

Supporting information

A new, efficient and recyclable [Ce(L-Pro)]₂(Oxa) as a heterogeneous catalyst used in Kabachnik-Fields reaction.

Caren Daniele Galeano da Silva,^a Aline Rufino de Oliveira,^a Mariana Pompilio Darbem Rocha,^a Ramesh Katla,^a Eriton Rodrigo Botero,^b Érica Cristina da Silva,^c Nelson Luís de Campos Domingues.^a

^a Organic Catalysis and Biocatalysis Laboratory – OCBL – Federal University of Grande Dourados – UFGD, Itahúm rod. Km 12 s/nº - Dourados/MS, Brazil.

Fax: +55(67) 3410 2072, Tel: +55(67) 3410 2081; e-mail: nelsondomingues@ufgd.edu.br or nelsonluis.domingues@hotmail.com

^b Grupo de Óptica Aplicada e Laboratório de Materiais Cerâmicos – Federal University of Grande Dourados – UFGD

^c State University of Campinas – Unicamp Institute of Chemistry.

1. Experiment Details	2
1.1. General Procedure	2
1.2. Catalyst -Procedure of [Ce(L-Pro)] ₂ (Oxa)	2
1.3 General Procedure of α-aminophosphonates	2
2.2. Solvents effects for the Kabachnik-Fields reaction.....	3
3. Characterization of the Kabachnik-Fields reaction.....	4
5. Characterization of Ce[(L-Pro) ₂ (Oxa)]	32

1. Experiment Details

1.1. General Procedure

The catalyst preparation was carried out using dry starting material under pressure. All other reactions were carried out using chemical reagents and solvents without any specific treatment. The respective reactions were monitored by Thin Layer Chromatography (TLC) MACHEREY-NAGEL (SIL G / UV₂₅₄) and were visualized by fluorescence quenching with UV light at 254 nm. The purification of the compounds was performed by recrystallization solvent using Chloroform / Hexane to 65°C. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on Bruker (300 MHz and 75 MHz respectively) spectrometer. ¹H NMR data are reported as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet), coupling constants (J) and assignment. The infrared spectra were recorded on FT/IR 4100 type A spectrometer of Jasco. The melting point was measured using DF-3600 of Instrutherm. It is important to mention that all spectral data matched with literature data.

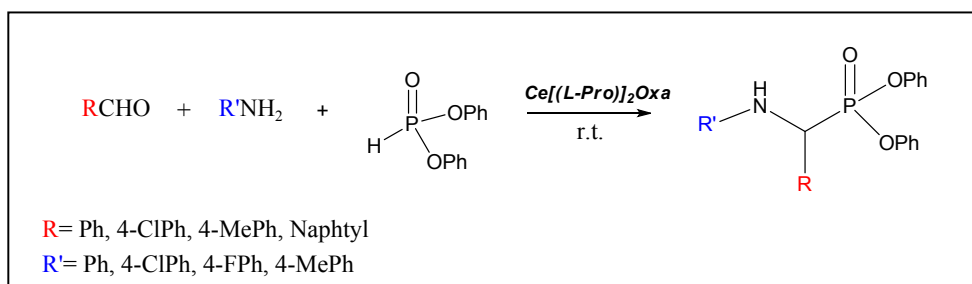
1.2. Catalyst -Procedure of [Ce(L-Pro)]₂(Oxa)

The cerium catalyst was prepared using L-proline (2.7 mmol) and sodium hydroxide (2.7 mmol) in methanol (10 mL) at room temperature, after 10 minutes then cerium (III) chloride (1.4 mmol) was added. The mixture was stirred at room temperature for 45 minutes, then was added a solution of sodium oxalate (0.1g/mL) as precipitate agent. After completion the reaction was centrifuged, washed with methanol and dried overnight at 40 °C and a pale yellow semi-solid was obtained. The infrared spectra were recorded on FT/IR 4100 type A spectrometer of Jasco. The X-Ray powder diffraction were done at room temperature with CuK_α in a conventional diffractometer. The analysis of Scanning electron microscopy (SEM), were done by a Phenom Pro X model of Anacom Científica brand, with an enlargement of 80 to 130,000 times, resolution ≤ 14 nm, CCD camera with a zoom of 20 to 135 times.

1.3 General Procedure of α-aminophosphonates

In a 50 mL round bottle flask was added cerium catalyst (0.02 mmol), benzaldehyde (2.2 mmol), aniline (2.0 mmol) and diphenyl phosphite (2.0 mmol), the mixture was magnetic stirred in toluene (10 mL) at room temperature. The progress of the reaction was monitored by TLC (eluent: EtOAc/hexane, 10:90), until the phosphite and aniline was completely consumed. After the reaction was completed a white solid was formed and then purified by recrystallization (chloroform/hexane) to obtain α-aminophosphonates, the catalyst was separated by filtration. All compounds were characterized by ¹H NMR, ¹³C NMR, FT / IR and melting point; all data are summarized as follow.

2. Reaction Optimization



2.1. Effects of catalyst

Table 1 Influence of catalyst loading over the Kabachnik-Fields reaction.^a

Cat (%mol) ^b	Yeld(%) ^b
0	^c
1	96
2	97

[a] Reaction conditions: benzaldehyde (2.2 mmol), aniline (2.0 mmol) and diphneylphosphite (2.0 mmol) at room temperature [b] Yields by recrystallization [c] No reaction.

2.2. Solvents effects for the Kabachnik-Fields reaction.

Table 2 Solvents and yields for the Kabachnik-Fields reaction.^a

Solvent ^a	Time (min)	Yeld (%) ^b
Toluene	10	96
DCM	10	90
CH ₃ CN	10	55
THF	60	80
No solvent	60	-

[a] Reaction conditions: benzaldehyde (2.2 mmol), aniline (2.0 mmol) and diphneyl phosphite (2.0 mmol) and 1 % mol catalyst at room temperature. [b] Yield of isolated product.

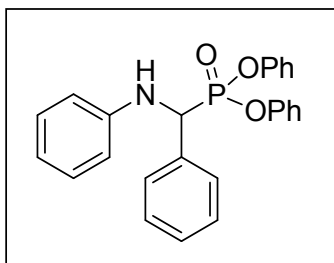
Table 3. Kabachnik-Fields reactions using [Ce(L-Pro)]₂(Oxa) recyclability.

Cycle	Yield ^a (%)	ΔYield (per cycle)
#1	94	-
#2	80	14
#3	65	15

^a. Yields by recrystallization.

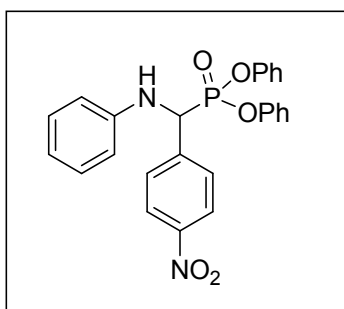
3. Characterization of the Kabachnik-Fields reaction.

Diphenyl (phenyl(phenylamino)methyl) phosphonate:



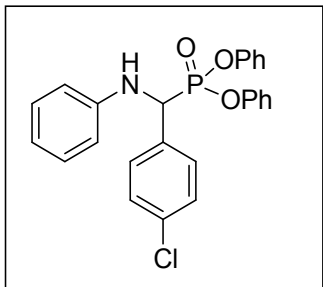
White solid, PM: 415.13 g/mol. $C_{25}H_{22}NO_3P$. M.p.: 159 °C. IR (KBr) ($\nu_{\max}$ cm^{-1}): 3343 (N-H), 1186.01 (P=O), 762.70 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 2.14-2.22 (d, J_{H-P} = 24.6 Hz, 1H, N-CH-P), 3.67-3.89 (m, 4H), 4.10-4.40 (m, 14H), 4.57-4.60 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 55.01 and 57.06 (d, J_{C-P} = 153.3 Hz), 76.66, 77.51, 114.08, 118.918, 120.34, 120.40, 120.70, 120.75, 125.29, 125.46, 125.47, 128.20, 128.28, 128.41, 128.45, 128.85, 128.89, 129.32, 129.68, 129.78, 134.82, 145.97, 150.29.

Diphenyl ((4-nitrophenyl)(phenylamino)methyl) phosphonate



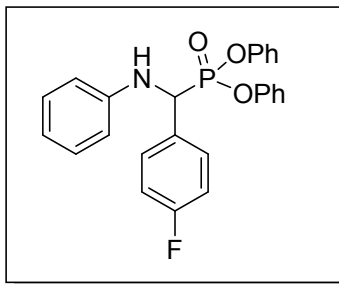
Yellow solid, MW: 460.12 g/mol. $C_{25}H_{21}N_2O_5P$. M.p.: 153-155 °C. IR (KBr) ($\nu_{\max}$ cm^{-1}): 3305.39(N-H), 1182.15 (P=O), 772 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 5.25-5.36 (d, J = 25,38 Hz, 1H, N-CH-P), 6.60-6.68 (m, 2H), 6.75-6.86 (m, 3H), 6.89-7.05 (m, 12H), 7.47-8.50 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.88 and 56.10 (d, J_{C-P} = 153.0 Hz), 114.03, 115.41, 119.58, 120.12, 120.16, 120.32, 120.51, 120.54, 123.18, 123.22, 123.48, 123.50, 125.75, 125.87, 129.53, 129.58, 129.96, 129.98, 134.11, 137.53, 137.54, 145.09, 145.21.

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



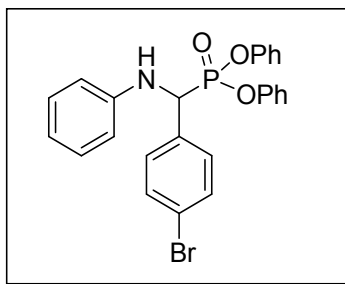
Green solid, PM: 449.09 g/mol. $C_{25}H_{21}ClNO_3P$. M.p.:131-132 °C. IR KBr ($\nu_{\text{máx}}$ cm^{-1}): 3299 (N-H), 1182.15 (P-O), 765.60 (C-P). ^1H NMR (300 MHz, DMSO): δ ppm 5.12-5.20 (d, $J = 24.9$ Hz, 1H, N-CH-P), 6.64-6.99 (m, 3H), 7.11-7.38 (m, 15H), 7.51-7.57 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 54.40 and 56.45 (d, $J_{\text{P-C}} = 153.0$ Hz), 76.57, 77.42, 113.98, 119.11, 120.20, 120.26, 120.53, 120.58, 125.39, 125.50, 128.97, 129.01, 129.31, 129.39, 129.46, 129.72, 129.77, 133.46, 134.23, 145.43, 145.61, 150.10, 150.12.

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



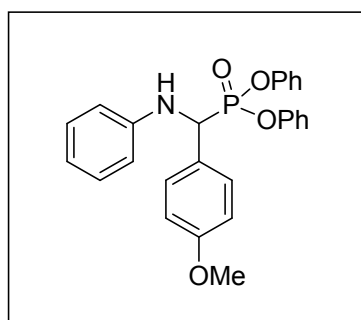
Blue solid, PM: 433.12 g/mol. $C_{25}H_{21}FNO_3P$. M.p.:104-105 °C. IR KBr ($\nu_{\text{máx}}$ cm^{-1}): 3453.29 (N-H), 1284.63 (P-O), 776.80 (C-O). ^1H NMR (300 MHz, CDCl_3): δ ppm 5.19-5.11 (d $J_{\text{H-P}} = 24,3$ Hz, 1H, N-CH-P), 6.63-6.94 (m, 6H), 7.03-7.33 (m, 12H), 7.52-7.58 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 54.27 and 56.32 (d, $J_{\text{P-C}} = 153.7$ 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-bromophenyl)(phenylamino)methyl) phosphonate:



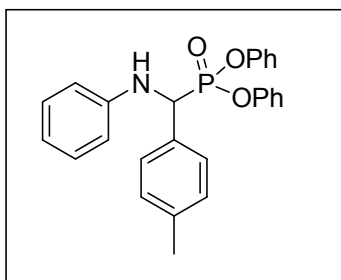
Green solid, MW:493.04 g/mol. $C_{25}H_{11}BrNO_3P$. M.p.:138-140 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3322.75(N-H), 1029.63 (P-O), 765.60 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 5.05-5.24 (d, $J = 24.9$ Hz, 1H, N-CH-P), 6.59-6.72 (m, 2H), 6.72-6.86 (m, 2H), 6.87-7.00 (m, 2H), 7.06-7.39 (m, 10H), 7.40-7.56 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.55 and 56.59 (d, $J_{P-C} = 153.55$ Hz), 114.07, 115.40, 119.13, 119.22, 120.28, 120.34, 120.62, 120.67, 122.51, 122.56, 125.54, 125.66, 129.40, 129.57, 129.87, 132.01, 132.04, 134.04, 145.50, 145.63, 150.12, 150.18, 150.30.

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



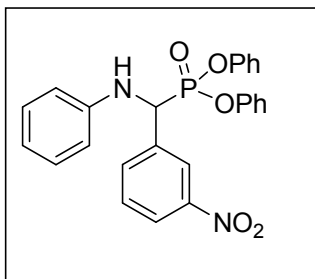
Yellow solid, MW:445.14 g/mol. $C_{26}H_{24}NO_4P$. M.p.:141-142 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3329.0 (N-H), 1252.0 (P-O), 770.4 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 3.80 (s, 3H), 5.08-5.16 (d, $J = 24.6$ Hz, 1H, N-CH-P), 6.66-6.92 (m, 6H), 7.09-7.33 (m, 11H), 7.45-7.51 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.19, 55.16 and 56.26 (d, $J_{P-C} = 73.52$ Hz), 76.57, 77.42, 113.98, 114.17, 114.20, 118.68, 120.25, 120.31, 120.58, 120.64, 125.11, 125.27, 126.45, 126.47, 129.14, 129.23, 129.31, 129.53, 129.63, 145.76, 145.96, 150.21, 150.23.

Diphenyl ((phenylamino)(*p*-tolyl)methyl) phosphonate:



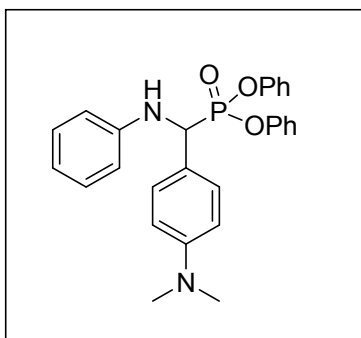
Yellow solid, MW: 429.15 g/mol. $C_{26}H_{24}NO_3P$. Mp: 120-125 °C. IR KBr (ν_{max} cm^{-1}): 3345.01 (N-H), 1215.14 (P=O), 764.63 (C-P). ^1H NMR (300 MHz, CDCl_3): δ ppm 2.34 (s, 3H), 5.09-5.17 (d, $J_{\text{H-P}} = 24.6$ Hz, 1H, N-CH-P), 6.64-6.92 (m, 5H), 7.08-7.32 (m, 12H), 7.42-7.40 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 55.33 and 57.28 (d, $J_{\text{P-C}} = 147.36$ Hz), 113.28, 114.25, 115.46, 120.27, 120.31, 120.42, 120.66, 120.78, 125.36, 125.52, 128.20, 128.28, 128.32, 128.45, 128.65, 128.82, 128.86, 129.60, 129.68, 129.77, 129.81, 134.92, 143.48, 143.60.

Diphenyl ((3-nitrophenyl)(phenylamino)methyl) phosphonate:



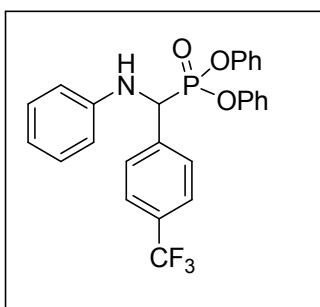
Red solid, MW: 460.12 g/mol. $C_{25}H_{21}N_2O_5P$. M.p.: 124-126 °C. ^1H NMR (300 MHz, CDCl_3): δ ppm 5.21 and 5.38 (d, $J_{\text{H-P}} = 25.9$ Hz, 1H, N-CH-P), 6.52-6.69 (m, 2H), 6.75-6.94 (m, 3H), 6.96-7.05 (m, 2H), 7.06-7.37 (m, 11H), 7.73-7.83 (m, 2H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 54.83 and 56.83 (d, $J_{\text{P-C}} = 151.22$ Hz), 113.92, 114.02, 115.43, 119.25, 119.57, 120.19, 120.25, 120.51, 120.56, 123.97, 124.01, 125.79, 125.88, 128.66, 128.80, 129.06, 129.13, 129.45, 129.51, 129.55, 129.97, 145.23, 145.39.

Diphenyl ((4-(dimethylamino)phenyl)(phenylamino)methyl) phosphonate:



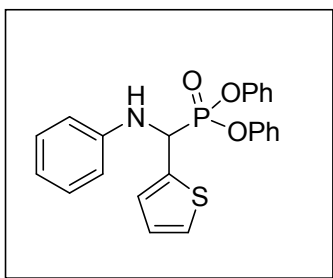
Orange solid MW: 458.18 g/mol. $C_{27}H_{27}N_2O_3P$. M.p: 97-98 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3399.12(N-H), 1188.9 (P=O), 772.3 (C-P). ^1H NMR (300 MHz, CDCl_3): δ ppm 2.94 (s, 1H), 3.09 (s, 3H), 5.06-5.13 (d, $J = 23.7$, 1H, N-CH-P), 6.66-6.94 (m, 6H), 7.10-7.32 (m, 12H), 7.39-7.79 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 40.54, 54.83 and 56.08 (d, $J_{P-C} = 93.7$ Hz), 76.82, 77.33, 111.03, 112.75, 112.77, 114.16, 115.52, 118.68, 119.83, 120.52, 120.55, 120.78, 120.82, 125.29, 128.98, 129.03, 129.70, 146.12, 146.24, 150.32, 150.40, 150.47, 150.55, 150.56.

