Supplementary Material

Photostimulated synthesis of 2-(diphenylphosphino)benzoic acid by the $S_{RN}1$ reaction

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Results and Discussion of Annex Material

To extend the studies, we conducted news experiments in liquid ammonia at -78 ºC with 1 equiv. of **1**, 1 equiv. of Ph_2P^- ions and 2.5 h of stirring before adding 2-chlorobenzoate ion **(1),** as those previously reported.[1] However, the reactions were carried out in a photochemical reactor equipped with two metal iodide lamps of 400 W (Philips, Model HPI-T, water refrigerated), and quenched by adding NH_4NO_3 in excess instead of adding THF at 30 min of reaction. Typically, product analyses were conducted by esterification of the phosphine to the corresponding esters (ethyl 2-(diphenylphosphoryl)benzoate (**4**), ethyl benzoate (**5)** and ethyl 2-chlorobenzoate (**6**)) with ensuing determination by GC. Results are summarized in Table S1.

When the photostimulated reaction of **1** with Ph_2P^- ions was carried out in this condition, the substitution product was obtained only in 11% yield and 75% of the substrate remained unaltered (entry 1, Table S1). The reaction did not occur in the dark (entry 2, Table S1). In addition, the photostimulated reactions were also inhibited by small amounts of electron acceptors (*m*-DNB) or free-radical traps (TEMPO) (entries 3 and 4, Table S1). Once again, all these results suggets that the reaction proceeds through the $S_{RN}1$ mechanism.

In adition, we shows that without quenched by adding NH_4NO_3 in excess, the reaction continue to progress beyond the addition of THF, during the time of solvent evaporation and consequente increase in temperature (-78 to -33 ºC) (compare entry 1, Table 2 with entry 1, Table S1).

Table S1. Reactions of **1** with Ph_2P^- ions under the experimental conditions reported in ref. 1 and quenched with NH_4NO_3

Entry	Conditions[a]	Cl^- (%)[b]	**4** (%)[c]	**6** (%)[c]	**5** (%)[c]
1	NH_3, -78ºC, *hv*, 30 min	26	11	75	>5
2[d]	NH_3, -78ºC, dark, 30 min	>1	--	ca100.	--
3[e]	NH_3, -78ºC, *hv*, 30 min	>1	--	ca100.	--
4[f]	NH_3, -78ºC, *hv*, 30 min	>1	--	ca100.	--

[a] Reactions carried out under N_2 in 10-15 mL of ammonia at -78ºC, with 1 equiv. (4.44 mmoles) of **1,** 1 equiv. (4.44 mmoles) of Ph_2P^- ions and 2.5 h of stirring before adding **1** and 0.5 h of stirring before adding of an excess of NH_4NO_3. Is important to note that *t*-BuOH was not added. Irradiation was conducted in a photochemical reactor equipped with two 400 W lamps refrigerated with air and water unless otherwise indicated. [b] Determined potentiometrically. [c] Yields were determined by GC (internal standard method). [d] 2-Chlorobenzoic acid was added in one portion. [e] 20 mol % of *m*-DNB was added. [f] 20 mol % of TEMPO was added.

Experimental Section

General. Gas chromatographic analyses were performed on a Hewlett Packard 5890 series II with a flame ionization detector and equipped with the following column: HP1 column (0.53 mm x 5m). Quantification by GC was performed by the internal standard method. Gas Chromatographic-Mass Spectrometer analyses were carried out on a Shimadzu QP-5050 spectrometer equipped with a quadrupole detector and a VF-5 ms column (30 m x 0.25 mm x 0.25 μm). ^{1}H NMR (400.16 MHz), ^{31}P NMR (162 MHz) and ^{13}C NMR (100.62 MHz) spectra were recorded on a High Resolution Spectrometer Bruker Advance 400 in $CDCl_3$ as solvent and against internal TMS (^{1}H) and external 85% phosphoric acid (^{31}P). Coupling constants (*J*) are given in Hz units. Irradiation was conducted in a reactor equipped with two 400-W lamps of metal iodide (Philips, Model HPI-T) refrigerated with water. An Orion 420A pHmeter with Ag/Ag^+ electrode was used for the potentiometric titration of halide ions in the aqueous phases.

Materials

$C_6H_5CO_2H$, 2-$ClC_6H_4CO_2H$, Na metal, Ph_3P, *t*-BuOH, NH_4NO_3, EtOH and H_2SO_4 were commercially available and used as received from the supplier. THF was dried over Na metal and benzophenone, and distilled under atmosphere of N_2. All solvents were analytical grade and used as received from the supplier. Silica gel (0.063-0.200 mm Macherey-Nagel) was used in column chromatography. Ethyl benzoate and ethyl 2-chlorobenzoate were prepared according to the literature procedure.[2]

Representative Procedure for Photostimulated Reactions of 1 with Ph_2P^- ions in Liquid Ammonia

Liquid ammonia (150 mL), previously dried with Na metal under N_2, was condensed into a 250 mL three-necked, round-bottomed flask equipped with a coldfinger condenser charged with ethanol, a nitrogen inlet, and a magnetic stirrer. PPh_3 (0.1442 g, 0.55 mmol) was then added, and Na metal was introduced in small pieces; addition was continued until the solution kept its dark brown color for at least 15 min. After its color turned red, *t*-BuOH (0.5 mL, 0.55 mmol) was added to eliminate the H_2N^- anions formed. An orange solution of Ph_2P^- ions was obtained. 2-Chlorobenzoic acid was added to the solution to form **1** (0.0783 g, 0.5 mmol), and the mixture was irradiated for 120 min with two metal iodide lamps of 400 W (Philips, Model HPI-T, water refrigerated). The reaction was quenched with an excess of NH_4NO_3 and the liquid ammonia was allowed to evaporate. Water (50 mL) was added to the residue and HCl was afterwards added until the aqueous phase reached pH 1-2. The aqueous phase was extrated with ethyl acetate (3 x 30 mL) and the combined organic layers were washed with H_2O (20 mL) and dried over anhydrous $MgSO_{4;}$ the solvent was evaporated under vacuum. The chloride ions in the aqueous solution were determined by potentiometry.

The crude products were mixed with EtOH (1.8 mL, 30.8 mmol) and concentrate H_2SO_4 (0.05 mL, 0.94 mmol) in a 10 mL tube sealed and equipped with a magnetic stirrer. The mixture was heated to 80°C for 4 days. The excess of EtOH was eliminated on a rotary evaporator and allowed cooling. The residue was dissolved with water (50 mL) and $NaHCO_3$ was then added until have pH 8-9.

