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Supporting information

Synthesis of α-aminophosphonates using a mesoporous silica catalyst produced from the sugarcane bagasse ash

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Experimental Section

Synthesis of SBA-16

Firstly, the sugarcane bagasse ash (SCBA) was collected from the sugar-alcohol plant located in the region of Maringá City, Paraná, Brazil. This material was placed in a horizontal furnace and heated at a rate of 20 °C•min^{-1} from room temperature up to 600°C, and holding for 4 h (SCBA600). The SCBA600 was used as the silica precursor to synthesis of SBA-16 where 4.0 g of SCBA600 were mixed with 6.0 g of NaOH (ratio of 1.5 w/w) to obtain a homogeneous mixture. Then, the mixture was heated in a nickel crucible at atmospheric pressure at 550°C for 40 minutes. The resultant fused mixture was dissolved in 50 mL of deionized water (solution 1). Then, 4.0 g of surfactant Pluronic F127 ($EO_{106}PO_{70}EO_{106}$, EO = ethylene oxide, PO = propylene oxide; Sigma Aldrich) was dissolved in 120 mL of HCl solution, 2 mol•L^{-1}, at room temperature. The mixture was stirred at room temperature until a homogeneous gel solution was formed (solution 2). Afterward, solution 2 was added to solution 1, and was kept under moderate stirring at room temperature for 20 h. The solid product was filtered, washed with deionized water, and air-dried at 80°C for 4 h. Finally, the as-prepared white powder was calcinated in air at 550°C for 6 h, with a heating ramp to reach 550°C of 1°C•min^{-1}, to remove the surfactant. The sample obtained was denoted by SBA-16.

Synthesis of functionalized SBA-16 sulfonic groups

The anchor of organic group into mesostructured silica surface occurred via post-synthesis procedure.[10a] Initially the SBA-16 was functionalized with thiol (RSH) group. It was carried out under batch reaction conditions using a 150 mL flask fitted with a stirrer, a thermometer and a reflux condenser at 60°C. In a typical reaction, 1.0 g SBA-16 was dissolved in 30 mL of toluene, then 1.0 mL of 3-mercaptopropyltrimethoxysilane (MPTMS) was added.

After stirring for 24 h, the SBA-16 powder functionalized with thiol group was recovered as described in 2.1 item. Then, the thiol functionalized SBA-16 was oxidized with slowly dropwise of 30 mL of 30 wt% H_2O_2 solution for 24 h with moderate stirring at room temperature. The solid products were recovered, as described in 2.1 item and was denoted by SBA-16/SO_3H.

α-aminophosphonates synthesis

Initially the reactions were carried out varying the amount of catalysts (0.003, 0.006, 0.008, 0.01 and 0.02 g). In a typical reaction, 2.0 mmol aniline, 2.2 mmol benzaldehyde and 2.0 mmol of diphenyl phosphite were mixed in the presence of SBA-16 and SBA-16/SO3H in amounts above indicated. In next, the aminophosphonates was synthesized in similar way, where 0.01 g of catalysts was used in present of different solvents (toluene, dichloromethane, chloroform, TFH, ethanol and methanol). Finally, establishing the standardization of reaction Kabachnik-Fields, other α-aminophosphonates were synthesized following the same protocol, but with benzaldehyde and aniline replaced as described in Figure S1.

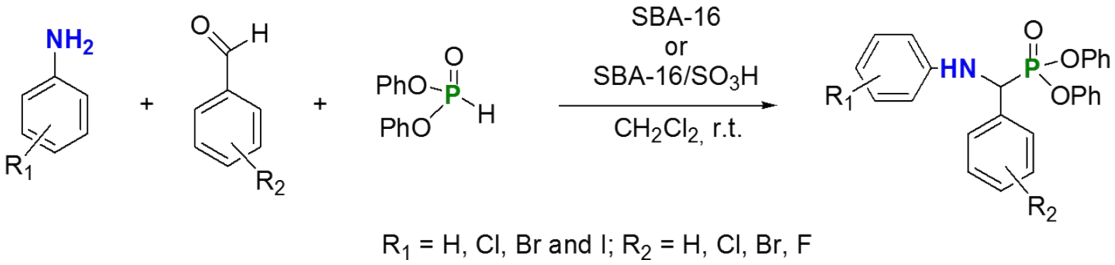


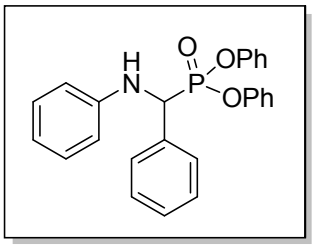
Figure S1 SBA-16 and SBA-16/SO3H catalyzed in a general scope of the Kabachnik–Fields reactions.

Characterization Techniques

Low-angle X-ray diffraction XRD patterns were obtained using a Bruker D8-Advance equipment with Cu-Kα radiation, wavelength of 1.5406 Å, operated at 40 kV and 35 mA, 0.01° step size and 2 s/step time over range 0.5°< 2θ < 5°. Nitrogen adsorption–desorption isotherms were measured at -196°C on a Quantachrome NOVA-1200E Surface and PoroAnalizer equipment. The specific surface areas were evaluated using Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH). Fourier transform infrared (FTIR) spectra were recorded with Thermo Fischer Scientific Nicolet IZ10 equipment in the range of 400-4000 cm^{-1} using KBr disc method. Scanning Electron Microscopy (SEM) images were obtained with Shimadzu SSX-550 Superscan equipment and Transmission Electron Microscopy (TEM) images were recorded on JEOL JEM-1400 equipment operated at 120 kV. Acid capacities of SBA-16 and SBA-16/SO_3H were indicated by temperature-programmed ammonium desorption (NH3-TPD) and was carried out with AutoChem II 2920 equipment. The α-aminophosphonates products were characterized using ^{1}H and ^{13}C nuclear magnetic resonance spectroscopy (NMR), using $CDCl_3$ as solvent and, recorded on a 300 MHz Bruker AVANCE III HD spectrometer. Chemical shifts were expressed in parts per million (ppm) and coupling constants (J) were reported in Hertz (Hz).

