Visible-light-initiated regio- & stereoselective C(sp^2)–H phosphorylation of enamides under transition-metal-free conditions

Ji-Yu Tao,[†a] Qing-Hong Zhang,[†a] Tong-Hao Zhu,[†a,d] Xin-Wen Xu,[†a] Kun Ni,[a] Qiao Zhao,[a] Zheng-Bao Qin,[a] Yu Zhang,[b] Lili Zhao,[a] and Kai Zhao*[a,c]

[a]Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 211816, China. E-mail: ias_kzhao@njtech.edu.cn

[b]College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

[c]Guangdong Provincial Key Laboratory of Catalysis, Southern University of Science and Technology, Shenzhen 518055, China

[d]Institute of Advanced Studies, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, China

[†]These authors contributed equally.

Supporting Information

Table of Contents

General Information

All photoredox-catalyzed reactions in Table 1 and Scheme 2-3 were carried out in oven-dried Schlenk tubes under nitrogen atmosphere using anhydrous solvent purchased from Energy Chemical. All enamides or enecarbamates were prepared using existing methods.[1] Phosphine oxides, dialkyl phosphonates, ethyl phenylphosphinate, eosin Y, *tert*-butyl peroxybenzoate (TBPB) and anhydrous acetonitrile were purchased from Energy Chemical. Melting points were recorded on an electrothermal digital melting point apparatus. ^{1}H, ^{19}F, ^{13}C NMR spectra were recorded in $CDCl_3$ or $(CD_3)_2SO$ on Bruker Avance 400 MHz spectrometers. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), t (triplet), dd (doublet of doublets), m (multiplet); coupling constants (J) are in Hertz (Hz). NMR spectra were taken using TMS (^{1}H, $\delta = 0$), $CDCl_3$ (^{1}H, $\delta = 7.26$), and $CDCl_3$ (^{13}C, CPD $\delta = 77.16$) as the internal standards, respectively. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions.

The photoredox-catalyzed transformations were carried out in a customized dark cassette equipped with three 15 W blue LEDs lamp from different directions for irradiation along with an electronic cooling fan for heat dissipation (**Figure S1**). A magnetic hotplate stirrer was placed in the dark cassette for stirring. The reaction vessel was placed in the center of the stirrer so that the average distance from the lamp to the reaction medium was 10 cm. The 15 W blue LEDs were purchased from Ctech Global Pte Ltd (Singapore) with the maximum absorption wavelength of 460-465 nm. The borosilicate made reaction vessels (Schlenk tubes) were all purchased from Synthware Glassware.

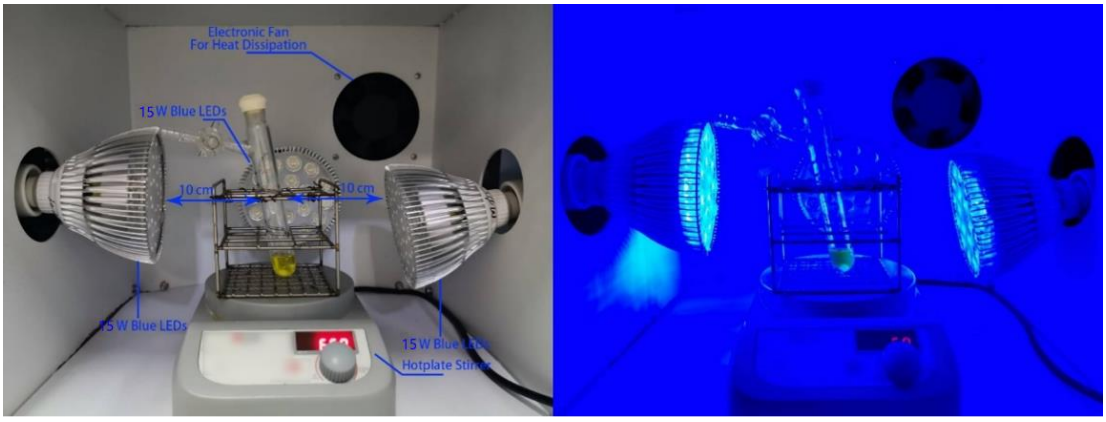
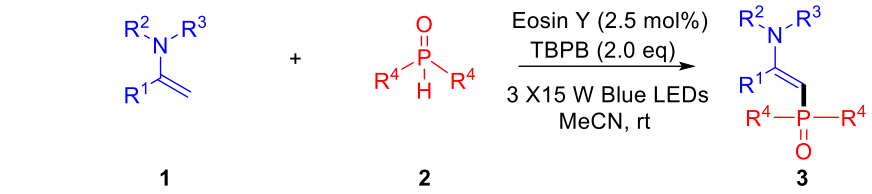


Figure S1 The customized dark cassette equipped with 15 W blue LEDs lamps

Abbreviations: Bn = benzyl, Ac = acetyl, DMF = *N*, *N*-dimethyl formamide, MeCN = acetonitrile, TBPB = *tert*-Butyl peroxybenzoate, Boc = *t*-butoxycarbonyl, TEMPO = 2,2,6,6-tetramethylpiperidinooxy.

General Procedures for the Synthesis of *β*-phosphonylated Enamides

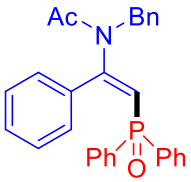


1 **2** **3**

R^1 = 4-BrC_6H_4, 4-$OMeC_6H_4$ 2-furyl, 2-thienyl, alkyl *etc.*
R^2 = Ac, Boc *etc.* R^3 = Bn, Boc, allyl *etc.*
R^4 = aryl, alkyl

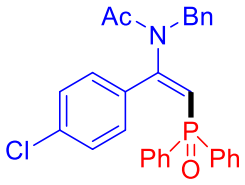
Enamides **1** (0.3 mmol), phosphine oxide **2** (0.45 mmol, 1.5 eq) and Eosin Y (0.0075 mmol, 2.5 mol%) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (120 μL, 0.6 mmol, 2.0 eq) and MeCN (1.5 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 15 W blue LEDs irradiation. Upon completion of the reactions as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash column chromatography using dichloromethane/methanol (100:1 *v*/*v*) as eluent to afford pure products **3**.

Analytical Data for the *β*-phosphorylated Enamides



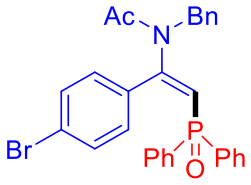
3aa

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (3aa):** 67.7 mg, 75% yield. (0.2 mmol scale) Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* ppm 7.47-7.43 (m, 4H), 7.43-7.42 (m, 2H), 7.41-7.36 (m, 2H), 7.34-7.30 (m, 4H), 7.29-7.26 (m, 4H), 5.97 (d, *J* = 15.3 Hz, 1H), 4.68 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* ppm 170.53, 156.14 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.04, 134.18 (d, $J_{C\text{-}P}$ = 3.5 Hz), 133.37 (d, $J_{C\text{-}P}$ = 107.6 Hz), 131.52, 131.14 (d, $J_{C\text{-}P}$ = 81.5 Hz), 130.80, 130.70, 129.67, 128.84, 128.58 (d, $J_{C\text{-}P}$ = 33.3 Hz), 128.43 (d, $J_{C\text{-}P}$ = 19.7 Hz), 127.72, 120.53 (d, $J_{C\text{-}P}$ = 98.5 Hz), 50.37, 23.21. ^{31}P NMR (162 MHz, $CDCl_3$) *δ* ppm 18.94. HRMS m/z: calcd for $C_{29}H_{27}NO_2P^+$ $[M+H]^+$ 452.1774, found: 452.1779.



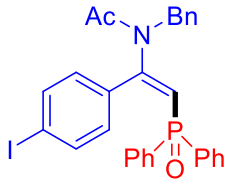
3ba

***(E)*-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (3ba):** 121.0 mg, 83% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47-7.38 (m, 9H), 7.35-7.26 (m, 7H), 7.24-7.19 (m, 2H), 7.13-7.09 (m, 2H), 5.89 (d, J = 15.5 Hz, 1H), 4.58 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.38, 155.81 (d, $J_{C\text{-}P}$ = 7.2 Hz), 135.57, 133.78, 133.73, 133.16 (d, $J_{C\text{-}P}$ = 91.6 Hz), 131.75, 131.32 (d, $J_{C\text{-}P}$ = 80.4 Hz), 130.77, 130.67, 130.38, 129.67, 128.70 (d, $J_{C\text{-}P}$ = 35.1 Hz), 128.55 (d, $J_{C\text{-}P}$ = 21.1 Hz), 121.00 (d, $J_{C\text{-}P}$ = 97.2 Hz), 49.38, 23.03. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.82. HRMS m/z: calcd for $C_{29}H_{26}ClNO_2P^+$ $[M+H]^+$ 486.1384, found: 486.1388.



3ca

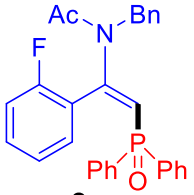
***(E)*-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (3ca):** 135.3 mg, 85% yield. Yellow solid. m.p. = 132–133 °C. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.75-7.66 (m, 2H), 7.54-7.47 (m, 2H), 7.46-7.39 (m, 6H), 7.35-7.32 (m, 6H), 7.32-7.24 (m, 1H), 7.21-7.16 (m, 2H). 5.97 (d, J = 15.4 Hz, 1H), 4.66 (s, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.43, 154.81 (d, $J_{C\text{-}P}$ = 7.1 Hz), 136.86, 133.20 (d, $J_{C\text{-}P}$ = 104.6 Hz), 133.10 (d, $J_{C\text{-}P}$ = 3.3 Hz), 132.68 (d, $J_{C\text{-}P}$ = 5.4 Hz), 131.78 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.42 (d, $J_{C\text{-}P}$ = 35.4 Hz), 130.87, 130.77, 129.07, 128.95, 128.87, 128.64 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.89, 125.44, 121.44 (d, $J_{C\text{-}P}$ = 98.2 Hz), 50.31, 23.19. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.38. HRMS m/z: calcd for $C_{29}H_{26}BrNO_2P^+$ $[M+H]^+$ 530.0879, found: 530.0888.



3da

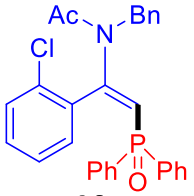
***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-iodophenyl)vinyl)acetamide (3da):** 143.8 mg, 83%

yield. White soild. m.p. = 128–129 ºC. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.56-7.54 (m, 2H), 7.46-7.39 (m, 6H), 7.37-7.29 (m, 7H), 7.21-7.16 (m, 2H), 7.14-7.10 (m, 2H), 5.95 (d, J = 15.4 Hz, 1H), 4.65 (s, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.56, 155.05 (d, $J_{C\text{-}P}$ = 6.9 Hz), 137.55, 136.79, 133.59 (d, $J_{C\text{-}P}$ = 3.4 Hz), 132.83 (d, $J_{C\text{-}P}$ = 78.7 Hz), 132.81, 131.84 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.20, 130.90, 130.80, 130.02, 128.85, 128.84, 128.65 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.08 (d, $J_{C\text{-}P}$ = 44.8 Hz), 121.09 (d, $J_{C\text{-}P}$ = 98.4 Hz), 97.75, 50.25, 23.19. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.09. HRMS m/z: calcd for $C_{29}H_{26}INO_2P^+$ $[M+H]^+$ 578.0740, found: 578.0745.



3ea

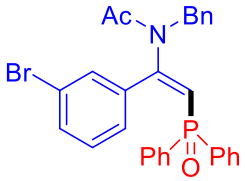
***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(2-fluorophenyl)vinyl)acetamide (3ea):** 131.0 mg, 93% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm δ 7.51-7.40 (m, 8H), 7.35-7.30 (m, 7H), 7.18-7.16 (m, 2H), 7.09-7.05 (m, 1H), 6.83-6.78 (m, 1H), 6.13 (d, J = 16.1 Hz, 1H), 4.58 (s, 2H), 2.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.30, 160.03 (d, $J_{C\text{-}F}$ = 251.5 Hz), 151.25 (d, $J_{C\text{-}F}$ = 7.1 Hz), 137.06, 133.64, 132.89 (d, $J_{C\text{-}P}$ = 74.3 Hz), 132.60, 130.73, 131.30 (d, $J_{C\text{-}P}$ = 90.3 Hz), 130.80 (d, $J_{C\text{-}F}$ = 9.9 Hz), 128.77, 128.66, 128.55, 127.68, 124.02 (d, $J_{C\text{-}F}$ = 3.7 Hz), 123.40 (d, $J_{C\text{-}P}$ = 98.6 Hz), 122.20, 115.65 (d, $J_{C\text{-}F}$ = 21.4 Hz), 49.67, 23.08 (d, $J_{C\text{-}F}$ = 2.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -111.75. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.41. HRMS m/z: calcd for $C_{29}H_{26}FNO_2P^+$ $[M+H]^+$ 470.1680, found:470.1671.



3fa

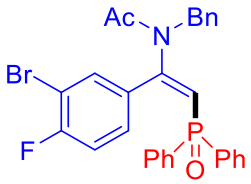
***(E)*-*N*-benzyl-*N*-(1-(2-chlorophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (3fa):** 118.1 mg, 81% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.59-7.55 (m, 4H), 7.52-7.49 (m, 1H), 7.40-7.36 (m, 2H), 7.33-7.27 (m, 5H), 7.26-7.24 (m, 2H), 7.20-7.12 (m, 2H), 7.10-7.08 (m, 2H), 7.00-6.98 (m, 1H), 6.34 (d, J =

14.6 Hz, 1H), 4.52 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.96, 137.02, 135.27 (d, $J_{C\text{-}P}$ = 0.9 Hz), 132.77 (d, $J_{C\text{-}P}$ = 62.1 Hz), 132.61 (d, $J_{C\text{-}P}$ = 0.9 Hz), 132.50, 131.58-131.57 (m), 129.94 (d, $J_{C\text{-}P}$ = 38.5 Hz), 128.74, 128.56, 128.44, 128.41, 127.64 (d, $J_{C\text{-}P}$ = 15.3 Hz), 126.64, 121.20 (d, $J_{C\text{-}P}$ = 102.6 Hz), 50.30, 23.72. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.93. HRMS m/z: calcd for $C_{29}H_{26}ClNO_2P^+$ $[M+H]^+$ 486.1384, found: 486.1389.



3ga

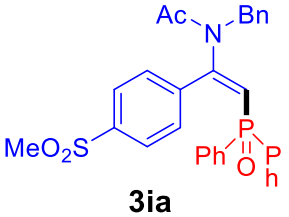
***(E)*-*N*-benzyl-*N*-(1-(3-bromophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (3ga):** 141.6 mg, 89% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.50-7.44 (m, 5H), 7.42-7.36 (m, 5H), 7.35-7.29 (m, 6H), 7.21-7.19 (m, 2H), 7.09-7.07 (m, 1H), 6.06 (d, J = 14.8 Hz, 1H), 4.67 (s, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.61, 154.54 (d, $J_{C\text{-}P}$ = 7.4 Hz), 136.84, 136.39 (d, $J_{C\text{-}P}$ = 3.4 Hz), 133.68, 133.17, 132.89 (d, $J_{C\text{-}P}$ = 108.3 Hz), 131.95, 131.85, 131.82, 130.87, 130.78, 130.15, 129.89, 128.92, 128.85, 128.82, 128.72, 128.60, 128.44, 128.01, 127.96, 122.04 (d, $J_{C\text{-}P}$ = 105.0 Hz), 50.63, 23.35. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.57. HRMS m/z: calcd for $C_{29}H_{26}BrNO_2P^+$ $[M+H]^+$ 530.0879, found: 530.0869.



3ha

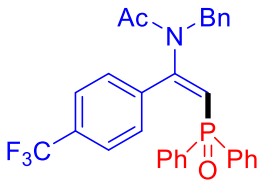
***(E)*-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-2-(diphenylphosphoryl)vinyl) acetamide (3ha):** 106.9 mg, 65% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.55-7.51 (m, 1H), 7.49-7.41 (m, 6H), 7.40-7.36 (m, 1H), 7.36-7.30 (m, 7H), 7.21-7.17 (m, 2H), 6.96-6.90 (m, 1H), 6.05 (d, J = 14.8 Hz, 1H), 4.67 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.41, 160.22 (d, $J_{C\text{-}F}$ = 252.9 Hz), 153.49 (d, $J_{C\text{-}P}$ = 6.9 Hz), 136.68, 134.42, 132.90 (d, $J_{C\text{-}P}$ = 107.9 Hz), 131.92, 131.88, 131.84 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.06 (d, $J_{C\text{-}F}$ = 7.8 Hz), 130.77, 130.67, 128.74 (d, $J_{C\text{-}P}$ = 33.1 Hz), 128.71, 128.70, 127.98, 122.08

(d, J_{C-P} = 97.7 Hz), 116.25 (d, J_{C-F} = 22.9 Hz), 109.29 (d, J_{C-F} = 21.6 Hz), 50.56, 23.27. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -103.16. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.69. HRMS m/z: calcd for $C_{29}H_{25}BrFNO_2P^+$ $[M+H]^+$ 548.0785, found: 548.0777.



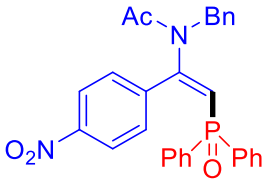
3ia

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-(methylsulfonyl)phenyl)vinyl) acetamide (3ia):** 139.8 mg, 88% yield. White solid. m.p. = 113–116 ºC. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.83-7.73 (m, 2H), 7.64-7.54 (m, 2H), 7.46-7.40 (m, 6H), 7.37-7.30 (m, 7H), 7.19-7.14 (m, 2H), 6.13 (d, J = 15.2 Hz, 1H), 4.64 (s, 2H), 3.00 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.30, 153.67 (d, J_{C-P} = 6.6 Hz), 142.02, 139.63 (d, J_{C-P} = 3.6 Hz), 136.52, 132.90 (d, J_{C-P} = 108.0 Hz), 131.98 (d, J_{C-P} = 2.8 Hz), 130.86, 130.76, 130.69, 128.98, 128.75 (d, J_{C-P} = 12.3 Hz), 128.74, 128.05, 127.28, 124.63 (d, J_{C-P} = 96.4 Hz), 50.38, 44.38, 23.17. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.91. HRMS m/z: calcd for $C_{30}H_{29}NO_4PS^+$ $[M+H]^+$ 530.1549, found: 530.1544.



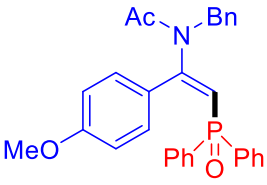
3ja

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)vinyl) acetamide (3ja):** 93.6 mg, 60% yield. Yellow solid. m.p. = 141–142 ºC. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51-7.49 (m, 2H), 7.46-7.40 (m, 8H), 7.35-7.29 (m, 7H), 7.20-7.17 (m, 2H), 6.10 (d, J = 15.1 Hz, 1H), 4.66 (s, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.47, 154.43 (d, J_{C-P} = 6.9 Hz), 137.80 (d, J_{C-P} = 2.6 Hz), 136.73, 132.86 (d, J_{C-P} = 108.3 Hz), 132.47, 132.14, 131.92 (d, J_{C-P} = 2.8 Hz), 130.84 (d, J_{C-P} = 9.8 Hz), 130.16, 128.94, 128.80, 128.76, 128.64, 126.16 (q, J_{C-F} = 270.5 Hz), 125.31 (q, J_{C-F} = 3.7 Hz), 122.70 (d, J_{C-P} = 97.5 Hz), 50.40, 23.26. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -62.96. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.16. HRMS m/z: calcd for $C_{30}H_{26}F_3NO_2P^+$ $[M+H]^+$ 520.1648, found: 520.1639.



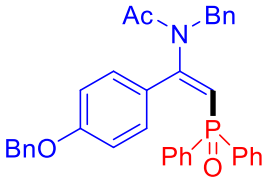
3ka

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-nitrophenyl)vinyl)acetamide (3ka):** 59.6 mg, 40% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09-8.06 (m, 2H), 7.57-7.54 (m, 2H), 7.47-7.40 (m, 6H), 7.37-7.32 (m, 7H), 7.18-7.16 (m, 2H), 6.14 (d, J = 15.2 Hz, 1H), 4.66 (s, 2H), 2.12 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.34, 153.32 (d, $J_{C\text{-}P}$ = 6.4 Hz), 148.80, 140.51 (d, $J_{C\text{-}P}$ = 3.4 Hz), 136.48, 132.78 (d, $J_{C\text{-}P}$ = 108.0 Hz), 132.12 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.89, 130.82, 130.79, 128.92 (d, $J_{C\text{-}P}$ = 28.4 Hz), 128.90, 128.15, 124.00 (d, $J_{C\text{-}P}$ = 95.7 Hz), 123.44, 50.41, 23.20. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.91. HRMS m/z: calcd for $C_{29}H_{26}N_2O_4P^+$ $[M+H]^+$ 497.1625, found: 497.1631.



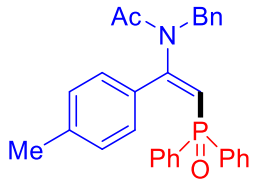
3la

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-methoxyphenyl)vinyl)acetamide (3la):** 78.0 mg, 54% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48-7.43 (m, 3H), 7.42-7.38 (m, 5H), 7.35-7.27 (m, 7H), 7.22-7.20 (m, 2H), 6.73 (d, J = 8.8 Hz, 2H), 5.80 (d, J = 15.7 Hz, 1H), 4.70 (s, 2H), 3.76 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.71, 161.70, 156.01 (d, $J_{C\text{-}P}$ = 7.3 Hz), 137.25, 133.67 (d, $J_{C\text{-}P}$ = 107.6 Hz), 131.58 (d, $J_{C\text{-}P}$ = 3.2 Hz), 131.49, 130.92, 130.83, 129.01, 128.64 (d, $J_{C\text{-}P}$ = 30.7 Hz), 128.61, 127.76, 126.53 (d, $J_{C\text{-}P}$ = 3.4 Hz), 118.62 (d, $J_{C\text{-}P}$ = 99.8 Hz), 113.85, 100.03, 55.44, 50.51, 23.25. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.38. HRMS m/z: calcd for $C_{30}H_{29}NO_3P^+$ $[M+H]^+$ 482.1880, found: 482.1872.



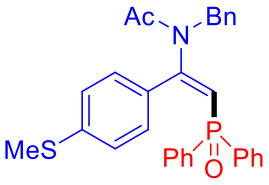
3ma

***(E)*-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-2-(diphenylphosphoryl)vinyl)acetamide (3ma):** 150.6 mg, 90% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.74-7.68 (m, 1H), 7.58-7.48 (m, 2H), 7.46-7.43 (m, 3H), 7.41-7.39 (m, 6H), 7.38-7.37 (m, 2H), 7.33-7.31 (m, 4H), 7.29-7.27 (m, 2H), 7.22-7.20 (m, 2H), 6.81-6.79 (m, 1H), 5.81 (d, J = 15.7 Hz), 5.02 (s, 2H), 4.69 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.68, 160.87, 155.96 (d, $J_{C\text{-}P}$ = 7.2 Hz), 136.85 (d, $J_{C\text{-}P}$ = 67.6 Hz), 133.54 (d, $J_{C\text{-}P}$ = 107.5 Hz), 132.70 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.57, 131.12 (d, $J_{C\text{-}P}$ = 68.1 Hz), 130.88, 129.08, 128.97, 128.76, 128.73, 128.58, 128.46, 128.23, 127.74, 127.54, 126.75, 118.68 (d, $J_{C\text{-}P}$ = 100.5 Hz), 114.66, 70.07, 50.51, 23.03.^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.29. HRMS m/z: calcd for $C_{36}H_{33}NO_3P^+$ $[M+H]^+$ 558.2193, found: 558.2181.



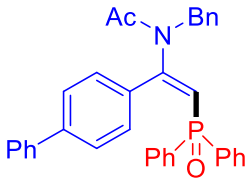
3na

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(p-tolyl)vinyl)acetamide (3na):** 88.0 mg, 63% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.47-7.37 (m, 7H), 7.34-7.32 (m, 5H), 7.30 (d, J = 2.2 Hz, 3H), 7.22-7.20 (m, 2H), 7.02 (d, J = 7.9 Hz, 2H), 5.85 (d, J = 15.8 Hz, 1H), 4.67 (s, 2H), 2.28 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.61, 156.22 (d, $J_{C\text{-}P}$ = 7.3 Hz), 141.27, 137.22, 133.65 (d, $J_{C\text{-}P}$ = 107.8 Hz), 131.56 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.24 (d, $J_{C\text{-}P}$ = 3.4 Hz), 130.88 (d, $J_{C\text{-}P}$ = 9.8 Hz), 129.73, 129.13, 129.00, 128.79, 128.59, 128.47, 127.75, 119.76 (d, $J_{C\text{-}P}$ = 99.7 Hz), 50.29, 23.22, 21.52. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.16. HRMS m/z: calcd for $C_{30}H_{29}NO_2P^+$ $[M+H]^+$ 466.1930, found: 466.1939.



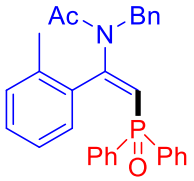
3oa

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-(methylthio)phenyl)vinyl) acetamide (3oa):** 64.2 mg, 43% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.39-7.33 (m, 6H), 7.28-7.26 (m, 5H), 7.25-7.22 (m, 3H), 7.19-7.18 (m, 1H), 7.15-7.12 (m, 2H), 6.99-6.97 (m, 2H), 5.79 (d, J = 15.7 Hz, 1H), 4.62 (s, 2H), 2.37 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.67, 155.63 (d, $J_{C\text{-}P}$ = 7.2 Hz), 142.83, 137.10, 133.43 (d, $J_{C\text{-}P}$ = 107.8 Hz), 131.71 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.89 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.08, 129.02, 128.85, 128.62 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.83, 125.33, 123.49, 119.80 (d, $J_{C\text{-}P}$ = 99.9 Hz), 50.36, 23.27, 15.08. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.30. HRMS m/z: calcd for $C_{30}H_{29}NO_2PS^+$ $[M+H]^+$ 498.1651, found: 498.1642.



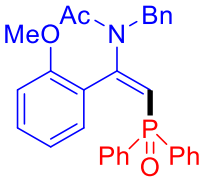
3pa

***(E)*-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(diphenylphosphoryl)vinyl)-*N*-benzylacetamide (3pa):** 142.5 mg, 90% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.08-8.06 (m, 1H), 7.57-7.52 (m, 3H), 7.46-7.41 (m, 8H), 7.35-7.31 (m, 8H), 7.19-7.17 (m, 2H), 7.13-7.10 (m, 2H), 5.96 (d, J = 15.6 Hz, 1H), 4.66 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.56, 155.05 (d, $J_{C\text{-}P}$ = 6.9 Hz), 137.55, 136.79, 133.59 (d, $J_{C\text{-}P}$ = 3.4 Hz), 132.83 (d, $J_{C\text{-}P}$ = 108.4 Hz), 132.81, 131.84 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.20, 130.90, 130.80, 130.02, 128.85, 128.84, 128.65 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.30, 127.86, 121.09 (d, $J_{C\text{-}P}$ = 98.4 Hz), 97.75, 50.25, 23.19. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.36. HRMS m/z: calcd for $C_{35}H_{31}NO_2P^+$ $[M+H]^+$ 528.2087, found: 528.2095.



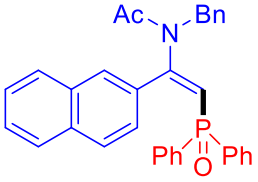
3qa

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(o-tolyl)vinyl)acetamide (3qa):** 108.9 mg, 78% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.57-7.52 (m, 4H), 7.38-7.35 (m, 3H), 7.31-7.26 (m, 6H), 7.15-7.08 (m, 5H), 6.80 (d, J = 7.3 Hz, 1H), 6.39 (d, J = 15.4 Hz, 1H), 4.49 (s, 2H), 2.30 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.87, 157.01 (d, $J_{C\text{-}P}$ = 9.2 Hz), 137.16, 136.27, 133.51, 130.99 (d, $J_{C\text{-}P}$ = 68.6 Hz), 130.74, 130.39 (d, $J_{C\text{-}P}$ = 3.7 Hz), 128.81, 128.35 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.58 (d, $J_{C\text{-}P}$ = 2.9 Hz), 125.75, 119.92 (d, $J_{C\text{-}P}$ = 103.9 Hz), 50.42, 23.83, 19.86. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.76. HRMS m/z: calcd for $C_{30}H_{29}NO_2P^+$ $[M+H]^+$ 466.1930, found: 466.1935.



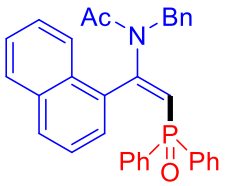
3ra

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(2-methoxyphenyl)vinyl)acetamide (3ra) :** 135.8 mg, 94% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51-7.46 (m, 4H), 7.40-7.35 (m, 3H), 7.31-7.28 (m, 4H), 7.26-7.24 (m, 3H), 7.22-7.18 (m, 1H), 7.15-7.13 (m, 2H), 6.88-6.84 (m, 1H), 6.46 (d, J = 8.3 Hz, 1H), 6.12 (d, J = 16.5 Hz, 1H), 4.53 (s, 2H), 3.44 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.64, 157.04, 154.94 (d, $J_{C\text{-}P}$ = 8.3 Hz), 137.48, 133.61 (d, $J_{C\text{-}P}$ = 107.7 Hz), 133.40, 131.98, 131.27 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.68 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.47, 128.26 (d, $J_{C\text{-}P}$ = 12.2 Hz), 127.31, 122.75 (d, J = 3.9 Hz), 121.71 (d, J = 102.4 Hz), 120.11, 110.01, 54.77, 49.50, 23.16. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.86. HRMS m/z: calcd for $C_{30}H_{29}NO_3P^+$ $[M+H]^+$ 482.1880, found: 482.1876.



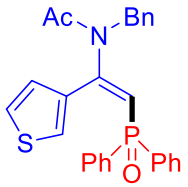
3sa

***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(naphthalen-2-yl)vinyl)acetamide (3sa):** 115.9 mg, 77% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.07(s, 1H), 7.83-7.66 (m, 2H), 7.62-7.60 (m, 1H), 7.52-7.40 (m, 6H), 7.35-7.28 (m, 6H), 7.24-7.19 (m, 6H), 6.09 (d, J = 15.1 Hz, 1H), 4.73 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.75, 156.29 (d, $J_{C\text{-}P}$ = 7.4 Hz), 137.13, 134.18, 133.39 (d, $J_{C\text{-}P}$ = 107.7 Hz), 132.47, 131.65 (d, $J_{C\text{-}P}$ = 3.4 Hz), 131.48 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.10, 130.81, 130.71, 129.00, 128.88, 128.85, 128.43 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.26, 127.83, 127.59 (d, $J_{C\text{-}P}$ = 1.6 Hz), 126.69, 125.31, 121.15 (d, $J_{C\text{-}P}$ = 100.0 Hz), 50.71, 23.43. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.01. HRMS m/z: calcd for $C_{33}H_{29}NO_2P^+$ $[M+H]^+$ 502.1930, found: 502.1922.



3ta

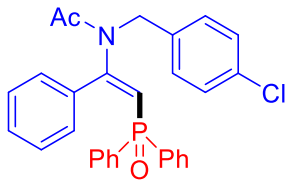
***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(naphthalen-1-yl)vinyl)acetamide (3ta):** 87.3 mg, 58% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.66-7.55 (m, 8H), 7.42-7.27 (m, 8H), 7.26-7.19 (m, 2H), 7.14-7.05 (m, 4H), 6.74 (d, J = 14.5 Hz, 1H), 4.38 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 171.21, 155.30 (d, $J_{C\text{-}P}$ = 5.9 Hz), 137.07, 132.77 (d, $J_{C\text{-}P}$ = 56.1 Hz), 131.31 (d, $J_{C\text{-}P}$ = 4.8 Hz), 131.01, 130.49 (d, $J_{C\text{-}P}$ = 10.1 Hz), 130.34, 128.87, 128.45, 127.88, 127.59, 127.03, 126.73, 126.09, 124.65 (d, $J_{C\text{-}P}$ = 48.6 Hz), 122.11 (d, $J_{C\text{-}P}$ = 104.5 Hz), 51.02, 24.04. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.39. HRMS m/z: calcd for $C_{33}H_{29}NO_2P^+$ $[M+H]^+$ 502.1930, found: 502.1934.



3ua

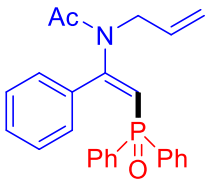
***(E)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(thiophen-3-yl)vinyl)acetamide (3ua):** 61.8 mg, 45%

yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.96-7.95 (m, 1H), 7.50-7.38 (m, 6H), 7.36-7.30 (m, 6H), 7.30-7.25 (m, 3H), 7.11-7.09 (m, 1H), 7.06-7.04 (m, 1H), 5.90 (d, J = 15.5 Hz, 1H), 4.80 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.61, 151.23 (d, $J_{C\text{-}P}$ = 7.5 Hz), 137.25, 136.32 (d, $J_{C\text{-}P}$ = 3.8 Hz), 133.29 (d, $J_{C\text{-}P}$ = 107.5 Hz), 131.67 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.08, 130.76 (d, $J_{C\text{-}P}$ = 9.9 Hz), 129.06, 128.87, 128.59 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.91, 127.49, 126.49, 119.72 (d, $J_{C\text{-}P}$ = 98.9 Hz), 50.99, 23.23. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.29. HRMS m/z: calcd for $C_{27}H_{25}NO_2PS^+$ $[M+H]^+$ 458.1338, found: 458.1346.



3va

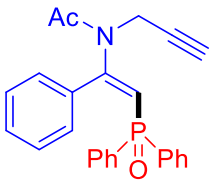
***(E)*-*N*-(4-chlorobenzyl)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (3va):** 106.4 mg, 73% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.48-7.40 (m, 9H), 7.35-7.28 (m, 6H), 7.26-7.21 (m, 2H), 7.14-7.11 (m, 2H), 5.90 (d, J = 15.5 Hz, 1H), 4.60 (s, 2H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.37, 155.80 (d, $J_{C\text{-}P}$ = 7.2 Hz), 135.56, 133.77 (d, $J_{C\text{-}P}$ = 1.5 Hz), 133.73, 133.16 (d, $J_{C\text{-}P}$ = 91.6 Hz), 131.75, 131.32 (d, $J_{C\text{-}P}$ = 80.4 Hz), 130.72 (d, $J_{C\text{-}P}$ = 9.9 Hz), 130.37, 129.66, 128.87, 128.65, 128.48 (d, $J_{C\text{-}P}$ = 9.0 Hz), 120.99 (d, $J_{C\text{-}P}$ = 97.9 Hz), 49.38, 23.02. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.82. HRMS m/z: calcd for $C_{29}H_{26}ClNO_2P^+$ $[M+H]^+$ 486.1384, found: 486.1389.



3wa

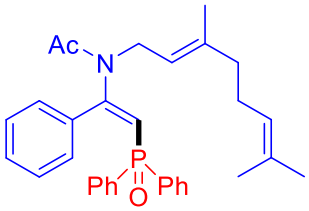
***(E)*-*N*-allyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (3wa):** 61.4 mg, 51% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.72-7.60 (m, 4H), 7.49-7.46 (m, 2H), 7.42-7.36 (m, 2H), 7.38-7.27 (m, 4H), 7.25-7.20 (m, 1H), 7.19-7.13 (m, 2H), 6.28 (d, J = 14.5 Hz, 1H), 5.93-5.73 (m, 1H), 5.22-5.03 (m, 2H), 4.10 (d, J = 6.2 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.43, 134.79 (d, $J_{C\text{-}P}$ = 3.6 Hz), 133.53 (d, $J_{C\text{-}P}$ = 107.7 Hz), 132.85, 131.56 (d, $J_{C\text{-}P}$ = 3.1 Hz), 130.83 (d, $J_{C\text{-}P}$ = 9.7

Hz), 130.71, 129.67, 129.66, 128.53 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.36, 120.01 (d, $J_{C\text{-}P}$ = 120.0 Hz), 118.58, 50.89, 23.37. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.68. HRMS m/z: calcd for $C_{25}H_{25}NO_2P^+$ $[M+H]^+$ 402.1617, found: 402.1608.



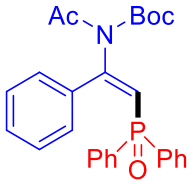
3xa

***(E)-N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-*N*-(prop-2-yn-1-yl)acetamide (3xa):** 64.7 mg, 54% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.79-7.66 (m, 4H), 7.59-7.53 (m, 2H), 7.44-7.29 (m, 6H), 7.26-7.14 (m, 3H), 6.43 (d, J = 13.9 Hz, 1H), 4.41 (d, J = 2.2 Hz, 2H), 2.34 (t, J = 2.5 Hz, 1H), 2.01(s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.17, 156.31 (d, $J_{C\text{-}P}$ = 7.9 Hz), 134.51 (d, $J_{C\text{-}P}$ = 3.4 Hz), 133.26 (d, $J_{C\text{-}P}$ = 108.0 Hz), 131.54 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.81, 130.77 (d, $J_{C\text{-}P}$ = 9.7 Hz), 129.63, 128.45 (d, $J_{C\text{-}P}$ = 12.2 Hz), 128.32, 119.83 (d, $J_{C\text{-}P}$ = 100.0 Hz), 78.70, 72.71, 37.37, 23.28. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.88. HRMS m/z: calcd for $C_{25}H_{23}NO_2P^+$ $[M+H]^+$ 400.1461, found: 400.1466.



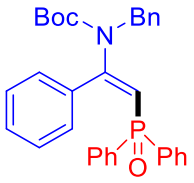
3ya

***N*-((*E*)-3,7-dimethylocta-2,6-dien-1-yl)-*N*-((*E*)-2-(diphenylphosphoryl)-1-phenylvinyl) acetamide (3ya):** 123.9 mg, 83% yield. White solid. m.p. = 152–156 ºC. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.71-7.61 (m, 4H), 7.52-7.48 (m, 2H), 7.43-7.37 (m, 2H), 7.35-7.29 (m, 4H), 7.24-7.13 (m, 3H), 6.24 (d, J = 14.8 Hz, 1H), 5.15 (dt, J = 75.2, 7.3 Hz, 2H), 4.13 (d, J = 6.9 Hz, 2H), 2.07 (s, 3H), 2.05-1.92 (m, 5H), 1.73-1.68 (m, 0.5H), 1.66 (s, 3H), 1.64-1.60 (m, 0.5H), 1.58 (s, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.48, 139.97, 134.90 (d, $J_{C\text{-}P}$ = 3.4 Hz), 133.52 (d, $J_{C\text{-}P}$ = 107.7 Hz), 131.95, 131.58 (d, $J_{C\text{-}P}$ = 3.1 Hz), 130.86 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.66, 129.77, 128.55 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.29, 123.87, 119.19, 46.16, 39.71, 26.55, 25.84, 23.47, 17.87, 16.28. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.03. HRMS m/z: calcd for $C_{32}H_{37}NO_2P^+$ $[M+H]^+$ 498.2556, found: 498.2564.



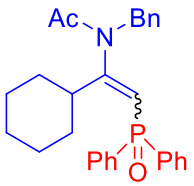
3za

***tert*-butyl *(E)*-acetyl(2-(diphenylphosphoryl)-1-phenylvinyl)carbamate (3za):** 132.9 mg, 96% yield. Yellow oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.86-7.78 (m, 2H), 7.73-7.65 (m, 2H), 7.55-7.48 (m, 3H), 7.47-7.41 (m, 5H), 7.38-7.33 (m, 2H), 7.28-7.20 (m, 1H), 6.62 (d, J = 17.7 Hz, 1H), 2.59 (s, 3H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 173.52, 152.90 (d, $J_{C\text{-}P}$ = 8.7 Hz), 151.78, 135.92 (d, $J_{C\text{-}P}$ = 3.4 Hz), 133.51 (d, $J_{C\text{-}P}$ = 108.0 Hz), 131.32, 131.29, 131.06, 130.96, 129.93, 129.14, 128.37 (d, $J_{C\text{-}P}$ = 12.4 Hz), 127.89, 126.15, 123.52 (d, $J_{C\text{-}P}$= 100.1 Hz), 84.36, 27.54, 26.58. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 27.66. HRMS m/z: calcd for $C_{27}H_{29}NO_4P^+$ $[M+H]^+$ 462.1829, found: 462.1821.



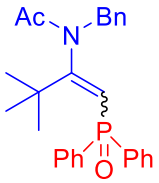
3a'a

***tert*-butyl *(E)*-benzyl(2-(diphenylphosphoryl)-1-phenylvinyl)carbamate (3a'a):** 73.3 mg, 48% yield. White solid. m.p. = 139–142 ºC. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.33 (m, 9H), 7.33-7.27 (m, 4H), 7.22-7.17 (m, 4H), 7.10-7.01 (m, 3H), 6.01 (d, J = 13.9 Hz, 1H), 4.81 (s, 2H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 157.29 (d, $J_{C\text{-}P}$ = 9.3 Hz), 154.44, 137.72, 137.09 (d, $J_{C\text{-}P}$ = 4.3 Hz), 134.06 (d, $J_{C\text{-}P}$ = 107.9 Hz), 130.96 (d, $J_{C\text{-}P}$ = 2.8 Hz), 130.88 (d, $J_{C\text{-}P}$ = 9.6 Hz), 129.56, 129.22, 128.79, 128.28, 128.11 (d, $J_{C\text{-}P}$ = 12.3 Hz), 127.78, 127.71, 113.73 (d, $J_{C\text{-}P}$ = 107.6 Hz), 100.02, 82.00, 52.65, 27.86. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.75. HRMS m/z: calcd for $C_{32}H_{33}NO_3P^+$ $[M+H]^+$ 510.2193, found: 510.2184.



3b'a

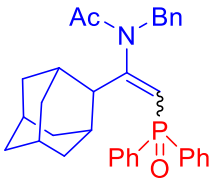
***N*-benzyl-*N*-(1-cyclohexyl-2-(diphenylphosphoryl)vinyl)acetamide (3b'a):** 113.9 mg, 83% yield, *Z*/*E* = 68:32. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.81-7.74 (m, 4H), 7.65-7.61 (m, 2H), 7.50-7.47 (m, 10H), 7.33-7.29 (m, 1H), 7.24-7.22 (m, 4H), 7.20-7.15 (m, 2H), 6.09 (d, *J* = 17.7 Hz, 1H, *Z*-isomer), 5.97 (d, *J* = 16.8 Hz, 0.47H, *E*-isomer), 4.94 (d, *J* = 15.4 Hz, 1H, *Z*-isomer), 4.78 (s, 1H, *E*-isomer), 3.83 (d, *J* = 15.4 Hz, 1H, *Z*-isomer), 2.06 (s, 3H), 1.85-1.82 (m, 2H), 1.67-1.57 (m, 7H), 1.20-0.96 (m, 7H), 0.91-0.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ Major: 170.15, 166.32, 138.16, 133.15 (d, $J_{C\text{-}P}$ = 30.6 Hz), 131.92 (d, $J_{C\text{-}P}$ = 2.9 Hz), 131.03 (d, $J_{C\text{-}P}$ = 10.0 Hz), 128.94, 128.88, 128.69, 128.42 (d, $J_{C\text{-}P}$ = 19.4 Hz), 127.30, 116.31 (d, $J_{C\text{-}P}$ = 100.7 Hz), 51.16, 46.65, 32.36, 31.51, 26.48, 25.86, 23.01. Minor: 166.32, 134.21 (d, $J_{C\text{-}P}$ = 31.2 Hz), 131.75 (d, $J_{C\text{-}P}$ = 2.3 Hz), 130.91 (d, $J_{C\text{-}P}$ = 2.8 Hz), 128.88, 128.76 (d, $J_{C\text{-}P}$ = 1.1 Hz), 128.59 (d, $J_{C\text{-}P}$ = 3.1 Hz), 127.55, 126.87, 126.13, 115.03 (d, $J_{C\text{-}P}$ = 32.2 Hz), 56.78, 45.55, 33.11, 29.81, 26.22, 26.03, 22.06. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.95 (*E*-isomer), 16.77 (*Z*-isomer). HRMS m/z: calcd for $C_{29}H_{33}NO_2P^+$ $[M+H]^+$ 458.2243, found: 458.2251.



3c'a

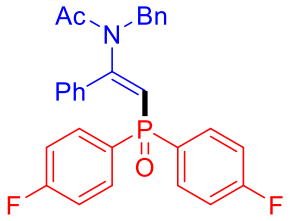
***N*-benzyl-*N*-(1-(diphenylphosphoryl)-3,3-dimethylbut-1-en-2-yl)acetamide (3c'a):** 98.4 mg, 76% yield, *Z*/*E* = 47:53. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.84-7.66 (m, 9H), 7.58-7.39 (m, 14H), 7.34-7.31 (m, 4H), 7.29-7.27 (m, 1H), 7.23-7.11 (m, 3H), 6.44 (d, *J* = 18.5 Hz, 1H, *Z*-isomer), 6.16 (d, *J* = 18.5 Hz, 1.12H, *E*-isomer), 5.34 (d, *J* = 15.6 Hz, 1.06H, *Z*-isomer), 5.15 (d, *J* = 17.0 Hz, 1.14H, *E*-isomer), 4.50 (d, *J* = 17.0 Hz, 1.13H, *E*-isomer), 3.96 (d, *J* = 15.6 Hz, 1H, *Z*-isomer), 1.96 (s, 3.52H, *E*-isomer), 1.91 (s, 3.13H, *Z*-isomer), 1.07 (s, 10.04H, *E*-isomer), 1.07 (s, 9.10H, *Z*-isomer). ^{13}C NMR (100 MHz, $CDCl_3$) δ Major: 171.46, 137.55, 132.09 (d, $J_{C\text{-}P}$ = 2.6 Hz), 131.90 (d, $J_{C\text{-}P}$ = 2.7 Hz), 131.31 (d, $J_{C\text{-}P}$ = 77.9 Hz), 131.04, 131.00, 129.01, 128.96, 128.89, 128.67, 128.51, 128.20, 127.95, 127.51, 118.92

(d, $J_{C\text{-}P}$ = 99.3 Hz), 57.67, 40.01, 29.65, 22.70. Minor: 168.98, 138.28, 132.03 (d, $J_{C\text{-}P}$ = 2.5 Hz), 131.82 (d, $J_{C\text{-}P}$ = 2.8 Hz), 131.25 (d, $J_{C\text{-}P}$ = 68.9 Hz), 130.01, 129.95, 128.98, 128.85, 127.11, 115.78 (d, $J_{C\text{-}P}$ = 101.7 Hz), 55.53, 39.98, 30.43, 23.36. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.72 (*E*-isomer), 16.73 (*Z*-isomer). HRMS m/z: calcd for $C_{27}H_{31}NO_2P^+$ $[M+H]^+$ 432.2087, found: 432.2092.



3d'a

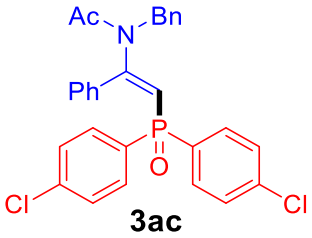
***N*-(1-((1r,3r,5r,7r)-adamantan-2-yl)-2-(diphenylphosphoryl)vinyl)-*N*-benzylacetamide (3d'a):** 84.1 mg, 55% yield, *Z/E* = 48:52. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.85-7.77 (m, 2H), 7.77-7.68 (m, 7H), 7.59-7.40 (m, 15H), 7.38-7.28 (m, 6H), 7.23-7.12 (m, 3H), 6.37 (d, *J* = 18.7 Hz, 1H, *Z*-isomer), 6.06 (d, *J* = 19.3 Hz, 1.1H, *E*-isomer), 5.35 (d, *J* = 15.5 Hz, 1.07H, *Z*-isomer), 5.21 (d, *J* = 17.2 Hz, 1.15H, *E*-isomer), 4.42 (d, *J* = 17.3 Hz, 1.15H, *E*-isomer), 3.89 (d, *J* = 15.5 Hz, 1.01H, *Z*-isomer), 1.97 (s, 3H), 1.90 (s, 9H), 1.81-1.66 (m, 10H), 1.62-1.58 (m, 10H), 1.54-1.52 (m, 1H), 1.43-1.40 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm Major: 174.03, 173.11, 171.89, 170.55, 137.82, 134.45 (d, $J_{C\text{-}P}$ = 85.3 Hz), 134.21, 133.16, 131.95 (d, $J_{C\text{-}P}$ = 7.3 Hz), 131.75 (d, $J_{C\text{-}P}$ = 7.7 Hz), 131.56, 131.03, 130.93 (d, $J_{C\text{-}P}$ = 4.9 Hz), 129.15, 128.87 (d, $J_{C\text{-}P}$ = 12.0 Hz), 128.59, 128.56, 127.79, 127.34, 115.05 (d, $J_{C\text{-}P}$ = 101.1 Hz), 57.63, 41.80, 41.60, 41.51, 36.43, 28.46, 23.54. Minor: 174.02, 173.17, 171.84, 170.54, 138.41, 134.32 (d, $J_{C\text{-}P}$ = 99.4 Hz), 133.76, 132.96, 131.93 (d, $J_{C\text{-}P}$ = 7.2 Hz), 131.78 (d, $J_{C\text{-}P}$ = 7.7 Hz), 131.67, 131.04, 130.97 (d, $J_{C\text{-}P}$ = 6.7 Hz), 128.85 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.47, 128.06, 127.03, 118.27 (d, $J_{C\text{-}P}$ = 99.6 Hz), 55.69, 41.90, 41.70, 41.49, 36.12, 28.43, 22.87. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 20.12 (*E*-isomer), 16.85 (*Z*-isomer). HRMS m/z: calcd for $C_{33}H_{37}NO_2P^+$ $[M+H]^+$ 510.2556, found: 510.2560.



3ab

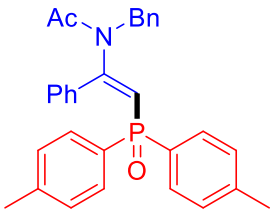
***(E)*-*N*-benzyl-*N*-(2-(bis(4-fluorophenyl)phosphoryl)-1-phenylvinyl)acetamide (3ab):** 128.7 mg,

88% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45-7.39 (m, 6H), 7.36-7.34 (m, 3H), 7.28-7.18 (m, 5H), 6.97 (m, 4H), 5.97 (d, J = 15.3 Hz, 1H), 4.70 (s, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.70, 164.69 (dd, $J_{C\text{-}F}$ = 253.4 Hz, $J_{C\text{-}P}$ = 3.3 Hz), 156.57 (d, $J_{C\text{-}P}$ = 7.9 Hz), 137.00, 134.31 (d, $J_{C\text{-}P}$ = 3.5 Hz), 133.31, 133.21 (dd, $J_{C\text{-}F}$ = 20.0 Hz, $J_{C\text{-}P}$ = 2.5 Hz), 130.92, 129.64, 128.84, 128.65, 128.44, 127.83, 119.79 (d, $J_{C\text{-}P}$ = 103.9 Hz), 115.98 (d, $J_{C\text{-}F}$ = 13.5 Hz), 115.77 (d, $J_{C\text{-}F}$ = 13.5 Hz), 50.71, 23.38. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.76. ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -106.89. HRMS m/z: calcd for $C_{29}H_{25}F_2NO_2P^+$ $[M+H]^+$ 488.1585, found: 488.1591.



3ac

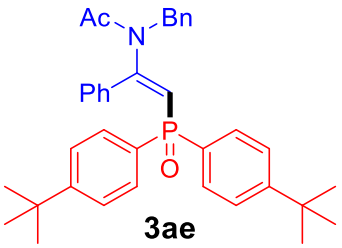
***(E)*-*N*-benzyl-*N*-(2-(bis(4-chlorophenyl)phosphoryl)-1-phenylvinyl)acetamide (3ac):** 74.9 mg, 48% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.40-7.34 (m, 8H), 7.31-7.29 (m, 4H), 7.25-7.20 (m, 6H), 5.95 (d, J = 15.5 Hz, 1H), 4.71 (s, 2H), 2.10 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.86, 138.33 (d, $J_{C\text{-}P}$ = 3.3 Hz), 137.01, 134.41 (d, $J_{C\text{-}P}$ = 3.4 Hz), 132.24, 131.61 (d, $J_{C\text{-}P}$ = 104.9 Hz), 129.70, 129.03, 128.96, 128.90, 128.70, 128.57, 127.97, 50.85, 23.54. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.95. HRMS m/z: calcd for $C_{29}H_{25}Cl_2NO_2P^+$ $[M+H]^+$ 520.0994, found: 520.0998.



3ad

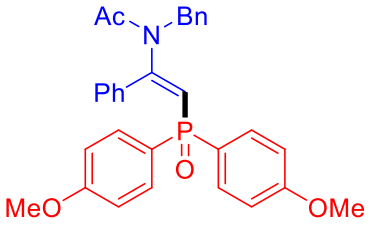
***(E)*-*N*-benzyl-*N*-(2-(di-p-tolylphosphoryl)-1-phenylvinyl)acetamide (3ad):** 86.3 mg, 60% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45-7.40 (m, 2H), 7.36-7.27 (m, 8H), 7.25-7.18 (m, 4H), 7.11-7.18 (m, 4H), 5.90 (d, J = 15.4 Hz, 1H), 4.65 (s, 2H), 2.32 (s, 6H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.54, 155.53 (d, $J_{C\text{-}P}$ = 7.3 Hz), 141.98 (d, $J_{C\text{-}P}$ = 3.0 Hz), 137.17, 134.12 (d, $J_{C\text{-}P}$ = 3.5 Hz), 130.84 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.22 (d, $J_{C\text{-}P}$ = 88.3 Hz), 129.27 (d, $J_{C\text{-}P}$ = 12.7 Hz), 129.01,

128.76, 128.32, 127.73, 121.34 (d, J_{C-P} = 98.3 Hz), 50.16, 23.17, 21.61, 21.60. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.37. HRMS m/z: calcd for $C_{31}H_{31}NO_2P^+$ $[M+H]^+$ 480.2087, found: 480.2082.



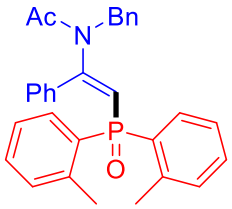
3ae

***(E)*-*N*-benzyl-*N*-(2-(bis(4-(*tert*-butyl)phenyl)phosphoryl)-1-phenylvinyl) acetamide (3ae):** 82.9 mg, 49% yield. White solid. m.p. = 113–115 °C. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.37 (m, 6H), 7.33-7.29 (m, 6H), 7.28-7.27 (m, 1H), 7.25-7.19 (m, 3H), 7.18-7.13 (m, 2H), 6.00 (d, J = 14.6 Hz, 1H), 4.65 (s, 2H), 2.14 (s, 3H), 1.26 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.47, 155.48 (d, J_{C-P} = 7.5 Hz), 154.74 (d, J_{C-P} = 3.0 Hz), 137.10, 134.25 (d, J_{C-P} = 3.5 Hz), 130.73, 130.45, 130.15 (d, J_{C-P} = 97.3 Hz), 129.55, 128.81, 128.67, 128.20, 127.62, 125.36 (d, J_{C-P} = 12.5 Hz), 121.71 (d, J_{C-P} = 98.3 Hz), 50.41, 34.89, 31.07, 23.22. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 18.79. HRMS m/z: calcd for $C_{37}H_{43}NO_2P^+$ $[M+H]^+$ 564.3026, found: 564.3032.



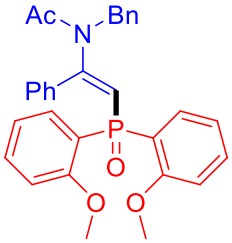
3af

***(E)*-*N*-benzyl-*N*-(2-(bis(4-methoxyphenyl)phosphoryl)-1-phenylvinyl)acetamide (3af):** 53.7 mg, 35% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.41 (m, 2H), 7.35-7.29 (m, 8H), 7.25-7.23 (m, 2H), 7.21-7.19 (m, 2H), 6.81-6.79 (m, 4H), 5.89 (d, J = 15.1 Hz, 1H), 4.65 (s, 2H), 3.80 (s, 6H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.45, 155.43 (d, J_{C-P} = 7.1 Hz), 141.92 (d, J_{C-P} = 3.0 Hz), 137.09, 134.04 (d, J_{C-P} = 3.5 Hz), 130.76 (d, J_{C-P} = 10.2 Hz), 130.71, 130.60, 129.71, 129.20 (d, J_{C-P} = 12.7 Hz), 128.93, 128.70, 128.26, 127.67, 121.27 (d, J_{C-P} = 98.1 Hz), 50.07, 23.10, 21.55, 21.54. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.41. HRMS m/z: calcd for $C_{31}H_{31}NO_4P^+$ $[M+H]^+$ 512.1985, found: 512.1991.



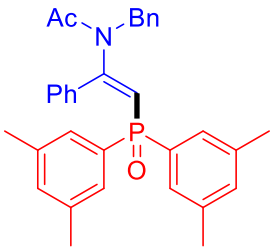
3ag

***(E)*-*N*-benzyl-*N*-(2-(di-o-tolylphosphoryl)-1-phenylvinyl)acetamide (3ag):** 67.6 mg, 47% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.46-7.40 (m, 2H), 7.36-7.31 (m, 4H), 7.31-7.26 (m, 4H), 7.25-7.18 (m, 4H), 7.11-7.08 (m, 4H), 5.91 (d, J = 15.4 Hz, 1H), 4.65 (s, 2H), 2.32 (s, 6H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm δ ppm 170.55, 155.55 (d, $J_{C\text{-}P}$ = 8.1 Hz), 142.00 (d, $J_{C\text{-}P}$ = 2.8 Hz), 137.18, 134.14 (d, $J_{C\text{-}P}$ = 3.3 Hz), 130.86 (d, $J_{C\text{-}P}$ = 10.2 Hz), 130.68, 129.80, 129.28 (d, $J_{C\text{-}P}$ = 12.6 Hz), 129.03, 128.56 (d, $J_{C\text{-}P}$ = 44.0 Hz), 127.74, 121.35 (d, $J_{C\text{-}P}$ = 98.0 Hz), 50.18, 23.18, 21.63, 21.61. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.37. HRMS m/z: calcd for $C_{31}H_{31}NO_2P^+$ $[M+H]^+$ 480.2087, found: 480.2096.



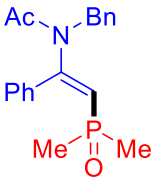
3ah

***(E)*-*N*-benzyl-*N*-(2-(bis(2-methoxyphenyl)phosphoryl)-1-phenylvinyl)acetamide (3ah):** 50.6 mg, 33% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.45-7.33 (m, 6H), 7.31-7.23 (m, 4H), 7.20 (m, 4H), 7.01-6.64 (m, 4H), 6.33 (d, J = 14.3 Hz, 1H), 4.62 (s, 2H), 3.53 (s, 6H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.85, 160.31 (d, $J_{C\text{-}P}$ = 3.1 Hz), 153.69 (d, $J_{C\text{-}P}$ = 7.7 Hz), 137.72, 134.28 (d, $J_{C\text{-}P}$ = 3.4 Hz), 134.14 (d, $J_{C\text{-}P}$ = 8.1 Hz), 133.50 (d, $J_{C\text{-}P}$ = 2.0 Hz), 130.15, 129.56, 128.53, 128.40 (d, $J_{C\text{-}P}$ = 76.7 Hz), 127.38, 121.96 (d, $J_{C\text{-}P}$ = 103.4 Hz), 121.24, 120.48, 120.45, 120.24, 120.66 (d, $J_{C\text{-}P}$ = 12.4 Hz), 120.14, 110.85 (d, $J_{C\text{-}P}$ = 6.7 Hz), 55.43, 50.24, 22.81. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 16.82. HRMS m/z: calcd for $C_{31}H_{31}NO_4P^+$ $[M+H]^+$ 512.1985, found: 512.1993.



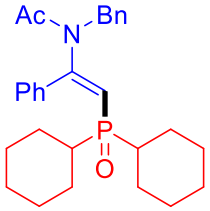
3ai

***(E)*-*N*-benzyl-*N*-(2-(bis(3,5-dimethylphenyl)phosphoryl)-1-phenylvinyl)acetamide (3ai):** 86.8 mg, 57% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43-7.39 (m, 2H), 7.35-7.26 (m, 4H), 7.25-7.18 (m, 4H), 7.11-6.99 (m, 6H), 5.95 (d, J = 15.0 Hz, 1H), 4.67 (s, 2H), 2.23 (s, 12H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.70, 155.61 (d, $J_{C\text{-}P}$ = 7.1 Hz), 138.21, 138.08, 137.10, 134.40 (d, $J_{C\text{-}P}$ = 3.2 Hz), 133.30 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.16 (d, $J_{C\text{-}P}$ = 106.8 Hz), 130.57, 129.69, 128.97, 128.68, 128.40 (d, $J_{C\text{-}P}$ = 9.7 Hz), 128.20, 127.79, 120.64 (d, $J_{C\text{-}P}$ = 98.0 Hz), 50.39, 23.29, 21.32, 21.31. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 19.35. HRMS m/z: calcd for $C_{33}H_{35}NO_2P^+$ $[M+H]^+$ 508.2400, found: 508.2404.