Diphenyl ((phenylamino)(4-(trifluoromethyl) phenyl)methyl) phosphonate:



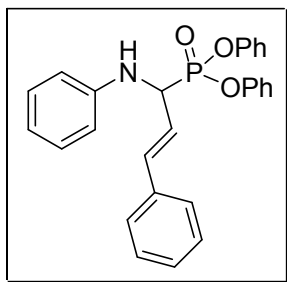
Green solid. MW: 483.12 g/mol. $C_{26}H_{21}F_3NO_3P$. Mp: 118-120 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3326.12 (N-H), 1209.63 (P=O), 752.1 (C-P). ^1H NMR (300 MHz, CDCl_3): δ ppm 5.18-5.26 (d, $J = 24.6$, 1H, N-CH-P), 6.62-6.95 (m, 6H), 7.08-7.33 (m, 10H), 7.55-7.73 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 55.08 and 56.30 (d, $J_{P-C} = 153.17$ Hz), 76.74, 77.25, 113.955, 115.31, 119.27, 120.12, 120.16, 120.28, 120.50, 120.53, 125.54, 125.55, 125.66, 125.67, 128.47, 128.51, 129.37, 129.50, 129.76, 129.77, 129.82, 139.03, 145.40, 150.02.

Diphenyl ((phenylamino)(thiophen-2-yl)methyl) phosphate:



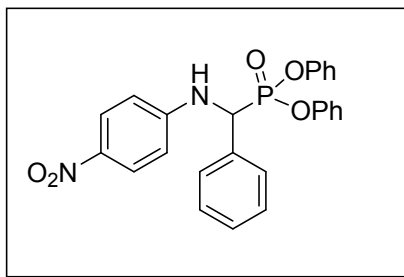
Brown solid. MW: 421.09 g/mol. $C_{23}H_{20}NO_3PS$. Mp. 93-95°C. IR KBr (ν_{max} cm^{-1}): 3365.1 (N-H), 1277.1 (P=O), 773.3 (C-P). ^1H NMR (300 MHz, CDCl_3): δ ppm 5.41-5.49 (d, $J = 24.4$, 1H, N-CH-P), 6.73-6.84 (m, 6H), 6.99-7.33 (m, 16H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 55.08-56.30 (d, $J_{\text{P-C}} = 153.17$ Hz), 76.745, 77.254, 113.955, 115.318, 119.278, 120.126, 120.160, 120.289, 120.504, 120.537, 125.543, 125.553, 125.665, 125.676, 128.470, 128.515, 129.373, 129.500, 129.767, 129.774, 129.829, 139.039, 145.406, 150.023.

(3-Phenyl-1-phenylamino-allyl)-phosphonic acid diphenyl ester:



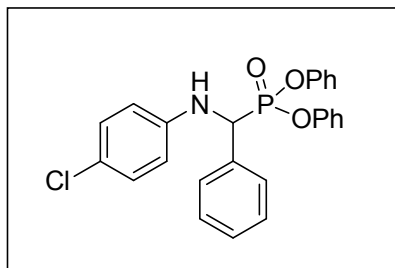
Brown solid. MW: 427.13 g/mol. $C_{26}H_{22}NO_3P$. Mp: 84-85 °C. IR KBr (ν_{max} cm^{-1}): 3295.75 (N-H), 1213.01 (P=O), 741.97 (C-P). ^1H NMR (300 MHz, CDCl_3): δ ppm 5.15-5.23 (d, $J_{\text{H-P}} = 14.1$ Hz, 1H, N-CH-P), 5.67 (s, N-H), 6.80-6.89 (m, 5H), 7.08-7.37 (m, 10H), 8.14-8.34 (m, 5H). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 76.63 and 77.48 (d, $J_{\text{P-C}} = 63.90$ Hz), 113.21, 115.33, 117.31, 117.70, 119.16, 119.98, 120.73, 121.20, 126.97, 129.45, 129.68, 132.26, 133.25, 133.86, 135.56, 137.21, 137.56, 146.02, 148.43, 155.62.

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



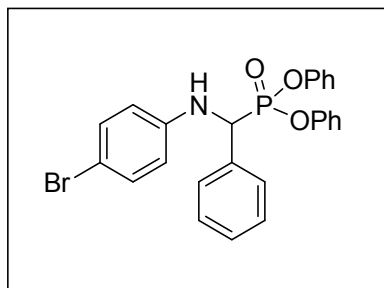
Yellow solid. PM: 460.12 g/mol. $C_{25}H_{21}N_2O_5P$. Mp.: 143-145 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3328.7 (N-H), 1257.9 (P-O), 770.4 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 5.18-5.26 (d, J_{H-P} = 24,5 Hz, 1H, N-CH-P), 6.59-6.77 (m, 4H), 7.10-7.39 (m, 11H), 7.55-7.58 (m, 3H), 7.98-8.03 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 53.45 and 55.51 (d, J_{C-P} = 154.5 Hz), 112.98, 113.10, 115.834, 120.82, 120.87, 121.04, 121.09, 125.91, 125.94, 126.37, 126.97, 128.90, 128.94, 129.10, 129.18, 129.26, 130.40, 135.09, 137.92, 150.30, 150.44, 153.76, 153.91.

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



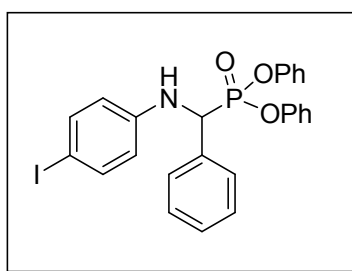
White solid, PM: 449.09. $C_{25}H_{21}ClNO_3P$. Mp.: 151-152 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3336.25 (N-H), 1185.53 (P=O), 775.72 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 3.82-3.90 (d, J_{H-P} = 24,6 Hz, 1H, N-CH-P), 5.32-5.64 (m, 4H), 5.84-6.17 (m, 14H), 6.28-6.33 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 53.77 and 55.84 (d, J_{C-P} = 156.3 Hz), 115.65, 120.75, 120.81, 121.05, 121.11, 121.18, 125.69, 125.75, 128.48, 128.52, 128.78, 128.81, 128.96, 129.12, 129.20, 130.26, 135.80, 146.33, 146.53, 150.30, 150.43, 150.51, 150.65.

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



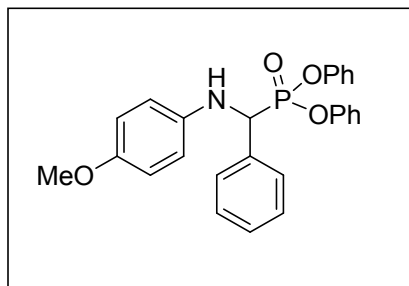
White solid. PM: 493.04 g/mol. $C_{25}H_{21}BrNO_3P$. Mp: 165-167 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3336.25 (N-H), 1185.53 (P=O), 775.72 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 5.09-5.18 (d, J_{H-P} = 24,6 Hz, 1H, N-CH-P), 6.55-6.90 (m, 4H), 7.13-7.45 (m, 14H), 7.55-7.60 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 55.50 and 57.56 (d, J_{C-P} = 154.12 Hz), 76.57, 77.42, 115.02, 115.12, 115.35, 115.55, 115.84, 120.01, 120.20, 120.26, 120.59, 120.64, 125.32, 125.51, 125.51, 128.19, 128.50, 128.86, 129.62, 129.73, 134.37, 142.12, 150.02.

Diphenyl (((4-iodophenyl)amino)(phenyl)methyl) phosphosnate:



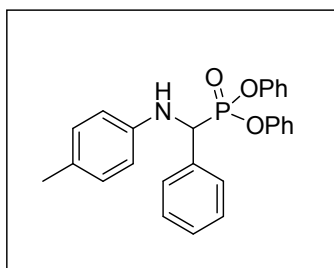
Yellow solid. PM: 541.03. $C_{25}H_{21}INO_3P$. Mp.: 154-155 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3339.62 (N-H), 1188.90 (P=O), 775.726 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 5.05-5.14 (d, J_{H-P} = 24.9 Hz, 1H, N-CH-P), 6.43-6.46 (m, 2H), 5.82-6.85 (m, 4H), 7.08-7.42 (m, 12H), 7.52-7.55 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 54.82 and 56.86 (d, J_{C-P} = 153.50 Hz), 115.37, 116.27, 117.39, 120.28, 120.35, 120.64, 120.75, 125.43, 125.63, 128.14, 128.21, 128.61, 128.67, 128.96, 129.06, 129.59, 129.66, 129.89, 134.30, 134.34, 137.88, 145.60.

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



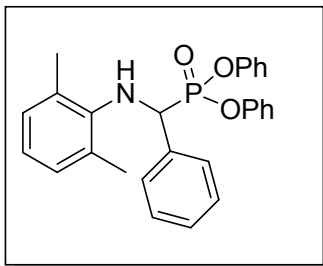
Light brown solid. PM: 445.14 g/mol. $C_{26}H_{24}NO_4P$. IR KBr ($\nu_{\max}$ cm^{-1}): 3454.8 (N-H), 1186.0 (P=O), 776.2 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 3.73 (s, 3H), 5.04-5.12 (d, J_{H-P} = 24.3 Hz, 1H, N-CH-P), 6.61-6.89 (m, 6H), 7.10-7.40 (m, 12H), 7.54-7.58 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 39.43, 54.15 and 56.22 (d, J_{C-P} = 155.7 Hz), 114.27, 115.01, 120.22, 120.27, 120.56, 120.62, 125.06, 125.11, 127.75, 127.79, 128.13, 128.15, 128.62, 128.70, 129.67, 135.74, 140.57, 140.79, 149.82, 149.96, 150.092, 150.22, 151.63.

Diphenyl (phenyl(*p*-tolylamino)methyl) phosphonate:



White solid. PM: 429.15 g/mol. $C_{26}H_{24}NO_3P$. Mp: 165-168 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3336.2 (N-H), 1185.5 (P=O), 775.7 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 3.06 (s, 3H), 5.77-5.85 (d, J_{H-P} = 25.2 Hz, 1H, N-CH-P), 6.79-7.43 (m, 18H), 7.65-7.68 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 34.82, 61.26 and 63.41 (d, J_{C-P} = 161.4 Hz), 76.57, 77.42, 114.37, 115.36, 118.66, 119.67, 120.46, 120.52, 120.59, 120.65, 125.11, 125.27, 128.35, 128.68, 128.95, 129.07, 129.23, 129.28, 129.54, 129.63, 133.02, 149.86, 149.98.

Diphenyl (((2,6-dimethylphenyl)amino)(phenyl) methyl) phosphonate:



Blue solid. PM: 443.17 g/mol. $C_{27}H_{26}NO_3P$. Mp.: 98-100 °C. IR KBr ($\nu_{\max}$ cm^{-1}): 3343.4 (N-H), 1213.0 (P=O), 755.4 (C-P). 1H NMR (300 MHz, $CDCl_3$): δ ppm 2.27 (s, 6H), 4.84-4.92 (d, J_{H-P} = 22,6 Hz, 1H, N-CH-P), 6.72-6.88 (m, 4H), 6.96-7.38 (m, 13H), 7.51-7.55 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 18.73, 57.98 and 59.96 (d, J_{C-P} = 161.4 Hz), 76.57, 77.42, 115.33, 119.83, 120.24, 120.55, 122.29, 122.78, 125.16, 125.34, 128.25, 128.37, 128.60, 129.05, 129.31, 129.47, 129.68, 131.58, 134.50, 135.397, 135.43, 143.40, 150.01, 156.13.

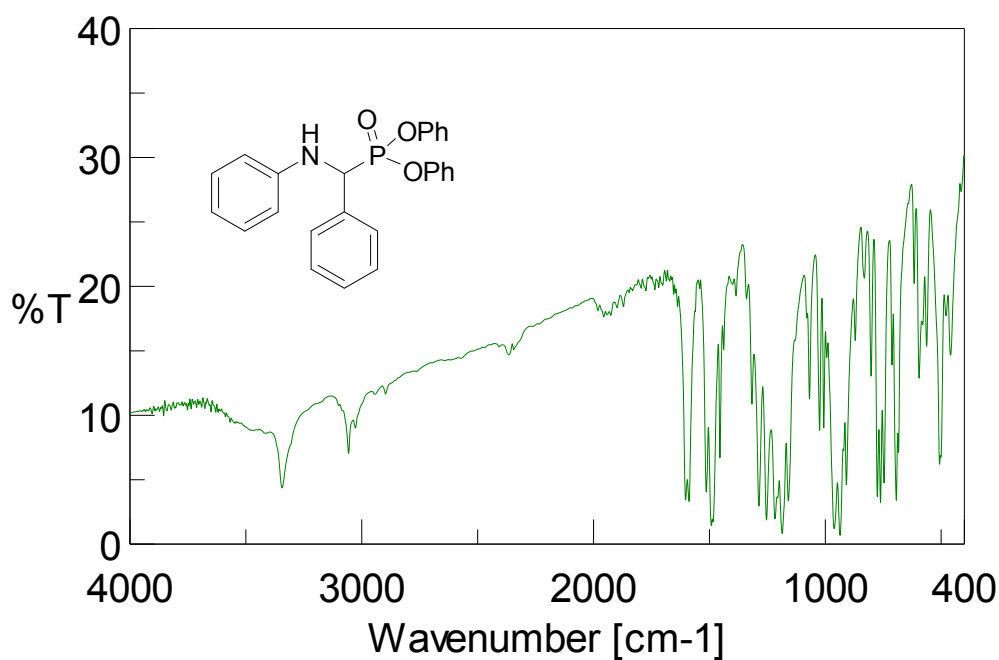


Figure 1. FTIR spectra for the **Diphenyl ((phenyl(phenylamino)methyl) phosphonate [A1]** in KBr.

4. ^1H and ^{13}C NMR spectra analysis

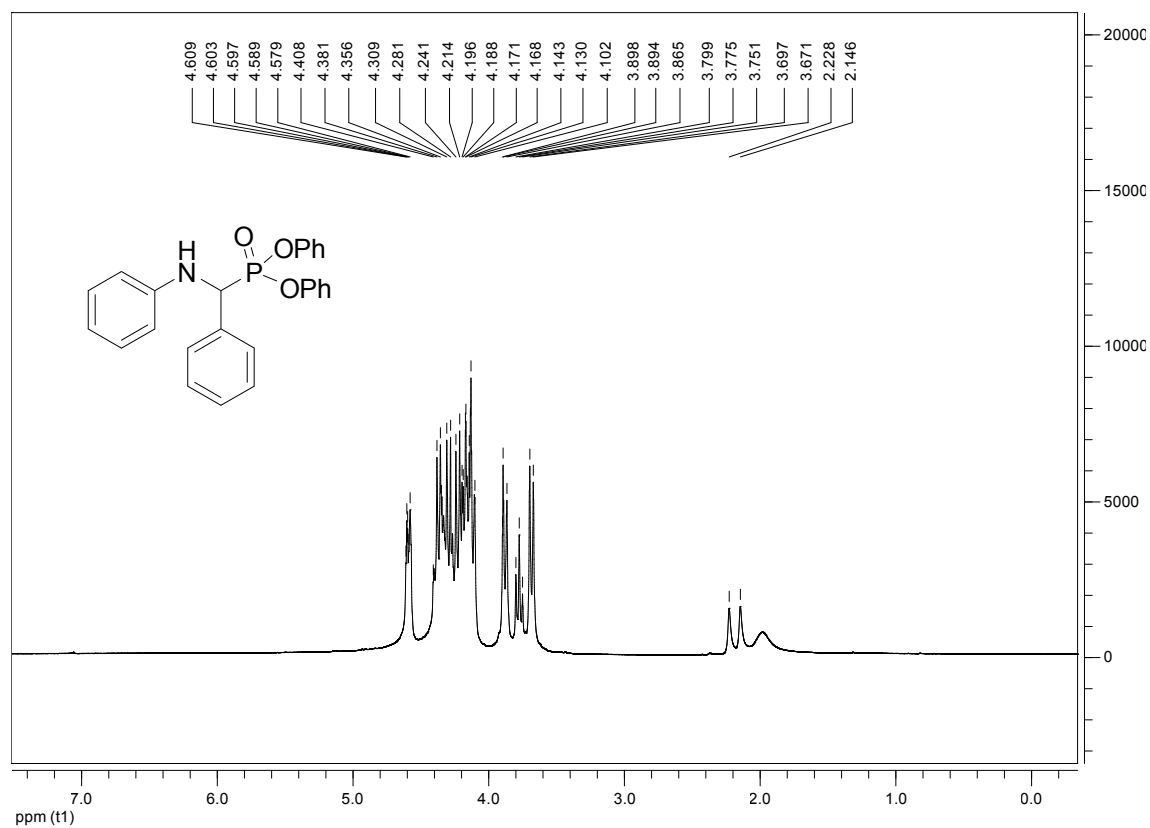


Figure 2. ^1H NMR spectra for the Diphenyl (phenyl(phenylamino)methyl) phosphonate in CDCl_3 .

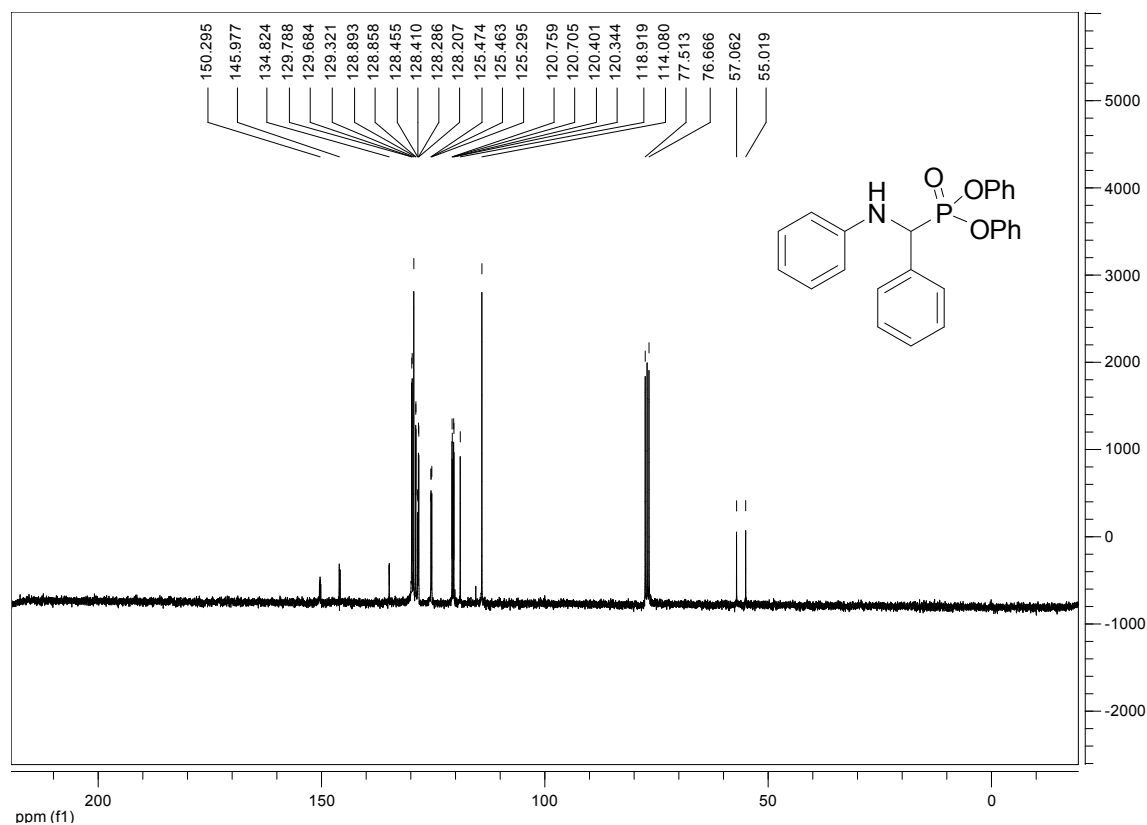


Figure 3. ^{13}C NMR spectra for the Diphenyl (phenyl(phenylamino)methyl) phosphonate in CDCl_3 .

