Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Material for

Palladium-Catalyzed Asymmetric Allylic Amination: Synthesis of chiral β-aminophosphonic acids derivatives

Xubin Wang, Xiaoming Wang, Zhaobin Han, Zheng Wang, Kuiling Ding*

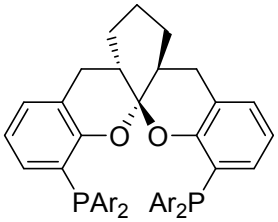
State Key Laboratory of Oganometallic Chemistry, Shanghai Institute of Organic Chemistry,

Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China.

kding@mail.sioc.ac.cn

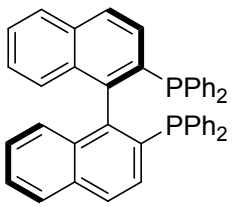
1. General

Unless otherwise noted, all reactions and manipulations involving air- and moisture-sensitive compounds were performed using standard Schlenk techniques. CH_2Cl_2, CH_3CN and THF were purified and dried using standard procedures. Melting points were measured on a RY-I apparatus and uncorrected. ^1H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on Varian Mercury 400 MHz or Agilent Technologies 400/54 premium shilded spectrometers. Chemical shifts (δ values) were reported in ppm downfield from internal TMS for ^1H NMR, $CDCl_3$ or CD_3OD for ^{13}C NMR, external 85% H_3PO_4 for ^{31}P NMR, and external CF_3CO_2H for ^{19}F NMR, respectively. Optical rotations were determined using Rudolph Autopol I polarimeter or JASCO P-1030 Polarimeter. The IR spectra were measured on a BRUKER TENSOR 27 FT-IR spectrometer. ESI-MS spectra were obtained on a Shimadzu LCMS-2010EV spectrometer. HRMS(ESI) were determined on Bruker APEXIII 7.0 TESLA FTMS spectrometer. HPLC analyses were performed on a JASCO 2089 liquid chromatograph. The chiral spiroketal-based diphosphine ligands (SKP) (*S*, *S*, *S*)-**1a**-**1e** were prepared by following our previously reported procedures,[1] while ligands **1f** [(*R*)-BINAP], **1g** [(*R*)-SDP] and **1h** [(*R*,*R*)-Trost ligand] were purchased from commercial sources and were used without further purification.

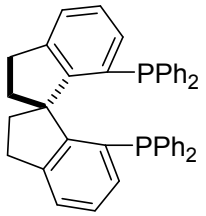


(*S,S,S*)-**1a-e**

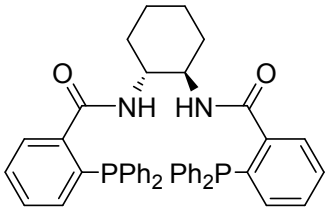
1a: Ar = C_6H_5
1b: Ar = 2-MeC_6H_4
1c: Ar = 3,5-$(Me)_2C_6H_3$
1d: Ar = 4-MeC_6H_4
1e: Ar = 4-$MeOC_6H_4$



1f
(*R*)-BINAP

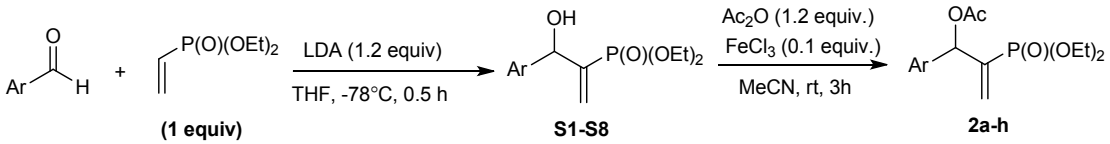


1g
(*R*)-SDP



1h
(*R,R*)-Trost ligand

1. Preparation of 2-(diethoxyphosphoryl)-1-arylallyl acetates 2a-2h



(1 equiv) **S1-S8** **2a-h**

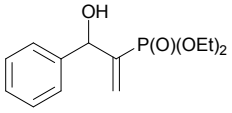
The allylic substrates for the amination reaction, 2-(diethoxyphosphoryl)-1-

arylallyl acetates **2a**-**2h**, were synthesized by acetylation of the Morita-Baylis-Hillman (MBH) adducts **S1**-**S8**, which were in turn prepared by the reaction of aromatic aldehydes with diethyl vinylphosphonate in the presence of LDA.

1.1. General procedure for the preparation of the MBH adducts S1-S8

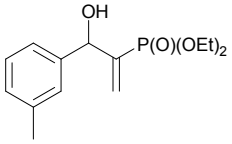
The MBH adducts **S1**-**S8** were prepared by following a literature procedure.[2] To a solution of the aromatic aldehyde (32.5 mmol) and diethyl vinylphosphonate (5.0 mL, 32.5 mmol) in THF (10 mL) was added dropwise a solution of LDA in THF (2.0 M, 19.5 mL, 39.0 mmmol) at -78°C. After stirring the mixture for 0.5 h under -78°C, the reaction was quenched with distilled water (10 mL), and the resulting mixture was extracted with CH_2Cl_2 (20 mL × 3). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and the solvent was evaporated in vacuo. Purification of the residue by flash chromatography [SiO_2: EtOAc/petroleum ether (1/5-2/1)] to yield the product.

Diethyl (3-hydroxy-3-phenylprop-1-en-2-yl)phosphonate (S1)[3]



Colorless oil, 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 5H), 6.10 (ddd, *J* = 46.2, 1.6, 1.6 Hz, 1H), 6.08 (ddd, *J* = 22.4, 1.6, 0.8 Hz, 1H), 5,41 (d, *J* = 10.4 Hz, 1H), 4.51 (*br* s, 1H), 3.93-3.79 (m, 3H), 3.65-3.59 (m, 1H), 1.19 (t, *J* = 6.8 Hz, 3H), 1.04 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (d, $J_{(P, C)}$ = 170.2 Hz), 141.1(d, $J_{(P, C)}$ = 3.5 Hz), 129.3 (d, $J_{(P, C)}$ = 7.1 Hz), 127.8, 127.3, 126.7, 73.2 (d, $J_{(P, C)}$ = 16.1 Hz), 61.7 (d, $J_{(P, C)}$ = 5.7 Hz), 61.6 (d, $J_{(P, C)}$ = 5.1 Hz), 15.9 (d, $J_{(P, C)}$ = 6.8 Hz), 15.6 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.3 ppm; IR (neat) ν 3556, 2983, 1453, 1392, 1226, 1195, 1179, 1016, 963, 799, 765, 698, 638 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{13}H_{19}NaO_4P^+$: 293.0913, Found: 293.0911 $[M+Na]^+$.

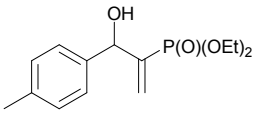
Diethyl (3-hydroxy-3-(*m-tolyl*)prop-1-en-2-yl)phosphonate (S2)



Light yellow oil, 42.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.13 (m, 3H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.08 (d, *J* = 21.6 Hz, 1H), 6.05 (d, *J* = 47.2 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), 4.16 (*br* s, 1H), 4.00-3.82 (m, 3H), 3.72-3.64 (m, 1H), 2.32 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7 (d, $J_{(P, C)}$ = 170.1 Hz), 140.8 (d, $J_{(P, C)}$ = 4.0 Hz), 137.5, 129.4 (d, $J_{(P, C)}$ = 6.9 Hz), 128.2, 127.9, 127.3, 123.8, 73.4 (d, $J_{(P, C)}$ = 15.1 Hz), 61.8 (d, $J_{(P, C)}$ = 5.6 Hz), 61.7 (d, $J_{(P, C)}$ = 5.7 Hz), 21.2, 15.9 (d, $J_{(P, C)}$ = 6.5 Hz), 15.7 (d, $J_{(P, C)}$ = 6.9 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.5 ppm; IR

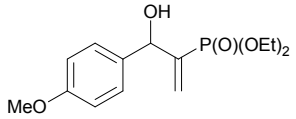
(neat) ν 3353, 2982, 1642, 1608, 1392, 1226, 1181, 1018, 963, 784, 703, 642 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_{21}NaO_4P^+$: 307.1070, Found: 307.1068 $[M+Na]^+$.

Diethyl (3-hydroxy-3-*(p-tolyl)*prop-1-en-2-yl)phosphonate (S3)



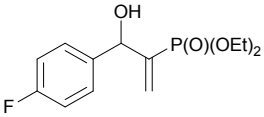
Light yellow oil, 35.7% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.07 (d, *J* = 22.0 Hz, 1H), 6.03 (d, *J* = 46.0 Hz, 1H), 5.40 (dd, *J* = 10.8, 4.8 Hz, 1H), 4.02 (d, *J* = 4.8 Hz, 1H), 3.98-3.82 (m, 3H), 3.73-3.63 (m, 1H), 2.32(s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 (d, $J_{(P, C)}$ = 169.6 Hz), 138.0 (d, $J_{(P, C)}$ = 4.0 Hz), 137.1, 129.3 (d, $J_{(P, C)}$ = 7.1 Hz), 128.7, 126.6, 73.3 (d, $J_{(P, C)}$ = 15.4 Hz), 61.9 (d, $J_{(P, C)}$ = 5.4 Hz), 61.8 (d, $J_{(P, C)}$ = 5.5 Hz). 20.9, 16.0 (d, $J_{(P, C)}$ = 6.5 Hz), 15.7 (d, $J_{(P, C)}$ = 6.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.5 ppm; IR (neat) ν 3349, 2982, 1642, 1512, 1392, 1227, 1017, 963, 823, 793, 736 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_{21}NaO_4P^+$: 307.1070, Found: 307.1066 $[M+Na]^+$.

Diethyl (3-hydroxy-3-(4-methoxyphenyl)prop-1-en-2-yl)phosphonate (S4)



White solid, 56.7% yield, m.p. 67-68 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 6.84-6.80 (m, 2H), 6.13 (ddd, *J* = 46.4, 1.2, 1.2 Hz, 1H), 6.07 (d, *J* = 22.4 Hz, 1H), 5.36 (dd, *J* = 8.4, 4.4 Hz, 1H), 4.54 (d, *J* = 4.4 Hz, 1H), 3.93-3.78 (m, 3H), 3.75 (s, 3H), 3.68-3.59 (m, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 141.8 (d, $J_{(P, C)}$ = 169.8 Hz), 133.2 (d, $J_{(P, C)}$ = 3.5 Hz), 128.7 (d, $J_{(P, C)}$ = 7.0 Hz), 127.9, 113.1, 72.3 (d, $J_{(P, C)}$ = 16.8 Hz), 61.5 (d, $J_{(P, C)}$ = 4.0 Hz), 61.4 (d, $J_{(P, C)}$ = 3.8 Hz), 54.8, 15.7 (d, $J_{(P, C)}$ = 6.1 Hz), 15.5 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.1 ppm; IR (neat) ν 3339, 2975, 2899, 1608, 1510, 1297, 1228, 1199, 1179, 1022, 961, 836, 816, 798, 750, 631 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_{21}NaO_5P^+$: 323.1019, Found: 323.1021 $[M+Na]^+$.

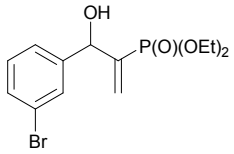
Diethyl (3-(4-fluorophenyl)-3-hydroxyprop-1-en-2-yl)phosphonate (S5)



Colorless oil, 33.1% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37-7.34 (m, 2H), 7.05-7.01 (m, 2H), 6.07 (d, *J* = 21.6 Hz, 1H), 5.98 (d, *J* = 45.6 Hz, 1H), 5.45 (dd, *J* = 12.0, 4.8 Hz, 1H), 4.03-3.88 (m, 4H), 3.82-3.72 (m, 1H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $J_{(F, C)}$ = 244.4 Hz), 141.6 (dd, $J_{(P, C)}$ = 171.2 Hz, $J_{(F, C)}$ = 0.8 Hz,), 137.0 (dd, $J_{(P, C)}$ = 3.4 Hz, $J_{(F, C)}$ = 3.4 Hz,), 129.1 (d, $J_{(P, C)}$ = 6.9 Hz), 128.5 (d, $J_{(F, C)}$ = 8.4 Hz),

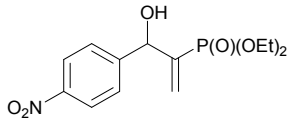
114.6 (d, $J_{(F, C)}$ = 21.3 Hz), 72.4 (d, $J_{(P, C)}$ = 16.4 Hz), 61.8 (d, $J_{(P, C)}$ = 2.3 Hz), 61.7 (d, $J_{(P, C)}$ = 2.4 Hz), 15.8 (d, $J_{(P, C)}$ = 6.6 Hz), 15.7 (d, $J_{(P, C)}$ = 6.3 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.0 ppm; IR (neat) ν 3349, 2984, 1644, 1603, 1508, 1393, 1219, 1157, 1016, 964, 838, 792 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{13}H_{18}FNaO_4P^+$: 311.0819, Found: 311.0809 $[M+Na]^+$.

Diethyl (3-(3-bromophenyl)-3-hydroxyprop-1-en-2-yl)phosphonate (S6)



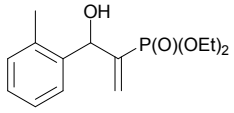
Light yellow solid, 28.7% yield, m.p. 62-63 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.11 (d, *J* = 44.8 Hz, 1H), 6.09 (d, *J* = 22.4 Hz, 1H), 5.37 (d, *J* = 10.4 Hz, 1H), 4.82 (*br*, s, 1H), 3.96-3.82 (m, 3H), 3.76-3.66 (m, 1H), 1.21 (t, *J* = 6.8 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.7 (d, $J_{(P, C)}$ = 3.4 Hz), 141.1 (d, $J_{(P, C)}$ = 171.3 Hz), 130.3, 129.8, 129.7, 129.5, 125.4, 121.9, 72.5 (d, $J_{(P, C)}$ = 15.9 Hz), 61.9 (d, $J_{(P, C)}$ = 2.2 Hz), 61.8 (d, $J_{(P, C)}$ = 2.0 Hz), 15.9 (d, $J_{(P, C)}$ = 6.8 Hz), 15.7 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.9 ppm; IR (neat) ν3286, 2987, 1567, 1391, 1287, 1229, 1189, 1019, 967, 943, 789, 765, 681 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{13}H_{19}BrO_4P^+$: 349.0199, Found: 349.0188 $[M+H]^+$.

Diethyl (3-hydroxy-3-(4-nitrophenyl)prop-1-en-2-yl)phosphonate (S7)



Brown oil, 7.8% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22-8.19 (m, 2H), 7.6-7.57 (m, 2H), 6.10 (d, *J* = 21.6 Hz, 1H), 5.98 (d, *J* = 45.2 Hz, 1H), 5.56 (d, *J* = 14.0 Hz, 1H), 4.42 (*br* s, 1H), 4.08-3.83 (m, 4H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.4 (d, $J_{(P, C)}$ = 4.6 Hz), 147.3, 141.0 (d, $J_{(P, C)}$ = 172.3 Hz), 130.4(d, $J_{(P, C)}$ = 7.0 Hz), 127.5, 123.3, 73.4 (d, $J_{(P, C)}$ = 13.9 Hz), 62.4 (d, $J_{(P, C)}$ = 5.9 Hz), 62.3 (d, $J_{(P, C)}$ = 6.1 Hz), 16.1 (d, $J_{(P, C)}$ = 6.4 Hz), 16.0 (d, $J_{(P, C)}$ = 6.4 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.2 ppm; IR (neat) ν 3467, 2983, 1739, 1608, 1512, 1370, 1225, 1175, 1016, 959, 833, 795 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{13}H_{19}NO_6P^+$: 316.0945, Found: 316.0931 $[M+H]^+$.

Diethyl (3-hydroxy-3-(*o-tolyl*)prop-1-en-2-yl)phosphonate (S8)



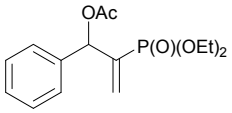
Light yellow oil, 38.2% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.24-7.11 (m, 3H), 6.07 (d, *J* = 22.0 Hz, 1H), 5.77 (d, *J* = 46.4 Hz, 1H), 5.67 (d, *J* = 7.6 Hz, 1H), 4.05-3.96 (m, 3H), 3.87-3.80 (m, 2H), 2.28 (s, 3H),

1.28 (t, J = 7.2 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9 (d, $J_{(P, C)}$ = 170.5 Hz), 138.5 (d, $J_{(P, C)}$ = 6.2 Hz), 135.2, 129.9, 129.6 (d, $J_{(P, C)}$ = 7.3 Hz), 127.3, 126.7, 125.7, 69.4 (d, $J_{(P, C)}$ = 5.3 Hz), 61.9 (d, $J_{(P, C)}$ = 5.8 Hz), 61.8 (d, $J_{(P, C)}$ = 5.8 Hz), 18.8, 16.0 (d, $J_{(P, C)}$ = 6.1 Hz), 15.8 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.6 ppm; IR (neat) ν 3334, 2980, 1392, 1228, 1186, 1018, 962, 788, 758, 728, 632 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_{21}NaO_4P^+$: 307.1070, Found: 307.1067 $[M+Na]^+$.

1.2. General procedure for acetylation of the MBH adducts S1-S8 for preparation of 2a-2h

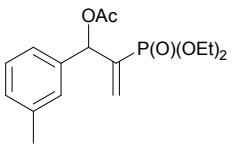
To an acetonitrile solution (40 mL) of the MBH adducts **S1-S8** (8.6 mmol, 1.0 equiv.) at ambient temperature was added acetic anhydride (1.05 mL, 10.3 mmol, 1.2 equiv.), followed by addition of ferric chloride (232.0 mg, 0.86 mmol, 0.1 equiv.). After stirring the mixture for 3 h, saturated aqueous $NaHCO_3$ solution (30 mL) was added, and the resulting mixture was stirred at ambient temperature until bubbling ceased. The resulting mixture was extracted with EtOAc (40 mL × 3), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and the solvent was evaporated in vacuo. Purification of the residue by flash chromatography [SiO_2: EtOAc/petroleum ether (1/1-2/1)] to yield the product **2**.

2-(diethoxyphosphoryl)-1-phenylallyl acetate (2a)[2]



Colorless oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.28 (m, 5H), 6.47 (d, J = 7.2 Hz, 1H), 6.31 (d, J = 22.4 Hz, 1H), 6.10 (ddd, J = 45.2, 1.2, 1.2 Hz, 1H), 4.06-3.88 (m, 3H), 3.74-3.64 (m, 1H), 2.10 (s, 3H), 1.28 (t, J = 6.8 Hz, 3H), 1.06 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 138.7 (d, $J_{(P, C)}$ = 174.6 Hz), 137.1 (d, $J_{(P, C)}$ = 3.5 Hz), 130.6 (d, $J_{(P, C)}$ = 7.1 Hz), 128.3, 128.2, 127.7, 73.8 (d, $J_{(P, C)}$ = 8.1 Hz), 61.9 (d, $J_{(P, C)}$ = 5.7 Hz), 61.6 (d, $J_{(P, C)}$ = 5.8 Hz), 20.9, 16.0 (d, $J_{(P, C)}$ = 6.5 Hz), 15.7 (d, $J_{(P, C)}$ = 6.7 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.6 ppm; IR (neat) ν 3473, 2983, 1741, 1371, 1225, 1016, 960, 797, 760, 698 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{15}H_{22}O_5P^+$: 313.1199, Found: 313.1193 $[M+H]^+$.

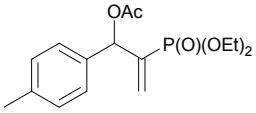
2-(diethoxyphosphoryl)-1-(*m-tolyl*)allyl acetate (2b)



Light yellow oil, 96% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.10 (m, 4H), 6.44 (d, J = 7.2 Hz, 1H), 6.31 (d, J = 22.4 Hz, 1H), 6.09 (d, J = 45.6 Hz, 1H), 4.07-3.89 (m, 3H), 3.75-3.65 (m, 1 H), 2.34 (s, 3H), 2.09 (s, 3H), 1.28 (t, J = 6.8

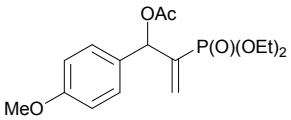
Hz, 3H), 1.07 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 138.5 (d, $J_{(P, C)}$ = 175.1 Hz), 137.6, 136.7 (d, $J_{(P, C)}$ = 3.3 Hz), 130.5 (d, $J_{(P, C)}$ = 7.5 Hz), 128.9, 128.2, 127.9, 124.6, 73.6 (d, $J_{(P, C)}$ = 18.0 Hz), 61.7 (d, $J_{(P, C)}$ = 5.2 Hz), 61.4 (d, $J_{(P, C)}$ = 5.1 Hz), 20.9, 20.6, 15.8 (d, $J_{(P, C)}$ = 6.6 Hz), 15.5 (d, $J_{(P, C)}$ = 7.2 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.2 ppm; IR (neat) ν 2983, 1743, 1370, 1224, 1017, 964, 789, 700 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{24}O_5P^+$: 327.1356, Found: 327.1351 $[M+H]^+$

2-(diethoxyphosphoryl)-1-(*p-tolyl*)allyl acetate (2c)



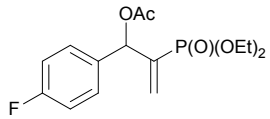
Light yellow oil, 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 7.6 Hz, 2H), 6.43 (d, J = 6.8 Hz, 1H), 6.29 (d, J = 22.4 Hz, 1H), 6.08 (d, J = 45.6 Hz, 1H), 4.07-3.88 (m, 3H), 3.74-3.64 (m, 1H), 2.33 (s, 3H), 2.09 (s, 3H), 1.29 (t, J = 6.8 Hz, 3H), 1.08 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 138.8 (d, $J_{(P, C)}$ = 174.6 Hz), 138.3, 134.1 (d, $J_{(P, C)}$ = 3.4 Hz), 130.6 (d, $J_{(P, C)}$ = 7.0 Hz), 128.9, 127.8, 73.7 (d, $J_{(P, C)}$ = 17.9 Hz), 62.0 (d, $J_{(P, C)}$ = 5.4 Hz), 61.7 (d, $J_{(P, C)}$ = 5.3 Hz), 21.1, 21.0, 16.1 (d, $J_{(P, C)}$ = 6.6 Hz), 15.8 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.3 ppm; IR (neat) ν 2983, 1742, 1371, 1226, 1017, 961, 821, 790, 731 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{24}O_5P^+$: 327.1356, Found: 327.1350 $[M+H]^+$

2-(diethoxyphosphoryl)-1-(4-methoxyphenyl)allyl acetate (2d)



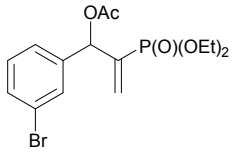
Compound **2d** was obtained as a mixture along with its regioisomer **6d** in a molar ratio of 3/1 (by ^{1}H NMR). Since the isomers were found hardly isolated from each other by regular flash chromatography, the mixture was used directly in the subsequent allylic amination reaction without further purification. Light yellow oil, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.42 (d, J = 6.4 Hz, 1H), 6.28 (d, J = 22.4 Hz, 1H), 6.10 (d, J = 45.6 Hz, 1H), 4.07-3.90 (m, 3H), 3.80 (s, 3H), 3.72-3.66 (m, 1H), 2.09 (s, 3H), 1.29 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 159.6, 139.0 (d, $J_{(P, C)}$ = 175.0 Hz), 130.2 (d, $J_{(P, C)}$ = 6.8 Hz), 129.3, 129.2 (d, $J_{(P, C)}$ = 2.9 Hz), 113.6, 73.6 (d, $J_{(P, C)}$ = 18.6 Hz), 62.0 (d, $J_{(P, C)}$ = 5.3 Hz), 61.7 (d, $J_{(P, C)}$ = 5.2 Hz), 55.2, 21.0, 16.1 (d, $J_{(P, C)}$ = 6.1 Hz), 15.9 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.6 ppm; IR (neat) ν 3304, 1599, 1519, 1345, 1228, 1020, 969, 956, 800, 700 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{14}H_{23}NaO_6P^+$: 365.1124, Found: 365.112 $[M+H]^+$.

2-(diethoxyphosphoryl)-1-(4-fluorophenyl)allyl acetate (2e)



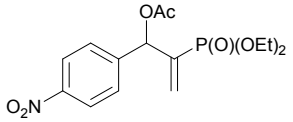
Light yellow oil, 89% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.06-7.01 (m, 2H), 6.46 (d, *J* = 7.2 Hz, 1H), 6.30 (d, *J* = 22.0 Hz, 1H), 6.12 (d, *J* = 45.2 Hz, 1H), 4.07-3.91 (m, 3H), 3.80-3.71 (m, 1H), 2.10 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 162.1 (d, $J_{(F, C)}$ = 245.7 Hz), 138.3 (d, $J_{(P, C)}$ = 174.9 Hz), 132.8 (dd, $J_{(P, C)}$ = 3.4 Hz, $J_{(F, C)}$ = 3.4 Hz), 130.0 (d, $J_{(P, C)}$ = 7.1 Hz), 129.3 (d, $J_{(F, C)}$ = 8.4 Hz), 114.7 (d, $J_{(F, C)}$ = 21.8 Hz), 72.8 (d, $J_{(P, C)}$ = 18.3 Hz), 61.6 (d, $J_{(P, C)}$ = 5.1 Hz), 61.4 (d, $J_{(P, C)}$ = 5.8 Hz), 20.4, 15.6 (d, $J_{(P, C)}$ = 6.5 Hz), 15.4 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.4 ppm; IR (neat) ν 2984, 1744, 1605, 1510, 1371, 1219, 1016, 961, 862, 798 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{15}H_{21}FO_5P^+$: 331.1105, Found: 331.1098 $[M+H]^+$.

1-(3-bromophenyl)-2-(diethoxyphosphoryl)allyl acetate (2f)



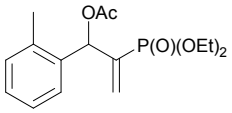
Light yellow oil, 78% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 1.6 Hz, 1H), 7.46-7.43 (m,1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.42 (d, *J* = 7.6 Hz, 1H), 6.32 (d, *J* = 22.0 Hz, 1H), 6.18-6.06 (ddd, *J* = 44.8, 1.2, 1.2 Hz, 1H), 4.05-3.94 (m, 3H), 3.82-3.73 (m, 1H), 2.12 (s, 3H), 1.28 (t, *J* = 6.8 Hz, 3H), 1.11(t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7,139.3 (d, $J_{(P, C)}$ = 3.1 Hz), 138.1 (d, $J_{(P, C)}$ = 176.2 Hz), 131.2, 130.8 (d, $J_{(P, C)}$ = 7.2 Hz), 130.4, 129.6, 126.3, 121.9, 72.8 (d, $J_{(P, C)}$ = 18.5 Hz), 61.8 (d, $J_{(P, C)}$ = 5.9 Hz), 61.6 (d, $J_{(P, C)}$ = 5.5 Hz), 20.6, 15.8 (d, $J_{(P, C)}$ = 6.8 Hz), 15.6 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.7 ppm; IR (neat) ν 2982, 1745, 1572, 1222, 1017, 963, 799, 784, 692 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{15}H_{21}BrO_5P^+$: 391.0304, Found: 391.0293 $[M+H]^+$.

2-(diethoxyphosphoryl)-1-(4-nitrophenyl)allyl acetate (2g)



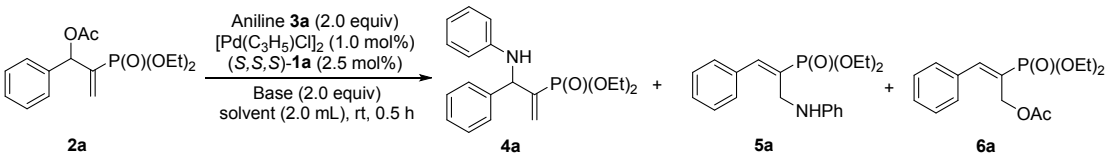
Brown oil, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.8 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 6.46 (d, *J* = 8.8 Hz, 1H), 6.25 (d, *J* = 22.0 Hz, 1H), 6.07 (d, *J* = 44.4 Hz, 1H), 3.99-3.88 (m, 3H), 3.80-3.72 (m, 1H), 2.07 (s, 3H), 1.18 (t, *J* = 6.8 Hz, 3H), 1.06 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 147.4, 144.4 (d, $J_{(P, C)}$ = 3.0 Hz), 137.8 (d, $J_{(P, C)}$ = 177.0 Hz), 131.3 (d, $J_{(P, C)}$ = 6.8 Hz), 128.3, 123.2 72.7 (d, $J_{(P, C)}$ = 17.9 Hz), 61.9 (d, $J_{(P, C)}$ = 5.6 Hz), 61.8 (d, $J_{(P, C)}$ = 6.1 Hz), 20.6, 15.9 (d, $J_{(P, C)}$ = 6.3 Hz), 15.7 (d, $J_{(P, C)}$ = 6.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.5 ppm; IR (neat) ν 2984, 1745, 1607, 1521, 1347, 1220, 1015, 963, 855, 834, 793, 750, 696 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{15}H_{21}NO_7P^+$: 358.1050, Found: 358.1039 $[M+H]^+$.

2-(diethoxyphosphoryl)-1-(*o-tolyl*)allyl acetate (2h)



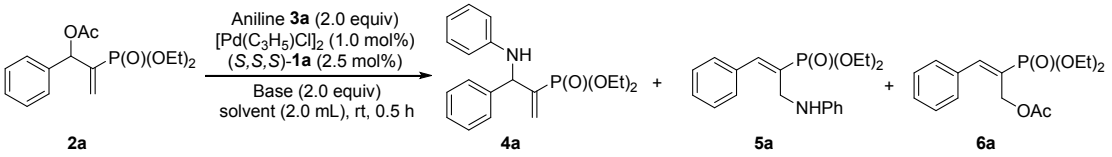
Light yellow oil, 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.30 (m, 1H), 7.20-7.13 (m, 3H), 6.73 (d, J = 6.4 Hz, 1H), 6.31 (d, J = 22.4 Hz, 1H), 5.94 (d, J = 45.2 Hz, 1H), 4.10-3.91 (m, 3H), 3.77-3.69 (m, 1H), 2.39 (s, 3H), 2.08 (s, 3H), 1.30 (t, J = 6.8 Hz, 3H), 1.09 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 137.9 (d, $J_{(P, C)}$ = 174.7 Hz), 135.9, 134.9 (d, $J_{(P, C)}$ = 4.7 Hz), 130.9 (d, $J_{(P, C)}$ = 7.4 Hz), 130.0, 127.9, 127.0, 125.5, 70.0 (d, $J_{(P, C)}$ = 16.7 Hz), 61.5 (d, $J_{(P, C)}$ = 5.3 Hz), 61.4 (d, $J_{(P, C)}$ = 5.4 Hz), 20.4, 18.6, 15.7 (d, $J_{(P, C)}$ = 6.7 Hz), 15.4 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.4 ppm; IR (neat) ν 2982, 1741, 1370. 1229, 1016, 959, 790, 758 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{16}H_{24}O_5P^+$: 327.1356, Found: 327.1361 $[M+H]^+$.

2. Preliminary survey of the conditions for the allylic amination



The solvent effect and the base additives were examined using reaction of MBH adduct **2a** (0.2 mmol) and aniline **3a** (0.4 mmol). The reactions were performed in the specified solvent (2 mL) under ambient temperature, in the presence of (*S*,*S*,*S*)-**1a** (0.005 mmol) and $[Pd(allyl)Cl]_2$ (0.002 mmol). The relative molar ratios of **4a**/**5a**/**6a** were determined by ^{1}H NMR analysis of the crude reaction mixture, and *ee* values of **4a** were determined by chiral HPLC with a Chiracel OD-H column.

Table S1. Effects of the base and the solvent[a]

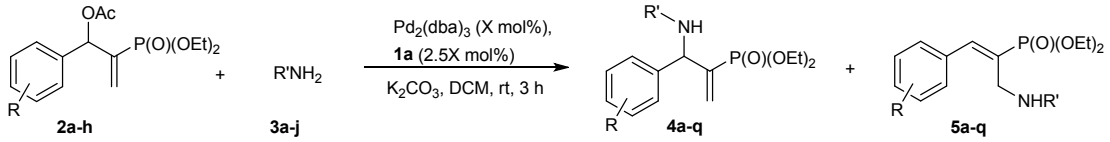


Entry	Base	Solvent	**4a/5a/6a**[b]	Yield of **4a** (%) [c]	*ee* (%)[d]
1	None	CH_2Cl_2	82/6/12	80	98
2	K_2CO_3	CH_2Cl_2	>98/<2/0	95	> 99
3	K_2CO_3 (aq)	CH_2Cl_2	97/3/0	93	98
4	Cs_2CO_3	CH_2Cl_2	70/4/26	66	98
5	NaOMe	CH_2Cl_2	41/49/10	30	96

6	KO^{t}Bu	CH_2Cl_2	---	0	---
7	K_3PO_4	CH_2Cl_2	83/0/17	80	98
8	NEt_3	CH_2Cl_2	71/0/29	68	98
9	K_2CO_3	THF	44/33/23	35	97
10	K_2CO_3	toluene	58/32/10	54	98
11	K_2CO_3	CH_3CN	95/0/5	93	98
12	K_2CO_3	DMF	65/14/21	63	> 99
13	K_2CO_3	DME	10/0/90	7	> 99
14	K_2CO_3	Et_2O	69/12/19	66	94
15	K_2CO_3	$CHCl_3$	85/4/11	82	> 99

[a] Unless otherwise noted, all reactions were conducted at rt in the specified solvent (2 mL) for 0.5 h, with **2a** (0.2 mmol), aniline (0.4 mmol), $[Pd(C_3H_5)Cl]_2$ (0.001 mmol), (*S*,*S*,*S*)-**1a** (0.0025 mmol), in the presence of the specified base (0.4 mmol). [b] Molar ratios were determined by ^{1}H NMR analysis. [c] Yield of the isolated **4a**. [d] Determined by chiral HPLC.