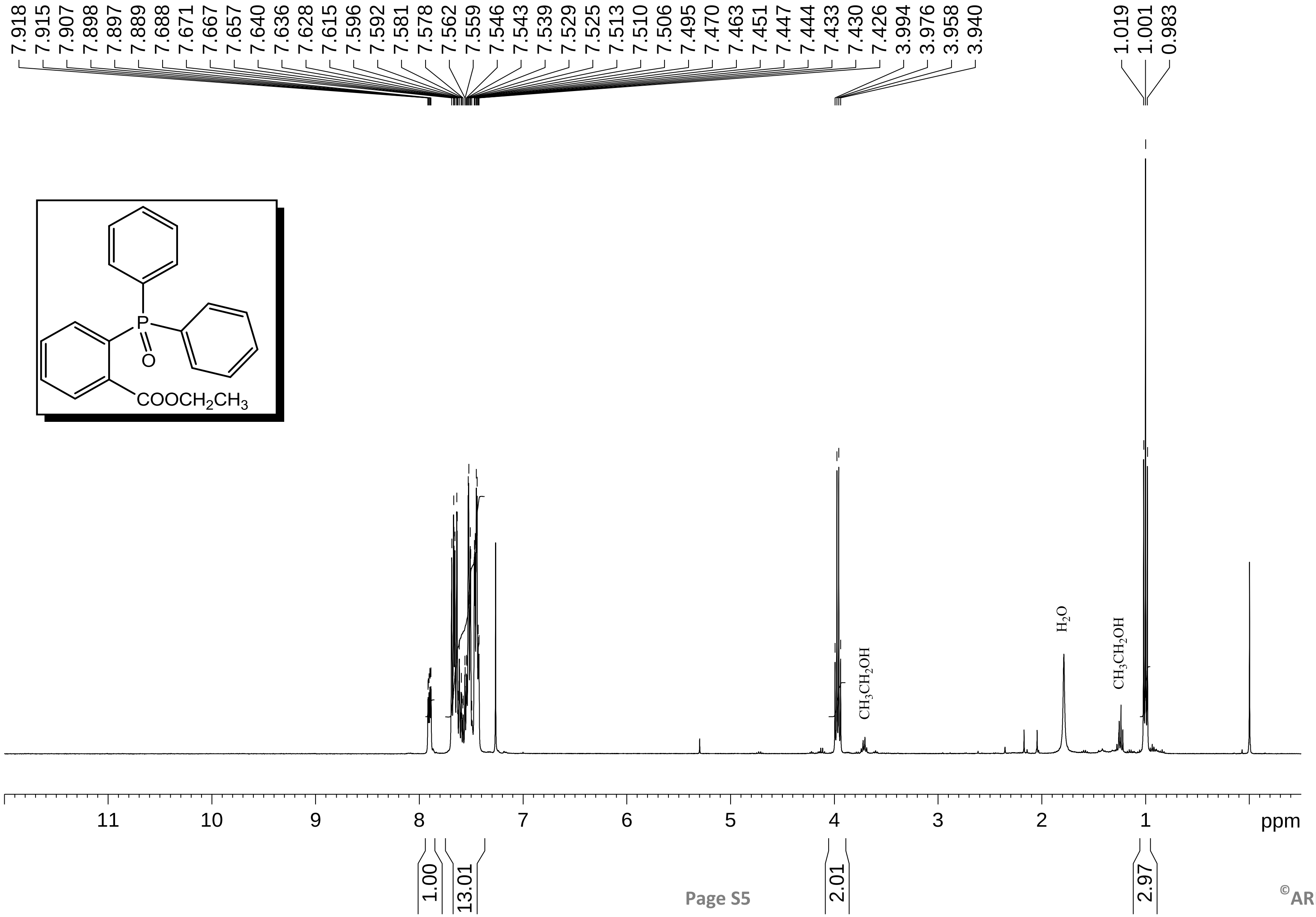
The aqueous phase was extracted with ethyl acetate (3 x 30 mL) and the combined organic layers were washed with H_2O (20 mL), dried over anhydrous $MgSO_4$ and then quantified by GC using the internal standard method.

Alternatively, in other runs the solvent was removed under reduced pressure and the product ethyl 2-(diphenylphosphoryl)benzoate (**4**)[3] was purified by column chromatography on silica gel eluting with a dichloromethane / etanol gradient (100:0 → 95:5) as a colourless liquid. ^1H NMR (400.16 MHz, $CDCl_3$): δ_H 7.92-7.89 (1H_{aro}, m, 1CH), 7.69-7.43 (13 H_{aro}, m, 13CH), 3.97 (2H, q, J_{HH} = 7.2 Hz, CH_2CH$_3$), 1.00 (3H, t, J_{HH} = 7.2 Hz, CH$_2$$CH_3$). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 167.26 (d, J = 3 Hz), 136.45 (d, J = 6 Hz), 134.76 (d, J = 10 Hz), 133.48 (d, J = 108 Hz), 132.12 (d, J = 99 Hz), 131.85 (d, J = 10 Hz), 131.57 (d, J = 3 Hz), 130.77 (d, J = 12 Hz), 130.39 (d, J = 8 Hz), 128.31 (d, J = 13 Hz), 61.61 (s, CH_2CH$_3$), 13.53 (s, CH$_2$$CH_3$). ^{31}P NMR (162 MHz, $CDCl_3$): δ_P 31.16. MS, *m/z* (%) = 350 (M^+, 2), 349 (4), 322 (30), 321 (88), 305 (21), 303 (25), 278 (11), 277 (35), 274 (20), 273 (100), 257 (16), 246 (17), 245 (87), 229 (25), 228 (13), 227 (31), 201 (15), 200 (16), 199 (35), 183 (12), 168 (11), 167 (22), 153 (17), 152 (51), 105 (12), 77 (56), 51(20). ESI-HRMS Anal. Calcd for $C_{21}H_{19}O_3PNa^+$ (M+ Na^+) 373.0964, found 373.0993.

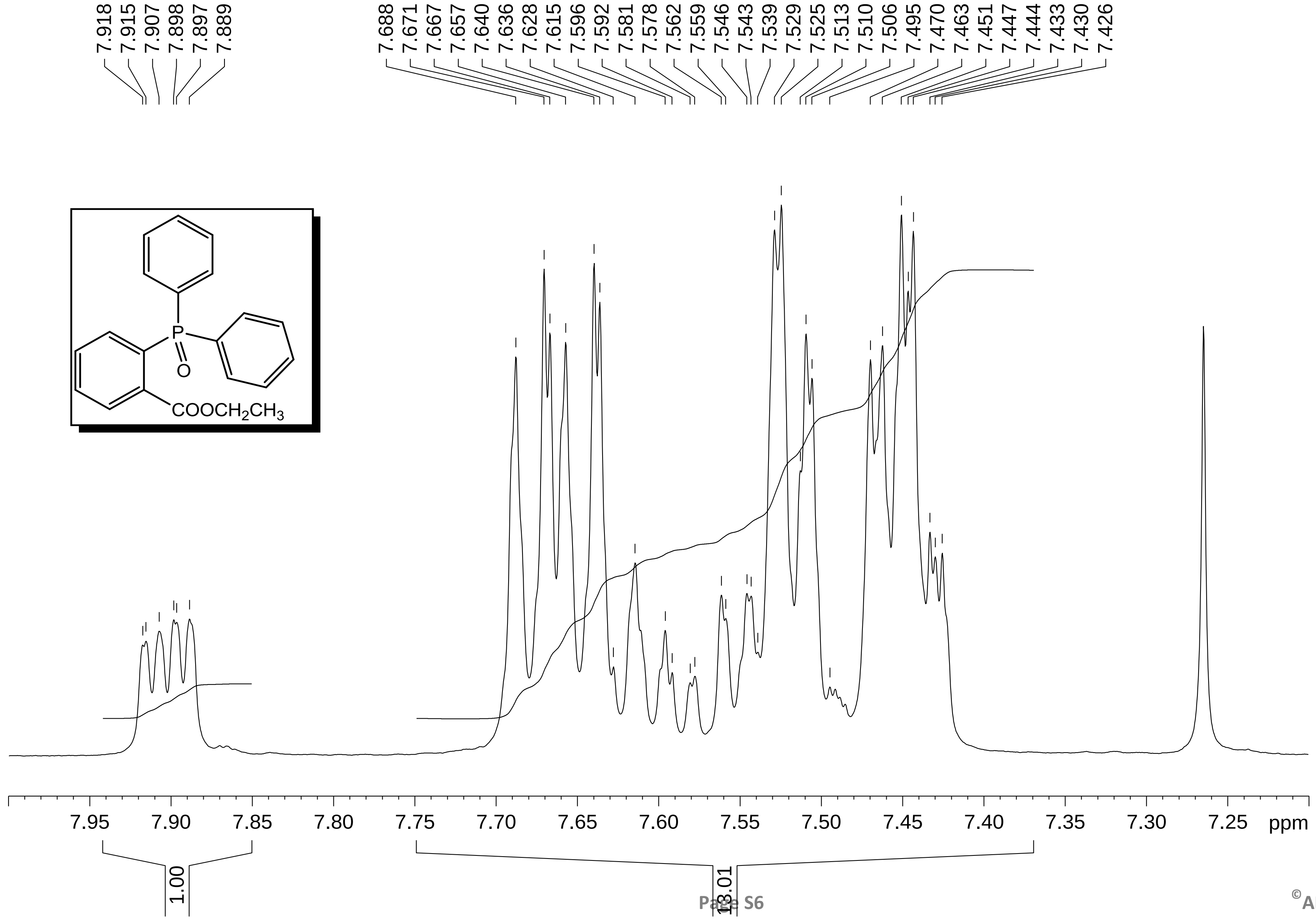
References

1. Kemme, S. T.; Schmidt, Y.; Grünanger, C. U.; Laungani, A. C.; Herber, C.; Breit, B. *Synthesis* **2010**, 1924.
2. Furniss, B. S.; Hannaford, A. J.; Smith P. W. G.; Tatchell, A. R. *Vogel´s Textbook of Practical Organic Chemistry*, 5th Edn., Addison-Wesley, 1989, pp 1076.
3. Crich, D.; Dyker, H. *Tetrahedron Lett.* **1989**, *30*, 475.

