Supplementary Information

Nickel/Brønsted Acid Dual-Catalyzed Regio- and Enantioselective Hydrophosphinylation of 1,3-Dienes: Access to Chiral Allylic Phosphine Oxides

Jiao Long,[a] *Yuqiang Li,*[a] *Weining Zhao,*[*,b] *Guoyin Yin*[*,a]

[a] The Institute for Advanced Studies, Wuhan University, Wuhan 430072, China

[b] College of Pharmacy, Shenzhen Technology University, Shenzhen 518118, China

[*]corresponding author,

E-mails: zhaoweining@sztu.edu.cn

yinguoyin@whu.edu.cn

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1. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers (Energy Chemical, Adamas-beta®, *J*&K, laajoo and so on) and used without further purification. All reactions were assembled on a Schlenk vacuum line or in a glovebox using oven-dried glass tube and were stirred with Teflon-coated magnetic stirring bars unless otherwise specified. Reactions were monitored using thin-layer chromatography (TLC), visualization of the developed plates was performed under UV light (254 nm) or $KMnO_4$ stain. Purification and isolation of products were performed *via* silica gel (300-400 mesh) chromatography. ^{1}H, ^{2}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on Bruker 400 MHz or 600 MHz spectrometer. ^{1}H NMR spectra were internally referenced to TMS. ^{13}C NMR spectra were internally referenced to the residual solvent signal. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, m = multiplet), coupling constants (Hz) and integration. GC analysis were performed on a Shimadzu GC-2010 Pro gas chromatograph with an FID detector. High resolution mass spectra (HRMS) were measured with a Thermo Orbitrap Elite instrument (ESI). High pressure liquid chromatography (HPLC) was performed on Agilent 1260 Series chromatographs using Daicel Chiralcel columns (250 mm). Optical rotations were measured on a Perkin Elmer 343 polarimeter using a 100 mm pathlength cell at 589 nm with $[\alpha]_D$ values reported in degrees; concentration (c) is in g/100 mL. Melting points (m.p.) were obtained on SGW® X-4 micro melting point apparatus.

2. Preparation of Substrates

Internal 1,3-dienes **1a**-**1j** used in this work were prepared according to literature procedure[1, 2] and were obtained in *E,Z*/*E,E* mixture form. The ratios of *E,Z*/*E,E* are listed as **Figure S1**. Terminal 1,3-dienes **1k**-**1r** used here have been reported in our previous work.[2] 1,3-Diene **1h** was commercially available (**Figure S2**).

Symmetric phosphine oxides **2c**-**2k** and **2r** used here were known compounds and synthesized according to reported methods,[3] **2a**, **2b**, **2h**, **2i** and **2q** were commercially available (**Figure S3**). Unsymmetric phosphine oxides **2l**-**2p** used here were prepared according to literature procedure (**Figure S4**).[4, 5]

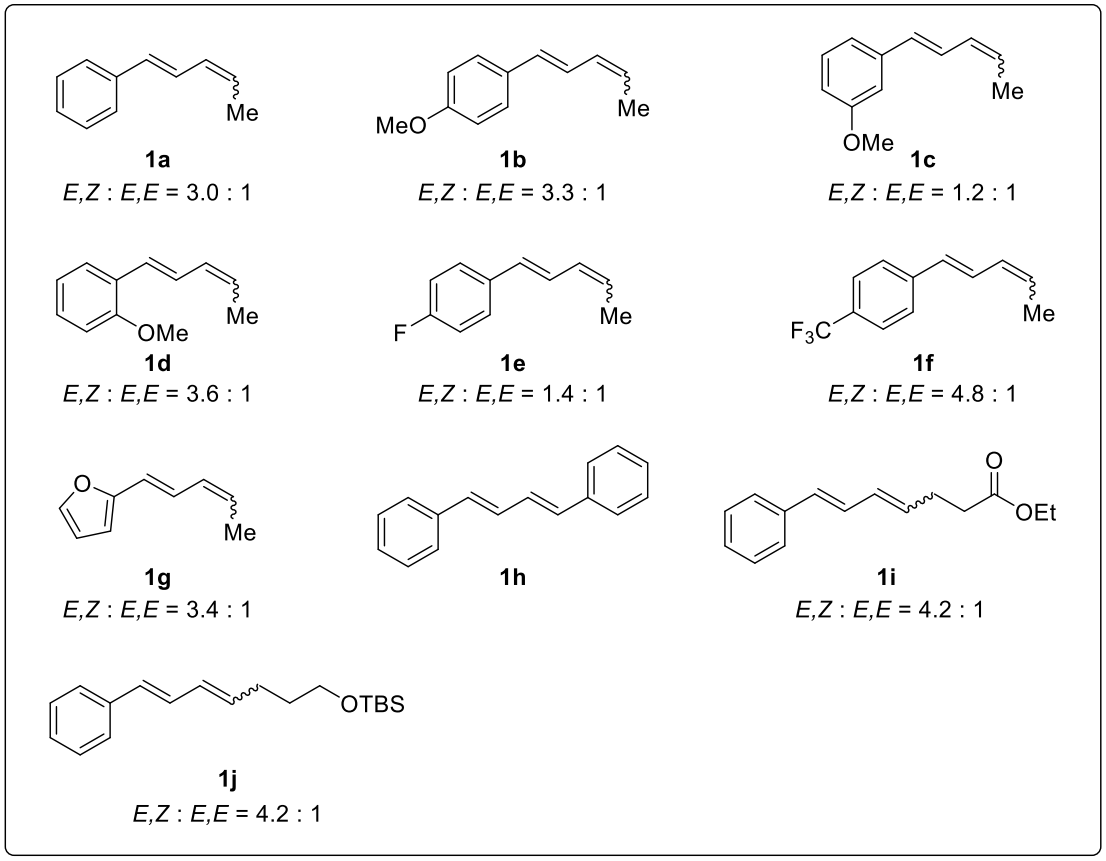


Figure S1. Internal 1,3-dienes used in this work.

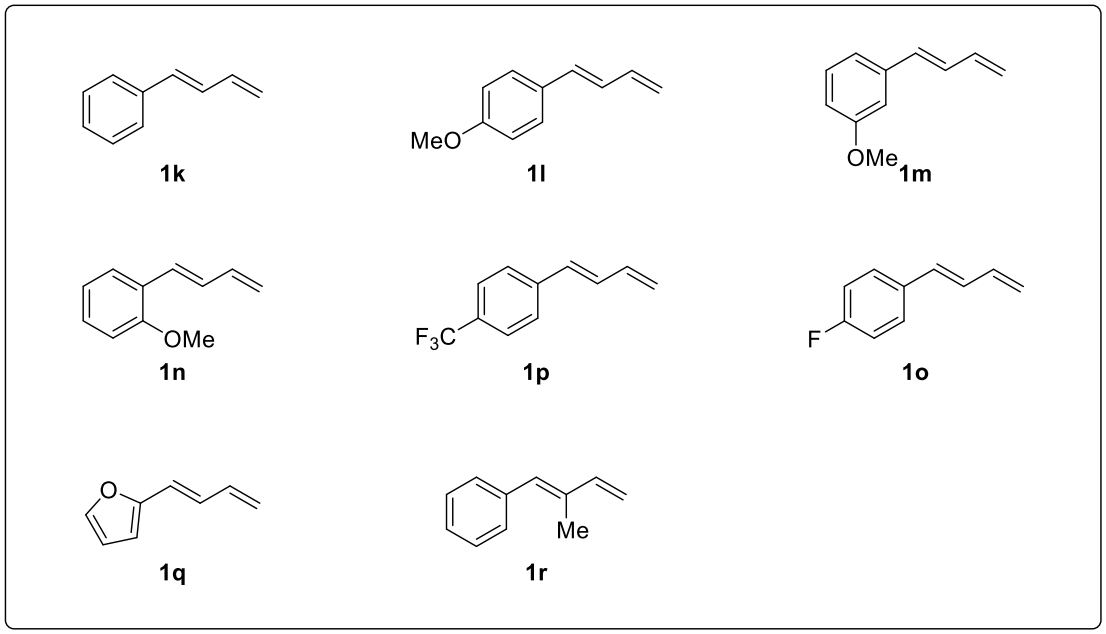


Figure S2. Terminal 1,3-dienes used in this work.

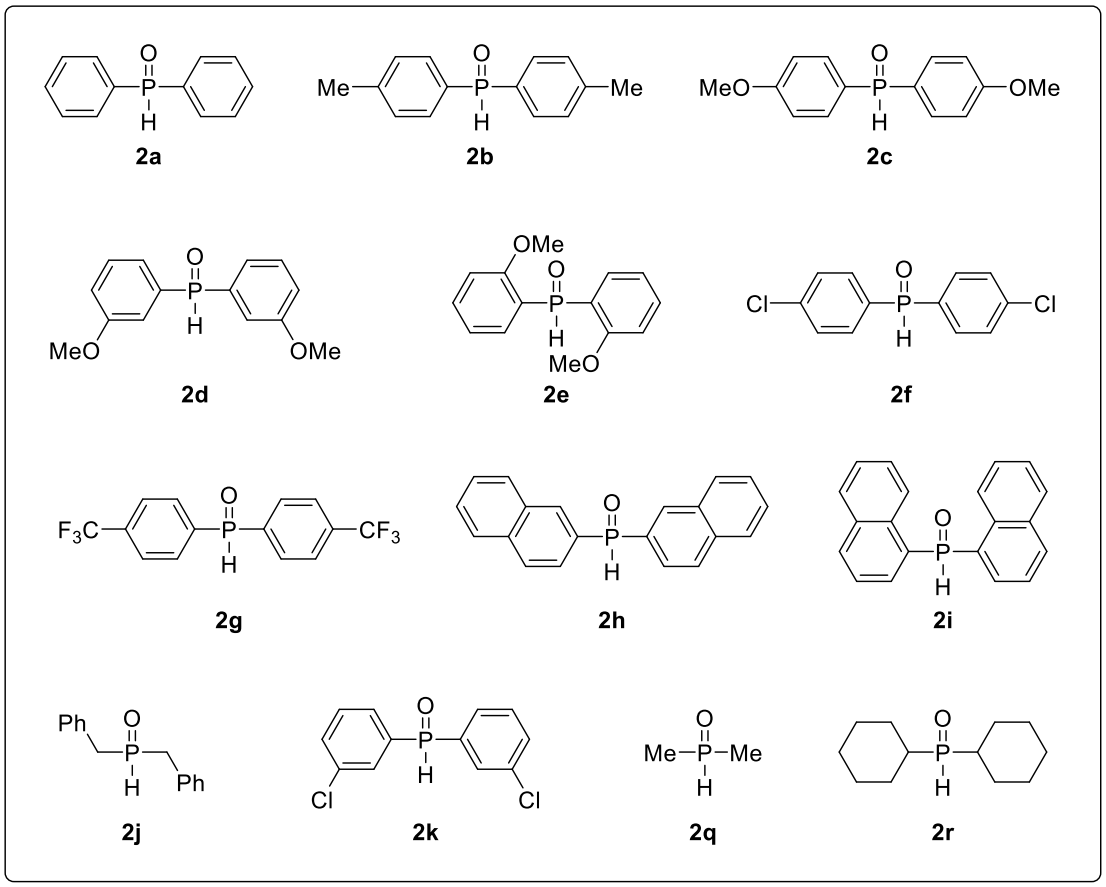


Figure S3. Symmetric phosphine oxides used in this work.

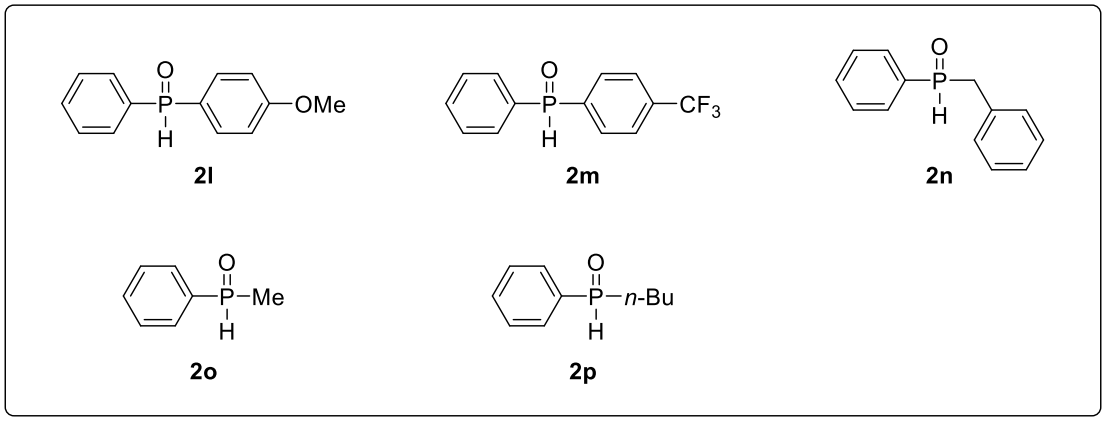


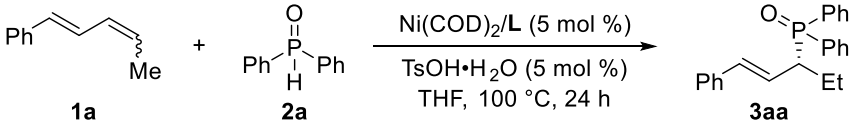
Figure S4. Unsymmetric phosphine oxides used in this work.

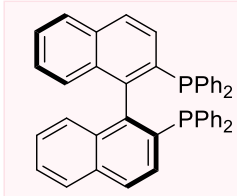
3. Reaction Optimization

General method A: a reaction tube was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.05 equiv *vs* SPO), chiral ligand (0.01 mmol, 0.05 equiv *vs* SPO), acid (0.01 mmol, 0.05 equiv *vs* SPO), diphenylphosphine oxide **2a** (0.2 mmol, 1.0 equiv) and 1.0 mL solvent in an argon-filled glovebox, then 1,3-dienes **1a** (38 μL, 0.24 mmol, 1.2 equiv *vs* SPO) was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was

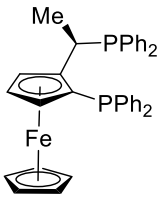
stirred at 100 °C for 24 h. The crude product was used to determine the regioselectivity by ^{31}P NMR analysis. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

Table S1. Ligand screening for Ni-catalyzed asymmetric hydrophosphinylation of **1a**.[a]

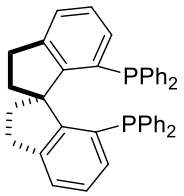




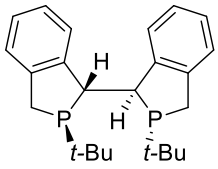
L1: (*S*)-BINAP[b]
98% yield, > 99% ee



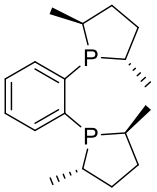
L2
35% yield, -47% ee



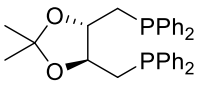
L3: (*R*)-SDP
6% yield, ND[c]



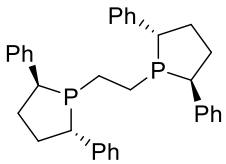
L4: (*R*c,*S*p)-DuanPhos
67% yield, 61% ee



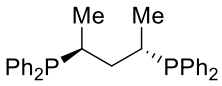
L5: (*S*,*S*)-Me-DuPhos
24% yield, -68% ee



L6: (*R*)-DIOP
16% yield, 15% ee



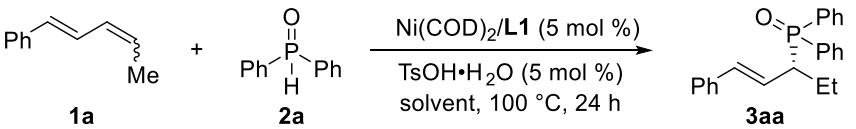
L7: (*S*,*S*)-Ph-BPE
62% yield, 93% ee



L8: (*S*,*S*)-BDPP
31% yield, 36% ee

[a] Unless otherwise noted, all reactions were carried out with 0.24 mmol **1a** (*E*,*Z* : *E*,*E* = 3.0:1), 0.20 mmol **2a**, 5.0 mol % $Ni(COD)_2$, 5.0 mol % ligand, 5.0 mol % $TsOH{\cdot}H_2O$ in 1 mL THF at 100 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. rr > 20:1, which is determined by ^{31}P NMR analysis of reaction mixture. ee values were determined by HPLC analysis using a chiral stationary phase. [b] Isolated yield. [c] Not determined.

Table S2. Solvent screening for the Ni-catalyzed asymmetric hydrophosphinylation of **1a**.[a]

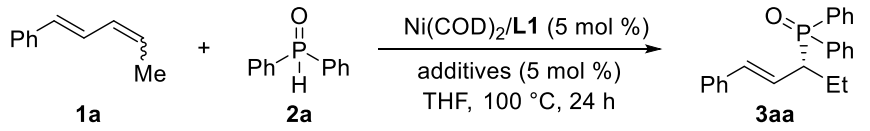


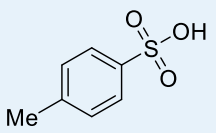
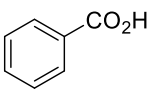
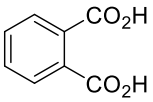
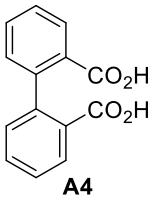
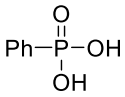
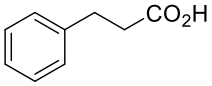
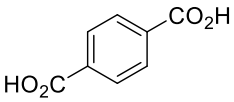
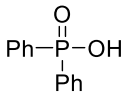
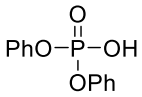
Entry	Solvent	Yield [%]	ee [%]
1	toluene	68	> 99
2	1,4-dioxane	59	98
3	THF	98[b]	> 99
4	MTBE	38	94
5	CpME	40	> 99
6	DMF	9	ND[c]
7	DCE	6	ND[c]

8	EA	71	95
9[d]	THF	92	> 99
10[e]	THF	33	> 99
11[f]	THF	trace	ND[c]

[a] Unless otherwise noted, all reactions were carried out with 0.24 mmol **1a** (*E,Z* : *E,E* = 3.0:1), 0.20 mmol **2a**, 5.0 mol % $Ni(COD)_2$, 5.0 mol % ligand, 5.0 mol % $TsOH·H_2O$ in 1 mL THF at 100 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. rr > 20:1, which is determined by ^{31}P NMR analysis of reaction mixture. ee values were determined by HPLC analysis using a chiral stationary phase. [b] Isolated yield. [c] Not determined. [d] 80 ℃. [e] 50 ℃. [f] 25 ℃.

Table S3. Acid additives screening for Ni-catalyzed asymmetric hydrophosphinylation of **1a**.[a]

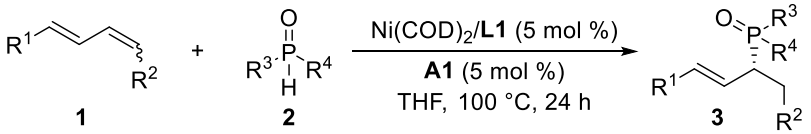


 **A1**[b] 98% yield, > 99% ee	 **A2** trace, ND	 **A3** trace, ND	 **A4** trace, ND	 **A5** trace, ND
 **A6** trace, ND	 **A7** trace, ND	 **A8** trace, ND	 **A9** 27% yield, > 99% ee	No Acid trace, ND

[a] Unless otherwise noted, all reactions were carried out with 0.24 mmol **1a** (*E,Z* : *E,E* = 3.0:1), 0.20 mmol **2a**, 5.0 mol % $Ni(COD)_2$, 5.0 mol % ligand, 5.0 mol % $TsOH·H_2O$ in 1 mL THF at 100 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. rr > 20:1, which is determined by ^{31}P NMR analysis of reaction mixture. ee values were determined by HPLC analysis using a chiral stationary phase. ND means not determined. [b] Isolated yield.

4. General Procedure for Ni-catalyzed Asymmetric Hydrophosphinylation of 1,3-Dienes

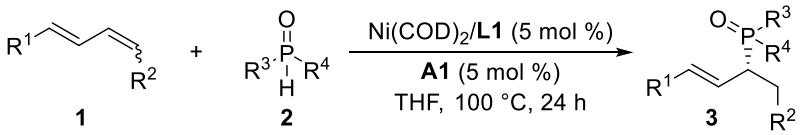
Scheme S1:



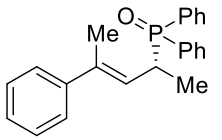
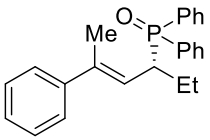
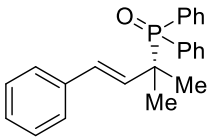
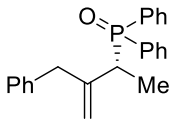
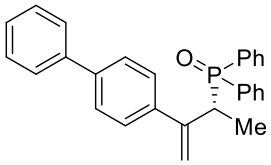
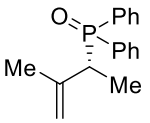
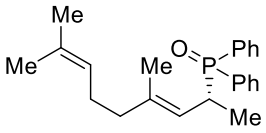
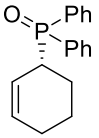
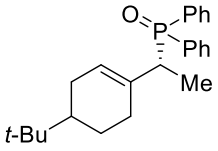
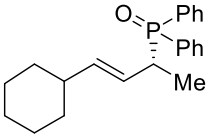
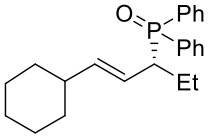
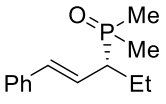
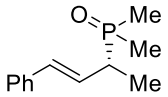
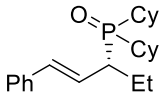
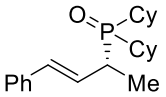
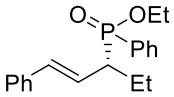
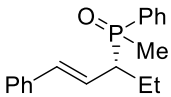
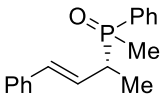
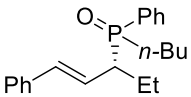
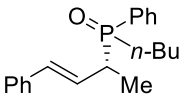
A reaction tube was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.05 equiv *vs* SPO), (*S*)-BINAP (6.3 mg, 0.01 mmol, 0.05 equiv *vs* SPO), $TsOH·H_2O$ (1.9 mg, 0.01 mmol, 0.05 equiv *vs* SPO), secondary phosphine oxides **2** (0.2 mmol, 1.0 equiv) and 1.0 mL THF in an argon-filled glovebox, then 1,3-dienes **1** (0.24 mmol, 1.2 equiv *vs* SPO) was added. The reaction vessel

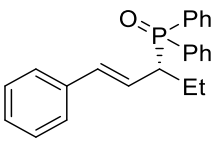
was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 100 °C for 24 h. After complete conversion, the resulting mixture was cooled to rt, and the crude product was used to determine the regioselectivity by ^{31}P NMR analysis. Then the residue was purified by SiO_2 column chromatography to give the desired product. The ee values of all compounds **3** were determined by HPLC on a chiral stationary phase.

Table S4. Non-reactive and inefficient substrates.



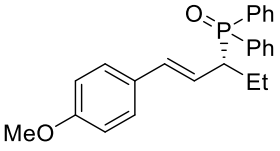
1 **2** **3**

 NP	 NP	 trace, ND	 NR
 mixture	 trace, ND	 NR	 NR
 mixture	 rr = 3.6:1 78% yield, 81% ee	 rr= 2.3:1 71% yield, 76% ee	 NR
 NR	 NR	 NR	 NR
 trace, ND	 trace, ND	 trace, ND	 trace, ND

(*R,E*)-diphenyl(1-phenylpent-1-en-3-yl)phosphine oxide (3aa): > 20:1 rr; white solid 67.6 mg;  m.p. 185.4-187.9 ℃; isolated yield 98%; > 99% ee; $[\alpha]_D^{25}$= +156.9 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, t_R = 16.2 min (major), 19.1 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.83 (m, 2H), 7.78-7.72 (m, 2H), 7.55-7.37 (m, 6H), 7.28-7.17 (m, 5H), 6.29 (dd,

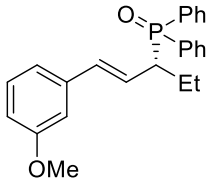
J = 15.9, 4.4 Hz, 1H), 6.06 (ddd, *J* = 15.7, 9.7, 5.8 Hz, 1H), 3.09-3.00 (m, 1H), 1.98-1.86 (m, 1H), 1.81-1.68 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.8 (d, *J* = 3.0 Hz), 135.0 (d, *J* = 12.1 Hz), 131.9 (dd, *J* = 94.5, 23.7 Hz), 131.6 (dd, *J* = 14.8, 2.8 Hz), 131.3 (dd, *J* = 16.6, 8.6 Hz), 128.43, 128.41 (dd, *J* = 32.4, 11.4 Hz), 127.4, 126.1 (d, *J* = 1.8 Hz), 124.4 (d, *J* = 7.5 Hz), 46.6 (d, *J* = 68.8 Hz), 21.0 (d, *J* = 2.5 Hz), 12.7 (d, *J* = 13.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.72 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}OP$ = 347.1559**,** found: 347.1550.

(*R,E*)-(1-(4-methoxyphenyl)pent-1-en-3-yl)diphenylphosphine oxide (3ba): > 20:1 rr; white



solid 56.6 mg; m.p.161.8-165.0 ℃; isolated yield 75%; 97% ee; $[\alpha]_D^{25}$ = +129.4 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 14.9 min (major), 17.8 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.77-7.72 (m, 2H), 7.55-7.37 (m, 6H), 7.18-7.14 (m, 2H), 6.82-6.78 (m, 2H), 6.22 (dd, *J* = 15.8, 4.4 Hz, 1H), 5.90 (ddd, *J* = 15.7, 9.7, 5.9 Hz, 1H), 3.78 (s, 3H), 3.05-2.97 (m, 1H), 1.97-1.84 (m, 1H), 1.78-1.65 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 134.4 (d, *J* = 12.3 Hz), 132.0 (dd, *J* = 94.9, 24.1 Hz), 131.5 (dd, *J* = 16.2, 2.7 Hz), 131.3 (dd, *J* = 18.0, 8.6 Hz), 129.6 (d, *J* = 2.9 Hz), 128.4 (dd, *J* = 33.6, 11.3 Hz), 127.3 (d, *J* = 1.0 Hz), 122.0 (d, *J* = 7.7 Hz), 113.8, 55.2, 46.5 (d, *J* = 69.1 Hz), 21.0 (d, *J* = 2.6 Hz), 12.6 (d, *J* = 13.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.91 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_2P$ = 377.1665**,** found: 377.1678.

(*R,E*)-(1-(3-methoxyphenyl)pent-1-en-3-yl)diphenylphosphine oxide (3ca): > 20:1 rr; white



solid 65.1 mg; m.p. 110.3-113.2 ℃; isolated yield 86%; 95% ee; $[\alpha]_D^{25}$= +138.3 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 9.1 min (major), 12.3 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.77-7.72 (m, 2H), 7.55-7.38 (m, 6H), 7.19-7.15 (m, 1H), 6.82-6.74 (m, 3H), 6.26 (dd, *J* = 15.9, 4.4 Hz, 1H), 6.06 (ddd, *J* = 15.7, 9.7, 5.8 Hz, 1H), 3.78 (s, 3H), 3.08-3.00 (m, 1H), 1.96-1.85 (m, 1H), 1.80-1.70 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.7, 138.2 (d, *J* = 3.2 Hz), 134.9 (d, *J* = 12.2 Hz), 131.9 (d, *J* = 94.9, 24.1 Hz), 131.6 (dd, *J* = 14.1, 2.7 Hz), 131.3 (dd, *J* = 17.0, 8.6 Hz), 129.4, 128.4 (dd, *J* = 32.3, 11.4 Hz), 124.8 (d, *J* = 7.4 Hz), 118.9, 113.2, 111.3, 55.2, 46.6 (d, *J* = 68.8 Hz), 21.0 (d, *J* = 2.7 Hz), 12.7 (d, *J* = 13.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.76 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_2P$ = 377.1665**,** found: 377.1680.

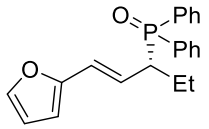
(*R,E*)-(1-(2-methoxyphenyl)pent-1-en-3-yl)diphenylphosphine oxide (3da): > 20:1 rr; white solid 60.2 mg; m.p. 154.8-158.1 ℃; isolated yield 80%; 96% ee; $[\alpha]_D^{25}$= +100.8 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 8.4 min (major), 11.0 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.83 (m, 2H), 7.80-7.75 (m, 2H), 7.53-7.37 (m, 6H), 7.27 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.19-7.15 (m, 1H), 6.86 (td, *J* = 7.5, 1.1 Hz, 1H), 6.80 (dd, *J* = 8.2, 1.1 Hz, 1H), 6.64 (dd, *J* = 16.0, 4.5 Hz, 1H), 6.04 (ddd, *J* = 15.8, 9.8, 5.9 Hz, 1H), 3.74 (s, 3H), 3.13-3.04 (m, 1H), 2.00-1.87 (m, 1H), 1.79-1.65 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 132.1 (dd, *J* = 96.3, 65.3 Hz), 131.4 (d, *J* = 16.3, 2.8 Hz), 131.3 (dd, *J* = 26.5, 8.6 Hz), 129.9 (d, *J* = 12.6 Hz), 128.4, 128.3 (dd, *J* = 33.3, 11.0 Hz), 126.6 (d, *J* = 1.9 Hz), 125.9 (d, *J* = 2.9 Hz), 124.8 (d, *J* = 7.2 Hz), 120.5, 110.8, 55.4, 47.0 (d, *J* = 69.0 Hz), 21.0 (d, *J* = 2.7 Hz), 12.6 (d, *J* = 13.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 35.56 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_2P$ = 377.1665**,** found: 377.1680.

(*R,E*)-(1-(4-fluorophenyl)pent-1-en-3-yl)diphenylphosphine oxide (3ea): > 20:1 rr; white solid 62.7 mg; m.p. 162.1-164.7 ℃; isolated yield 86%; 95% ee; $[\alpha]_D^{25}$= +144.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 18.4 min (major), 20.5 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-783 (m, 2H), 7.77-7.72 (m, 2H), 7.56-7.37 (m, 6H), 7.20-7.16 (m, 2H), 6.97-6.92 (m, 2H), 6.24 (dd, *J* = 15.9, 4.4 Hz, 1H), 5.98 (ddd, *J* = 15.7, 9.7, 5.8 Hz, 1H), 3.07-2.98 (m, 1H), 1.95-1.82 (m, 1H), 1.80-1.71 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.7 Hz), 133.8 (d, *J* = 12.1 Hz), 132.9 (t, *J* = 3.1 Hz), 131.9 (d, *J* = 92.9, 3.7 Hz), 131.6 (dd, *J* = 17.8, 2.9 Hz), 131.2 (dd, *J* = 11.8, 8.5 Hz), 128.4 (dd, *J* = 34.1, 11.4 Hz), 127.6 (d, *J* = 8.0 Hz), 124.1 (dd, *J* = 7.6, 1.7 Hz), 115.3 (d, *J* = 21.6 Hz), 46.5 (d, *J* = 68.9 Hz), 21.0 (d, *J* = 2.4 Hz), 12.7 (d, *J* = 13.6 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.90 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.38 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{23}FOP$ = 365.1465**,** found: 365.1478.

(*R,E*)-diphenyl(1-(4-(trifluoromethyl)phenyl)pent-1-en-3-yl)phosphine oxide (3fa): > 20:1 rr; white solid 60.9 mg; m.p. 178.3-181.7 ℃; isolated yield 73%; 95% ee; $[\alpha]_D^{25}$= +124.9 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 5.5 min (major), 7.8 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.76-7.72 (m, 2H), 7.57-7.54 (m, 1H), 7.53-7.50 (m, 4H), 7.47-7.45 (m, 1H), 7.43-7.40 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.30 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.19 (ddd, *J* = 15.7, 9.6, 5.7 Hz, 1H), 3.10-3.04 (m, 1H), 1.94-1.86 (m, 1H), 1.84-1.75 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.1, 133.7 (d, *J* = 12.0 Hz), 131.8 (dd, *J* = 97.5, 10.1 Hz), 131.7 (dd, *J* = 27.2, 2.7 Hz), 131.2 (dd, *J* = 10.6, 8.6 Hz), 129.2 (q, *J* = 32.3 Hz), 128.5 (dd, *J* = 50.7, 11.4 Hz), 127.4

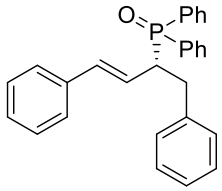
(d, *J* = 7.5 Hz), 126.3 (d, *J* = 1.9 Hz), 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.8 Hz), 46.7 (d, *J* = 68.5 Hz), 21.0 (d, *J* = 2.6 Hz), 12.7 (d, *J* = 13.6 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 33.15 ppm; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.48 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{23}F_3OP$ = 415.1433**,** found: 415.1426.

(*R,E*)-(1-(furan-2-yl)pent-1-en-3-yl)diphenylphosphine oxide (3ga): > 20:1 rr; yellowish-



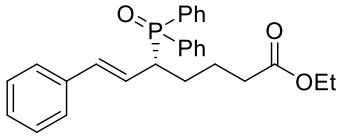
brown solid 36.9 mg; m.p. 109.2-113.7 ℃; isolated yield 55%; >99% ee; $[\alpha]_D^{25}$= +134.5 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 7.3 min (major), 19.2 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.73 (m, 4H), 7.55-7.40 (m, 6H), 7.28-7.26 (m, 1H), 6.31 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.13 (dd, *J* = 15.9, 4.1 Hz, 2H), 6.00 (ddd, *J* = 15.8, 9.5, 6.0 Hz, 1H), 3.04-2.95 (m, 1H), 1.96-1.88 (m, 1H), 1.76-1.63 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.3 (d, *J* = 3.8 Hz), 141.8, 131.8 (d, *J* = 98.0, 41.1 Hz), 131.6 (dd, *J* = 10.0, 2.6 Hz), 131.3 (dd, *J* = 20.2, 8.6 Hz), 128.4 (dd, *J* = 25.7, 11.4 Hz), 123.2 (d, *J* = 12.4 Hz), 123.0 (d, *J* = 7.8 Hz), 111.1, 107.4 (d, *J* = 2.8 Hz), 46.4 (d, *J* = 69.0 Hz), 21.1 (d, *J* = 2.5 Hz), 12.7 (d, *J* = 13.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.57 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{21}H_{22}O_2P$ = 337.1352**,** found: 337.1365.

(*R,E*)-(1,4-diphenylbut-3-en-2-yl)diphenylphosphine oxide (3ha): > 20:1 rr; white solid 57.0



mg; m.p. 177.2-178.7 ℃; isolated yield 35%; 83% ee; $[\alpha]_D^{25}$= +11.5 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 18.8 min (major), 20.8 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.91 (m, 2H), 7.80-7.75 (m, 2H), 7.58-7.51 (m, 3H), 7.48-7.38 (m, 3H), 7.24-7.16 (m, 5H), 7.15-7.06 (m, 5H), 6.11 (ddd, *J* = 16.1, 9.2, 5.7 Hz, 1H), 6.00 (dd, *J* = 15.9, 4.0 Hz, 1H), 3.44-3.36 (m, 1H), 3.22 (ddd, *J* = 14.2, 9.6, 2.7 Hz, 1H), 2.97 (ddd, *J* = 14.1, 11.3, 5.0 Hz, 1H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.2 (d, *J* = 14.1 Hz), 136.8 (d, *J* = 2.7 Hz), 135.5 (d, *J* = 11.8 Hz), 131.8 (dd, *J* = 21.4, 2.8 Hz), 131.7 (d, *J* = 98.0, 12.0 Hz), 131.3 (dd, *J* = 12.9, 8.7 Hz), 128.8 (d, *J* = 11.2 Hz), 128.7 (d, *J* = 59.7 Hz), 128.4, 128.3, 127.4, 126.3, 126.2 (d, *J* = 1.0 Hz), 123.8 (d, *J* = 7.5 Hz), 46.8 (d, *J* = 67.3 Hz), 34.2 ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.90 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{28}H_{26}OP$ = 409.1716**,** found: 409.1725.

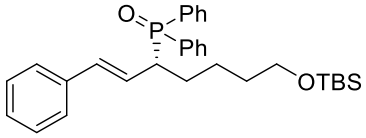
ethyl (*R,E*)-5-(diphenylphosphoryl)-7-phenylhept-6-enoate (3ia): > 20:1 rr; white solid 51.3



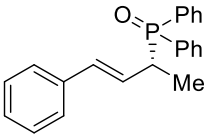
mg; m.p. 138.3-141.9 ℃; isolated yield: 59%; 94% ee; $[\alpha]_D^{25}$= +110.7 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 21.4 min (minor), 24.3 min (major); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.76-7.71 (m, 2H), 7.54-7.46

(m, 3H), 7.45-7.37 (m, 3H), 7.26-7.19 (m, 5H), 6.28 (dd, *J* = 15.9, 4.5 Hz, 1H), 6.06 (ddd, *J* = 15.7, 9.6, 5.6 Hz, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.21-3.12 (m, 1H), 2.28-2.24 (m, 2H), 1.87-1.77 m, 3H), 1.64-1.55 (m, 1H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.1, 136.6 (d, *J* = 3.0 Hz), 135.2 (d, *J* = 11.9 Hz), 131.7 (dd, *J* = 17.4, 2.0 Hz), 131.6 (d, *J* = 98.2, 17.4 Hz), 131.2 (dd, *J* = 17.9, 8.5 Hz), 128.5 (dd, *J* = 36.4, 11.4 Hz), 128.4, 127.6, 126.2, 124.0 (d, *J* = 7.8 Hz), 60.3, 44.6 (d, *J* = 68.8 Hz), 33.7, 27.0, 23.3 (d, *J* = 13.5 Hz), 14.1 ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.91 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{27}H_{30}O_3P$ = 433.1927**,** found: 433.1943.

(*R,E*)-(7-((tert-butyldimethylsilyl)oxy)-1-phenylhept-1-en-3-yl)diphenylphosphine oxide (3ja): > 20:1 rr; white solid 75.9 mg; m.p. 109.7-111.3 ℃; isolated yield: 75%; 94% ee; $[\alpha]_D^{25}$= +88.9 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 96:4, flow rate = 0.5 mL/min, UV detection at 254 nm, t_R = 14.1 min (major), 15.3 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.77-7.72 (m, 2H), 7.54-7.38 (m, 6H), 7.27-7.17 (m, 5H), 6.26 (dd, *J* = 15.9, 4.4 Hz, 1H), 6.05 (ddd, *J* = 15.7, 9.7, 5.7 Hz, 1H), 3.56-3.47 (m, 2H), 3.19-3.10 (m, 1H), 1.87-1.71 (m, 2H), 1.58-1.37 (m, 3H), 1.35-1.26 (m, 1H), 0.83 (s, 9H), -0.02 (s, 6H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.7 (d, *J* = 2.9 Hz), 135.0 (d, *J* = 12.1 Hz), 131.8 (d, *J* = 97.0, 18.0 Hz), 131.6 (dd, *J* = 17.2, 2.8 Hz), 131.3 (dd, *J* = 18.1, 8.6 Hz), 128.43 (dd, *J* = 35.0, 11.4 Hz), 128.41, 127.5, 126.2 (d, *J* = 1.8 Hz), 124.5 (d, *J* = 7.6 Hz), 62.7, 44.8 (d, *J* = 68.8 Hz), 32.2, 27.2 (d, *J* = 2.5 Hz), 25.9, 24.1 (d, *J* = 13.0 Hz), 18.2, -5.4 ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.01 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{42}O_2PSi$ = 505.2686**,** found: 505.2701.



(*R,E*)-diphenyl(4-phenylbut-3-en-2-yl)phosphine oxide (3ka): > 20:1 rr; white solid 62.2 mg; m.p. 80.1-82.5 ℃; isolated yield 94%; 96% ee; $[\alpha]_D^{25}$= +90.0 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 9.5 min (major), 12.2 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.75 (m, 4H), 7.56-7.39 (m, 6H), 7.28-7.17 (m, 5H), 6.33 (dd, *J* = 15.9, 4.2 Hz, 1H), 6.19 (ddd, *J* = 15.9, 8.2, 5.7 Hz, 1H), 3.40-3.30 (m, 1H), 1.41 (dd, *J* = 16.0, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.8 (d, *J* = 2.9 Hz), 133.2 (d, *J* = 11.7 Hz), 131.7 (dd, *J* = 8.7, 2.8 Hz), 131.5 (dd, *J* = 92.8 Hz, 43.5 Hz).131.3 (dd, *J* = 21.8, 8.5 Hz), 128.47 (dd, *J* = 28.0, 11.4 Hz), 128.45, 127.5, 126.2, 125.8 (d, *J* = 7.3 Hz), 38.5 (d, *J* = 68.8 Hz), 13.4 (d, *J* = 3.8 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.83 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{22}OP$ = 333.1403**,** found: 333.1401.



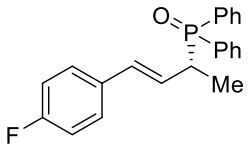
(*R,E*)-(4-(4-methoxyphenyl)but-3-en-2-yl)diphenylphosphine oxide (3la): 18:1 rr; white solid 60.3 mg; m.p. 137.9-141.6 ℃; isolated yield 83%; > 99% ee; $[\alpha]_D^{25}$ = +113.3 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 16.0 min (major), 21.1 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 2H), 7.79-7.74 (m, 2H), 7.53-7.41 (m, 6H), 7.15 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 6.26 (dd, *J* = 15.9, 4.4 Hz, 1H), 6.03 (ddd, *J* = 15.9, 8.3, 5.8 Hz, 1H), 3.77 (s, 3H), 3.37-3.27 (m, 1H), 1.39 (dd, *J* = 16.0, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.1, 132.5 (d, *J* = 11.6 Hz), 131.7 (dd, *J* = 96.3, 44.6 Hz), 131.6 (dd, *J* = 9.2, 2.5 Hz), 131.4 (dd, *J* = 23.4, 8.6 Hz), 129.6 (d, *J* = 2.8 Hz), 128.4 (dd, *J* = 29.1, 11.4 Hz), 127.3 (d, *J* = 0.8 Hz), 123.5 (d, *J* = 7.4 Hz), 113.9, 55.2, 38.4 (d, *J* = 69.1 Hz), 13.4 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.80 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}O_2P$ = 363.1508**,** found: 363.1503.

(*R,E*)-(4-(3-methoxyphenyl)but-3-en-2-yl)diphenylphosphine oxide (3ma): > 20:1 rr; colorless oil 63.4 mg; isolated yield 88%; 94% ee; $[\alpha]_D^{25}$= +99.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 13.8 min (major), 21.1 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 4H), 7.55-7.39 (m, 6H), 7.16 (td, *J* = 7.4, 1.6 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.76-6.74 (m, 2H), 6.30 (dd, *J* = 16.0, 4.1 Hz, 1H), 6.18 (ddd, *J* = 15.9, 8.1, 5.6 Hz, 1H), 3.76 (s, 3H), 3.39-3.29 (m, 1H), 1.40 (dd, *J* = 16.0, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.6, 138.2 (d, *J* = 2.9 Hz), 133.0 (d, *J* = 11.6 Hz), 131.7 (dd, *J* = 8.8, 2.7 Hz), 131.5 (dd, *J* = 96.5, 40.4 Hz), 131.3 (dd, *J* = 21.6, 8.7 Hz), 129.4, 128.4 (dd, *J* = 28.1, 11.4 Hz), 126.1 (d, *J* = 7.3 Hz), 118.8, 113.2, 111.3 (d, *J* = 0.8 Hz), 55.1, 38.4 (d, *J* = 68.8 Hz), 13.3 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.72 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}O_2P$ = 363.1508**,** found: 363.1506.

(*R,E*)-(4-(2-methoxyphenyl)but-3-en-2-yl)diphenylphosphine oxide (3na): > 20:1 rr; white solid 70.7 mg; m.p. 96.2-98.4 ℃; isolated yield 98%; 95% ee; $[\alpha]_D^{25}$= +81.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 14.3 min (major), 22.0 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.77 (m, 4H), 7.54-7.39 (m, 6H), 7.26-7.24 (m, 1H), 7.19-7.15 (m, 1H), 6.87-6.84 (m, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.67 (dd, *J* = 16.0, 4.5 Hz, 1H), 6.18 (ddd, *J* = 16.1, 8.4, 5.8 Hz, 1H), 3.75 (s, 3H), 3.43-3.33 (m, 1H), 1.41 (dd, *J* = 16.0, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 131.7 (dd, *J* = 96.3, 65.3 Hz), 131.6 (dd, *J* = 9.4, 3.6 Hz), 131.4 (dd, *J* = 31.2, 8.5 Hz), 128.5, 128.4 (dd, *J* = 29.4, 11.1 Hz), 128.1 (d, *J* = 11.9 Hz), 126.7 (d, *J* = 1.0 Hz), 126.4 (d, *J* = 7.1 Hz), 125.9 (d, *J* = 3.0 Hz), 120.6, 110.7, 55.3, 39.0 (d, *J* = 68.9 Hz), 13.4

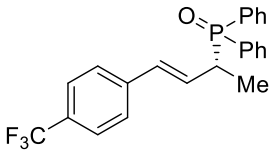
(d, *J* = 3.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.79 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}O_2P$ = 363.1508, found: 363.1502.

(*R,E*)-(4-(4-fluorophenyl)but-3-en-2-yl)diphenylphosphine oxide (3oa): > 20:1 rr; colorless



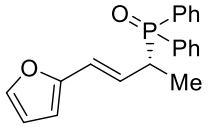
oil 56.7 mg; isolated yield 81%; 94% ee; $[\alpha]_D^{25}$= +75.2 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 17.3 min (minor), 22.3 min (major); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.82 (m, 2H), 7.79-7.74 (m, 2H), 7.56-7.40 (m, 6H), 7.19-7.14 (m, 2H), 6.96-6.90 (m, 2H), 6.28 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.10 (ddd, *J* = 15.9, 8.3, 5.7 Hz, 1H), 3.38-3.28 (m, 1H), 1.40 (dd, *J* = 16.0, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.1 (d, *J* = 246.9 Hz), 132.9 (t, *J* = 3.2 Hz), 131.9 (d, *J* = 11.5 Hz), 131.7 (dd, *J* = 10.6, 2.6 Hz), 131.5 (dd, *J* = 96.7, 19.1 Hz), 131.2 (dd, *J* = 15.9, 8.6 Hz), 128.5 (dd, *J* = 28.0, 11.4 Hz), 127.6 (dd, *J* = 8.0, 1.3 Hz), 125.5 (dd, *J* = 7.4, 2.3 Hz), 115.3 (d, *J* = 21.6 Hz), 38.3 (d, *J* = 68.8 Hz), 13.3 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.67 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.36 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{21}FOP$ = 351.1309**,** found: 351.1039.

(*R,E*)-diphenyl(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)phosphine oxide (3pa): > 20:1 rr;



white solid 60.9 mg; m.p. 135.0-137.1 ℃; isolated yield 76%; 94% ee; $[\alpha]_D^{25}$= +98.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 6.8 min (major), 8.2 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.83 (m, 2H), 7.79-7.74 (m, 2H), 7.58-7.47 (m, 6H), 7.46-7.41 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.38-6.26 (m, 2H), 3.42-3.32 (m, 1H), 1.42 (dd, *J* = 15.9, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 140.1, 131.82, 131.81 (dd, *J* = 16.0, 2.7 Hz), 131.4 (d, *J* = 97.5 Hz), 131.2 (dd, *J* = 16.3, 8.7 Hz), 129.2 (q, *J* = 32.2 Hz), 128.8, 128.5 (dd, *J* = 40.6, 11.5 Hz), 126.3 (d, *J* = 1.7 Hz), 125.4 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.7 Hz), 38.6 (d, *J* = 68.2 Hz), 13.2 (d, *J* = 3.4 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.36 ppm; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -62.48 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{21}F_3OP$ = 401.1277**,** found: 401.1271.

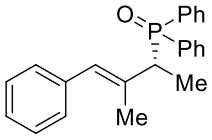
(*R,E*)-(4-(furan-2-yl)but-3-en-2-yl)diphenylphosphine oxide (3qa): > 20:1 rr; yellowish-



brown solid 31.4 mg; m.p. 91.2-93.6 ℃; isolated yield 49%; 93% ee; $[\alpha]_D^{25}$= +52.8 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 11.5 min (major), 26.1 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85-7.75 (m, 4H), 7.56-7.42 (m, 6H), 7.27-7.26 (m, 1H), 6.31 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.21-6.09 (m, 3H), 3.37-3.27 (m, 1H), 1.38 (dd, *J* = 15.9, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 152.4 (d, *J* = 3.9 Hz), 141.9, 131.7 (t, *J* = 3.3 Hz), 131.5 (dd, *J* = 95.7, 67.5 Hz), 131.4 (dd, *J* = 26.6, 8.6 Hz), 128.5 (dd, *J* = 22.6, 11.4 Hz), 124.3 (d, *J* = 7.5 Hz), 121.4 (d, *J* = 11.8 Hz), 111.2, 107.6 (d, *J* = 2.5 Hz), 38.1 (d, *J* = 68.8 Hz), 13.1 (d, *J* = 3.4 Hz) ppm; **^{31}P NMR**

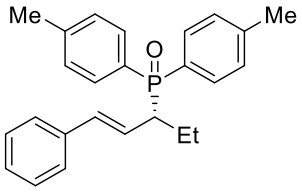
(162 MHz, $CDCl_3$) δ 34.35 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{20}H_{20}O_2P$ = 323.1195**,** found: 323.1189.

(*R,E*)-(3-methyl-4-phenylbut-3-en-2-yl)diphenylphosphine oxide (3ra): > 20:1 rr; white solid



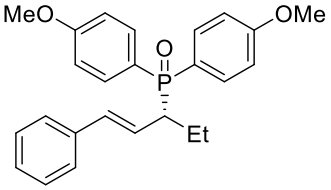
24.3 mg; m.p. 133.0-134.6 ℃; isolated yield 35%; 96% ee; $[\alpha]_D^{25}$= +129.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 10.8 min (major), 14.1 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94-7.89 (m, 2H), 7.80-7.75 (m, 2H), 7.55-7.50 (m, 3H), 7.48-7.38 (m, 3H), 7.27-7.23 (m, 2H), 7.17-7.14 (m, 1H), 6.96 (d, *J* = 7.4 Hz, 2H), 6.27 (d, *J* = 3.5 Hz, 1H), 3.24-3.17 (m, 1H), 1.86-1.85 (m, 3H), 1.46 (dd, *J* = 16.3, 7.3 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.6 (d, *J* = 2.3 Hz), 135.4 (d, *J* = 7.4 Hz), 132.4 (d, *J* = 97.8, 29.7 Hz), 131.5 (dd, *J* = 23.4, 2.6 Hz), 131.2 (d, *J* = 8.4 Hz), 129.7 (d, *J* = 10.4 Hz), 128.7 (d, *J* = 2.2 Hz), 128.4 (d, *J* = 48.1, 11.5 Hz), 127.9, 126.22, 44.2 (d, *J* = 66.9 Hz), 17.0 (d, *J* = 2.6 Hz), 13.1 (d, *J* = 3.4 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.27 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}OP$ = 347.1559**,** found: 347.1568.

(*R,E*)-(1-phenylpent-1-en-3-yl)di-p-tolylphosphine oxide (3ab): > 20:1 rr; white solid 72.4



mg; m.p. 167.9-169.1 ℃; isolated yield: 97%; 94% ee; $[\alpha]_D^{25}$= +157.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 10.9 min (major), 12.6 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 10.7, 8.0 Hz, 2H), 7.62 (dd, *J* = 10.7, 8.0 Hz, 2H), 7.29-7.18 (m, 9H), 6.30 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.06 (ddd, *J* = 15.8, 9.7, 5.9 Hz, 1H), 3.03-2.97 (m, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1.95-1.87 (m, 1H), 1.74-1.66 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 141.9 (dd, *J* = 25.6, 2.7 Hz), 136.9 (d, *J* = 2.7 Hz), 134.8 (d, *J* = 12.1 Hz), 131.3 (dd, *J* = 29.2, 8.9 Hz), 129.1 (dd, *J* = 43.4, 11.7 Hz), 128.8 (dd, *J* = 98.2, 48.3 Hz), 128.4, 127.4, 126.2 (d, *J* = 1.7 Hz), 124.8 (d, *J* = 7.1 Hz), 46.7 (d, *J* = 69.2 Hz), 21.5 (d, *J* = 5.9 Hz), 21.0 (d, *J* = 2.6 Hz), 12.7 (d, *J* = 13.6 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 33.44 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{28}OP$ = 375.1872**,** found: 375.1887.

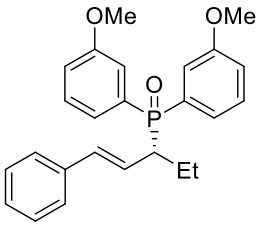
(*R,E*)-bis(4-methoxyphenyl)(1-phenylpent-1-en-3-yl)phosphine oxide (3ac): > 20:1 rr;



white solid 59.9 mg; m.p. 141.6-143.9 ℃; isolated yield: 74%; 96% ee; $[\alpha]_D^{25}$= +123.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 12.7 min (major), 14.9 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2H), 7.67-7.63 (m, 2H), 7.28-7.24 (m, 4H), 7.21-7.18 (m, 1H), 7.00-6.97 (m, 2H), 6.92-

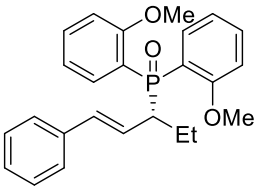
6.90 (m, 2H), 6.29 (dd, *J* = 15.9, 4.4 Hz, 1H), 6.04 (ddd, *J* = 15.7, 9.7, 5.9 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.00-2.94 (m, 1H), 1.97-1.89 (m, 1H), 1.73-1.64 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.1 (dd, *J* = 20.3, 2.9 Hz), 136.9 (d, *J* = 2.8 Hz), 134.7 (d, *J* = 12.4 Hz), 133.1 (dd, *J* = 34.0, 9.8 Hz), 128.4, 127.4, 126.2 (d, *J* = 1.7 Hz), 125.0 (d, *J* = 7.1 Hz), 123.3 (dd, *J* = 101.2, 36.2 Hz), 113.9 (dd, *J* = 45.1, 12.4 Hz), 55.2 (d, *J* = 9.3 Hz), 47.1 (d, *J* = 69.8 Hz), 21.0 (d, *J* = 2.5 Hz), 12.7 (d, *J* = 13.4 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 33.35 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{28}O_3P$ = 407.1771**,** found: 407.1768.

(*R,E*)-bis(3-methoxyphenyl)(1-phenylpent-1-en-3-yl)phosphine oxide (3ad): > 20:1 rr;



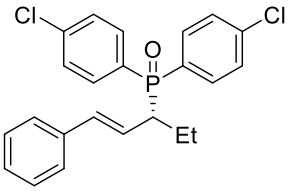
colorless oil 63.4 mg; isolated yield: 78%; 96% ee; $[\alpha]_D^{25}$= +116.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, t_R = 27.0 min (major), 30.4 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46-7.17 (m, 11H), 7.07-7.04 (m, 1H), 6.98-6.95 (m, 1H), 6.30 (dd, *J* = 15.9, 4.4 Hz, 1H), 6.10 (ddd, *J* = 15.7, 9.7, 5.8 Hz, 1H), 3.82 (s, 3H), 3.71 (s, 3H), 3.04-2.96 (m, 1H), 1.96-1.83 (m, 1H), 1.81-1.70 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5 (dd, *J* = 32.2, 13.9 Hz), 136.7 (d, *J* = 2.9 Hz), 135.0 (d, *J* = 12.1 Hz), 133.3 (dd, *J* = 94.9, 5.6 Hz), 129.5 (dd, *J* = 34.8, 13.6 Hz), 128.4, 127.5, 126.1 (d, *J* = 1.8 Hz), 124.4 (d, *J* = 7.6 Hz), 123.1 (dd, *J* = 20.5, 8.9 Hz), 117.9 (dd, *J* = 6.7, 2.7 Hz), 116.2 (d, *J* = 9.2 Hz), 55.3 (d, *J* = 13.6 Hz), 46.6 (d, *J* = 68.9 Hz), 21.0 (d, *J* = 2.6 Hz), 12.7 (d, *J* = 13.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.15 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{28}O_3P$ = 407.1771**,** found: 407.1769.

(*R,E*)-bis(2-methoxyphenyl)(1-phenylpent-1-en-3-yl)phosphine oxide (3ae): > 20:1 rr;

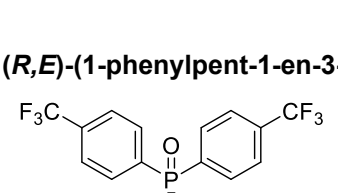


white solid 54.0 mg; m.p. 145.7-149.3 ℃; isolated yield: 66%; 95% ee; $[\alpha]_D^{25}$ = +150.8 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 26.7 min (major), 40.4 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 12.7, 7.6, 1.8 Hz, 1H), 7.75 (ddd, *J* = 12.8, 7.6, 1.8 Hz, 1H), 7.45-7.42 (m, 1H), 7.39-7.36 (m, 1H), 7.23-7.19 (m, 4H), 7.16-7.13 (m, 1H), 7.03-6.97 (m, 2H), 6.88 (dd, *J* = 8.1, 5.1 Hz, 1H), 6.78 (dd, *J* = 8.1, 5.2 Hz, 1H), 6.40 (dd, *J* = 15.8, 4.6 Hz, 1H), 6.17 (ddd, *J* = 15.8, 10.0, 7.0 Hz, 1H), 3.78 (s, 3H), 3.66 (s, 3H), 3.56-3.48 (m, 1H), 1.95-1.87 (m, 1H), 1.77-1.68 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.1 (dd, *J* = 26.7, 3.4 Hz), 137.4 (d, *J* = 2.8 Hz), 134.2 (dd, *J* = 6.0, 2.8 Hz), 133.3 (d, *J* = 13.6 Hz), 133.0 (d, *J* = 2.1 Hz), 128.3, 127.0, 126.6 (d, *J* = 7.3 Hz), 126.1 (d, *J* = 1.8 Hz), 121.1 (dd, *J* = 96.6, 14.3 Hz), 120.6 (dd, *J* = 15.9, 10.9 Hz), 110.6 (dd, *J* = 39.2, 6.6 Hz), 55.2 (d, *J* = 20.0 Hz), 46.6 (d, *J* = 72.5 Hz), 21.8 (d, *J* = 2.5 Hz), 12.9 (d, *J* = 14.8 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 35.46 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{28}O_3P$ = 407.1771**,** found: 407.1770.

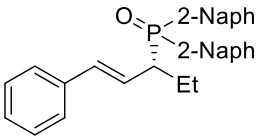
(*R,E*)-bis(4-chlorophenyl)(1-phenylpent-1-en-3-yl)phosphine oxide (3af): > 20:1 rr; white solid 22.3 mg; m.p. 134.6-136.9 ℃; isolated yield: 27%; > 99% ee; $[\alpha]_D^{25}$ = +135.5 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 7.0 min (major), 8.3 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.73 (m, 2H), 7.69-7.63 (m, 2H), 7.51-7.47 (m, 2H), 7.42-7.38 (m, 2H), 7.31-7.27 (m, 2H), 7.25-7.22 (m, 3H), 6.31 (dd, *J* = 15.9, 4.5 Hz, 1H), 6.03 (ddd, *J* = 15.9, 9.8, 6.0 Hz, 1H), 3.04-2.95 (m, 1H), 1.90-1.83 (m, 1H), 1.77-1.68 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 138.5 (dd, *J* = 26.7, 3.3 Hz), 136.4 (d, *J* = 2.8 Hz), 135.6 (d, *J* = 12.5 Hz), 132.6 (dd, *J* = 24.5, 9.3 Hz), 130.2 (d, *J* = 95.4, 33.2 Hz), 129.0 (dd, *J* = 47.5, 11.9 Hz), 128.6, 127.8, 126.2, 123.7 (d, *J* = 7.6 Hz), 46.6 (d, *J* = 69.8 Hz), 21.0 (d, *J* = 2.6 Hz), 12.6 (d, *J* = 13.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 32.60 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{22}Cl_2OP$ = 415.0780**,** found: 415.0796.



(*R,E*)-(1-phenylpent-1-en-3-yl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3ag): > 20:1 rr; white solid 29.6 mg; m.p. 149.9-151.7 ℃; isolated yield 28%; 92% ee; $[\alpha]_D^{25}$= +81.4 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 12.6 min (minor), 13.5 min (major); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 10.4, 8.1 Hz, 2H), 7.90 (dd, *J* = 10.5, 8.1 Hz, 2H), 7.78 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.69 (dd, *J* = 8.3, 2.4 Hz, 2H), 7.30-7.26 (m, 2H), 7.24-7.22 (m, 3H), 6.35 (dd, *J* = 15.9, 4.5 Hz, 1H), 6.07 (ddd, *J* = 15.8, 9.8, 6.0 Hz, 1H), 3.14-3.08 (m, 1H), 1.90-1.76 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.2 (d, *J* = 3.1 Hz), 136.1 (d, *J* = 12.5 Hz), 135.8 (dd, *J* = 93.0, 34.7 Hz), 133.7 (ddq, *J* = 33.2, 30.5, 2.8 Hz), 131.7 (dd, *J* = 17.1, 8.9 Hz), 128.6, 127.9, 126.2 (d, *J* = 1.7 Hz), 125.5 (ddq, *J* = 47.2, 11.4, 3.7 Hz), 123.6 (dq, *J* = 272.8, 3.5 Hz), 122.9 (d, *J* = 7.7 Hz), 46.2 (d, *J* = 69.7 Hz), 21.0 (d, *J* = 2.7 Hz), 12.5 (d, *J* = 13.8 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 31.06 ppm; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -63.19, -63.20 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{22}F_6OP$ = 483.1307**,** found: 483.1307.

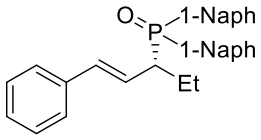


(*R,E*)-di(naphthalen-2-yl)(1-phenylpent-1-en-3-yl)phosphine oxide (3ah): > 20:1 rr; white solid 56.0 mg; m.p. 184.8-185.9 ℃; isolated yield: 63%; 94% ee; $[\alpha]_D^{25}$ = +153.7 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 11.0 min (major), 12.4 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.49 (dd, *J* = 40.8, 12.9 Hz, 2H), 7.96-7.92 (m, 2H), 7.88-7.75 (m, 6H), 7.60-7.47 (m, 4H), 7.22-7.14 (m, 5H), 6.41 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.17 (ddd, *J* = 15.8, 9.7, 5.9 Hz, 1H), 3.32-3.24 (m, 1H), 2.05-1.93 (m, 1H), 1.89-1.76 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.7 (d, *J* = 2.8 Hz), 135.2 (d, *J* = 12.3 Hz), 134.5 (dd,



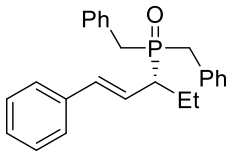
J = 8.1, 2.5 Hz), 133.5 (dd, *J* = 13.8, 7.5 Hz), 132.5 (dd, *J* = 14.9, 12.5 Hz), 129.0 (dd, *J* = 121.2, 23.6 Hz), 128.9 (d, *J* = 3.2 Hz), 128.4, 128.3, 128.1, 128.0 (d, *J* = 11.2 Hz), 127.7 (dd, *J* = 29.1, 21.9 Hz), 126.8 (d, *J* = 18.2 Hz), 126.2 (dd, *J* = 5.1, 4.0 Hz), 125.8 (d, *J* = 9.9 Hz), 124.5 (d, *J* = 7.4 Hz), 46.5 (d, *J* = 69.1 Hz), 21.1 (d, *J* = 1.9 Hz), 12.7 (d, *J* = 13.8 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.99 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{28}OP$ = 447.1872**,** found: 447.1890.

(*R,E*)-di(naphthalen-1-yl)(1-phenylpent-1-en-3-yl)phosphine oxide (3ai): > 20:1 rr; white



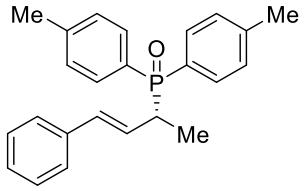
solid 35.7 mg; m.p. 181.6-184.9 ℃; isolated yield: 40%; 93% ee; $[\alpha]_D^{25}$ = +78.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 10.2 min (major), 18.0 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.4 Hz, 2H), 8.04-7.93 (m, 3H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.86-7.84 (m, 1H), 7.78-7.75 (m, 1H), 7.54-7.49 (m, 1H), 7.48-7.35 (m, 5H), 7.20-7.12 (m, 3H), 7.07-7.05 (m, 2H), 6.30 (dd, *J* = 15.9, 4.0 Hz, 1H), 6.14 (ddd, *J* = 15.9, 9.6, 6.3 Hz, 1H), 3.53-3.45 (m, 1H), 2.18-2.06 (m, 1H), 1.95-1.85 (m, 1H), 1.01 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.8 (d, *J* = 2.5 Hz), 134.5 (d, *J* = 12.9 Hz), 134.0 (d, *J* = 8.5 Hz), 133.8 (dd, *J* = 12.1, 8.9 Hz), 132.8 (dd, *J* = 14.9, 2.9 Hz), 131.7 (dd, *J* = 25.2, 9.8 Hz), 129.3 (dd, *J* = 94.9, 5.6 Hz), 128.8 (d, *J* = 14.3 Hz), 128.3, 127.3 (d, *J* = 6.0 Hz), 127.0, 126.9 (d, *J* = 4.6 Hz), 126.3, 126.1, 125.3 (d, *J* = 6.7 Hz), 124.2 (dd, *J* = 13.4, 10.6 Hz), 47.1 (d, *J* = 70.0 Hz), 21.8 (d, *J* = 1.8 Hz), 12.7 (d, *J* = 13.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 39.16 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{31}H_{28}OP$ = 447.1872**,** found: 447.1868.

(*R,E*)-dibenzyl(1-phenylpent-1-en-3-yl)phosphine oxide (3aj): > 20:1 rr; white solid 37.4 mg;



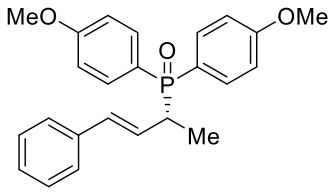
m.p. 124.2-128.3 ℃; isolated yield: 50%; 94% ee; $[\alpha]_D^{25}$= +140.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 10.5 min (major), 12.0 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 15H), 6.38 (dd, *J* = 15.8, 4.5 Hz, 1H), 5.93 (ddd, *J* = 15.5, 9.9, 5.0 Hz, 1H), 3.25-3.16 (m, 1H), 3.13-3.07 (m, 2H), 3.04-3.01 (m, 1H), 2.52-2.43 (m, 1H), 2.09-1.97 (m, 1H), 1.52-1.39 (m, 1H), 0.88 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.4 (d, *J* = 2.4 Hz), 135.0 (d, *J* = 12.4 Hz), 131.9 (d, *J* = 6.7 Hz), 130.0 (dd, *J* = 5.5, 2.3 Hz), 128.71, 128.68, 127.8, 126.9 (d, *J* = 2.6 Hz), 126.2 (d, *J* = 1.0 Hz), 124.6 (d, *J* = 5.9 Hz), 45.7 (d, *J* = 62.6 Hz), 34.1 (dd, *J* = 59.8, 12.4 Hz), 20.6, 12.7 (d, *J* = 12.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 45.23 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{25}H_{28}OP$ = 375.1872**,** found: 375.1868.

(*R,E*)-(4-phenylbut-3-en-2-yl)di-p-tolylphosphine oxide (3kb): > 20:1 rr; white solid 50.6 mg;



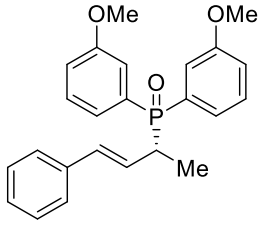
m.p. 160.3-164.0 ℃; isolated yield: 70%; 95% ee; $[\alpha]_D^{25}$= +107.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 23.3 min (minor), 26.1 min (major); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.62 (m, 4H), 7.30-7.27 (m, 2H), 7.26-7.16 (m, 7H), 6.33 (dd, *J* = 15.9, 4.2 Hz, 1H), 6.19 (ddd, *J* = 16.0, 8.2, 5.7 Hz, 1H), 3.36-3.26 (m, 1H), 2.39 (s, 3H), 2.35 (s, 3H), 1.39 (dd, *J* = 15.9, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.0 (dd, *J* = 10.5, 2.8 Hz), 136.9 (d, *J* = 2.9 Hz), 132.8 (d, *J* = 11.6 Hz), 131.4 (dd, *J* = 24.8, 8.9 Hz), 129.2 (dd, *J* = 25.3, 11.8 Hz), 128.5 (dd, *J* = 100.0, 55.3 Hz), 128.4, 127.4, 126.3 (d, *J* = 7.1 Hz), 126.2 (d, *J* = 0.7 Hz), 38.6 (d, *J* = 69.0 Hz), 21.5, 13.4 (d, *J* = 3.4 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.92 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}OP$ = 361.1716**,** found: 361.1715.

(*R,E*)-bis(4-methoxyphenyl)(4-phenylbut-3-en-2-yl)phosphine oxide (3kc): > 20:1 rr; white



solid 33.8 mg; m.p. 135.7-138.9 ℃; isolated yield: 43%; 95% ee; $[\alpha]_D^{25}$= +42.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 18.6 min (major), 23.8 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H), 7.69-7.65 (m, 2H), 7.28-7.23 (m, 4H), 7.21-7.18 (m, 1H), 7.00-6.98 (m, 2H), 6.94-6.92 (m, 2H), 6.32 (dd, *J* = 16.0, 4.2 Hz, 1H), 6.18 (ddd, *J* = 15.9, 8.2, 5.8 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.31-3.24 (m, 1H), 1.38 (dd, *J* = 15.9, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 162.2 (dd, *J* = 11.3, 2.9 Hz), 136.9 (d, *J* = 2.9 Hz), 133.2 (dd, *J* = 43.6, 9.8 Hz), 132.7 (d, *J* = 11.5 Hz), 128.5, 127.4, 126.4 (d, *J* = 7.0 Hz), 126.2 (d, *J* = 1.4 Hz), 122.9 (d, *J* = 101.2, 86.8 Hz), 114.0 (dd, *J* = 39.9, 12.3 Hz), 55.3 (d, *J* = 7.6 Hz), 38.9 (d, *J* = 69.8 Hz), 13.4 (d, *J* = 3.4 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.88 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_3P$ = 393.1614**,** found: 393.1612.

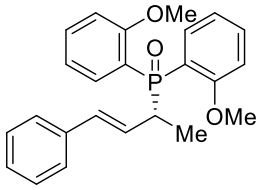
(*R,E*)-bis(3-methoxyphenyl)(4-phenylbut-3-en-2-yl)phosphine oxide (3kd): > 20:1 rr;



colorless oil 71.4 mg; isolated yield: 91%; 95% ee; $[\alpha]_D^{25}$= +73.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 11.5 min (major), 13.7 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44-7.22 (m, 10H), 7.21-7.18 (m, 1H), 7.07-7.05 (m, 1H), 7.01-6.99 (m, 1H), 6.34 (dd, *J* = 15.9, 4.2 Hz, 1H), 6.21 (ddd, *J* = 15.9, 8.3, 5.8 Hz, 1H), 3.82 (s, 3H), 3.72 (s, 3H), 3.34-3.27 (m, 1H), 1.42 (dd, *J* = 16.1, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 159.5 (dd, *J* = 42.2, 13.9 Hz), 136.8 (d, *J* = 2.8 Hz), 133.1 (d, *J* = 11.5 Hz), 133.0 (dd, *J* = 93.6, 38.7 Hz), 129.6 (dd, *J* = 43.9, 13.5 Hz), 128.4, 127.5,

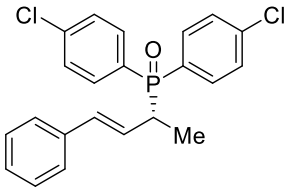
126.2 (d, *J* = 1.9 Hz), 125.9 (d, *J* = 7.5 Hz), 123.2 (dd, *J* = 34.2, 8.9 Hz), 118.0 (dd, *J* = 24.6, 2.7 Hz), 116.2 (d, *J* = 9.2 Hz), 55.3 (d, *J* = 17.5 Hz), 38.6 (d, *J* = 69.0 Hz), 13.4 (d, *J* = 3.7 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 34.17 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_3P$ = 393.1614**,** found: 393.1613.

(*R,E*)-bis(2-methoxyphenyl)(4-phenylbut-3-en-2-yl)phosphine oxide (3ke): > 20:1 rr;



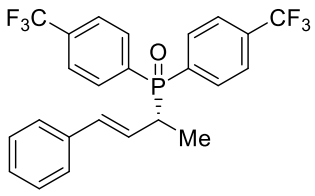
colorless oil 64.9 mg; isolated yield: 83%; 92% ee; $[\alpha]_D^{25}$=+94.1 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 80:20, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 25.5 min (major), 29.4 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (ddd, *J* = 12.8, 7.6, 1.8 Hz, 1H), 7.77 (ddd, *J* = 12.8, 7.6, 1.7 Hz, 1H), 7.46-7.43 (m, 1H), 7.42-7.38 (m, 1H), 7.23-7.18 (m, 4H), 7.16-7.13 (m, 1H), 7.04-6.98 (m, 2H), 6.89 (dd, *J* = 8.1, 5.1 Hz, 1H), 6.81 (dd, *J* = 8.1, 5.2 Hz, 1H), 6.42 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.33 (ddd, *J* = 15.7, 8.4, 6.9 Hz, 1H), 3.86-3.78 (m, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 1.41 (dd, *J* = 17.2, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 160.2 (dd, *J* = 20.0, 3.5 Hz), 137.5 (d, *J* = 2.8 Hz), 134.3 (dd, *J* = 10.2, 6.2 Hz), 133.1 (d, *J* = 2.1 Hz), 131.1 (d, *J* = 13.0 Hz), 128.4 (d, *J* = 6.9 Hz), 128.3, 127.0, 126.1 (d, *J* = 1.8 Hz), 120.9 (dd, *J* = 96.5, 44.8 Hz), 120.6 (dd, *J* = 17.1, 11.1 Hz), 110.7 (dd, *J* = 37.7, 6.6 Hz), 55.3 (d, *J* = 20.1 Hz), 38.4 (d, *J* = 72.4 Hz), 14.2 (d, *J* = 3.6 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 36.19 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_3P$ = 393.1614**,** found: 393.1612.

(*R,E*)-bis(4-chlorophenyl)(4-phenylbut-3-en-2-yl)phosphine oxide (3kf): > 20:1 rr; white

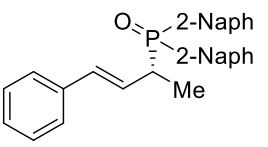


solid 31.2 mg; m.p. 144.8-145.9 ℃; isolated yield: 39%; 95% ee; $[\alpha]_D^{25}$= +114.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 10.3 min (major), 13.6 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.72 (m, 2H), 7.71-7.65 (m, 2H), 7.51-7.47 (m, 2H), 7.44-7.40 (m, 2H), 7.30-7.26 (m, 2H), 7.24-7.20 (m, 3H), 6.35 (dd, *J* = 15.9, 4.3 Hz, 1H), 6.15 (ddd, *J* = 15.9, 8.4, 5.9 Hz, 1H), 3.36-3.25 (m, 1H), 1.40 (dd, *J* = 16.3, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.6 (dd, *J* = 10.2, 3.3 Hz), 136.4 (d, *J* = 2.9 Hz), 133.7 (d, *J* = 11.8 Hz), 132.7 (dd, *J* = 22.1, 9.2 Hz), 129.8 (d, *J* = 99.0, 43.0 Hz), 129.0 (dd, *J* = 27.8, 11.9 Hz), 128.6, 127.8, 126.2, 125.0 (d, *J* = 7.5 Hz), 38.5 (d, *J* = 69.8 Hz), 13.4 (d, *J* = 3.7 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 33.49 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{20}Cl_2OP$ = 401.0623**,** found: 401.0636.

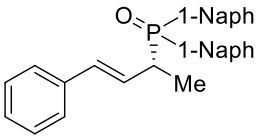
(*R,E*)-(4-phenylbut-3-en-2-yl)bis(4-(trifluoromethyl)phenyl)phosphine oxide (3kg): > 20:1 rr; white solid 66.3 mg; m.p. 150.6-152.6 ℃; isolated yield 64%; 84% ee; $[\alpha]_D^{25}$= +71.5 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 16.2 min (major), 17.8 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 10.5, 8.0 Hz, 2H), 7.93 (dd, *J* = 10.5, 8.1 Hz, 2H), 7.79 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.72 (dd, *J* = 8.4, 2.3 Hz, 2H), 7.29-7.27 (m, 2H), 7.24-7.21 (m, 3H), 6.39 (dd, *J* = 15.9, 4.4 Hz, 1H), 6.19 (ddd, *J* = 15.9, 8.6, 6.0 Hz, 1H), 3.46-3.39 (m, 1H), 1.44 (dd, *J* = 16.5, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.2 (d, *J* = 3.0 Hz), 135.5 (dd, *J* = 92.9, 51.4 Hz), 134.2 (d, *J* = 11.9 Hz), 133.8 (ddq, *J* = 32.8, 20.6, 3.0 Hz), 131.7 (dd, *J* = 24.7, 8.9 Hz), 128.6, 127.9, 126.2 (d, *J* = 1.4 Hz), 125.5 (ddq, *J* = 40.5, 11.4, 3.6 Hz), 124.3 (d, *J* = 7.6 Hz), 123.4 (dq, *J* = 271.5, 2.3 Hz), 38.3 (d, *J* = 69.6 Hz), 13.3 (d, *J* = 3.6 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 31.92 ppm; **^{19}F NMR** (565 MHz, $CDCl_3$) δ -63.19, -63.21 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{20}F_6OP$ = 469.1151, found: 469.1147.



(*R,E*)-di(naphthalen-2-yl)(4-phenylbut-3-en-2-yl)phosphine oxide (3kh): > 20:1 rr; white solid 72.2 mg; m.p. 136.4-137.8 ℃; isolated yield: 83%; 93% ee; $[\alpha]_D^{25}$ = +95.7 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 15.6 min (major), 18.8 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 22.5, 12.8 Hz, 2H), 7.95-7.91 (m, 2H), 7.89-7.77 (m, 6H), 7.59-7.47 (m, 4H), 7.21-7.13 (m, 5H), 6.43 (dd, *J* = 16.0, 4.2 Hz, 1H), 6.29 (ddd, *J* = 15.9, 8.1, 5.7 Hz, 1H), 3.63-3.53 (m, 1H), 1.48 (dd, *J* = 16.0, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.7 (d, *J* = 2.9 Hz), 134.5 (dd, *J* = 4.4, 2.3 Hz), 133.6 (dd, *J* = 28.0, 7.7 Hz), 133.2 (d, *J* = 11.6 Hz), 132.5 (t, *J* = 12.7 Hz), 128.84, 128.83 (dd, *J* = 94.9, 42.8 Hz), 128.40, 128.39 (d, *J* = 11.1 Hz), 128.1, 128.0 (d, *J* = 11.4 Hz), 127.7 (dd, *J* = 31.6, 25.9 Hz), 126.8 (d, *J* = 14.7 Hz), 126.1 (dd, *J* = 6.1, 5.1 Hz), 125.9 (d, *J* = 2.5 Hz), 125.8, 38.4 (d, *J* = 68.9 Hz), 13.5 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 34.83 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{30}H_{26}OP$ = 433.1716**,** found: 433.1732.

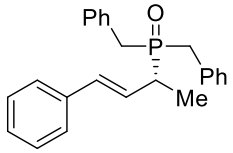


(*R,E*)-di(naphthalen-1-yl)(4-phenylbut-3-en-2-yl)phosphine oxide (3ki): > 20:1 rr; white solid 66.6 mg; m.p. 177.2-178.9 ℃; isolated yield: 77%; 95% ee; $[\alpha]_D^{25}$ = +42.9 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 14.7 min (major), 22.6 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.2 Hz, 2H), 8.01-7.90 (m, 4H), 7.85-7.82 (m, 1H), 7.79-7.76 (m, 1H), 7.51-7.34 (m, 6H), 7.20-7.11 (m, 3H), 7.08-7.05 (m, 2H), 6.38 (dd, *J* = 16.0, 3.4 Hz, 1H), 6.30 (ddd, *J* = 15.9, 7.7, 5.9 Hz, 1H), 3.85-3.75 (m, 1H), 1.56 (dd, *J* = 16.0, 7.0 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.8 (d, *J* = 2.4 Hz), 134.0 (dd, *J* = 8.0, 2.4 Hz), 133.8 (dd, *J* = 8.2, 5.0 Hz), 132.9 (dd, *J* = 9.9, 3.0 Hz), 132.4 (d, *J* = 12.0 Hz),



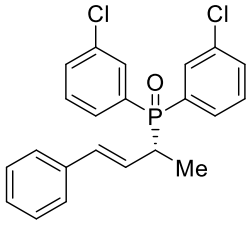
131.7 (dd, *J* = 9.9, 2.7 Hz), 129.0 (dd, *J* = 92.1, 5.2 Hz), 128.7 (d, *J* = 14.3 Hz), 128.3, 127.2 (d, *J* = 7.6 Hz), 127.1, 127.0 (d, *J* = 6.3 Hz), 126.9 (d, *J* = 6.5 Hz), 126.3, 126.1 (d, *J* = 4.8 Hz), 124.2 (dd, *J* = 13.4, 8.3 Hz), 39.1 (d, *J* = 69.9 Hz), 14.6 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 39.99 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{30}H_{26}OP$ = 433.1716**,** found: 433.1710.

(*R,E*)-dibenzyl(4-phenylbut-3-en-2-yl)phosphine oxide (3kj): > 20:1 rr; white solid 32.5 mg;



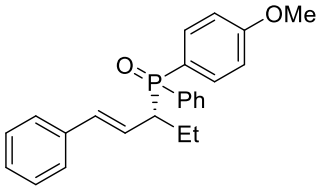
m.p. 119.4-121.8 ℃; isolated yield: 45%; 93% ee; $[\alpha]_D^{25}$= +79.6 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 18.3 min (major), 19.2 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.27 (m, 15H), 6.41 (dd, *J* = 15.9, 3.8 Hz, 1H), 6.14 (ddd, *J* = 15.9, 8.4, 5.1 Hz, 1H), 3.22-3.15 (m, 1H), 3.13-3.08 (m, 2H), 3.05-3.01 (m, 1H), 2.84-2.72 (m, 1H), 1.33 (dd, *J* = 15.1, 7.1 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 136.6 (d, *J* = 2.7 Hz), 132.9 (d, *J* = 11.6 Hz), 131.8 (dd, *J* = 7.1, 4.0 Hz), 129.9 (dd, *J* = 10.1, 4.0 Hz), 128.8, 128.7, 127.8, 126.9 (dd, *J* = 7.1, 3.0 Hz), 126.2, 126.1 (d, *J* = 6.3 Hz), 37.2 (d, *J* = 62.6 Hz), 33.8 (dd, *J* = 59.6, 32.8 Hz), 13.1 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 45.88 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}OP$ = 361.1716**,** found: 361.1712.

(*R,E*)-bis(3-chlorophenyl)(4-phenylbut-3-en-2-yl)phosphine oxide (3kk): > 20:1 rr; white



solid 43.3 mg; m.p. 113.4-116.7 ℃; isolated yield: 54%; 94% ee; $[\alpha]_D^{25}$= +118.0 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 8.3 min (major), 11.9 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.83 (dt, *J* = 11.1, 1.7 Hz, 1H), 7.75 (dt, *J* = 11.2, 1.7 Hz, 1H), 7.70 (ddt, *J* = 10.3, 7.5, 1.3 Hz, 1H), 7.63 (ddt, *J* = 10.3, 7.6, 1.2 Hz, 1H), 7.53 (ddt, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.48-7.44 (m, 2H), 7.38 (td, *J* = 7.8, 3.3 Hz, 1H), 7.29-7.20 (m, 5H), 6.38 (dd, *J* = 15.9, 4.5 Hz, 1H), 6.15 (ddd, *J* = 15.9, 8.6, 6.0 Hz, 1H), 3.36-3.29 (m, 1H), 1.42 (dd, *J* = 16.5, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.4 (d, *J* = 3.1 Hz), 135.2 (dd, *J* = 44.7, 14.7 Hz), 134.0 (d, *J* = 11.9 Hz), 133.6 (dd, *J* = 95.1, 55.0 Hz), 132.2 (dd, *J* = 17.4, 2.7 Hz), 131.2 (dd, *J* = 29.5, 9.3 Hz), 130.1 (dd, *J* = 44.7, 12.4 Hz), 129.2 (dd, *J* = 30.7, 8.1 Hz), 128.5, 127.8, 126.3 (d, *J* = 1.8 Hz), 124.8 (d, *J* = 7.6 Hz), 38.4 (d, *J* = 69.4 Hz), 13.4 (d, *J* = 3.8 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 31.94 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{22}H_{20}Cl_2OP$ = 401.0623**,** found: 401.0618.

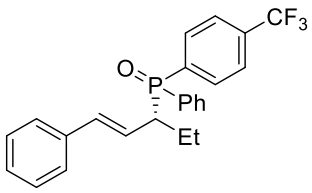
(4-methoxyphenyl)(phenyl)((*R,E*)-1-phenylpent-1-en-3-yl)phosphine oxide (3al): > 20:1 rr;



white solid 55.8 mg (a mixture of diastereomer); isolated yield 74%; dr = 1.1:1; 97% ee, 98% ee; The enantiomeric excess was determined by HPLC on Chiralpak IC-H column, hexane: isopropanol = 85:15, flow rate = 0.4 mL/min, UV detection at 254 nm, diastereomer 1: t_R = 76.8 min (major), 127.4 min (minor);

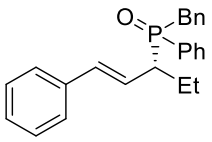
diastereomer 2: t_R = 80.5 min (major), 117.3 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 7.85-7.81 (m, 2H), 7.80-7.75 (m, 2.2H), 7.75-7.71 (m, 2.2H), 7.69-7.65 (m, 2H), 7.53-7.50 (m, 1.1H), 7.49-7.45 (m, 2.2H), 7.44-7.42 (m, 1H), 7.41-7.37 (m, 2H), 7.28-7.18 (m, 10.5H), 7.00 (dd, J = 8.8, 2.2 Hz, 2.2H), 6.91 (dd, J = 8.8, 2.3 Hz, 2H), 6.32-6.26 (m, 2.1H), 6.09-6.02 (m, 2.1H), 3.83 (s, 3.3H), 3.78 (s, 3H), 3.05-2.97 (m, 2.1H), 1.98-1.87 (m, 2.1H), 1.76-1.67 (m, 2.1H), 0.97-0.94 (m, 6.3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 162.2 (d, *J* = 2.8 Hz), 162.0 (d, *J* = 2.7 Hz), 136.8 (d, *J* = 2.9 Hz), 134.9 (d, *J* = 2.7 Hz), 134.8 (d, *J* = 2.5 Hz), 133.2 (d, *J* = 9.8 Hz), 133.0 (d, *J* = 9.8 Hz), 132.4 (d, *J* = 94.8 Hz), 132.1 (d, *J* = 97.4 Hz), 131.5 (d, *J* = 2.7 Hz), 131.34 (d, *J* = 2.8 Hz), 131.30 (d, *J* = 8.7 Hz), 131.1 (d, *J* = 8.7 Hz), 128.47 (d, *J* = 11.3 Hz), 128.41, 128.40, 128.2 (d, *J* = 11.4 Hz), 127.4 (d, *J* = 3.0 Hz), 126.12, 126.11, 126.10, 126.09, 124.6 (d, *J* = 7.6 Hz), 122.8 (d, *J* = 100.5 Hz) 122.6 (d, *J* = 103.1 Hz), 114.1 (d, *J* = 12.2 Hz), 113.8 (d, *J* = 12.3 Hz), 55.24, 55.17, 46.8 (d, *J* = 69.5 Hz), 46.7 (d, *J* = 69.4 Hz), 21.0, 12.7 (d, *J* = 13.6 Hz), 12.6 (d, *J* = 13.6 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 33.31 ppm (the peaks of the two diastereomers overlap totally). **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}O_2P$ = 377.1665**,** found: 377.1661.

phenyl((*R,E*)-1-phenylpent-1-en-3-yl)(4-(trifluoromethyl)phenyl)phosphine oxide (3am): >



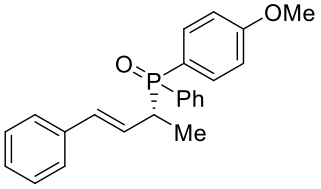
20:1 rr; white solid 60.5 mg (a mixture of diastereomer); isolated yield 73%; dr = 1.1:1; 95% ee, 95% ee; The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 94:6, flow rate = 0.3 mL/min, UV detection at 254 nm, diastereomer 1: t_R = 25.4 min (major), 36.8 min (minor); diastereomer 2: t_R = 27.1 min (major), 29.9 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 8.02-7.97 (m, 1H), 7.90-7.83 (m, 2H), 7.78-7.73 (m, 2H), 7.67-7.65 (m, 1H), 7.57-7.42 (m, 3H), 7.29-7.26 (m, 2H), 7.24-7.19 (m, 3H), 6.36-6.27 (m, 1H), 6.11-6.02 (m, 1H), 3.11-3.03 (m, 1H), 1.92-1.72 (m, 2H), 1.00-0.96 (m, 3H) ppm (the peaks of the two diastereomers overlap totally); **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 136.8 (d, *J* = 90.7 Hz), 136.6 (d, *J* = 93.7 Hz), 136.5 (d, *J* = 2.8 Hz), 136.4 (d, *J* = 3.2 Hz), 135.6 (d, *J* = 12.5 Hz), 135.5 (d, *J* = 12.4 Hz), 133.43 (q, *J* = 31.0 Hz), 133.41 (q, *J* = 31.1 Hz), 132.1 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 8.7 Hz), 131.7 (d, *J* = 8.8 Hz), 131.24 (d, *J* = 8.7 Hz), 131.18 (d, *J* = 95.1 Hz), 131.08 (d, *J* = 8.6 Hz), 130.95 (d, *J* = 97.0 Hz), 128.9 (d, *J* = 11.4 Hz), 128.54, 128.53 (d, *J* = 11.7 Hz), 128.52, 127.72, 127.68, 126.19 (d, *J* = 1.8 Hz), 126.15 (d, *J* = 1.7 Hz), 125.3 (dq, *J* = 48.1, 3.4 Hz), 125.2 (dq, *J* = 48.5, 3.7 Hz), 123.67 (d, *J* = 7.6 Hz), 123.66 (d, *J* = 7.6 Hz), 123.53 (q, *J* = 272.6 Hz), 123.51 (q, *J* = 272.7 Hz), 46.5 (d, *J* = 69.4 Hz), 46.3 (d, *J* = 69.3 Hz), 21.02 (d, *J* = 2.7 Hz), 20.99 (d, *J* = 2.6 Hz), 12.63 (d, *J* = 13.5 Hz), 12.62 (d, *J* = 13.6 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 32.89, 32.65 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ -63.00, -63.02 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{23}F_3OP$ = 415.1433**,** found: 415.1427.

benzyl(phenyl)((*R,E*)-1-phenylpent-1-en-3-yl)phosphine oxide (3an): > 20:1 rr; white solid



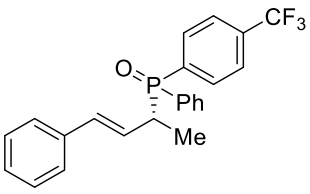
37.9 mg (a mixture of diastereomer); isolated yield 53%; dr = 1.3:1; 97% ee, 96% ee; The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, diastereomer 1: t_R = 14.3 min (minor), 23.1 min (major); diastereomer 2: t_R = 10.1 min (major), 20.3 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 7.70-7.67 (m, 2H), 7.60-7.56 (m, 2.6H), 7.53-7.49 (m, 1.3H), 7.49-7.43 (m, 5.6H), 7.42-7.39 (m, 2.6H), 7.37-7.25 (m, 12.6H), 7.23-7.20 (m, 1.3H), 7.15-7.11 (m, 3.9H), 7.03-7.01 (m, 2.6H), 6.57 (dd, *J* = 15.8, 4.1 Hz, 1.3H), 6.40 (dd, *J* = 15.9, 4.7 Hz, 1H), 6.30 (ddd, *J* = 15.8, 10.1, 5.7 Hz, 1.3H), 5.77 (ddd, *J* = 15.5, 10.0, 5.1 Hz, 1H), 3.54-3.40 (m, 3.3H), 3.28 (dd, *J* = 14.7, 10.6 Hz, 1.3H), 2.77-2.65 (m, 2.3H), 2.21-2.11 (m, 1H), 1.71-1.64 (m, 2.6H), 1.36-1.28 (m, 1H), 0.90-0.87 (m, 6.9H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 136.51 (d, *J* = 1.2 Hz). 136.50 (d, *J* = 2.2 Hz), 135.2 (d, *J* = 12.0 Hz), 134.6 (d, *J* = 12.7 Hz), 131.7 (d, *J* = 2.8 Hz), 131.53 (d, *J* = 2.7 Hz), 131.47 (d, *J* = 6.6 Hz), 131.4 (d, *J* = 7.6 Hz), 131.3 (d, *J* = 7.3 Hz), 131.1 (d, *J* = 8.2 Hz), 130.6 (d, *J* = 90.4 Hz), 130.2 (d, *J* = 90.0 Hz), 130.1 (d, *J* = 5.1 Hz), 129.9 (d, *J* = 5.2 Hz), 128.7, 128.6, 128.5 (d, *J* = 2.2 Hz), 128.26 (d, *J* = 2.2 Hz), 128.25, 128.2, 127.97 (d, *J* = 72.5 Hz), 127.95 (d, *J* = 68.5 Hz), 126.8 (d, *J* = 2.7 Hz), 126.5 (d, *J* = 2.9 Hz), 126.3 (d, *J* = 1.3 Hz), 126.1 (d, *J* = 2.0 Hz), 125.3 (d, *J* = 5.6 Hz), 124.6 (d, *J* = 7.3 Hz), 47.0 (d, *J* = 65.8 Hz), 46.2 (d, *J* = 65.4 Hz), 36.2 (d, *J* = 63.2 Hz), 34.7 (d, *J* = 63.6 Hz), 21.0 (d, *J* = 2.8 Hz), 20.3 (d, *J* = 3.1 Hz), 12.6 (d, *J* = 13.1 Hz), 12.4 (d, *J* = 13.0 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 39.09, 38.16 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{24}H_{26}OP$ = 361.1716**,** found: 361.1711.