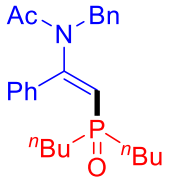
3aj

***(E)*-*N*-benzyl-*N*-(2-(dimethylphosphoryl)-1-phenylvinyl)acetamide (3aj):** 50.1 mg, 51% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61-7.59 (m, 2H), 7.54-7.41 (m, 3H), 7.33-7.27 (m, 3H), 7.25-7.16 (m, 2H), 5.65 (d, J = 14.1 Hz, 1H), 4.63 (s, 2H), 2.13 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 172.82, 137.00, 134.95 (d, $J_{C\text{-}P}$ = 3.4 Hz), 131.31, 129.60, 129.29, 129.13, 128.82, 128.76, 128.48, 127.86, 122.48 (d, $J_{C\text{-}P}$ = 94.0 Hz), 50.70, 23.18, 18.08 (d, $J_{C\text{-}P}$ = 75.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 28.81. HRMS m/z: calcd for $C_{19}H_{23}NO_2P^+$ $[M+H]^+$ 328.1461, found: 328.1451.



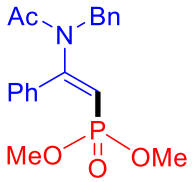
3ak

***(E)*-*N*-benzyl-*N*-(2-(dicyclohexylphosphoryl)-1-phenylvinyl)acetamide (3ak):** 80.7 mg, 58% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.64-7.55 (m, 2H), 7.52-7.38 (m, 4H), 7.36-7.22 (m, 3H), 7.23-7.15 (m, 1H), 5.18 (d, J = 16.8 Hz, 1H), 4.57 (s, 2H), 2.28 (s, 3H), 1.92-1.68 (m, 9H), 1.60-1.47 (m, 4H), 1.25-1.00 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 169.75, 137.23, 133.44 (d, $J_{C\text{-}P}$ = 2.3 Hz), 130.54, 129.80, 128.97, 128.65, 128.15, 127.68, 119.93 (d, $J_{C\text{-}P}$ = 77.8 Hz), 49.45, 36.87 (d, $J_{C\text{-}P}$ = 70.7 Hz), 26.63, 26.48 (d, $J_{C\text{-}P}$ = 4.1 Hz), 26.46, 26.33, 26.17, 25.86 (d, $J_{C\text{-}P}$ = 3.4 Hz), 25.01 (d, $J_{C\text{-}P}$ = 3.5 Hz), 23.09. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 40.77. HRMS m/z: calcd for $C_{29}H_{39}NO_2P^+$ $[M+H]^+$ 464.2713, found: 464.2722.



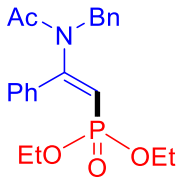
3al

***(E)*-*N*-benzyl-*N*-(2-(dibutylphosphoryl)-1-phenylvinyl)acetamide (3al):** 37.0 mg, 30% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61-7.55 (m, 2H), 7.49-7.39 (m, 3H), 7.33-7.27 (m, 3H), 7.21-7.19 (m, 2H), 5.48 (d, J = 13.5 Hz, 1H), 4.63 (s, 2H), 2.17 (s, 3H), 1.52-1.42 (m, 4H), 1.34-1.26 (m, 5H), 1.24-1.19 (m, 3H), 0.80 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.30, 154.85 (d, J = 6.8 Hz), 137.09, 134.73 (d, J = 2.9 Hz), 131.00, 129.51, 128.79, 128.68, 127.77, 120.75 (d, J = 90.6 Hz), 50.41, 29.08 (d, J = 70.0 Hz), 24.16, 24.00, 23.83, 23.79, 23.13, 13.59. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 36.92. HRMS m/z: calcd for $C_{25}H_{35}NO_2P^+$ $[M+H]^+$ 412.2400, found: 412.2410.



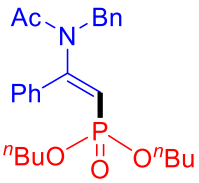
3am

Dimethyl *(E)*-(2-(N-benzylacetamido)-2-phenylvinyl)phosphonate (3am): 39.9 mg, 37% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53-7.39 (m, 5H), 7.32-7.27 (m, 2H), 7.26-7.22 (m, 1H), 7.17 (m, 2H), 5.46 (d, J = 10.3 Hz, 1H), 4.60 (s, 2H), 3.46 (s, 3H), 3.43 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.46, 156.45 (d, $J_{C\text{-}P}$ = 15.2 Hz), 136.86, 134.59 (d, $J_{C\text{-}P}$ = 3.7 Hz), 130.98, 129.31 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.70, 128.67, 128.66, 127.72, 114.04 (d, $J_{C\text{-}P}$ = 191.9 Hz), 52.47, 52.41, 50.35, 23.10. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.83. HRMS m/z: calcd for $C_{19}H_{23}NO_4P^+$ $[M+H]^+$ 360.1359, found: 360.1364.



3an

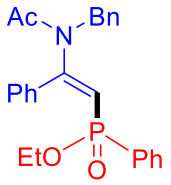
Diethyl *(E)*-(2-(*N*-benzylacetamido)-2-phenylvinyl)phosphonate (3an): 44.2 mg, 38% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.51-7.37 (m, 5H), 7.30-7.25 (m, 2H), 7.24-7.20 (m, 1H), 7.18-7.14 (m, 2H), 5.45 (d, J = 10.3 Hz, 1H), 4.57 (s, 2H), 3.93-3.62 (m, 4H), 2.18 (s, 3H), 1.07-1.02 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.46, 155.68 (d, $J_{C\text{-}P}$ = 14.7 Hz), 136.95, 134.72 (d, $J_{C\text{-}P}$ = 3.6 Hz), 130.82, 129.41 (d, $J_{C\text{-}P}$ = 1.5 Hz), 128.76, 128.64, 128.60, 127.68, 115.57 (d, $J_{C\text{-}P}$ = 190.4 Hz), 62.02, 61.96, 50.28, 23.08, 16.20, 16.13. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 14.83. HRMS m/z: calcd for $C_{21}H_{27}NO_4P^+$ $[M+H]^+$ 388.1672, found: 388.1664.



3ao

Dibutyl *(E)*-(2-(*N*-benzylacetamido)-2-phenylvinyl)phosphonate (3ao): 46.6 mg, 35% yield.

Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53-7.38 (m, 5H), 7.29-7.26 (m, 2H), 7.26-7.22 (m, 1H), 7.17-7.15 (m, 2H), 5.47 (d, J = 10.2 Hz, 1H), 4.60 (s, 2H), 3.94-3.55 (m, 4H), 2.19 (s, 3H), 1.52-1.34 (m, 4H), 1.22-1.17 (m, 4H), 0.83 (t, J = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.50, 155.64 (d, $J_{C\text{-}P}$ = 14.8 Hz), 136.92, 134.74 (d, $J_{C\text{-}P}$ = 3.5 Hz), 130.81, 129.42 (d, $J_{C\text{-}P}$ = 1.3 Hz), 128.80, 128.63, 128.60, 127.68, 115.51 (d, $J_{C\text{-}P}$ = 190.3 Hz), 65.77, 65.70, 50.31, 32.32, 32.25, 23.08, 18.71, 13.67. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 14.93. HRMS m/z: calcd for $C_{25}H_{35}NO_4P^+$ $[M+H]^+$ 444.2298, found: 444.2292.

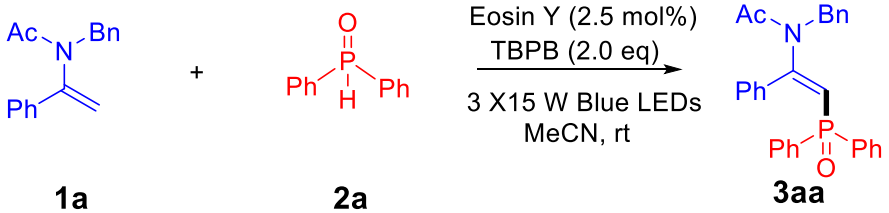


3ap

ethyl *(E)*-(2-(*N*-benzylacetamido)-2-phenylvinyl)(phenyl)phosphinate (3ap): 54.1 mg, 43% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.42-7.27 (m, 9H), 7.26-7.20 (m, 4H), 7.19-7.14 (m, 2H), 5.78 (d, J = 9.4 Hz, 1H), 4.55 (dd, J = 137.8, 14.7 Hz, 2H), 3.99-3.64 (m, 2H), 2.14 (s, 3H), 1.13 (t, J = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.37, 155.48 (d, $J_{C\text{-}P}$ = 14.4 Hz), 136.94, 134.55 (d, $J_{C\text{-}P}$ = 3.7 Hz), 131.97 (d, $J_{C\text{-}P}$ = 3.0 Hz), 131.42, 131.31, 130.55, 129.56 (d, $J_{C\text{-}P}$ = 1.2 Hz), 128.76, 128.60, 128.35, 128.24, 128.11, 127.61, 120.38 (d, $J_{C\text{-}P}$ = 139.4 Hz), 60.69 (d, $J_{C\text{-}P}$ = 5.6 Hz), 50.16, 23.17, 16.32 (d, $J_{C\text{-}P}$ = 6.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 28.82. HRMS m/z: calcd for $C_{25}H_{27}NO_3P^+$ $[M+H]^+$ 420.1723, found: 420.1731.

Synthetic Applications

(a) Gram-Scale Synthesis of *β*-phosphonylated Enamide



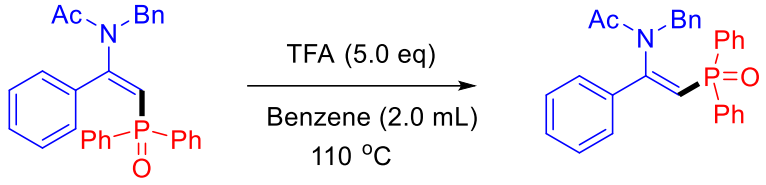
1a **2a** **3aa**

1.005 g, 4 mmol **1.517 g, 84% yield**

Enamides **1a** (1.01 g, 4.0 mmol), diphenyl phosphine oxide **2a** (6.0 mmol, 1.5 eq) and Eosin Y (0.1 mmol, 2.5 mol%) were added sequentially into Schlenk tube under nitrogen, the tube was then

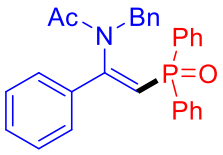
capped with a rubber stopper. TBPB (1.6 mL, 8 mmol, 2.0 eq) and MeCN (20.0 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 15 W blue LEDs irradiation. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash column chromatography using dichloromethane/methanol (100:1 *v*/*v*) as the eluent to afford pure products **3aa** (1.517 g, 84% yield).

(b) Conversion of Stereochemistry of Enamides



3aa **Z-3aa**
65.0 mg, 48% yield

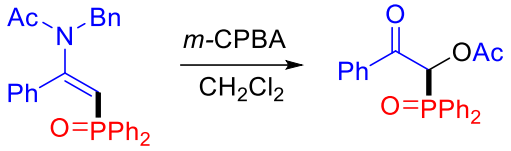
0.3 mmol of the enamide **3aa** was dissolved in dry benzene (2.0 mL) in a screw cap vial. 102.6 mg (1.5 mmol, 5.0 eq) of trifluoroacetic acid were then added to the solution and the vial was heated to 110 °C using a magnetic hotplate stirrer equipped with an oil bath. Upon completion of the reaction as monitored by TLC, the solvent was removed under vacuum and the residue was purified by flash column chromatography using dichloromethane/methanol (100:1 *v*/*v*) as the eluent to afford pure products ***Z*-3aa**.



***Z*-3aa**

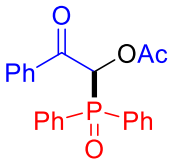
***(Z)*-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (*Z*-3aa):** 65.0 mg, 48% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.79-7.55 (m, 4H), 7.53-7.47 (m, 6H), 7.36-7.33 (m, 1H), 7.25-7.21 (m, 4H), 7.17-7.15 (m, 2H), 7.09-7.07 (m, 3H), 6.58 (d, J = 16.8 Hz, 1H), 4.80 (s, 2H), 1.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.23, 156.95 (d, $J_{C\text{-}P}$ = 2.8 Hz), 137.36 (d, $J_{C\text{-}P}$ = 12.5 Hz), 136.78, 131.59 (d, $J_{C\text{-}P}$ = 95.3 Hz), 131.00, 130.63, 130.54, 128.93, 128.48 (d, $J_{C\text{-}P}$ = 62.9 Hz), 127.64, 127.23, 117.69 (d, $J_{C\text{-}P}$ = 100.0 Hz), 52.58, 22.89. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 17.36. HRMS m/z: calcd for $C_{29}H_{27}NO_2P^+$ $[M+H]^+$ 452.1774, found: 452.1782.

(c) The Synthesis of *α*-acyloxyketone



3aa **4**

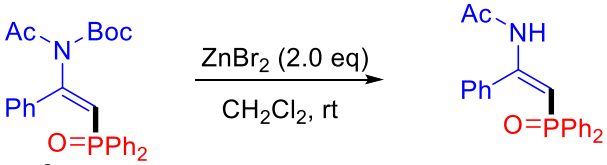
Enamide **3aa** (0.2 mmol) was added into a reaction tube. *m*-CPBA (3.0 eq) was then added to the stirred solution of the enamide in CH_2Cl_2 at 0 °C and the resultant suspension was stirred for 30 min before warming to room temperature. The resulting mixture was stirred at room temperature. Upon completion, the solvent was then removed under vacuum. The residue was purified directly by silica gel chromatography, eluting with dichloromethane/methanol (100:1 *v*/*v*) to give *α*-acyloxyketone **4**.



4

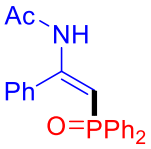
1-(diphenylphosphoryl)-2-oxo-2-phenylethyl acetate (4): 37.8 mg, 50% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 8.09-7.96 (m, 2H), 7.91-7.75 (m, 4H), 7.62-7.34 (m, 10H), 6.78 (d, J = 11.8 Hz, 1H), 2.05(s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.53, 133.46, 133.28, 131.73, 129.50, 129.20, 129.04, 128.95, 128.76, 128.09, 128.07, 127.81, 127.72, 127.08, 121.27, 44.31, 25.66. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 28.11. HRMS m/z: calcd for $C_{22}H_{20}O_4P^+$ $[M+H]^+$ 379.1094, found: 379.1103.

(d) Cleavage of *N*-Boc Group[2]



3za **5**

Enamide **3za** (0.2 mmol) was added into a reaction tube. $ZnBr_2$ (90.1 mg, 0.4 mmol) and CH_2Cl_2 (1.0 mL) were then added sequentially. The resulting mixture was stirred at room temperature for 4 hours. Upon completion as monitored by TLC, the solvent was then removed under vacuum. The residue was purified directly by flash chromatography, eluting with dichloromethane/methanol (100:1 *v*/*v*) to give **5**.



5

***(E)*-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (5):** 37.6 mg, 52% yield. Colorless oil. Eluents for flash column chromatography dichloromethane/methanol (100:1 *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.73-7.68 (m, 1H), 7.63-7.55 (m, 4H), 7.42 (d, J = 15.7 Hz, 1H), 7.33-7.28 (m, 4H), 7.26-7.20 (m, 4H), 7.19-7.14 (m, 1H), 7.14-7.03 (m, 2H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 170.19, 151.57 (d, $J_{C\text{-}P}$ = 10.0 Hz), 135.60 (d, $J_{C\text{-}P}$ = 5.9 Hz), 134.88 (d, $J_{C\text{-}P}$ = 107.8 Hz), 130.91 (d, $J_{C\text{-}P}$ = 9.8 Hz), 130.36 (d, $J_{C\text{-}P}$ = 105.1 Hz), 129.19, 128.18 (d, $J_{C\text{-}P}$ = 12.3 Hz), 128.14, 105.15 (d, $J_{C\text{-}P}$ = 111.6 Hz), 100.04, 25.19. ^{31}P NMR (162 MHz, $CDCl_3$) δ ppm 20.70. HRMS m/z: calcd for $C_{22}H_{21}NO_2P^+$ $[M+H]^+$ 362.1304, found: 362.1292.

Preliminary Mechanistic Studies

(a) Radical-Trapping Experiment

1a **2a** **3aa, trace** **Detected by GC-MS**

Enamides **1** (0.3 mmol), phosphine oxide **2** (0.45 mmol, 1.5 eq), Eosin Y (0.0075 mmol, 2.5 mol%) and TEMPO (0.6 mmol, 2.0 eq) were added sequentially into Schlenk tube under nitrogen, the tube was then capped with a rubber stopper. TBPB (120 μL, 0.6 mmol, 2.0 eq) and MeCN (1.5 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 15 W blue LEDs irradiation for 24 hours. Then the solvent was removed under vacuum and the residue was determined by ^{1}H NMR analysis of the crude reaction mixture by using mesitylene as an internal standard. It was observed that the transformation was completely inhibited by TEMPO, along with the interception of the phosphinoyl radical species as detected by GC-MS (**Figure S2**), implying the involvement of a radical species.

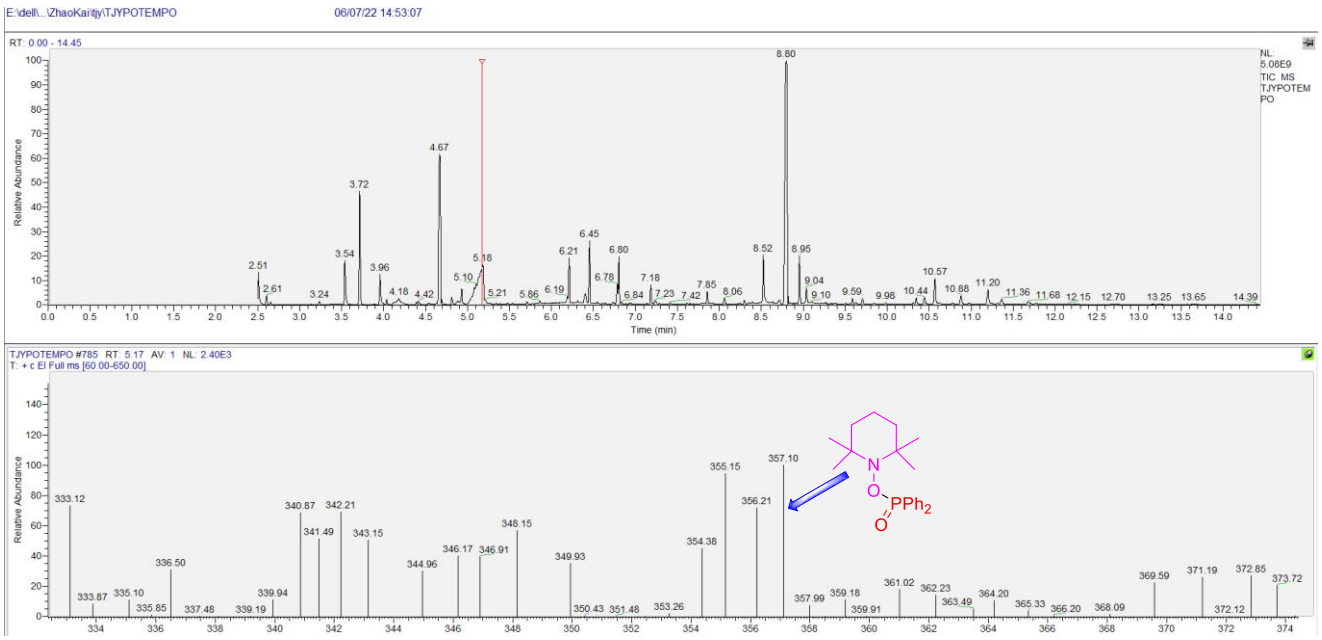


Figure S2 The GC-MS Spectra for the Radical-Trapping Experiment with TEMPO

(b) Quantum Yield Measurement

In order to determine whether a radical-chain reaction is involved, the quantum yield measurement was conducted, which gives the quantum yield (Φ) of the photoreaction of 0.78, implying that the reaction is highly possible to proceed in a photoredox catalytic pathway rather than a radical-chain mechanism.

The actinometry measurements were done as follows based on previous literature[3]:

(i) The actinometry measurements were determined by standard ferrioxalate actinometry. A solution of ferrioxalate was prepared by dissolving 73.7 mg of potassium ferrioxalate hydrate and 67.0 μL of concentrated sulfuric acid in a 25.0 mL volumetric flask and filled to the mark with water (HPLC grade). A buffered solution of phenanthroline was prepared by dissolving 25.0 mg of phenanthroline, 5.2 g of sodium acetate and 0.56 mL of concentrated sulfuric acid in a 50.0 mL volumetric flask and filled to the mark with water (HPLC grade). Both solutions were stored in the dark.

(ii) The actinometry solutions (V_1, 1.0 mL) were irradiated with 80 W blue LEDs for specified time intervals (30 s, 60 s, 90 s, 120 s, and 150 s). After irradiation, 40.0 μL (V_2) of the actionmeter solutions were removed and placed in 10.0 mL (V_3) volumetric flasks. 1.5 mL of buffered solutions were added to these flasks and filled to the mark with water (HPLC grade). The UV-Vis spectra of actinometry samples were recorded for each time interval (**Figure S3, a**). The absorbance of the actinometry solutions were monitored at 510 nm. A non-irradiated sample was also prepared and the absorbance at

510 nm measured in cuvette (l = 1 cm). ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). Based on the data, we got the graph (**Figure S3, b**).

$$\text{mol } Fe^{2+} = \frac{V_1 \times V_3 \times \Delta A\ (510\ nm)}{10^3 \times V_2 \times L \times \varepsilon\ (510\ nm)} = \frac{1\ mL \times 10\ mL \times \Delta A\ (510\ nm)}{10^3 \times (40 \times 10^{-3}\ mL) \times 1\ cm \times 11100} = \frac{\Delta A\ (510\ nm)}{44400} = 1.69565 \times 10^{-8}$$

The quantum yield for Fe^{2+} ($\Phi_{Fe^{2+}} = 1.13$), F = mol $Fe^{2+}/\Phi_{Fe^{2+}}$.Then, the irradiated light intensity was estimated to 1.70×10^{-8} einstein S^{-1} by using $K_3[Fe(C_2O_4)_3]$ as an actinometer.

(iii) For five clean tubes, according to the general procedure, the 0.3 mmol scale model reaction solution was irradiated with 80 W blue LEDs for specified time intervals (30 min, 60 min, 90 min, 120 min and 150 min). The moles of products formed were determined by ^1H NMR yield with mesitylene as reference standard. The number of moles of products (y axis) per unit time is related to the number of photons (x axis, calculated from the light intensity) (**Figure S3, c**). The slope gives the quantum yield (Φ) of the photoreaction, 0.78.

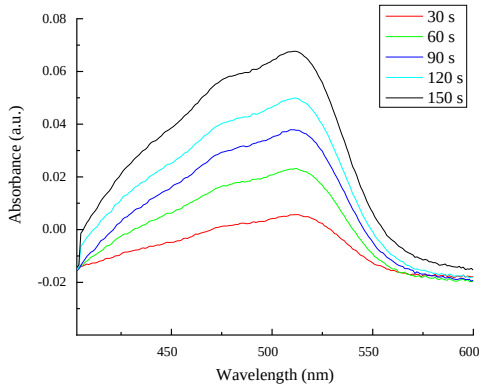


Figure a

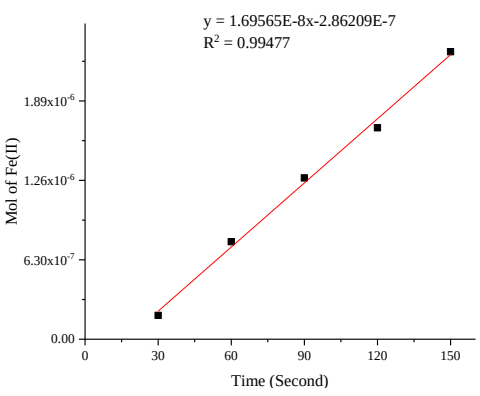


Figure b

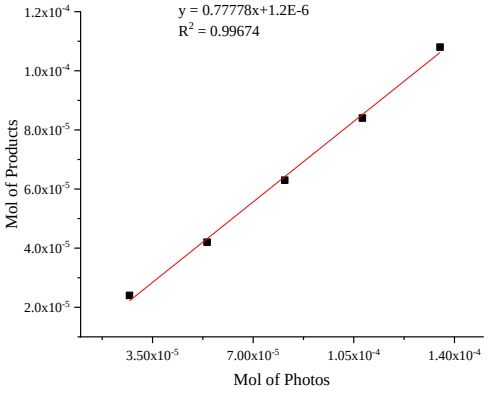
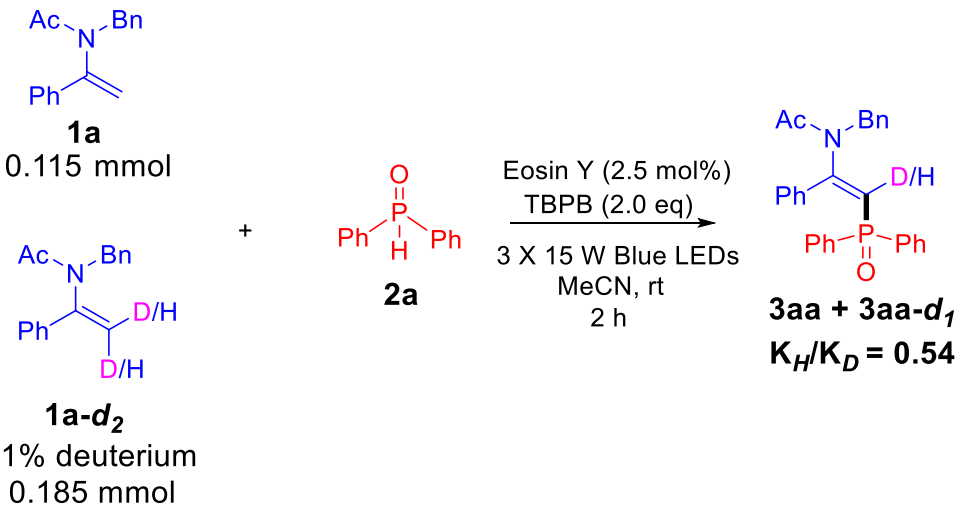


Figure c

Figure S3 The UV-Vis Spectra and Data of Quantum Yield Measurement

(c) Intermolecular Kinetic Isotopic Effect (KIE) Study

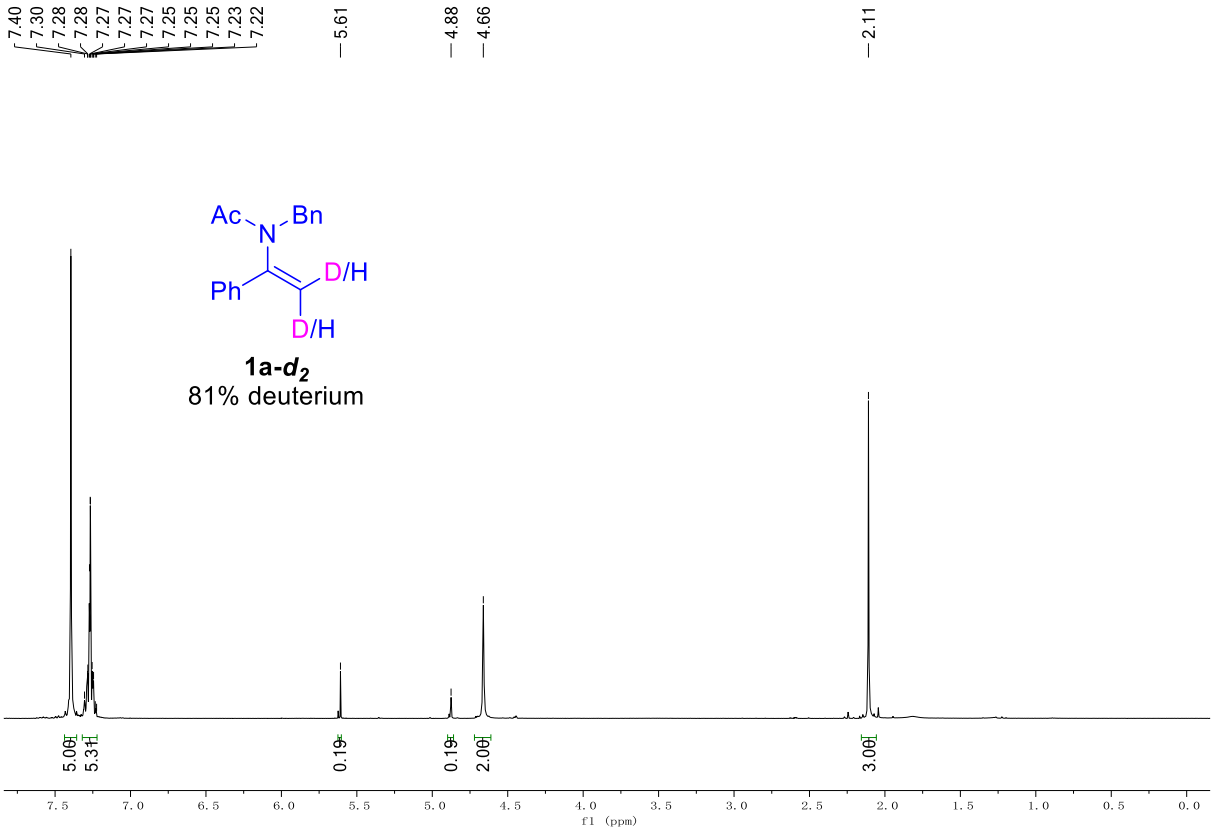


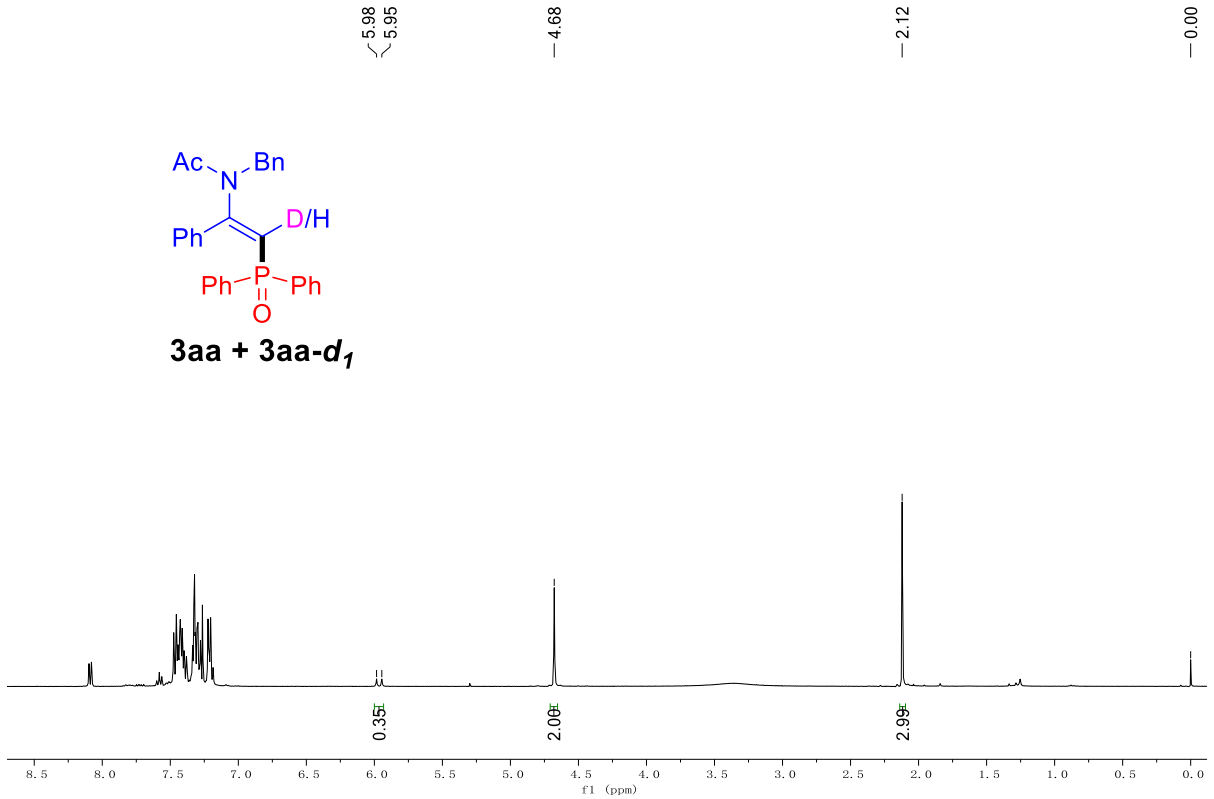
Enamide **1a-*d*$_2$** was prepared according to the literatures,[1b,4] as a light yellow oil with 81% deuterium. Enamide **1a** (0.115 mmol), **1a-*d*$_2$** (0.185 mmol), Eosin Y (0.005 mmol, 2.5 mol%)were added sequentially into an oven-dried Schlenk tube under nitrogen atmosphere, the tube was then capped with a rubber stopper. TBPB (120 μL, 0.6 mmol, 2.0 eq) and MeCN (1.5 mL) were then added by syringe. The resulting mixture was allowed to stir at room temperature under 15 W blue LEDs irradiation for 2 hours. The product was isolated through thin-layer chromatography (dichloromethane/methanol 100:1 *v*/*v*) to afford crude mixture (10% yield) as light yellow oil. The KIE value (K_H/K_D = 0.54) was determined by ^{1}H NMR.

In consideration of the 81% deuterated ratio of **1a-*d*$_2$**, 0.185 mmol of **1a-*d*$_2$** (a H-D mixture containing 81% deuterated enamide and 19% undeuterated one) was added along with 0.115 mmol of undeuterated enamide **1a** in the same reaction vessel, so that the real amount of pure deuterated enamide (and its undeuterated competitor) was calculated to be 0.15 mmol approximately. The ratio of deuterated enamide **2a-*d*$_1$** *vs* **2a** in the isolated mixture was 65:35 as determined by ^{1}H NMR, thus giving a calculated K_H/K_D = 0.35/0.65 = 0.54.

Notably, an inverse secondary KIE (KIE<1) is observed, which might be attributed to the change of the hybridization state of the olefinic carbon of the substrate. Based on the mechanism as depicted in Figure 1, the addition of the phosphinoyl radical species to the double bonds of enamides to form intermediate **A** changes the hybridization state of the *β*-olefinic carbon from sp^2 to sp^3, leading to an increase of the force constant of the C-H or C-D bonds bending vibrations (which means the C-H bending vibrations became more rigid and difficult). In this pattern, the difference between the zero-point energy in the transition state (ΔG_{TS}) (between the H-containing compound and a D-containing

one) is greater than the difference between the starting enamide substrates (ΔG_s), implying that the reaction rate of a deuterium-labelled substrate would surpass the rate of the non-deuterium one at a relatively low conversion, resulting to an inverse KIE of 0.54.

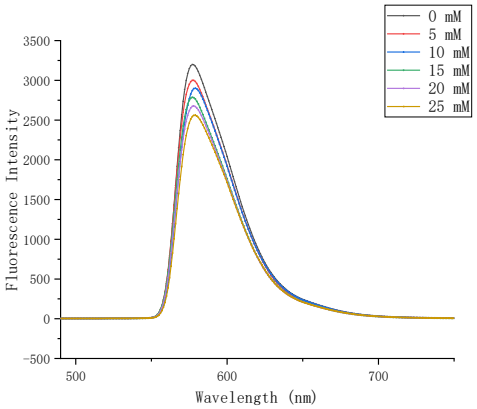




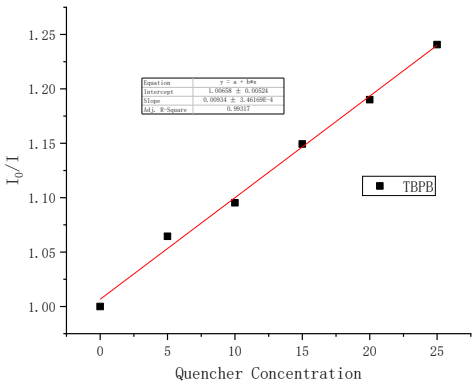
(d) Stern-Volmer Experiment

The Stern-Volmer fluorescence quenching experiments of Eosin Y with TBPB was conducted by the following procedures. Firstly, the emission and excitation spectra of the photocatalyst Eosin Y was investigated. The luminescence quenching experiment was taken using an F97 pro Fluorescence spectrophotometer (Shanghai, China). A solution of Eosin Y (1.0 mM) in DMSO was chosen as the model. The excitation wavelength was 451 nm and the emission intensity was collected at 578 nm.

Next, the fluorescence quenching experiments of Eosin Y with TBPB was conducted respectively: In a typical experiment, 1.0 mL of solution of Eosin Y (1.0 mM) in DMSO was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette, 1 M solution of the quencher (oxidants) was added into the cuvette by 5 μL, and the emission of the sample was collected (**Figure S4a**). The solution was excited at λ = 451 nm (excitation maximum of Eosin Y) and the emission intensity at 578 nm (emission maximum of Eosin Y) was observed (**Figure S4b**). Linear quenching was observed when TBPB was used as the oxidant, showing that the oxidative quenching of the excited Eosin Y by TBPB is highly plausible.



a) The fluorescence emission spectra of Eosin Y with different concentration of added quencher (TBPB) excited at 451 nm.



b) Eosin Y emission quenching by TBPB. Linear quenching is observed.

Figure S4 Stern-Volmer Experiments

(e) Alternative Mechanism Using Mes-AcrClO$_4$ as a Photocatalyst

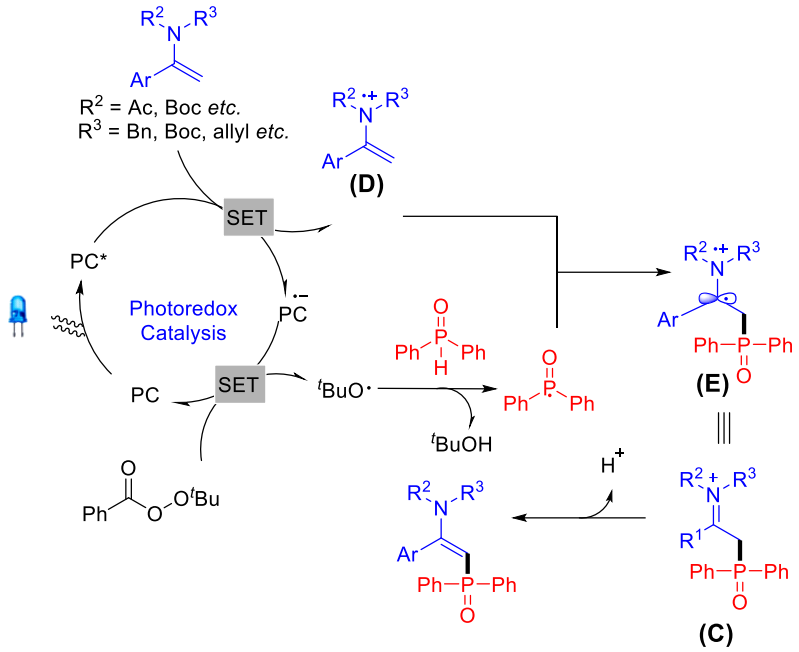


Figure S5 An Alternative Reductive Quenching Cycle Using Mes-AcrClO$_4$ as a Photocatalyst

In the case of Eosin Y, an oxidative quenching of Eosin Y* has been proposed. However, when using the oxidative photocatalyst Mes-AcrClO$_4$ as the catalyst ($E_{1/2}^{red}$ = +2.06 V *vs* SCE), a reductive quenching of the photocatalyst (PC) is more feasible, as depicted in **Figure S5**. Initially, the photocatalyst is excited into PC* upon blue LEDs irradiation. Then, PC* is reductively quenched by enamides to generate a radical cation **D** and a radical anion $PC^{\bullet-}$. Subsequently, TBPB is reduced by $PC^{\bullet-}$ to furnish a *tert*-butyloxy radical, along with the regeneration of the ground state PC to complete the photocatalytic cycle. Next, the hydrogen abstraction of phosphine oxides by *tert*-butyloxy radical occurs to give a P-centered phosphinoyl radical, which would be regioselectively intercepted by radical cation **D** to forge intermediate **E** (the resonanced equivalent of iminium ion **C**). Finally, the deprotonation of **C** gives the desired β-phosphorylated enamides.

References

1. (a) Berg, M. v. d.; Haak, R. M.; Minnaard, A. J.; de Vries, A. H. M.; de Vries, J. G.; Feringa, B. L. *Adv. Synth. Catal.* **2002**, *344*, 1003; (b) Pankajakshan, S.; Xu, Y.-H.; Cheng, J.-K.; Low, M.-T.; Loh, T.-P. *Angew. Chem., Int. Ed.* **2012**, *51*, 5701. (c) Chang, X. H.; Wang, Z. L.; Zhao, M.; Yang, C.; Li, J. J.; Ma, W. W.; Xu, Y.-H. *Org. Lett.* **2020**, *22*, 1326.

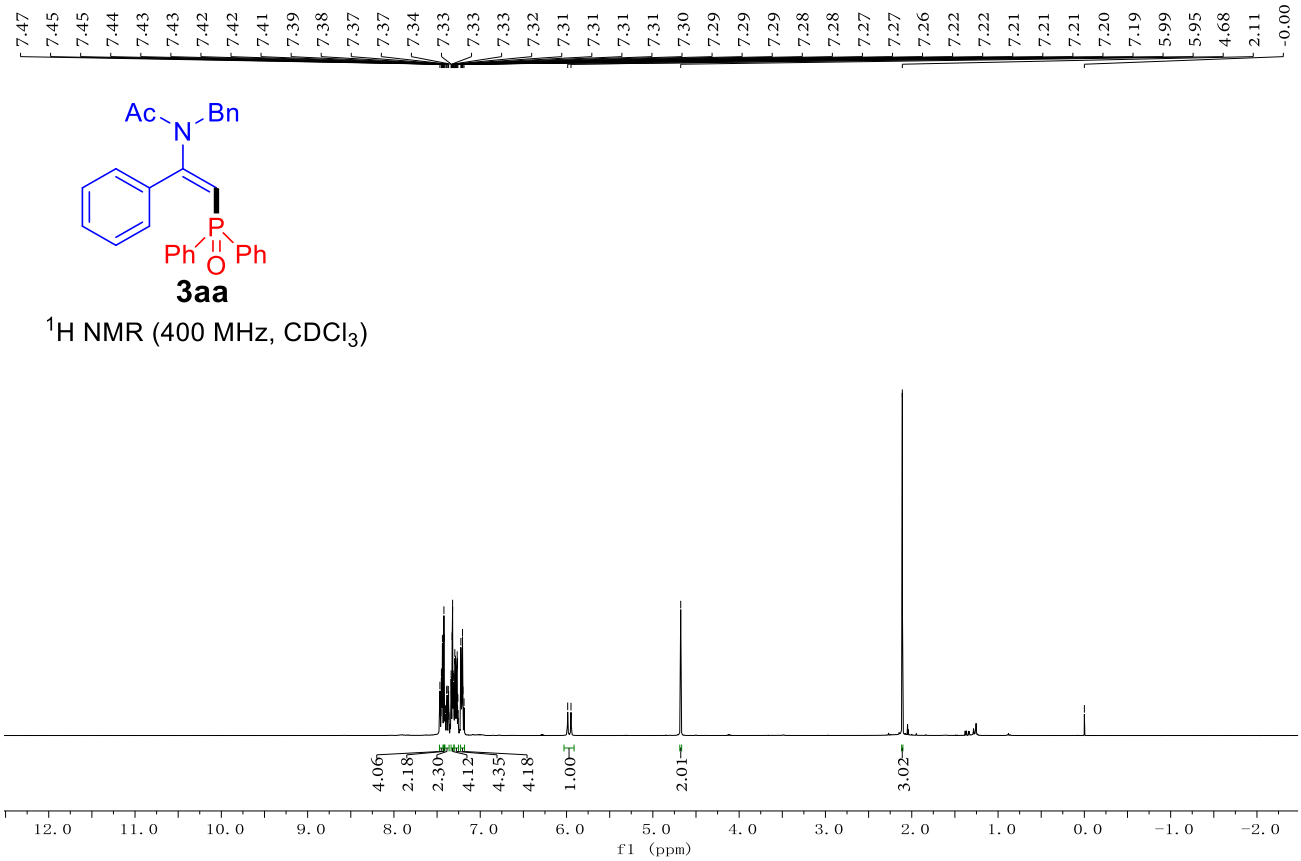
2. Nigama, S. C.; Mann, A.; Taddei, M.; Wermutha, C.-G. *Synth. Commun*. **1989**, *19*, 3139.

3. Cismesiaa, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426.

4. Yu, W.-L.; Chen, J.; Liu, Z.-X.; Zhang, Y.-H. *Org. Lett*. **2014**, *16*, 4870.

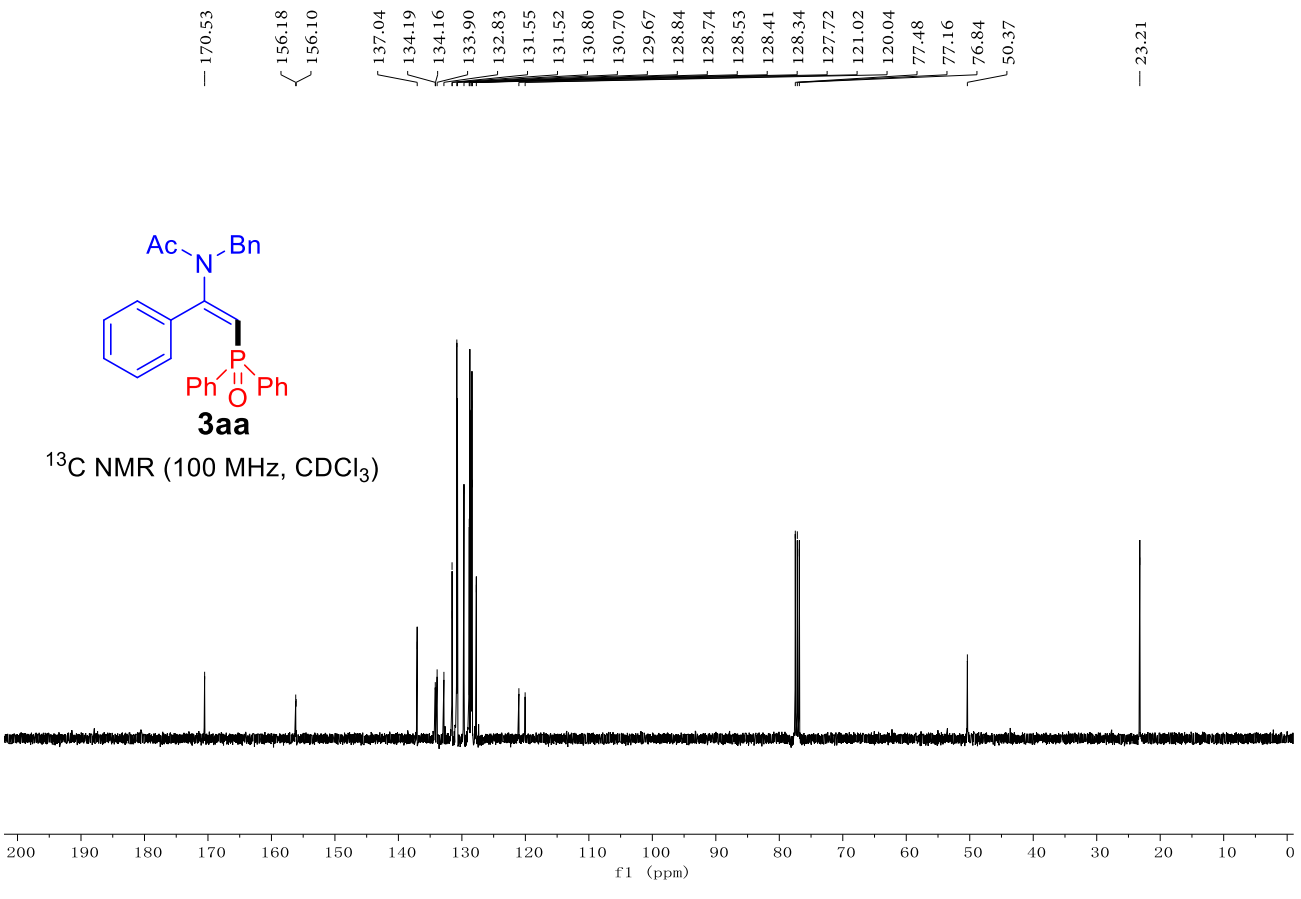
Copies of ^{1}H NMR, ^{13}C NMR, ^{19}F NMR and ^{31}P NMR Spectra

(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (**3aa**)



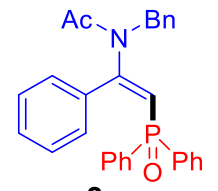
3aa

^{1}H NMR (400 MHz, $CDCl_3$)



3aa

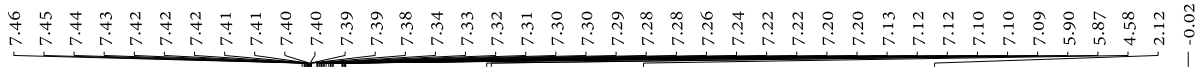
^{13}C NMR (100 MHz, $CDCl_3$)

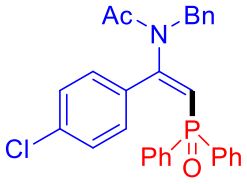


3aa

^{31}P NMR (162 MHz, $CDCl_3$)

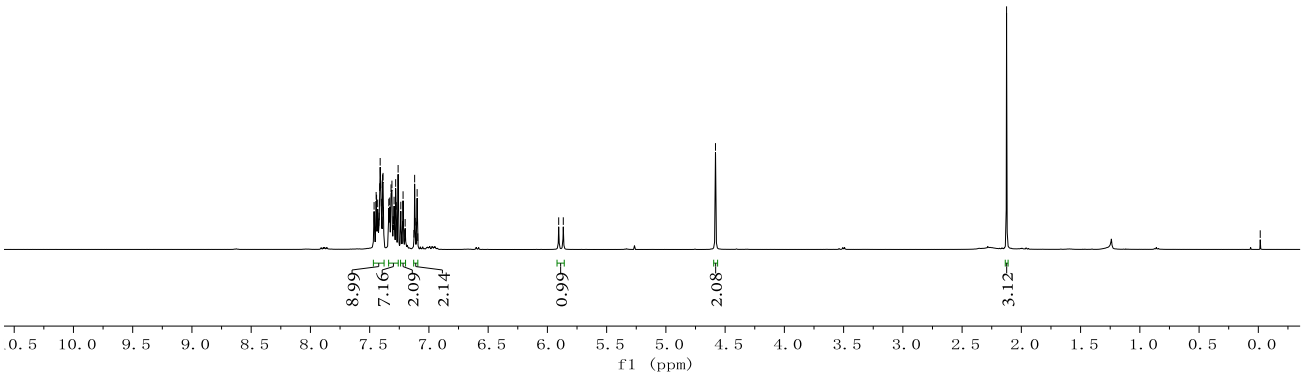
(E)-*N*-benzyl-*N*-(1-(4-chlorophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (**3ba**)

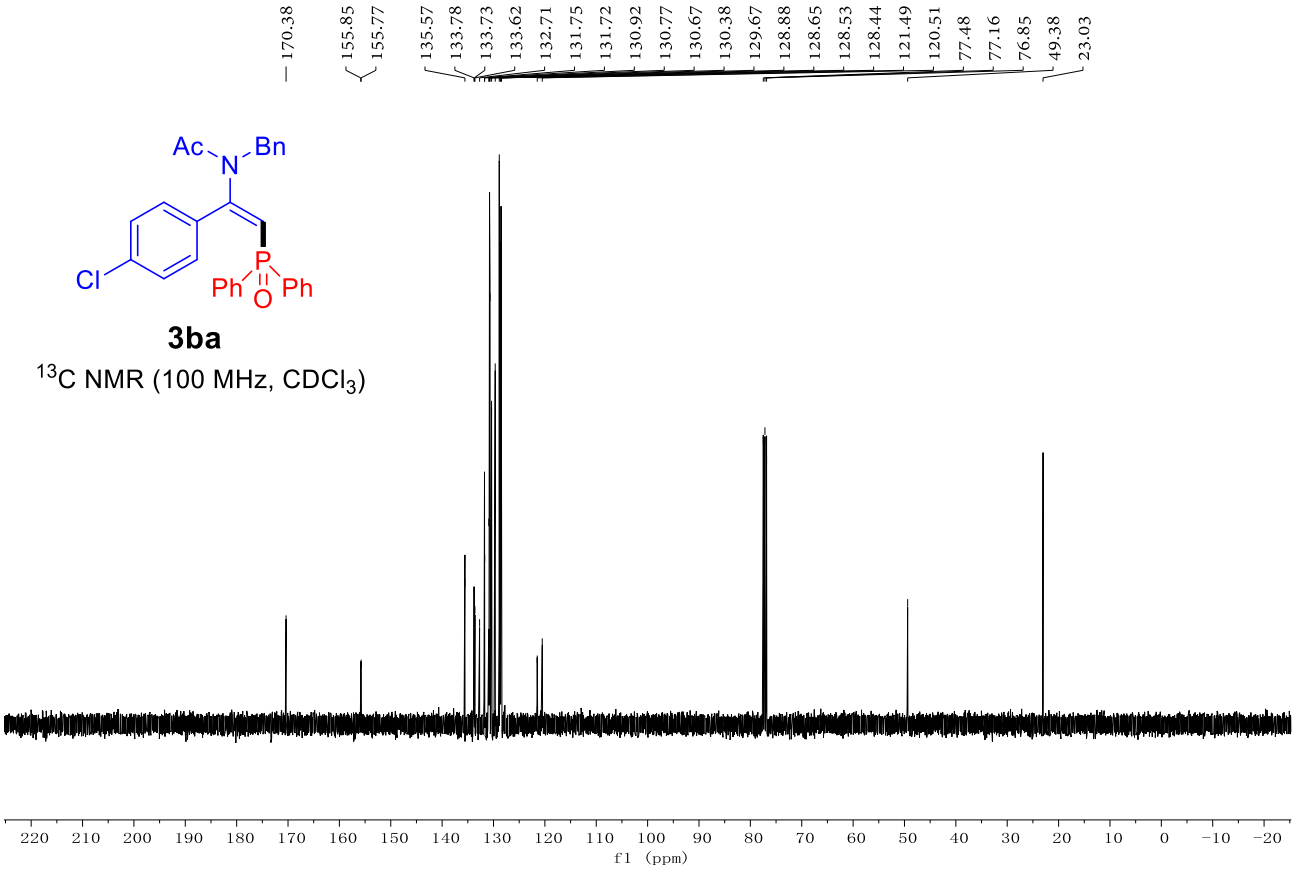




3ba

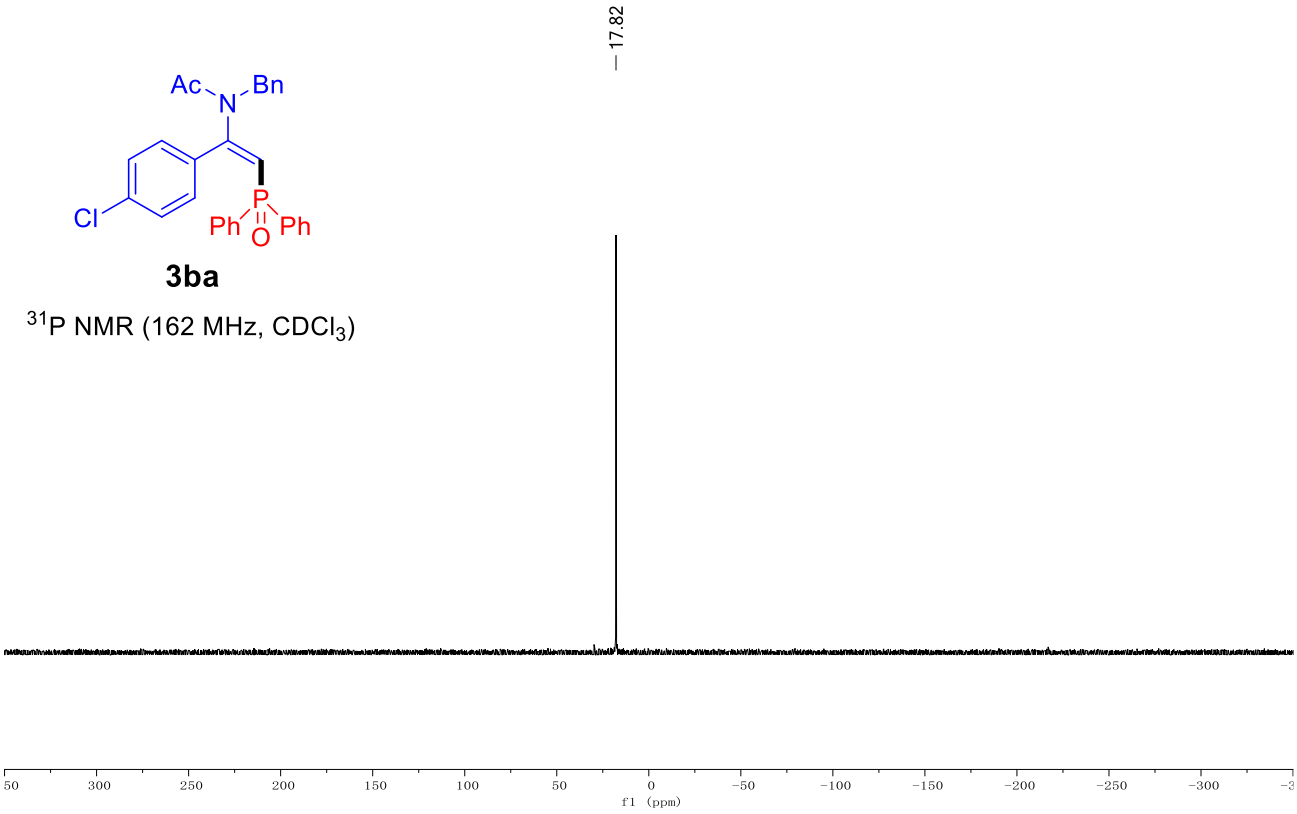
^{1}H NMR (400 MHz, $CDCl_3$)





3ba

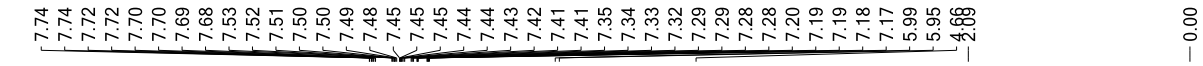
^{13}C NMR (100 MHz, $CDCl_3$)

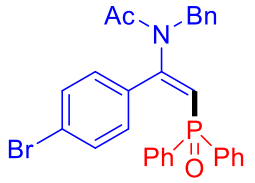


3ba

^{31}P NMR (162 MHz, $CDCl_3$)

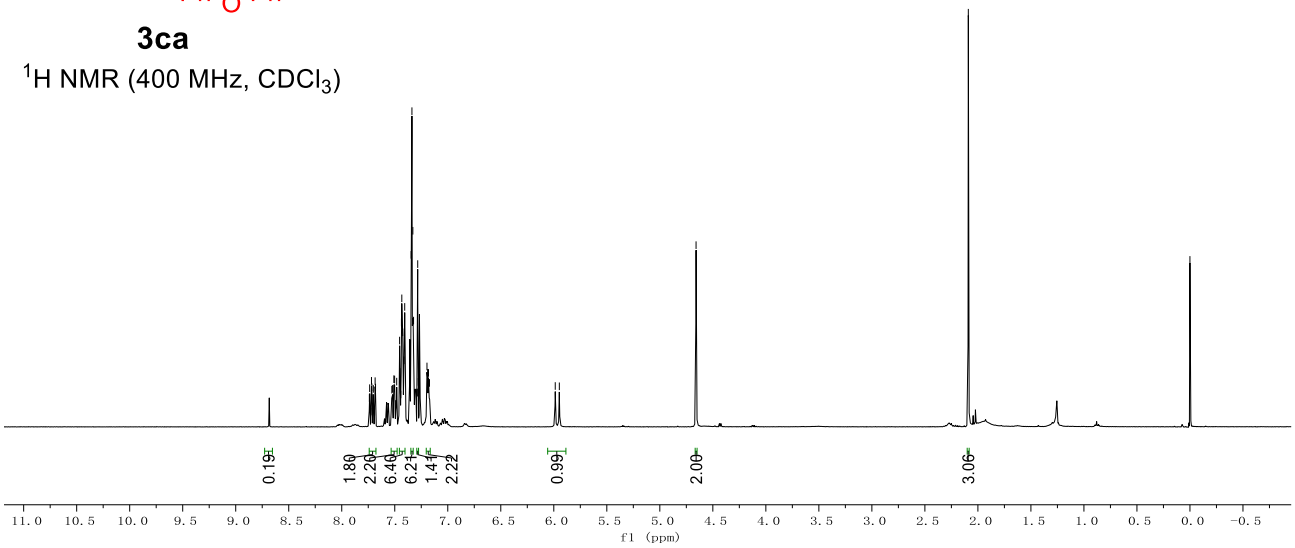
(E)-*N*-benzyl-*N*-(1-(4-bromophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (**3ca**)

