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Supplementary Information

CAMDOL-Enabled Diastereoselective Synthesis of α-Substituted Phosphonates

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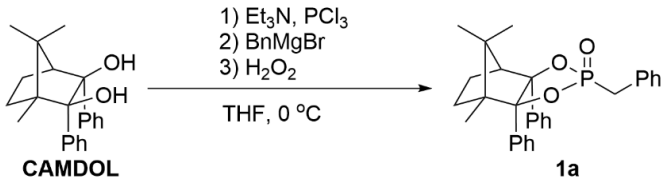
Contents

General Experimental

Tetrahydrofuran (THF), acetonitrile (MeCN) and methanol (MeOH) were obtained by passing the previously degassed solvents through an activated alumina column. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. Reactions weremonitored by thin layer chromatography (TLC), GC/MS, GC/FID, or LC/MS. TLC was performed using 0.25 mm E. Merck silica plates (60F-254), using short-wave UV light as the visualizing agent, andphosphomolybdic acid, *p*-anisaldehyde, or $KMnO_4$ and heat as developing agents. NMR spectra were recorded on Bruker DRX-300 instruments and are calibrated using residual undeuterated solvent ($CHCl_3$, CH_2Cl_2, DMSO, MeOH, acetone at 7.26, 5.32, 2.50, 3.31 and 2.05 ppm for ^{1}H NMR, respectively, and 77.16, 53.84, 39.52, 49.00 and 29.84 ppm for ^{13}C NMR, respectively). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck silica gel (60, particle size 0.043–0.063 mm), and preparative TLC (pTLC) was performed on Merck silica plates (60F-254). High-resolution mass spectra (HRMS) were recorded on an Agilent LC/Xevo G2-XS QTOF mass spectrometer by electrospray ionization time of flight reflectron experiments. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected. The enantiomeric ratios were determined with Waters UPC2 SFC equipped with a photodiode array detector or an Agilent Technologies 1220 Infinity II LC HPLC. Optical rotation data was recorded on an Anton Paar 100 Modular Circular Polarimeter.

General procedure for synthesis of 1-4

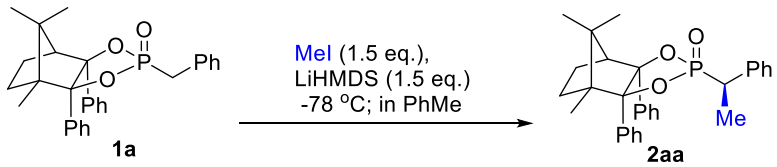
Synthesis of 1a



CAMDOL **1a**

To a 500 mL three-necked flask containing CAMDOL (6.44 g, 20 mmol) under a nitrogen atmosphere, THF (200 mL) was added and cooled to 0 °C in an ice-water bath. Then triethylamine (6.95 mL, 50 mmol) and phosphorus trichloride (2.62 mL, 30 mmol) was slowly added to the mixture, the mixture was stirred at 0 °C for 0.5 h. To the mixture at 0 °C was slowly added BnMgBr (80 mL, 80 mmol) and the mixture was at 0 °C for 1 h. Finally, the solution was oxidized with conc. H_2O_2 with ^{31}P NMR analysis of a small aliquot showed complete consumption. To the resulting mixture was filtered and concentrated. The residue was purified by silica gel chromatography to afford the desired product **1a**.

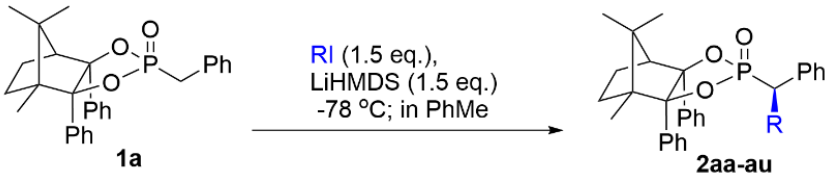
Synthesis of 2aa (10 mmol scale)



1a **2aa**

To a 500 mL three-necked flask containing **1a** (4.58 g, 10 mmol) under a nitrogen atmosphere, toluene (150 mL) was added and cooled to -78 °C. Then LiHMDS (15 mL, 15 mmol) was slowly added to the mixture, the mixture was stirred at -78 °C for 0.5 h. To the mixture at -78 °C was slowly added MeI (2.13 g, 15 mmol) and the mixture was at -78 °C for 12 h. Finally, ^{31}P NMR analysis of a small aliquot showed complete consumption. To the resulting mixture was added saturated aqueous NH_4Cl solution (50 mL) and EtOAc (100 mL). The layers were separated, and the aqueous layer was washed with EtOAc (2 × 100 mL). The combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography to afford the desired product **2aa**.

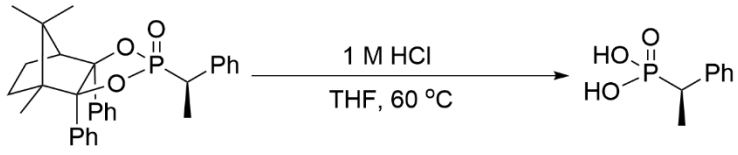
Synthesis of 2aa-2au



A Schlenk tube was dried under vacuum. After cooling, the tube was placed under nitrogen atmosphere. Under nitrogen atmosphere, to a stirred solution of **1a** (1 mmol) in dry THF was slowly added LiHMDS (1.5 eq) at -78 °C, the mixture was stirred at -78 °C for 0.5 h. Then RI (1.5 eq) was slowly added to the mixture, The mixture was stirred at -78 °C for 12 h. Finally, ^{31}P NMR analysis of a small aliquot showed complete consumption. To the resulting mixture was added saturated aqueous NH_4Cl solution (10 mL) and EtOAc (10 mL). The layers were separated, and the aqueous layer was washed with EtOAc (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography to afford the desired product **2aa**-**2au**.

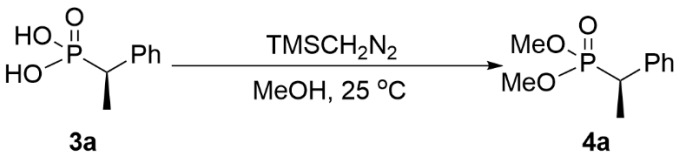
Compounds **2ba-2bl** were obtained by the similar procedures of **1a** and **2a**.

Synthesis of 3a



To a 50 mL flask containing **2aa** (1 mmol) was added THF (10 mL). Then HCl (5 mL, 5 mmol) was added to the mixture, the mixture was stirred at 60 °C for 2 h. Then, ^{31}P NMR analysis of a small aliquot showed complete consumption. To the resulting mixture was added water (10 mL) and DCM (10 mL). The layers were separated, and the aqueous layer was washed with DCM (2 × 10 mL). The combined organic layers were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by silica gel chromatography to afford the desired product **3a**.

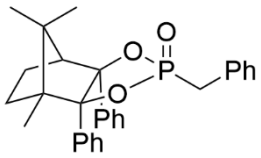
Synthesis of 4a



3a **4a**

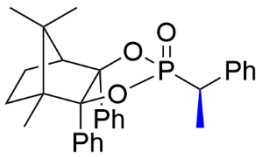
To a 50 mL flask containing **3a** (1 mmol) was added MeOH (10 mL). Then $TMSCH_2N_2$ (2 eq) was added to the mixture, the mixture was stirred at 25 °C for 1 h. Then, ^{31}P NMR analysis of a small aliquot showed complete consumption. The mixture was concentrated in vacuum, and the crude product was purified by silica gel chromatography to afford the desired product **4a**.

2,3-Diphenyl camphor benzylphosphonate 1a:



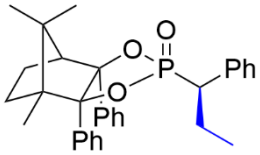
89% yield, white solid, **m.p.** = 113–119 °C, R_f = 0.38 (PE/EA= 1:1), $\mathbf{[\alpha]^{25}_D}$ = 105.4° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 38.9 Hz, 13H), 6.98 (s, 2H), 3.10 (dd, *J* = 20.8, 11.0 Hz, 3H), 2.07 (s, 1H), 1.77 (s, 3H), 1.69 – 1.46 (m, 1H), 1.31 (d, *J* = 30.6 Hz, 2H), 1.15 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.52 (d, *J* = 3.1 Hz), 136.49 (d, *J* = 4.0 Hz), 131.18 , 131.06 , 130.56 – 130.35 (m), 130.27 , 129.82 (d, *J* = 6.8 Hz), 128.55 – 128.25 (m), 128.07 , 127.70 , 126.85 (d, *J* = 3.4 Hz), 126.37 , 100.25 , 98.51 , 55.61 , 52.16 (d, *J* = 3.2 Hz), 48.28 , 36.92 , 35.24 , 29.59 , 26.43 , 24.44 , 21.51 , 9.95; ^{31}P NMR (122 MHz, $CDCl_3$) δ 38.71; HRMS (ESI-MS) $[M+H]^+$: found 458.2011; calculated for $C_{29}H_{31}O_3P$: 458.2011.

2,3-Diphenyl camphor (1-phenylethyl)phosphonate 2aa:



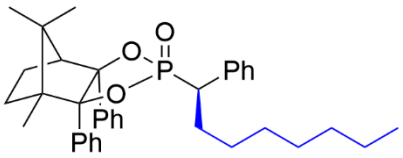
85% yield, white solid, **m.p.** = 110–115 °C, R_f = 0.48 (PE/EA= 1:1), $\mathbf{[\alpha]^{25}_D}$ = 102.4° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.28 (s, 10H), 7.08 – 6.92 (m, 3H), 6.91 – 6.76 (m, 2H), 2.96 (hept, *J* = 7.2 Hz, 2H), 2.09 – 1.96 (m, 1H), 1.77 (s, 3H), 1.69 (dd, *J* = 18.7, 7.1 Hz, 3H), 1.49 (dt, *J* = 14.1, 7.4 Hz, 1H), 1.32 (dq, *J* = 14.4, 8.2, 7.2 Hz, 2H), 1.13 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.26 (d, *J* = 3.3 Hz), 137.15 (d, *J* = 7.1 Hz), 136.98 , 130.43 (d, *J* = 42.9 Hz), 128.63 – 128.27 (m), 128.19 (d, *J* = 2.4 Hz), 128.06 , 127.60 , 126.81 (d, *J* = 3.0 Hz), 126.41 , 100.15 , 98.77 (d, *J* = 1.6 Hz), 55.63 (d, *J* = 2.8 Hz), 52.24 (d, *J* = 3.3 Hz), 48.25 , 40.77 , 39.10 , 29.76 , 26.52 , 24.39 , 21.50 , 16.97 (d, *J* = 5.4 Hz), 9.97; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.49; HRMS (ESI-MS) $[M+H]^+$: found 472.2169; calculated for $C_{30}H_{33}O_3P$:472.2167.

2,3-Diphenyl camphor (1-phenylpropyl)phosphonate 2ab:



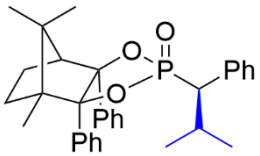
92% yield, white solid, **m.p.** = 82-93 °C, R_f = 0.48 (PE/EA= 1:1), **[α]$^{25}_{D}$** = 67.4° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.14 (m, 10H), 7.05 – 6.85 (m, 5H), 2.93 (d, *J* = 5.3 Hz, 1H), 2.61 (ddd, *J* = 17.0, 10.6, 3.9 Hz, 1H), 2.38 (dddt, *J* = 13.4, 10.3, 6.8, 3.9 Hz, 1H), 2.15 – 1.93 (m, 2H), 1.78 (s, 3H), 1.48 (dq, *J* = 16.2, 9.1, 8.3 Hz, 1H), 1.32 (ddd, *J* = 19.9, 11.3, 4.3 Hz, 2H), 1.12 (s, 3H), 0.89 (s, 3H), 0.80 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.22 , 136.92 , 135.09 (d, *J* = 5.0 Hz), 130.69 , 130.14 , 129.27 (d, *J* = 7.4 Hz), 128.09 (d, *J* = 3.8 Hz), 127.46 , 126.54 (d, *J* = 34.8 Hz), 100.17 , 98.56 , 55.60 , 52.21 , 49.19 , 48.21 , 47.50 , 29.66 , 26.46 , 25.46 , 24.49 , 21.46 , 12.62 (d, *J* = 16.9 Hz), 10.01; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.42; HRMS (ESI-MS) $[M+H]^+$: found 486.2322; calculated for C31H35O3P: 486.2324.

2,3-Diphenyl camphor (1-phenylheptyl)phosphonate 2ac:



78% yield, white solid, **m.p.** = 98-103 °C, R_f = 0.33 (PE/EA= 1:1), **[α]$^{25}_{D}$** = 89.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 10H), 7.05 – 6.96 (m, 3H), 6.93 – 6.84 (m, 2H), 2.95 (d, *J* = 5.3 Hz, 1H), 2.73 (ddd, *J* = 17.8, 11.0, 3.5 Hz, 1H), 2.27 (d, *J* = 9.4 Hz, 1H), 2.12 – 1.93 (m, 2H), 1.77 (s, 3H), 1.49 (tt, *J* = 13.7, 6.4 Hz, 1H), 1.40 – 1.31 (m, 2H), 1.25 (d, *J* = 5.5 Hz, 2H), 1.16 (d, *J* = 15.4 Hz, 11H), 0.89 (d, *J* = 6.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.22 (d, *J* = 3.3 Hz), 136.90 (d, *J* = 4.1 Hz), 135.25 (d, *J* = 6.8 Hz), 130.48 (d, *J* = 37.2 Hz), 129.26 (d, *J* = 7.3 Hz), 128.06, 127.49, 126.75 (d, *J* = 2.9 Hz), 126.31, 100.13, 98.57, 55.59 (d, *J* = 3.0 Hz), 52.24 (d, *J* = 3.3 Hz), 48.25, 47.01, 45.34, 31.81, 31.44 (d, *J* = 4.0 Hz), 29.72, 28.98 (d, *J* = 7.9 Hz), 27.37 (d, *J* = 14.9 Hz), 26.50, 24.43, 22.61, 21.52, 14.21, 10.01; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.68; HRMS (ESI-MS) $[M+H]^+$: found 556.3104; calculated for $C_{36}H_{45}O_3P$: 556.3106.

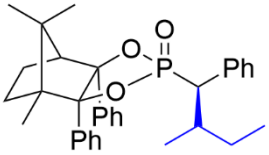
2,3-Diphenyl camphor (2-methyl-1-phenylpropyl)phosphonate 2ad:



90% yield, white solid, **m.p.** = 95–100 °C, R_f = 0.44 (PE/EA= 1:1), **[α]$^{25}_{D}$** = 90.5° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.01 (m, 9H), 6.89 (s, 5H), 2.82 (d, *J* = 5.3 Hz, 1H), 2.50 – 2.24 (m, 2H), 1.94 (d, *J* = 16.9 Hz, 1H), 1.73 (s, 3H), 1.41 (d, *J* = 14.5 Hz, 1H), 1.22 (d, *J* = 6.3 Hz, 5H), 1.04 (s, 3H), 0.83 (s, 3H), 0.62 (d, *J* = 6.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.73, 134.99 (d, *J* = 5.7 Hz), 130.50, 129.88 (d, *J* = 8.3 Hz), 127.91 , 127.76 (d, *J* = 1.3 Hz), 127.37, 126.58 (d, *J* = 2.2 Hz), 100.69 , 98.15 (d, *J* = 1.8 Hz), 55.90–54.92 (m), 53.94 , 51.96 (d, *J* = 3.4 Hz), 48.10 , 32.05 (d, *J* = 3.2 Hz), 29.88 , 26.60 , 24.48 , 23.27 (d, *J* = 6.5 Hz), 21.50 , 20.88

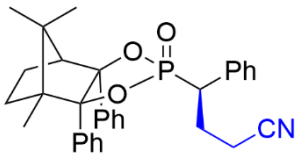
(d, *J* = 13.0 Hz), 9.93 ; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.54; HRMS (ESI-MS) $[M+H]^+$: found 500.2482; calculated for $C_{32}H_{37}O_3P$:500.2480.

2,3-Diphenyl camphor (2-methyl-1-phenylbutyl)phosphonate 2ae:



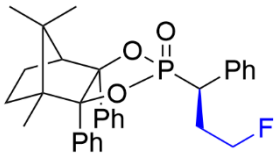
82% yield, white solid, **m.p.** = 105-108 °C, R_f = 0.55 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 103.5° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.01 (m, 10H), 6.89 (d, *J* = 1.6 Hz, 5H), 2.83 (d, *J* = 5.4 Hz, 1H), 2.63 (dd, *J* = 18.5, 5.8 Hz, 1H), 2.21 (tq, *J* = 8.5, 6.0 Hz, 1H), 1.91 (ddd, *J* = 14.9, 8.0, 4.1 Hz, 1H), 1.73 (s, 3H), 1.56 (ddd, *J* = 13.2, 7.4, 5.6 Hz, 1H), 1.37 (dt, *J* = 14.3, 7.2 Hz, 1H), 1.25 – 1.11 (m, 3H), 1.04 (s, 3H), 0.87 – 0.70 (m, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.75 (d, *J* = 3.3 Hz), 135.83 (d, *J* = 4.4 Hz), 132.69 (d, *J* = 5.2 Hz), 129.33 (d, *J* = 8.9 Hz), 126.86 (d, *J* = 2.1 Hz), 126.57 , 126.30 , 125.53 (d, *J* = 2.0 Hz), 125.03 , 99.45 (d, *J* = 1.2 Hz), 97.13 (d, *J* = 1.7 Hz), 54.45 (d, *J* = 2.9 Hz), 51.76 , 51.00 (d, *J* = 3.4 Hz), 50.09 , 47.05 , 36.37 (d, *J* = 2.8 Hz), 28.78 , 28.00 (d, *J* = 10.8 Hz), 25.48 , 23.34 , 20.42 , 15.69 (d, *J* = 8.2 Hz), 11.24 , 8.88; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.59; HRMS (ESI-MS) $[M+H]^+$: found 514.2637; calculated for $C_{33}H_{39}O_3P$:514.2637.

2,3-Diphenyl camphor (2-cyano-1-phenylethyl)phosphonate 2ag:



82% yield, white solid, **m.p.** = 98-100 °C, R_f = 0.45 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 103.5° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 6.94 (m, 15H), 3.34 – 2.88 (m, 4H), 2.03 (dp, *J* = 11.9, 4.5 Hz, 1H), 1.75 (s, 3H), 1.50 (td, *J* = 15.9, 14.2, 8.7 Hz, 1H), 1.33 (dd, *J* = 10.4, 6.6 Hz, 2H), 1.13 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.43 (d, *J* = 3.4 Hz), 136.23 (d, *J* = 4.3 Hz), 132.53 (d, *J* = 6.6 Hz), 130.15 (d, *J* = 49.2 Hz), 128.83 (d, *J* = 6.9 Hz), 128.68 (d, *J* = 1.5 Hz), 128.56 (d, *J* = 2.8 Hz), 128.16 (d, *J* = 2.3 Hz), 127.78 , 126.78 , 117.30 (d, *J* = 21.2 Hz), 101.22 , 99.91 (d, *J* = 1.3 Hz), 55.76 (d, *J* = 2.9 Hz), 52.10 (d, *J* = 3.5 Hz), 48.20 , 43.68 , 41.95 , 29.64 , 26.50 , 24.41 , 21.42 (d, *J* = 8.6 Hz), 9.94; ^{31}P NMR (122 MHz, $CDCl_3$) δ 37.27; HRMS (ESI-MS) $[M+H]^+$: found 497.2120; calculated for $C_{31}H_{32}NO_3P$:497.2120.

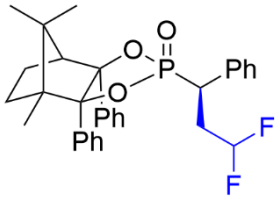
2,3-Diphenyl camphor (3-fluoro-1-phenylpropyl)phosphonate 2ah:



73% yield, white solid, **m.p.** = 100-105 °C, R_f = 0.32 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 150.5° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (s, 10H), 6.92 (d, *J* = 15.5 Hz, 5H), 4.34 (d, *J* = 46.6 Hz, 1H), 3.94 (d, *J* = 47.8 Hz, 1H), 3.10 – 2.82 (m, 2H), 2.67 (s, 1H), 2.38 – 2.07 (m, 1H), 1.96 (s,

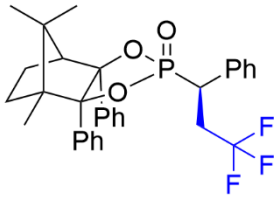
1H), 1.70 (s, 3H), 1.44 – 1.19 (m, 3H), 1.06 (s, 3H), 0.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.97 (d, *J* = 3.3 Hz), 136.40 (d, *J* = 4.1 Hz), 133.85 (d, *J* = 6.8 Hz), 130.63 , 130.03 , 129.43 (d, *J* = 7.4 Hz), 128.57 – 127.91 (m), 127.55 , 127.20 (d, *J* = 2.6 Hz), 126.36 , 100.51 , 98.99 (d, *J* = 1.4 Hz), 81.59 (d, *J* = 15.9 Hz), 79.39 (d, *J* = 15.8 Hz), 55.64 (d, *J* = 3.0 Hz), 52.18 (d, *J* = 3.4 Hz), 48.24 , 42.80 (d, *J* = 3.4 Hz), 41.08 (d, *J* = 3.3 Hz), 32.77 (dd, *J* = 20.2, 3.5 Hz), 29.69 , 26.49 , 24.46 , 21.48 , 9.99; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.76; ^{19}F NMR (282 MHz, $CDCl_3$) δ -221.87 (tdd, J = 47.1, 37.2, 15.2 Hz); HRMS (ESI-MS) $[M+H]^+$: found 504.5723; calculated for $C_{31}H_{34}FO_3P$:504.5720.

2,3-Diphenyl camphor (3,3-difluoro-1-phenylpropyl)phosphonate 2ai:



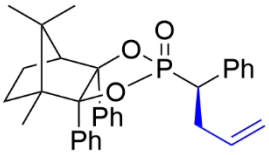
79% yield, white solid, **m.p.** = 114-118 °C, R_f = 0.33 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 159.2° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 – 7.17 (m, 10H), 7.03 (dd, *J* = 5.3, 2.0 Hz, 3H), 6.94 (dt, *J* = 7.8, 2.2 Hz, 2H), 5.68 – 5.13 (m, 1H), 3.15 – 2.90 (m, 2H), 2.81 – 2.51 (m, 2H), 2.16 – 1.94 (m, 1H), 1.76 (s, 3H), 1.40 (m, 3H), 1.14 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.83 (d, *J* = 3.3 Hz), 136.23 (d, *J* = 4.2 Hz), 133.23 (d, *J* = 7.4 Hz), 130.28 (d, *J* = 48.0 Hz), 129.06 (d, *J* = 7.3 Hz), 128.72 – 128.26 (m), 127.60, 126.49, 118.61 (d, *J* = 20.5 Hz), 115.43 (d, *J* = 20.3 Hz), 112.25 (d, *J* = 20.4 Hz), 100.78, 99.37 (d, *J* = 1.5 Hz), 55.70 (d, *J* = 3.0 Hz), 52.22 (d, *J* = 3.5 Hz), 48.26, 41.68 (d, *J* = 8.6 Hz), 39.95 (d, *J* = 7.2 Hz), 36.42 (d, *J* = 21.6 Hz), 29.69, 26.49, 24.40, 21.51, 9.95; ^{31}P NMR (122 MHz, $CDCl_3$) δ 39.64; ^{19}F NMR (282 MHz, $CDCl_3$) δ -103.80 – -136.08 (m); HRMS (ESI-MS) $[M+H]^+$: found 522.2136; calculated for $C_{31}H_{33}F_2O_3P$: 522.2135.

2,3-Diphenyl camphor (4,4,4-trifluoro-1-phenylbutyl)phosphonate 2aj:



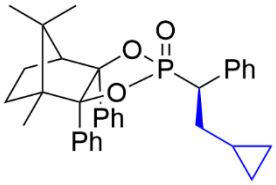
83% yield, white solid, **m.p.** = 103-110 °C, R_f = 0.43 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 103.2° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.17 (m, 10H), 7.11 – 6.72 (m, 6H), 2.97 (d, *J* = 5.3 Hz, 1H), 2.91 – 2.72 (m, 1H), 2.56 (d, *J* = 7.3 Hz, 1H), 2.48 – 2.26 (m, 1H), 2.14 – 1.89 (m, 2H), 1.76 (s, 4H), 1.63 – 1.42 (m, 2H), 1.36 (dd, *J* = 16.8, 6.0 Hz, 3H), 1.14 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.67 (d, *J* = 5.2 Hz), 129.93 , 129.17 (d, *J* = 7.1 Hz), 128.48 (d, *J* = 2.1 Hz), 128.38 , 128.18 , 127.59 , 127.41 (d, *J* = 2.8 Hz), 126.48 , 100.51 , 99.11 , 55.65 (d, *J* = 2.9 Hz), 52.21 (d, *J* = 3.4 Hz), 48.24 , 45.66 , 43.96 , 29.66 , 26.44 , 24.36 , 23.89 , 21.45 , 9.93; ^{31}P NMR (122 MHz, $CDCl_3$) δ 40.56; ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.13 (dd, J = 32.8, 16.7 Hz); HRMS (ESI-MS) $[M+H]^+$: found 554.2198; calculated for $C_{32}H_{34}F_3O_3P$: 554.2198.

2,3-Diphenyl camphor (1-phenylbut-3-en-1-yl)phosphonate 2ak:



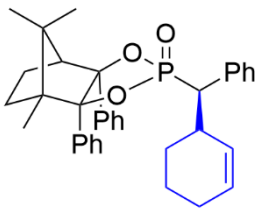
83% yield, white solid, **m.p.** = 95-98 °C, R_f = 0.45 (PE/EA= 1:1), **[α]$^{25}_{D}$** = 123.5° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 10H), 7.04 – 6.97 (m, 3H), 6.91 (dd, *J* = 5.6, 2.6 Hz, 2H), 5.67 – 5.44 (m, 1H), 5.16 – 4.82 (m, 2H), 3.14 – 2.94 (m, 2H), 2.88 – 2.71 (m, 2H), 2.12 – 1.96 (m, 1H), 1.78 (s, 3H), 1.57 – 1.42 (m, 1H), 1.33 (ddd, *J* = 20.6, 11.0, 5.1 Hz, 2H), 1.14 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.12 (d, *J* = 3.3 Hz), 136.74 (d, *J* = 4.1 Hz), 135.17 (d, *J* = 16.0 Hz), 134.64 (d, *J* = 6.7 Hz), 130.67 , 130.20 , 129.30 (d, *J* = 7.3 Hz), 128.39 – 127.98 (m), 127.53 , 126.91 (d, *J* = 2.7 Hz), 126.35 , 117.25 , 100.33 , 98.79 (d, *J* = 1.4 Hz), 55.64 (d, *J* = 3.0 Hz), 52.23 (d, *J* = 3.3 Hz), 48.25 , 47.67 , 46.00 , 36.28 (d, *J* = 3.4 Hz), 29.67 , 26.51 , 24.50 , 21.51 , 10.04; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.47; HRMS (ESI-MS) $[M+H]^+$: found 498.5923;calculated for $C_{32}H_{35}O_3P$:498.5923.

2,3-Diphenyl camphor (2-cyclopropyl-1-phenylethyl)phosphonate 2al:



92% yield, white solid, **m.p.** = 115-118 °C, R_f = 0.35 (PE/EA= 1:1), **[α]$^{25}_{D}$** = 113.4° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.15 (m, 10H), 7.06 – 6.84 (m, 5H), 3.12 – 2.71 (m, 2H), 2.47 – 2.28 (m, 1H), 2.05 – 1.98 (m, 1H), 1.77 (s, 3H), 1.56 – 1.43 (m, 1H), 1.38 – 1.22 (m, 3H), 1.13 (s, 3H), 0.88 (s, 3H), 0.55 – 0.18 (m, 3H), 0.06 (dt, *J* = 9.1, 4.6 Hz, 1H), -0.22 (dq, *J* = 9.4, 4.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.17 (d, *J* = 3.3 Hz), 136.86 (d, *J* = 4.1 Hz), 135.43 (d, *J* = 6.6 Hz), 130.47 (d, *J* = 36.5 Hz), 129.26 (d, *J* = 7.5 Hz), 128.64 – 127.83 (m), 127.48 , 126.74 (d, *J* = 2.7 Hz), 126.25 , 100.15 , 98.55 (d, *J* = 1.5 Hz), 68.01 , 55.56 (d, *J* = 3.0 Hz), 52.21 (d, *J* = 3.3 Hz), 48.10 (d, *J* = 19.4 Hz), 46.30 , 37.24 (d, *J* = 3.4 Hz), 29.67 , 26.44 , 24.45 , 21.44 , 10.50 – 8.59 (m), 5.39 , 3.93; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.18; HRMS (ESI-MS) $[M+H]^+$: found 512.2480; calculated for $C_{33}H_{37}O_3P$:512.2480.

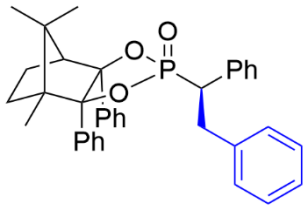
2,3-Diphenyl camphor (cyclohex-2-en-1-yl(phenyl)methyl)phosphonate 2am:



84% yield, white solid, **m.p.** = 102-108 °C, R_f = 0.33 (PE/EA= 1:1), **[α]$^{25}_{D}$** = 113.8° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 – 6.95 (m, 15H), 6.32 (d, *J* = 8.9 Hz, 1H), 5.98 (d, *J* = 9.6 Hz, 1H), 2.89 (d, *J* = 5.0 Hz, 2H), 2.64 (dd, *J* = 16.5, 9.2 Hz, 1H), 2.00 (d, *J* = 10.4 Hz, 4H), 1.82 (s, 3H), 1.47 – 1.28 (m, 6H), 1.12 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.75 (d, *J* = 3.4 Hz), 136.59 (d, *J* = 4.2 Hz), 135.17 (d, *J* = 5.7 Hz), 130.72 , 130.14 (d, *J* = 5.4 Hz),

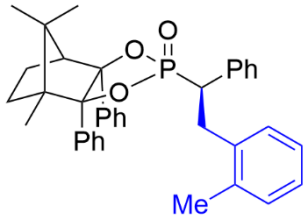
129.74 (d, *J* = 8.3 Hz), 129.41 , 127.90 (d, *J* = 6.5 Hz), 127.35 , 126.67 (d, *J* = 1.8 Hz), 126.00 , 100.76 (d, *J* = 1.1 Hz), 98.13 (d, *J* = 1.4 Hz), 55.56 (d, *J* = 2.9 Hz), 53.39 , 52.34 – 51.03 (m), 48.20 , 39.10 (d, *J* = 3.0 Hz), 29.71 , 26.62 , 25.95 (d, *J* = 13.3 Hz), 25.40 , 24.61 , 21.62 , 19.84 , 10.08; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.06; HRMS (ESI-MS) $[M+H]^+$: found 538.2634; calculated for $C_{35}H_{39}O_3P$: 538.2637.

2,3-Diphenyl camphor (1,2-diphenylethyl)phosphonate 2an:



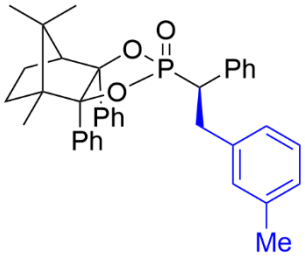
84% yield, white solid, **m.p.** = 112-114 °C, R_f = 0.55 (PE/EA= 1:1), **[α]$^{25}_D$** = 13.8° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.09 (m, 13H), 6.88 (dd, *J* = 29.6, 13.1 Hz, 7H), 3.77 – 3.58 (m, 1H), 3.31 – 3.11 (m, 1H), 3.05 – 2.85 (m, 2H), 2.04 (t, *J* = 11.9 Hz, 1H), 1.82 (s, 3H), 1.57 – 1.46 (m, 1H), 1.32 (dd, *J* = 17.7, 7.7 Hz, 2H), 1.15 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.86 (d, *J* = 16.0 Hz), 138.02 (d, *J* = 3.3 Hz), 136.80 (d, *J* = 4.1 Hz), 134.48 (d, *J* = 6.1 Hz), 130.39 (d, *J* = 30.1 Hz), 129.44 (d, *J* = 7.6 Hz), 129.11 , 128.64 – 127.74 (m), 127.46 , 127.20 – 125.96 (m), 100.35 , 98.75 , 55.63 (d, *J* = 3.0 Hz), 52.21 (d, *J* = 3.2 Hz), 50.24 , 48.41 (d, *J* = 25.1 Hz), 38.82 , 29.63 , 26.48 , 24.55 , 21.51 , 10.01; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.43; HRMS (ESI-MS) $[M+H]^+$: found 548.2480;calculated for $C_{36}H_{37}O_3P$: 548.2480.

2,3-Diphenyl camphor (1-phenyl-2-(*o*-tolyl)ethyl)phosphonate 2ao:



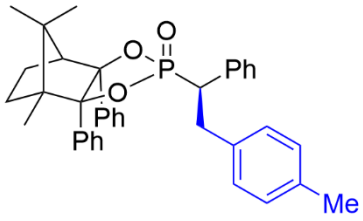
87% yield, white solid, **m.p.** = 100-102 °C, R_f = 0.65 (PE/EA= 1:1), **[α]$^{25}_D$** = 102.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 6.84 (m, 19H), 3.60 (ddd, *J* = 13.9, 9.1, 5.0 Hz, 1H), 3.25 (td, *J* = 13.7, 9.7 Hz, 1H), 3.04 (ddd, *J* = 16.4, 9.6, 5.0 Hz, 1H), 2.92 (d, *J* = 5.2 Hz, 1H), 2.09 – 1.96 (m, 1H), 1.94 (s, 3H), 1.83 (s, 3H), 1.47 (dt, *J* = 14.5, 7.2 Hz, 1H), 1.28 (t, *J* = 7.0 Hz, 2H), 1.12 (s, 3H), 0.87 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.90 (d, *J* = 3.3 Hz), 136.82 (dd, *J* = 9.0, 4.8 Hz), 136.48, 135.10 (d, *J* = 5.6 Hz), 130.25 (d, *J* = 9.3 Hz), 129.37 (d, *J* = 8.0 Hz), 128.29 – 127.90 (m), 127.49, 126.56, 125.83, 100.51, 98.67 (d, *J* = 1.7 Hz), 55.60 (d, *J* = 2.8 Hz), 52.10 (d, *J* = 3.4 Hz), 49.01, 48.21, 47.34, 36.27 (d, *J* = 3.2 Hz), 29.81, 26.61, 24.53, 21.63, 19.59, 9.97; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.62; HRMS (ESI-MS) $[M+H]^+$: found 562.2639.;calculated for $C_{37}H_{39}O_3P$: 562.2637.

2,3-Diphenyl camphor (1-phenyl-2-(*m*-tolyl)ethyl)phosphonate 2ap:



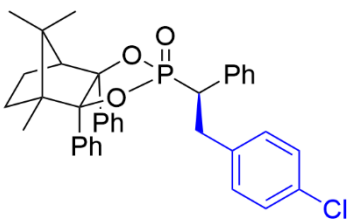
87% yield, white solid, **m.p.** = 100-102 °C, R_f = 0.65 (PE/EA= 1:1), **[α]$^{25}_D$** = 102.3° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.09 (m, 10H), 6.90 (dd, *J* = 22.4, 6.0 Hz, 7H), 6.69 – 6.45 (m, 2H), 3.74 – 3.55 (m, 1H), 3.14 (q, *J* = 11.0 Hz, 1H), 2.92 (dd, *J* = 18.8, 8.3 Hz, 2H), 2.20 (s, 3H), 2.11 – 1.95 (m, 1H), 1.82 (s, 3H), 1.51 (dt, *J* = 14.3, 7.0 Hz, 1H), 1.31 (dd, *J* = 19.4, 10.1 Hz, 2H), 1.14 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.86 (d, *J* = 15.9 Hz), 138.06 , 137.71 , 136.86 , 134.68 (d, *J* = 6.0 Hz), 130.46 (d, *J* = 28.2 Hz), 130.02 , 129.49 (d, *J* = 7.6 Hz), 128.54 – 127.87 (m), 127.49 , 127.15 – 126.72 (m), 126.32 (d, *J* = 29.2 Hz), 100.37 , 98.78 (d, *J* = 1.6 Hz), 55.65 (d, *J* = 3.0 Hz), 52.24 (d, *J* = 3.3 Hz), 50.36 , 48.70 , 48.27 , 38.91 (d, *J* = 3.4 Hz), 29.66 , 26.53 , 24.59 , 21.47 (d, *J* = 15.0 Hz), 10.06; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.58; HRMS (ESI-MS) $[M+H]^+$: found 562.6775;calculated for $C_{37}H_{39}O_3P$: 562.2637.

2,3-Diphenyl camphor (1-phenyl-2-(*p*-tolyl)ethyl)phosphonate 2ar:



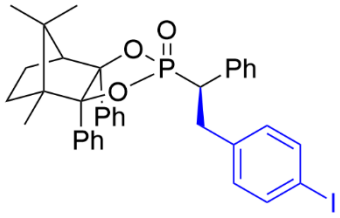
83% yield, white solid, **m.p.** = 112-114 °C, R_f = 0.63 (PE/EA= 1:1), **[α]$^{25}_D$** = 113.8° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.24 – 6.96 (m, 12H), 6.81 – 6.70 (m, 6H), 6.54 (d, *J* = 7.6 Hz, 1H), 3.62 – 3.45 (m, 1H), 3.03 (dt, *J* = 13.4, 9.9 Hz, 1H), 2.81 (dd, *J* = 11.7, 3.9 Hz, 2H), 2.08 (s, 3H), 1.87 (t, *J* = 12.0 Hz, 1H), 1.68 (s, 3H), 1.43 – 1.34 (m, 1H), 1.21 – 1.12 (m, 2H), 0.99 (s, 3H), 0.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.06 (d, *J* = 3.3 Hz), 136.83 (d, *J* = 4.0 Hz), 135.79 (t, *J* = 8.1 Hz), 134.66 (d, *J* = 6.0 Hz), 130.46 (d, *J* = 30.8 Hz), 129.55 (d, *J* = 7.5 Hz), 128.98 (d, *J* = 4.7 Hz), 128.18 (d, *J* = 4.6 Hz), 128.01 , 127.53 , 126.89 (d, *J* = 2.3 Hz), 126.52 , 100.39 , 98.81 (d, *J* = 1.3 Hz), 68.03 , 55.68 (d, *J* = 3.0 Hz), 52.27 (d, *J* = 3.1 Hz), 50.37 , 48.71 , 48.29 , 38.48 (d, *J* = 3.0 Hz), 29.69 , 26.57 , 25.89 (d, *J* = 26.6 Hz), 24.62 , 21.77 (d, *J* = 21.9 Hz), 21.19 (d, *J* = 7.3 Hz), 9.88 (d, *J* = 35.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.06; HRMS (ESI-MS) $[M+H]^+$: found 562.2637; calculated for $C_{37}H_{39}O_3P$: 562.2637.

2,3-Diphenyl camphor (2-(4-chlorophenyl)-1-phenylethyl)phosphonate 2as:



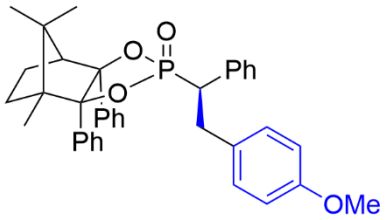
88% yield, white solid, **m.p.** = 118-120 °C, R_f = 0.38 (PE/EA= 1:1), **$[\alpha]^{25}_D$** = 123.2° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 – 6.43 (m, 20H), 3.00 (dt, *J* = 13.5, 10.3 Hz, 1H), 2.79 (d, *J* = 5.2 Hz, 1H), 1.88 (s, 1H), 1.65 (s, 3H), 1.35 (dd, *J* = 14.4, 7.6 Hz, 1H), 1.20 (s, 3H), 0.99 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.89 (d, *J* = 3.3 Hz), 137.35 (d, *J* = 16.0 Hz), 136.76 (d, *J* = 4.1 Hz), 134.14 (d, *J* = 6.1 Hz), 132.16 , 130.47 (d, *J* = 12.5 Hz), 129.38 (d, *J* = 7.6 Hz), 128.35 , 128.21 , 128.11 , 127.52 , 127.06 , 126.47 , 100.43 , 98.88 , 55.64 (d, *J* = 3.0 Hz), 52.18 (d, *J* = 3.3 Hz), 50.15 , 48.49 , 48.22 , 38.20 , 29.61 , 26.48 , 24.51 , 21.50 , 10.01; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.01; HRMS (ESI-MS) $[M+H]^+$: found 582.2091; calculated for $C_{36}H_{36}ClO_3P$: 582.2091.

2,3-Diphenyl camphor (2-(4-iodophenyl)-1-phenylethyl)phosphonate 2at:



80% yield, white solid, **m.p.** = 102-110 °C, R_f = 0.33 (PE/EA= 1:1), **$[\alpha]^{25}_D$** = 100.1° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 – 7.11 (m, 12H), 6.95 (d, *J* = 7.0 Hz, 3H), 6.88 – 6.80 (m, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 3.60 (ddd, *J* = 13.2, 9.1, 3.8 Hz, 1H), 3.13 (dt, *J* = 13.4, 10.1 Hz, 1H), 2.99 – 2.79 (m, 2H), 2.04 (ddt, *J* = 15.0, 10.0, 5.2 Hz, 1H), 1.80 (s, 3H), 1.50 (dt, *J* = 14.2, 7.2 Hz, 1H), 1.35 (dd, *J* = 7.7, 3.9 Hz, 2H), 1.15 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.57 (d, *J* = 16.0 Hz), 137.93 (d, *J* = 3.4 Hz), 137.28, 136.79 (d, *J* = 4.1 Hz), 134.20 (d, *J* = 6.0 Hz), 131.14, 130.36 (d, *J* = 31.7 Hz), 129.40 (d, *J* = 7.6 Hz), 128.17 (dd, *J* = 7.4, 2.6 Hz), 127.54, 127.08, 126.50, 100.43, 98.87 (d, *J* = 1.6 Hz), 91.86, 55.66 (d, *J* = 3.0 Hz), 52.21 (d, *J* = 3.3 Hz), 48.25, 38.42 (d, *J* = 3.2 Hz), 29.64, 26.52, 24.54, 21.54, 10.04; ^{31}P NMR (122 MHz, $CDCl_3$) δ 40.92; HRMS (ESI-MS) $[M+H]^+$: found 674.1448; calculated for $C_{36}H_{36}IO_3P$: 674.1447.

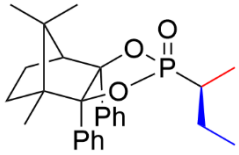
2,3-Diphenyl camphor (2-(4-methoxyphenyl)-1-phenylethyl)phosphonate 2au:



83% yield, white solid, **m.p.** = 111-114 °C, R_f = 0.63 (PE/EA= 1:1), **$[\alpha]^{25}_D$** = 88.1° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 40.6 Hz, 5H), 7.15 (d, *J* = 7.9 Hz, 8H), 7.02 – 6.85 (m, 5H), 6.78 (d, *J* = 8.1 Hz, 2H), 3.30 – 3.07 (m, 1H), 3.01 – 2.80 (m, 2H), 1.80 (s, 3H), 1.33 (dd, *J* = 9.7, 4.0 Hz, 2H), 1.25 (s, 3H), 1.13 (s, 3H), 0.90 (s, 2H), 0.86 (d, *J* = 5.4 Hz, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.08 , 138.02 (d, *J* = 3.5 Hz), 136.73 (d, *J* = 4.0 Hz), 135.67 (d, *J* = 15.5 Hz), 134.64 (d, *J* = 6.0 Hz), 129.42 (d, *J* = 7.7 Hz), 128.86 , 128.06 (d, *J* = 4.5 Hz), 127.94 (d, *J* = 1.5 Hz), 127.46 , 126.79 (d, *J* = 2.4 Hz), 125.04 , 100.31 , 98.69 , 55.59 (d, *J* = 3.0 Hz), 52.15 , 50.17 , 48.52 , 48.22 , 38.36 , 34.39 , 31.38 , 29.59 , 26.49 , 25.73 (d, *J* = 2.0 Hz), 24.59 , 21.49 , 9.97 , -

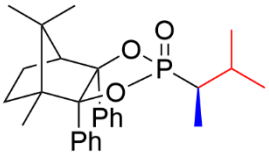
2.90 , -3.52; ^{31}P NMR (122 MHz, $CDCl_3$) δ 41.67; HRMS (ESI-MS) $[M+H]^+$: found 578.2586; calculated for C37H39O4P: 578.2586.