(4-methoxyphenyl)(phenyl)((*R,E*)-4-phenylbut-3-en-2-yl)phosphine oxide (3kl): > 20:1 rr;

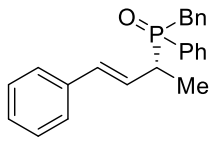


white solid 40.2 mg (a mixture of diastereomer); isolated yield 55%; dr = 1.3:1; 95% ee, 92% ee; The enantiomeric excess was determined by HPLC on Chiralpak IA-H column, hexane: isopropanol = 80:20, flow rate = 0.3 mL/min, UV detection at 254 nm, diastereomer 1: t_R = 50.6 min (minor), 66.9 min (major); diastereomer 2: t_R = 57.9 min (major), 61.7 min (minor); **^{1}H NMR** (600 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 7.84-7.80 (m, 2H), 7.78-7.73 (m, 5H), 7.72-7.68 (m, 2H), 7.54-7.51 (m, 1H), 7.50-7.46 (m, 3.3H), 7.43-7.40 (m, 2.6H), 7.28-7.18 (m, 11.7H), 7.02-6.99 (m, 2.6H), 6.95-6.92 (m, 2H), 6.35-6.29 (m, 2.3H), 6.22-6.16 (m, 2.3H), 3.84 (s, 3.9H), 3.81 (s, 3H), 3.34-3.28 (m, 2.3H), 1.42-1.37 (m, 6.9H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 162.3 (d, *J* = 2.8 Hz), 162.2 (d, *J* = 2.8 Hz), 136.8 (d, *J* = 3.0 Hz), 133.3 (d, *J* = 9.8 Hz), 133.1 (d, *J* = 9.8 Hz), 132.88 (d, *J* = 11.4 Hz), 132.87 (d, *J* = 11.3 Hz), 132.2 (d, *J* = 95.0 Hz), 131.7 (d, *J* = 97.4 Hz), 131.6 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 2.7 Hz), 131.4 (d, *J* = 8.6 Hz), 131.2 (d, *J* = 8.7 Hz), 128.52 (d, *J* = 11.2 Hz), 128.45, 128.43, 128.2 (d, *J* = 11.3 Hz), 127.42, 127.41, 126.16, 126.14, 126.13, 126.08, 122.7 (d, *J* = 100.9 Hz), 122.1 (d, *J* = 102.9 Hz), 114.2 (d, *J* = 12.2 Hz), 113.9 (d, *J* = 12.3 Hz), 55.3, 55.2, 38.70 (d, *J* = 69.1 Hz), 38.68 (d, *J* = 69.2 Hz).13.4 (d, *J* = 3.5 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 34.13 ppm (the peaks of the two diastereomers overlap totally). **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}O_2P$ = 363.1508**,** found: 363.1506.

phenyl((*R,E*)-4-phenylbut-3-en-2-yl)(4-(trifluoromethyl)phenyl)phosphine oxide (3km): > 20:1 rr; white solid 71.7 mg (a mixture of diastereomer); isolated yield 90%; dr = 1.3:1; 91% ee, 94% ee; The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, diastereomer 1: t_R = 16.6 min (major), 21.6 min (minor); diastereomer 2: t_R = 13.1 min (minor), 25.7 min (major); **^{1}H NMR** (400 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 8.01-7.97 (m, 1H), 7.93-7.72 (m, 4H), 7.69-7.67 (m, 1H), 7.60-7.44 (m, 3H), 7.29-7.25 (m, 2H), 7.23-7.21 (m, 3H), 6.39-6.30 (m, 1H), 6.22-6.14 (m, 1H), 3.43-3.33 (m, 1H), 1.46-1.39 (m, 3H) ppm (the peaks of the two diastereomers overlap totally); **^{13}C NMR** (150 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 136.6 (d, *J* = 91.6 Hz), 136.5 (d, *J* = 2.9 Hz), 136.4 (d, *J* = 2.7 Hz), 136.1 (d, *J* = 97.6 Hz), 133.68 (d, *J* = 11.8 Hz), 133.66 (d, *J* = 11.6 Hz), 133.43 (dq, *J* = 32.9, 20.2 Hz), 133.41 (dq, *J* = 32.9, 20.0 Hz), 132.2 (d, *J* = 2.8 Hz), 132.1 (d, *J* = 2.7 Hz), 131.9 (d, *J* = 8.7 Hz), 131.7 (d, *J* = 8.8 Hz), 131.3 (d, *J* = 8.6 Hz), 131.1 (d, *J* = 8.7 Hz), 131.0 (d, *J* = 98.8 Hz), 130.6 (d, *J* = 97.9 Hz), 128.9 (d, *J* = 11.4 Hz), 128.60 (d, *J* = 11.5 Hz), 128.55, 128.52, 127.73, 127.68, 126.20 (d, *J* = 1.4 Hz), 126.17 (d, *J* = 1.4 Hz), 125.4 (dq, *J* = 42.5, 3.4 Hz), 125.2 (dq, *J* = 42.6, 3.5 Hz), 125.1, 125.0, 123.5 (q, *J* = 272.5 Hz), 38.43 (d, *J* = 69.2 Hz), 38.40 (d, *J* = 69.2 Hz), 13.41 (d, *J* = 3.5 Hz), 13.36 (d, *J* = 3.6 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ 33.69, 33.46 ppm; **^{19}F NMR** (376 MHz, $CDCl_3$, reported as a mixture of diastereomers) δ -63.01, -63.02 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{21}F_3OP$ = 401.1277**,** found: 401.1270.

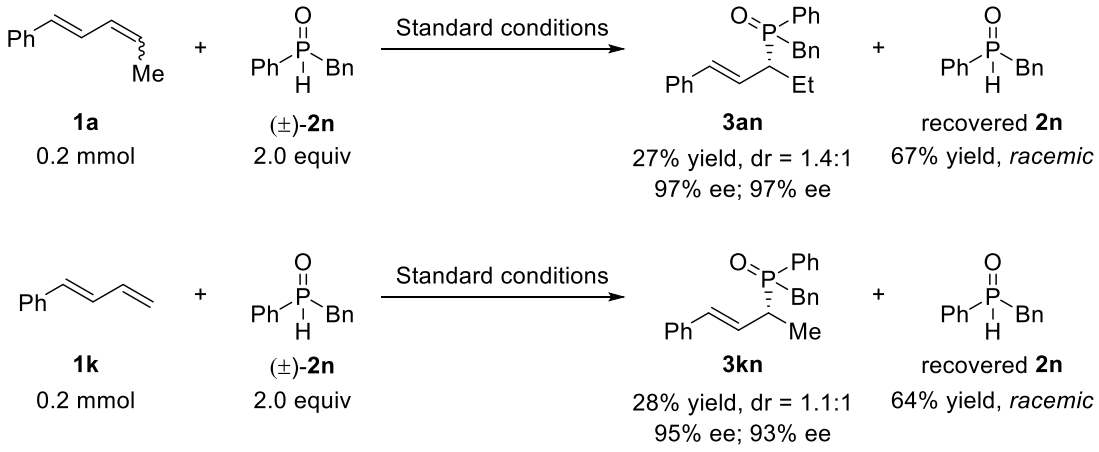


benzyl(phenyl)((*R,E*)-4-phenylbut-3-en-2-yl)phosphine oxide (3kn): > 20:1 rr; white solid 24.4 mg; isolated yield 35%; dr = 1.1:1; 96% ee, 94% ee; The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, diastereomer 1: t_R = 17.8 min (minor), 24.9 min (major); diastereomer 2: t_R = 11.2 min (major), 14.3 min (minor); diastereomer 1: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.51-7.48 (m, 1H), 7.43-7.40 (m, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28-7.25 (m, 1H), 7.18-7.12 (m, 3H), 7.08-7.06 (m, 2H), 6.55 (dd, *J* = 15.9, 4.1 Hz, 1H), 6.39 (ddd, *J* = 15.8, 9.0, 5.5 Hz, 1H), 3.48 (dd, *J* = 16.3, 14.7 Hz, 1H), 3.32 (dd, *J* = 14.7, 11.1 Hz, 1H), 3.00-2.93 (m, 1H), 1.27 (dd, *J* = 15.9, 7.1 Hz, 3H) ppm; **^{13}C NMR** (150 MHz, $CDCl_3$) δ 136.6 (d, *J* = 2.6 Hz), 133.3 (d, *J* = 11.4 Hz), 131.6 (d, *J* = 2.7 Hz), 131.5 (d, *J* = 7.5 Hz), 131.2 (d, *J* = 8.2 Hz), 130.3 (d, *J* = 90.4 Hz), 129.9 (d, *J* = 5.0 Hz), 128.6, 128.3 (d, *J* = 4.4 Hz), 128.2, 128.0 (d, *J* = 91.1 Hz), 126.6 (d, *J* = 2.9 Hz), 126.3 (d, *J* = 1.2 Hz), 126.1 (d, *J* = 7.4 Hz), 38.9 (d, *J* = 65.6 Hz), 35.7 (d, *J* = 62.8 Hz), 13.8 (d, *J* = 3.7 Hz) ppm; **^{31}P NMR** (243 MHz, $CDCl_3$) δ 39.87 ppm. Another diastereomer is mixed with an unknown impurity and cannot be purified. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{24}OP$ = 347.1559**,** found: 347.1557.



5. Kinetic Resolution/Dynamic Kinetic Resolution Investigations

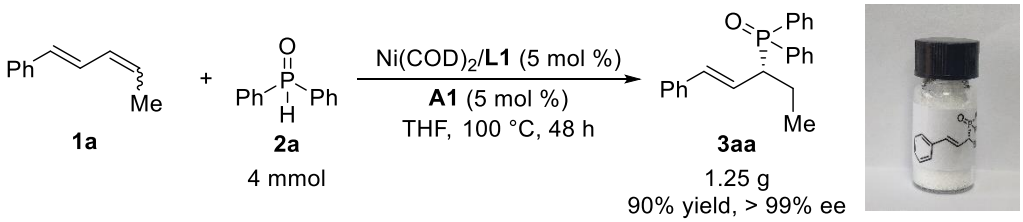
Scheme S2:

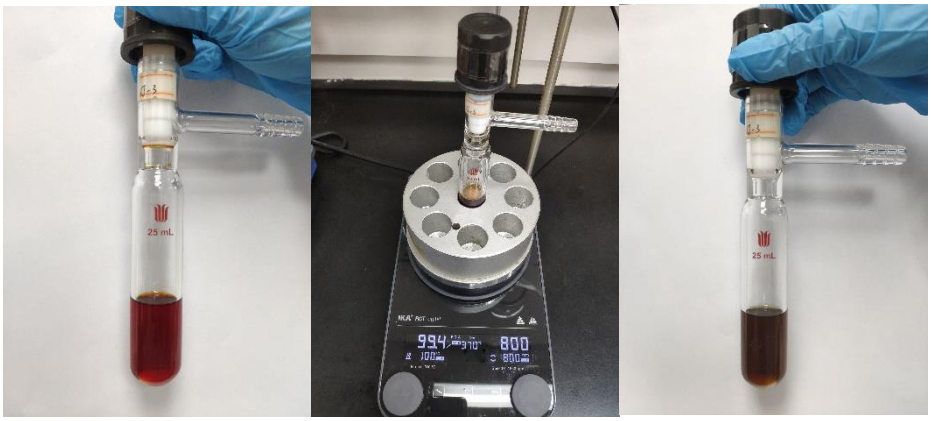


The kinetic resolution or dynamic kinetic resolution investigations were carried out with 1,3-dienes **1a** (or **1k**) and 2.0 equivalent (±)-**2n** under the standard conditions, the desired chiral allylic phosphine oxide products **3an** and **3kn** were obtained with a diastereomer ratio of about 1:1, and the recovered **2n** were totally racemic in both cases. Yields were calculated based on the dosage of (±)-**2n**, dr was determined by ^{31}P NMR analysis. The ee values of **3an**, **3kn** and recovered **2n** were determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min.

6. Scale-up Reaction and Derivatization of the Product

Scheme S3. Scale-up reaction.



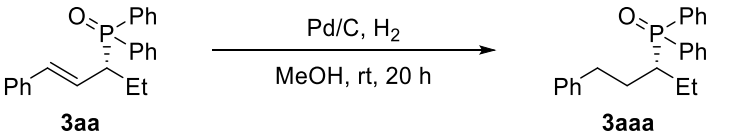


Before reaction After reaction

A 25 mL Schlenk tube was charged with $Ni(COD)_2$ (55.0 mg, 0.2 mmol, 0.05 equiv *vs* SPO), (*S*)-BINAP (124.5 mg, 0.2 mmol, 0.05 equiv *vs* SPO), $TsOH{\cdot}H_2O$ (38.0 mg, 0.2 mmol, 0.05

equiv *vs* SPO), secondary phosphine oxides **2a** (808.8 mg, 4.0 mmol, 1.0 equiv) and 10 mL THF in an argon-filled glovebox, then 1,3-dienes **1a** (743 μL, 4.8 mmol, 1.2 equiv *vs* SPO) was added. The reaction vessel was sealed and removed from the glovebox, and the mixture was stirred at 100 °C for 48 h. After complete conversion, the resulting mixture was cooled to rt, and then the residue was purified by SiO_2 column chromatography to give the desired product **3aa** 1.25 g (90% yield, > 99% ee), the enantiomeric excess was determined by HPLC on Chiralpak OJ-H column.

Scheme S4. Derivatization of the product.



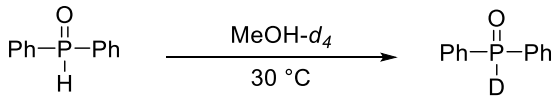
3aa → **3aaa**

> 99% yield, > 99% ee

12 mg of Pd/C was added to a solution of **3aa** (69.3 mg, 0.2 mmol) in MeOH (2.0 mL). The mixture was hydrogenated under a balloon pressure of hydrogen for 20 h. The reaction progress was monitored by ^{1}H NMR analysis. The reaction mixture was filtered through celite and the filtrate was evaporated to give the crude product. The residue was purified by SiO_2 column chromatography to give the desired product **3aaa** as a white solid : 69.7 mg, > 99% yield; > 99% ee; m.p. 135.9-137.0 ℃; $[\alpha]_D^{25}$= +14.5 (c = 1.0, $CHCl_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm, t_R = 21.7 min (major), 23.0 min (minor); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.68 (m, 4H), 7.51-7.40 (m, 6H), 7.27-7.22 (m, 2H), 7.20-7.16 (m, 1H), 7.02-6.99 (m, 2H), 2.78 (ddd, *J* = 14.2, 9.2, 5.4 Hz, 1H), 2.53 (ddd, *J* = 13.8, 9.2, 7.4 Hz, 1H), 2.25-2.17 (m, 1H), 2.03-1.88 (m, 2H), 1.86-1.75 (m, 1H), 1.74-1.60 (m, 1H), 0.97 (t, *J* = 7.5 Hz, 3H) ppm; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 132.8 (dd, *J* = 93.9, 20.2 Hz), 131.3 (t, *J* = 2.5 Hz), 130.8 (dd, *J* = 8.3, 3.8 Hz), 128.5, 128.4, 128.3, 125.9, 37.3 (d, *J* = 70.9 Hz), 33.5 (d, *J* = 9.7 Hz), 28.4, 20.2, 12.3 (d, *J* = 8.8 Hz) ppm; **^{31}P NMR** (162 MHz, $CDCl_3$) δ 36.84 ppm. **HRMS (ESI)** calculated $[M+H]^+$ for $C_{23}H_{26}OP$ = 349.1716**,** found: 349.1710.

7. Deuterium-Labeled Experiments

Scheme S5. Synthesis of *d*-**2a**.[6, 7]



2a (2 mmol) → *d*-**2a** (> 99% yield, > 99% D)

An oven dried flask (20 mL) was rinsed with MeOH-d_4 twice, and then charged with diphenylphosphine oxide (404.4 mg, 2 mmol). MeOH-d_4 (99.8 % D, 2 mL) was added and the

mixture was concentrated using rotatory evaporator (400 mbar) for 6 minutes (This process was repeated six times); The residual solvent was evaporated with high vacuum and resulted in quantitative (>99%) yield of the title compound *d*-**2a**. ^{1}H NMR spectrum showed > 99% D incorporation. **^{1}H NMR** (400 MHz, MeOH-d_4) δ 7.76-7.70 (m, 4H), 7.67-7.62 (m, 2H), 7.59-7.54 (m, 4H) ppm.

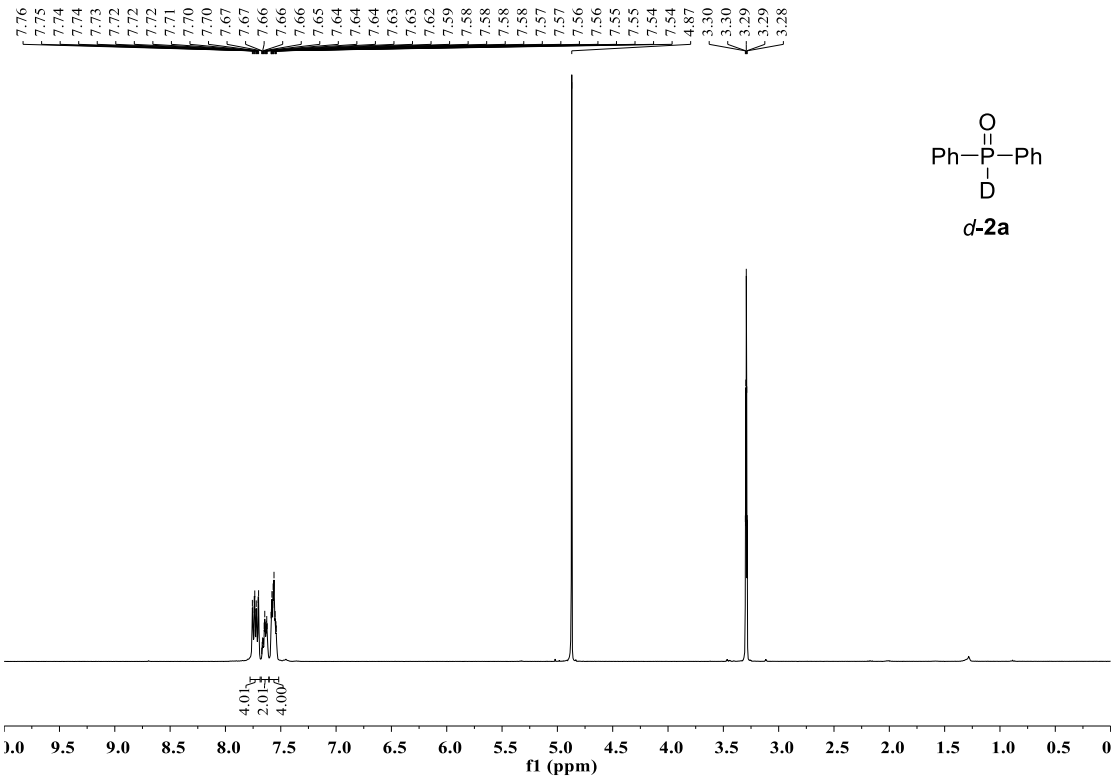
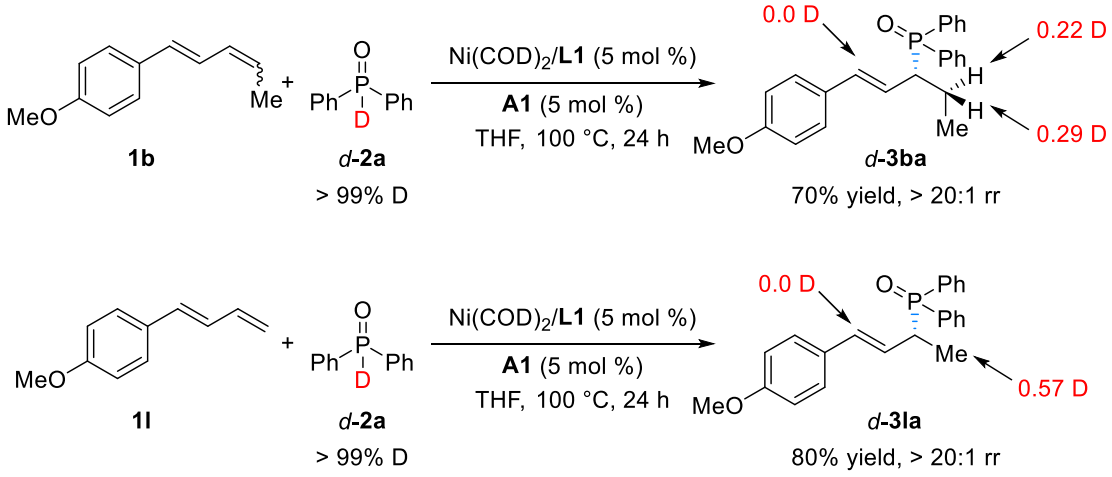


Figure S5. ^{1}H NMR spectra of ***d*-2a**.

Scheme S6. Synthesis of *d*-**3ba** and *d*-**3la**.



A reaction tube was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.05 equiv *vs* SPO), (*S*)-BINAP (6.3 mg, 0.01 mmol, 0.05 equiv *vs* SPO), $TsOH{\cdot}H_2O$ (1.9 mg, 0.01 mmol, 0.05 equiv *vs* SPO), *d*-**2a** (40.6 mg, 0.2 mmol, 1.0 equiv) and 1.0 mL THF in an argon-filled glovebox, then

1,3-diene **1b** or **1l** (0.24 mmol, 1.2 equiv *vs* SPO) was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 100 °C for 24 h. After complete conversion, the resulting mixture was cooled to rt, and the crude product was used to determine the regioselectivity by ^{31}P NMR analysis. Then the residue was purified by SiO_2 column chromatography to give the desired product *d*-**3ba** (White solid, 70% yield, >20:1 rr) or *d*-**3la** (White solid, 80% yield, >20:1 rr). The *d*-**3ba** and *d*-**3la** were determined by ^{1}H NMR and ^{2}H NMR analysis. Deuterium incorporation was determined by ^{1}H NMR. Percent deuterium (% D) incorporation is depicted as the amount of deuterium in place of a single hydrogen atom at that site.

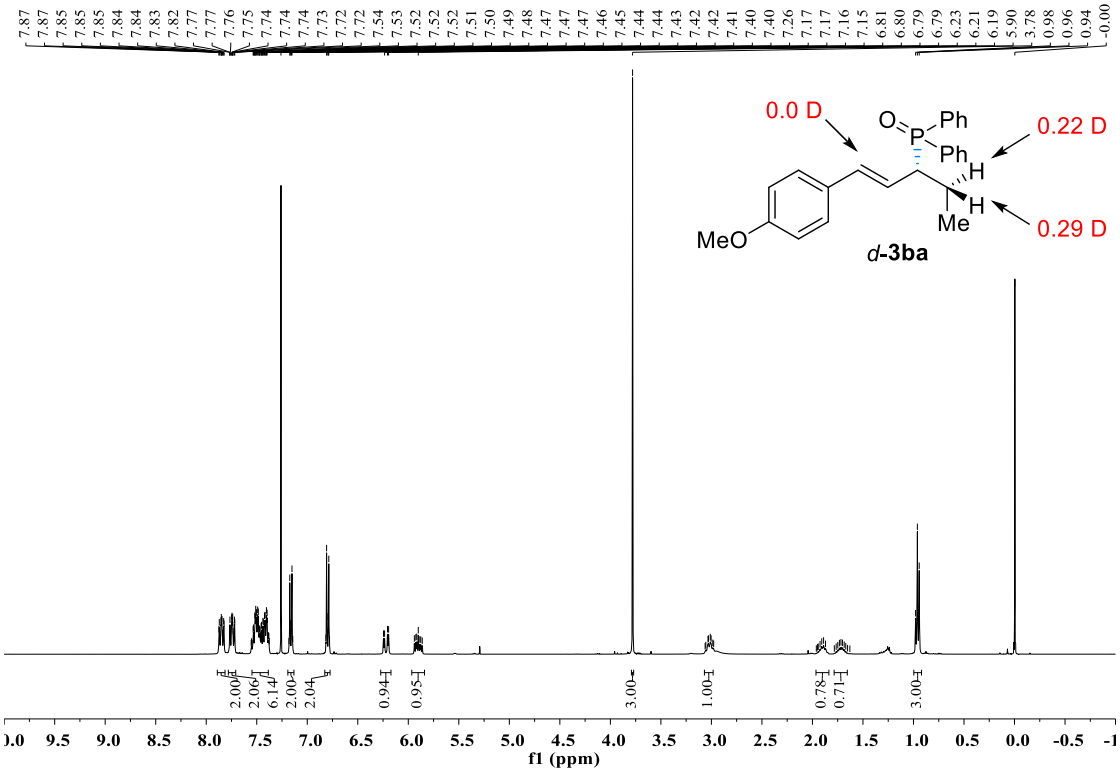


Figure S6. ^{1}H NMR spectra of *d*-**3ba**.

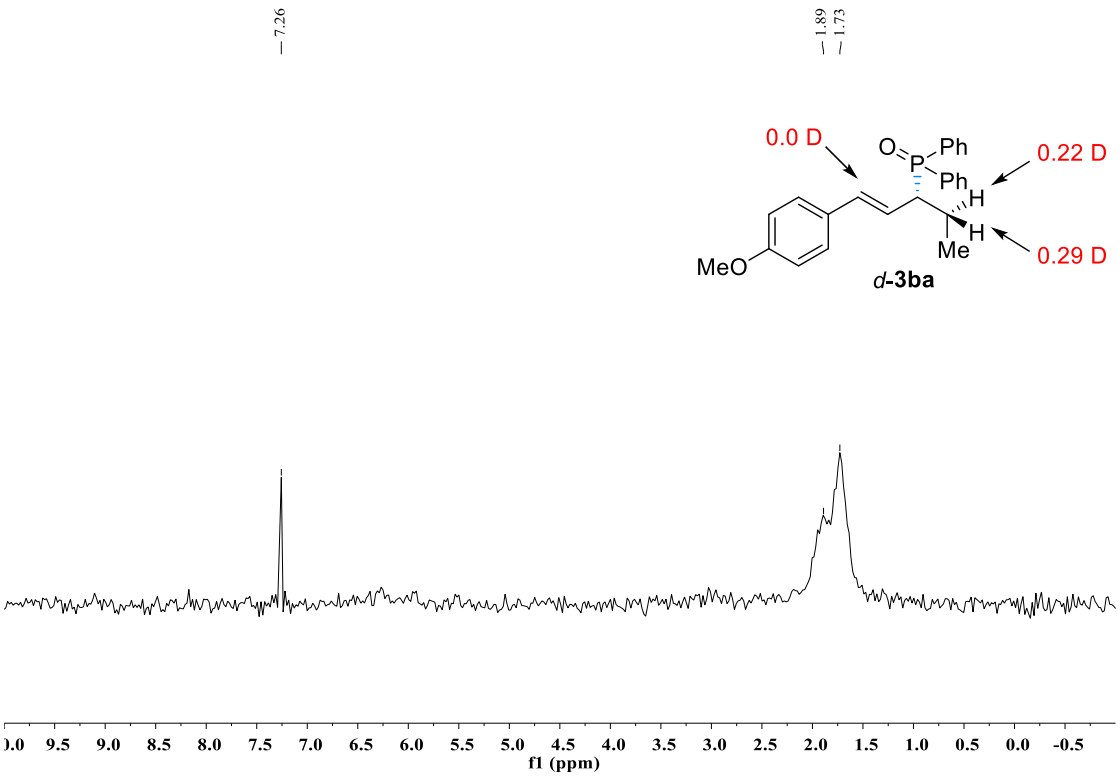


Figure S7. ^{2}H NMR spectra of *d*-**3ba**.

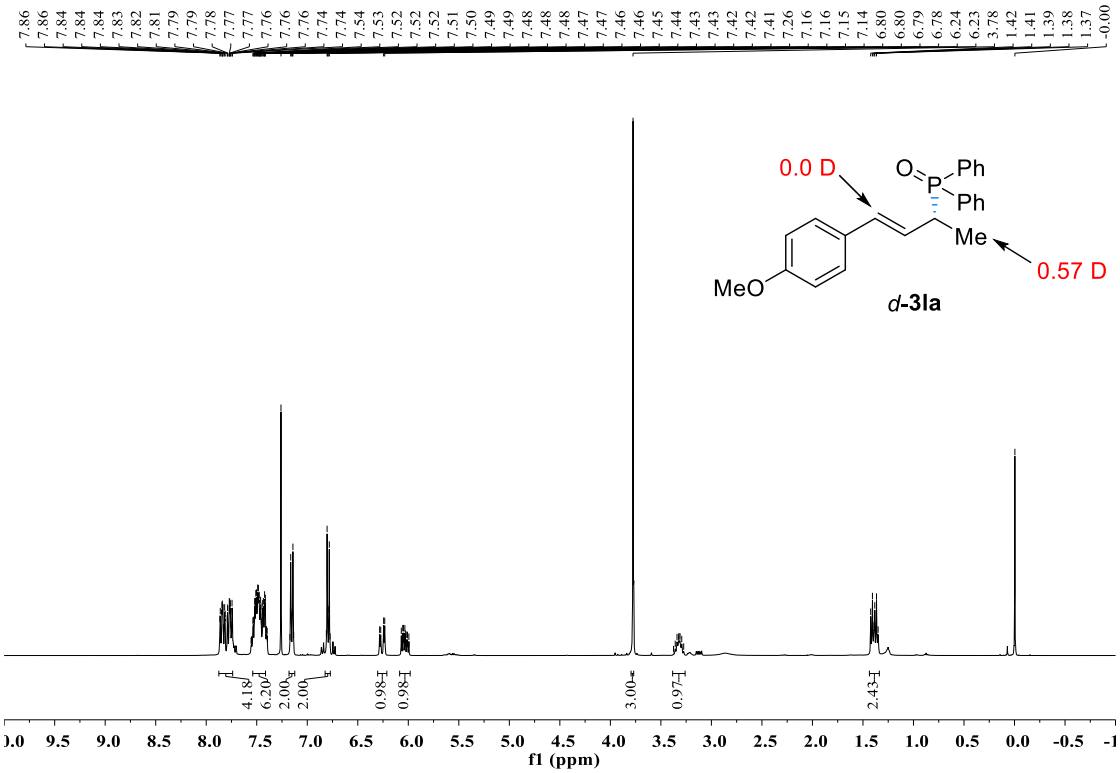


Figure S8. ^{1}H NMR spectra of *d*-**3la**.

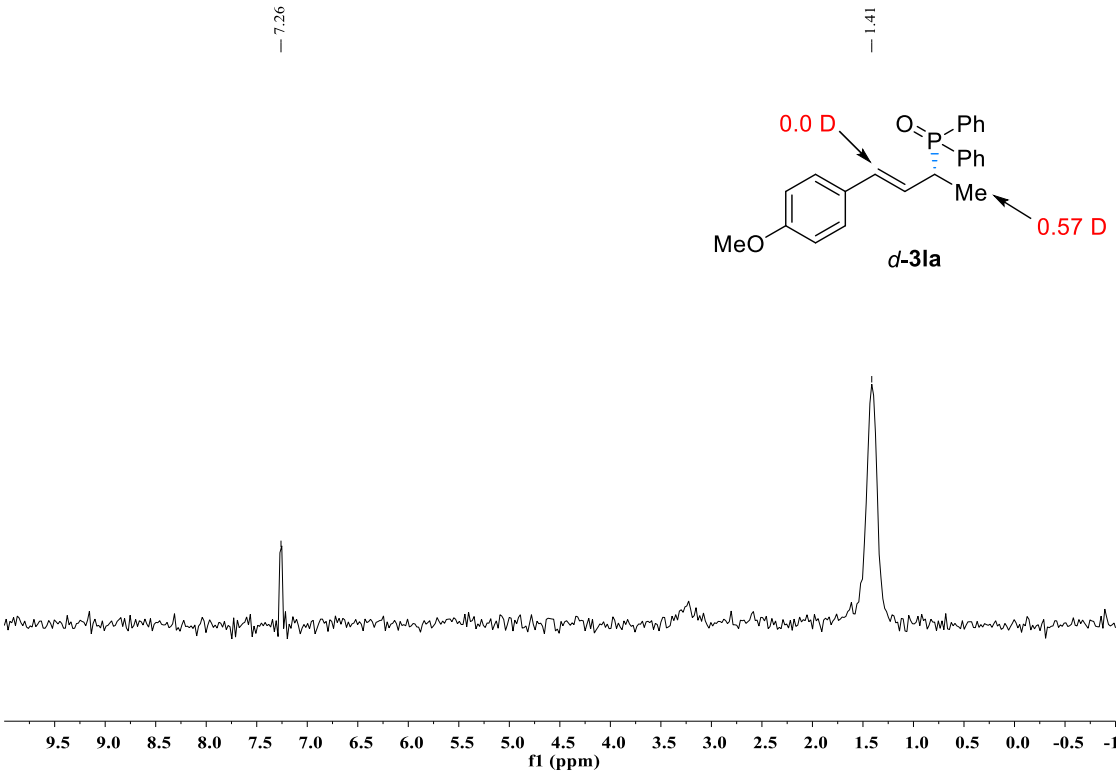
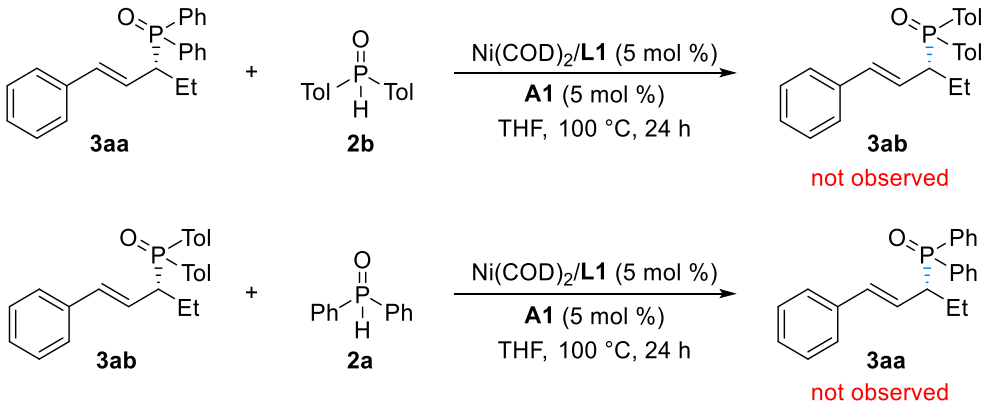


Figure S9. ^{2}H NMR spectra of *d*-**3la**.

8. Cross-Over Experiments

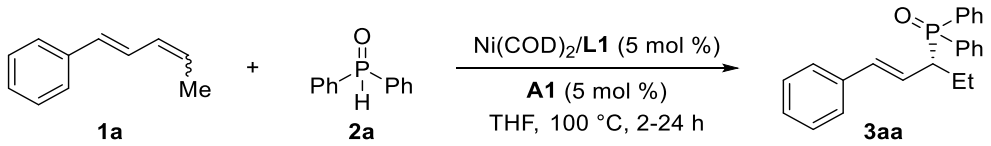
Scheme S7:



A reaction tube was charged with $Ni(COD)_2$ (1.4 mg, 0.005 mmol, 0.05 equiv *vs* SPO), (*S*)-BINAP (3.2 mg, 0.005 mmol, 0.05 equiv *vs* SPO), $TsOH{\cdot}H_2O$ (1.0 mg, 0.005 mmol, 0.05 equiv *vs* SPO), **2b** (or **2a**) (0.1 mmol, 1.0 equiv) and **3aa** (or **3ab**) (0.1 mmol, 1.0 equiv) in an argon-filled glovebox, then 1.0 mL THF was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 100 °C for 24 h. Then the resulting mixture was cooled to rt, we observe no reactivity, but rather remaining starting materials (determined by ^{31}P NMR analysis).

9. Reaction Profiles

Scheme S8:

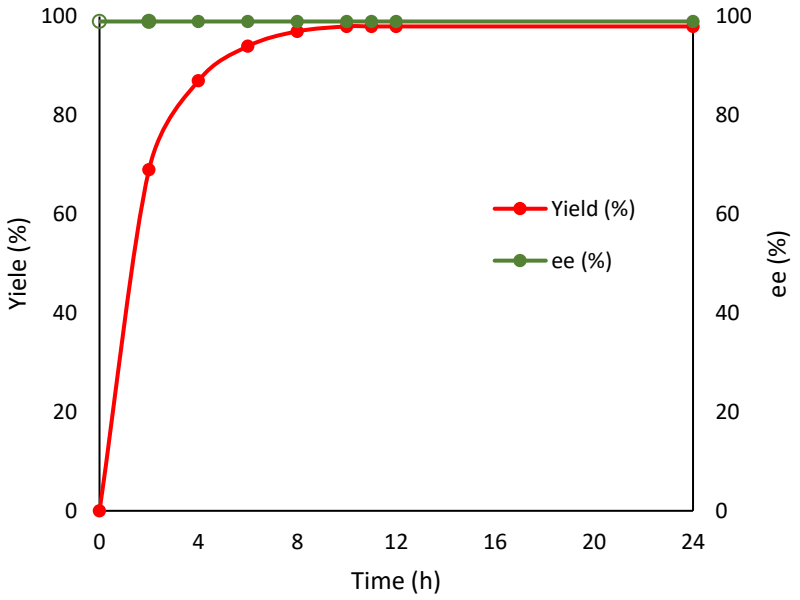


1a **2a** **3aa**

A reaction tube was charged with $Ni(COD)_2$ (2.8 mg, 0.01 mmol, 0.05 equiv *vs* **2a**), (*S*)-BINAP (0.01 mmol, 0.05 equiv *vs* **2a**), $TsOH{\cdot}H_2O$ (0.01 mmol, 0.05 equiv *vs* **2a**), Diphenylphosphine oxide **2a** (0.2 mmol, 1.0 equiv) and 1.0 mL THF in an argon-filled glovebox, then 1,3-diene **1a** (38 μL, 0.24 mmol, 1.2 equiv *vs* **2a**) was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 100 °C for 24 h. The reaction progress was monitored by GC with naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

Table S5. Reaction Profiles.

Entry	Time (h)	Yield (%)	ee (%)
1	2	69	99
2	4	87	99
3	6	91	99
4	8	97	99
5	10	98	99
6	11	98	99
7	12	98	99
8	24	98	99



10. DFT Calculation

Computational Methods: All of the density functional theory (DFT) calculations were performed with the Gaussian 09 series of programs.[8] The B3-LYP functional[9, 10] with the standard 6-31G(d) basis set (LANL08(f) basis set for Ni) was used for the geometry optimizations in the gas phase. Harmonic vibrational frequency calculations were performed for all of the stationary points to determine whether they are local minima or transition structures and to derive the thermochemical corrections for the enthalpies and free energies. The M06 functional[11] proposed by Truhlar *et al*. with the 6-311+G(d,p) basis set (LANL08(f) basis set for Ni) was used to calculate the single-point energies in THF solvent to provide more accurate energy information. The solvent effect was considered by single-point calculations based on the gas-phase stationary points with the SMD[12, 13] continuum solvation model. The Gibbs free energies of the stationary points calculated using the M06 functional are used to discuss the energies. The 3D images of the calculated structures were prepared using CYLview.[14]

In this hydrophosphinylation reaction, high enantioselectivity was observed regardless of the *E,Z*/*E,E* ratio of the starting 1,3-dienes. To explore the origin of the enantioselectivity, we calculated the energies of the transition states of the diene insertion step for reaction of (*E,Z*)-**1a** and (*E,E*)-**1a** to afford (*R*)-**3aa** and (*S*)-**3aa**, respectively. Comparison of the energies of transition states **TS-1** and **TS-3** indicated that the formation of (*R*)-**3aa** was favored over the formation of (*S*)-**3aa** by 5.2 kcal/mol. Comparison of the energies of transition states **TS-2** and **TS-4** indicated that the formation of (*R*)-**3aa** was favored over the formation of (*S*)-**3aa** by 4.5 kcal/mol. Thus, both (*E,Z*)-**1a** and (*E,E*)-**1a** underwent the enantiodetermining step to give (*R*)-**3aa** as the predominant product.

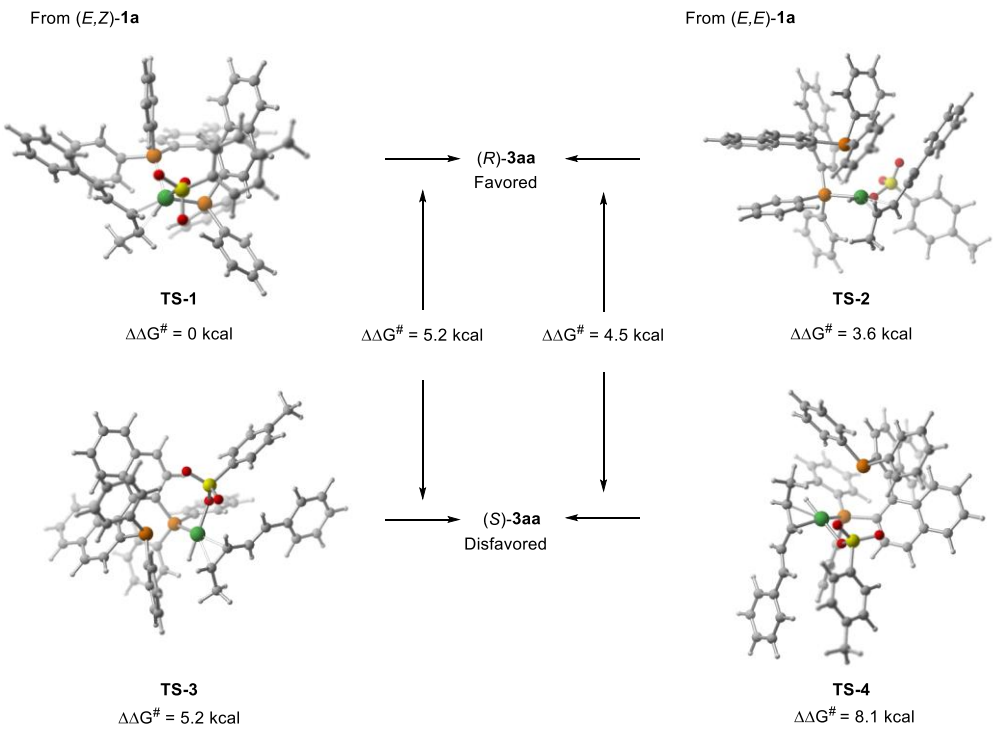


Figure S10. Calculated energies of transition states of diene insertion step for reactions of (*E,Z*)-**1a** and (*E,E*)-**1a**.

Cartesian coordinates of the calculated transition states.

TS-1

Thermal Correction to Free Energy: 0.858325 Hartree

SCF energy: -3868.542788 Hartree

Gibbs free energy: -3867.684463 Hartree

Coordinates:

C	-2.76980100	1.90276700	4.81608900
C	-3.02224300	2.48698800	3.59711600
C	-2.80331300	1.77598800	2.38628700
C	-2.31795300	0.42861500	2.43065100
C	-2.06614600	-0.14017000	3.71314500
C	-2.28151100	0.57569300	4.86926800
H	-3.42737400	3.39096300	1.08720500
H	-2.93844400	2.45574000	5.73628700
H	-3.38981900	3.50845700	3.53633000
C	-3.06005100	2.36902800	1.12730200
C	-2.10175100	-0.30019900	1.20465300
H	-1.68676900	-1.15258600	3.77731300
H	-2.07143600	0.11770700	5.83203600

C	-2.32654000	0.34336700	-0.01863500
C	-2.81122200	1.68134700	-0.03193700
C	-1.79535700	-1.77194200	1.33782900
C	-2.89864100	-2.60860800	1.75637000
C	-0.52945800	-2.34128200	1.16431400
C	-4.22099300	-2.10477900	1.93464600
C	-2.68964300	-4.00443500	1.99760600
C	-0.35083600	-3.73068200	1.43609900
C	-5.25843900	-2.92643200	2.31743200
H	-4.41454400	-1.05280200	1.76367900
C	-3.77739400	-4.82723200	2.39607900
C	-1.38642600	-4.53326000	1.83972900
C	-5.03951800	-4.30425400	2.55359000
H	-6.25431800	-2.51009700	2.44391000
H	-3.58885900	-5.88337000	2.57419000
H	-1.21366400	-5.58702700	2.04634100
H	-5.86508200	-4.94106400	2.85969800
H	0.63404900	-4.16687500	1.32830000
H	-2.97688900	2.17329700	-0.98262800
P	0.92982900	-1.34173200	0.55141100
P	-1.70367100	-0.31645400	-1.63158700
C	1.54260900	-0.51029800	2.08003000
C	1.42590600	-1.08586100	3.35656800
C	2.18811900	0.72759300	1.94311500
C	1.94720000	-0.43494900	4.47478500
H	0.93175500	-2.04598500	3.47667900
C	2.71385300	1.37273300	3.06581800
H	2.27386300	1.19677400	0.97008400
C	2.59331600	0.79605200	4.33073600
H	1.85042400	-0.88924200	5.45773100
H	3.21477300	2.32884300	2.94064200
H	2.99976300	1.30163200	5.20309400
C	2.20790000	-2.65669500	0.26255300
C	3.40428500	-2.73175700	0.98922200
C	2.00700900	-3.57101400	-0.78893000
C	4.36951200	-3.69480100	0.67746700
H	3.59302600	-2.03556100	1.79882400
C	2.96258200	-4.54053300	-1.08958700

H	1.08710400	-3.53151000	-1.36670300
C	4.15285700	-4.60348400	-0.35770400
H	5.29243700	-3.72795400	1.25008900
H	2.78007700	-5.24516700	-1.89714500
H	4.90176100	-5.35436400	-0.59510600
C	-2.49248400	0.71905300	-2.95077700
C	-3.79213000	0.48817900	-3.43213200
C	-1.73643900	1.76231700	-3.51125900
C	-4.32479800	1.28695900	-4.44424900
H	-4.38962700	-0.32255200	-3.02868800
C	-2.27610600	2.56145300	-4.52249200
H	-0.73326100	1.97187700	-3.15361400
C	-3.56855900	2.32605900	-4.99220400
H	-5.33080800	1.09321500	-4.80757800
H	-1.67552200	3.36523600	-4.93972300
H	-3.98488700	2.94418000	-5.78349300
C	-2.48720400	-1.96119800	-1.91740000
C	-1.81353600	-2.90859500	-2.70334600
C	-3.77210600	-2.27212300	-1.44623700
C	-2.40930800	-4.13206300	-3.01386900
H	-0.81810000	-2.68652000	-3.07672600
C	-4.36527400	-3.49853100	-1.74907400
H	-4.30785200	-1.55871700	-0.82891200
C	-3.68636100	-4.43065700	-2.53575500
H	-1.87312100	-4.85276000	-3.62575500
H	-5.35489300	-3.72554500	-1.36242500
H	-4.14813600	-5.38569200	-2.77150500
Ni	0.57750900	-0.05801600	-1.52394600
C	2.47453800	0.35003500	-2.47748000
H	2.33678900	1.42399700	-2.54492400
C	3.68160800	-0.10388600	-1.80982600
H	3.90879600	-1.16677400	-1.84111000
C	4.52472500	0.75271400	-1.18314700
H	4.22593500	1.79824900	-1.13072600
C	1.70765100	-0.42533700	-3.37641200
C	5.79496500	0.43043200	-0.53321700
C	6.40968000	-0.83716000	-0.59945100
C	6.45555900	1.44349300	0.19011800

C	7.62319200	-1.07744100	0.03831000
H	5.93754800	-1.63796900	-1.16013100
C	7.66997200	1.20197400	0.82953900
H	5.99831200	2.42829000	0.24752100
C	8.26077900	-0.06102600	0.75771700
H	8.08039100	-2.06162400	-0.03087900
H	8.15648200	2.00140500	1.38256300
H	9.20996900	-0.25215900	1.25132400
O	0.35419800	1.73032200	-0.64206000
S	1.02978100	3.06275400	-0.99508100
O	0.95720100	3.34069900	-2.45027000
O	2.37178600	3.16866800	-0.37945400
C	-0.00698100	4.28162900	-0.17426800
C	-0.89757800	5.05096900	-0.92195100
C	0.09606200	4.45836700	1.20688000
C	-1.69167000	6.00100400	-0.27791900
H	-0.95332000	4.90838100	-1.99568100
C	-0.70326800	5.41005300	1.83653000
H	0.79629700	3.85881200	1.77900400
C	-1.60545400	6.19929400	1.10678700
H	-2.38269400	6.60439500	-0.86273300
H	-0.62250400	5.54621600	2.91269500
C	-2.43431200	7.26172000	1.79157500
H	-3.37692300	7.43976700	1.26275800
H	-2.67094100	6.98425000	2.82466900
H	-1.89758100	8.21928700	1.82922600
H	1.04534000	0.14691700	-4.02442600
C	2.18874800	-1.72648200	-3.99858500
H	2.91286100	-1.49296100	-4.79012000
H	2.67629500	-2.38644400	-3.27818500
H	1.36127500	-2.27641800	-4.46035800
H	0.64647800	-1.23476200	-2.41287700

Cartesian coordinates of the calculated transition states.

TS-2

Thermal Correction to Free Energy: 0.855774 Hartree

SCF energy: -3868.534947 Hartree

Gibbs free energy: -3867.679173 Hartree

Coordinates:

C	3.02596400	0.99776700	5.39517000
C	2.18555800	-0.05161300	5.10631200
C	1.97308000	-0.46872300	3.76498200
C	2.64410900	0.20641600	2.69431700
C	3.49443100	1.29892900	3.03348400
C	3.68151500	1.68007100	4.34341900
H	0.53284600	-2.01701300	4.25031800
H	3.18184400	1.30978700	6.42439600
H	1.66337100	-0.58018300	5.90003100
C	1.09276400	-1.53241100	3.45562400
C	2.43872700	-0.22143900	1.32981900
H	3.99887700	1.84387300	2.24517400
H	4.33506900	2.51807100	4.57032500
C	1.59890200	-1.31110800	1.07691800
C	0.91114800	-1.93708000	2.15950900
C	3.17445200	0.54667200	0.26541700
C	4.58578200	0.31554800	0.11016300
C	2.54426300	1.54747300	-0.47970500
C	5.28543900	-0.67651800	0.85521300
C	5.33433700	1.09930800	-0.82641000
C	3.31906600	2.32946100	-1.38384200
C	6.63548000	-0.88491100	0.67697600
H	4.74106000	-1.27272900	1.57908700
C	6.72465200	0.85802800	-0.99143300
C	4.66384500	2.11239900	-1.55549500
C	7.36645200	-0.11313200	-0.25773200
H	7.14523500	-1.64589500	1.26206200
H	7.27441400	1.46286900	-1.70890800
H	5.23302200	2.72676800	-2.24977500
H	8.43132100	-0.28599700	-0.38841200
H	2.83625500	3.11692900	-1.95075100
H	0.19719000	-2.72464000	1.96221200
P	0.69691400	1.77661800	-0.31624000
P	1.04977800	-1.91239000	-0.58730900
C	0.53539700	2.81149000	1.20497300
C	1.35043100	3.92339000	1.47941000

C	-0.45199300	2.44133200	2.13132300
C	1.17273200	4.65795700	2.65093400
H	2.12609100	4.21443100	0.77571400
C	-0.62478000	3.17972200	3.30604100
H	-1.07870600	1.57209900	1.94624500
C	0.18287400	4.28647000	3.56623500
H	1.80759900	5.51732400	2.85252000
H	-1.38866200	2.87903200	4.01795900
H	0.04819300	4.85751600	4.48148800
C	0.31230900	2.96197300	-1.68755000
C	-0.32940500	4.19050000	-1.47168600
C	0.54123000	2.56044500	-3.01895400
C	-0.71477100	4.99714900	-2.54645300
H	-0.53788400	4.52115700	-0.46019700
C	0.16748300	3.37018400	-4.09104200
H	1.03769400	1.61402600	-3.21729200
C	-0.46559700	4.59493000	-3.85820300
H	-1.21492800	5.94159200	-2.35009800
H	0.37132100	3.04552500	-5.10868900
H	-0.76082400	5.22603400	-4.69233300
C	0.85565900	-3.74239800	-0.38770200
C	1.66358700	-4.52246400	0.45403900
C	-0.10735200	-4.38305400	-1.18050200
C	1.51420700	-5.90907200	0.49481800
H	2.39494700	-4.04870200	1.10136100
C	-0.25116400	-5.77087700	-1.14557200
H	-0.75488800	-3.78824900	-1.81807200
C	0.55975900	-6.53738200	-0.30744000
H	2.14195500	-6.49743800	1.15874000
H	-1.00310400	-6.25072300	-1.76653100
H	0.44379600	-7.61730700	-0.27286900
C	2.47023000	-1.86180100	-1.77434100
C	2.32763600	-1.25235500	-3.02784800
C	3.67333800	-2.52798500	-1.48830900
C	3.35940600	-1.29650800	-3.96825000
H	1.40010000	-0.74572800	-3.27321900
C	4.70463000	-2.57132300	-2.42430900
H	3.81095400	-3.01695400	-0.53038000

C	4.55070100	-1.95598300	-3.66864700
H	3.22780900	-0.81590400	-4.93412900
H	5.63062600	-3.08328700	-2.17851000
H	5.35450300	-1.99275100	-4.39900000
Ni	-0.95316200	-1.00409300	-1.12552000
C	-2.80366300	-0.36770600	-1.87168700
H	-3.33762600	-1.29334400	-1.65684900
C	-3.28752700	0.82144700	-1.16489700
H	-3.63000700	0.63781800	-0.15251400
C	-3.37987800	2.06807100	-1.67571200
H	-3.09764400	2.24427100	-2.71338700
C	-1.94925800	-0.36165500	-2.97656300
H	-1.60627600	0.60582500	-3.33988600
C	-3.88911600	3.24256700	-0.95834900
C	-4.01291400	3.28277900	0.44534900
C	-4.27597700	4.38110300	-1.69001800
C	-4.52282100	4.41208600	1.08080700
H	-3.68828600	2.43334600	1.03925400
C	-4.78784300	5.50999200	-1.05228500
H	-4.17624000	4.37111400	-2.77301600
C	-4.91642100	5.52981800	0.33800900
H	-4.60384500	4.42455400	2.16467400
H	-5.08620200	6.37418000	-1.64071700
H	-5.31121800	6.40943200	0.83957900
C	-1.93041400	-1.48064200	-3.99258700
H	-2.61740800	-1.23477600	-4.81459700
H	-0.93634200	-1.63038100	-4.42642400
H	-2.26166200	-2.42702700	-3.55365100
H	-0.28536700	-0.45702100	-2.31105700
O	-1.75973000	-1.96329100	0.36358500
S	-2.61293700	-1.62514600	1.59953200
O	-2.72811400	-0.16685100	1.83040400
O	-2.18237000	-2.44994900	2.74085200
C	-4.25316800	-2.20354900	1.12868200
C	-5.37190000	-1.41615000	1.39304200
C	-4.40217200	-3.47052100	0.55344600
C	-6.64366000	-1.89375700	1.06678100
H	-5.24194600	-0.43982700	1.84772800

C	-5.67525300	-3.93267900	0.23254300
H	-3.52634300	-4.08212800	0.36031700
C	-6.81695000	-3.15262900	0.48135300
H	-7.51421100	-1.27508200	1.27205000
H	-5.78881100	-4.91781800	-0.21535500
C	-8.19120900	-3.66317900	0.11490600
H	-8.97771000	-3.00835500	0.50300800
H	-8.31742400	-3.72336300	-0.97402200
H	-8.36387800	-4.66994900	0.51401500

Cartesian coordinates of the calculated transition states.

TS-3

Thermal Correction to Free Energy: 0.855630 Hartree

SCF energy: -3868.532399 Hartree

Gibbs free energy: -3867.676769 Hartree

Coordinates:

C	-2.97074400	4.55491400	-3.01516900
C	-1.81660100	3.89673800	-3.36934500
C	-1.53333100	2.59934400	-2.86561000
C	-2.46402600	1.95786000	-1.98645200
C	-3.64693400	2.67379600	-1.64006100
C	-3.88944800	3.93531200	-2.13527500
H	0.35864300	2.39051300	-3.89268900
H	-3.17542000	5.55039900	-3.39987200
H	-1.09344100	4.36281800	-4.03415400
C	-0.34704800	1.91450800	-3.21648400
C	-2.18703900	0.63625800	-1.47598500
H	-4.35694500	2.22670500	-0.95487000
H	-4.79249900	4.46266800	-1.84059200
C	-0.97454300	0.01686400	-1.80900800
C	-0.07168200	0.67997300	-2.69087800
C	-3.31107600	-0.03241600	-0.72373500
C	-4.41937400	-0.52302000	-1.50944000
C	-3.37298300	-0.09459000	0.66828500
C	-4.44366400	-0.45669400	-2.93297100
C	-5.55049100	-1.10841500	-0.85490200
C	-4.52068100	-0.66651700	1.29268200

C	-5.50739200	-0.95029500	-3.65702300
H	-3.60829200	-0.00534400	-3.45571300
C	-6.63211800	-1.60980700	-1.62747400
C	-5.56830900	-1.16339000	0.56125200
C	-6.61570200	-1.53650600	-3.00135300
H	-5.49735000	-0.88230100	-4.74164200
H	-7.47892100	-2.05142900	-1.10720900
H	-6.43293100	-1.59361300	1.06181600
H	-7.45021700	-1.91950600	-3.58250100
H	-4.56590600	-0.70986200	2.37477000
H	0.86027900	0.19500700	-2.95252700
P	-1.98406900	0.64388400	1.67120600
P	-0.25140700	-1.47117000	-0.96598900
C	-2.61154600	2.37092900	1.93306600
C	-3.90690000	2.65628400	2.40135300
C	-1.74450800	3.43155800	1.63266800
C	-4.32340600	3.97542900	2.57081100
H	-4.59292100	1.84659500	2.63403500
C	-2.16700000	4.75402200	1.80630300
H	-0.75054500	3.22844100	1.24407300
C	-3.45102900	5.02833700	2.27418900
H	-5.32702200	4.18360700	2.93389000
H	-1.48566400	5.56607100	1.56711900
H	-3.77693800	6.05718800	2.40652300
C	-2.24081900	-0.11681100	3.34322600
C	-2.11196000	0.65508100	4.51042900
C	-2.39209500	-1.50978300	3.48642100
C	-2.14969500	0.05965200	5.77373200
H	-1.98497500	1.73031400	4.43372000
C	-2.44527400	-2.10166200	4.74932200
H	-2.47951300	-2.13764500	2.60354300
C	-2.32265400	-1.31921100	5.90035800
H	-2.04990800	0.68055400	6.66033900
H	-2.58279700	-3.17711400	4.83318200
H	-2.36058600	-1.78022000	6.88369500
C	1.03031300	-2.12139800	-2.14851800
C	0.68439400	-2.80160000	-3.32823900
C	2.39075500	-1.95426100	-1.84111500

C	1.67169600	-3.29727700	-4.17915800
H	-0.35763900	-2.95920700	-3.58441600
C	3.37775600	-2.45608900	-2.69404900
H	2.68212100	-1.41304300	-0.94826400
C	3.02200500	-3.12802900	-3.86320400
H	1.38428200	-3.82155500	-5.08686200
H	4.42433400	-2.31851500	-2.43609300
H	3.79020000	-3.52044300	-4.52447700
C	-1.47804700	-2.84964100	-0.97837300
C	-1.41290000	-3.82831800	0.02490300
C	-2.40464500	-3.01793300	-2.01843900
C	-2.25277600	-4.94271300	-0.00859900
H	-0.69741400	-3.71936700	0.83375600
C	-3.25118700	-4.12683300	-2.04801700
H	-2.48201600	-2.27314200	-2.80237100
C	-3.17683600	-5.09316200	-1.04364200
H	-2.18585200	-5.69062700	0.77719400
H	-3.97411800	-4.22606800	-2.85281900
H	-3.83652700	-5.95644300	-1.06632600
Ni	0.81610400	-0.89430700	0.93636700
C	2.18181100	-0.96025500	2.53994200
H	2.18753500	0.10552100	2.75605300
C	3.42766600	-1.53811700	2.05745600
H	3.45954300	-2.61673600	1.91710100
C	4.52462300	-0.79506000	1.78171400
H	4.44299400	0.28342100	1.90499900
C	1.08603100	-1.71659000	2.97930300
H	0.33299500	-1.17401900	3.54467400
C	5.82144600	-1.27803600	1.30358500
C	6.16671400	-2.64373500	1.23571800
C	6.78311400	-0.33587500	0.88823500
C	7.41312000	-3.04493100	0.76440700
H	5.45853300	-3.39754800	1.56786500
C	8.03116500	-0.73845700	0.41630900
H	6.53460800	0.72171500	0.92706000
C	8.35337400	-2.09522400	0.35102400
H	7.65693600	-4.10363300	0.72517800
H	8.75375200	0.00944400	0.09988700

H	9.32724700	-2.41172700	-0.01280100
C	1.13513500	-3.20391000	3.27119400
H	1.65351100	-3.36540300	4.22566600
H	0.12648500	-3.61656400	3.36854600
H	1.66513400	-3.77166200	2.50173400
H	0.04335200	-1.94923500	1.61680400
O	1.83705000	0.50656800	0.03131700
S	1.99653100	1.97570200	0.46961300
O	2.22551500	2.10682200	1.92667100
O	0.93892000	2.83175500	-0.10029800
C	3.54044100	2.43476600	-0.33531000
C	4.48447000	3.17017400	0.37968100
C	3.76602200	2.11347200	-1.67671000
C	5.66174400	3.57939400	-0.25230000
H	4.29245500	3.41427100	1.41916600
C	4.94507600	2.52412400	-2.29234700
H	3.02689800	1.54111000	-2.22687000
C	5.91291000	3.26255400	-1.59248300
H	6.39422200	4.15711900	0.30717100
H	5.11980500	2.26806500	-3.33531000
C	7.19500000	3.68728000	-2.27038000
H	7.74609000	4.41425500	-1.66529000
H	7.85801800	2.82907800	-2.44230300
H	6.99932100	4.14219100	-3.24858600

Cartesian coordinates of the calculated transition states.

TS-4

Thermal Correction to Free Energy: 0.857359 Hartree

SCF energy: -3868.529741 Hartree

Gibbs free energy: -3867.672382 Hartree

Coordinates:

C	-2.90012000	3.23279300	-4.40630800
C	-1.67548300	2.60776400	-4.42052000
C	-1.38359300	1.55531400	-3.51276400
C	-2.37573700	1.12462000	-2.57538300
C	-3.63165000	1.79944300	-2.59049000
C	-3.88314400	2.82456700	-3.47458900

H	0.62593200	1.21150400	-4.23575400
H	-3.11232100	4.04215200	-5.09973400
H	-0.90341500	2.91469100	-5.12197000
C	-0.12771500	0.90661500	-3.51370900
C	-2.09034700	0.04839100	-1.65286800
H	-4.39617600	1.51724300	-1.87729200
H	-4.84482800	3.32957400	-3.44983200
C	-0.81048600	-0.52535100	-1.64984700
C	0.15116700	-0.07786500	-2.60400400
C	-3.27455600	-0.45516300	-0.86511300
C	-4.24260400	-1.24996900	-1.58409000
C	-3.52859900	-0.08922200	0.45589000
C	-4.06243800	-1.63892700	-2.94338200
C	-5.43554000	-1.68605900	-0.92273700
C	-4.72982600	-0.52967100	1.08594200
C	-4.99461000	-2.41518900	-3.59768100
H	-3.17320000	-1.31604300	-3.47243000
C	-6.37991500	-2.48295200	-1.62367000
C	-5.64916200	-1.30298900	0.42533500
C	-6.16833500	-2.84471400	-2.93444300
H	-4.82925400	-2.69435100	-4.63489500
H	-7.27885900	-2.80089100	-1.10045700
H	-6.56041600	-1.62239000	0.92629700
H	-6.89875100	-3.45215900	-3.46205700
H	-4.92100600	-0.24486500	2.11433700
H	1.13486000	-0.52746300	-2.61440900
P	-2.30819100	1.01636000	1.33007400
P	-0.07270700	-1.63485700	-0.34437700
C	-3.00354600	2.69341600	0.95045300
C	-4.35573000	3.03189100	1.13885700
C	-2.12434500	3.65840800	0.43755100
C	-4.81580900	4.31039300	0.82785200
H	-5.05188000	2.29577100	1.53153700
C	-2.59046700	4.94019700	0.12677600
H	-1.08223200	3.40825600	0.26125600
C	-3.93115400	5.26865600	0.32148200
H	-5.86318500	4.56031900	0.97955500
H	-1.89799200	5.67590900	-0.27323000

H	-4.29110700	6.26551200	0.07861100
C	-2.77278600	0.78704900	3.11055700
C	-2.90337600	1.88080300	3.98170300
C	-2.83903800	-0.50777600	3.66067400
C	-3.10897500	1.68817200	5.35016000
H	-2.84677900	2.89145500	3.59032300
C	-3.06100800	-0.69926100	5.02495100
H	-2.72844700	-1.37593900	3.01586700
C	-3.19534000	0.39949600	5.87782000
H	-3.20819500	2.55205200	6.00259100
H	-3.12611300	-1.70939100	5.42245200
H	-3.36391100	0.25124700	6.94115900
C	1.22369600	-2.64301400	-1.23518300
C	0.95417000	-3.88518300	-1.83142300
C	2.54402500	-2.15716300	-1.26942900
C	1.97048700	-4.61429100	-2.45146000
H	-0.04514800	-4.30298000	-1.80534100
C	3.55808600	-2.88888500	-1.89094500
H	2.78060600	-1.19902900	-0.82046700
C	3.27500200	-4.11985900	-2.48373300
H	1.73834700	-5.57459900	-2.90483800
H	4.57063900	-2.49541800	-1.89770900
H	4.06557800	-4.69262300	-2.96146700
C	-1.29334900	-2.93164000	0.13558100
C	-1.30744400	-3.41541700	1.45219100
C	-2.14128400	-3.53505000	-0.80676000
C	-2.14595000	-4.47053200	1.81818100
H	-0.65610800	-2.96531100	2.19417200
C	-2.98435100	-4.58489000	-0.44130900
H	-2.15370100	-3.17987700	-1.83099800
C	-2.98780700	-5.05687200	0.87249400
H	-2.14048600	-4.83080800	2.84353800
H	-3.64347200	-5.02471400	-1.18438000
H	-3.64441700	-5.87464200	1.15725600
Ni	1.13167300	-0.51812400	1.23779500
C	2.66719900	-0.21044200	2.58946700
H	2.79454500	0.86654600	2.52095700
C	3.75482300	-1.06460700	2.13941500

H	3.64706700	-2.13155300	2.33546300
C	4.85457300	-0.59851700	1.50294600
H	4.90330200	0.47075800	1.30176100
C	1.59939000	-0.69187800	3.36990900
C	5.99763700	-1.37191700	1.01716300
C	6.17287600	-2.74821000	1.27045000
C	6.98236000	-0.71379600	0.25331600
C	7.27961700	-3.43138500	0.77583200
H	5.44109900	-3.28600900	1.86616700
C	8.08994000	-1.39915200	-0.24288000
H	6.86490900	0.34752400	0.04686000
C	8.24496700	-2.76239300	0.01571200
H	7.39357000	-4.49166500	0.98674300
H	8.83369500	-0.86732000	-0.83067700
H	9.10903400	-3.29909100	-0.36656800
H	0.52877600	-1.37692000	2.29138800
O	1.92127500	0.72863900	-0.03054900
S	1.84404600	2.26276300	0.14206000
O	1.75228800	2.64515700	1.56946700
O	0.85439000	2.85632400	-0.77316900
C	3.46467500	2.78363300	-0.44257600
C	4.40413700	3.28473000	0.45682500
C	3.77302800	2.67737700	-1.80135600
C	5.66480200	3.66834400	-0.00806800
H	4.13996700	3.38102300	1.50470800
C	5.03379700	3.06106800	-2.25045200
H	3.02632400	2.30542500	-2.49563400
C	6.00040600	3.56279900	-1.36370500
H	6.39524500	4.06270800	0.69491600
H	5.27348100	2.97565400	-3.30817200
C	7.35248500	4.01067800	-1.86905300
H	8.09752100	4.02111400	-1.06675000
H	7.72074700	3.35553900	-2.66650400
H	7.30381200	5.02676800	-2.28302900
C	0.75929900	0.25415700	4.19641300
H	-0.24363700	-0.13700600	4.37872800
H	1.24572800	0.39827000	5.17137200
H	0.67484500	1.22771400	3.70709000

H	1.69150900	-1.70530800	3.76500900

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12. NMR Spectra

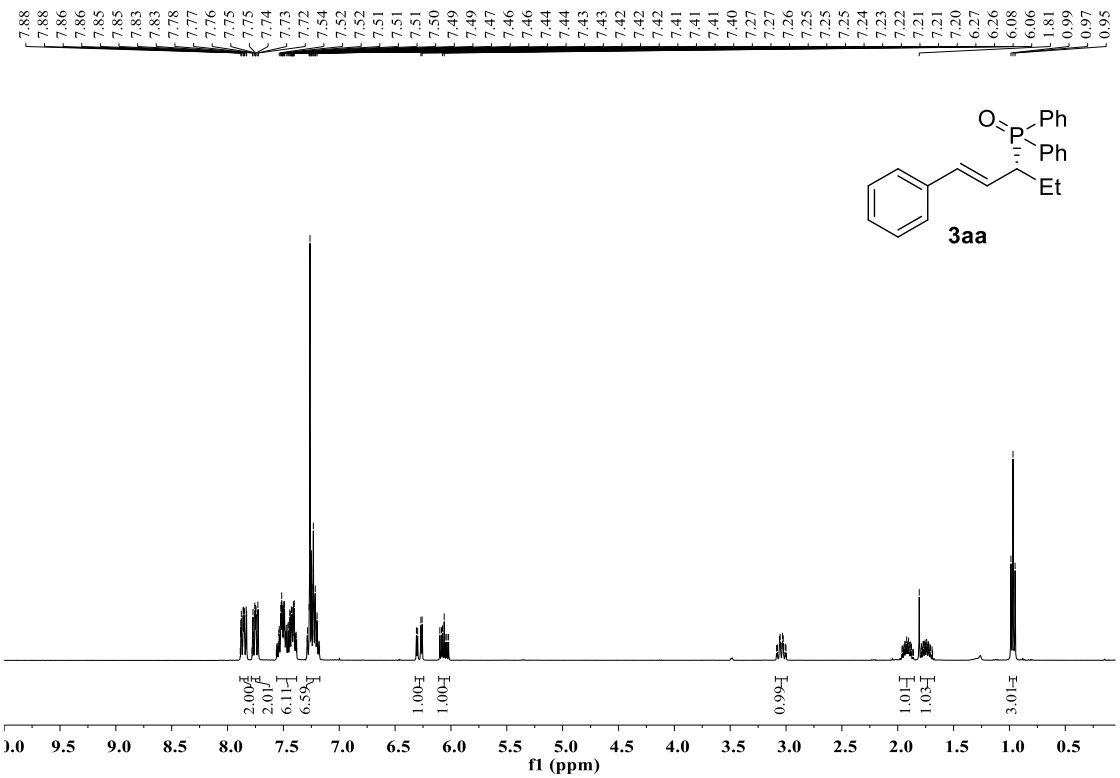

Figure S11. ^{1}H NMR spectra of **3aa**.

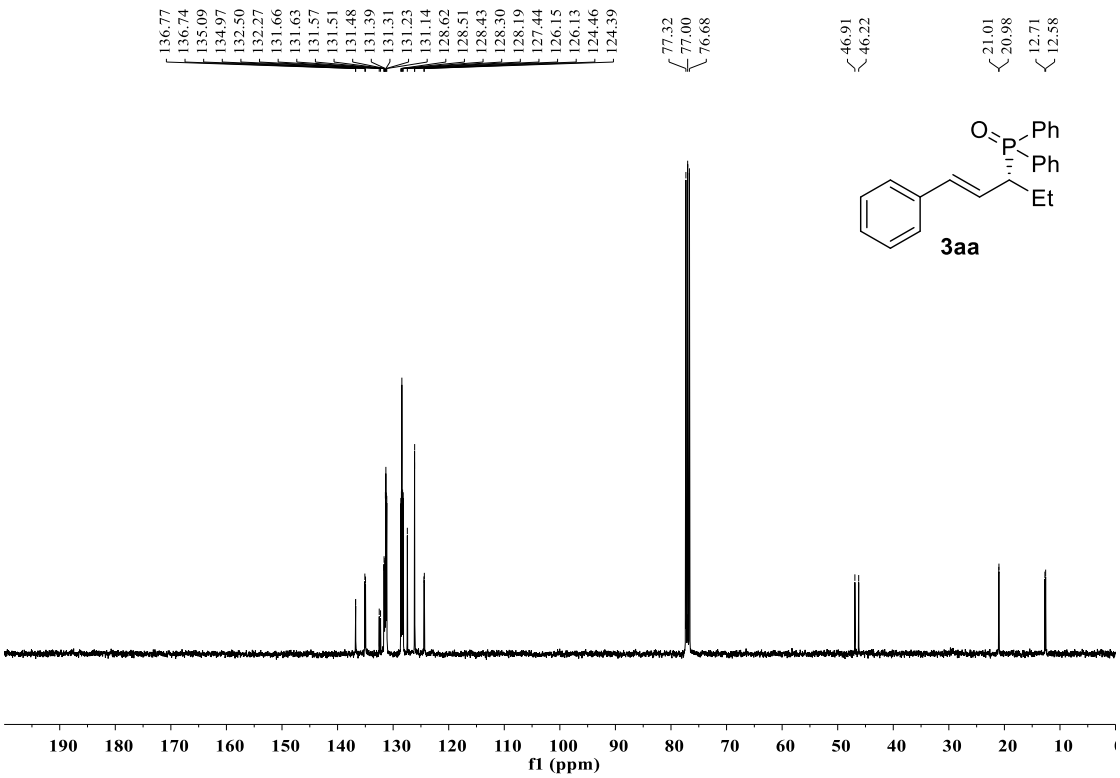

Figure S12. ^{13}C NMR spectra of **3aa**.

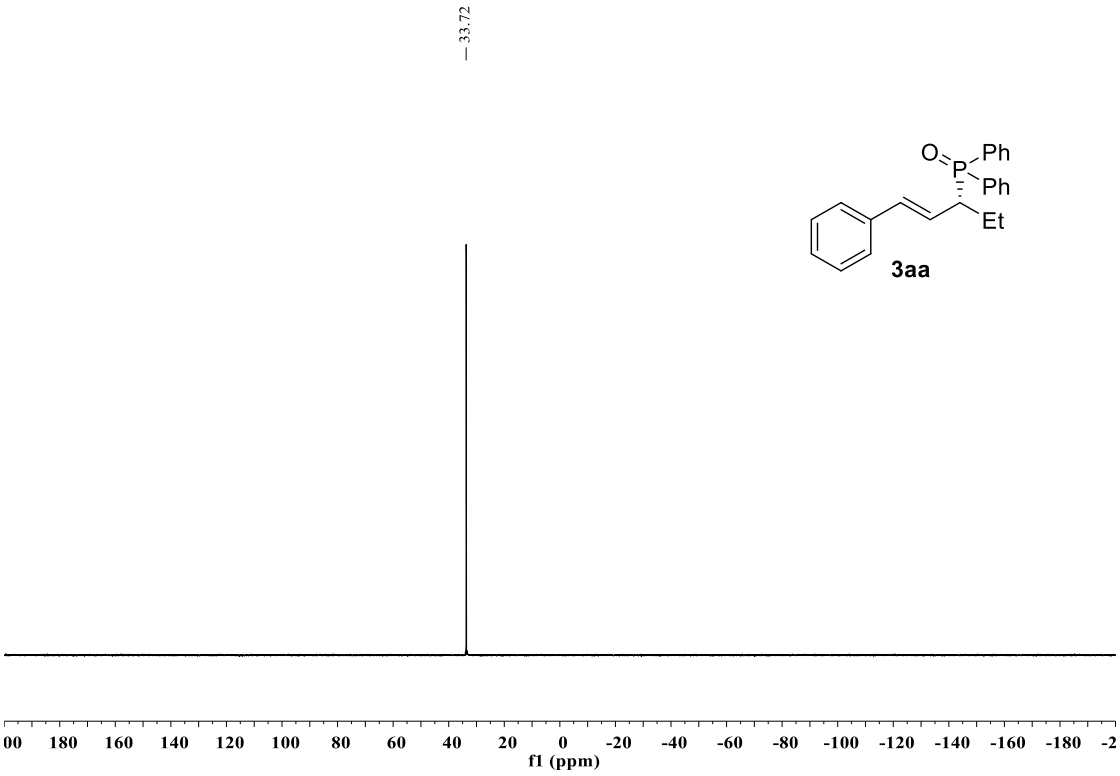

Figure S13. ^{31}P NMR spectra of **3aa**.

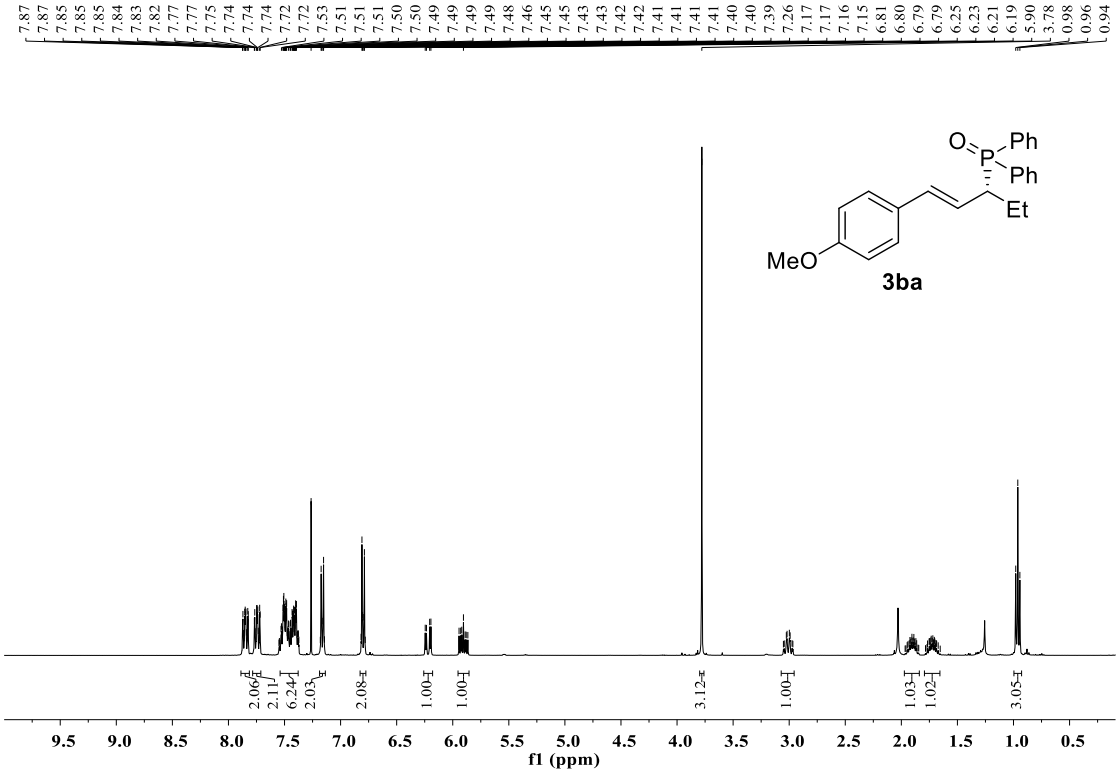

Figure S14. ^{1}H NMR spectra of **3ba**.

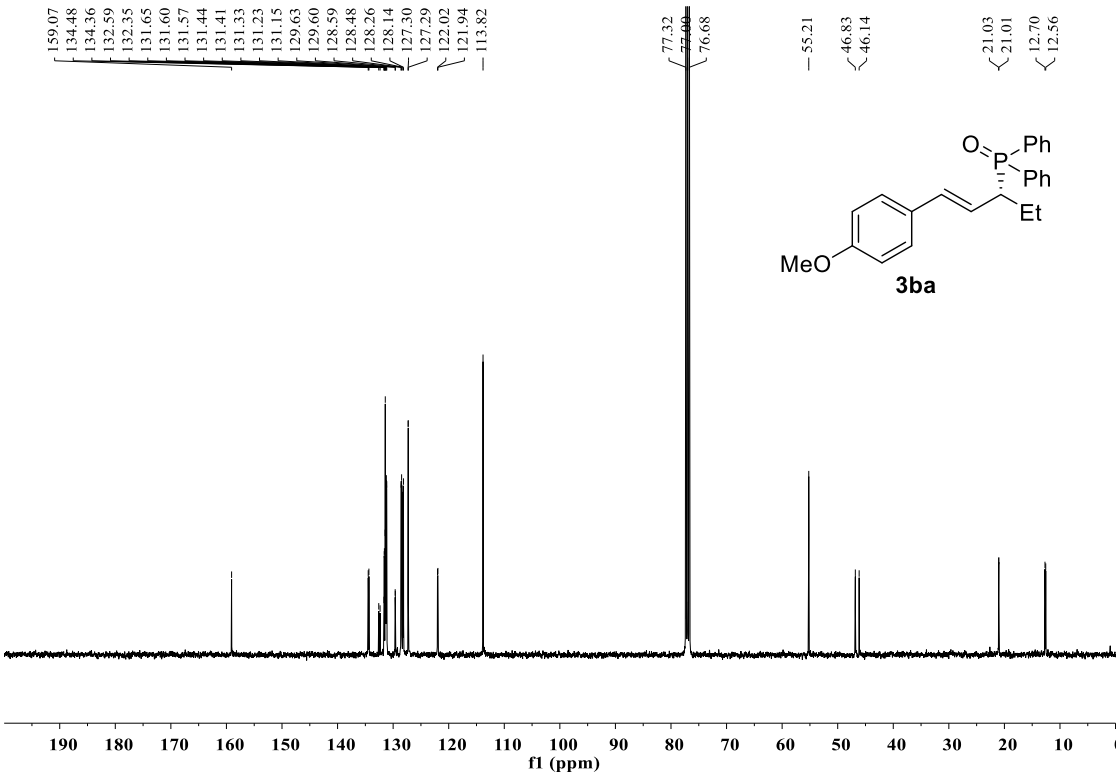

Figure S15. ^{13}C NMR spectra of **3ba**.

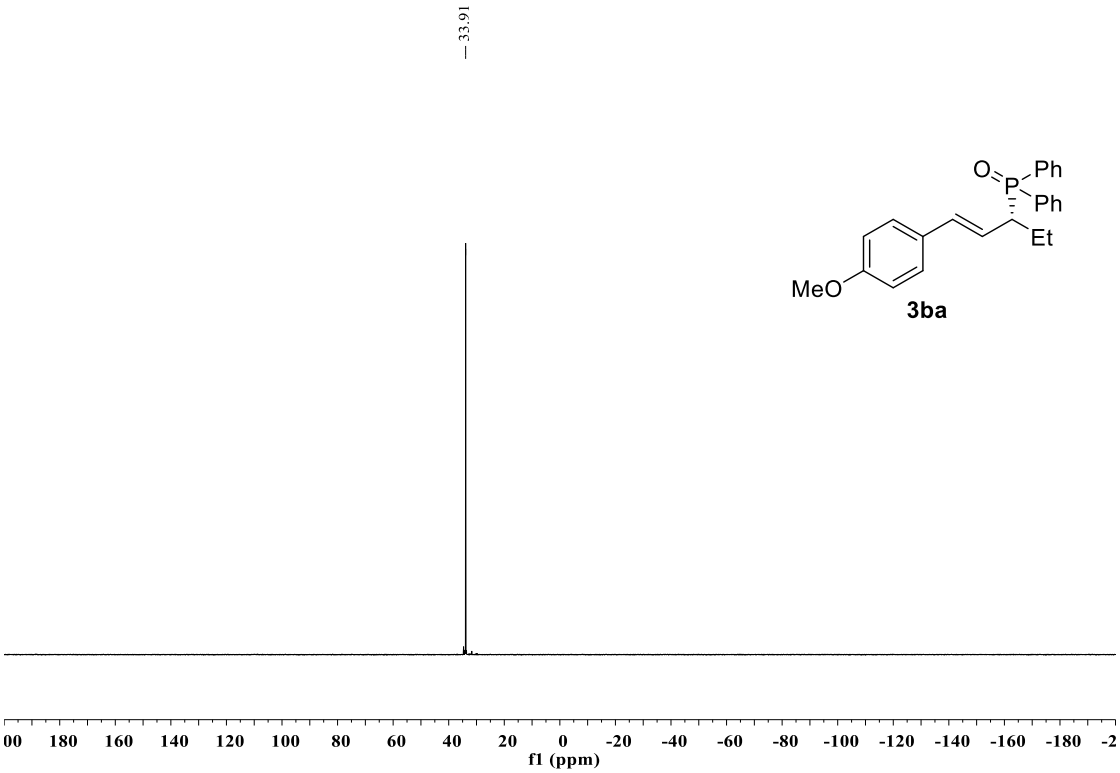

Figure S16. ^{31}P NMR spectra of **3ba**.

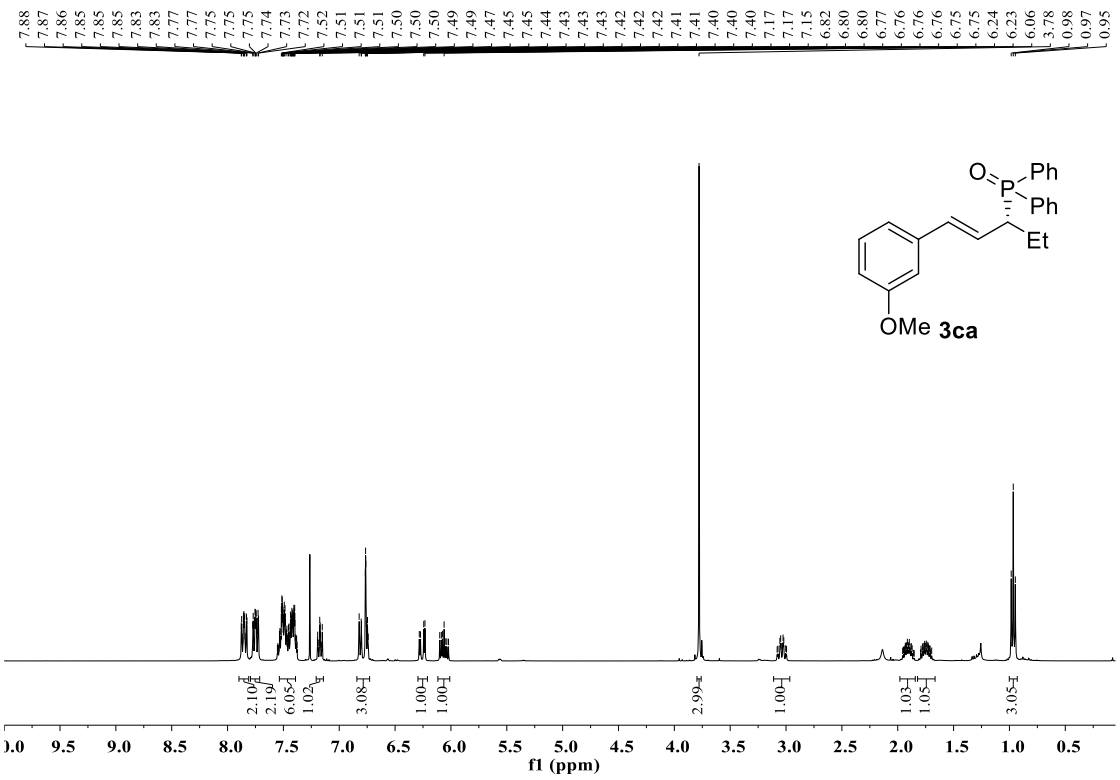

Figure S17. ^{1}H NMR spectra of **3ca**.

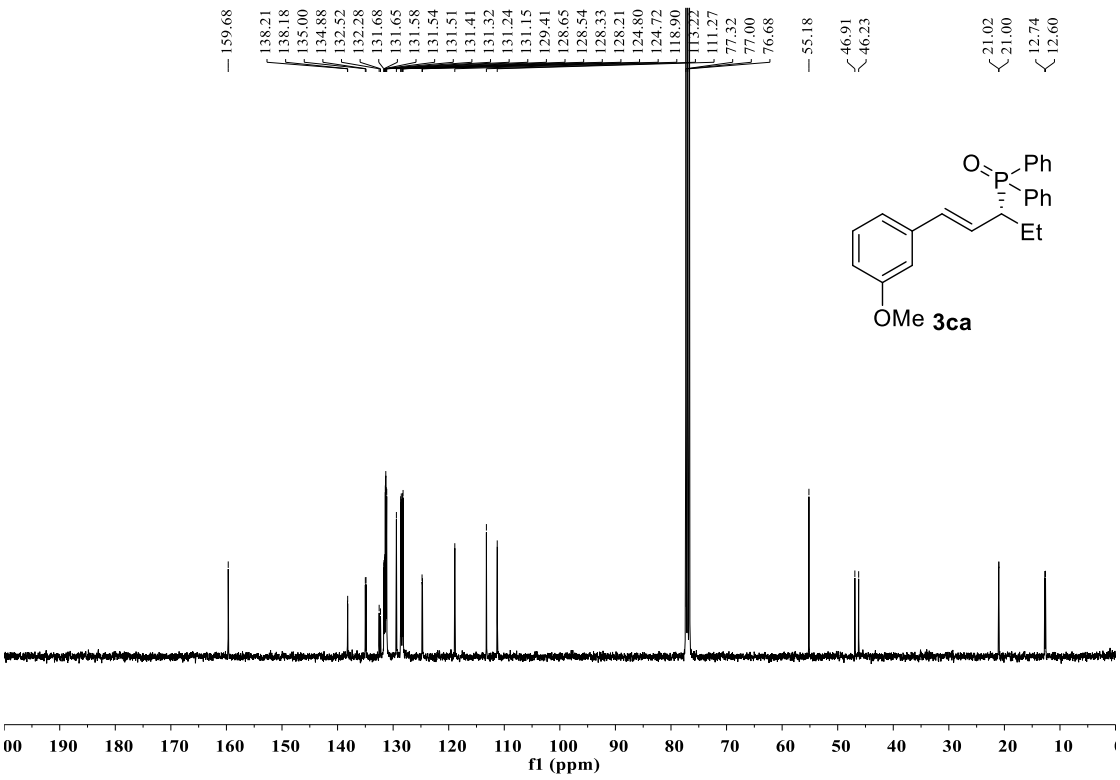

Figure S18. ^{13}C NMR spectra of **3ca**.

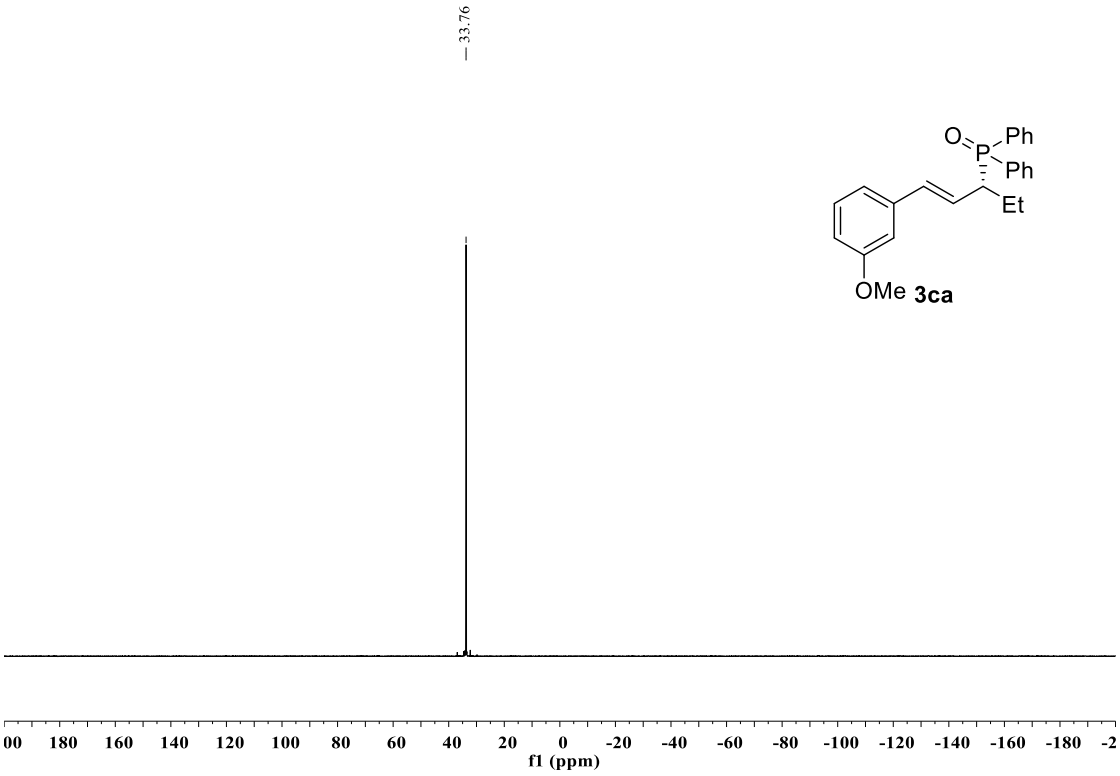

Figure S19. ^{31}P NMR spectra of **3ca**.

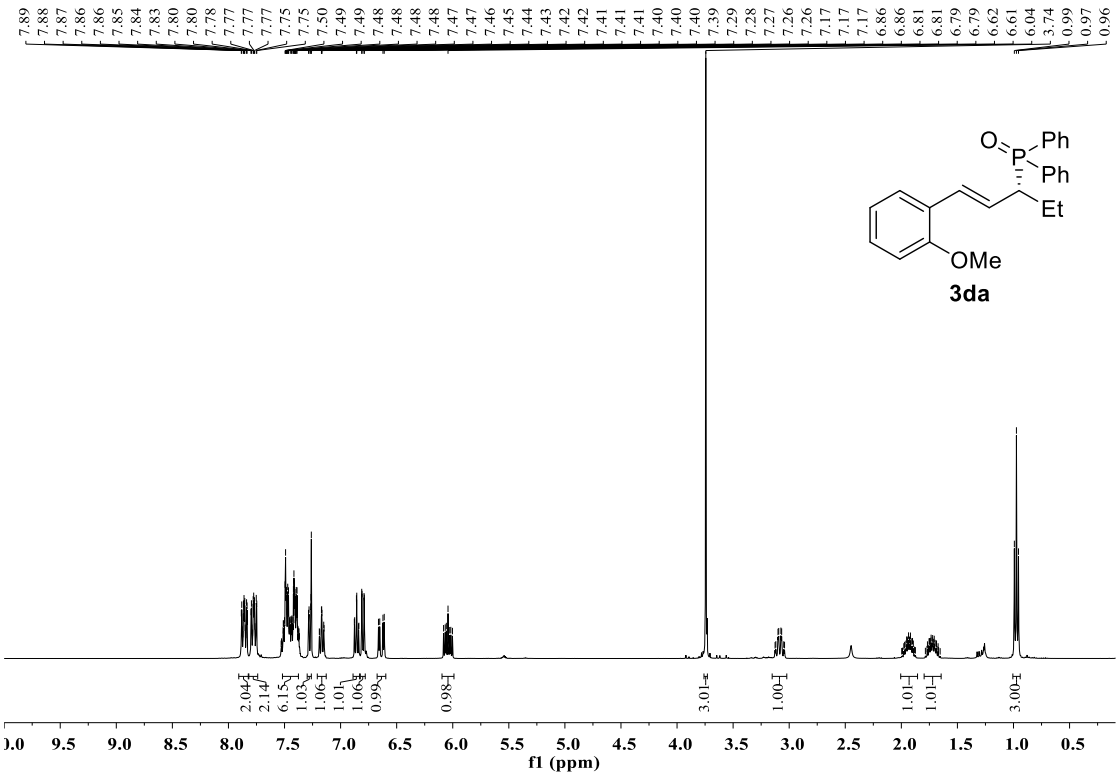

Figure S20. ^{1}H NMR spectra of **3da**.

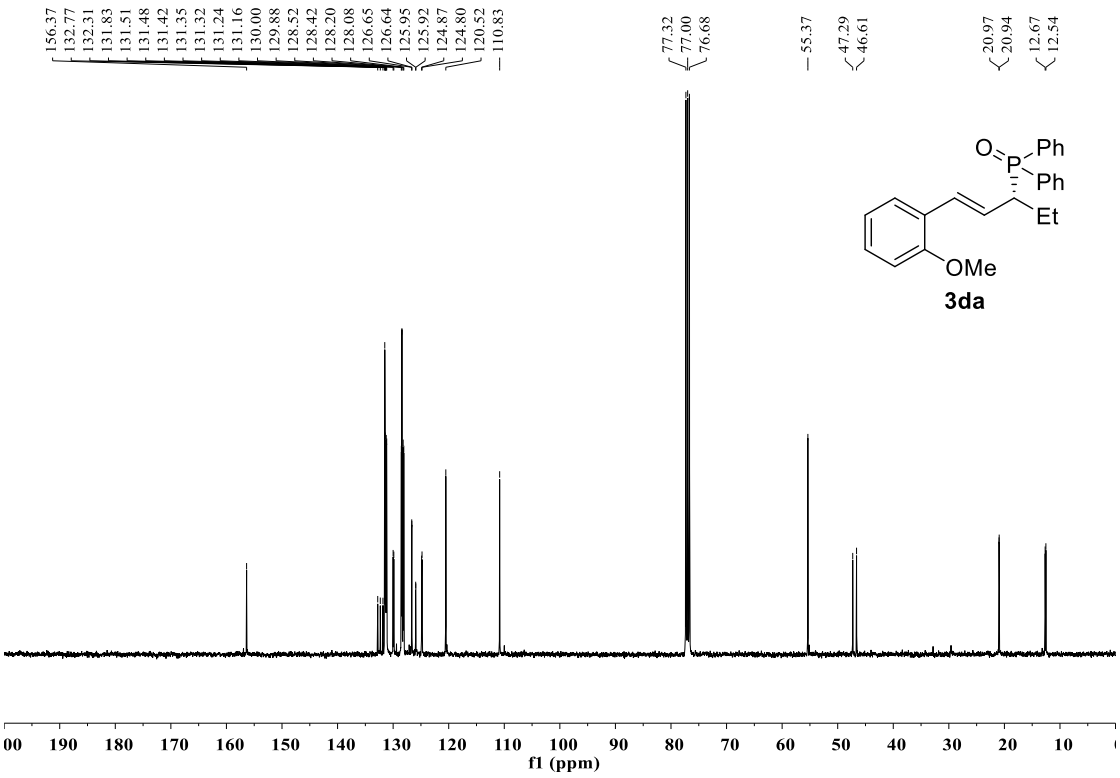

Figure S21. ^{13}C NMR spectra of **3da**.