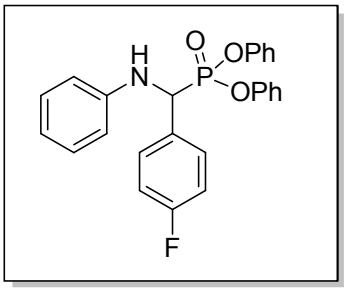
^{1}H and ^{13}C NMR spectra analysis

Diphenyl (phenyl(phenylamino)methyl) phosphonate:



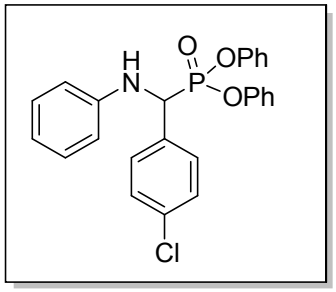
Light yellow, PM: 415,13 g/mol. $C_{25}H_{22}NO_3P$. M.p.:159-16 °C. IR (KBr) ($\nu_{máx}$ cm^{-1}): 3343 (N-H), 1186.01 (P=O), 762.70 (C-P). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 54.49-55.73 (d, J_{H-P}= 24.6 Hz, 1H, N-C**H**-P), 3.67-3.89 (m, 4H), 4.10-4.40 (m, 12H), 4.57-4.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 55.10 and 56.99 (d, J_{C-P}= *158.6* Hz), 76.57, 77.42, 118.82, 120.25, 120.31, 120.61, 120.66, 125.21, 125.38, 128.11, 128.19, 128.28, 128.76, 128.80, 129.23, 129.59, 129.70, 134.78, 145.97, 150.17.

Diphenyl ((4-fluorophenyl)(phenylamino)methyl) phosphonate:



Light yellow, PM: 433,12 g/mol. $C_{25}H_{21}FNO_3P$. M.p.:104-105 °C. IR KBr ($\nu_{máx}$ cm^{-1}): 3453.30 (N-H), 1284.65 (P-O), 776.80 (C-P). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 5.11-5.19 (d J_{H-P} = 24,0 Hz, 1H, N-C**H**-P), 6.63-6.66 (m, 2H), 6.76-6.94 (m, 4H), 7.03-7.33 (m, 12H), 7.52-7.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.27 and 56.32 (d, J_{P-C} = 153.7 Hz) 76.57, 77.42, 113.98, 115.65, 115.68, 115.94, 115.97, 119.04, 120.19, 120.25, 120.55, 120.60, 125.33, 125.47, 129.30, 129.70, 129.77, 129.81, 129.89, 145.51, 145.71, 150.14, 150.17.

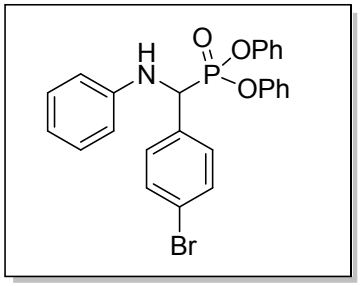
Diphenyl ((4-chlorophenyl)(phenylamino)methyl) phosphonate:



Brown, PM: 449,09 g/mol. $C_{25}H_{21}ClNO_3P$. M.p:131-132 °C. IR KBr ($\nu_{máx}$ cm^{-1}): 3299 (N-H), 1182.15 (P-O), 765.60 (C-P). ^{1}H NMR (300 MHz, DMSO): δ ppm 5.12 – 5.20 (d, *J* = 24.9 Hz, 1H, N-C**H**-P), 6.64-6.98 (m, 5H), 7.11-7.38 (m, 12

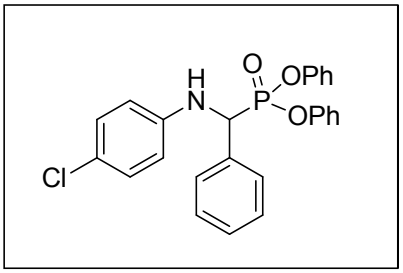
H), 7.51-7.57 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.40 and 56.45 (d, J_{P-C} = 153.0 Hz), 76.57, 77.42, 113.98, 119.11, 120.20, 120.26, 120.53, 120.58, 125.38, 125.50, 128.97, 129.01, 129.31, 129.39, 129.46, 129.72, 129.77, 133.46, 134.23, 145.48, 145.56, 149.99, 150.12.

Diphenyl ((4-bromophenyl)(phenylamino)methyl) phosphonate:



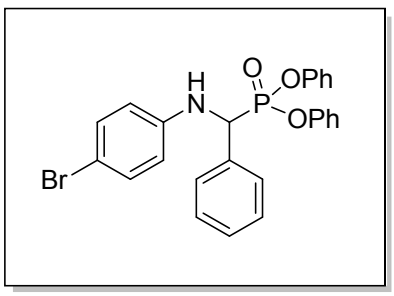
Light brown, PM:493,04 g/mol. $C_{25}H_{11}BrNO_3P$. M.p.:138-140 °C. IR KBr ($\nu_{máx}$ cm^{-1}): 3322.75(N-H), 1029.63 (P-O), 765.60 (C-P).^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 5.06-5.14 (d, *J* = 24.9 Hz, 1H, N-C**H**-P), 6.61-6.63 (m, 2H), 6.75-6.83 (m, 1H), 6.91-6.95 (m, 2H), 7.07-7.32 (m, 9H), 7.42-7.50 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.47 and 56.49 (d, J_{P-C} = 151.5 Hz), 76.57, 76.99, 77.42, 100.0, 113.9, 119.11, 120.16, 120.23, 120.48, 120.55, 122.41, 125.40,125.52, 129.33, 129.68, 129.72, 129.79, 131.90, 131.95, 134.00, 134.97, 145.46, 145.67.

Diphenyl (((4-Chlorophenyl) amino)(phenyl)methyl) phosphonate:



White. PM: 449,09. $C_{25}H_{21}ClNO_3P$. Mp:151-152 °C. IR KBr ($\nu_{máx}$ cm^{-1}): 3336.25 (N-H), 1185.53 (P=O), 775.72 (C-P). ^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 3.82-3.90 (d, J_{H-P}= 24,6 Hz, 1H, N-C**H**-P), 5.32-5.37 (m, 2H), 5.60-5.64 (m, 2H), 5.84-6.17 (m, 14H), 6.28-6.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 55.02 and 57.16 (d, J_{C-P}= 160.5 Hz), 76.57, 77.42, 115.13, 120.21, 120.56, 120.53, 120.62, 123.56, 125.28, 125.52, 128.07, 128.15, 128.53, 128.53, 128.88, 128.91, 129.13, 129.64, 129.77, 134.35, 144.25, 144.52, 150.11.