3. Palladium-catalyzed asymmetric allylic amination of racemic MBH adducts 2a-h with amines 3a-j



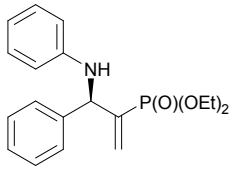
R	R'	R, R'	R, R'
2a: H	**3a**: Ph	**4a**: H, Ph	**4j**: H, Bn
2b: *m*-CH_3	**3b**: *p*-$CH_3C_6H_4$	**4b**: H, *p*-$CH_3C_6H_4$	**4k**: *m*-CH_3, Ph
2c: *p*-CH_3	**3c**: *p*-FC_6H_4	**4c**: H, *p*-FC_6H_4	**4l**: *p*-CH_3, Ph
2d: *p*-OCH_3	**3d**: *p*-BrC_6H_4	**4d**: H, *p*-BrC_6H_4	**4m**: *p*-OCH_3, Ph
2e: *p*-F	**3e**: *m*-$CH_3C_6H_4$	**4e**: H, *m*-$CH_3C_6H_4$	**4n**: *p*-F, Ph
2f: *m*-Br	**3f**: *p*-$OCH_3C_6H_4$	**4f**: H, R' = *p*-$OCH_3C_6H_4$	**4o**: *m*-Br, Ph
2g: *p*-NO_2	**3g**: *o*-$CH_3C_6H_4$	**4g**: H, *o*-$CH_3C_6H_4$	**4p**: *p*-NO_2, Ph
2h: *o*-CH_3	**3h**: *p*-ClC_6H_4	**4h**: H, *p*-ClC_6H_4	**4q**: *o*-CH_3, Ph
	3i: 3,4,5-$(OCH_3)_3(C_6H_2)$	**4i**: H, 3,4,5-$(OCH_3)_3(C_6H_2)$	
	3j: Bn		

General procedure: Into a schlenk tube equipped with magnetic stirring bar were added $Pd_2(dba)_3$ (1.8 mg, 0.005 mmol), (*S,S,S*)-**1a** (9.6 mg, 0.0125 mmol) and CH_2Cl_2 (5 mL) under a stream of argon. The solution was stirred for 5 min, followed by addition of **2** (0.5 mmol), K_2CO_3 (138 mg, 1.0 mmol) and **3** (1.0 mmol). The mixture was stirred for 3 h at room temperature, then the solid residue was removed by filtration through a pad of celite. The ratio of **4**/**5** was determined by ^{1}H NMR analysis of an aliquot of the filtrate. The solvent was

removed in vacuo, and the residue was purified by flash chromatography on silica gel with petroleum ether/EA (1/2) as the eluent to afford optically enriched α-methylene β-amino phosphonate esters **4**.

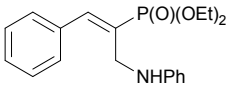
Characterization data:

(*R*)-diethyl (3-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (4a)



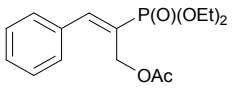
White solid, 94% yield, m.p. 95-97 °C, >99% *ee*. $[\alpha]_D^{26}$ = -84.7 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5H), 7.15-7.11 (m, 2H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 8.0 Hz, 2H), 6.24 (d, *J* = 22.4 Hz, 1H), 6.10 (d, *J* = 44.8 Hz, 1H), 5.21 (dd, *J* = 8.8, 4.4 Hz, 1H), 4.36 (d, *J* = 4.4 Hz, 1H), 4.05-3.85 (m, 3H), 3.71-3.61 (m, 1H), 1.24 (t, *J* = 6.8 Hz, 3H), 1.06 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.0 (d, $J_{(P, C)}$ = 3.2 Hz), 139.5 (d, $J_{(P, C)}$ = 171.1 Hz), 130.6 (d, $J_{(P, C)}$ = 8.4 Hz), 129.0, 128.5, 127.8, 127.7, 117.7, 113.4, 61.8 (d, $J_{(P, C)}$ = 6.4 Hz), 61.7 (d, $J_{(P, C)}$ = 6.1 Hz), 59.9 (d, $J_{(P, C)}$ = 15.7 Hz), 16.1 (d, $J_{(P, C)}$ = 6.6 Hz), 15.9 (d, $J_{(P, C)}$ = 6.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.0 ppm; IR (neat) ν 3294, 1601, 1496, 1235, 1018, 958, 798, 746, 694 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{25}NO_3P^+$: 346.1567, Found: 346.1557 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.50 min; t_R (major) = 7.42 min.

(*E*)-diethyl (1-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (5a)



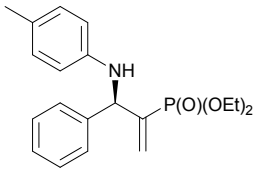
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 24.0 Hz, 1H), 7.47-7.34 (m, 5H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 2H), 4.18-4.09 (m, 4H), 4.05 (d, *J* = 22.4 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.8, 146.3 (d, $J_{(P, C)}$ = 11.8 Hz), 134.6 (d, $J_{(P, C)}$ = 22.3 Hz), 129.4 (d, $J_{(P, C)}$ = 1.6 Hz), 129.2, 129.1, 128.6, 127.1 (d, $J_{(P, C)}$ = 178.9 Hz), 117.8, 113.2, 62.1 (d, $J_{(P, C)}$ = 5.3 Hz), 41.6 (d, $J_{(P, C)}$ = 9.1 Hz), 16.3 (d, $J_{(P, C)}$ = 5.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.6 ppm; IR (neat) ν 3397, 3335, 3054, 2981, 2930, 2906, 1601, 1503, 1255, 1230, 1048, 1021, 966, 794, 750, 694 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{25}NO_3P^+$: 346.1567, Found: 346.1574 $[M+H]^+$.

(*E*)-2-(diethoxyphosphoryl)-3-phenylallyl acetate (6a)



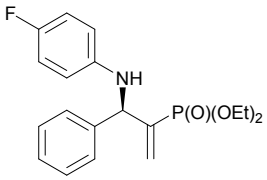
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, J = 24.0 Hz, 1H), 7,47-7.31 (m, 5H), 4.89 (d, J = 18.0 Hz, 2H), 4.15 (q, J = 7.2 Hz, 4H), 2.11 (s, 3H), 1.36 (t, J = 7.2 Hz, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 148.9 (d, $J_{(P, C)}$ = 10.7 Hz), 133.8 (d, $J_{(P, C)}$ = 21.6 Hz), 129.1, 128.9, 128.3, 124.4 (d, $J_{(P, C)}$ = 181.7 Hz), 61.7 (d, $J_{(P, C)}$ = 6.2 Hz), 59.0 (d, $J_{(P, C)}$ = 9.1 Hz), 20.5, 15.9 (d, $J_{(P, C)}$ = 7.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.7 ppm; IR (neat) ν 3466, 2983, 2934, 2907, 1739, 1621, 1222, 1162, 1015, 962, 789, 755, 697 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{15}H_{22}O_5P^+$: 313.1199, Found: 313.1206 $[M+H]^+$.

(*R*)-diethyl (3-phenyl-3-(*p*-tolylamino)prop-1-en-2-yl)phosphonate (4b)



Yellow oil, 91% yield, 95% *ee*. $[\alpha]_D^{26}$ = -97.7 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.24 (m, 5H), 6.94 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 8.4 Hz, 2H), 6.23 (d, J = 22.0 Hz, 1H), 6.11(d, J = 46.4 Hz, 1H), 5.18 (d, J = 8.8 Hz, 1H), 4.23 (*br* s, 1H), 4.00-3.85 (m, 3H), 3.69-3.59 (m, 1H), 2.21 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 140.2, 140.1, 139.6 (d, $J_{(P, C)}$ = 170.8 Hz), 130.5 (d, $J_{(P, C)}$ = 8.2 Hz), 129.4, 128.5, 127.7, 126.9, 113.4, 61.8 (d, $J_{(P, C)}$ = 6.4 Hz), 61.7 (d, $J_{(P, C)}$ = 5.5 Hz), 60.0 (d, $J_{(P, C)}$ = 15.9 Hz), 20.2 (d, $J_{(P, C)}$ = 1.4 Hz), 16.1 (d, $J_{(P, C)}$ = 6.7 Hz), 15.8 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 ppm; IR (neat) ν 3327, 2980, 1616, 1518, 1237, 1018, 961, 803, 697 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1722 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 5.94 min; t_R (major) = 7.02 min.

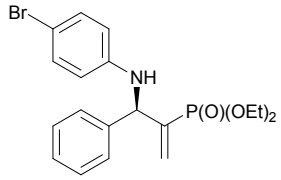
(*R*)-diethyl (3-((4-fluorophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4c)



Light yellow solid, 94% yield, m.p. 55-56 °C, 96% *ee*. $[\alpha]_D^{26}$ = -68.1 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 6.83 (t, J = 8.8 Hz, 2H), 6.53-6.50 (m, 2H), 6.21 (d, J = 22.0 Hz, 1H), 6.06 (d, J = 46.0 Hz, 1H), 5.14 (d, J = 9.6 Hz, 1H), 4.36 (*br*, s, 1H), 4.04-3.85 (m, 3H), 3.72-3.62 (m, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8(d, $J_{(F, C)}$ = 233.5 Hz), 142.8 (d, $J_{(F, C)}$ = 2.3 Hz), 139.8 (d, $J_{(P, C)}$ =

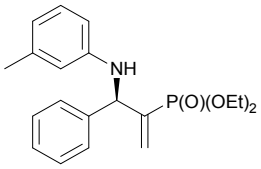
3.2 Hz), 139.5 (d, $J_{(P, C)}$ = 171.6 Hz), 130.5 (d, $J_{(P, C)}$ = 8.7 Hz), 128.5, 127.8, 127.6, 115.3 (d, $J_{(F, C)}$ = 22.6 Hz), 114.1 (d, $J_{(F, C)}$ = 7.2 Hz), 61.9 (d, $J_{(P, C)}$ = 11.6 Hz), 61.8, 60.4 (d, $J_{(P, C)}$ = 15.1 Hz), 16.1 (d, $J_{(P, C)}$ = 6.3 Hz), 15.8 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.3 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -127.5 ppm; IR (neat) ν 3289, 2984, 1519, 1235, 1047, 1018, 963, 954, 822, 782, 698 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{24}FNO_3P^+$: 364.1472, Found: 364.1467 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90: 10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.11 min; t_R (major) = 7.70 min.

(*R*)-diethyl (3-((4-bromophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4d)



White solid, 87% yield, m.p. 82-83 °C, 98% *ee*. $[\alpha]_D^{26}$ = -82.6 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 7.19 (d, *J* = 8.8 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 21.6 Hz, 1H), 6.04 (d, *J* = 45.6 Hz, 1H), 5.16 (d, *J* = 9.6 Hz, 1H), 4.53 (*br* s, 1H), 4.04-3.84 (m, 3H), 3.72-3.62 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 139.4 (d, $J_{(P, C)}$ = 2.7 Hz), 139.2 (d, $J_{(P, C)}$ = 171.2 Hz), 131.6, 130.5 (d, $J_{(P, C)}$ = 8.1 Hz), 128.6, 127.8, 127.5, 114.9, 109.3, 61.9 (d, $J_{(P, C)}$ = 5.9 Hz), 61.8 (d, $J_{(P, C)}$ = 5.7 Hz), 59.8 (d, $J_{(P, C)}$ = 5.3 Hz), 16.1 (d, $J_{(P, C)}$ = 6.7 Hz), 15.8 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.1 ppm; IR (neat) ν 3315, 2976, 1592, 1505, 1487, 1316, 1237, 1021, 964, 817, 699 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{24}BrNO_3P^+$: 424.0672, Found: 424.0665 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.80 min; t_R (major) = 8.54 min.

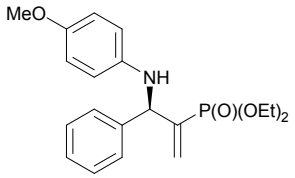
(*R*)-diethyl (3-phenyl-3-(*m*-tolylamino)prop-1-en-2-yl)phosphonate (4e)



Light yellow solid, 83% yield, m.p. 63-64 °C, 94% *ee*. $[\alpha]_D^{26}$ = -99.4 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 6.38 (d, *J* = 8.0 Hz, 1H), 6.24(d, *J* = 22.0, 1H), 6.13(d, *J* = 46.8 Hz, 1H), 5.20 (d, *J* = 8.8 Hz, 1H), 4.32 (*br* s, 1H), 4.10-3.85 (m, 3H), 3.66-3.56 (m, 1H), 2.23 (s, 3H), 1.25 (t, *J* = 6.8 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.4, 140.0 (d, $J_{(P, C)}$ = 2.7 Hz), 139.4(d, $J_{(P, C)}$ = 170.5 Hz), 138.5, 130.5, 130.4, 128.7, 128.4, 127.6, 118.5, 114.0, 110.4, 61.6 (d, $J_{(P, C)}$ = 6.1 Hz), 61.5 (d, $J_{(P, C)}$ = 5.6 Hz), 59.7 (d,

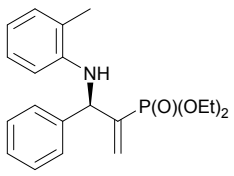
$J_{(P, C)}$ = 15.8 Hz), 21.4, 16.1 (d, $J_{(P, C)}$ = 6.6 Hz), 15.7 (d, $J_{(P, C)}$ = 7.2 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 ppm; IR (neat) ν 3327, 2980, 1604, 1489, 1237, 1167, 1049, 1018, 961, 800, 768, 694 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1736 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.09 min; t_R (major) = 7.16 min.

(*R*)-diethyl (3-((4-methoxyphenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4f)



Brown oil, 88% yield, 96% *ee*. $[\alpha]_D^{26}$ = -82.3 (c 0.70, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.25 (m, 5H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.4 Hz, 2H), 6.22 (d, *J* = 21.6 Hz, 1H), 6.10 (d, *J* = 46.4 Hz, 1H), 5.14 (d, *J* = 9.2 Hz, 1H), 4.16 (*br* s, 1H), 4.04-3.85 (m, 3H), 3.70 (s, 3H), 3.68-3.63 (m, 1H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 140.6, 140.1 (d, $J_{(P, C)}$ = 2.9 Hz), 139.7 (d, $J_{(P, C)}$ = 170.9 Hz), 130.5, 130.4, 128.4, 127.6, 114.53, 114.50, 61.7 (d, $J_{(P, C)}$ = 6.2 Hz), 61.6 (d, $J_{(P, C)}$ = 5.6 Hz), 60.4 (d, $J_{(P, C)}$ = 15.4 Hz), 55.5, 16.0 (d, $J_{(P, C)}$ = 6.8 Hz), 15.8 (d, $J_{(P, C)}$ = 6.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 ppm; IR (neat) ν 3328, 2982, 1510, 1233, 1021, 964, 818, 699 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_4P^+$: 376.1672, Found: 376.1675 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 8.01 min; t_R (major) = 10.07 min.

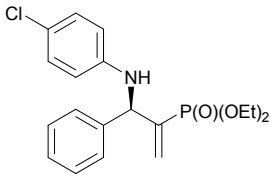
(*R*)-diethyl (3-phenyl-3-(*o*-tolylamino)prop-1-en-2-yl)phosphonate (4g)



Light yellow oil, 70% yield, 98% *ee*. $[\alpha]_D^{26}$ = -63.5 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.33-7.22 (m, 3H), 7.03-6.98 (m, 2H), 6.62 (t, *J* = 7.2 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 6.20 (d, *J* = 21.6 Hz, 1H), 6.04 (d, *J* = 46.4 Hz, 1H), 5.29 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.40 (*br* s, 1H), 4.03-3.83 (m, 3H), 3.73-3.63 (m, 1H), 2.17 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.1, 139.8 (d, $J_{(P, C)}$ = 3.0 Hz), 139.5 (d, $J_{(P, C)}$ = 171.0 Hz), 130.3 (d, $J_{(P, C)}$ = 8.3 Hz), 129.6, 128.2, 127.4, 127.2, 126.5, 121.7, 117.0, 110.6, 61.6 (d, $J_{(P, C)}$ = 5.7 Hz), 61.5 (d, $J_{(P, C)}$ = 6.2 Hz), 59.7 (d, $J_{(P, C)}$ = 14.5 Hz), 17.2, 15.8 (d, $J_{(P, C)}$ = 6.5 Hz), 15.6 (d, $J_{(P, C)}$ = 6.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.5 ppm; IR (neat) ν 3437, 3372, 2980,

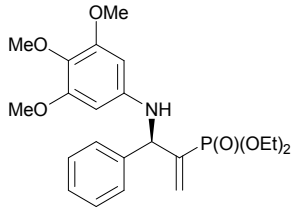
1604, 1586, 1510, 1452, 1311, 1239, 1017, 960, 793, 745, 698 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1726 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 98:2, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 16.95 min; t_R (major) = 18.62 min.

(*R*)-diethyl (3-((4-chlorophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4h)



White solid, 84% yield, m.p. 73-74 °C, 98% *ee*. $[\alpha]_D^{26}$ = -82.6 (c 1.00, $CHCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.25 (m, 5H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.4 Hz, 2H), 6.18 (d, *J* = 22.0 Hz, 1H), 5.99 (d, *J* = 46.0 Hz, 1H), 5.17 (dd, *J* = 8.4, 3.6 Hz, 1H), 4.71 (d, *J* = 4.0 Hz, 1H), 3.97-3.81 (m, 3H), 3.67-3.61 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 139.2 (d, $J_{(P, C)}$ = 3.1 Hz), 139.0 (d, $J_{(P, C)}$ = 171.3 Hz), 130.2 (d, $J_{(P, C)}$ = 8.1 Hz), 128.6, 128.2, 127.5, 127.3, 121.7, 114.1, 61.6 (d, $J_{(P, C)}$ = 6.2 Hz), 61.5 (d, $J_{(P, C)}$ = 5.8 Hz), 59.5 (d, $J_{(P, C)}$ = 5.1 Hz), 15.8 (d, $J_{(P, C)}$ = 7.6 Hz), 15.5 (d, $J_{(P, C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.8 ppm; IR (neat) ν 3282, 2984, 1597, 1511, 1491, 1313, 1234, 1017, 963, 950, 818, 791, 765, 698 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{24}ClNO_3P^+$: 380.1177, Found: 380.1161 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.42 min; t_R (major) = 8.03 min.

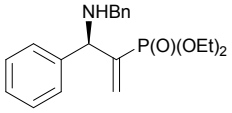
(*R*)-diethyl (3-phenyl-3-((3,4,5-trimethoxyphenyl)amino)prop-1-en-2-yl)phosphonate (4i)



Light gray solid, 89% yield, m.p. 109-110 °C, 98% *ee*. $[\alpha]_D^{26}$ = -96.7 (c 1.00, $CHCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.25 (m, 5H), 6.24 (d, *J* = 21.6 Hz, 1H), 6.19 (d, *J* = 46.4 Hz, 1H), 5.87 (s, 2H), 5.19 (dd, *J* = 8.4, 4.0 Hz, 1H), 4.50 (d, *J* = 4.4 Hz, 1H), 4.03-3.83 (m, 3H), 3.72 (s, 6H), 3.71 (s, 3H), 3.63-3.55 (m, 1H), 1.22 (t, *J* = 6.8 Hz, 3H), 1.04 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 142.9, 139.5 (d, $J_{(P, C)}$ = 2.5 Hz), 139.1 (d, $J_{(P, C)}$ = 171.2 Hz), 130.0 (d, $J_{(P, C)}$ = 8.0 Hz), 129.6, 128.2, 127.4, 127.3, 90.6, 61.5 (d, $J_{(P, C)}$ = 5.8 Hz), 61.4 (d, $J_{(P, C)}$ = 6.0 Hz), 60.4, 59.8 (d, $J_{(P, C)}$ = 16.5 Hz), 55.3, 15.8 (d, $J_{(P, C)}$ = 6.2 Hz), 15.5 (d, $J_{(P, C)}$ = 6.7 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.1 ppm; IR (neat) ν 3300, 2977, 1607, 1505, 1232, 1122, 1013, 962, 816, 783, 704

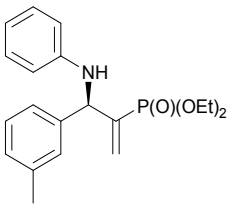
cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{22}H_{31}NO_6P^+$: 436.1884, Found: 436.1896 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel PA-2 column; n-Hex/*i*-PrOH = 70 : 30, 0.7 mL/min, UV-vis detection at λ = 214 nm; t_R (major) = 33.49 min; t_R (minor) = 61.36 min.

(*R*)-diethyl (3-(benzylamino)-3-phenylprop-1-en-2-yl)phosphonate (4j)



Light yellow oil, 84% yield, 95% *ee*. $[\alpha]_D^{26}$ = -25.6 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 10H), 6.25 (d, *J* = 22.0 Hz, 1H), 6.19 (d, *J* = 46.8 Hz, 1H), 4.56 (d, *J* = 10.0 Hz, 1H), 3.98-3.83 (m, 3H), 3.73-3.57 (m, 3H), 2.08 (*br*, s, 1H), 1.19 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (d, $J_{(P,\ C)}$ = 171.1 Hz), 140.7 (d, $J_{(P,\ C)}$ = 3.7 Hz), 139.9, 130.2 (d, $J_{(P,\ C)}$ = 8.0 Hz), 128.2, 128.1, 127.9, 127.8, 127.3, 126.7, 62.4 (d, $J_{(P,\ C)}$ = 14.4 Hz), 61.6 (d, $J_{(P,\ C)}$ = 5.6 Hz), 61.5 (d, $J_{(P,\ C)}$ = 5.2 Hz), 51.4, 16.0 (d, $J_{(P,\ C)}$ = 6.2 Hz), 15.8 (d, $J_{(P,\ C)}$ = 6.8 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.8 ppm; IR (neat) ν 3442, 2981, 1619, 1453, 1235, 1048, 1018, 958, 792, 746, 697, 611 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1715 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 5.95 min; t_R (major) = 6.48 min.

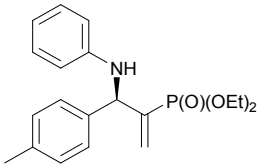
(*R*)-diethyl (3-(phenylamino)-3-(*m*-tolyl)prop-1-en-2-yl)phosphonate (4k)



Colorless oil, 75% yield, 94% *ee*. $[\alpha]_D^{26}$ = -102.3 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.08 (m, 6H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 2H), 6.23 (d, *J* = 21.2 Hz, 1H), 6.11(ddd, *J* = 46.0, 1.2, 1.2 Hz, 1H), 5.17 (dd, *J* = 8.8, 4.8 Hz, 1H), 4.33 (d, *J* = 4.4 Hz, 1H), 4.07-3.86 (m, 3H), 3.71-3.61 (m, 1H), 2.33 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 139.8 (d, $J_{(P,\ C)}$ = 3.2 Hz), 139.5 (d, $J_{(P,\ C)}$ = 170.7 Hz), 138.1, 130.4 (d, $J_{(P,\ C)}$ = 8.2 Hz), 128.9, 128.5, 128.4, 128.3, 124.7, 117.6, 113.3, 61.7 (d, $J_{(P,\ C)}$ = 6.5 Hz), 61.6 (d, $J_{(P,\ C)}$ = 5.6 Hz), 59.7 (d, $J_{(P,\ C)}$ = 15.0 Hz), 21.3, 16.0 (d, $J_{(P,\ C)}$ = 6.8 Hz), 15.8 (d, $J_{(P,\ C)}$ = 6.9 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.3 ppm; IR (neat) ν 3318, 2976, 1602, 1513, 1497, 1309, 1236, 1179, 1053, 1019, 949, 906, 758, 697 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1721 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, 254 nm; t_R (minor) = 5.81 min; t_R (major) = 6.47 min. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 5.81 min; t_R

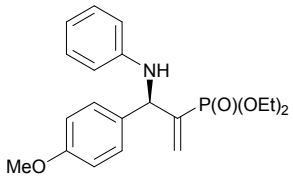
(major) = 6.47 min.

(*R*)-diethyl (3-(phenylamino)-3-(p-tolyl)prop-1-en-2-yl)phosphonate (4l)



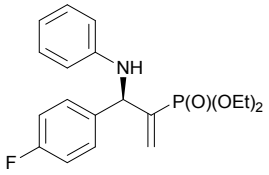
White solid, 92% yield, m.p. 74-75 °C, 97% *ee*. $[\alpha]_D^{26}$ = -91.9 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.0 Hz, 2H), 7.14-7.09 (m, 4H), 6.67 (t, *J* = 7.2Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 2H), 6.21 (d, *J* = 21.6 Hz, 1H), 6.08(d, *J* = 46.4 Hz, 1H), 5.18 (d, *J* = 8.8 Hz, 1H), 4.36 (*br* s, 1H), 4.04-3.87 (m, 3H), 3.71-3.62 (m, 1H), 2.32 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 139.5 (d, $J_{(P, C)}$ = 170.4 Hz), 137.3, 136.9 (d, $J_{(P, C)}$ = 3.3 Hz), 130.2 (d, $J_{(P, C)}$ = 8.2 Hz), 129.0, 128.8, 127.5, 117.5, 113.2, 61.7 (d, $J_{(P, C)}$ = 6.0 Hz), 61.6 (d, $J_{(P, C)}$ = 5.7 Hz), 59.4 (d, $J_{(P, C)}$ = 15.7 Hz), 20.8, 16.0 (d, $J_{(P, C)}$ = 6.3 Hz), 15.7 (d, $J_{(P, C)}$ = 6.6 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 ppm; IR (neat) ν 3308, 2978, 1601, 1513, 1498, 1317, 1021, 959, 794, 742, 692 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1708 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.19 min; t_R (major) = 6.94 min.

(*R*)-diethyl (3-(4-methoxyphenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4m)



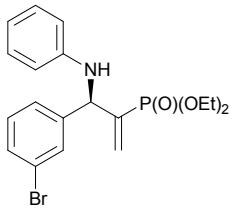
Light gray solid, 80% yield, m.p. 85-86 °C, 94% *ee*. $[\alpha]_D^{26}$ = -98.0 (c 0.50, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.8 Hz, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.70 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 7.6 Hz, 2H), 6.21 (d, *J* = 22.0 Hz, 1H), 6.12 (d, *J* = 46.4 Hz, 1H), 5.16 (d, *J* = 8.8 Hz, 1H), 4.68 (*br* s, 1H), 4.04-3.87 (m, 3H), 3.78 (s, 3H), 3.74-3.64 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.1, 146.1, 139.5 (d, $J_{(P, C)}$ = 170.9 Hz), 131.8 (d, $J_{(P, C)}$ = 2.8 Hz), 130.2 (d, $J_{(P, C)}$ = 8.2 Hz), 128.95, 128.90, 117.9, 113.8, 113.6, 61.8 (d, $J_{(P, C)}$ = 6.2 Hz), 61.7 (d, $J_{(P, C)}$ = 7.0 Hz), 59.4 (d, $J_{(P, C)}$ = 16.0 Hz), 55.1, 16.1 (d, $J_{(P, C)}$ = 6.5 Hz), 15.9 (d, $J_{(P, C)}$ = 6.5 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 ppm; IR (neat) ν 3317, 2983, 1602, 1510, 1304, 1271, 1233, 1185, 1177, 1027, 961, 747, 695 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_4P^+$: 376.1672, Found: 376.1660 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 9.17 min; t_R (major) = 10.74 min.

(*R*)-diethyl (3-(4-fluorophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4n)



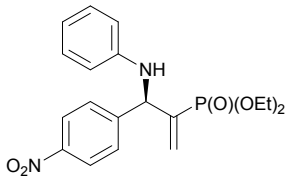
White solid, 70% yield, m.p. 93-94 °C 96% *ee*. $[\alpha]_D^{26}$ = -61.9 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.13 (t, *J* = 8.0 Hz, 2H), 7.02 (t, *J* = 9.2 Hz, 2H), 6.72-6.68 (m, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 21.6 Hz, 1H), 6.06 (d, *J* = 46.0 Hz, 1H), 5.21 (dd, *J* = 9.6, 4.4 Hz, 1H), 4.42 (d, *J* = 4.4 Hz, 1H), 4.05-3.88 (m, 3H), 3.79-3.69 (m, 1H), 1.24 (t, *J* = 6.8 Hz, 3H), 1.10 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1 (d, $J_{(F,\ C)}$ = 245.4 Hz), 146.2, 139.5 (d, $J_{(P,\ C)}$ = 171.4 Hz), 135.8 (dd, $J_{(P,\ C)}$ = 3.1 Hz, $J_{(F,\ C)}$ = 3.1 Hz), 130.5 (d, $J_{(P,\ C)}$ = 8.9 Hz), 129.2 (d, $J_{(F,\ C)}$ = 8.2 Hz), 128.9, 117.8, 115.3 (d, $J_{(F,\ C)}$ = 22.2 Hz), 113.3, 61.9 (d, $J_{(P,\ C)}$ = 5.3 Hz), 61.8 (d, $J_{(P,\ C)}$ = 6.1 Hz), 59.1 (d, $J_{(P,\ C)}$ = 15.2 Hz), 16.0 (d, $J_{(P,\ C)}$ = 6.4 Hz), 15.9 (d, $J_{(P,\ C)}$ = 6.2 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.5 ppm; IR (neat) ν 3308, 2981, 1601, 1519, 1498, 1236, 1216, 1157, 1016, 960, 793, 751, 695 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{24}FNO_3P^+$: 364.1472, Found: 364.1475 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 6.96 min; t_R (major) = 7.75 min.

(*R*)-diethyl (3-(3-bromophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4o)



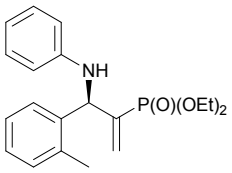
Colorless oil, 84% yield, 98% *ee*. $[\alpha]_D^{26}$ = -60.1 (c 1.00, $CHCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 7.6 Hz, 1H), 7.20 (t, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 8.4 Hz, 2H), 6.71(t, *J* = 7.2 Hz, 1H), 6.57 (d, *J* = 7.6 Hz, 2H), 6.23 (d, *J* = 21.6 Hz, 1H), 6.05 (d, *J* = 46.4 Hz, 1H), 5.19 (dd, *J* = 10.4, 4.8 Hz, 1H), 4.47 (d, *J* = 5.2 Hz, 1H), 4.06-3.89 (m, 3H), 3.82-3.73 (m, 1H), 1.24 (t, *J* = 6.8 Hz, 3H), 1.12 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.1, 142.4 (d, $J_{(P,\ C)}$ = 3.3 Hz), 139.2 (d, $J_{(P,\ C)}$ = 172.4 Hz), 131.1 (d, $J_{(P,\ C)}$ = 8.6 Hz), 130.7, 130.5, 130.0, 129.0, 126.2, 122.5, 117.9, 113.3, 61.9 (d, $J_{(P,\ C)}$ = 6.2 Hz), 61.8 (d, $J_{(P,\ C)}$ = 6.2 Hz), 59.4 (d, $J_{(P,\ C)}$ = 16.9 Hz), 16.0 (d, $J_{(P,\ C)}$ = 6.6 Hz), 15.8 (d, $J_{(P,\ C)}$ = 7.4 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.6 ppm; IR (neat) ν 3318, 2980, 1600, 1499, 1309, 1236, 1018, 962, 797, 747, 691 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{24}BrNO_3P^+$: 424.0672, Found: 424.0656$[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel IC column; n-Hex/*i*-PrOH = 95:5, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (major) = 23.5 min; t_R (minor) = 25.3 min.

(*R*)-diethyl (3-(4-nitrophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4p)



Yellow oil, 75% yield, >99% *ee*. $[\alpha]_D^{26}$ = -5.5 (c 1.00, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.6 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.23 (d, *J* = 21.6 Hz, 1H), 5.99 (d, *J* = 45.2 Hz, 1H), 5.35 (dd, *J* = 12.4, 5.2 Hz, 1H), 4.69 (d, *J* = 5.2 Hz, 1H), 4.07-3.86 (m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.6 (d, $J_{(P, C)}$ = 3.1 Hz), 147.2, 145.9, 139.2 (d, $J_{(P, C)}$ = 174.0 Hz), 131.6 (d, $J_{(P, C)}$ = 7.9 Hz), 129.0, 128.3, 123.6, 118.3, 113.4, 62.2 (d, $J_{(P, C)}$ = 5.9 Hz), 62.0 (d, $J_{(P, C)}$ = 6.1 Hz), 59.5 (d, $J_{(P, C)}$ = 13.9 Hz), 16.0 (d, $J_{(P, C)}$ = 6.4 Hz), 15.9 (d, $J_{(P, C)}$ = 6.5 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.4 ppm; IR (neat) ν 3409, 3320, 2982, 2923, 2851, 1600, 1519, 1344, 1314, 1236, 1017, 968, 854, 795, 750, 693 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{19}H_{24}N_2O_5P^+$: 391.1417, Found: 391.1415 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel IC−3 column; n-Hex/*i*-PrOH = 80:20, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 18.16 min; t_R (major) = 19.89 min.