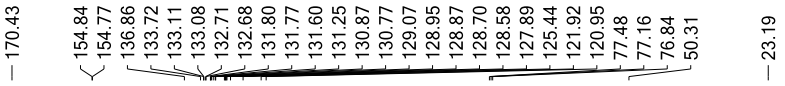


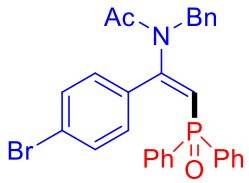


3ca

^{1}H NMR (400 MHz, $CDCl_3$)

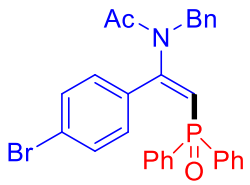






3ca

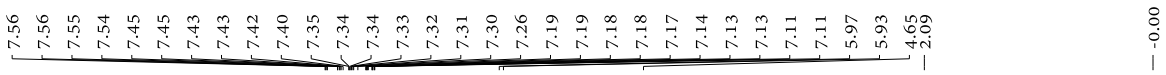
^{13}C NMR (100 MHz, $CDCl_3$)

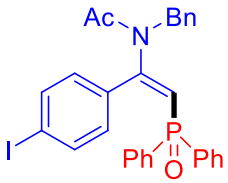


3ca

^{31}P NMR (162 MHz, $CDCl_3$)

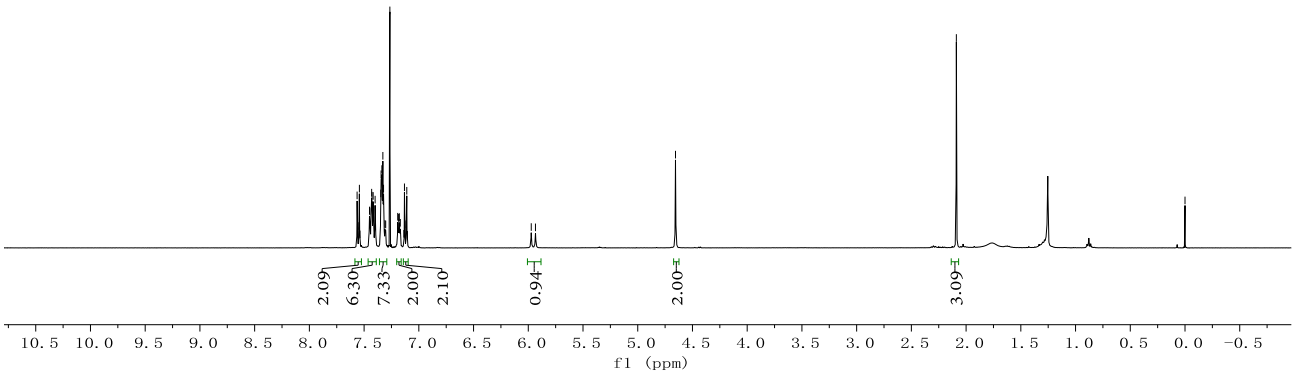
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-iodophenyl)vinyl)acetamide (**3da**)

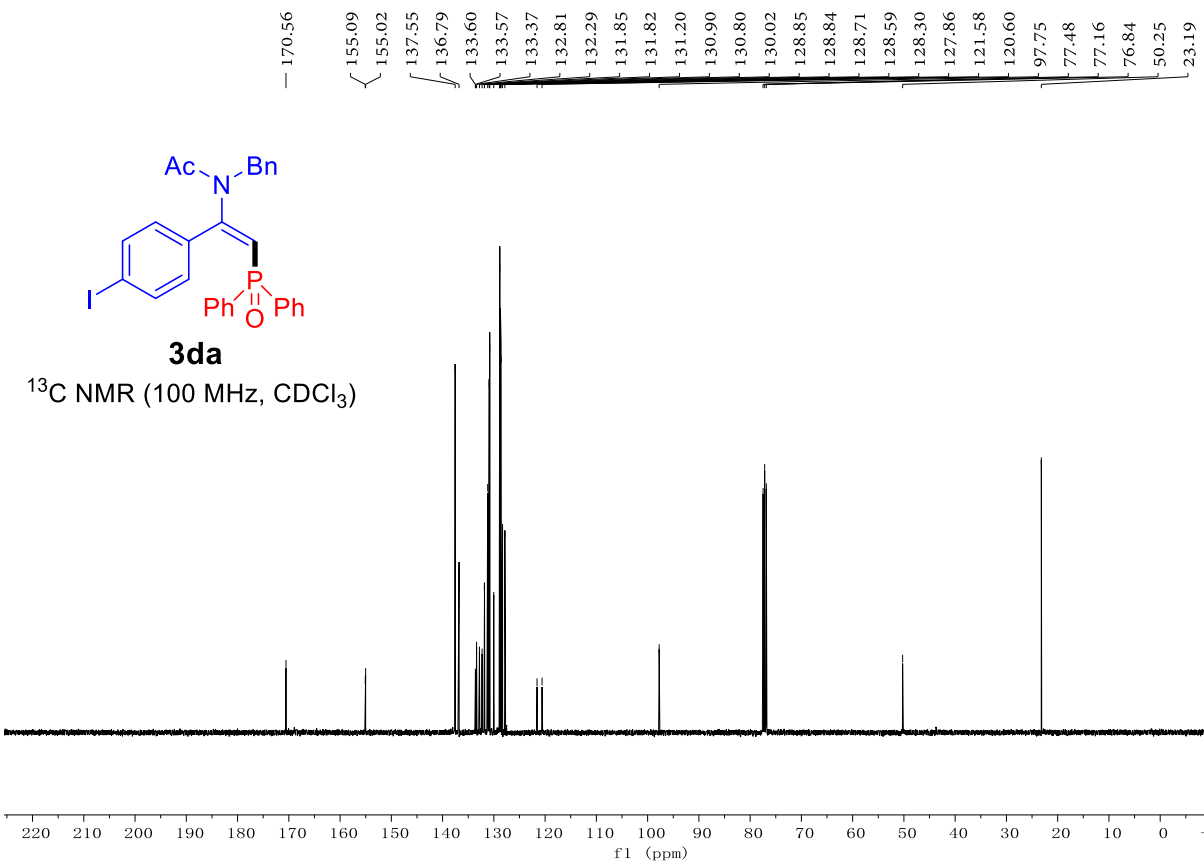




3da

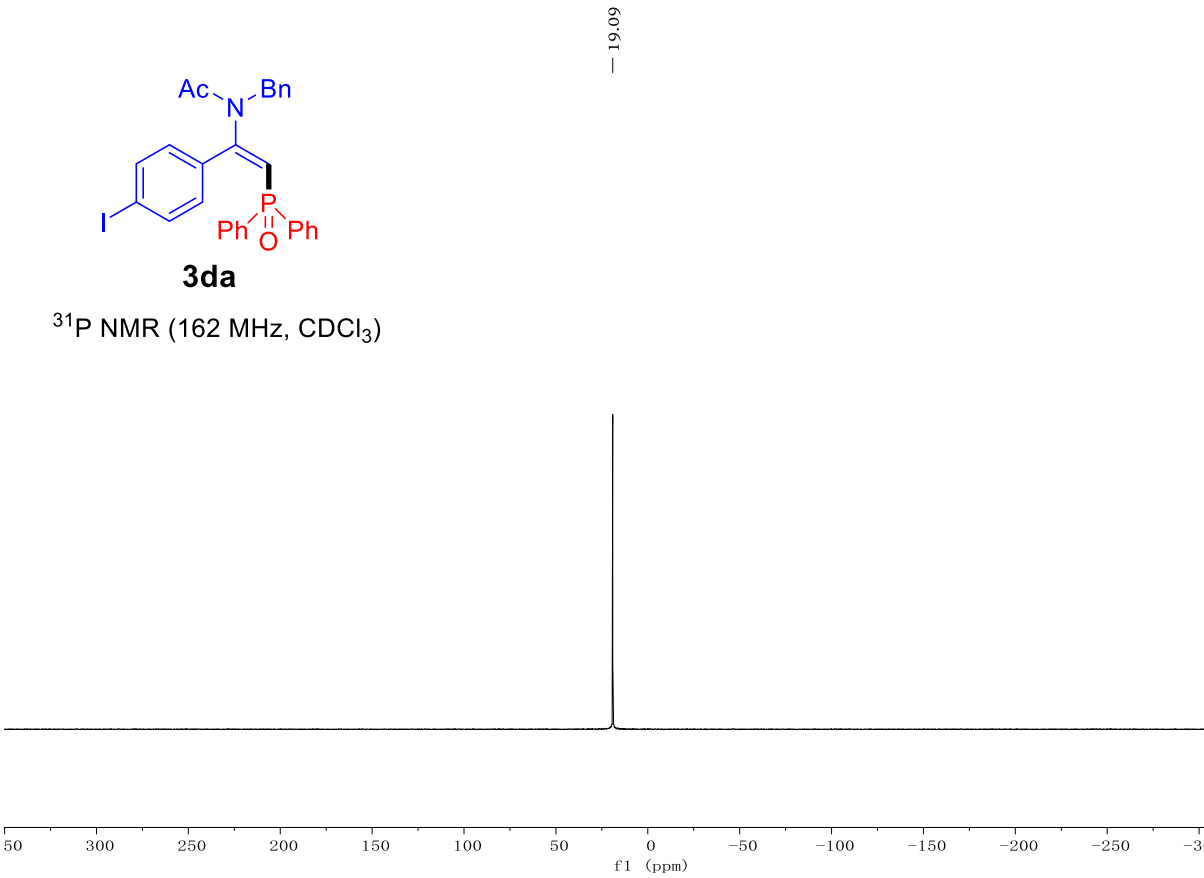
^{1}H NMR (400 MHz, $CDCl_3$)





3da

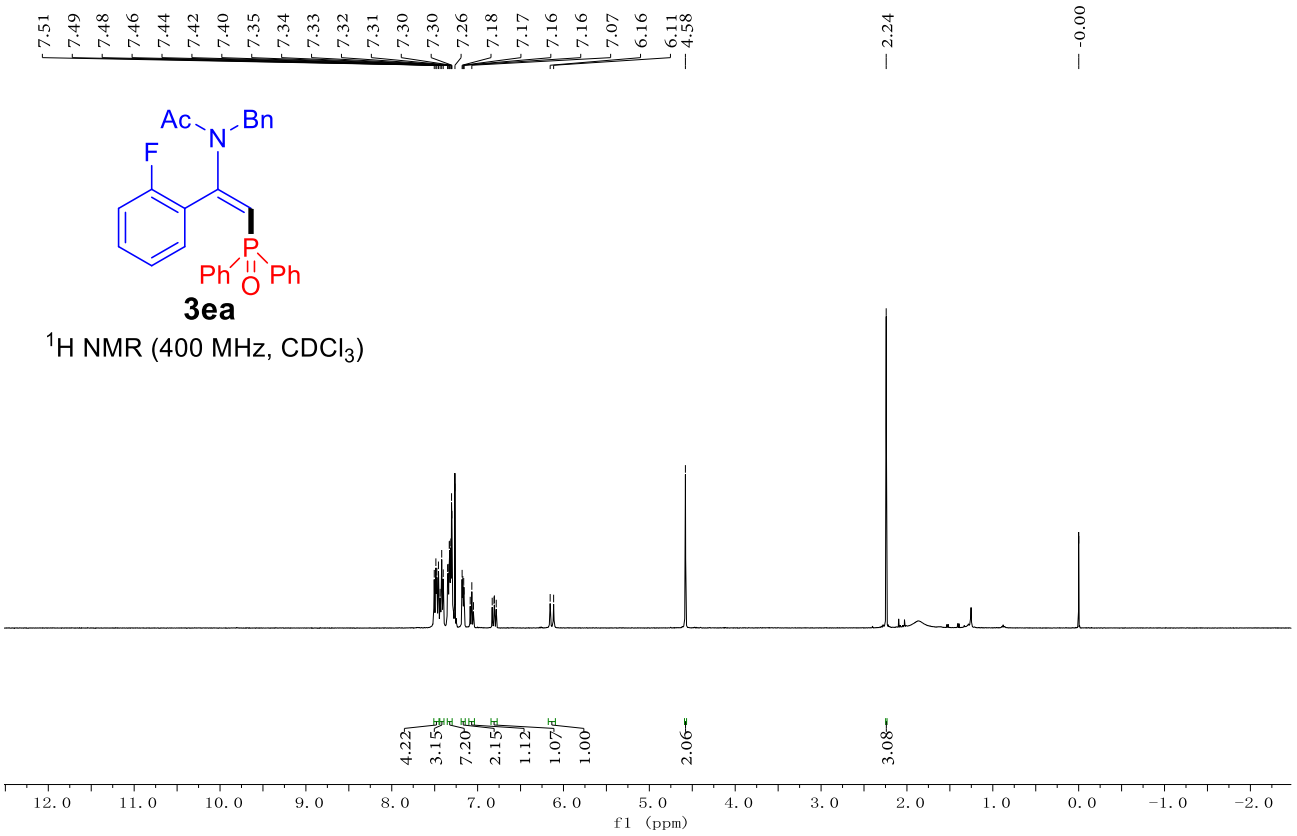
^{13}C NMR (100 MHz, $CDCl_3$)

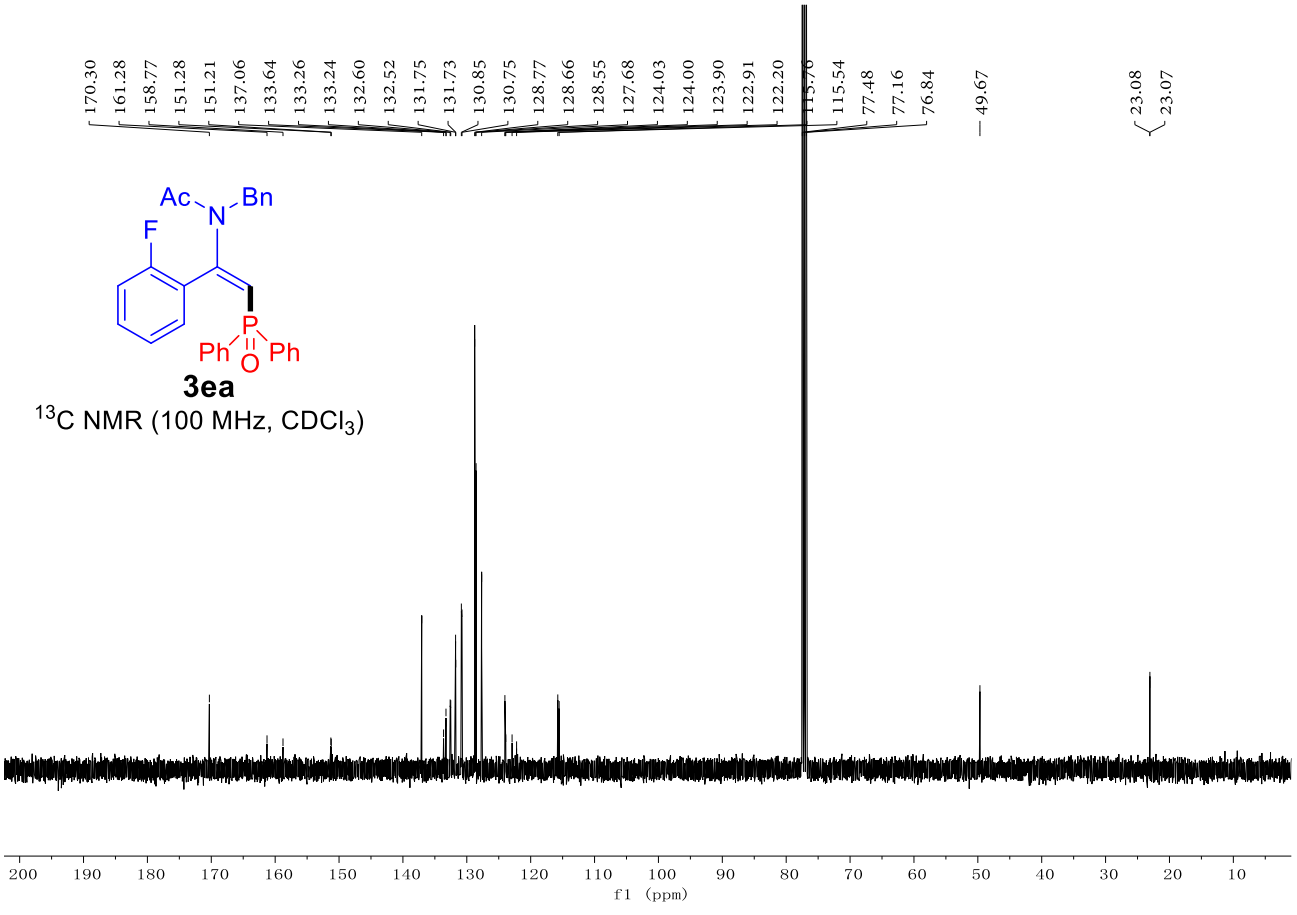


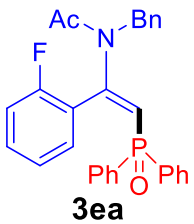
3da

^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(2-fluorophenyl)vinyl)acetamide (**3ea**)

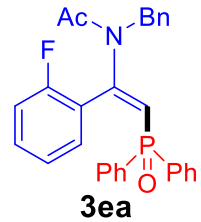






3ea

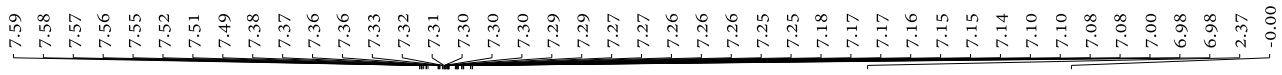
^{19}F NMR (376 MHz, $CDCl_3$)

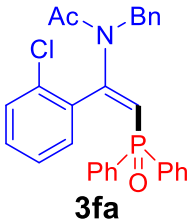


3ea

^{31}P NMR (162 MHz, $CDCl_3$)

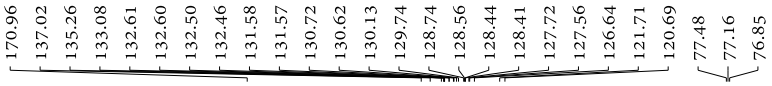
(E)-*N*-benzyl-*N*-(1-(2-chlorophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (**3fa**)

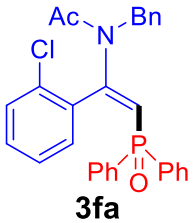




3fa

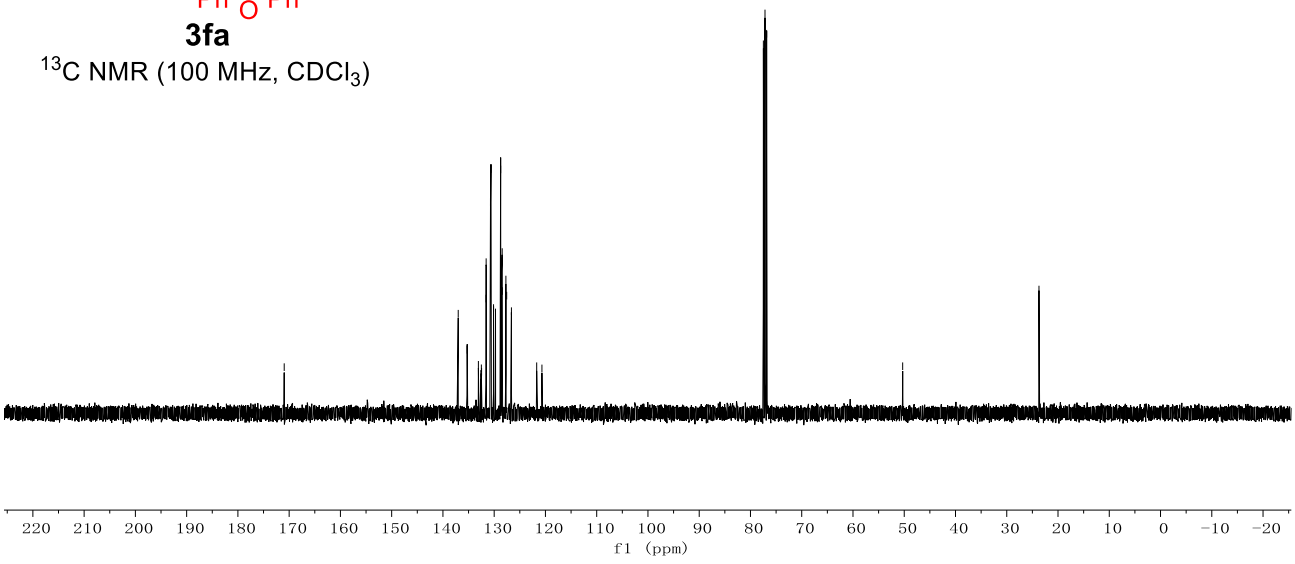
^{1}H NMR (400 MHz, $CDCl_3$)

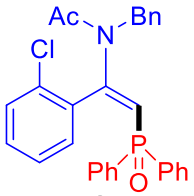




3fa

^{13}C NMR (100 MHz, $CDCl_3$)

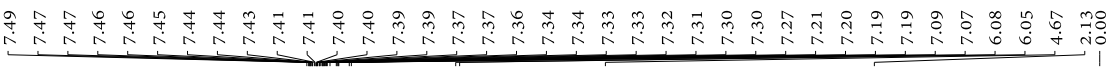


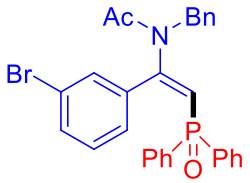


3fa

^{31}P NMR (162 MHz, $CDCl_3$)

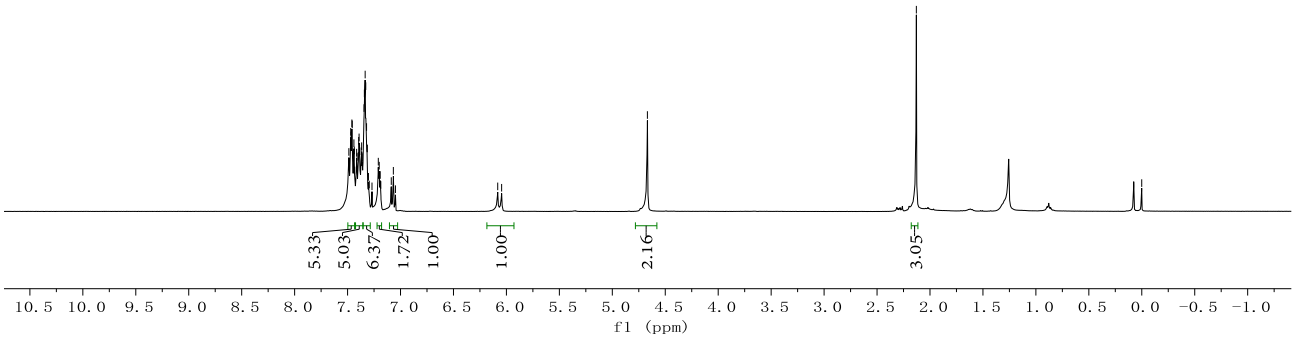
(E)-*N*-benzyl-*N*-(1-(3-bromophenyl)-2-(diphenylphosphoryl)vinyl)acetamide (**3ga**)

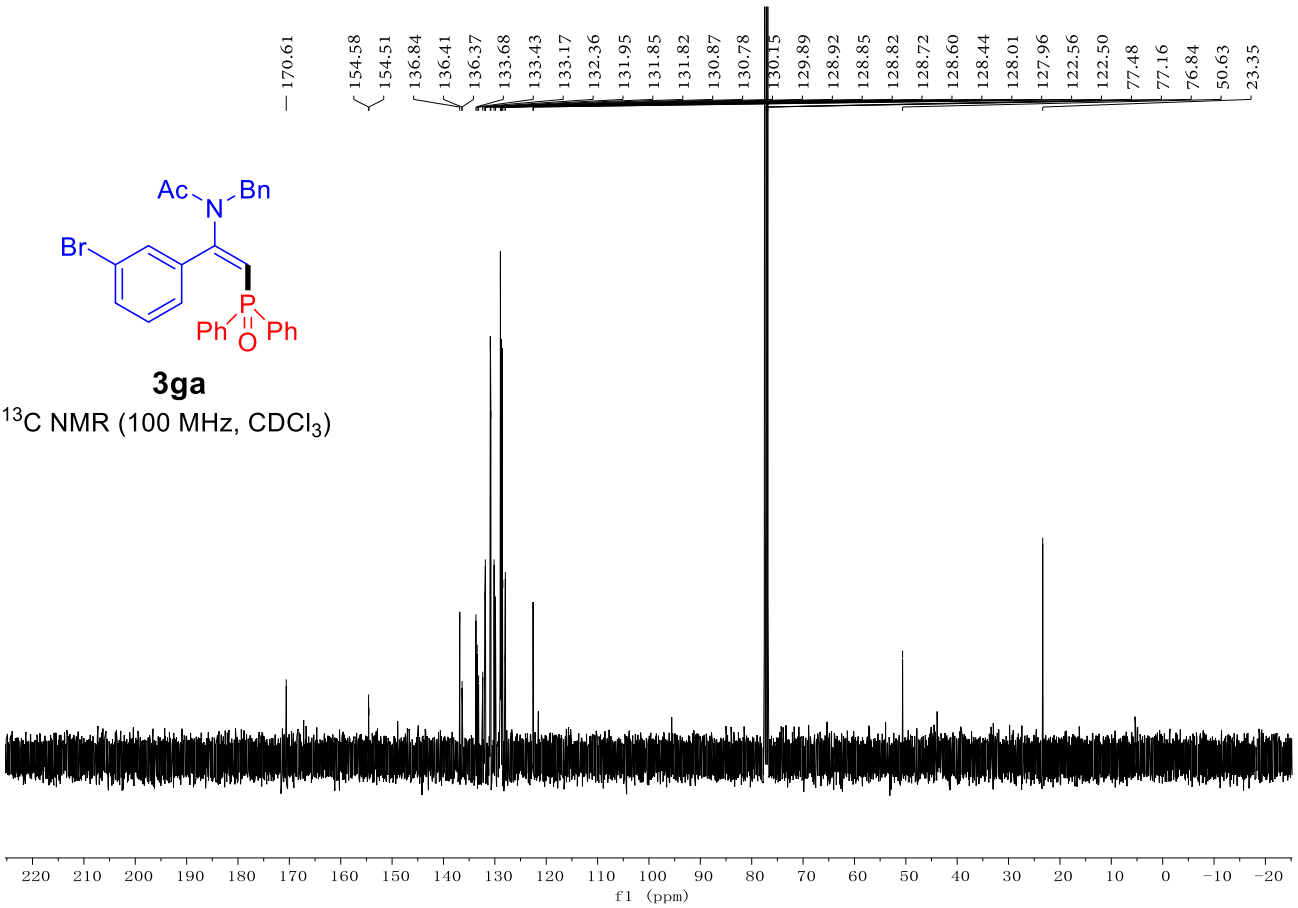




3ga

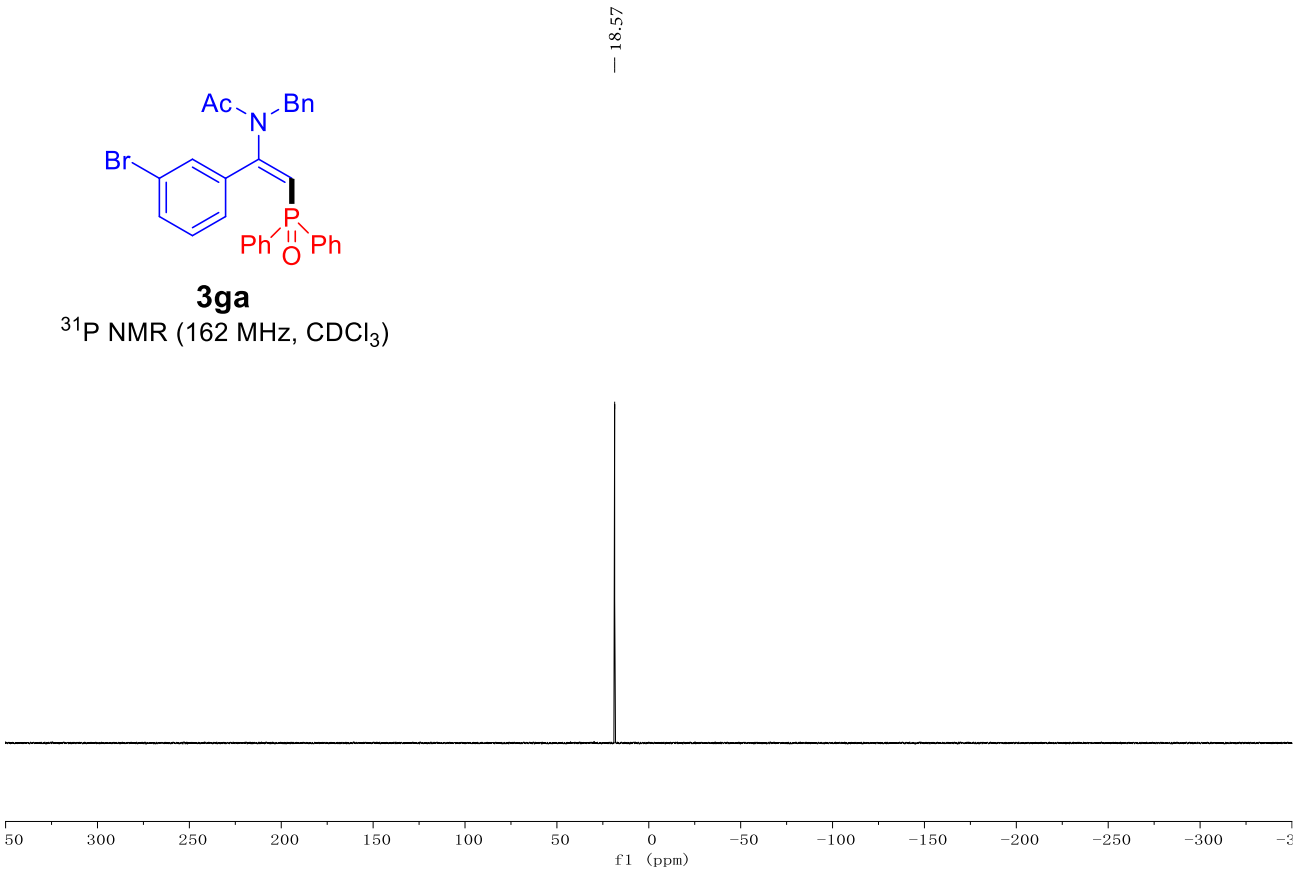
^{1}H NMR (400 MHz, $CDCl_3$)





3ga

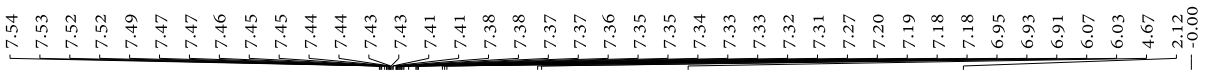
^{13}C NMR (100 MHz, $CDCl_3$)

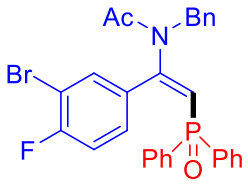


3ga

^{31}P NMR (162 MHz, $CDCl_3$)

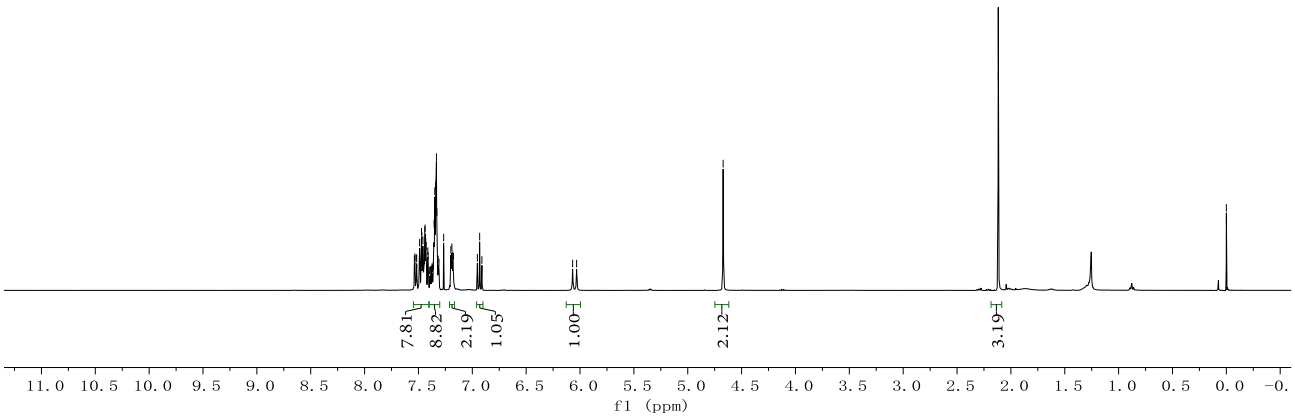
(E)-*N*-benzyl-*N*-(1-(3-bromo-4-fluorophenyl)-2-(diphenylphosphoryl)vinyl) acetamide (**3ha**)

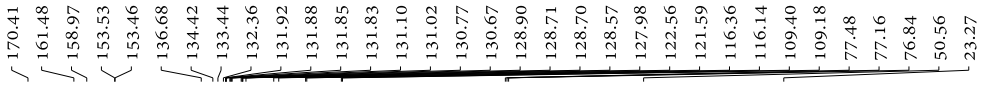


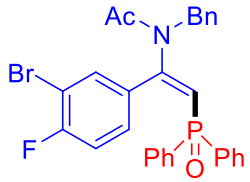


3ha

^{1}H NMR (400 MHz, $CDCl_3$)

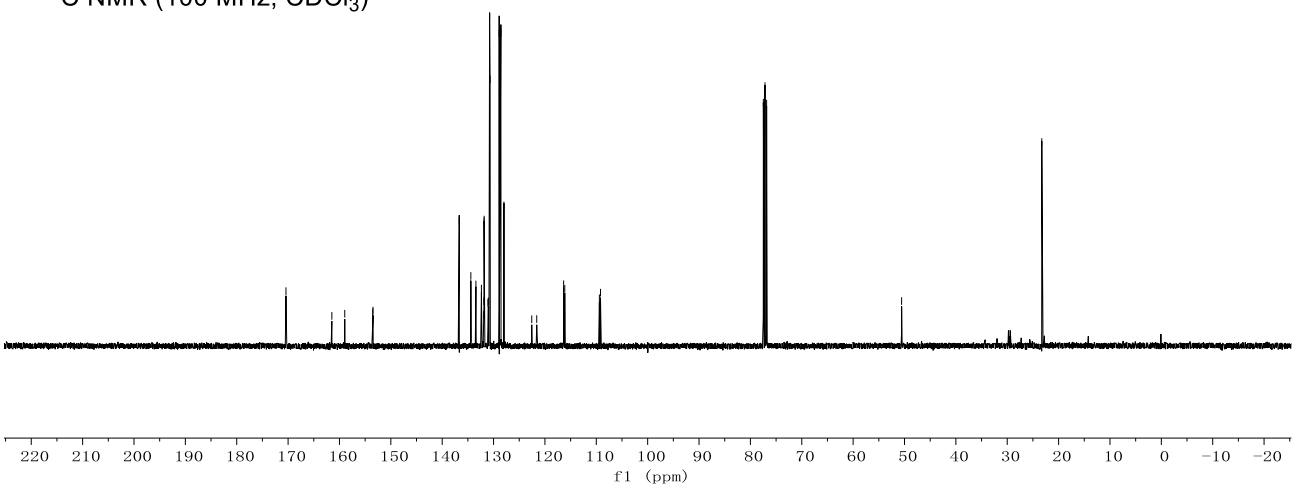


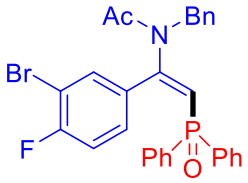




3ha

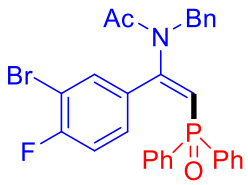
^{13}C NMR (100 MHz, $CDCl_3$)





3ha

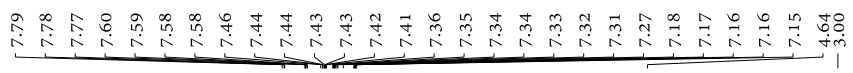
^{19}F NMR (376 MHz, $CDCl_3$)

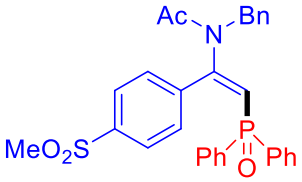


3ha

^{31}P NMR (162 MHz, $CDCl_3$)

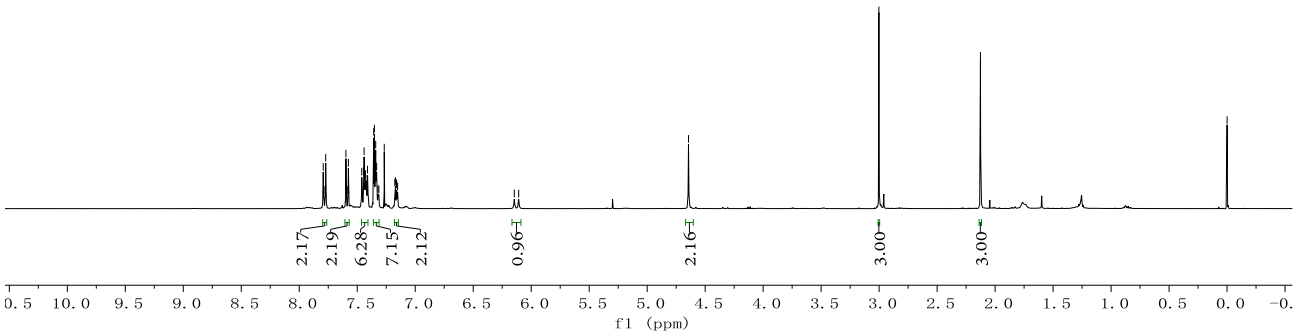
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-(methylsulfonyl)phenyl)vinyl) acetamide (**3ia**)

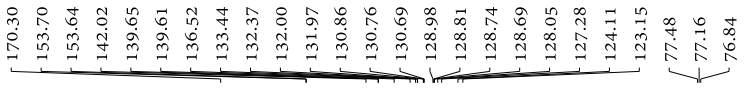


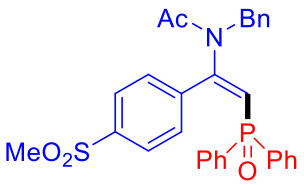


3ia

^{1}H NMR (400 MHz, $CDCl_3$)

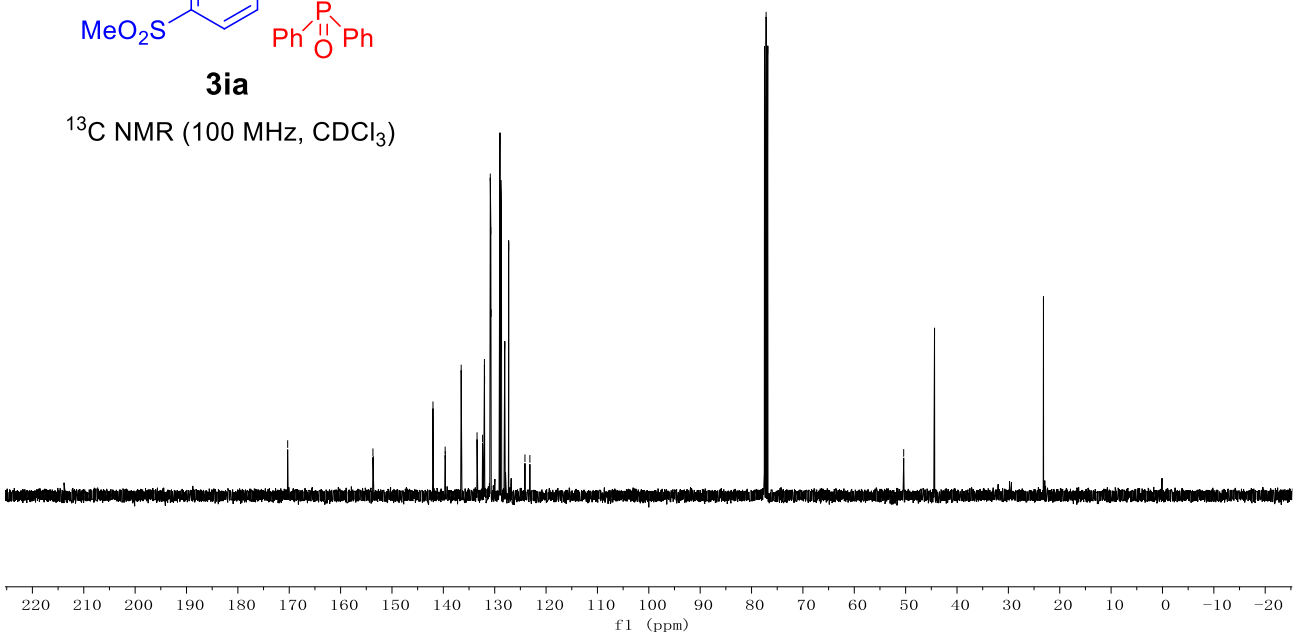


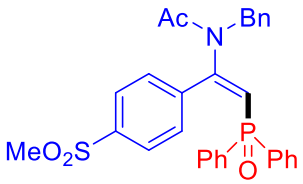




3ia

^{13}C NMR (100 MHz, $CDCl_3$)

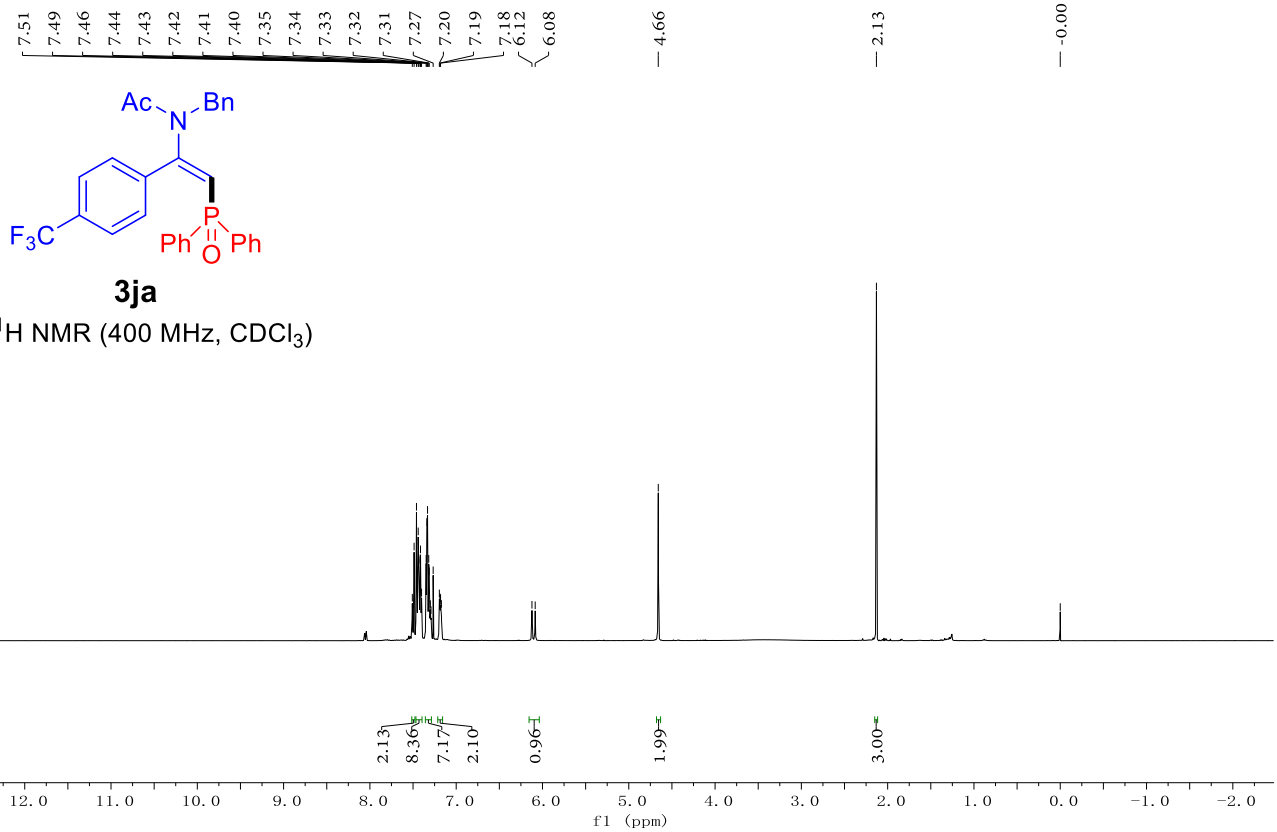




3ia

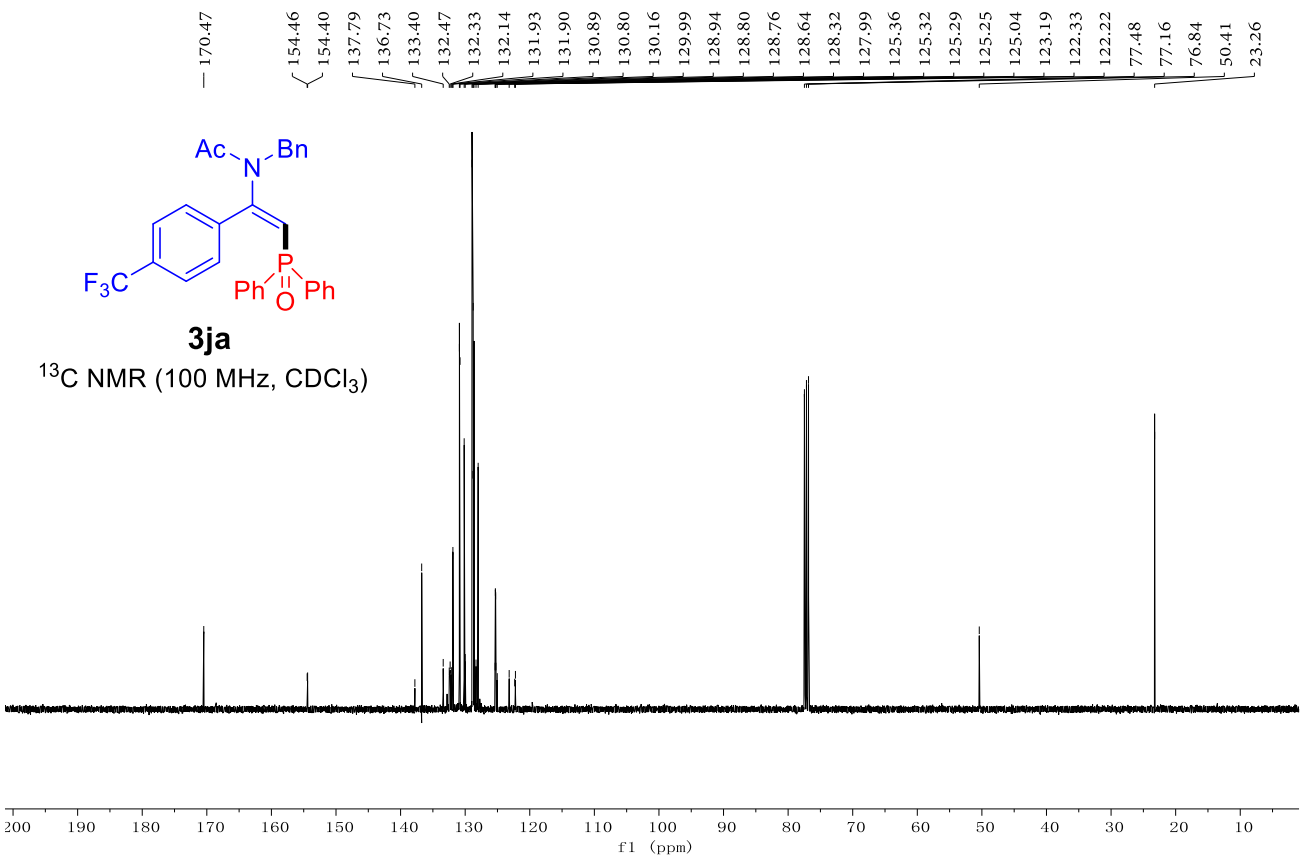
^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-(trifluoromethyl)phenyl)vinyl) acetamide (**3ja**)



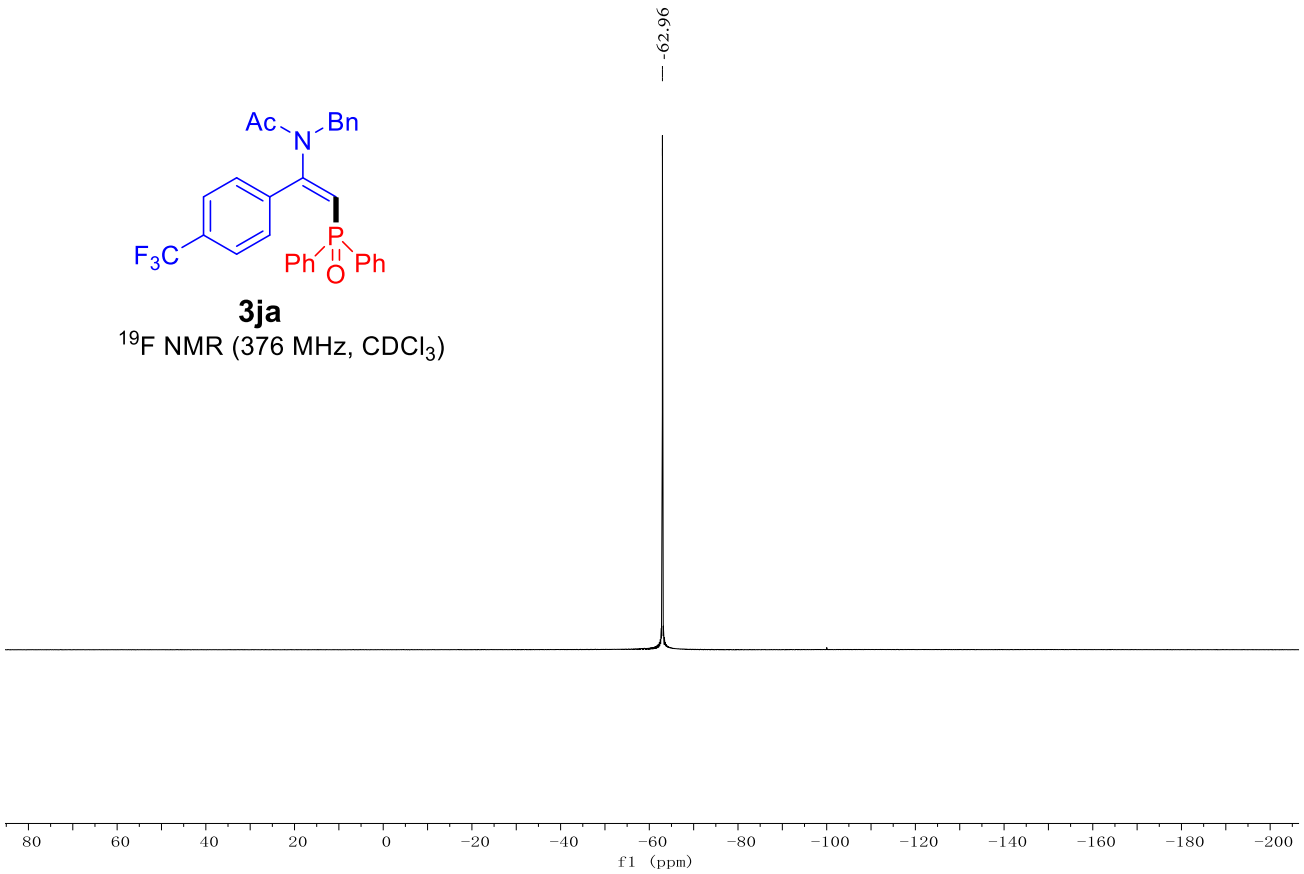
3ja

^{1}H NMR (400 MHz, $CDCl_3$)



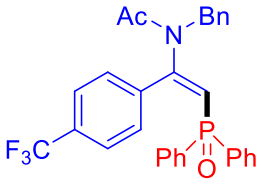
3ja

^{13}C NMR (100 MHz, $CDCl_3$)



3ja

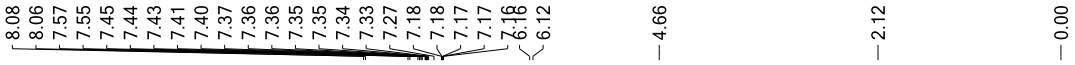
^{19}F NMR (376 MHz, $CDCl_3$)

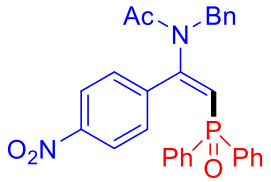


3ja

^{31}P NMR (162 MHz, $CDCl_3$)

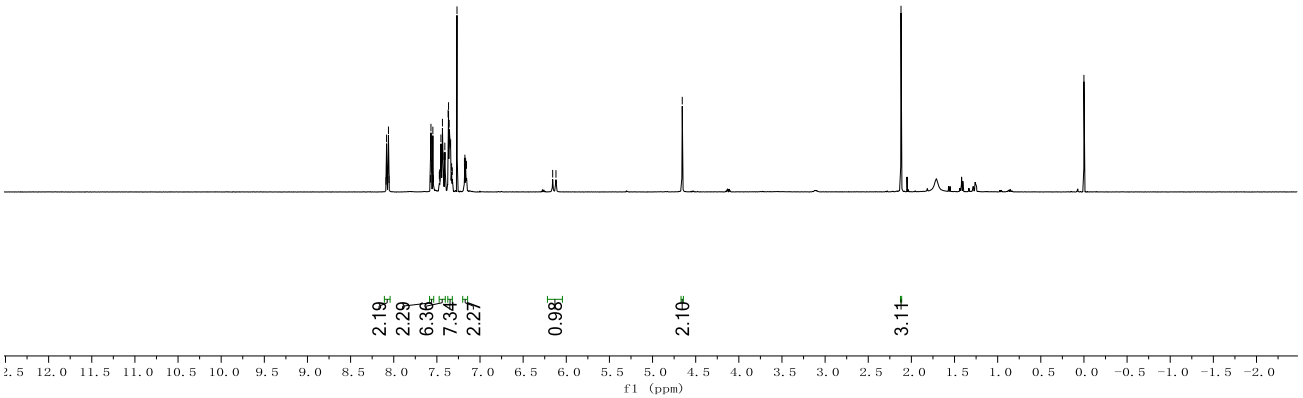
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-nitrophenyl)vinyl)acetamide (**3ka**)

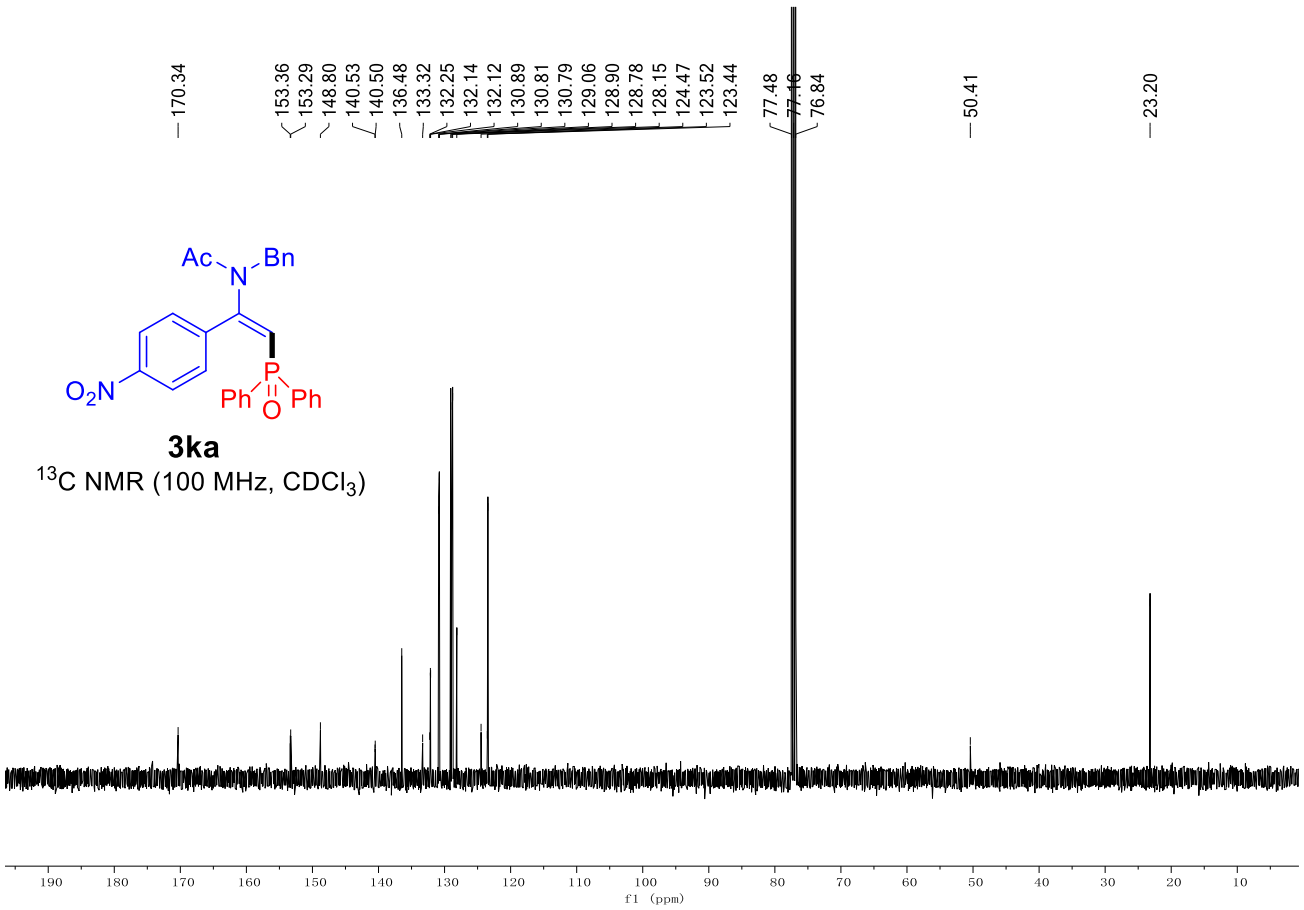




3ka

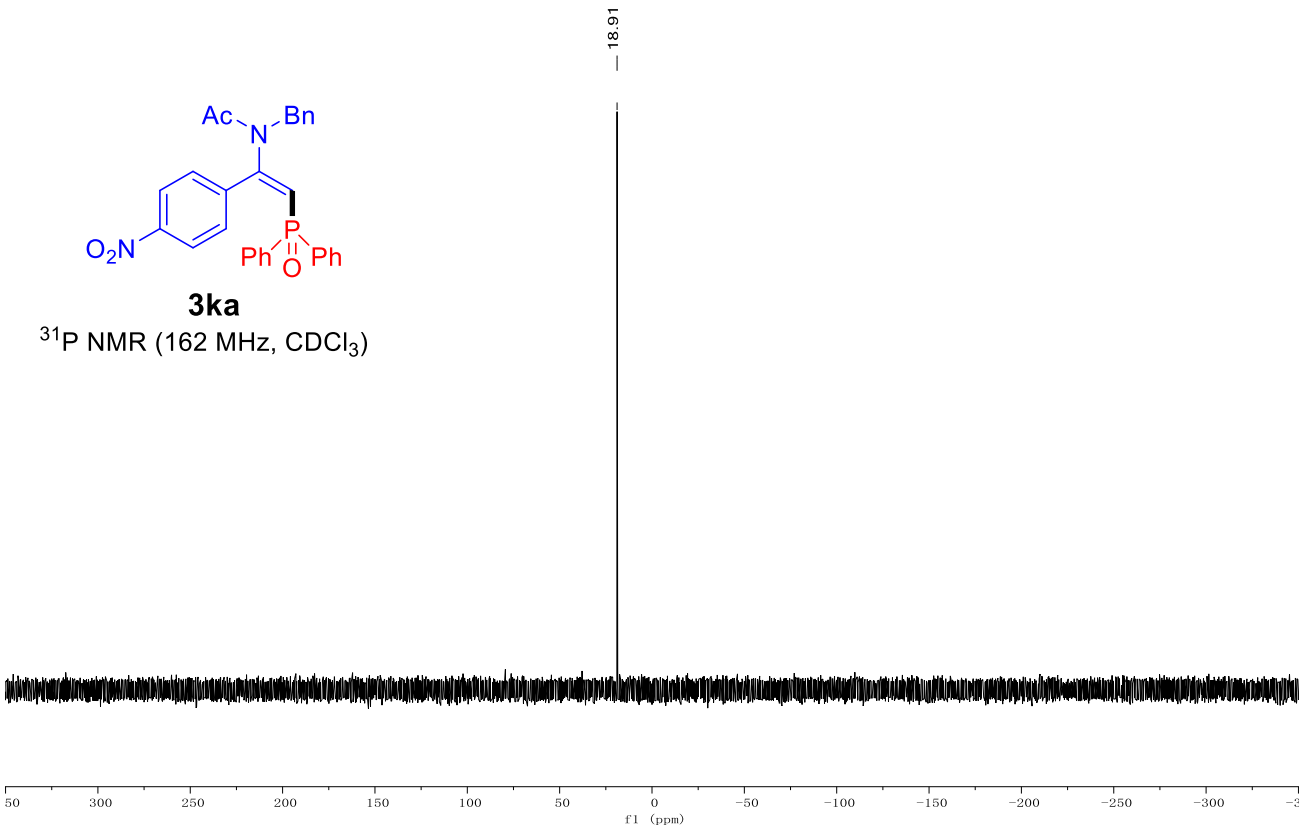
^{1}H NMR (400 MHz, $CDCl_3$)