Dipheny (((4-bromophenyl)amino)(phenyl)methyl) phosphonate:



White. PM: 493,04 g/mol. $C_{25}H_{21}BrNO_3P$. Mp:165-167 °C. IR KBr ($\nu_{máx}$ cm^{-1}): 3336.25 (N-H), 1185.53 (P=O), 775.72

(C-P).[1]H NMR (300 MHz, $CDCl_3$): δ ppm 5.09-5.18 (d, $J_{H\text{-}P}$= 24,6 Hz, 1H, N-C**H**-P), 6.55-6.60 (m, 2H), 6.86-6.91 (m, 2H), 7.13-7.45 (m, 14H), 7.55-7.60 (m, 2H). [13]C NMR (75 MHz, $CDCl_3$): δ ppm 54.89 and 57.01 (d, $J_{C\text{-}P}$= 159 Hz), 76.57, 77.00, 77.42, 110.65, 115.59, 120.17, 120.23, 120.53, 120.59, 125.24, 125.44, 128.03, 128.11, 128.48, 128.53, 128.84, 128.89, 129.60, 129.73, 132.00, 144.72, 144.93, 150.22.

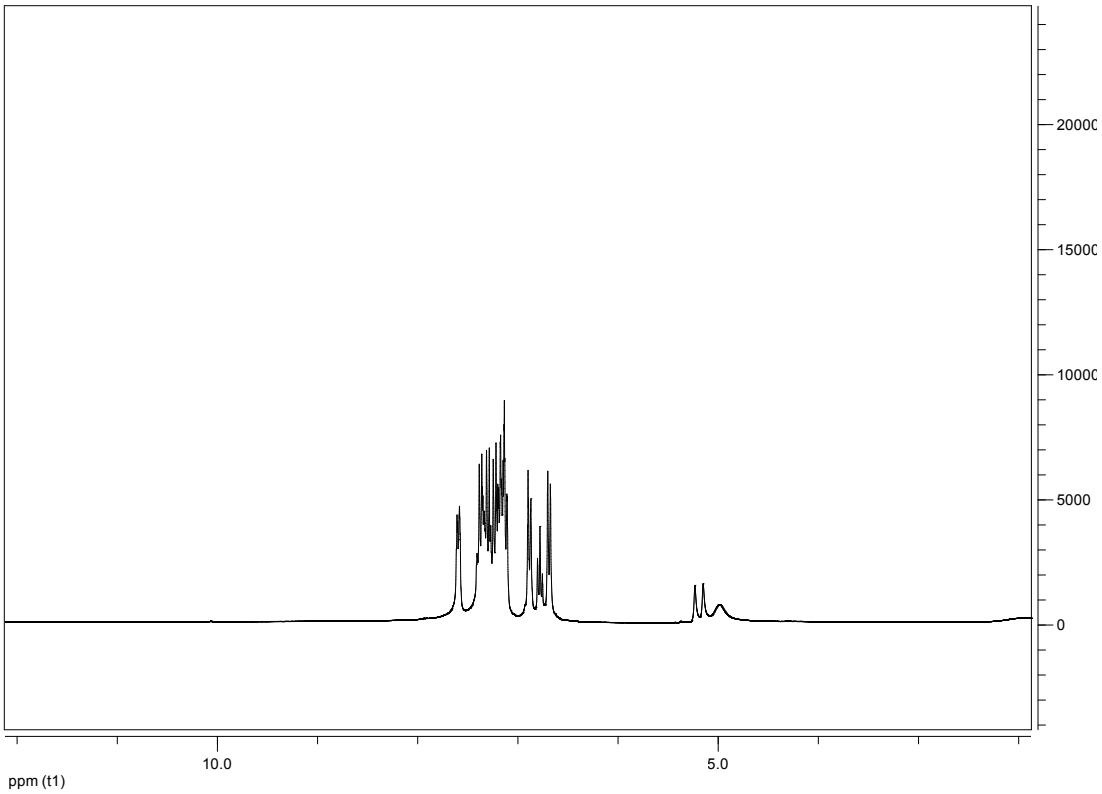


Figure S2 [1]H NMR spectra for the **Diphenyl (phenyl(phenylamino)methyl) phosphonate** in $CDCl_3$.

