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Palladium catalyzed stereocontrolled synthesis of *C*-aryl glycosides using arenediazonium salts at room temperature

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List of Contents

1. EXPERIMENTAL SECTION

General methods

All the reactions were carried out using oven dried glasswares. Solvents were evaporated with the help of rotary evaporator keeping the bath temperature below 50 °C. Thin layer chromatography was performed using pre-coated plates contained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV), then further analyzed by charring in stain solution (5% H_2SO_4 in MeOH). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate and hexane as an eluent. The NMR spectra were recorded on Bruker Avence 500 MHz NMR spectrometer. HRMS spectra were recorded on UHD Q-TOF using water's Quattro Micro V 4.1. The TMS signals were taken as the reference 0.00 ppm for 1H NMR spectra and 77.0 ppm for 13C NMR spectra in $CDCl_3$. Sometimes the residual solvent $CDCl_3$ signal at 7.26 ppm was used an internal standard for 1H NMR spectra. Starting materials were purchased or prepared

using literature procedures as stated below. Solvents and chemicals were purchased from commercial sources and used without further purification. The palladium catalysts were purchased from Sigma Aldrich.

Preparation of 3,4,6-tri-*O*-methyl-D-glucal (1aa):[1]

The commercially available 3,4,6-tri-*O*-acetyl-D-glucal (**1ae**) (5 g, 18.3 mmol) was stirred in MeOH (150 mL) at 0^{o}C to which NaOMe (108 mg, 2.0 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (100 mL) was added and cooled to 0 ^{o}C after which NaH (3.6 g, 60% in mineral oil, 91 mmol) was added portion wise. The resulting mixture was stirred for 30 min at the same temperature to which methyl iodide (5.2 mL, 80 mmol) was added slowly dropwise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (15 mL) and diluted with ethyl acetate (500 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 4:1) to afford **1aa** as a colorless oil in 80% yield (2.45 g). NMR spectra were identical with literature data.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.34 (d, *J* = 5.5 Hz, 1H), 4.78-4.77 (m, 1H), 3.91 (m, 1H), 3.83 (m, 1H), 3.64-3.57 (m, 2H), 3.49 (s, 3H), 3.41 (t, *J* = 7.0 Hz, 1H), 3.36-3.35 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.4, 99.4, 76.5, 76.1, 75.7, 70.6, 59.1, 59.0, 55.6.

Preparation of tri-*O*-benzyl-D-glucal (1ab):[1]

The commercially available 3,4,6-tri-*O*-acetyl-D-glucal (1 g, 3.6 mmol) was stirred in MeOH (30 mL) at 0^{o}C to which NaOMe (22 mg, 0.2 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (15 mL) was added and cooled to 0 ^{o}C followed by NaH (720 mg, 60% in mineral oil, 18 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which benzyl bromide (1.8 mL, 16 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (6 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 20:1) to afford **1ab** as a white solid in 87% yield (1.3 g). NMR spectra were identical with literature data.[1] ^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.38-7.26 (m, 15H), 6.43 (d, *J* = 5.5 Hz, 1H), 4.89-4.88 (m, 1H), 4.84 (d, *J* = 11.5 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 2H), 4.59-4.55 (m, 3H), 4.22 (m, 1H), 4.07 (m, 1H), 3.87 (t, *J* = 7.0 Hz, 1H), 3.83-3.76 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.6, 138.3, 138.1, 137.9, 128.3, 128.3, 128.3, 127.8, 127.7, 127.7, 127.6, 99.9, 76.7, 75.7, 74.3, 73.7, 73.4, 70.4, 68.4.

Preparation of 3,4,6-tri-*O*-ethyl-D-glucal (1ac):[15]

The compound **1ac** is prepared using the literature procedure employed for the preparation of **1aa**.[1] To a solution of commercially available 3,4,6-tri-*O*-acetyl-D-glucal **1ag** (500 mg, 1.8 mmol) in MeOH (15 mL), NaOMe (10.8 mg, 0.2 mmol) was added at 0^{o}C. The mixture was stirred for 3 h and evaporated to dryness. To the same flask, dry DMF (10 mL) was added and cooled to 0 ^{o}C followed by NaH (360 mg, 60% in mineral oil, 9 mmol) was added portion wise. The mixture was stirred for 20 min at the same temperature to which ethyl bromide (0.6 mL, 9 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (3 mL) and diluted with ethyl acetate (180 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 4:1) to afford **1ac** as a colorless oil in 75% yield (310 mg). NMR spectra were identical with literature data.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.34 (d, *J* = 5.5 Hz, 1H), 4.76-4.75 (m, 1H), 3.95-3.90 (m, 2H), 3.81 (t, *J* = 7.5, 1H), 3.68 (s, 2H), 3.65-3.61 (m, 2H), 3.57-3.48 (m, 4H), 1.20-1.17 (m, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 100.4, 76.8,76.0, 74.7, 68.9, 67.1, 66.8, 63.9, 15.6, 15.5, 15.0.

Preparation of 3,4,6-tri-*O*-methoxymethyl-D-glucal (1ad):[3]

To a solution of commercially available 3,4,6-tri-*O*-acetyl-D-glucal **1ag** (500 mg, 1.8 mmol) in MeOH (15 mL), NaOMe (10.8 mg, 0.2 mmol) was added at 0^{o}C. The mixture was stirred for 3 h and evaporated to dryness to obtain crude D-glucal. It was purified by a short silica chromatography using DCM-methanol. The pure D-glucal was dissolved in anhydrous DCM (20 mL) and cooled to 0^{o}C after which diisopropylethyl amine (2.0 mL, 11 mmol) was added followed by the dropwise addition of chloromethyl methyl ether (0.8 mL). The reaction mixture was allowed to stir for 12 h at room temperature and again diisopropylethyl amine (2.0 mL, 11 mmol) was added followed by the

dropwise addition of chloromethyl methyl ether (0.8 mL). Further the reaction was allowed to stir for 12 h and diluted with DCM (100 ml).The organic layer was washed with solution of 1M HCl (50 mL), $NaHCO_3$ (50 mL), dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 20:1) to afford **1ad** as a colorless oil in 60% yield (300 mg). NMR spectra were identical with literature data.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37(d, *J* = 5.5 Hz, 1H), 4.84 (m, 1H), 4.78 (d, *J* = 6.0 Hz, 1H), 4.71 (d, *J* = 6.5 Hz, 1H), 4.67 (s, 2H), 4.63 (s, 2H), 4.13-4.08 (m, 2H), 3.83-3.77 (m, 3H), 3.37 (s, 3H), 3.34 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 99.9, 96.6, 96.5, 95.3, 76.1, 72.5, 71.6, 65.7, 55.9, 55.4, 55.2.

Preparation of 3,4,6-tri-*O*-methyl-D-galactal (1af):[1]

The commercially available 3,4,6-tri-*O*-acetyl-D-galactal (**1ae**) (2 g, 7.2 mmol) was stirred in MeOH (40 mL) at 0^{o}C to which NaOMe (44 mg, 0.8 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (25 mL) was added and cooled to 0 ^{o}C to which NaH (1.5 g, 60% in mineral oil, 36 mmol) was added portion wise. The mixture was stirred for 30 min at the same temperature to which methyl iodide (2.6 mL, 40 mmol) was added slowly drop wise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (7 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 4:1) to afford **1af** as a colorless oil in 74% yield (1.05 g). NMR spectra were identical with literature data.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.28 (d, *J* = 6.0 Hz, 1H), 4.77-4.75 (m, 1H), 4.11 (m, 1H), 3.92 (s, 1H), 3.65-3.63 (m, 2H), 3.55-3.52 (m, 1H), 3.50 (s, 3H), 3.36 (s, 3H), 3.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.8, 99.1, 74.9, 73.4, 72.1, 70.3, 59.6, 58.9, 56.4.

Preparation of 3,4,6-tri-*O*-benzyl-D-galactal (1ag):[1]

The commercially available 3,4,6-tri-*O*-acetyl-D-galactal (1 g, 3.6 mmol) was stirred in MeOH (25 mL) at 0^{o}C to which NaOMe (22 mg, 0.4 mmol) was added. The mixture was stirred for 3 h and the solvent was evaporated to dryness. To the same flask, dry DMF (10 mL) was added and cooled to 0 ^{o}C followed by NaH (720 mg, 60% in mineral oil, 18 mmol) was added portion wise. The mixture was stirred for 20 min at the

same temperature to which benzyl bromide (1.8 mL, 16 mmol) was added slowly dropwise. The resulting mixture was stirred for overnight and quenched by saturated aqueous NH_4Cl (3 mL) and diluted with ethyl acetate (250 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to afford **1ag** as a white solid in 73% yield (1.1 g). NMR spectra were identical with literature data.[1] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 15H), 6.43 (d, *J* = 6.0 Hz, 1H), 4.95-4.92 (m, 2H), 4.71-4.65 (m, 3H), 4.56 (d, *J* = 12.0Hz, 1H), 4.48 (d, *J* = 12.0 Hz, 1H), 4.24 (m, 2H), 4.00 (s, 1H), 3.85 (t, *J* = 9.0 Hz, 1H), 3.72 (dd, *J* = 9.5, 4.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.0, 138.3, 138.2, 137.8, 128.2, 128.2, 128.0, 127.7, 127.5, 127.4, 127.3, 99.8, 75.5, 73.2, 73.1, 71.1, 70.7, 70.6, 68.3.

Preparation of 3,4-di-*O*-benzyl-L-rhamnal (1ah):[4]

L-Rhamnose (5.0 g, 30.5 mmol) was suspended in acetic anhydride (22 mL) and cooled to 0 ^{o}C after which perchloric acid (0.25 mL) was added dropwise. The mixture was allowed to stir for 3 h at room temperature and cooled to 0 ^{o}C to which hydrobromic acid (44 mL, 33% in AcOH) was added dropwise. The resulting mixture was stirred for overnight at room temperature and concentrated. The crude glycopyranosyl bromide was dissolved in CH_3CN and then Zinc dust (15 g, 228 mmol) and ammonium chloride (12 g, 228 mmol) were added and stirred at 60^{o}C for 2.5 h. Upon completion of the reaction, the reaction mixture is filtrated and the filtrate was concentrated and purified by column chromatography (SiO_2, hexane:ethyl acetate = 2:1) to afford 3,4-di-*O*-acetyl-L-rhamnose as colorless oil in 75% yield (4.9 g). NMR spectra were identical with literature. [18a] To a solution of 3,4-di-O-acetyl-L-rhamnal (1 g, 4.6 mmol) in THF (30 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 5 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 2:1) to afford 3,4-di-*O*-benzyl-L-rhamnose **1ah** as colourless oil in 50% yield (720 g).[4b] NMR spectra were identical with literature data.[15] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 10H), 6.39 (d, *J* = 5.5 Hz, 1H), 4.92-4.88 (m, 2H), 4.73 (d, *J* = 11.5 Hz, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.60

(d, *J* = 11.5 Hz, 1H), 4.24 (d, *J* = 6.0 Hz, 1H), 3.99-3.97 (m, 1H), 3.51 (t, *J* = 7.5 Hz, 1H), 1.41 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 138.3, 138.2, 128.3, 127.9, 127.7, 127.7, 127.5, 100.0, 79.4, 76.3, 74.0, 73.9, 70.4, 17.4.

Preparation of 3,4-di-*O*-benzyl-D-xylal (1ai):[4]

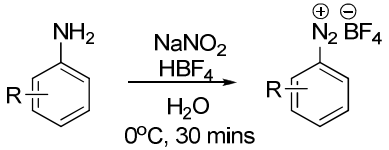
D-xylose (5.0 g, 33.5 mmol) was suspended in acetic anhydride (25 mL), perchloric acid (0.3 mL) was added dropwise at 0 ^{o}C. The mixture was allowed to stir for 3 h at room temperature and cooled to 0 ^{o}C to which hydrobromic acid (48 mL, 33% in AcOH) was added dropwise. The resulting mixture was stirred for overnight at room temperature and concentrated. The crude glycopyranosyl bromide was dissolved in CH_3CN and then Zinc dust (15 g, 228 mmol) and ammonium chloride (12 g, 228 mmol) were added and stirred at 60^{o}C for 2.5 h. Upon completion of the reaction, the reaction mixture is filtrated and the filtrate was concentrated and purified by column chromatography (SiO_2, hexane:ethyl acetate = 2:1) to afford 3,4-di-*O*-acetyl-D-xylal as colorless oil in 50% yield (3.3 g).[4a] To a solution of 3,4-di-*O*-acetyl- D-xylal (1 g, 5 mmol) in THF (30 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 3 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to afford 3,4-di-*O*-benzyl-D- xylal **1ai** as colourless oil in 51% yield (743 mg).[18b] NMR spectra were identical with literature data.[5] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.30 (m, 10H), 6.57 (d, *J* = 5.5 Hz, 1H), 4.96 (m, 1H), 4.68-4.65 (m, 2H), 4.62 (d, *J* = 11.5 Hz, 1H), 4.54 (d, *J* = 11.5 Hz, 1H), 4.13 (d, *J* = 11.5 Hz, 1H), 3.98 (d, *J* = 12.0 Hz, 1H), 3.86 (s, 1H), 3.69 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 138.3, 137.8, 128.4, 128.3, 127.8, 127.7, 127.6, 127.6, 98.9, 72.6, 71.2, 69.9, 69.0, 63.9.

Preparation of 3,5-di-*O*-benzyl-D-ribal (1aj):[6]

D-Ribose (3.0 g., 20 mmol) was suspended in DCM (20 mL) to which acetic anhydride (11.23 g., 110 mmol) followed by pyridine (9.49 g., 120 mmol) was added at 0 ^{o}C. The resulting mixture was stirred for 12 hours at room temperature and quenched with water (20 mL). The aqueous layer was extracted with DCM (2X30 mL), washed with water, dried over saturated Na_2SO_4 and concentrated. The crude product was purified

by short silica chromatography using 20% ethyl acetate in hexane to obtain D-ribofuranose 1,2,3,5-tetraacetate. Further, the ribose tetra-acetate was dissolved in HBr solution (33 wt % in acetic acid, 10.36 mL, 60 mmol) and stirred for 5 hours at room temperature. The reaction mixture was diluted with acetonitrile (25 mL) to which sodium acetate (3.28 g., 40 mmol), ammonium chloride (3.21 g., 60 mmol), and zinc dust (3.93 g., 40 mmol) were added successively. The reaction is allowed to stir for 2 hours at room temperature, then quenched with water, extracted with ethyl acetate (3X25 mL). The organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to obtain 3,5-di-*O*-acetyl-D-ribal in 27.5 % yield. (1.1 g).[20] To a solution of 3,5-di-*O*-acetyl-D-ribal (1 g, 5 mmol) in THF (25 mL), NaOH (736 mg, 18.4 mmol,), TBAI (50 mg, 0.13 mmol) and benzyl bromide (2.2 mL, 18.4 mmol) were added successively and the reaction mixture was allowed to stir for 3 h at room temperature. After completion, the reaction mixture was diluted with water and extracted with DCM. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and evaporated. The crude residue was purified by column chromatography (SiO_2, hexane:ethyl acetate = 9:1) to afford 3,5-di-*O*-benzyl-D-ribal **1aj** as colourless oil in 55% yield (801 mg). NMR spectra were identical with literature data.[7] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 10H), 6.41 (d, *J* = 5.0 Hz, 1H), 4.88-4.87 (m, 1H), 4.72 (s, 2H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.09-4.39 (m, 3H), 3.76-3.74 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.5, 138.7, 137.9, 128.4, 128.3, 127.8, 127.7, 127.6, 127.5, 98.7, 73.1, 71.0, 70.7, 66.6, 63.2.

Preparation of aryldiazonium tetrafluoroborates:



Aryldiazonium tetrafluoroborates were prepared using literature procedure.[8] To a stirred solution of aniline (10 mmol) in 48% aq. HBF_4 (4 ml), a solution of $NaNO_2$ (0.69 g in 5 ml of deionized water, 10 mmol) was added at 0 °C. The reaction mixture was stirred at 700 RPM for 30 min at 0°C. The resulting solid was filtered off, dissolved in 5 ml of acetone and precipitated by addition of 5 ml of diethyl ether. The resulting crystals

were dried in high vacuum to obtain pure aryldiazonium tetrafluoroborates. All the compounds gave identical NMR spectra to those reported previously. 4-bromobenzenediazonium tetrafluoroborate **2aa**[8] (pink solid, 72%); 2-chlorobenzenediazonium tetrafluoroborate **2ab**[8] (white solid, 64%); benzenediazonium tetrafluoroborate **2ac**[8] (white solid, 70%); 1-napthyldiazonium tetrafluoroborate **2ad**[9] (Purple solid, 55%); 4-methylbenzenediazonium tetrafluoroborate **2ae**[8] (white solid, 80%); 4-methoxybenzenediazonium tetrafluoroborate **2af**[9] (white solid, 75%); 4-nitrobenzenediazonium tetrafluoroborate **2ag**[8] (yellow solid, 69%); 4-(trifluoromethyl)benzenediazonium tetrafluoroborate **2ah**[10] (white solid, 70%); 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate **2ai**[8] (white solid, 30%); 4-acetylbenzenediazonium tetrafluoroborate **2aj**[9] (white solid, 75%); 4-cyanobenzenediazonium tetrafluoroborate **2ak**[8] (light yellow solid, 70%); 4-fluorobenzenediazonium tetrafluoroborate **2al**[8] (white solid, 69%); 4-chlorobenzenediazonium tetrafluoroborate **2am**[11] (white solid, 80%); 4-iodobenzenediazonium tetrafluoroborate **2an**[12] (brown solid, 80%); 2-ethylbenzenediazonium tetrafluoroborate **2ao**[13] (white solid, 64%); 2,4-dimethylbenzenediazonium tetrafluoroborate **2ap**[14] (white solid, 60%); 2,5-dimethylbenzenediazonium tetrafluoroborate **2aq**[15] (white solid, 70%); 3-fluorobenzenediazonium tetrafluoroborate **2ar**[16] (white solid, 40%); 3-chlorobenzenediazonium tetrafluoroborate **2as**[8] (pink solid, 59%); 3-bromobenzenediazonium tetrafluoroborate **2at**[12] (orange solid, 65%); 3,5-dichlorobenzenediazonium tetrafluoroborate **2au**[16] (white solid, %); 4-bromo-3-methylbenzenediazonium tetrafluoroborate **2av**[14] (white solid, 30%); 3-acetylbenzenediazonium tetrafluoroborate **2aw**[14] (white solid, 54%); 3-nitrobenzenediazonium tetrafluoroborate **2ax**[16] (white solid, 50%); 3-(trifluoromethyl)benzenediazonium tetrafluoroborate **2ay**[7] (Pink solid, 65%); 3,5-dimethylbenzenediazonium tetrafluoroborate **2az**[16] (white solid, 20%); 2,4-dimethoxybenzenediazonium tetrafluoroborate **2ba**[17] (purple solid, 60%).

General procedure used in the optimization table:

The glycal, 3,4,6-tri-*O*-methyl-D-glucal (95 mg, 0.5 mmol) was stirred in an appropriate solvent (4 mL) in a oven dried 25 ml round bottom flask. 4-Bromobenzenediazonium tetrafluoroborate (152 mg, 0.56 mmol) and palladium acetate (5.5 mg, 0.05 mmol) was successively added at room temperature under open air atmosphere. The mixture was stirred and monitored by TLC. After completion (or appropriate time mentioned in the table), the reaction mixture was diluted with ethyl acetate (150 mL) and washed with water (100 mL) and filtered, dried over anhydrous

Na_2SO_4, The organic layer was concentrated and purified by silica column chromatography (100-200 mess) on silica gel using 20 % ethyl acetate in hexane which furnished **3aa** as white foam.

General procedure for the preparation of *C*-glycosides:

Glycal (0.25-0.5 mmol) was dissolved in acetonitrile (3 mL) to which water (1 mL) was added. To the above solution, aryldiazonium tetrafluoroborate (1.1 equiv.) and palladium acetate (5-10 mol%) was successively added at room temperature under open air atmosphere. of the above mixture were added simultaneously aryldiazoniumtetrafluoroborate and palladium acetate at room temperature in an open air atmosphere. The reaction mixture was stirred for appropriate time (2-8 h), diluted with ethyl acetate (150 mL) and washed with water (100 mL). The organic layer was filtered, dried over anhydrous Na_2SO_4, concentrated and purified by silica column chromatography (100-200 mess) on silica gel using ethyl acetate in hexane.

(2R,3R,6S)-6-(4-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aa]

The compound **3aa** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-bromobenzenediazonium tetrafluoroborate **2aa** (152 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3aa** as white foam (147 mg, 90%); TLC R_f = 0.35 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.34-5.32 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.54-3.49 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 2.99-2.92 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 137.4, 131.8, 129.1, 122.3, 81.6, 74.6, 74.6, 71.5, 59.4, 59.4, 43.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 329.0388; found, 329.0359.

(2R,3R,6S)-6-(2-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ab]

The compound **3ab** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate **2ab** (127 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ab** as colourless semi solid (126 mg, 89%); TLC R_f = 0.40 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.39 (m, 1H), 7.31-7.29 (m, 1H), 7.20-7.16 (m, 2H), 5.64 (t, *J* = 5.5 Hz, 1H), 3.87 (d, *J* = 7.0 Hz, 1H), 3.77-3.74 (m, 1H), 3.57-3.51 (m, 2H), 3.43 (s, 3H), 3.32 (s, 3H), 2.91 (dd, *J* = 15.0, 5.5 Hz, 1H), 2.78 (dd, *J* = 15.0, 6.0 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 136.9, 133.3, 129.9, 129.4, 128.2, 126.8, 81.4, 75.5, 71.9, 71.9, 59.3, 59.0, 44.3. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0868.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3ac]

The compound **3ac** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (97 mg, 0.5 mmol) and benzenediazonium tetrafluoroborate **2ac** (108 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.8 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ac** as white foam (107 mg, 85%); TLC R_f = 0.5 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.25 (m, 4H), 7.22-7.19 (m, 1H), 5.39-5.38 (m, 1H), 3.89 (d, *J* = 8.0 Hz, 1H), 3.54-3.49 (m, 3H), 3.43 (d, *J* = 2.0 Hz, 3H), 3.35 (d, *J* = 2.0 Hz, 3H), 3.05-2.93 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 138.3, 128.6, 128.0, 127.3, 81.6, 75.1, 74.2, 71.4, 59.4, 59.3, 43.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{19}O_4$ 251.1283; found, 251.1265.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(naphthalen-1-yl)dihydro-2H-pyran-4(3H)-one [3ad]

The compound **3ad** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 1-napthyldiazonium tetrafluoroborate **2ad** (135 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.7 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ad** as white foam (131 mg, 87%); TLC R_f = 0.48 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.77-7.71 (m, 2H), 7.49 – 7.27 (m, 4H), 6.03-6.02 (m, 1H), 4.01 (d, *J* = 9.0 Hz, 1H), 3.46 (s, 3H), 3.40-3.38 (m, 1H), 3.32-3.30 (m, 5H), 3.18-3.11 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 133.9, 133.5, 131.5, 129.5, 128.5, 126.3, 126.2, 125.9, 124.8, 124.7, 81.5, 73.8, 72.8, 71.1, 59.7, 59.3, 44.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{21}O_4$ 301.1440; found, 301.1437.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3ae] The compound **3ae** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (115 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ae** as white foam (116 mg, 87%); TLC R_f = 0.4 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 5.36 (d, *J* = 6.0 Hz, 1H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.52-3.46 (m, 3H), 3.42 (s, 3H), 3.34 (s, 3H), 3.02-2.93 (m, 2H), 2.24 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.7, 137.9, 135.2, 129.2, 127.4, 81.6, 75.0, 73.9, 71.4, 59.5, 59.3, 43.7, 20.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{21}O_4$ 265.1440; found, 265.1417.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(4-methoxyphenyl)dihydro-2H-pyran-4(3H)-one [3af]

The compound **3af** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-methoxybenzenediazonium tetrafluoroborate **2af** (124 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in

hexane which furnished **3af** as white foam (118 mg, 84%); TLC R_f = 0.28 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 2H), 6.79-6.77 (m, 2H), 5.35 (dd, *J* = 6.5, 2.5 Hz, 1H), 3.89-3.87 (m, 1H), 3.70 (s, 3H), 3.53-3.47 (m, 3H), 3.43 (s, 3H), 3.34 (s, 3H), 3.01-2.93 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.8, 159.3, 130.3, 128.8, 113.9, 81.7, 74.8, 73.8, 71.4, 59.5, 59.3, 55.1, 43.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{21}O_5$ 281.1389; found, 281.1370

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(4-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3ag]

The compound **3ag** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-nitrobenzenediazonium tetrafluoroborate **2ag** (132 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4h. Column chromatography purification was performed using 25 % ethyl acetate in hexane which furnished **3ag** as white foam (98 mg, 69%); TLC R_f = 0.25 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 5.44 (t, *J* = 4.5 Hz, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.61-3.57 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.02-2.94 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 147.5, 145.9, 127.9, 123.8, 81.4, 75.7, 74.4, 71.7, 59.3, 59.2, 43.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1108.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(4-(trifluoromethyl)phenyl)dihydro-2H-pyran-4(3H)-one [3ah]

The compound **3ah** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-(trifluoromethyl)benzenediazonium tetrafluoroborate **2ah** (145 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3ah** as viscous oil (127 mg, 79%); TLC R_f = 0.30 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H), 5.41 (m, 1H), 3.88 (d, *J* = 7.0 Hz, 1H), 3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.03-2.94 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 142.5, 130.4 (q, $J_{C\text{-}F}$ = 32.5 Hz), 127.5, 126.7 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272 Hz), 81.5, 75.2, 74.6, 71.6, 59.3, 59.3, 43.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}F_3O_4$ 319.1157; found, 319.1139.

Methyl 4-((2S,5R,6R)-5-methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzoate [3ai]

The compound **3ai** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate **2ai** (140 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3ai** as white foam (118 mg, 76%); TLC R_f = 0.24 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.41 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.84 (s, 3H), 3.53 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.04-2.94 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 166.6, 143.5, 130.0, 129.9, 127.2, 81.6, 75.0, 74.9, 71.6, 59.4, 52.2, 43.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_6$ 309.1338; found, 309.1339.

(2R,3R,6S)-6-(4-Acetylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aj]

The compound **3aj** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-acetylbenzenediazonium tetrafluoroborate **2aj** (130 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 3h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3aj** as yellowish foam (115 mg, 78%); TLC R_f = 0.40 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 5.41 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.53 (s, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.04-3.94 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 197.4, 143.6, 136.6, 128.6, 127.3, 81.5, 75.0, 74.7, 71.5, 59.3, 59.3, 43.6, 26.5. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_5$ 293.1389; found, 293.1393.

4-((2S,5R,6R)-5-Methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzonitrile [3ak]

The compound **3ak** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **2ak** (121 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$

(5.5 mg, 0.025 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3ak** as white foam (111 mg, 80%); TLC R_f = 0.26 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 5.40 (t, *J* = 5.0 Hz, 1H), 3.87 (d, *J* = 7.0 Hz, 1H), 3.59-3.55 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.00-2.93 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.3, 143.9, 132.5, 127.8, 118.3, 112.0, 81.4, 75.5, 74.6, 71.7, 59.4, 59.3, 43.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}NO_4$ 276.1236; found, 276.1229.

(2R,3R,6S)-6-(4-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3al]

The compound **3al** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-fluorobenzenediazonium tetrafluoroborate **2al** (116 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3al** as white foam (114 mg, 84%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (t, J=7.0 Hz, 2H), 6.99 (t, *J* = 8.0 Hz, 2H), 5.40 (m, 1H), 3.93 (d, *J* = 8.5 Hz, 1H), 3.58-3.50 (m, 3H), 3.47 (s, 3H), 3.39 (s, 3H), 3.07-2.98 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 162.4 (d, $J_{C\text{-}F}$ = 247.5 Hz), 134.2(d, $J_{C\text{-}F}$ = 3.3 Hz), 129.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 116.0 (d, $J_{C\text{-}F}$ = 21.5 Hz), 81.6, 74.6, 74.4, 71.5, 59.5, 59.4, 43.8. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{14}H_{17}FO_4Na$ 291.1009; found, 291.0985.

(2R,3R,6S)-6-(4-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3am]

The compound **3am** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-chlorobenzenediazonium tetrafluoroborate **2am** (126 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished 3am as white foam (123 mg, 85%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (s, 4H), 5.44-5.43 (m, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.62-3.55 (m, 3H), 3.51 (s, 3H), 3.43 (s, 3H), 3.08-3.01 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ

206.1, 136.9, 134.1, 128.8, 128.8, 81.6, 74.6, 74.6, 71.5, 59.5, 59.4, 43.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0870.

(2R,3R,6S)-6-(4-Iodophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3an]

The compound **3an** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-iodobenzenediazonium tetrafluoroborate **2an** (177 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3an** as brownish foam (170 mg, 90%); TLC R_f = 0.63 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 5.31 (m, 1H), 3.86 (d, *J* = 8.5 Hz, 1H), 3.56-3.51 (m, 3H), 3.41 (s, 3H), 3.34 (s, 3H), 2.97-2.90 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 138.1, 137.7, 129.2, 94.0, 81.5, 74.7, 74.6, 71.5, 59.4, 59.3, 43.5. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}IO_4$ 377.0250; found, 377.0250.

(2R,3R,6S)-6-(2-Ethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ao]

The compound **3ao** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 2-ethylbenzenediazonium tetrafluoroborate **2ao** (123 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ao** as semi solid (106 mg, 76%); TLC R_f = 0.47 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.17 (m, 3H), 7.07-7.04 (m, 1H), 5.59 (t, *J* = 4.5 Hz, 1H), 3.93 (d, *J* = 9.0 Hz, 1H), 3.50-3.41 (m, 6H), 3.32 (s, 3H), 2.94 (d, *J* = 4.5 Hz, 2H), 2.80-2.67 (m, 2H), 1.16 (t, *J* = 7.5 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 143.6, 135.8, 129.2, 128.7, 127.6, 125.7, 81.6, 73.9, 72.3, 71.6, 59.6, 59.4, 44.4, 25.1, 15.41. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1575.

(2R,3R,6S)-6-(2,4-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ap]

The compound **3ap** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 2,4-dimethylbenzenediazonium tetrafluoroborate **2ap** (123 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ap** as white foam (100 mg, 71%); TLC R_f = 0.48 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.0 Hz, 1H), 6.94 (s, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 5.48 (t, *J* = 4.5 Hz, 1H), 3.91 (d, *J* = 9.0 Hz, 1H), 349-3.37 (m, 6H), 3.33 (s, 3H), 2.99-2.93 (m, 2H), 2.32 (s, 3H), 2.20 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 207.7, 138.2, 137.7, 133.3, 131.9, 127.6, 126.2, 81.6, 73.4, 72.8, 71.4, 59.6, 59.3, 44.0, 20.9, 19.4. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1575.

(2R,3R,6S)-6-(2,5-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aq]

The compound **3aq** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 2,5-dimethylbenzenediazonium tetrafluoroborate **2aq** (122 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3aq** as semi solid (113 mg, 81%); TLC R_f = 0.65 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00-6.99 (m, 2H), 6.94-6.93 (m, 1H), 5.48-5.47 (m, 1H), 3.91 (d, *J* = 9.0 Hz, 1H), 3.51-3.42 (m, 6H), 3.33 (s, 3H), 2.99-2.90 (m, 2H), 2.30 (s, 3H), 2.20 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 207.4, 136.3, 135.2, 134.4, 130.9, 129.0, 128.1, 81.8, 73.8, 72.9, 71.6, 59.6, 59.3, 44.0, 21.0, 19.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1596.

(2R,3R,6S)-6-(3-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3ar]

The compound **3ar** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3-fluorobenzenediazonium tetrafluoroborate **2ar** (117 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$

(5.5 mg, 0.025 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ar** as brownish semi solid (112 mg, 83%); TLC R_f = 0.6 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1H), 7.06 (t, *J* = 8.5 Hz, 2H), 6.90 (t, *J* = 8.5 Hz, 1H), 5.35 (m, 1H), 3.88 (d, *J* = 7.5 Hz, 1H), 3.55-3.54 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 3.00-2.92 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 162.9 (d, J_{C-F} = 247.0 Hz), 141.11 (d, J_{C-F} = 6.7 Hz), 130.2 (d, J_{C-F} = 8.2 Hz), 122.7 (d, J_{C-F} = 2.8 Hz) , 115.1 (d, J_{C-F} = 22.1 Hz), 114.4 (d, J_{C-F} = 22.1 Hz) 81.5, 74.8, 74.6, 71.5, 59.3, 59.3, 43.6. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{14}H_{18}FO_4$ 269.1189; found, 269.1199.

(2R,3R,6S)-6-(3-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3as]

The compound **3as** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3-chlorobenzenediazonium tetrafluoroborate **2as** (125 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3as** as viscous oil (122 mg, 85%); TLC R_f = 0.46 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.16 (m, 3H), 5.33 (dd, *J* = 6.0, 3.5 Hz, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.58-3.54 (m, 3H), 3.42 (s, 3H), 3.35 (s, 3H), 2.99-2.90 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 140.7, 134.8, 129.9, 128.3, 127.5, 125.2, 81.5, 74.9, 74.6, 71.6, 59.3, 43.7. HRMS (ESI-TOF) (m/z): [M + H]$^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0876.

(2R,3R,6S)-6-(3-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3at]

The compound **3at** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3-bromobenzenediazonium tetrafluoroborate **2at** (152 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3at** as brownish oil (138 mg, 83%); TLC R_f = 0.64 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (m, *J* = 7.5 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 5.32 (m, 1H), 3.87 (d, *J* = 8.0 Hz, 1H), 3.58-3.54 (m, 3H), 3.41

(s, 3H), 3.35 (s, 3H), 2.98-2.89 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 140.9, 131.2, 130.3, 130.1, 125.6, 122.9, 81.5, 74.9, 74.5, 71.5, 59.3, 43.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 329.0388; found, 329.0393.

(2R,3R,6S)-6-(3,5-Dichlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3au]

The compound **3au** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3,5-dichlorobenzenediazonium tetrafluoroborate **2au** (145 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3au** as colourless oil (105 mg, 65%); TLC R_f = 0.64 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (m, 3H), 5.28 (m, 1H), 3.86 (d, *J* = 7.5 Hz, 1H), 3.64-3.63 (m, 1H), 3.56 (s, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 2.93-2.86 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 142.3, 135.4, 128.3, 125.5, 81.4, 75.5, 74.1, 71.7, 59.4, 59.2, 43.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{17}Cl_2O_4$ 319.0504; found, 319.0506.

(2R,3R,6S)-6-(4-Bromo-3-methylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3av]

The compound **3av** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 4-bromo-3-methylbenzenediazonium tetrafluoroborate **2av** (160 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3av** as brownish oil (145 mg, 84%); TLC R_f = 0.3 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.16 (s, 1H), 6.97 (d, *J* = 8.0 Hz, 1H), 5.29 (m, 1H), 3.86 (d, *J* = 7.5 Hz, 1H), 3.54-3.49 (m, 3H), 3.41 (s, 3H), 3.34 (s, 3H), 2.97-2.89 (m, 2H), 2.29 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 138.1, 137.7, 132.4, 129.6, 126.2, 124.6, 81.5, 74.5, 74.5, 71.5, 59.3, 59.2, 43.6, 22.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{20}BrO_4$ 343.0545; found, 343.0547.

(2R,3R,6S)-6-(3-Acetylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3aw]

The compound **3aw** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3-acetylbenzenediazonium tetrafluoroborate **2aw** (130 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3aw** as colourless oil (131 mg, 89%); TLC R_f = 0.3 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 5.42 (m, 1H), 3.88 (d, *J* = 8.0 Hz, 1H), 3.57-3.54 (m, 3H), 3.41 (s, 3H), 3.35 (s, 3H), 3.06-2.95 (m, 2H), 2.53 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 197.7, 139.2, 137.5, 131.5, 129.0, 127.9, 127.2, 81.6, 75.0, 74.8, 71.6, 59.3, 59.3, 43.8, 26.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_5$ 293.1389; found, 293.1391.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(3-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3ax]

The compound **3ax** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3-nitrobenzenediazonium tetrafluoroborate **2ax** (132 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4h. Column chromatography purification was performed using 25 % ethyl acetate in hexane which furnished **3ax** as yellowish oil (103 mg, 69%); TLC R_f = 0.30 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 5.45 (t, *J* = 5.0 Hz, 1H), 3.89 (d, *J* = 7.5 Hz, 1H), 3.65-3.55 (m, 3H), 3.41 (s, 3H), 3.36 (s, 3H), 3.04-2.95 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.0, 148.5, 141.1, 132.8, 129.7, 123.0, 122.1, 81.4, 75.7, 74.3, 71.8, 59.4, 59.2, 43.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1068.

(2R,3R,6S)-3-Methoxy-2-(methoxymethyl)-6-(3-(trifluoromethyl)phenyl)dihydro-2H-pyran-4(3H)-one [3ay]

The compound **3ay** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3-(trifluoromethyl)benzenediazonium tetrafluoroborate **2ay** (144 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of

$Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ay** as colourless oil (135 mg, 84%); TLC R_f = 0.6 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.49-7.47 (m, 2H), 7.40 (t, *J* = 7.5 Hz, 1H), 5.41-5.39 (m, 1H), 3.87 (d, *J* = 8.0 Hz, 1H), 3.62-3.59 (m, 1H), 3.56-3.55 (m, 2H), 3.41 (s, 3H), 3.35 (s, 3H), 3.03-2.92 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 139.8, 131.3 (q, $J_{C\text{-}F}$ = 32.4 Hz), 129.1, 124.9 (q, $J_{C\text{-}F}$ = 3.7 Hz) , 124.0 (q, $J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $J_{C\text{-}F}$ = 272 Hz), 81.5, 75.3, 74.7, 71.7, 59.3, 59.2, 43.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}F_3O_4$ 319.1157; found, 319.1160.

(2R,3R,6S)-6-(3,5-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3az]

The compound **3az** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 3,5-dimethylbenzenediazonium tetrafluoroborate **2az** (122 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 3.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3az** as colourless solid (86 mg, 61%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90-6.83 (m, 3H), 5.30-5.29 (m, 1H), 3.87 (d, *J* = 8.5 Hz, 1H), 3.57-3.49 (m, 3H), 3.43 (s, 3H), 3.34 (s, 3H), 3.01-2.98 (m, 1H), 2.90-2.88 (m, 1H), 2.21 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.5, 138.4, 138.1, 129.7, 125.1, 81.7, 75.1, 74.2, 71.5, 59.4, 59.2, 43.7, 21.2. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1595.

(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3ba]

The compound **3ba** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and benzenediazonium tetrafluoroborate **2ac** (52 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 5 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3ba** as white foam (77 mg, 80%); TLC R_f = 0.28 (20 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.5 Hz, 2H), 7.26-7.19 (m, 13H), 5.40-5.39 (m, 1H), 4.76 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.39 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz,

1H), 4.17 (d, *J* = 8.5 Hz, 1H), 3.65-3.56 (m, 3H), 3.05-2.93 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 138.5, 137.7, 137.3, 128.6, 128.3, 128.3, 128.1, 128.1, 127.8, 127.8, 127.7, 127.3, 79.5, 75.1, 74.5, 73.5, 73.3, 69.0, 43.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{27}O_4$ 403.1909; found, 403.1916.

(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bb]

The compound **3bb** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (55 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bb** as white foam (89 mg, 89%); TLC R_f = 0.65 (30 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.18 (m, 12H), 7.06 (d, *J* = 7.5 Hz, 2H), 5.39-5.37 (m, 1H), 4.77 (d, *J* = 11.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 4.16 (d, *J* = 8.5 Hz, 1H), 3.63-3.57 (m, 3H), 3.04-2.94 (m, 2H), 2.23 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 137.9, 137.8, 137.3, 135.4, 129.3, 128.3, 128.33, 128.1, 127.8, 127.8, 127.7, 127.4, 79.6, 75.0, 74.3, 73.5, 73.4, 69.0, 43.9, 21.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{29}O_4$ 417.2066; found, 417.2070.

(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-methoxyphenyl)dihydro-2H-pyran-4(3H)-one [3bc]

The compound **3bc** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-methoxybenzenediazonium tetrafluoroborate **2af** (60 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 12 % ethyl acetate in hexane which furnished **3bc** as white foam (88 mg, 85%); TLC R_f = 0.25 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26-7.18 (m, 12H), 6.77 (d, *J* = 8.5 Hz, 2H), 5.37 (dd, *J* = 6.5, 2.5 Hz, 1H), 4.77 (d, *J* = 11 Hz, 1H), 4.51 (d, *J* = 12. Hz, 1H), 4.39 (d, *J* = 12. Hz, 1H), 4.34 (d, *J* = 11. Hz, 1H), 4.16 (d, *J* = 9 Hz, 1H), 3.69 (s, 3H), 3.62-3.54 (m, 3H), 3.03-2.94 (m Hz, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.7, 159.3,

137.8, 137.3, 130.5, 128.8, 128.3, 128.3, 128.1, 127.8, 127.8, 127.7, 113.9, 79.6, 74.8, 74.0, 73.5, 73.4, 68.9, 55.2, 43.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 433.2015; found, 433.2000.

(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-fluorophenyl)dihydro-2H-pyran-4(3H)-one [3bd]

The compound **3bd** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-fluorobenzenediazonium tetrafluoroborate **2al** (56 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3bd** as white foam (85 mg, 84%); TLC R_f = 0.62 (30 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.17 (m, 12H), 6.93 (t, *J* = 8.0 Hz, 2H), 5.37 (m, 1H), 4.75 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.0 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.62-3.55 (m, 3H), 3.01-2.93 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.2, 162.4 (d, J_{C-F} = 247.5 Hz), 137.7, 137.2, 134.2 (d, J_{C-F} = 3.3 Hz), 129.3 (d, J_{C-F} = 8.2 Hz), 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 115.5 (d, J_{C-F} = 21.5 Hz), 79.4, 74.6, 74.6, 73.5, 73.3, 69.0, 44.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}FO_4$ 421.1815; found, 421.1813.

(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-chlorophenyl)dihydro-2H-pyran-4(3H)-one [3be]

The compound **3be** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-chlorobenzenediazonium tetrafluoroborate **2am** (60 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3be** as white foam (89 mg, 85%); TLC R_f = 0.4 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25-7.17 (m, 14H), 5.36 (m, 1H), 4.75 (d, *J* = 11.0 Hz, 1H), 4.50 (d, *J* = 12.0 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.15 (d, *J* = 8.5 Hz, 1H), 3.62-3.56 (m, 3H), 3.00-2.92 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.0, 137.7, 137.2, 137.1, 134.1, 128.8, 128.7, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 79.4, 74.8, 74.5, 73.5, 73.3, 69.0, 43.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}ClO_4$ 437.1520; found, 437.1521.

(2R,3R,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl)dihydro-2H-pyran-4(3H)-one [3bf]

The compound **3bf** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-bromobenzenediazonium tetrafluoroborate **2aa** (72 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bf** as white foam (94 mg, 82%); TLC R_f = 0.29 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.31-7.13 (m, 12H), 5.34 (m, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.5 Hz, 1H), 4.39 (d, *J* = 12.5 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.14 (d, *J* = 8.5 Hz, 1H), 3.63-3.56 (m, 3H), 2.99-2.91 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.9, 137.7, 137.6, 137.1, 131.8, 129.0, 128.3, 128.3, 128.1, 127.9, 127.8, 127.7, 122.2, 79.3, 74.9, 74.6, 73.5, 73.3, 69.0, 43.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}BrO_4$ 481.1014; found, 481.1020.

4-((2S,5R,6R)-5-(Benzyloxy)-6-(benzyloxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzonitrile [3bg]

The compound **3bg** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **2ak** (58 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bg** as white foam (72 mg, 70%); TLC R_f = 0.25 (30 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.25-7.18 (m, 10H), 5.40 (m, 1H), 4.72 (d, *J* = 11.0 Hz, 1H), 4.49 (d, *J* = 12.5 Hz, 1H), 4.40 (d, *J* = 12.5 Hz, 1H), 4.33 (d, *J* = 11.0 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.67-3.66 (m, 1H), 3.61 (s, 2H), 3.00-2.92 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.2, 144.1, 137.5, 136.9, 132.4, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 118.3, 112.0, 79.1, 75.7, 74.5, 73.5, 73.2, 69.1, 43.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{26}NO_4$ 428.1862; found, 428.1858.

Methyl 4-((2S,5R,6R)-5-(benzyloxy)-6-(benzyloxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzoate [3bh]

The compound **3bh** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-glucal **1ab** (100 mg, 0.24 mmol) and 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate **2ai** (67 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bh** as white foam (83 mg, 75%); TLC R_f = 0.24 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.5 Hz, 2H), 7.38 (d, *J* = 7.5 Hz, 2H), 7.26-7.17 (m, 10H), 5.41 (m, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 12.5 Hz, 1H), 4.40 (d, *J* = 12.0 Hz, 1H), 4.34 (d, *J* = 11.5 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 3.67-3.60 (m, 3H), 3.04-2.93 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.7, 166.5, 143.7, 137.6, 137.1, 129.9, 129.8, 128.3, 128.3, 128.1, 127.9, 127.7, 127.7, 127.1, 79.3, 75.2, 74.8, 73.5, 73.2, 69.1, 52.1, 43.9. HRMS (ESI-TOF) (m/z): $[M + Na]^+$ calcd for $C_{28}H_{28}O_6Na$ 483.1784; found, 483.1778.

(2R,3R,6S)-3-Ethoxy-2-(ethoxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bi]

The compound **3bi** was prepared using the general procedure. The reaction was carried out between tri-*O*-ethyl-D-glucal **1ac** (115 mg, 0.5 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (113 mg, 0.55 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.025 mmol) at room temperature for 2 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bi** as white foam (131 mg, 90%); TLC R_f = 0.64 (30 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (d, *J*= 8.0 Hz, 2H), 7.05 (d, *J* = 7.5 Hz, 2H), 5.36 (d, *J* = 6.0 Hz, 1H), 4.03 (d, *J* = 8.5 Hz, 1H), 3.78-3.75 (m, 1H), 3.56-3.50 (m, 4H), 3.44-3.38 (m, 2H), 3.01-2.99 (m, 2H), 2.23 (s, 3H), 1.17-1.11 (m, 6H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.9, 137.7, 135.4, 129.2, 127.3, 80.2, 74.9, 74.2, 69.1, 67.2, 66.9, 43.6, 20.9, 15.0, 14.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{25}O_4$ 293.1753; found, 293.1748.

(2R,3R,6S)-3-(Methoxymethoxy)-2-((methoxymethoxy)methyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bj]

The compound **3bj** was prepared using the general procedure. The reaction was carried out between tri-*O*-(methoxymethyl ether)-D-glucal **1ad** (100 mg, 0.35 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (82 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8 mg, 0.035 mmol) at room temperature for 7 h. Column chromatography purification was performed using 30 % ethyl acetate in hexane which furnished **3bj** as colorless solid (75 mg, 60%); TLC R_f = 0.45 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.18 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.38 (d, *J* = 6.0 Hz, 1H), 4.71 (d, *J* = 6.5 Hz, 2H), 4.64-4.61 (m, 3H), 4.29 (d, *J* = 8.0 Hz, 1H), 3.70-3.65 (m, 2H), 3.61 (d, *J* = 9.0 Hz, 1H), 3.35 (s, 3H), 3.31 (s, 3H), 3.04 (d, *J* = 9.5 Hz, 21H), 2.98-2.94 (m, 2H), 2.25 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.8, 138.0, 135.3, 129.3, 127.3, 96.9, 96.7, 76.7, 75.0, 74.2, 66.7, 56.3, 55.5, 43.9, 21.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{17}H_{25}O_6$ 325.1651; found, 325.1661.

((2R,3R,6S)-3-Acetoxy-4-oxo-6-p-tolyltetrahydro-2H-pyran-2-yl)methyl acetate [3bk]

The reaction was carried out between 3,4,6-tri-*O*-acetyl-D-glucal **1ag** (100 mg, 0.37 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (83 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) at room temperature for 5 h. The desired product **3bk** was not obtained.

