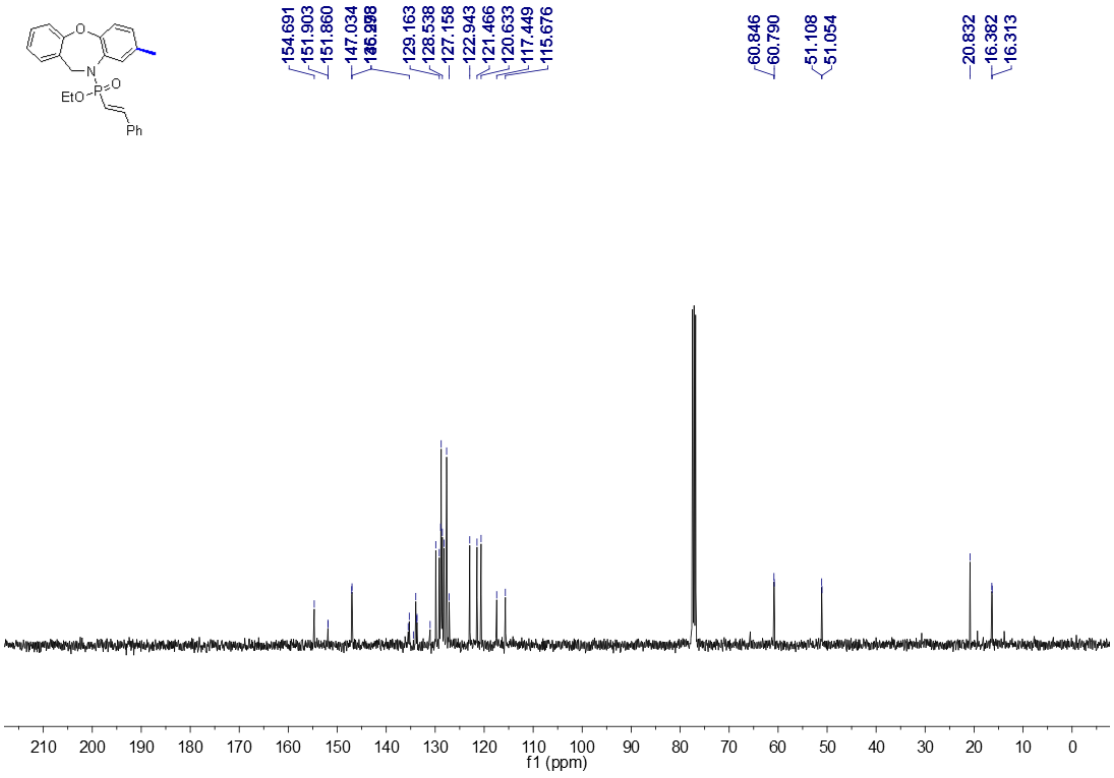
^{13}C NMR Spectrum of Compound **3ac**



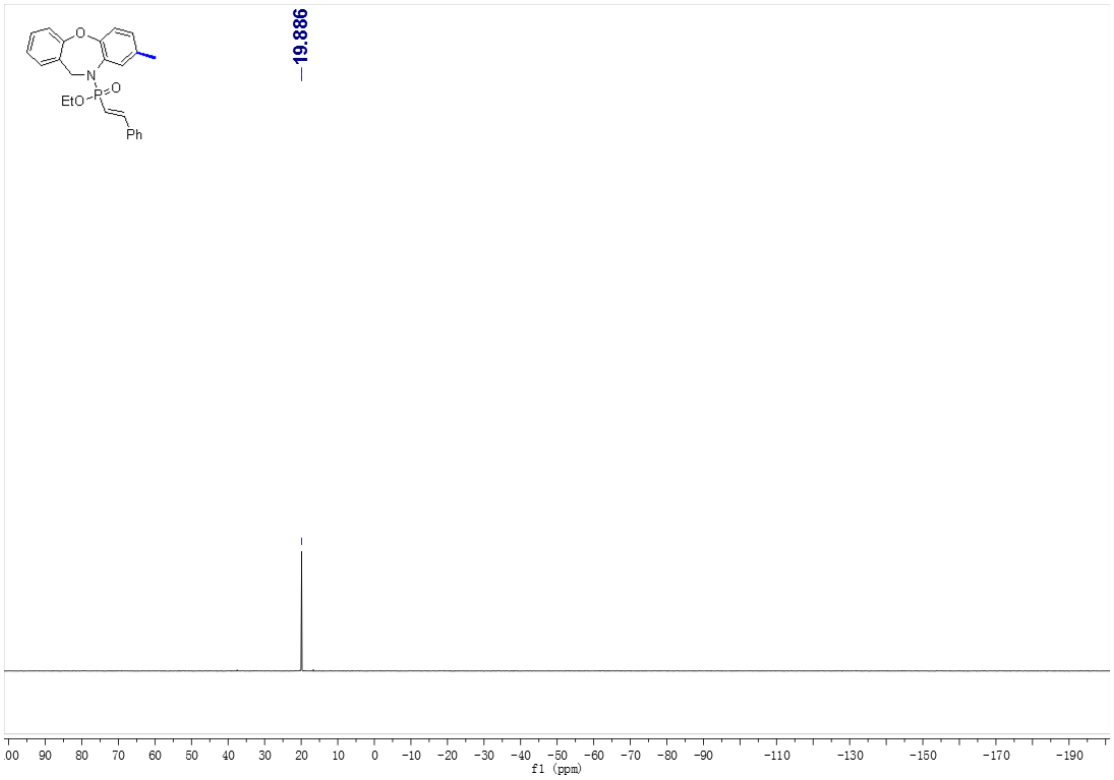
^{31}P NMR Spectrum of Compound **3ac**



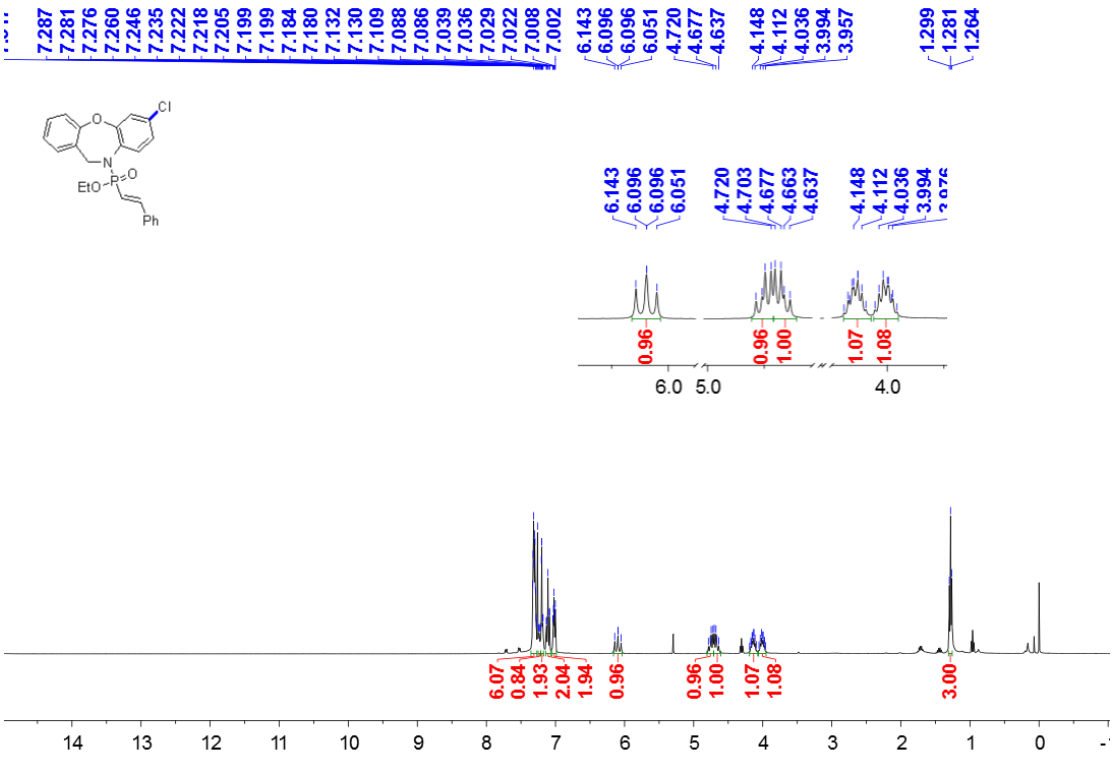
^{1}H NMR Spectrum of Compound **3ad**



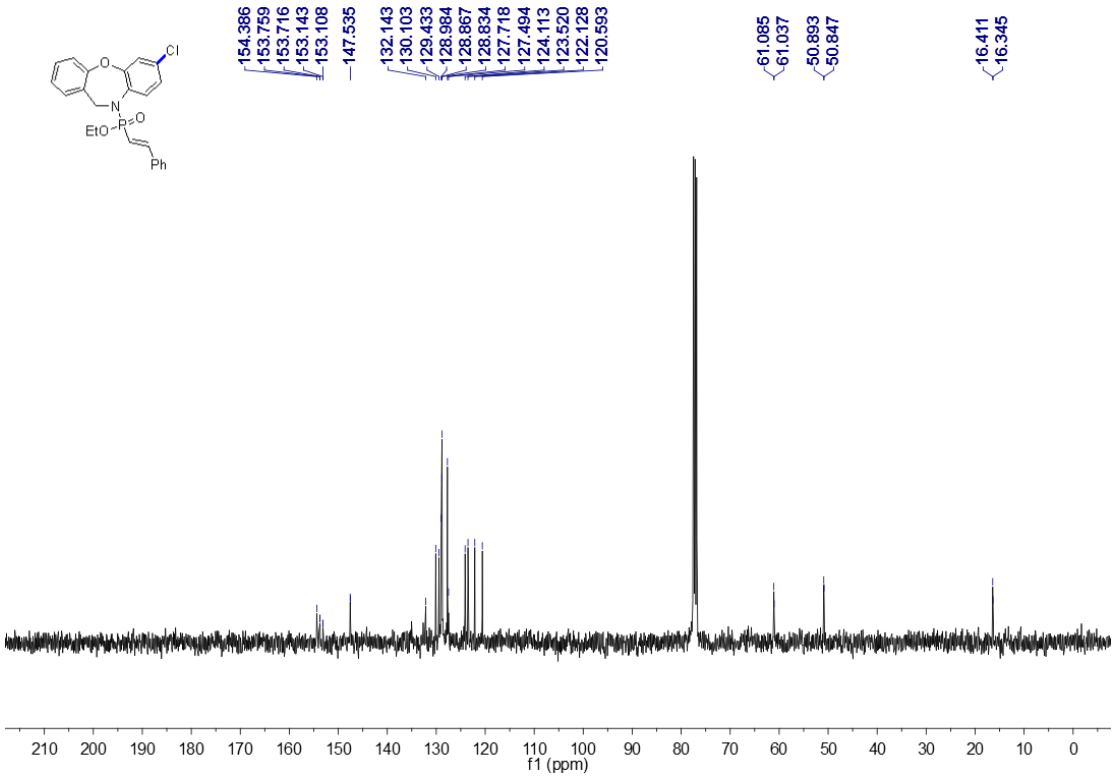
^{31}C NMR Spectrum of Compound **3ad**



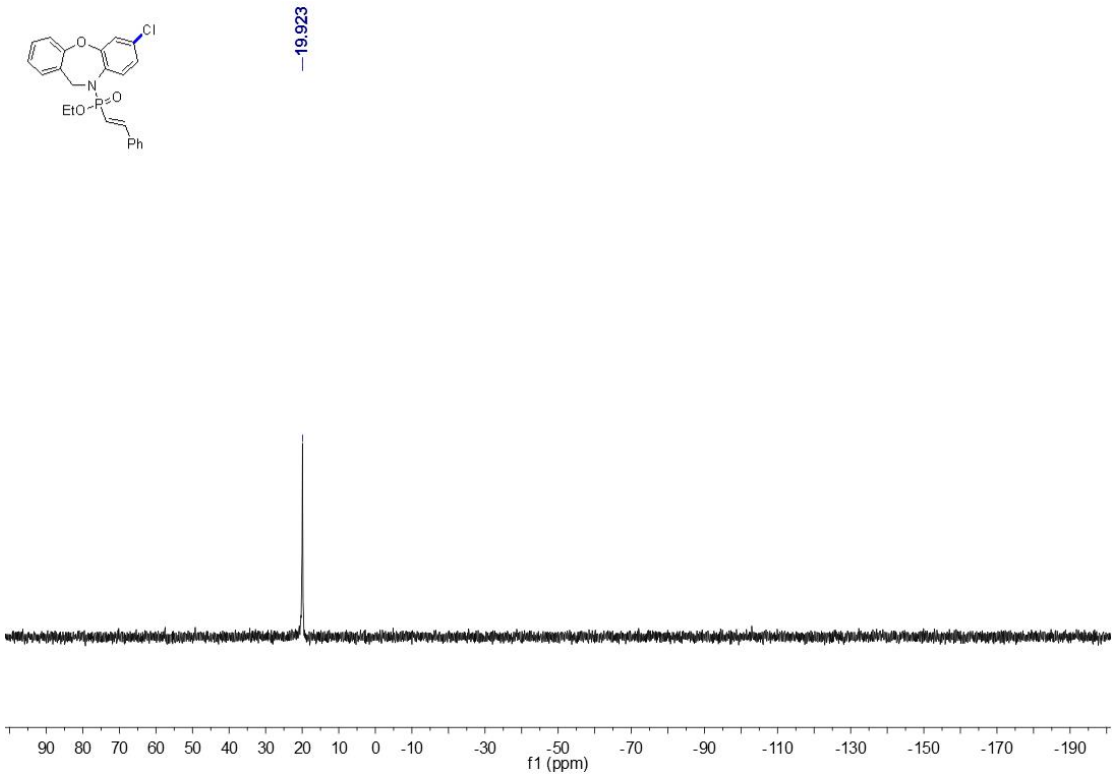
^{31}P NMR Spectrum of Compound **3ad**



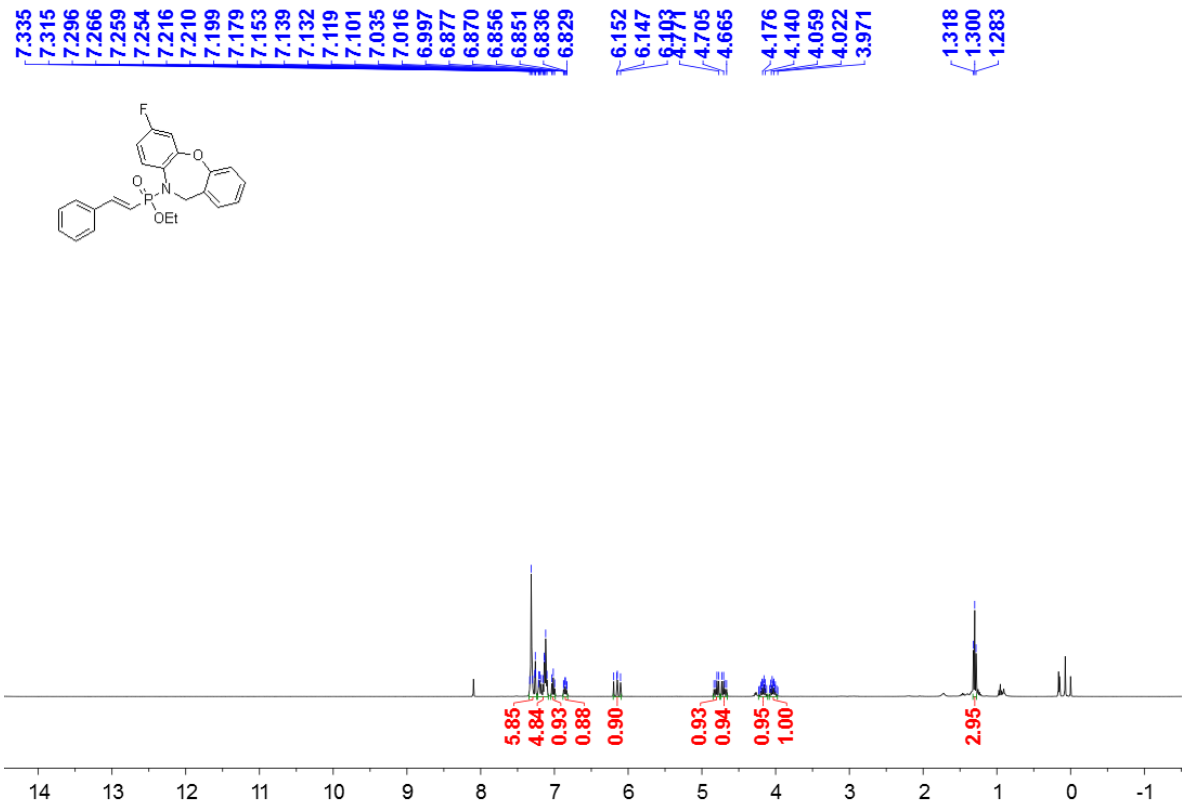
^{1}H NMR Spectrum of Compound **3ae**



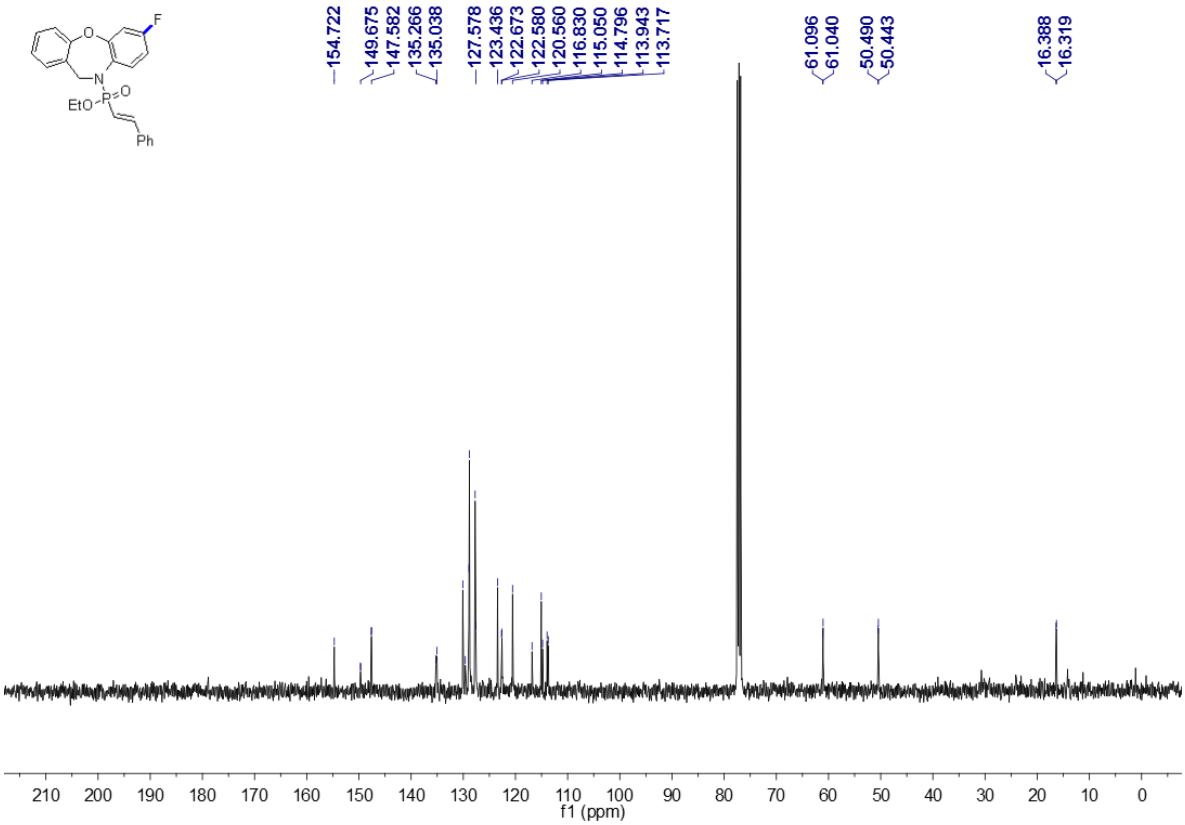
^{31}C NMR Spectrum of Compound **3ae**



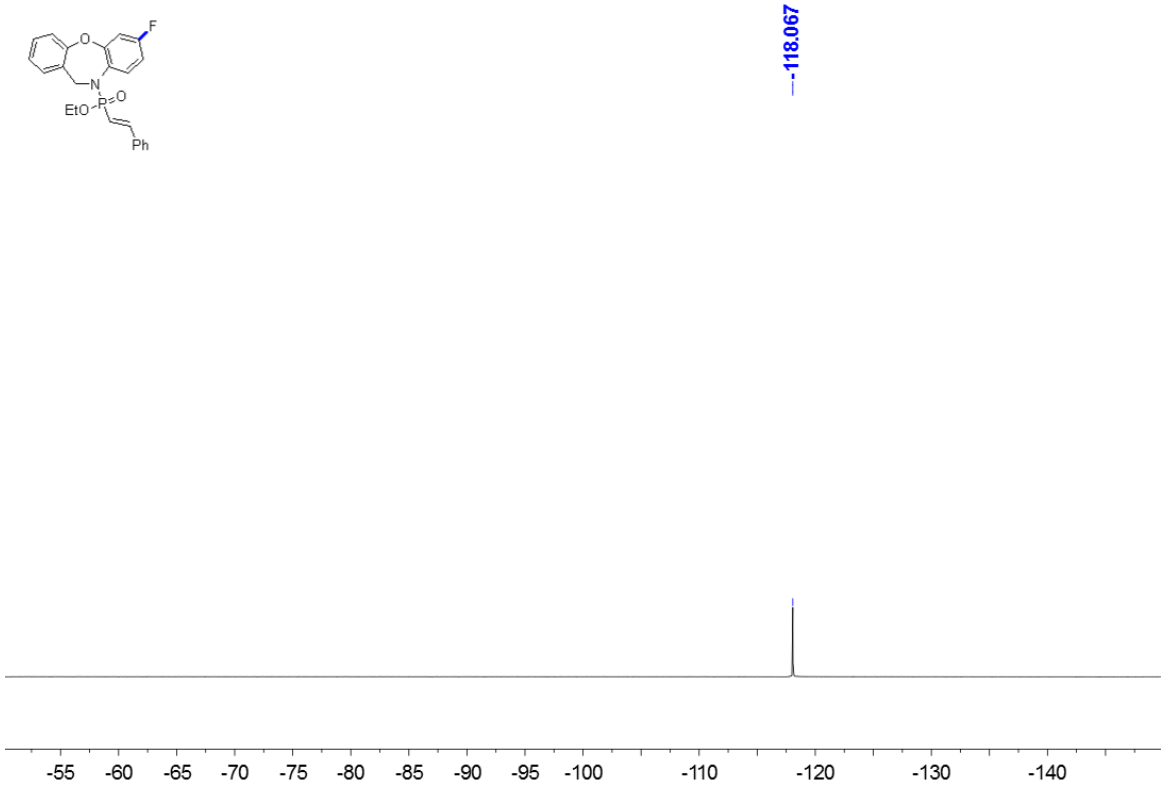
^{31}P NMR Spectrum of Compound **3ae**



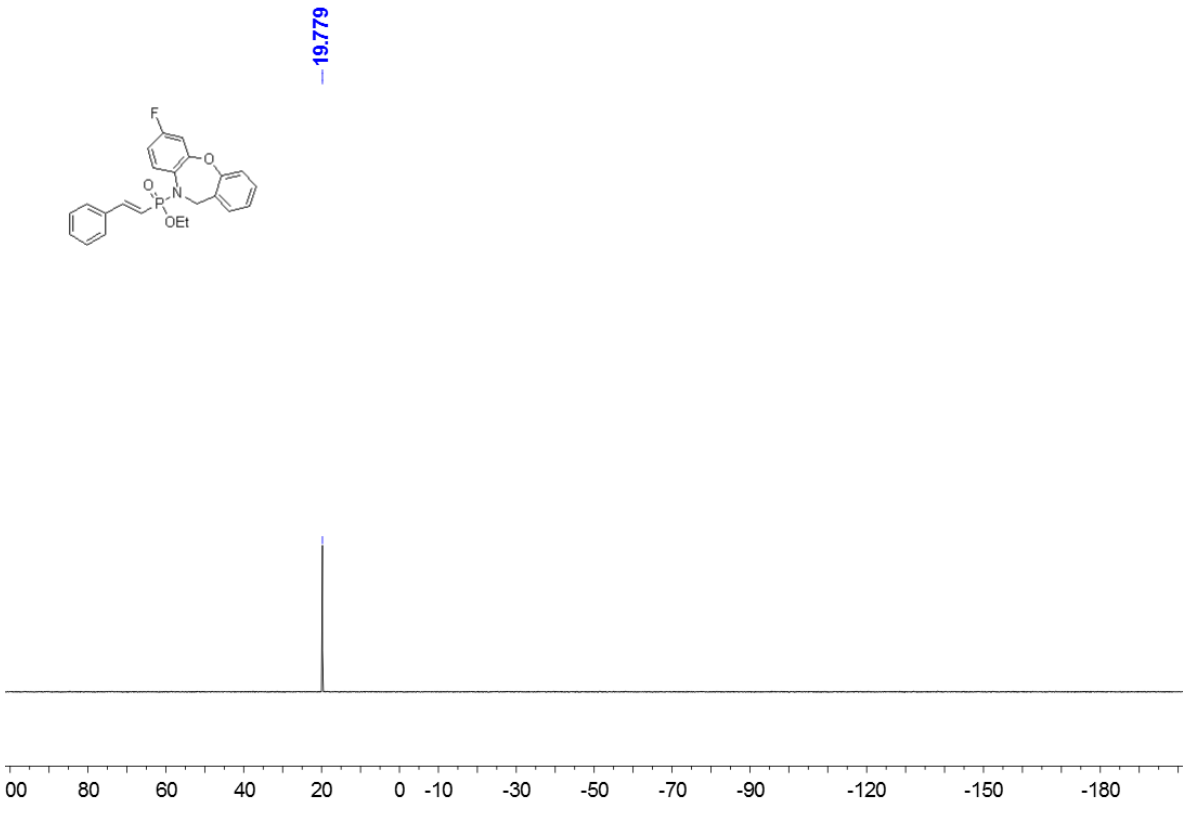
^{1}H NMR Spectrum of Compound **3af**



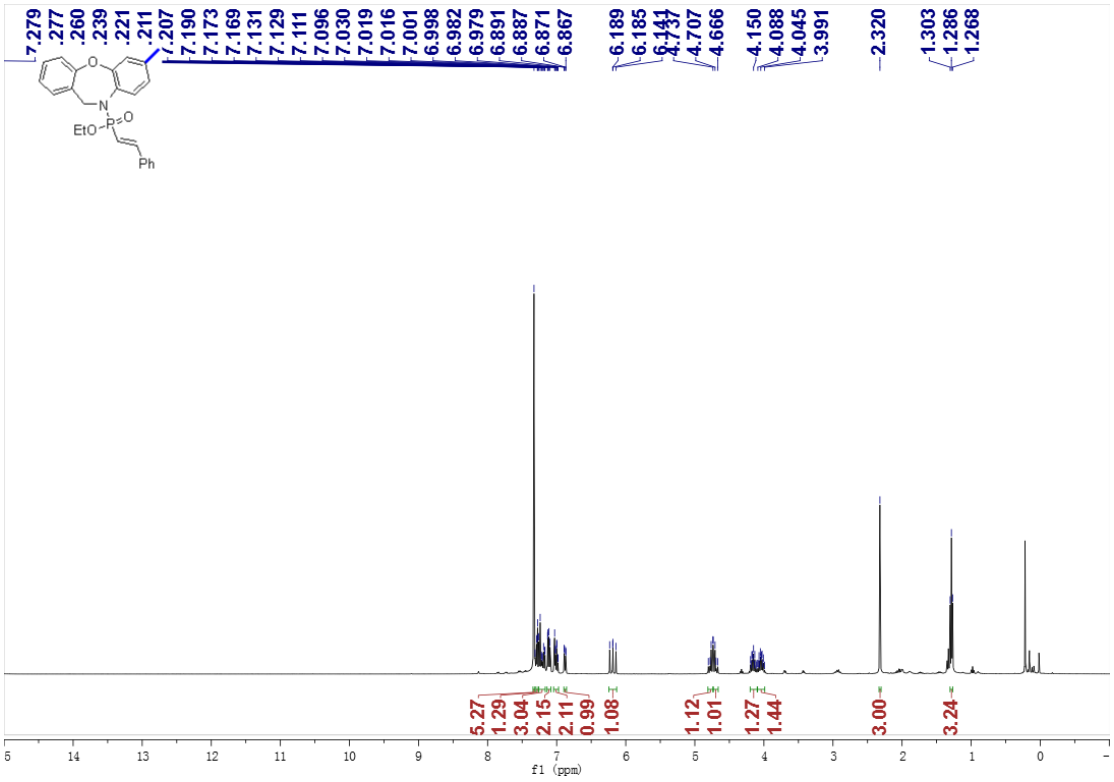
^{31}C NMR Spectrum of Compound **3af**



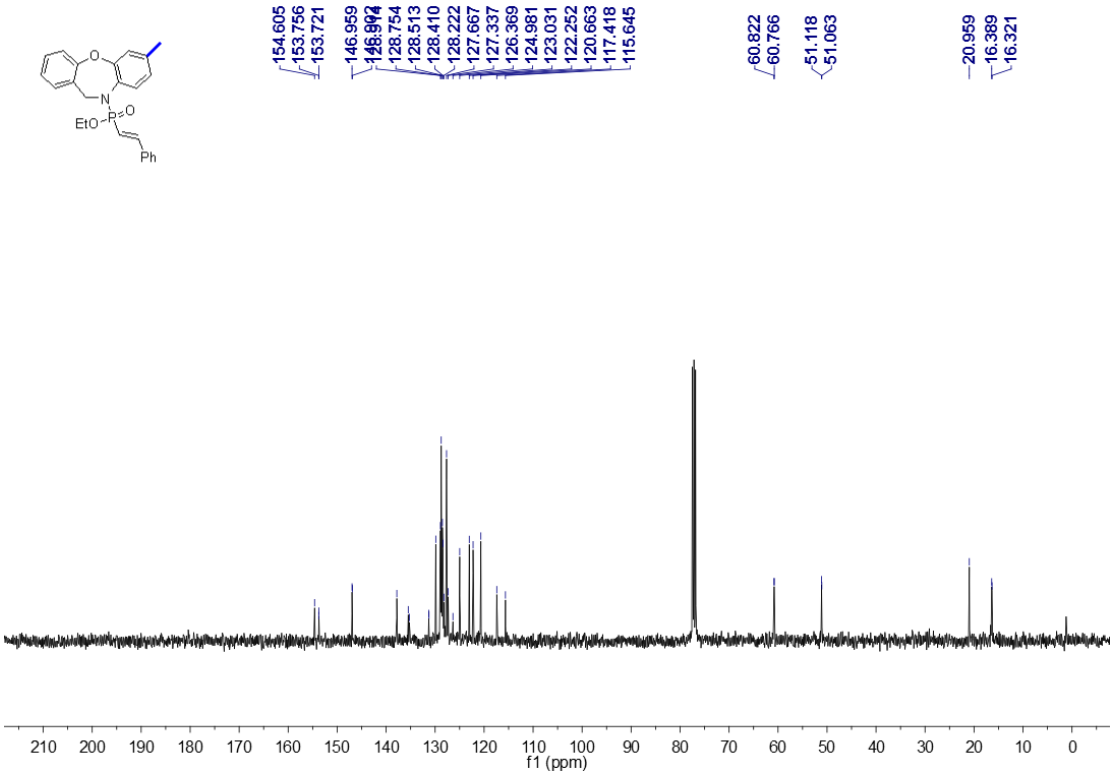
^{19}F NMR Spectrum of Compound **3af**



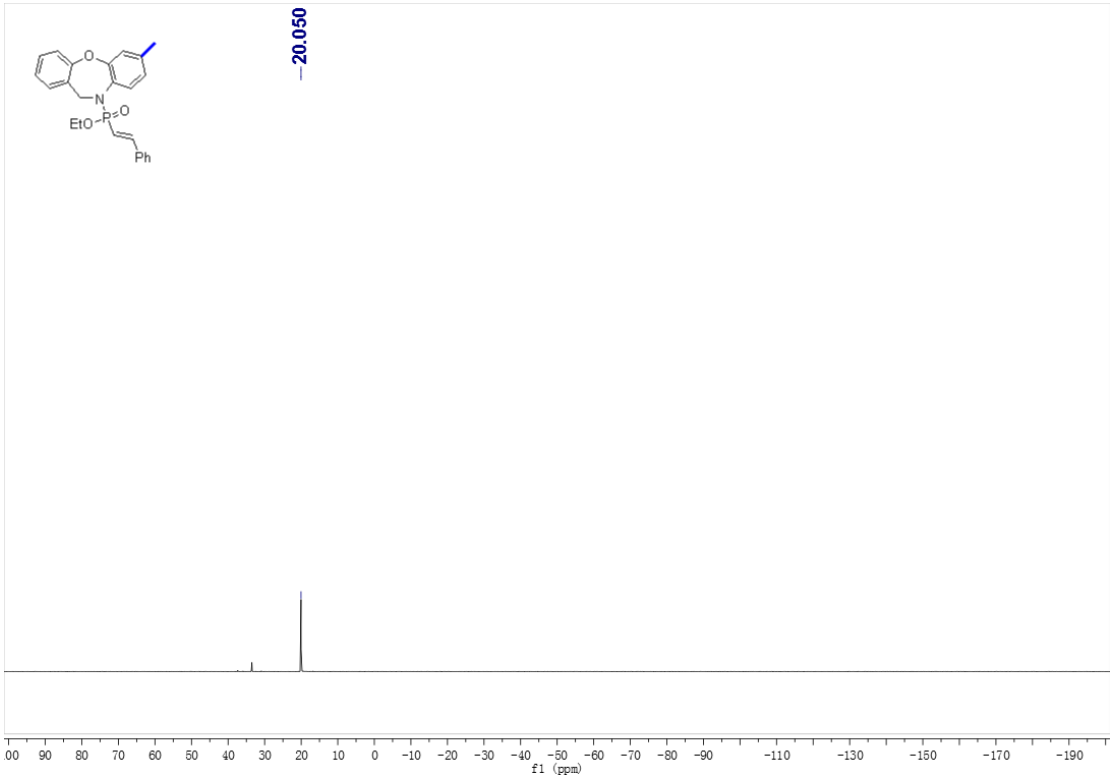
^{31}P NMR Spectrum of Compound **3af**



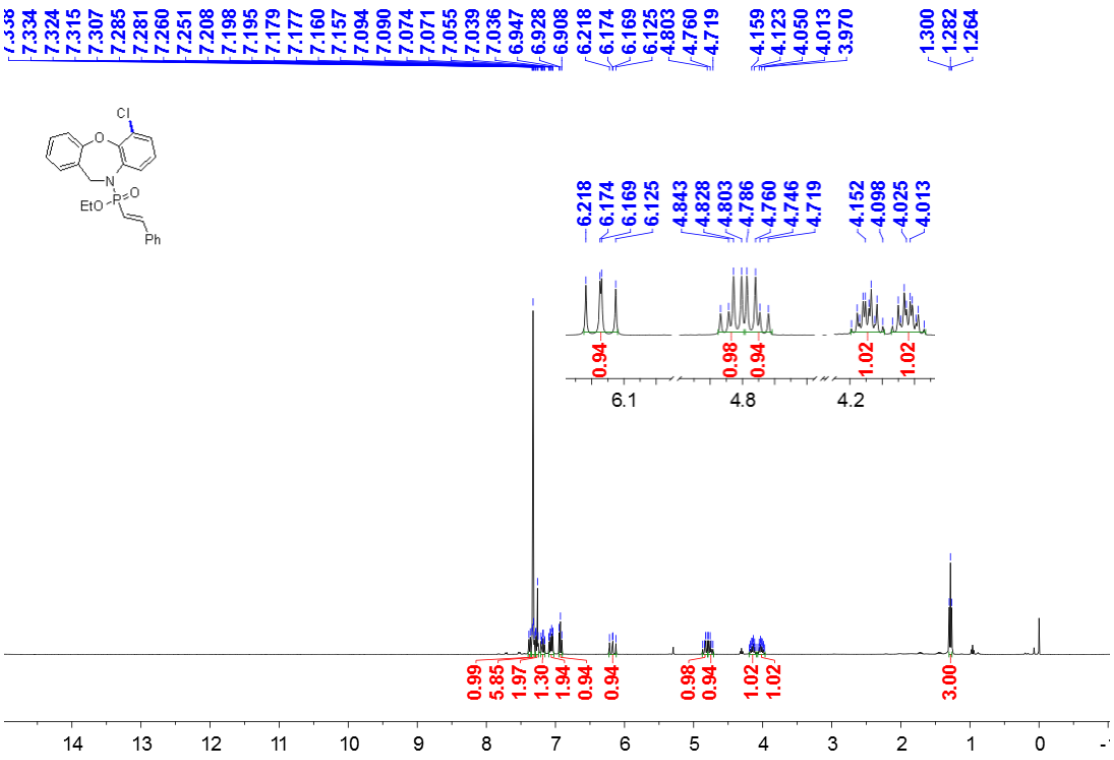
^{1}H NMR Spectrum of Compound **3ag**



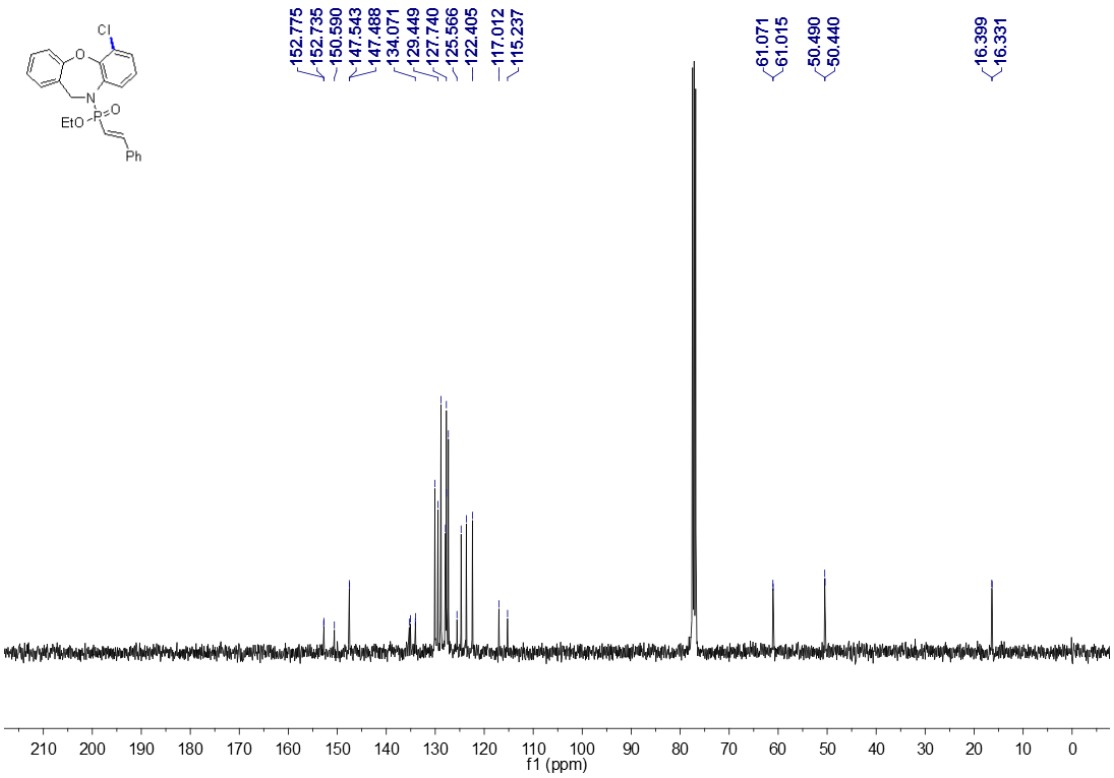
^{31}C NMR Spectrum of Compound **3ag**



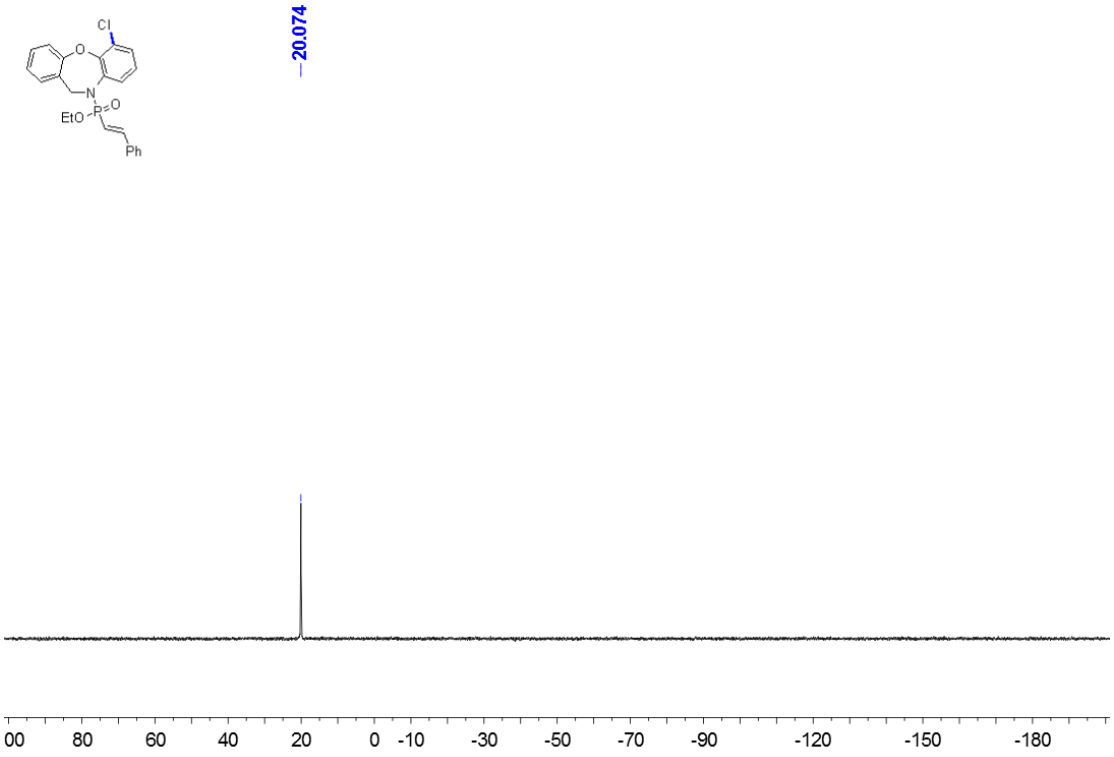
^{31}P NMR Spectrum of Compound **3ag**



