Supplementary Material (ESI) for Chemical Communications

Enantioselective Organocatalytic Phospha-Michael Reaction of α, β-Unsaturated Ketones

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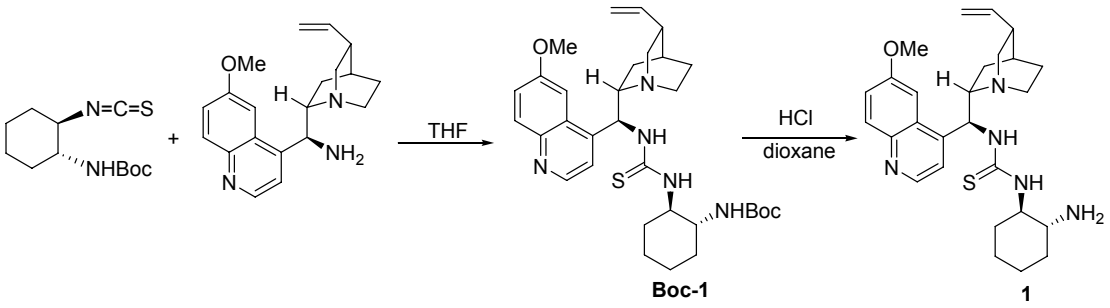
A: General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV-400 spectrometer (400 MHz and 100 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CDCl_3$: δ 7.26) Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ($CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t =triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). Mass spectra (EI) were measured on a Waters Micromass GCT spectrometer. High performance liquid chromatography (HPLC) was performed on an Agilent 1200 Series chromatographs using a Chiracel AS-H column (0.46cm x 25 cm), Chiralpak OD-H (0.46cm x 25 cm), Chiralpak AD-H (0.46cm x 25 cm) and Chiralpak IA (0.46cm x 25 cm) as noted.

Starting Materials. All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. Aromatic enones were prepared following the literature procedures[1]. Different substituted diphenylphospine oxides were prepared following the literature procedures[2].

B: **General Procedure for Preparing Catalysts.**



To a solution of 9-amino(9-deoxy)epiquinine[3] (3.23g, 10mmol) in THF (40 mL) was slowly added a solution of tert-butyl(*1R,2R*)-2-isothio-cyanatocyclohexyl-carbamate[4] (3.07g, 12mmol) 40mL of dry THF at 0°C temperature. The mixture was stirred overnight at room temperature, and the solvent was removed in vacuo. The residue was purified by column chromatography on silica gel affording the compound (**Boc-1**) as a yellowish solid (4.92 g, 85%).

To a solution of **Boc-1** (2.90, 5.0mmol) in dioxane (100 mL) at room temperature was added 4N hydrochloric acid (100 mL) in one portion. The reaction mixture was stirred overnight. Solvents were removed in vacuo and the residue was dissolved in CH_2Cl_2 and water (1:1, 200mL).The aqueous phase was washed with CH_2Cl_2 (3 × 100 mL). Then the aqueous phase PH value was adjusted to 13 with 1N NaOH. The aqueous layer was extracted dichloromethane (4 × 50 mL) and the combined oganic phase was dried by anhydrous Na_2SO_4. Solvent was removed in vacuo affording the product (2.26g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.74 (d, J = 4.8 Hz, 1H), 8.05-7.97 (m, 2H), 7.67-7.38 (m, 2H), 7.36-7.35 (m, 1H), 5.76 (m, 1H), 5.05-4.99 (m, 3H), 4.03 (s, 3H), 3.89-3.79 (m, 2H), 3.32-3.12 (m, 3H), 2.91-2.50 (m, 3H), 2.33 (m, 2H), 2.01-1.88 (m, 2H), 1.69-1.60 (m, 4H), 1.43-1.21 (m, 4H), 0.96-0.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 182.4, 158.4, 148.0, 145.2, 140.9, 132.3, 131.8, 128.8, 122.0, 121.8, 115.2, 102.8, 73.0, 60.7, 56.6, 56.3, 55.8, 55.5, 41.9, 41.2, 40.1, 39.4, 34.2, 32.5, 27.5, 25.9, 25.0.

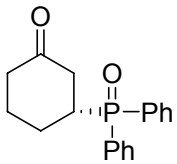
Catalyst **8** was synthesized by 9-amino(9-deoxy)epiquinidine and tert-butyl(*1S,2S*)-2-isothio-cyanatocyclohexylcarbamate. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 8.73 (d, J = 4.0 Hz, 1H), 8.03-8.01 (m, 2H), 7.41-7.39 (m, 2H), 7.36-7.35 (m, 1H), 5.92-5.85 (m, 1H), 5.14-5.10 (m, 3H), 4.02 (s, 3H), 3.98 (m, 2H), 2.99-2.90 (m, 6H), 2.31-2.29 (m, 2H), 1.91-1.79 (m, 2H), 1.67-1.64 (m, 4H), 1.56-1.52 (m, 4H), 0.91-0.81 (m, 1H). ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 182.3, 158.0, 147.4, 144.7, 140.0, 131.2, 128.3, 122.5, 121.5, 120.0, 114.9, 102.4, 73.0, 60.5, 59.3, 57.9, 55.8, 55.7, 48.8, 47.2, 38.9, 32.3, 31.5, 27.2, 26.2, 25.4, 24.7. HRMS (EI): exact mass calculated for M+ (C27H37N5OS) requires m/z 479.2719, found m/z 479.2726.

C: General Procedure for Asymmetric Michael Addition

To a solution of α, β-unsaturated ketone (3.0 mmol) in DCM (2.0 mL) was added diphenylphosphine oxide (1.0 mmol), catalyst (0.10 mmol). The reaction mixture was stirred at gived temperature. After completion monitored by TLC, the product was purified by silica gel chromatography to yield the desired addition product. The enantiomeric excess of the product was determined by HPLC analysis on chiral column.

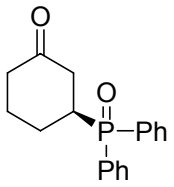
D: Characterization Data of Michael Addition Products

3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 1)



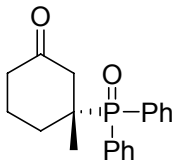
Prepared according to general procedure. The reaction was carried out in dried DCM for 2 days. The product was obtained in 94% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.78-7.73 (m, 4H), 7.52-7.50 (m, 6H), 2.81-2.62 (m, 2H), 2.39-2.34 (m, 2H), 2.30-2.28 (m, 1H), 2.21-2.17 (m, 1H), 1.96-1.83 (m, 2H), 1.72-1.69 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.8; 131.9; 131.9; 130.9; 130.8; 128.9; 128.8; 41.2; 39.3; 38.1; 26.4; 23.3. HRMS (ESI): exact mass calculated for M^+ ($C_{18}H_{19}O_2P$+H) requires m/z 299.1201, found m/z 299.1195. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/i-PrOH = 9/1, 0.8 ml/min]: 28.228 min (major), 24.078 min (minor), ee=90%.

3-(diphenylphosphoryl)cyclohexanone (Table 1, entry 16)



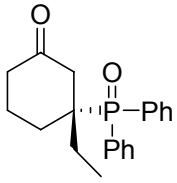
Prepared according to general procedure. The reaction was carried out in dried DCM for 2 days. The product was obtained in 90% yield, white solid. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 7.75-7.66 (m, 4H), 7.42-7.33 (m, 6H), 2.70-2.52 (m, 2H), 2.31-2.17 (m, 3H), 2.08-2.04 (m, 1H), 1.92-1.80 (m, 1H), 1.76-1.55 (m, 2H). ^{13}C NMR (100 MHz, CDCl3): δ (ppm) 209.5, 131.9, 131.6, 131.1, 130.8, 130.8, 130.7, 130.7, 130.6, 130.2, 128.8, 128.7, 41.0, 39.3, 37.9, 37.2, 23.3. HRMS (EI): exact mass calculated for M+ (C18H19O2P) requires m/z 298.1123, found m/z 298.1120. The enantiomeric excess was determined by HPLC. [AS-H column, 220nm, hexane/i-PrOH = 9/1, 0.8 ml/min]: 21.039 min (major), 18.944 min (minor), ee=90%.

3-(diphenylphosphoryl)-3-methylcyclohexanone (Table 2, entry 2)



Prepared according to general procedure. The reaction was carried out in dried DCM for 6 days. The product was obtained in 96% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92-7.87 (m, 2H), 7.79-7.74 (m, 2H), 7.49-7.47 (m, 6H), 2.78-2.64 (m, 2H), 2.54-2.49 (m, 1H), 2.35-2.31 (m, 1H), 2.23-2.18 (m, 1H), 1.76-1.69 (m, 3H), 0.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.8; 134.8; 132.4; 131.6; 131.5; 130.8; 130.7; 130.6; 130.5; 128.8; 128.7; 128.5; 45.2; 42.5; 37.7; 34.5; 31.0; 22.3. HRMS (ESI): exact mass calculated for M^+ ($C_{19}H_{21}O_2P$+H) requires m/z 313.1357, found m/z 313.1359. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/i-PrOH = 9/1, 0.8 ml/min]: 25.748 min (major), 33.770 min (minor), ee=98%.

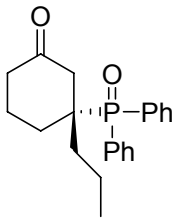
3-(diphenylphosphoryl)-3-ethylcyclohexanone (Table 2, entry 3)



Prepared according to general procedure. The reaction was carried out in dried DCM for 6 days. The product was obtained in 95% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02-7.93 (m, 4H), 7.57-7.48 (m, 6H), 2.68-2.62 (m, 2H), 2.50-2.44 (m, 1H), 2.32-2.15

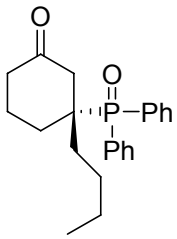
(m, 3H), 2.10-2.05 (m, 2H), 1.89-1.73 (m, 2H), 0.82 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.7; 132.2; 132.1; 132.1; 132.0; 128.6; 128.5; 128.4; 46.1; 44.3; 40.3; 26.7; 25.9; 21.3; 8.7. HRMS (ESI): exact mass calculated for M^+ ($C_{20}H_{23}O_2P$+H) requires m/z 327.1514, found m/z 327.1511. The enantiomeric excess was determined by HPLC. [IC-H column, 254nm, hexane/EtOH = 7/3, 0.8 ml/min]: 20.282 min (major), 16.369 min (minor), ee=94%.

3-(diphenylphosphoryl)-3-propylcyclohexanone (Table 2, entry 4)



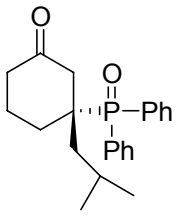
Prepared according to general procedure. The reaction was carried out in dried DCM for 6 days. The product was obtained in 87% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01-7.92 (m, 4H), 7.54-7.42 (m, 6H), 2.65-2.45 (m, 2H), 2.33-2.02 (m, 5H), 1.89-1.78 (m, 1H), 1.64-1.15 (m, 4H), 0.70 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.8; 132.1; 132.1; 132.0; 131.9; 131.0; 130.1; 128.6; 128.5; 128.5; 128.4; 46.5; 45.0; 40.3; 35.4; 27.1; 21.3; 17.3; 14.6. HRMS (ESI): exact mass calculated for M^+ ($C_{21}H_{25}O_2P$+H) requires m/z 341.1670, found m/z 341.1666. The enantiomeric excess was determined by HPLC. [AS-H column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]: 7.131 min (major), 7.791 min (minor), ee=94%.

3-butyl-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 5)



Prepared according to general procedure. The reaction was carried out in dried DCM for 7 days. The product was obtained in 85% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.99-7.94 (m, 4H), 7.54-7.50 (m, 6H), 2.62-1.84 (m, 8H), 1.65-0.67 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.6, 209.5; 132.2; 132.1; 132.1; 132.0; 131.8; 131.8; 128.6; 128.5; 128.4; 46.7; 44.8; 40.4; 32.8; 27.1; 25.9; 23.1; 21.4; 13.5. HRMS (ESI): exact mass calculated for M^+ ($C_{22}H_{27}O_2P$+H) requires m/z 355.1827, found m/z 327.1833. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/EtOH = 9/1, 0.8 ml/min]: 23.339 min (major), 16.357 min (minor), ee=97%.

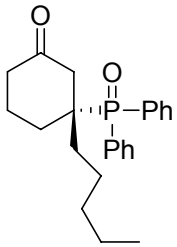
3-(diphenylphosphoryl)-3-isobutylcyclohexanone (Table 2, entry 6)



Prepared according to general procedure. The reaction was carried out in dried DCM for 8 days. The product was obtained in 88% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02-7.90 (m, 4H), 7.59-7.49 (m, 6H), 2.59-2.57 (m, 2H), 2.28-2.23 (m, 3H), 2.08-1.91 (m, 4H), 1.62-1.41 (m, 2H), 0.79-0.78 (d, J = 8 Hz, 3H), 0.71-0.69 (d, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.3; 132.2; 132.1; 132.1; 132.0; 131.8; 131.7; 131.3; 130.4; 128.6; 128.5; 128.4; 47.1; 45.8; 42.4; 40.2; 28.3; 25.1; 24.7; 24.4; 21.4. HRMS (ESI): exact mass calculated for M^+ ($C_{22}H_{27}O_2P$+H) requires m/z 355.1827, found m/z 355.1820. The enantiomeric excess

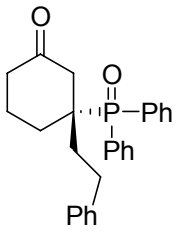
was determined by HPLC. [AS-H column, 220nm, hexane/EtOH = 9/1, 0.8 ml/min]: 11.126 min (major), 14.486 min (minor), ee=94%.

3-(diphenylphosphoryl)-3-pentylcyclohexanone (Table 2, entry 7)



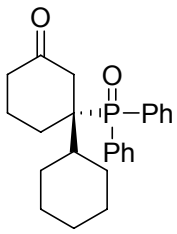
Prepared according to general procedure. The reaction was carried out in dried DCM for 8 days. The product was obtained in 94% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02-7.93 (m, 4H), 7.67-7.49 (m, 6H), 2.67-2.45 (m, 2H), 2.29-2.05 (m, 5H), 1.86-1.82 (m, 1H), 1.70-1.42 (m, 2H), 1.35-1.00 (m, 6H), 0.76-0.73 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.8; 132.2; 132.1; 132.0; 131.9; 131.1; 130.2; 128.6; 128.5; 128.5; 128.4; 46.7; 44.2; 40.4; 33.0; 32.3; 29.6; 27.0; 23.4; 22.0; 13.8. HRMS (ESI): exact mass calculated for M^+ ($C_{23}H_{29}O_2P$+H) requires m/z 369.1983, found m/z 369.1985. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/i-PrOH = 9/1, 0.8 ml/min]: 22.070 min (major), 16.301 min (minor), ee=92%.

3-(diphenylphosphoryl)-3-phenethylcyclohexanone (Table 2, entry 8)



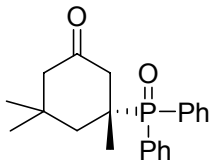
Prepared according to general procedure. The reaction was carried out in dried DCM for 15 days. The product was obtained in 82% yield, white solid. ^{1}H NMR (400 MHz, CDCl3): δ (ppm) 8.06-7.97 (m, 4H), 7.57-7.51 (m, 6H), 7.17-6.81 (m, 5H), 2.74-2.46 (m, 4H), 2.32-2.29 (m, 2H), 2.24-2.14 (m, 1H), 2.09-1.93 (m, 2H), 1.92-1.69 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.3; 141.1; 132.1; 128.8; 128.7; 128.7; 128.3; 128.0; 125.9; 46.8; 45.0; 40.5; 35.3; 30.5; 27.2; 21.4. HRMS (ESI): exact mass calculated for M+ (C26H27O2P+H) requires m/z 403.1827, found m/z 403.1819. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]: 9.839 min (major), 8.508 min (minor), ee=92%.

3-cyclohexyl-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 9)



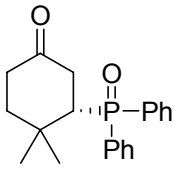
Prepared according to general procedure. The reaction was carried out in dried DCM for 6 days. The product was obtained in 85% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02-7.93 (m, 4H), 7.58-7.51 (m, 6H), 2.66-2.45 (m, 2H), 2.33-2.19 (m, 3H), 2.08-2.04 (m, 2H), 1.86-1.83 (m, 1H), 1.15-1.04 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.7; 132.2; 132.1; 132.1; 131.8; 131.8; 131.1; 130.2; 128.6; 128.5; 128.5; 128.4; 46.7; 44.2; 40.4; 33.1; 31.1; 29.7; 27.1; 23.7; 23.7; 22.3; 13.9. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{29}O_2P$+H) requires m/z 381.1983, found m/z 383.200. The enantiomeric excess was determined by HPLC. [AS-H column, 254nm, hexane/EtOH = 4/1, 0.8 ml/min]: 18.840 min (major), 16.997 min (minor), ee=90%.

3-(diphenylphosphoryl)-3,5,5-trimethylcyclohexanone (Table 2, entry 10)



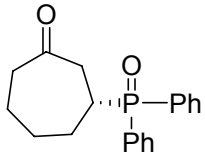
Prepared according to general procedure. The reaction was carried out in dried DCM for 8 days. The product was obtained in 90% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02-7.85 (m, 4H), 7.58-7.48 (m, 6), 2.49-2.33 (m, 2H), 2.13-2.10 (m, 2H), 1.69-1.64 (m, 2H), 1.42-1.37 (m, 3H), 1.05 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 210.5; 132.4; 132.0; 131.9; 130.1; 129.2; 129.1; 128.6; 128.5; 53.5; 45.1; 41.4; 37.1; 33.9; 28.8; 22.1. HRMS (ESI): exact mass calculated for M^+ ($C_{21}H_{25}O_2P$+Na) requires m/z 341.1670, found m/z 341.1667. The enantiomeric excess was determined by HPLC. [IC column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]:18.838 min (major), 16.102 min (minor), ee=96%.

3-(diphenylphosphoryl)-4,4-dimethylcyclohexanone (Table 2, entry 11)



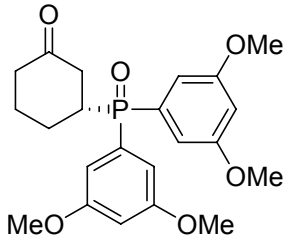
Prepared according to general procedure. The reaction was carried out in dried DCM for 2.5 days. The product was obtained in 95% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91-7.87 (m, 2H), 7.78-7.74 (m, 2H), 7.75-7.47 (m, 6H), 2.75-2.68 (m, 1H), 2.58-2.49 (m, 1H), 2.35-2.17 (m, 2H), 1.77-1.75 (m, 3H), 1.42 (s, 3H), 0.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.9; 131.6; 131.5; 130.8; 130.7; 130.6; 128.8; 128.7; 128.6; 42.7; 42.6; 37.9; 37.8; 34.4; 31.0; 22.2. HRMS (ESI): exact mass calculated for M^+ ($C_{20}H_{23}O_2P$+H) requires m/z 327.1514, found m/z 327.1527. The enantiomeric excess was determined by HPLC. [AS-H column, 220nm, hexane/EtOH = 92/8, 0.8 ml/min]: 14.553 min (major), 12.361 min (minor), ee=98%.

3-(diphenylphosphoryl)cycloheptanone (Table 2, entry 12)



Prepared according to general procedure. The reaction was carried out in dried DCM for 6 days. The product was obtained in 87% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.79-7.77 (m, 4H), 7.51-7.49 (m, 6H), 2.79-2.77 (m, 1H), 2.56-2.51 (m, 4H), 2.07-1.92 (m, 3H), 1.66-1.63 (m, 2H), 1.37-1.34 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 212.2; 131.9; 131.8; 131.1; 130.9; 130.9; 130.8; 128.8; 128.7; 128.6; 43.6; 41.7; 34.9; 29.2; 28.8; 23.6. HRMS (ESI): exact mass calculated for M^+ ($C_{19}H_{21}O_2P$+H) requires m/z 313.1357, found m/z 313.1344. The enantiomeric excess was determined by HPLC. [AD-H column, 220nm, hexane/EtOH = 4/1, 0.8 ml/min]: 28.104 min (major), 23.236 min (minor), ee=90%.

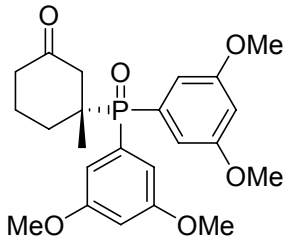
3-(bis(3,5-dimethoxyphenyl)phosphoryl)cyclohexanone (Table 2, entry 13)



Prepared according to general procedure. The reaction was carried out in dried DCM for 2.5 days. The product was obtained in 86% yield, white solid. ^{1}H NMR (400 MHz,

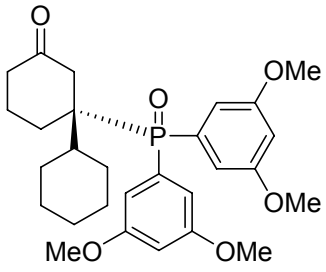
$CDCl_3$): δ (ppm) 6.90-6.54 (m, 6H), 3.77 (s, 12H), 2.60-2.55 (m, 2H), 2.35-2.16 (m, 3H), 1.92-1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.5, 209.4; 161.0; 108.3; 103.5; 55.4; 40.9; 39.1; 37.8; 26.2; 23.2. HRMS (ESI): exact mass calculated for M^+ ($C_{22}H_{27}O_6P$+H) requires m/z 419.1624, found m/z 419.1640. The enantiomeric excess was determined by HPLC. [AS-H column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]: 8.416 min (major), 12.238 min (minor), ee=91%.

3-(bis(3,5-dimethoxyphenyl)phosphoryl)-3-methylcyclohexanone (Table 2, entry 14)



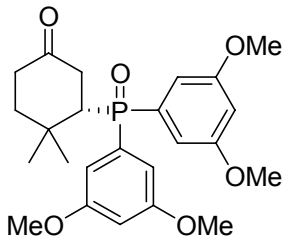
Prepared according to general procedure. The reaction was carried out in dried DCM for 3.0 days. The product was obtained in 84% yield, white solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.09-7.00 (m, 4H), 6.60-6.58 (m, 2H), 3.81 (s, 12H), 2.95-2.89 (m, 1H), 2.30-2.17 (m, 4H), 2.06-2.04 (m, 1H), 1.88-1.83 (m, 1H), 1.83-1.71 (m, 1H), 1.24-1.20 (d, J = 16.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 210.1; 160.8; 131.7; 130.8; 110.0; 109.9; 103.7; 55.5; 46.5; 42.1; 40.7; 29.0; 21.7; 18.9. HRMS (ESI): exact mass calculated for M^+ ($C_{23}H_{29}O_6P$+H) requires m/z 433.1780, found m/z 433.1776. The enantiomeric excess was determined by HPLC. [IA column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]: 13.115 min (major), 10.396 min (minor), ee=94%.

3-(bis(3,5-dimethoxyphenyl)phosphoryl)-3-cyclohexylcyclohexanone (Table 2, entry 15)



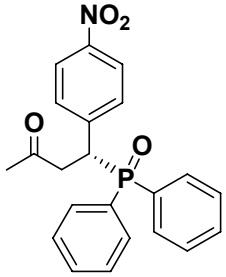
Prepared according to general procedure. The reaction was carried out in dried DCM for 4 days.The product was obtained in 92% yield, white solid. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.10-7.05 (m, 4H), 6.60 (s, 2H), 3.83 (s, 12H), 2.67-2.45 (m, 2H), 2.32-2.04 (m, 6H), 1.87-1.26 (m, 4H), 1.16-1.07 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.8; 160.8; 160.8; 160.7; 160.6; 132.8; 132.7; 131.8; 109.9; 109.8; 109.7; 103.6; 55.5; 46.6; 44.3; 40.4; 33.0; 31.2; 29.7; 27.2; 23.7; 22.3; 21.4; 13.9. HRMS (ESI): exact mass calculated for M^+ ($C_{28}H_{37}O_6P$+H) requires m/z 501.2406, found m/z 501.2411. The enantiomeric excess was determined by HPLC. [IA column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]: 10.277 min (major), 9.656 min (minor), ee=94%.

3-(bis(3,5-dimethoxyphenyl)phosphoryl)-4,4-dimethylcyclohexanone (Table 2, entry 16)



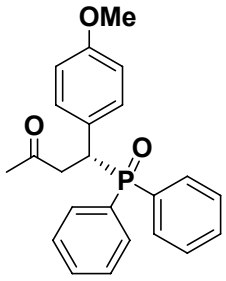
Prepared according to general procedure. The reaction was carried out in dried DCM for 2.5 days. The product was obtained in 90% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.98 (d, *J* = 12.0 Hz, 2H), 6.58 (d, *J* = 12.0 Hz, 2H), 6.51 (d, *J* = 12.0 Hz, 2H), 3.77 (d, *J* = 12.0 Hz, 12H), 2.70-2.45 (m, 3H), 2.31-2.20 (m, 2H), 1.75-1.68 (m, 2H), 1.38 (s, 3H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 209.9; 161.1; 160.9; 136.6; 134.3; 108.6; 108.2; 108.1; 103.4; 103.3; 55.5; 45.0; 42.3; 37.7; 34.4; 30.8; 22.3. HRMS (ESI): exact mass calculated for M^+ ($C_{24}H_{31}O_6P$+H) requires m/z 447.1937, found m/z 447.1920. The enantiomeric excess was determined by HPLC. [AS-H column, 220nm, hexane/EtOH = 7/3, 0.8 ml/min]: 8.005 min (major), 6.664 min (minor), ee=98%.

4-(diphenylphosphoryl)-4-(4-nitrophenyl)butan-2-one (Table 2, entry 17)



Prepared according to general procedure. The reaction was carried out in dried DCM for 2 days. The product was obtained in 90% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.04-7.92 (m, 4H), 7.59-7.29 (m, 10H), 4.36-4.30 (m, 1H), 3.31-3.09 (m, 1H), 3.03-2.95 (m, 1H), 2.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 204.5; 146.8; 144.0; 144.0; 132.4; 131.9; 131.1; 131.0; 130.7; 130.6; 130.5; 130.5; 129.1; 128.4; 128.3; 123.3; 43.4; 41.4, 40.7; 30.3. HRMS (ESI): exact mass calculated for M^+ ($C_{22}H_{20}NO_4P$+H) requires m/z 394.1208, found m/z 394.1204. The enantiomeric excess was determined by HPLC. [IC column, 220nm, hexane/EtOH = 4/1, 0.8 ml/min]: 30.587 min (major), 16.530 min (minor), ee=92%.

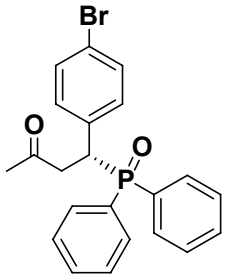
4-(diphenylphosphoryl)-4-(4-methoxyphenyl)butan-2-one (Table 2, entry 18)



Prepared according to general procedure. The reaction was carried out in dried DCM for 2 days. The product was obtained in 97% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94-7.92 (m, 2H), 7.55-7.21 (m, 10H), 6.72-6.70 (m, 2H), 4.36-4.30 (m, 1H), 3.37 (s, 3H), 3.30-3.24 (m, 1H), 2.93-2.86 (m, 1H) ,1.96 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.5; 158.5; 132.0; 131.9; 131.9; 131.4; 131.3; 131.2; 131.1; 130.9; 130.7; 130.6; 128.9; 128.7; 128.1; 128.0; 127.6, 127.5; 113.7; 55.0; 43.6; 40.4, 39.7; 30.6. HRMS (ESI): exact mass calculated for M^+ ($C_{23}H_{23}O_3P$+H) requires m/z 379.1463, found m/z 379.1468. The enantiomeric excess was determined by HPLC. [AS-H column, 220nm,

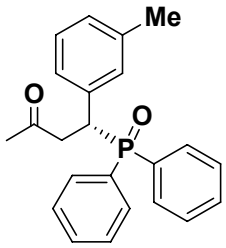
hexane/EtOH = 9/1, 0.8 ml/min]: 13.057 min (major), 14.241 min (minor), ee=85%.

4-(4-bromophenyl)-4-(diphenylphosphoryl)butan-2-one (Table 2, entry 19)



Prepared according to general procedure. The reaction was carried out in dried DCM for 2 days. The product was obtained in 94% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93-7.92 (m, 2H), 7.57-7.19 (m, 12H), 4.22-4.17 (m, 1H), 3.31-3.23 (m, 1H), 2.97-2.89 (m, 1H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.1; 135.0; 132.1; 131.6; 131.5; 131.4; 131.3; 131.2; 131.1; 130.8; 130.7; 130.6; 130.5; 43.4; 40.7, 40.0; 30.5. HRMS (ESI): exact mass calculated for M^+ ($C_{22}H_{20}BrO_2P$+H) requires m/z 427.0463, found m/z 427.0450. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/i-PrOH = 9/1, 0.8 ml/min]: 18.353 min (major), 13.833 min (minor), ee=94%.