(2R,3S,6S)-3-Methoxy-2-(methoxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3bl]

The compound **3bl** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and benzenediazonium tetrafluoroborate **2ac** (107 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bl** as colourless semi solid (76 mg, 60%); TLC R_f = 0.50 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.19 (m, 5H), 5.25 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.43-4.40 (m, 1H), 3.92 (dd, *J* = 6.5, 1.0 Hz, 1H), 3.69-3.62 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.76-2.72

(m, 1H), 2.61-2.56 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 140.4, 128.5, 127.9, 125.8, 82.1, 75.8, 74.8, 71.0, 59.3, 59.0, 47.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{19}O_4$ 251.1283; found, 251.1265

(2R,3S,6S)-3-Methoxy-2-(methoxymethyl)-6-(naphthalen-1-yl)dihydro-2H-pyran-4(3H)-one [3bm]

The compound **3bm** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 1-naphthyldiazonium tetrafluoroborate **2ad** (135 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bm** as light purple solid (88 mg, 58%); TLC R_f = 0.5 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.80.-7.73 (m, 2H), 7.56 (d, *J* = 6.5 Hz, 1H), 7.48-7.38 (m, 3H), 6.02 (d, *J* = 9.0 Hz, 1H), 4.42 (s, 1H), 3.97 (d, *J* = 5.5 Hz, 1H), 3.77-3.66 (m, 2H), 3.50 (s, 3H), 3.28 (s, 3H), 2.98-2.95 (m, 1H), 2.78-2.74 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 204.4, 135.8, 133.8, 130.4, 128.8, 128.7, 126.3, 125.7, 125.2, 123.4, 123.2, 82.2, 75.7, 71.9, 70.9, 59.3, 59.1, 46.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{18}H_{21}O_4$ 301.1440; found, 301.1390.

(2R,3S,6S)-3-Methoxy-2-(methoxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3bn]

The compound **3bn** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (114 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bn** as colourless semi solid (86 mg, 65%); TLC R_f = 0.52 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20-7.18 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.21 (dd, *J* = 9.5, 3.5 Hz, 1H), 4.38 (m, 1H), 3.89 (d, *J* = 5.5 Hz, 3H), 3.67-3.63 (m, 2H), 3.47 (s, 3H), 3.26 (s, 3H), 2.73 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.61-2.57 (m, 1H), 2.26 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 204.1, 137.7, 137.5, 129.2, 125.9, 82.2, 75.7, 74.8, 71.1, 59.3, 59.0, 47.75, 21.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{21}O_4$ 265.1440; found, 265.1436.

(2R,3S,6S)-6-(4-Fluorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bo]

The compound **3bo** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-fluorobenzenediazonium tetrafluoroborate **2al** (117 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 3h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bo** as colourless semi solid (79 mg, 59%); TLC R_f = 0.65 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.27 (m, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 5.23 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.41-4.38 (m, 1H), 3.91 (d, *J* = 5.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.72 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.57-2.52 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 162.4 (d, J_{C-F} = 247.5 Hz), 136.4 (d, J_{C-F} = 3.3 Hz), 127.6 (d, J_{C-F} = 8.2 Hz), 115.4 (d, J_{C-F} = 21.5 Hz), 82.1, 75.9, 74.3, 71.0, 59.3, 59.1, 47.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}FO_4$ 269.1189; found, 269.1154.

(2R,3S,6S)-6-(4-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bp]

The compound **3bp** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-chlorobenzenediazonium tetrafluoroborate **2am** (126 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bp** as colourless semi solid (87 mg, 61%); TLC R_f = 0.60 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.23 (m, 4H), 5.23 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.40-4.39 (m, 1H), 3.90 (d, *J* = 5.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.72 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.54-2.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.4, 139.1, 133.6, 128.7, 127.2, 82.0, 75.9, 74.2, 71.1, 59.3, 59.1, 47.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0874.

(2R,3S,6S)-6-(4-Bromophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bq]

The compound **3bq** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-bromobenzenediazonium tetrafluoroborate **2aa** (150 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 3 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bq** as brownish semi solid (91 mg, 55%); TLC R_f = 0.48 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 5.22 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.41 (t, *J* = 5.5 Hz, 1H), 3.90 (d, *J* = 6.5 Hz, 1H), 3.69-3.61 (m, 2H), 3.48 (s, 3H), 3.25 (s, 3H), 2.72 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.53-2.48 (m, 2H).^{13}C NMR (125 MHz, $CDCl_3$) δ 203.5, 139.6, 131.6, 127.5, 121.8, 82.0, 75.9, 74.3, 71.1, 59.3, 59.2, 47.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}BrO_4$ 329.0388; found, 329.0361.

(2R,3S,6S)-3-Methoxy-2-(methoxymethyl)-6-(4-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3br]

The compound **3br** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-nitrobenzenediazonium tetrafluoroborate **2ag** (131 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 8 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3br** as semi solid (72 mg, 48%); TLC R_f = 0.40 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 5.49 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.48-4.47 (m, 1H), 3.95 (d, *J* = 6.5 Hz, 1H), 3.74-3.64 (m, 2H), 3.51 (s, 3H), 3.26 (s, 3H), 2.78-2.75 (m, 1H), 2.50-2.45 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 202.6, 148.0, 147.4, 126.4, 123.8, 81.8, 76.3, 74.0, 71.3, 59.4, 59.3, 48.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1143.

4-((2S,5S,6R)-5-Methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl) benzonitrile [3bs]

The compound **3bs** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-cyanobenzenediazonium tetrafluoroborate **2ak** (120 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$

(11 mg, 0.05 mmol) at room temperature for 6 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bs** as colourless semi solid (68 mg, 49%); TLC R_f = 0.42 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 5.33 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.45 (m, 1H), 3.92 (d, *J* = 6.0 Hz, 1H), 3.72-3.70 (m, 1H), 3.66-3.63 (m, 1H), 3.49 (s, 3H), 3.25 (s, 3H), 2.74 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.49-2.44 (m, 1H).^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 146.0, 132.4, 126.3, 118.5, 111.7, 81.8, 76.2, 74.1, 71.3, 59.4, 59.3, 47.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{15}H_{18}NO_4$ 276.1236; found, 276.1223.

Methyl 4-((2S,5S,6R)-5-methoxy-6-(methoxymethyl)-4-oxotetrahydro-2H-pyran-2-yl)benzoate [3bt]

The compound **3bt** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 4-(methoxycarbonyl)benzenediazonium tetrafluoroborate **2ai** (139 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography purification was performed using 18 % ethyl acetate in hexane which furnished **3bt** as yellowish solid (80 mg, 52%); TLC R_f = 0.45 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 5.32 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.44 (m, 1H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.84 (s, 3H), 3.71-3.63 (m, 2H), 3.49 (s, 3H), 3.26 (s, 3H), 2.75 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.54-2.49 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 166.6, 145.7, 129.9, 129.7, 125.6, 82.0, 76.1, 74.4, 71.2, 59.3, 59.2, 52.1, 47.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{21}O_6$ 309.1338; found, 309.1375.

(2R,3S,6S)-6-(2,4-Dimethylphenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bu]

The compound **3bu** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 2,4-dimethylbenzenediazonium tetrafluoroborate **2ap** (122 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 5 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3bu** as colourless solid (76 mg, 54%); TLC R_f = 0.40 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J*=7.5Hz,1H), 6.91(s, 1H). 5.44 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.36-4.35 (m, 1H), 3.92 (d, *J*=6.5 Hz, 1H), 3.68-3.64 (m, 2H), 3.47 (s, 3H), 3.25 (s, 3H), 2.67 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.62-2.58 (m, 1H), 2.25 (s, 3H), 2.22 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ

204.4, 137.6, 135.3, 135.2, 131.3, 126.9, 125.5, 82.2, 75.66 71.6, 71.1, 59.2, 59.0, 46.5, 20.9, 18.9. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{23}O_4$ 279.1596; found, 279.1610.

(2R,3S,6S)-6-(2-Chlorophenyl)-3-methoxy-2-(methoxymethyl)dihydro-2H-pyran-4(3H)-one [3bv]

The compound **3av** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate **2ba** (127 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 4 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3av** as yellowish semi solid (60 mg, 43%); TLC R_f = 0.60 (15 % ethyl acetate in chloroform); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.54 (m, 1H), 7.28-7.14 (m, 3H), 5.62 (dd, *J* = 10.5, 2.5 Hz, 1H), 4.52-4.50 (m, 1H), 3.99(d, *J* = 6.0 Hz, 1H), 3.69-3.68 (m, 2H), 3.51 (s, 3H), 3.27 (s, 3H), 2.84 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.40-2.34 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 203.2, 138.5, 131.8, 129.4, 128.9, 127.2, 126.8, 82.0, 76.3, 71.4, 70.9, 59.3, 59.3, 46.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}ClO_4$ 285.0894; found, 285.0890.

(2R,3S,6S)-3-Methoxy-2-(methoxymethyl)-6-(3-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3bw]

The compound **3bw** was prepared using the general procedure. The reaction was carried out between tri-*O*-methyl-D-galactal **1ae** (95 mg, 0.5 mmol) and 3-nitrobenzenediazonium tetrafluoroborate **2ax** (140 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (11 mg, 0.05 mmol) at room temperature for 8 h. Column chromatography purification was performed using 20 % ethyl acetate in hexane which furnished **3bw** as yellowish semi solid (60 mg, 40%); TLC R_f = 0.3 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.19 (d, *J* = 7.0 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 5.39 (dd, *J* = 10.0, 2.5 Hz, 1H), 4.49 (t, *J* = 4.5 Hz, 1H), 3.97 (d, *J* = 6.5 Hz, 1H), 3.74-3.64 (m, 2H), 3.51 (s, 3H), 3.27 (s, 3H), 2.77 (dd, *J* = 14.5, 3.5 Hz, 1H), 2.53-2.48 (m, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 148.4, 143.1, 131.7, 129.5, 122.8, 120.8, 81.8, 76.3, 73.9, 71.3, 59.4, 59.3, 48.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{14}H_{18}NO_6$ 296.1134; found, 296.1115.

(2R,3S,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-phenyldihydro-2H-pyran-4(3H)-one [3bx]

The compound **3bx** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-galactal **1af** (100 mg, 0.24 mmol) and benzenediazonium tetrafluoroborate **2ac** (66 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol) at room temperature for 4h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bx** as colourless semi solid (48 mg, 50%); TLC R_f = 0.48 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28-7.17 (m, 15H), 5.25 (dd, *J* = 9.5, 2.5 Hz, 1H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 4.5 Hz, 1H), 4.48 (d, *J* = 4.5 Hz, 1H), 4.42 (d, *J* = 12.0 Hz, 1H), 4.37 (s, 1H), 4.09 (d, *J* = 6.5 Hz, 1H), 3.78-3.71 (m, 2H), 2.73 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.59-2.54 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.1, 140.5, 137.9, 137.4, 128.5, 128.4, 128.3, 128.0, 12.9, 127.8, 127.6, 127.5, 125.9, 79.2, 76.4, 74.7, 73.5, 72.6, 68.4, 47.9 HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{27}O_4$ 403.1909; found, 403.1916.

(2R,3S,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-p-tolyldihydro-2H-pyran-4(3H)-one [3by]

The compound **3by** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-galactal **1af** (100 mg, 0.24 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (55 mg, 0.27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3by** as semi solid (52 mg, 52%); TLC R_f = 0.47 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.14 (m, 13H), 7.08 (d, *J* = 7.5 Hz, 2H), 5.22 (d, *J* = 9.0 Hz, 1H), 4.85 (d, *J* = 12.5 Hz, 1H), 4.49 (d, *J* = 13.0 Hz, 2H), 4.42 (d, *J* = 12.5 Hz, 1H), 4.34 (s, 1H), 4.08 (d, *J* = 6.0 Hz, 1H), 3.77-3.70 (m, 2H), 2.74-2.71 (m, 1H), 2.60-2.55 (m, 1H), 2.25 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 204.3, 137.9, 137.8, 137.4, 137.4, 129.2, 128.4, 128.3, 127.9, 127.8, 127.6, 127.5, 126.0, 79.2, 76.3, 74.7, 73.5, 72.6, 68.4, 47.8, 21.1 HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{27}H_{29}O_4$ 417.2066; found, 417.2061.

(2R,3S,6S)-3-(Benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl)dihydro-2H-pyran-4(3H)-one [3bz]

The compound **3bz** was prepared using the general procedure. The reaction was carried out between tri-*O*-benzyl-D-galactal **1af** (100 mg, 0.24 mmol) and 4-bromobenzenediazonium tetrafluoroborate **2aa** (72 mg, 0. 27 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (5.5 mg, 0.024 mmol) at room temperature for 4 h. Column chromatography purification was performed using 10 % ethyl acetate in hexane which furnished **3bz** as yellowish foam (58 mg, 50%); TLC R_f = 0.50 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.39-7.28 (m, 11H), 7.23 (d, *J* = 8.0 Hz, 2H), 5.31 (dd, *J* = 10.0, 3.0 Hz, 1H), 4.97 (d, *J* = 12.0 Hz, 1H), 4.62-4.58 (m, 2H), 4.52 (d, *J* = 12.5 Hz, 1H), 4.46 (s, 1H), 4.18 (d, *J* = 6.5 Hz, 1H), 3.88-3.81 (m, 2H), 2.81 (dd, *J* = 14.5, 3.0 Hz, 1H), 2.62-2.57 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.7, 139.6, 137.8, 137.3, 131.6, 128.5, 128.3, 128.0, 127.8, 127.6, 127.6, 121.8, 79.0, 76.5, 74.1, 73.6, 72.7, 68.5, 47.8. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{26}BrO_4$ 481.1014; found, 481.1019.

(2S,3S,6R)-3-(Benzyloxy)-2-methyl-6-phenyldihydro-2H-pyran-4(3H)-one [3ca]

The compound **3ca** was prepared using the general procedure. The reaction was carried out between 3,4-di-*O*-benzyl-L-rhamnal **1ag** (110 mg, 0.35 mmol) and benzenediazonium tetrafluoroborate **2ac** (75 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8 mg, 0.035 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3ca** as white foam (73 mg, 69%); TLC R_f = 0.25 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.28 (m, 10H), 5.33 (t, *J*= 4.0 Hz, 1H), 4.89 (d, *J* = 11.5 Hz, 1H), 4.52 (d, *J* = 11.5 Hz, 1H), 3.87-3.84 (m, 1H), 3.70 (d, *J* = 7.5 Hz, 1H), 3.18 (dd, *J* = 14.0, 3.5 Hz, 1H), 2.96 (dd, *J* = 14.5, 6.5 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.3, 139.0, 137.2, 128.6, 128.3, 128.1, 128.0, 127.9, 127.1, 84.7, 74.6, 73.0, 71.9, 44.4, 18.0. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{21}O_3$ 297.1491; found, 297.1499.

(2S,3S,6R)-3-(Benzyloxy)-2-methyl-6-p-tolyldihydro-2H-pyran-4(3H)-one [3cb]

The compound **3cb** was prepared using the general procedure. The reaction was carried out between 3,4-di-*O*-benzyl-L-rhamnal **1ag** (110 mg, 0.35 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (81 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8 mg, 0.035 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3cb** as white foam (79 mg, 72%); TLC R_f = 0.40 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27-7.19 (m, 7H), 7.07 (d, *J* = 7.5 Hz, 2H), 5.20 (m, 1H), 4.78 (d, *J* = 11.5 Hz, 1H), 4.41 (d, *J* = 11.5 Hz, 1H), 3.73-3.70 (m, 1H), 3.58 (d, *J* = 8.0 Hz, 1H), 3.05 (d, *J* = 14.0 Hz, 1H), 2.85 (dd, *J* = 14.0, 6.5 Hz, 1H), 2.24 (s, 3H), 1.21 (m, *J* = 7.4 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.6, 137.9, 137.3, 136.0, 129.3, 128.4, 128.2, 128.0, 127.2, 84.8, 74.6, 73.0, 71.6, 44.5, 21.0, 18.2. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{20}H_{23}O_3$ 311.1647; found, 311.1639.

(2S,3S,6R)-3-(Benzyloxy)-2-methyl-6-(4-nitrophenyl)dihydro-2H-pyran-4(3H)-one [3cc]

The compound **3cc** was prepared using the general procedure. The reaction was carried out between 3,4-di-*O*-benzyl-L-rhamnal **1ag** (110 mg, 0.35 mmol) and 4-nitrobenzenediazonium tetrafluoroborate **2ag** (93 mg, 0.4 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8 mg, 0.035 mmol) at room temperature for 1.5 h. Column chromatography purification was performed using 12 % ethyl acetate in hexane which furnished **3cc** as white foam (78 mg, 64%); TLC R_f = 0.24 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.34-7.28 (m, 5H), 5.29 (t, *J* = 2.5 Hz, 1H), 4.79 (d, *J* = 11.5 Hz, 1H), 4.46 (d, *J* = 11.5 Hz, 1H), 3.88-3.84 (m, 1H), 3.66 (d, *J* = 6.5 Hz, 1H), 3.11 (dd, *J* = 14.0, 5.0 Hz, 1H), 2.91 (dd, *J* = 14.0, 6.0 Hz, 1H), 1.29 (d, *J* = 6.5 Hz, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 205.4, 147.6, 146.4, 136.9, 128.4, 128.2, 128.1, 127.7, 123.8, 84.1, 73.6, 73.2, 72.9, 44.5, 17.5. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{20}NO_5$ 342.1341; found, 342.1341.

(2S,5R)-5-(Benzyloxy)-2-p-tolyldihydro-2H-pyran-4(3H)-one [3cd]

The compound **3cd** was prepared using the general procedure. The reaction was carried out between di-*O*-benzyl-D-xylal **1ah** (110 mg, 0.37 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (85 mg, 0.56 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8.5 mg, 0.037 mmol) at room temperature for 4 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3cd** as colourless semi solid (45 mg, 41%); TLC R_f= 0.24 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 7H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.73-4.69 (m, 2H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.33 (dd, *J* = 12.5, 2.5 Hz, 1H), 3.86-3.83 (m, 1H), 3.75 (s, 1H), 3.20 (dd, *J* = 13.5, 10.0 Hz, 1H), 2.63 (d, *J* = 13.5 Hz, 1H), 2.37 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 206.4, 138.0, 137.0, 129.3, 128.5, 128.1, 128.1, 126.0, 80.1, 79.6, 71.7, 70.5, 47.2, 21.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{21}O_3$ 297.1491; found, 297.1501.

(2R,5S)-2-(Benzyloxymethyl)-5-p-tolyldihydrofuran-3(2H)-one [3ce]

The compound **3ce** was prepared using the general procedure. The reaction was carried out between di-*O*-benzyl-D-ribal **1ai** (100 mg, 0.34 mmol) and 4-methylbenzenediazonium tetrafluoroborate **2ae** (77 mg, 0.37 mmol) in acetonitrile-water (4 mL, 3:1) in the presence of $Pd(OAc)_2$ (8 mg, 0.034 mmol) at room temperature for 2.5 h. Column chromatography purification was performed using 8 % ethyl acetate in hexane which furnished **3ce** as white foam (31 mg, 31%); TLC R_f= 0.25 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.24 (t, 5H), 7.14 (d, *J* = 7.5 Hz, 2H), 7.09 (d, *J* = 7.5 Hz, 2H), 4.86 (d, *J* = 12.0 Hz, 1H), 4.54-4.51 (m, 2H), 4.35-4.32 (m, 1H), 4.13-4.09 (m, 1H), 3.54 (t, *J* = 11.0 Hz, 1H), 2.66-2.59 (m, 2H), 2.26 (s, 3H).^{13}C NMR (125 MHz, $CDCl_3$) δ 204.9, 138.0, 137.3, 136.8, 129.3, 128.5, 128.4, 128.0, 127.9, 125.5, 80.6, 78.9, 72.7, 70.5, 49.7, 21.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{19}H_{21}O_3$ 297.1491; found, 297.1482.

(2R,3R,6S)-6-(2-Chlorophenyl)-3,4,4-trimethoxy-2-(methoxymethyl)tetrahydro-2H-pyran [4ab]

The compound **4ab** was prepared using the general procedure while methanol is used as the solvent. The reaction was carried out between tri-*O*-methyl-D-glucal **1aa** (95 mg, 0.5 mmol) and 2-chlorobenzenediazonium tetrafluoroborate **2ab** (127 mg, 0.56 mmol) in methanol (4 mL) in the

presence of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol) at room temperature for 1 h. Column chromatography purification was performed using 15 % ethyl acetate in hexane which furnished **3ab** as viscous liquid (157 mg, 94%); TLC R_f = 0.38 (35 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.5 Hz, 1H), 7.23-7.18 (m, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.98 (d, *J* = 11.5 Hz, 1H), 4.40 (t, *J* = 6.0 Hz, 1H), 3.80-3.77 (m, 1H), 3.52 (dd, *J* = 10.5, 5.0 Hz, 1H), 3.43 (s, 3H), 3.32 (s, 3H), 3.27 (s, 3H), 3.18 (s, 4H), 2.06 (d, *J* = 14.0 Hz, 1H), 1.68 (t, *J* = 13.0 Hz, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 131.2, 128.9, 128.4, 127.8, 127.2, 98.7, 75.7, 74.5, 70.6, 67.0, 59.0, 57.3, 47.7, 47.5, 34.1. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{16}H_{24}ClO_5$ 331.1312; found, 331.1331.

Procedure for the deprotection of dimethyl acetal 4ab:

To a solution of acetal **4ab** (76 mg 0.23 mmol) in methanol (2 mL), 6N HCl (5 mL) was added at room temperature and stirred for 1h. The resulting solution was diluted with ethyl acetate (100 mL) and washed with saturated $NaHCO_3$ and brine solutions. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified by column chromatography using 15 % ethyl acetate in hexane which furnished a mixture of inseparable **3ab** and **5ab** (α/β=6:1) in 76% yield (51 mg).

(2R,3S,4S,6S)-3-(benzyloxy)-2-(benzyloxymethyl)-6-phenyltetrahydro-2H-pyran-4-ol [4ba]

To a stirred solution of ketone **3ba** (150 mg, 0.37 mmol) in methanol (7 mL), sodium borohydride (15 mg, 0.4 mmol) was added at 0-4 ^{o}C. The reaction mixture was stirred for 30 mins at the same temperature, diluted with ethyl acetate (50 mL) and washed with saturated ammonium chloride solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified in column chromatography using 15 % ethyl acetate in hexane which furnished **4ba** as a white foam in 72% yield (108 mg). TLC R_f = 0.25 (20 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.16 (m, 15H), 4.67-4.64 (m, 2H), 4.52-4.44 (m, 3H), 4.29 (s, 1H), 4.03-4.01 (m, 1H), 3.68-3.63 (m, 3H), 2.01-1.99 (m, 2H), 1.92 (d, *J* = 13.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 137.8, 137.8, 128.4, 128.4, 128.2, 127.8, 127.8, 127.7, 127.6, 127.4, 126.0, 75.4, 73.4, 73.0, 72.6, 71.5, 69.2, 66.0, 36.6. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{29}O_4$ 405.2066; found, 405.2019.

(2R,3S,4S,6S)-3-(benzyloxy)-2-(benzyloxymethyl)-6-(4-bromophenyl)tetrahydro-2H-pyran-4-ol [4bf]

To a stirred solution of ketone **3bf** (100 mg, 0.21 mmol) in methanol (7 mL), sodium borohydride (11 mg, 0.28 mmol) was added at 0-4 ^{o}C. The reaction mixture was stirred for 30 mins at the same temperature, diluted with ethyl acetate (50 mL) and washed with saturated ammonium chloride solution. The organic layer was dried over anhydrous Na_2SO_4, concentrated and purified in column chromatography using 20 % ethyl acetate in hexane which furnished **4bf** as viscous oil in 82% yield (83 mg). TLC R_f = 0.26 (15 % ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.5 Hz, 2H), 7.25-7.18 (m, 12H), 4.63 (d, *J* = 10.5 Hz, 2H), 4.50 (d, *J* = 12 Hz, 1H), 4.44 (d, *J* = 12.5 Hz, 1H), 4.22 (s, 1H), 4.02-4.01 (m, 1H), 3.65-3.61 (m, 3H), 2.14 (bs, 1H), 2.01-1.88 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.8, 137.7, 137.7, 131.2, 128.5, 128.4, 127.9, 127.8, 127.7, 127.6, 121.1, 75.3, 73.4, 72.4, 72.3, 71.5, 69.1, 65.8, 36.3. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{26}H_{28}BrO_4$ 483.1171; found, 483.1163.

(2R,3S,4S,6S)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-6-phenyltetrahydro-2H-pyran (5ba)

The alcohol **4ba** (100 mg, 0.25 mmol) was stirred in dry DMF (3 mL) was added and cooled to 0 ^{o}C after which NaH (12 mg, 60% in mineral oil) was added. The mixture was stirred for 5 min at the same temperature to which benzyl bromide (0.038 mL, 1.5 equiv.) was added. The resulting mixture was stirred for 60 mins and quenched by saturated aqueous NH_4Cl (1 mL) and diluted with ethyl acetate (50 mL). The organic phase was washed with H_2O, brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by column chromatography using 10% ethyl acetate in hexane to afford **5ba** as viscous oil in 81% yield (100 mg). TLC R_f = 0.34 (20 % ethyl acetate in hexane);; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.28 (m, 20H), 4.78-4.75 (m, 3H), 4.55 (d, *J* = 17.5 Hz, 4H), 4.47 (s, 1H), 4.95 (d, *J* = 10 Hz, 1H), 3.91 (s, 1H), 3.75-3.68 (m, 2H), 2.45-2.38 (m, 1H), 2.04 (d, *J* = 12.5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 138.6, 138.4, 137.9, 128.40, 128.2, 128.2, 127.8, 127.6, 127.5, 127.4, 127.3, 126.0, 74.5, 73.7, 73.5, 73.2, 72.6, 71.6, 70.0, 68.9, 33.7. HRMS (ESI-TOF) (m/z): $[M + H]^+$ calcd for $C_{33}H_{35}O_4$ 495.2535; found, 495.2515.

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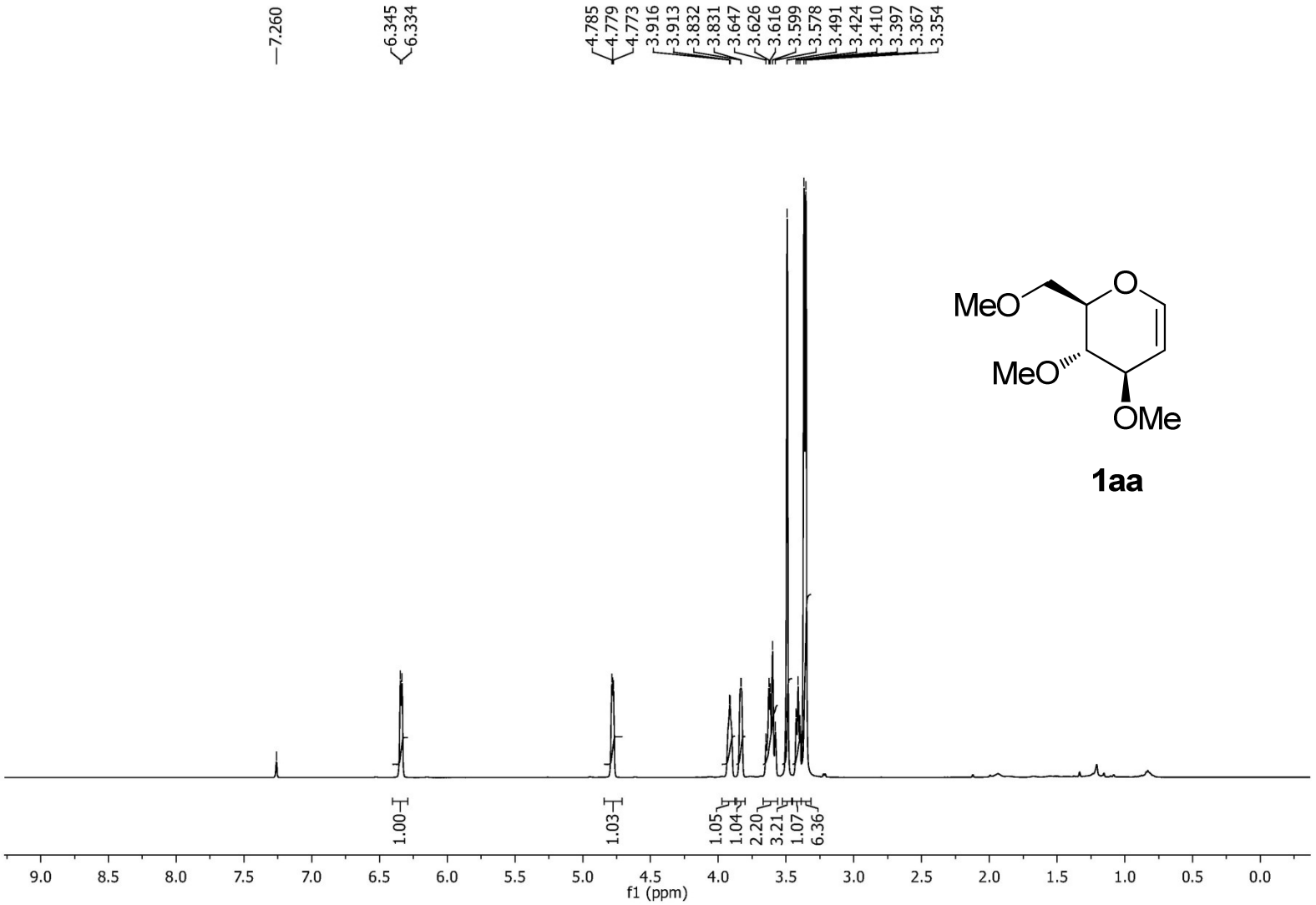