^{1}H-NMR ($CDCl_3$). Ethyl 2-(diphenylphosphoryl)benzoate (**4**)



^{1}H-NMR ($CDCl_3$). Ethyl 2-(diphenylphosphoryl)benzoate (**4**)



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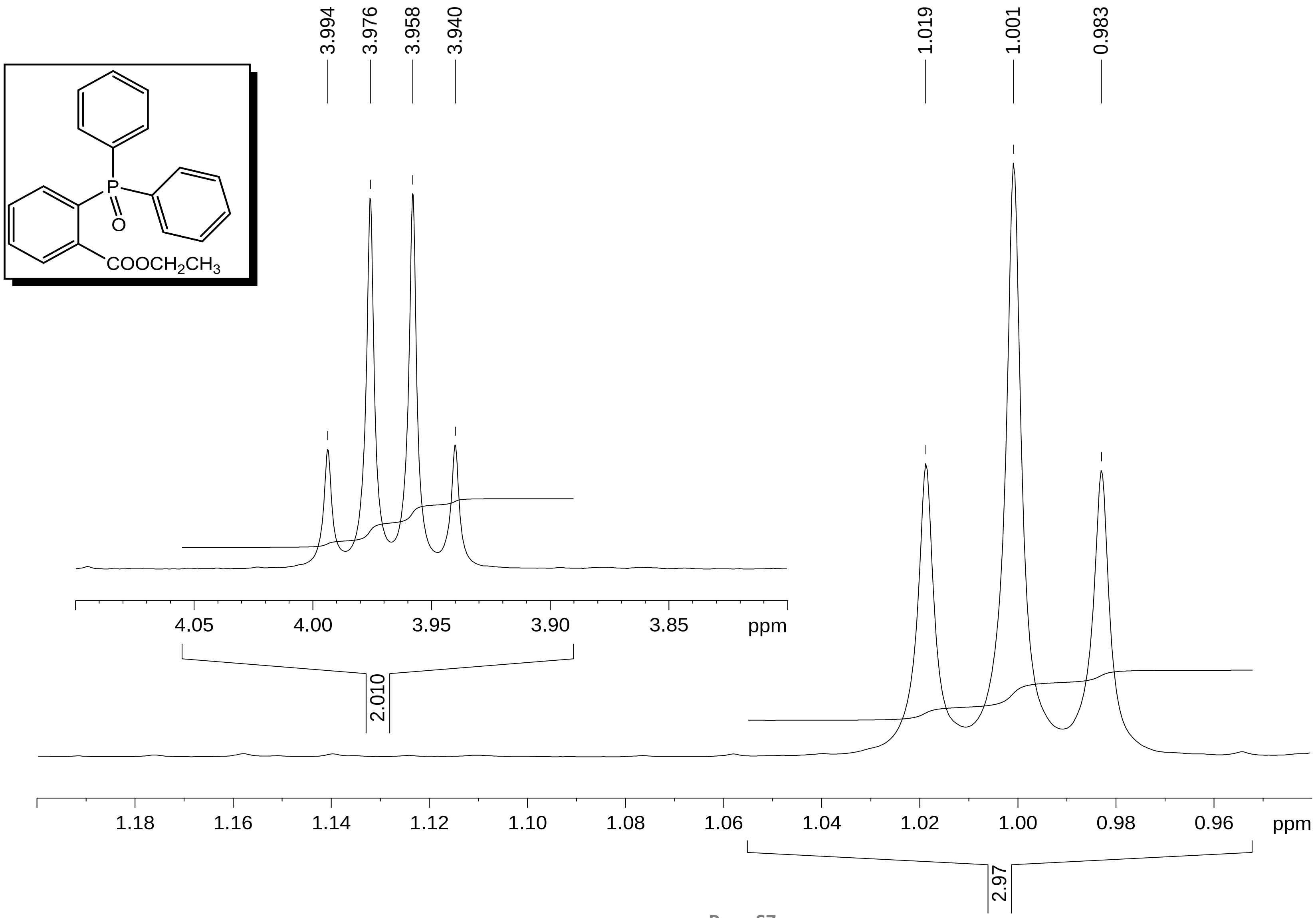