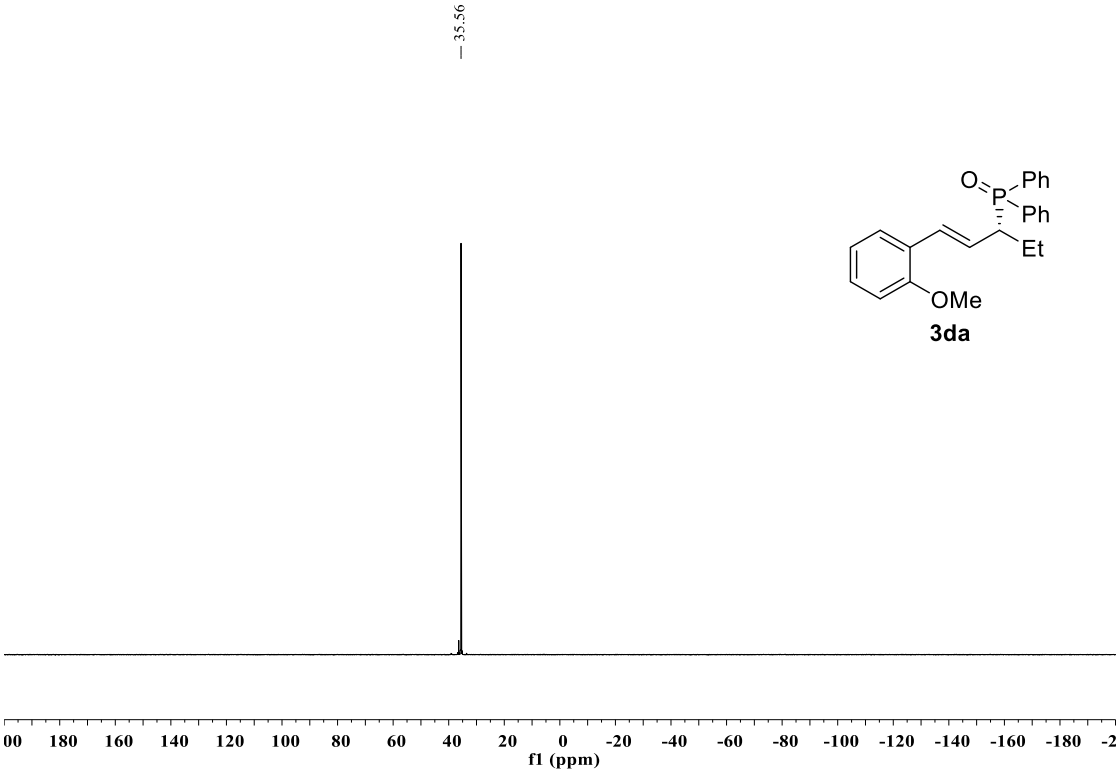

Figure S22. ^{31}P NMR spectra of **3da**.

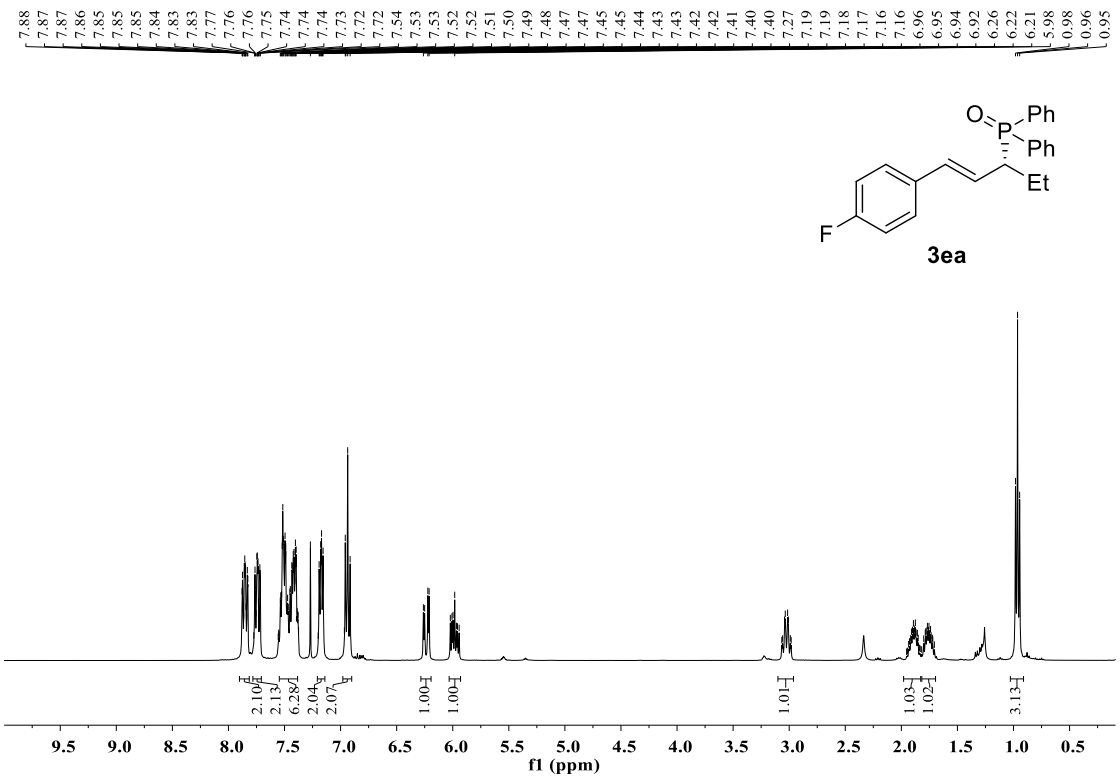

Figure S23. ^{1}H NMR spectra of **3ea**.

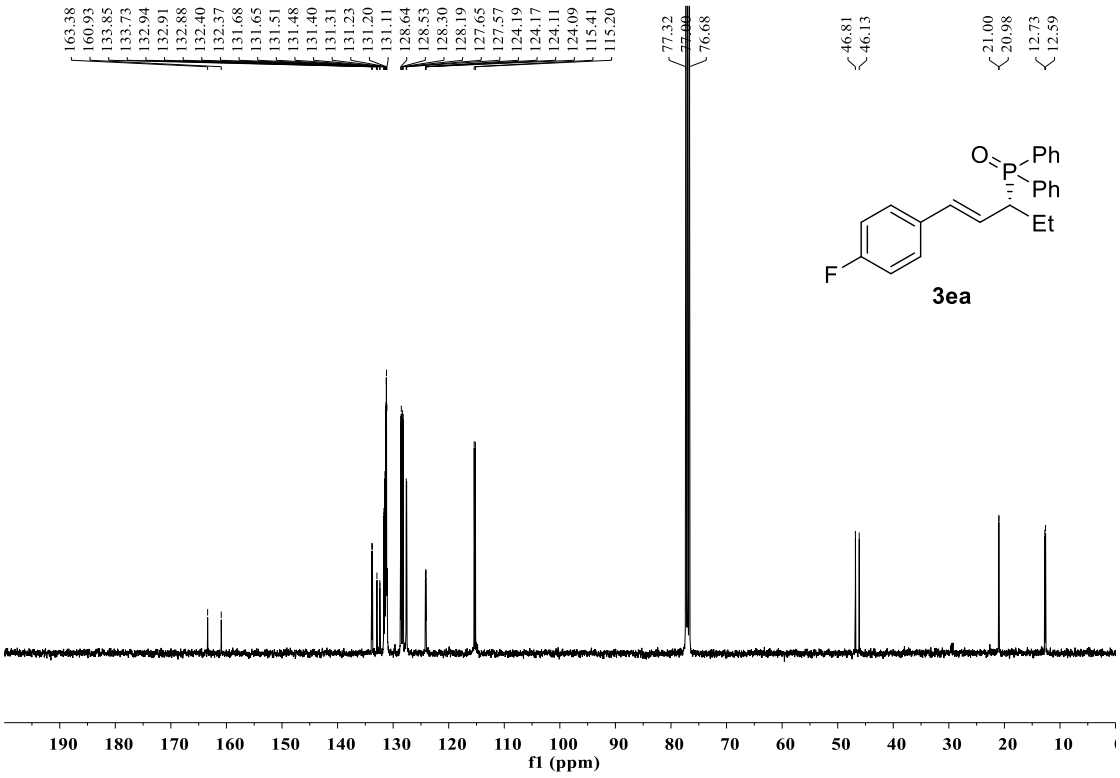

Figure S24. ^{13}C NMR spectra of **3ea**.

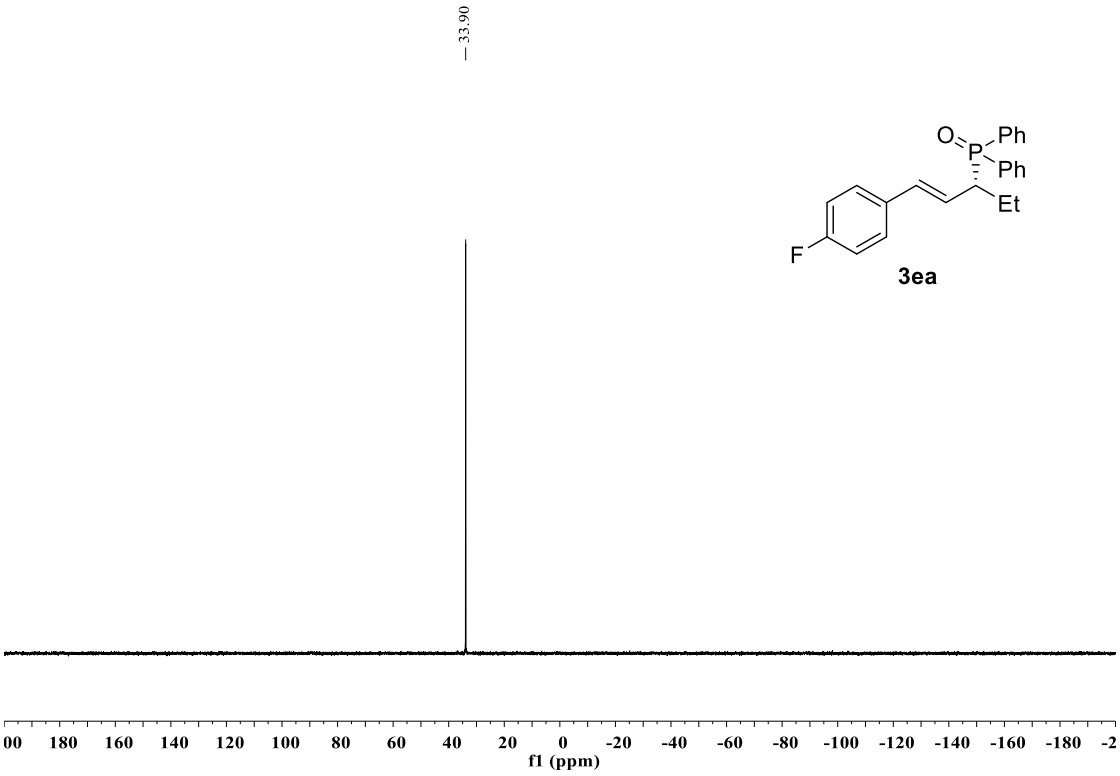

Figure S25. ^{31}P NMR spectra of **3ea**.

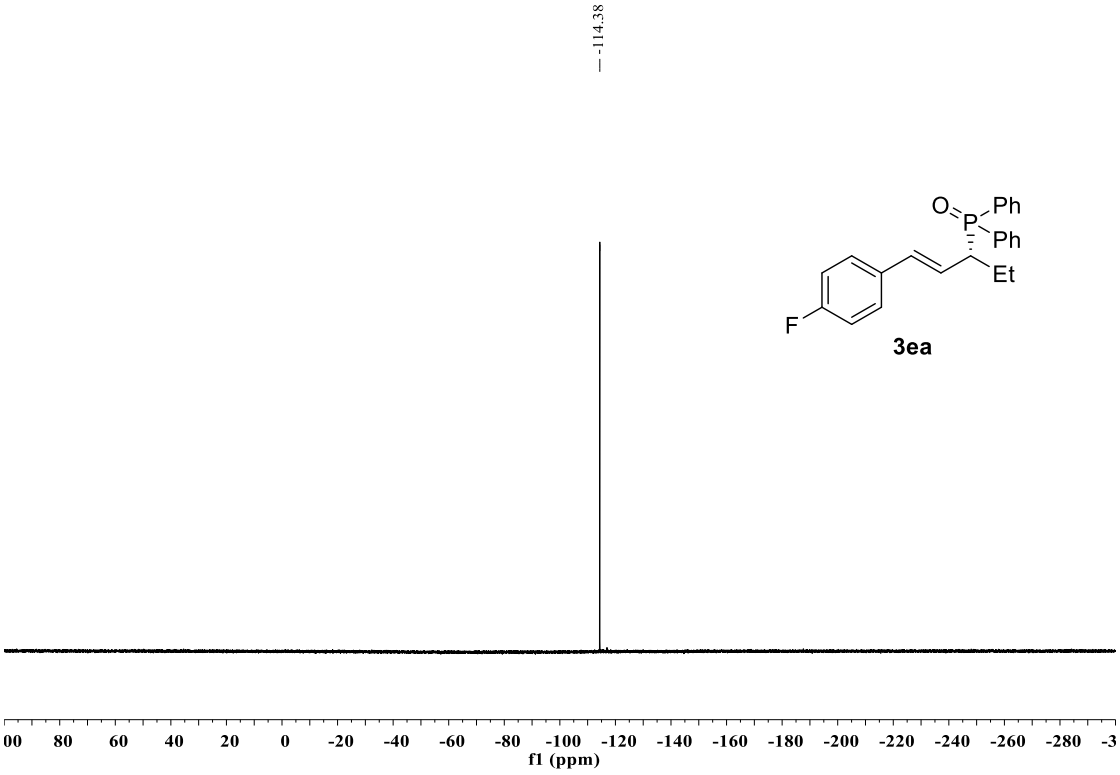

Figure S26. ^{19}F NMR spectra of **3ea**.

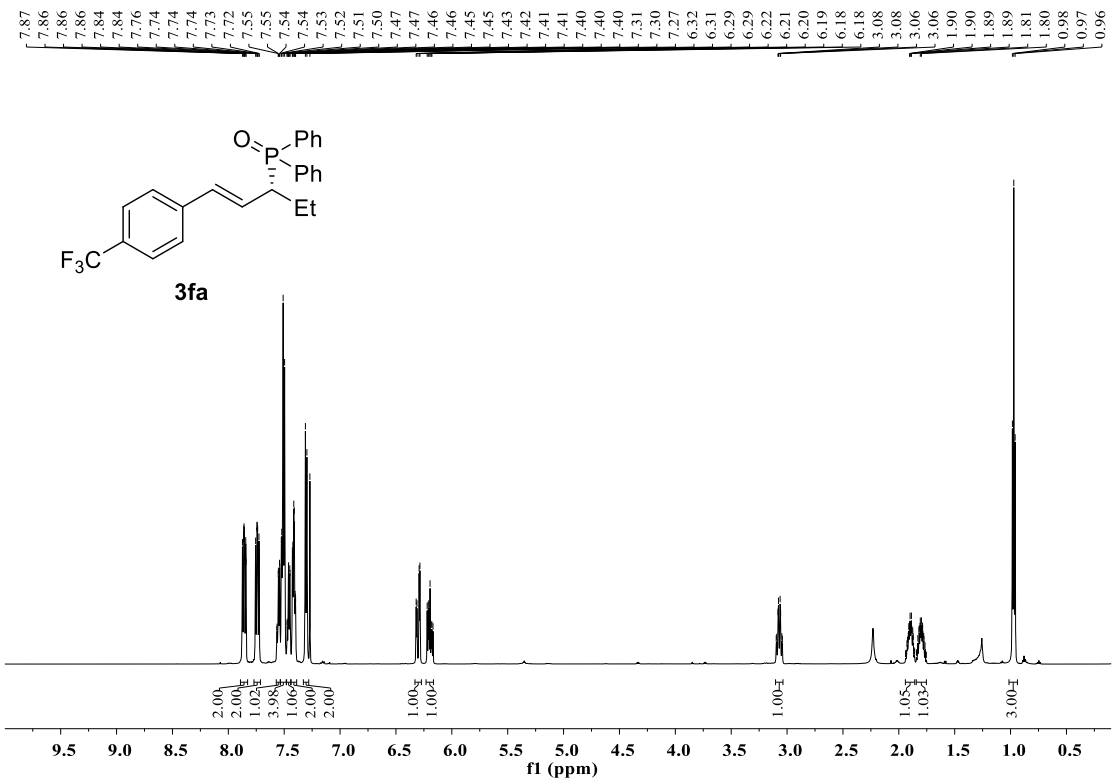

Figure S27. ^{1}H NMR spectra of **3fa**.

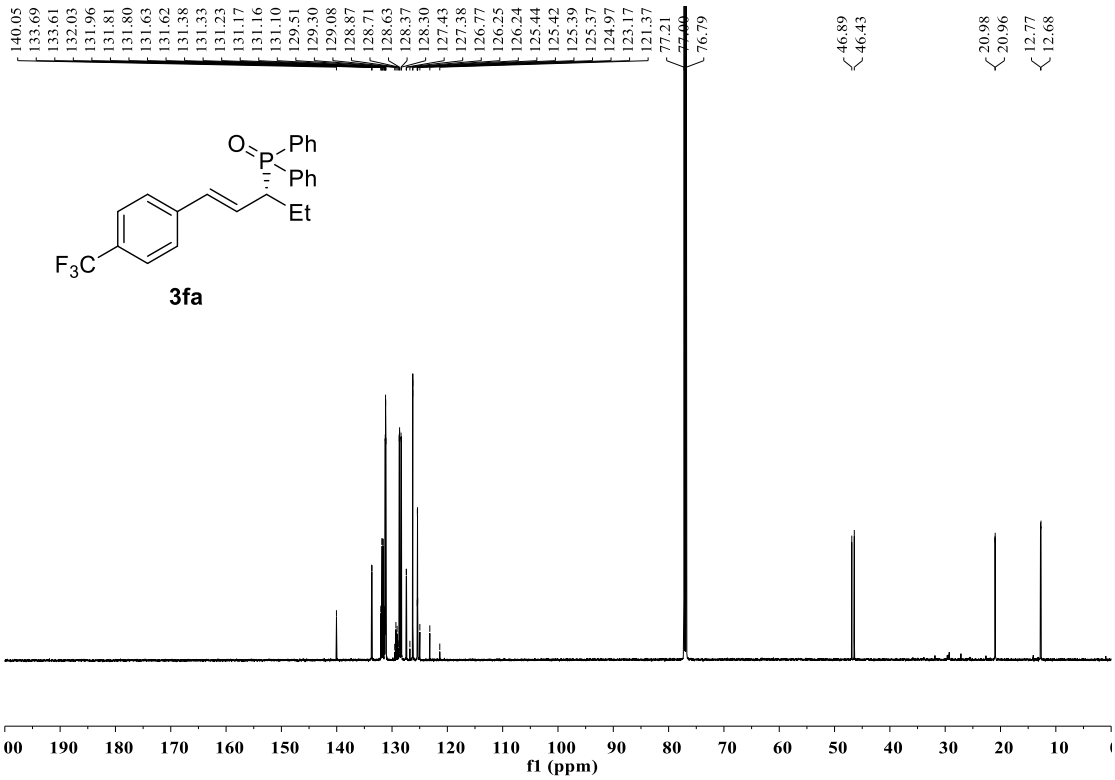

Figure S28. ^{13}C NMR spectra of **3fa**.

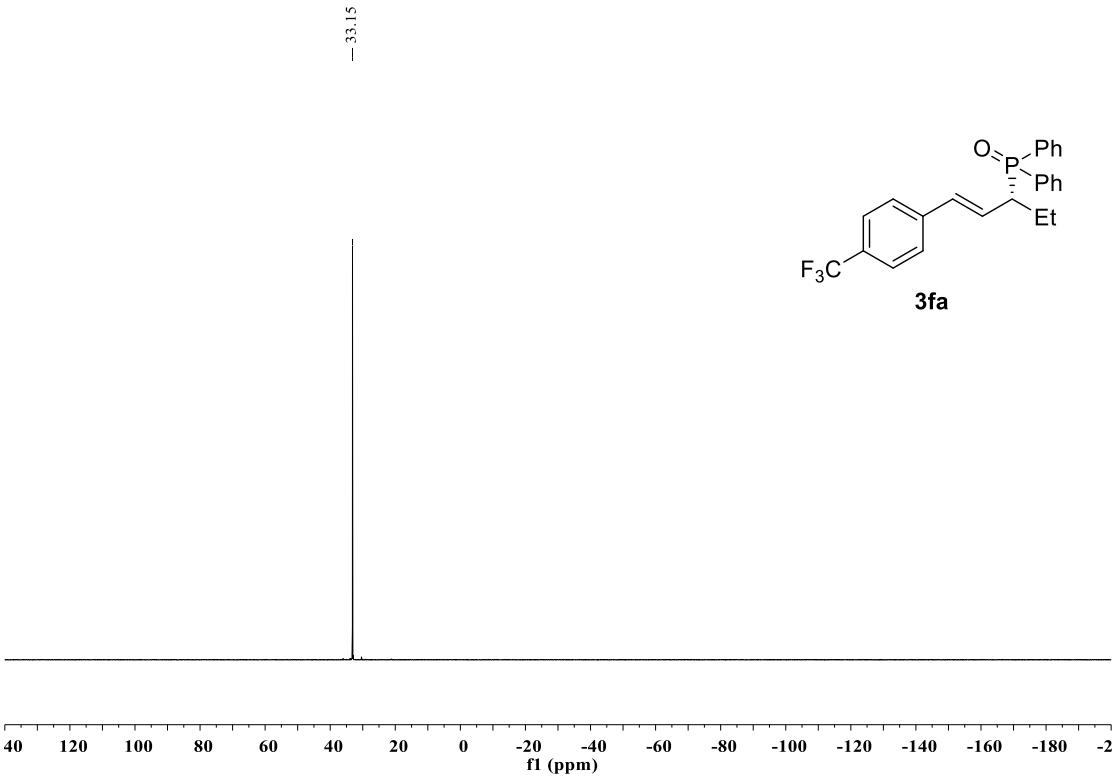

Figure S29. ^{31}P NMR spectra of **3fa**.

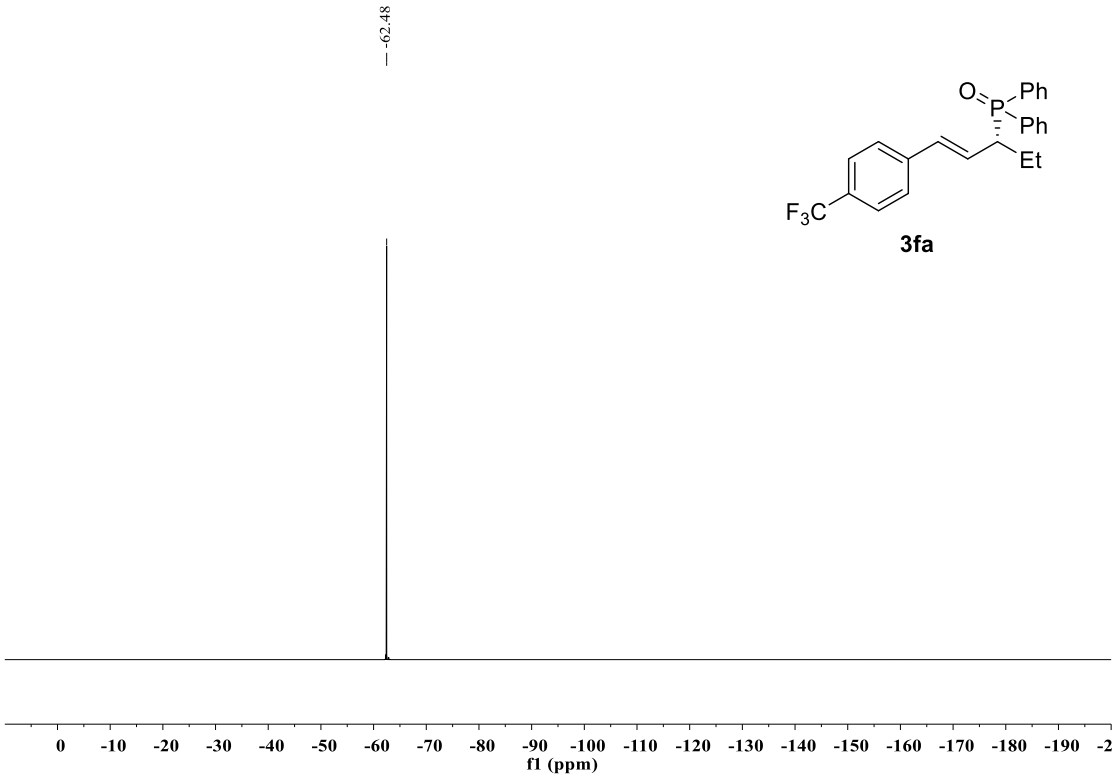

Figure S30. ^{19}F NMR spectra of **3fa**.

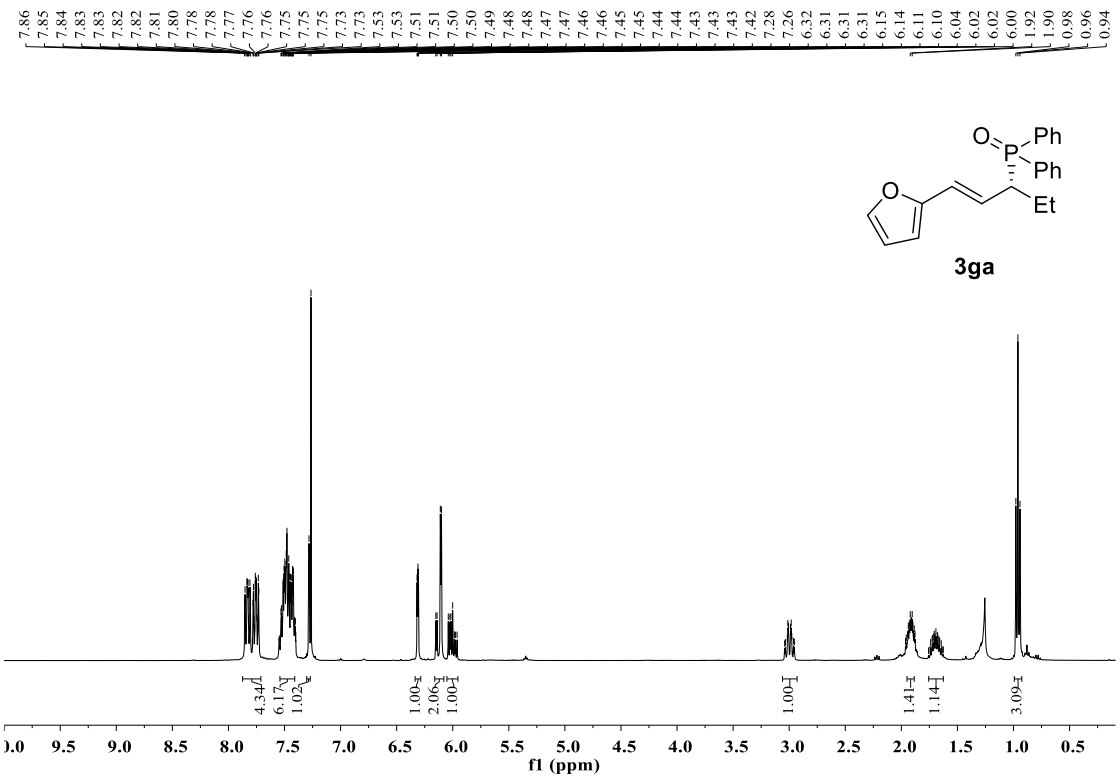

Figure S31. ^{1}H NMR spectra of **3ga**.

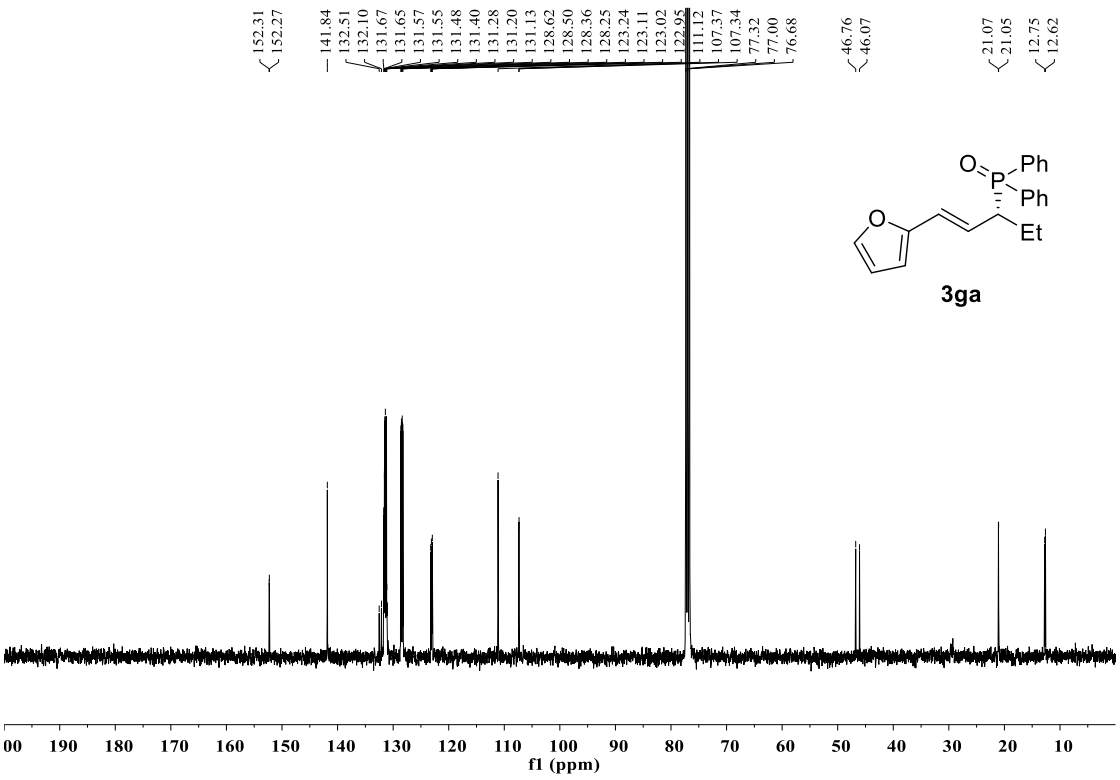

Figure S32. ^{13}C NMR spectra of **3ga**.

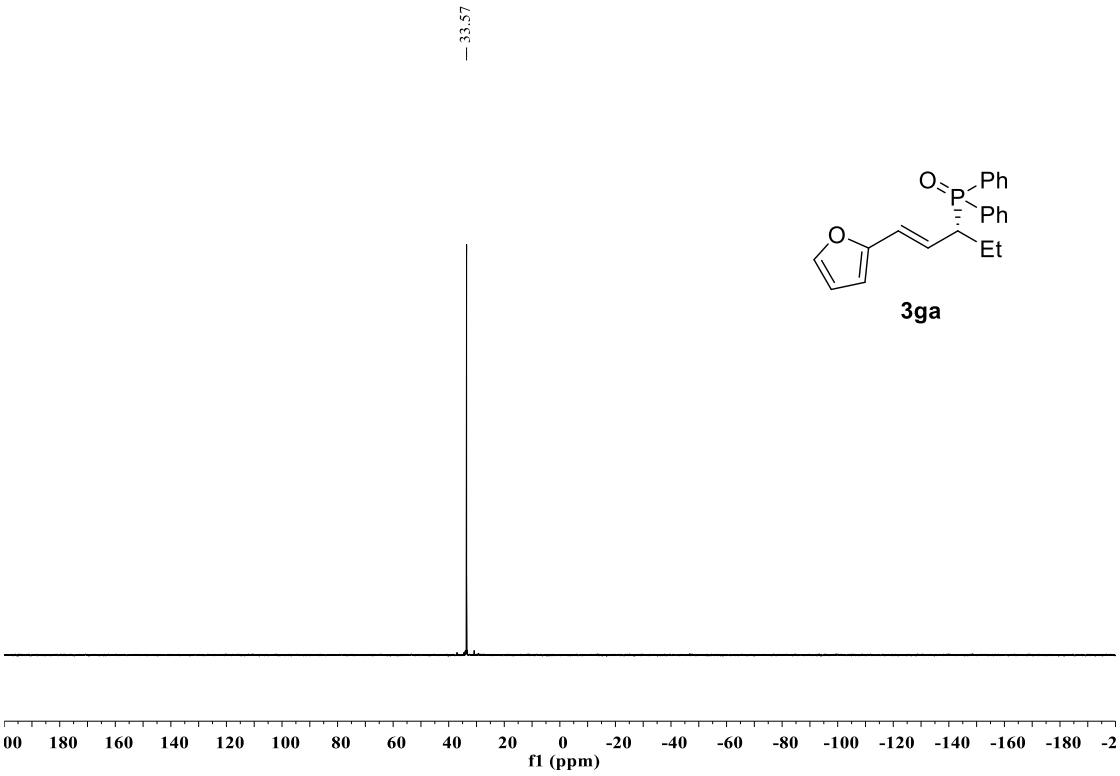

Figure S33. ^{31}P NMR spectra of **3ga**.

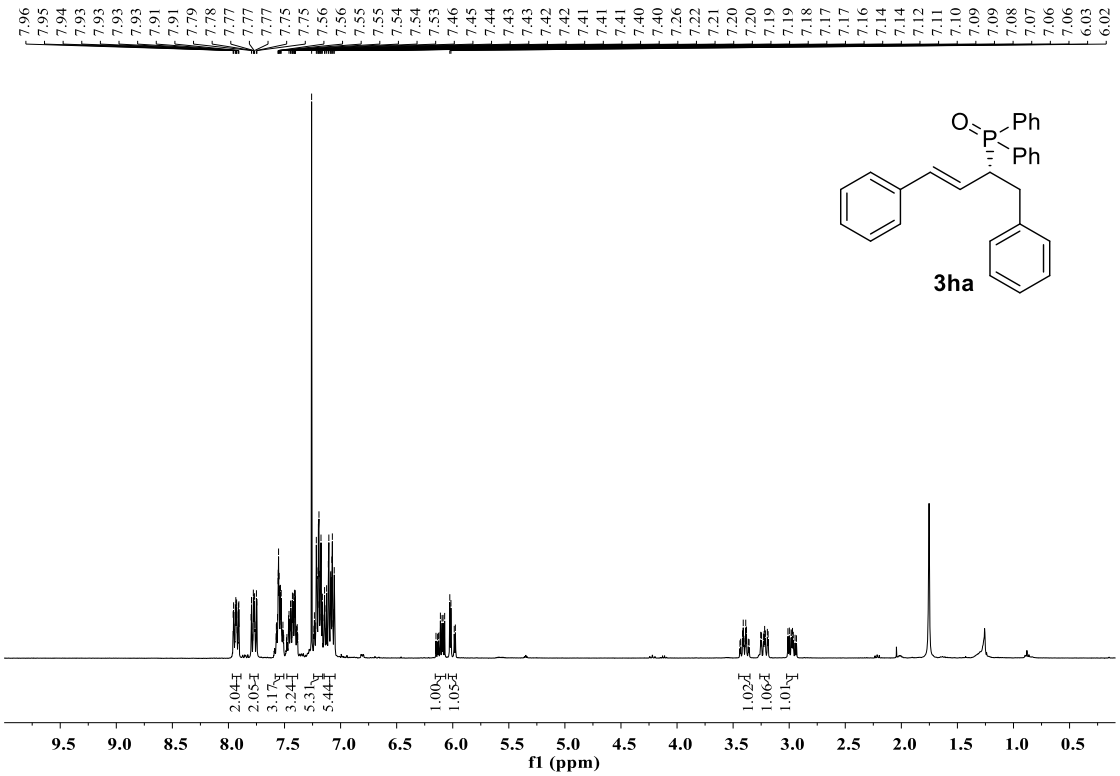

Figure S34. ^{1}H NMR spectra of **3ha**.

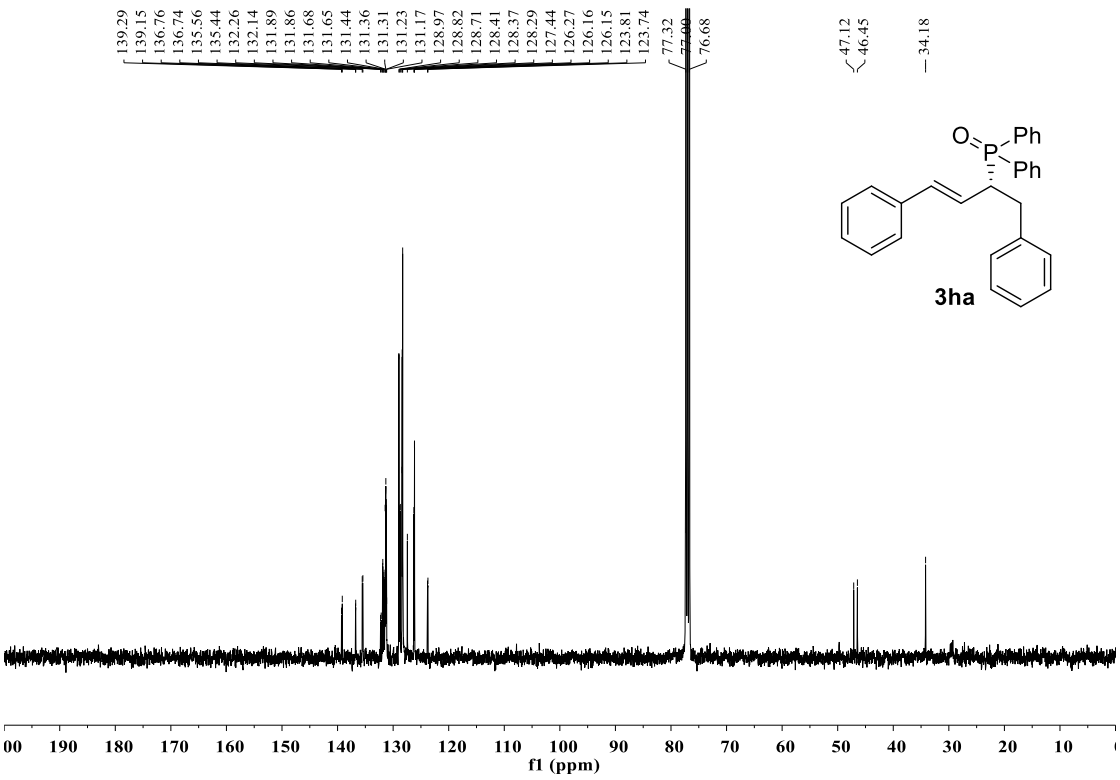

Figure S35. ^{13}C NMR spectra of **3ha**.

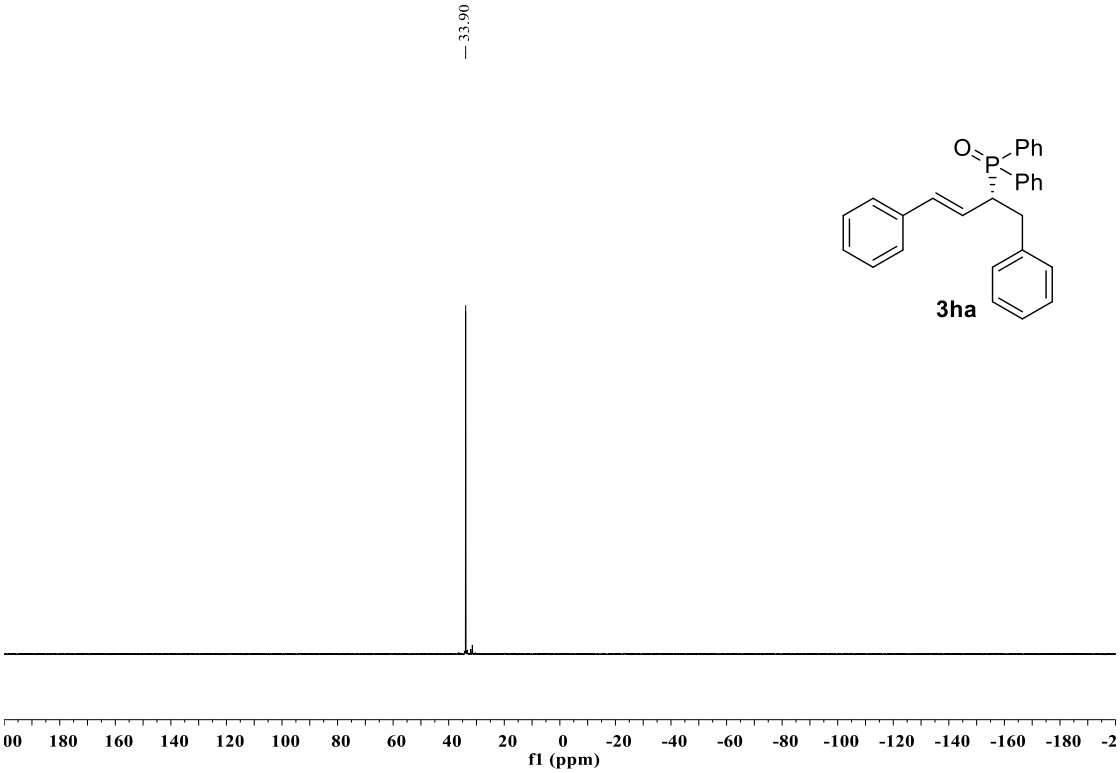

Figure S36. ^{31}P NMR spectra of **3ha**.

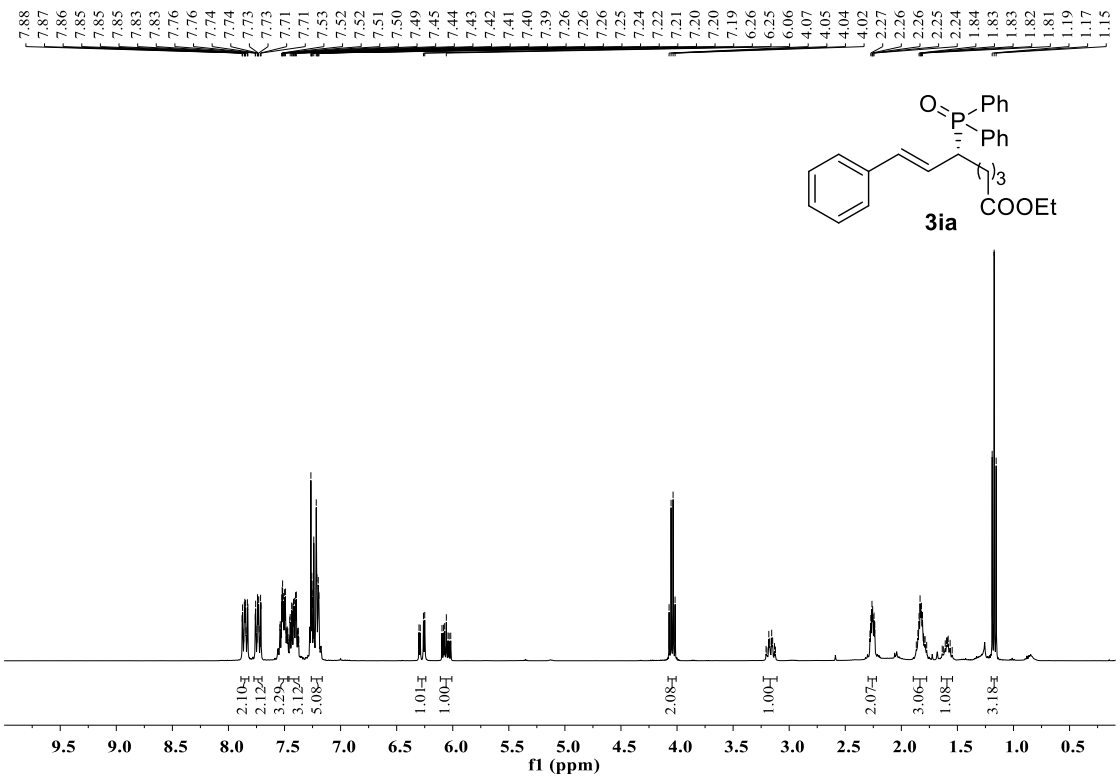

Figure S37. ^{1}H NMR spectra of **3ia**.

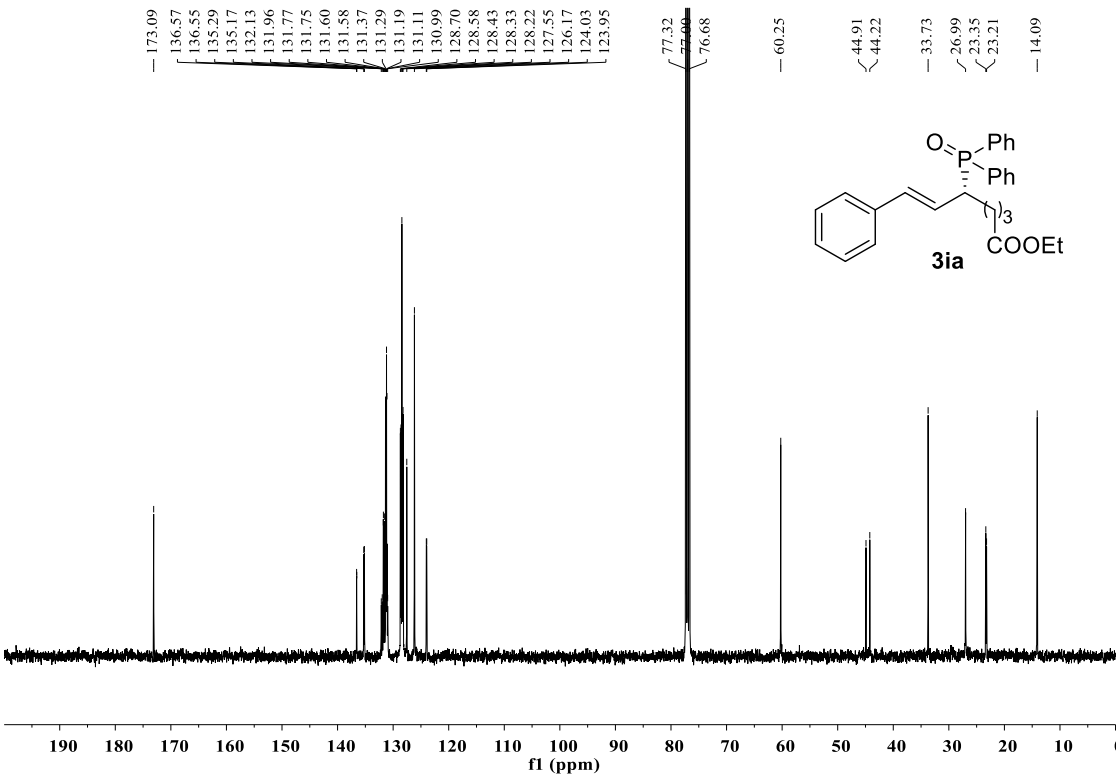

Figure S38 ^{13}C NMR spectra of **3ia**.

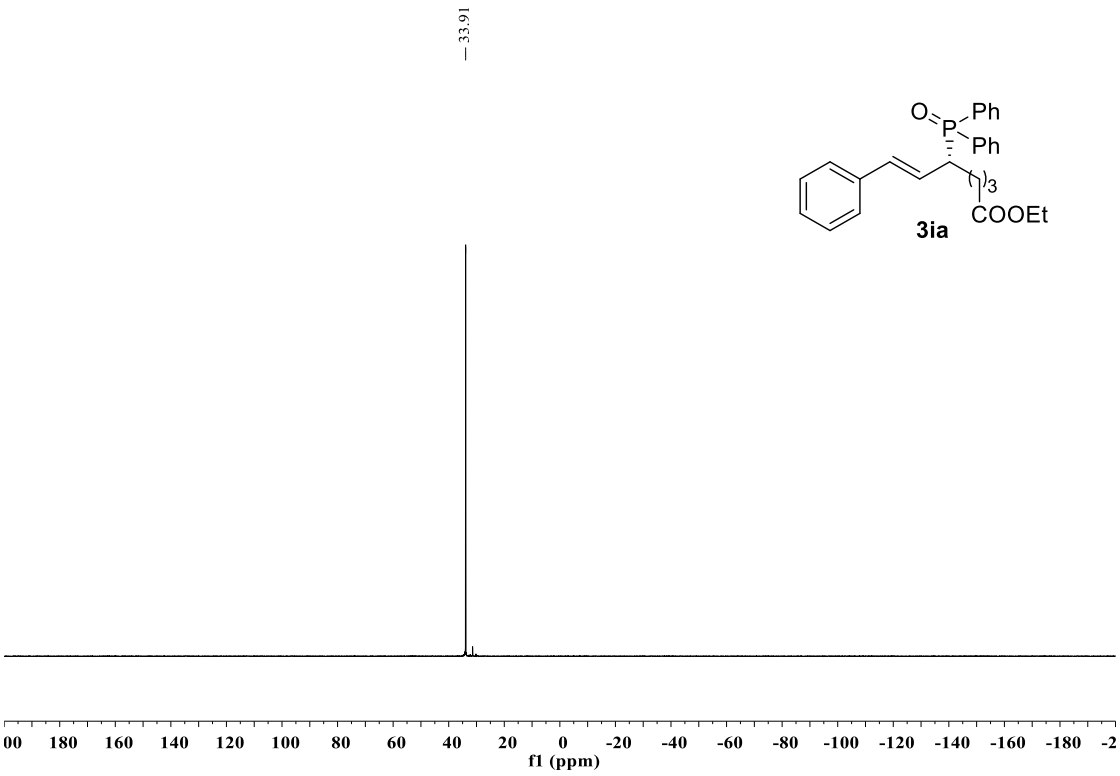

Figure S39. ^{31}P NMR spectra of **3ia**.

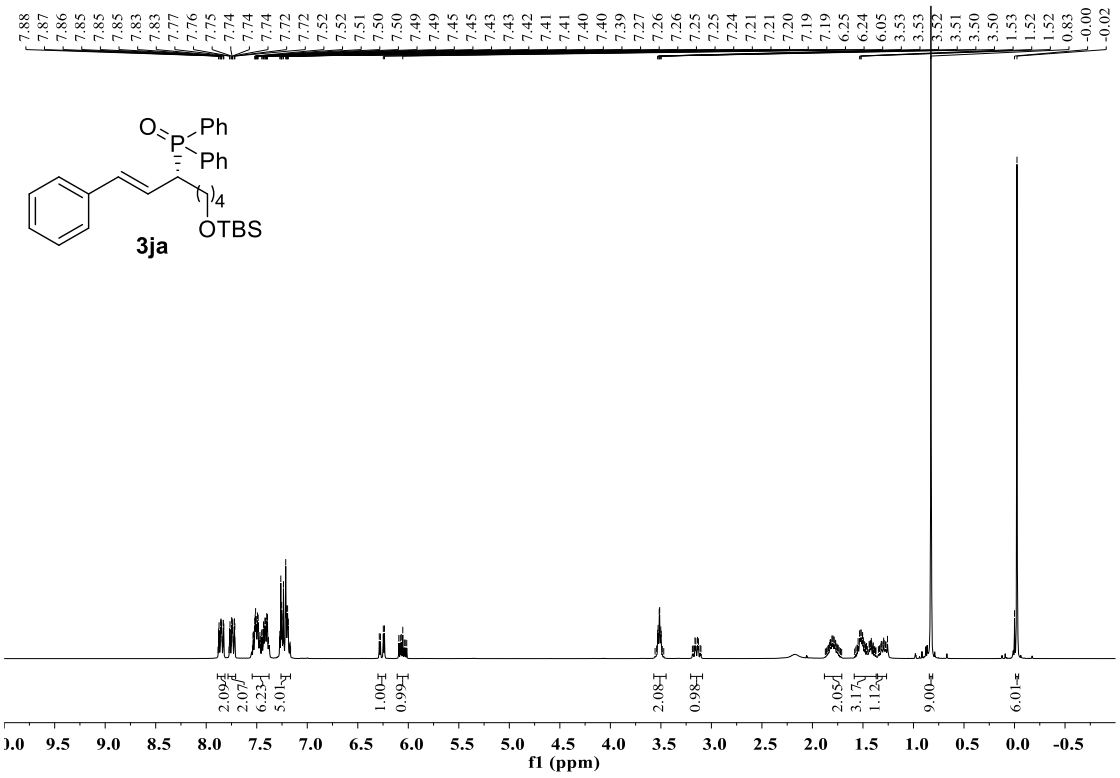

Figure S40. ^{1}H NMR spectra of **3ja**.

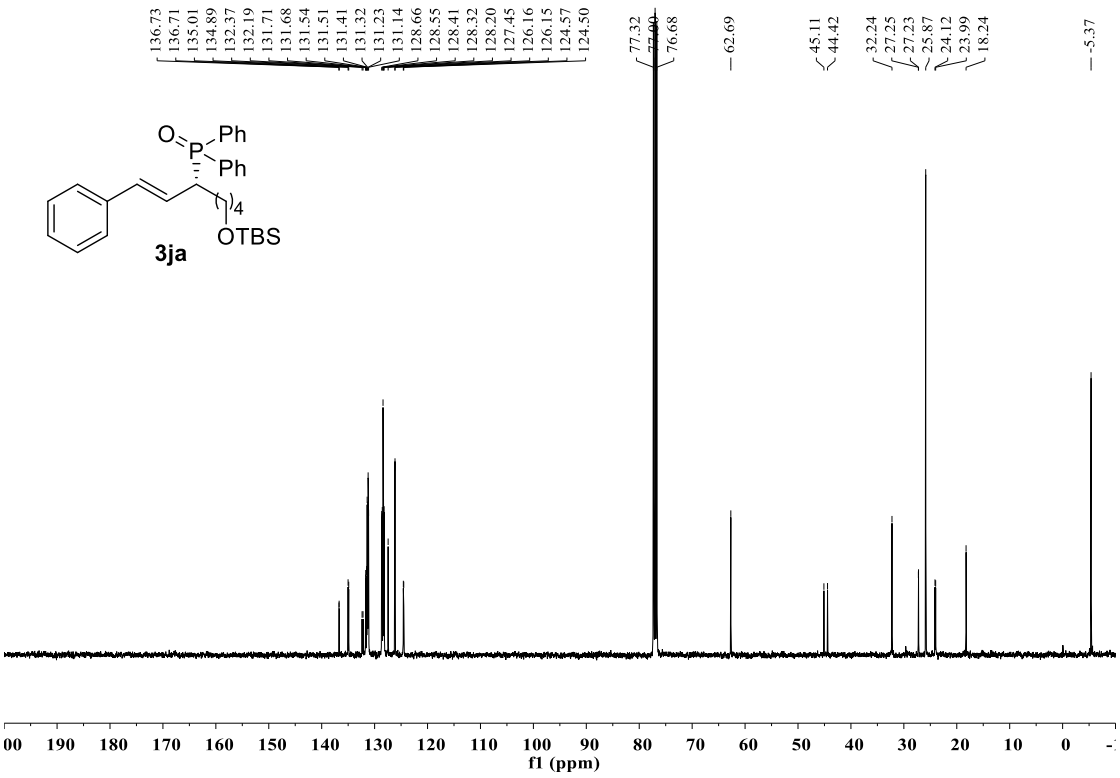

Figure S41. ^{13}C NMR spectra of **3ja**.

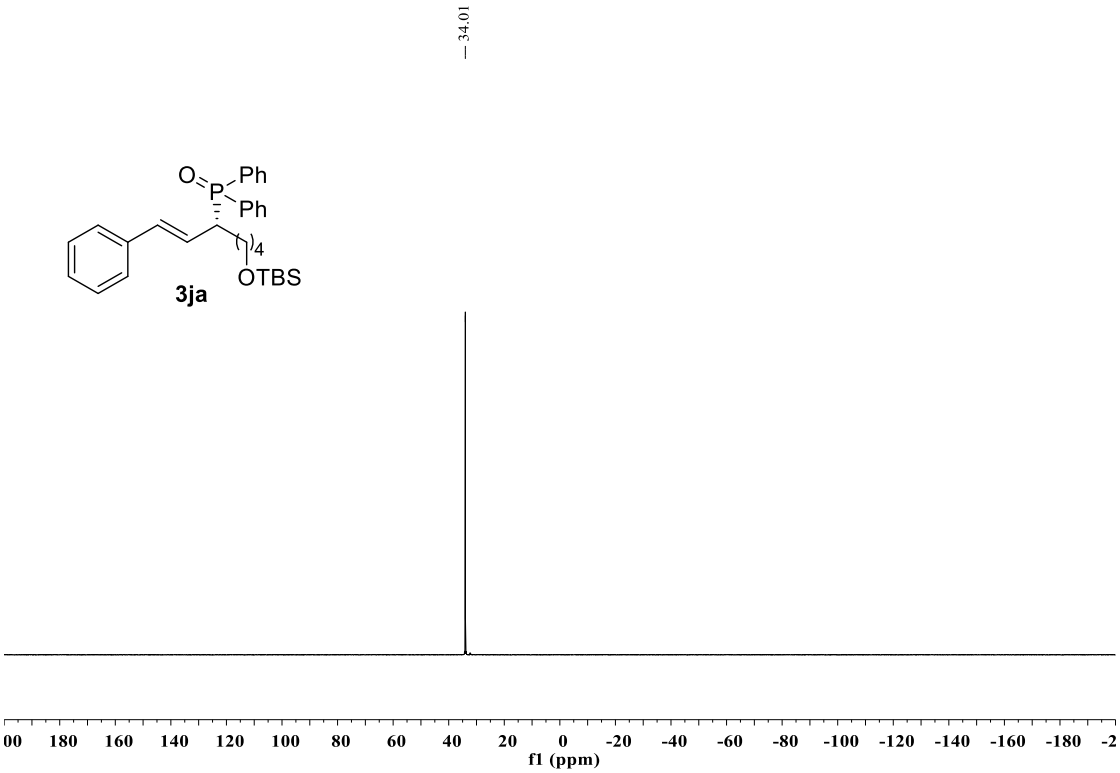

Figure S42. ^{31}P NMR spectra of **3ja**.

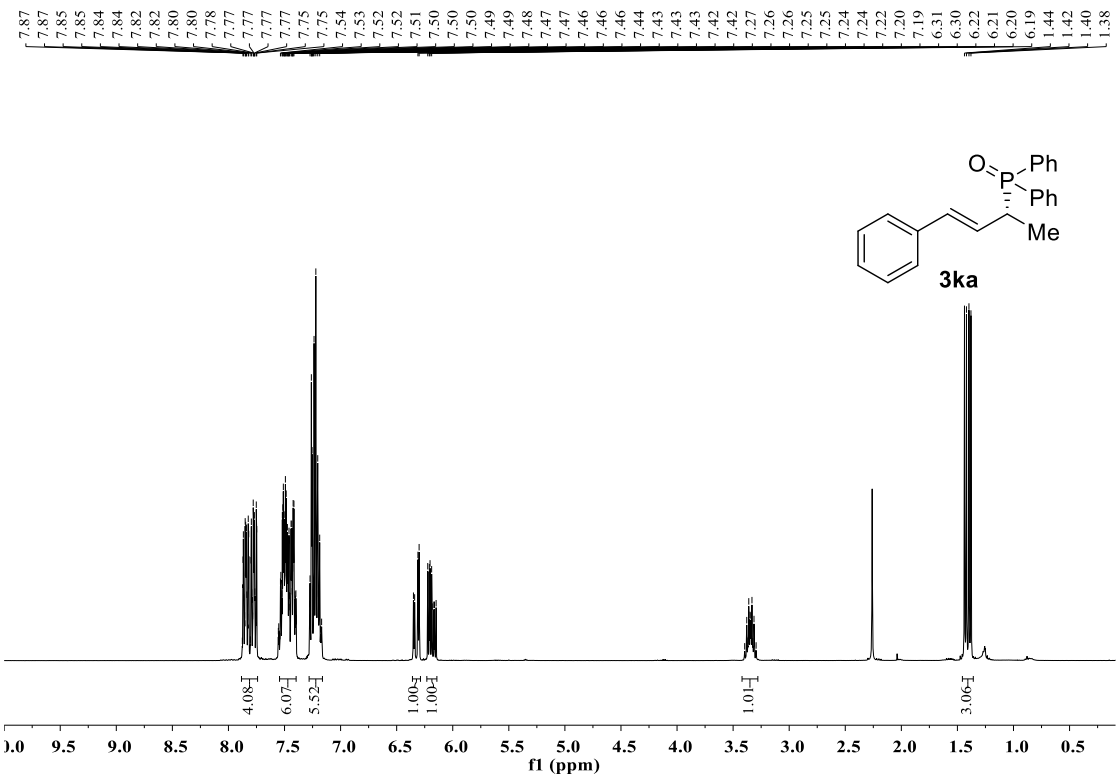

Figure S43. ^{1}H NMR spectra of **3ka**.

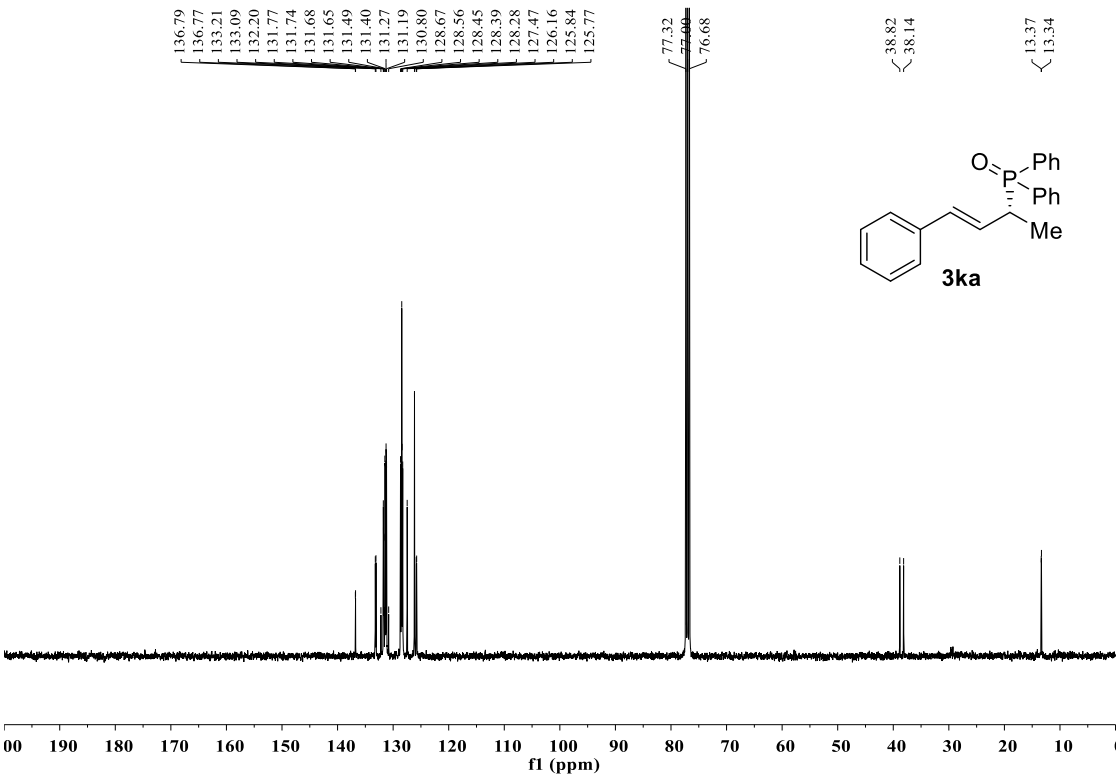

Figure S44. ^{13}C NMR spectra of **3ka**.

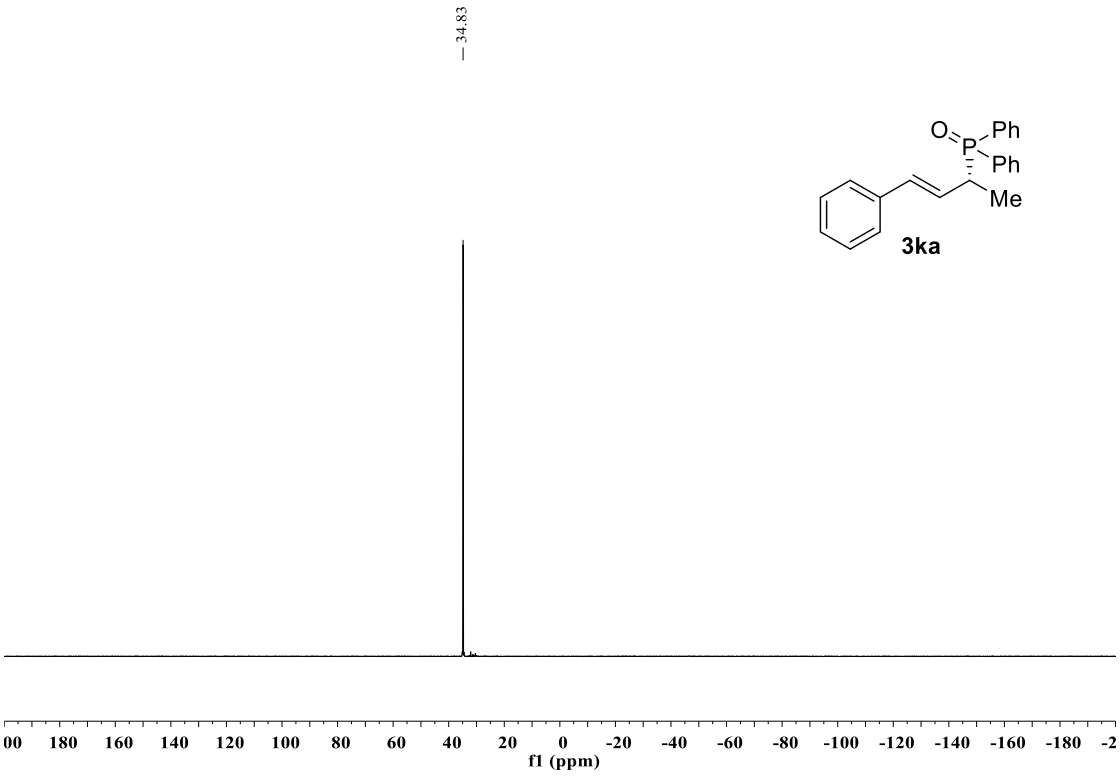

Figure S45. ^{31}P NMR spectra of **3ka**.

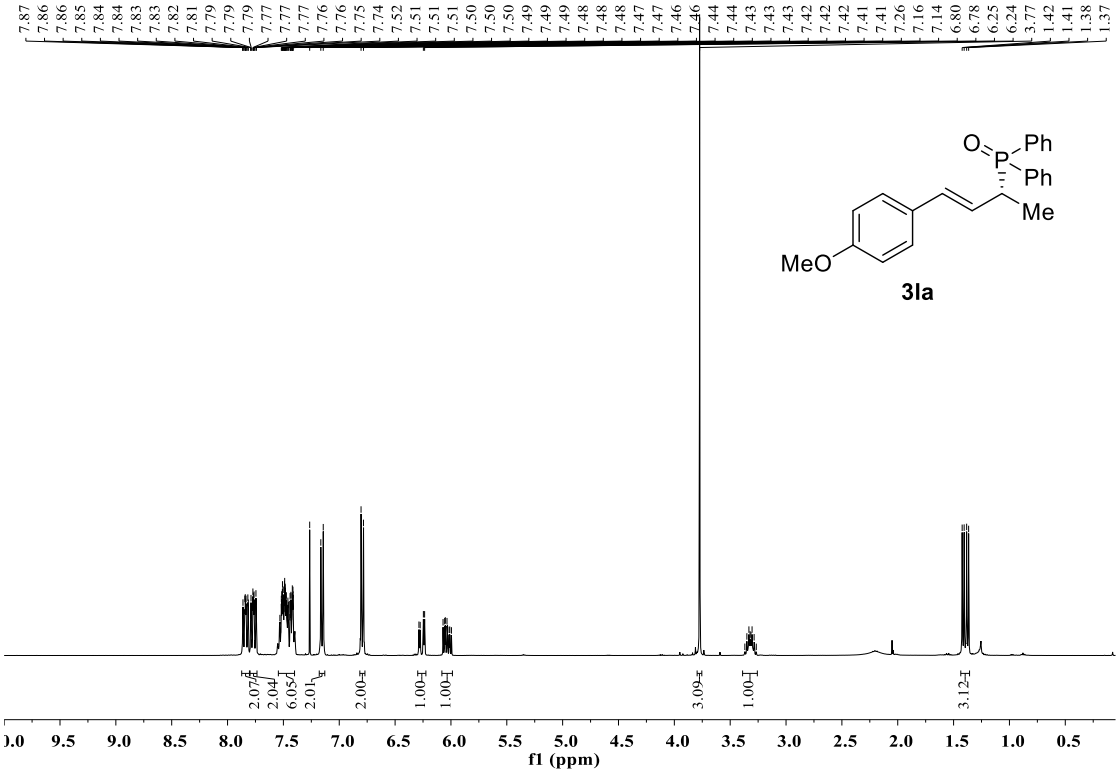

Figure S46. ^{1}H NMR spectra of **3la**.

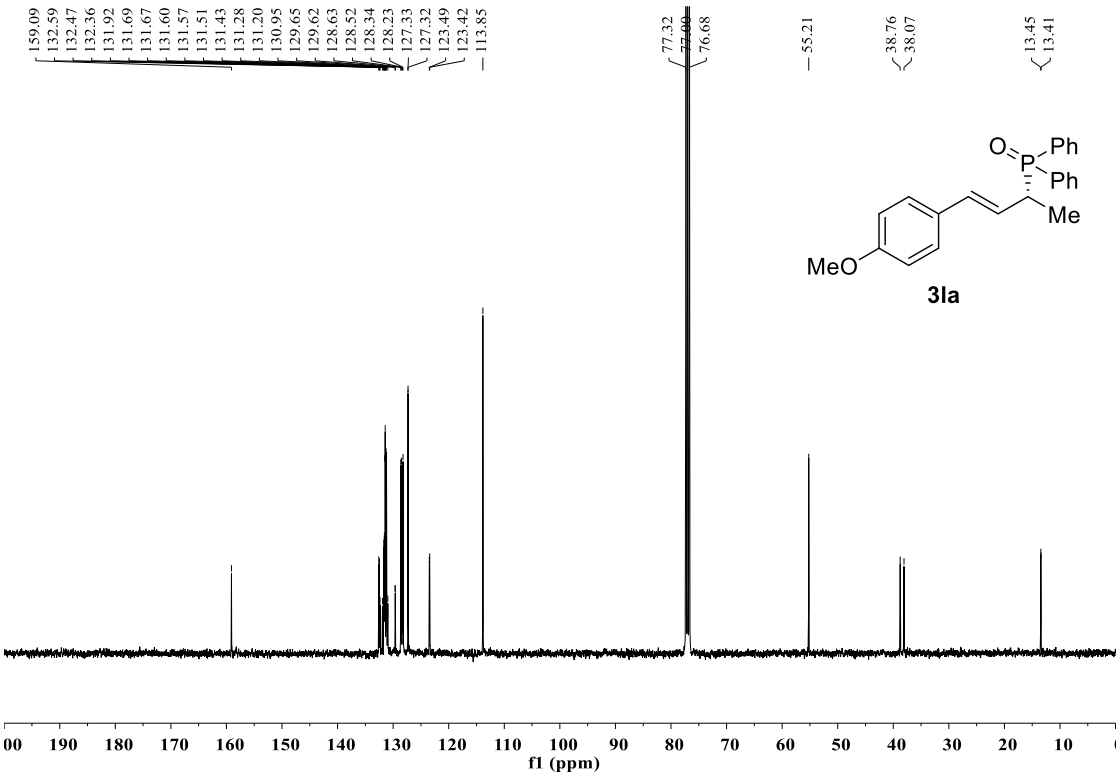

Figure S47. ^{13}C NMR spectra of **3la**.

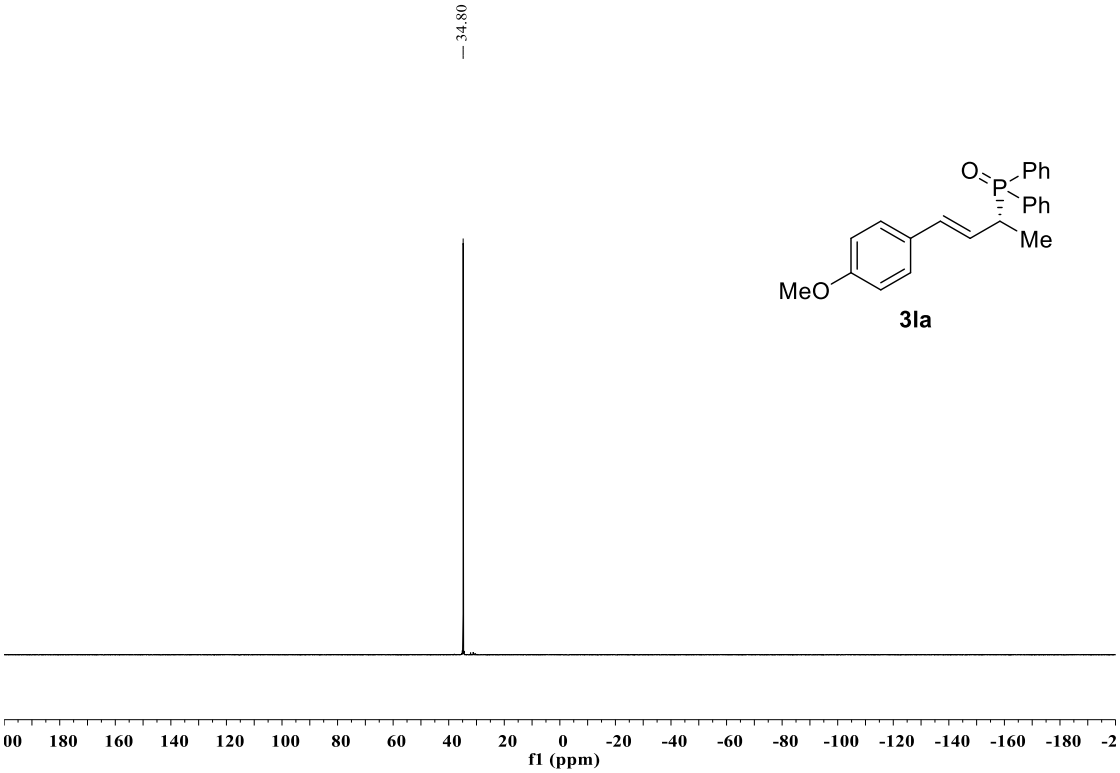

Figure S48. ^{31}P NMR spectra of **3la**.

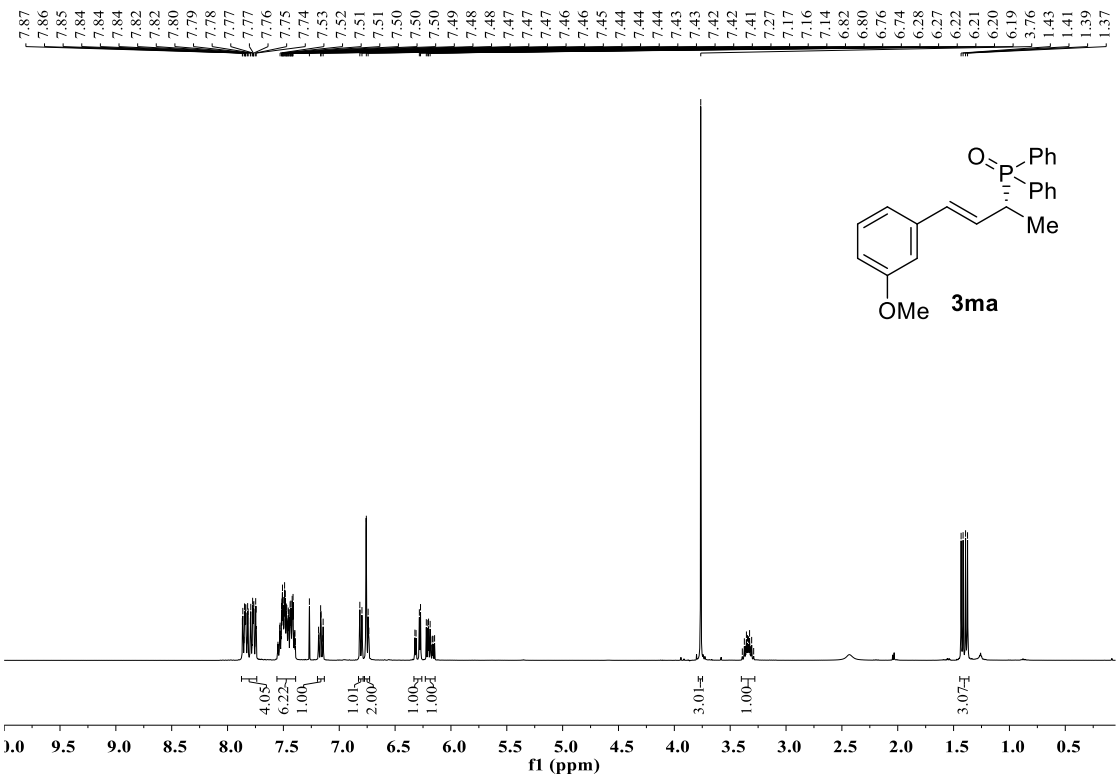

Figure S49. ^{1}H NMR spectra of **3ma**.

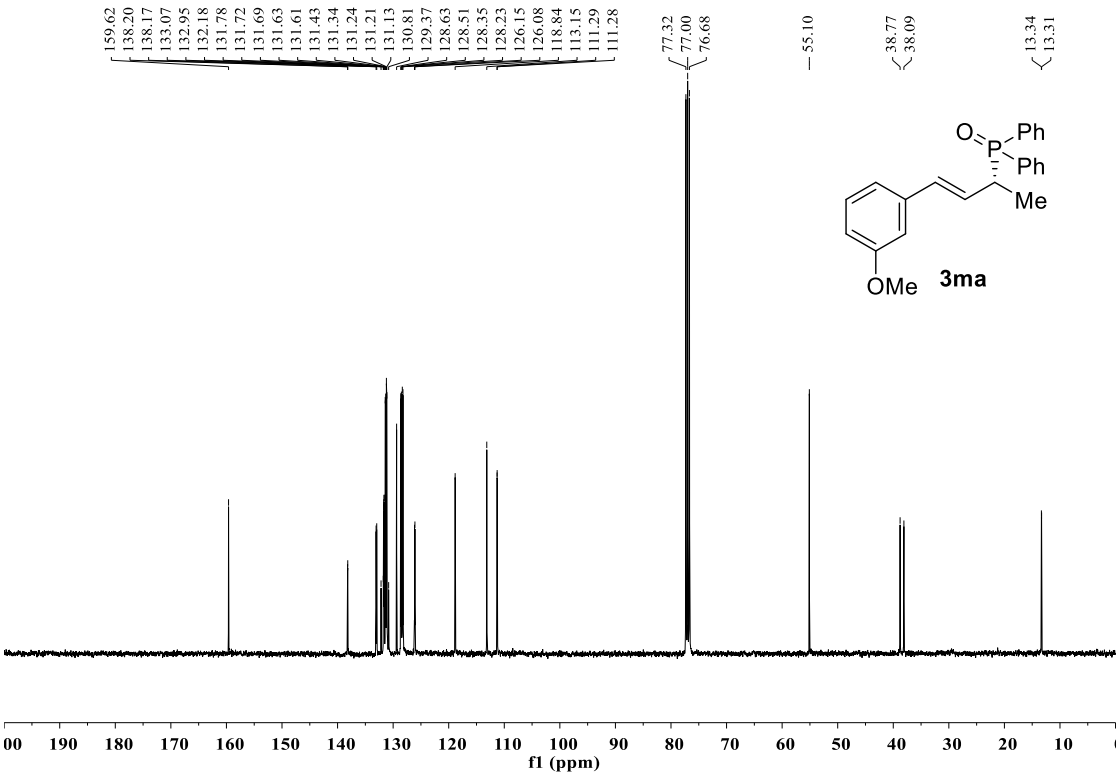

Figure S50. ^{13}C NMR spectra of **3ma**.

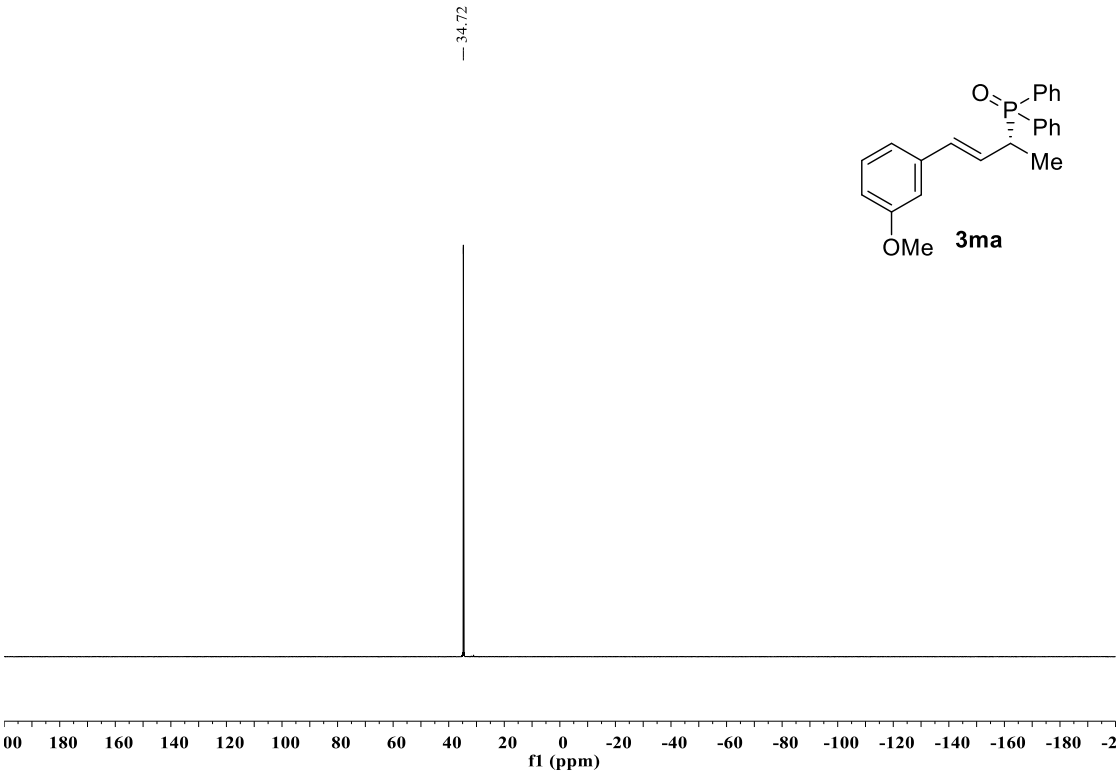

Figure S51. ^{31}P NMR spectra of **3ma**.

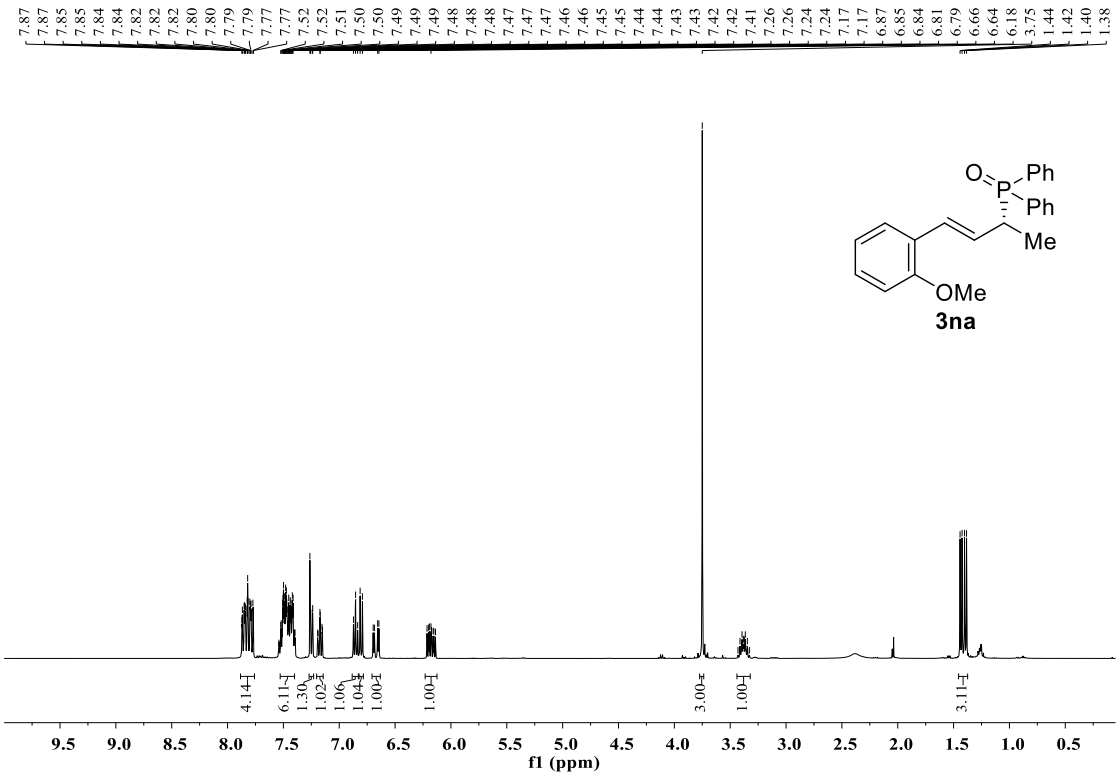

Figure S52. ^{1}H NMR spectra of **3na**.

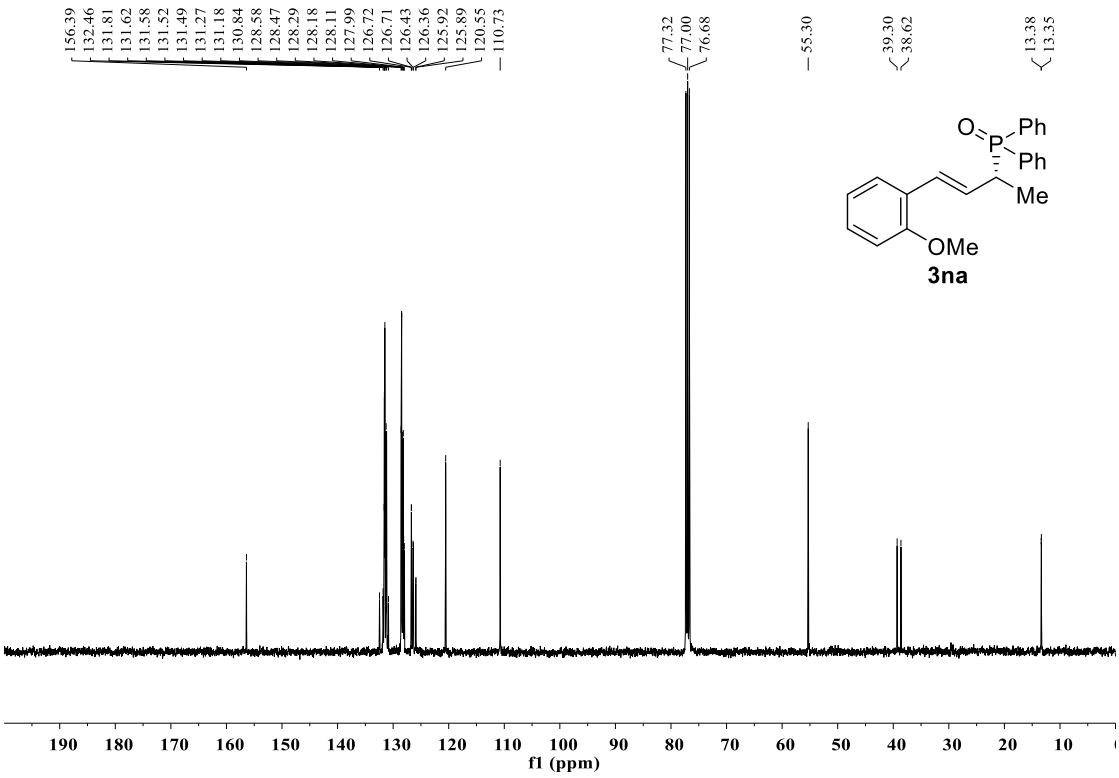

Figure S53. ^{13}C NMR spectra of **3na**.

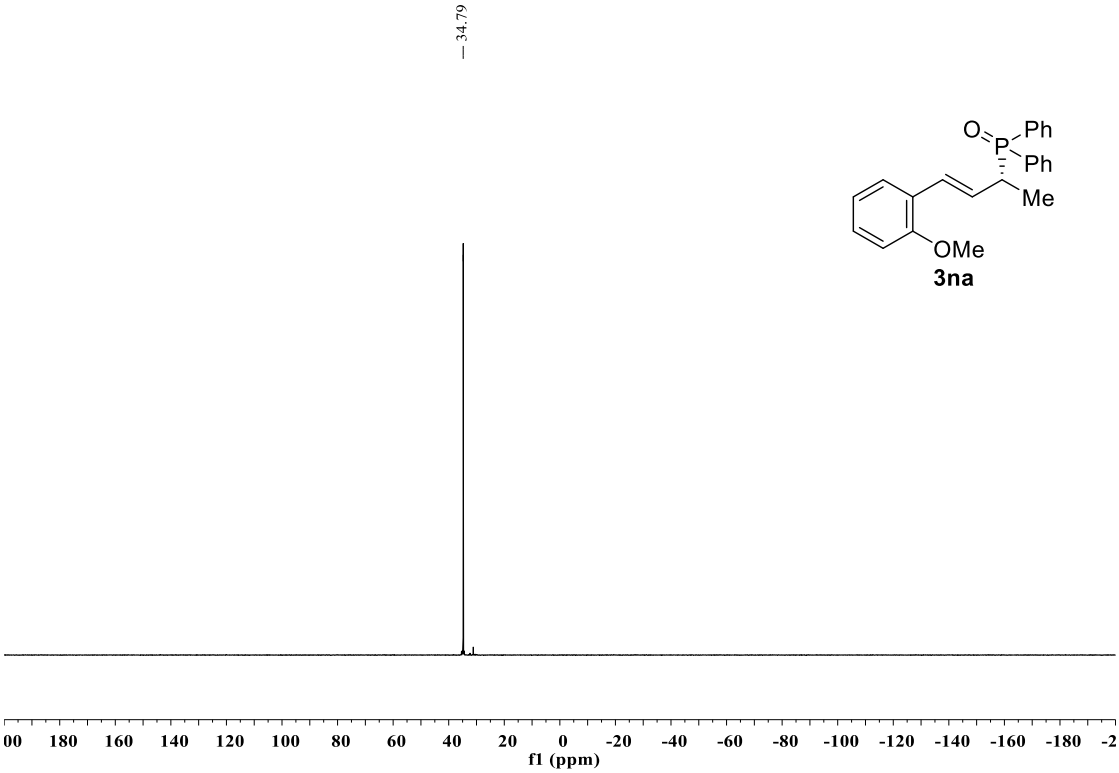

Figure S54. ^{31}P NMR spectra of **3na**.

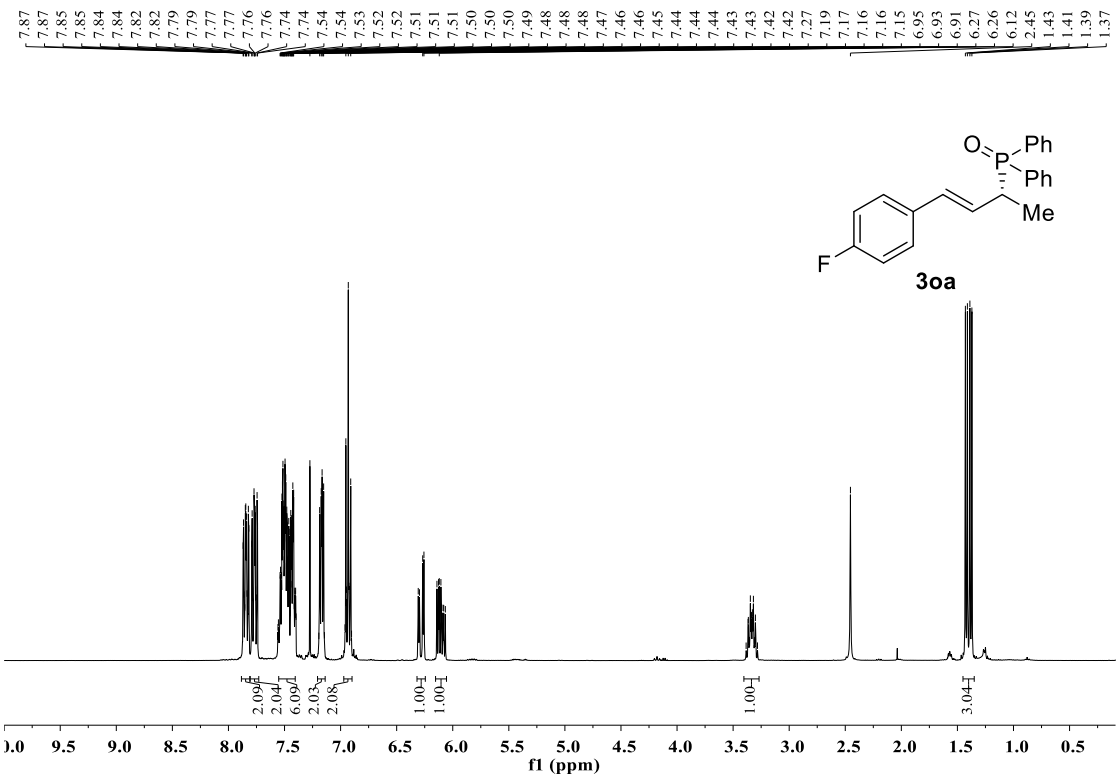

Figure S55. ^{1}H NMR spectra of **3oa**.

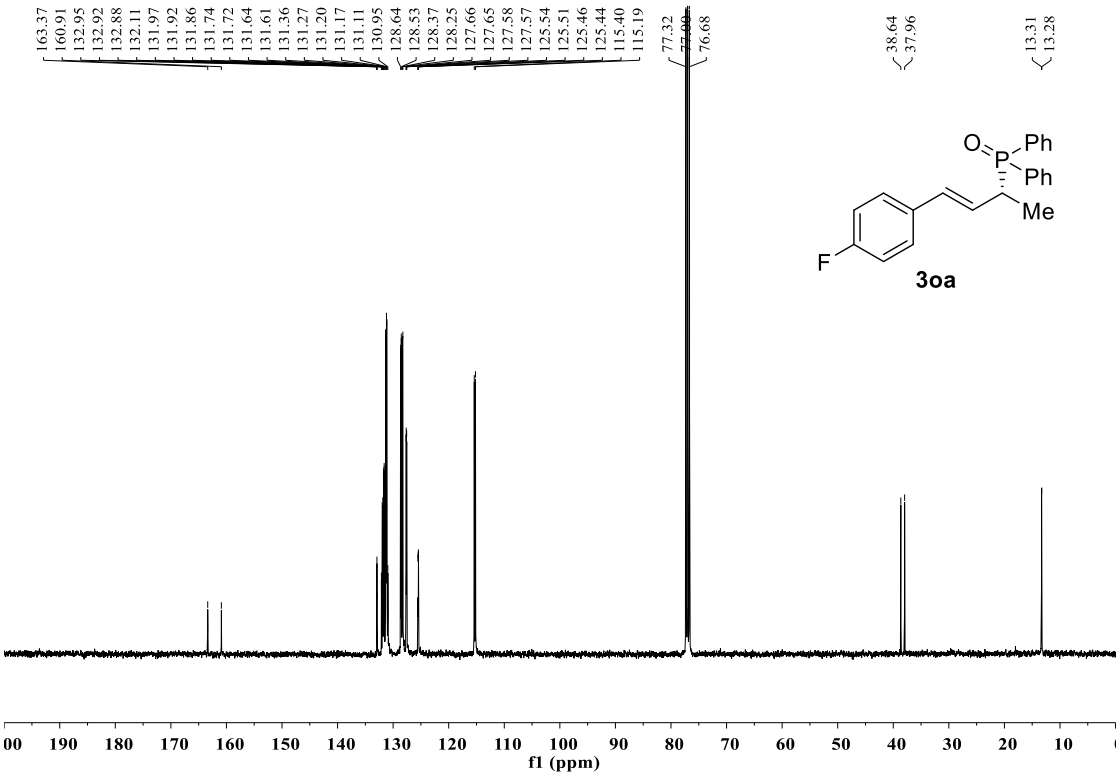

Figure S56. ^{13}C NMR spectra of **3oa**.