Figure S1: ^{1}H-NMR spectrum of compound 1aa in $CDCl_3$

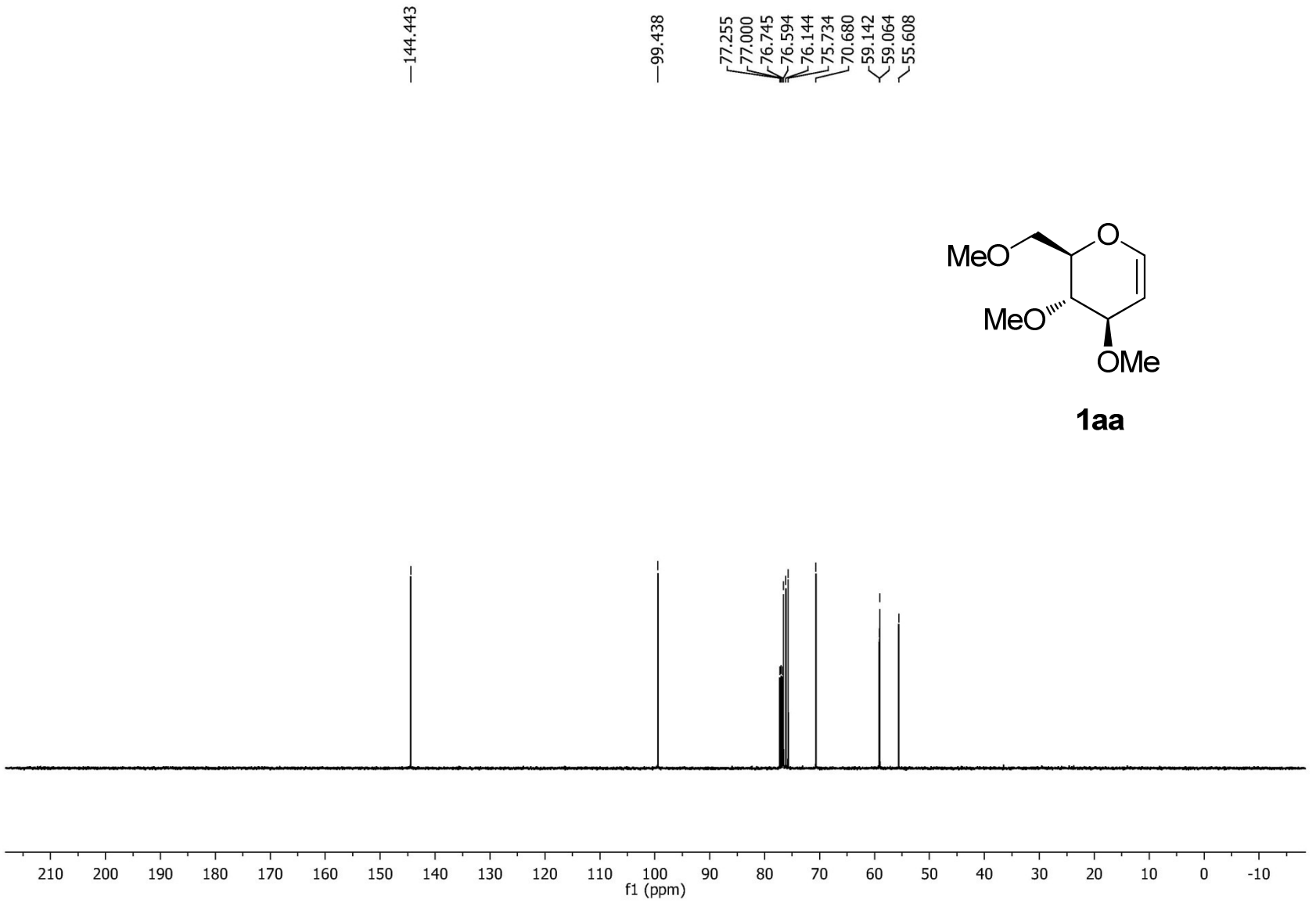

Figure S2: ^{13}C-NMR spectrum of compound 1aa in $CDCl_3$

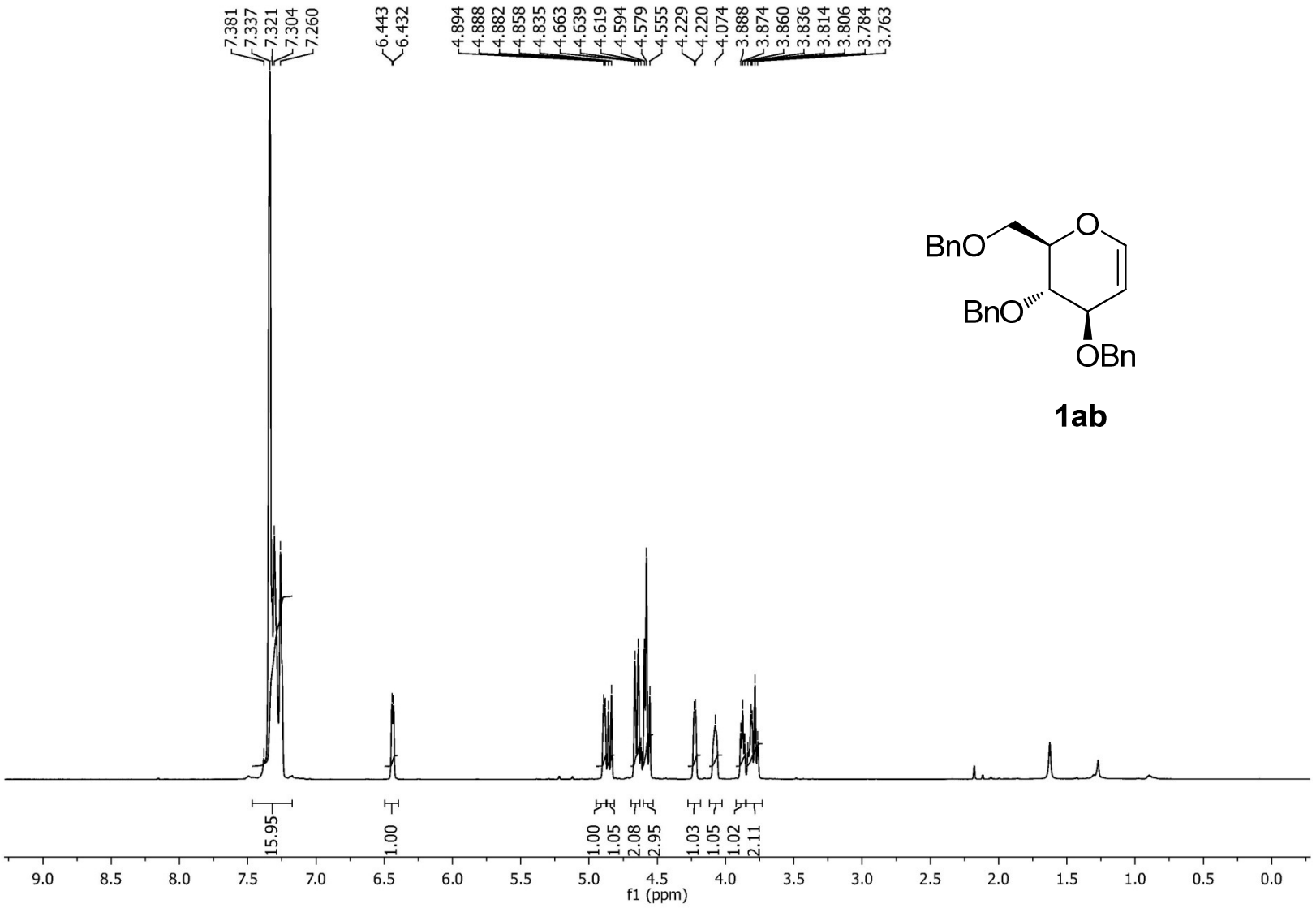

Figure S3: ^{1}H-NMR spectrum of compound 1ab in $CDCl_3$

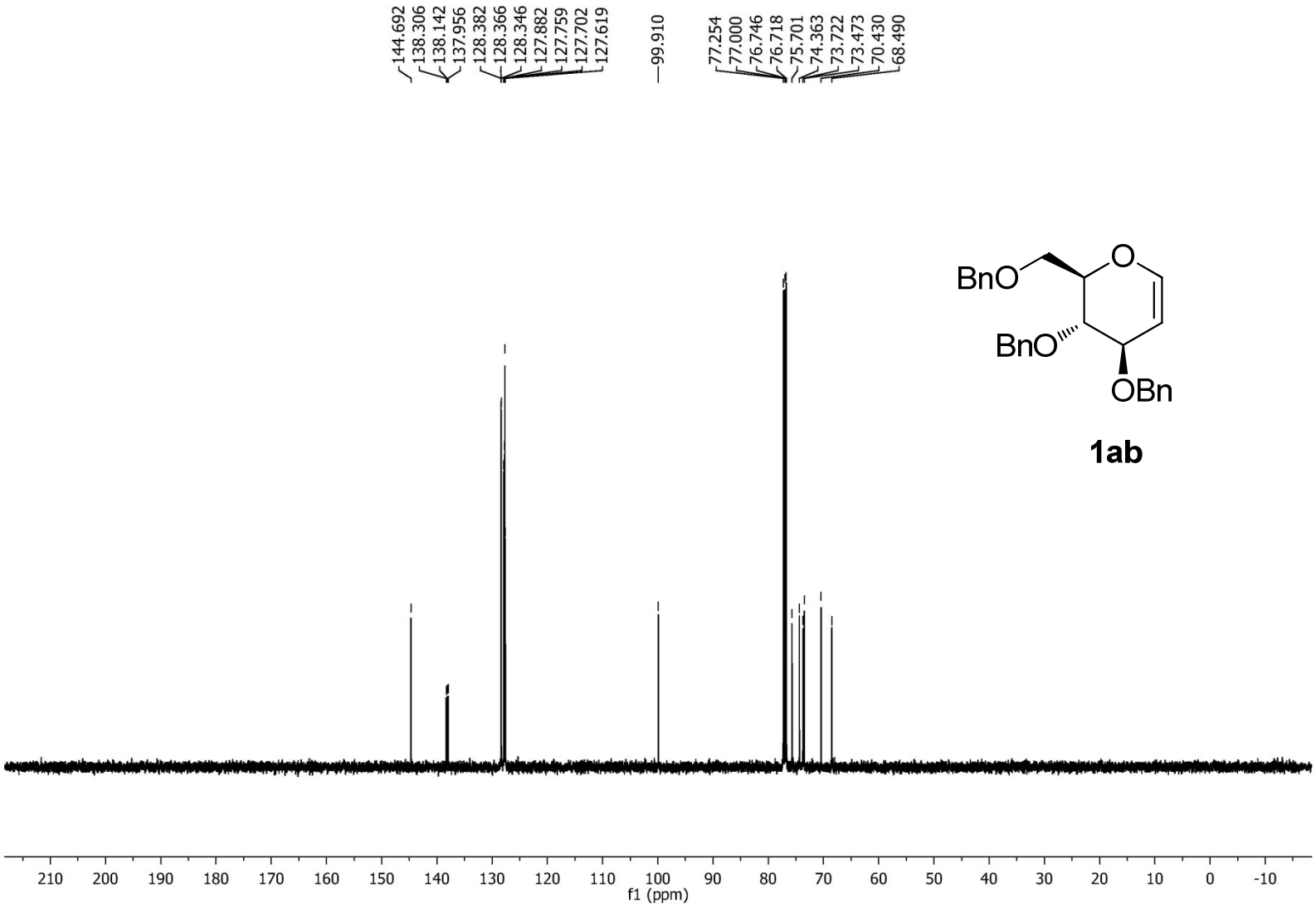

Figure S4: ^{13}C-NMR spectrum of compound 1ab in $CDCl_3$

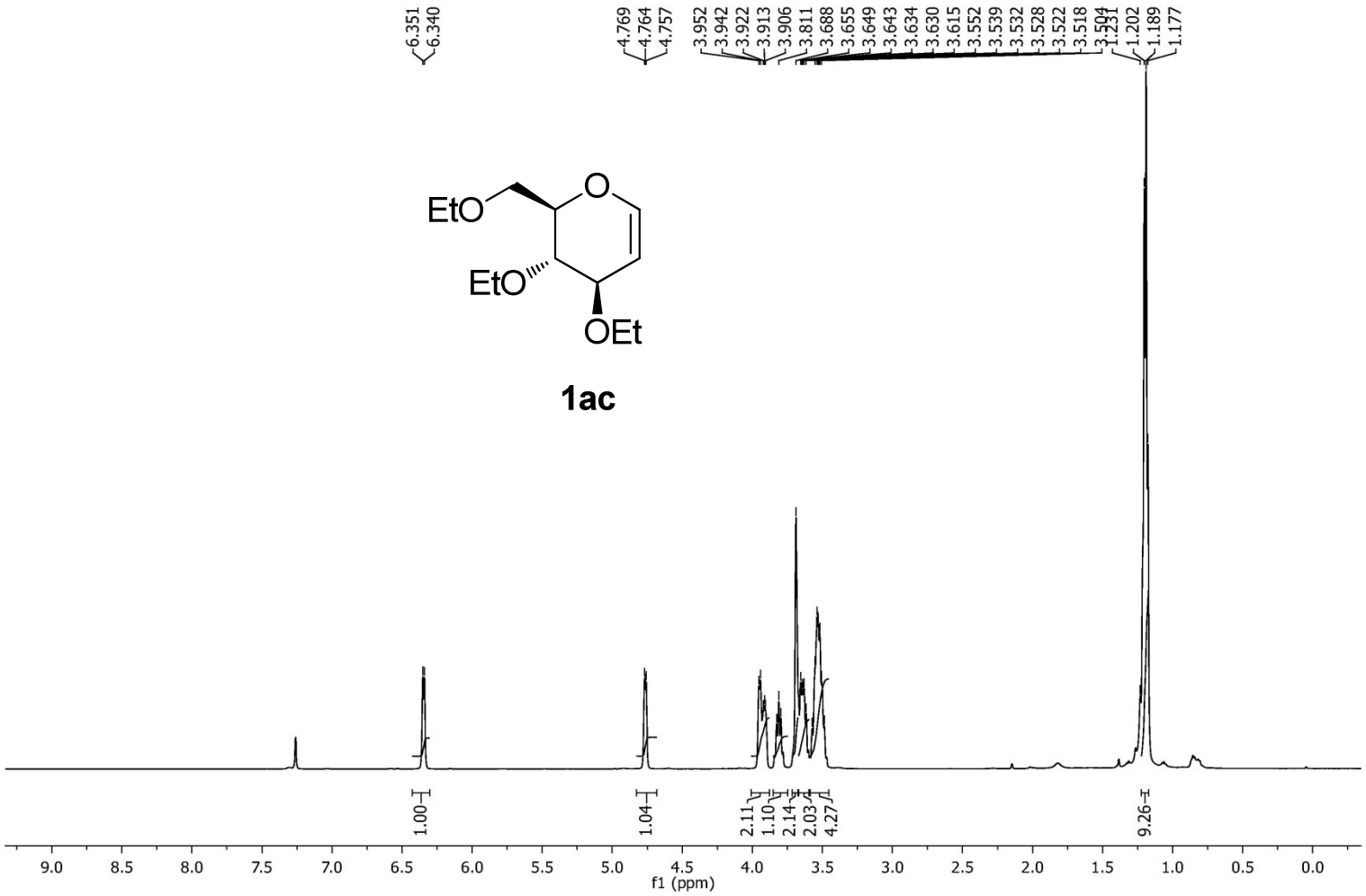

Figure S5: ^{1}H-NMR spectrum of compound 1ac in $CDCl_3$

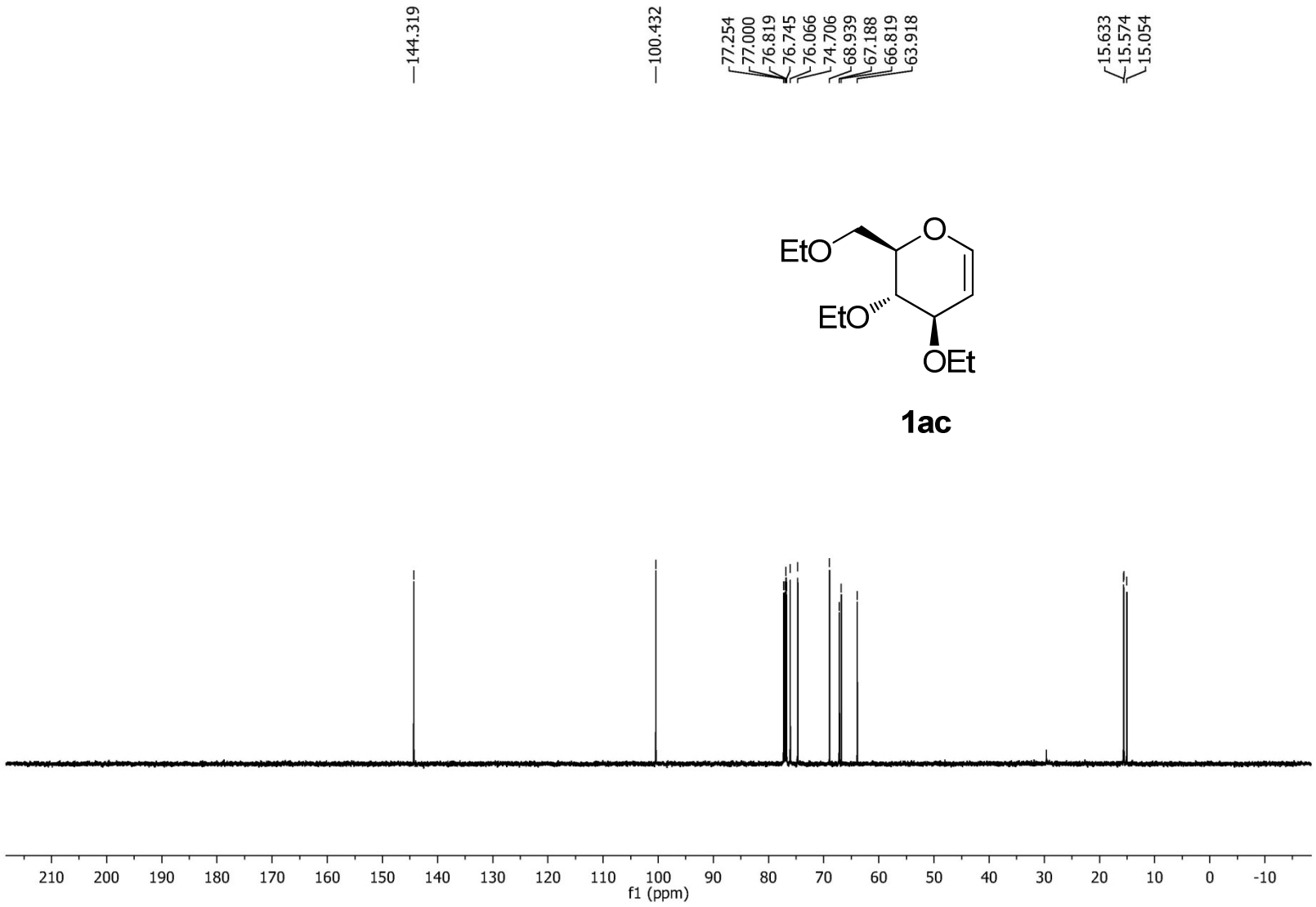

Figure S6: ^{13}C-NMR spectrum of compound 1ac in $CDCl_3$

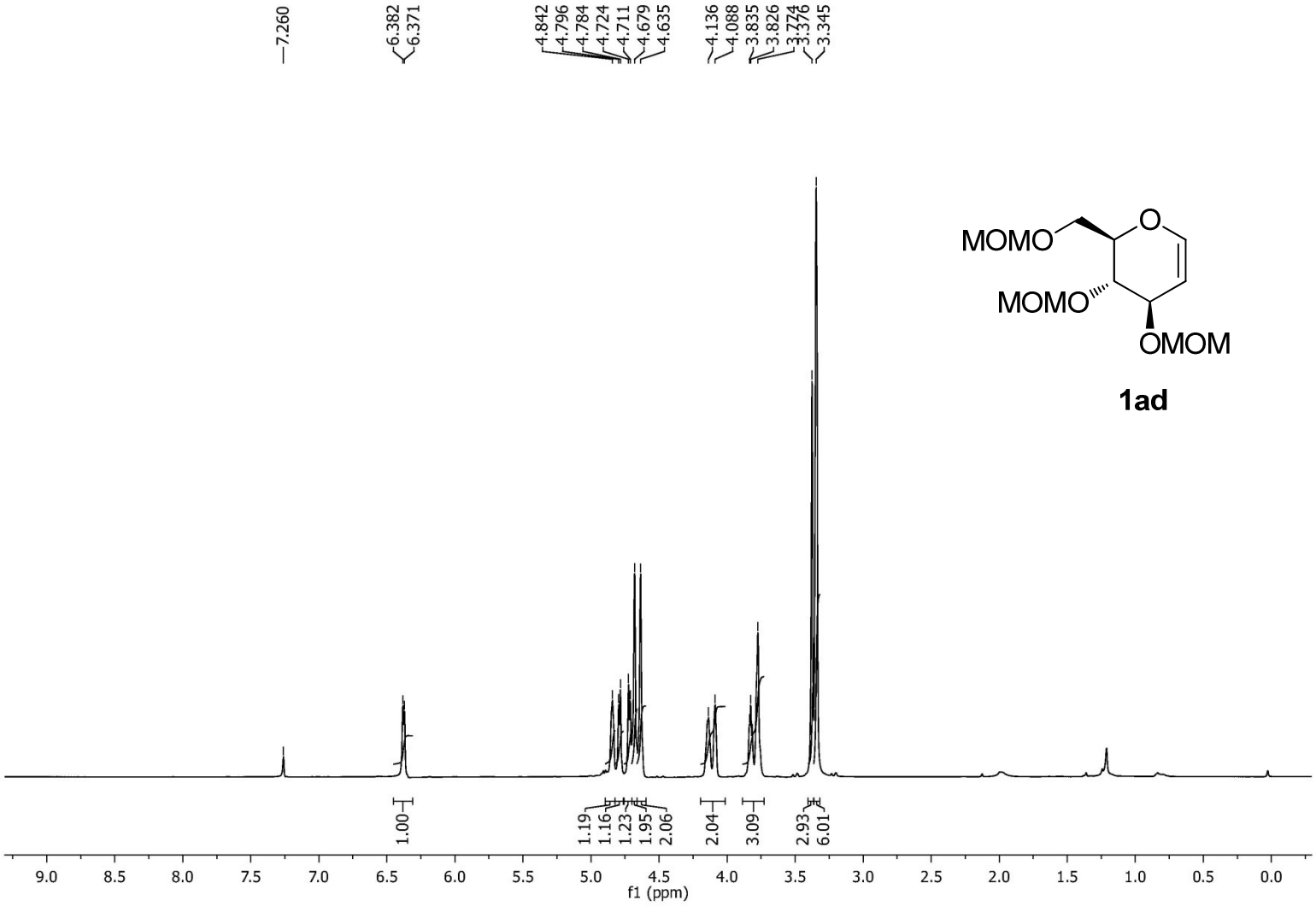

Figure S7: ^{1}H-NMR spectrum of compound 1ad in $CDCl_3$

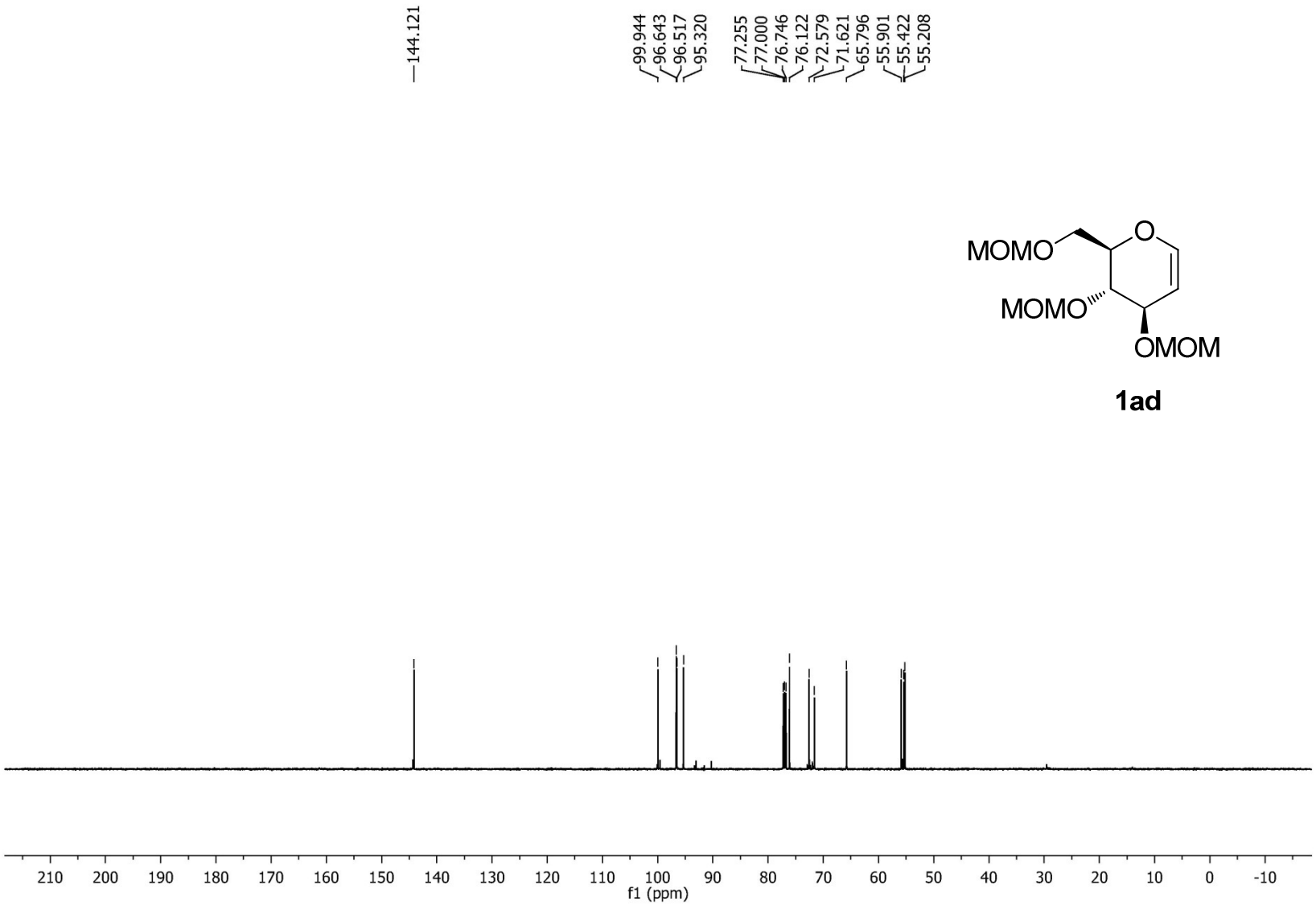

Figure S8: ^{13}C-NMR spectrum of compound 1ad in $CDCl_3$

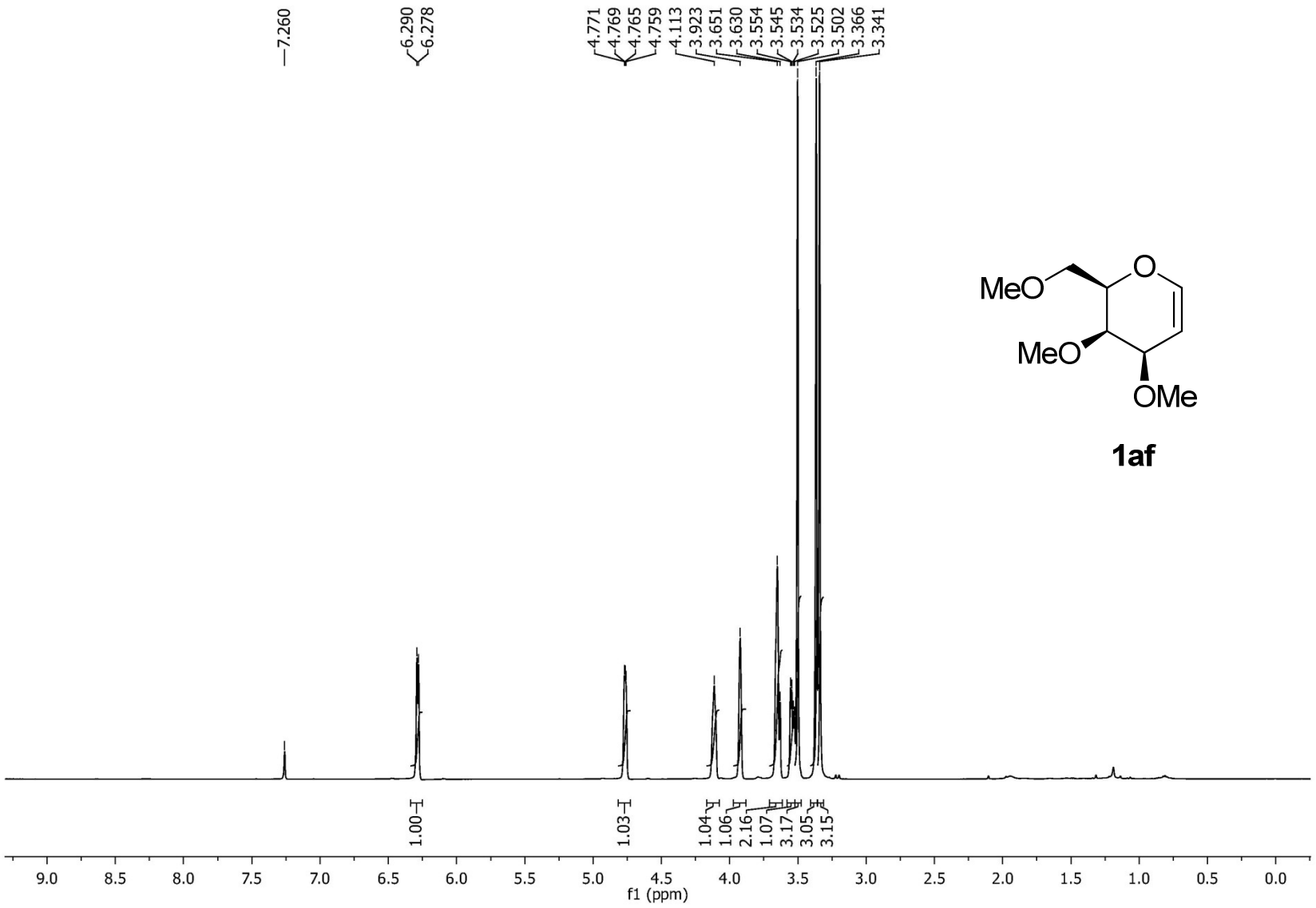

Figure S9: ^{1}H-NMR spectrum of compound 1af in $CDCl_3$

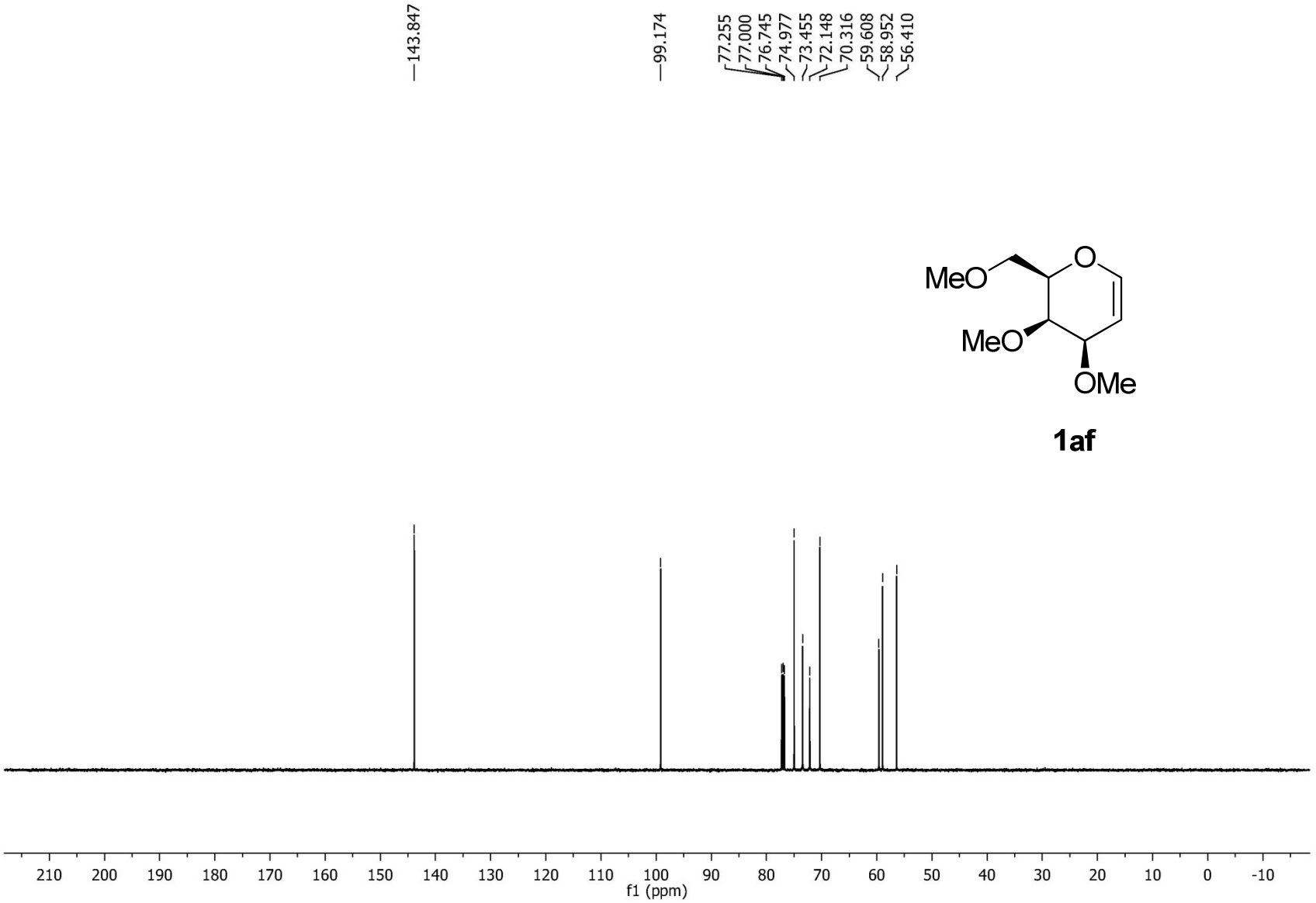

Figure S10: ^{13}C-NMR spectrum of compound 1af in $CDCl_3$

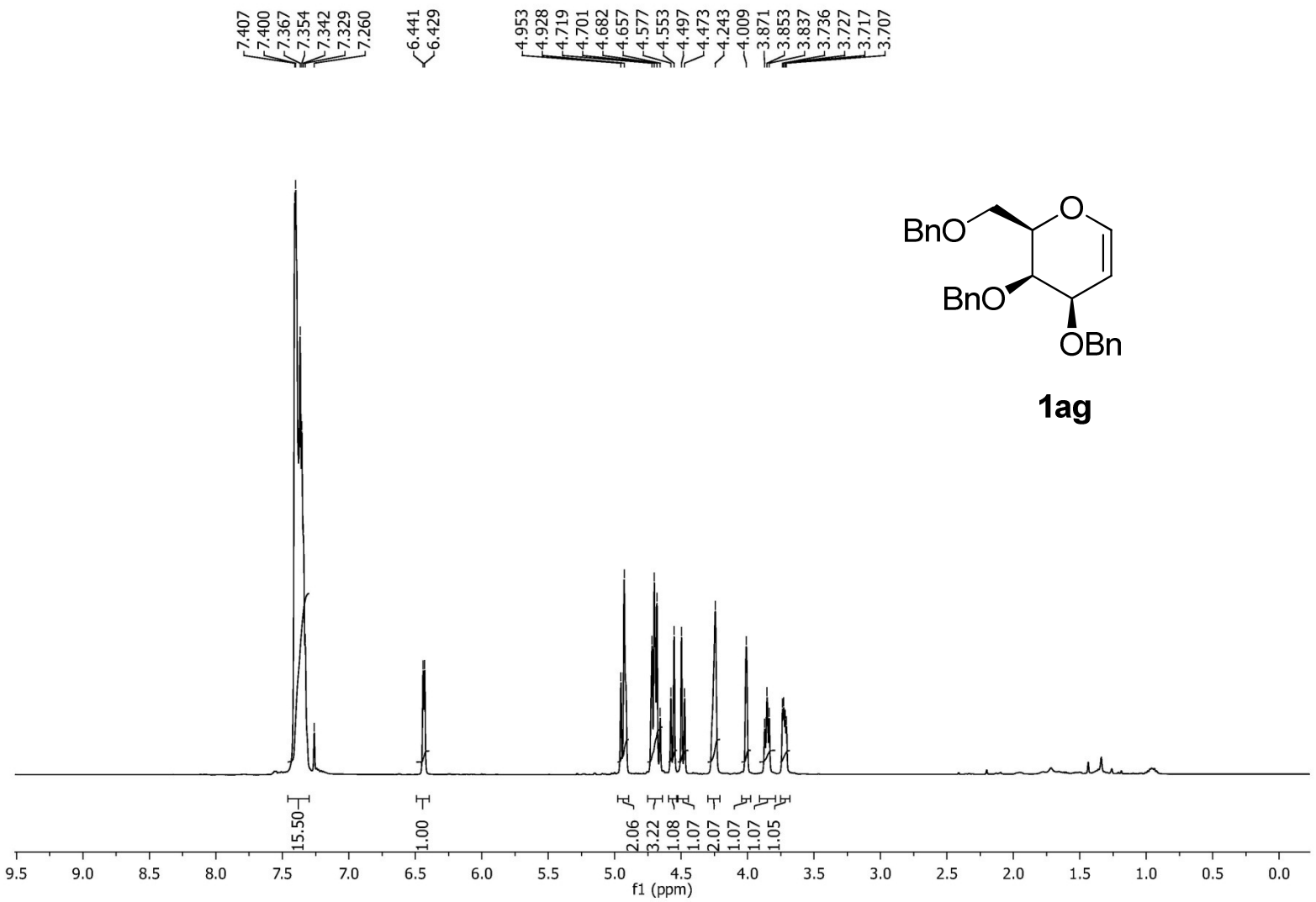

Figure S11: ^{1}H-NMR spectrum of compound 1ag in $CDCl_3$

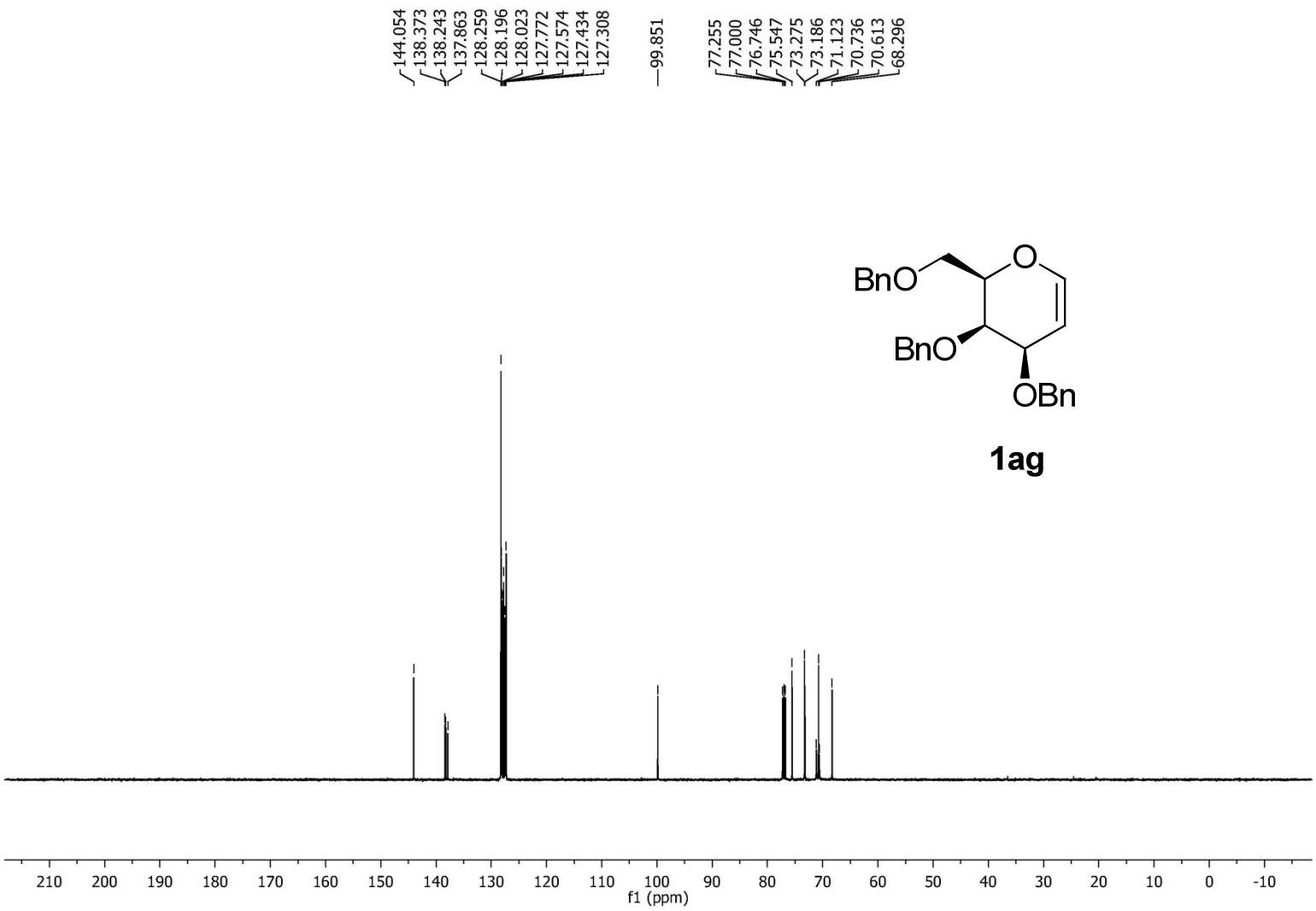

Figure S12: ^{13}C-NMR spectrum of compound 1ag in $CDCl_3$

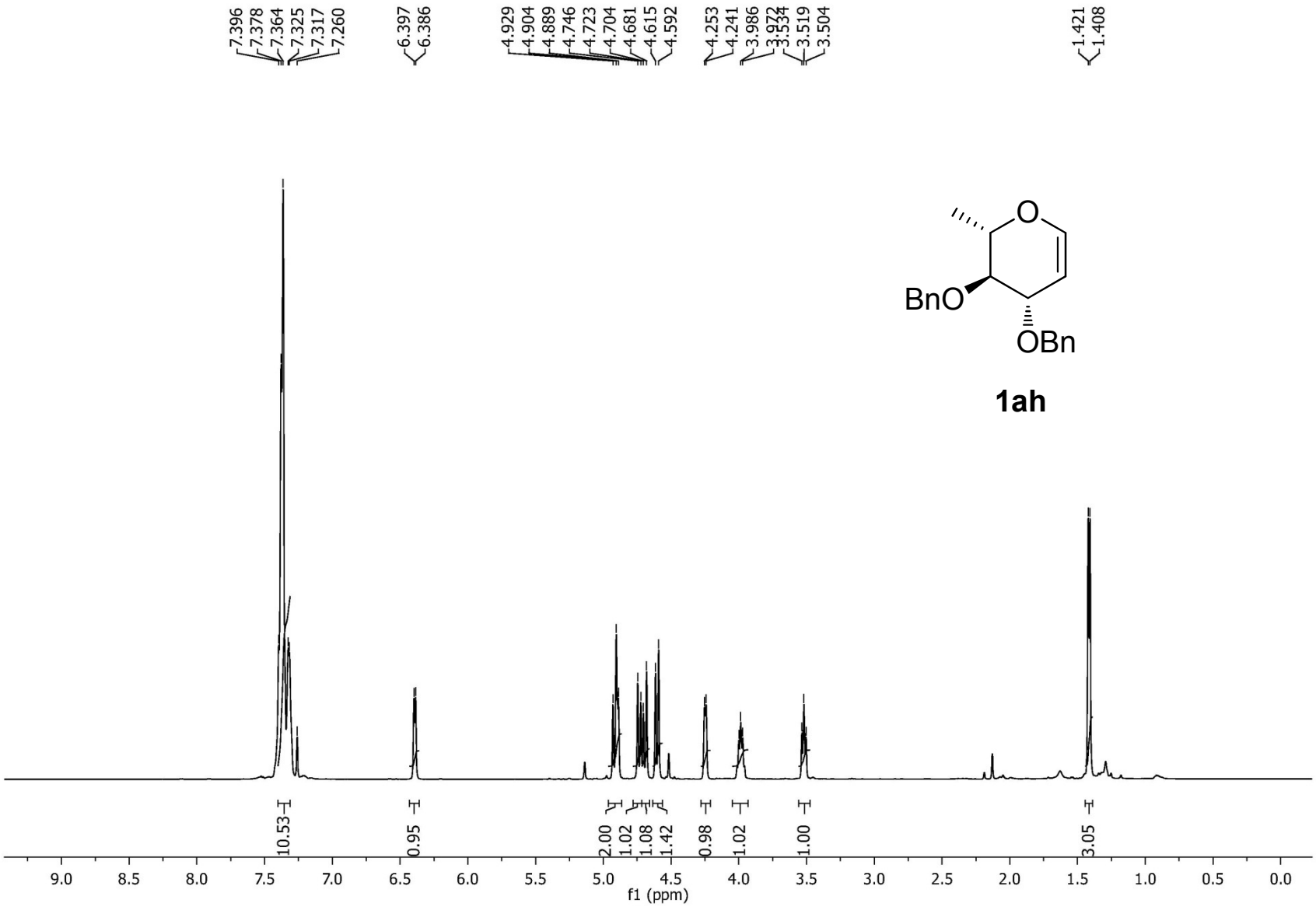

Figure S13: ^{1}H-NMR spectrum of compound 1ah in $CDCl_3$

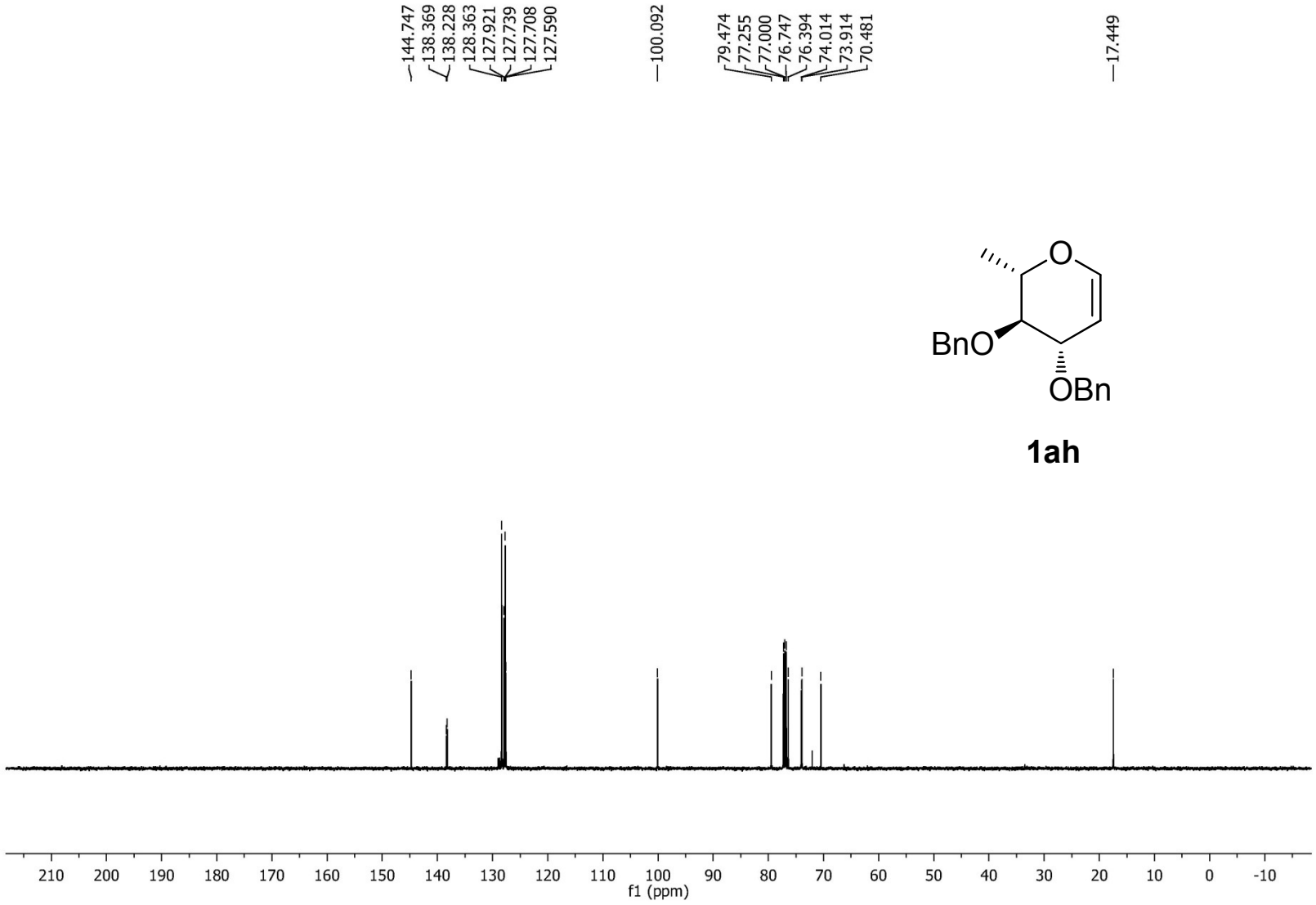

Figure S14: ^{13}C-NMR spectrum of compound 1ah in $CDCl_3$

