Metal-Free Visible Light Photoredox Enables Generation of Carbyne Equivalents via Phosphonium Ylides C-H Activation

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General Information

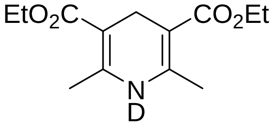
All the reactions were carried out in oven-dried glassware under inert atmosphere. All the anhydrous solvents and commercially available chemicals were purchased and used without further purification. Thin layer chromatography (TLC) were performed on Merck 60 F254 precoated silica gel (0.2 mm thickness) to monitor the reactions. TLC were visualized through irradiation with UV light at 254 nm and/or by staining with *p*-anisaldehyde or basic solution of potassium permanganate. Flash column chromatography was performed to purify the products with distilled technical grade solvents using silica gel 60 (40-60 μm). High resolution mass spectrometry was recorded on a Waters Q-Tof premier^{TM} machine. ^{1}H and ^{13}C-NMR spectra were recorded on Bruker 400MHz and 500MHz NMR spectrometers. For ^{1}H-NMR spectra, the chemical shifts are reported as δ in ppm (parts per million), calibrated to the peak of $CHCl_3$ residue (δ 7.26, singlet) and the coupling constants (*J*) are reported in Hz. Peak multiplicities are reported as follows: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublet); dt (doublet of triplet); m (multiplet). For ^{13}C-NMR spectra the chemical shifts are also reported as δ in ppm (parts per million), calibrated to the peak of $CHCl_3$ residue (δ 77.00, triplet). All the reactions were irradiated with blue light using 34W Blue LEDs 150 made by Kessil.

1. Catalytic phosphonium ylide addition to electron rich alkenes

To an oven dried 8 ml vial was charged with 9-mesityl-10-methylacridinium tetrafluoroborate (5 mol %), Hantzsch ester (1.2 equiv.) and ylide substrate (0.1 mmol). The mixture was dissolved in anhydrous DCM (0.025 M), followed by the addition of thiophenol (10 mol %) and alkene substrate (0.3 mmol). The reaction mixture was subsequently degassed by freeze-pump-thaw technique (three cycles). The reaction vial was then irradiated by using 34W Kessil Blue LEDs (10 cm distance to the light source) and the surroundings temperature was cooled by using USB powered cooling fan. After 12 hours, reaction mixture was concentrated and purified by flash column chromatography (ethyl acetate : hexane).

2. Synthesis of deuterated Hantzsch esters

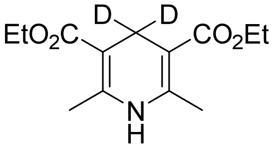
(a) 1-deuterated diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate



Compound **a** was synthesized according to the reported literature procedure.[1] In an oven dried round bottom flask, diethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (0.25 g, 0.98 mmol) and CD_3OD (3 ml) were mixed and stirred overnight under argon atmosphere. The solvent was evaporated and the desired compound was obtained as a pale green solid (0.24 g, 96%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.16 (q, *J* = 7.2 Hz, 4H), 3.26 (s, 2H), 2.19 (s, 6H), 1.28 (t, *J* = 6.8 Hz, 6H).

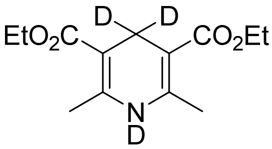
(b) 4,4-dideuterio-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine



Compound **b** was synthesized according to the reported literature procedure.[2] An oven dried round bottom flask was charged with ethyl acetoacetate (1.6 ml, 12.48 mmol, 4 equiv.), d_2-paraformaldehyde (0.1 g, 3.12 mmol, 1 equiv.), ammonium acetate (0.48 g, 6.24 mmol, 2 equiv.) and water (6.5 ml), then the mixture was heated at 86 °C. After 3 hours, the reaction mixture was allowed to cool down to room temperature and filtered. The precipitate was dried in vacuo to afford the desired compound as yellow solid (0.4 g, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.13 (s, 1H), 4.16 (q, *J* = 7.2 Hz, 4H), 2.19 (s, 6H), 1.28 (t, *J* = 6.8Hz, 6H).

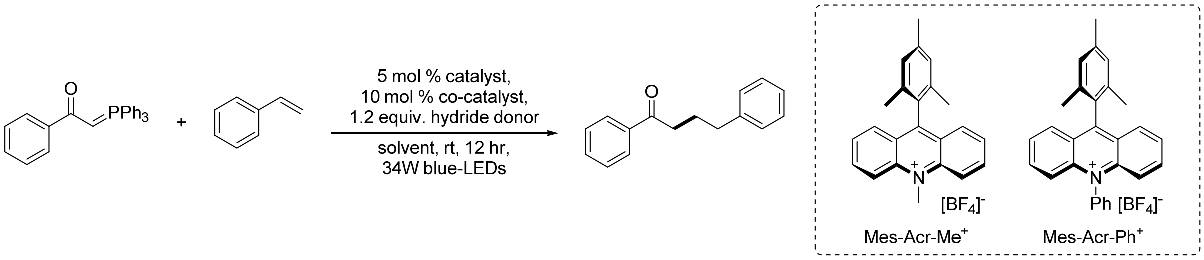
(c) 1,4,4-trideuterio-2,6-dimethyl-3,5-dicarbethoxy-1,4-dihydropyridine



Compound **c** was synthesized by following the reported literature procedure.[1] In an oven dried round bottom flask compound **b** (0.1g, 0.39 mmol) and CD_3OD (1 ml) were mixed and stirred for overnight under argon atmosphere. The solvent was evaporated and the desired compound was obtained as a pale green solid (0.096 g, 97%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 4.16 (q, *J* = 7.5 Hz, 4H), 2.19 (s, 6H), 1.28 (t, *J* = 7.0 Hz, 6H).

3. Solvent evaluation



Entry	Photocatalyst	Co-catalyst	Hydride Donor	Solvent (conc.)	NMR Yields
1	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	DCM (0.1 M)	57%
2	Mes-Acr-Ph$^+$	PhSH	Hantzsch ester	DCM (0.1 M)	49%
3	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	DCE (0.1 M)	10%
4	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	$CHCl_3$ (0.1 M)	54%
5	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	MeCN (0.1 M)	-
6	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	THF (0.1 M)	-
7	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	Dioxane (0.1 M)	-
8	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	DMSO (0.1 M)	-
9	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	MeOH (0.1 M)	41%
10	Mes-Acr-Me$^+$	PhSH	Hantzsch ester	DME (0.1 M)	-
11	Mes-Acr-Me$^+$	PhSH	Hantsch ester	$PhCF_3$ (0.1 M)	-

4. TEMPO Trapping Experiment

To an oven dried 8 ml vial was charged with 9-mesityl-10-methylacridinium tetrafluoroborate (1 equiv.), Hantzsch ester (1.2 equiv.), chloro substituted ylide substrate **1b** (0.05 mmol) and TEMPO (1.2 equiv.). The mixture was dissolved in anhydrous DCM (0.025 M), followed by the addition of thiophenol (5 mol%) and alkene substrate (0.3 mmol). The reaction mixture was subsequently degassed by freeze-pump-thaw technique (three cycles). The reaction vial was then irradiated by using 34W Kessil Blue LEDs (10 cm distance to the light source) and the surroundings temperature was cooled by using USB powered cooling fan. After 8 hrs the blue LEDs was turned off and the reaction mixture was taken for mass spectrometry analysis (using MeOH solvent, ESI method).

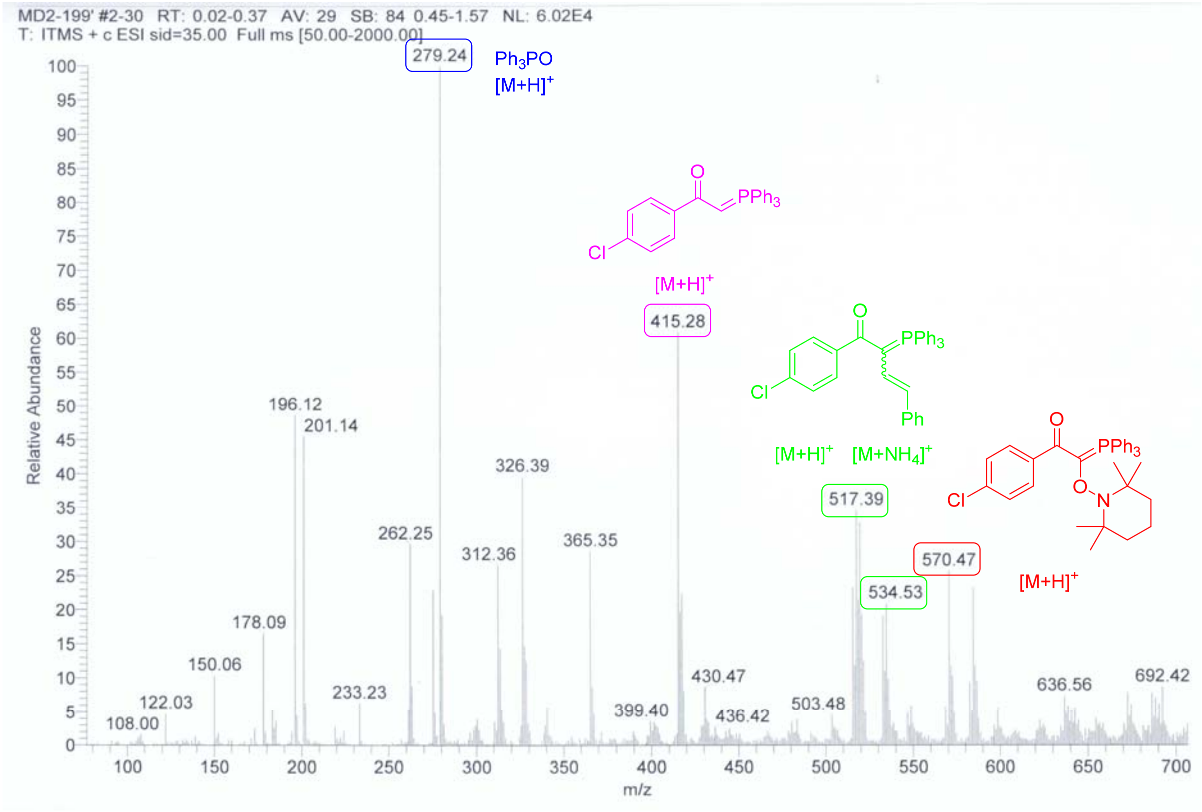


Figure 1. Analysis of mass spectrum of the reaction mixture with TEMPO scavenger

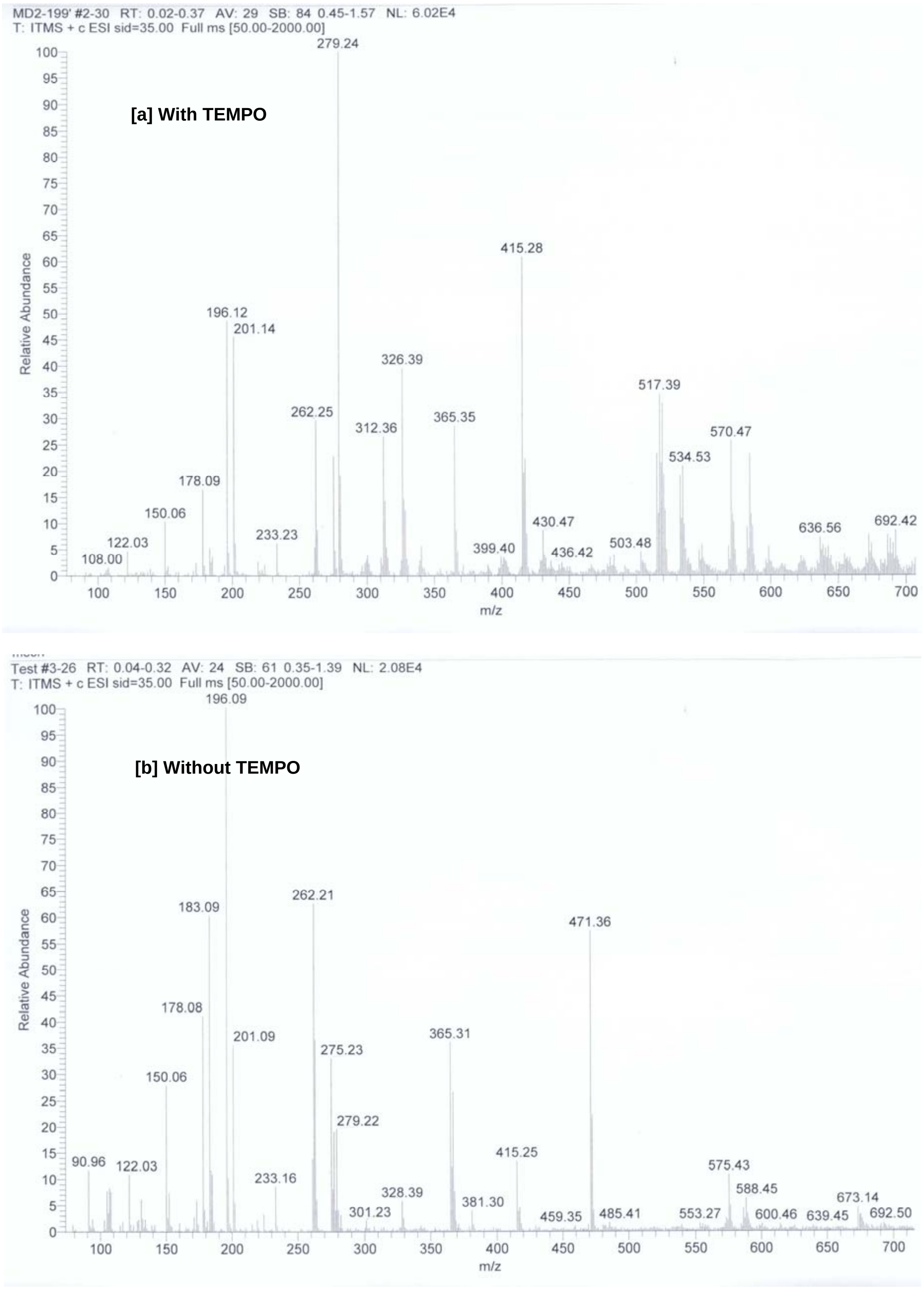
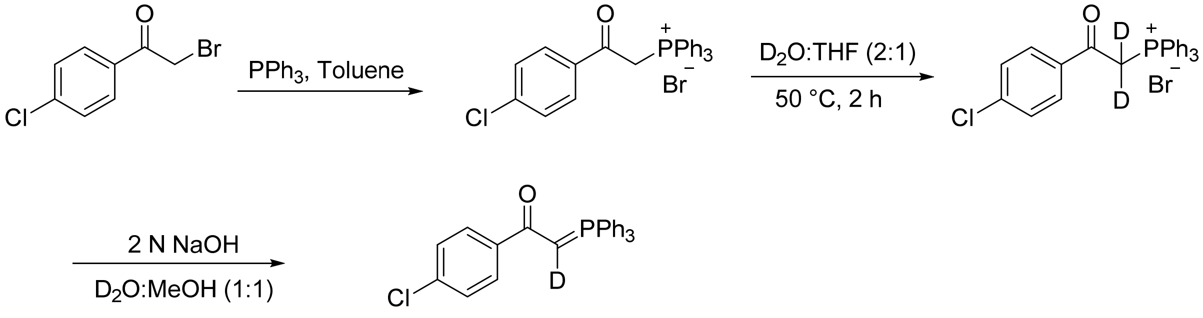


Figure 2. Comparison of mass spectra of the reaction mixture with and without TEMPO scavenger

5. Synthesis of Deuterium Labelled Ylide (1b)



1b

Compound **1b** was synthesized according to the reported literature.[3] In an oven dried round bottom flask 2-bromo-4'-chloroacetophenone (0.5 g, 2.14 mmol) was dissolved in toluene (15 ml), then triphenylphosphine (0.56 g, 2.14 mmol) was added to it and stirred for overnight under argon atmosphere. The white phosphonium salt was filtered and washed with diethyl ether and dried under vacuum. Dried phosphonium salt was dissolved in D_2O : THF (2:1) and heated at 50 °C for 2 hours. Then the solution was cooled to room temperature and the solvent was evaporated in vacuum. Then the deuterated phosphonium salt was dissolved in D_2O : MeOH (1:1) and 2 N NaOH solution was added dropwise and stirred for 10 minutes. The reaction mixture was extracted with DCM and the organic layer was extracted with saturated NaCl solution. Then the organic layer was dried with anhydrous sodium sulfate and evaporated to dryness. The desired compound 1b was obtained as white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89 (d, J = 8.05 Hz, 2H), 7.72-7.68 (m, 6H), 7.58-7.55 (m, 3H), 7.49-7.46 (m, 6H), 7.30 (d, J = 8.1 Hz, 2H).

6. Fluorescence Quenching Studies

Fluorescence quenching studies were performed on RF-5301PC Spectro-fluorophotometer. The experiments were carried out by mixing a 5×10^{-4} M solution of 9-mesityl-10-phenylacridinium (Mes-Acr^{+}-Me) tetrafluoroborate in degased dichloromethane with varoius amount of quencher in quartz cuvette. All the solutions were irradiated at $\lambda = 455$ nm and the emission intensity at $\lambda = 504$ nm was observed.

a. Stern-Volmer Quenching Studies with Alkene

Increasing amounts of alkene were added to a solution of 9-mesityl-10-phenylacridinium (Mes-Acr^{+}-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

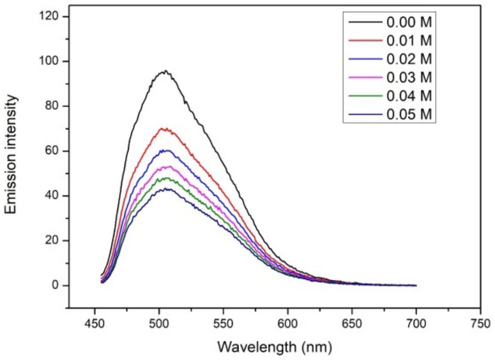


Figure 3. Emission spectrum of Mes-Acr^{+}-Me while changing the concentration of styrene.

b. Stern-Volmer Quenching Studies with Ylide

Increasing amounts of alkene were added to a solution of 9-mesityl10-phenylacridinium (Mes-Acr^{+}-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

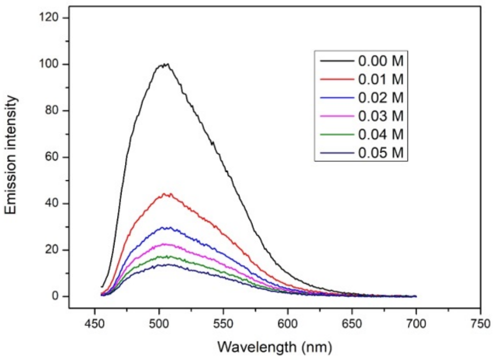


Figure 4. Emission spectrum of Mes-Acr$^+$-Me while changing the concentration of ylide **1b**.

c. Stern-Volmer Quenching Studies with Hantzsch Ester

Increasing amounts of alkene were added to a solution of 9-mesityl10-phenylacridinium (Mes-Acr$^+$-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

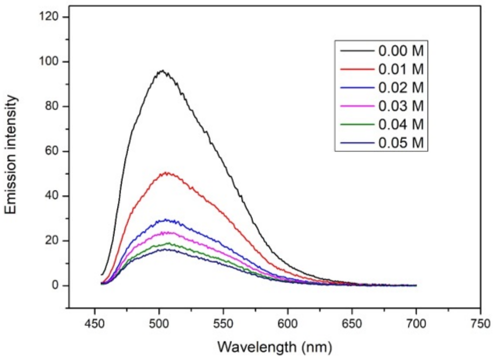


Figure 5. Emission spectrum of Mes-Acr$^+$-Me while changing the concentration of Hantzsch ester.

d. Stern-Volmer Quenching Studies with Thiol

Increasing amounts of alkene were added to a solution of 9-mesityl10-phenylacridinium (Mes-Acr$^+$-Me) tetrafluoroborate in dichloromethane. After each addition, the absorption and emission spectrum of the solution were recorded.

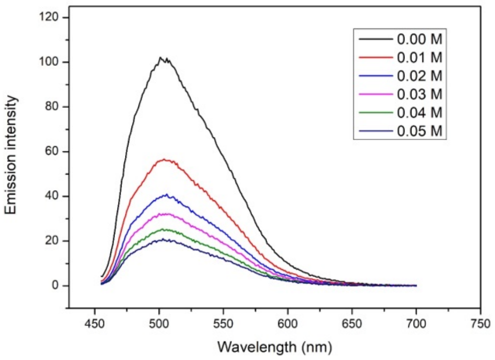


Figure 6. Emission spectrum of Mes-Acr$^+$-Me while changing the concentration of thiophenol.

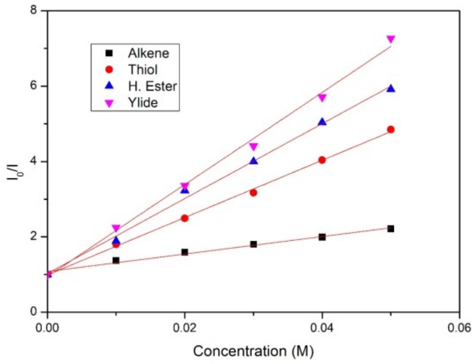
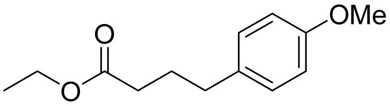


Figure 7. Overall Stern-Volmer plot.

7. Characterization of compounds

Compound 4.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), ethyl 2-(triphenyl-λ5-phosphaneylidene)acetate (34.8 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography gave compound 4 as a colourless oil (18.7 mg, 84%).

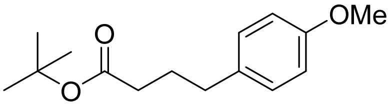
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 3H), 2.59 (t, *J* = 7.4 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.91 (quint, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.7, 158.0, 133.6, 129.5, 113.9, 60.3, 55.3, 34.3, 33.7, 26.9, 14.3.

HRMS: m/z for $C_{13}H_{18}O_3$ $[M+H]^+$ calculated 223.1334, found 223.1335.

Spectra matches with reported literature.[4]

Compound 5.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), *tert*-butyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (37.6 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for

12 hrs. Purification by flash column chromatography furnished compound **5** as a colourless oil (15.5 mg, 62%).

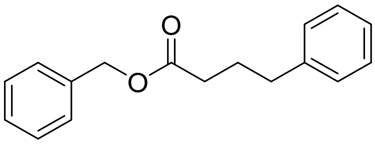
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.57 (t, *J* = 7.5 Hz, 2H), 2.21 (t, *J* = 7.4 Hz, 2H), 1.86 (quint, *J* = 7.6 Hz, 2H), 1.44 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 173.1, 158.0, 133.9, 129.5, 113.9, 80.2, 55.4, 35.0, 34.3, 28.2, 27.1.

HRMS: m/z for $C_{15}H_{22}O_3$ $[M+H]^+$ calculated 251.1647, found 251.1641.

Spectra matches with reported literature.[5]

Compound 6.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), benzyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (41.0 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **6** as a colourless oil (18.1 mg, 71%).

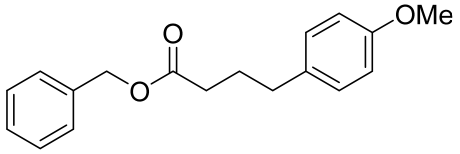
^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 5H), 7.28-7.25 (m, 2H), 7.20-7.14 (m, 3H), 5.11 (s, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 1.97 (quint, *J* = 7.7 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.4, 141.4, 136.2, 128.7, 128.6, 128.5, 128.3, 126.1, 66.3, 35.2, 33.7, 26.6.

HRMS: m/z for $C_{17}H_{18}O_2$ $[M+H]^+$ calculated 255.1385, found 255.1384.

Spectra matches with reported literature.[6]

Compound 7.



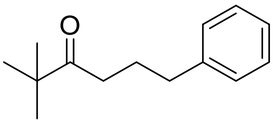
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), benzyl 2-(triphenyl-λ^5-phosphaneylidene)acetate (41.0 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **7** as a colourless oil (22.2 mg, 78%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.38-7.30 (m, 5H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.11 (s, 2H), 3.78 (s, 3H), 2.58 (t, *J* = 7.4 Hz, 2H), 2.36 (t, *J* = 7.4 Hz, 2H), 1.94 (quint, *J* = 7.6 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 173.5, 158.0, 136.2, 133.5, 129.5, 128.7, 128.3, 113.9, 66.3, 55.4, 34.3, 33.7, 26.8.

HRMS: m/z for $C_{18}H_{20}O_3$ $[M+H]^+$ calculated 285.1491, found 285.1494.

Compound 8.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 3,3-dimethyl-1-(triphenyl-λ^5-phosphaneylidene)butan-2-one (36.0 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **8** as a colourless oil (9.8 mg, 48%).

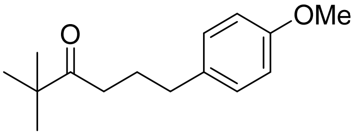
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.89 (quint, *J* = 7.3 Hz, 2H), 1.11 (s, 9H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 215.9, 142.0, 128.6, 128.4, 126.0, 44.2, 35.7, 35.3, 26.5, 25.5.

HRMS: m/z for $C_{14}H_{20}O$ $[M+H]^+$ calculated 205.1592, found 203.1590.

Spectra matches with reported literature.[7]

Compound 9.



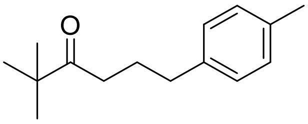
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 3,3-dimethyl-1-(triphenyl-λ^5-phosphaneylidene)butan-2-one (36.0 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **9** as a colourless oil (13.8 mg, 59%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.54 (t, *J* = 7.4 Hz, 2H), 2.48 (t, *J* = 7.1 Hz, 2H), 1.85 (quint, *J* = 7.3 Hz, 2H), 1.11 (s, 9H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 215.9, 157.9, 134.1, 129.4, 113.9, 55.4, 44.2, 35.7, 34.4, 26.5, 25.7.

HRMS: m/z for $C_{15}H_{22}O_2$ $[M+H]^+$ calculated 235.1698, found 235.1699.

Compound 10.



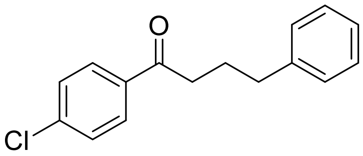
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 3,3-dimethyl-1-(triphenyl-λ^5-phosphaneylidene)butan-2-one (36.0 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **10** as a colourless oil (10.7 mg, 49%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.09-7.05 (m, 4H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.87 (quint, *J* = 7.3 Hz, 2H), 1.11 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 215.9, 138.9, 135.4, 129.1, 128.4, 44.2, 35.8, 34.9, 26.5, 25.6, 21.1.

HRMS: m/z for $C_{15}H_{22}O$ $[M+H]^+$ calculated 219.1749, found 219.1751.

Compound 11.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **11** as a white solid (18.6 mg, 72%).

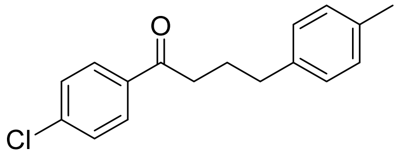
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.21-7.19 (m, 3H), 2.94 (t, *J* = 7.2 Hz, 3H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.08 (quint, *J* = 7.3 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.9, 141.6, 169.5, 135.4, 129.5, 129.0, 128.6, 128.5, 126.1, 37.7, 35.2, 25.7.

HRMS: m/z for $C_{16}H_{15}ClO$ $[M+H]^+$ calculated 259.0890, found 259.0891.

Spectra matches with reported literature.[8]

Compound 12.



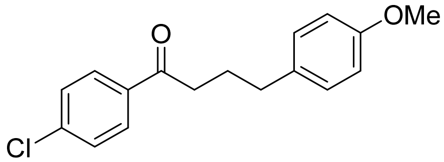
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **12** as a white solid (20.7 mg, 76%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 4H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.05 (quint, *J* = 7.5 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 199.0, 139.4, 138.5, 135.6, 135.4, 129.5, 129.2, 128.9, 128.5, 37.7, 34.7, 25.8, 21.1.

HRMS: m/z for $C_{17}H_{17}ClO$ $[M+H]^+$ calculated 273.1046, found 273.1043.

Compound 13.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by

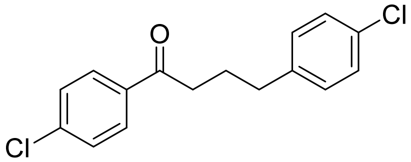
Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **13** as a white solid (24.8 mg, 86%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.03 (quint, *J* = 7.4 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 199.0, 158.0, 139.4, 135.4, 133.6, 129.6, 129.5, 128.9, 113.9, 55.3, 37.7, 34.3, 25.9.

HRMS: m/z for $C_{17}H_{17}ClO_2$ $[M+H]^+$ calculated 289.0995, found 289.0998.

Compound 14.



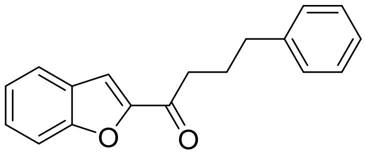
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 4-chlorostyrene (36.0 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **14** as a colourless oil (16.4 mg, 56%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 2.04 (quint, *J* = 7.4 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.7, 140.1, 139.6, 135.3, 129.9, 129.5, 129.0, 128.6, 37.5, 34.5, 25.5.

HRMS: m/z for $C_{16}H_{14}Cl_2O$ $[M+H]^+$ calculated 293.0500, found 293.0502.

Compound 15.



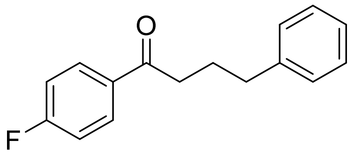
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(benzofuran-2-yl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (42.1 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **15** as a yellow solid (9.3 mg, 35%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.69 (d, *J* = 7.8 MHz, 1H), 7.57 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.48-7.44 (m, 2H), 7.32-7.28 (m, 3H), 7.22-7.19 (m, 3H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.12 (quint, *J* = 7.6 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 191.3, 155.7, 152.7, 141.6, 128.6, 128.5, 128.3, 127.1, 126.1, 124.0, 123.3, 112.7, 112.6, 38.2. 35.2, 25.7.

HRMS: m/z for $C_{18}H_{16}O_2$ $[M+H]^+$ calculated 265.1229, found 265.1231.

Compound 16.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-fluorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (39.8 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **16** as a white solid (14.8 mg, 61%).

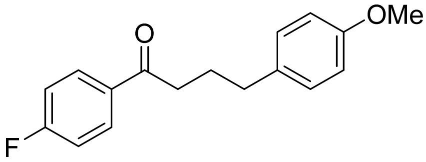
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.94 (t, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 3H), 7.11 (t, *J* = 8.4 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.08 (quint, *J* = 7.4 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.6, 165.8 (d, $J_{C,F}$ = 253.0 Hz), 141.7, 133.5, 130.7 (d, $J_{C,F}$ = 9.0 Hz), 128.6 (t, $J_{C,F}$ = 8.0 Hz), 126.1, 115.7 (d, $J_{C,F}$ = 22.0 Hz), 37.7, 35.2, 25.7.

HRMS: m/z for $C_{16}H_{15}FO$ $[M+H]^+$ calculated 243.1185, found 243.1186.

Spectra matches with reported literature.[8]

Compound 17.



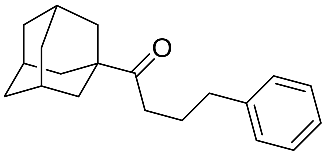
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-fluorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (39.8 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **16** as a white solid (17.7 mg, 65%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.11 (t, *J* = 7.4 Hz, 4H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.04 (quint, *J* = 6.9 Hz, 2H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 198.7, 165.8 (d, $J_{C,F}$ = 253.0 Hz), 158.0, 133.6 (d, $J_{C,F}$ = 15.0 Hz), 130.7 (d, $J_{C,F}$ = 9.0 Hz), 129.5, 115.7 (d, $J_{C,F}$ = 21.0 Hz), 113.9, 55.4, 37.6, 34.3, 26.0.

HRMS: m/z for $C_{17}H_{17}FO_2$ $[M+H]^+$ calculated 273.1291, found 243.1288.

Compound 18.



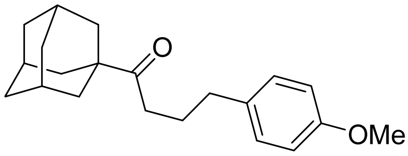
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(adamantan-1-yl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (43.9 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **18** as a colourless oil (17.5 mg, 62%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 2.59 (t, *J* = 7.2 Hz, 2H), 2.45 (t, 7.2 Hz, 2H), 2.03 (br, 3H), 1.87 (quint, *J* = 7.3 Hz, 2H), 1.78-1.66 (m, 12 H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 215.6, 142.0, 128.6, 128.4, 125.9, 46.4, 38.3, 36.7, 35.4, 35.3, 28.1, 25.2.

HRMS: m/z for $C_{20}H_{26}O$ $[M+H]^+$ calculated 283.2062, found 283.2063.

Compound 19.



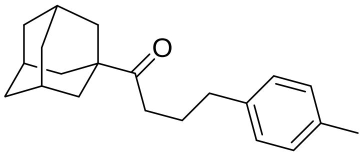
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(adamantan-1-yl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (43.9 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **19** as a colourless oil (18.8 mg, 60%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.08 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.6 Hz, 2H), 3.78 (s, 3H), 2.53 (t, *J* = 7.4 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.02 (br, 3H), 1.87-1.65 (m, 14H).

^{13}C-NMR (100 MHz, CDCl$_3$): δ 215.6, 157.9, 134.1, 129.4, 113.8, 55.4, 46.4, 38.4, 36.7, 35.2, 34.4, 28.1, 25.5.

HRMS: m/z for $C_{21}H_{28}O_2$ $[M+H]^+$ calculated 313.2168, found 313.2170.

Compound 20.



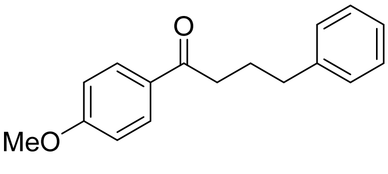
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(adamantan-1-yl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (43.9 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **20** as a colourless oil (15.7 mg, 53%).

^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.09-7.05 (m, 4H), 2.55 (t, *J* = 7.4 Hz, 2H), 2.44 (t, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 2.02 (br, 3H), 1.85 (quint, *J* = 7.3 Hz, 2H), 1.78-1.66 (m, 12H).

^{13}C-NMR (125 MHz, CDCl$_3$): δ 215.6, 138.9, 135.3, 129.1, 128.4, 46.4, 38.4, 36.7, 35.3, 34.9, 28.1, 25.4, 21.1.

HRMS: m/z for $C_{21}H_{28}O$ $[M+H]^+$ calculated 297.2218, found 297.2221.

Compound 21.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-methoxyphenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.1 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 μl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **21** as a colourless oil (16.1 mg, 63%).

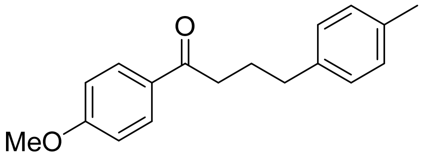
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21-7.18 (m, 3H), 6.91 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.07 (quint, *J* = 7.5 Hz, 2H).

^{13}C- NMR (125 MHz, $CDCl_3$): δ 198.8, 163.5, 141.9, 130.4, 130.2, 128.6, 128.5, 126.0, 113.8, 55.5, 37.5, 35.4, 26.0.

HRMS: m/z for $C_{17}H_{18}O_2$ $[M+H]^+$ calculated 255.1385, found 255.1382.

Spectra matches with reported literature.[9]

Compound 22.



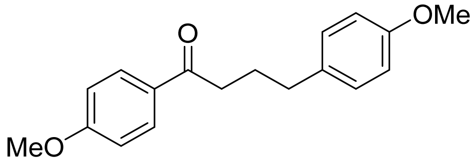
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-methoxyphenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.1 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **22** as a white solid (17.7 mg, 66%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 6.5 Hz, 2H), 7.10 (s, 4H), 6.91 (d, *J* = 8.9 Hz), 3.87 (s, 3H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.67 (t, *J* = 7.3 Hz, 2H), 2.32 (s, 3H), 2.05 (quint, *J* = 7.5 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.9, 163.4, 138.8, 135.4, 130.4, 130.3, 129.1, 128.5, 113.8, 55.5, 37.5, 34.9, 26.1, 21.1.

HRMS: m/z for $C_{18}H_{20}O_2$ $[M+H]^+$ calculated 269.1542, found 269.1535.

Compound 23.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-methoxyphenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.1 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **23** as a white solid (20.2 mg, 71%).

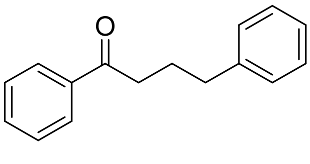
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.6, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.65 (t, *J* = 7.4 Hz, 2H), 2.03 (quint, *J* = 7.5 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.9, 163.4, 157.9, 133.9, 130.4, 130.3, 129.5, 125.4, 113.9, 113.8, 55.5, 55.4, 37.4, 34.4, 26.3.

HRMS: m/z for $C_{18}H_{20}O_3$ $[M+H]^+$ calculated 285.1491, found 285.1496.

Spectra matches with reported literature.[7]

Compound 24.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and styrene (34.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **24** as a white solid (14.2 mg, 63%).

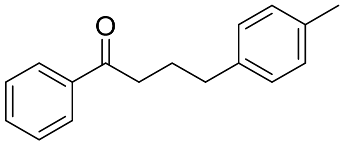
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.22-7.19 (m, 3H), 2.98 (t, *J* = 7.3 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.09 (quint, *J* = 7.5 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.2, 141.8, 137.1, 133.0, 128.6, 128.6, 128.5, 128.1, 126.0, 37.8, 35.3, 25.8.

HRMS: m/z for $C_{16}H_{16}O$ $[M+H]^+$ calculated 225.1274, found 225.1271.

Spectra matches with reported literature.[10]

Compound 25.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and 4-methylstyrene (39.5 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **25** as a colourless oil (17.9 mg, 75%).

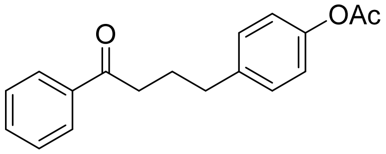
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.10 (s, 4H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.06 (quint, *J* = 7.5 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.3, 138.7, 137.1, 135.5, 133.0, 129.2, 128.6, 128.5, 128.1, 37.8, 34.8, 25.9, 21.1.

HRMS: m/z for $C_{17}H_{18}O$ $[M+H]^+$ calculated 239.1430, found 239.1433.

Spectra matches with reported literature.[11]

Compound 26.



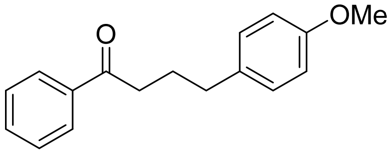
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and 4-acetoxystyrene (45.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **26** as a white solid (17.5 mg, 62%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 9.3 Hz, 2H), 7.55 (t, *J* = 9.1 Hz, 1H), 7.45 (t, *J* = 9.8 Hz, 2H), 7.20 (d, *J* = 10.4, 2H), 7.00 (d, *J* = 10.5 Hz, 2H), 2.98 (t, *J* = 9.0 Hz, 2H), 2.71 (t, *J* = 9.2 Hz, 2H), 2.29 (s, 3H), 2.07 (quint, *J* = 9.4 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.1, 169.8, 149.0, 139.4, 137.1, 133.1, 129.5, 128.7, 128.1, 121.5, 37.7, 34.6, 25.7, 21.2.

HRMS: m/z for $C_{18}H_{18}O_3$ $[M+H]^+$ calculated 283.1334, found 283.1337.

Compound 27.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and 4-methoxystyrene (39.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **27** as a colourless oil (20.4 mg, 80%).

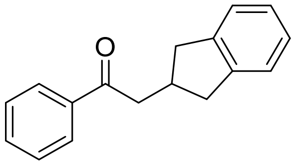
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.1 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.67 (t, 7.5 Hz, 2H), 2.04 (quint, *J* = 7.4 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.3, 157.9, 137.1, 133.8, 133.0, 129.5, 128.6, 128.1, 113.9, 55.3, 37.7, 34.4, 26.0.

HRMS: m/z for $C_{17}H_{18}O_2$ $[M+H]^+$ calculated 255.1380, found 255.1381.

Spectra matches with reported literature.[12]

Compound 28.



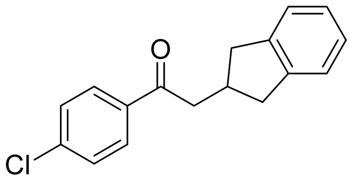
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and indene (35.0 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **28** as a white solid (7.1 mg, 30%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.97 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.20-7.14 (m, 4H), 3.24-3.16 (m, 4H), 3.13-3.07 (m, 1H), 2.67 (dd, *J* = 15.6, 6.6 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 199.8, 142.9, 137.2, 133.1, 128.7, 128.1, 126.3, 124.6, 44.4, 39.3, 35.4.

HRMS: m/z for $C_{17}H_{16}O$ $[M+H]^+$ calculated 237.1274, found 237.1272.

Compound 29.



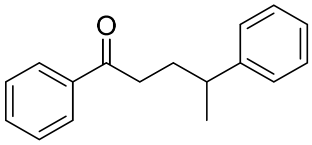
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and indene (35.0 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **29** as a white solid (9.5 mg, 35%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4, 2H), 7.25-7.13 (m, 4H), 3.22 (dd, *J* = 15.5, 7.5 Hz, 2H), 3.13 (d, *J* = 7.0 Hz, 2H), 3.10-3.03 (m, 1H), 2.65 (dd, *J* = 15.4, 6.5 Hz, 2H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.6, 142.8, 139.6, 135.5, 129.6, 129.0, 126.4, 124.6, 44.4, 39.3, 35.3.

HRMS: m/z for $C_{17}H_{15}ClO$ $[M+H]^+$ calculated 271.0890, found 271.0884.

Compound 30.



Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-phenyl-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (38.1 mg, 0.1 mmol, 1 equiv.) and α-methylstyrene (39.0 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **30** as a colourless oil (16.7 mg, 70%).

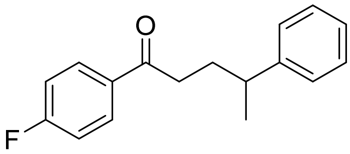
^{1}H- NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.3 Hz, 3H), 2.90-2.76 (m, 3H), 2.11-1.95 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 200.5, 146.6, 137.0, 133.0, 128.6, 128.1, 127.2, 126.3, 39.6, 36.8, 32.6, 22.7.

HRMS: m/z for $C_{17}H_{18}O$ $[M+H]^+$ calculated 239.1430, found 239.1428.

Spectra matches with reported literature.[13]

Compound 31.