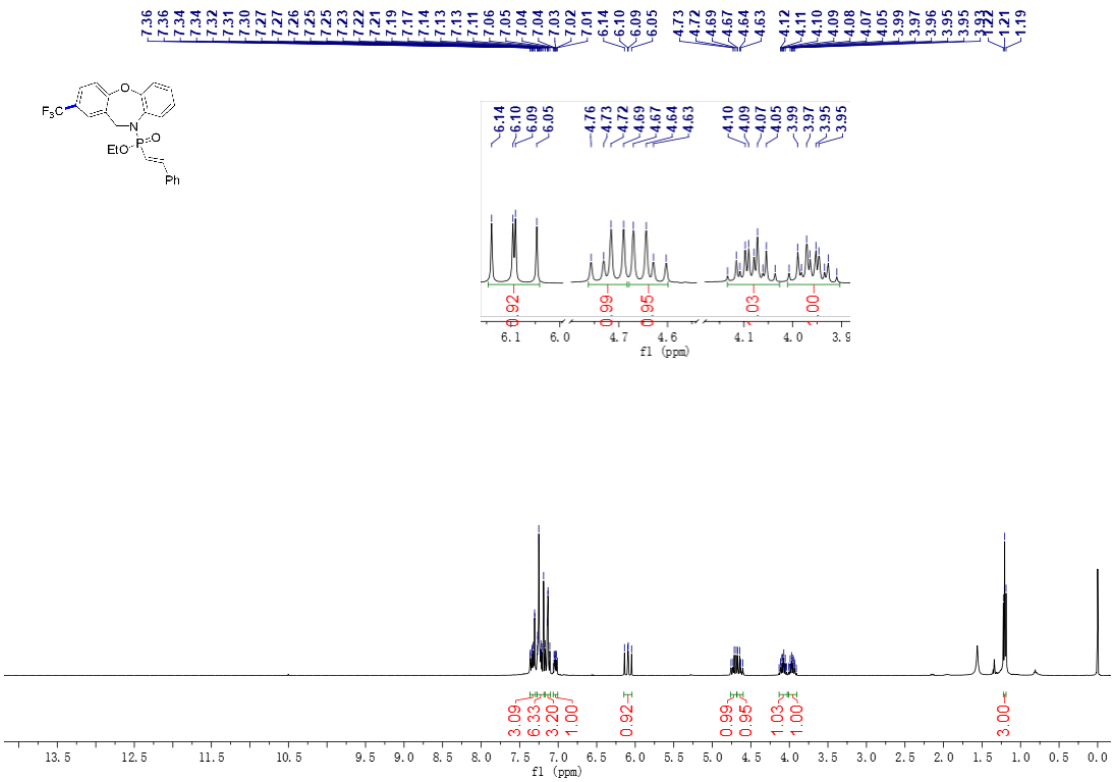
^{1}H NMR Spectrum of Compound **3ah**



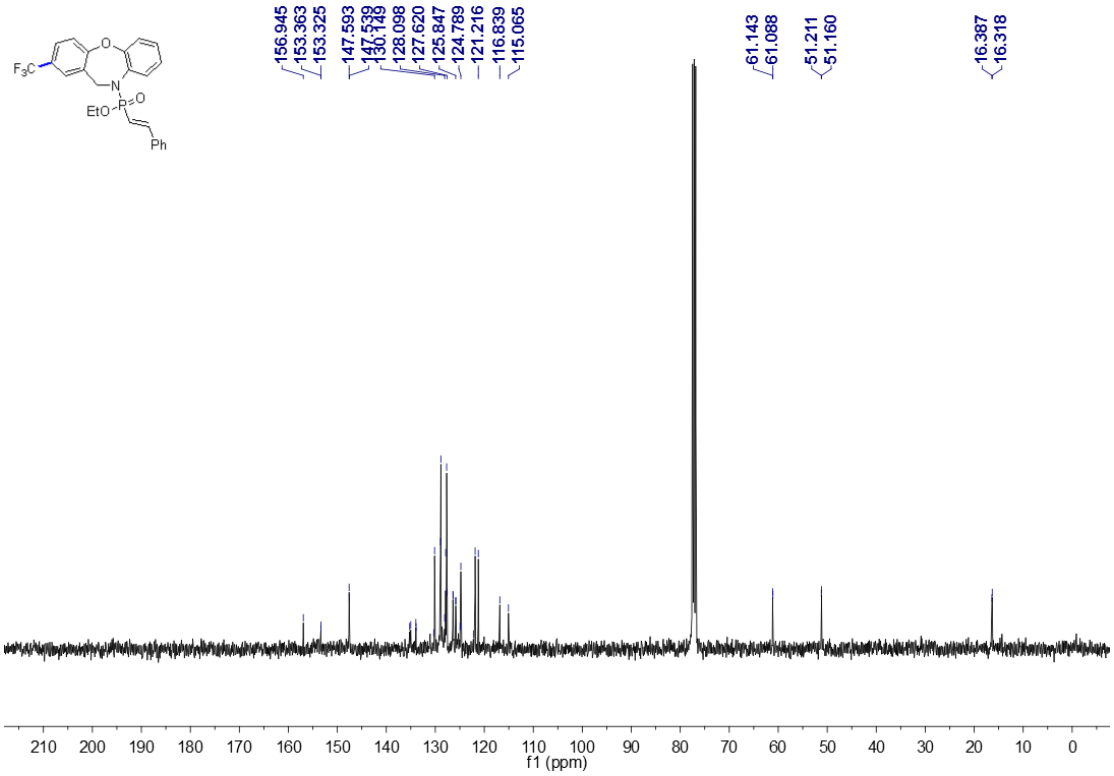
^{13}C NMR Spectrum of Compound **3ah**



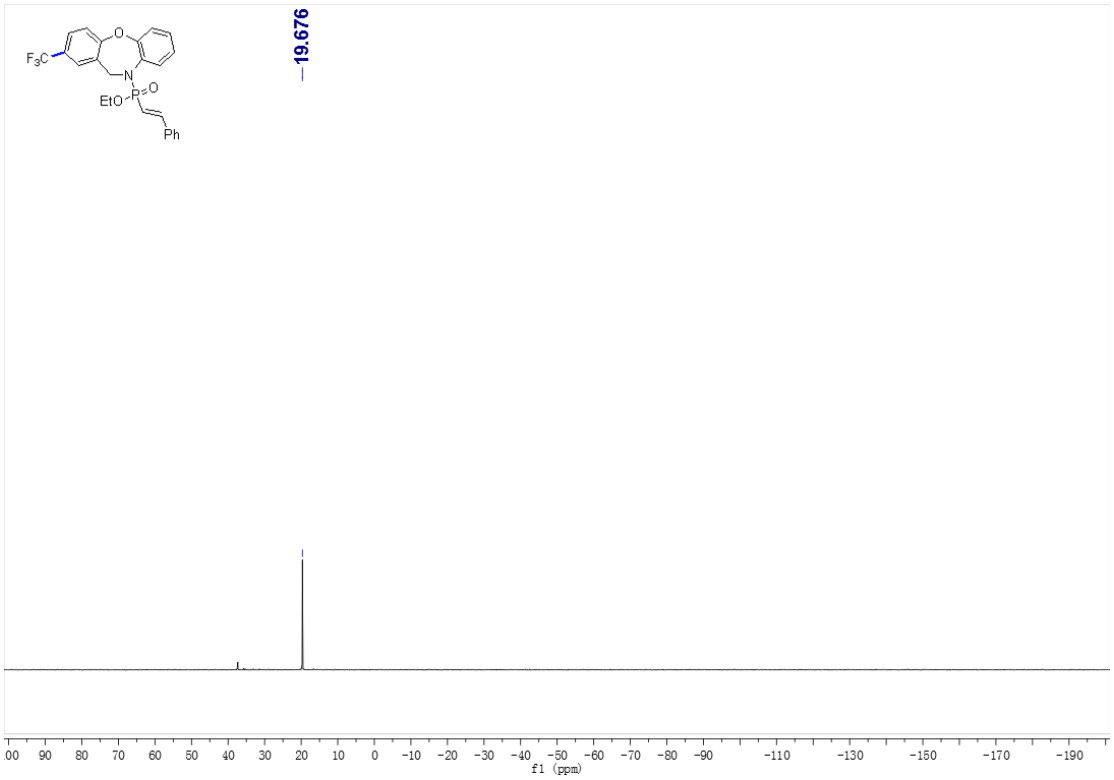
^{31}P NMR Spectrum of Compound **3ah**



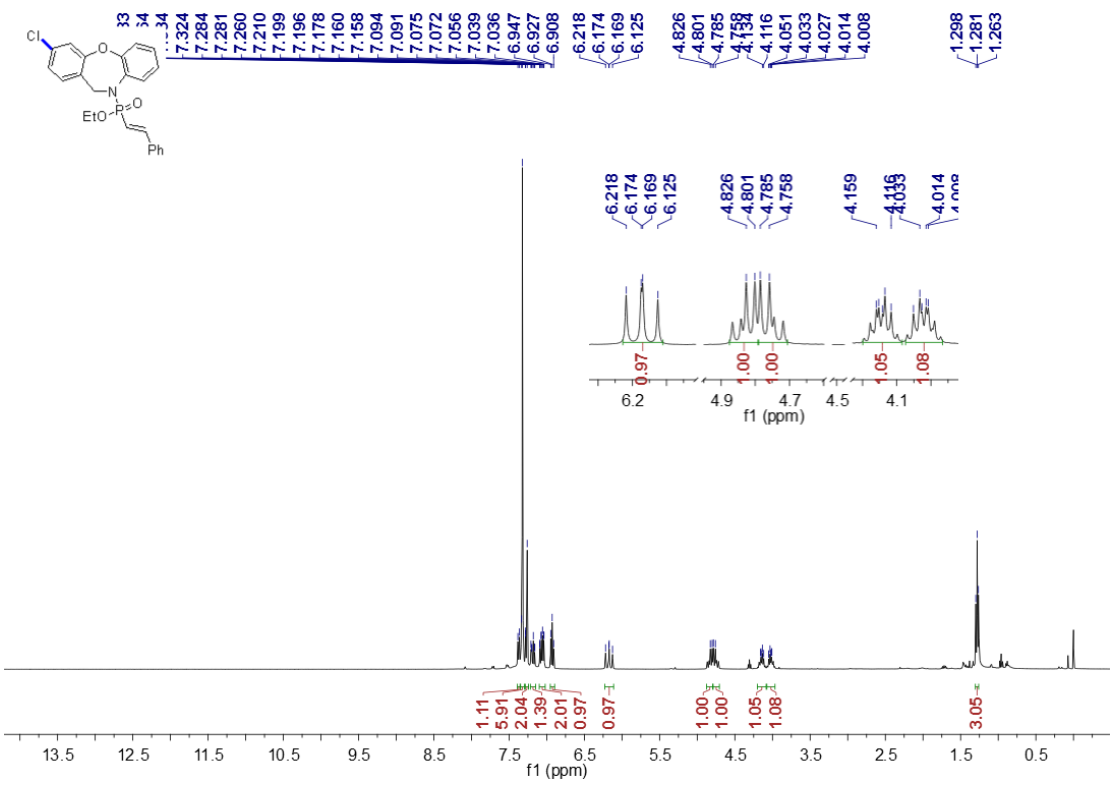
^{1}H NMR Spectrum of Compound **3ai**



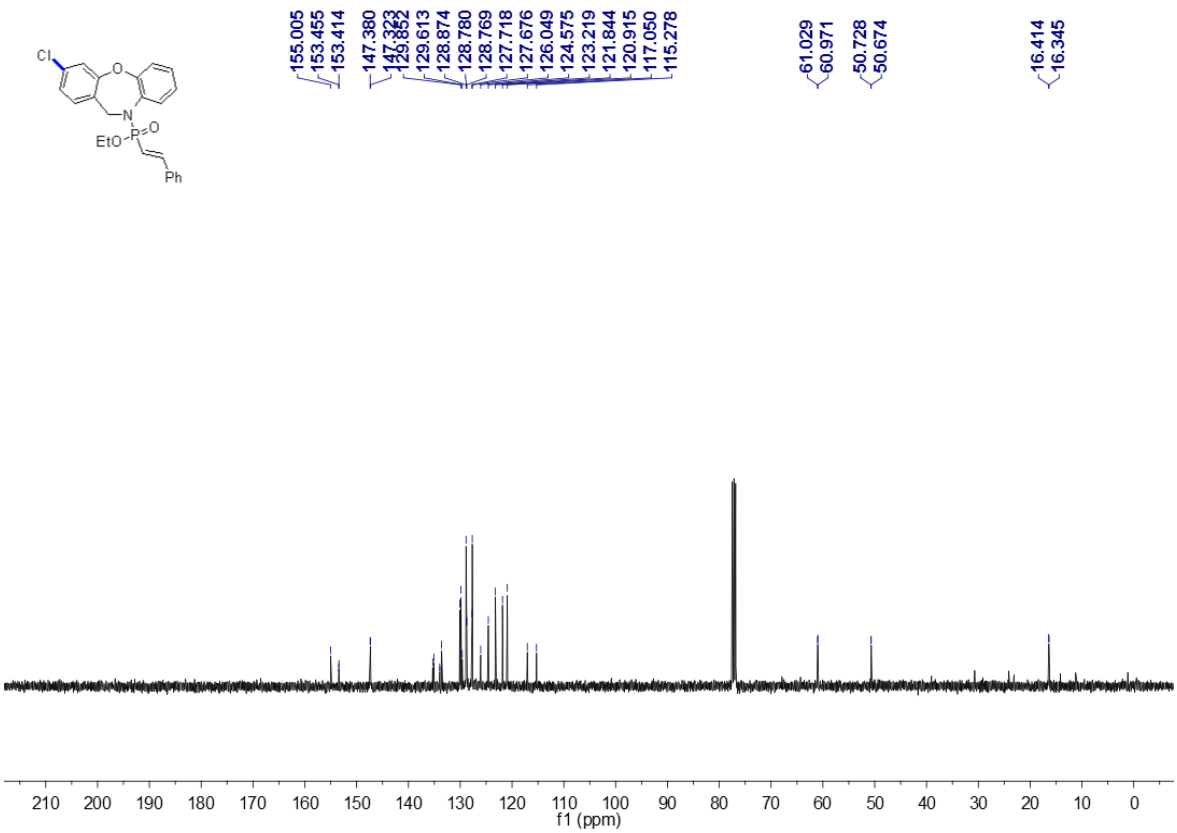
^{13}C NMR Spectrum of Compound **3ai**



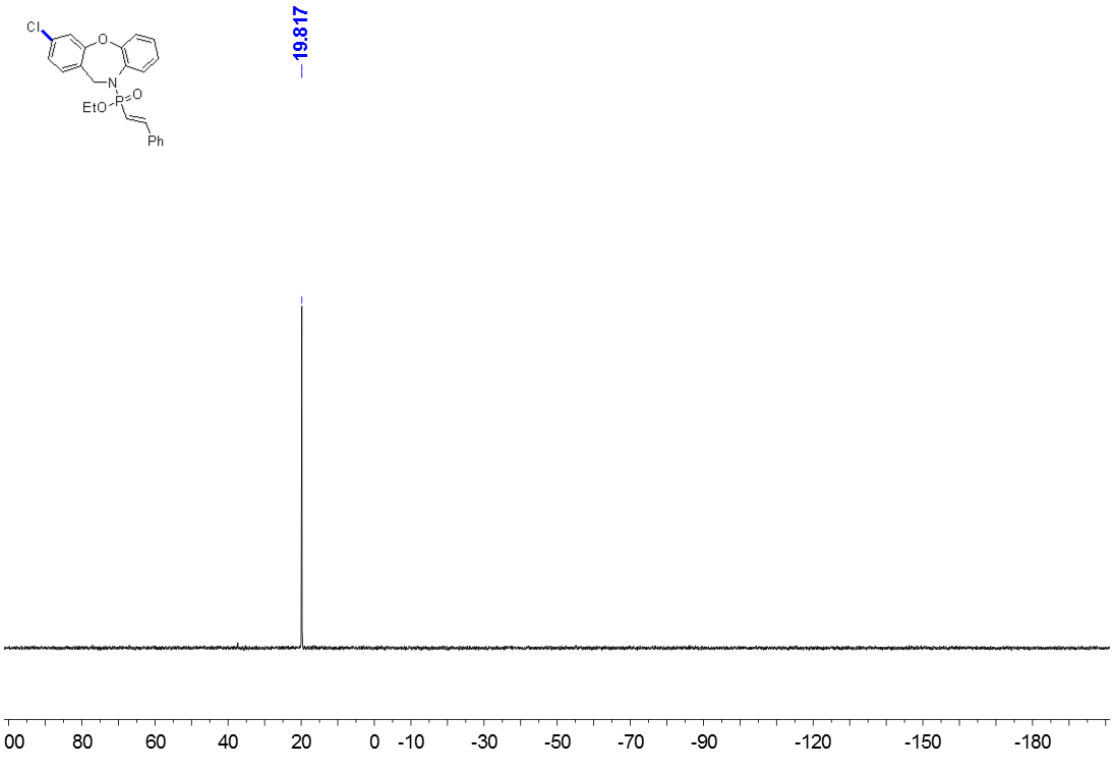
^{31}P NMR Spectrum of Compound **3ai**



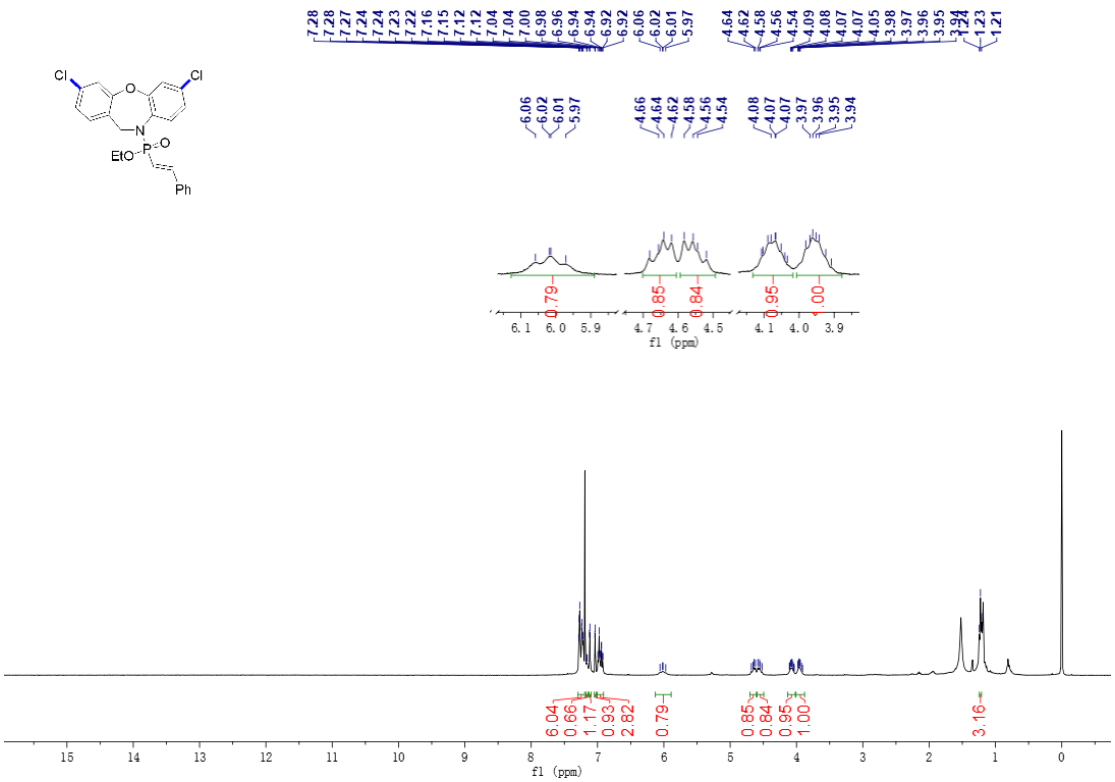
^{1}H NMR Spectrum of Compound **3aj**



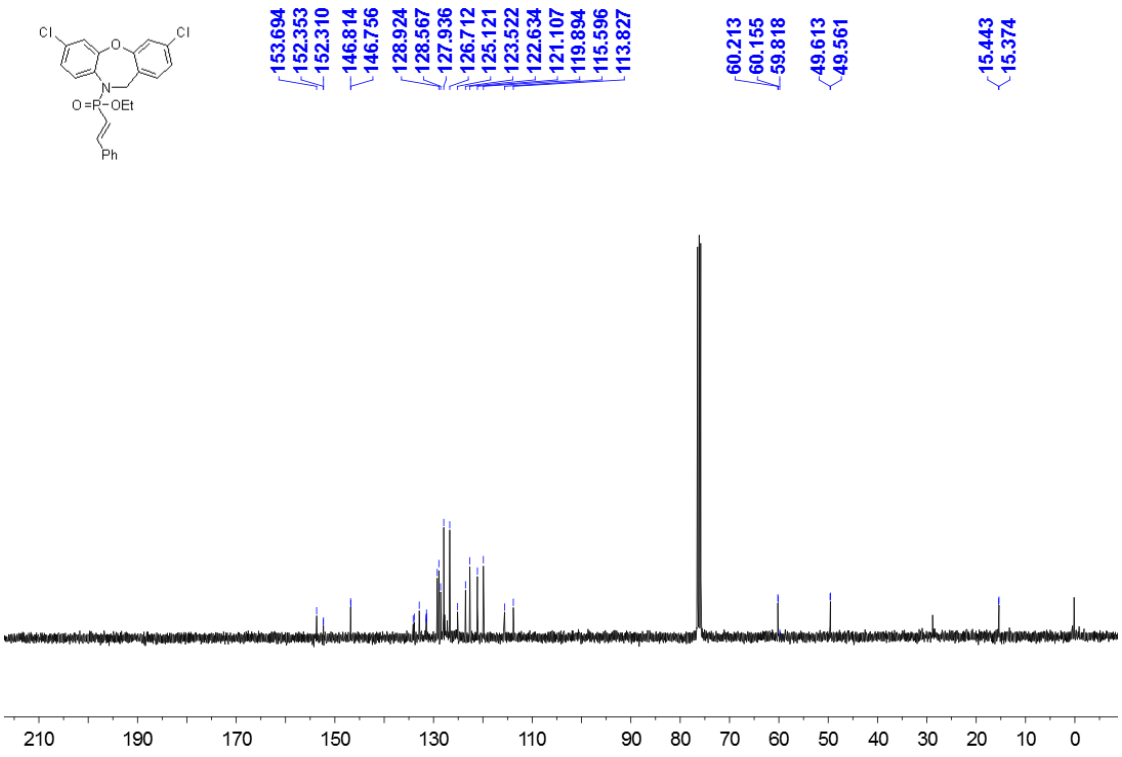
^{13}C NMR Spectrum of Compound **3aj**



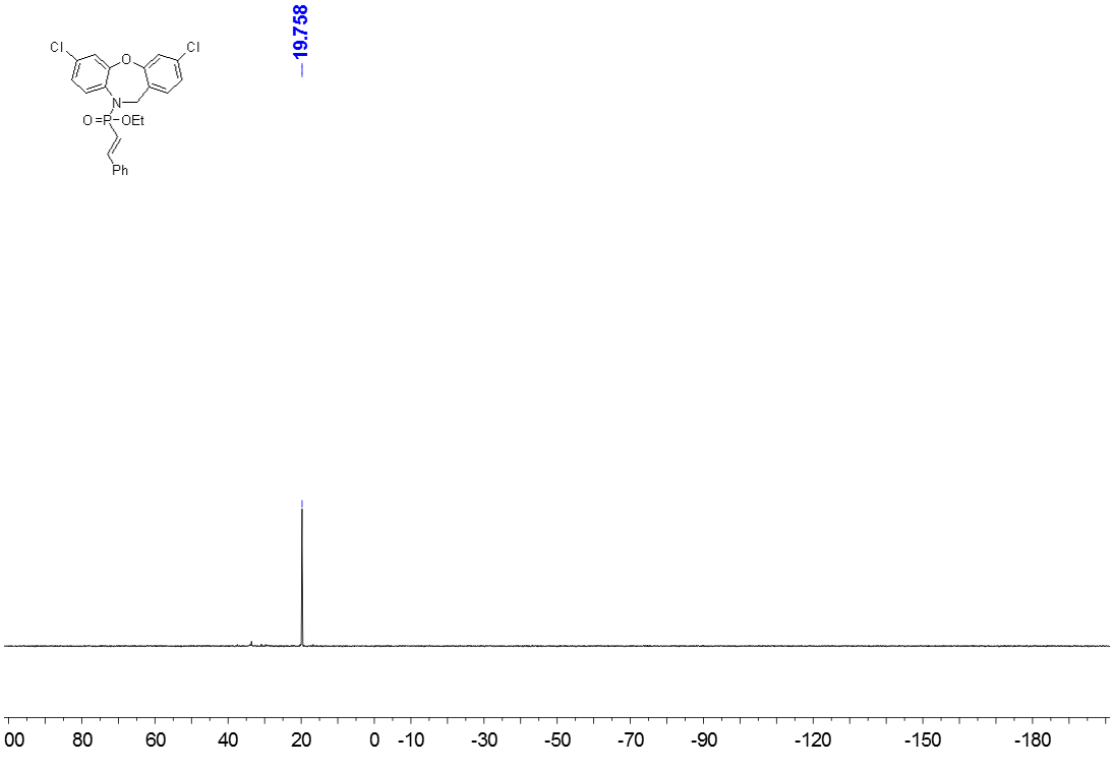
^{31}P NMR Spectrum of Compound **3aj**



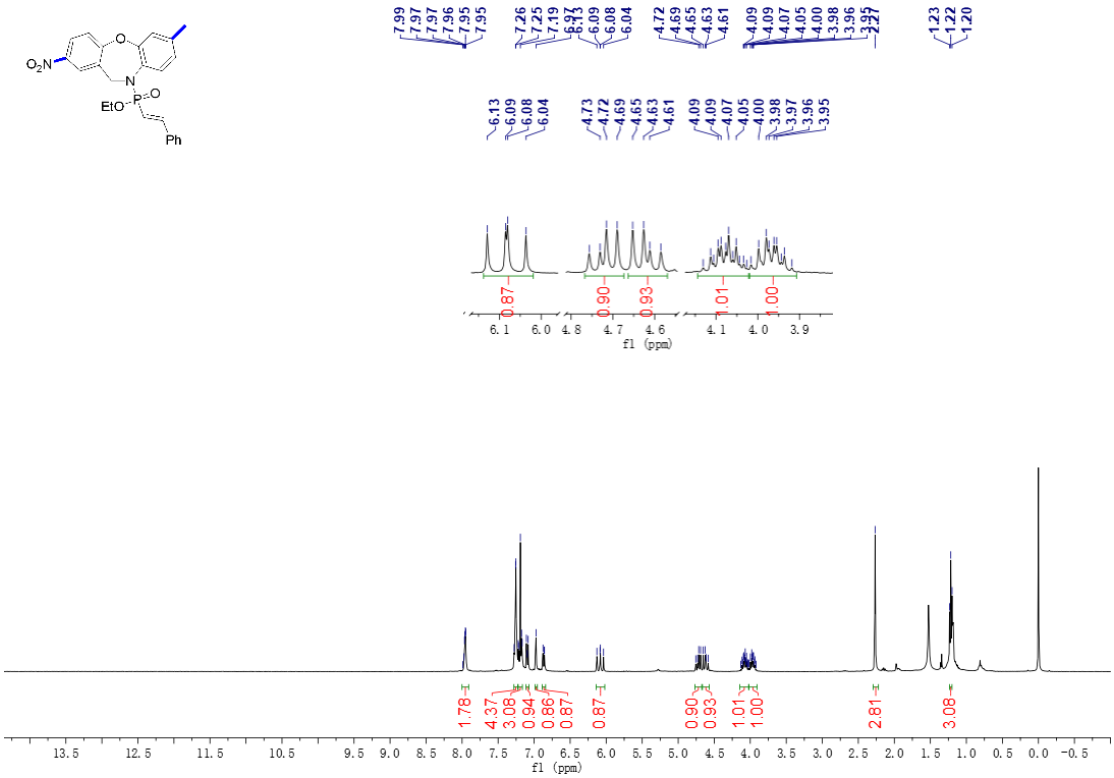
^{1}H NMR Spectrum of Compound **3ak**



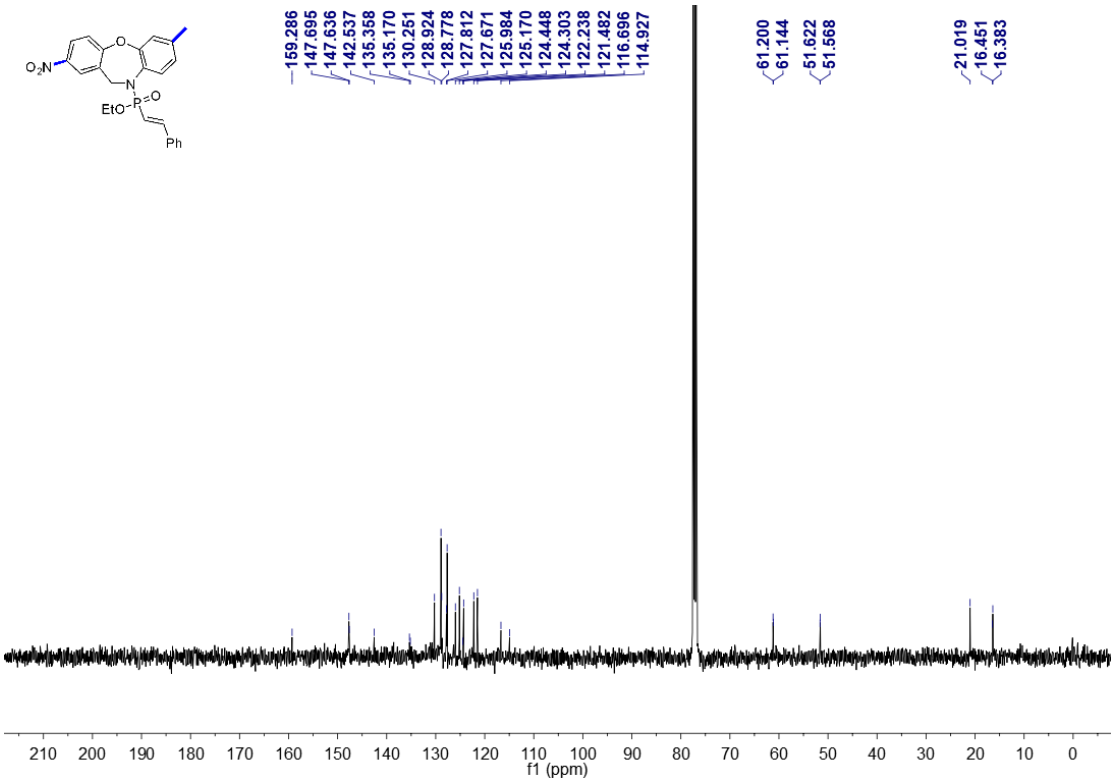
^{13}C NMR Spectrum of Compound **3ak**



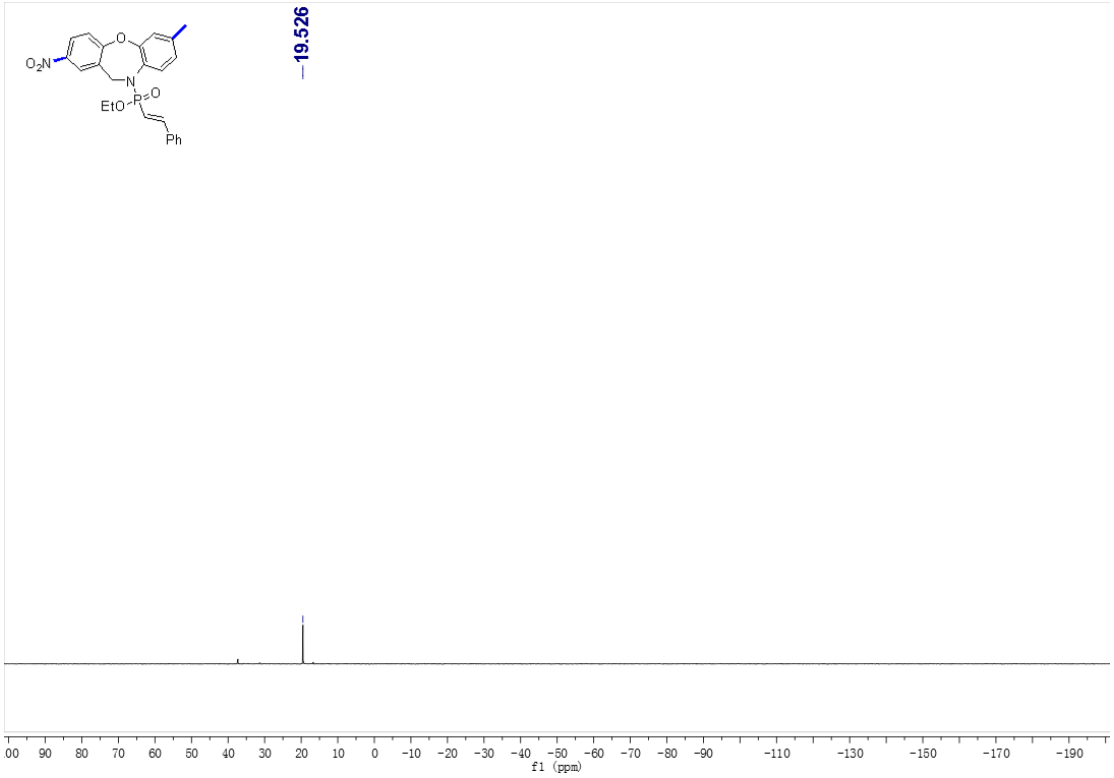
^{31}P NMR Spectrum of Compound **3ak**



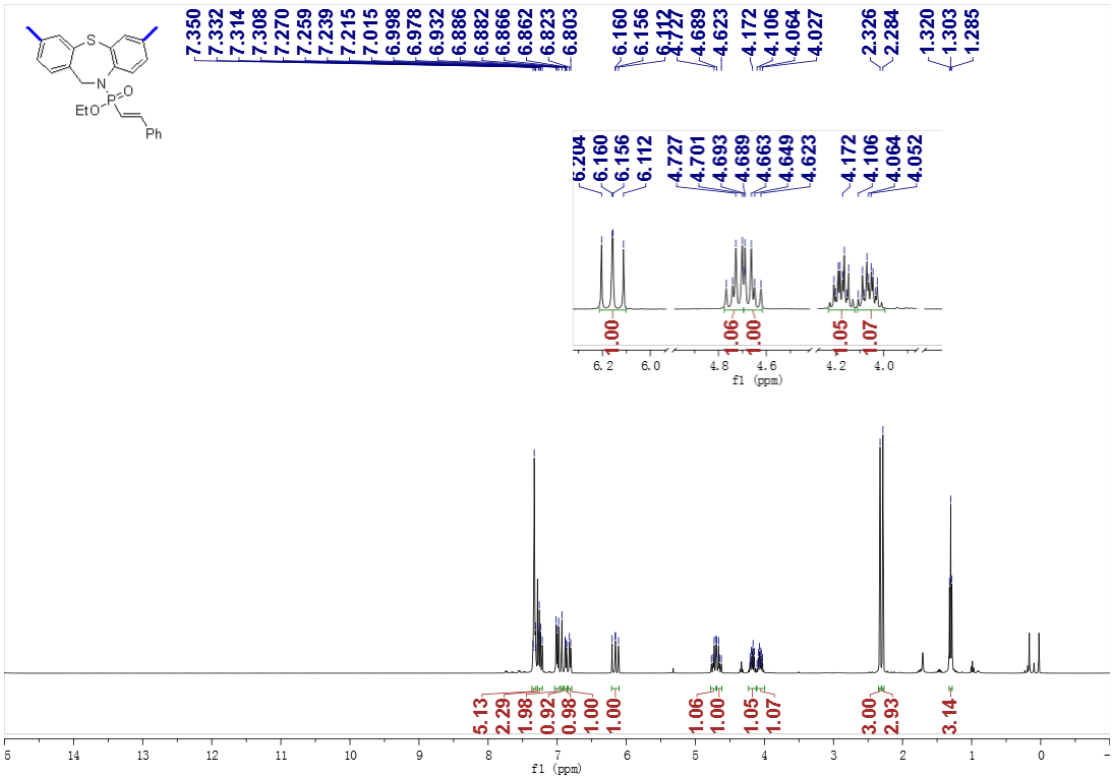
^{1}H NMR Spectrum of Compound **3al**



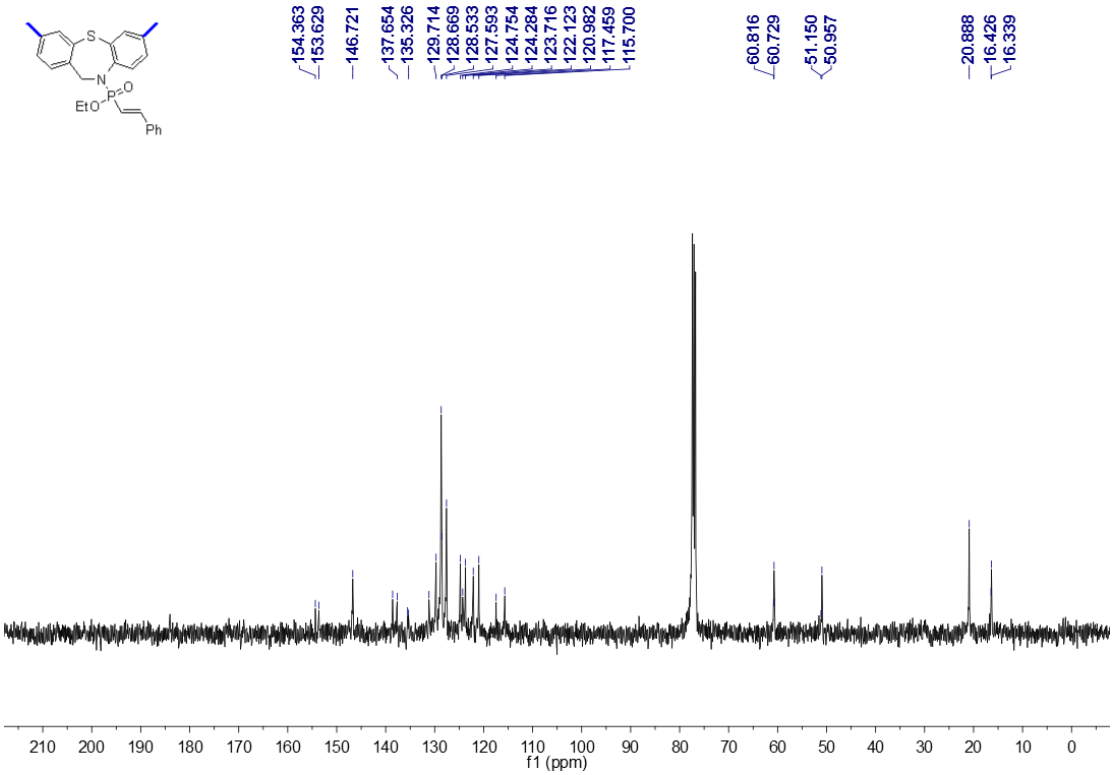
^{13}C NMR Spectrum of Compound **3al**



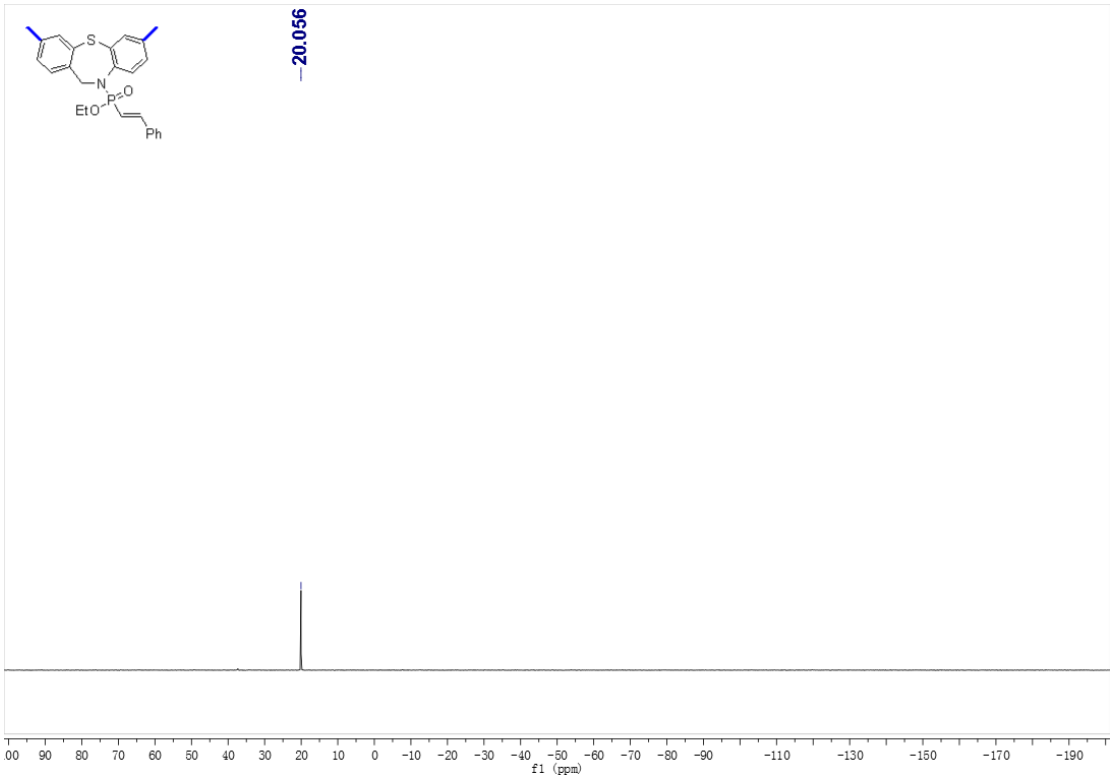
^{31}P NMR Spectrum of Compound **3al**



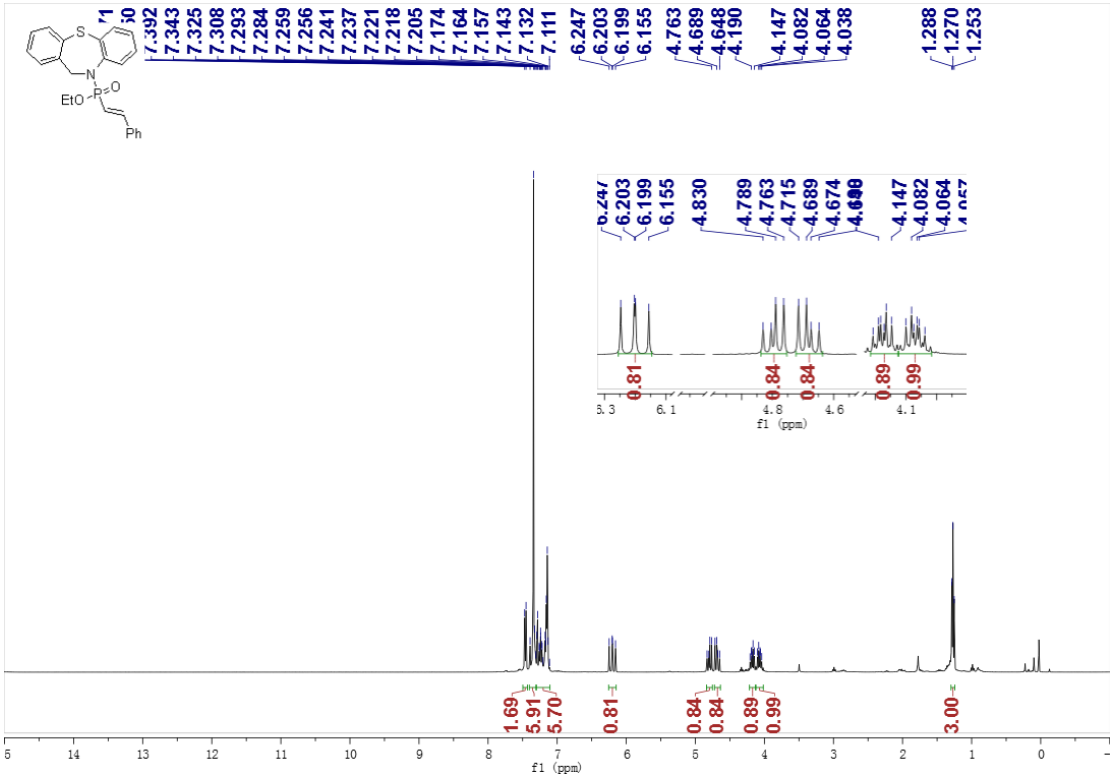