2,3-Diphenyl camphor sec-butylphosphonate 2ba:



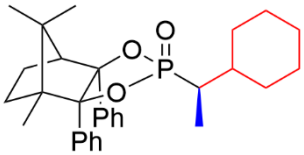
80% yield, white solid, **m.p.** = 88-91 °C, R_f = 0.48 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 73.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 6.92 (m, 10H), 2.93 (d, *J* = 5.3 Hz, 1H), 2.08 (tdd, *J* = 20.8, 14.5, 7.2 Hz, 3H), 1.76 (ttd, *J* = 19.4, 11.5, 11.0, 5.8 Hz, 3H), 1.46 (s, 3H), 1.34 – 1.17 (m, 6H), 1.13 (s, 3H), 0.95 (t, *J* = 7.5 Hz, 1H), 0.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.14 , 136.43 (d, *J* = 70.4 Hz), 126.62 , 126.30 , 125.93 , 100.47 – 94.22 (m), 66.94 , 59.37 , 54.10 (d, *J* = 5.4 Hz), 50.59 , 46.81 , 33.25 (d, *J* = 127.8 Hz), 28.35 , 24.86 , 24.34 (d, *J* = 3.7 Hz), 23.57 , 20.17 (d, *J* = 22.3 Hz), 13.30 (d, *J* = 18.6 Hz), 11.63 (d, *J* = 8.2 Hz), 8.90; ^{31}P NMR (122 MHz, $CDCl_3$) δ 49.72; HRMS (ESI-MS) $[M+H]^+$: found 424.2167; calculated for $C_{26}H_{33}O_3P$: 424.2167.

2,3-Diphenyl camphor (1-isobutylethyl)phosphonate 2bc:



79% yield, white solid, R_f = 0.45 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 83.2° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 3H), 7.22 – 7.17 (m, 7H), 2.92 (d, *J* = 5.3 Hz, 1H), 2.17 – 1.92 (m, 3H), 1.83 – 1.73 (m, 2H), 1.47 (dd, *J* = 10.7 Hz, 4 H), 1.44 – 1.34 (m, 2H), 1.28 – 1.25 (dd, *J* = 7.0, 2.7 Hz, 3H), 1.20 (d, *J* = 7.1 Hz, 1H), 1.13 (s, 3H), 0.97 (dd, *J* = 8.9, 6.3 Hz, 3H), 0.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.04 (d, *J* = 11.7 Hz), 137.08, 127.60 (d, *J* = 6.4 Hz), 127.30 (d, *J* = 3.9 Hz), 126.94, 100.17 (d, *J* = 3.4 Hz), 98.55 (dd, *J* = 9.1, 3.5 Hz), 97.00 (d, *J* = 3.7 Hz), 55.10 (t, *J* = 5.7 Hz), 51.66 (dd, *J* = 12.7, 5.4 Hz), 47.81 (d, *J* = 2.4 Hz), 40.50 (d, *J* = 20.6 Hz), 38.84 (d, *J* = 20.4 Hz), 30.20 – 28.53 (m), 25.91 (d, *J* = 1.8 Hz), 24.65 (d, *J* = 6.3 Hz), 22.67 (d, *J* = 7.3 Hz), 22.22 (d, *J* = 6.8 Hz), 21.50 (d, *J* = 12.7 Hz), 19.93 (dd, *J* = 26.9, 12.1 Hz), 11.91 (d, *J* = 4.7 Hz), 9.99; ^{31}P NMR (122 MHz, $CDCl_3$) δ 49.33; HRMS (ESI-MS) $[M+H]^+$: found 438.2321; calculated for $C_{27}H_{35}O_3P$: 438.2324.

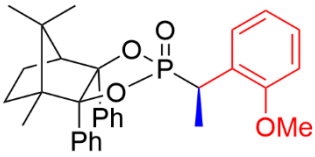
2,3-Diphenyl camphor (1-cyclohexylethyl)phosphonate 2bd:



87% yield, white solid, **m.p.** = 113-116 °C, R_f = 0.49 (PE/EA= 1:1), $[\alpha]^{25}_D$ = 105.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 – 6.67 (m, 10H), 2.92 (d, *J* = 5.3 Hz, 1H), 2.20 – 1.94 (m, 3H), 1.89 – 1.74 (m, 3H), 1.71 – 1.54 (m, 4H), 1.49 (d, *J* = 7.2 Hz, 1H), 1.45 (s, 3H), 1.36 (dt,

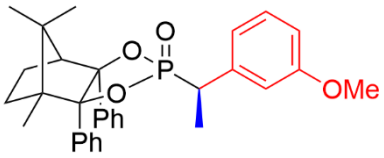
J = 8.6, 4.2 Hz, 2H), 1.32 – 1.17 (m, 4H), 1.13 (s, 3H), 1.09 – 0.91 (m, 2H), 0.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.01, 143.39, 141.90, 138.09, 137.07, 130.29, 128.42, 128.06, 127.86, 127.52, 127.43 – 127.08 (m), 126.94, 126.33, 103.89, 98.53 (d, J = 21.4 Hz), 90.70, 60.65, 55.64, 55.08 (d, J = 5.5 Hz), 51.77 (d, J = 5.5 Hz), 47.77, 40.95, 40.04, 38.27 (d, J = 15.3 Hz), 32.75 (d, J = 6.3 Hz), 30.70 (d, J = 19.3 Hz), 30.04 (d, J = 5.5 Hz), 29.84, 29.39, 26.47, 26.24, 26.12, 25.93, 25.55 (d, J = 3.9 Hz), 25.14 – 24.34 (m), 21.64 , 20.94, 11.87, 10.00; ^{31}P NMR (122 MHz, $CDCl_3$) δ 49.49; HRMS (ESI-MS) $[M+H]^+$: found 478.2637; calculated for $C_{30}H_{39}O_3P$: 478.2637.

2,3-Diphenyl camphor (1-(2-methoxyphenyl)ethyl)phosphonate 2be:



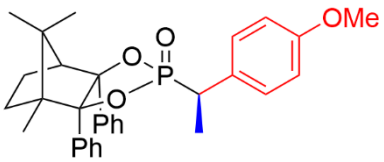
82% yield, white solid, R_f = 0.39 (PE/EA= 5:1), **[α]$^{25}_D$** = 57.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (s, 10H), 6.85 (t, J = 8.0 Hz, 1H), 6.45 (dd, J = 16.5, 8.0 Hz, 2H), 6.22 (s, 1H), 3.77 – 3.52 (m, 1H), 3.36 (s, 3H), 2.87 (dd, J = 20.2, 6.4 Hz, 1H), 1.72 – 1.57 (m, 3H), 1.31 – 1.13 (m, 4H), 1.05 (s, 3H), 0.80 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.18, 138.97 – 138.12 (m), 136.95 (d, J = 4.2 Hz), 130.81, 130.16, 129.16, 128.33, 128.01, 127.58, 126.36, 120.73, 113.49, 100.17, 98.78, 55.61 (d, J = 3.0 Hz), 55.00, 52.22, 48.22, 40.75, 39.08, 31.62, 29.75, 26.48, 24.39, 22.68, 21.45, 16.59 (d, J = 5.5 Hz), 14.16, 9.92; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.25; HRMS (ESI-MS) $[M+H]^+$: found 502.2275; calculated for $C_{31}H_{35}O_4P$: 502.2273.

2,3-Diphenyl camphor (1-(3-methoxyphenyl)ethyl)phosphonate 2bf:



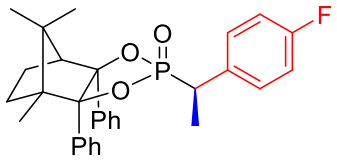
80% yield, white solid, R_f = 0.37 (PE/EA= 5:1), **[α]$^{25}_D$** = 67.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 – 6.82 (m, 14H), 3.85 (s, 3H), 3.67 – 3.47 (m, 1H), 2.94 (dd, J = 22.5, 5.4 Hz, 1H), 2.17 – 2.01 (m, 1H), 1.88 – 1.69 (m, 1H), 1.68 – 1.52 (m, 6H), 1.43 – 1.22 (m, 2H), 1.16 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.80 (d, J = 2.4 Hz), 139.28 (d, J = 6.6 Hz), 137.83, 136.76, 129.70 (d, J = 2.4 Hz), 127.78, 127.29, 127.04, 120.96 (d, J = 6.7 Hz), 114.01 (d, J = 6.9 Hz), 113.15 (d, J = 3.0 Hz), 99.77 (d, J = 2.5 Hz), 98.48 (d, J = 4.1 Hz), 55.83 – 54.70 (m), 51.69 (d, J = 5.5 Hz), 47.83, 39.88, 38.20, 29.33, 25.93, 24.64, 21.88, 16.85 (d, J = 4.7 Hz), 9.85; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.57; HRMS (ESI-MS) $[M+H]^+$: found 502.2276; calculated for $C_{31}H_{35}O_4P$: 502.2273.

2,3-Diphenyl camphor (1-(4-methoxyphenyl)ethyl)phosphonate 2bg:



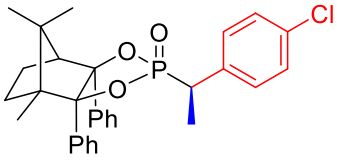
83% yield, white solid, **m.p.** = 101-105 °C, R_f = 0.38 (PE/EA= 5:1), **$[\alpha]^{25}_D$** = 57.8° (c = 1.00 in $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 10H), 6.74 (d, *J* = 6.7 Hz, 2H), 6.54 (d, *J* = 8.5 Hz, 2H), 3.63 (s, 3H), 2.98 (d, *J* = 5.1 Hz, 1H), 2.03 (ddt, *J* = 14.9, 9.7, 5.0 Hz, 1H), 1.76 (s, 2H), 1.66 (dd, *J* = 18.7, 7.1 Hz, 3H), 1.49 (dd, *J* = 13.5, 6.9 Hz, 1H), 1.43 – 1.23 (m, 2H), 1.13 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.97 (d, *J* = 3.3 Hz), 136.40 (d, *J* = 4.1 Hz), 133.85 (d, *J* = 6.8 Hz), 130.63 , 130.03 , 129.43 (d, *J* = 7.4 Hz), 128.57 – 127.91 (m), 127.55 , 127.20 (d, *J* = 2.6 Hz), 126.36 , 100.51 , 98.99 (d, *J* = 1.4 Hz), 81.59 (d, *J* = 15.9 Hz), 79.39 (d, *J* = 15.8 Hz), 55.64 (d, *J* = 3.0 Hz), 52.18 (d, *J* = 3.4 Hz), 48.24 , 42.80 (d, *J* = 3.4 Hz), 41.08 (d, *J* = 3.3 Hz), 32.77 (dd, *J* = 20.2, 3.5 Hz), 29.69 , 26.49 , 24.46 , 21.48 , 9.99; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.78; HRMS (ESI-MS) $[M+H]^+$: found 502.2278; calculated for $C_{31}H_{35}O_4P$: 502.2273.

2,3-Diphenyl camphor (1-(4-fluorophenyl)ethyl)phosphonate 2bh:



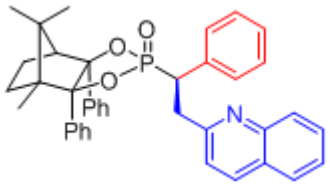
80% yield, white solid, R_f = 0.33 (PE/EA= 5:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (s, 10H), 6.91 – 6.49 (m, 4H), 2.95 (dd, *J* = 20.3, 6.2 Hz, 2H), 2.03 (ddt, *J* = 14.2, 9.4, 4.5 Hz, 1H), 1.76 (s, 3H), 1.67 (dd, *J* = 18.6, 6.8 Hz, 3H), 1.48 (tt, *J* = 15.6, 7.4 Hz, 1H), 1.40 – 1.23 (m, 2H), 1.14 (s, 3H), 0.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.31 (d, *J* = 3.3 Hz), 160.06 (d, *J* = 3.3 Hz), 138.29 (d, *J* = 3.3 Hz), 136.86 (d, *J* = 4.2 Hz), 131.84 – 129.61 (m), 128.75 – 127.31 (m), 126.41, 115.01 (dd, *J* = 21.2, 2.4 Hz), 100.26, 98.77, 55.64 (d, *J* = 2.8 Hz), 52.24 (d, *J* = 3.4 Hz), 48.25, 39.98, 38.29, 29.74, 26.46, 24.32, 21.46, 16.96 (d, *J* = 5.4 Hz), 9.91; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.10; ^{19}F NMR (282 MHz, $CDCl_3$) δ -116.10 (dt, *J* = 8.6, 4.6 Hz); HRMS (ESI-MS) $[M+H]^+$: found 490.2152; calculated for $C_{31}H_{35}O_4P$: 490.2073.

2,3-Diphenyl camphor (1-(4-chlorophenyl)ethyl)phosphonate 2bi:



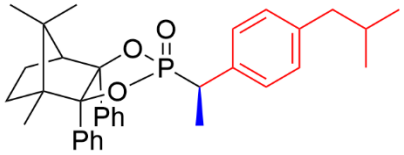
82% yield, white solid, R_f = 0.32 (PE/EA= 5:1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (s, 10H), 6.97 (d, *J* = 8.2 Hz, 2H), 6.75 (dd, *J* = 8.6, 2.4 Hz, 2H), 3.11 – 2.83 (m, 2H), 2.12 – 1.94 (m, 1H), 1.75 (s, 3H), 1.67 (dd, *J* = 18.6, 7.1 Hz, 3H), 1.56 – 1.41 (m, 1H), 1.40 – 1.24 (m, 2H), 1.13 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.27 (d, *J* = 3.3 Hz), 136.82 (d, *J* = 4.3 Hz), 135.71 (d, *J* = 7.3 Hz), 132.68 (d, *J* = 3.7 Hz), 129.78 (d, *J* = 6.7 Hz), 128.69 – 127.89 (m), 126.43, 100.32, 98.83 (d, *J* = 1.6 Hz), 55.65 (d, *J* = 2.9 Hz), 52.24 (d, *J* = 3.5 Hz), 48.24, 40.17, 38.49, 29.73, 26.46, 24.31, 21.45, 16.78 (d, *J* = 5.5 Hz), 9.91; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.72; HRMS (ESI-MS) $[M+H]^+$: found 506.1858; calculated for $C_{31}H_{35}O_4P$: 506.1778.

2,3-Diphenyl camphor (2-(quinolin-2-yl)-1-phenylethyl)phosphonate 2bj:



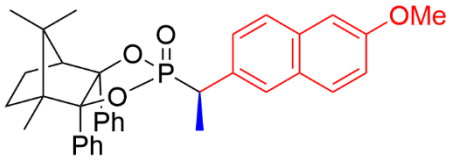
82% yield, white solid, R_f = 0.25 (PE/EA= 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (t, *J* = 8.8 Hz, 1H), 8.00 – 7.84 (m, 1H), 7.83 – 7.63 (m, 4H), 7.55 – 7.33 (m, 3H), 7.22 (dd, *J* = 5.5, 2.0 Hz, 3H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.03 – 6.85 (m, 7H), 4.11 – 3.82 (m, 2H), 3.64 – 3.37 (m, 1H), 2.95 (d, *J* = 5.3 Hz, 1H), 2.00 (ddt, *J* = 18.6, 9.9, 4.6 Hz, 1H), 1.83 (s, 3H), 1.50 (dq, *J* = 14.3, 7.4, 6.8 Hz, 1H), 1.40 – 1.20 (m, 2H), 1.12 (s, 3H), 0.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.71 (d, *J* = 14.0 Hz), 155.41, 147.92, 137.97 (d, *J* = 3.3 Hz), 136.63, 136.40 (d, *J* = 4.1 Hz), 135.83, 135.62 (d, *J* = 6.3 Hz), 134.66, 129.96 (d, *J* = 6.1 Hz), 129.31 (dd, *J* = 20.1, 8.2 Hz), 128.22 – 127.93 (m), 127.56 (d, *J* = 5.6 Hz), 127.05 – 126.62 (m), 125.99 (d, *J* = 17.3 Hz), 122.16, 119.60, 100.45, 98.88 (d, *J* = 1.6 Hz), 55.58 (d, *J* = 2.9 Hz), 52.16 (d, *J* = 3.5 Hz), 48.27, 46.56, 44.86, 41.46 (d, *J* = 2.7 Hz), 29.76, 26.53, 24.42, 21.64, 9.93; ^{31}P NMR (122 MHz, $CDCl_3$) δ 42.29; HRMS (ESI-MS) $[M+H]^+$: found 599.2595; calculated for $C_{31}H_{35}O_4P$: 599.2589.

2,3-Diphenyl camphor (1-(4-isobutyphenyl)ethyl)phosphonate 2bk:



75% yield, white solid, R_f = 0.38 (PE/EA= 5:1), $[\alpha]^{25}_D$ = 102.8° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.17 (m, 10H), 6.85 – 6.59 (m, 4H), 3.05 – 2.81 (m, 2H), 2.26 (d, *J* = 7.1 Hz, 2H), 2.11 – 1.96 (m, 1H), 1.77 (s, 3H), 1.74 – 1.62 (m, 4H), 1.51 (dq, *J* = 14.2, 7.3, 6.8 Hz, 1H), 1.40 – 1.24 (m, 2H), 1.13 (s, 3H), 0.89 (s, 3H), 0.78 (dd, *J* = 6.6, 1.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 140.11 (d, *J* = 3.2 Hz), 138.28 (d, *J* = 3.2 Hz), 136.99 (d, *J* = 4.2 Hz), 134.18 (d, *J* = 7.4 Hz), 130.45 (d, *J* = 43.8 Hz), 128.92 (d, *J* = 2.5 Hz), 128.28, 128.12, 128.02 (d, *J* = 1.9 Hz), 127.56, 126.37, 100.07, 98.69 (d, *J* = 1.6 Hz), 55.61 (d, *J* = 2.8 Hz), 52.24 (d, *J* = 3.4 Hz), 48.24, 44.96, 40.33, 38.66, 30.40 – 28.81 (m), 26.49, 24.37, 22.41 (d, *J* = 1.9 Hz), 21.48, 16.78 (d, *J* = 5.3 Hz), 9.95; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.77; HRMS (ESI-MS) $[M+H]^+$: found 528.2795; calculated for $C_{31}H_{35}O_4P$: 528.2793.

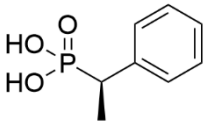
2,3-Diphenyl camphor (1-(4-methoxynaphthyl)ethyl)phosphonate 2bl:



73% yield, white solid, R_f = 0.38 (PE/EA= 3:1), $[\alpha]^{25}_D$ = 87.3° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 – 7.21 (m, 12H), 7.14 – 6.85 (m, 4H), 3.80 (s, 3H), 3.07 (dt, *J* = 17.8, 7.1 Hz, 1H), 2.95 (d, *J* = 5.3 Hz, 1H), 2.02 (m, 1H), 1.85 – 1.69 (m, 3H), 1.56 – 1.29 (m, 3H), 1.26 (s, 3H), 1.12 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.41 (d, *J* = 1.3 Hz), 138.43 (d, *J* = 3.2 Hz), 136.99 (d, *J* = 4.2 Hz), 133.43 (d, *J* = 2.2 Hz), 132.07 (d, *J* = 7.7 Hz), 130.51 (d, *J* = 48.2 Hz), 129.17 (d, *J* = 1.3 Hz), 128.58 (d, *J* = 2.5 Hz), 128.31, 128.07, 127.68, 127.44 (d, *J* = 8.6 Hz), 126.85 – 126.58 (m), 126.42, 118.52, 105.27 (d, *J* = 1.4 Hz), 100.19, 98.69 (d, *J* = 1.5 Hz), 55.66 (d, *J* = 2.9 Hz), 55.23, 52.29 (d, *J* = 3.4 Hz), 48.26, 40.63, 38.95, 29.75, 26.45, 24.30, 21.49, 16.76 (d, *J* =

5.3 Hz), 9.95; ^{31}P NMR (122 MHz, $CDCl_3$) δ 43.33; HRMS (ESI-MS) $[M+H]^+$: found 552.2431; calculated for $C_{31}H_{35}O_4P$: 552.2429.

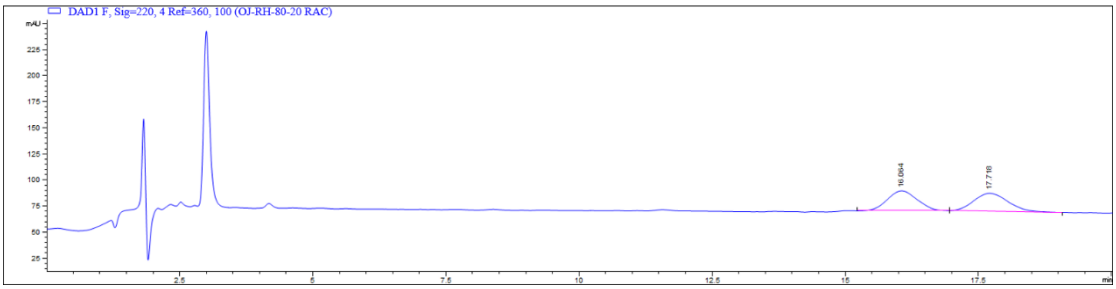
(1-phenylethyl)phosphonic acid 3a:



99% yield, white solid, **m.p.** = 70-76 °C, R_f = 0.26 (PE/EA= 0:1), **$[\alpha]^{25}_D$** = 4.8° (c = 1.00 in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.24 (d, *J* = 8.8 Hz, 2H), 3.16 – 2.76 (m, 0H), 1.39 (dd, *J* = 18.8, 7.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.33 (d, *J* = 6.9 Hz), 128.71 (d, *J* = 5.8 Hz), 128.40, 127.11, 38.49, 36.63, 14.86; ^{31}P NMR (122 MHz, $CDCl_3$): δ =34.05; HRMS (ESI-MS) $[M+H]^+$: found 186.0446; calculated for $C_8H_{11}O_3P$: 186.0446.

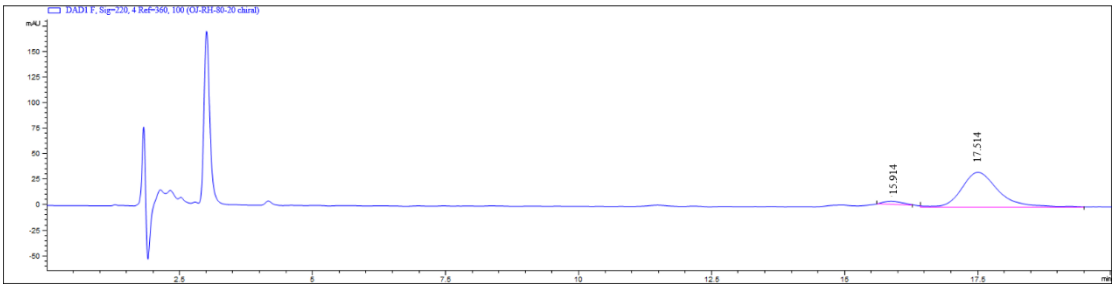
Chiral HPLC: The enantiomeric excess was determined by HPLC on Chiralpak OJ-RH column after esterification with $TMSCH_2N_2$, Water/Acetonitrile = 80/20, flow rate = 1.0 mL/min, λ = 220 nm.

RAC-3a



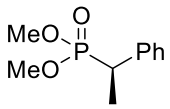
	Retention Time (min)	Relative Area (%)
Peak 1	16.064	49.012
Peak 2	17.718	50.988

Chiral-3a



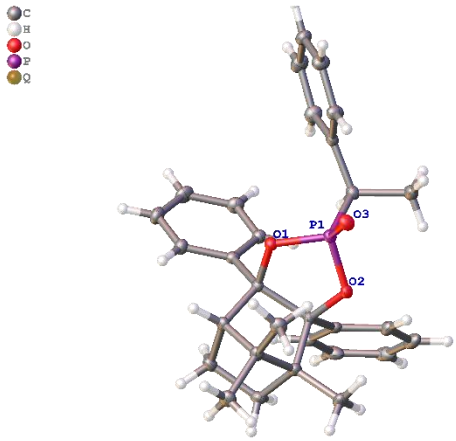
	Retention Time (min)	Relative Area (%)
Peak 1	15.914	1.585
Peak 2	17.514	98.415

(1-phenylethyl)phosphonic acid 4a:



99% yield, white solid, R_f = 0.36 (PE/EA= 0:1), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.22 (m, 5H), 3.69 (d, *J* = 10.6 Hz, 3H), 3.53 (d, *J* = 10.5 Hz, 3H), 3.22 (dq, *J* = 22.4, 7.4 Hz, 1H), 1.59 (dd, *J* = 18.6, 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.65 (d, *J* = 7.0 Hz), 128.78 – 128.40 (m), 127.21 (d, *J* = 3.3 Hz), 53.33 (d, *J* = 7.0 Hz), 52.84 (d, *J* = 7.3 Hz), 38.97, 37.15, 15.56 (d, *J* = 5.2 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ =32.16; HRMS (ESI-MS) $[M+H]^+$: found 214.0756; calculated for $C_8H_{11}O_3P$: 214.0759.

X-ray crystal structure of 2aa



Crystal data for compound **2aa**

Identification code	**2aa**
Empirical formula	$C_{30}H_{33}O_3P$
Formula weight	472.53
Temperature/K	179.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.97433(16)

b/Å	9.78846(14)
c/Å	11.7517(2)
α/°	90
β/°	102.0231(16)
γ/°	90
Volume/Å^3	1234.69(3)
Z	2
ρ_{calc}g/cm^3	1.271
μ/mm^{-1}	1.217
F(000)	504.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.692 to 146.96
Index ranges	-13 ≤ h ≤ 12, -12 ≤ k ≤ 12, -14 ≤ l ≤ 12
Reflections collected	7634
Independent reflections	4546 [R_{int} = 0.0209, R_{sigma} = 0.0303]
Data/restraints/parameters	4546/1/311
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0301, wR_2 = 0.0786
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0790
Largest diff. peak/hole / e Å^{-3}	0.15/-0.28
Flack/Hooft parameter	0.025(10)/0.023(9)

NMR Spectra of 1-4

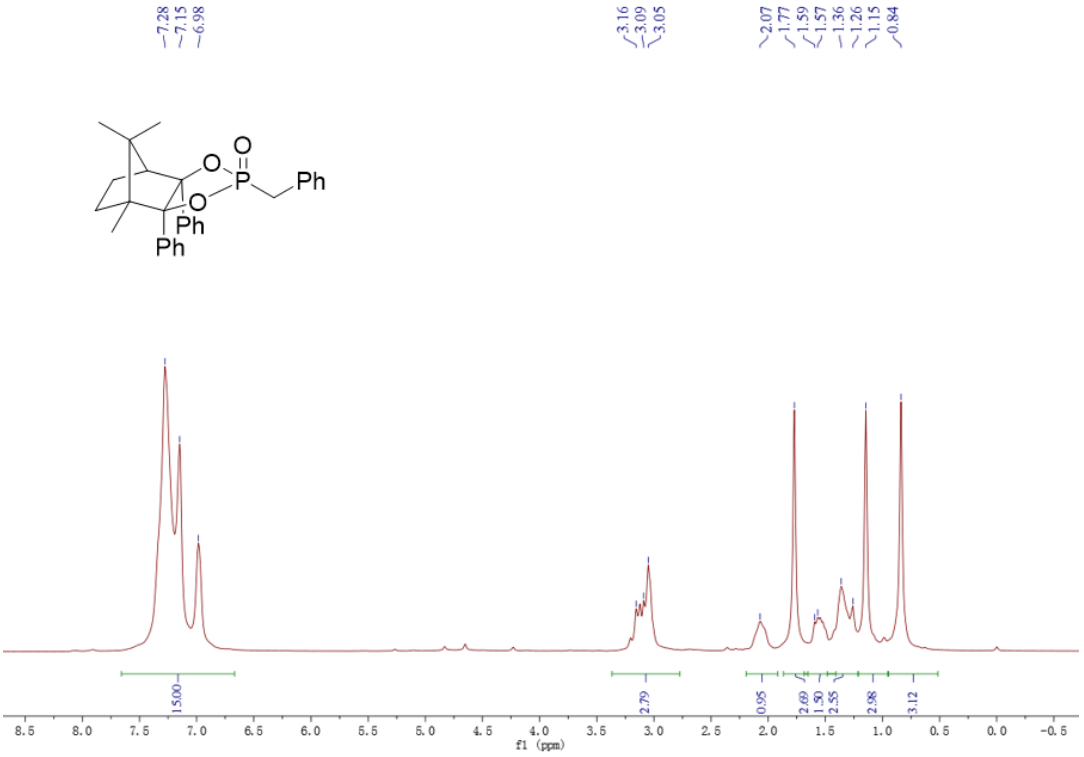


Figure1: ^{1}H NMR of **1a**

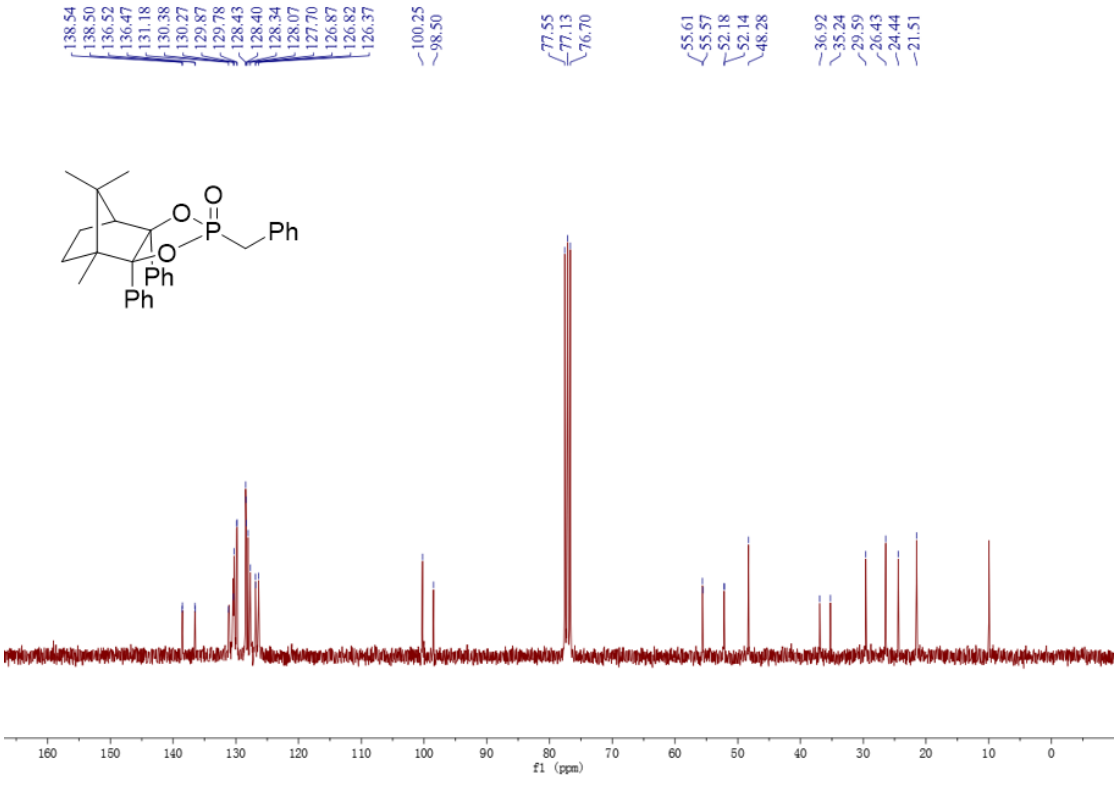


Figure 2: ^{13}C NMR of **1a**

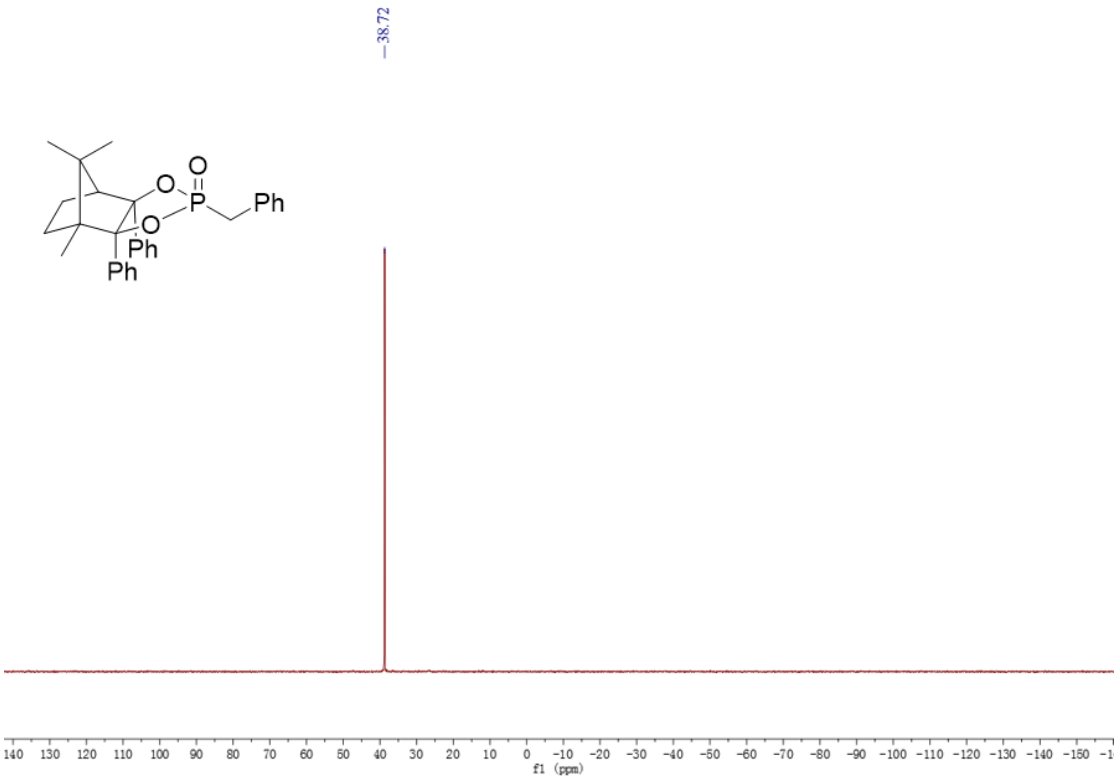


Figure 3: ^{31}P NMR of **1a**

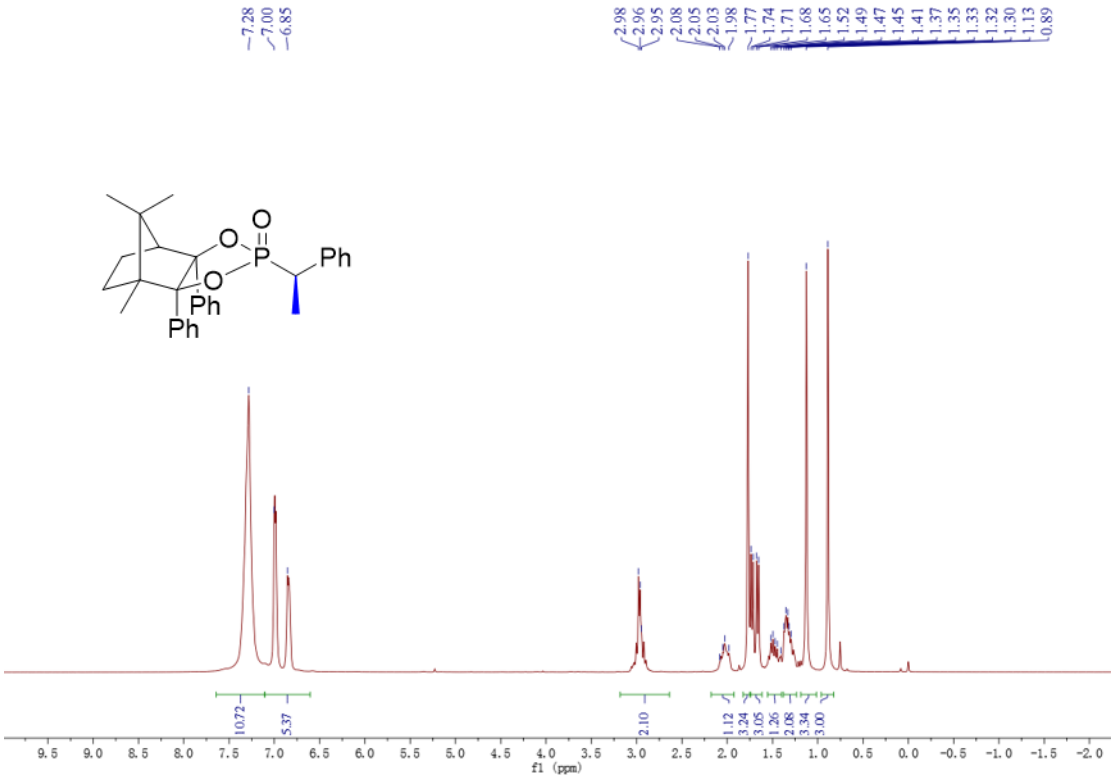
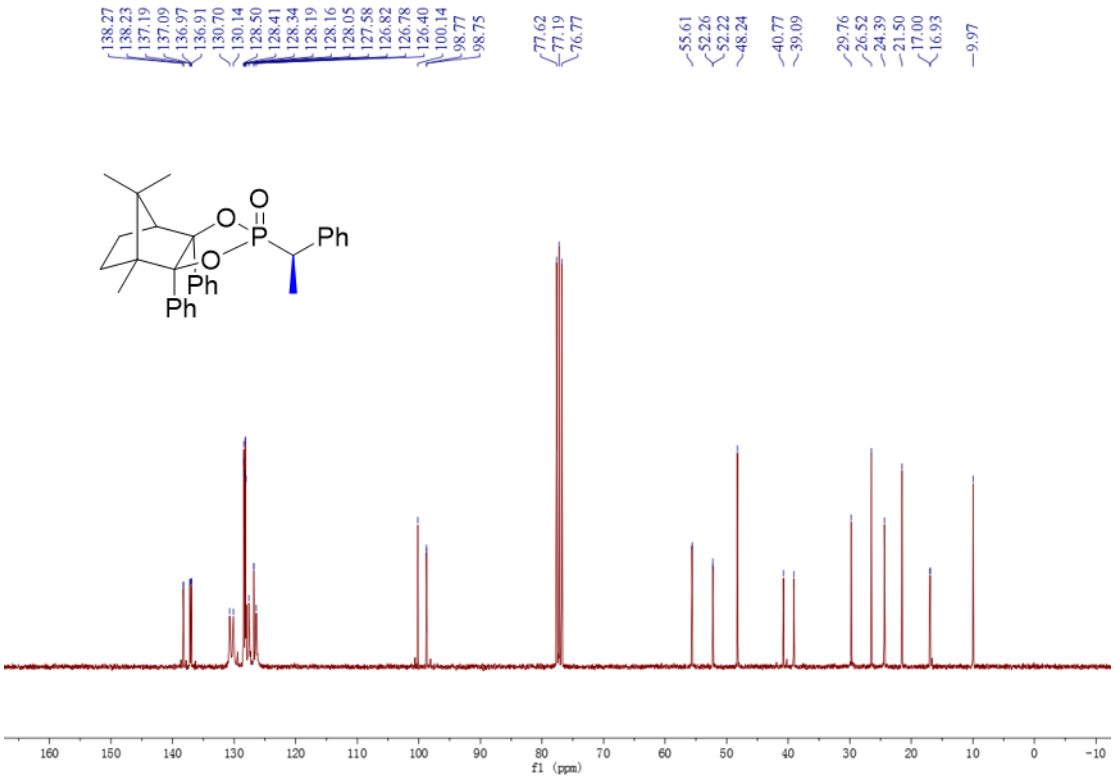
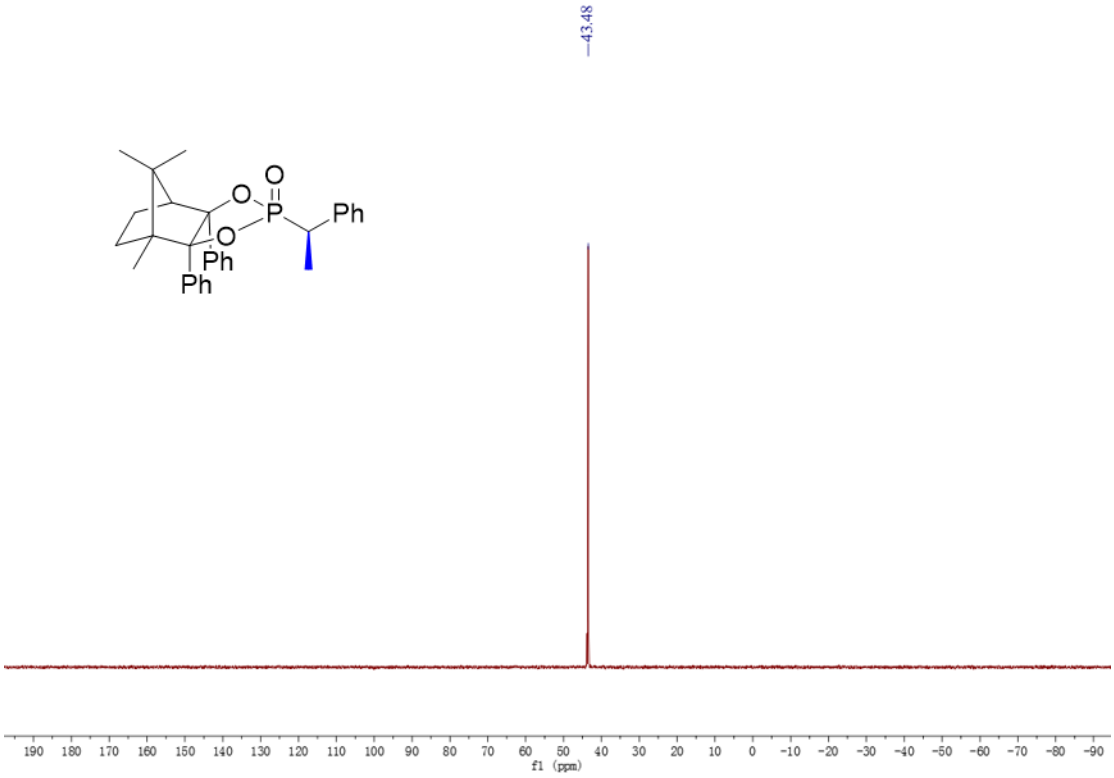