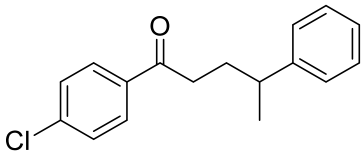
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-fluorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (39.8 mg, 0.1 mmol, 1 equiv.) and α-methylstyrene (39.0 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **31** as a colourless oil (12.3 mg, 48%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.86 (t, *J* = 6.6 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 3H), 7.07 (t, *J* = 8.4 Hz, 2H), 2.86-2.72 (m, 3H), 2.10-1.94 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.8, 165.7 (d, $J_{C,F}$ = 253.0 Hz), 146.5, 133.5, 130.7 (d, $J_{C,F}$ = 9.0 Hz), 128.6, 127.2, 126.3, 115.7 (d, $J_{C,F}$ = 22.0 Hz), 39.6, 36.7, 32.6, 22.7.

HRMS: m/z for $C_{17}H_{17}FO$ $[M+H]^+$ calculated 257.1336, found 257.1337.

Compound 32.



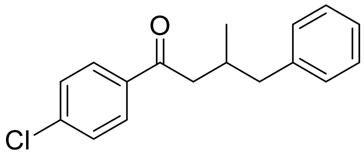
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and α-methylstyrene (39.0 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **32** as a colourless oil (17.7 mg, 65%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 7.7 Hz, 3H), 2.79-2.72 (m, 3H), 2.10-1.93 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 199.2, 146.5, 139.4, 135.3, 129.5, 128.9, 128.6, 127.2, 126.4, 39.6, 39.7, 32.5, 22.7.

HRMS: m/z for $C_{17}H_{17}ClO$ $[M+H]^+$ calculated 273.1046, found 273.1045.

Compound 33.



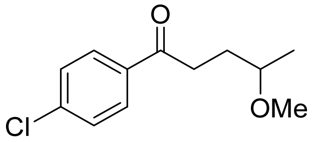
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and β-methylstyrene (38.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **33** as a colourless oil (5.7 mg, 21%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 6.3 Hz, 3H), 2.93 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.73-2.56 (m, 3H), 2.50-2.41 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 198.9, 140.4, 139.4, 135.7, 132.5, 129.6, 129.4, 128.9, 128.4, 126.2, 45.0, 43.4, 31.9, 29.8, 20.1.

HRMS: m/z for $C_{17}H_{17}ClO$ $[M+H]^+$ calculated 273.1046, found 273.1041.

Compound 34.



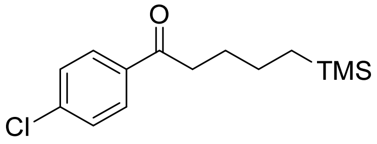
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and 2-methoxypropene (47.9 µl, 0.5 mmol, 5 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **34** as a colourless oil (13.2 mg, 58%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 3.43-3.36 (m, 1H), 3.29 (s, 3H), 3.06-3.00 (m, 2H), 1.99-1.79 (m, 2H), 1.18 (d, *J* = 6.1 Hz, 3H).

^{13}C-NMR (125 MHz, $CDCl_3$): δ 199.2, 139.4, 135.5, 129.6, 129.0, 75.9, 56.1, 34.3, 30.7, 19.1.

HRMS: m/z for $C_{12}H_{15}ClO_2$ $[M+H]^+$ calculated 227.0839, found 227.0840.

Compound 35.



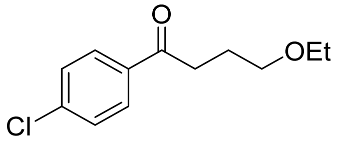
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and allyltrimethylsilane (79.5 µl, 0.5 mmol, 5 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **35** as a white solid (15.1 mg, 56%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 2.93 (t, *J* = 7.3 Hz, 2H), 1.74 (quint, *J* = 7.4 Hz, 2H), 1.42-1.34 (m, 2H), 0.53 (t, *J* = 8.5 Hz, 2H), -0.02 (s, 9H).

^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.4, 139.4, 135.5, 129.6, 129.0, 38.5, 28.2, 23.9, 16.7, -1.5.

HRMS: m/z for $C_{14}H_{21}ClOSi$ $[M+H]^+$ calculated 269.1128, found 269.1128.

Compound 36



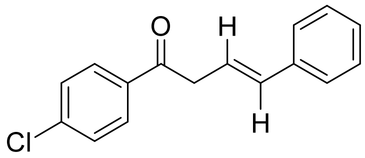
Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and ethyl vinyl ether (47.9 µl, 0.5 mmol, 5 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **36** as a white solid (11.6 mg, 51%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.3 Hz, 2H), 3.51-3.43 (m, 4H), 3.04 (t, *J* = 7.1 Hz, 2H), 2.00 (quint, *J* = 6.4 Hz, 2H), 1.17 (t, *J* = 6.9 Hz, 3H).

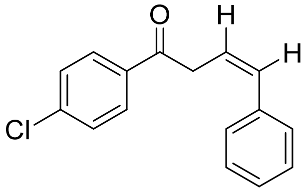
^{13}C-NMR (100 MHz, $CDCl_3$): δ 199.0, 139.4, 135.5, 129.6, 128.9, 69.5, 66.2, 35.3, 24.4, 15.3.

HRMS: m/z for $C_{12}H_{15}ClO_2$ $[M+H]^+$ calculated 227.0839, found 227.0834.

Compound 37.



Trans-



Cis-

White solid

Colourless oil

Following the general procedure, a mixture of 9-mesityl-10-methylacridinium tetrafluoroborate (2.0 mg, 0.005 mmol), Hantzsch ester (30.4 mg, 0.12 mmol, 1.2 equiv.), 1-(4-chlorophenyl)-2-(triphenyl-λ^5-phosphaneylidene)ethan-1-one (41.5 mg, 0.1 mmol, 1 equiv.) and phenylacetylene (32.9 µl, 0.3 mmol, 3 equiv.) in DCM (4 ml) is irradiated by Blue LEDs for 12 hrs. Purification by flash column chromatography furnished compound **37** as a mixture of two isomers (*Z* : *E* = 1.3 : 1, 40%).

^{1}H-NMR-*trans*- isomer (500 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.6 Hz, 2H), 7.38 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.24-7.21 (m, 1H), 6.55 (d, *J* = 16.0 Hz, 1H), 6.44 (dt, *J* = 15.9, 6.6 Hz, 1H), 3.88 (dd, *J* = 6.7, 1.2 Hz, 2H).

^{13}C-NMR-*trans*-isomer (125 MHz, $CDCl_3$): δ 196.9, 139.8, 136.9, 135.0, 133.9, 129.9, 129.1, 128.7, 127.7, 126.4, 122.2, 42.8.

^{1}H-NMR-*cis*- isomer (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.6 Hz, 2H), 7.41 (d, *J* = 8.6 Hz, 2H), 7.38-7.35 (m, 2H), 7.29-7.25 (m, 3H), 6.73 (d, *J* = 11.5 Hz, 1H), 6.02 (dt, *J* = 11.5, 7.1 Hz, 1H), 3.95 (dd, *J* = 7.0, 1.7 Hz, 2H).

^{13}C-NMR-*cis*-isomer (100 MHz, $CDCl_3$): δ 196.8, 136.9, 134.9, 132.5, 129.8, 129.1, 128.7, 128.5, 127.3, 123.6, 38.4.

HRMS: m/z for $C_{16}H_{13}ClO$ $[M+H]^+$ calculated 257.0733, found 257.0735.

8. References

1. Zhang, D.; Wu, L.-Z.; Zhou, L.; Han, X.; Yang, Q.-Z.; Zhang, L.-P.; Tung, C.-H. *Journal of the American Chemical Society* **2004,** *126*, 3440-3441.

2. Larraufie, M.-H.; Pellet, R.; Fensterbank, L.; Goddard, J.-P.; Lacôte, E.; Malacria, M.; Ollivier, C. *Angewandte Chemie International Edition* **2011,** *50*, 4463-4466.

3. Zugui, S.; Qinjie, T.; Yi, L. W. W.; Guofu, Z. *Chem. Eur. J.* **2012,** *18*, 9802-9806.

4. Everson, D. A.; Jones, B. A.; Weix, D. J. *Journal of the American Chemical Society* **2012,** *134*, 6146-6159.

5. Dai; Dai, X.-J.; Wang, H.; Li, C.-J. *Angewandte Chemie (International ed.)* **2017,** *56*, 6302-6306.

6. Lu; Lu, B.; Zhu, F.; Sun, H.-M.; Shen, Q. *Organic letters* **2017,** *19*, 1132-1135.

7. Montignoul, C.; Richard, M.-J.; Vigne, C.; Giral, L. *Journal of Heterocyclic Chemistry* **1984,** *21*, 1509-1519.

8. Murphy; Murphy, J.; Commeureuc, A. G. J.; Snaddon, T.; McGuire, T.; Khan, T.; Hisler, K.; Dewis, M.; Carling, R. *Organic letters* **2005,** *7*, 1427-1429.

9. (a) Colbon; Colbon, P.; Ruan, J.; Purdie, M.; Xiao, J. *Organic letters* **2010,** *12*, 3670-3673; (b) Kogan; Kogan, T.; Dupré, B.; Bui, H.; McAbee, K.; Kassir, J.; Scott, I.; Hu, X.; Vanderslice, P.; Beck, P.; Dixon, R. A. F. *Journal of medicinal chemistry* **1998,** *41*, 1099-1111.

10. Hsieh, J.-C.; Chen, Y.-C.; Cheng, A.-Y.; Tseng, H.-C. *Organic Letters* **2012,** *14*, 1282-1285.

11. Paira *Indian journal of chemistry. Sect. B* **2010,** *49*, 573.

12. Sumida, Y.; Yorimitsu, H.; Oshima, K. *The Journal of Organic Chemistry* **2009,** *74*, 3196-3198.

13. Hornback, J. M.; Proehl, G. S. *Journal of the American Chemical Society* **1979,** *101*, 7367-7373.

9. Cyclic Voltammetry Data

Equipment Model: EC-Lab ASCII

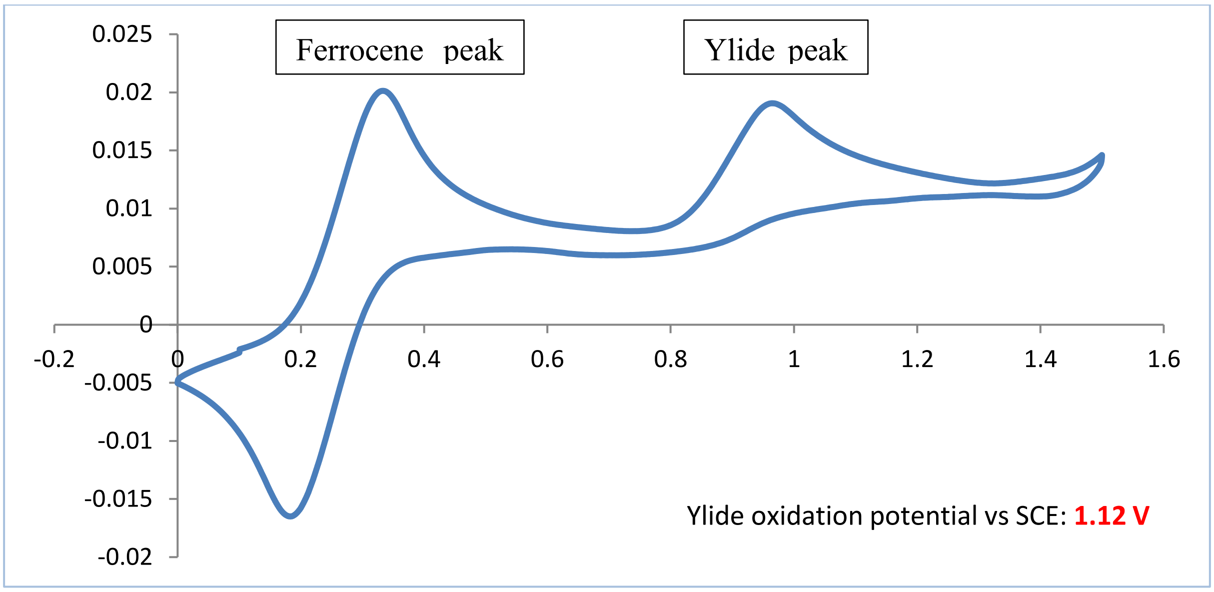
Working Electrode: Glassy Carbon

Auxiliary Electrode: Platinum

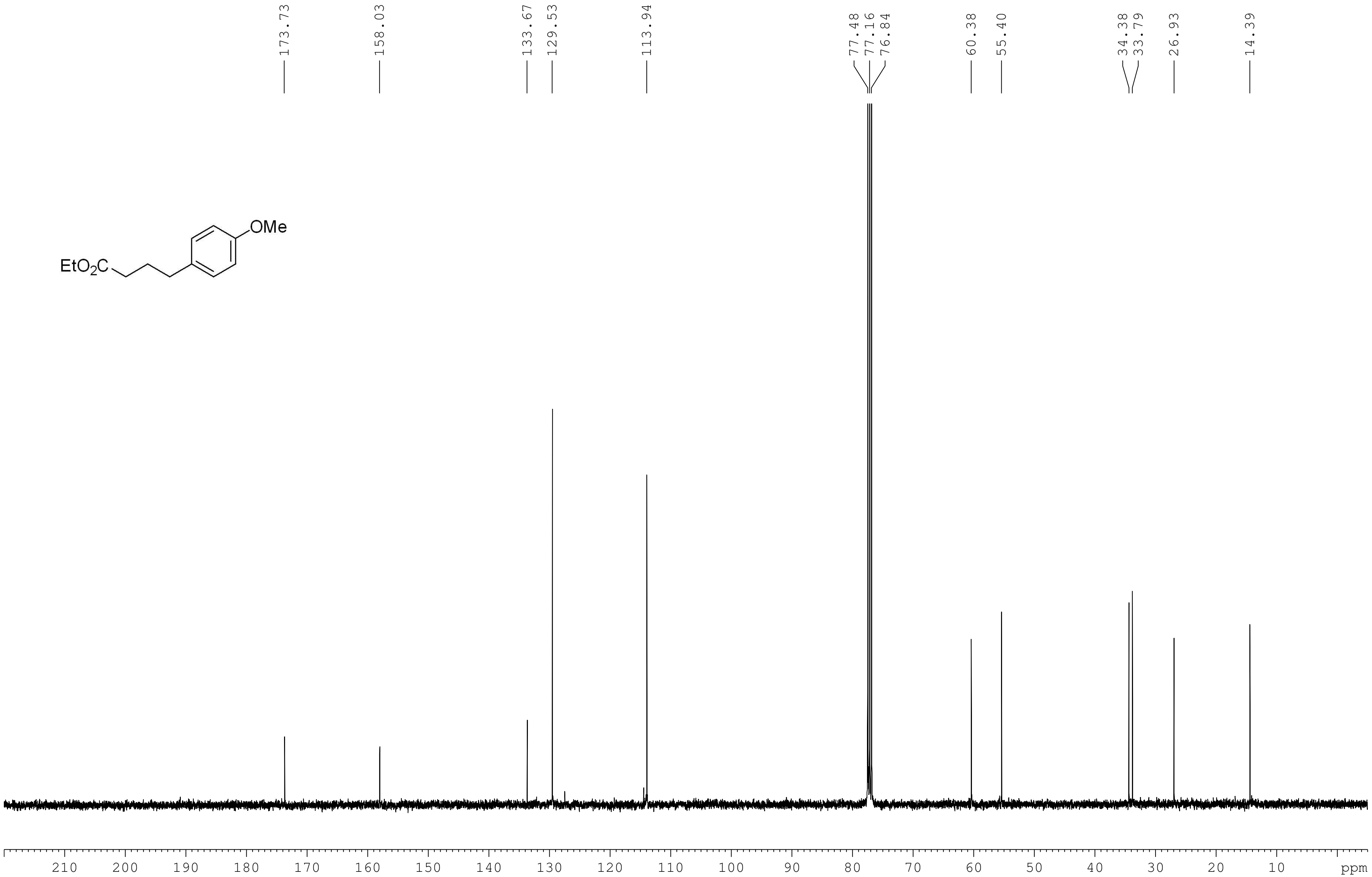
Reference Electrode: Platinum

Scan rate: 100 mV/s

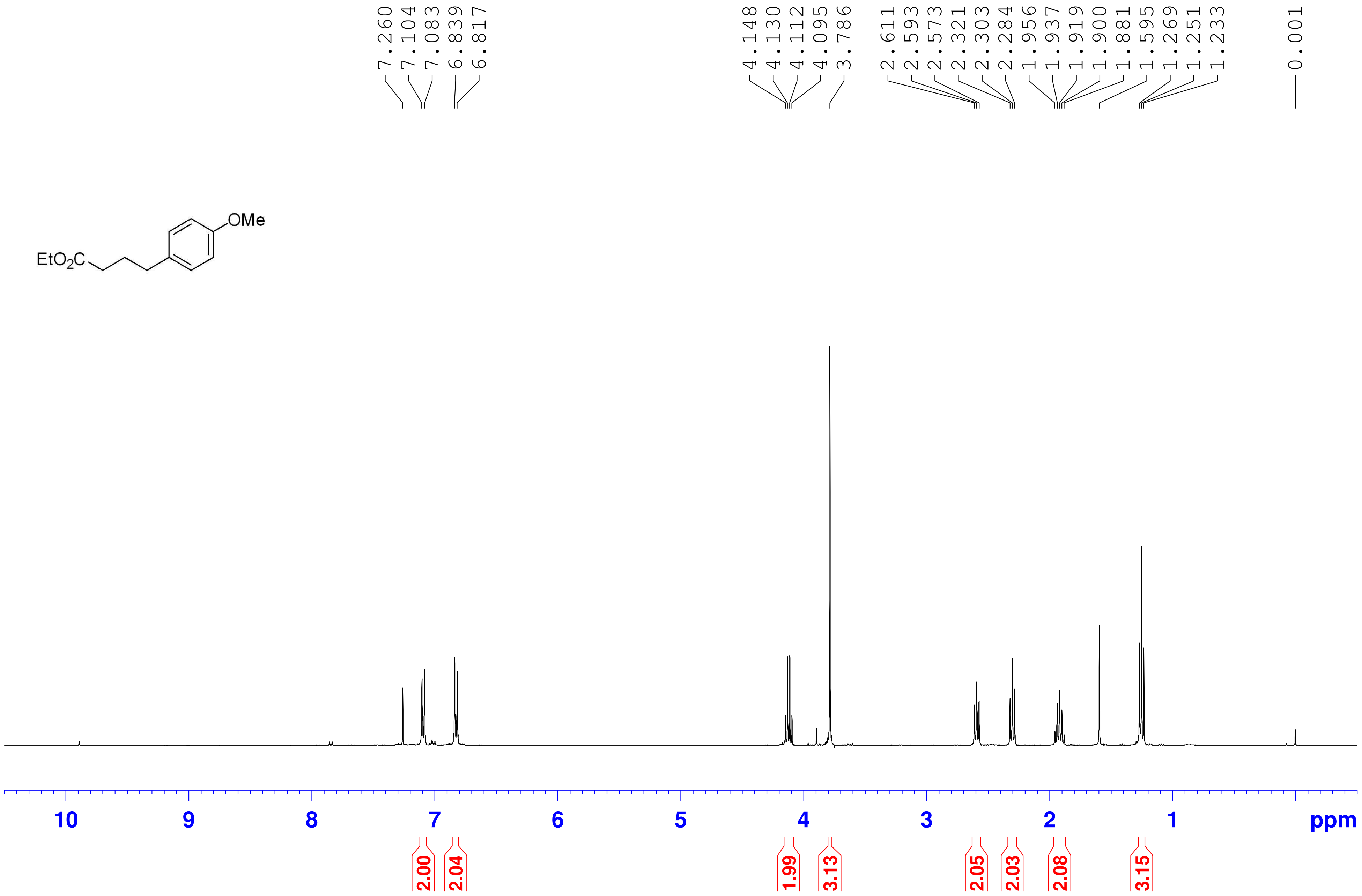
C_{Ylide} = 0.9 mM $C_{Bu_4NPF_6}$ = 0.1 M $C_{Ferrocene}$ = 0.9 mM