^{1}H NMR Spectrum of Compound **3am**



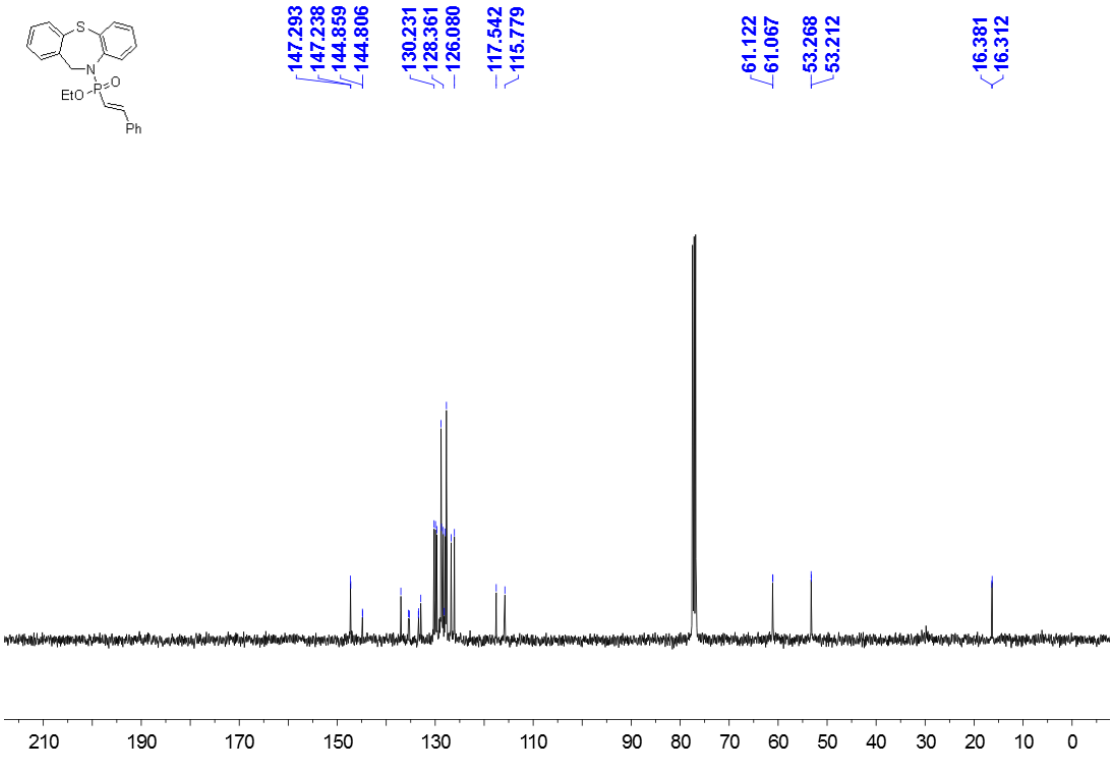
^{13}C NMR Spectrum of Compound **3am**



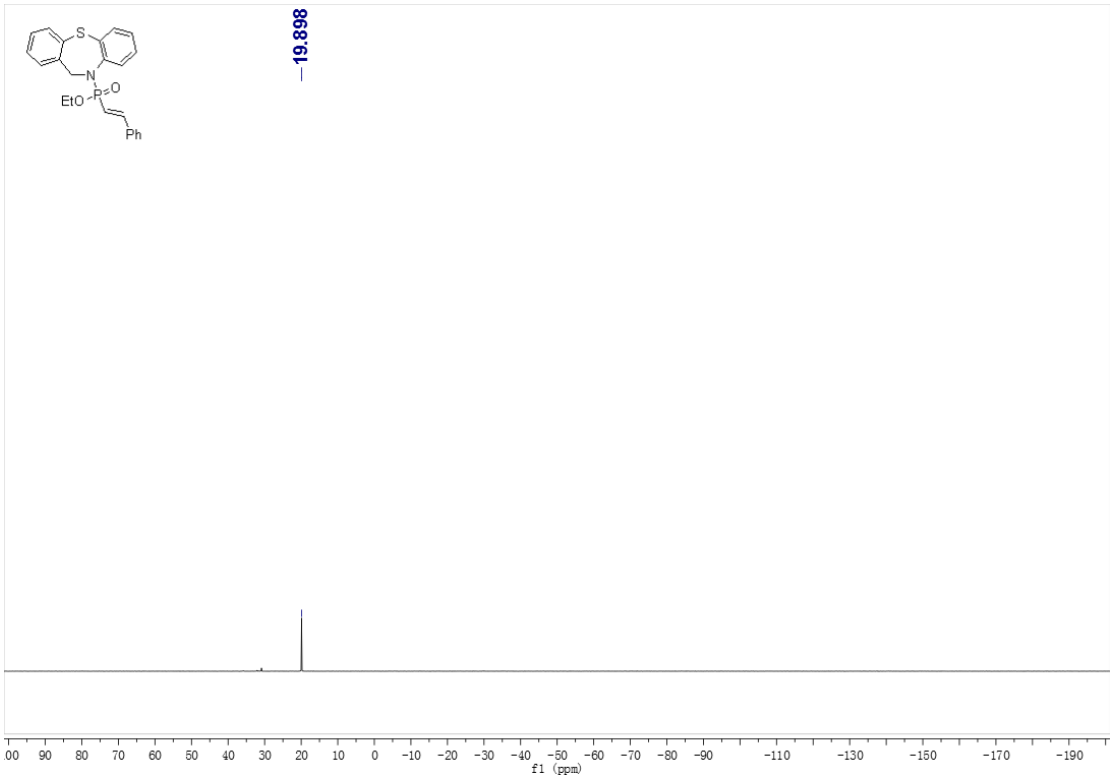
^{31}P NMR Spectrum of Compound **3am**



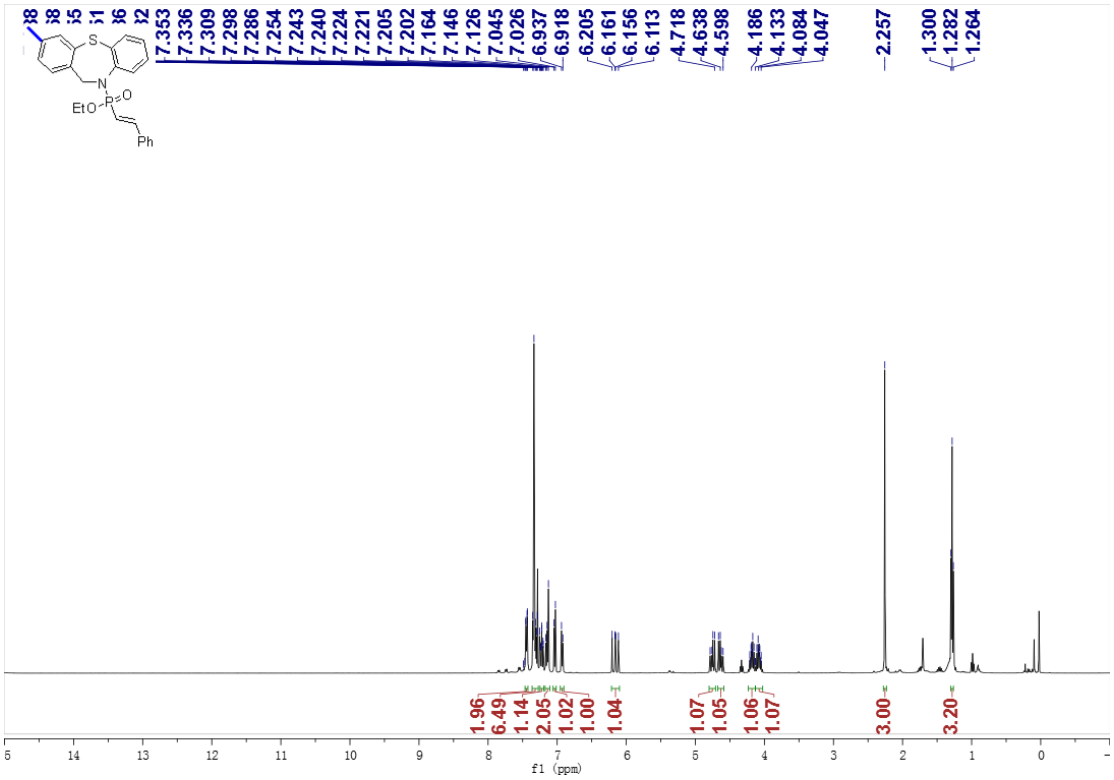
^{1}H NMR Spectrum of Compound **3an**



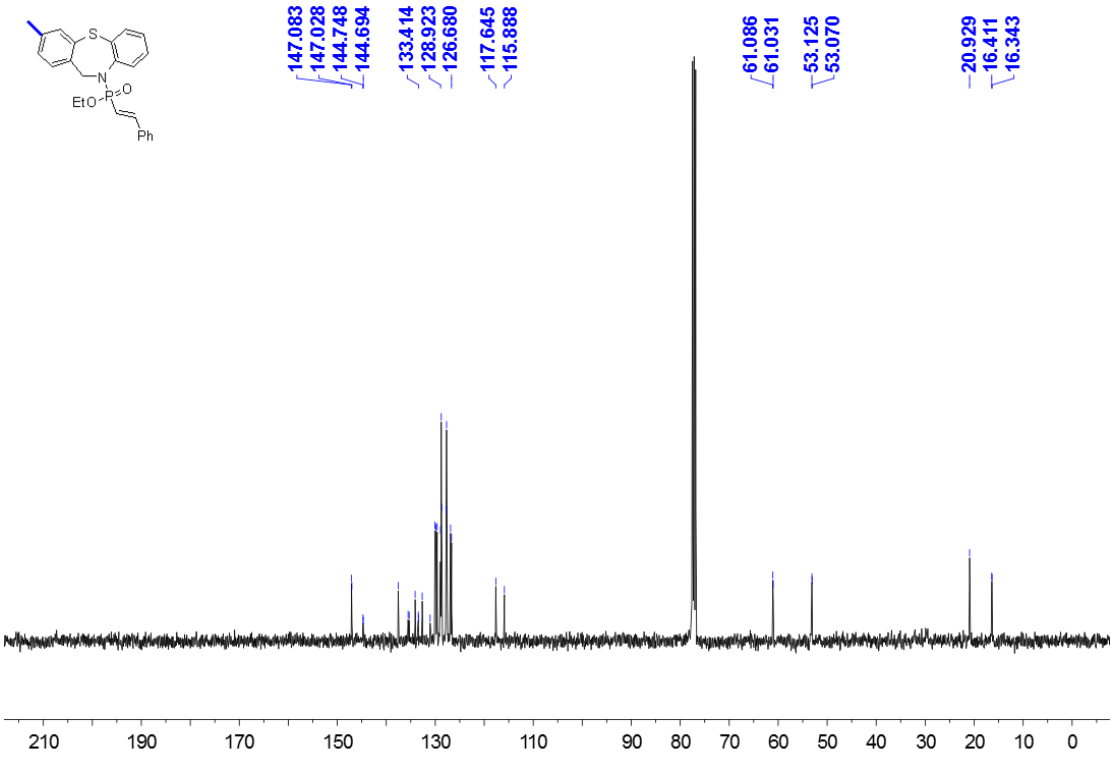
^{13}C NMR Spectrum of Compound **3an**



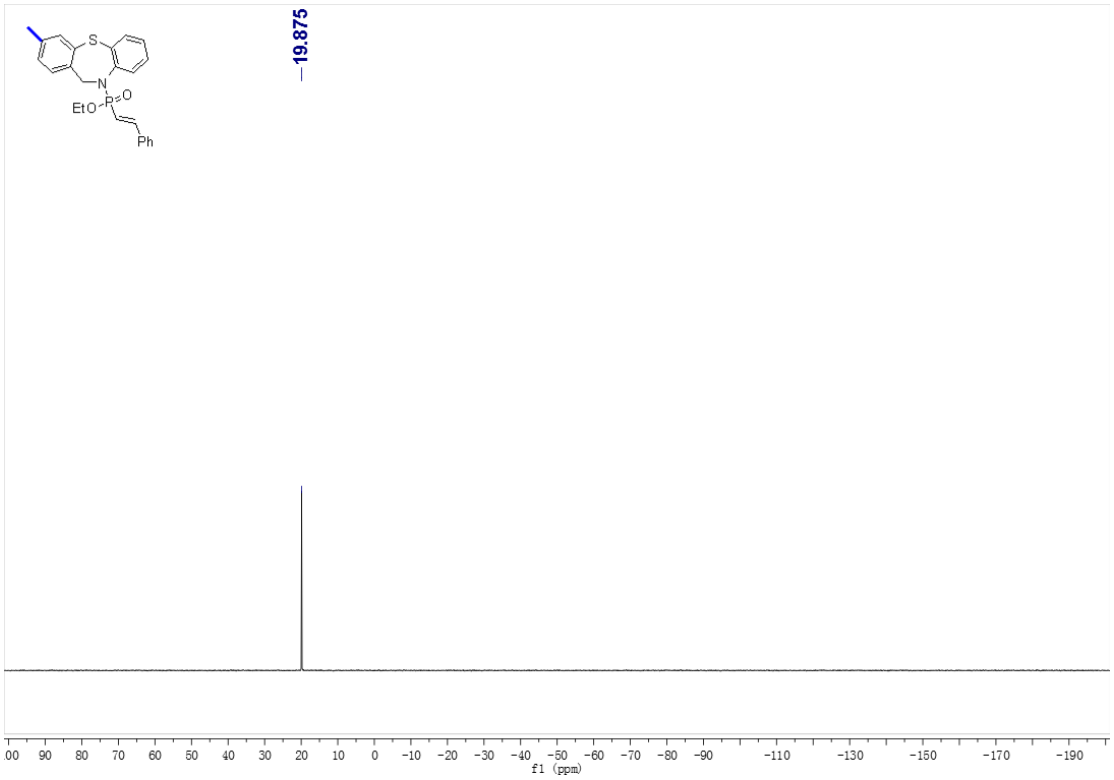
^{31}P NMR Spectrum of Compound **3an**



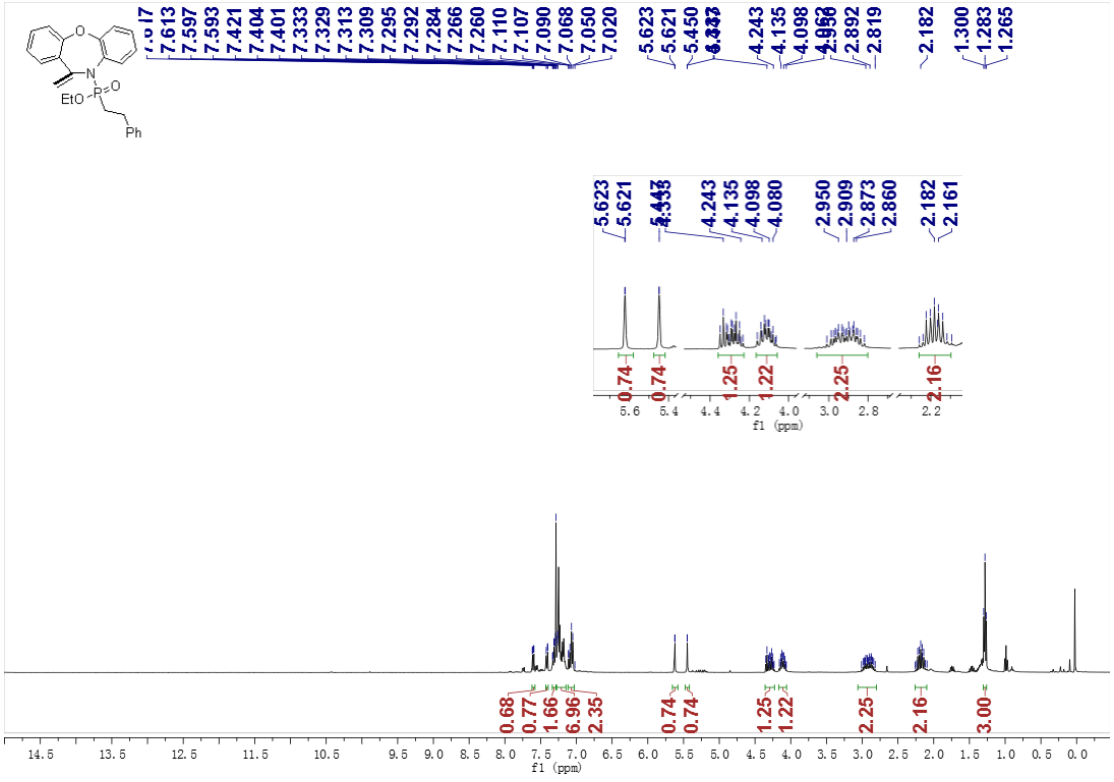
^{1}H NMR Spectrum of Compound **3ao**



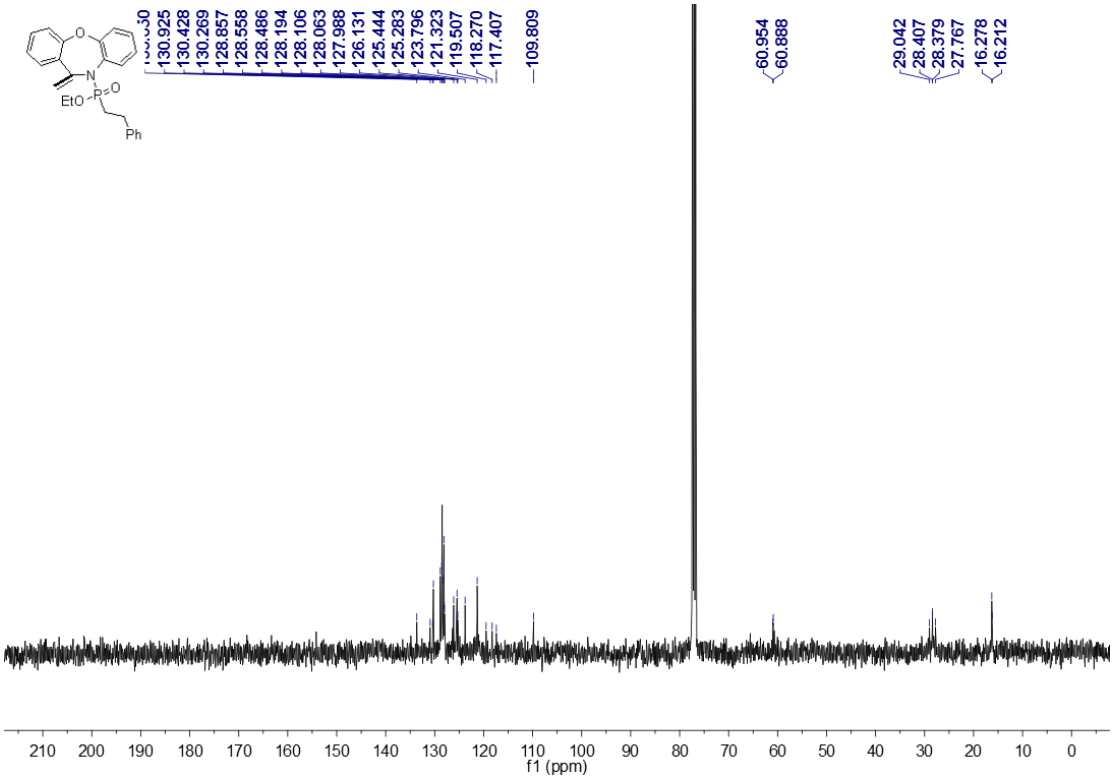
^{13}C NMR Spectrum of Compound **3ao**



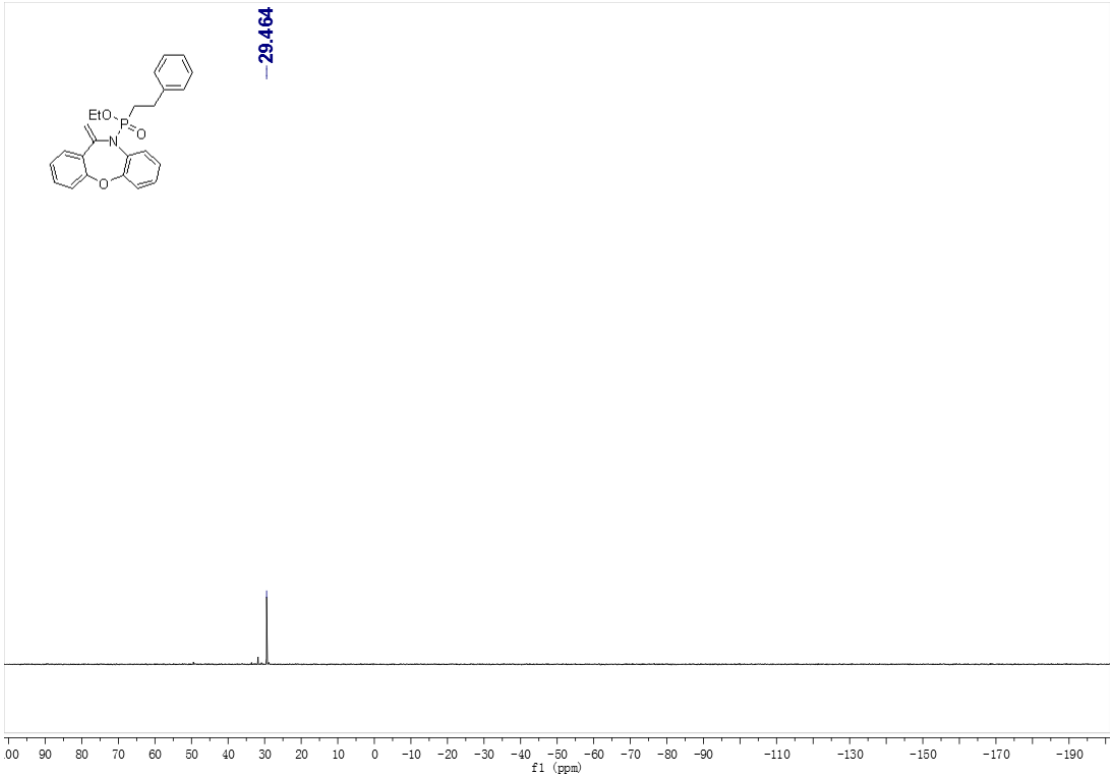
^{31}P NMR Spectrum of Compound **3ao**



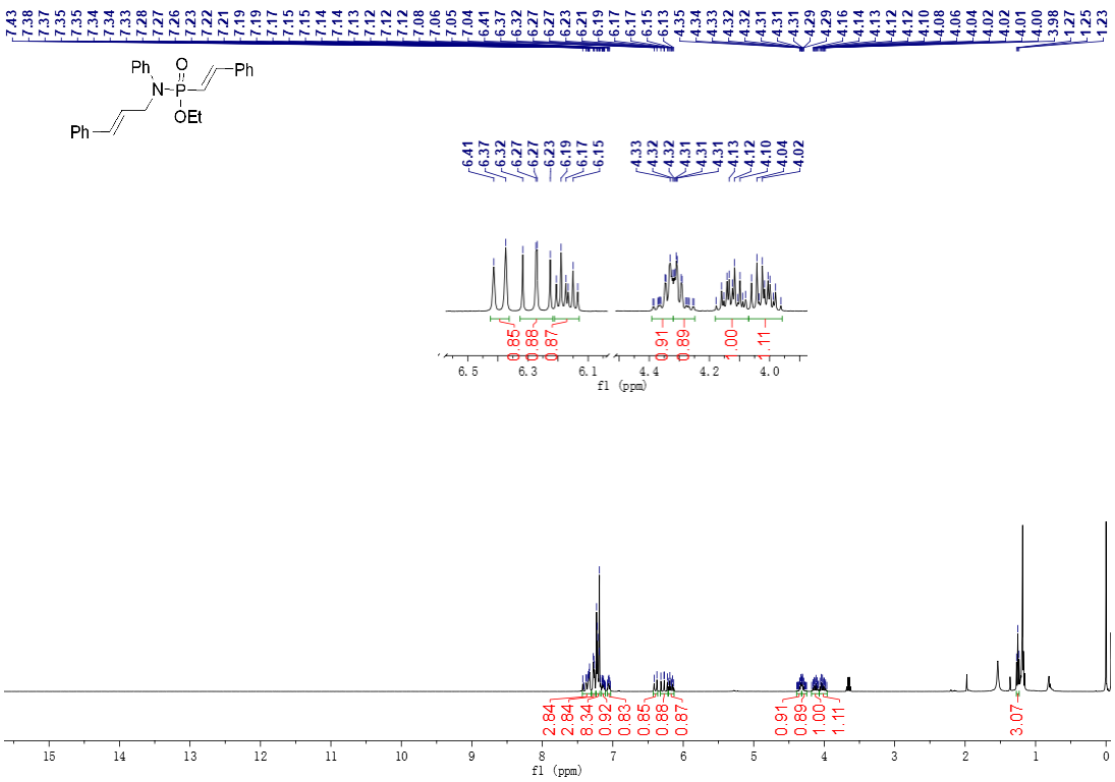
^{1}H NMR Spectrum of Compound **4**



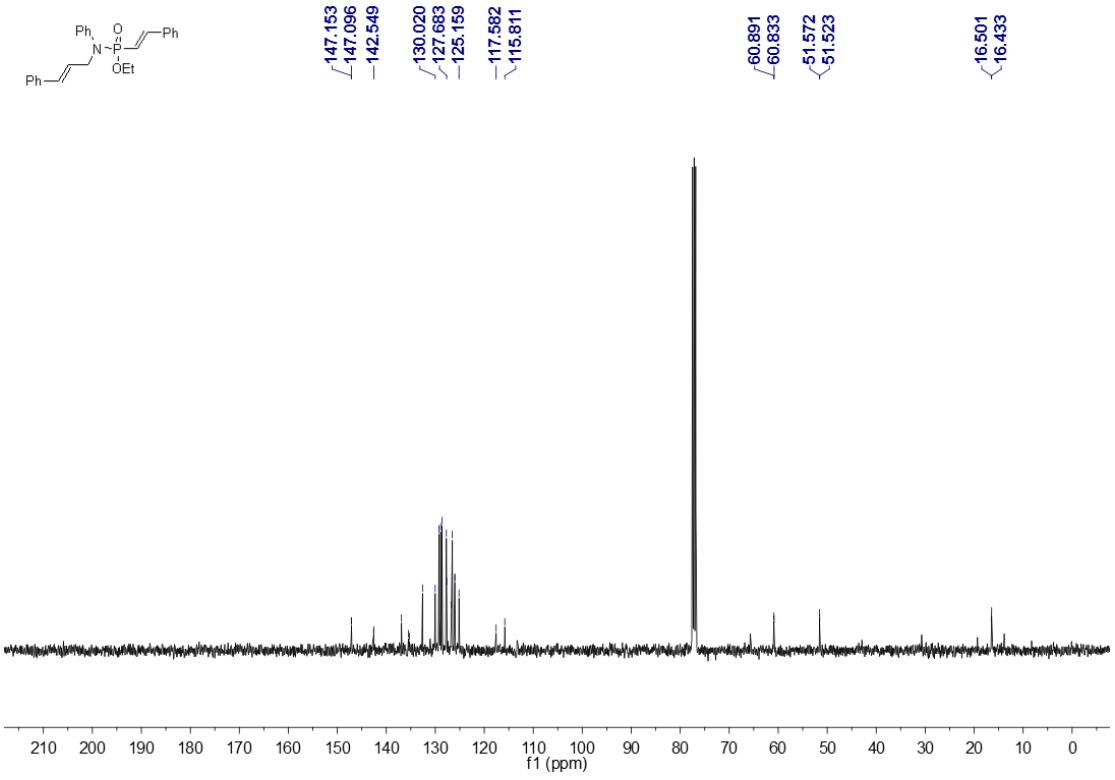
^{31}C NMR Spectrum of Compound **4**



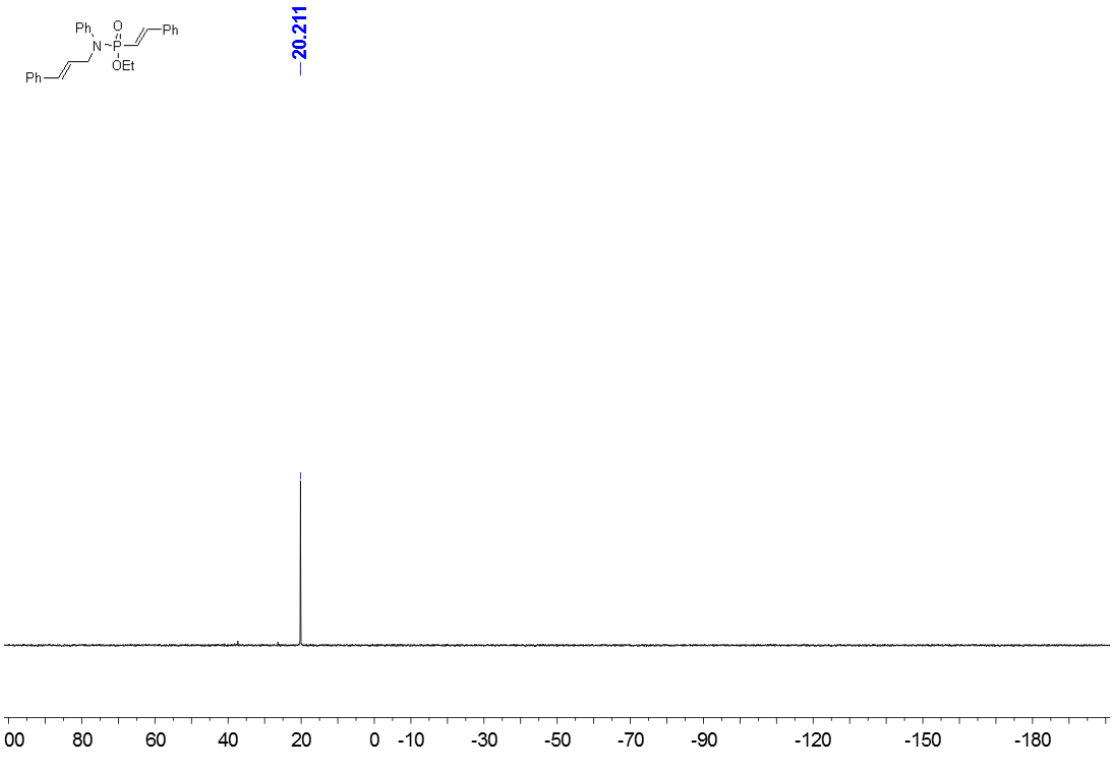
^{31}P NMR Spectrum of Compound **4**



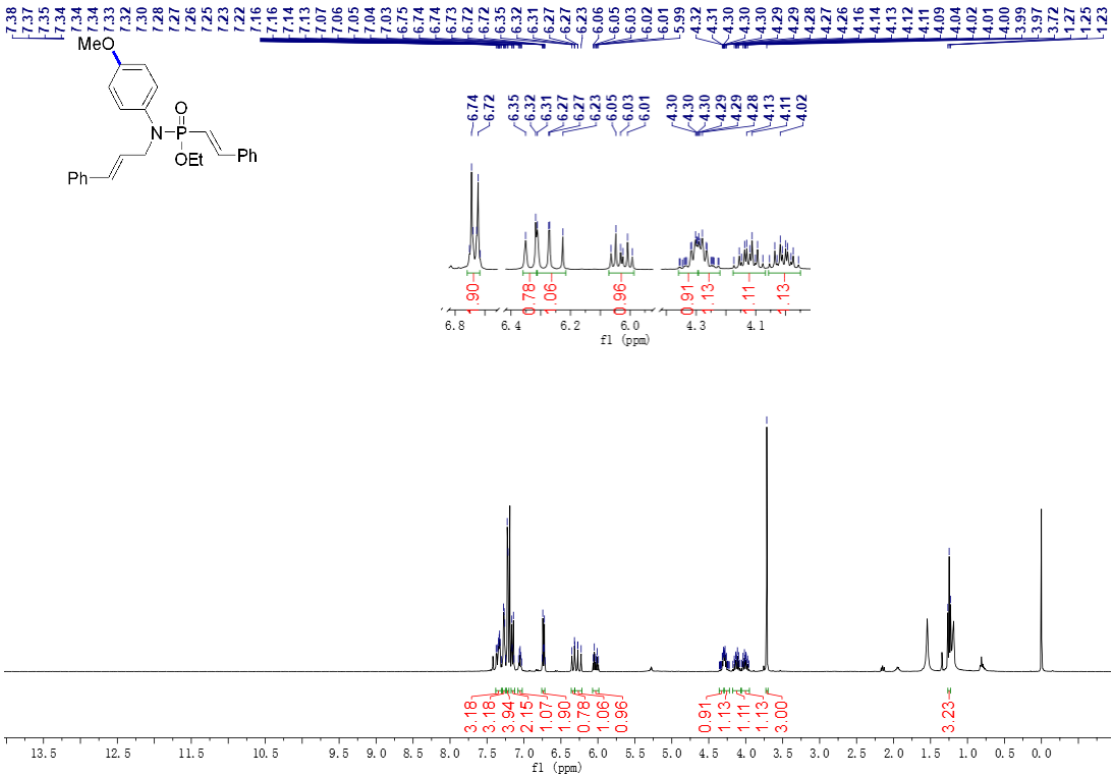
^{1}H NMR Spectrum of Compound **3aA**



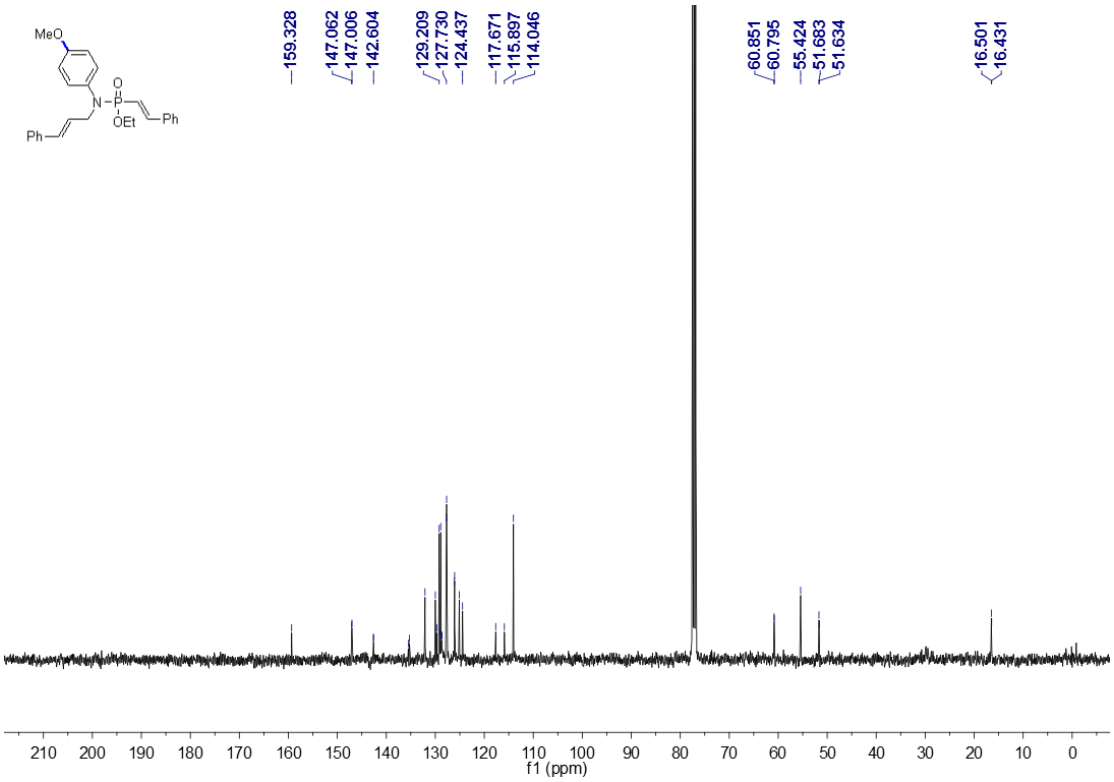
^{13}C NMR Spectrum of Compound **3aA**



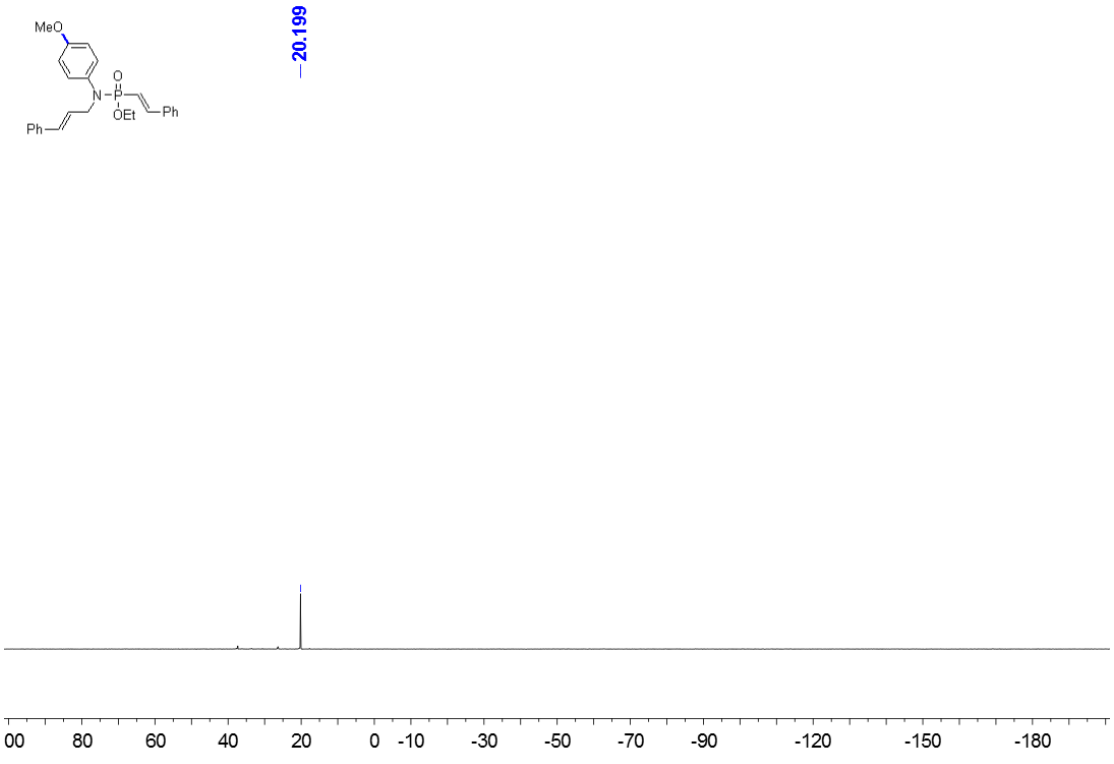
^{31}P NMR Spectrum of Compound **3aA**



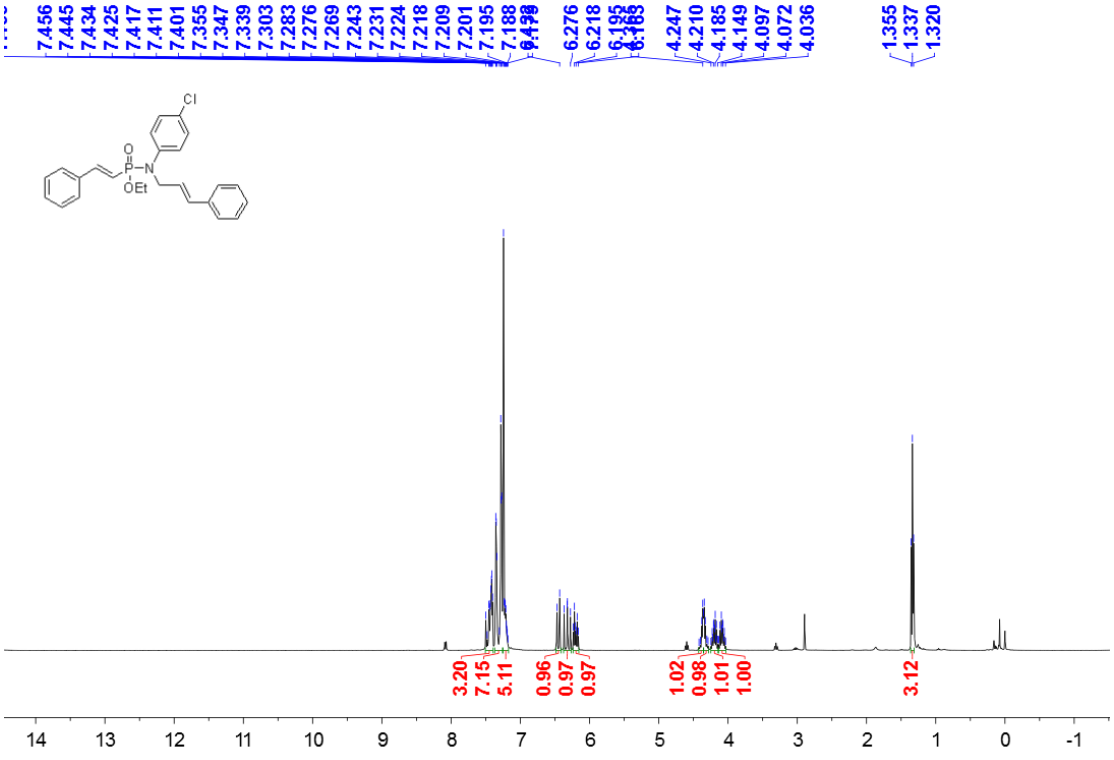