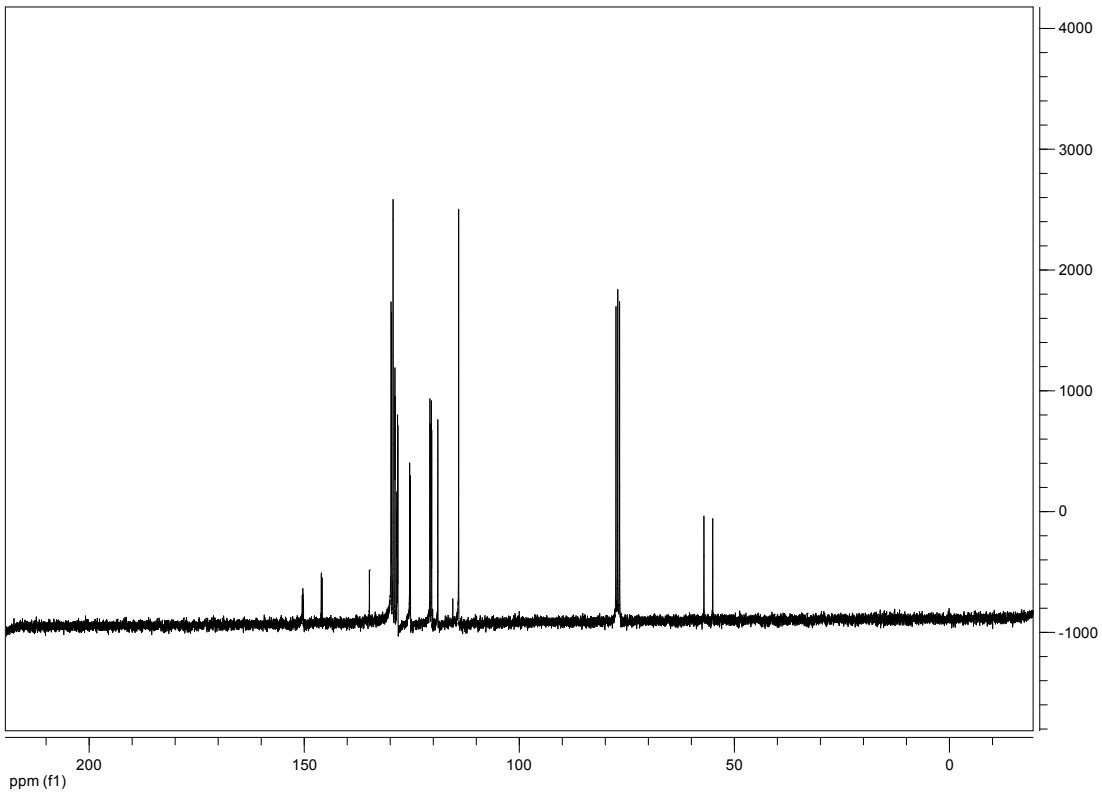


Figure S3 ^{13}C NMR spectra for the **Diphenyl (phenyl(phenylamino)methyl) phosphonate** in $CDCl_3$.

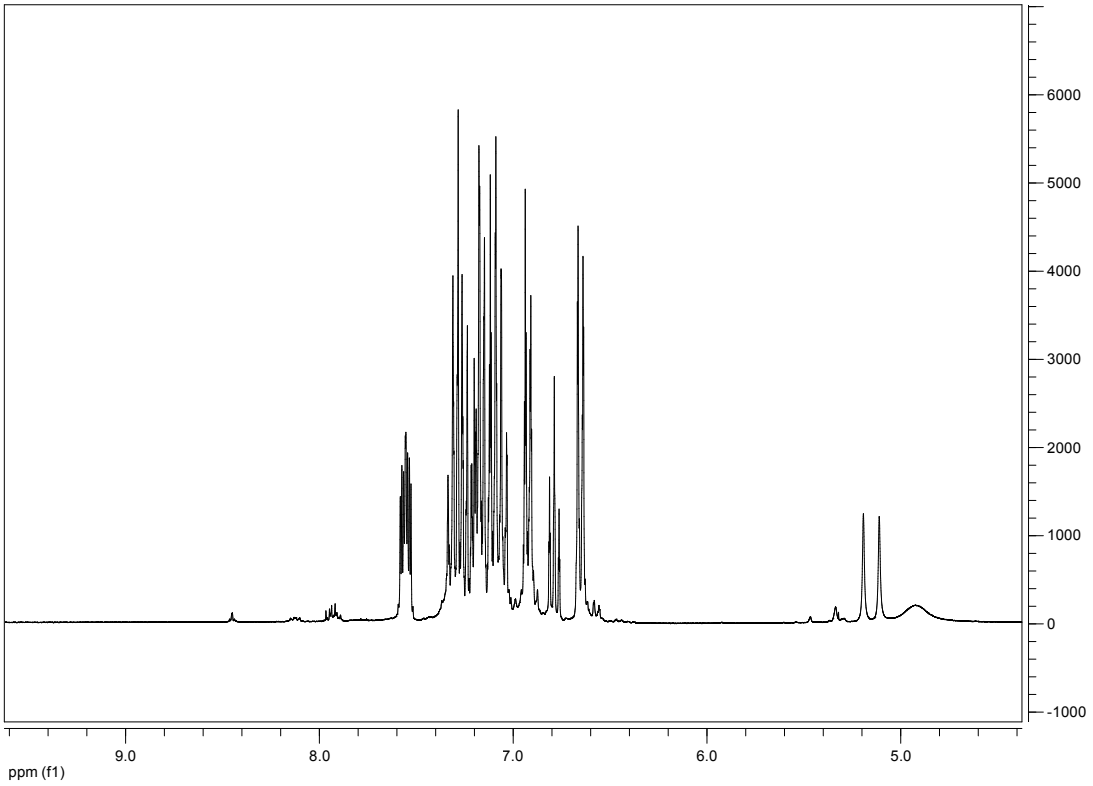


Figure S4 ^{1}H NMR spectra for the **Diphenyl ((4-fluorophenyl)(phenylamino)methyl) phosphonate** in $CDCl_3$.

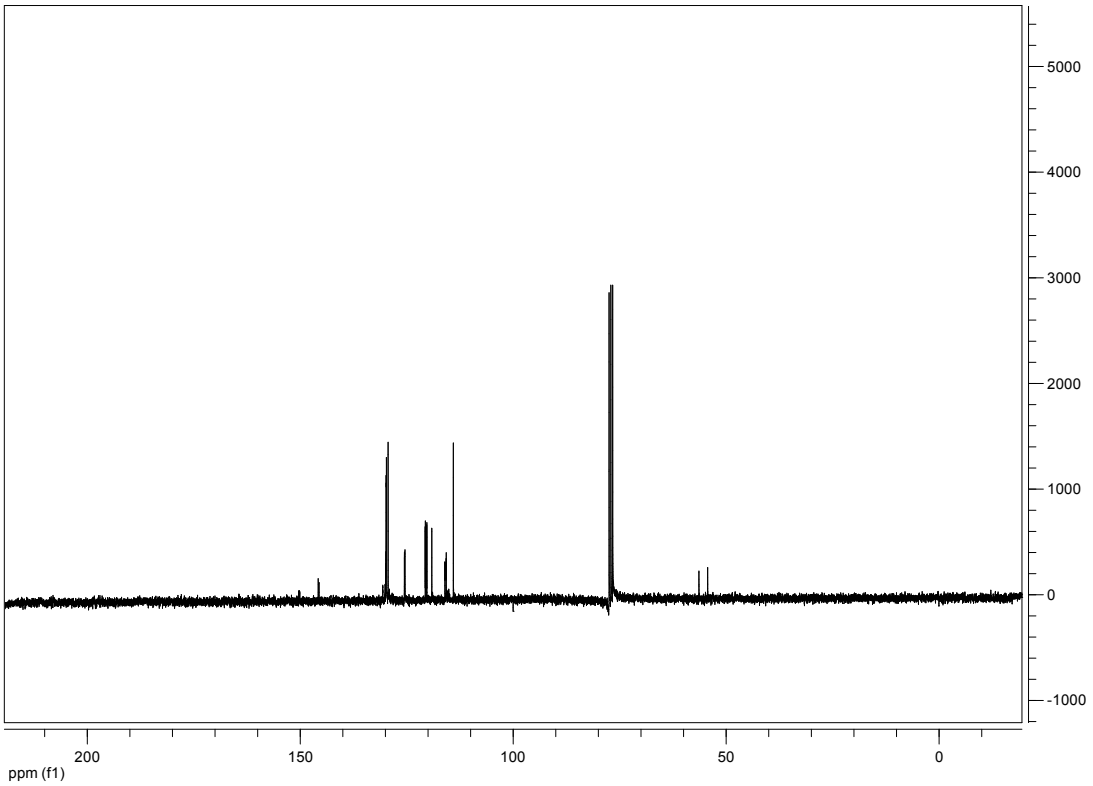


Figure S5 ^{13}C NMR spectra for the **Diphenyl ((4-fluorophenyl)(phenylamino)methyl) phosphonate** in $CDCl_3$.