Figure 4: ^{1}H NMR of **2aa**



491

492 **Figure 5:** ^{13}C NMR of **2aa**



493

494 **Figure 6:** ^{31}P NMR of **2aa**

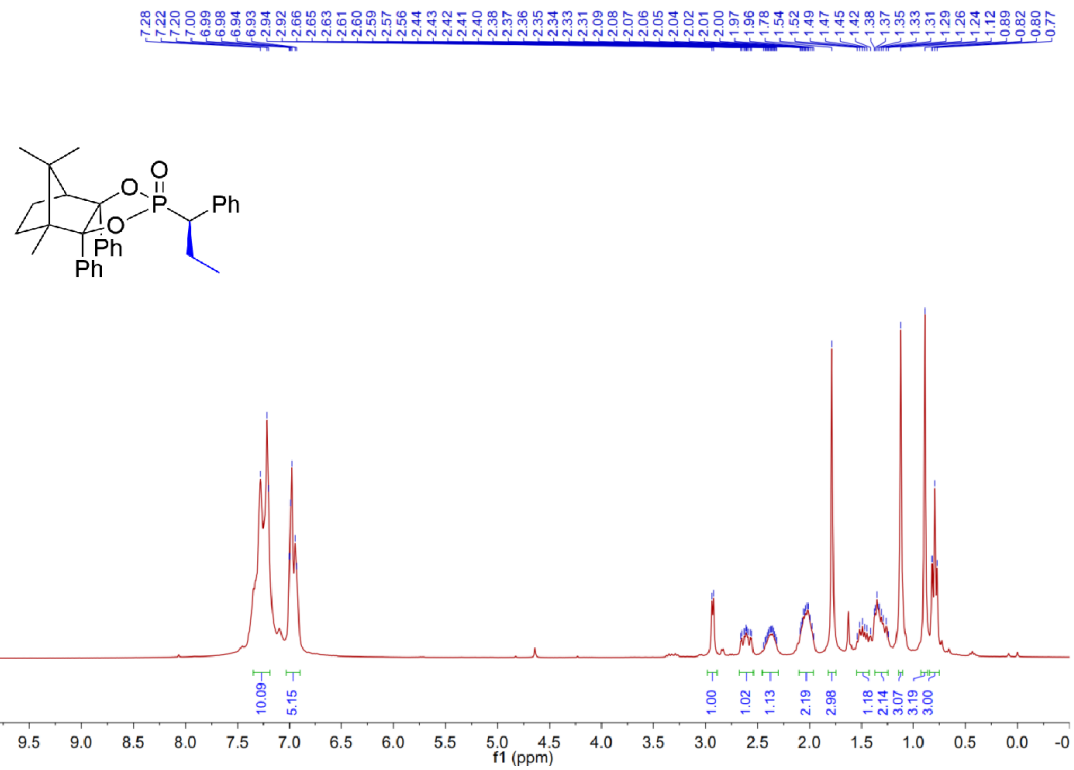


Figure 7: ^{1}H NMR of **2ab**

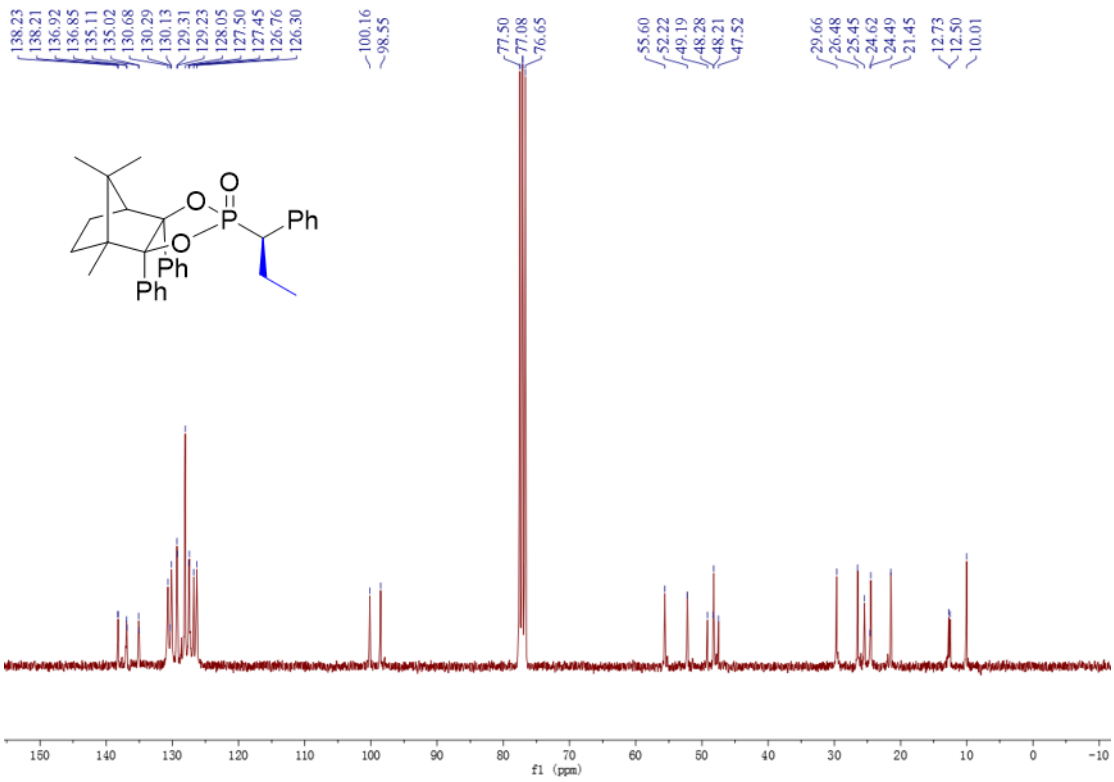


Figure 8: ^{13}C NMR of **2ab**

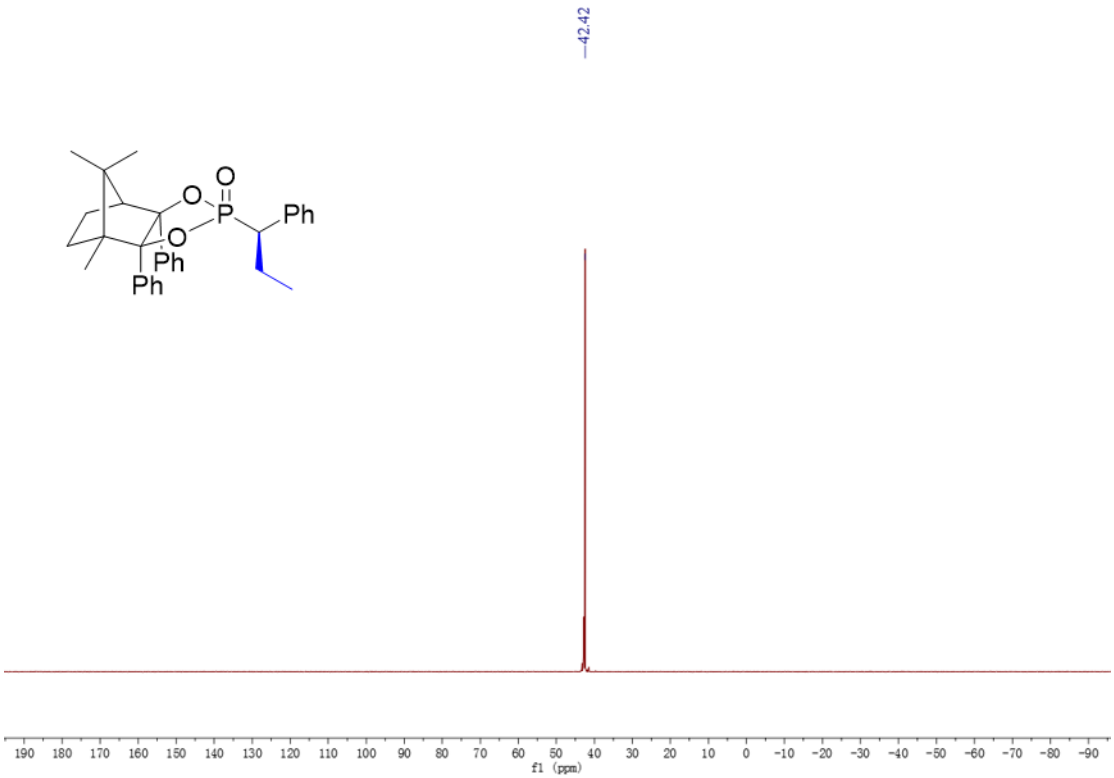


Figure 9: ^{31}P NMR of **2ab**

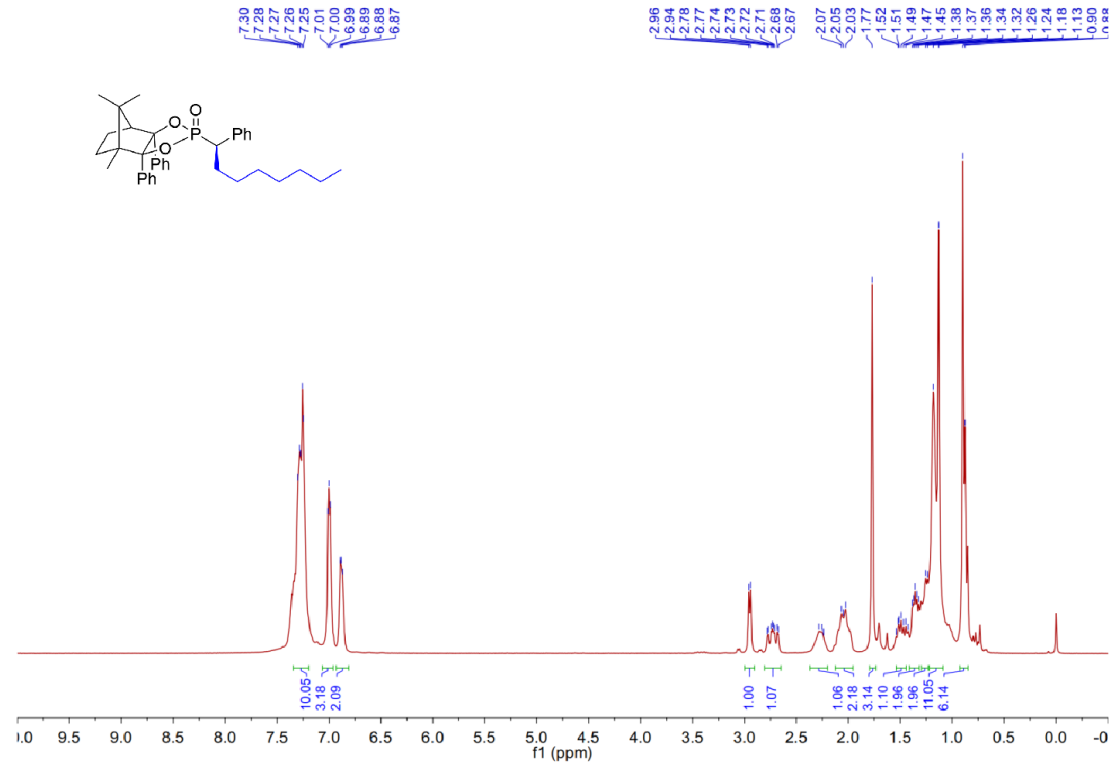
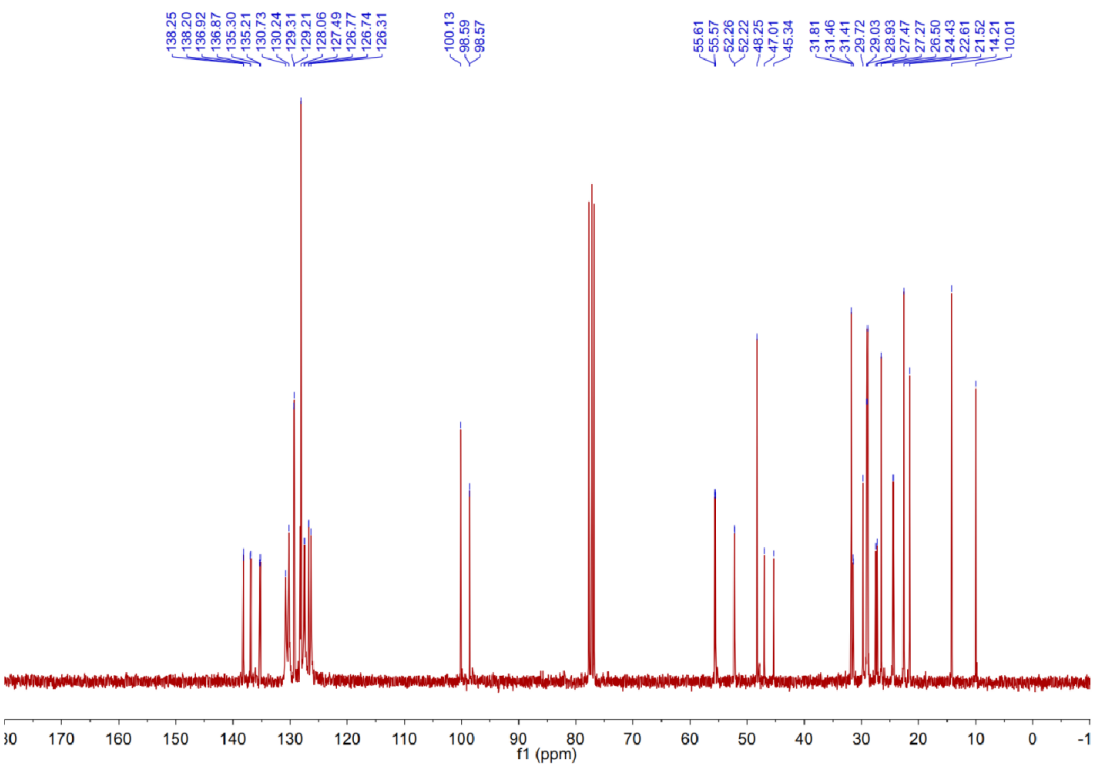
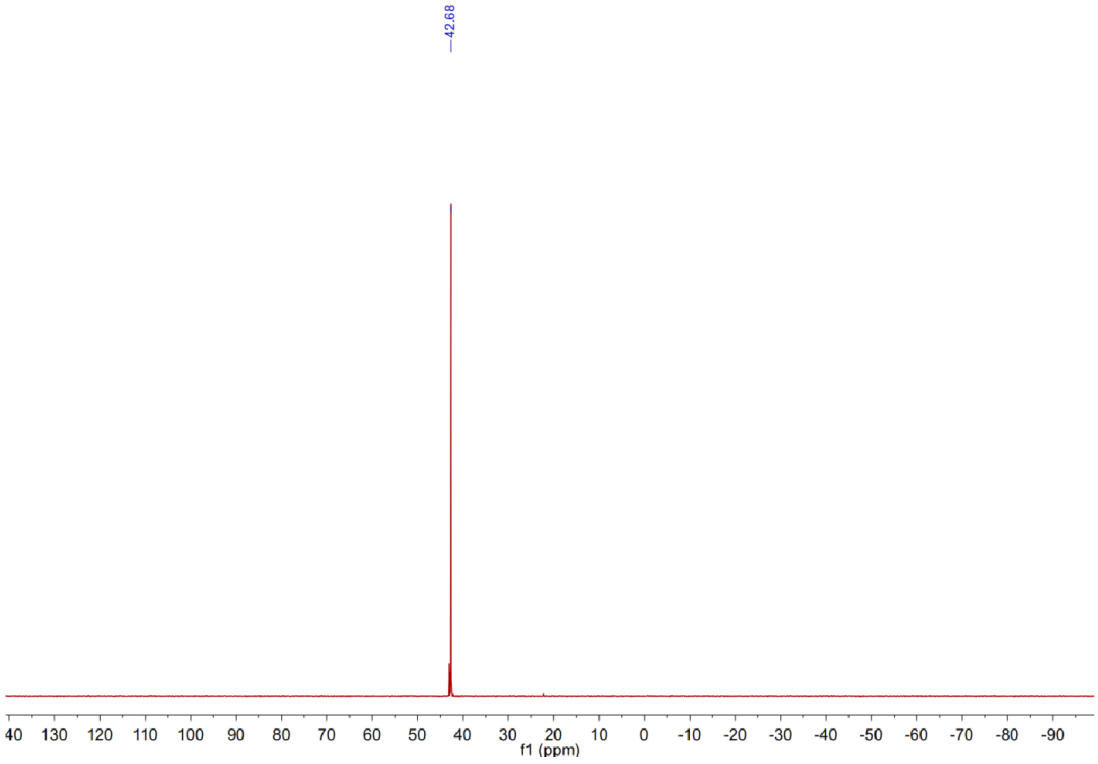


Figure 10: ^{1}H NMR of **2ac**



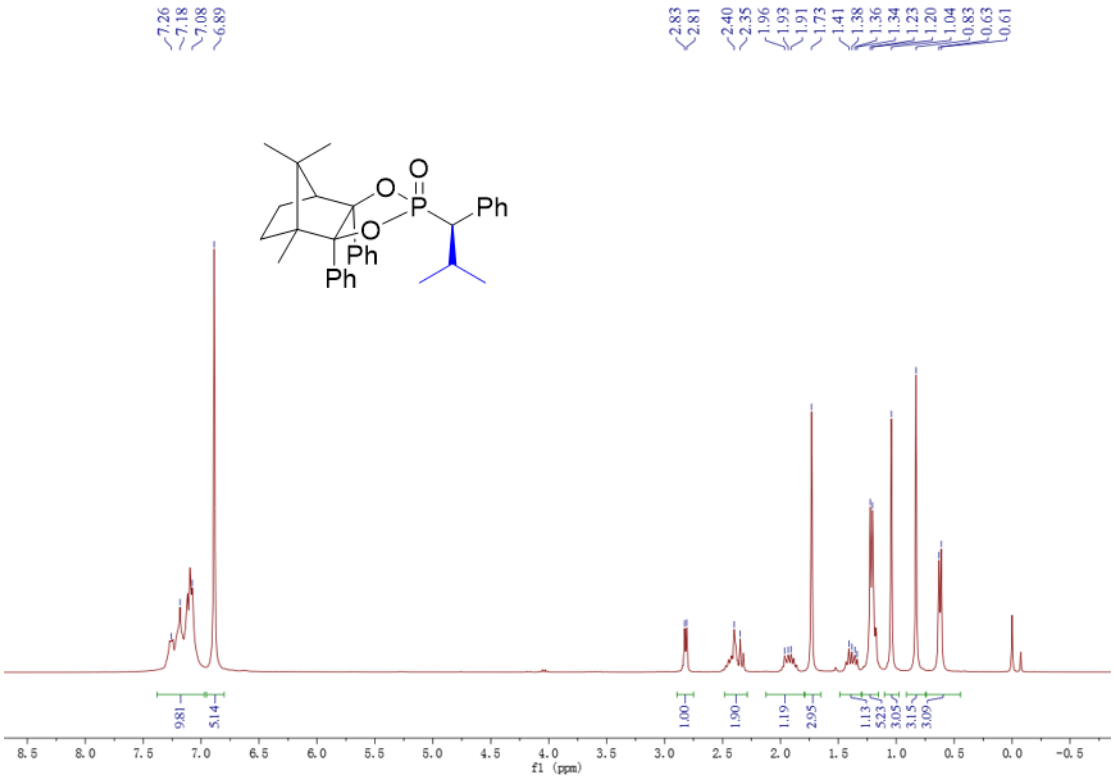
505

506 **Figure 11:** ^{13}C NMR of **2ac**



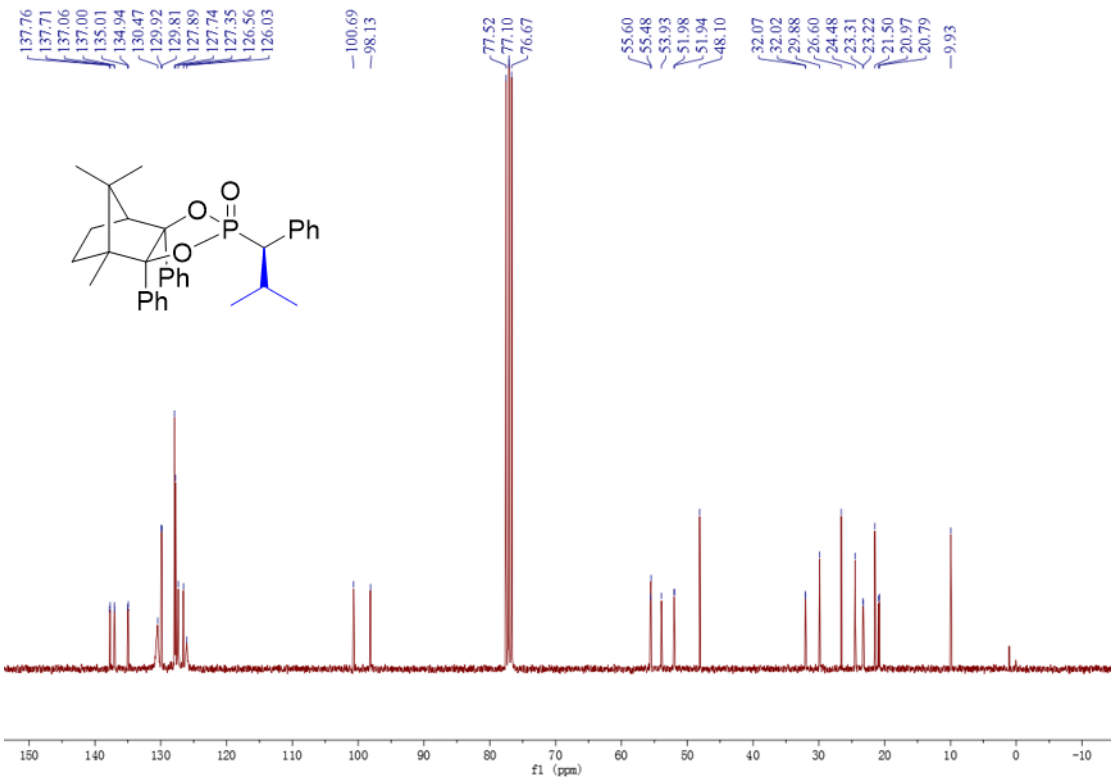
507

508 **Figure 12:** ^{31}P NMR of **2ac**



509

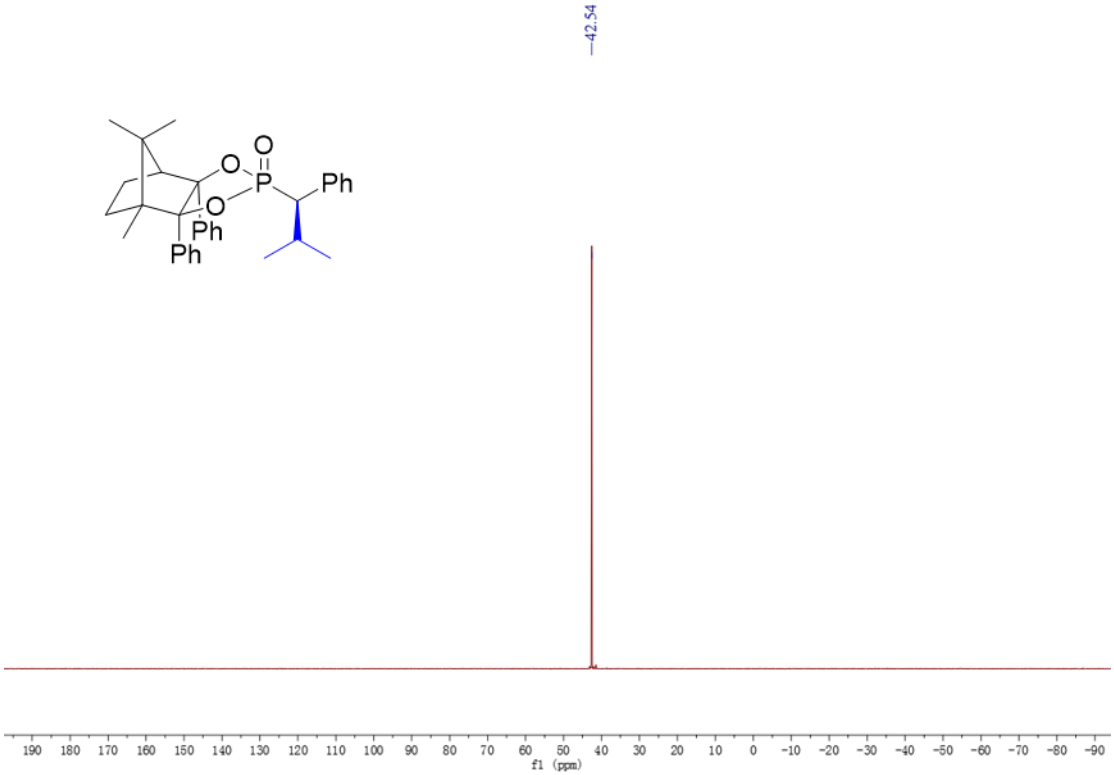
510 **Figure 13:** ^{1}H NMR of **2ad**



511

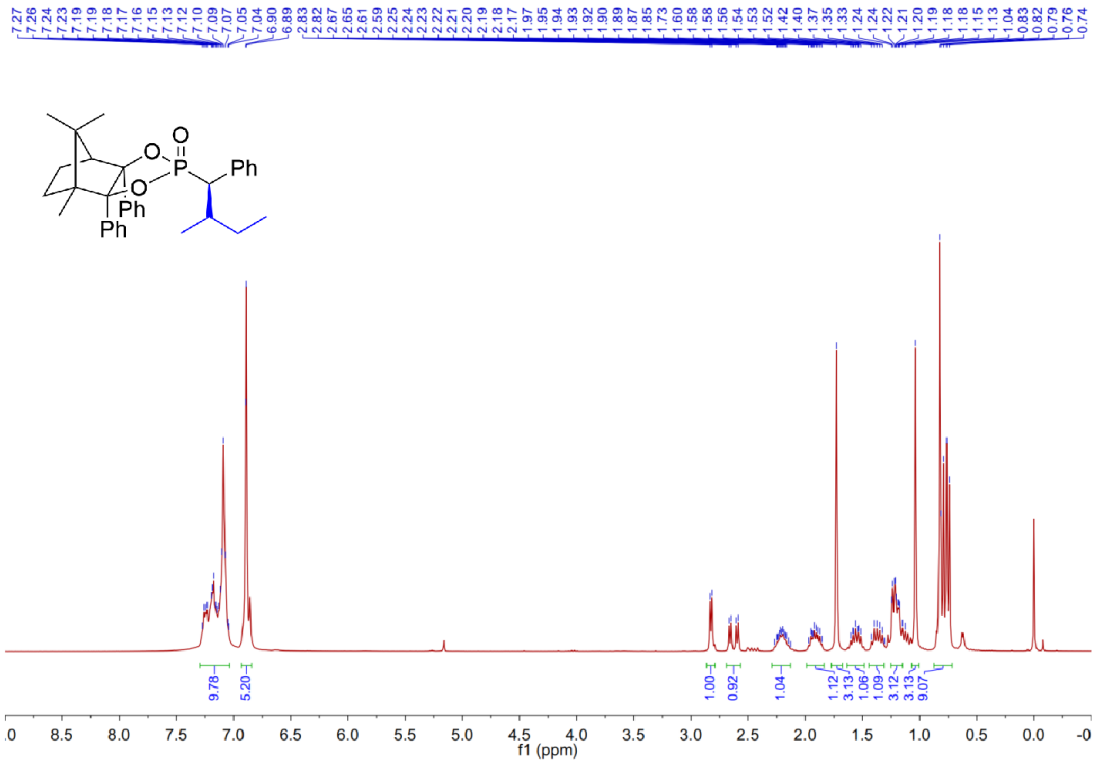
512 **Figure 14:** ^{13}C NMR of **2ad**

513



514

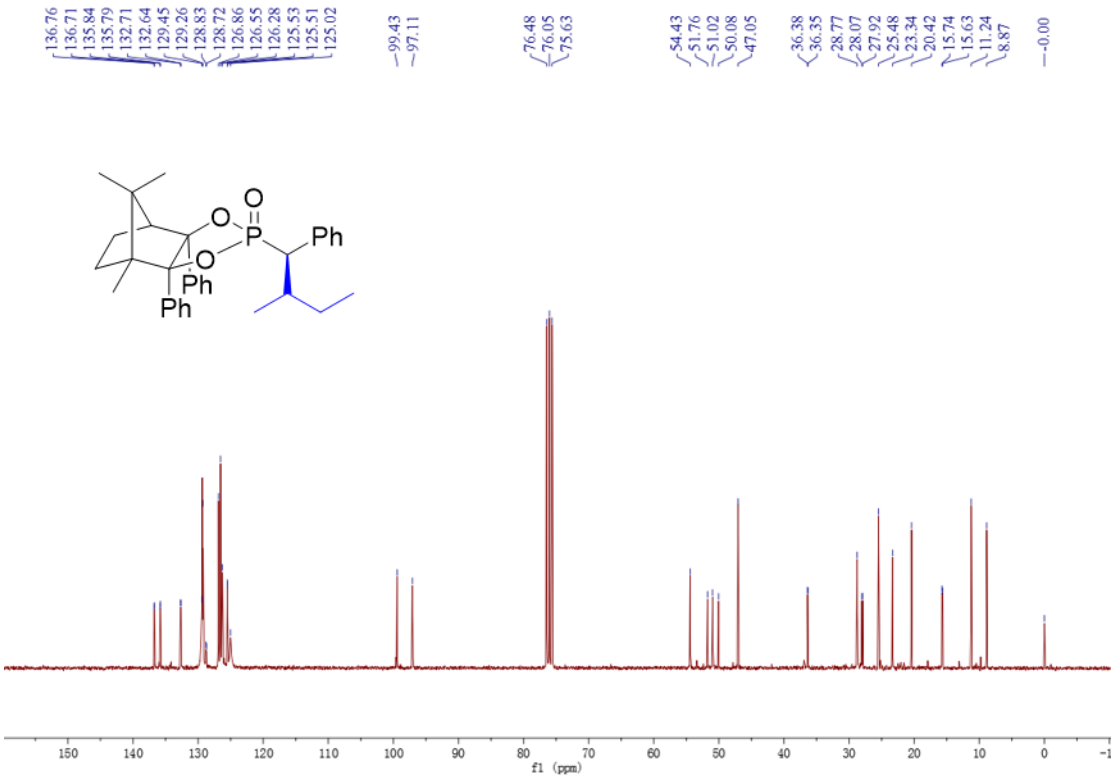
515 **Figure 15:** ^{31}P NMR of **2ad**



516

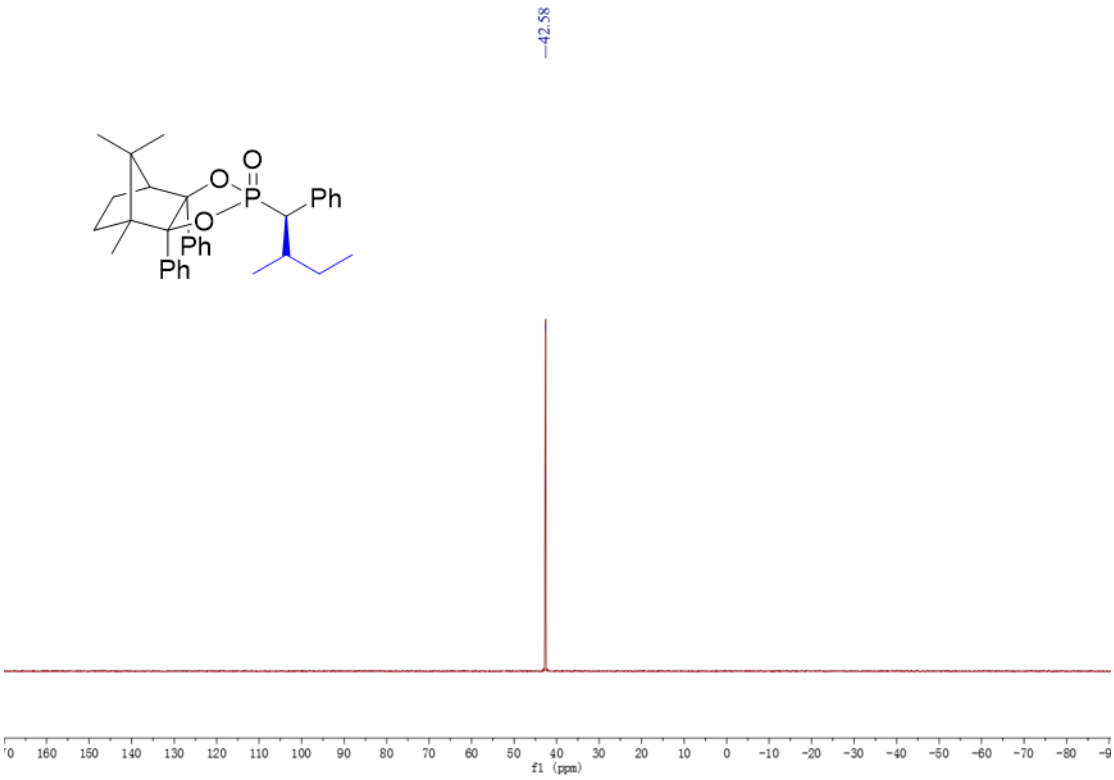
517 **Figure 16:** ^{1}H NMR of **2ae**

518



519

520 **Figure 17:** ^{13}C NMR of **2ae**



521

522 **Figure 18:** ^{31}P NMR of **2ae**

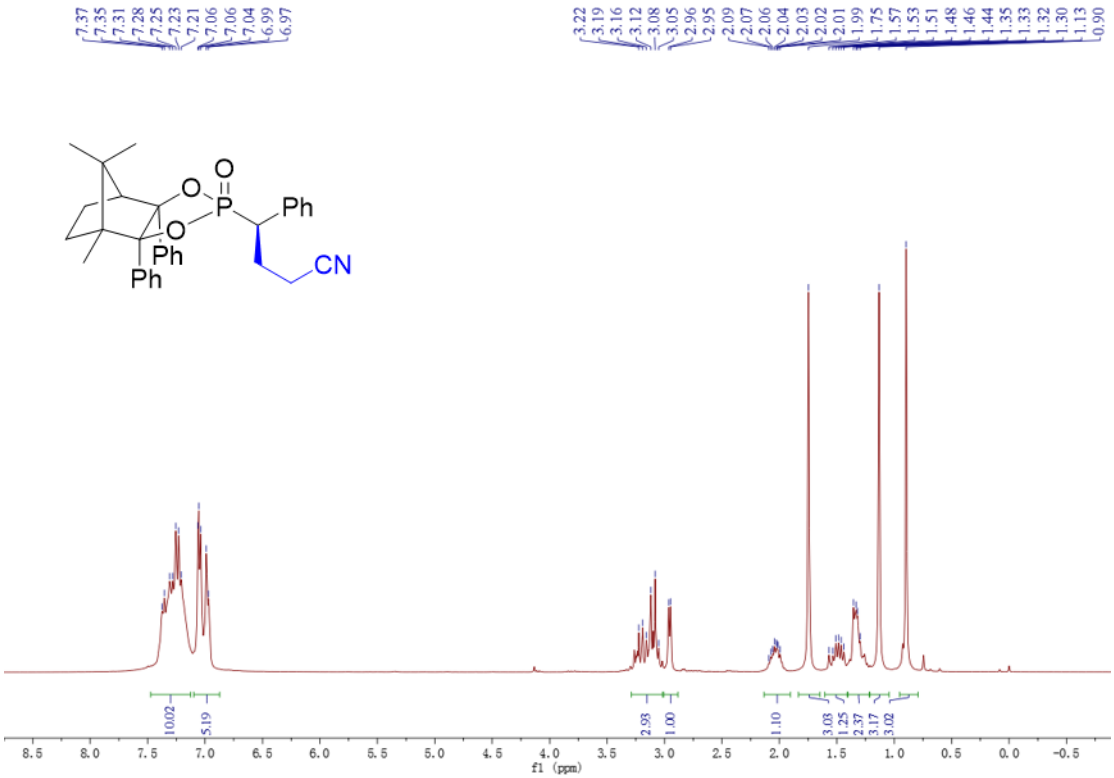


Figure 19: ^{1}H NMR of **2ag**

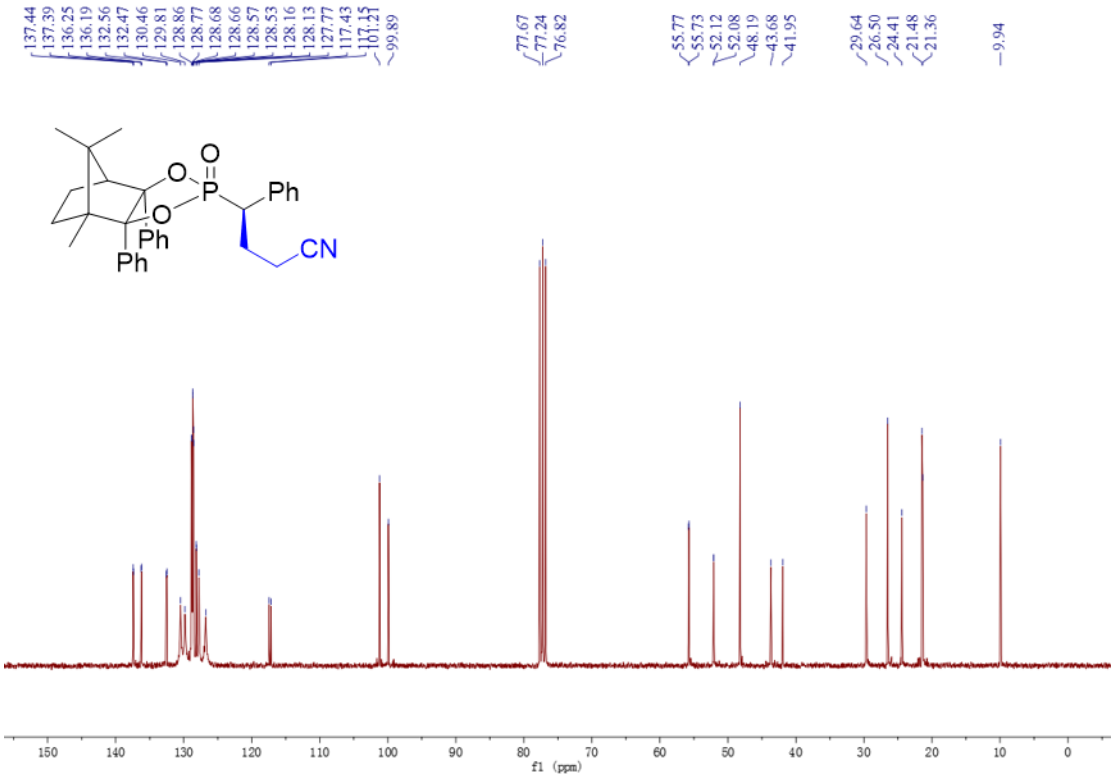
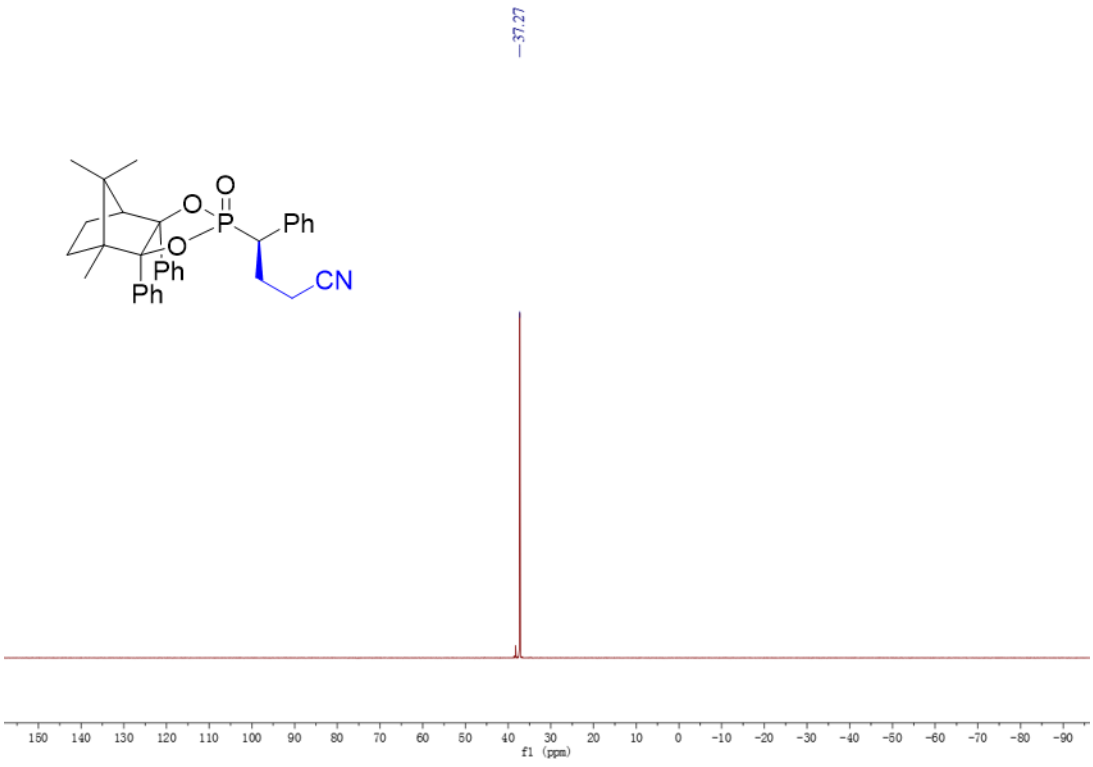
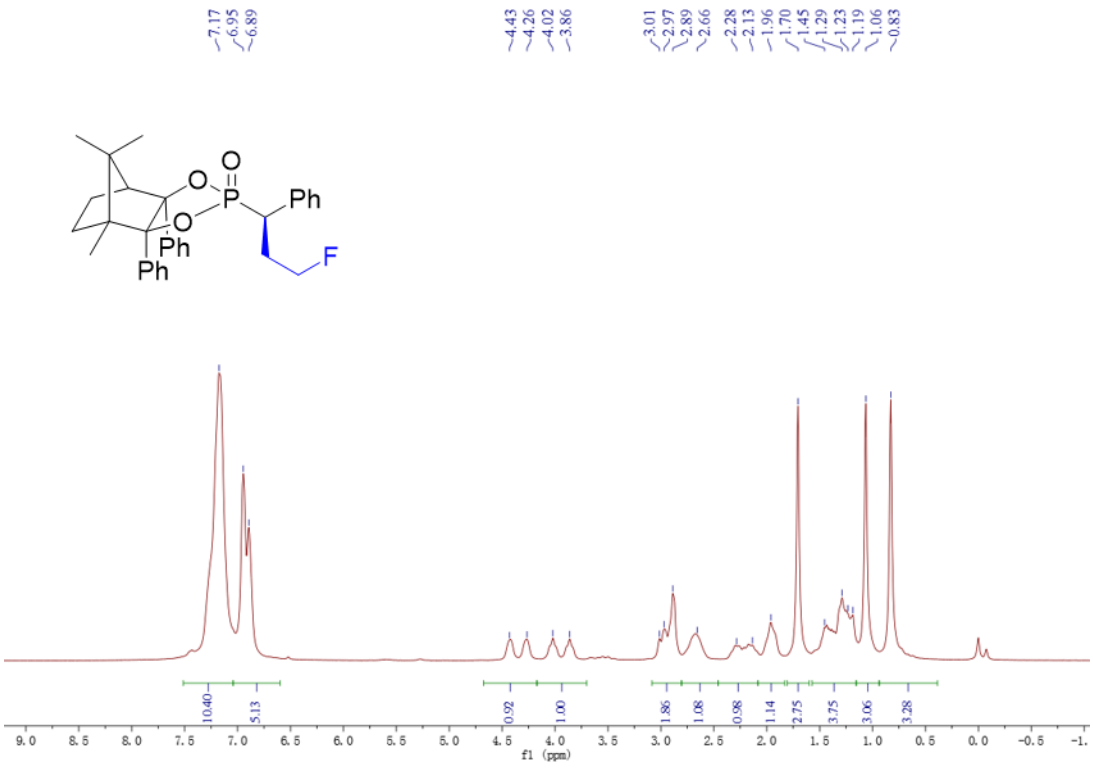


Figure 20: ^{13}C NMR of **2ag**



529

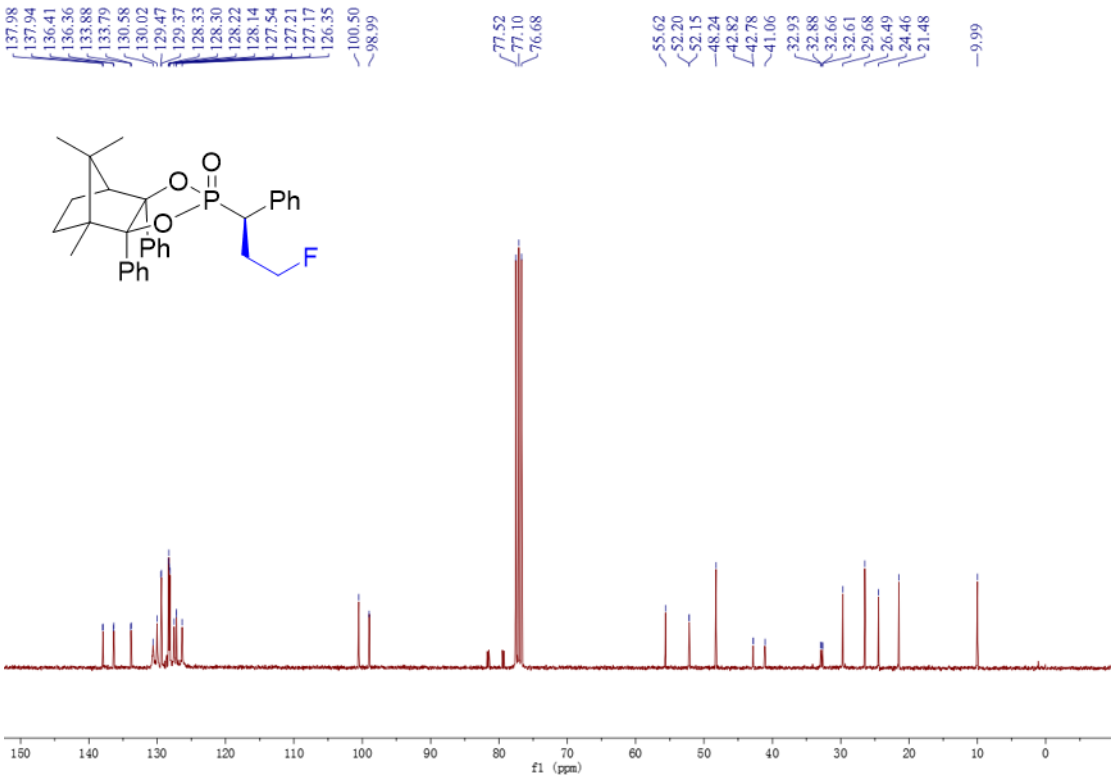
530 **Figure 21:** ^{31}P NMR of **2ag**