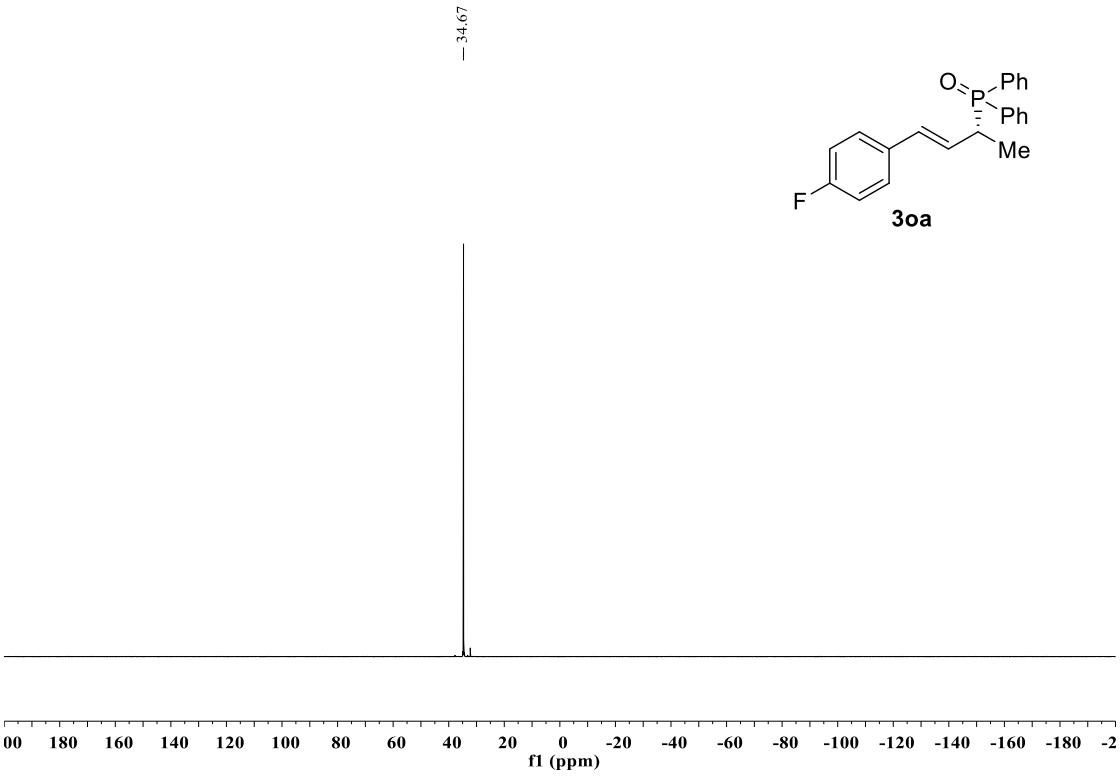

Figure S57. ^{31}P NMR spectra of **3oa**.

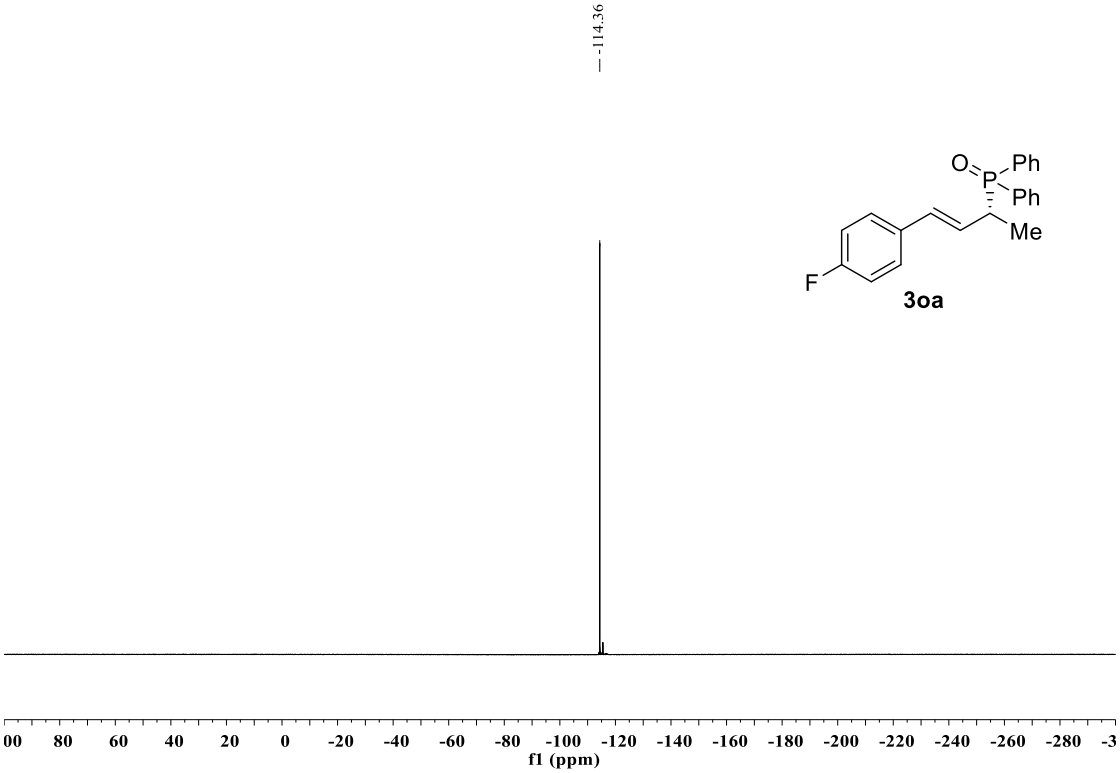

Figure S58. ^{19}F NMR spectra of **3oa**.

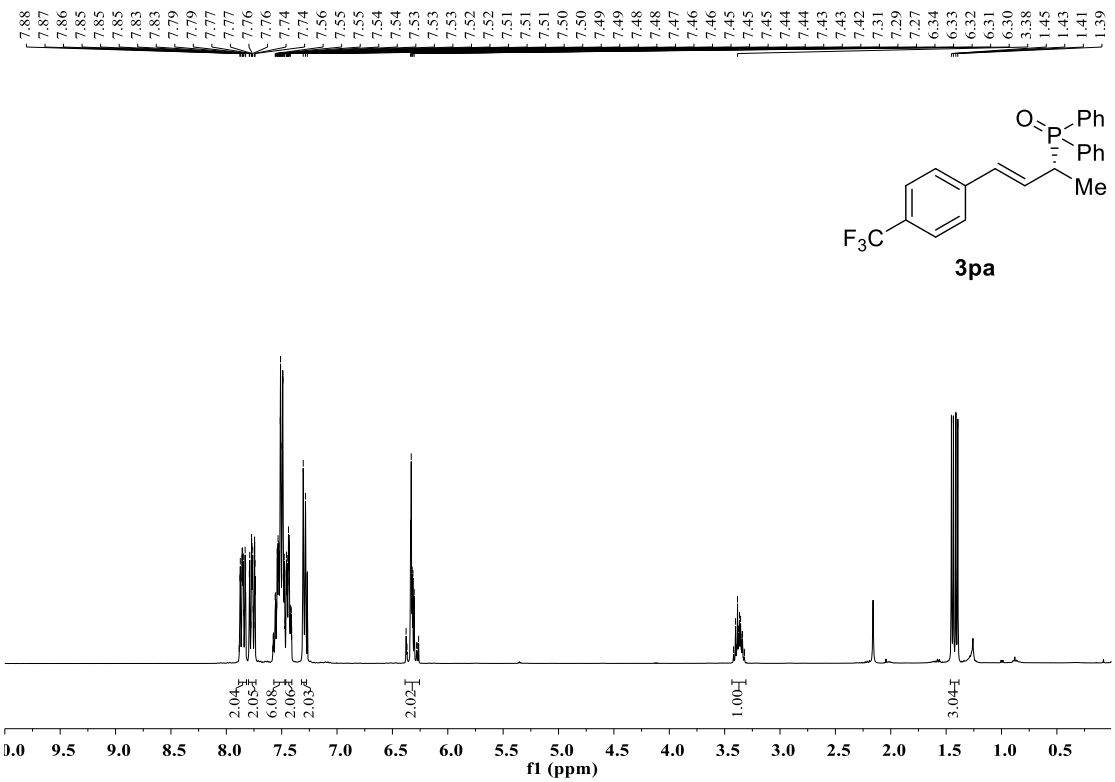

Figure S59. ^{1}H NMR spectra of **3pa**.

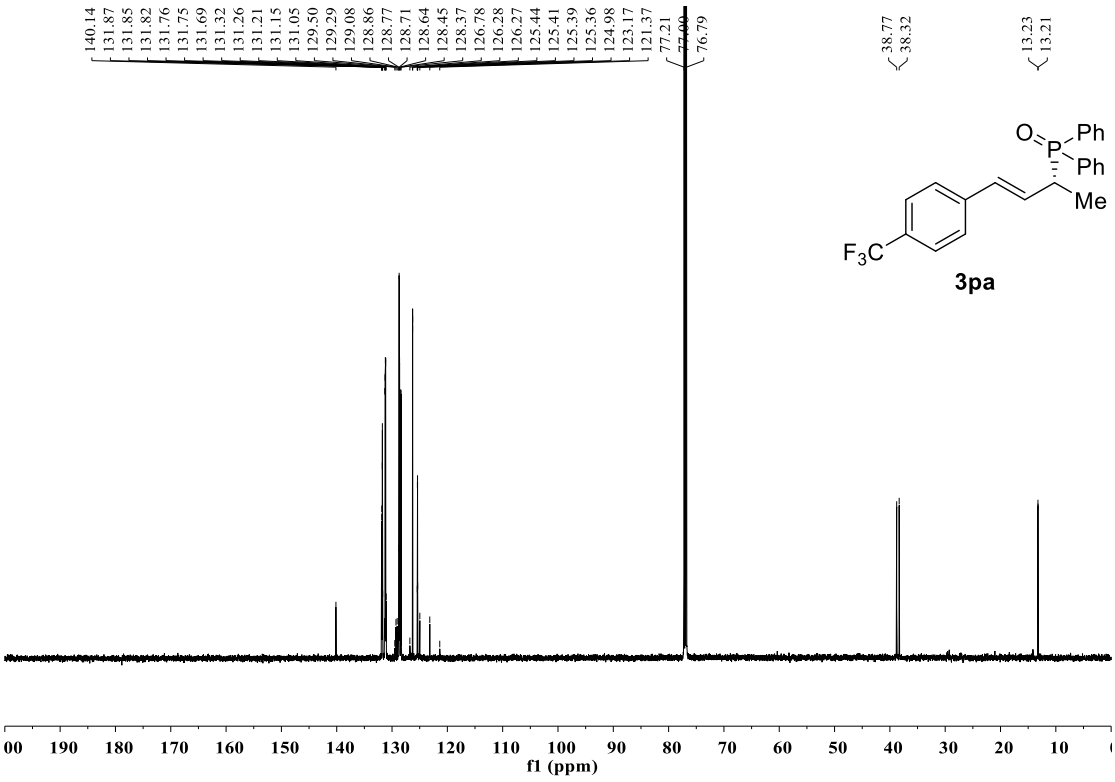

Figure S60. ^{13}C NMR spectra of **3pa**.

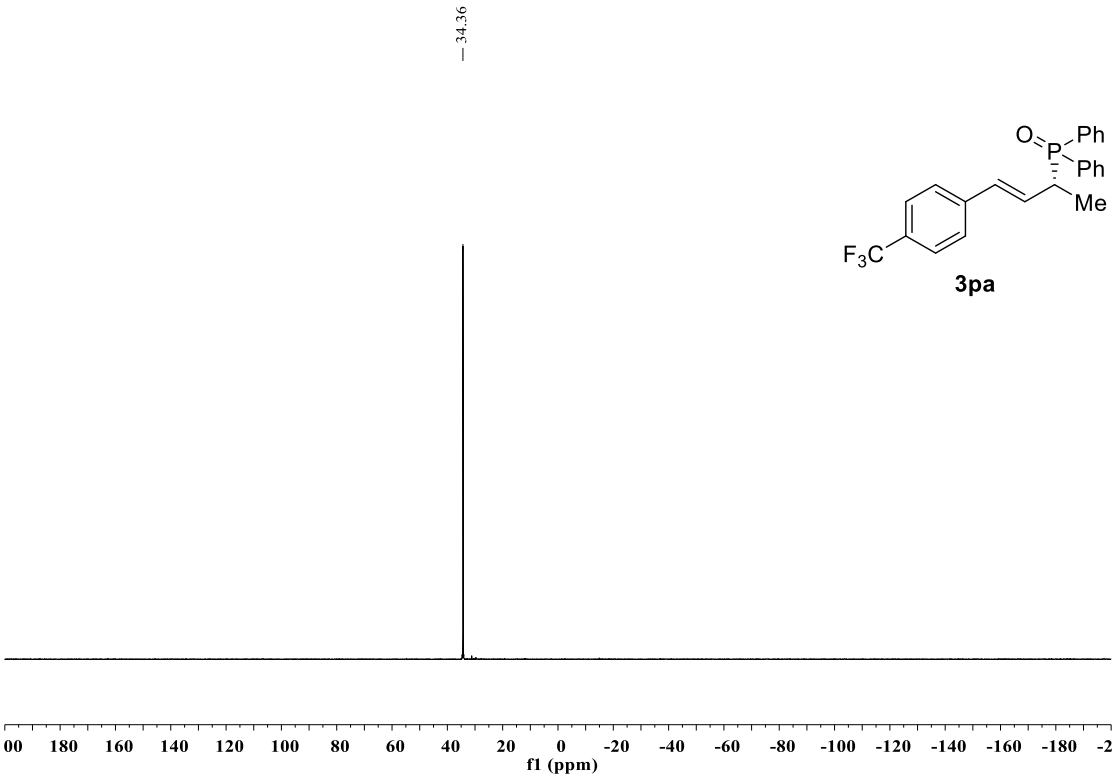

Figure S61. ^{31}P NMR spectra of **3pa**.

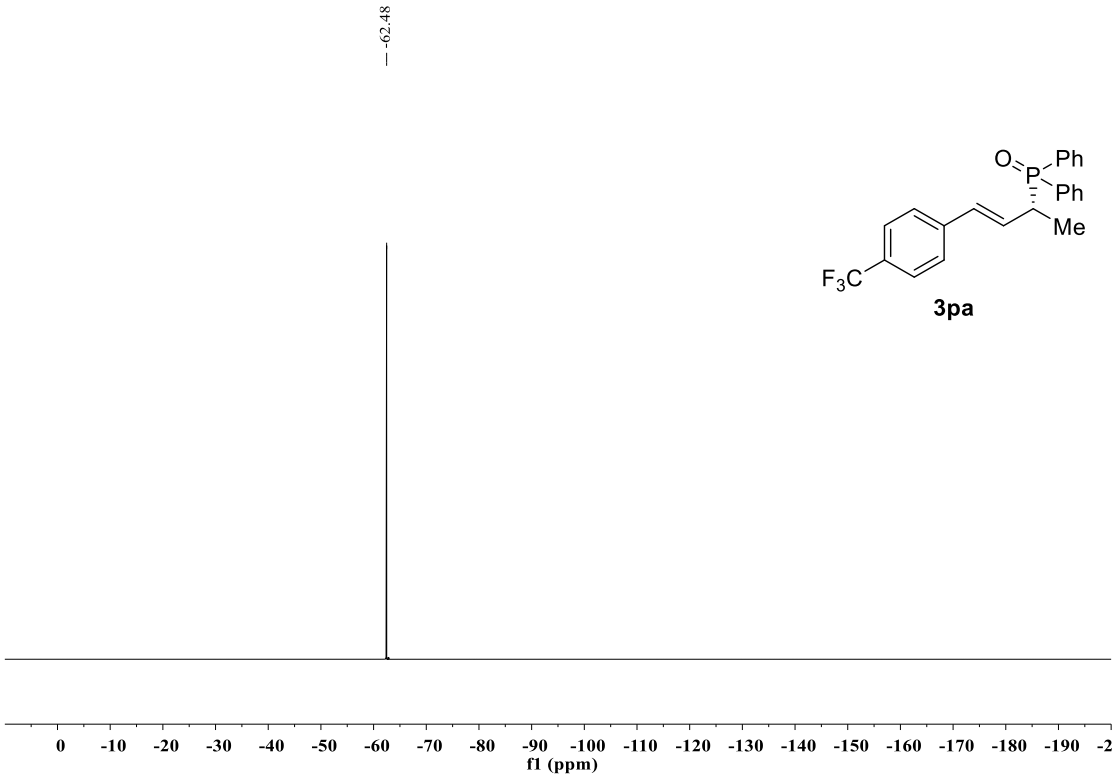

Figure S62. ^{19}F NMR spectra of **3pa**.

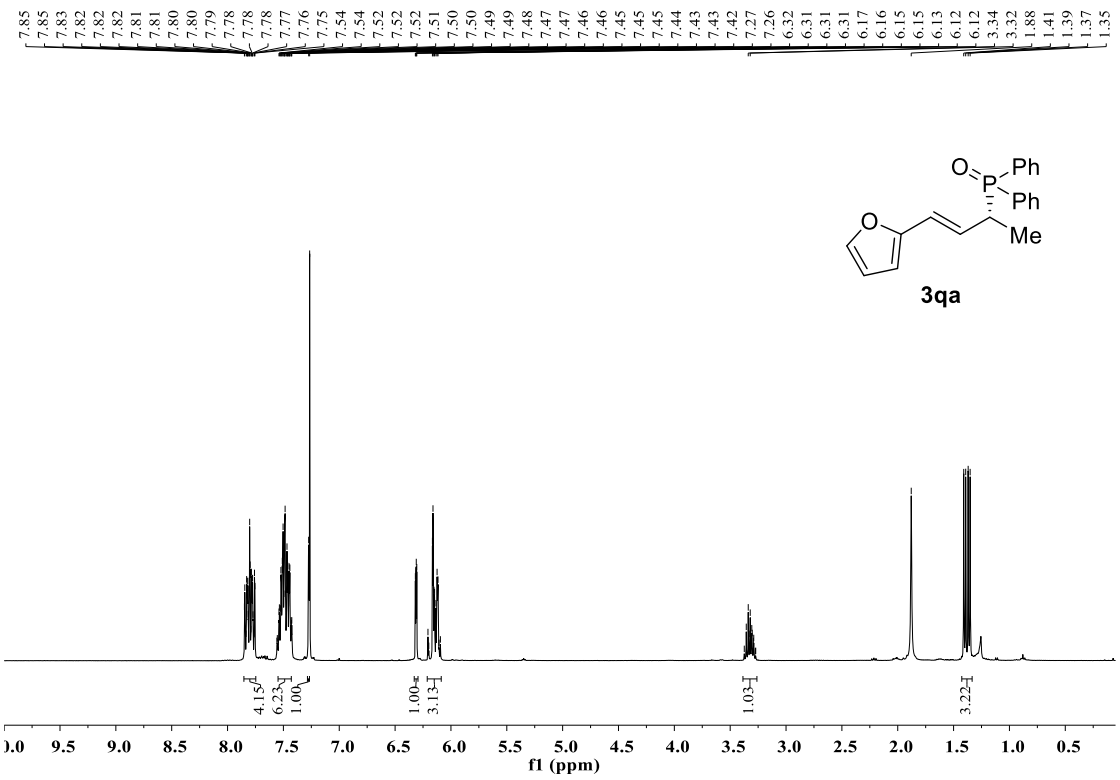

Figure S63. ^{1}H NMR spectra of **3qa**.

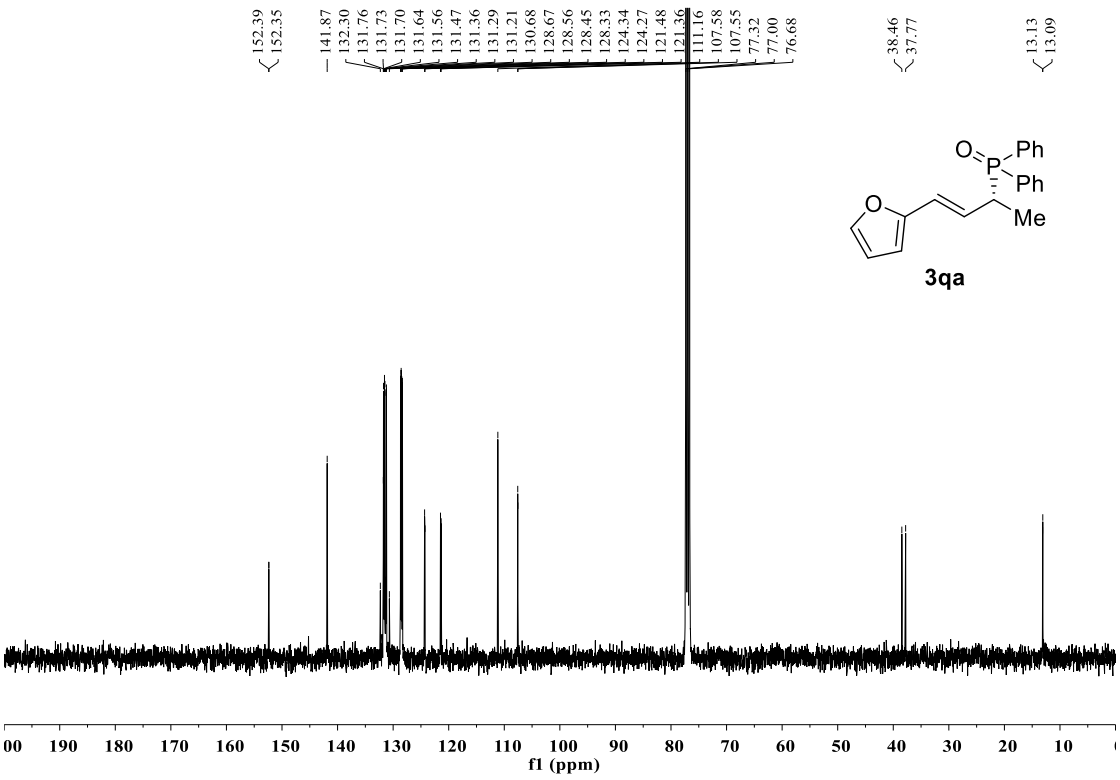

Figure S64. ^{13}C NMR spectra of **3qa**.

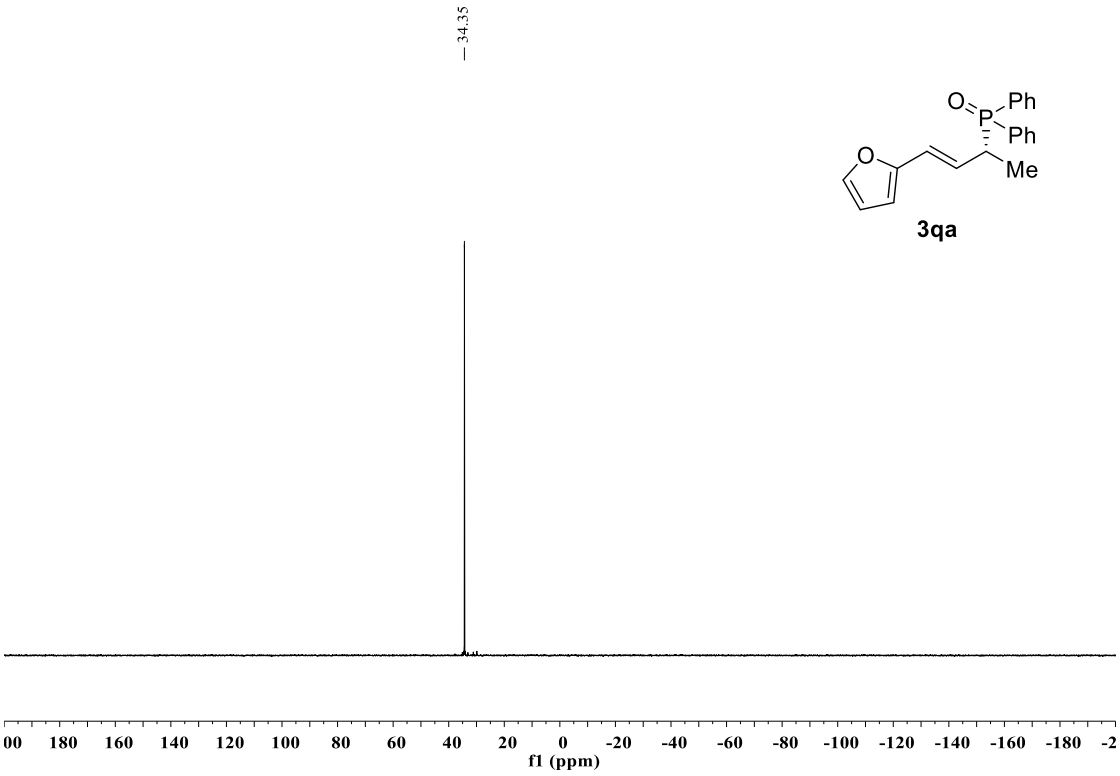

Figure S65. ^{31}P NMR spectra of **3qa**.

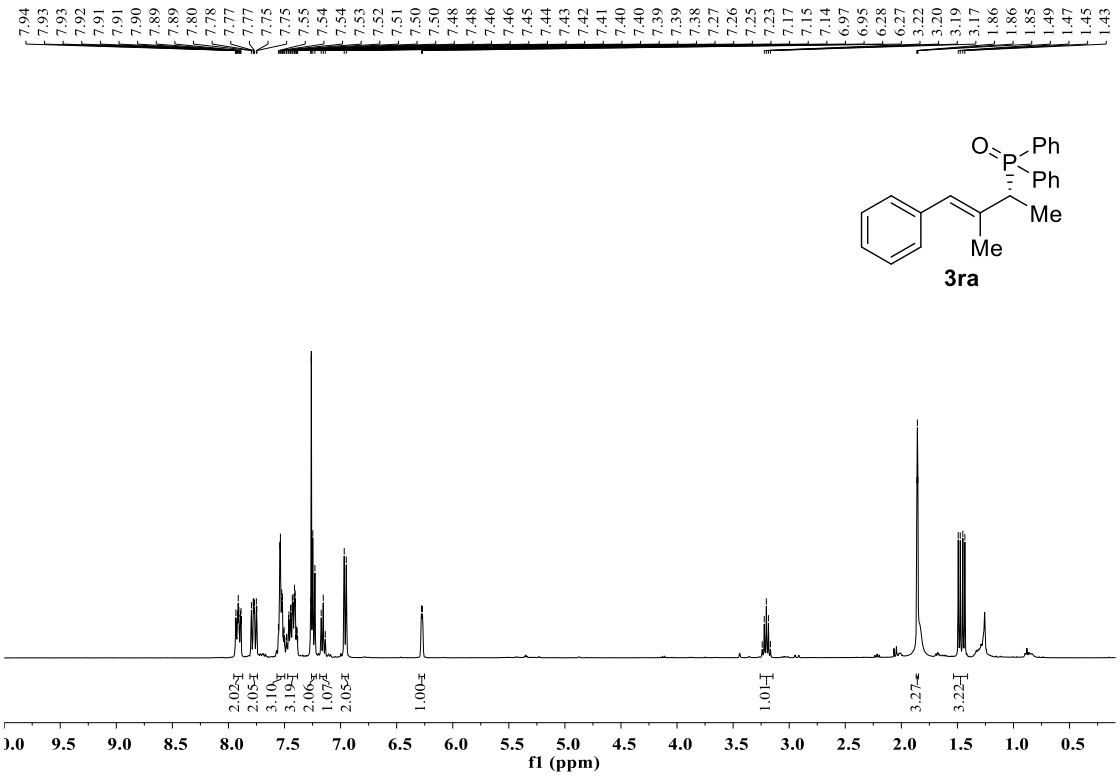

Figure S66. ^{1}H NMR spectra of **3ra**.

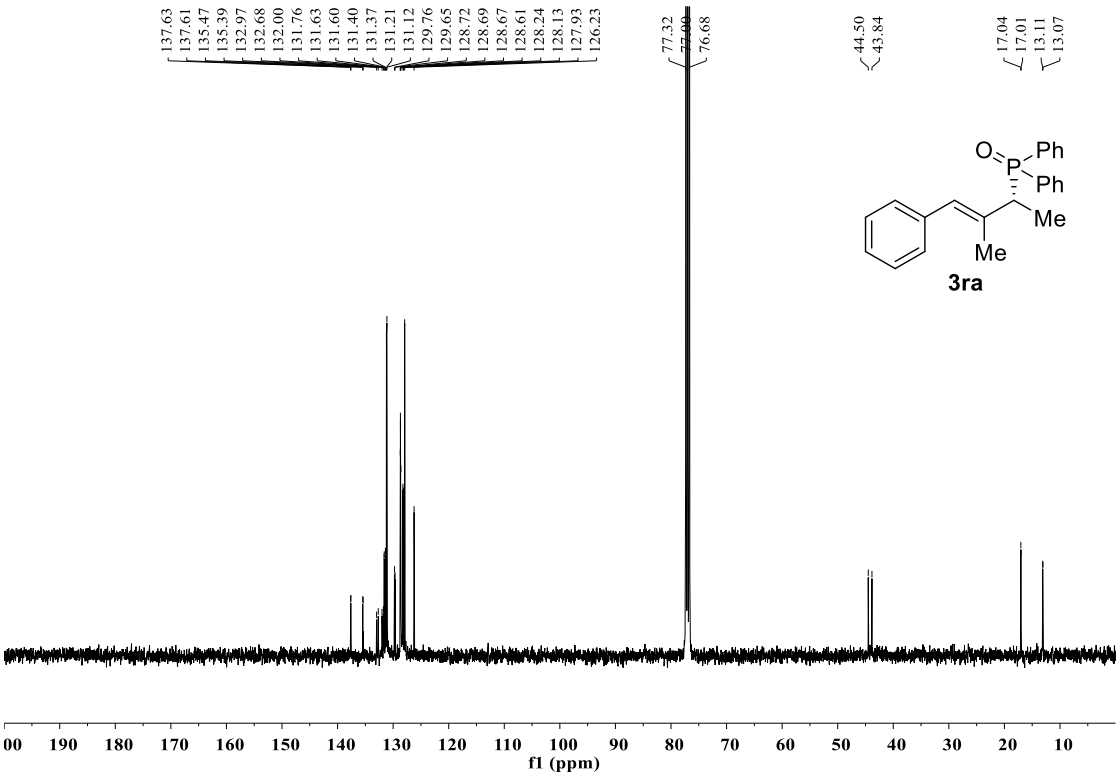

Figure S67. ^{13}C NMR spectra of **3ra**.

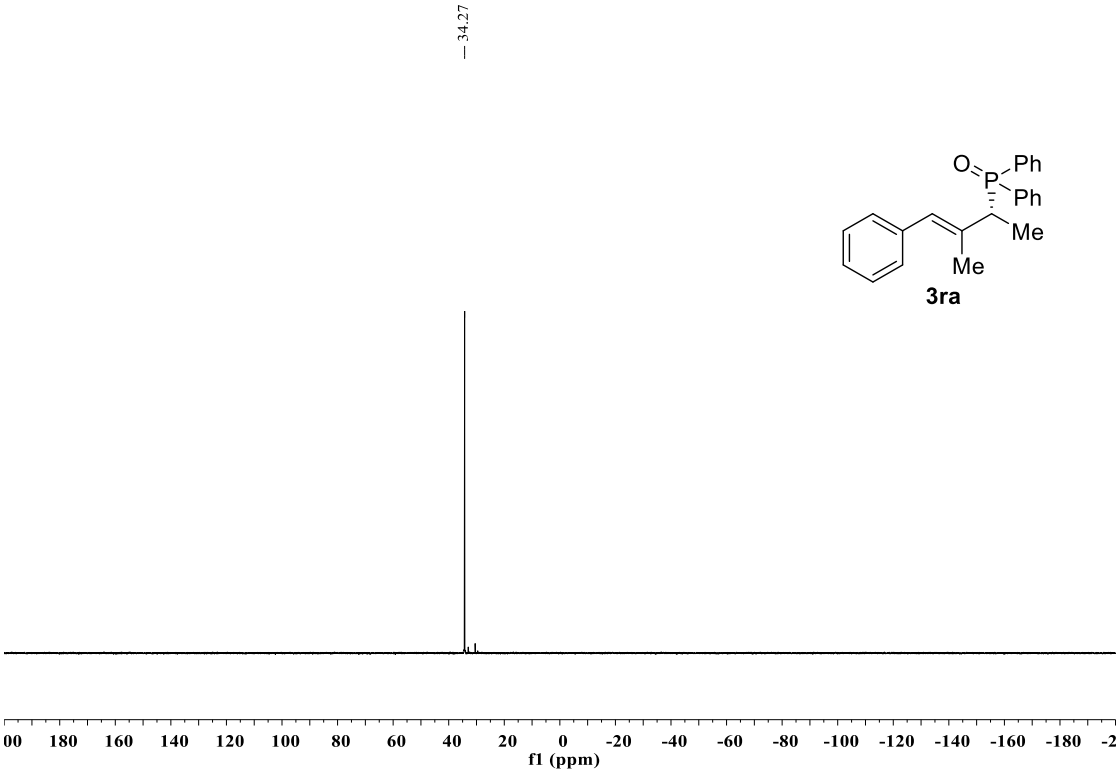

Figure S68. ^{31}P NMR spectra of **3ra**.

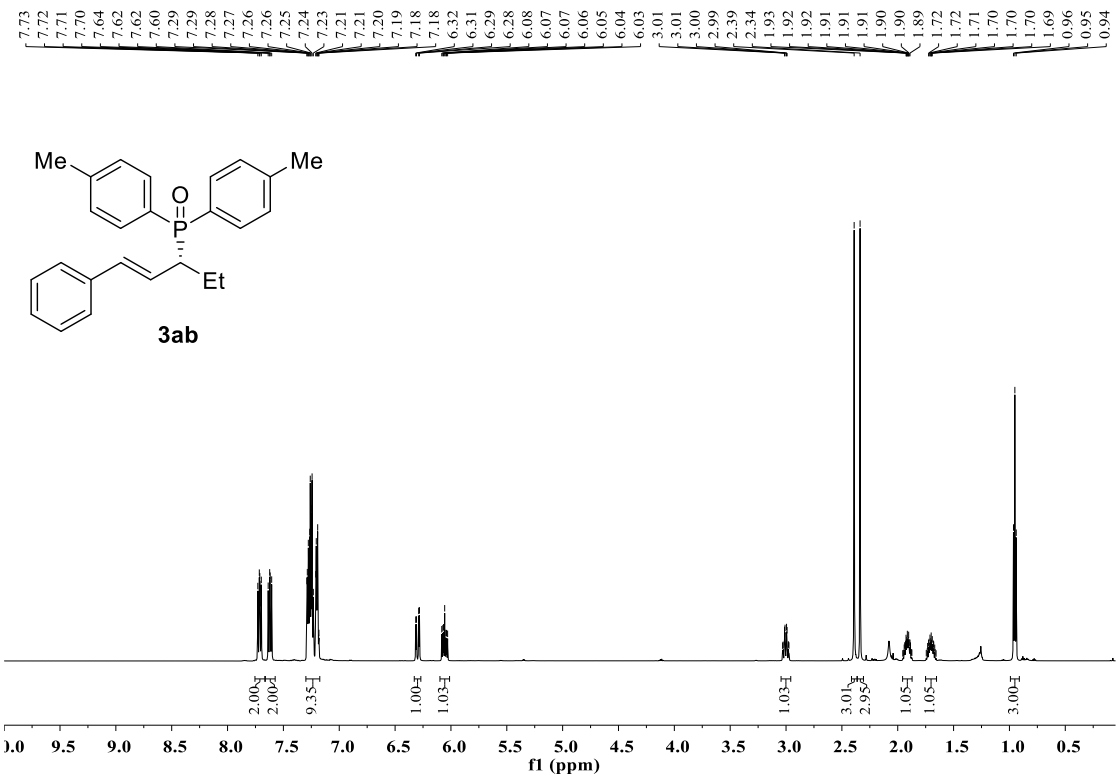

Figure S69. ^{1}H NMR spectra of **3ab**.

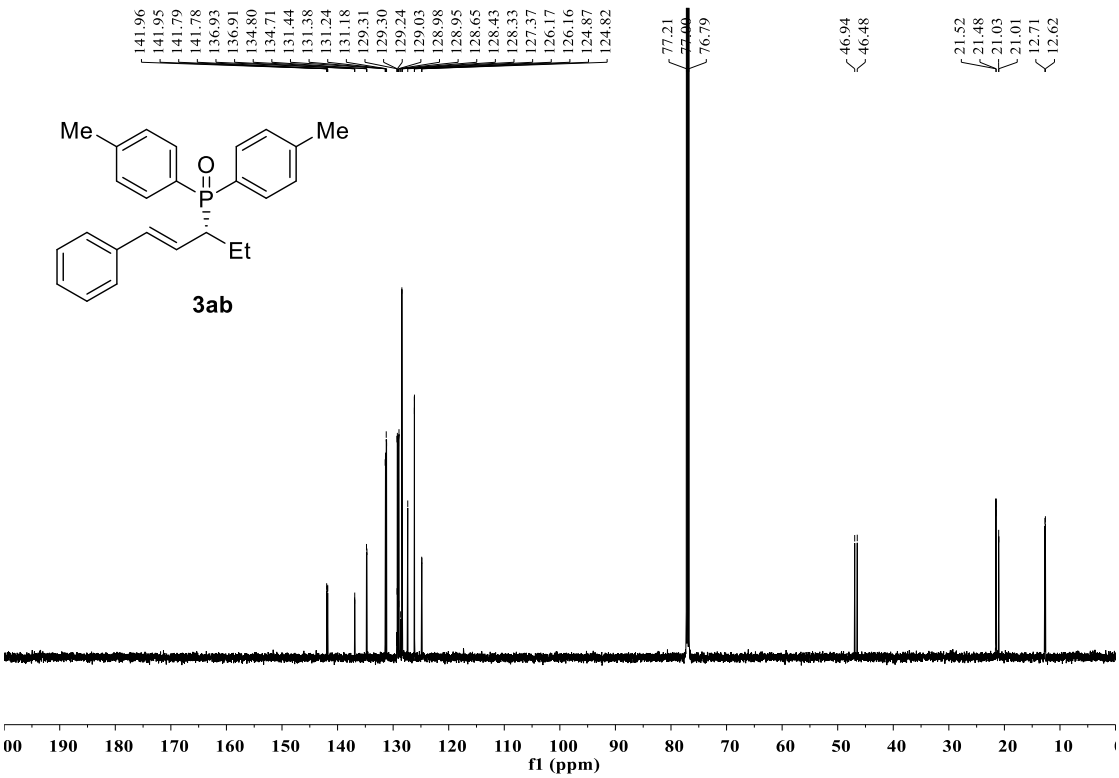

Figure S70. ^{13}C NMR spectra of **3ab**.

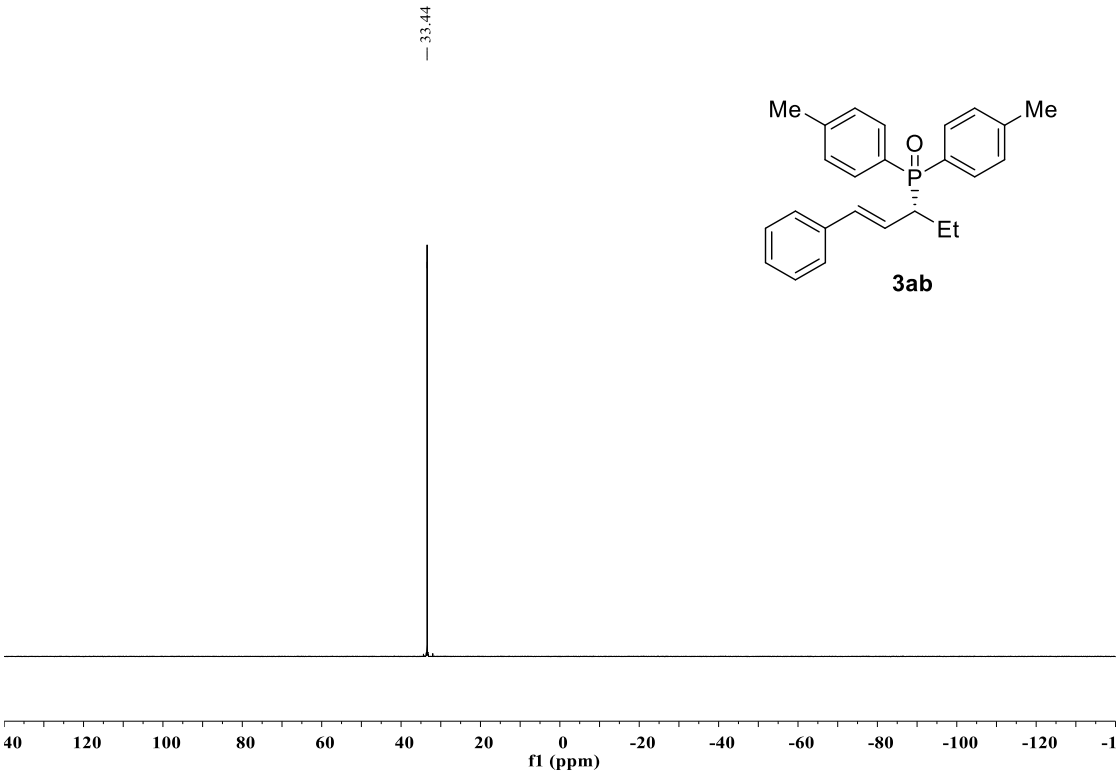

Figure S71. ^{31}P NMR spectra of **3ab**.

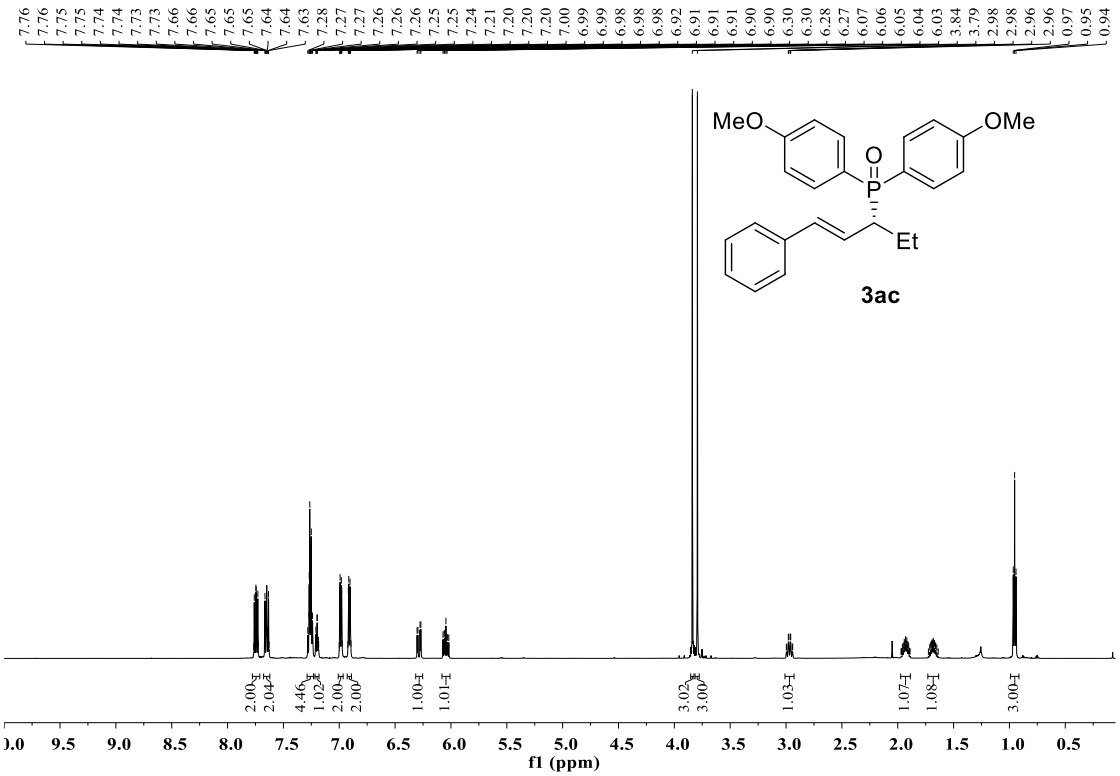

Figure S72. ^{1}H NMR spectra of **3ac**.

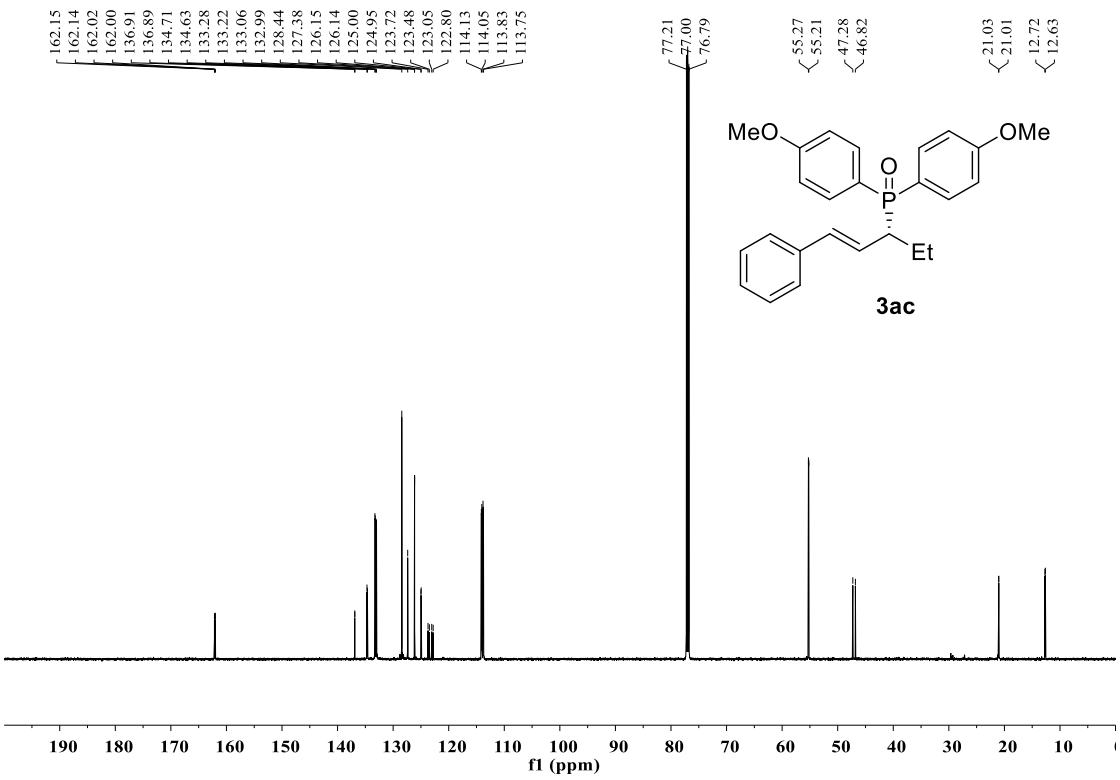

Figure S73. ^{13}C NMR spectra of **3ac**.

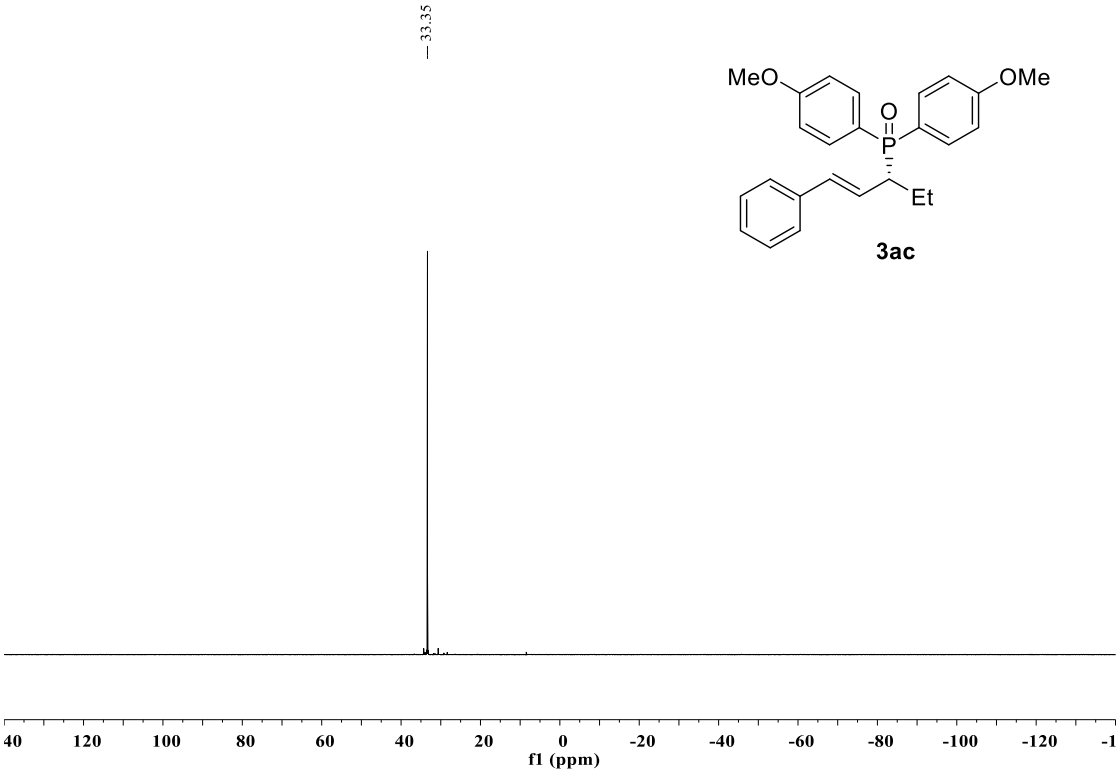

Figure S74. ^{13}P NMR spectra of **3ac**.

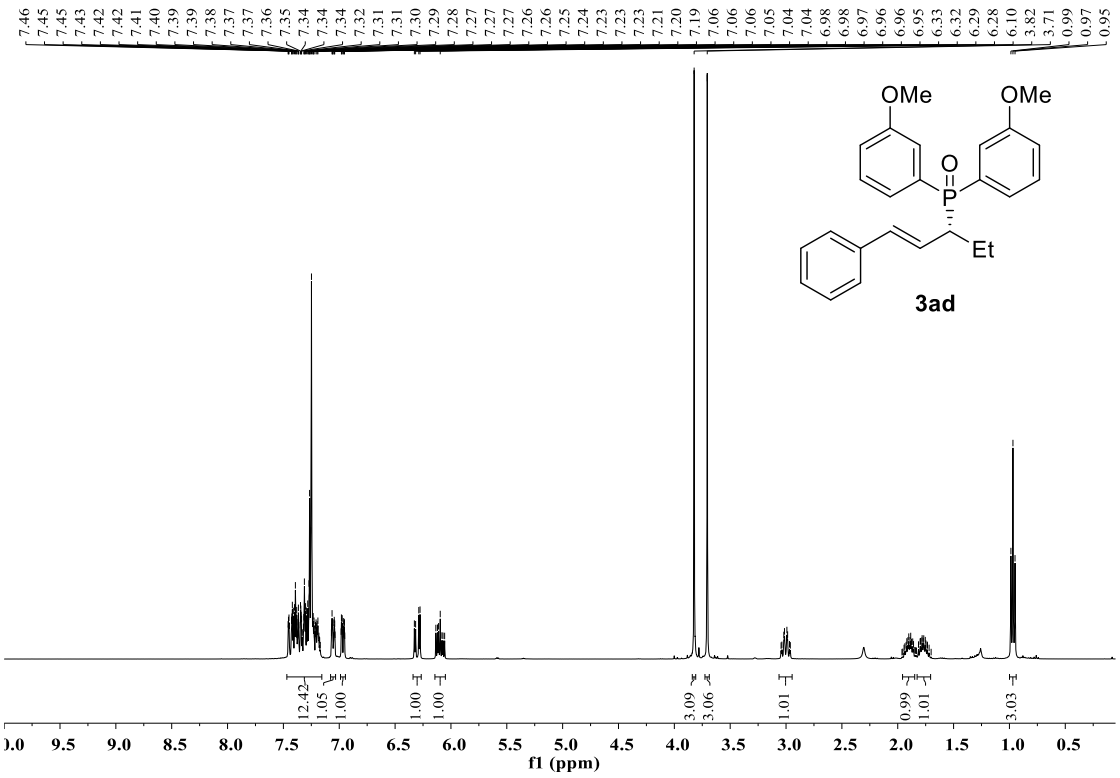

Figure S75. ^{1}H NMR spectra of **3ad**.

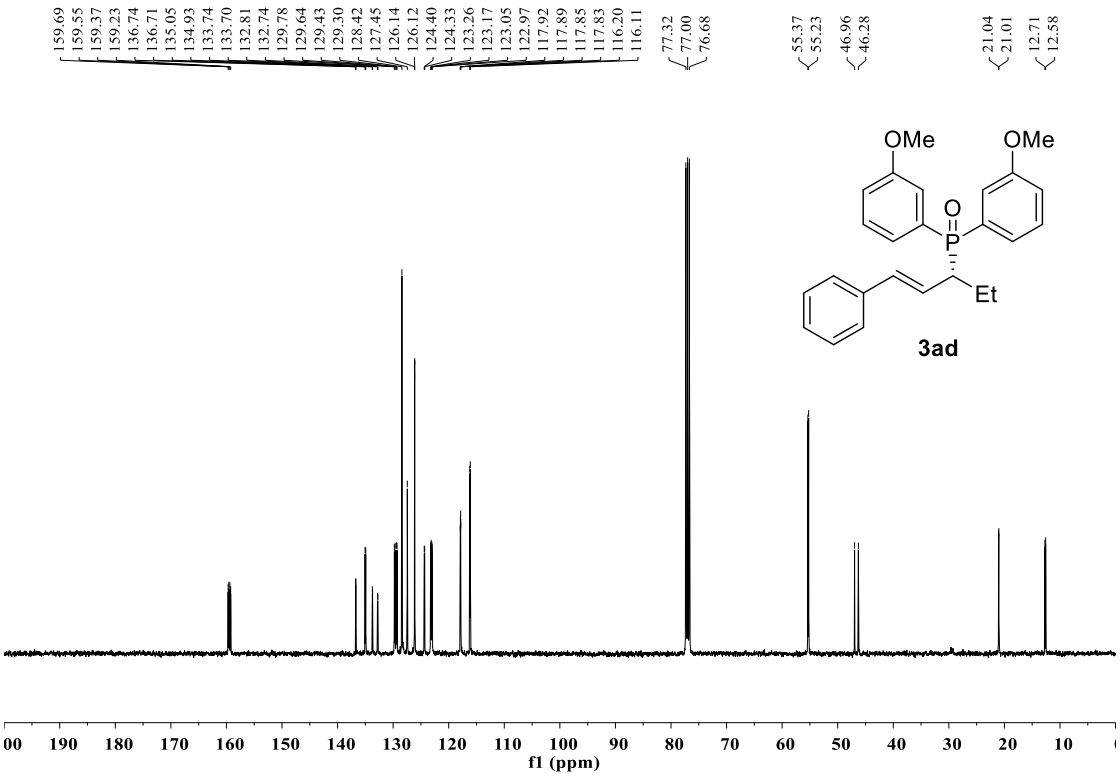

Figure S76. ^{13}C NMR spectra of **3ad**.

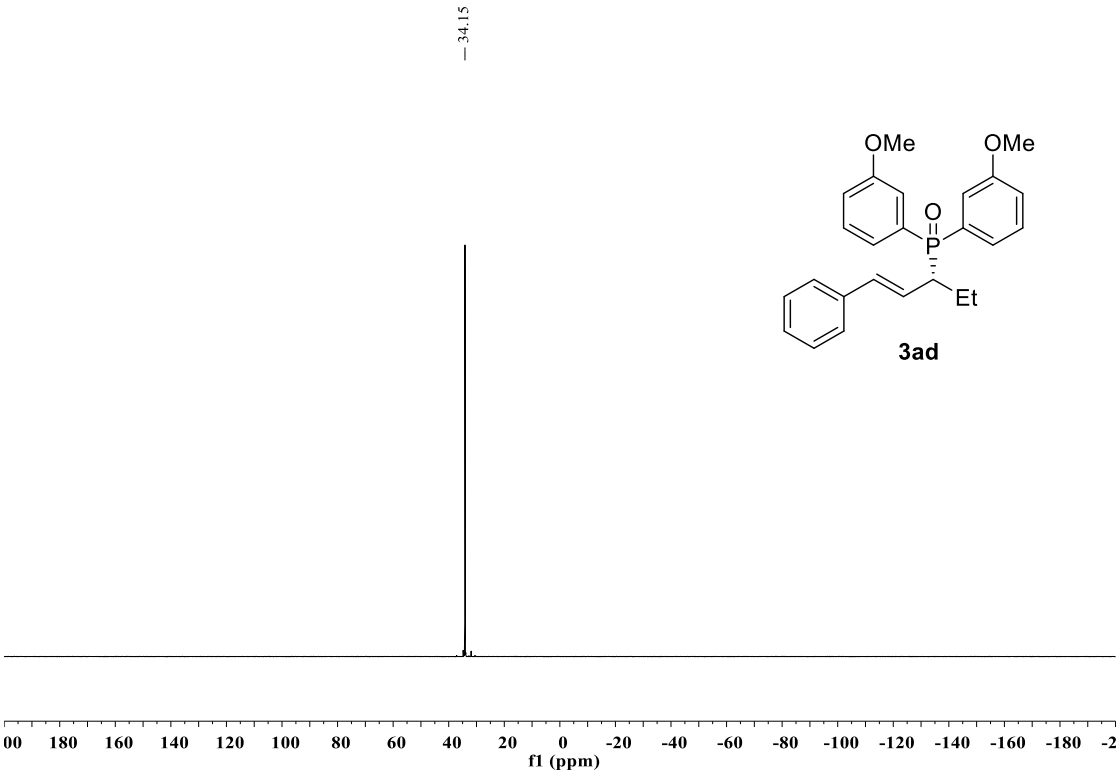

Figure S77. ^{31}P NMR spectra of **3ad**.

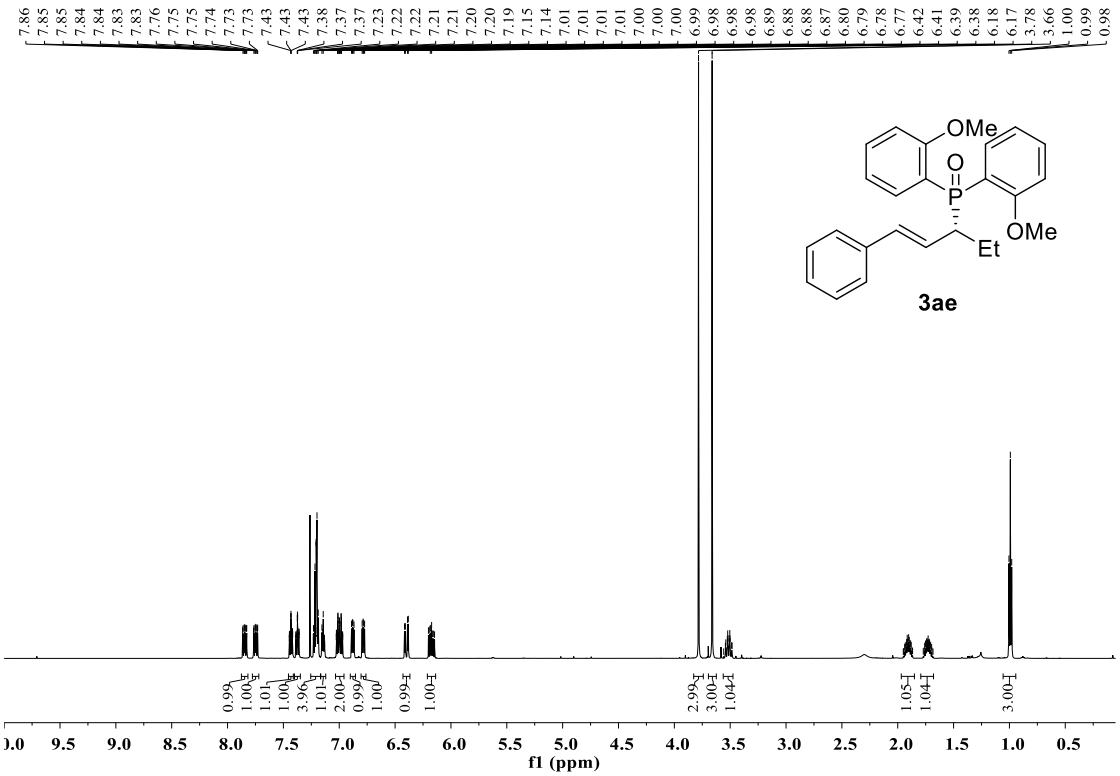

Figure S78. ^{1}H NMR spectra of **3ae**.

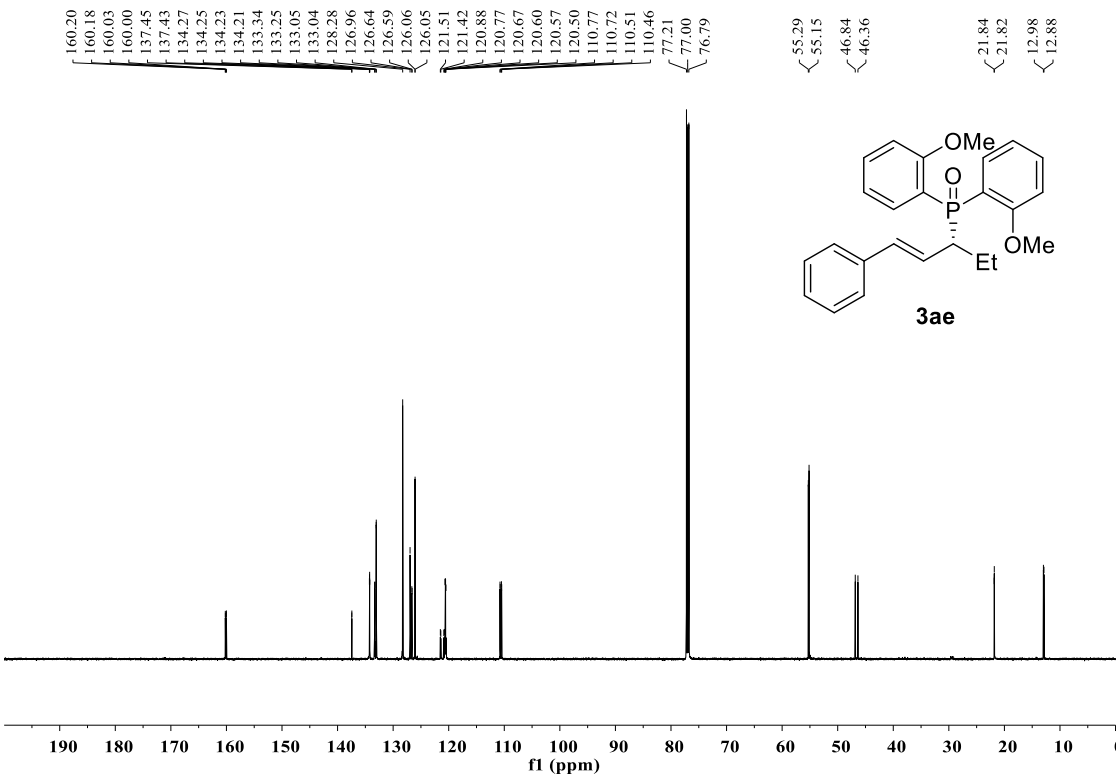

Figure S79. ^{13}C NMR spectra of **3ae**.

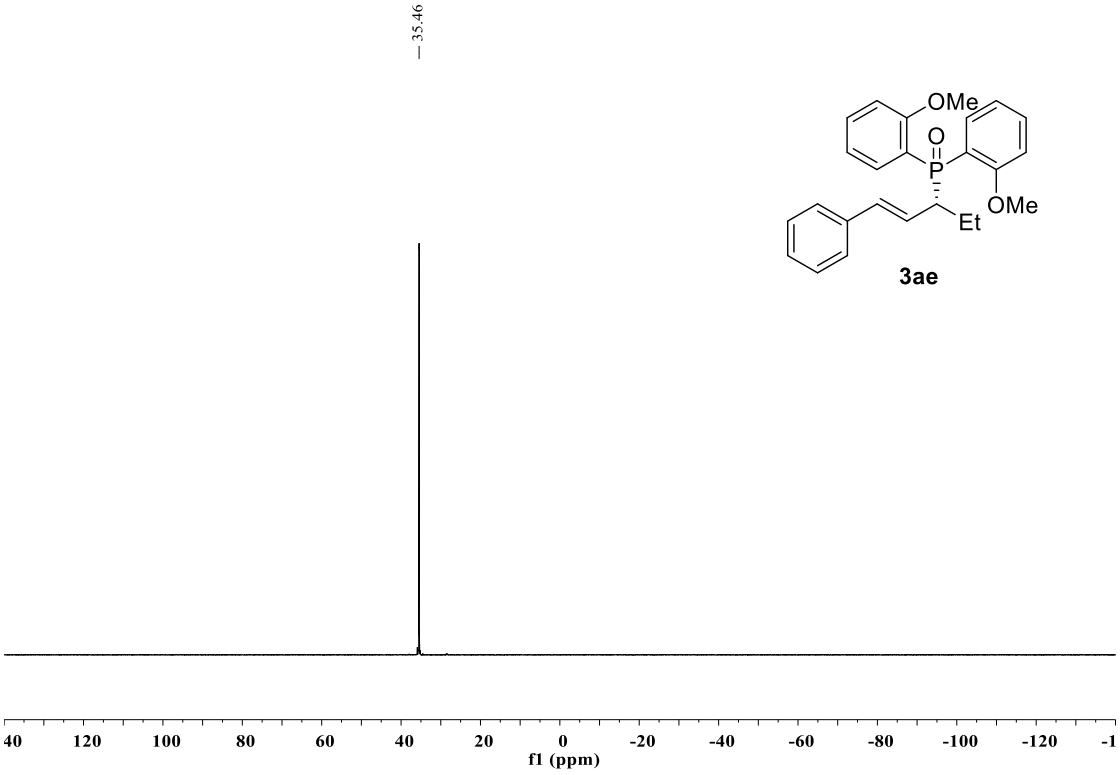

Figure S80. ^{31}P NMR spectra of **3ae**.

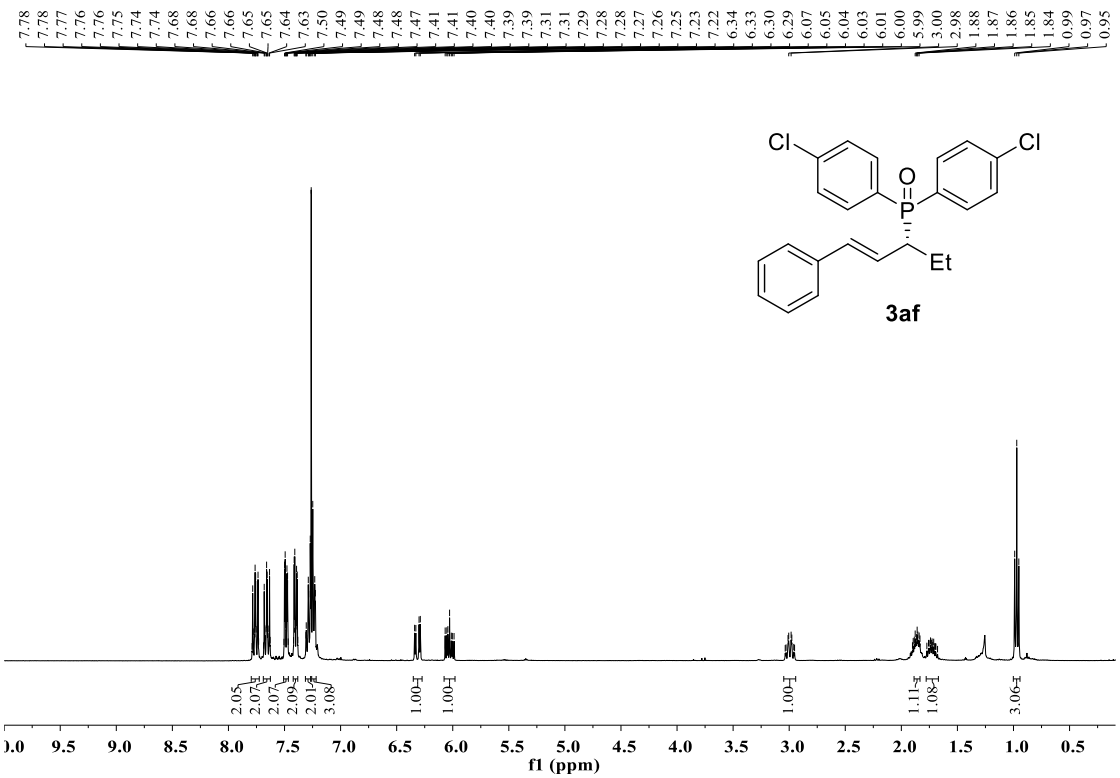

Figure S81. ^{1}H NMR spectra of **3af**.

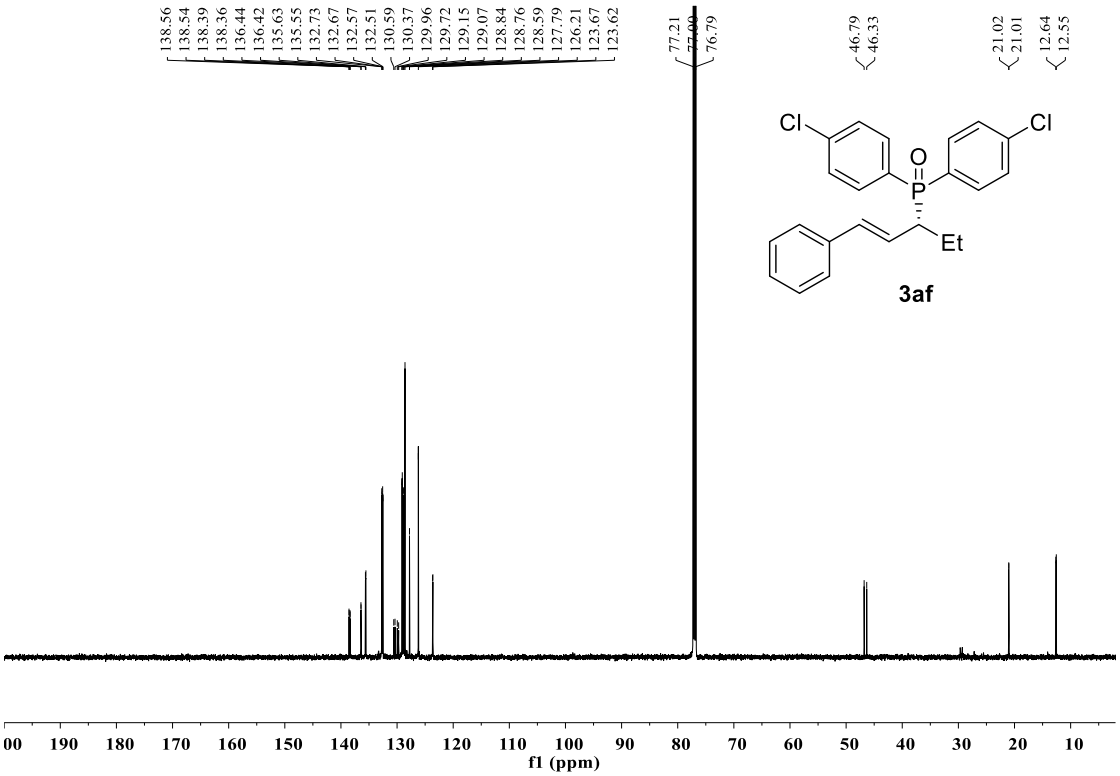

Figure S82. ^{13}C NMR spectra of **3af**.

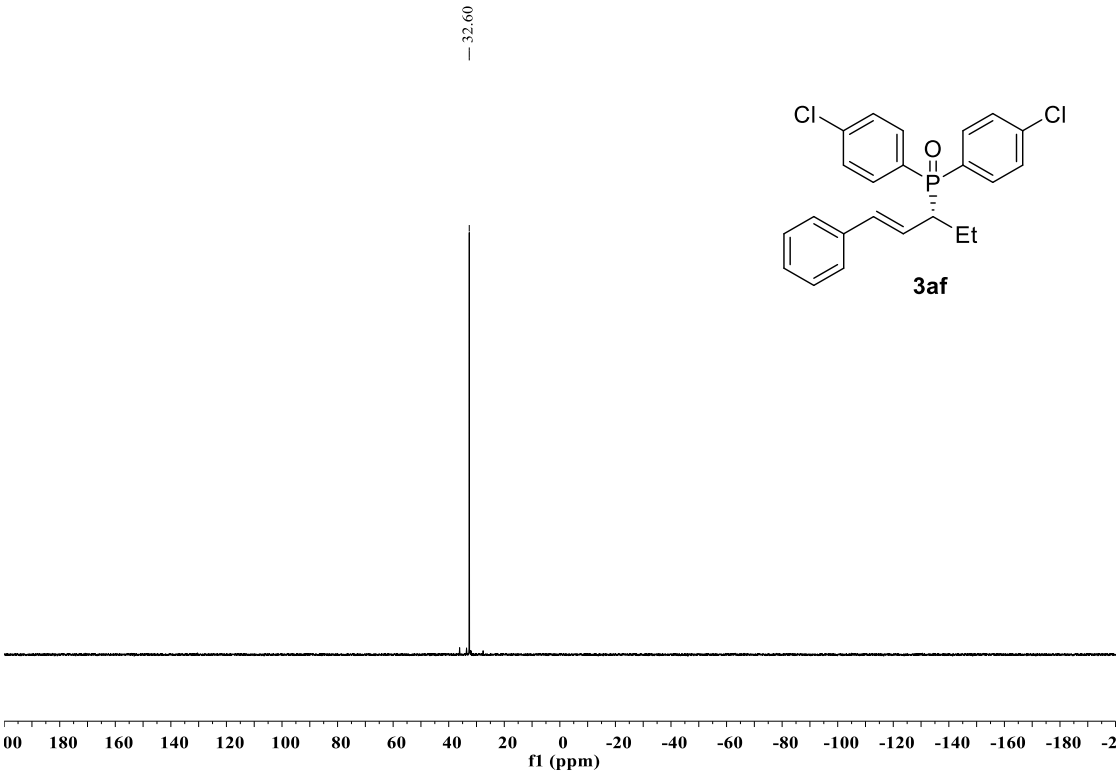

Figure S83. ^{31}P NMR spectra of **3af**.

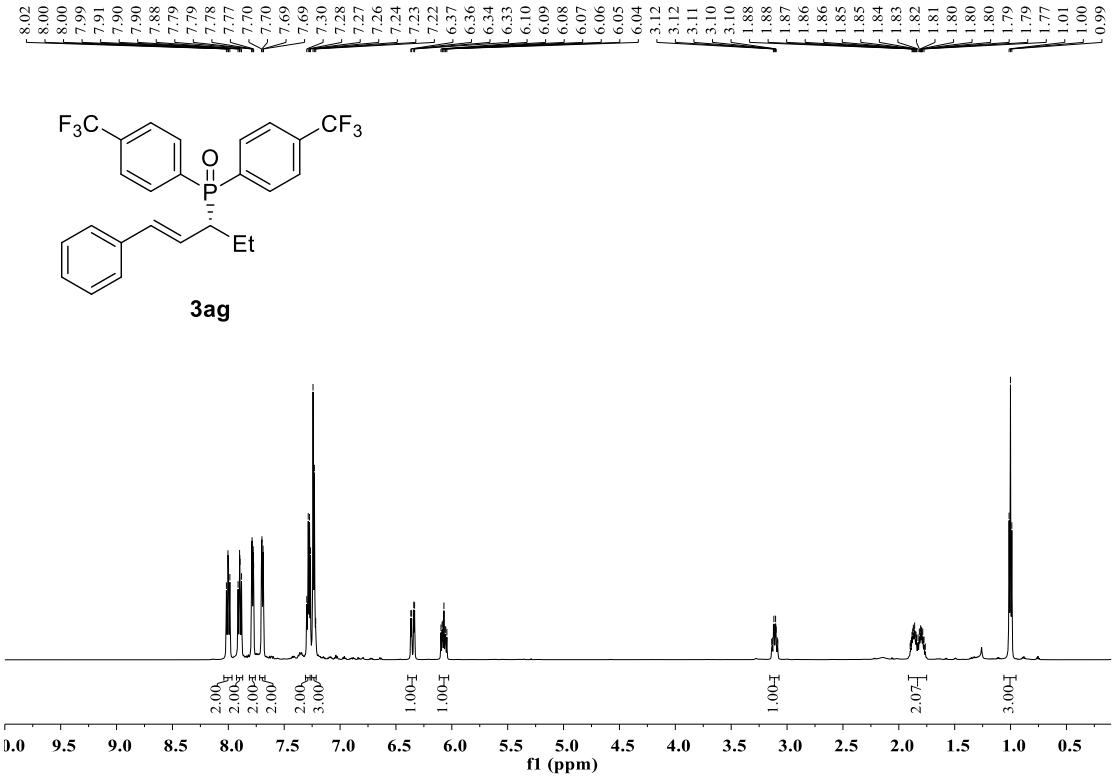

Figure S84. ^{1}H NMR spectra of **3ag**.

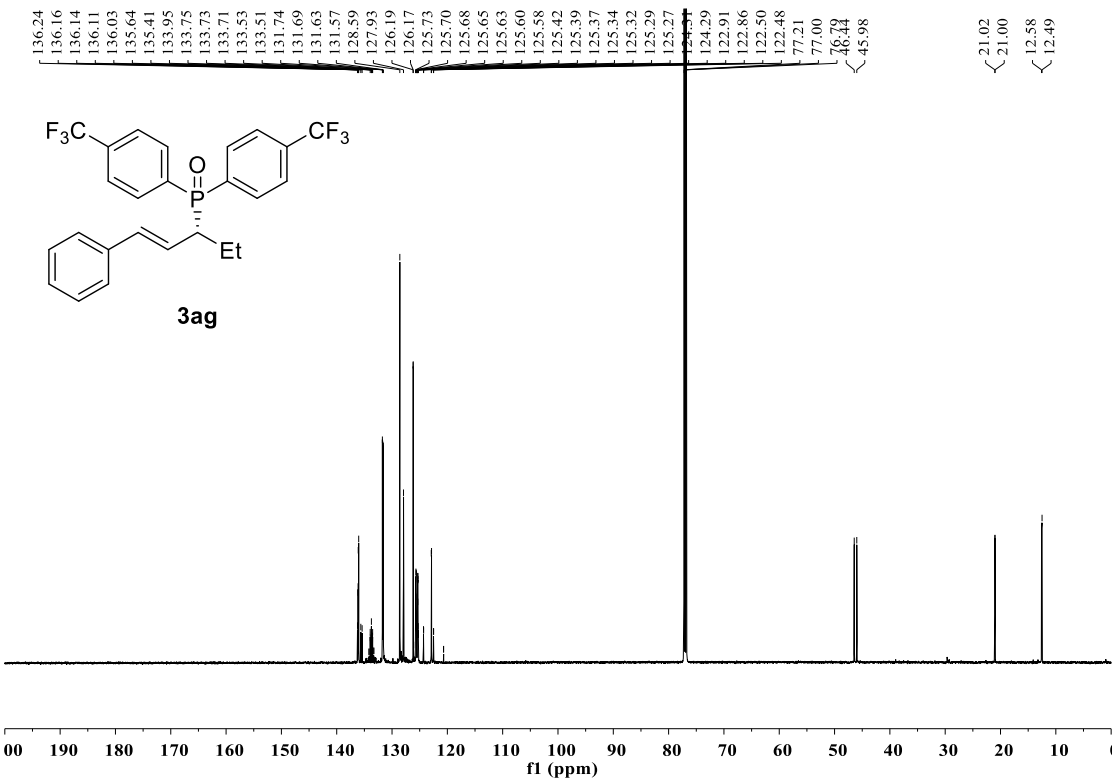

Figure S85. ^{13}C NMR spectra of **3ag**.

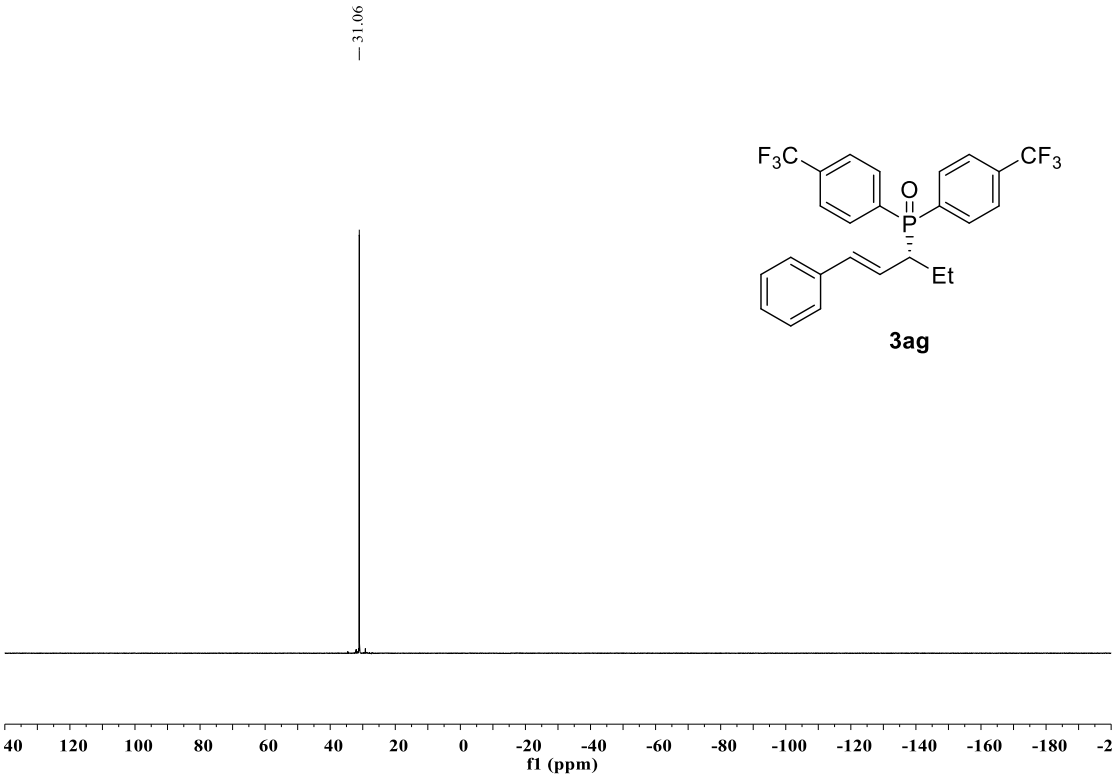

Figure S86. ^{31}P NMR spectra of **3ag**.

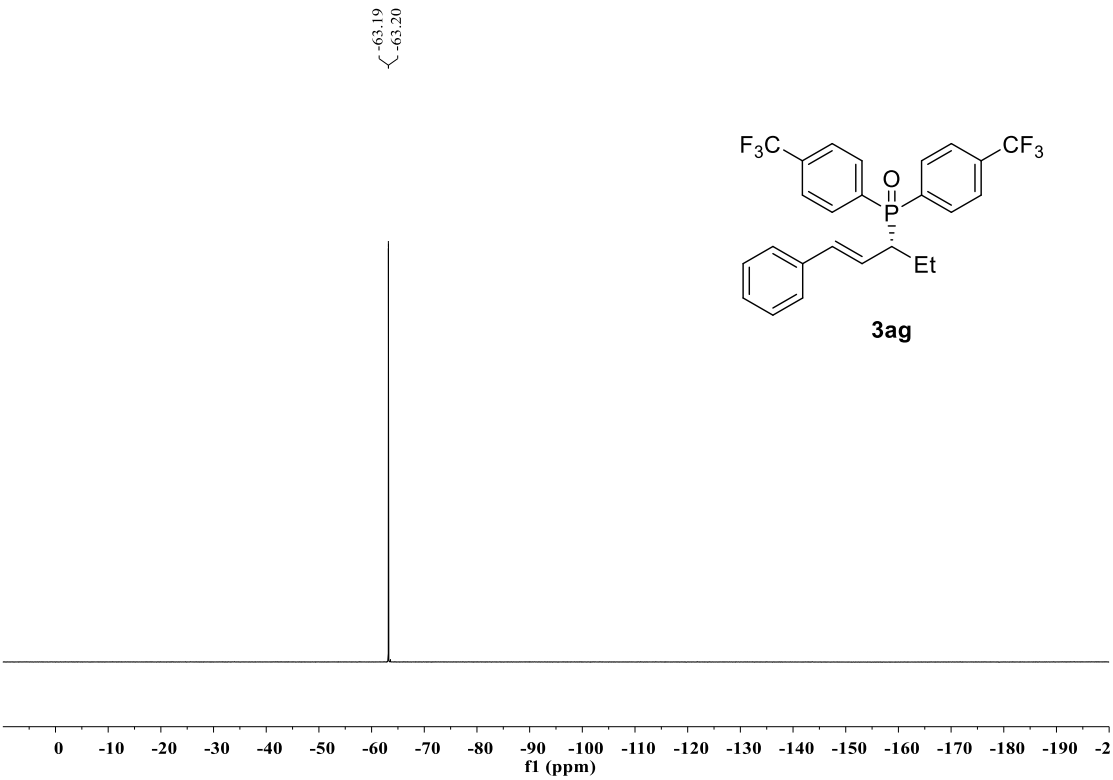

Figure S87. ^{19}F NMR spectra of **3ag**.

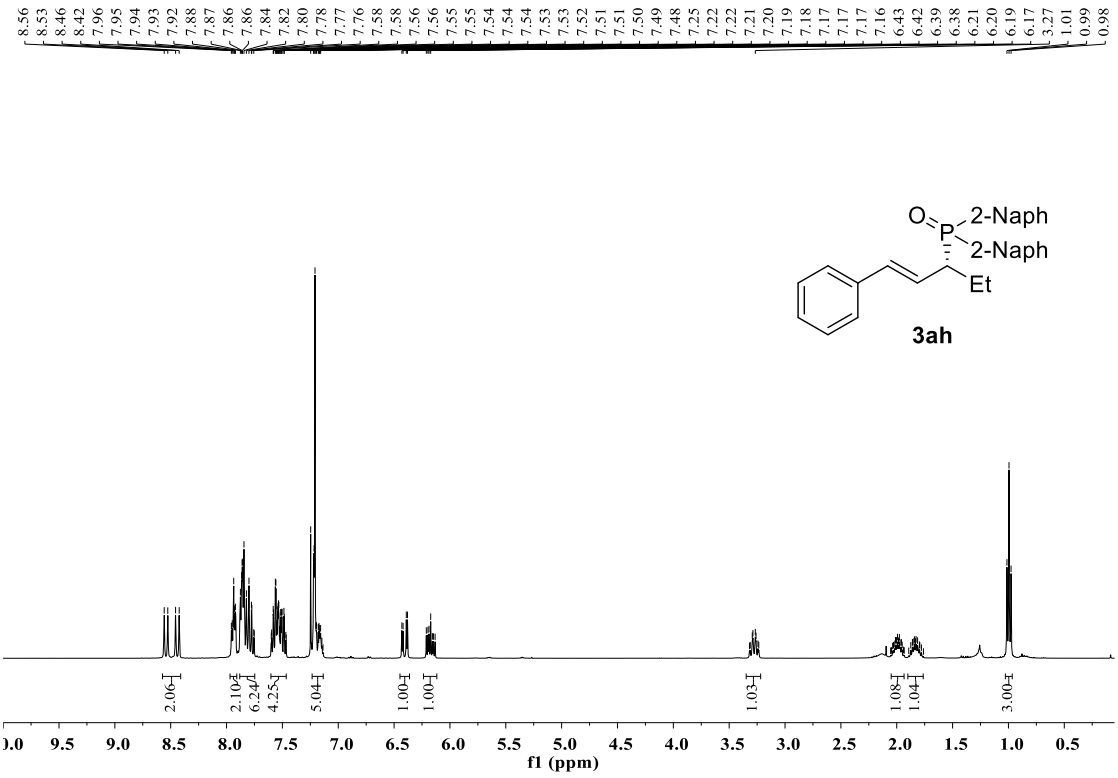

Figure S88. ^{1}H NMR spectra of **3ah**.

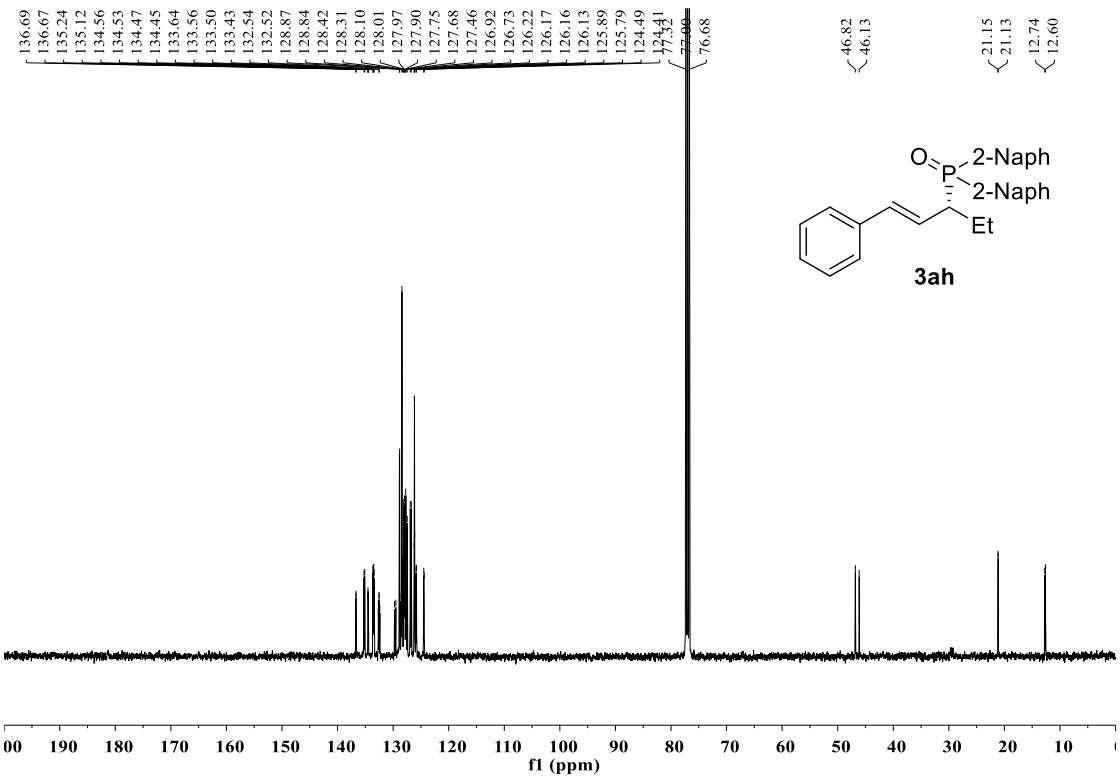

Figure S89. ^{13}C NMR spectra of **3ah**.

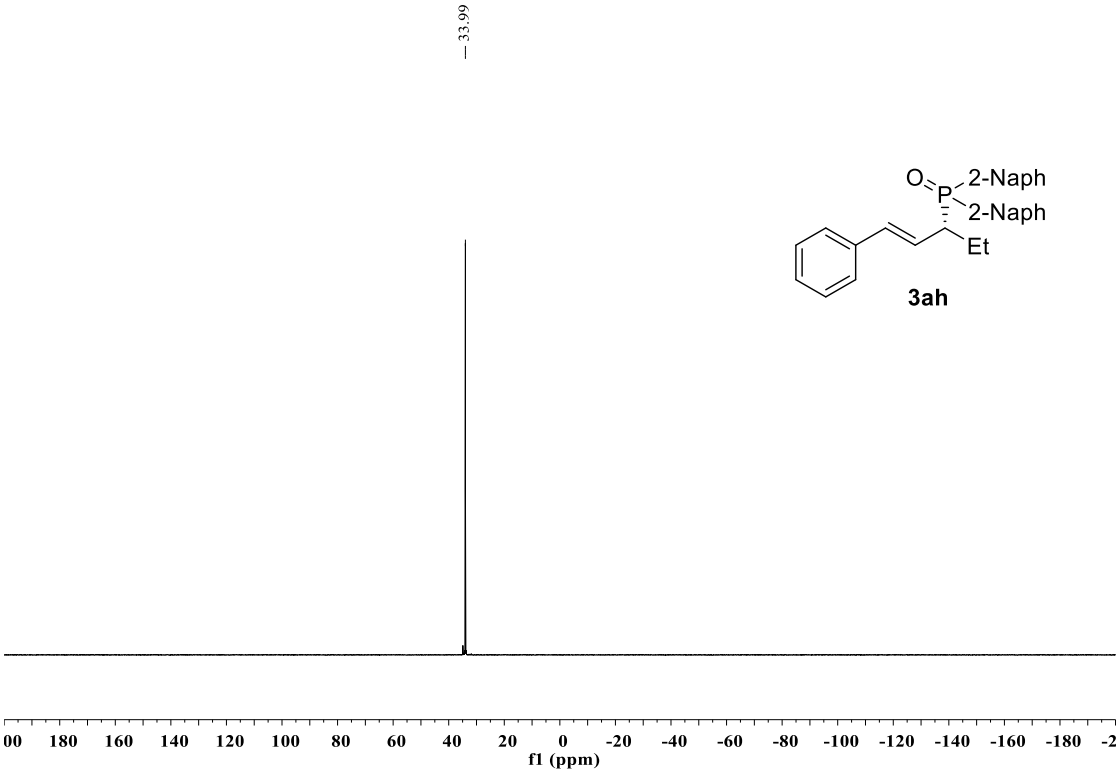

Figure S90. ^{31}P NMR spectra of **3ah**.

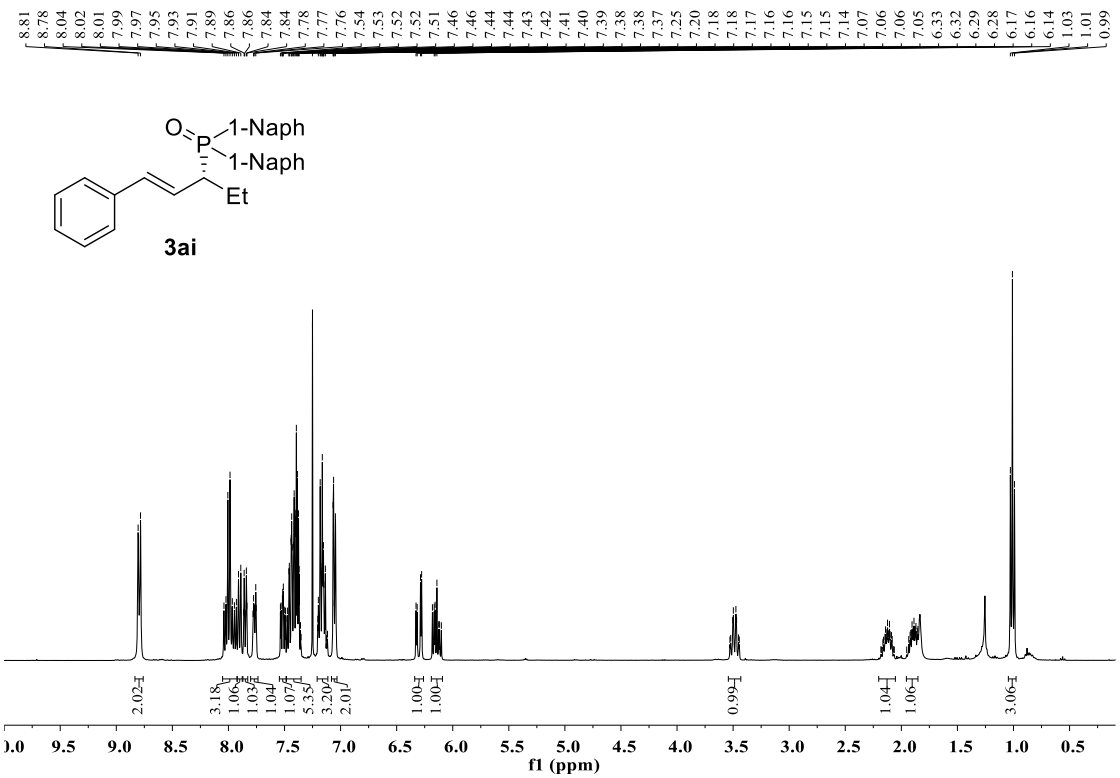

Figure S91. ^{1}H NMR spectra of **3ai**.