3ka

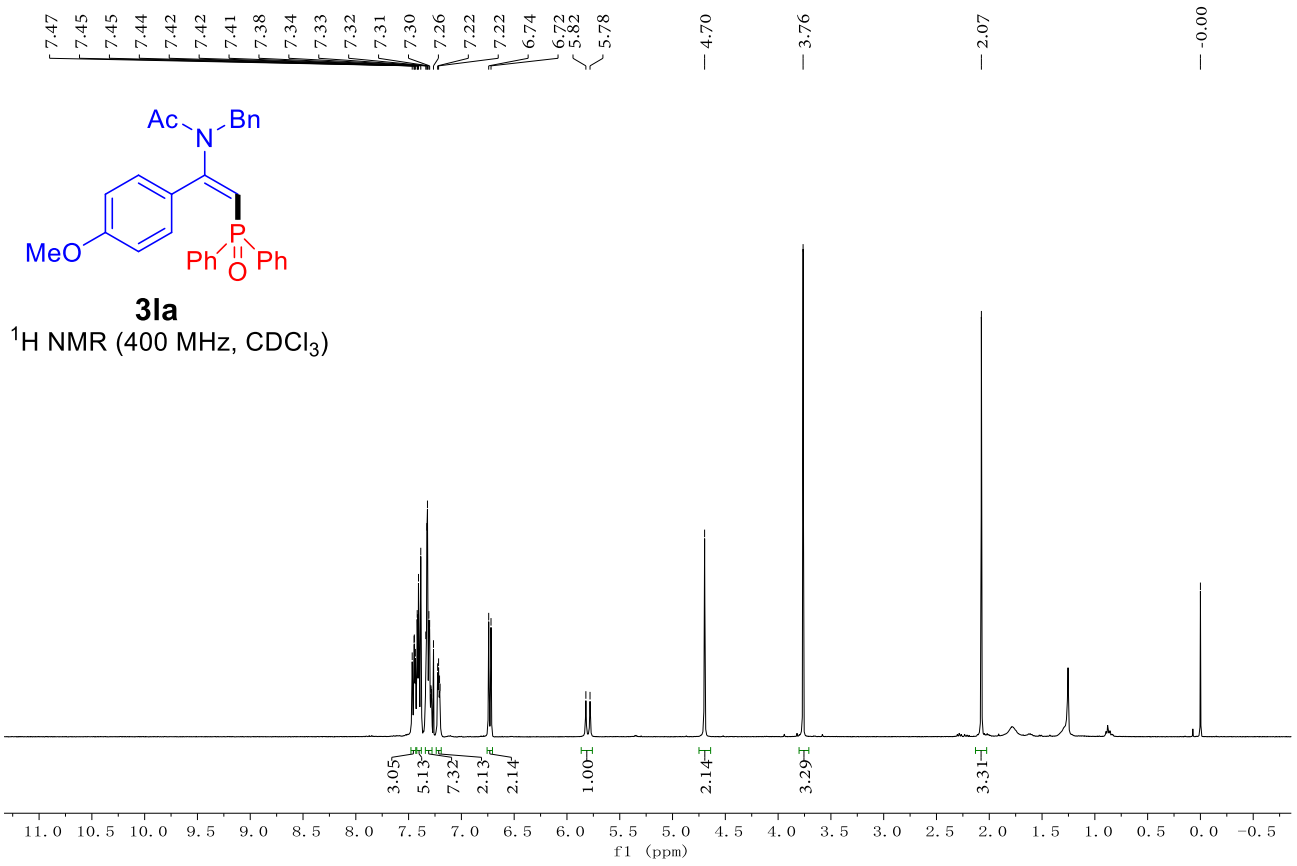
^{13}C NMR (100 MHz, $CDCl_3$)



3ka

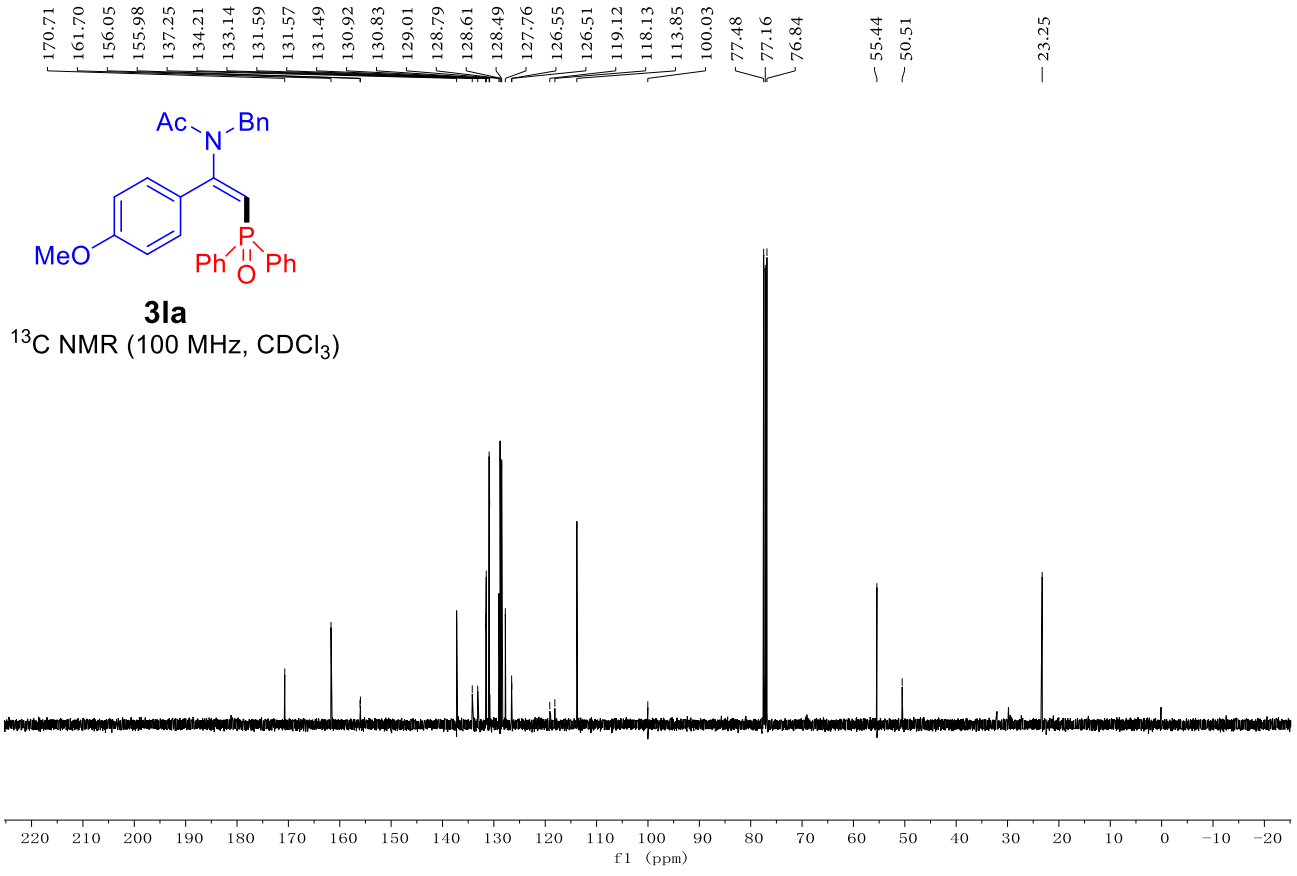
^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-methoxyphenyl)vinyl)acetamide (**3la**)



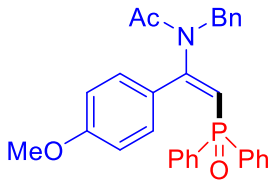
3la

^{1}H NMR (400 MHz, $CDCl_3$)



3la

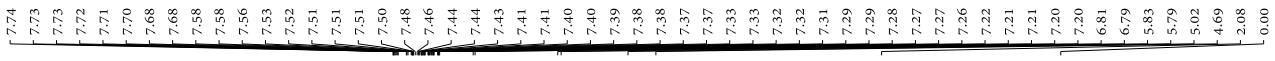
^{13}C NMR (100 MHz, $CDCl_3$)

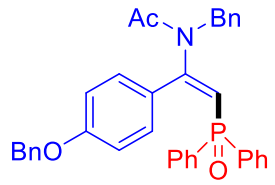


3la

^{31}P NMR (162 MHz, $CDCl_3$)

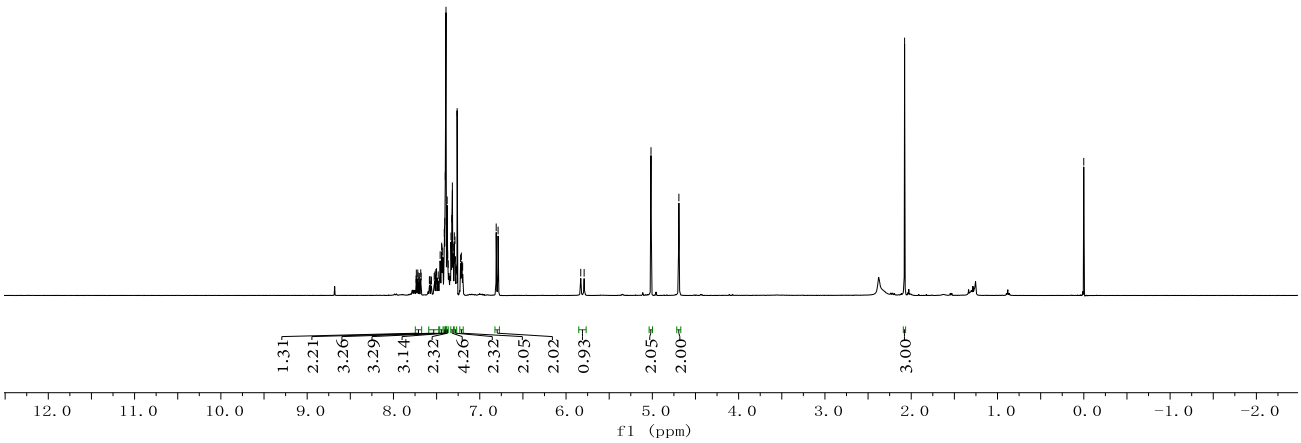
(E)-*N*-benzyl-*N*-(1-(4-(benzyloxy)phenyl)-2-(diphenylphosphoryl)vinyl)acetamide (**3ma**)

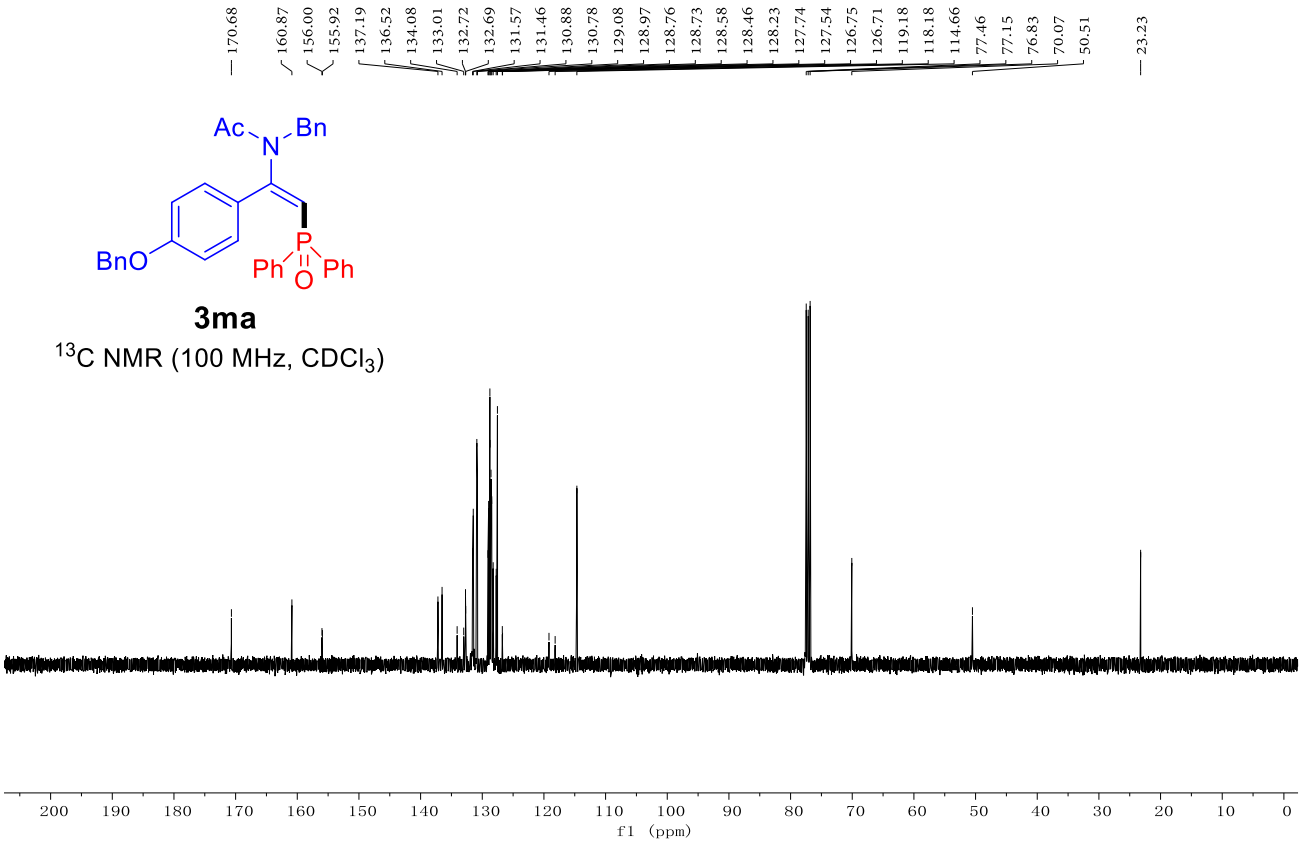




3ma

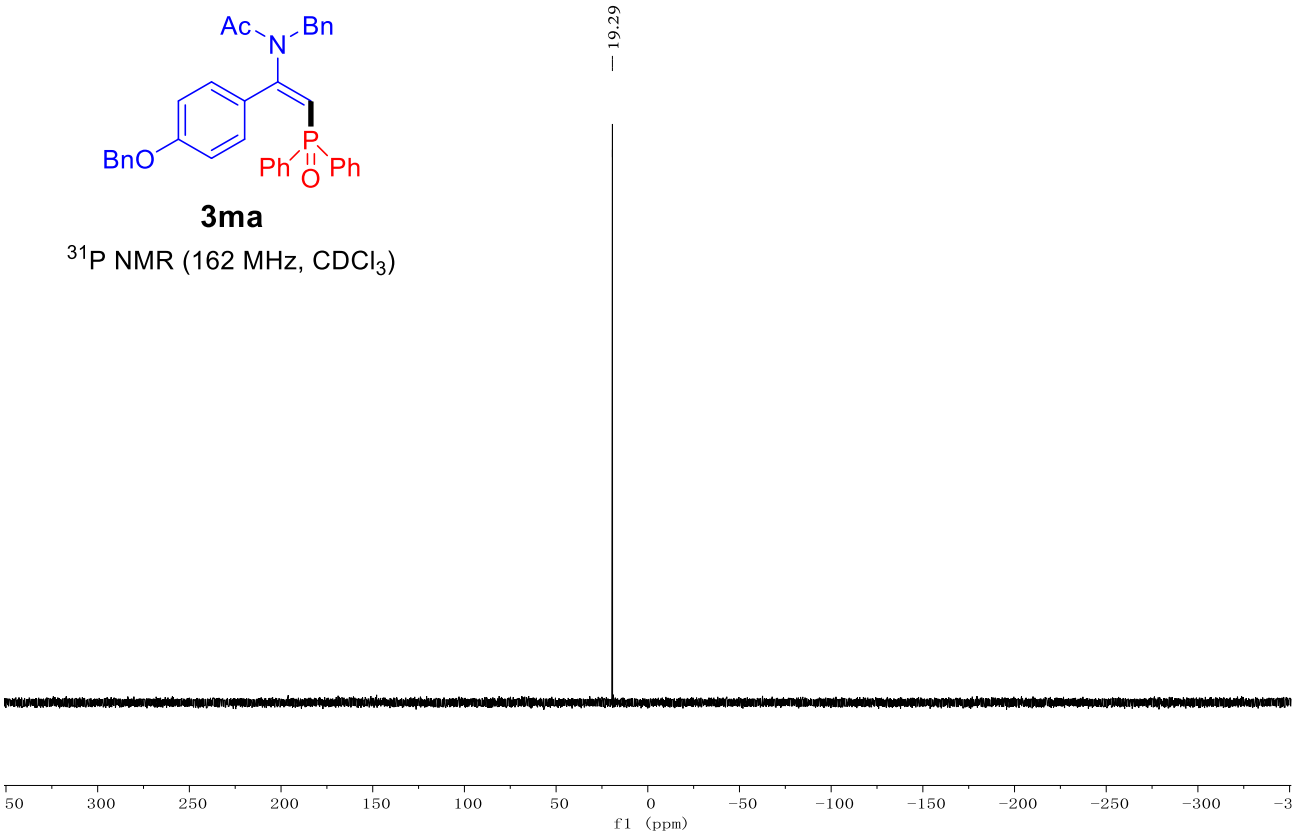
^{1}H NMR (400 MHz, $CDCl_3$)





3ma

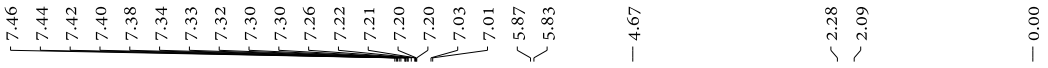
^{13}C NMR (100 MHz, $CDCl_3$)

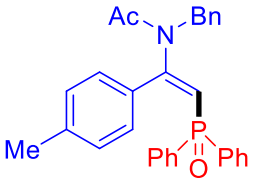


3ma

^{31}P NMR (162 MHz, $CDCl_3$)

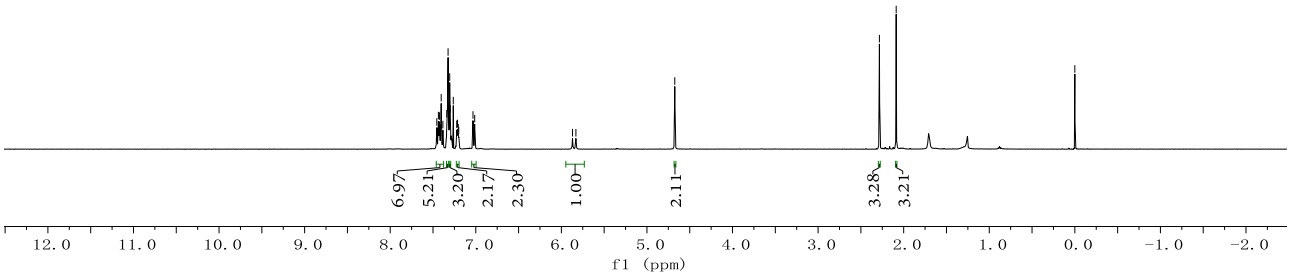
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(p-tolyl)vinyl)acetamide (**3na**)

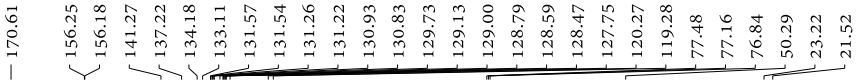


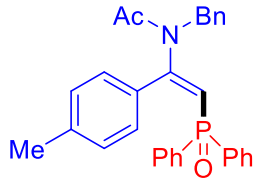


3na

^{1}H NMR (400 MHz, $CDCl_3$)

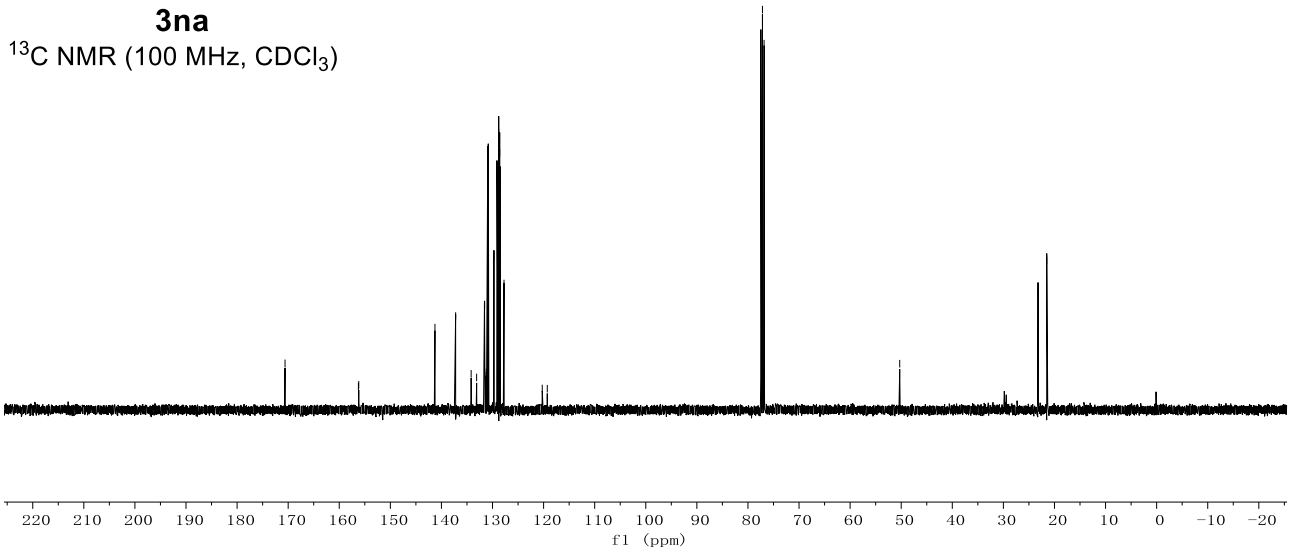


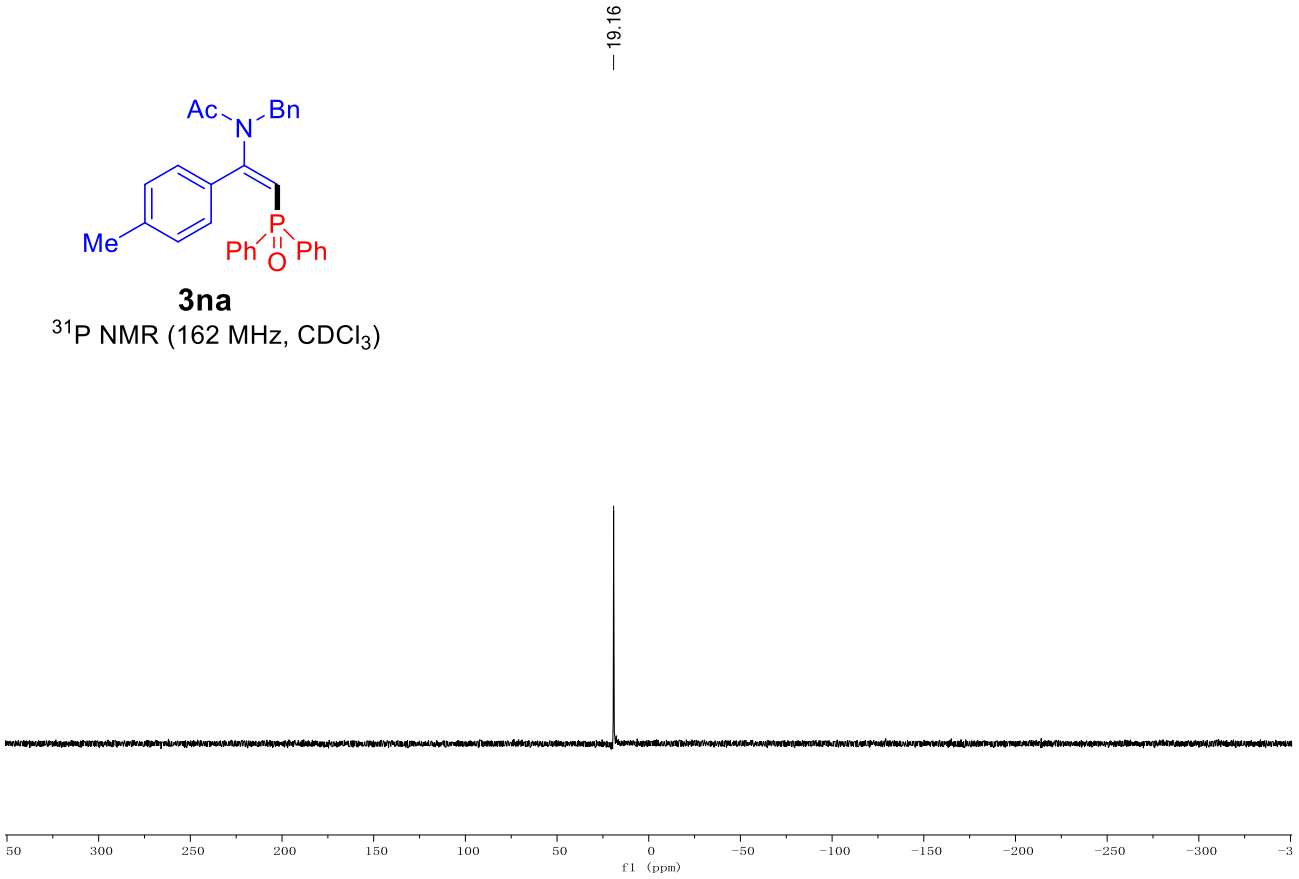




3na

^{13}C NMR (100 MHz, $CDCl_3$)

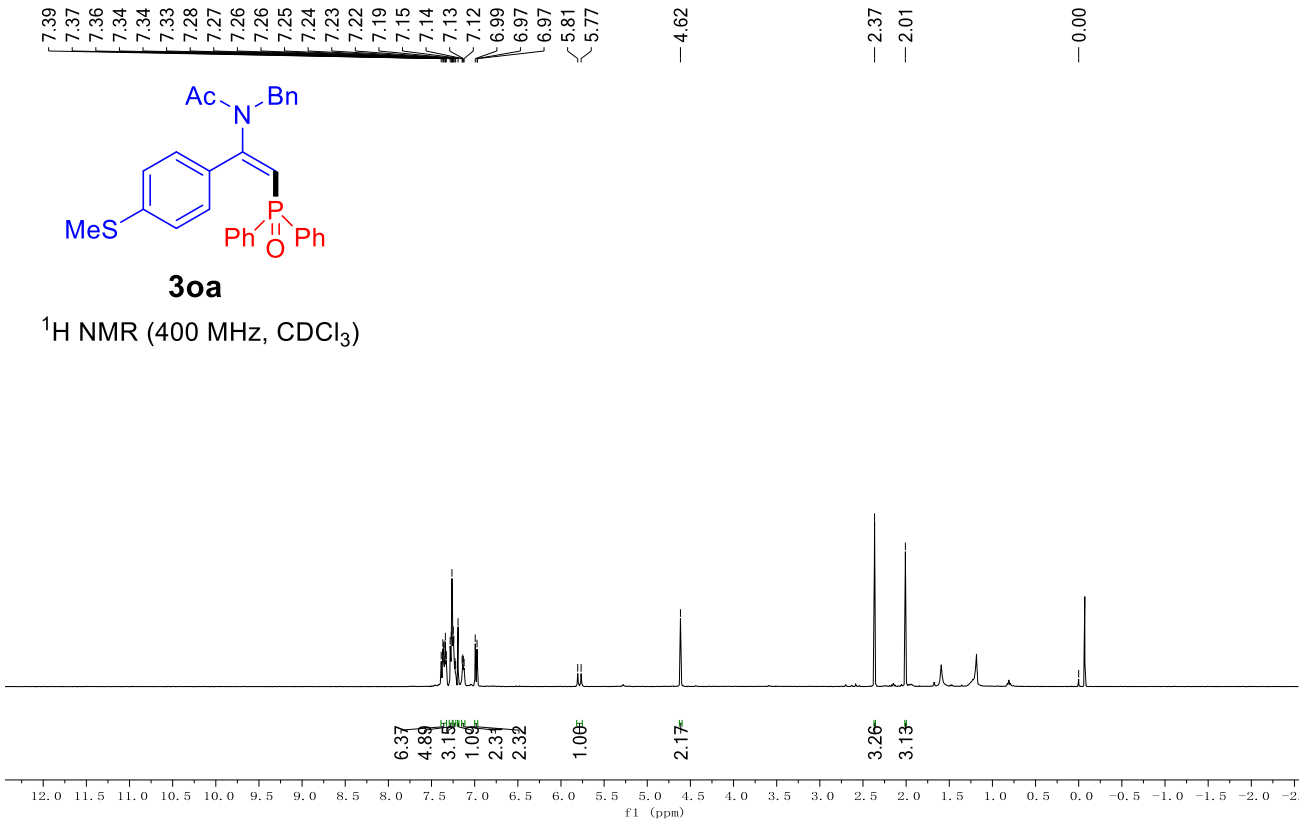




3na

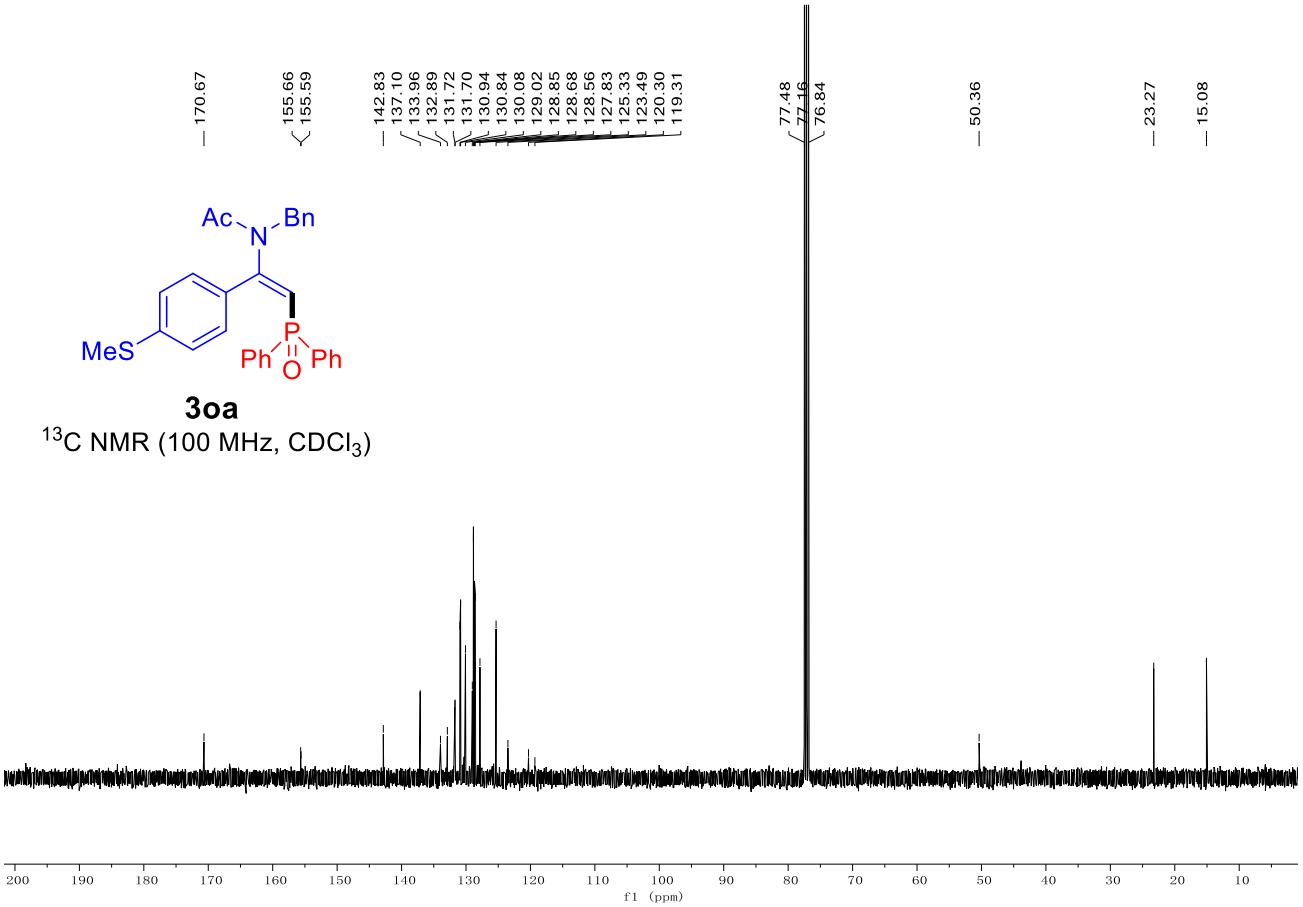
^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(4-(methylthio)phenyl)vinyl) acetamide (**3oa**)



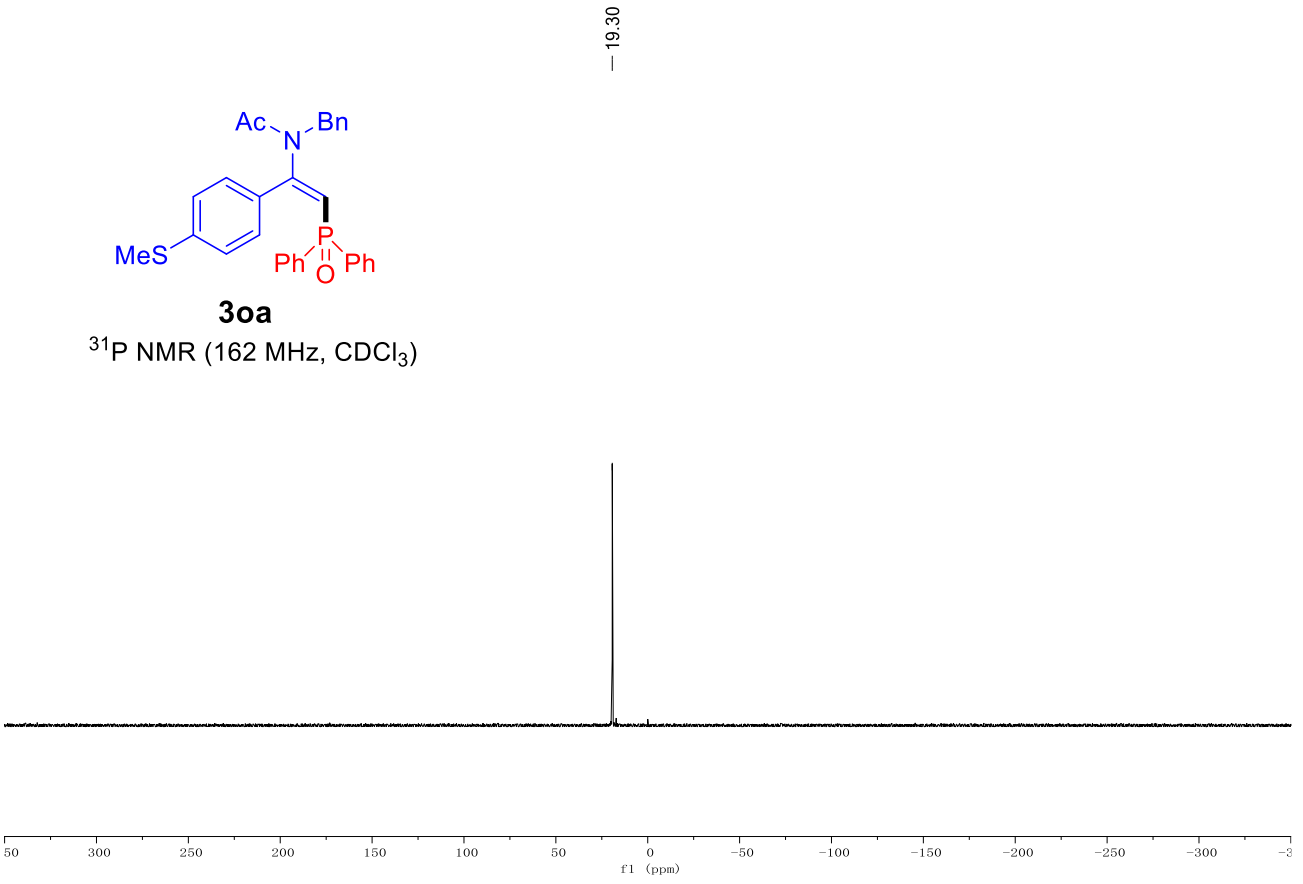
3oa

^{1}H NMR (400 MHz, $CDCl_3$)



3oa

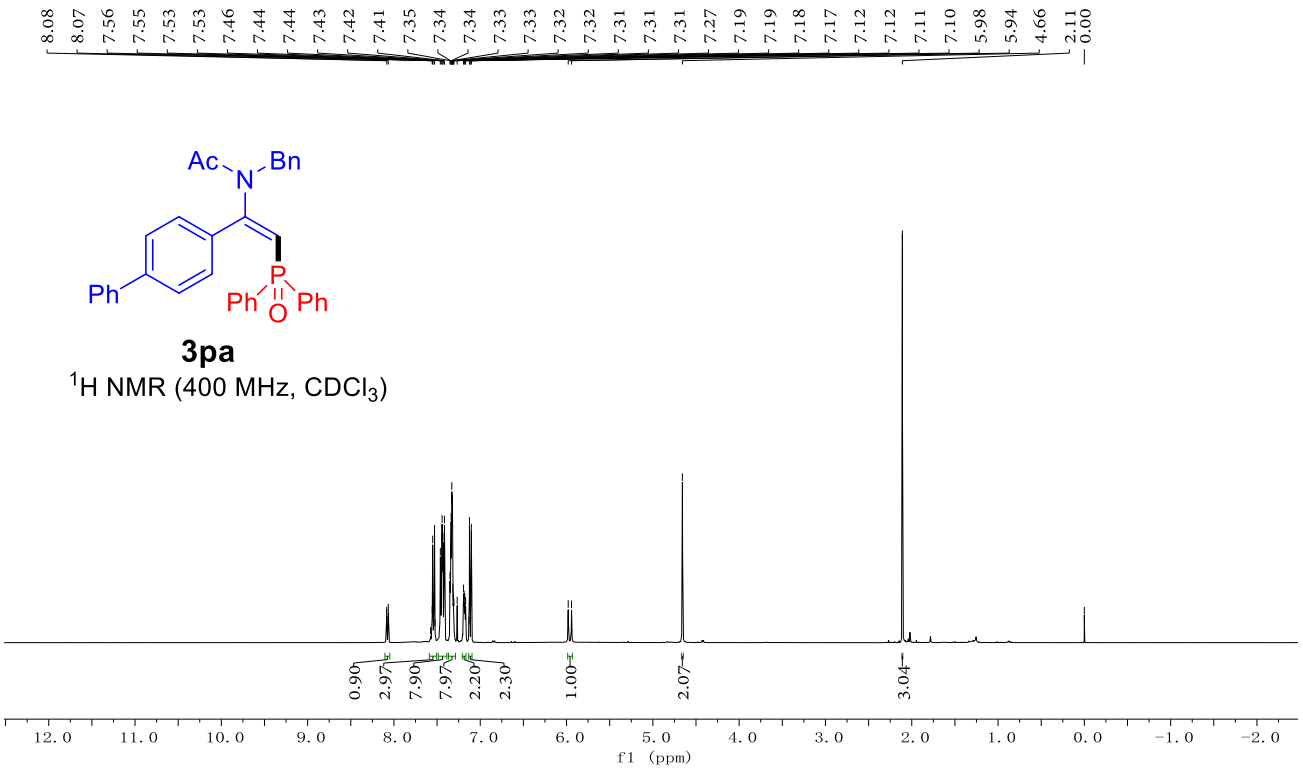
^{13}C NMR (100 MHz, $CDCl_3$)

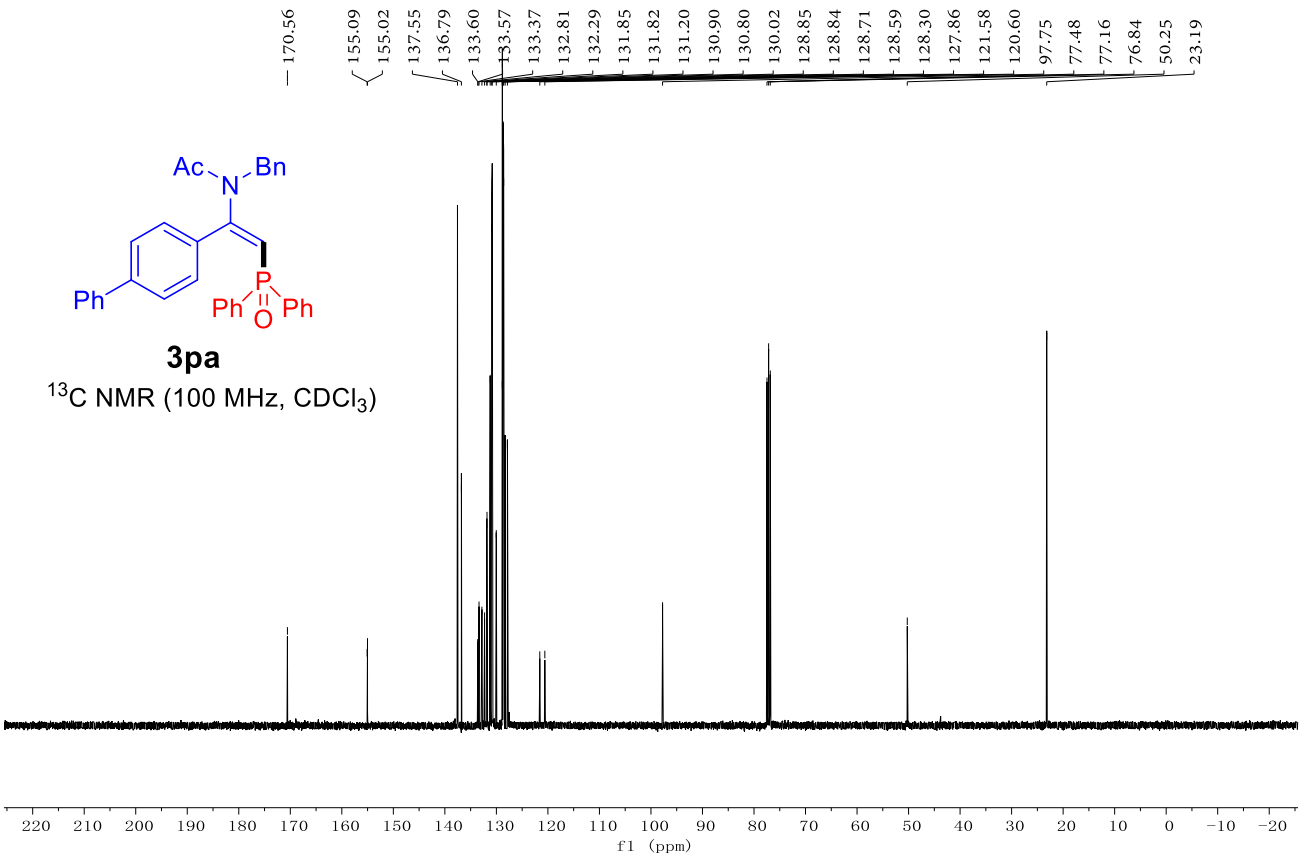


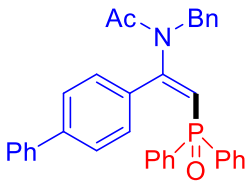
3oa

^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-(1-([1,1'-biphenyl]-4-yl)-2-(diphenylphosphoryl)vinyl)-*N*-benzylacetamide (**3pa**)



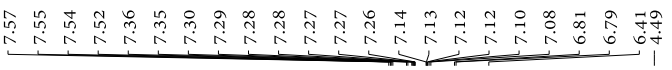


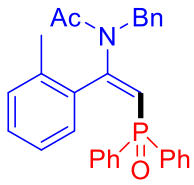


3pa

^{31}P NMR (162 MHz, $CDCl_3$)

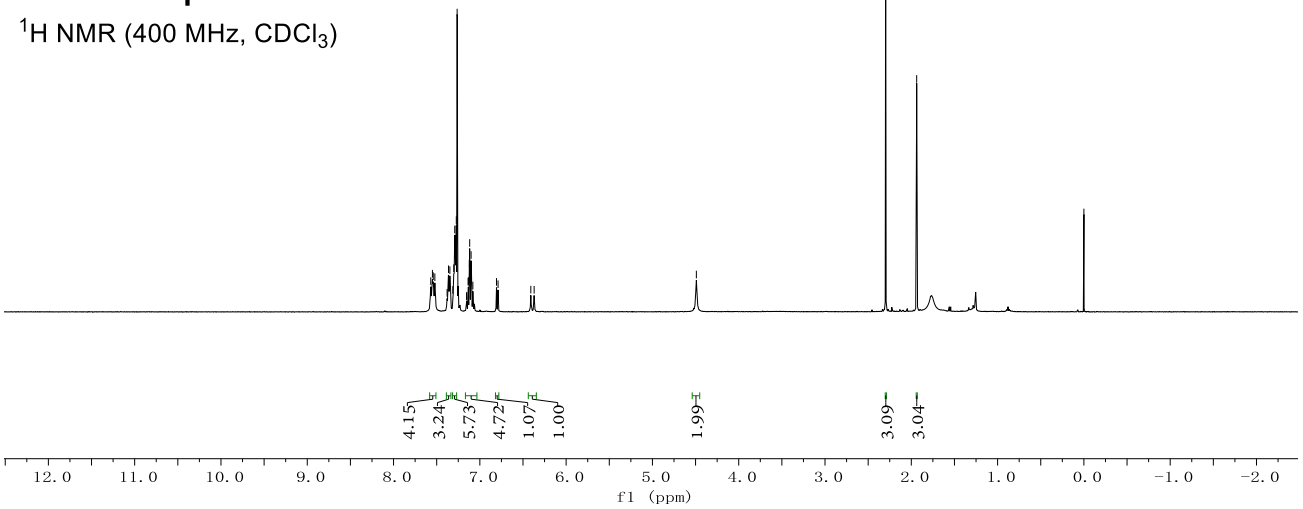
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(o-tolyl)vinyl)acetamide (**3qa**)

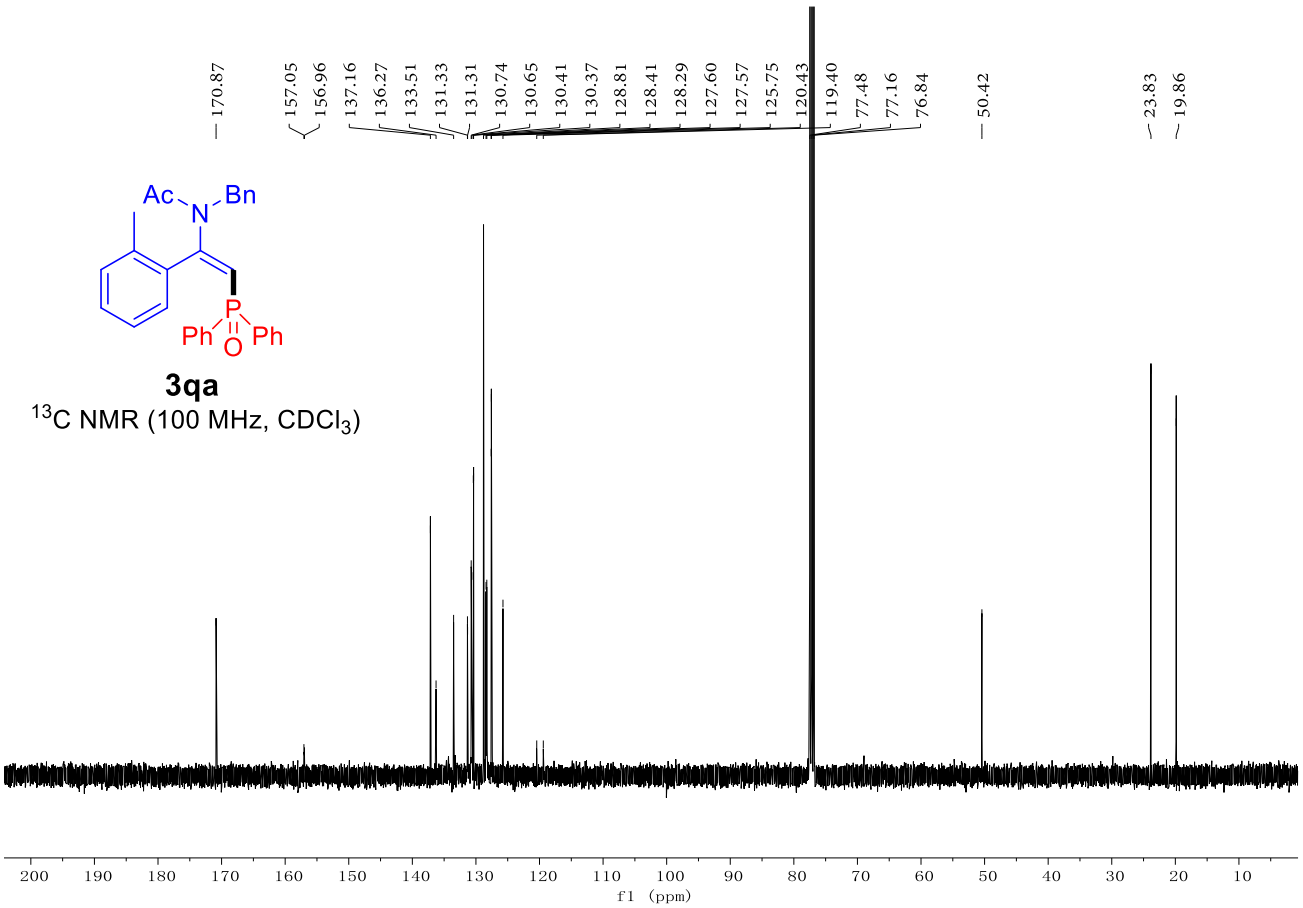




3qa

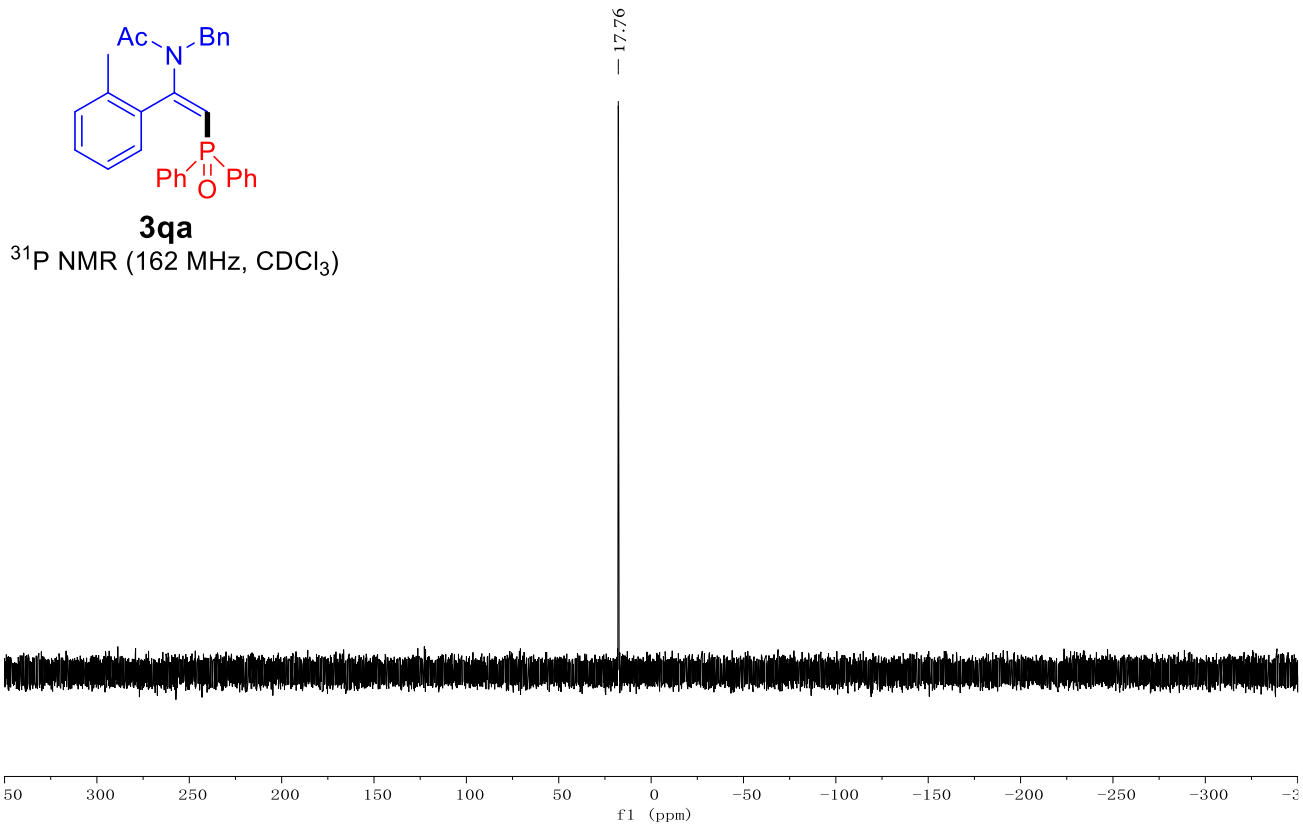
^{1}H NMR (400 MHz, $CDCl_3$)





3qa

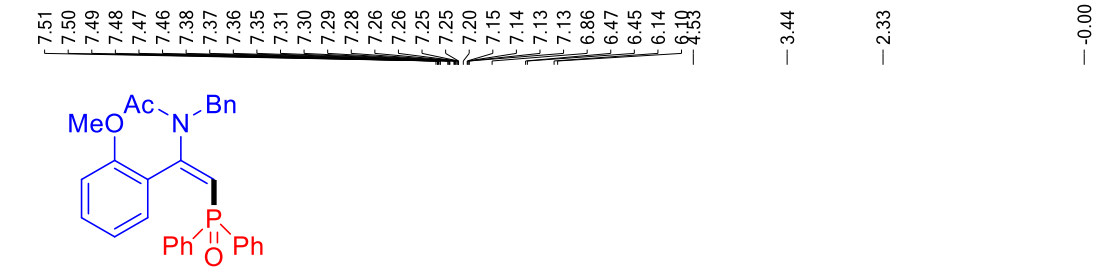
^{13}C NMR (100 MHz, $CDCl_3$)



3qa

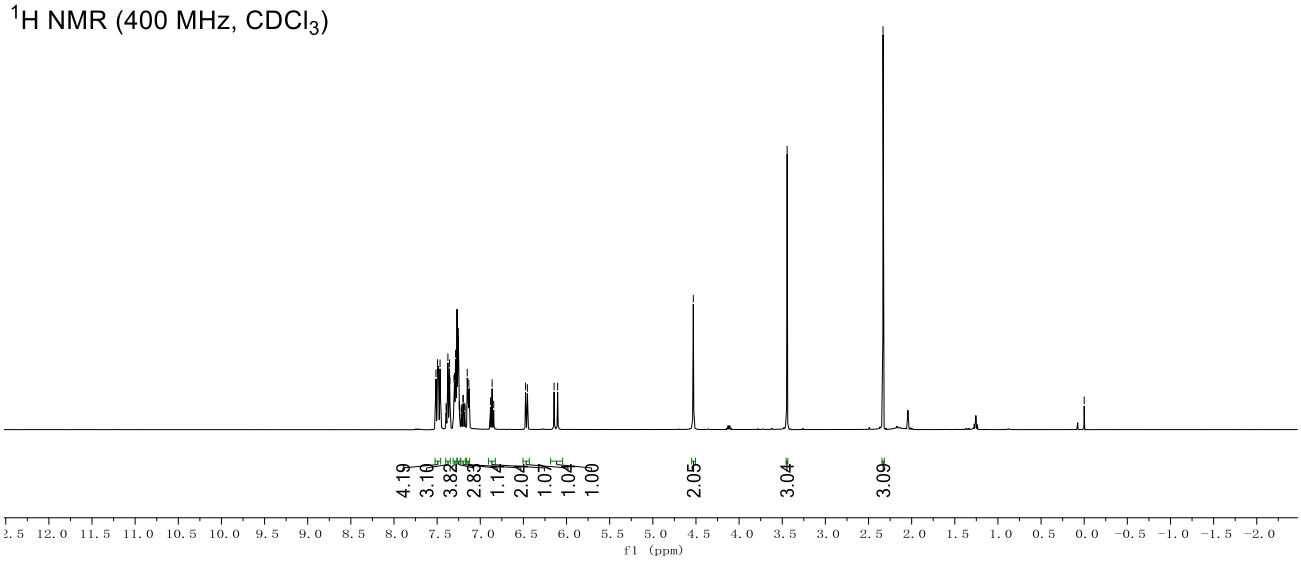
^{31}P NMR (162 MHz, $CDCl_3$)

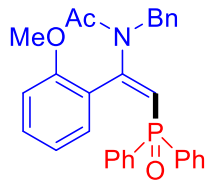
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(2-methoxyphenyl)vinyl)acetamide (**3ra**)



3ra

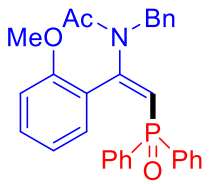
^{1}H NMR (400 MHz, $CDCl_3$)





3ra

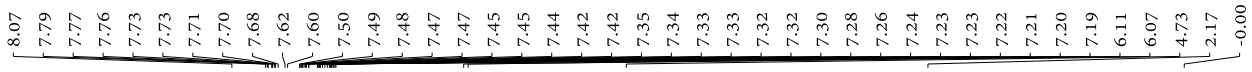
^{13}C NMR (100 MHz, $CDCl_3$)

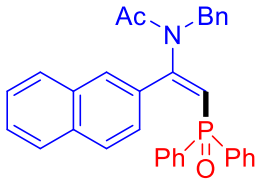


3ra

^{31}P NMR (162 MHz, $CDCl_3$)