(*R*)-diethyl (3-(phenylamino)-3-(*o*-tolyl)prop-1-en-2-yl)phosphonate (4q)



Light yellow oil, 40% yield, 94% *ee*. $[\alpha]_D^{26}$ = -25.0 (c 1.00, $CHCl_3$) ^1H NMR (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 1H), 7.25-7.12 (m, 5H), 6.70(t, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 2H), 6.28 (d, *J* = 22.0 Hz, 1H), 6.03 (d, *J* = 46.8 Hz, 1H), 5.43 (d, *J* = 6.8 Hz, 1H), 4.08-3.89 (m, 3H), 3.73-3.64 (m, 1H), 2.38 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.06 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.5, 139.8 (d, $J_{(P, C)}$ = 171.7 Hz), 137.8 (d, $J_{(P, C)}$ = 3.6 Hz), 136.3, 130.8 (d, $J_{(P, C)}$ = 8.3 Hz), 130.6, 129.1, 127.7, 127.0, 126.2, 117.6, 113.0, 61.9, 61.8, 55.4 (d, $J_{(P, C)}$ = 16.4 Hz), 19.2, 16.2 (d, $J_{(P, C)}$ = 6.8 Hz), 15.9 (d, $J_{(P, C)}$ = 7.0 Hz) ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.8 ppm; IR (neat) ν 3321, 2980, 1601, 1500, 1241, 1049, 1021, 965, 799, 749, 692 cm^{-1}; HRMS (ESI) m/z: calcd. for $C_{20}H_{27}NO_3P^+$: 360.1723, Found: 360.1722 $[M+H]^+$. The *ee* value was determined by HPLC analysis using a Chiralcel OD−H column; n-Hex/*i*-PrOH = 90:10, 1.0 mL/min, UV-vis detection at λ = 254 nm; t_R (minor) = 5.46 min; t_R (major) = 6.36 min.

4. Determination of absolute configurations of the amination products 4a-q

The absolute configuration of (*R*)-**4d** was determined by X-ray single-crystal diffractional analysis, while those of **4a-c** and **4e-q** were all found to the (*R*) by comparison of their CD spectra with that of (*R*)-**4d** (*vide infra*).

4. 1. Crystal structural data of (R)-4d

Single crystals of (*R*)-**4d** were obtained by recrystallization from ethyl acetate/petroleum ether. The X-ray diffractional data and the refinement were shown in Table S3, and the solid-state structure was shown in Figure S1.

Table S2. X-ray Crystallographic Data for (*R*)-4d

Empirical formula	C_{19} H_{23} Br N O_3 P
Temperature	133(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Orthorhombic, P 21 21 2
Unit cell dimensions	a = 9.8916(7) Å α = 90°. b = 26.4389(19) Å β = 90°. c = 7.7778(6) Å γ = 90°.
Volume	2034.1(3) $Å^3$
Z, Calculated density	4, 1.385 Mg/m^3
Absorption coefficient	2.116 mm^{-1}
F(000)	872
Crystal size	0.300 x 0.250 x 0.100 mm^3
Theta range for data collection	1.540 to 30.535°.
Index ranges	-14<=h<=13, -37<=k<=37, -11<=l<=11
Reflections collected	20495
Independent reflections	6186 [R(int) = 0.0361]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5154
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6186 / 12 / 228
Goodness-of-fit on F^2	1.092
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1077
R indices (all data)	R1 = 0.0629, wR2 = 0.1145
Absolute structure parameter	0.024(5)
Extinction coefficient	n/a
Largest diff. peak and hole	1.535 and -0.681 $e.Å^{-3}$

CIF file of (*R*)-**4d** can be obtained from the Cambridge Crystallographic Data Centre using deposition number 1012761. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

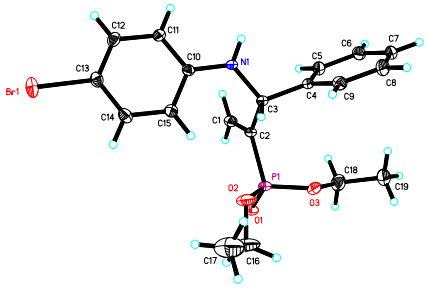
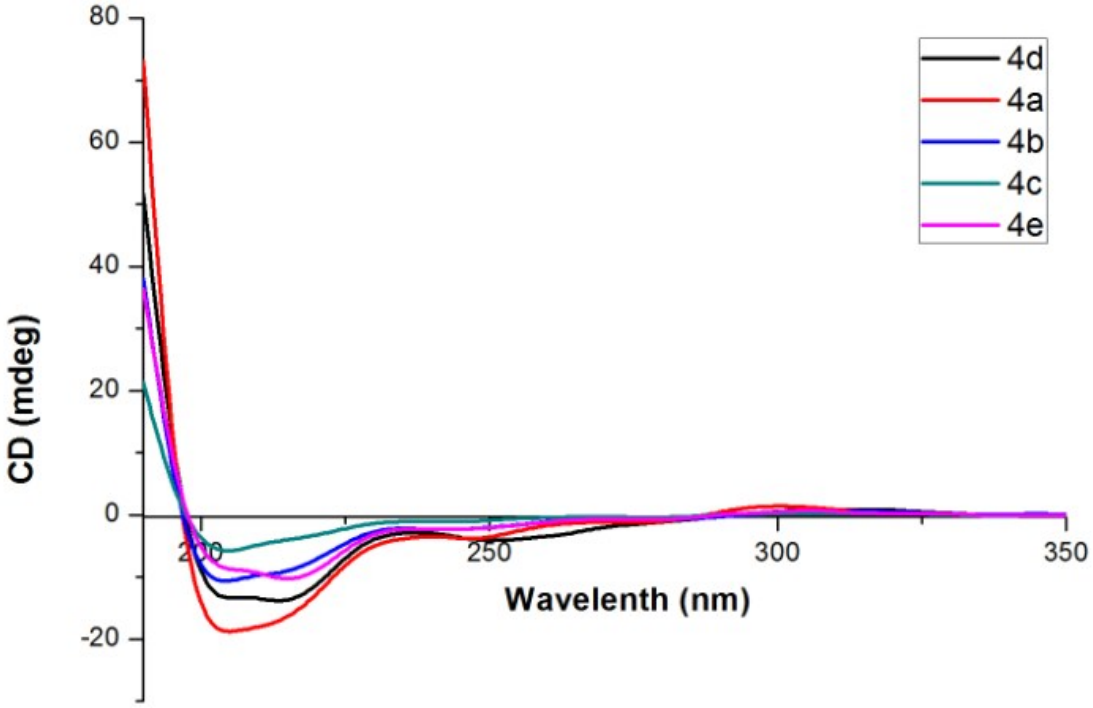


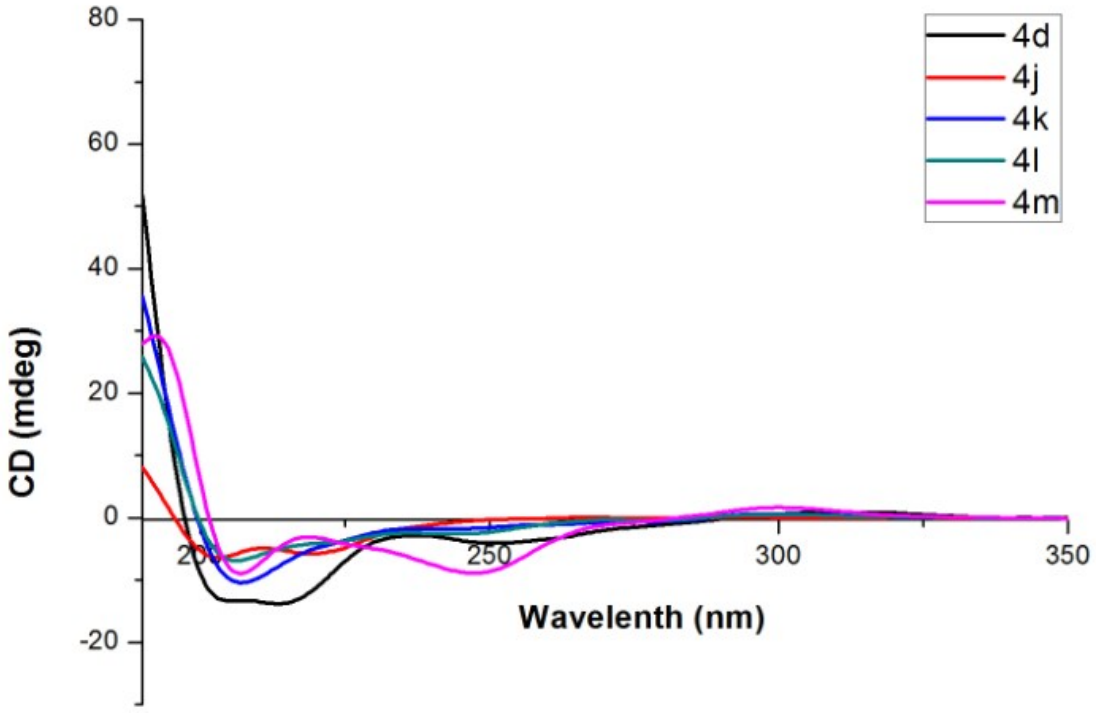
Figure S1. X-ray single crystal structure of (*R*)-**4d**

4. 2. CD spectra of the amination products 4a-q

Electronic circular dichroism (ECD) was applied for the determination of absolute configurations of the amination products 4a-q, and the assignments were made on the basis of their CD spectra (Figure S2) measured in their acetonitrile solutions with uv-vis wavelength ranging from 190-350 nm.




80
60
40
20
0
-20
CD (mdeg)
200
250
300
350
Wavelenth (nm)
4d
4f
4g
4h
4i


80
60
40
20
0
-20
CD (mdeg)
250
300
350
Wavelenth (nm)
4d
4j
4k
4l
4m

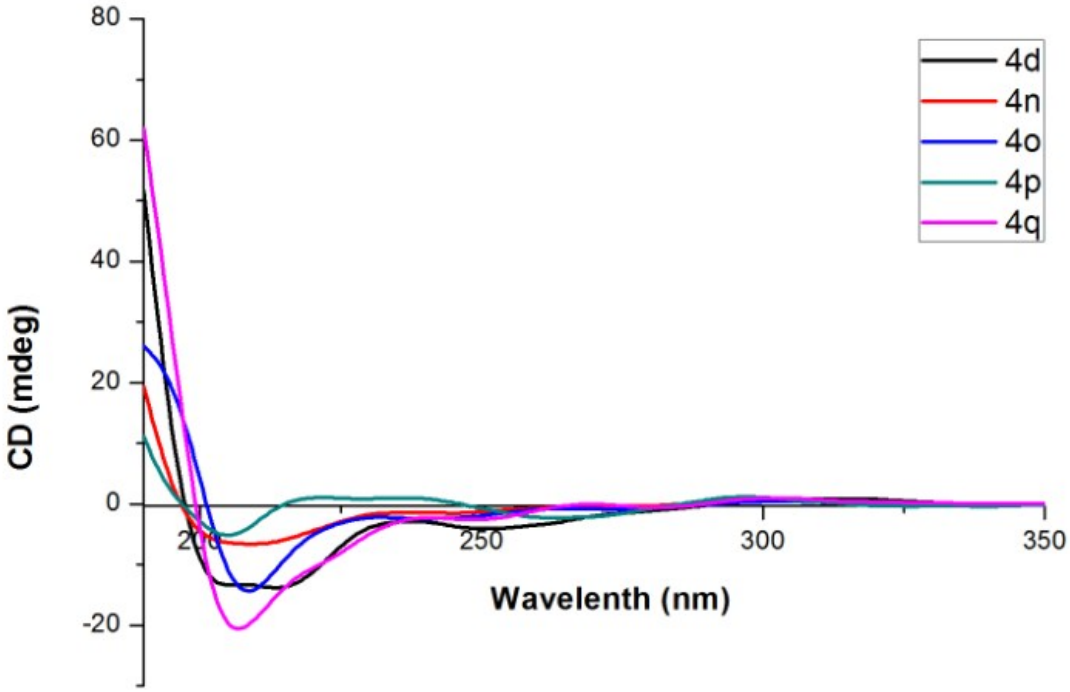


Figure S2. CD spectra of 4a-q measured in acetonitrile solutions

References

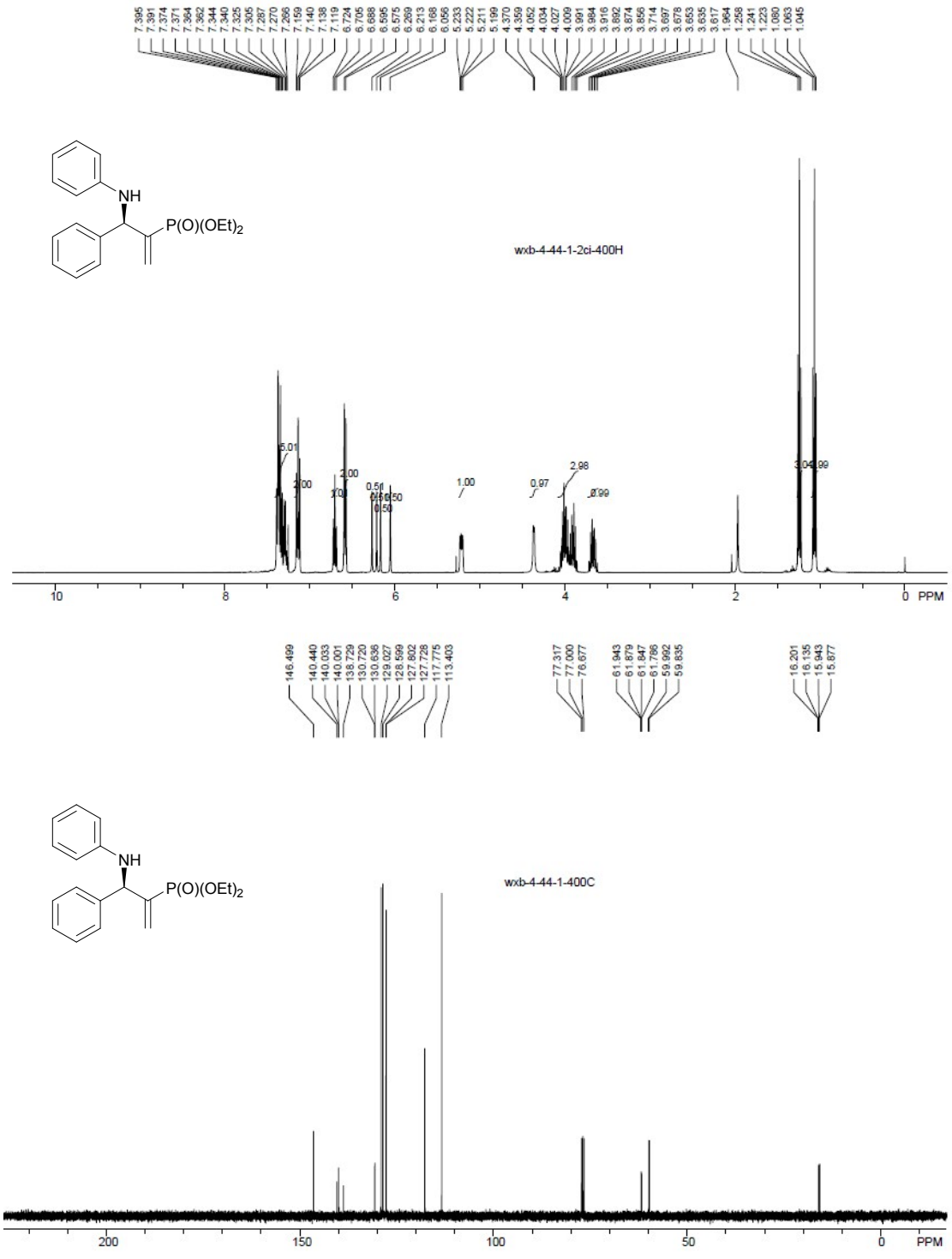
[1] a) X. Wang, Z. Han, Z. Wang, K. Ding, *Angew. Chem. Int. Ed.* **2012**, *51*, 936; b) X. Wang, P. Guo, X. Wang, Z. Wang, K. Ding, *Adv. Synth. Catal.* **2013**, *355*, 2900; c) X. Wang, F. Meng, Y. Wang, Z. Han, Y.-J. Chen, L. Liu, Z. Wang, K. Ding, *Angew. Chem. Int. Ed.* **2012**, *51*, 9276.

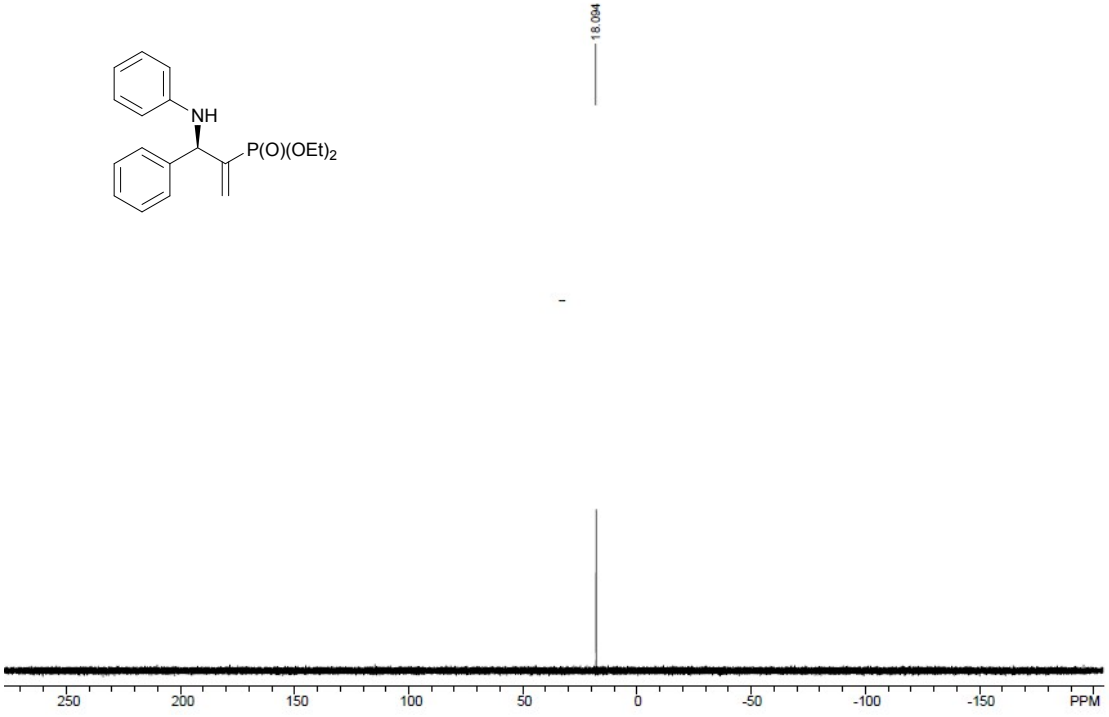
[2] H. Park, C.-W. Cho, M. J. Krische, *J. Org. Chem.* **2006**, *71*, 7892.

[3] B. Zhu, L. Yan, Y. Pan, R. Lee, H. Liu, Z. Han, K.-W. Huang, C.-H. Tan, Z. Jiang, *J. Org. Chem.* **2011**, *76*, 6894.

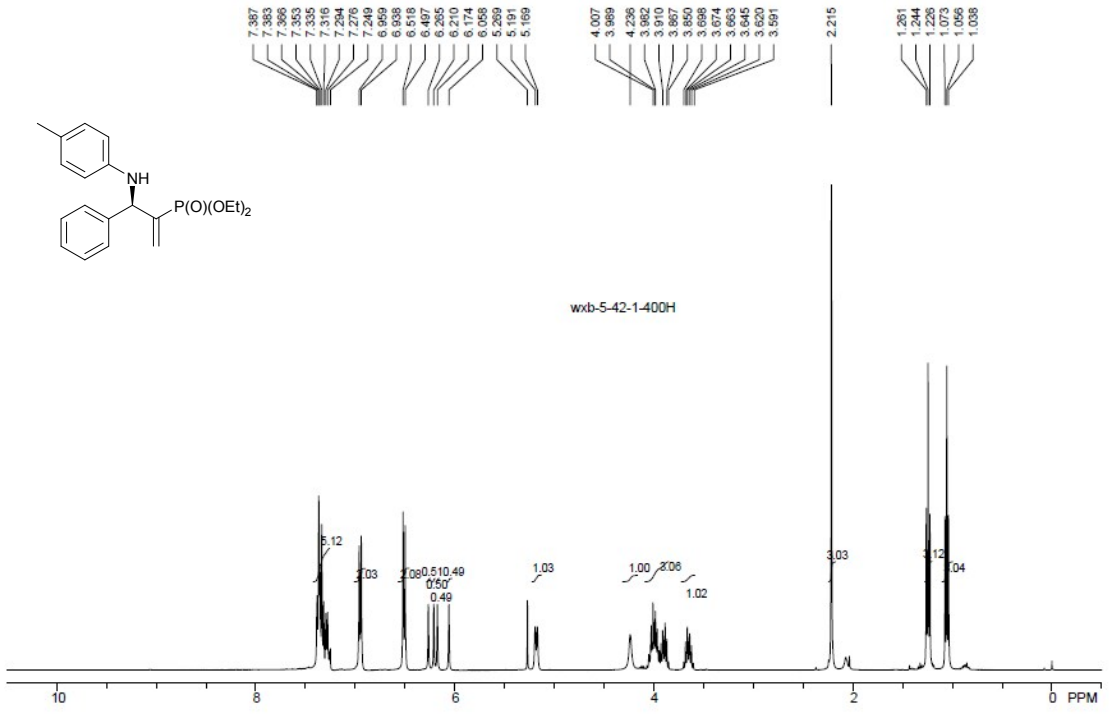
NMR spectra of 4a-q

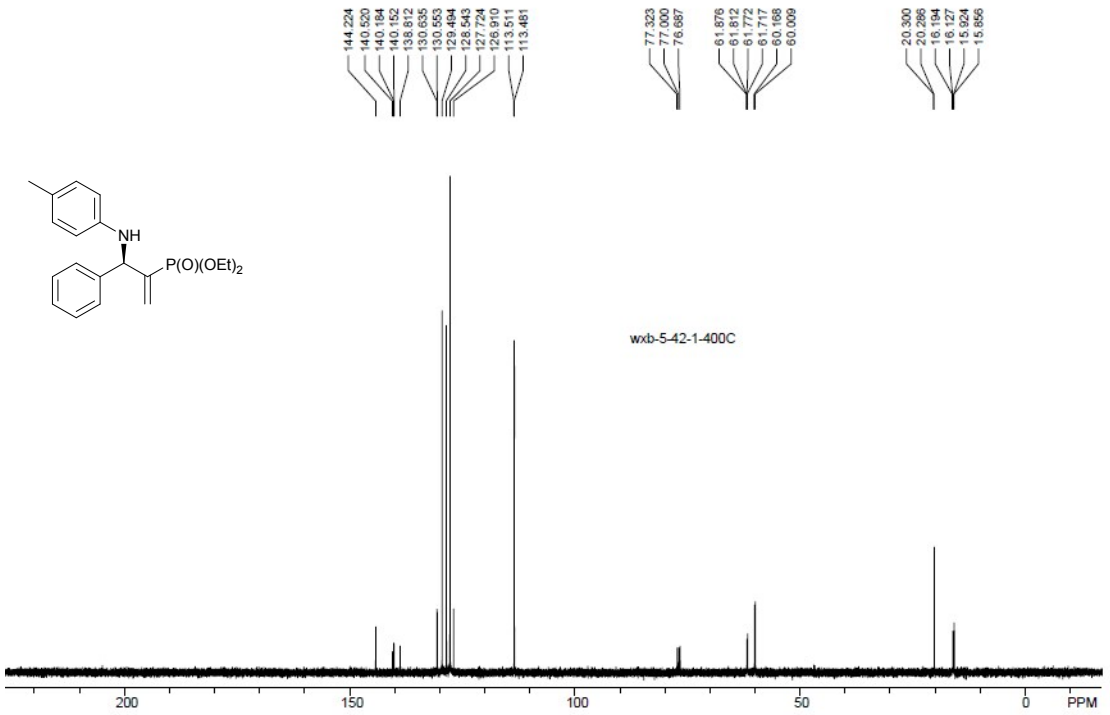
diethyl (3-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (4a)





diethyl (3-phenyl-3-(p-tolylamino)prop-1-en-2-yl)phosphonate (4b)

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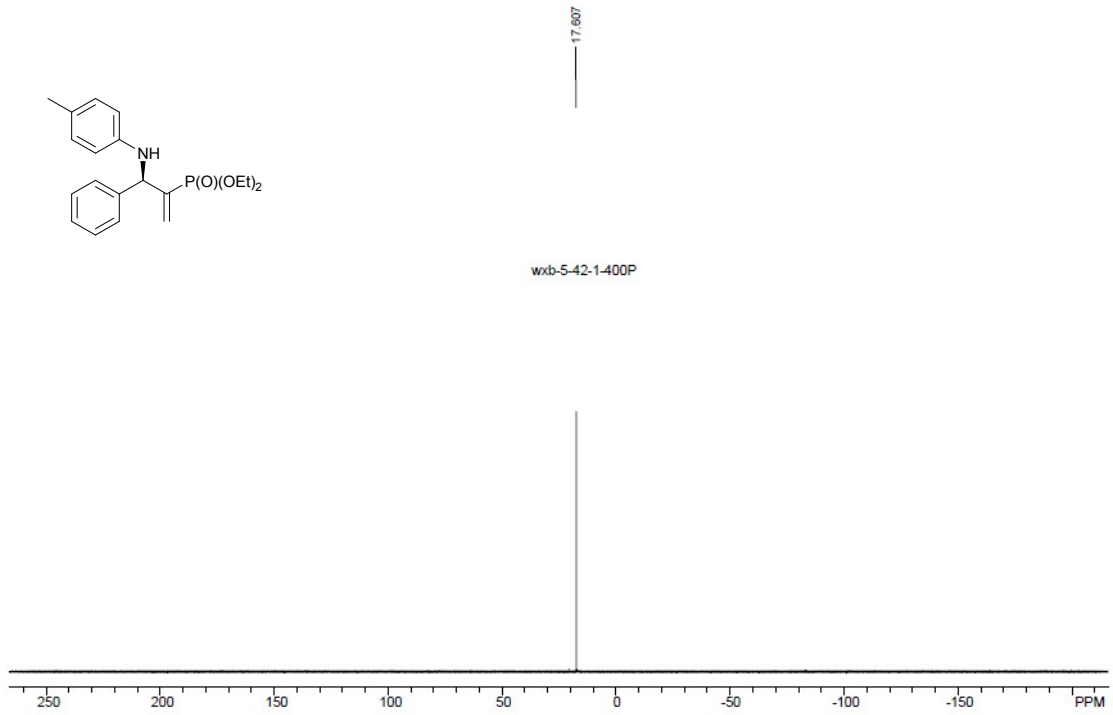
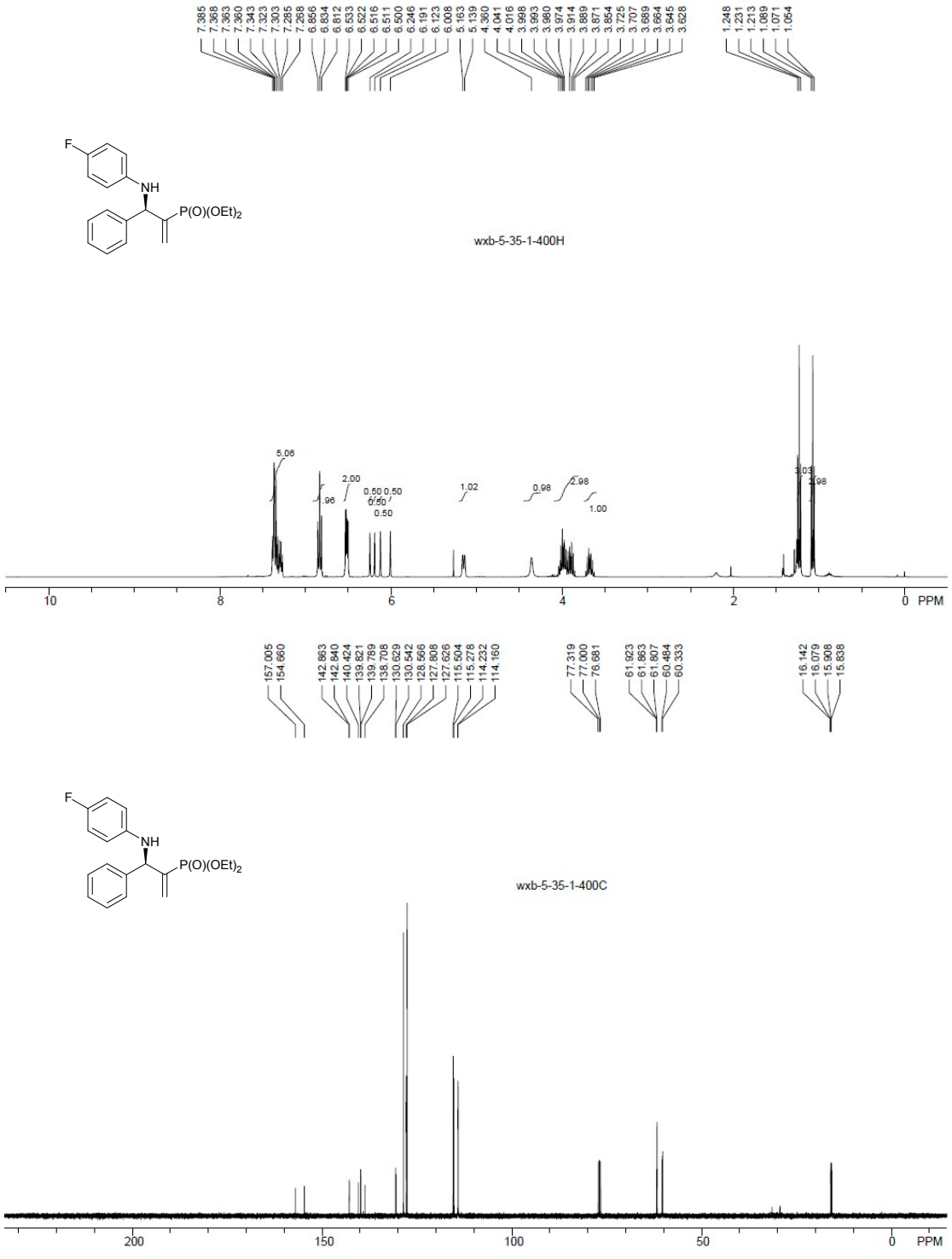
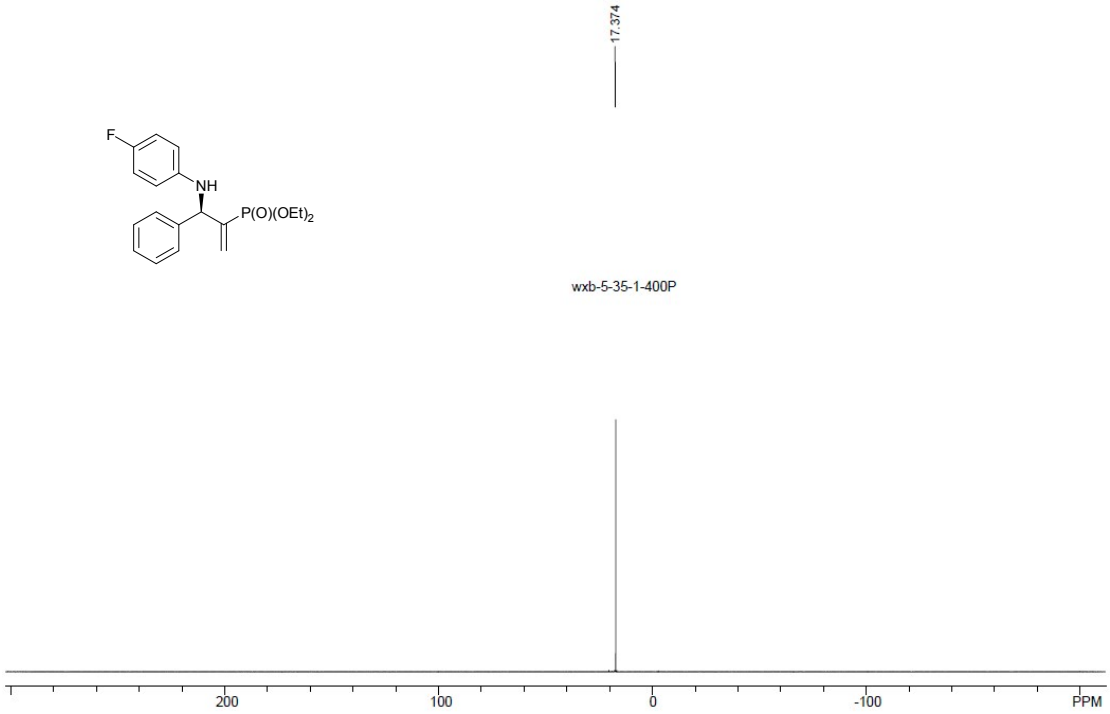
140.184
140.152
138.812
130.635
130.553
129.494
128.543
127.724
126.910
113.511
113.481
77.323
77.000
76.687
61.878
61.812
61.772
61.717
60.168
60.009
20.300
20.286
16.194
16.127
15.924
15.856
NH
P(O)(OEt)2
wxb-5-42-1-400C
200
150
100
50
0
PPM