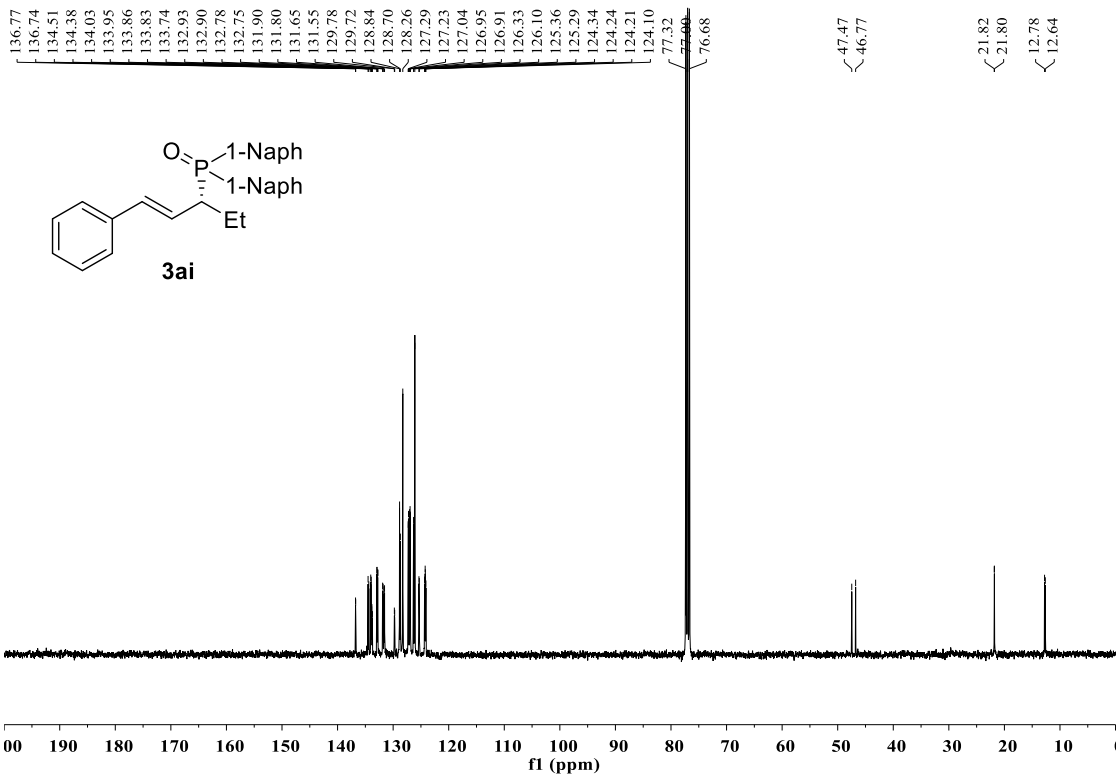

Figure S92. ^{13}C NMR spectra of **3ai**.

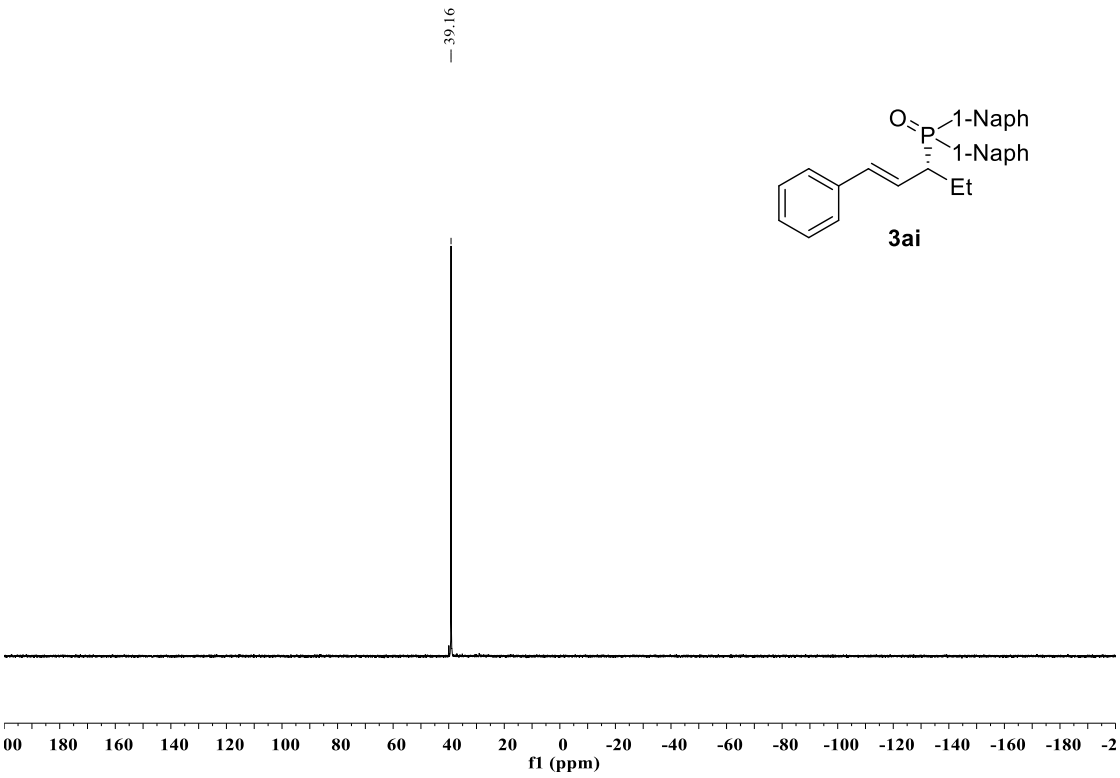

Figure S93. ^{31}P NMR spectra of **3ai**.

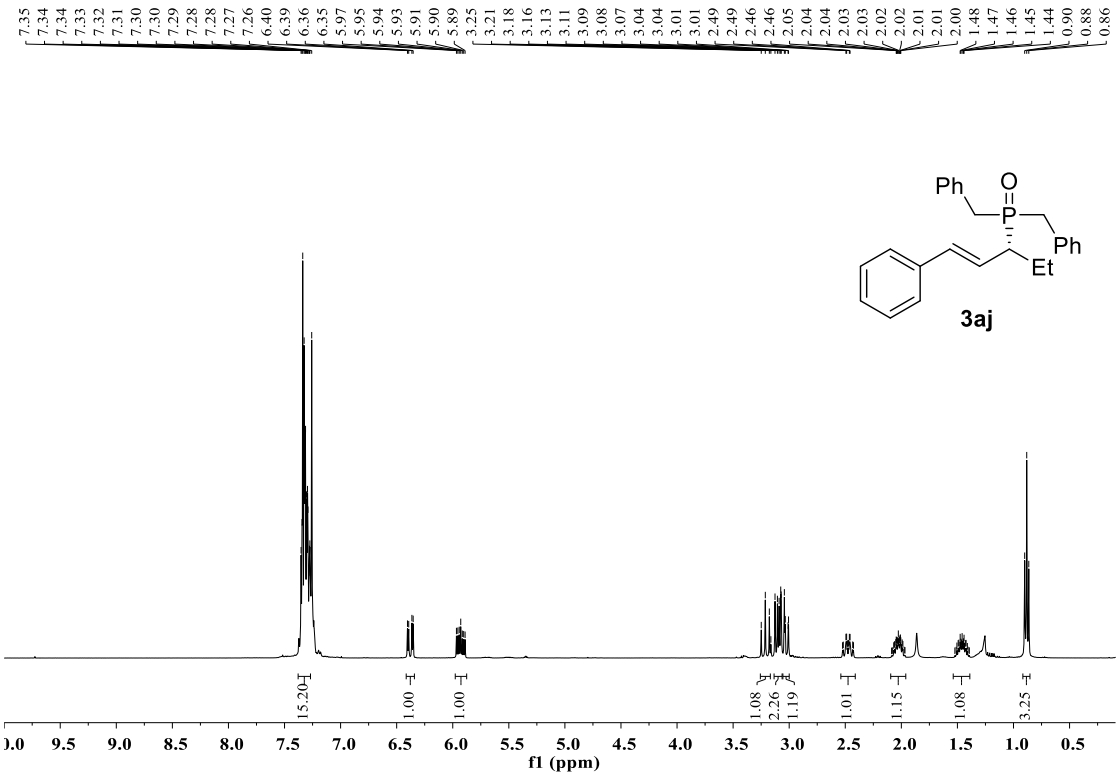

Figure S94. ^{1}H NMR spectra of **3aj**.

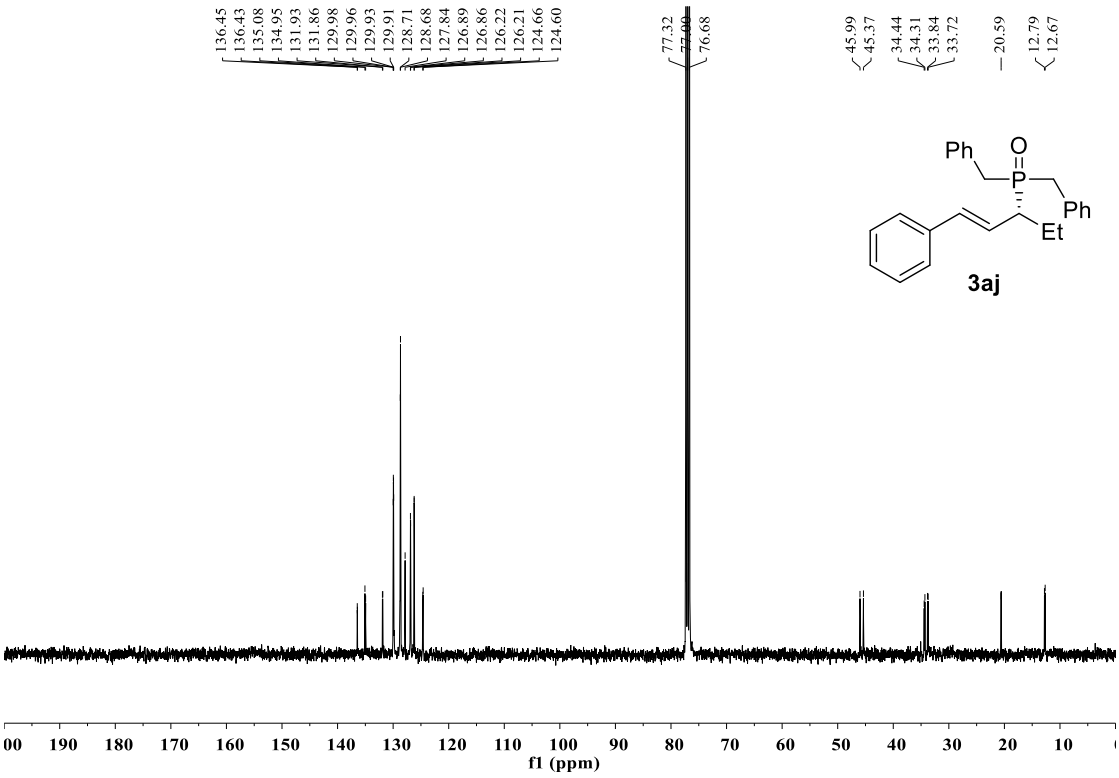

Figure S95. ^{13}C NMR spectra of **3aj**.

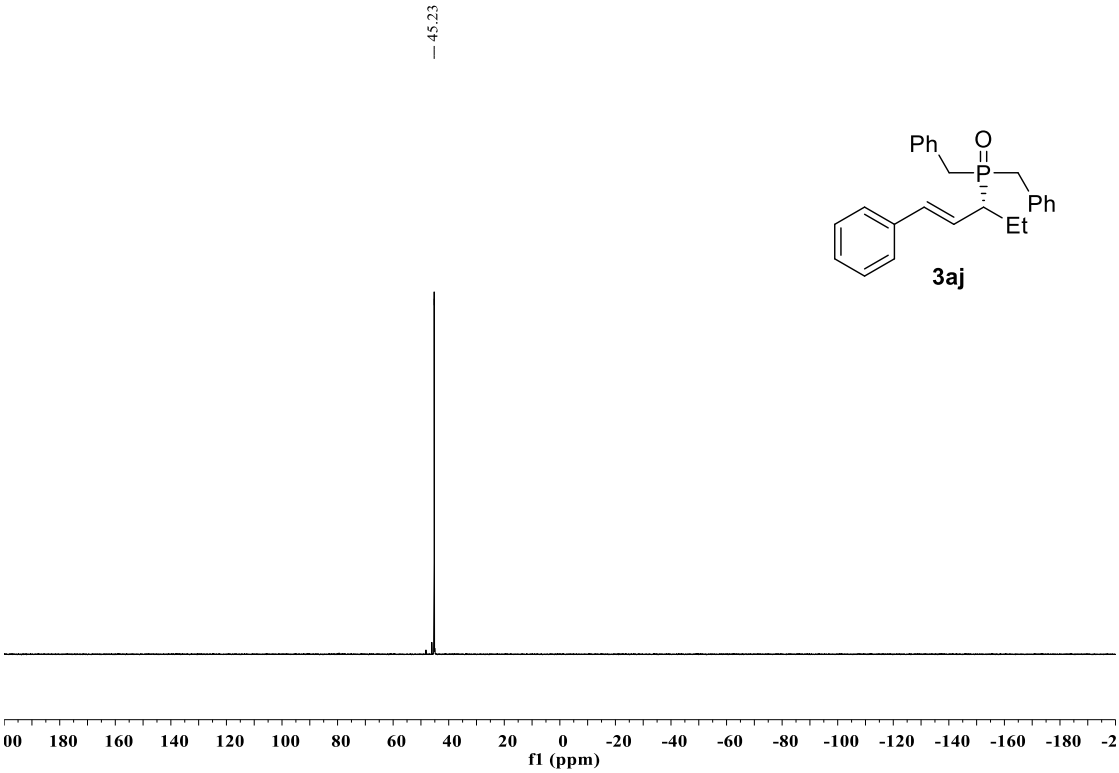

Figure S96. ^{31}P NMR spectra of **3aj**.

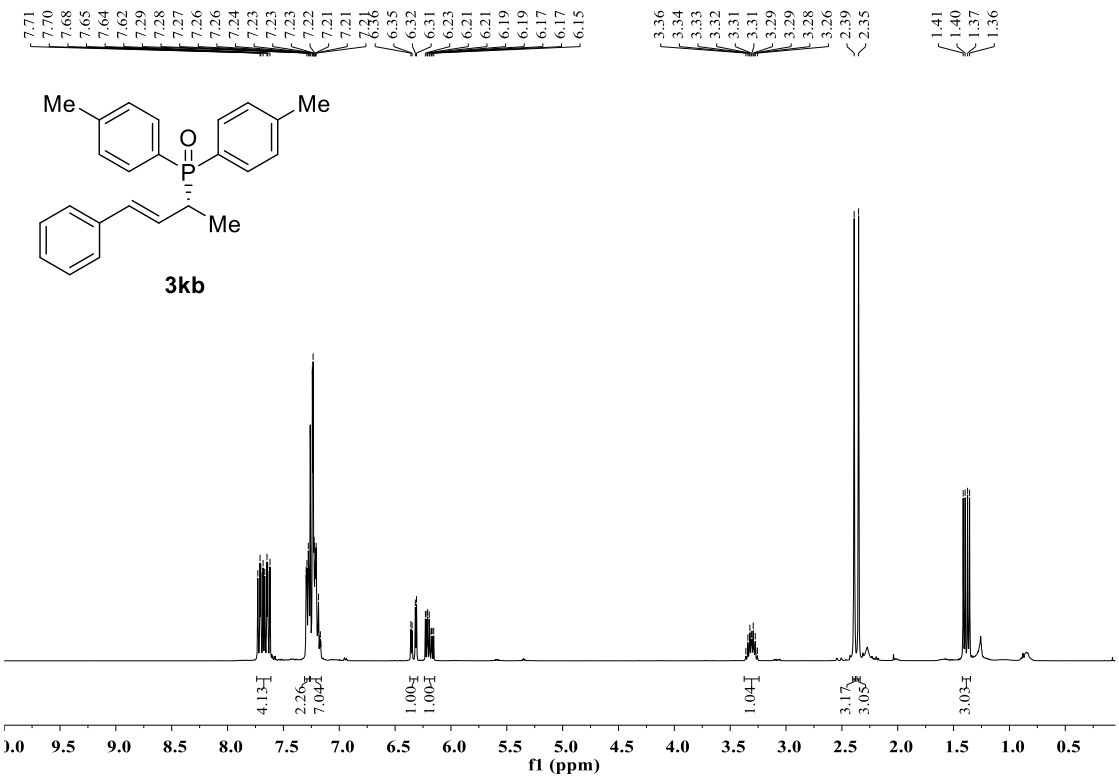

Figure S97. ^{1}H NMR spectra of **3kb**.

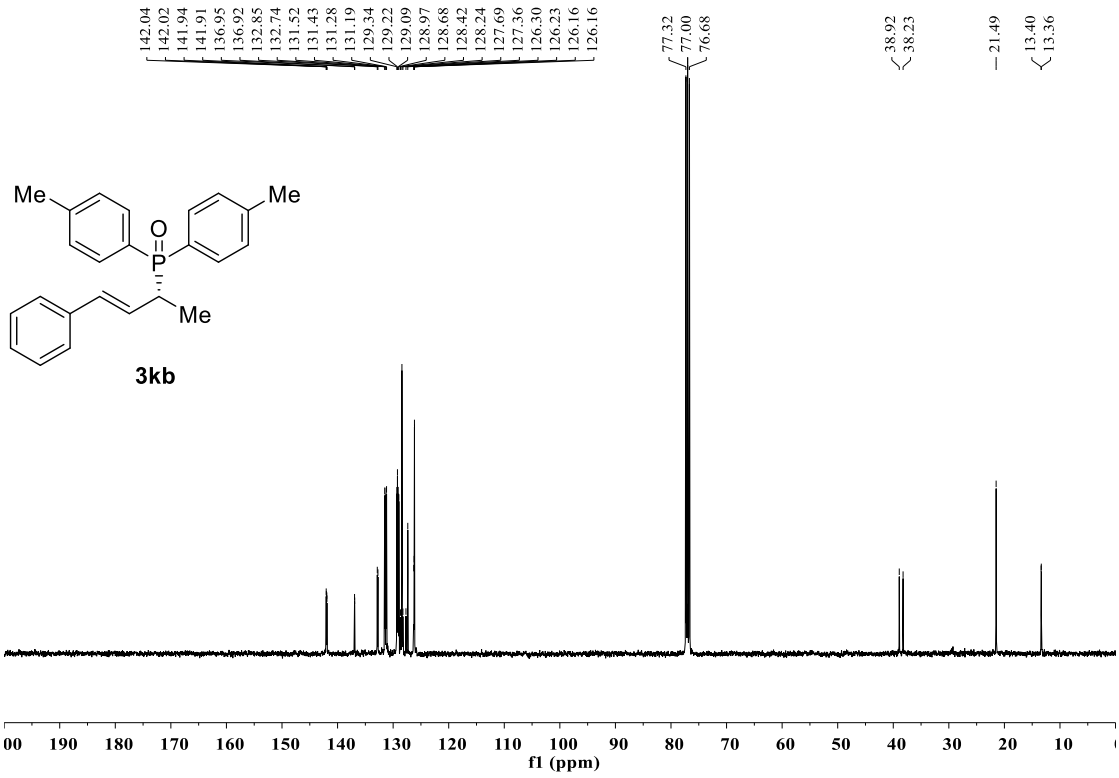

Figure S98. ^{13}C NMR spectra of **3kb**.

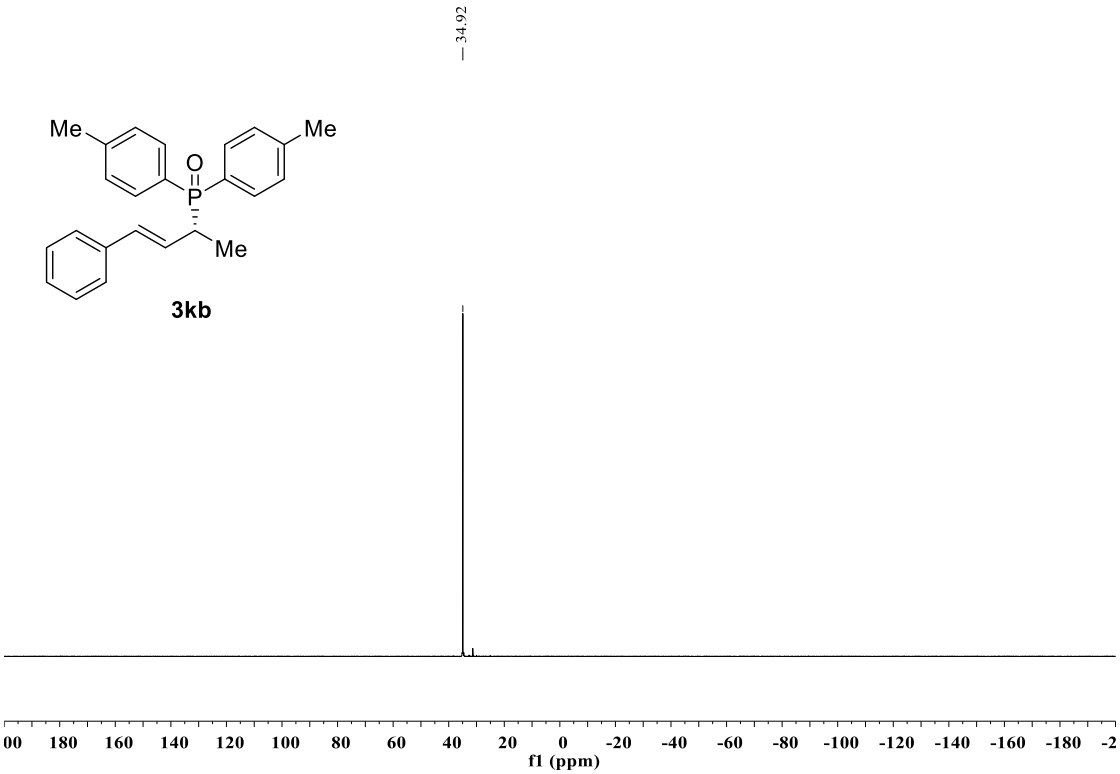

Figure S99. ^{31}P NMR spectra of **3kb**.

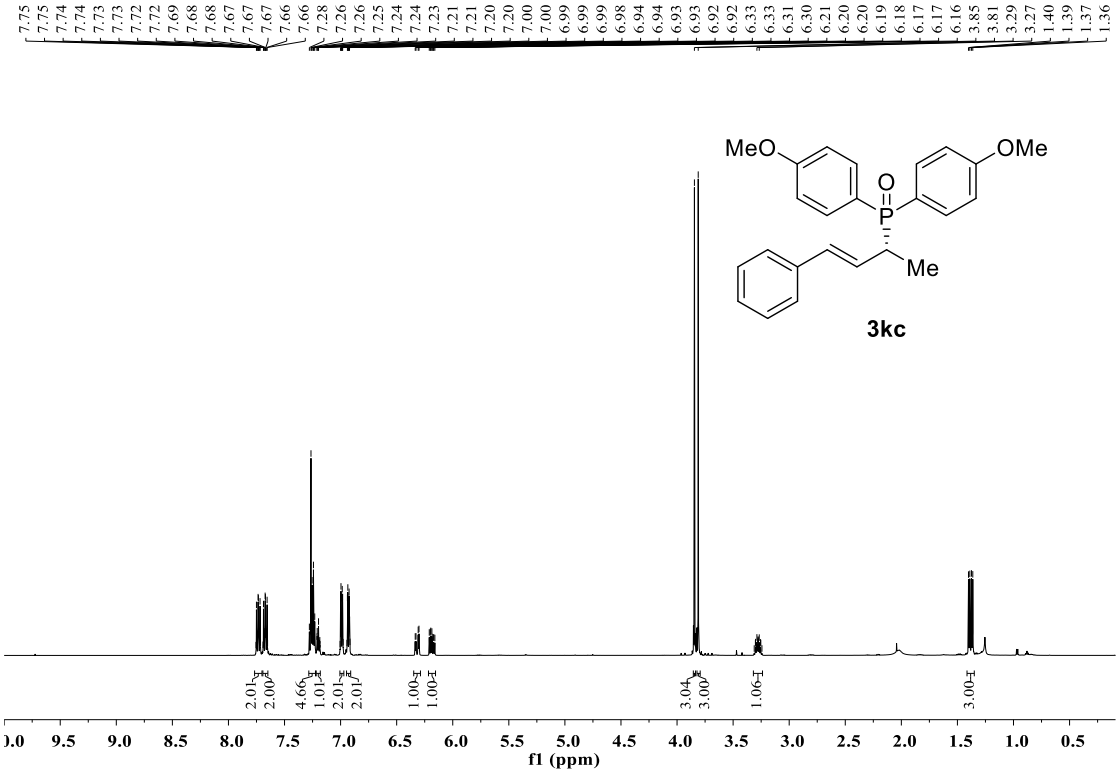

Figure S100. ^{1}H NMR spectra of **3kc**.

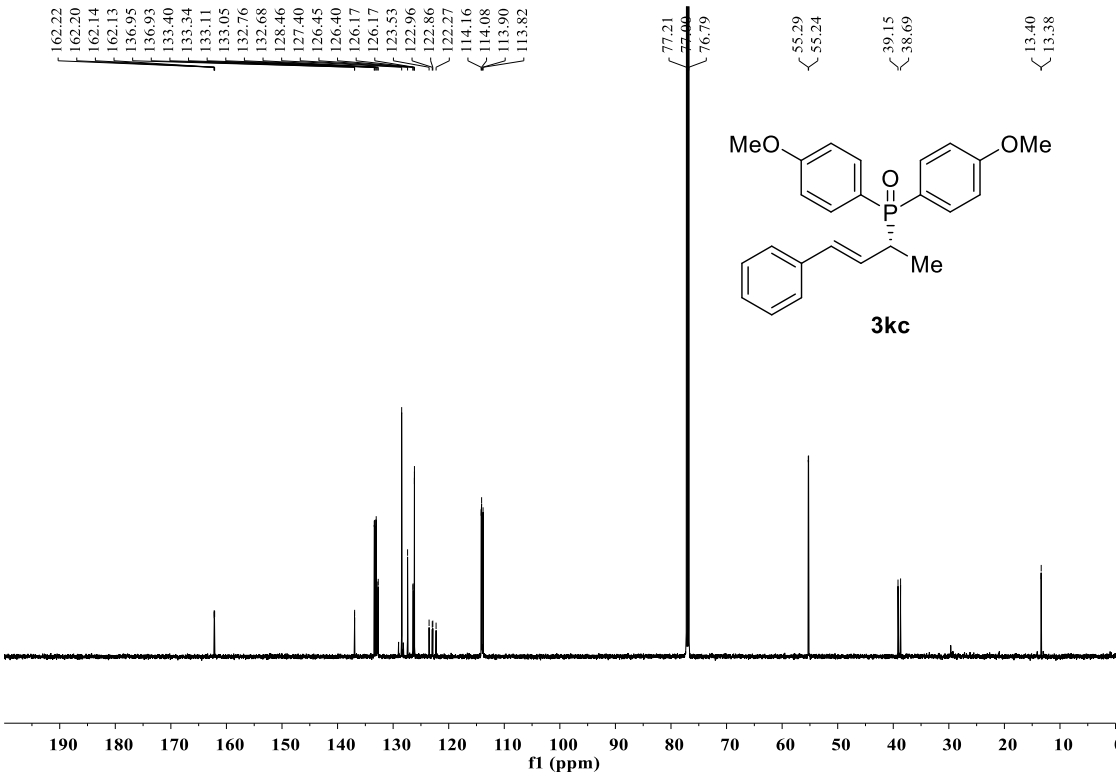

Figure S101. ^{13}C NMR spectra of **3kc**.

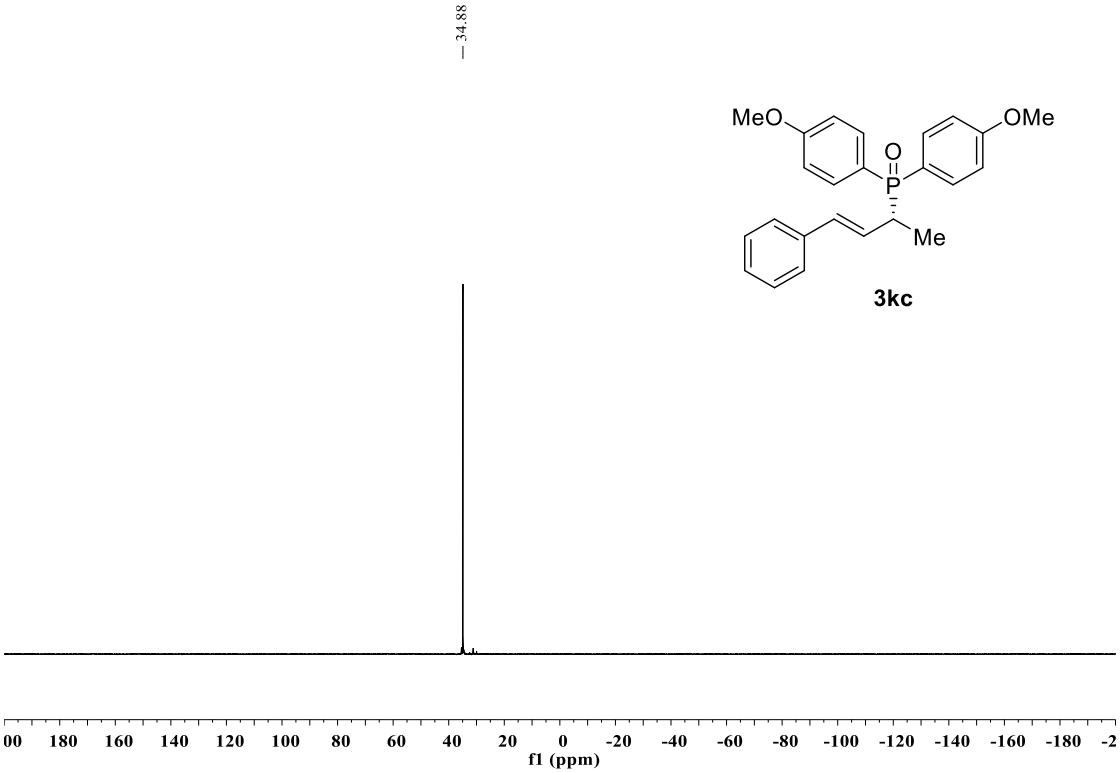

Figure S102. ^{31}P NMR spectra of **3kc**.

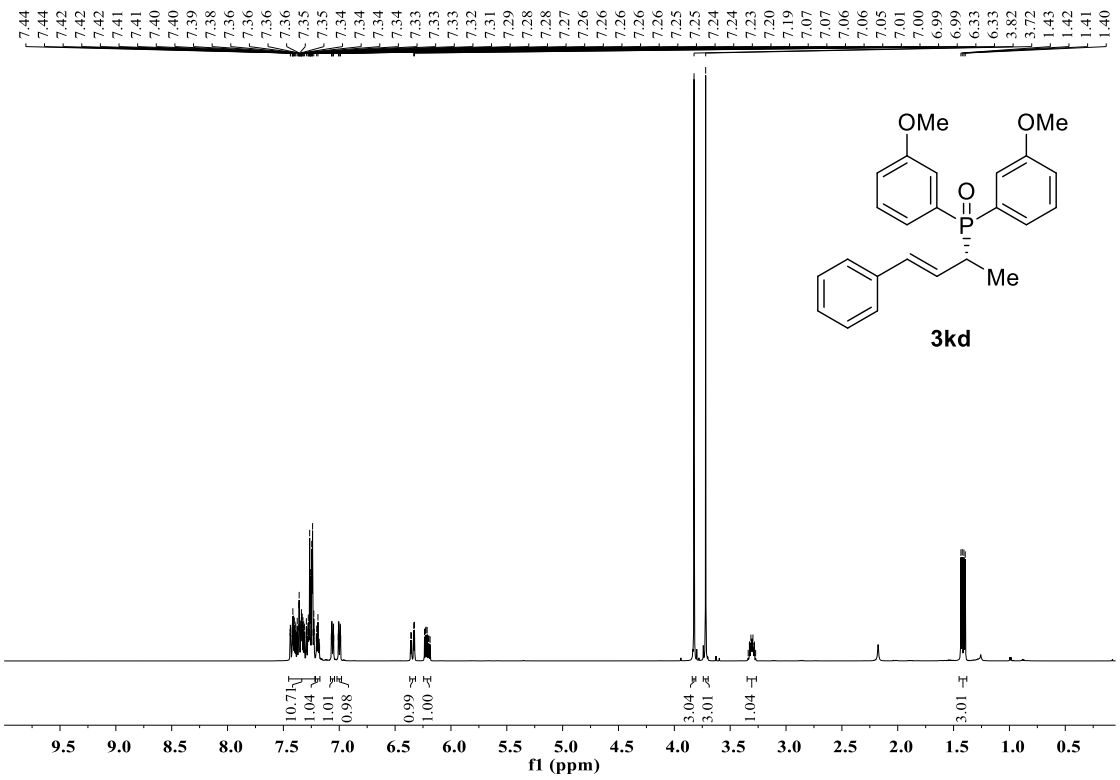

Figure S103. ^{1}H NMR spectra of **3kd**.

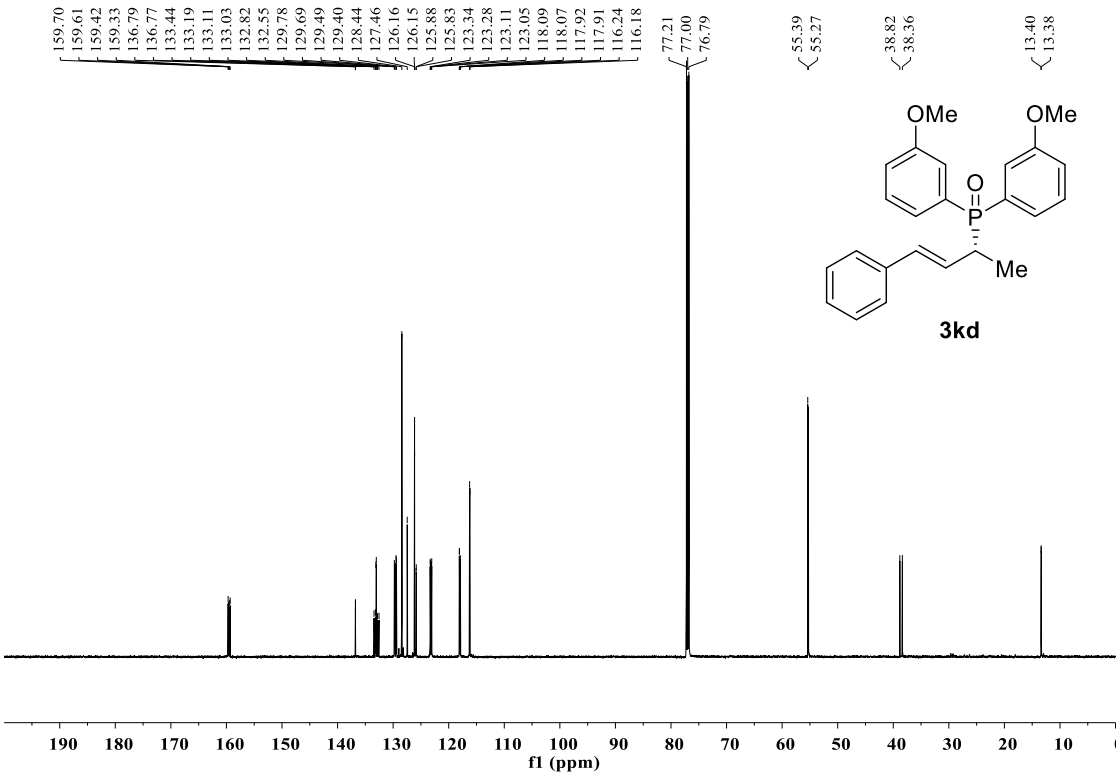

Figure S104. ^{13}C NMR spectra of **3kd**.

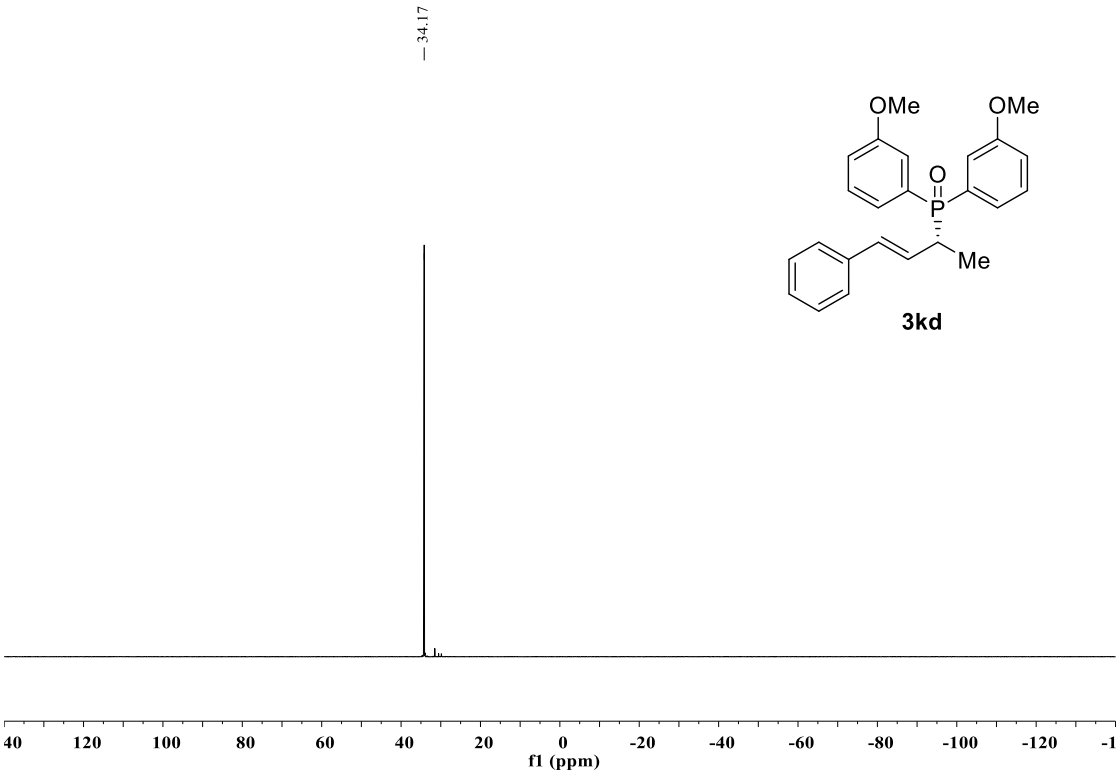

Figure S105. ^{31}P NMR spectra of **3kd**.

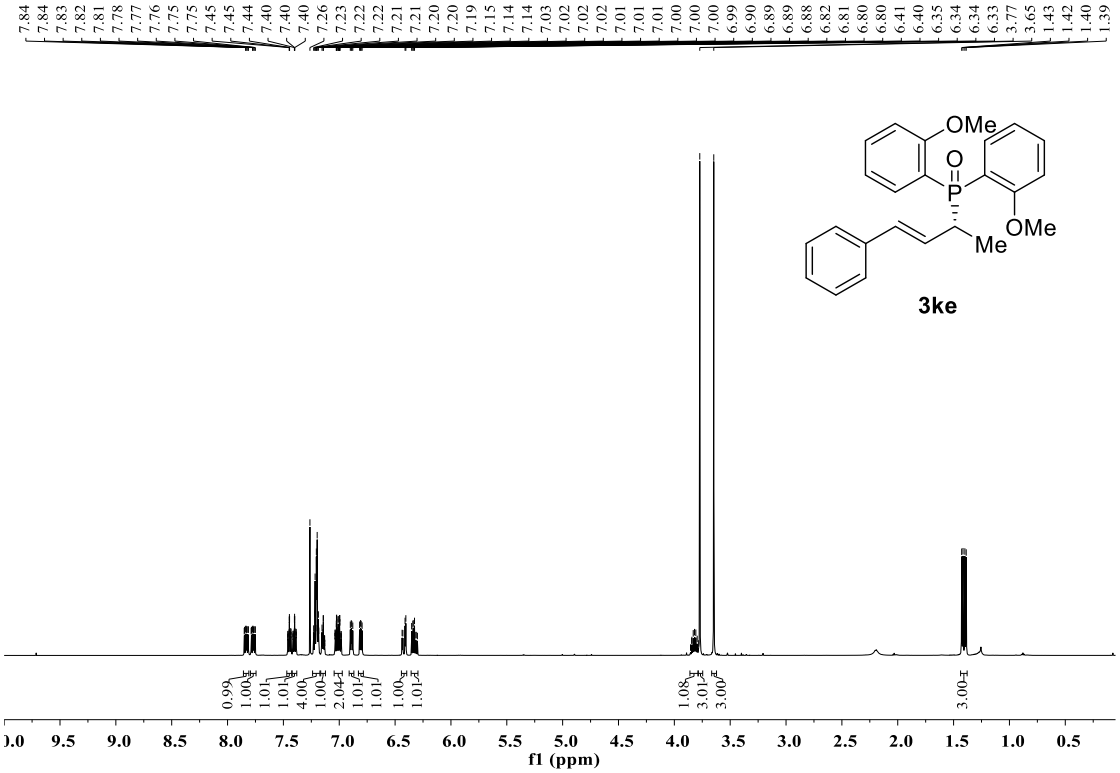

Figure S106. ^{1}H NMR spectra of **3ke**.

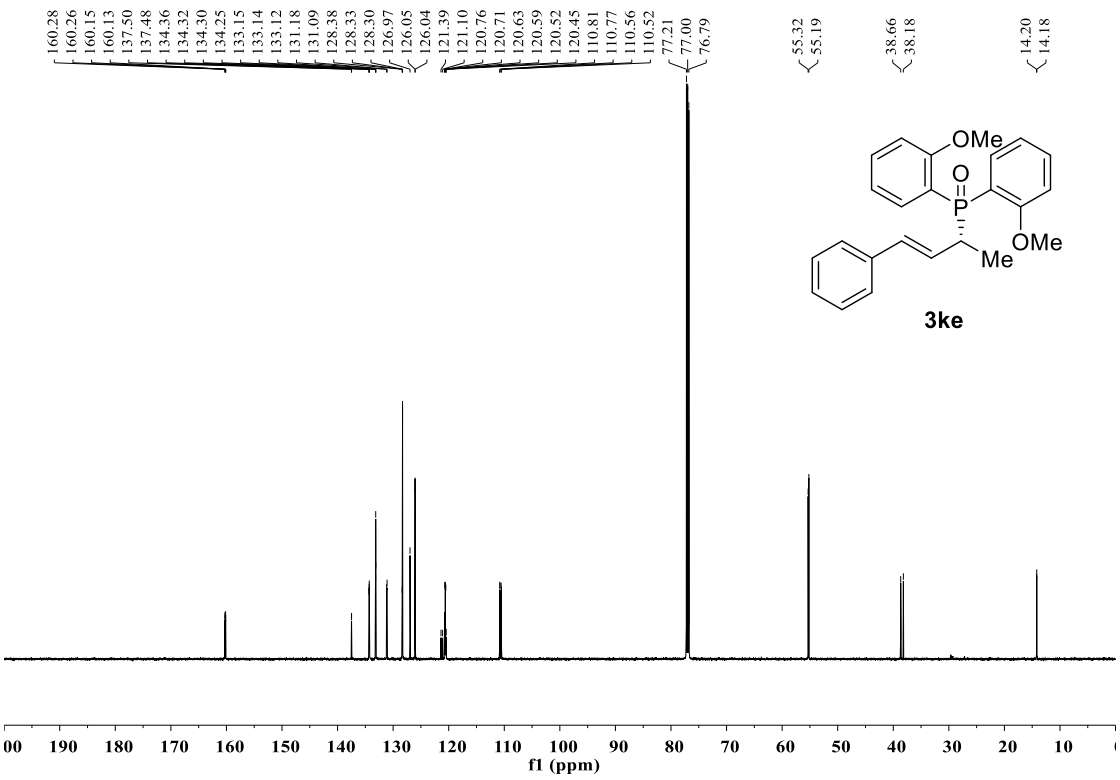

Figure S107. ^{13}C NMR spectra of **3ke**.

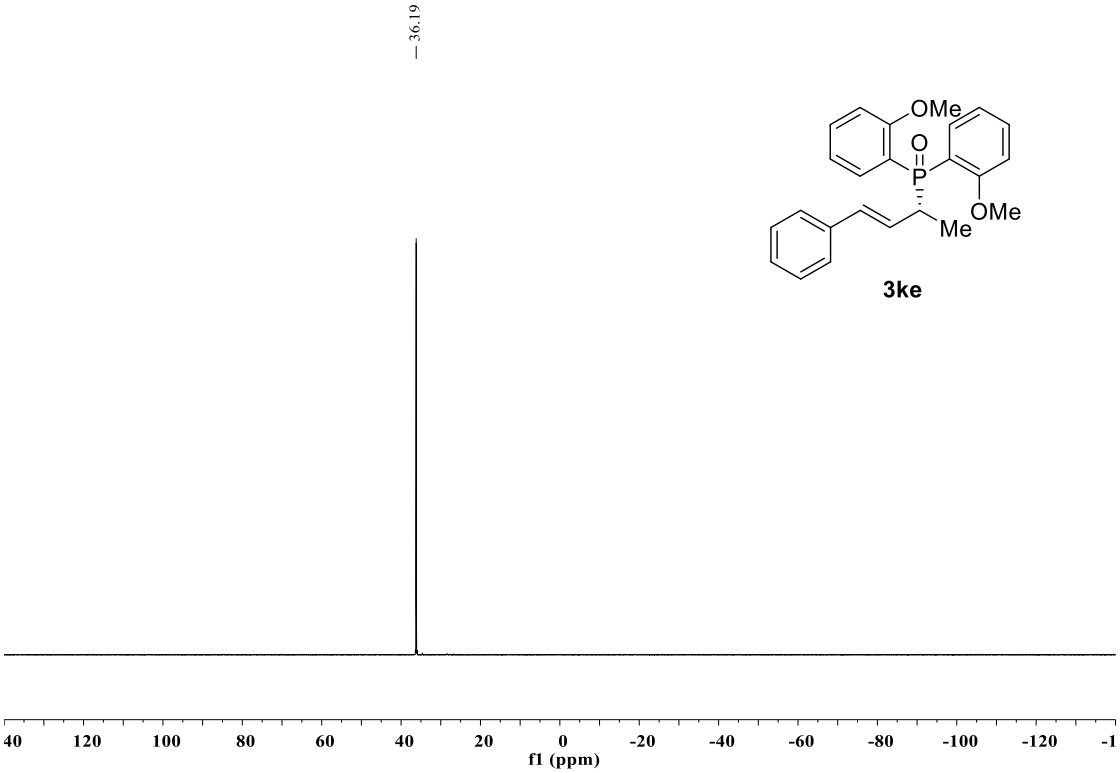

Figure S108. ^{31}P NMR spectra of **3ke**.

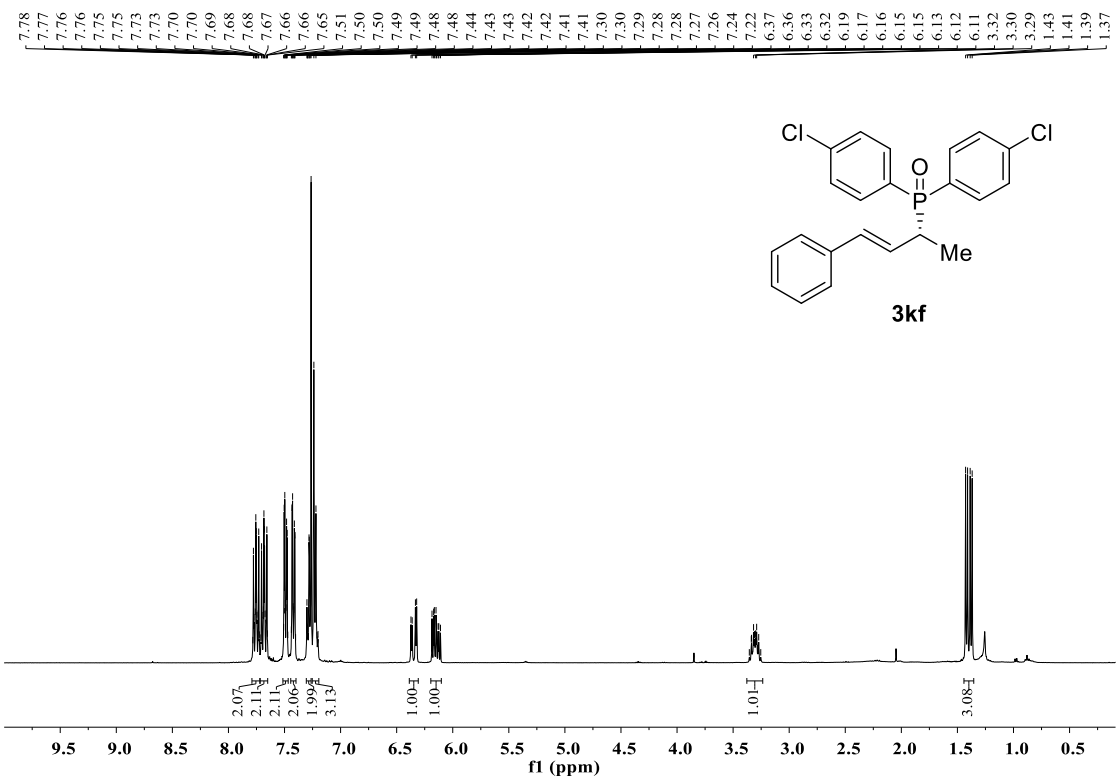

Figure S109. ^{1}H NMR spectra of **3kf**.

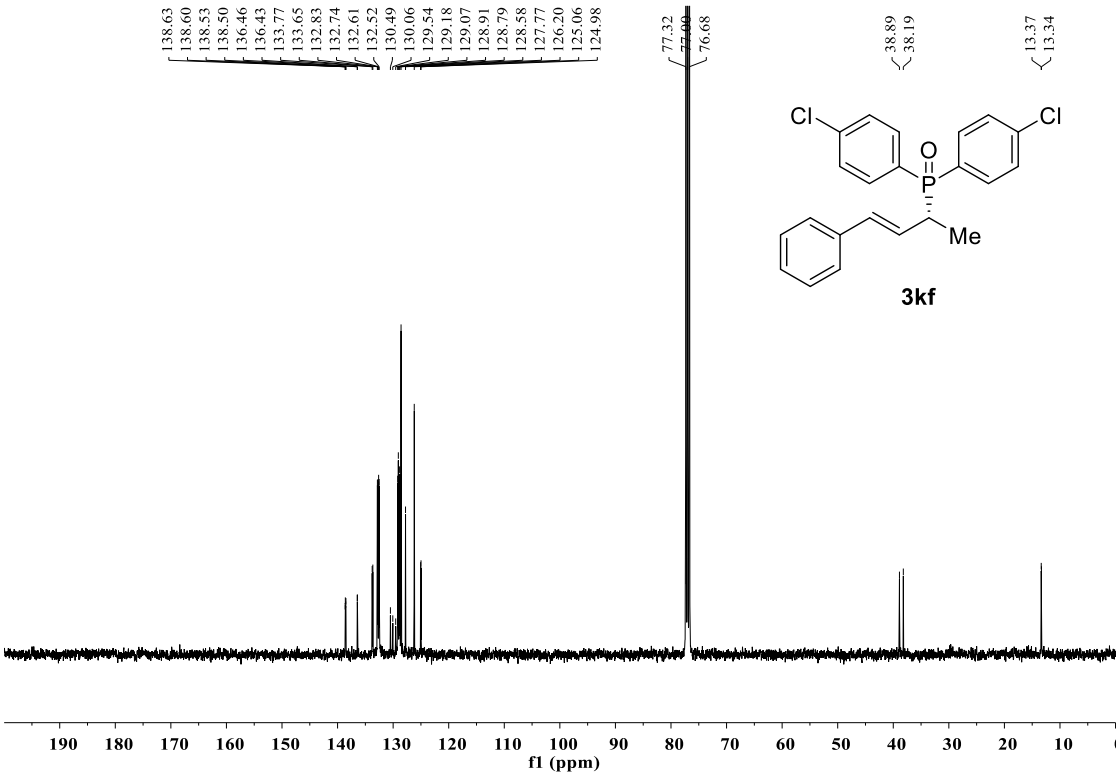

Figure S110. ^{13}C NMR spectra of **3kf**.

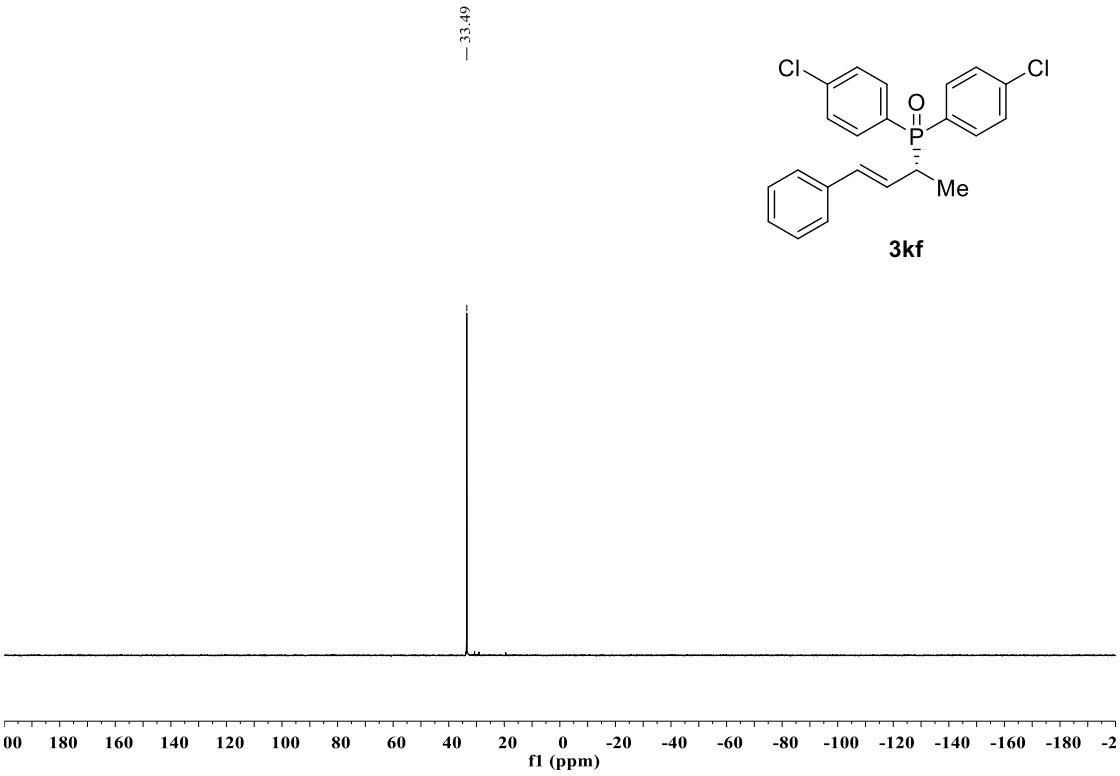

Figure S111. ^{31}P NMR spectra of **3kf**.

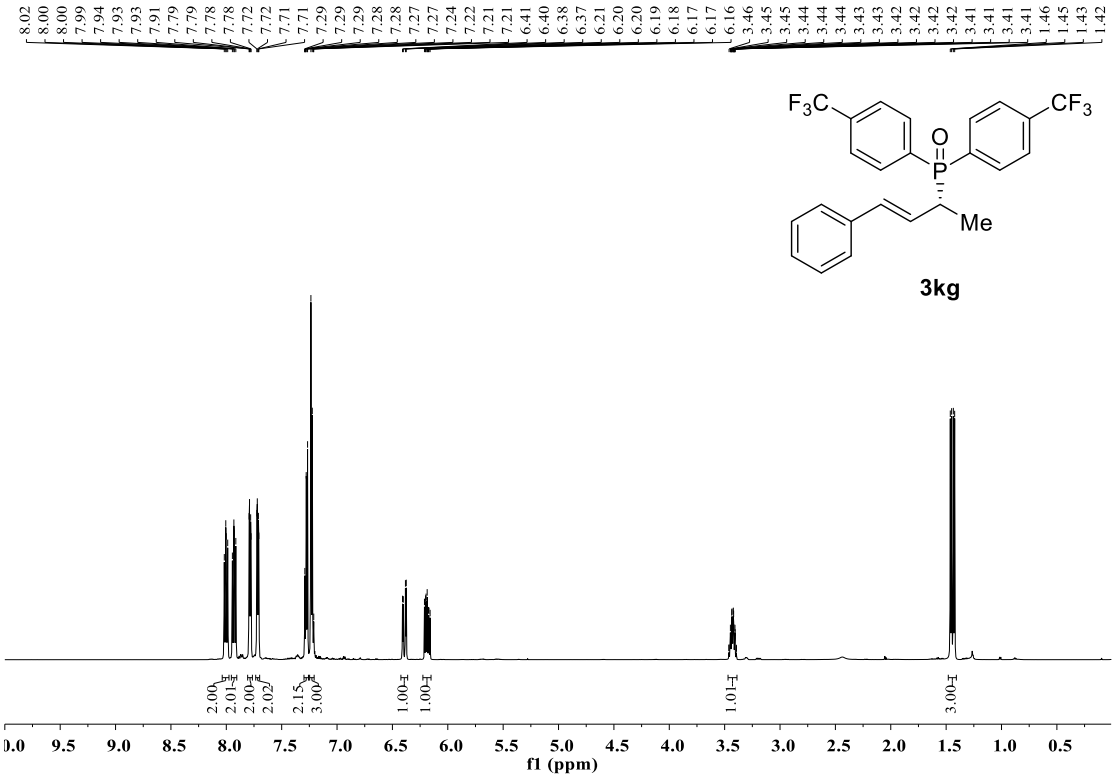

Figure S112. ^{1}H NMR spectra of **3kg**.

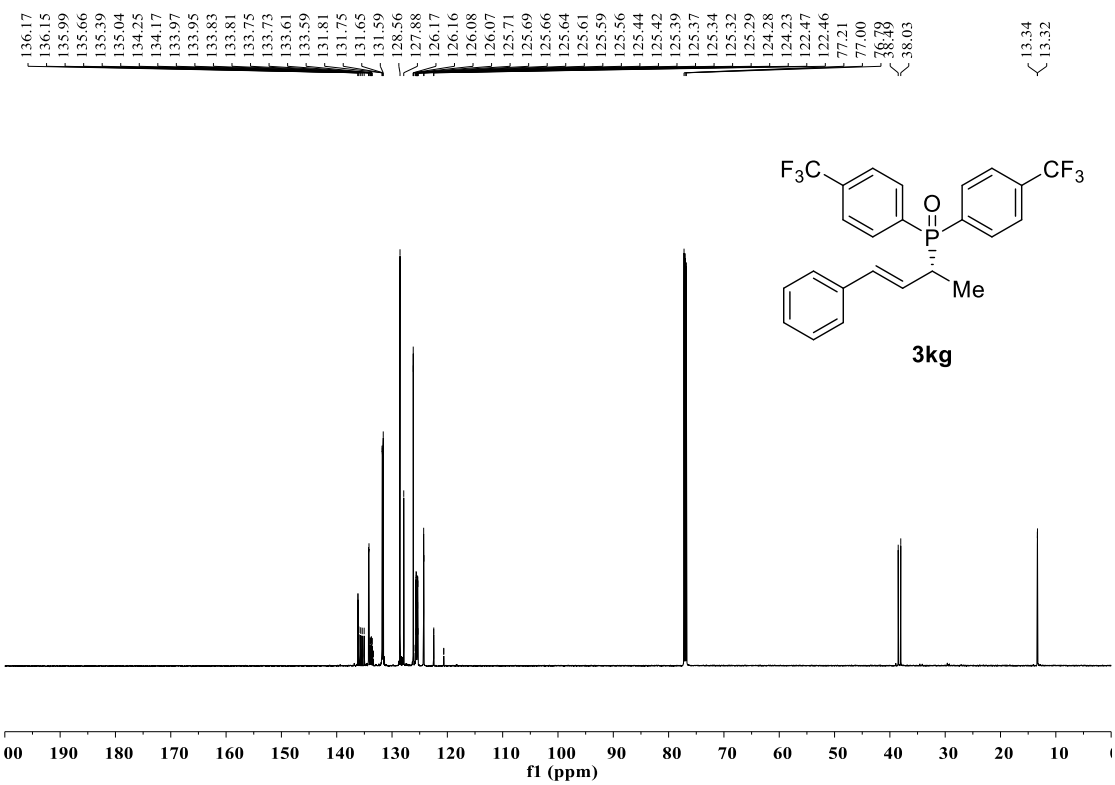

Figure S113. ^{13}C NMR spectra of **3kg**.

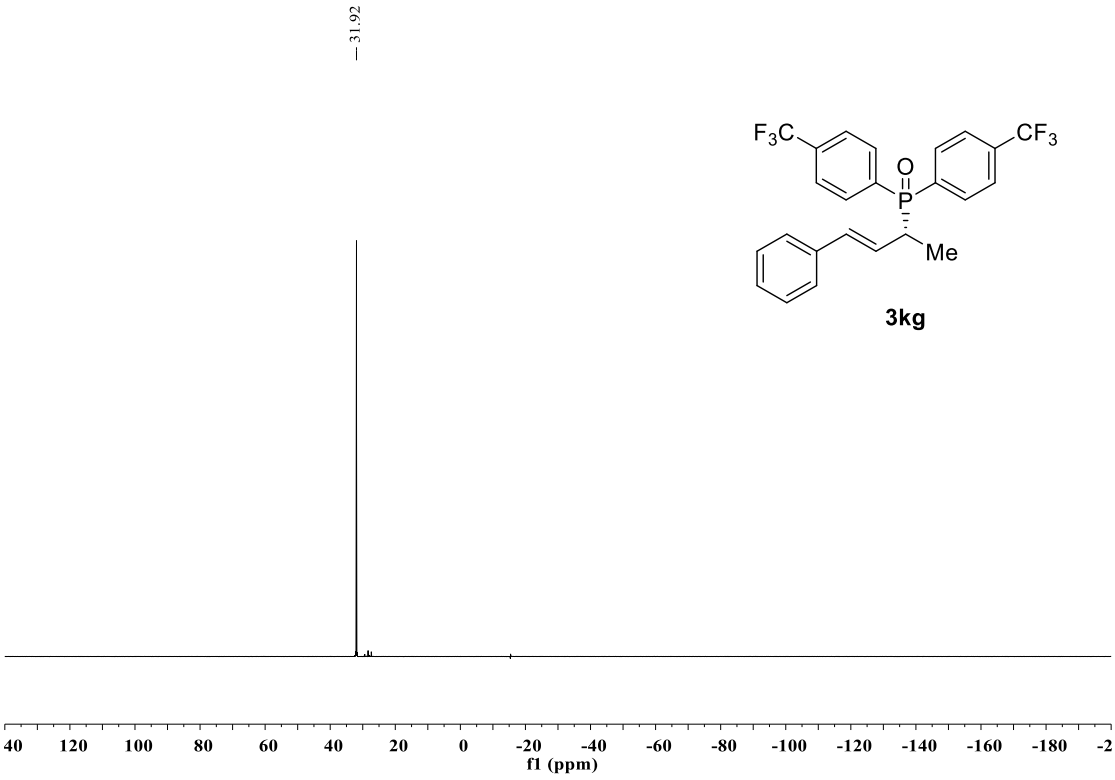

Figure S114. ^{31}P NMR spectra of **3kg**.

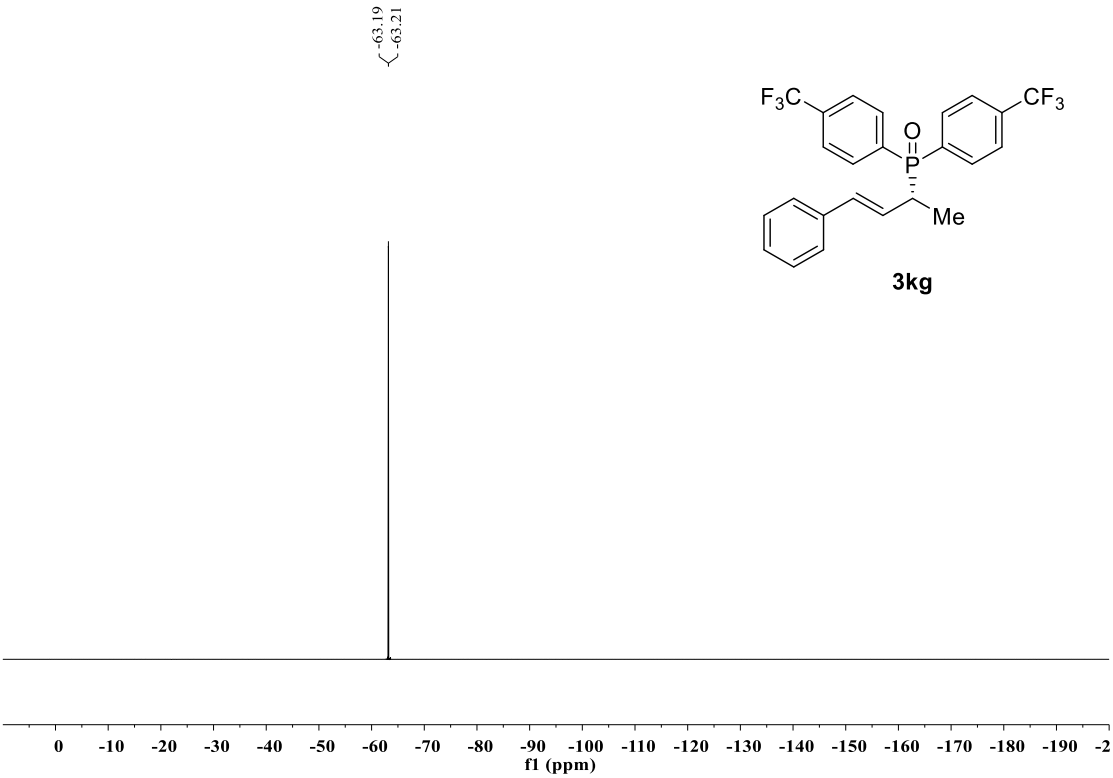

Figure S115. ^{19}F NMR spectra of **3kg**.

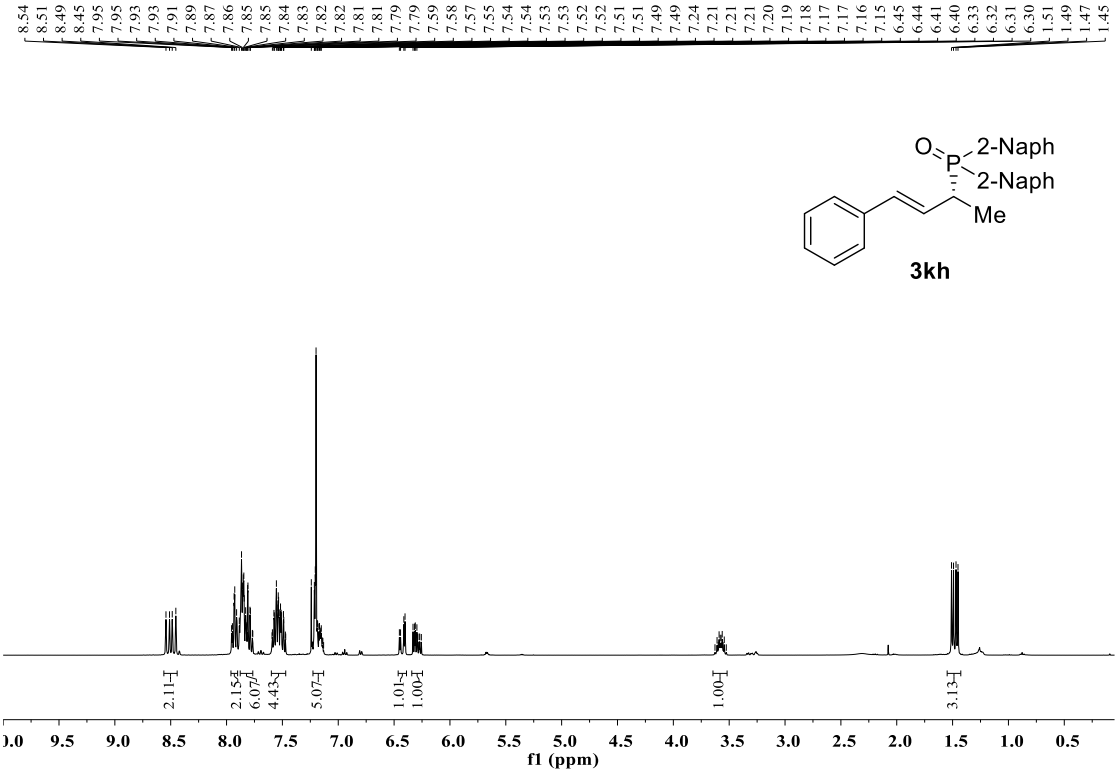

Figure S116. ^{1}H NMR spectra of **3kh**.

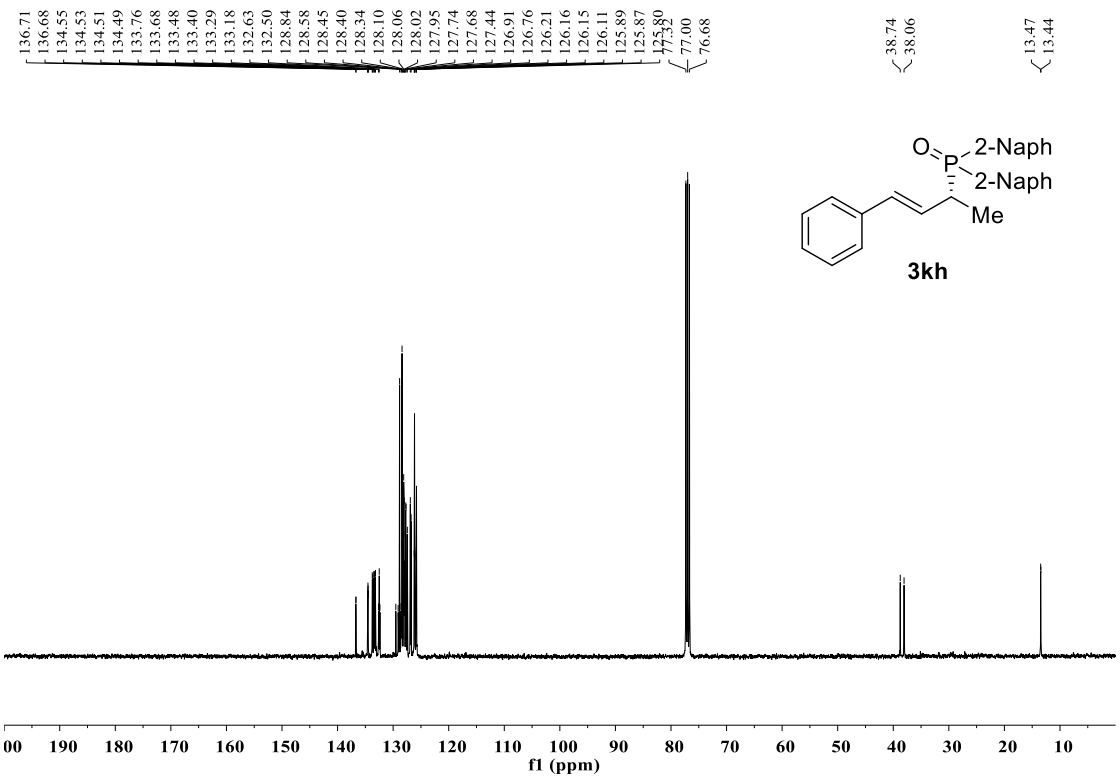

Figure S117. ^{13}C NMR spectra of **3kh**.

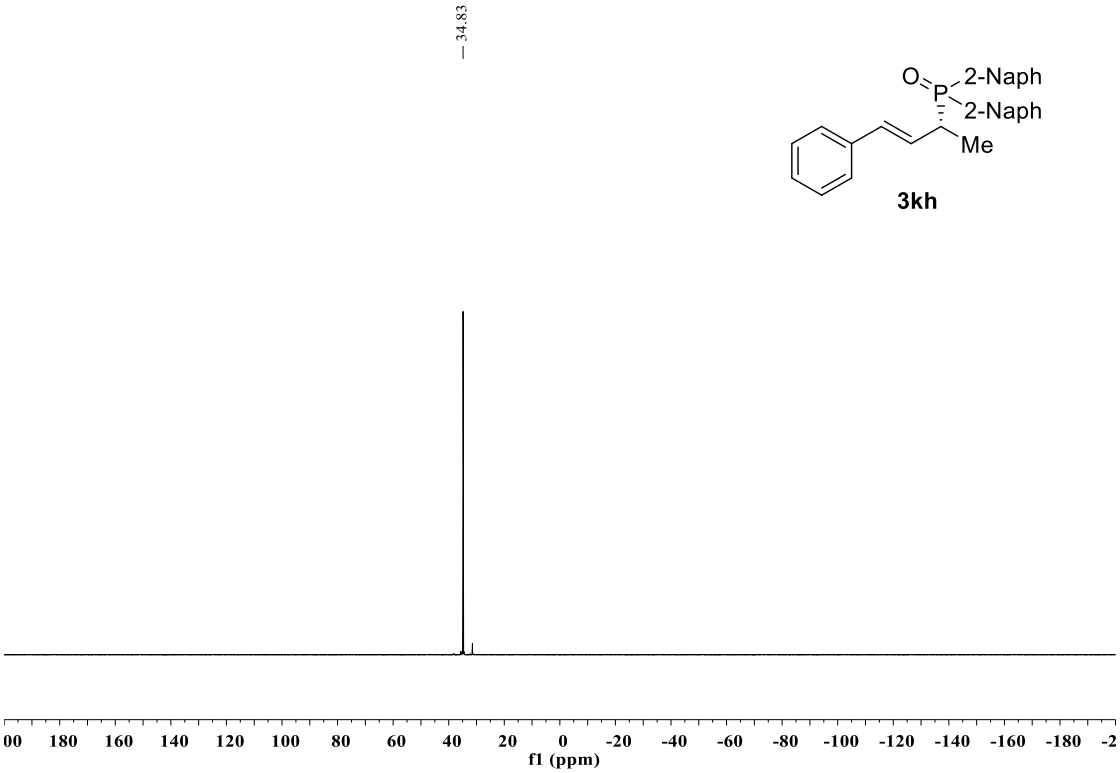

Figure S118. ^{31}P NMR spectra of **3kh**.

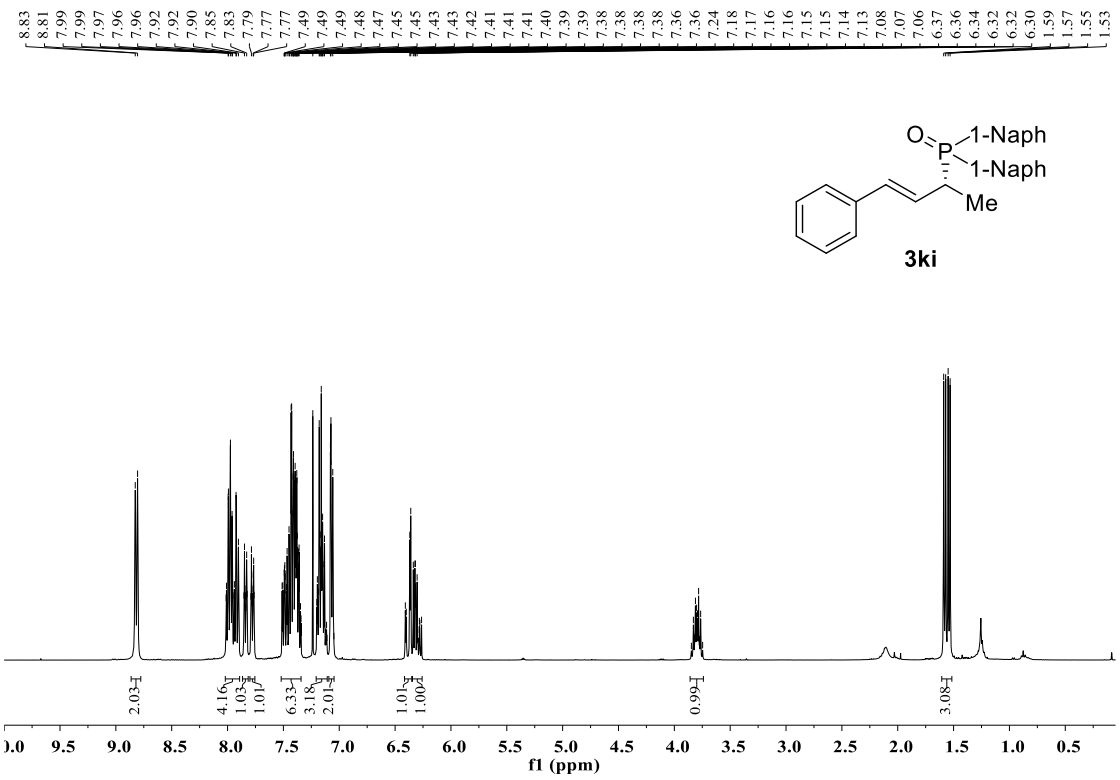

Figure S119. ^{1}H NMR spectra of **3ki**.

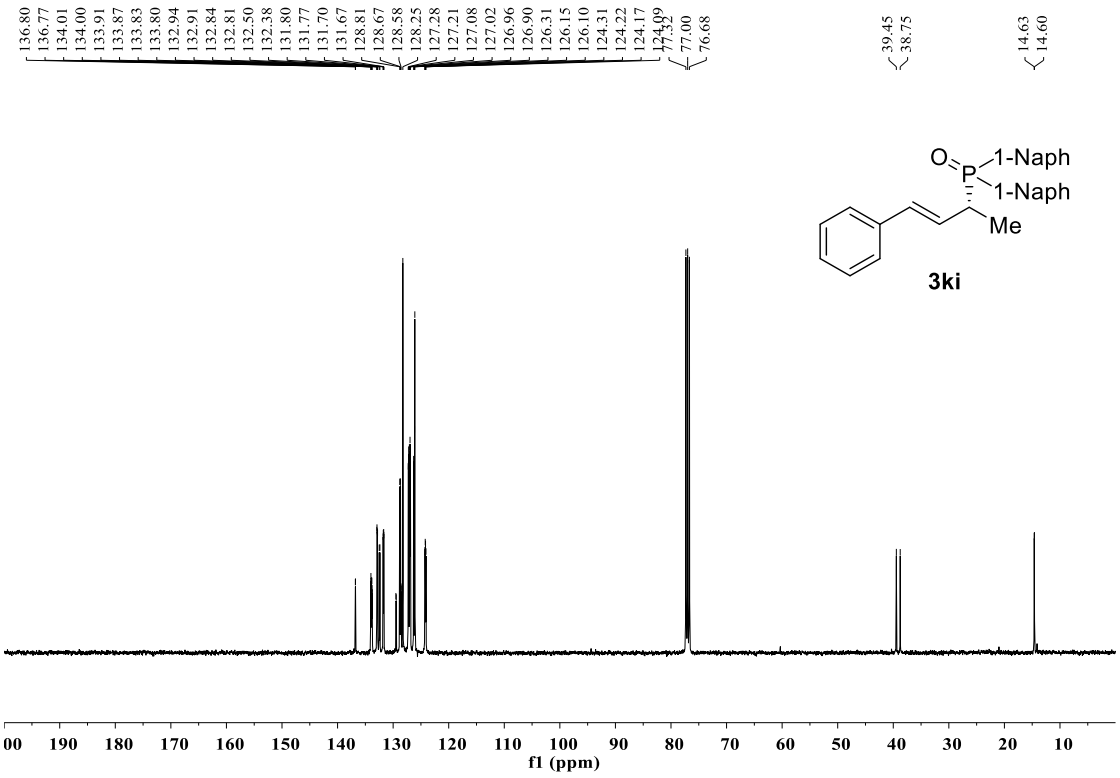

Figure S120. ^{13}C NMR spectra of **3ki**.

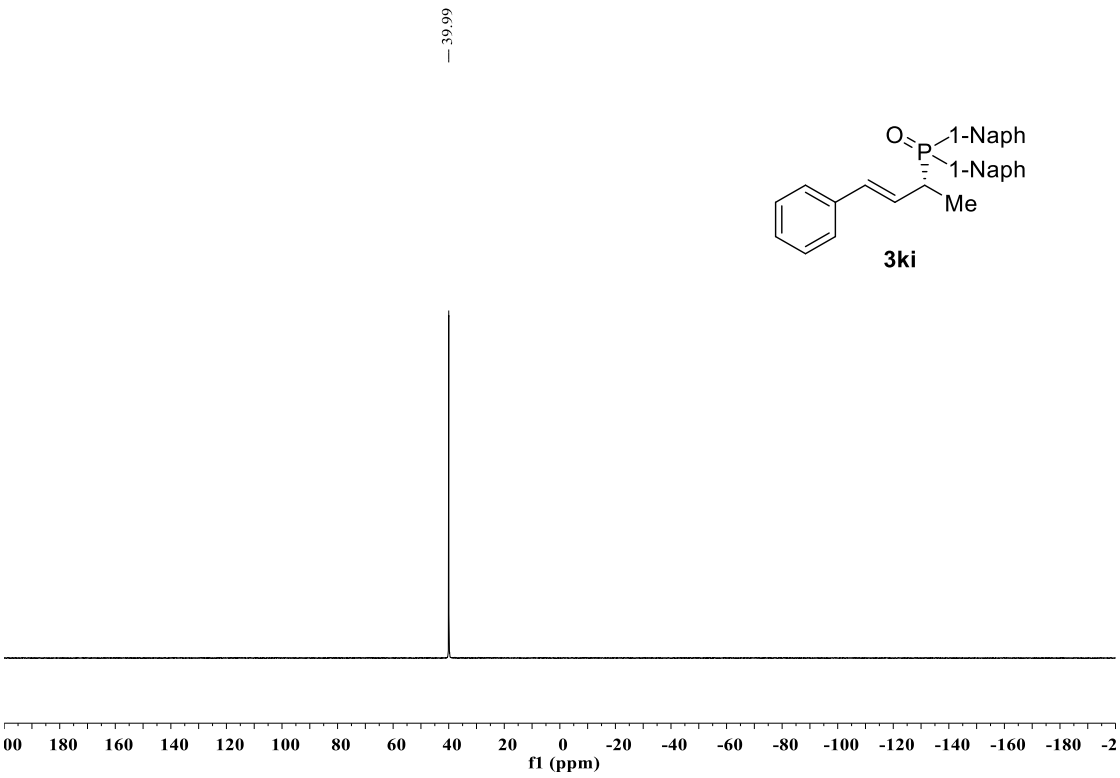

Figure S121. ^{31}P NMR spectra of **3ki**.

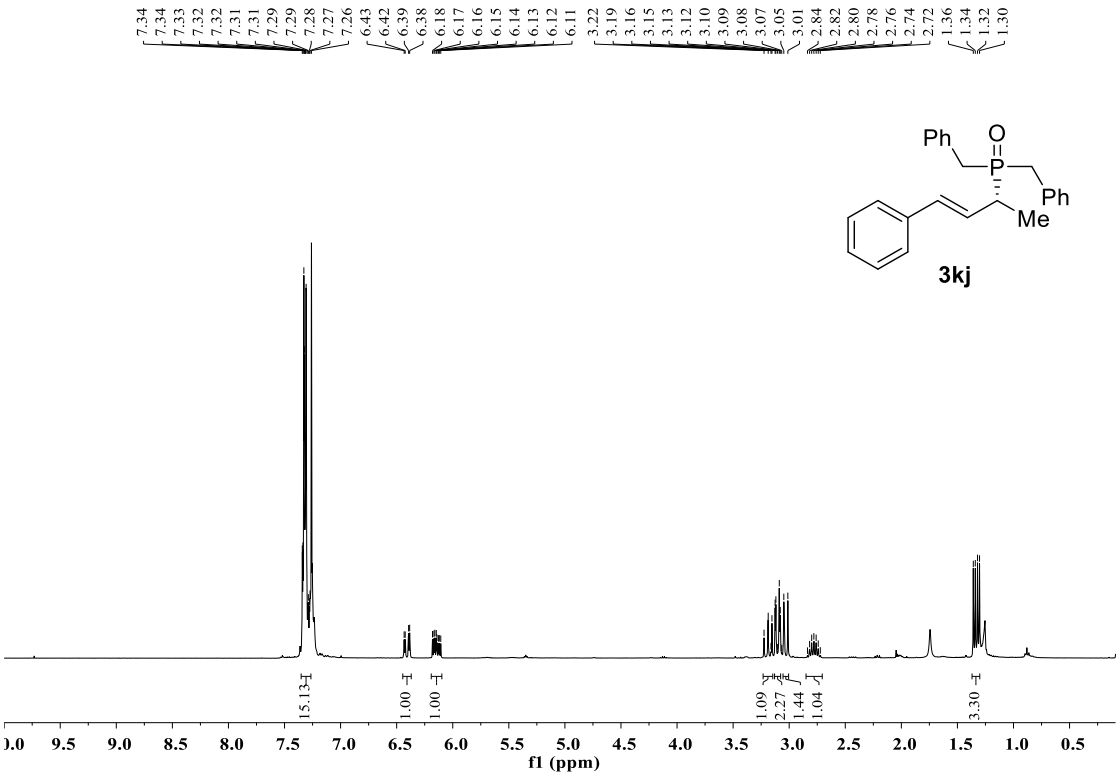

Figure S122. ^{1}H NMR spectra of **3kj**.

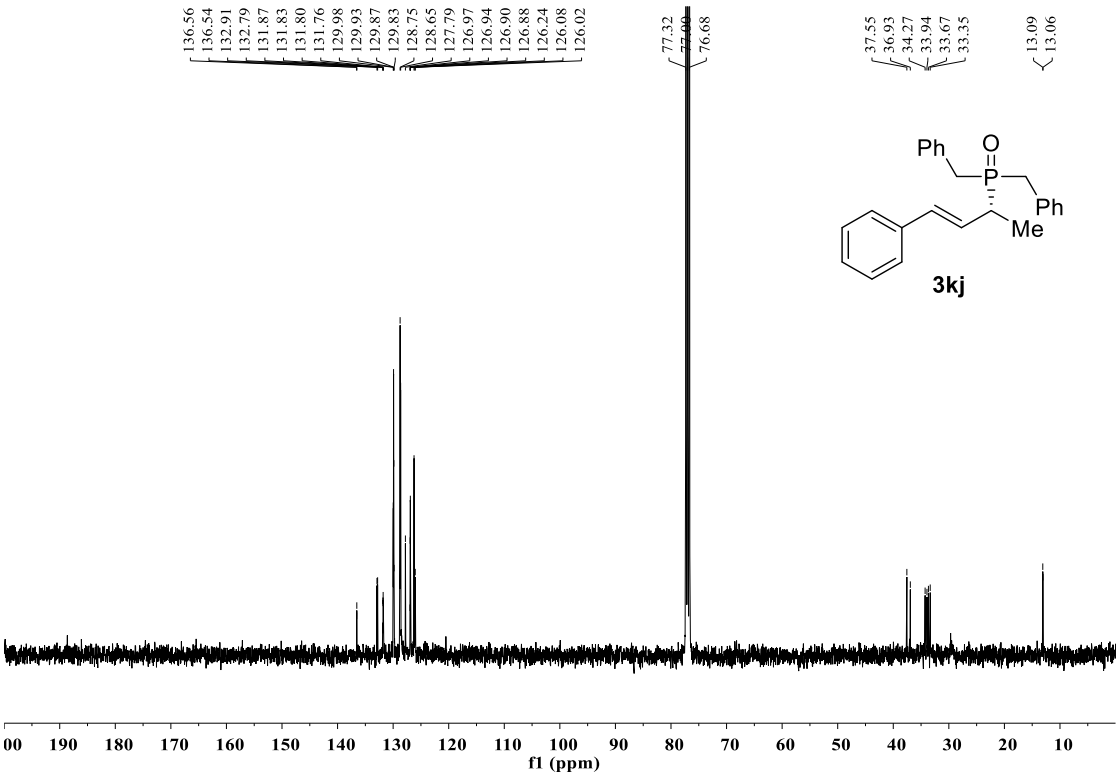

Figure S123. ^{13}C NMR spectra of **3kj**.

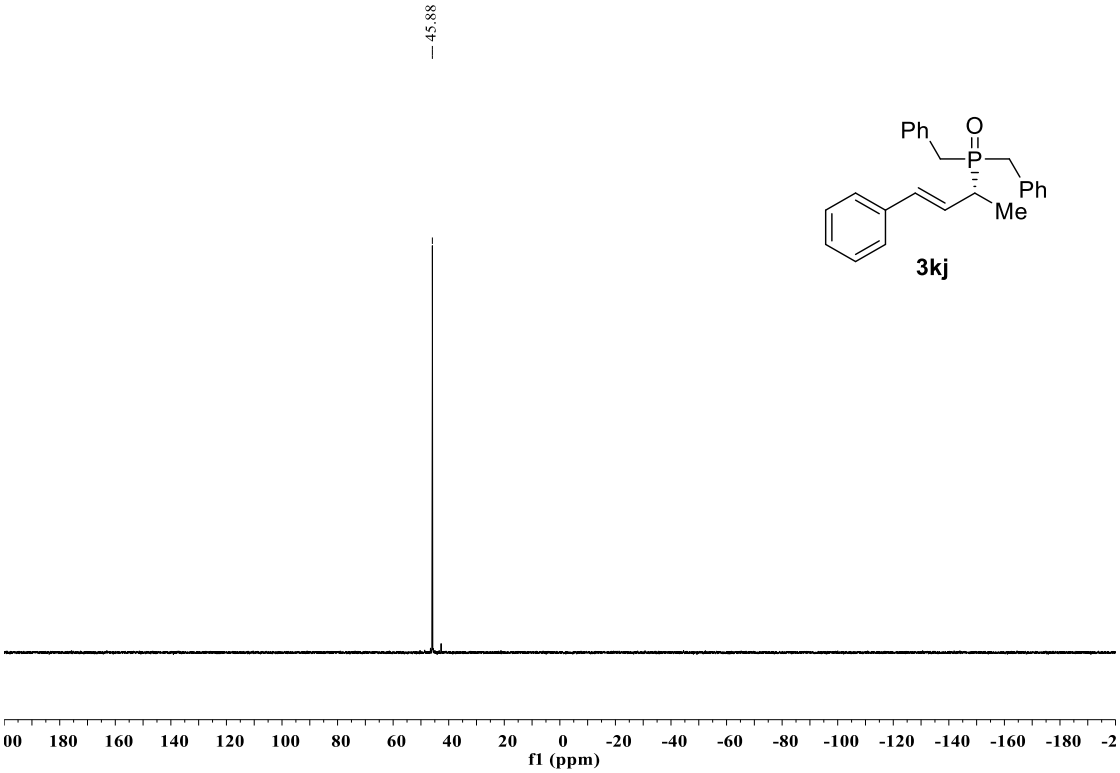

Figure S124. ^{31}P NMR spectra of **3kj**.

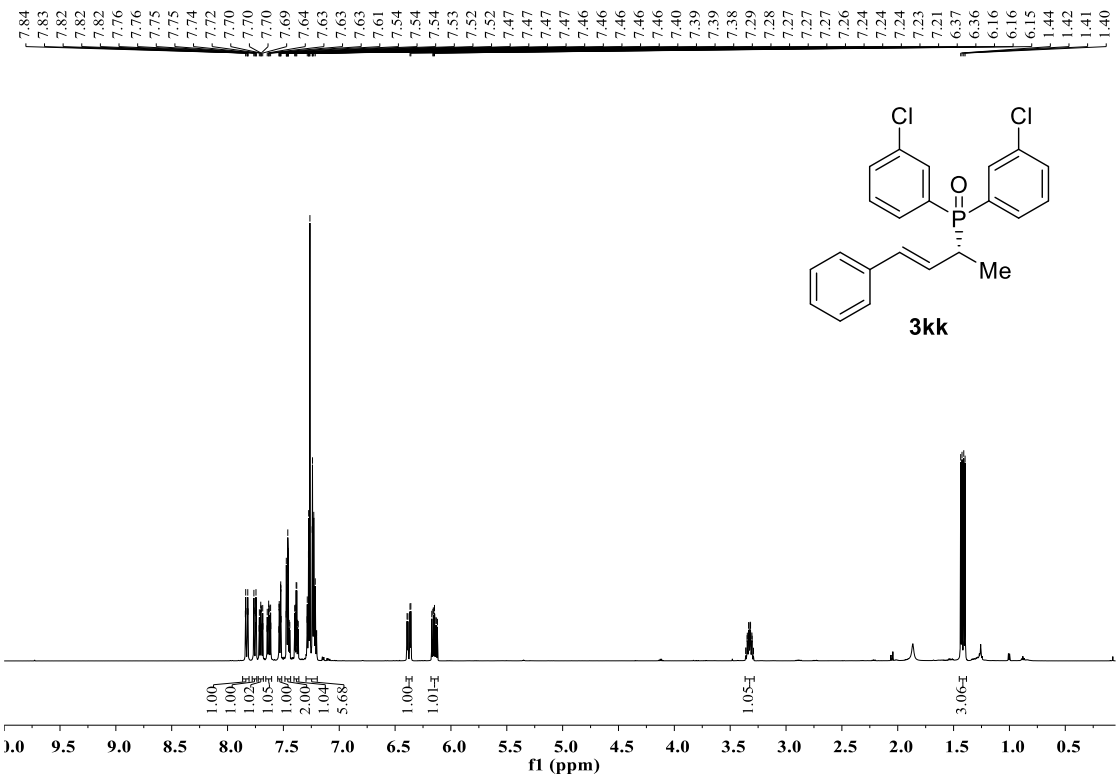

Figure S125. ^{1}H NMR spectra of **3kk**.

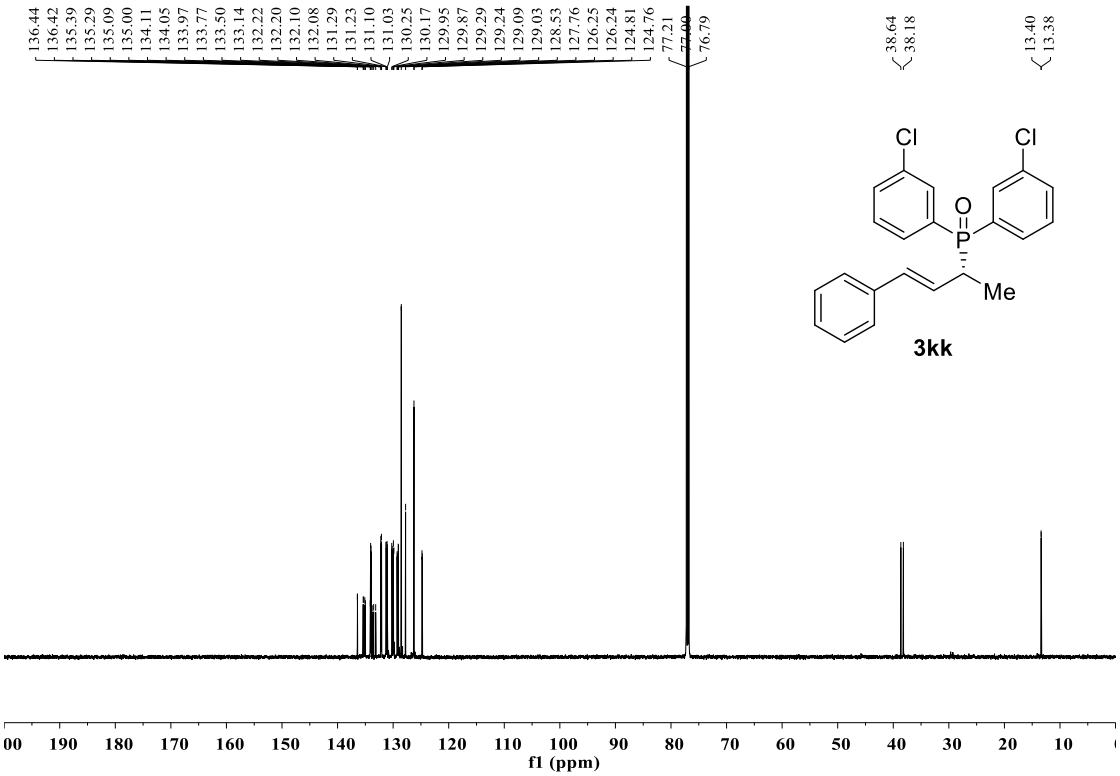

Figure S126. ^{13}C NMR spectra of **3kk**.