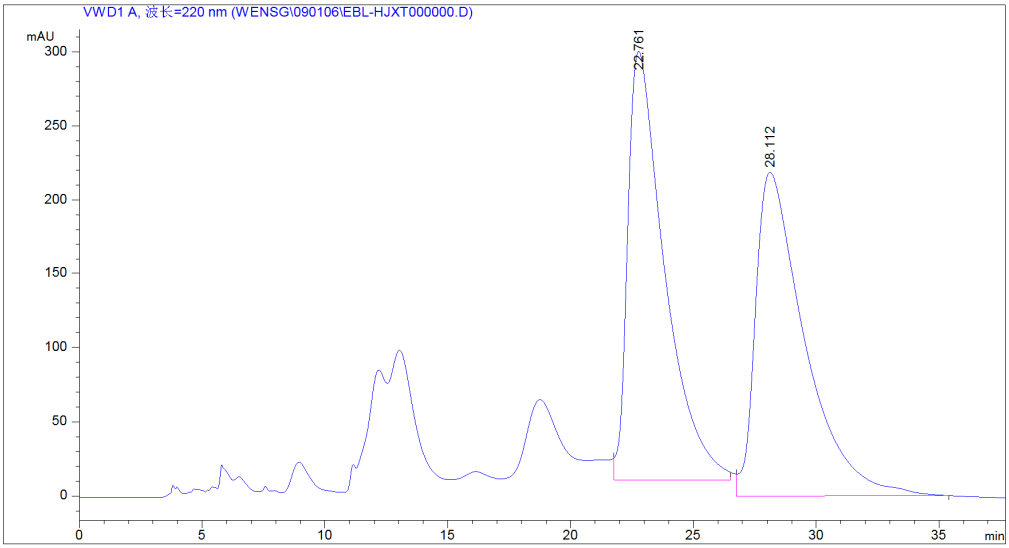
4-(diphenylphosphoryl)-4-m-tolylbutan-2-one (Table 2, entry 20)



Prepared according to general procedure. The reaction was carried out in dried DCM for 2 days. The product was obtained in 92% yield, white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95-7.91 (m, 2H), 7.59-7.23 (m, 8H), 7.10-7.04 (m, 3H), 6.96-6.94 (m, 1H), 4.22-4.16 (m, 1H), 3.36-3.28 (m, 1H), 2.98-2.91 (m, 1H), 2.22 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 205.5; 137.8; 135.5; 135.4; 132.0; 131.3; 131.2; 131.0; 130.9; 128.9; 128.8; 128.1; 128.0; 127.9; 126.7; 43.3; 41.3, 40.6; 30.6; 21.2. HRMS (ESI): exact mass calculated for M^+ ($C_{23}H_{23}O_2P$+H) requires m/z 363.1514, found m/z 363.1496. The enantiomeric excess was determined by HPLC. [OD-H column, 220nm, hexane/i-PrOH = 9/1, 0.8 ml/min]: 13.096 min (major), 12.008 min (minor), ee=84%.

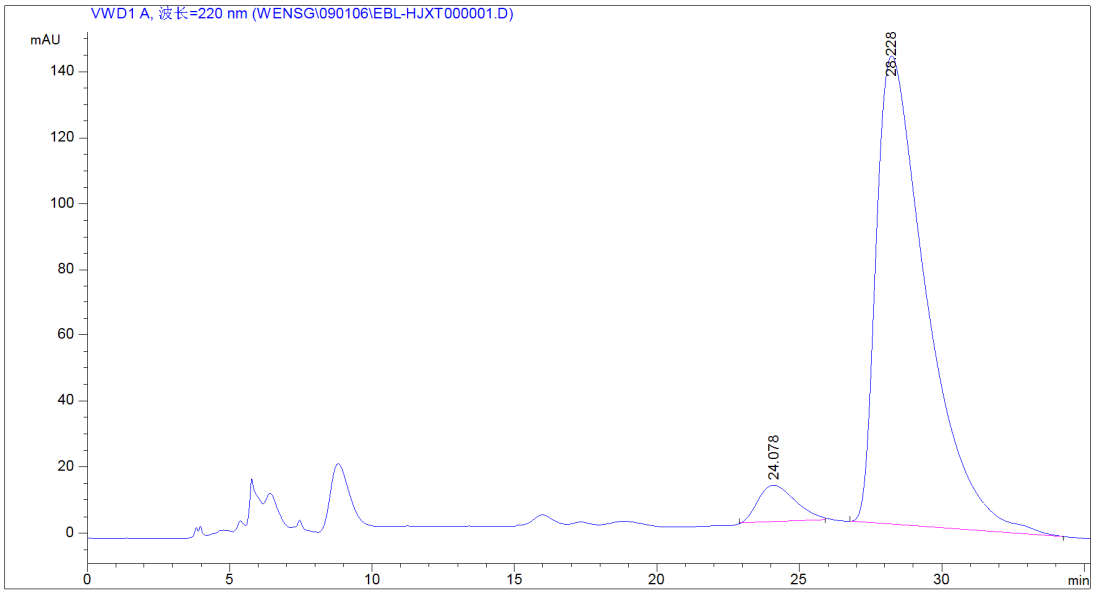
E: HPLC Analysis of Michael Addition Products

(R)-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 1)



Racemic adduct (sample in EtOH)

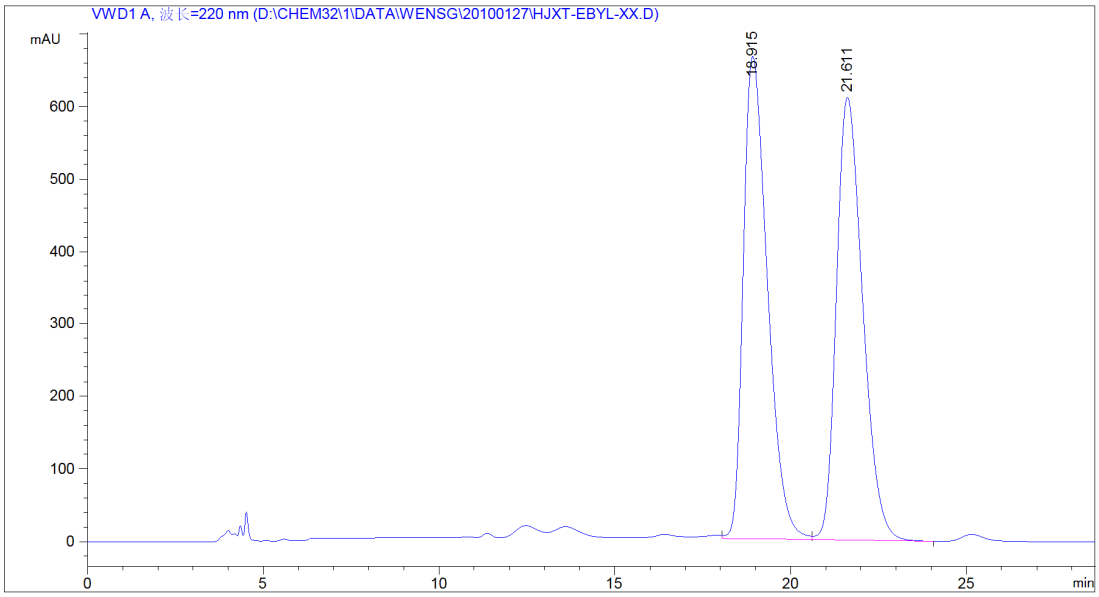
#	time	Area	Height	Width	Area%
1	22.761	30201.5	289.57	1.7363	49.8190
2	28.112	30420.9	218.77	2.0198	50.1610



Asymmetric adduct (sample in EtOH)

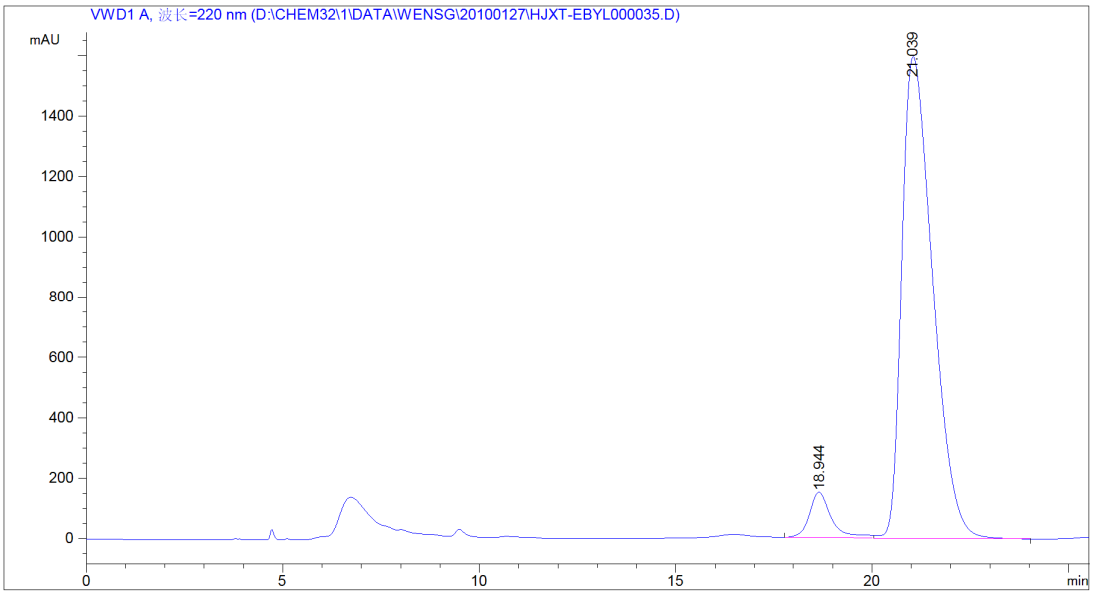
#	time	Area	Height	Width	Area%
1	24.078	1011.54	11.11	1.5163	4.9770
2	26.228	17457.3	142.1	1.7941	95.0230

(S)-3-(diphenylphosphoryl)cyclohexanone (Table 1, entry 16)



Racemic adduct (sample in EtOH)

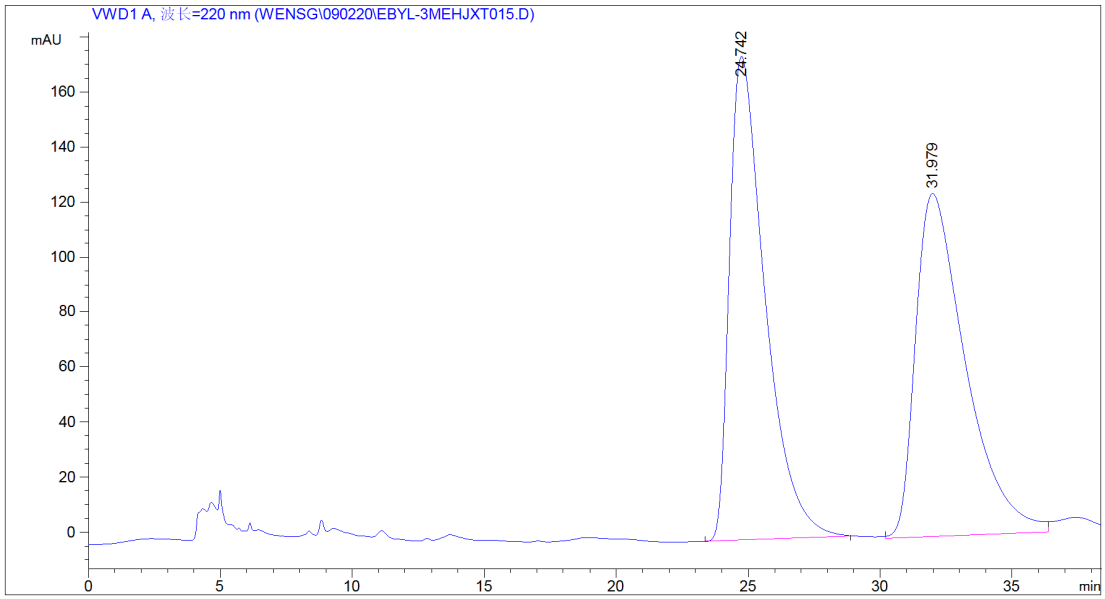
#	Time	Area	Height	Width	Area %
1	18.915	31785.6	665.7	0.7391	50.0860
2	21.611	31676.5	610.9	0.8073	49.9140



Asymmetric adduct (sample in EtOH)

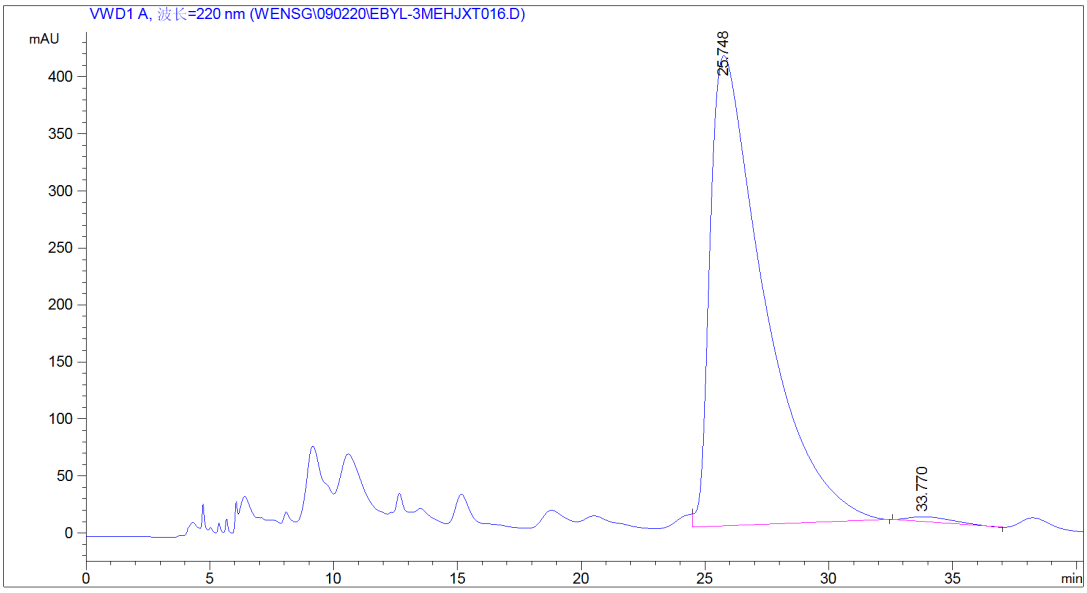
#	Time	Area	Height	Width	Area %
1	18.944	3580.6	158.65	0.6349	4.7943
2	21.039	87322.8	1596.81	0.8477	95.2057

3-(diphenylphosphoryl)-3-methylcyclohexanone (Table 2, entry 2)



Racemic adduct (sample in EtOH)

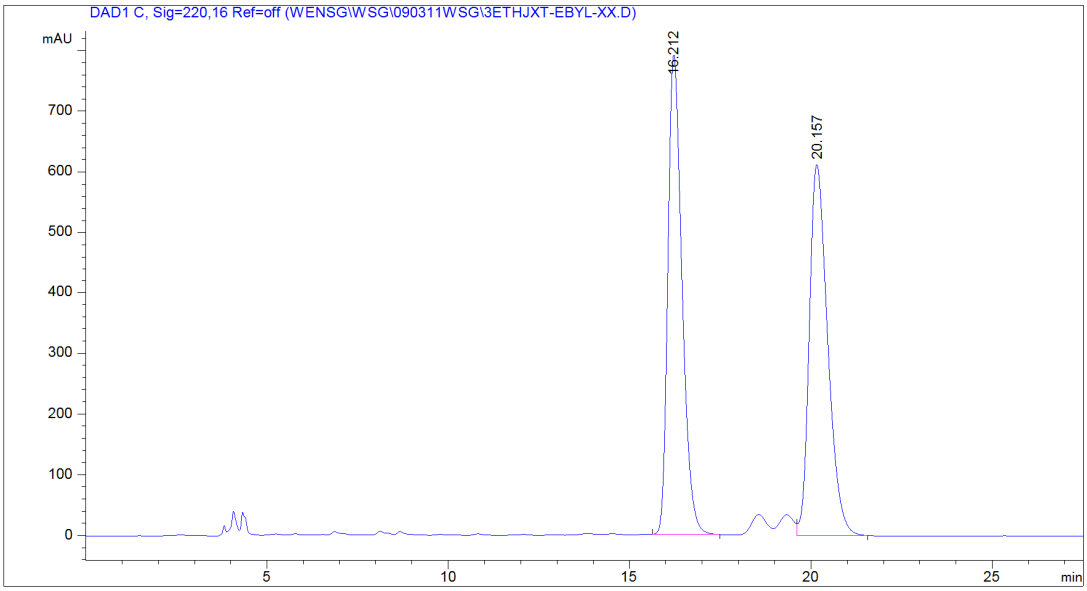
#	time	Area	Height	Width	Area%
1	24.742	16479.0	175.8	1.3920	50.095
2	34.997	16415.9	124.7	2.1930	49.904



Asymmetric adduct (sample in EtOH)

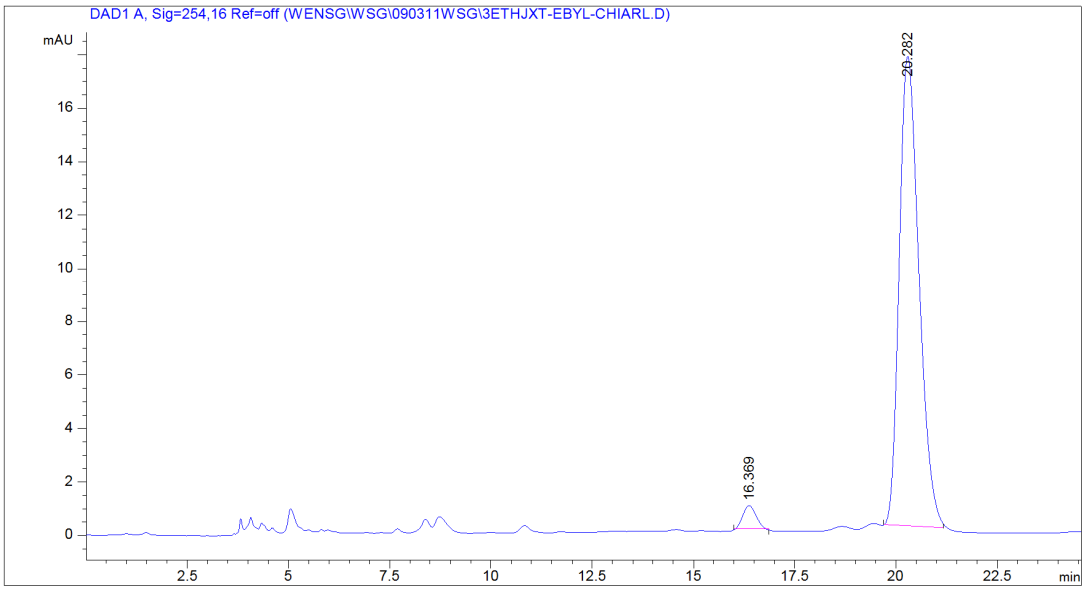
#	time	Area	Height	Width	Area%
1	25.748	62551.7	412.5	2.5268	99.0854
2	33.770	577.3	4.4	1.5376	0.9146

3-(diphenylphosphoryl)-3-ethylcyclohexanone (Table 2, entry 3)



Racemic adduct (sample in EtOH)

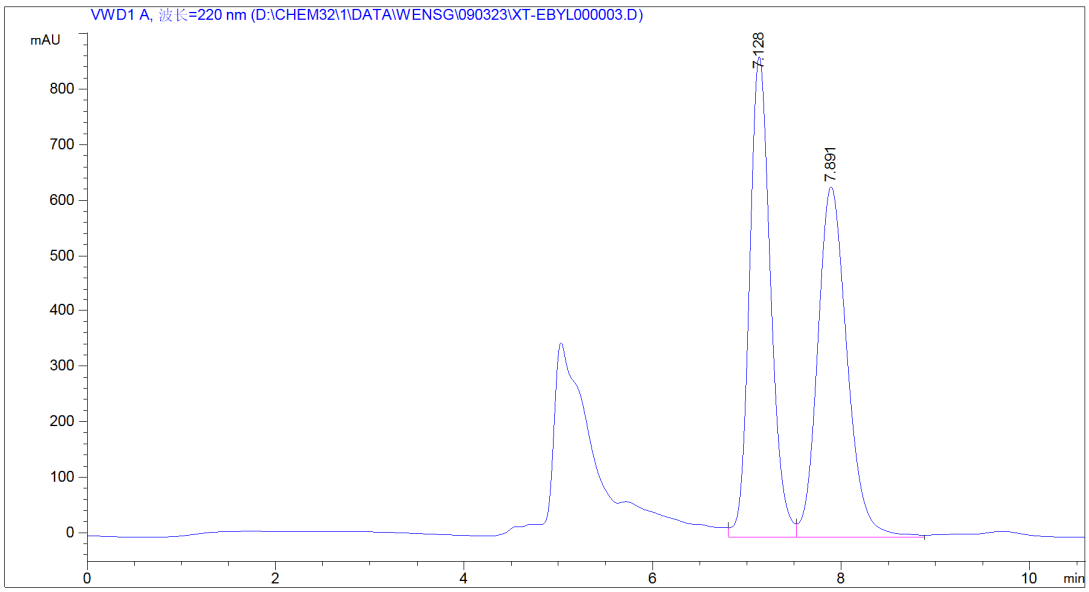
#	time	Area	Height	Width	Area%
1	16.212	21414.7	791.2	0.4158	49.8518
2	20.157	21541.9	611.7	0.5388	50.1482



Asymmetric adduct (sample in EtOH)

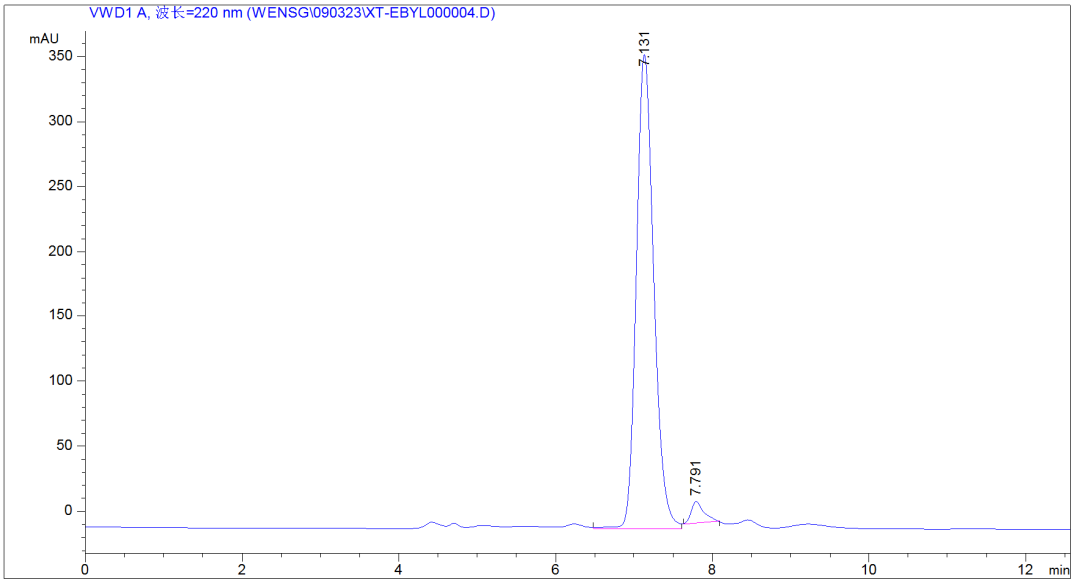
#	time	Area	Height	Width	Area%
1	16.369	19.5	0.8	0.3754	3.1711
2	20.282	595.7	17.5	0.5252	96.8289

3-(diphenylphosphoryl)-3-propylcyclohexanone (Table 2, entry 4)



Racemic adduct (sample in EtOH)

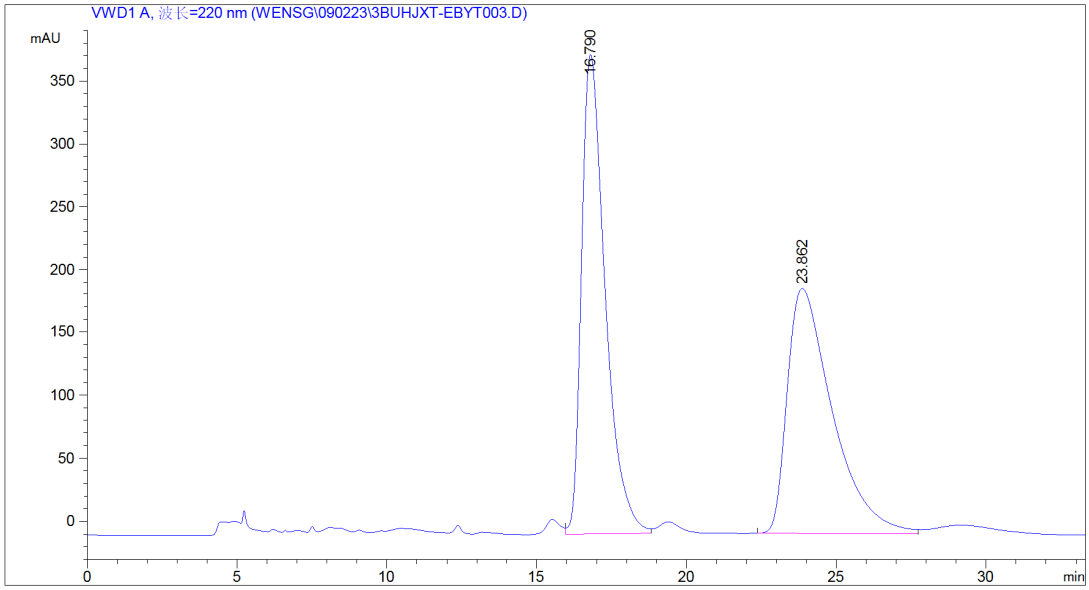
#	time	Area	Height	Width	Area%
1	7.128	13500.6	866.3	0.2399	49.5848
2	7.891	13726.7	632.7	0.3361	50.4152



Asymmetric adduct (sample in EtOH)

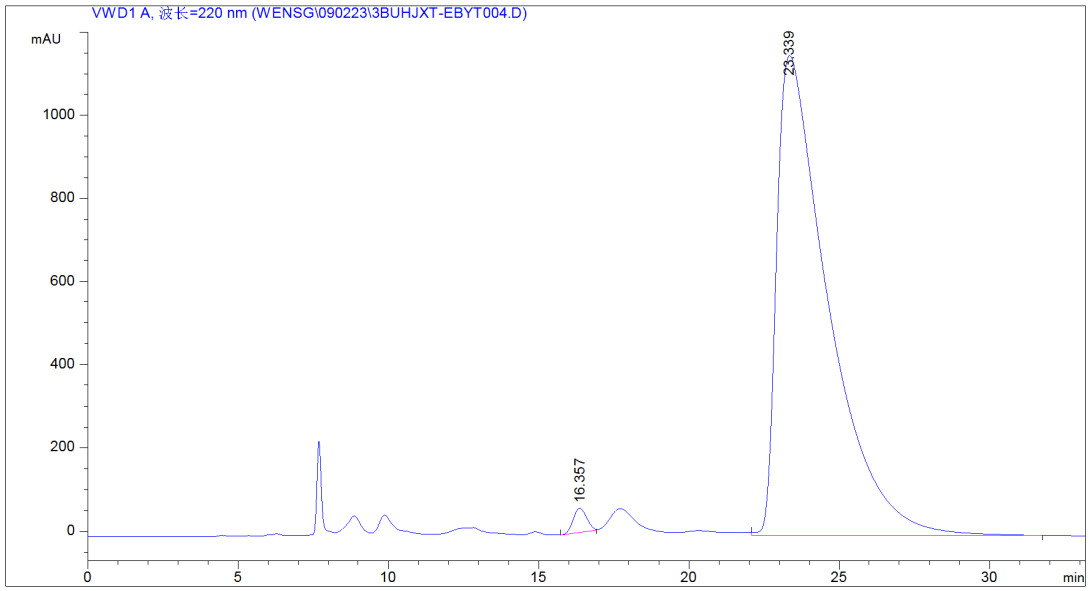
#	time	Area	Height	Width	Area%
1	7.131	5634.4	364.7	0.2370	96.7217
2	7.791	190.9	16.7	0.1896	3.2783

3-butyl-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 5)



Racemic adduct (sample in EtOH)

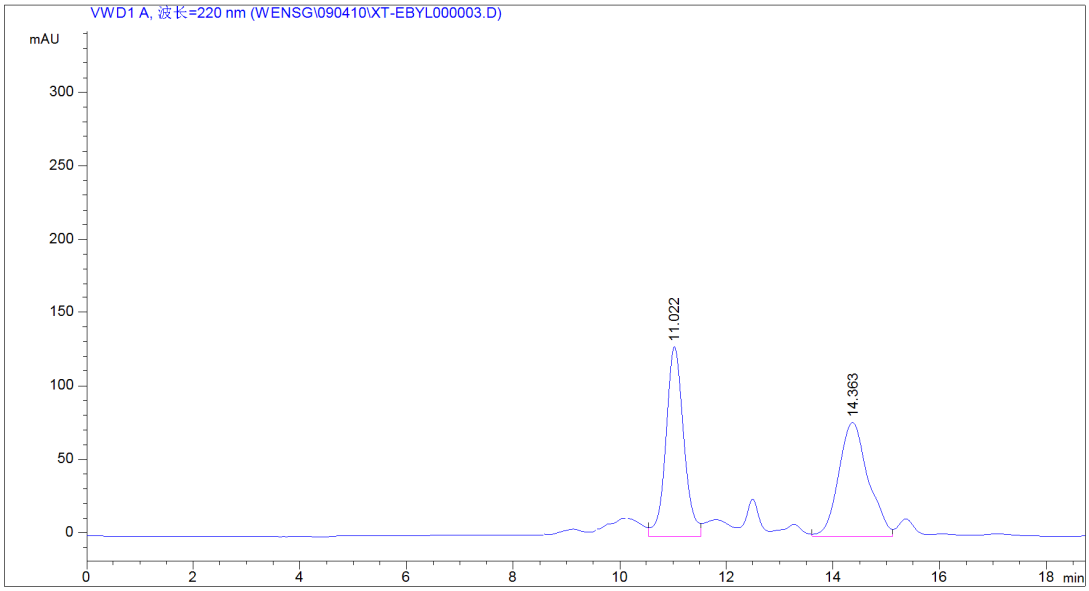
#	time	Area	Height	Width	Area%
1	16.790	20951.2	381.0	0.8292	50.7288
2	23.862	20349.3	194.0	1.5292	49.2712



Asymmetric adduct (sample in EtOH)