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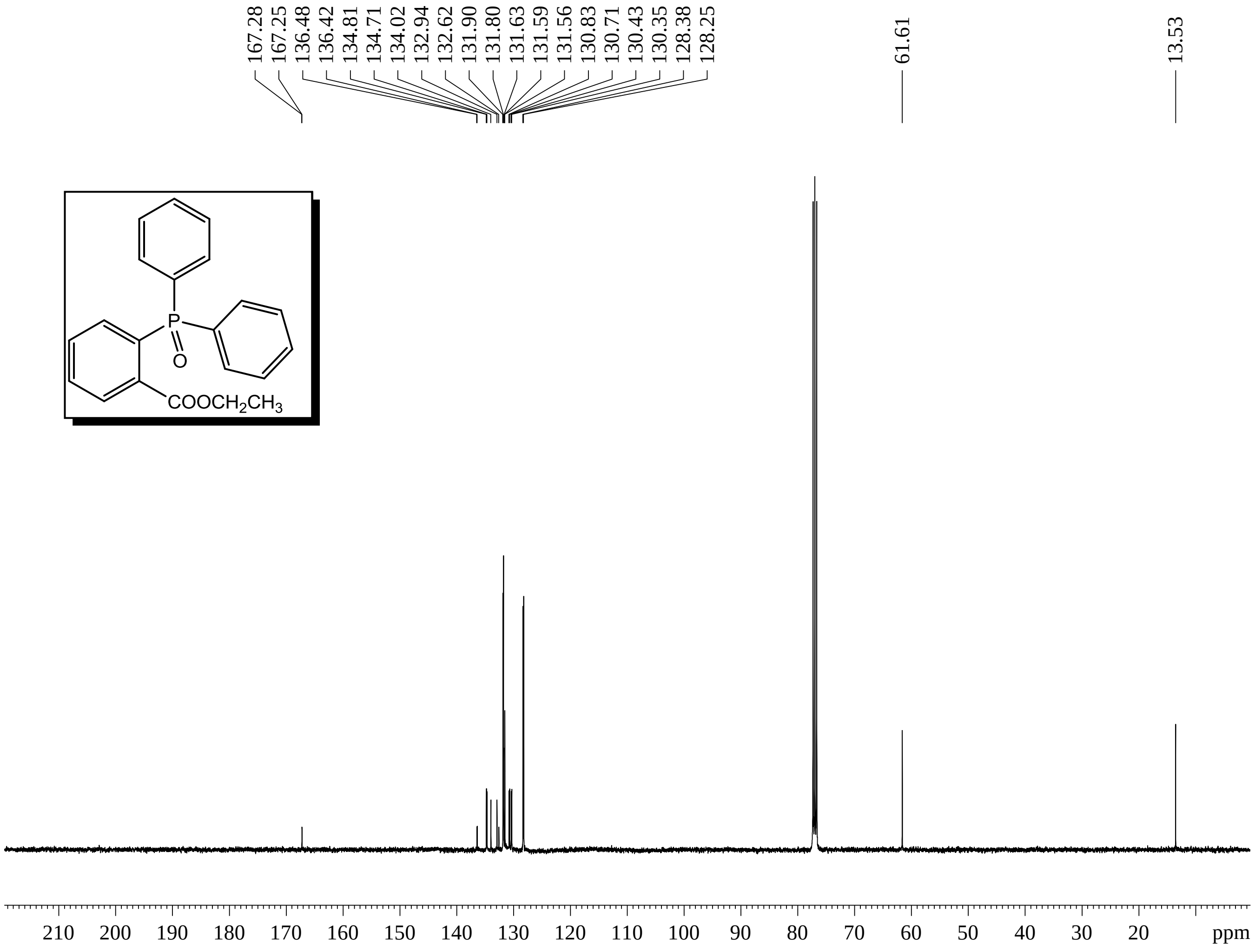
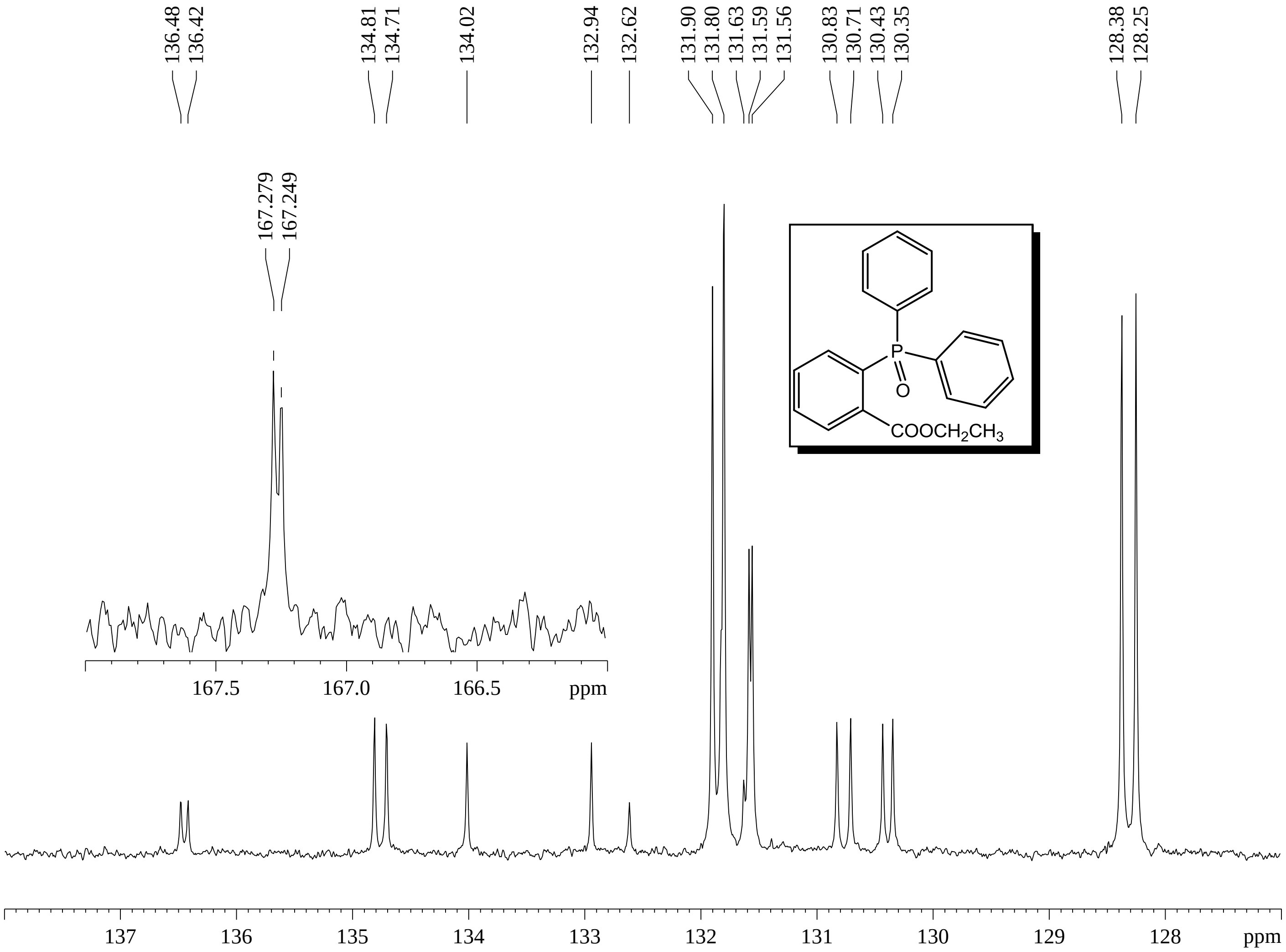
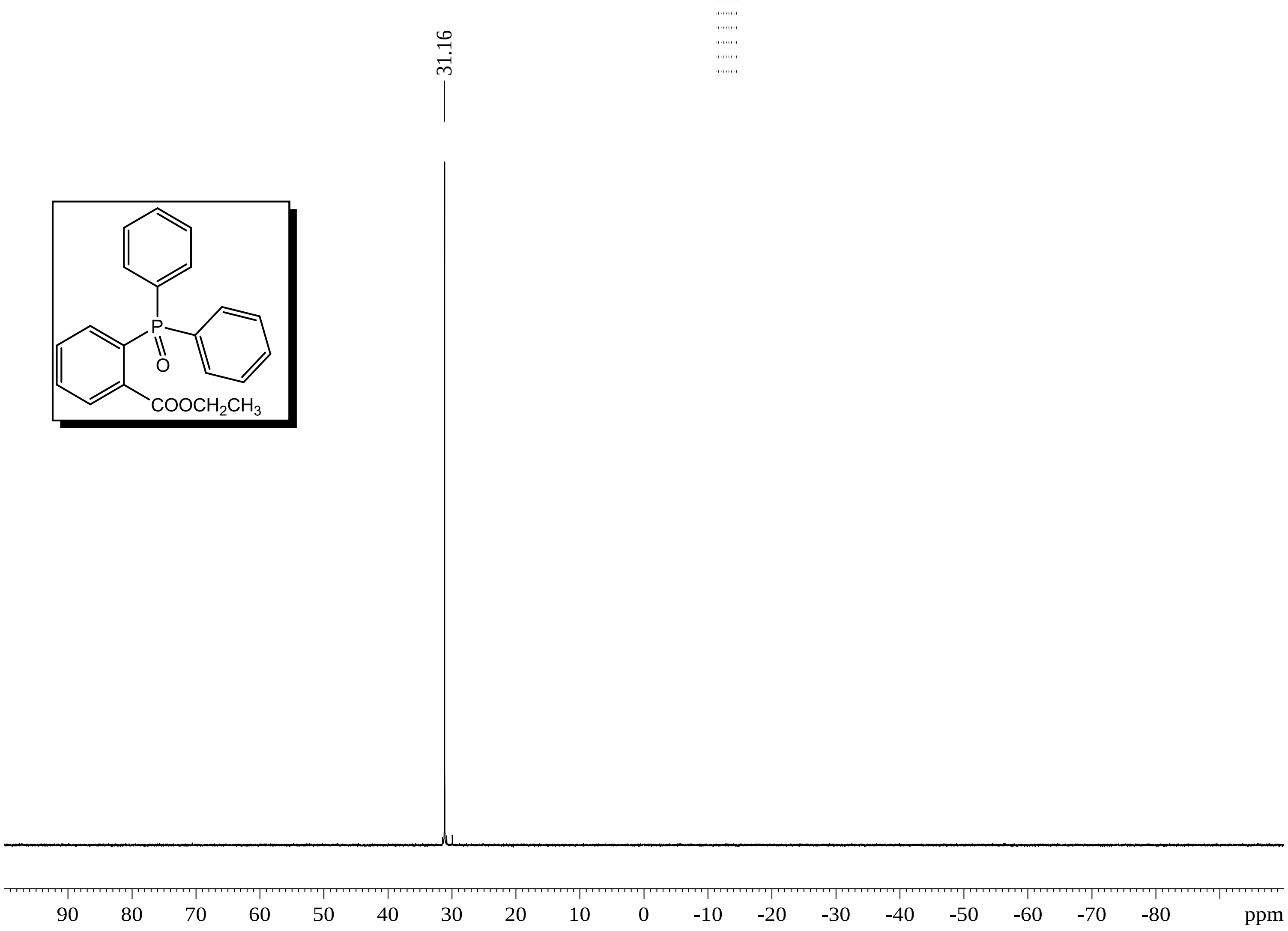