17.607
NH
P(O)(OEt)2
wxb-5-42-1-400P
250
200
150
100
50
0
-50
-100
-150
PPM

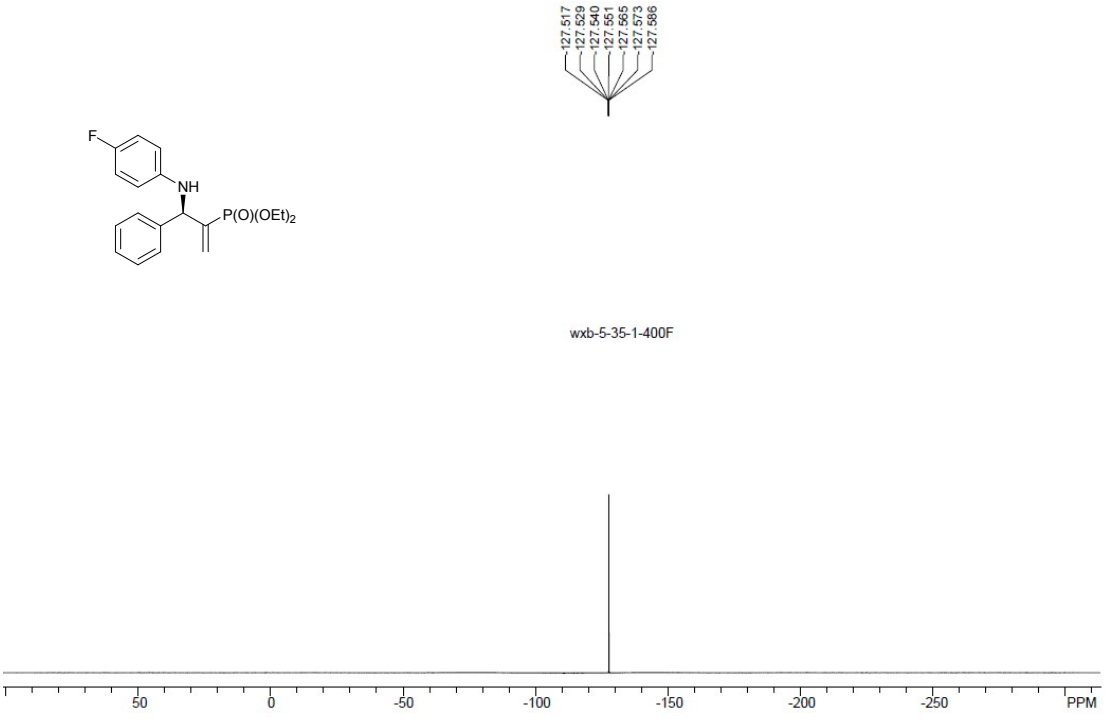
diethyl (3-((4-fluorophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4c)



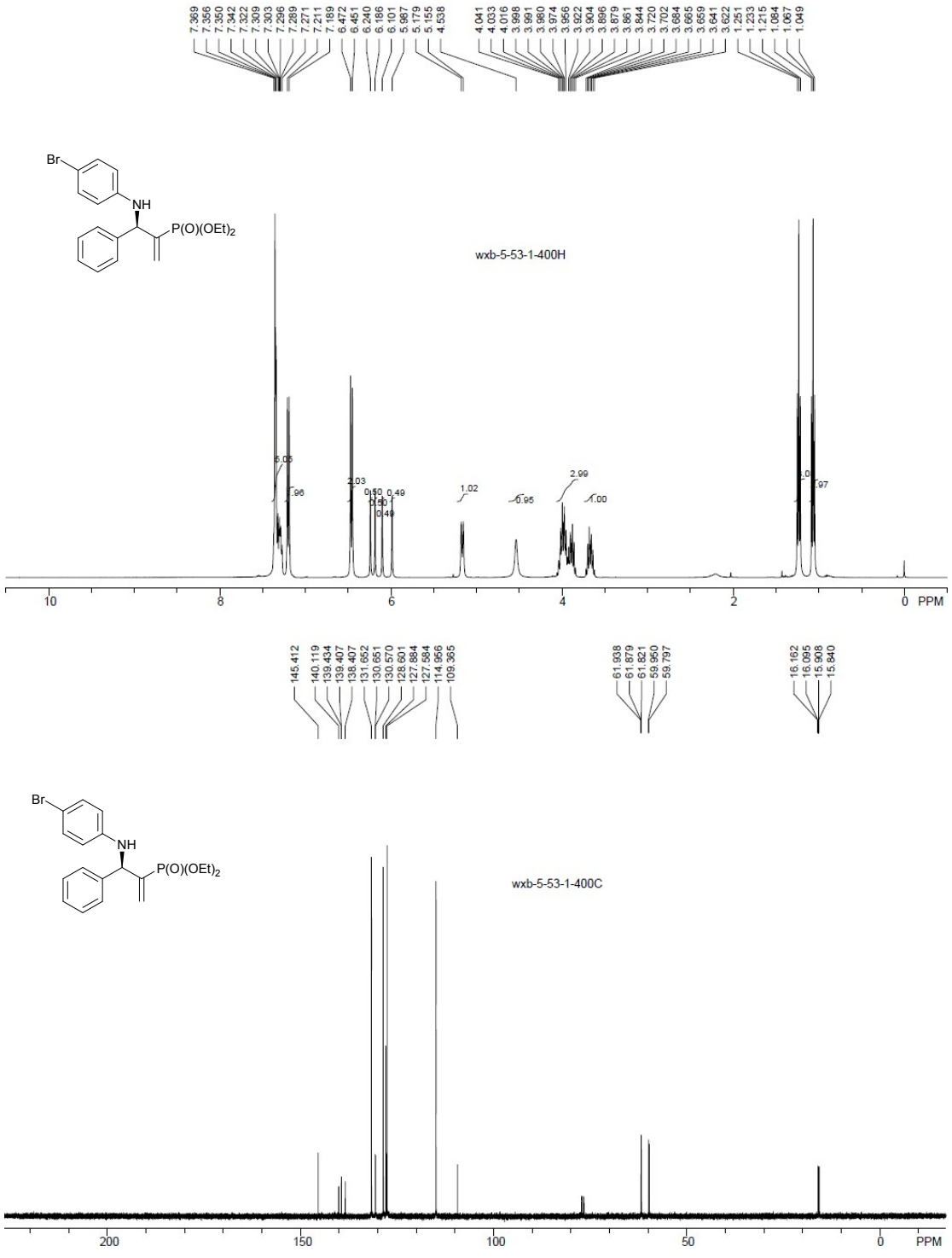
F
NH
P(O)(OEt)2

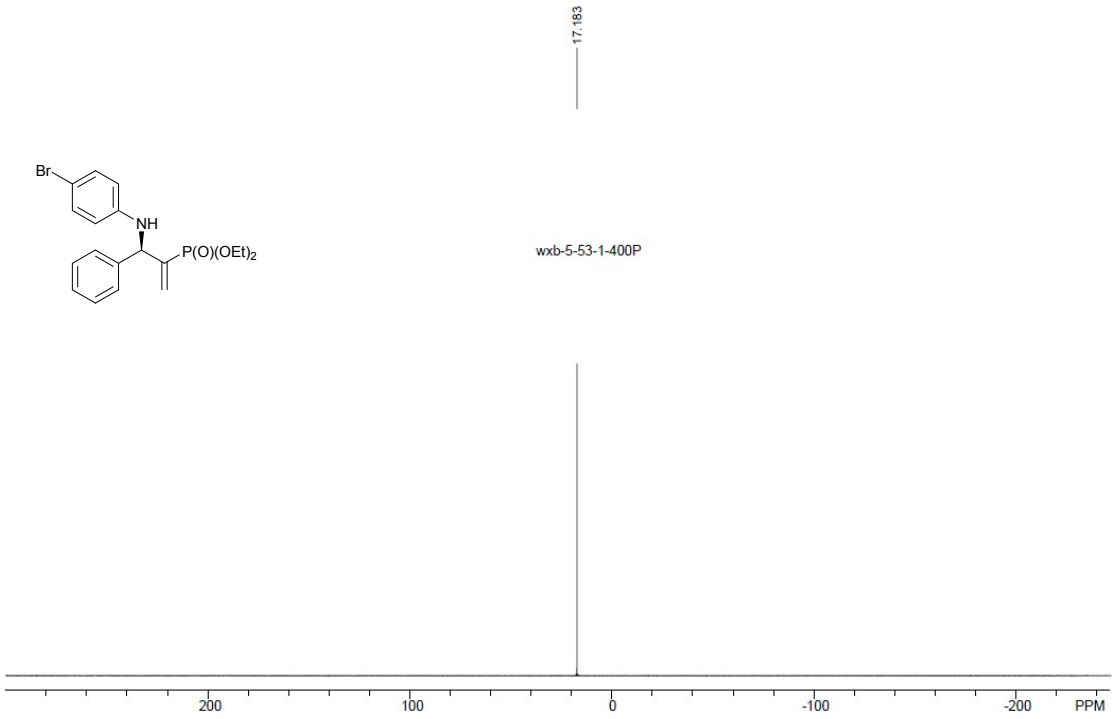

17.374
wxb-5-35-1-400P
200
100
0
-100
PPM

F
NH
P(O)(OEt)2

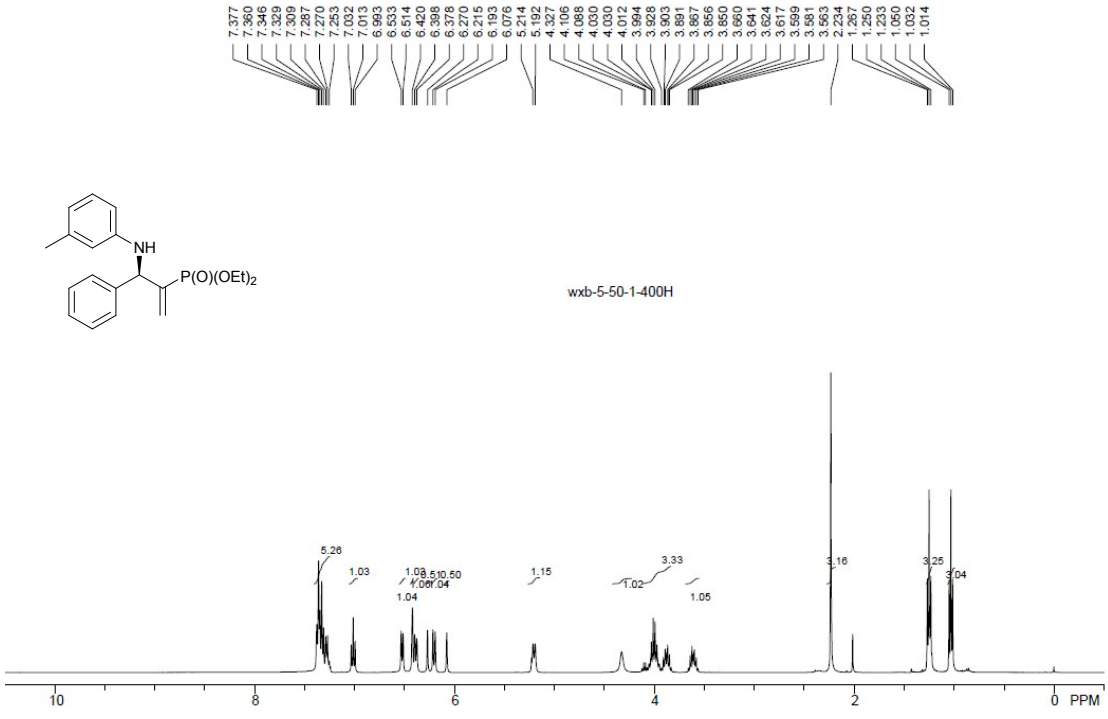

127.517
127.529
127.540
127.551
127.565
127.573
127.586
wxb-5-35-1-400F
50
0
-50
-100
-150
-200
-250
PPM

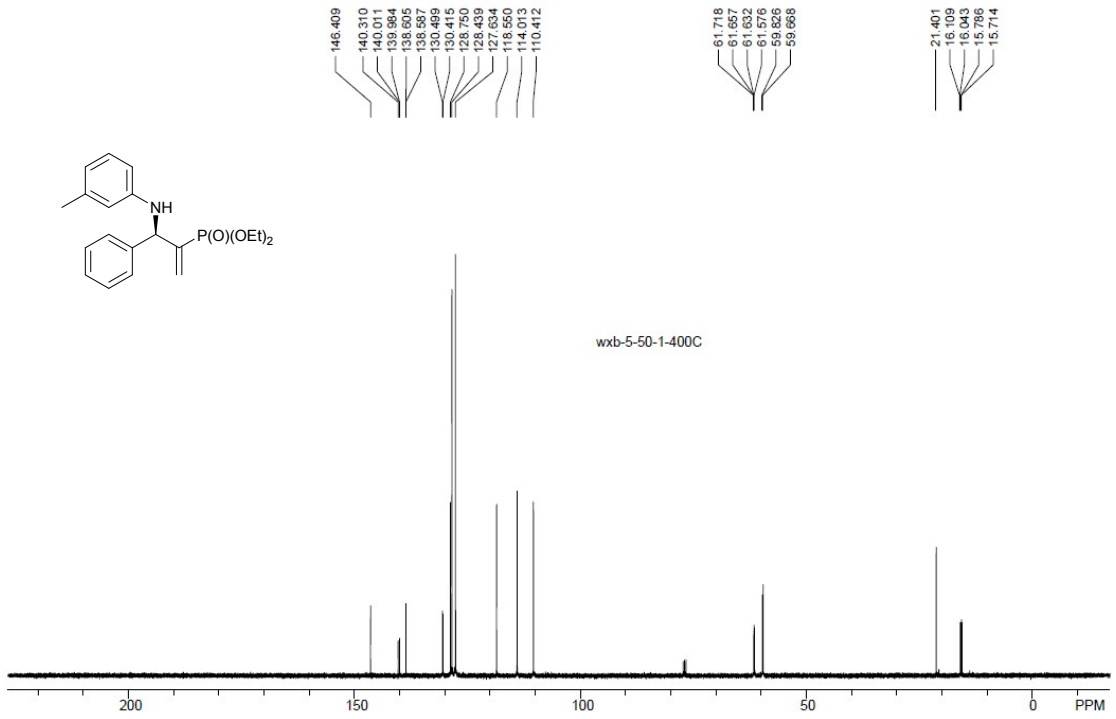
diethyl (3-((4-bromophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4d)





diethyl (3-phenyl-3-(m-tolylamino)prop-1-en-2-yl)phosphonate (4e)

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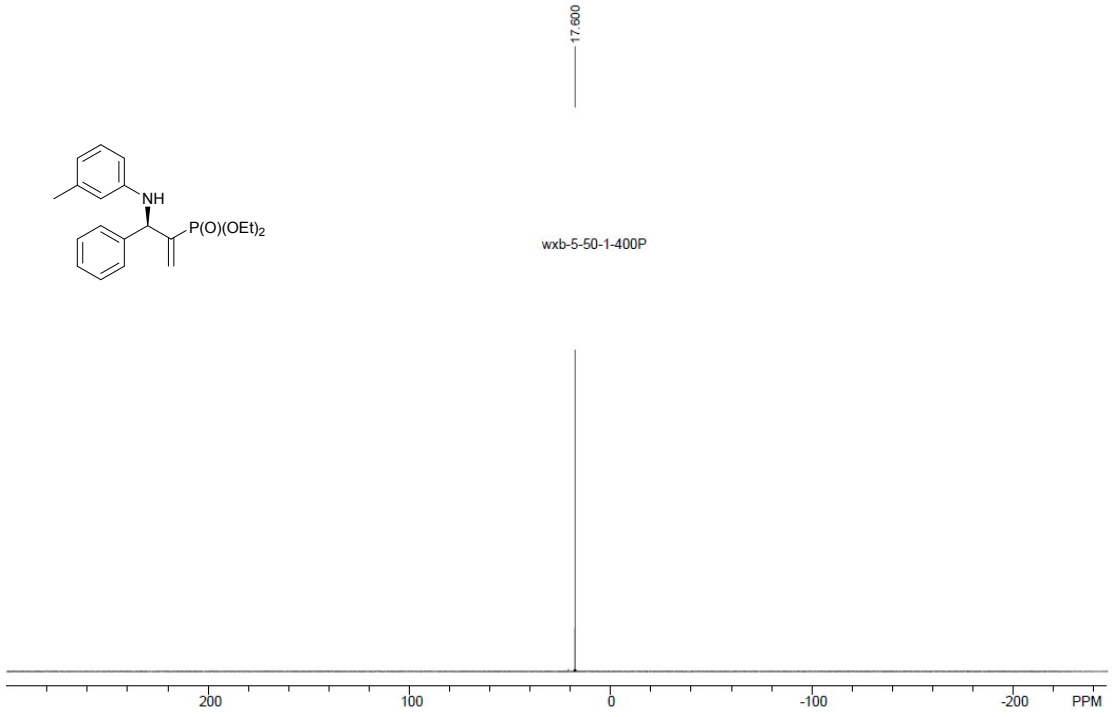
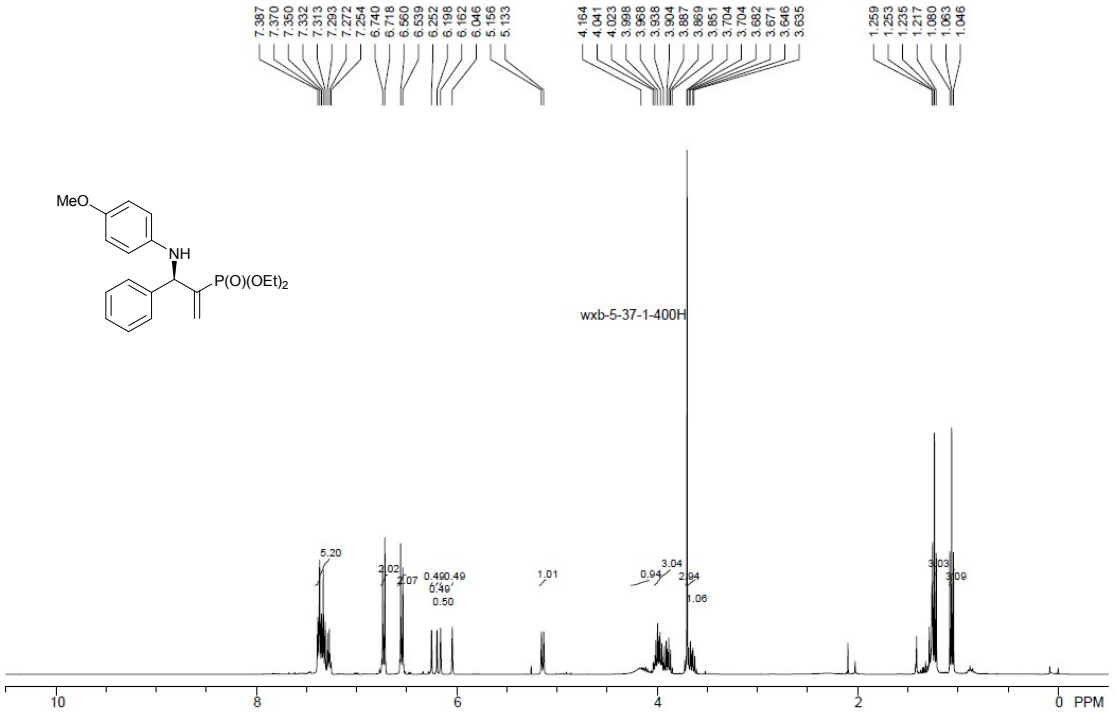
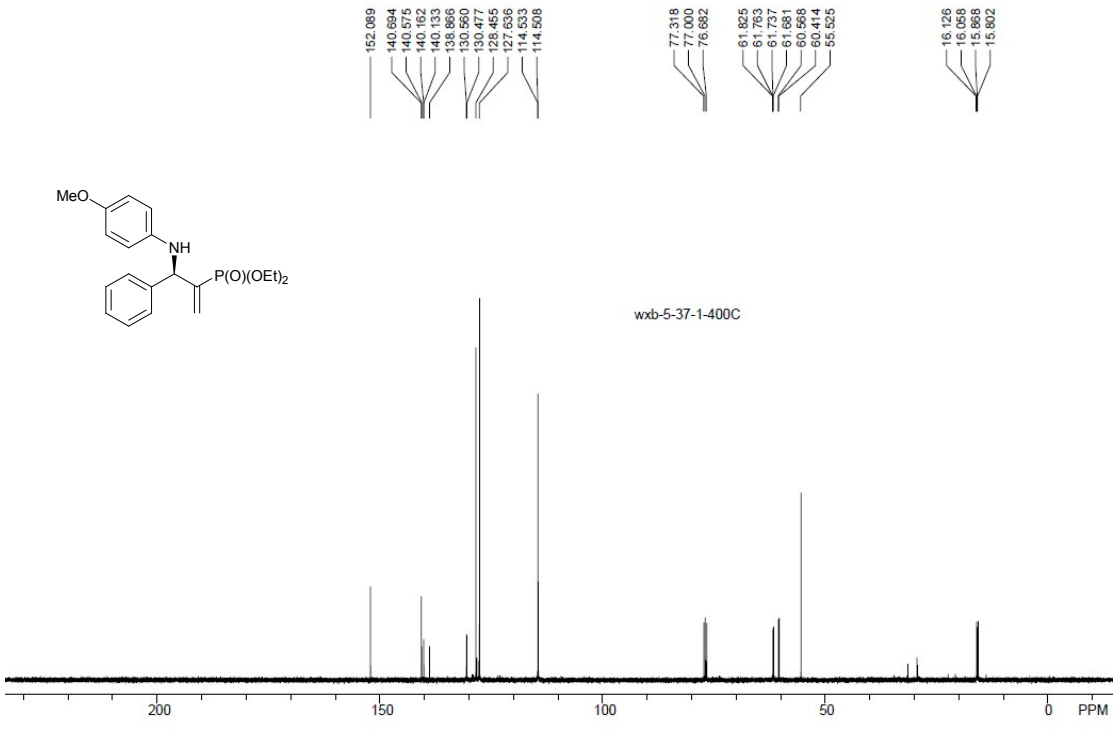
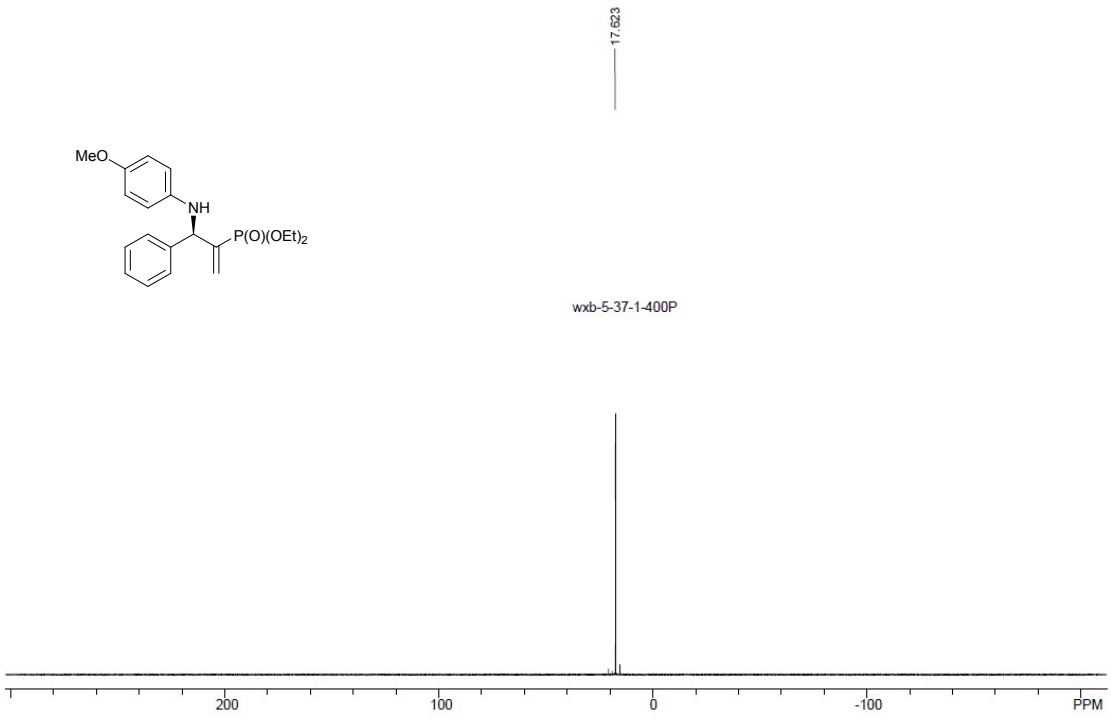
140.310
140.011
139.984
138.605
138.587
130.499
130.415
128.750
128.439
127.634
118.550
114.013
110.412
61.718
61.657
61.632
61.576
59.826
59.668
21.401
16.109
16.043
15.786
15.714
NH
P(O)(OEt)2
wxb-5-50-1-400C
200
150
100
50
0
PPM


17.600
NH
P(O)(OEt)2
wxb-5-50-1-400P
200
100
0
-100
-200
PPM

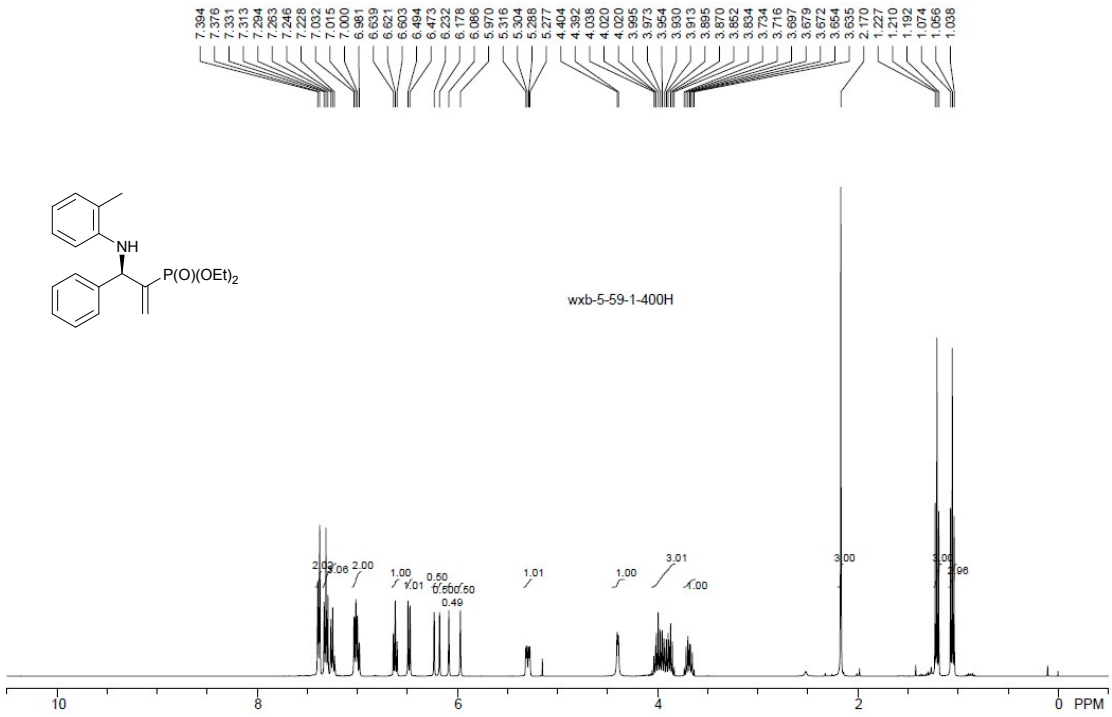
diethyl (3-((4-methoxyphenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4f)

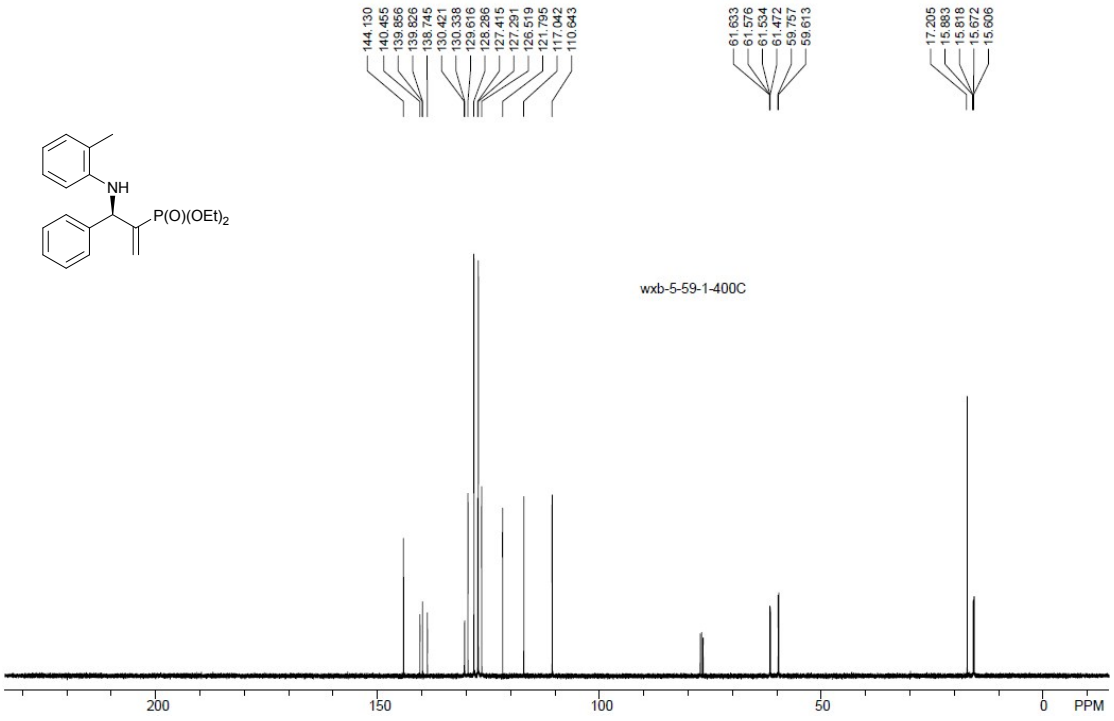


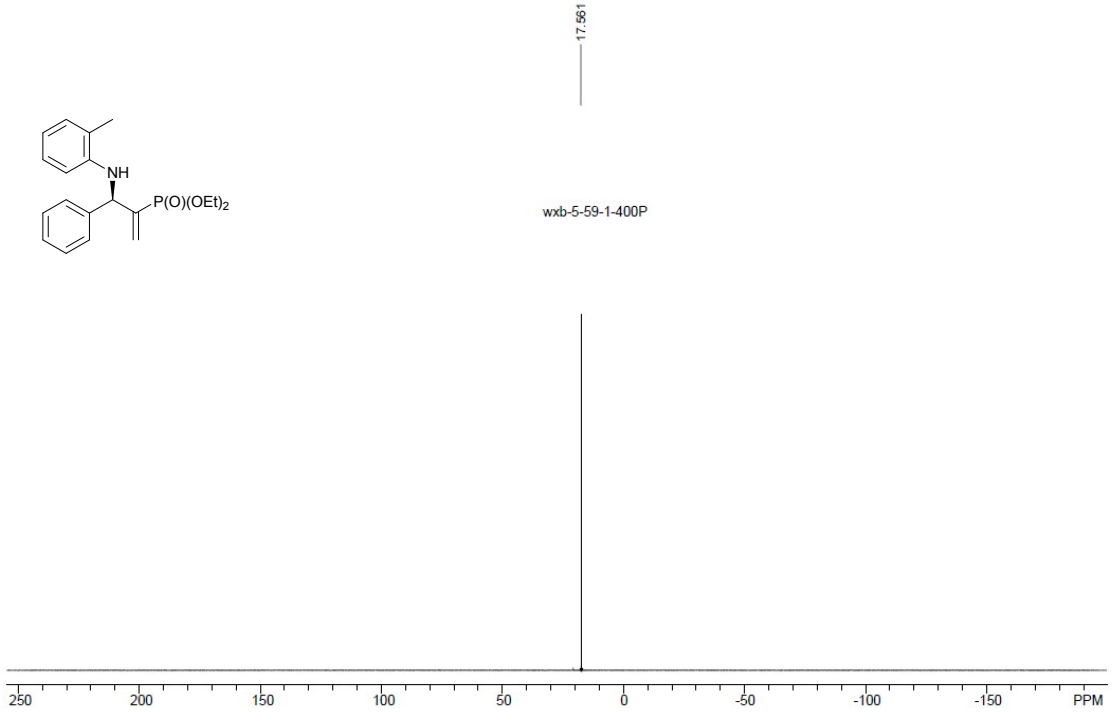




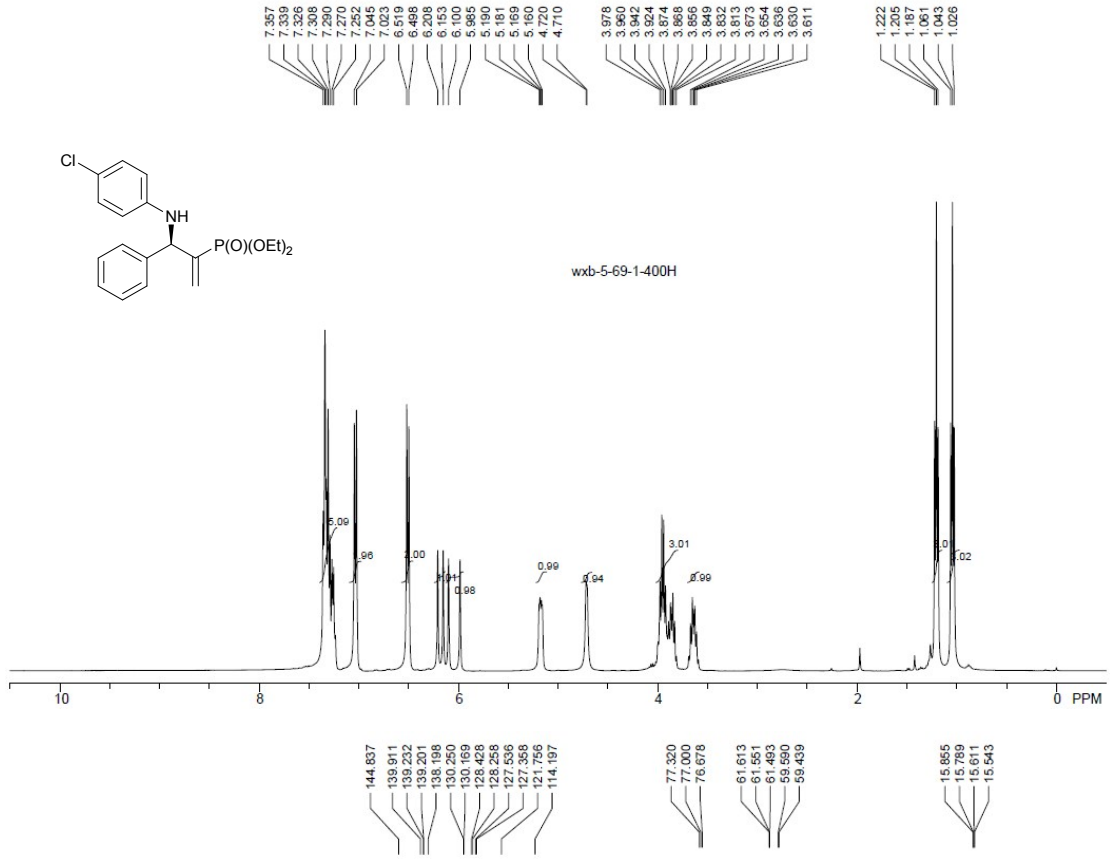
diethyl (3-phenyl-3-(o-tolylamino)prop-1-en-2-yl)phosphonate (4g)