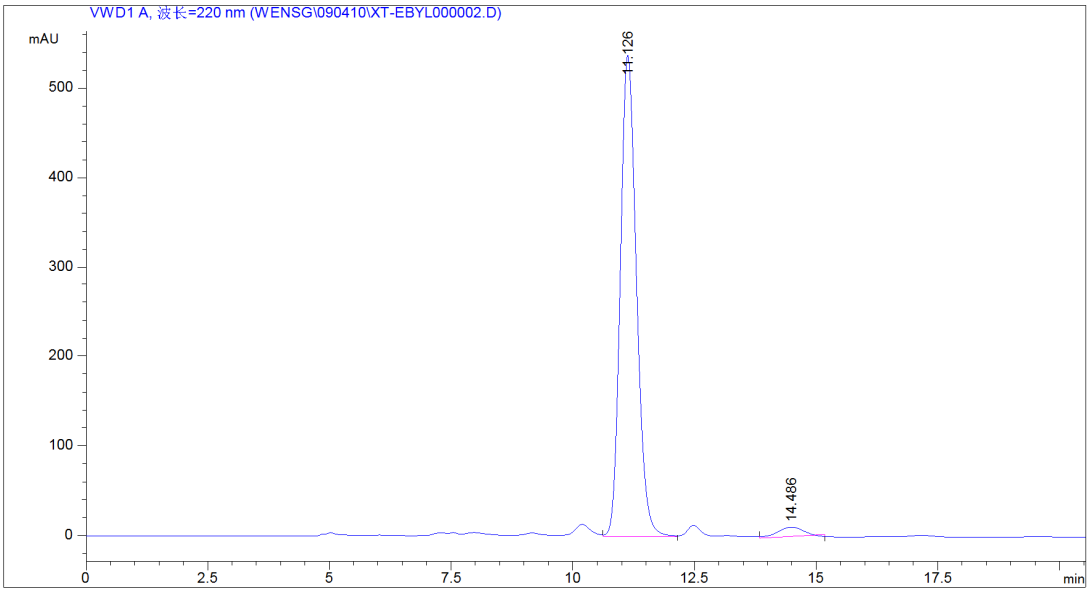
#	time	Area	Height	Width	Area%
1	16.357	1874.0	58.6	0.5326	1.3480
2	23.339	137153	1153.6	1.6652	98.6520

3-(diphenylphosphoryl)-3-isobutylcyclohexanone (Table 2, entry 6)



Racemic adduct (sample in EtOH)

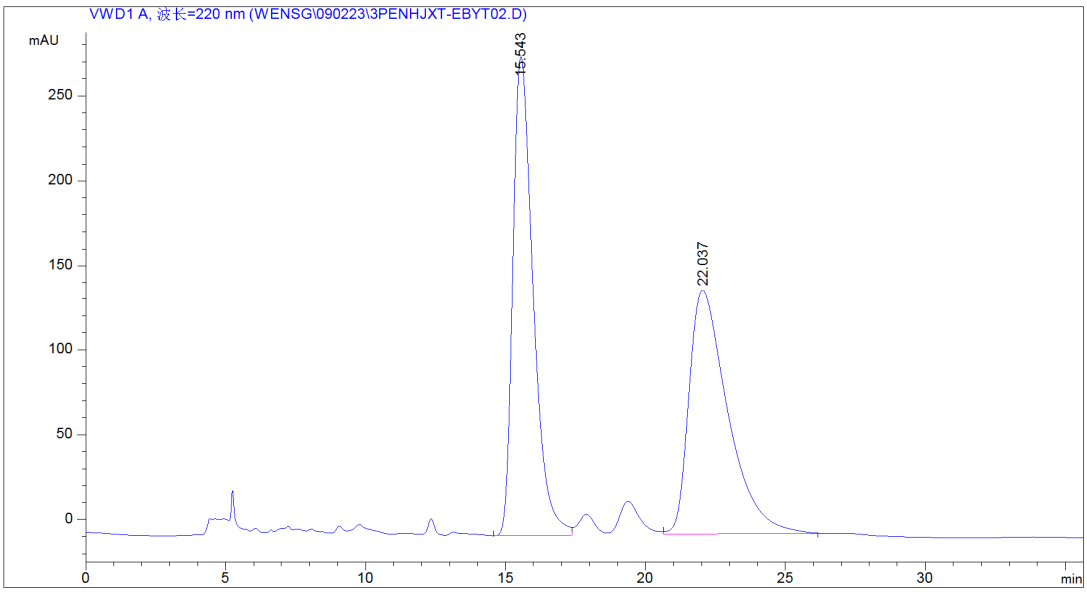
#	time	Area	Height	Width	Area%
1	11.022	2994.4	128.8	0.3557	50.1081
2	14.363	2981.5	77.3	0.5836	49.8919



Asymmetric adduct (sample in EtOH)

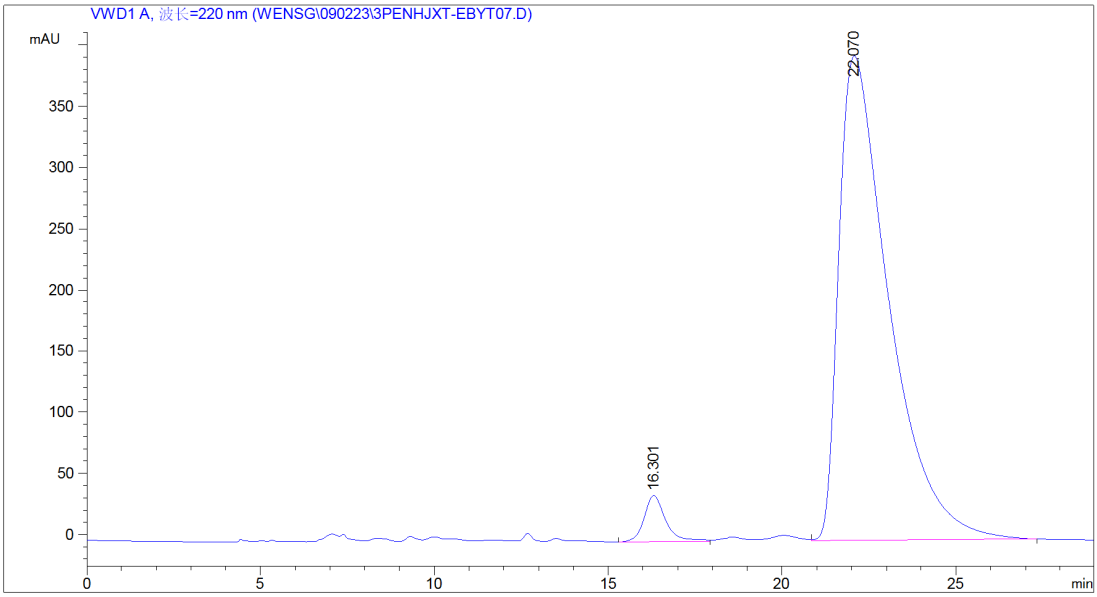
#	time	Area	Height	Width	Area%
1	11.126	12396.2	537.9	0.3562	96.9696
2	14.486	387.3	10.6	0.6025	3.0304

3-(diphenylphosphoryl)-3-pentylcyclohexanone (Table 2, entry 7)



Racemic adduct (sample in EtOH)

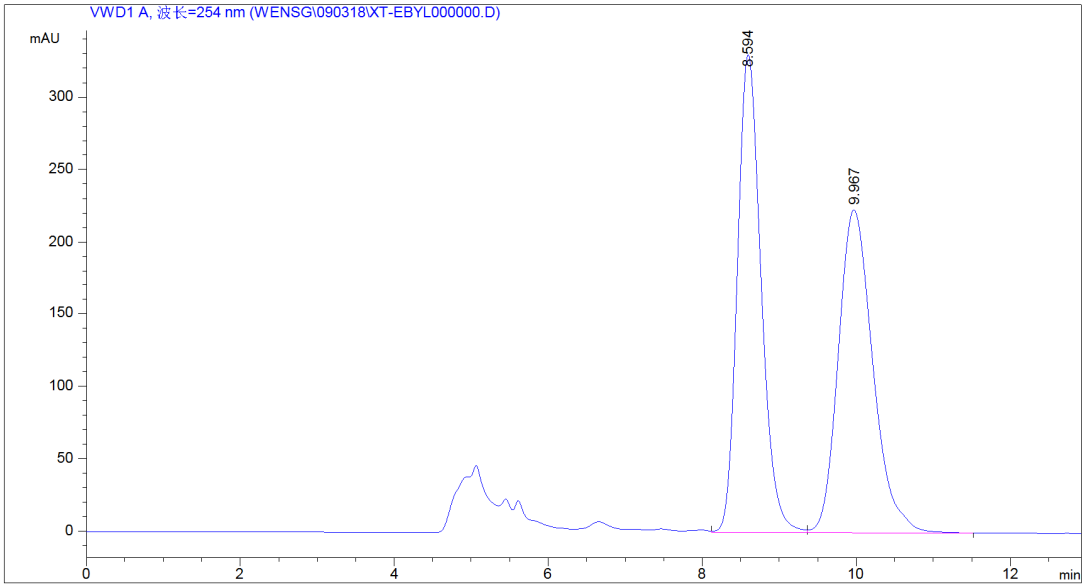
#	time	Area	Height	Width	Area%
1	15.543	14240.2	282.4	0.7654	50.6635
2	22.037	13867.2	143.6	1.4076	49.3365



Asymmetric adduct (sample in EtOH)

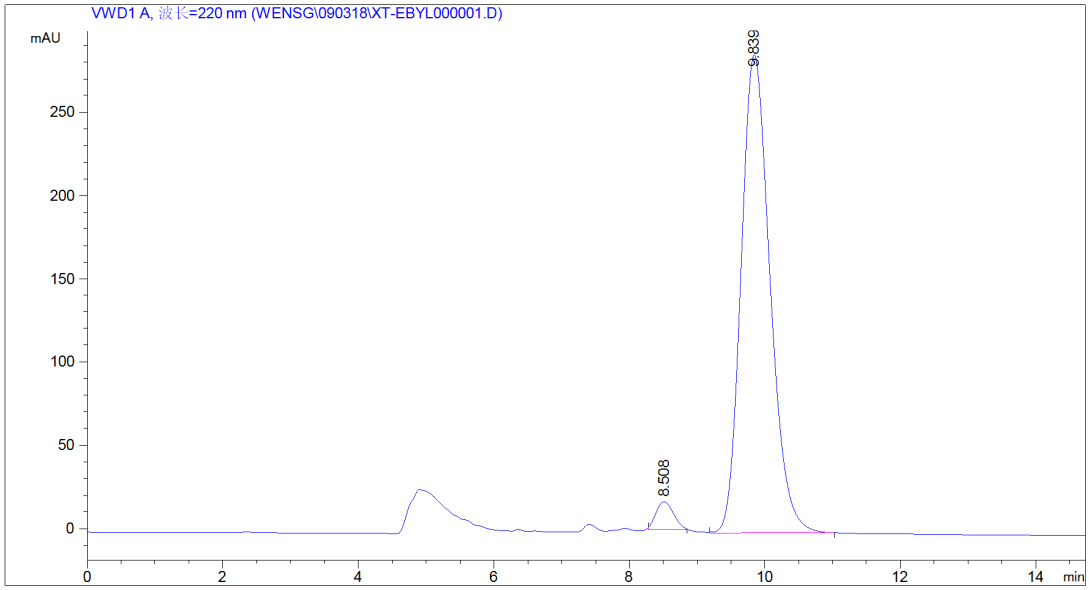
#	time	Area	Height	Width	Area%
1	16.301	1628.8	37.7	0.6349	3.9392
2	22.070	39721.6	395.6	1.4508	96.0608

3-(diphenylphosphoryl)-3-phenethylcyclohexanone (Table 2, entry 8)



Racemic adduct (sample in EtOH)

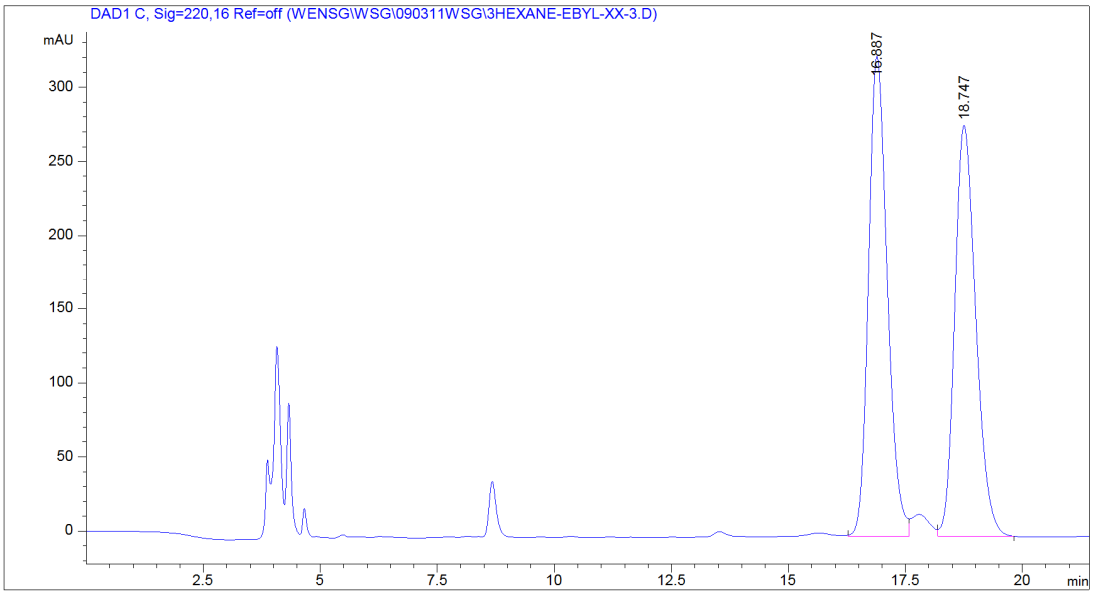
#	time	Area	Height	Width	Area%
1	8.594	7074.2	330.5	0.3312	50.4036
2	9.967	6960.9	223.4	0.4785	49.5964



Asymmetric adduct (sample in EtOH)

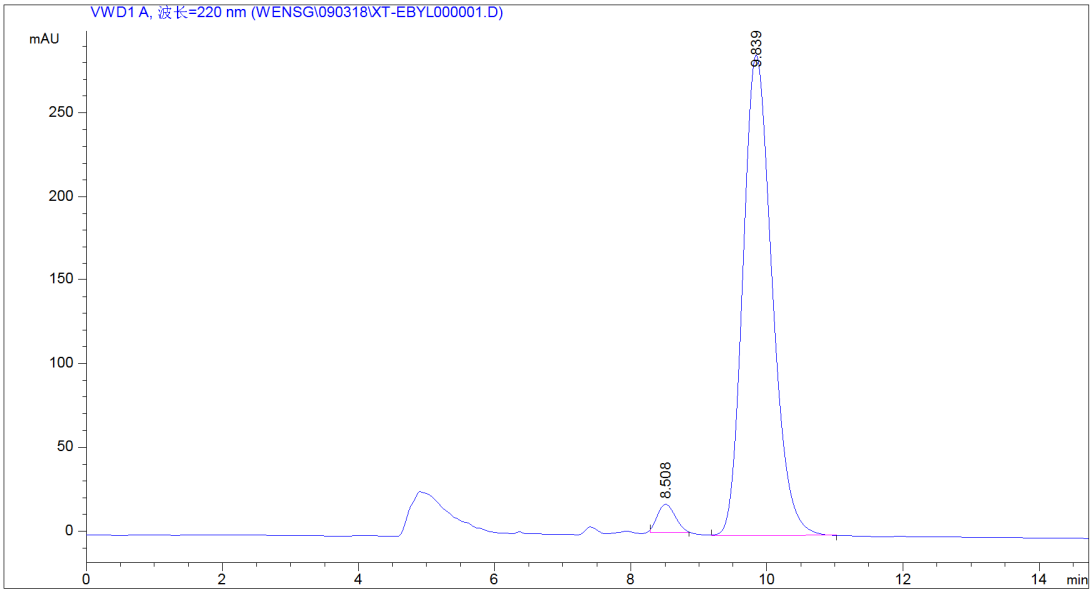
#	time	Area	Height	Width	Area%
1	8.508	309.3	16.8	0.3055	3.5106
2	9.839	8503.1	287.0	0.4578	96.4894

3-cyclohexyl-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 9)



Racemic adduct (sample in EtOH)

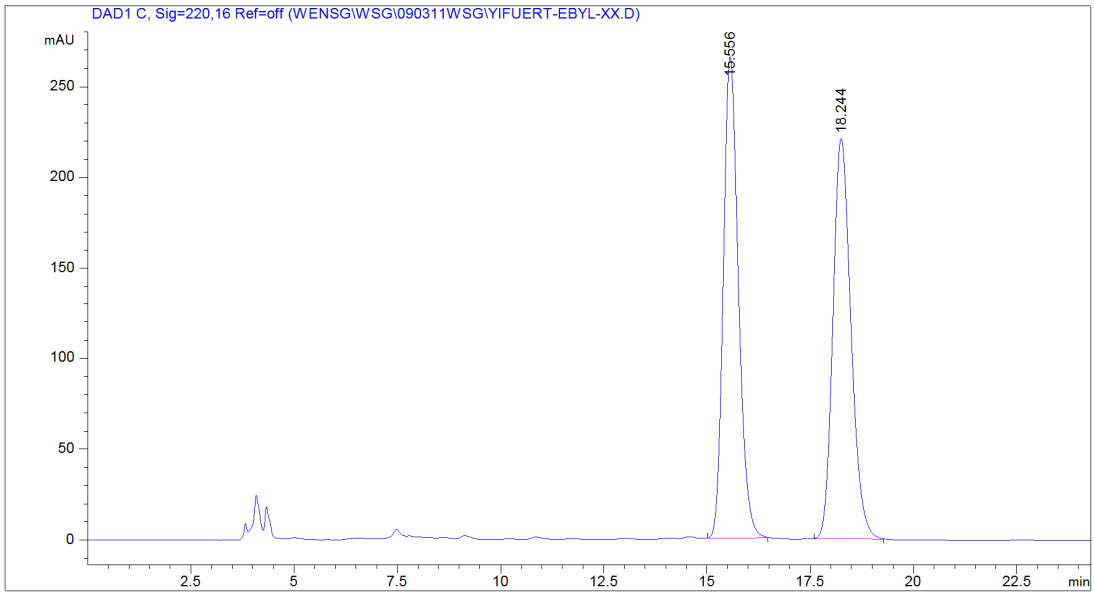
#	time	Area	Height	Width	Area%
1	16.887	9073.0	324.4	0.4304	50.9953
2	18.747	8718.9	277.8	0.4841	49.0047



Asymmetric adduct (sample in EtOH)

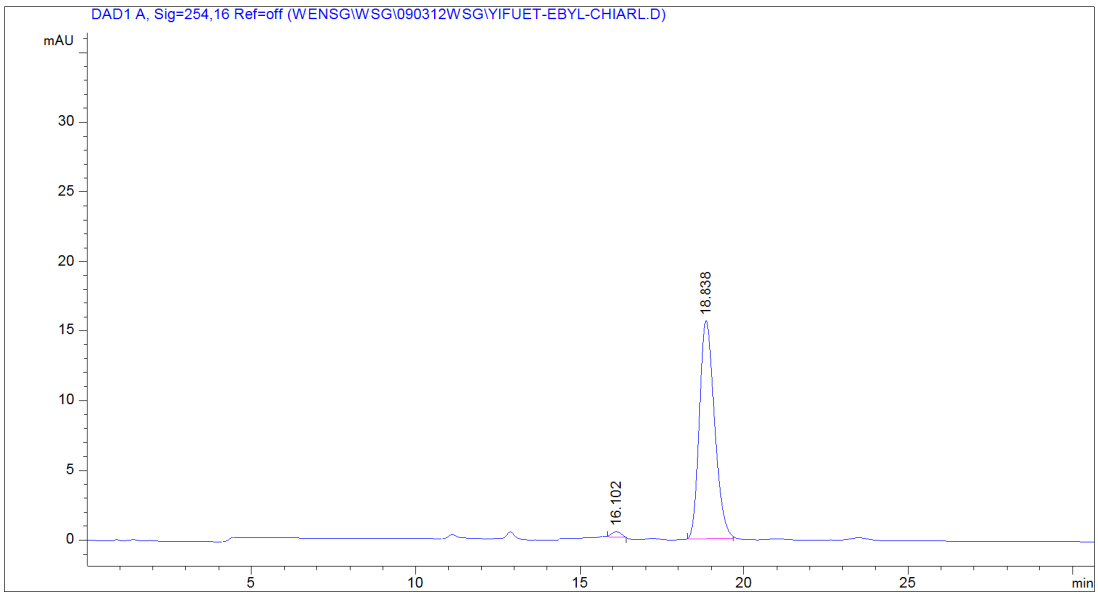
#	time	Area	Height	Width	Area%
1	16.997	390.0	13.8	0.4679	5.0811
2	18.840	7286.7	232.7	0.4833	94.9189

3-(diphenylphosphoryl)-3,5,5-trimethylcyclohexanone (Table 2, entry 10)



Racemic adduct (sample in EtOH)

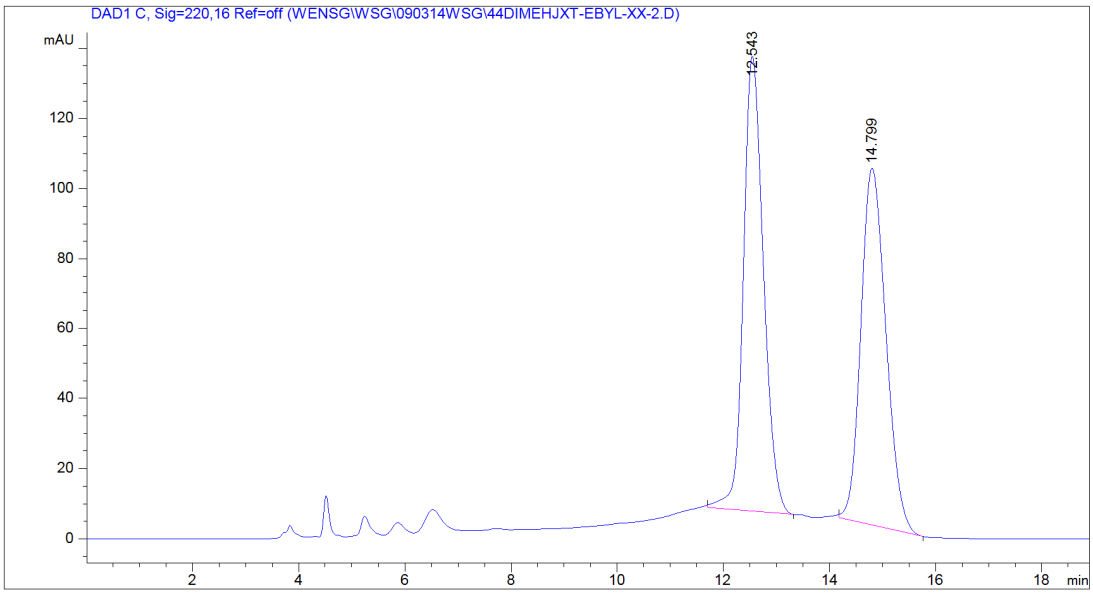
#	time	Area	Height	Width	Area%
1	15.556	6727.7	265.5	0.3895	50.0637
2	18.244	6710.6	220.9	0.4684	49.9363



Asymmetric adduct (sample in EtOH)

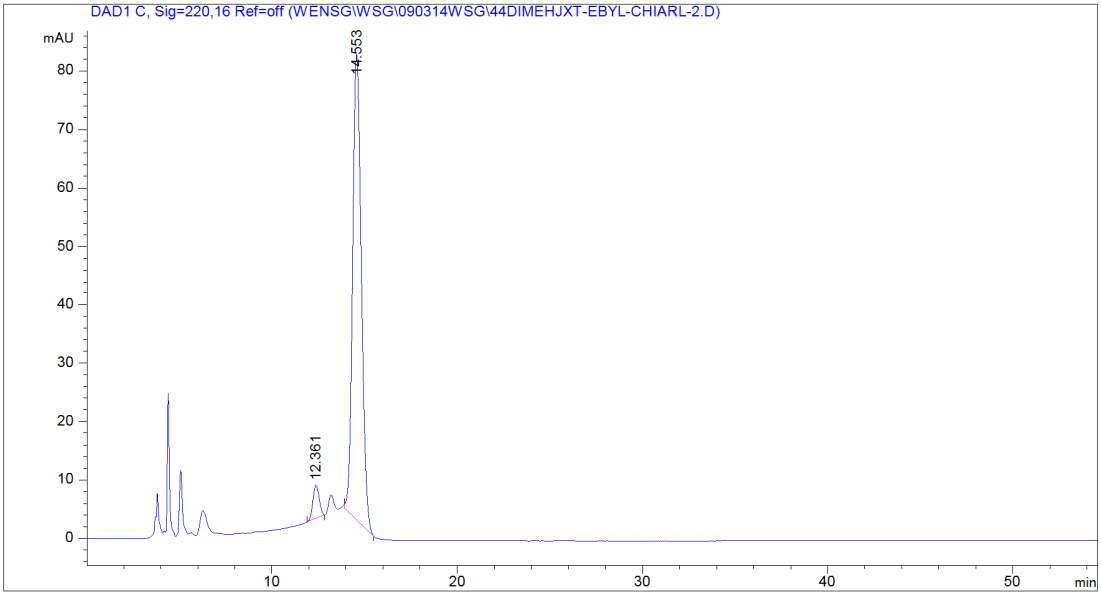
#	time	Area	Height	Width	Area%
1	16.102	7.724	0.3931	0.3274	1.5182
2	18.836	501.05	15.61	0.4963	98.4818

3-(diphenylphosphoryl)-4,4-dimethylcyclohexanone (Table 2, entry 11)



Racemic adduct (sample in EtOH)

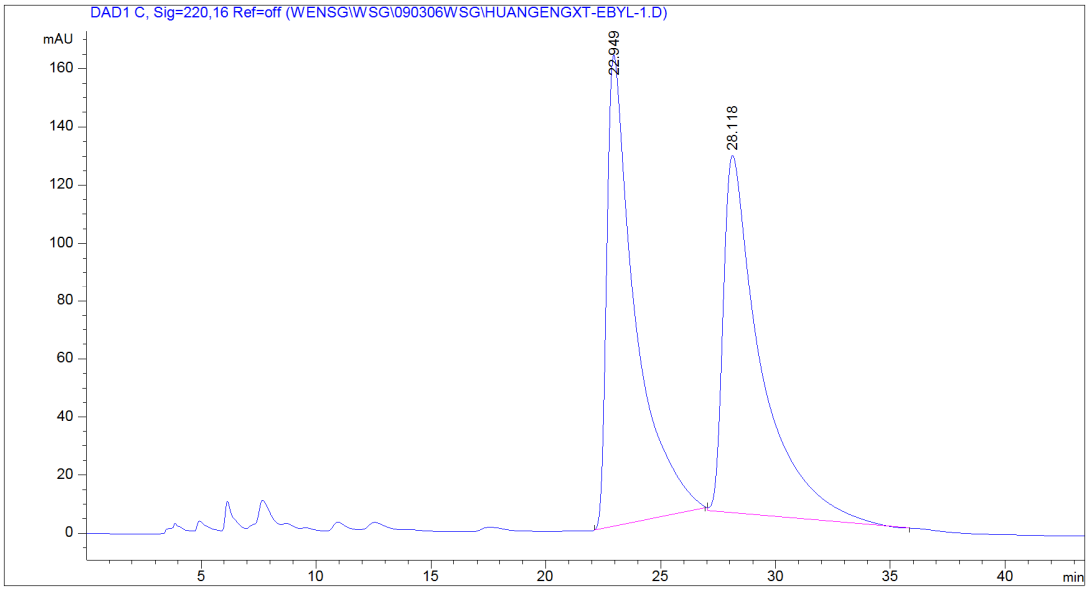
#	time	Area	Height	Width	Area%
1	6.643	7856.9	497.3	0.2411	50.1923
2	8.008	7796.7	255.9	0.5078	49.8077



Asymmetric adduct (sample in EtOH)

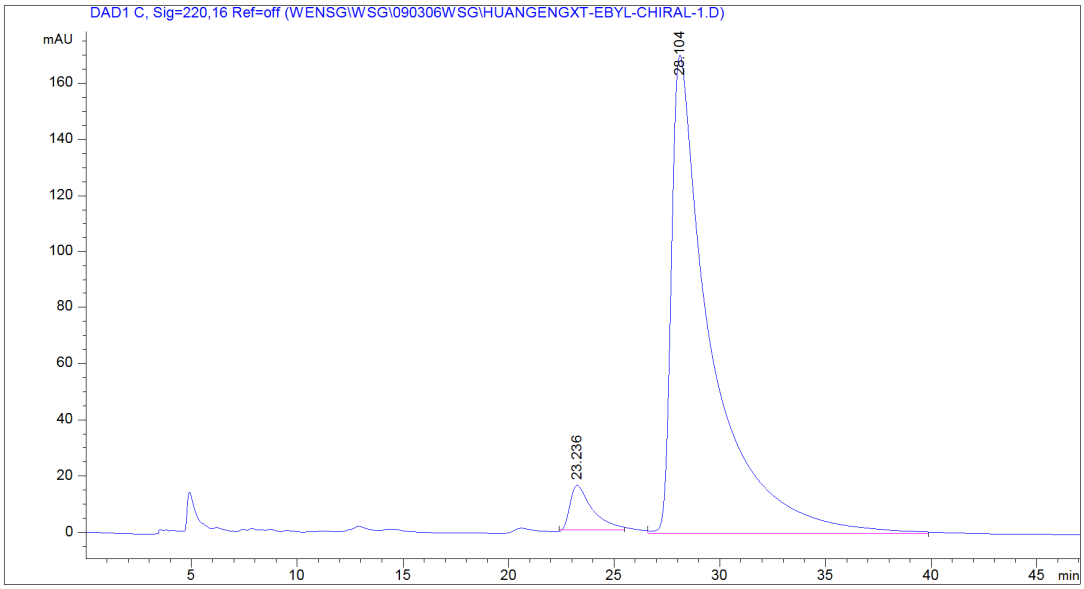
#	time	Area	Height	Width	Area%
1	6.664	405.1	31.0	0.2172	0.7631
2	8.005	52680.5	1685.7	0.5208	99.2369