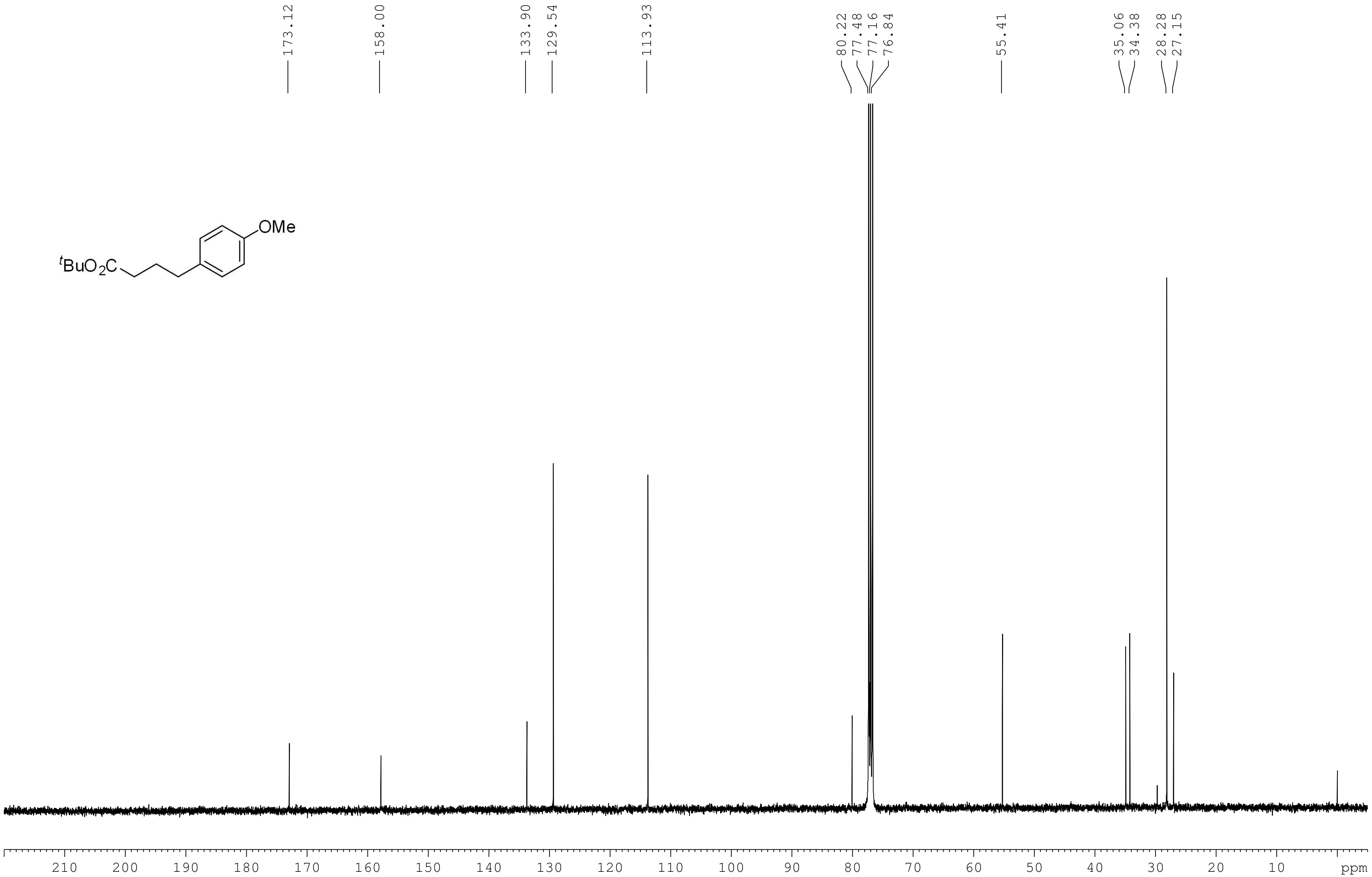
CDCl3, 100 MHz



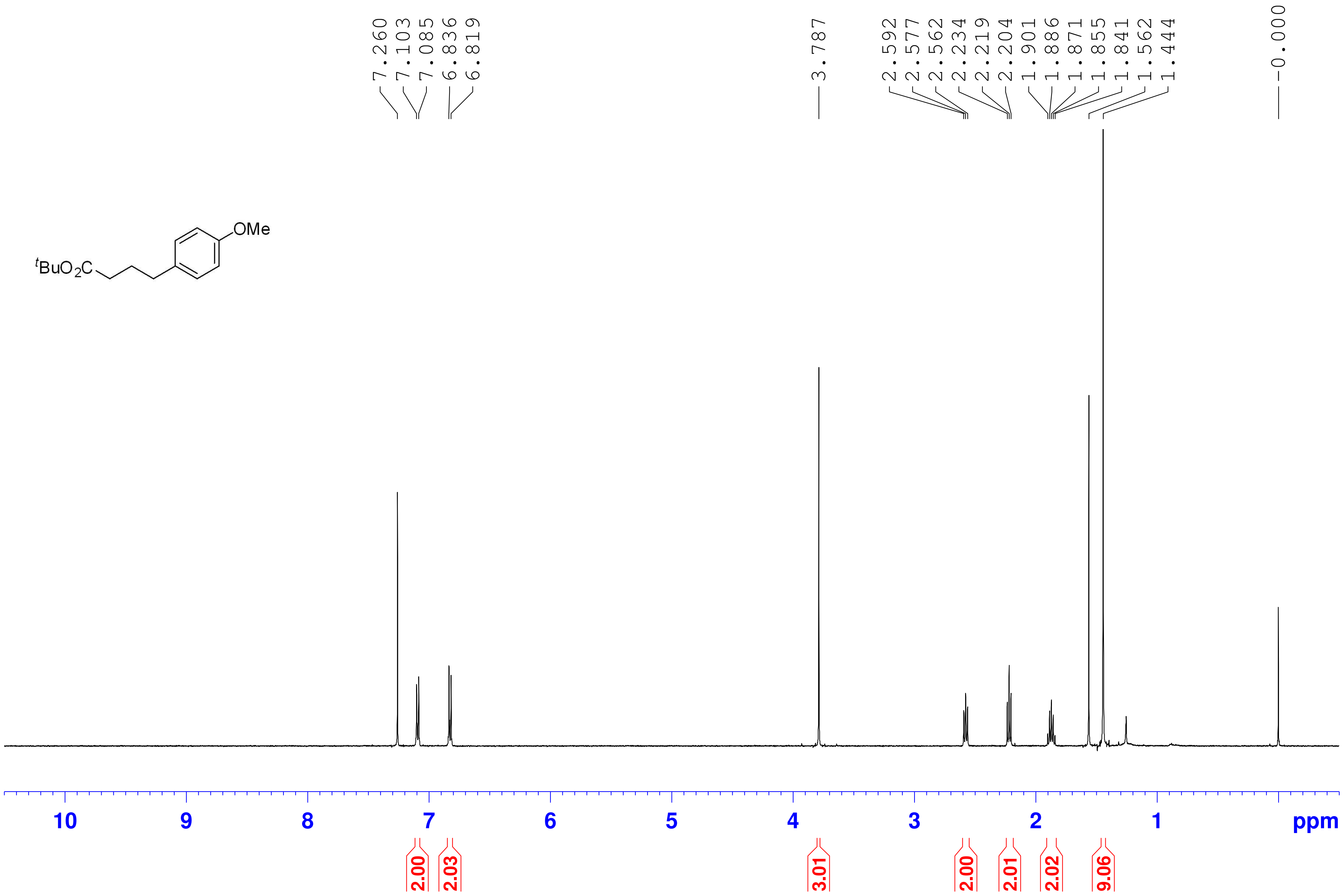
CDCl3,400 MHz



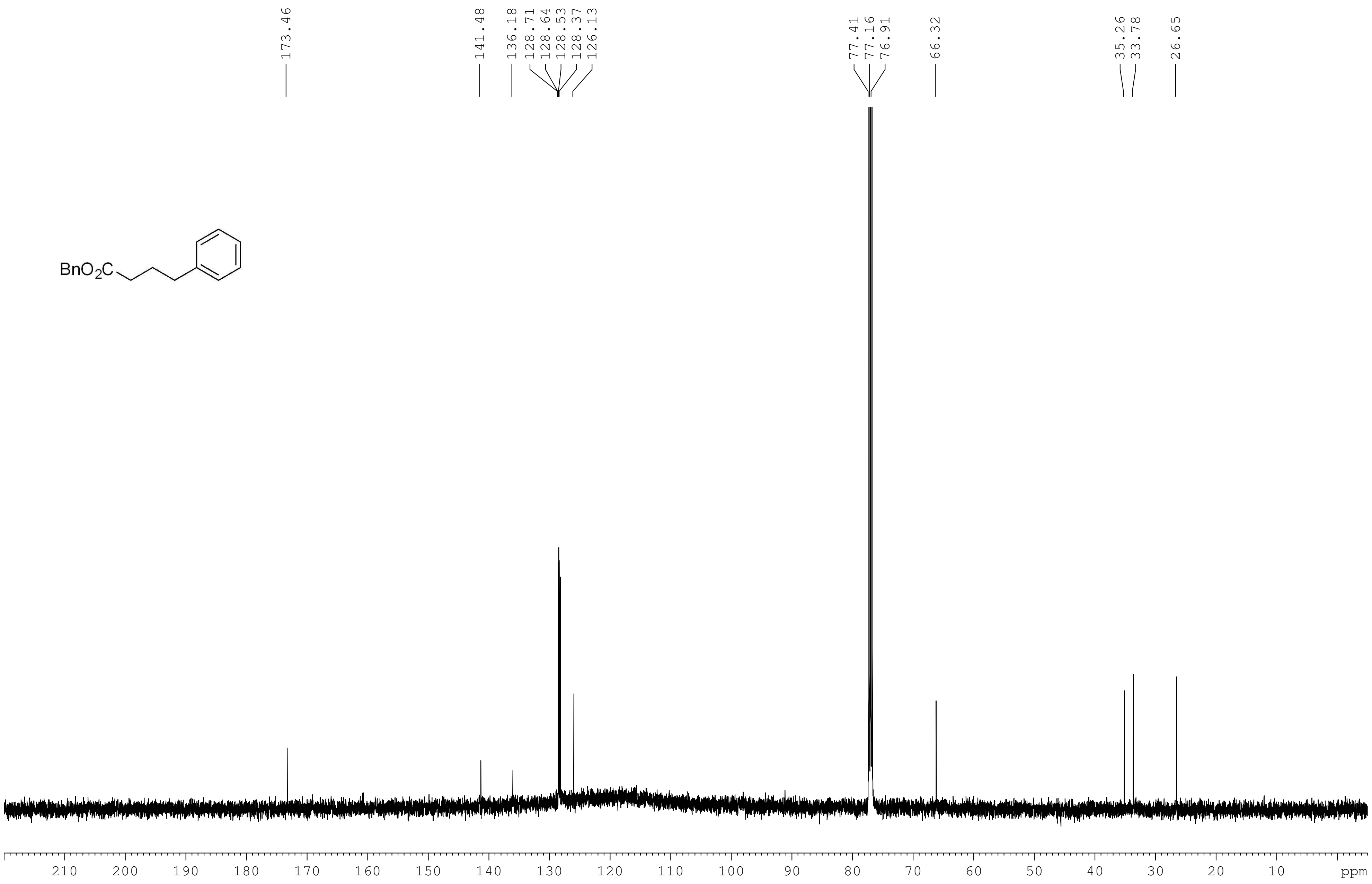
CDCl3, 100 MHz



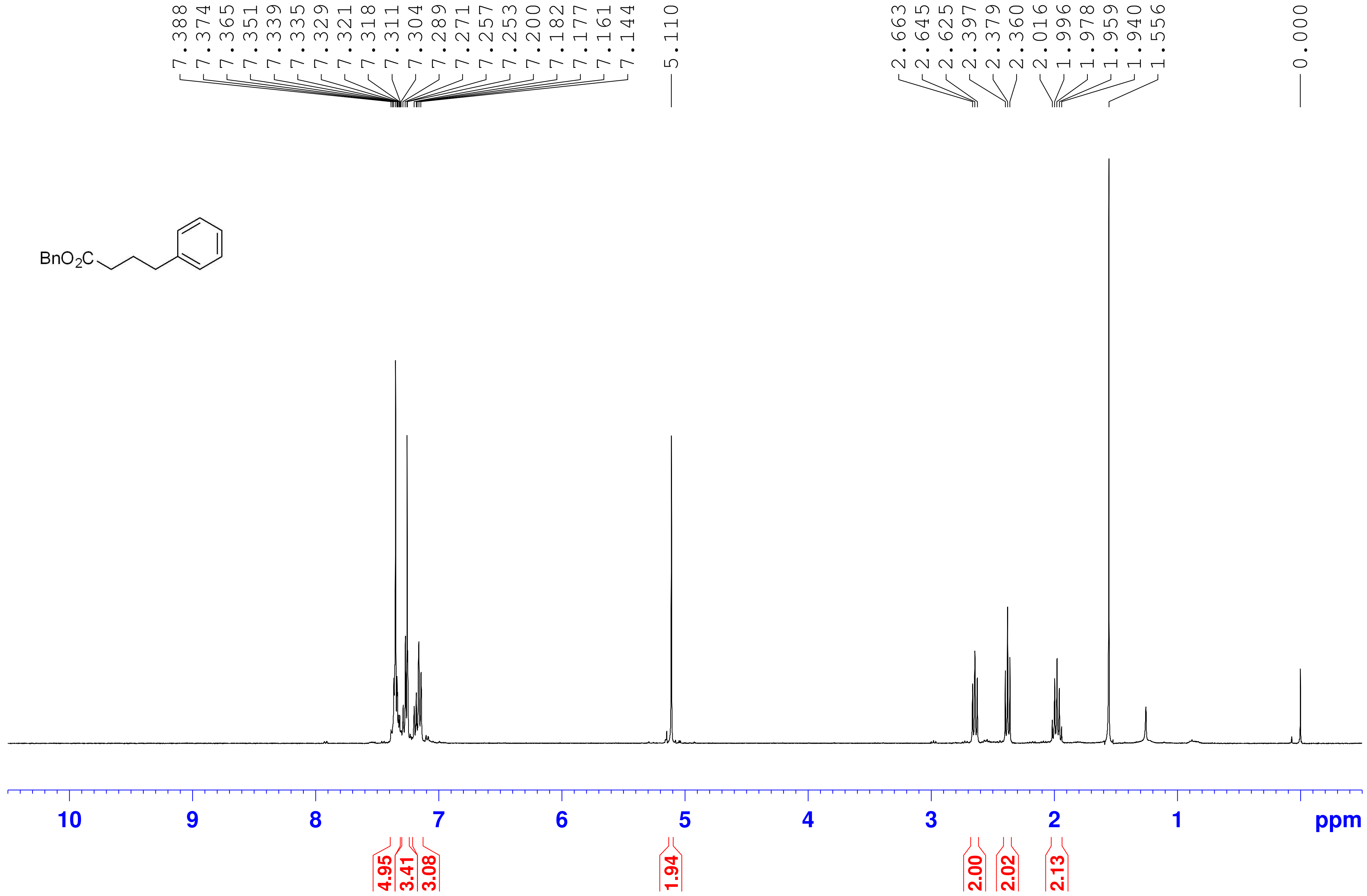
CDCl3, 500 MHz



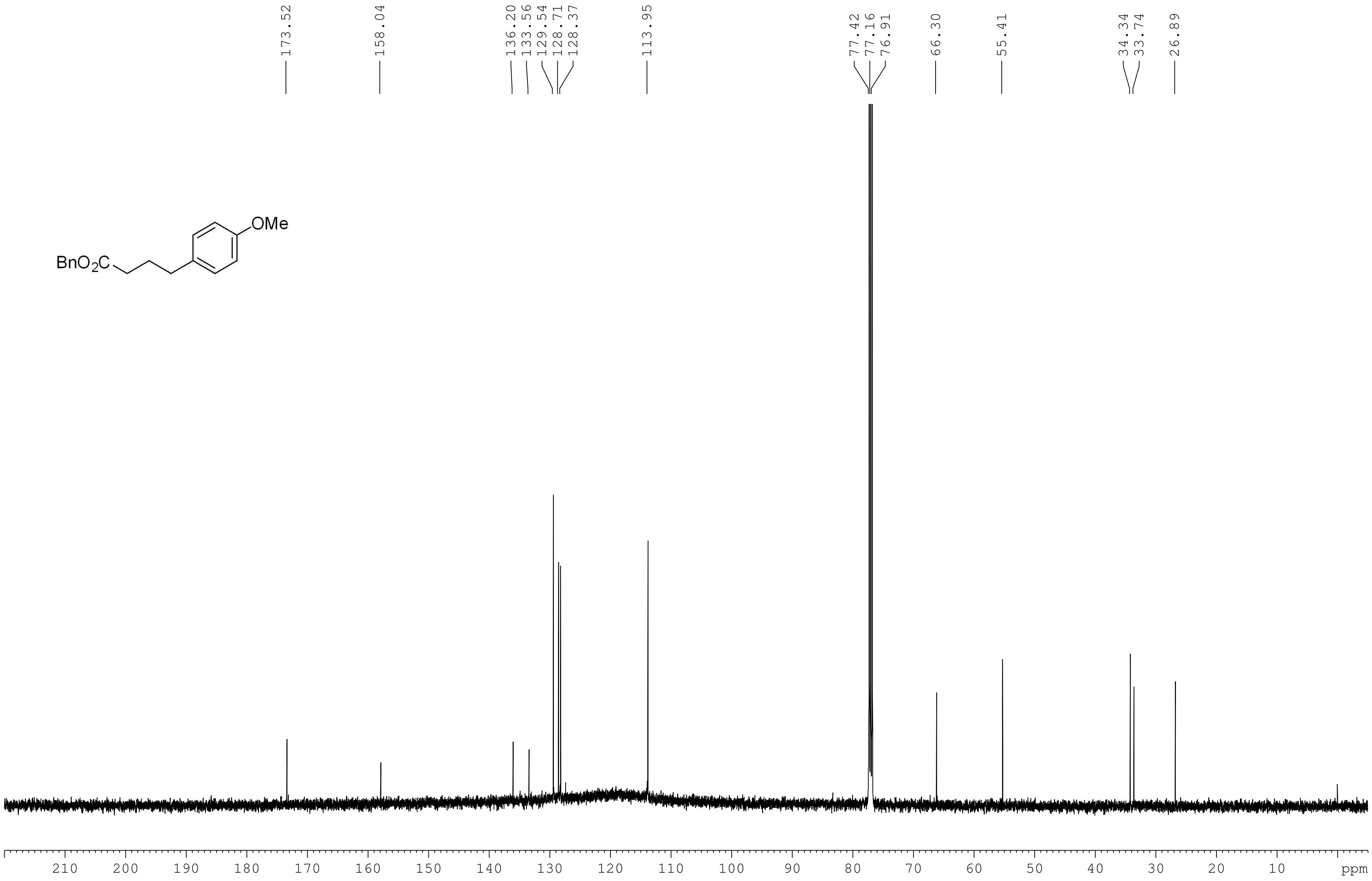
CDCl3, 125 MHz



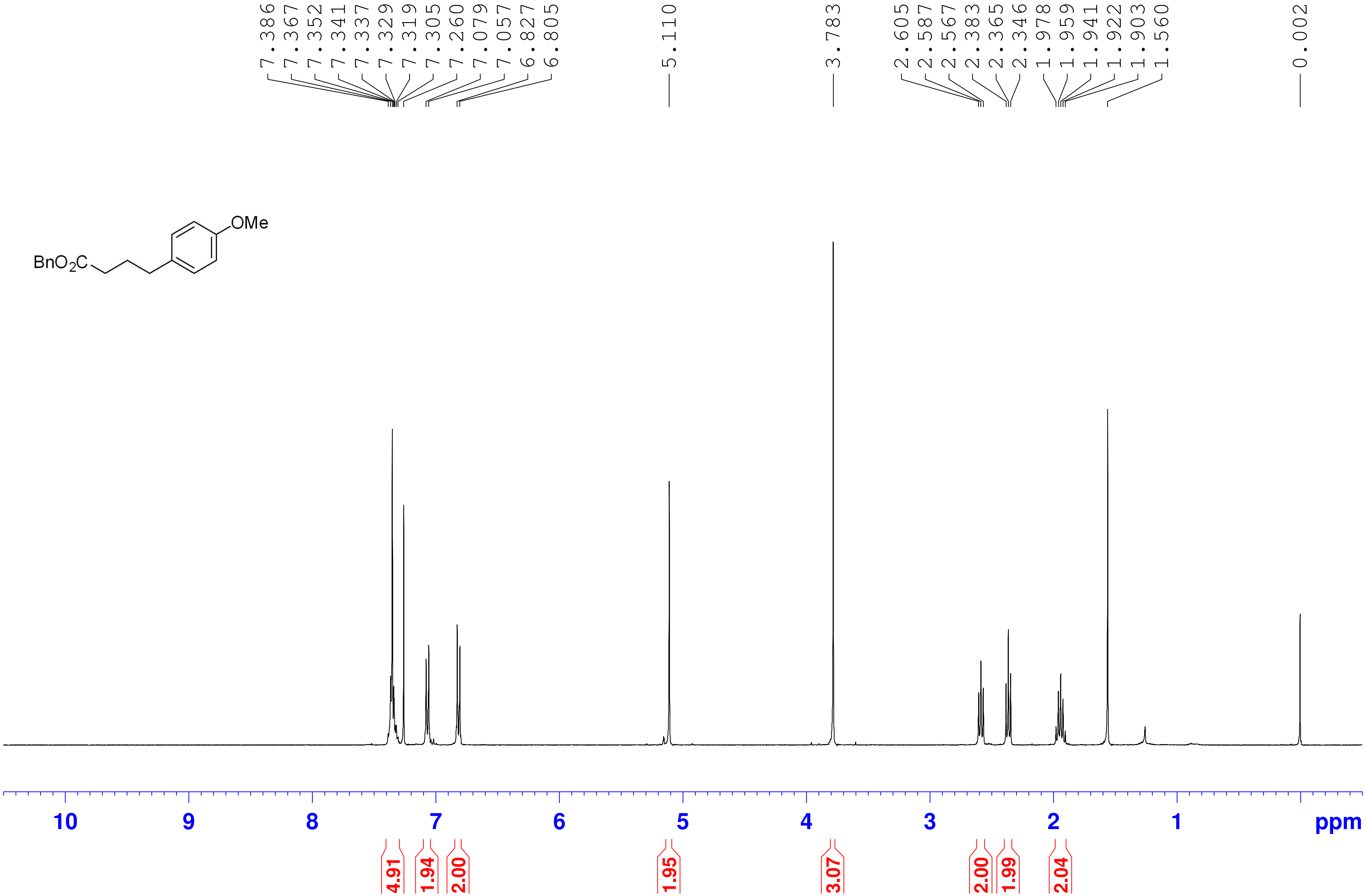
CDCl3, 400 MHz



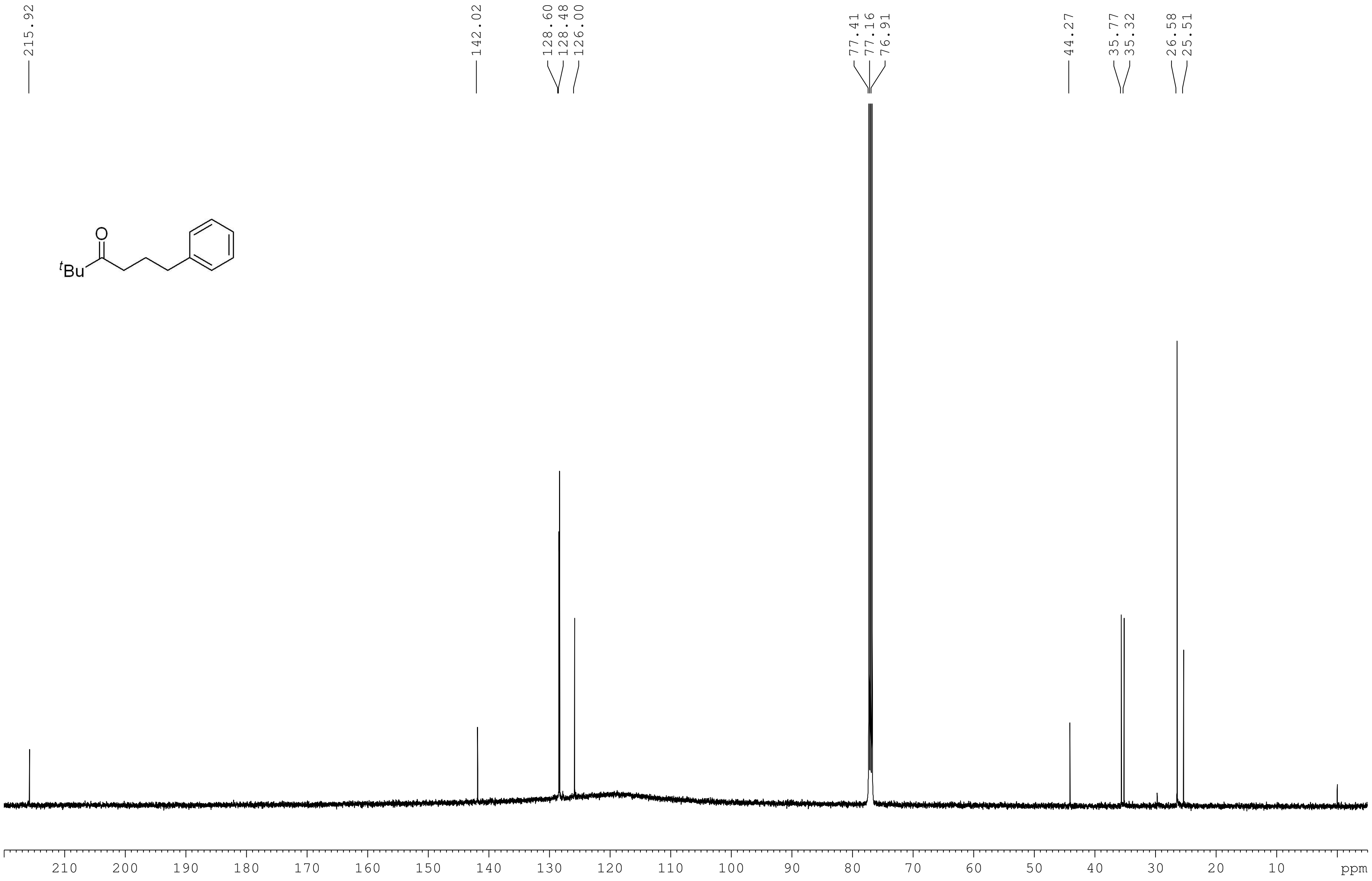
CDCl3, 125 MHz



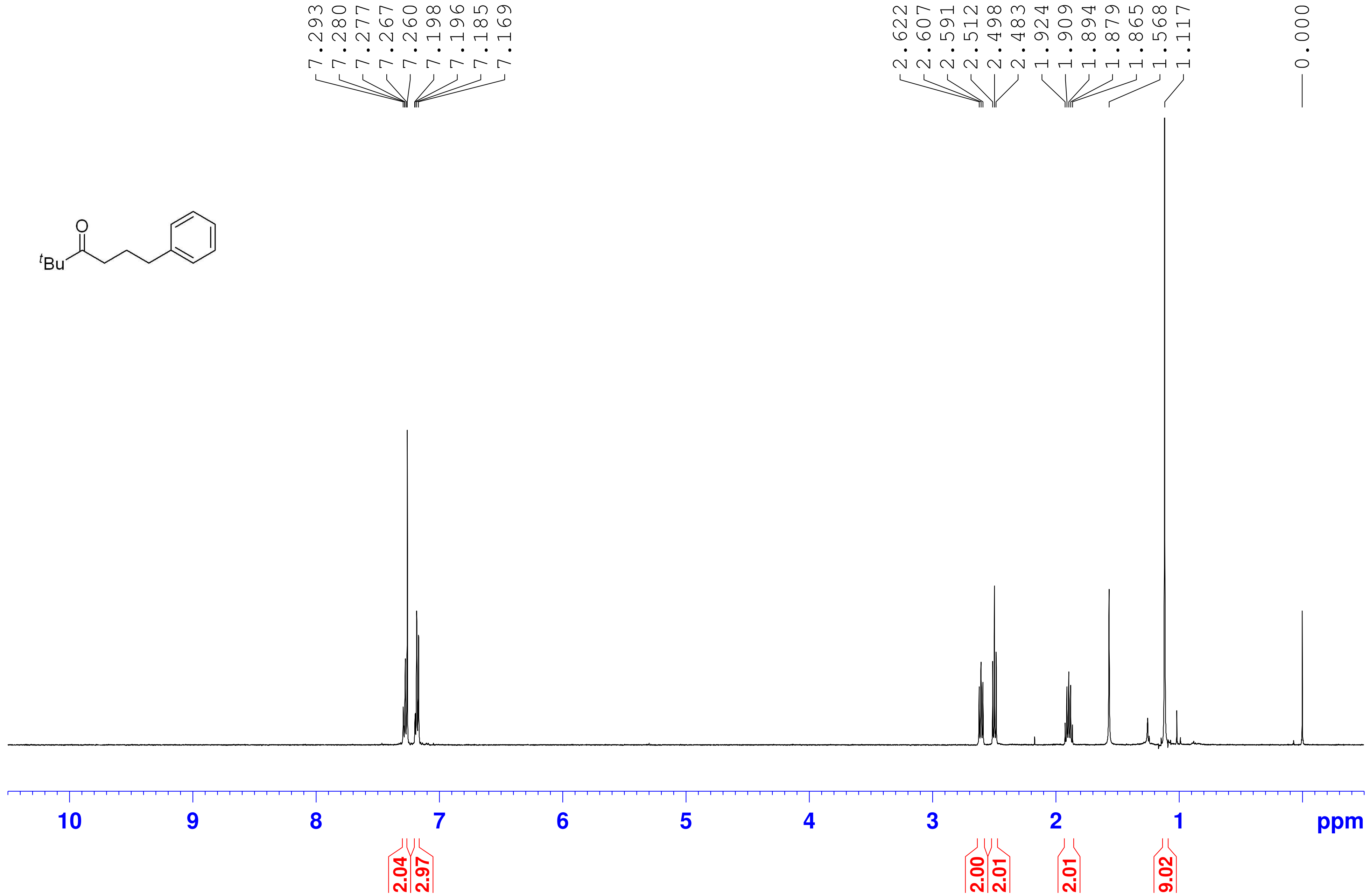
CDCl3, 400 MHz



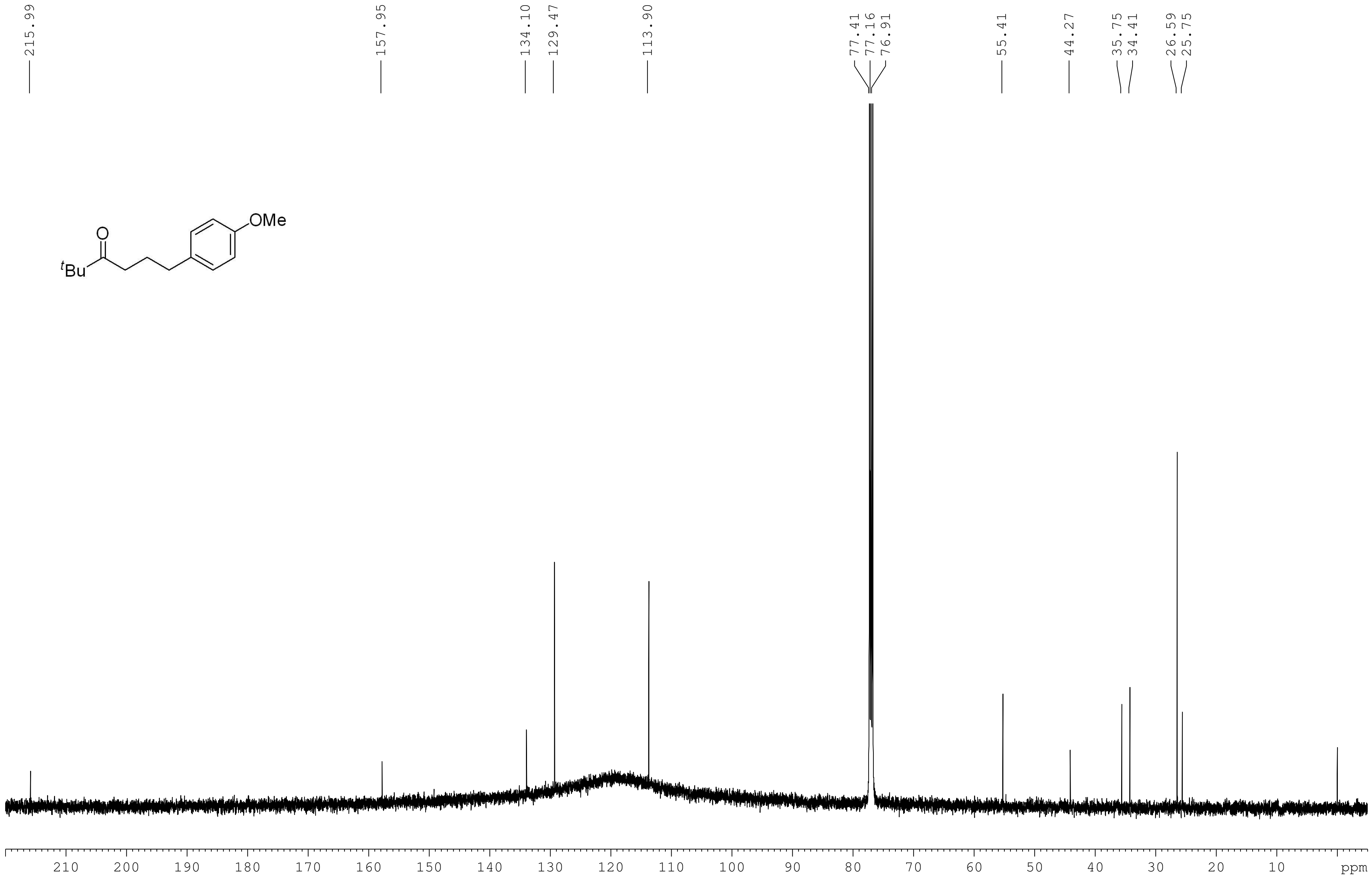
CDCl3, 125 MHz



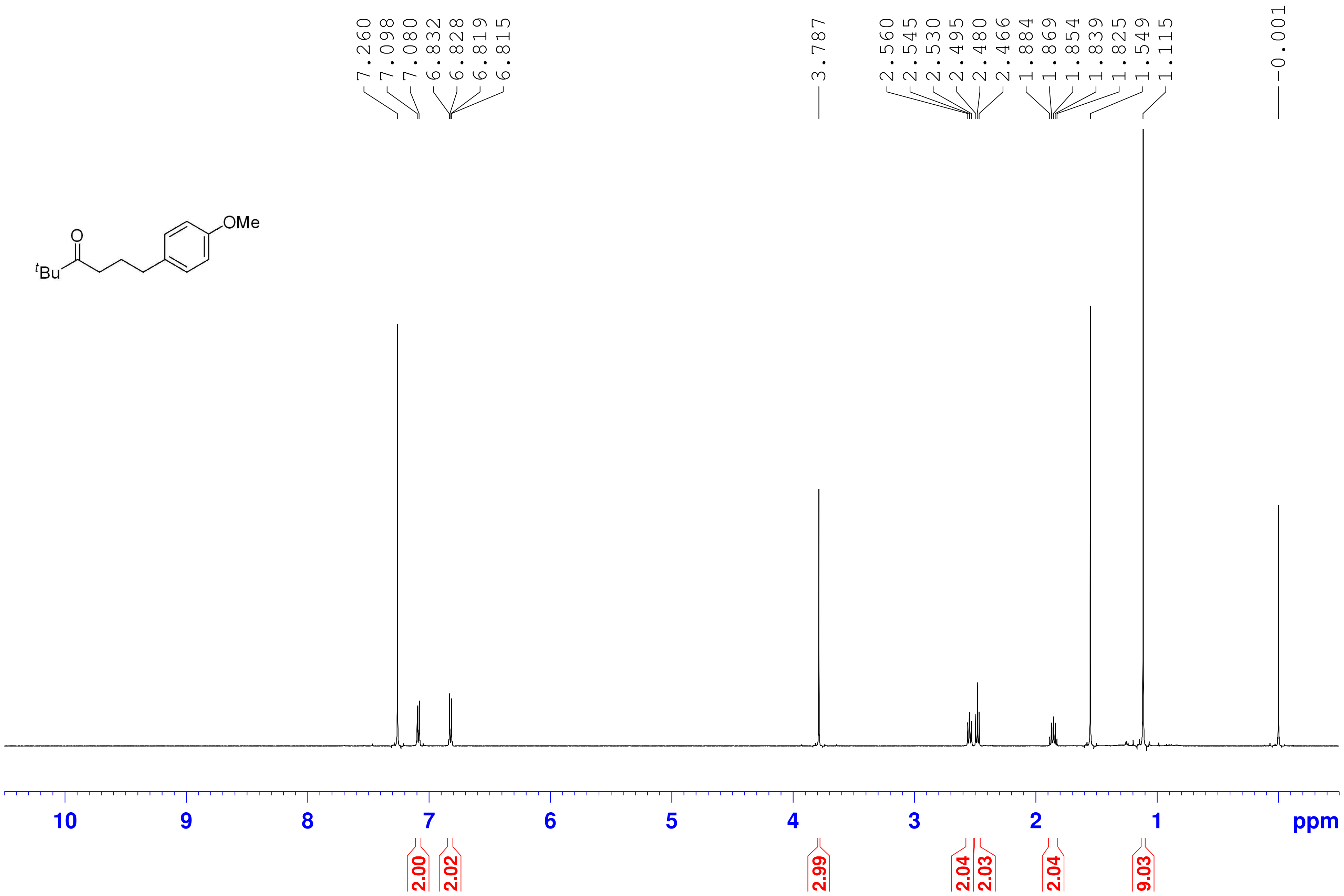
CDCl3, 500 MHz



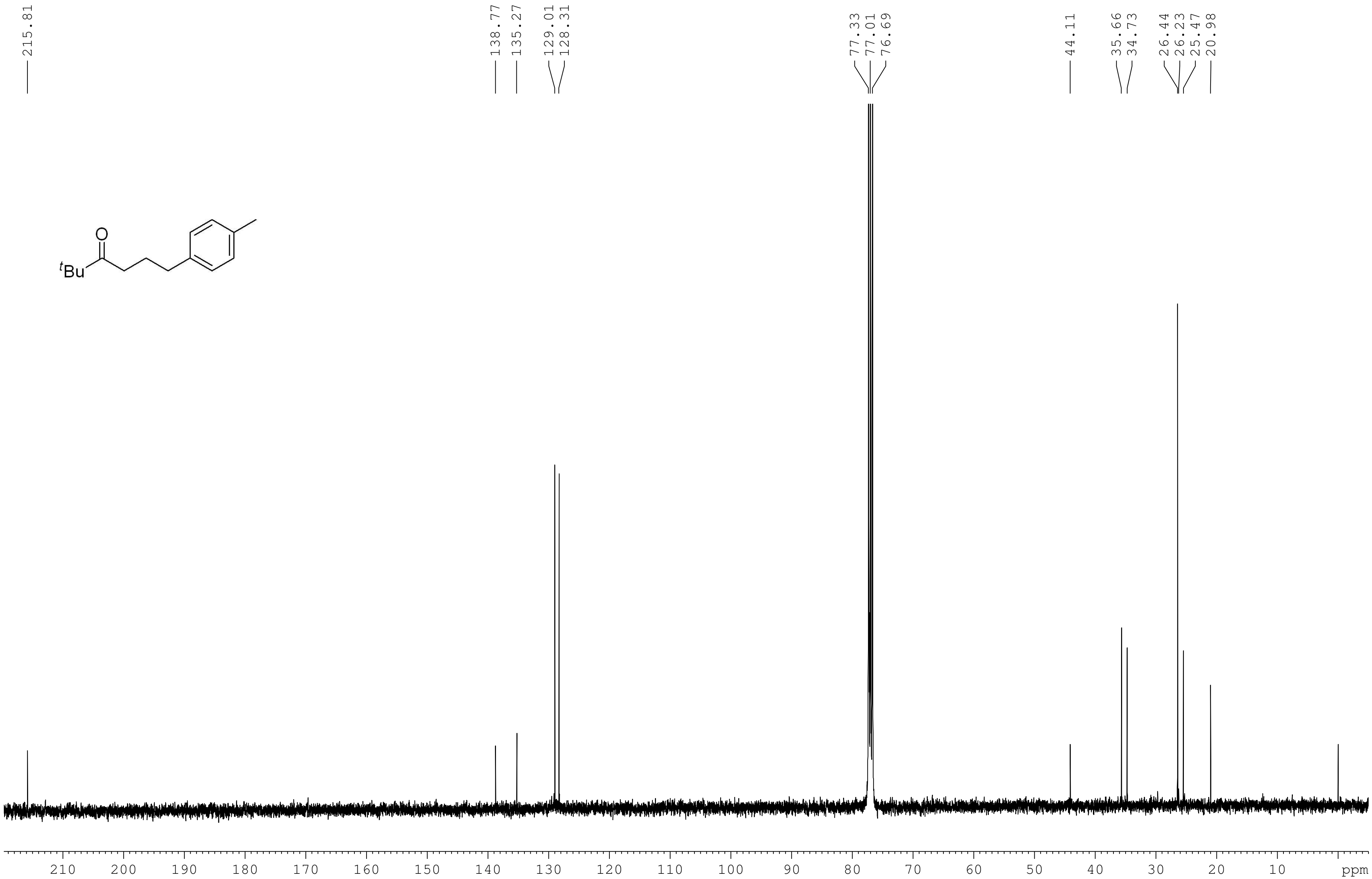
CDCl3, 125 MHz



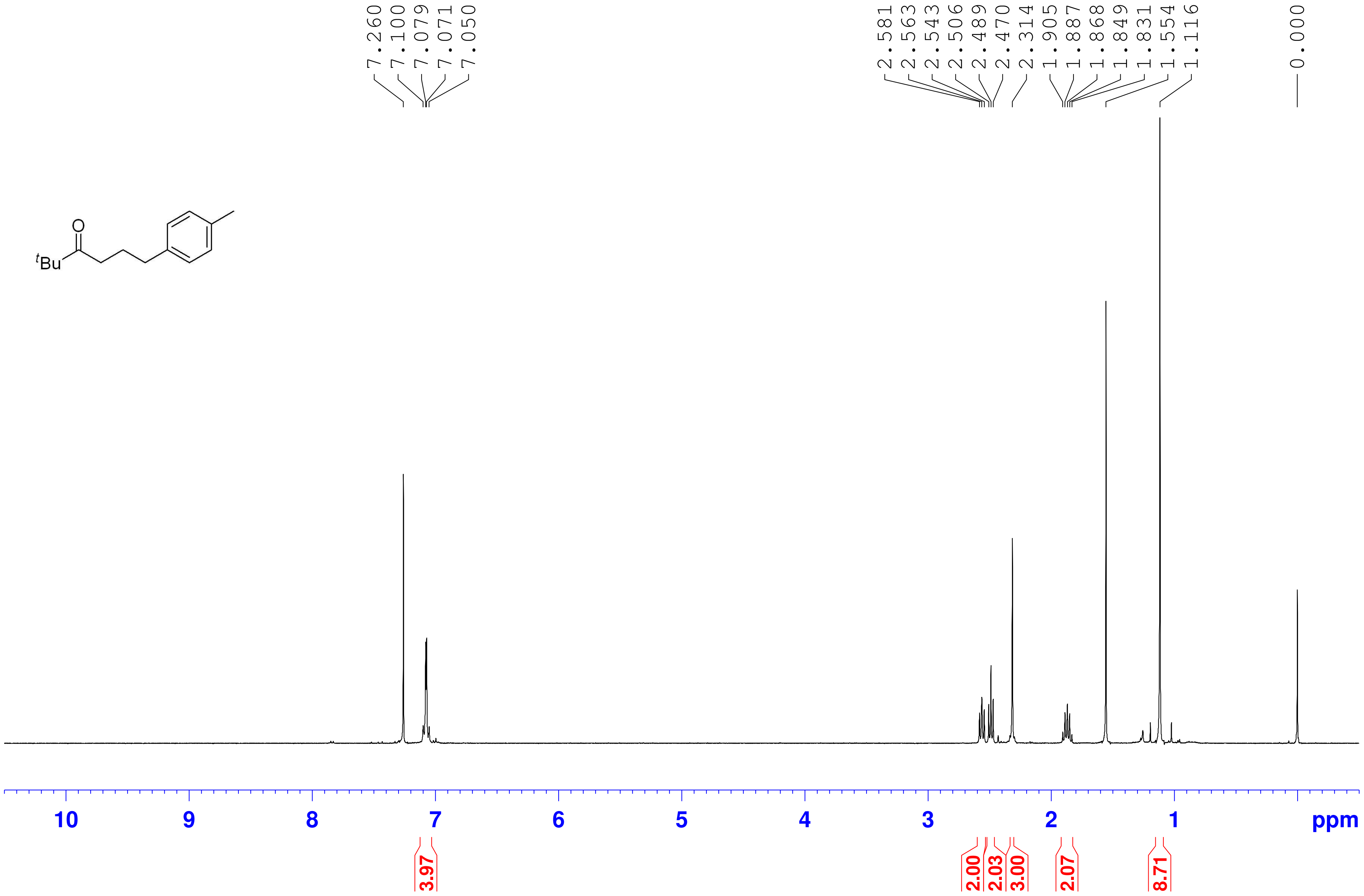
CDCl3, 500 MHz



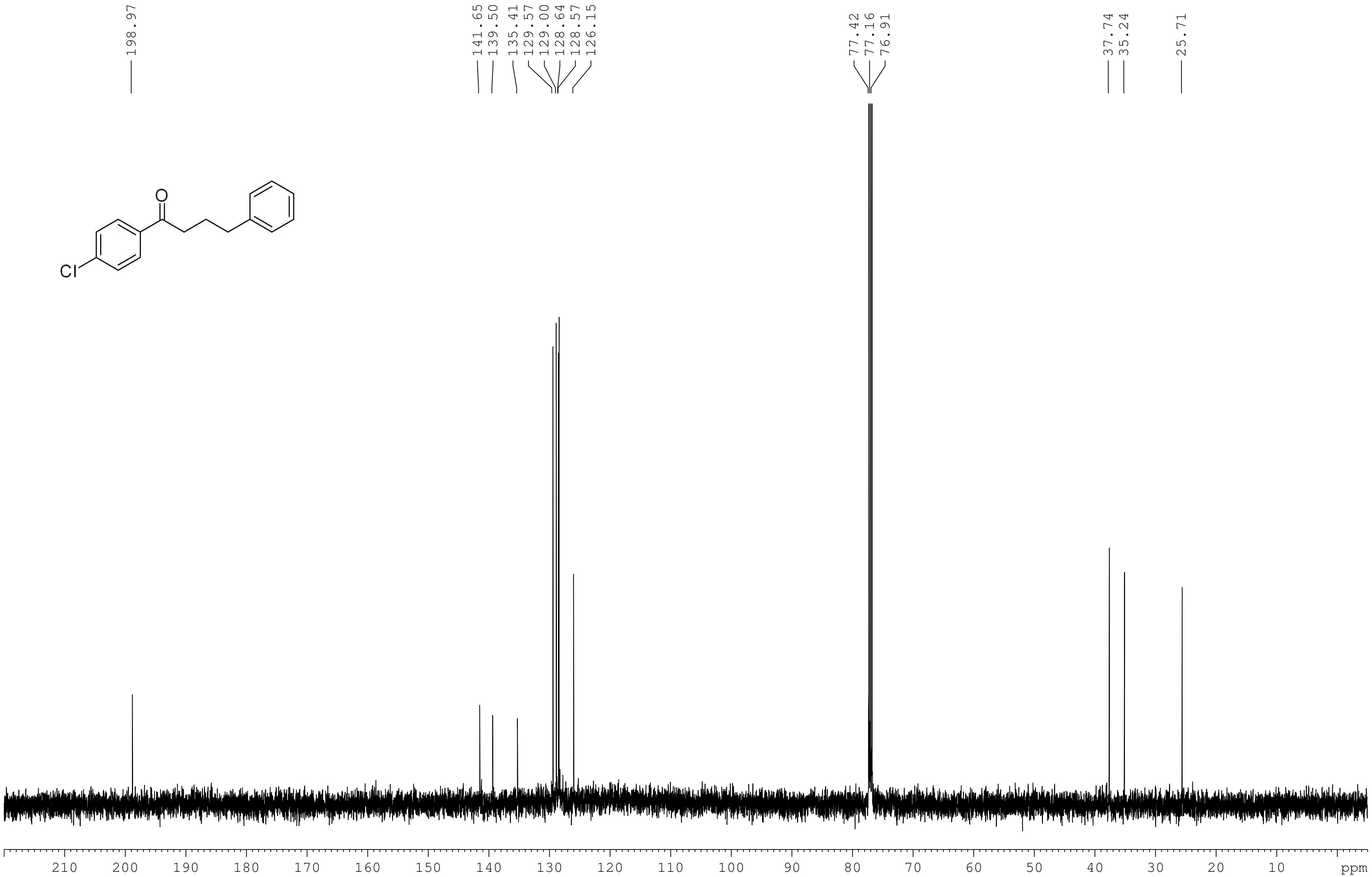
CDCl3, 100 MHz

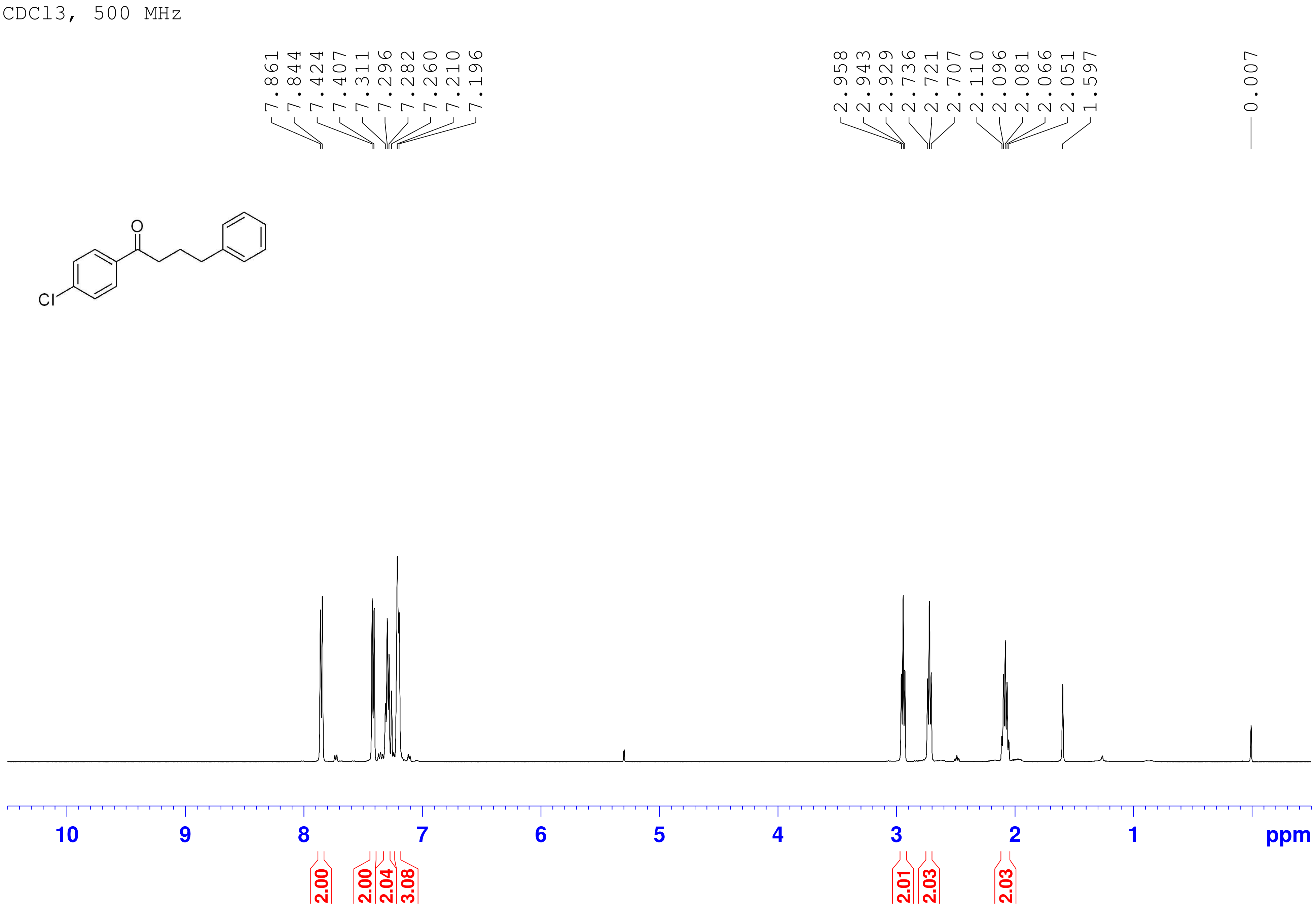


CDCl3, 400 MHz

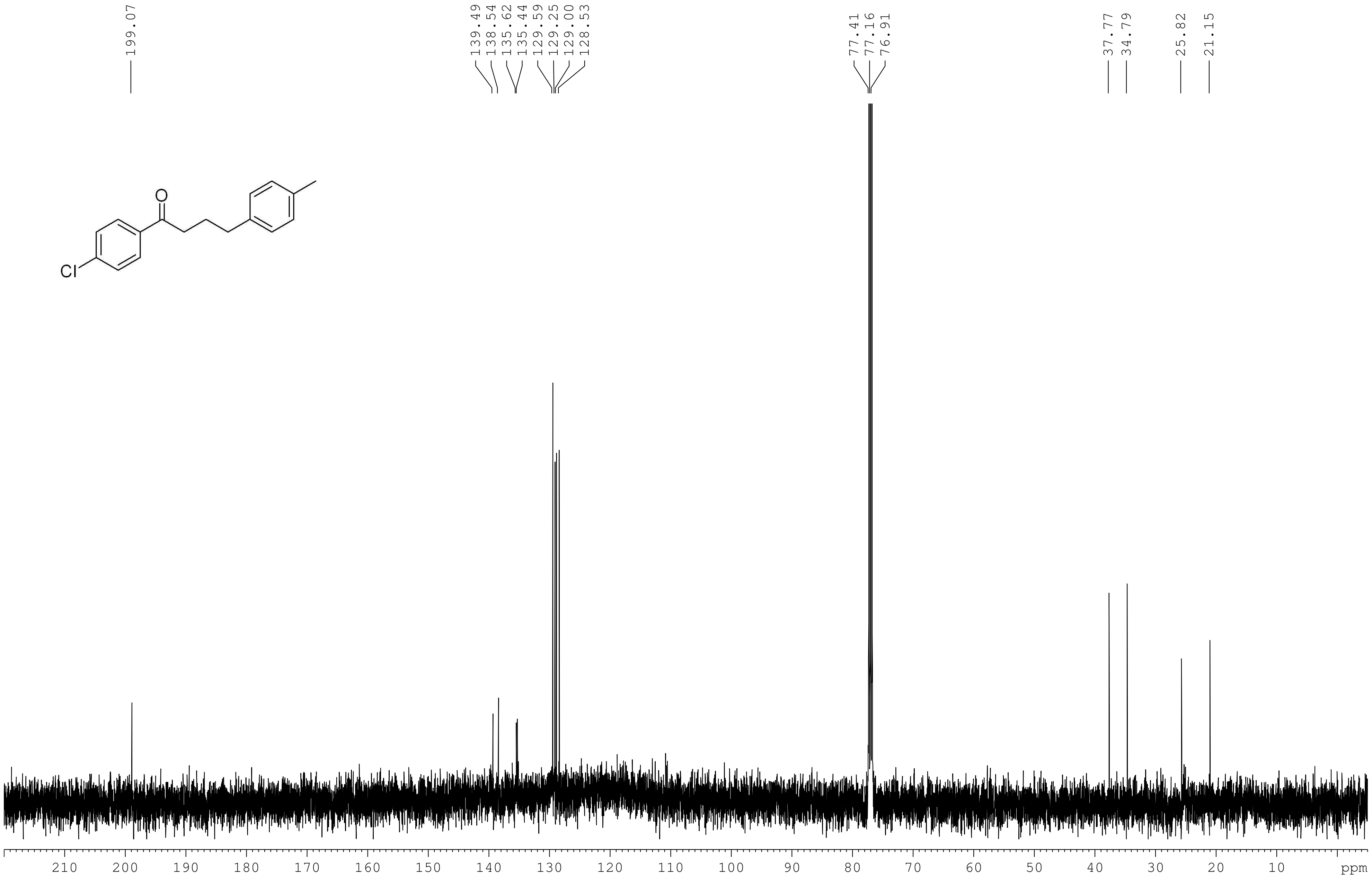


CDCl3, 125 MHz

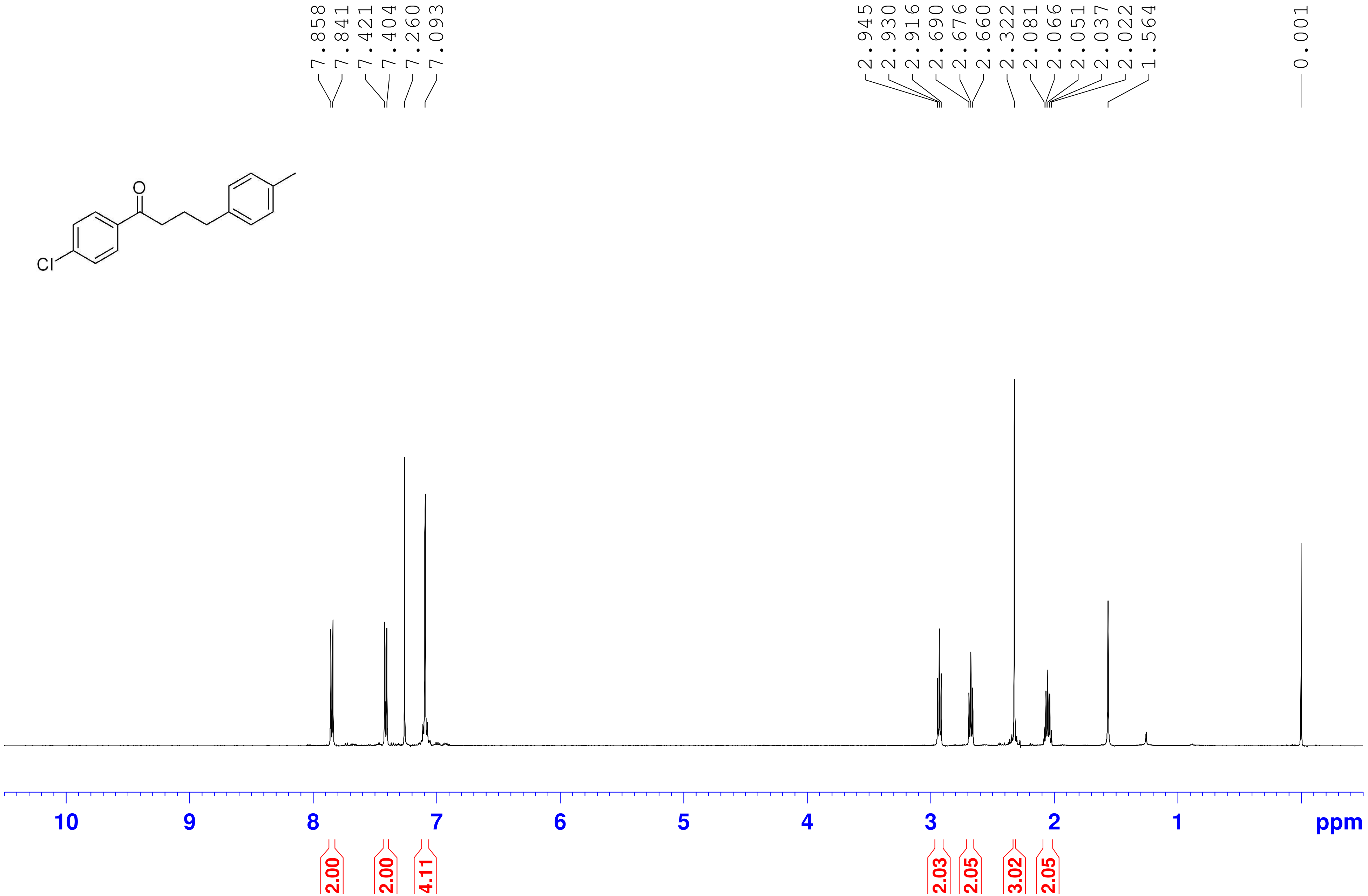



CDCl3, 500 MHz
7.861
7.844
7.424
7.407
7.311
7.296
7.282
7.260
7.210
7.196
2.958
2.943
2.929
2.736
2.721
2.707
2.110
2.096
2.081
2.066
2.051
1.597
0.007
O
Cl
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.00
2.04
3.08
2.01
2.03
2.03