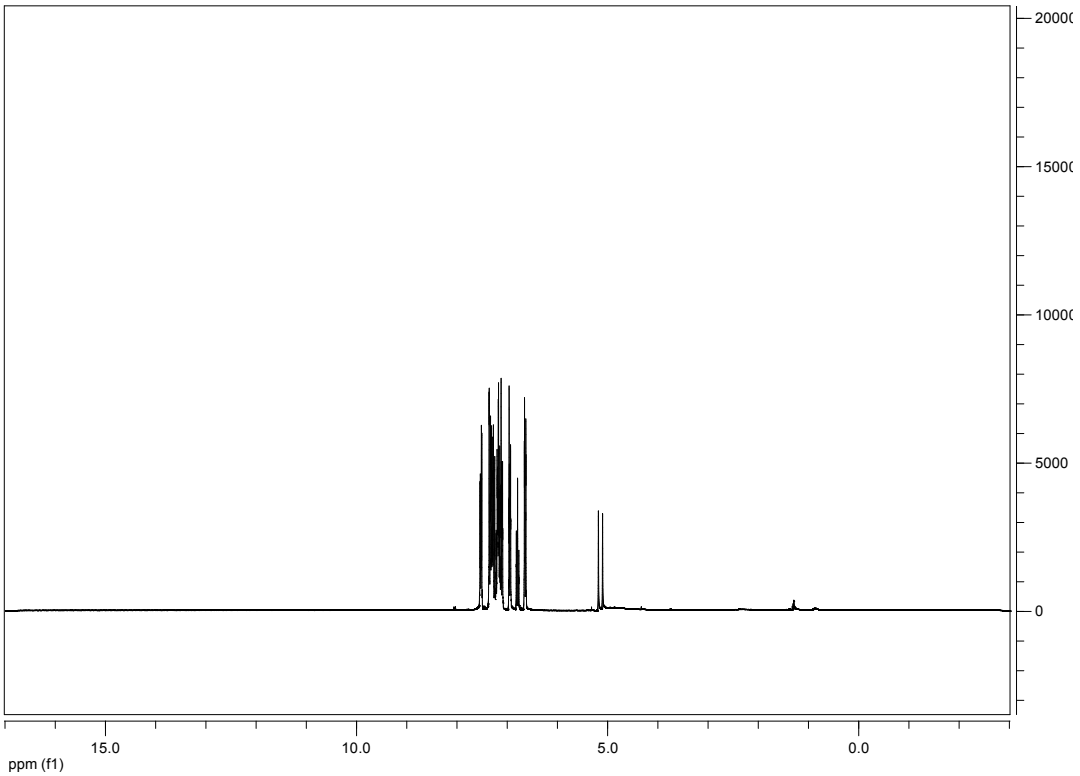


Figure S6 ^{1}H NMR spectra for the **Diphenyl ((4-chlorophenyl)(phenylamino)methyl) phosphonate** in $CDCl_3$.

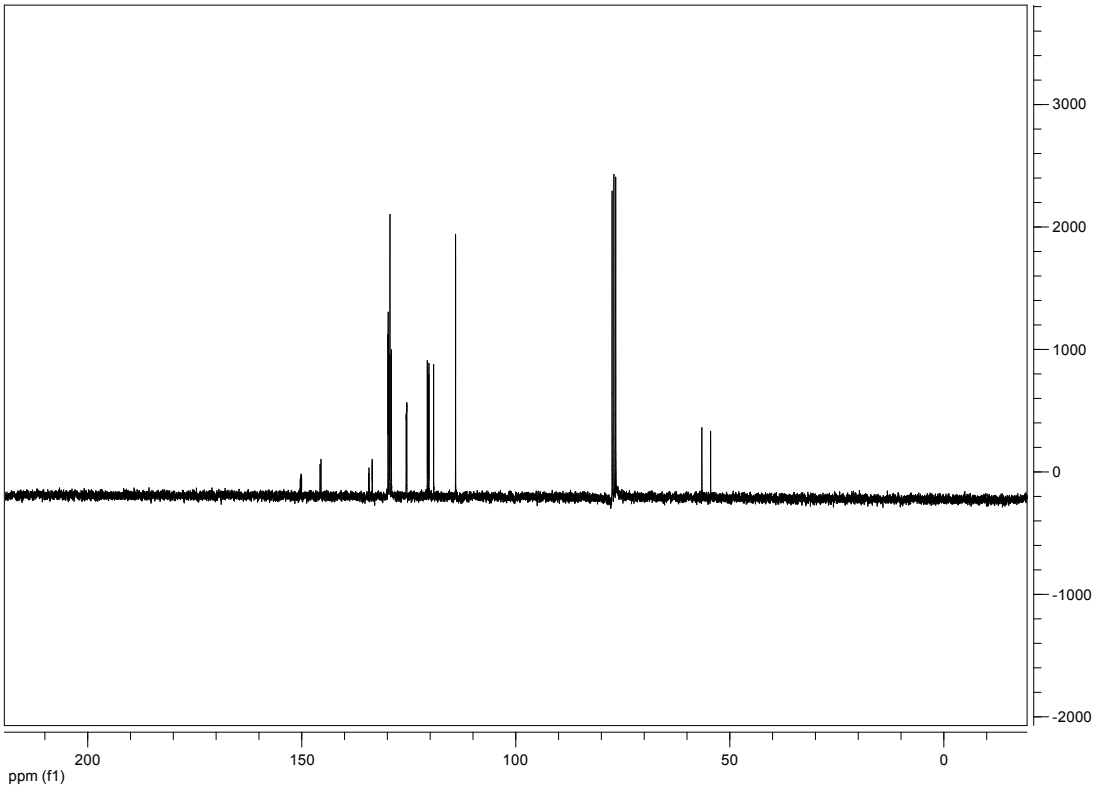


Figure S7 ^{13}C NMR spectra for the **Diphenyl ((4-chlorophenyl)(phenylamino)methyl) phosphonate** in $CDCl_3$.