531

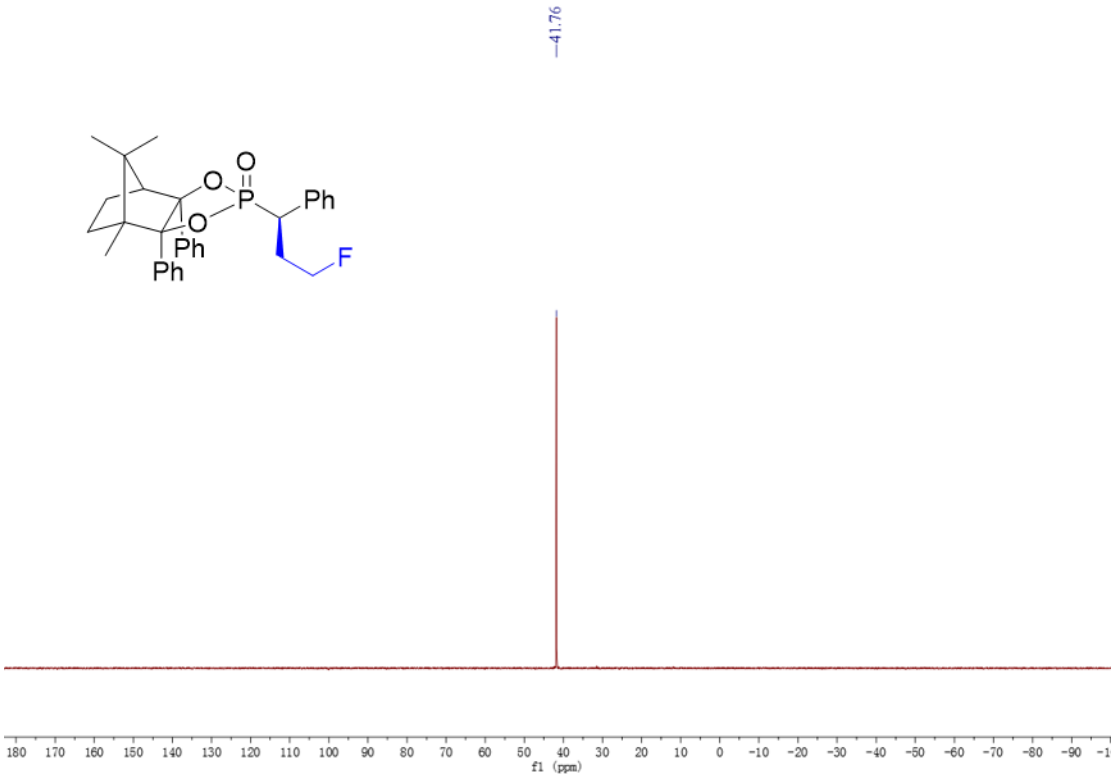
532 **Figure 22:** ^{1}H NMR of **2ah**

533



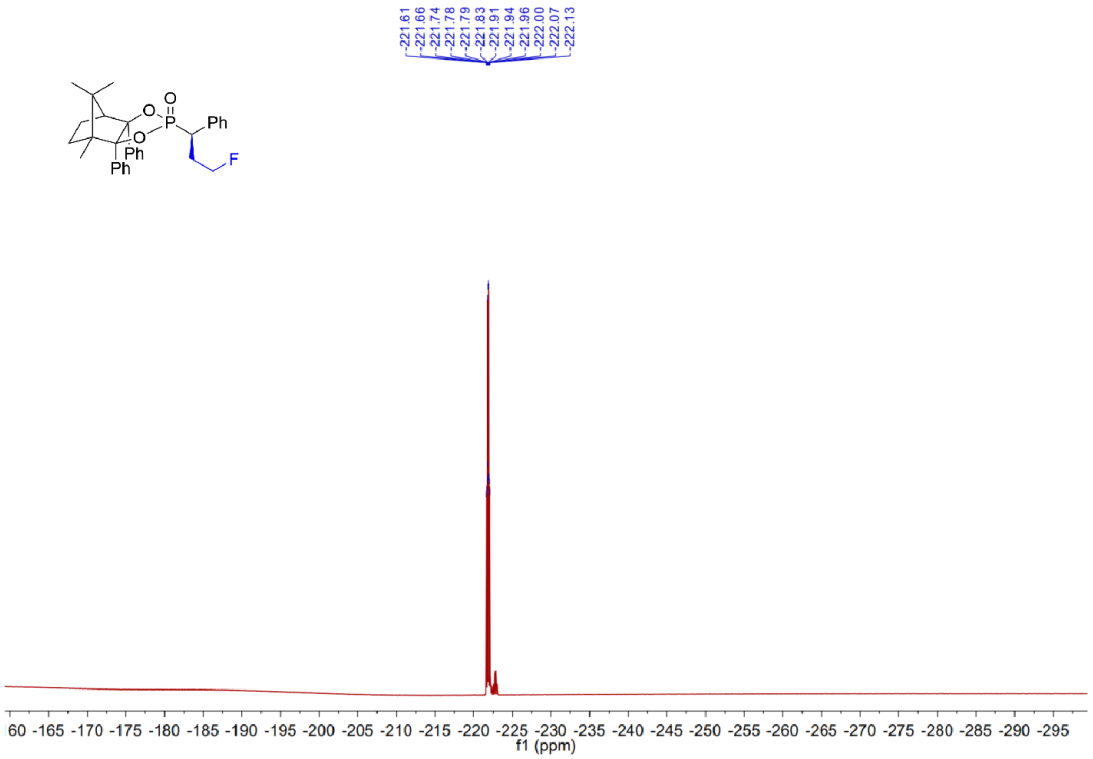
534
535

536 **Figure 23:** ^{13}C NMR of **2ah**



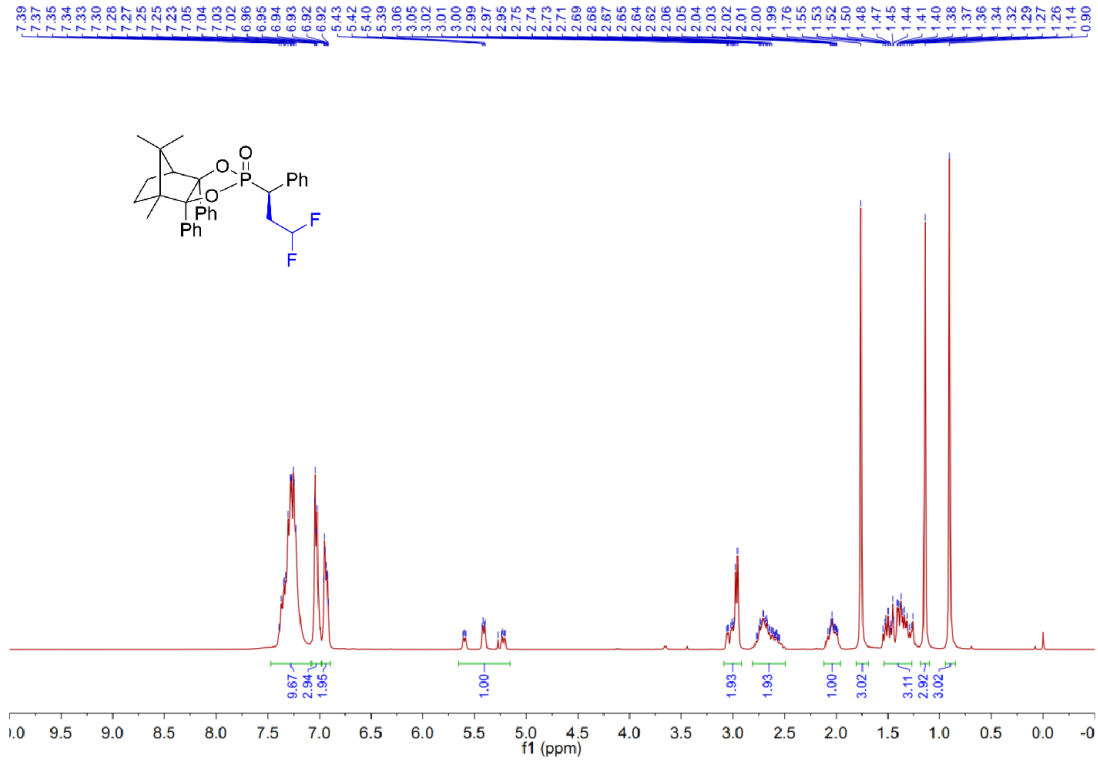
537

538 **Figure 24:** ^{31}P NMR of **2ah**



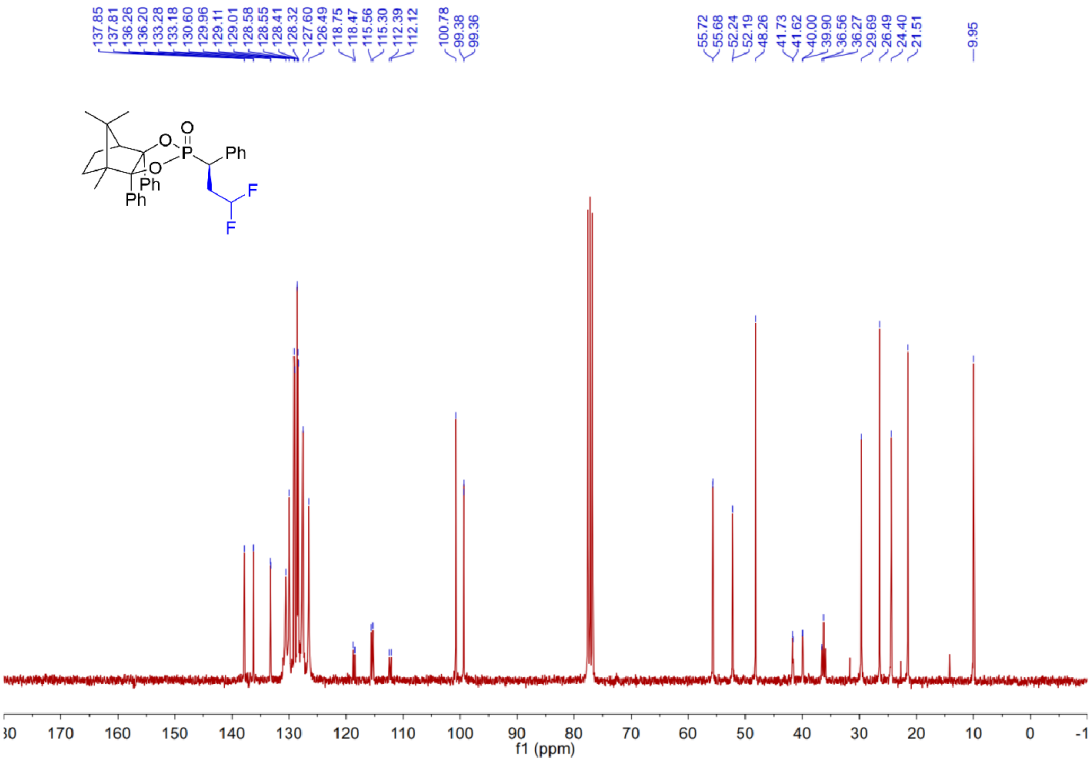
539

540 **Figure 25:** ^{19F} NMR of **2ah**



541

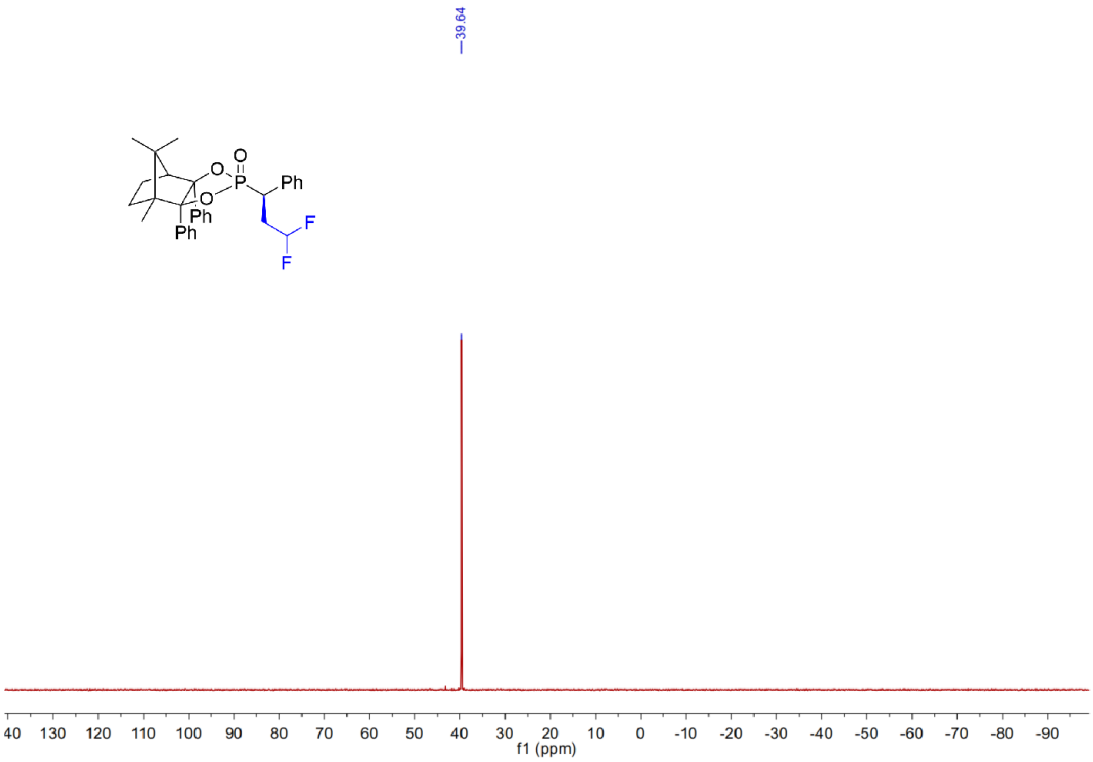
542 **Figure 26:** ^{1}H NMR of **2ai**



543

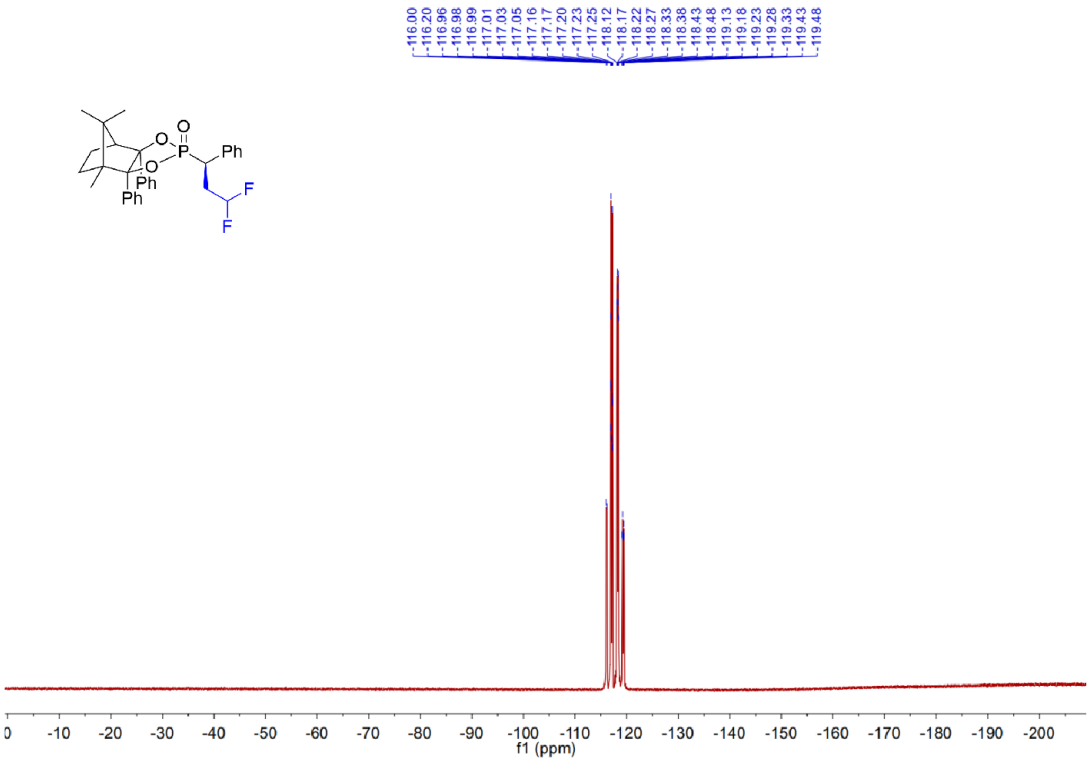
544 **Figure 27:** ^{13}C NMR of **2ai**

545



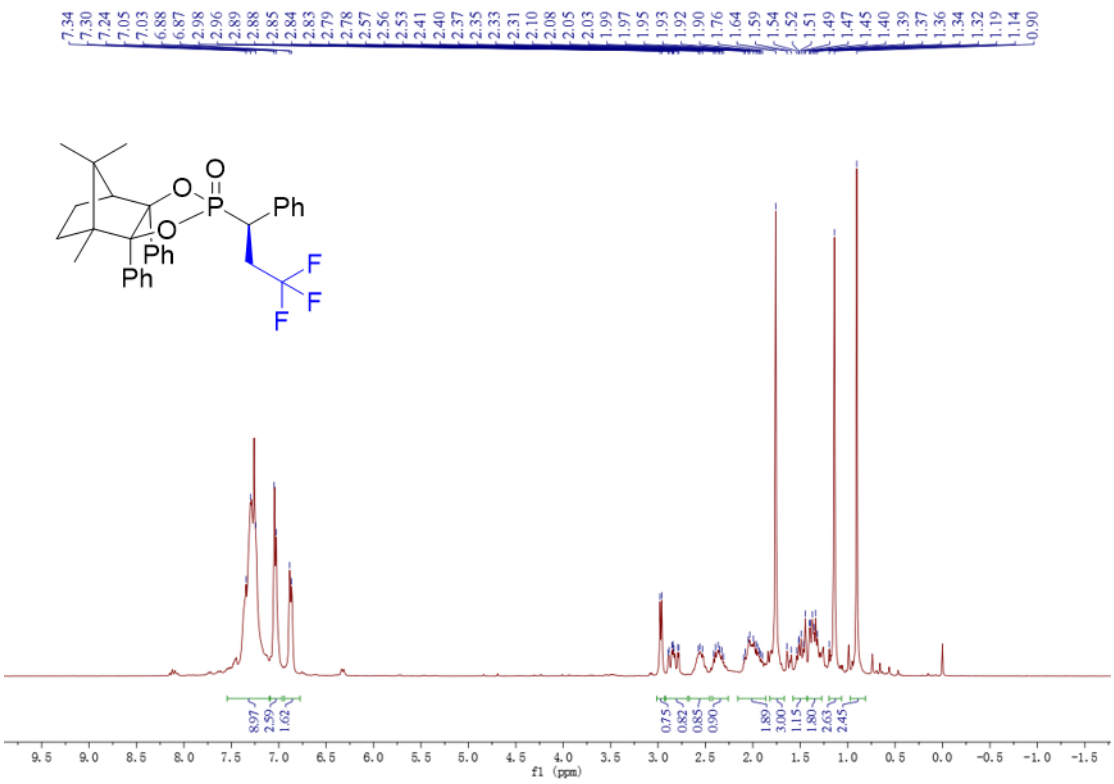
546

547 **Figure 28:** ^{31}P NMR of **2ai**



548

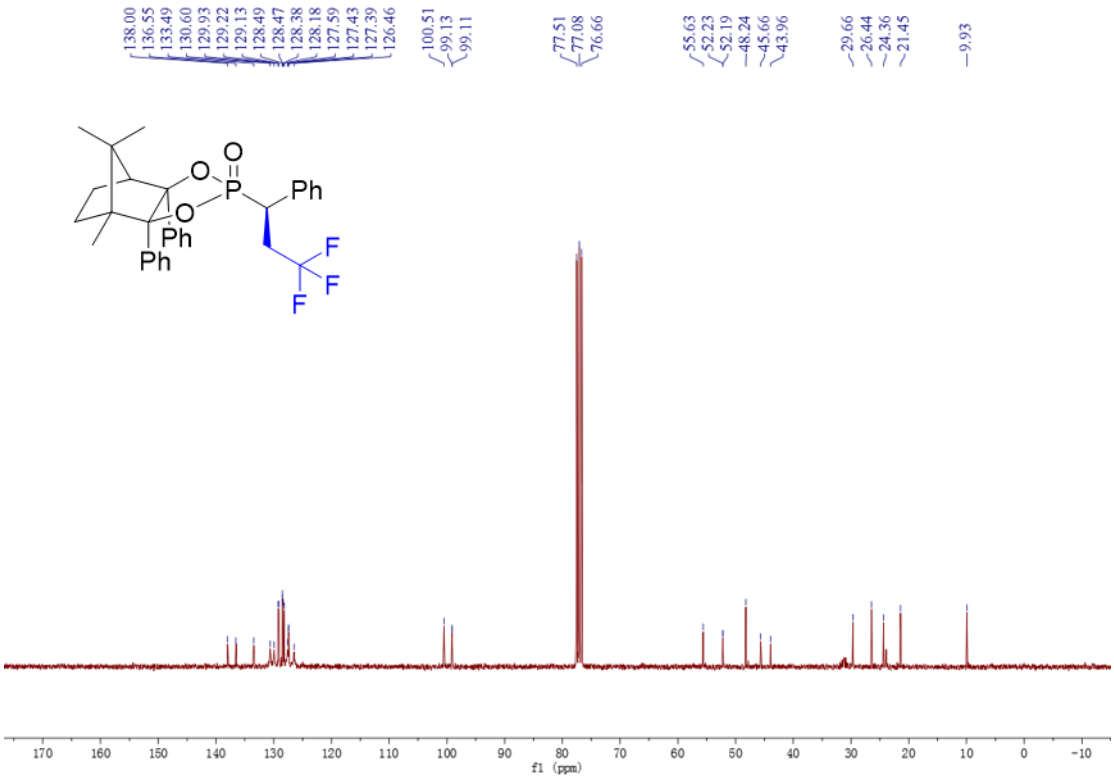
549 **Figure 29:** ^{19}F NMR of **2ai**



550

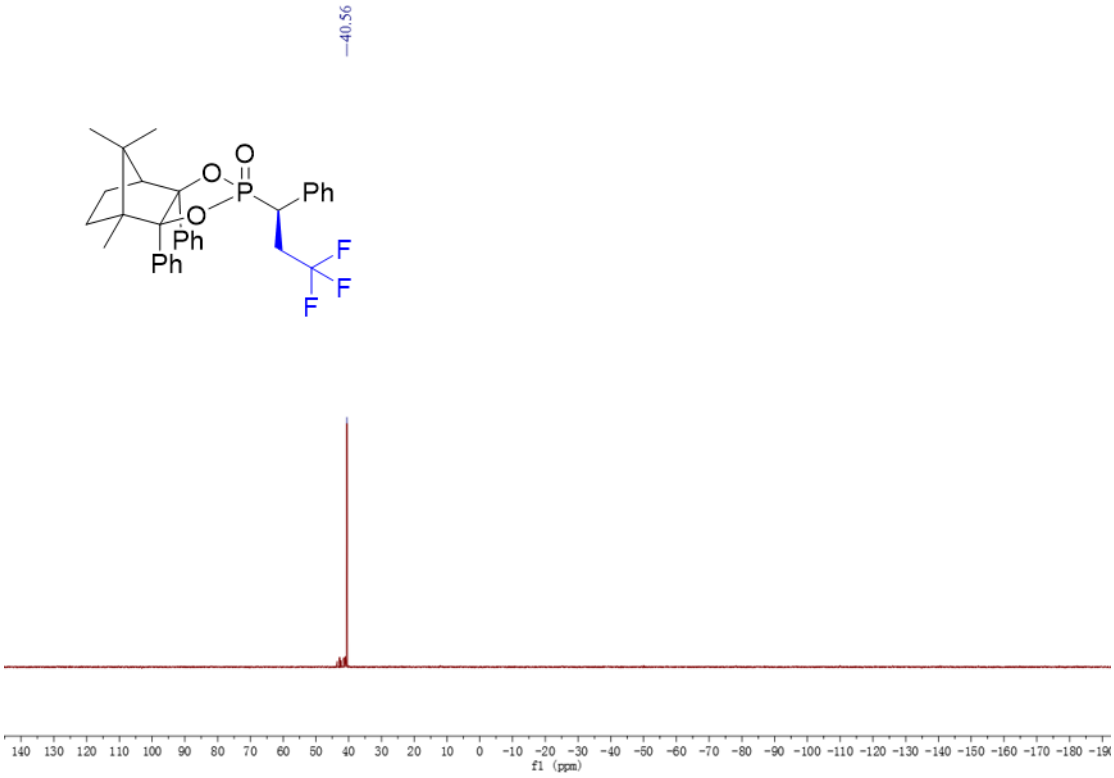
551 **Figure 30:** ^{1}H NMR of **2aj**

552



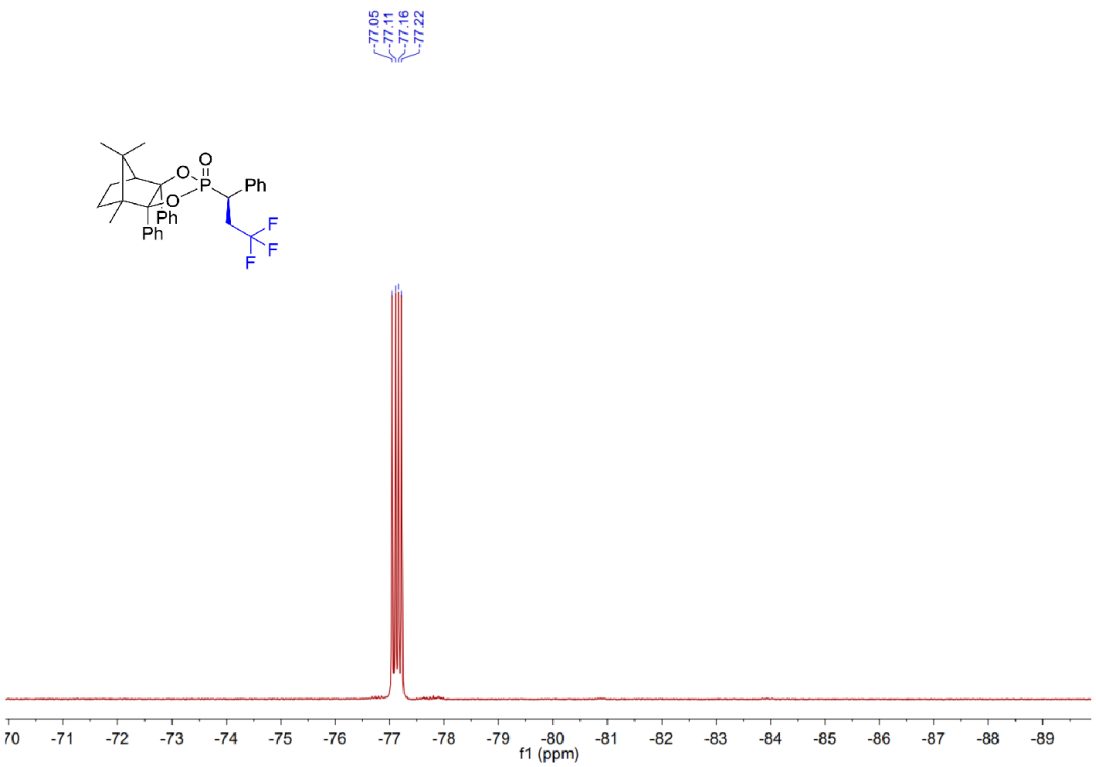
553

554 **Figure 31:** ^{13}C NMR of **2aj**



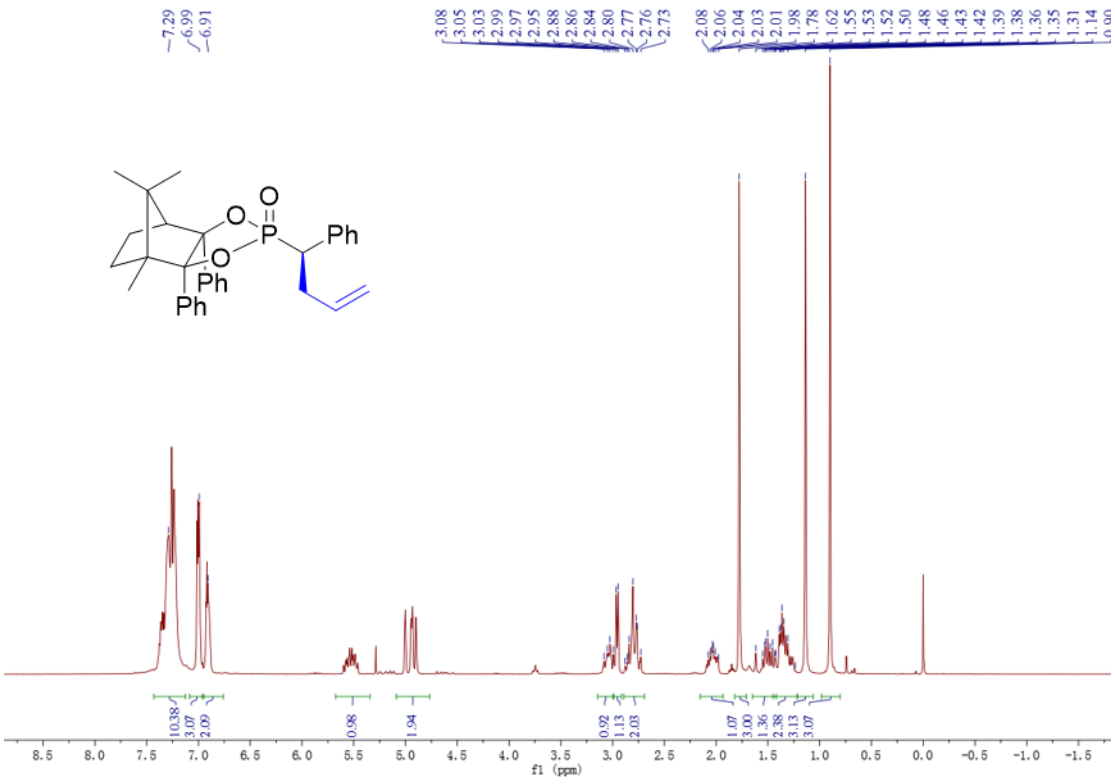
555

556 **Figure 32:** ^{31}P NMR of **2aj**



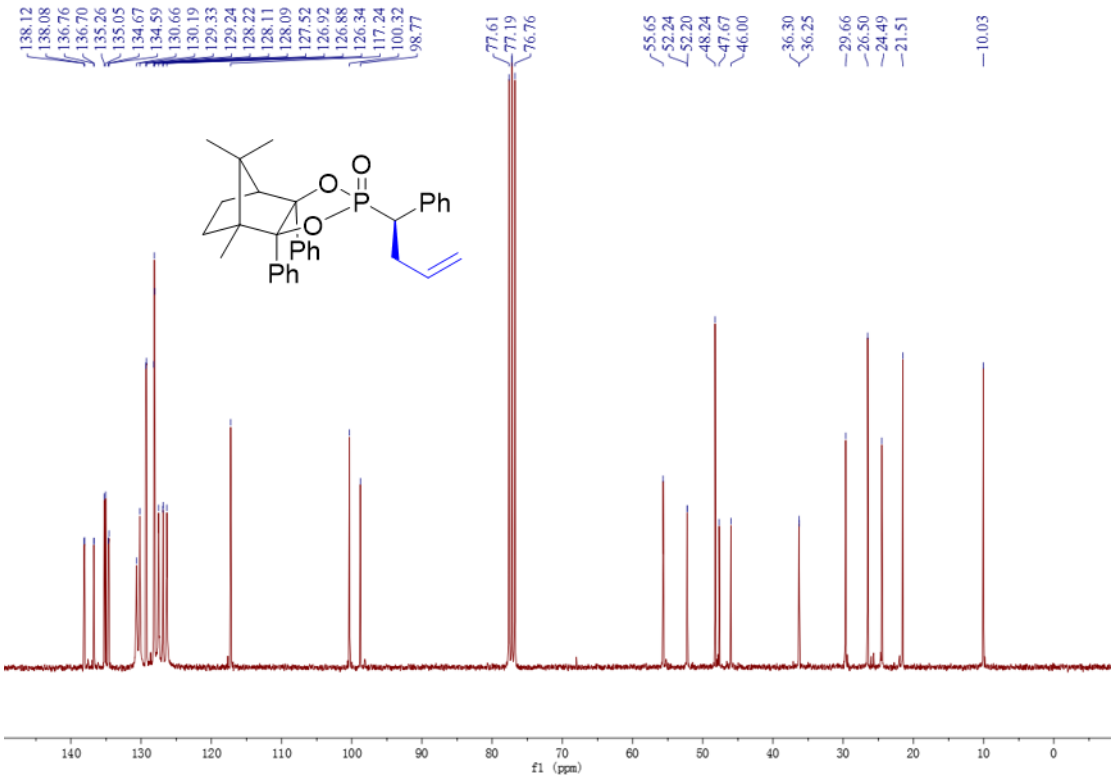
557

558 **Figure 33:** ^{19}F NMR of **2aj**



559

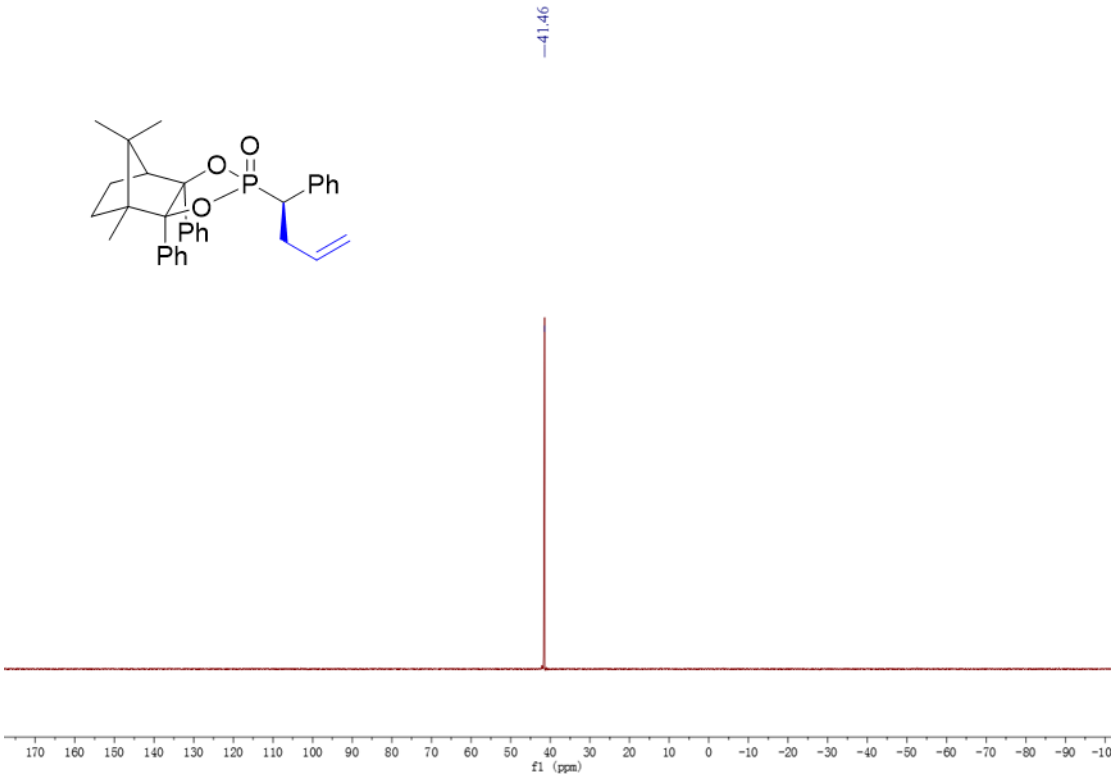
560 **Figure 34:** ^{1}H NMR of **2ak**



561

562 **Figure 35:** ^{13}C NMR of **2ak**

563



564

565 **Figure 36:** ^{31}P NMR of **2ak**

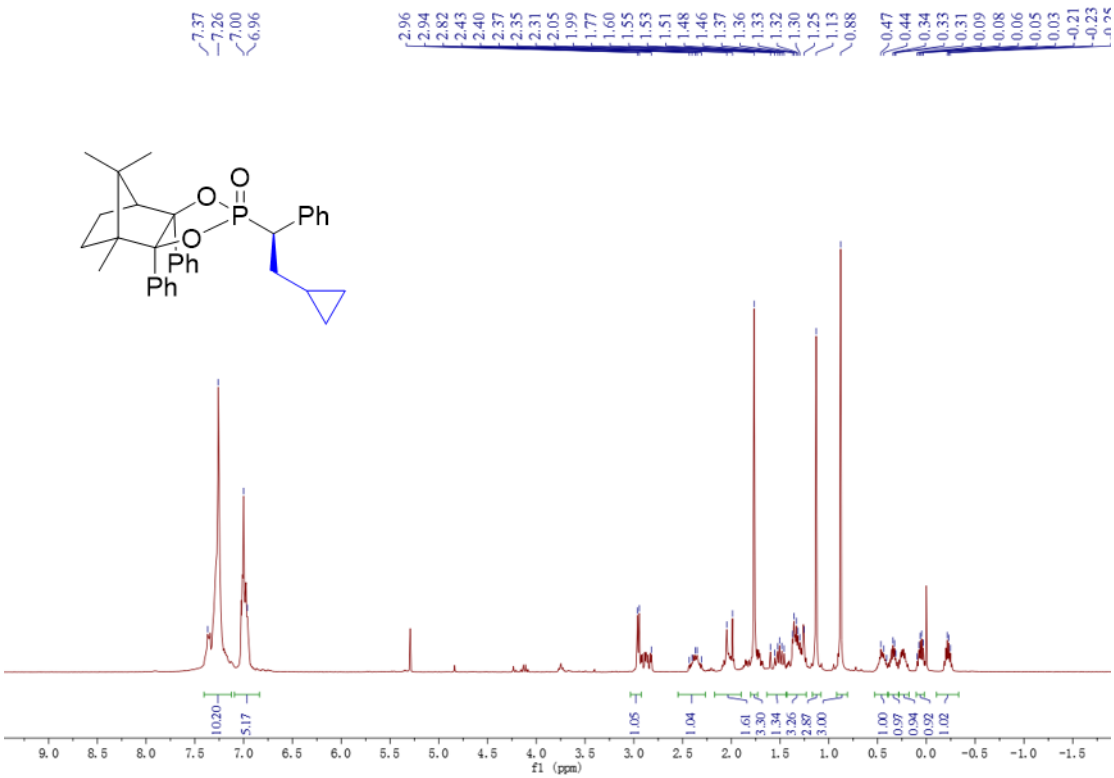


Figure 37: ^{1}H NMR of **2al**

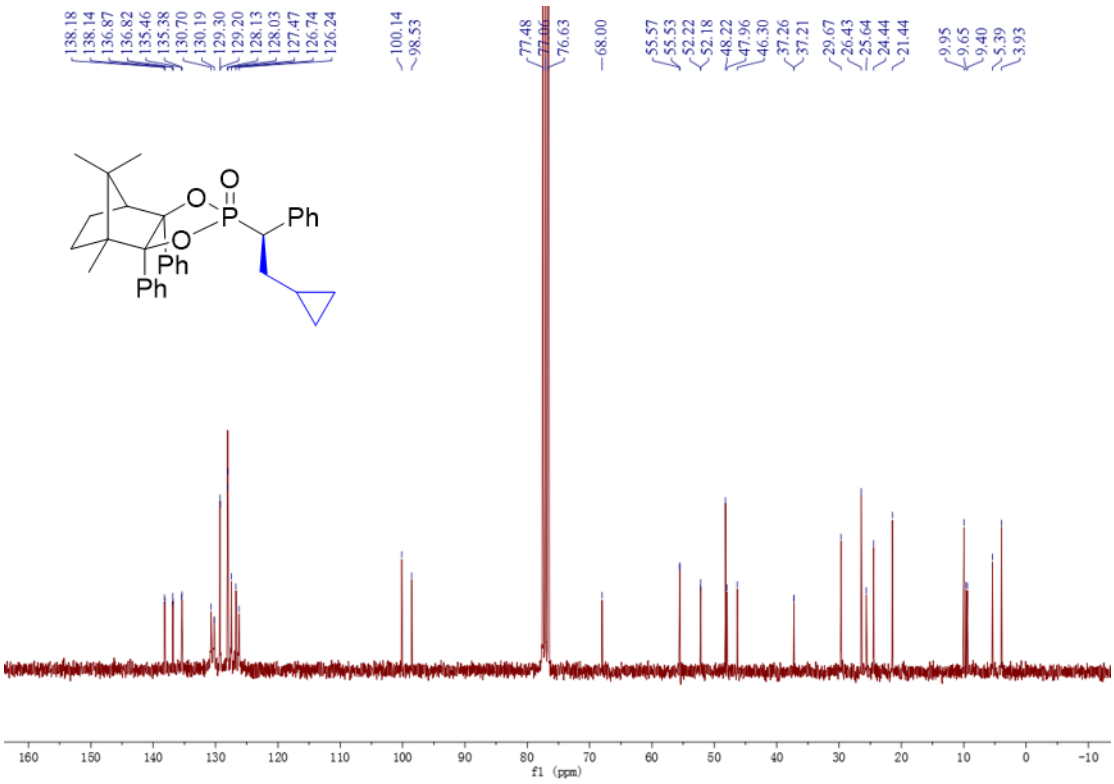
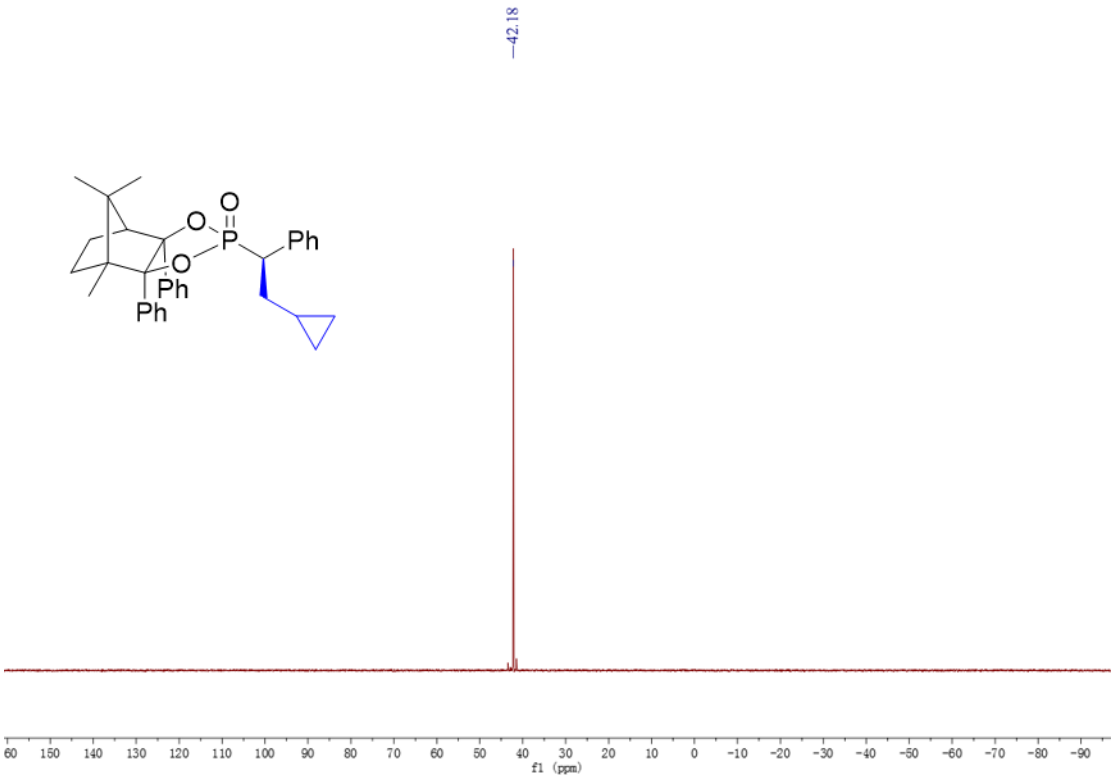
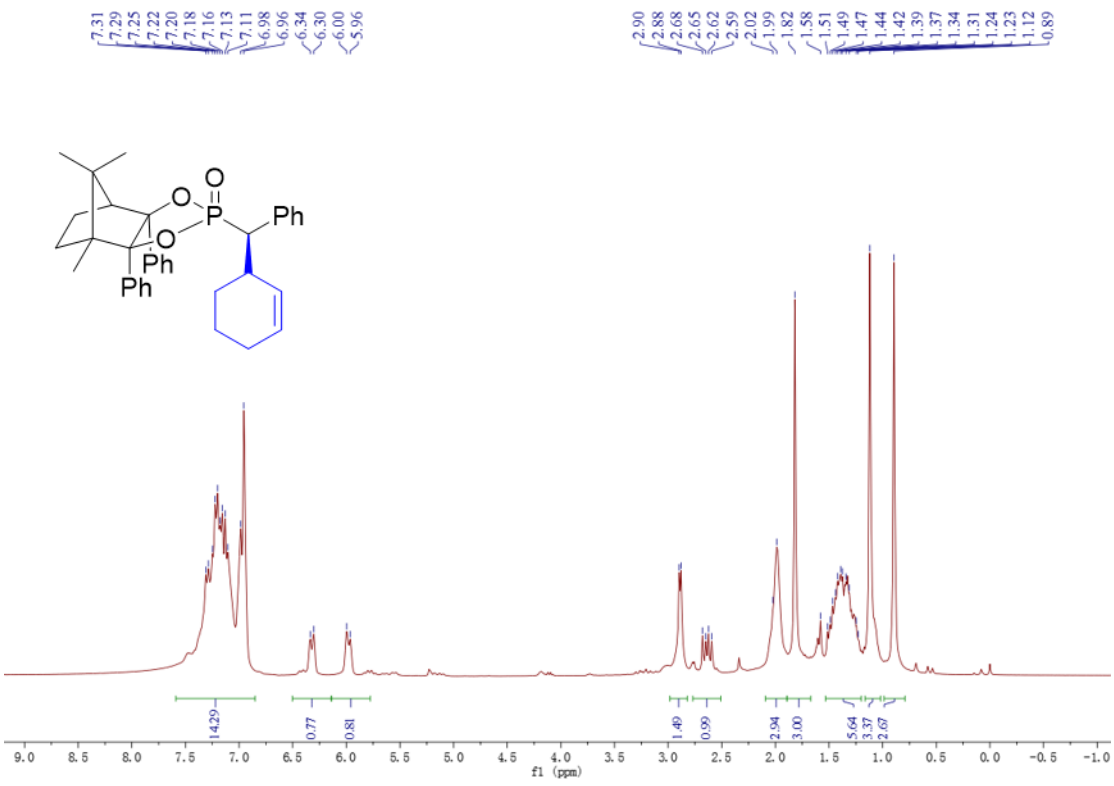