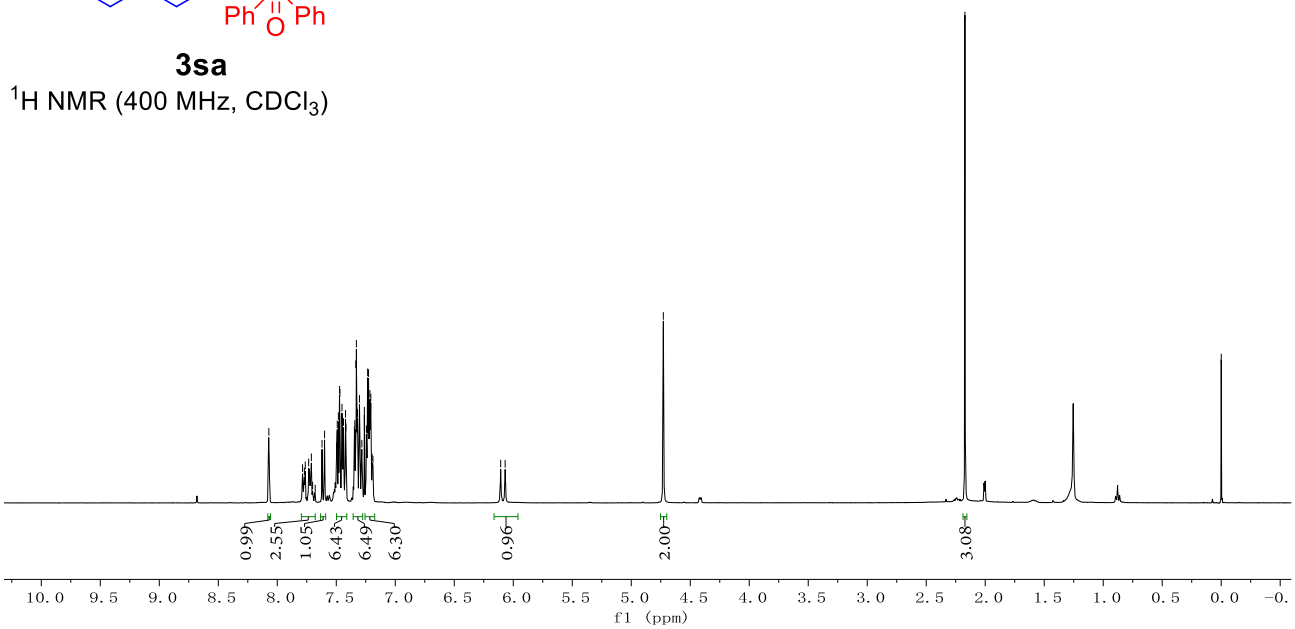
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(naphthalen-2-yl)vinyl)acetamide (**3sa**)

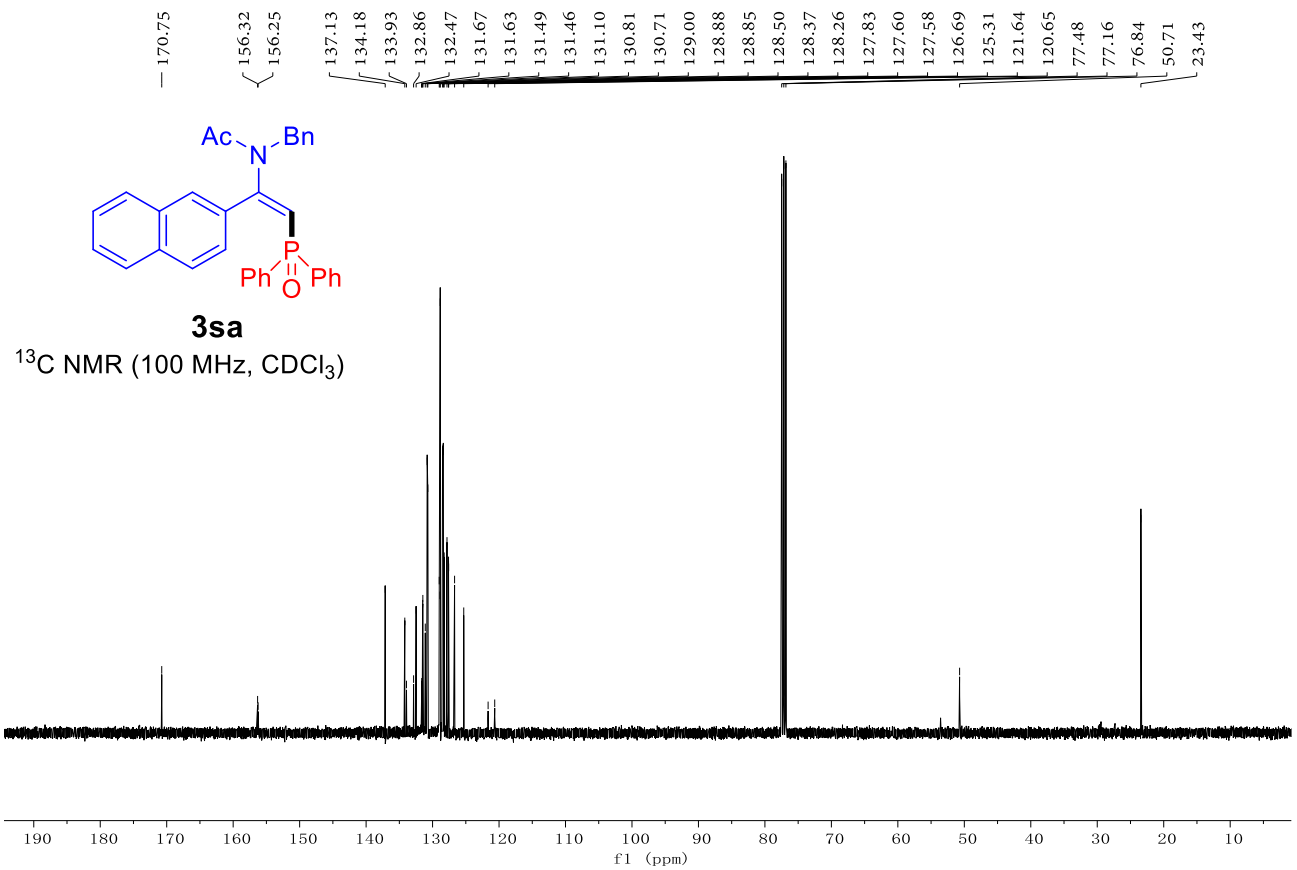




3sa

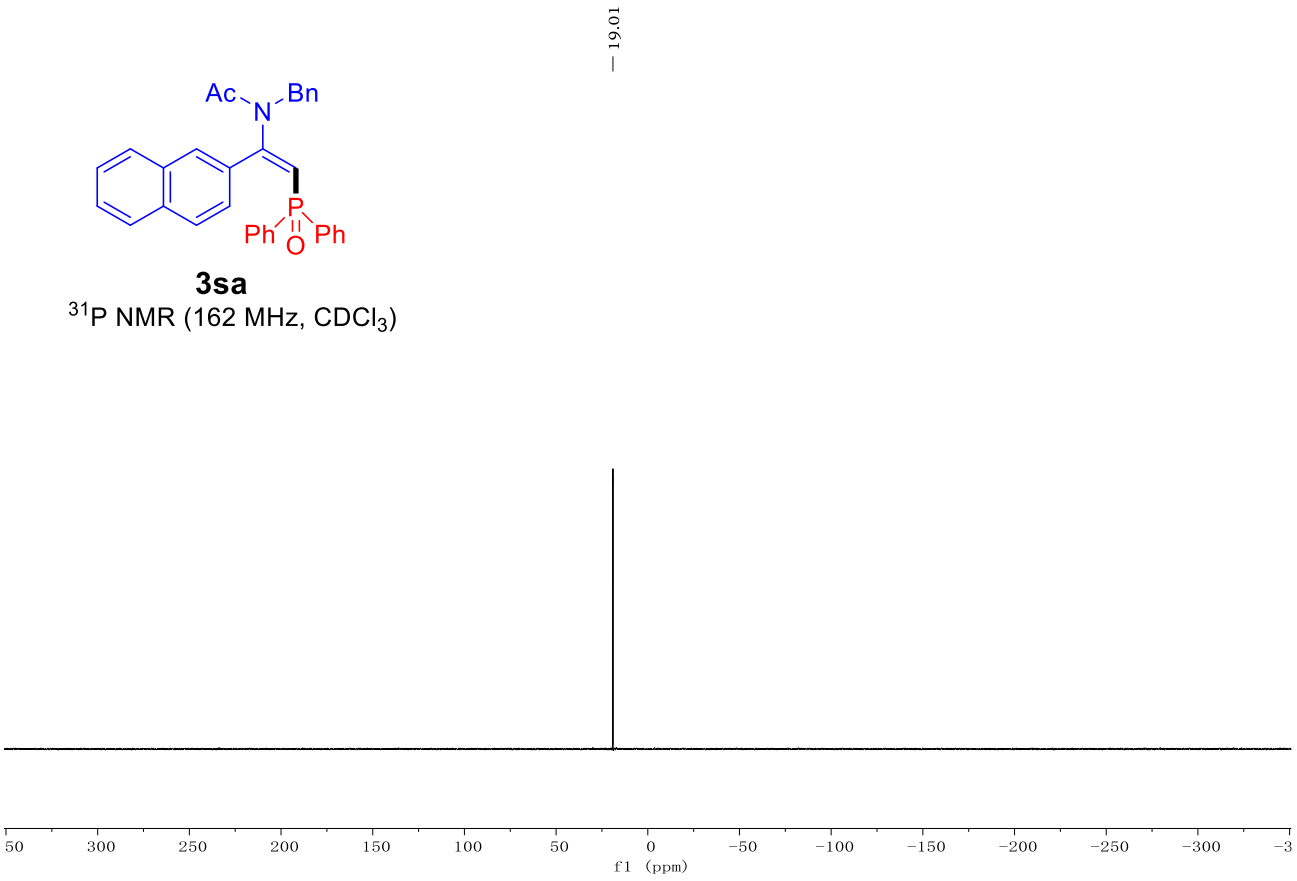
^{1}H NMR (400 MHz, $CDCl_3$)





3sa

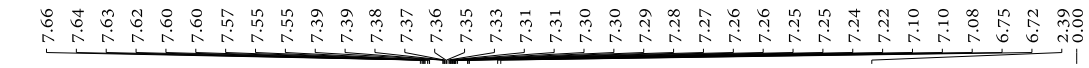
^{13}C NMR (100 MHz, $CDCl_3$)

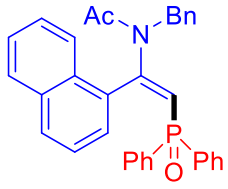


3sa

^{31}P NMR (162 MHz, $CDCl_3$)

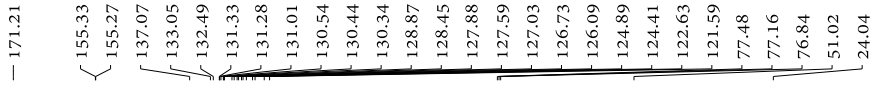
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(naphthalen-1-yl)vinyl)acetamide (**3ta**)

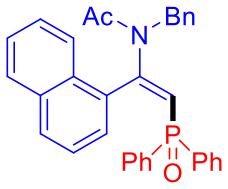




3ta

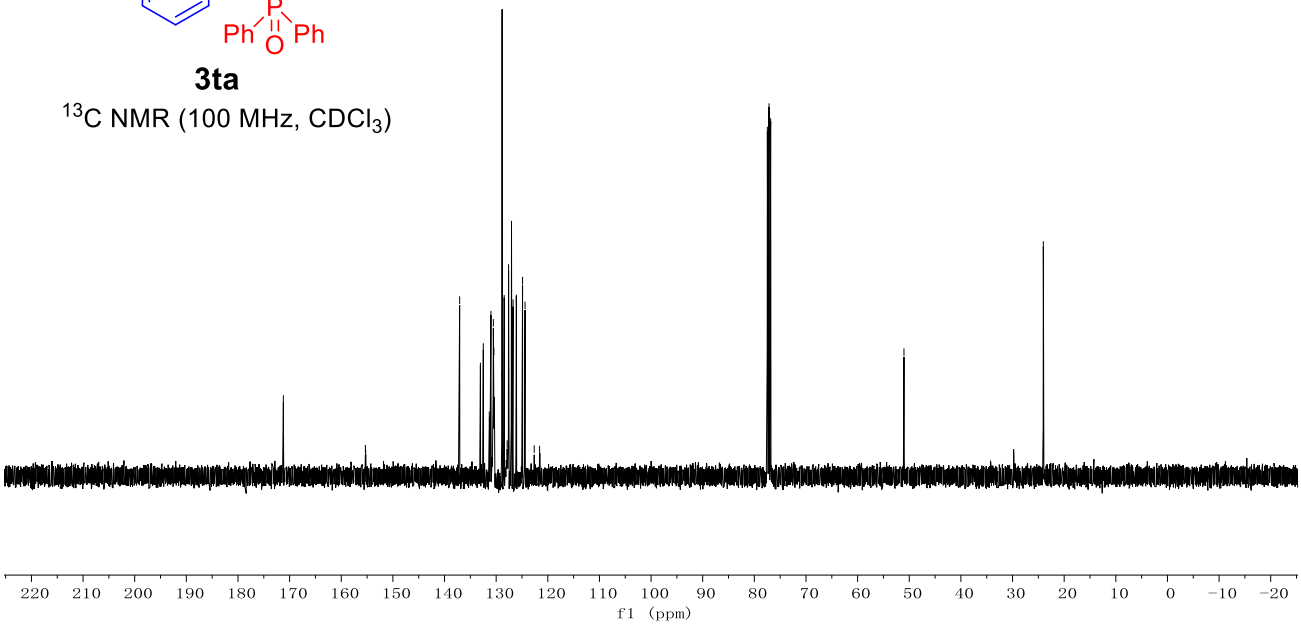
^{1}H NMR (400 MHz, $CDCl_3$)

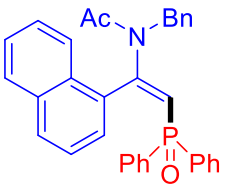




3ta

^{13}C NMR (100 MHz, $CDCl_3$)

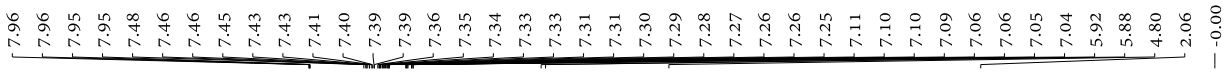


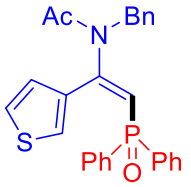


3ta

^{31}P NMR (162 MHz, $CDCl_3$)

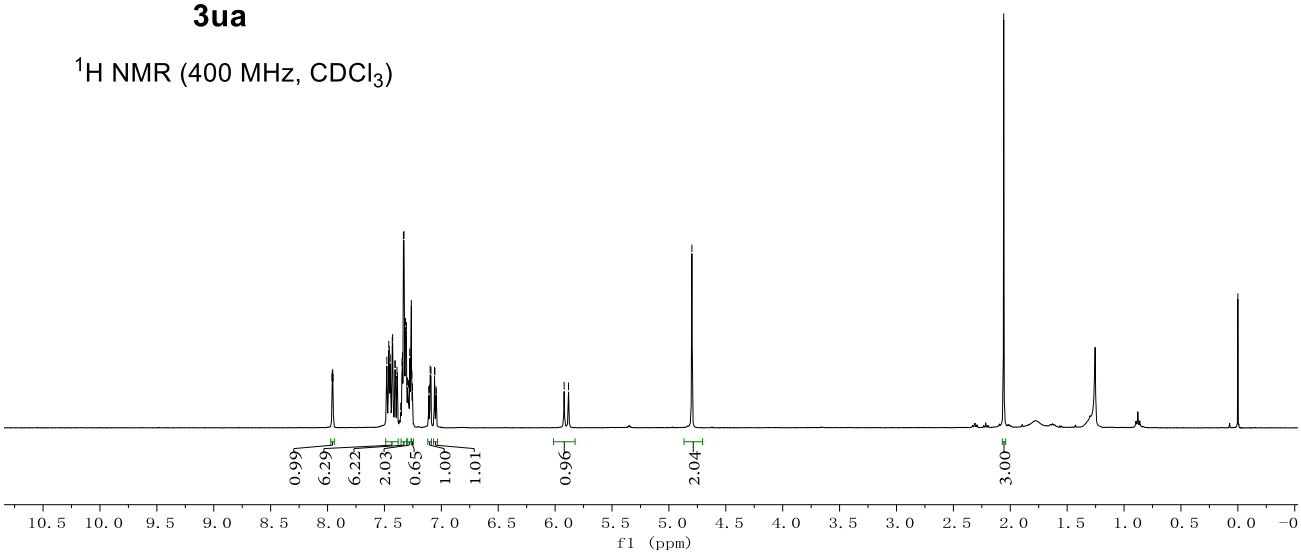
(E)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-(thiophen-3-yl)vinyl)acetamide (**3ua**)

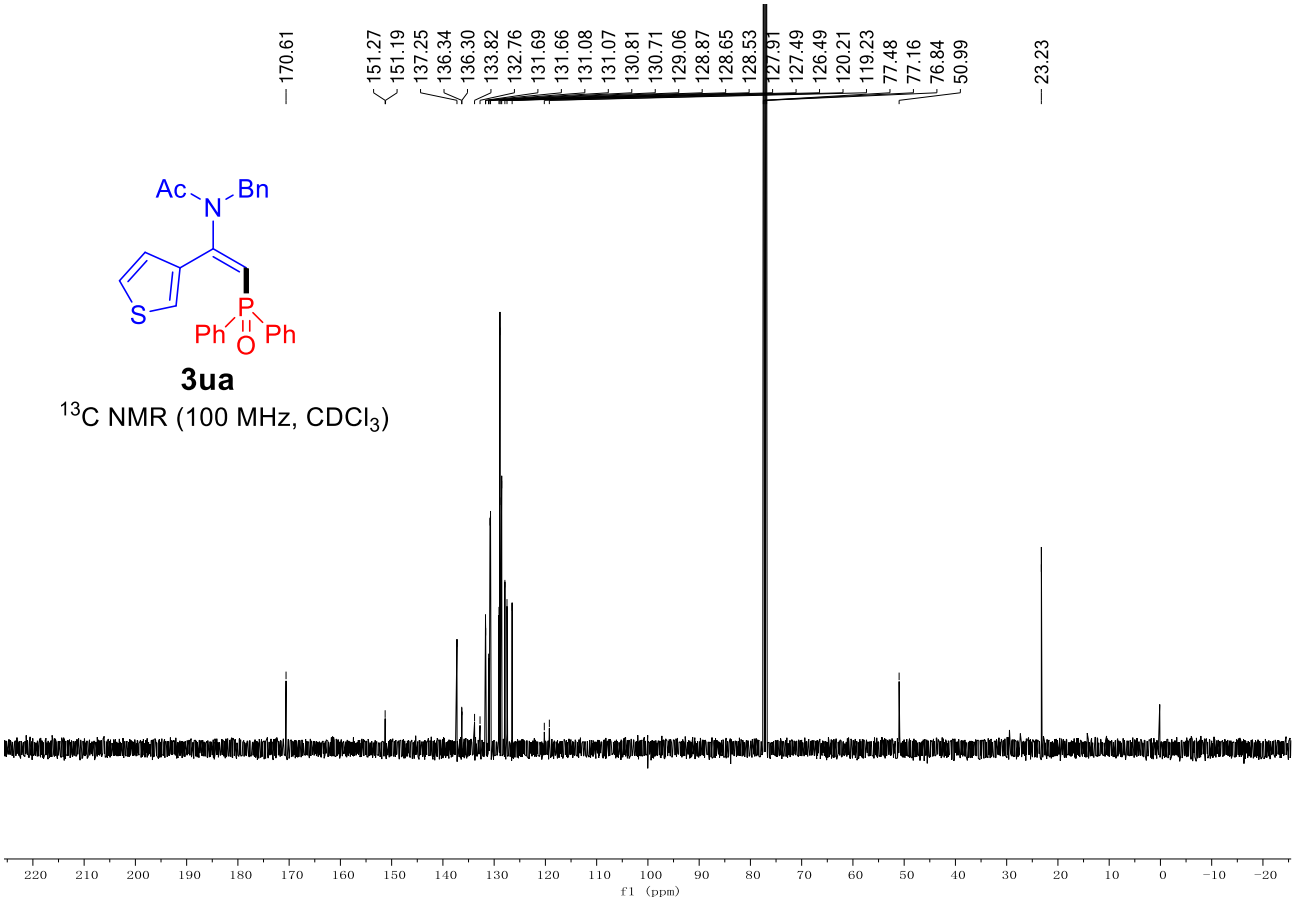




3ua

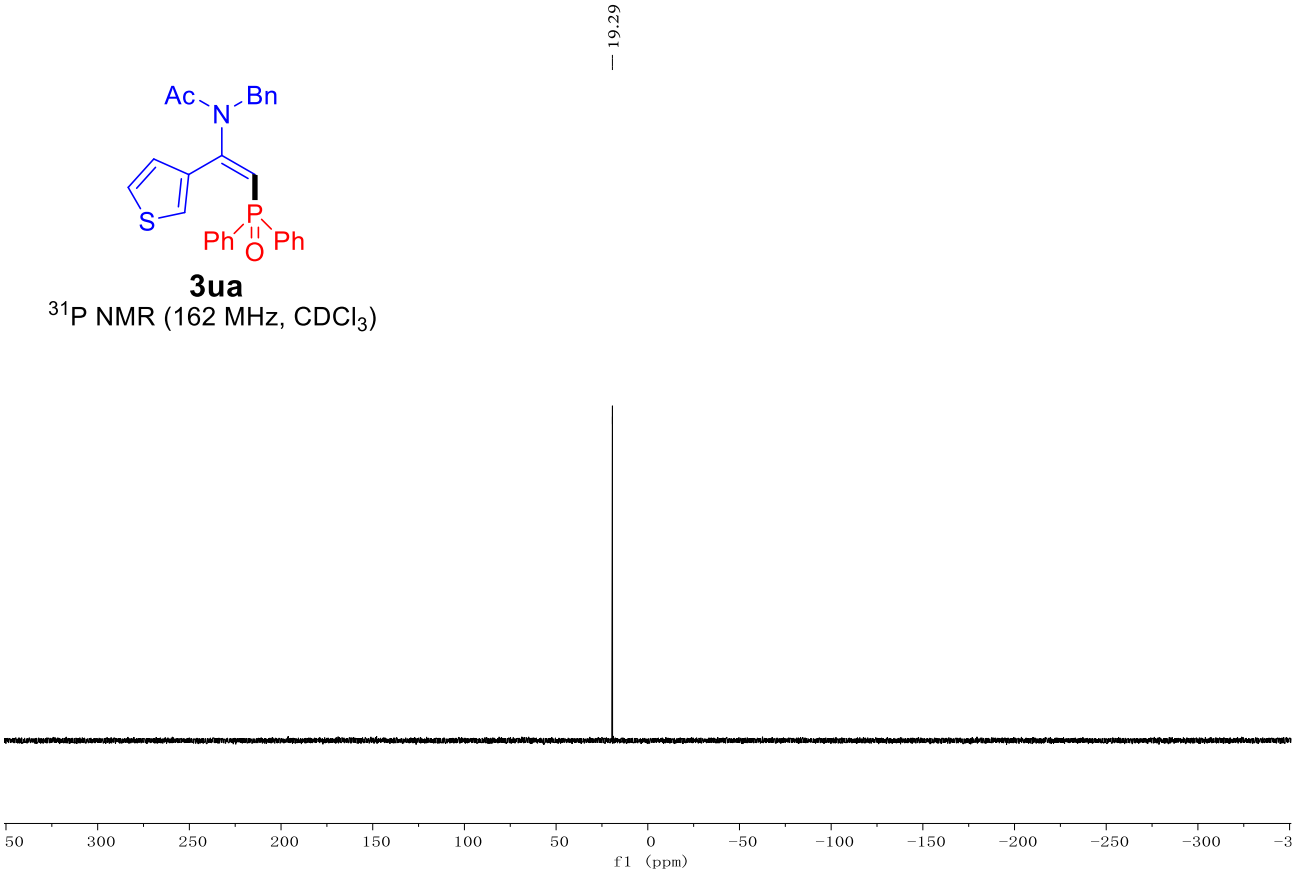
^{1}H NMR (400 MHz, $CDCl_3$)





3ua

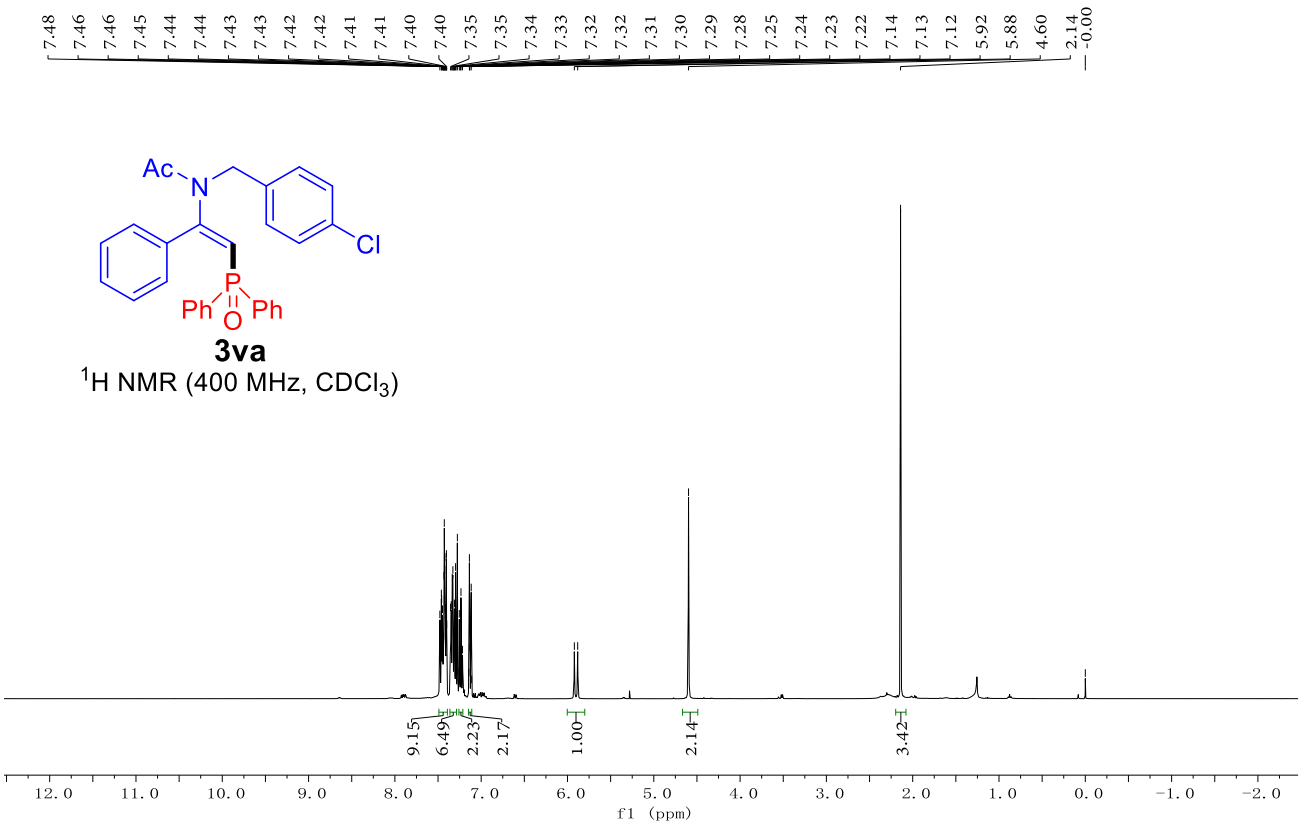
^{13}C NMR (100 MHz, $CDCl_3$)

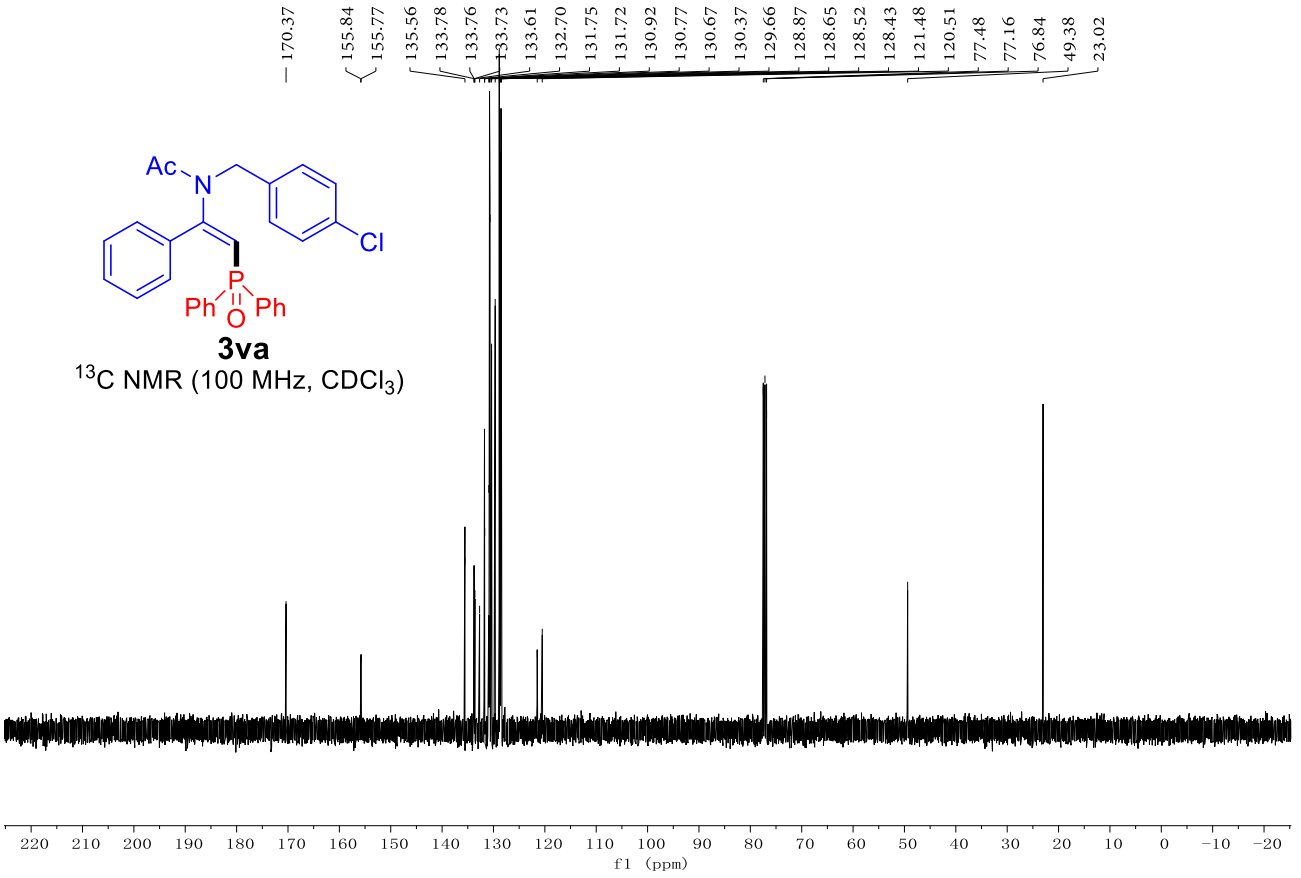


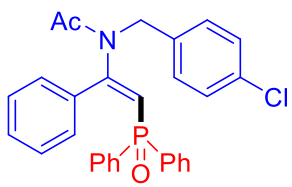
3ua

^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-(4-chlorobenzyl)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (**3va**)



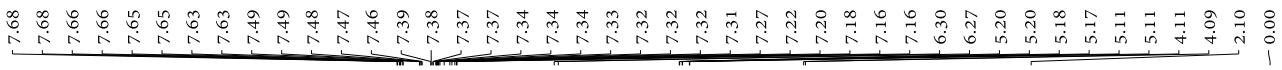


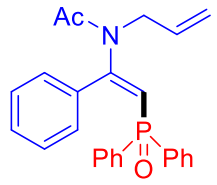


3va

^{31}P NMR (162 MHz, $CDCl_3$)

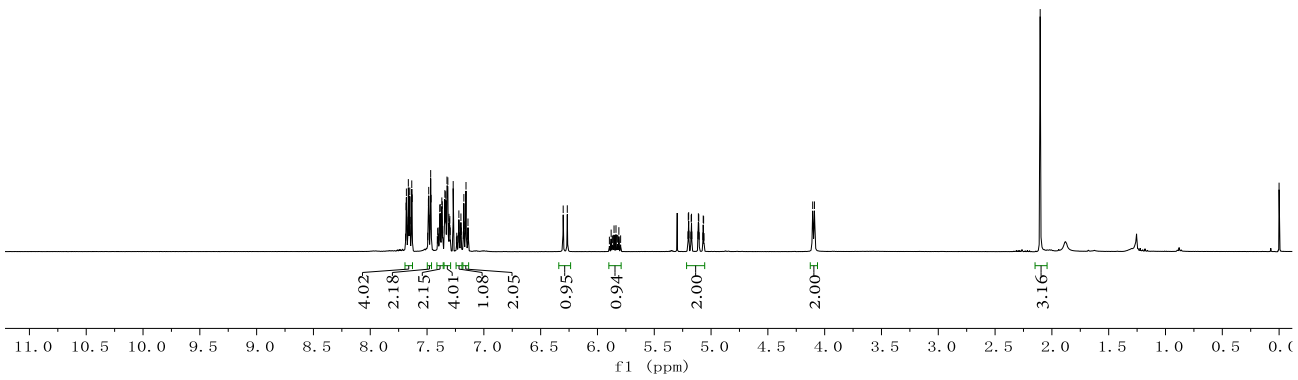
(E)-*N*-allyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (**3wa**)

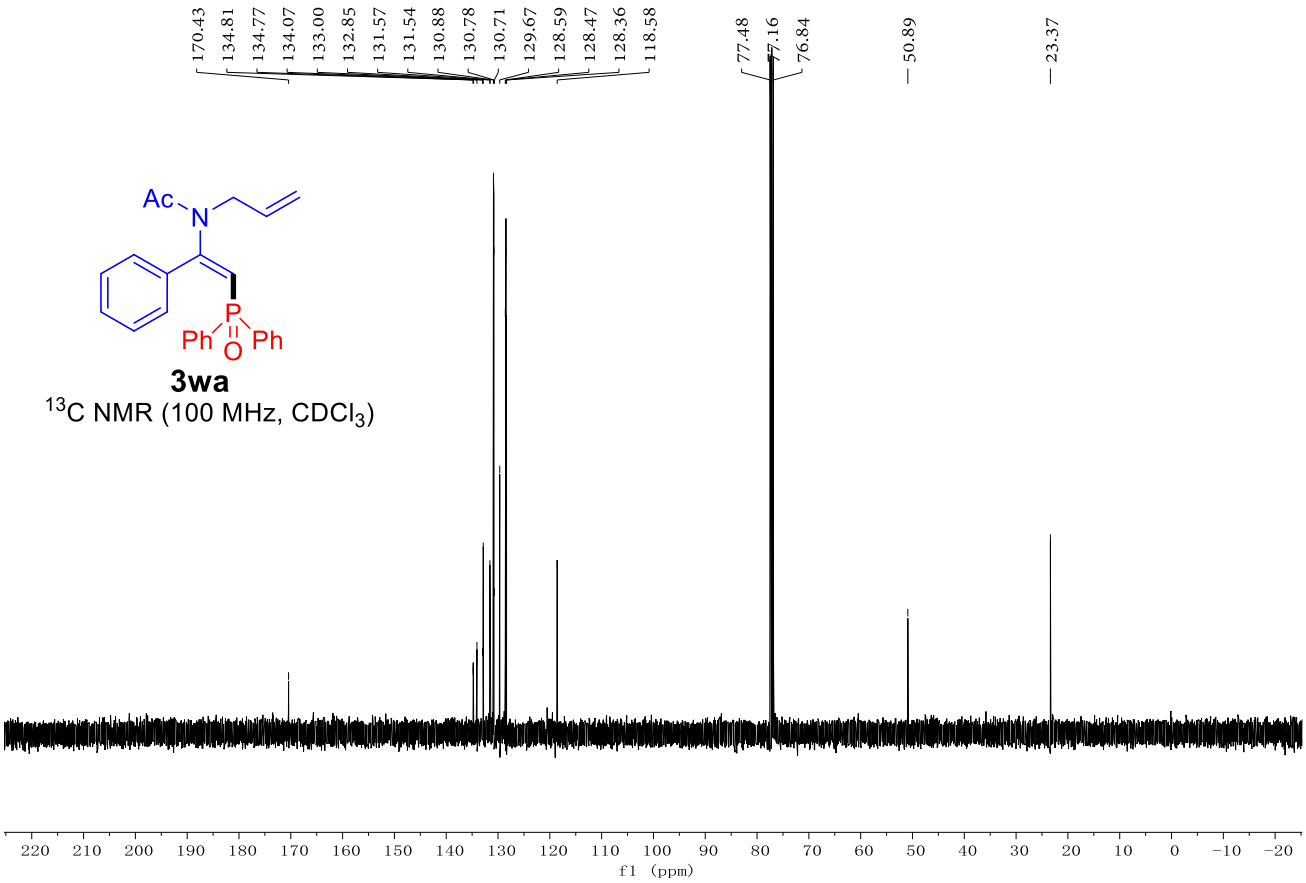




3wa

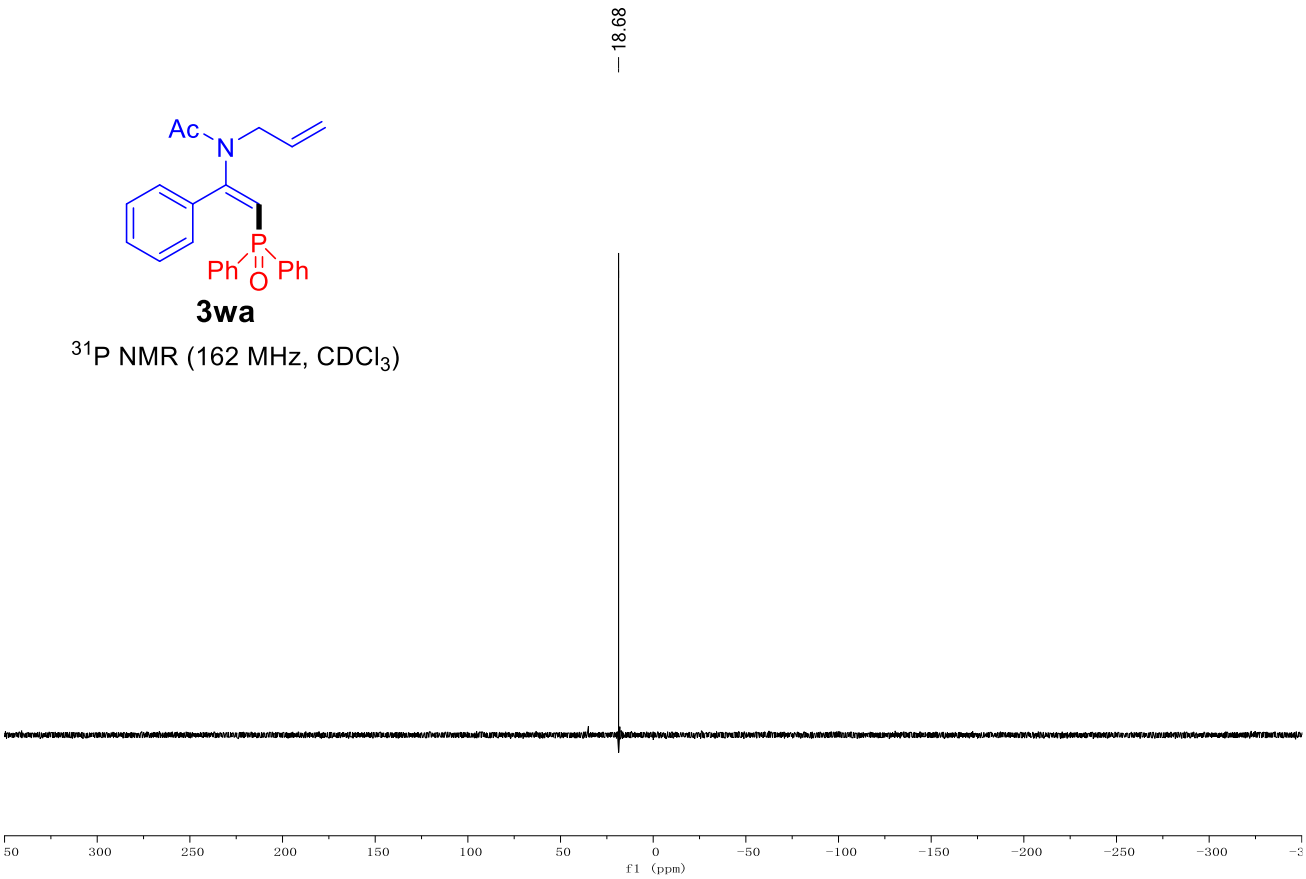
^{1}H NMR (400 MHz, $CDCl_3$)





3wa

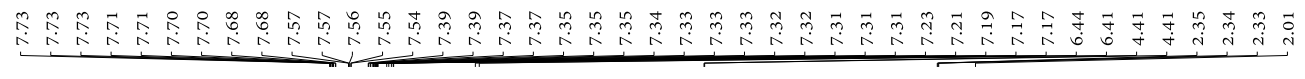
^{13}C NMR (100 MHz, $CDCl_3$)

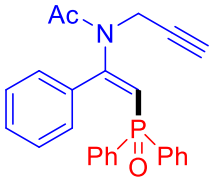


3wa

^{31}P NMR (162 MHz, $CDCl_3$)

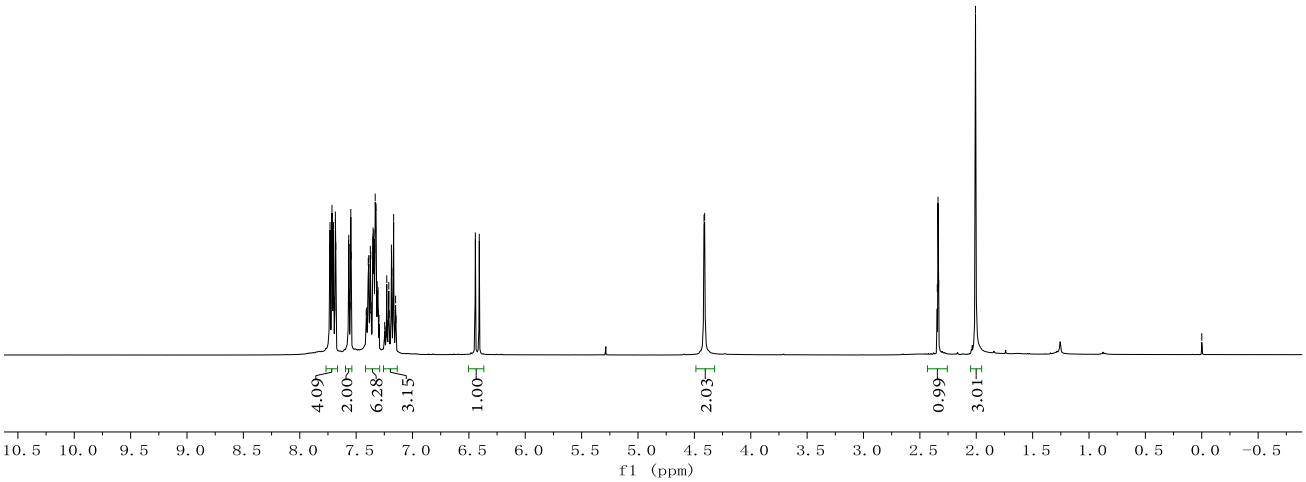
(E)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)-*N*-(prop-2-yn-1-yl)acetamide (**3xa**)

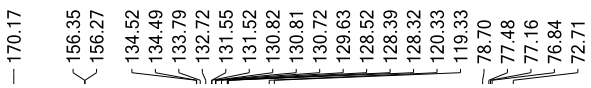


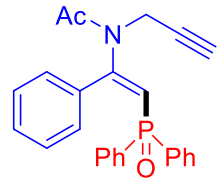


3xa

^{1}H NMR (400 MHz, $CDCl_3$)

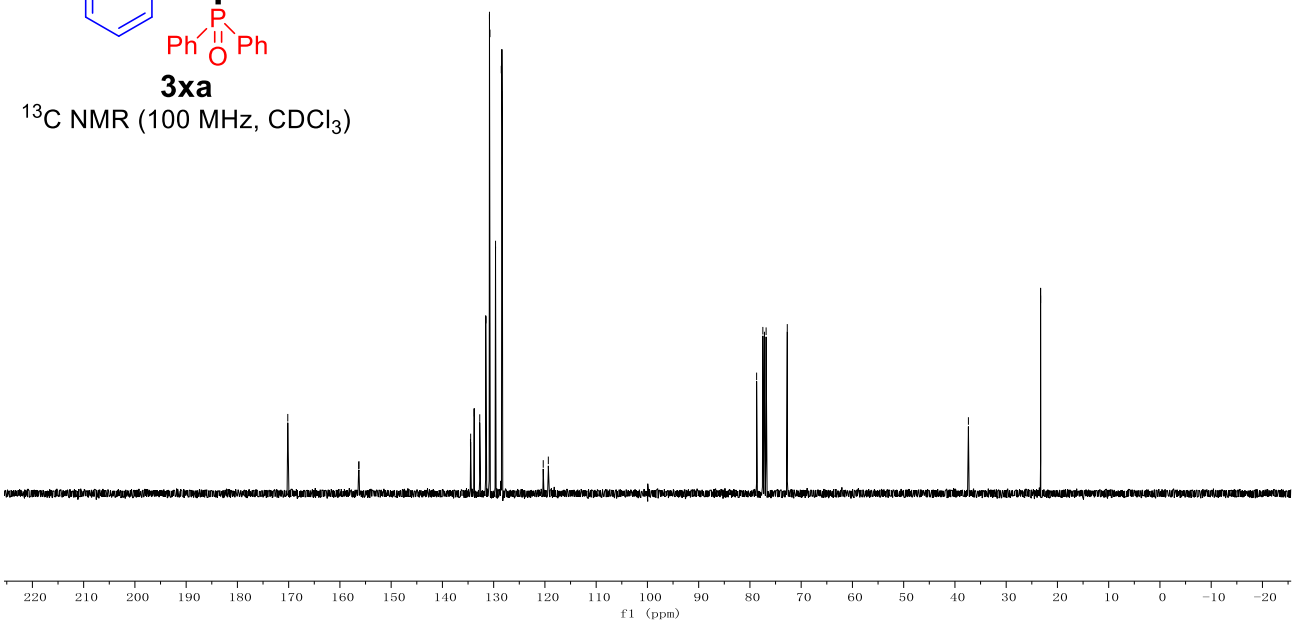


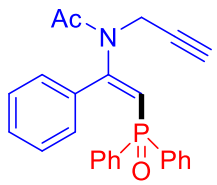




3xa

^{13}C NMR (100 MHz, $CDCl_3$)

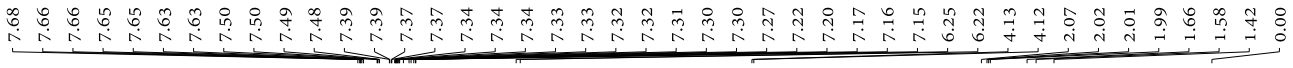


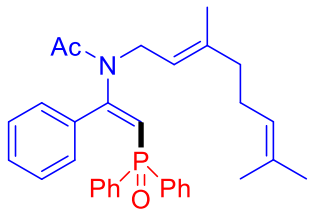


3xa

^{31}P NMR (162 MHz, $CDCl_3$)

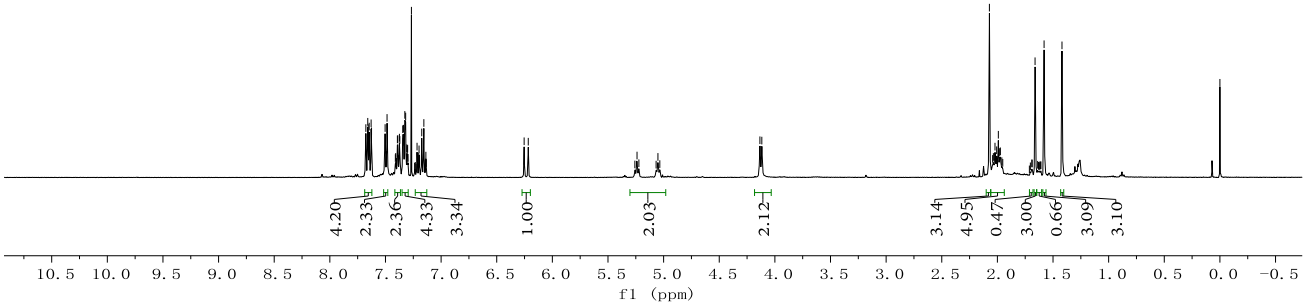
N-((*E*)-3,7-dimethylocta-2,6-dien-1-yl)-*N*-((*E*)-2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (**3ya**)

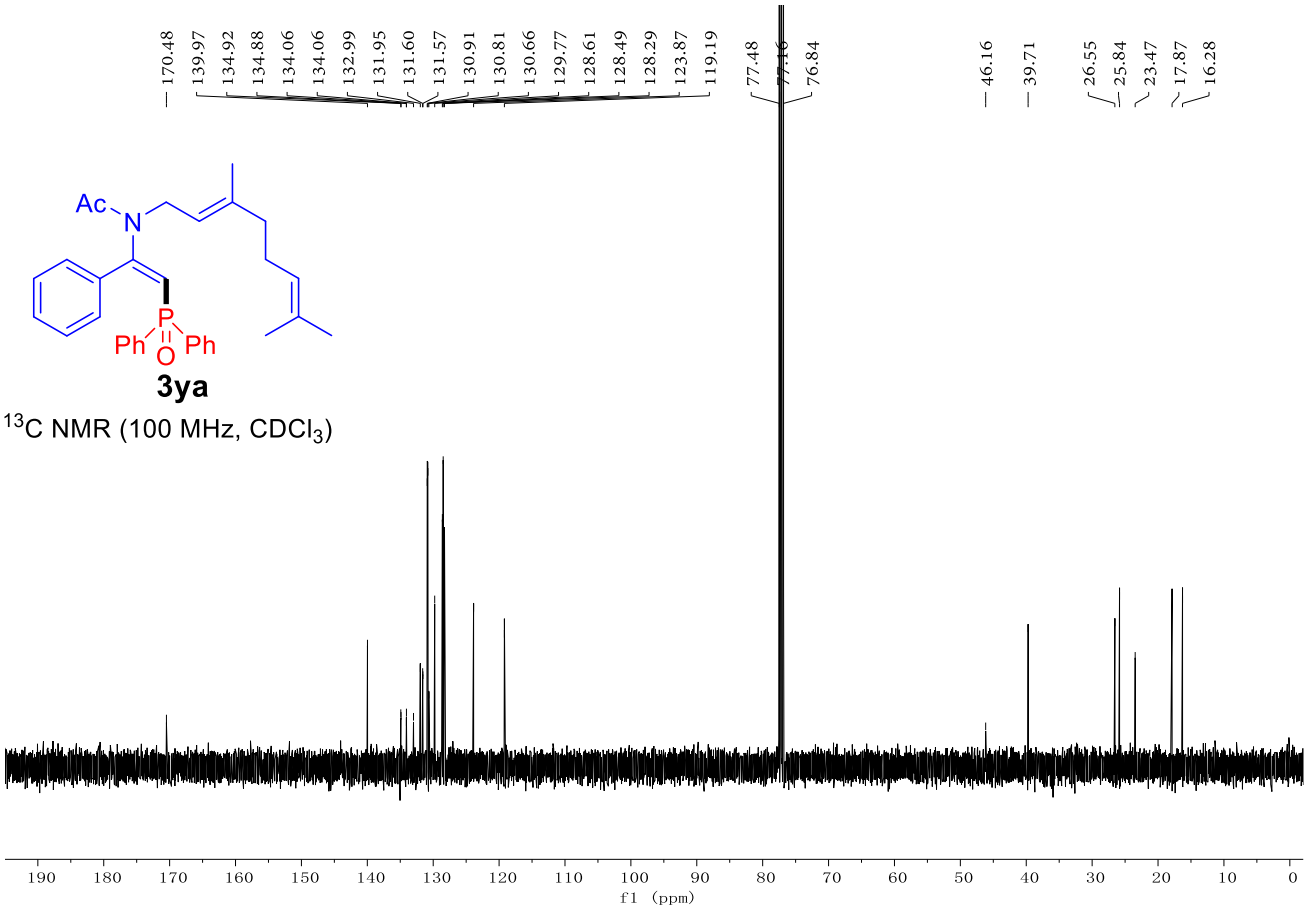




3ya

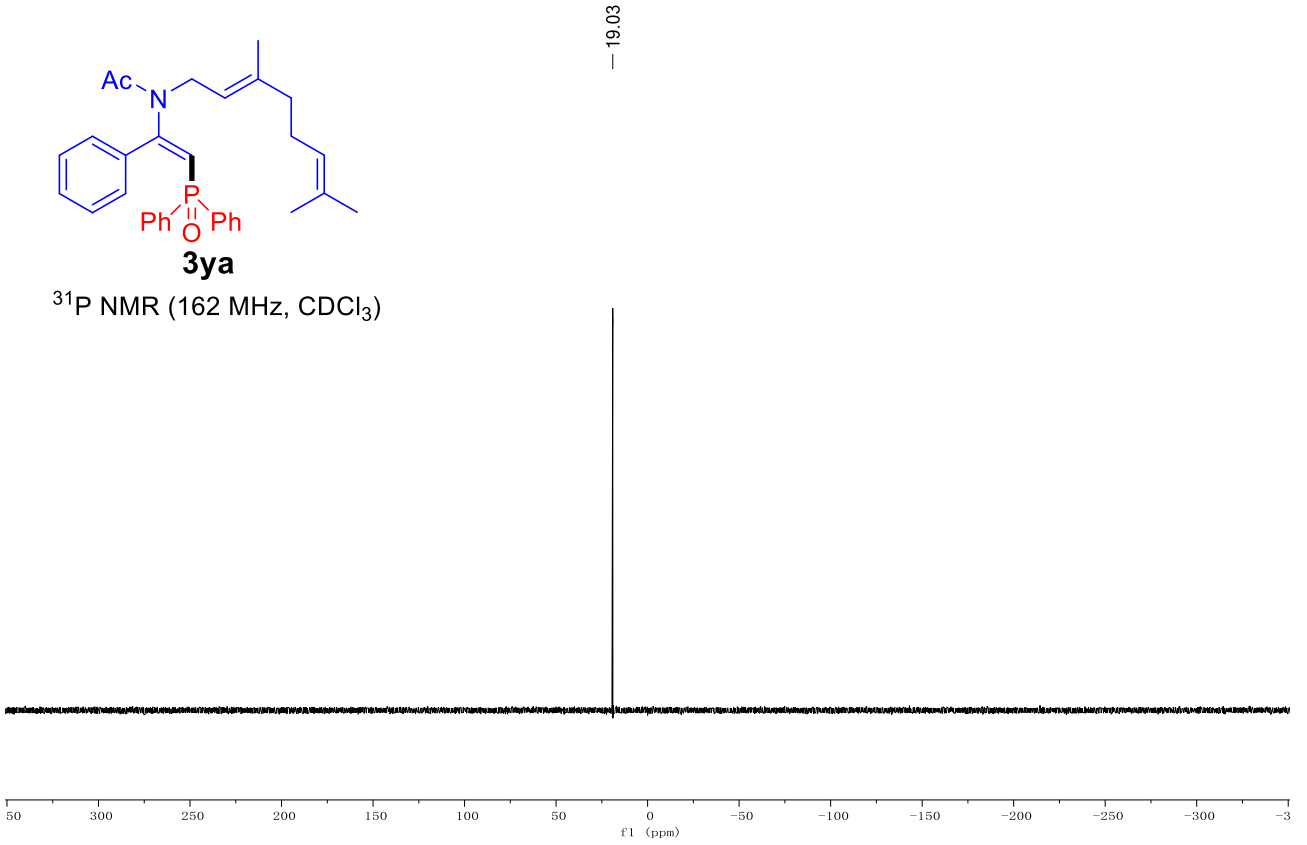
^{1}H NMR (400 MHz, $CDCl_3$)





3ya

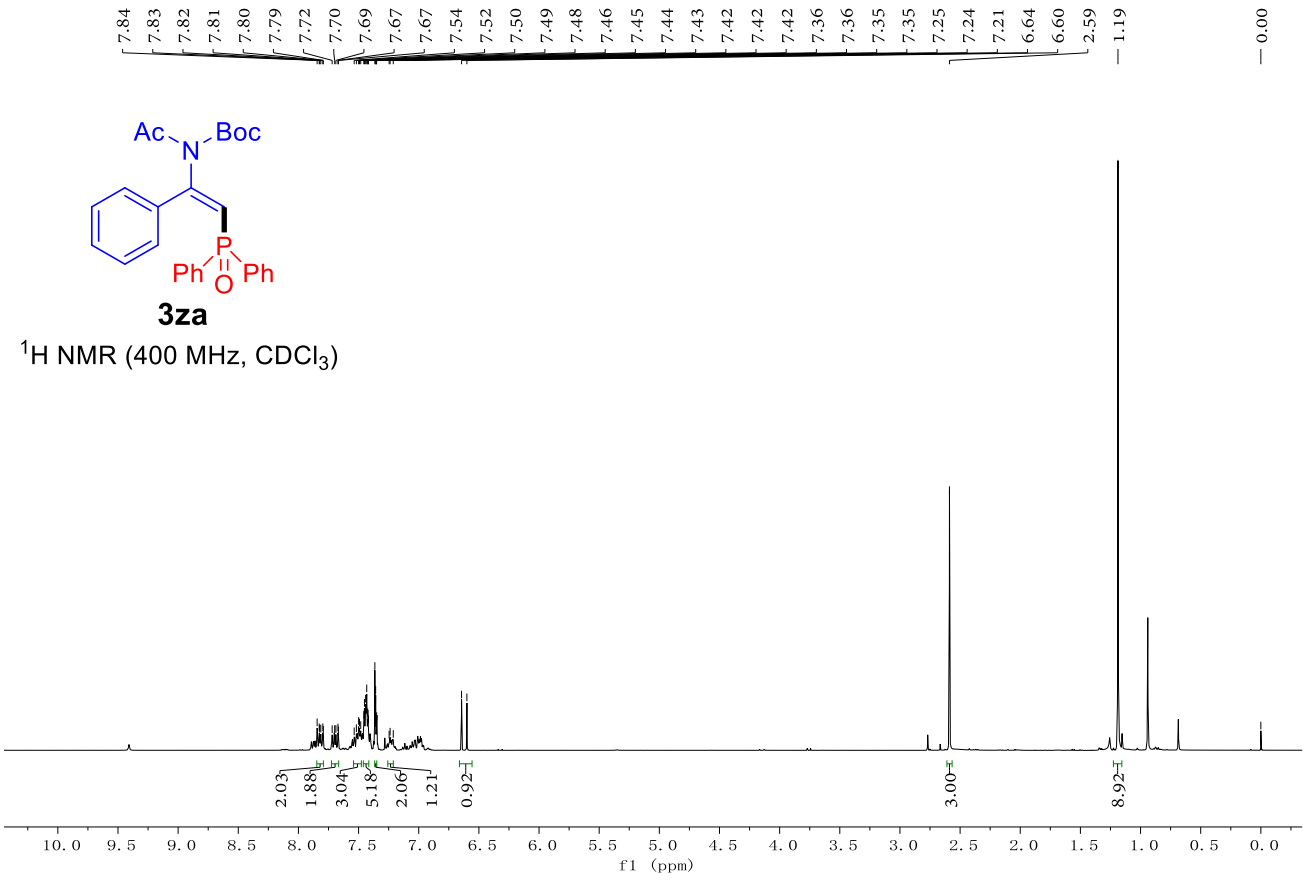
^{13}C NMR (100 MHz, $CDCl_3$)