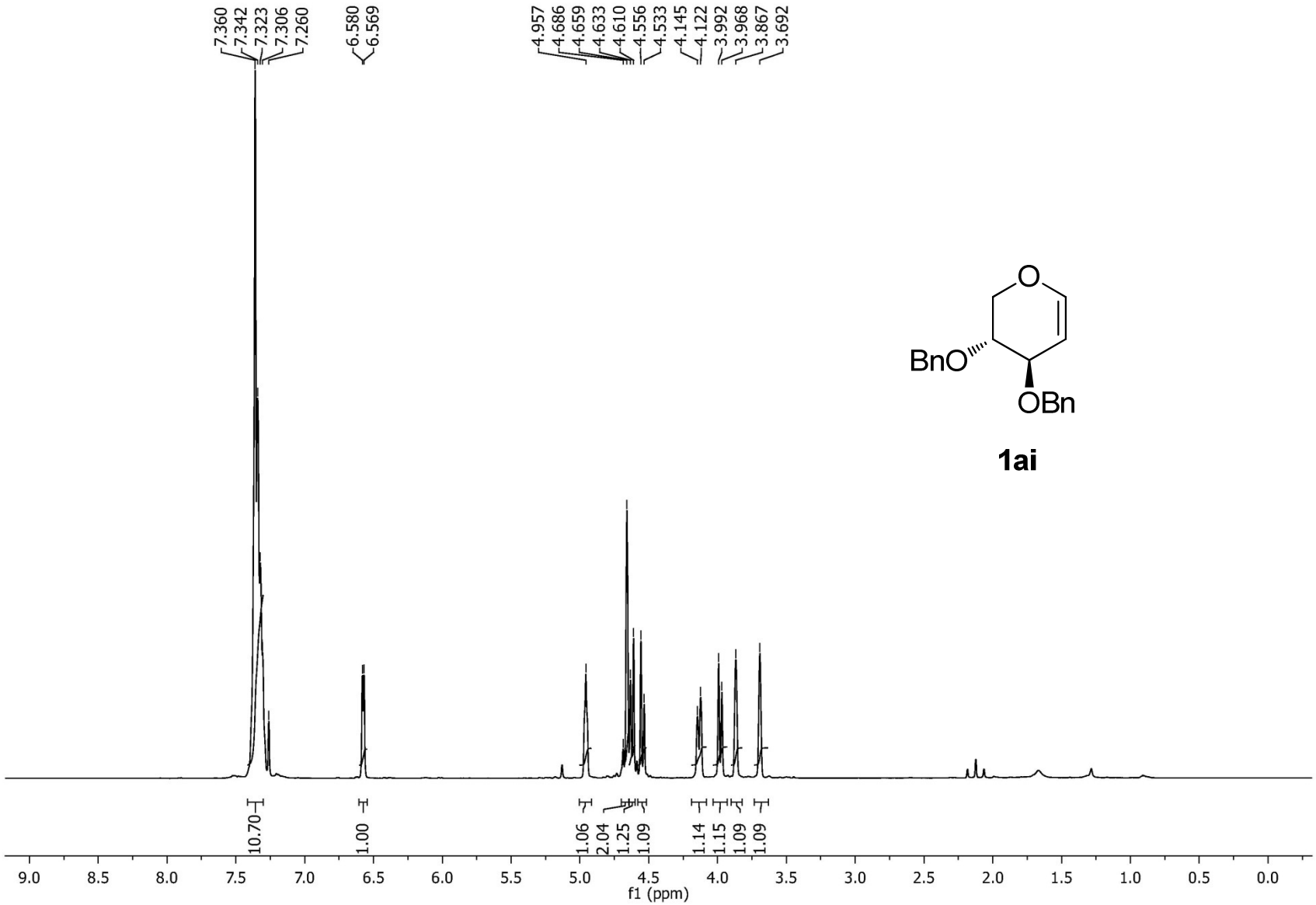

Figure S15: ^{1}H-NMR spectrum of compound 1ai in $CDCl_3$

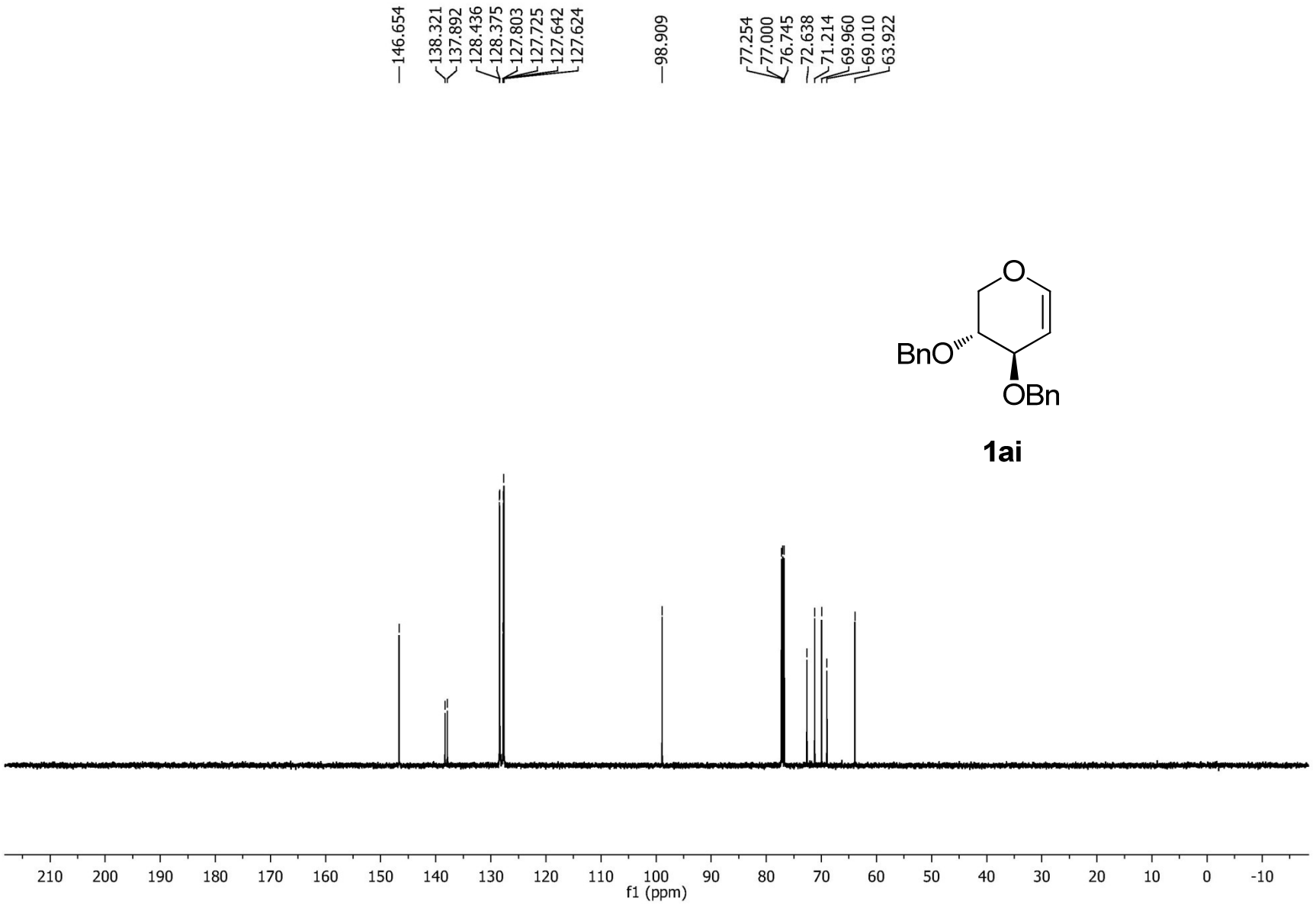

Figure S16: ^{13}C-NMR spectrum of compound 1ai in $CDCl_3$

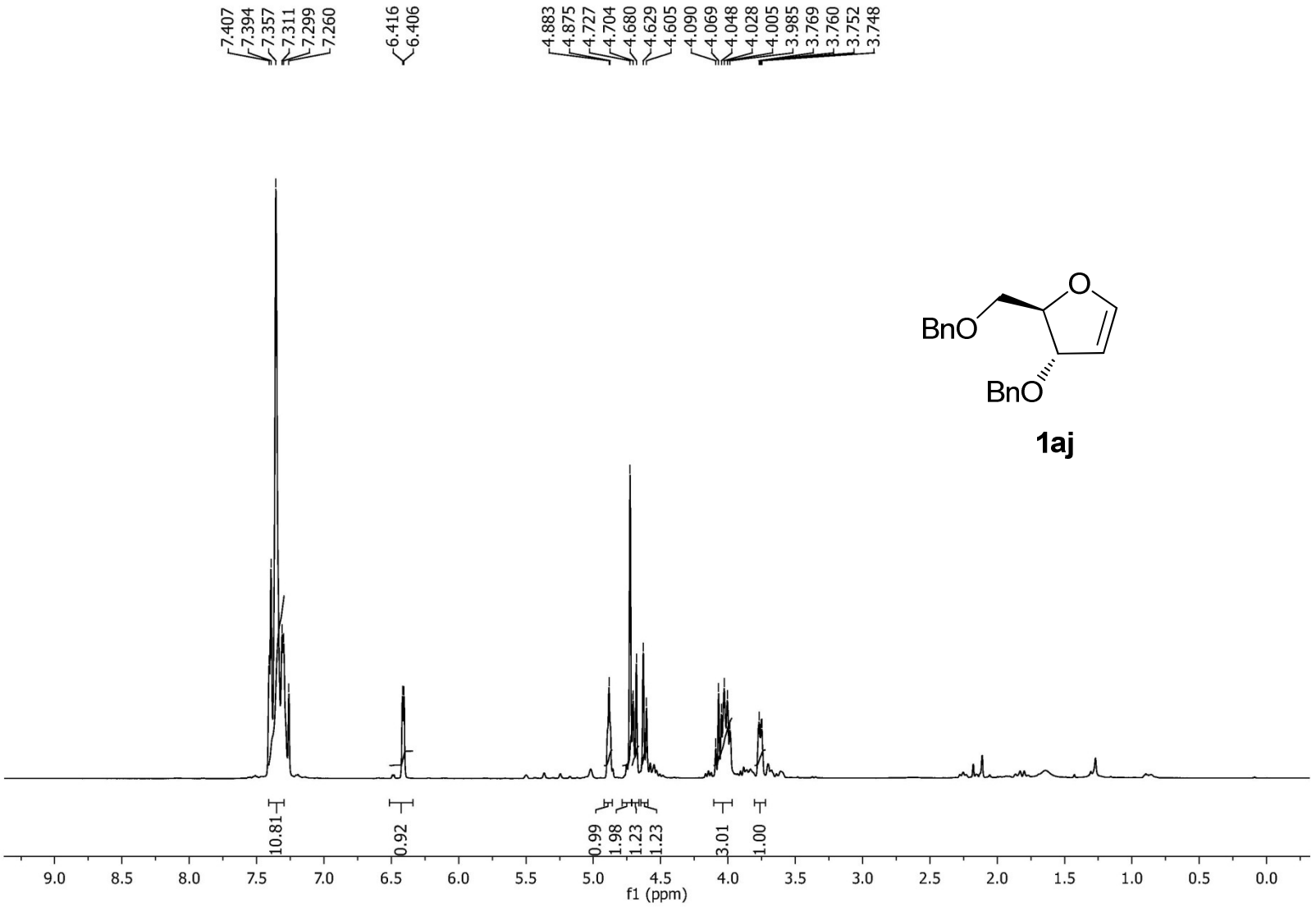

Figure S17: ^{1}H-NMR spectrum of compound 1aj in $CDCl_3$

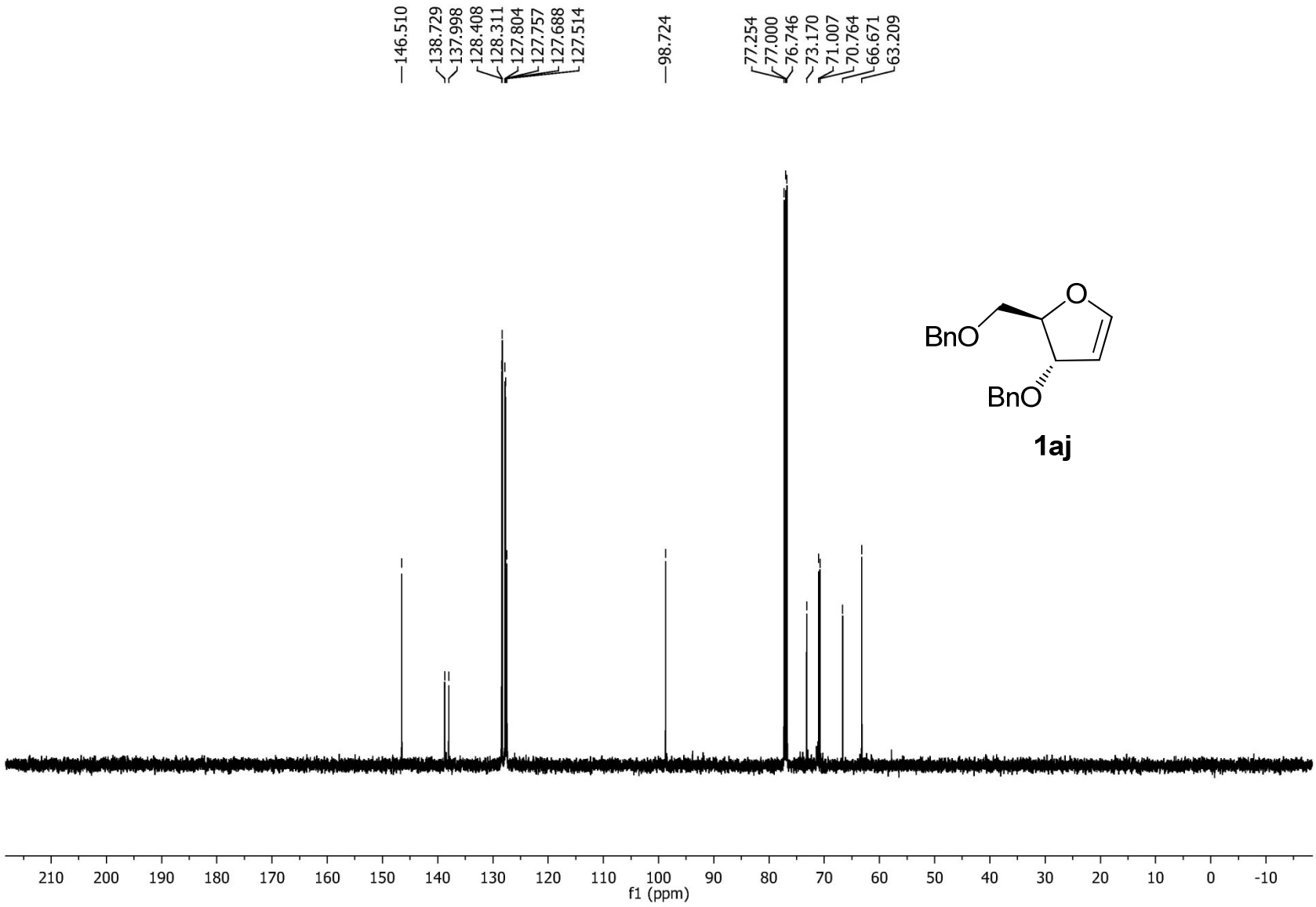

Figure S18: ^{13}C-NMR spectrum of compound 1aj in $CDCl_3$

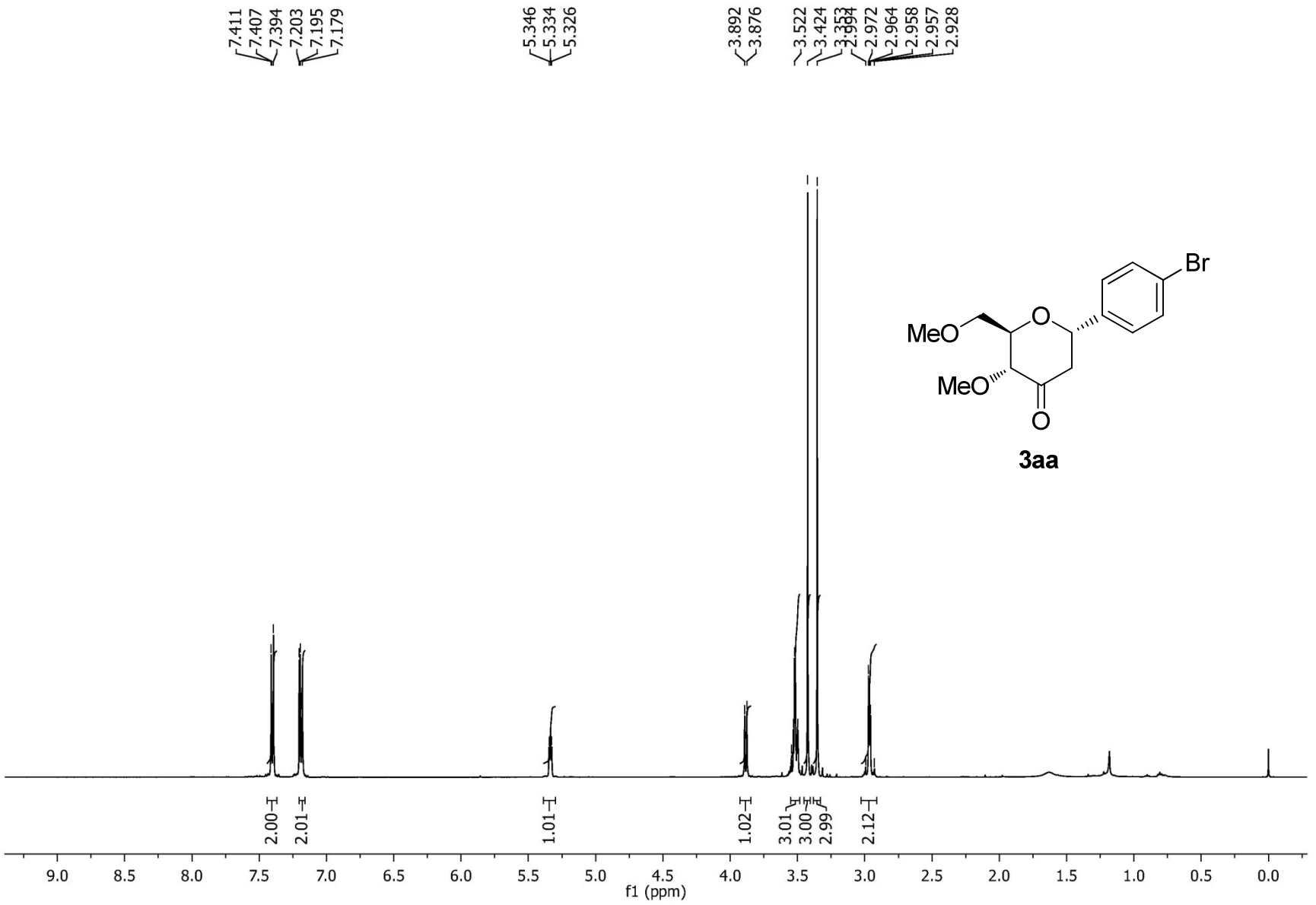

Figure S19: ^{1}H-NMR spectrum of compound 3aa in CDCl

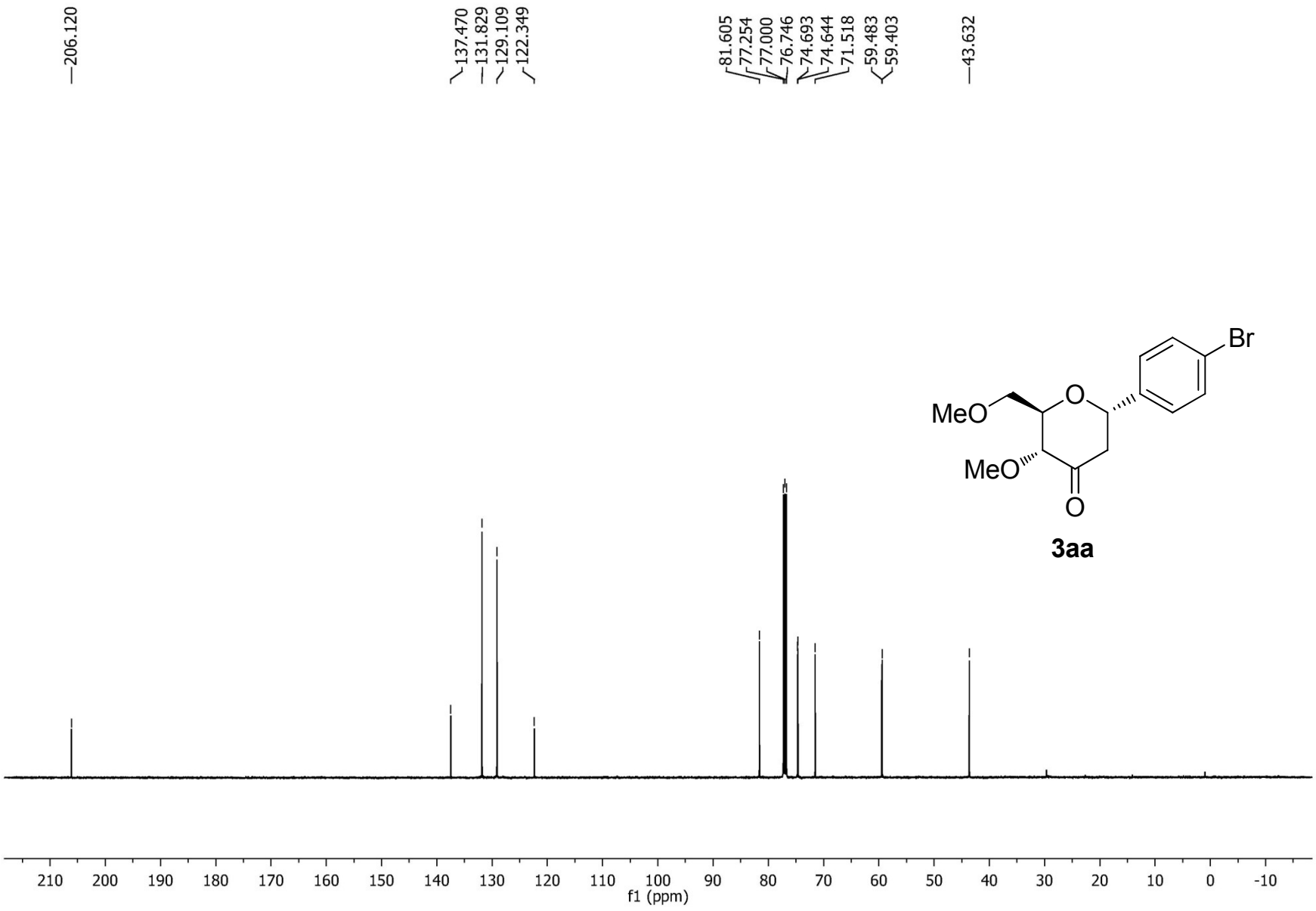

Figure S20: ^{13}C-NMR spectrum of compound 3aa in $CDCl_3$

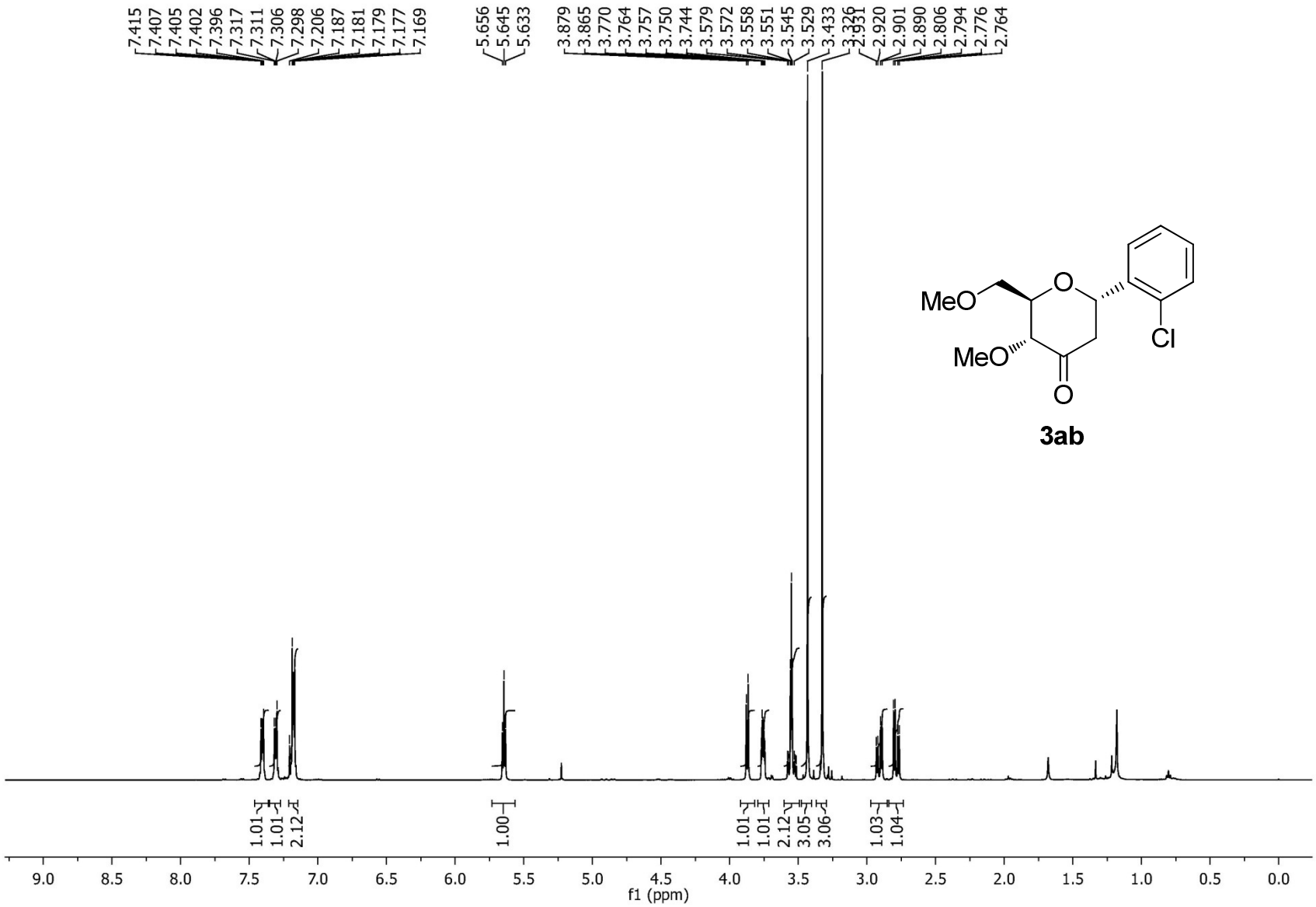

Figure S21: ^{1}H-NMR spectrum of compound 3ab in $CDCl_3$

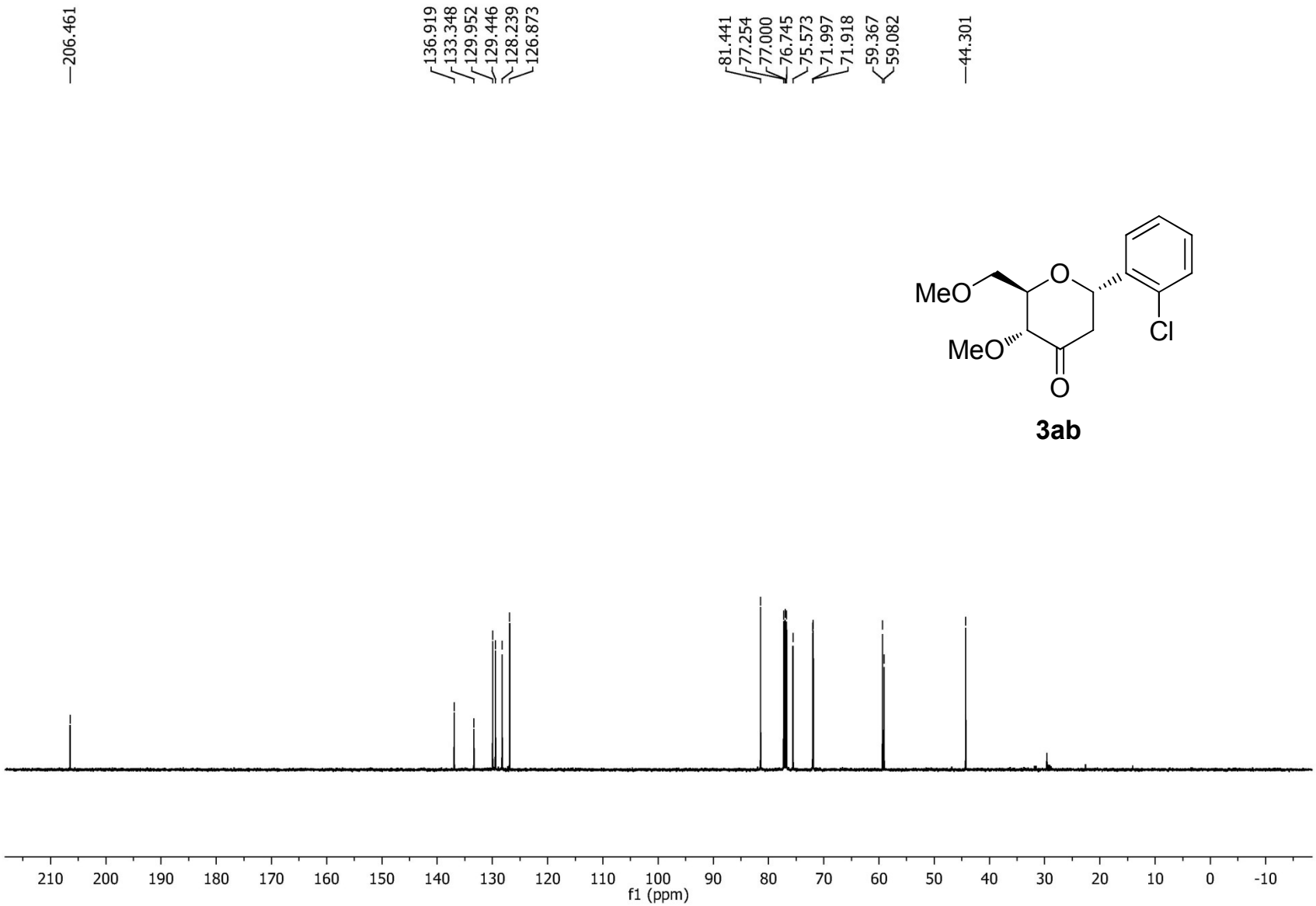

Figure S22: ^{13}C-NMR spectrum of compound 3ab in $CDCl_3$

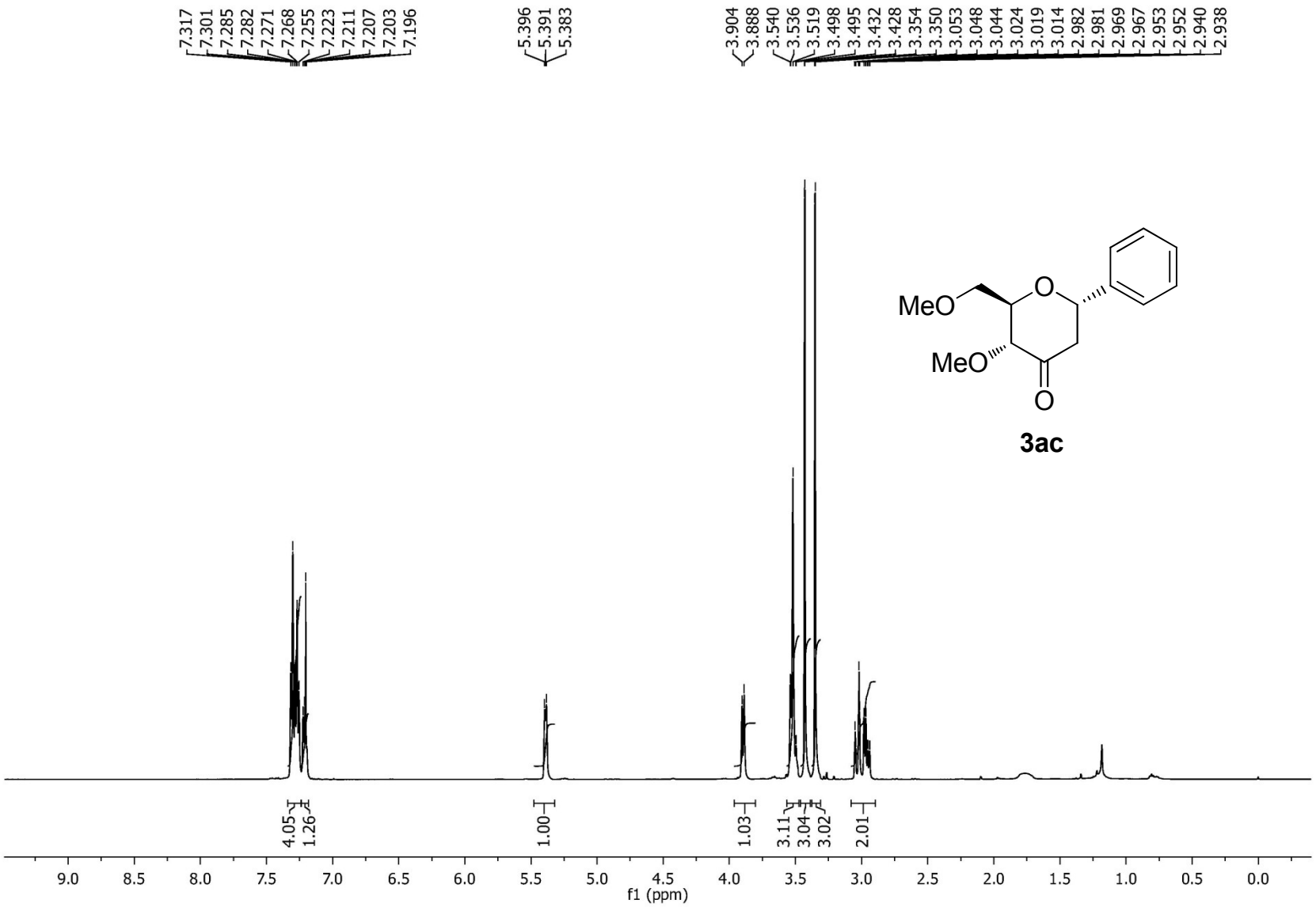

Figure S23: ^{1}H-NMR spectrum of compound 3ac in $CDCl_3$

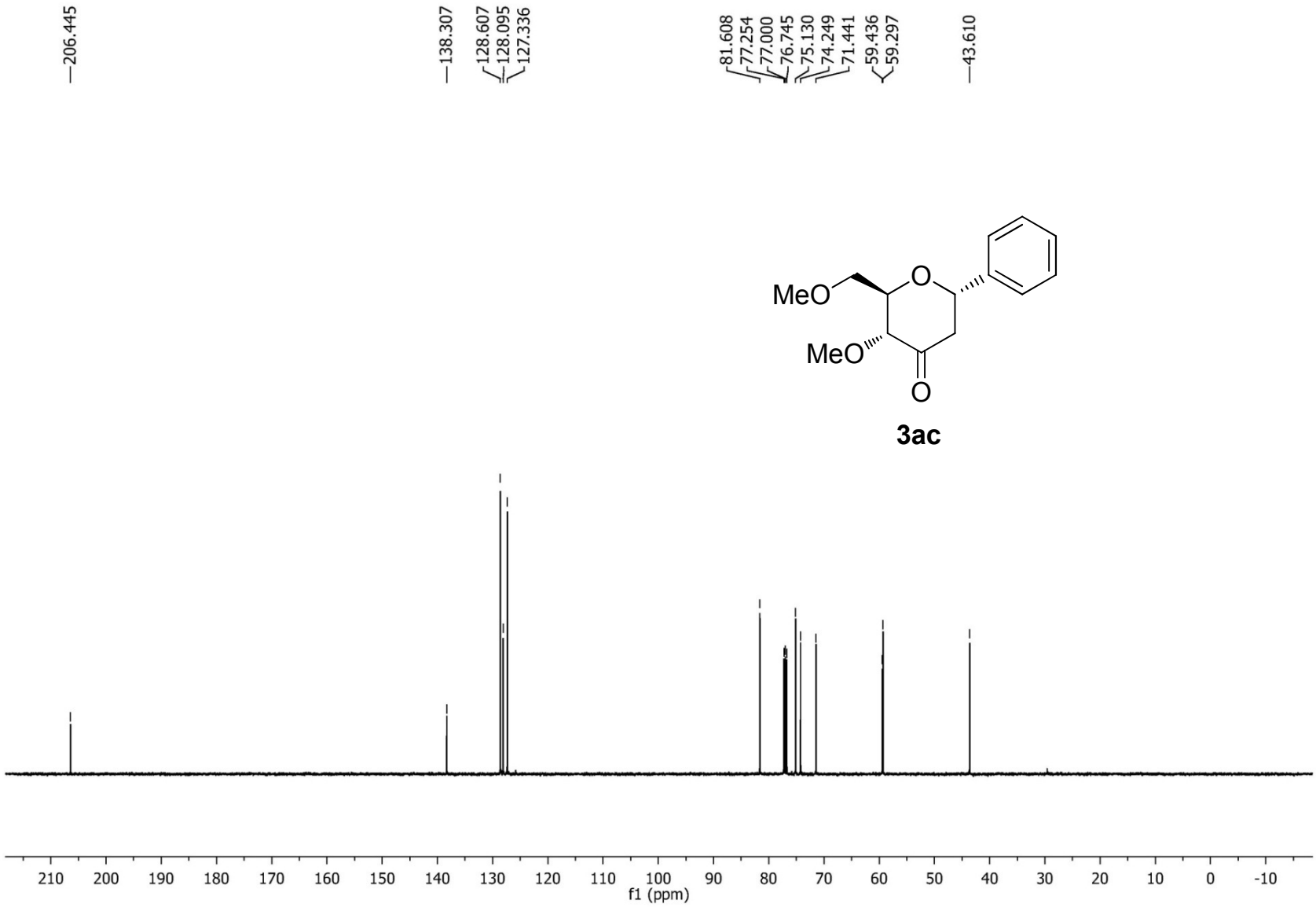

Figure S24: ^{13}C-NMR spectrum of compound 3ac in $CDCl_3$

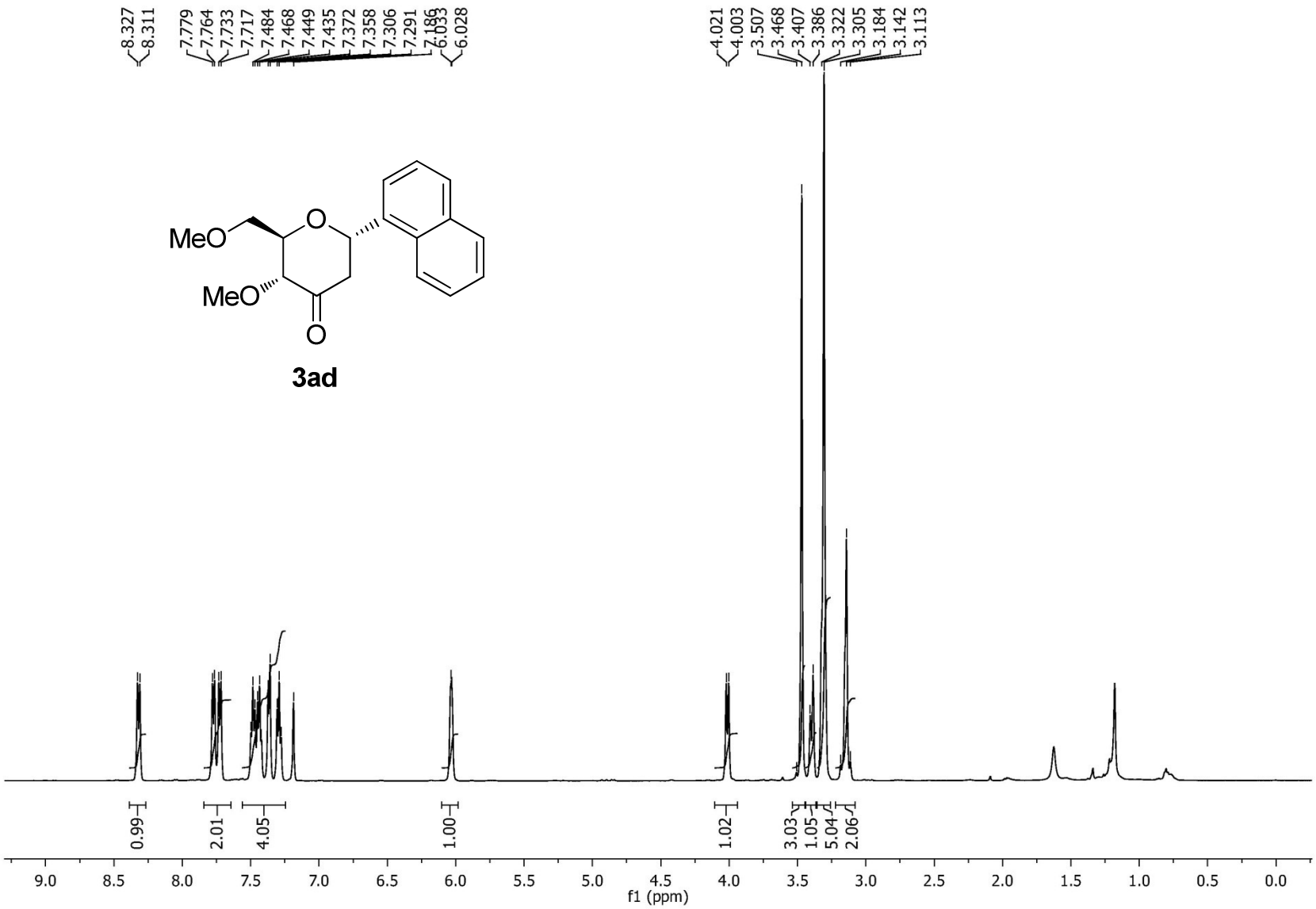

Figure S25: ^{1}H-NMR spectrum of compound 3ad in $CDCl_3$

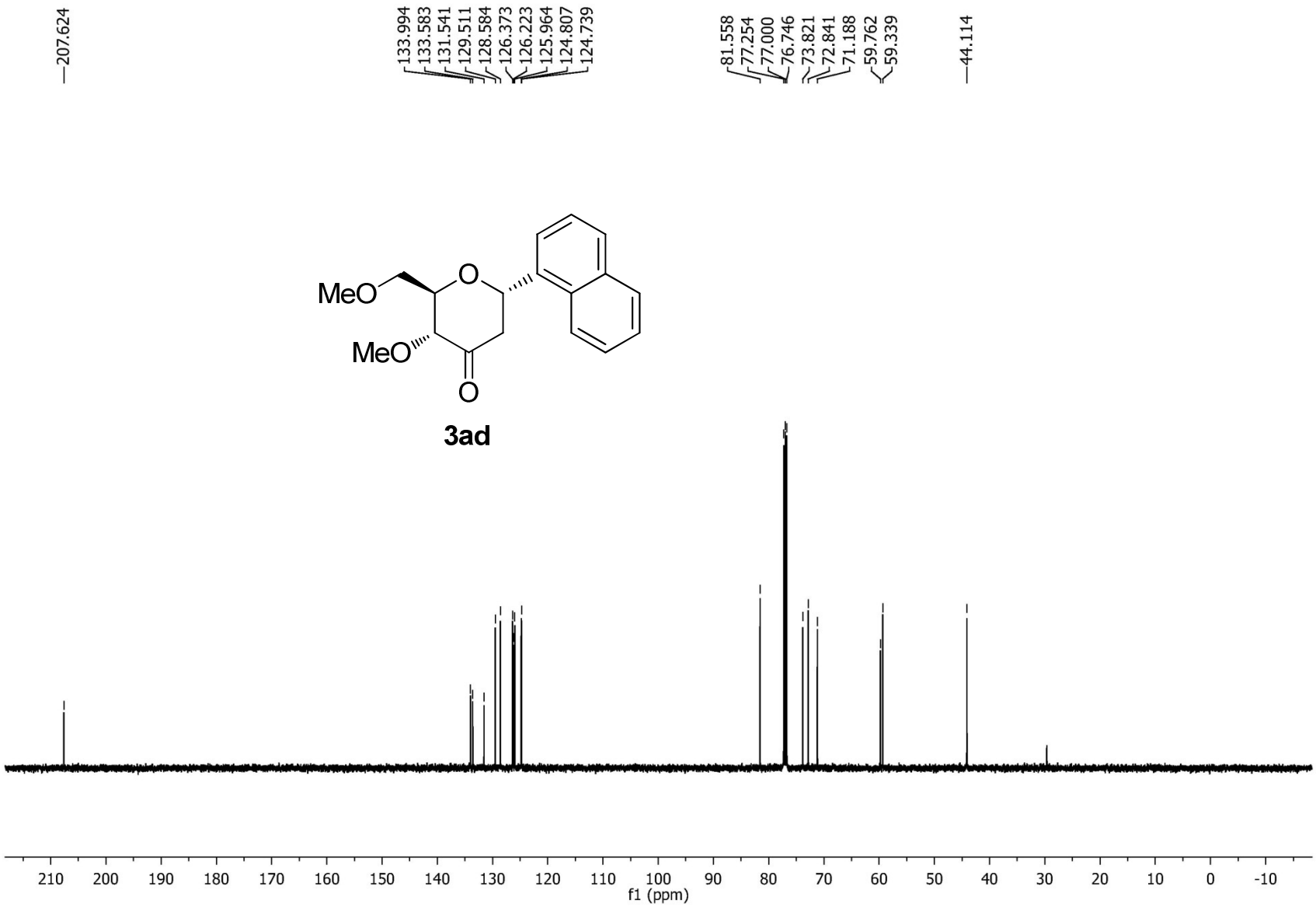

Figure S26: ^{13}C-NMR spectrum of compound 3ad in $CDCl_3$

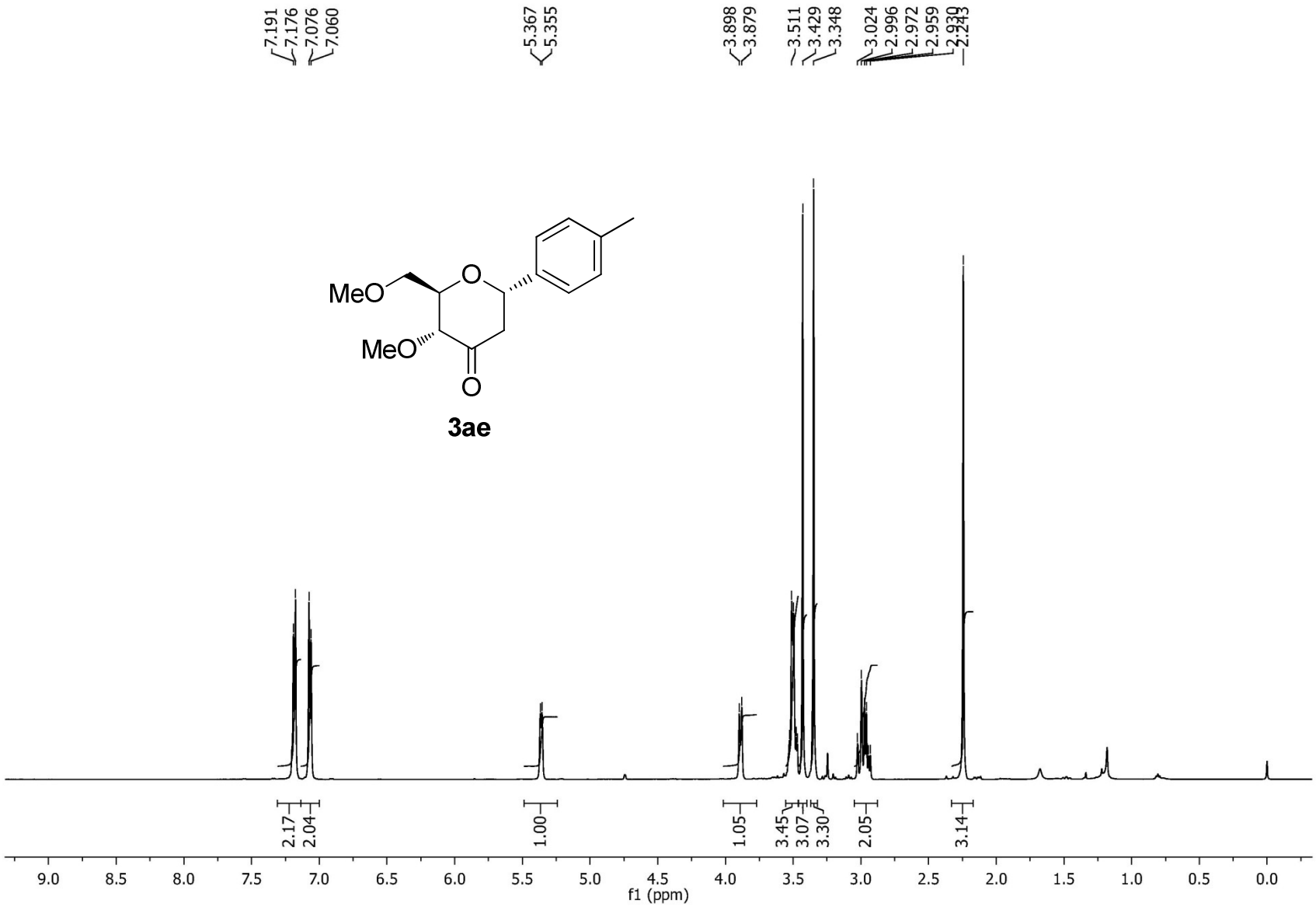

Figure S27: ^{1}H-NMR spectrum of compound 3ae in $CDCl_3$

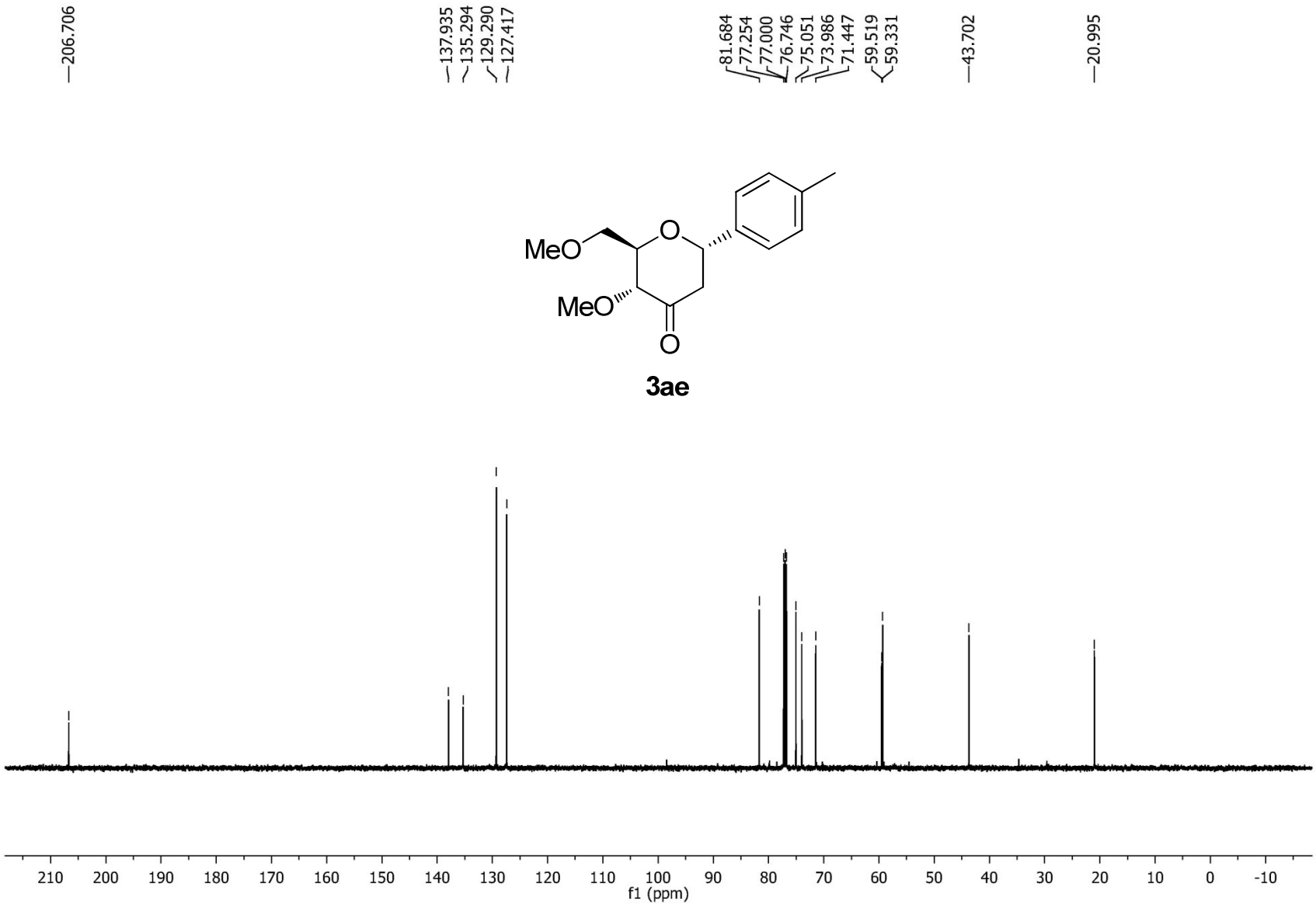