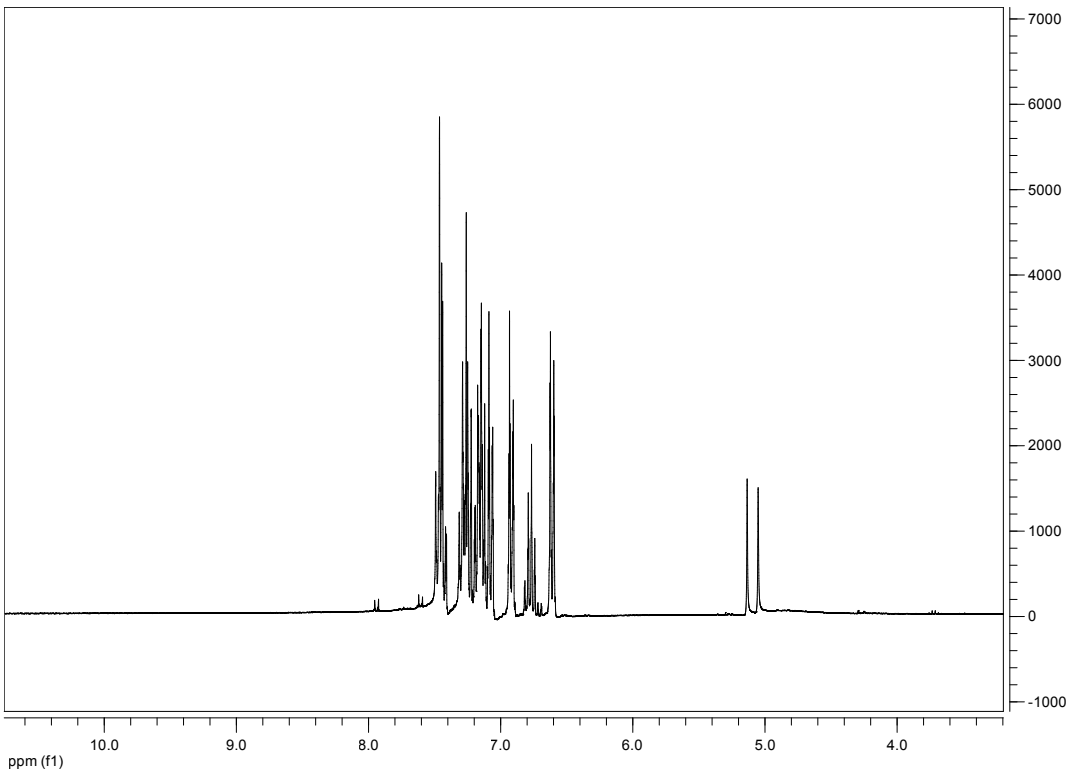


Figure S8 ^{1}H NMR spectra for the **Diphenyl ((4-bromophenyl)(phenylamino)methyl) phosphonate** in $CDCl_3$

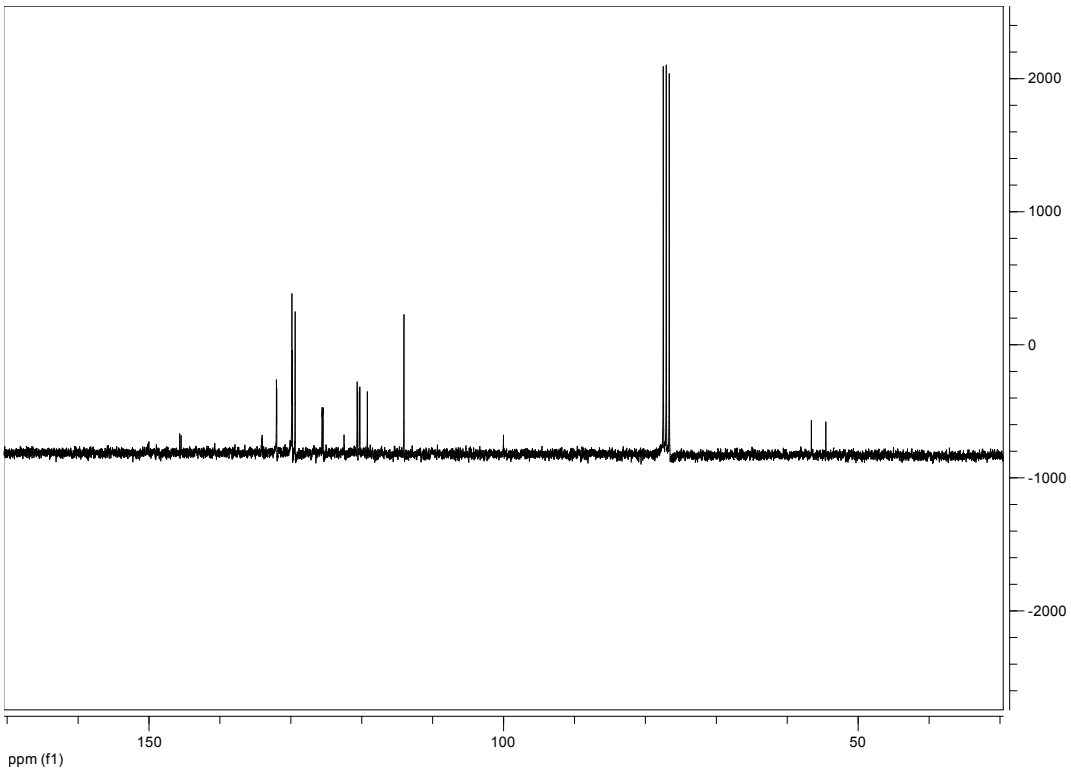


Figure S9 ^{13}C NMR spectra for the **Diphenyl ((4-bromophenyl)(phenylamino)methyl) phosphonate** in $CDCl_3$.