Figure 38: ^{13}C NMR of **2al**



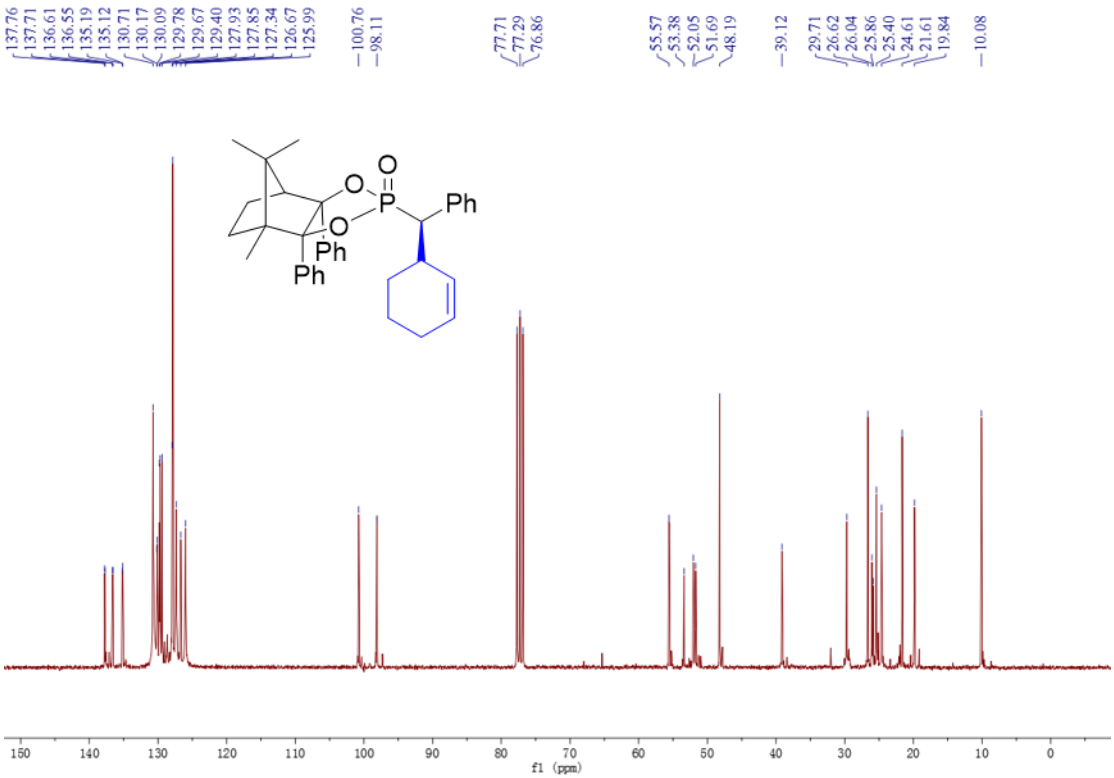
571

572 **Figure 39:** ^{31}P NMR of **2al**



573

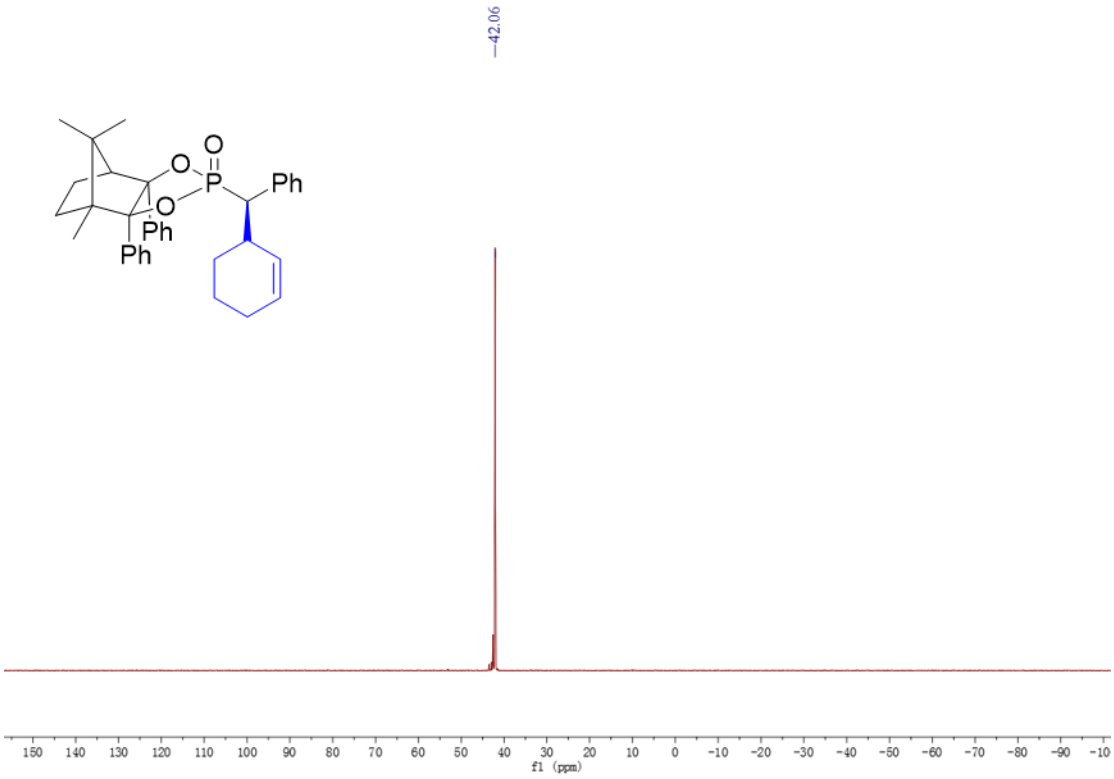
574 **Figure 40:** ^{1}H NMR of **2am**



575

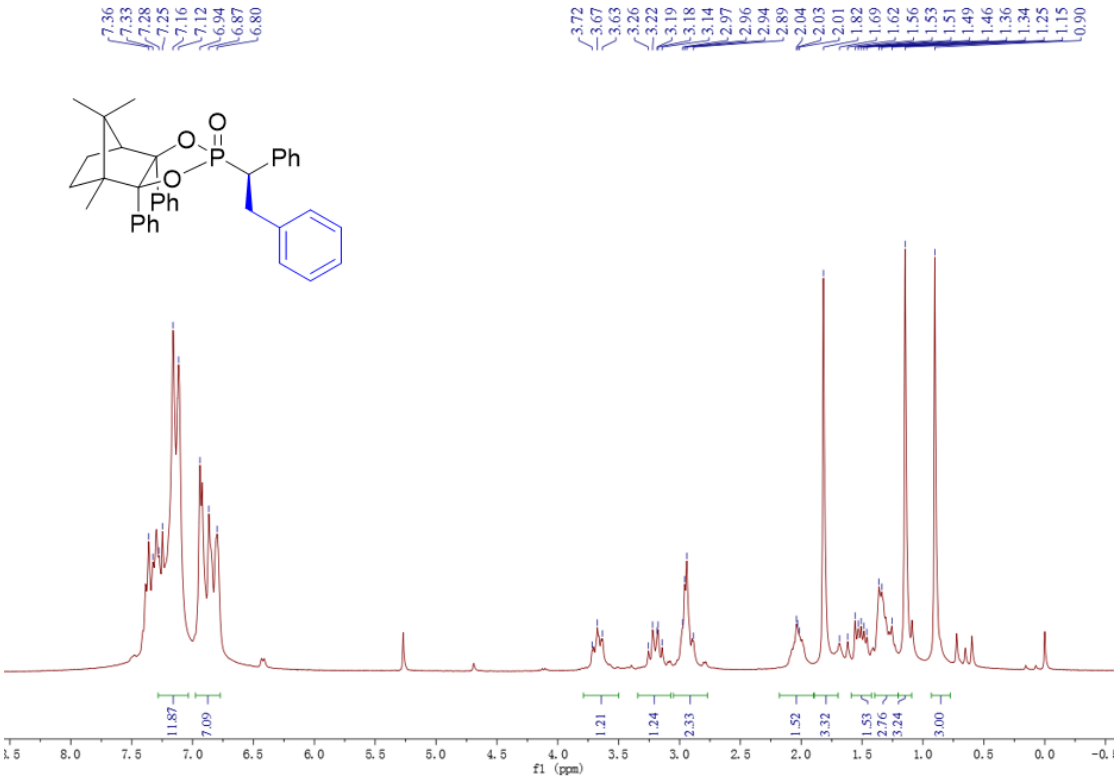
576 **Figure 41:** ^{13}C NMR of **2am**

577



578

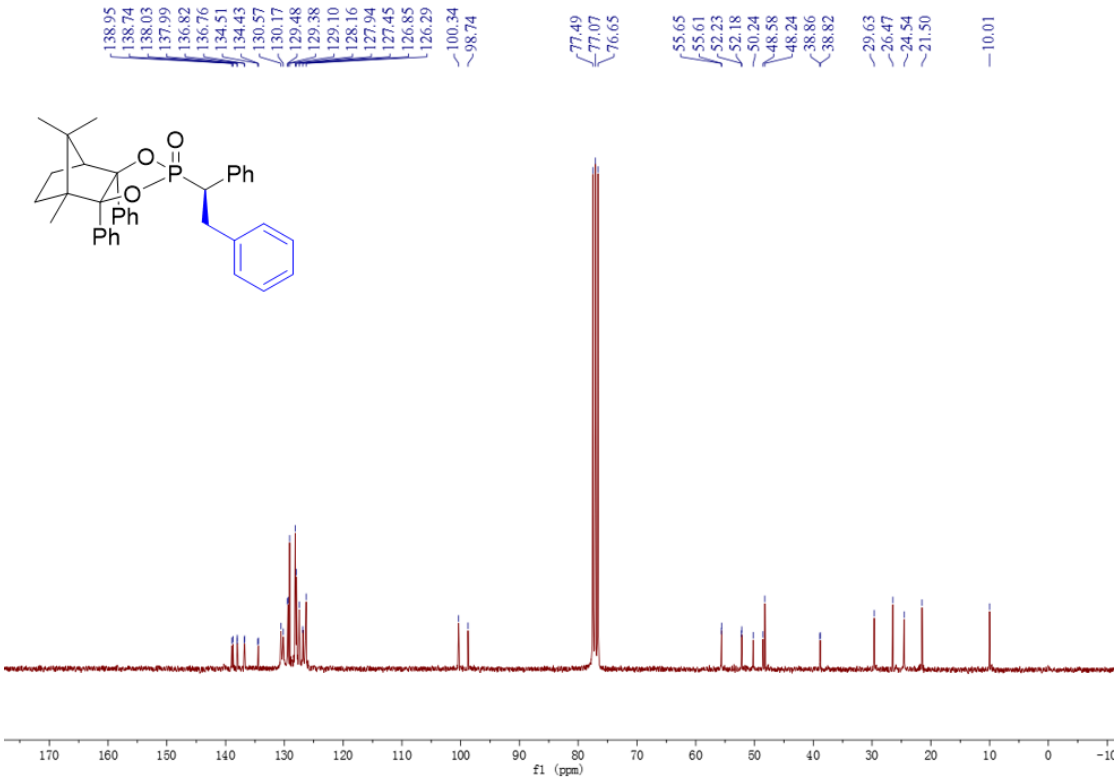
579 **Figure 42:** ^{31}P NMR of **2am**



580

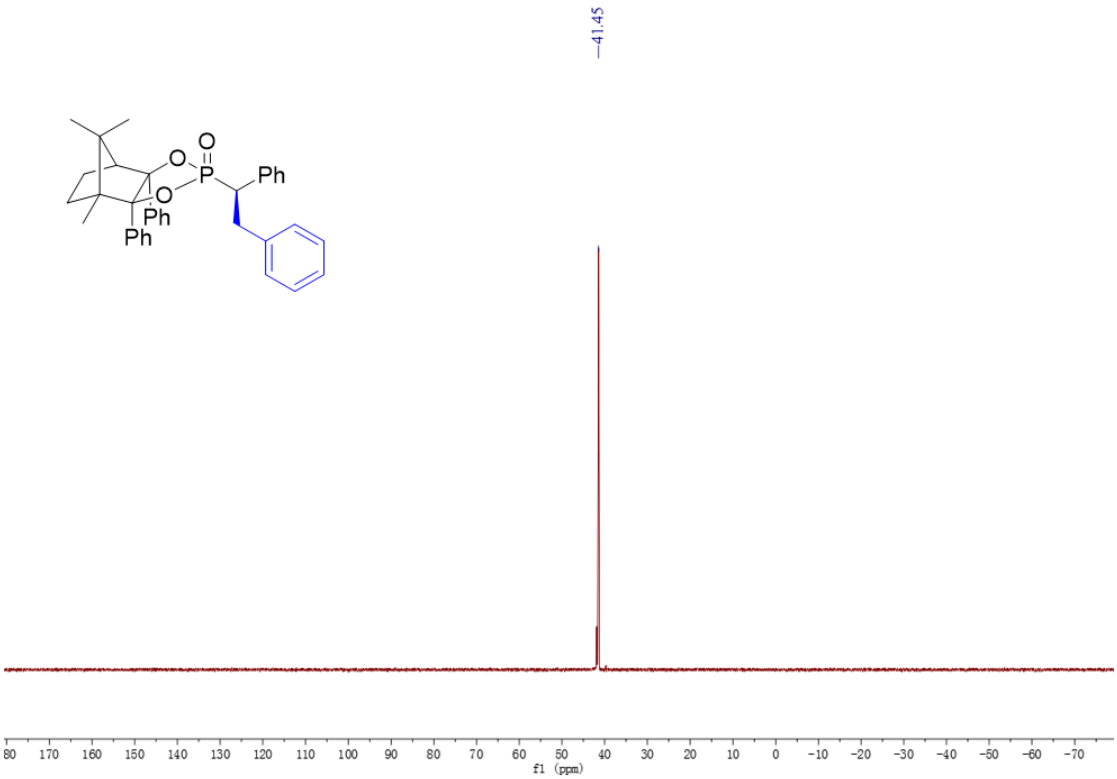
581 **Figure 43:** ^{1}H NMR of **2an**

582



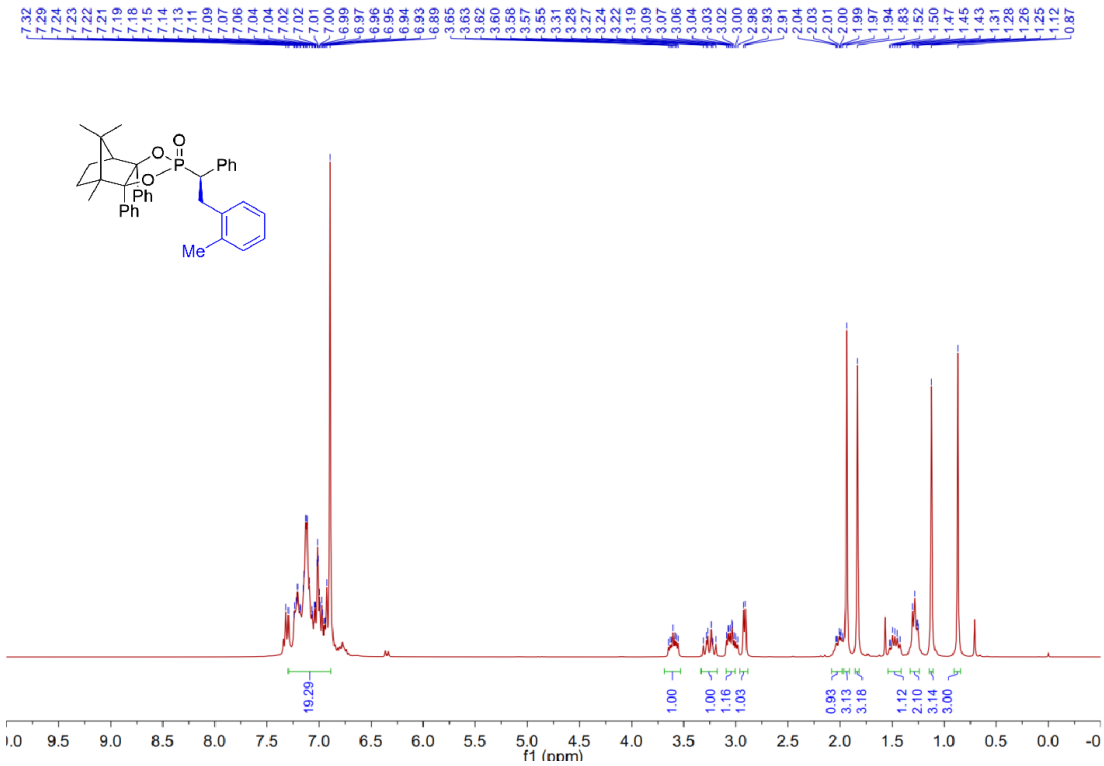
583

584 **Figure 44:** ^{13}C NMR of **2an**



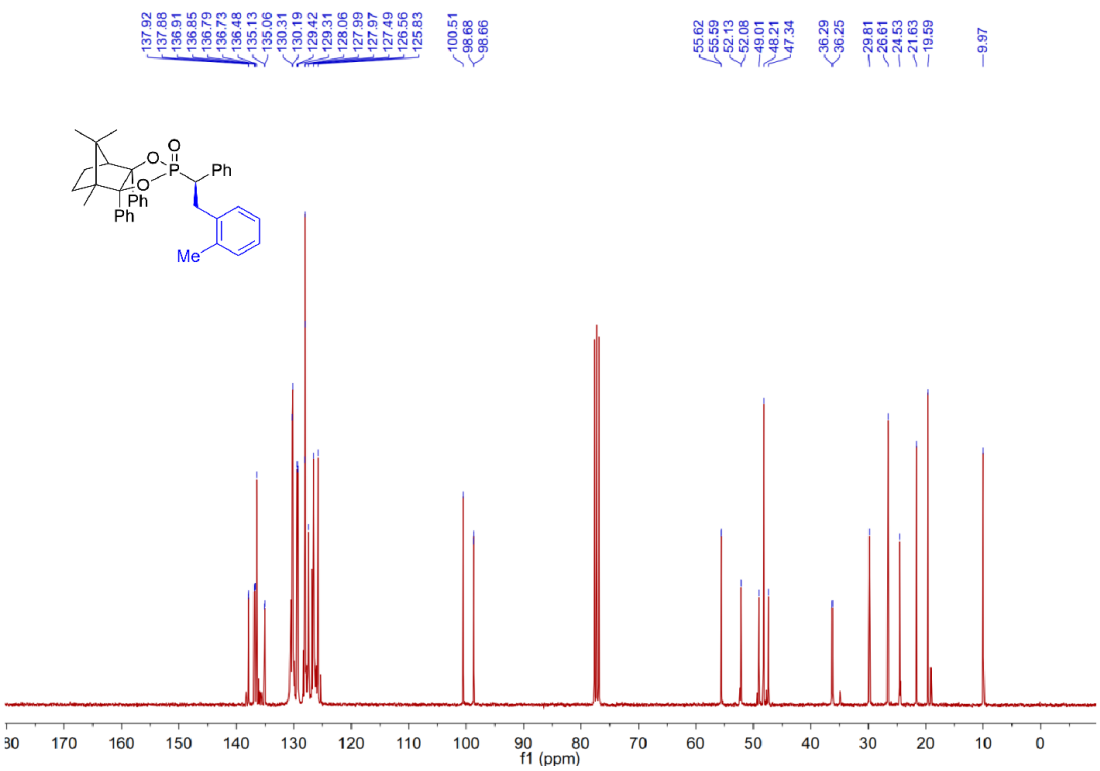
585

586 **Figure 45:** ^{31}P NMR of **2an**



587

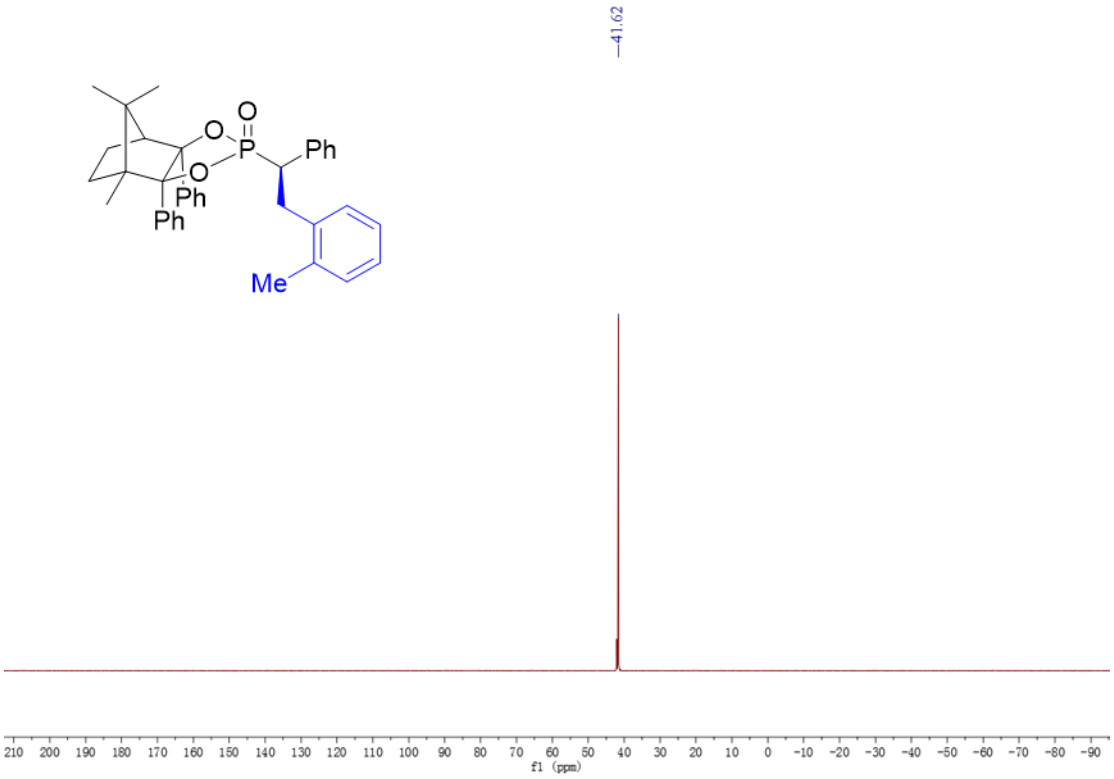
588 **Figure 46:** ^{1}H NMR of **2ao**



589

590 **Figure 47:** ^{13}C NMR of **2ao**

591



592

593 **Figure 48:** ^{31}P NMR of **2ao**

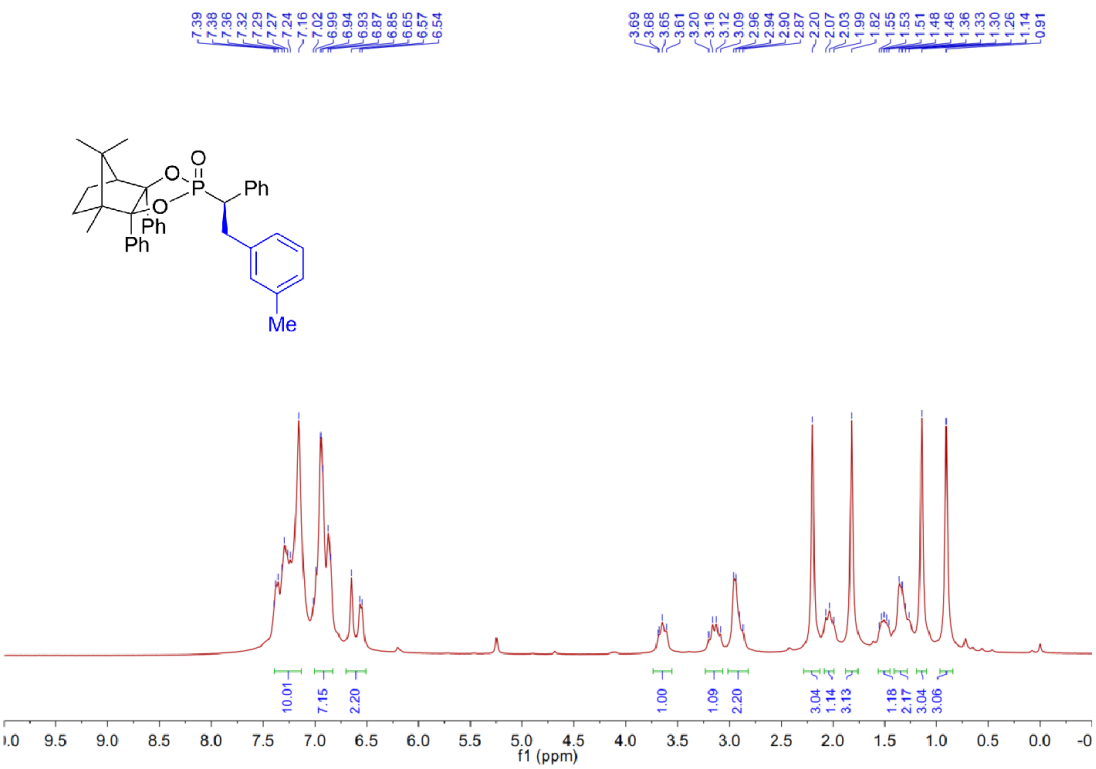


Figure 49: ^{1}H NMR of **2ap**

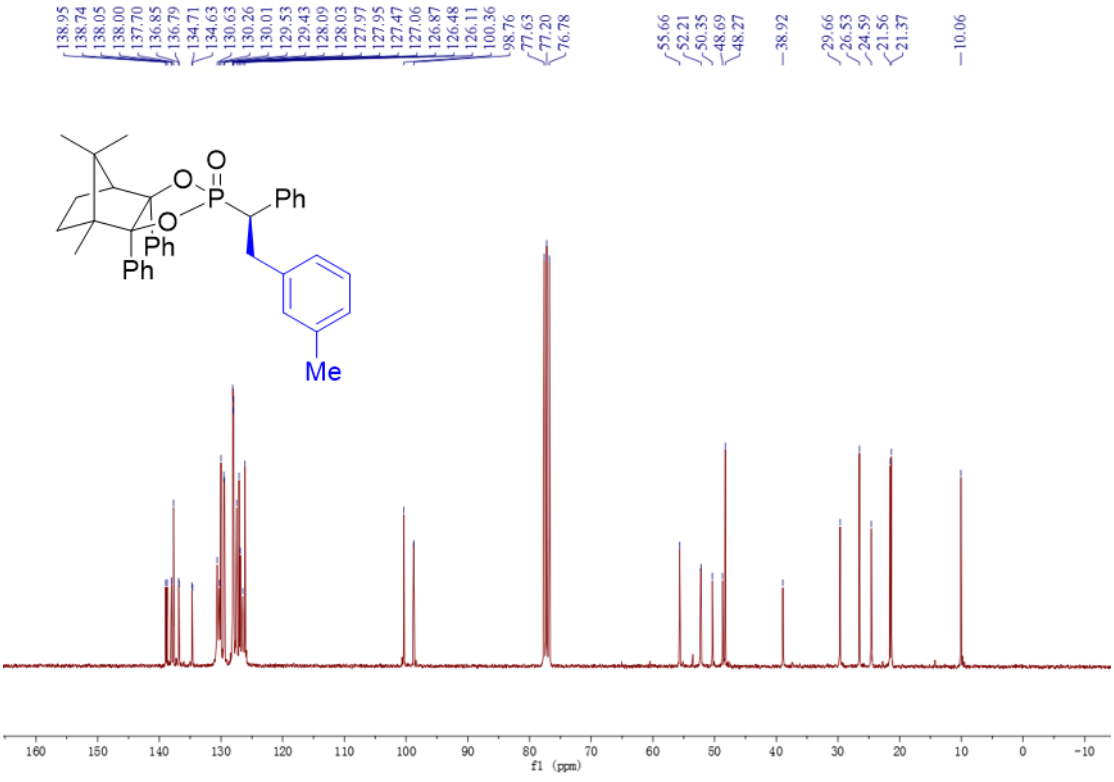
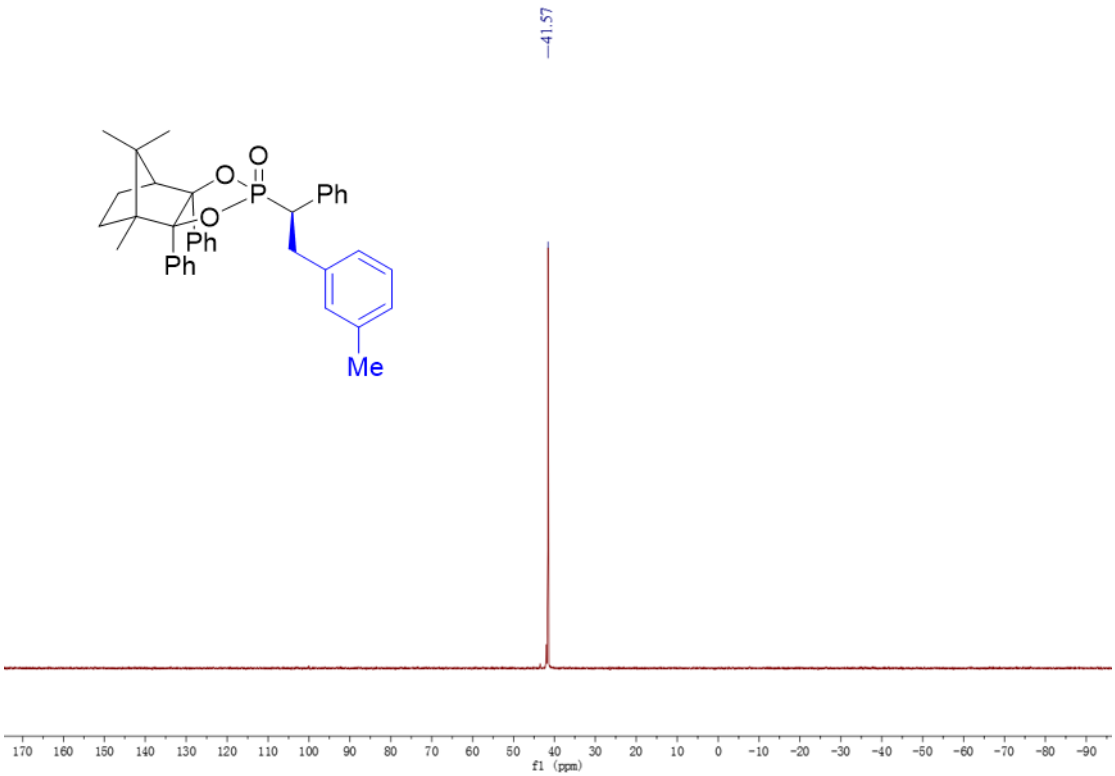
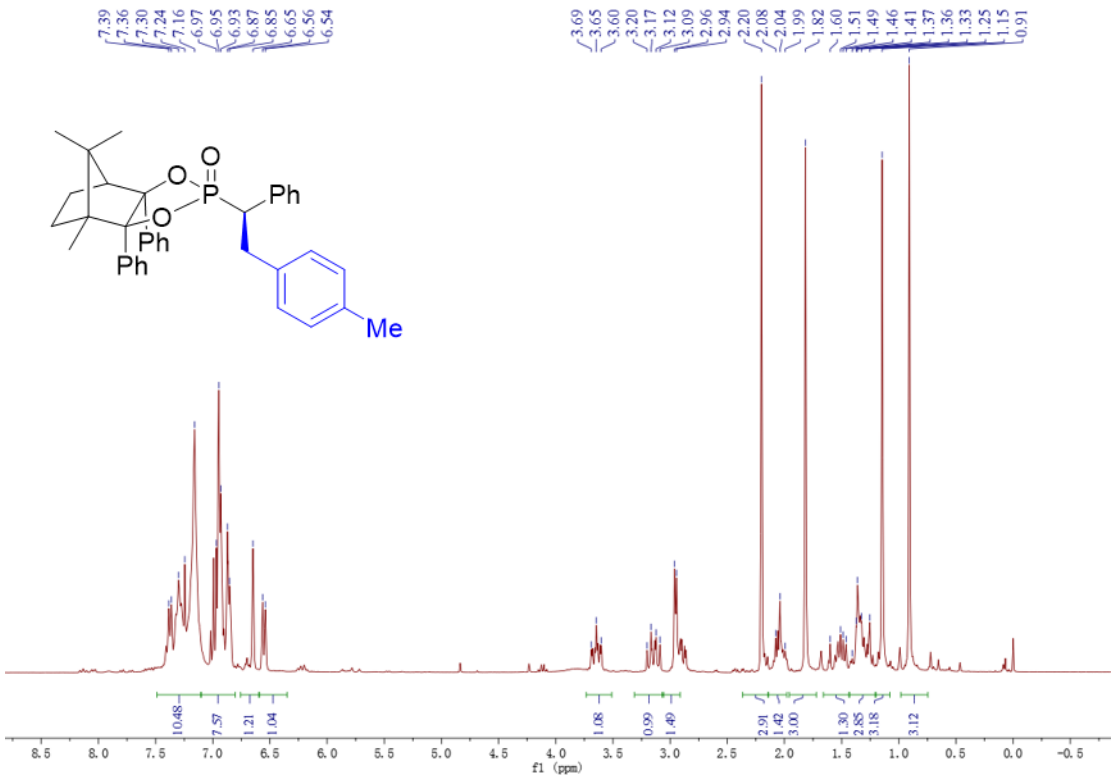


Figure 50: ^{13}C NMR of **2ap**



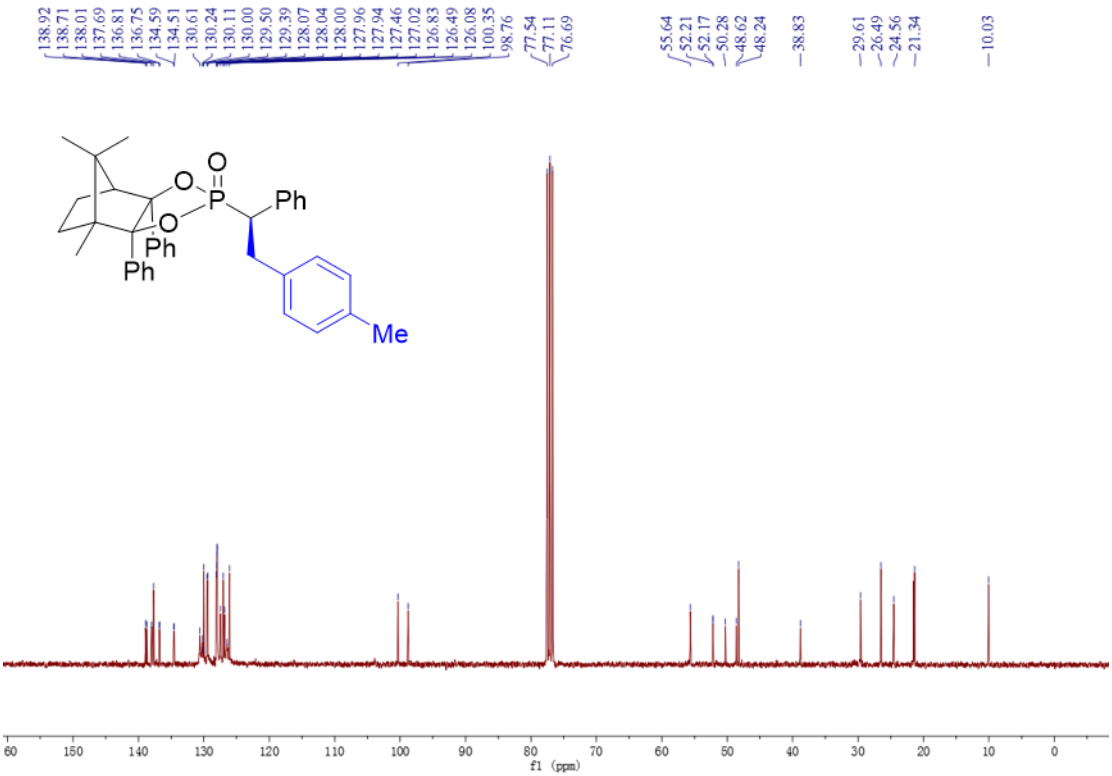
600

601 **Figure 51:** ^{31}P NMR of **2ap**



602

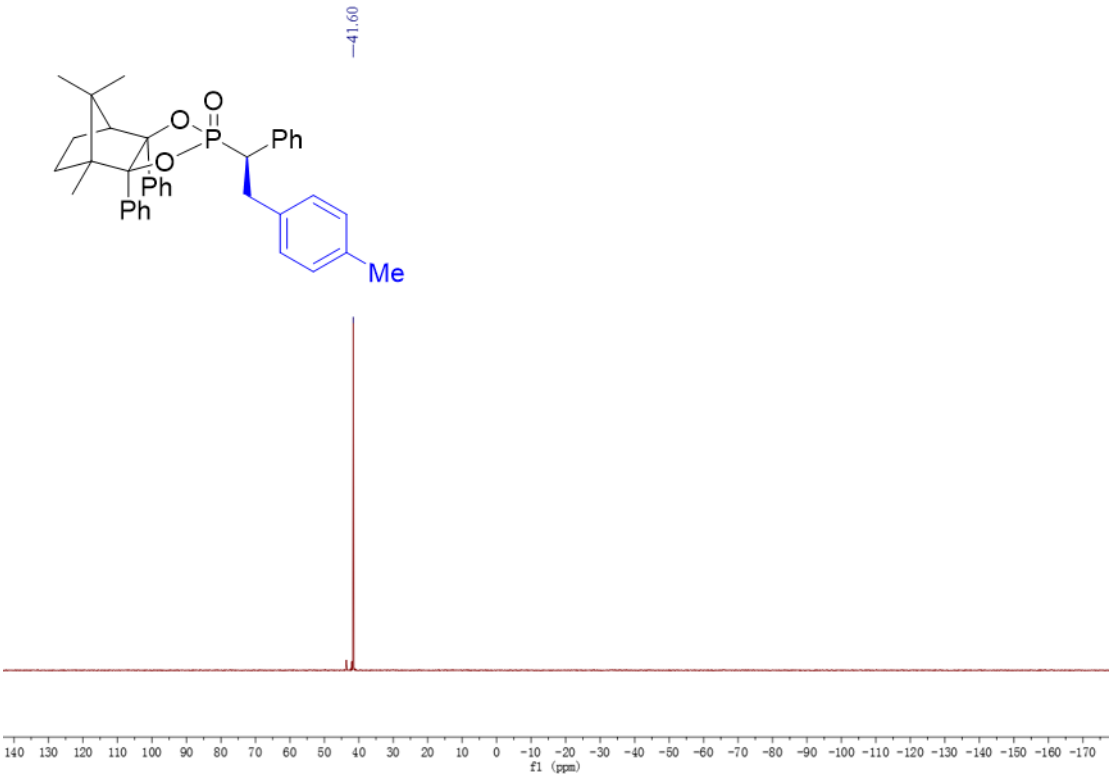
603 **Figure 52**: ^{1}H NMR of **2ar**



604

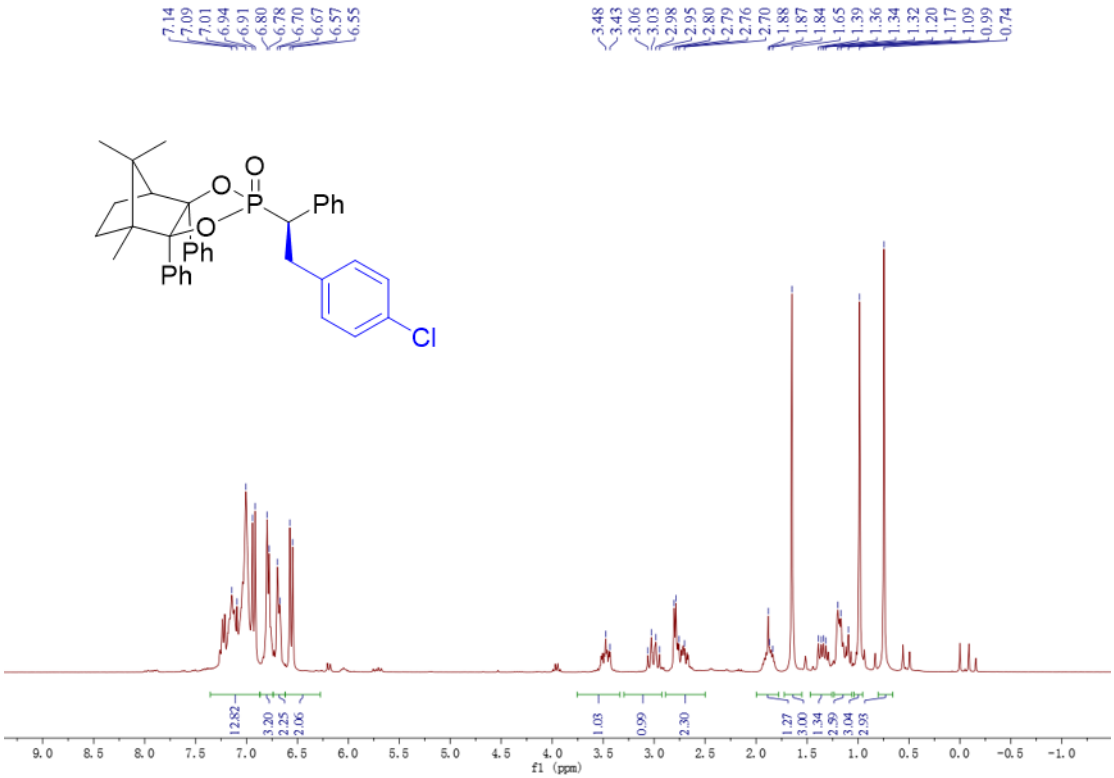
605 **Figure 53:** ^{13}C NMR of **2ar**

606



607

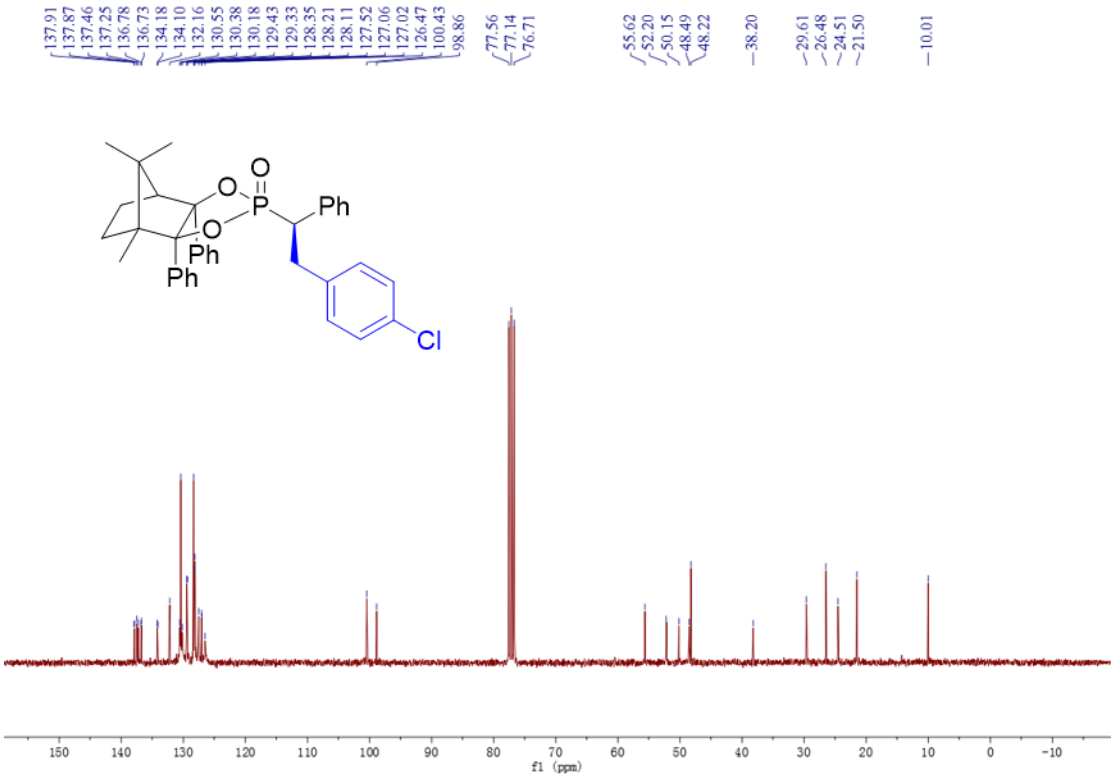
608 **Figure 54:** ^{31}P NMR of **2ar**