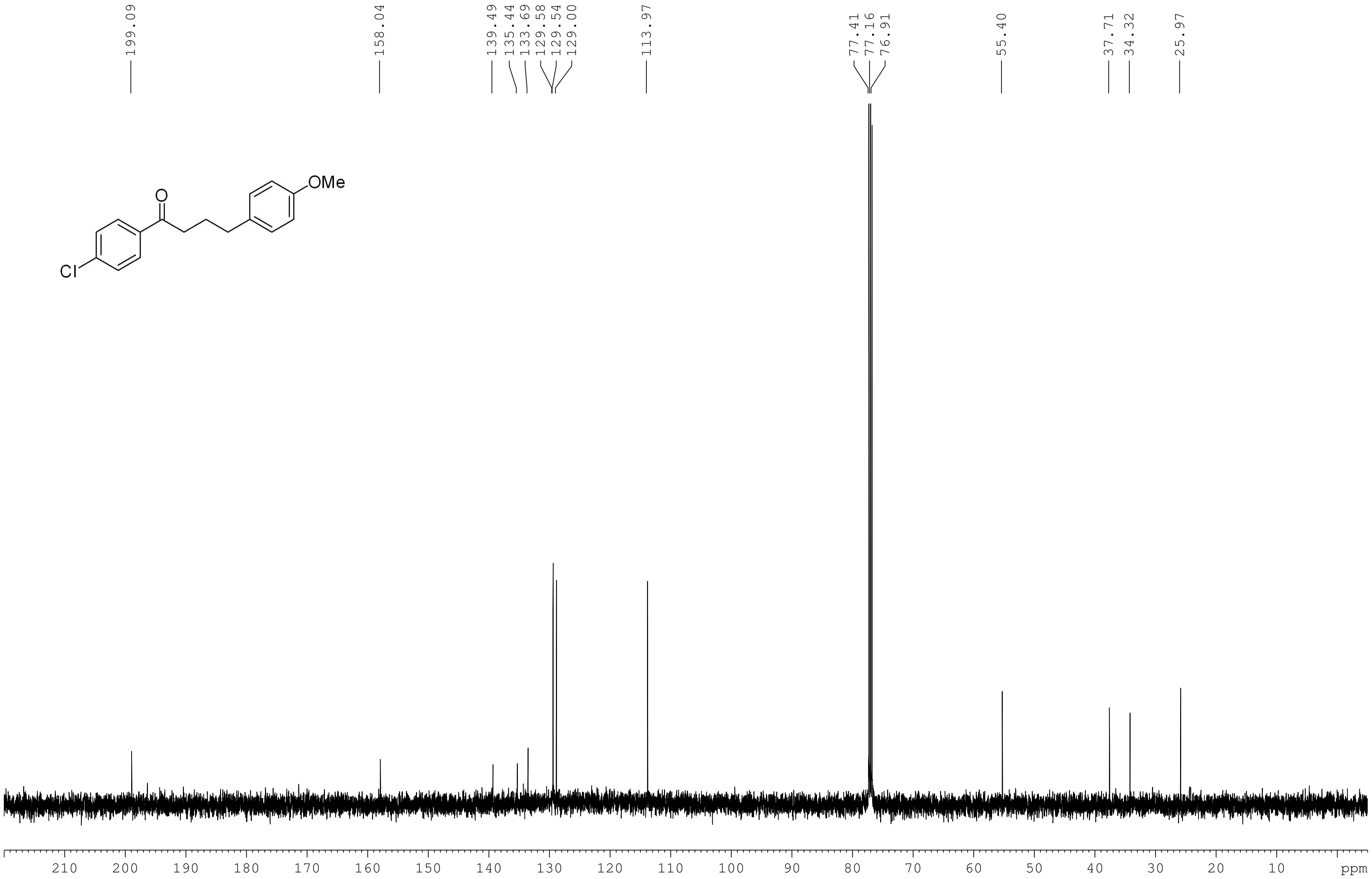
CDCl3, 125 MHz



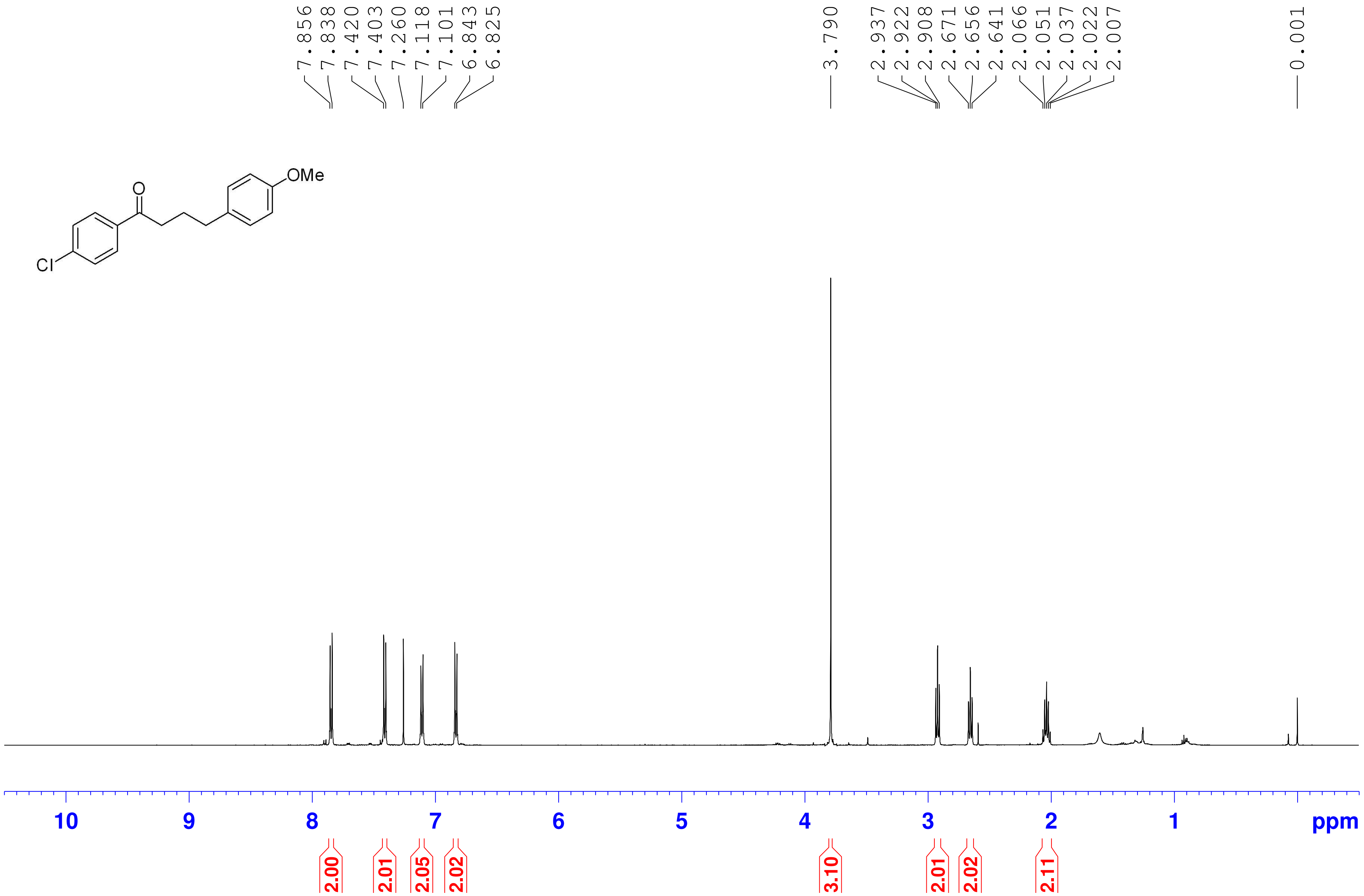
CDCl3,500 MHz



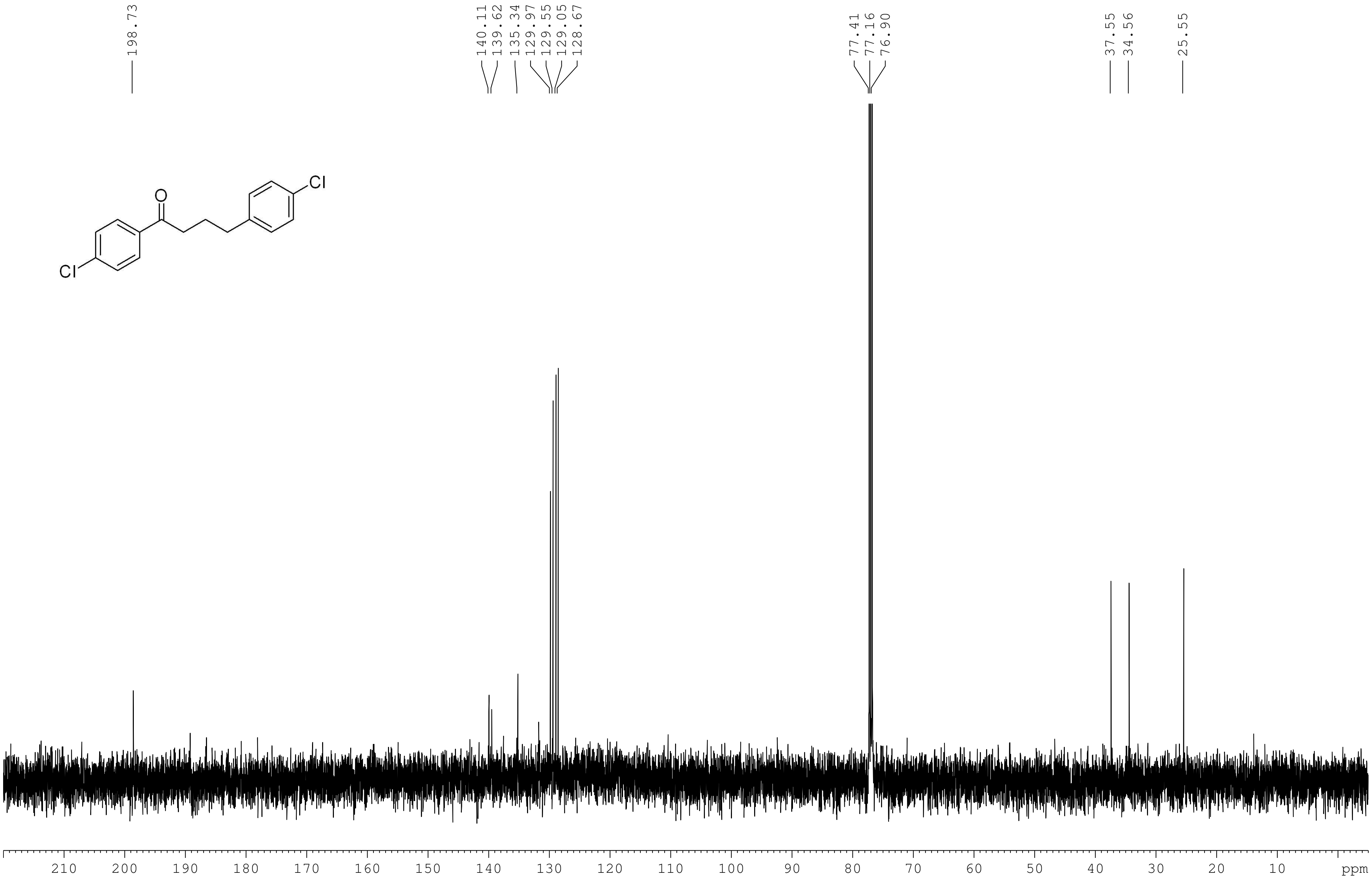
CDCl3, 125 MHz

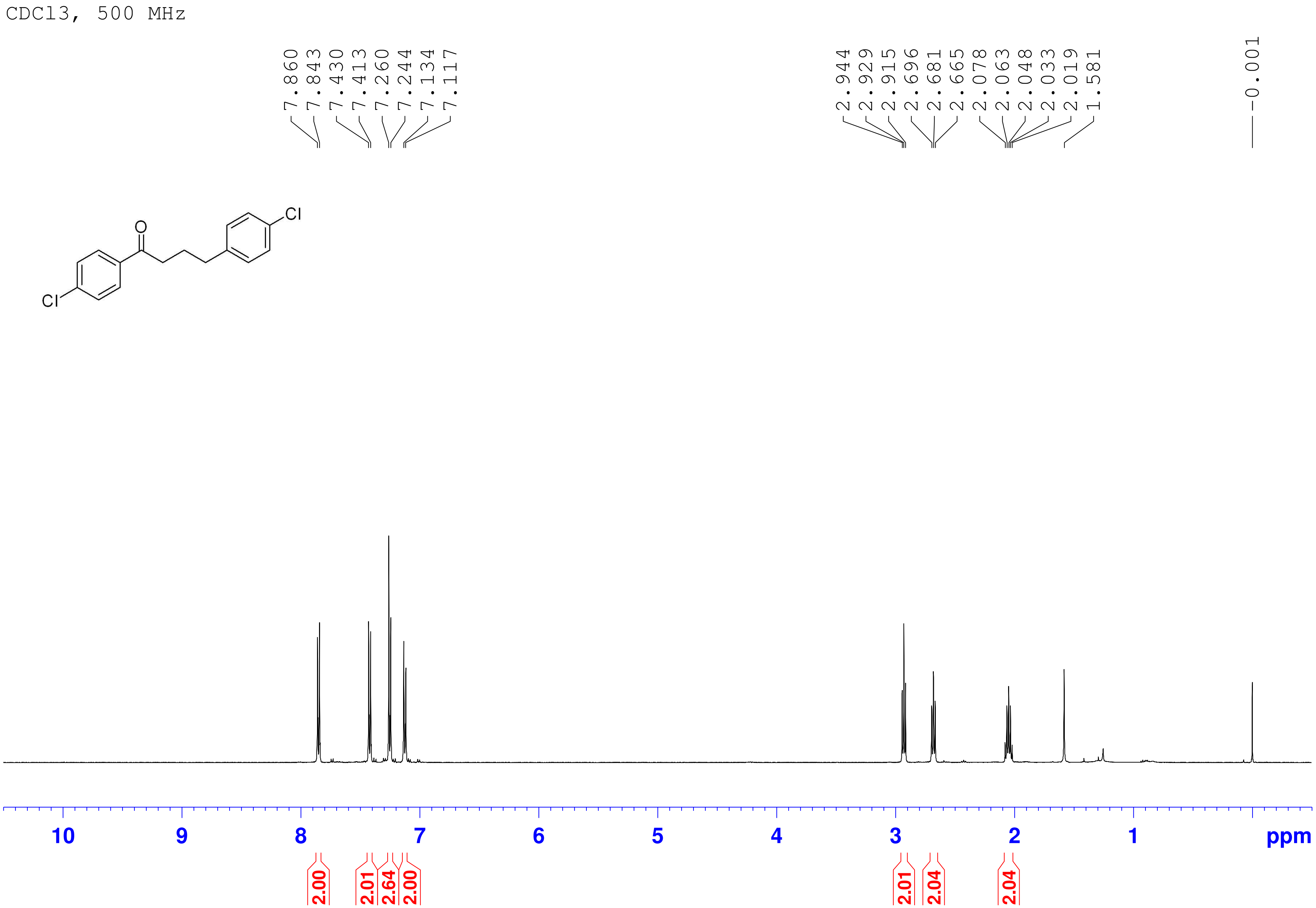


CDCl3, 500 MHz

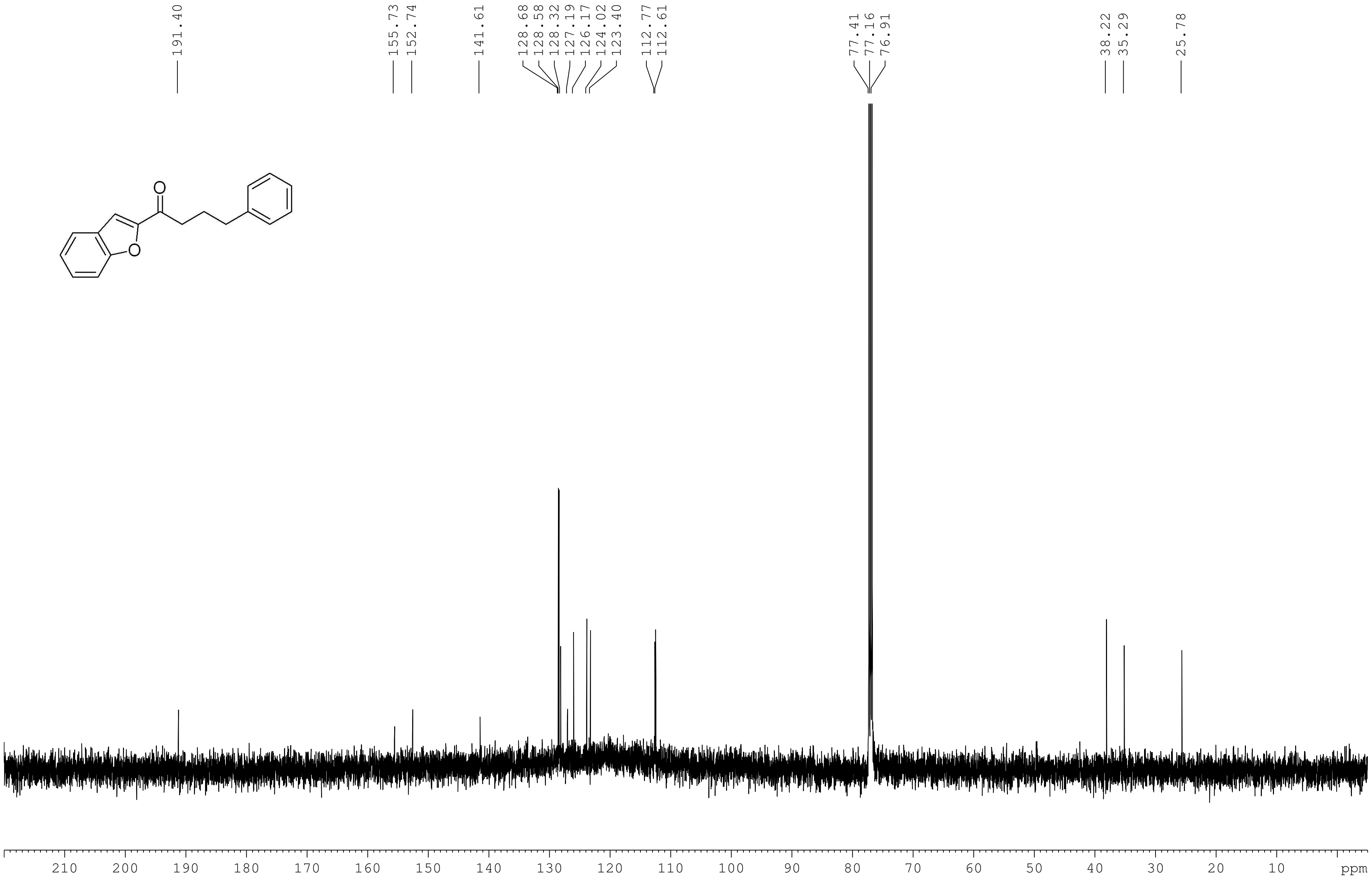


CDCl3, 125 MHz

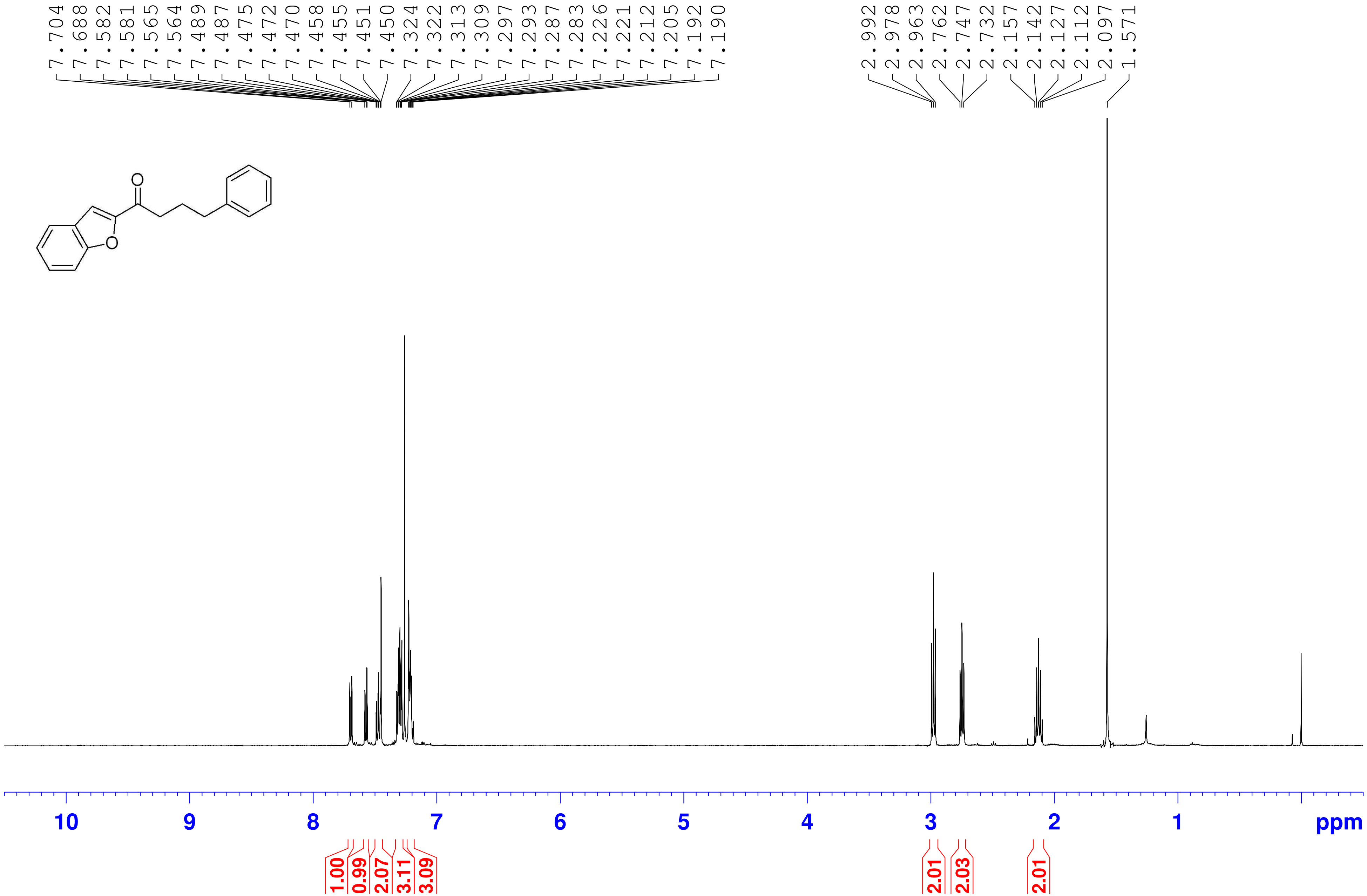



CDCl3, 500 MHz
7.860
7.843
7.430
7.413
7.260
7.244
7.134
7.117
2.944
2.929
2.915
2.696
2.681
2.665
2.078
2.063
2.048
2.033
2.019
1.581
-0.001
O
Cl
Cl
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.01
2.64
2.00
2.01
2.04
2.04