3ya

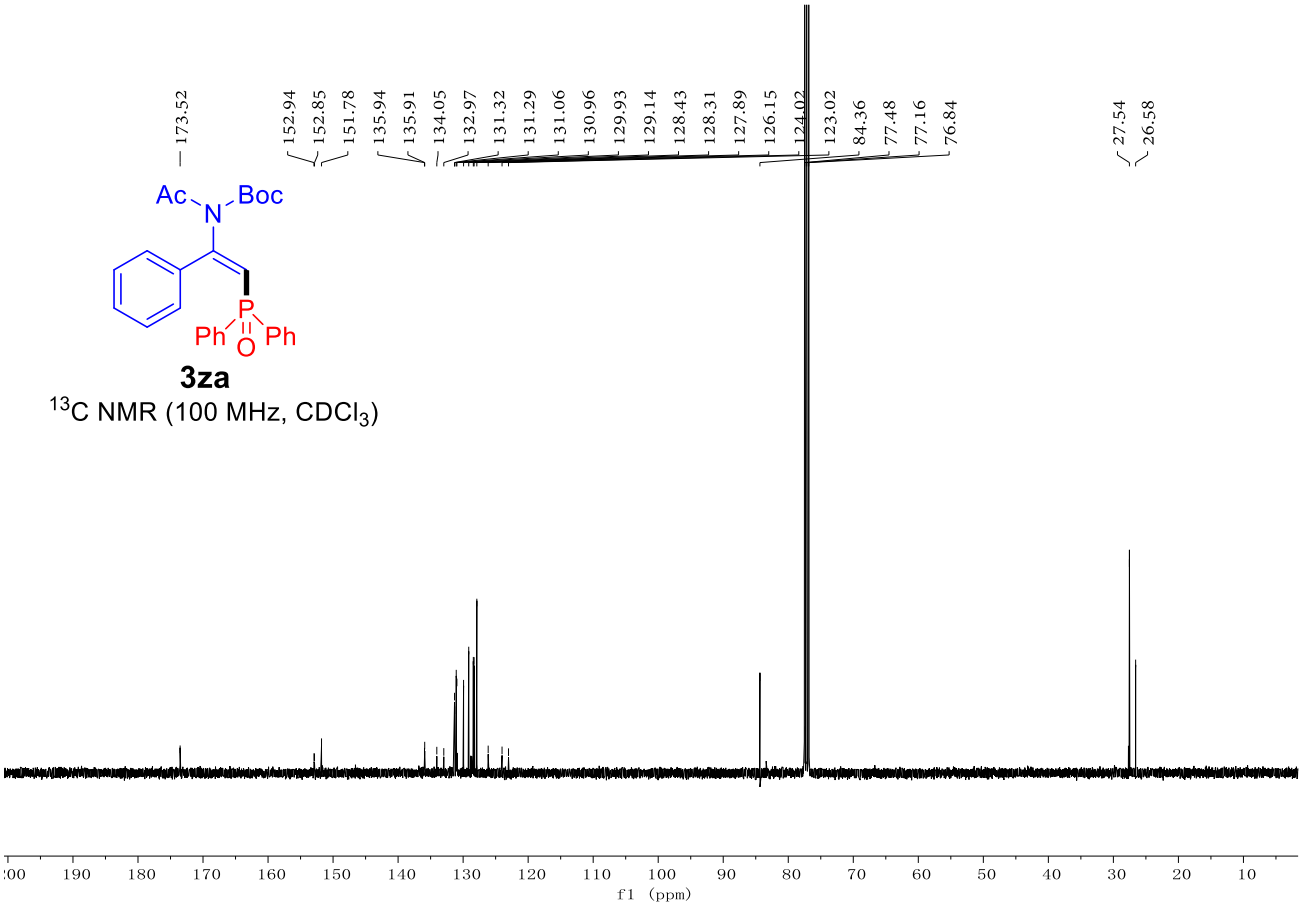
^{31}P NMR (162 MHz, $CDCl_3$)

tert-butyl *(E)*-acetyl(2-(diphenylphosphoryl)-1-phenylvinyl)carbamate (**3za**)



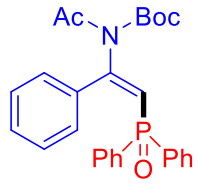
3za

^{1}H NMR (400 MHz, $CDCl_3$)



3za

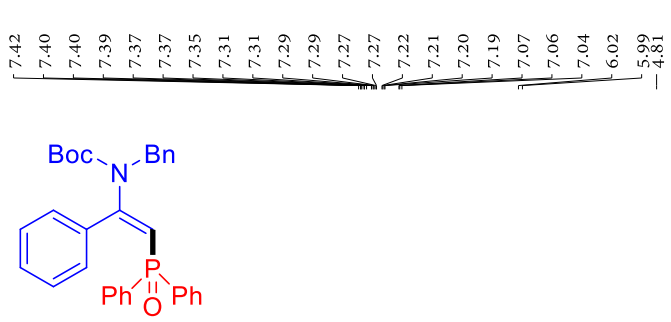
^{13}C NMR (100 MHz, $CDCl_3$)



3za

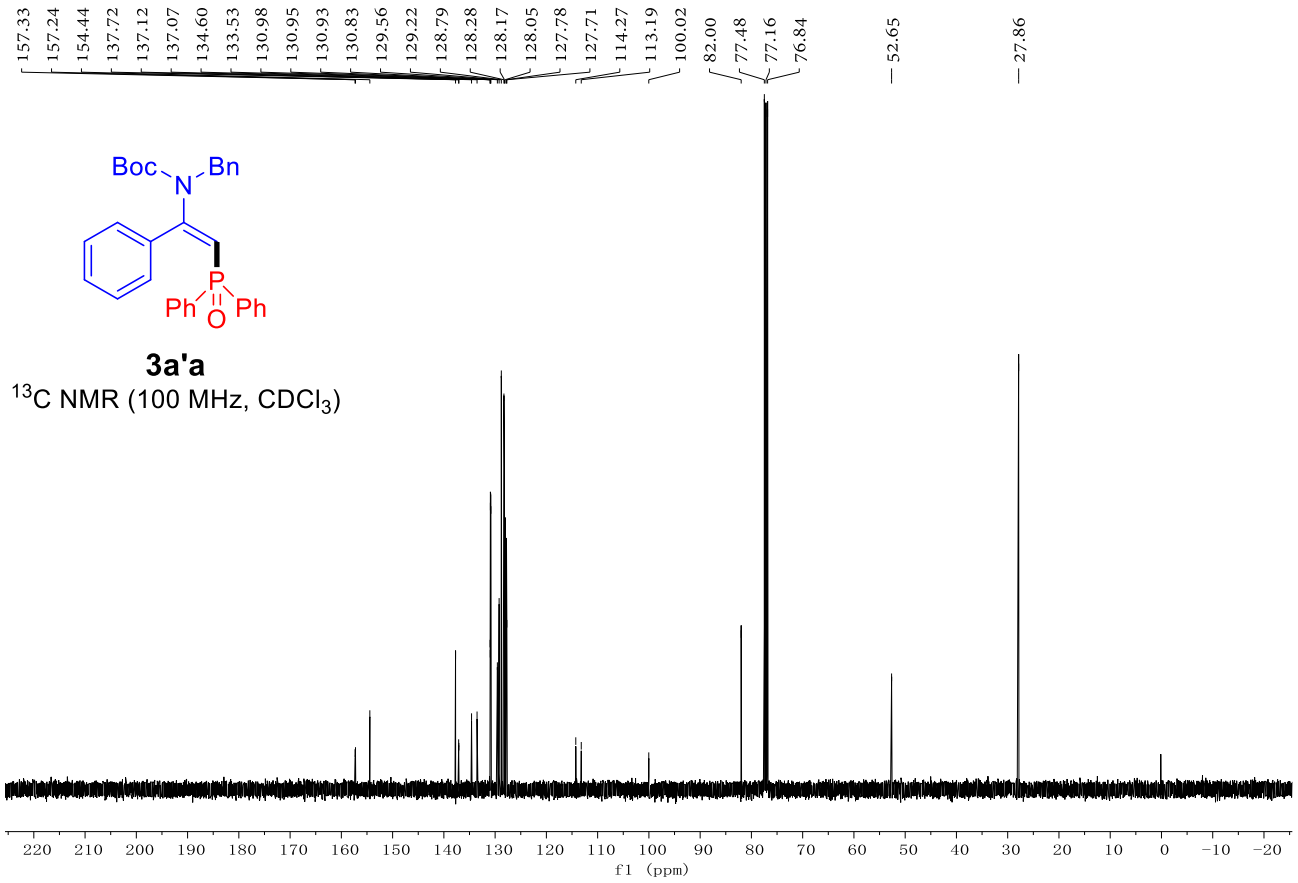
^{31}P NMR (162 MHz, $CDCl_3$)

tert-butyl *(E)*-benzyl(2-(diphenylphosphoryl)-1-phenylvinyl)carbamate (**3a'a**)



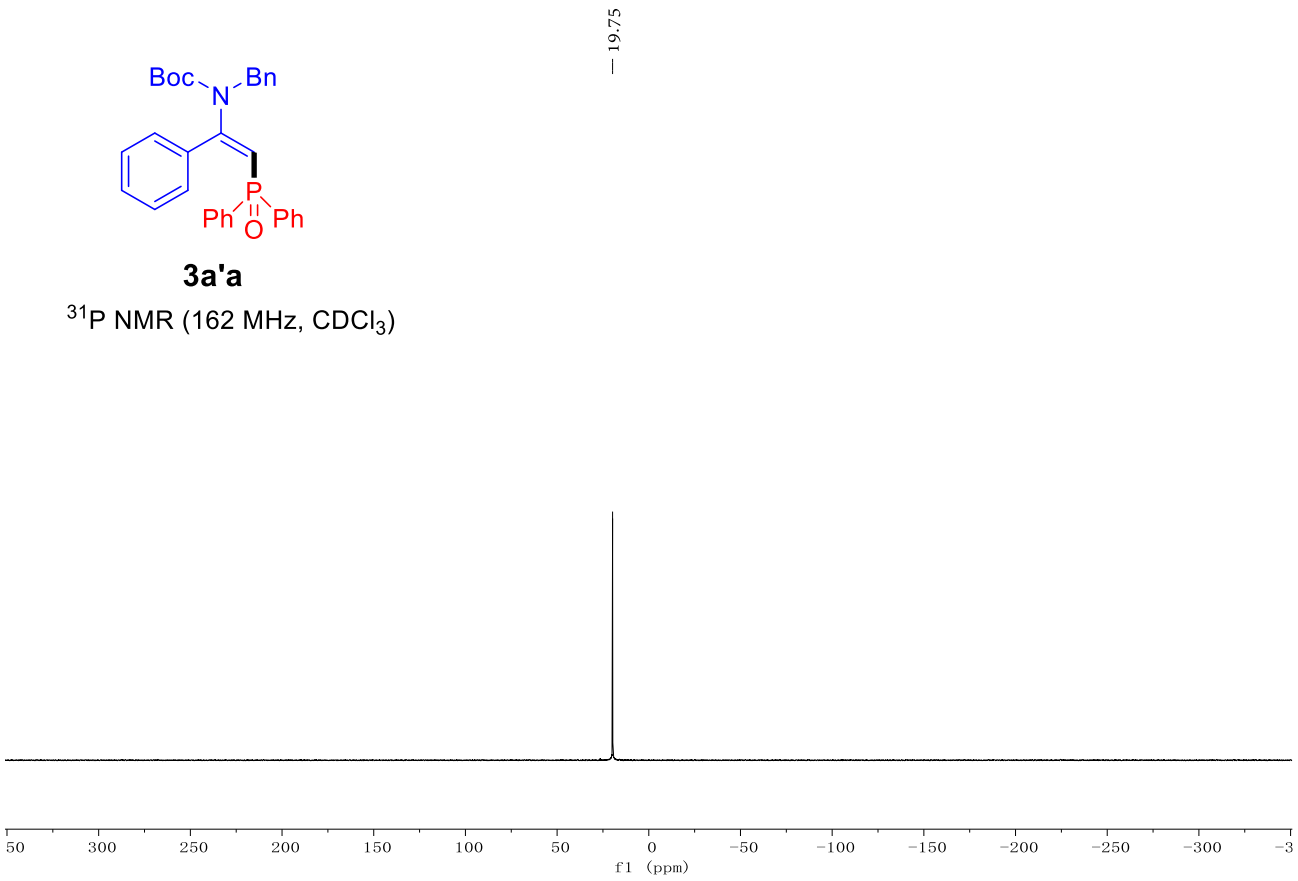
3a'a

^{1}H NMR (400 MHz, $CDCl_3$)



3a'a

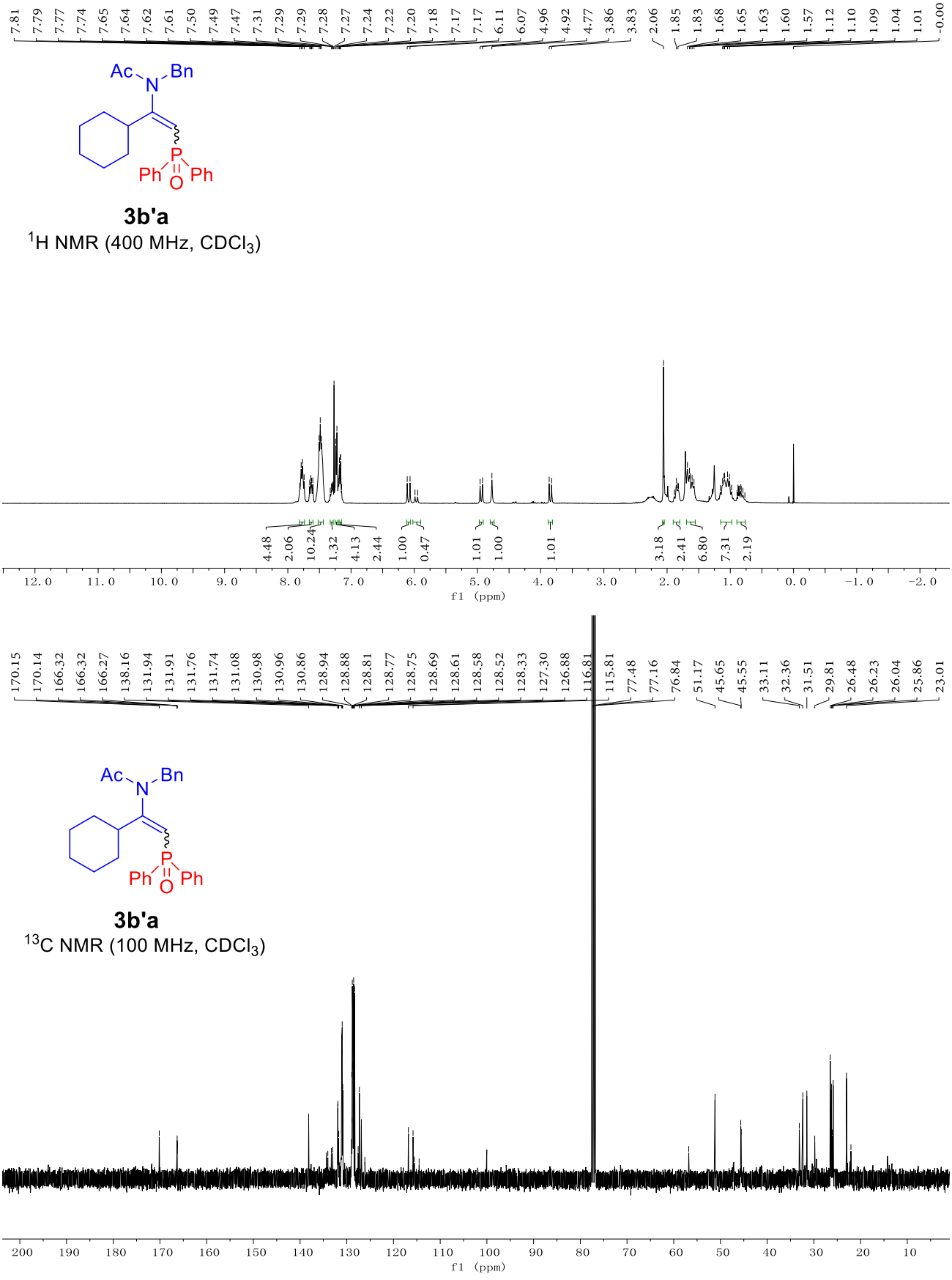
^{13}C NMR (100 MHz, $CDCl_3$)

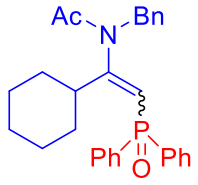


3a'a

^{31}P NMR (162 MHz, $CDCl_3$)

N-benzyl-*N*-(1-cyclohexyl-2-(diphenylphosphoryl)vinyl)acetamide (**3b'a**)

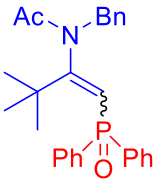




3b'a

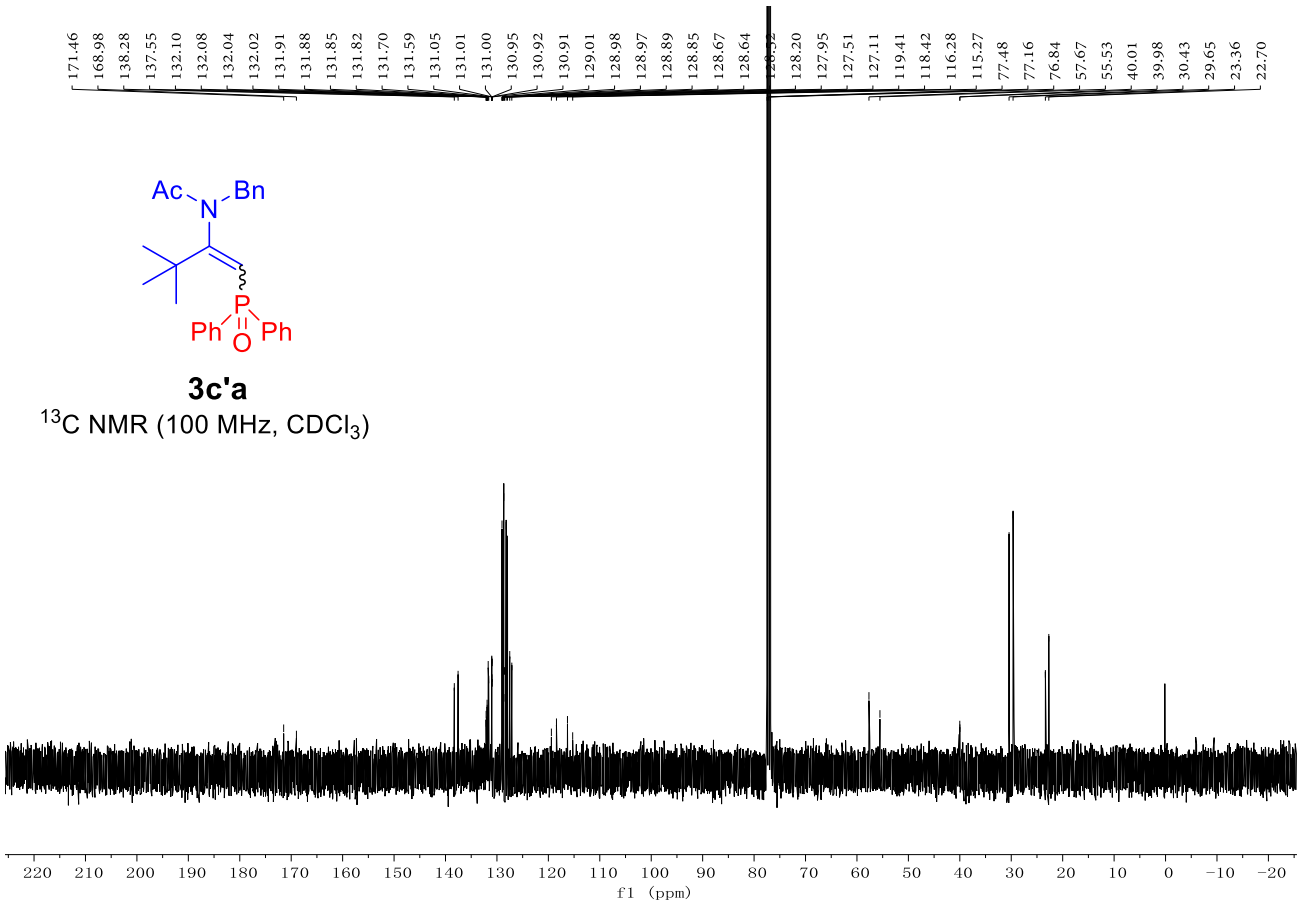
^{31}P NMR (162 MHz, $CDCl_3$)

N-benzyl-*N*-(1-(diphenylphosphoryl)-3,3-dimethylbut-1-en-2-yl)acetamide (**3c'a**)



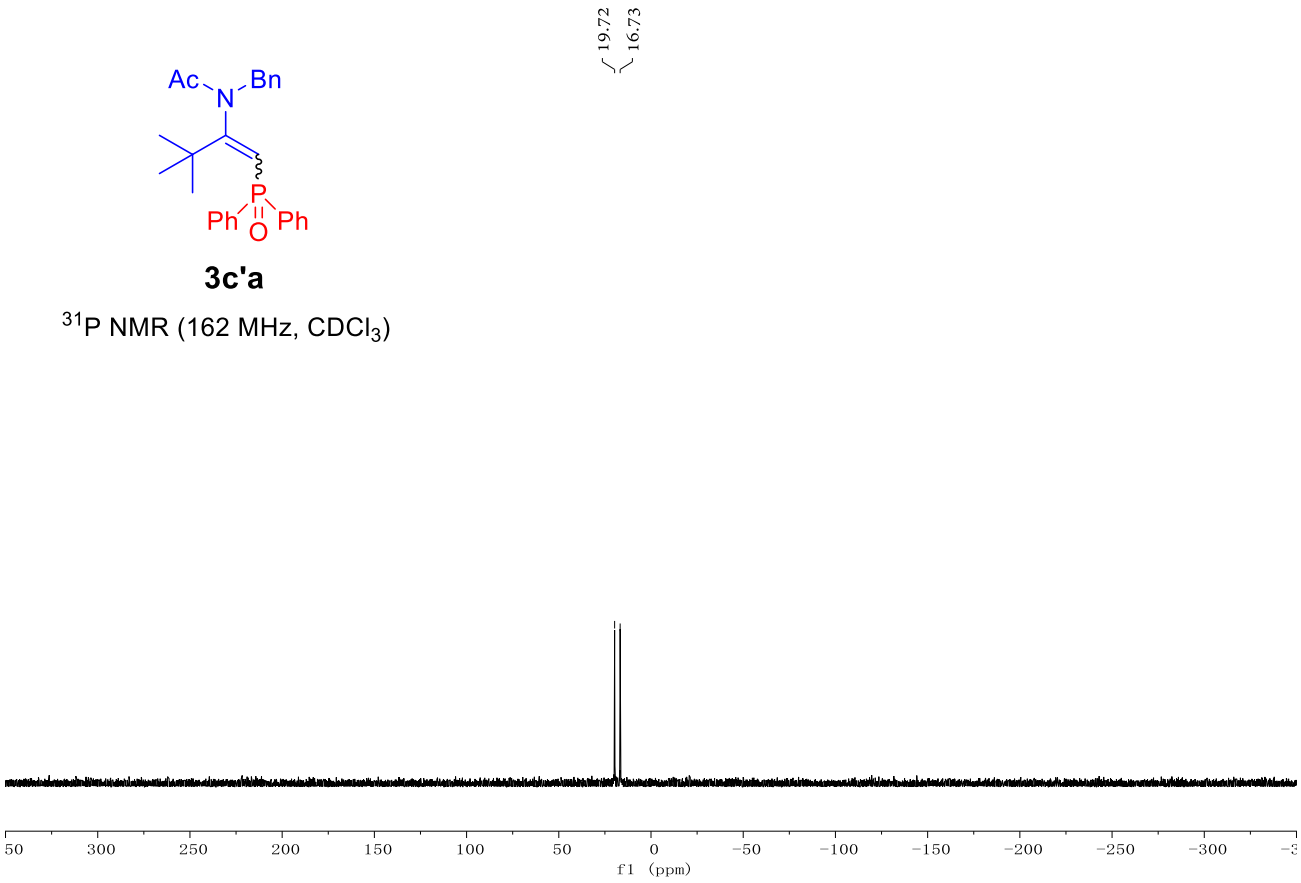
3c'a

^{1}H NMR (400 MHz, $CDCl_3$)



3c'a

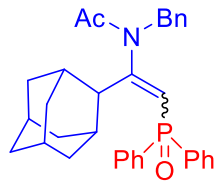
^{13}C NMR (100 MHz, $CDCl_3$)



3c'a

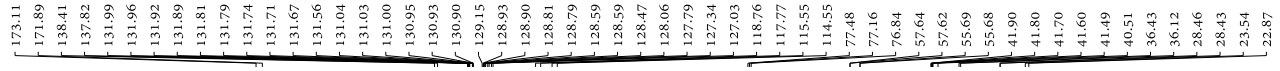
^{31}P NMR (162 MHz, $CDCl_3$)

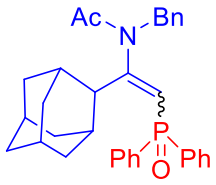
N-(1-((1r,3r,5r,7r)-adamantan-2-yl)-2-(diphenylphosphoryl)vinyl)-*N*-benzylacetamide (**3d'a**)



3d'a

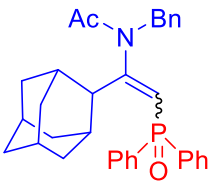
^{1}H NMR (400 MHz, $CDCl_3$)





3d'a

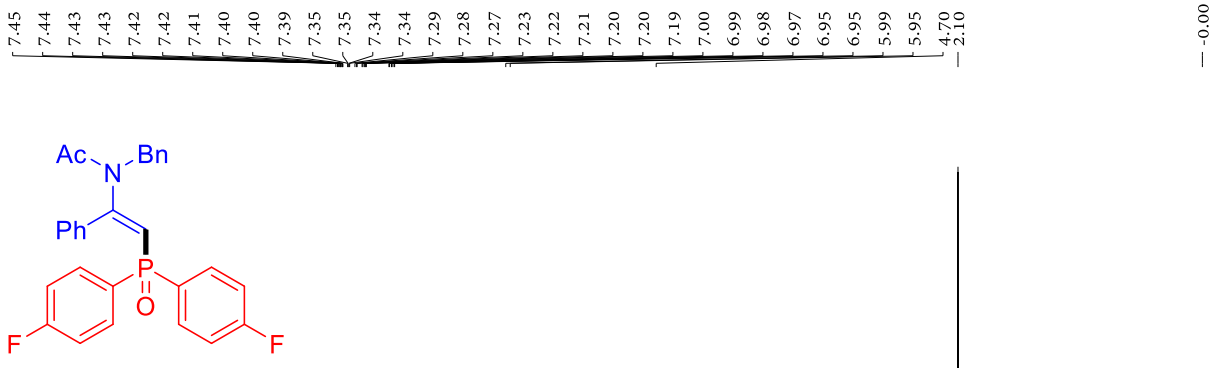
^{13}C NMR (100 MHz, $CDCl_3$)



3d'a

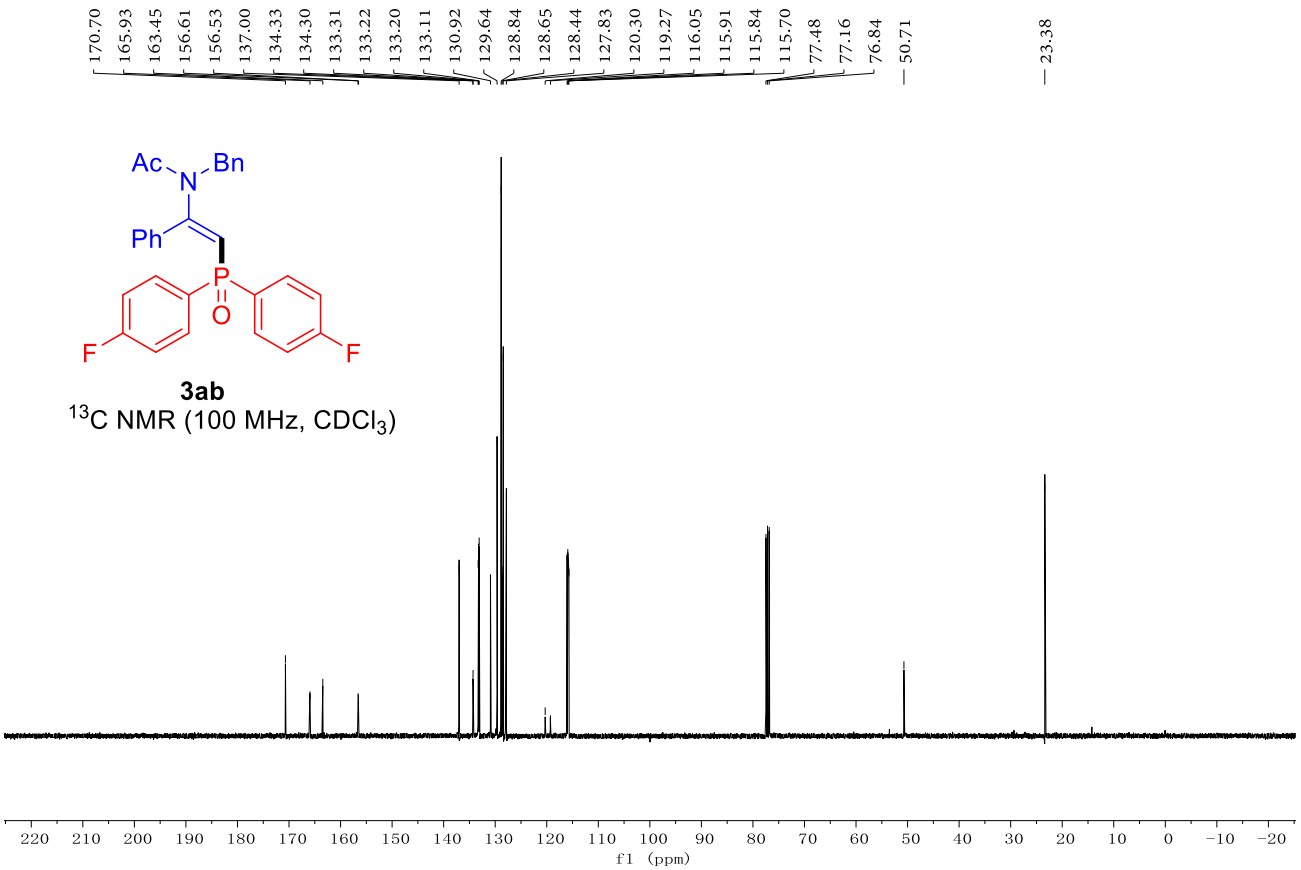
^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(bis(4-fluorophenyl)phosphoryl)-1-phenylvinyl)acetamide (**3ab**)



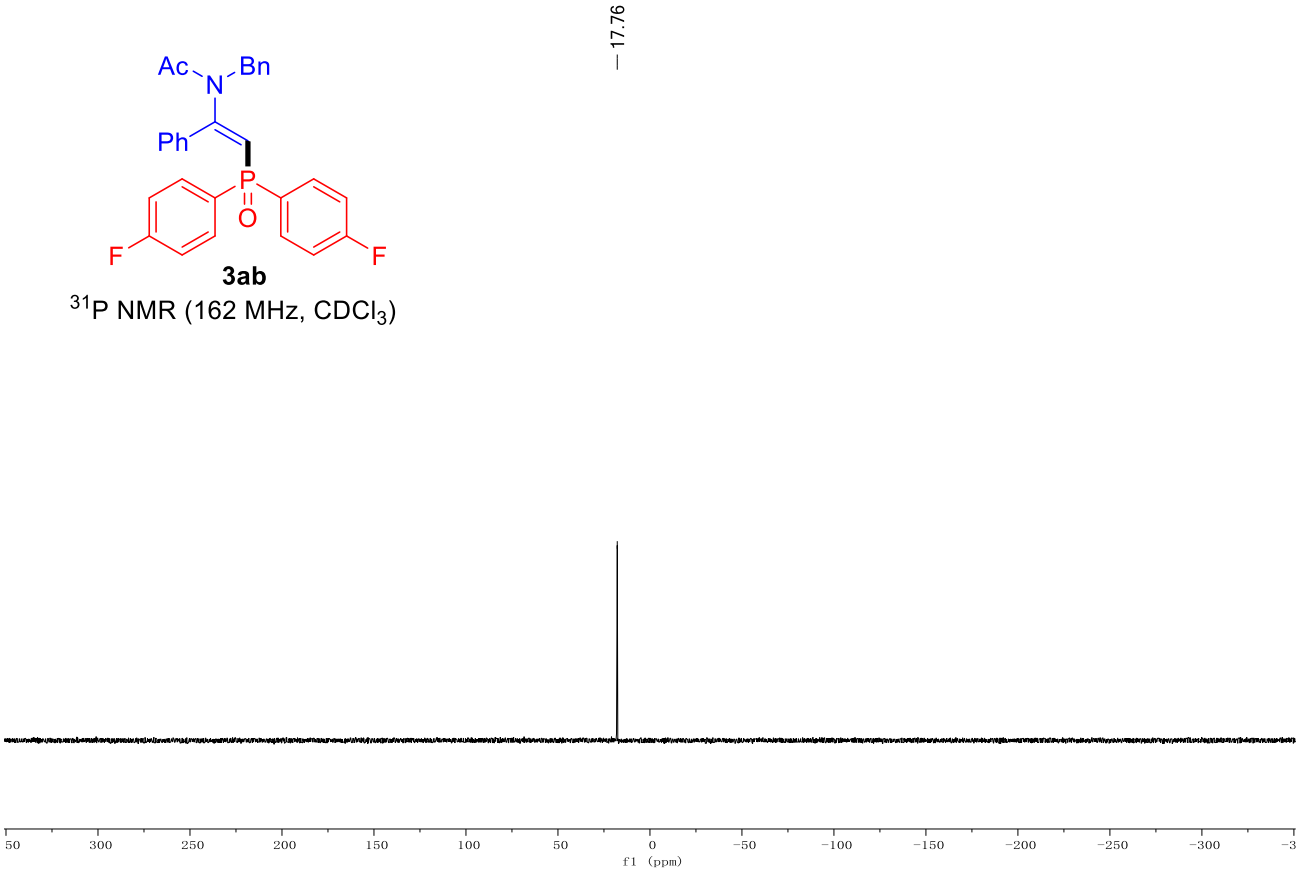
3ab

^{1}H NMR (400 MHz, $CDCl_3$)



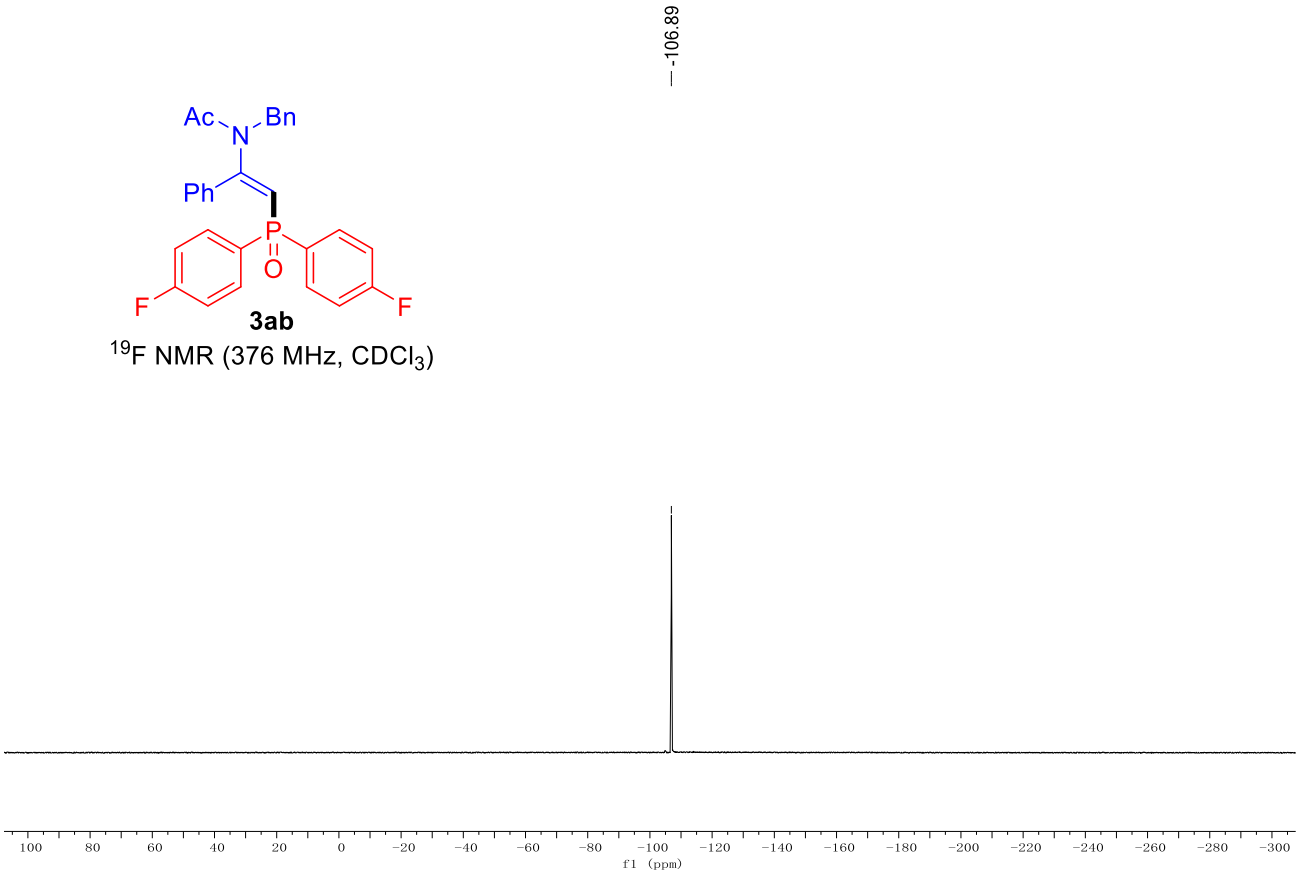
3ab

^{13}C NMR (100 MHz, $CDCl_3$)

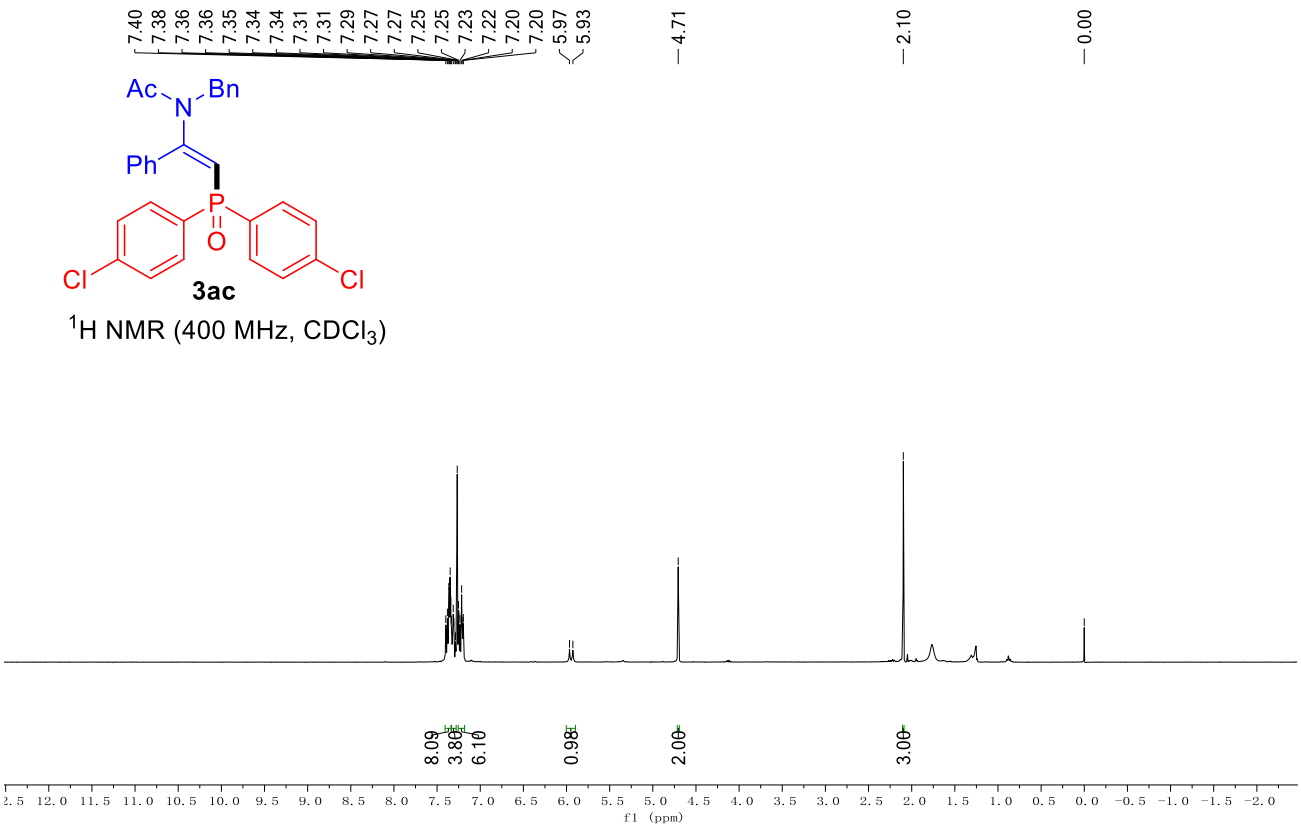


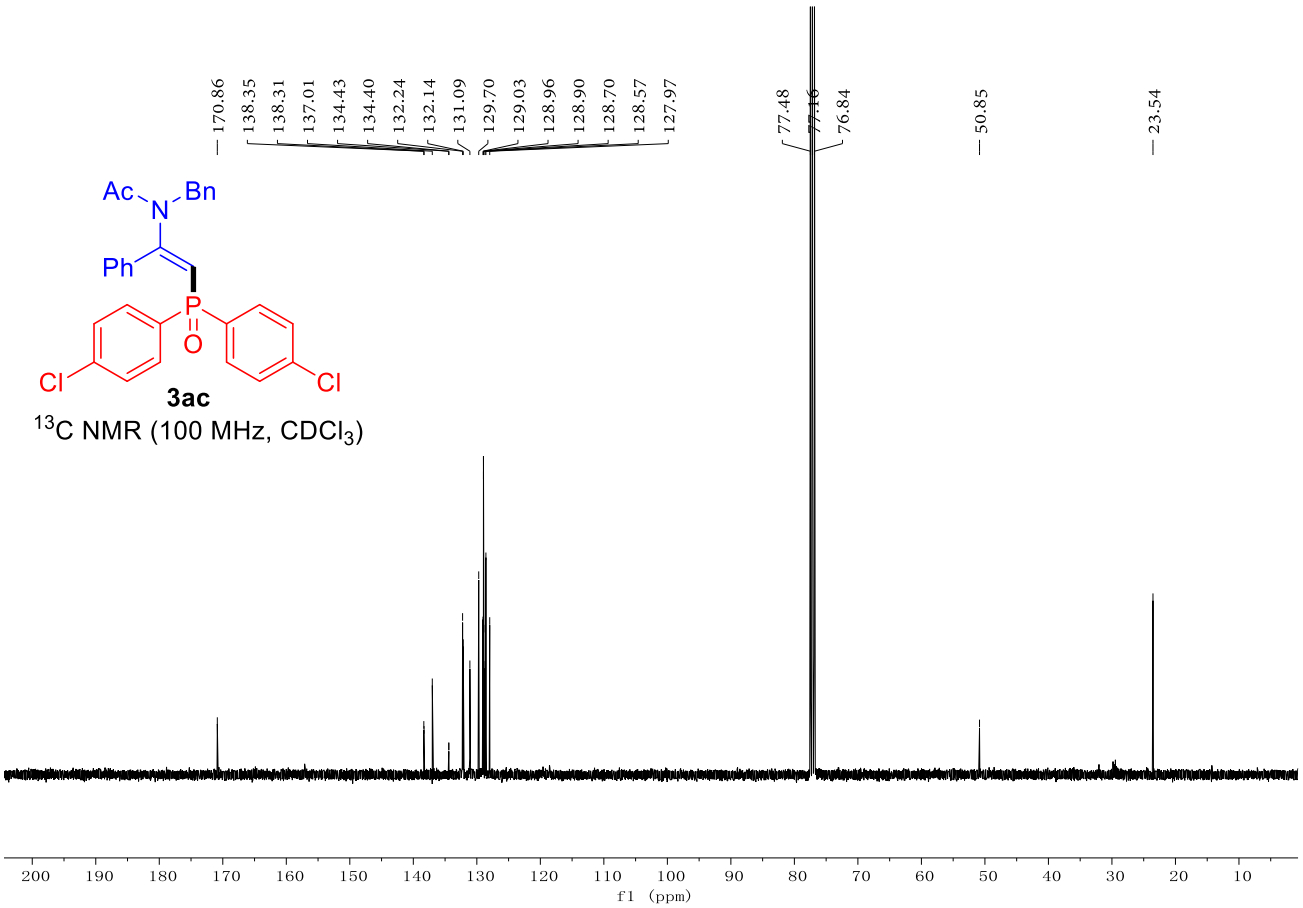
3ab

^{31}P NMR (162 MHz, $CDCl_3$)



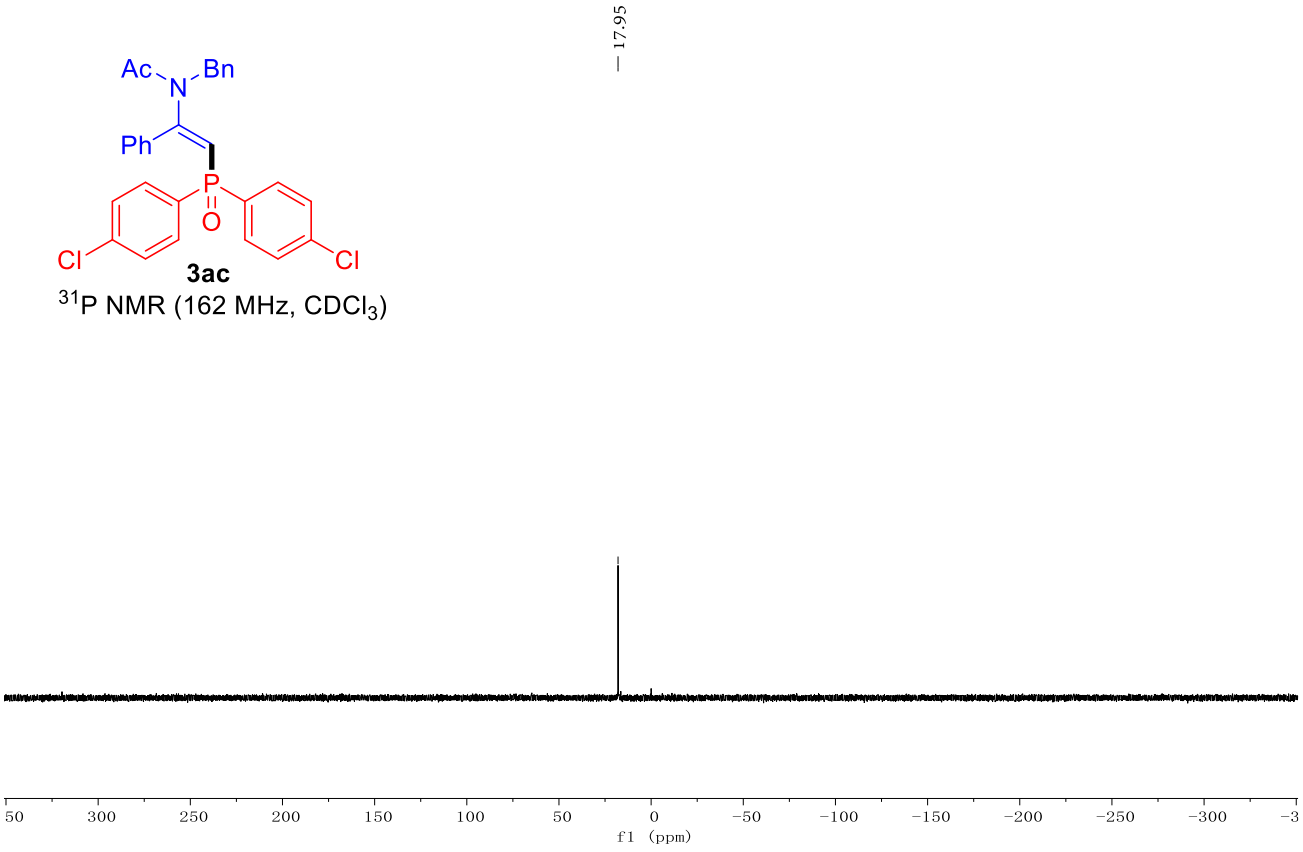
(E)-*N*-benzyl-*N*-(2-(bis(4-chlorophenyl)phosphoryl)-1-phenylvinyl)acetamide (**3ac**)





3ac

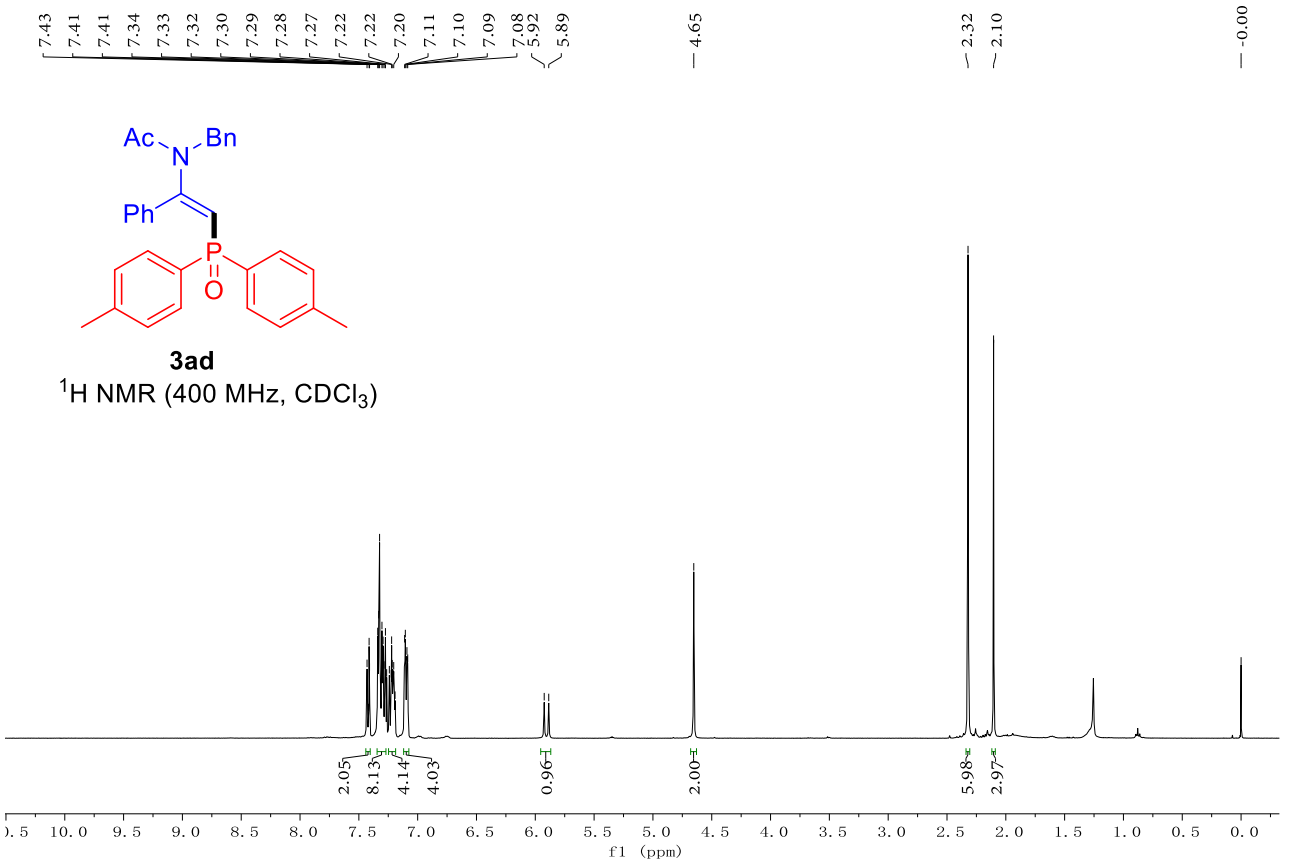
^{13}C NMR (100 MHz, $CDCl_3$)

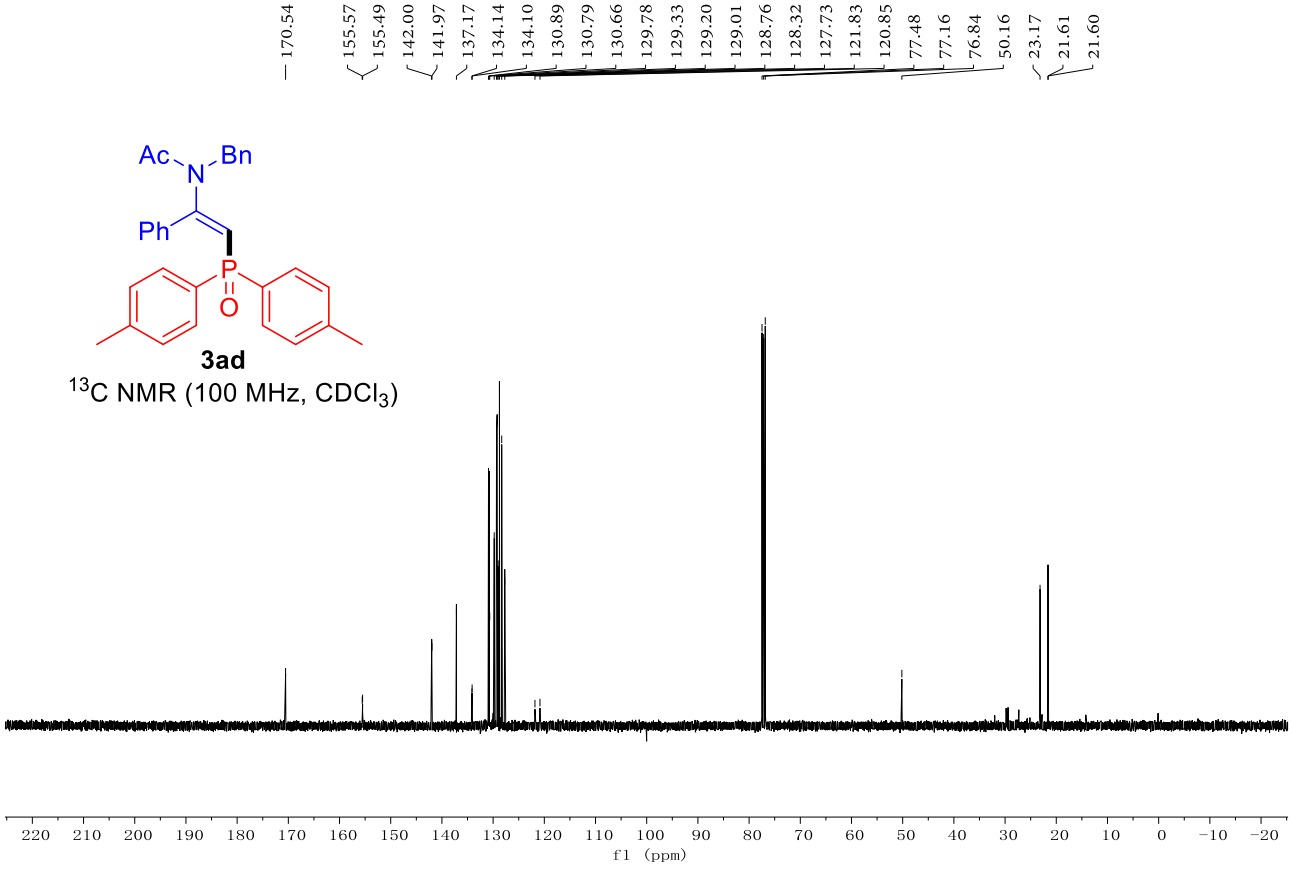


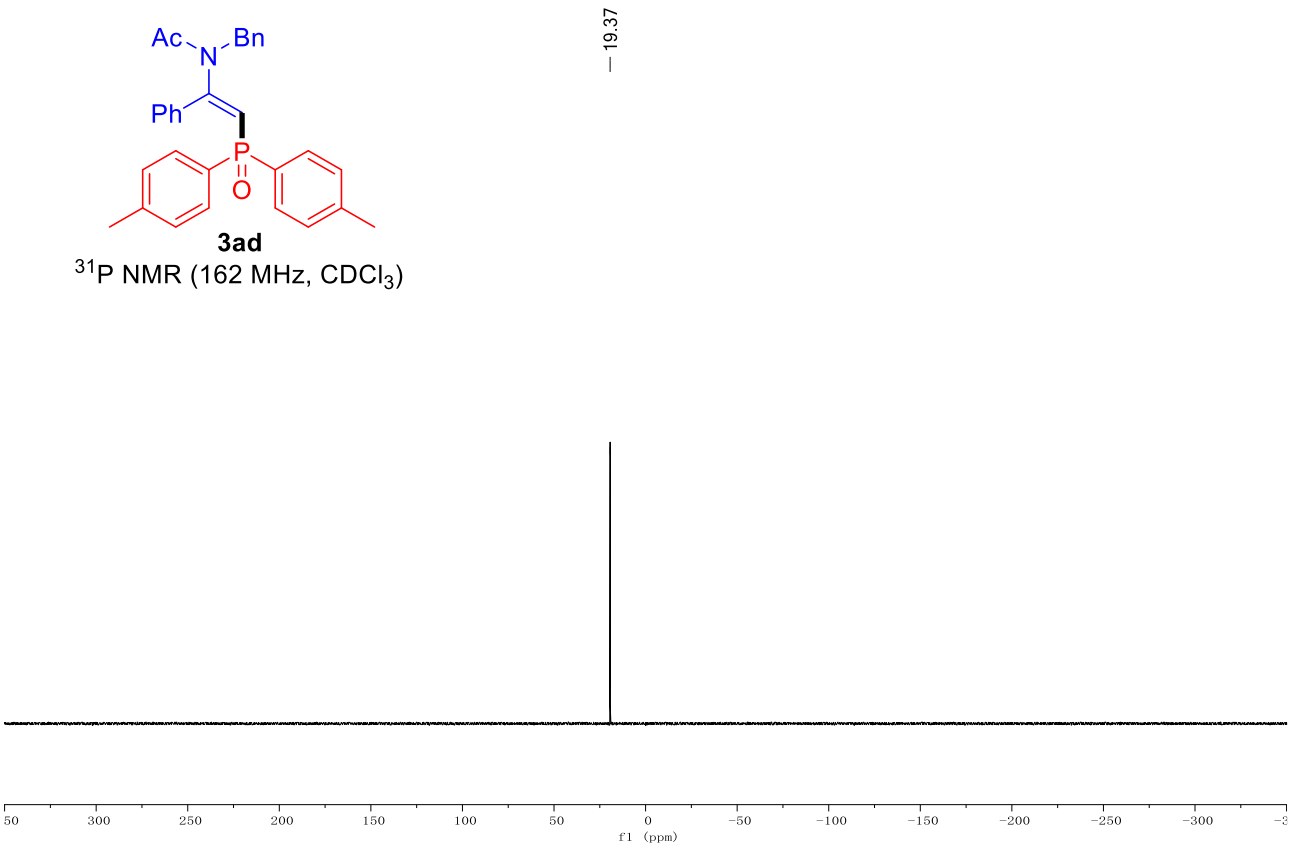
3ac

^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(di-p-tolylphosphoryl)-1-phenylvinyl)acetamide (**3ad**)