^{1}H NMR Spectrum of Compound **3aB**



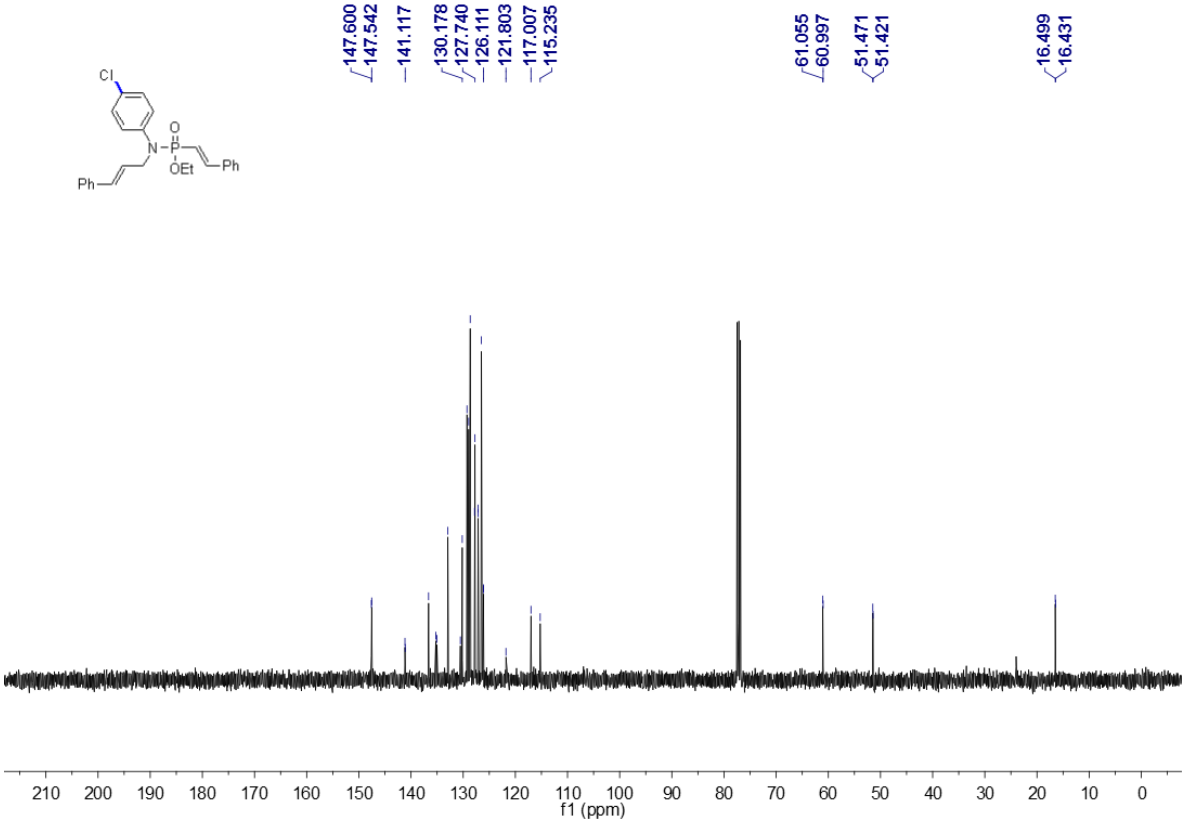
^{13}C NMR Spectrum of Compound **3aB**



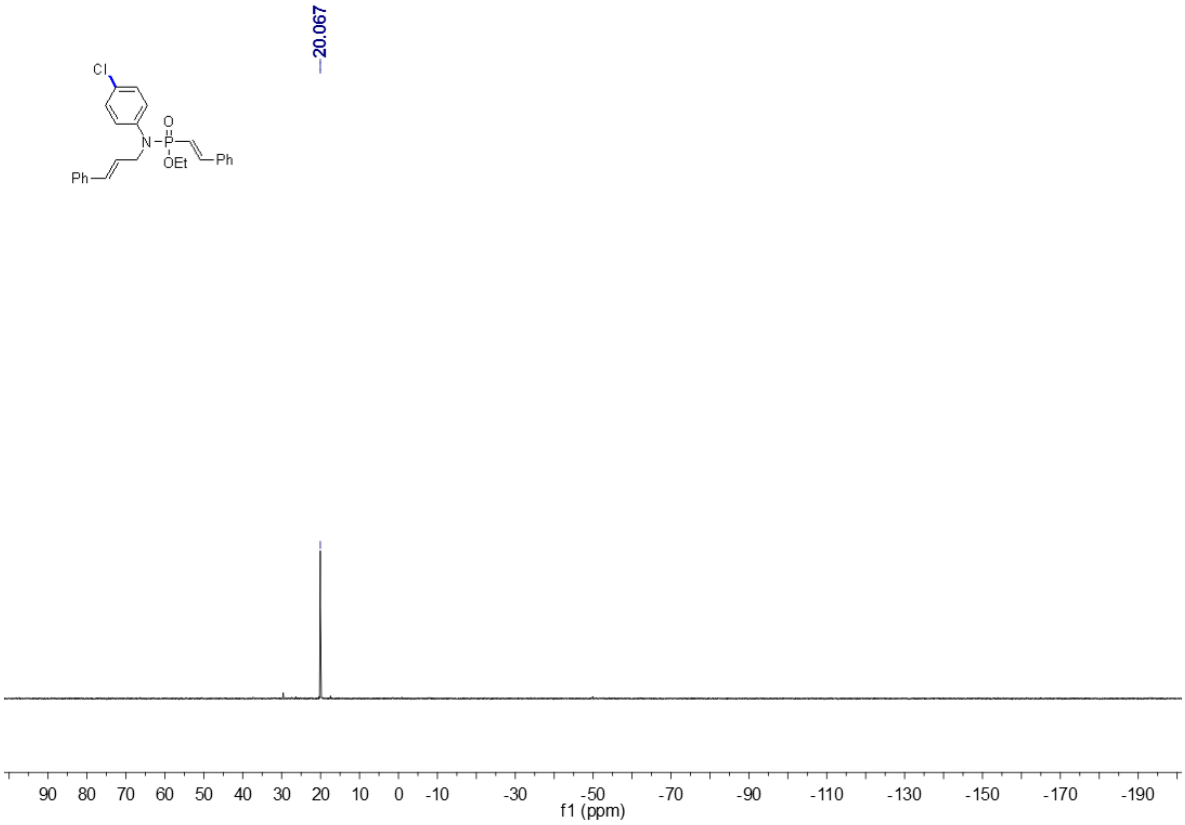
^{31}P NMR Spectrum of Compound **3aB**



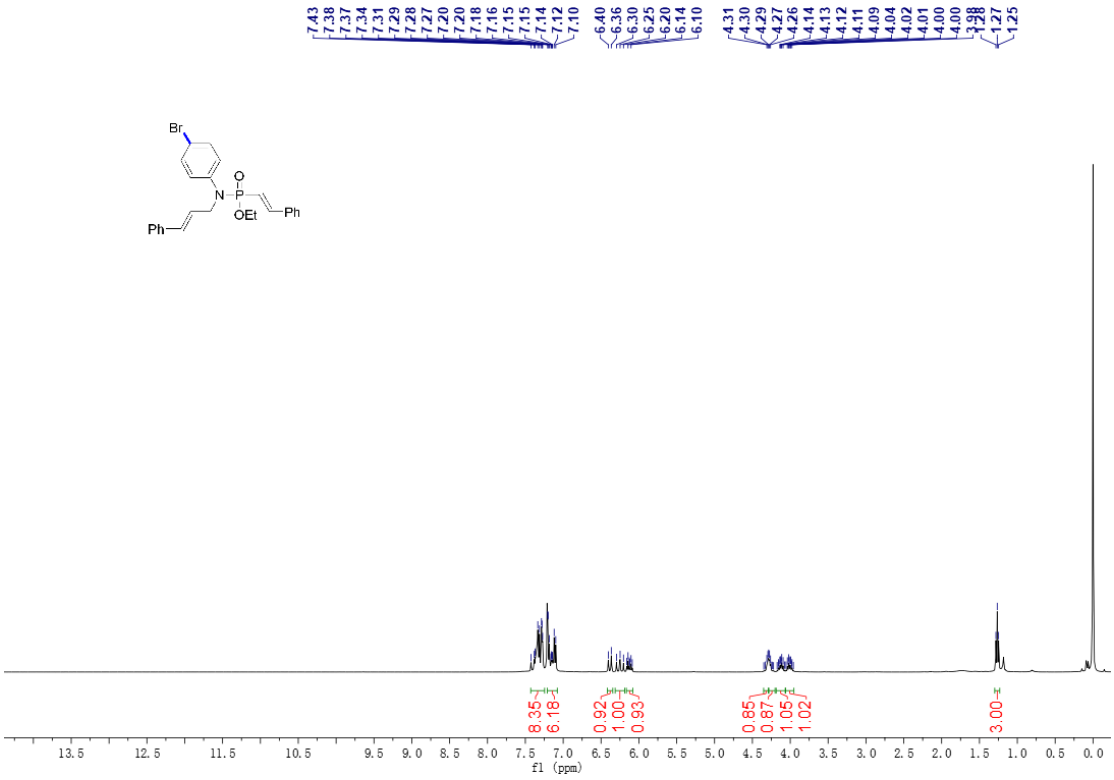
^{1}H NMR Spectrum of Compound **3aC**



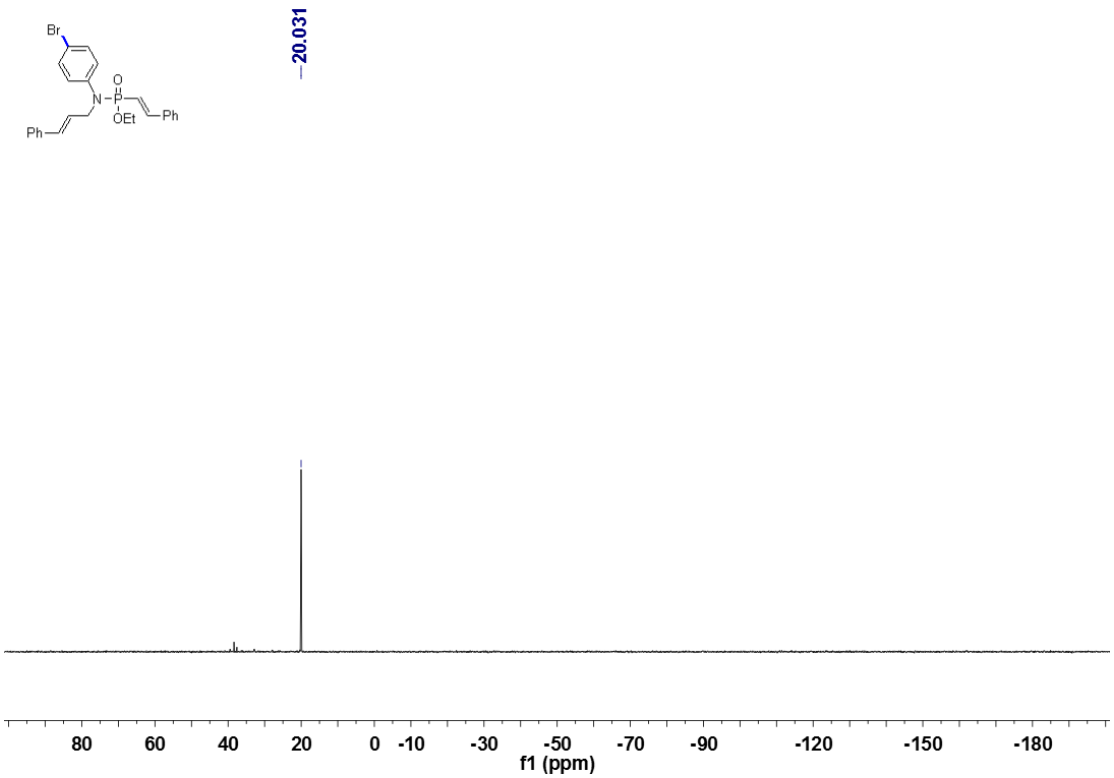
^{13}C NMR Spectrum of Compound **3aC**



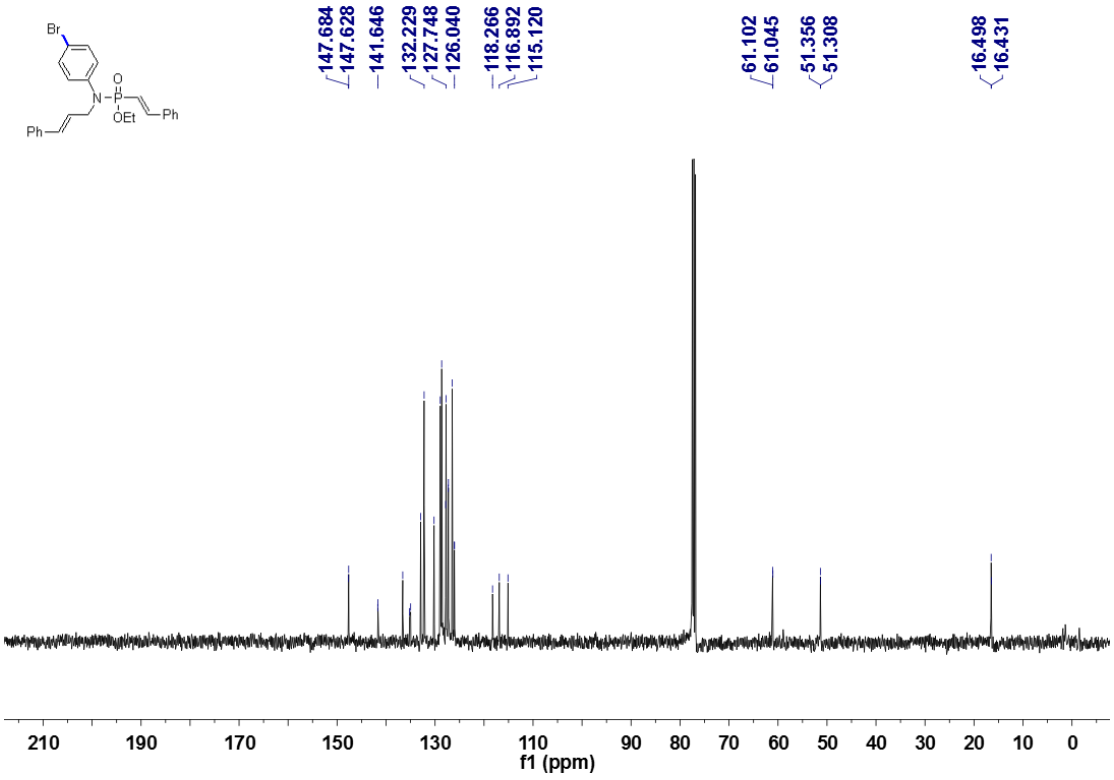
^{31}P NMR Spectrum of Compound **3aC**



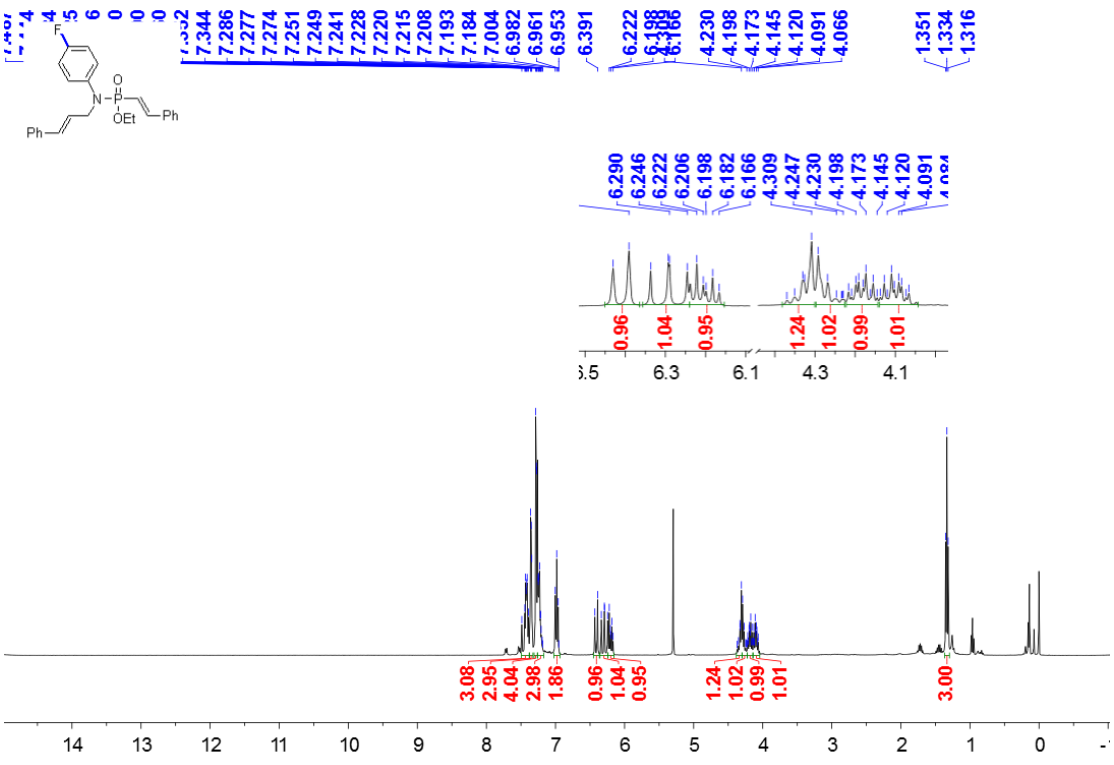
^{1}H NMR Spectrum of Compound **3aD**



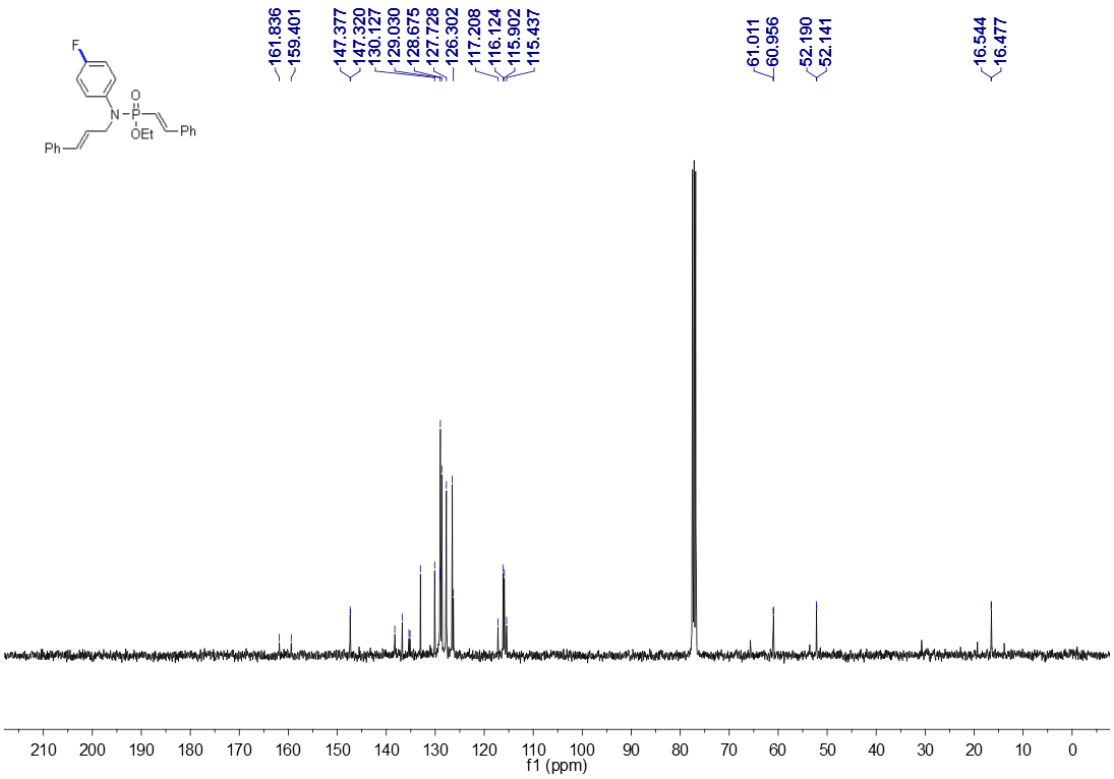
^{31}P NMR Spectrum of Compound **3aD**



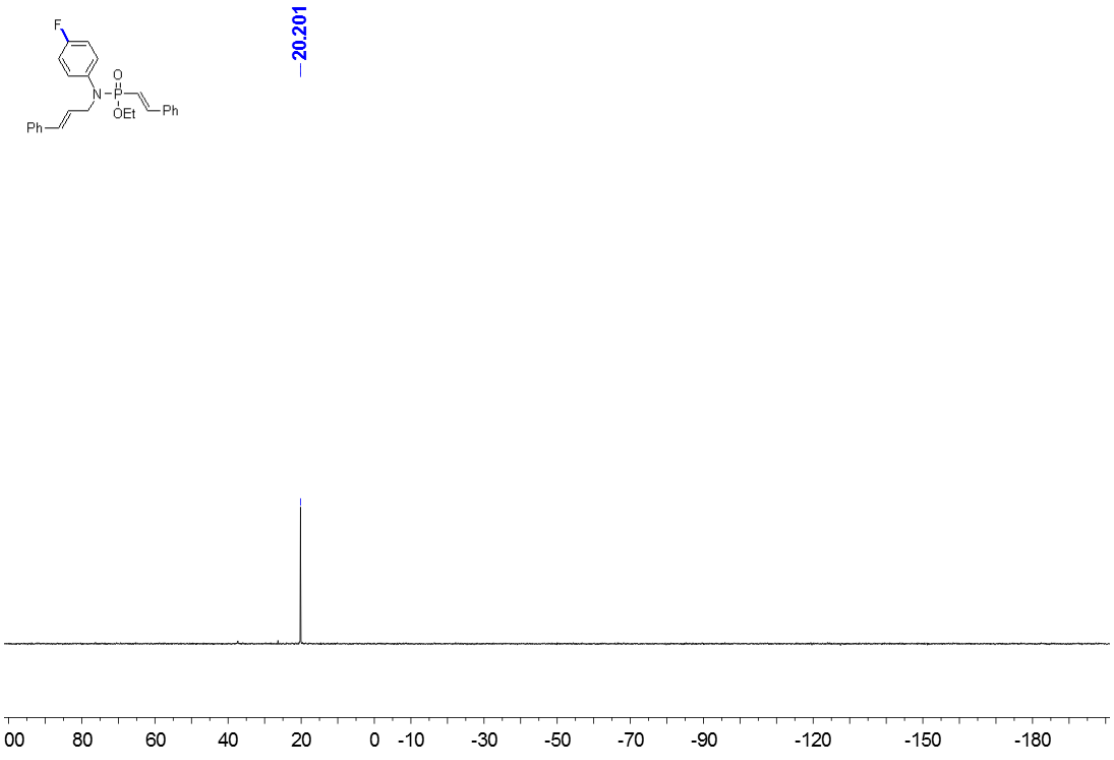
^{13}C NMR Spectrum of Compound **3aD**



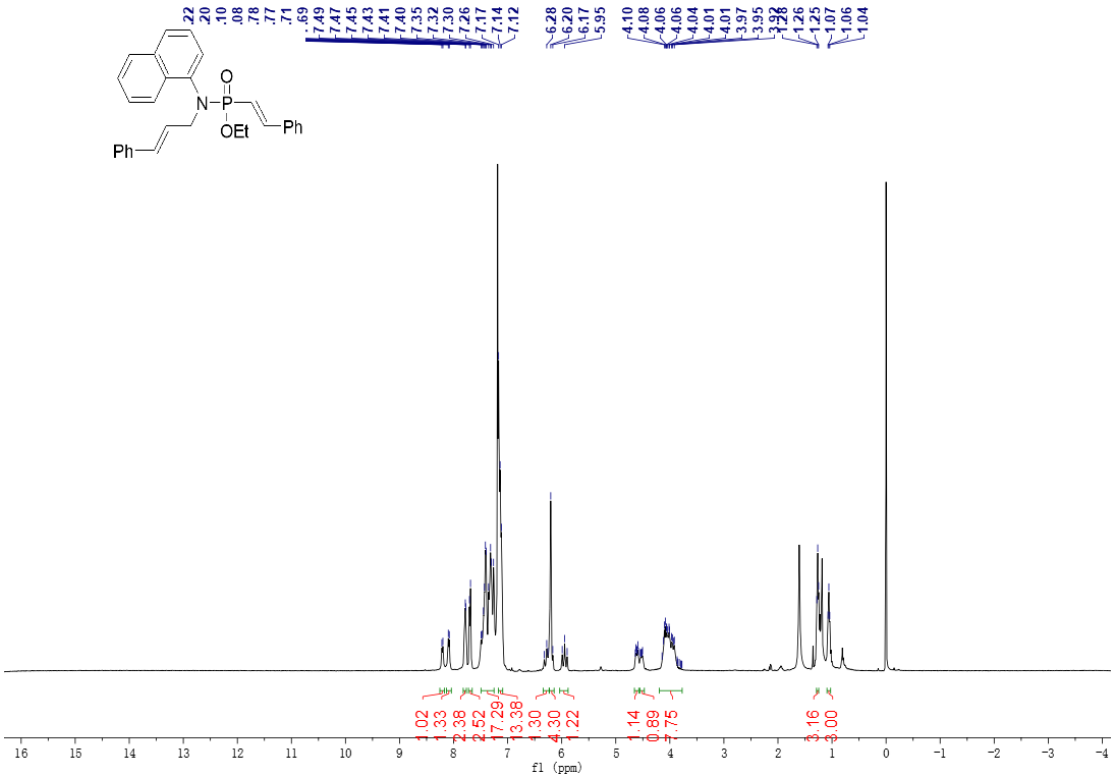
^{1}H NMR Spectrum of Compound **3aE**



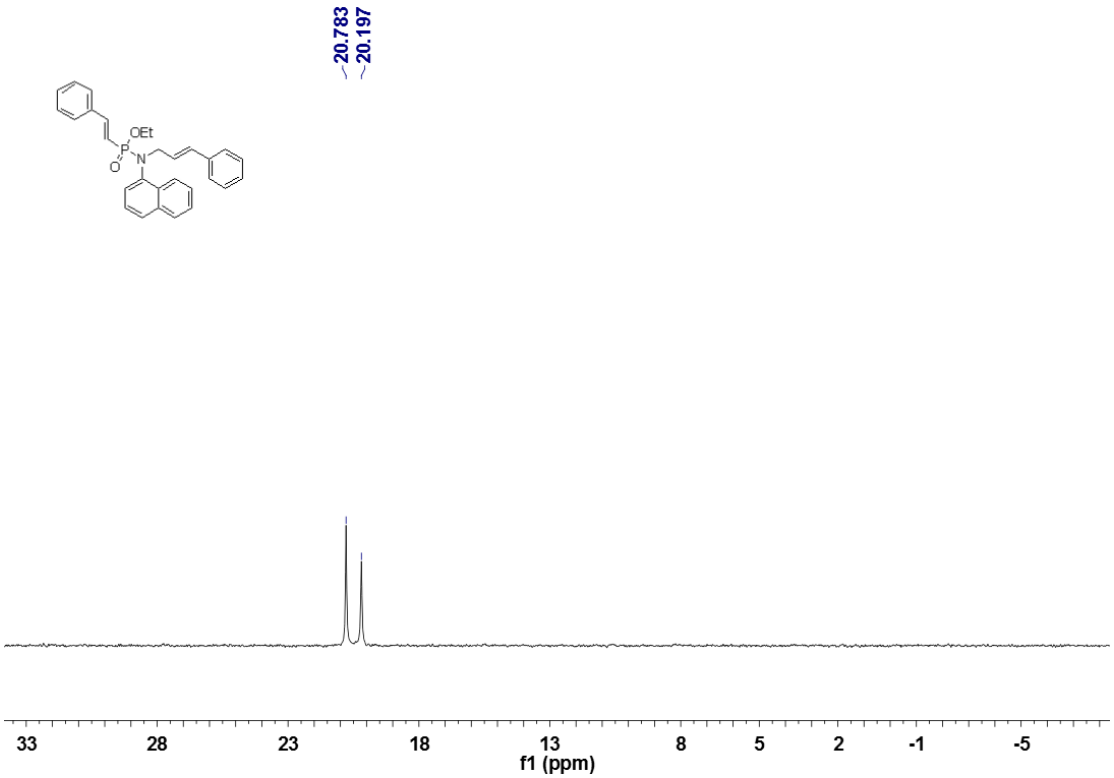
^{13}C NMR Spectrum of Compound **3aE**



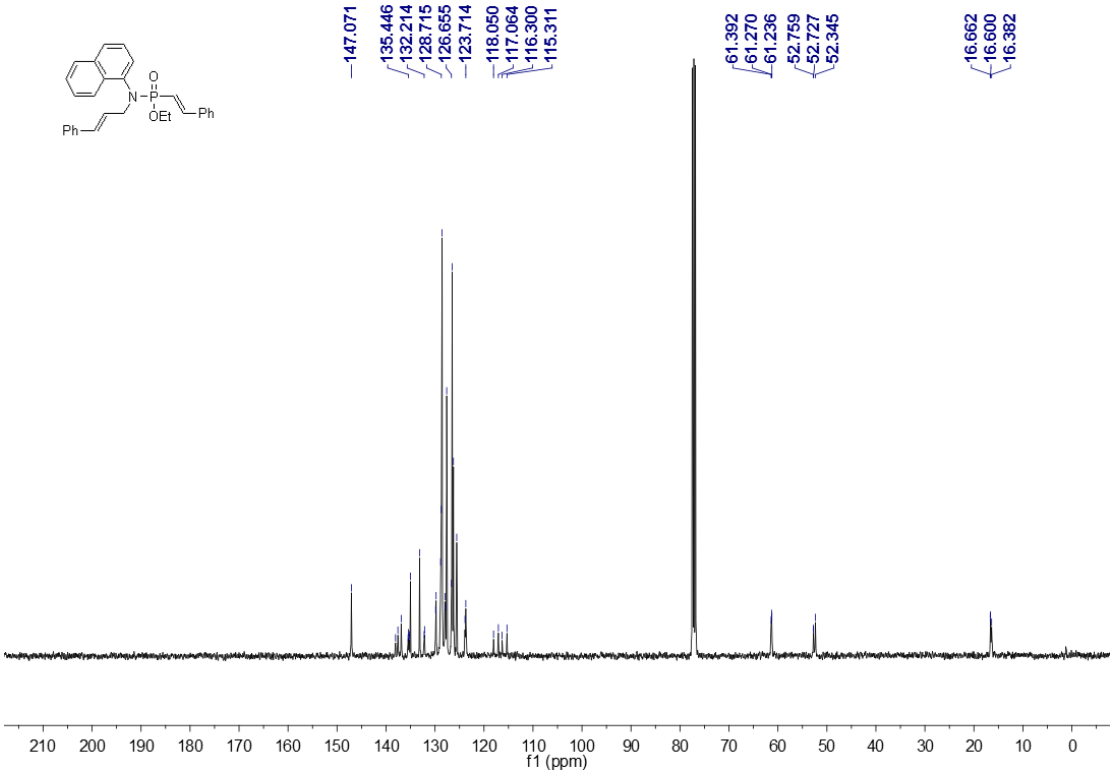
^{31}P NMR Spectrum of Compound **3aE**



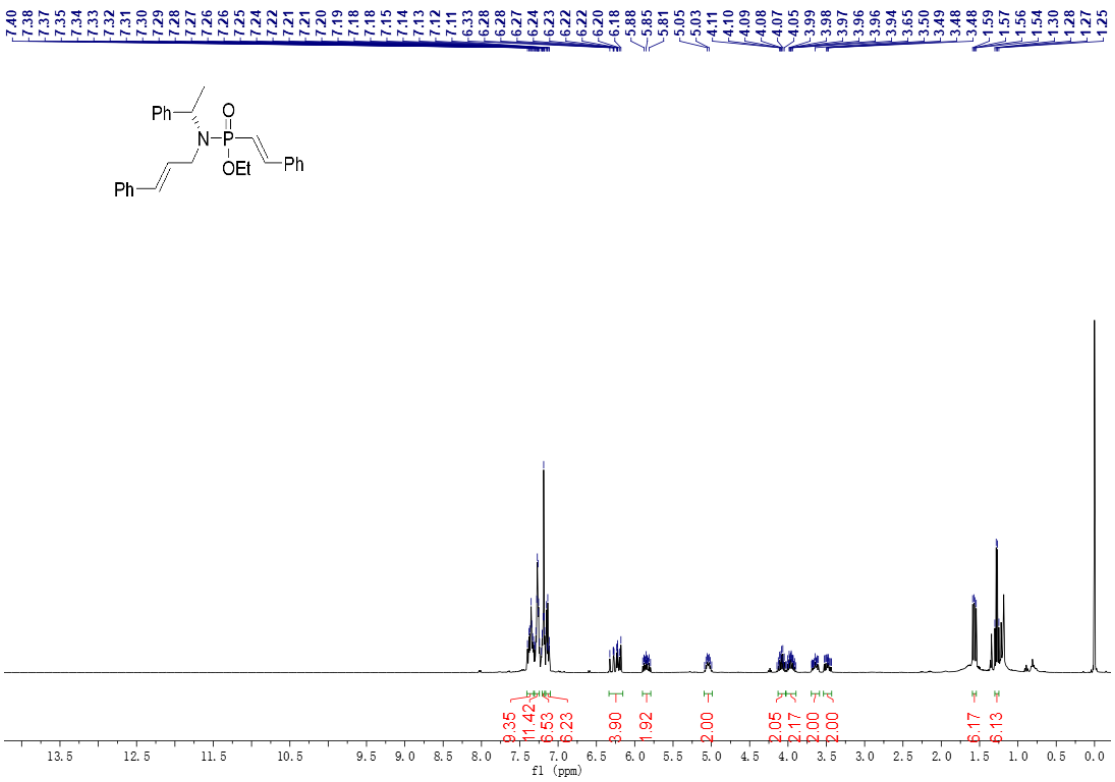
^{1}H NMR Spectrum of Compound **3aF**



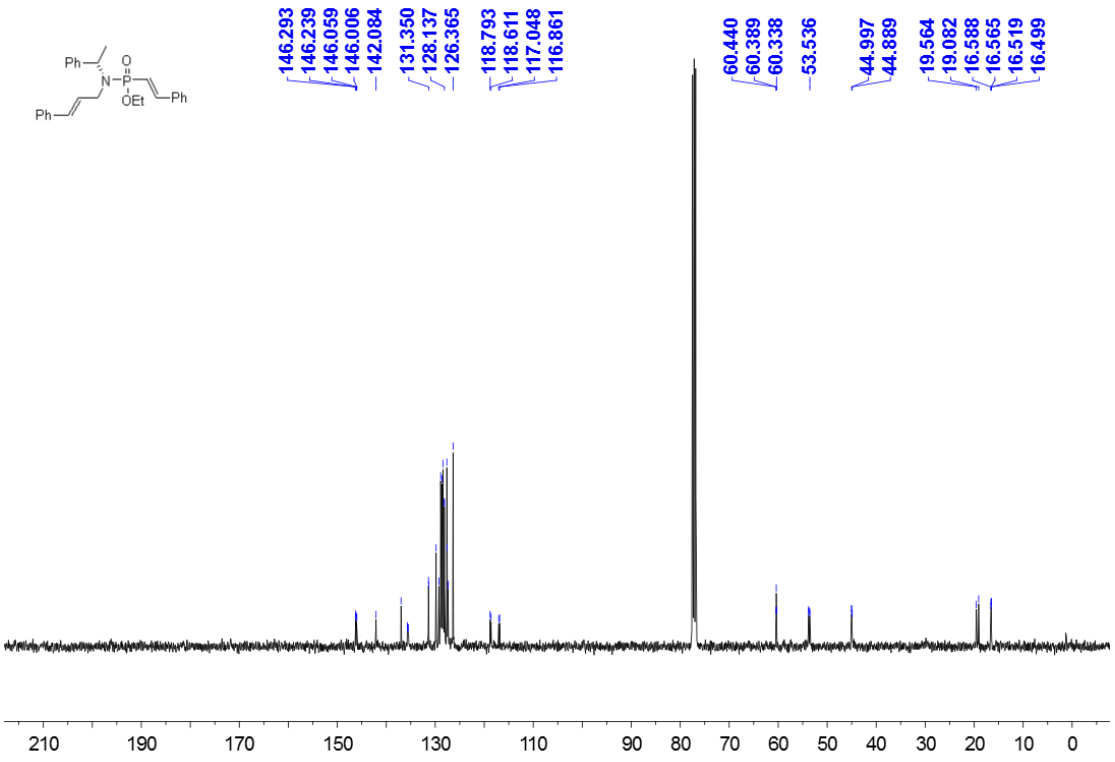
^{31}P NMR Spectrum of Compound **3aF**



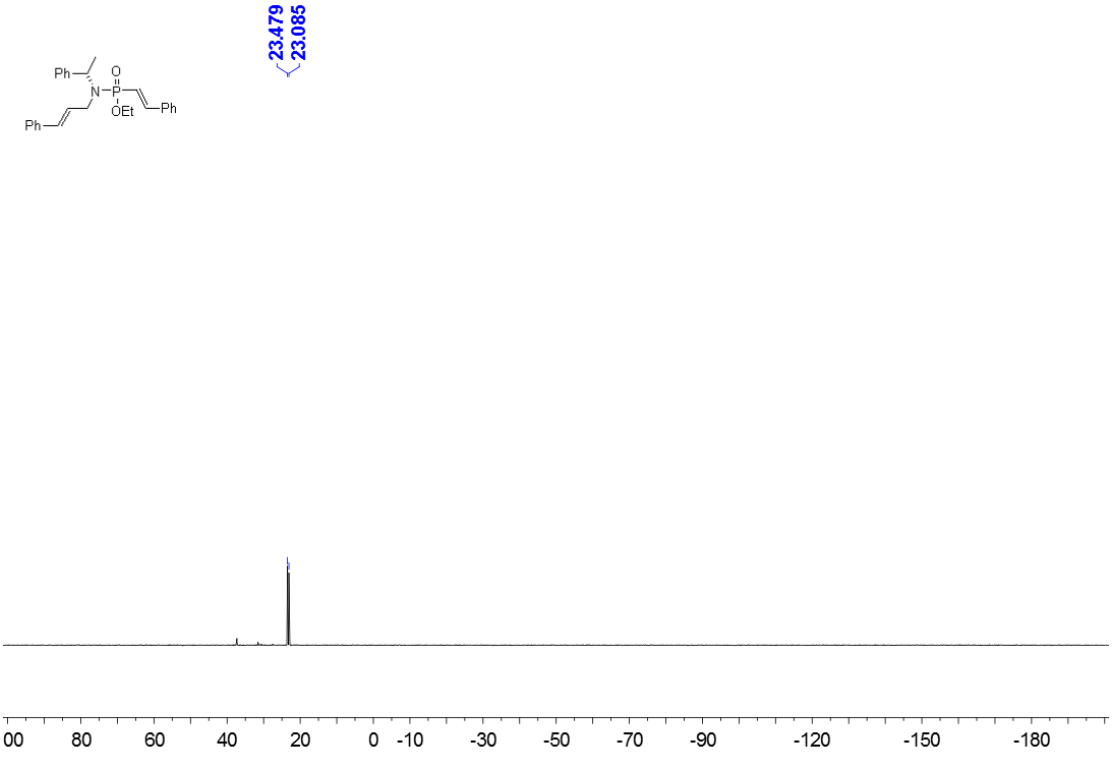
^{13}C NMR Spectrum of Compound **3aF**



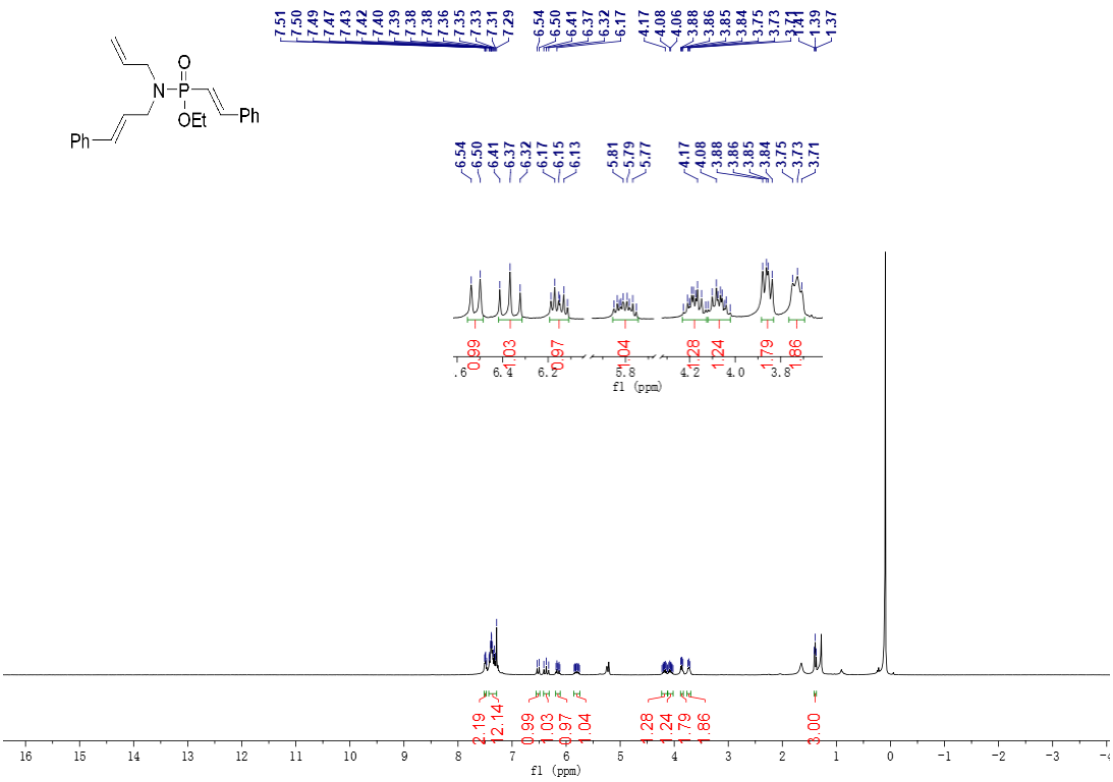