Figure S28: ^{13}C-NMR spectrum of compound 3ae in $CDCl_3$

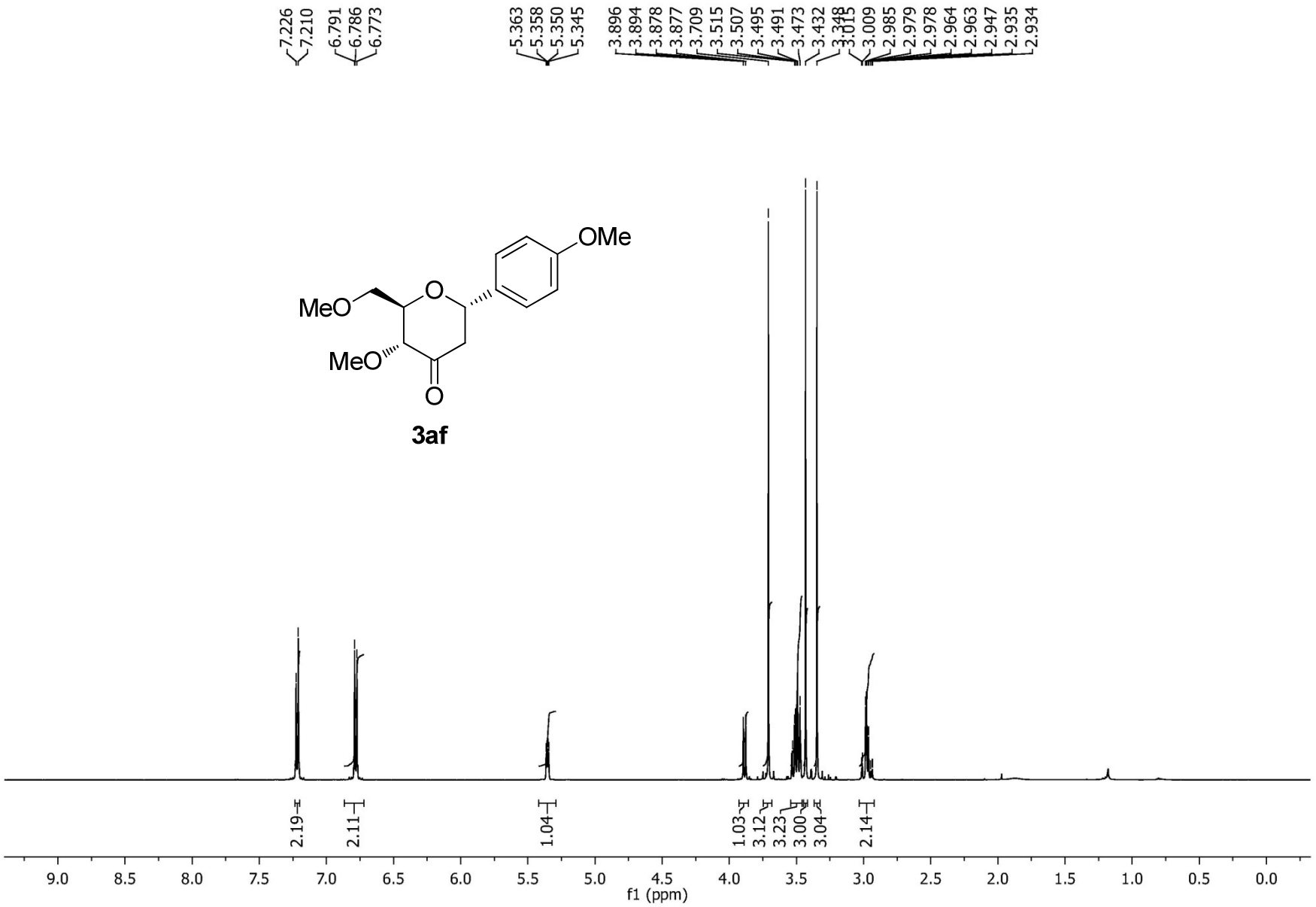

Figure S29: ^{1}H-NMR spectrum of compound 3af in $CDCl_3$

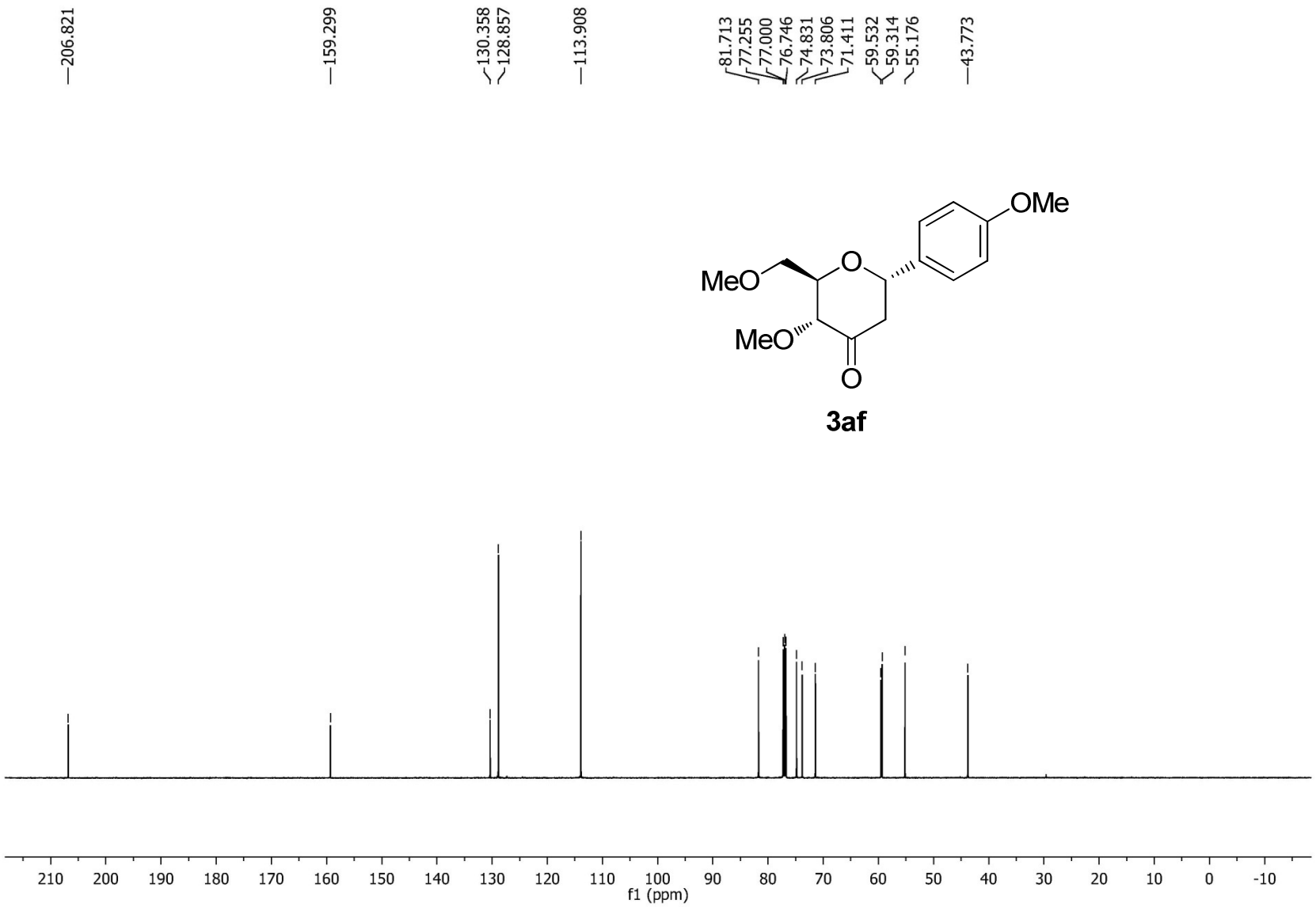

Figure S30: ^{13}C-NMR spectrum of compound 3af in $CDCl_3$

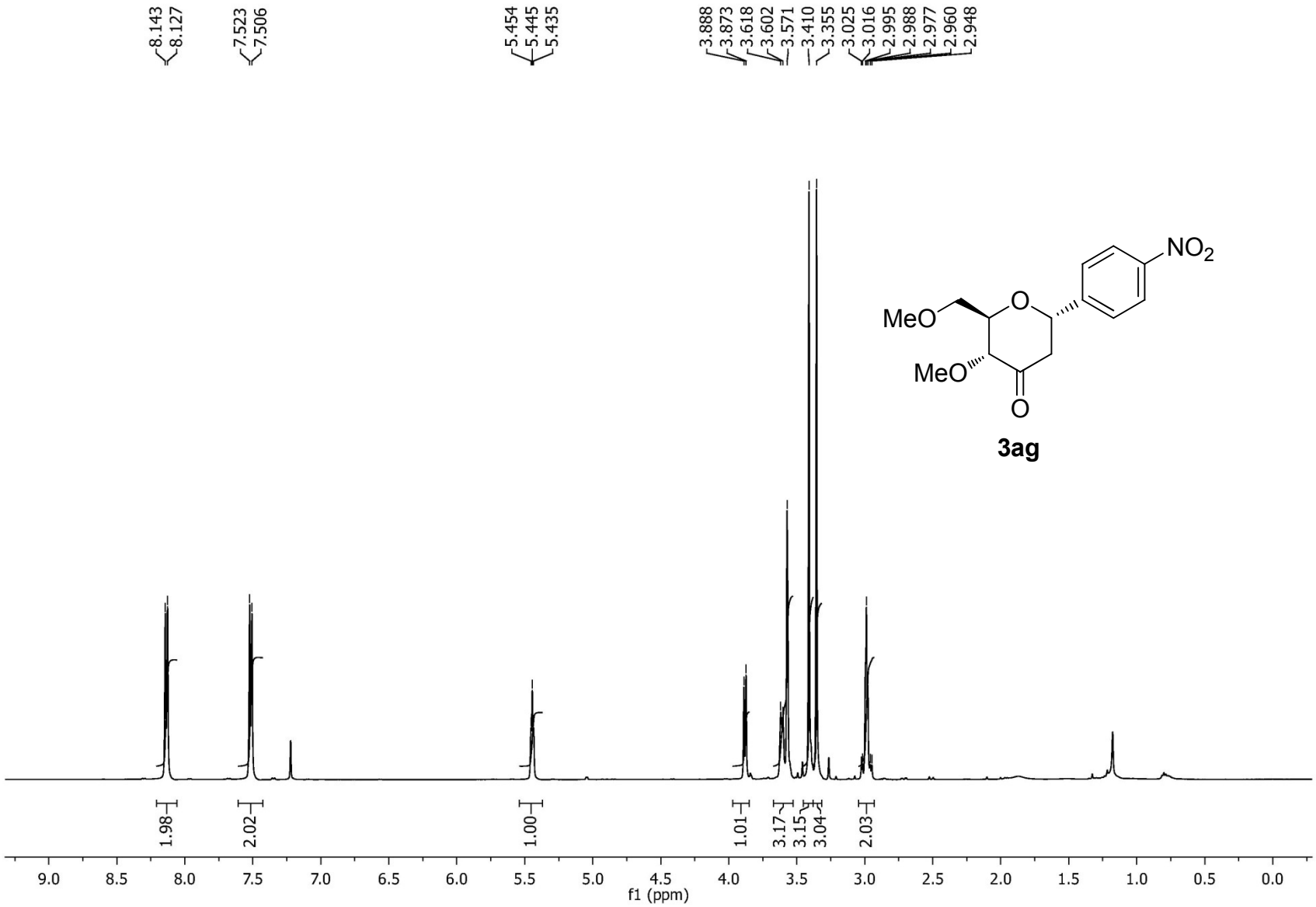

Figure S31: ^{1}H-NMR spectrum of compound 3ag in $CDCl_3$

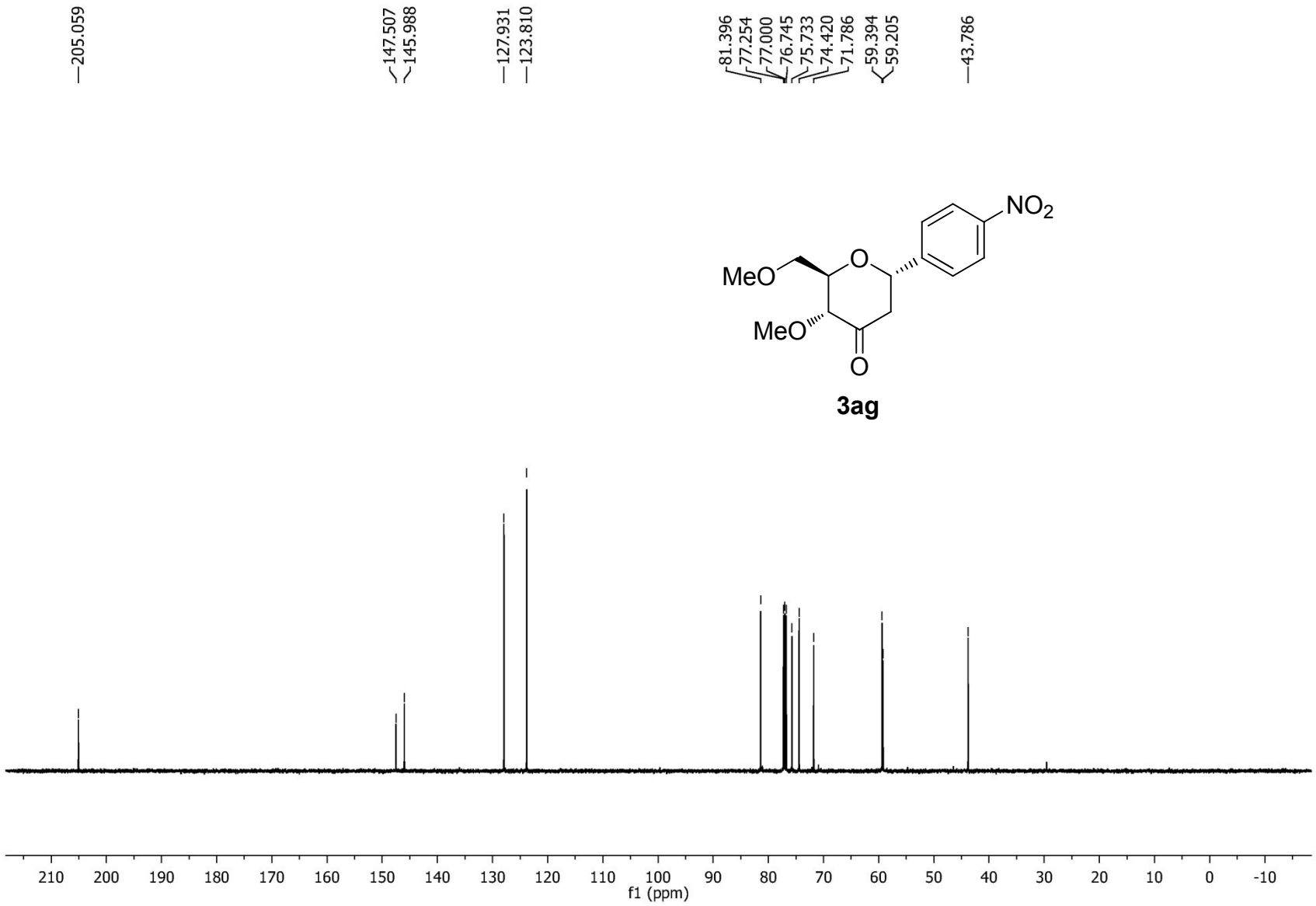

Figure S32: ^{13}C-NMR spectrum of compound 3ag in $CDCl_3$

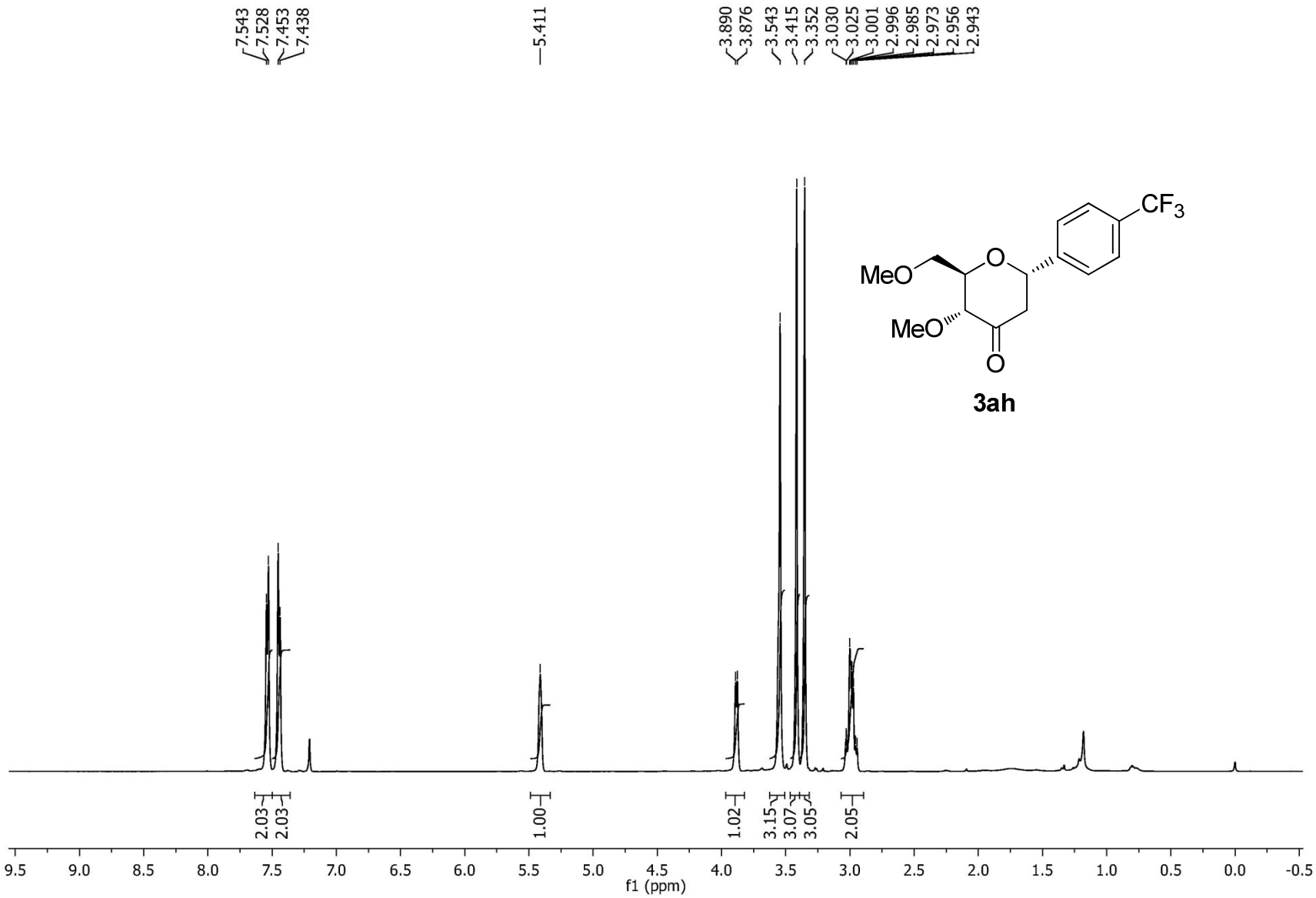

Figure S33: ^{1}H-NMR spectrum of compound 3ah in $CDCl_3$

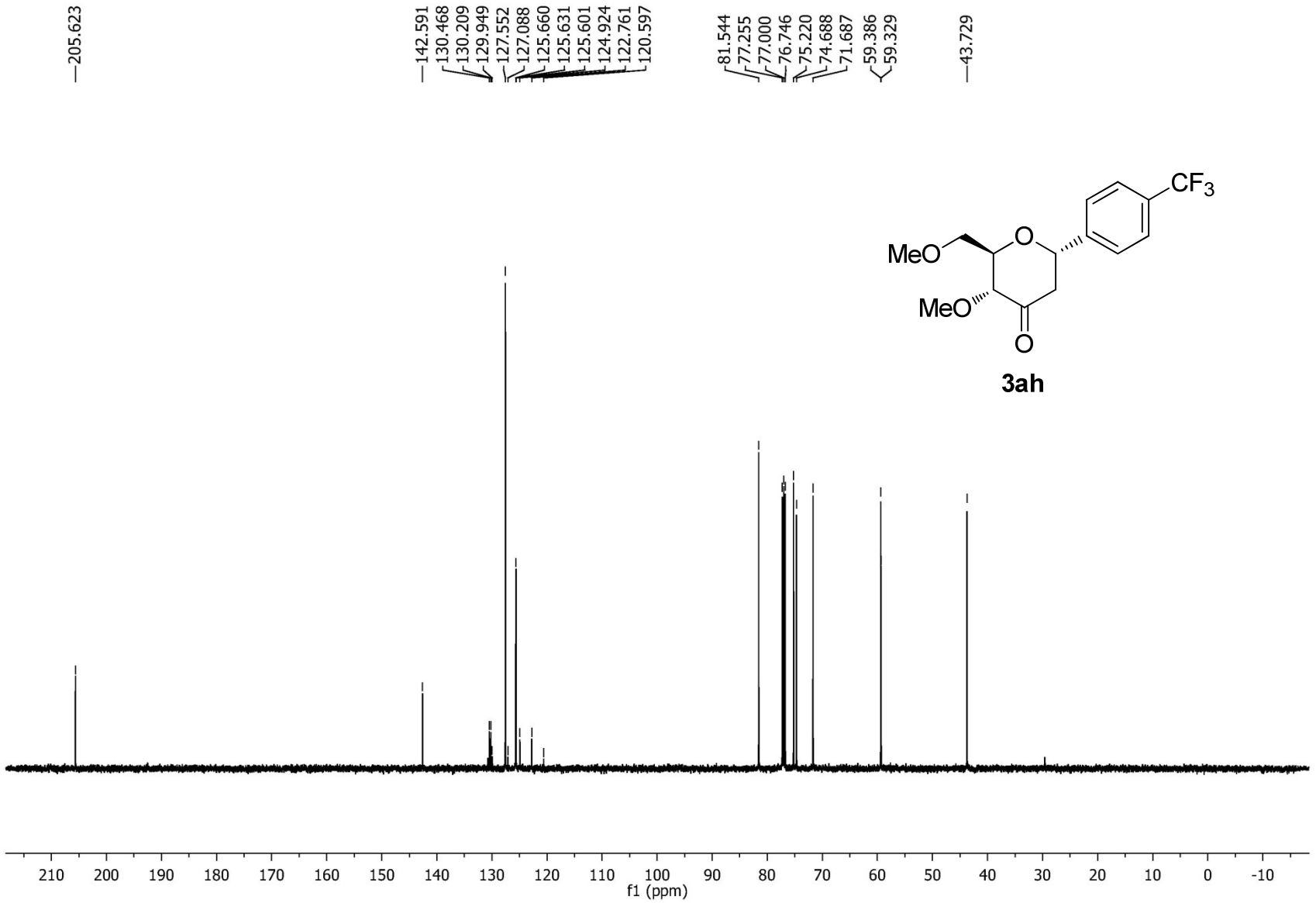

Figure S34: ^{13}C-NMR spectrum of compound 3ah in $CDCl_3$

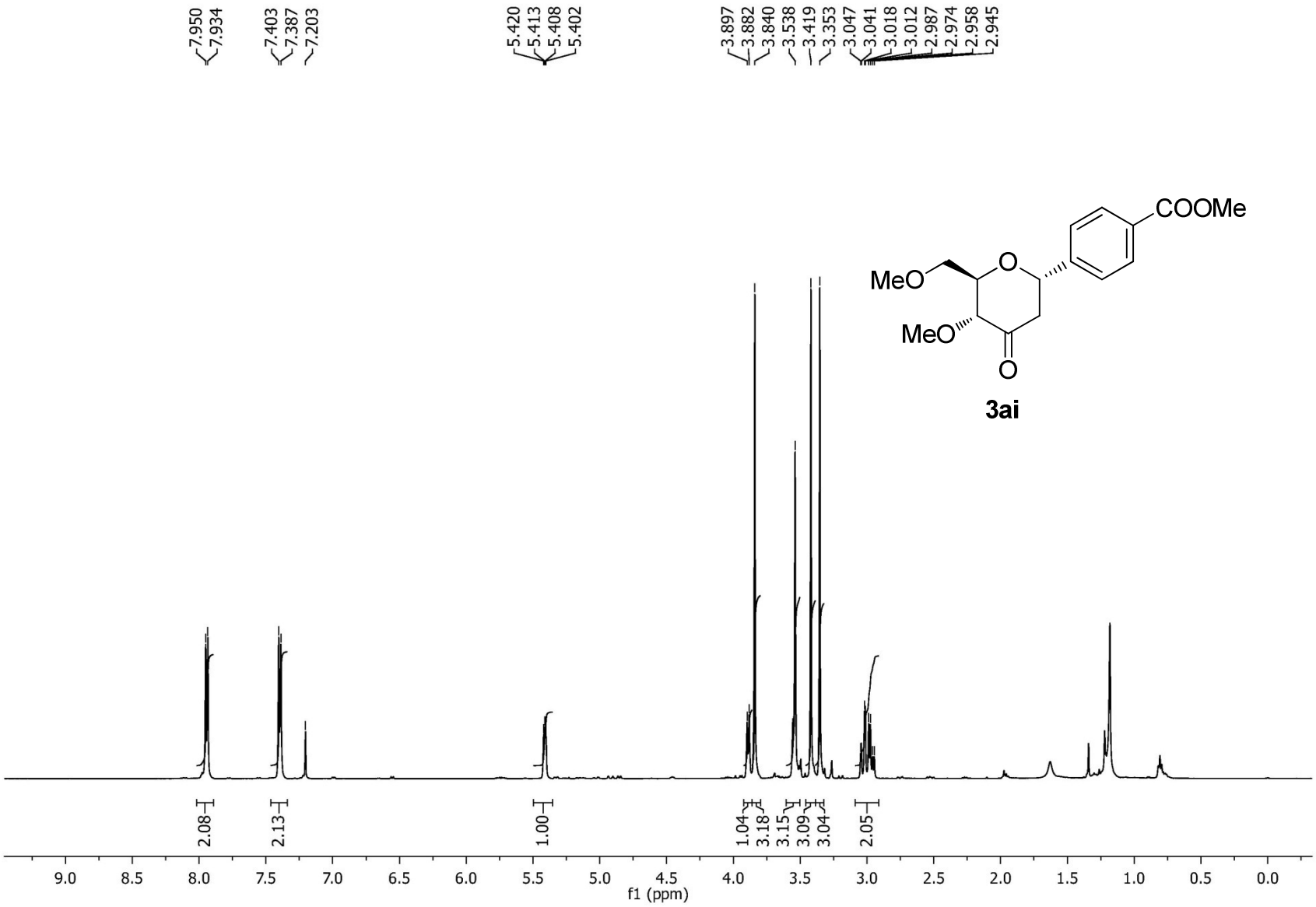

Figure S35: ^{1}H-NMR spectrum of compound 3ai in $CDCl_3$

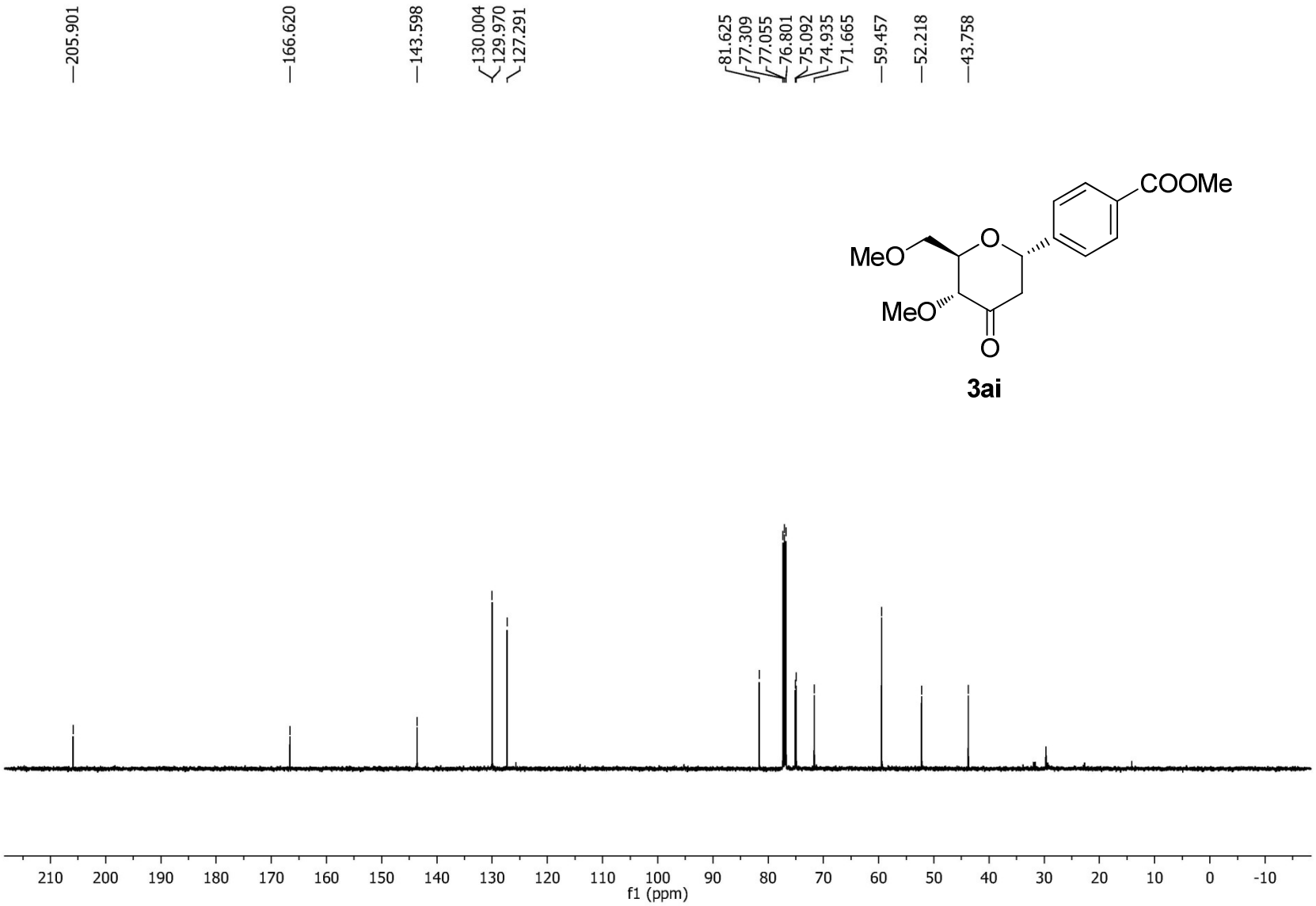

Figure S36: ^{13}C-NMR spectrum of compound 3ai in $CDCl_3$

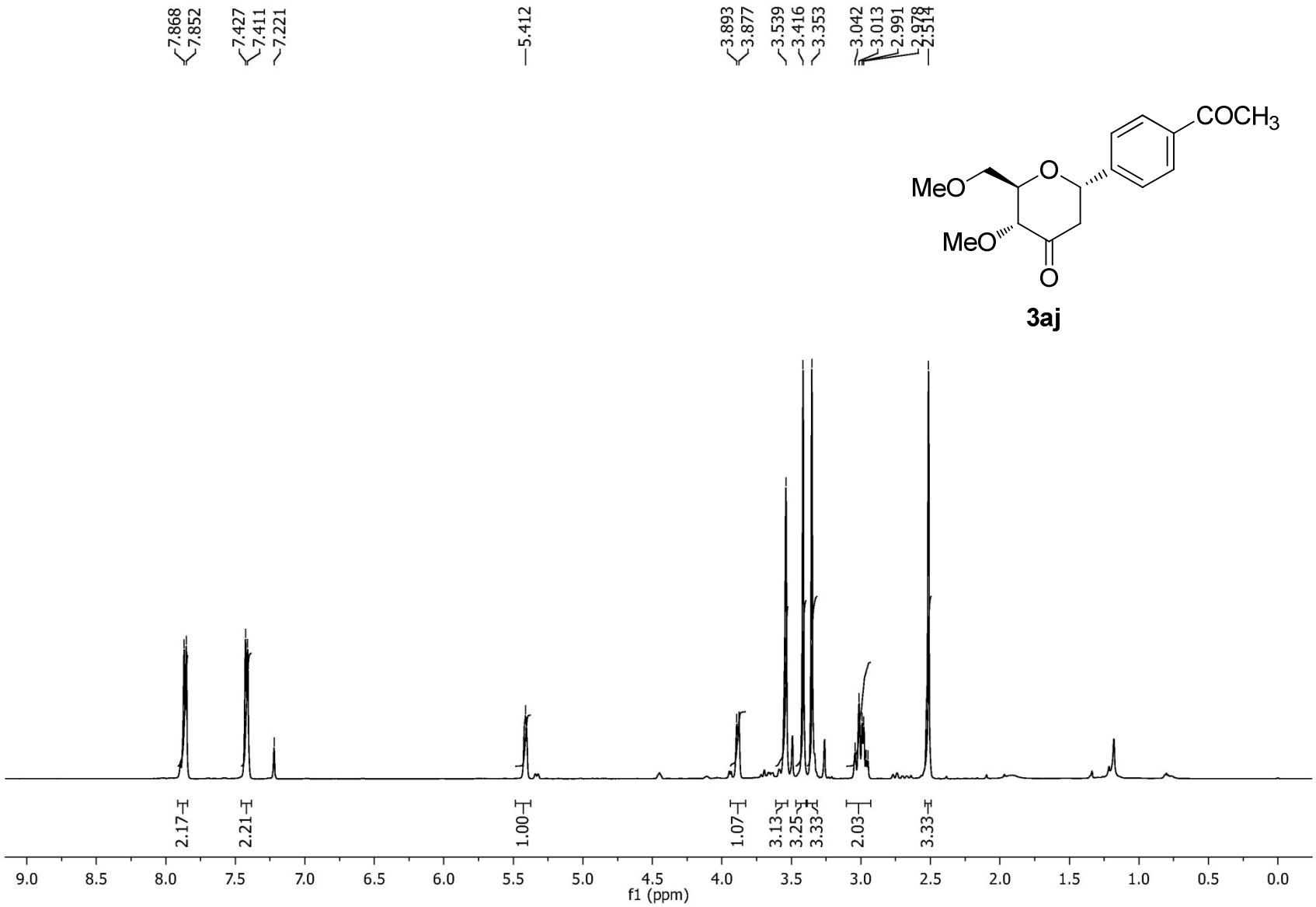

Figure S37: ^{1}H-NMR spectrum of compound 3aj in $CDCl_3$

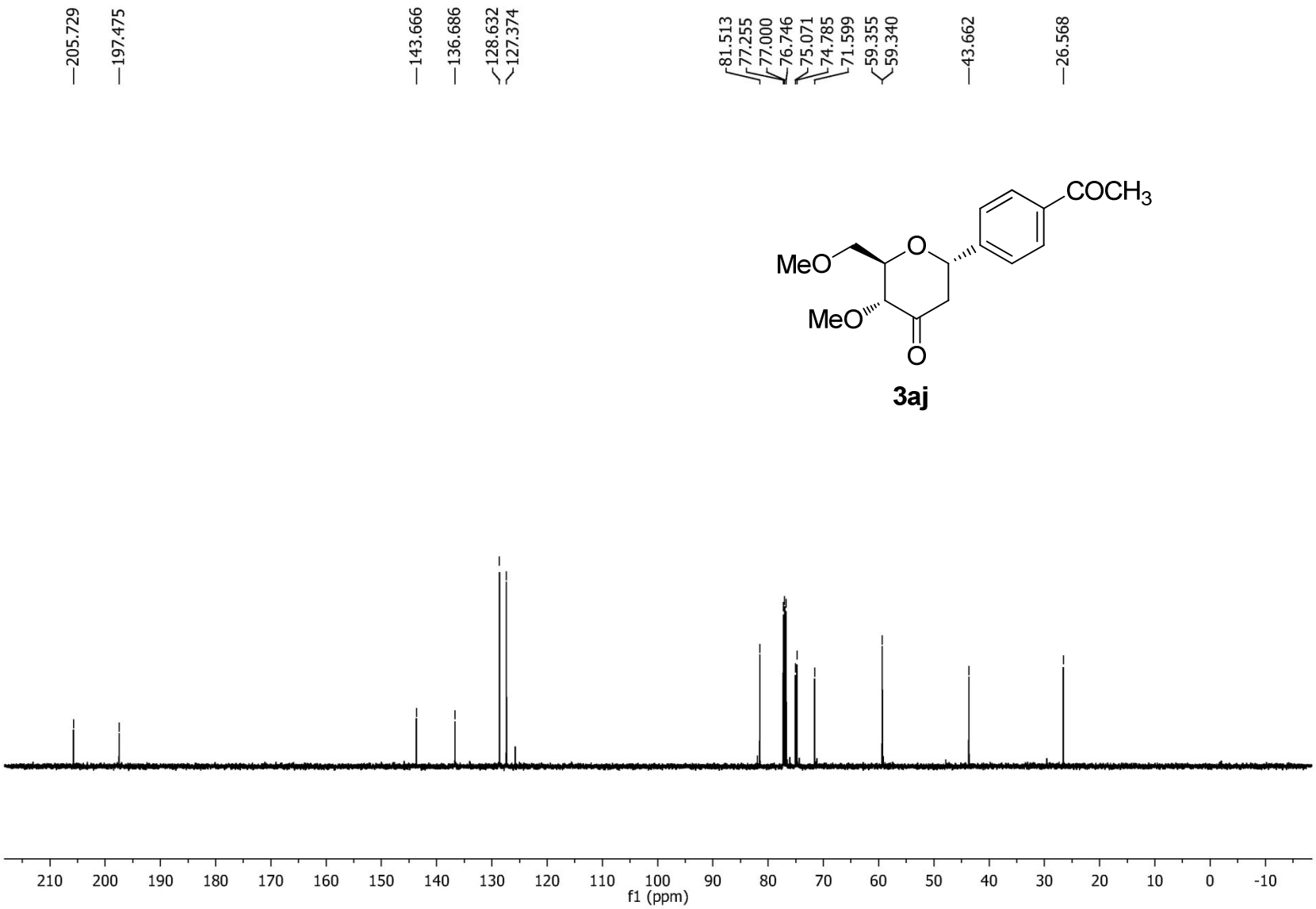

Figure S38: ^{13}C-NMR spectrum of compound 3aj in $CDCl_3$

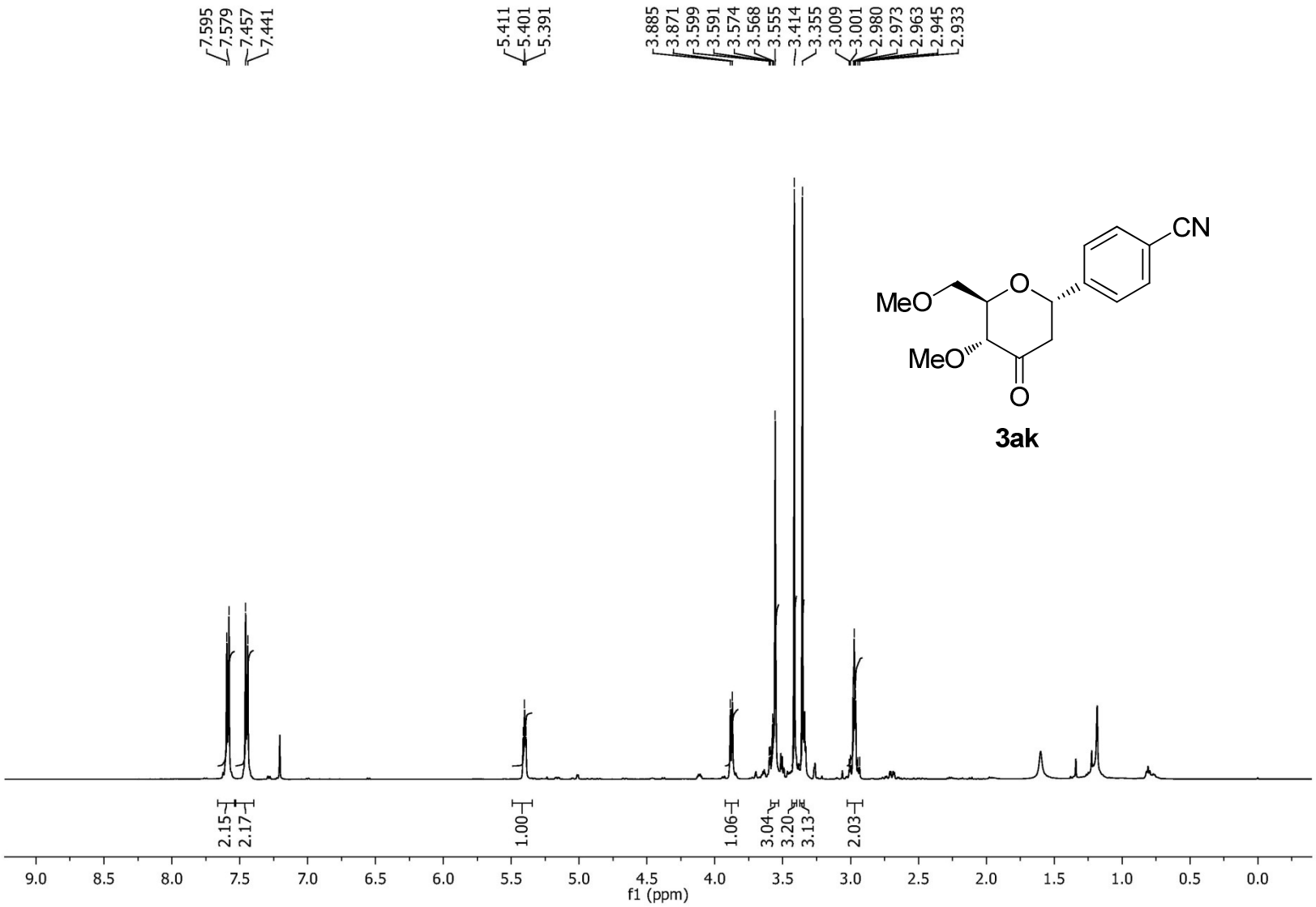

Figure S39: ^{1}H-NMR spectrum of compound 3ak in $CDCl_3$

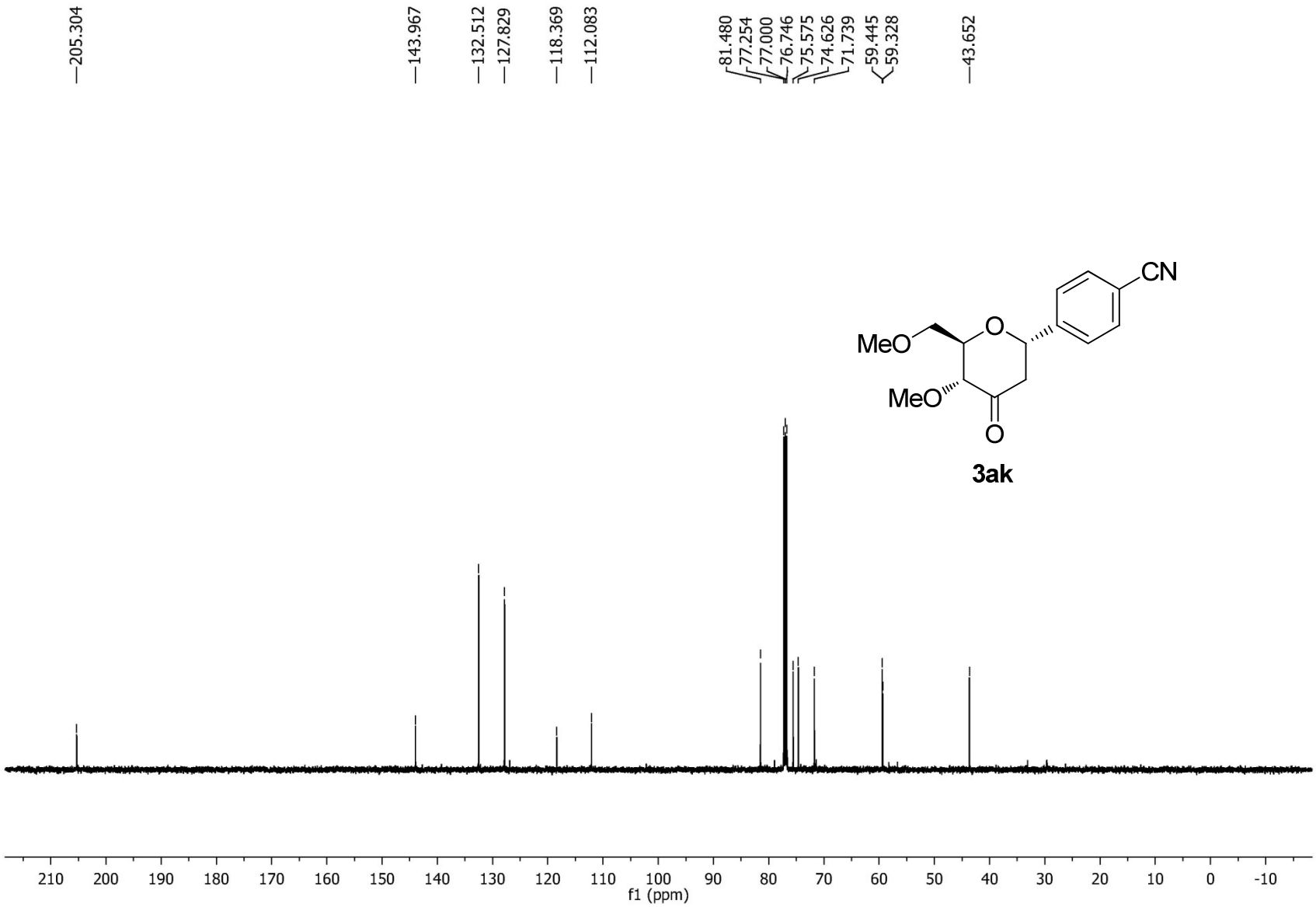

Figure S40: ^{13}C-NMR spectrum of compound 3ak in $CDCl_3$

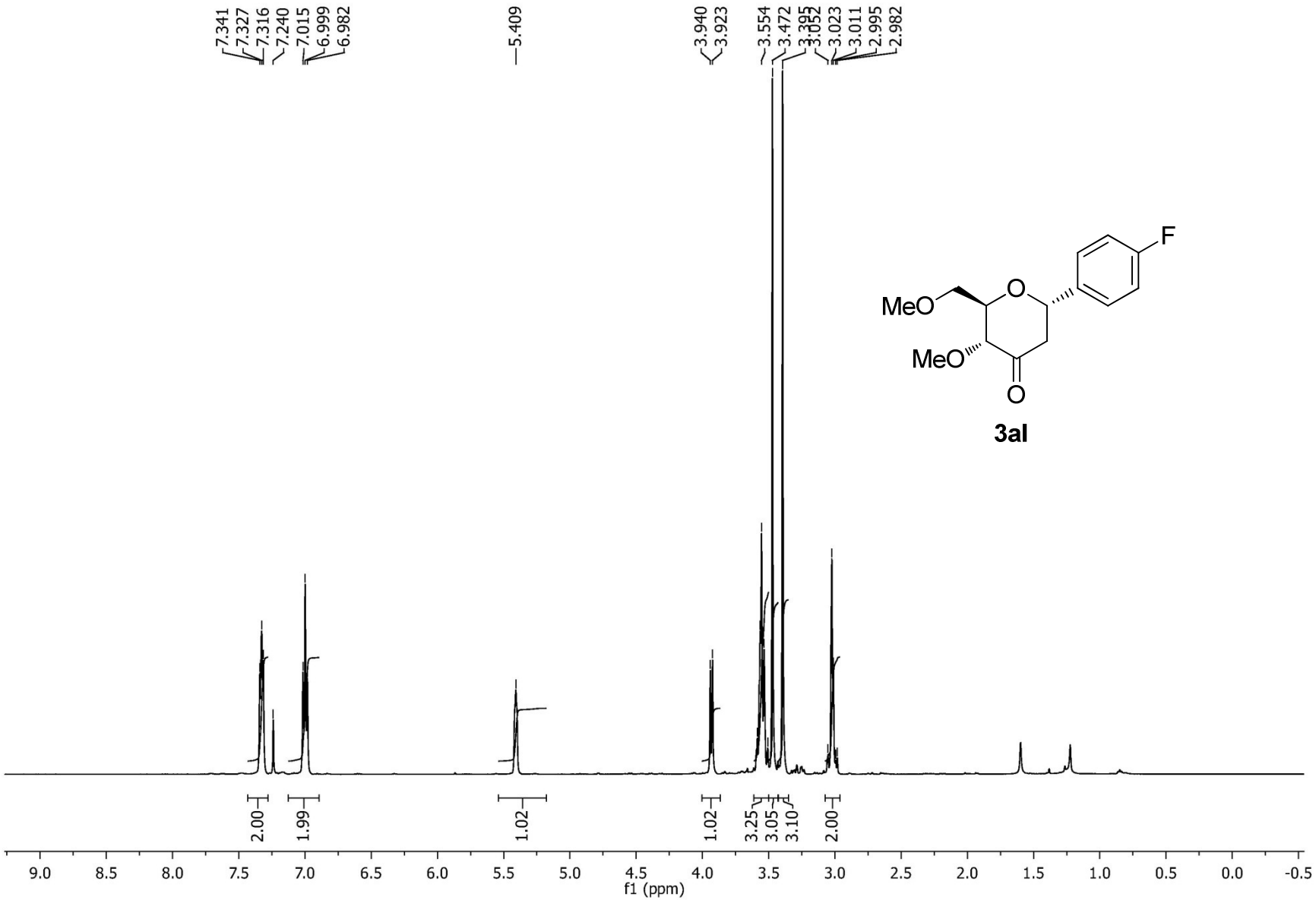

Figure S41: ^{1}H-NMR spectrum of compound 3al in $CDCl_3$

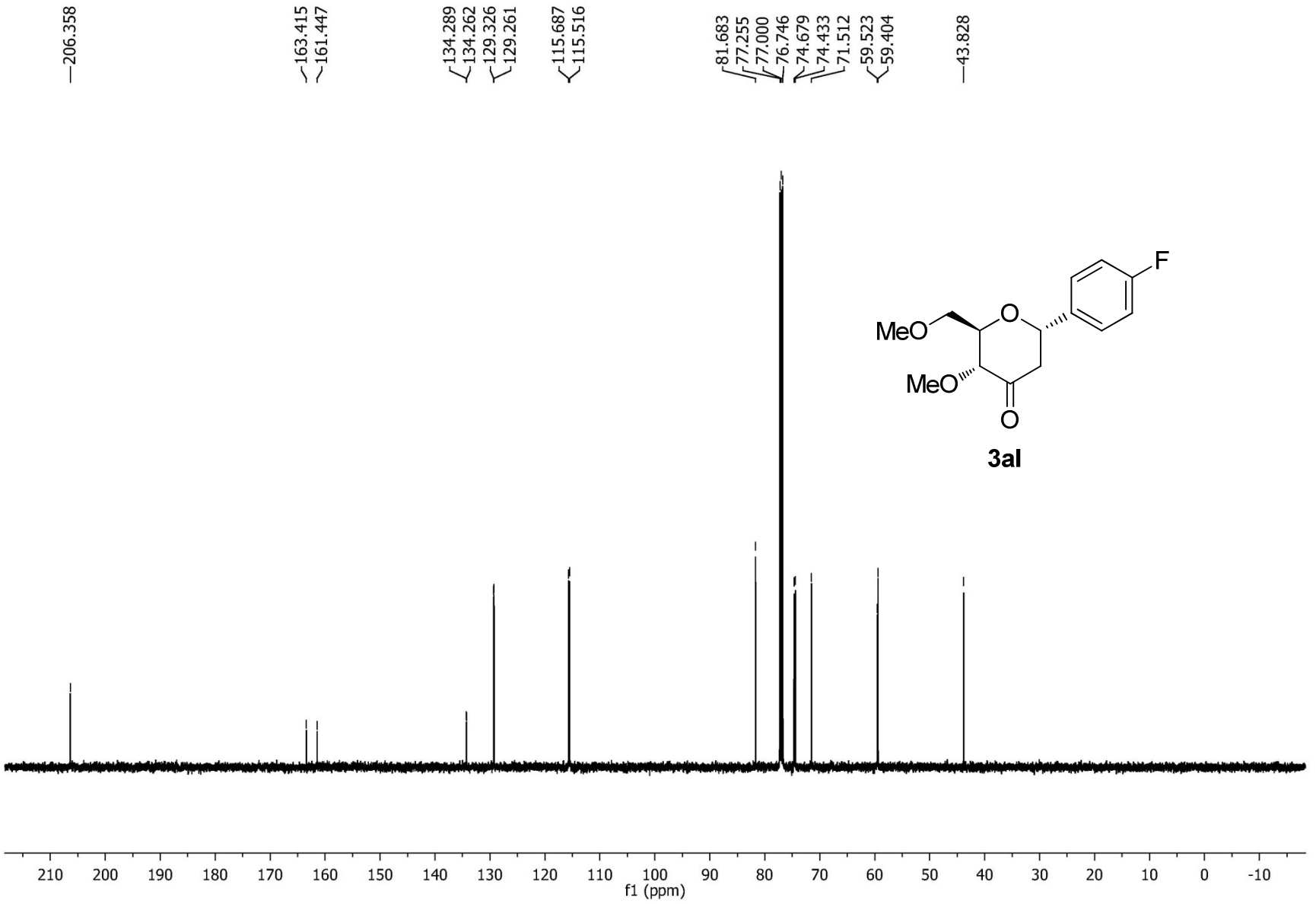