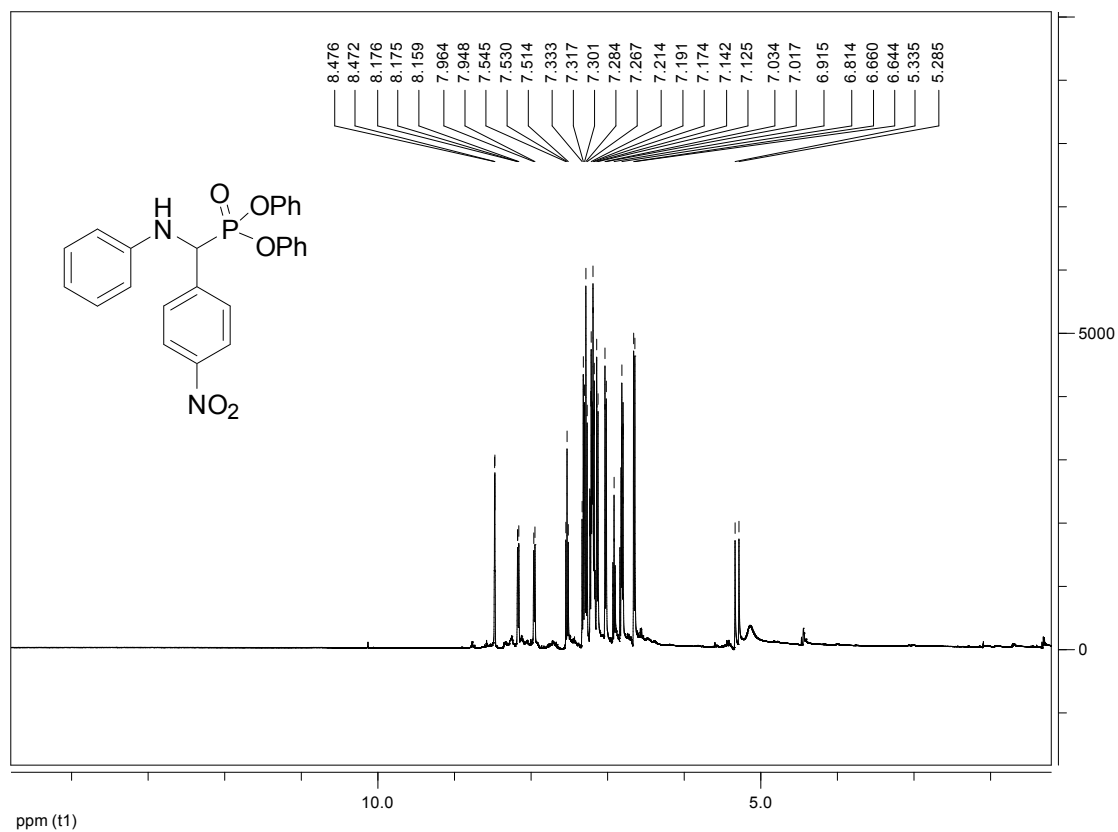


Figure 4. ¹H NMR spectra for the Diphenyl ((4-nitrophenyl)(phenylamino)methyl) phosphonate in CDCl₃.

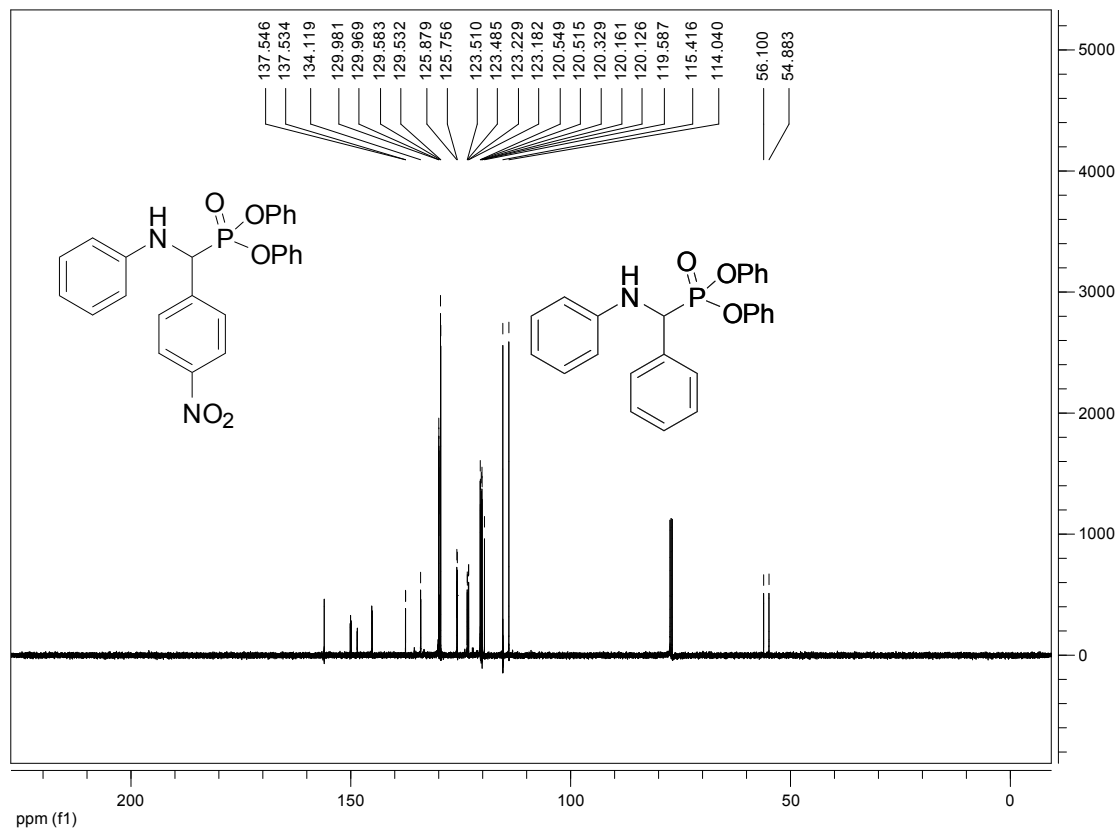


Figure 5. ¹³C NMR spectra for the Diphenyl ((4-nitrophenyl)(phenylamino)methyl) phosphonate in CDCl₃.

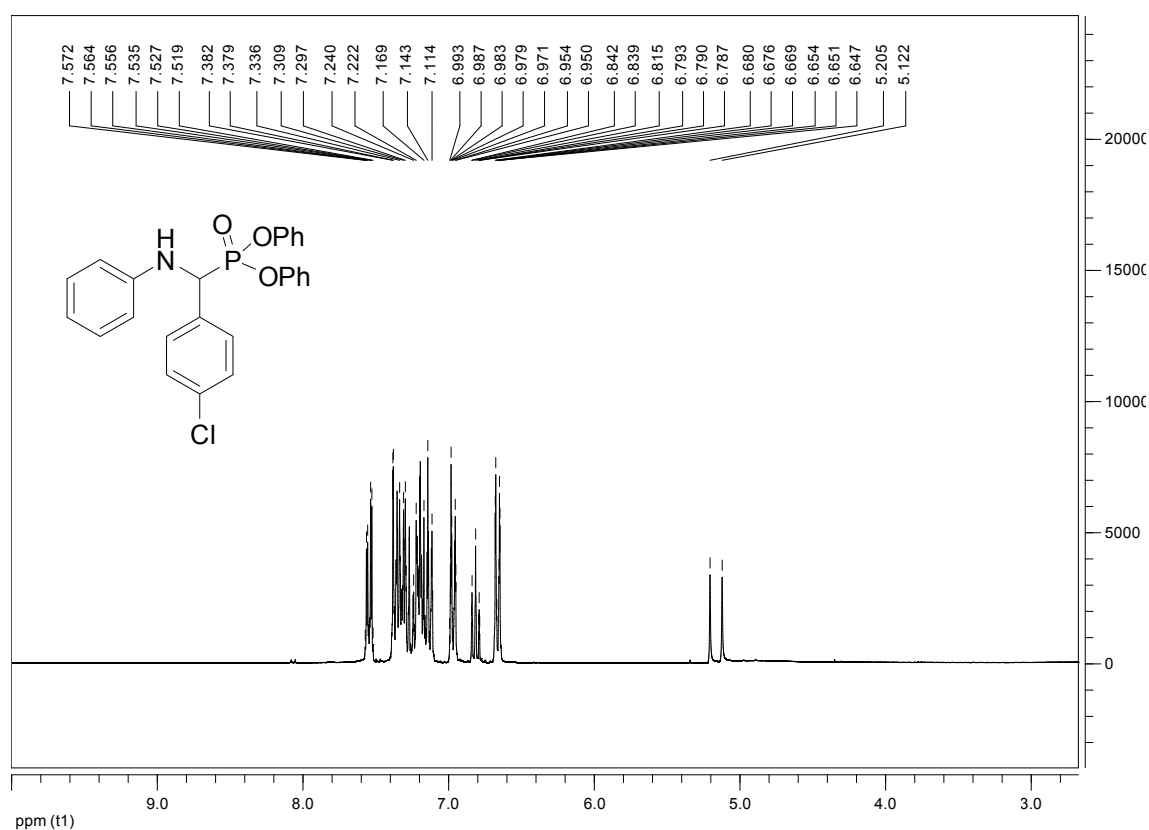


Figure 6. ¹H NMR spectra for the Diphenyl ((4-chlorophenyl)(phenylamino)methyl) phosphonate in CDCl₃.

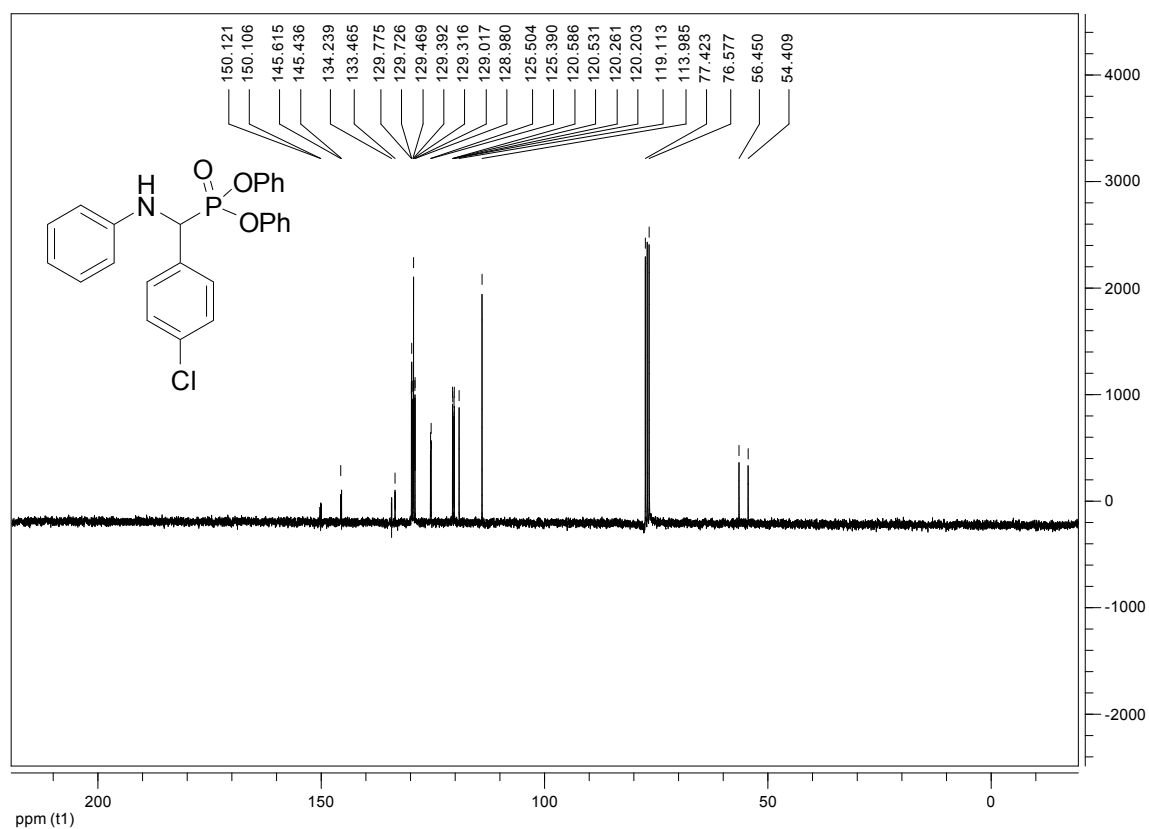


Figure 7. ¹³C NMR spectra for the Diphenyl ((4-chlorophenyl)(phenylamino)methyl) phosphonate in CDCl₃.

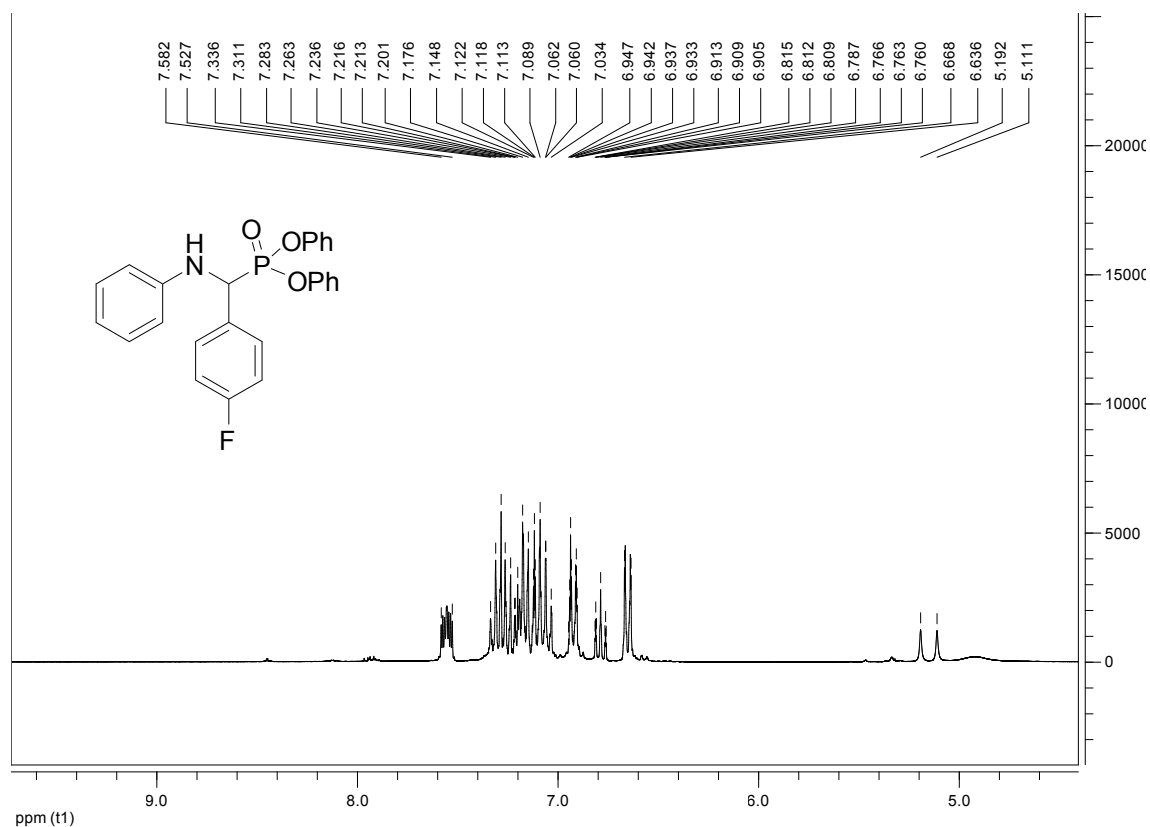


Figure 8. ¹H NMR spectra for the Diphenyl ((4-fluorophenyl)(phenylamino)methyl) phosphonate in CDCl₃.