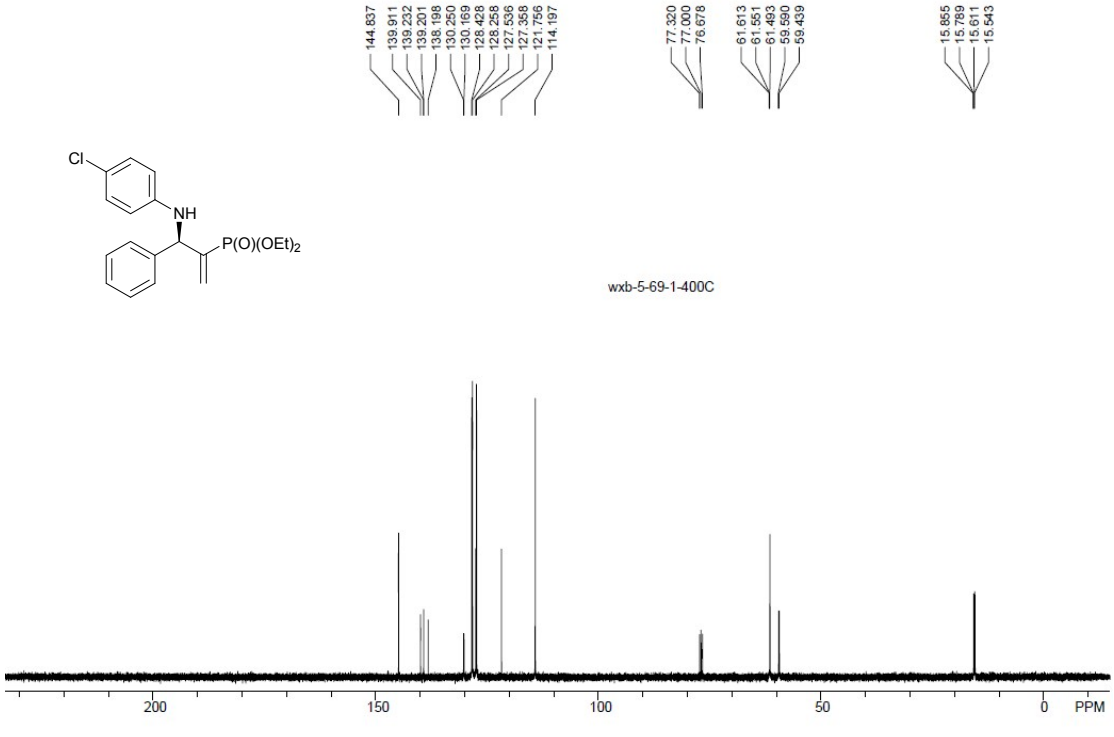


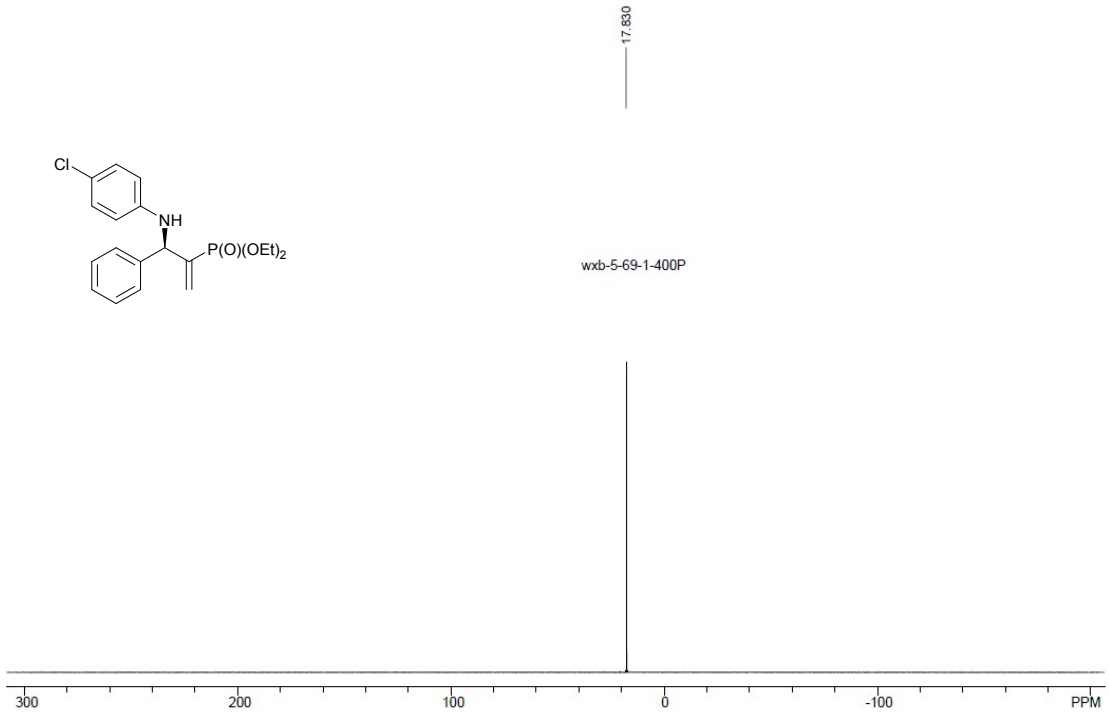

144.130
140.455
139.856
139.826
138.745
130.421
130.338
129.616
128.286
127.415
127.291
126.519
121.795
117.042
110.643
61.633
61.576
61.534
61.472
59.757
59.613
17.205
15.883
15.818
15.672
15.606
NH
P(O)(OEt)2
wxb-5-59-1-400C
200
150
100
50
0
PPM


17.561
NH
P(O)(OEt)2
wxb-5-59-1-400P
250
200
150
100
50
0
-50
-100
-150
PPM

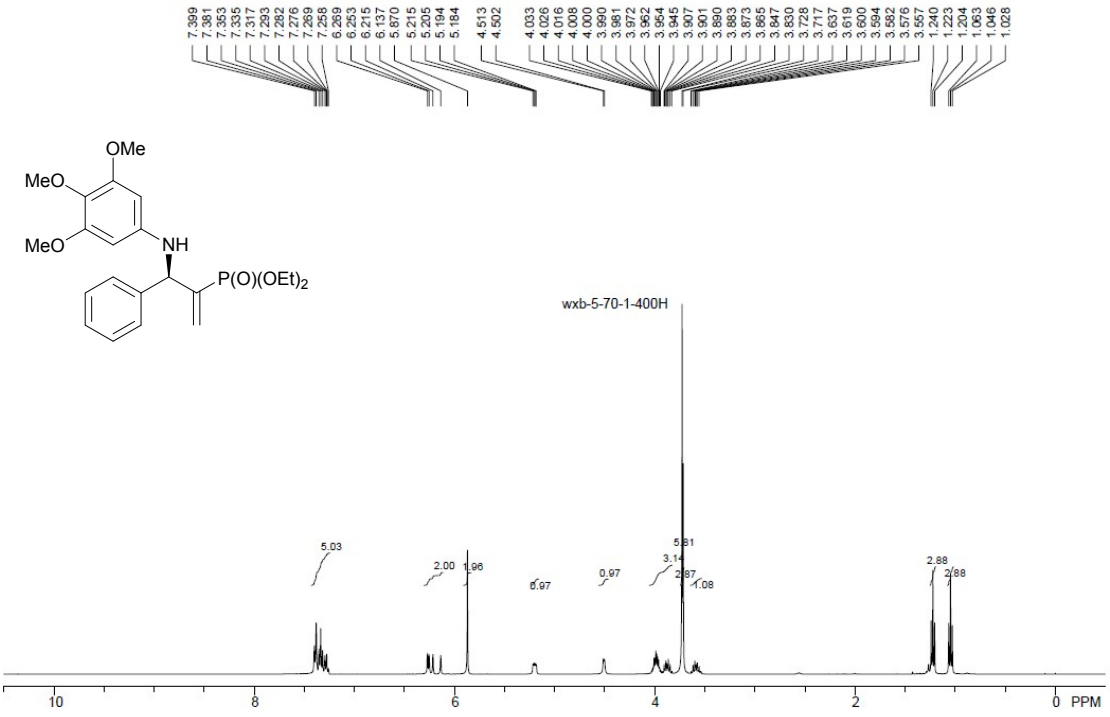
diethyl (3-((4-chlorophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4h)

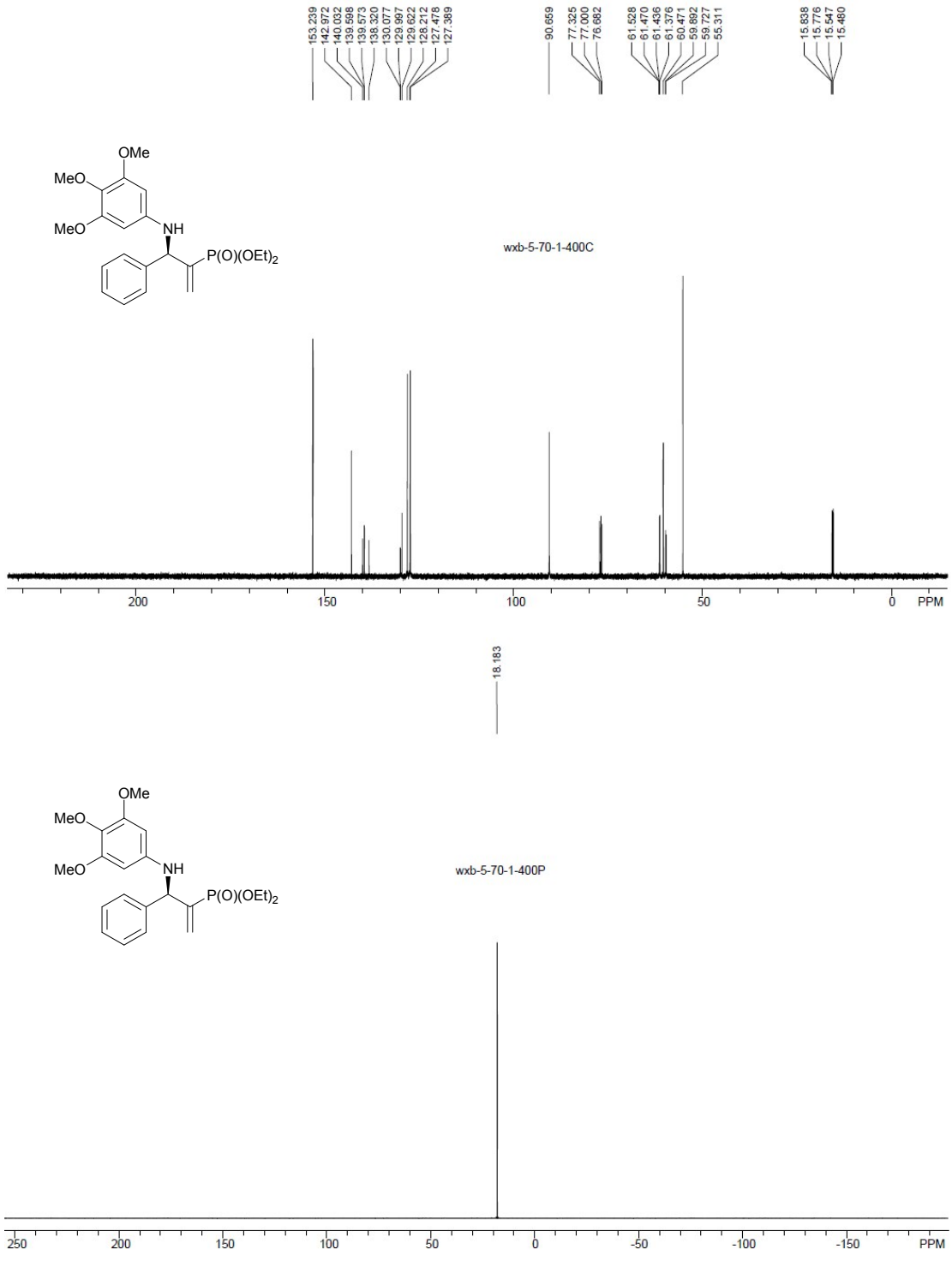






diethyl (3-phenyl-3-((3,4,5-trimethoxyphenyl)amino)prop-1-en-2-yl)phosphonate (4i)

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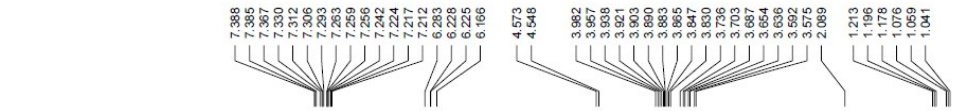
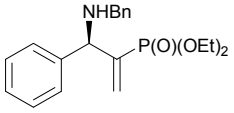
140.032
139.598
139.573
138.320
130.077
129.997
129.622
128.212
127.478
127.389
90.659
77.325
77.000
76.682
61.528
61.470
61.436
61.376
60.471
59.892
59.727
55.311
15.638
15.776
15.547
15.480
OMe
MeO
MeO
NH
P(O)(OEt)2
wxb-5-70-1-400C
200
150
100
50
0
PPM
18.183
OMe
MeO
MeO
NH
P(O)(OEt)2
wxb-5-70-1-400P
250
200
150
100
50
0
-50
-100
-150
PPM

diethyl (3-(benzylamino)-3-phenylprop-1-en-2-yl)phosphonate (4j)





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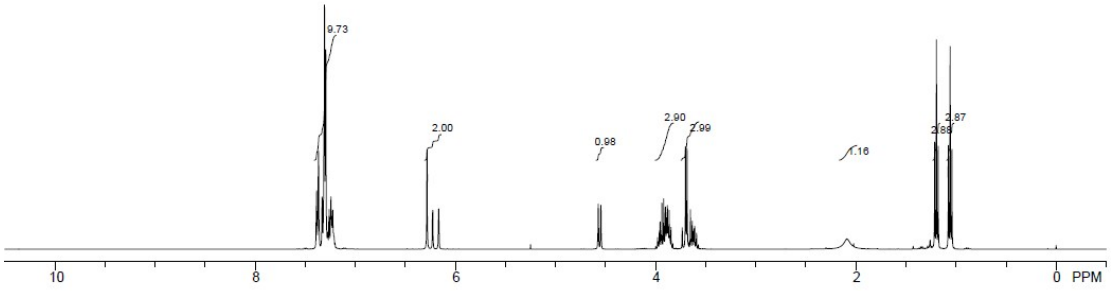
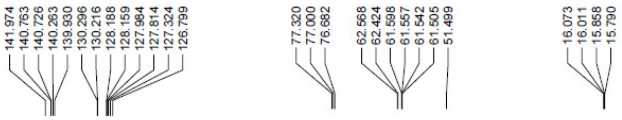
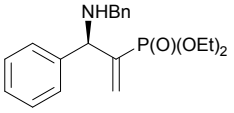
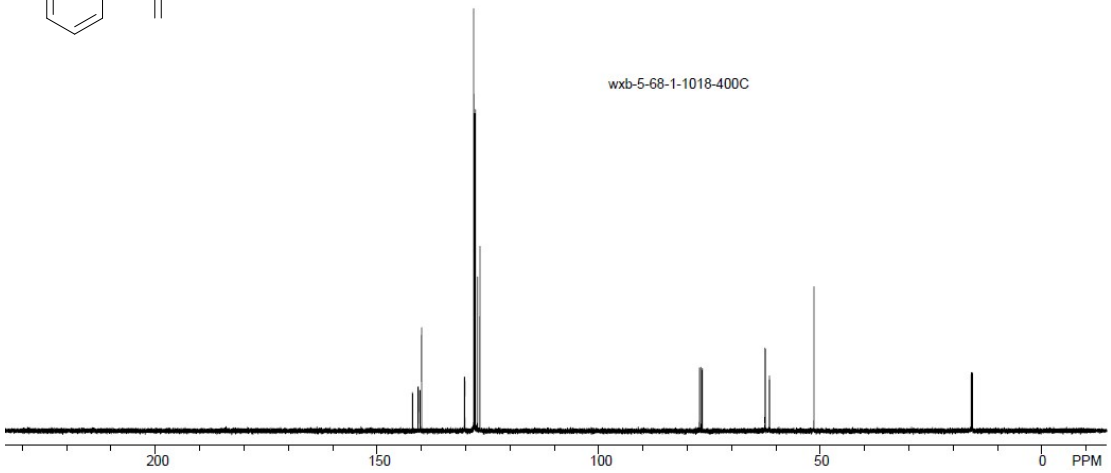
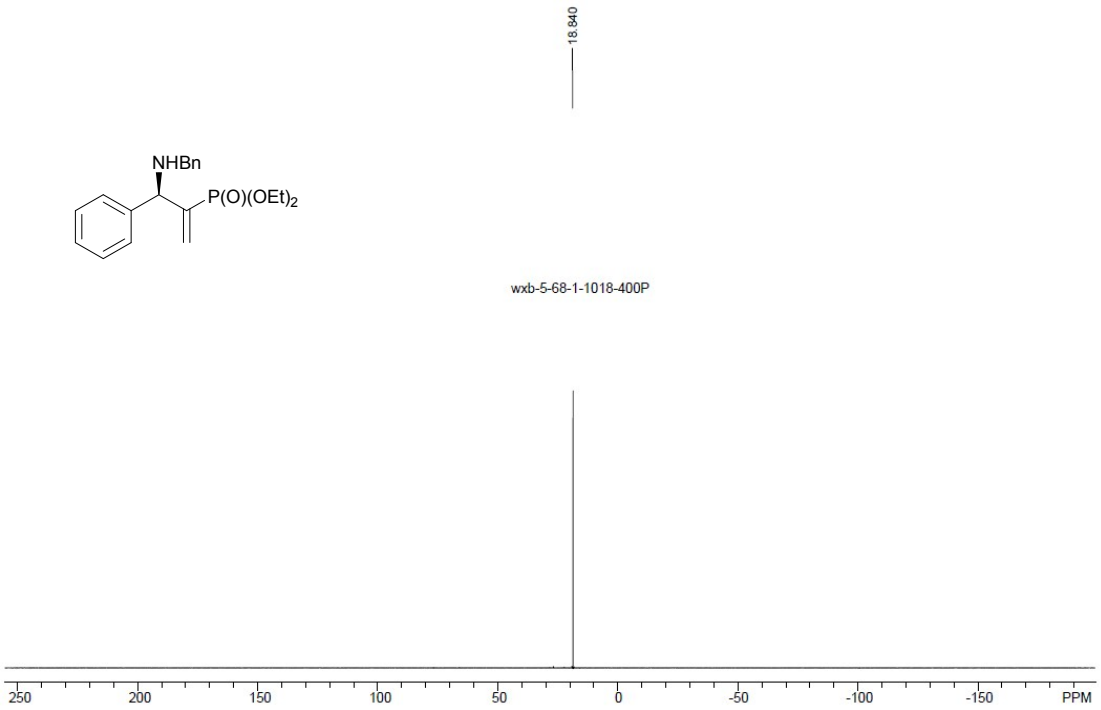




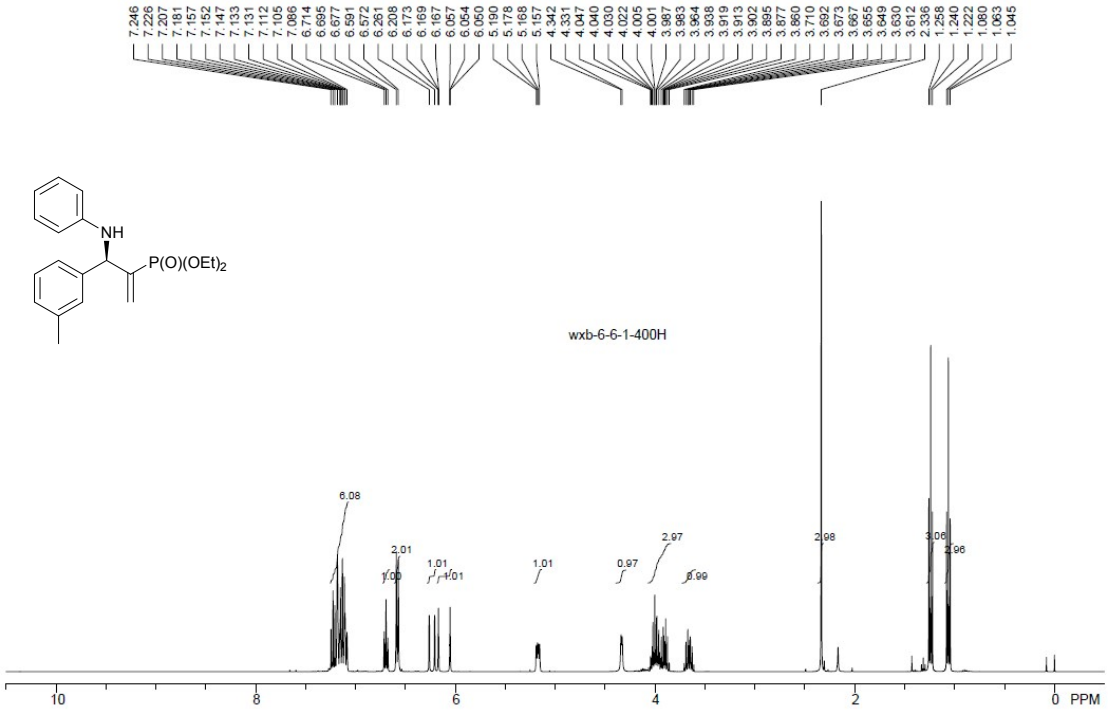


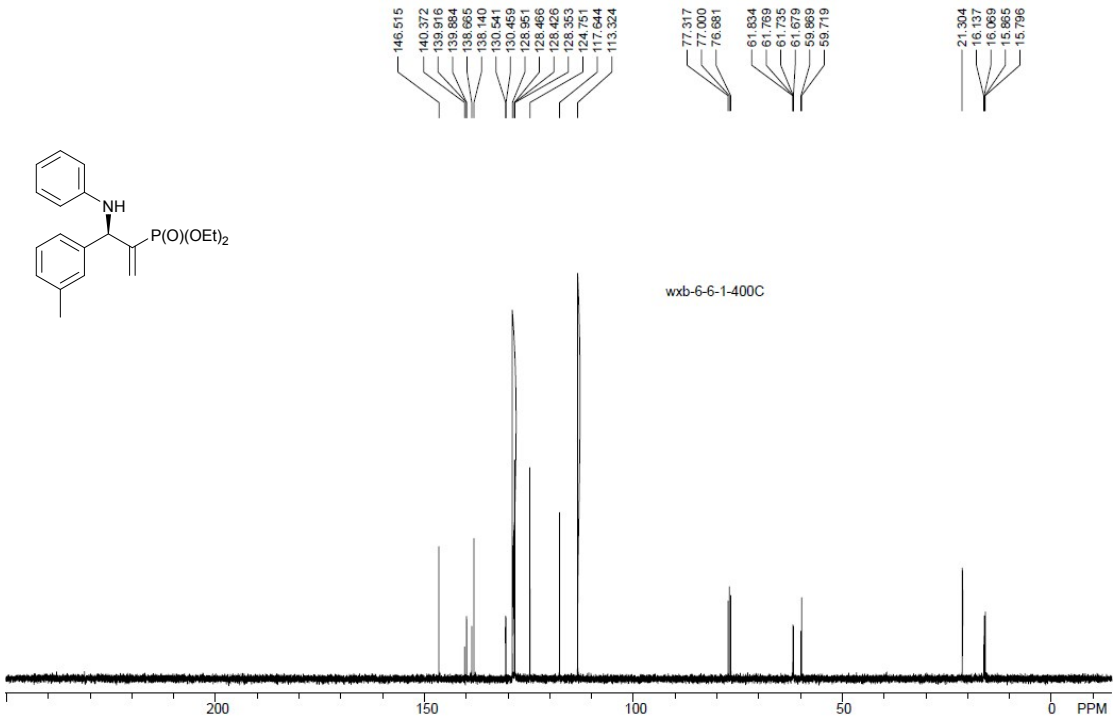
wxb-5-68-1-1018-400C





diethyl (3-(phenylamino)-3-(m-tolyl)prop-1-en-2-yl)phosphonate (4k)

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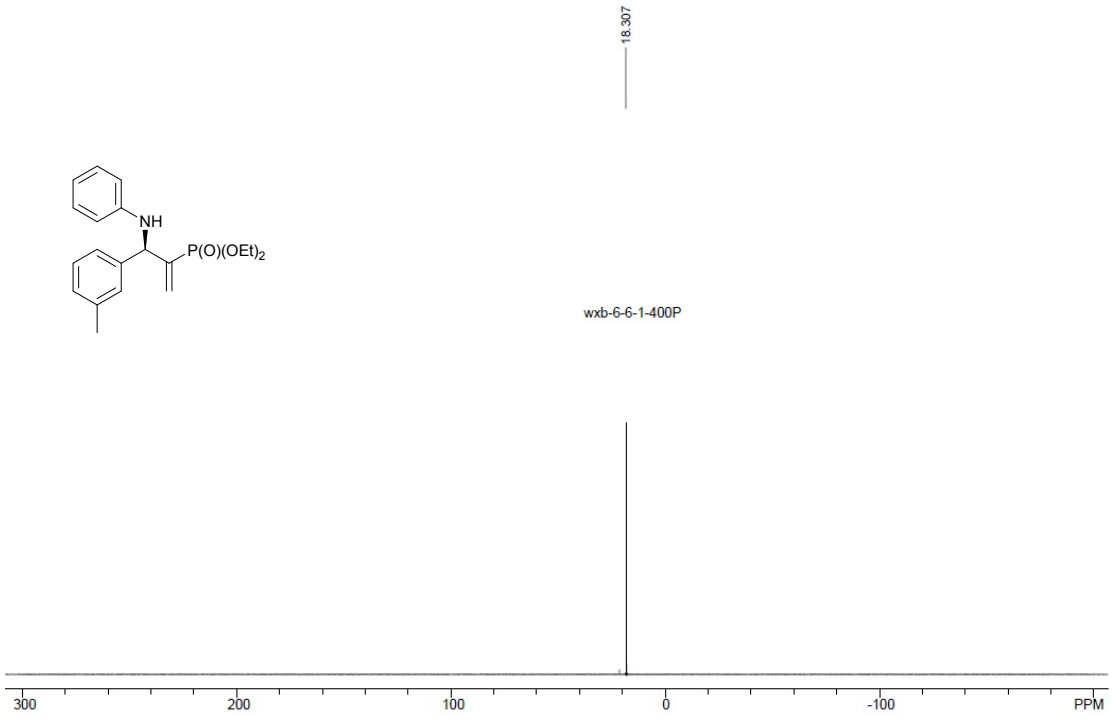
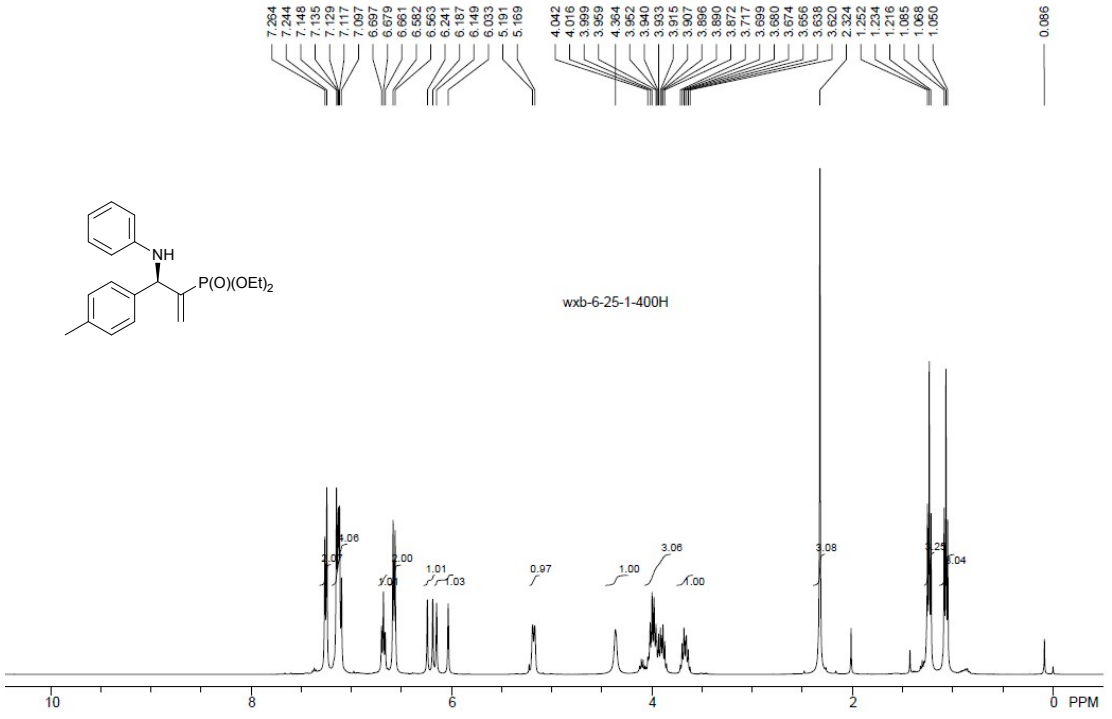
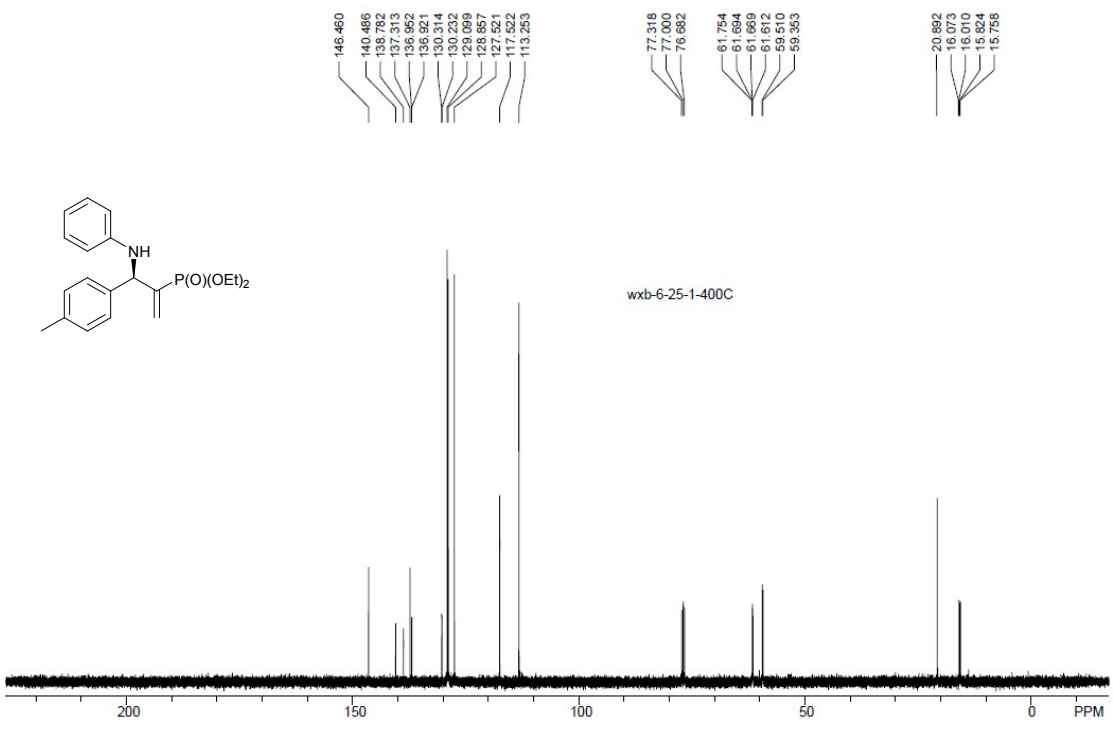
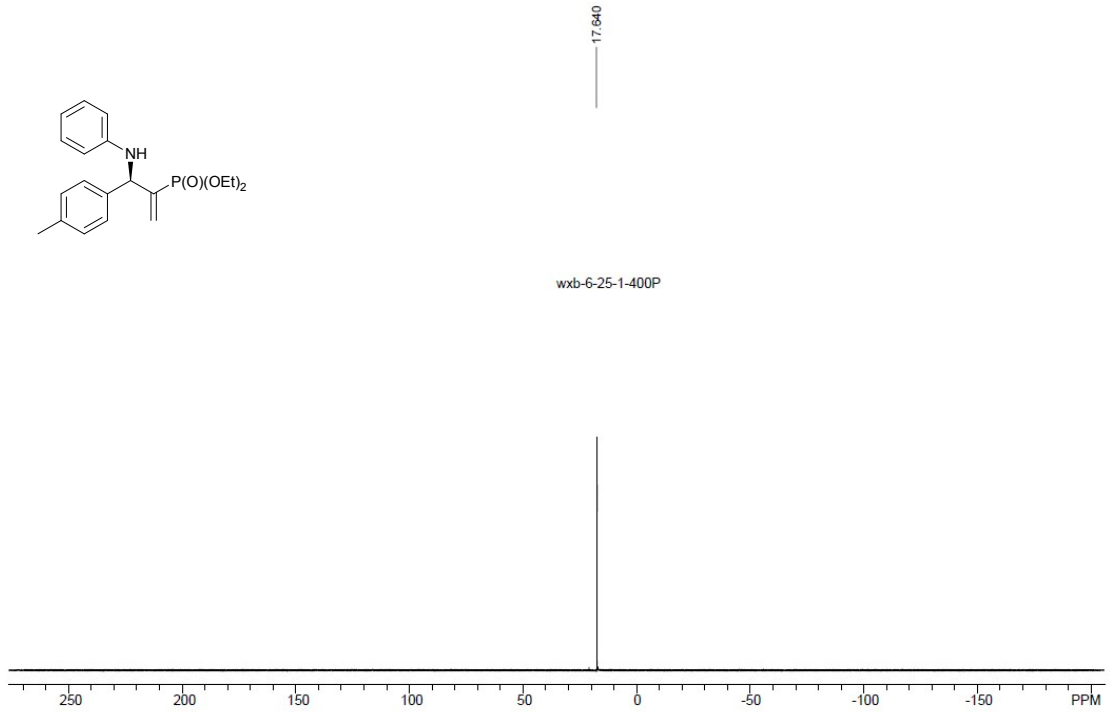
139.916
139.884
138.665
138.140
130.541
130.459
128.951
128.466
128.426
128.353
124.751
117.644
113.324
77.317
77.000
76.681
61.834
61.769
61.735
61.679
59.869
59.719
21.304
16.137
16.069
15.865
15.796
NH
P(O)(OEt)2
wxb-6-6-1-400C
200
150
100
50
0
PPM