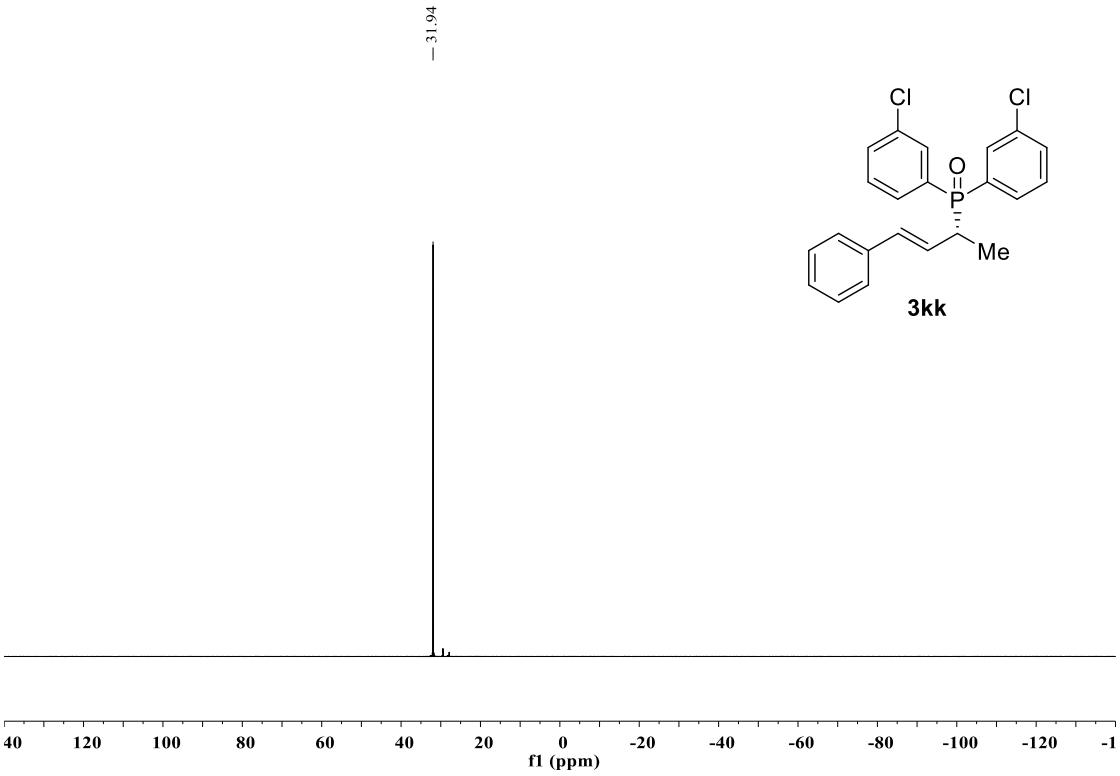

Figure S127. ^{31}P NMR spectra of **3kk**.

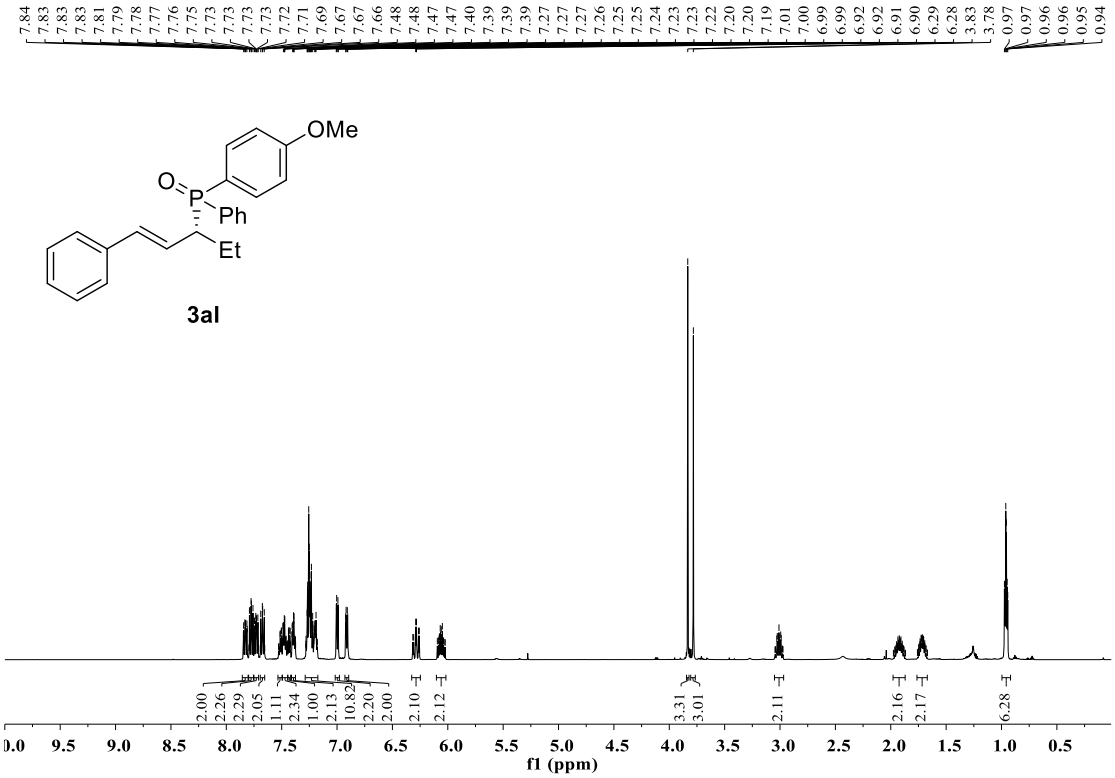

Figure S128. ^{1}H NMR spectra of **3al**.

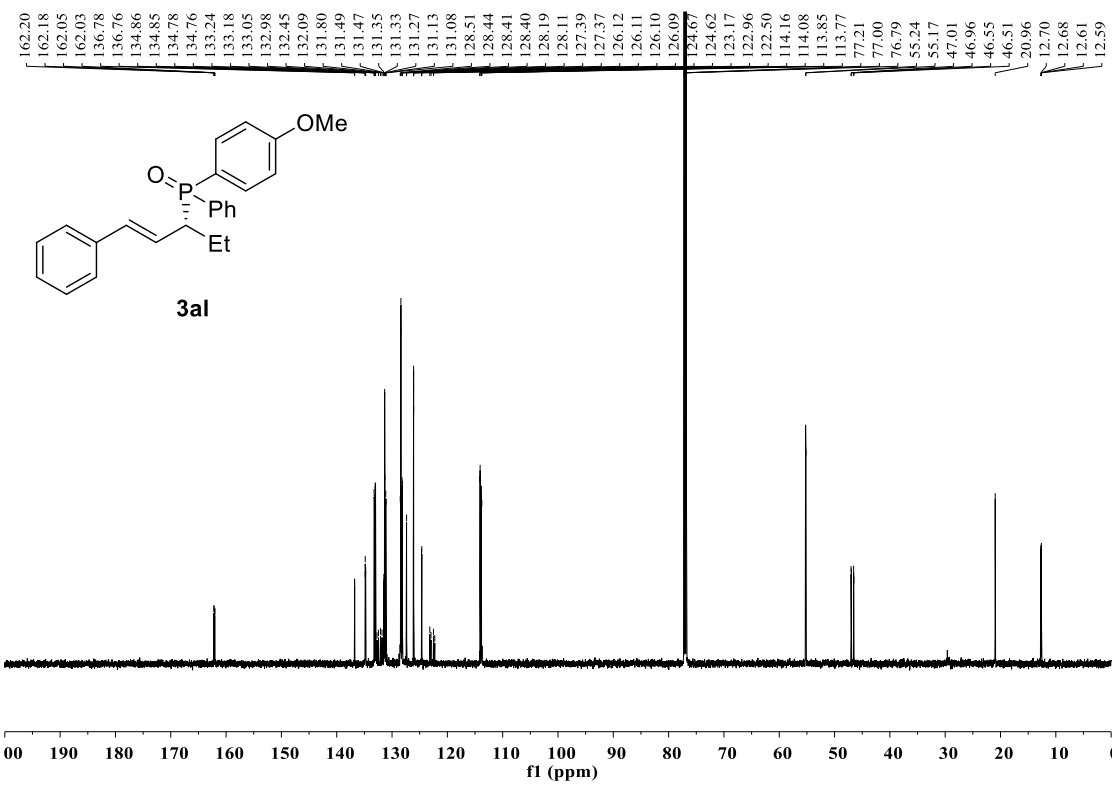

Figure S129. ^{13}C NMR spectra of **3al**.

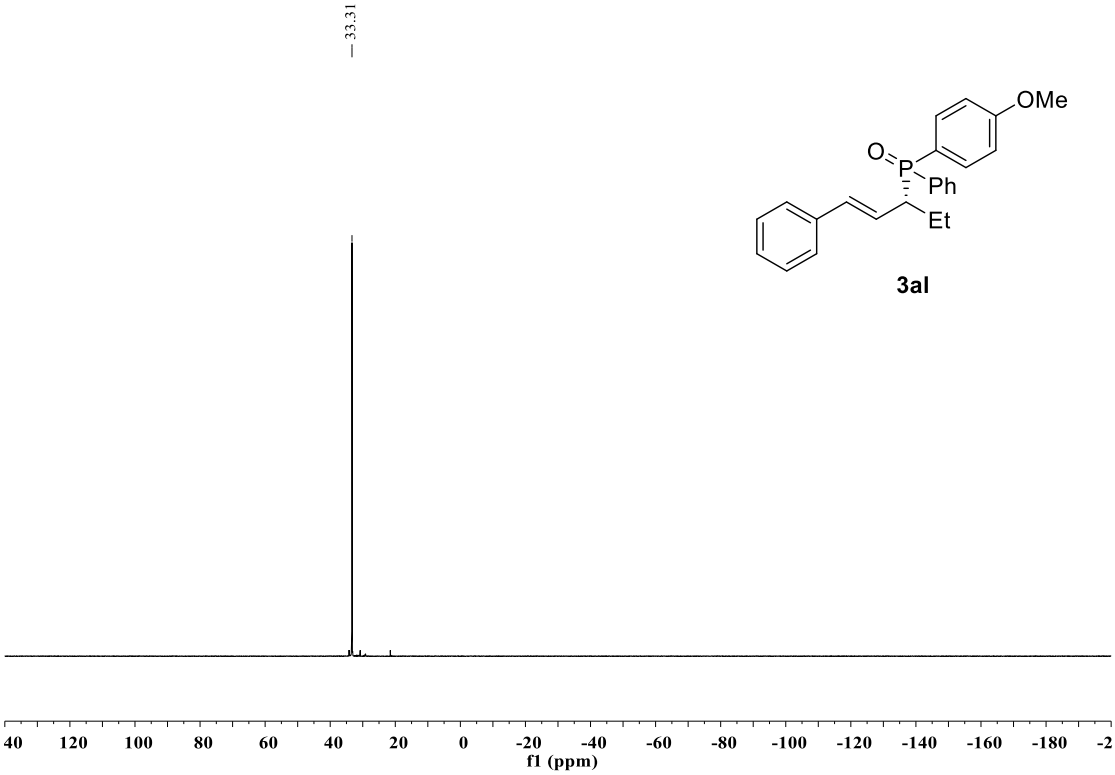

Figure S130. ^{31}P NMR spectra of **3al**.

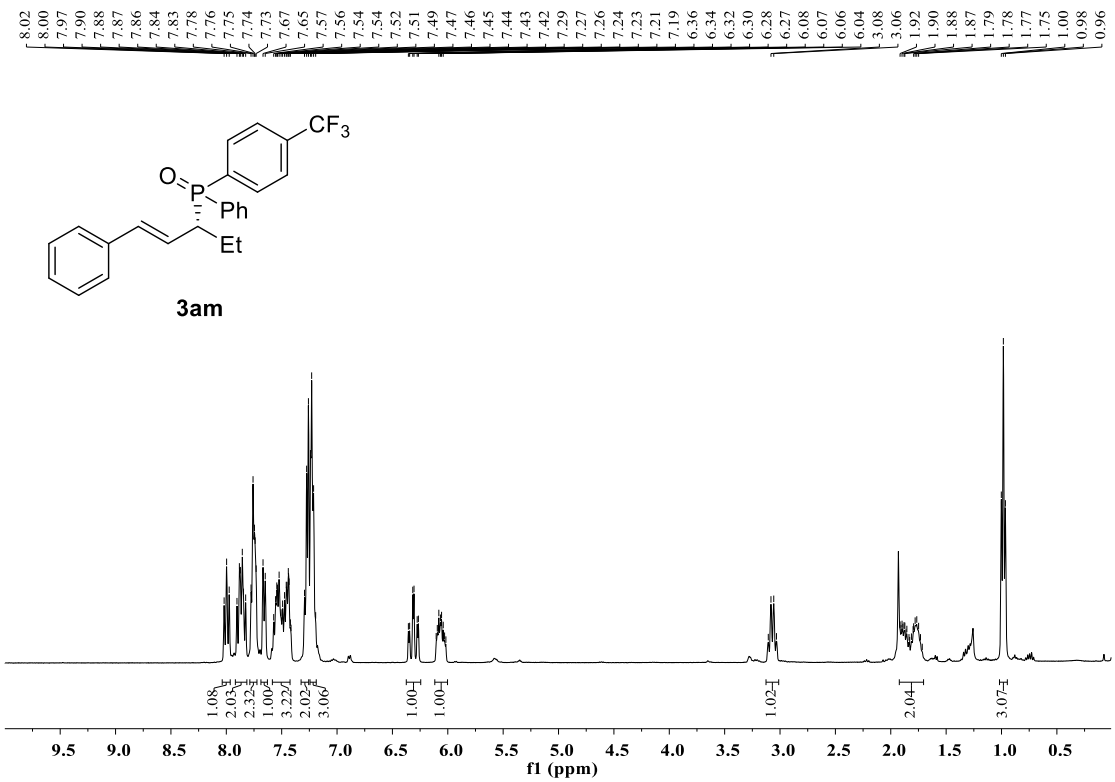

Figure S131. ^{1}H NMR spectra of **3am**.

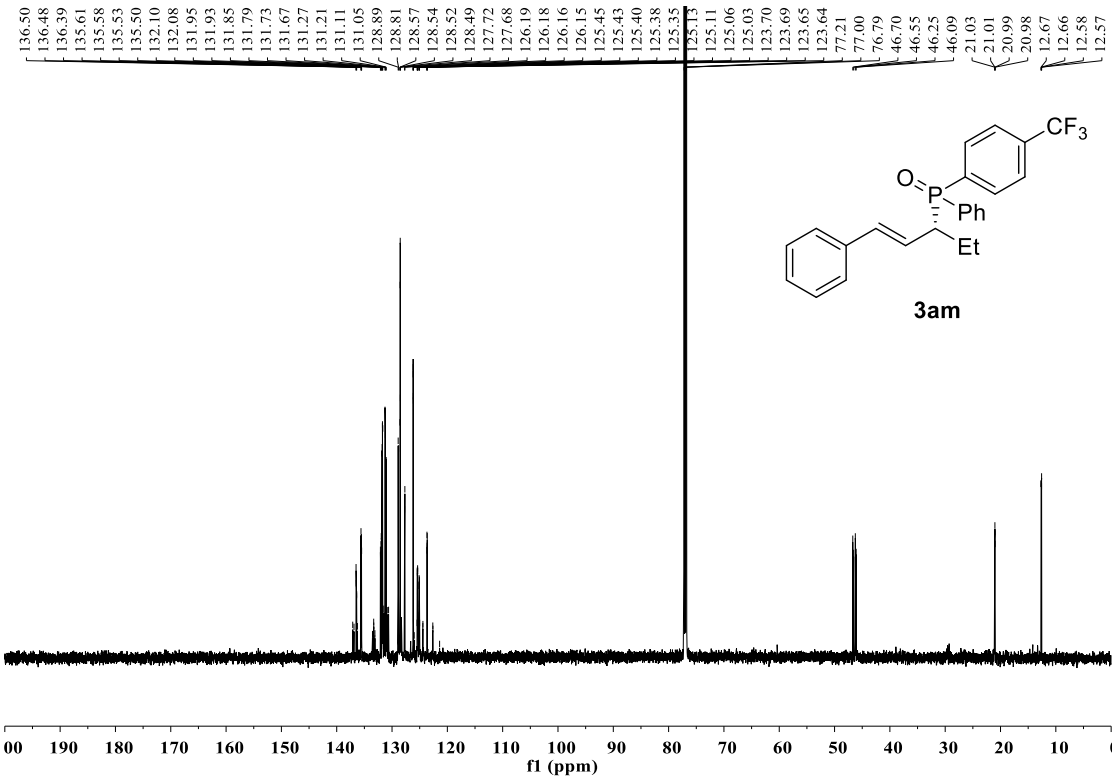

Figure S132. ^{13}C NMR spectra of **3am**.

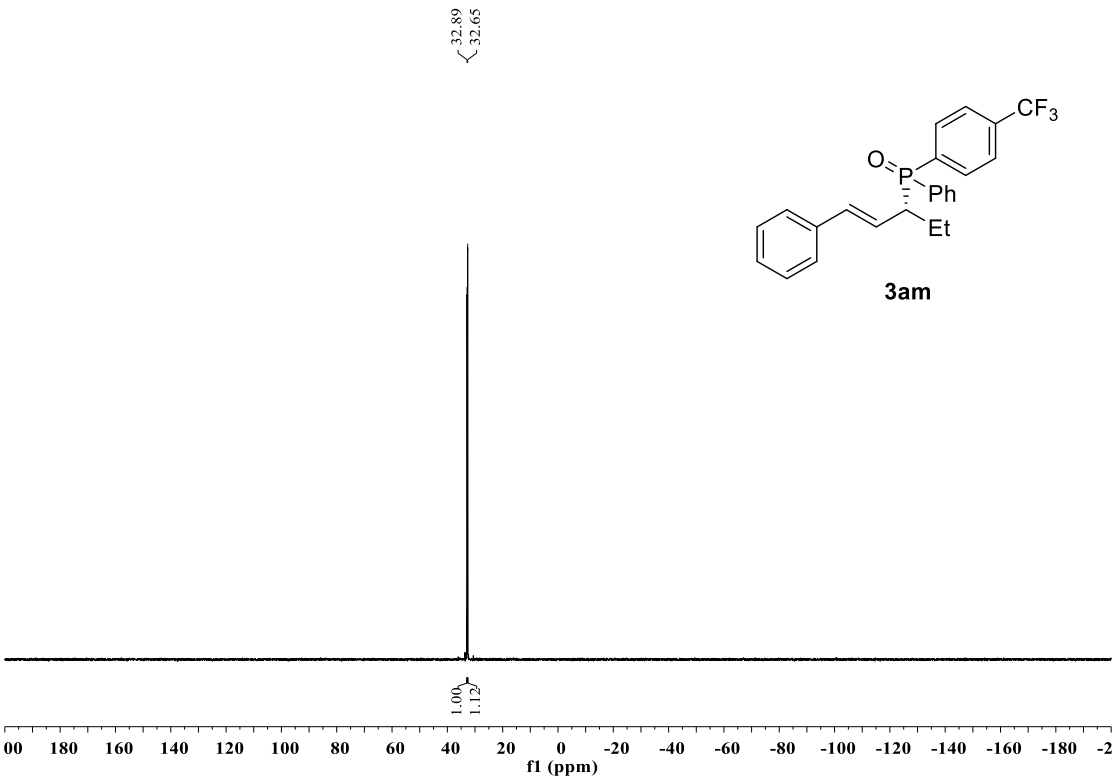

Figure S133. ^{31}P NMR spectra of **3am**.

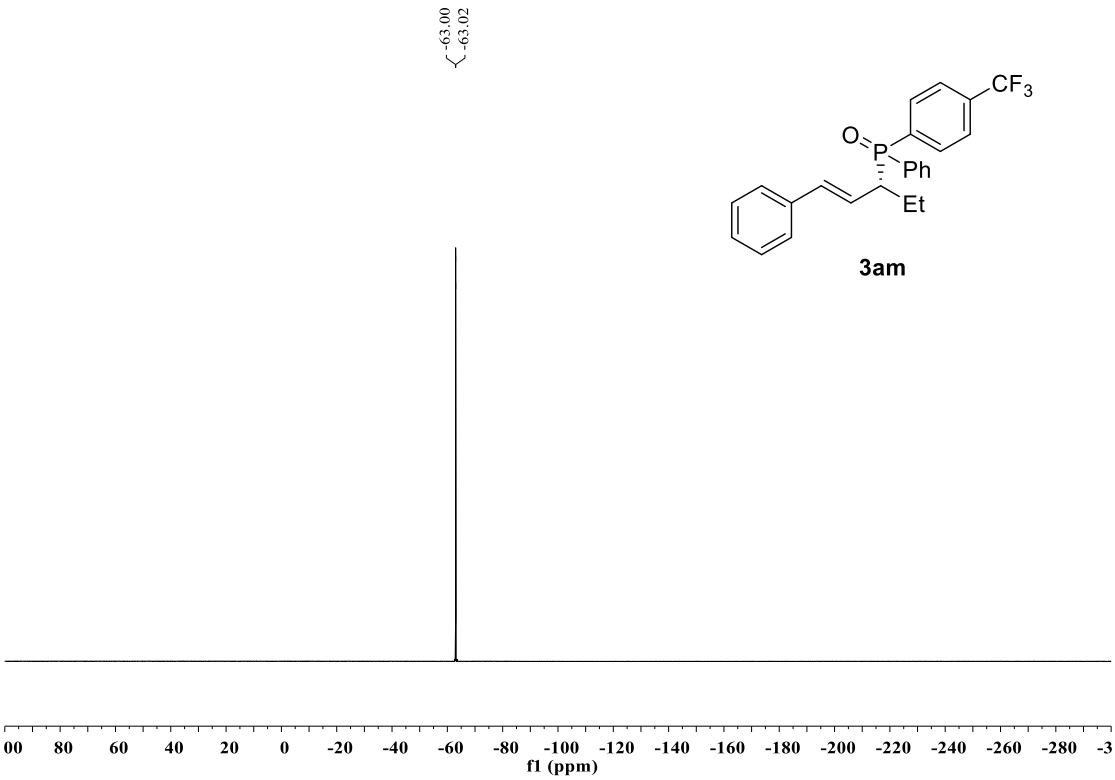

Figure S134. ^{19}F NMR spectra of **3am**.

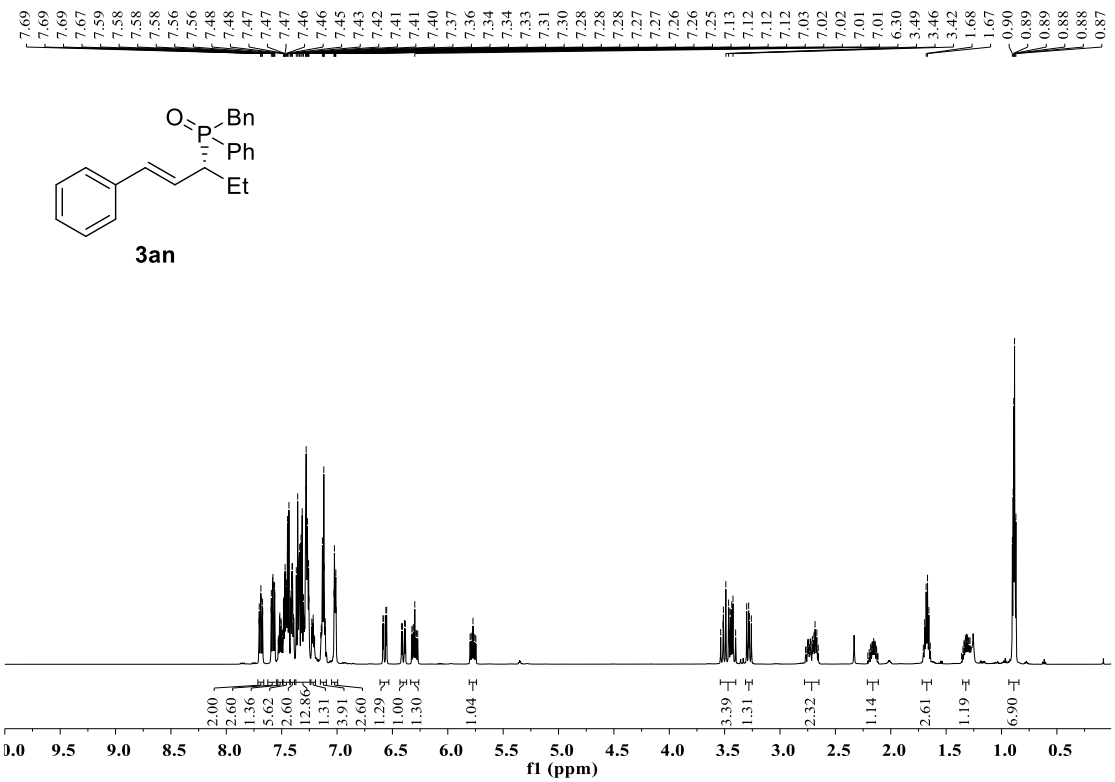

Figure S135. ^{1}H NMR spectra of **3an**.

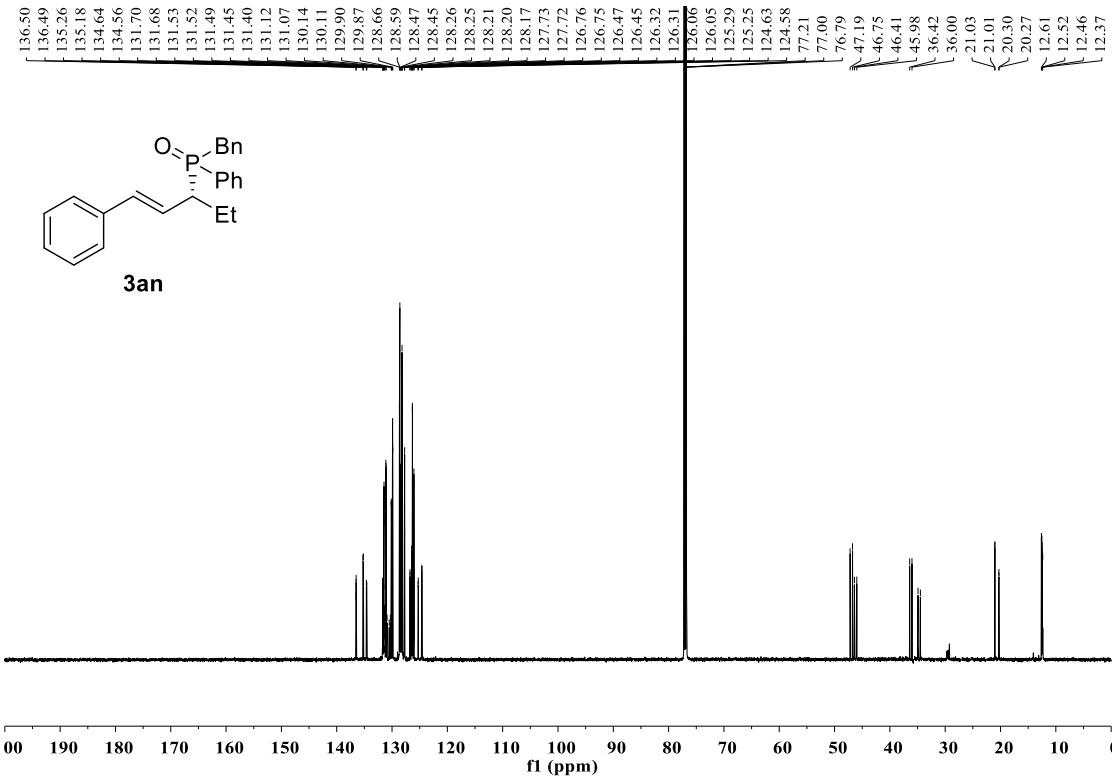

Figure S136. ^{13}C NMR spectra of **3an**.

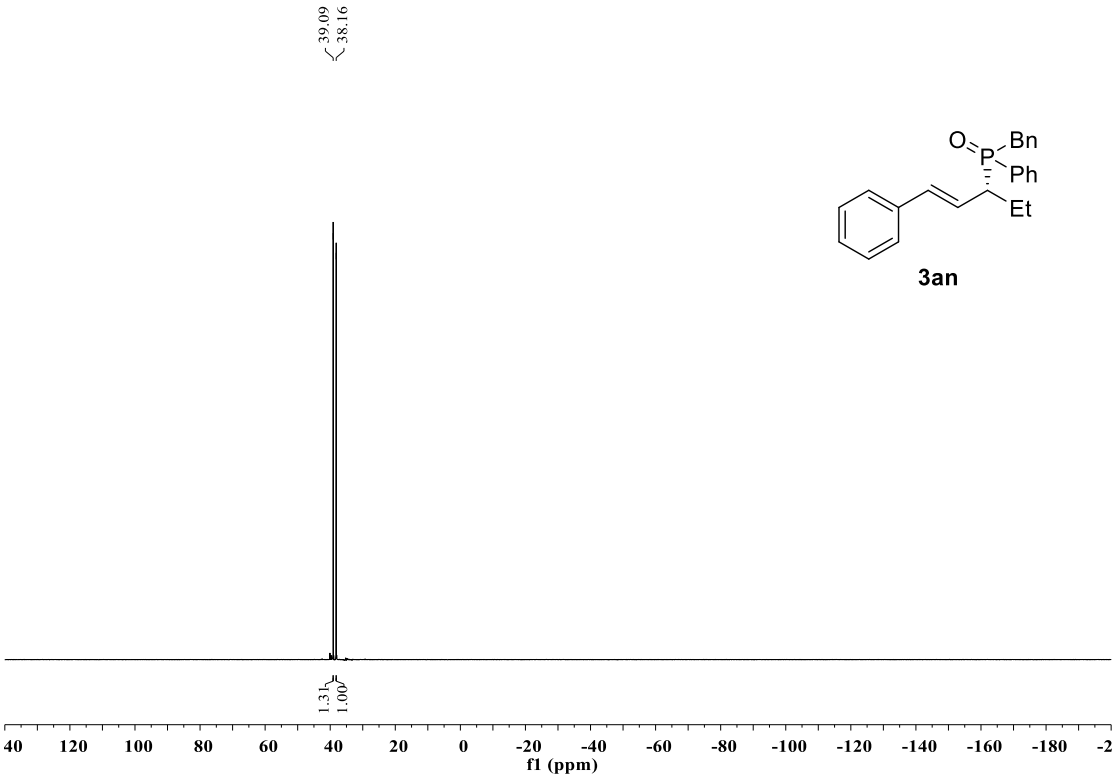

Figure S137. ^{31}P NMR spectra of **3an**.

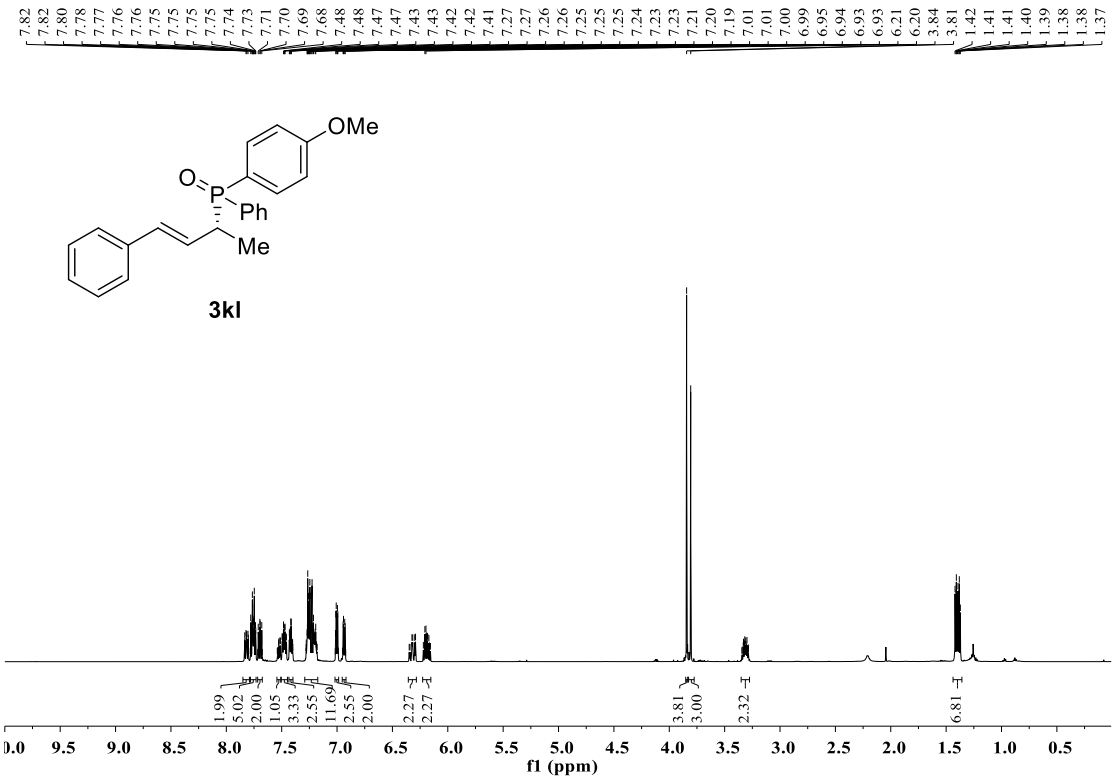

Figure S138. ^{1}H NMR spectra of **3kl**.

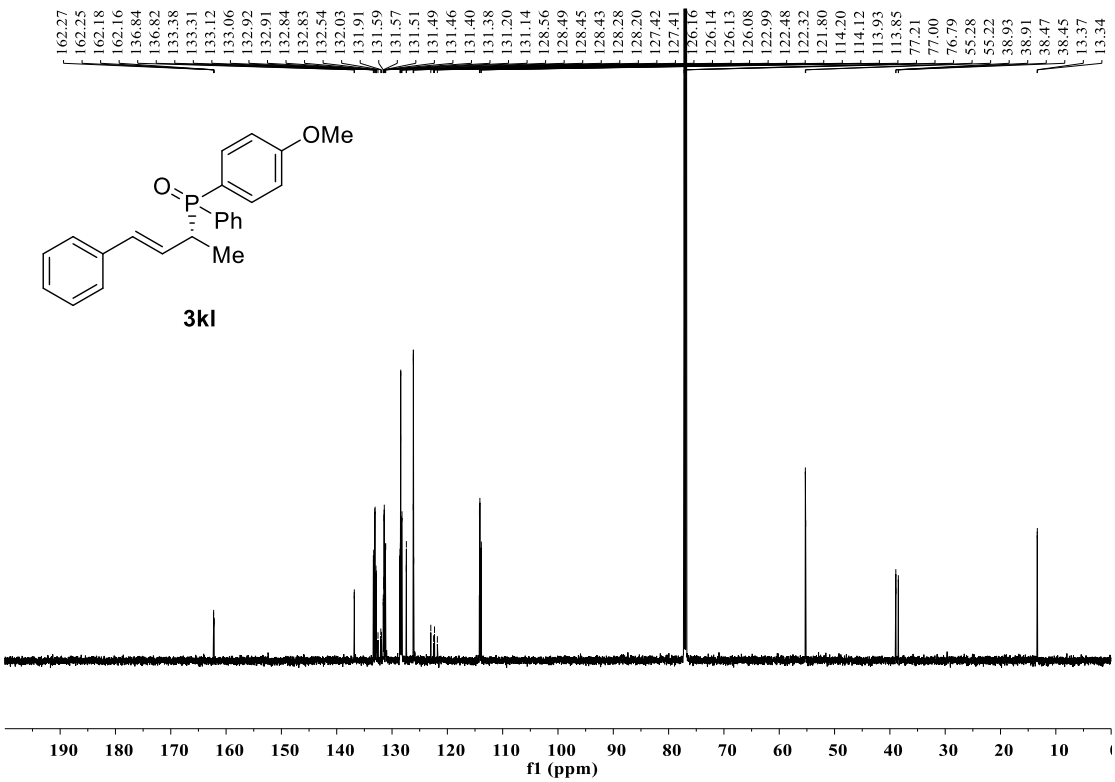

Figure S139. ^{13}C NMR spectra of **3kl**.

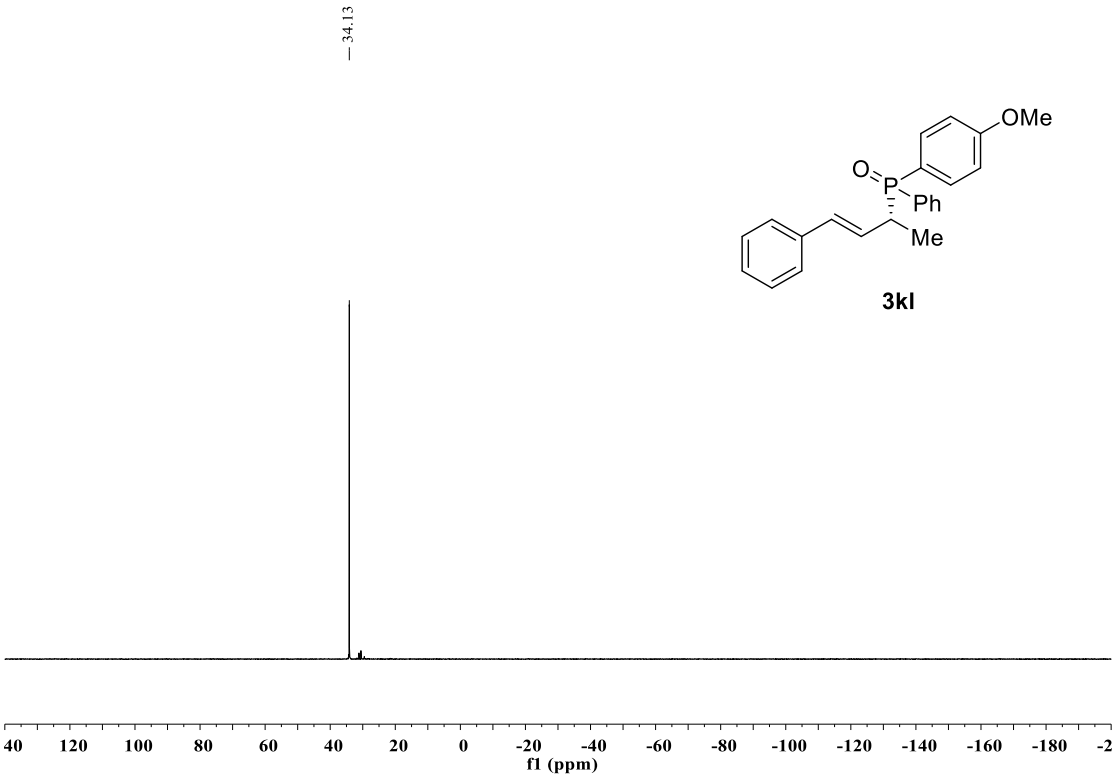

Figure S140. ^{31}P NMR spectra of **3kl**.

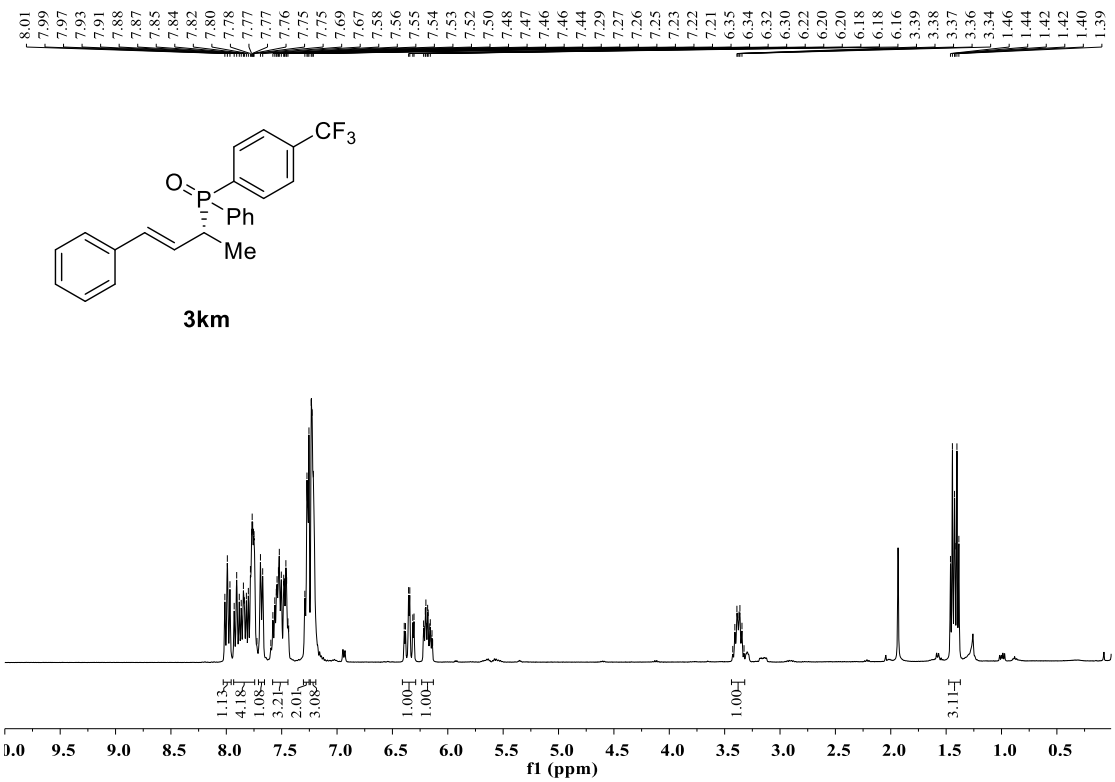

Figure S141. ^{1}H NMR spectra of **3km**.

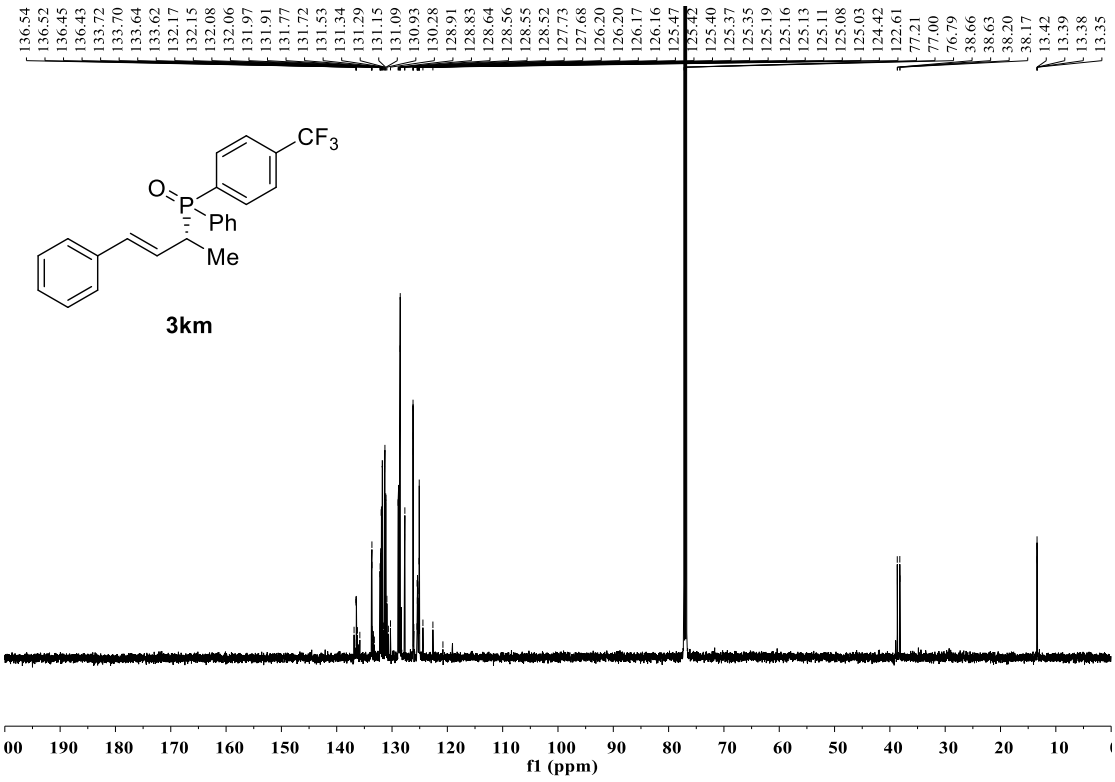

Figure S142. ^{13}C NMR spectra of **3km**.

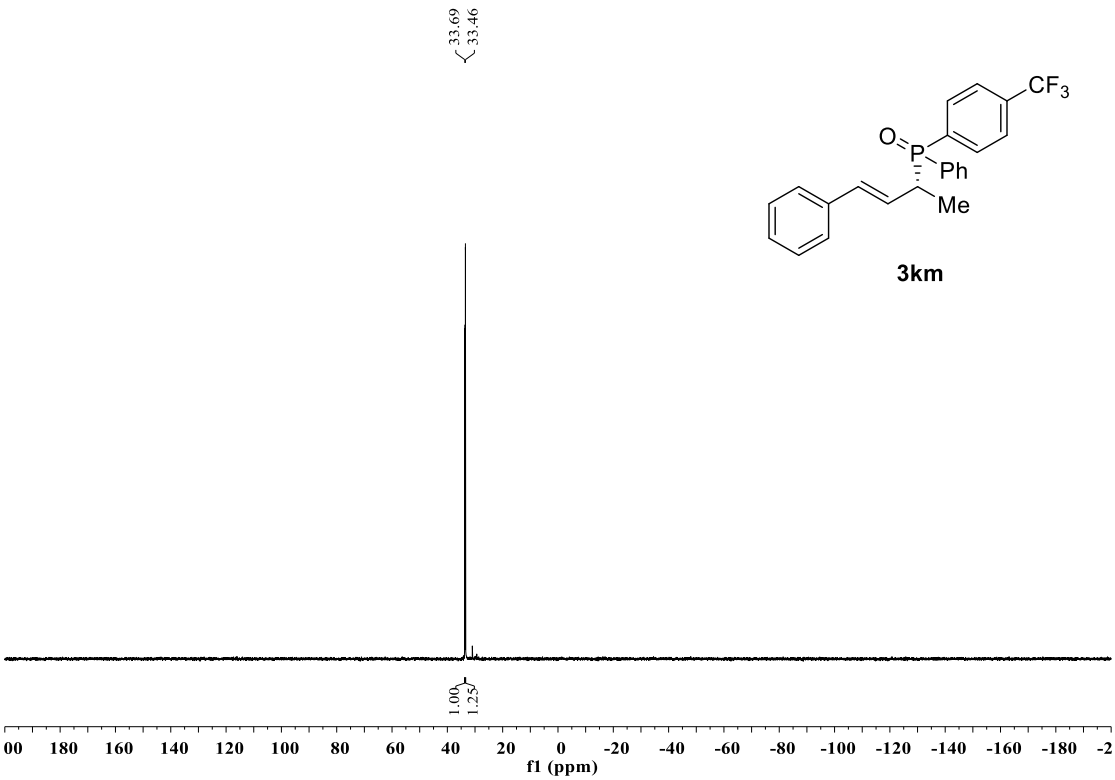

Figure S143. ^{31}P NMR spectra of **3km**.

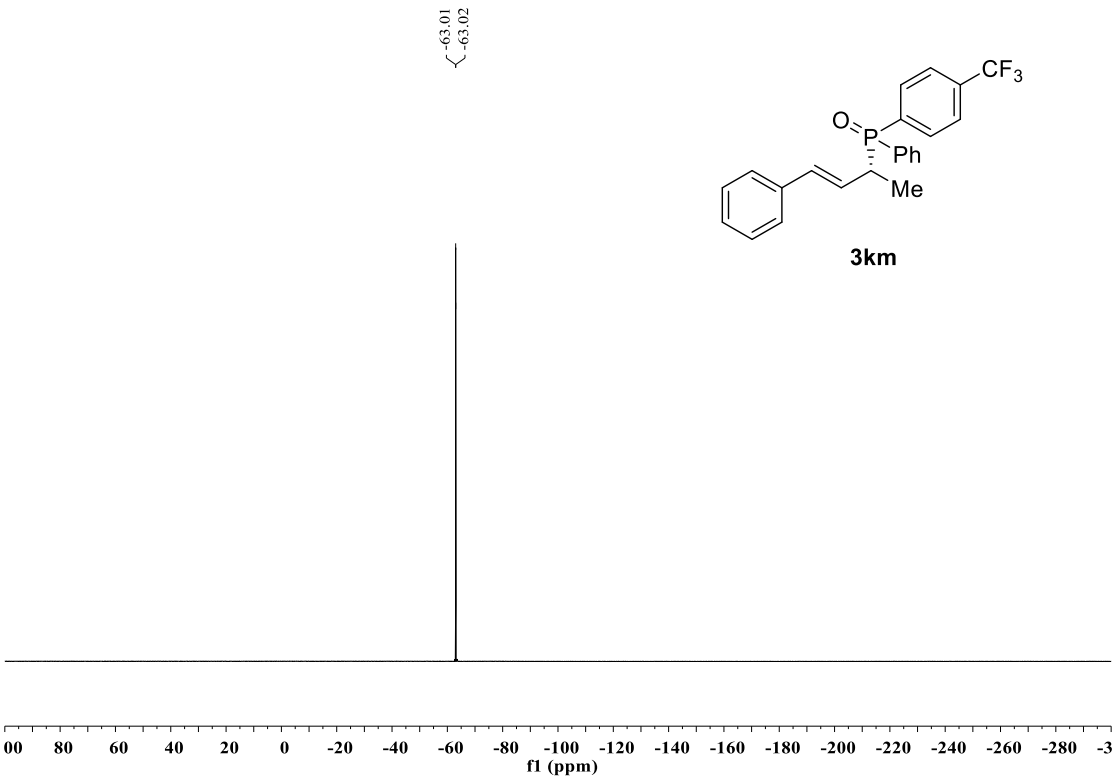

Figure S144. ^{19}F NMR spectra of **3km**.

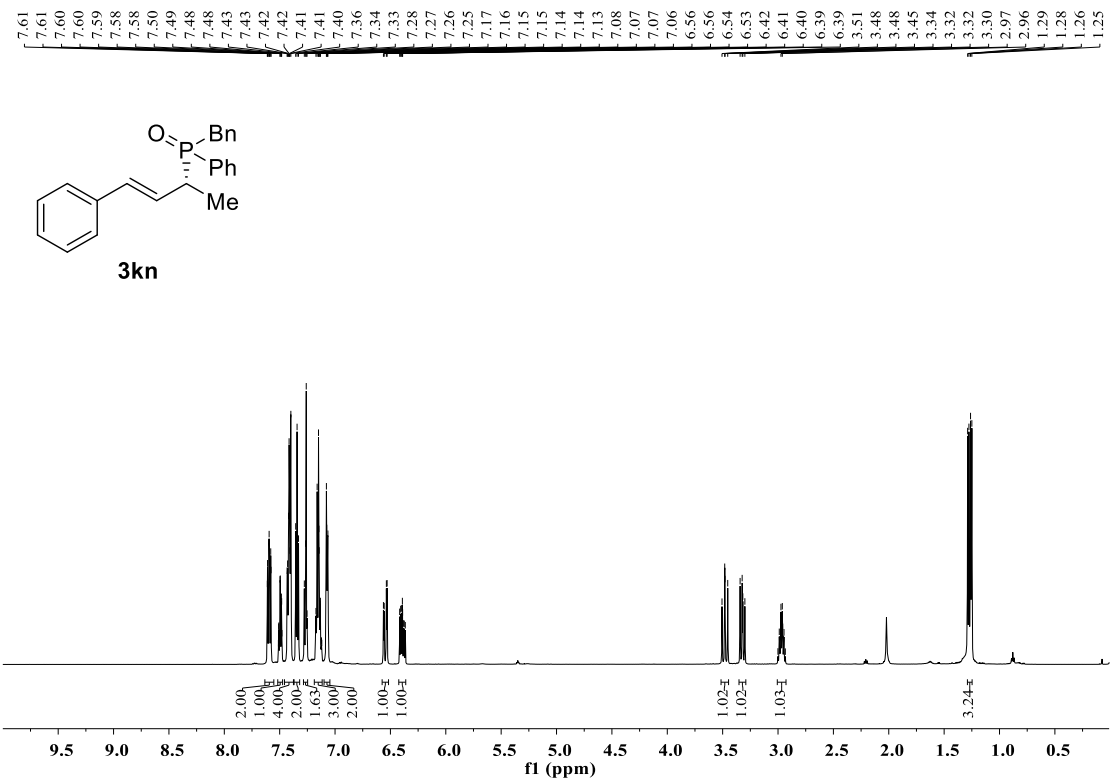

Figure S145. ^{1}H NMR spectra of **3kn**.

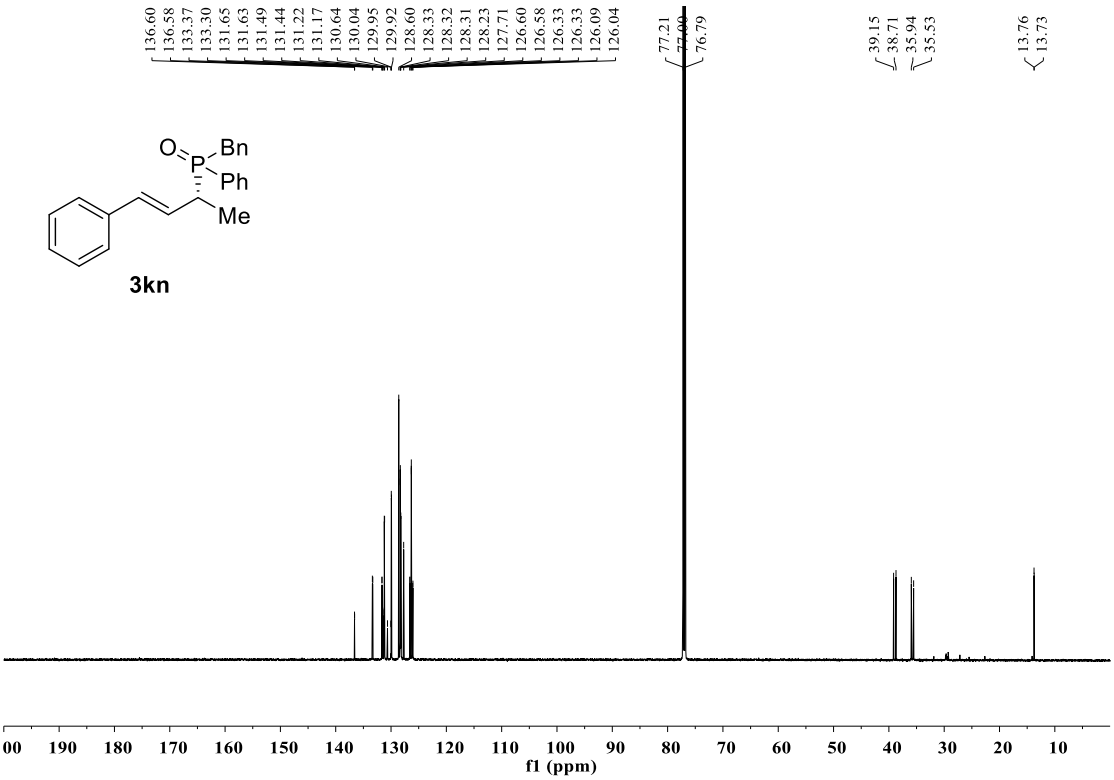

Figure S146. ^{13}C NMR spectra of **3kn**.

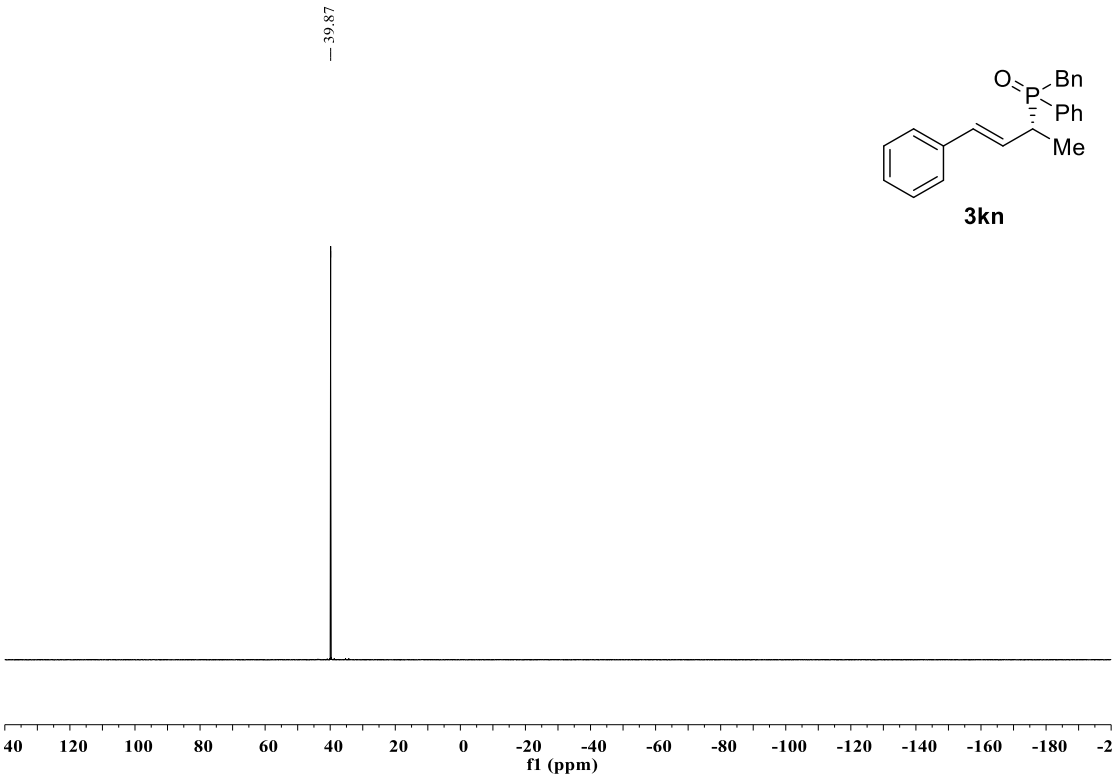

Figure S147. ^{31}P NMR spectra of **3kn**.

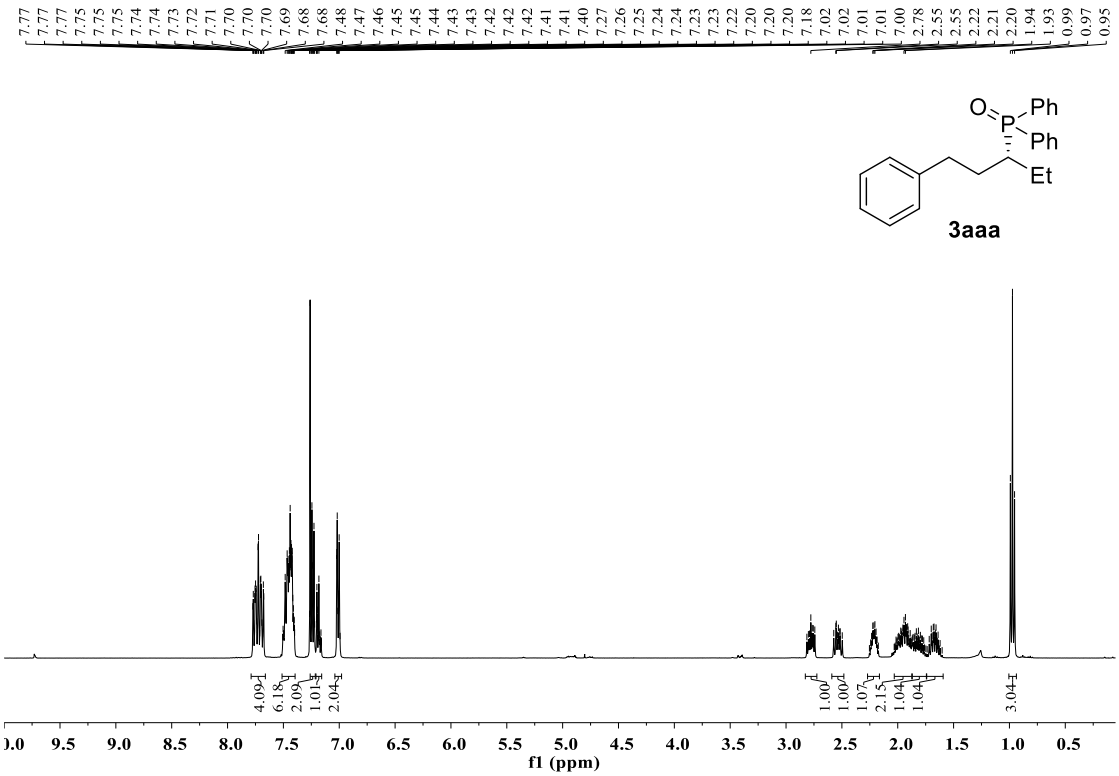

Figure S148. ^{1}H NMR spectra of **3aaa**.

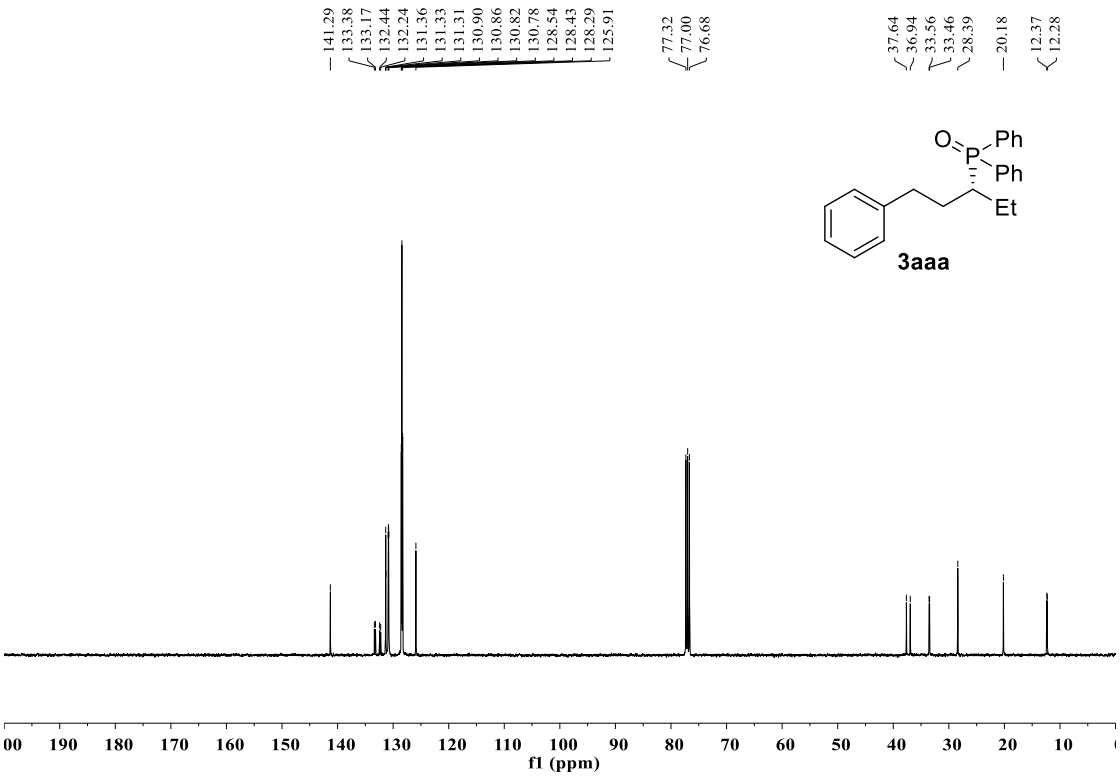

Figure S149. ^{13}C NMR spectra of **3aaa**.

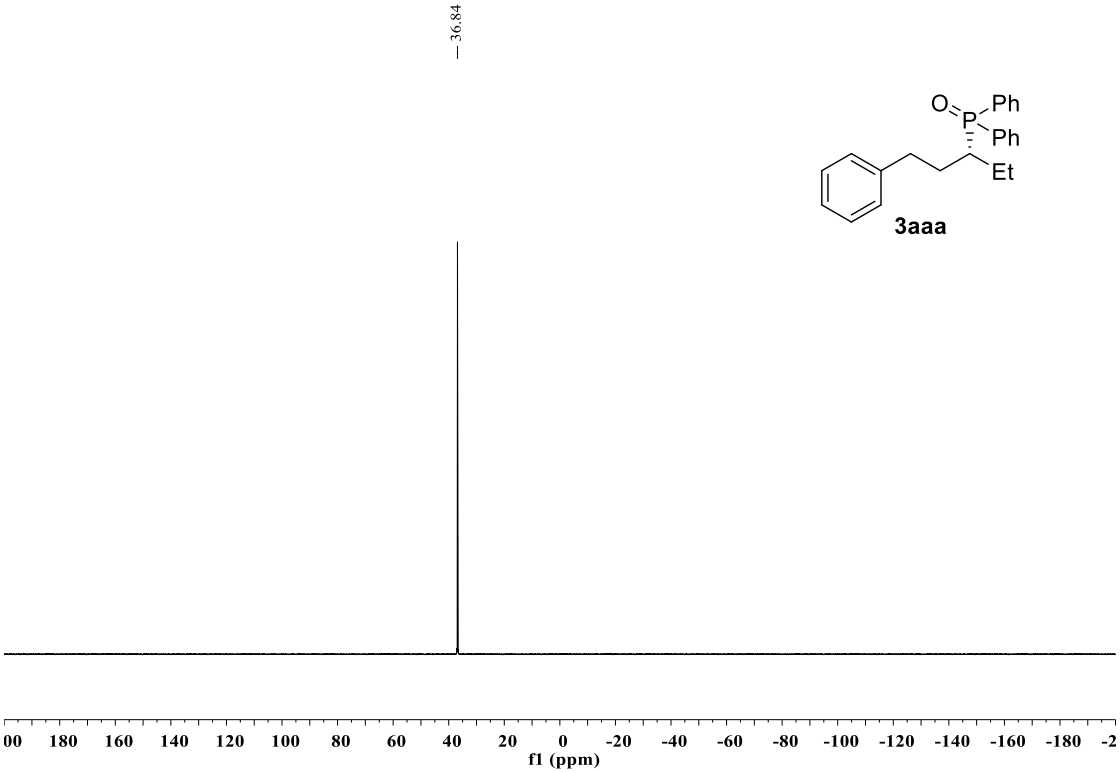

Figure S150. ^{31}P NMR spectra of **3aaa**.

13. HPLC Spectra

```
Data File D:\DATA\LJ\LJ-3-8\LJ-3-8 2020-10-17 22-06-17\009-72-LJ-2-132-2-RAC.D
Sample Name: LJ-2-132-2-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   9
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   72
    Injection Date  : 10/18/2020 1:55:34 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-8\LJ-3-8 2020-10-17 22-06-17\P1-95-5-0.5ML-5UL-220NM-254NM-
                      30MIN.M
    Last changed    : 10/17/2020 10:04:53 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-8\LJ-3-8 2020-10-17 22-06-17\P1-95-5-0.5ML-5UL-220NM-254NM-
                      30MIN.M (Sequence Method)
    Last changed    : 10/18/2020 3:01:51 AM by SYSTEM
                      (modified after loading)
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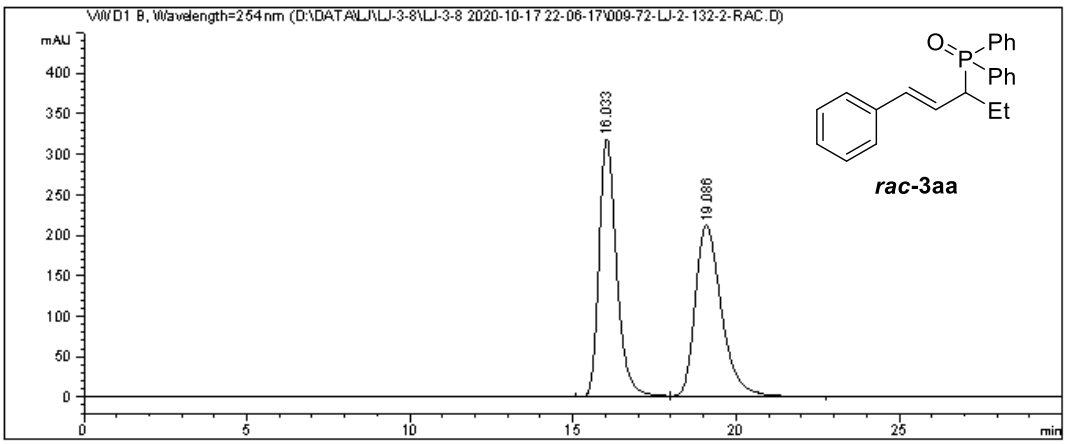


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                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.033 BV    0.5696 1.19378e4   318.28809  50.0390
       2  19.086 VB    0.8681 1.19192e4   211.93512  49.9610

    Totals :                  2.38569e4   530.22321


    ======================================================================
                              *** End of Report ***

1260 10/18/2020 3:01:58 AM SYSTEM                          Page 1 of 1
```

Figure S151. HPLC spectra of ***rac*-3aa**.

```
Data File D:\Data\LJ\LJ-3-8\LJ-3-8 2020-10-17 22-06-17\008-71-LJ-2-132-2.D
Sample Name: LJ-2-132-2
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   71
    Injection Date  : 10/18/2020 1:24:51 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-8\LJ-3-8 2020-10-17 22-06-17\P1-95-5-0.5ML-5UL-220NM-254NM-
                      30MIN.M
    Last changed    : 10/17/2020 10:04:53 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-8\LJ-3-8 2020-10-17 22-06-17\P1-95-5-0.5ML-5UL-220NM-254NM-
                      30MIN.M (Sequence Method)
    Last changed    : 10/18/2020 3:04:16 AM by SYSTEM
                      (modified after loading)
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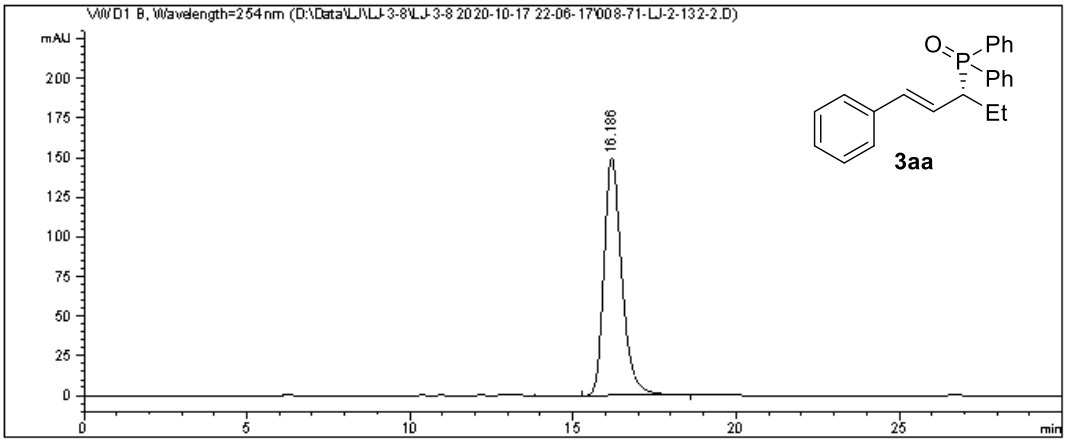


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    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.186 BB    0.5797 5700.87891  149.88394 100.0000

    Totals :                  5700.87891  149.88394


    ======================================================================
                              *** End of Report ***


1260 10/18/2020 3:04:20 AM SYSTEM                          Page 1 of 1
```

Figure S152. HPLC spectra of **3aa**.

```
Data File D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\006-72-LJ-2-195-RAC.D
Sample Name: LJ-2-195-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   72
    Injection Date  : 10/7/2020 10:25:29 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P1-95-5-1.0ML-5UL-220NM-
                      254NM-30MIN.M
    Last changed    : 10/7/2020 10:22:46 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P1-95-5-1.0ML-5UL-220NM-
                      254NM-30MIN.M (Sequence Method)
    Last changed    : 10/15/2020 8:42:23 AM by SYSTEM
                      (modified after loading)
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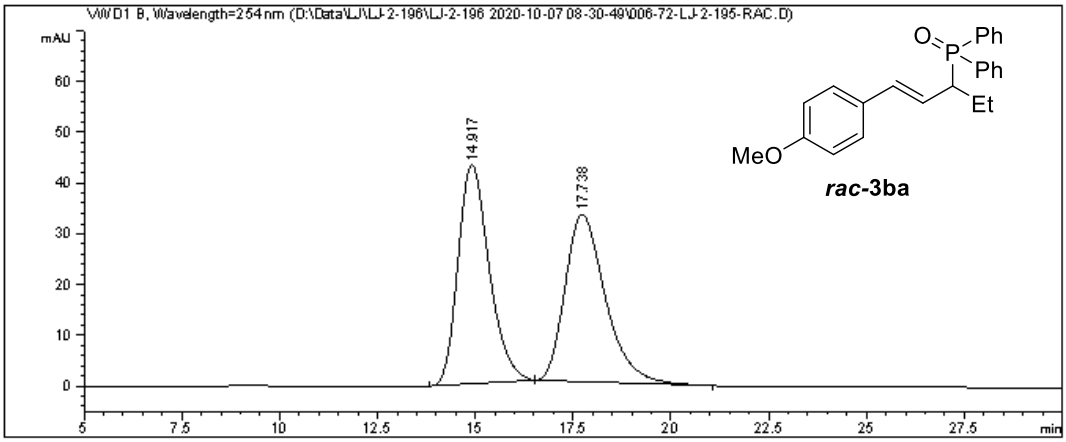

***rac*-3ba**

```
    ======================================================================
                              Area Percent Report
    ======================================================================

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    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.917 BB    0.8539 2394.27393   43.11356  50.3637
       2  17.738 BB    1.1058 2359.69214   32.85833  49.6363

    Totals :                  4753.96606   75.97188

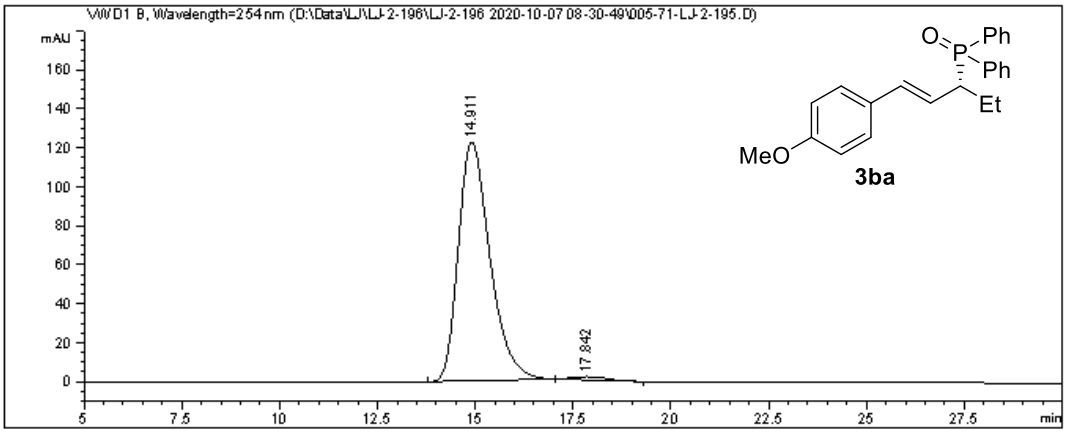

    ======================================================================
                              *** End of Report ***

1260 10/15/2020 8:42:39 AM SYSTEM                          Page 1 of 1
```

Figure S153. HPLC spectra of ***rac*-3ba**.

Data File D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\005-71-LJ-2-195.D
Sample Name: LJ-2-195

Acq. Operator	: SYSTEM	Seq. Line :	5
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location :	71
Injection Date	: 10/7/2020 9:54:47 AM	Inj :	1
		Inj Volume :	5.000 µl
Acq. Method	: D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P1-95-5-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 10/7/2020 10:22:46 AM by SYSTEM (modified after loading)		
Analysis Method	: D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P1-95-5-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 10/15/2020 8:43:53 AM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.911	BB	0.8631	6900.83252	122.52628	98.4446
2	17.842	BB	0.9353	109.03064	1.82416	1.5554
Totals :				7009.86316	124.35044	

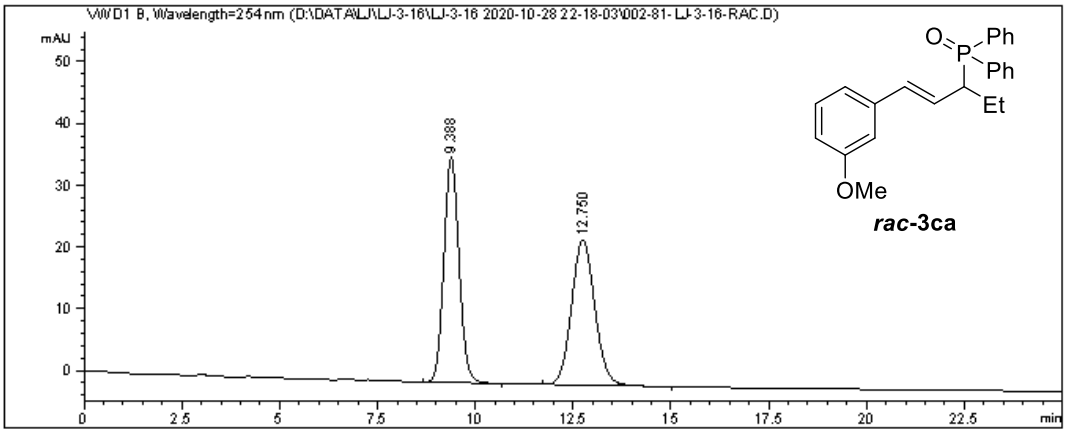
*** End of Report ***

1260 10/15/2020 8:43:59 AM SYSTEM

Figure S154. HPLC spectra of **3ba**.

Data File D:\DATA\LJ\LJ-3-16\LJ-3-16 2020-10-28 22-18-03\002-81-LJ-3-16-RAC.D
Sample Name: LJ-3-16-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 81
Injection Date	: 10/28/2020 10:30:07 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-16\LJ-3-16 2020-10-28 22-18-03\P2-85-15-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 10/28/2020 10:46:29 PM by SYSTEM (modified after loading)		
Analysis Method	: D:\Data\LJ\LJ-3-16\LJ-3-16 2020-10-28 22-18-03\P2-85-15-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 10/28/2020 11:44:57 PM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.388	BB	0.4203	984.67834	36.55403	50.2927
2	12.750	BB	0.6473	973.21716	23.49186	49.7073
Totals :				1957.89551	60.04589	

*** End of Report ***

1260 10/28/2020 11:45:07 PM SYSTEM Page 1 of 1

Figure S155. HPLC spectra of ***rac*-3ca**.

Data File D:\Data\LJ\LJ-3-16\LJ-3-16 2020-10-28 22-18-03\003-82-LJ-3-16.D
Sample Name: LJ-3-16

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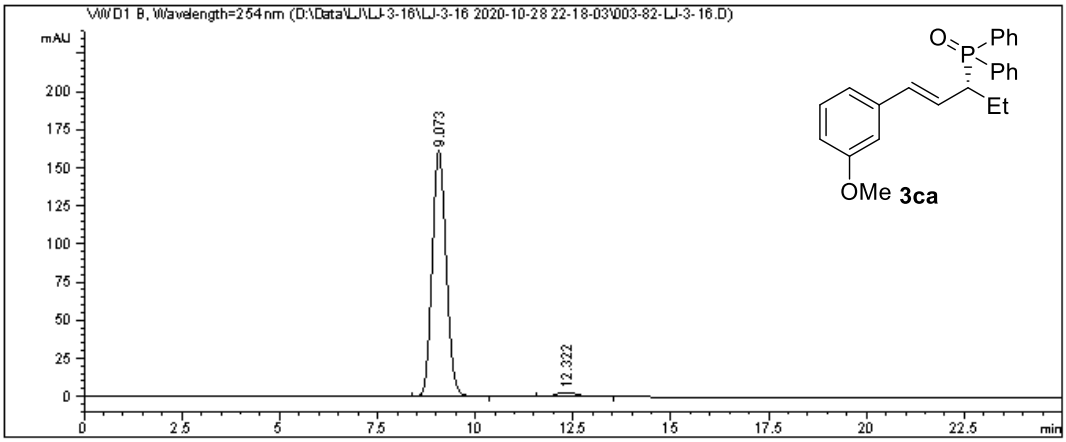
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 82
Injection Date	: 10/28/2020 10:55:50 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-16\LJ-3-16 2020-10-28 22-18-03\P2-85-15-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 10/28/2020 10:46:29 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-16\LJ-3-16 2020-10-28 22-18-03\P2-85-15-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 10/28/2020 11:47:19 PM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.073	BB	0.3833	3971.97510	161.29582	97.2567
2	12.322	BB	0.5950	112.03732	2.92413	2.7433
Totals :				4084.01242	164.21995	

*** End of Report ***

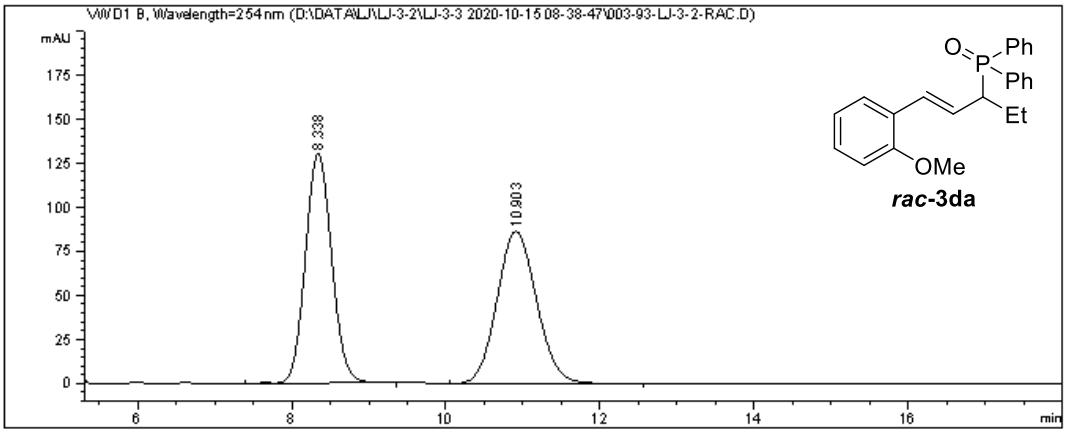
1260 10/28/2020 11:47:27 PM SYSTEM Page 1 of 1

Figure S156. HPLC spectra of **3ca**.

Data File D:\DATA\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\003-93-LJ-3-2-RAC.D
Sample Name: LJ-3-2-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 3
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 93
Injection Date	: 10/15/2020 9:06:11 AM	Inj	: 1
		Inj Volume	: 5.000 µl

Acq. Method : D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-85-15-1.0ML-5UL-220NM-254NM-30MIN.M
Last changed : 10/15/2020 8:59:14 AM by SYSTEM
Analysis Method : D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-85-15-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)
Last changed : 10/15/2020 9:31:56 AM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated



***rac*-3da**

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.338	VB R	0.3707	3081.69141	129.95374	50.0623
2	10.903	BB	0.5554	3074.02612	86.34139	49.9377
Totals :				6155.71753	216.29513	

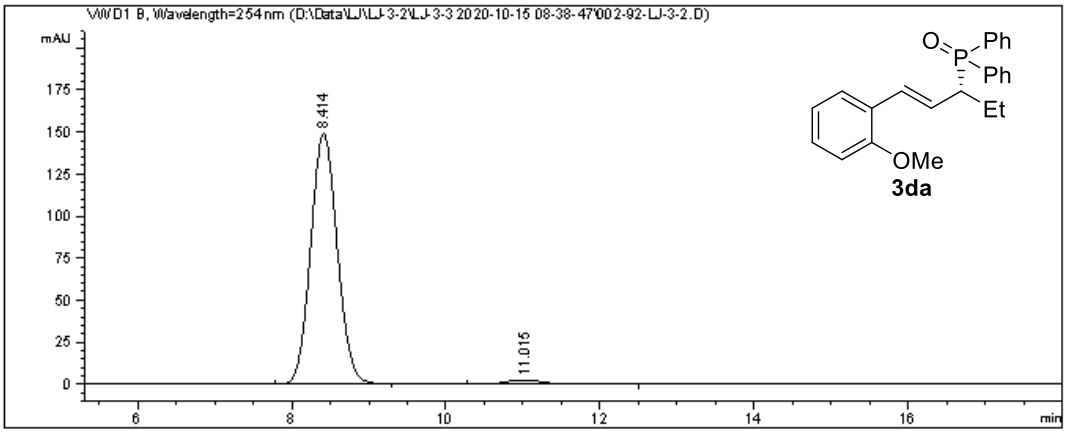
*** End of Report ***

1260 10/15/2020 9:32:03 AM SYSTEM

Figure S157. HPLC spectra of ***rac*-3da**.

Data File D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\002-92-LJ-3-2.D
Sample Name: LJ-3-2

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 92
Injection Date	: 10/15/2020 8:45:27 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-85-15-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 10/15/2020 8:59:14 AM by SYSTEM (modified after loading)		
Analysis Method	: D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-85-15-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 10/15/2020 9:38:36 AM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.414	BB	0.3727	3553.77881	148.78304	97.7306
2	11.015	BB	0.5579	82.52254	2.30399	2.2694
Totals :				3636.30135	151.08703	

*** End of Report ***

1260 10/15/2020 9:38:40 AM SYSTEM

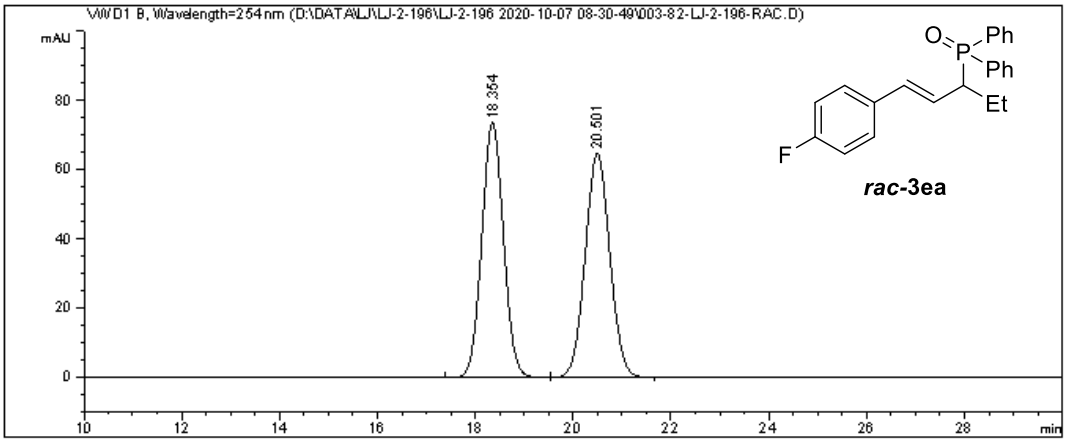
Page 1 of 1

Figure S158. HPLC spectra of **3da**.

Data File D:\DATA\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\003-82-LJ-2-196-RAC.D
Sample Name: LJ-2-196-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 3
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 82
Injection Date	: 10/7/2020 9:13:11 AM	Inj	: 1
		Inj Volume	: 5.000 µl

Acq. Method : D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P2-80-20-1.0ML-5UL-220NM-254NM-40MIN.M
Last changed : 10/7/2020 9:12:02 AM by SYSTEM
Analysis Method : D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P2-80-20-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)
Last changed : 10/7/2020 10:01:24 AM by SYSTEM (modified after loading)



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.354	BB	0.4798	2258.16870	73.62626	49.9582
2	20.501	BB	0.5414	2261.95190	64.77413	50.0418
Totals :				4520.12061	138.40039	

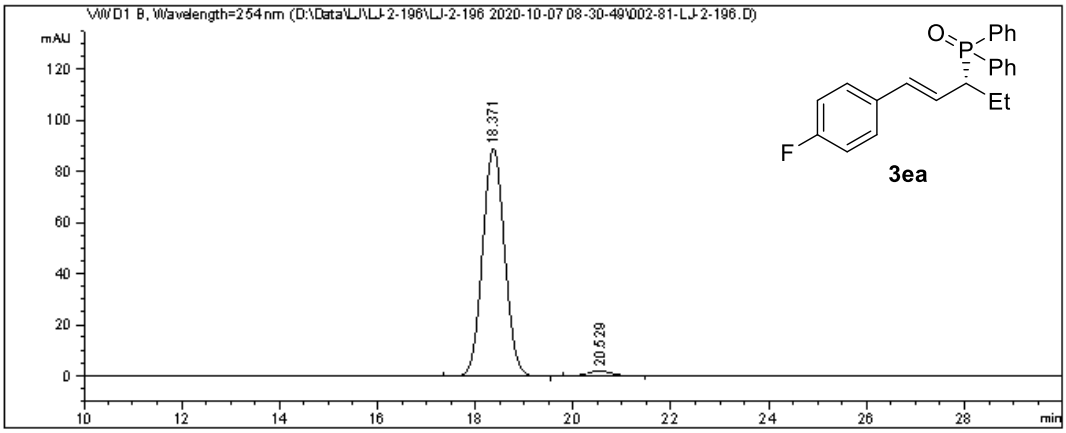
*** End of Report ***

1260 10/7/2020 10:01:34 AM SYSTEM Page 1 of 1

Figure S159. HPLC spectra of ***rac*-3ea**.

Data File D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\002-81-LJ-2-196.D
Sample Name: LJ-2-196

Acq. Operator	: SYSTEM	Seq. Line :	2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location :	81
Injection Date	: 10/7/2020 8:42:28 AM	Inj :	1
		Inj Volume :	5.000 µl
Acq. Method	: D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P2-80-20-1.0ML-5UL-220NM-254NM-40MIN.M		
Last changed	: 10/7/2020 9:12:02 AM by SYSTEM (modified after loading)		
Analysis Method	: D:\Data\LJ\LJ-2-196\LJ-2-196 2020-10-07 08-30-49\P2-80-20-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)		
Last changed	: 10/7/2020 10:03:22 AM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

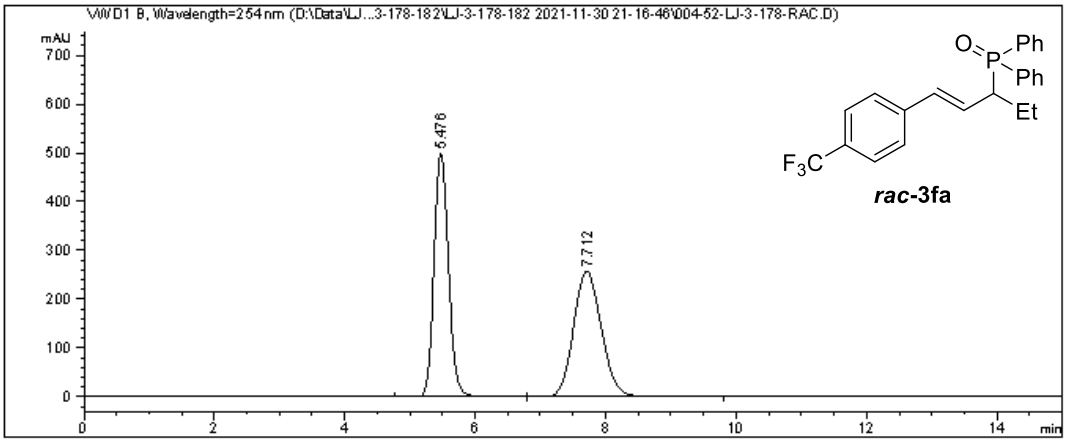
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.371	BB	0.4896	2777.86963	89.13638	97.5137
2	20.529	BB	0.5455	70.82655	2.00804	2.4863
Totals :				2848.69618	91.14442	

*** End of Report ***

1260 10/7/2020 10:03:29 AM SYSTEM Page 1 of 1

Figure S160. HPLC spectra of **3ea**.

```
Data File D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\004-52-LJ-3-178-RAC.D
Sample Name: LJ-3-178-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   52
    Injection Date  : 11/30/2021 10:02:15 PM            Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P1-85-15-1.0ML-5UL
                      -220NM-254NM-20MIN.M
    Last changed    : 11/30/2021 9:15:18 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P1-85-15-1.0ML-5UL
                      -220NM-254NM-20MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:32:42 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.476 VB R  0.2364 7623.68555  498.66730  50.0396
       2   7.712 BB    0.4612 7611.61133  257.26355  49.9604

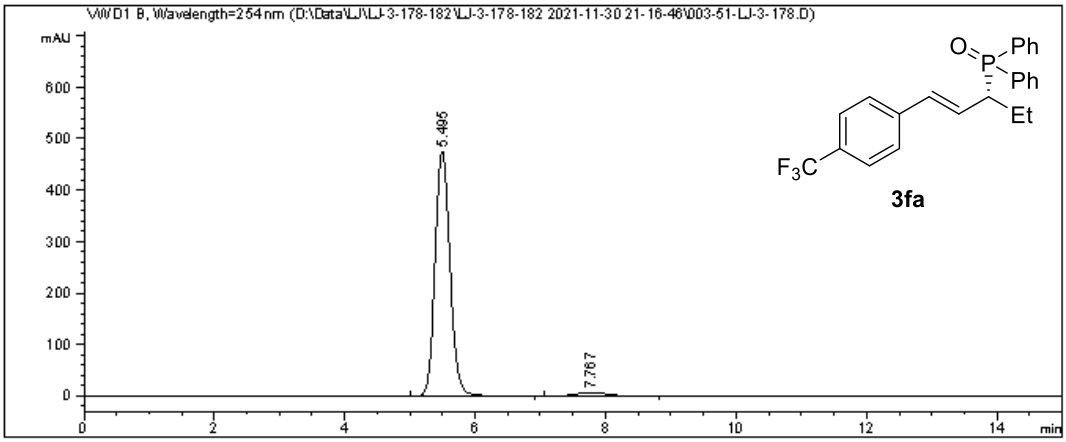
    Totals :                  1.52353e4   755.93085


    ======================================================================
                               *** End of Report ***

1260 11/30/2021 10:32:49 PM SYSTEM                          Page 1 of 1
```

Figure S161. HPLC spectra of ***rac*-3fa**.

```
Data File D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\003-51-LJ-3-178.D
Sample Name: LJ-3-178
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   51
    Injection Date  : 11/30/2021 9:41:32 PM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P1-85-15-1.0ML-5UL
                      -220NM-254NM-20MIN.M
    Last changed    : 11/30/2021 9:15:18 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P1-85-15-1.0ML-5UL
                      -220NM-254NM-20MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:33:53 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   5.495 BB    0.2460 7504.95313  475.97095  97.3743
       2   7.767 BB    0.5152  202.37331    6.03594   2.6257

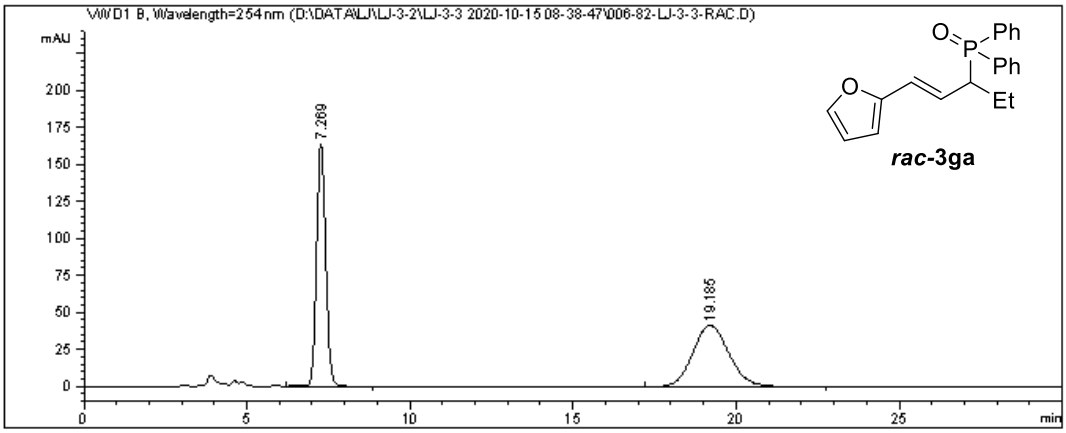
    Totals :                   7707.32643  482.00689


    ======================================================================
                            *** End of Report ***

1260 11/30/2021 10:34:02 PM SYSTEM                          Page 1 of 1
```

Figure S162. HPLC spectra of **3fa**.