3-(diphenylphosphoryl)cycloheptanone (Table 2, entry 12)



Racemic adduct (sample in EtOH)

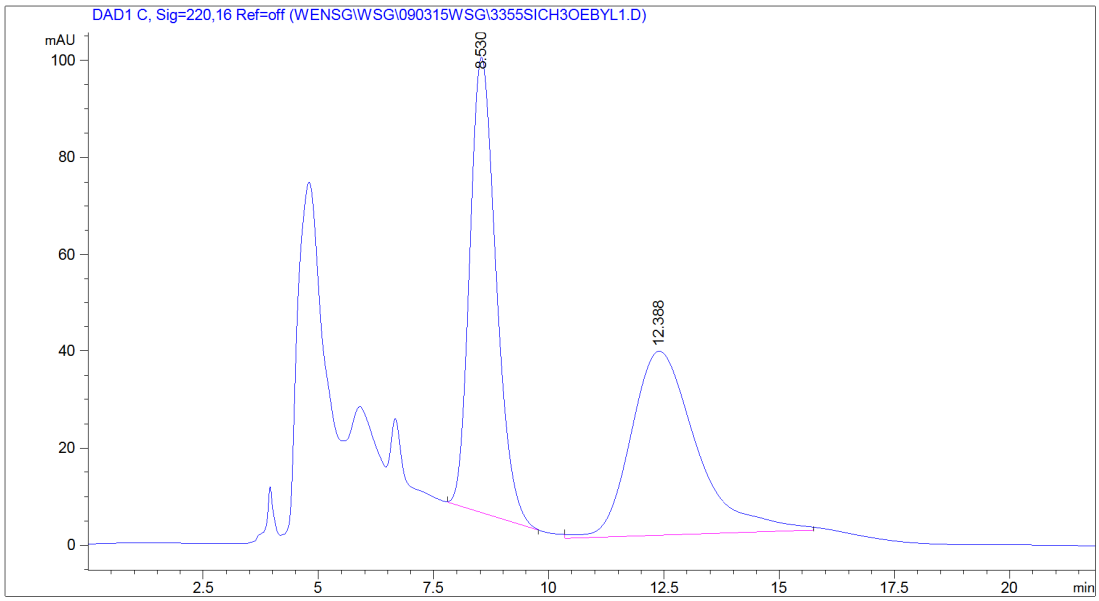
#	time	Area	Height	Width	Area%
1	22.949	1194.0	162.3	1.1940	50.0610
2	26.118	1884.3	123.2	1.8843	49.9390



Asymmetric adduct (sample in EtOH)

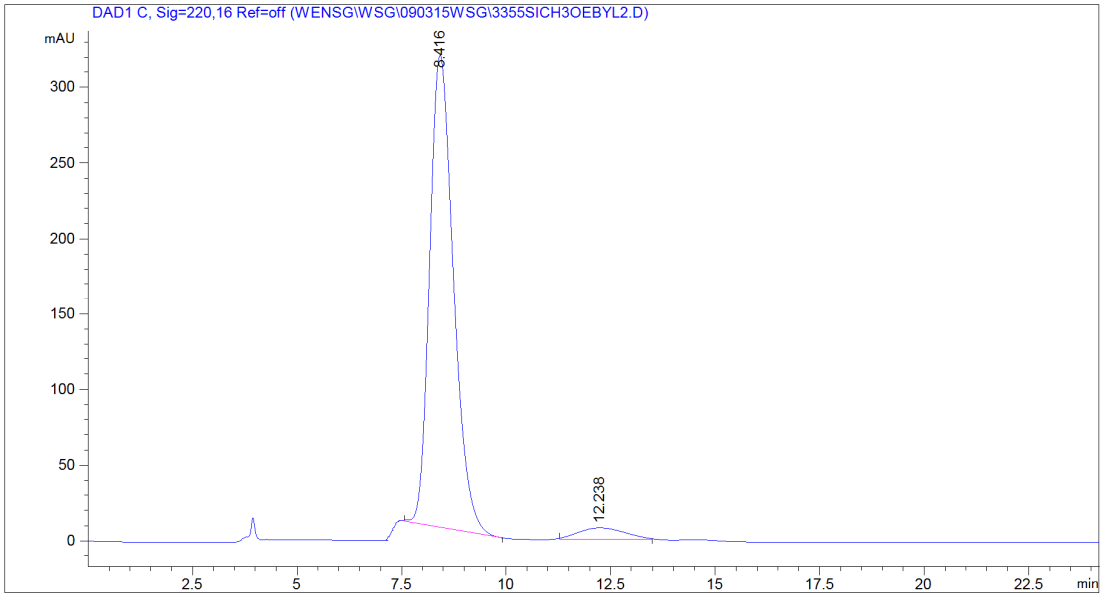
#	time	Area	Height	Width	Area%
1	23.236	1196.0	16.05	1.2414	5.0390
2	26.104	22078.1	170.23	2.1616	94.9610

3-(bis(3,5-dimethoxyphenyl)phosphoryl)cyclohexanone (Table 2, entry 13)



Racemic adduct (sample in EtOH)

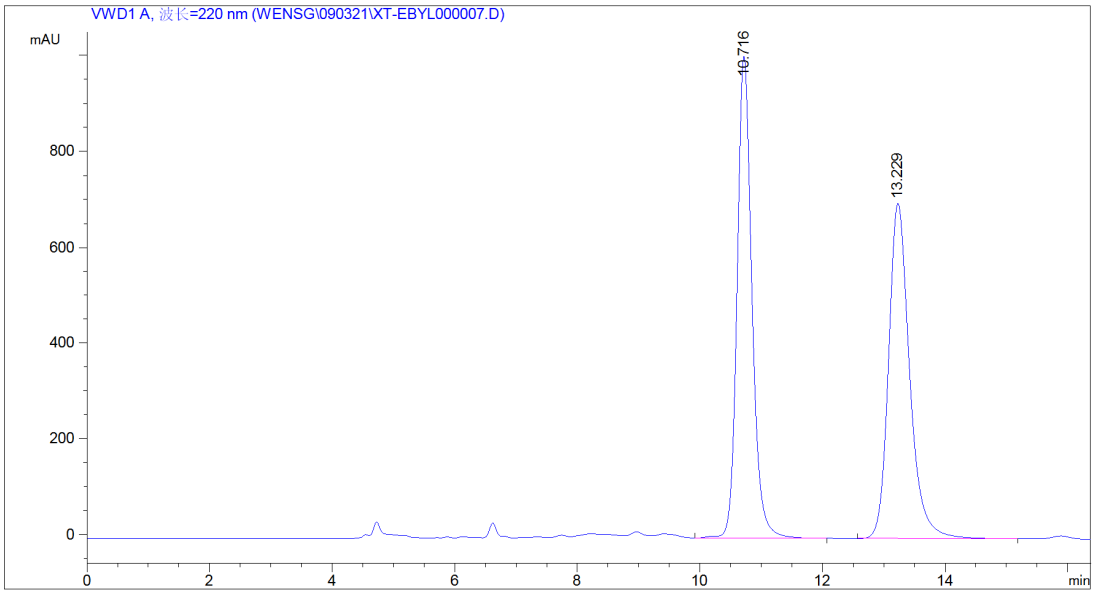
#	time	Area	Height	Width	Area%
1	8.530	3721.9	93.91	0.6124	49.4845
2	12.388	3754.1	37.92	1.6500	50.2155



Asymmetric adduct (sample in EtOH)

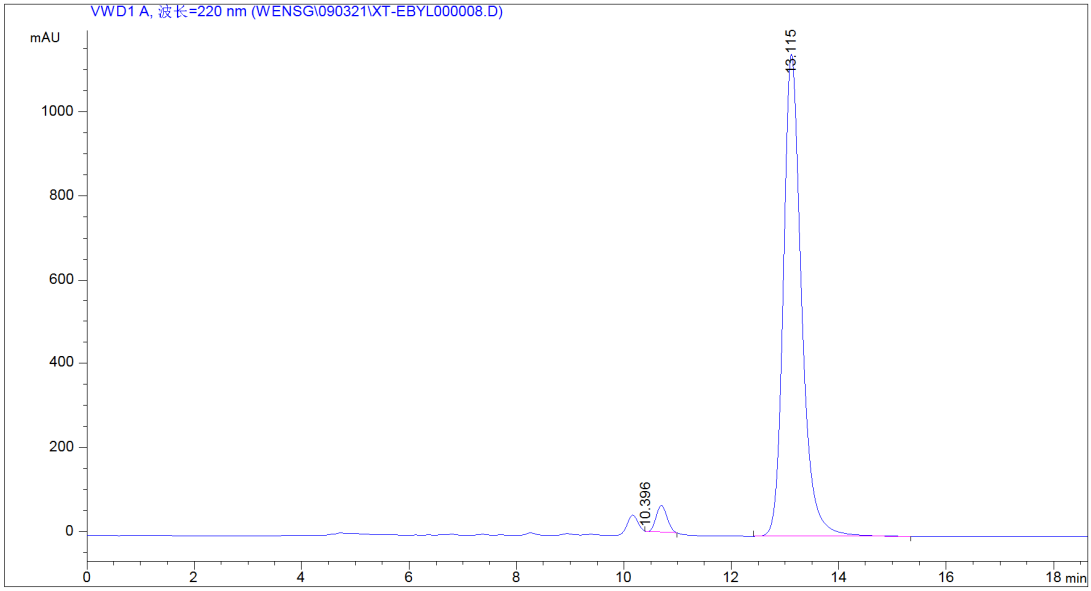
#	time	Area	Height	Width	Area%
1	8.416	12377.8	312.22	0.6125	95.5946
2	12.238	570.4	7.44	1.2770	4.4054

3-(bis(3,5-dimethoxyphenyl)phosphoryl)-3-methylcyclohexanone (Table 2, entry 14)



Racemic adduct (sample in EtOH)

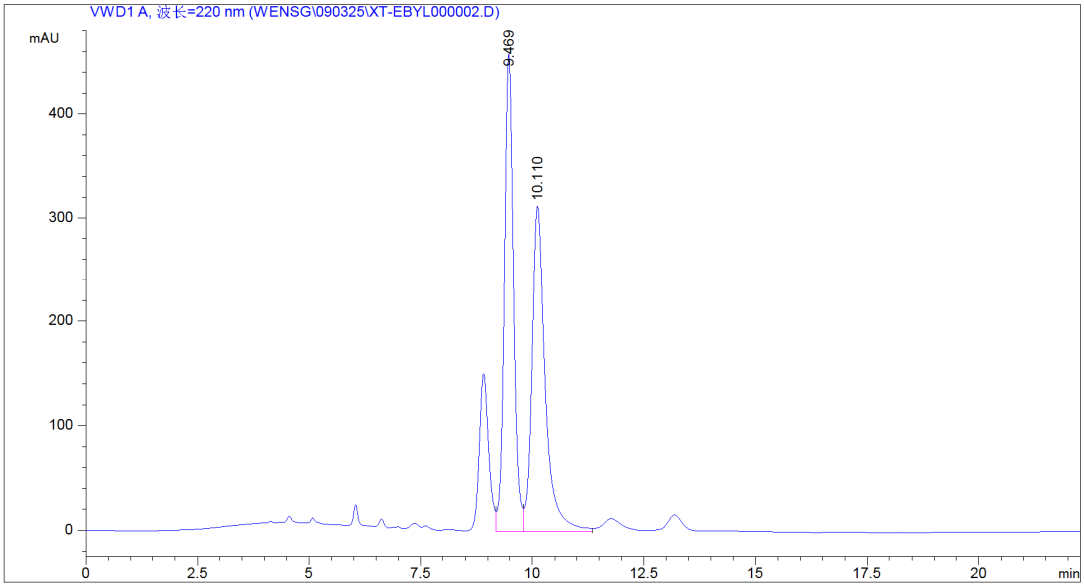
#	time	Area	Height	Width	Area%
1	10.716	17032.1	1006.9	0.2385	50.3873
2	13.229	16770.3	700.9	0.3607	49.6127



Asymmetric adduct (sample in EtOH)

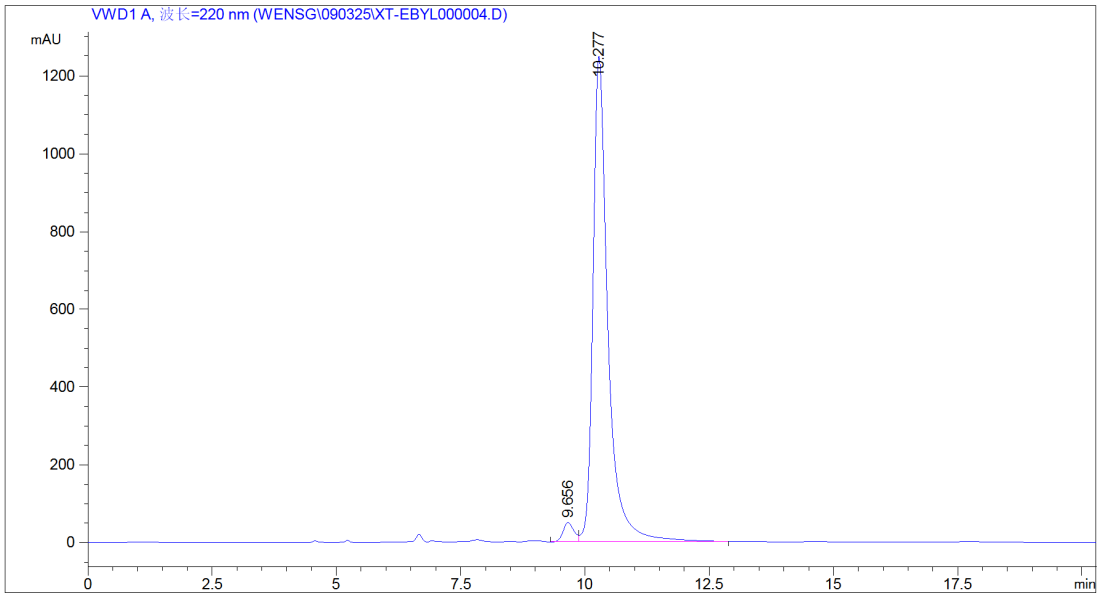
#	time	Area	Height	Width	Area%
1	10.396	887.4	0.2942	0.2353	3.1859
2	13.115	26968.5	1148.7	0.3554	96.8141

3-(bis(3,5-dimethoxyphenyl)phosphoryl)-3-cyclohexylcyclohexanone (Table 2, entry 15)



Racemic adduct (sample in EtOH)

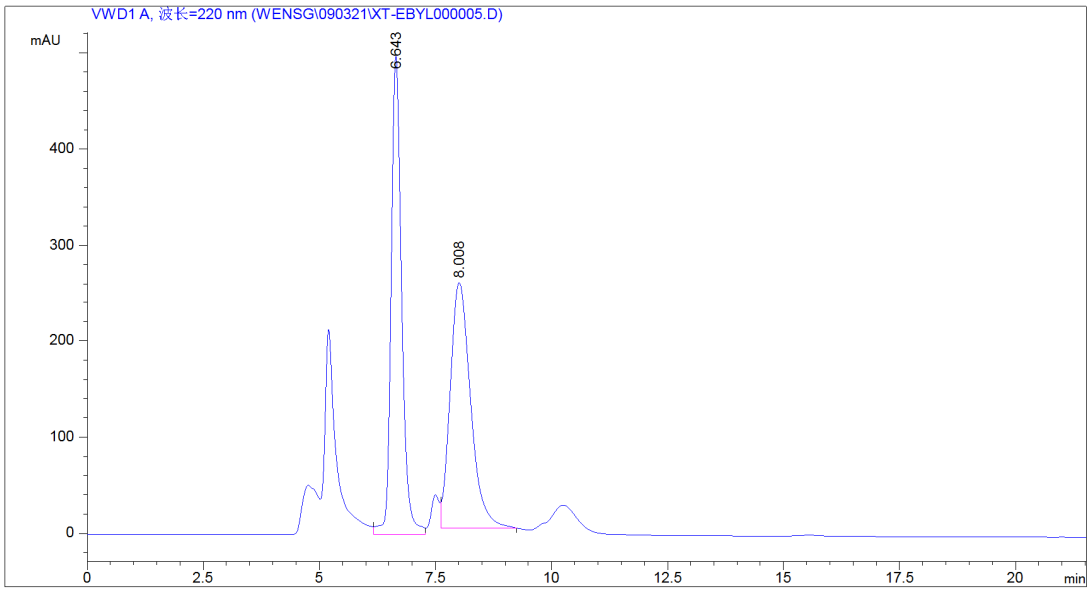
#	time	Area	Height	Width	Area%
1	9.469	6543.4	458.7	0.2174	50.0924
2	10.110	6519.2	312.7	0.3073	49.9076



Asymmetric adduct (sample in EtOH)

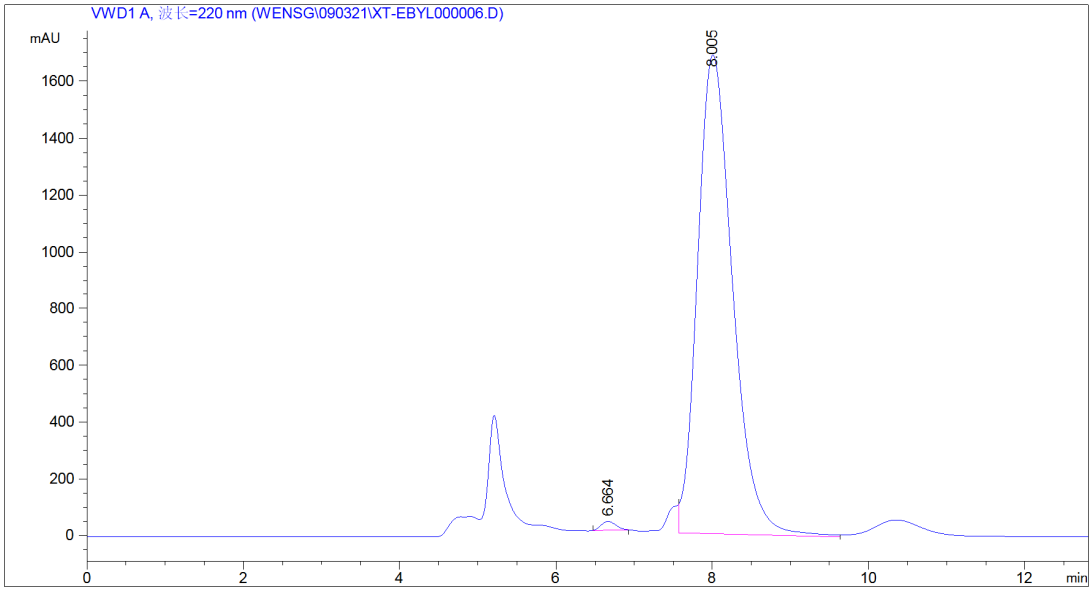
#	time	Area	Height	Width	Area%
1	9.656	764.7	49.86	0.2313	2.8489
2	10.277	2.607	1247.1	0.3080	97.1511

3-(bis(3,5-dimethoxyphenyl)phosphoryl)-4,4-dimethylcyclohexanone (Table 2, entry 16)



Racemic adduct (sample in EtOH)

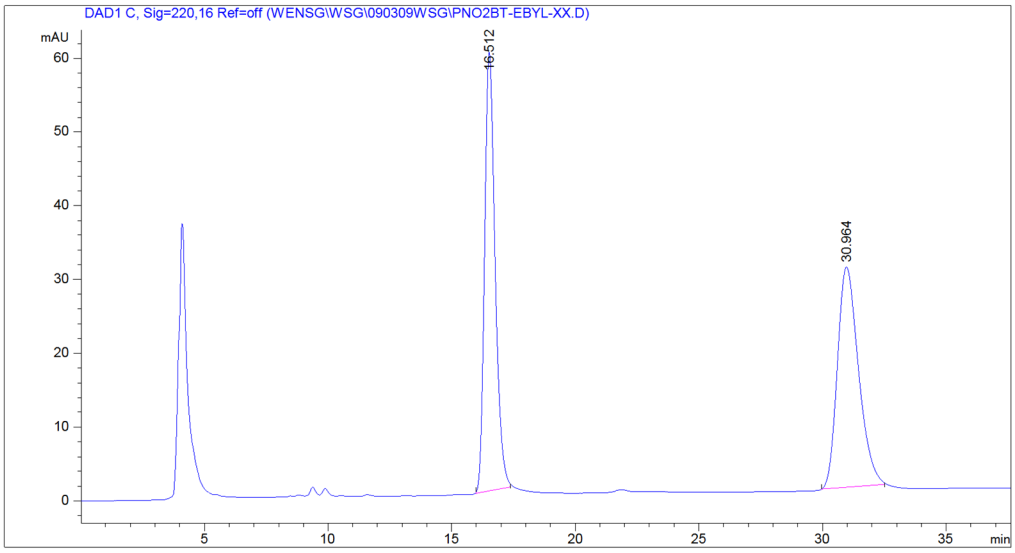
#	time	Area	Height	Width	Area%
1	6.643	7856.9	497.3	0.2411	50.1923
2	8.008	7796.7	255.9	0.5078	49.8077



Asymmetric adduct (sample in EtOH)

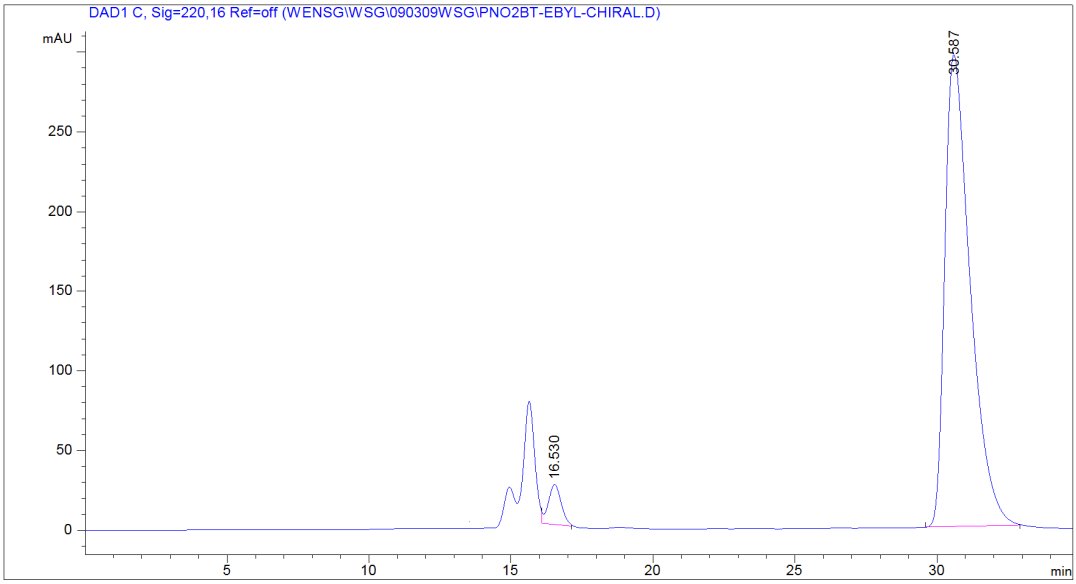
#	time	Area	Height	Width	Area%
1	6.664	405.1	31.08	0.2172	0.7631
2	8.005	52680.5	1685.7	0.5208	99.2369

4-(diphenylphosphoryl)-4-(4-nitrophenyl)bu tan-2-one (Table 2, entry 17)



Racemic adduct (sample in EtOH)

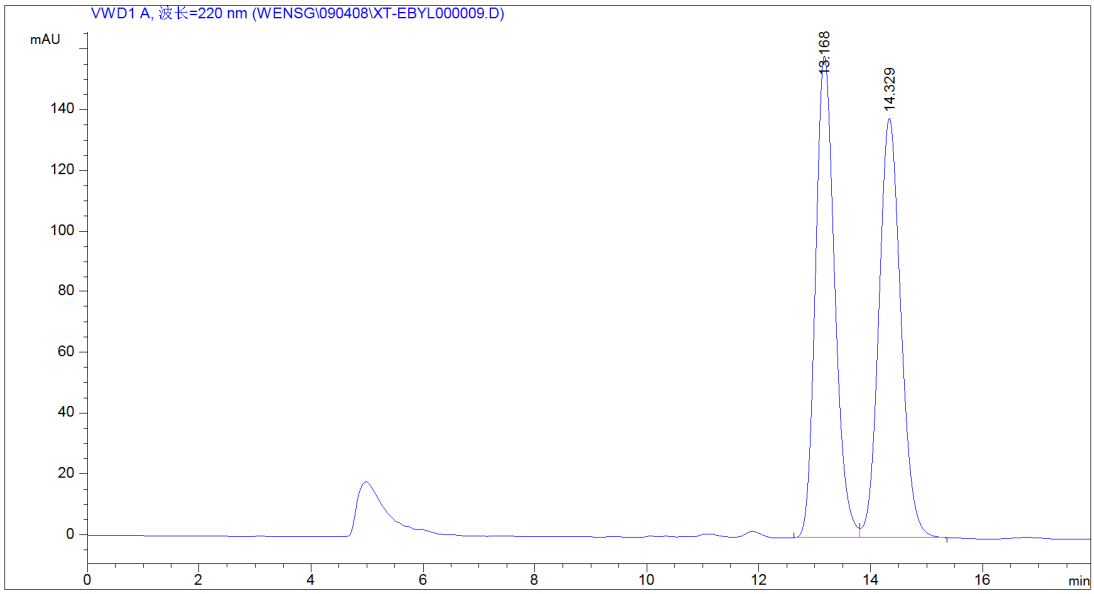
#	time	Area	Height	Width	Area%
1	16.512	1754.3	59.45	0.4502	49.7796
2	30.964	1769.8	29.86	0.8953	50.2204



Asymmetric adduct (sample in EtOH)

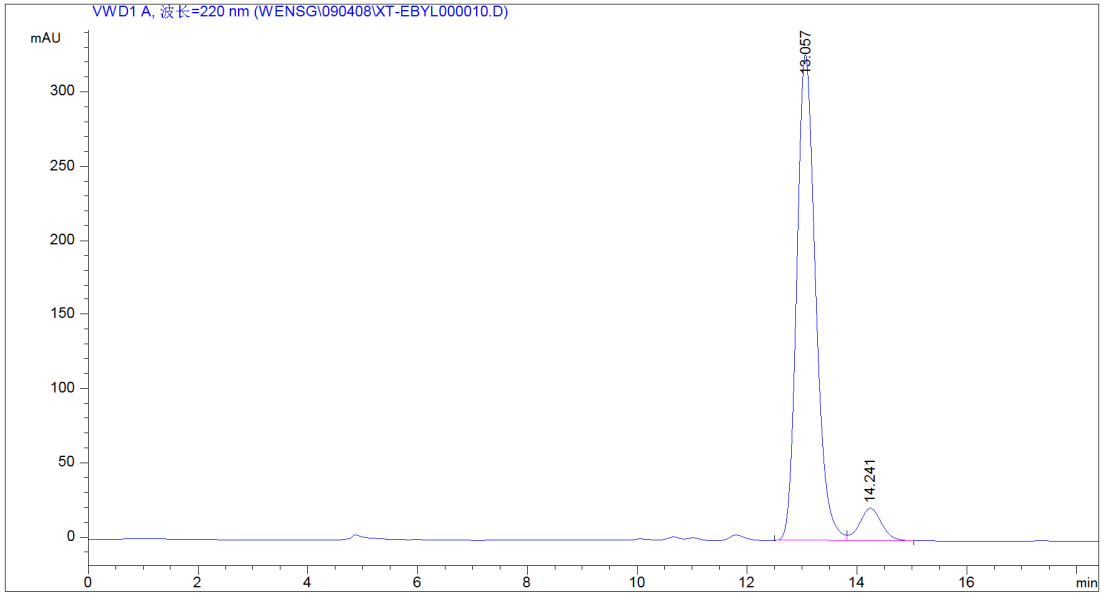
#	time	Area	Height	Width	Area%
1	16.530	796.5	25.17	0.5273	4.1415
2	30.587	1843.7	296.0	0.9604	95.8585

4-(diphenylphosphoryl)-4-(4-methoxyphenyl)butan-2-one (Table 2, entry 18)



Racemic adduct (sample in EtOH)