Figure S42: ^{13}C-NMR spectrum of compound 3al in $CDCl_3$

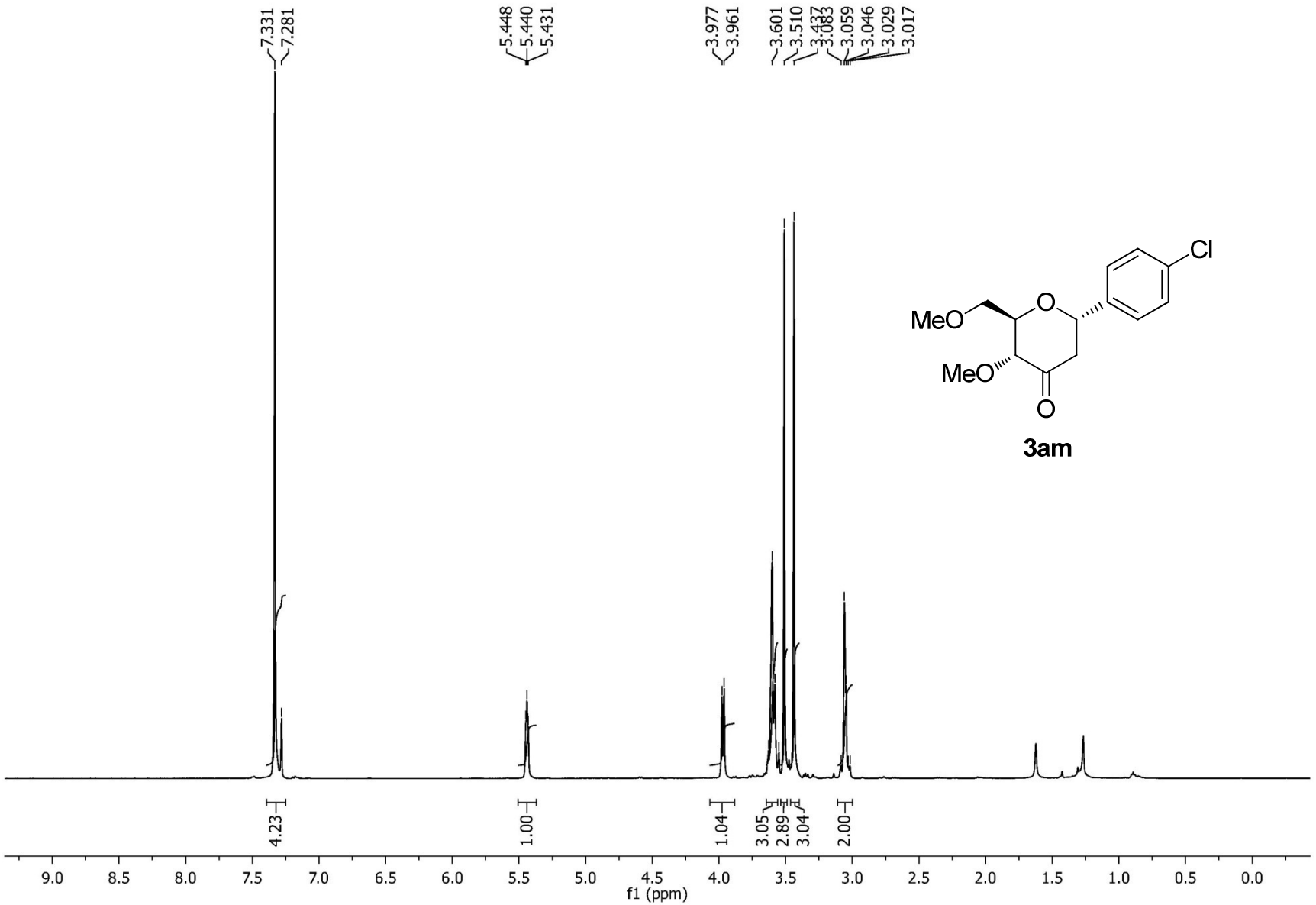

Figure S43: ^{1}H-NMR spectrum of compound 3am in $CDCl_3$

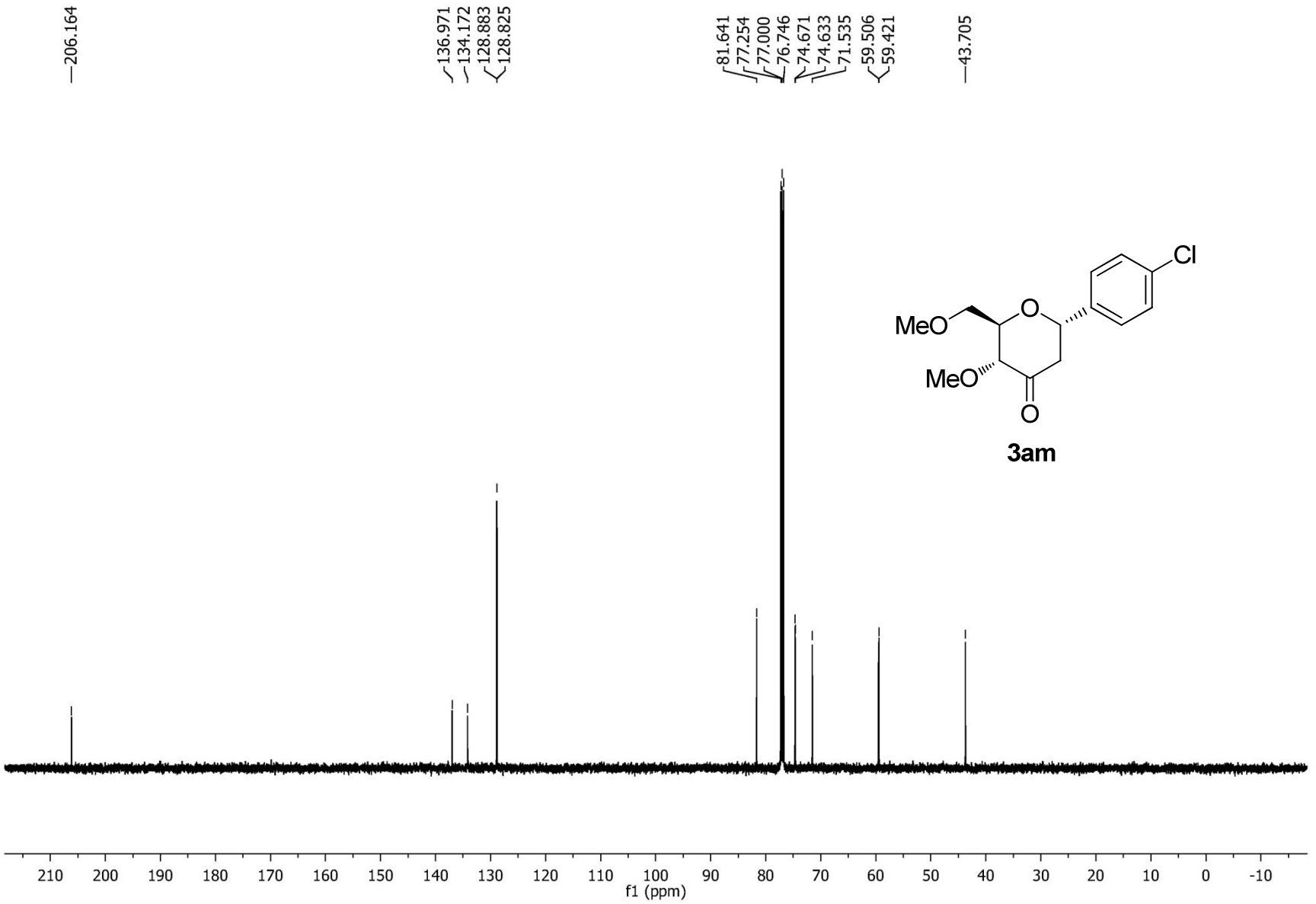

Figure S44: ^{13}C-NMR spectrum of compound 3am in $CDCl_3$

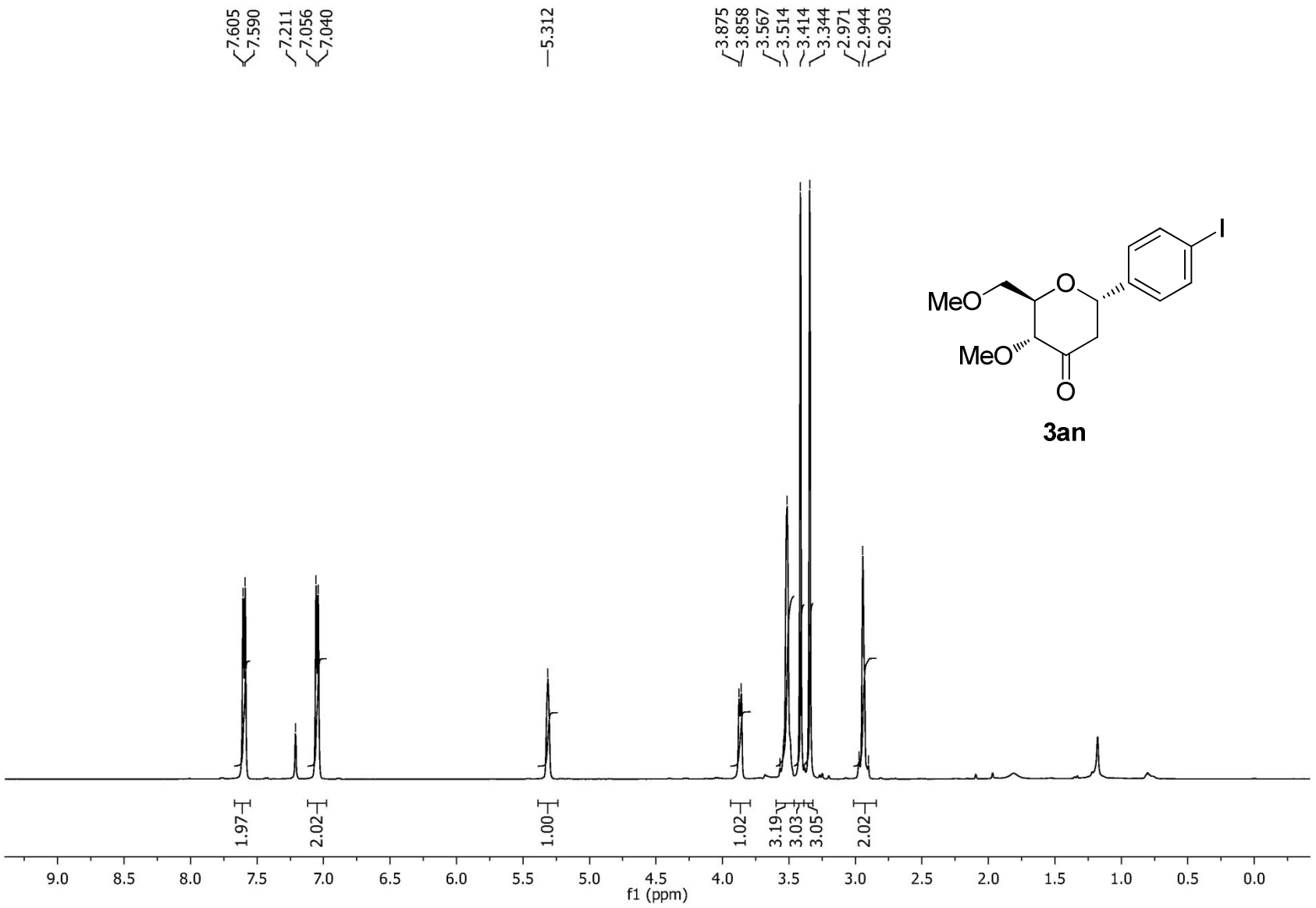

Figure S45: ^{1}H-NMR spectrum of compound 3an in $CDCl_3$

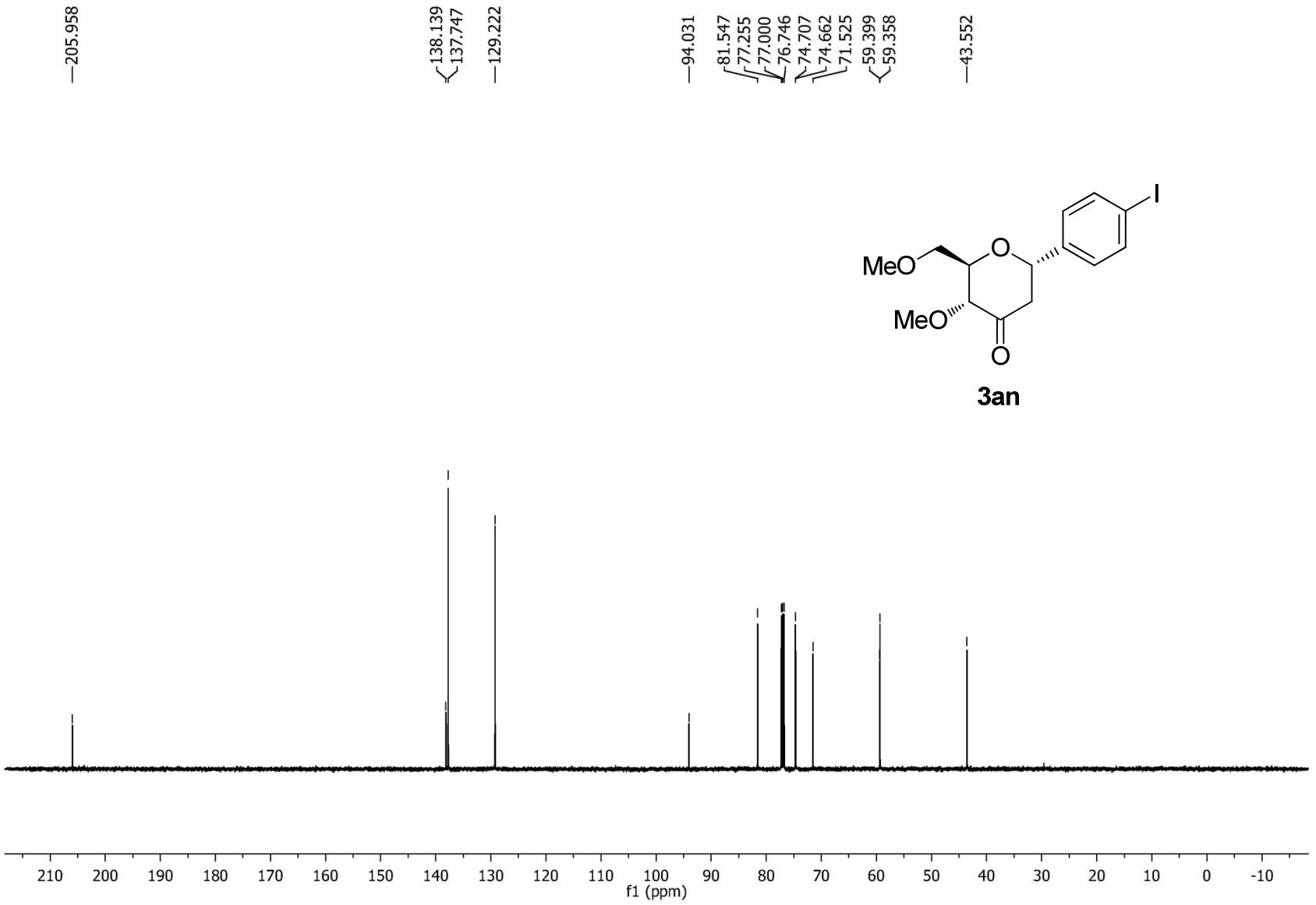

Figure S46: ^{13}C-NMR spectrum of compound 3an in $CDCl_3$

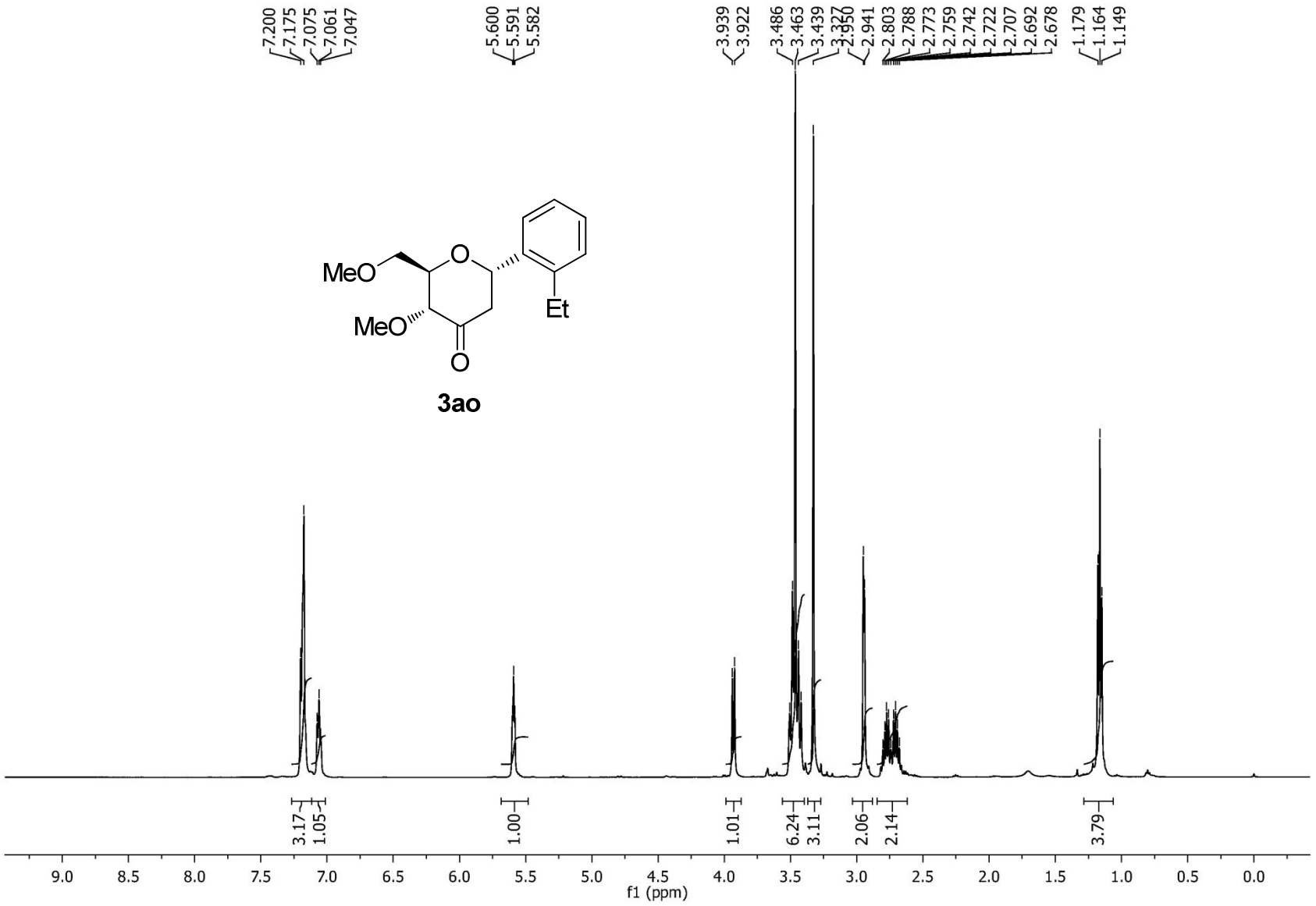

Figure S47: ^{1}H-NMR spectrum of compound 3ao in $CDCl_3$

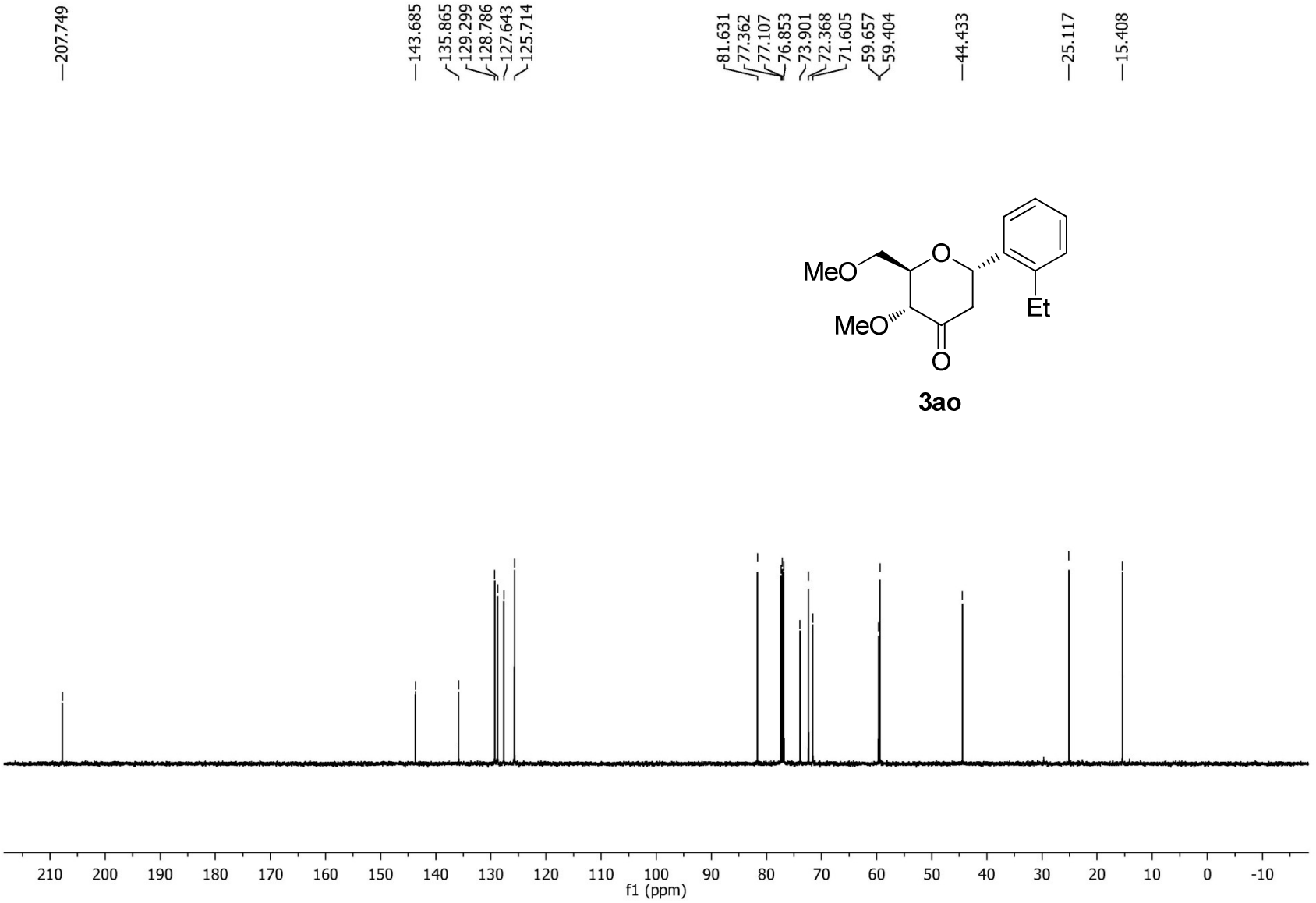

Figure S48: ^{13}C-NMR spectrum of compound 3ao in $CDCl_3$

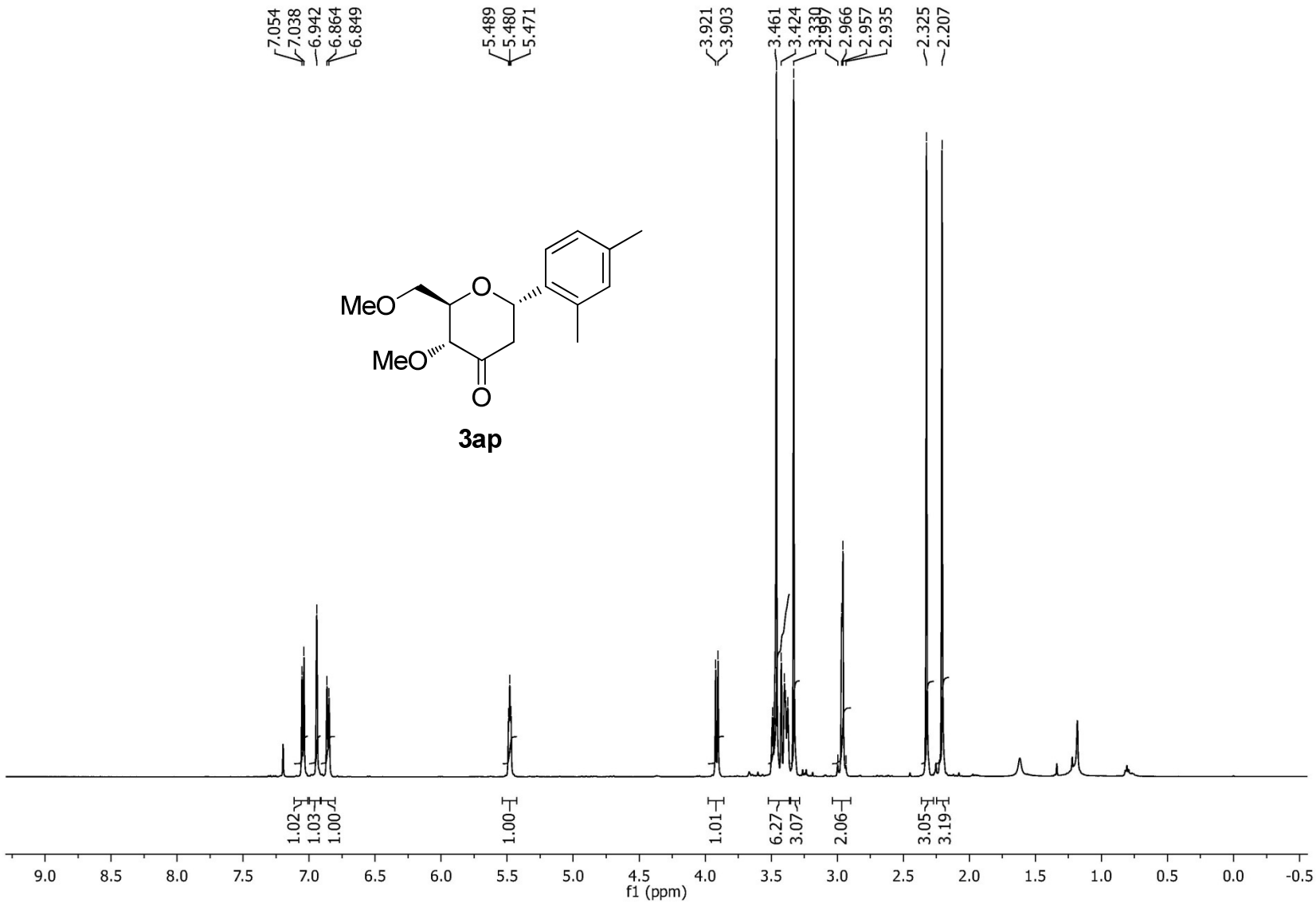

Figure S49: ^{1}H-NMR spectrum of compound 3ap in $CDCl_3$

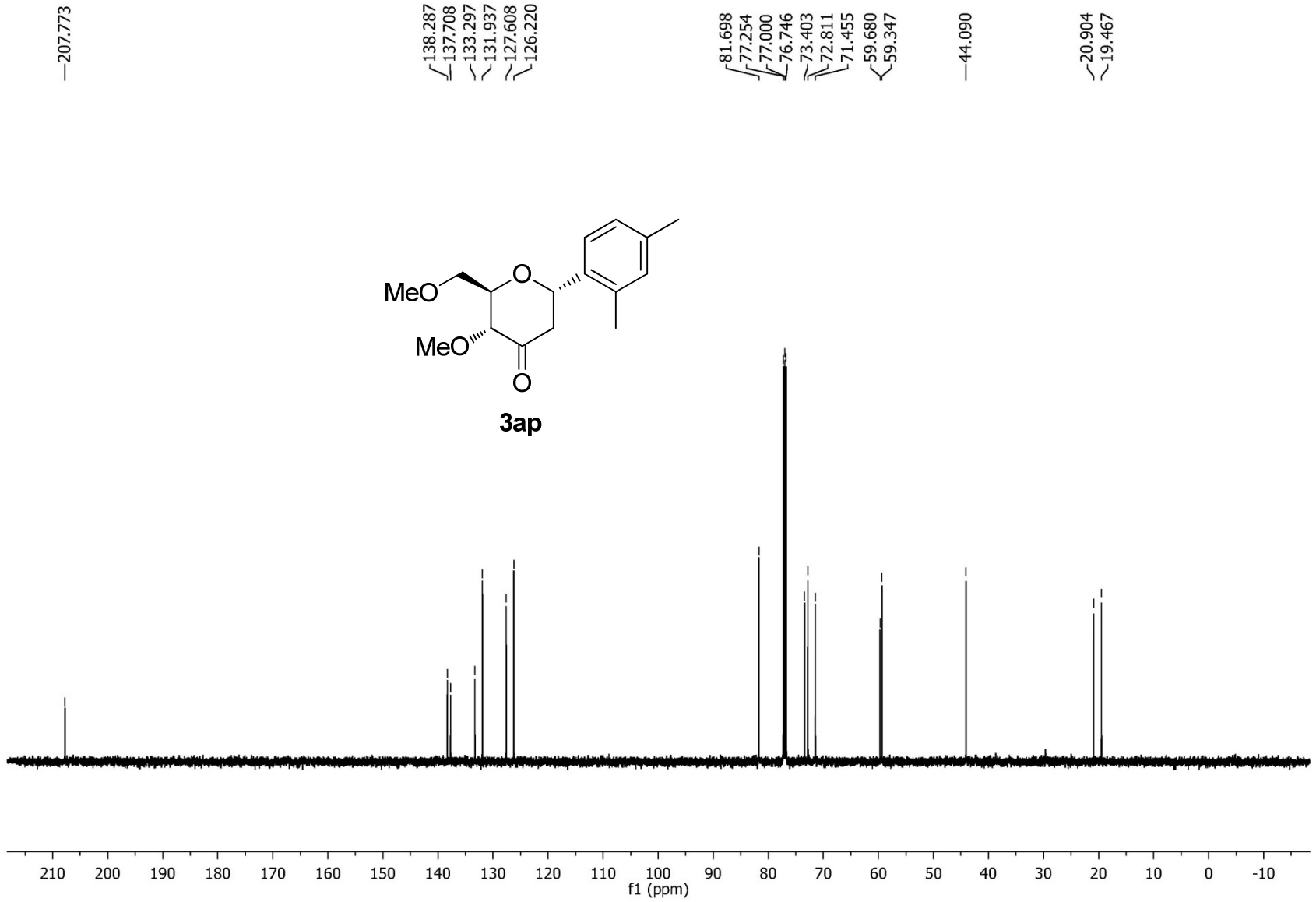

Figure S50: ^{13}C-NMR spectrum of compound 3ap in $CDCl_3$

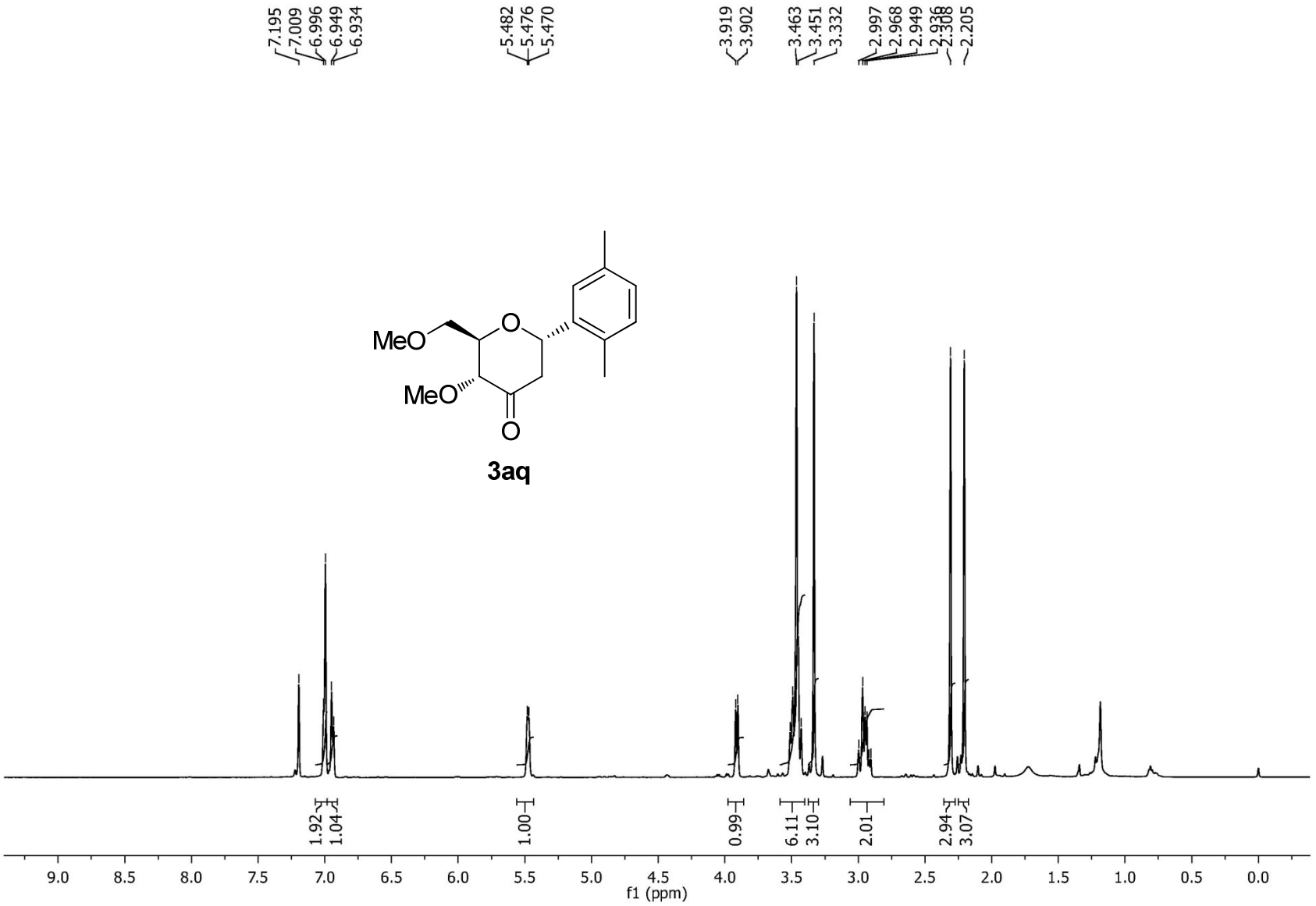

Figure S51: ^{1}H-NMR spectrum of compound 3aq in $CDCl_3$

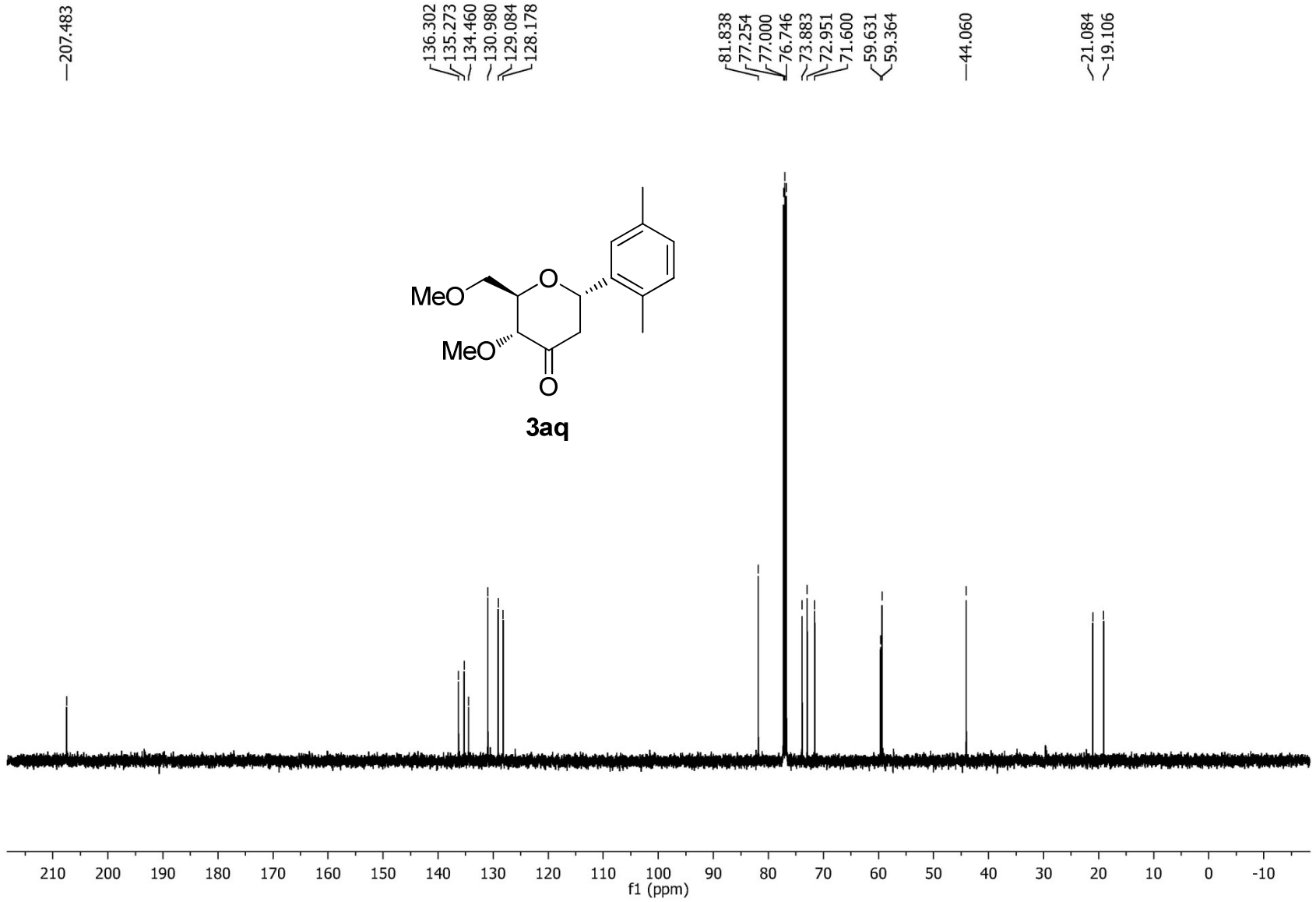

Figure S52: ^{13}C-NMR spectrum of compound 3aq in $CDCl_3$

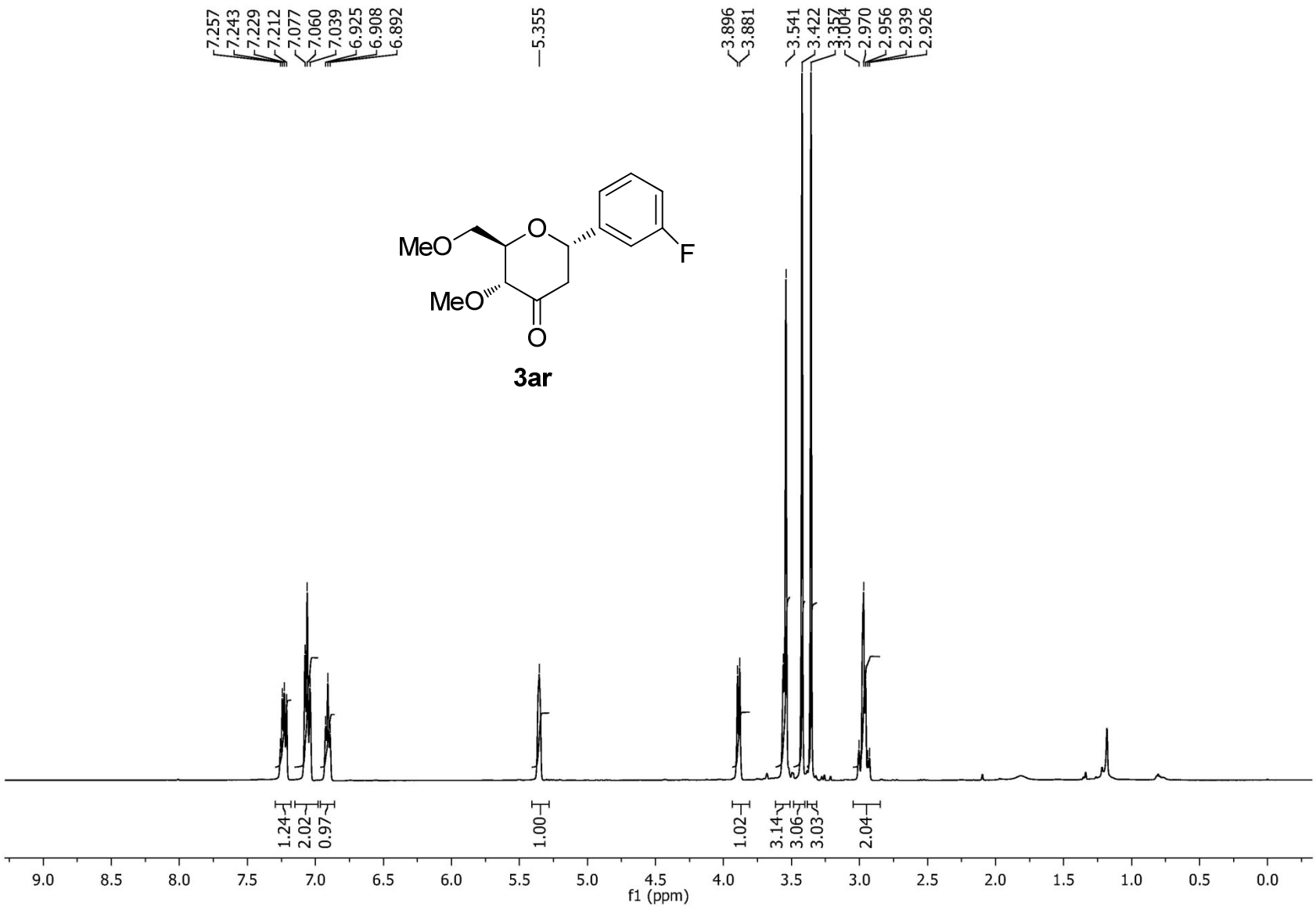

Figure S53: ^{1}H-NMR spectrum of compound 3ar in $CDCl_3$

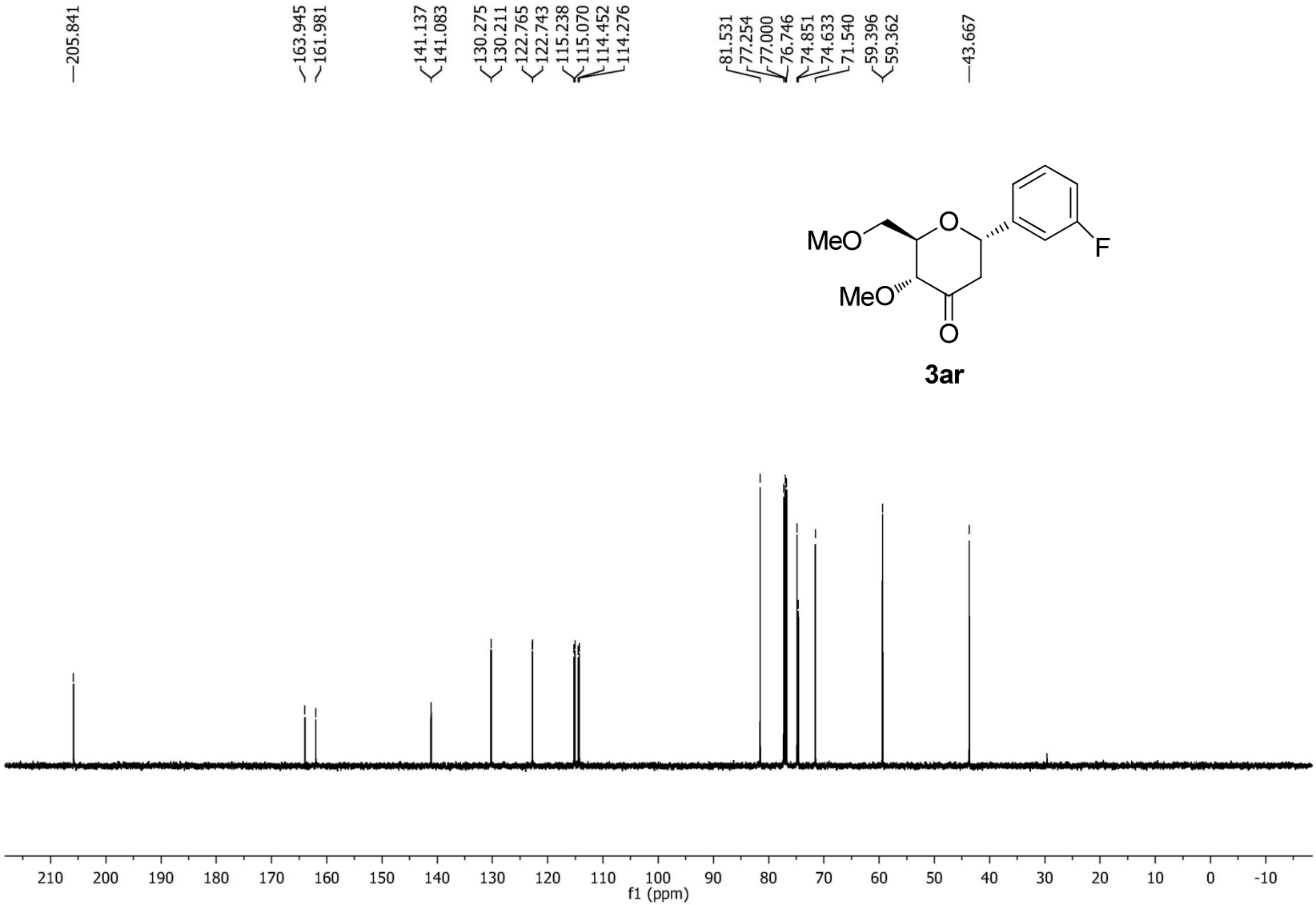

Figure S54: ^{13}C-NMR spectrum of compound 3ar in $CDCl_3$

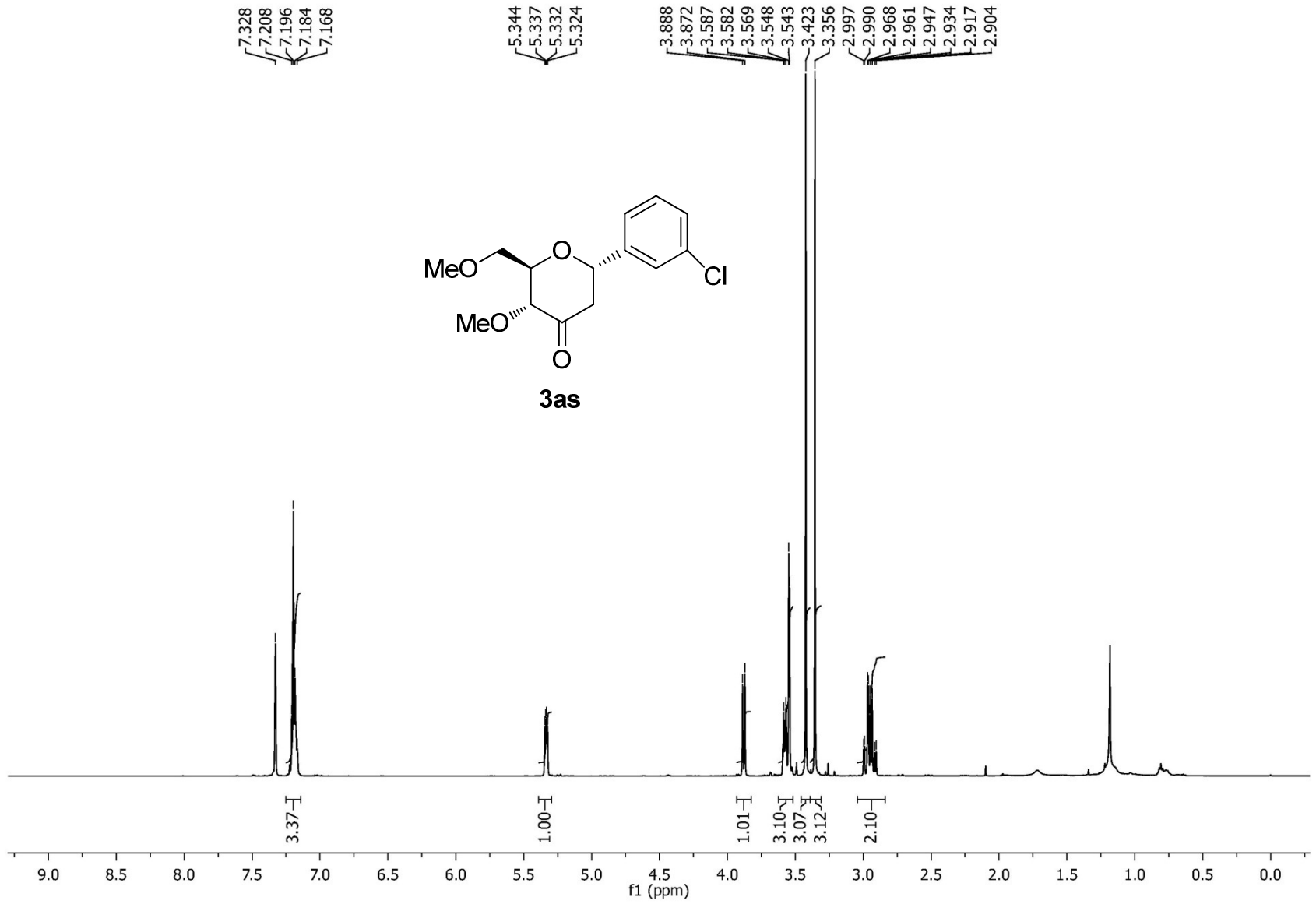

Figure S55: ^{1}H-NMR spectrum of compound 3as in $CDCl_3$