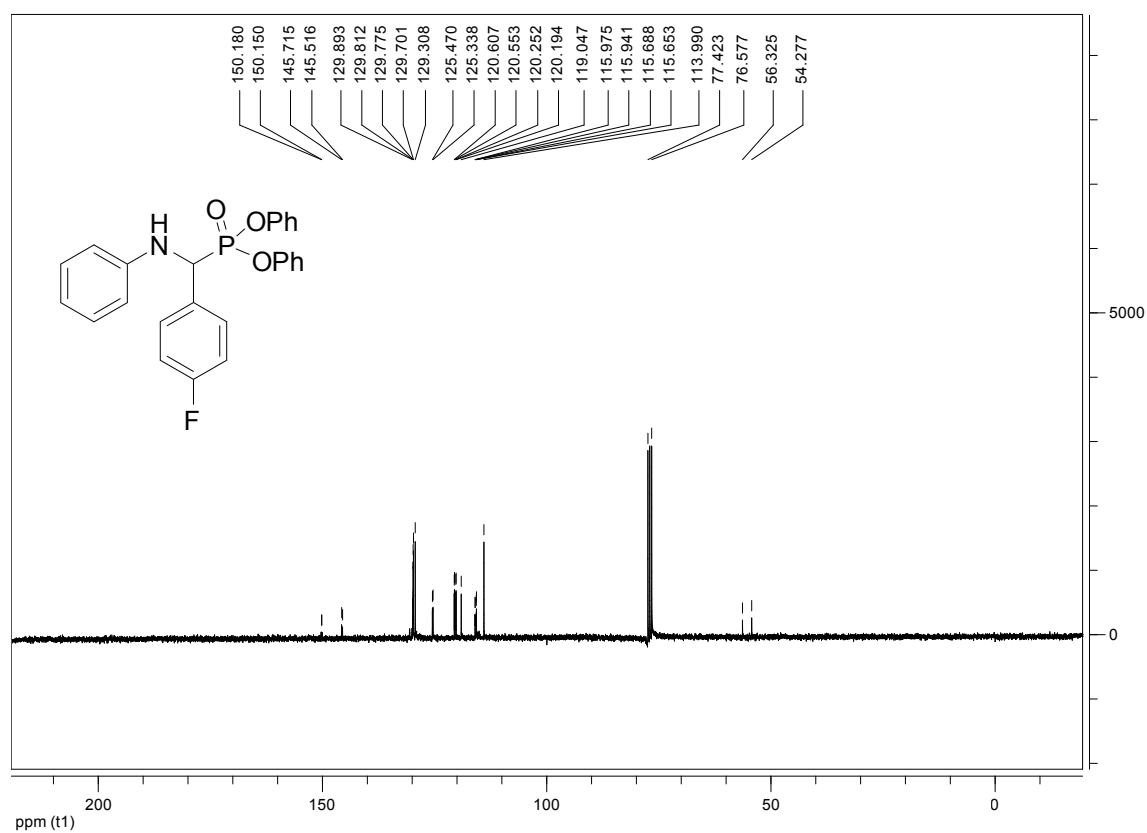


Figure 9. ¹³C NMR spectra for the Diphenyl ((4-fluorophenyl)(phenylamino)methyl) phosphonate in CDCl₃.

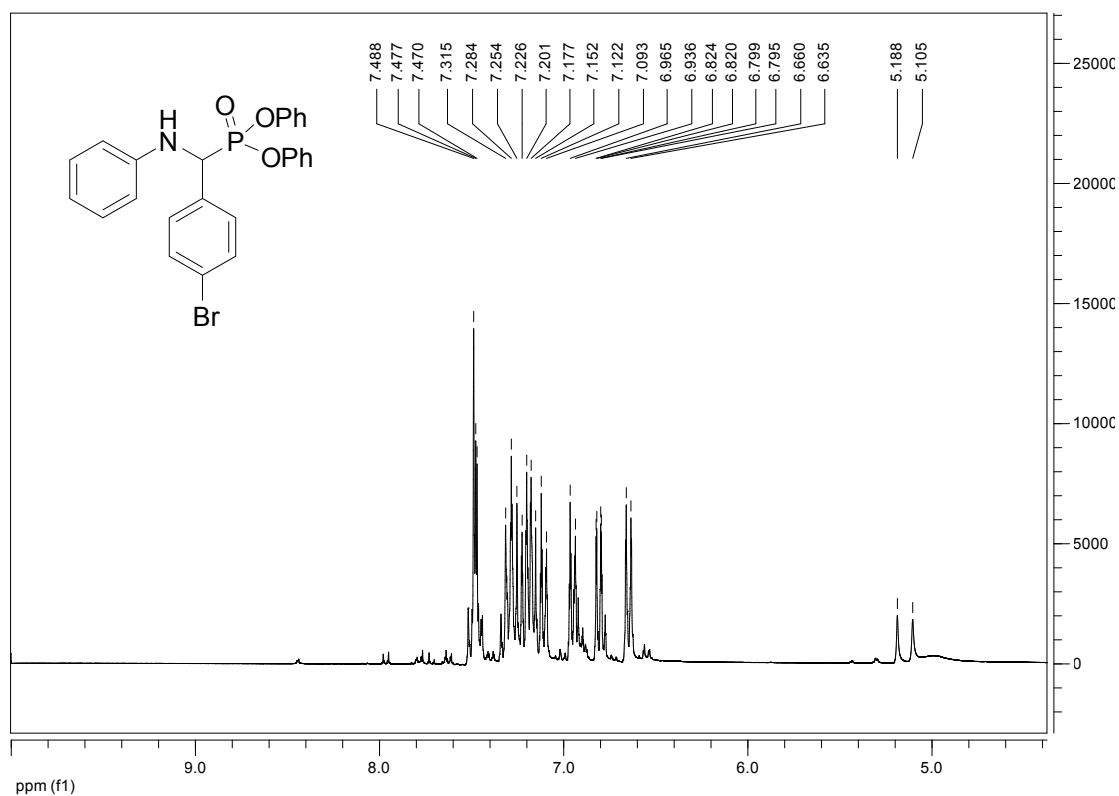


Figure 10. ¹H NMR spectra for the Diphenyl ((4-bromophenyl)(phenylamino)methyl) phosphonate [A5] in CDCl₃.

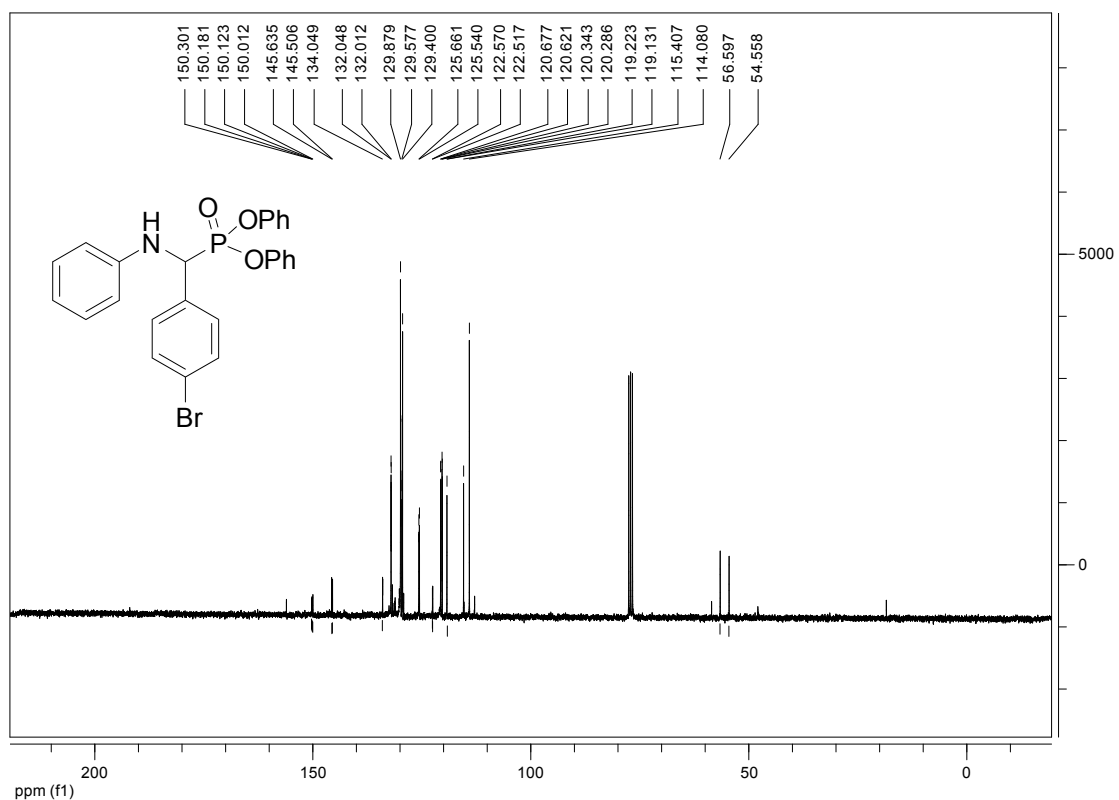


Figure 11. ¹³C NMR spectra for the Diphenyl ((4-bromophenyl)(phenylamino)methyl) phosphonate [A5] in CDCl₃.

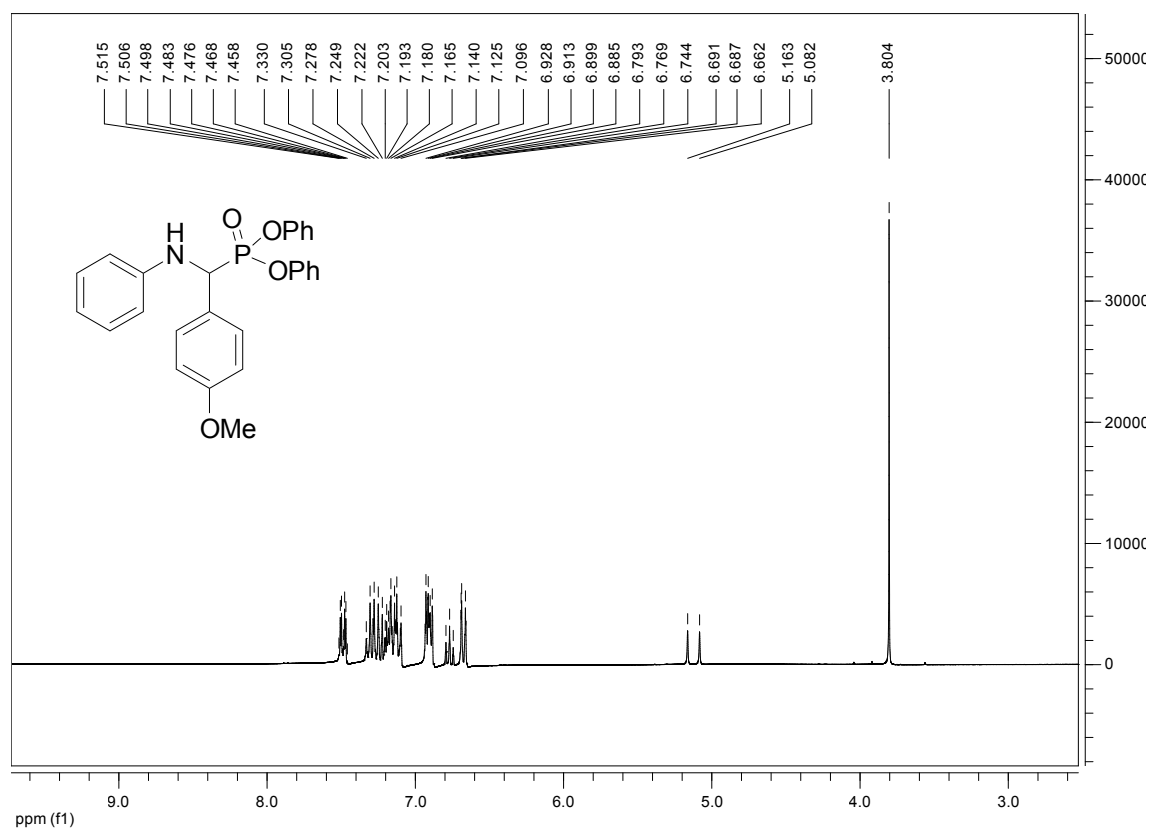


Figure 12. ¹H NMR spectra for the Diphenyl ((4-methoxyphenyl)(phenylamino)methyl) phosphonate in CDCl₃.

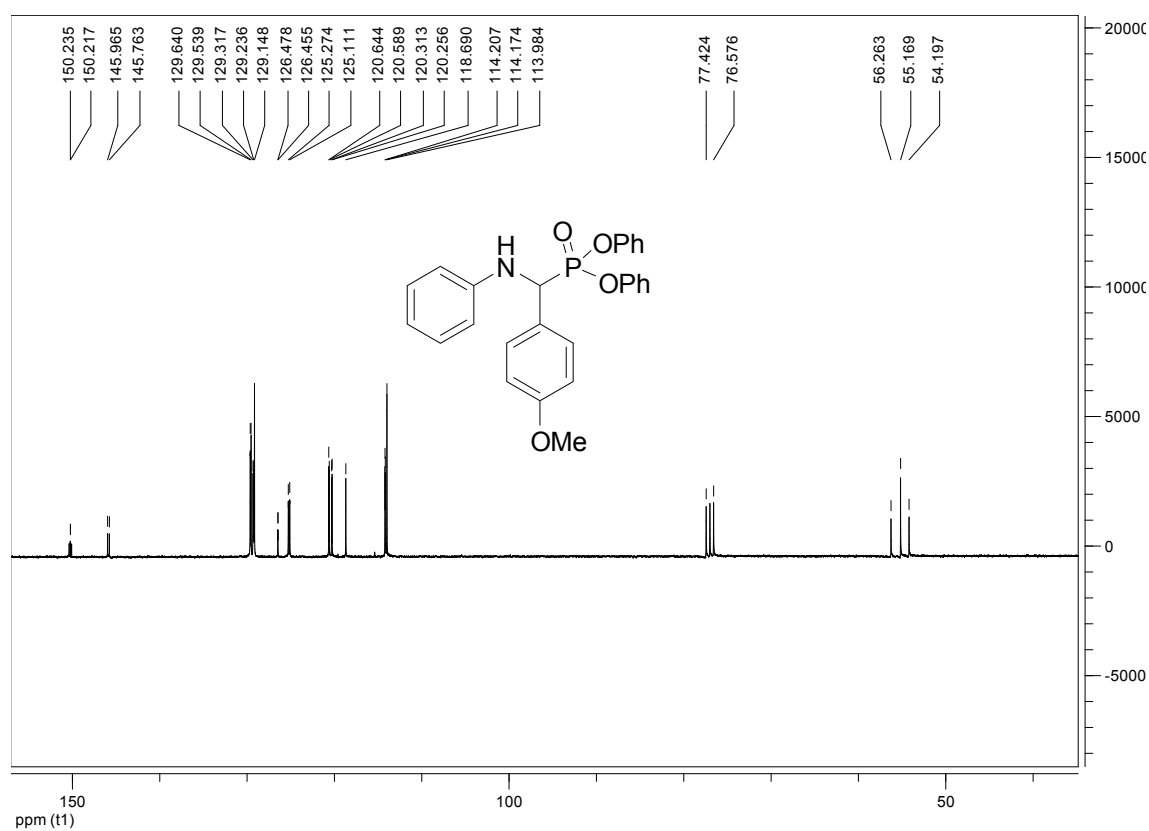


Figure 13. ¹³C NMR spectra for the Diphenyl ((4-methoxyphenyl)(phenylamino)methyl) phosphonate in CDCl₃.

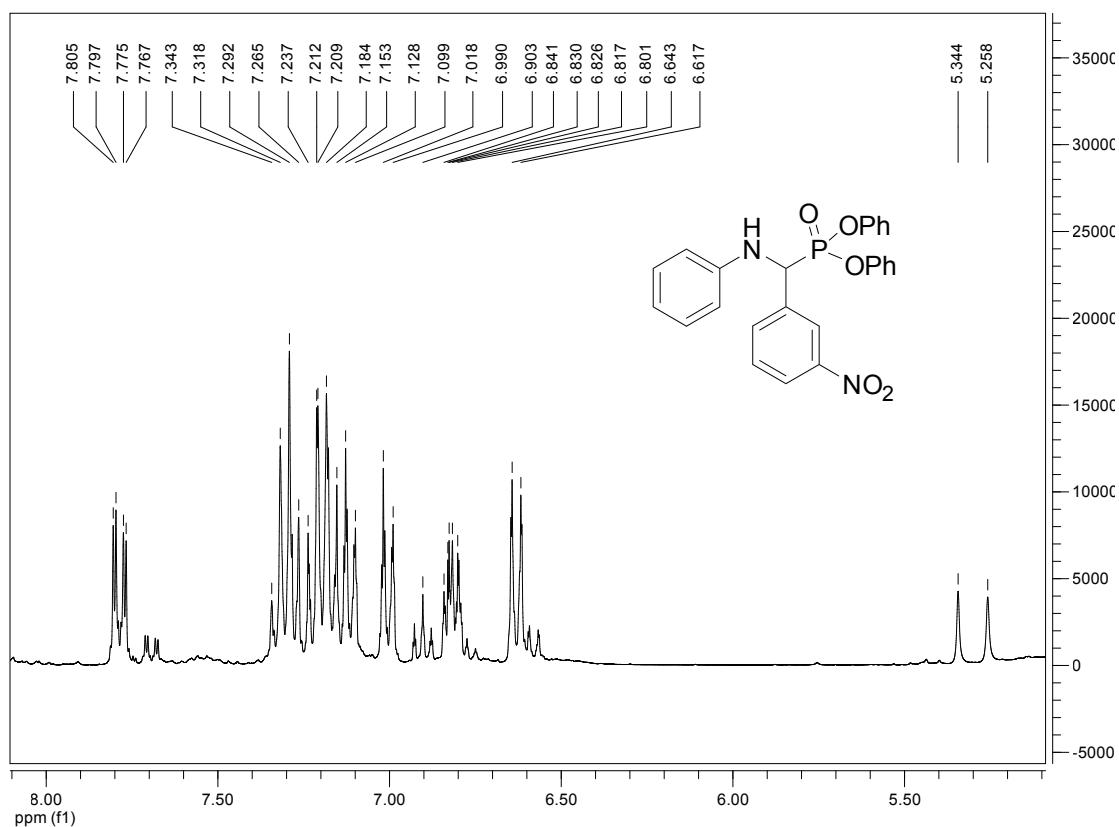


Figure 14. ^1H NMR spectra for the **Diphenyl ((3-nitrophenyl)(phenylamino)methyl) phosphonate** in CDCl_3 .