609

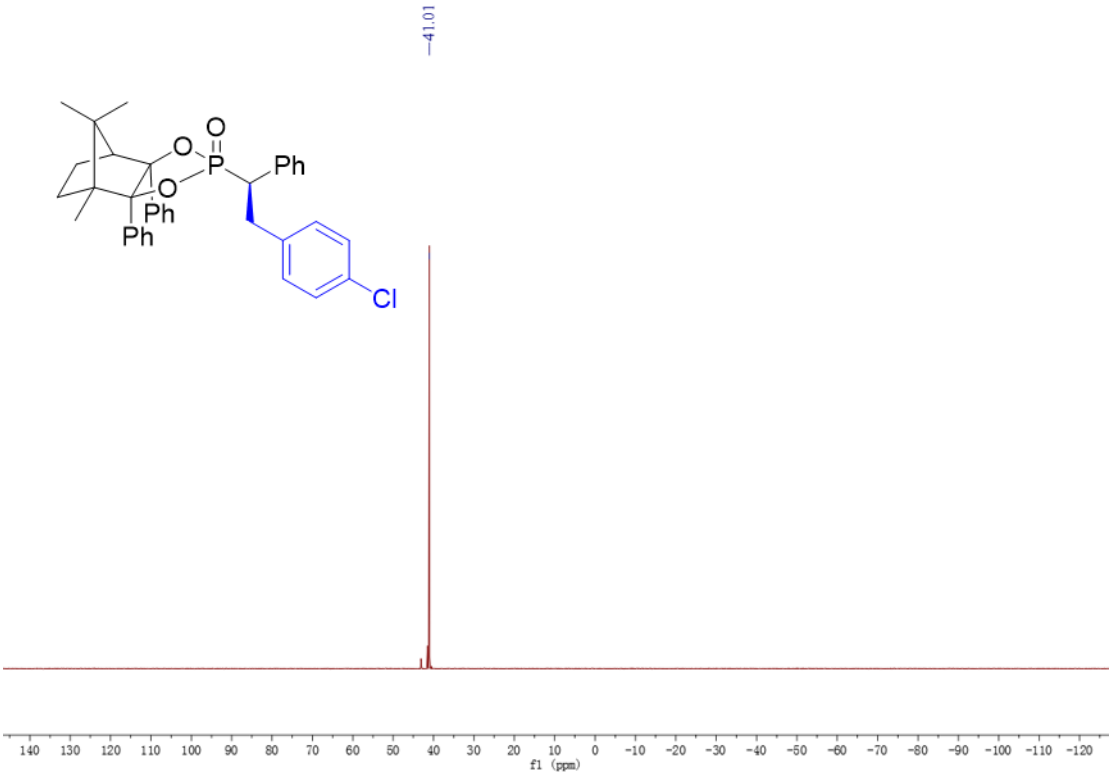
610 **Figure 55:** ^{1}H NMR of **2as**

611



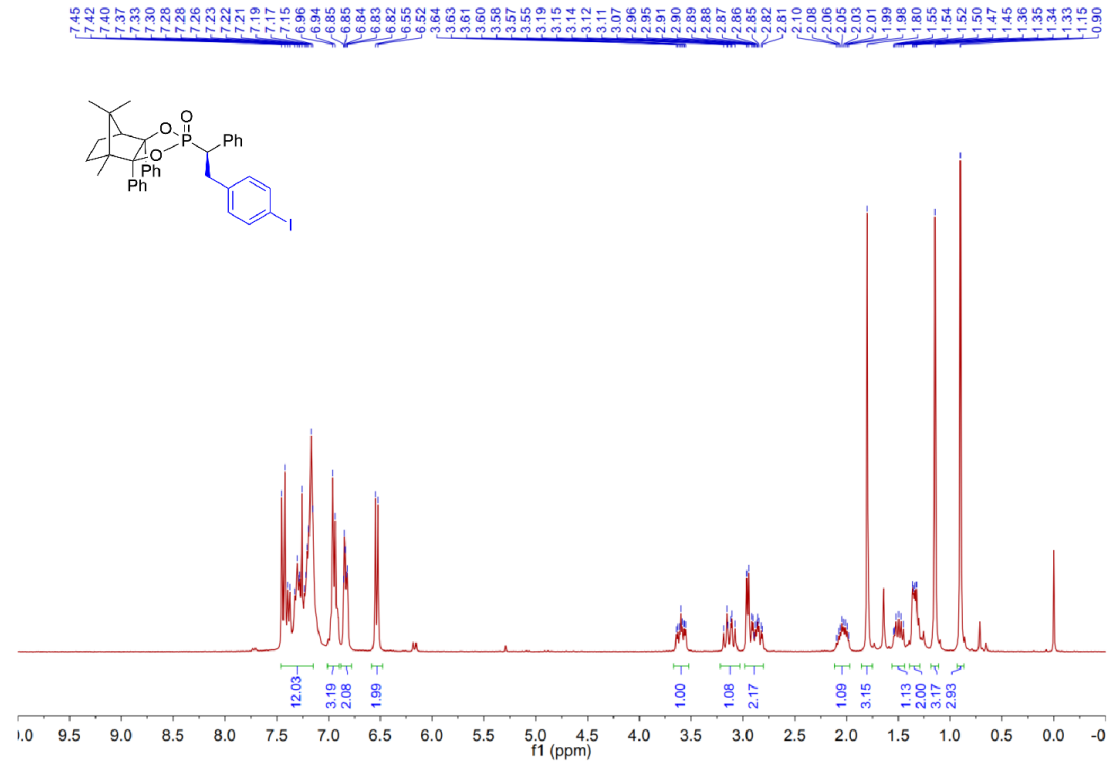
612

613 **Figure 56:** ^{13}C NMR of **2as**



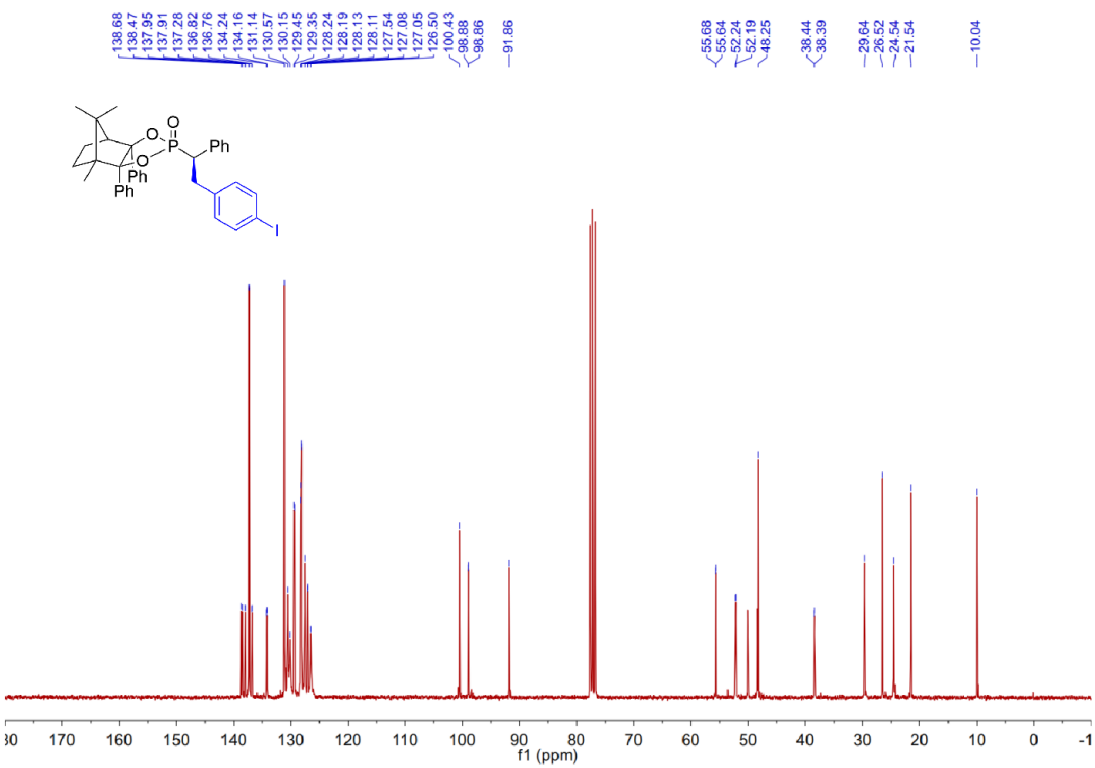
614

615 **Figure 57:** ^{31}P NMR of **2as**



616

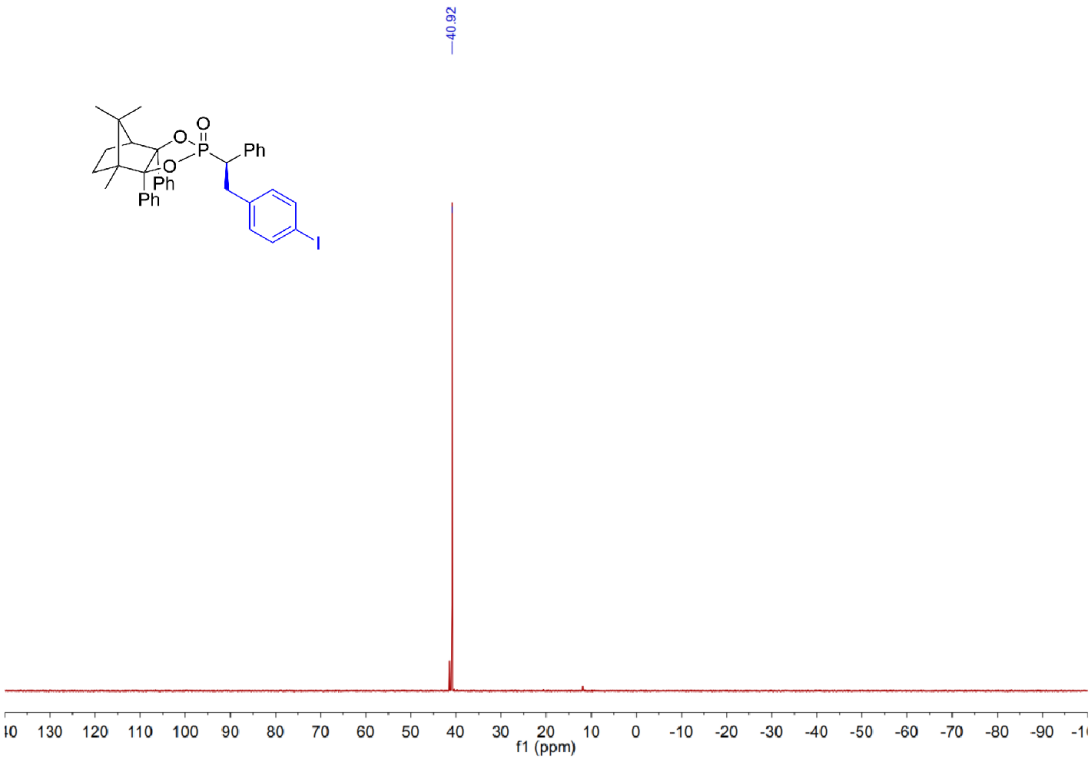
617 **Figure 58:** ^{1}H NMR of **2at**



618

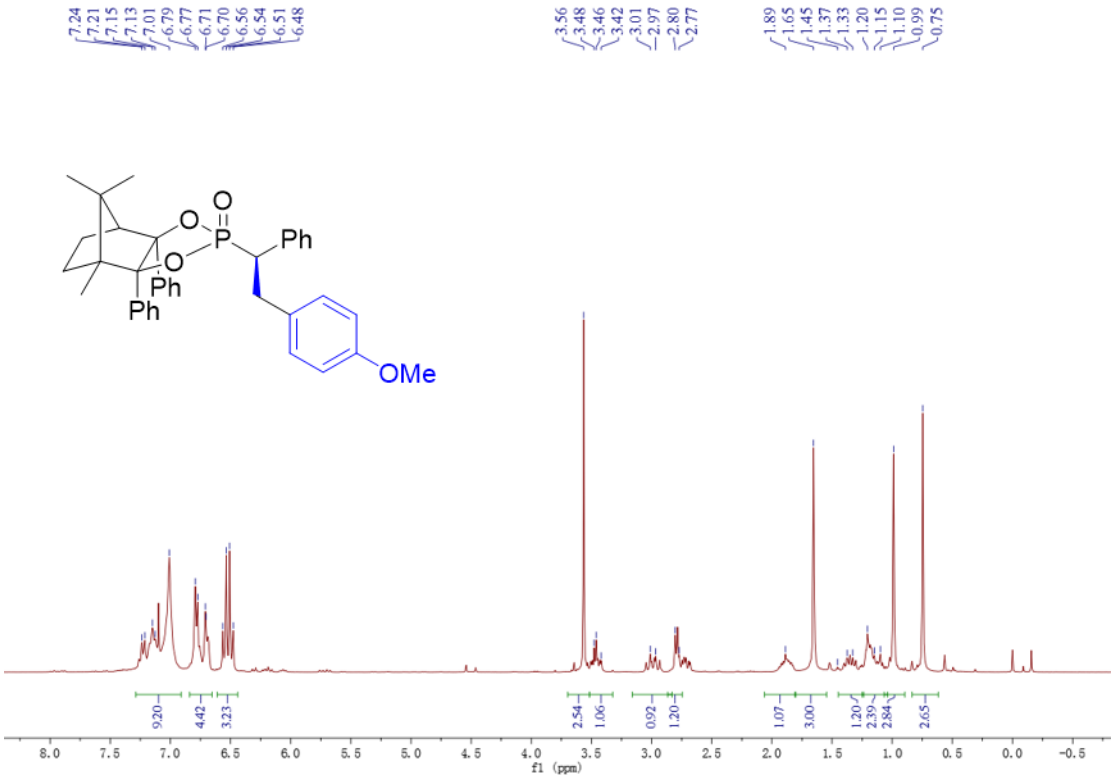
619 **Figure 59:** ^{13}C NMR of **2at**

620



621

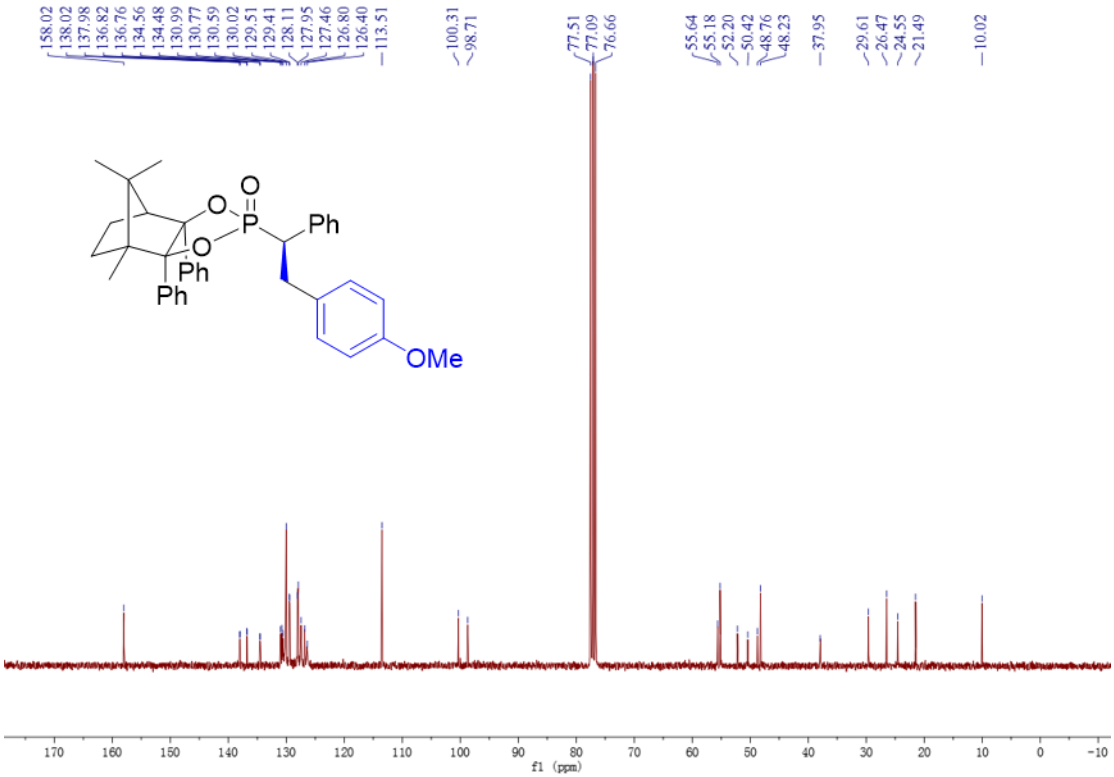
622 **Figure 60:** ^{31}P NMR of **2at**



623

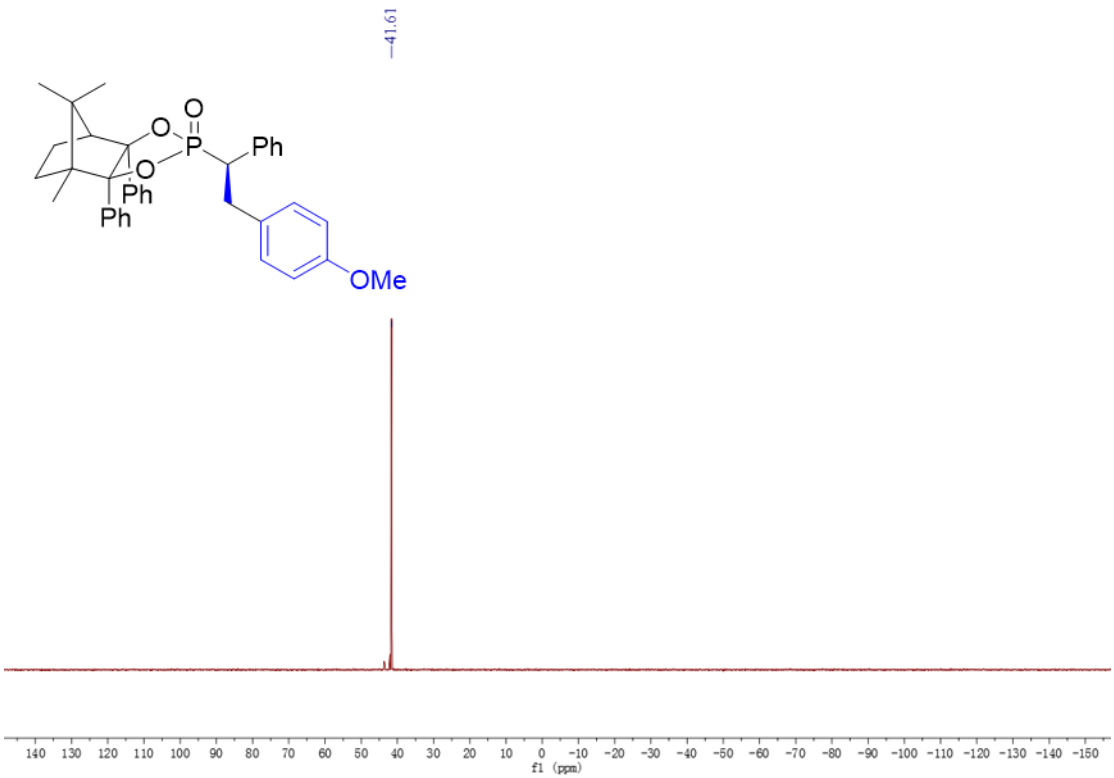
624 **Figure 61:** ^{1}H NMR of **2au**

625



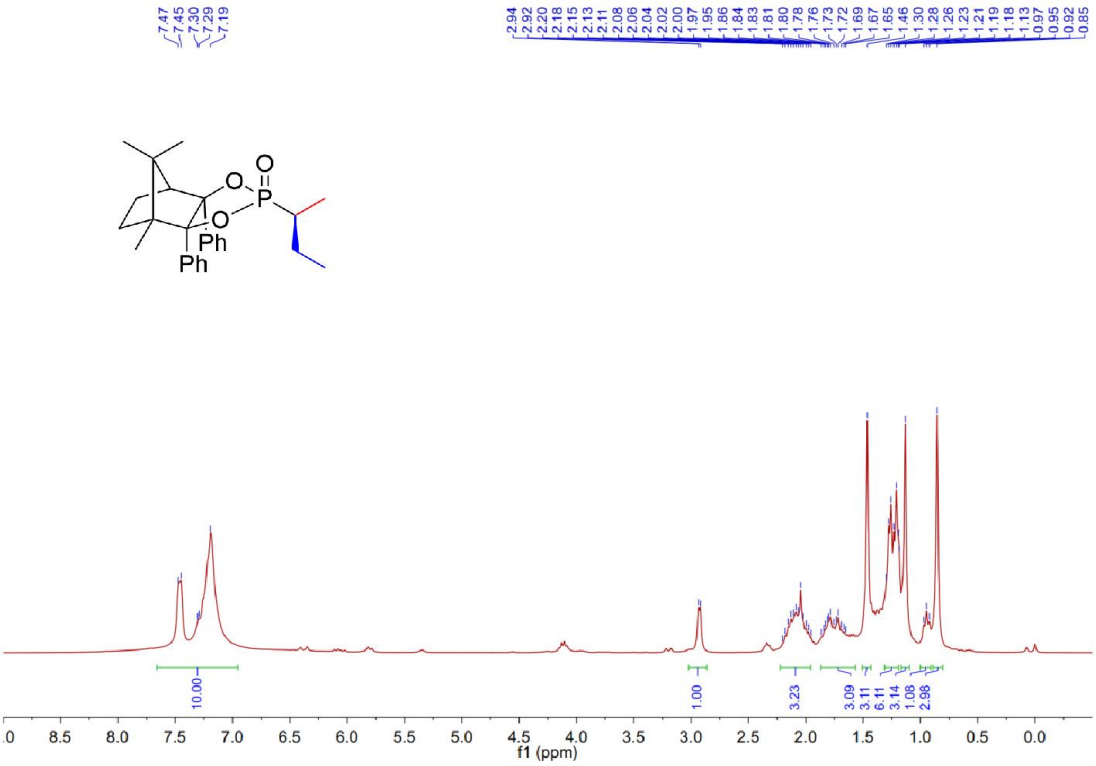
626

627 **Figure 62:** ^{13}C NMR of **2au**



628

629 **Figure 63:** ^{31}P NMR of **2au**



630

631 **Figure 64:** ^{1}H NMR of **2ba**

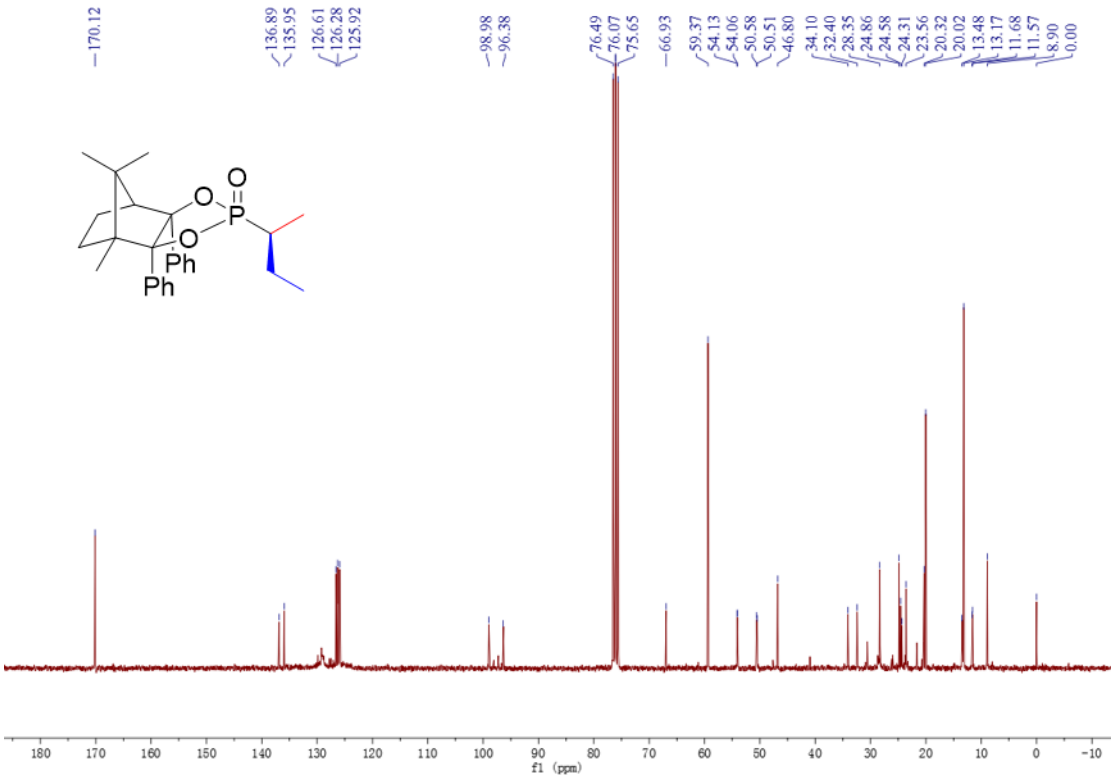


Figure 65: ^{13}C NMR of **2ba**

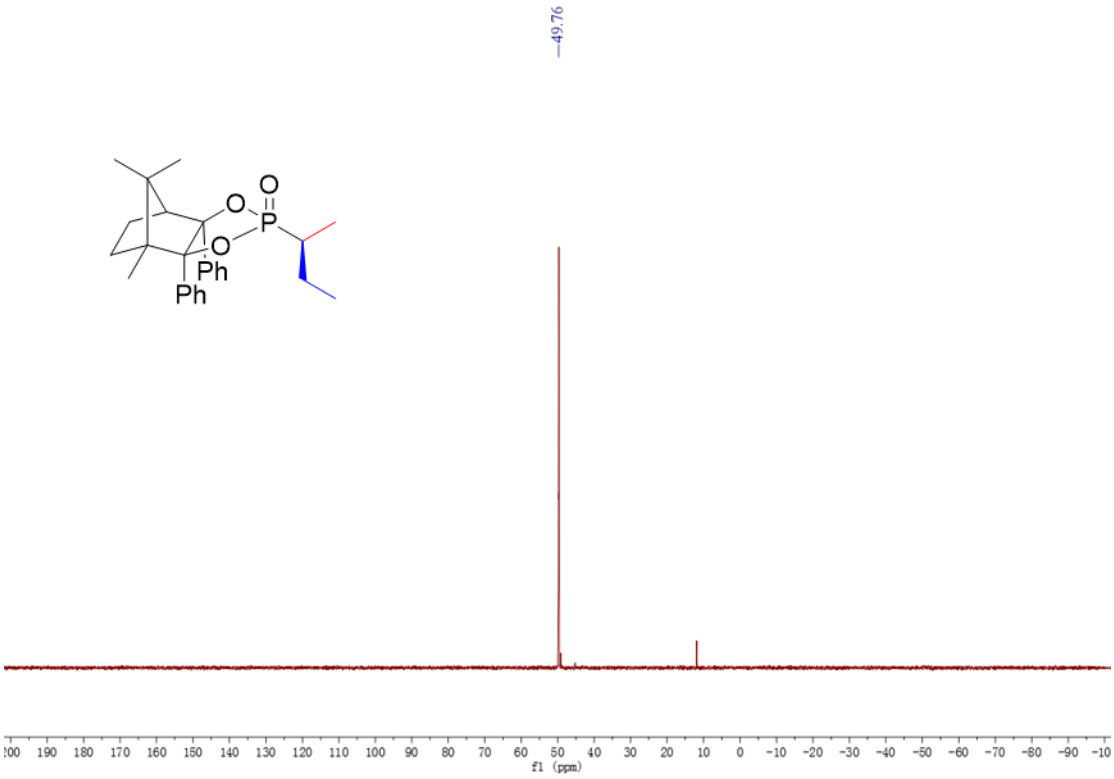


Figure 66: ^{31}P NMR of **2ba**

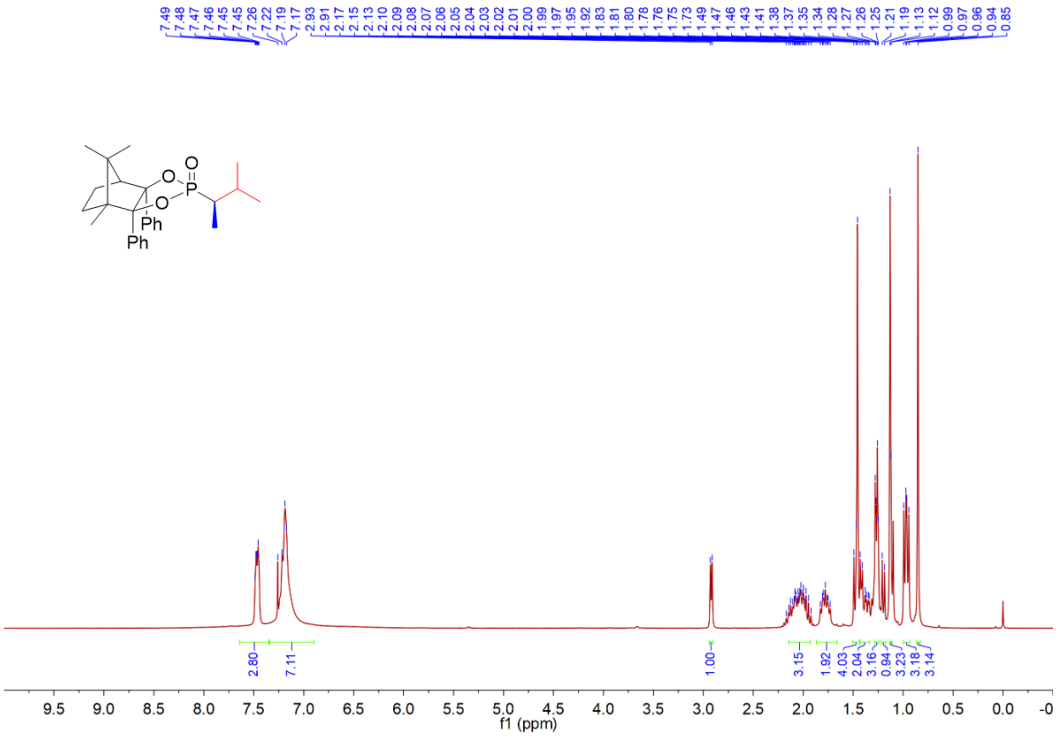


Figure 67: ^{1}H NMR of **2bc**

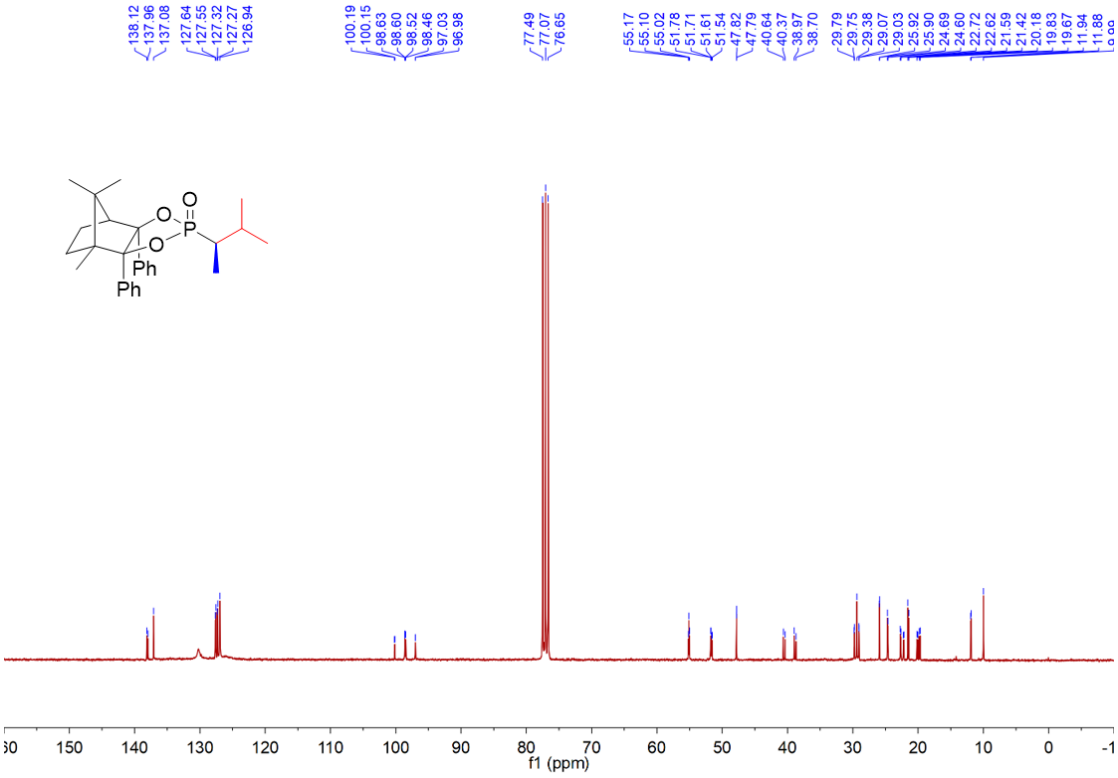
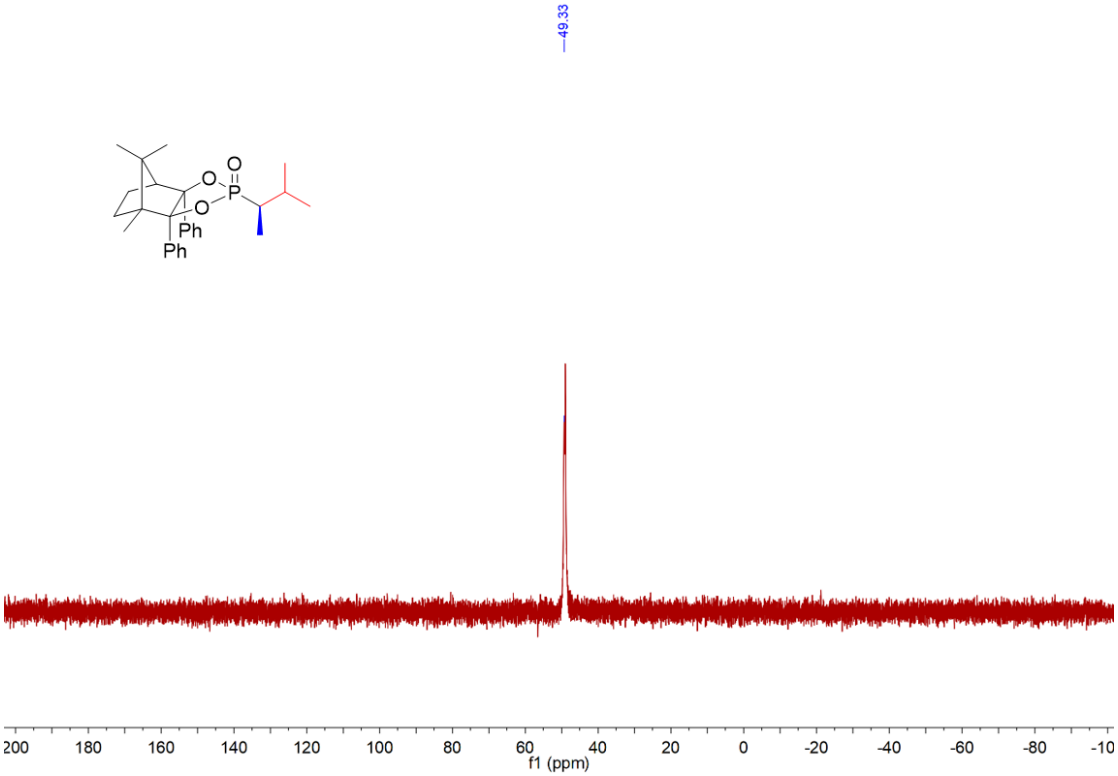


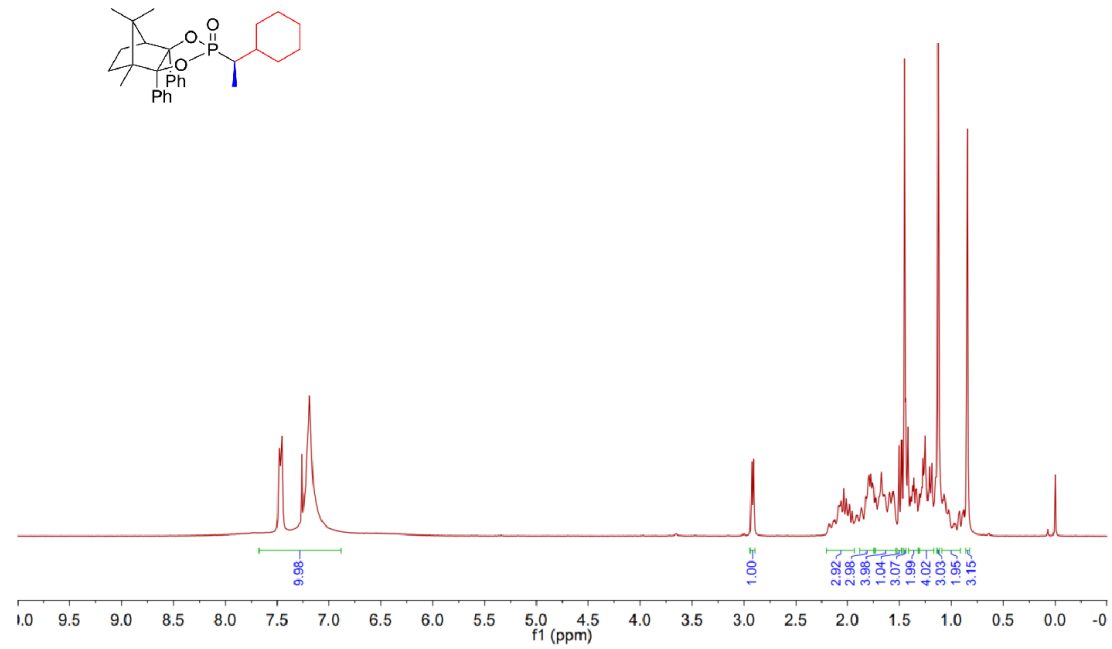
Figure 68: ^{13}C NMR of **2bc**



642

643 **Figure 69:** ^{31}P NMR of **2bc**

644



645

646 **Figure 70:** ^{1}H NMR of **2bd**

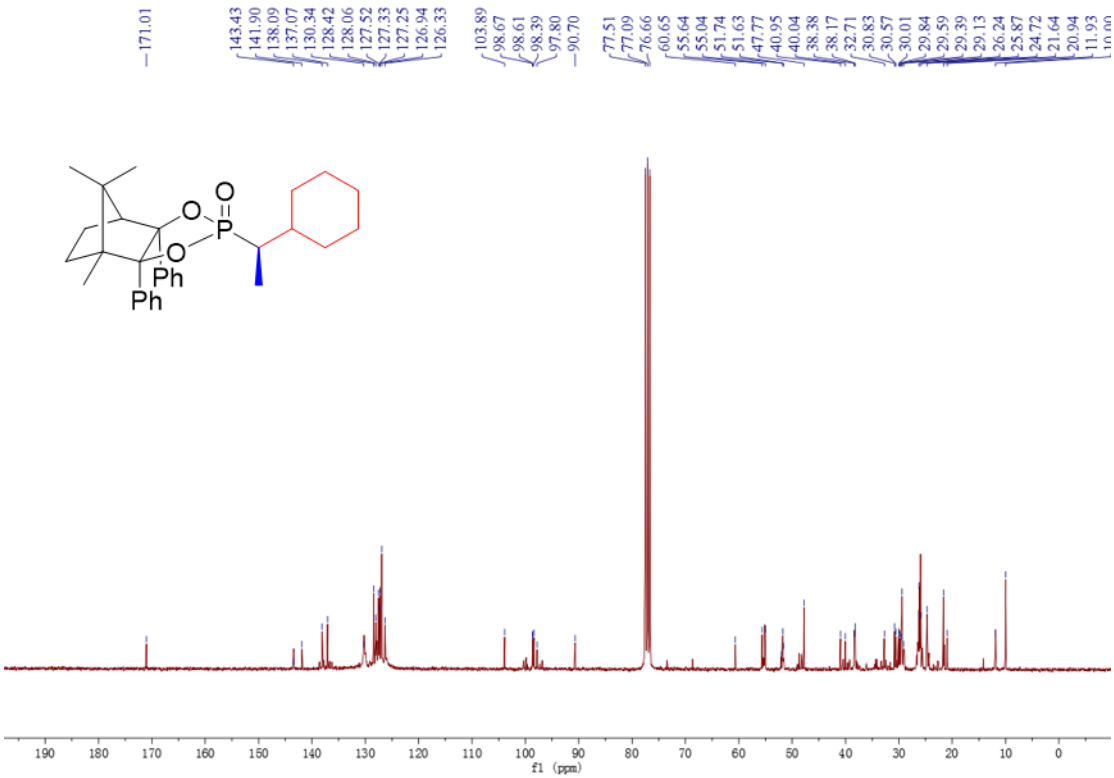


Figure 71: ^{13}C NMR of **2bd**

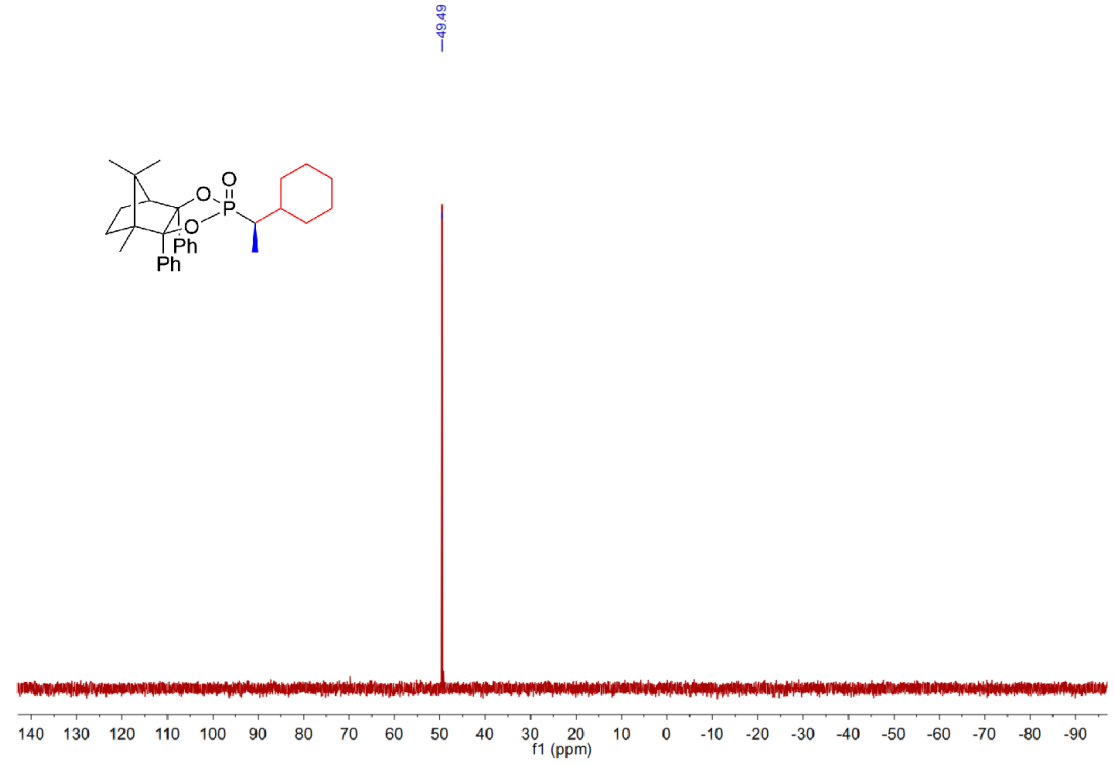
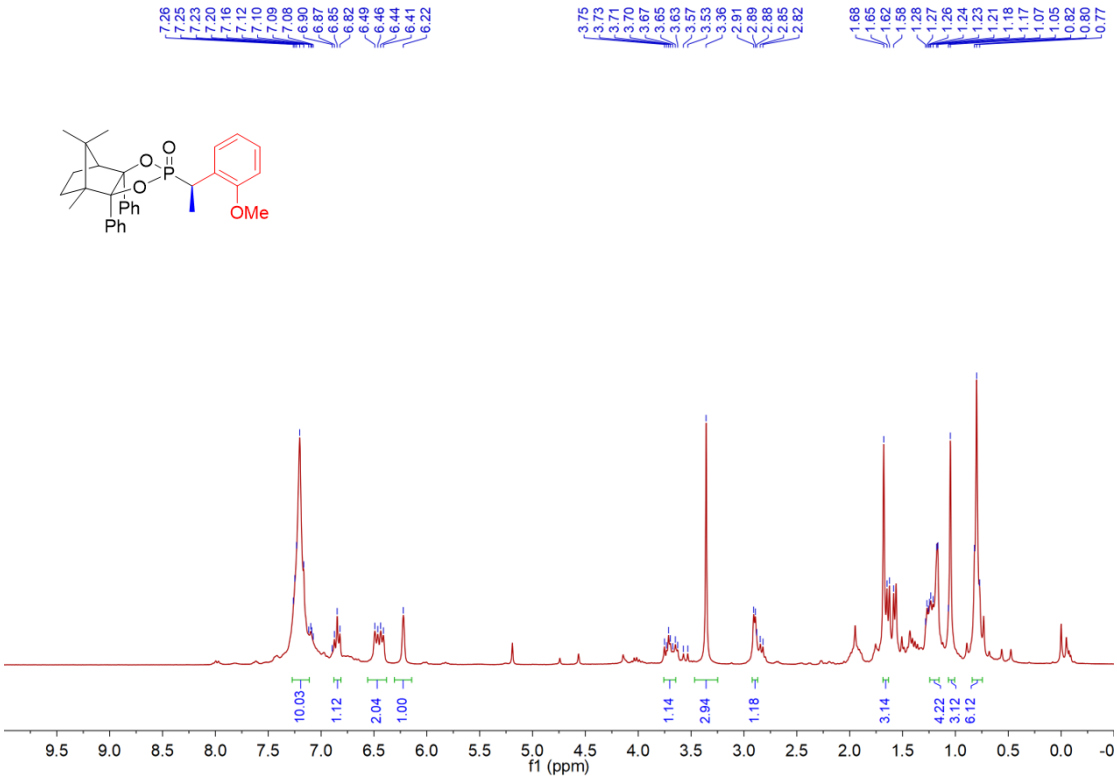
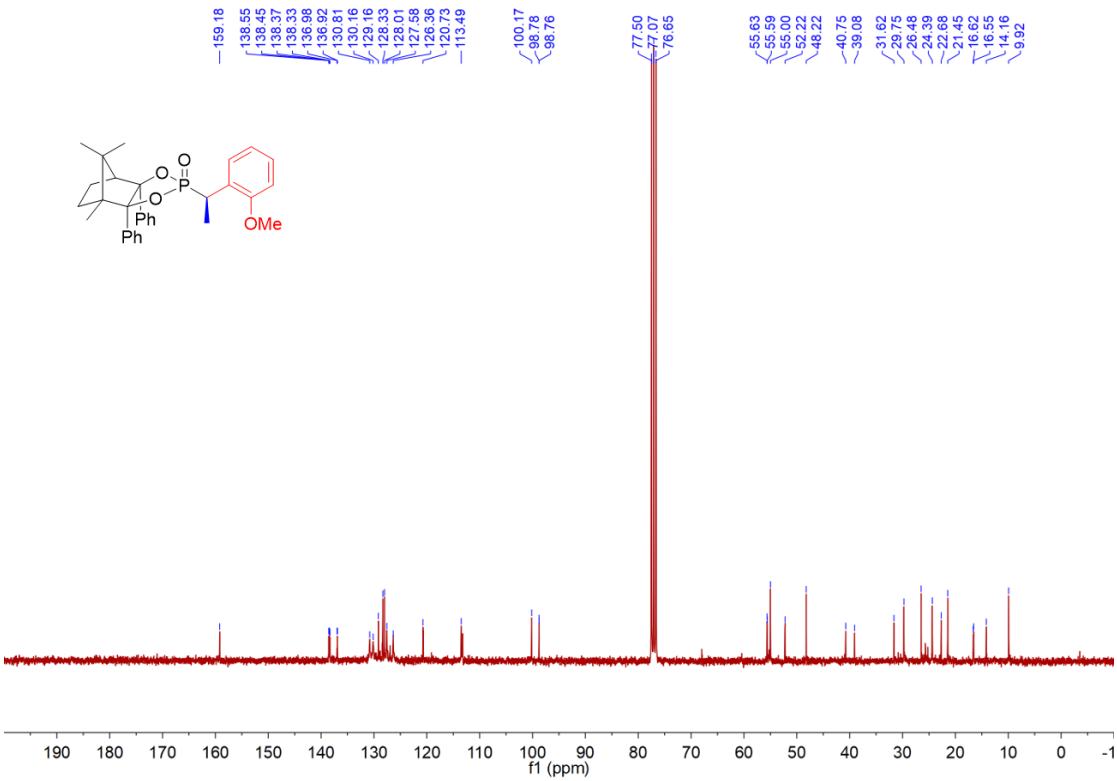