```
Data File D:\DATA\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\006-82-LJ-3-3-RAC.D
Sample Name: LJ-3-3-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   82
    Injection Date  : 10/15/2020 10:03:30 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-80-20-1.0ML-5UL-220NM-254NM
                      -30MIN.M
    Last changed    : 8/13/2020 11:36:50 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-80-20-1.0ML-5UL-220NM-254NM
                      -30MIN.M (Sequence Method)
    Last changed    : 10/17/2020 8:58:45 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.269 VB R  0.3037 3194.40552  163.67488  50.2858
       2  19.185 BB    1.1749 3158.10034   41.07947  49.7142

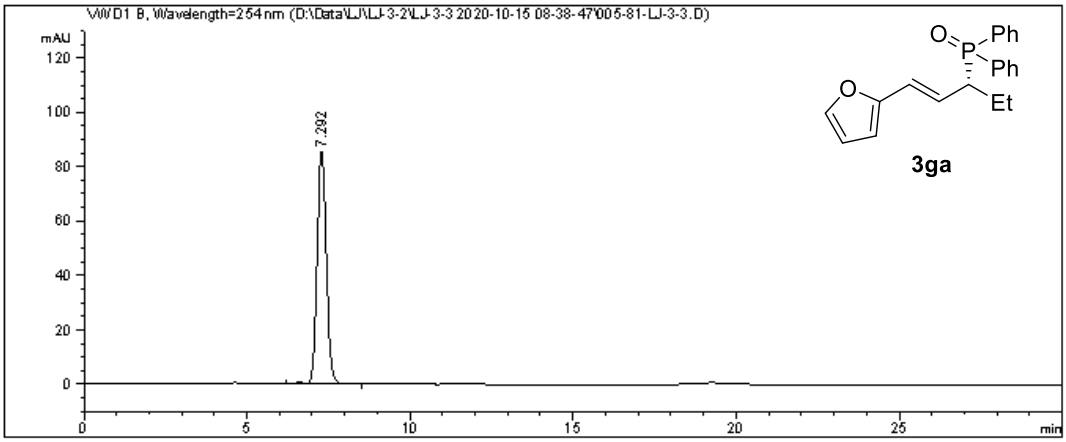
    Totals :                  6352.50586  204.75435


    ======================================================================
                              *** End of Report ***

1260 10/17/2020 8:58:54 AM SYSTEM                          Page 1 of 1
```

Figure S163. HPLC spectra of ***rac*-3ga**.

```
Data File D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\005-81-LJ-3-3.D
Sample Name: LJ-3-3
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   81
    Injection Date  : 10/15/2020 9:32:46 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-80-20-1.0ML-5UL-220NM-254NM
                      -30MIN.M
    Last changed    : 8/13/2020 11:36:50 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-2\LJ-3-3 2020-10-15 08-38-47\P1-80-20-1.0ML-5UL-220NM-254NM
                      -30MIN.M (Sequence Method)
    Last changed    : 10/17/2020 9:00:24 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   7.292 VB R  0.3056 1691.00940   85.92770 100.0000

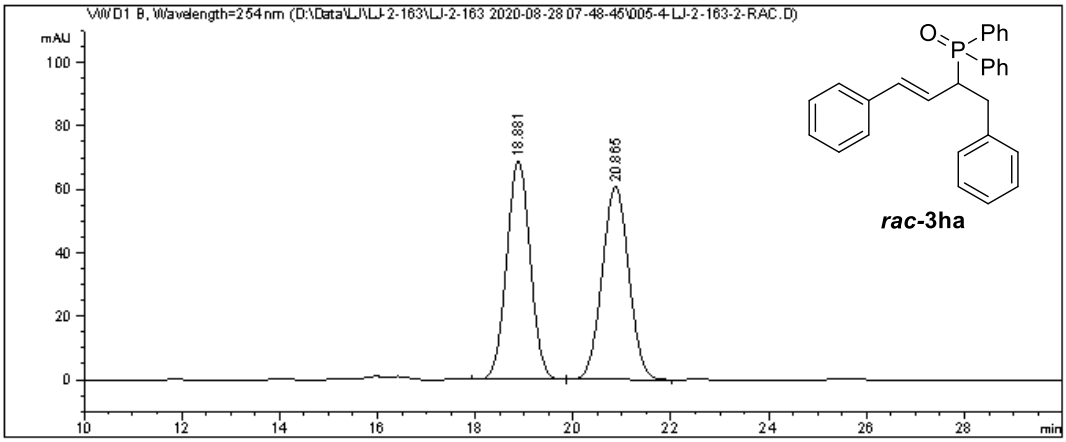
    Totals :                  1691.00940   85.92770


    ======================================================================
                            *** End of Report ***


1260 10/17/2020 9:00:34 AM SYSTEM                          Page 1 of 1
```

Figure S164. HPLC spectra of **3ga**.

```
Data File D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\005-4-LJ-2-163-2-RAC.D
Sample Name: LJ-2-163-2-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   4
    Injection Date  : 8/28/2020 9:22:25 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M
    Last changed    : 8/14/2020 1:43:33 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M (Sequence Method)
    Last changed    : 10/15/2020 8:19:44 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  18.881 BB    0.5230 2308.32568   68.87173  50.0140
       2  20.865 BB    0.5923 2307.03101   60.85109  49.9860

    Totals :                  4615.35669  129.72282

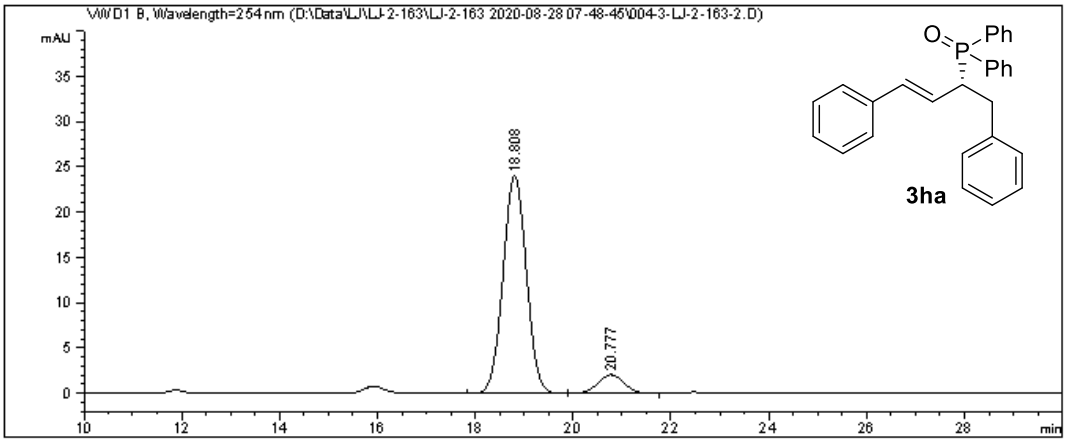

    ======================================================================
                            *** End of Report ***

1260 10/15/2020 8:19:50 AM SYSTEM                          Page 1 of 1
```

Figure S165. HPLC spectra of ***rac*-3ha**.

Data File D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\004-3-LJ-2-163-2.D
Sample Name: LJ-2-163-2

Acq. Operator	: SYSTEM	Seq. Line :	4
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location :	3
Injection Date	: 8/28/2020 8:41:42 AM	Inj :	1
		Inj Volume :	5.000 µl
Acq. Method	: D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-254NM-40MIN.M		
Last changed	: 8/14/2020 1:43:33 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)		
Last changed	: 10/15/2020 8:22:10 AM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.808	BB	0.5164	793.68976	23.96498	91.3799
2	20.777	BB	0.5755	74.87100	2.01502	8.6201
Totals :				868.56076	25.98000	

*** End of Report ***

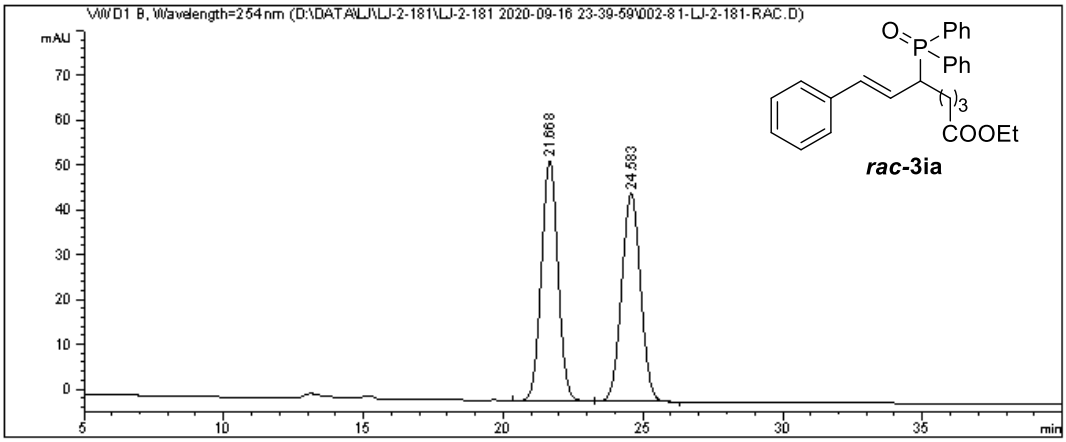
1260 10/15/2020 8:22:17 AM SYSTEM

Page 1 of 1

Figure S166. HPLC spectra of **3ha**.

Data File D:\DATA\LJ\LJ-2-181\LJ-2-181 2020-09-16 23-39-59\002-81-LJ-2-181-RAC.D
Sample Name: LJ-2-181-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                       Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   81
    Injection Date  : 9/16/2020 11:53:47 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-181\LJ-2-181 2020-09-16 23-39-59\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M
    Last changed    : 8/14/2020 1:43:33 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-181\LJ-2-181 2020-09-16 23-39-59\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M (Sequence Method)
    Last changed    : 9/17/2020 2:25:37 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                           Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.668 BB    0.6354 2206.69604   53.47410  50.3713
       2  24.583 BB    0.7397 2174.16772   46.48447  49.6287

    Totals :                  4380.86377   99.95857

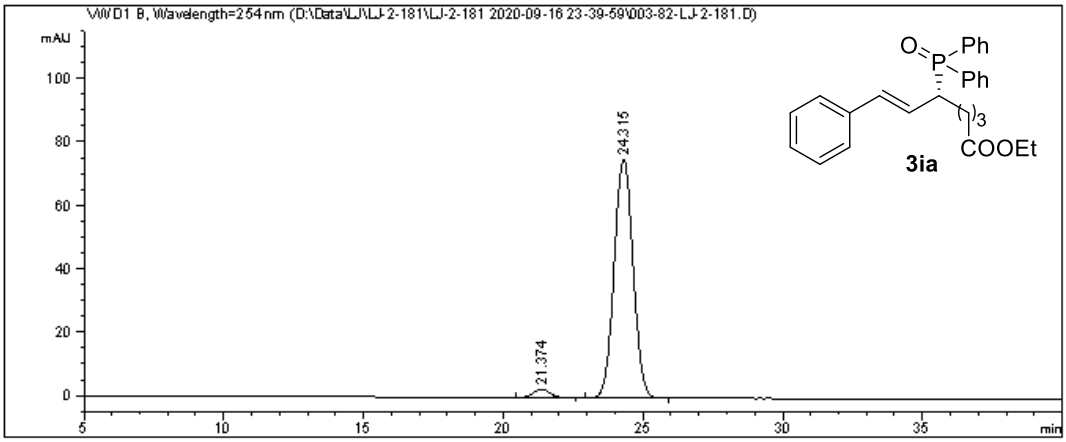

    ======================================================================
                           *** End of Report ***

1260 9/17/2020 2:25:43 AM SYSTEM                              Page 1 of 1
```

Figure S167. HPLC spectra of ***rac*-3ia**.

Data File D:\Data\LJ\LJ-2-181\LJ-2-181 2020-09-16 23-39-59\003-82-LJ-2-181.D
Sample Name: LJ-2-181

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                           Location :   82
    Injection Date  : 9/17/2020 12:34:30 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-181\LJ-2-181 2020-09-16 23-39-59\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M
    Last changed    : 8/14/2020 1:43:33 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-181\LJ-2-181 2020-09-16 23-39-59\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M (Sequence Method)
    Last changed    : 9/17/2020 2:27:41 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  21.374 BB    0.6222  108.74841    2.68690   2.9898
       2  24.315 BB    0.7281 3528.58472   75.10789  97.0102

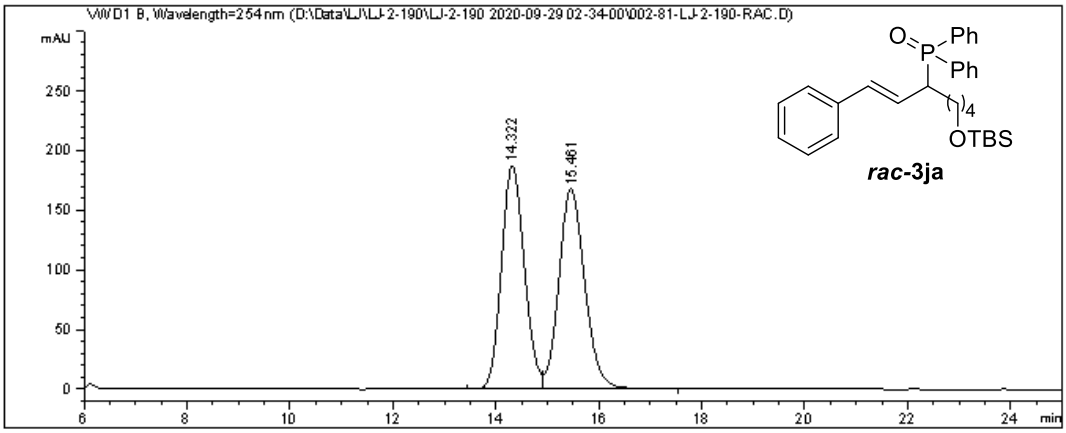
    Totals :                  3637.33313   77.79479


    ======================================================================
                            *** End of Report ***

1260 9/17/2020 2:27:51 AM SYSTEM                              Page 1 of 1
```

Figure S168. HPLC spectra of **3ia**.

```
Data File D:\Data\LJ\LJ-2-190\LJ-2-190 2020-09-29 02-34-00\002-81-LJ-2-190-RAC.D
Sample Name: LJ-2-190-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   81
    Injection Date  : 9/29/2020 2:45:40 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-190\LJ-2-190 2020-09-29 02-34-00\P1-96-4-0.5ML-5UL-220NM-
                      254NM-40MIN.M
    Last changed    : 9/29/2020 2:32:25 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-190\LJ-2-190 2020-09-29 02-34-00\P1-96-4-0.5ML-5UL-220NM-
                      254NM-40MIN.M (Sequence Method)
    Last changed    : 9/30/2020 12:14:12 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.322 BV    0.4858 5799.62646  186.99374  49.6232
       2  15.461 VB    0.5417 5887.70947  167.65469  50.3768

    Totals :                  1.16873e4   354.64844


    ======================================================================
                              *** End of Report ***

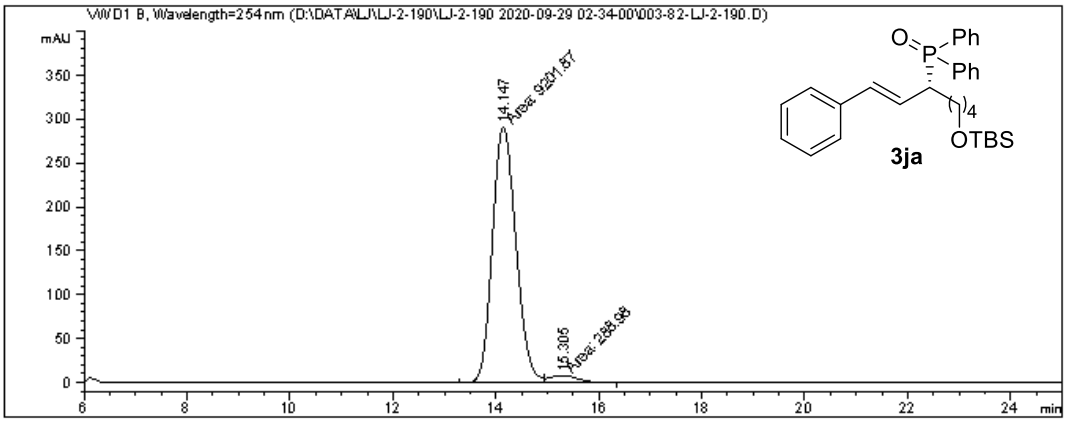
1260 9/30/2020 12:14:20 AM SYSTEM                          Page 1 of 1
```

Figure S169. HPLC spectra of ***rac*-3ja**.

Data File D:\DATA\LJ\LJ-2-190\LJ-2-190 2020-09-29 02-34-00\003-82-LJ-2-190.D
Sample Name: LJ-2-190

Acq. Operator	: SYSTEM	Seq. Line	: 3
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 82
Injection Date	: 9/29/2020 3:26:23 AM	Inj	: 1
		Inj Volume	: 5.000 µl

Acq. Method : D:\Data\LJ\LJ-2-190\LJ-2-190 2020-09-29 02-34-00\P1-96-4-0.5ML-5UL-220NM-254NM-40MIN.M
Last changed : 9/29/2020 3:30:12 AM by SYSTEM
(modified after loading)
Analysis Method : D:\Data\LJ\LJ-2-190\LJ-2-190 2020-09-29 02-34-00\P1-96-4-0.5ML-5UL-220NM-254NM-40MIN.M (Sequence Method)
Last changed : 9/30/2020 12:12:33 AM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.147	MF	0.5274	9201.87402	290.79672	96.9552
2	15.305	FM	0.5977	288.97983	8.05860	3.0448
Totals :				9490.85385	298.85532	

*** End of Report ***

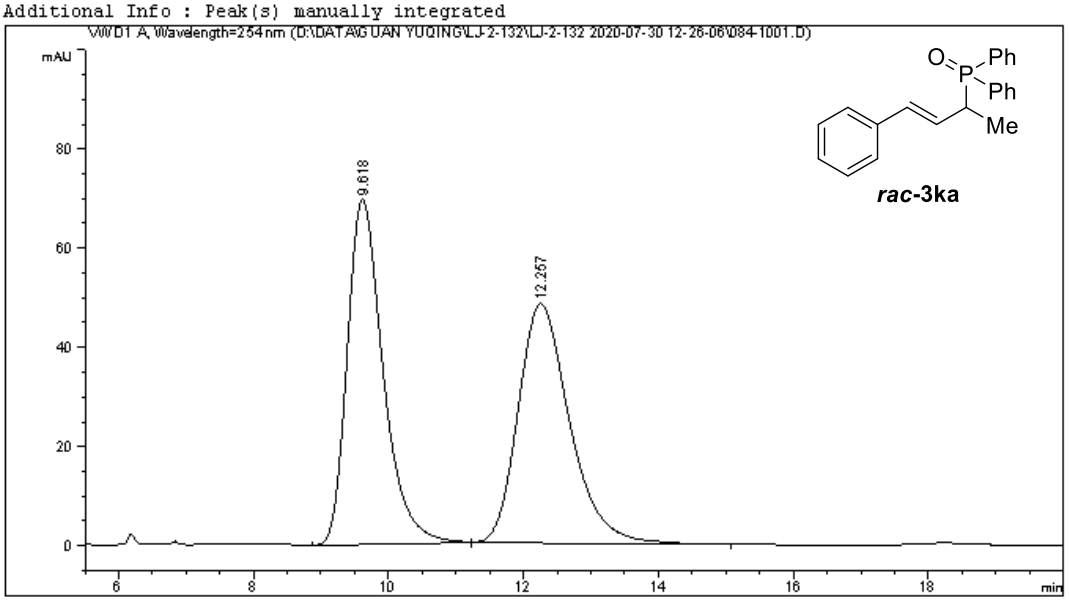
1260 9/30/2020 12:12:44 AM SYSTEM

Page 1 of 1

Figure S170. HPLC spectra of **3ja**.

Data File D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\084-1001.D
Sample Name: LJ-2-132-1-RAC

```
    ======================================================================
    Acq. Operator   :                              Seq. Line :  10
    Acq. Instrument : Instrument 1                  Location : Vial 84
    Injection Date  : 7/30/2020 4:37:44 PM               Inj :  1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\VWD-0J(1-2)-90-10
                      -1ML-5UL-254NM-20MIN.M
    Last changed    : 7/30/2020 12:30:41 PM
    Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-0J(1-2)-90-10-1ML-5UL-254NM-10MIN.M
    Last changed    : 7/30/2020 9:00:12 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   9.618 BB    0.5623 2564.64697   69.53281  50.1132
       2  12.257 BB    0.8094 2553.05811   48.24146  49.8868

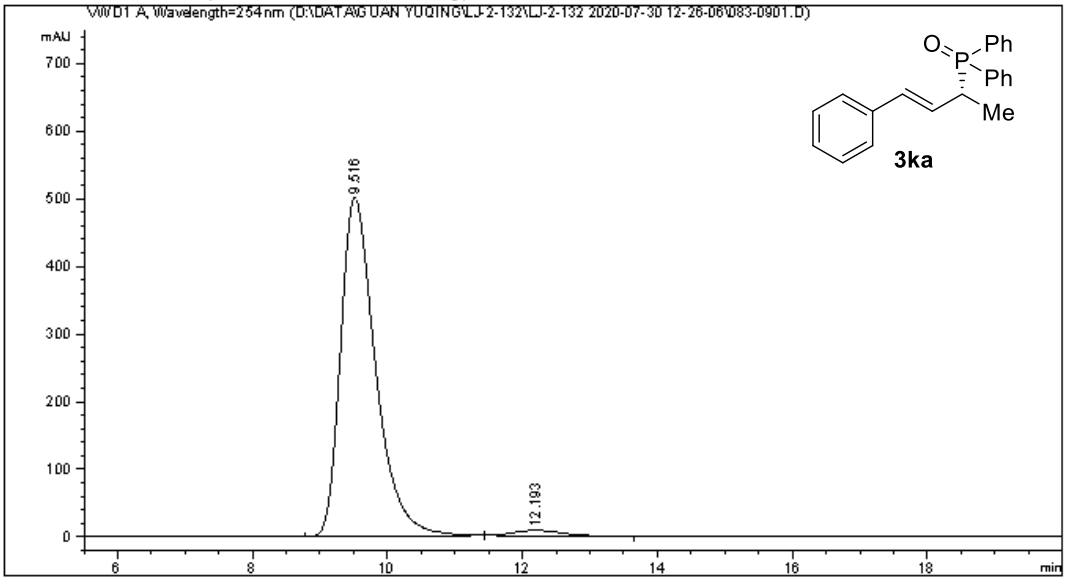
    Totals :                  5117.70508  117.77426


Instrument 1 7/30/2020 9:00:27 PM                          Page 1 of 2
```

Figure S171. HPLC spectra of ***rac*-3ka**.

Data File D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\083-0901.D
Sample Name: LJ-2-132-1

```
    ======================================================================
    Acq. Operator   :                              Seq. Line :   9
    Acq. Instrument : Instrument 1                  Location : Vial 83
    Injection Date  : 7/30/2020 4:16:54 PM               Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\VWD-0J(1-2)-90-10
                      -1ML-5UL-254NM-20MIN.M
    Last changed    : 7/30/2020 12:30:41 PM
    Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-0J(1-2)-90-10-1ML-5UL-254NM-10MIN.M
    Last changed    : 7/30/2020 9:01:40 PM
                      (modified after loading)
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1   9.516 BB    0.5455 1.80094e4   500.83066  97.8336
       2  12.193 BB    0.7482  398.79898    8.16037   2.1664

    Totals :                  1.84082e4   508.99102

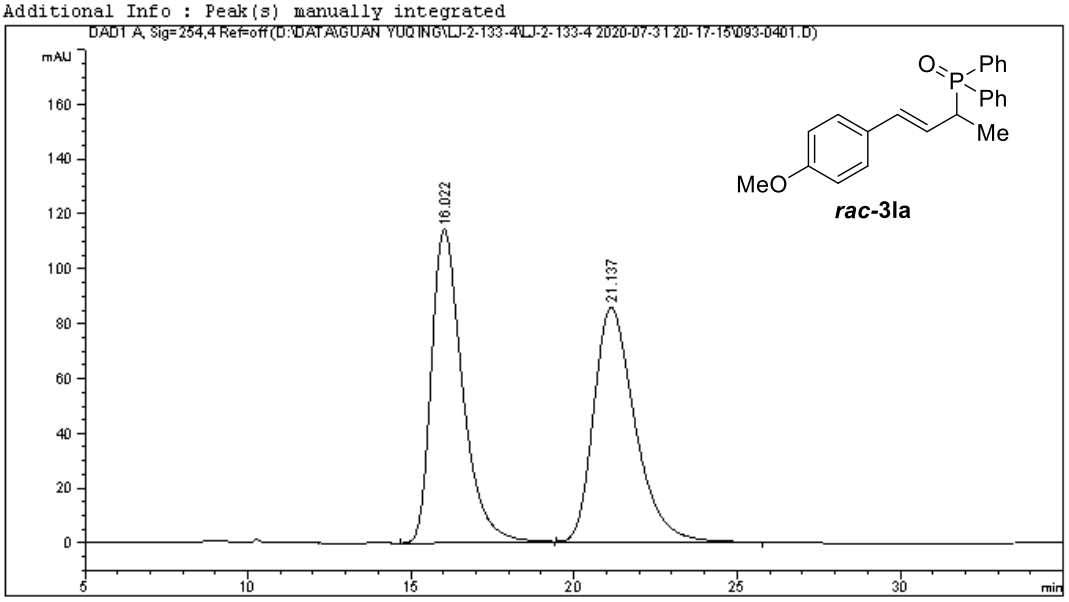

    ======================================================================
```

Instrument 1 7/30/2020 9:02:03 PM

Figure S172. HPLC spectra of **3ka**.

Data File D:\DATA\GUAN YUQING\LJ-2-133-4\LJ-2-133-4 2020-07-31 20-17-15\093-0401.D
Sample Name: LJ-2-133-4-RAC

```
    ======================================================================
    Acq. Operator   :                               Seq. Line :   4
    Acq. Instrument : Instrument 2                   Location : Vial 93
    Injection Date  : 7/31/2020 9:31:29 PM                Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-133-4\LJ-2-133-4 2020-07-31 20-17-15\DAD-0J(1-2)-
                      90-10-1.0ML-5UL-ALL-40MIN.M
    Last changed    : 7/24/2020 12:08:24 PM
    Analysis Method : D:\METHOD\LGY\DAD-0D(1-2)-90-10-1ML-5UL-ALL-20MIN.M
    Last changed    : 8/1/2020 5:39:24 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

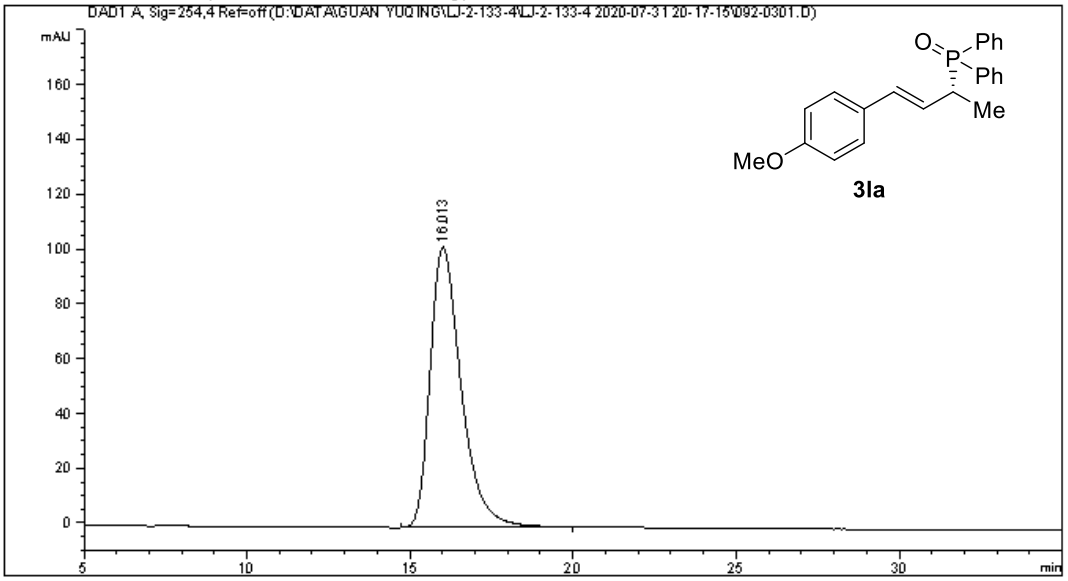
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.022 BB    0.9915 7557.32324  114.27718  50.1070
       2  21.137 BB    1.2985 7525.04199   85.69373  49.8930

    Totals :                  1.50824e4   199.97092
```


Figure S173. HPLC spectra of ***rac*-3la**.

Data File D:\DATA\GUAN YUQING\LJ-2-133-4\LJ-2-133-4 2020-07-31 20-17-15\092-0301.D
Sample Name: LJ-2-133-4

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   3
    Acq. Instrument : Instrument 2                    Location : Vial 92
    Injection Date  : 7/31/2020 8:50:29 PM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-133-4\LJ-2-133-4 2020-07-31 20-17-15\DAD-0J(1-2)-
                      90-10-1.0ML-5UL-ALL-40MIN.M
    Last changed    : 7/24/2020 12:08:24 PM
    Analysis Method : D:\METHOD\LGY\DAD-0D(1-2)-90-10-1ML-5UL-ALL-20MIN.M
    Last changed    : 8/1/2020 5:41:13 PM
                      (modified after loading)
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  16.013 BB    1.0103 6793.58789  102.36721 100.0000

    Totals :                  6793.58789  102.36721

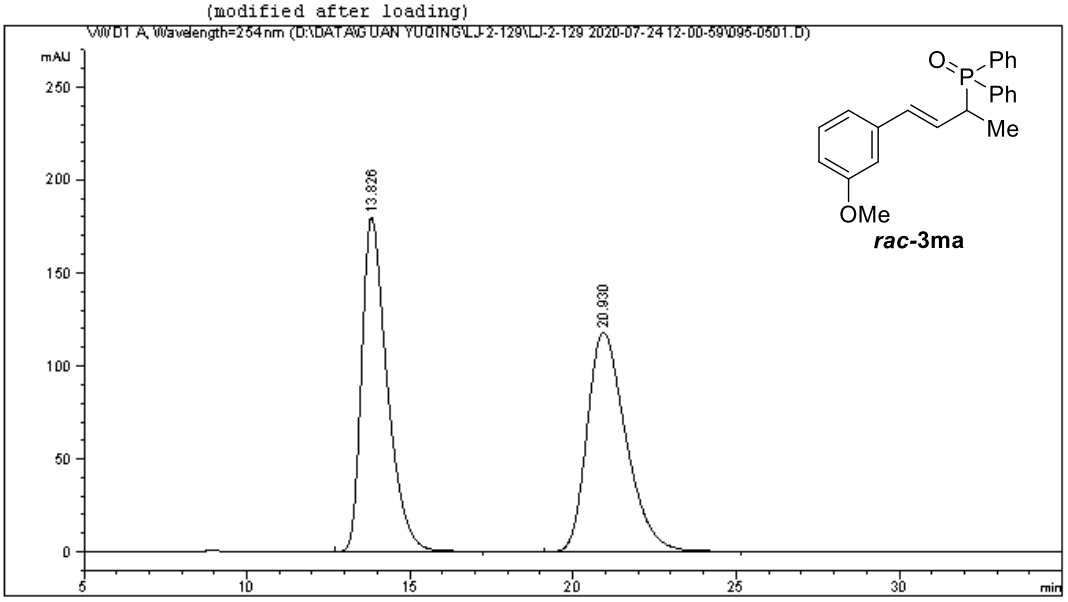

    ======================================================================
                              *** End of Report ***

Instrument 2 8/1/2020 5:41:18 PM                                Page 1 of 1
```

Figure S174. HPLC spectra of **3la**.

Data File D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\095-0501.D
Sample Name: LJ-2-129-5-RAC

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   5
    Acq. Instrument : Instrument 1                    Location : Vial 95
    Injection Date  : 7/24/2020 2:18:52 PM                 Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\VWD-AS(1-6)-85-15
                      -1ML-5UL-254NM-40MIN.M
    Last changed    : 7/24/2020 2:56:42 PM
                      (modified after loading)
    Analysis Method : D:\METHOD\LWD\DAD-IC(1-6)-90-10-0.5ML-2UL-ALL-60MIN.M
    Last changed    : 7/25/2020 4:14:21 PM
                      (modified after loading)
```



***rac*-3ma**

```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.826 BB    0.8144 9742.17090  179.72826  50.0212
       2  20.930 BB    1.2608 9733.93164  117.95081  49.9788

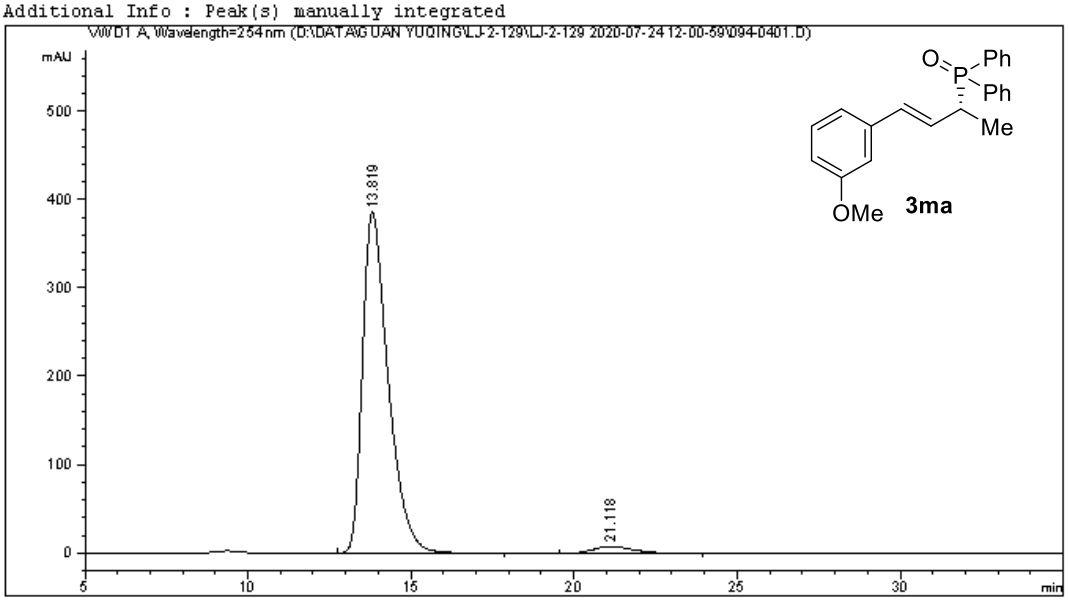
    Totals :                  1.9476le4   297.67906


Instrument 2 7/25/2020 4:14:25 PM                                Page 1 of 2
```

Figure S175. HPLC spectra of ***rac*-3ma**.

Data File D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\094-0401.D
Sample Name: LJ-2-129-5

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   4
    Acq. Instrument : Instrument 1                    Location : Vial 94
    Injection Date  : 7/24/2020 1:37:59 PM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\VWD-AS(1-6)-85-15
                      -1ML-5UL-254NM-40MIN.M
    Last changed    : 6/27/2019 10:00:11 PM
    Analysis Method : D:\METHOD\LWD\DAD-IC(1-6)-90-10-0.5ML-2UL-ALL-60MIN.M
    Last changed    : 7/25/2020 4:15:41 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

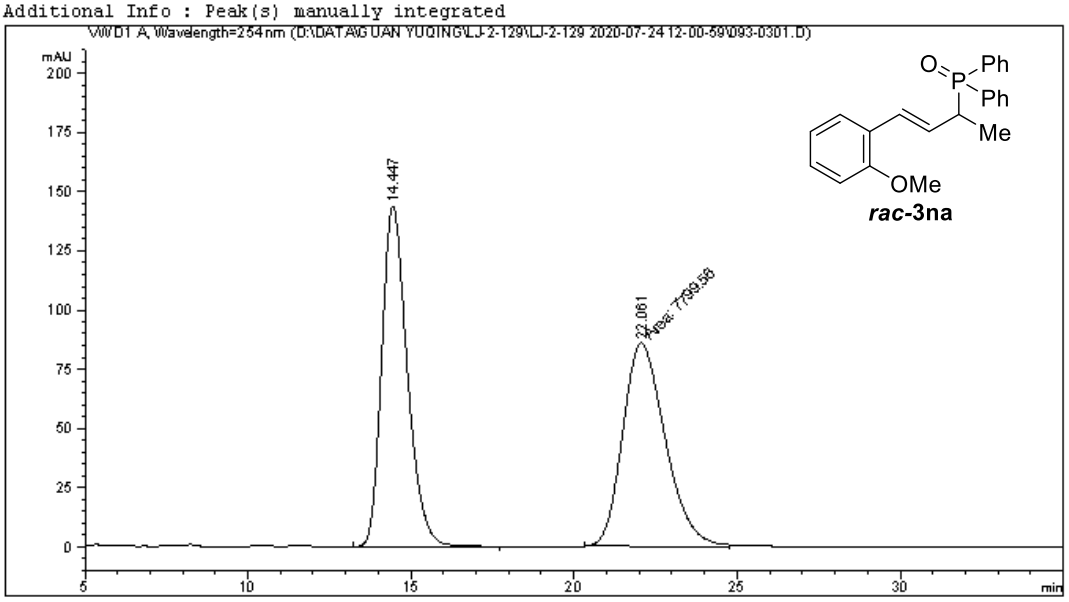
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.819 BB    0.8284 2.11235e4   386.01627  97.0550
       2  21.118 BB    1.1325  640.96503    7.75334   2.9450

    Totals :                  2.17644e4   393.76960
```


Figure S176. HPLC spectra of **3ma**.

Data File D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\093-0301.D
Sample Name: LJ-2-129-4-RAC

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   3
    Acq. Instrument : Instrument 1                    Location : Vial 93
    Injection Date  : 7/24/2020 12:57:05 PM              Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\VWD-AS(1-6)-85-15
                      -1ML-5UL-254NM-40MIN.M
    Last changed    : 6/27/2019 10:00:11 PM
    Analysis Method : D:\METHOD\LWD\DAD-IC(1-6)-90-10-0.5ML-2UL-ALL-60MIN.M
    Last changed    : 7/25/2020 4:11:47 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.447 BB    0.8360 7804.19092  143.84839  50.0148
       2  22.061 MM    1.5134 7799.55664   85.89545  49.9852

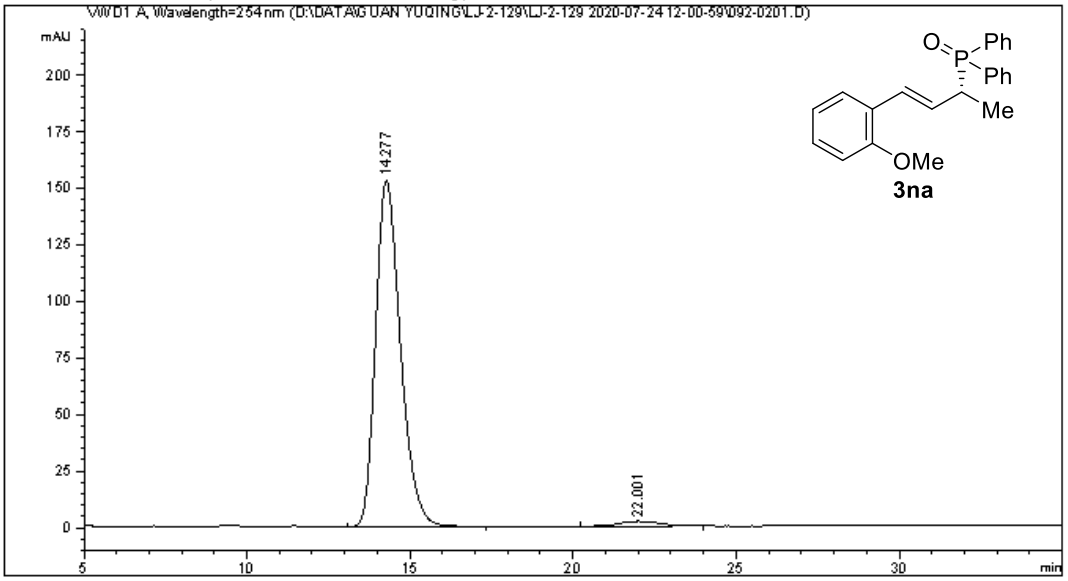
    Totals :                  1.56037e4   229.74384


Instrument 2 7/25/2020 4:11:52 PM                              Page 1 of 2
```

Figure S177. HPLC spectra of ***rac*-3na**.

Data File D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\092-0201.D
Sample Name: LJ-2-129-4

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   2
    Acq. Instrument : Instrument 1                    Location : Vial 92
    Injection Date  : 7/24/2020 12:16:14 PM              Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-129\LJ-2-129 2020-07-24 12-00-59\VWD-AS(1-6)-85-15
                      -1ML-5UL-254NM-40MIN.M
    Last changed    : 6/27/2019 10:00:11 PM
    Analysis Method : D:\METHOD\LWD\DAD-IC(1-6)-90-10-0.5ML-2UL-ALL-60MIN.M
    Last changed    : 7/25/2020 4:13:03 PM
                      (modified after loading)
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  14.277 BB    0.8129 8097.00342  152.87758  97.6878
       2  22.001 BB    1.0197  191.64929    2.21440   2.3122

    Totals :                  8288.65271  155.09198


    ======================================================================
```

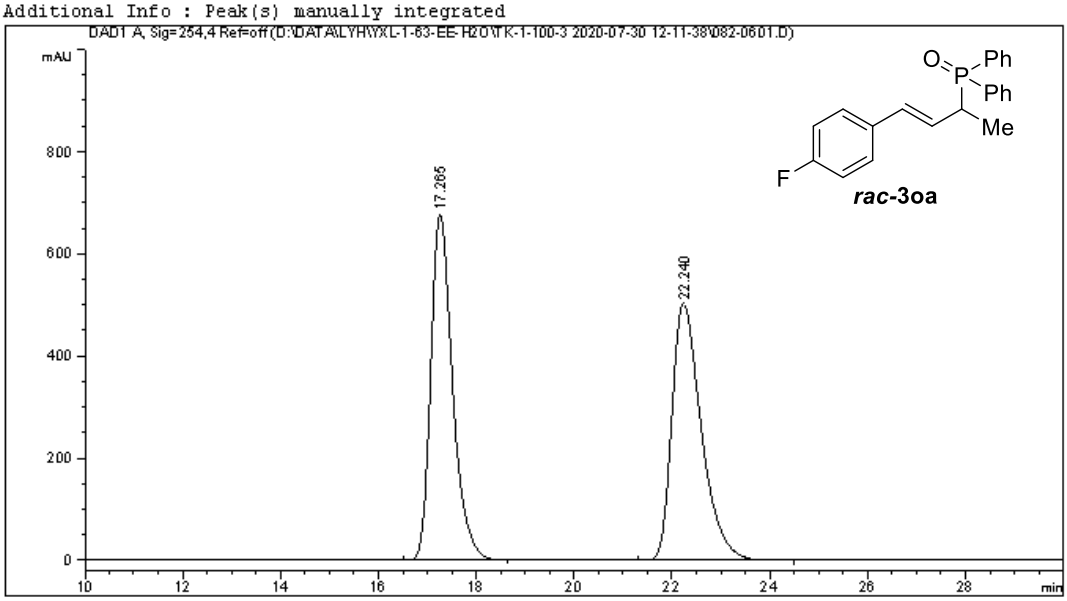
Instrument 2 7/25/2020 4:13:10 PM

Page 1 of 1

Figure S178. HPLC spectra of **3na**.

Data File D:\DATA\LYH\YXL-1-63-EE-H20\TK-1-100-3 2020-07-30 12-11-38\082-0601.D
Sample Name: LJ-2-132-3-RAC

```
    ======================================================================
    Acq. Operator   :                               Seq. Line :   6
    Acq. Instrument : Instrument 2                   Location : Vial 82
    Injection Date  : 7/30/2020 2:27:46 PM               Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\LYH\YXL-1-63-EE-H20\TK-1-100-3 2020-07-30 12-11-38\DAD-AD(1-6)-80-
                      20-1.0ML-5UL-ALL-30MIN.M
    Last changed    : 7/24/2020 10:44:13 PM
    Analysis Method : D:\METHOD\LGY\DAD-OD(1-2)-90-10-1ML-5UL-ALL-20MIN.M
    Last changed    : 7/30/2020 8:47:21 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

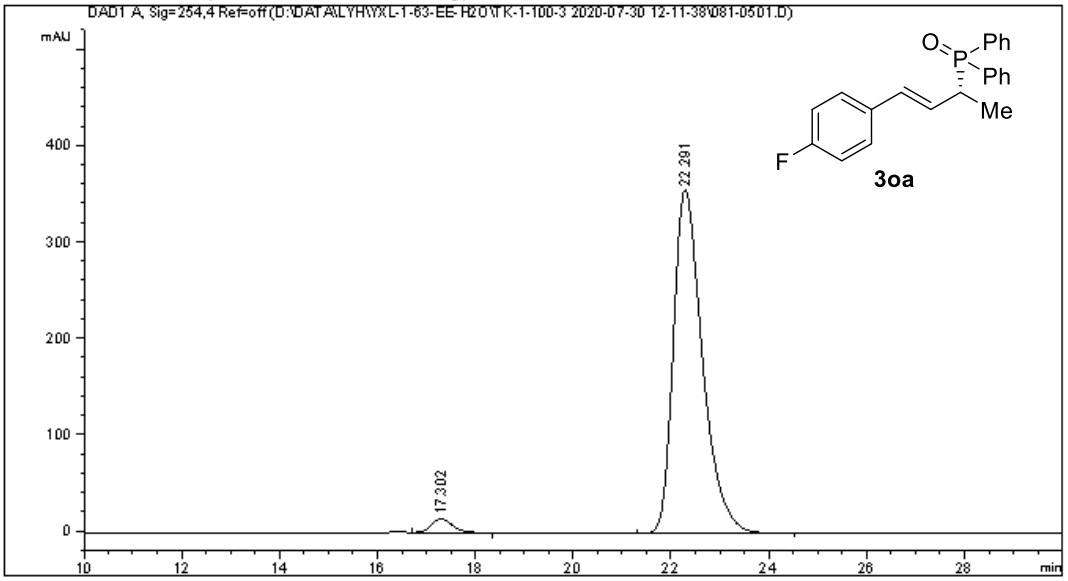
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  17.265 BB    0.4704 2.09296e4   677.53448  49.8831
       2  22.240 BB    0.6373 2.10277e4   503.44644  50.1169

    Totals :                  4.19572e4  1180.98093
```


Figure S179. HPLC spectra of ***rac*-3oa**.

Data File D:\DATA\LYH\YXL-1-63-EE-H20\TK-1-100-3 2020-07-30 12-11-38\081-0501.D
Sample Name: LJ-2-132-3

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   5
    Acq. Instrument : Instrument 2                    Location : Vial 81
    Injection Date  : 7/30/2020 1:56:47 PM                 Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\LYH\YXL-1-63-EE-H20\TK-1-100-3 2020-07-30 12-11-38\DAD-AD(1-6)-80-
                      20-1.0ML-5UL-ALL-30MIN.M
    Last changed    : 7/24/2020 10:44:13 PM
    Analysis Method : D:\METHOD\LGY\DAD-OD(1-2)-90-10-1ML-5UL-ALL-20MIN.M
    Last changed    : 7/30/2020 8:44:49 PM
                      (modified after loading)
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: DAD1 A, Sig=254,4 Ref=off

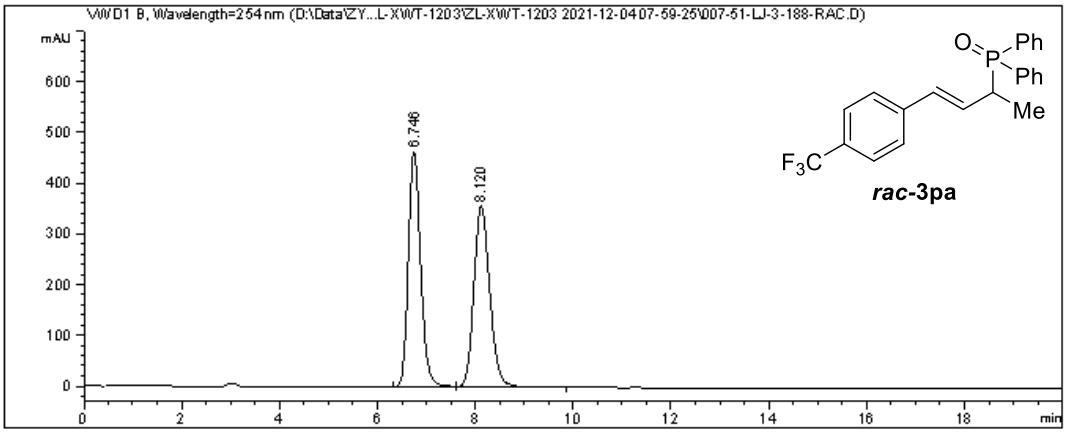
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  17.302 BB    0.4531  434.54437   14.43926   2.8747
       2  22.291 BB    0.6296 1.46817e4   355.67935  97.1253

    Totals :                  1.51163e4   370.11861


    ======================================================================
```


Figure S180. HPLC spectra of **3oa**.

```
Data File D:\Data\ZYF\ZL-XWT-1203\ZL-XWT-1203 2021-12-04 07-59-25\007-51-LJ-3-188-RAC.D
Sample Name: LJ-3-188-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   7
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   51
    Injection Date  : 12/4/2021 9:50:44 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\ZYF\ZL-XWT-1203\ZL-XWT-1203 2021-12-04 07-59-25\P2-85-15-1.0ML-5UL-
                      220NM-254NM-20MIN.M
    Last changed    : 9/11/2020 5:47:12 AM by SYSTEM
    Analysis Method : D:\Data\ZYF\ZL-XWT-1203\ZL-XWT-1203 2021-12-04 07-59-25\P2-85-15-1.0ML-5UL-
                      220NM-254NM-20MIN.M (Sequence Method)
    Last changed    : 12/4/2021 9:35:23 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   6.746 BV    0.2683 8046.23926  464.07693  49.9377
       2   8.120 VB    0.3521 8066.31104  356.29480  50.0623

    Totals :                  1.61126e4   820.37173

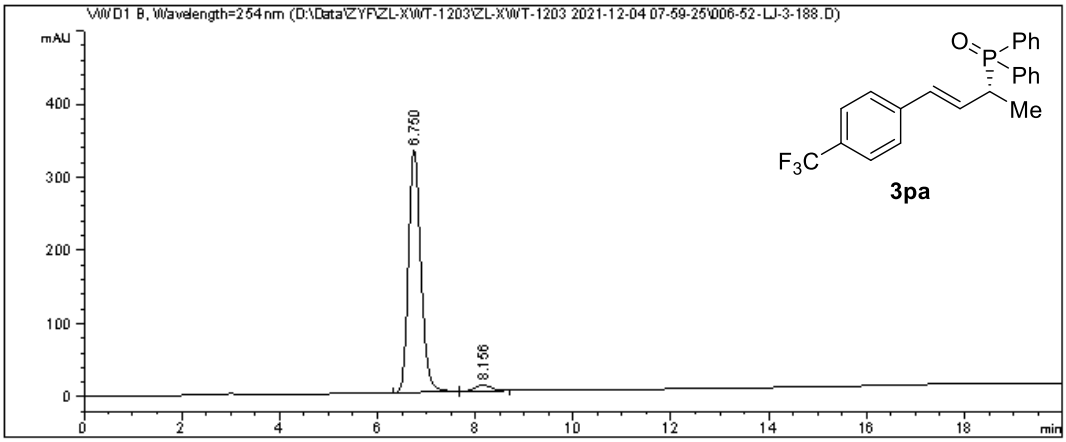

    ======================================================================
                              *** End of Report ***

1260 12/4/2021 9:36:06 PM SYSTEM                                Page 1 of 1
```

Figure S181. HPLC spectra of ***rac*-3pa**.

Data File D:\Data\ZYF\ZL-XWT-1203\ZL-XWT-1203 2021-12-04 07-59-25\006-52-LJ-3-188.D
Sample Name: LJ-3-188

Acq. Operator	: SYSTEM	Seq. Line :	6
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location :	52
Injection Date	: 12/4/2021 9:30:03 AM	Inj :	1
		Inj Volume :	5.000 µl
Acq. Method	: D:\Data\ZYF\ZL-XWT-1203\ZL-XWT-1203 2021-12-04 07-59-25\P2-85-15-1.0ML-5UL-220NM-254NM-20MIN.M		
Last changed	: 9/11/2020 5:47:12 AM by SYSTEM		
Analysis Method	: D:\Data\ZYF\ZL-XWT-1203\ZL-XWT-1203 2021-12-04 07-59-25\P2-85-15-1.0ML-5UL-220NM-254NM-20MIN.M (Sequence Method)		
Last changed	: 12/4/2021 9:37:57 PM by SYSTEM (modified after loading)		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.750	BV	0.2711	5823.78467	331.26373	96.7432
2	8.156	VB	0.3594	196.05597	8.42705	3.2568
Totals :				6019.84064	339.69078	

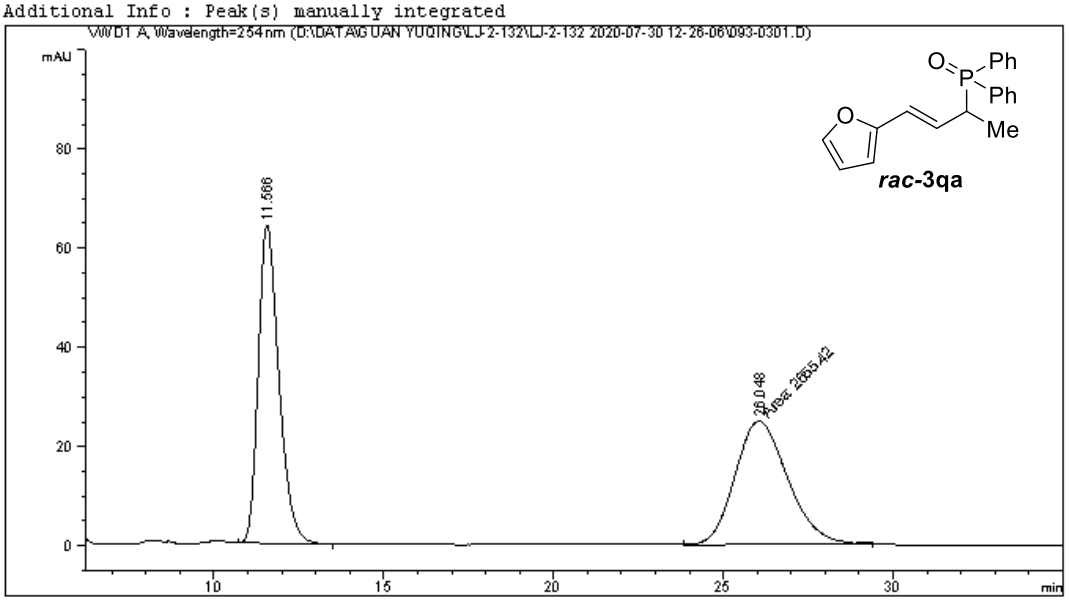
*** End of Report ***

1260 12/4/2021 9:38:11 PM SYSTEM Page 1 of 1

Figure S182. HPLC spectra of **3pa**.

Data File D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\093-0301.D
Sample Name: LJ-2-132-4-RAC

```
    ======================================================================
    Acq. Operator   :                              Seq. Line :   3
    Acq. Instrument : Instrument 1                  Location : Vial 93
    Injection Date  : 7/30/2020 1:31:28 PM               Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\VWD-AS(1-6)-80-20
                      -1ML-5UL-254NM-40MIN.M
    Last changed    : 7/28/2020 6:04:24 PM
    Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-0J(1-2)-90-10-1ML-5UL-254NM-10MIN.M
    Last changed    : 7/30/2020 9:04:38 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.566 BB    0.6449 2703.24878   64.11257  50.4462
       2  26.048 MM    1.7823 2655.42310   24.83125  49.5538

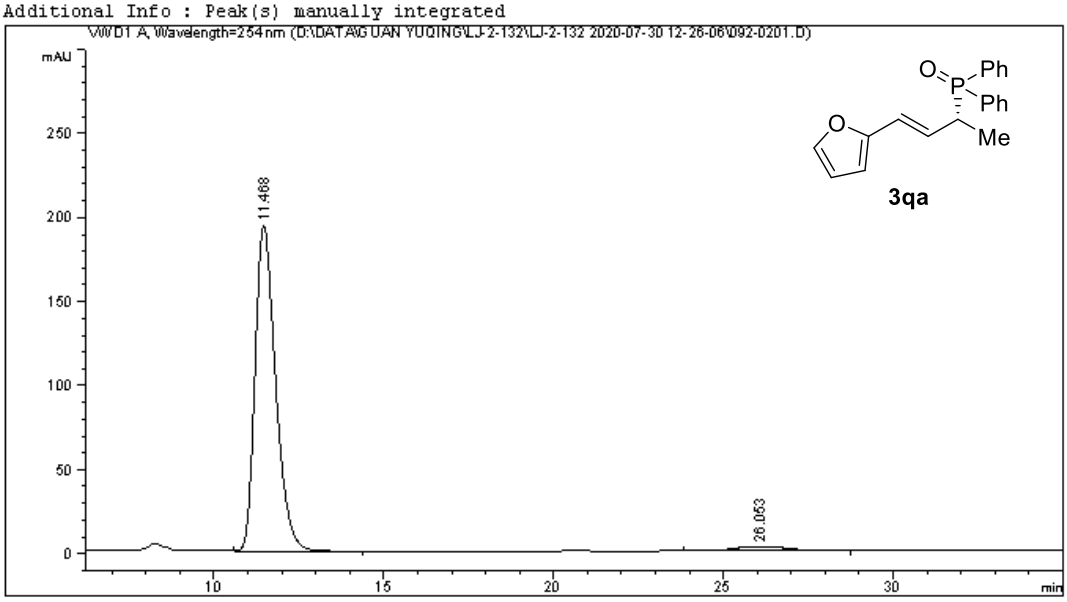
    Totals :                  5358.67188   88.94382


Instrument 1 7/30/2020 9:04:52 PM                              Page 1 of 2
```

Figure S183. HPLC spectra of ***rac*-3qa**.

Data File D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\092-0201.D
Sample Name: LJ-2-132-4

```
    ======================================================================
    Acq. Operator   :                                Seq. Line :   2
    Acq. Instrument : Instrument 1                    Location : Vial 92
    Injection Date  : 7/30/2020 12:50:37 PM              Inj :   1
                                                    Inj Volume : 5.000 µl
    Acq. Method     : D:\DATA\GUAN YUQING\LJ-2-132\LJ-2-132 2020-07-30 12-26-06\VWD-AS(1-6)-80-20
                      -1ML-5UL-254NM-40MIN.M
    Last changed    : 7/28/2020 6:04:24 PM
    Analysis Method : D:\METHOD\GUAN YUQING\LONGJIAO\VWD-0J(1-2)-90-10-1ML-5UL-254NM-10MIN.M
    Last changed    : 7/30/2020 9:06:19 PM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Use Multiplier & Dilution Factor with ISTDs

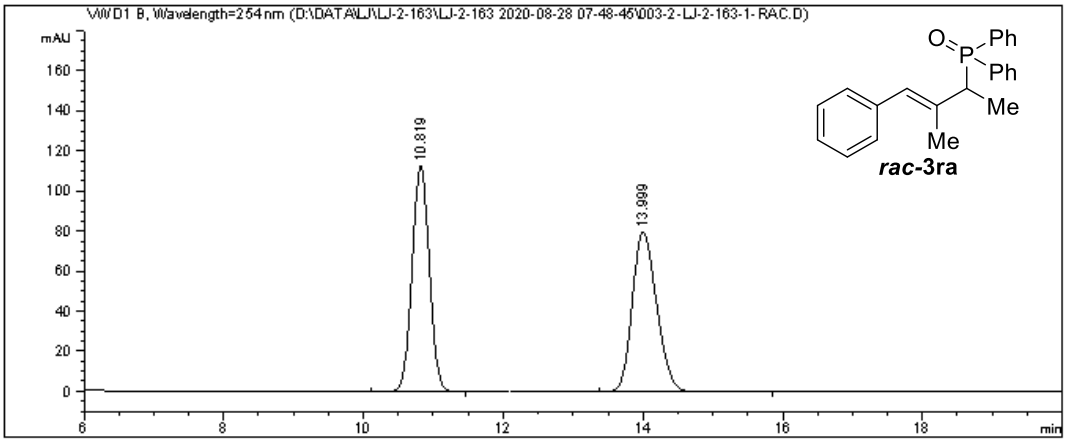

    Signal 1: VWD1 A, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]        %
    ----|-------|----|-------|----------|----------|--------|
       1  11.468 BB    0.6433 8141.77295  193.73189  96.4885
       2  26.053 BB    1.2660  296.30133    2.75892   3.5115

    Totals :                  8438.07428  196.49080
```


Figure S184. HPLC spectra of **3qa**.

```
Data File D:\DATA\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\003-2-LJ-2-163-1-RAC.D
Sample Name: LJ-2-163-1-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                       Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   2
    Injection Date  : 8/28/2020 8:20:55 AM              Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/23/2020 2:24:42 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 8/28/2020 8:57:04 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.819 BB    0.2660 1935.23633  112.87365  49.9959
       2  13.999 BB    0.3787 1935.55420   79.86952  50.0041

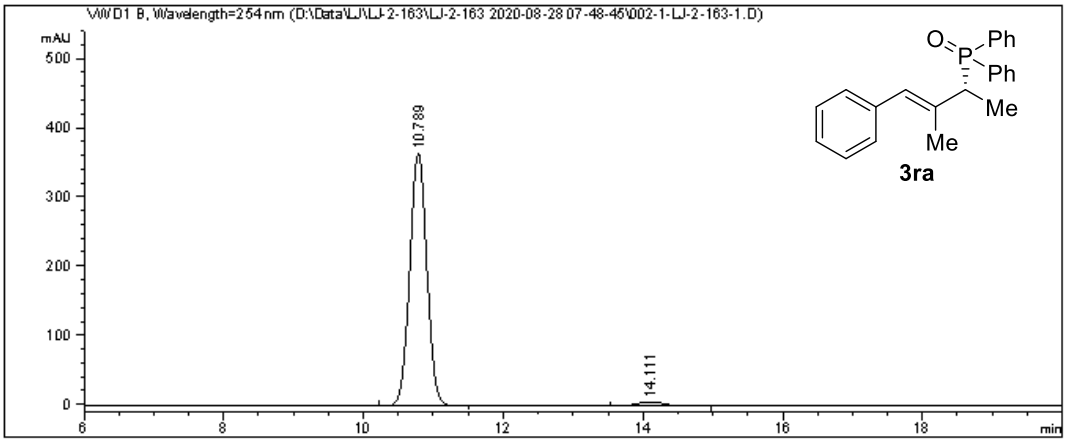
    Totals :                  3870.79053  192.74317


    ======================================================================
                            *** End of Report ***

1260 8/28/2020 8:57:11 AM SYSTEM                              Page 1 of 1
```

Figure S185. HPLC spectra of ***rac*-3ra**.

```
Data File D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\002-1-LJ-2-163-1.D
Sample Name: LJ-2-163-1
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   1
    Injection Date  : 8/28/2020 8:00:11 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/23/2020 2:24:42 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-163\LJ-2-163 2020-08-28 07-48-45\P2-80-20-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 8/28/2020 8:59:42 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.789 BB    0.2641 6184.39893  364.23044  97.7191
       2  14.111 BB    0.3776  144.34955    5.93810   2.2809

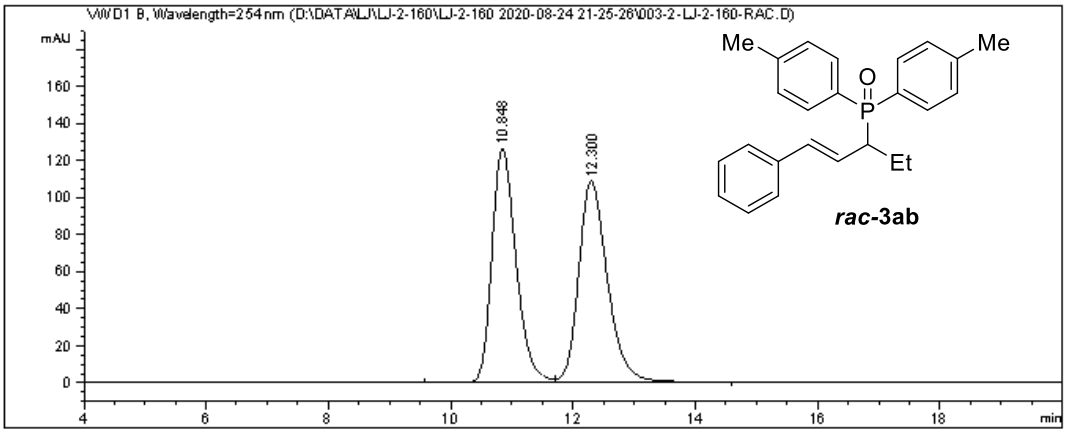
    Totals :                  6328.74847  370.16853


    ======================================================================
                            *** End of Report ***

1260 8/28/2020 8:59:50 AM SYSTEM                          Page 1 of 1
```

Figure S186. HPLC spectra of **3ra**.

```
Data File D:\DATA\LJ\LJ-2-160\LJ-2-160 2020-08-24 21-25-26\003-2-LJ-2-160-RAC.D
Sample Name: LJ-2-160-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   2
    Injection Date  : 8/24/2020 9:58:46 PM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-160\LJ-2-160 2020-08-24 21-25-26\P1-95-5-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/13/2020 11:44:53 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-160\LJ-2-160 2020-08-24 21-25-26\P1-95-5-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 8/24/2020 10:22:58 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.848 BV    0.4204 3454.18530  126.55992  49.3569
       2  12.300 VB    0.4985 3544.19946  108.66531  50.6431

    Totals :                  6998.38477  235.22523

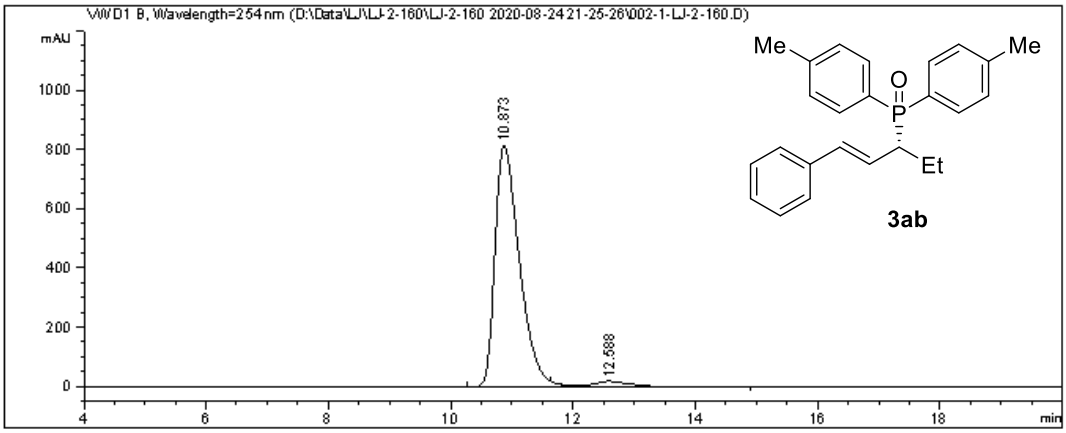

    ======================================================================
                              *** End of Report ***

1260 8/24/2020 10:23:04 PM SYSTEM                          Page 1 of 1
```

Figure S187. HPLC spectra of ***rac*-3ab**.

Data File D:\Data\LJ\LJ-2-160\LJ-2-160 2020-08-24 21-25-26\002-1-LJ-2-160.D
Sample Name: LJ-2-160

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 1
Injection Date	: 8/24/2020 9:38:00 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-2-160\LJ-2-160 2020-08-24 21-25-26\P1-95-5-1.0ML-5UL-220NM-254NM-20MIN.M		
Last changed	: 8/13/2020 11:44:53 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-2-160\LJ-2-160 2020-08-24 21-25-26\P1-95-5-1.0ML-5UL-220NM-254NM-20MIN.M (Sequence Method)		
Last changed	: 8/24/2020 10:28:58 PM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

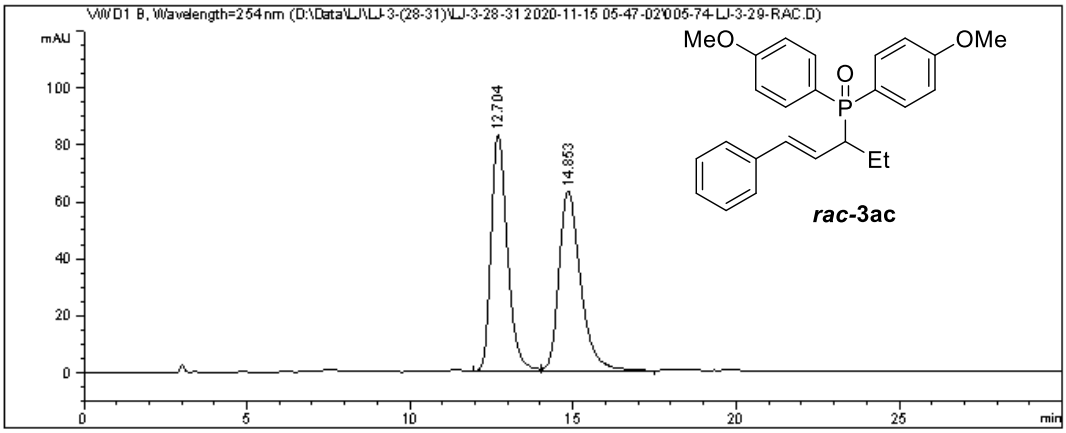
Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.873	BV R	0.4233	2.25448e4	813.49200	96.8350
2	12.588	VB E	0.6498	736.87665	17.26945	3.1650
Totals :				2.32817e4	830.76145	

*** End of Report ***

Figure S188. HPLC spectra of **3ab**.

```
Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\005-74-LJ-3-29-RAC.D
Sample Name: LJ-3-29-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   74
    Injection Date  : 11/15/2020 7:50:50 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-
                      220NM-254NM-30MIN.M
    Last changed    : 8/23/2020 2:17:04 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-
                      220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/15/2020 8:40:52 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.704 BV    0.5324 2874.15918   82.91635  49.8198
       2  14.853 VB    0.6969 2894.94653   63.14737  50.1802

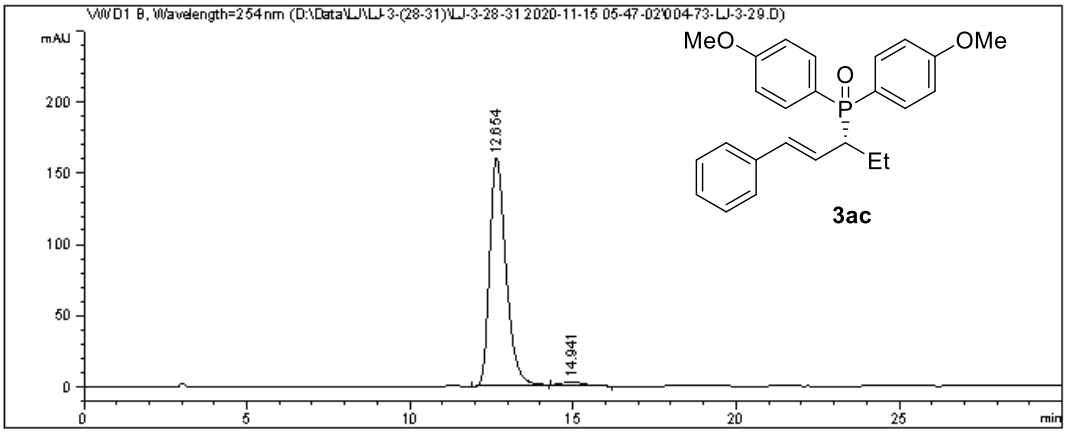
    Totals :                  5769.10571  146.06372


    ======================================================================
                               *** End of Report ***

1260 11/15/2020 8:41:02 AM SYSTEM                          Page 1 of 1
```

Figure S189. HPLC spectra of ***rac*-3ac**.

```
Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\004-73-LJ-3-29.D
Sample Name: LJ-3-29
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   73
    Injection Date  : 11/15/2020 7:20:08 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-
                      220NM-254NM-30MIN.M
    Last changed    : 8/23/2020 2:17:04 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-
                      220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/15/2020 8:43:03 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.654 BB    0.5322 5561.73242  159.75887  98.0703
       2  14.941 BB    0.6682  109.43578    2.47338   1.9297

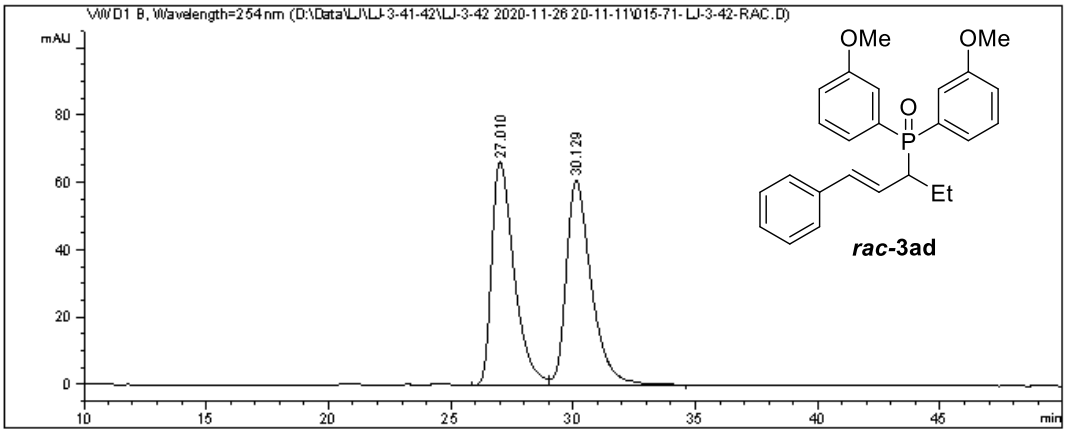
    Totals :                  5671.16820  162.23224


    ======================================================================
                              *** End of Report ***

1260 11/15/2020 8:43:08 AM SYSTEM                          Page 1 of 1
```

Figure S190. HPLC spectra of **3ac**.

```
Data File D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\015-71-LJ-3-42-RAC.D
Sample Name: LJ-3-42-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  15
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   71
    Injection Date  : 11/27/2020 1:26:37 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-95-5-0.5ML-5UL-220NM-
                      254NM-60MIN.M
    Last changed    : 10/17/2020 10:05:29 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-95-5-0.5ML-5UL-220NM-
                      254NM-60MIN.M (Sequence Method)
    Last changed    : 11/27/2020 3:36:20 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  27.010 BV    0.9829 4225.00928   66.16904  49.4354
       2  30.129 VB    1.0919 4321.51172   60.75058  50.5646

    Totals :                  8546.52100  126.91962

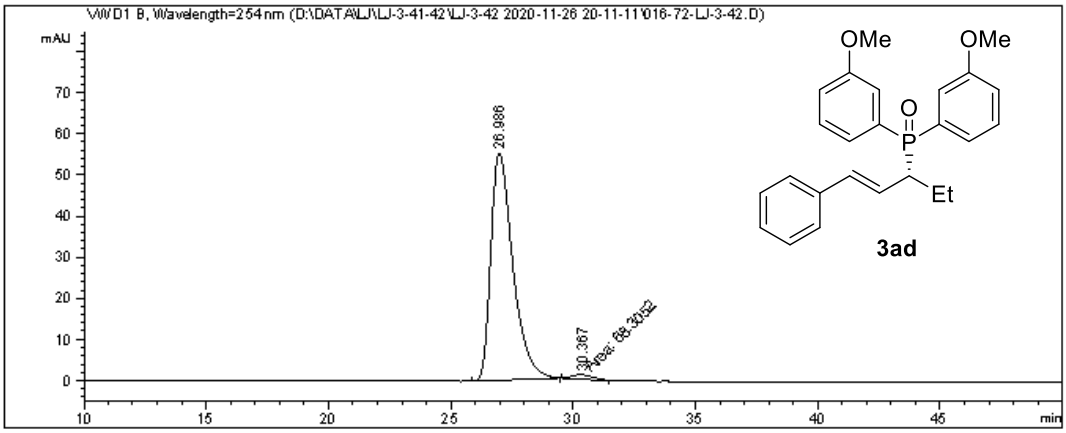

    ======================================================================
                              *** End of Report ***

1260 11/27/2020 3:36:28 AM SYSTEM                          Page 1 of 1
```

Figure S191. HPLC spectra of ***rac*-3ad**.

Data File D:\DATA\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\016-72-LJ-3-42.D
Sample Name: LJ-3-42

Acq. Operator : SYSTEM Seq. Line : 16
Sample Operator : SYSTEM
Acq. Instrument : 1260 Location : 72
Injection Date : 11/27/2020 2:27:19 AM Inj : 1
Inj Volume : 5.000 µl
Acq. Method : D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-95-5-0.5ML-5UL-220NM-254NM-60MIN.M
Last changed : 10/17/2020 10:05:29 PM by SYSTEM
Analysis Method : D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-95-5-0.5ML-5UL-220NM-254NM-60MIN.M (Sequence Method)
Last changed : 11/27/2020 3:34:22 AM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

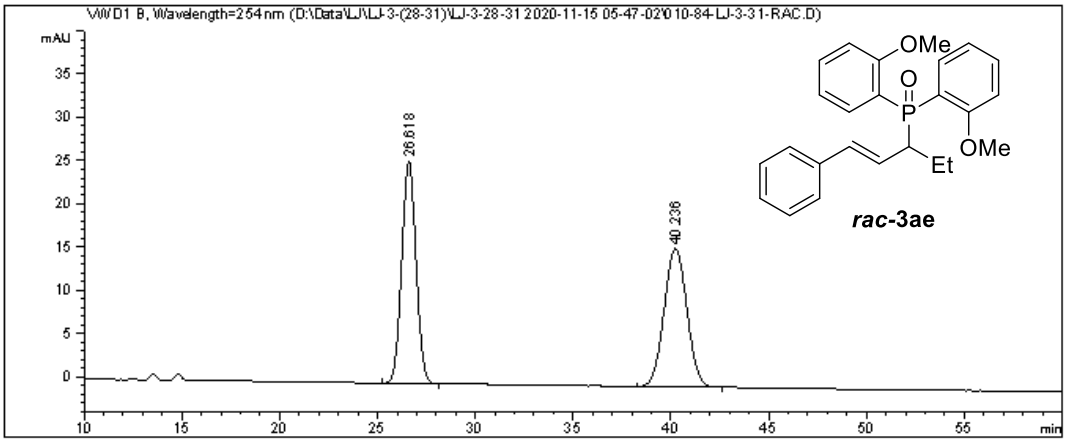
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.986	BB	0.9641	3457.84937	55.25288	98.0629
2	30.367	MM	1.0559	68.30518	1.07817	1.9371
Totals :				3526.15454	56.33105	

*** End of Report ***

1260 11/27/2020 3:34:27 AM SYSTEM Page 1 of 1

Figure S192. HPLC spectra of **3ad**.

```
Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\010-84-LJ-3-31-RAC.D
Sample Name: LJ-3-31-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  10
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   84
    Injection Date  : 11/15/2020 11:34:36 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-
                      220NM-254NM-60MIN.M
    Last changed    : 8/23/2020 2:25:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-
                      220NM-254NM-60MIN.M (Sequence Method)
    Last changed    : 11/16/2020 2:07:44 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  26.618 BB    0.8026 1299.05530   25.66140  50.0266
       2  40.236 BB    1.2548 1297.67444   15.99031  49.9734

    Totals :                  2596.72974   41.65171

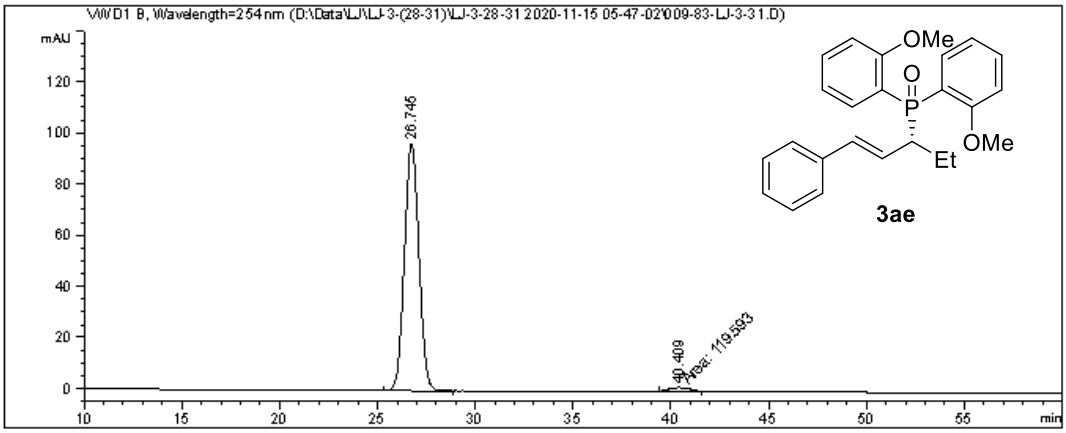

    ======================================================================
                              *** End of Report ***

1260 11/16/2020 2:08:00 AM SYSTEM                          Page 1 of 1
```

Figure S193. HPLC spectra of ***rac*-3ae**.

Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\009-83-LJ-3-31.D
Sample Name: LJ-3-31

Acq. Operator	: SYSTEM	Seq. Line	: 9
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 83
Injection Date	: 11/15/2020 10:33:52 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-220NM-254NM-60MIN.M		
Last changed	: 8/23/2020 2:25:51 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-220NM-254NM-60MIN.M (Sequence Method)		
Last changed	: 11/16/2020 2:09:18 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.745	BB	0.8142	4927.49365	96.75091	97.6304
2	40.409	MM	1.2519	119.59342	1.59221	2.3696
Totals :				5047.08707	98.34312	

*** End of Report ***

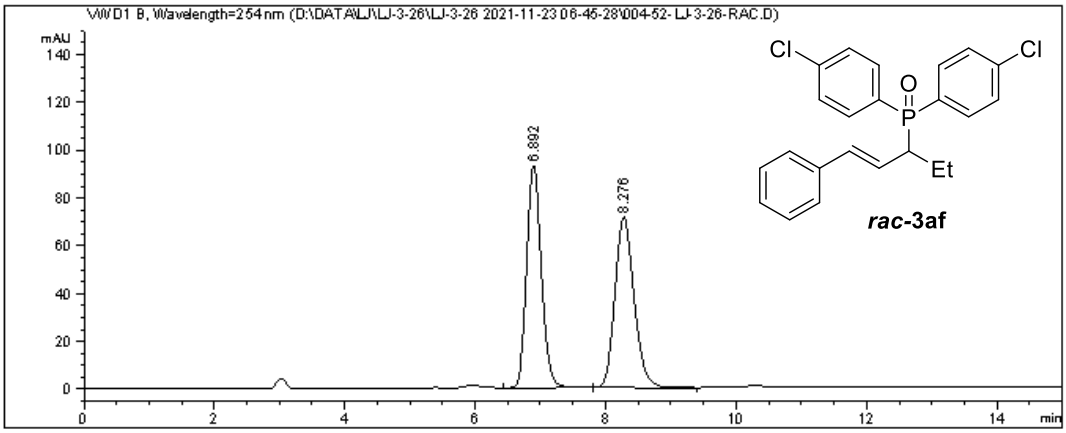
1260 11/16/2020 2:09:32 AM SYSTEM

Page 1 of 1

Figure S194. HPLC spectra of **3ae**.

Data File D:\DATA\LJ\LJ-3-26\LJ-3-26 2021-11-23 06-45-28\004-52-LJ-3-26-RAC.D
Sample Name: LJ-3-26-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 4
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 52
Injection Date	: 11/23/2021 7:28:19 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-26\LJ-3-26 2021-11-23 06-45-28\P2-90-10-1.0ML-5UL-220NM-254NM-20MIN.M		
Last changed	: 8/23/2020 2:28:48 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-26\LJ-3-26 2021-11-23 06-45-28\P2-90-10-1.0ML-5UL-220NM-254NM-20MIN.M (Sequence Method)		
Last changed	: 11/30/2021 9:44:41 PM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.892	BB	0.2437	1465.94177	93.12042	50.1376
2	8.276	BB	0.3143	1457.89392	71.36427	49.8624
Totals :				2923.83569	164.48470	

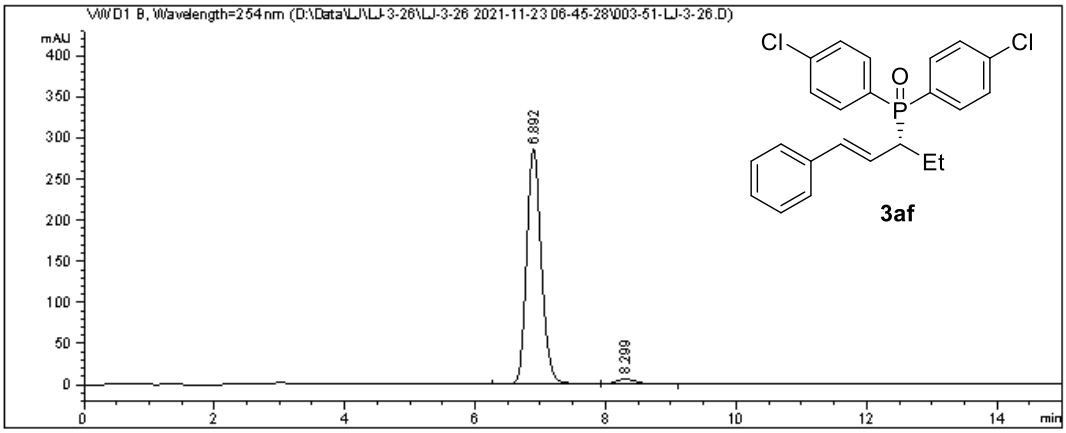
*** End of Report ***

1260 11/30/2021 9:44:52 PM SYSTEM

Figure S195. HPLC spectra of ***rac*-3af**.

Data File D:\Data\LJ\LJ-3-26\LJ-3-26 2021-11-23 06-45-28\003-51-LJ-3-26.D
Sample Name: LJ-3-26

Acq. Operator	: SYSTEM	Seq. Line	: 3
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 51
Injection Date	: 11/23/2021 7:07:37 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-26\LJ-3-26 2021-11-23 06-45-28\P2-90-10-1.0ML-5UL-220NM-254NM-20MIN.M		
Last changed	: 8/23/2020 2:28:48 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-26\LJ-3-26 2021-11-23 06-45-28\P2-90-10-1.0ML-5UL-220NM-254NM-20MIN.M (Sequence Method)		
Last changed	: 11/30/2021 9:48:11 PM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

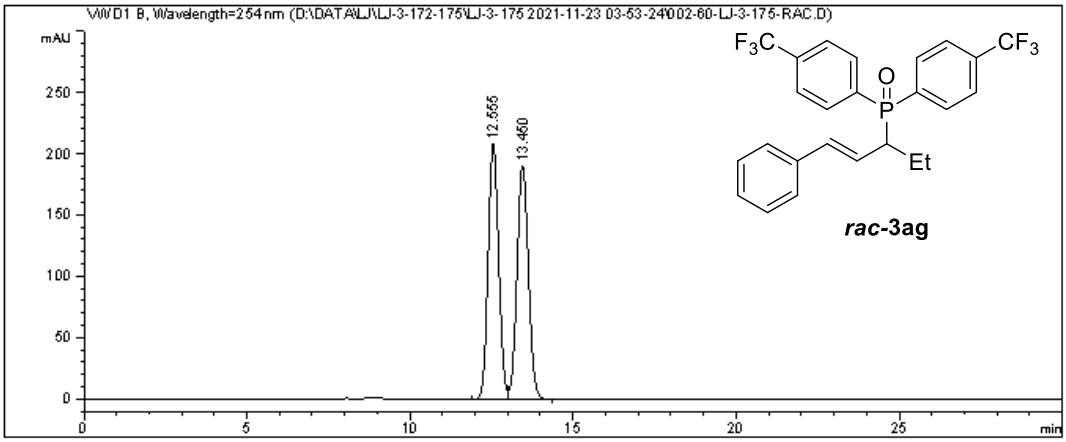
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.892	BV	0.2415	4498.04150	285.97031	97.0984
2	8.299	VB	0.3346	134.41620	6.11198	2.9016
Totals :				4632.45770	292.08229	

*** End of Report ***

1260 11/30/2021 9:48:29 PM SYSTEM Page 1 of 1

Figure S196. HPLC spectra of **3af**.

```
Data File D:\DATA\LJ\LJ-3-172-175\LJ-3-175 2021-11-23 03-53-24\002-60-LJ-3-175-RAC.D
Sample Name: LJ-3-175-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   60
    Injection Date  : 11/23/2021 4:04:59 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-175 2021-11-23 03-53-24\P1-85-15-1.0ML-5UL-
                      220NM-254NM-30MIN.M
    Last changed    : 10/15/2020 8:06:11 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-175 2021-11-23 03-53-24\P1-85-15-1.0ML-5UL-
                      220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:26:39 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  12.555 BV    0.3494 4659.98291  207.95580  50.3178
       2  13.450 VB    0.3763 4601.12646  190.17068  49.6822

    Totals :                  9261.10938  398.12648

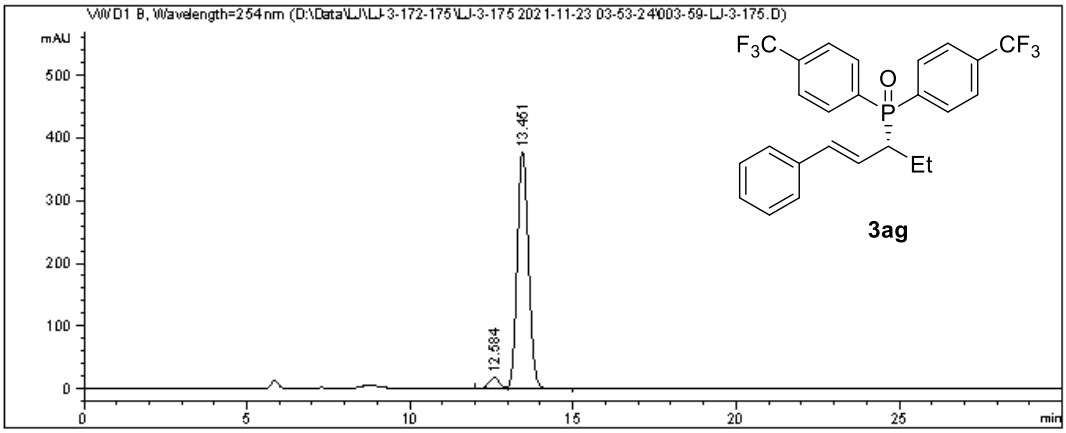

    ======================================================================
                            *** End of Report ***

1260 11/30/2021 10:26:48 PM SYSTEM                          Page 1 of 1
```

Figure S197. HPLC spectra of ***rac*-3ag**.

Data File D:\Data\LJ\LJ-3-172-175\LJ-3-175 2021-11-23 03-53-24\003-59-LJ-3-175.D
Sample Name: LJ-3-175

Acq. Operator	: SYSTEM	Seq. Line	: 3
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 59
Injection Date	: 11/23/2021 4:35:42 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-172-175\LJ-3-175 2021-11-23 03-53-24\P1-85-15-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 10/15/2020 8:06:11 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-172-175\LJ-3-175 2021-11-23 03-53-24\P1-85-15-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 11/30/2021 10:28:33 PM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

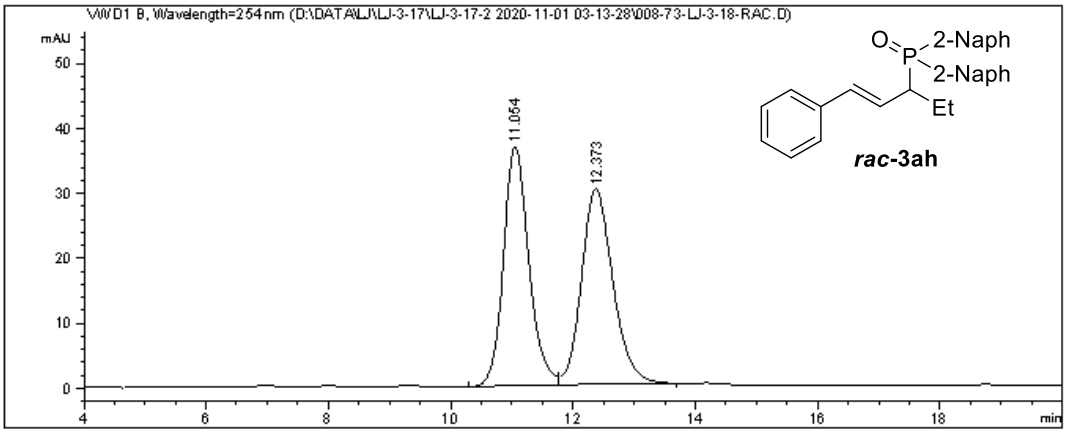
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.584	BV E	0.3404	388.81024	17.83380	4.1124
2	13.451	VB R	0.3718	9065.77051	378.01227	95.8876
Totals :				9454.58075	395.84606	

*** End of Report ***

1260 11/30/2021 10:29:12 PM SYSTEM Page 1 of 1

Figure S198. HPLC spectra of **3ag**.

```
Data File D:\DATA\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\008-73-LJ-3-18-RAC.D
Sample Name: LJ-3-18-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   73
    Injection Date  : 11/1/2020 6:11:44 AM              Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/23/2020 2:15:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 11/3/2020 4:10:35 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.054 BV    0.4444 1061.16504   36.80175  49.7449
       2  12.373 VB    0.5453 1072.04785   30.11871  50.2551

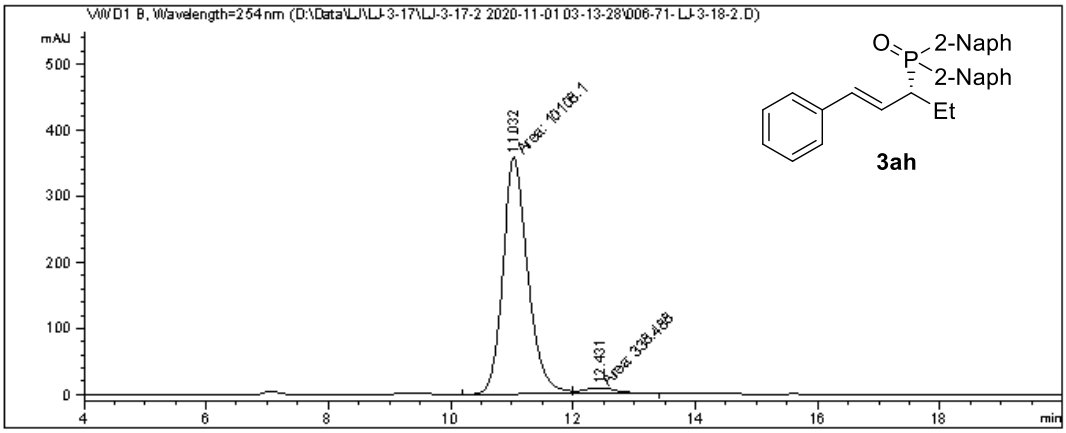
    Totals :                  2133.21289   66.92046


    ======================================================================
                              *** End of Report ***

1260 11/3/2020 4:10:40 AM SYSTEM                                Page 1 of 1
```

Figure S199. HPLC spectra of ***rac*-3ah**.