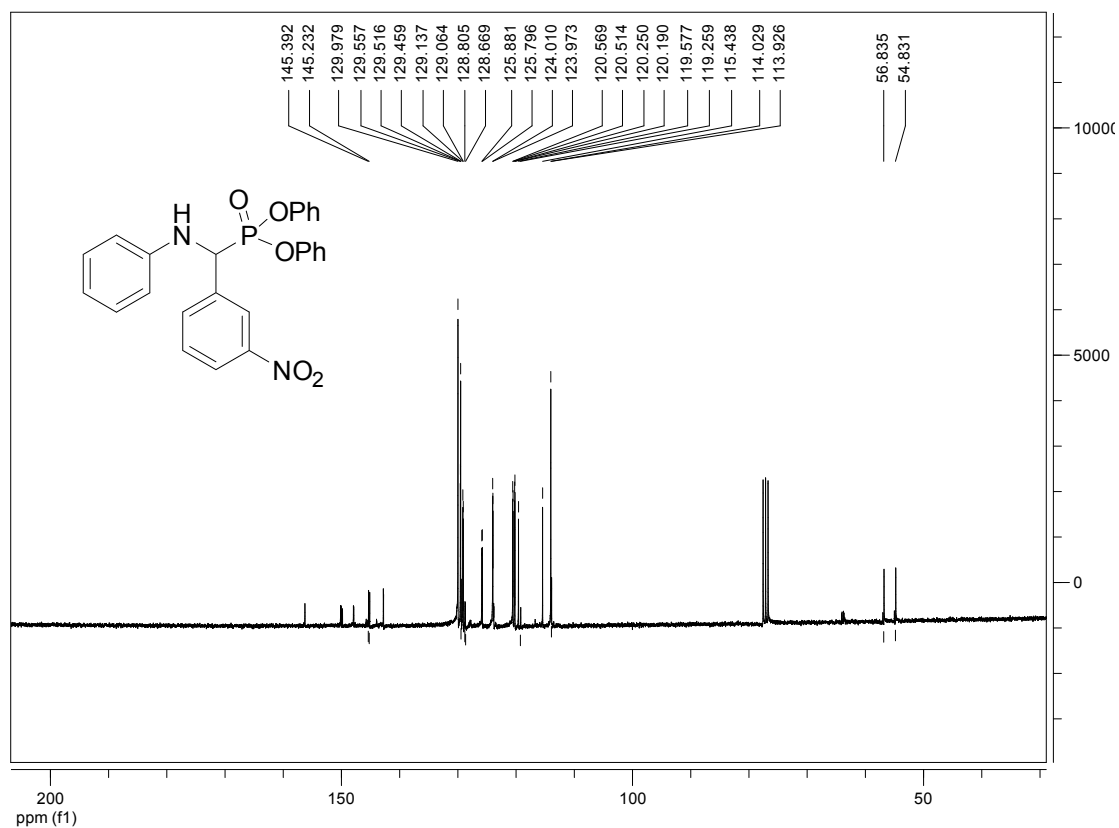


Figure 15. ^{13}C NMR spectra for the **Diphenyl ((3-nitrophenyl)(phenylamino)methyl) phosphonate** in CDCl_3 .

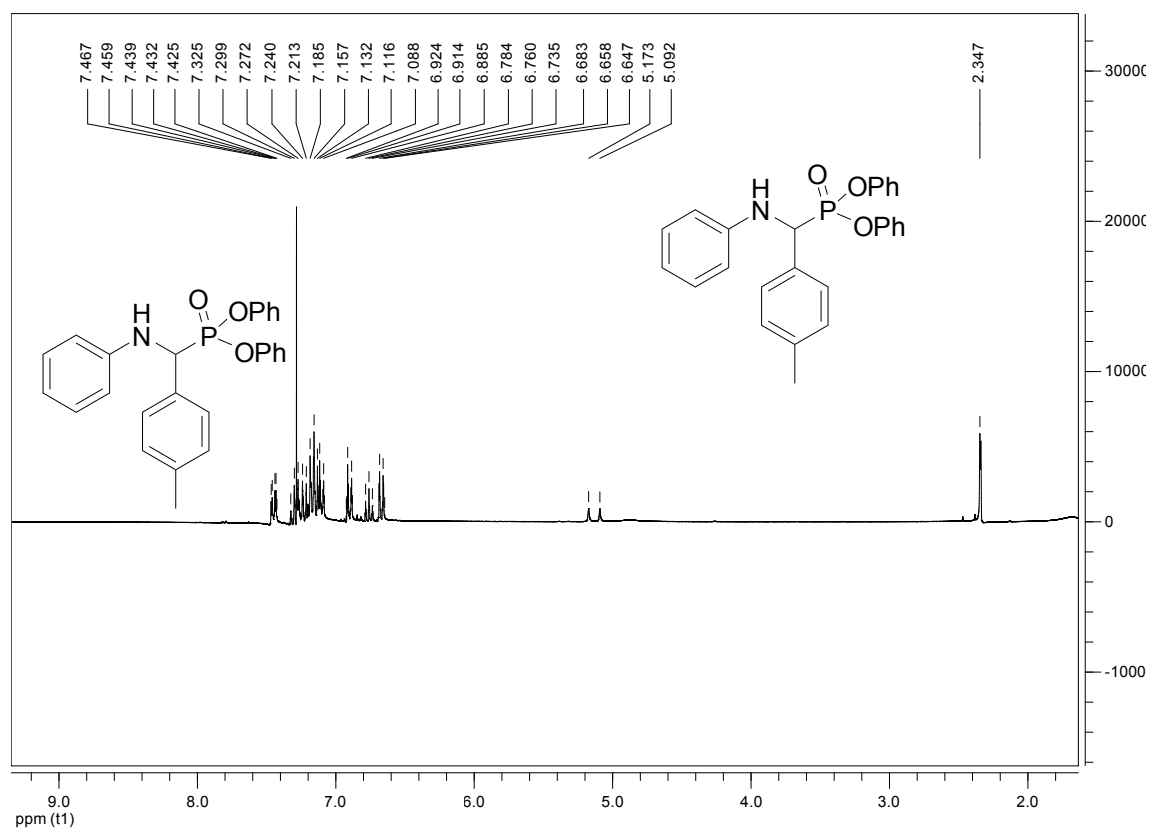


Figure 16. ¹H NMR spectra for the Diphenyl ((phenylamino)(*p*-tolyl)methyl) phosphonate in CDCl₃.

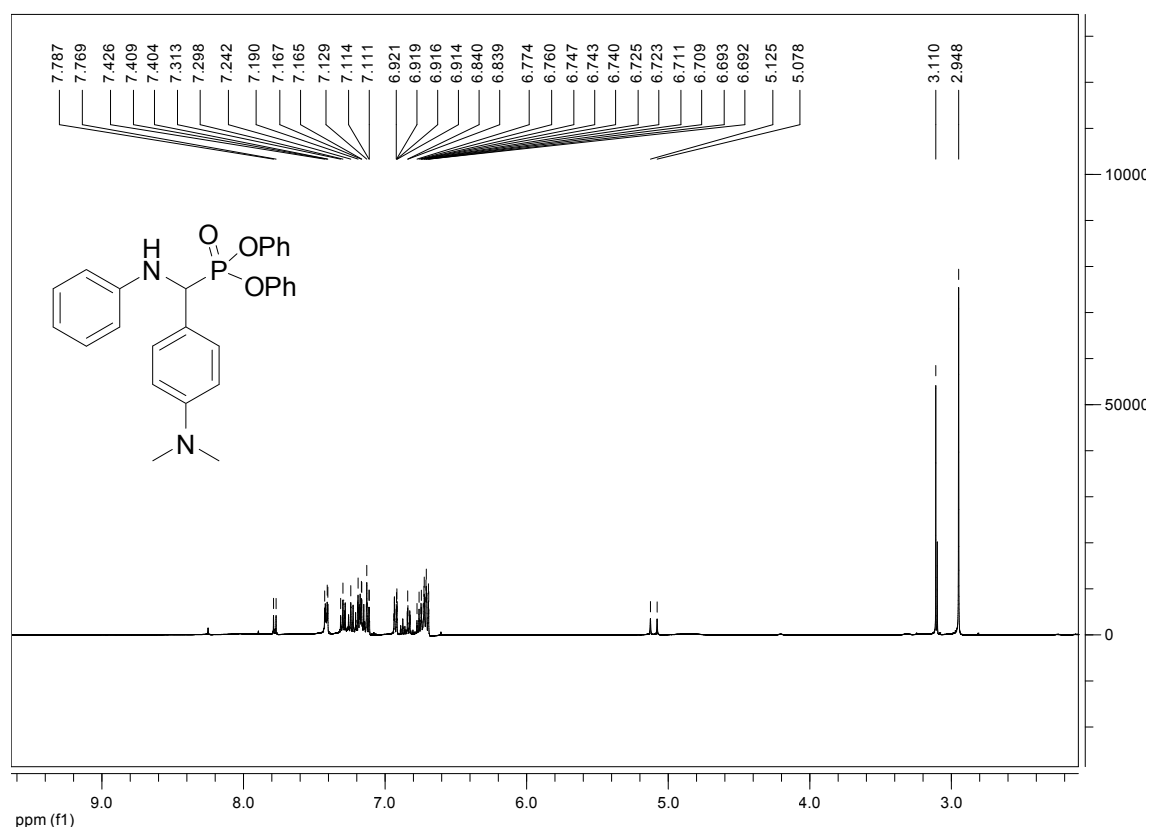


Figure 17. ¹H NMR spectra for the Diphenyl ((4-(dimethylamino)phenyl)(phenylamino)methyl) phosphonate in CDCl₃.

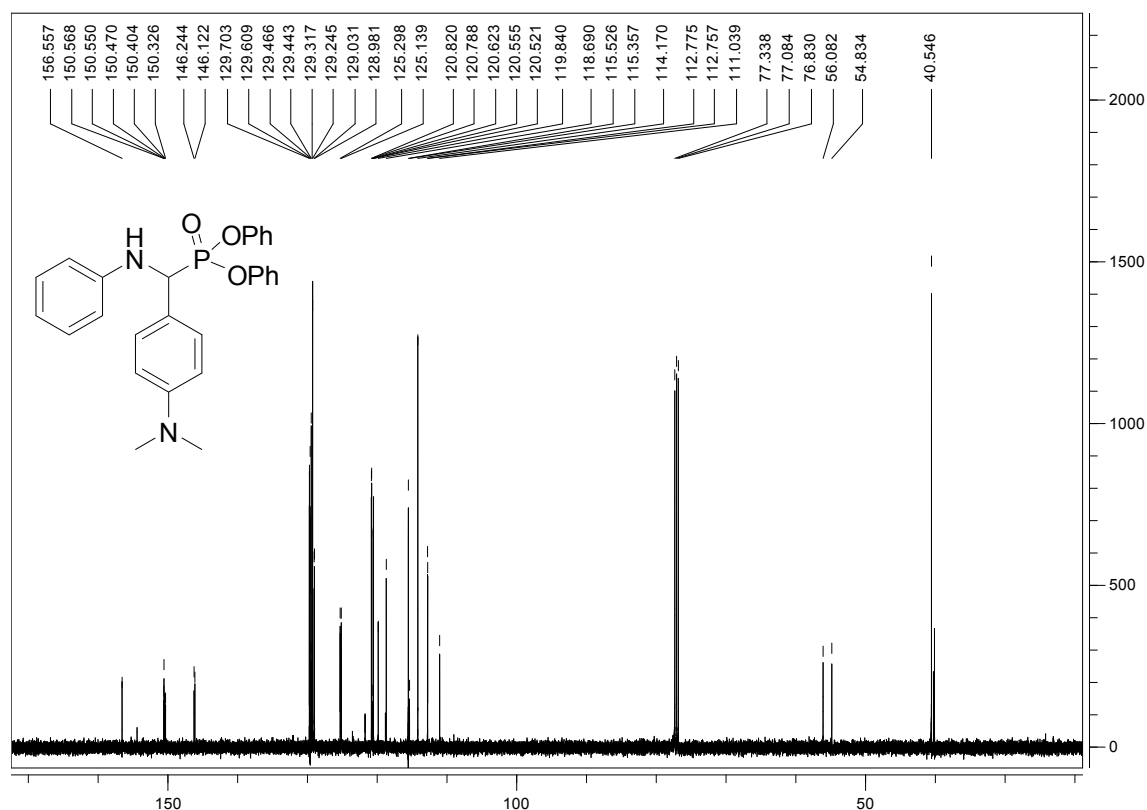


Figure 18. ¹³C NMR spectra for the Diphenyl ((4-(dimethylamino)phenyl)(phenylamino)methyl) phosphonate in CDCl₃.

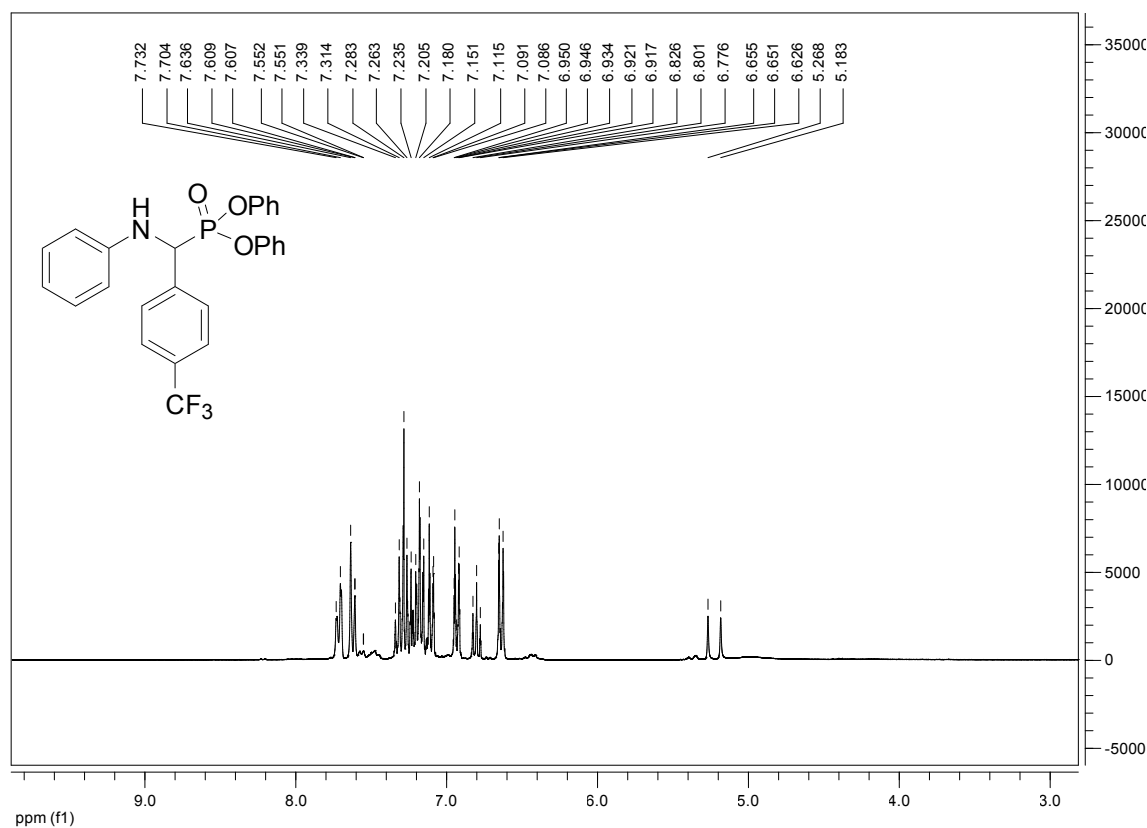


Figure 19. ¹H NMR spectra for the Diphenyl ((phenylamino)(4-(trifluoromethyl)phenyl)methyl) phosphonate in CDCl₃.

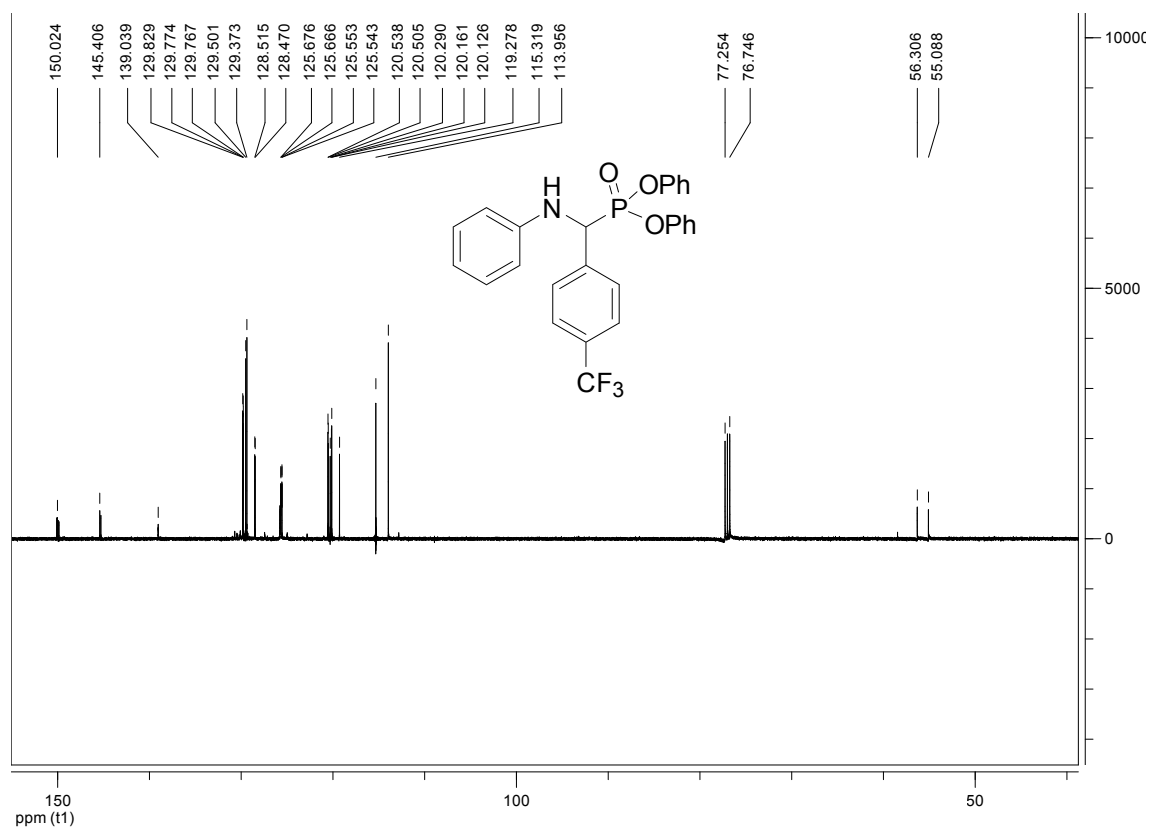


Figure 20. ¹³C NMR spectra for the Diphenyl ((phenylamino)(4-(trifluoromethyl) phenyl)methyl) phosphonate in CDCl₃.