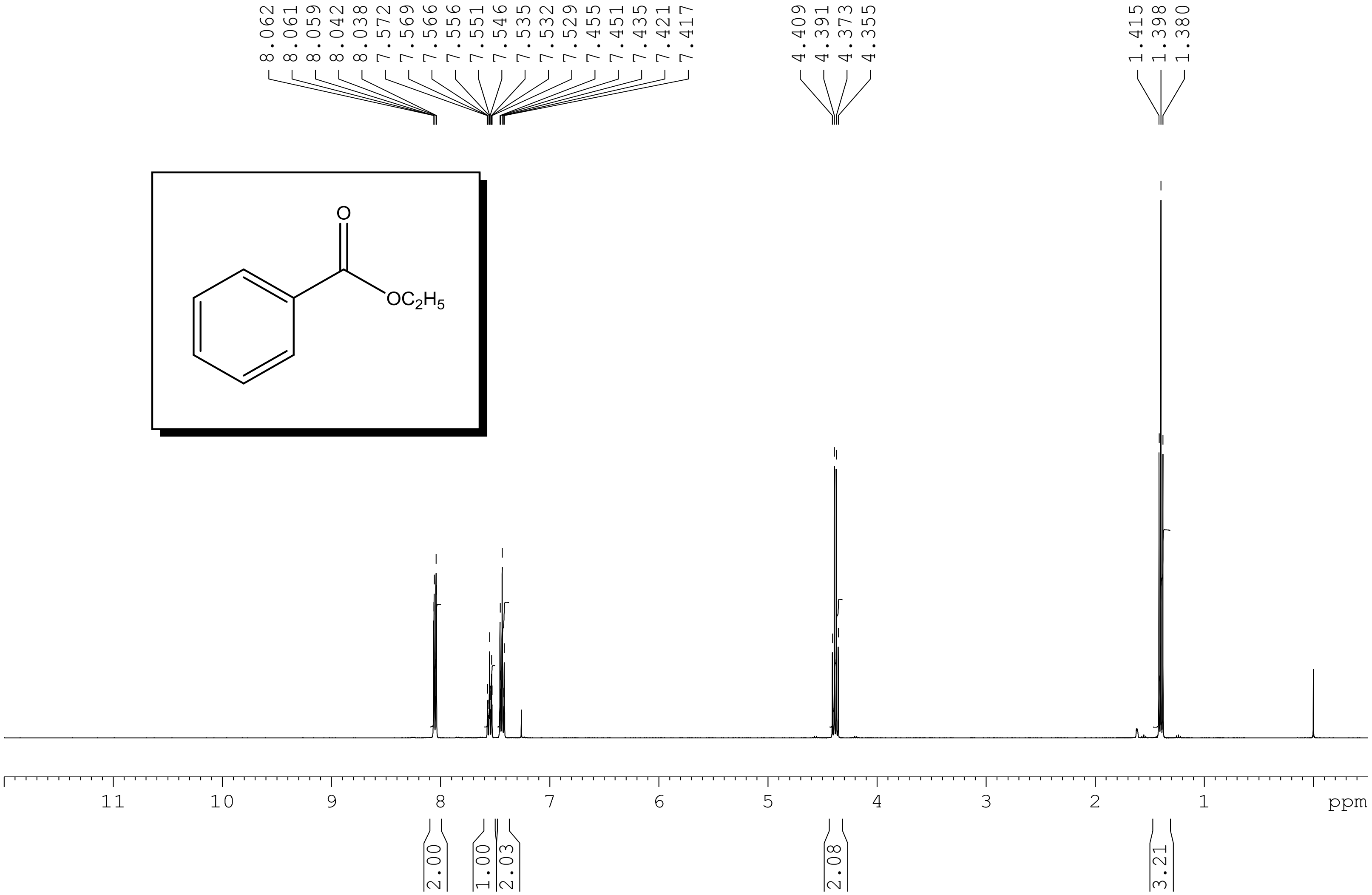
^{13}C-NMR ($CDCl_3$). Ethyl 2-(diphenylphosphoryl)benzoate (**4**)



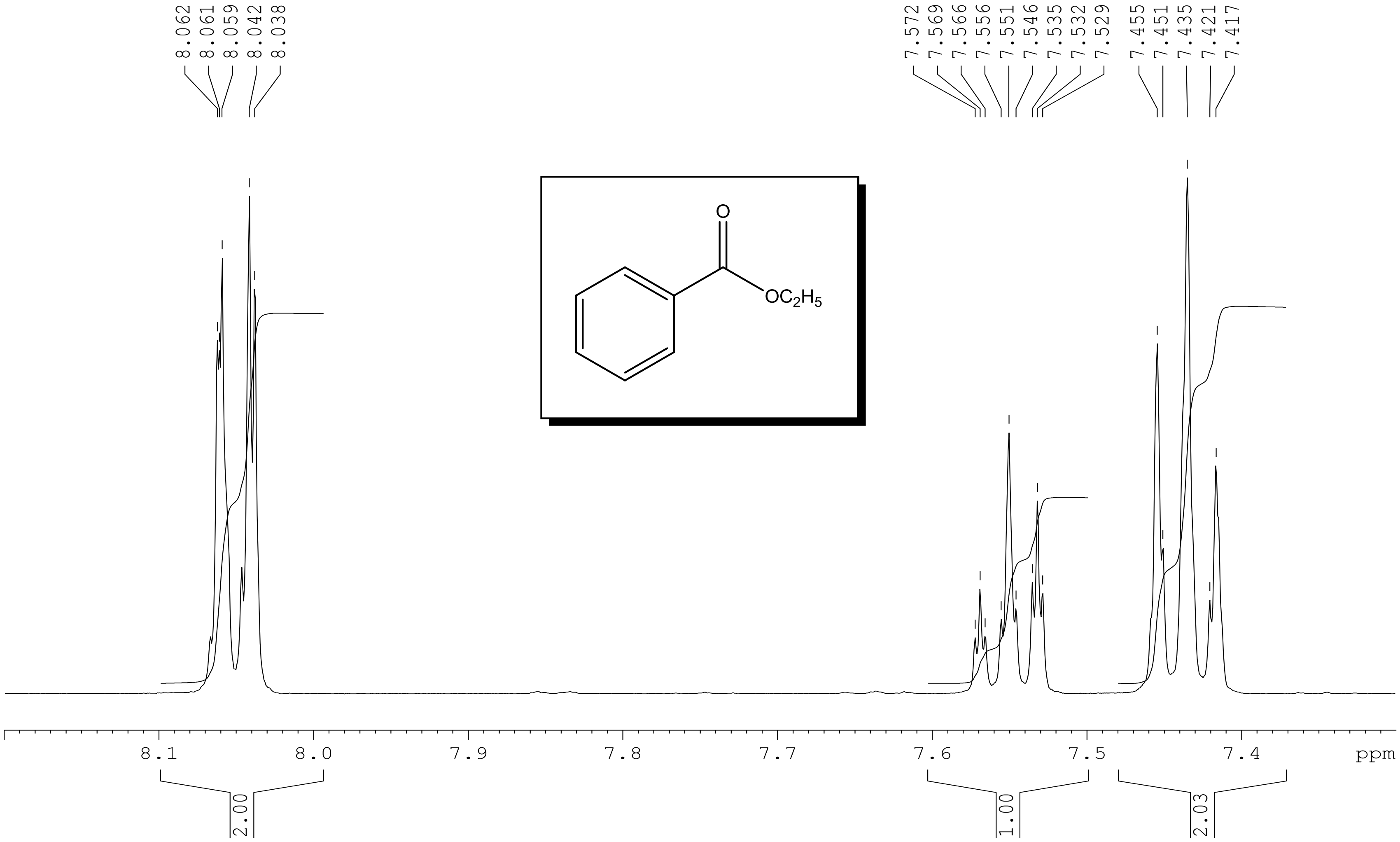
^{31}P-NMR ($CDCl_3$). Ethyl 2-(diphenylphosphoryl)benzoate (**4**)