Figure 72: ^{31}P NMR of **2bd**



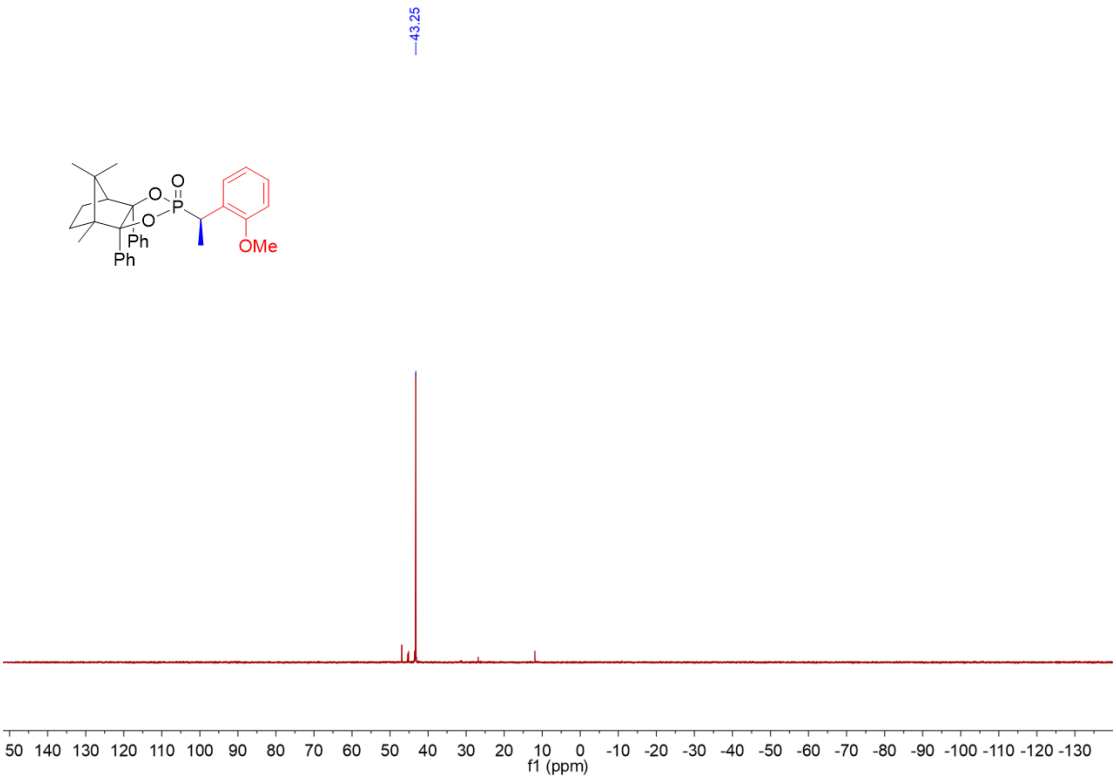
651

652 **Figure 73:** ^{1}H NMR of **2be**



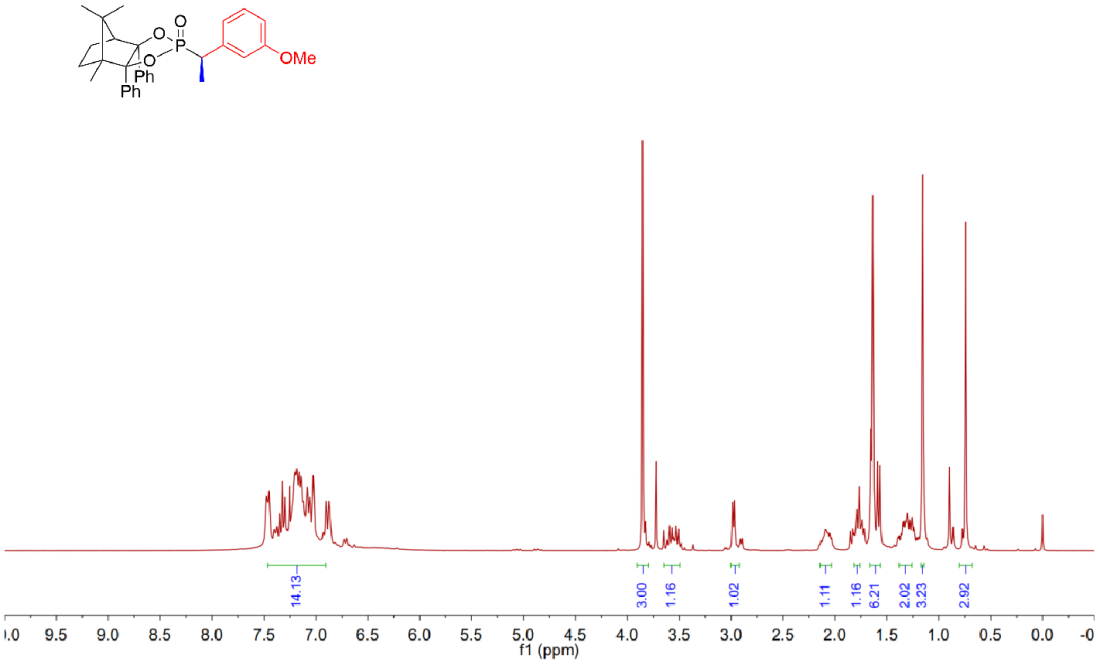
653

654 **Figure 74:** ^{13}C NMR of **2be**



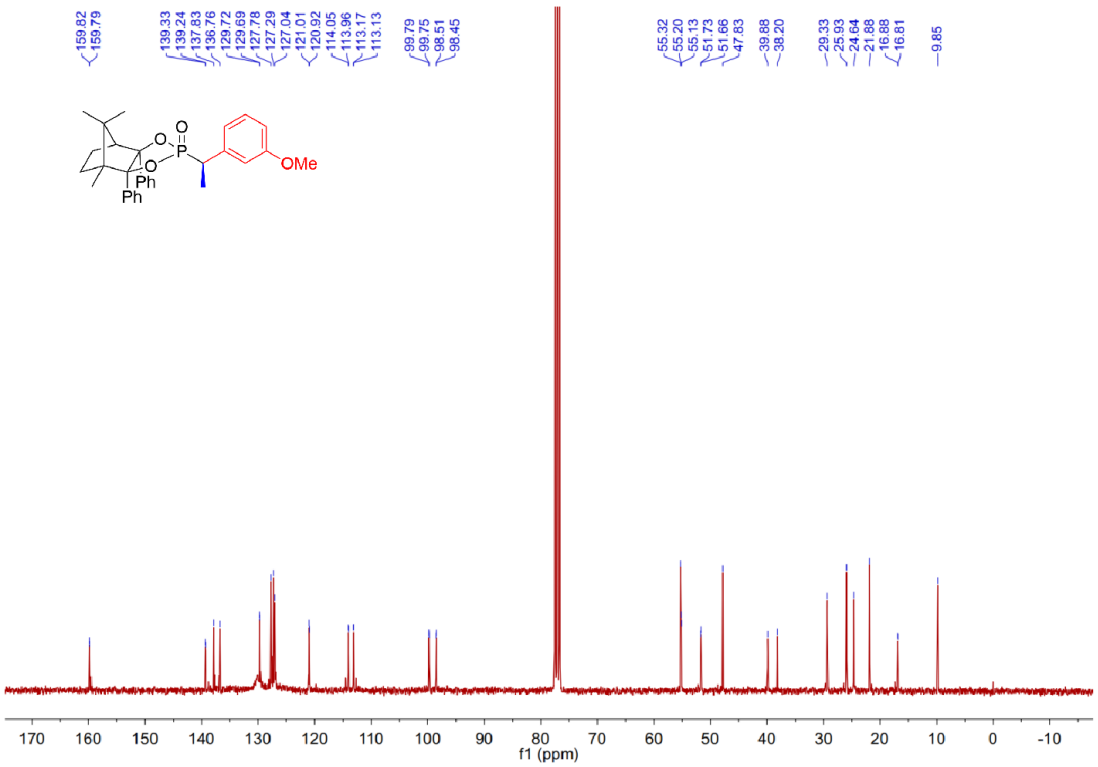
655

656 **Figure 75:** ^{31}P NMR of **2be**



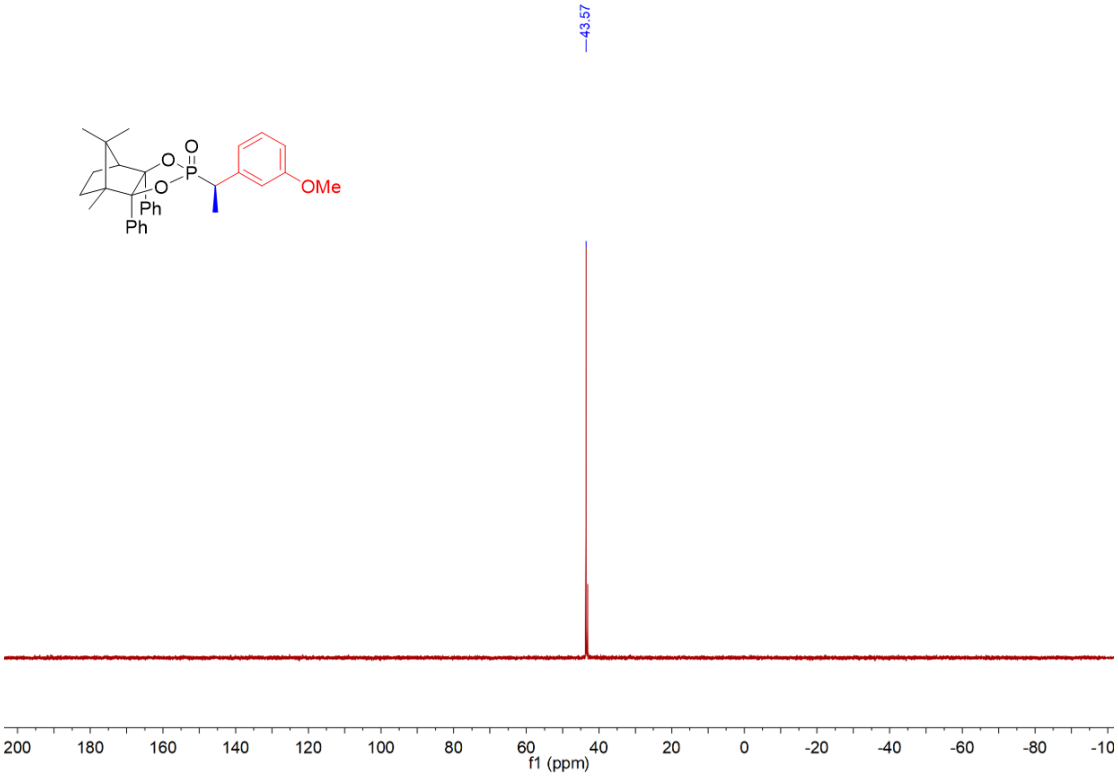
657

658 **Figure 76:** ^{1}H NMR of **2bf**



659

660 **Figure 77:** ^{13}C NMR of **2bf**



661

662 **Figure 78:** ^{31}P NMR of **2bf**

663

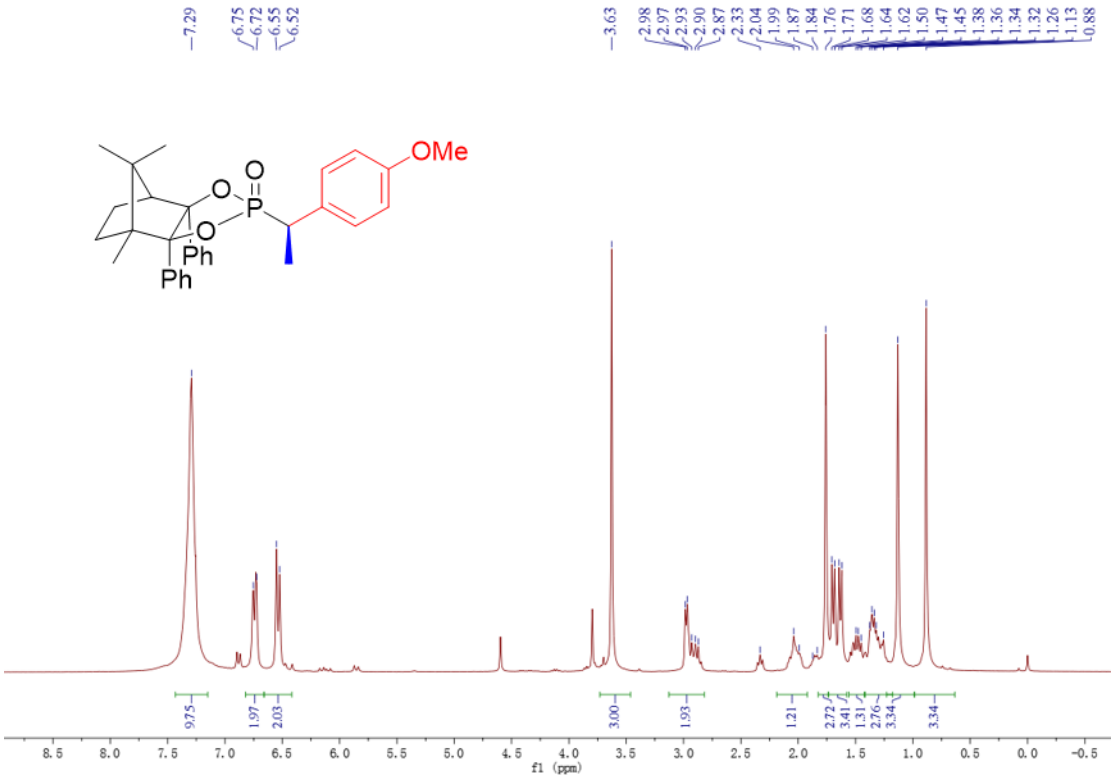


Figure 79: ^{1}H NMR of **2bg**

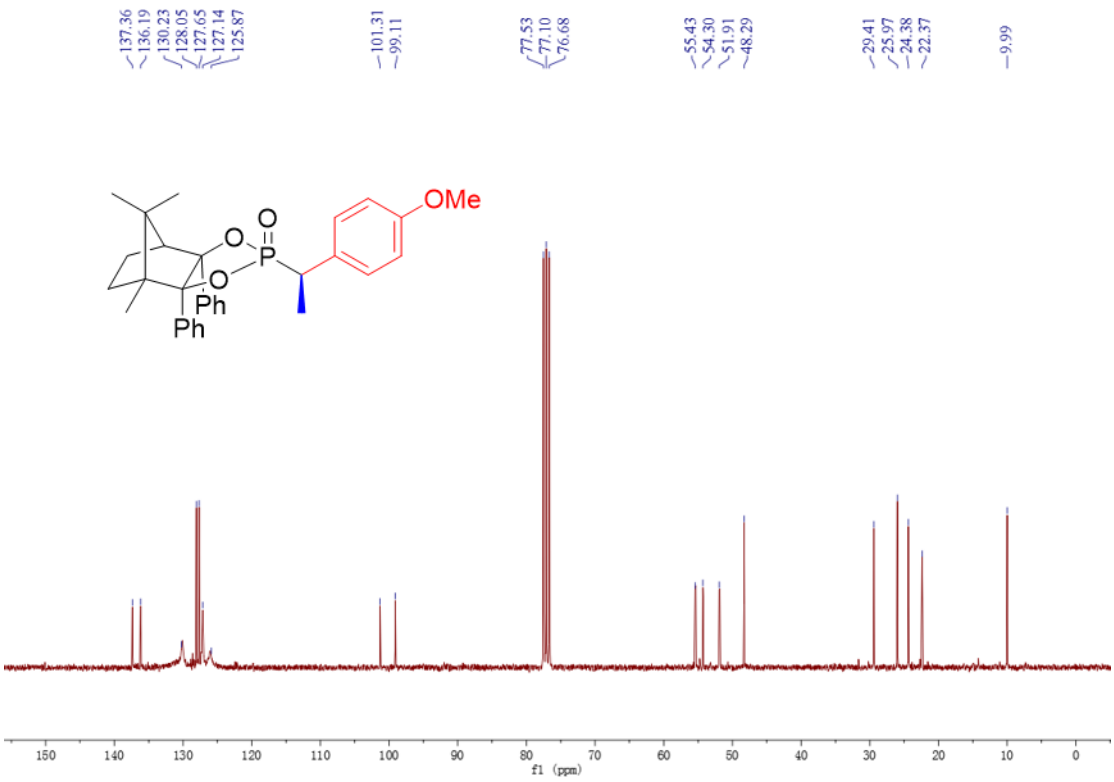
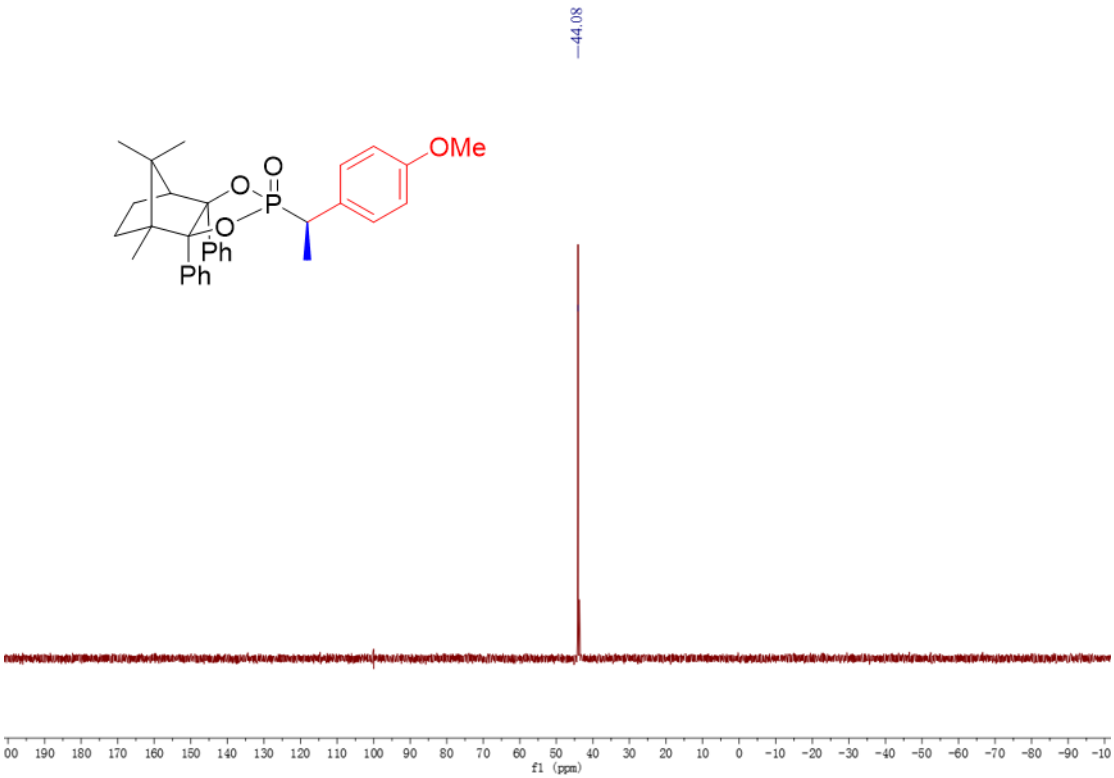


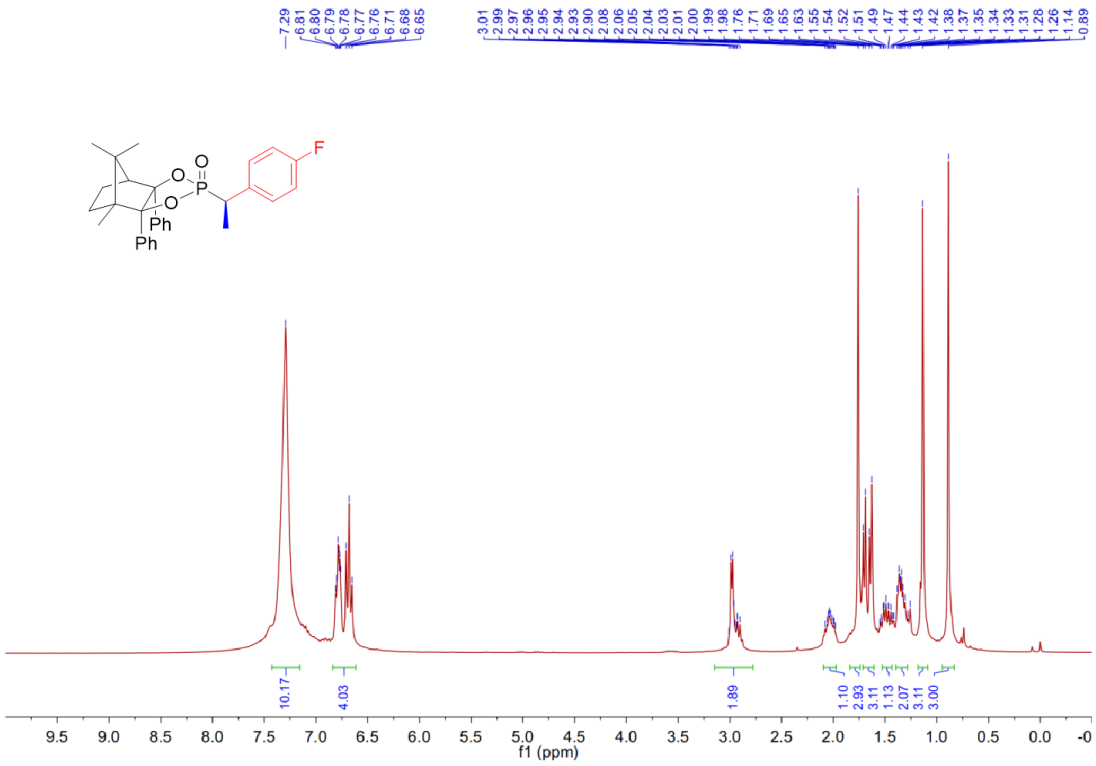
Figure 80: ^{13}C NMR of **2bg**



668

669 **Figure 81:** ^{31}P NMR of **2bg**

670



671

672 **Figure 82:** ^{1}H NMR of **2bh**

673

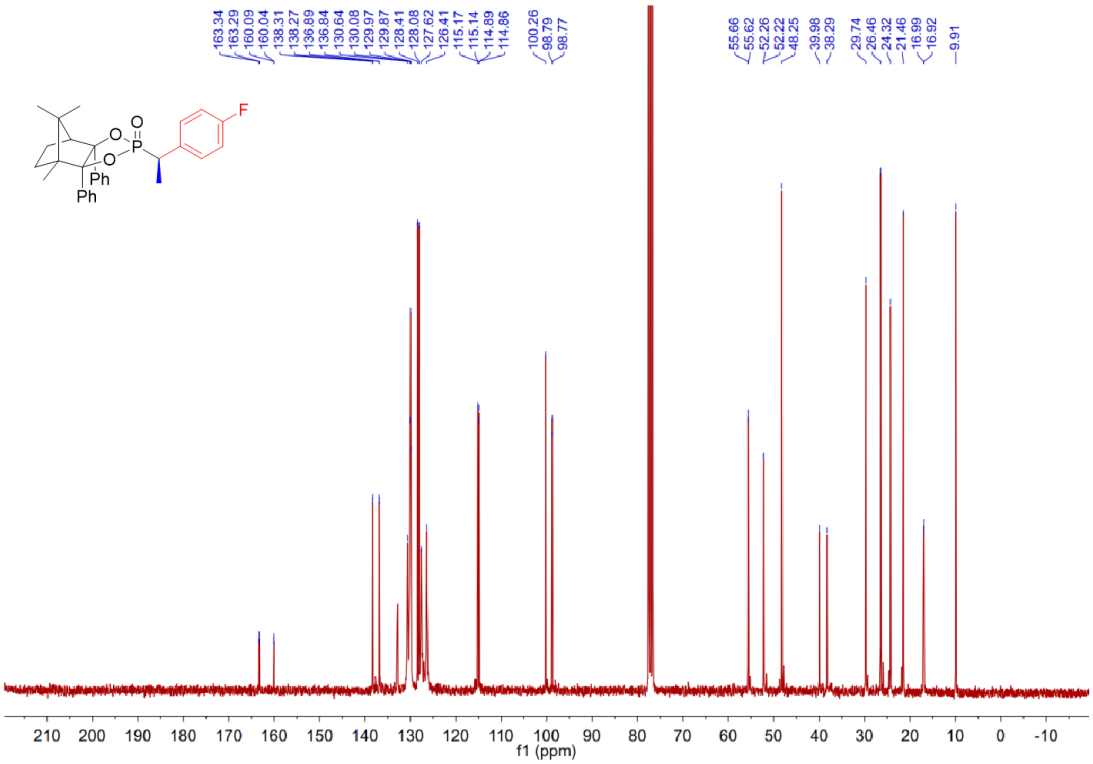


Figure 83: ^{13}C NMR of **2bh**

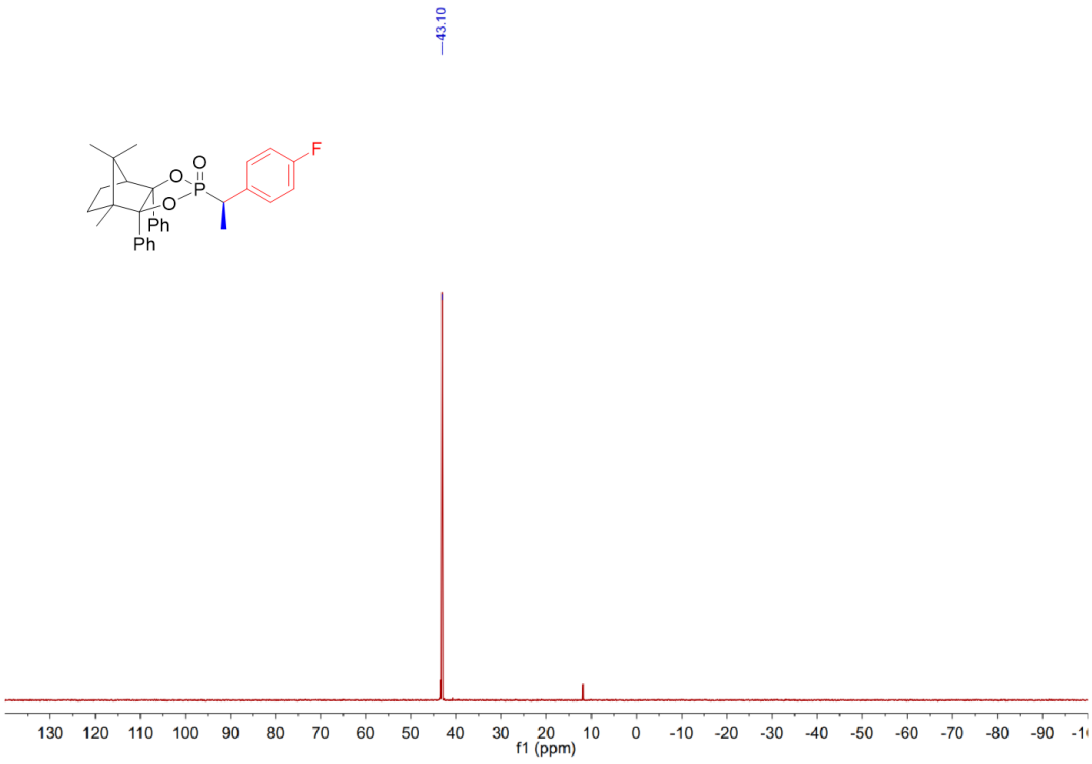


Figure 84: ^{31}P NMR of **2bh**

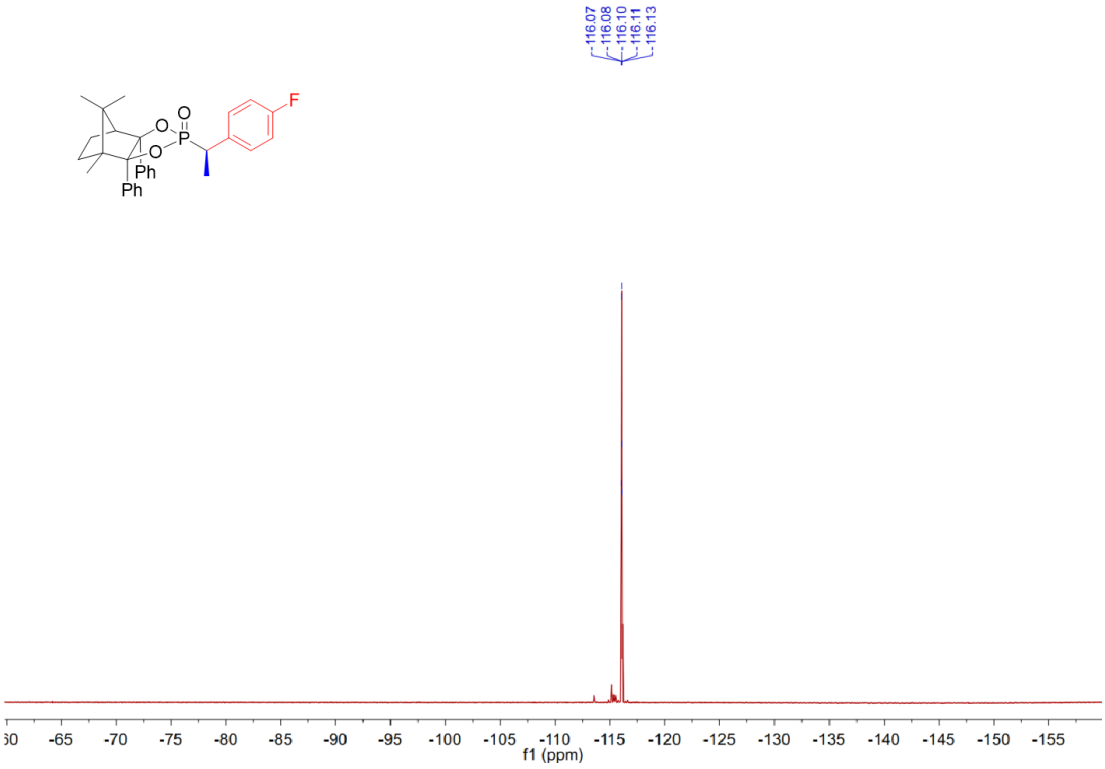


Figure 85: ^{19}F NMR of **2bh**

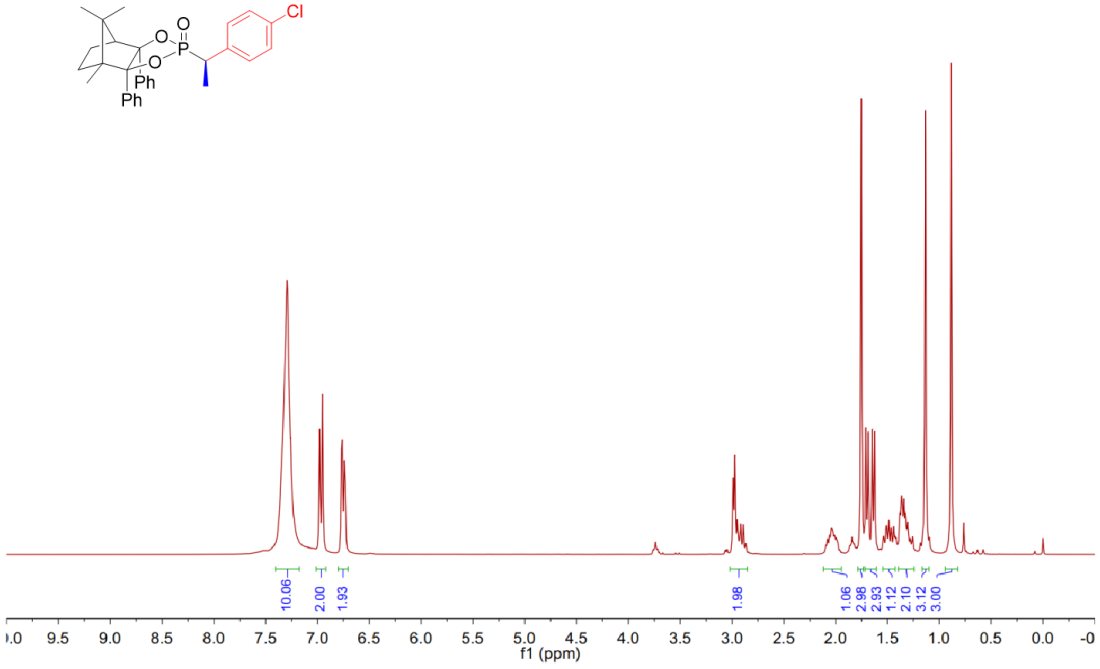
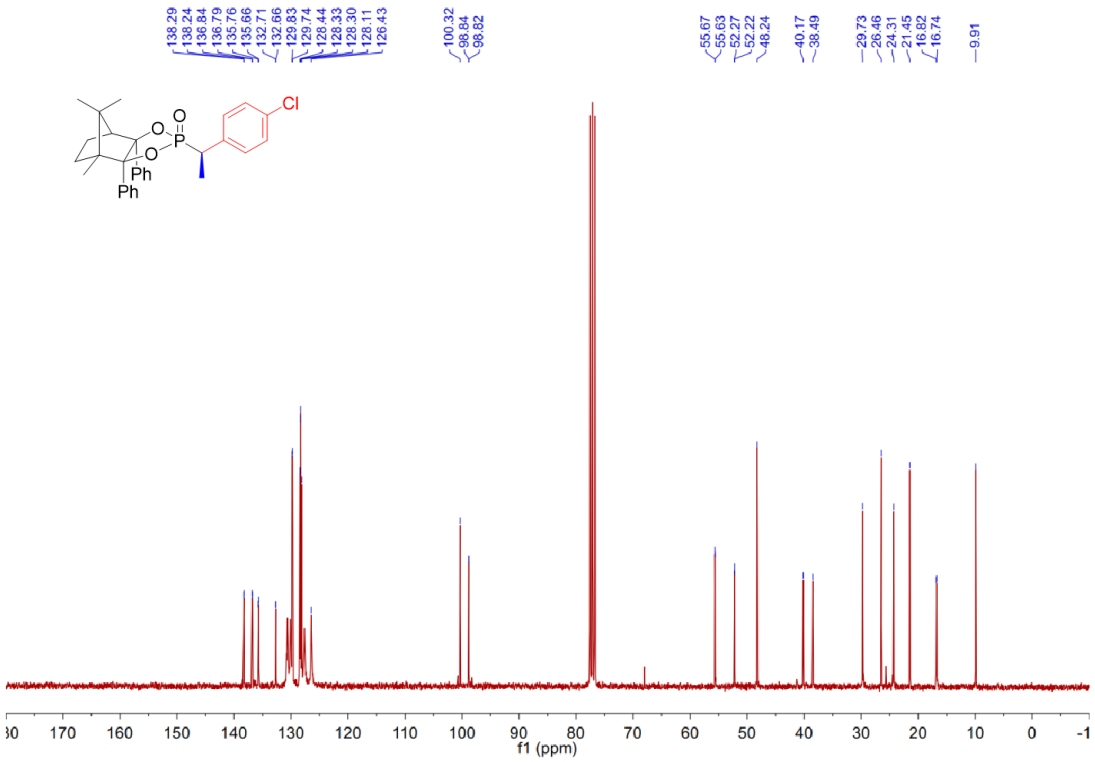


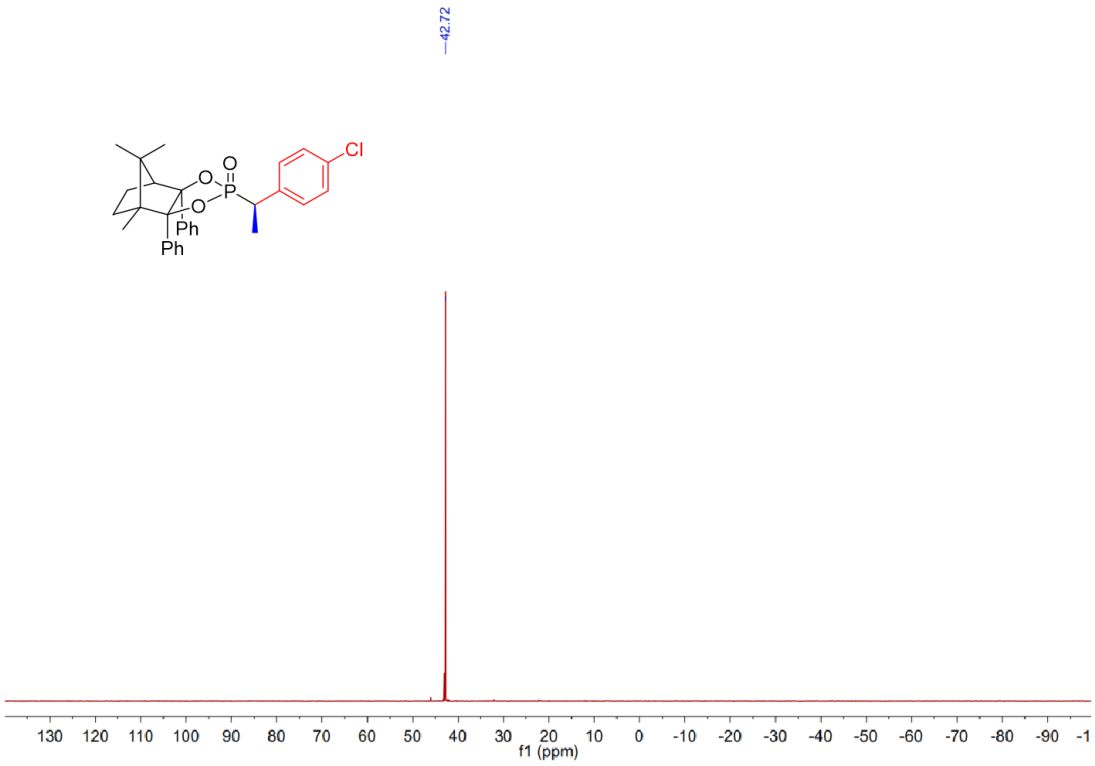
Figure 86: ^{1}H NMR of **2bi**



685

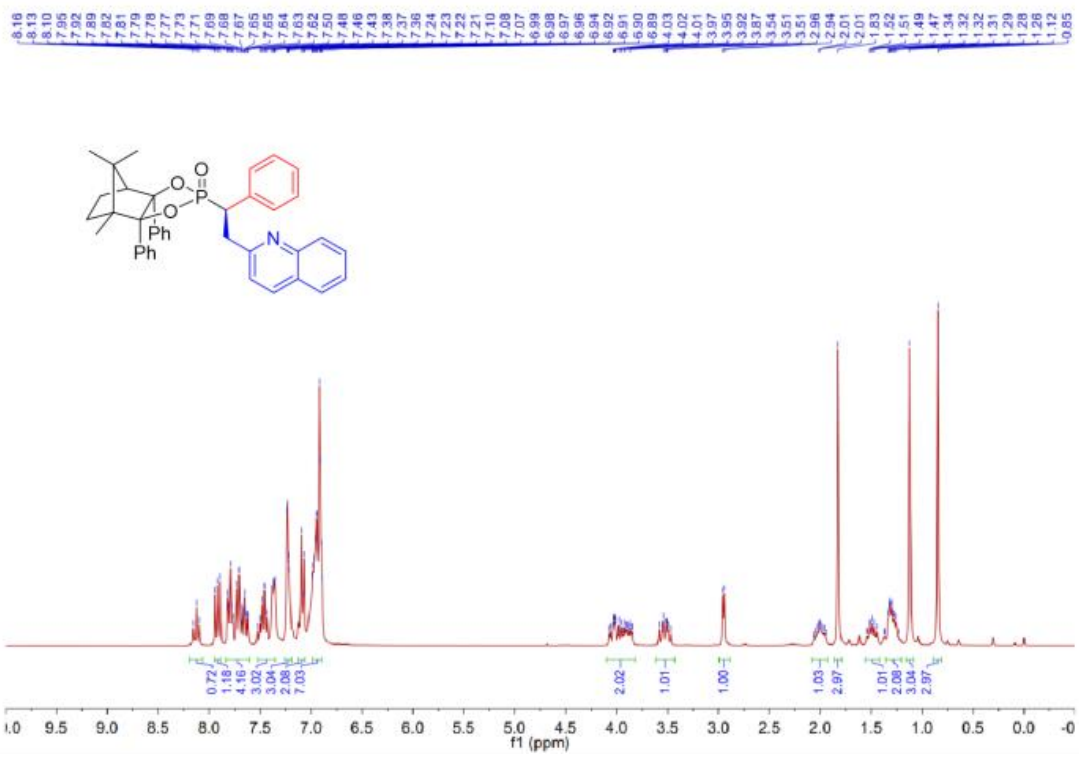
686 **Figure 87:** ^{13}C NMR of **2bi**