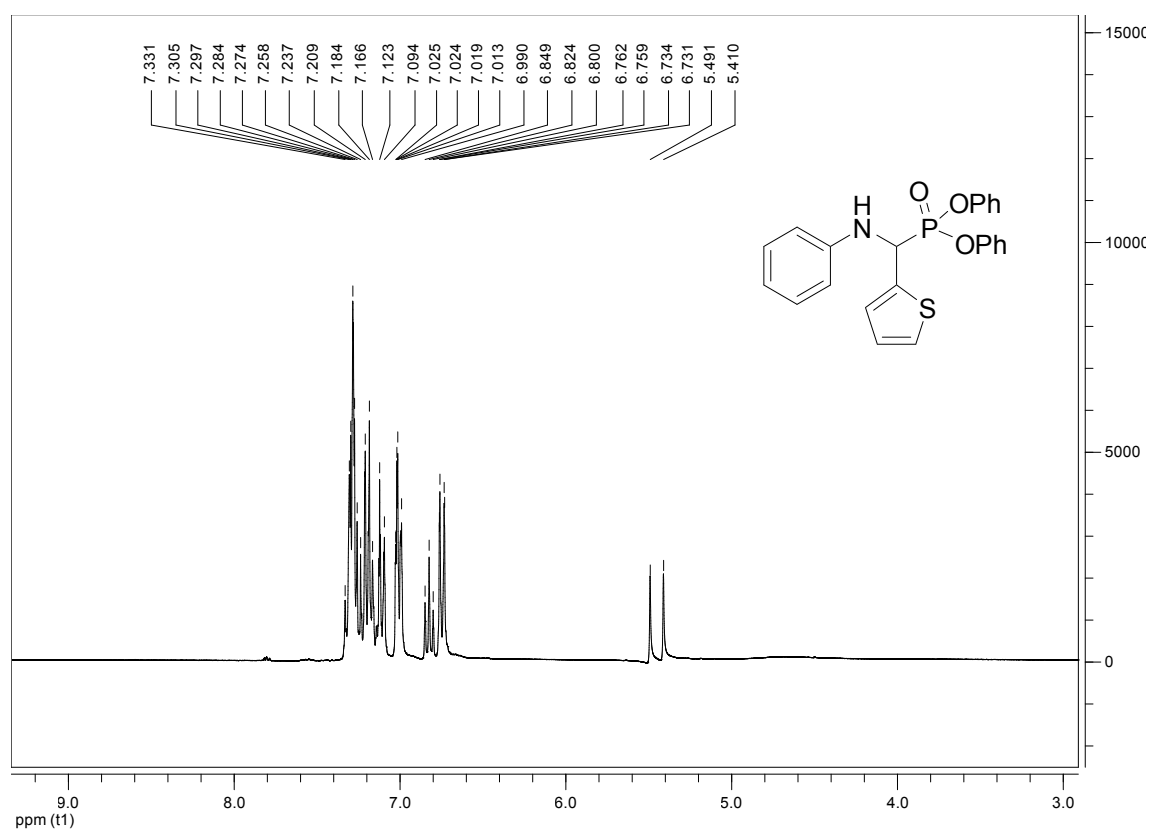


Figure 21. ¹H NMR spectra for the Diphenyl ((phenylamino)(thiophen-2-yl)methyl) phosphate in CDCl₃.

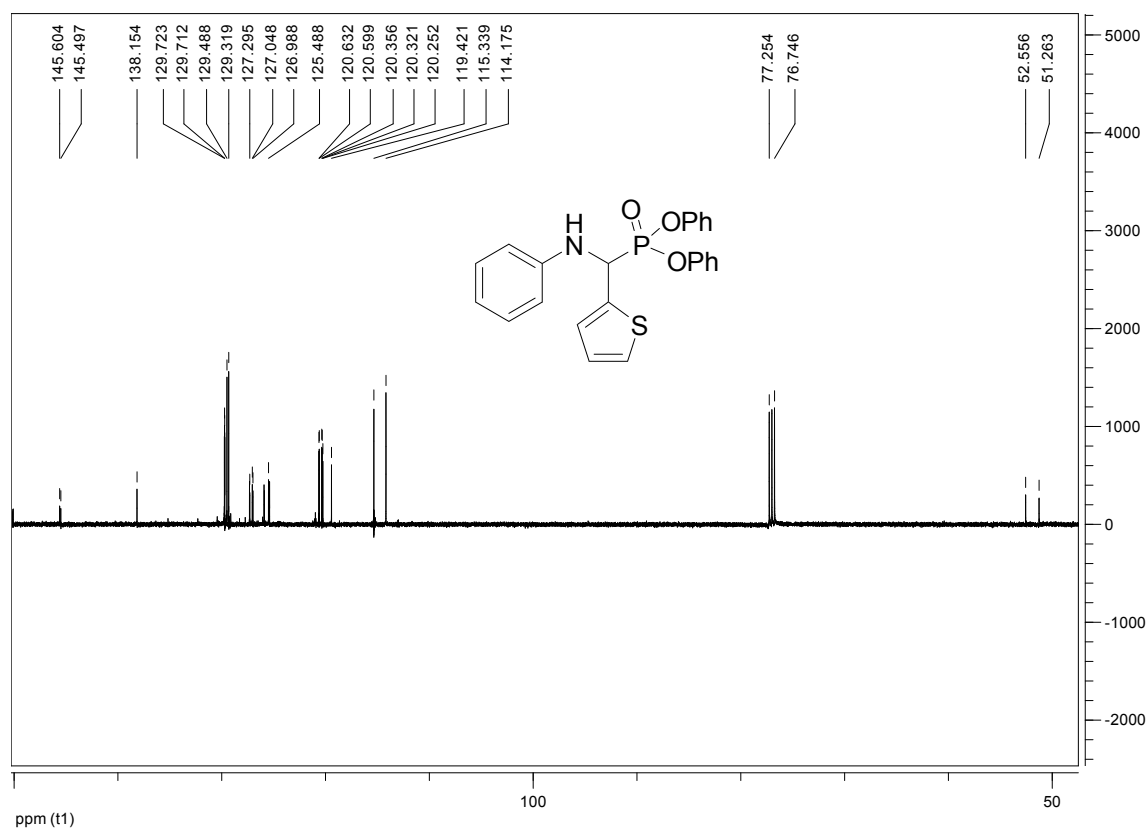


Figure 22. ¹³C NMR spectra for the Diphenyl ((phenylamino)(thiophen-2-yl)methyl) phosphate in CDCl₃.

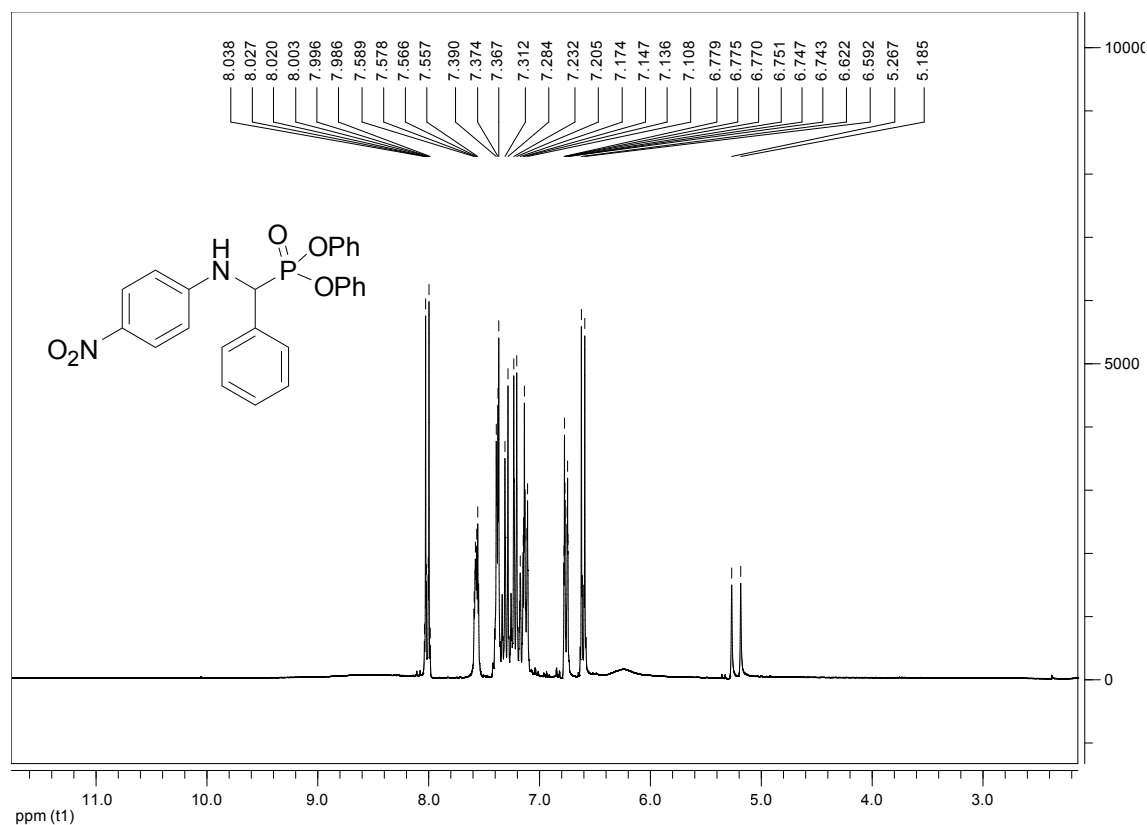


Figure 23. ¹H NMR spectra for the Diphenyl (((4-nitrophenyl)amino)(phenyl)methyl) phosphonate in CDCl₃.

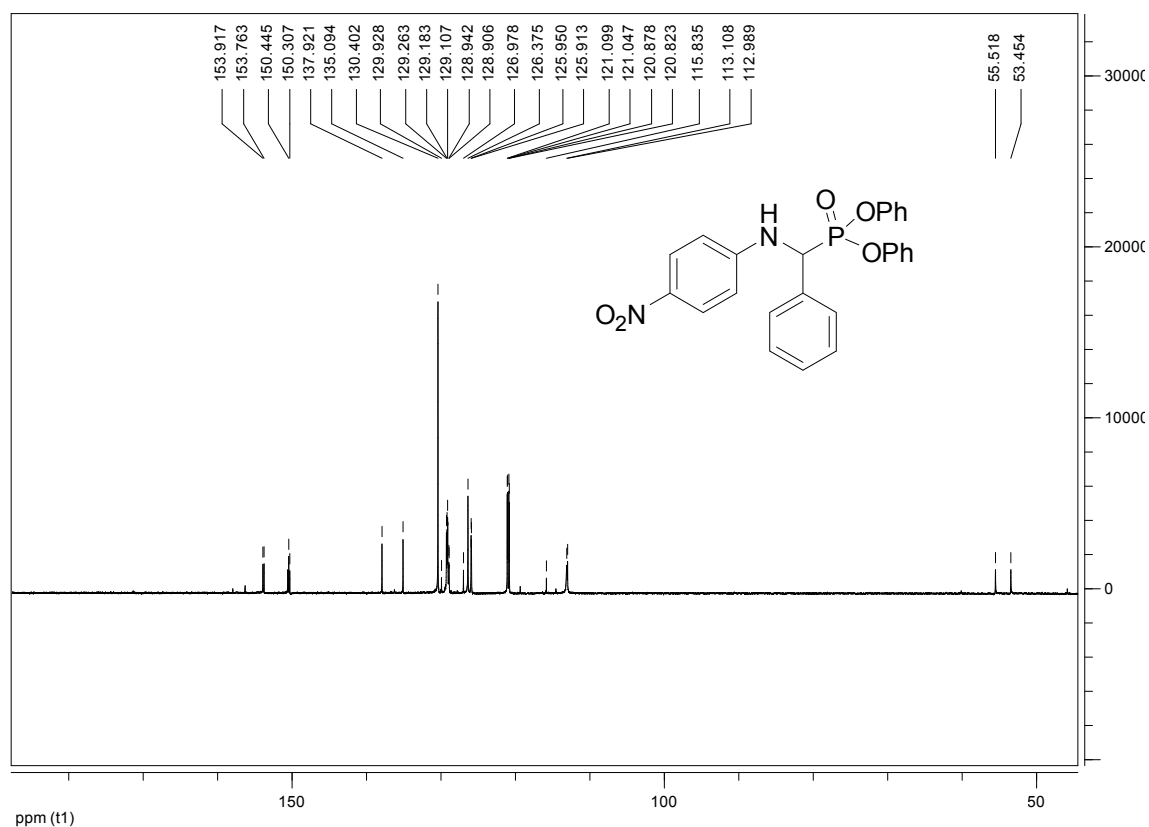


Figure 24. ¹³C NMR spectra for the Diphenyl (((4-nitrophenyl)amino)(phenyl)methyl) phosphonate in CDCl₃.

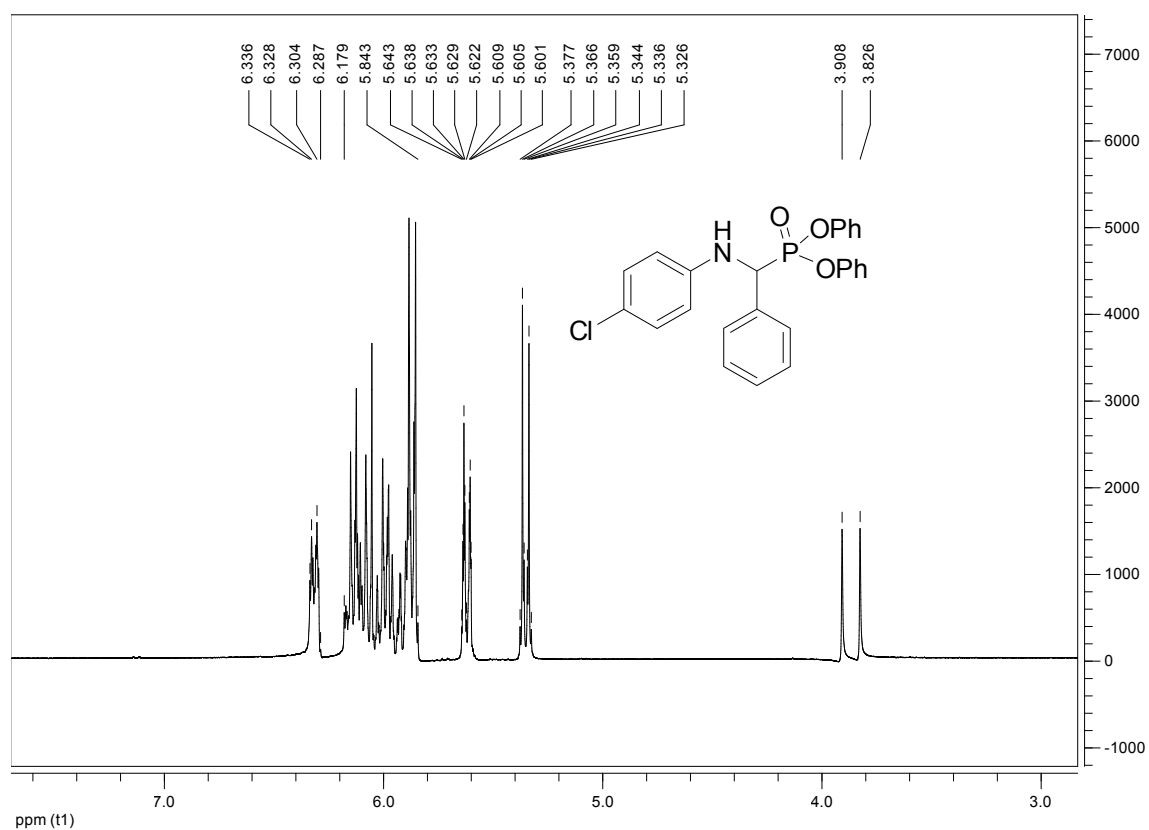


Figure 25. ¹H NMR spectra for the Diphenyl (((4-Chlorophenyl) amino)(phenyl)methyl) phosphonate in CDCl₃.

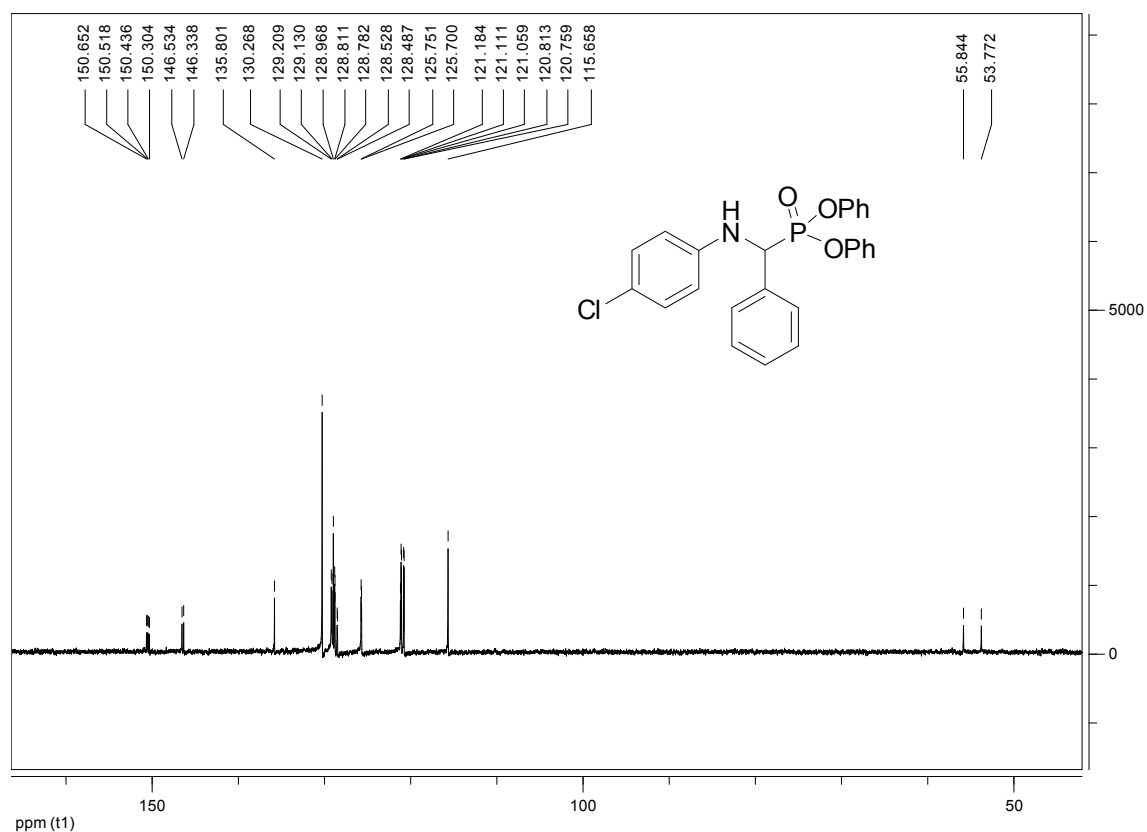


Figure 26. ¹³C NMR spectra for the Diphenyl (((4-chlorophenyl) amino)(phenyl)methyl) phosphonate in CDCl₃.