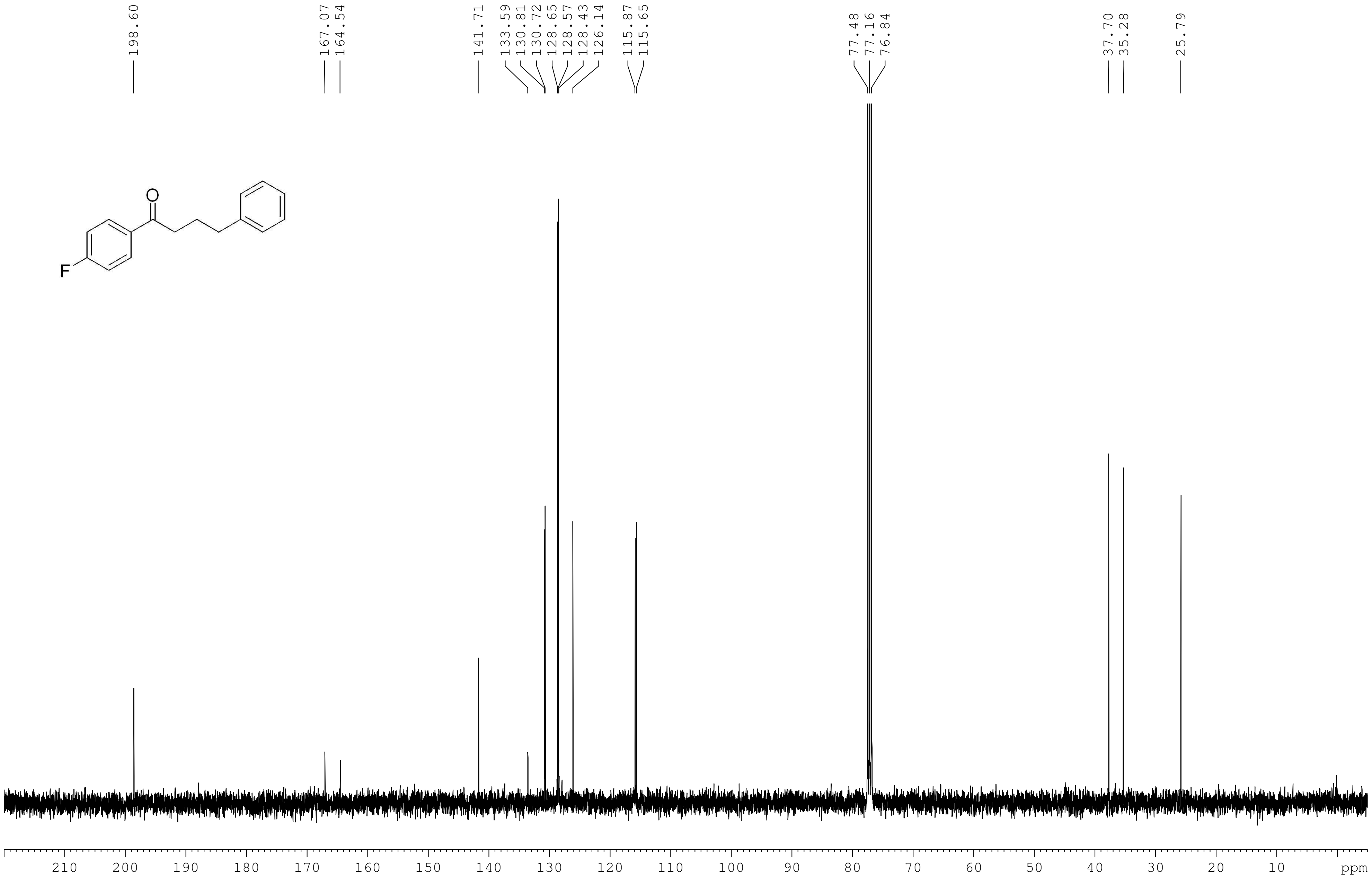
CDCl3, 125 MHz



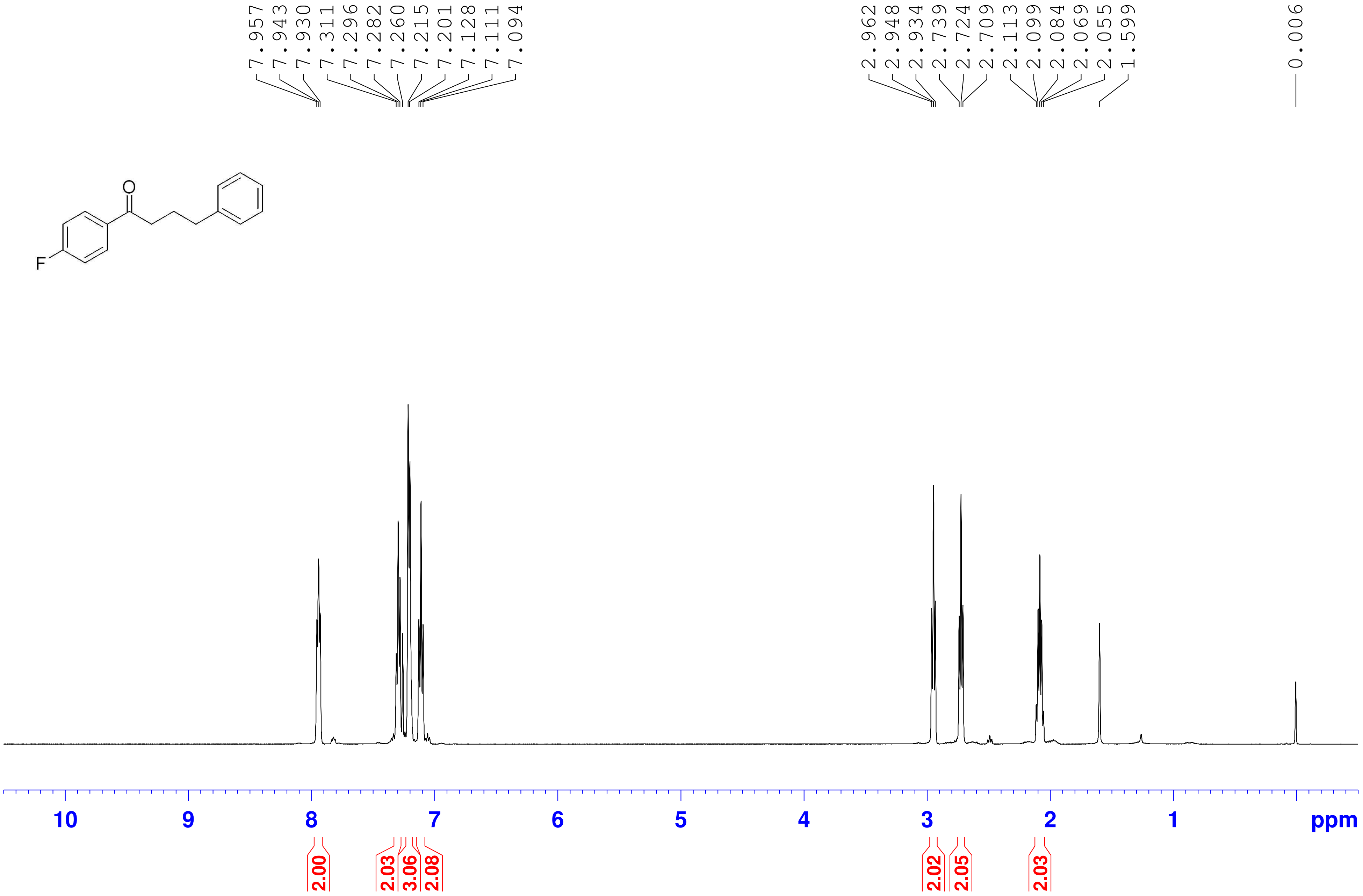
CDCl3, 500 MHz



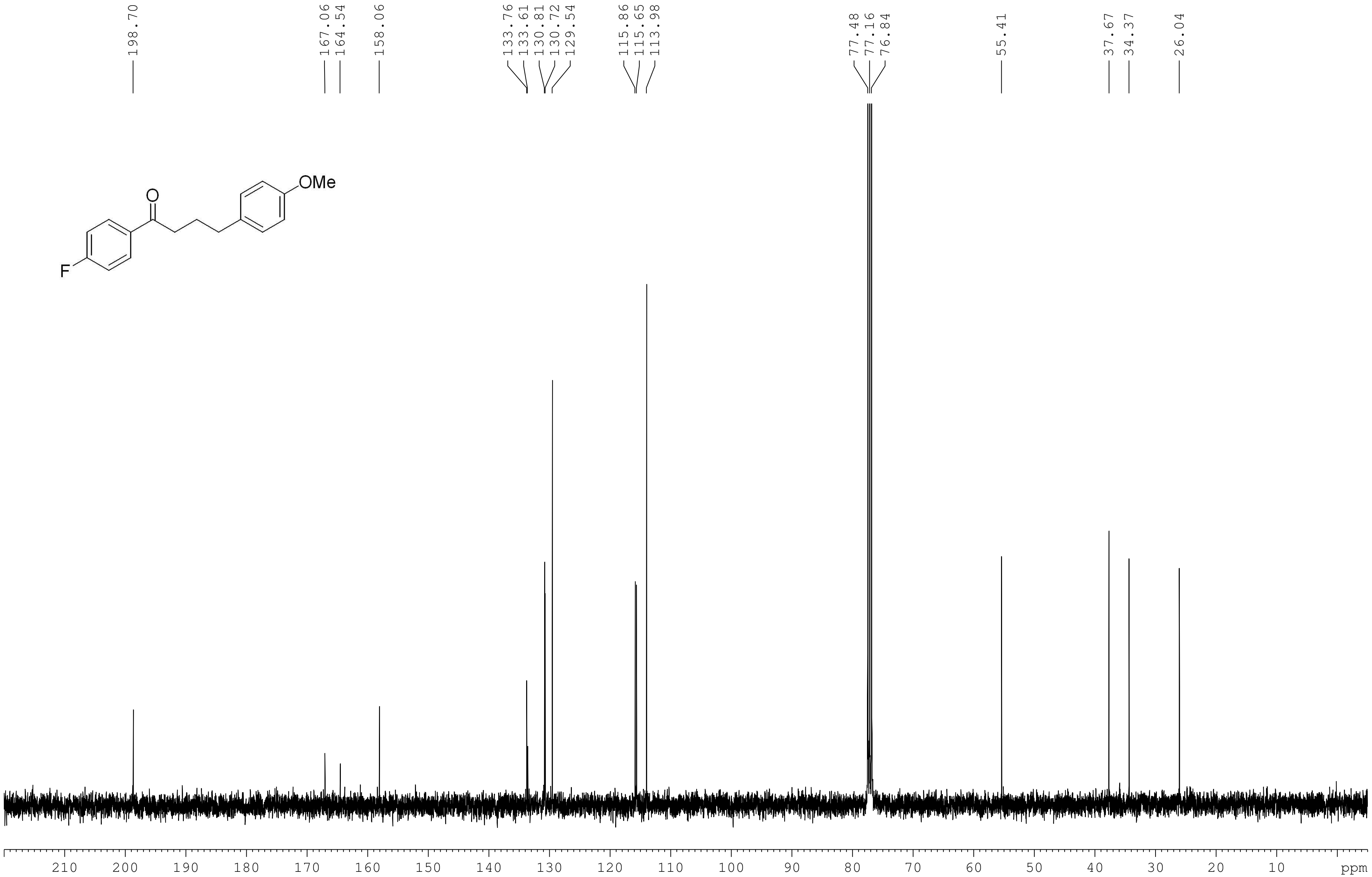
CDCl3, 100 MHz



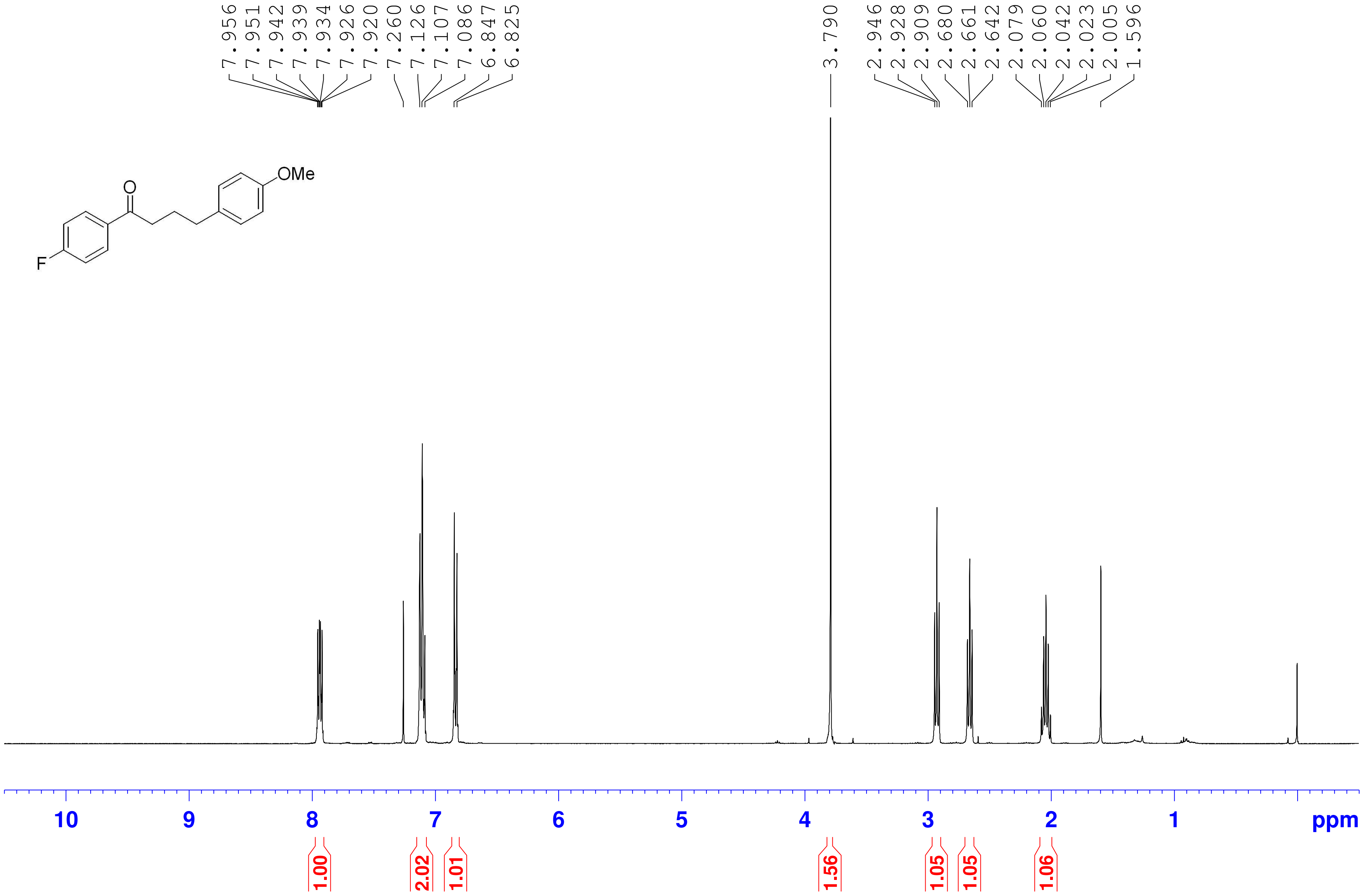
CDCl3, 500 MHz



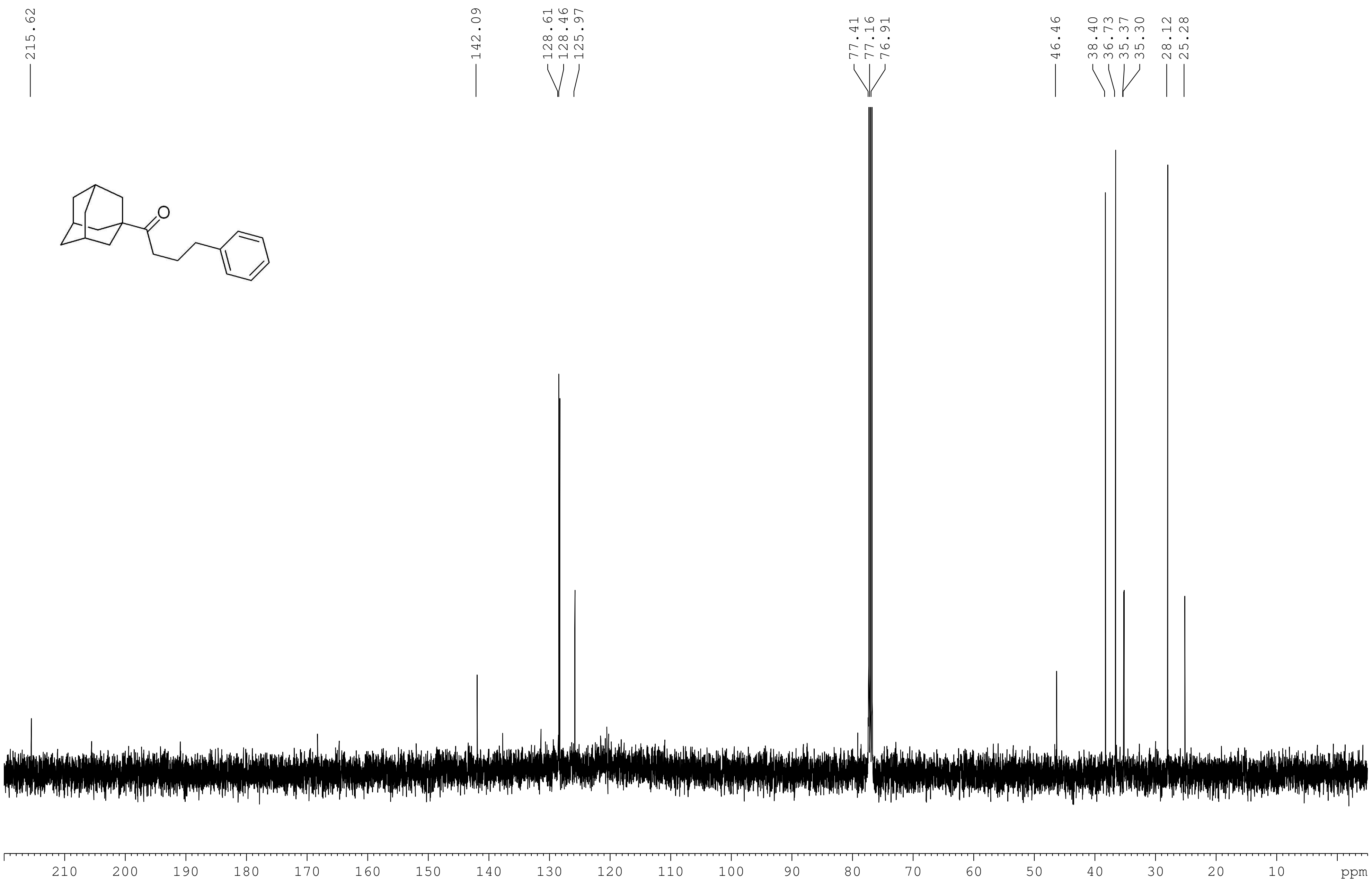
CDCl3, 100 MHz



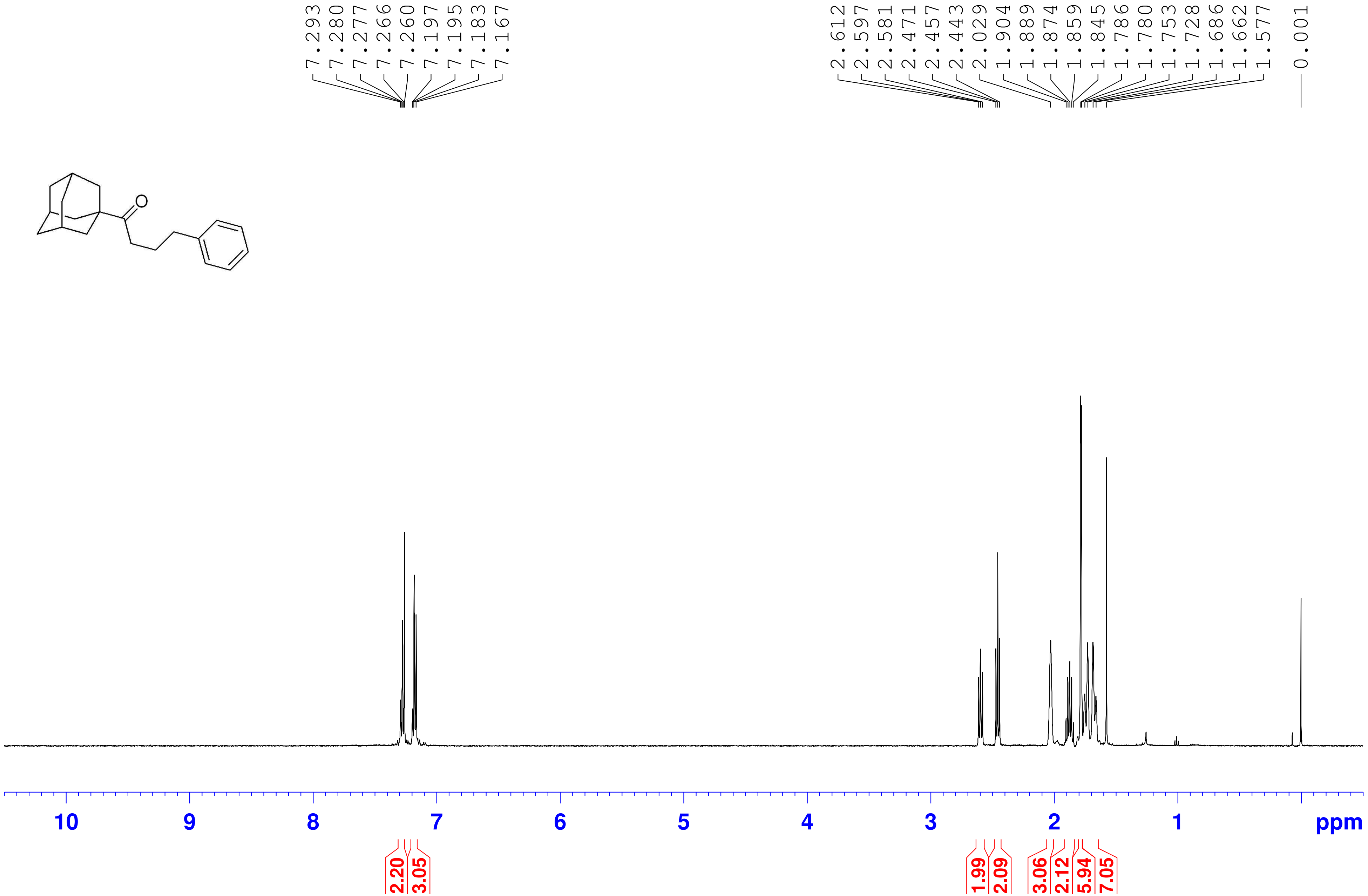
CDCl3, 400 MHz



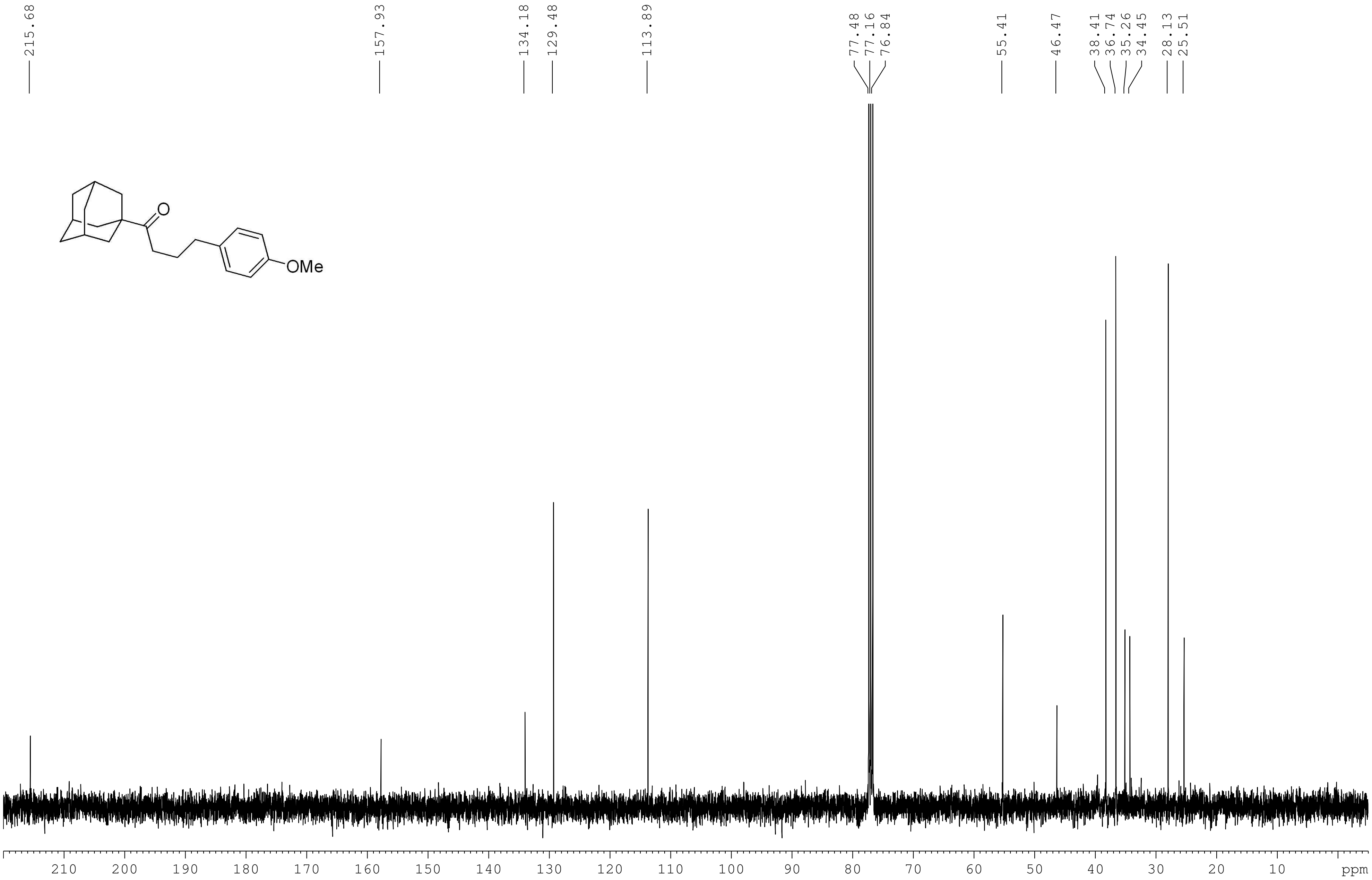
CDCl3, 125 MHz



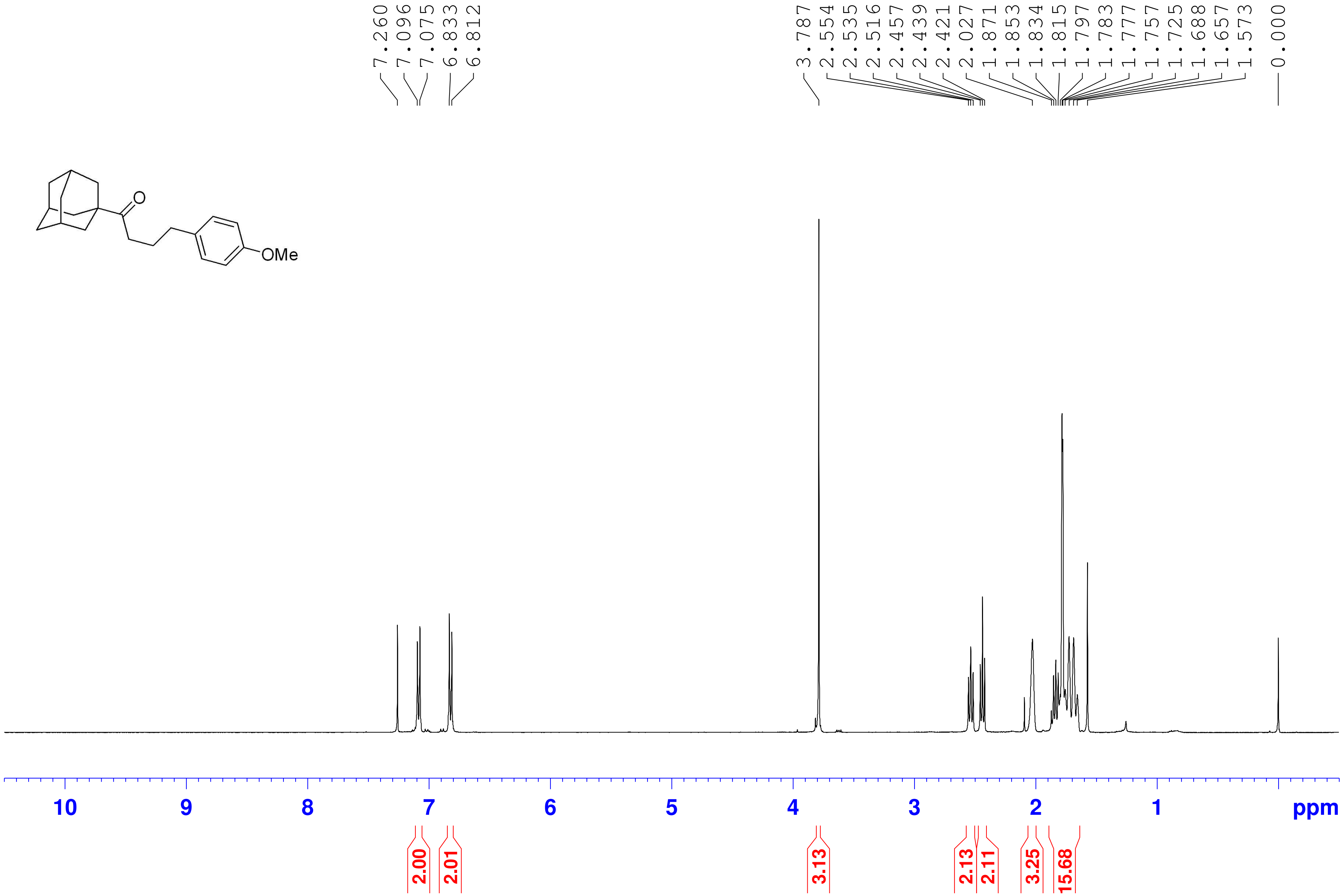
CDCl3, 500 MHz



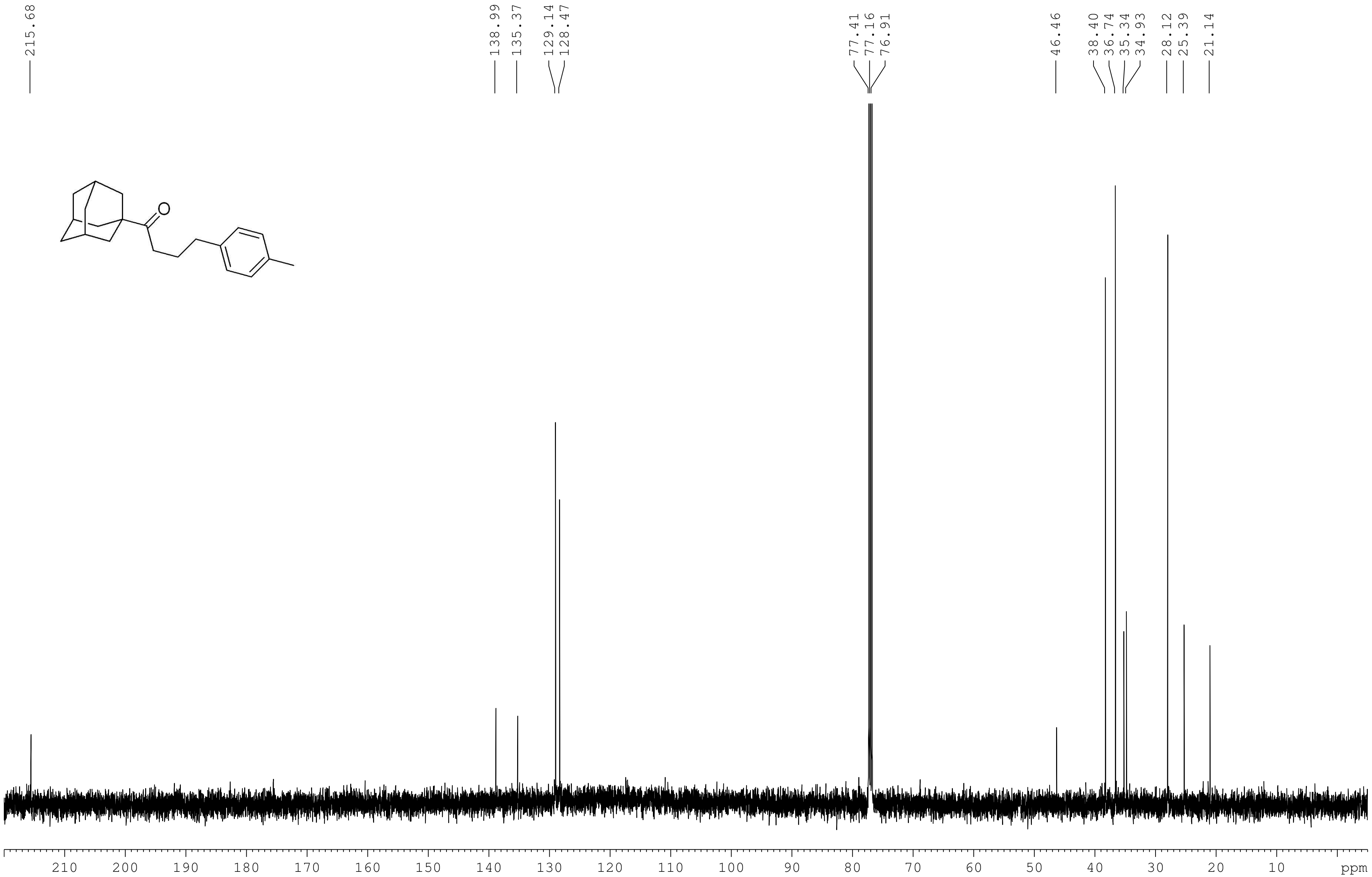
CDCl3, 100 MHz



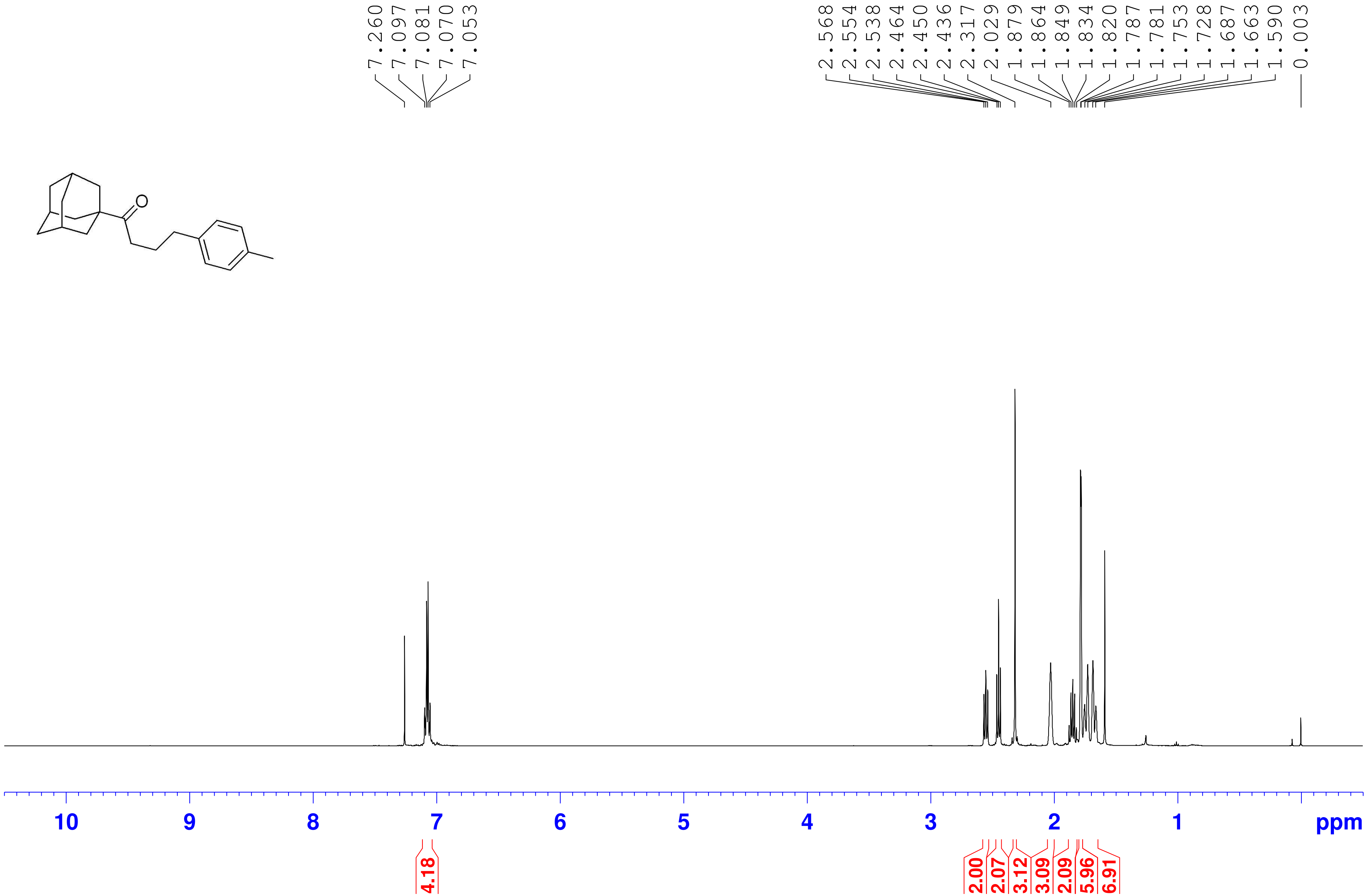
CDCl3, 400 MHz



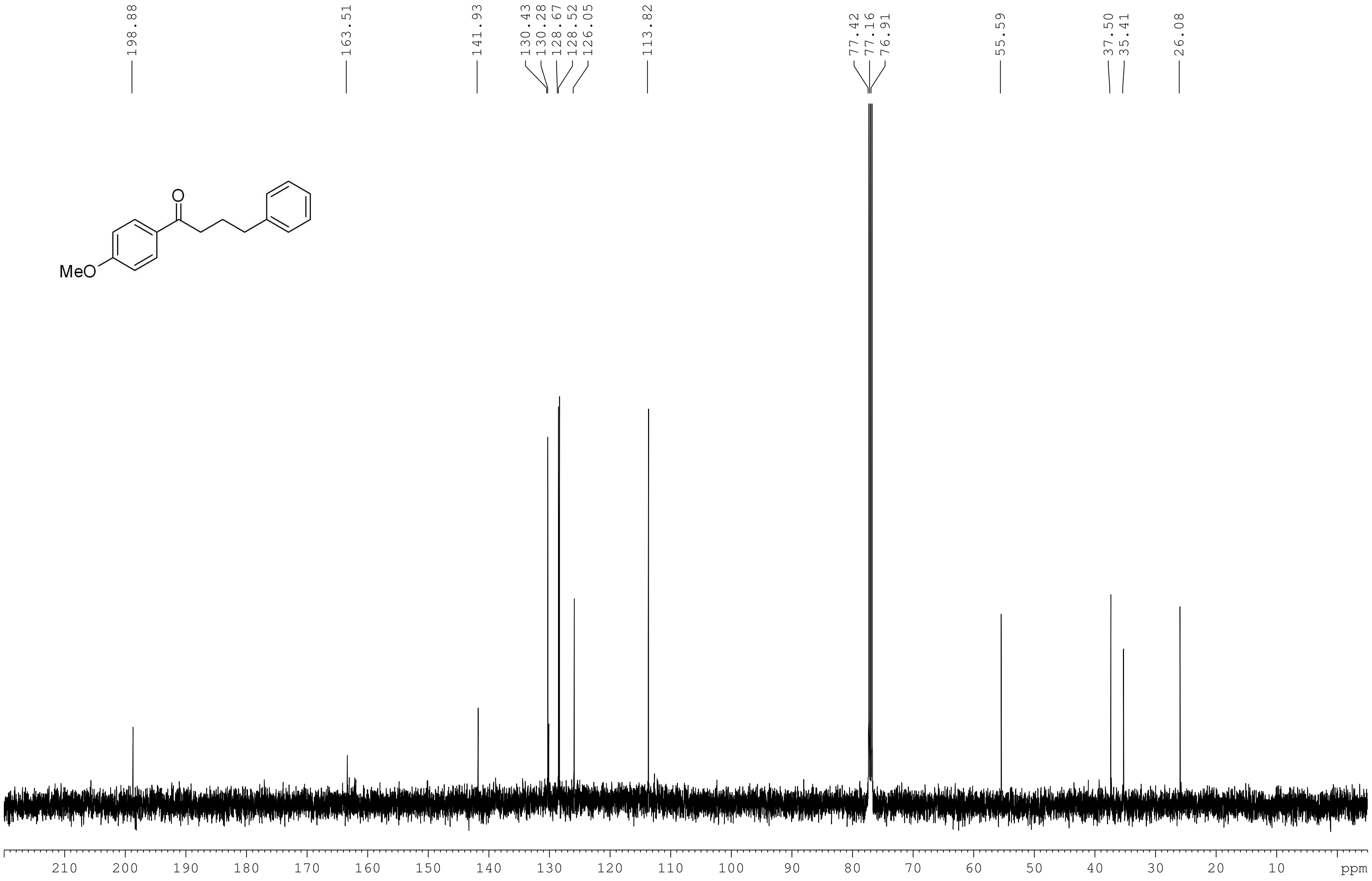
CDCl3, 125 MHz



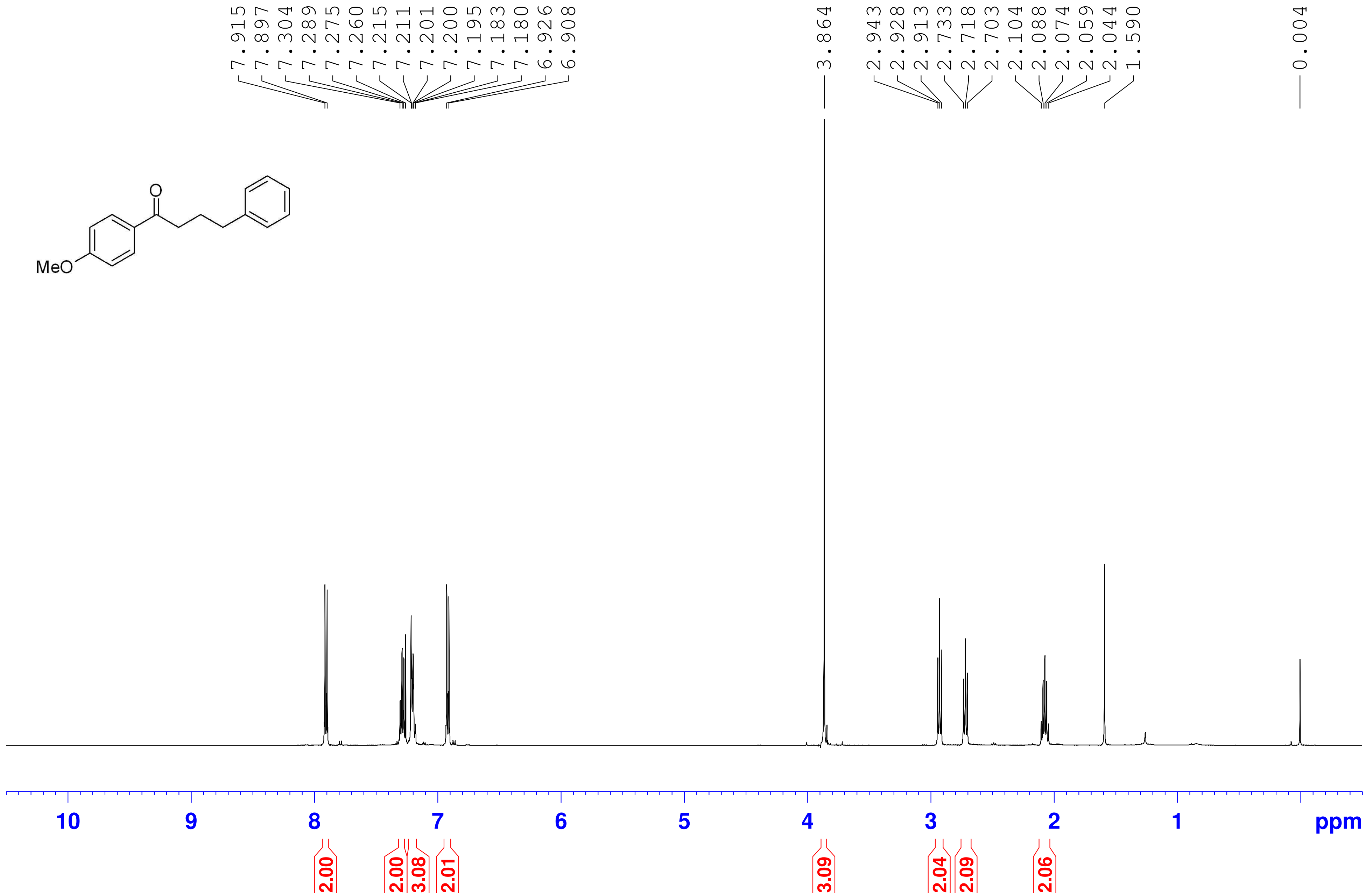
CDCl3, 500 MHz

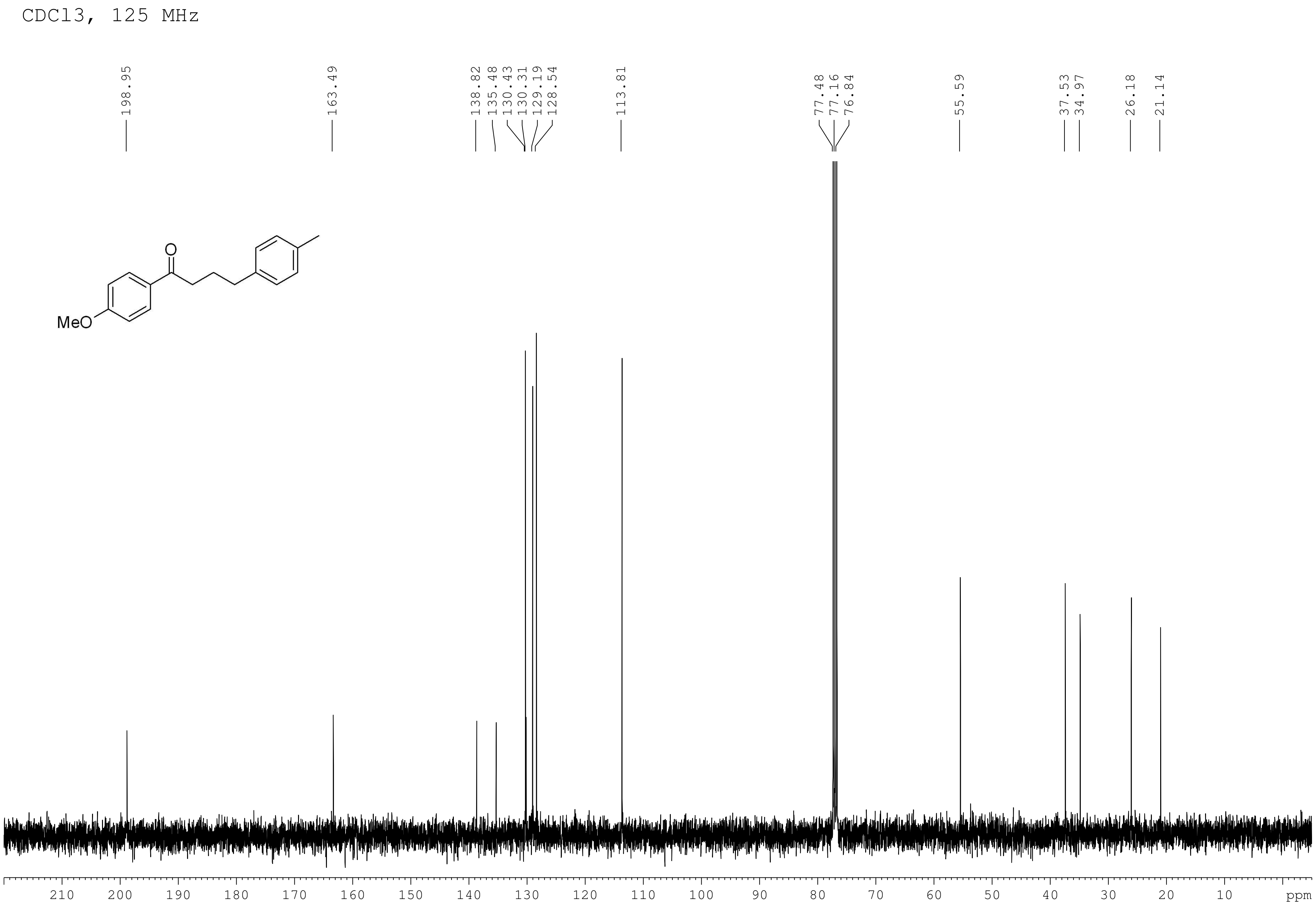


CDCl3, 125 MHz

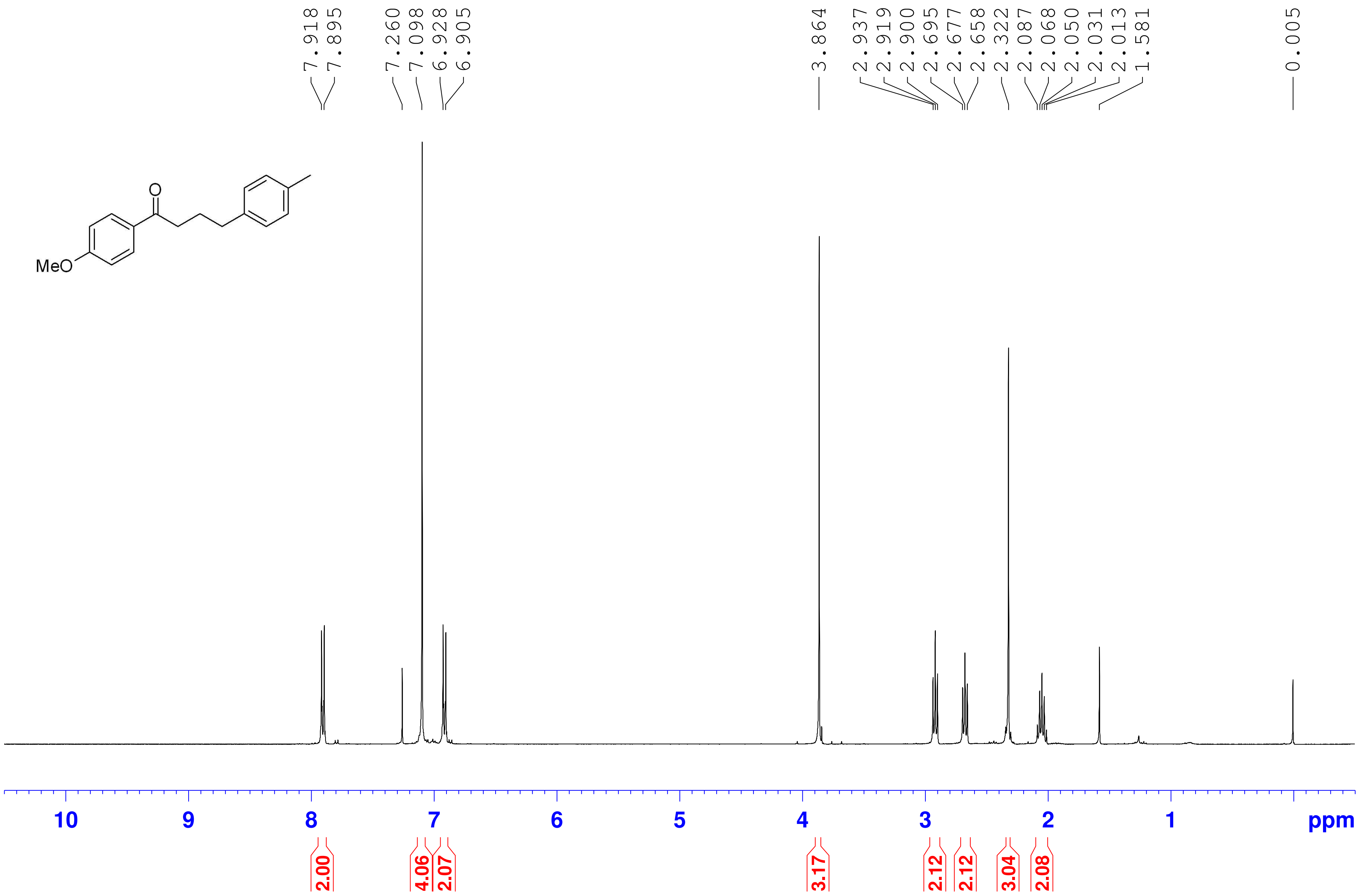


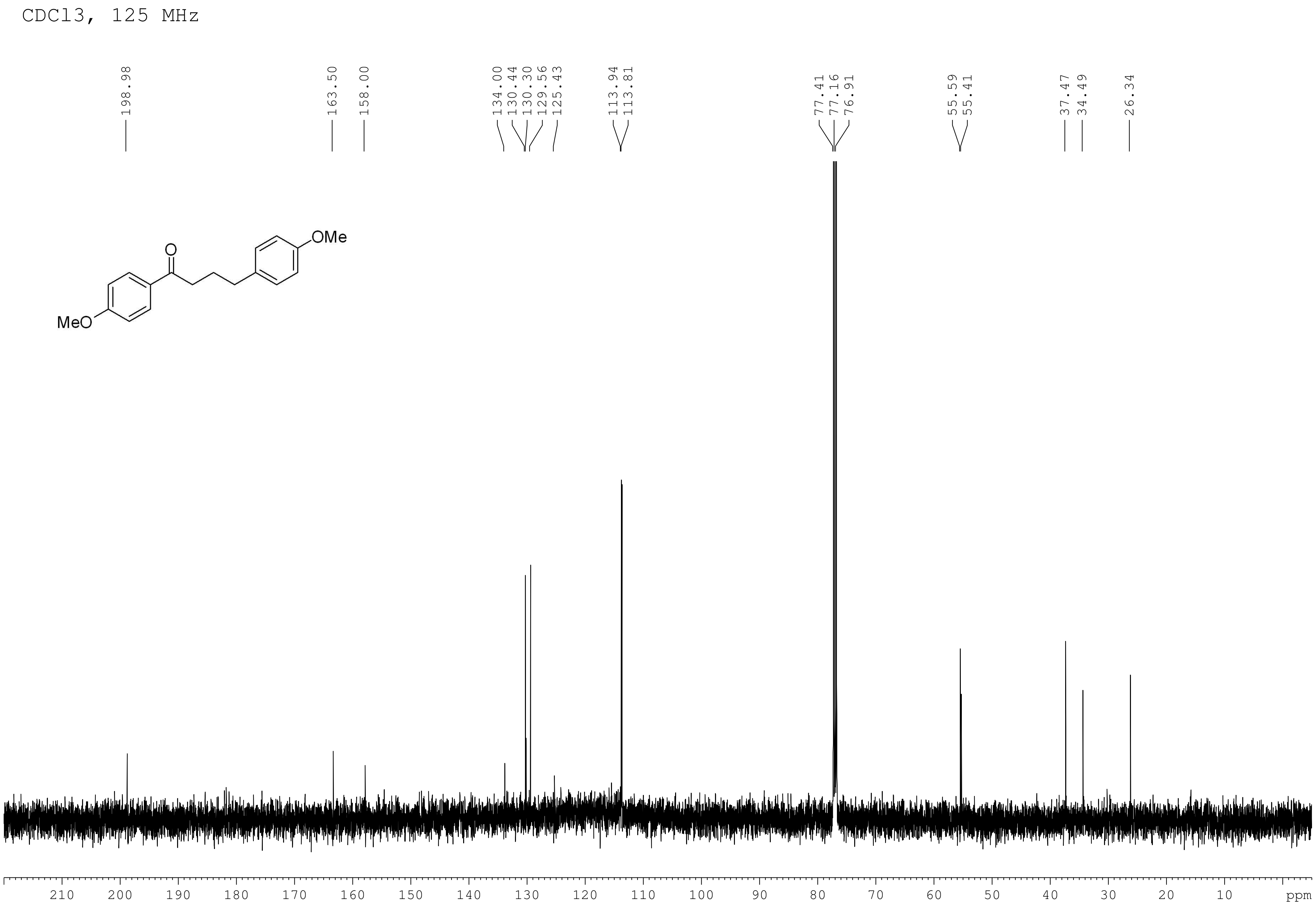
CDCl3, 500 MHz



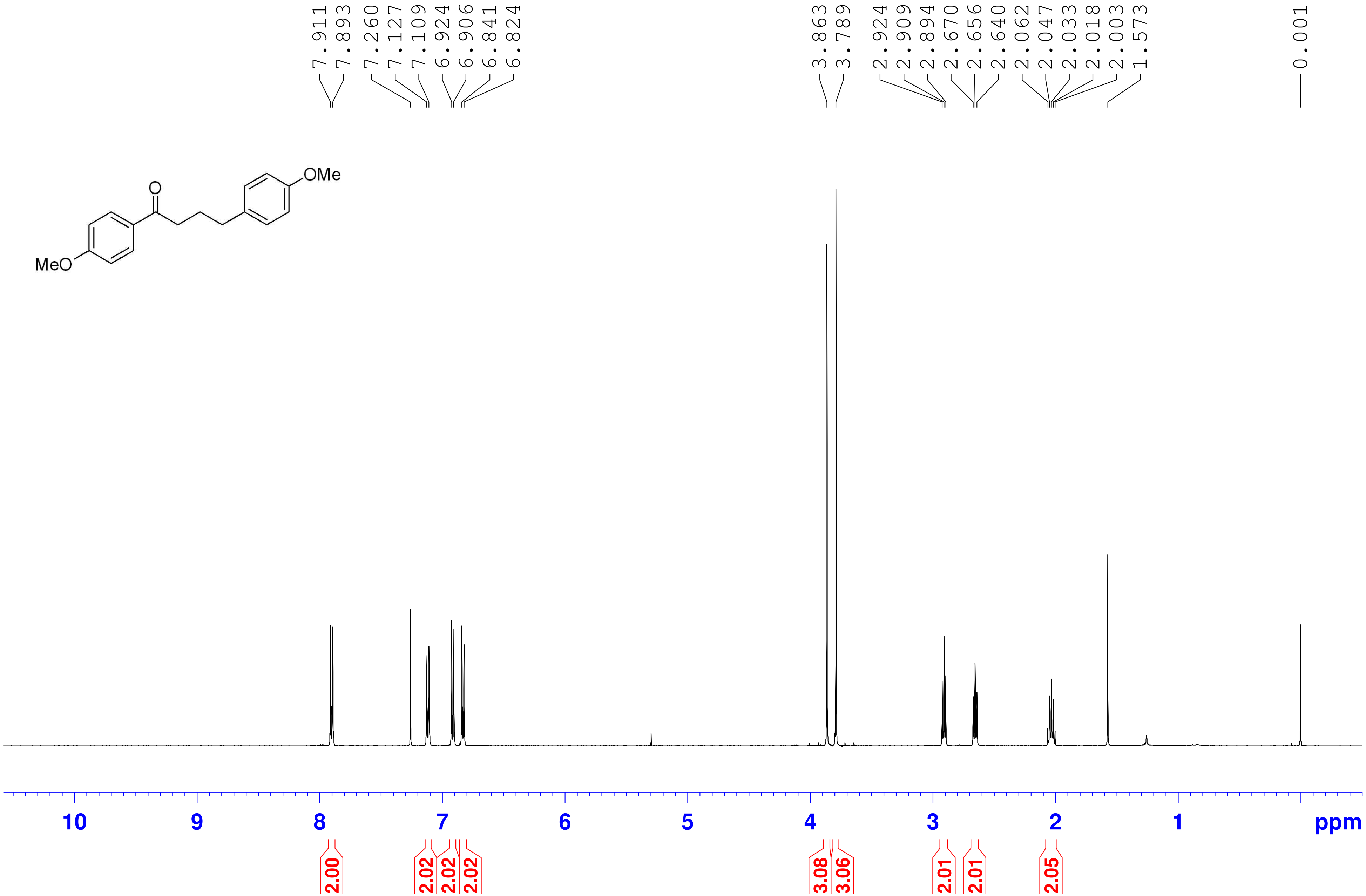

CDCl3, 125 MHz
198.95
163.49
138.82
135.48
130.43
130.31
129.19
128.54
113.81
77.48
77.16
76.84
55.59
37.53
34.97
26.18
21.14
O
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CDCl3, 400 MHz

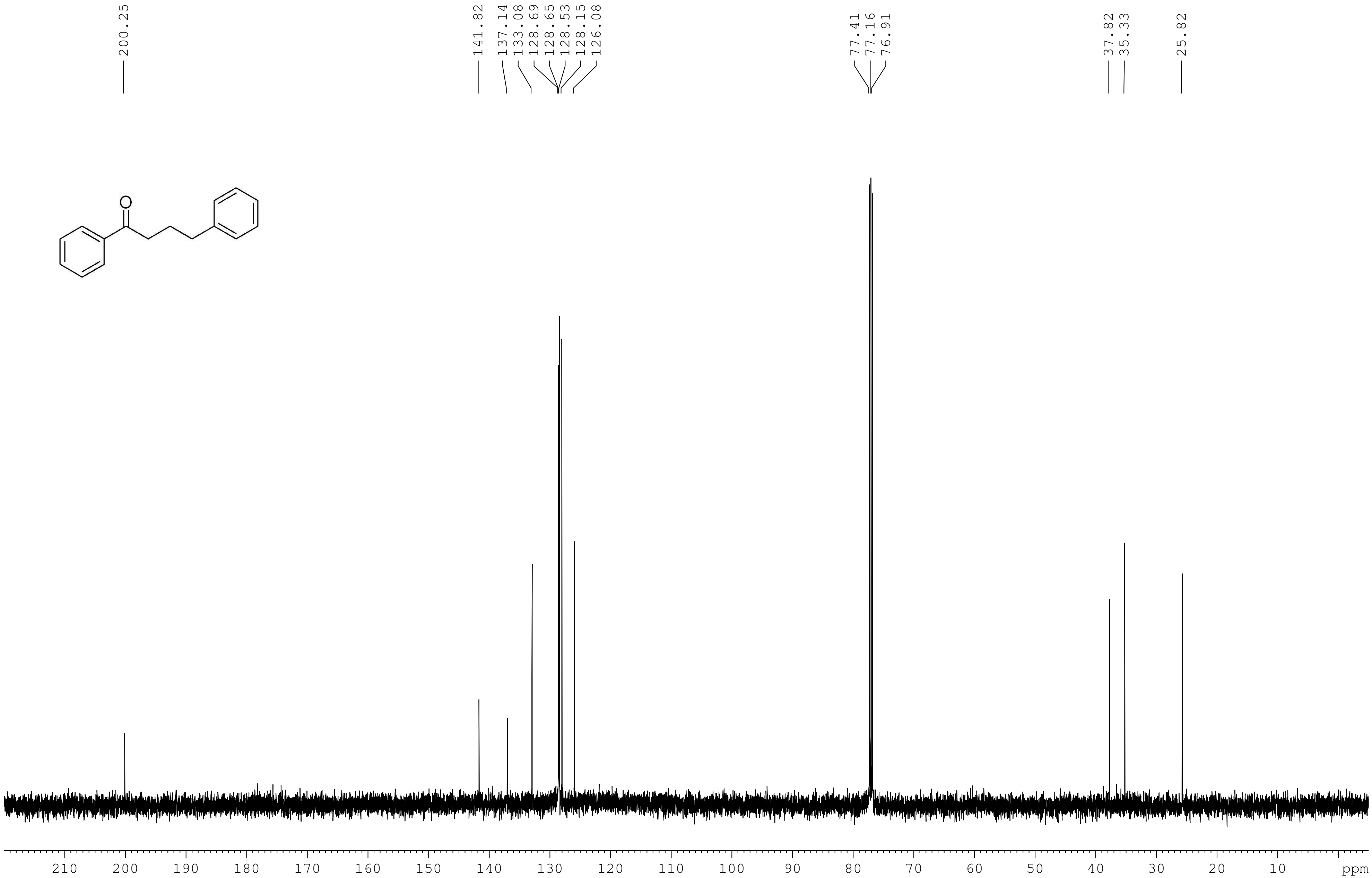


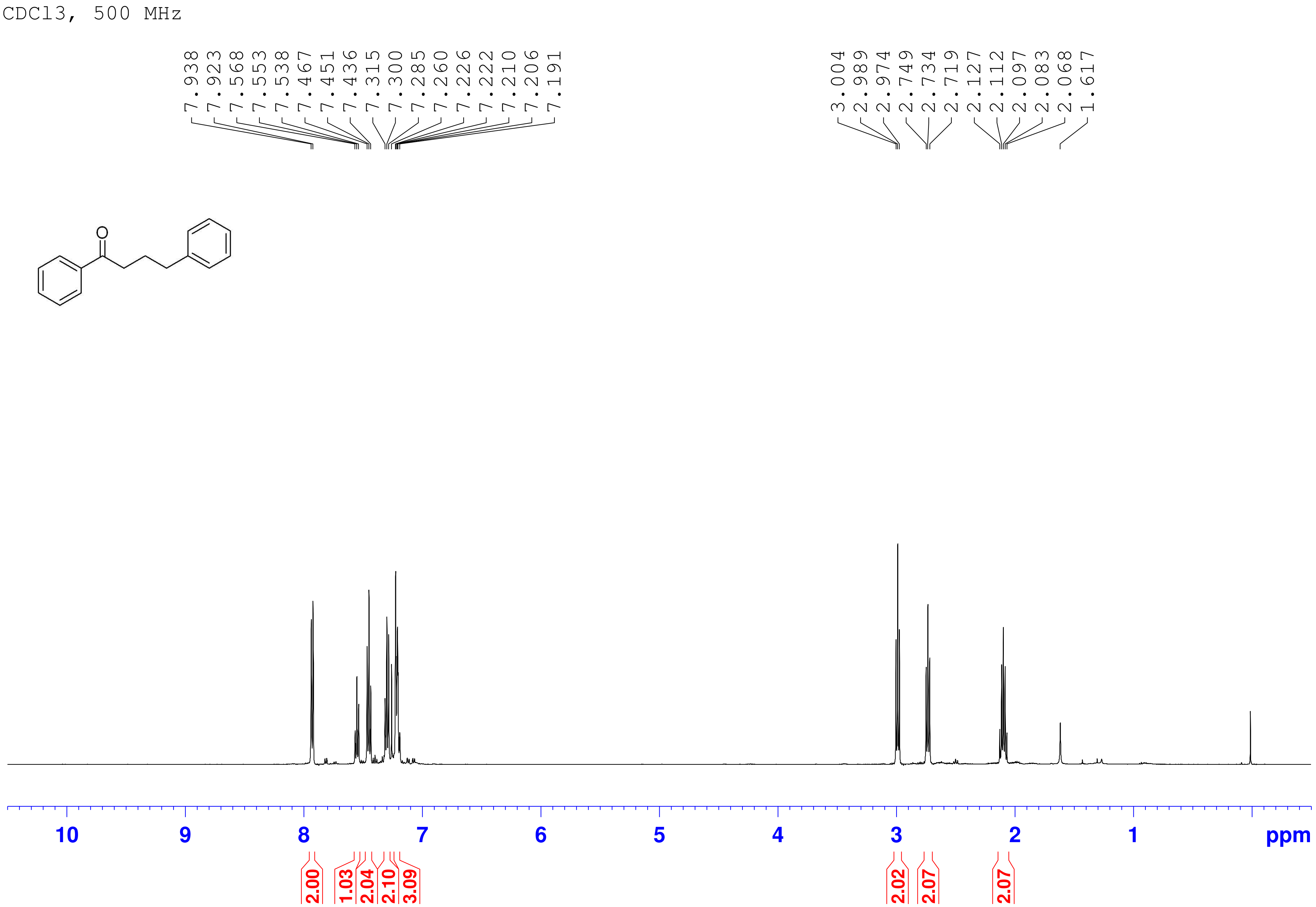

CDCl3, 125 MHz
198.98
163.50
158.00
134.00
130.44
130.30
129.56
125.43
113.94
113.81
77.41
77.16
76.91
55.59
55.41
37.47
34.49
26.34
O
OMe
MeO
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