18.307
NH
P(O)(OEt)2
wxb-6-6-1-400P
300
200
100
0
-100
PPM

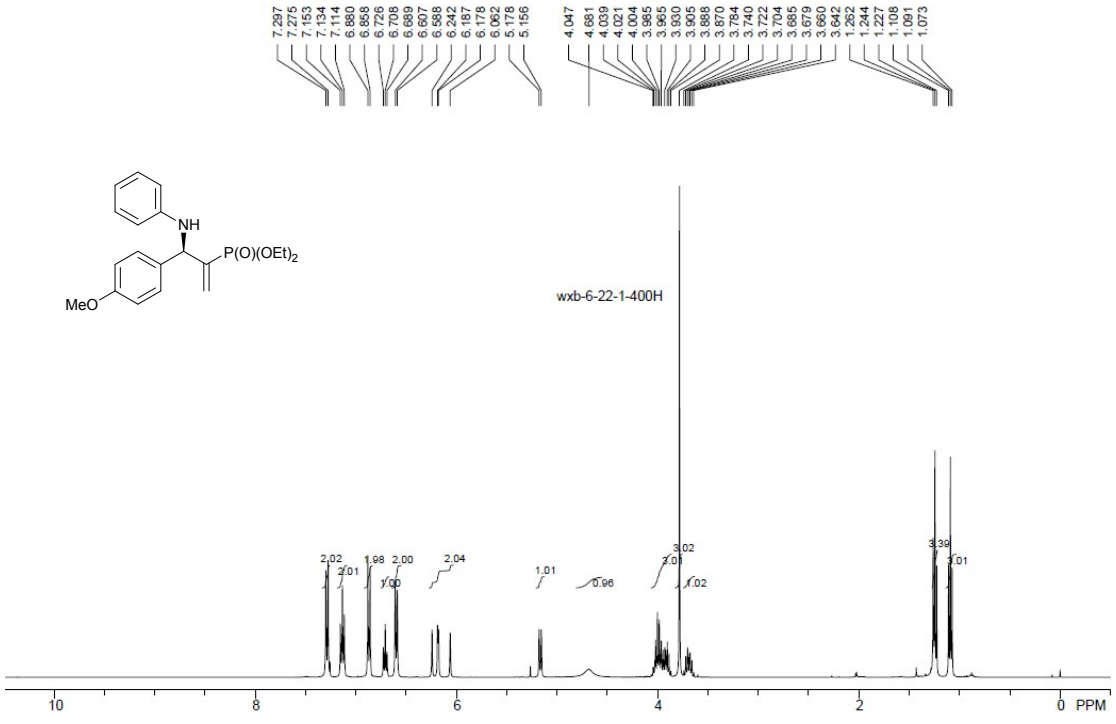
diethyl (3-(phenylamino)-3-(p-tolyl)prop-1-en-2-yl)phosphonate (4l)

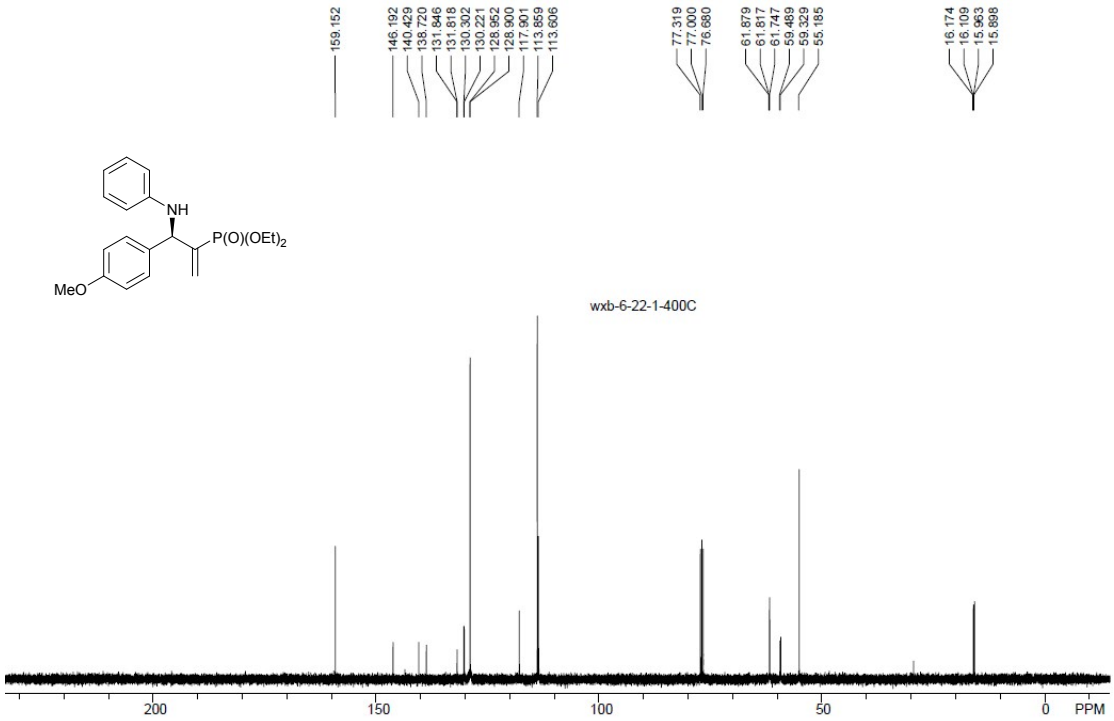






diethyl (3-(4-methoxyphenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4m)

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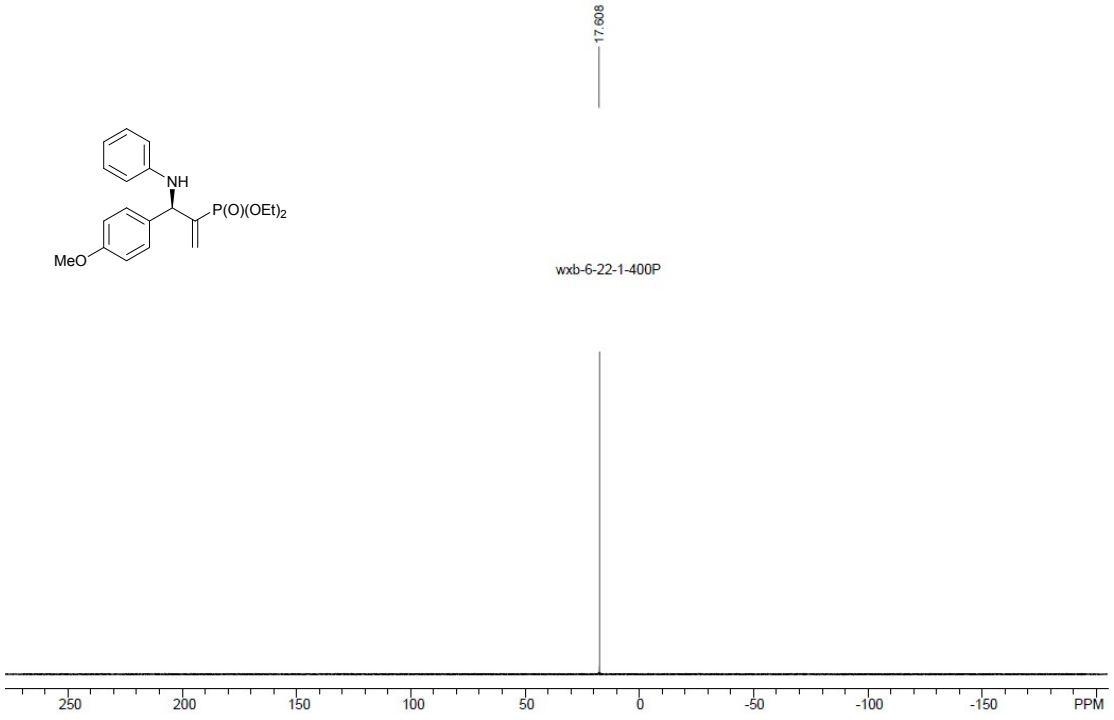
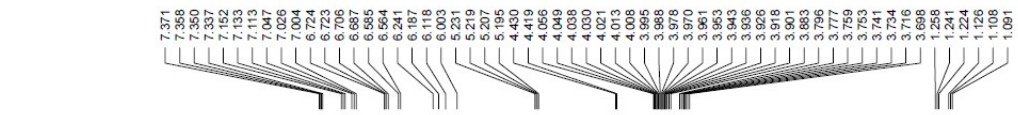
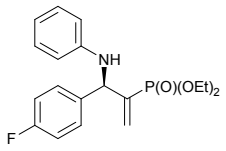
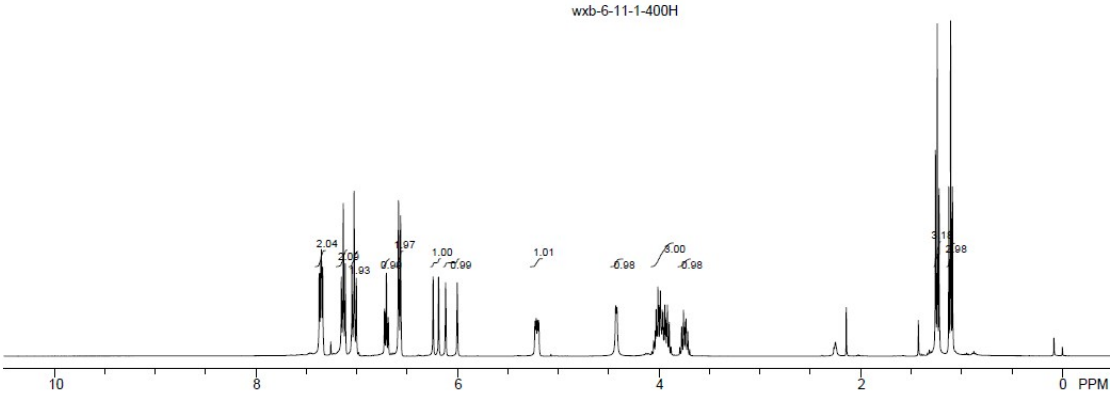
146.192
140.429
138.720
131.846
131.818
130.302
130.221
128.952
128.900
117.901
113.859
113.606
77.319
77.000
76.680
61.879
61.817
61.747
59.489
59.329
55.185
16.174
16.109
15.963
15.898
NH
P(O)(OEt)2
MeO
wxb-6-22-1-400C
200
150
100
50
0
PPM

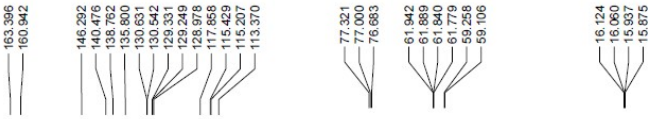

17.608
NH
P(O)(OEt)2
MeO
wxb-6-22-1-400P
250
200
150
100
50
0
-50
-100
-150
PPM

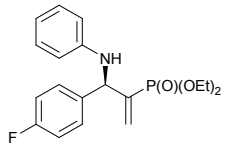
diethyl (3-(4-fluorophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4n)

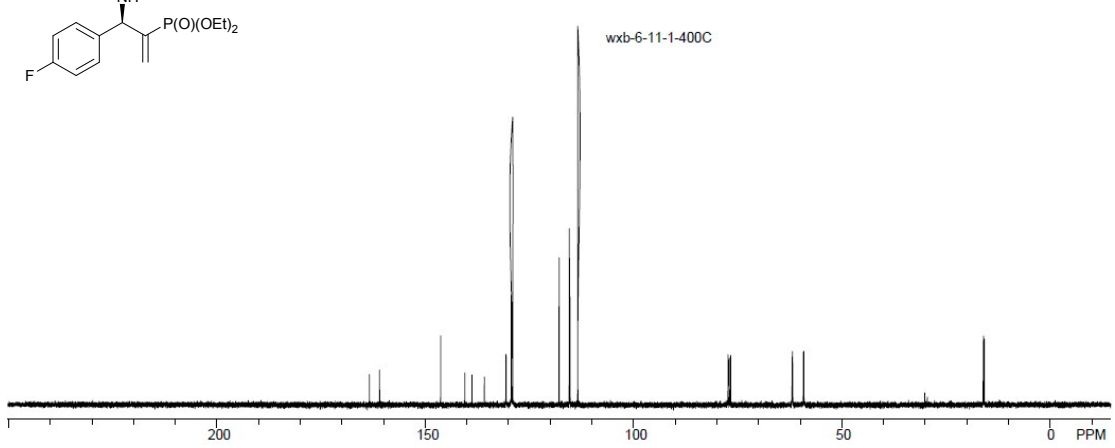




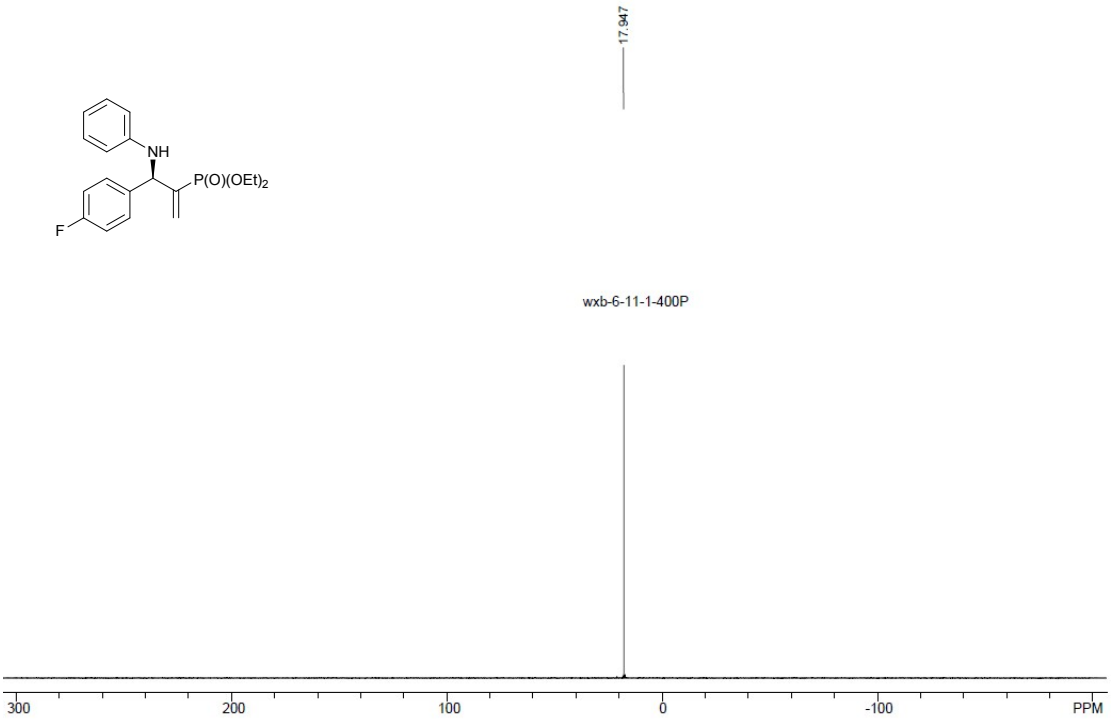




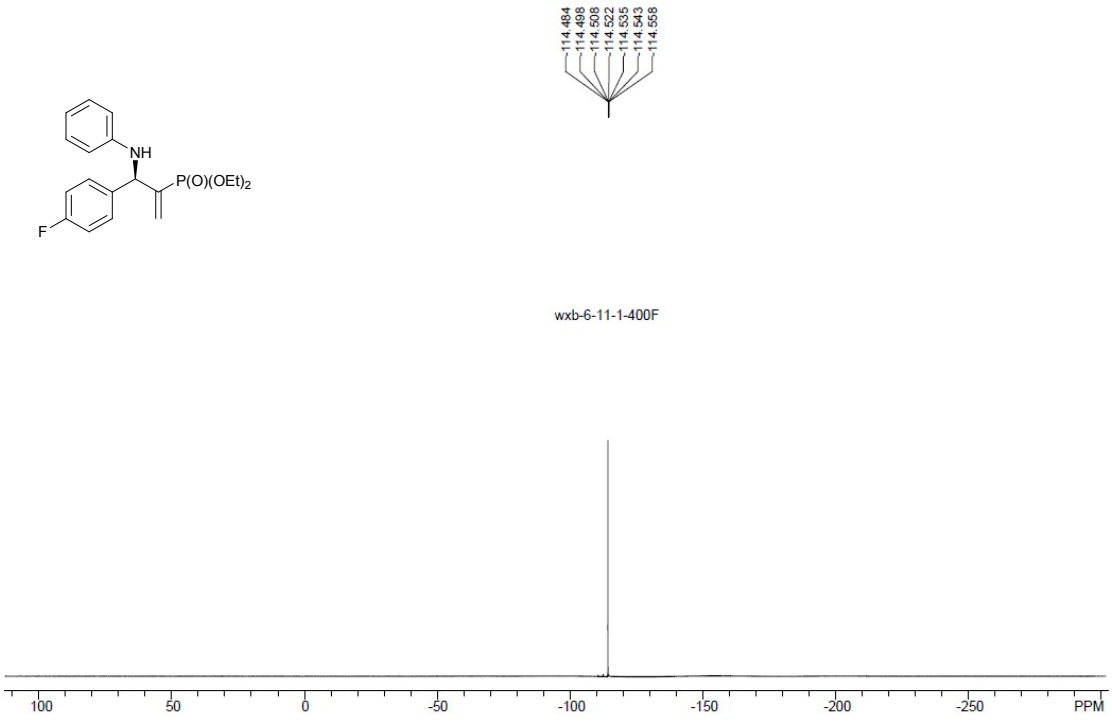




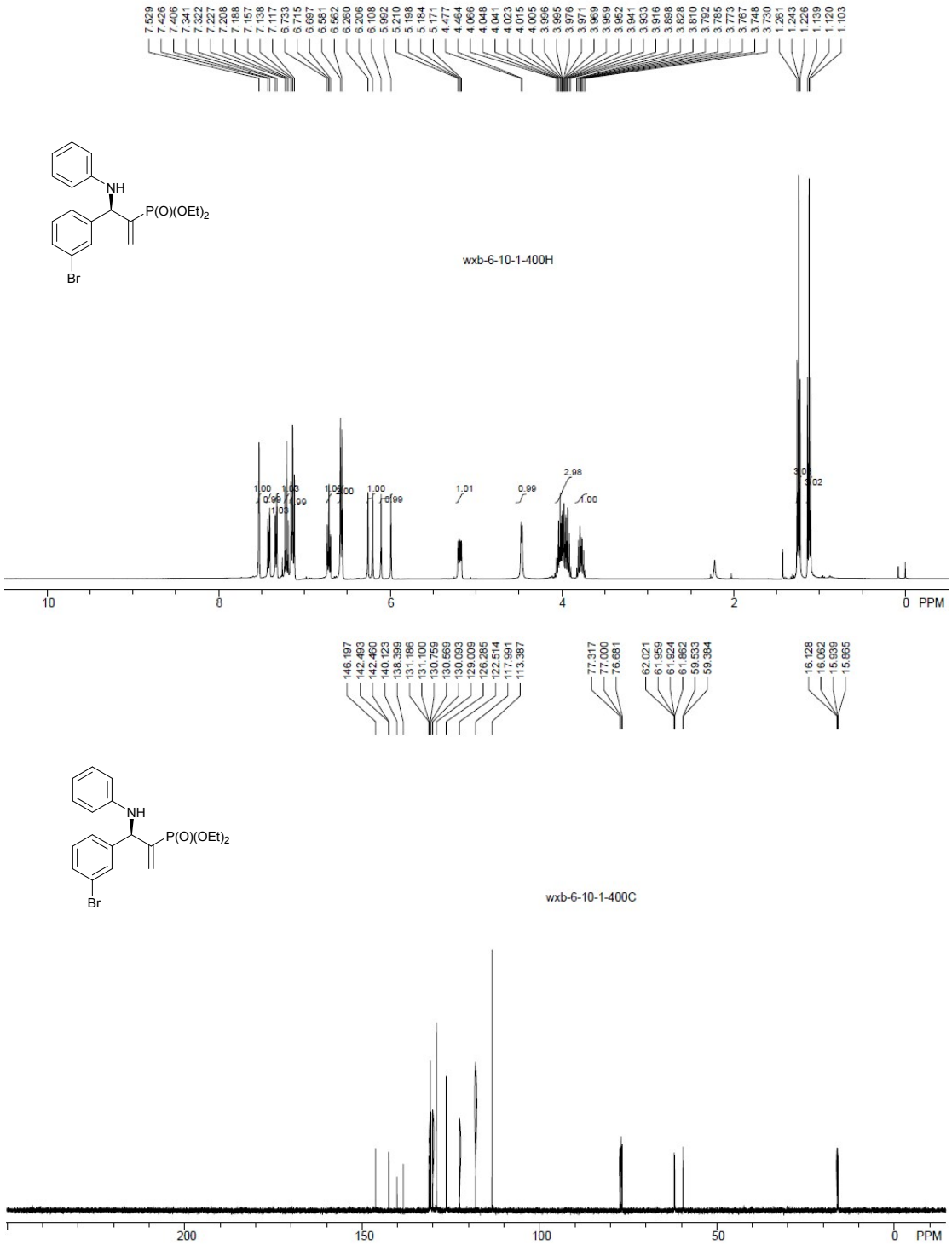
NH
P(O)(OEt)2
F

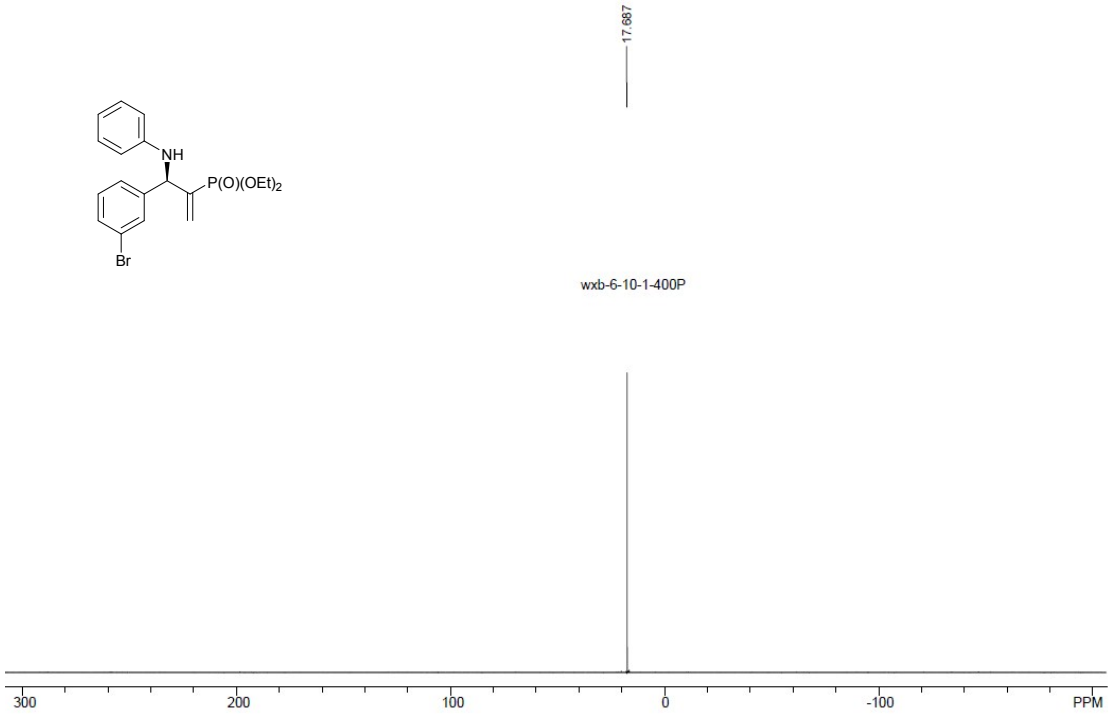

17.947
wxb-6-11-1-400P
300
200
100
0
-100
PPM

NH
P(O)(OEt)2
F

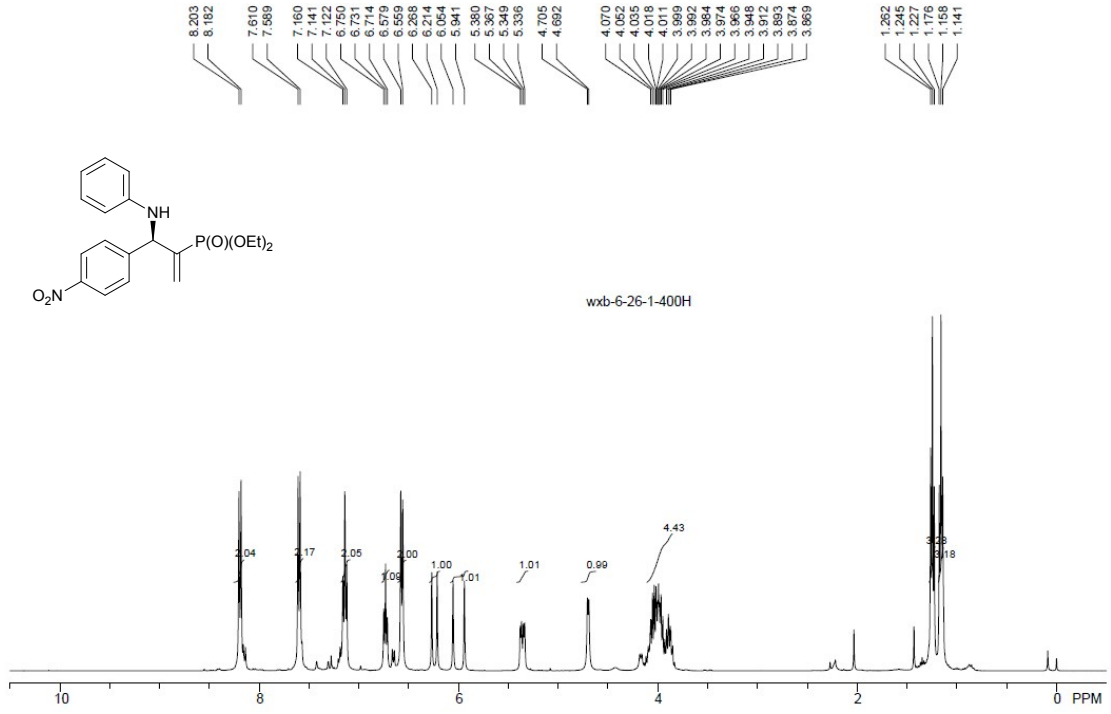

114.484
114.498
114.508
114.522
114.535
114.543
114.558
wxb-6-11-1-400F
100
50
0
-50
-100
-150
-200
-250
PPM

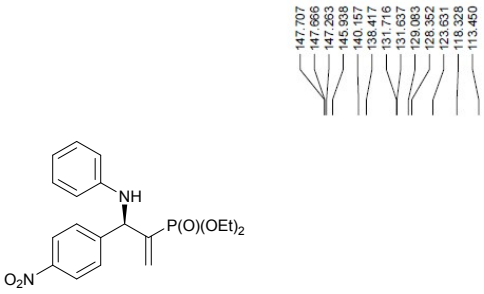
diethyl (3-(3-bromophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4o)



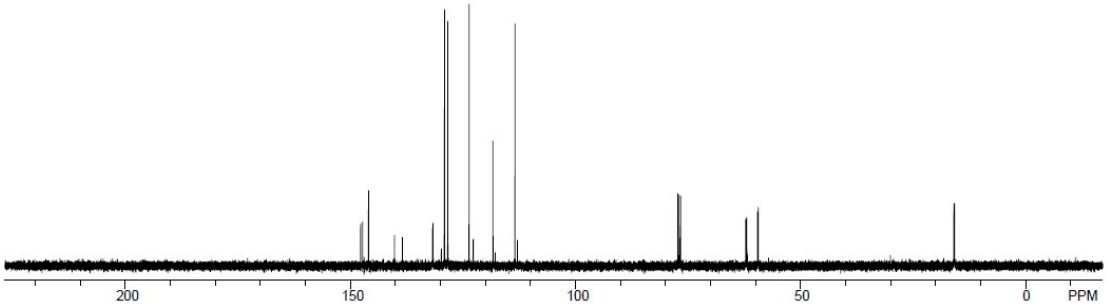


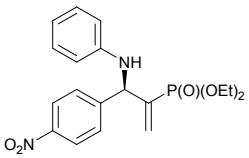
diethyl (3-(4-nitrophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4p)