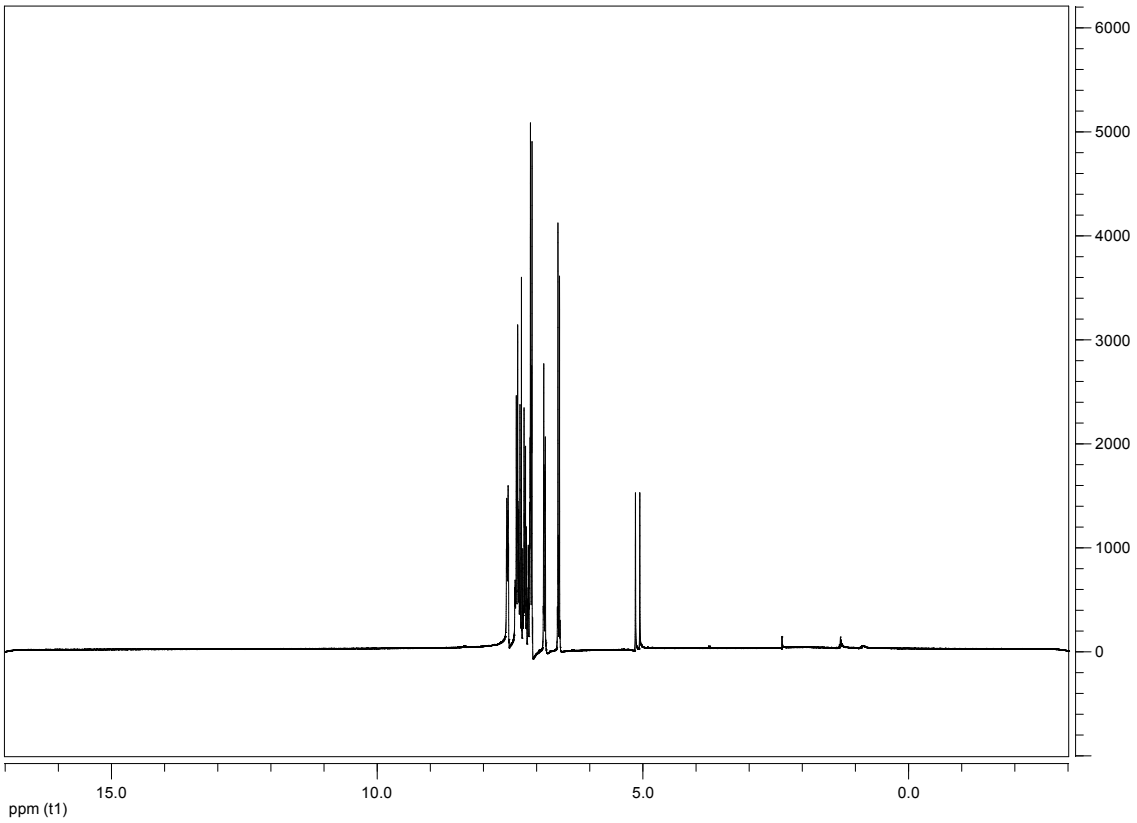


Figure S10 ^{1}H NMR spectra for the **Diphenyl (((4-Chlorophenyl) amino)(phenyl)methyl) phosphonate** in $CDCl_3$.

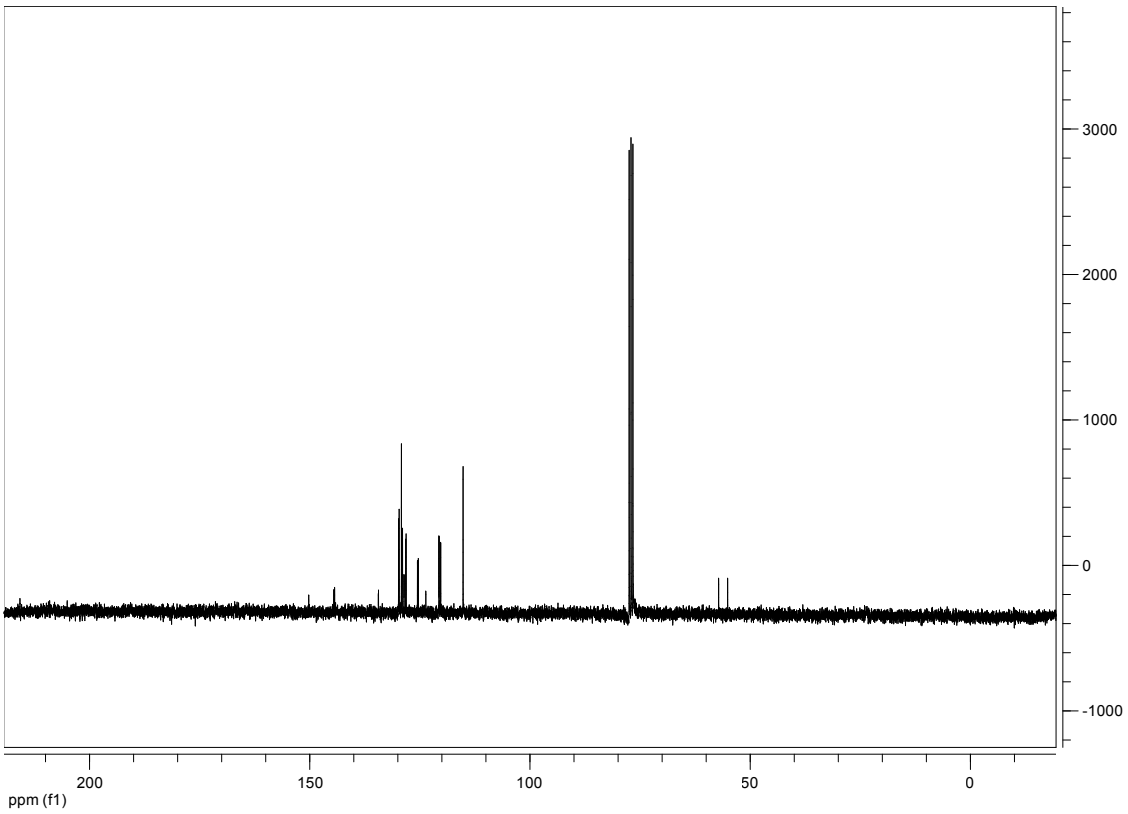


Figure S11 ^{13}C NMR spectra for the **Diphenyl (((4-Chlorophenyl) amino)(phenyl)methyl) phosphonate** in $CDCl_3$.