CDCl3, 500 MHz

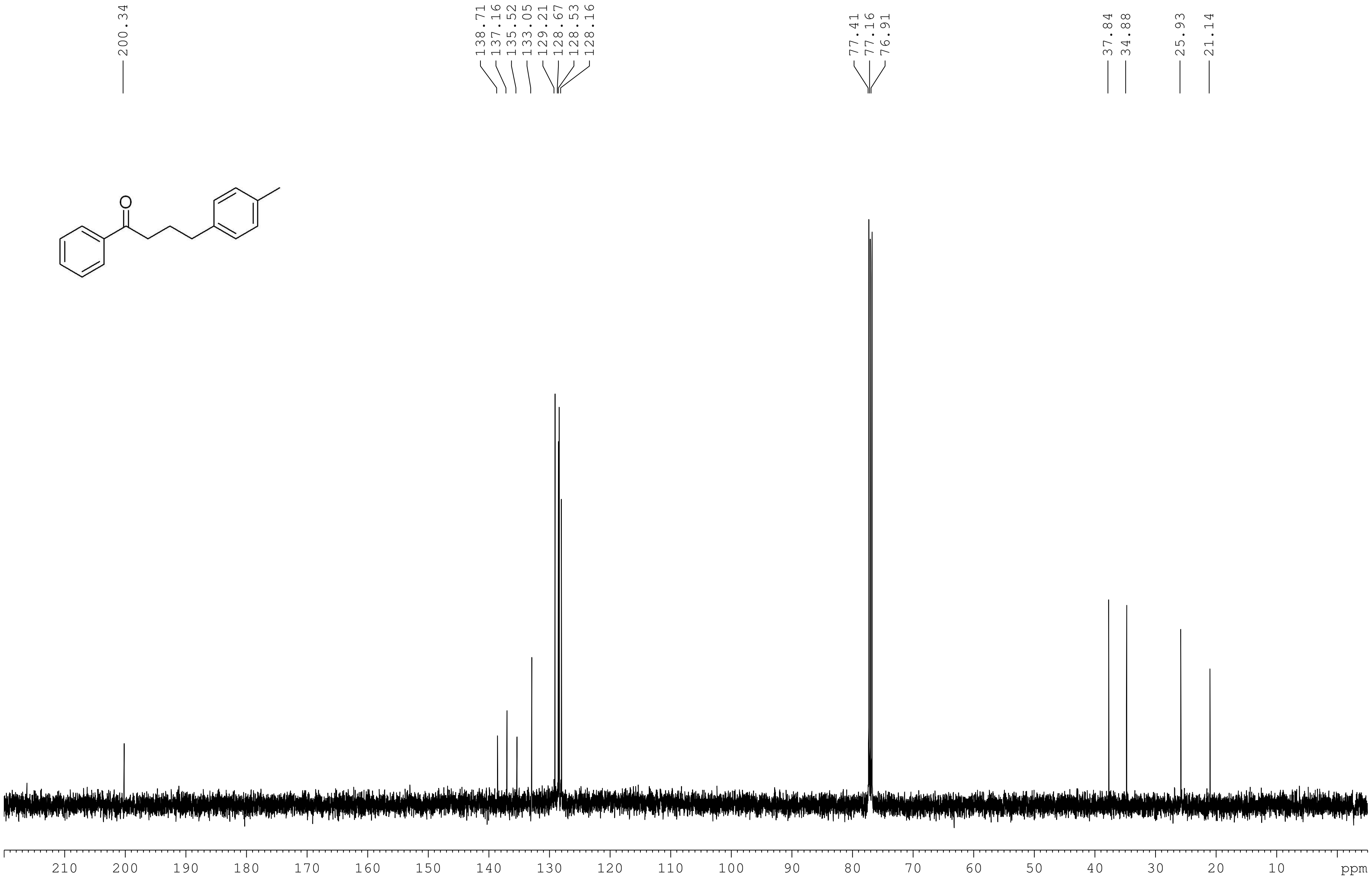


CDCl3, 125 MHz

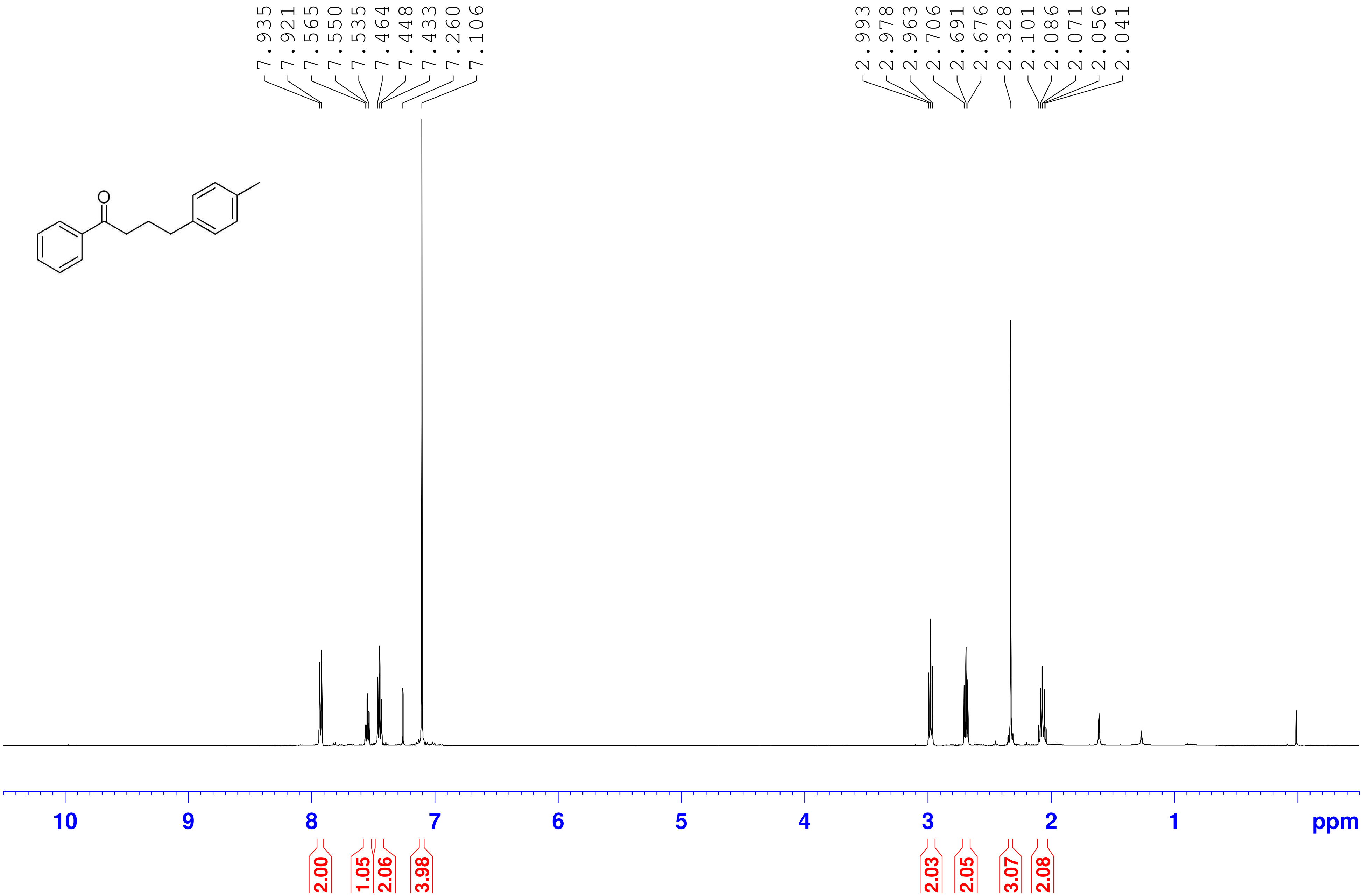


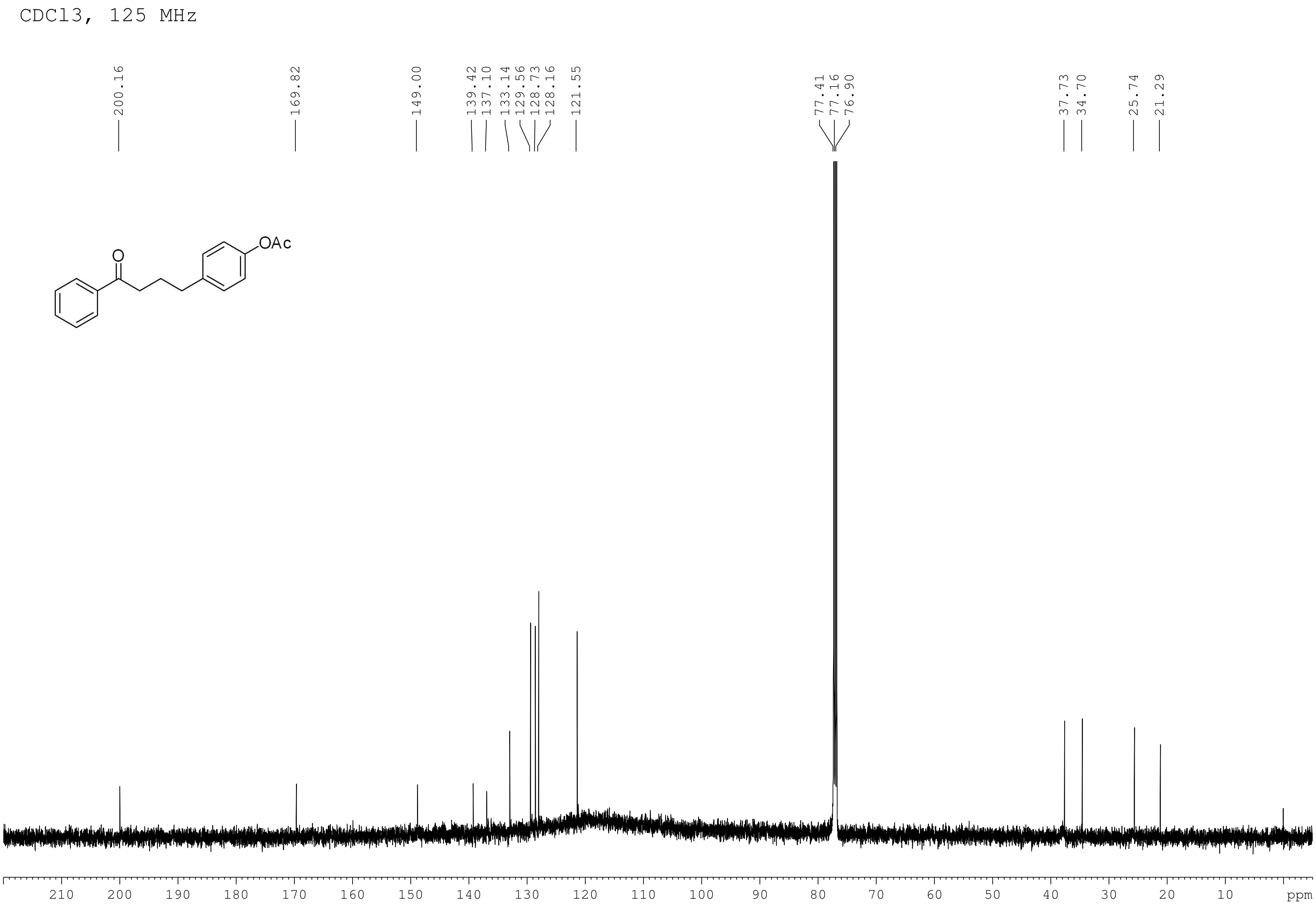

CDCl3, 500 MHz
7.938
7.923
7.568
7.553
7.538
7.467
7.451
7.436
7.315
7.300
7.285
7.260
7.226
7.222
7.210
7.206
7.191
3.004
2.989
2.974
2.749
2.734
2.719
2.127
2.112
2.097
2.083
2.068
1.617
O
10
9
8
7
6
5
4
3
2
1
ppm
2.00
1.03
2.04
2.10
3.09
2.02
2.07
2.07

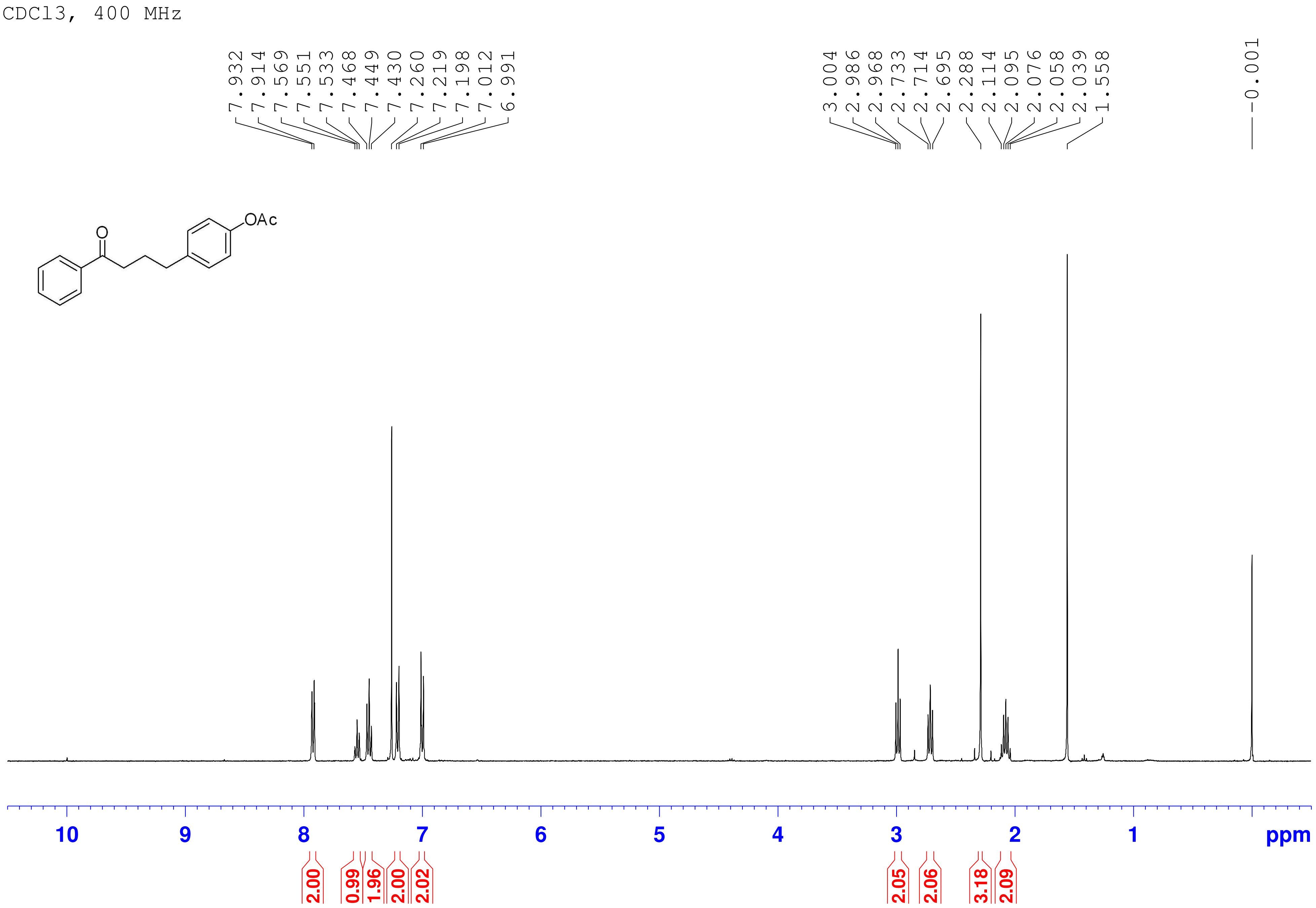
$CDCl_3$, 125 MHz



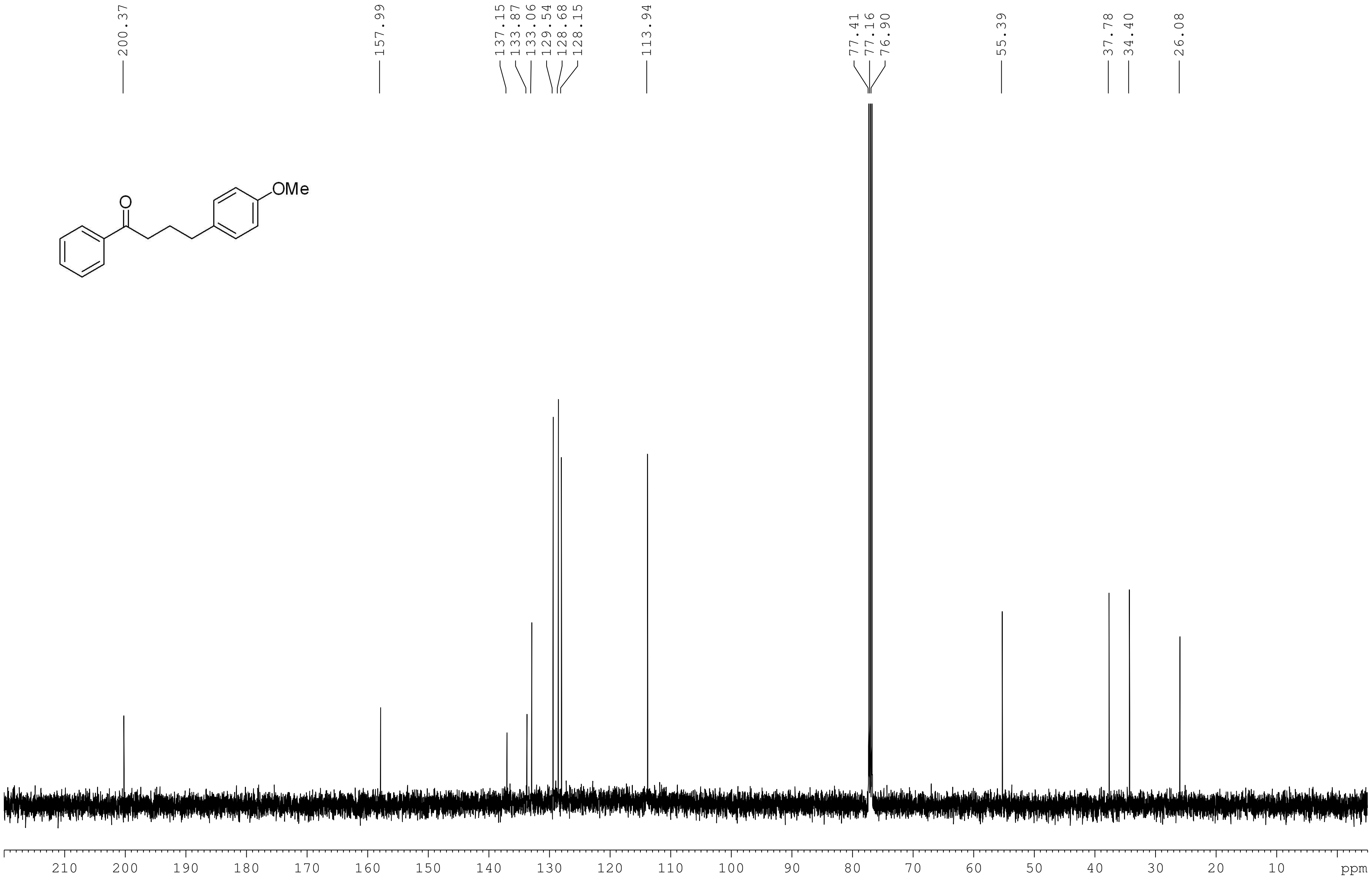
CDCl3, 500 MHz



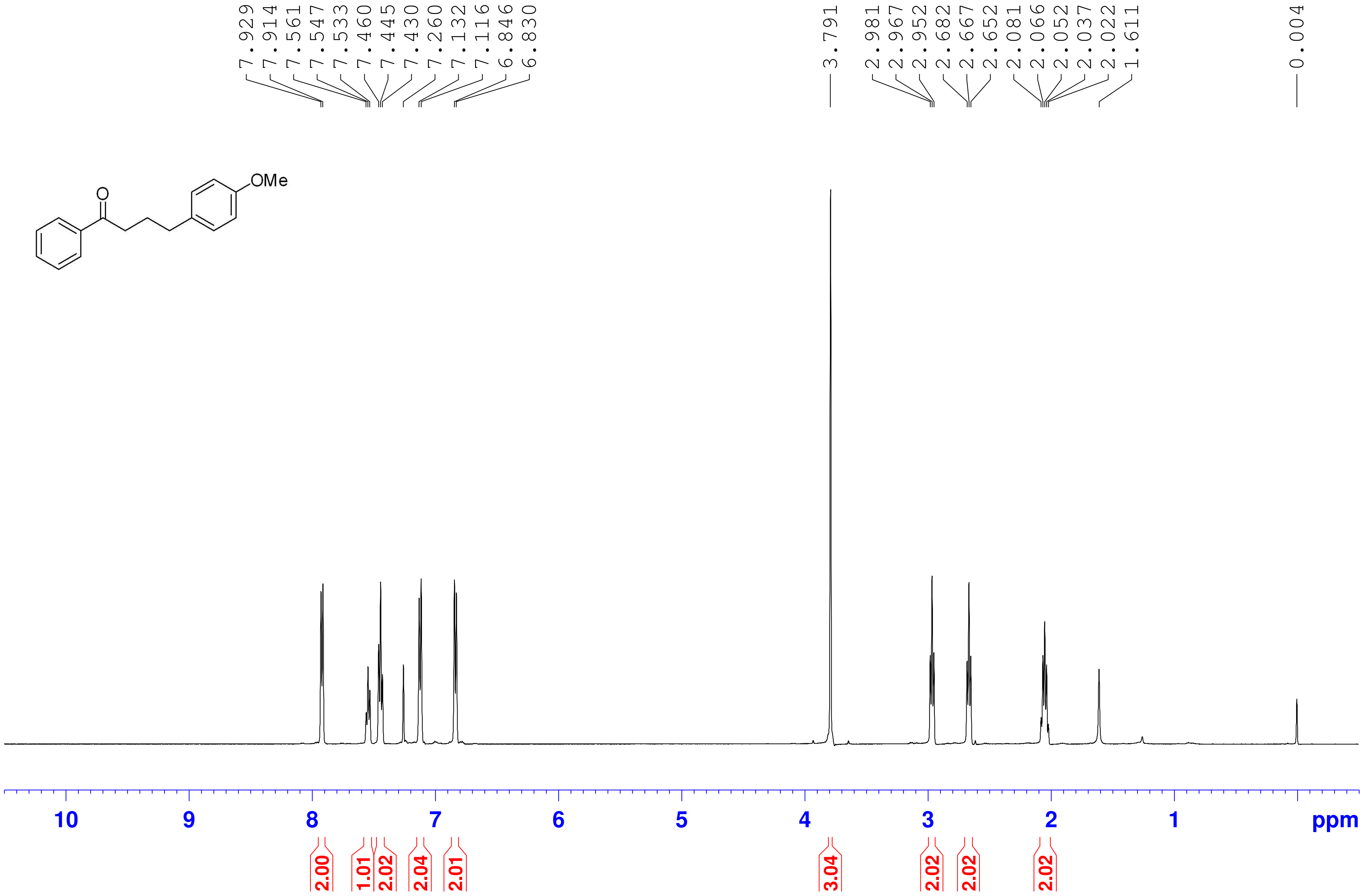

CDCl3, 125 MHz
200.16
169.82
149.00
139.42
137.10
133.14
129.56
128.73
128.16
121.55
77.41
77.16
76.90
37.73
34.70
25.74
21.29
O
OAc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


CDCl3, 400 MHz
7.932
7.914
7.569
7.551
7.533
7.468
7.449
7.430
7.260
7.219
7.198
7.012
6.991
3.004
2.986
2.968
2.733
2.714
2.695
2.288
2.114
2.095
2.076
2.058
2.039
1.558
-0.001
O
OAc
10
9
8
7
6
5
4
3
2
1
ppm
2.00
0.99
1.96
2.00
2.02
2.05
2.06
3.18
2.09