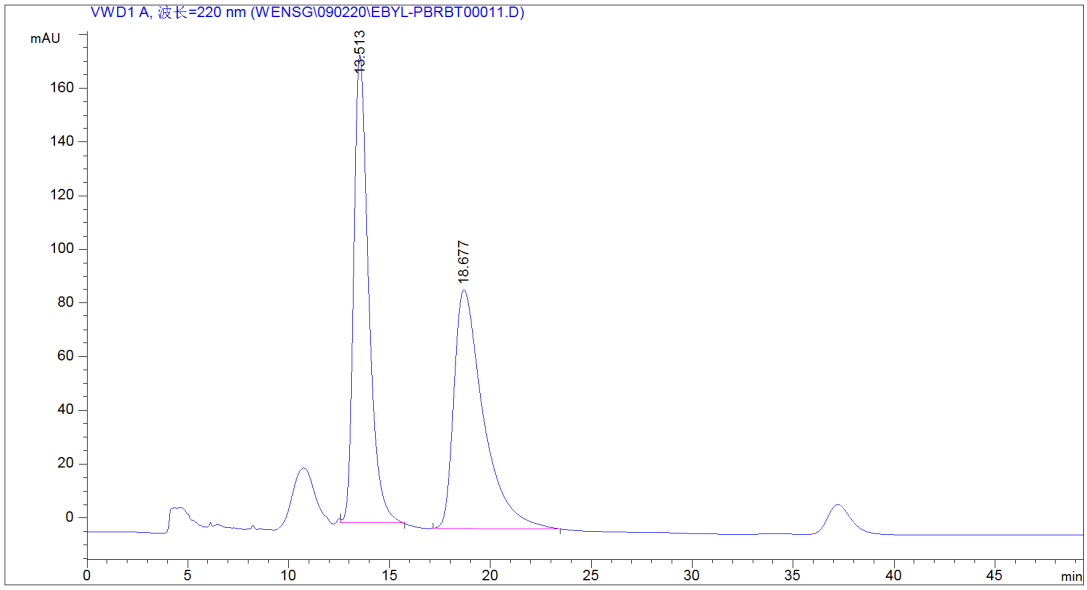
#	time	Area	Height	Width	Area%
1	13.168	3784.6	158.6	0.3671	50.1915
2	14.329	3755.7	138.1	0.4175	49.8085



Asymmetric adduct (sample in EtOH)

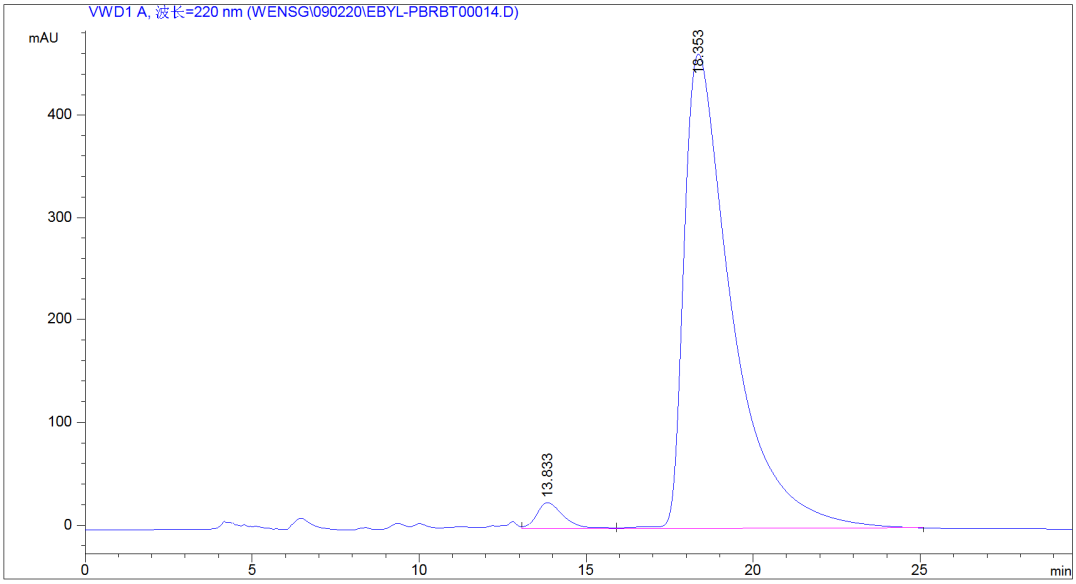
#	time	Area	Height	Width	Area%
1	13.057	7774.4	327.3	0.3659	92.7468
2	14.241	607.9	21.85	0.4251	7.2532

4-(4-bromophenyl)-4-(diphenylphosphoryl)butan-2-one (Table 2, entry 19)



Racemic adduct (sample in EtOH)

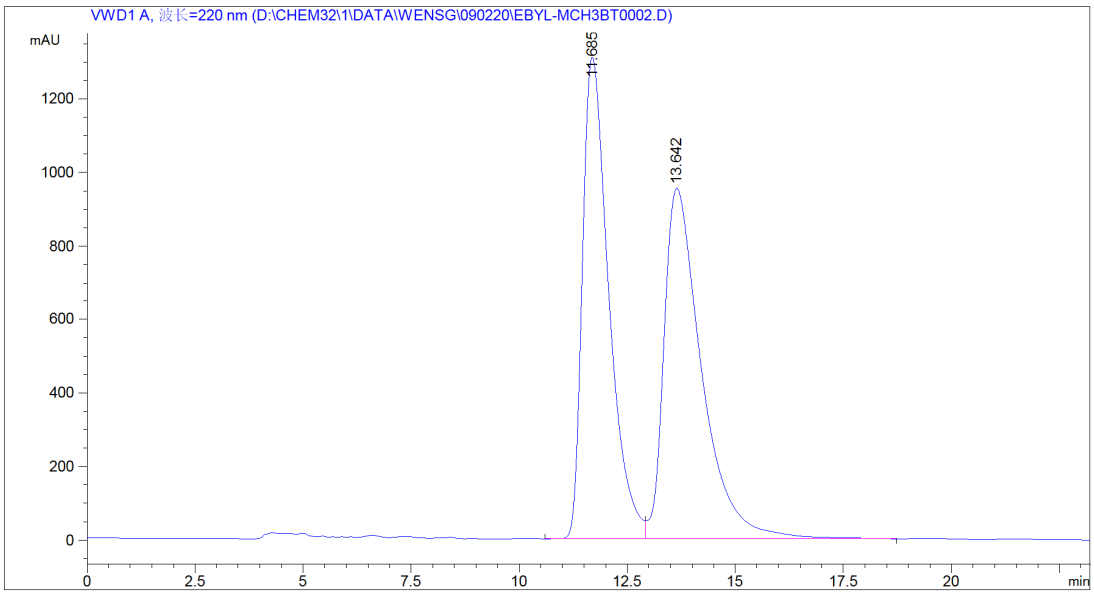
#	time	Area	Height	Width	Area%
1	13.513	8932.8	174.1	0.8547	49.8443
2	18.677	8988.6	88.8	1.4832	50.1557



Asymmetric adduct (sample in EtOH)

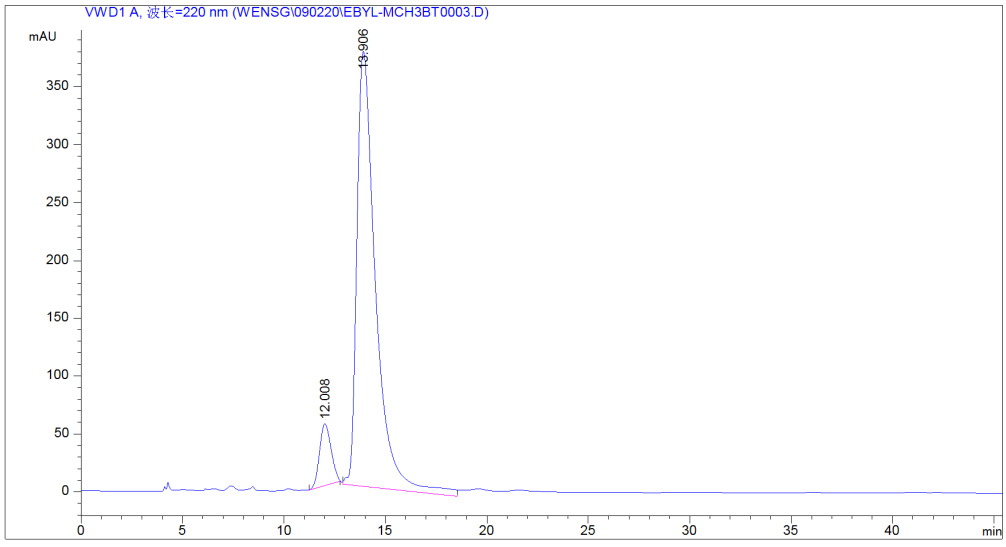
#	time	Area	Height	Width	Area%
1	13.833	1516.0	25.83	0.8624	3.1727
2	18.353	4.626	463.0	1.4541	96.8273

4-(diphenylphosphoryl)-4-m-tolylbutan-2-one (Table 2, entry 20)



Racemic adduct (sample in EtOH)

#	time	Area	Height	Width	Area%
1	11.685	55488.2	1310.12	0.6441	49.0045
2	13.642	57742.6	953.63	0.8972	50.9955

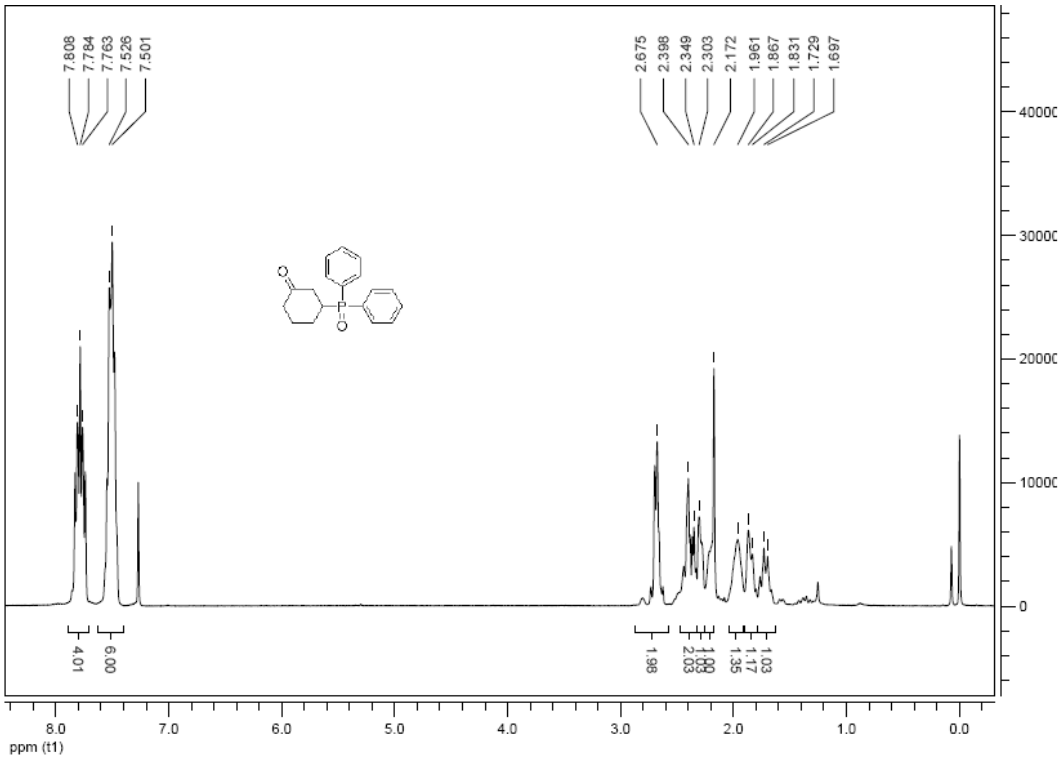


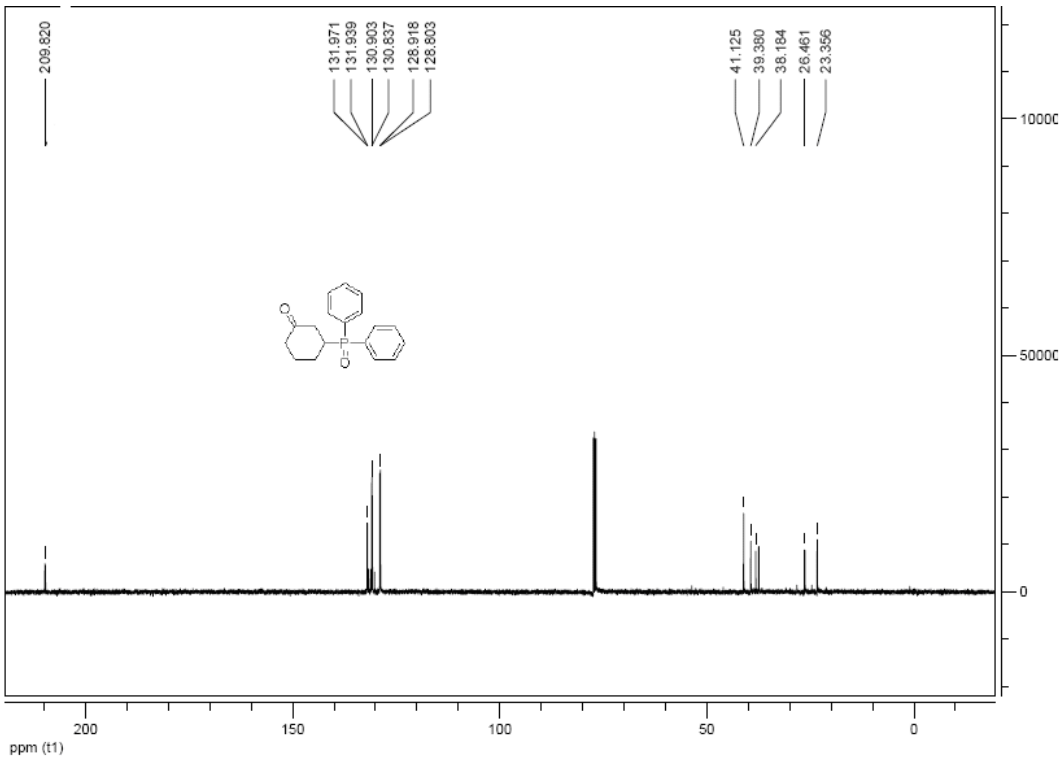
Asymmetric adduct (sample in EtOH)

#	time	Area	Height	Width	Area%
1	12.008	2132.05	53.42	0.6651	8.1256
2	13.906	24106.5	375.41	1.0702	91.8744

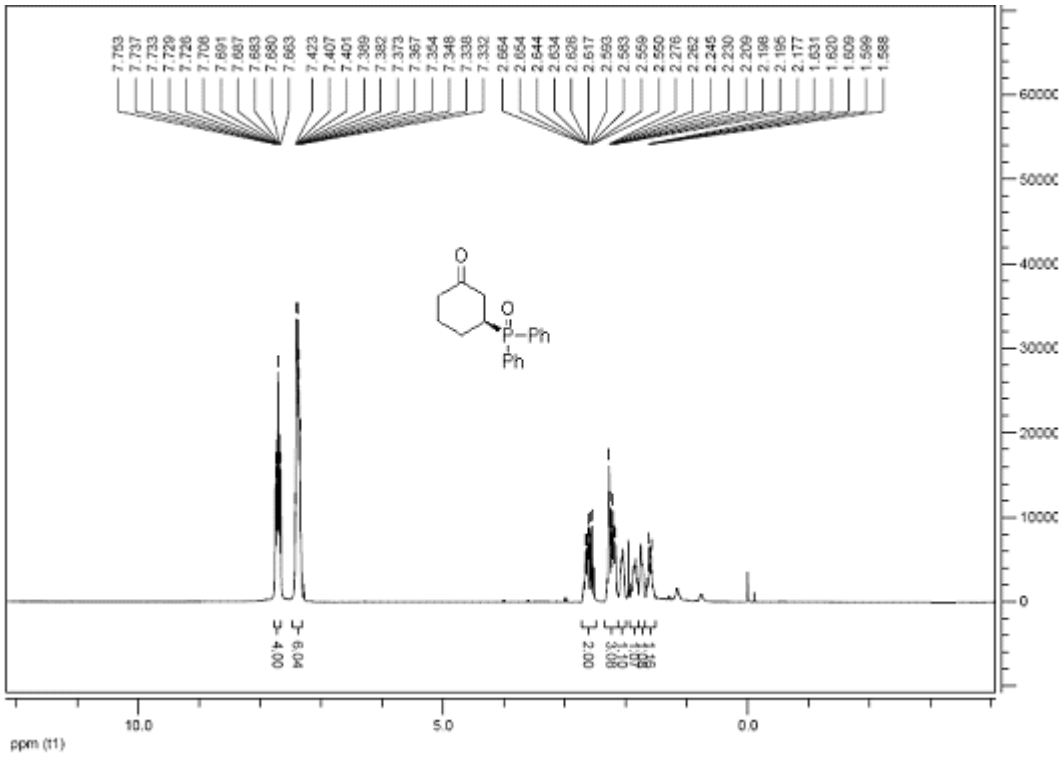
F: NMRAnalysis of Michael Addition Products

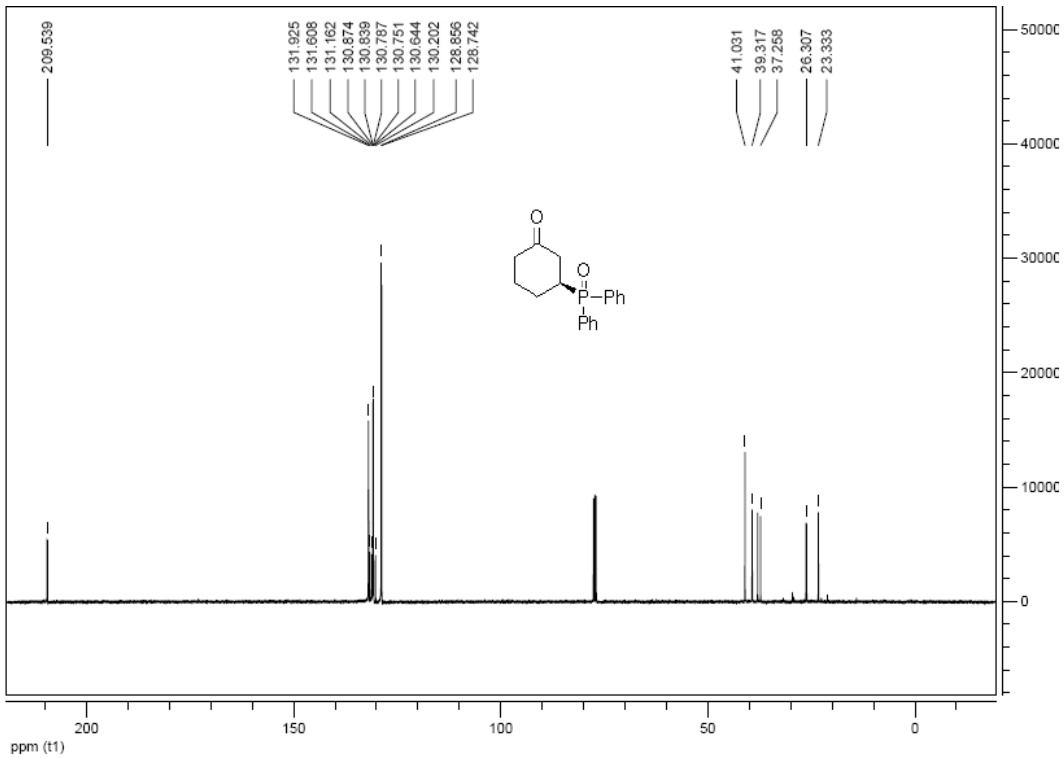
(R)-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 1)



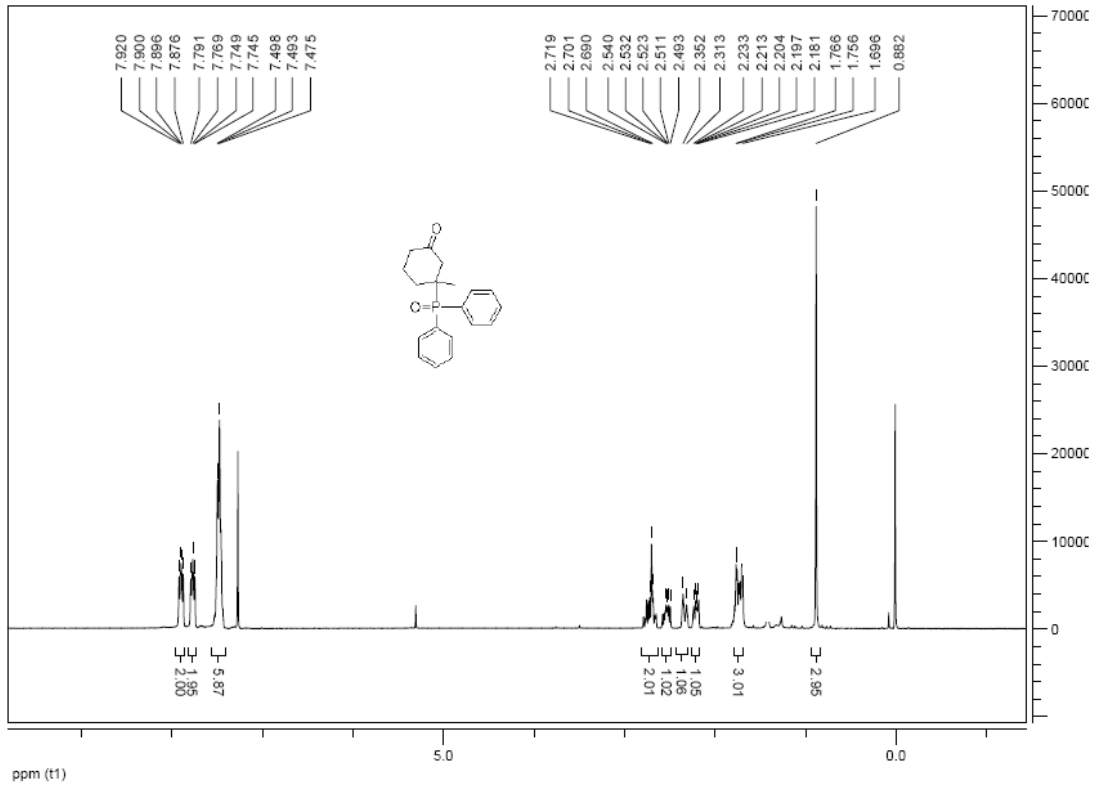


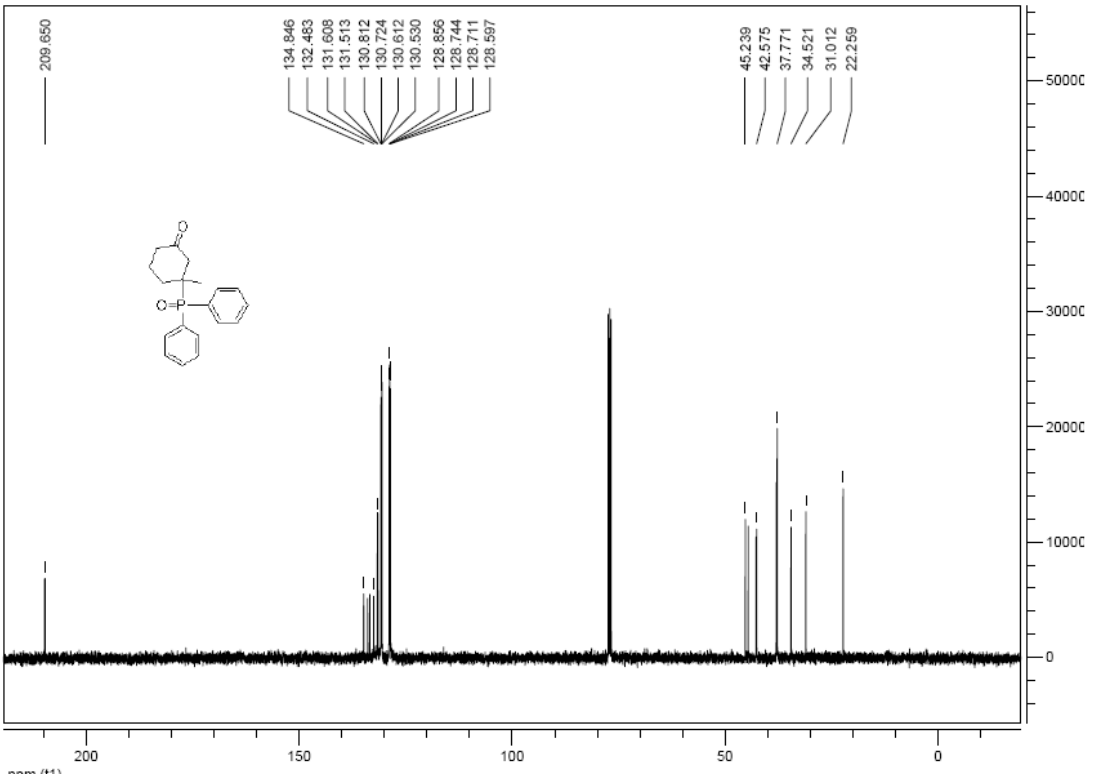
(S)-3-(diphenylphosphoryl)cyclohexanone (Table 1, entry 16)



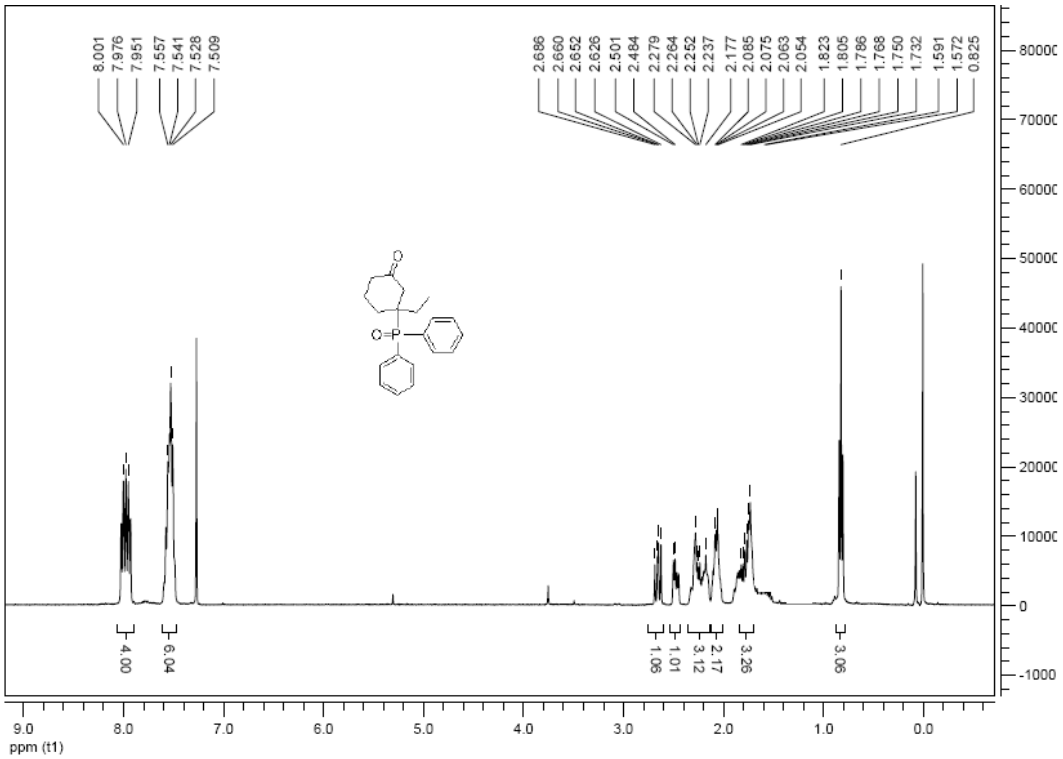


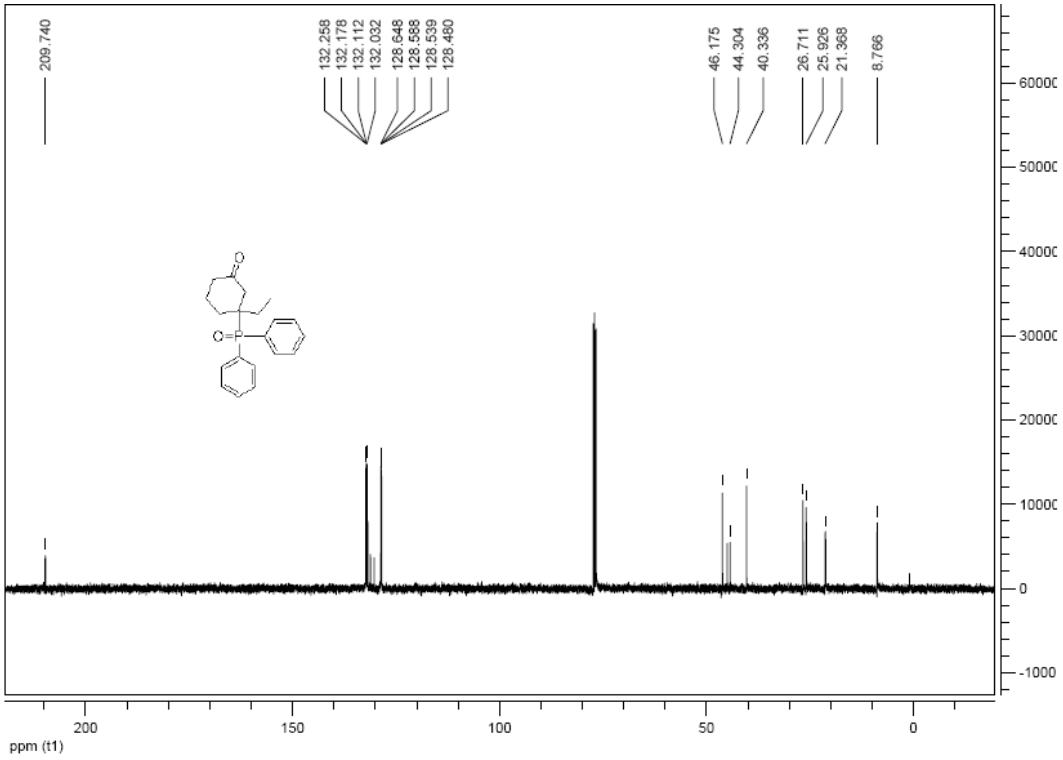
3-(diphenylphosphoryl)-3-methylcyclohexanone (Table 2, entry 2)