^{1}H NMR Spectrum of Compound **3aG**



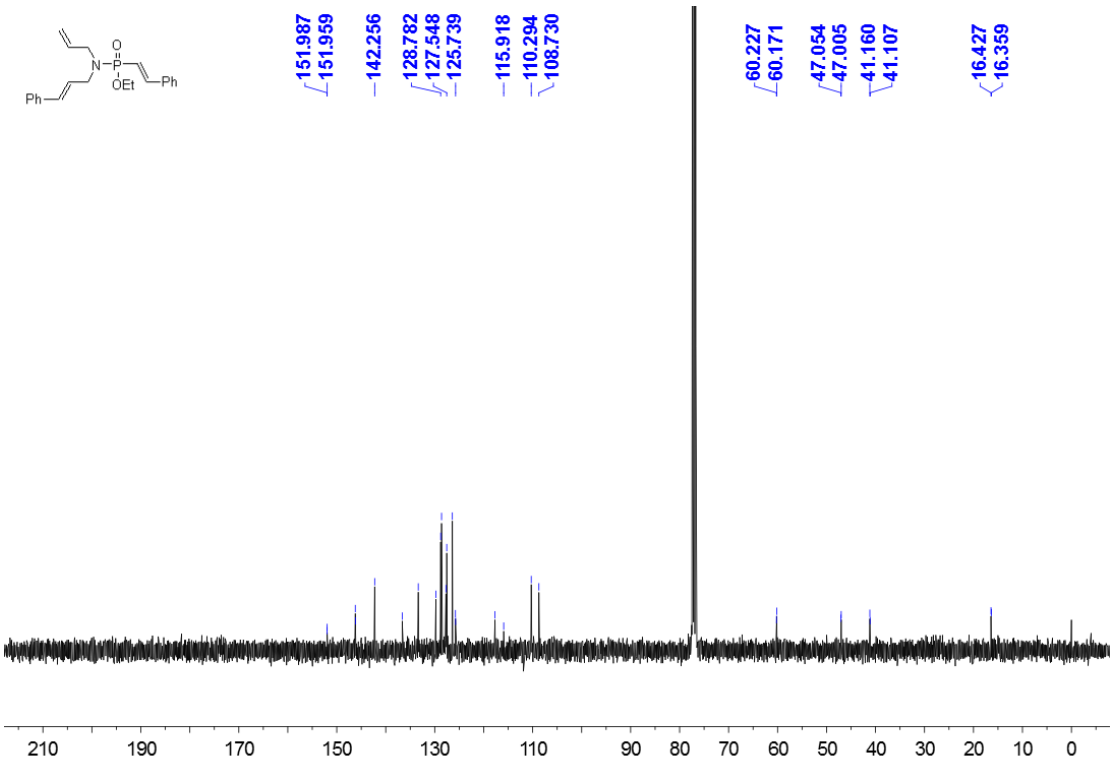
^{13}C NMR Spectrum of Compound **3aG**



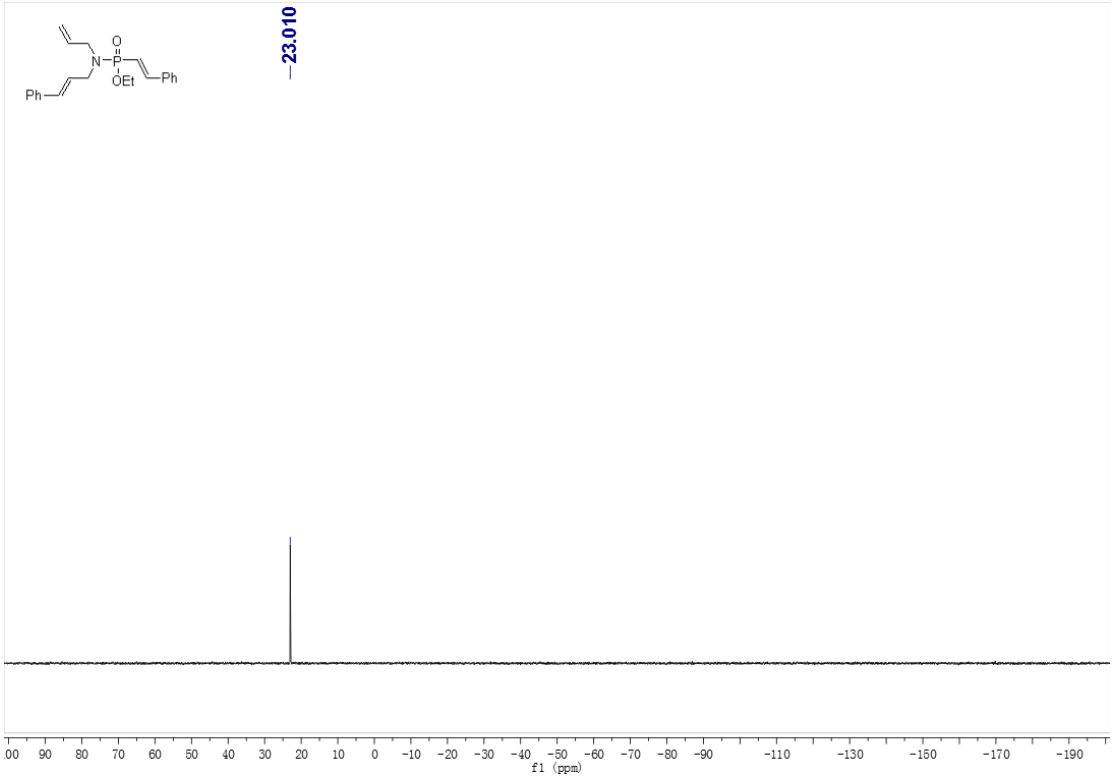
^{31}P NMR Spectrum of Compound **3aG**



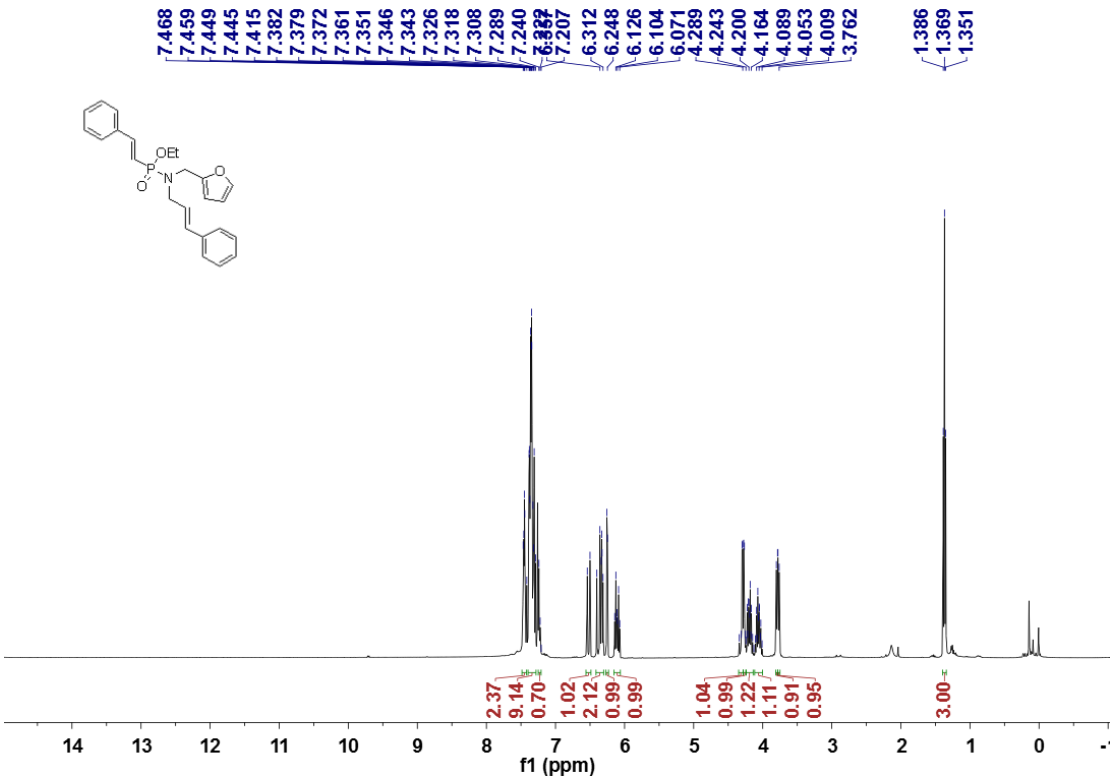
^{1}H NMR Spectrum of Compound **3aH**



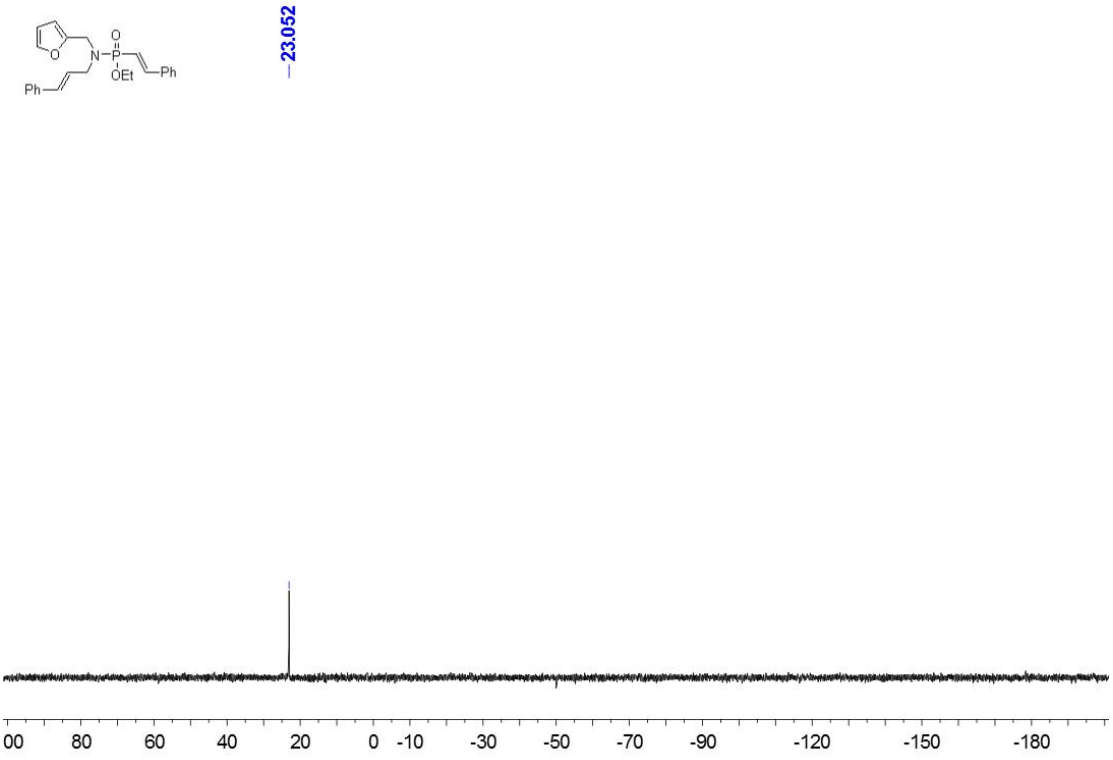
^{13}C NMR Spectrum of Compound **3aH**



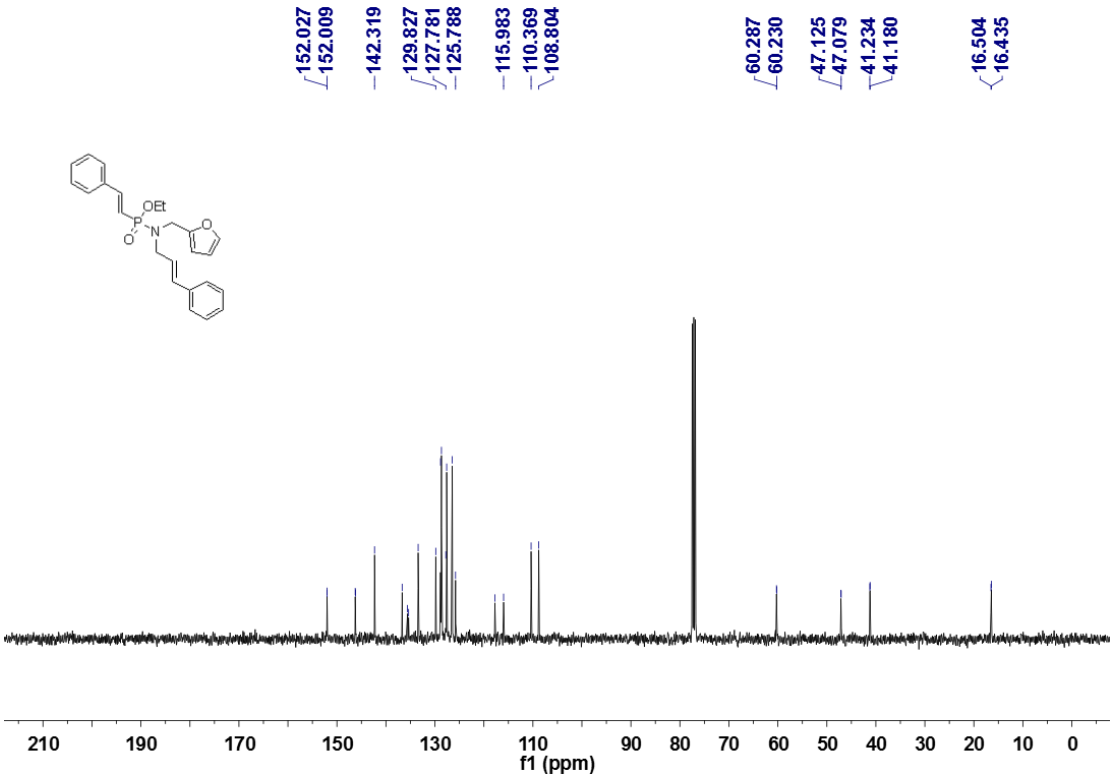
^{31}P NMR Spectrum of Compound **3aH**



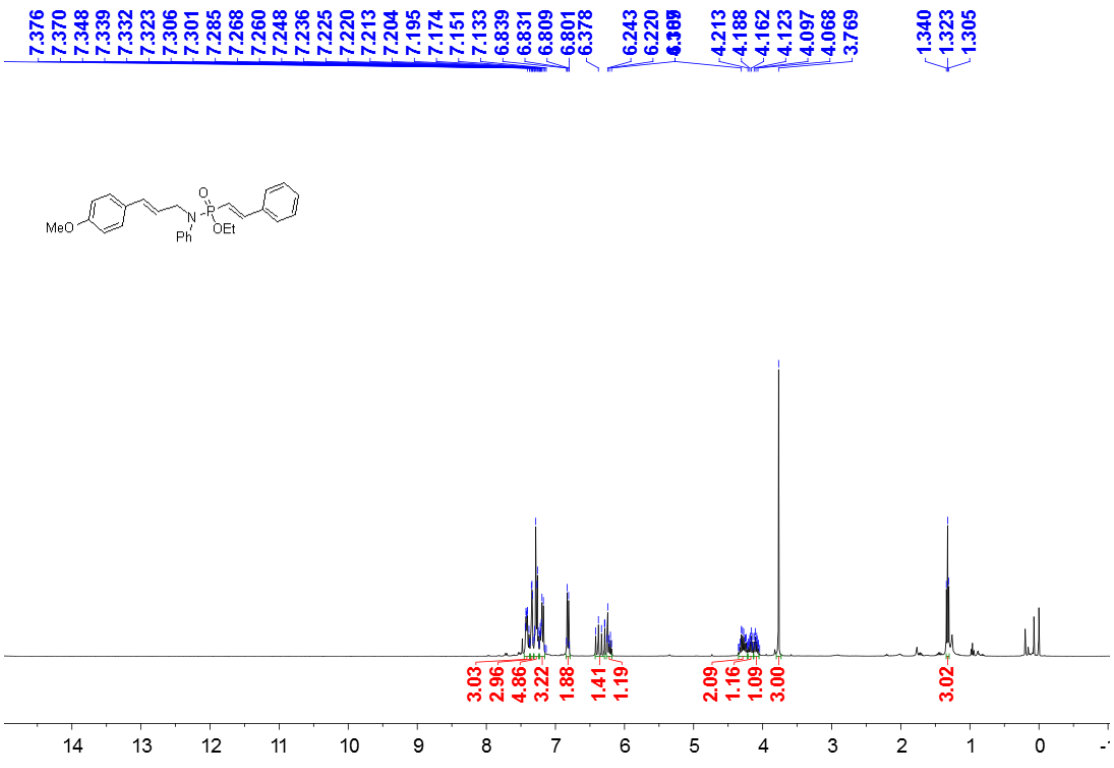
^{1}H NMR Spectrum of Compound **3aI**



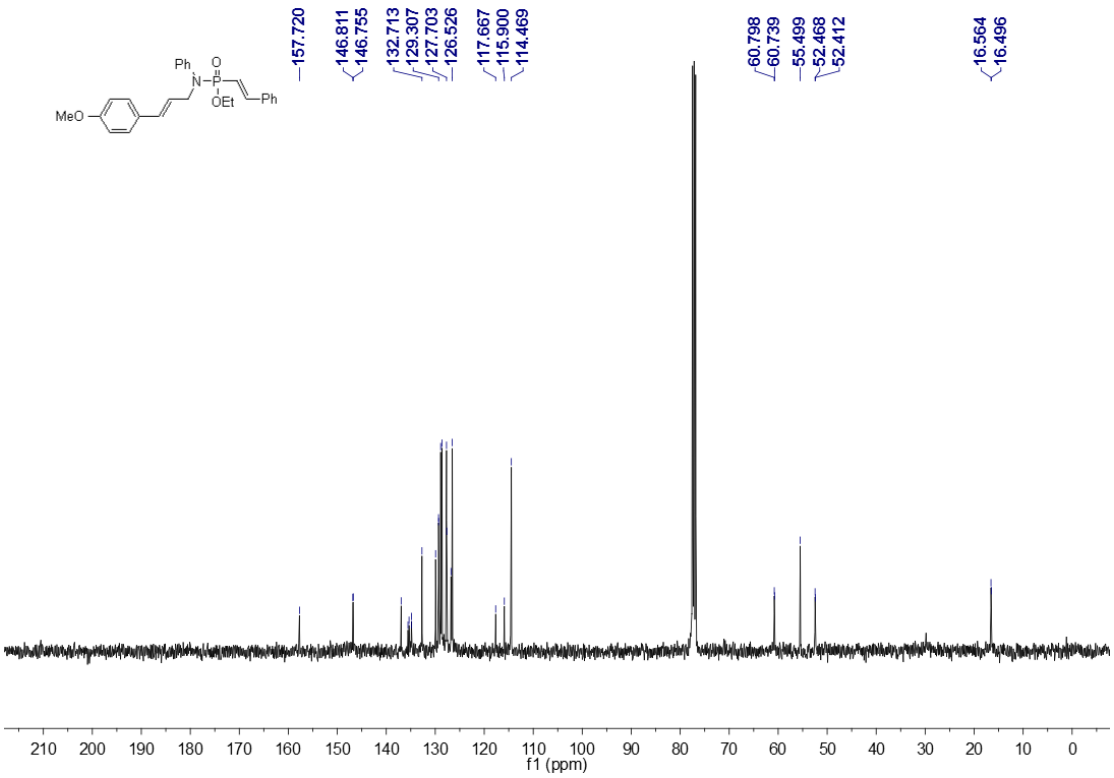
^{13}C NMR Spectrum of Compound **3aI**



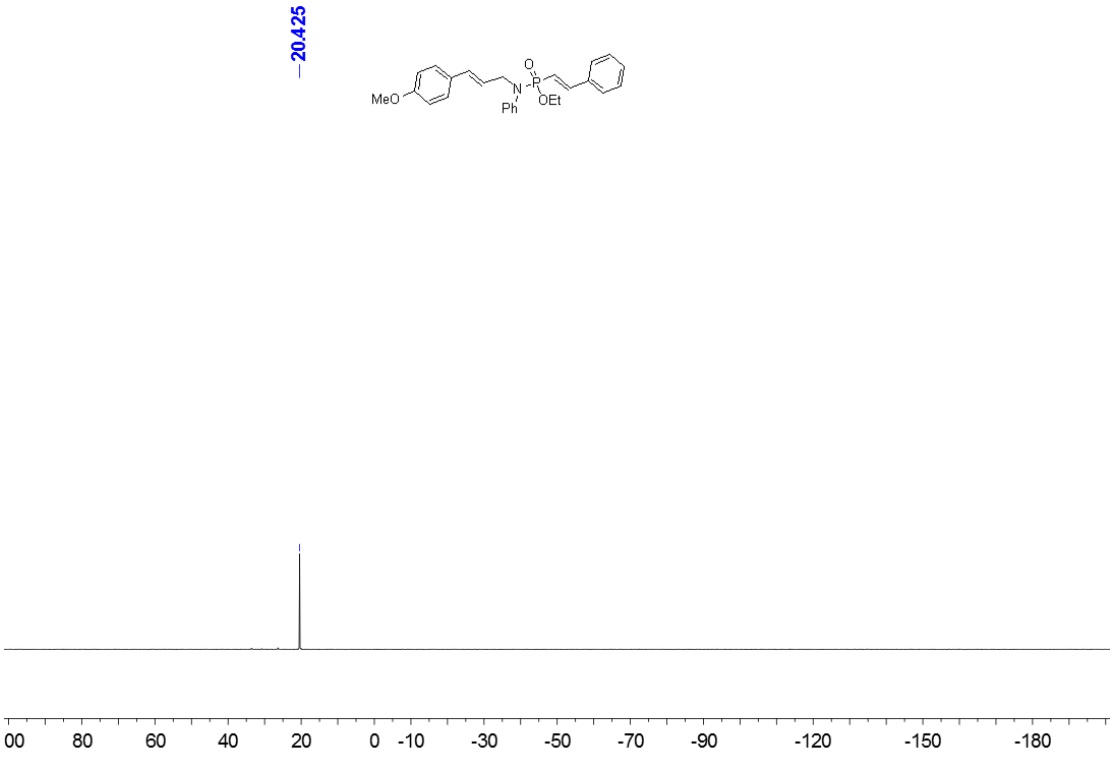
^{13}C NMR Spectrum of Compound **3aI**



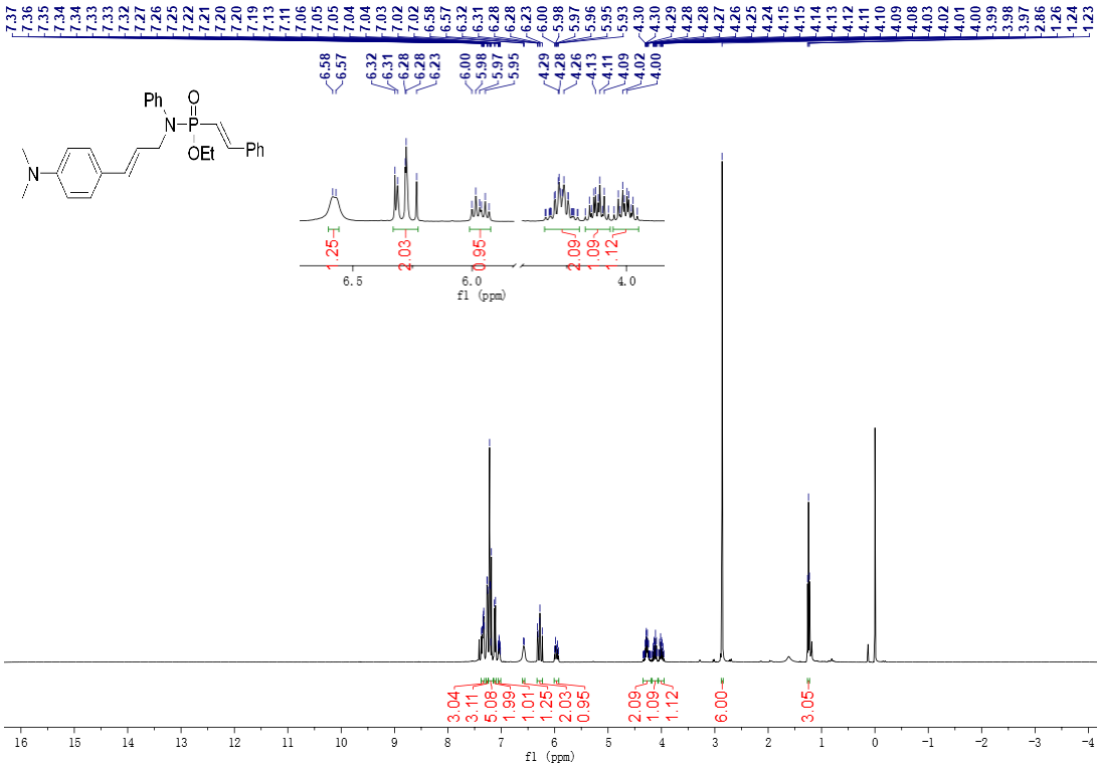
^{1}H NMR Spectrum of Compound **3aJ**



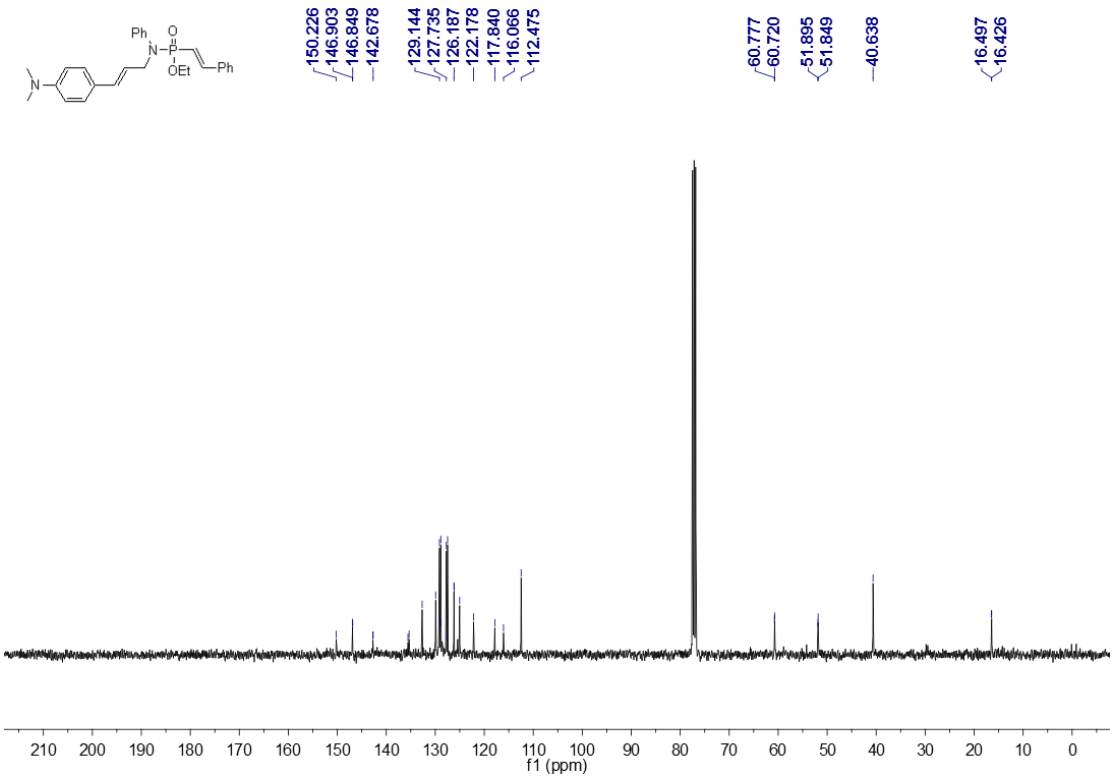
^{13}C NMR Spectrum of Compound **3aJ**



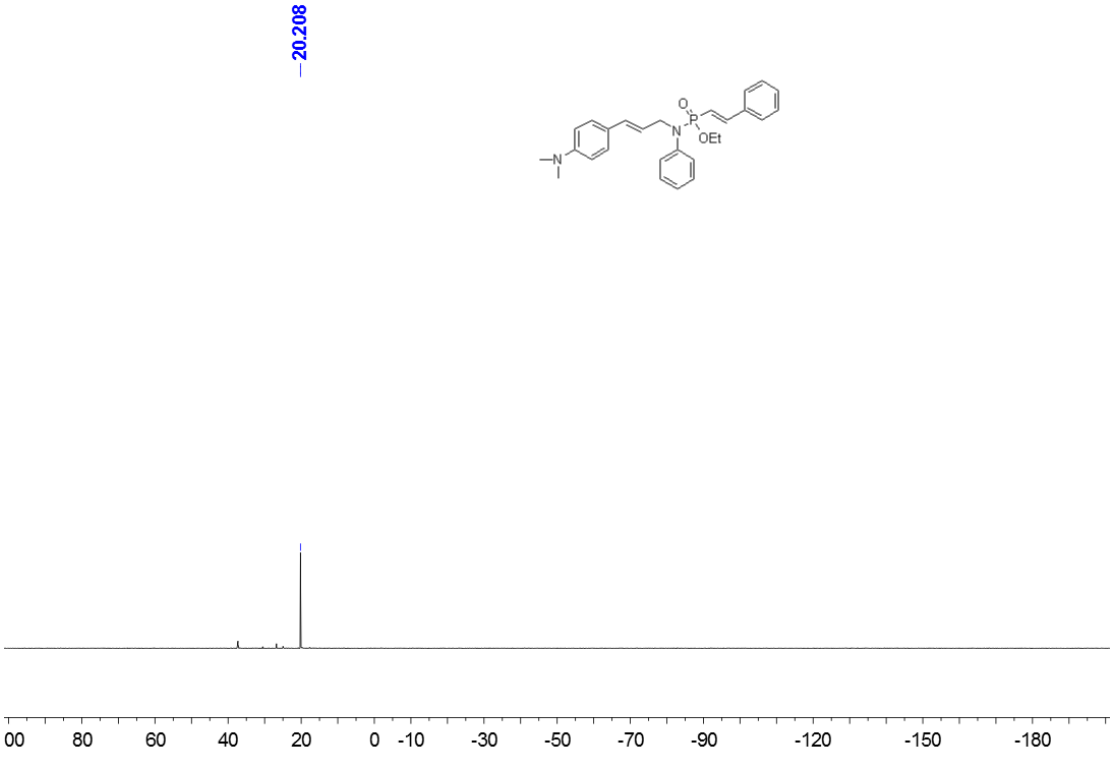
^{31}P NMR Spectrum of Compound **3aJ**



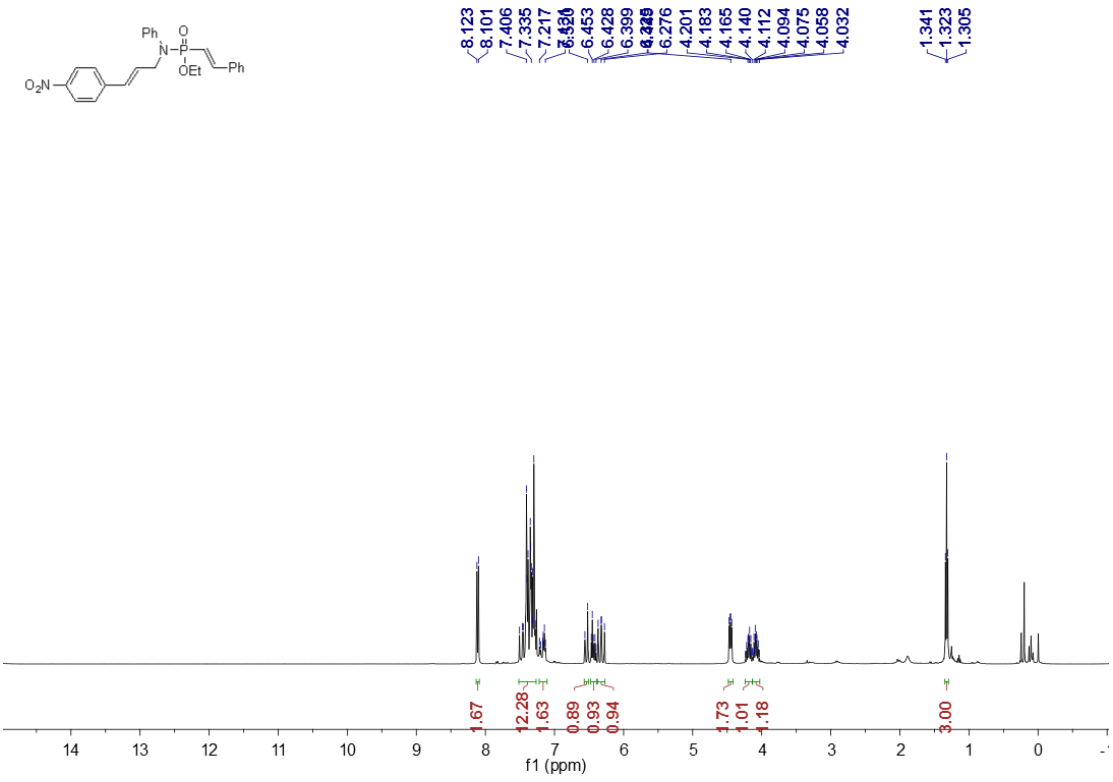
^{1}H NMR Spectrum of Compound **3aK**



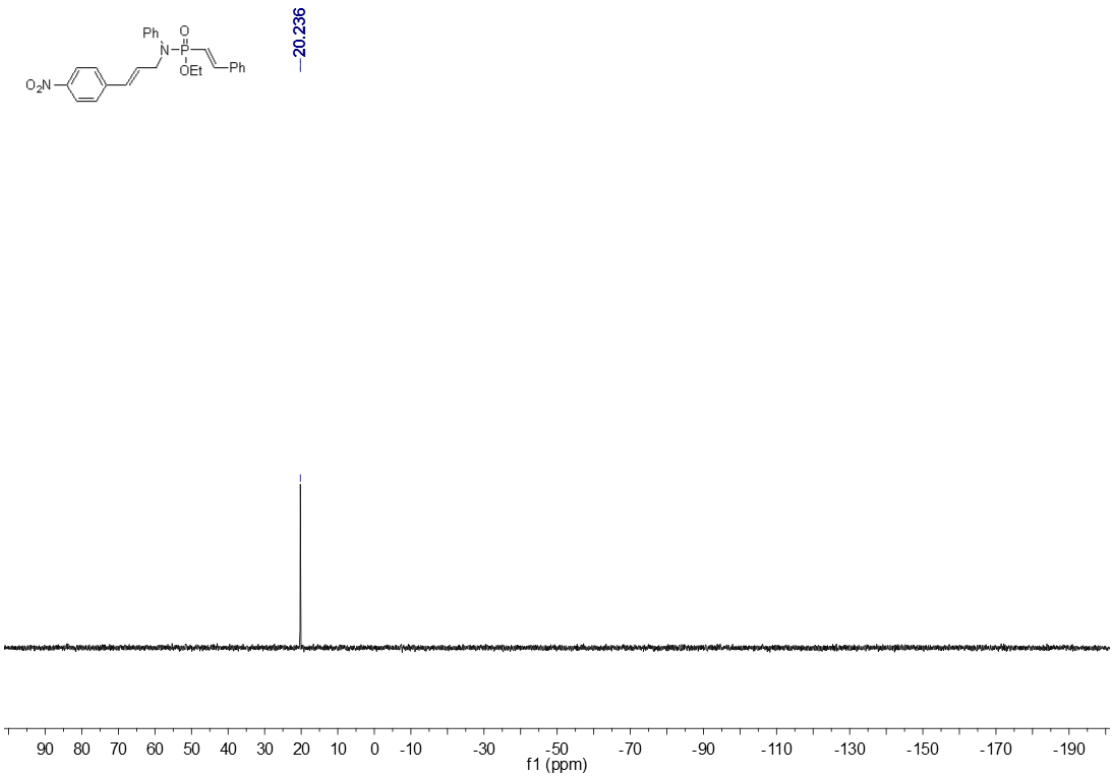
^{13}C NMR Spectrum of Compound **3aK**



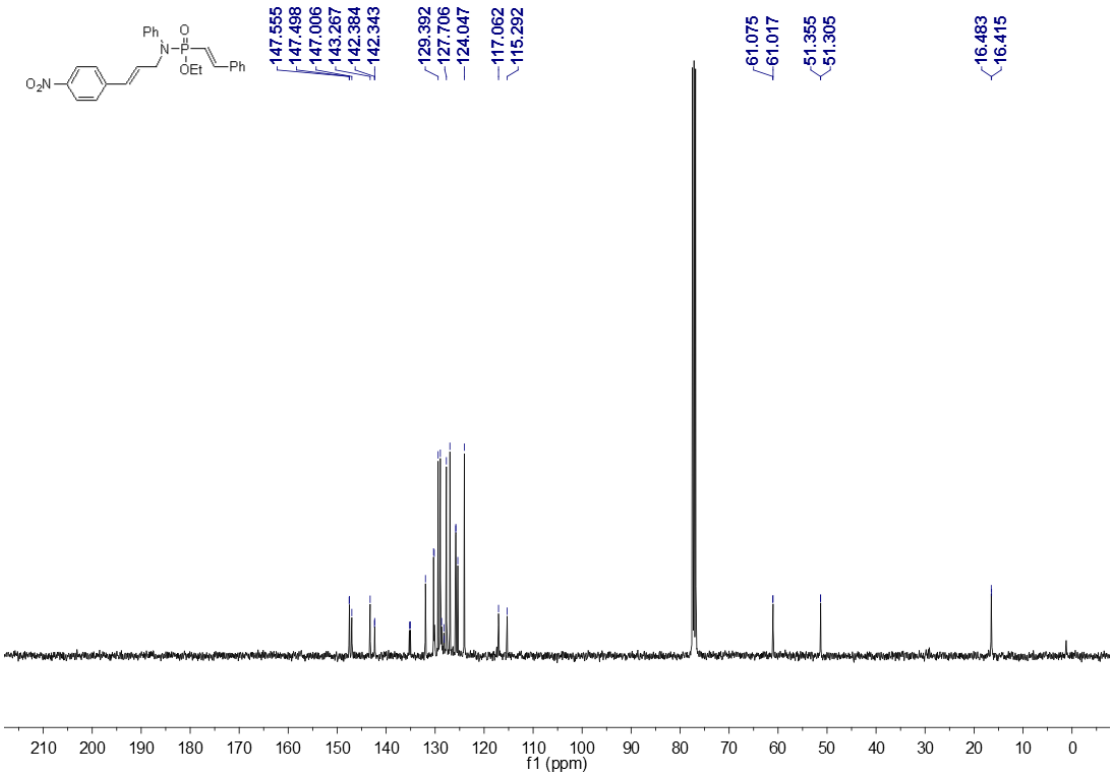
^{31}P NMR Spectrum of Compound **3aK**



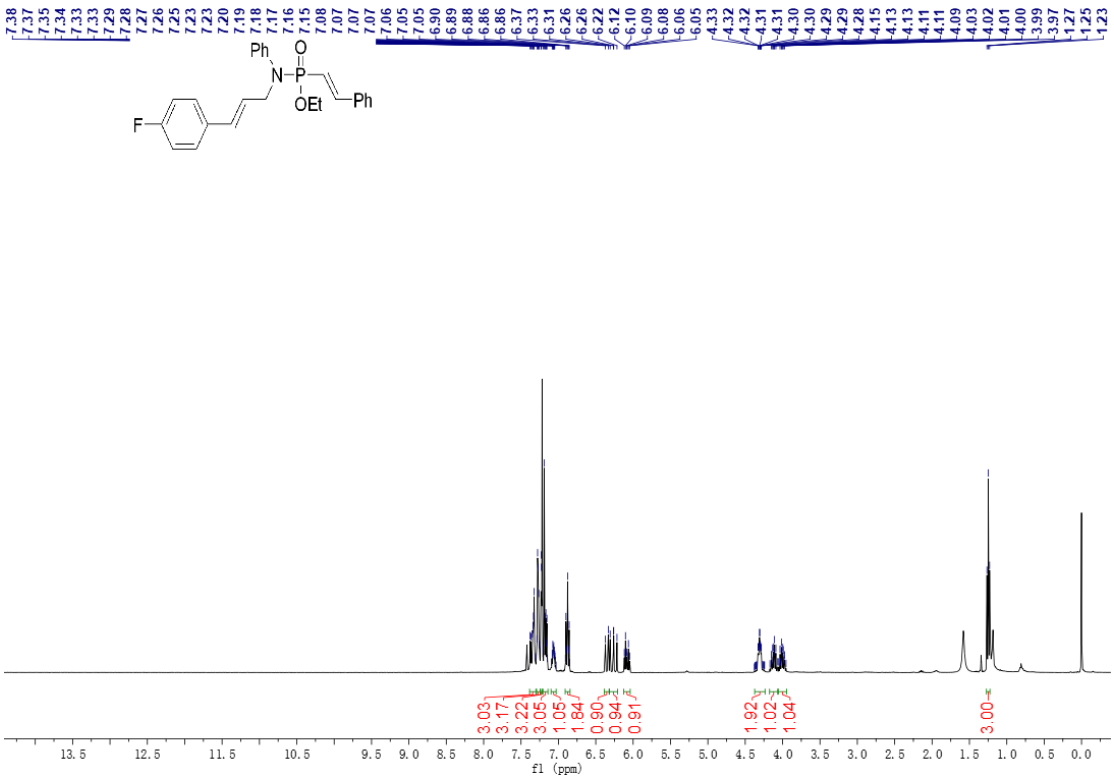
^{1}H NMR Spectrum of Compound **3aL**