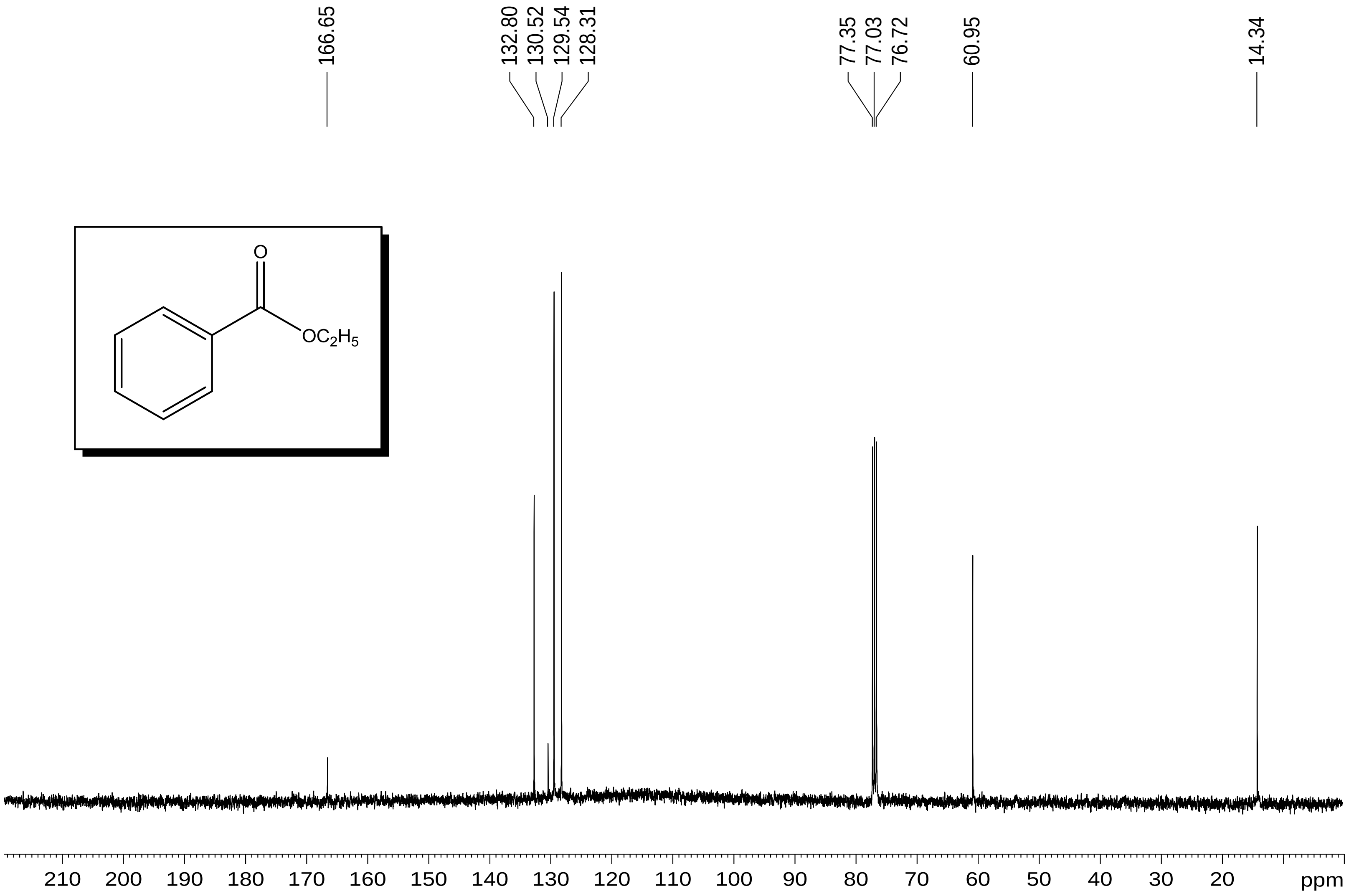
^{1}H-NMR ($CDCl_3$). Ethyl benzoate (**5**)



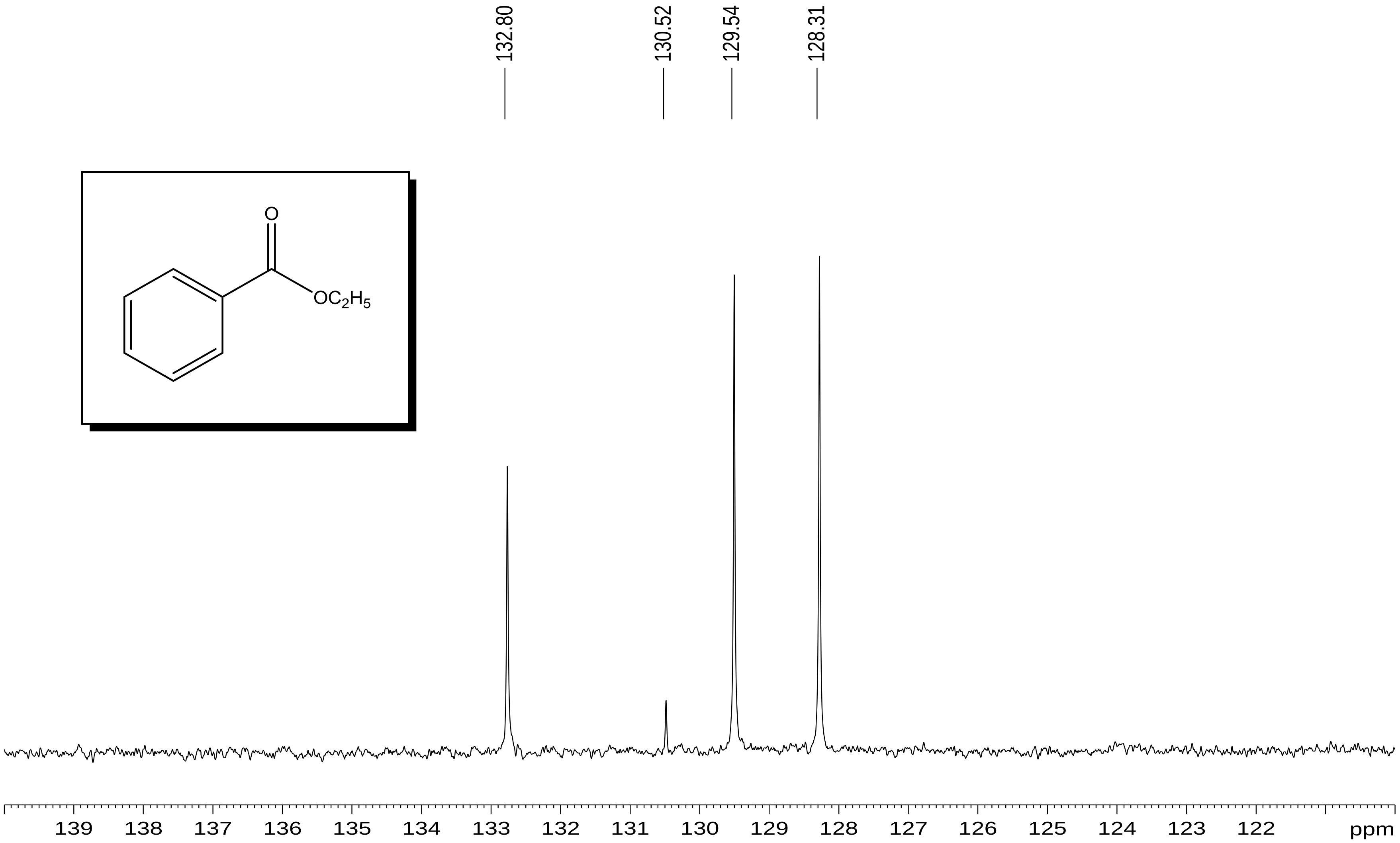
^{1}H-NMR ($CDCl_3$). Ethyl benzoate (**5**)