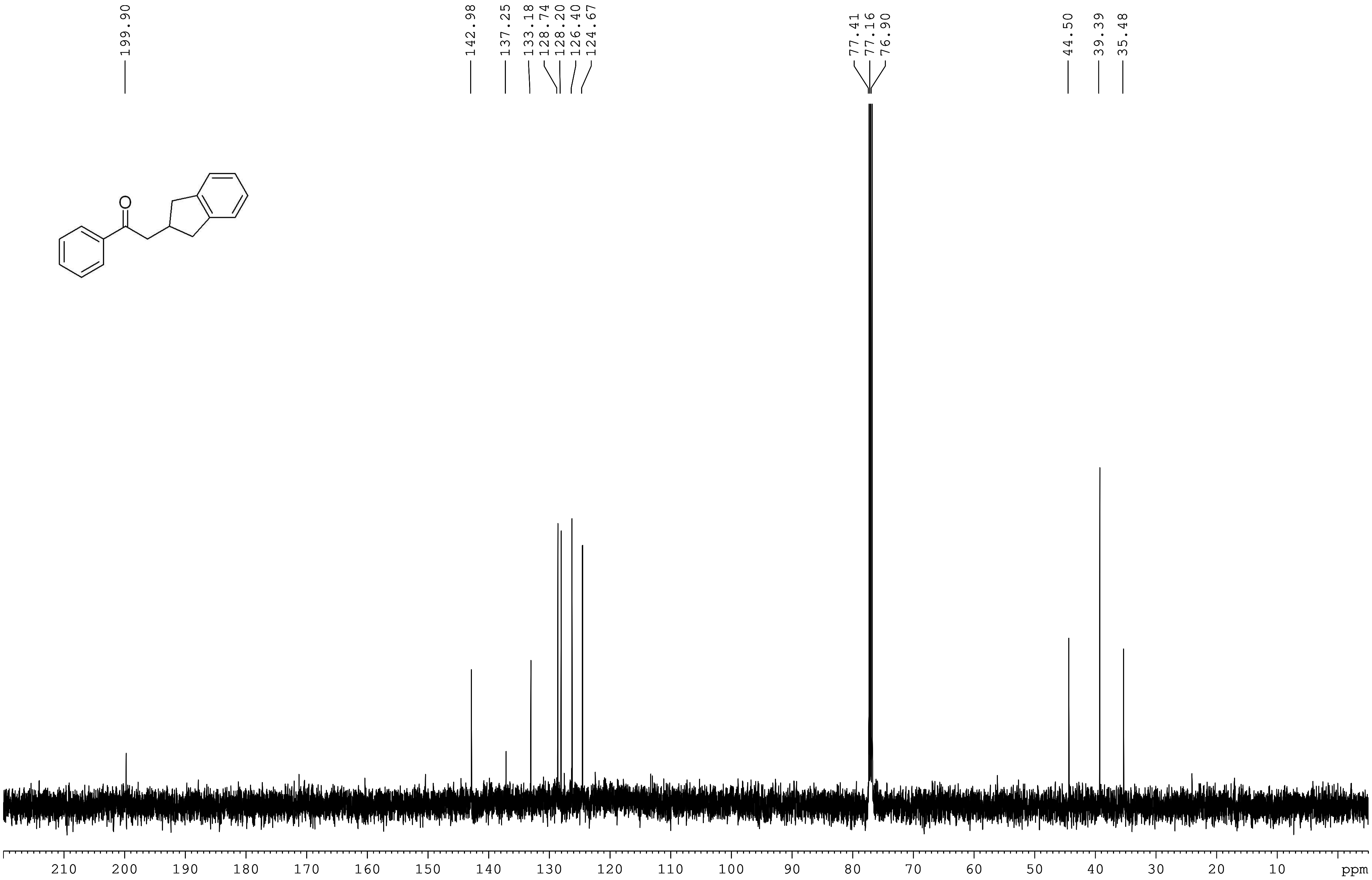
CDCl3, 125 MHz



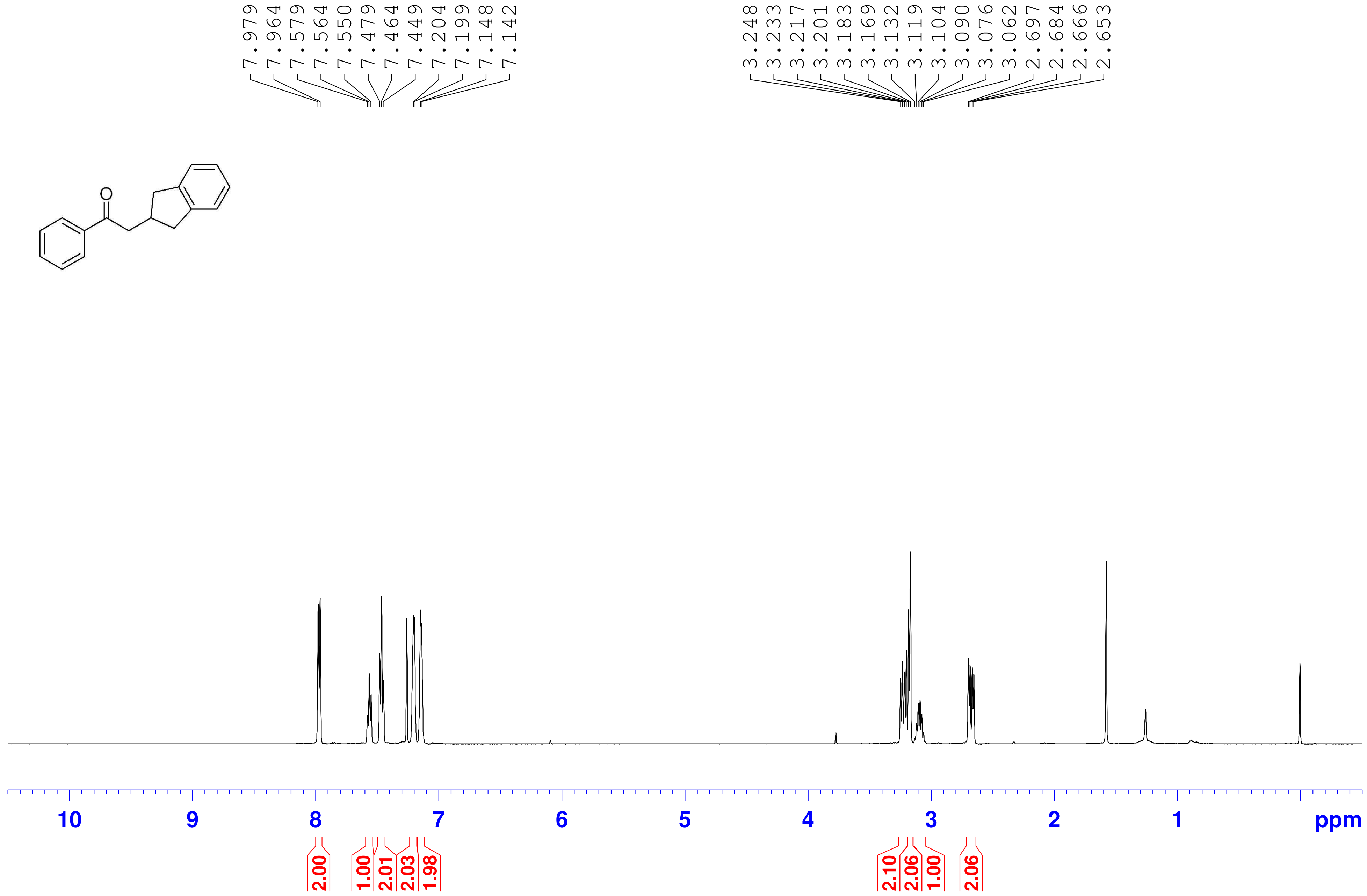
CDCl3, 500 MHz



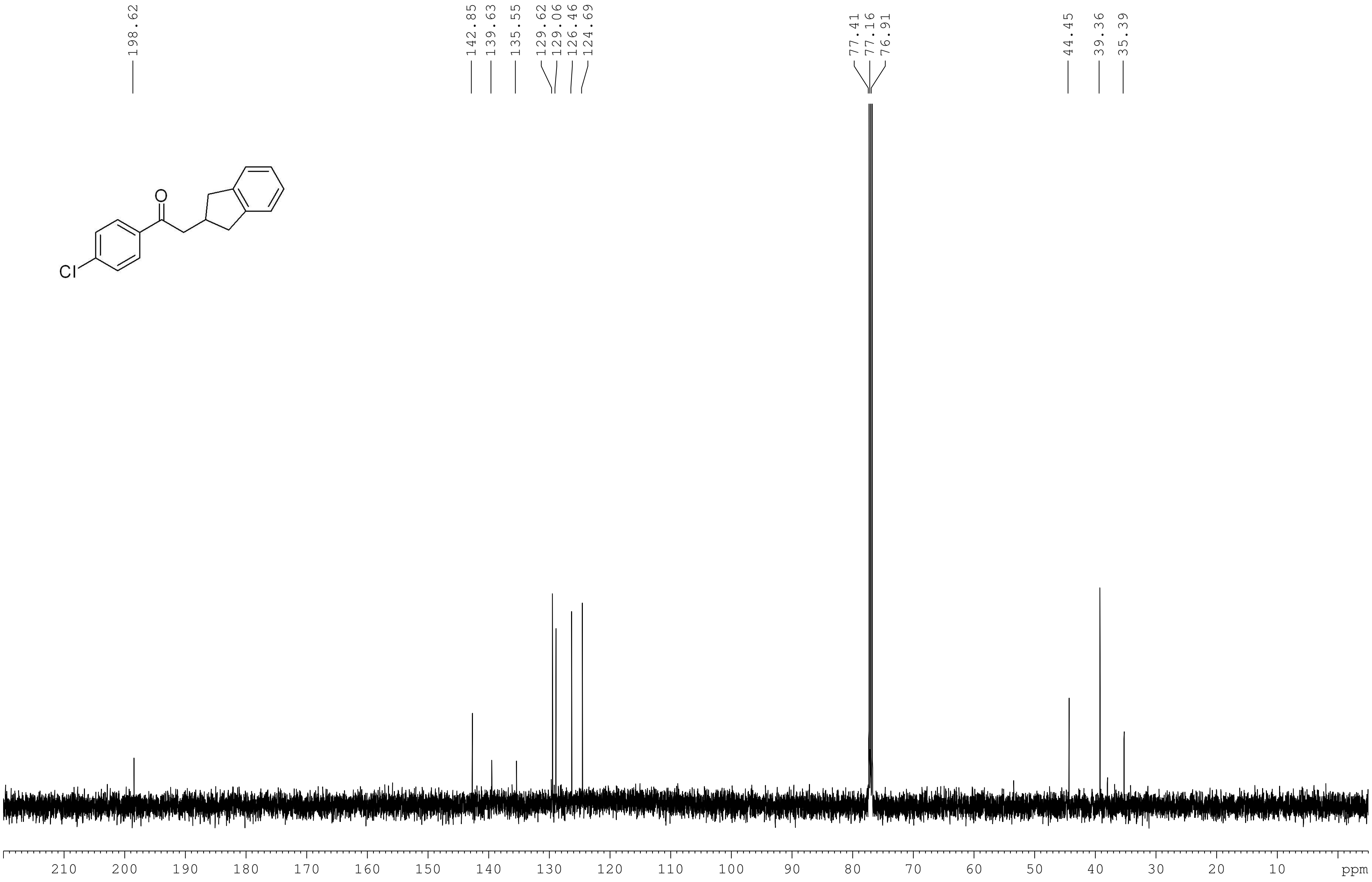
CDCl3, 125 MHz



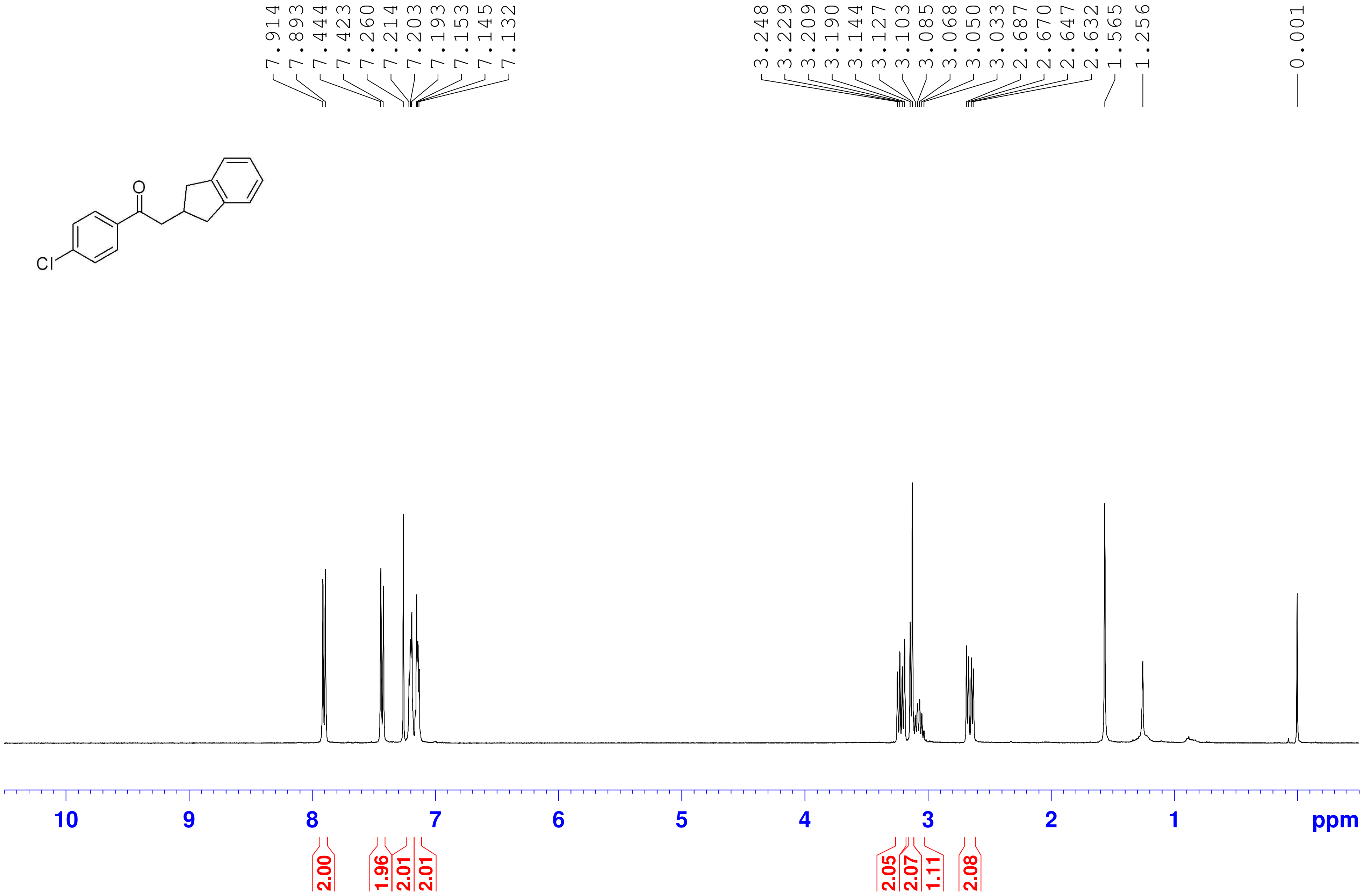
CDCl3, 500 MHz



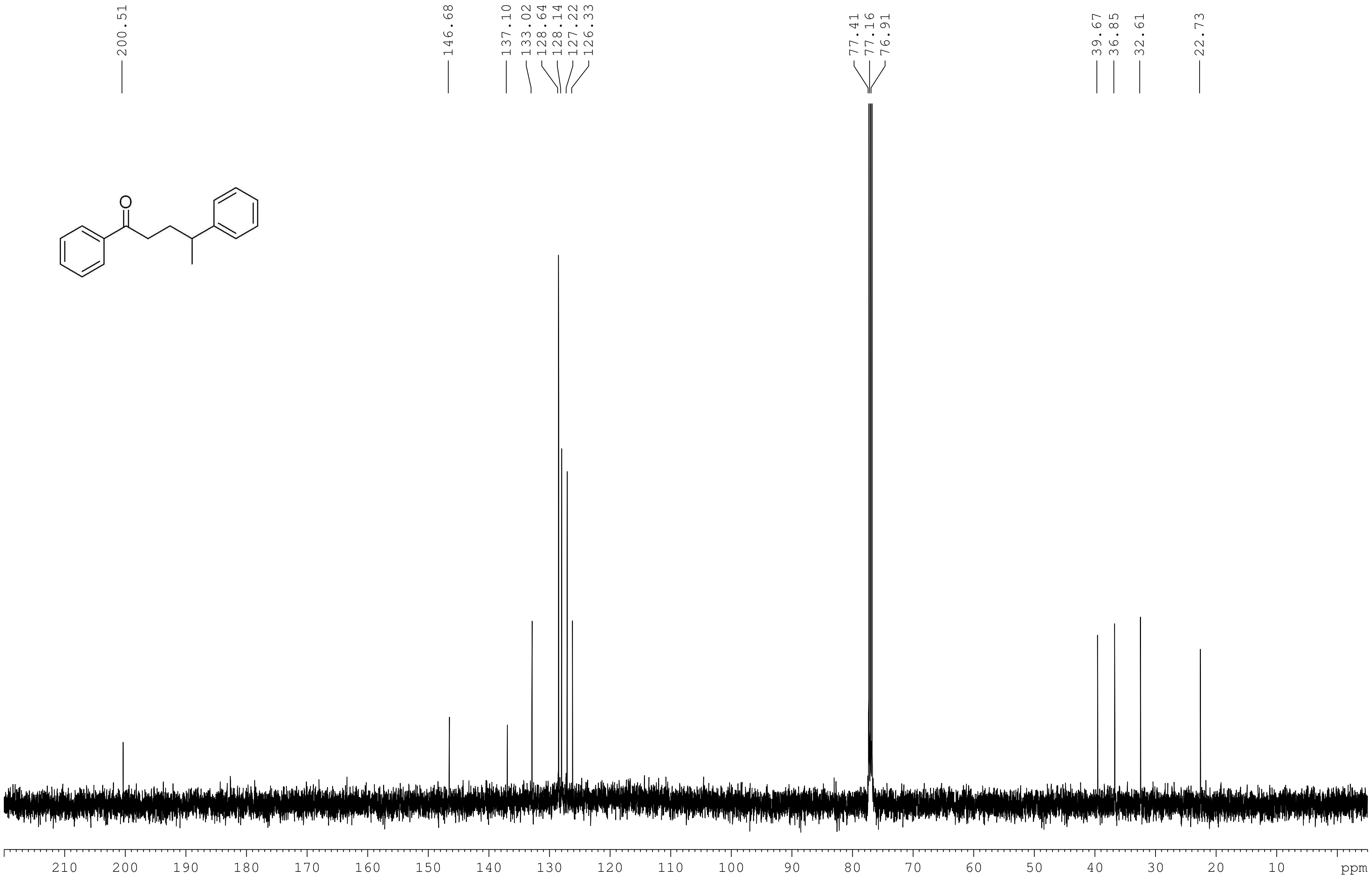
CDCl3, 125 MHz



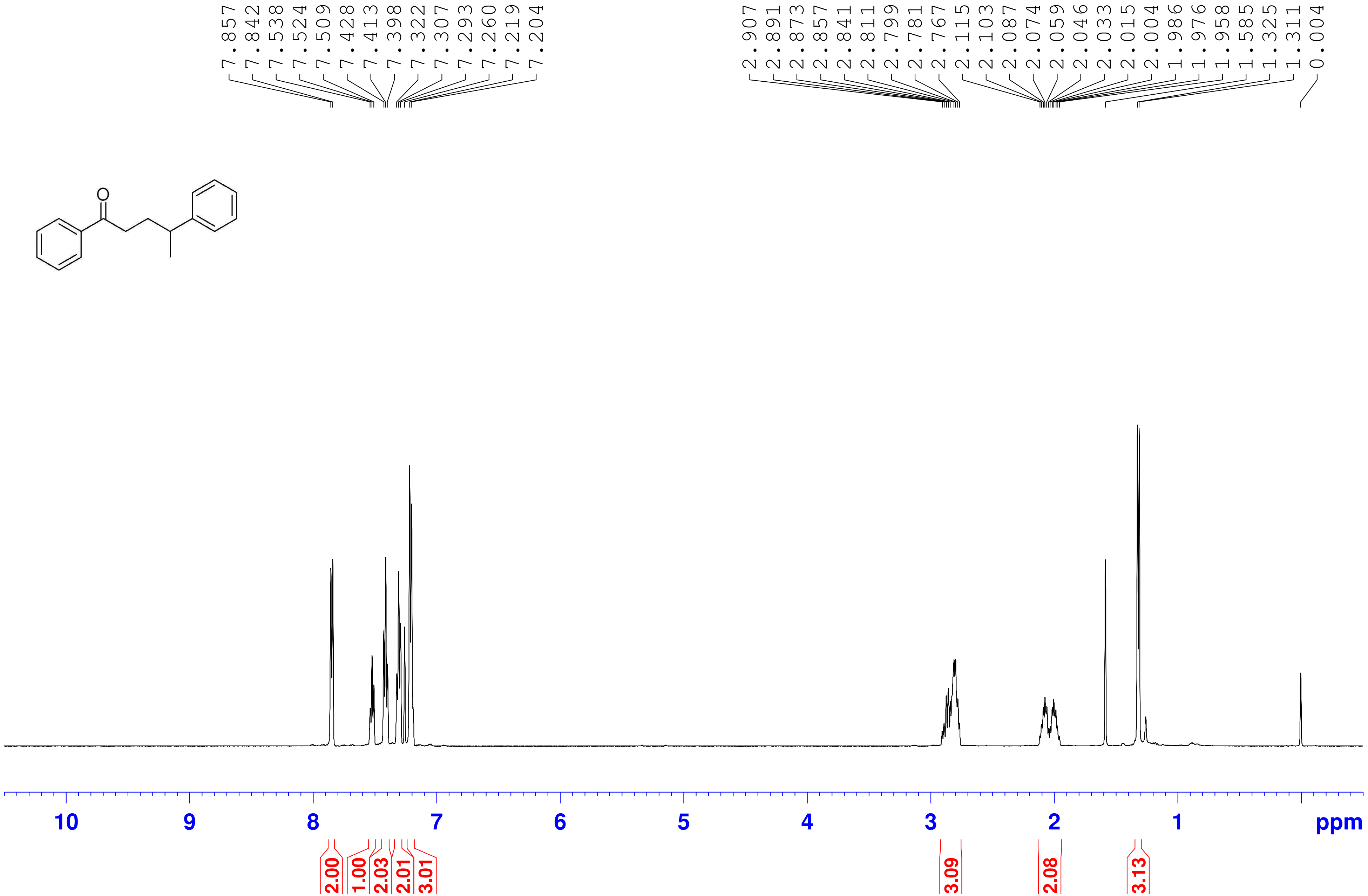
CDCl3, 400 MHz



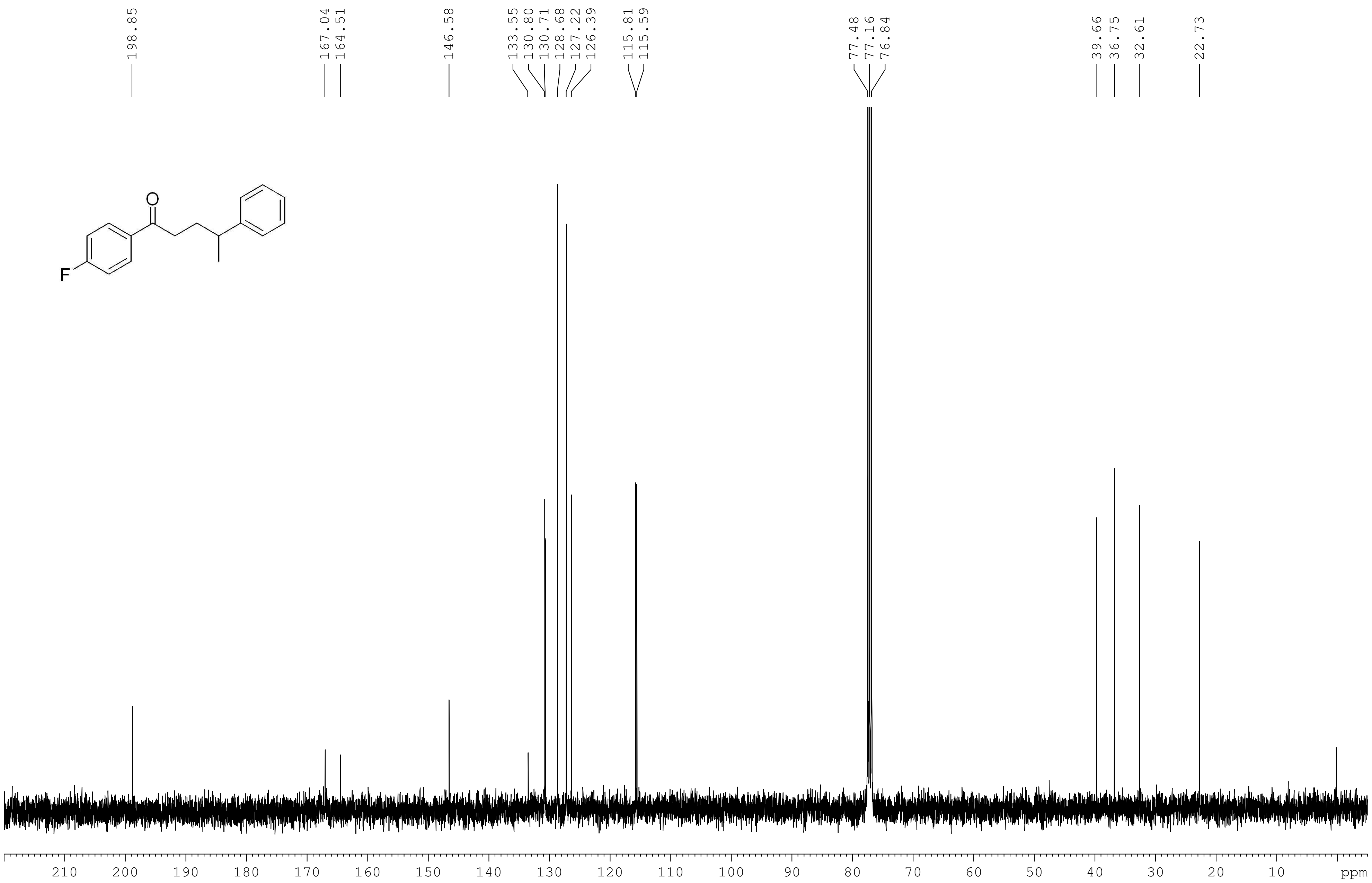
CDCl3, 125 MHz



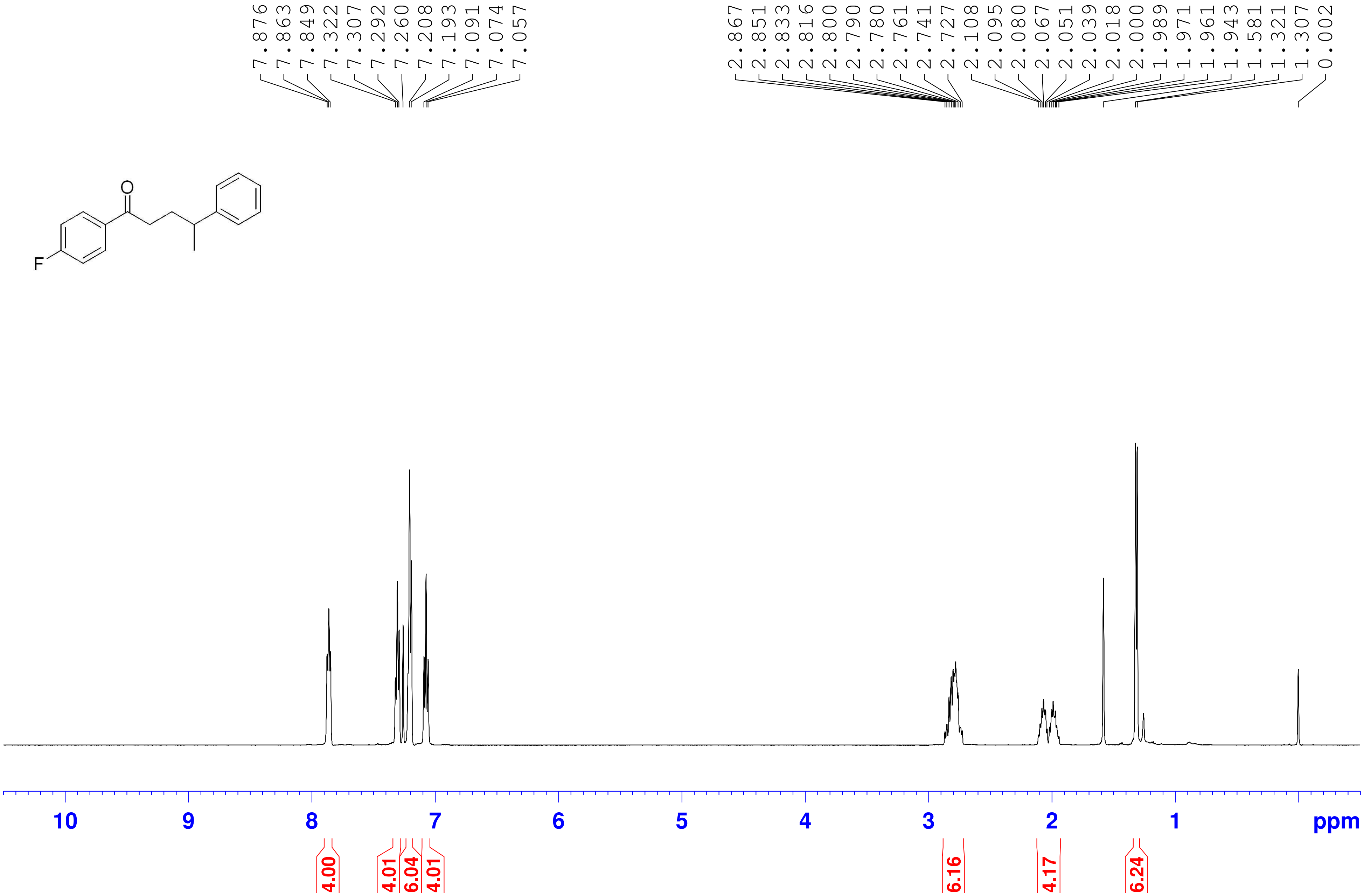
CDCl3, 500 MHz



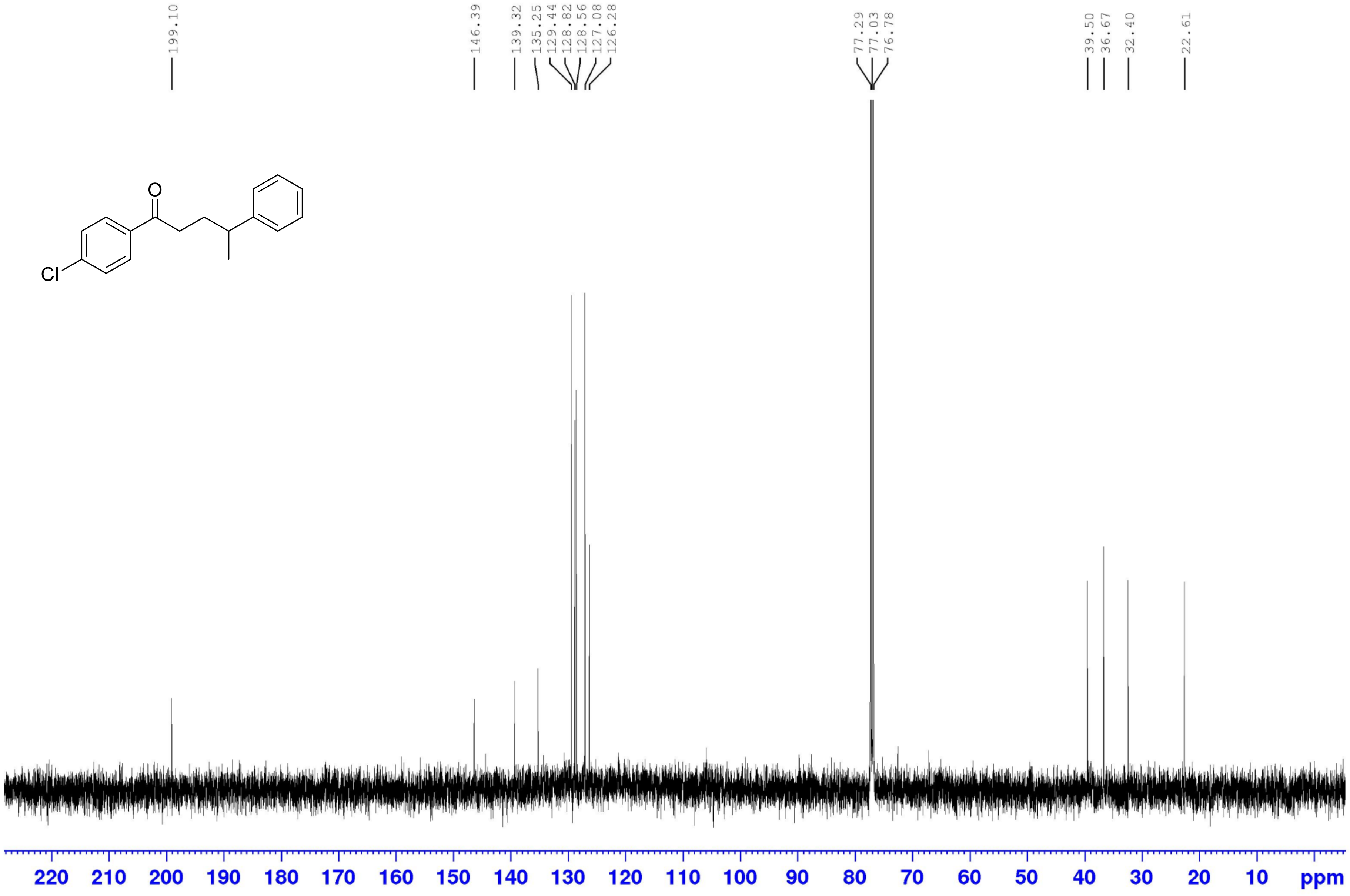
CDCl3, 100 MHz



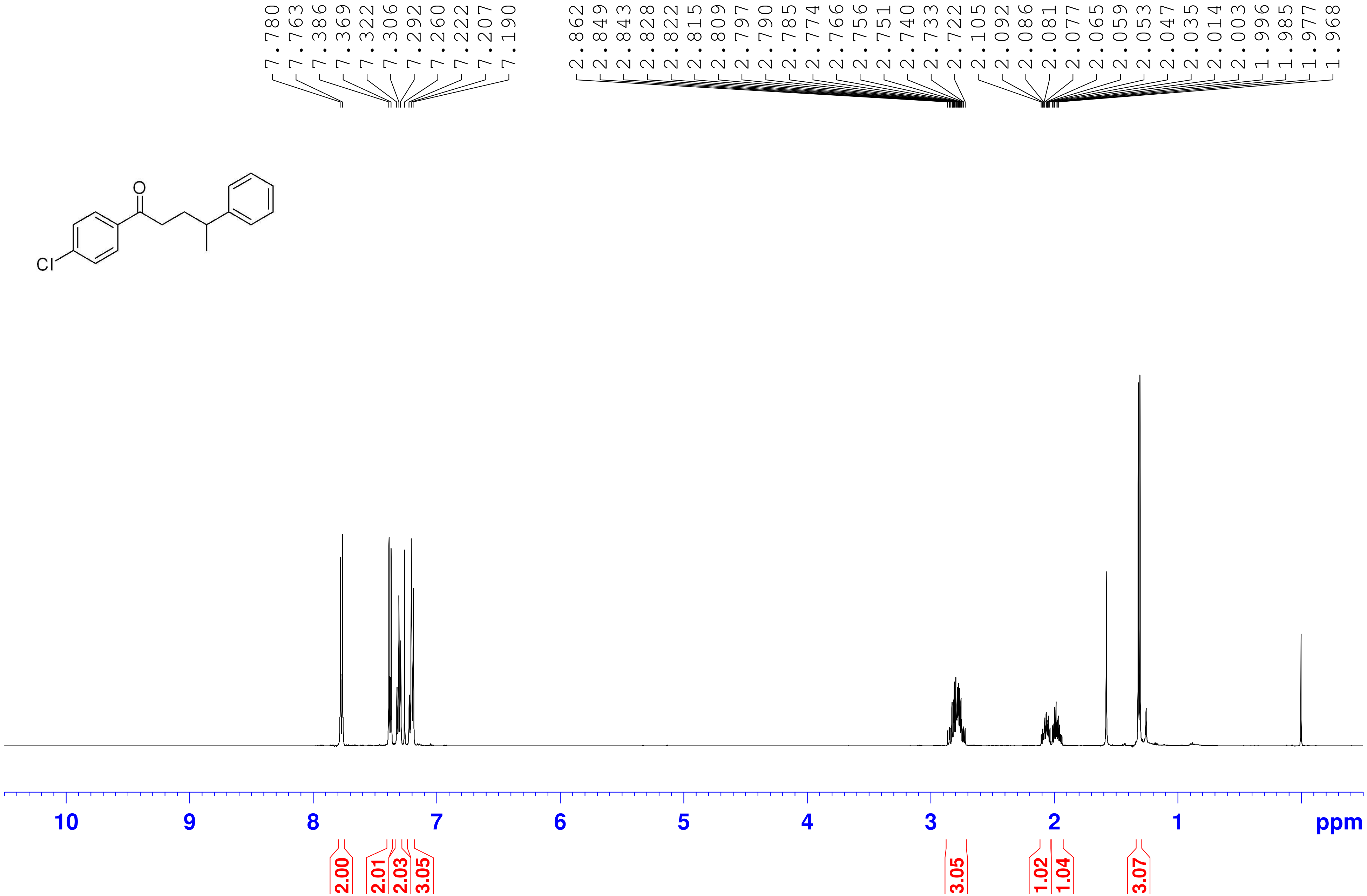
CDCl3, 500 MHz



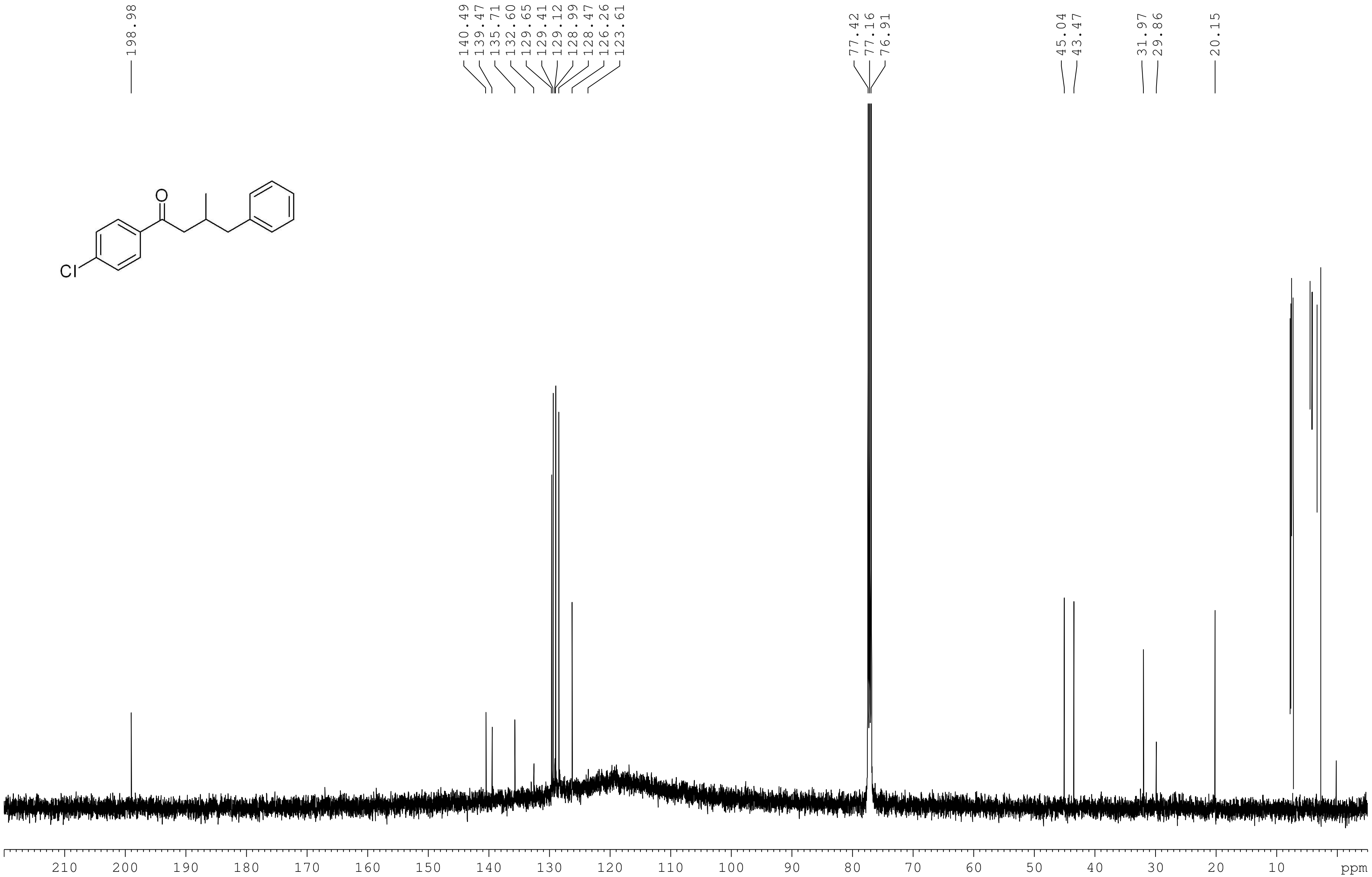
CDCl3, 125 MHz

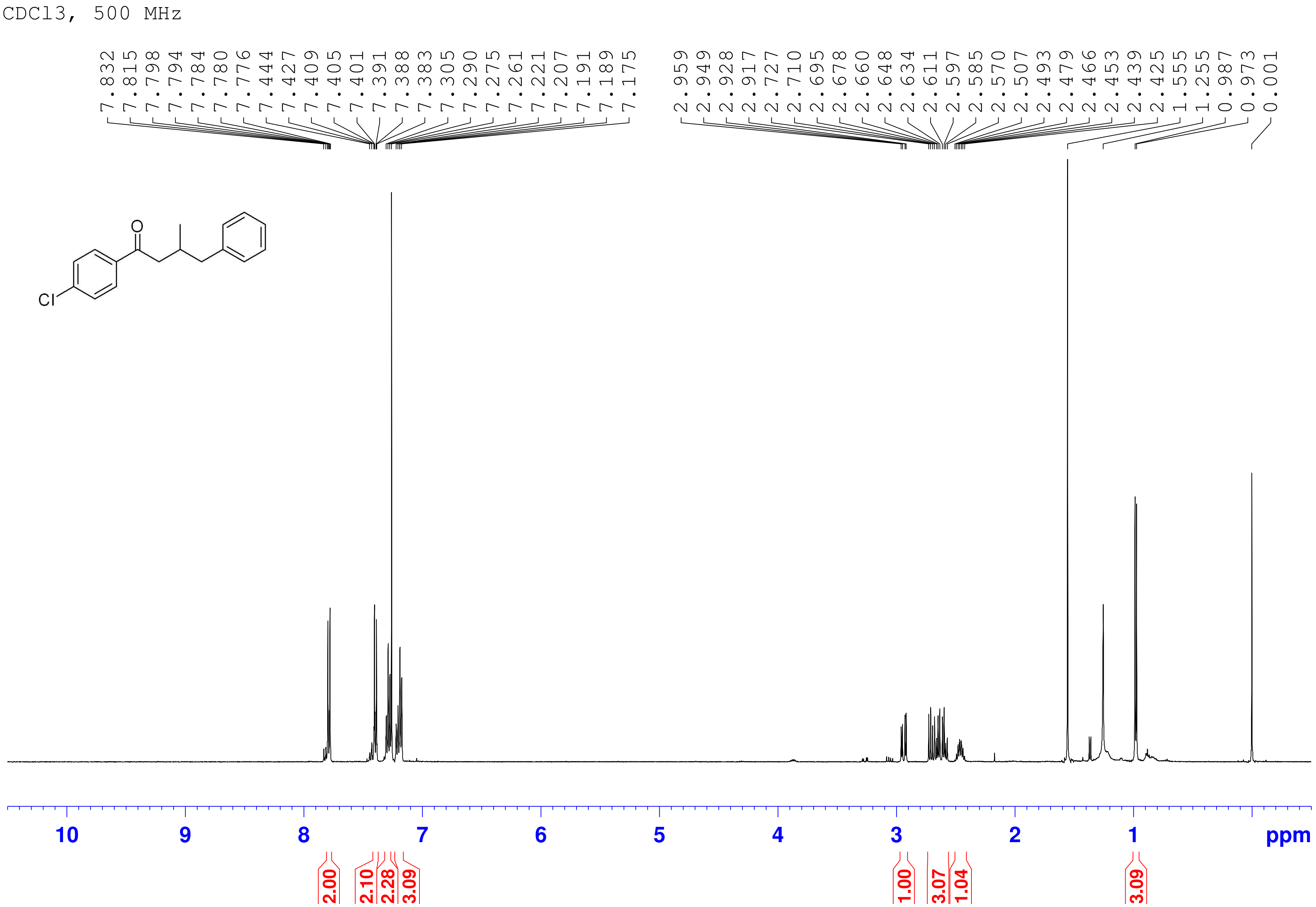


CDCl3, 500 MHz

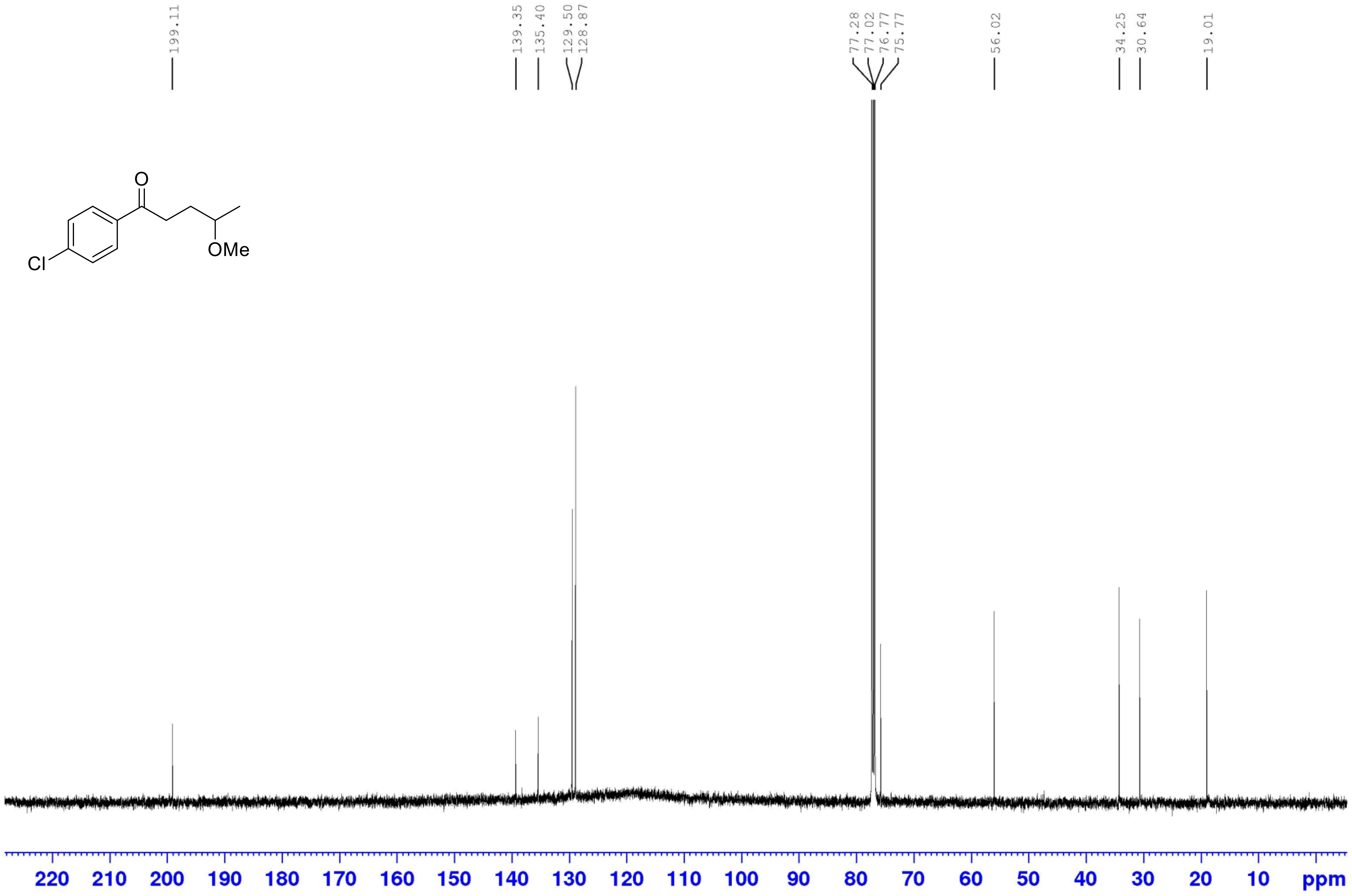


CDCl3, 125 MHz

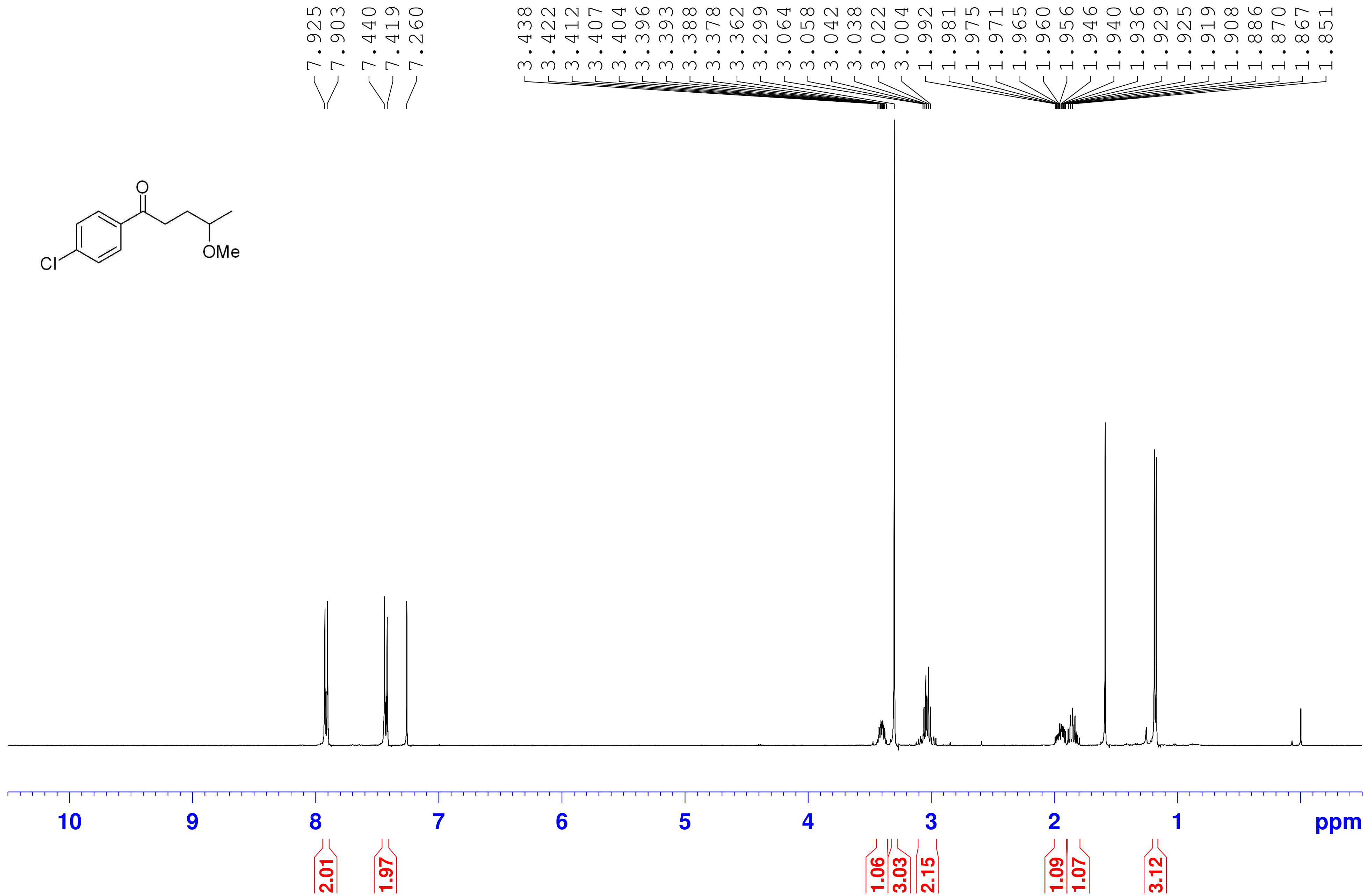



CDCl3, 500 MHz
7.832
7.815
7.798
7.794
7.784
7.780
7.776
7.444
7.427
7.409
7.405
7.401
7.391
7.388
7.383
7.305
7.290
7.275
7.261
7.221
7.207
7.191
7.189
7.175
2.959
2.949
2.928
2.917
2.727
2.710
2.695
2.678
2.660
2.648
2.634
2.611
2.597
2.585
2.570
2.507
2.493
2.479
2.466
2.453
2.439
2.425
1.555
1.255
0.987
0.973
0.001
O
Cl
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.10
2.28
3.09
1.00
3.07
1.04
3.09