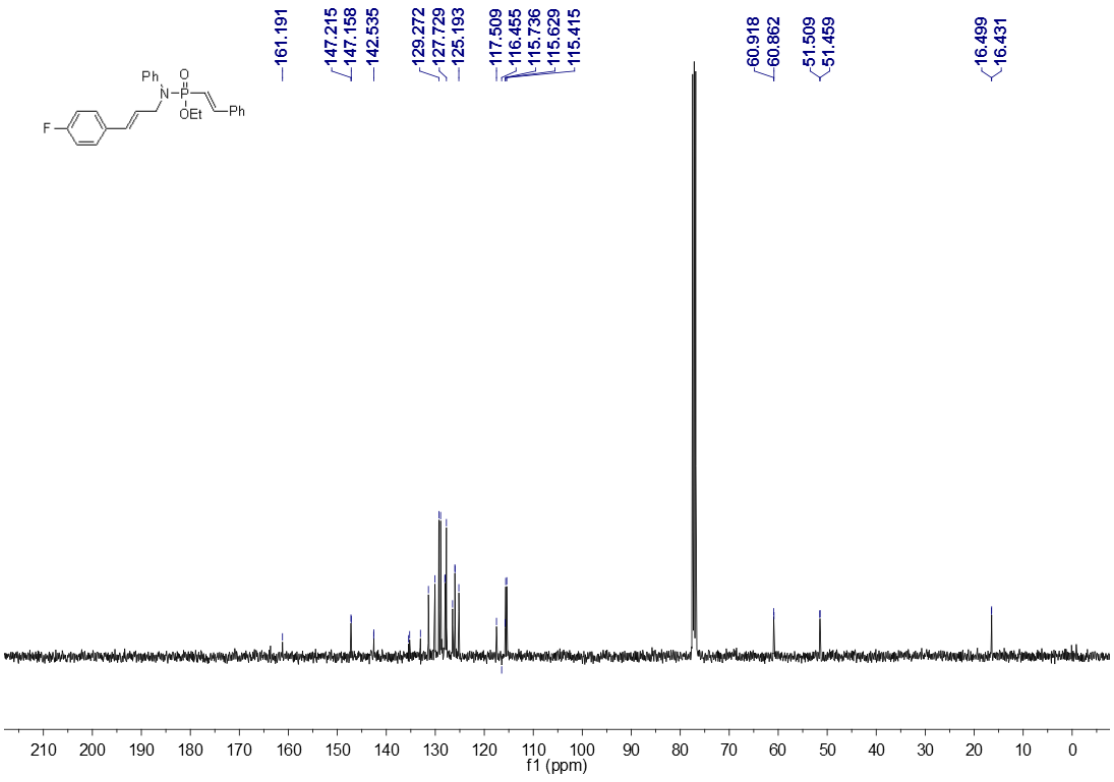
^{31}P NMR Spectrum of Compound **3aL**



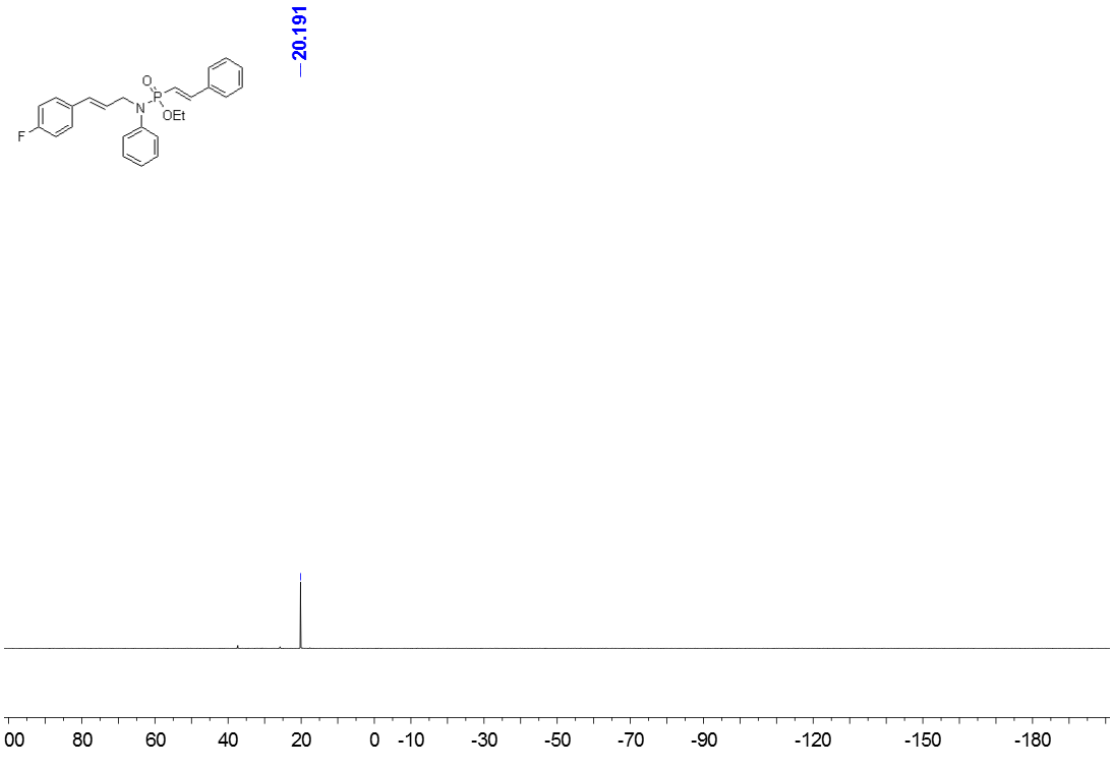
^{13}C NMR Spectrum of Compound **3aL**



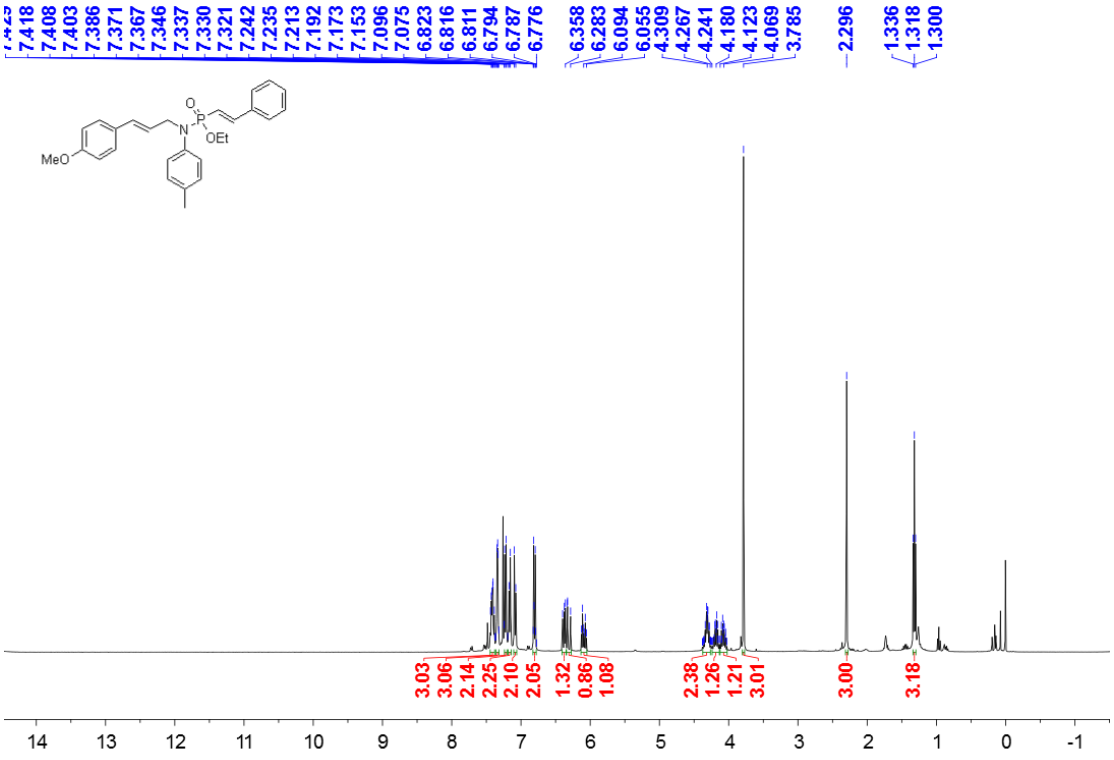
^{1}H NMR Spectrum of Compound **3aM**



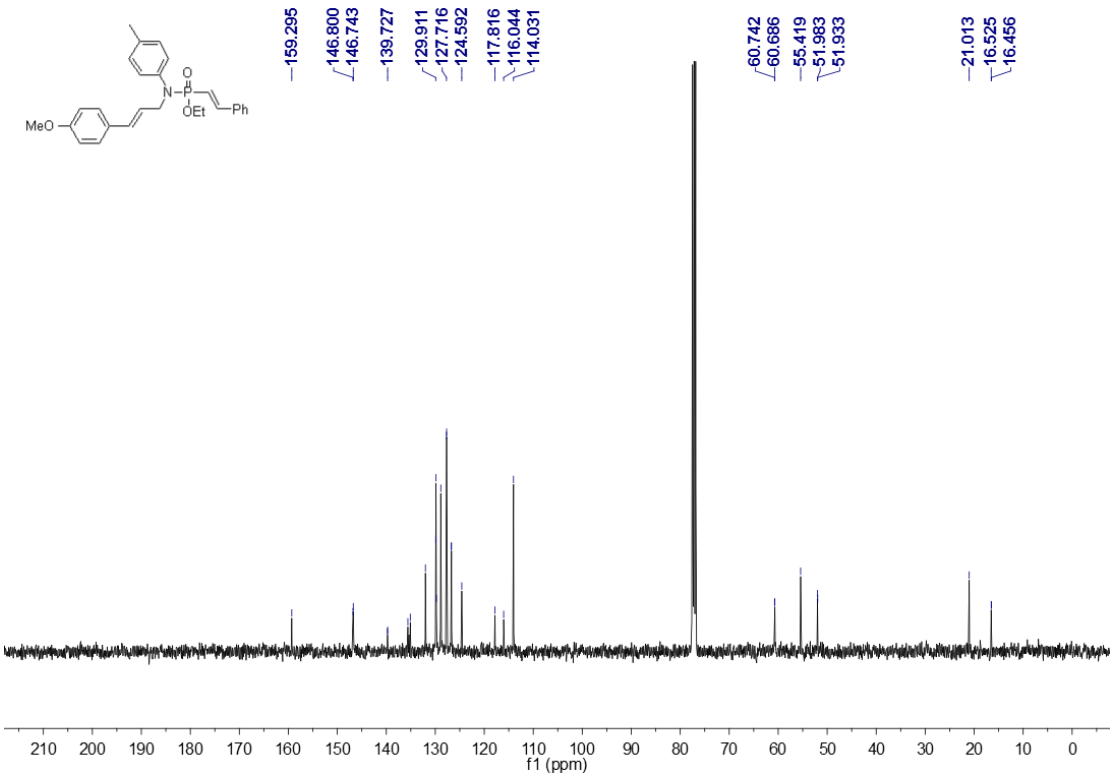
^{13}C NMR Spectrum of Compound **3aM**



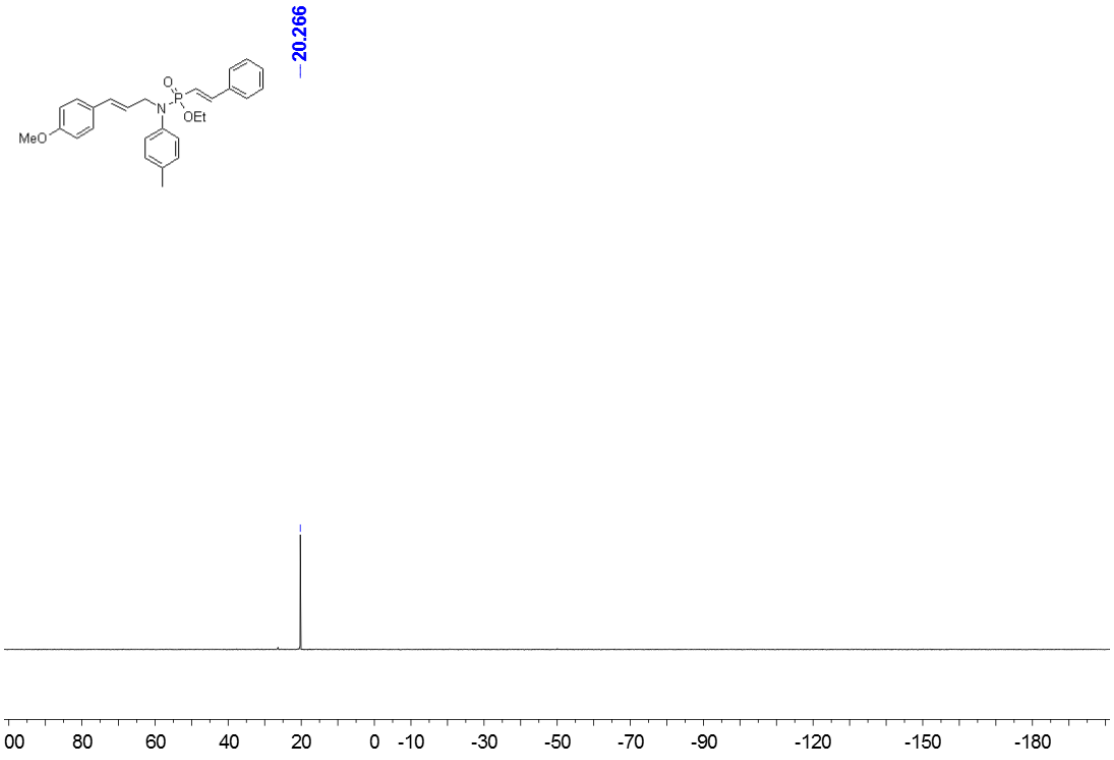
^{31}P NMR Spectrum of Compound **3aM**



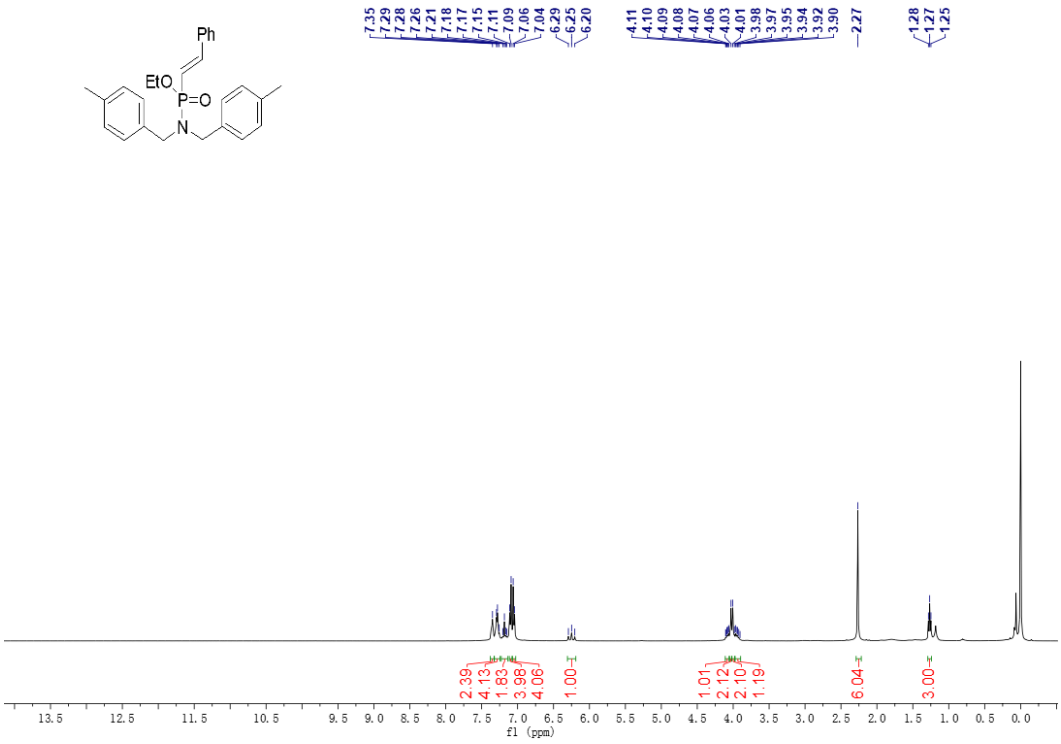
^{1}H NMR Spectrum of Compound **3aN**



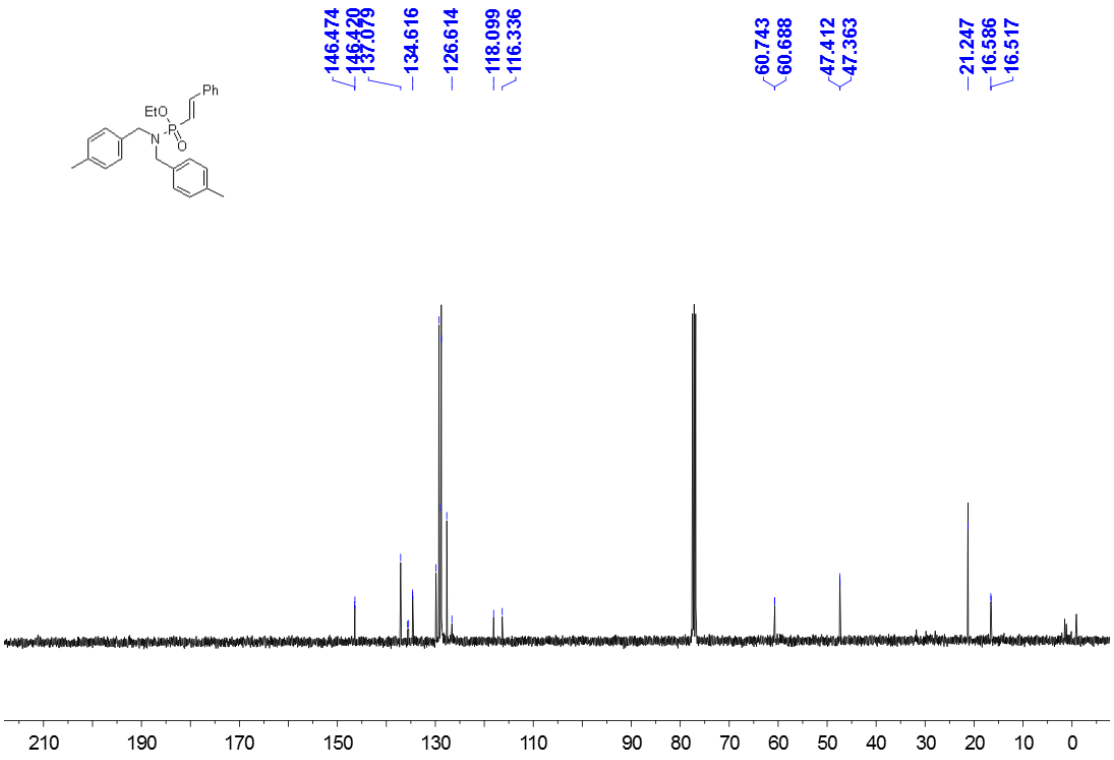
^{13}C NMR Spectrum of Compound **3aN**



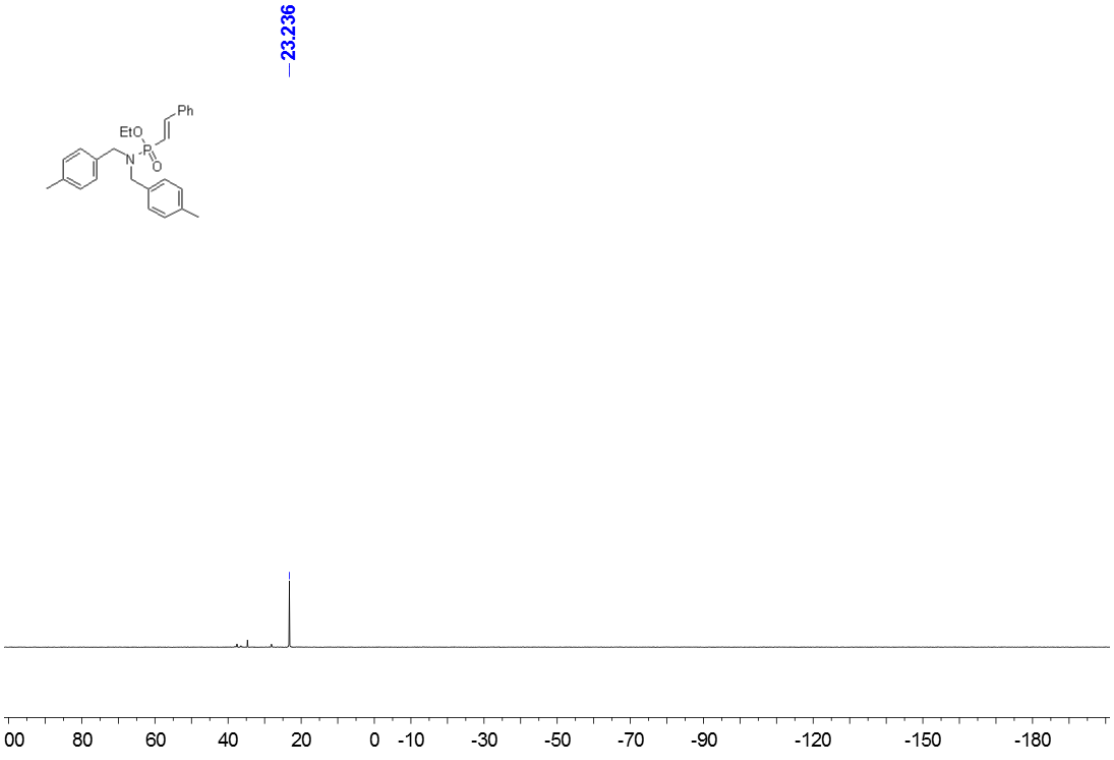
^{31}P NMR Spectrum of Compound **3aN**



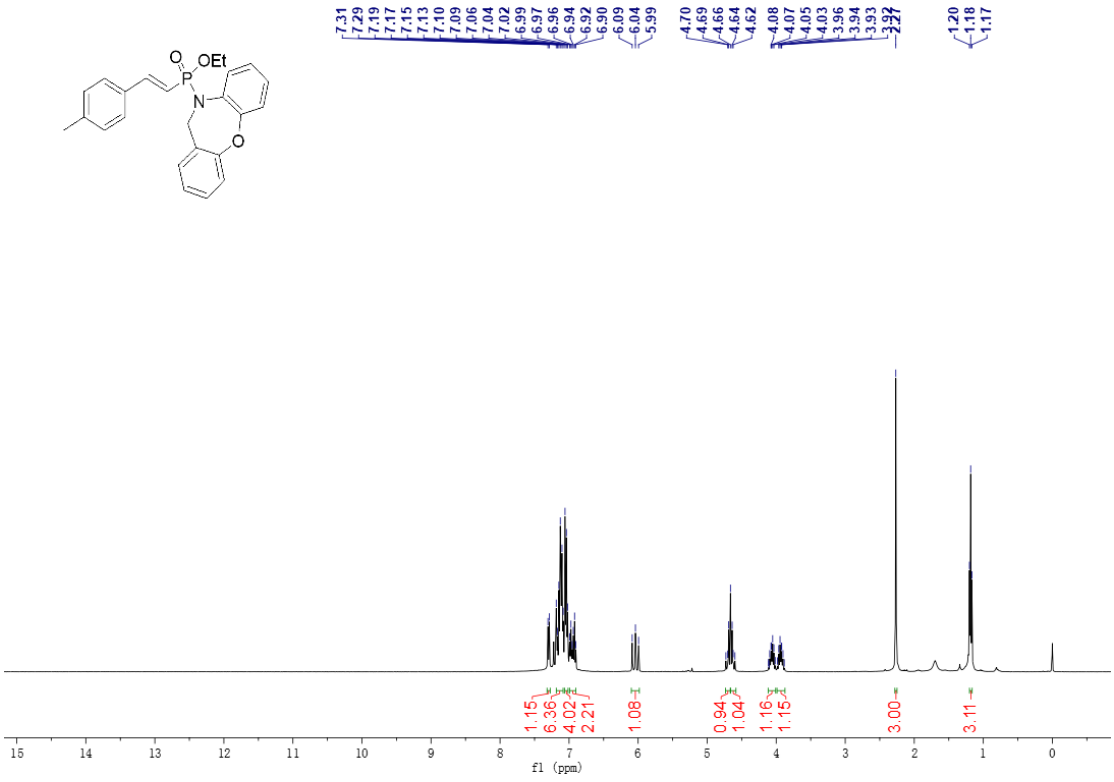
[1]H NMR Spectrum of Compound **3aO**



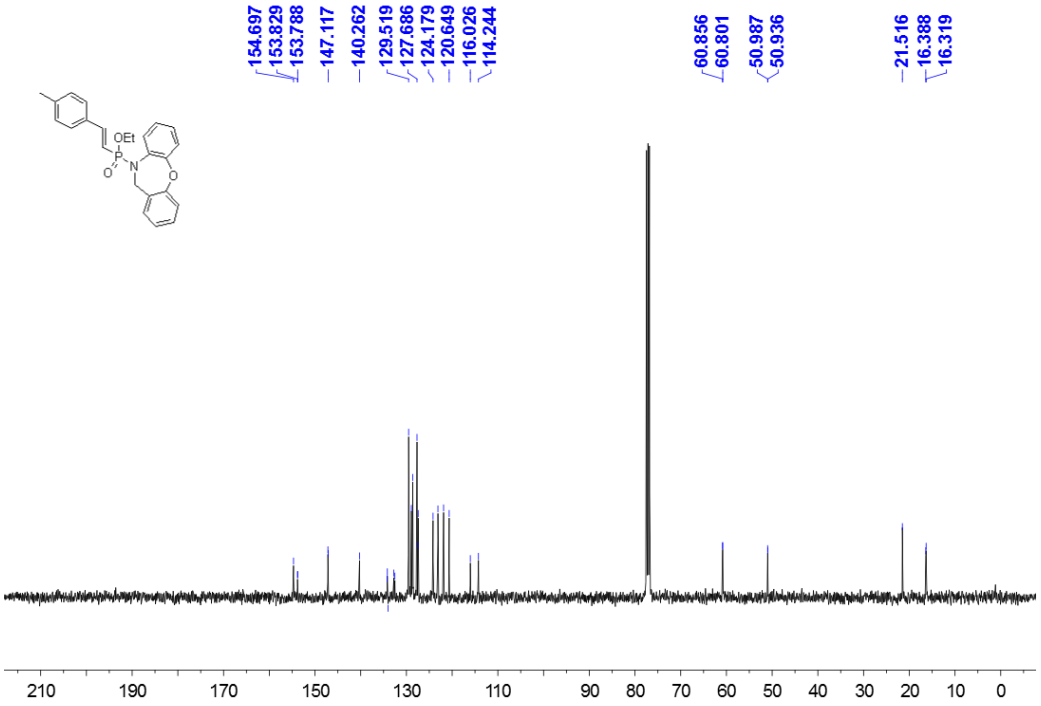
[13]C NMR Spectrum of Compound **3aO**



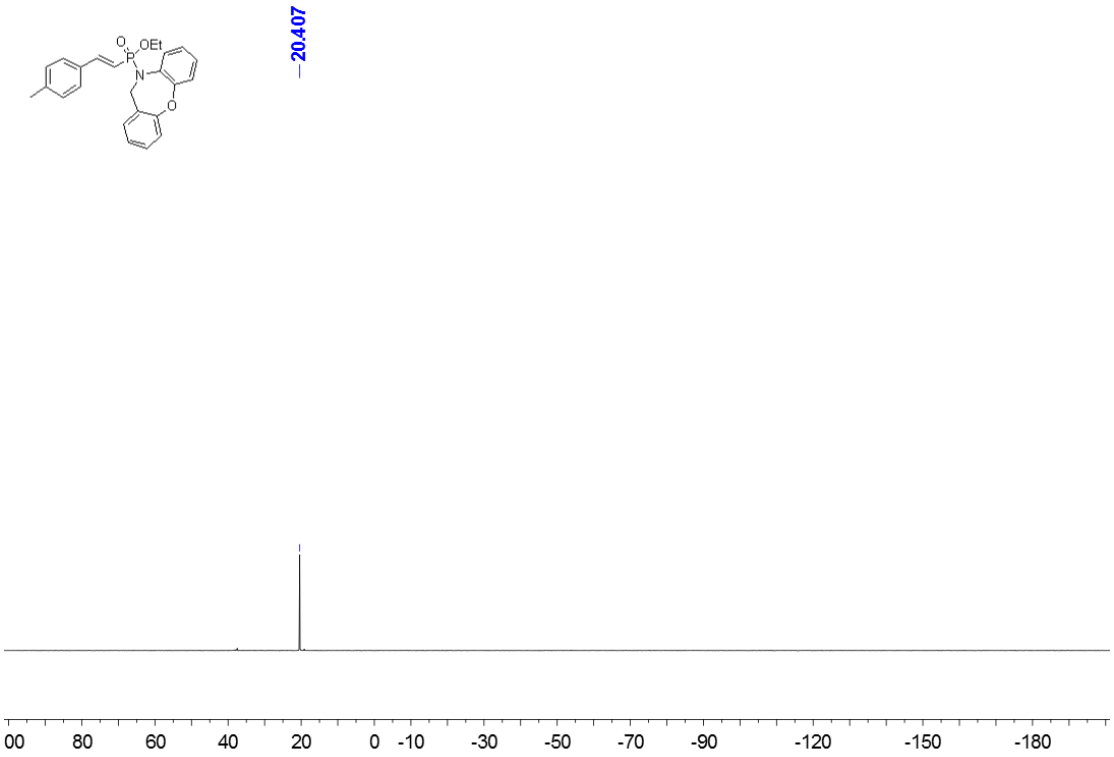
^{31}P NMR Spectrum of Compound **3aO**



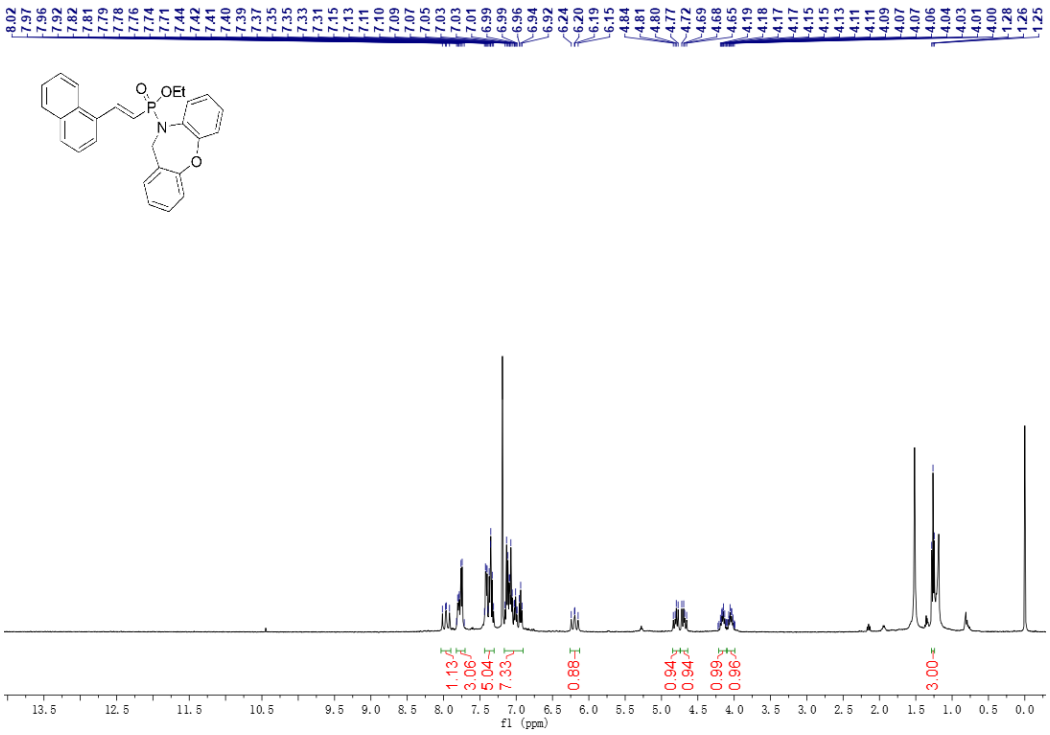
^{1}H NMR Spectrum of Compound **3ba**



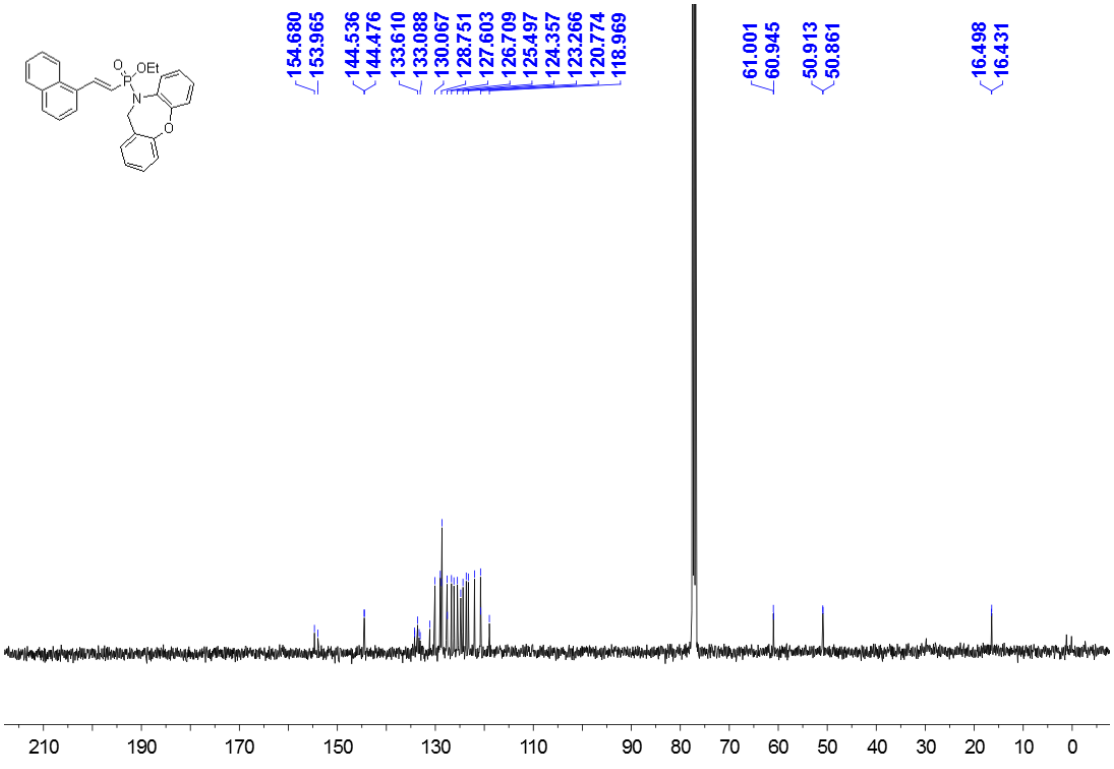
^{13}C NMR Spectrum of Compound **3ba**



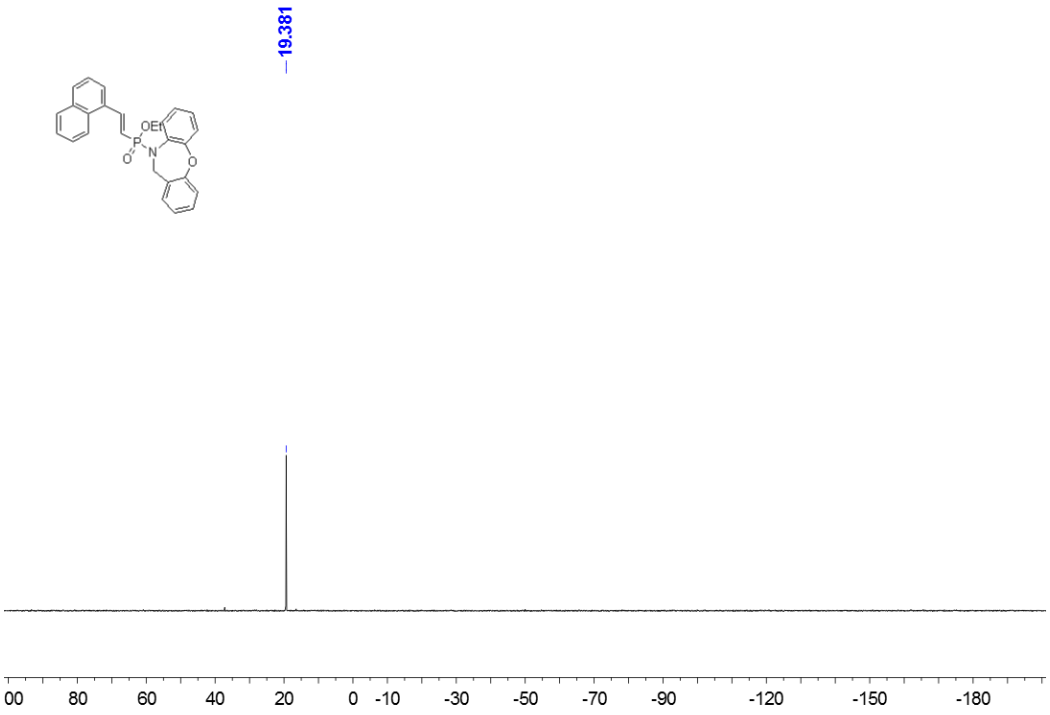
^{31}P NMR Spectrum of Compound **3ba**



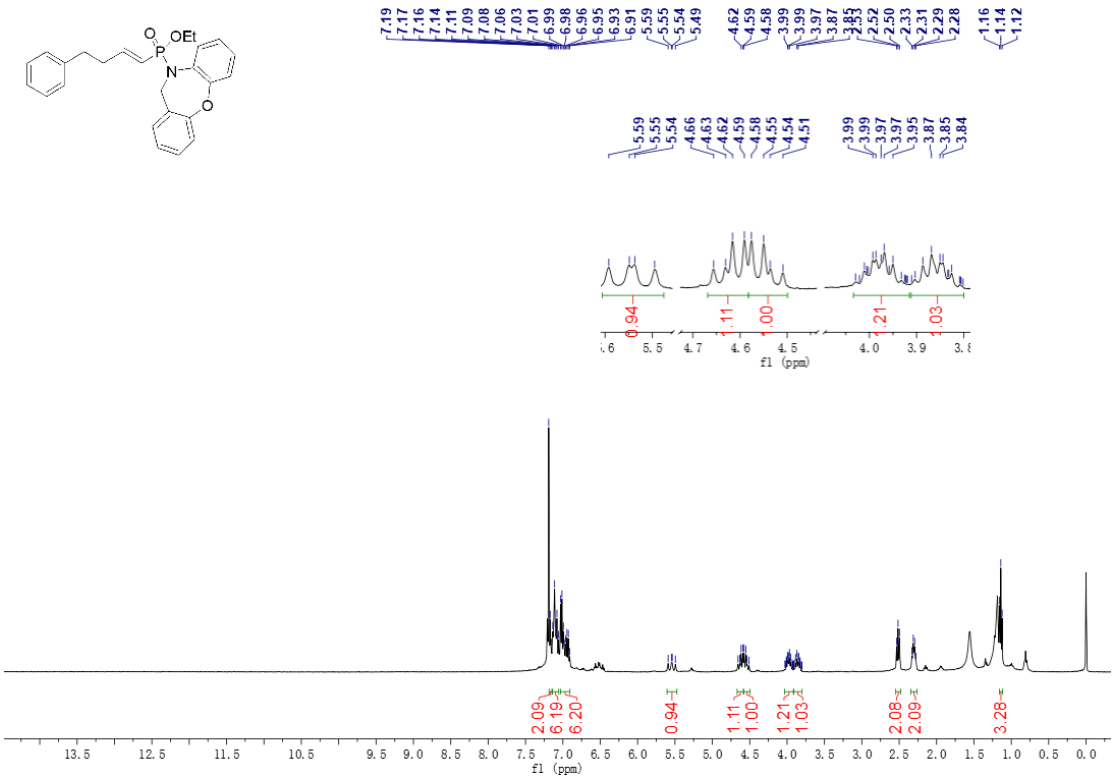
^{1}H NMR Spectrum of Compound **3ca**