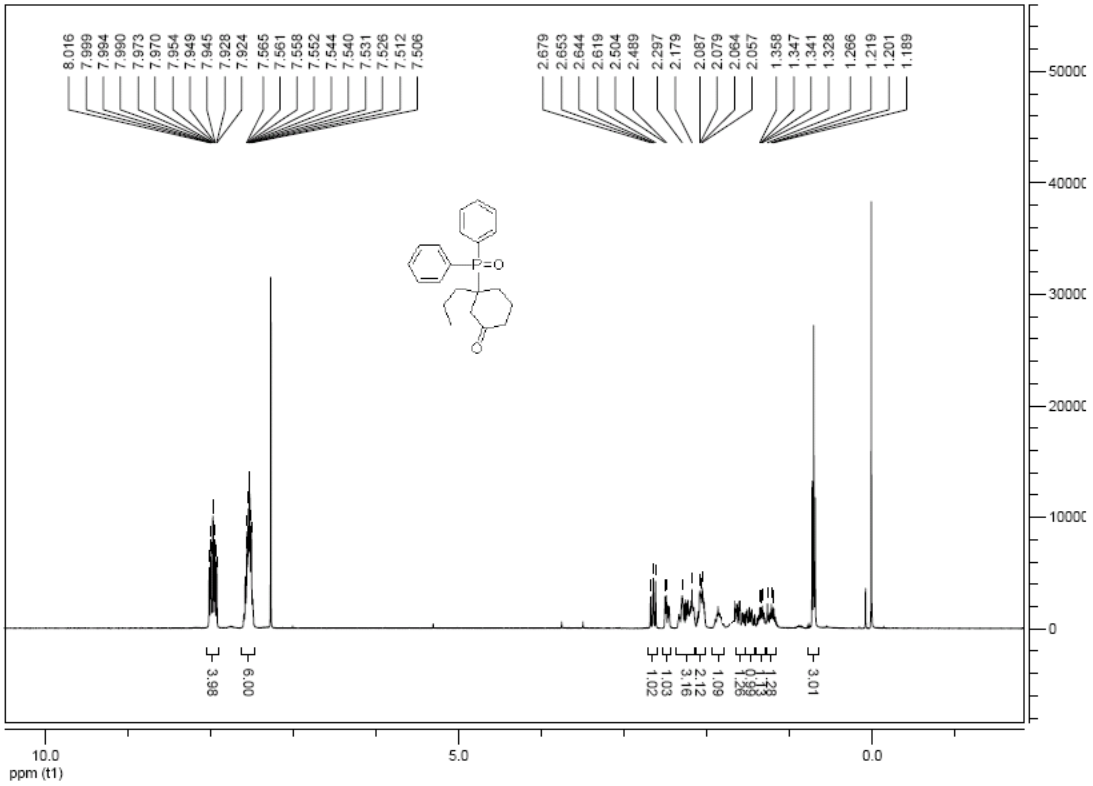


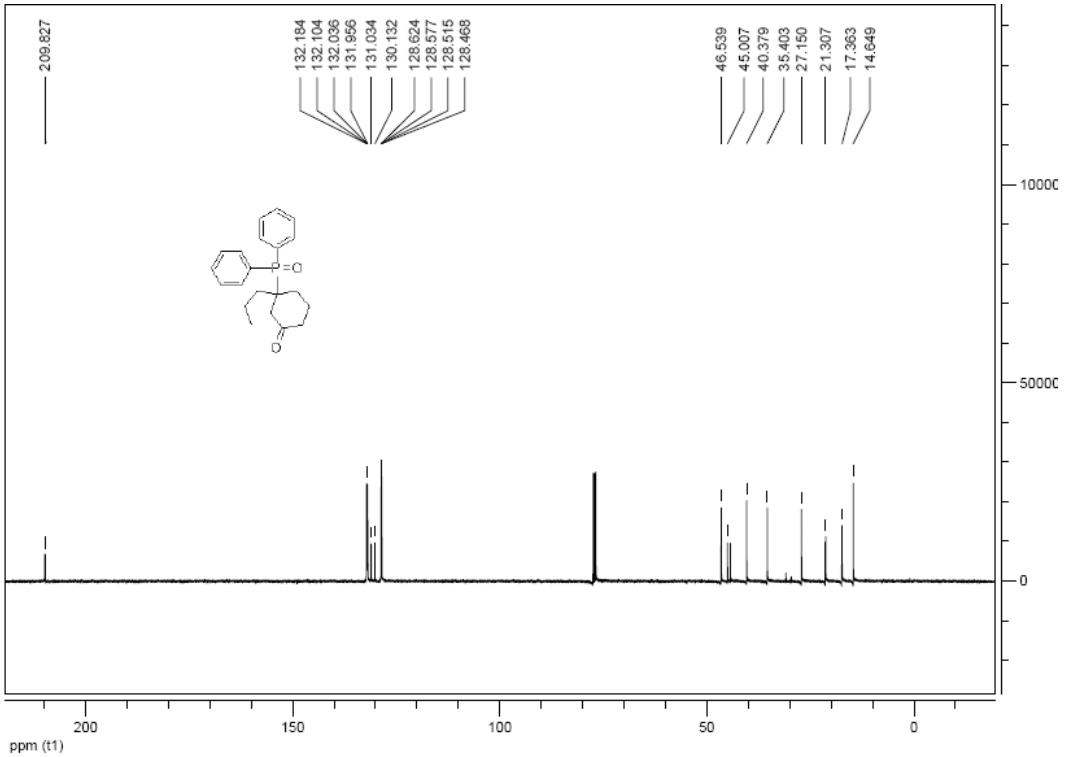
3-(diphenylphosphoryl)-3-ethylcyclohexanone (Table 2, entry 3)



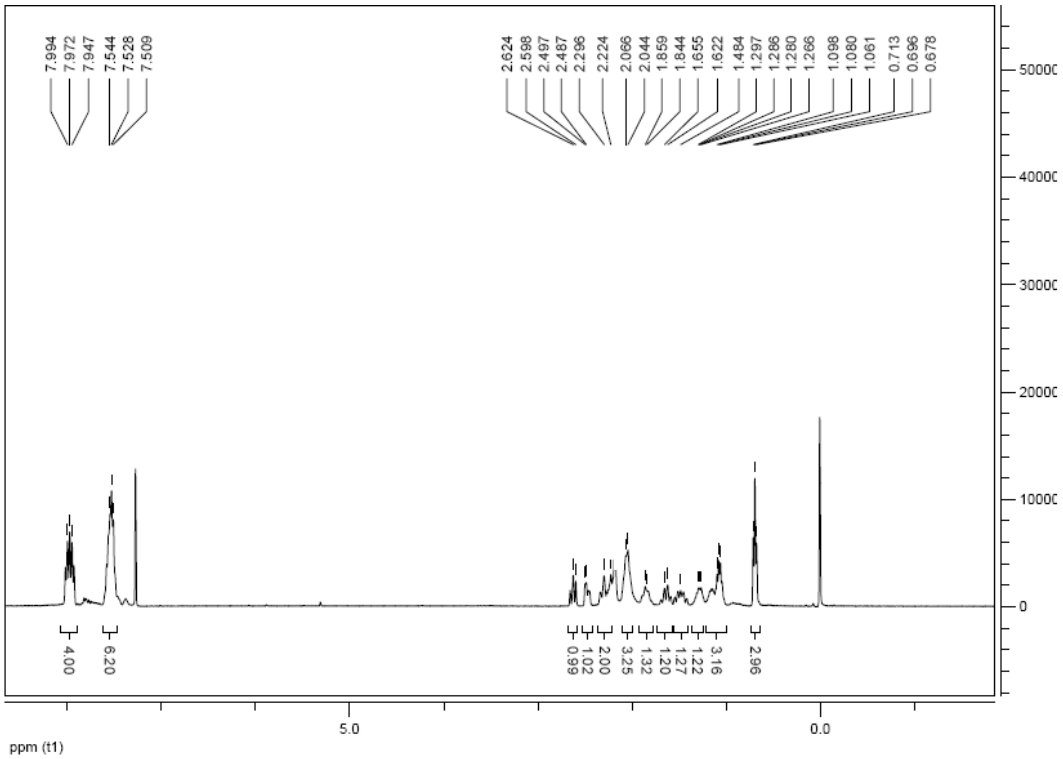


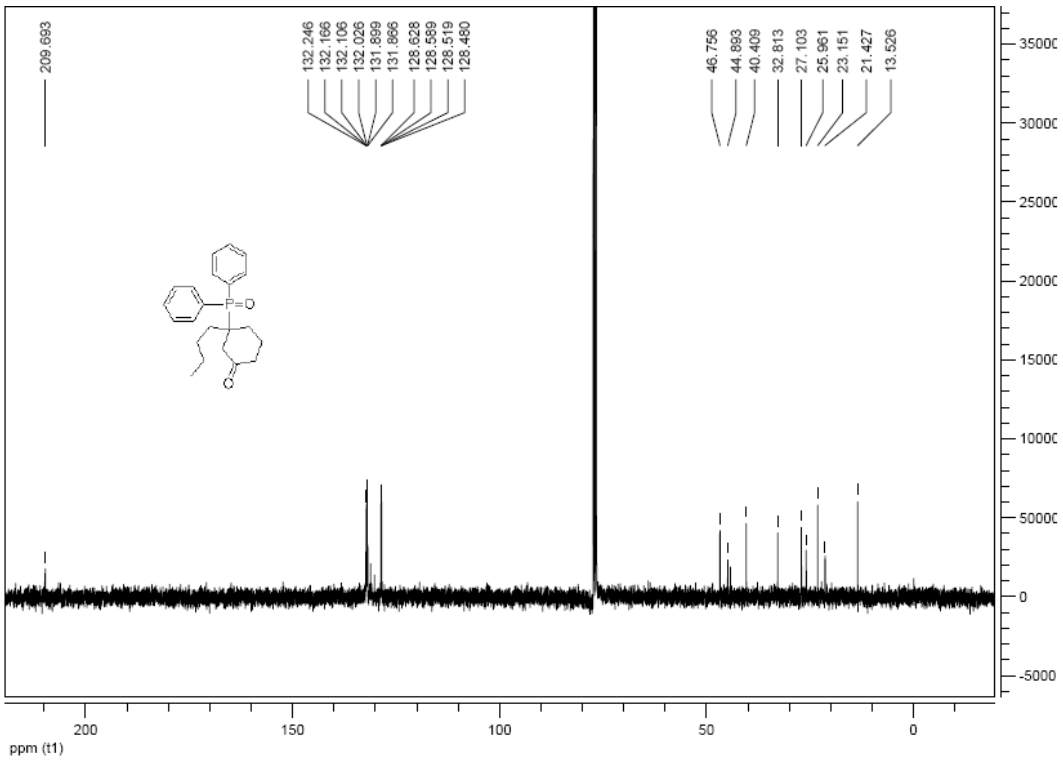
3-(diphenylphosphoryl)-3-propylcyclohexanone (Table 2, entry 4)



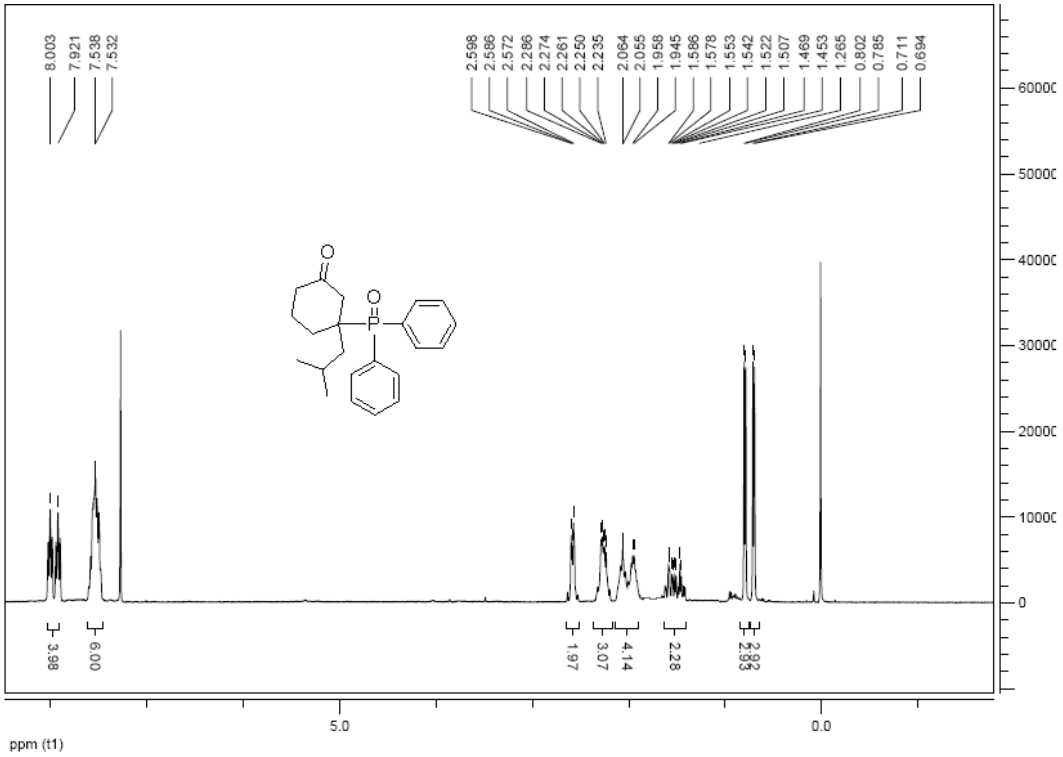


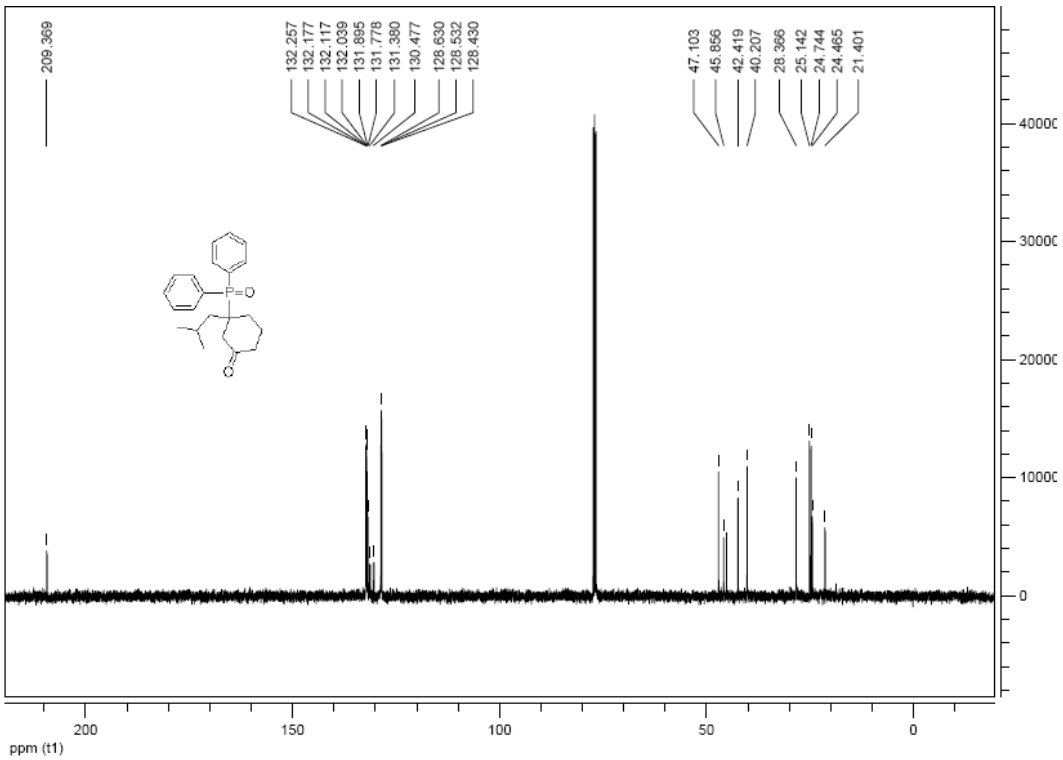
3-butyl-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 5)



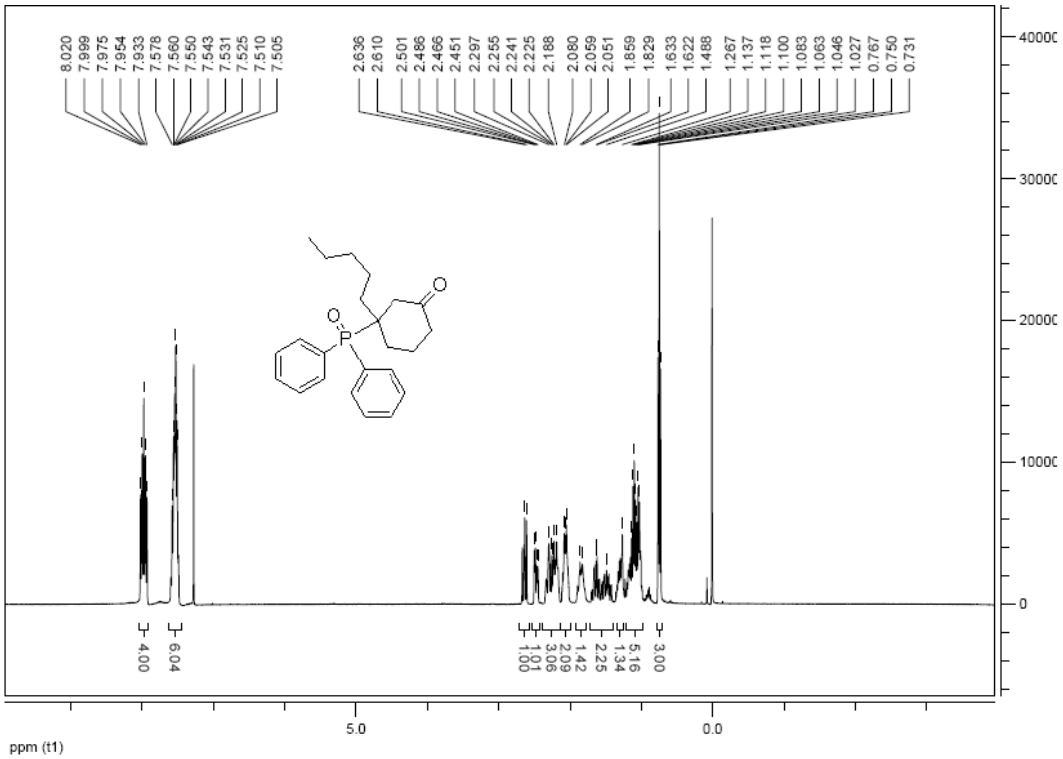


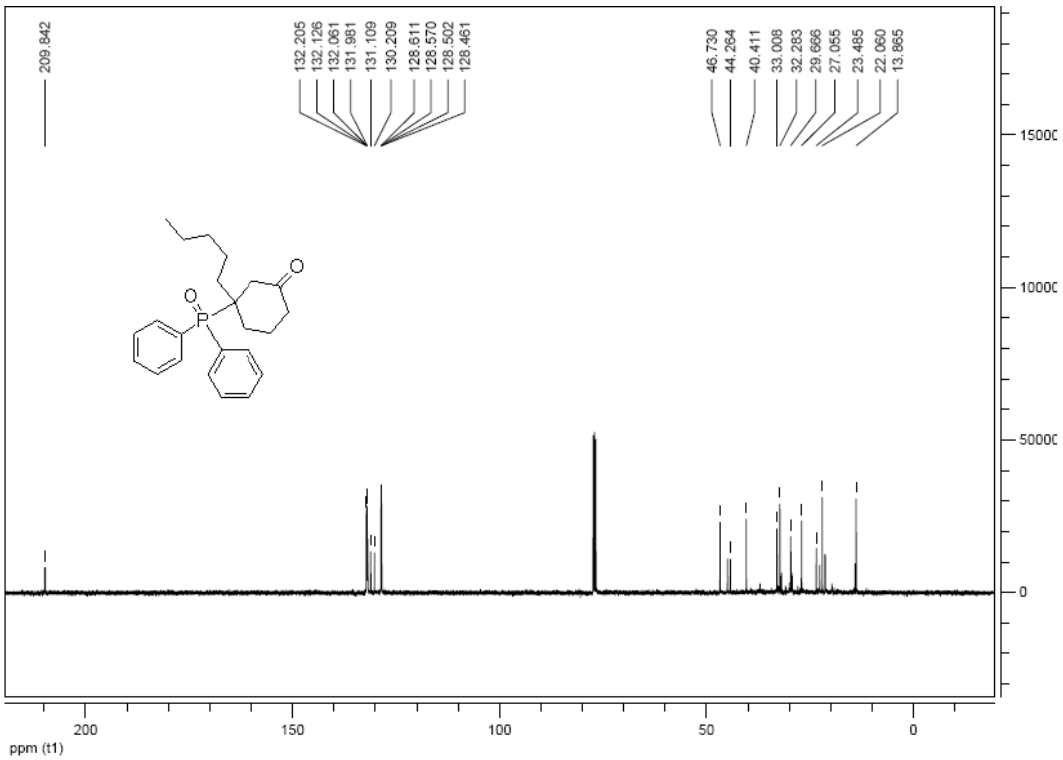
3-(diphenylphosphoryl)-3-isobutylcyclohexanone (Table 2, entry 6)



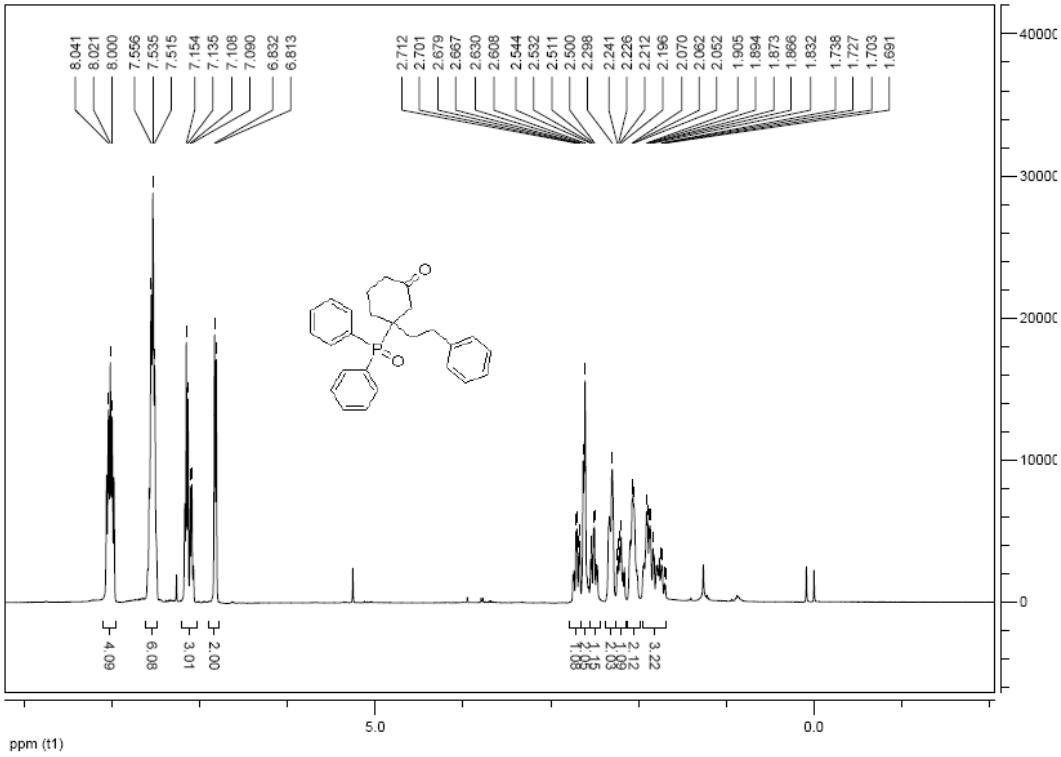


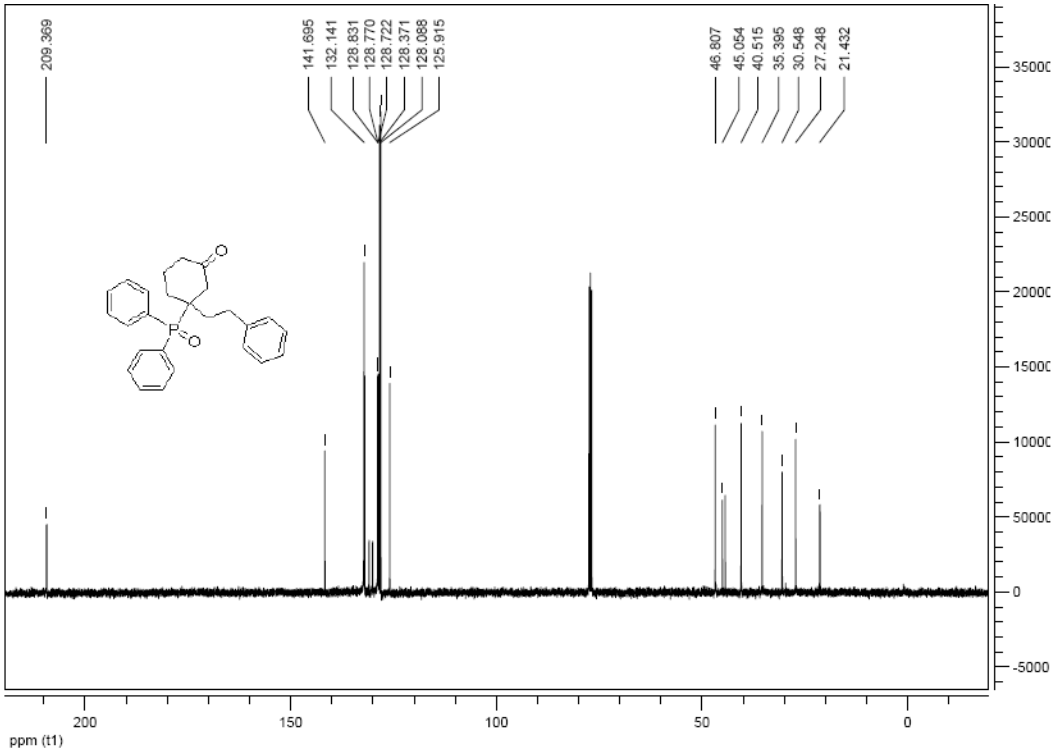
3-(diphenylphosphoryl)-3-pentylcyclohexanone (Table 2, entry 7)



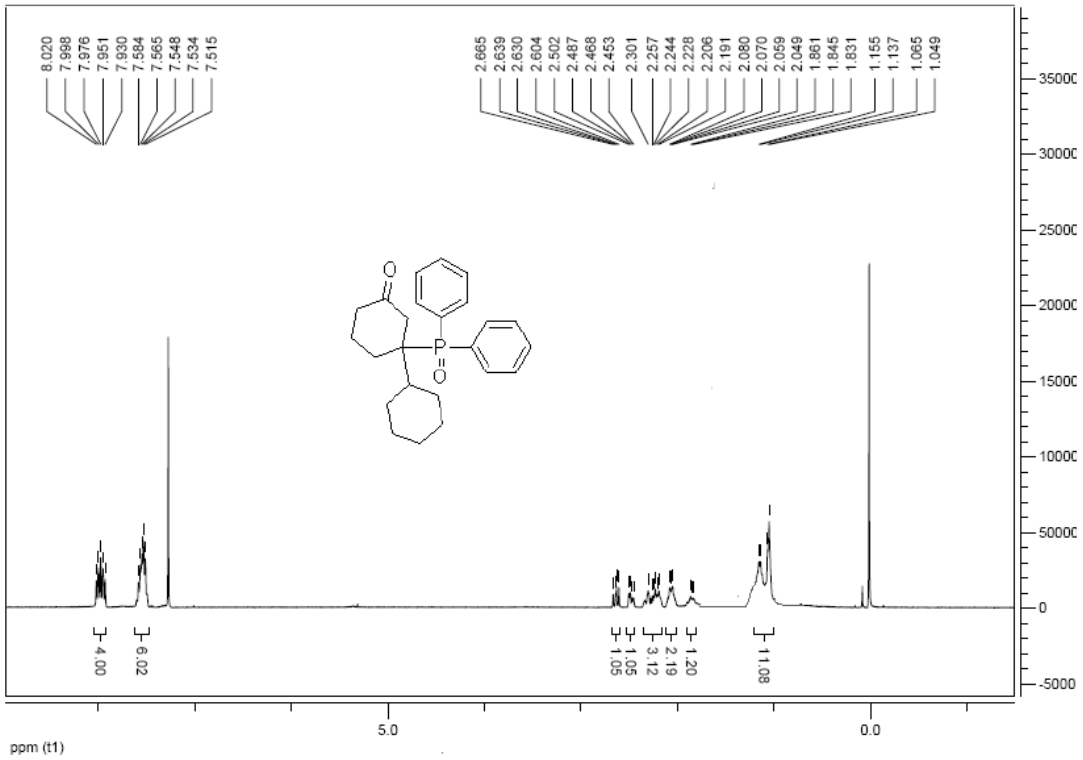


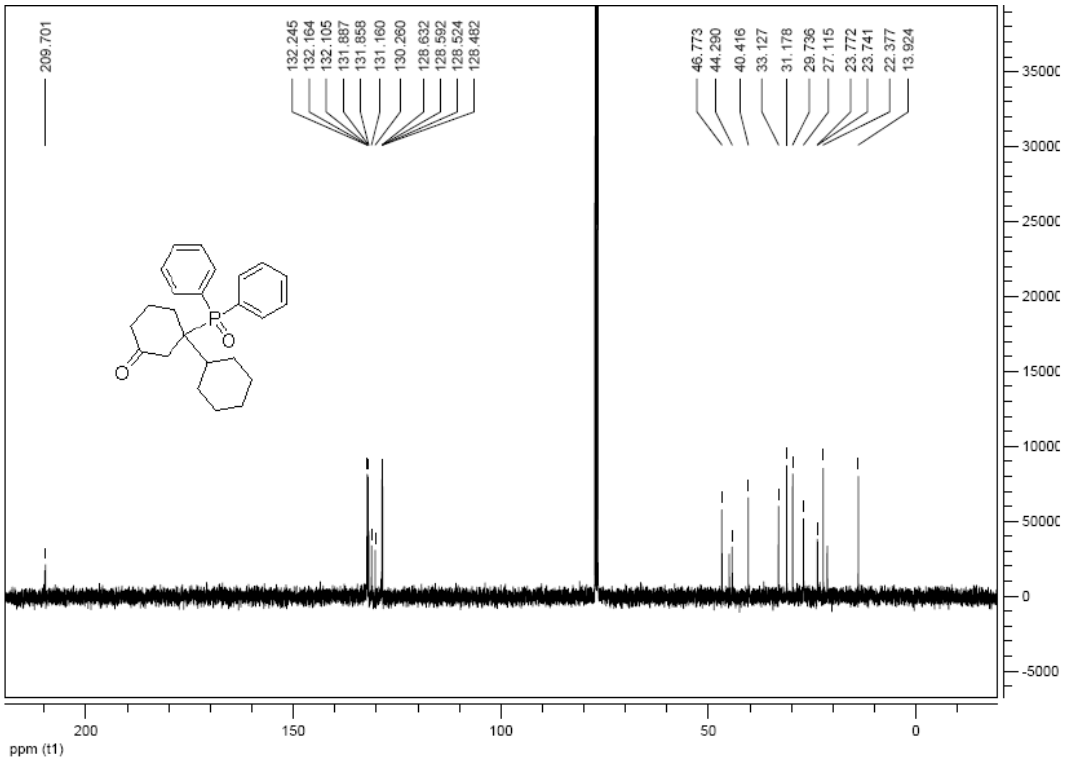
3-(diphenylphosphoryl)-3-phenethylcyclohexanone (Table 2, entry 8)