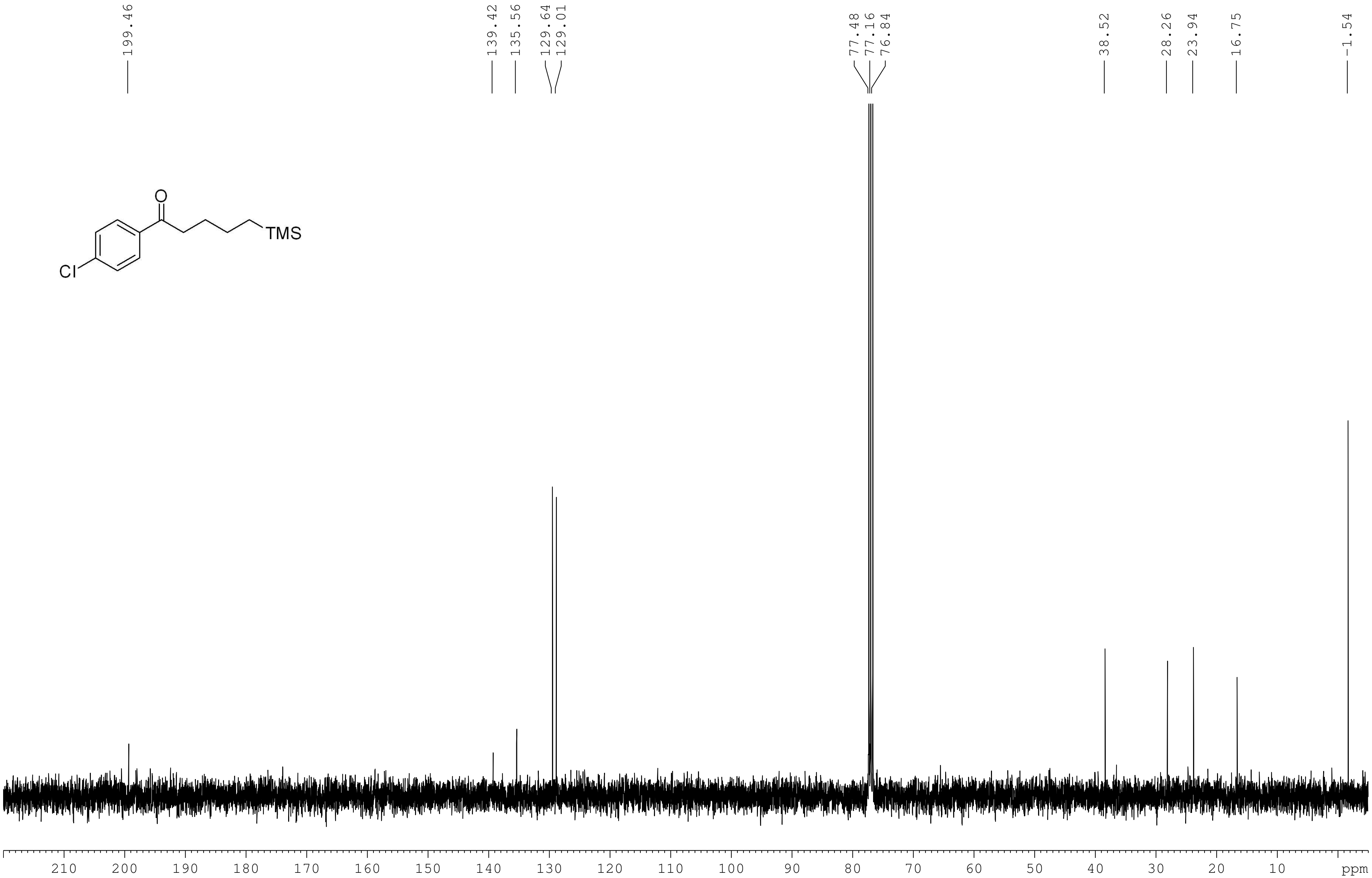
CDCl3, 125 MHz



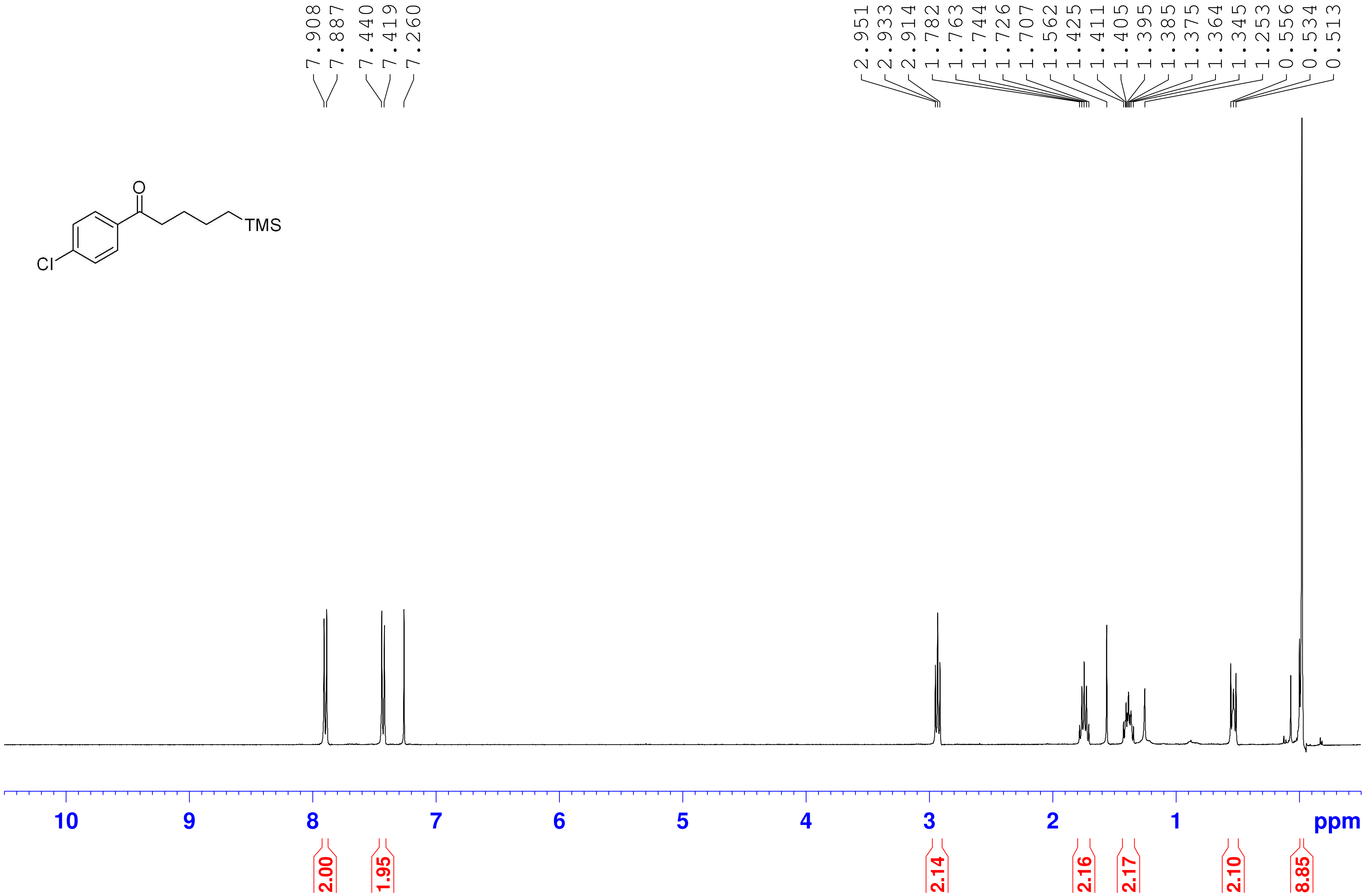
CDCl3, 400 MHz



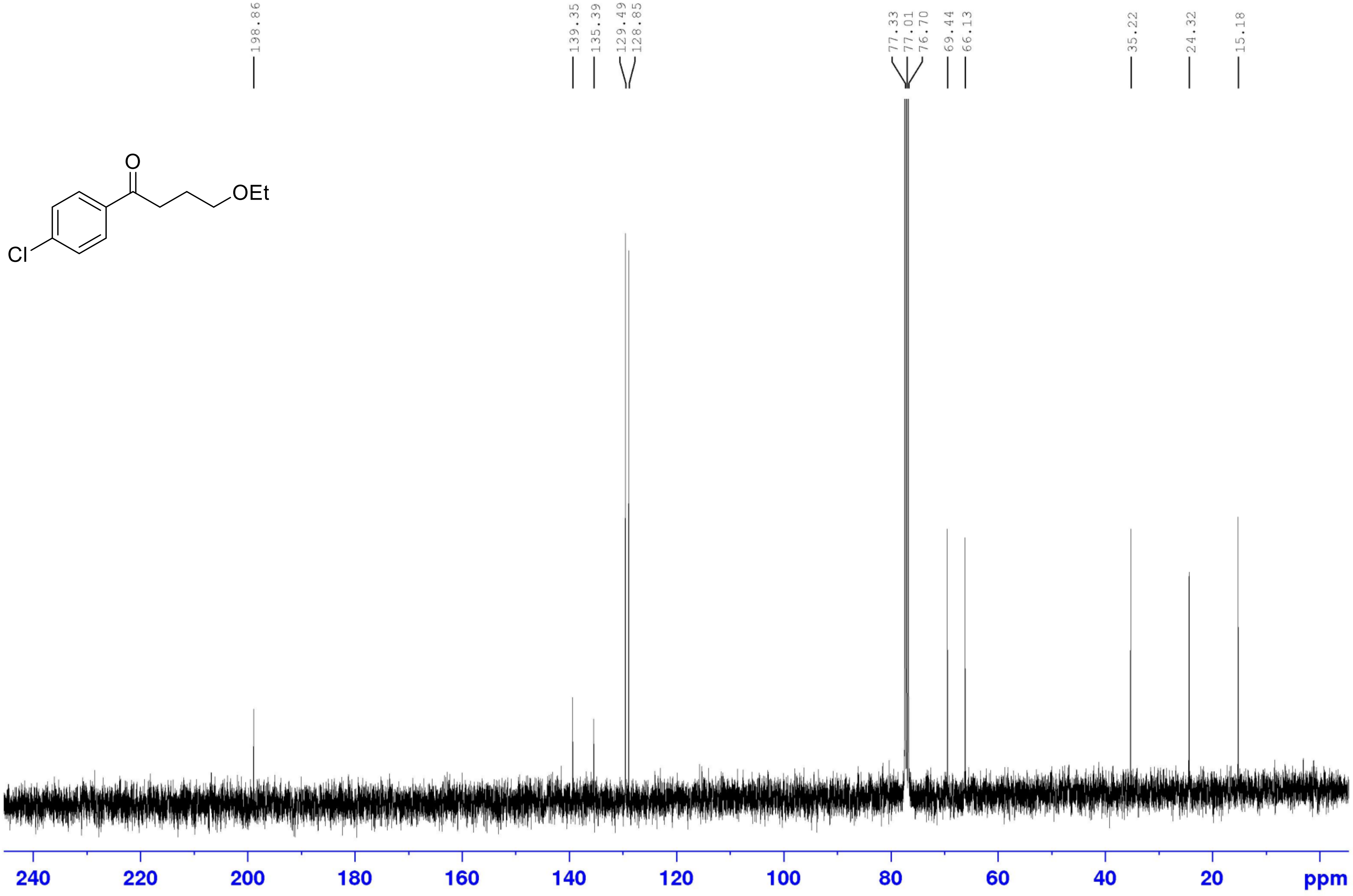
CDCl3, 100 MHz



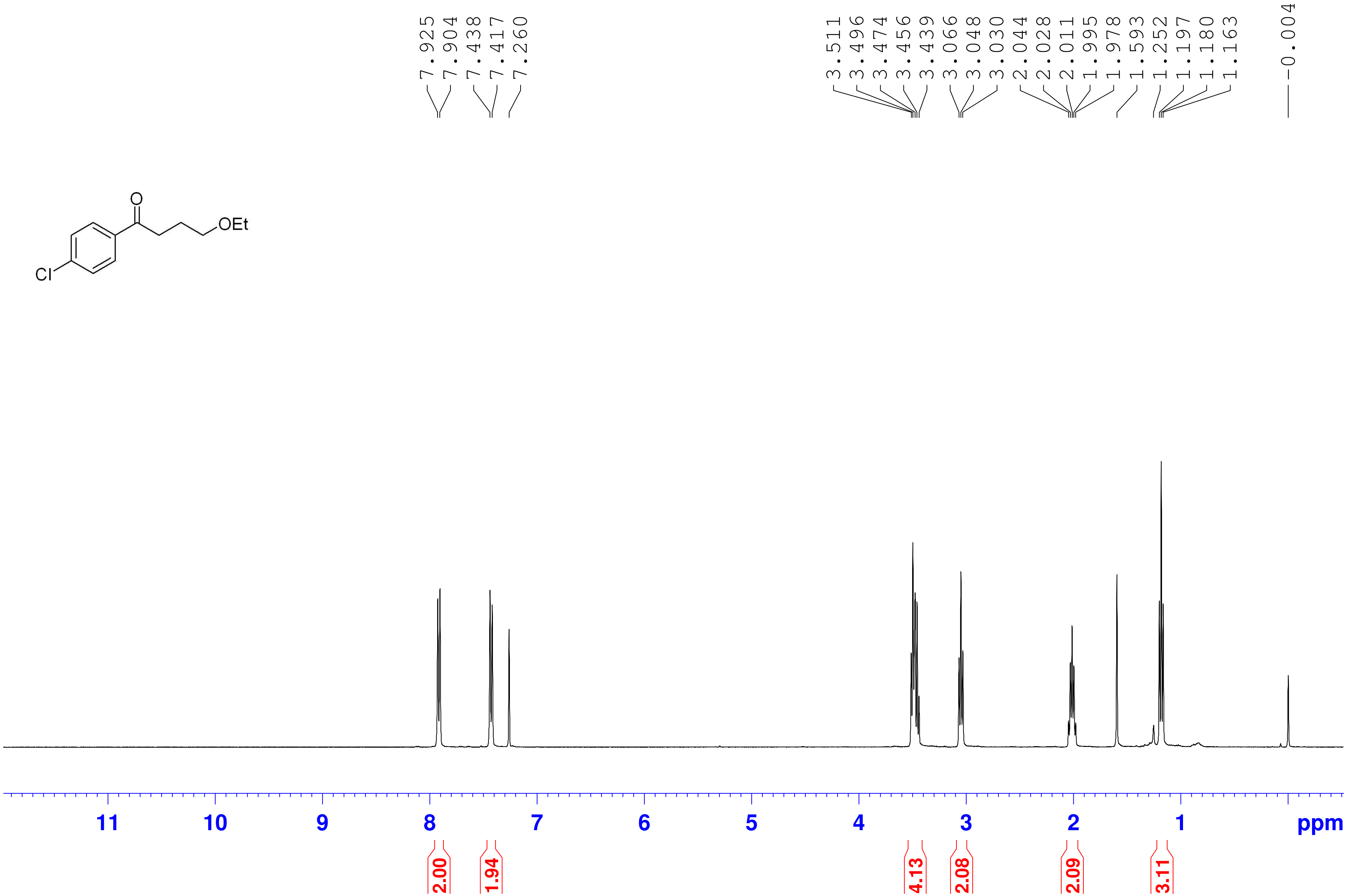
CDCl3, 400 MHz



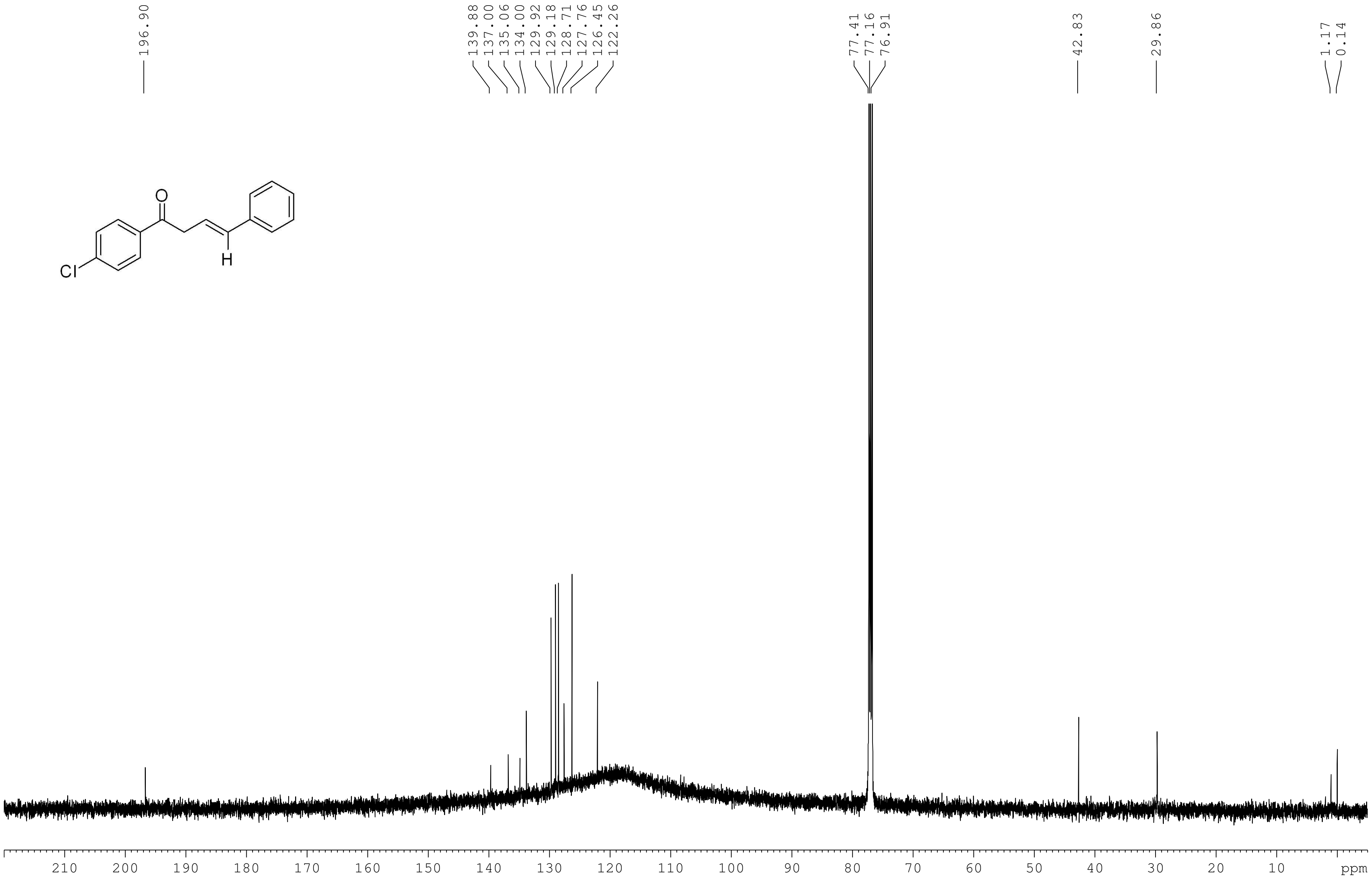
CDCl3, 100 MHz



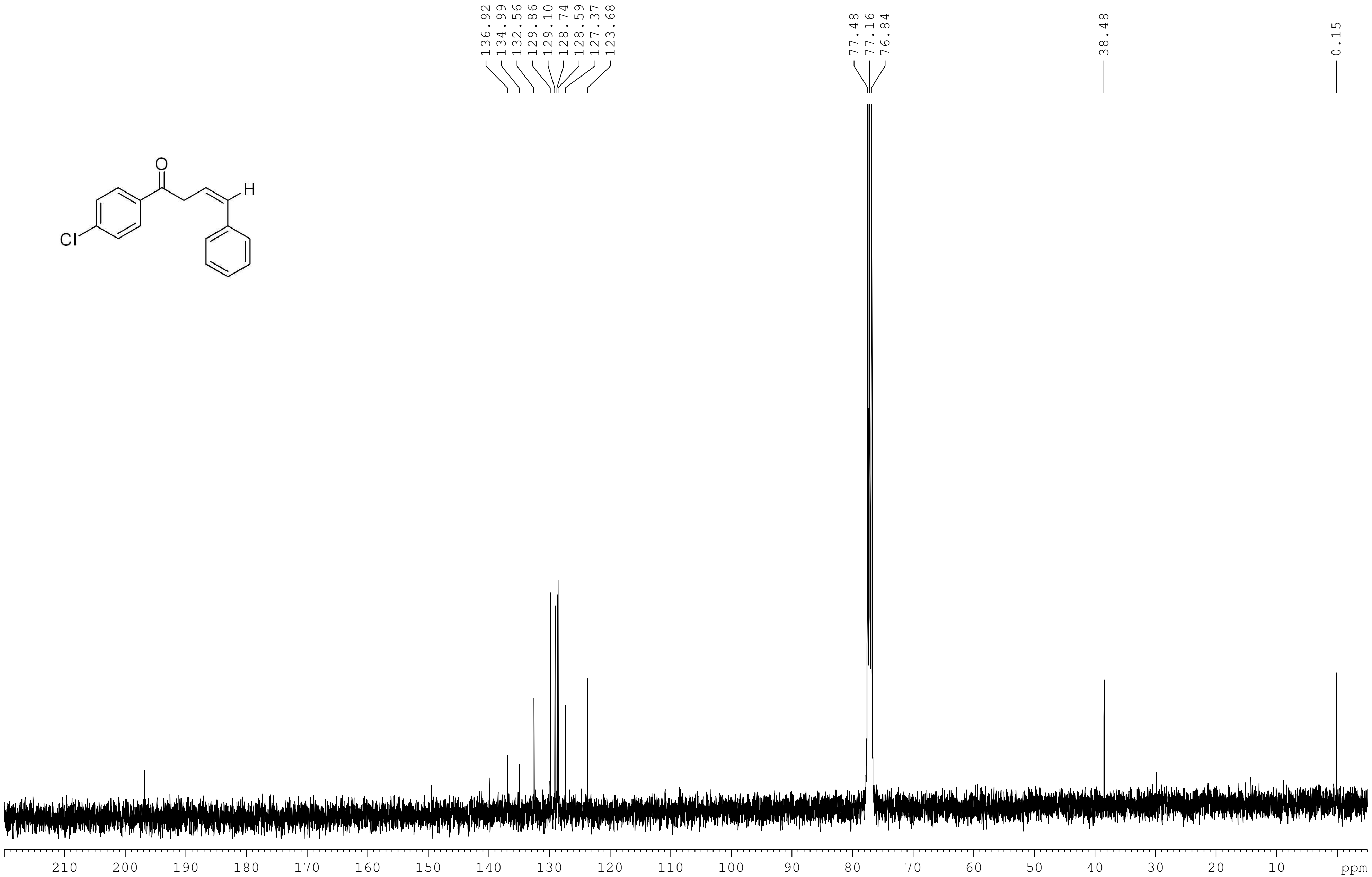
CDCl3, 400 MHz

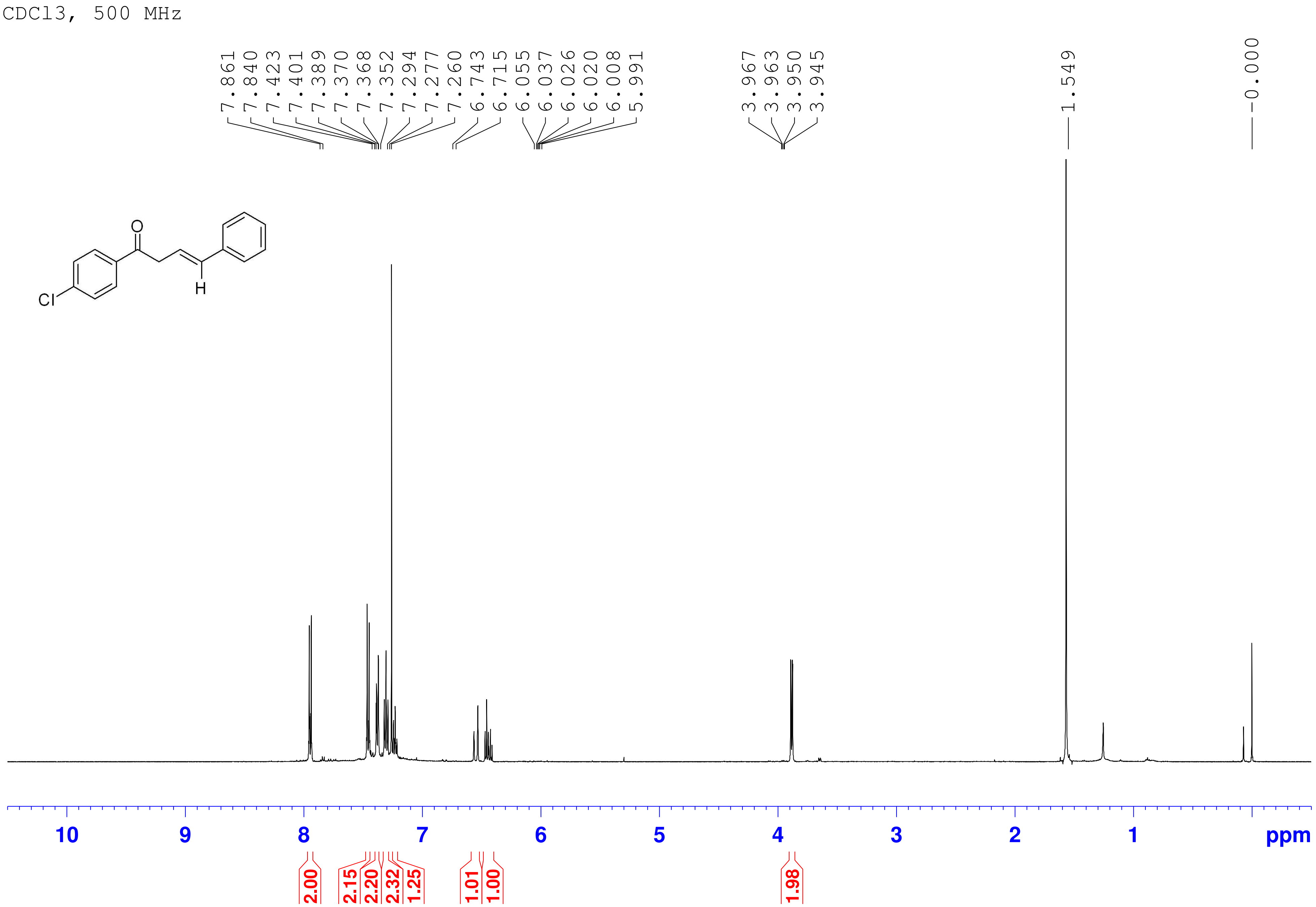


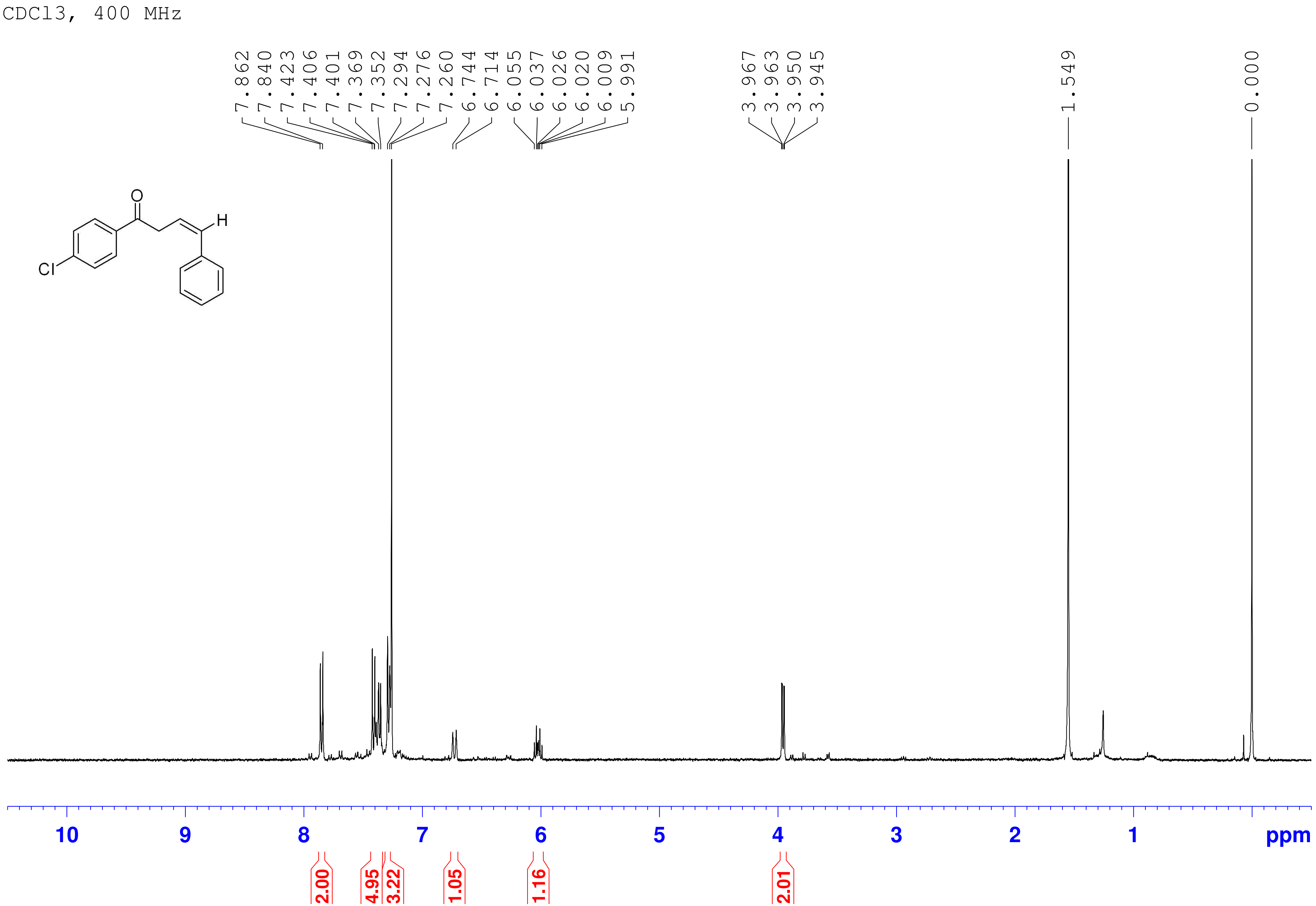
CDCl3, 125 MHz



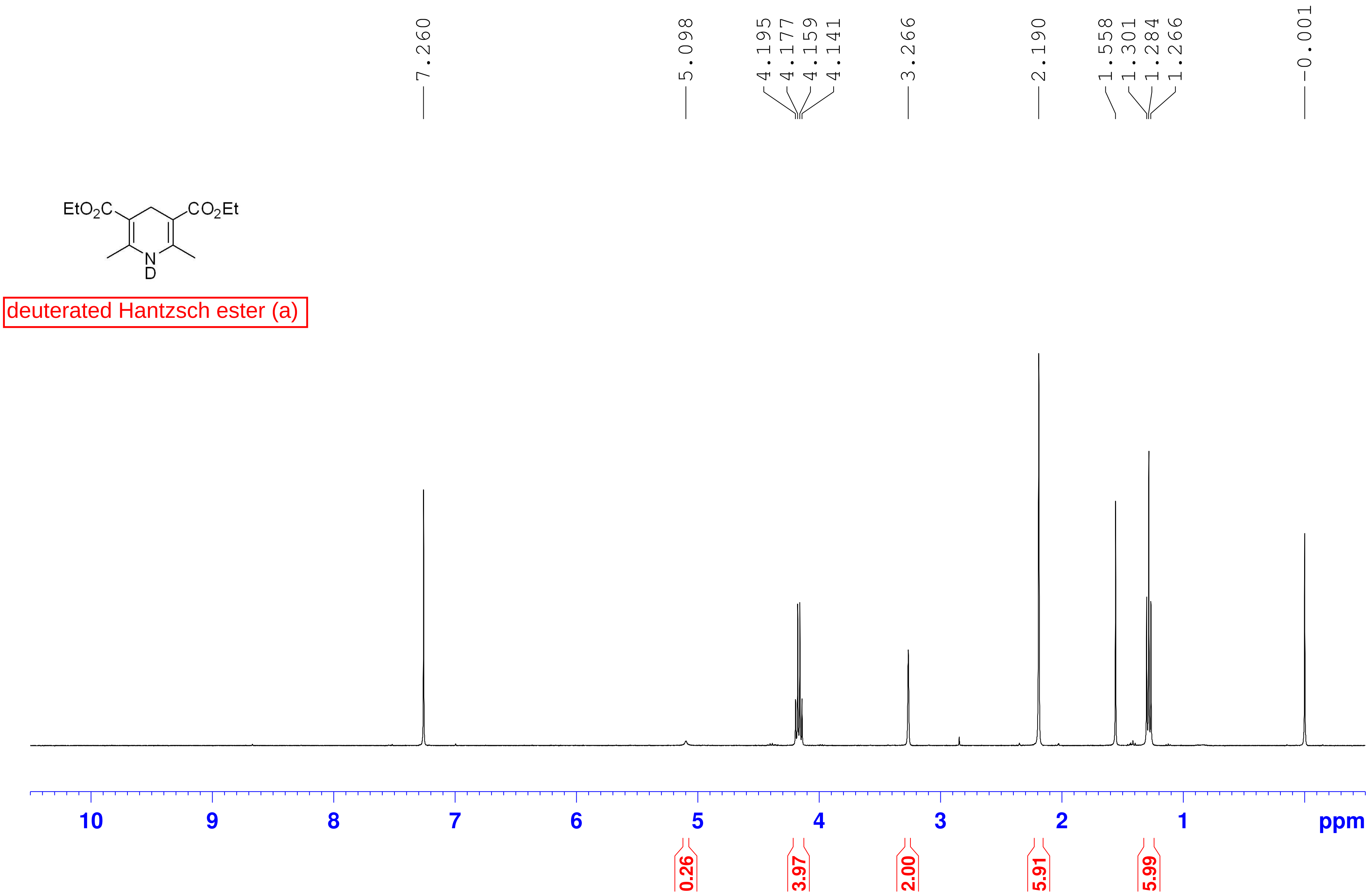
CDCl3, 100 MHz




CDCl3, 500 MHz
7.861
7.840
7.423
7.401
7.389
7.370
7.368
7.352
7.294
7.277
7.260
6.743
6.715
6.055
6.037
6.026
6.020
6.008
5.991
3.967
3.963
3.950
3.945
1.549
-0.000
O
Cl
H
10
9
8
7
6
5
4
3
2
1
ppm
2.00
2.15
2.20
2.32
1.25
1.01
1.00
1.98

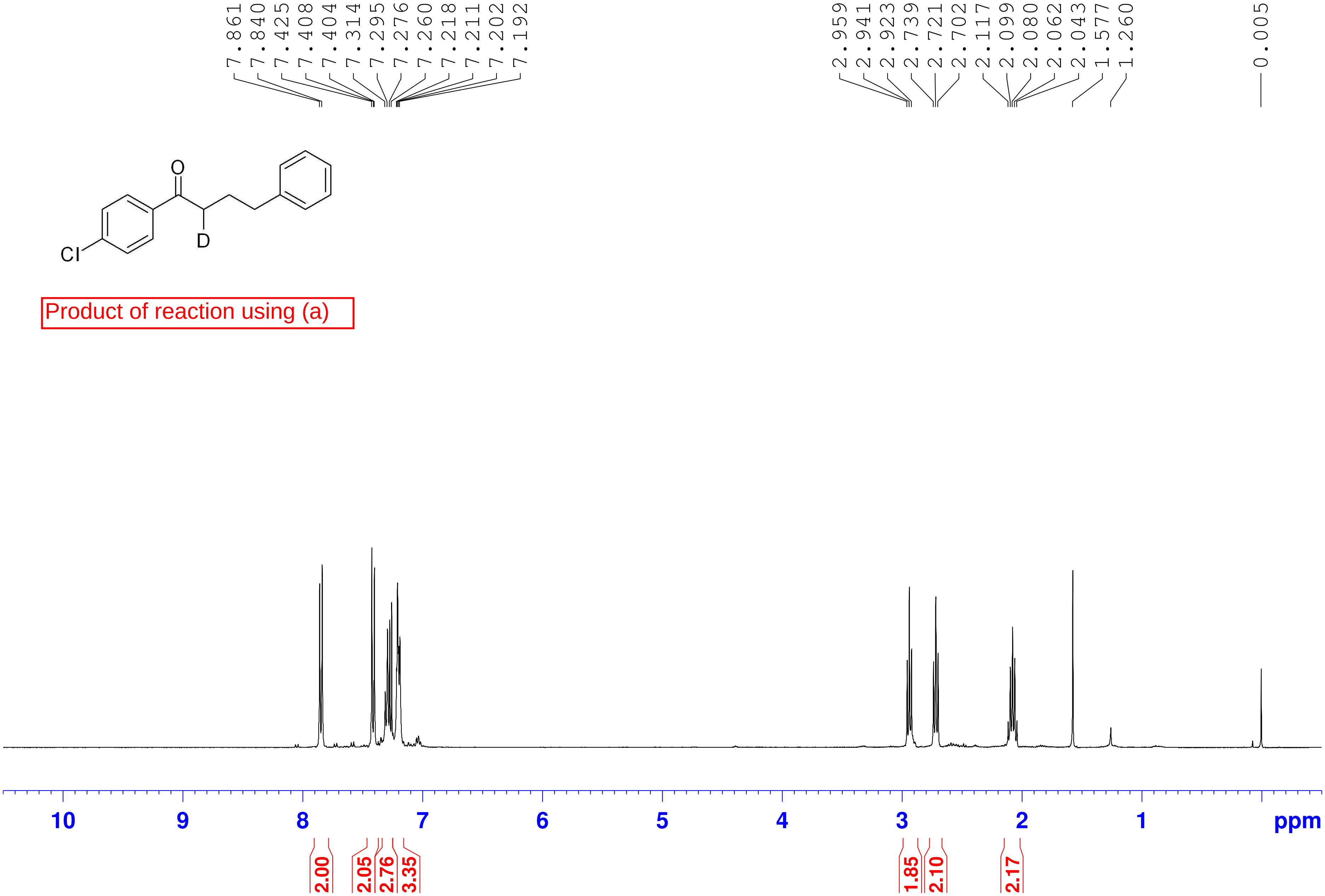

CDCl3, 400 MHz
7.862
7.840
7.423
7.406
7.401
7.369
7.352
7.294
7.276
7.260
6.744
6.714
6.055
6.037
6.026
6.020
6.009
5.991
3.967
3.963
3.950
3.945
1.549
0.000
O
H
Cl
10
9
8
7
6
5
4
3
2
1
ppm
2.00
4.95
3.22
1.05
1.16
2.01

CDCl3, 400 MHz



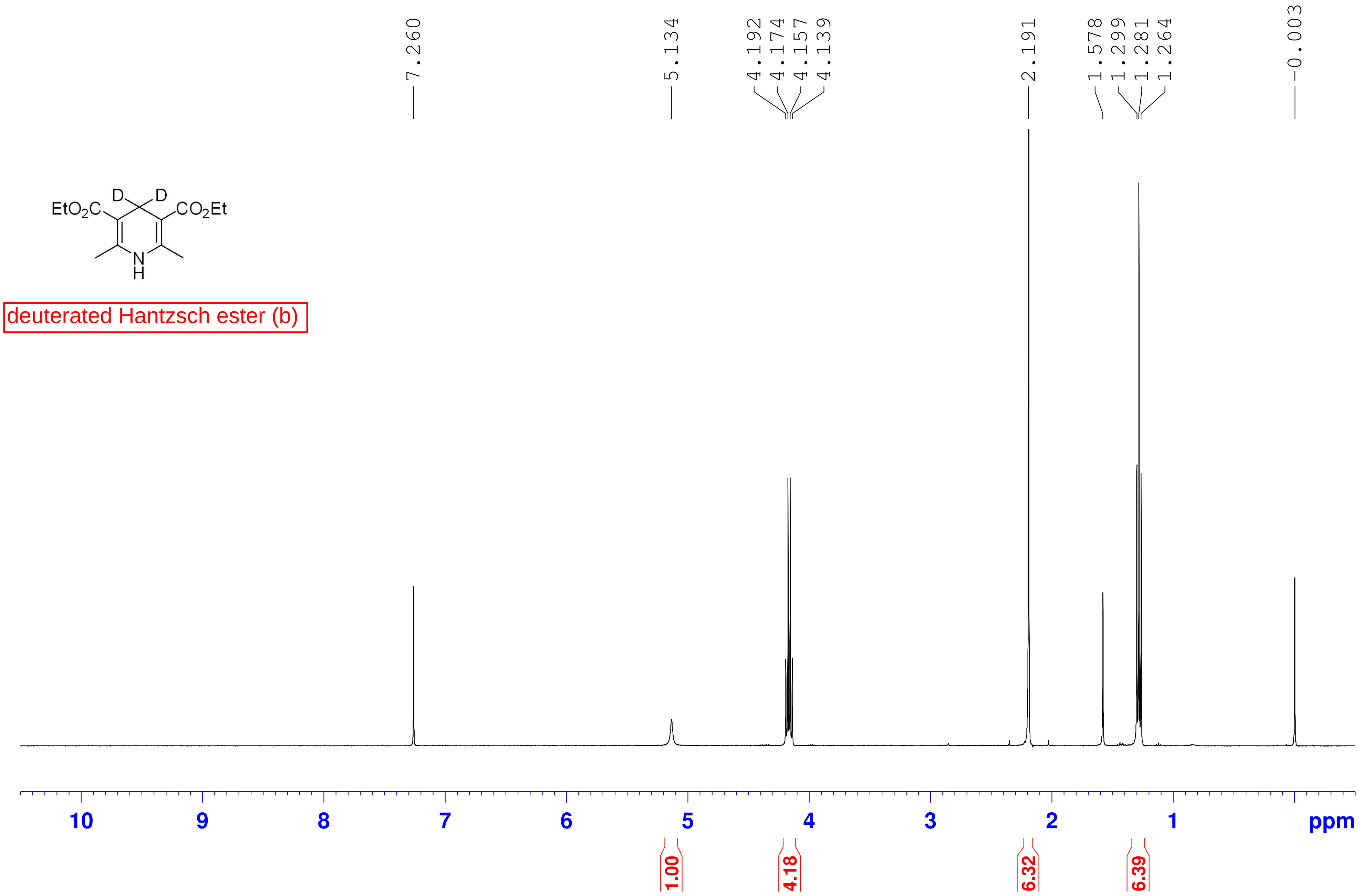
deuterated Hantzsch ester (a)

CDCl3, 400 MHz



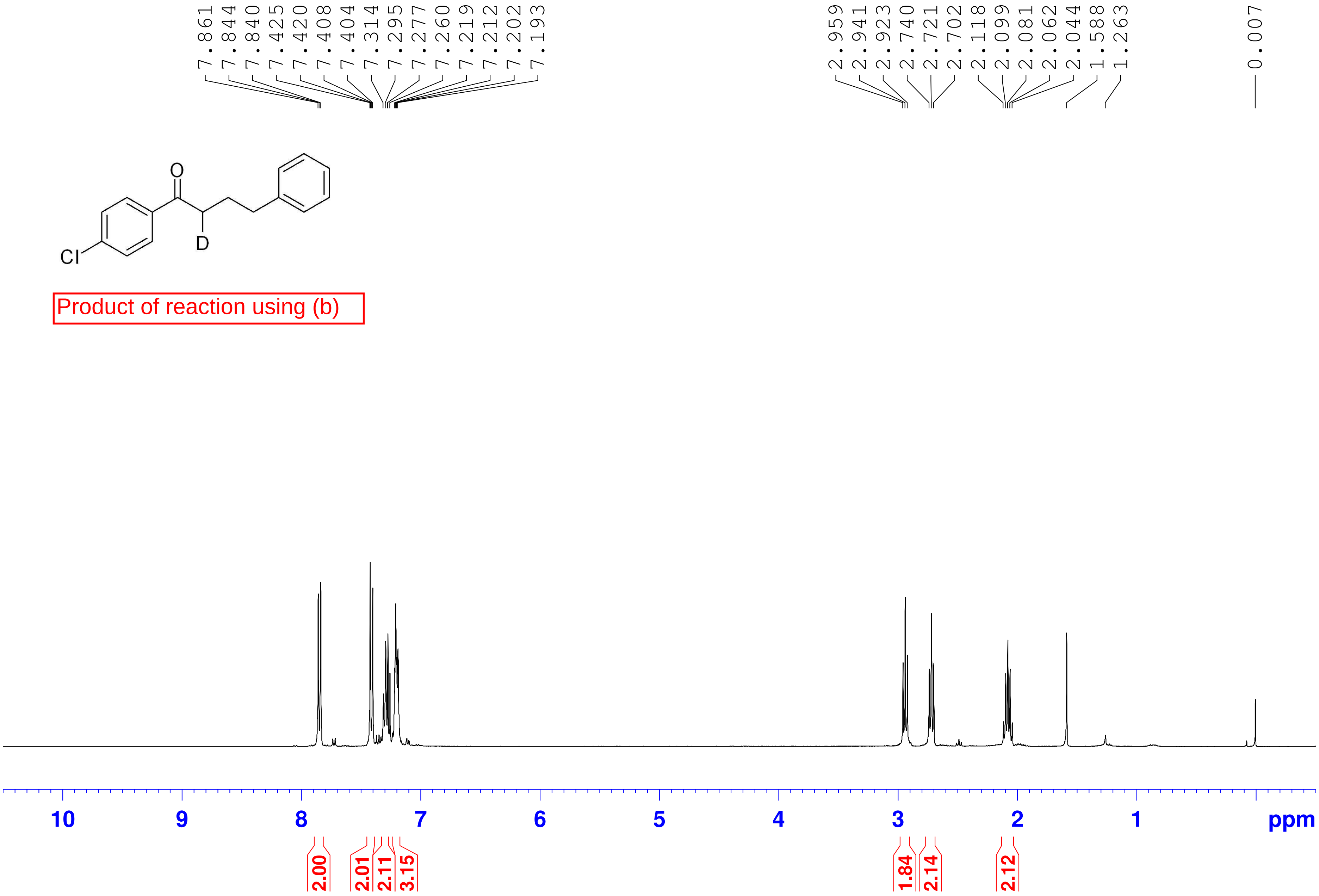
Product of reaction using (a)

CDCl3, 400 MHz

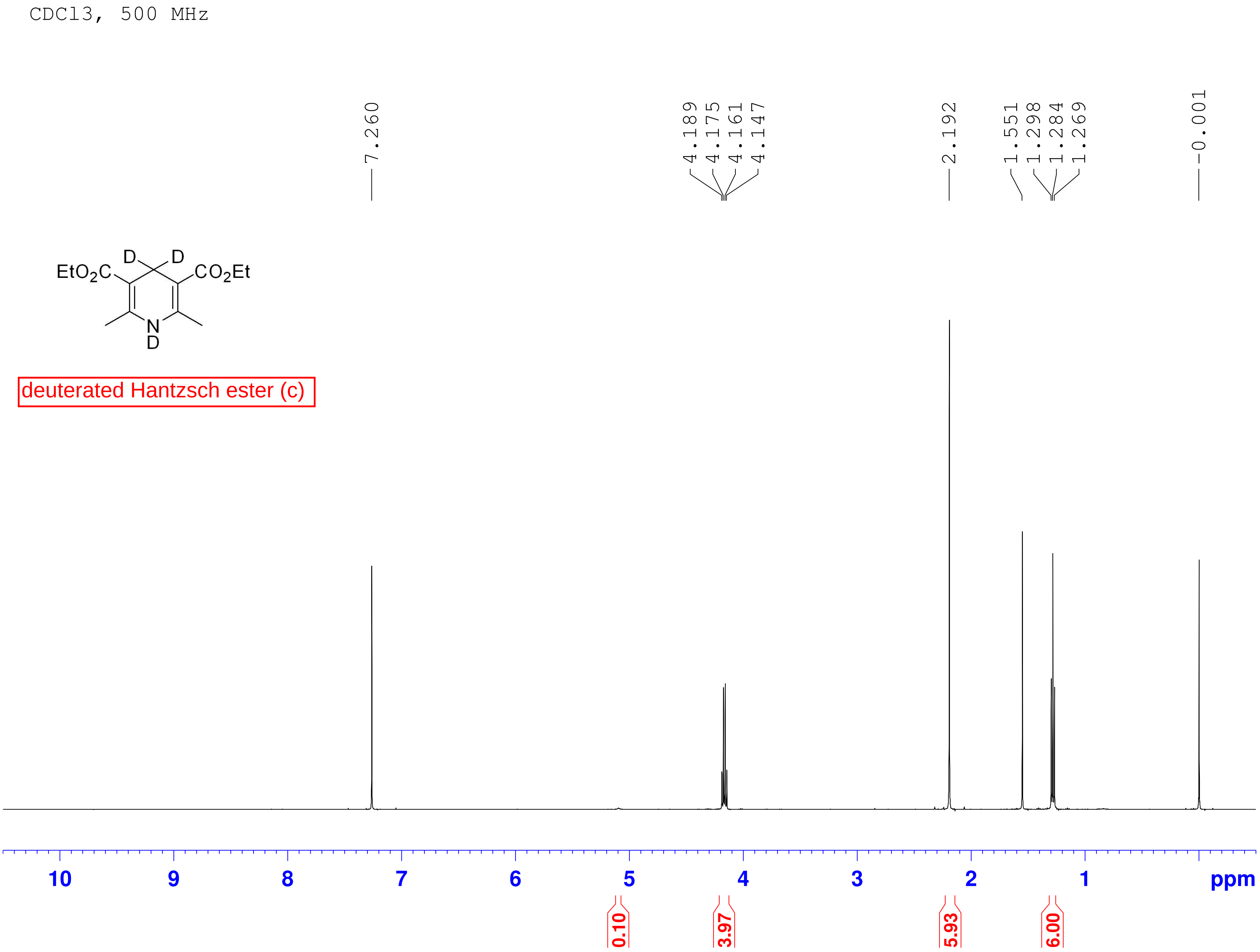


deuterated Hantzsch ester (b)

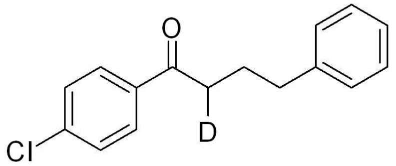
CDCl3, 400 MHz



Product of reaction using (b)


CDCl3, 500 MHz
7.260
4.189
4.175
4.161
4.147
2.192
1.551
1.298
1.284
1.269
-0.001
EtO2C
CO2Et
D
D
N
D
deuterated Hantzsch ester (c)
10
9
8
7
6
5
4
3
2
1
ppm
0.10
3.97
5.93
6.00

CDCl3, 400 MHz



Product of reaction using (c)