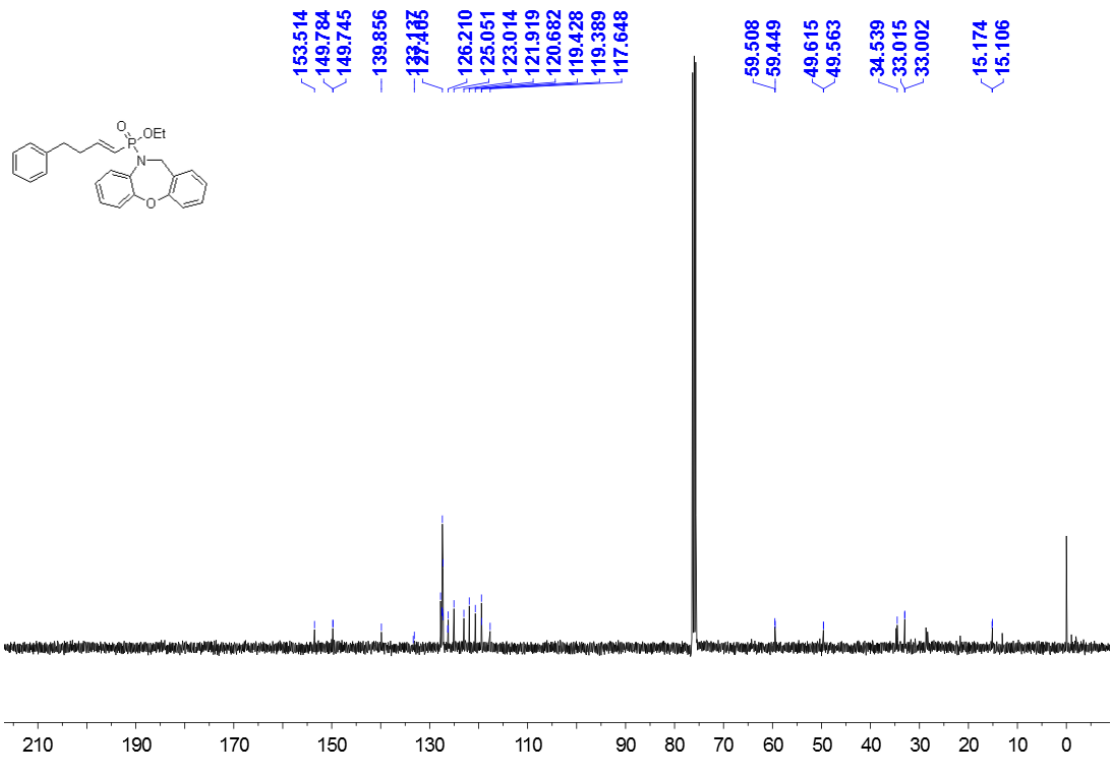
^{13}C NMR Spectrum of Compound **3ca**



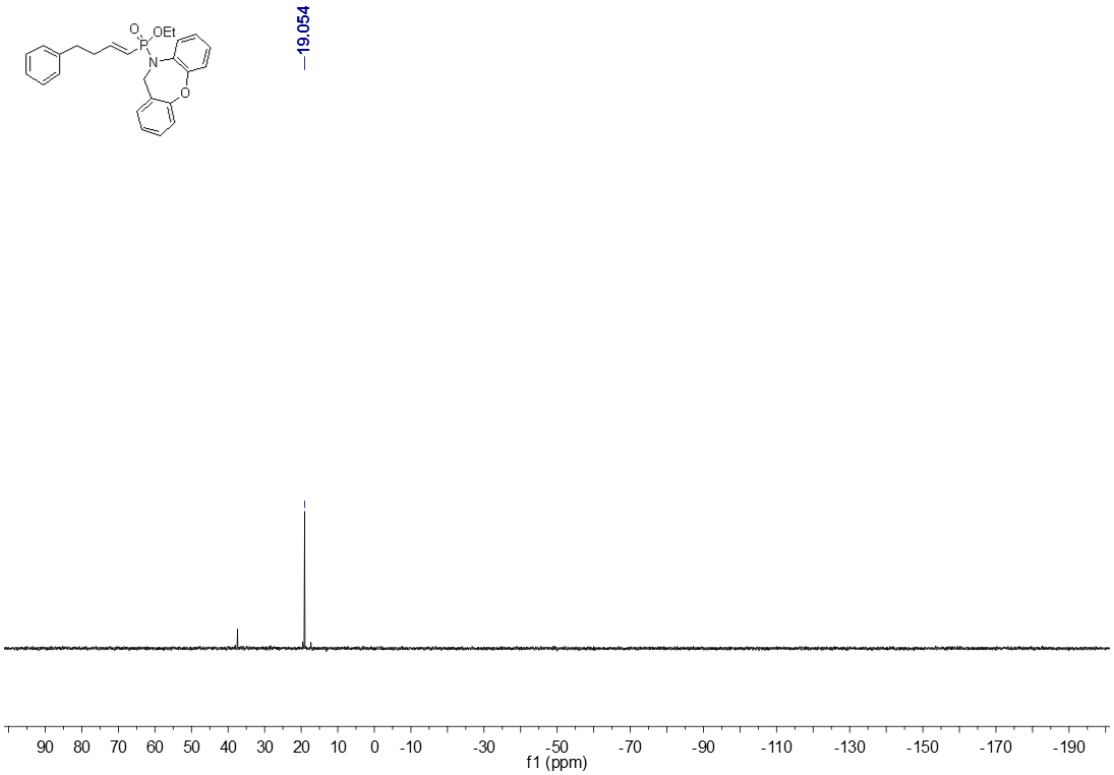
^{31}P NMR Spectrum of Compound **3ca**



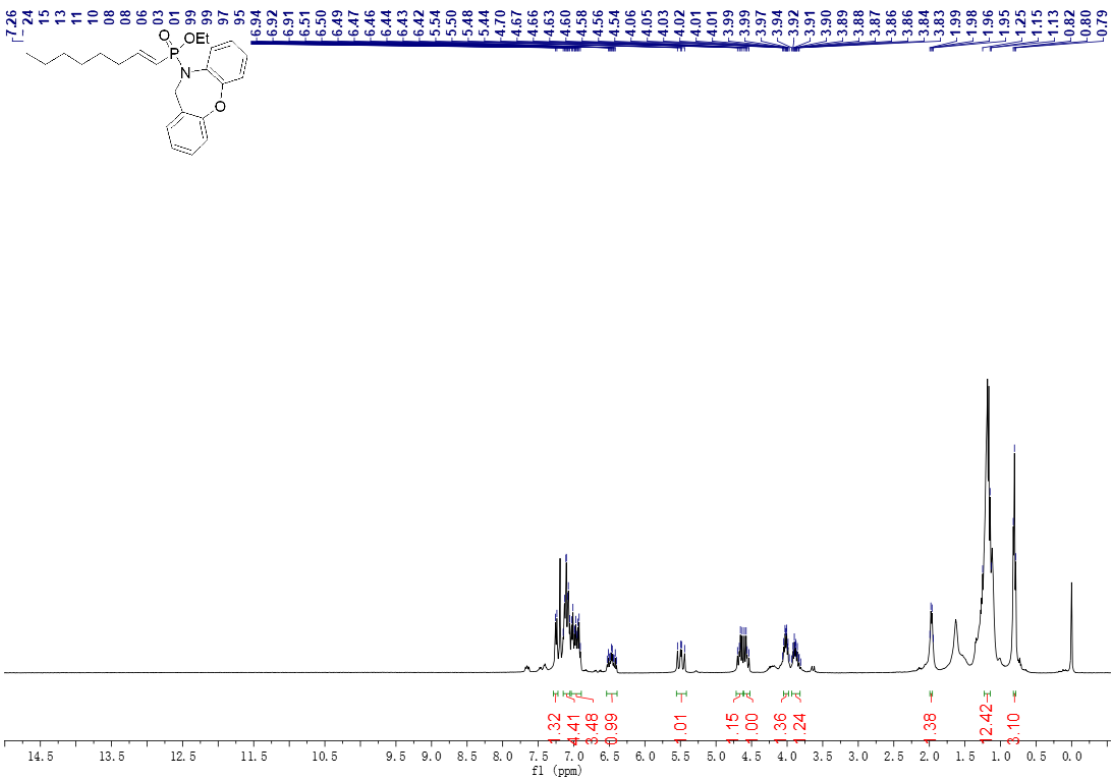
^{1}H NMR Spectrum of Compound **3da**



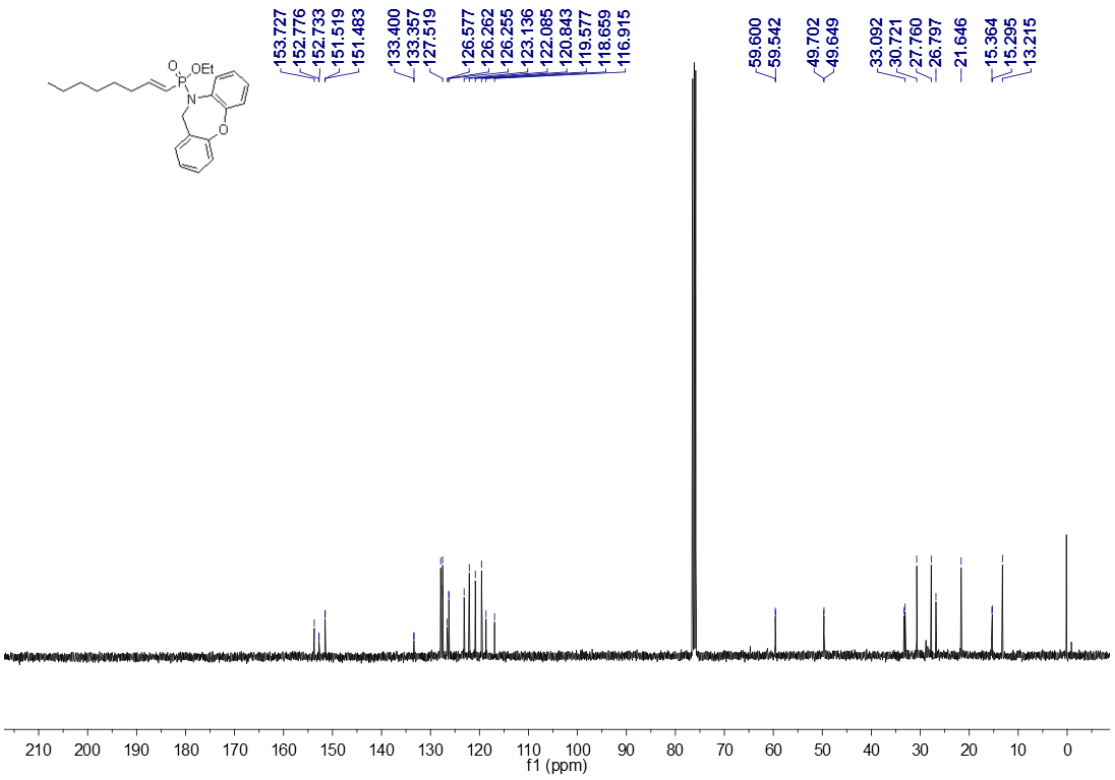
^{13}C NMR Spectrum of Compound **3da**



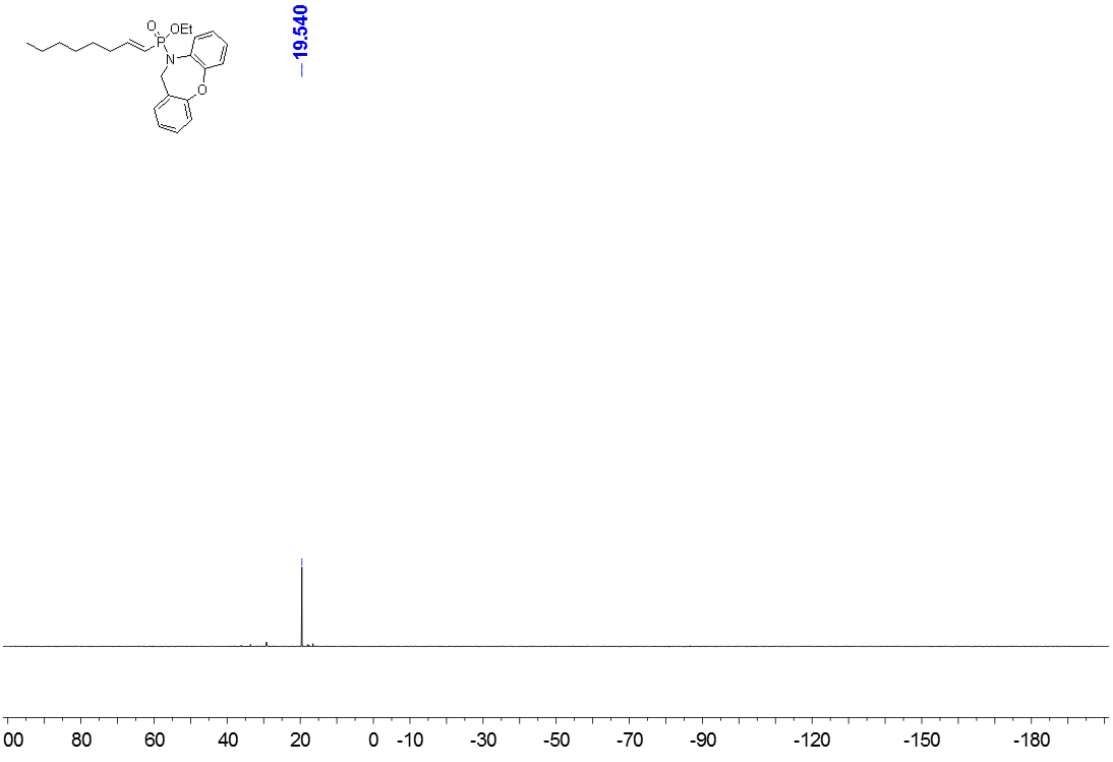
^{31}P NMR Spectrum of Compound **3da**



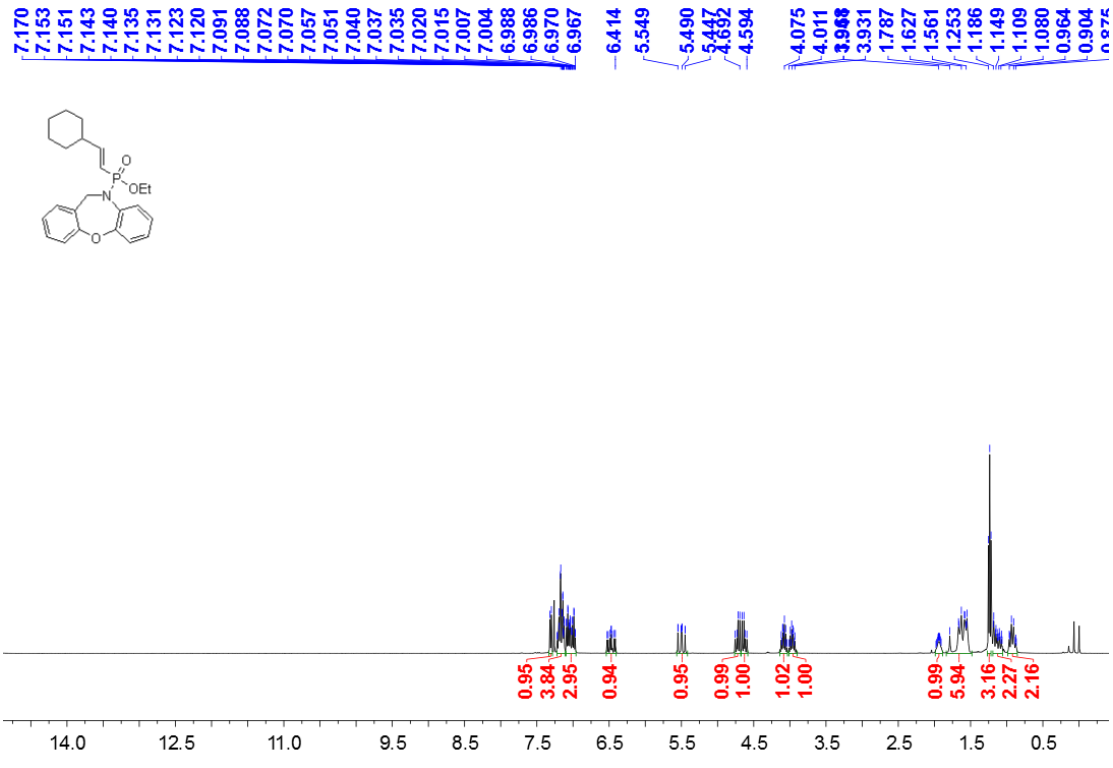
^{1}H NMR Spectrum of Compound **3ea**



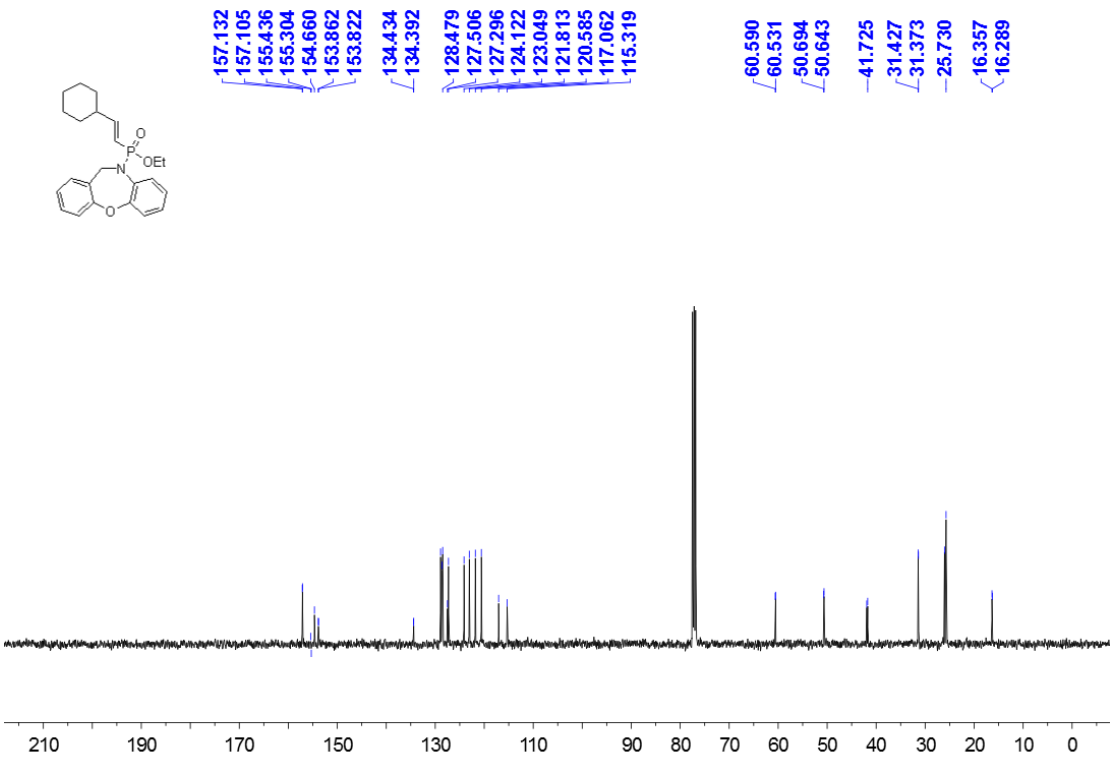
^{13}C NMR Spectrum of Compound **3ea**



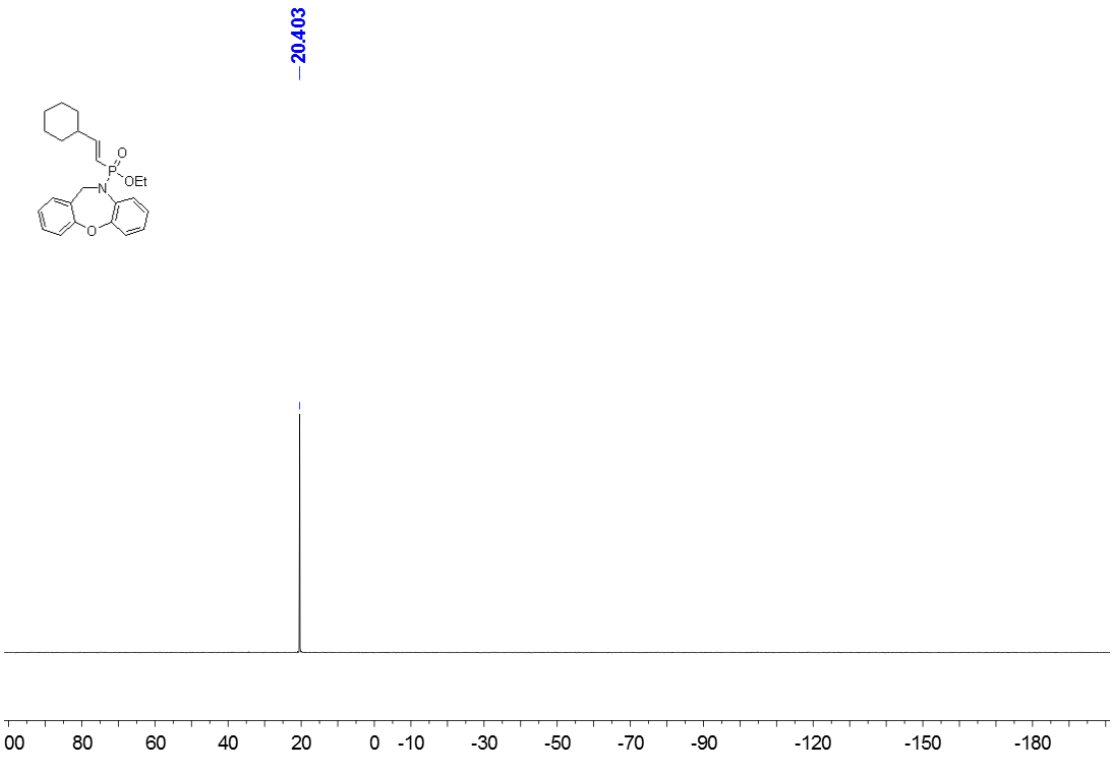
^{31}P NMR Spectrum of Compound **3ea**



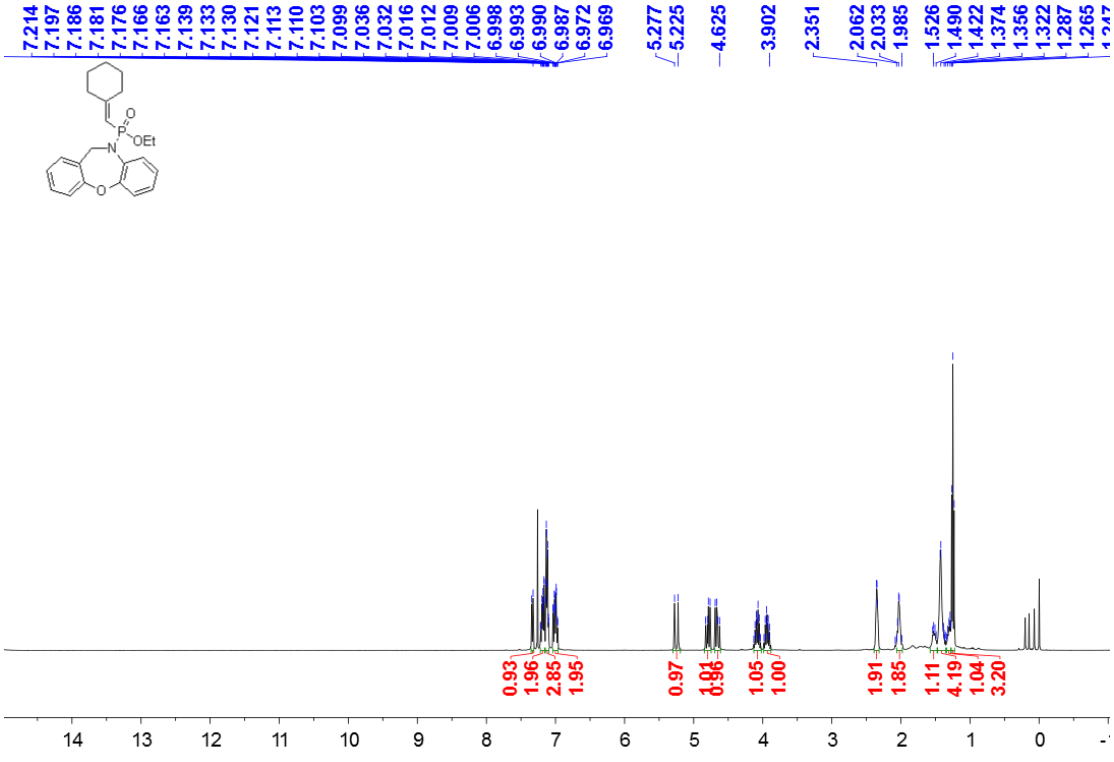
^{1}H NMR Spectrum of Compound **3fa**



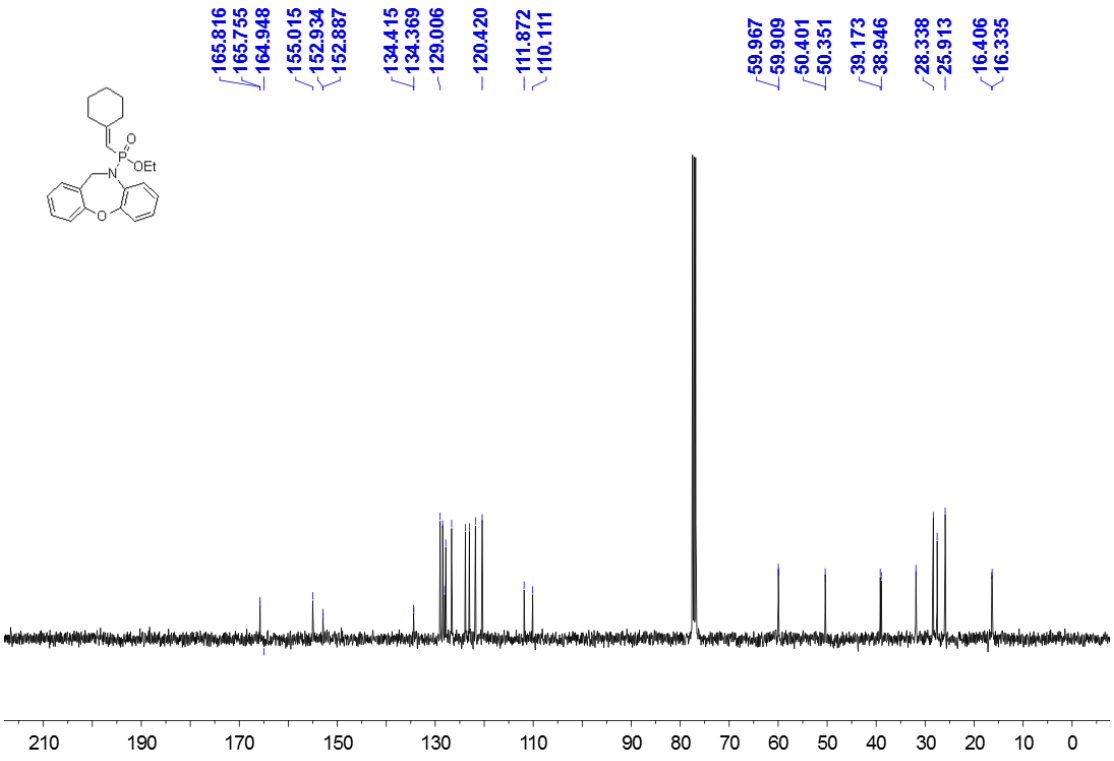
^{13}C NMR Spectrum of Compound **3fa**



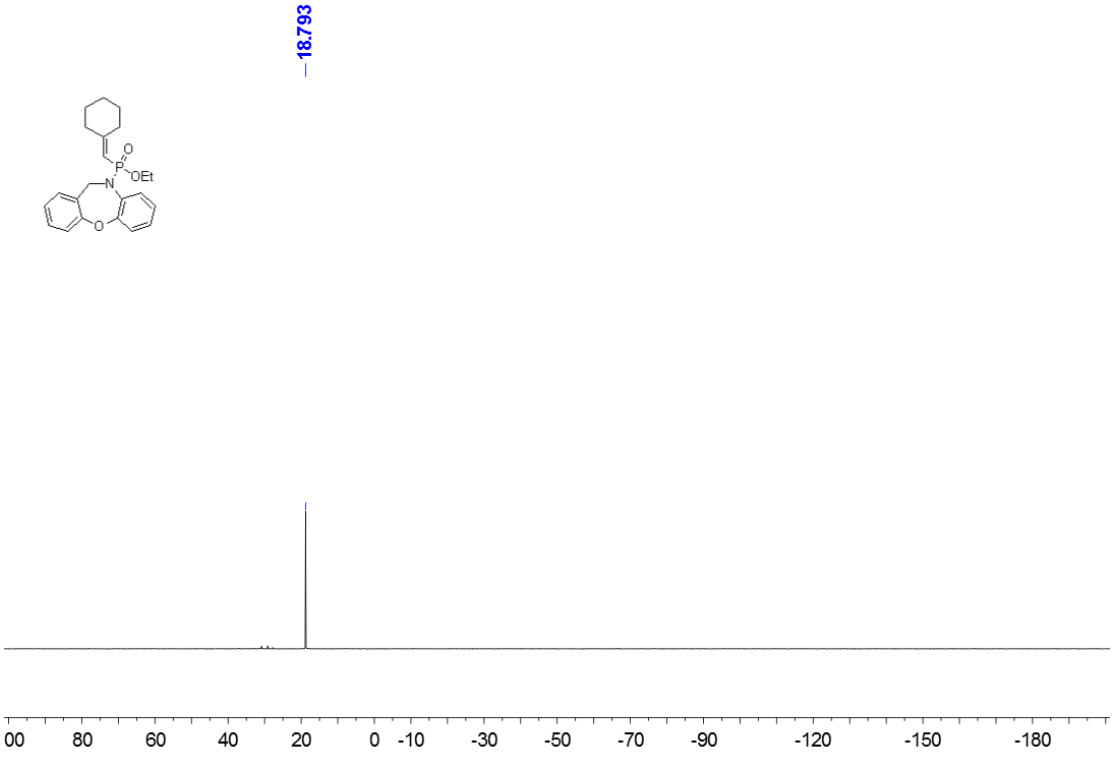
^{31}P NMR Spectrum of Compound **3fa**



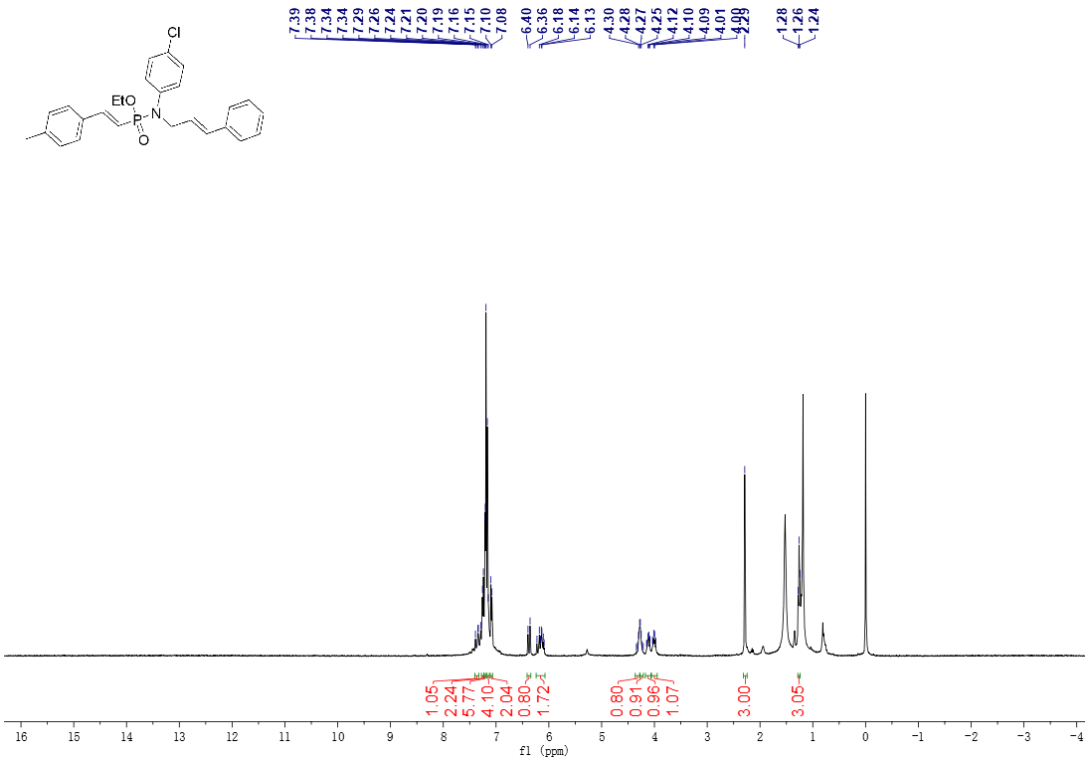
^{1}H NMR Spectrum of Compound **3ga**



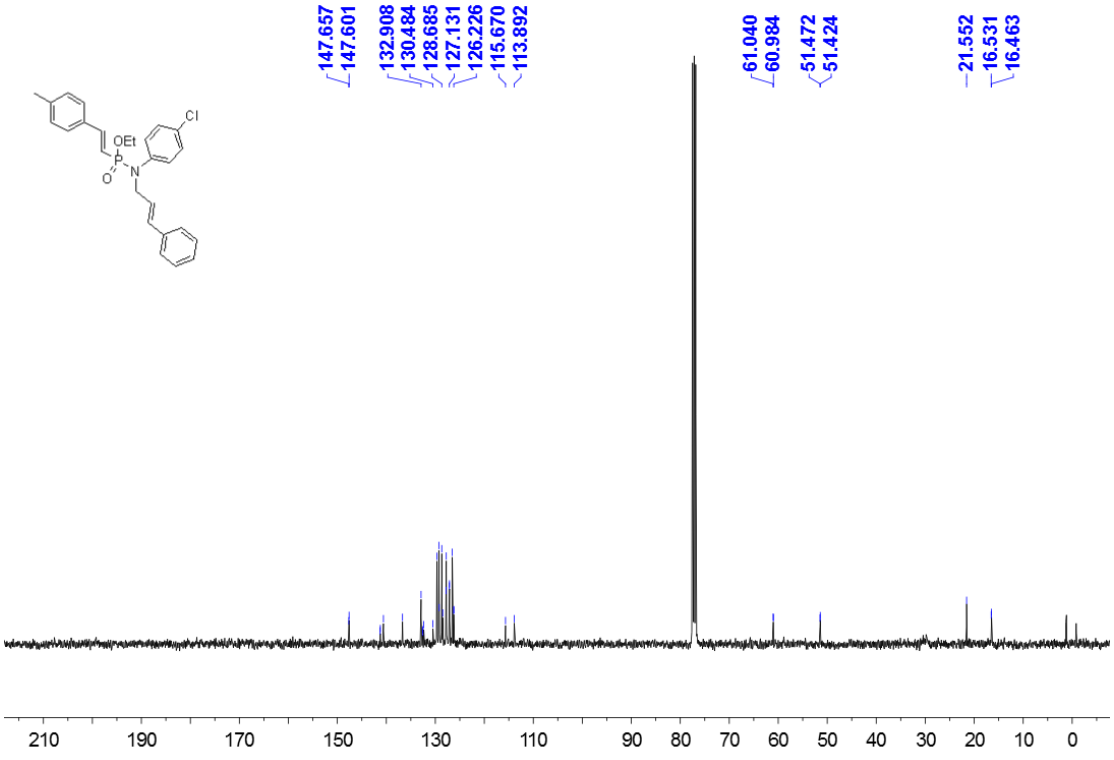
^{13}C NMR Spectrum of Compound **3ga**



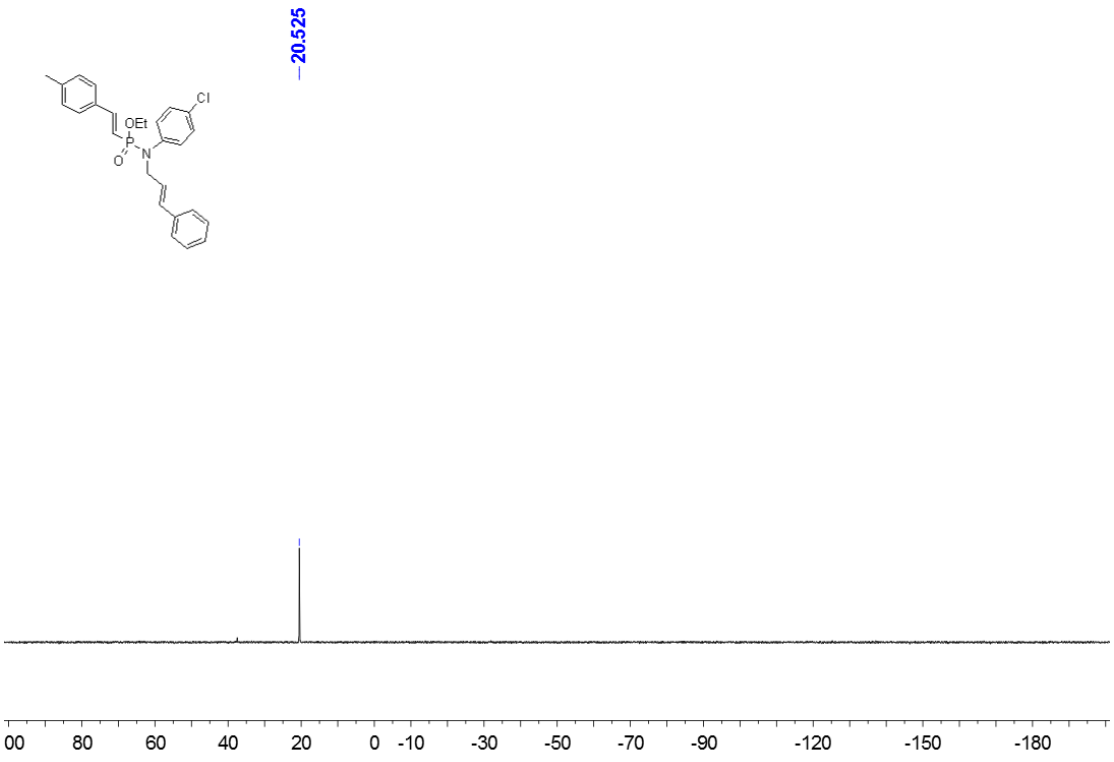
^{31}P NMR Spectrum of Compound **3ga**



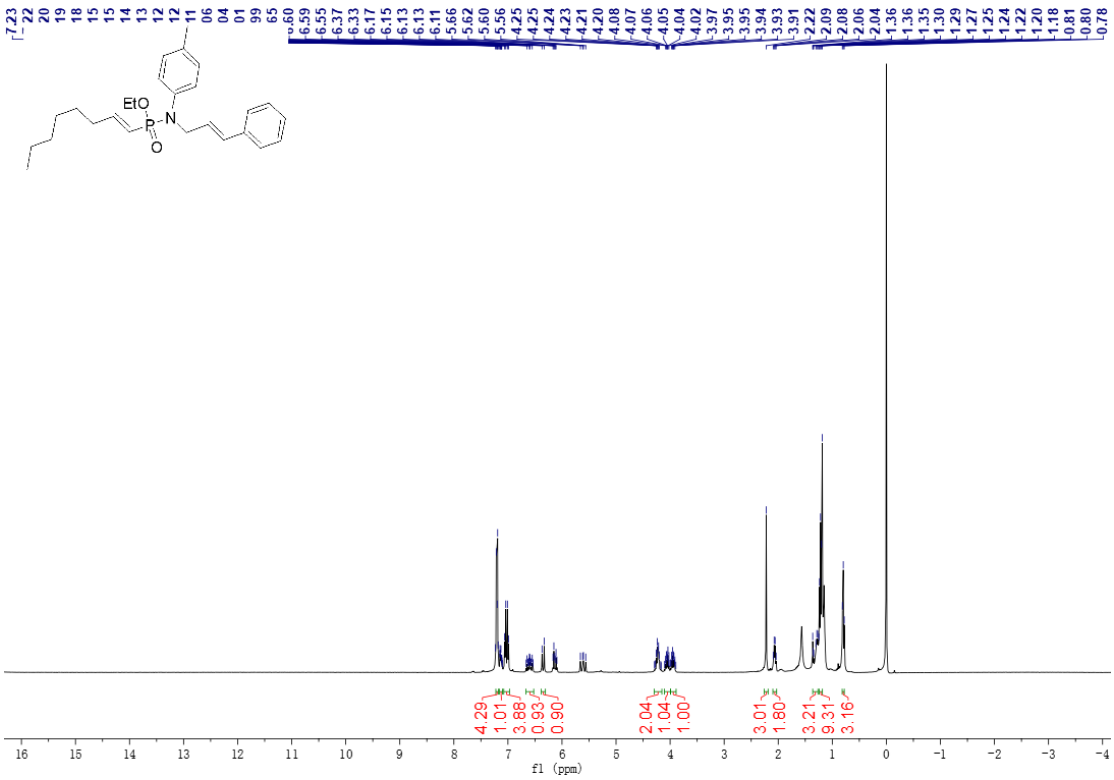
^{1}H NMR Spectrum of Compound **3bC**