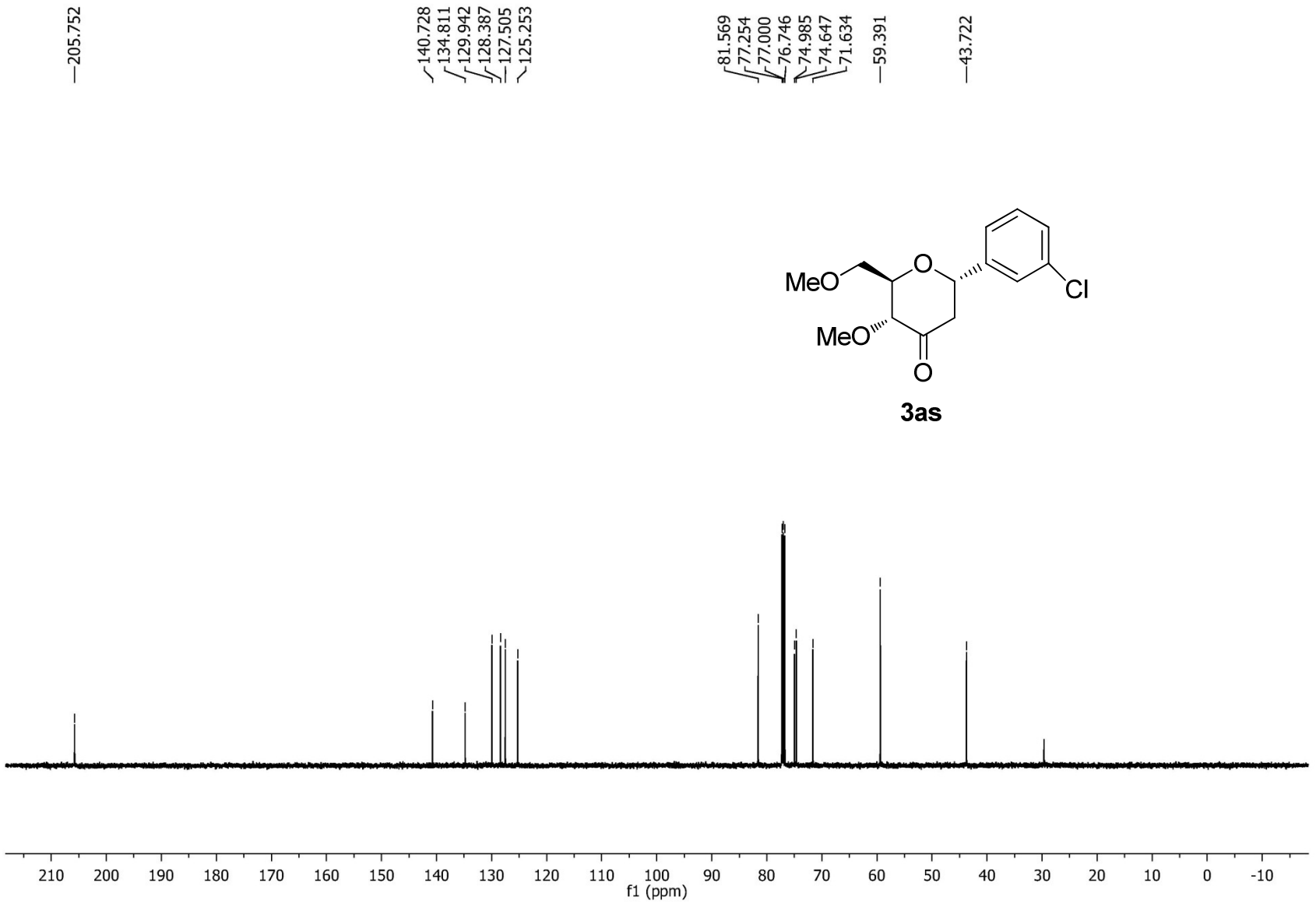

Figure S56: ^{13}C-NMR spectrum of compound 3as in $CDCl_3$

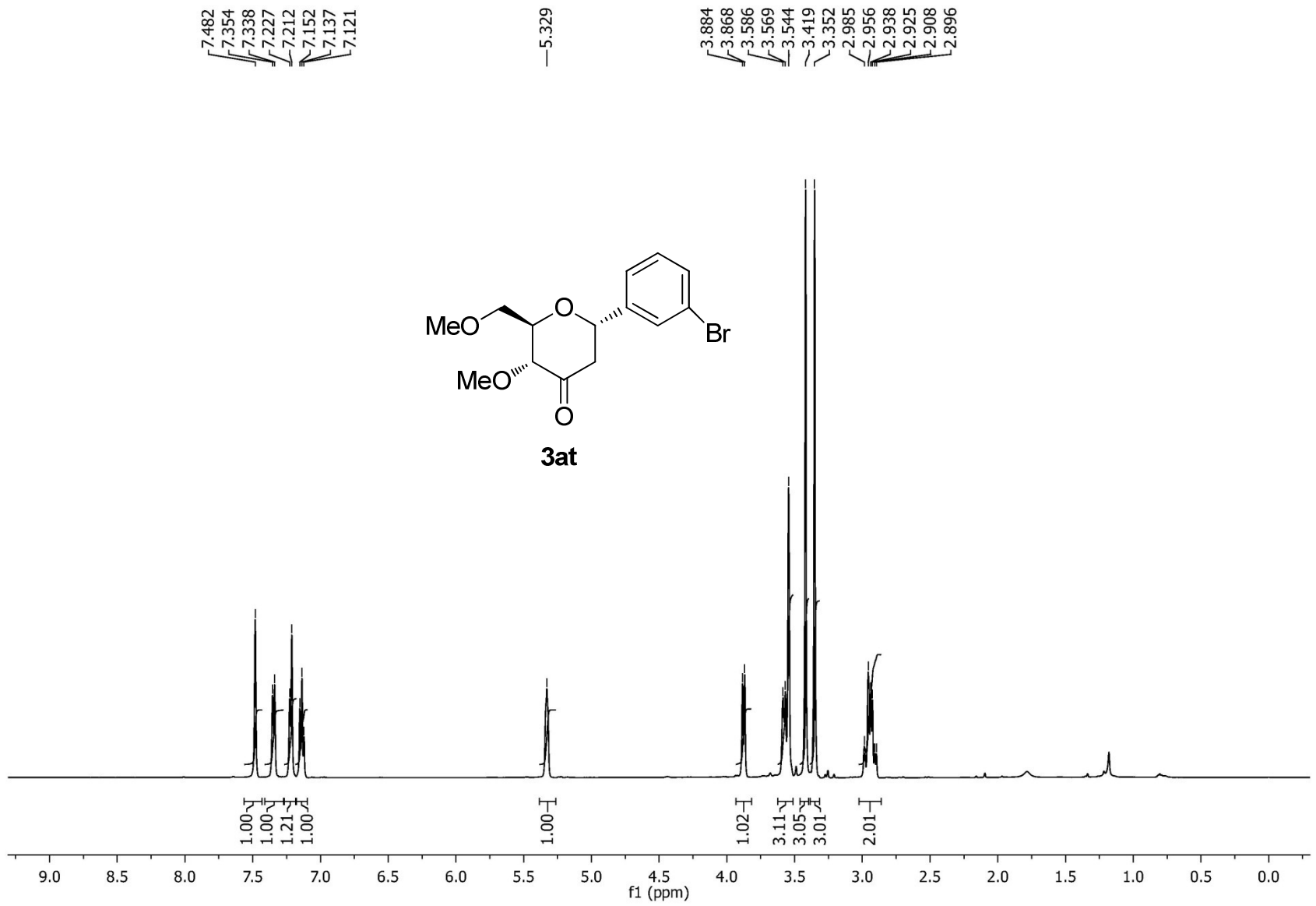

Figure S57: ^{1}H-NMR spectrum of compound 3at in $CDCl_3$

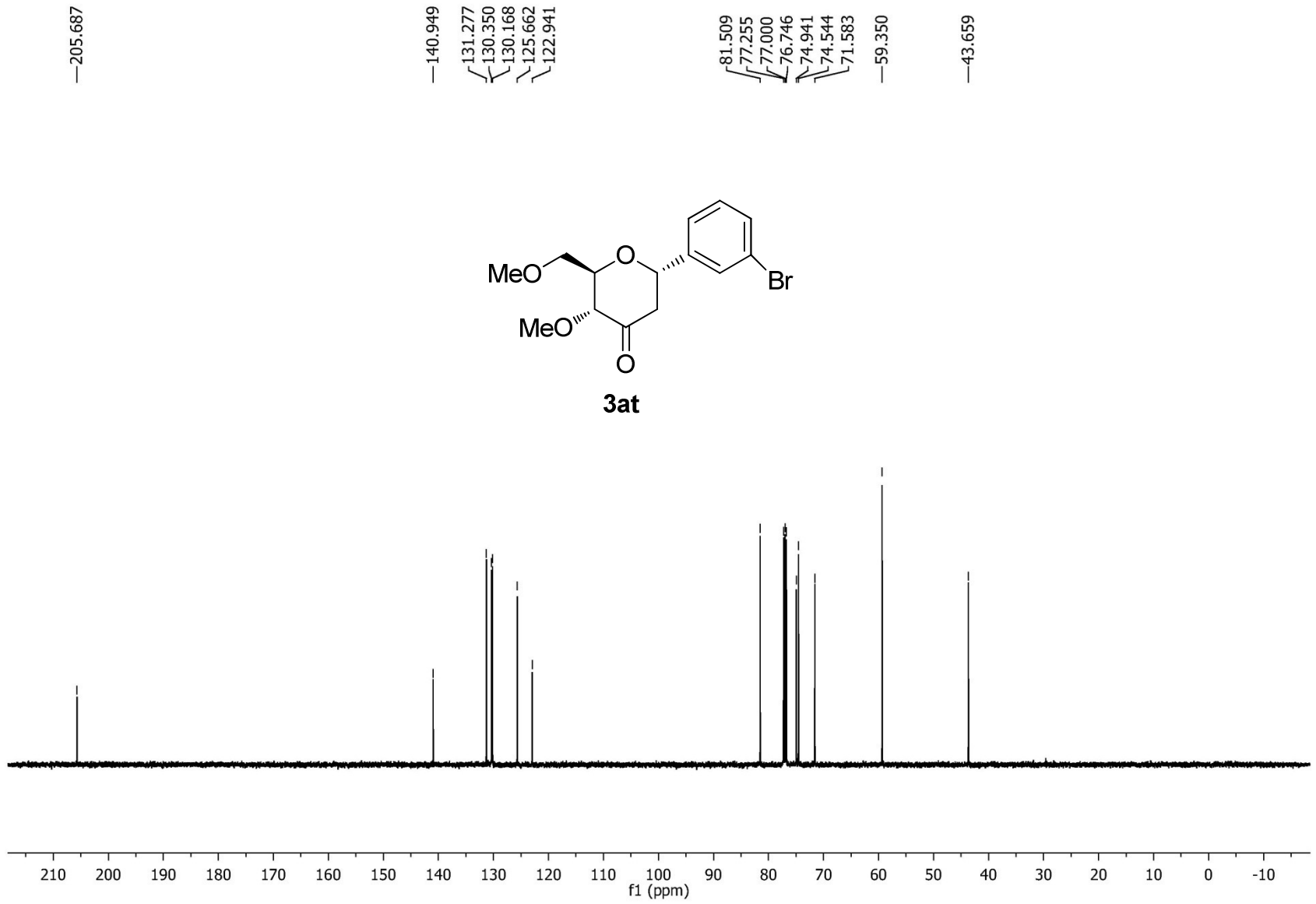

Figure S58: ^{13}C-NMR spectrum of compound 3at in $CDCl_3$

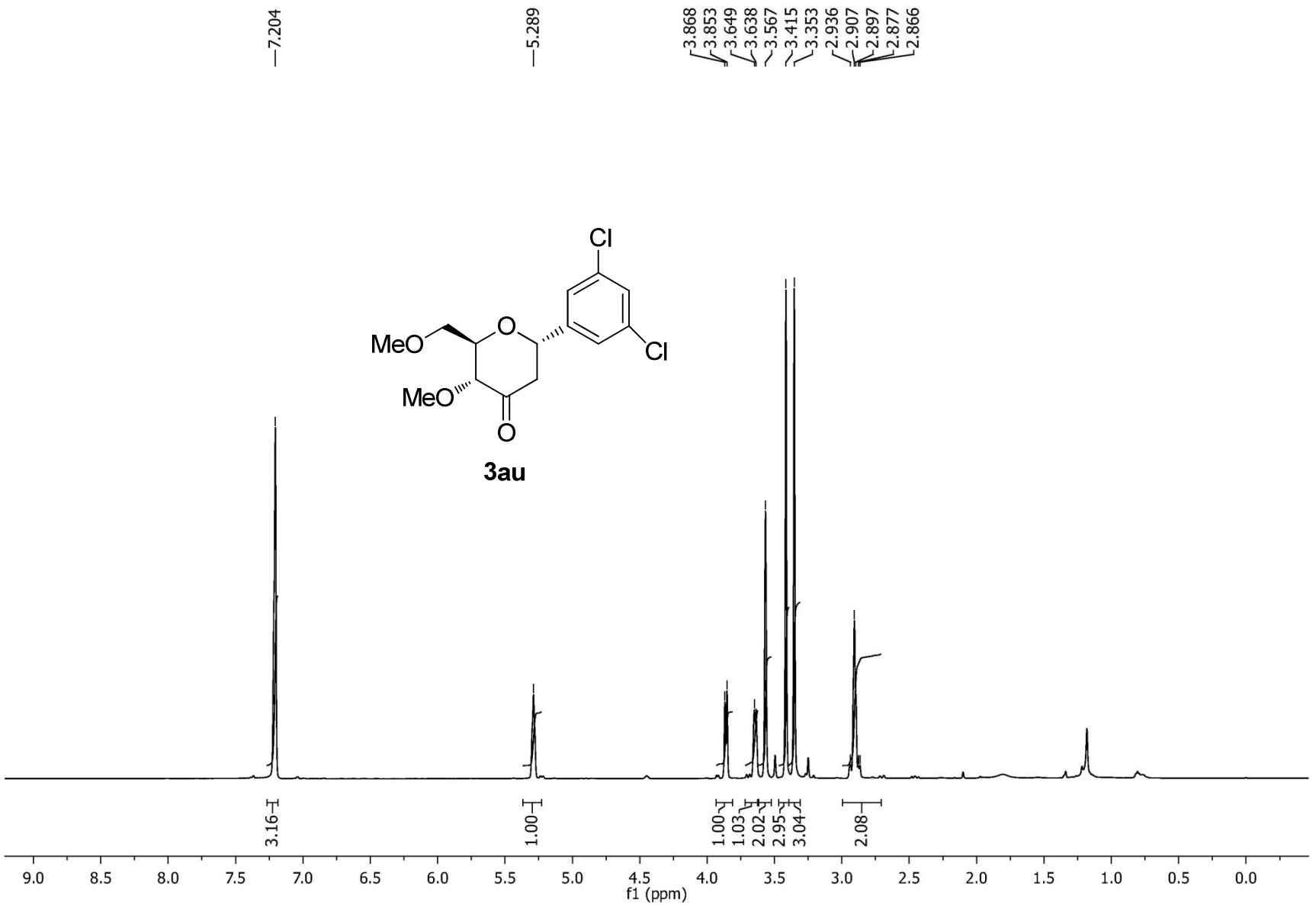

Figure S59: ^{1}H-NMR spectrum of compound 3au in $CDCl_3$

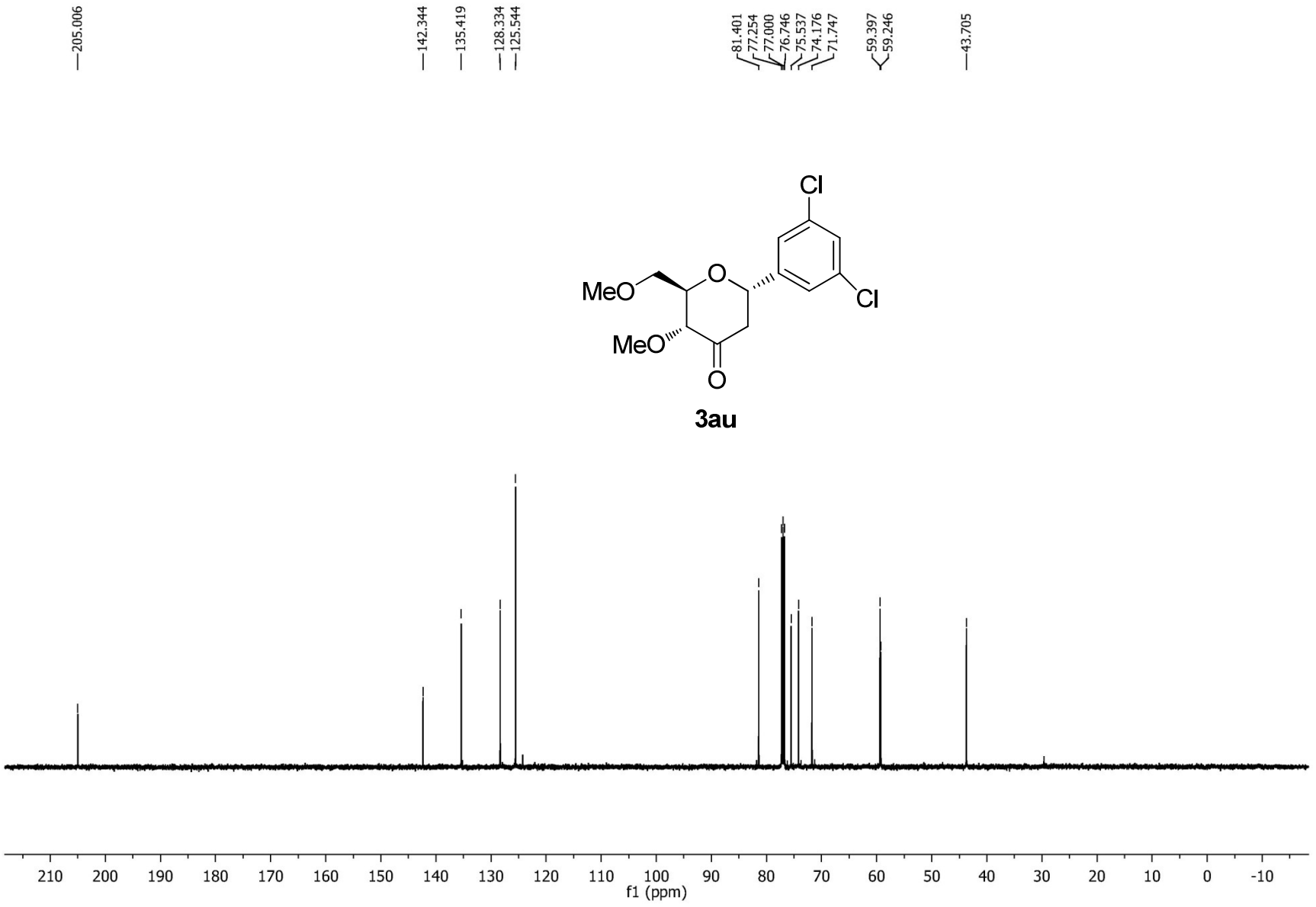

Figure S60: ^{13}C-NMR spectrum of compound 3au in $CDCl_3$

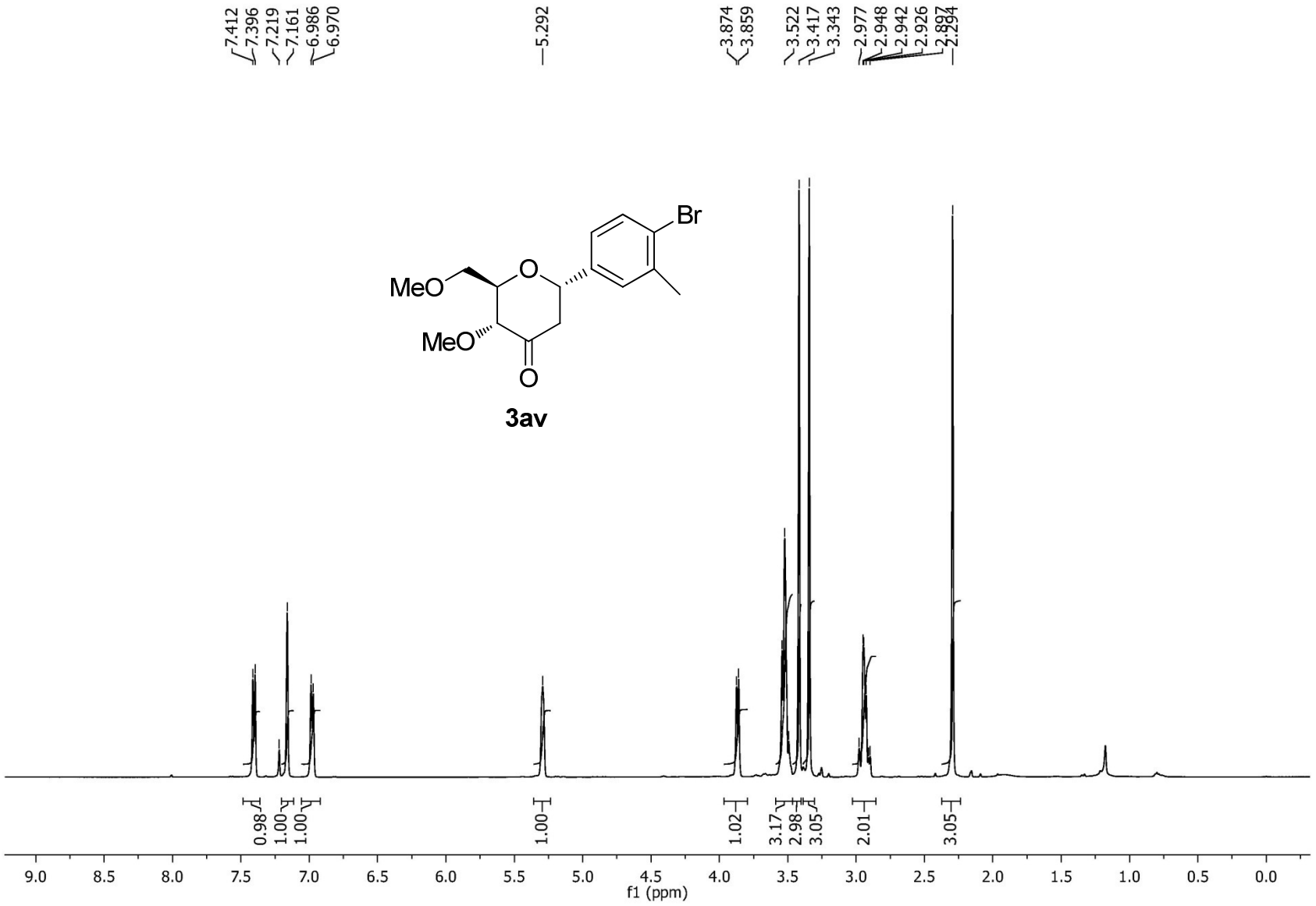

Figure S61: ^{1}H-NMR spectrum of compound 3av in $CDCl_3$

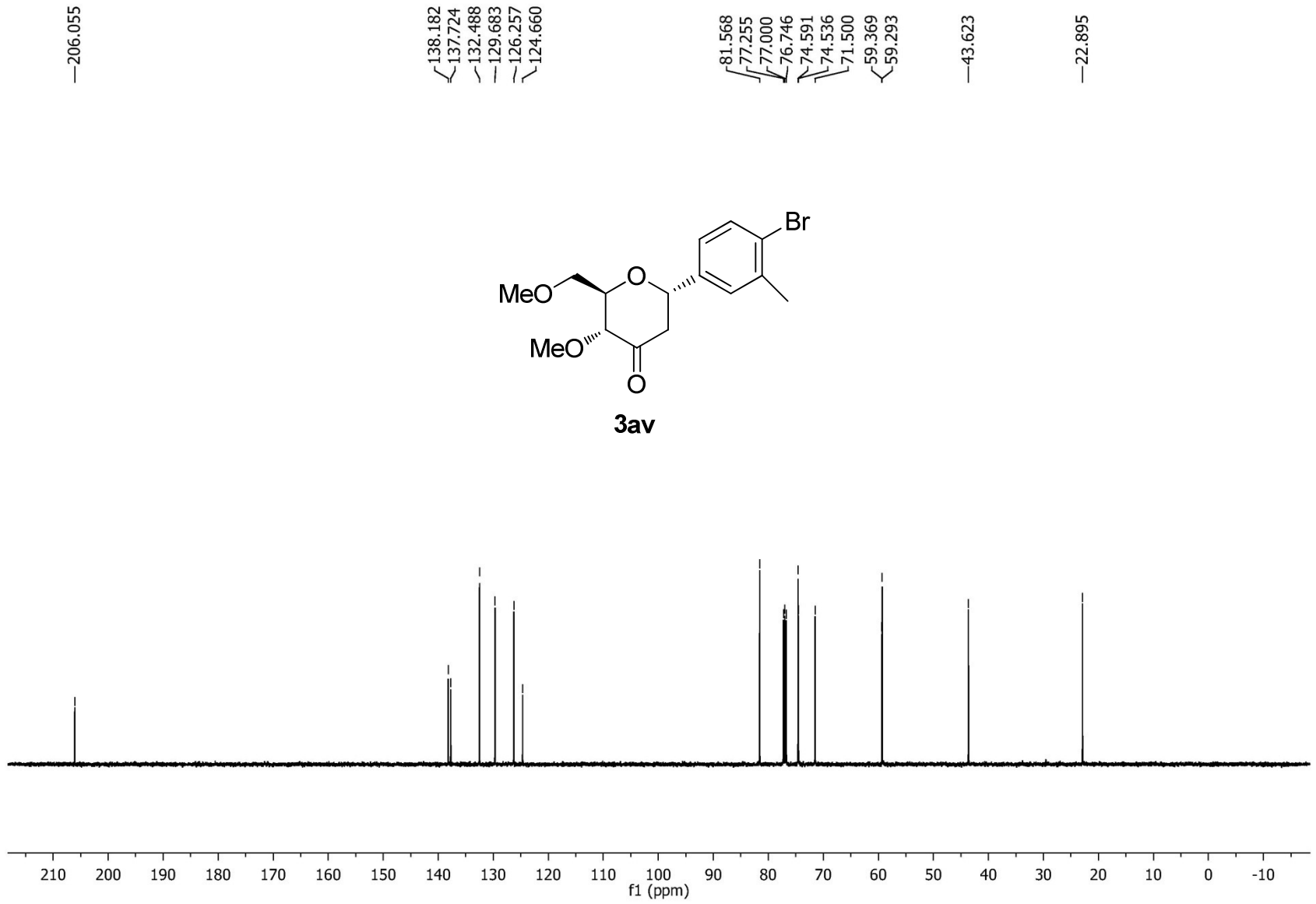

Figure S62: ^{13}C-NMR spectrum of compound 3av in $CDCl_3$

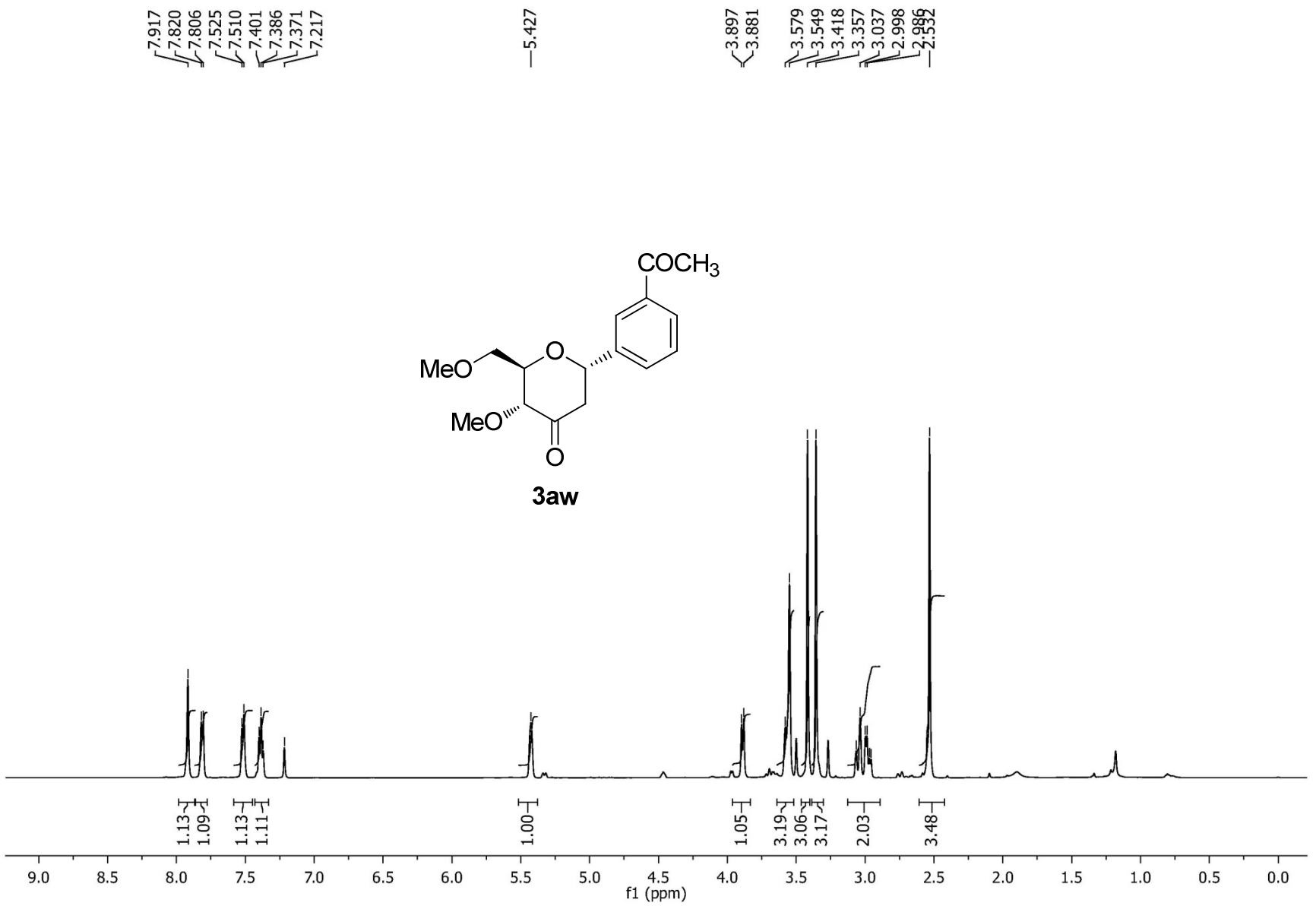

Figure S63: ^{1}H-NMR spectrum of compound 3aw in $CDCl_3$

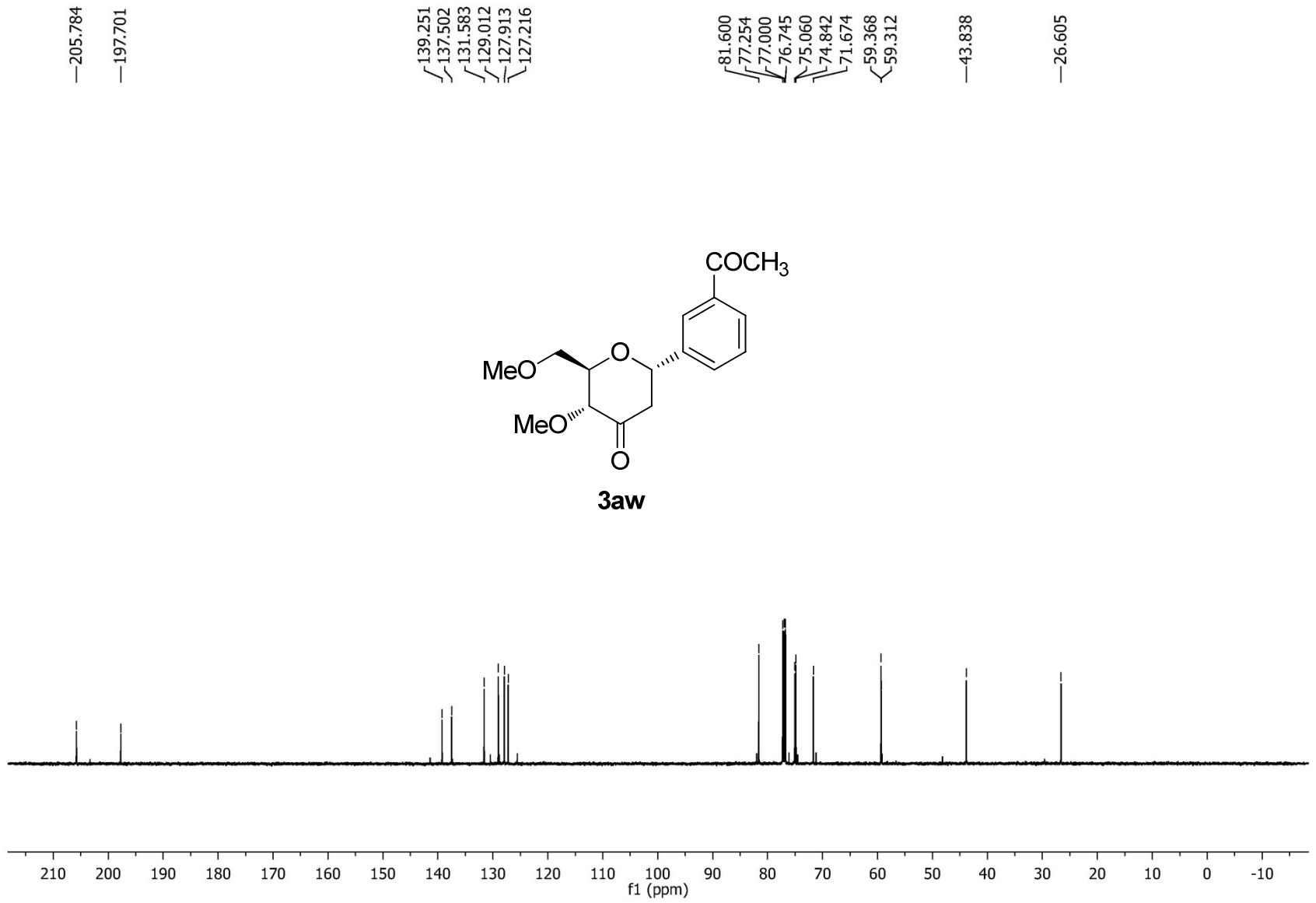

Figure S64: ^{13}C-NMR spectrum of compound 3aw in $CDCl_3$

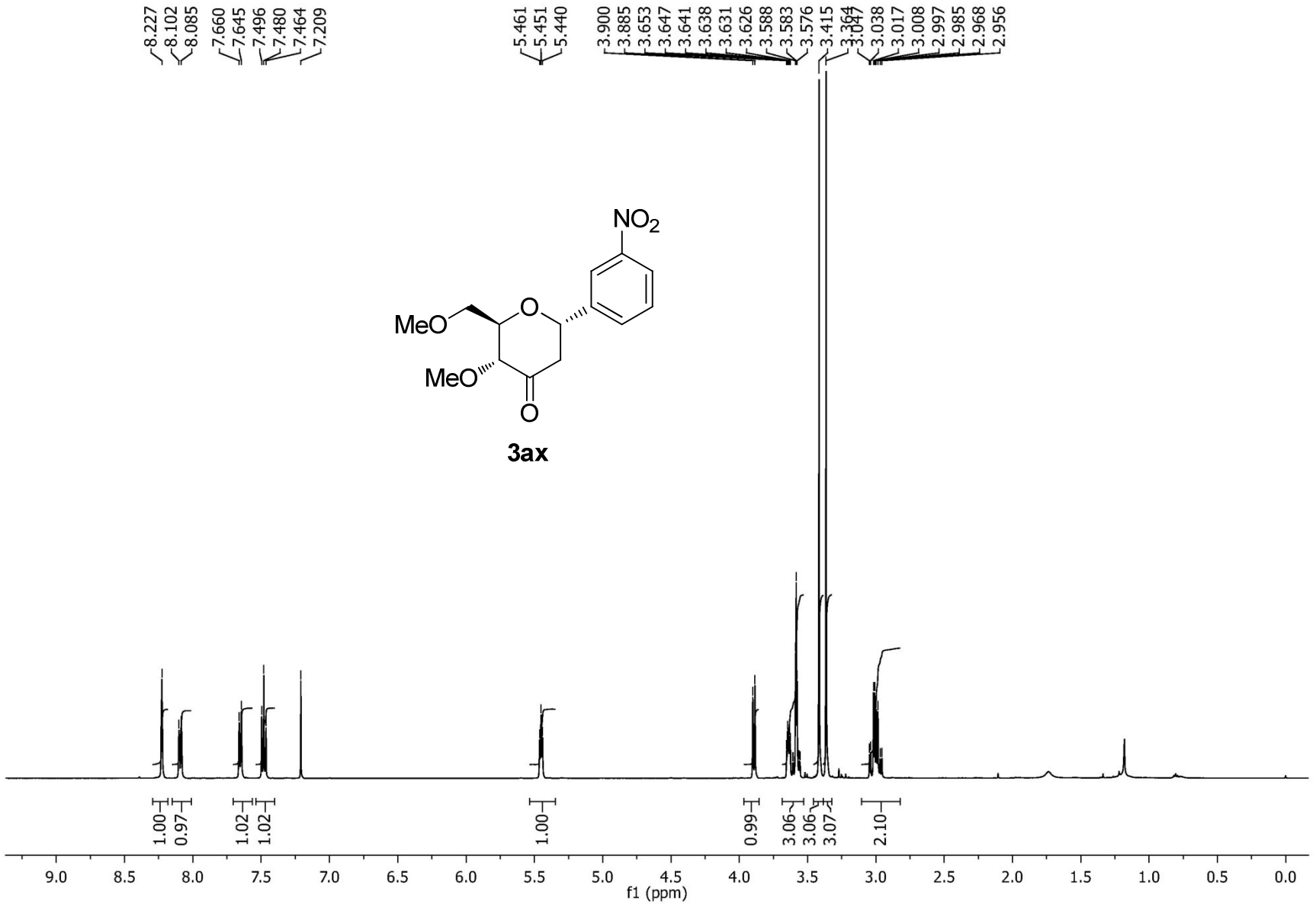

Figure S65: ^{1}H-NMR spectrum of compound 3ax in $CDCl_3$

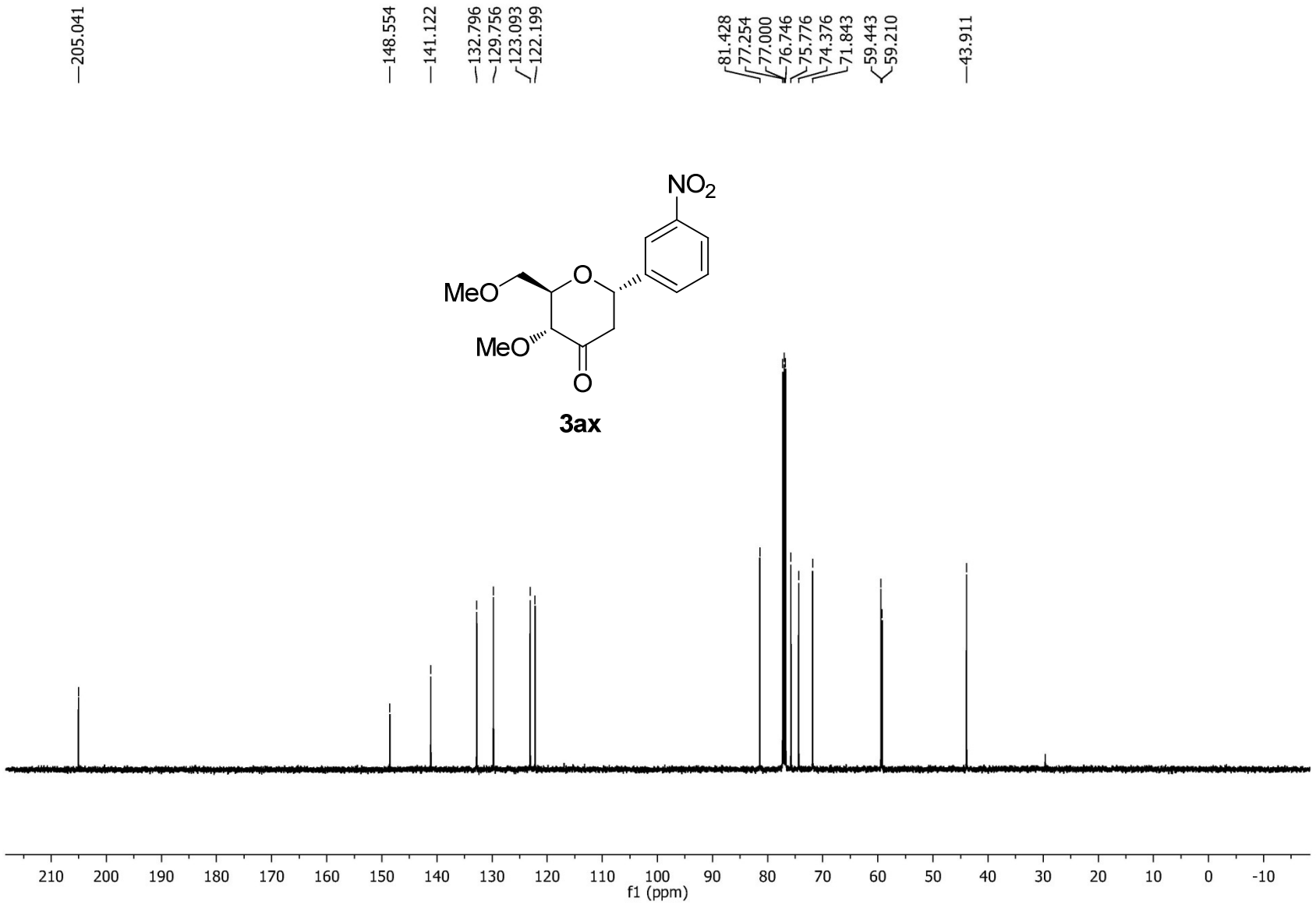

Figure S66: ^{13}C-NMR spectrum of compound 3ax in $CDCl_3$

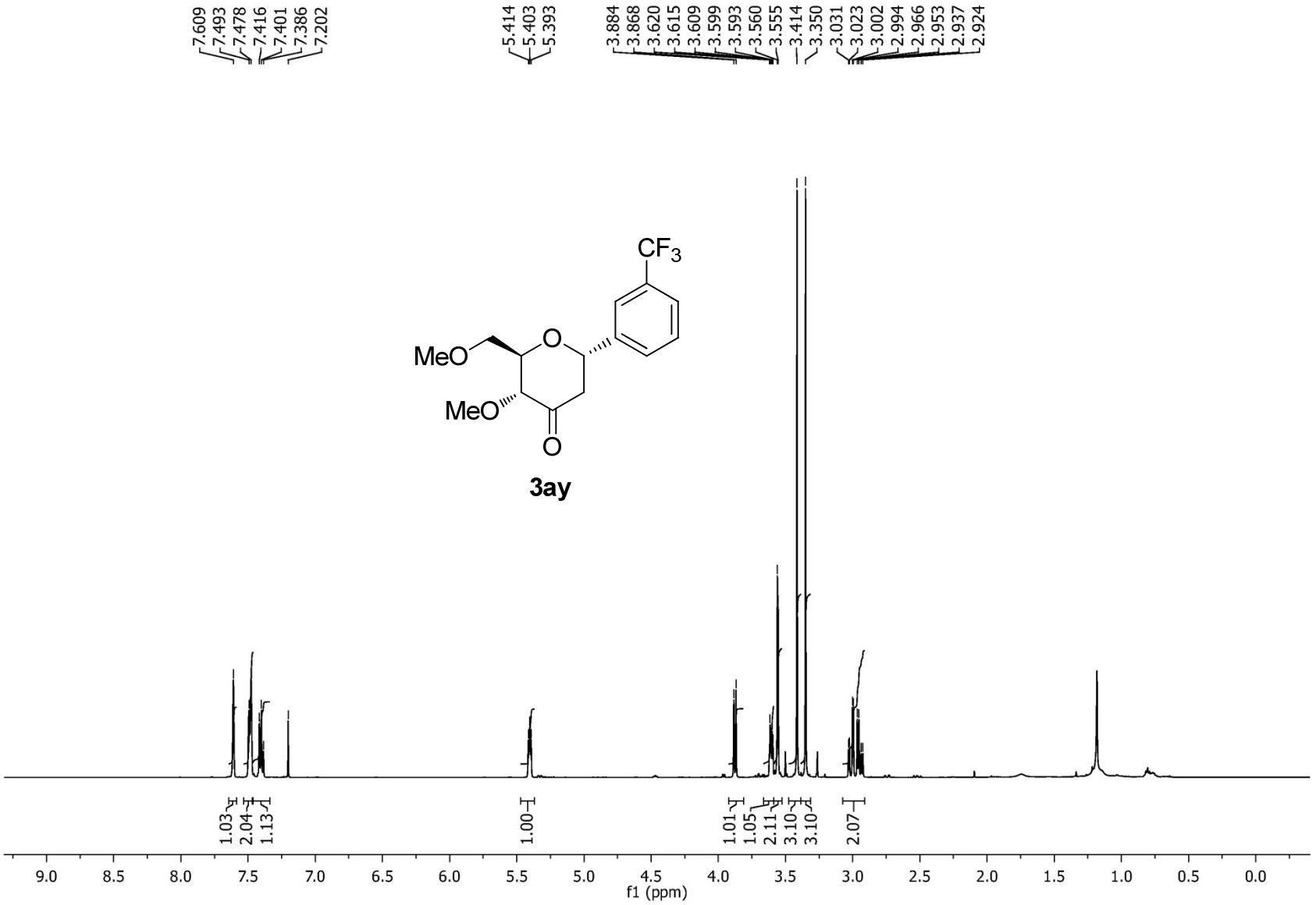

Figure S67: ^{1}H-NMR spectrum of compound 3ay in $CDCl_3$

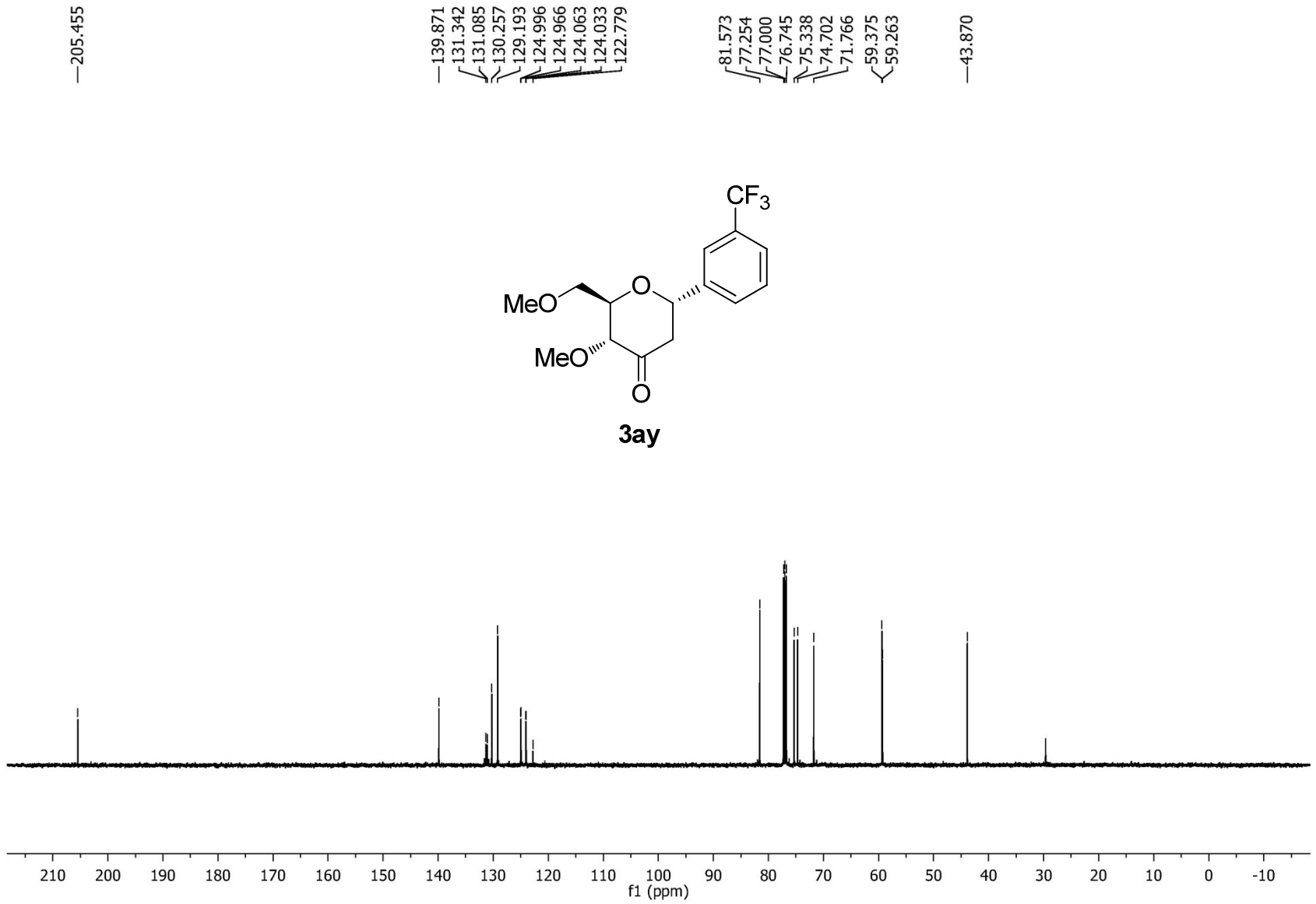

Figure S68: ^{13}C-NMR spectrum of compound 3ay in $CDCl_3$

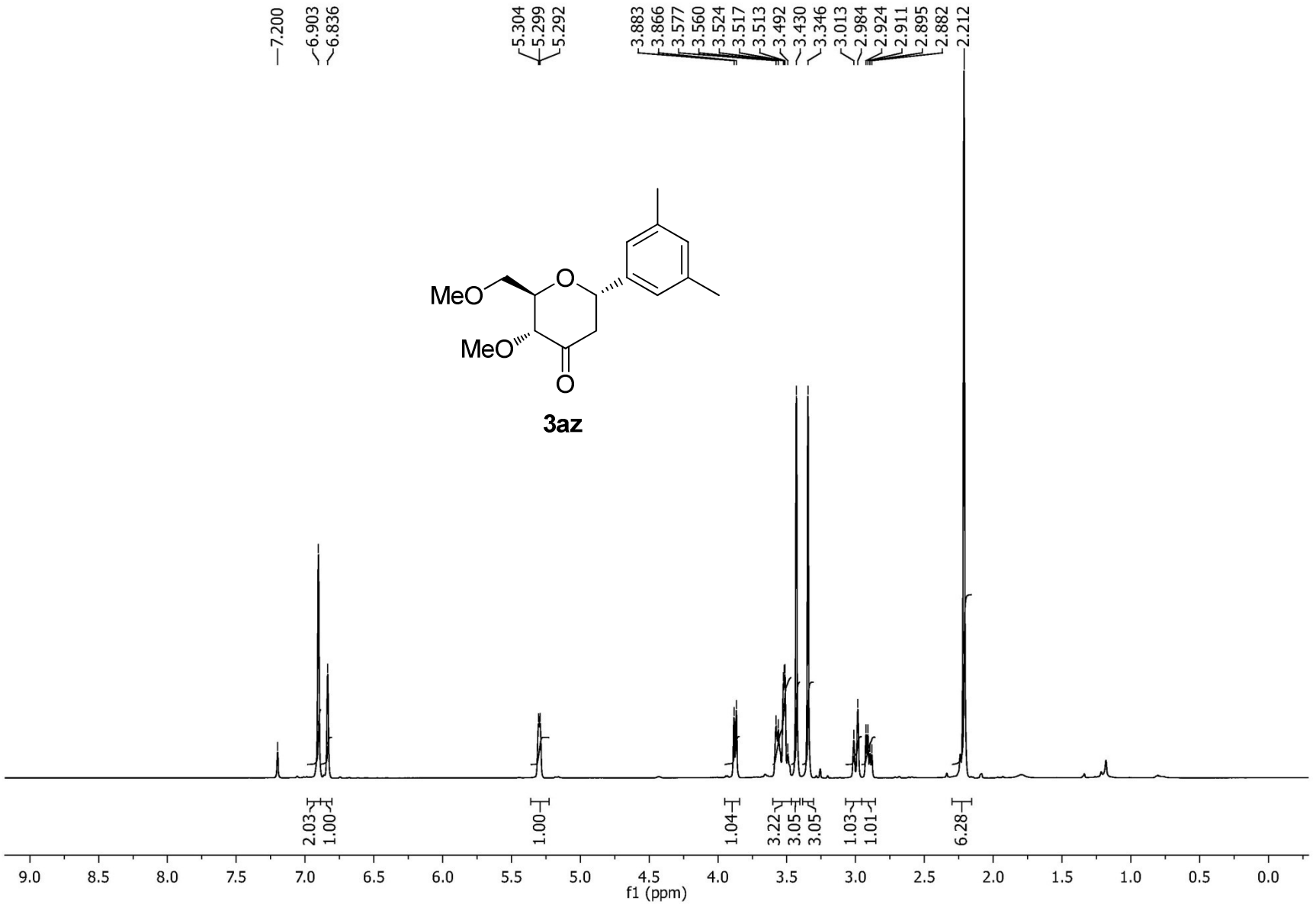