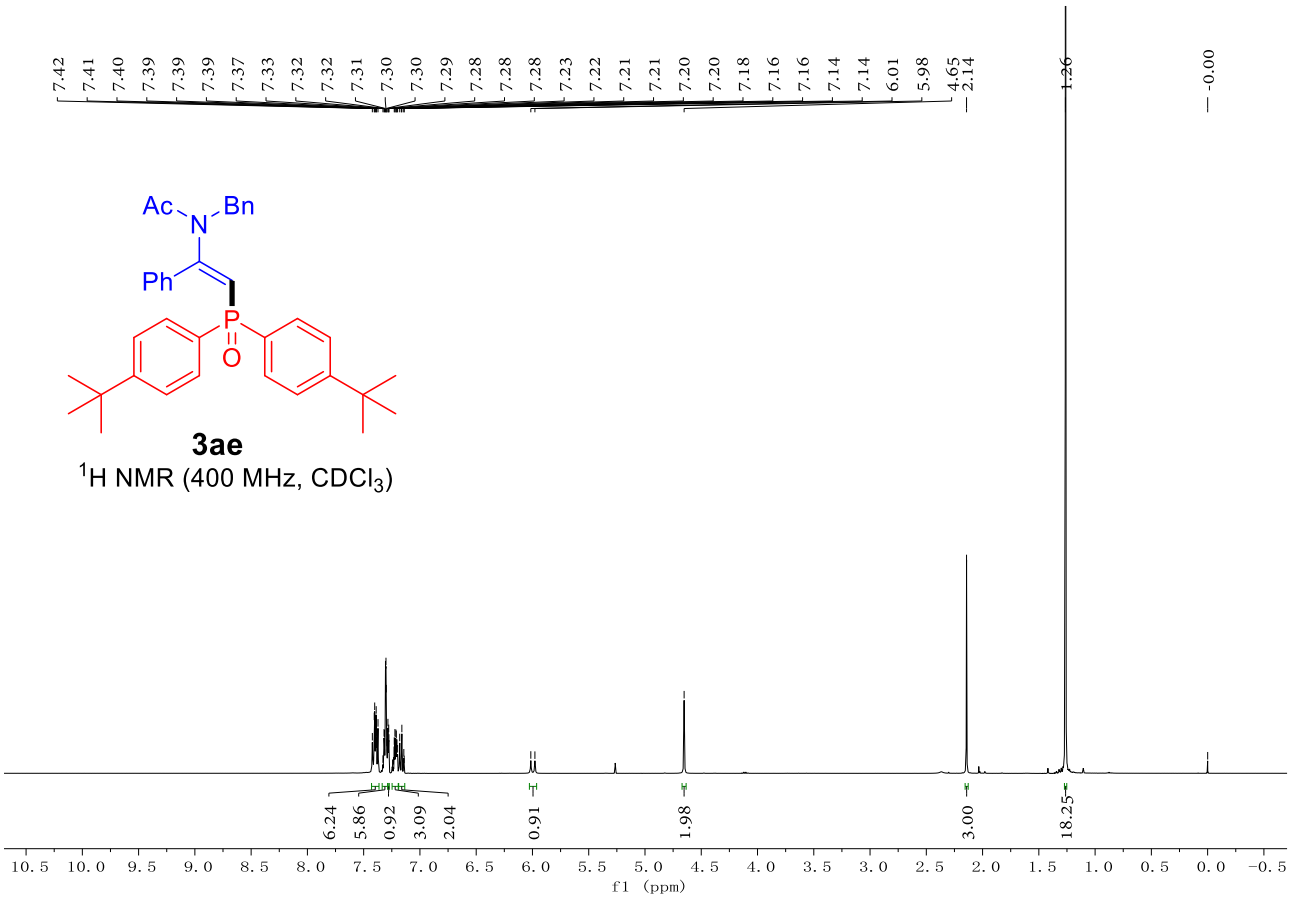




3ad

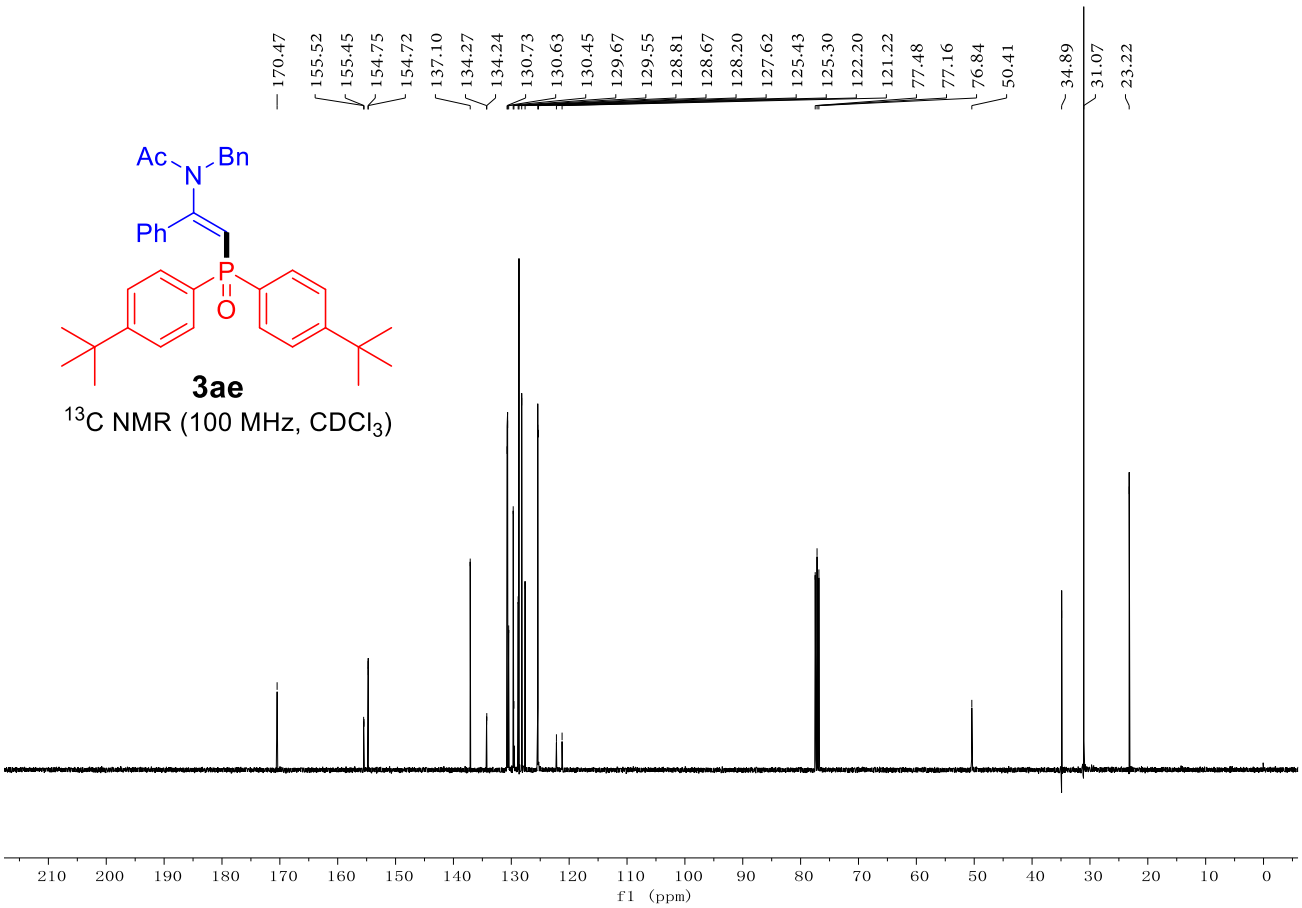
^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-benzyl-*N*-(2-(bis(4-(tert-butyl)phenyl)phosphoryl)-1-phenylvinyl) acetamide (**3ae**)



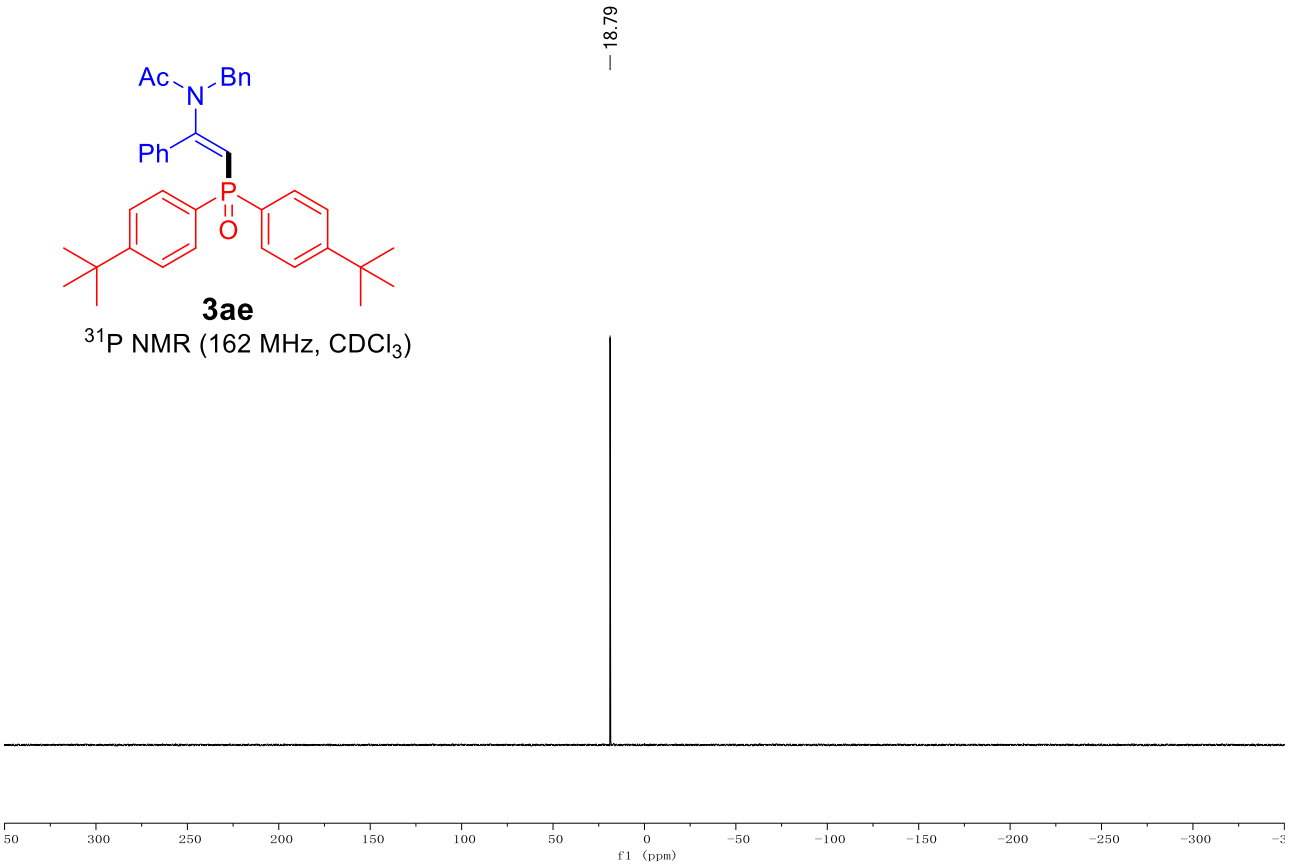
3ae

^{1}H NMR (400 MHz, $CDCl_3$)



3ae

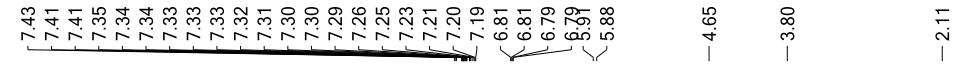
^{13}C NMR (100 MHz, $CDCl_3$)

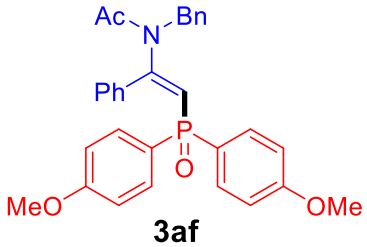


3ae

^{31}P NMR (162 MHz, $CDCl_3$)

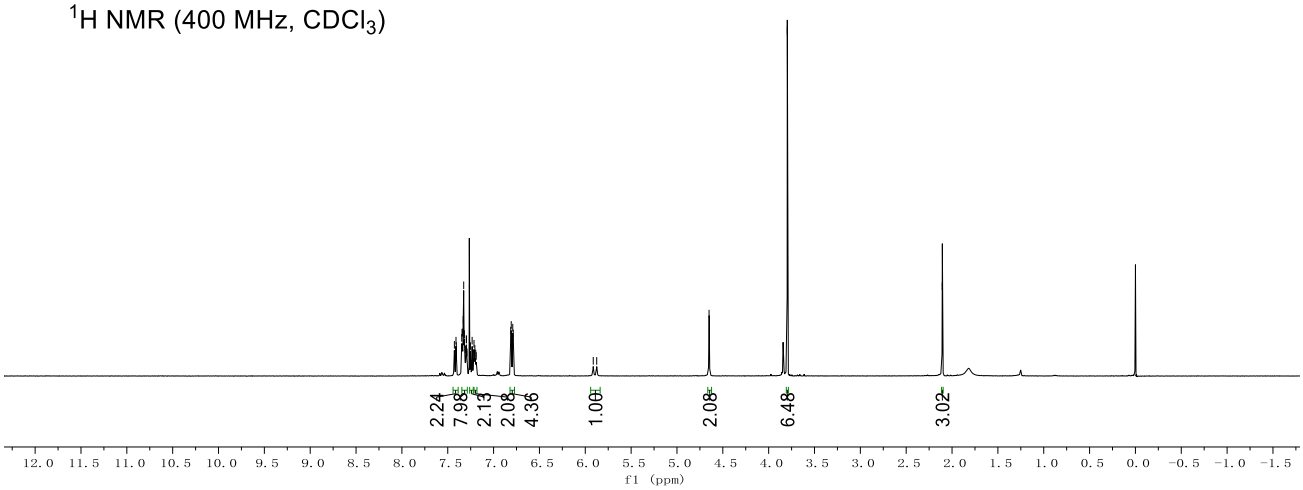
(E)-*N*-benzyl-*N*-(2-(bis(4-methoxyphenyl)phosphoryl)-1-phenylvinyl)acetamide (**3af**)

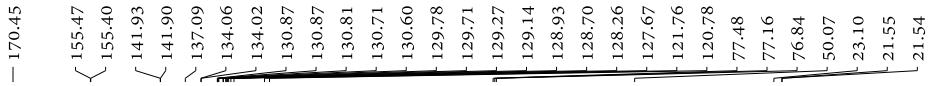


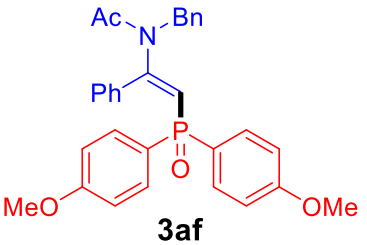


3af

^{1}H NMR (400 MHz, $CDCl_3$)

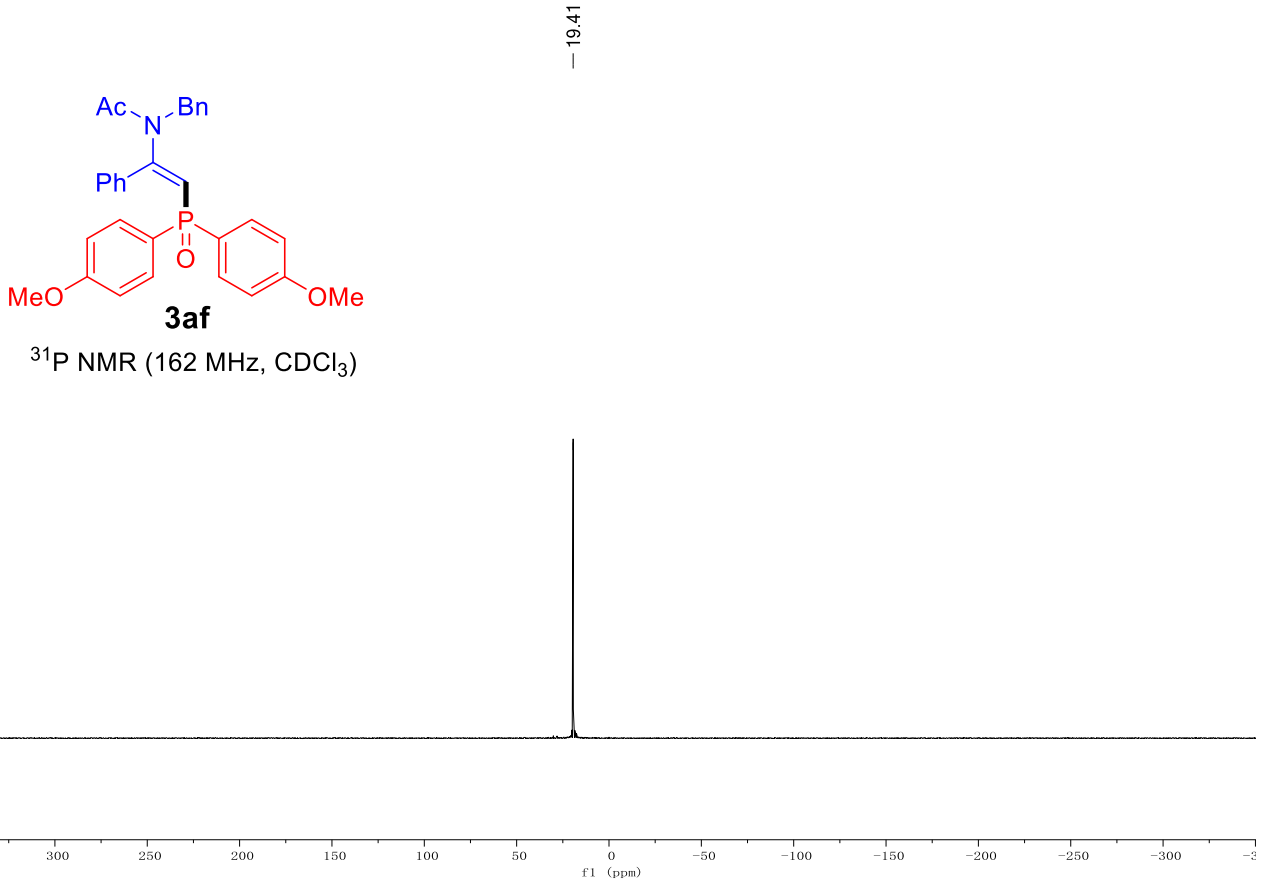




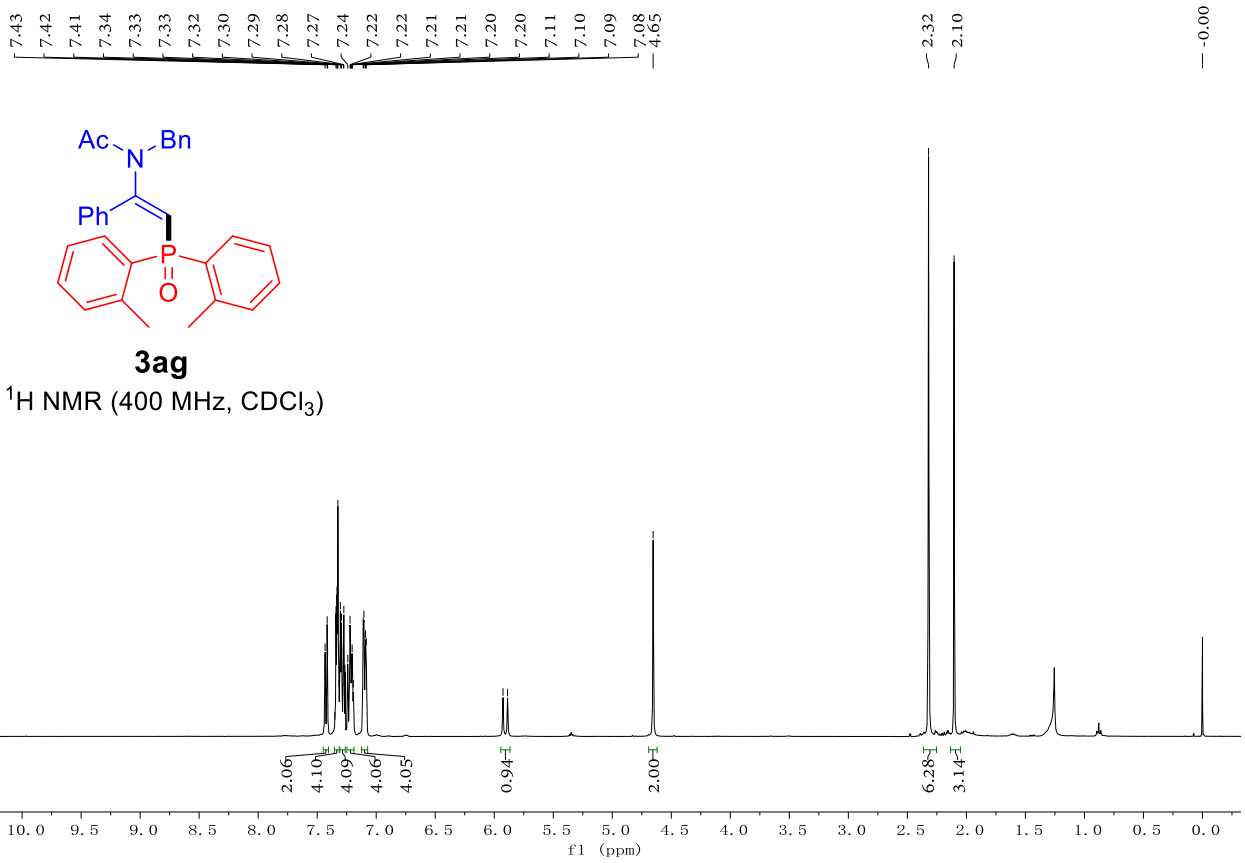


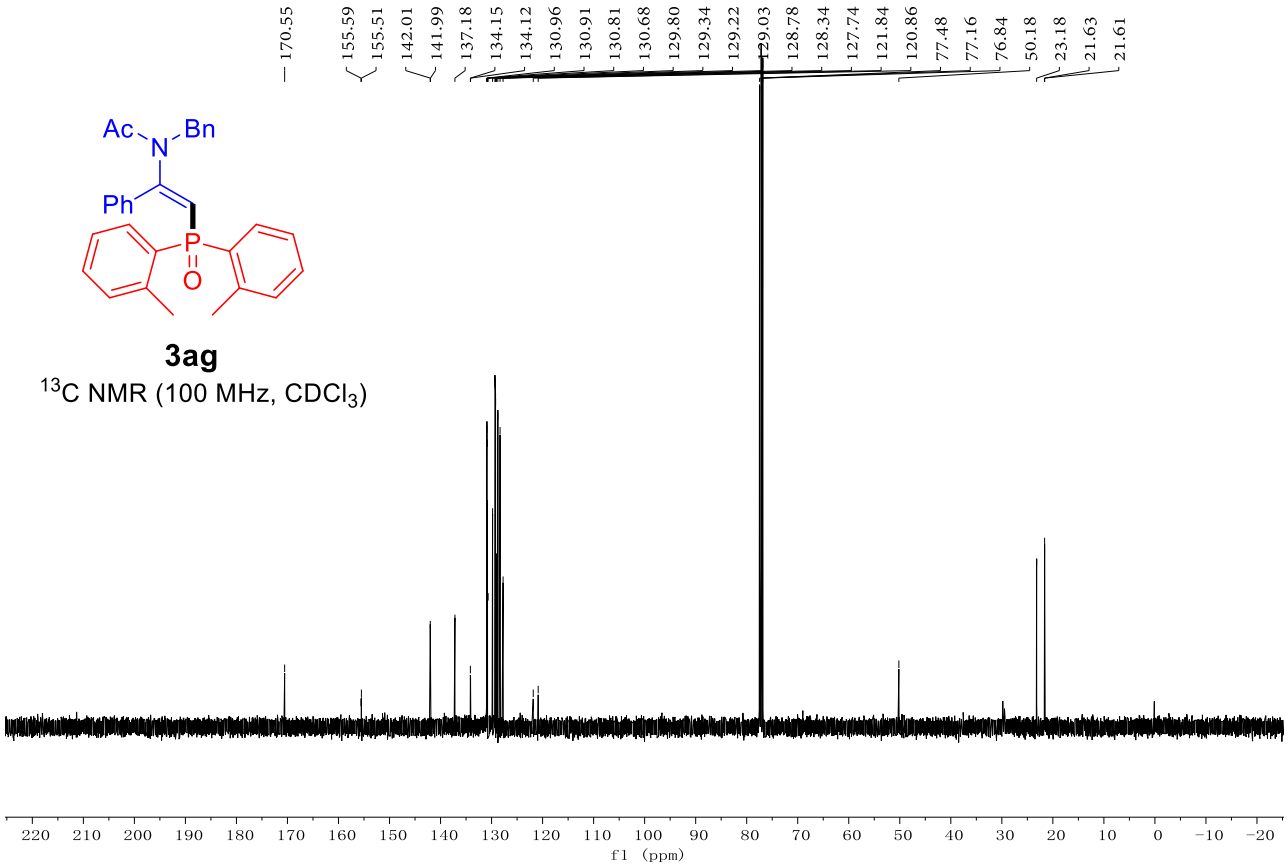
3af

^{13}C NMR (100 MHz, $CDCl_3$)



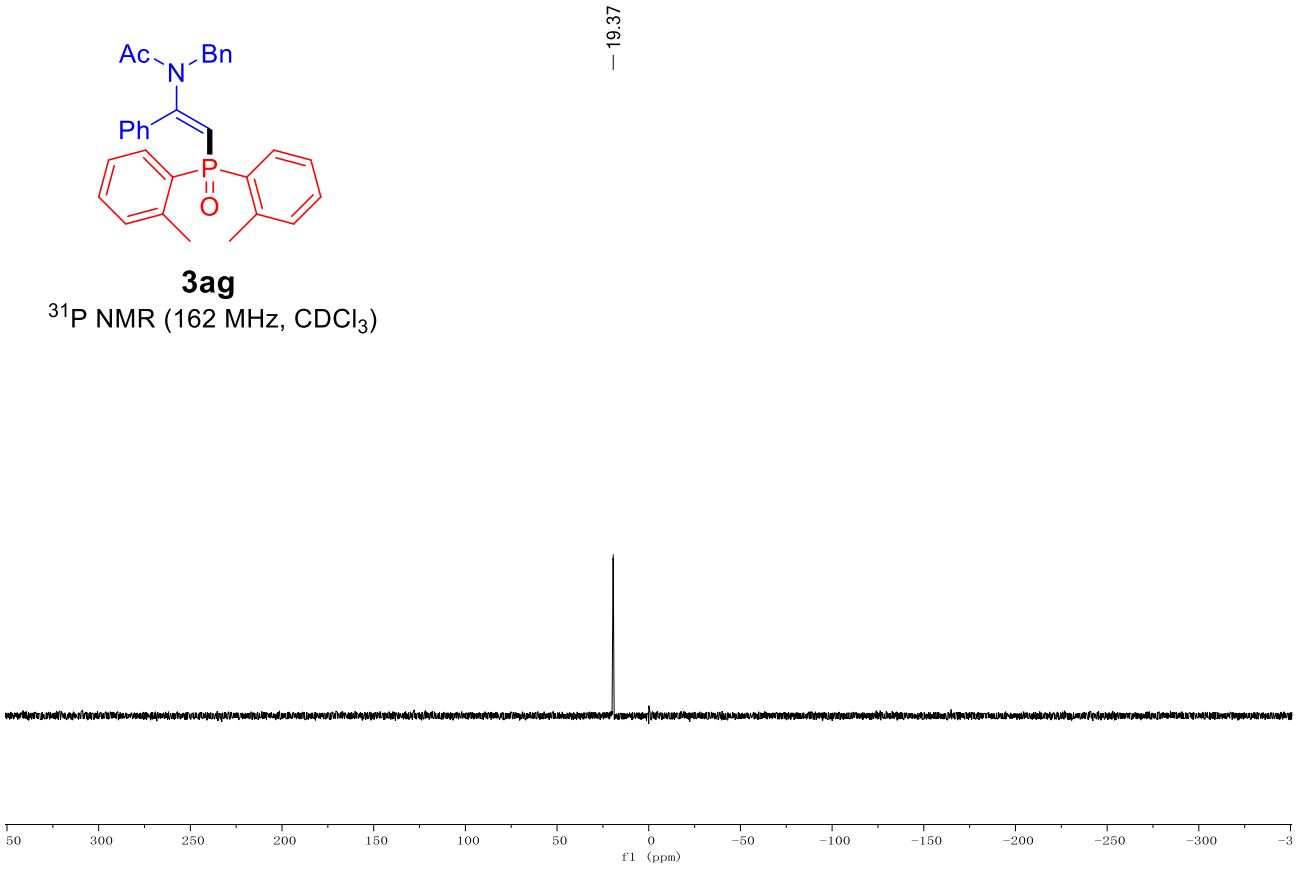
(E)-*N*-benzyl-*N*-(2-(di-o-tolylphosphoryl)-1-phenylvinyl)acetamide (**3ag**)





3ag

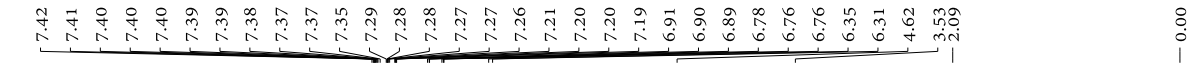
^{13}C NMR (100 MHz, $CDCl_3$)

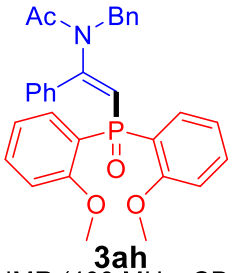


3ag

^{31}P NMR (162 MHz, $CDCl_3$)

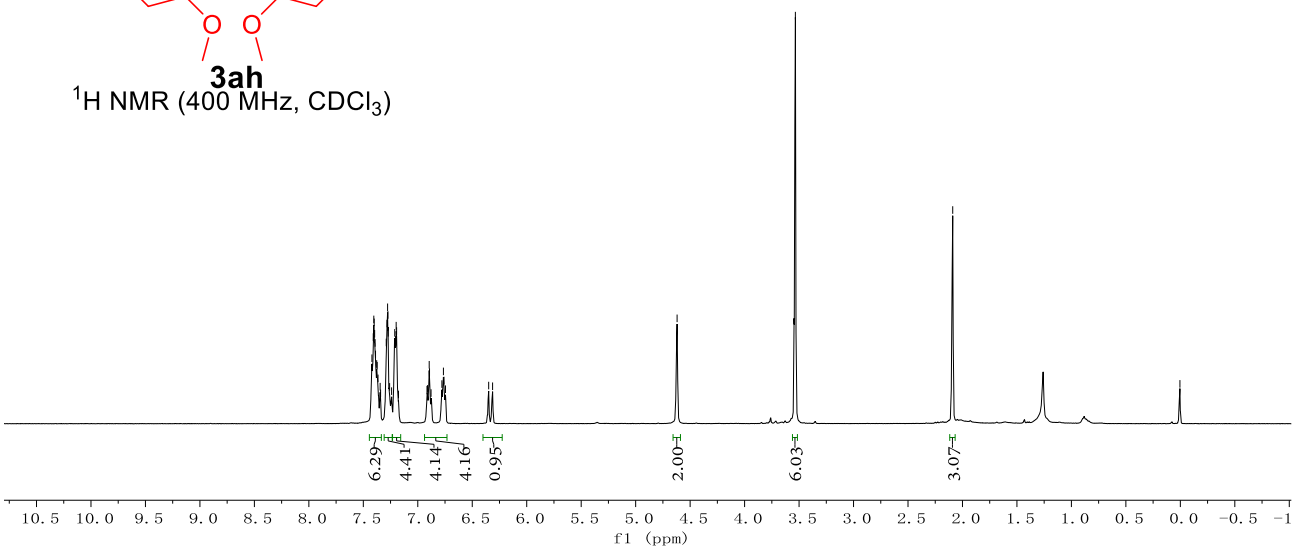
(E)-*N*-benzyl-*N*-(2-(bis(2-methoxyphenyl)phosphoryl)-1-phenylvinyl)acetamide (**3ah**)

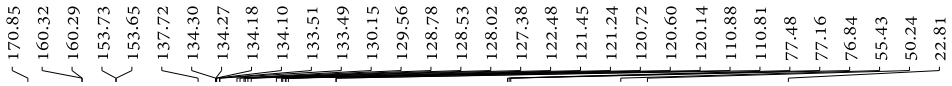


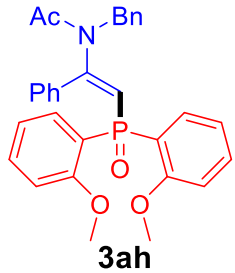


3ah

^{1}H NMR (400 MHz, $CDCl_3$)

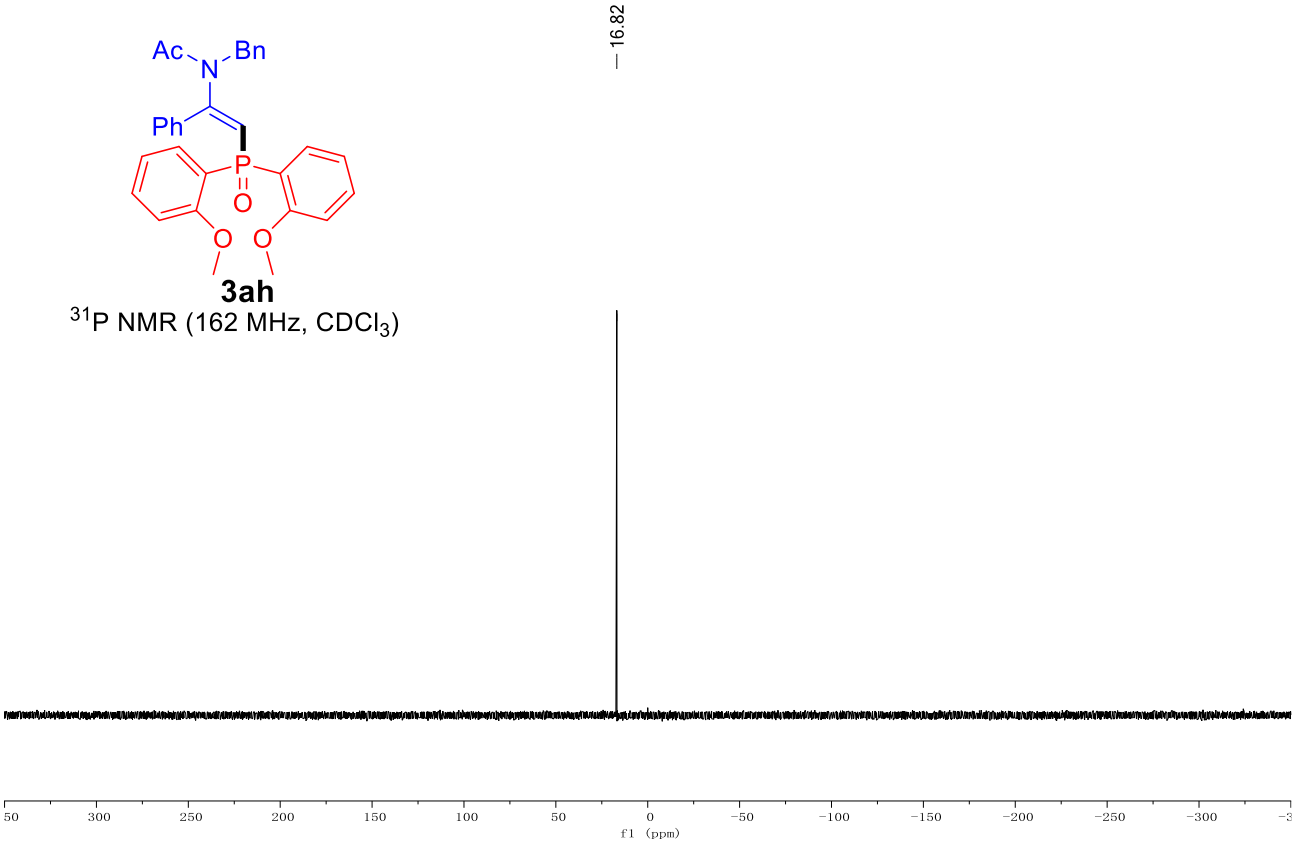




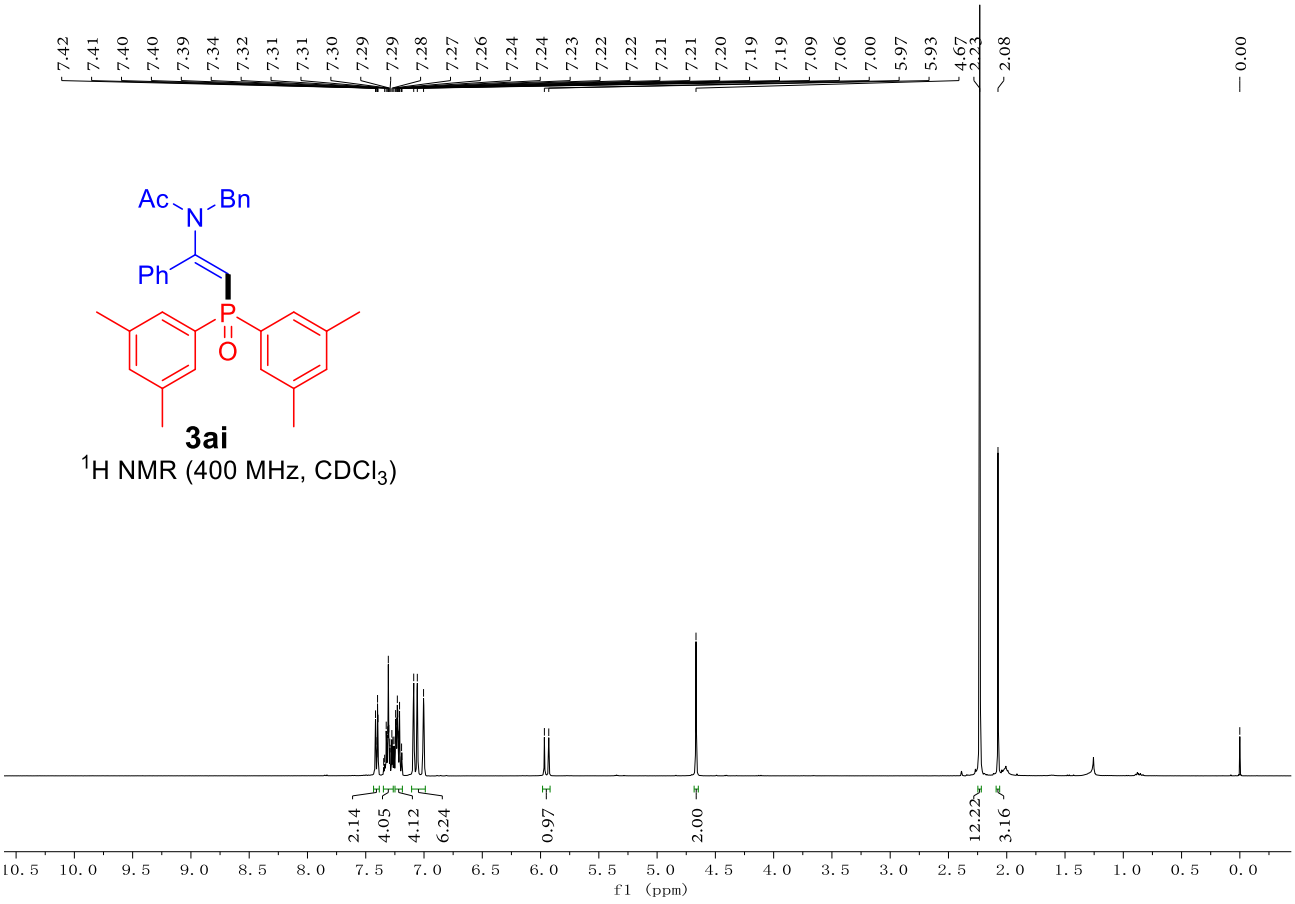


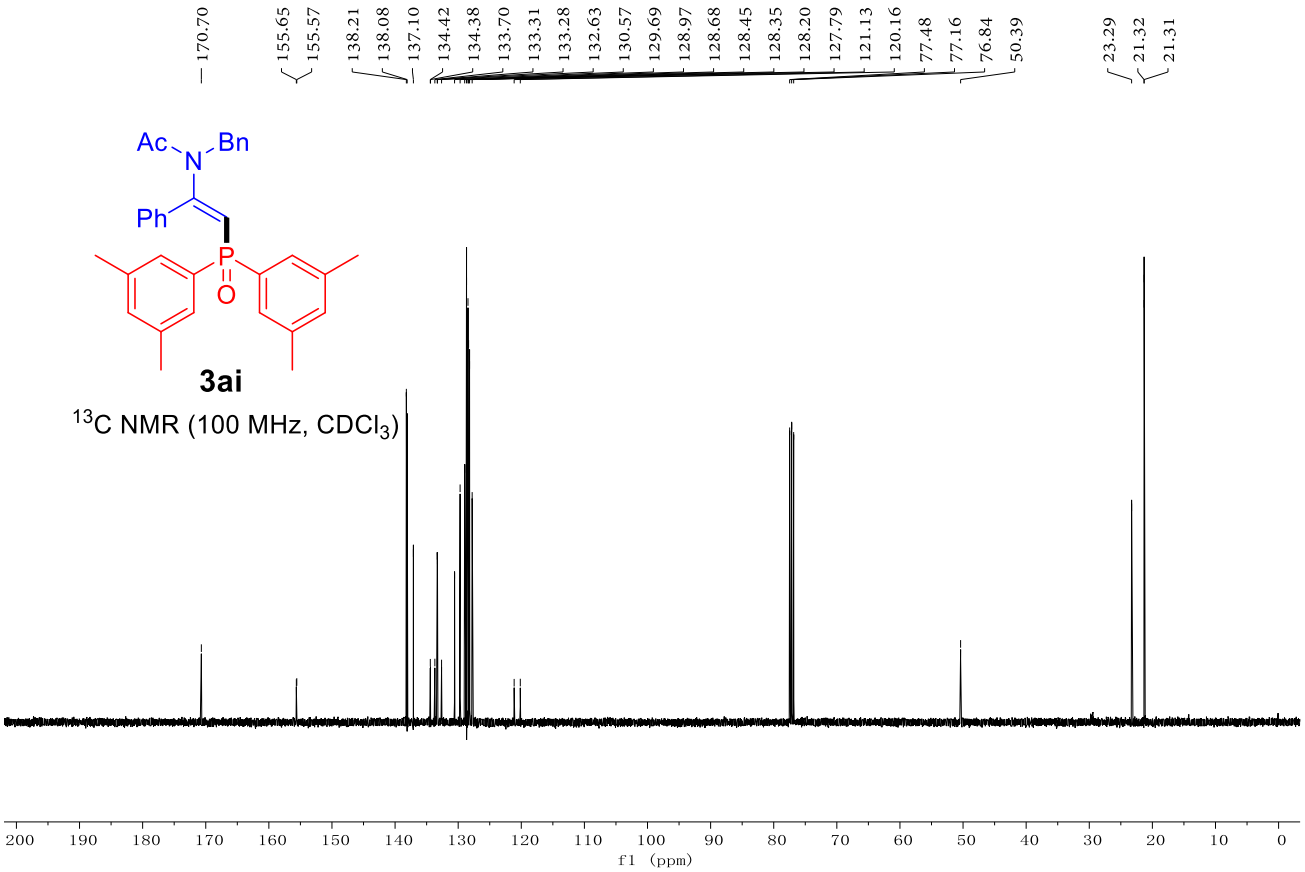
3ah

^{13}C NMR (100 MHz, $CDCl_3$)



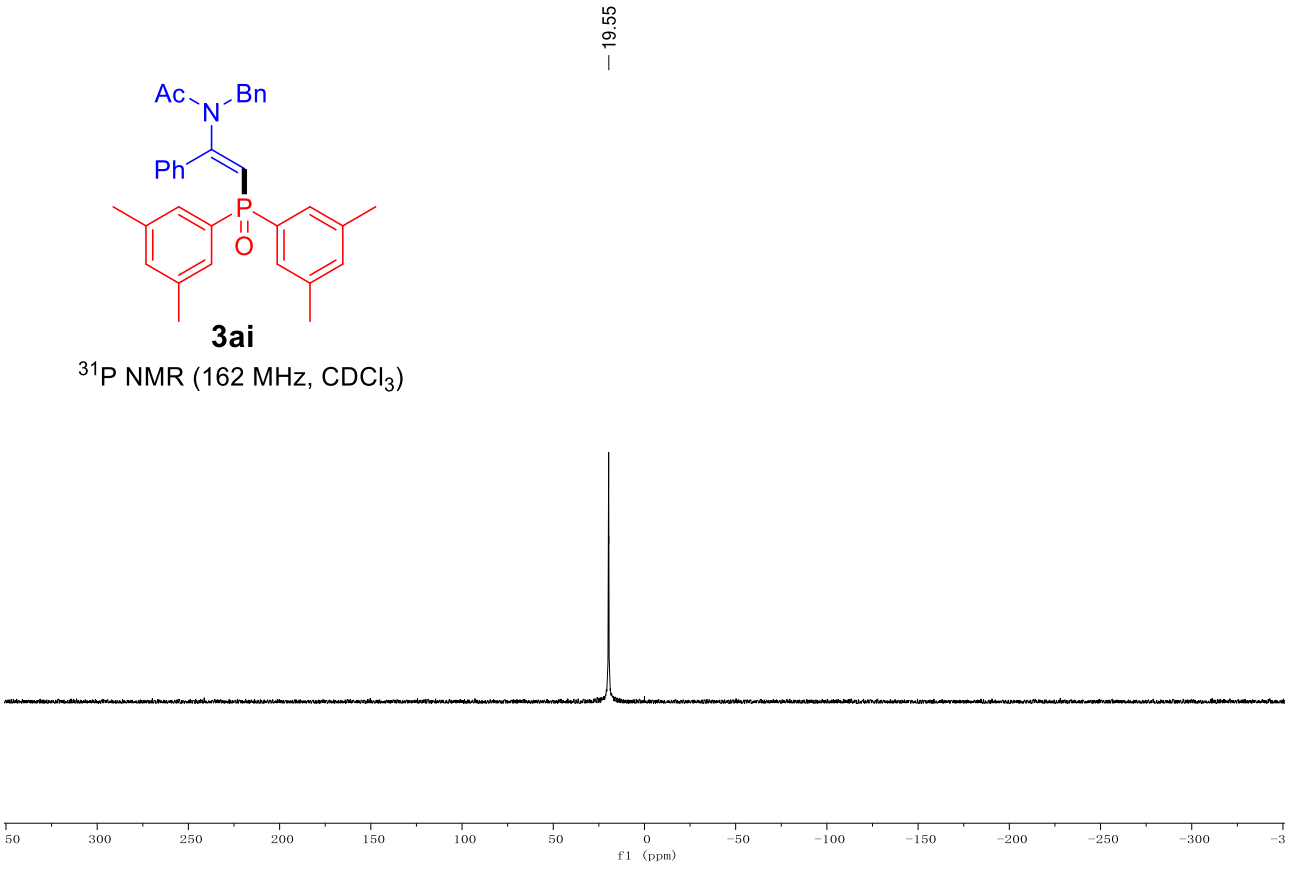
(E)-*N*-benzyl-*N*-(2-(bis(3,5-dimethylphenyl)phosphoryl)-1-phenylvinyl)acetamide (**3ai**)





3ai

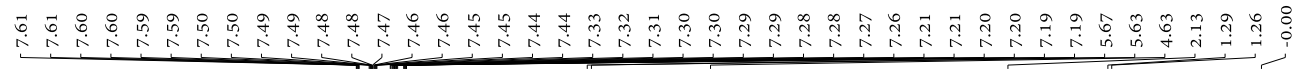
^{13}C NMR (100 MHz, $CDCl_3$)

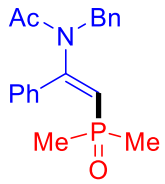


3ai

^{31}P NMR (162 MHz, $CDCl_3$)

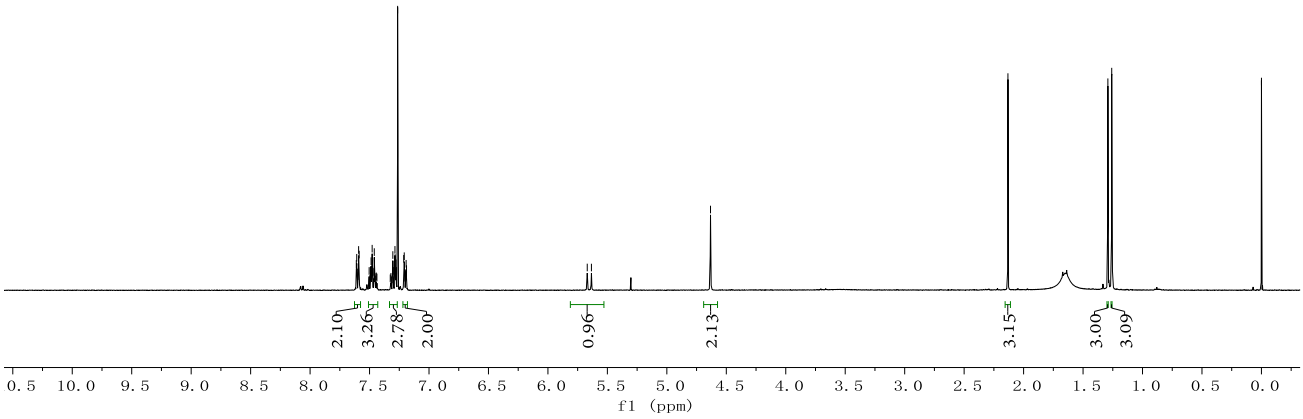
(E)-*N*-benzyl-*N*-(2-(dimethylphosphoryl)-1-phenylvinyl)acetamide (**3aj**)

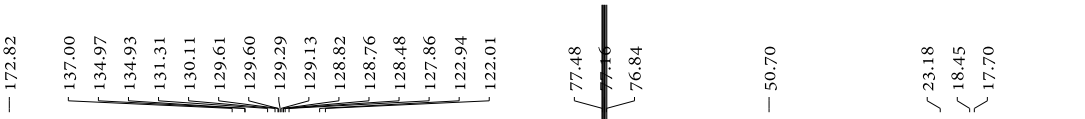


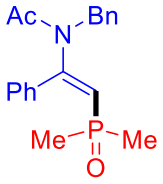


3aj

^{1}H NMR (400 MHz, $CDCl_3$)

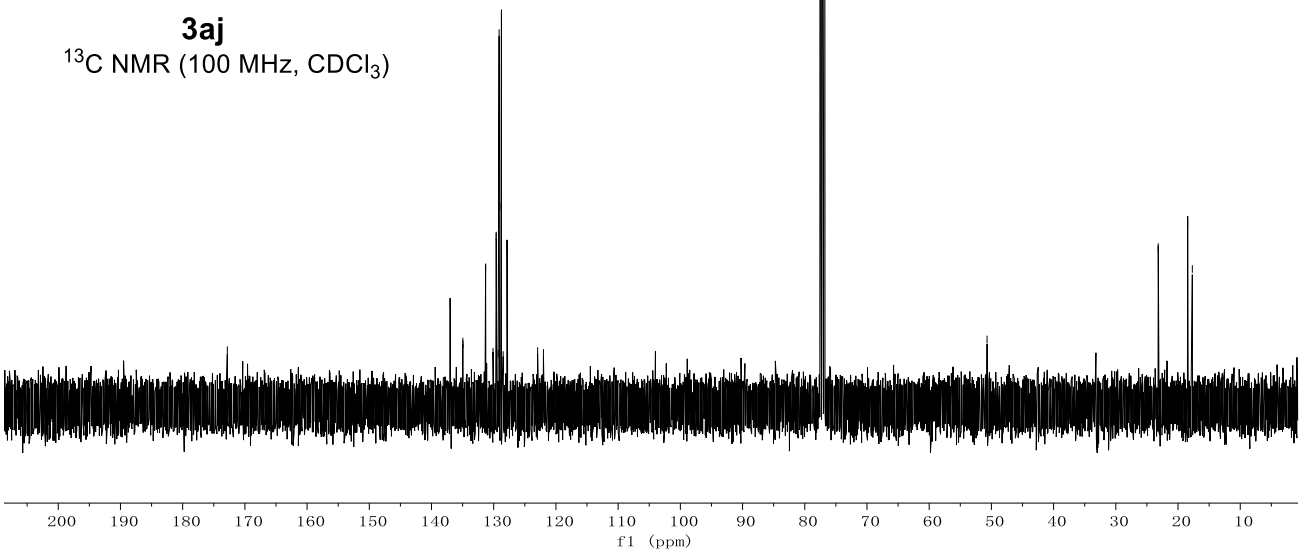


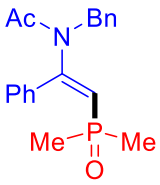




3aj

^{13}C NMR (100 MHz, $CDCl_3$)

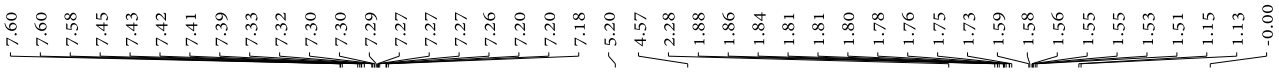


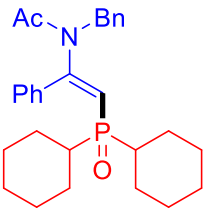


3aj

^{31}P NMR (162 MHz, $CDCl_3$)

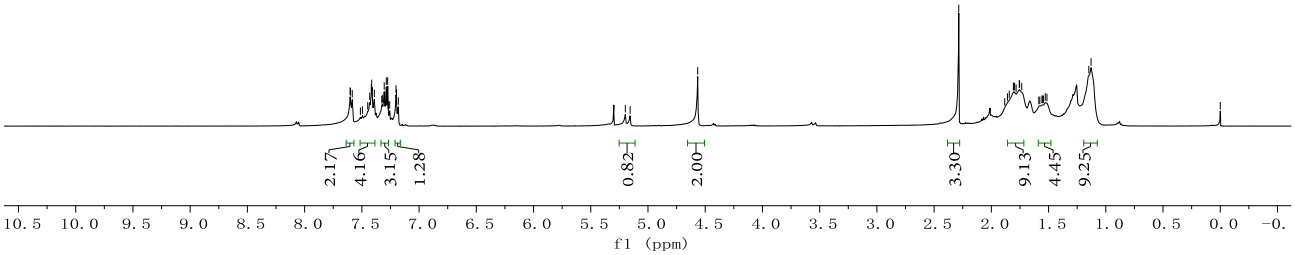
(E)-*N*-benzyl-*N*-(2-(dicyclohexylphosphoryl)-1-phenylvinyl)acetamide (**3ak**)

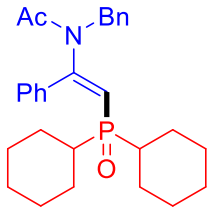




3ak

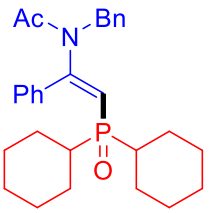
^{1}H NMR (400 MHz, $CDCl_3$)





3ak

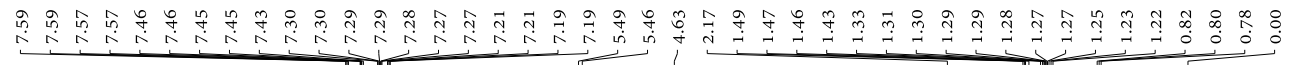
^{13}C NMR (100 MHz, $CDCl_3$)

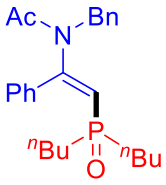


3ak

^{31}P NMR (162 MHz, $CDCl_3$)

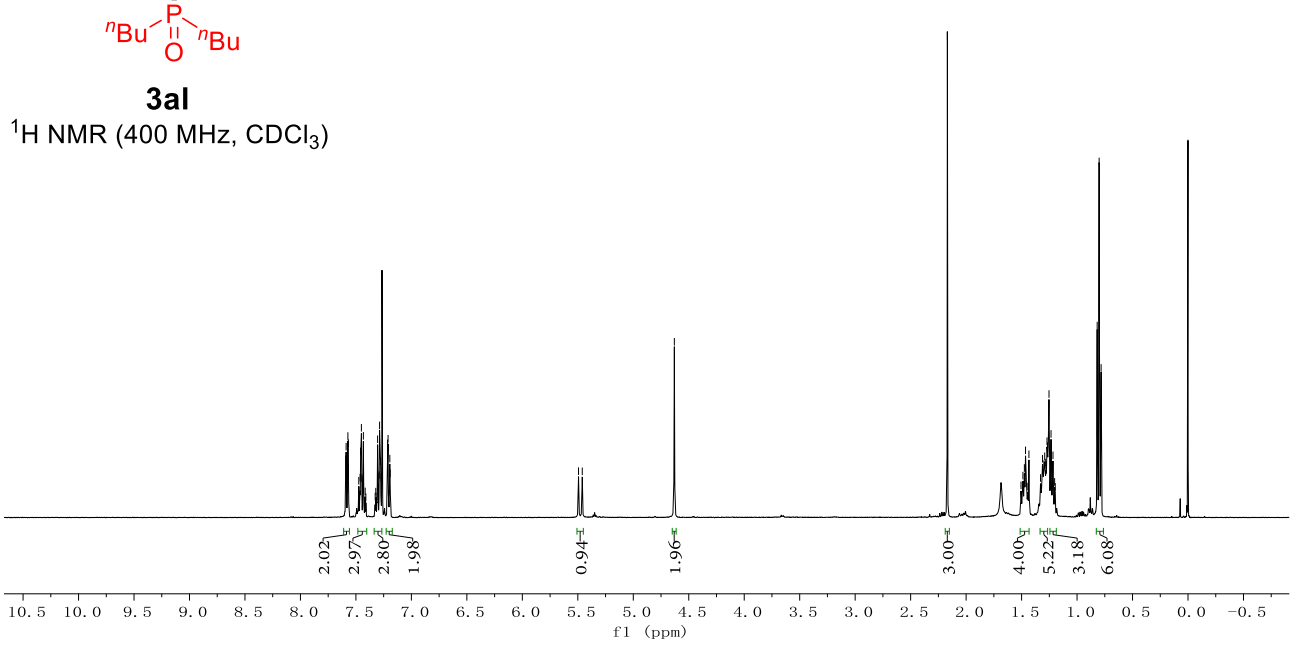
(E)-*N*-benzyl-*N*-(2-(dibutylphosphoryl)-1-phenylvinyl)acetamide (**3al**)

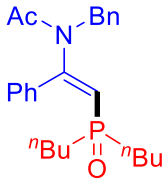




3al

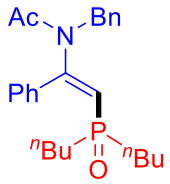
^{1}H NMR (400 MHz, $CDCl_3$)





3al

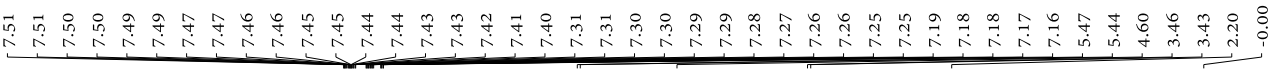
^{13}C NMR (100 MHz, $CDCl_3$)

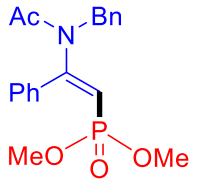


3al

^{31}P NMR (162 MHz, $CDCl_3$)

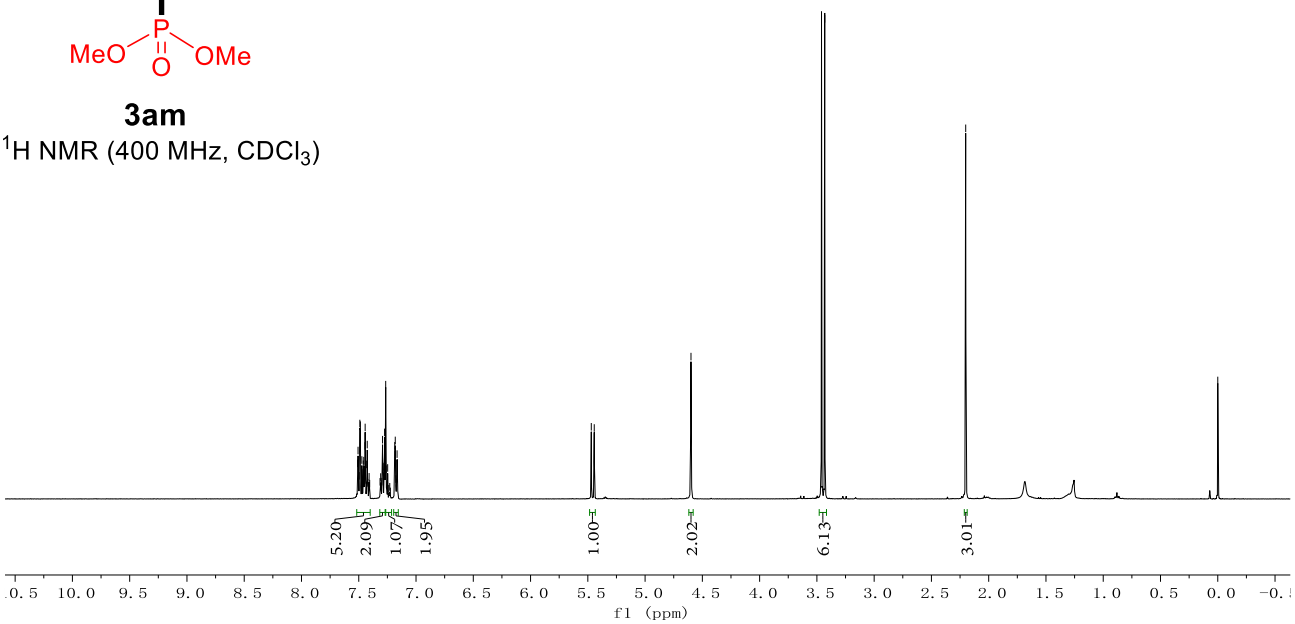
dimethyl *(E)*-(2-(N-benzylacetamido)-2-phenylvinyl)phosphonate (**3am**)