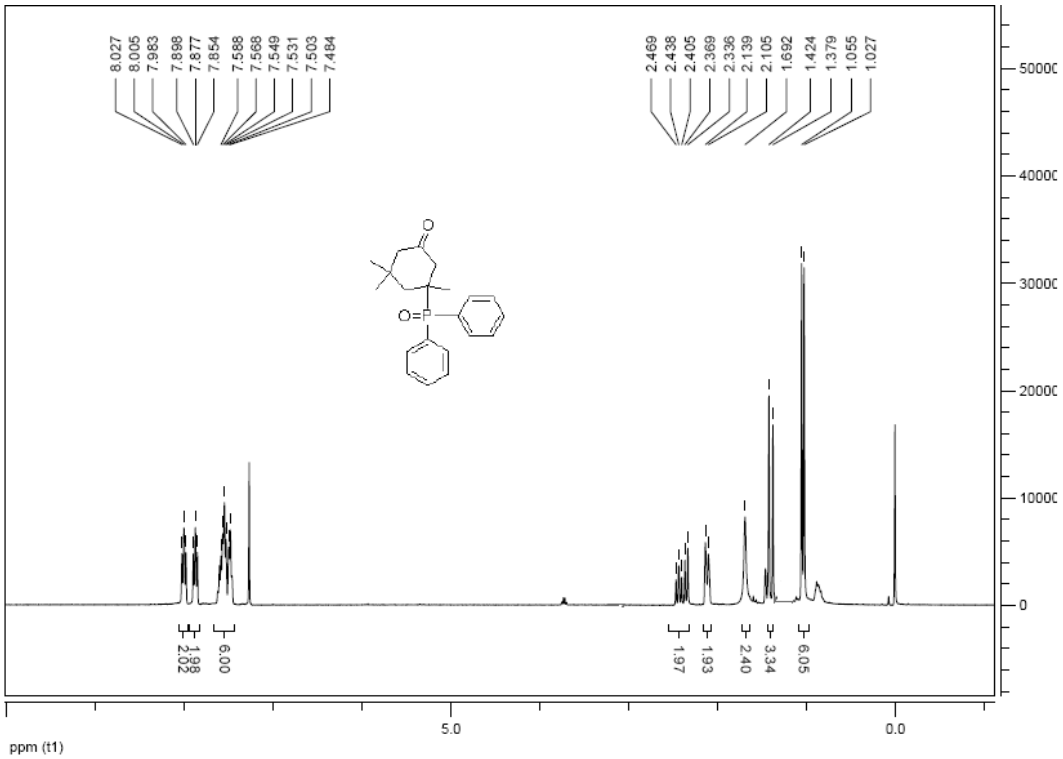


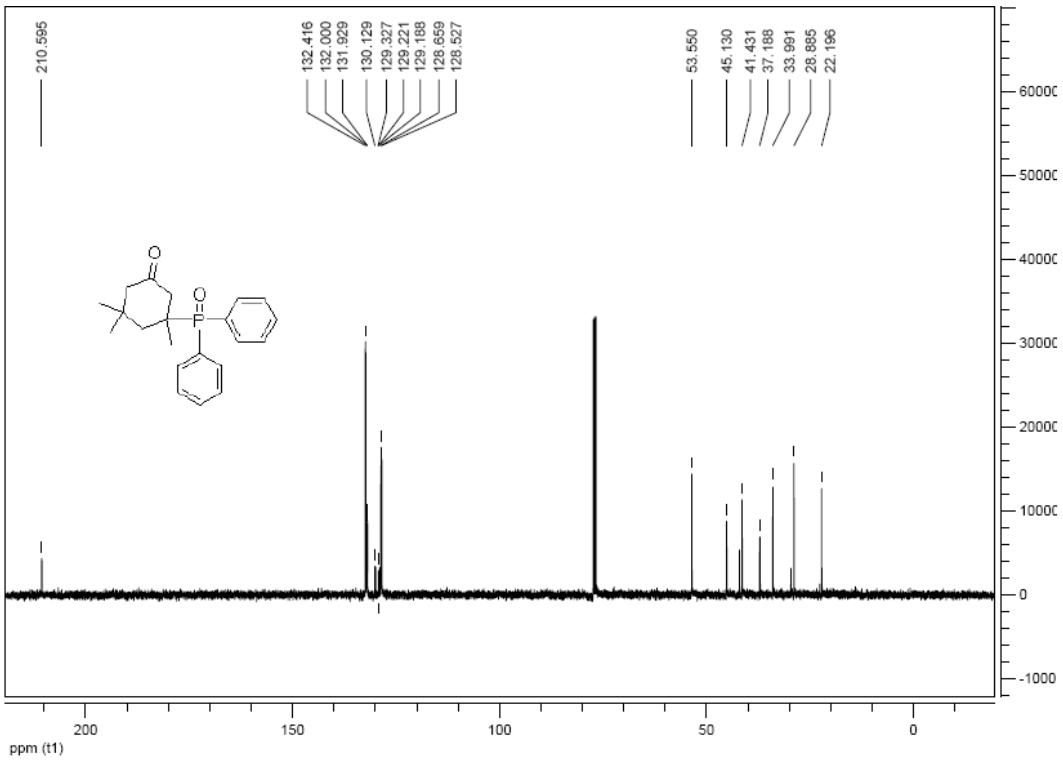
3-cyclohexyl-3-(diphenylphosphoryl)cyclohexanone (Table 2, entry 9)



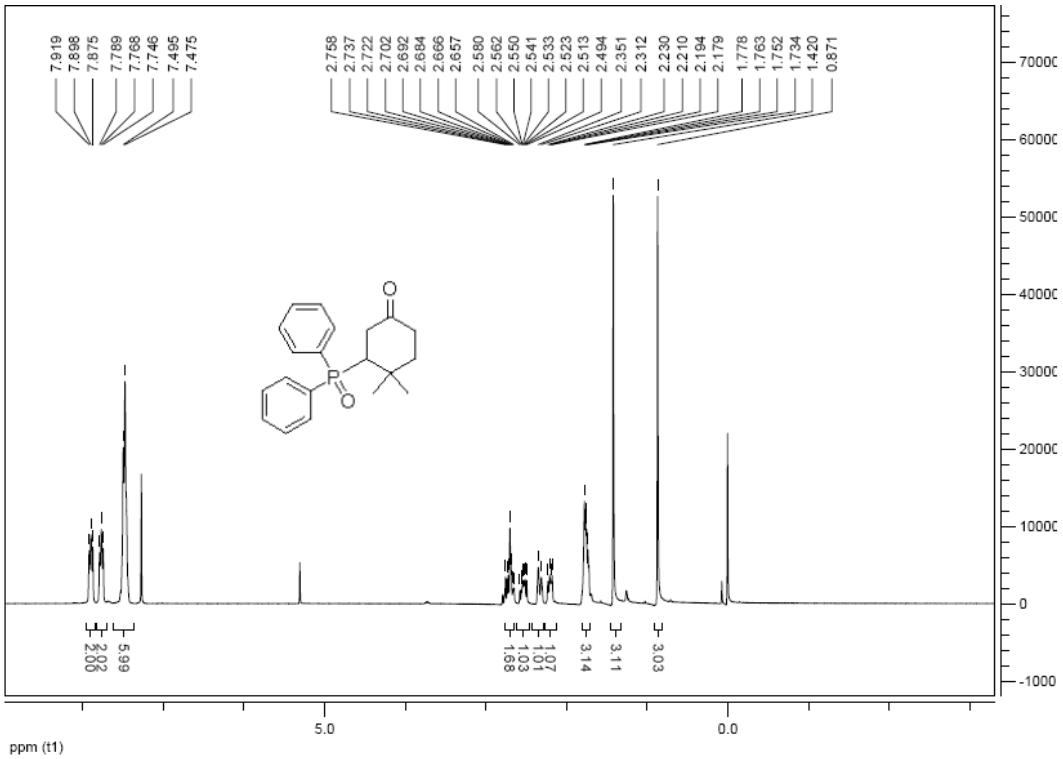


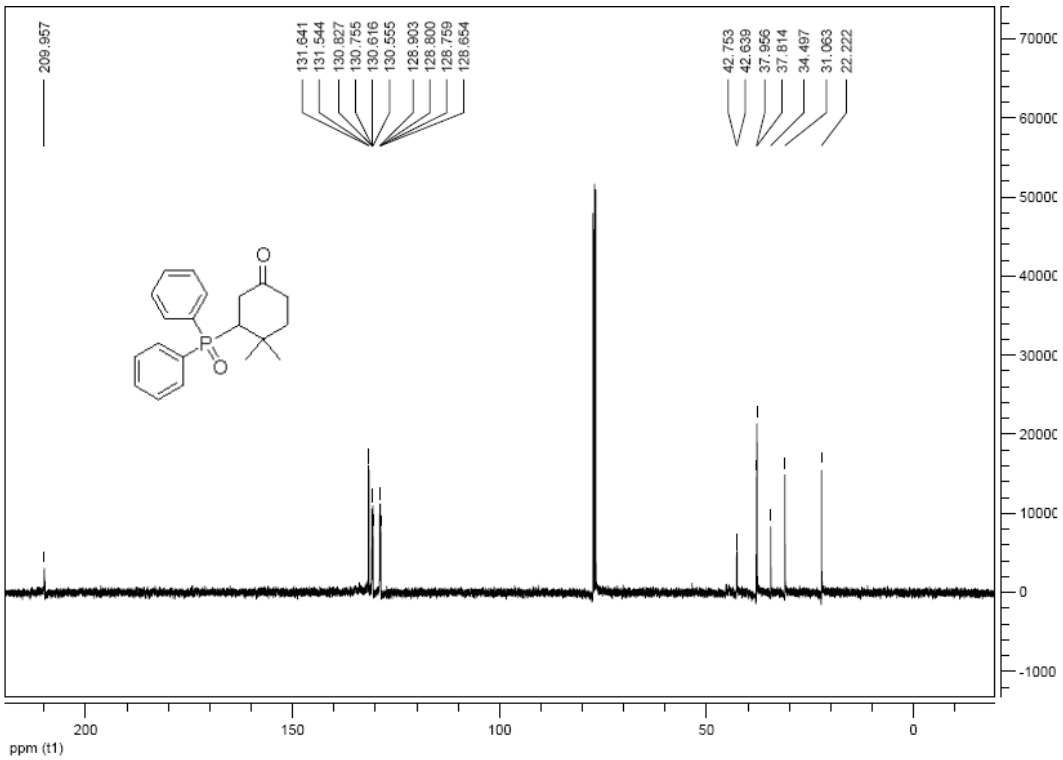
3-(diphenylphosphoryl)-3,5,5-trimethylcyclohexanone (Table 2, entry 10)



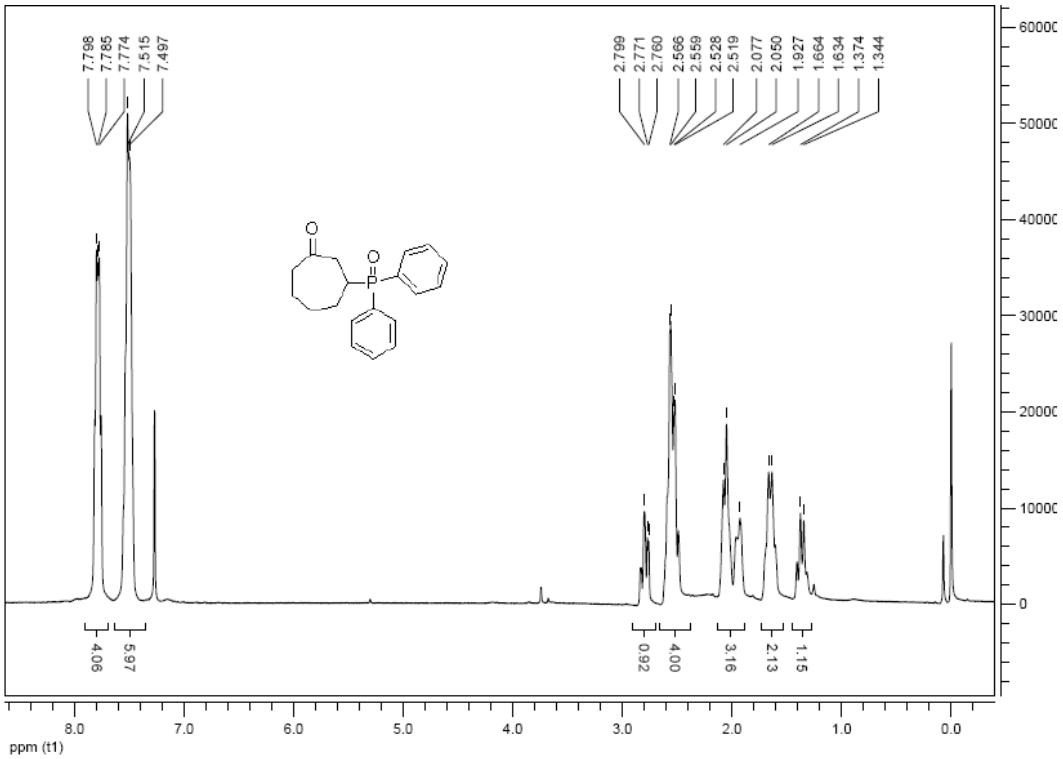


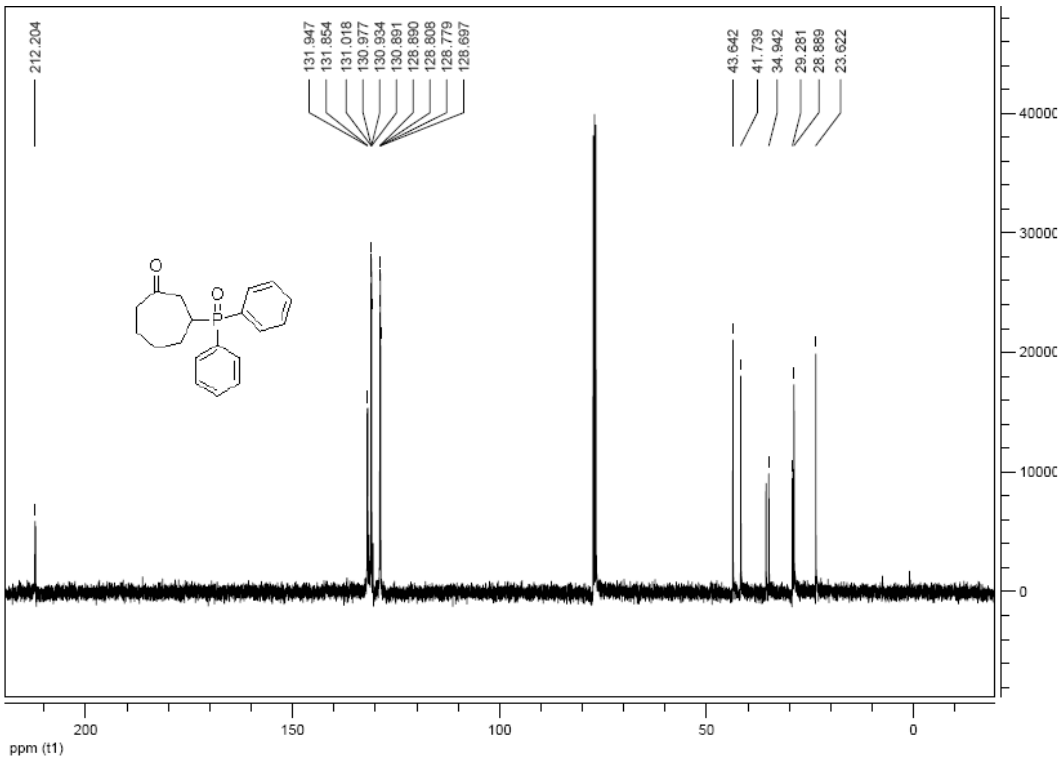
3-(diphenylphosphoryl)-4,4-dimethylcyclohexanone (Table 2, entry 11)



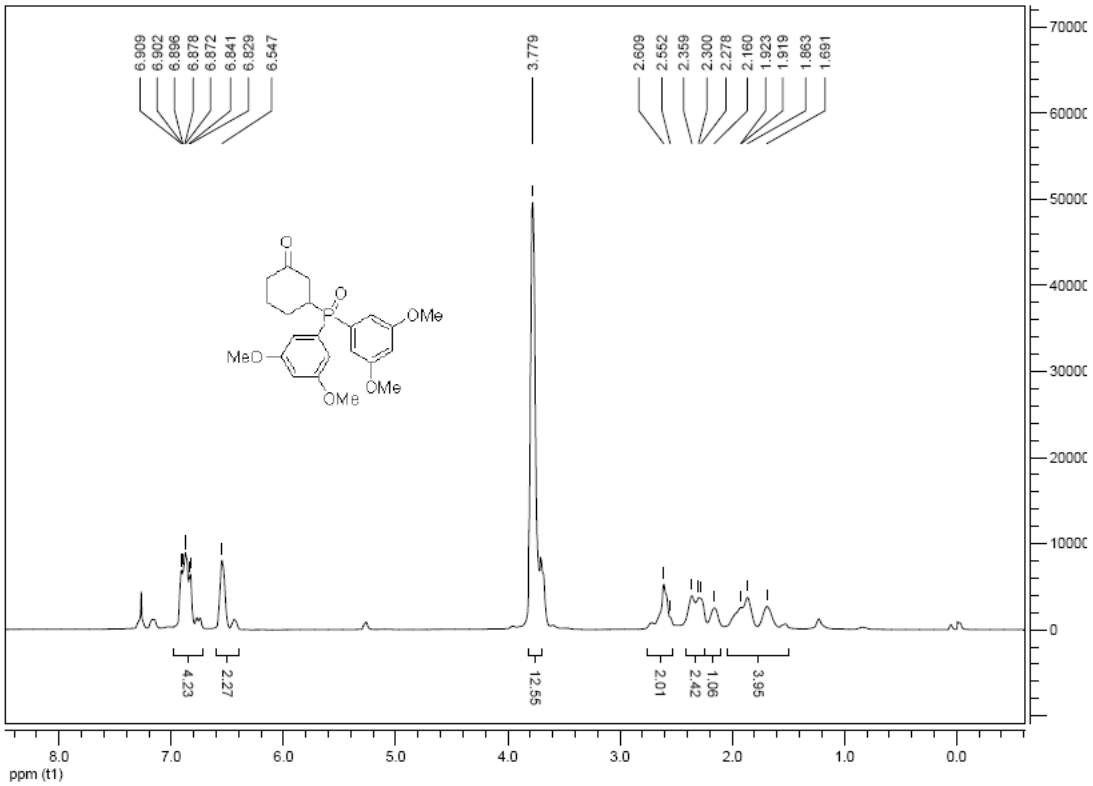


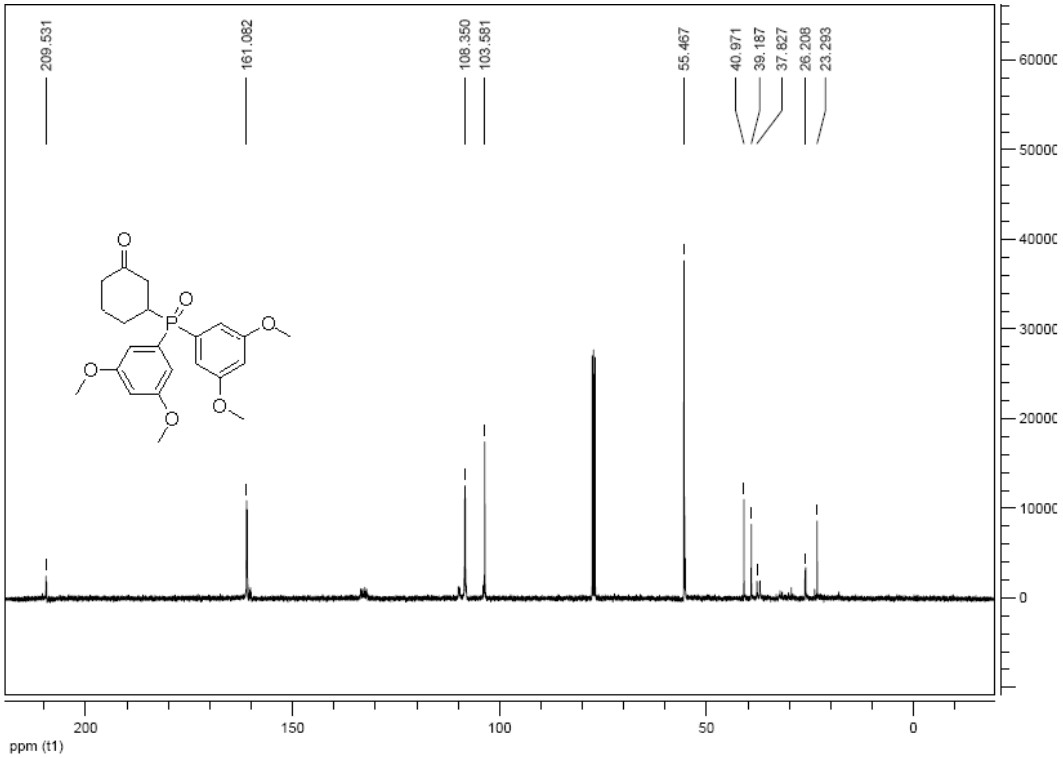
3-(diphenylphosphoryl)cycloheptanone (Table 2, entry 12)



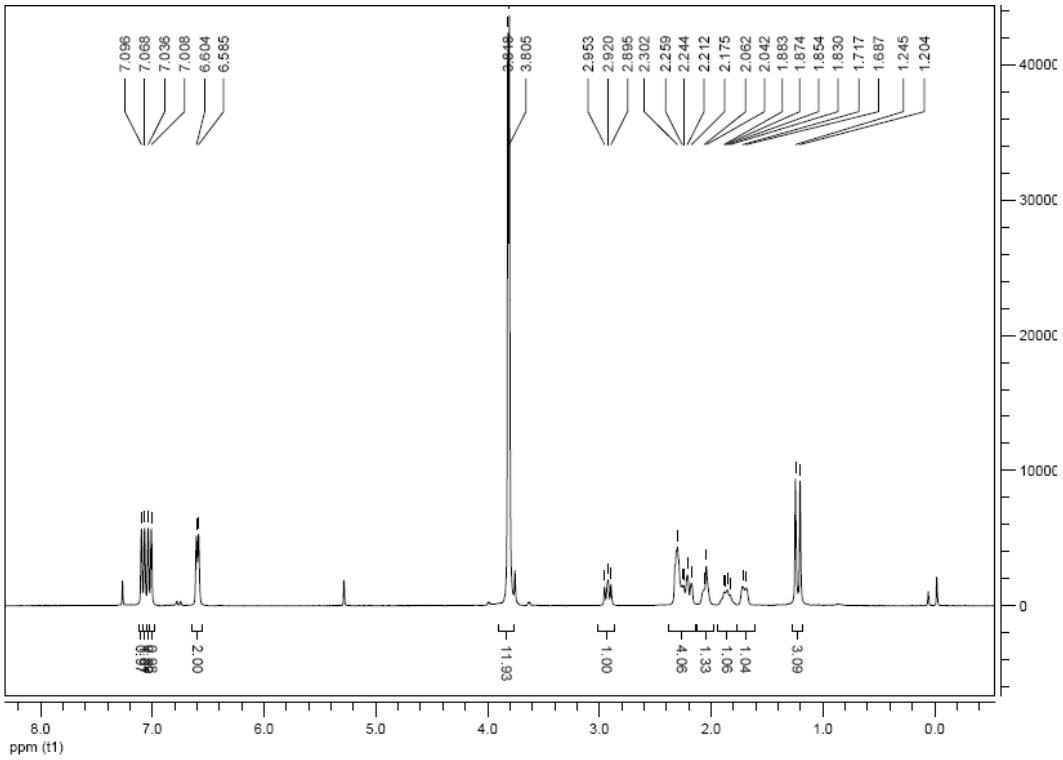


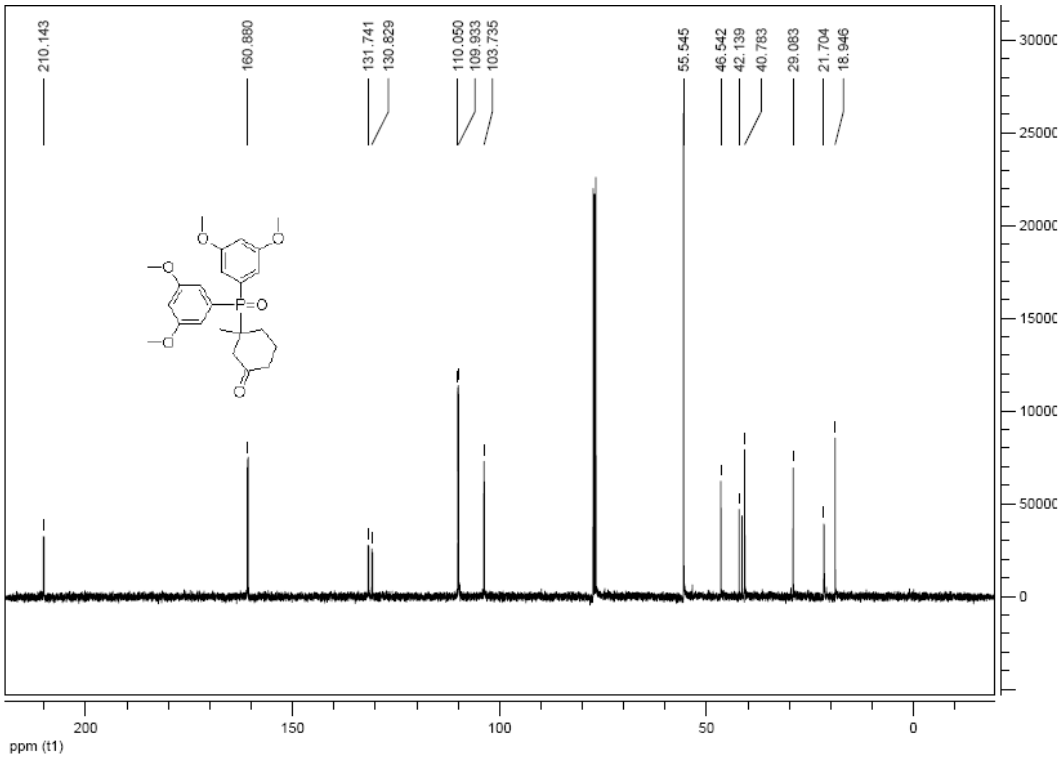
3-(bis(3,5-dimethoxyphenyl)phosphoryl)cyclohexanone (Table 2, entry 13)