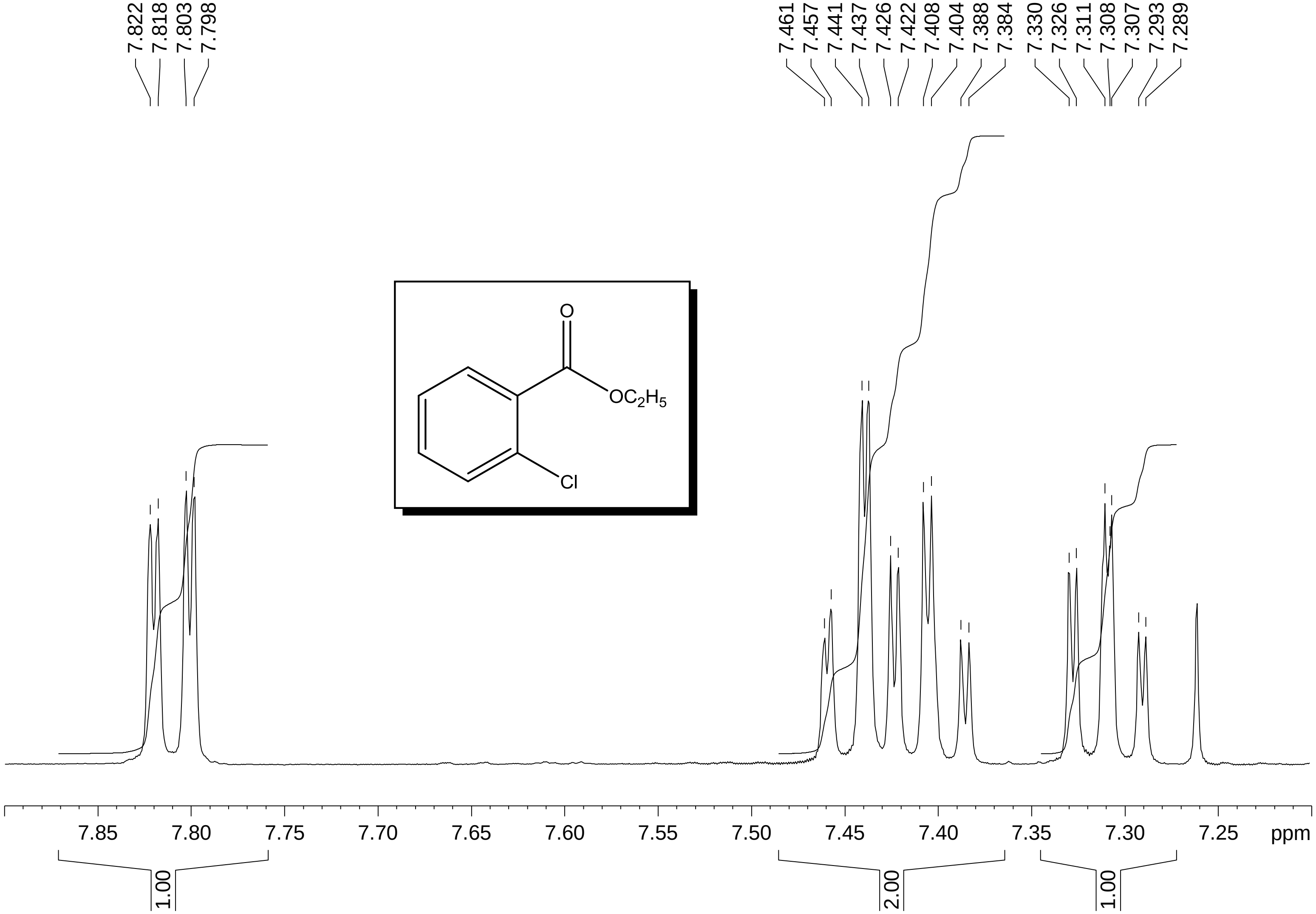
^{13}C-NMR (CDCl$_3$). Ethyl benzoate (**5**)



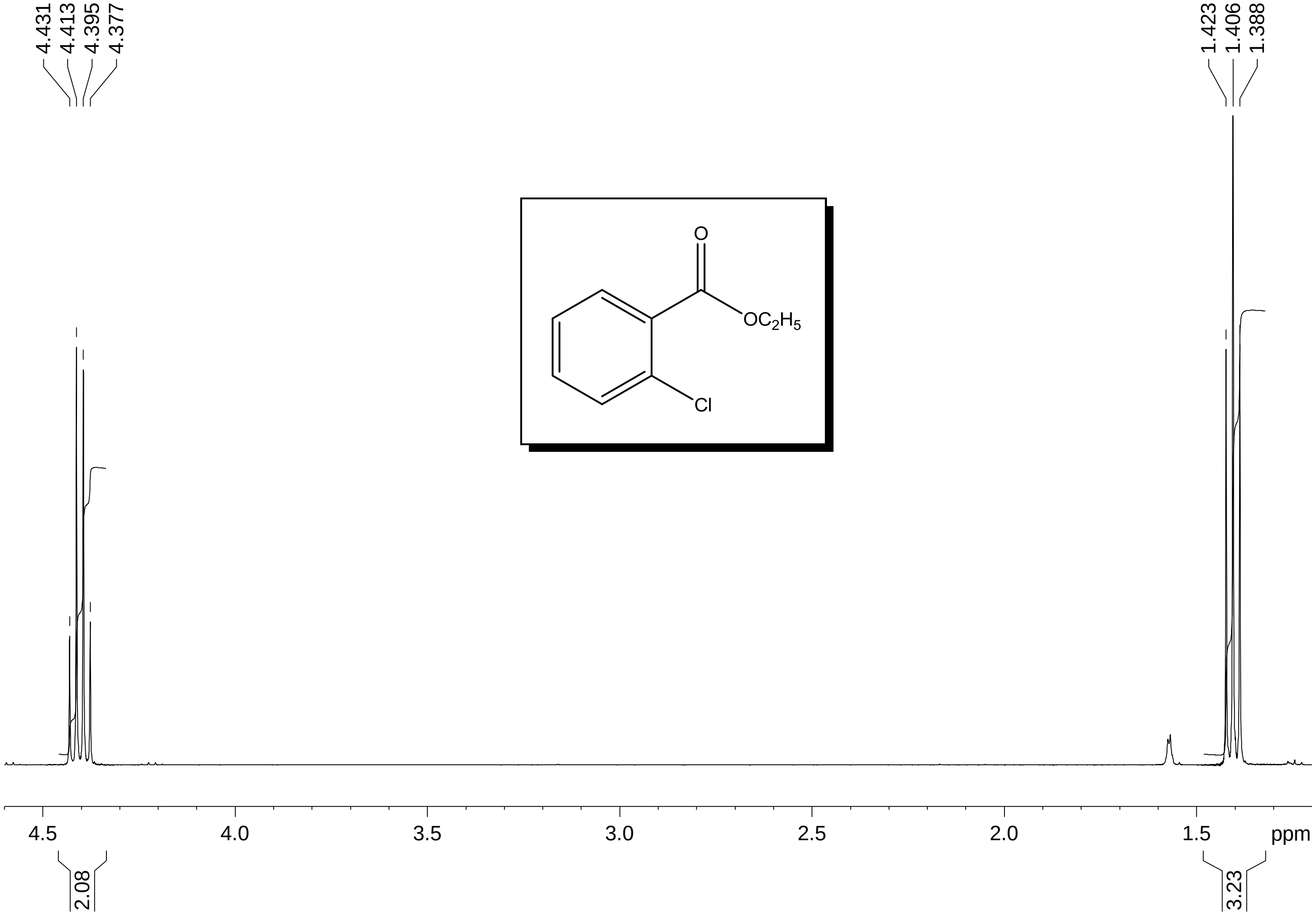
^{13}C-NMR ($CDCl_3$). Ethyl benzoate (**5**)