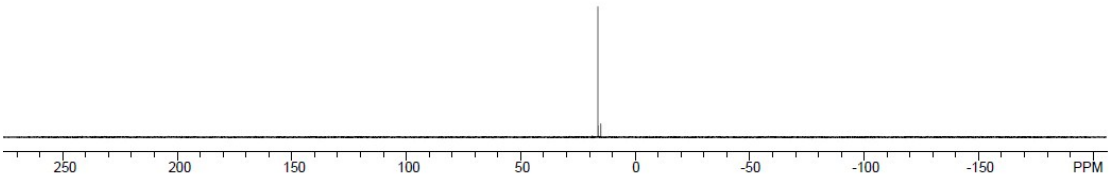


wxb-6-26-1-400C

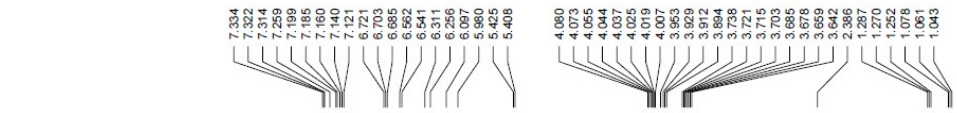


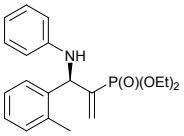


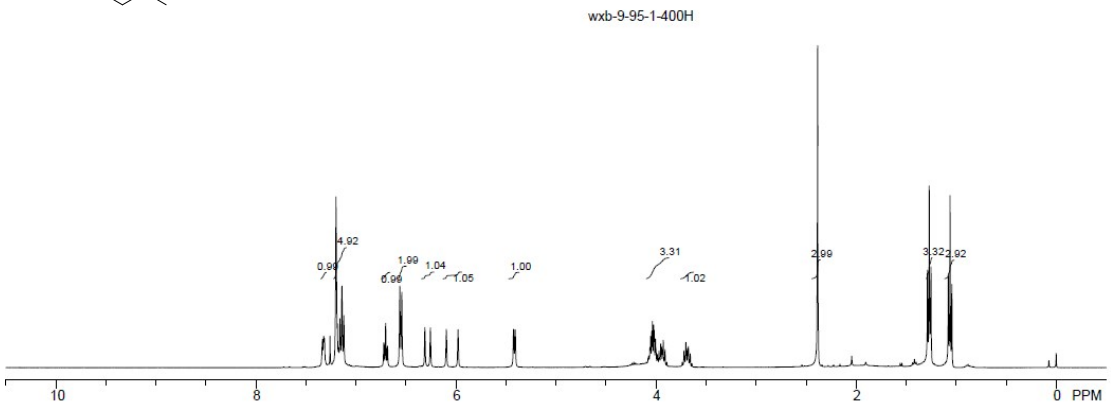
wxb-6-26-1-400P

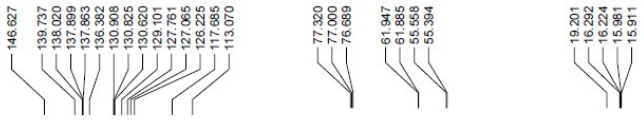


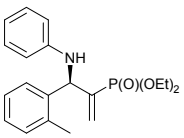
diethyl (3-(phenylamino)-3-(o-tolyl)prop-1-en-2-yl)phosphonate (4q)

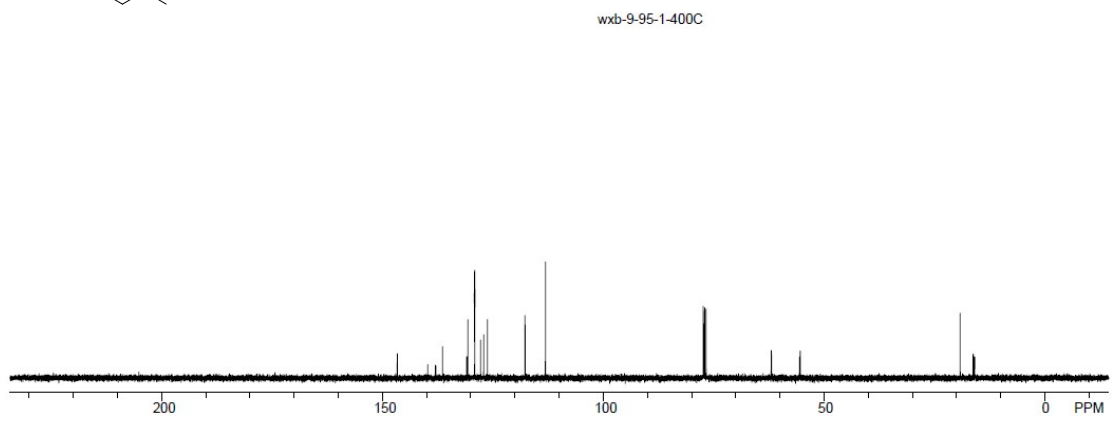


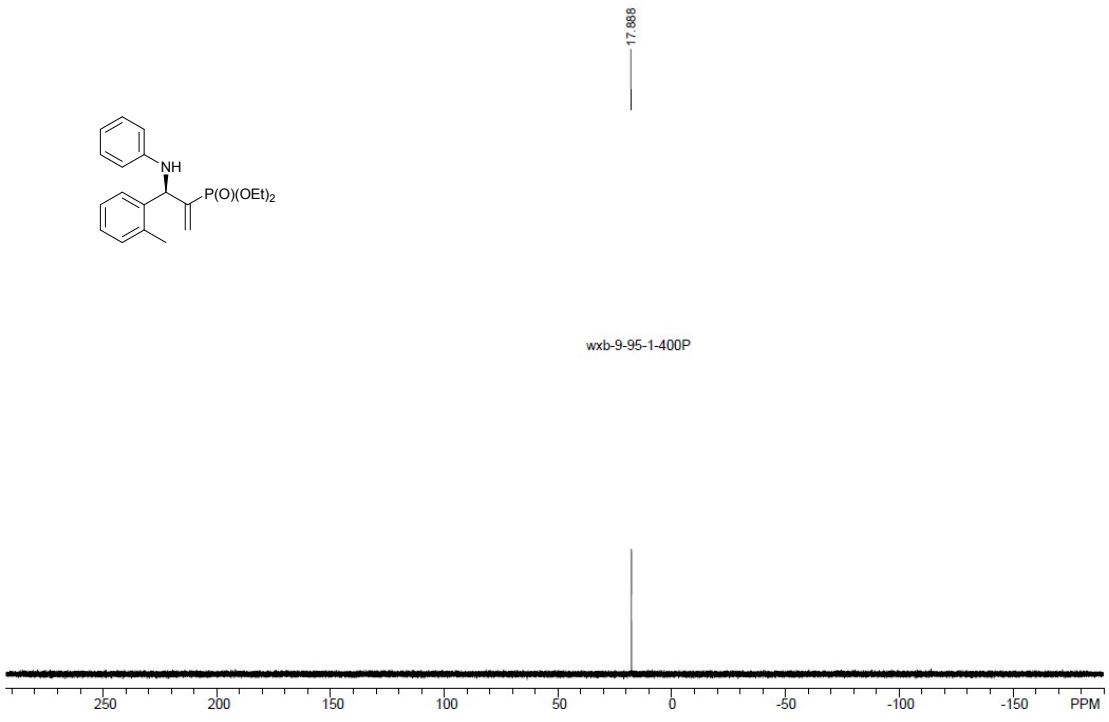






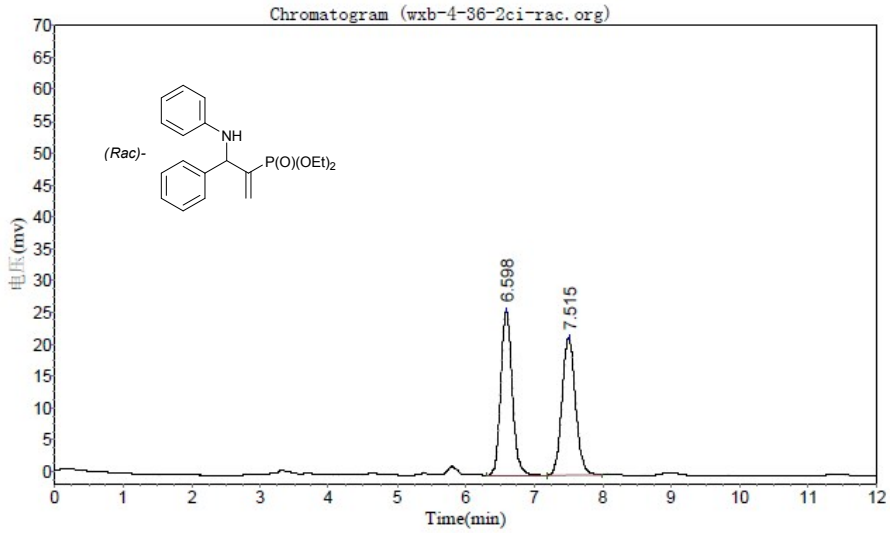





17.888
NH
P(O)(OEt)2
wxb-9-95-1-400P
250
200
150
100
50
0
-50
-100
-150
PPM

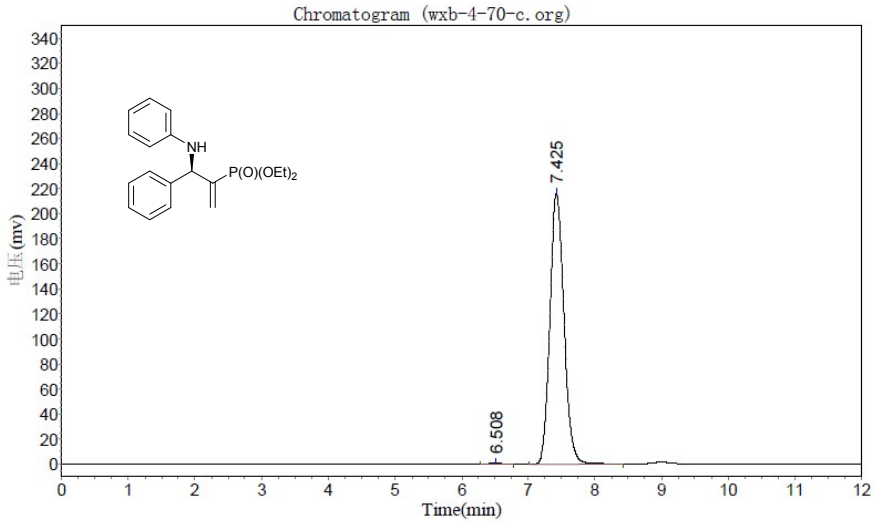
HPLC chromatograms for 4a-q

diethyl (3-phenyl-3-(phenylamino)prop-1-en-2-yl)phosphonate (4a)



Results

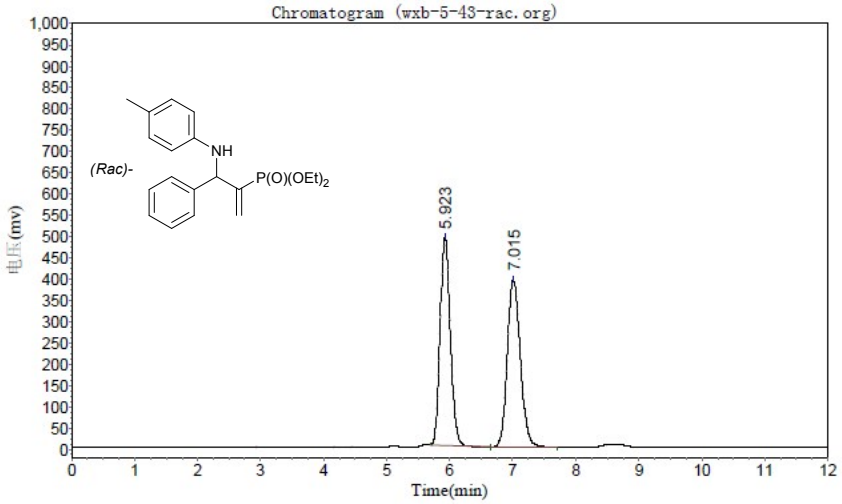
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.598	25710.432	301483.906	50.0586
2		7.515	21540.574	300778.125	49.9414
Total			47251.006	602262.031	100.0000



Results

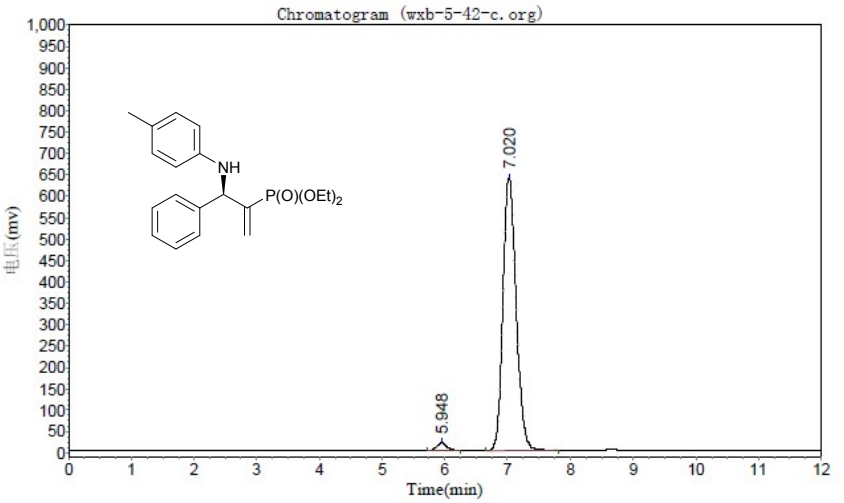
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.508	1316.432	15512.200	0.4840
2		7.425	216702.203	3189788.000	99.5160
Total			218018.635	3205300.200	100.0000

diethyl (3-phenyl-3-(p-tolylamino)prop-1-en-2-yl)phosphonate (4b)



Results

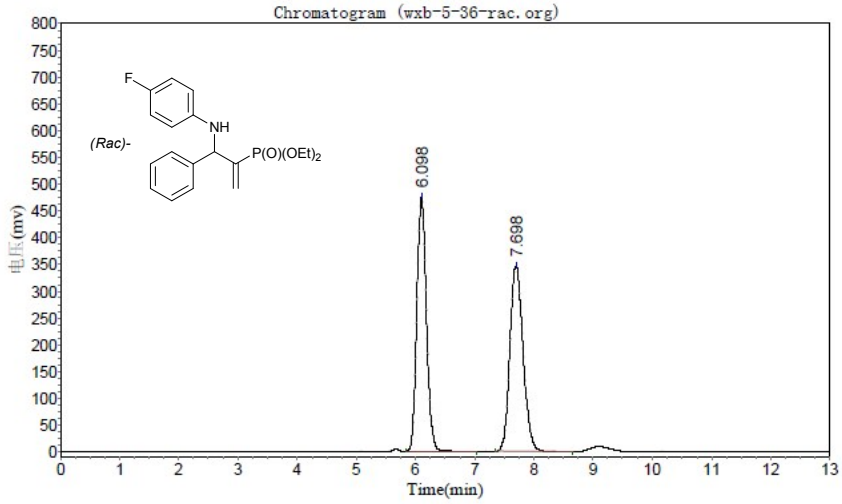
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.923	491459.938	5617868.500	49.7486
2		7.015	391248.563	5674654.000	50.2514
Total			882708.500	11292522.500	100.0000



Results

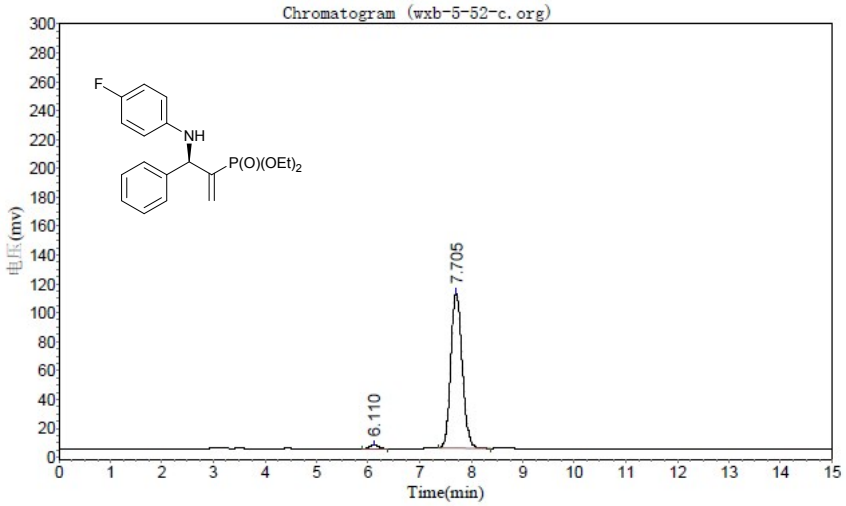
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.948	17215.313	195055.406	2.0570
2		7.020	636527.500	9287262.000	97.9430
Total			653742.813	9482317.406	100.0000

diethyl (3-((4-fluorophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4c)



Results

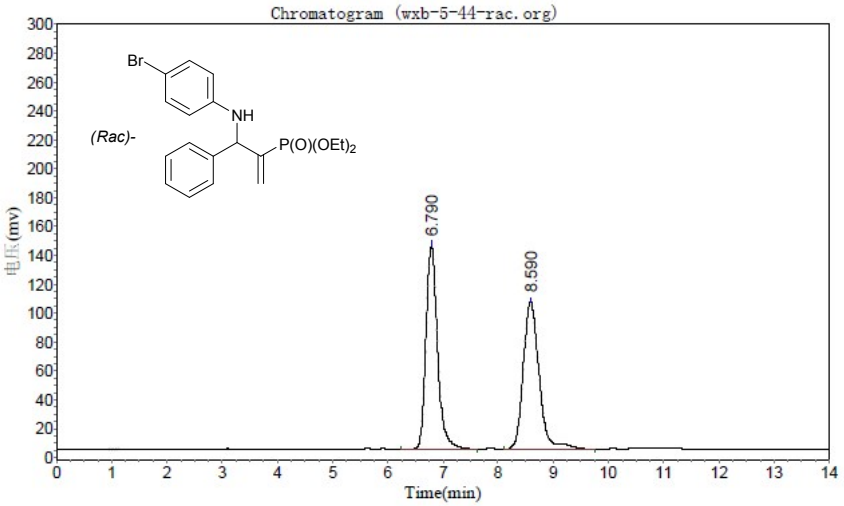
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.098	471959.531	5374903.500	49.8374
2		7.698	345383.500	5409976.500	50.1626
Total			817343.031	10784880.000	100.0000



Results

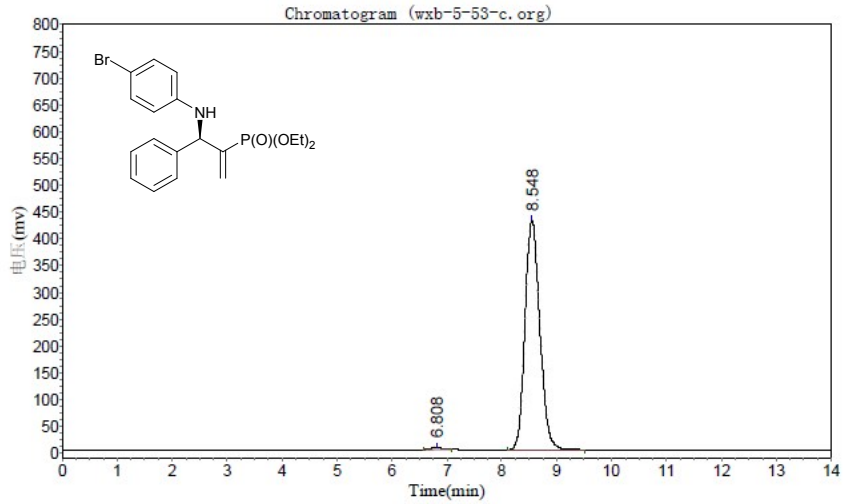
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.110	2601.353	29198.596	1.7358
2		7.705	107426.117	1652917.500	98.2642
Total			110027.470	1682116.096	100.0000

diethyl (3-((4-bromophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4d)



Results

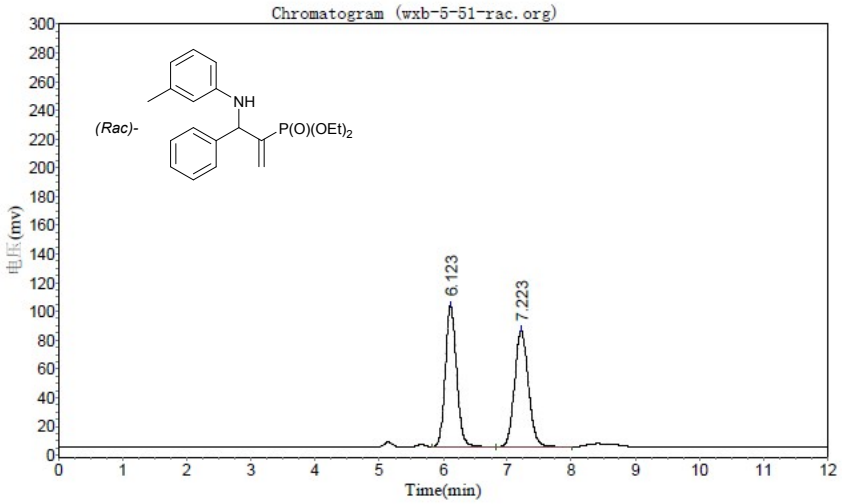
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.790	141015.891	2040434.250	50.0765
2		8.590	102190.594	2034198.375	49.9235
Total			243206.484	4074632.625	100.0000



Results

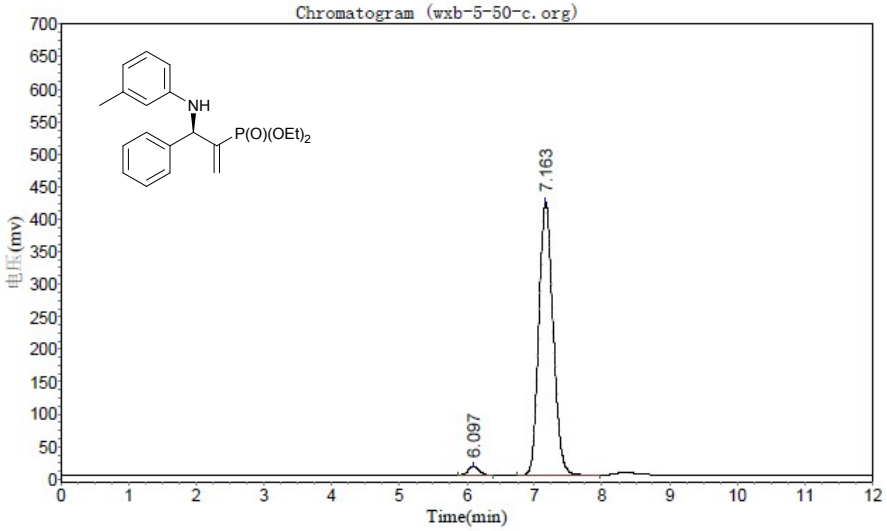
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.808	4556.941	60148.695	0.7434
2		8.548	429321.000	8031034.500	99.2566
Total			433877.941	8091183.195	100.0000

diethyl (3-phenyl-3-(m-tolylamino)prop-1-en-2-yl)phosphonate (4e)



Results

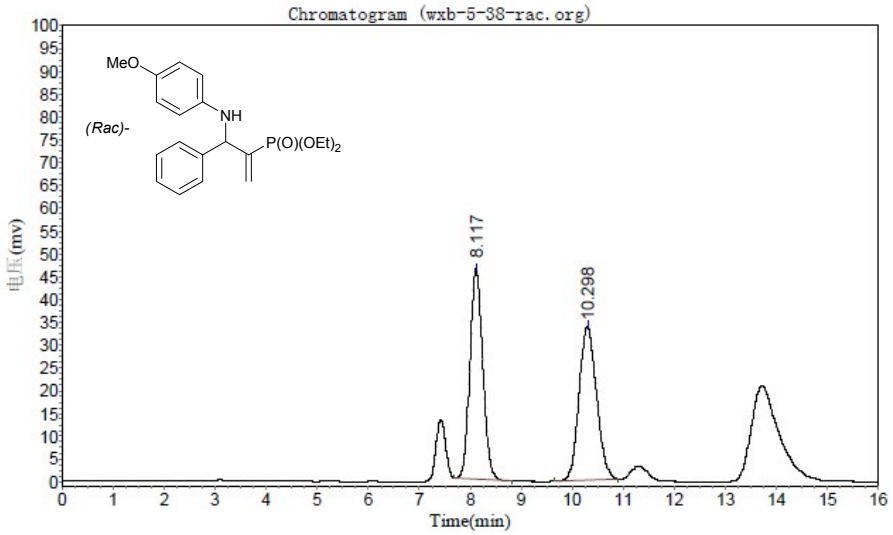
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.123	98202.539	1205067.625	49.7379
2		7.223	81254.156	1217767.250	50.2621
Total			179456.695	2422834.875	100.0000



Results

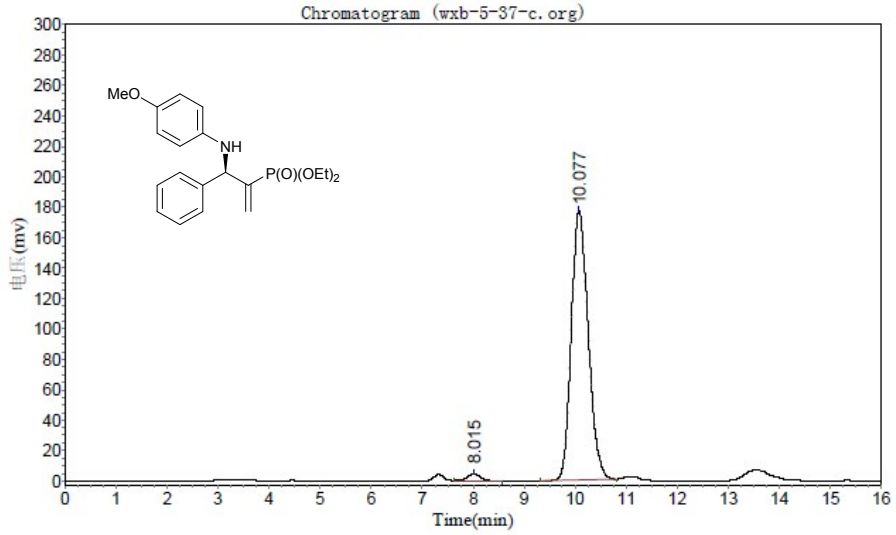
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.097	13408.692	159335.188	2.5169
2		7.163	420163.875	6171373.000	97.4831
Total			433572.567	6330708.188	100.0000

diethyl (3-((4-methoxyphenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4f)



Results

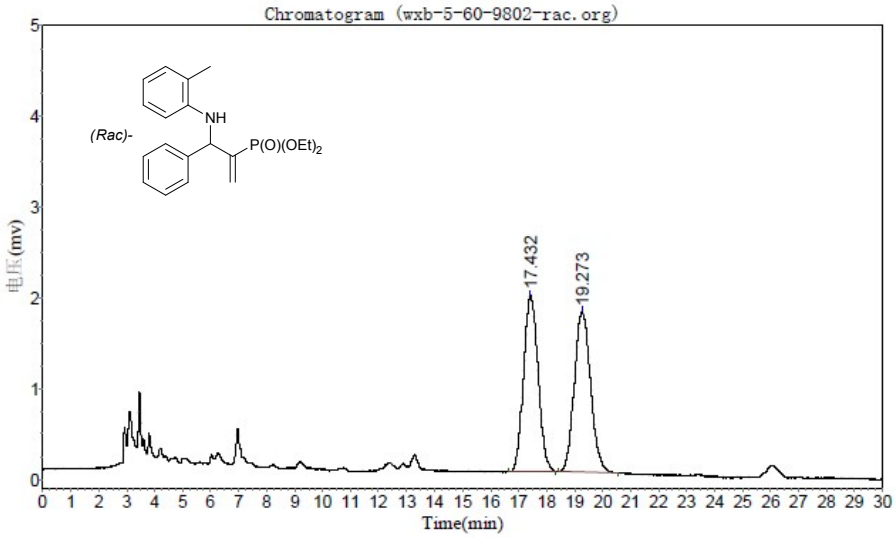
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.117	46212.832	807181.188	50.1584
2		10.298	33773.387	802082.125	49.8416
Total			79986.219	1609263.313	100.0000



Results

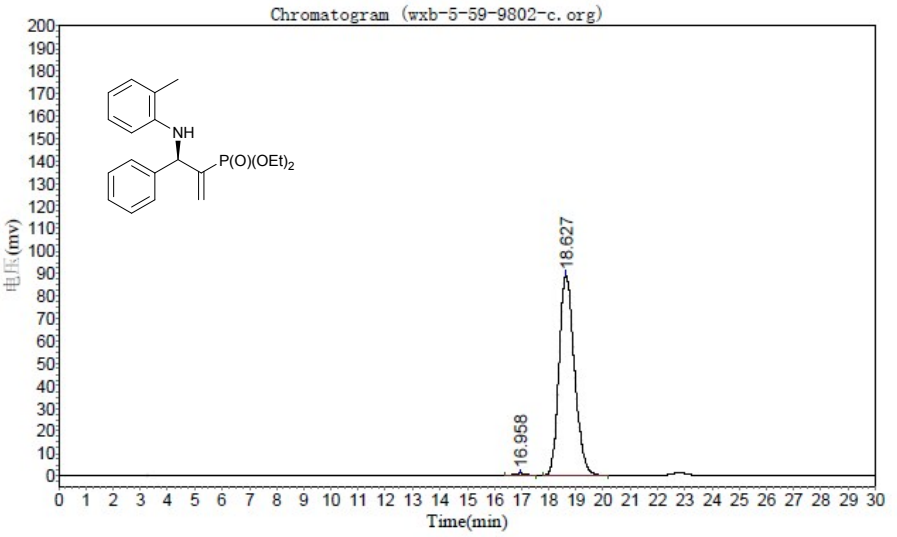
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.015	4412.016	77170.000	1.8627
2		10.077	177095.719	4065684.000	98.1373
Total			181507.735	4142854.000	100.0000

diethyl (3-phenyl-3-(o-tolylamino)prop-1-en-2-yl)phosphonate (4g)



Results

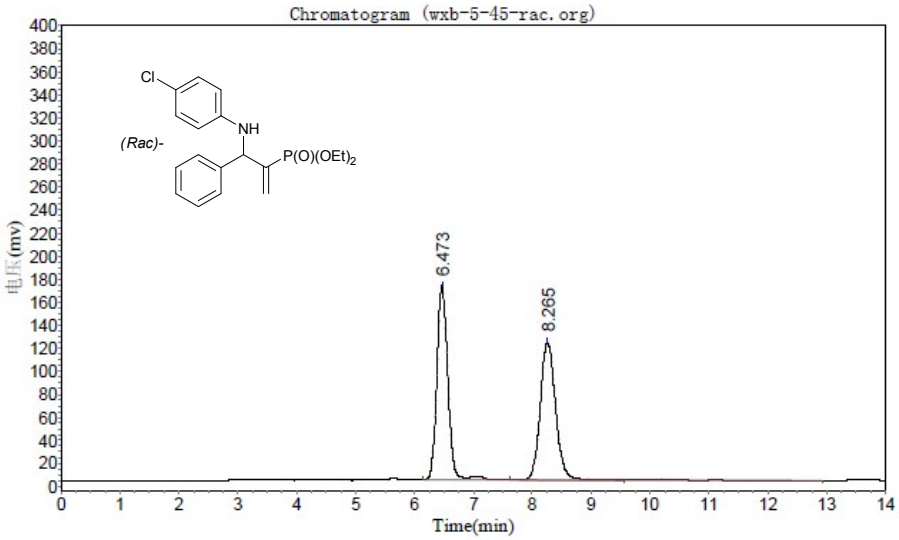
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.432	1946.533	69802.250	49.2915
2		19.273	1774.231	71808.898	50.7085
Total			3720.764	141611.148	100.0000



Results

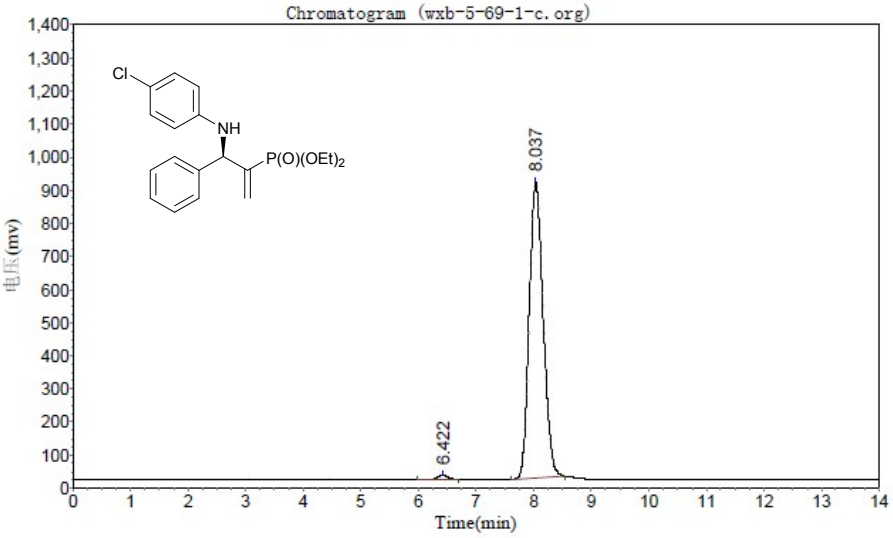
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.958	872.032	28281.898	0.7985
2		18.627	89011.305	3513537.250	99.2015
Total			89883.337	3541819.148	100.0000

diethyl (3-((4-chlorophenyl)amino)-3-phenylprop-1-en-2-yl)phosphonate (4h)