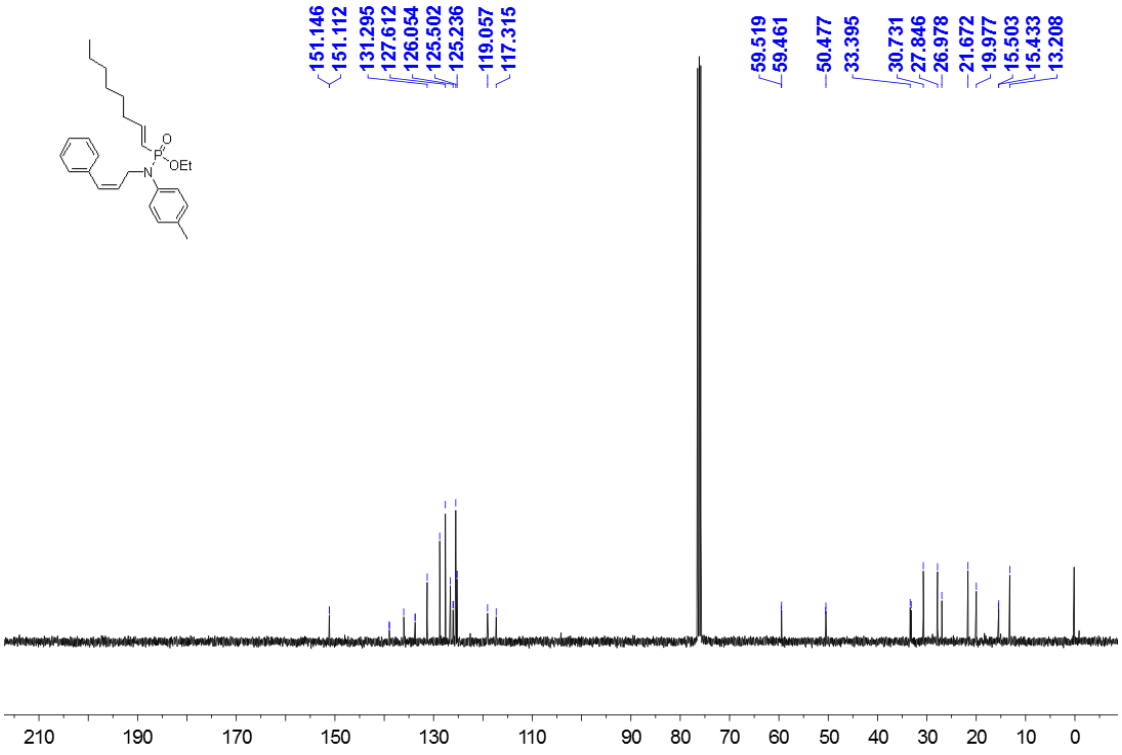
^{13}C NMR Spectrum of Compound **3bC**



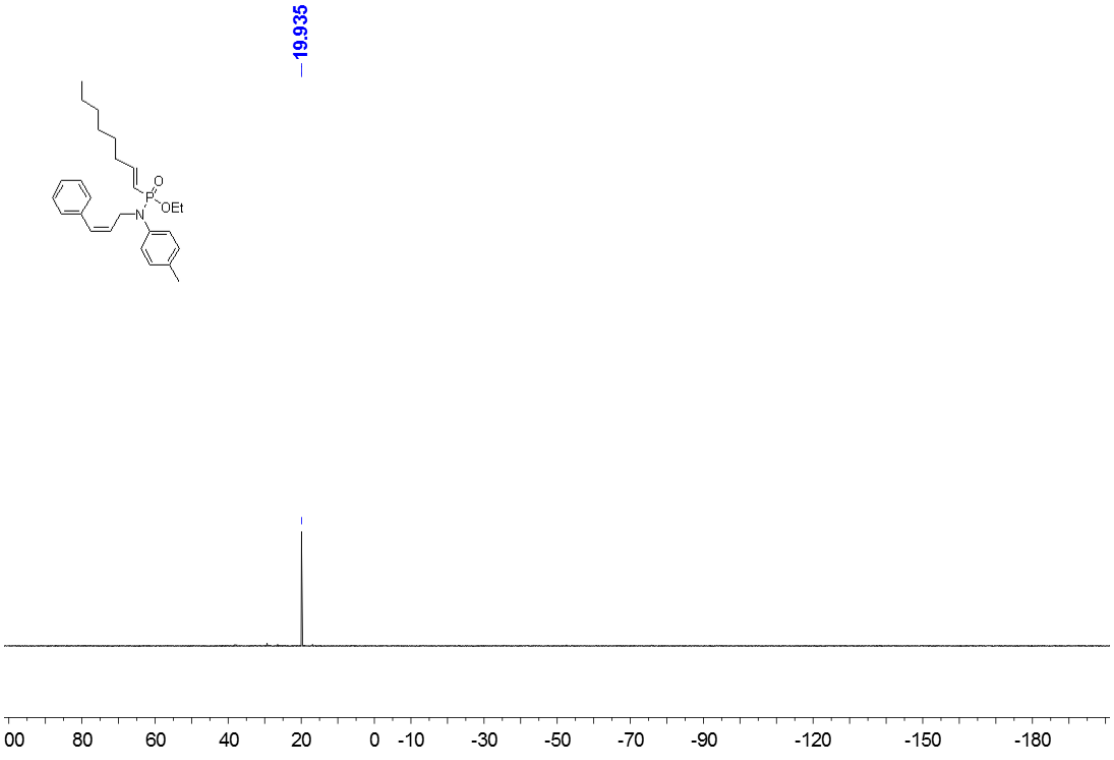
^{31}P NMR Spectrum of Compound **3bC**



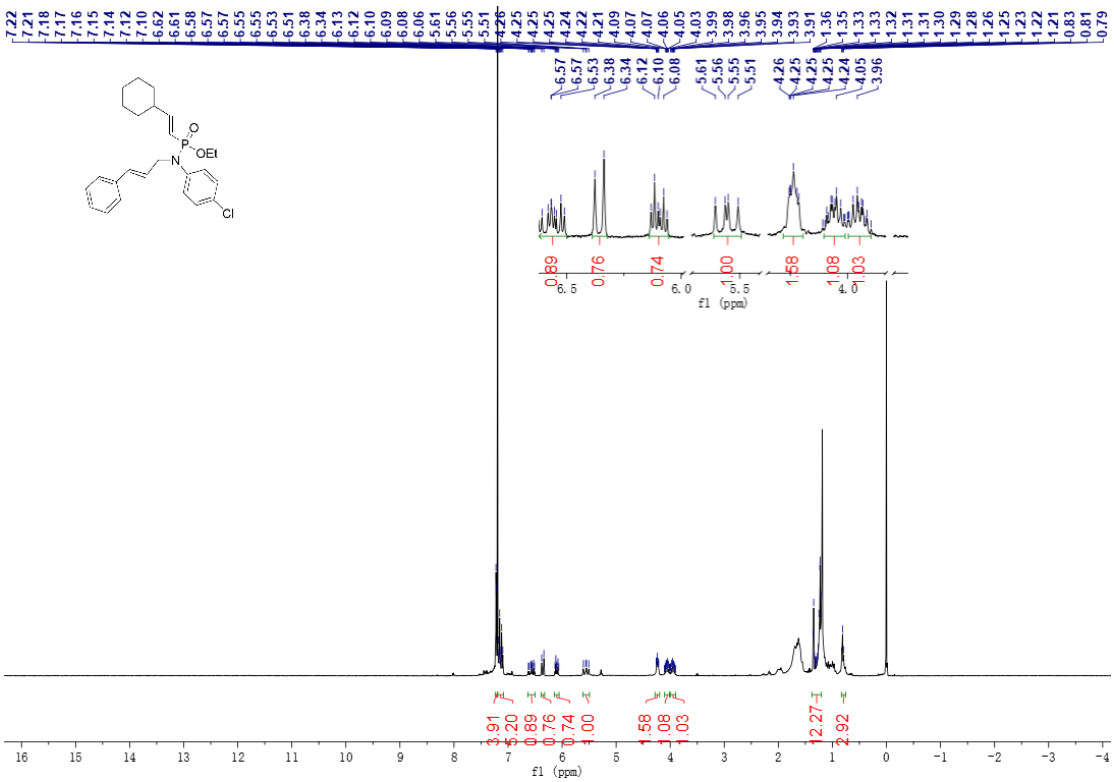
^{1}H NMR Spectrum of Compound **3eP**



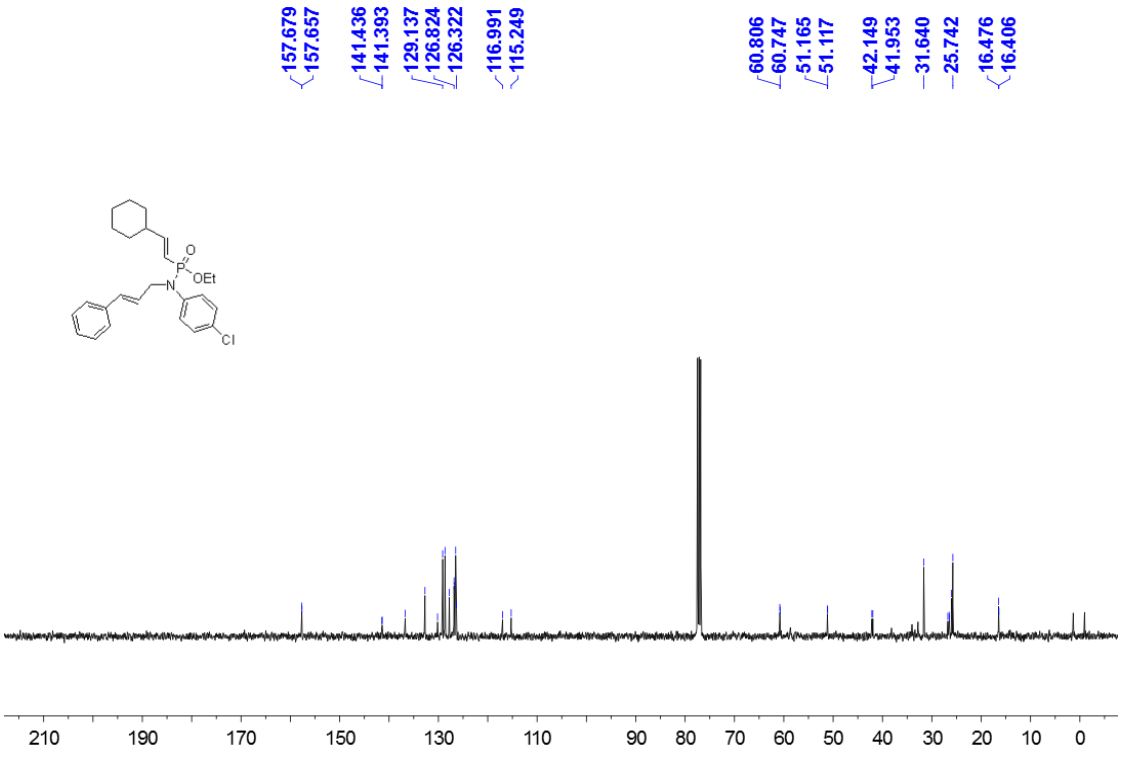
^{13}C NMR Spectrum of Compound **3eP**



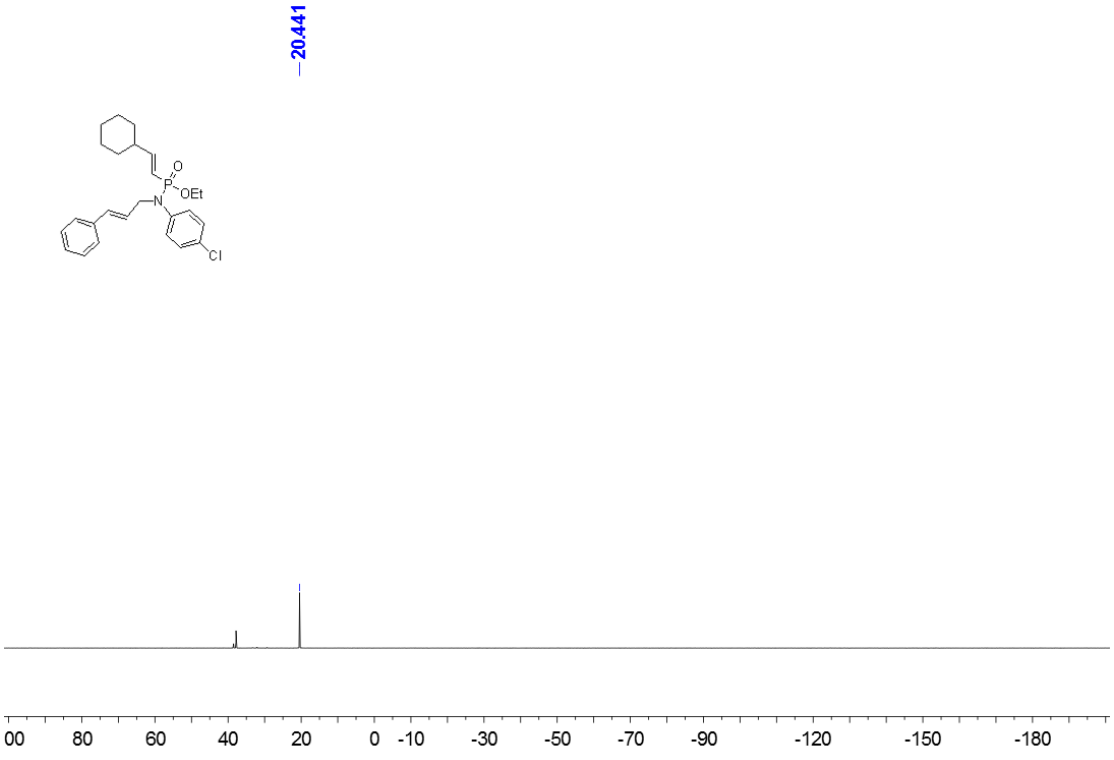
^{31}P NMR Spectrum of Compound **3eP**



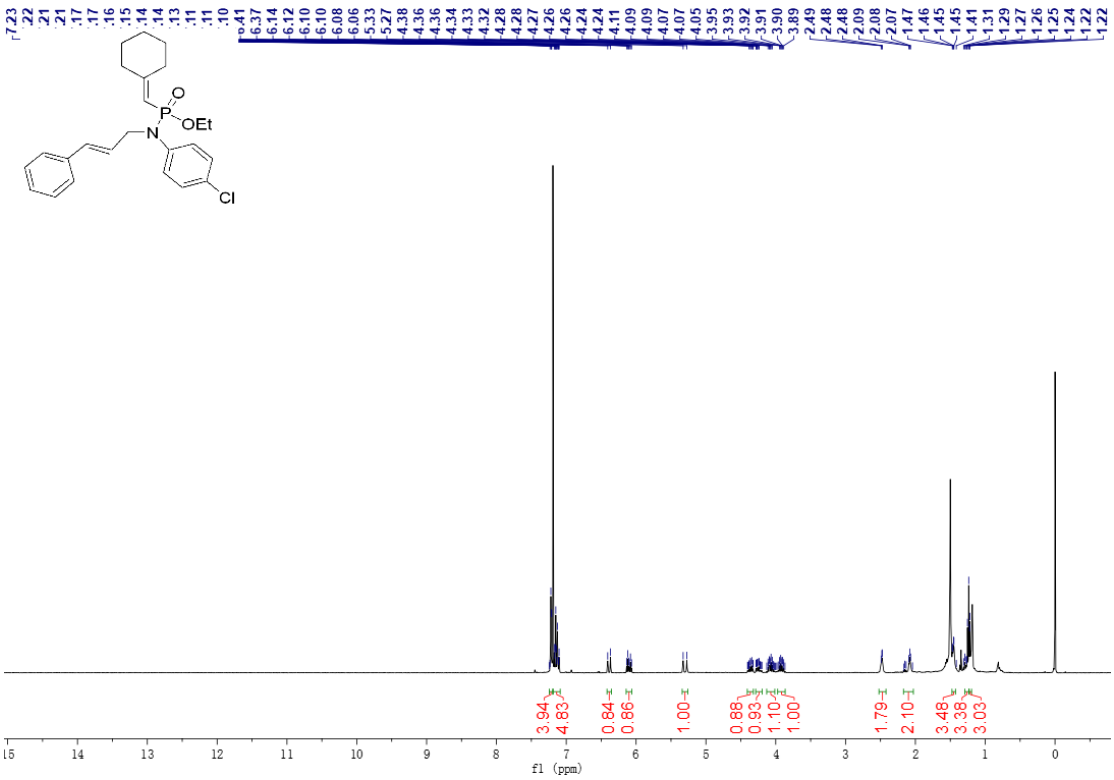
^{1}H NMR Spectrum of Compound **3fC**



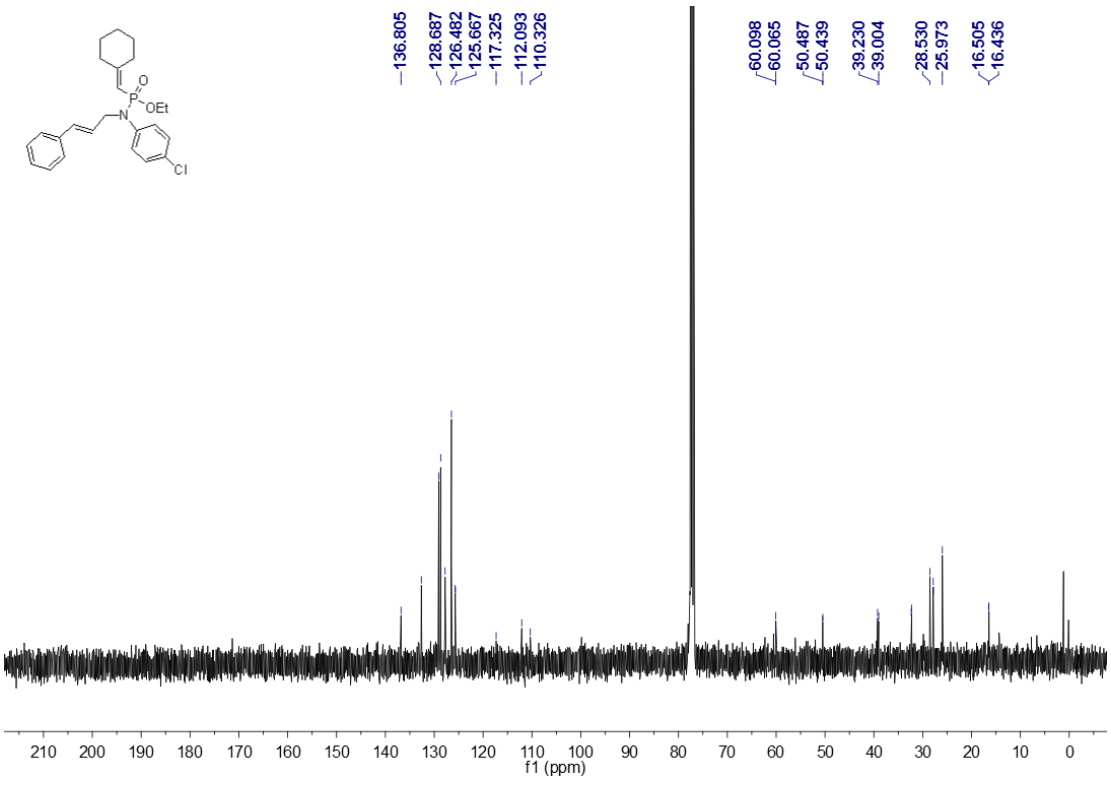
^{13}C NMR Spectrum of Compound **3fC**



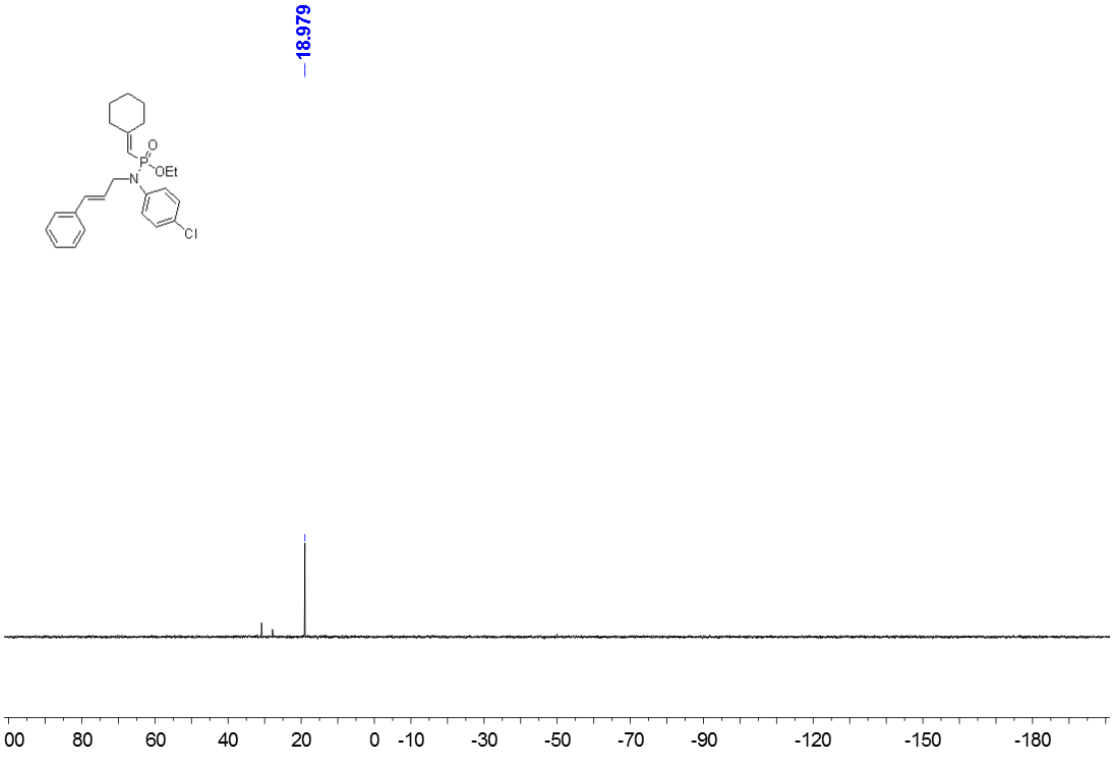
^{31}P NMR Spectrum of Compound **3fC**



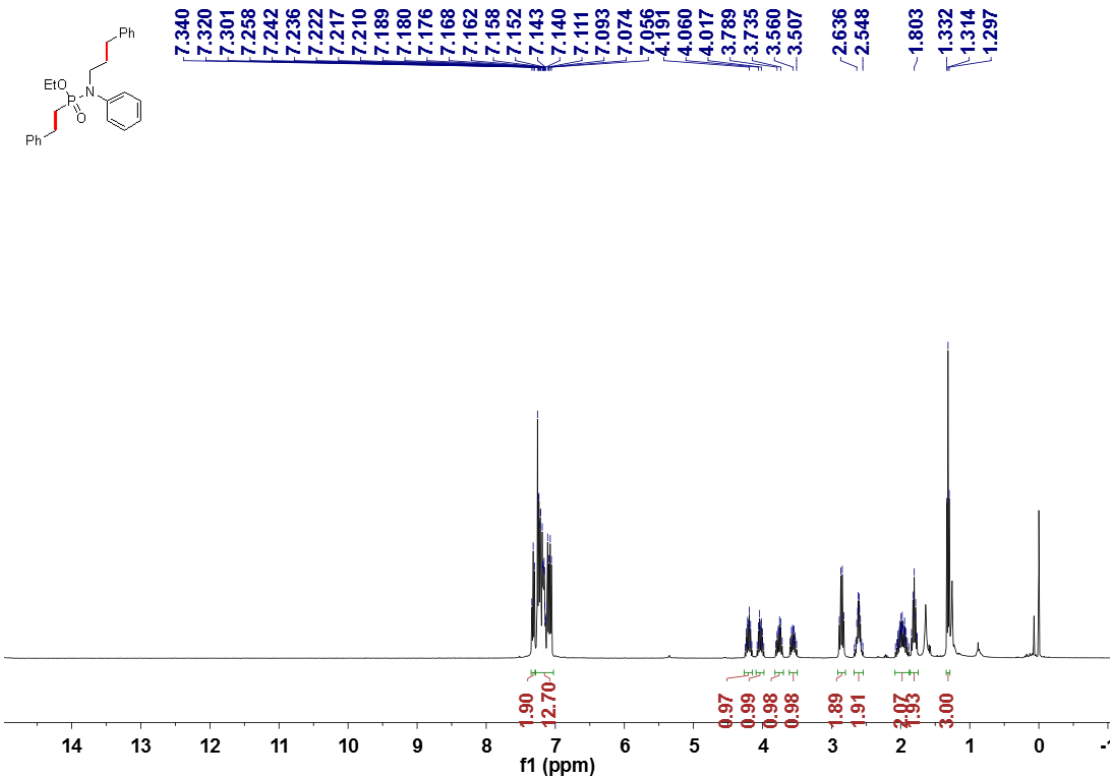
^{1}H NMR Spectrum of Compound **3gC**



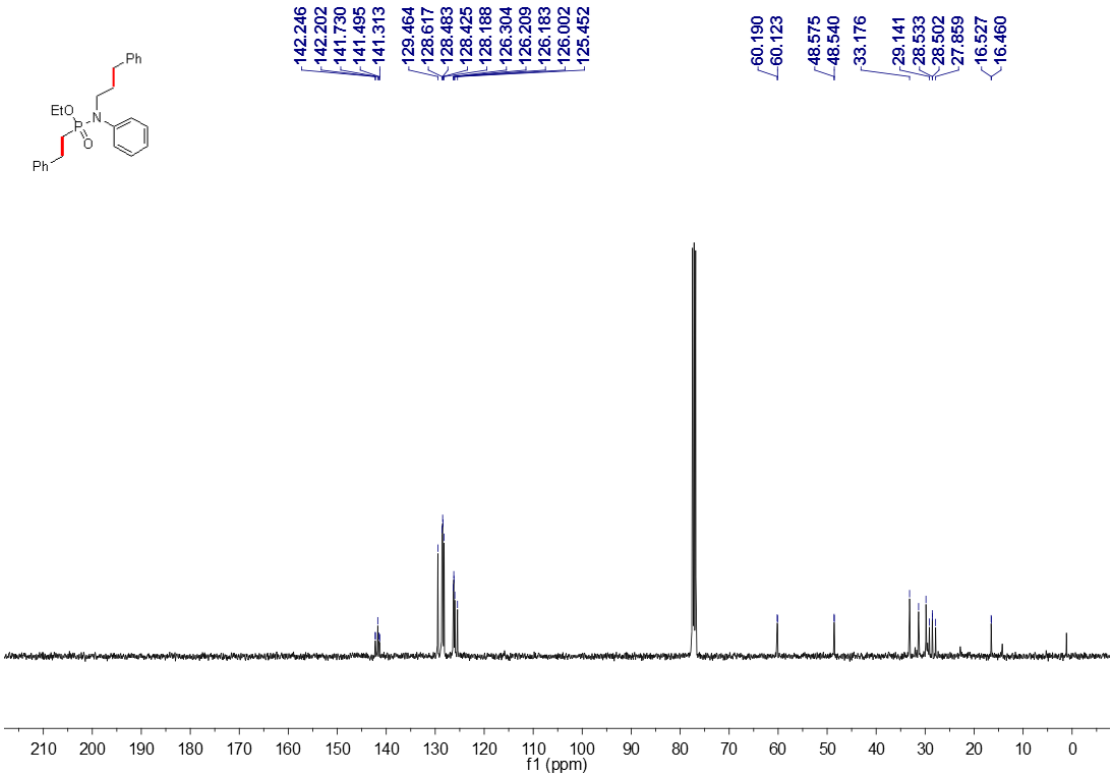
^{31}C NMR Spectrum of Compound **3gC**



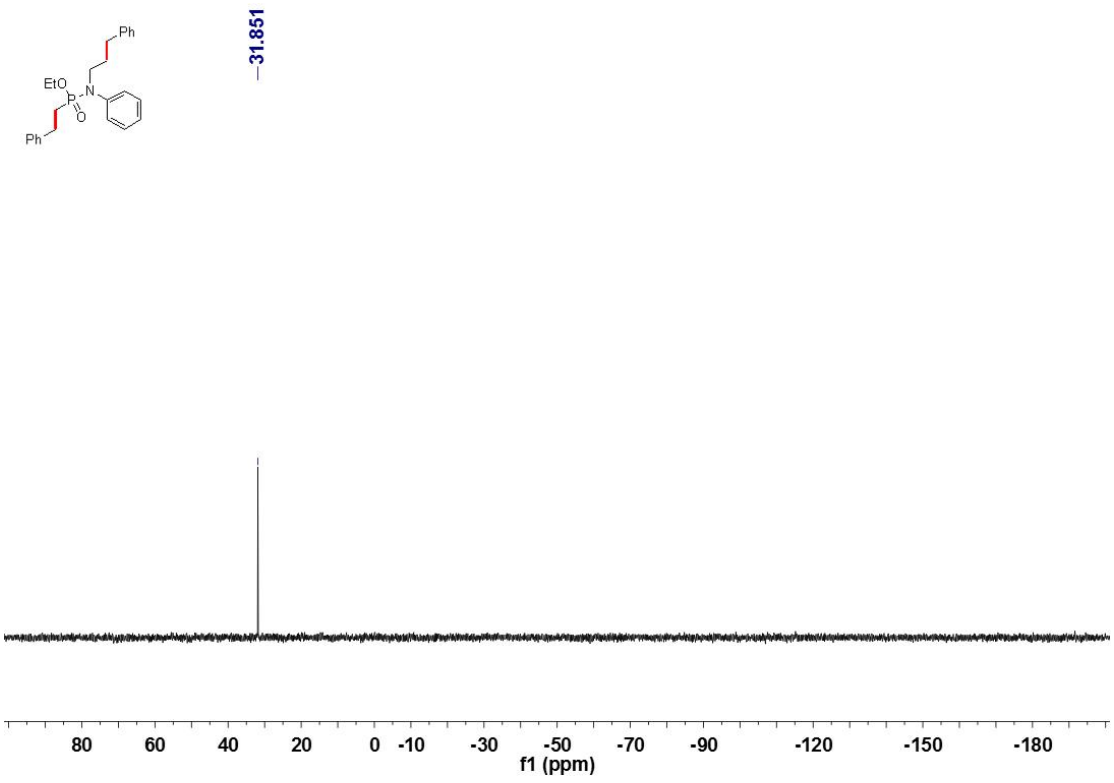
^{31}P NMR Spectrum of Compound **3gC**



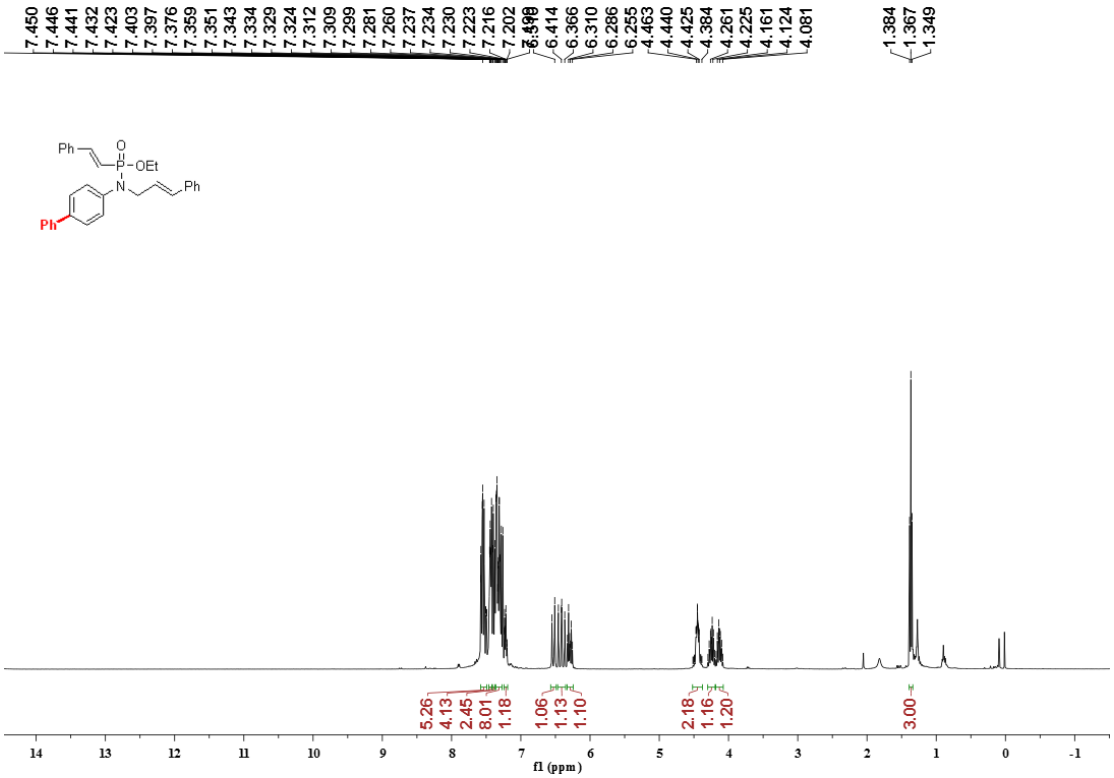
^{1}H NMR Spectrum of Compound **8**



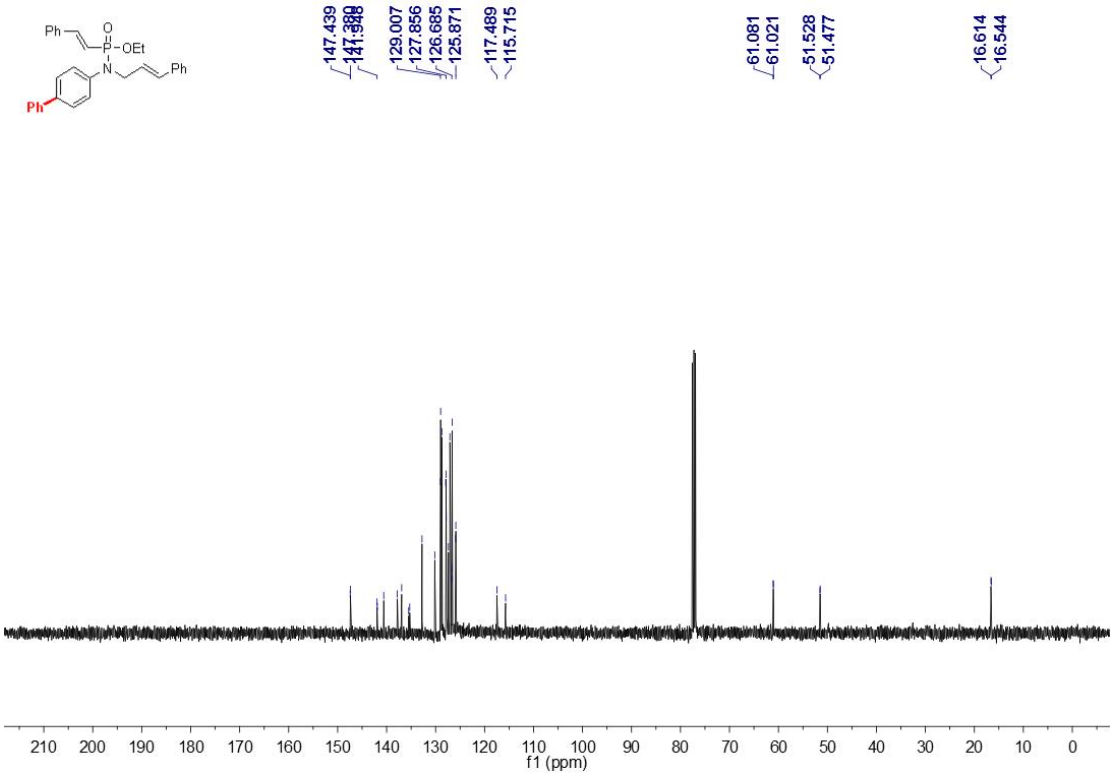
^{13}C NMR Spectrum of Compound **8**



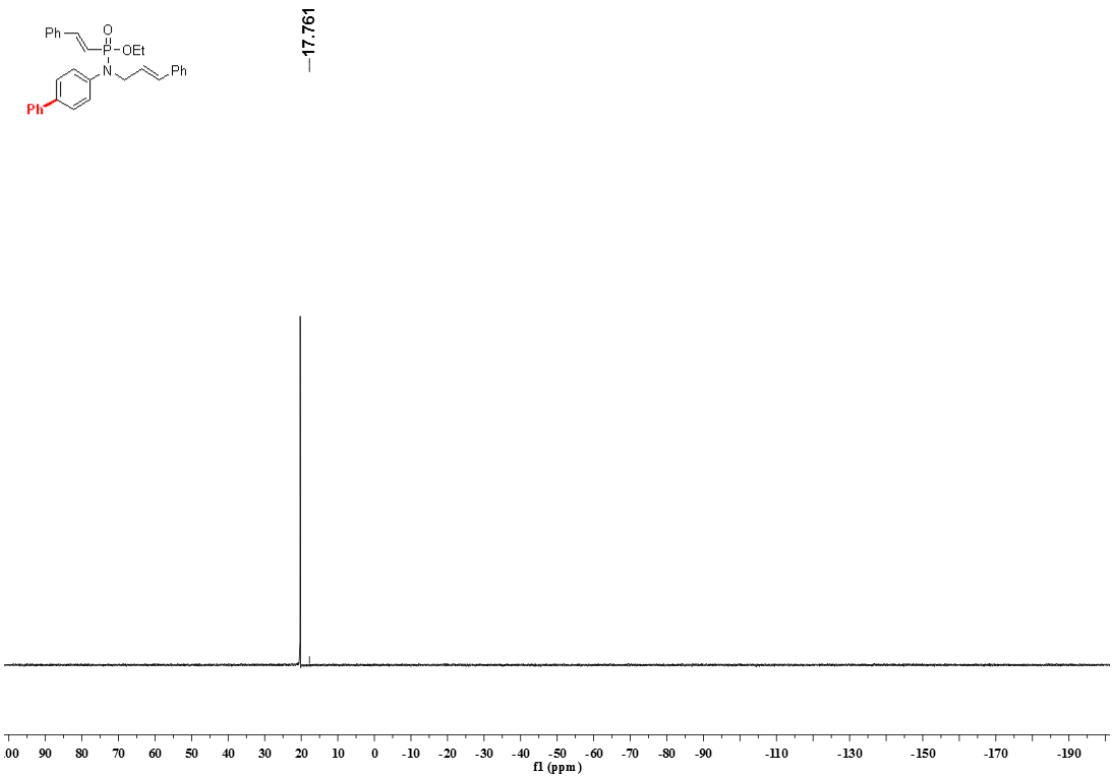
^{31}P NMR Spectrum of Compound **8**



^{1}H NMR Spectrum of Compound **9**



^{13}C NMR Spectrum of Compound **9**



^{31}P NMR Spectrum of Compound **9**