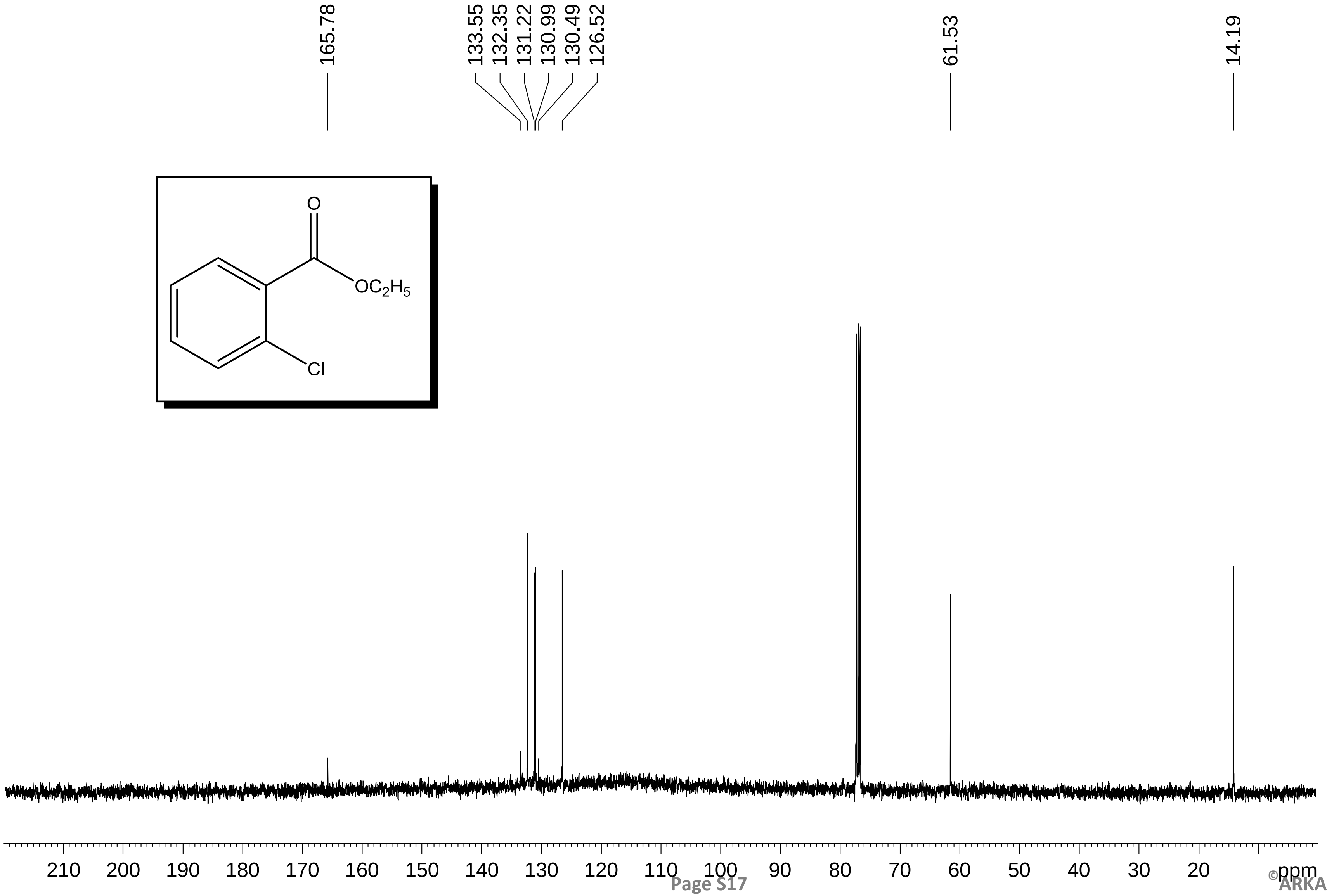
^{1}H-NMR ($CDCl_3$). Ethyl 2-chlorobenzoate (**6**)



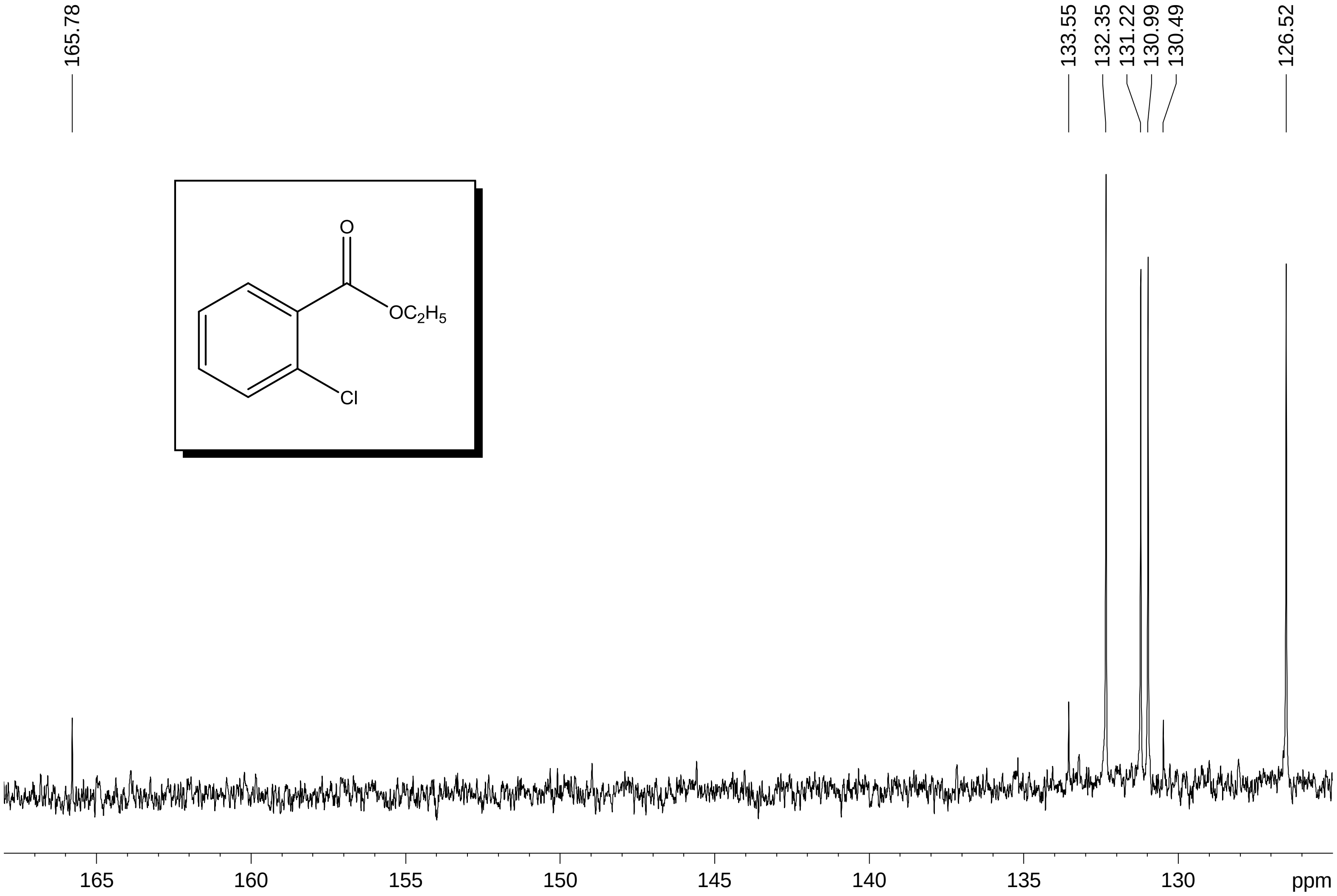
^{1}H-NMR ($CDCl_3$). Ethyl 2-chlorobenzoate (**6**)



^{13}C-NMR ($CDCl_3$). Ethyl 2-chlorobenzoate (**6**)



^{13}C-NMR ($CDCl_3$) Ethyl 2-chlorobenzoate (**6**)



Ethyl benzoate (**5**). MS: *m/z* (%) = 151 (2); 150 (19); 122 (28); 106 (9); 105 (100); 84 (7); 78 (6); 77 (49); 76 (6); 51 (28); 50 (9); 49 (7).
Ethyl 2-chlorobenzoate (**6**). MS: *m/z* (%) =185 (3); 184 (12); 158 (8); 156 (26); 141 (31); 140 (10); 139 (100); 113 (10); 111 (27); 76 (10); 75 (31); 74 (7); 51 (7); 50 (16); 49 (7).