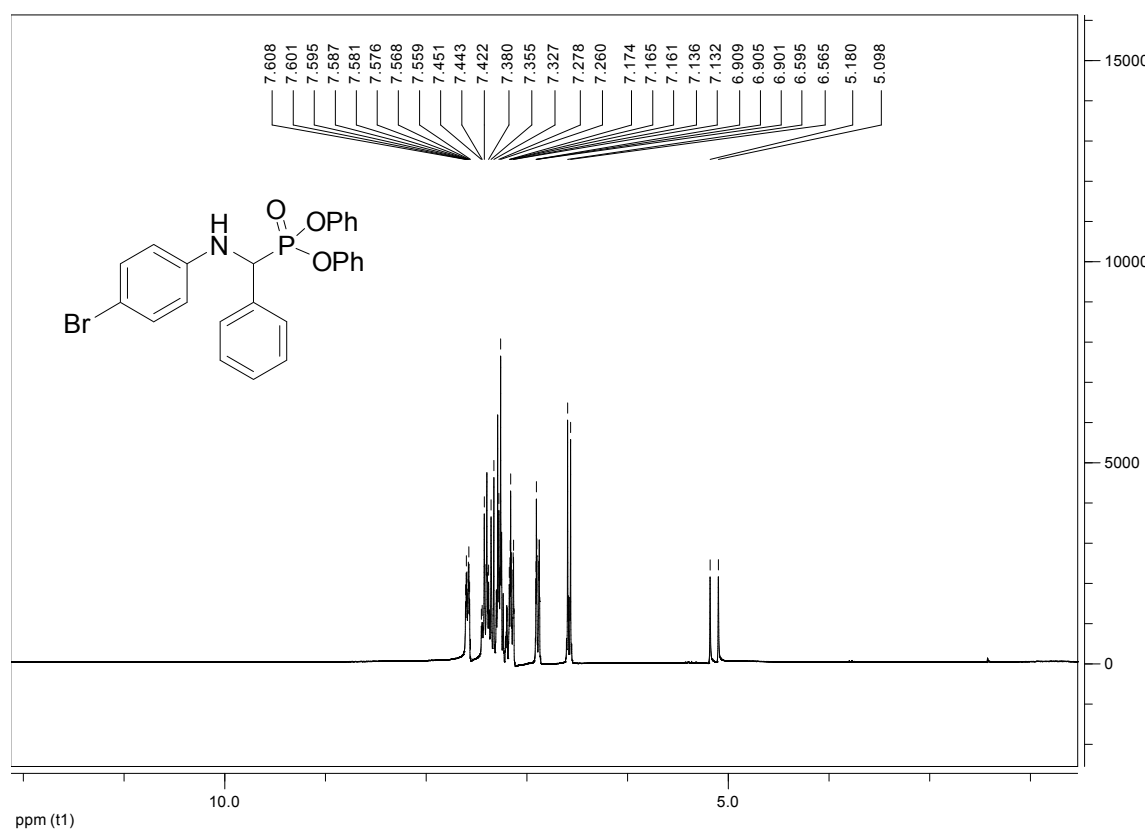
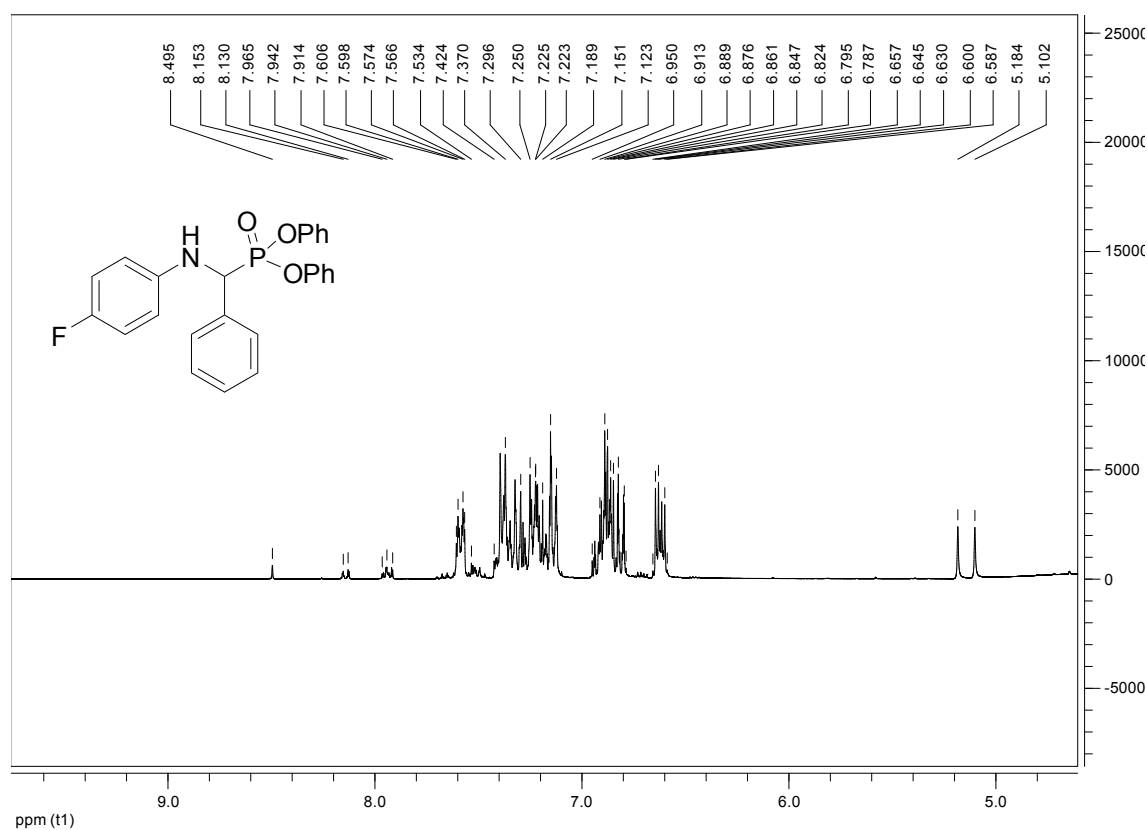
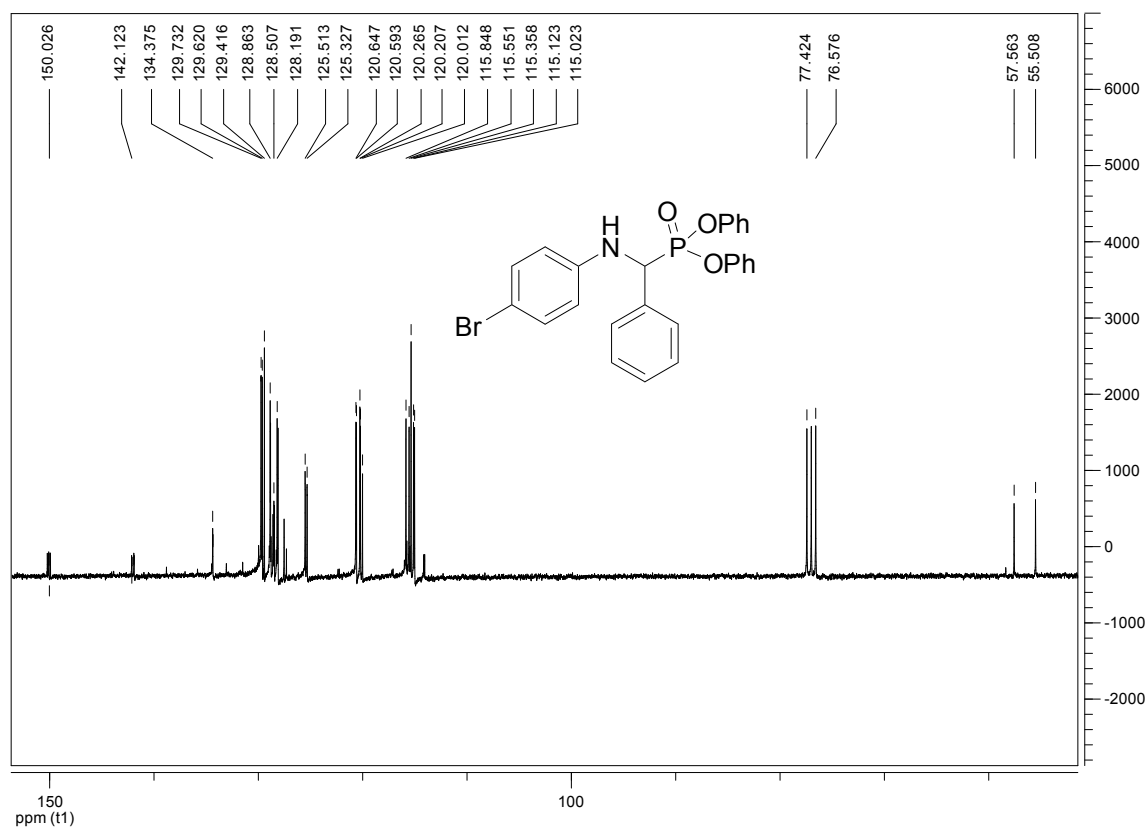


Figure 27. ¹H NMR spectra for the Diphenyl (((4-bromophenyl) amino)(phenyl)methyl) phosphonate in CDCl₃.



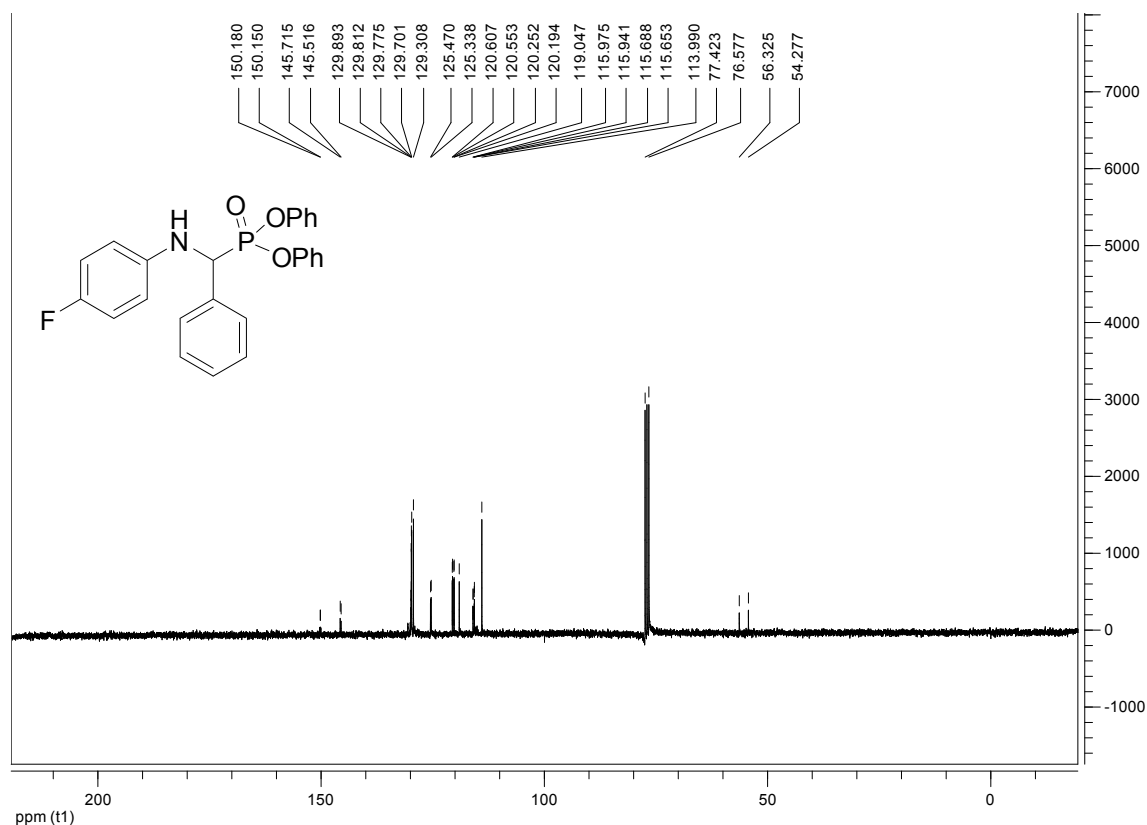


Figure 30. ¹³C NMR spectra for the Diphenyl (((4-fluorophenyl)amino)(phenyl)methyl) phosphonate in CDCl₃.

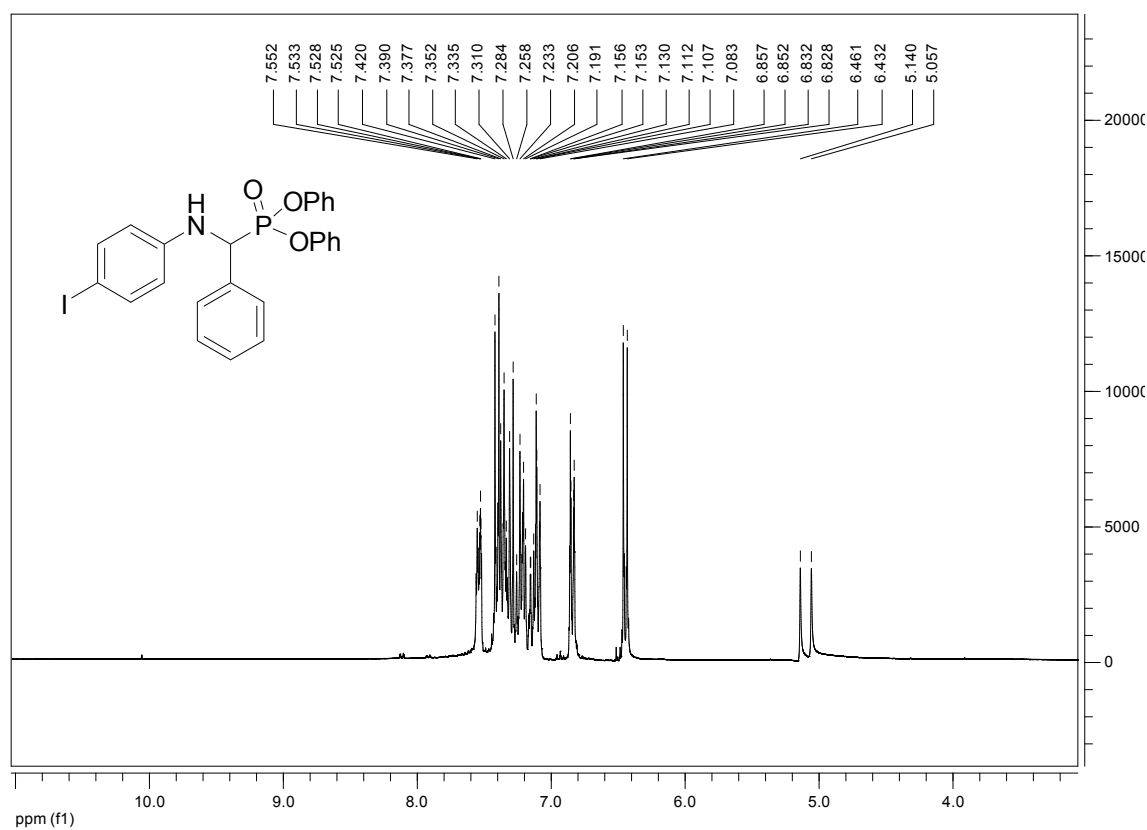
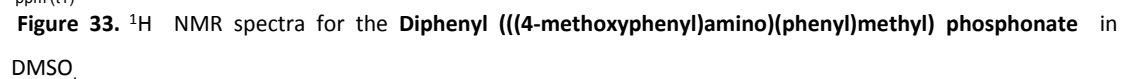
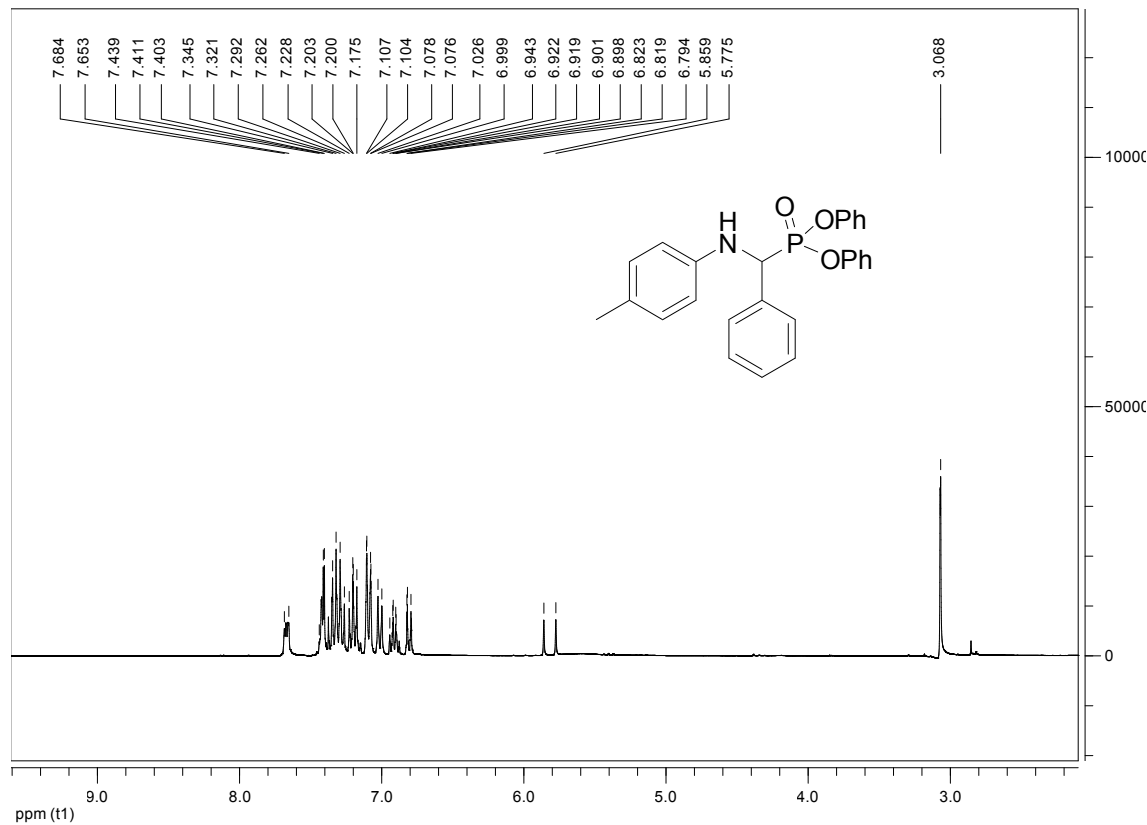
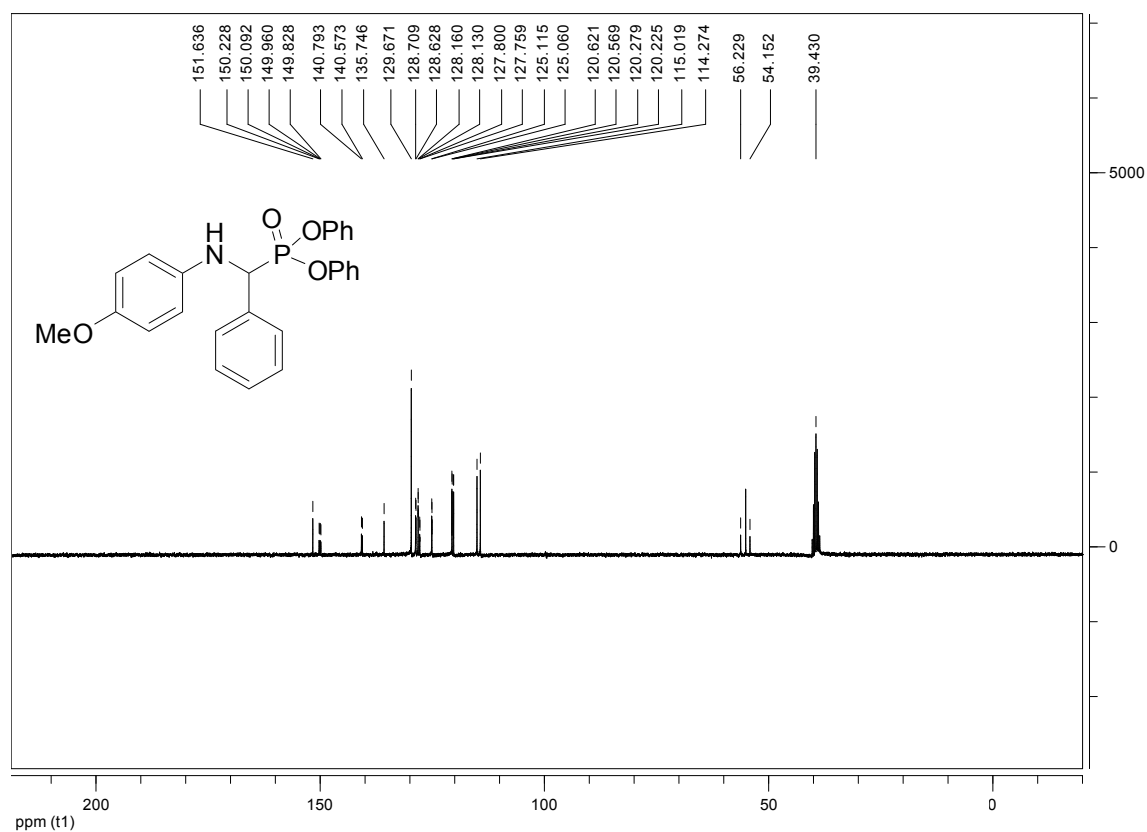