687



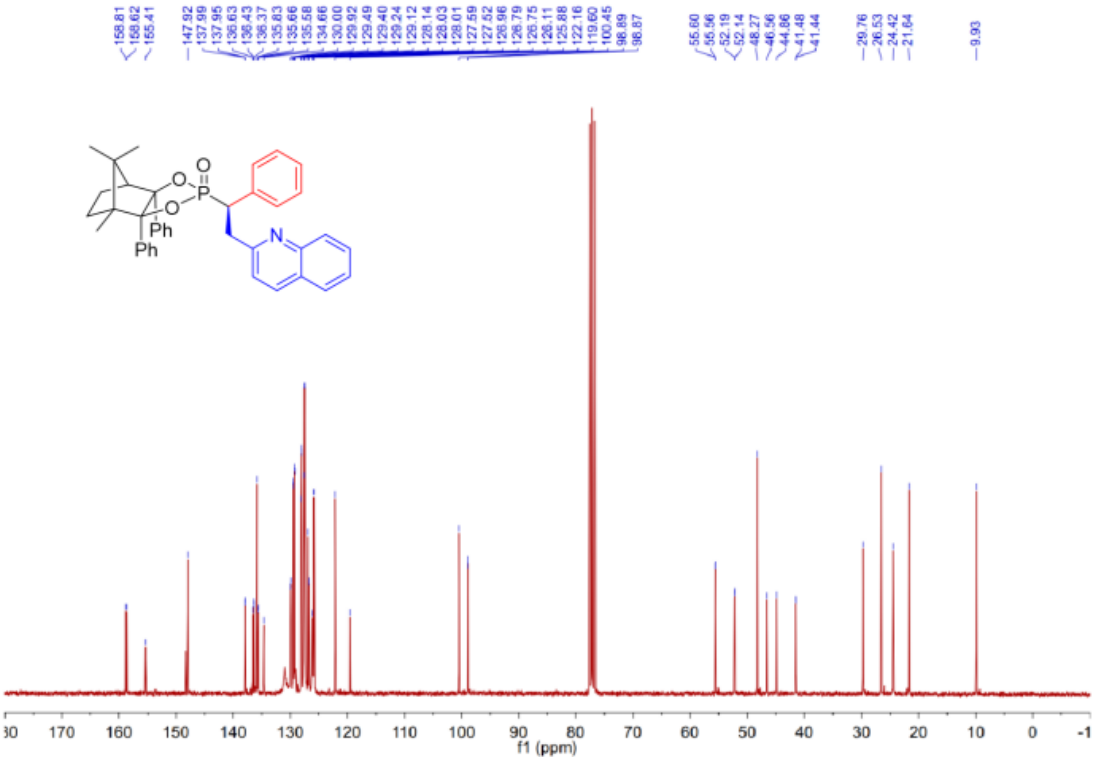
688

689 **Figure 88:** ^{31}P NMR of **2bi**



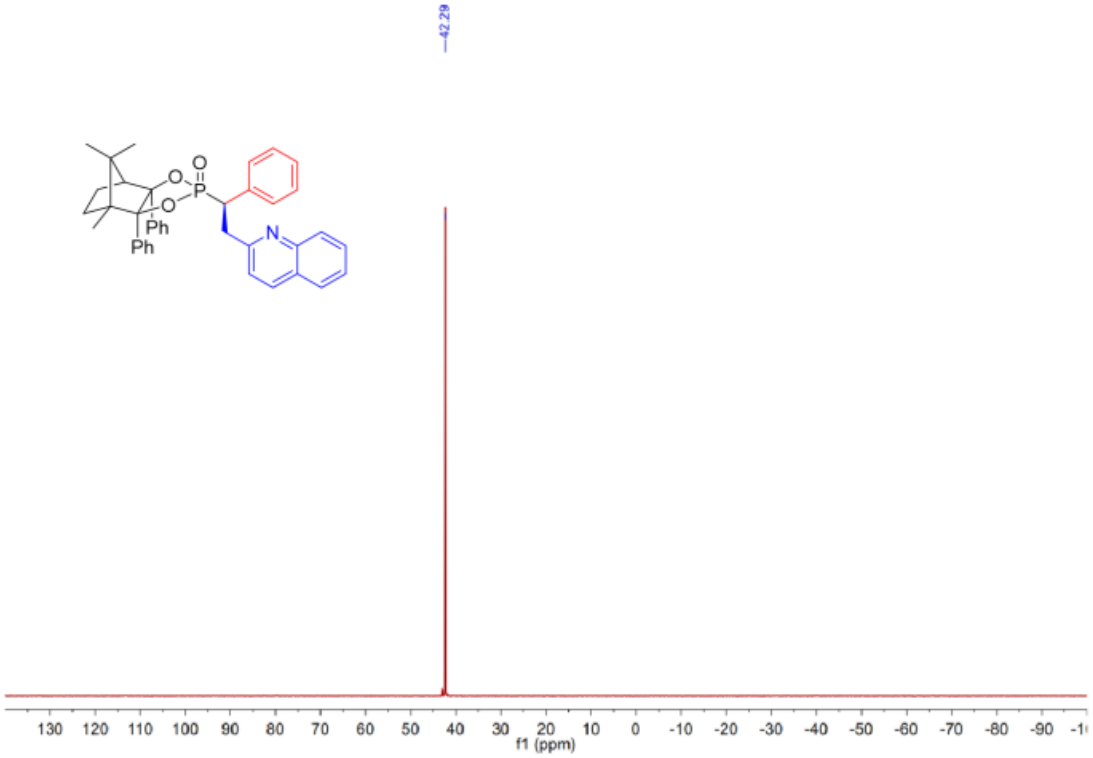
690

691 **Figure 89:** ^{1}H NMR of **2bj**



692

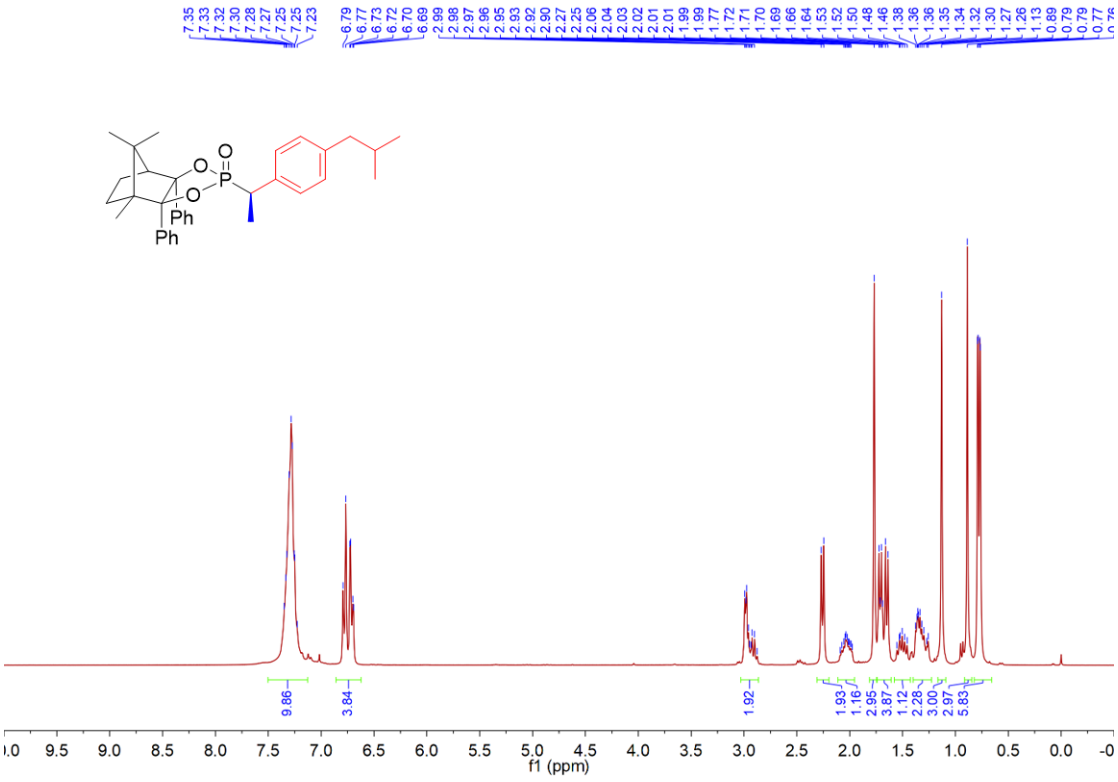
693 **Figure 90:** ^{13}C NMR of **2bj**



694

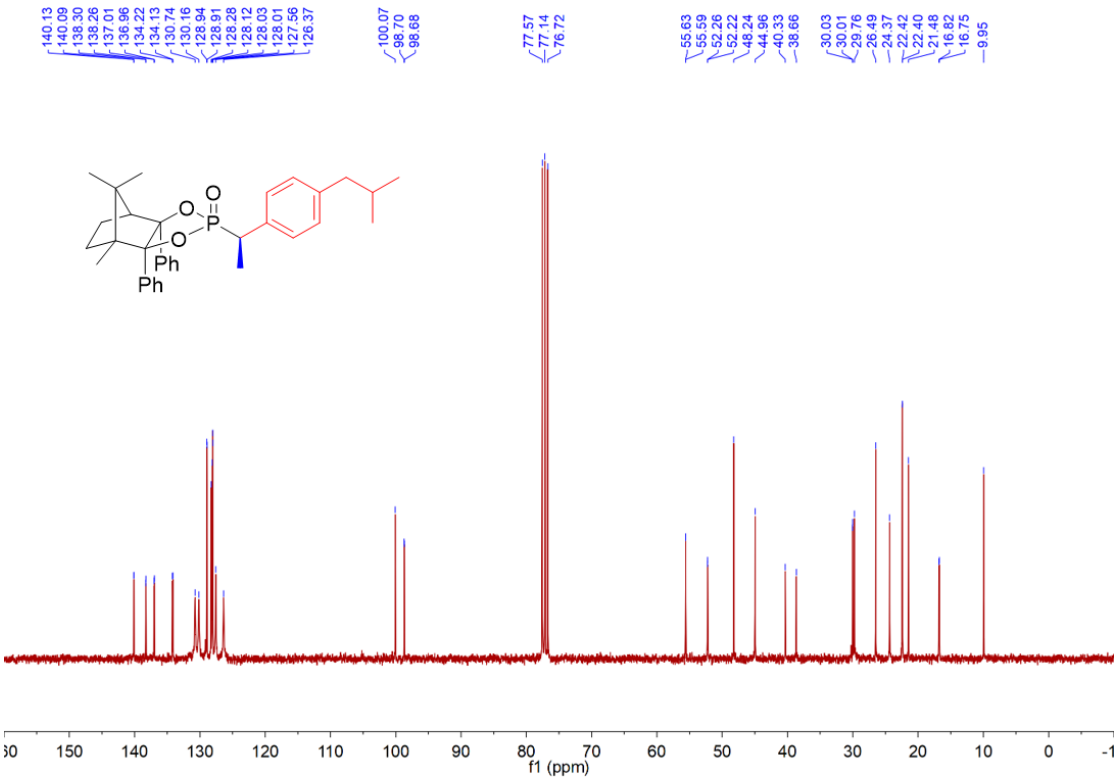
695 **Figure 91:** ^{31}P NMR of **2bj**

696



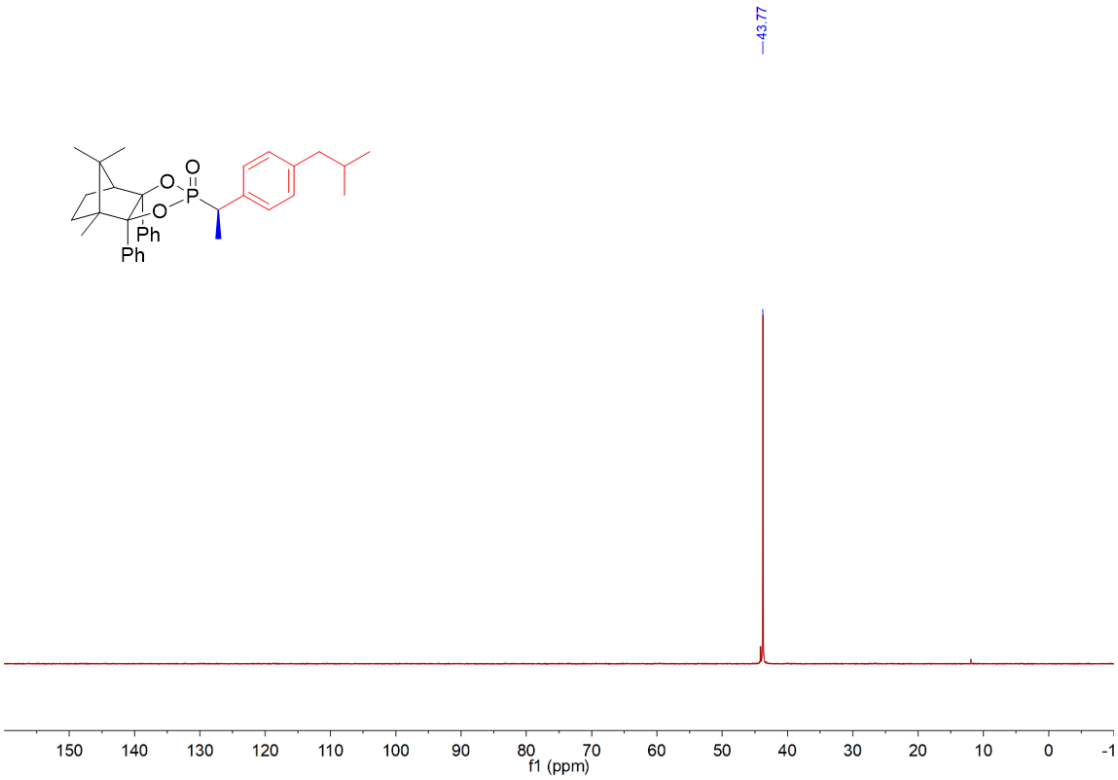
697

698 **Figure 92:** ^{1}H NMR of **2bk**



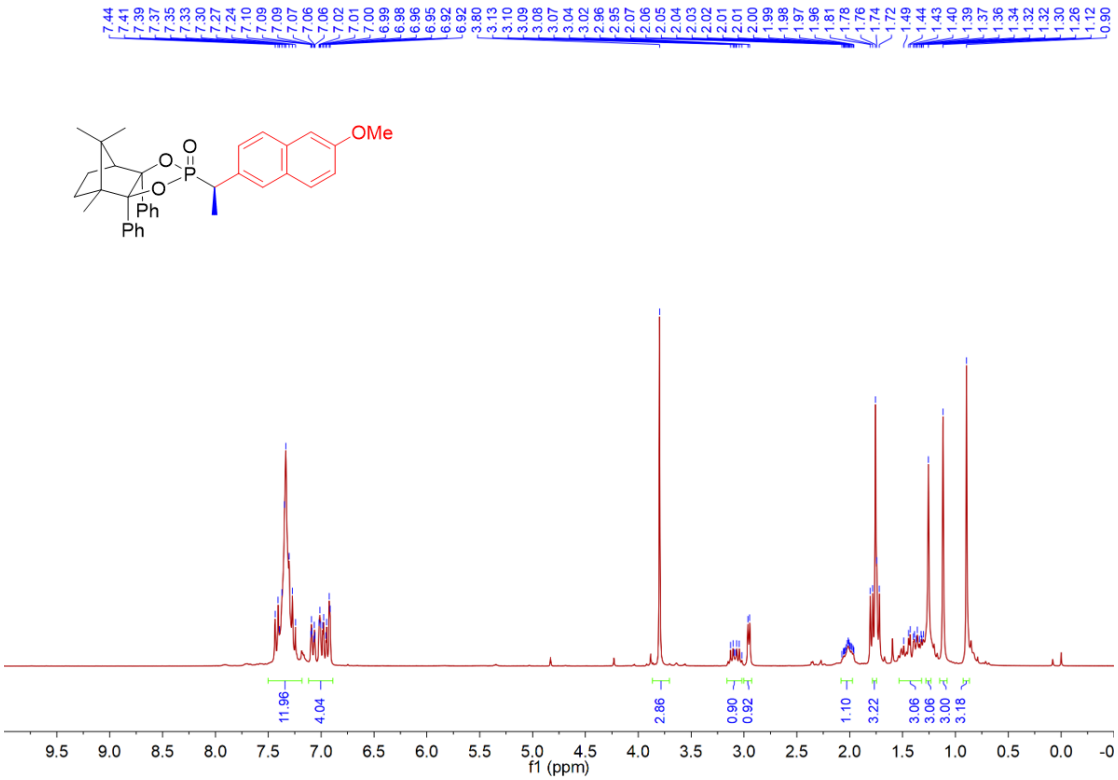
699

700 **Figure 93:** ^{13}C NMR of **2bk**



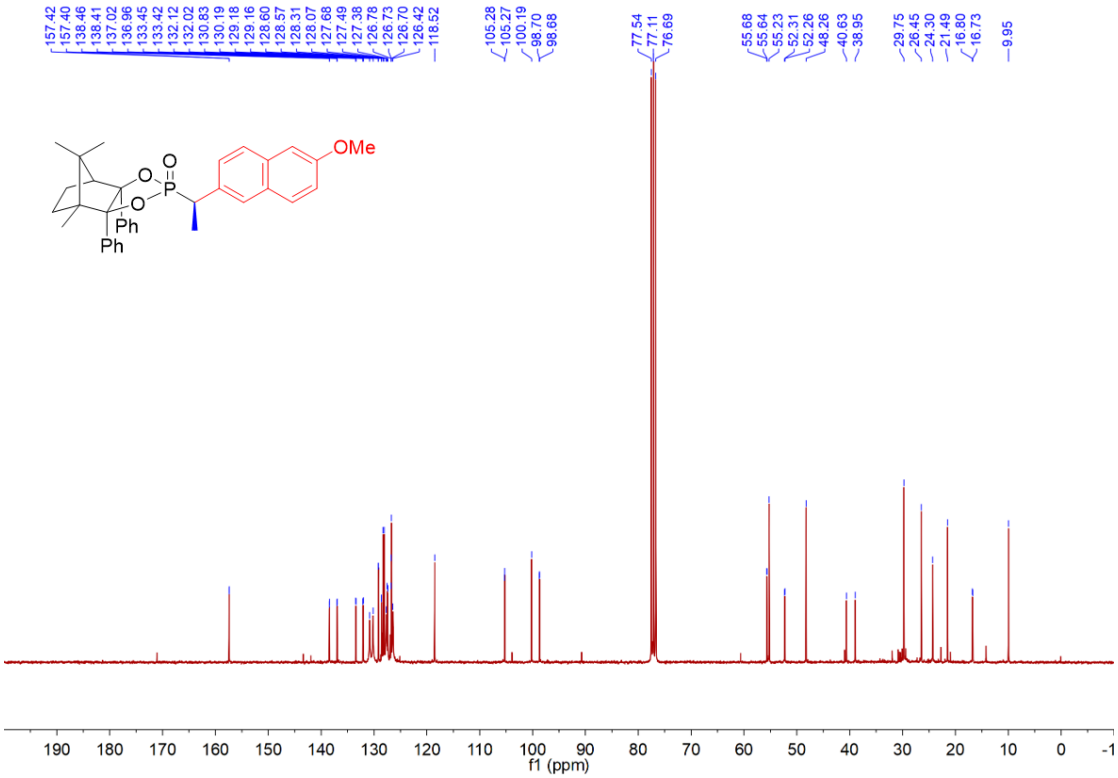
701

702 **Figure 94:** ^{31}P NMR of **2bk**



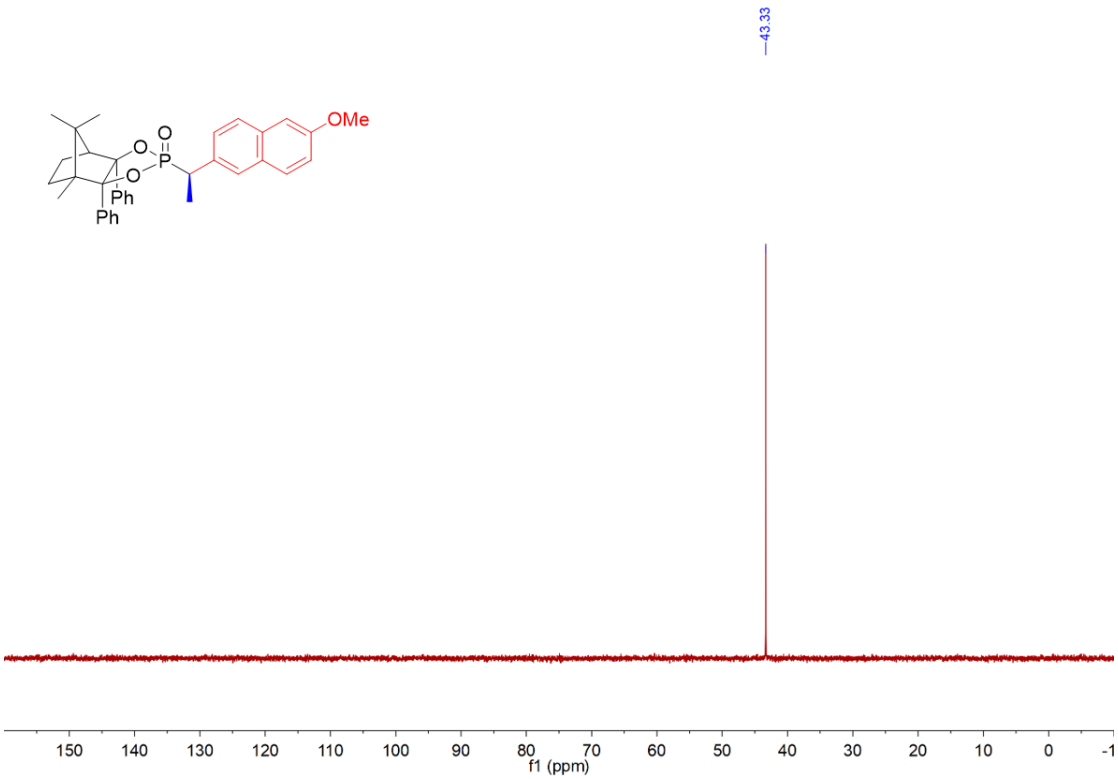
703

704 **Figure 95:** ^{1}H NMR of **2bl**



705

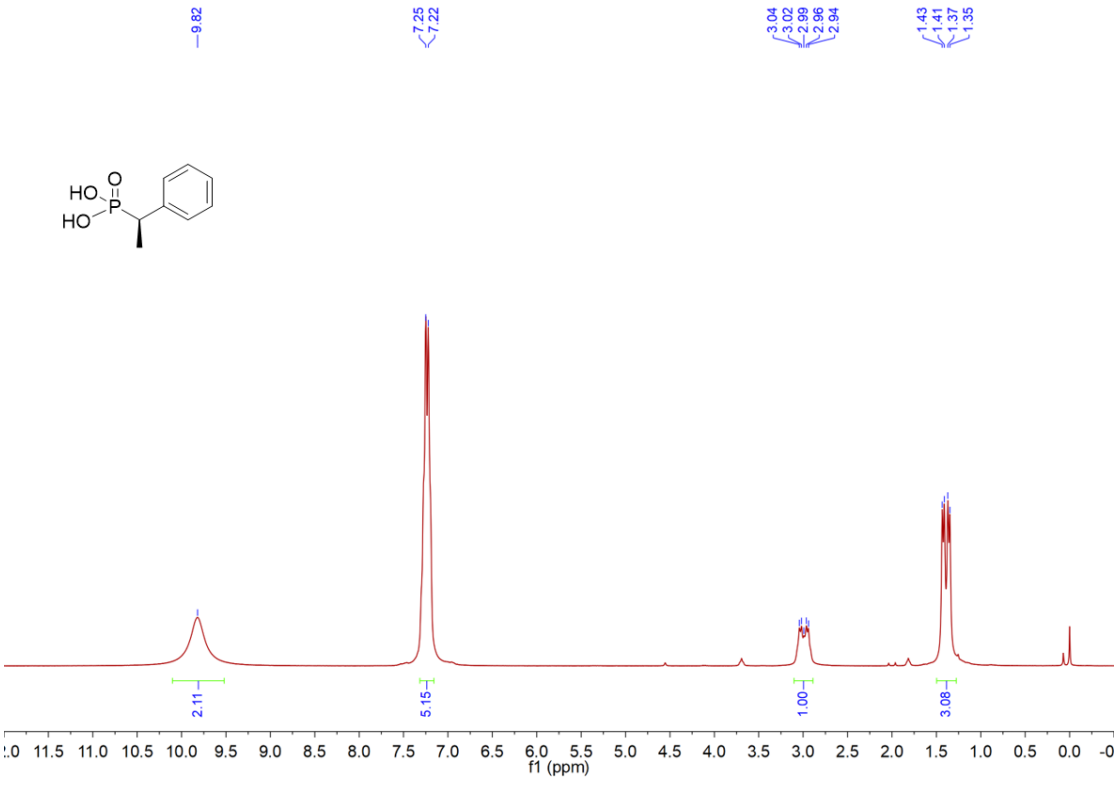
706 **Figure 96:** ^{13}C NMR of **2bl**



707

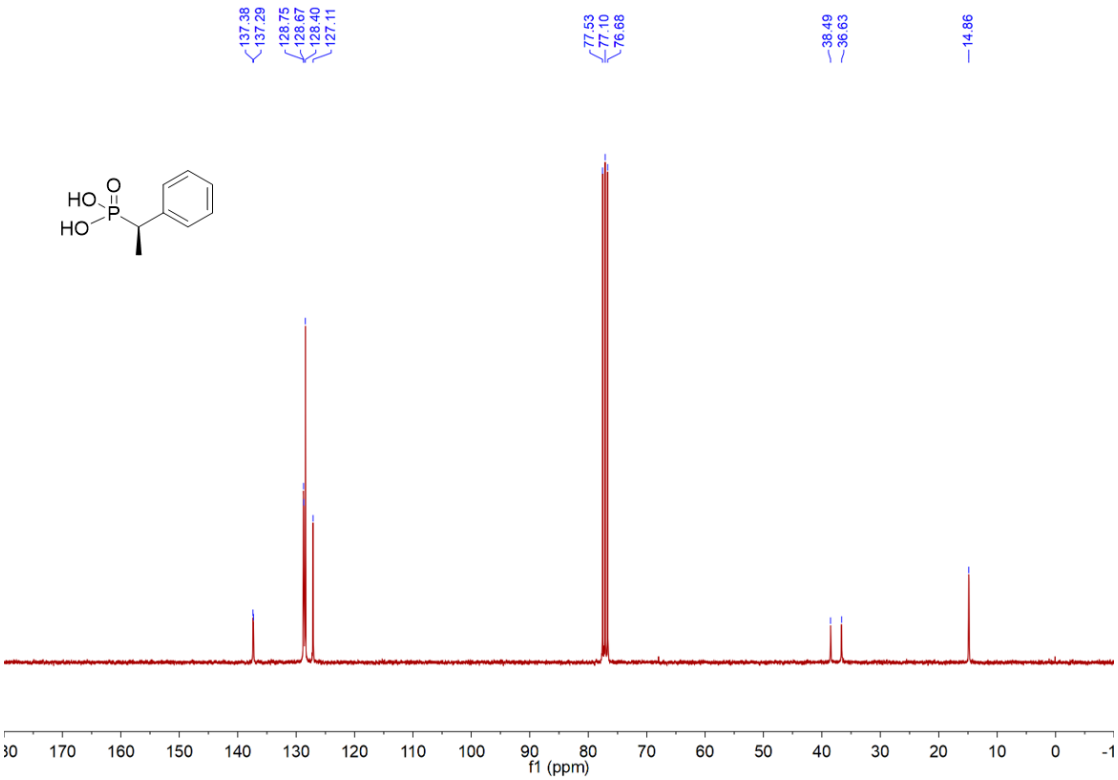
708 **Figure 97:** ^{31}P NMR of **2bl**

709



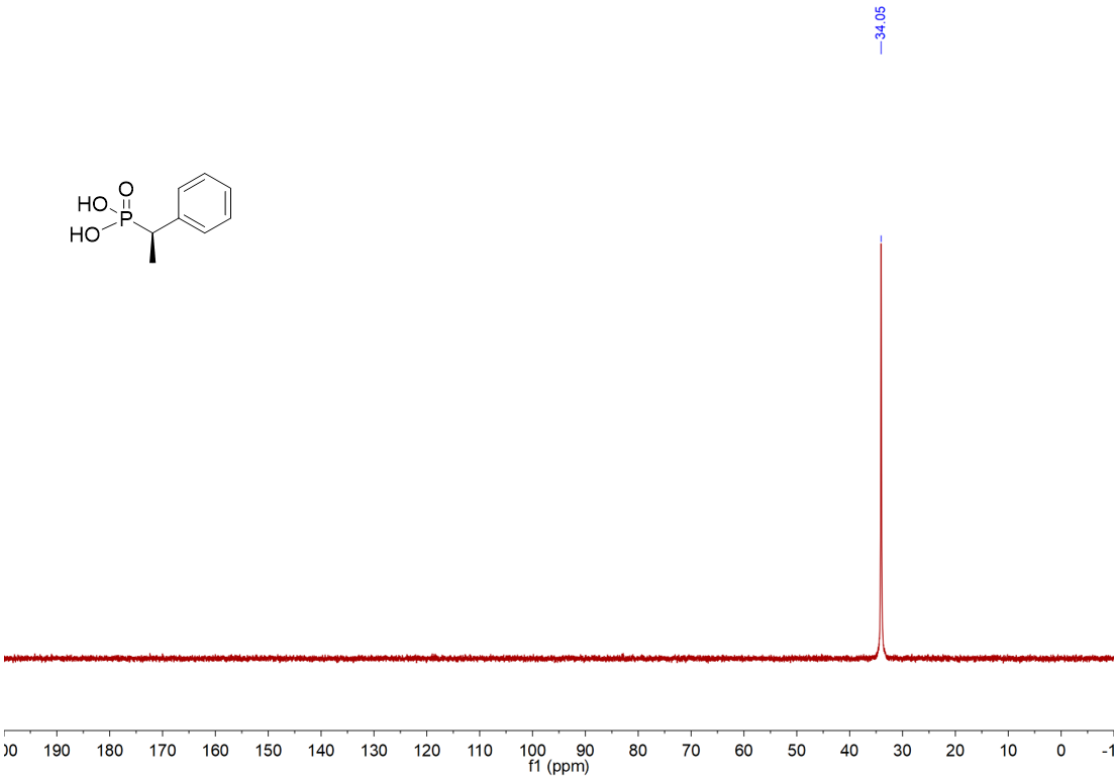
710

711 **Figure 98:** ^{1}H NMR of **3a**



712

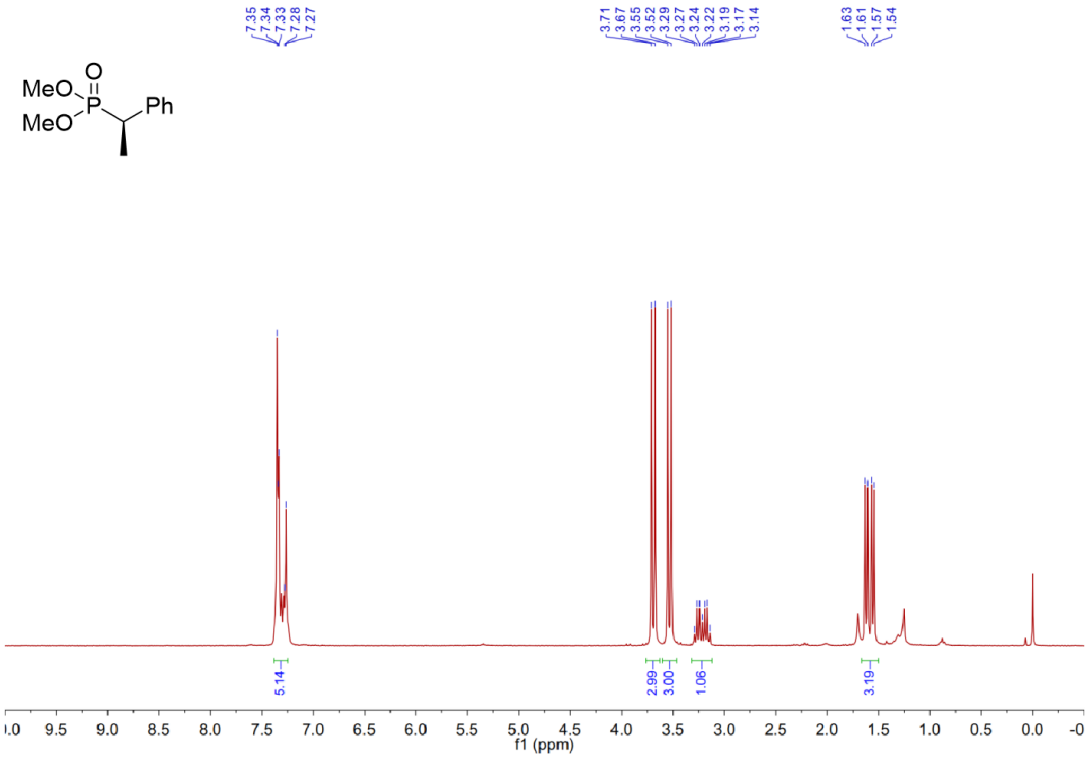
713 **Figure 99:** ^{13}C NMR of **3a**



714

715 **Figure 100:** ^{31}P NMR of **3a**

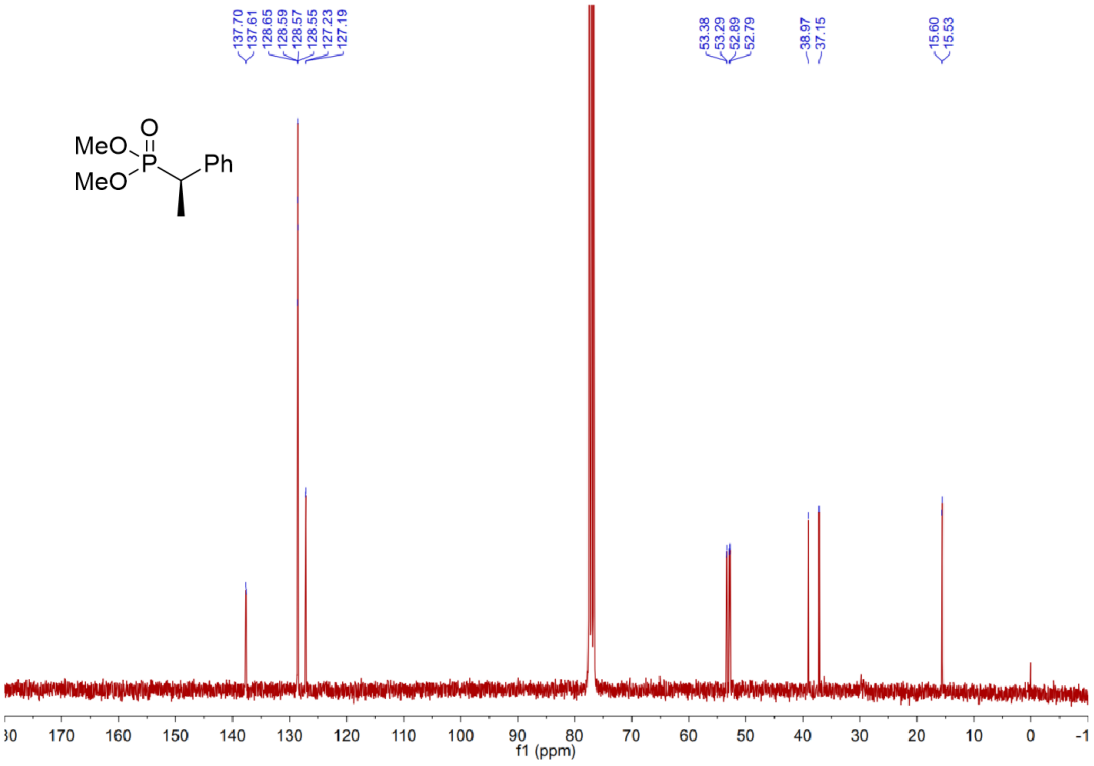
716



717

718 **Figure 101:** ^{1}H NMR of **4a**

719



720

721 **Figure 102:** ^{13}C NMR of **4a**

722

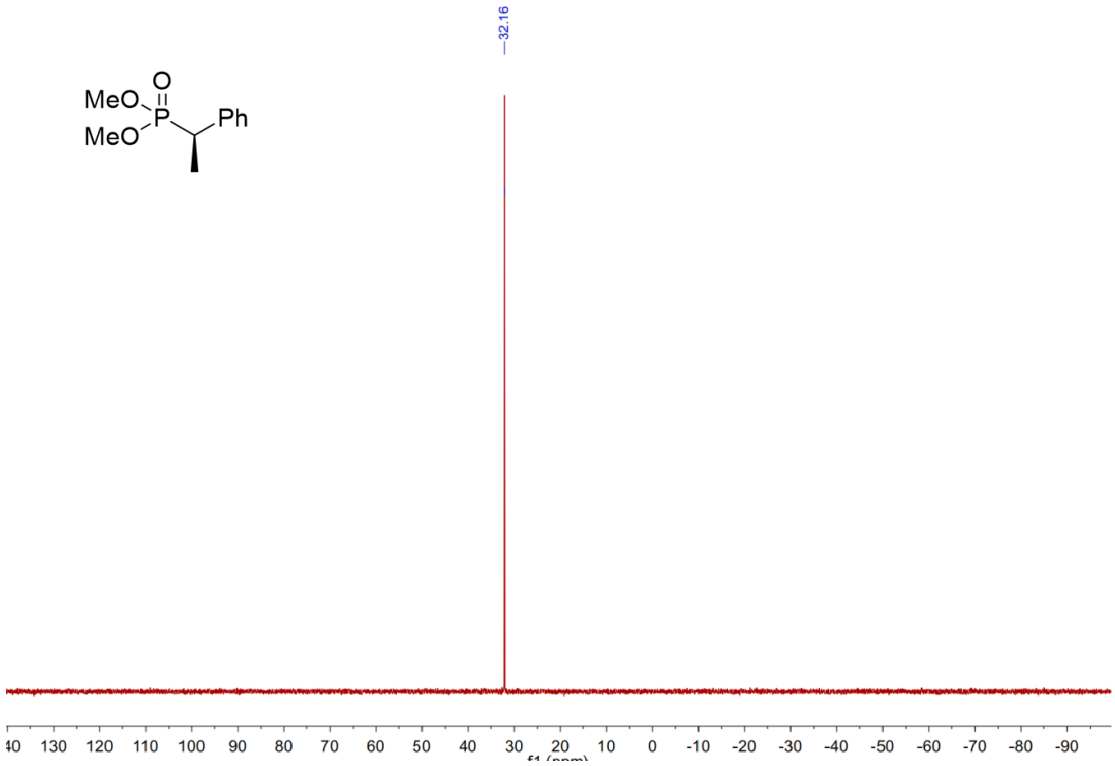
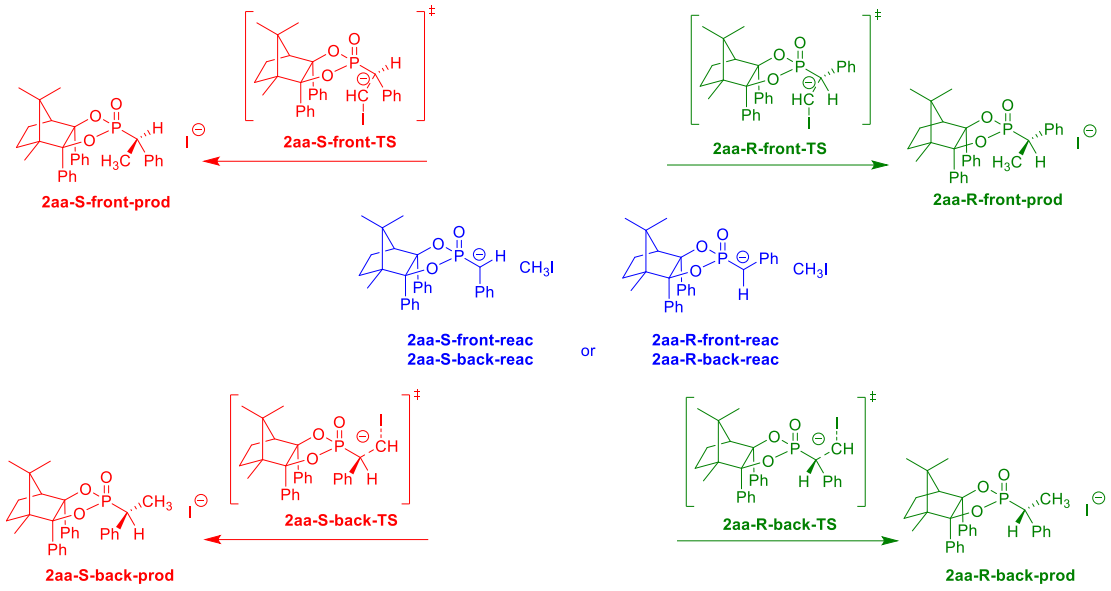


Figure 103: ^{31}P NMR of **4a**

DFT calculation

All calculations were carried out with the density functional theory (DFT) at the M06-2X level [1] of theory using Gaussian 16 series of programs [2]. The def2-SV basis set was used for all the atoms. The gas-phase geometries of all intermediates and transition states were fully optimized without any symmetry restriction, following harmonic frequency calculations to ensure that the local minima had zero imaginary frequencies and the transition state one and to derive the thermal corrections for Gibbs free energies. The transition states had been verified by intrinsic reaction coordinate (IRC) calculation and imaginary vibration modes, which linked reactants and products. Double hybrid functional (B2PLYP method) [3], which could give more accurate energetic information, was used to calculate single point energies with def2-TZVPP basis set. Gibbs free energies of all stationary points were obtained by the thermal correction to Gibbs free energy in gas phase and single point energy in gas phase.

Figure 104. 2D Structures of all stationary points



Supplementary Table 1. Gibbs free energies of all stationary points

Geometry[a]	$E_{(gas\text{-}B2PLYP)}$[b] (Hartree)	$G_{(corr\text{-}M062X)}$ [c] (Hartree)	IF[d]	ΔG[e] (kcal/mol)
2aa-R-front-reac	-2026.95218565100	0.499028	-	0.0
2aa-R-front-TS	-2026.94497415150	0.499980	-437.54	5.1
2aa-R-front-prod	-2027.01999207280	0.505861	-	-38.4
2aa-R-back-reac	-2026.95264002040	0.499799	-	0.0
2aa-R-back-TS	-2026.93311744560	0.502254	-445.16	13.78
2aa-R-back-prod	-2027.01440687890	0.507926	-	-33.64
2aa-S-front-reac	-2026.94130891500	0.499994	-	0.0
2aa-S-front-TS	-2026.93358206540	0.502438	-443.68	6.4
2aa-S-front-prod	-2027.00926694740	0.506250	-	-38.7
2aa-S-back-reac	-2026.96484110940	0.498696	-	0.0
2aa-S-back-TS	-2026.95317654780	0.499763	-458.03	7.98
2aa-S-back-prod	-2027.04060291320	0.505468	-	-43.27

[a] **2aa-R-front-reac**, **2aa-R-back-reac**, **2aa-S-front-reac** and **2aa-S-back-reac** have the same 2D structures and different 3D geometries. [b] The electronic energy calculated by B2PLYP in gas phase. [c] The thermal correction to Gibbs free energy calculated by M062X in gas phase. [d] The M062X calculated imaginary frequencies for the transition states. [e] $\Delta G = [G_{(corr\text{-}M062X)} + E_{(gas\text{-}B2PLYP)}]$ (Sum of electronic and thermal free energies for transition state) - $[G_{(corr\text{-}M062X)} + E_{(gas\text{-}B2PLYP)}]$ (Sum of electronic and thermal free energies for reactant) or $\Delta G = [G_{(corr\text{-}M062X)} + E_{(gas\text{-}B2PLYP)}]$ (Sum of electronic and thermal free energies for product) - $[G_{(corr\text{-}M062X)} + E_{(gas\text{-}B2PLYP)}]$ (Sum of electronic and thermal free energies for reactant)

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[2] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

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