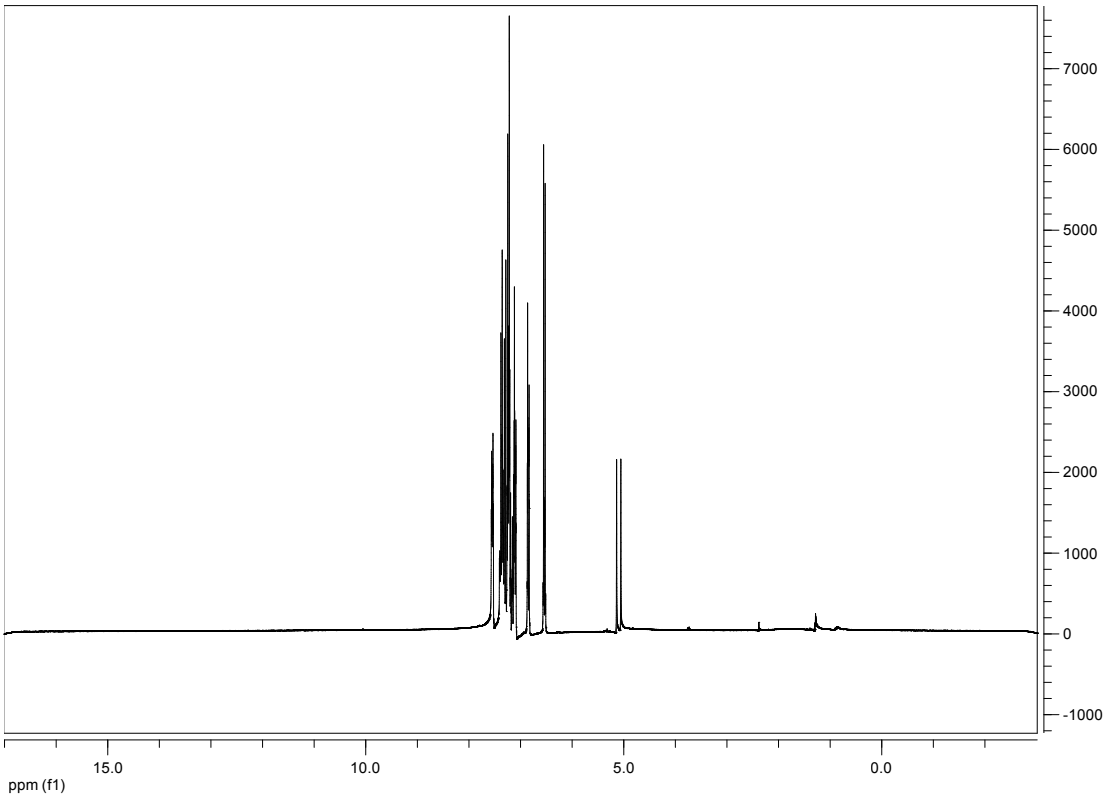


Figure S12 ^{1}H NMR spectra for the **Dipheny (((4-bromophenyl)amino)(phenyl)methyl) phosphonate** in $CDCl_3$.

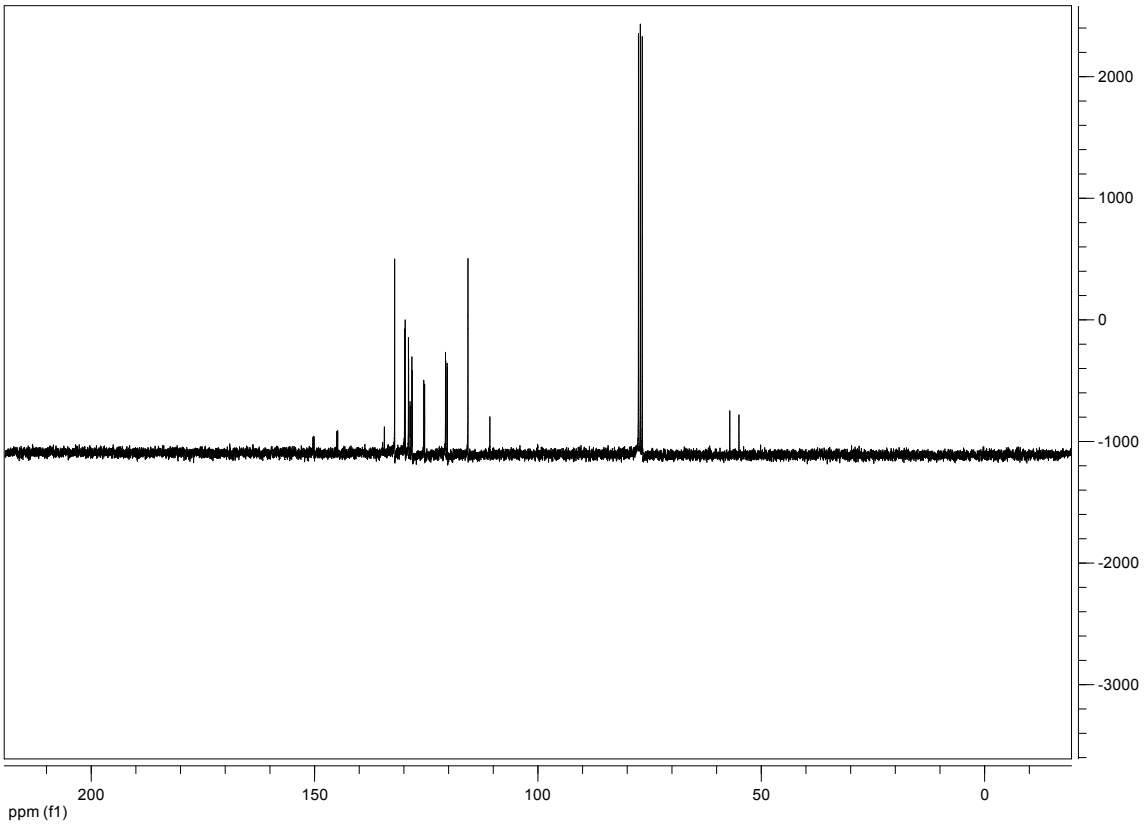


Figure S13 ^{13}C NMR spectra for the **Dipheny (((4-bromophenyl)amino)(phenyl)methyl) phosphonate** in $CDCl_3$.