Figure 31. ¹H NMR spectra for the Diphenyl (((4-iodophenyl)amino)(phenyl)methyl) phosphosnate in CDCl₃.





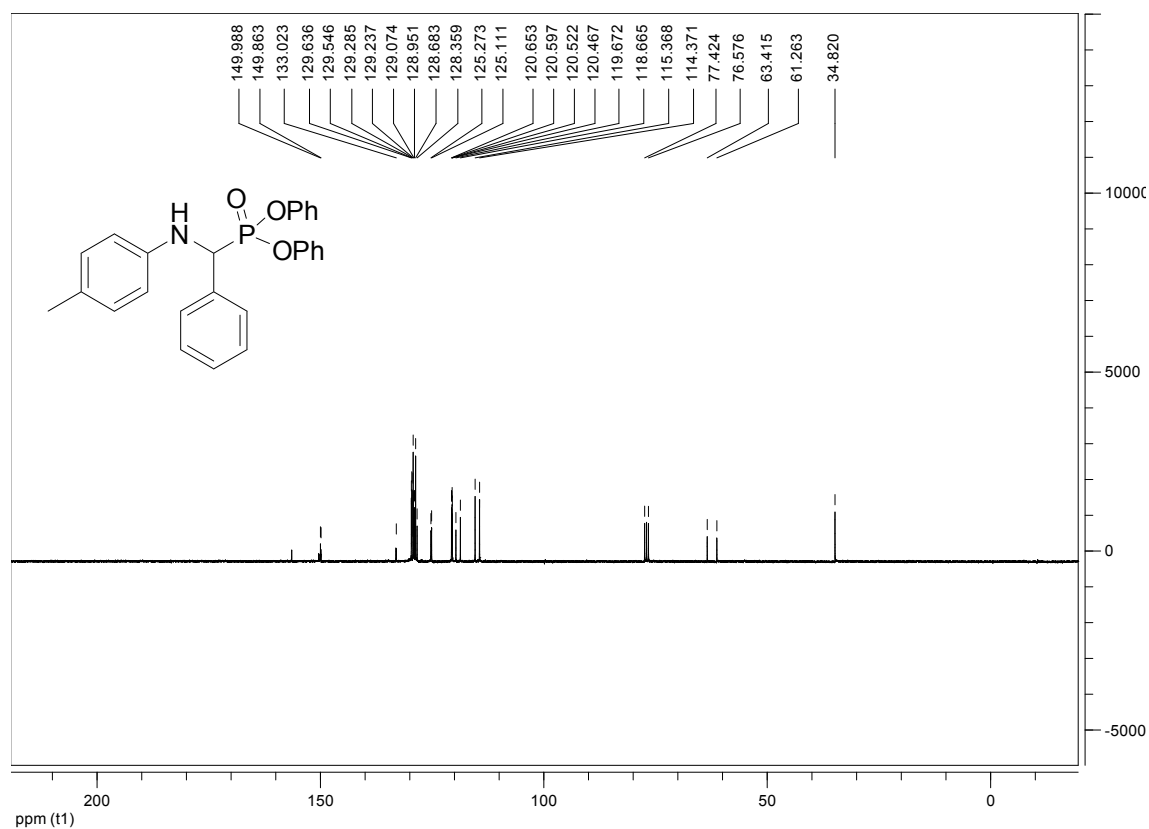


Figure 36. ¹³C NMR spectra for the Diphenyl (phenyl(*p*-tolylamino)methyl) phosphonate in CDCl₃.

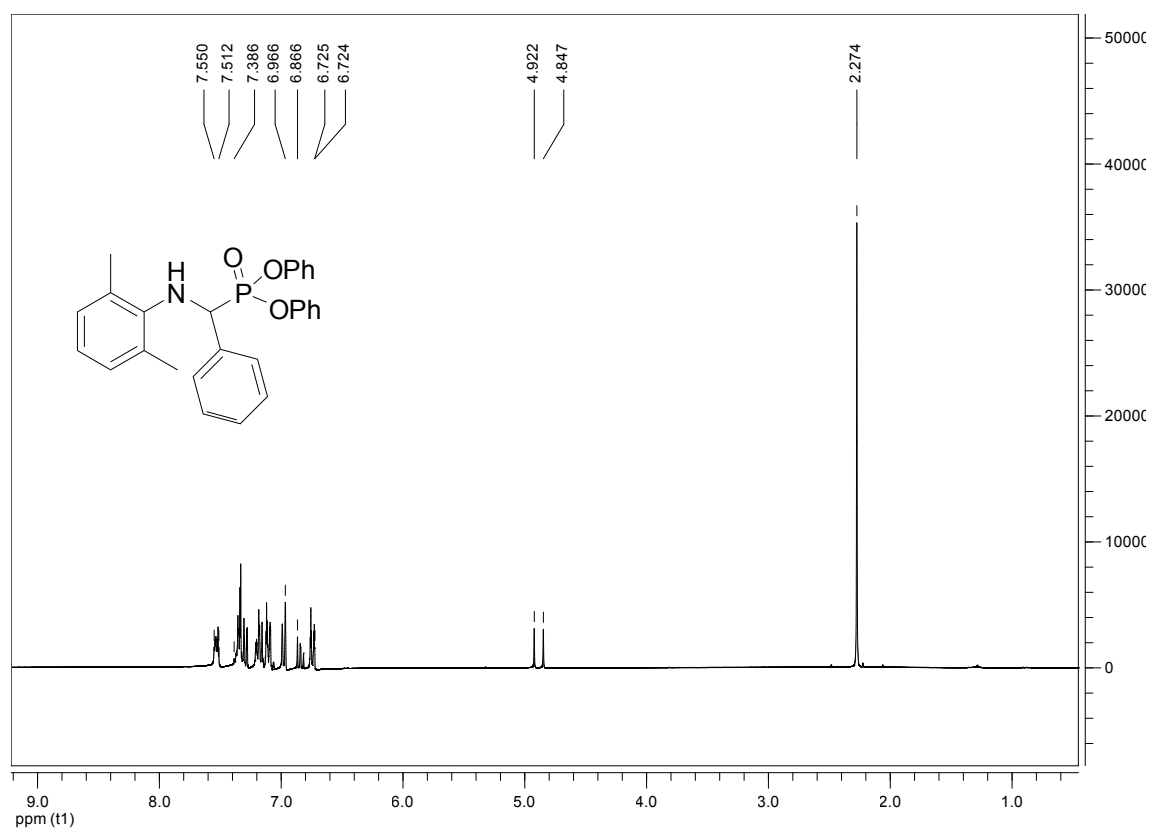


Figure 37. ¹H NMR spectra for the Diphenyl (((2,6-dimethylphenyl)amino)(phenyl) methyl) phosphonate in CDCl₃.

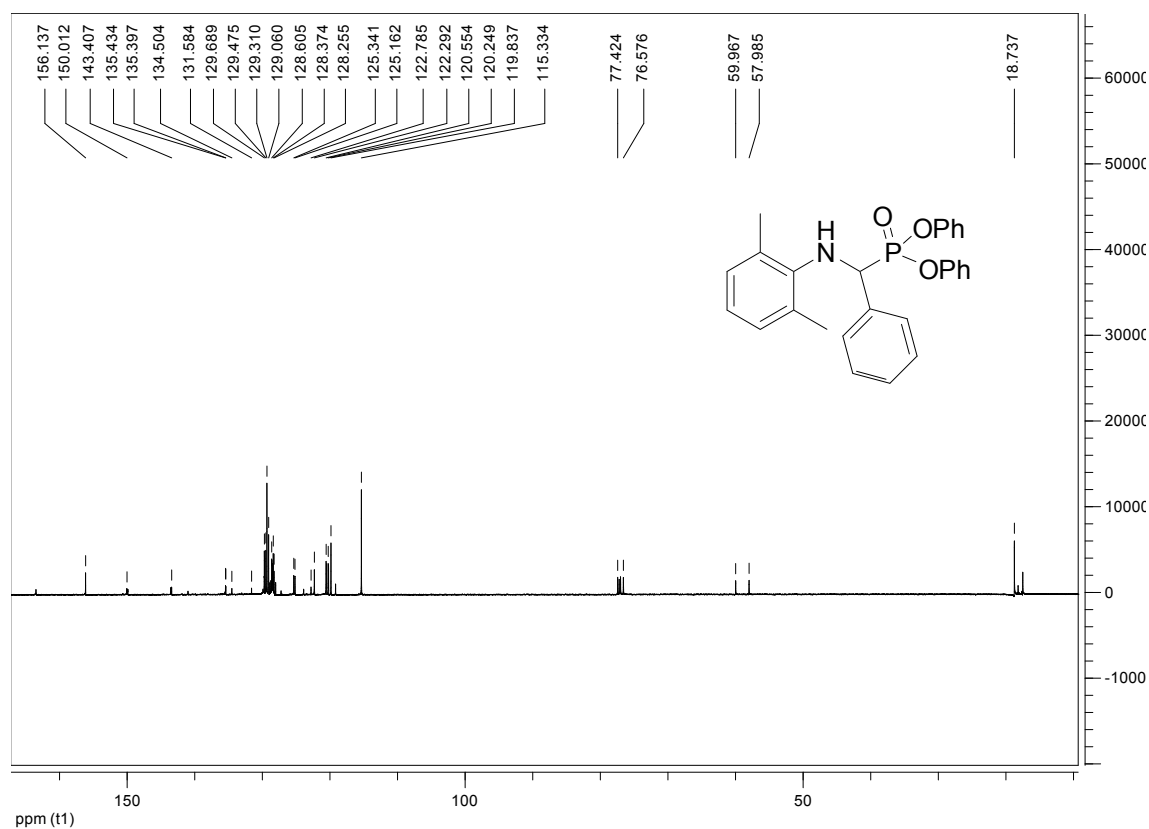


Figure 38. ¹³C NMR spectra for the Diphenyl (((2,6-dimethylphenyl)amino)(phenyl) methyl) phosphonate in CDCl₃.

5. Characterization of Ce[(L-Pro)₂(Oxa)]

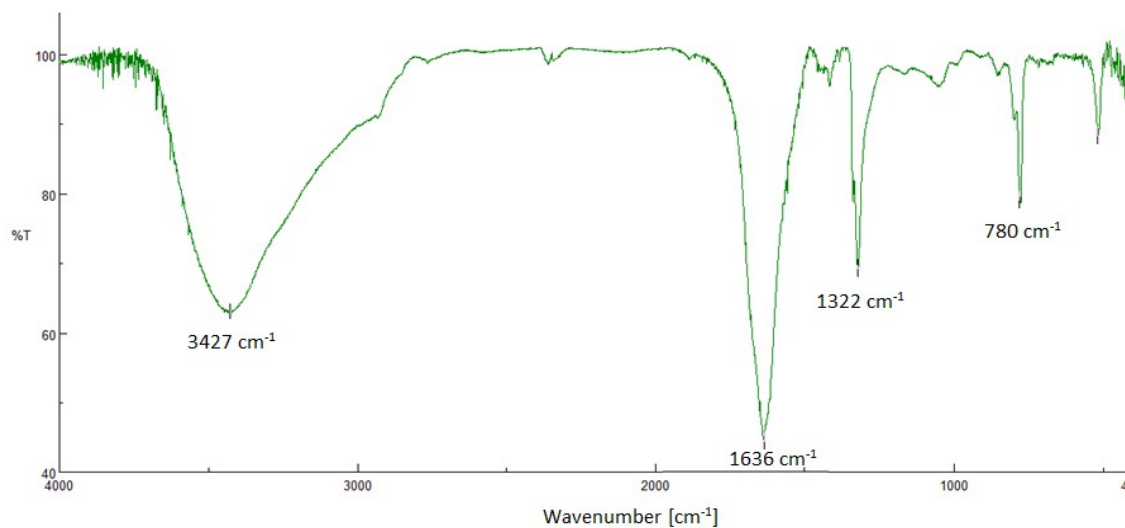


Figure 39. IR for Ce[(L-Pro)₂(Oxa)] in KBr spectroscopic.

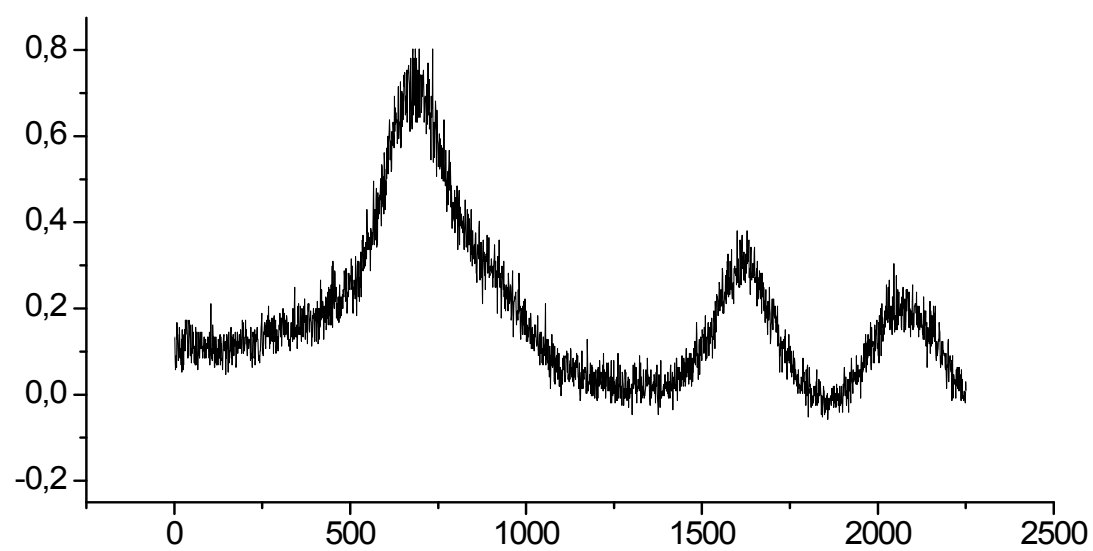


Figure 40. X-Ray diffraction patterns of $[\text{Ce}(\text{L-Pro})]_2(\text{Oxa})$.