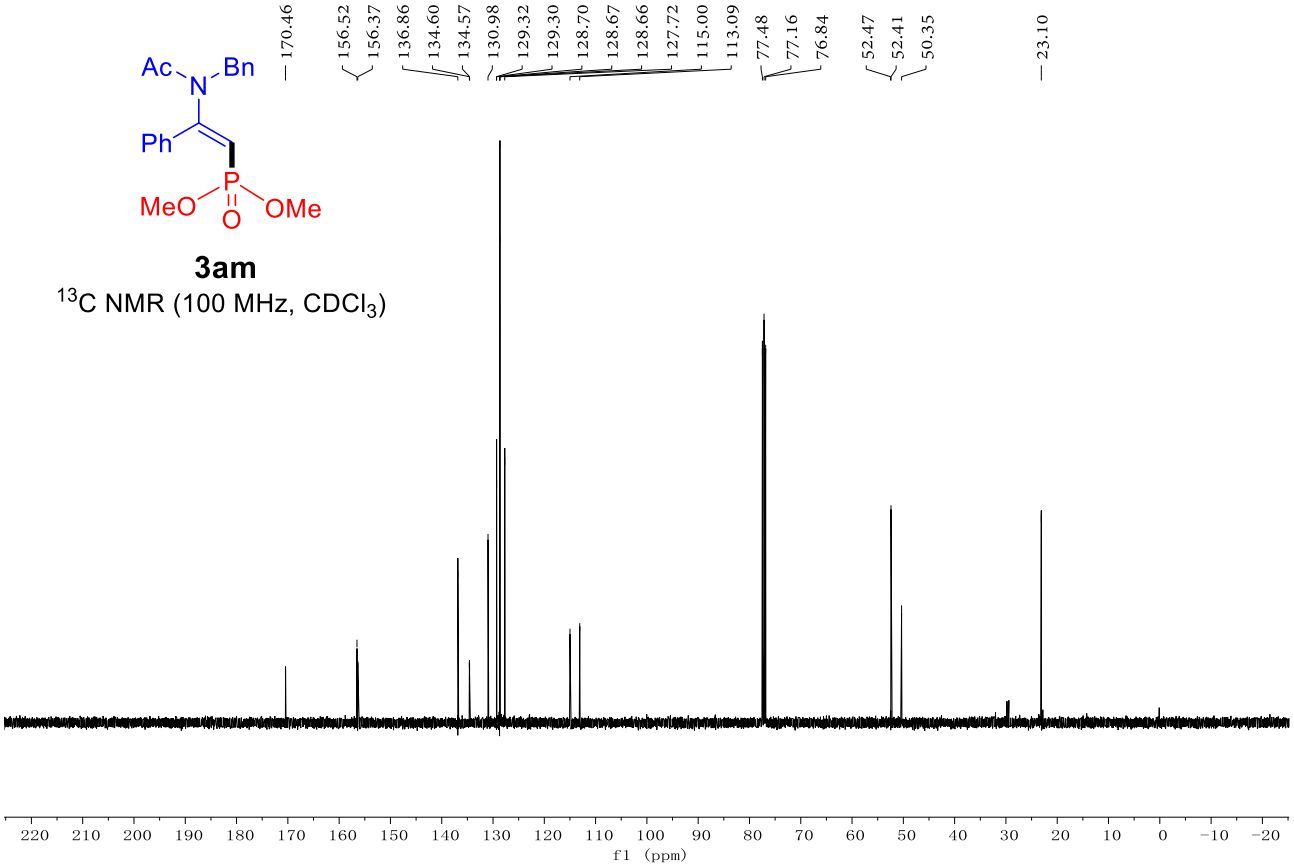




3am

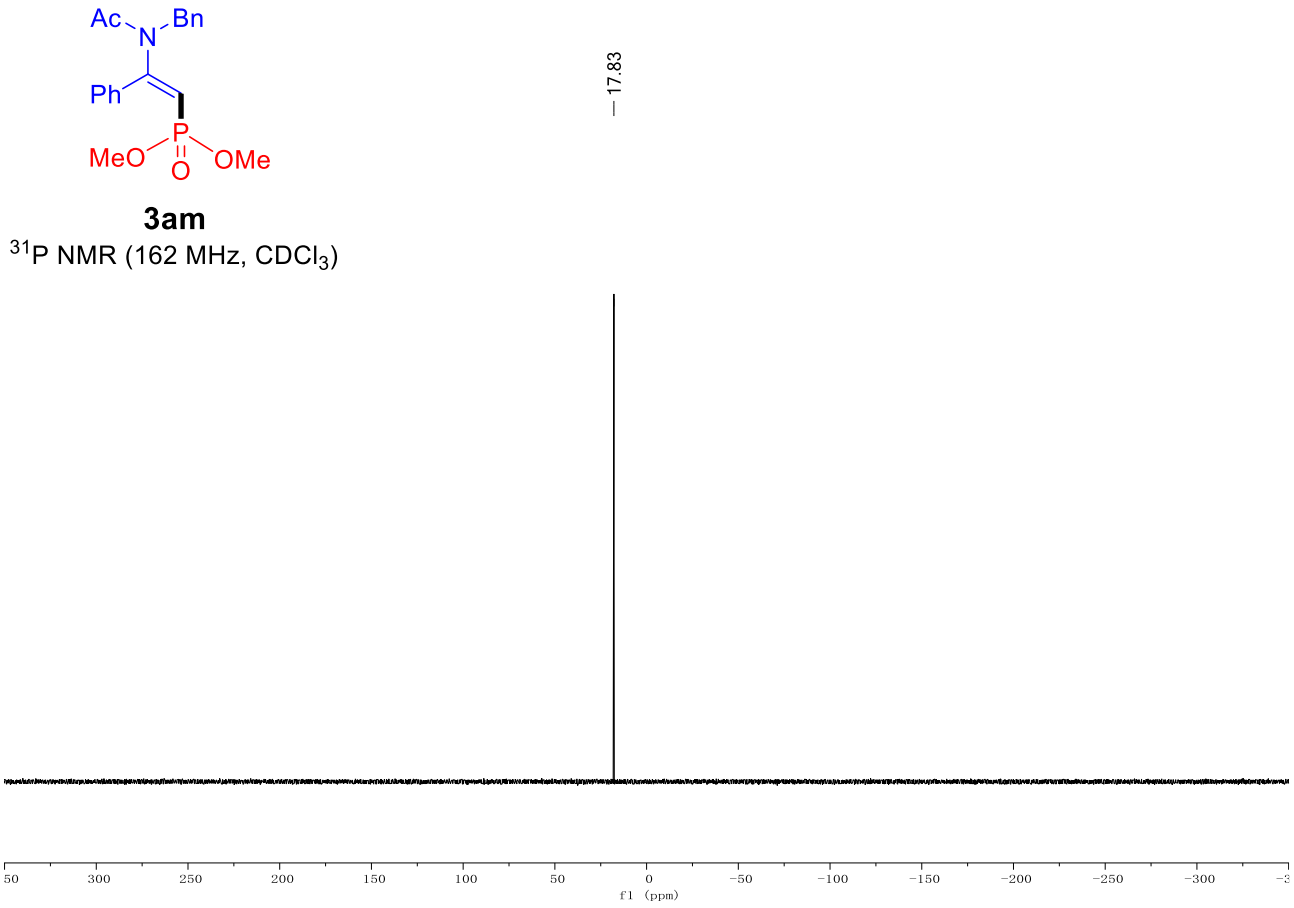
^{1}H NMR (400 MHz, $CDCl_3$)





3am

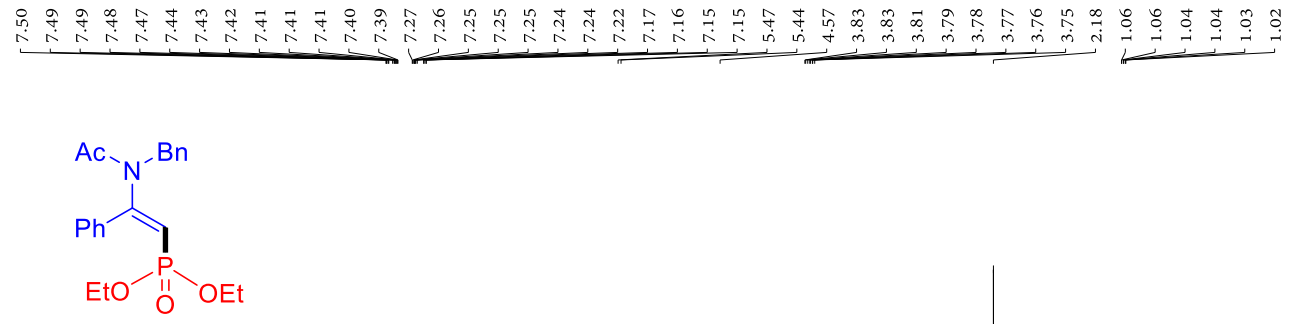
^{13}C NMR (100 MHz, $CDCl_3$)



3am

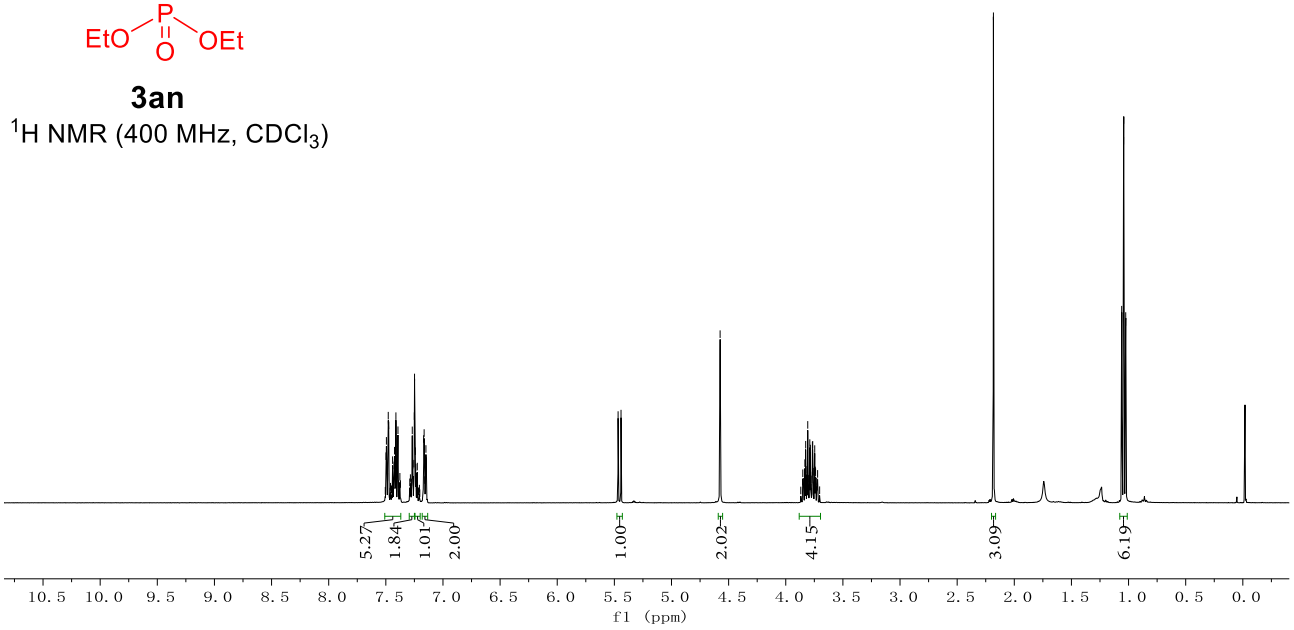
^{31}P NMR (162 MHz, $CDCl_3$)

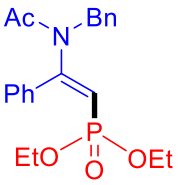
diethyl *(E)*-(2-(N-benzylacetamido)-2-phenylvinyl)phosphonate (**3an**)



3an

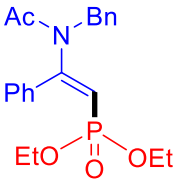
^{1}H NMR (400 MHz, $CDCl_3$)





3an

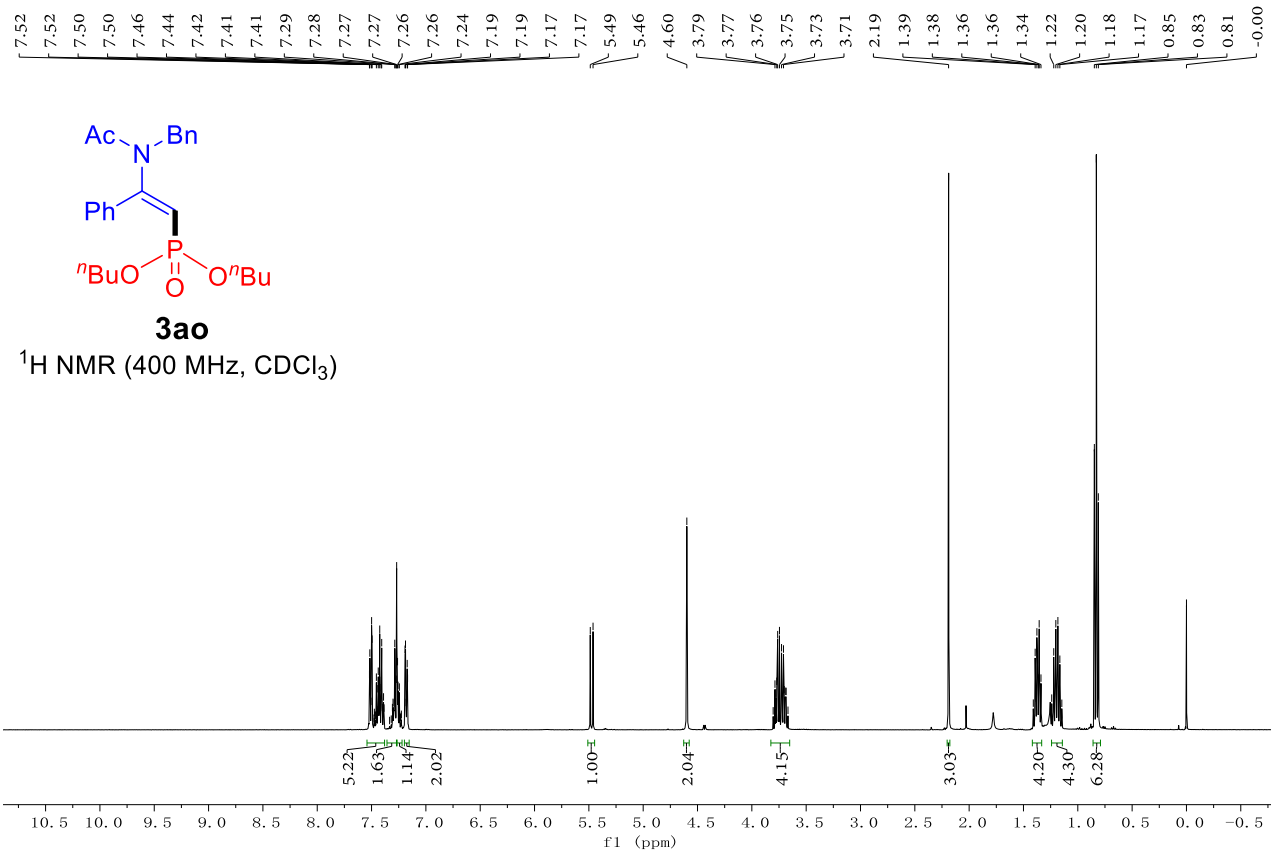
^{13}C NMR (100 MHz, $CDCl_3$)



3an

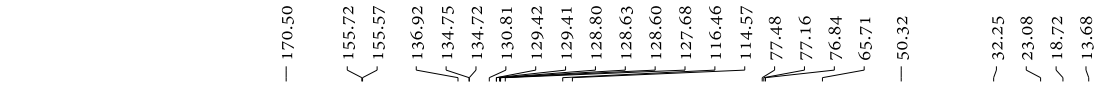
^{31}P NMR (162 MHz, $CDCl_3$)

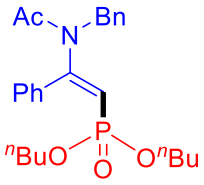
dibutyl *(E)*-(2-(*N*-benzylacetamido)-2-phenylvinyl)phosphonate (**3ao**)



3ao

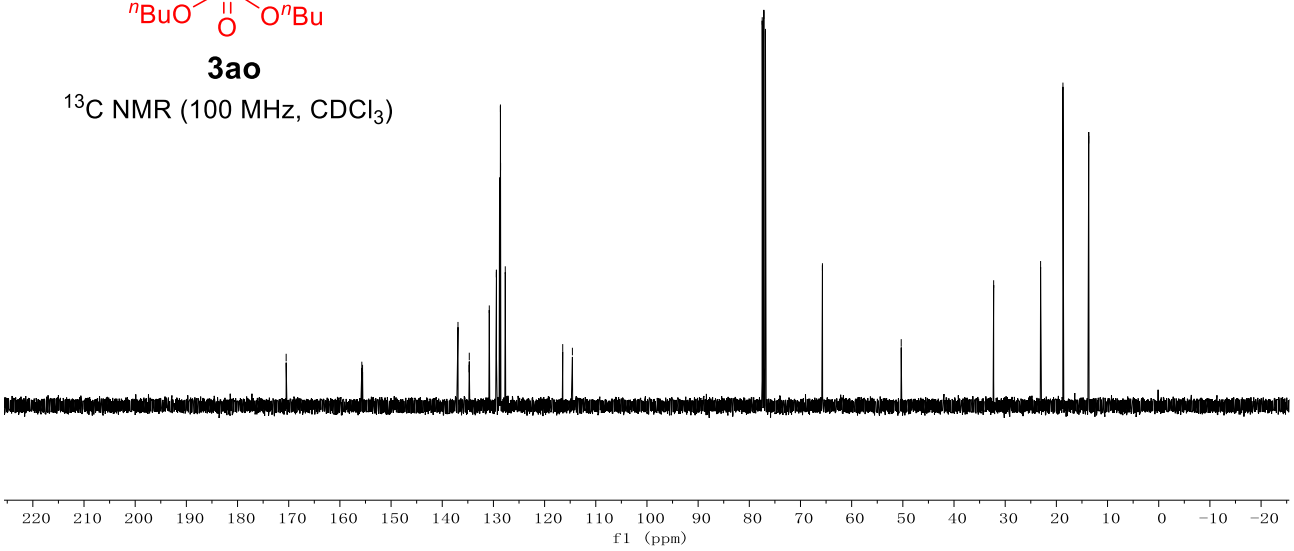
^{1}H NMR (400 MHz, $CDCl_3$)

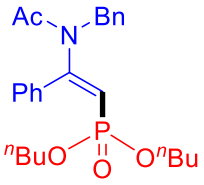




3ao

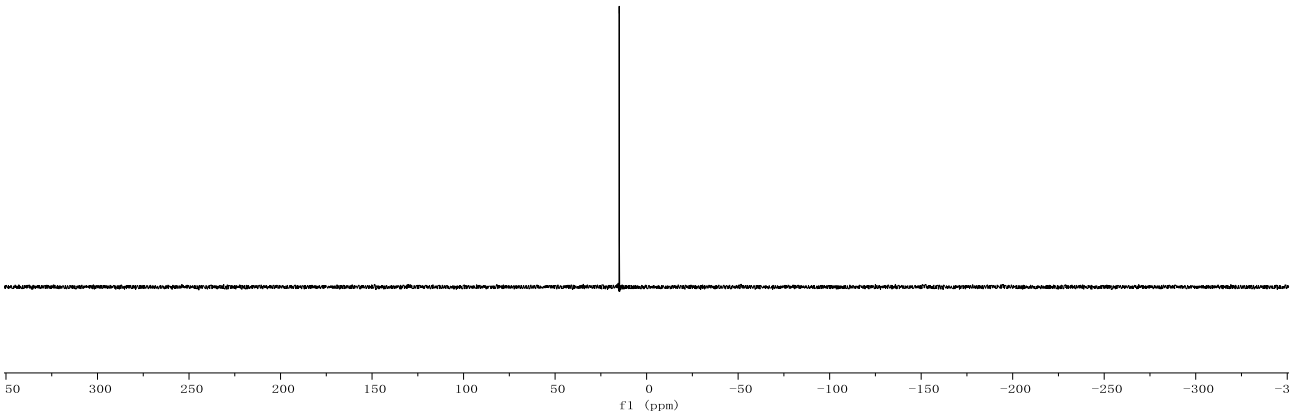
^{13}C NMR (100 MHz, $CDCl_3$)



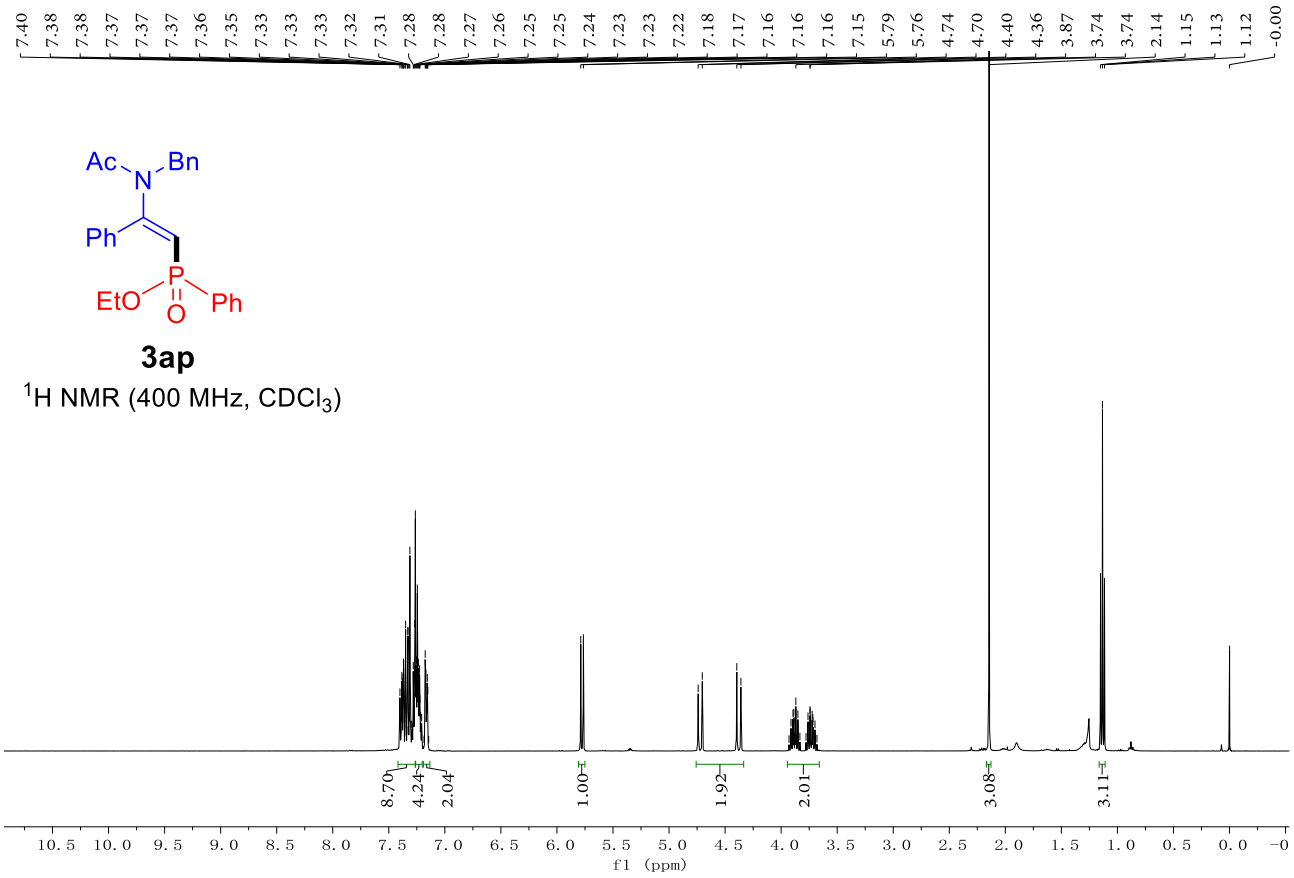


3ao

^{31}P NMR (162 MHz, $CDCl_3$)

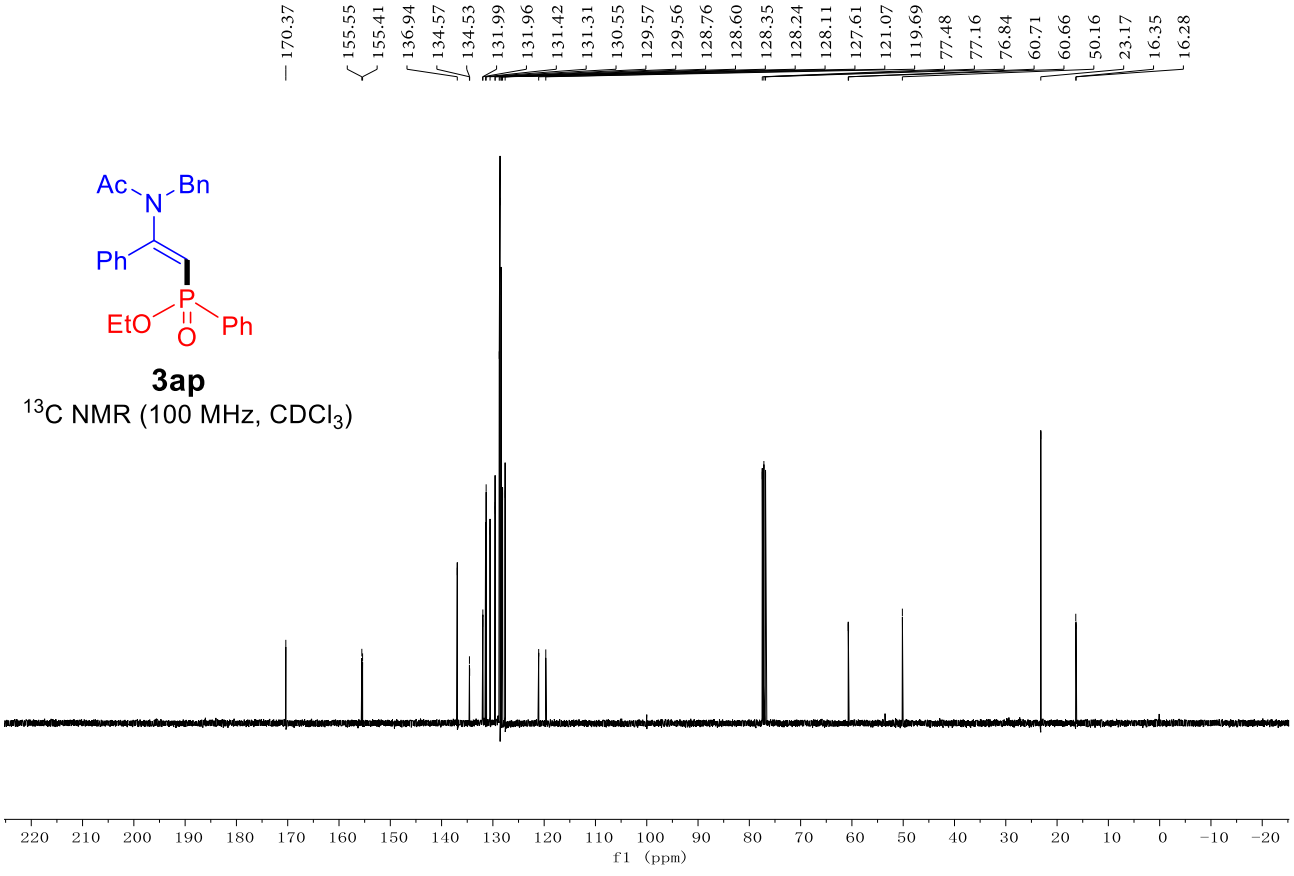


ethyl *(E)*-(2-(*N*-benzylacetamido)-2-phenylvinyl)(phenyl)phosphinate (**3ap**)



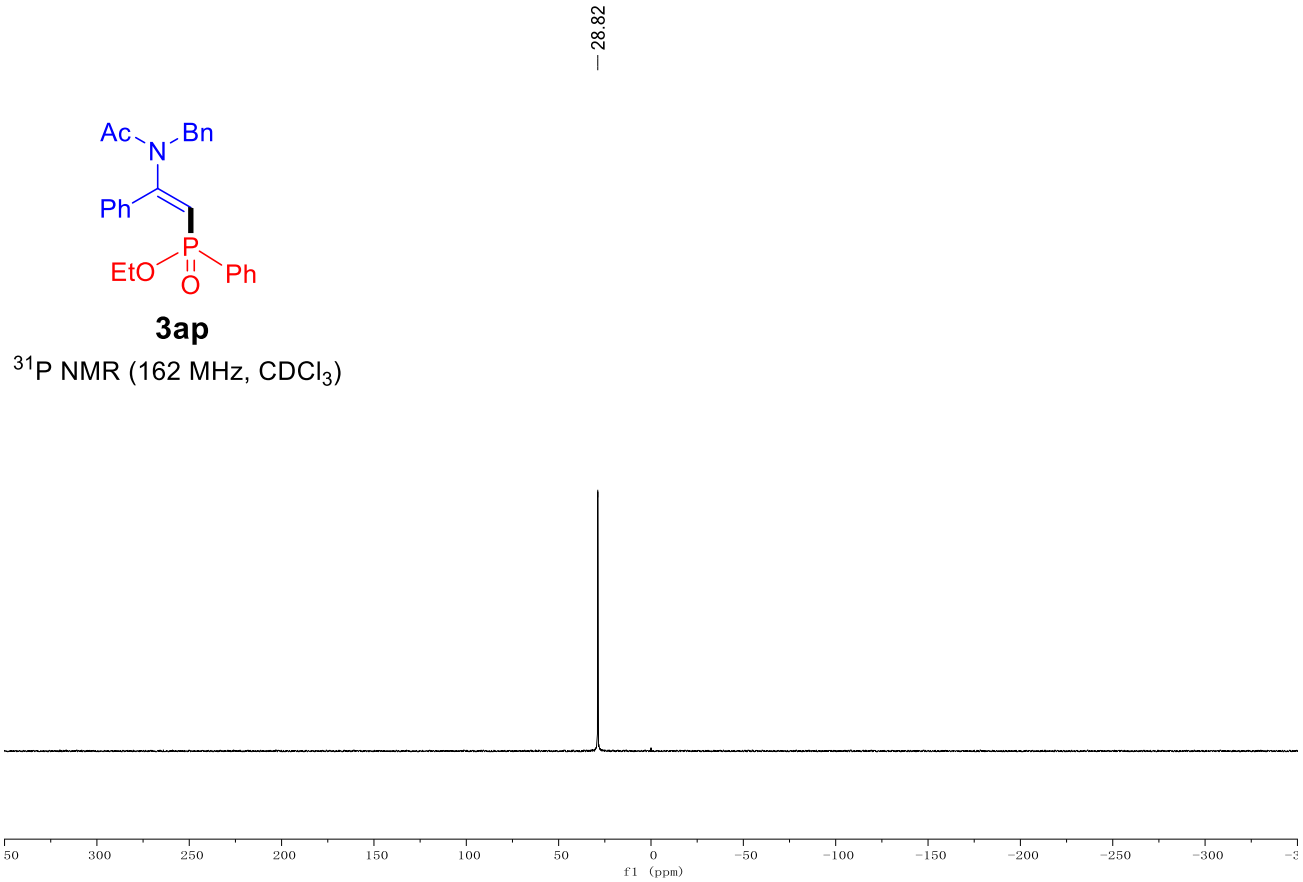
3ap

^{1}H NMR (400 MHz, $CDCl_3$)



3ap

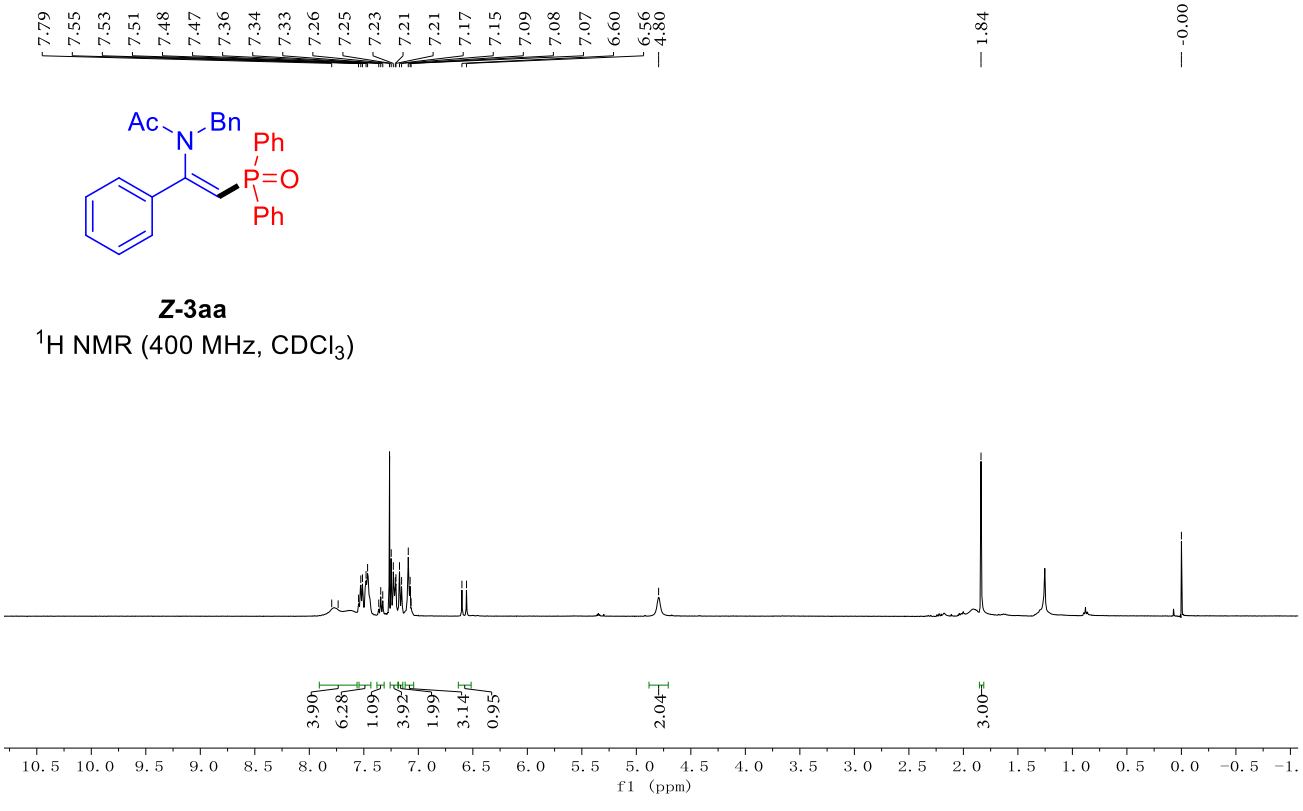
^{13}C NMR (100 MHz, $CDCl_3$)



3ap

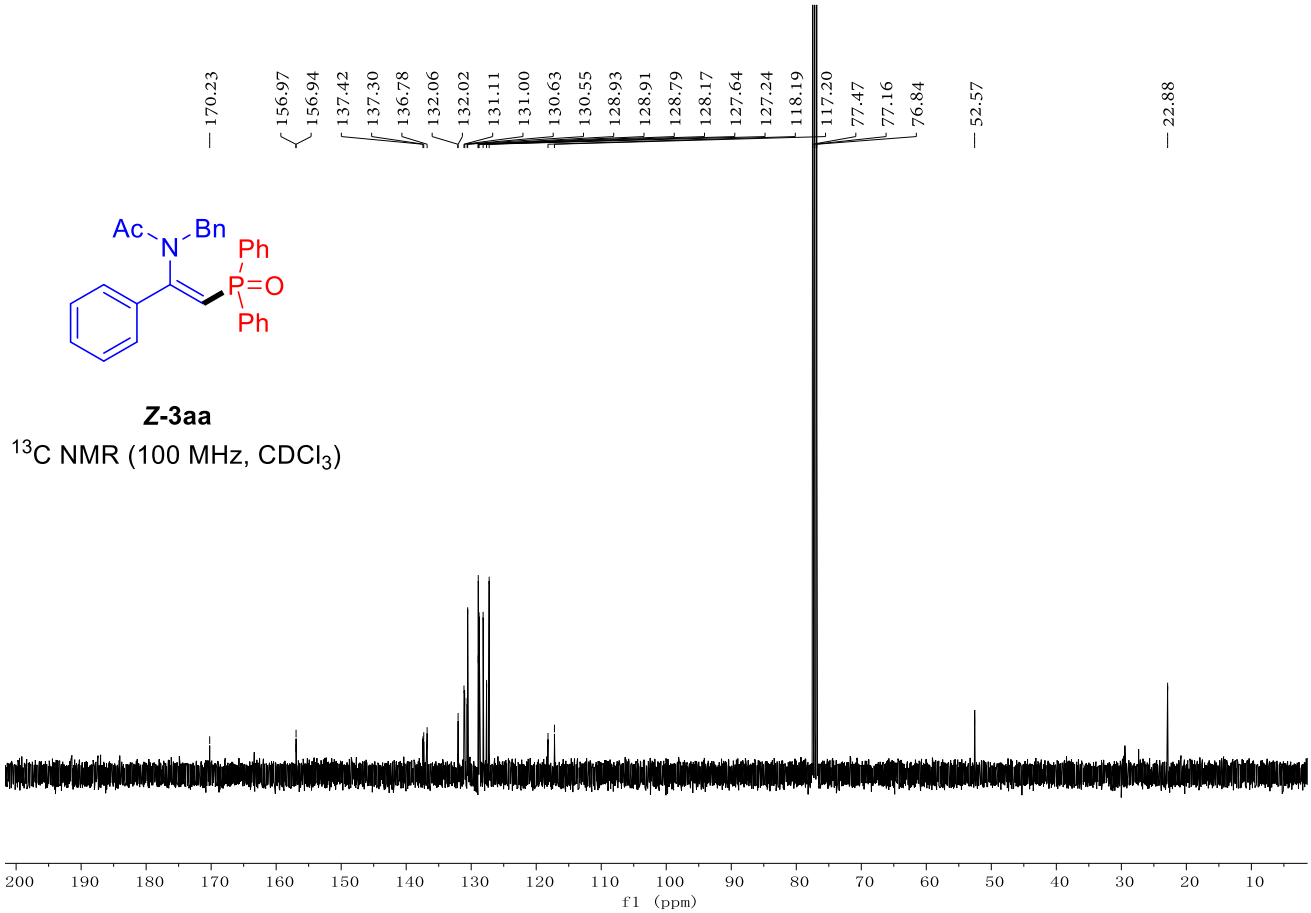
^{31}P NMR (162 MHz, $CDCl_3$)

(Z)-*N*-benzyl-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (***Z*-3aa**)



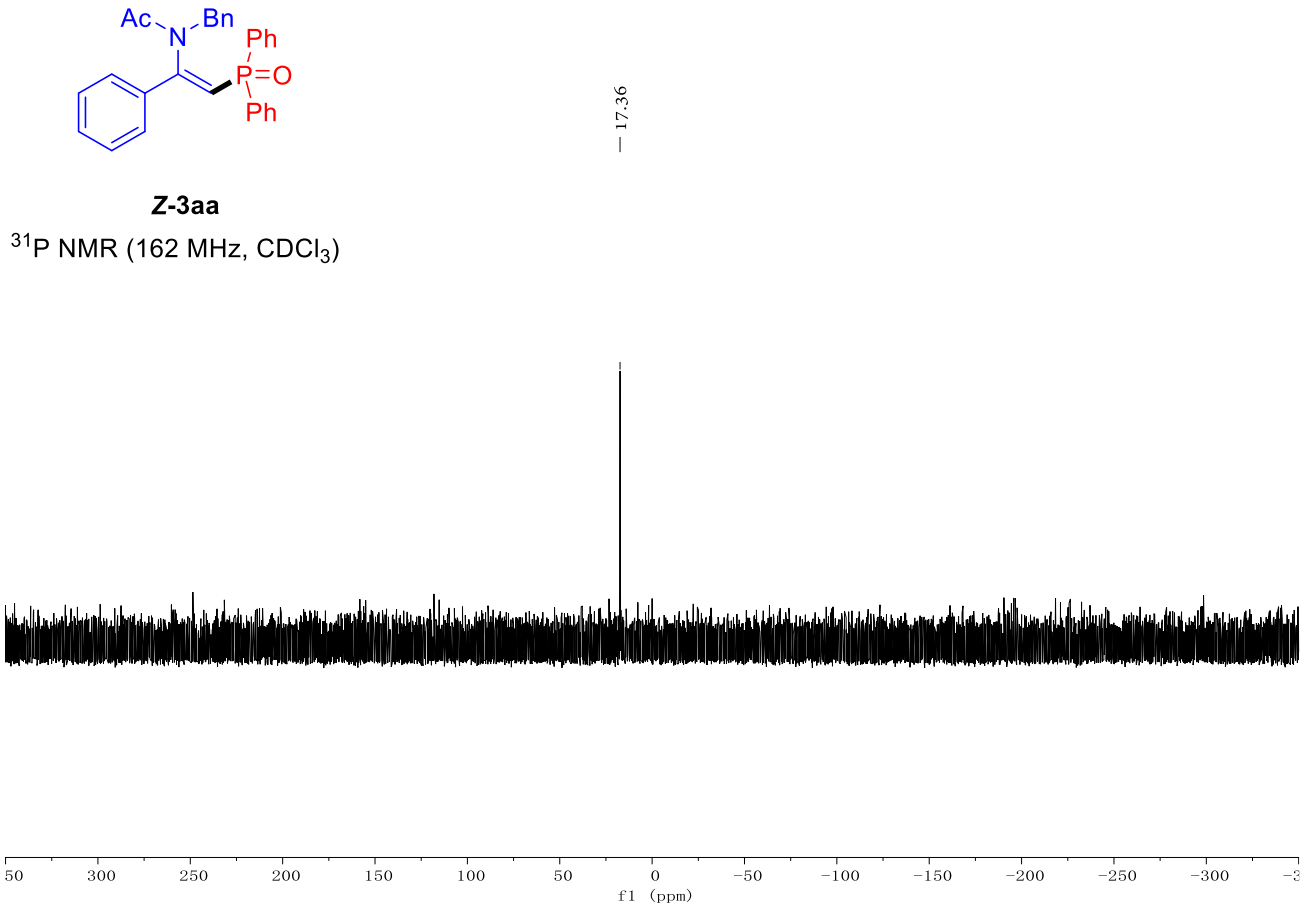
***Z*-3aa**

^{1}H NMR (400 MHz, $CDCl_3$)



***Z*-3aa**

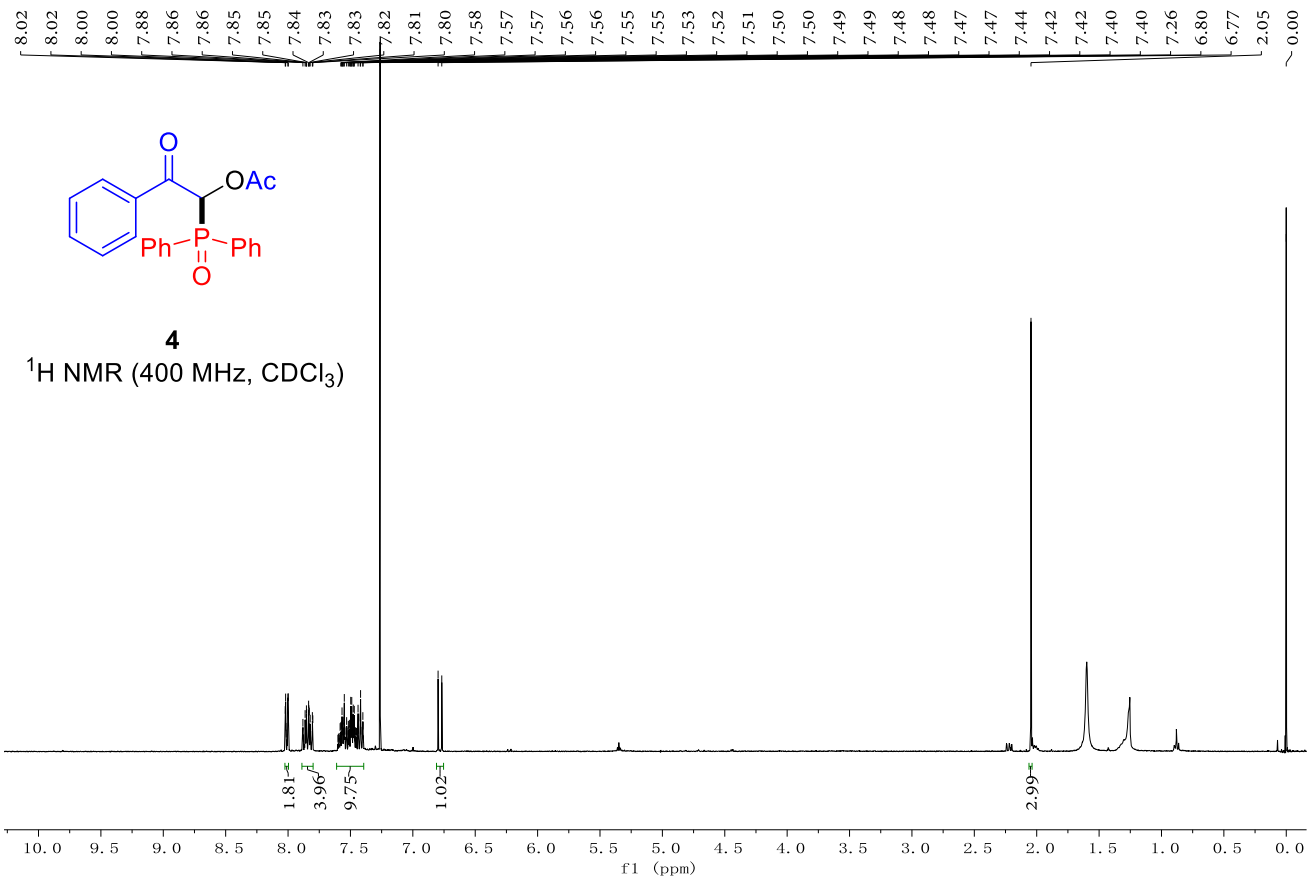
^{13}C NMR (100 MHz, $CDCl_3$)

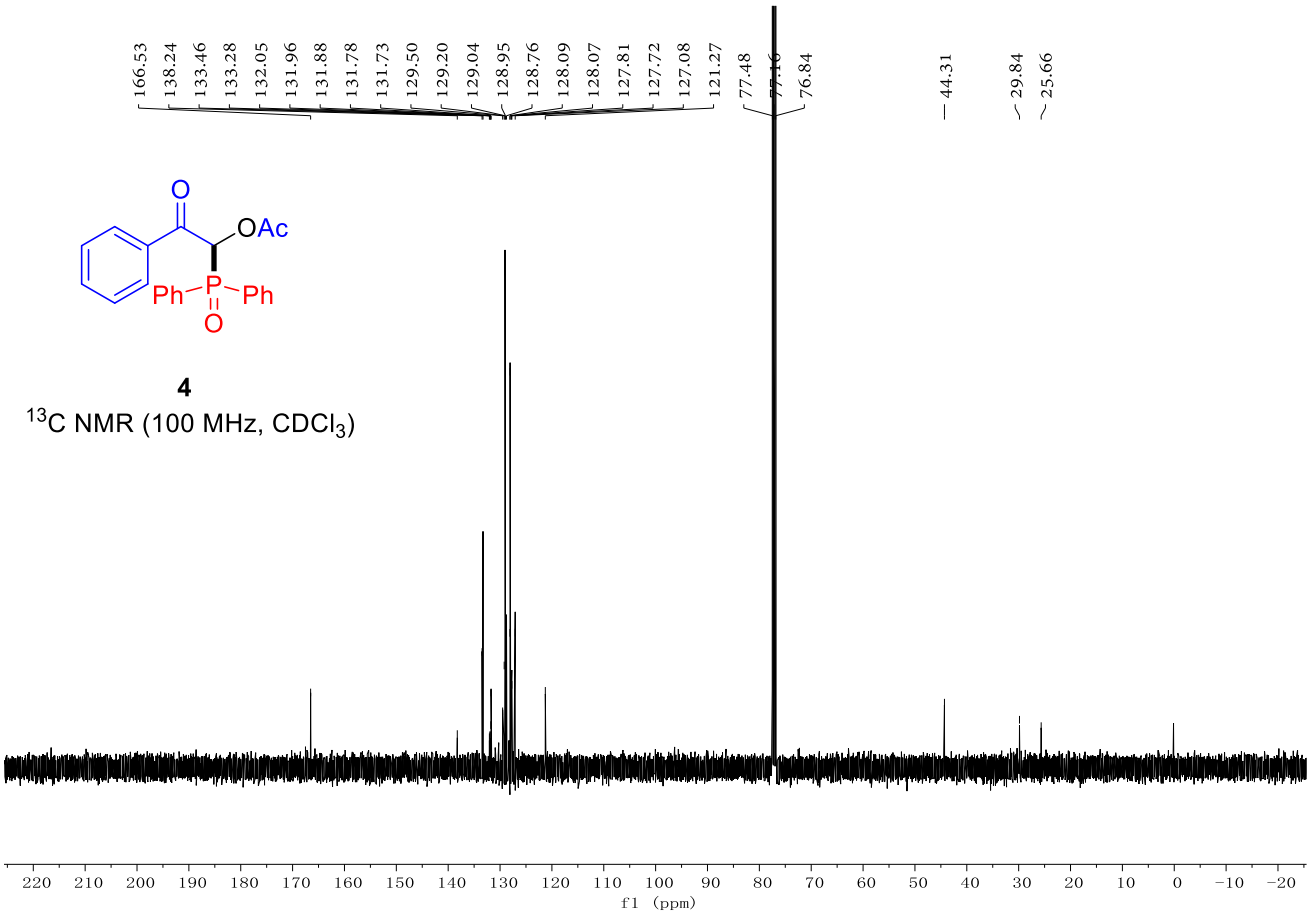


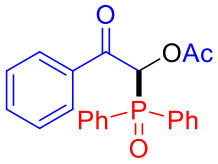
***Z*-3aa**

^{31}P NMR (162 MHz, $CDCl_3$)

1-(diphenylphosphoryl)-2-oxo-2-phenylethyl acetate (**4**)



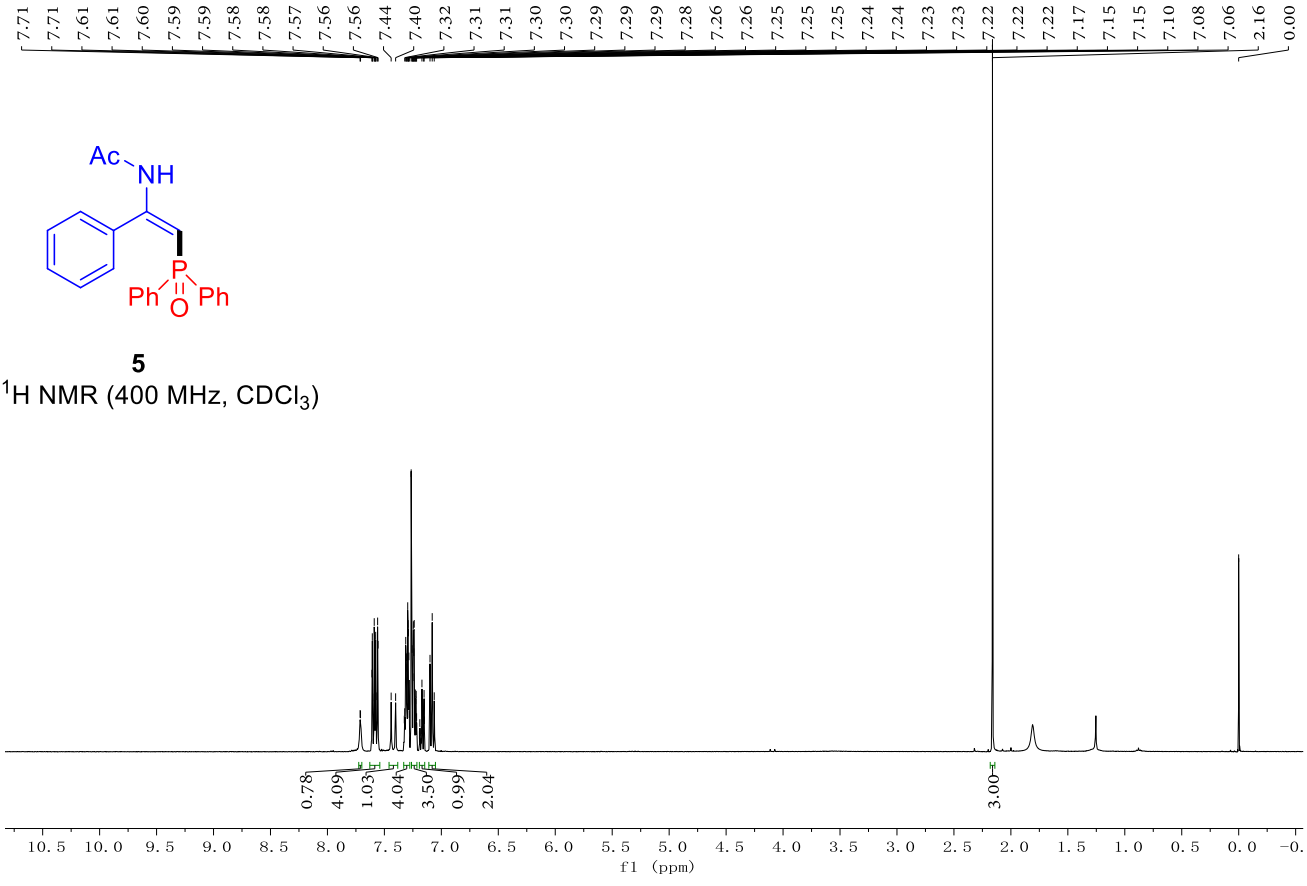




4

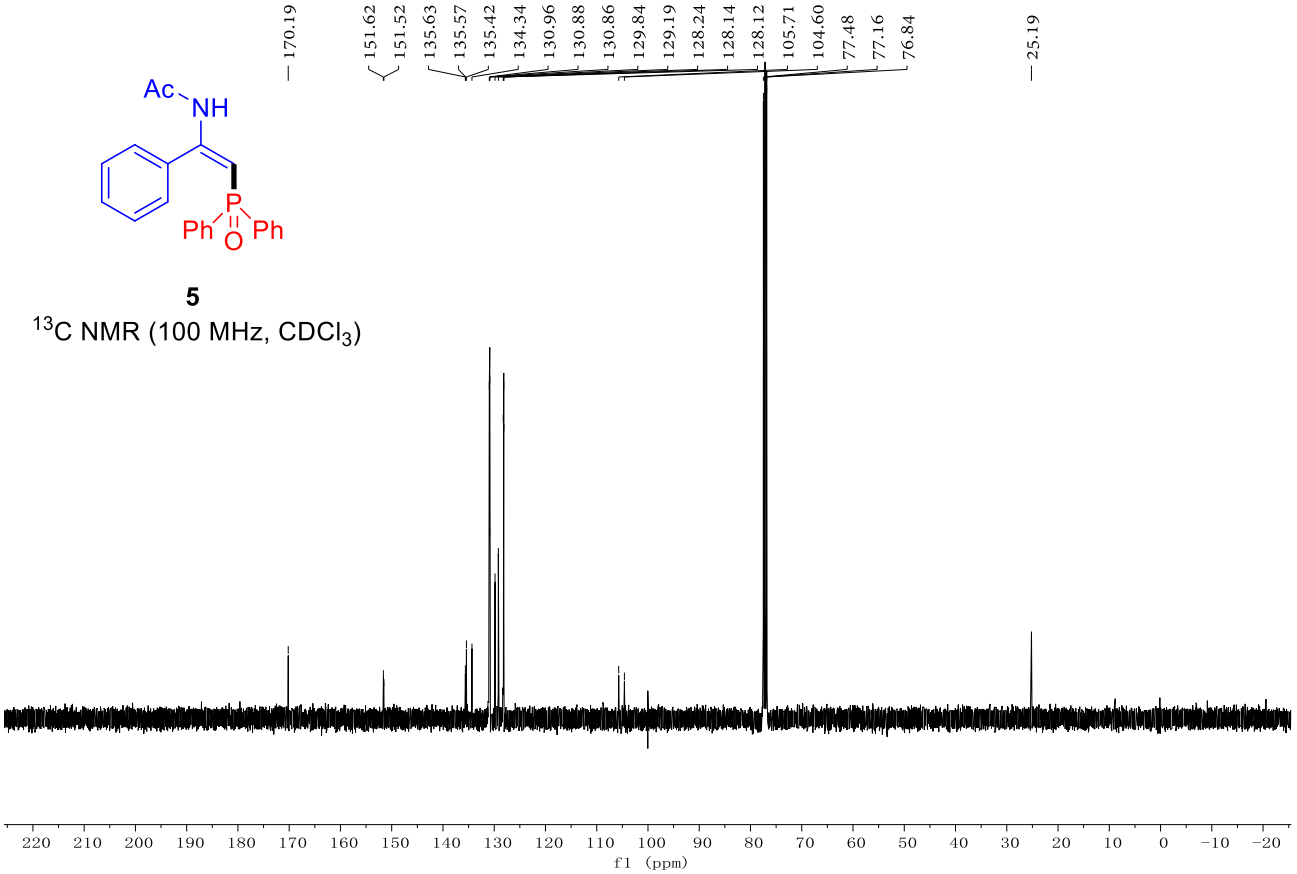
^{31}P NMR (162 MHz, $CDCl_3$)

(E)-*N*-(2-(diphenylphosphoryl)-1-phenylvinyl)acetamide (**5**)



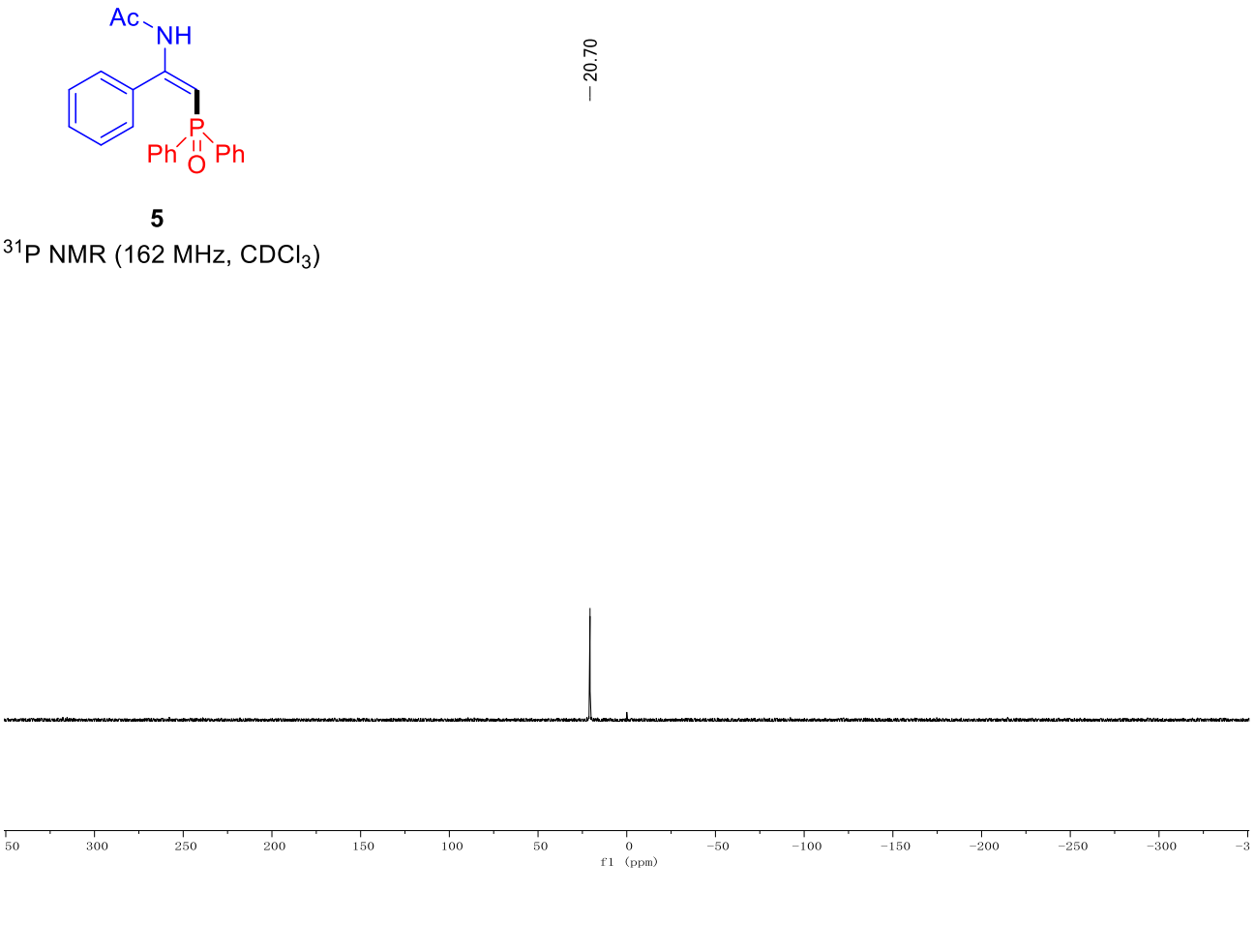
5

^{1}H NMR (400 MHz, $CDCl_3$)



5

^{13}C NMR (100 MHz, $CDCl_3$)



5

^{31}P NMR (162 MHz, $CDCl_3$)