Results

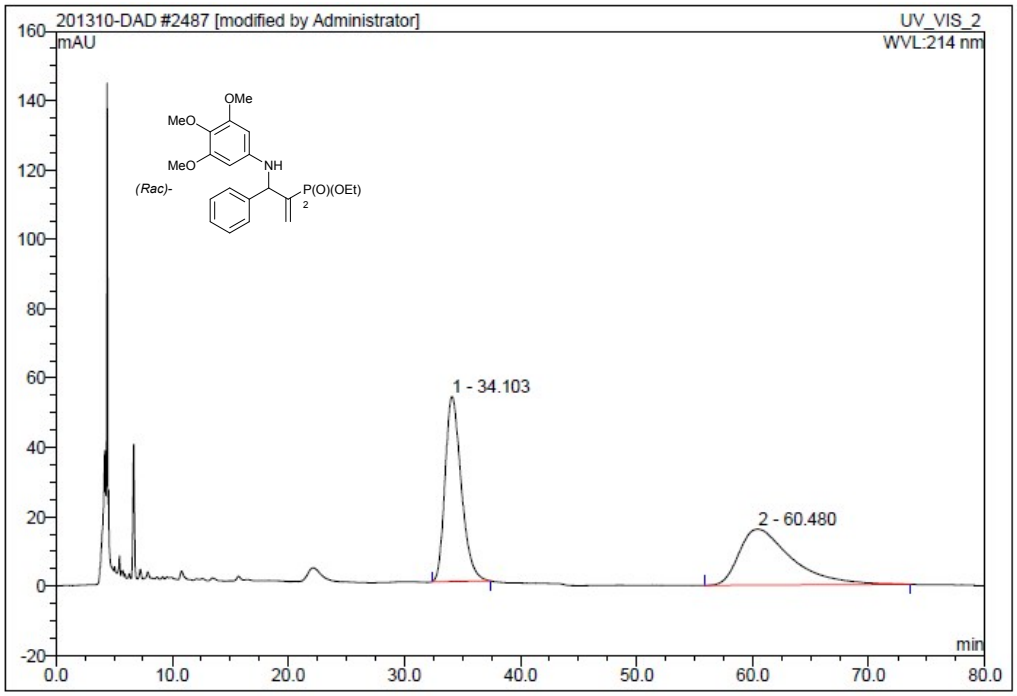
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.473	168346.922	2198725.000	50.5419
2		8.265	119339.320	2151577.000	49.4581
Total			287686.242	4350302.000	100.0000



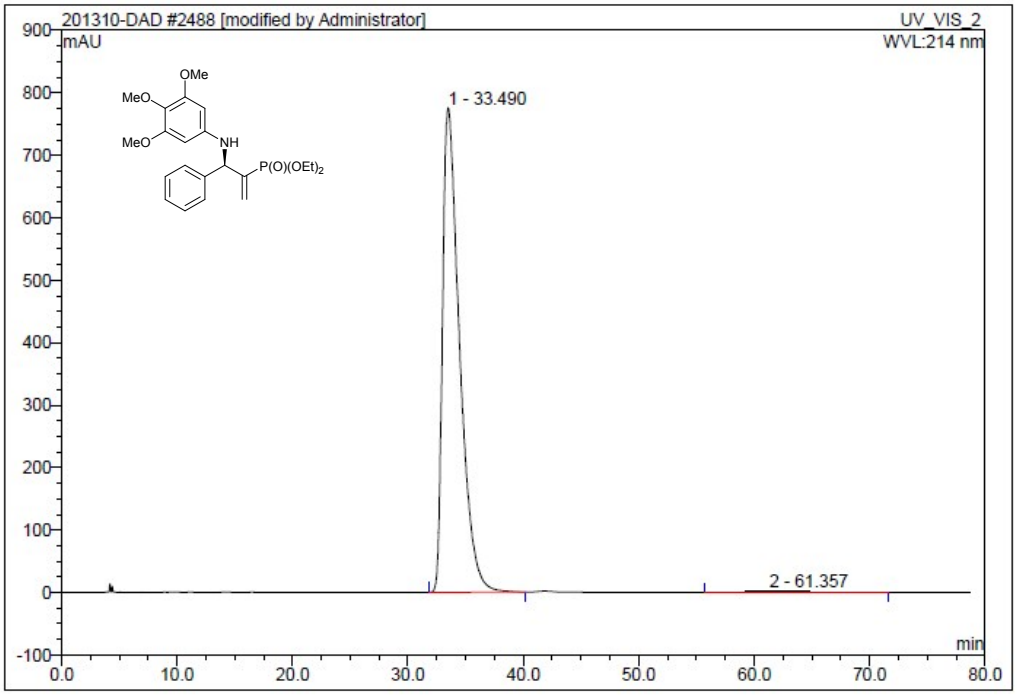
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.422	11700.917	145632.781	0.9649
2		8.037	892849.563	14946775.000	99.0351
Total			904550.479	15092407.781	100.0000

diethyl (3-phenyl-3-((3,4,5-trimethoxyphenyl)amino)prop-1-en-2-yl)phosphonate (4i)

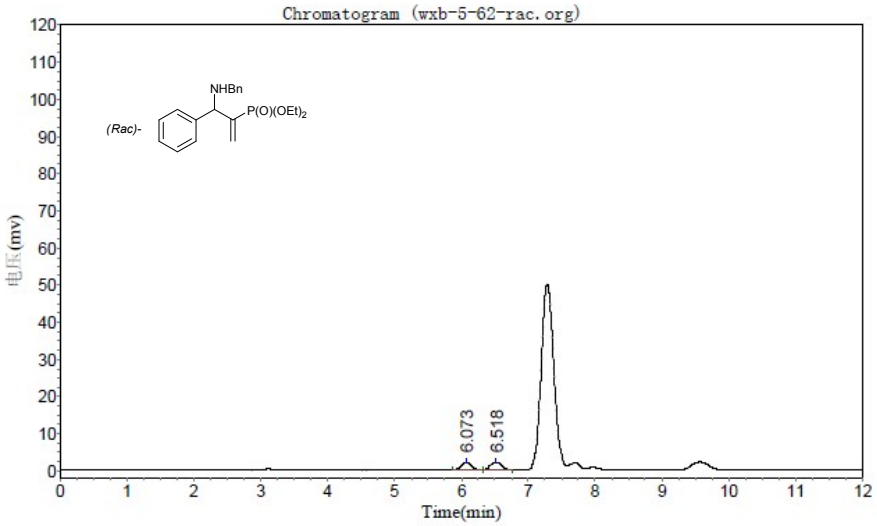


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	34.10	n.a.	53.303	86.559	50.62	n.a.	BMB
2	60.48	n.a.	16.234	84.456	49.38	n.a.	BMB*
Total:			69.537	171.015	100.00	0.000	



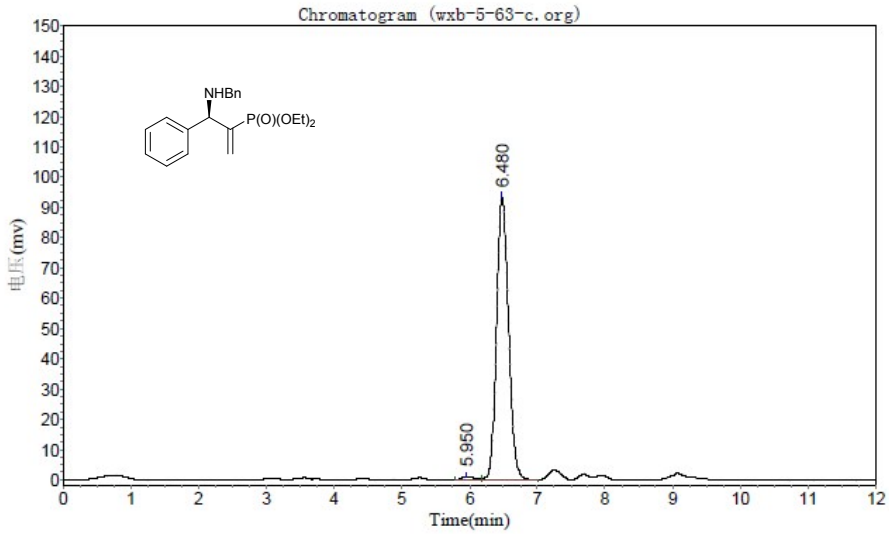
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	33.49	n.a.	776.218	1323.340	99.01	n.a.	BMB*
2	61.36	n.a.	2.534	13.290	0.99	n.a.	BMB*
Total:			778.752	1336.630	100.00	0.000	

diethyl (3-(benzylamino)-3-phenylprop-1-en-2-yl)phosphonate (4j)



Results

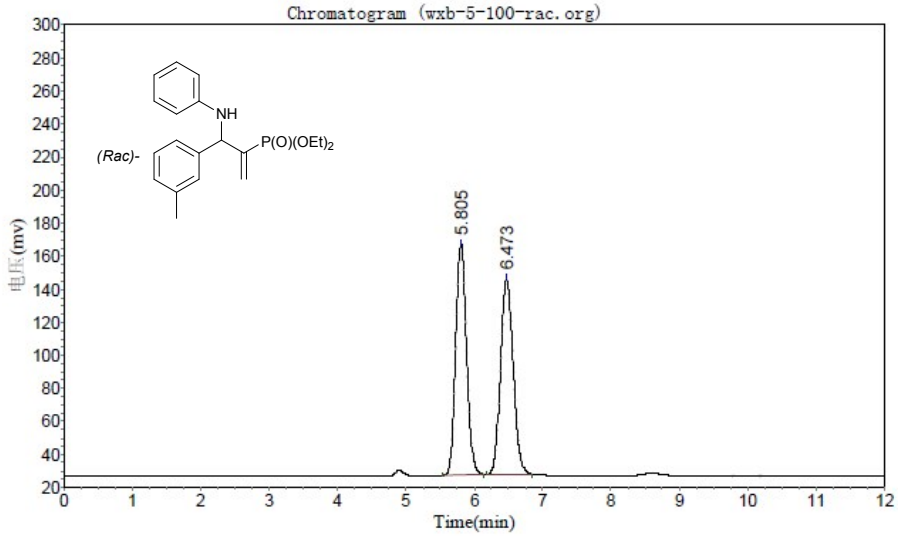
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.073	1969.000	20991.400	46.3015
2		6.518	2080.259	24344.900	53.6985
Total			4049.259	45336.301	100.0000



Results

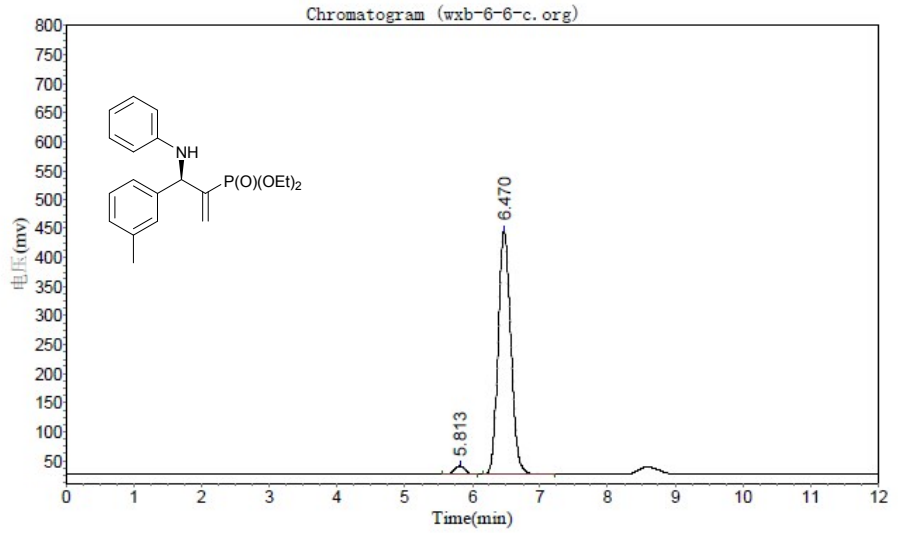
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.950	728.046	10296.364	0.8941
2		6.480	93426.414	1141238.000	99.1059
Total			94154.460	1151534.364	100.0000

diethyl (3-(phenylamino)-3-(m-tolyl)prop-1-en-2-yl)phosphonate (4k)



Results

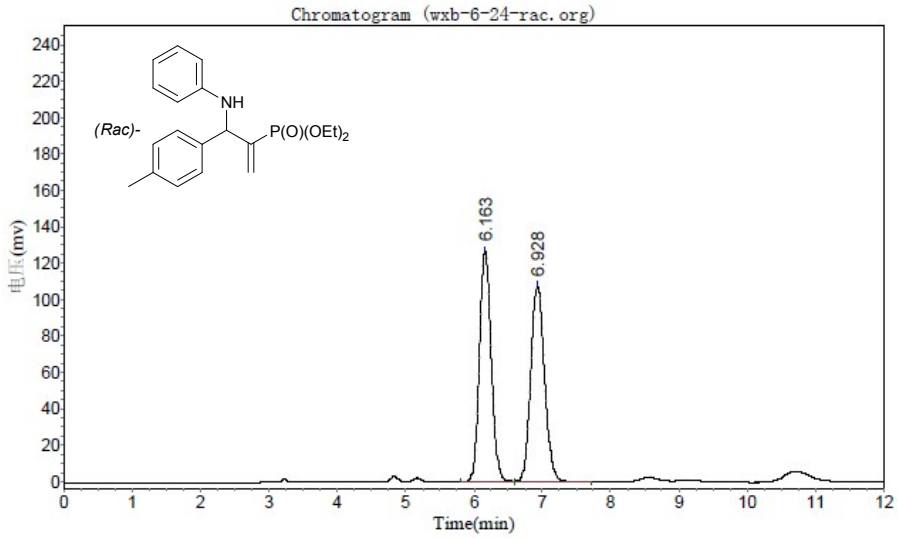
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.805	139465.500	1530979.500	50.1420
2		6.473	118370.500	1522307.000	49.8580
Total			257836.000	3053286.500	100.0000



Results

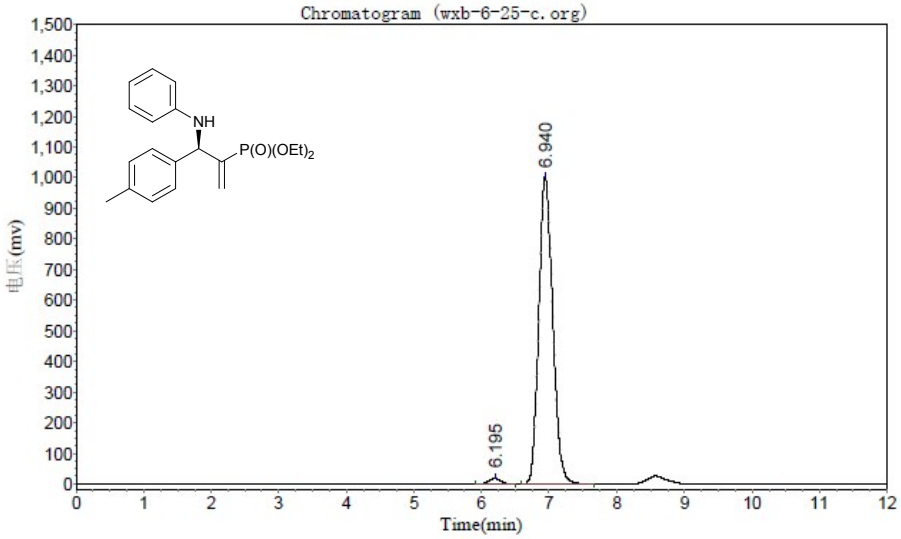
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.813	14369.791	156578.797	2.7898
2		6.470	420234.938	5455897.500	97.2102
Total			434604.729	5612476.297	100.0000

diethyl (3-(phenylamino)-3-(p-tolyl)prop-1-en-2-yl)phosphonate (4l)



Results

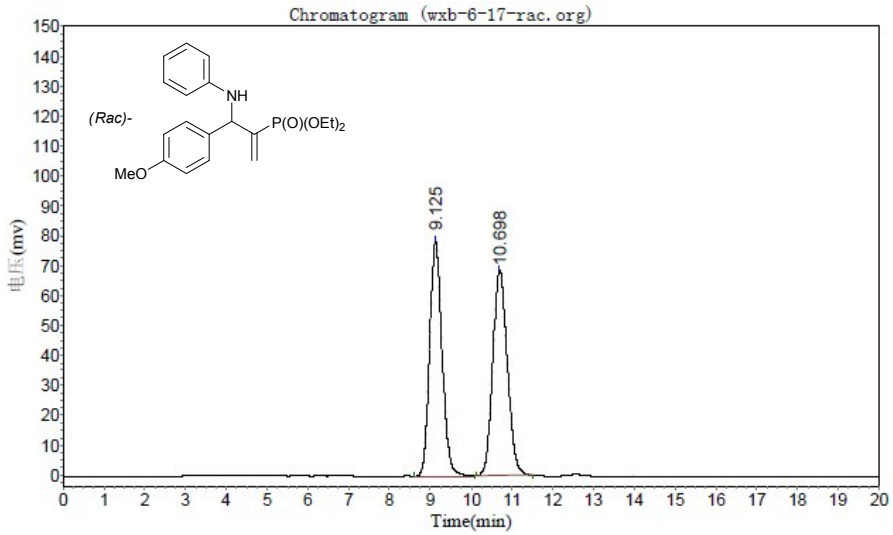
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.163	126575.531	1512709.500	49.9078
2		6.928	107588.117	1518301.125	50.0922
Total			234163.648	3031010.625	100.0000



Results

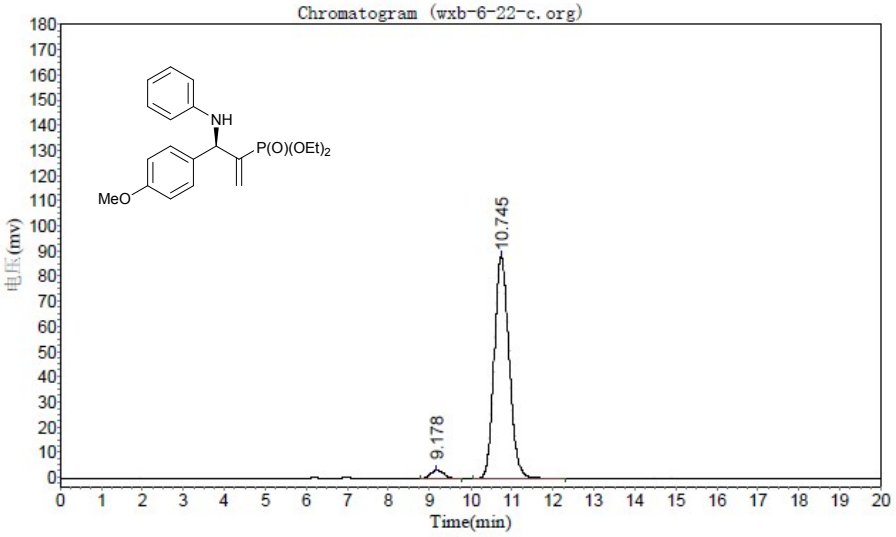
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.195	18024.211	212166.547	1.4570
2		6.940	1001216.875	14349540.000	98.5430
Total			1019241.086	14561706.547	100.0000

diethyl (3-(4-methoxyphenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4m)



Results

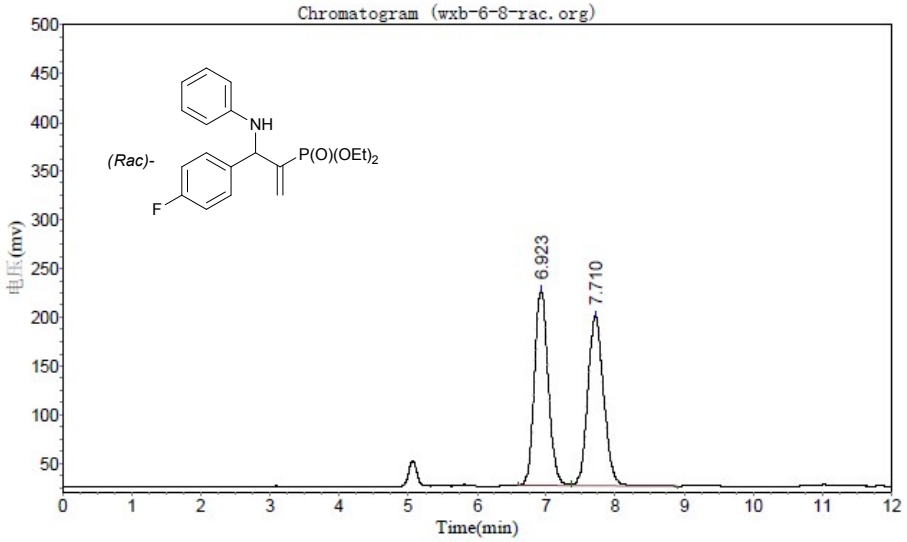
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.125	78854.406	1661678.375	49.4336
2		10.698	68631.875	1699756.625	50.5664
Total			147486.281	3361435.000	100.0000



Results

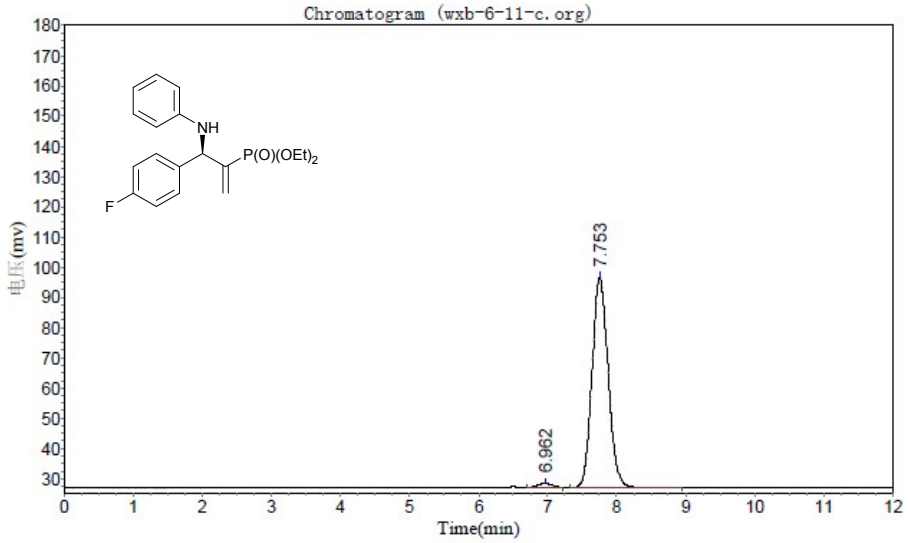
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.178	3224.273	67871.703	2.9649
2		10.745	88407.289	2221315.750	97.0351
Total			91631.562	2289187.453	100.0000

diethyl (3-(4-fluorophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4n)



Results

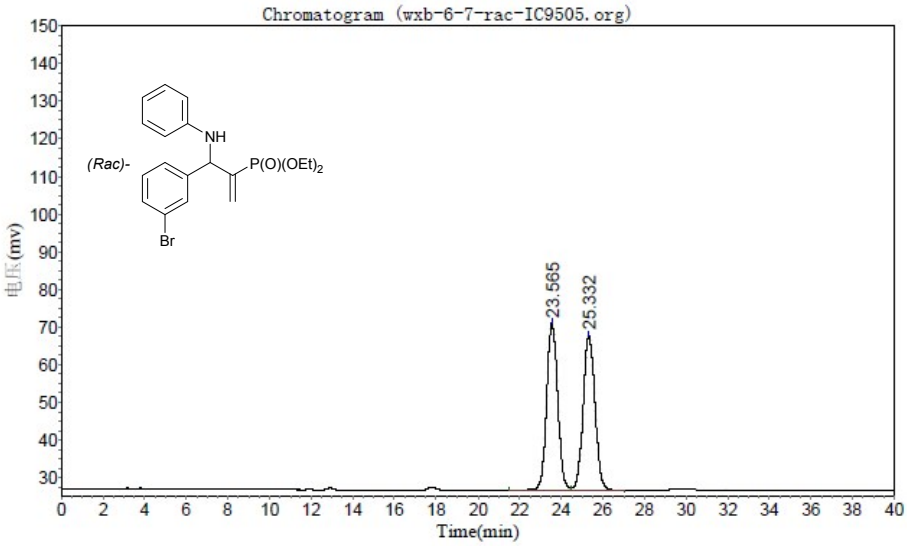
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.923	200054.813	2764174.500	49.9092
2		7.710	173848.391	2774234.750	50.0908
Total			373903.203	5538409.250	100.0000



Results

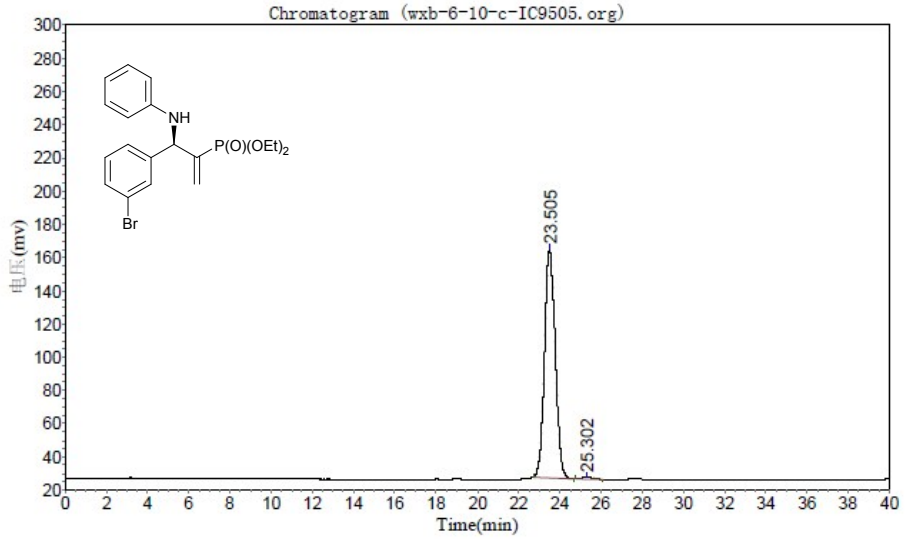
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.962	1374.563	18753.189	1.6372
2		7.753	69743.492	1126713.500	98.3628
Total			71118.055	1145466.689	100.0000

diethyl (3-(3-bromophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4o)



Results

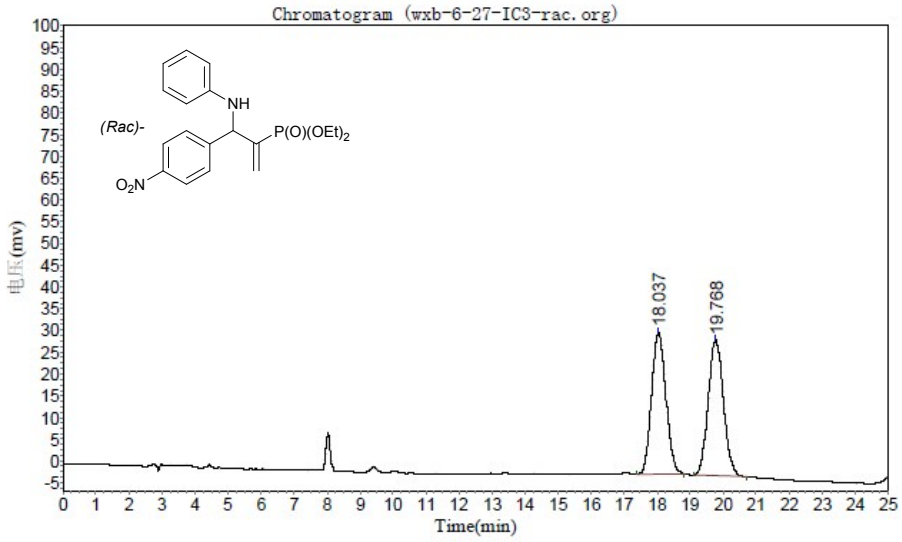
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.565	44426.133	1629510.875	50.2532
2		25.332	41078.535	1613092.375	49.7468
Total			85504.668	3242603.250	100.0000



Results

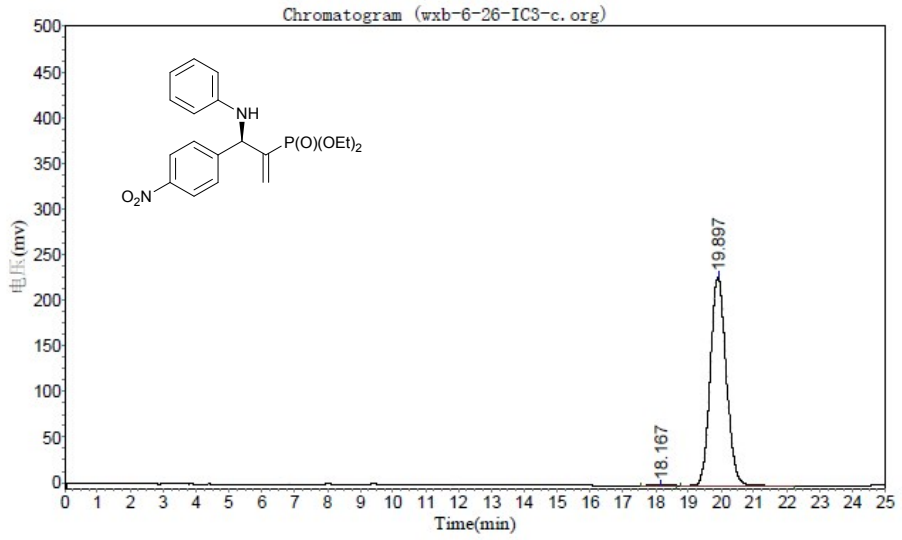
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.505	137967.000	4973829.000	99.4434
2		25.302	797.460	27840.672	0.5566
Total			138764.460	5001669.672	100.0000

diethyl (3-(4-nitrophenyl)-3-(phenylamino)prop-1-en-2-yl)phosphonate (4p)



Results

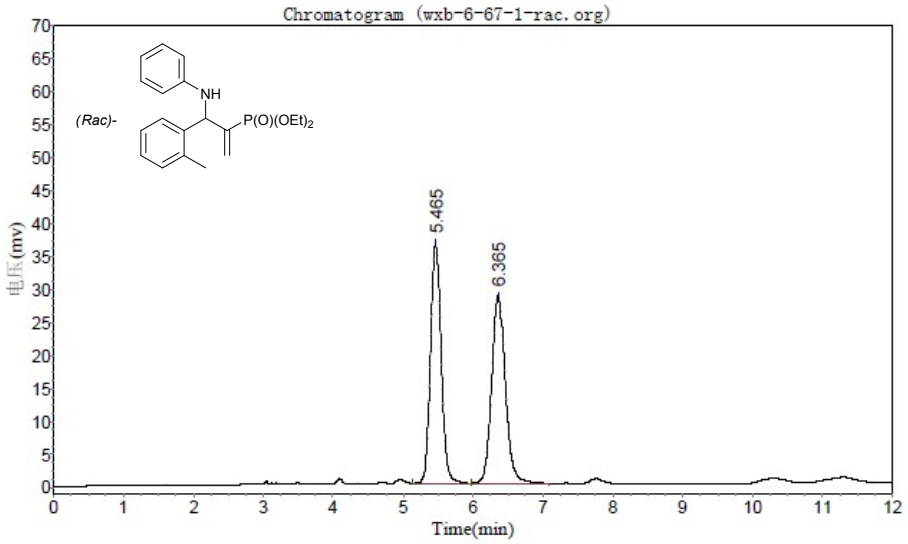
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.037	32635.557	982520.688	49.4757
2		19.768	31178.234	1003344.125	50.5243
Total			63813.791	1985864.813	100.0000



Results

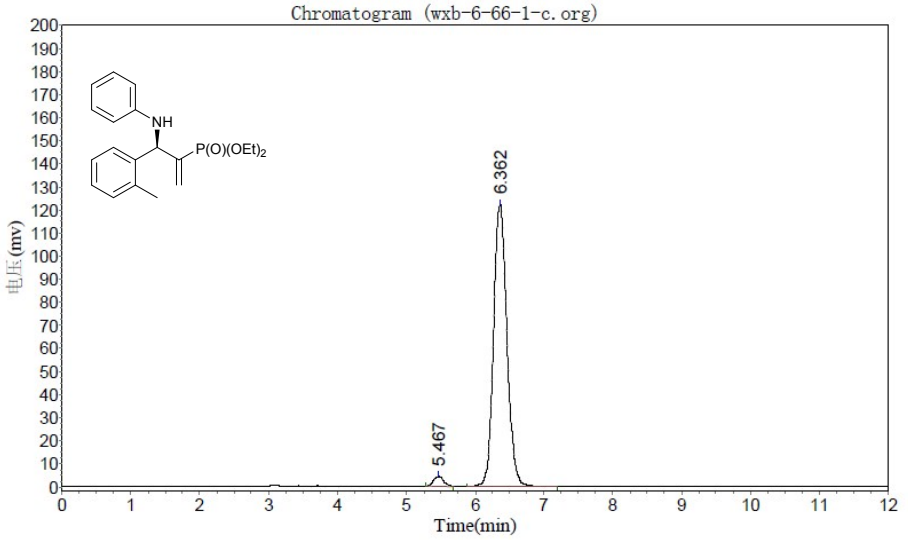
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.167	1242.568	35995.508	0.4638
2		19.897	228884.188	7725528.000	99.5362
Total			230126.755	7761523.508	100.0000

diethyl (3-(phenylamino)-3-(o-tolyl)prop-1-en-2-yl)phosphonate (4q)



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.465	36108.188	387258.875	49.8535
2		6.365	28359.361	389534.719	50.1465
Total			64467.549	776793.594	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.467	4267.333	42852.148	2.5327
2		6.362	122419.727	1649089.250	97.4673
Total			126687.060	1691941.398	100.0000