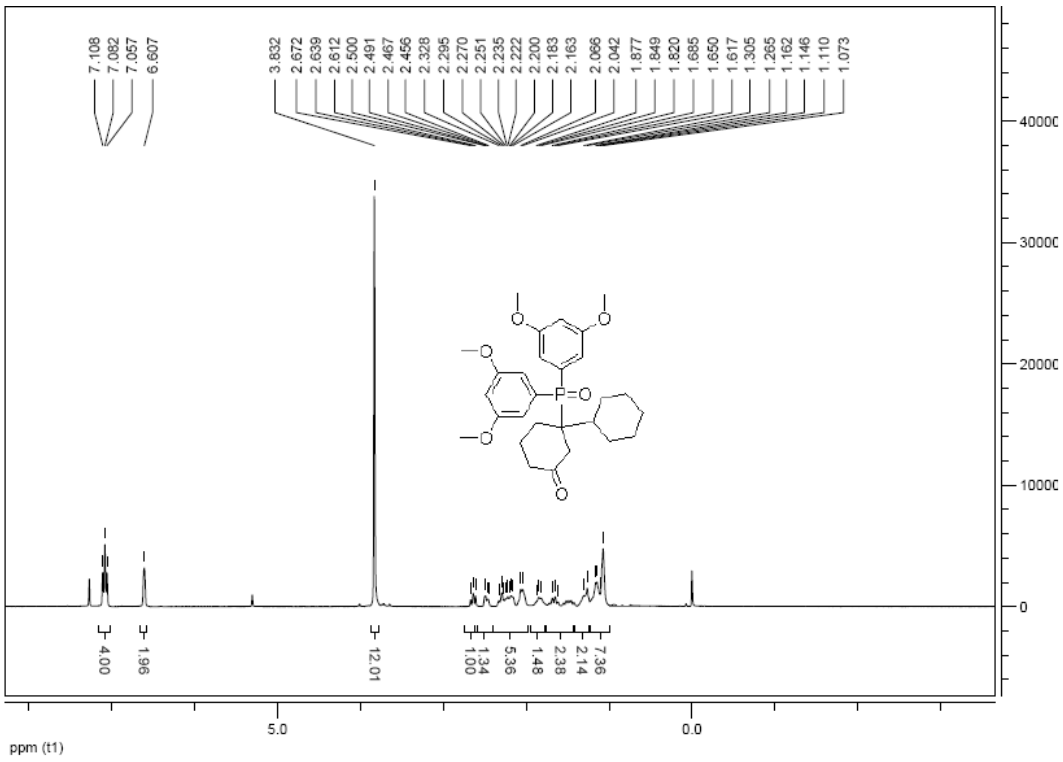


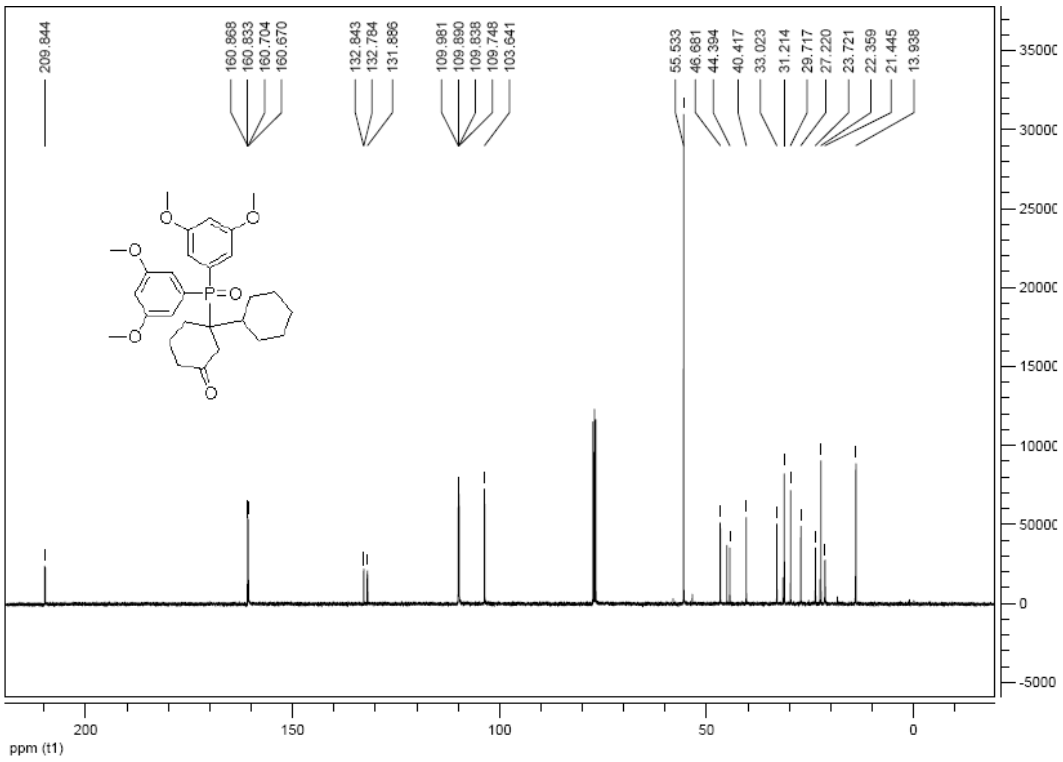
3-(bis(3,5-dimethoxyphenyl)phosphoryl)-3-methylcyclohexanone (Table 2, entry 14)



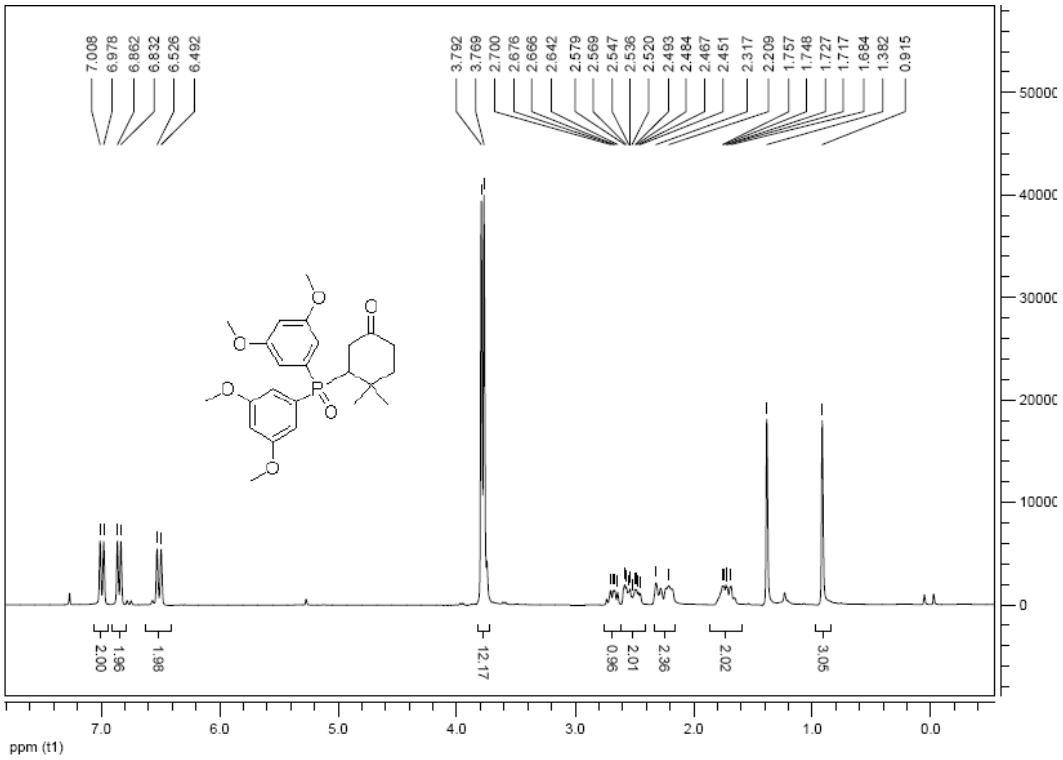


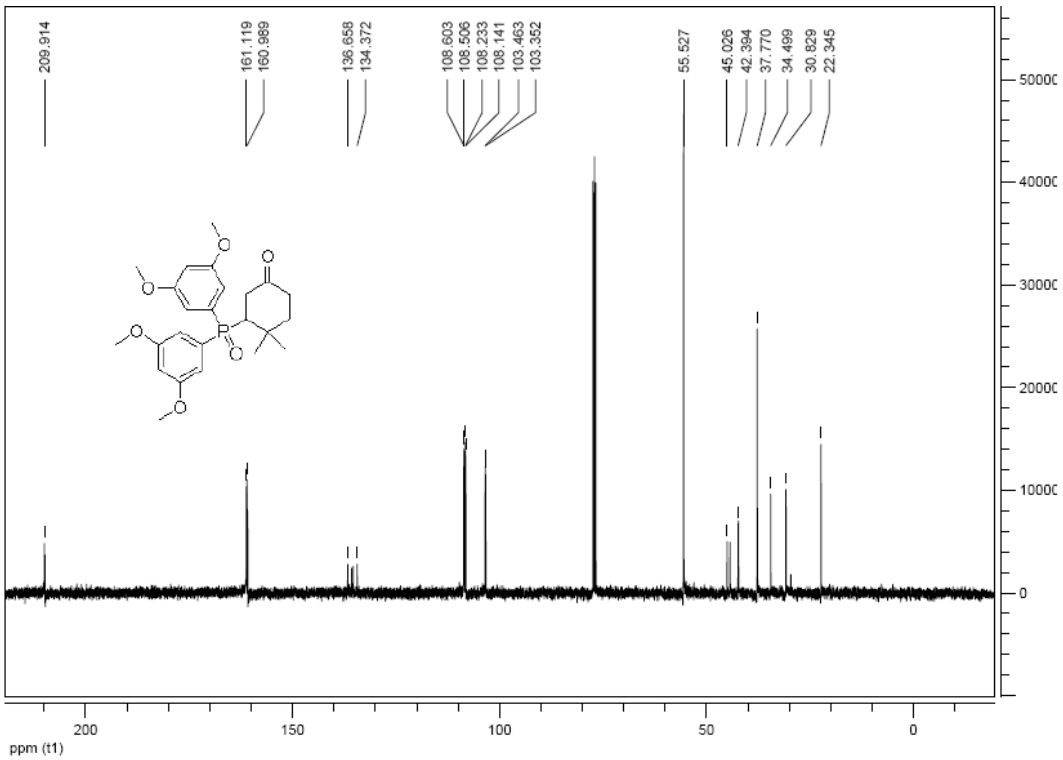
3-(bis(3,5-dimethoxyphenyl)phosphoryl)-3-cyclohexylcyclohexanone (Table 2, entry 15)



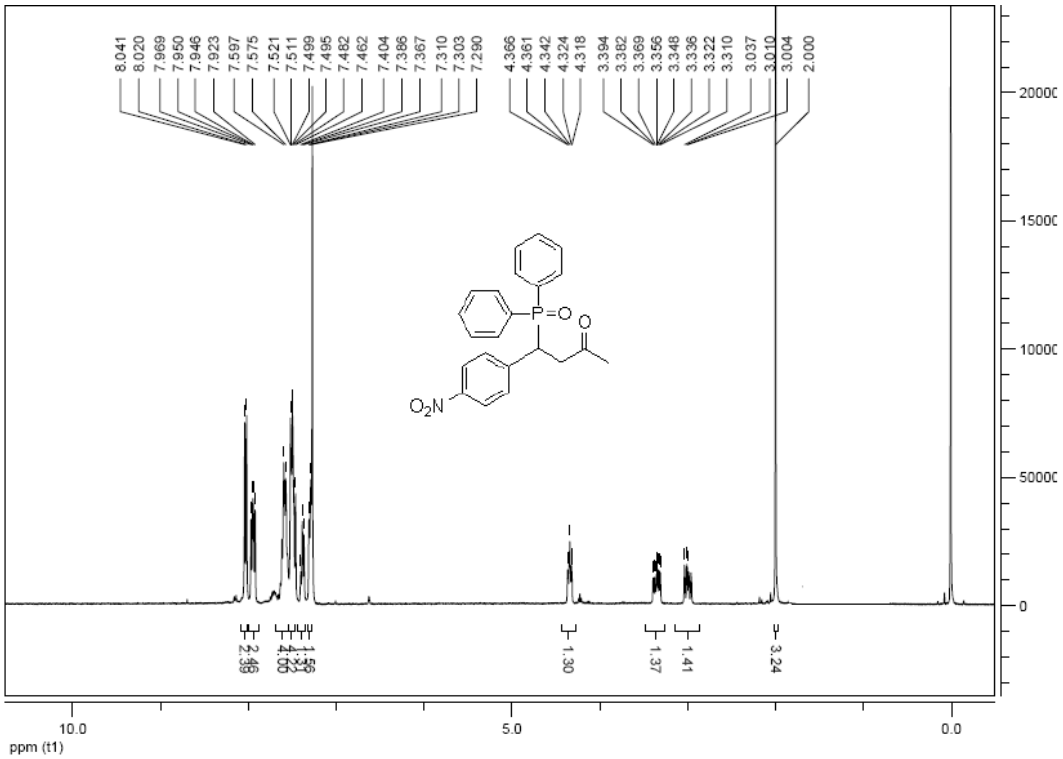


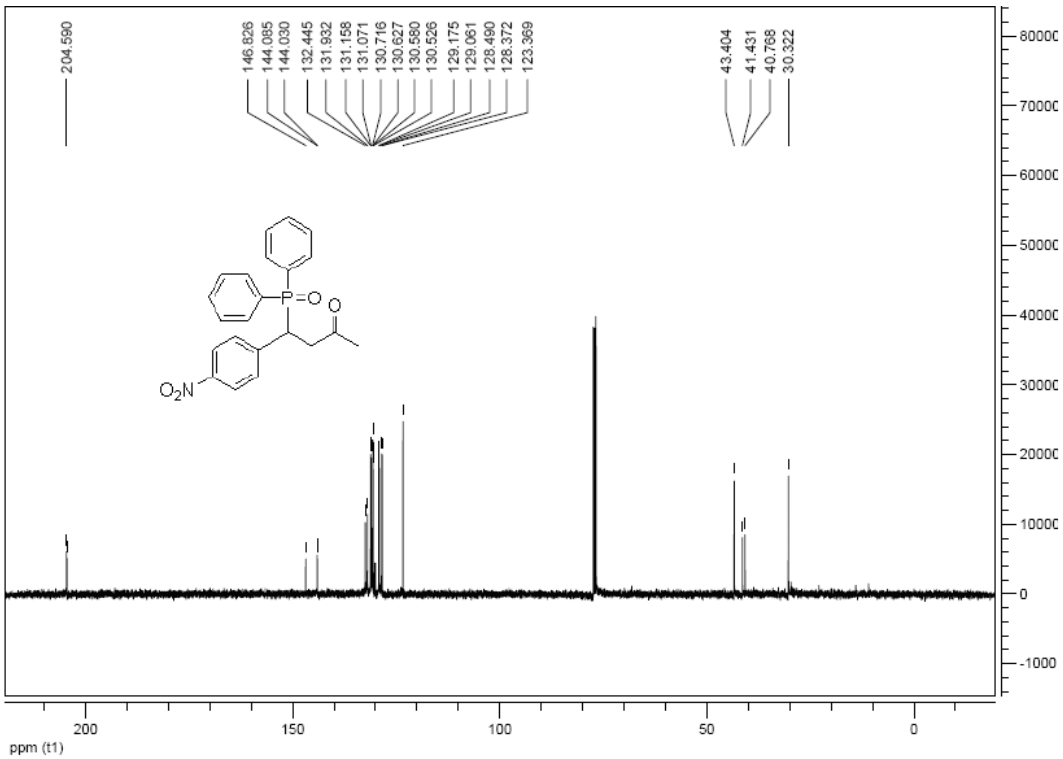
3-(bis(3,5-dimethoxyphenyl)phosphoryl)-4,4-dimethylcyclohexanone (Table 2, entry 16)



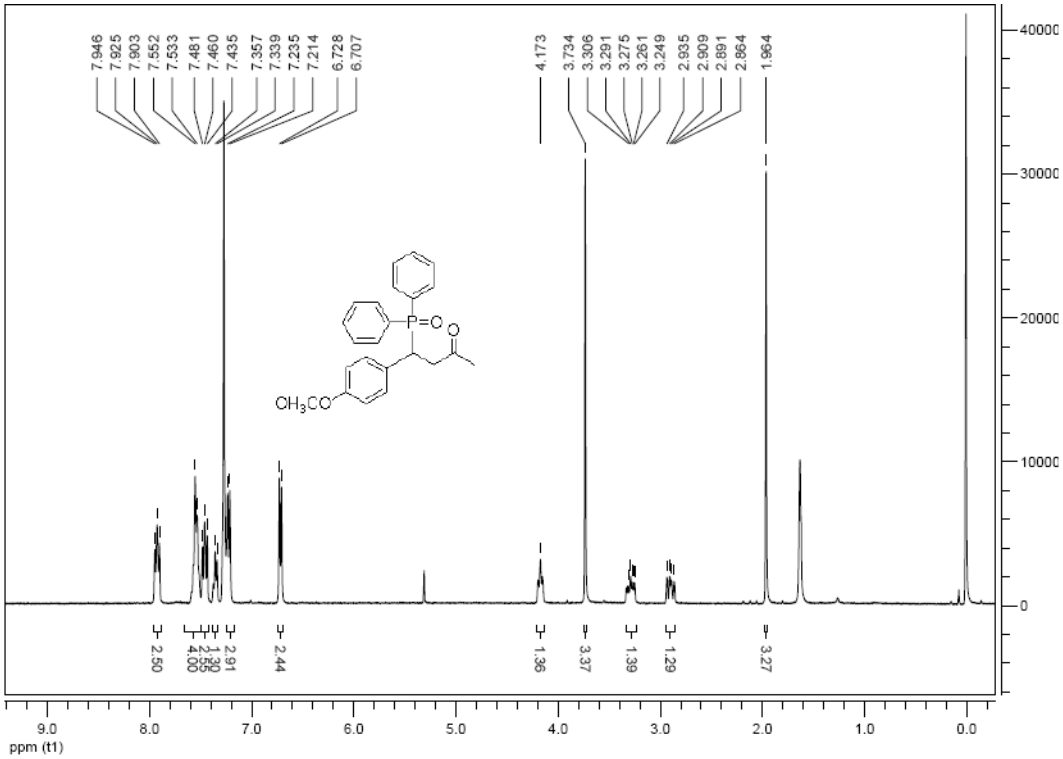


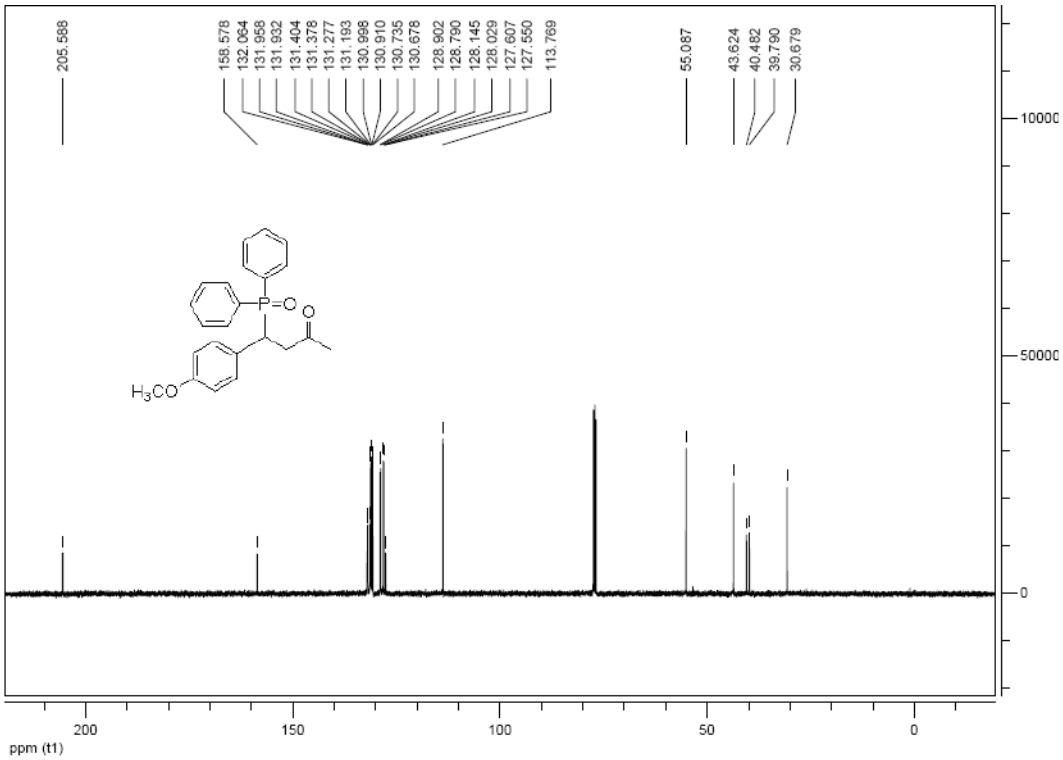
4-(diphenylphosphoryl)-4-(4-nitrophenyl)butan-2-one (Table 2, entry 17)



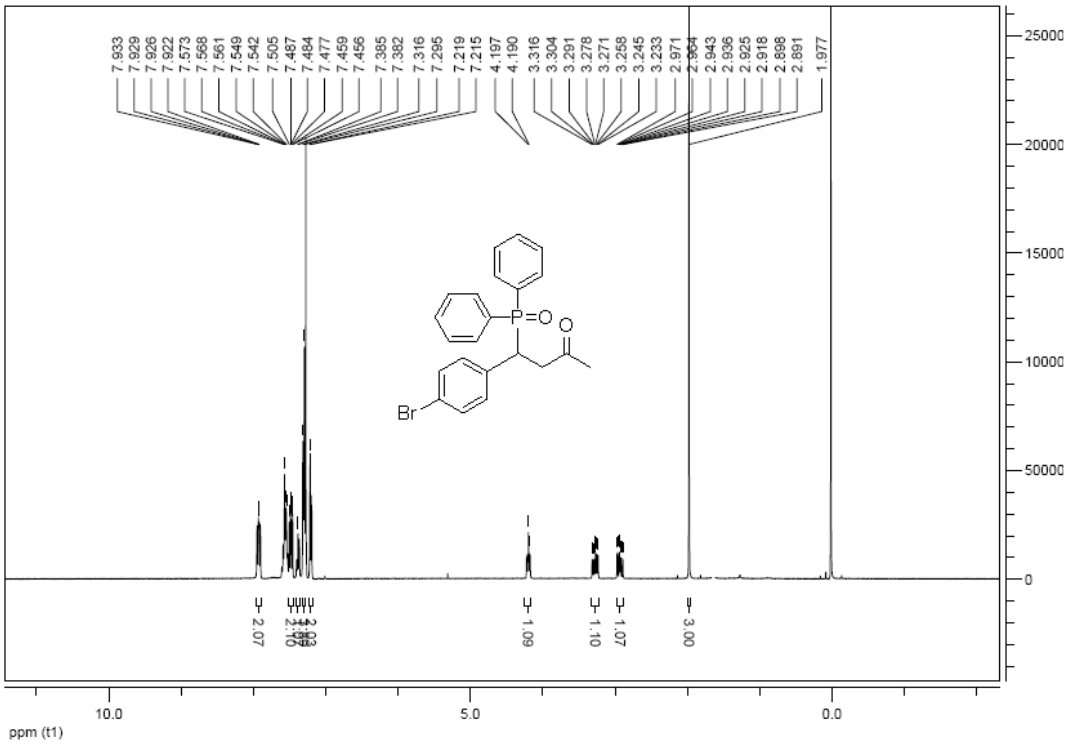


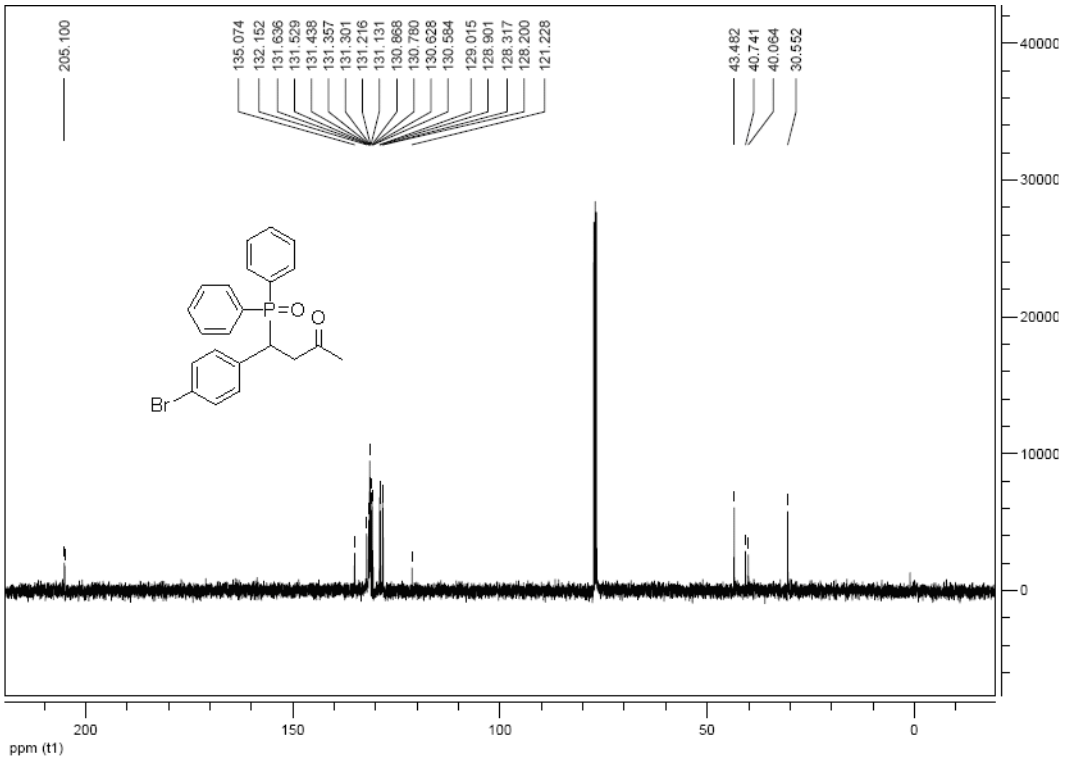
4-(diphenylphosphoryl)-4-(4-methoxyphenyl)butan-2-one (Table 2, entry 18)



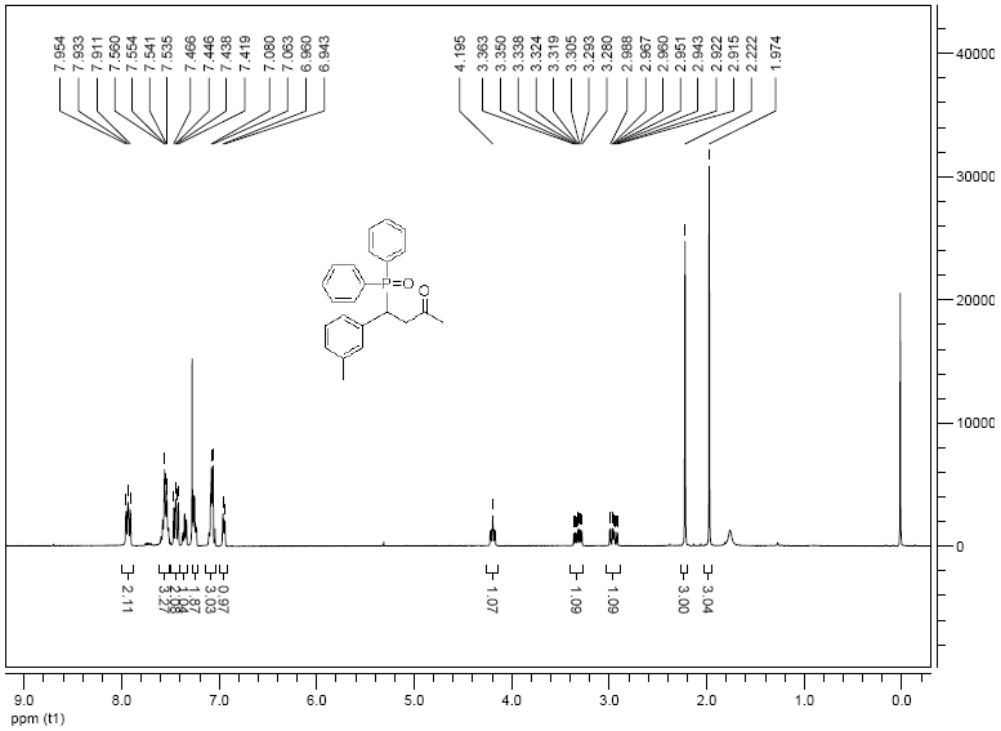


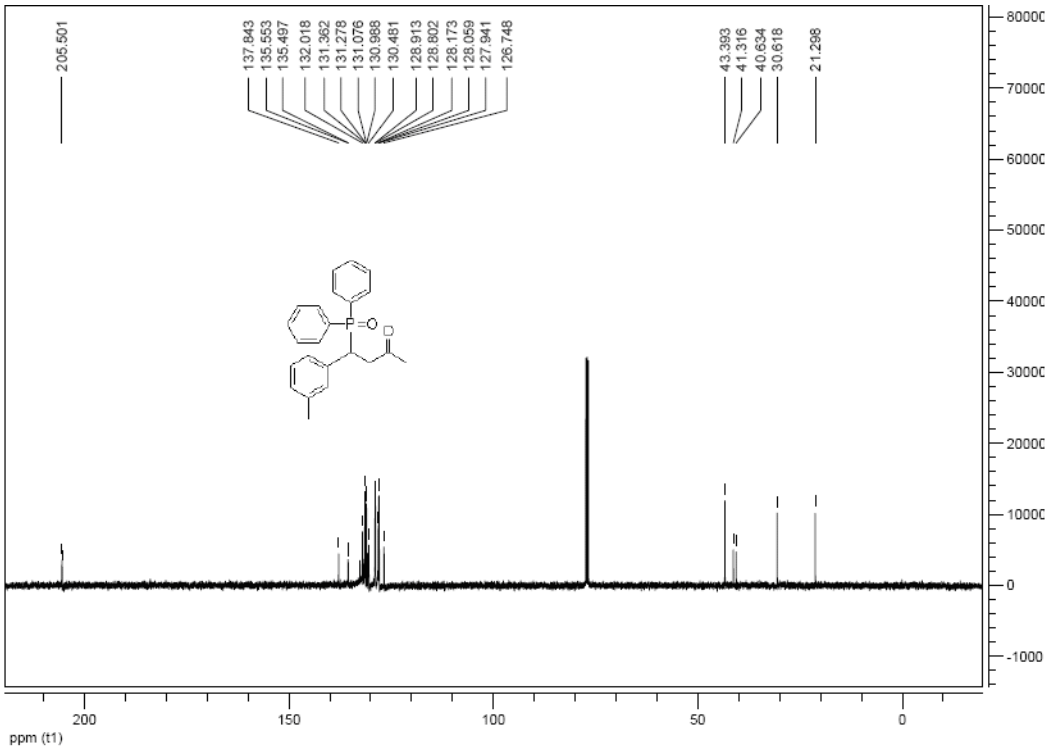
4-(4-bromophenyl)-4-(diphenylphosphoryl)butan-2-one (Table 2, entry 19)





4-(diphenylphosphoryl)-4-m-tolylbutan-2-one (Table 2, entry 20)





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