```
Data File D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\006-71-LJ-3-18-2.D
Sample Name: LJ-3-18-2
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   71
    Injection Date  : 11/1/2020 5:30:19 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/23/2020 2:15:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 11/3/2020 4:12:44 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.032 MF    0.4704 1.01081e4   358.12711  96.7598
       2  12.431 FM    0.6509  338.48846    8.66681   3.2402

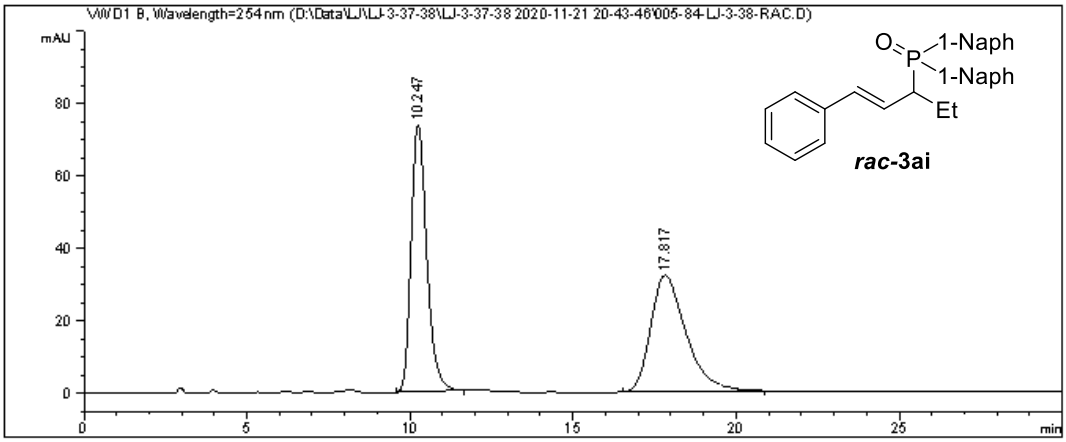
    Totals :                  1.04466e4   366.79392


    ======================================================================
                              *** End of Report ***

1260 11/3/2020 4:12:52 AM SYSTEM                                Page 1 of 1
```

Figure S200. HPLC spectra of **3ah**.

```
Data File D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\005-84-LJ-3-38-RAC.D
Sample Name: LJ-3-38-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   84
    Injection Date  : 11/21/2020 11:00:33 PM            Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M
    Last changed    : 11/21/2020 8:41:36 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/24/2020 2:33:33 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.247 BB    0.5134 2454.84033   73.55507  50.4260
       2  17.817 BB    1.1408 2413.35889   32.03956  49.5740

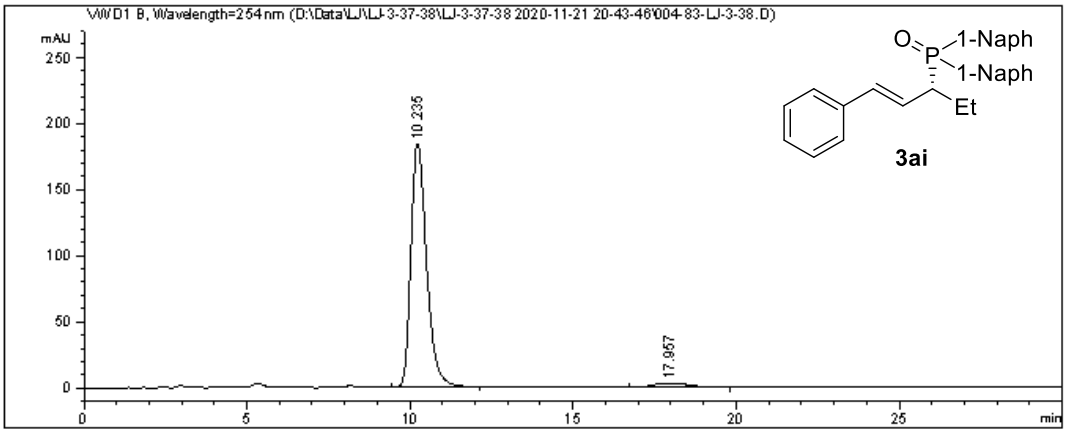
    Totals :                  4868.19922  105.59463


    ======================================================================
                            *** End of Report ***

1260 11/24/2020 2:33:42 AM SYSTEM                          Page 1 of 1
```

Figure S201. HPLC spectra of ***rac*-3ai**.

```
Data File D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\004-83-LJ-3-38.D
Sample Name: LJ-3-38
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   83
    Injection Date  : 11/21/2020 10:19:51 PM            Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M
    Last changed    : 11/21/2020 8:41:36 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/24/2020 2:34:57 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.235 BB    0.5097 6136.83301  184.66354  96.2812
       2  17.957 BB    1.1030  237.03291    3.12476   3.7188

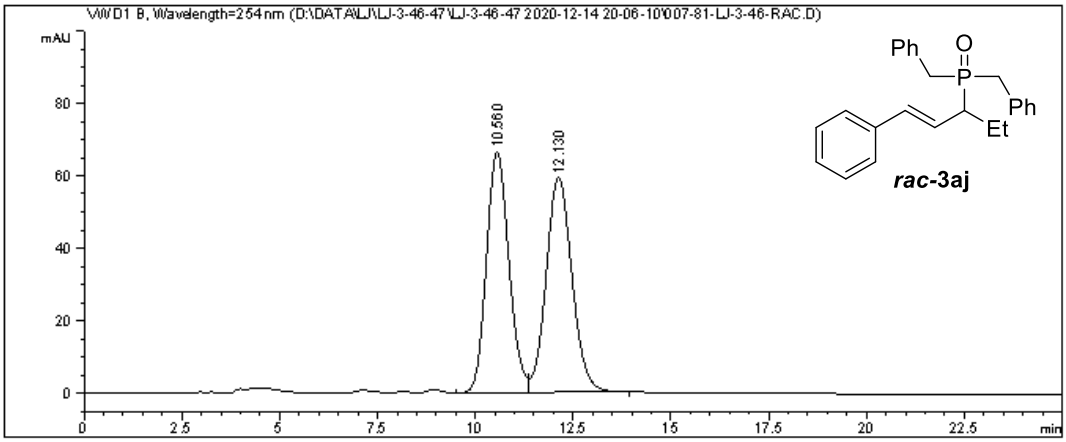
    Totals :                  6373.86592  187.78830


    ======================================================================
                               *** End of Report ***

1260 11/24/2020 2:35:06 AM SYSTEM                          Page 1 of 1
```

Figure S202. HPLC spectra of **3ai**.

```
Data File D:\DATA\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\007-81-LJ-3-46-RAC.D
Sample Name: LJ-3-46-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   7
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   81
    Injection Date  : 12/14/2020 10:09:17 PM            Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P2-85-15-1.0ML-5UL-
                      220NM-254NM-30MIN.M
    Last changed    : 9/11/2020 5:47:45 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P2-85-15-1.0ML-5UL-
                      220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 12/15/2020 1:19:37 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.560 BV    0.6171 2645.31274   66.35674  49.3712
       2  12.130 VB    0.7077 2712.69653   59.30025  50.6288

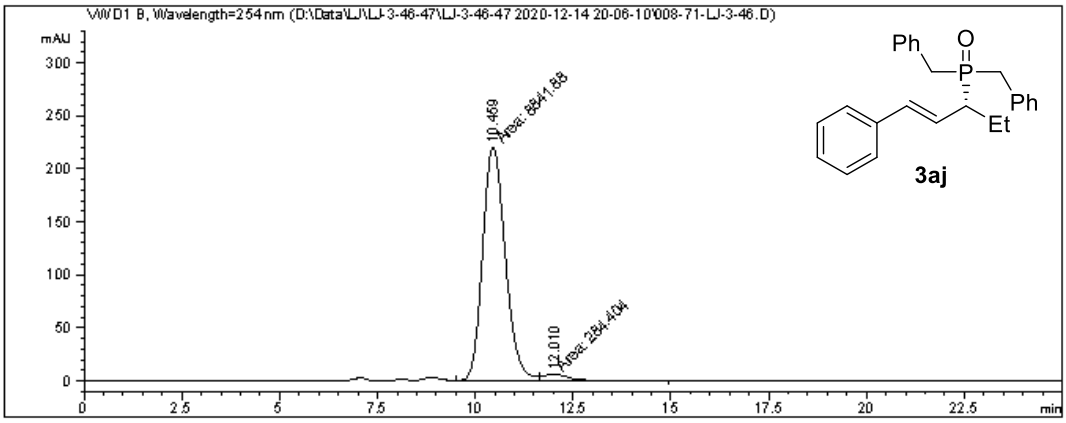
    Totals :                  5358.00928  125.65700


    ======================================================================
                            *** End of Report ***

1260 12/15/2020 1:19:42 AM SYSTEM                          Page 1 of 1
```

Figure S203. HPLC spectra of ***rac*-3aj**.

```
Data File D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\008-71-LJ-3-46.D
Sample Name: LJ-3-46
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   71
    Injection Date  : 12/14/2020 10:40:01 PM            Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P2-85-15-1.0ML-5UL-
                      220NM-254NM-30MIN.M
    Last changed    : 12/14/2020 10:43:23 PM by SYSTEM
                      (modified after loading)
    Analysis Method : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P2-85-15-1.0ML-5UL-
                      220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 12/15/2020 1:20:58 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  10.459 MF    0.6676 8841.87695  220.74631  96.8837
       2  12.010 FM    0.7659  284.40363    6.18870   3.1163

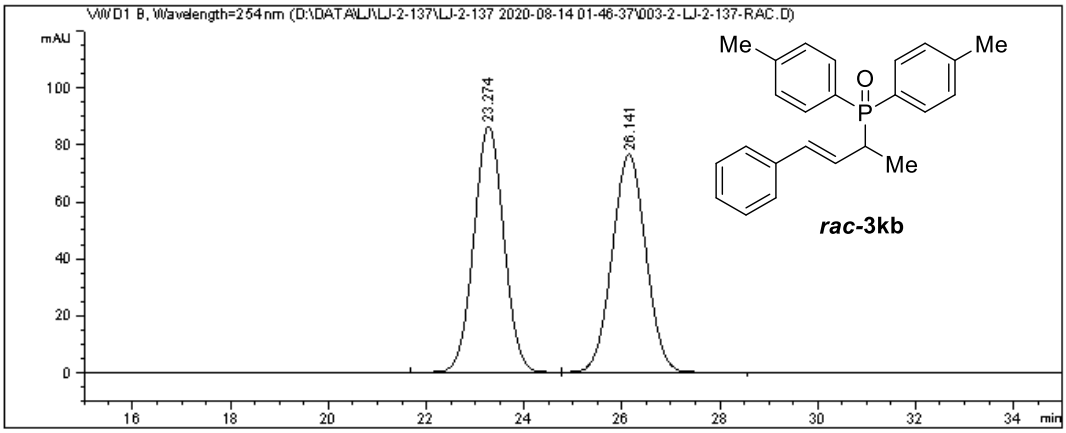
    Totals :                  9126.28058  226.93501


    ======================================================================
                            *** End of Report ***

1260 12/15/2020 1:21:04 AM SYSTEM                          Page 1 of 1
```

Figure S204. HPLC spectra of **3aj**.

```
Data File D:\DATA\LJ\LJ-2-137\LJ-2-137 2020-08-14 01-46-37\003-2-LJ-2-137-RAC.D
Sample Name: LJ-2-137-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   2
    Injection Date  : 8/14/2020 2:38:49 AM              Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-137\LJ-2-137 2020-08-14 01-46-37\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M
    Last changed    : 8/14/2020 1:43:33 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-137\LJ-2-137 2020-08-14 01-46-37\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M (Sequence Method)
    Last changed    : 8/24/2020 10:34:29 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  23.274 BB    0.6647 3671.11426   86.23427  50.0542
       2  26.141 BB    0.7466 3663.16650   76.50616  49.9458

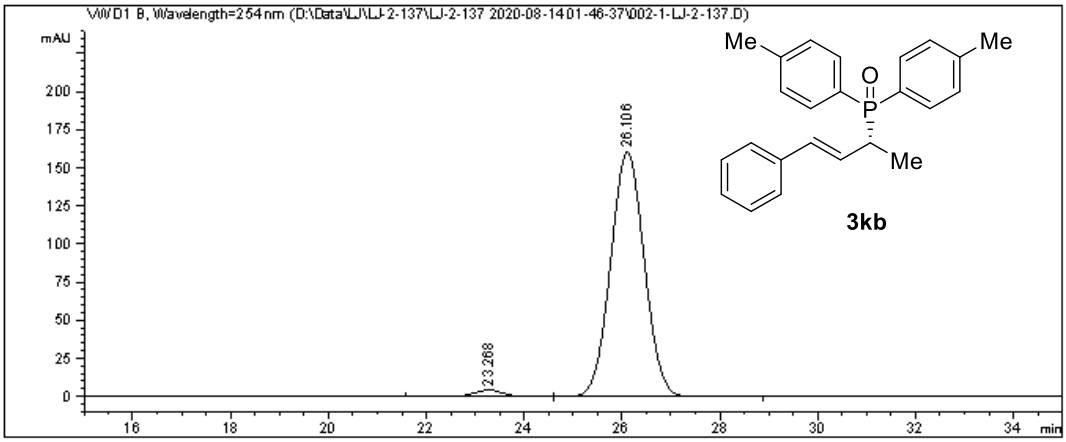
    Totals :                  7334.28076  162.74043


    ======================================================================
                              *** End of Report ***

1260 8/24/2020 10:34:40 PM SYSTEM                          Page 1 of 1
```

Figure S205. HPLC spectra of ***rac*-3kb**.

```
Data File D:\Data\LJ\LJ-2-137\LJ-2-137 2020-08-14 01-46-37\002-1-LJ-2-137.D
Sample Name: LJ-2-137
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   1
    Injection Date  : 8/14/2020 1:58:03 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-2-137\LJ-2-137 2020-08-14 01-46-37\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M
    Last changed    : 8/14/2020 1:43:33 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-2-137\LJ-2-137 2020-08-14 01-46-37\P2-80-20-1.0ML-5UL-220NM-
                      254NM-40MIN.M (Sequence Method)
    Last changed    : 8/24/2020 10:37:03 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  23.268 BB    0.6702  188.35468    4.34128   2.3880
       2  26.106 BB    0.7482 7699.27930  160.91919  97.6120

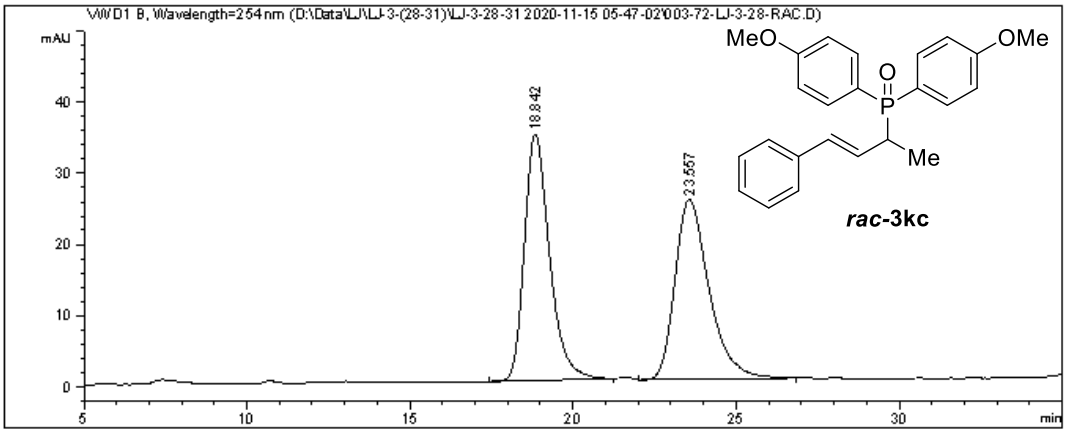
    Totals :                  7887.63397  165.26047


    ======================================================================
                            *** End of Report ***

1260 8/24/2020 10:37:08 PM SYSTEM                          Page 1 of 1
```

Figure S206. HPLC spectra of **3kb**.

```
Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\003-72-LJ-3-28-RAC.D
Sample Name: LJ-3-28-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   72
    Injection Date  : 11/15/2020 6:39:23 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-
                      220NM-254NM-40MIN.M
    Last changed    : 8/23/2020 2:17:41 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-
                      220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/15/2020 8:46:10 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  18.842 BB    0.8074 1857.59900   34.54003  50.3459
       2  23.557 BB    1.0851 1832.07605   25.23262  49.6541

    Totals :                  3689.67505   59.77265

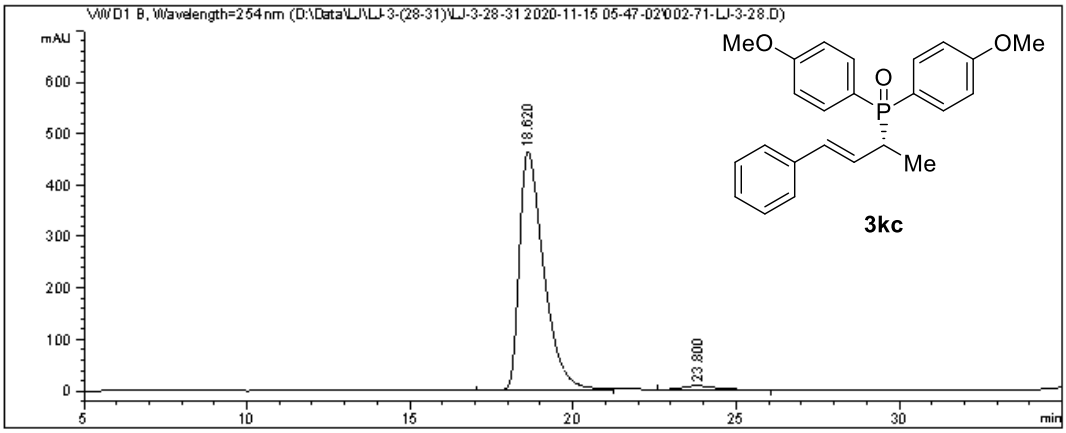

    ======================================================================
                               *** End of Report ***

1260 11/15/2020 8:46:18 AM SYSTEM                          Page 1 of 1
```

Figure S207. HPLC spectra of ***rac*-3kc**.

Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\002-71-LJ-3-28.D
Sample Name: LJ-3-28

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 71
Injection Date	: 11/15/2020 5:58:41 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-220NM-254NM-40MIN.M		
Last changed	: 8/23/2020 2:17:41 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P1-90-10-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)		
Last changed	: 11/15/2020 8:47:50 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.620	BB	0.7920	2.39771e4	463.17120	97.5451
2	23.800	BB	1.0673	603.44043	8.36791	2.4549
Totals :				2.45806e4	471.53912	

*** End of Report ***

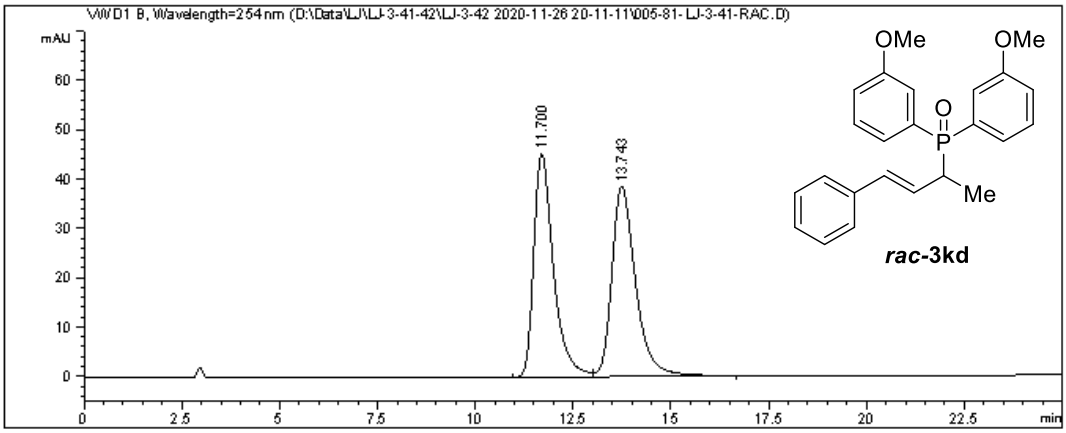
1260 11/15/2020 8:47:56 AM SYSTEM

Page 1 of 1

Figure S208. HPLC spectra of **3kc**.

Data File D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\005-81-LJ-3-41-RAC.D
Sample Name: LJ-3-41-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 5
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 81
Injection Date	: 11/26/2020 9:59:12 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 8/23/2020 2:17:04 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 11/27/2020 3:40:24 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.700	BV	0.5288	1585.78796	45.25752	49.3502
2	13.743	VB	0.6394	1627.55164	38.48030	50.6498
Totals :				3213.33960	83.73782	

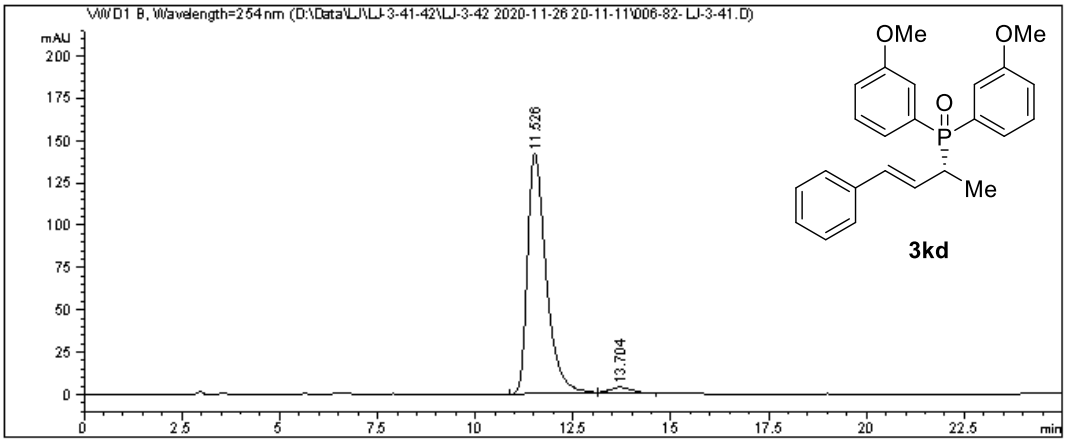
*** End of Report ***

1260 11/27/2020 3:40:32 AM SYSTEM

Page 1 of 1

Figure S209. HPLC spectra of ***rac*-3kd**.

```
Data File D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\006-82-LJ-3-41.D
Sample Name: LJ-3-41
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   82
    Injection Date  : 11/26/2020 10:29:55 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-90-10-1.0ML-5UL-220NM-
                      254NM-30MIN.M
    Last changed    : 8/23/2020 2:17:04 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-41-42\LJ-3-42 2020-11-26 20-11-11\P1-90-10-1.0ML-5UL-220NM-
                      254NM-30MIN.M (Sequence Method)
    Last changed    : 11/27/2020 3:41:52 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                           Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.526 BB    0.5040 4712.57764  141.68825  97.5494
       2  13.704 BB    0.5836  118.38741    3.15595   2.4506

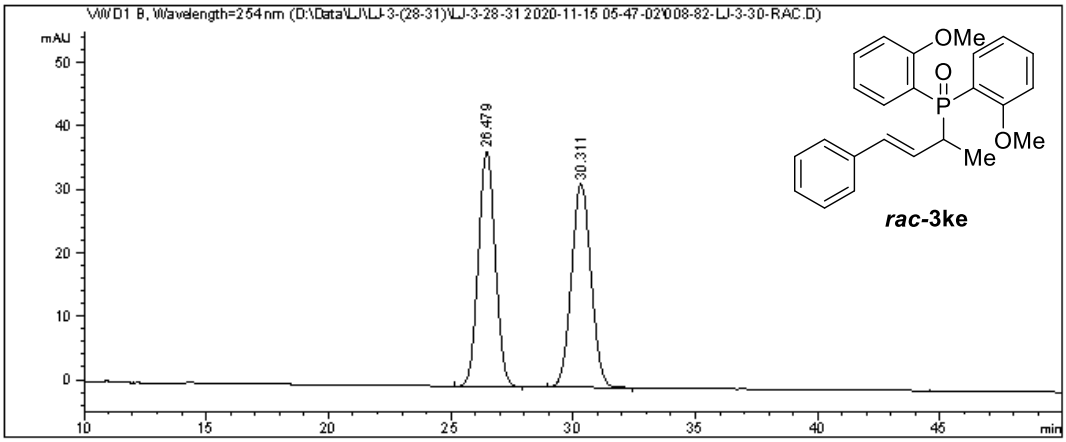
    Totals :                  4830.96505  144.84420


    ======================================================================
                           *** End of Report ***

1260 11/27/2020 3:42:00 AM SYSTEM                          Page 1 of 1
```

Figure S210. HPLC spectra of **3kd**.

```
Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\008-82-LJ-3-30-RAC.D
Sample Name: LJ-3-30-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   8
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   82
    Injection Date  : 11/15/2020 9:33:10 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-
                      220NM-254NM-60MIN.M
    Last changed    : 8/23/2020 2:25:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-
                      220NM-254NM-60MIN.M (Sequence Method)
    Last changed    : 11/16/2020 2:03:20 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  26.479 BB    0.7273 1782.61914   36.91867  50.0178
       2  30.311 BB    0.8797 1781.34717   31.98925  49.9822

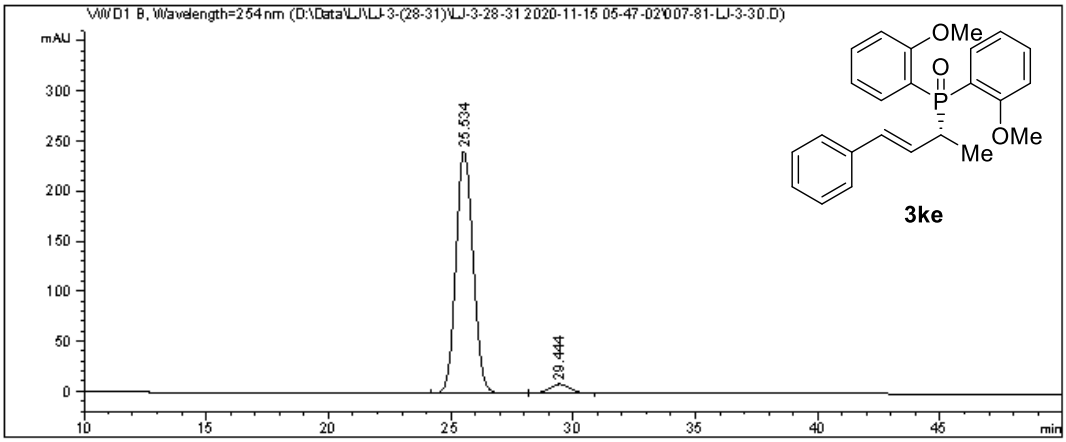
    Totals :                  3563.96631   68.90792


    ======================================================================
                            *** End of Report ***

1260 11/16/2020 2:03:25 AM SYSTEM                          Page 1 of 1
```

Figure S211. HPLC spectra of ***rac*-3ke**.

```
Data File D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\007-81-LJ-3-30.D
Sample Name: LJ-3-30
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   7
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   81
    Injection Date  : 11/15/2020 8:32:26 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-
                      220NM-254NM-60MIN.M
    Last changed    : 8/23/2020 2:25:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-(28-31)\LJ-3-28-31 2020-11-15 05-47-02\P2-80-20-1.0ML-5UL-
                      220NM-254NM-60MIN.M (Sequence Method)
    Last changed    : 11/16/2020 2:04:57 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  25.534 BB    0.7543 1.17393e4   240.99101  95.9858
       2  29.444 BB    0.8453  490.94220    8.71404   4.0142

    Totals :                  1.22303e4   249.70505


    ======================================================================
                              *** End of Report ***

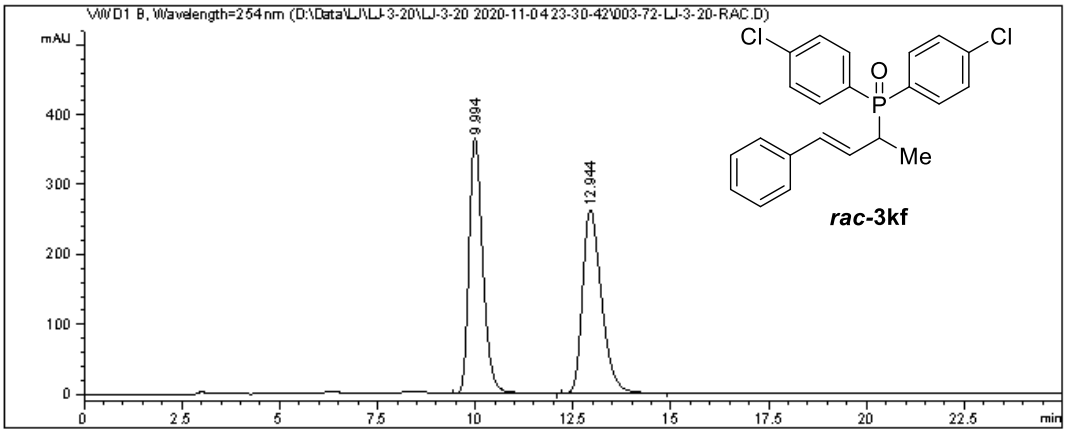
1260 11/16/2020 2:05:05 AM SYSTEM                          Page 1 of 1
```

Figure S212. HPLC spectra of **3ke**.

Data File D:\Data\LJ\LJ-3-20\LJ-3-20 2020-11-04 23-30-42\003-72-LJ-3-20-RAC.D
Sample Name: LJ-3-20-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 3
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 72
Injection Date	: 11/5/2020 12:15:38 AM	Inj	: 1
		Inj Volume	: 5.000 µl

Acq. Method : D:\Data\LJ\LJ-3-20\LJ-3-20 2020-11-04 23-30-42\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M
Last changed : 8/23/2020 2:17:04 AM by SYSTEM
Analysis Method : D:\Data\LJ\LJ-3-20\LJ-3-20 2020-11-04 23-30-42\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)
Last changed : 11/5/2020 1:39:03 AM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.994	BB	0.3790	8991.90918	365.49130	50.0701
2	12.944	BB	0.5194	8966.74414	263.22888	49.9299
Totals :				1.79587e4	628.72018	

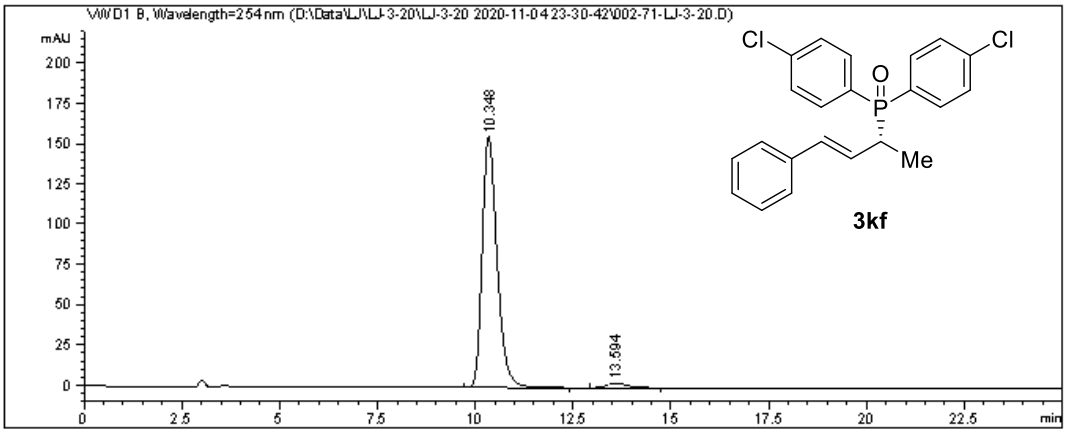
*** End of Report ***

1260 11/5/2020 1:39:09 AM SYSTEM

Figure S213. HPLC spectra of ***rac*-3kf**.

Data File D:\Data\LJ\LJ-3-20\LJ-3-20 2020-11-04 23-30-42\002-71-LJ-3-20.D
Sample Name: LJ-3-20

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 71
Injection Date	: 11/4/2020 11:44:56 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-20\LJ-3-20 2020-11-04 23-30-42\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 8/23/2020 2:17:04 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-20\LJ-3-20 2020-11-04 23-30-42\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 11/5/2020 1:41:48 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.348	BB	0.4063	4116.49121	155.77254	97.3663
2	13.594	BB	0.5849	111.35025	2.89402	2.6337
Totals :				4227.84146	158.66656	

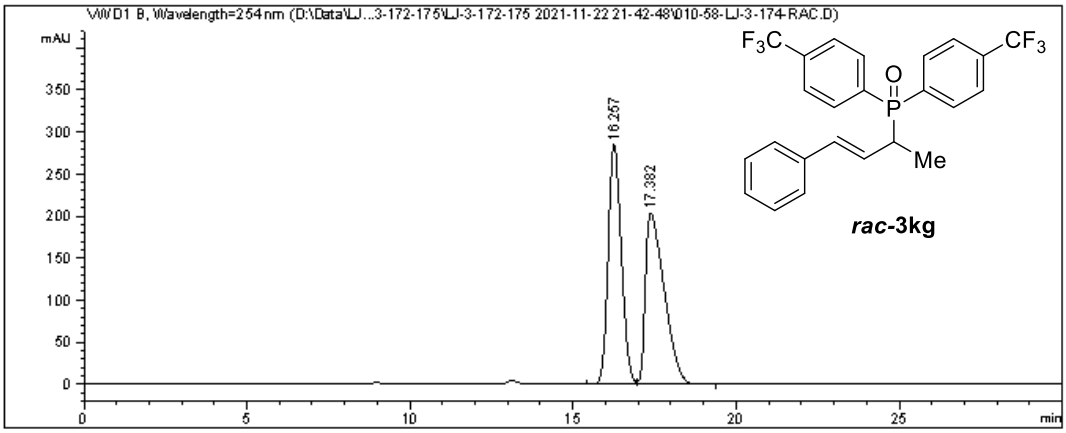
*** End of Report ***

1260 11/5/2020 1:41:55 AM SYSTEM Page 1 of 1

Figure S214. HPLC spectra of **3kf**.

Data File D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\010-58-LJ-3-174-RAC.D
Sample Name: LJ-3-174-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  10
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                           Location :  58
    Injection Date  : 11/23/2021 2:30:17 AM              Inj :  1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M
    Last changed    : 10/15/2020 8:06:11 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:22:39 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.257 BV    0.4399 8012.74365  285.11063  49.6146
       2  17.382 VB    0.6224 8137.24121  203.56592  50.3854

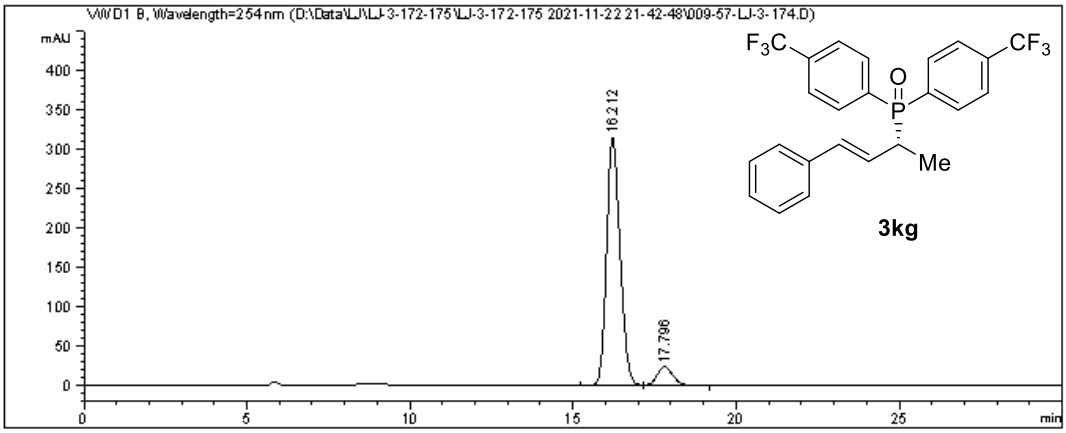
    Totals :                  1.61500e4   488.67654


    ======================================================================
                              *** End of Report ***

1260 11/30/2021 10:22:52 PM SYSTEM                          Page 1 of 1
```

Figure S215. HPLC spectra of ***rac*-3kg**.

```
Data File D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\009-57-LJ-3-174.D
Sample Name: LJ-3-174
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   9
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   57
    Injection Date  : 11/23/2021 1:59:35 AM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M
    Last changed    : 10/15/2020 8:06:11 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:24:40 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  16.212 BV    0.4476 9031.64258  313.98929  92.0705
       2  17.796 VB    0.5130  777.84515   23.56837   7.9295

    Totals :                  9809.48773  337.55766

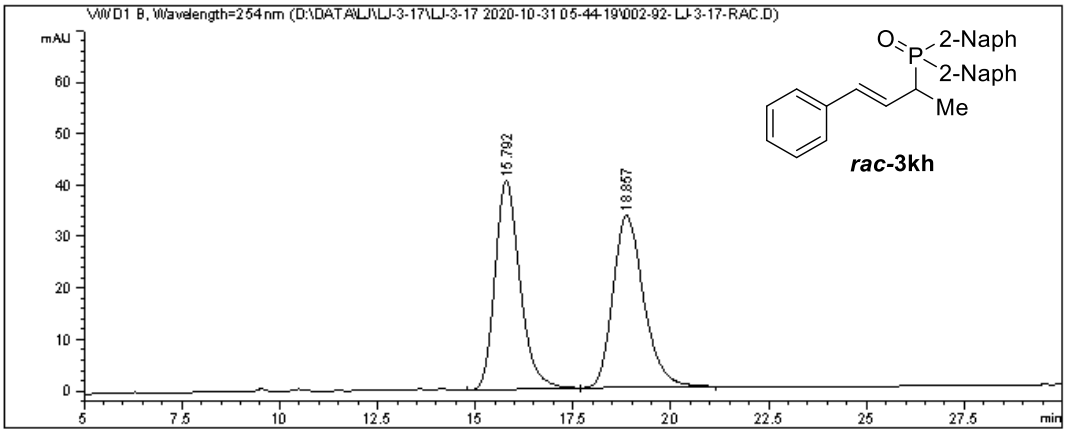

    ======================================================================
                              *** End of Report ***

1260 11/30/2021 10:24:44 PM SYSTEM                          Page 1 of 1
```

Figure S216. HPLC spectra of **3kg**.

Data File D:\DATA\LJ\LJ-3-17\LJ-3-17 2020-10-31 05-44-19\002-92-LJ-3-17-RAC.D
Sample Name: LJ-3-17-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 92
Injection Date	: 10/31/2020 5:55:58 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-17\LJ-3-17 2020-10-31 05-44-19\P1-90-10-1.0ML-5UL-220NM-254NM-40MIN.M		
Last changed	: 8/23/2020 2:17:41 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-17\LJ-3-17 2020-10-31 05-44-19\P1-90-10-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)		
Last changed	: 11/3/2020 4:05:38 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.792	BB	0.6843	1801.55627	40.54876	49.5166
2	18.857	BB	0.8497	1836.73120	33.49660	50.4834
Totals :				3638.28748	74.04536	

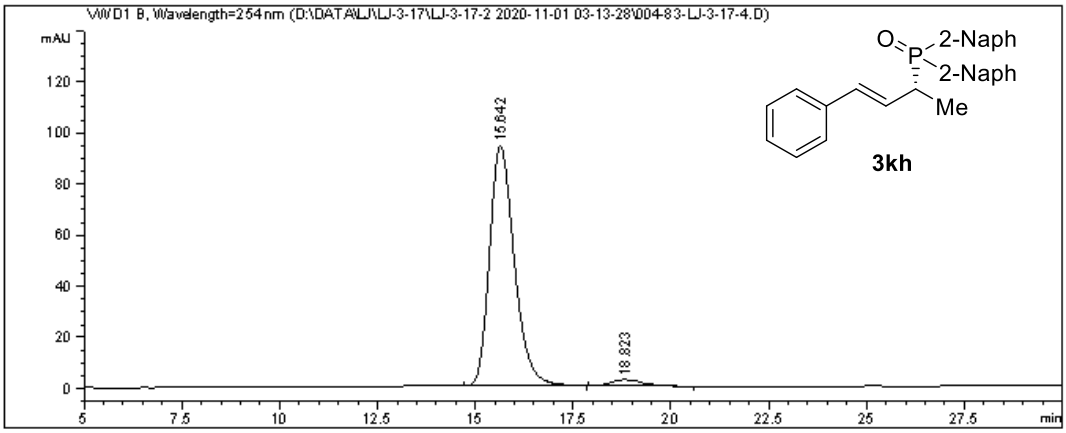
*** End of Report ***

1260 11/3/2020 4:05:43 AM SYSTEM Page 1 of 1

Figure S217. HPLC spectra of ***rac*-3kh**.

Data File D:\DATA\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\004-83-LJ-3-17-4.D
Sample Name: LJ-3-17-4

Acq. Operator	: SYSTEM	Seq. Line	: 4
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 83
Injection Date	: 11/1/2020 4:28:48 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M		
Last changed	: 8/23/2020 2:17:04 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-17\LJ-3-17-2 2020-11-01 03-13-28\P1-90-10-1.0ML-5UL-220NM-254NM-30MIN.M (Sequence Method)		
Last changed	: 11/3/2020 4:07:54 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

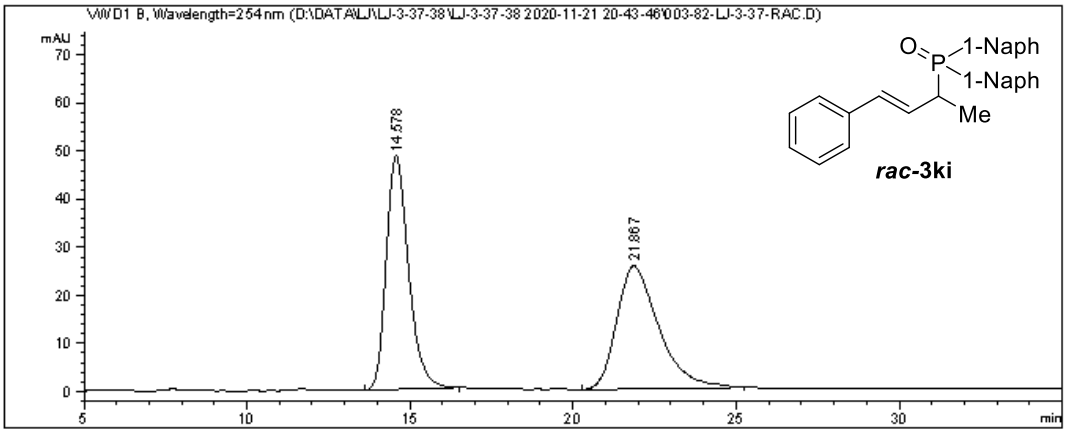
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.642	BB	0.6761	4126.66162	94.01119	96.6910
2	18.823	BB	0.8704	141.22437	2.48738	3.3090
Totals :				4267.88599	96.49857	

*** End of Report ***

1260 11/3/2020 4:07:58 AM SYSTEM Page 1 of 1

Figure S218. HPLC spectra of **3kh**.

```
Data File D:\DATA\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\003-82-LJ-3-37-RAC.D
Sample Name: LJ-3-37-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   82
    Injection Date  : 11/21/2020 9:39:08 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M
    Last changed    : 11/21/2020 8:41:36 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/24/2020 2:29:34 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.578 BB    0.7375 2310.86719   48.53537  50.2512
       2  21.867 BB    1.3524 2287.76343   25.65475  49.7488

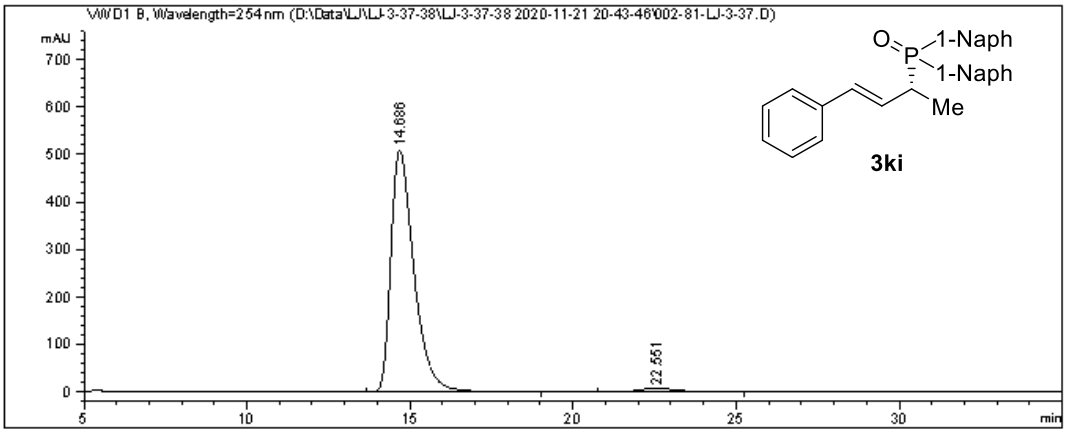
    Totals :                  4598.63062   74.19011


    ======================================================================
                              *** End of Report ***

1260 11/24/2020 2:29:49 AM SYSTEM                          Page 1 of 1
```

Figure S219. HPLC spectra of ***rac*-3ki**.

```
Data File D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\002-81-LJ-3-37.D
Sample Name: LJ-3-37
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   2
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   81
    Injection Date  : 11/21/2020 8:58:25 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M
    Last changed    : 11/21/2020 8:41:36 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-37-38\LJ-3-37-38 2020-11-21 20-43-46\P1-85-15-1.0ML-5UL-
                      220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/24/2020 2:31:35 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  14.686 BB    0.7652 2.51427e4   509.98615  97.4042
       2  22.551 BB    1.3913  670.06018    7.21651   2.5958

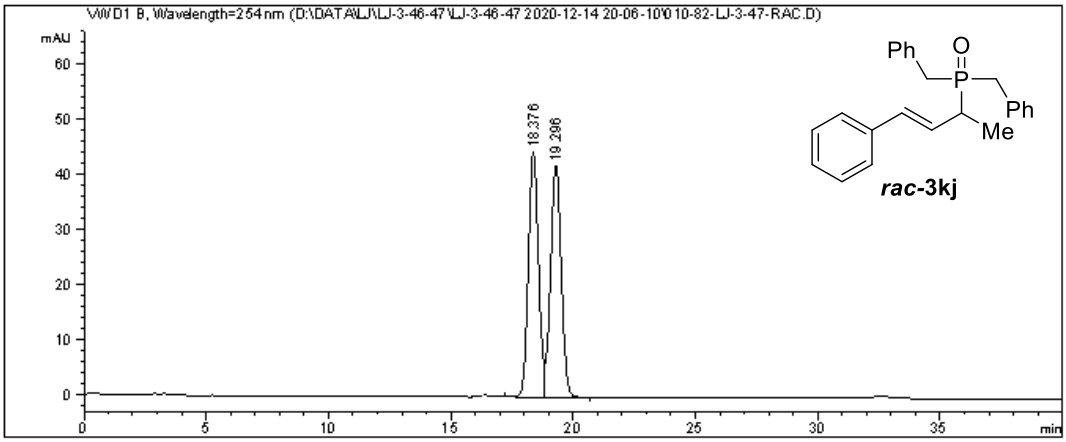
    Totals :                  2.58128e4   517.20266


    ======================================================================
                               *** End of Report ***

1260 11/24/2020 2:31:42 AM SYSTEM                          Page 1 of 1
```

Figure S220. HPLC spectra of **3ki**.

```
Data File D:\DATA\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\010-82-LJ-3-47-RAC.D
Sample Name: LJ-3-47-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  10
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   82
    Injection Date  : 12/14/2020 11:16:35 PM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P1-90-10-1.0ML-5UL-
                      220NM-254NM-60MIN.M
    Last changed    : 8/22/2020 11:49:17 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P1-90-10-1.0ML-5UL-
                      220NM-254NM-60MIN.M (Sequence Method)
    Last changed    : 12/15/2020 1:23:51 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  18.376 BV    0.4521 1288.17224   44.45259  50.0087
       2  19.296 VB    0.4770 1287.72363   42.08435  49.9913

    Totals :                  2575.89587   86.53694

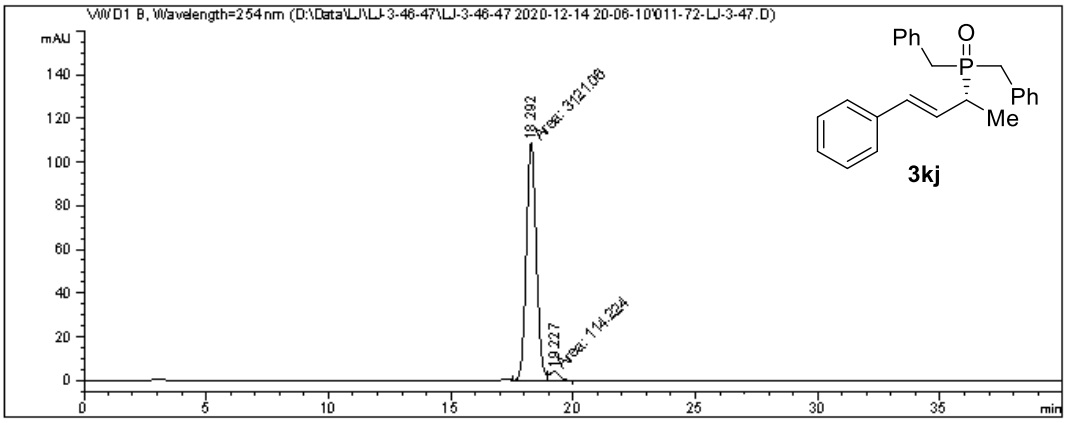

    ======================================================================
                            *** End of Report ***

1260 12/15/2020 1:23:55 AM SYSTEM                          Page 1 of 1
```

Figure S221. HPLC spectra of ***rac*-3kj**.

Data File D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\011-72-LJ-3-47.D
Sample Name: LJ-3-47

```
    ======================================================================
    Acq. Operator   : SYSTEM                       Seq. Line :  11
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :  72
    Injection Date  : 12/15/2020 12:17:17 AM            Inj :  1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P1-90-10-1.0ML-5UL-
                      220NM-254NM-60MIN.M
    Last changed    : 12/15/2020 1:11:34 AM by SYSTEM
                      (modified after loading)
    Analysis Method : D:\Data\LJ\LJ-3-46-47\LJ-3-46-47 2020-12-14 20-06-10\P1-90-10-1.0ML-5UL-
                      220NM-254NM-60MIN.M (Sequence Method)
    Last changed    : 12/15/2020 1:25:46 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  18.292 MF    0.4791 3121.05933  108.56474  96.4694
       2  19.227 FM    0.4691  114.22372    4.05869   3.5306

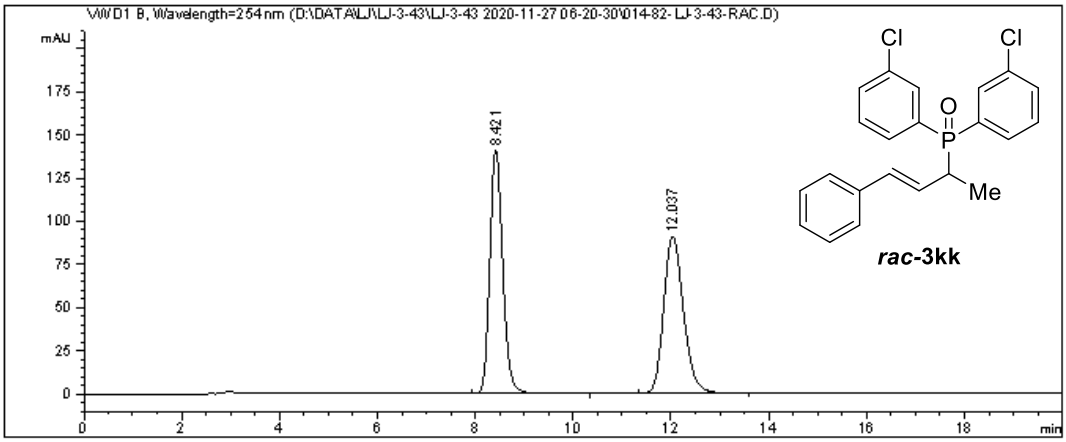
    Totals :                  3235.28305  112.62343


    ======================================================================
                              *** End of Report ***

1260 12/15/2020 1:25:56 AM SYSTEM                          Page 1 of 1
```

Figure S222. HPLC spectra of **3kj**.

```
Data File D:\DATA\LJ\LJ-3-43\LJ-3-43 2020-11-27 06-20-30\014-82-LJ-3-43-RAC.D
Sample Name: LJ-3-43-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  14
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   82
    Injection Date  : 11/27/2020 11:51:29 AM            Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-43\LJ-3-43 2020-11-27 06-20-30\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/23/2020 2:15:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-43\LJ-3-43 2020-11-27 06-20-30\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 11/27/2020 8:11:36 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.421 BB    0.2832 2566.82593  140.47169  50.2088
       2  12.037 BB    0.4341 2545.47729   90.52120  49.7912

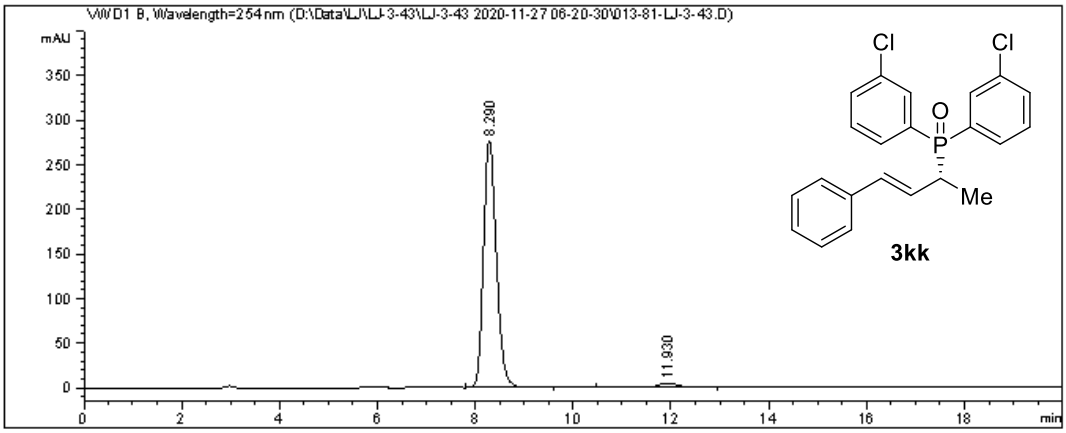
    Totals :                  5112.30322  230.99290


    ======================================================================
                              *** End of Report ***

1260 11/27/2020 8:11:43 PM SYSTEM                          Page 1 of 1
```

Figure S223. HPLC spectra of ***rac*-3kk**.

```
Data File D:\Data\LJ\LJ-3-43\LJ-3-43 2020-11-27 06-20-30\013-81-LJ-3-43.D
Sample Name: LJ-3-43
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  13
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :  81
    Injection Date  : 11/27/2020 11:30:45 AM            Inj :  1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-43\LJ-3-43 2020-11-27 06-20-30\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M
    Last changed    : 8/23/2020 2:15:51 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-43\LJ-3-43 2020-11-27 06-20-30\P1-90-10-1.0ML-5UL-220NM-
                      254NM-20MIN.M (Sequence Method)
    Last changed    : 11/27/2020 8:13:12 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1   8.290 BB    0.2808 5053.92236  277.09402  96.7203
       2  11.930 VB R  0.4950  171.37312    5.11349   3.2797

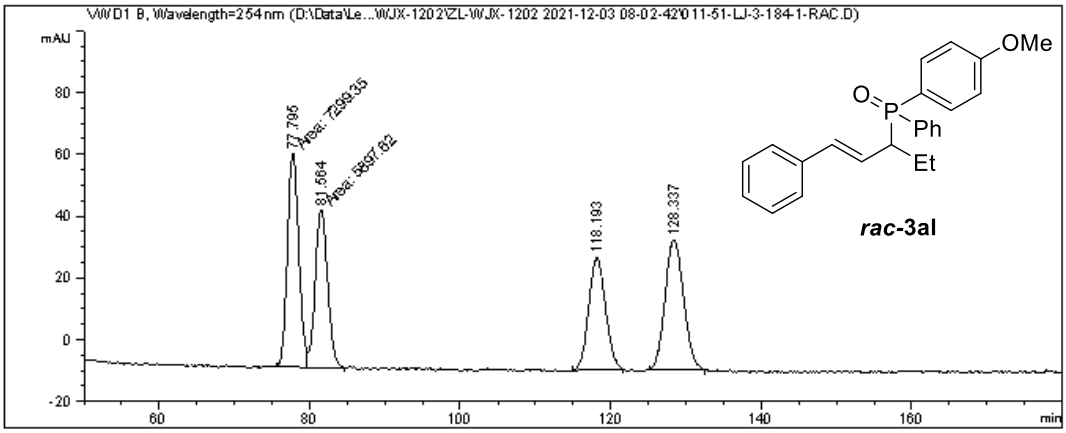
    Totals :                  5225.29549  282.20752


    ======================================================================
                              *** End of Report ***

1260 11/27/2020 8:13:18 PM SYSTEM                          Page 1 of 1
```

Figure S224. HPLC spectra of **3kk**.

```
Data File D:\Data\Le...ZL-WJX-1202\ZL-WJX-1202 2021-12-03 08-02-42\011-51-LJ-3-184-1-RAC.D
Sample Name: LJ-3-184-1-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :  11
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                           Location :  51
    Injection Date  : 12/3/2021 2:51:10 PM               Inj :  1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\Lei-ZL\ZL-WJX-1202\ZL-WJX-1202 2021-12-03 08-02-42\P2-85-15-0.4ML-
                      5UL-220NM-254NM-180MIN.M
    Last changed    : 12/2/2021 10:17:06 PM by SYSTEM
    Analysis Method : D:\Data\Lei-ZL\ZL-WJX-1202\ZL-WJX-1202 2021-12-03 08-02-42\P2-85-15-0.4ML-
                      5UL-220NM-254NM-180MIN.M (Sequence Method)
    Last changed    : 12/4/2021 9:11:47 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  77.795 MF    1.7497 7299.35010   69.53131  27.9604
       2  81.564 FM    1.9208 5897.62158   51.17248  22.5910
       3 118.193 BB    2.0967 5670.98242   36.45900  21.7229
       4 128.337 BB    2.1230 7238.05859   42.11659  27.7256

    Totals :                  2.61060e4   199.27939

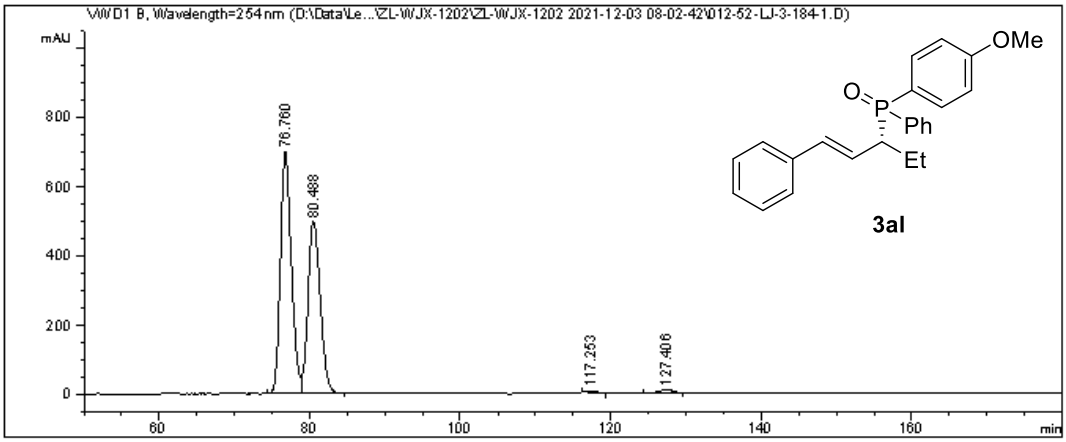

    ======================================================================

1260 12/4/2021 9:12:02 AM SYSTEM                                  Page 1 of 2
```

Figure S225. HPLC spectra of ***rac*-3al** (reported as a mixture of diastereomers).

Data File D:\Data\Lei-ZL\ZL-WJX-1202\ZL-WJX-1202 2021-12-03 08-02-42\012-52-LJ-3-184-1.D
Sample Name: LJ-3-184-1

```
    ======================================================================
    Acq. Operator   : SYSTEM                       Seq. Line :  12
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :  52
    Injection Date  : 12/3/2021 5:51:53 PM              Inj :  1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\Lei-ZL\ZL-WJX-1202\ZL-WJX-1202 2021-12-03 08-02-42\P2-85-15-0.4ML-
                      5UL-220NM-254NM-180MIN.M
    Last changed    : 12/2/2021 10:17:06 PM by SYSTEM
    Analysis Method : D:\Data\Lei-ZL\ZL-WJX-1202\ZL-WJX-1202 2021-12-03 08-02-42\P2-85-15-0.4ML-
                      5UL-220NM-254NM-180MIN.M (Sequence Method)
    Last changed    : 12/4/2021 9:21:32 AM by SYSTEM
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  76.760 BV    1.5672 7.07890e4   699.16571  54.6711
       2  80.488 VB    1.7111 5.70595e4   496.38150  44.0676
       3 117.253 BB    1.2645  429.20178    4.38280   0.3315
       4 127.406 BB    1.7488 1203.95593    8.19103   0.9298

    Totals :                  1.29482e5  1208.12105

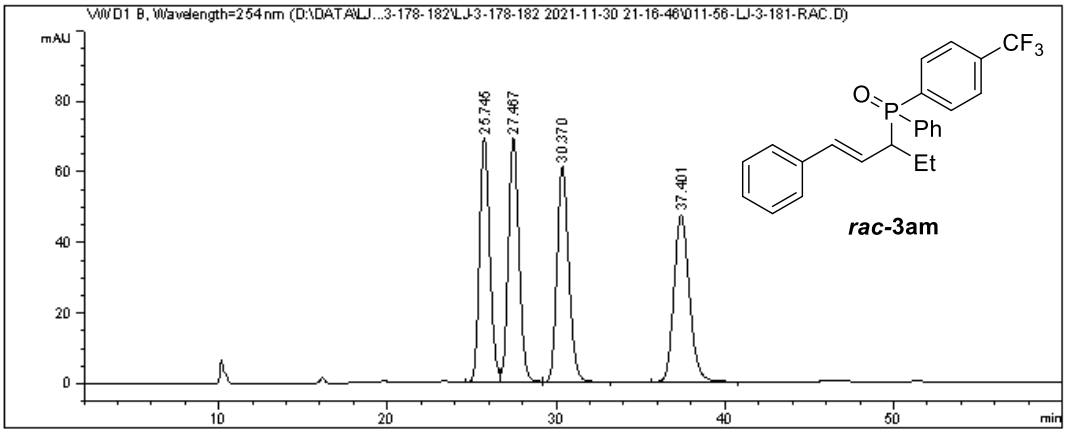

    ======================================================================

1260 12/15/2021 3:48:20 AM SYSTEM                                Page 1 of 2
```

Figure S226. HPLC spectra of **3al** (reported as a mixture of diastereomers).

Data File D:\DATA\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\011-56-LJ-3-181-RAC.D
Sample Name: LJ-3-181-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 11
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 56
Injection Date	: 12/1/2021 1:37:46 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P2-94-6-0.3ML-5UL-220NM-254NM-70MIN.M		
Last changed	: 11/30/2021 9:34:00 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P2-94-6-0.3ML-5UL-220NM-254NM-70MIN.M (Sequence Method)		
Last changed	: 12/1/2021 4:52:05 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

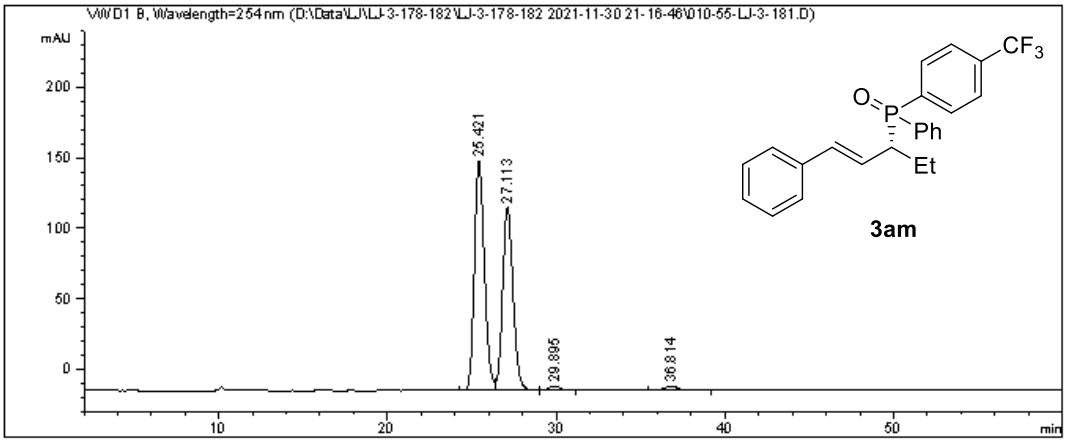
Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.745	BV	0.6574	2927.42236	69.21364	24.4981
2	27.467	VB	0.6830	3030.03589	69.18124	25.3568
3	30.370	BB	0.7534	2978.47266	61.02335	24.9253
4	37.401	BB	0.9739	3013.66919	47.38910	25.2198
Totals :				1.19496e4	246.80732	

Figure S227. HPLC spectra of ***rac*-3am** (reported as a mixture of diastereomers).

Data File D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\010-55-LJ-3-181.D
Sample Name: LJ-3-181

Acq. Operator	: SYSTEM	Seq. Line	: 10
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 55
Injection Date	: 12/1/2021 12:27:02 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P2-94-6-0.3ML-5UL-220NM-254NM-70MIN.M		
Last changed	: 11/30/2021 9:34:00 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P2-94-6-0.3ML-5UL-220NM-254NM-70MIN.M (Sequence Method)		
Last changed	: 12/1/2021 4:59:37 AM by SYSTEM		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 B, Wavelength=254 nm

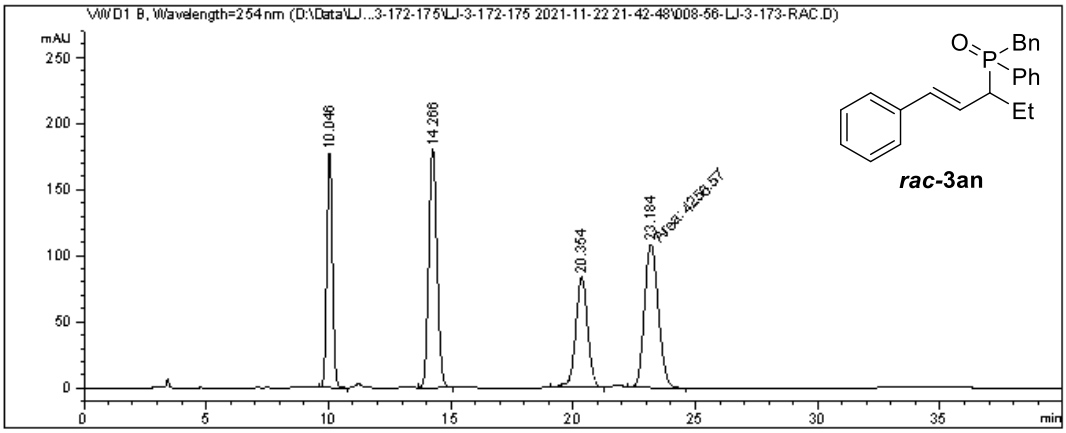
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.421	BV	0.6450	6762.35156	162.68384	53.1273
2	27.113	VB	0.6829	5642.90283	129.86325	44.3325
3	29.895	BB	0.7082	139.01546	2.99115	1.0922
4	36.814	BB	0.9868	184.31906	2.81894	1.4481
Totals :				1.27286e4	298.35718	

Figure S228. HPLC spectra of **3am** (reported as a mixture of diastereomers).

Data File D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\008-56-LJ-3-173-RAC.D
Sample Name: LJ-3-173-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 8
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 56
Injection Date	: 11/23/2021 1:18:50 AM	Inj	: 1
		Inj Volume	: 5.000 µl

Acq. Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL-220NM-254NM-40MIN.M
Last changed : 11/21/2020 8:41:36 PM by SYSTEM
Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)
Last changed : 11/30/2021 10:12:27 PM by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

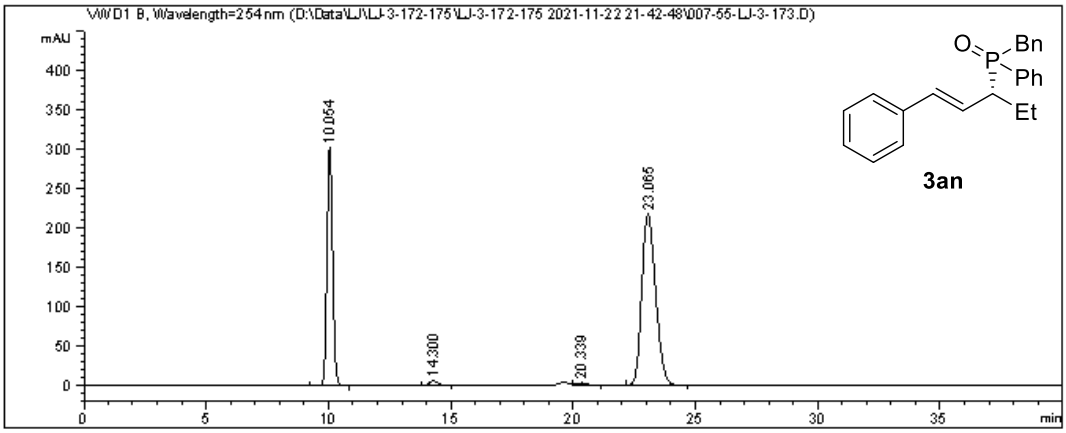
Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.046	BB	0.2479	2826.78516	177.36853	19.8758
2	14.266	BB	0.3697	4257.12500	180.12068	29.9329
3	20.354	BB	0.5346	2881.76514	83.51828	20.2624
4	23.184	FM	0.6543	4256.56836	108.41961	29.9290
Totals :				1.42222e4	549.42710	

Figure S229. HPLC spectra of ***rac*-3an** (reported as a mixture of diastereomers).

Data File D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\007-55-LJ-3-173.D
Sample Name: LJ-3-173

Acq. Operator	: SYSTEM	Seq. Line	: 7
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 55
Injection Date	: 11/23/2021 12:38:07 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL-220NM-254NM-40MIN.M		
Last changed	: 11/21/2020 8:41:36 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)		
Last changed	: 12/15/2021 3:57:56 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

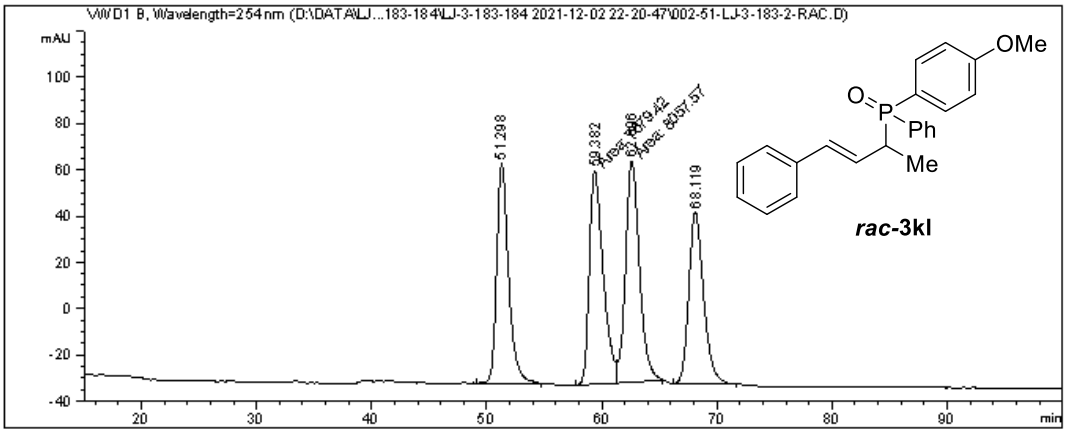
Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.054	VB R	0.2490	4829.73291	301.40018	35.4779
2	14.300	BB	0.3689	135.81970	5.64183	0.9977
3	20.339	VB	0.4981	108.77480	3.32131	0.7990
4	23.065	BB	0.6176	8539.01855	216.76474	62.7253
Totals :				1.36133e4	527.12806	

Figure S230. HPLC spectra of **3an** (reported as a mixture of diastereomers).

Data File D:\DATA\LJ\LJ-3-183-184\LJ-3-183-184 2021-12-02 22-20-47\002-51-LJ-3-183-2-RAC.D
Sample Name: LJ-3-183-2-RAC

Acq. Operator	: SYSTEM	Seq. Line	: 2
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 51
Injection Date	: 12/2/2021 10:35:02 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-183-184\LJ-3-183-184 2021-12-02 22-20-47\P1-80-20-0.3ML-5UL-220NM-254NM-100MIN.M		
Last changed	: 12/2/2021 10:14:26 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-183-184\LJ-3-183-184 2021-12-02 22-20-47\P1-80-20-0.3ML-5UL-220NM-254NM-100MIN.M (Sequence Method)		
Last changed	: 12/4/2021 9:23:09 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

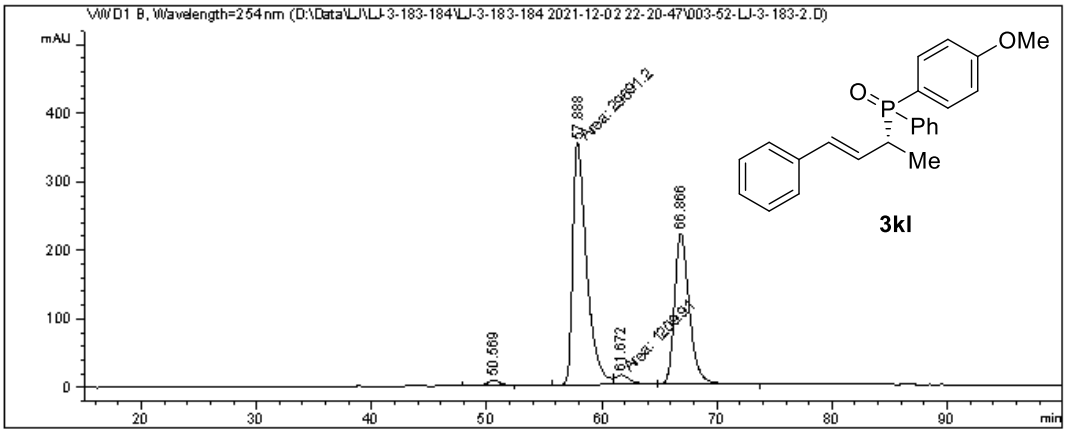
Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	51.298	BB	1.0836	6820.30273	95.00307	23.3709
2	59.382	MF	1.3888	7679.42578	92.15852	26.3148
3	62.606	FM	1.4069	8057.56592	95.45222	27.6106
4	68.119	BB	1.3641	6625.58594	74.03111	22.7037
Totals :				2.91829e4	356.64492	

Figure S231. HPLC spectra of ***rac*-3kl** (reported as a mixture of diastereomers).

Data File D:\Data\LJ\LJ-3-183-184\LJ-3-183-184 2021-12-02 22-20-47\003-52-LJ-3-183-2.D
Sample Name: LJ-3-183-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                           Location :   52
    Injection Date  : 12/3/2021 12:15:45 AM              Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-183-184\LJ-3-183-184 2021-12-02 22-20-47\P1-80-20-0.3ML-5UL
                      -220NM-254NM-100MIN.M
    Last changed    : 12/2/2021 10:14:26 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-183-184\LJ-3-183-184 2021-12-02 22-20-47\P1-80-20-0.3ML-5UL
                      -220NM-254NM-100MIN.M (Sequence Method)
    Last changed    : 12/15/2021 4:03:06 AM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

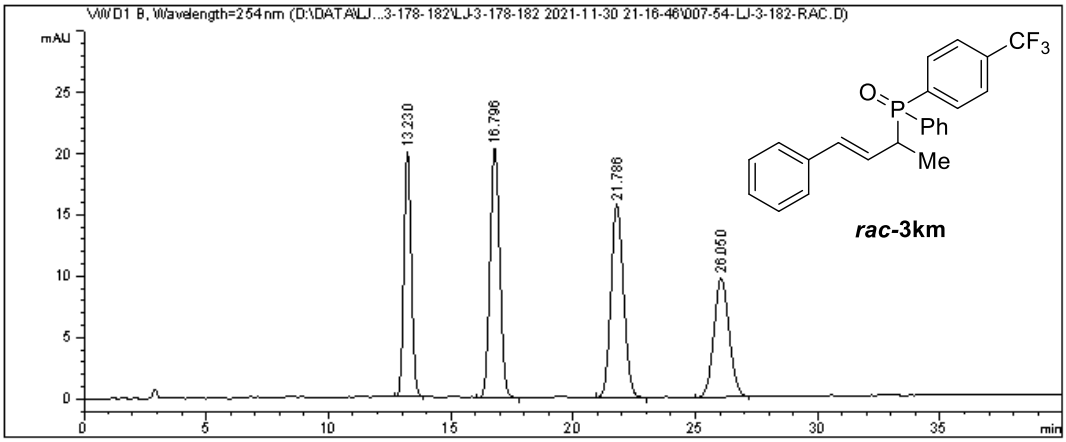
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  50.569 BB    1.0631  549.42023    7.67573   1.0776
       2  57.888 MF    1.4039 2.96912e4   352.49017  58.2340
       3  61.672 FM    1.4777 1209.90979   13.64621   2.3730
       4  66.866 BB    1.3697 1.95355e4   219.62827  38.3154

    Totals :                  5.09860e4   593.44038


    ======================================================================
```


Figure S232. HPLC spectra of **3kl** (reported as a mixture of diastereomers).

```
Data File D:\DATA\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\007-54-LJ-3-182-RAC.D
Sample Name: LJ-3-182-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   7
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   54
    Injection Date  : 11/30/2021 11:14:35 PM            Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P3-85-15-1.0ML-5UL
                      -220NM-254NM-40MIN.M
    Last changed    : 11/30/2021 9:25:06 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P3-85-15-1.0ML-5UL
                      -220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 12/1/2021 4:34:52 AM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                              Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  13.230 BB    0.3302  420.33923   19.91744  21.3994
       2  16.796 BB    0.4267  558.74255   20.32564  28.4455
       3  21.786 BB    0.5551  562.65295   15.73732  28.6446
       4  26.050 BB    0.6710  422.52240    9.68475  21.5105

    Totals :                  1964.25714   65.66514

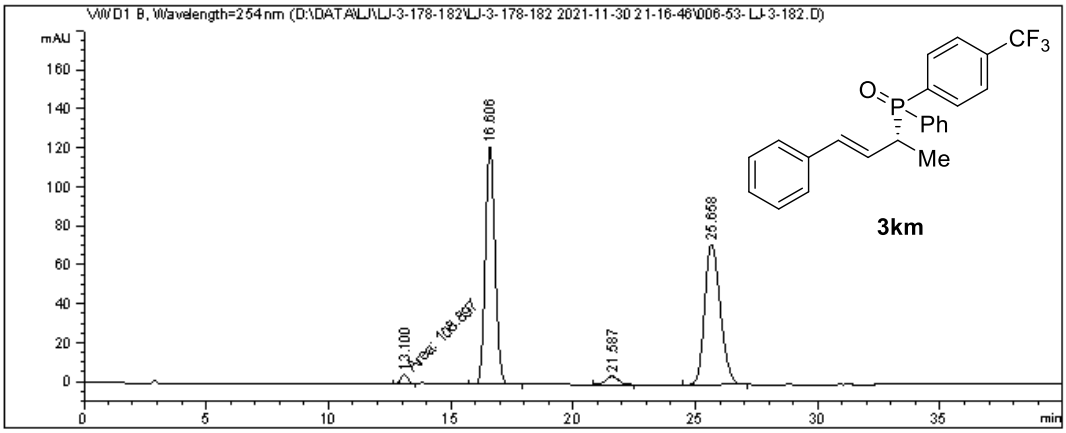

    ======================================================================

1260 12/1/2021 4:34:59 AM SYSTEM                                Page 1 of 2
```

Figure S233. HPLC spectra of ***rac*-3km** (reported as a mixture of diastereomers).

Data File D:\DATA\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\006-53-LJ-3-182.D
Sample Name: LJ-3-182

Acq. Operator	: SYSTEM	Seq. Line	: 6
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 53
Injection Date	: 11/30/2021 10:33:51 PM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P3-85-15-1.0ML-5UL-220NM-254NM-40MIN.M		
Last changed	: 11/30/2021 9:25:06 PM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-178-182\LJ-3-178-182 2021-11-30 21-16-46\P3-85-15-1.0ML-5UL-220NM-254NM-40MIN.M (Sequence Method)		
Last changed	: 12/15/2021 3:54:54 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

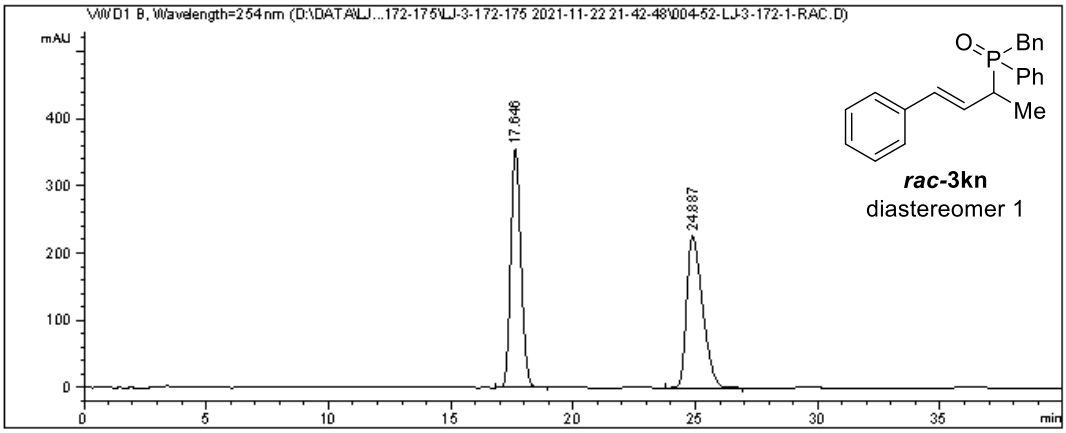
Signal 1: VWD1 B, Wavelength=254 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.100	MF	0.3559	108.89713	5.09988	1.5992
2	16.606	BB	0.4241	3334.39648	122.28763	48.9656
3	21.587	BB	0.5479	153.75826	4.33413	2.2579
4	25.658	BB	0.6863	3212.61450	72.03767	47.1773
Totals :				6809.66637	203.75930	

Figure S234. HPLC spectra of **3km** (reported as a mixture of diastereomers).

Data File D:\DATA\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\004-52-LJ-3-172-1-RAC.D
Sample Name: LJ-3-172-1-RAC

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   4
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                           Location :   52
    Injection Date  : 11/22/2021 10:55:55 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-40MIN.M
    Last changed    : 11/21/2020 8:41:36 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/30/2021 9:53:52 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

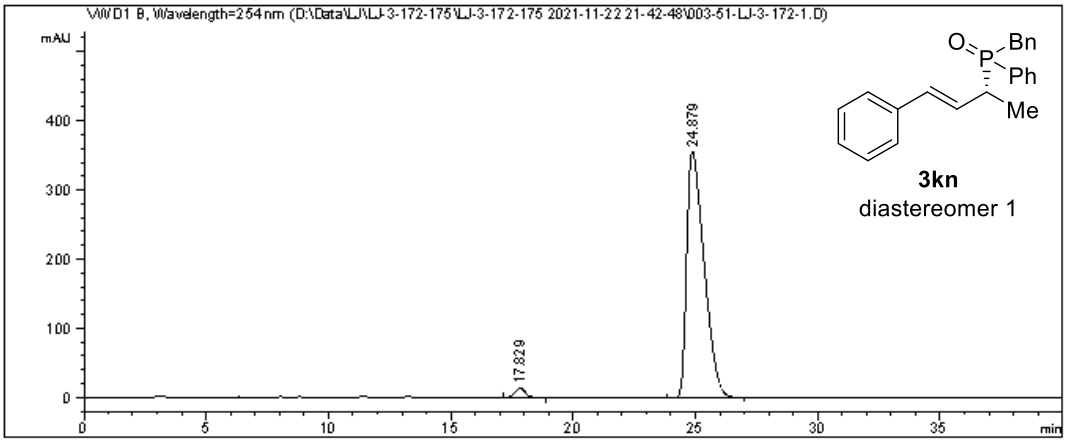
    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  17.646 BB    0.4404 1.01723e4   354.93857  50.0216
       2  24.887 BB    0.7049 1.01635e4   225.88161  49.9784

    Totals :                  2.03358e4   580.82018


    ======================================================================
                               *** End of Report ***
```


Figure S235. HPLC spectra of ***rac*-3kn** diastereomer 1.

```
Data File D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\003-51-LJ-3-172-1.D
Sample Name: LJ-3-172-1
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   3
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   51
    Injection Date  : 11/22/2021 10:15:12 PM             Inj :   1
                                                  Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-40MIN.M
    Last changed    : 11/21/2020 8:41:36 PM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-40MIN.M (Sequence Method)
    Last changed    : 11/30/2021 9:53:52 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  17.829 BB    0.4540  388.21075   13.32161   2.1605
       2  24.879 BB    0.7459 1.75801e4   356.12793  97.8395

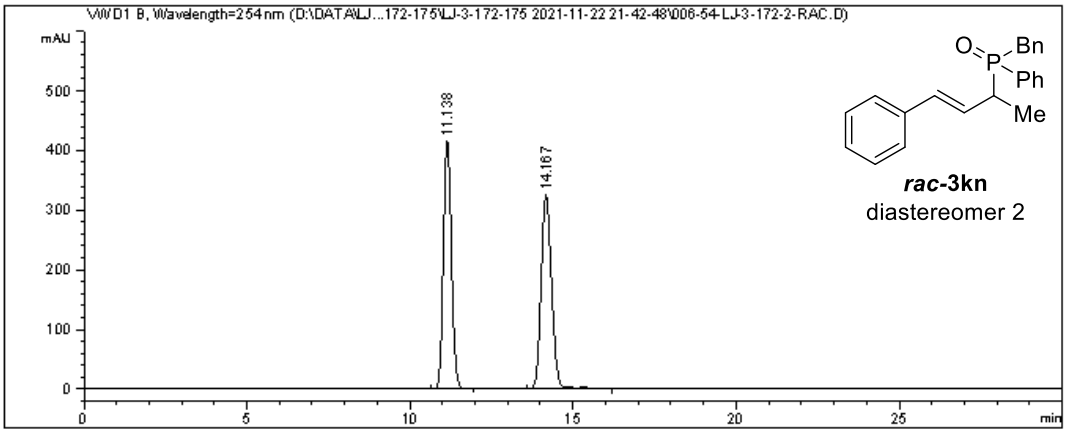
    Totals :                  1.79683e4   369.44954


    ======================================================================
                            *** End of Report ***

1260 11/30/2021 9:56:35 PM SYSTEM                          Page 1 of 1
```

Figure S236. HPLC spectra of **3kn** diastereomer 1.

```
Data File D:\DATA\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\006-54-LJ-3-172-2-RAC.D
Sample Name: LJ-3-172-2-RAC
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   6
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                          Location :   54
    Injection Date  : 11/23/2021 12:07:22 AM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M
    Last changed    : 10/15/2020 8:06:11 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:00:10 PM by SYSTEM
                      (modified after loading)
    Additional Info : Peak(s) manually integrated
    ======================================================================
```




```
    ======================================================================
                               Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.138 BB    0.2664 7134.98096  415.35880  49.5609
       2  14.167 BV R  0.3421 7261.41455  325.44089  50.4391

    Totals :                  1.43964e4   740.79968

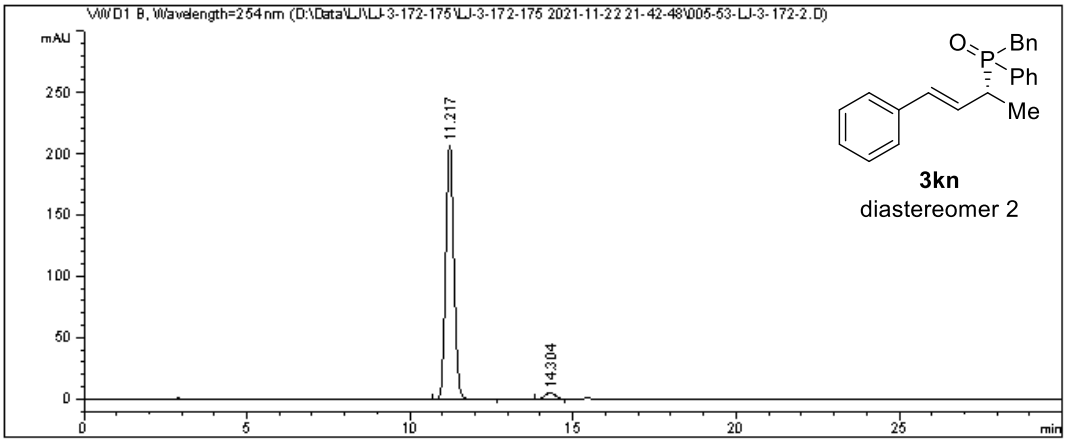

    ======================================================================
                               *** End of Report ***

1260 11/30/2021 10:00:22 PM SYSTEM                          Page 1 of 1
```

Figure S237. HPLC spectra of ***rac*-3kn** diastereomer 2.

Data File D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\005-53-LJ-3-172-2.D
Sample Name: LJ-3-172-2

```
    ======================================================================
    Acq. Operator   : SYSTEM                        Seq. Line :   5
    Sample Operator : SYSTEM
    Acq. Instrument : 1260                           Location :   53
    Injection Date  : 11/22/2021 11:36:39 PM             Inj :   1
                                                   Inj Volume : 5.000 µl
    Acq. Method     : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M
    Last changed    : 10/15/2020 8:06:11 AM by SYSTEM
    Analysis Method : D:\Data\LJ\LJ-3-172-175\LJ-3-172-175 2021-11-22 21-42-48\P1-85-15-1.0ML-5UL
                      -220NM-254NM-30MIN.M (Sequence Method)
    Last changed    : 11/30/2021 10:01:44 PM by SYSTEM
                      (modified after loading)
    ======================================================================
```




```
    ======================================================================
                            Area Percent Report
    ======================================================================

    Sorted By             :      Signal
    Multiplier            :      1.0000
    Dilution              :      1.0000
    Do not use Multiplier & Dilution Factor with ISTDs


    Signal 1: VWD1 B, Wavelength=254 nm

    Peak RetTime Type  Width     Area      Height     Area
      #   [min]        [min]   [mAU*s]     [mAU]       %
    ----|-------|----|-------|----------|----------|--------|
       1  11.217 BB    0.2717 3616.38062  207.07549  97.1375
       2  14.304 BB    0.3324  106.56946    5.04674   2.8625

    Totals :                  3722.95007  212.12222

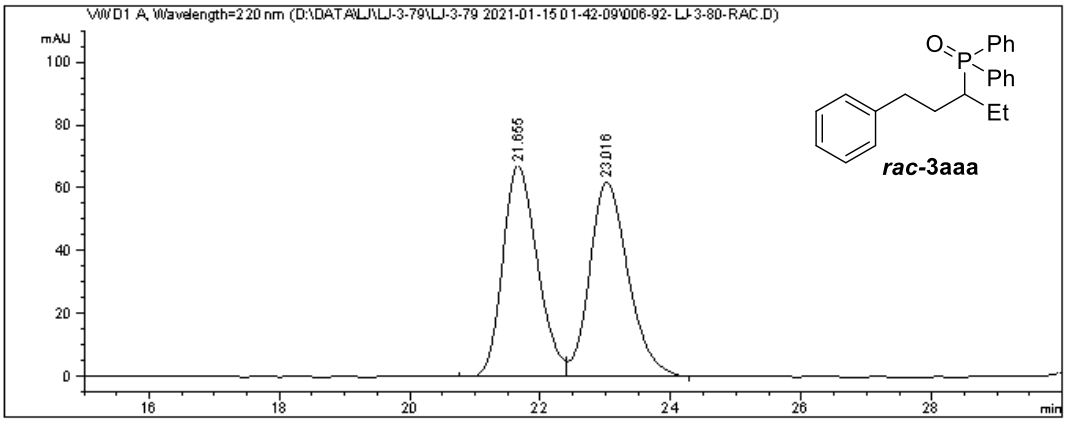

    ======================================================================
                            *** End of Report ***

1260 11/30/2021 10:02:06 PM SYSTEM                          Page 1 of 1
```

Figure S238. HPLC spectra of **3kn** diastereomer 2.

Data File D:\DATA\LJ\LJ-3-79\LJ-3-79 2021-01-15 01-42-09\006-92-LJ-3-80-RAC.D
Sample Name: LJ-3-80-RAC

Acq. Operator	: SYSTEM	Seq. Line :	6
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location :	92
Injection Date	: 1/15/2021 3:23:22 AM	Inj :	1
		Inj Volume :	5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-79\LJ-3-79 2021-01-15 01-42-09\P2-95-5-0.5ML-5UL-220NM-254NM-60MIN.M		
Last changed	: 1/15/2021 4:00:18 AM by SYSTEM (modified after loading)		
Analysis Method	: D:\Data\LJ\LJ-3-79\LJ-3-79 2021-01-15 01-42-09\P2-95-5-0.5ML-5UL-220NM-254NM-60MIN.M (Sequence Method)		
Last changed	: 1/15/2021 6:21:22 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.655	BV	0.5728	2490.86865	67.45312	49.4368
2	23.016	VB	0.6310	2547.62671	62.05661	50.5632
Totals :				5038.49536	129.50972	

*** End of Report ***

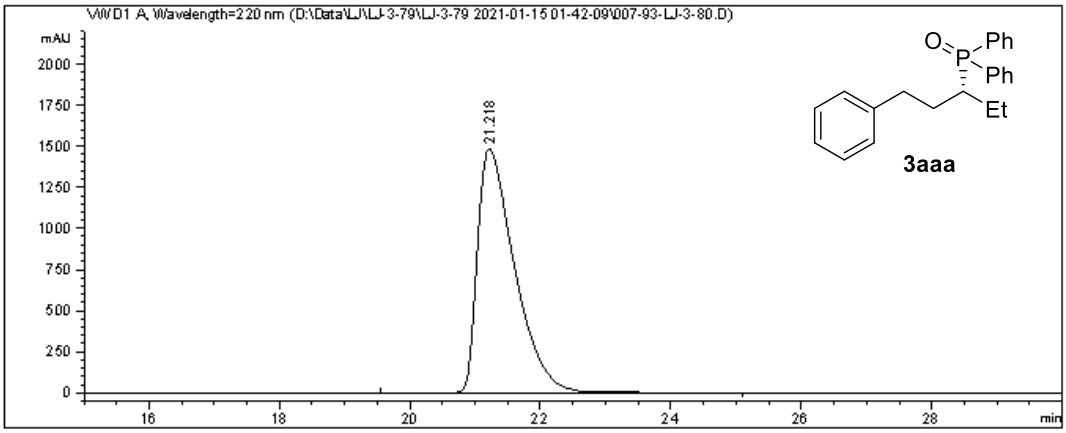
1260 1/15/2021 6:21:28 AM SYSTEM

Page 1 of 1

Figure S239. HPLC spectra of ***rac*-3aaa**.

Data File D:\Data\LJ\LJ-3-79\LJ-3-79 2021-01-15 01-42-09\007-93-LJ-3-80.D
Sample Name: LJ-3-80

Acq. Operator	: SYSTEM	Seq. Line	: 7
Sample Operator	: SYSTEM		
Acq. Instrument	: 1260	Location	: 93
Injection Date	: 1/15/2021 4:01:01 AM	Inj	: 1
		Inj Volume	: 5.000 µl
Acq. Method	: D:\Data\LJ\LJ-3-79\LJ-3-79 2021-01-15 01-42-09\P2-95-5-0.5ML-5UL-220NM-254NM-60MIN.M		
Last changed	: 1/15/2021 4:00:18 AM by SYSTEM		
Analysis Method	: D:\Data\LJ\LJ-3-79\LJ-3-79 2021-01-15 01-42-09\P2-95-5-0.5ML-5UL-220NM-254NM-60MIN.M (Sequence Method)		
Last changed	: 1/15/2021 6:23:25 AM by SYSTEM (modified after loading)		
Additional Info	: Peak(s) manually integrated		



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.218	VB R	0.6017	5.87598e4	1484.88403	100.0000
Totals :				5.87598e4	1484.88403	

*** End of Report ***

1260 1/15/2021 6:23:36 AM SYSTEM Page 1 of 1

Figure S240. HPLC spectra of **3aaa**.