Figure S69: ^{1}H-NMR spectrum of compound 3az in $CDCl_3$

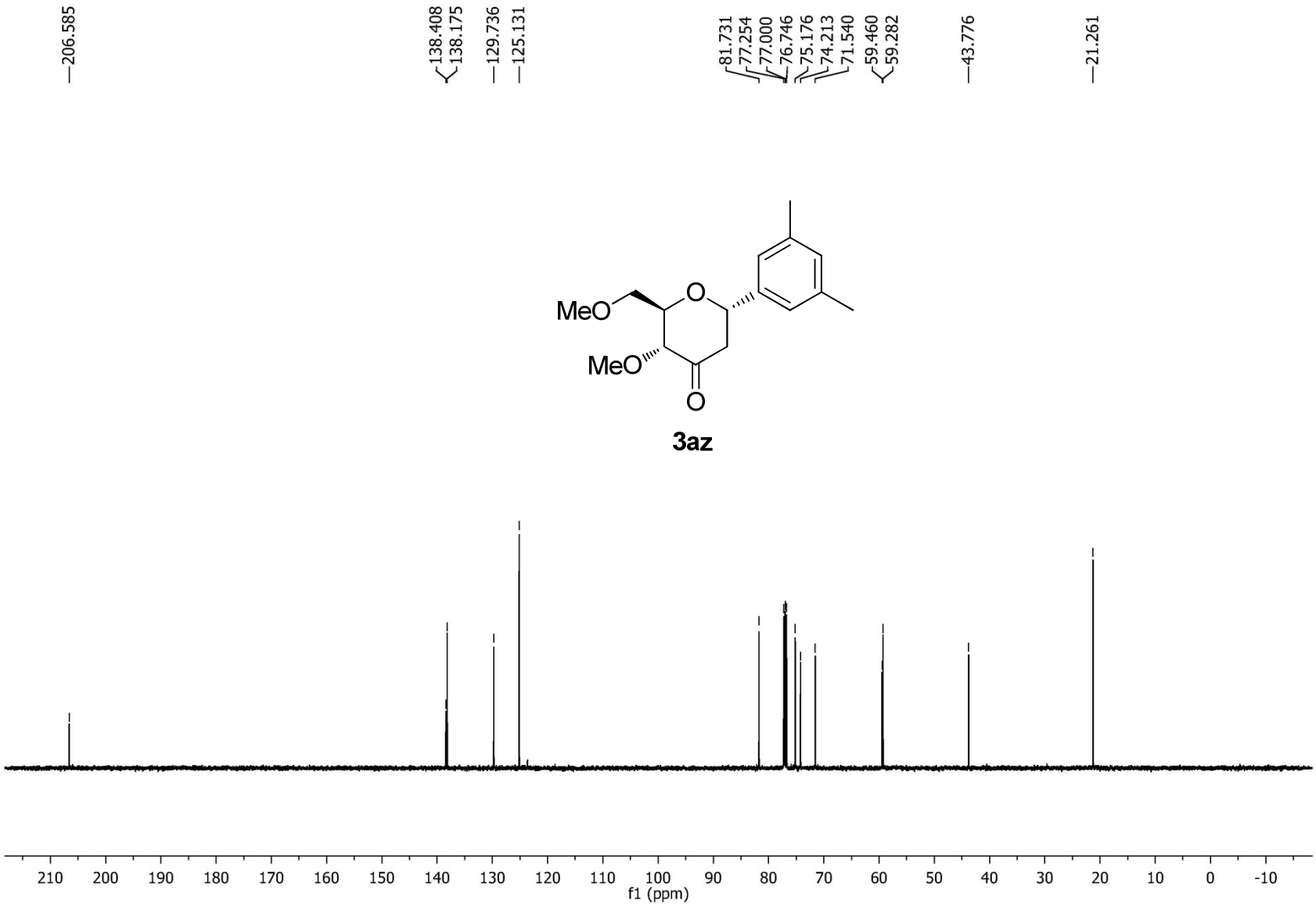

Figure S70: ^{13}C-NMR spectrum of compound 3az in $CDCl_3$

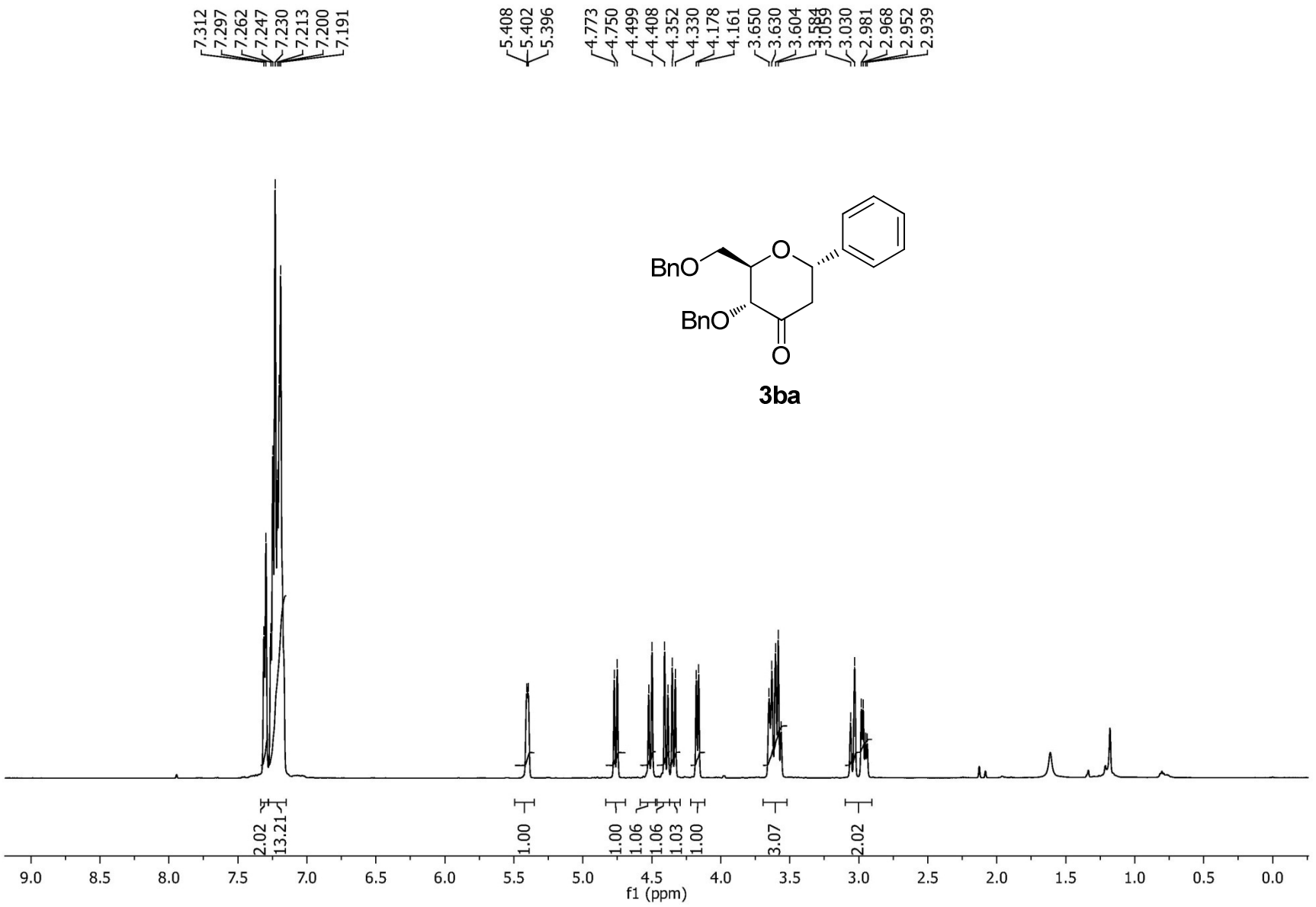

Figure S71: ^{1}H-NMR spectrum of compound 3ba in $CDCl_3$

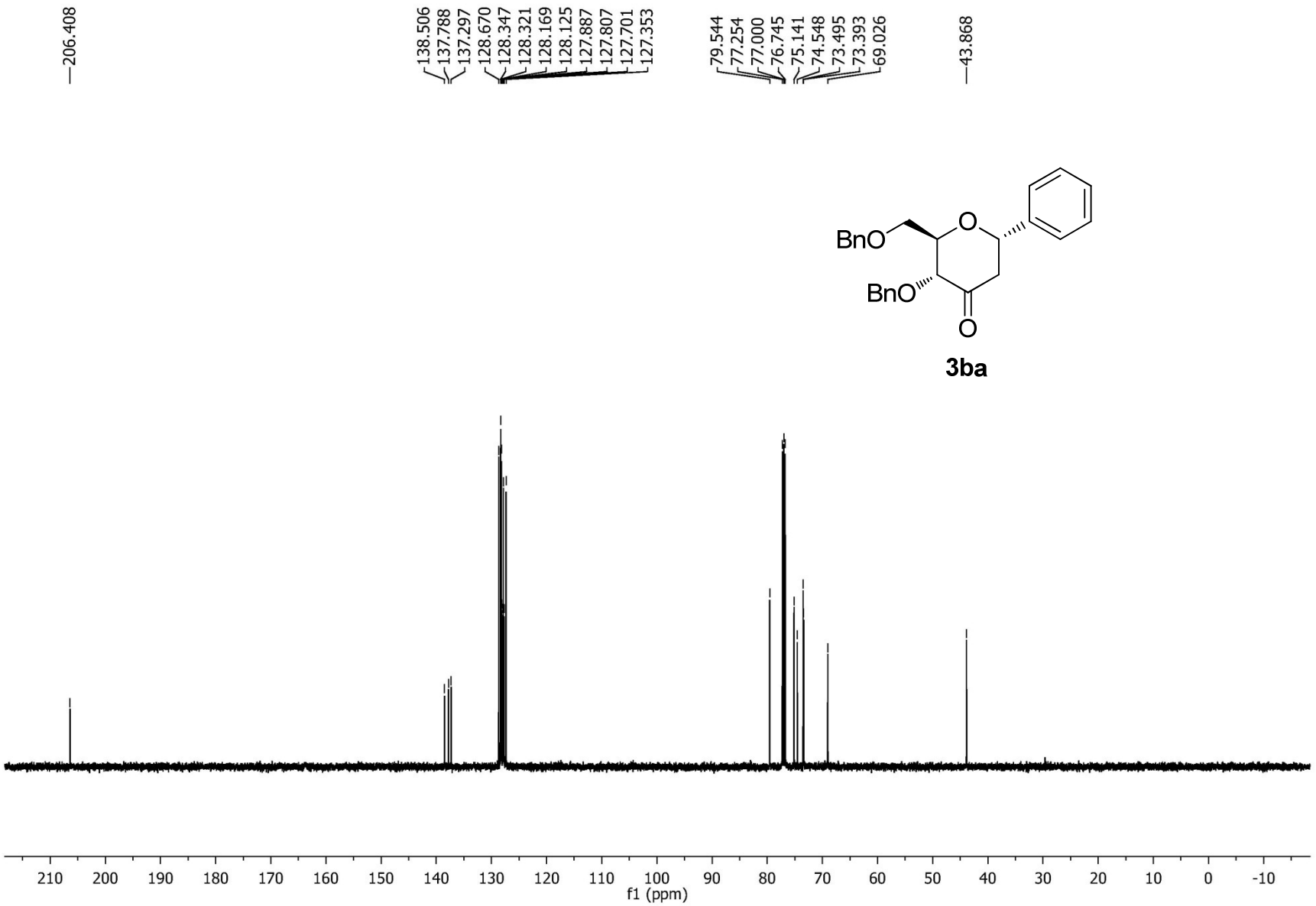

Figure S72: ^{13}C-NMR spectrum of compound 3ba in $CDCl_3$

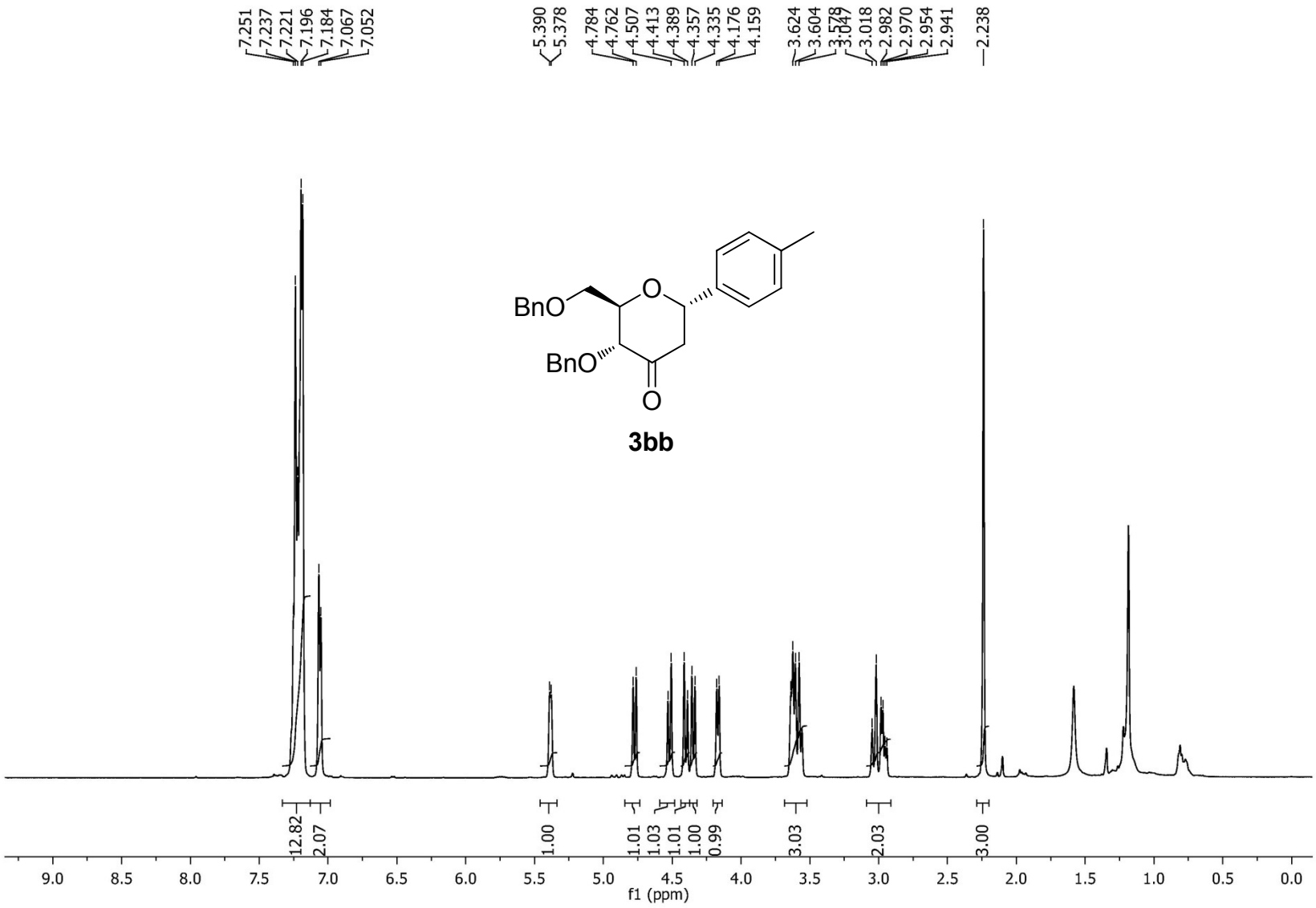

Figure S73: ^{1}H-NMR spectrum of compound 3bb in $CDCl_3$

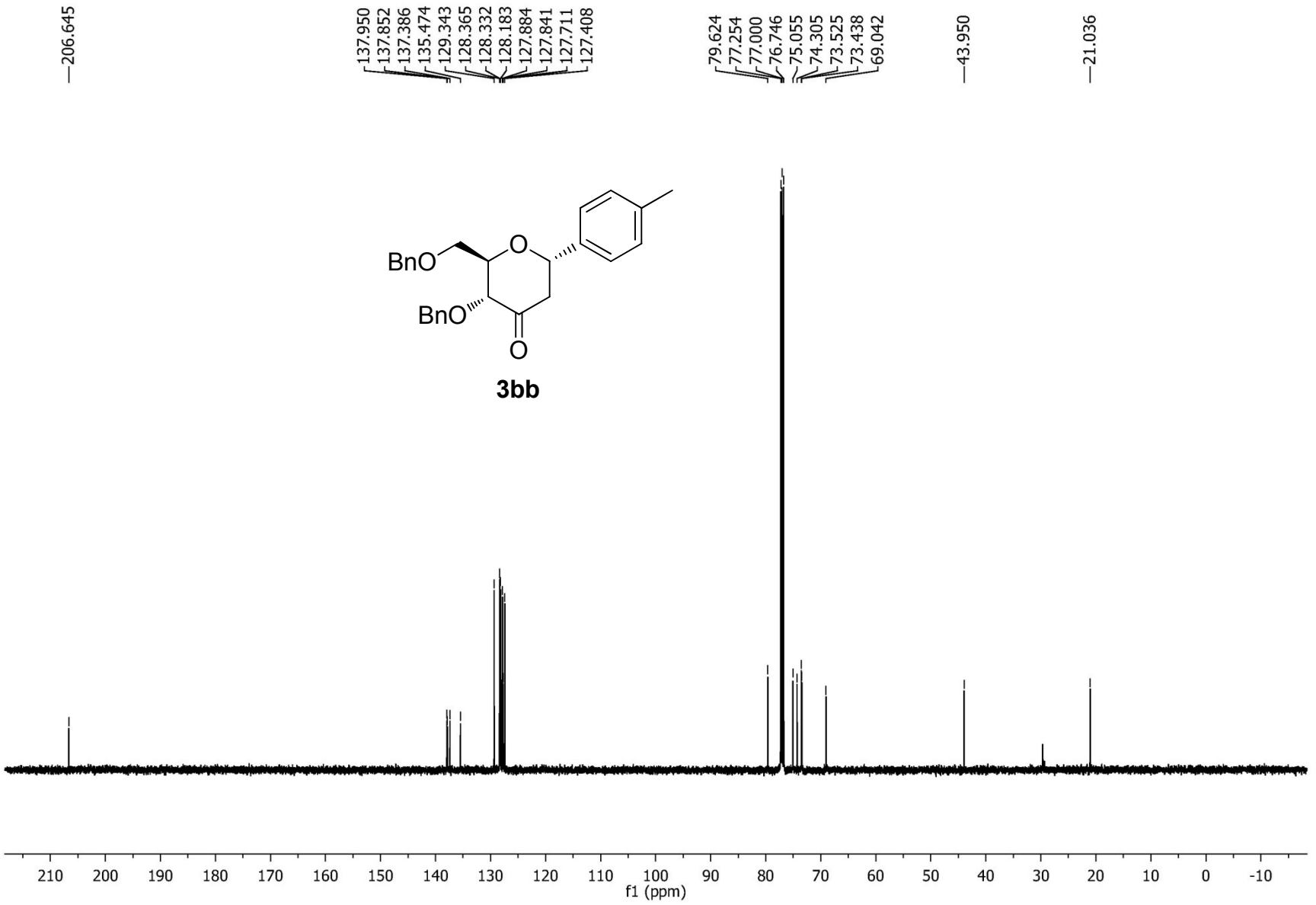

Figure S74: ^{13}C-NMR spectrum of compound 3bb in $CDCl_3$

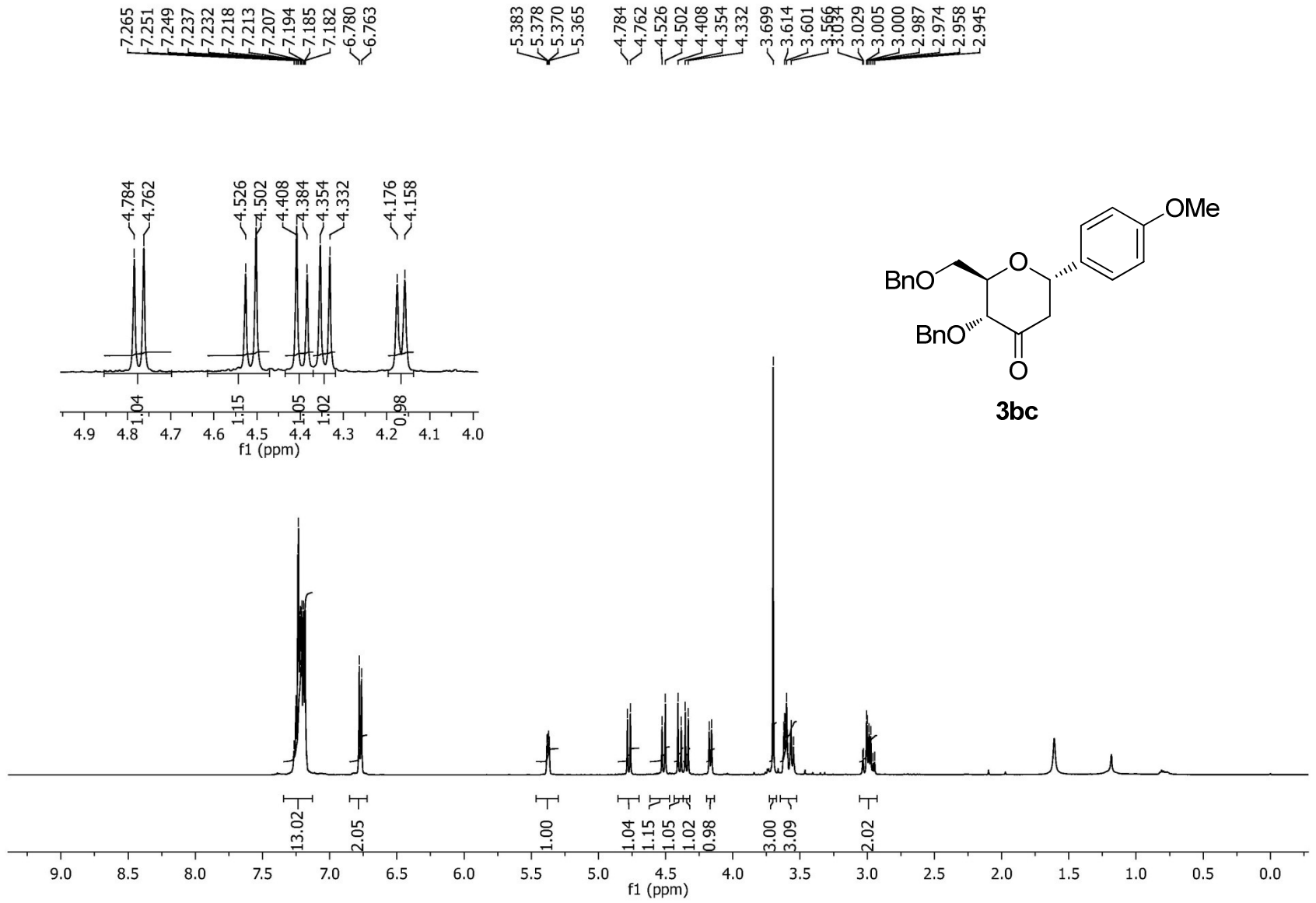

Figure S75: ^{1}H-NMR spectrum of compound 3bc in $CDCl_3$

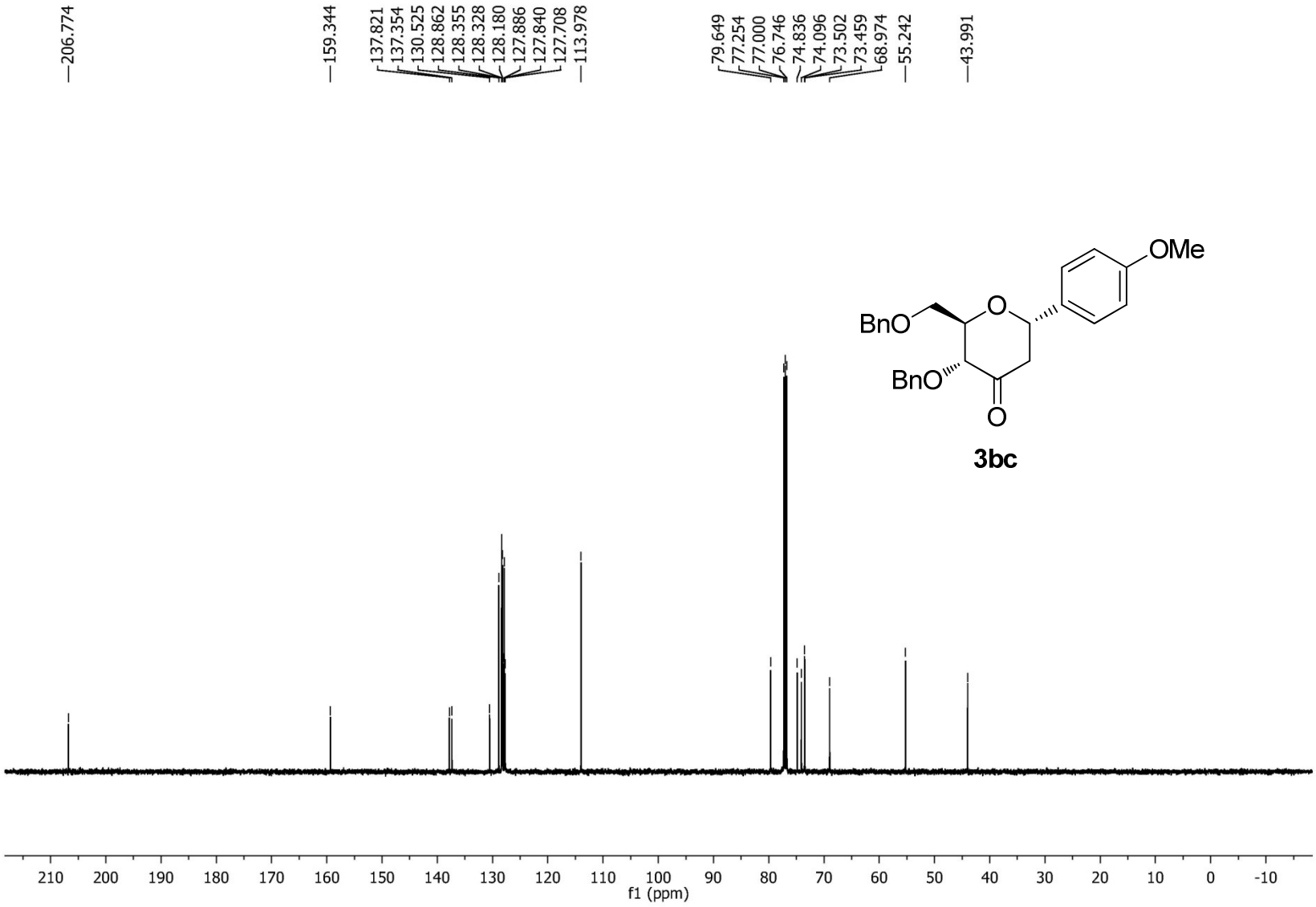

Figure S76: ^{13}C-NMR spectrum of compound 3bc in $CDCl_3$

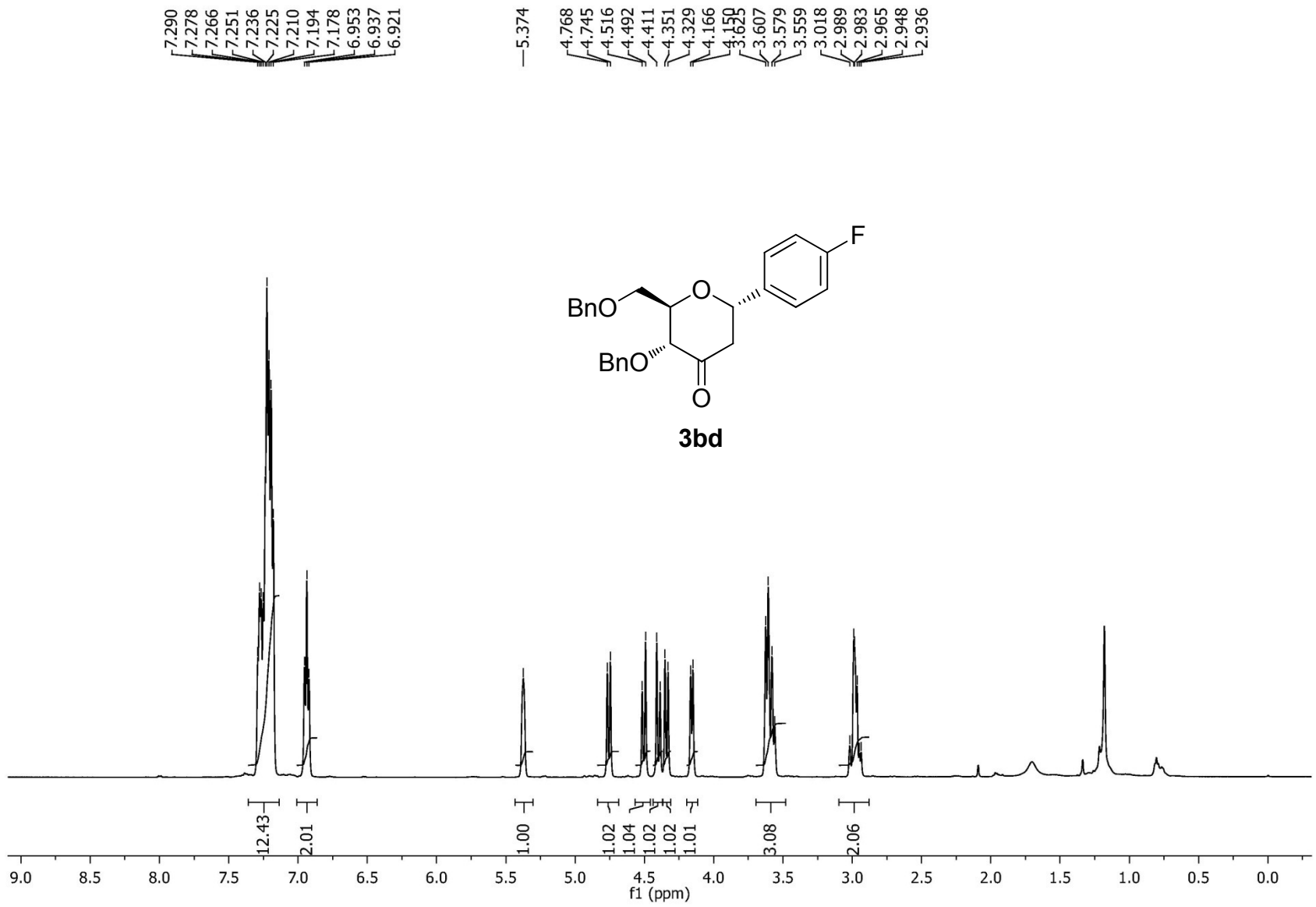

Figure S77: ^{1}H-NMR spectrum of compound 3bd in $CDCl_3$

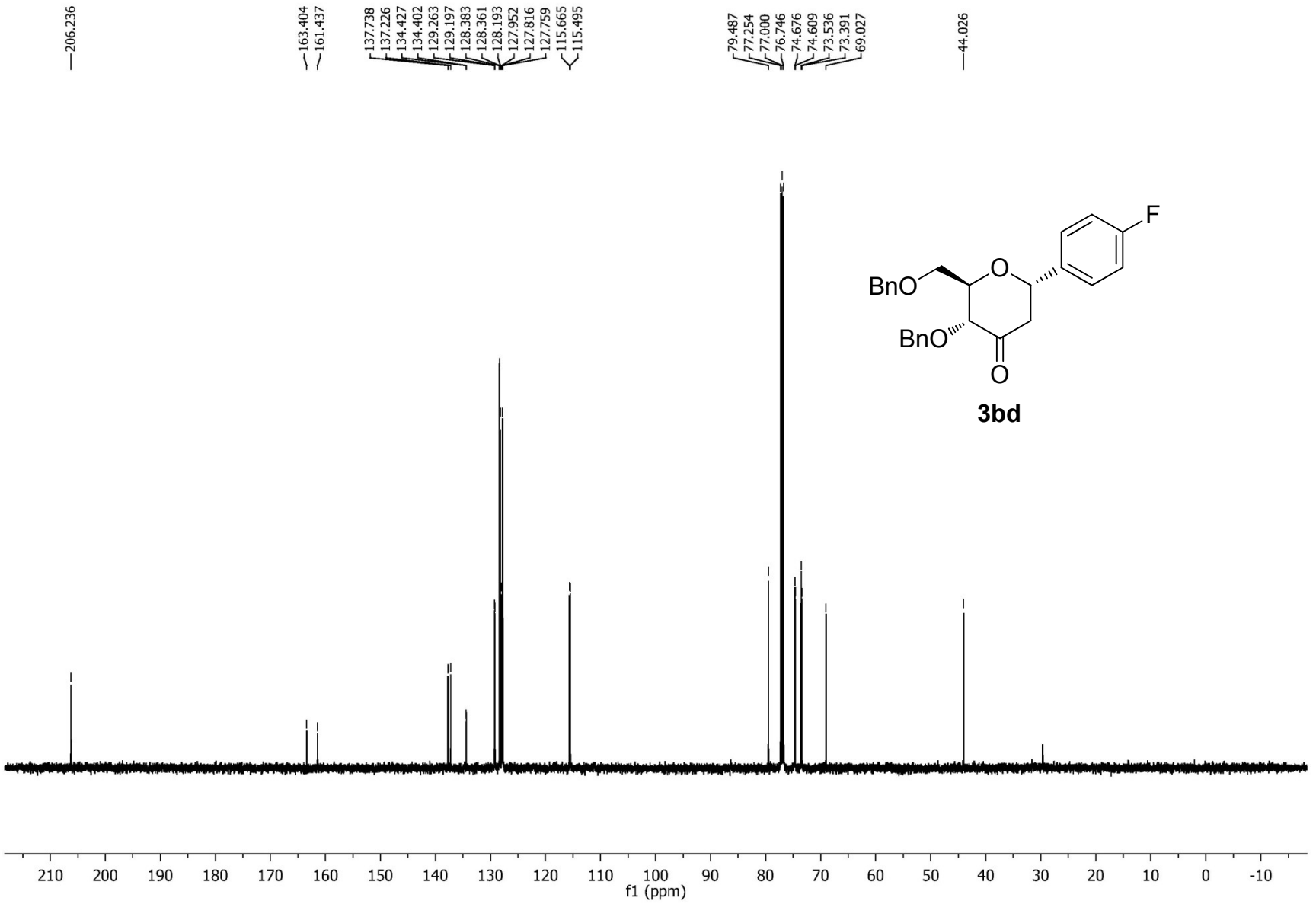

Figure S78: ^{13}C-NMR spectrum of compound 3bd in $CDCl_3$

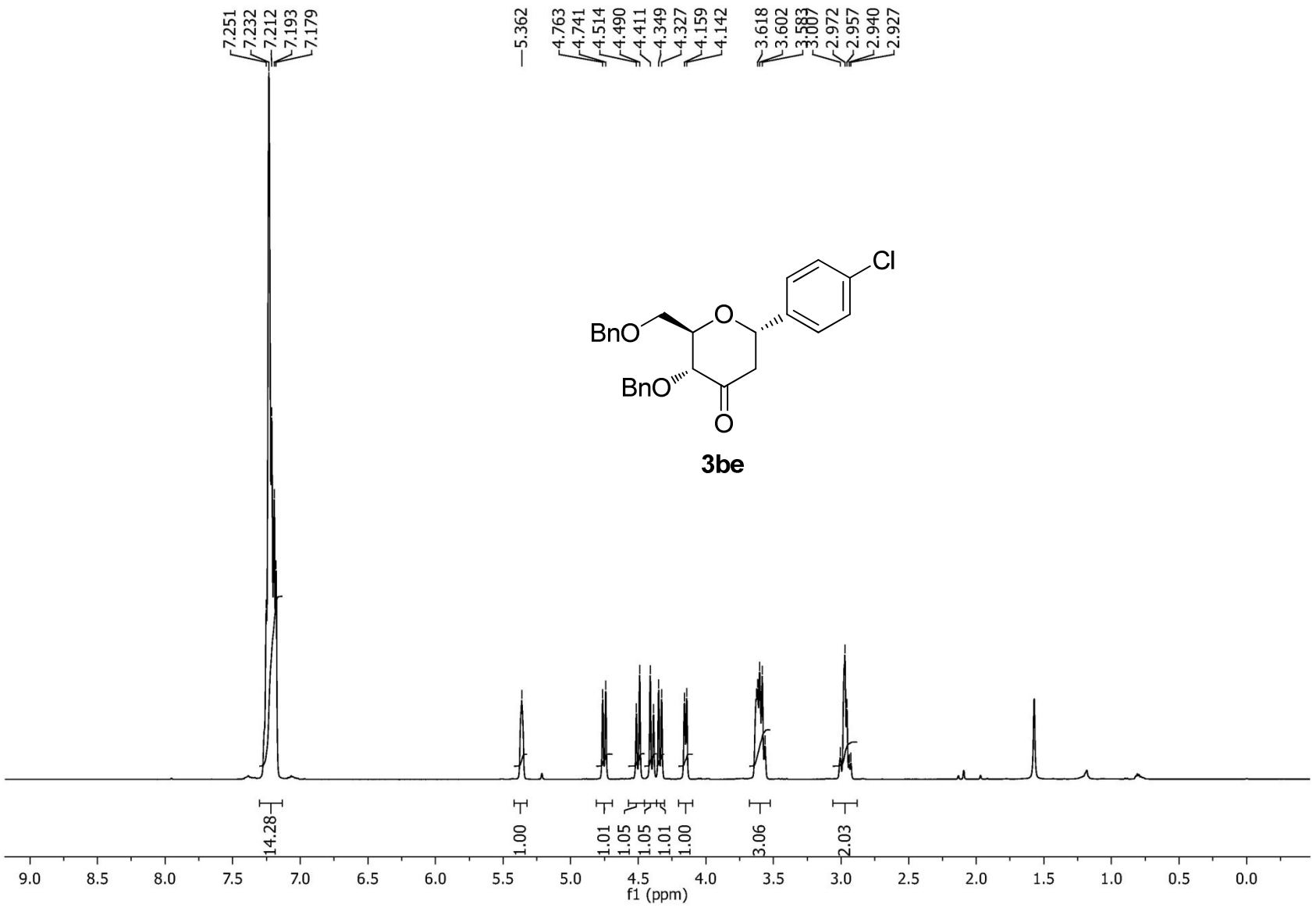

Figure S79: ^{1}H-NMR spectrum of compound 3be in $CDCl_3$

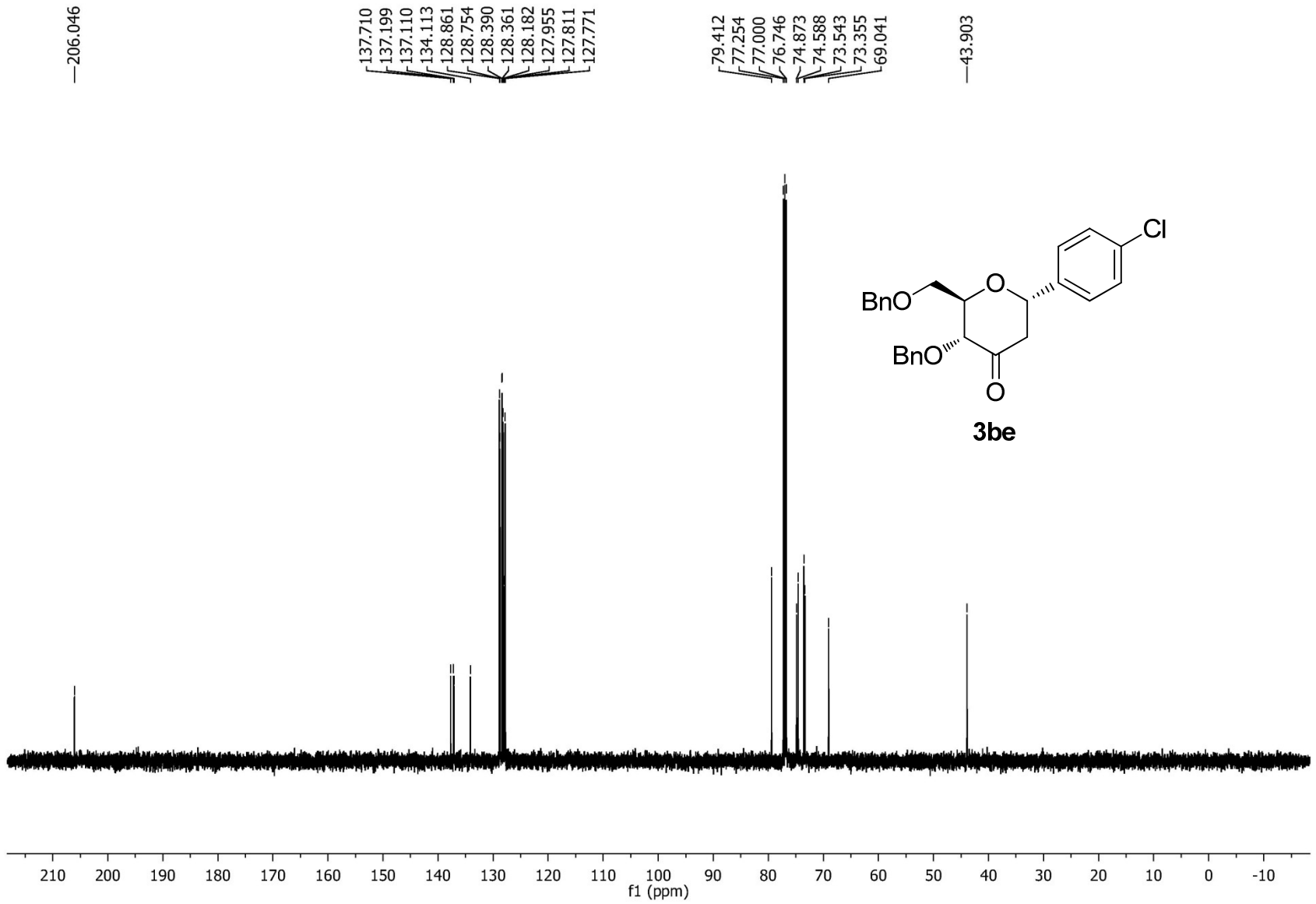

Figure S80: ^{13}C-NMR spectrum of compound 3be in $CDCl_3$

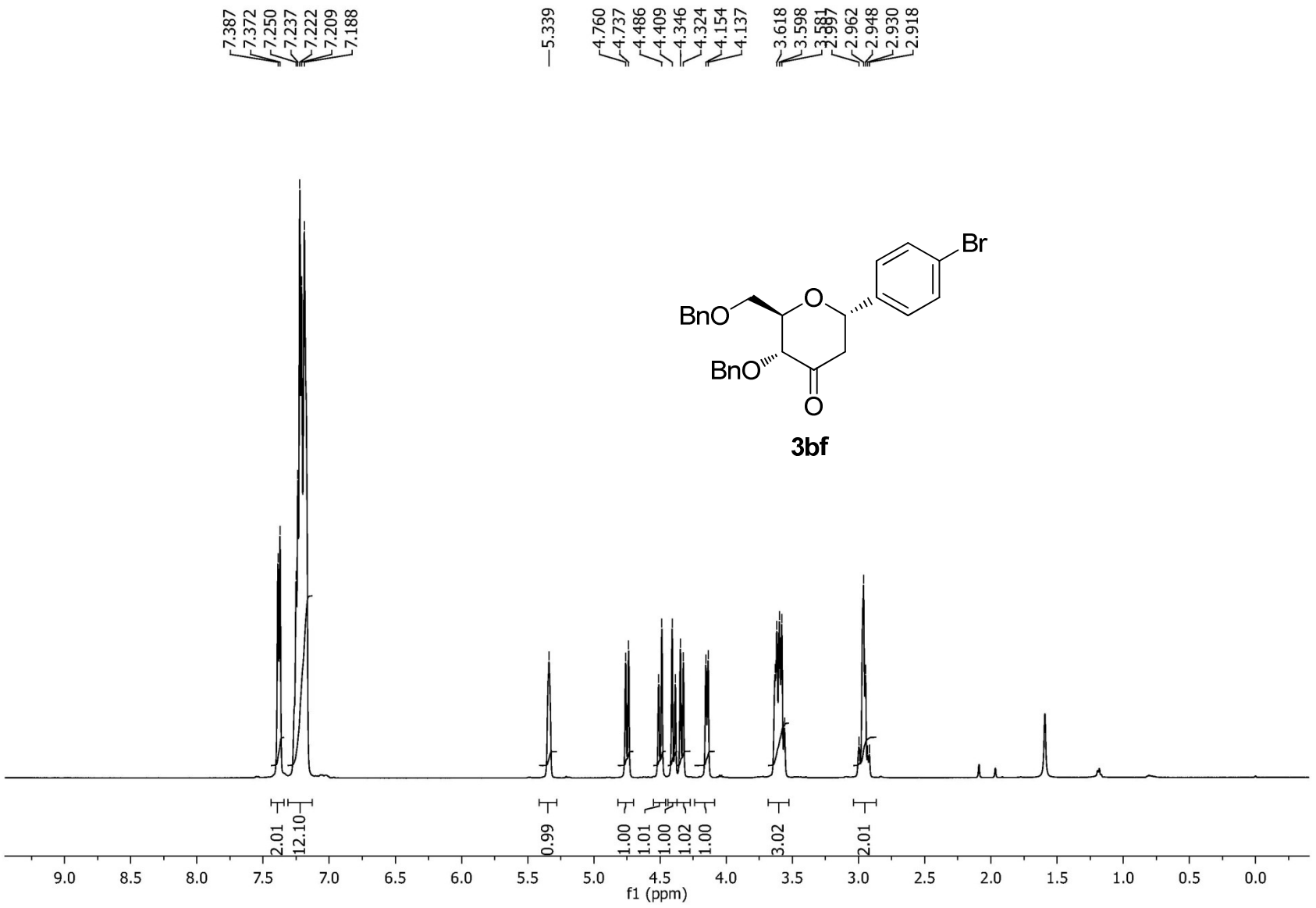

Figure S81: ^{1}H-NMR spectrum of compound 3bf in $CDCl_3$

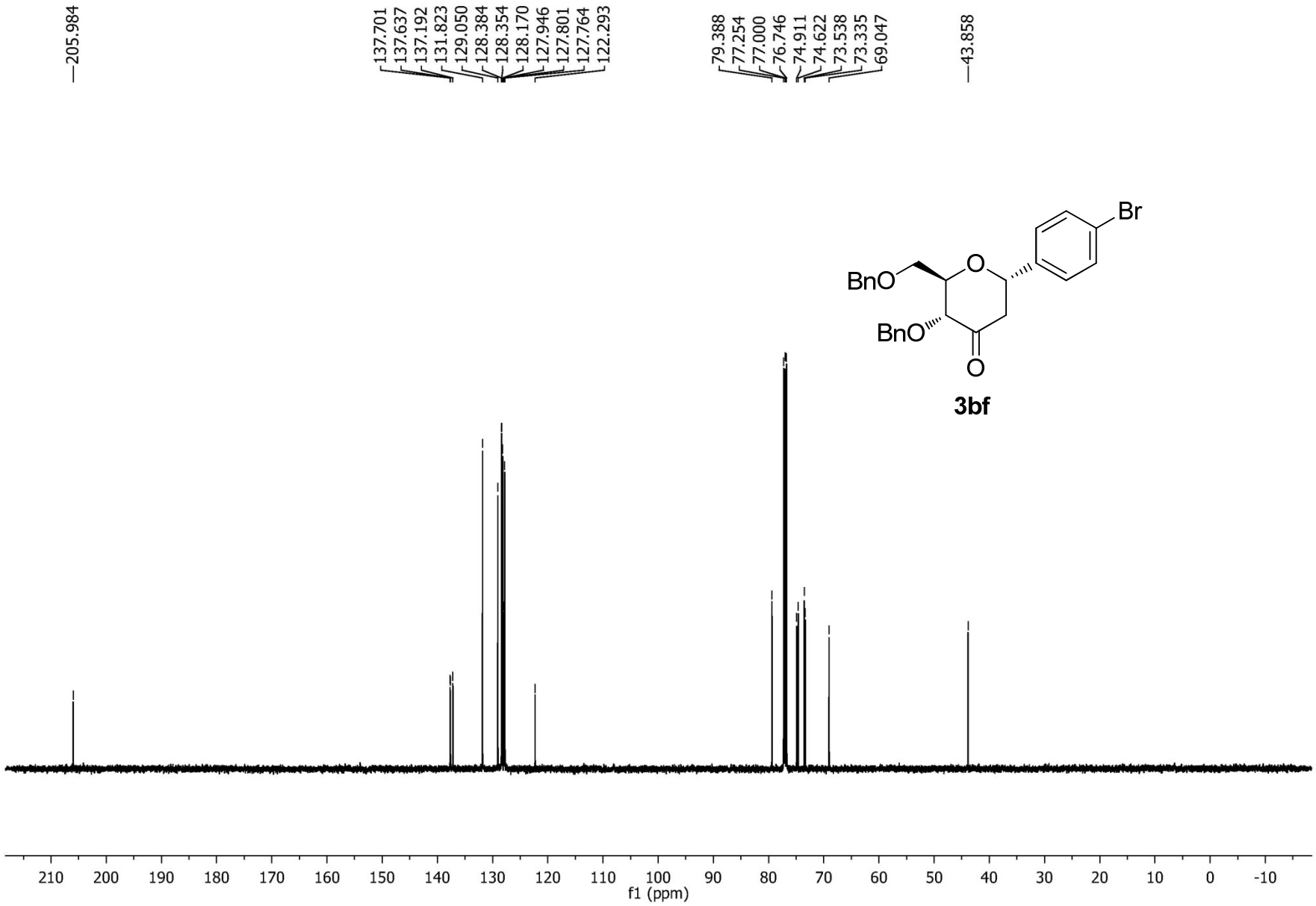

Figure S82: ^{13}C-NMR spectrum of compound 3bf in $CDCl_3$

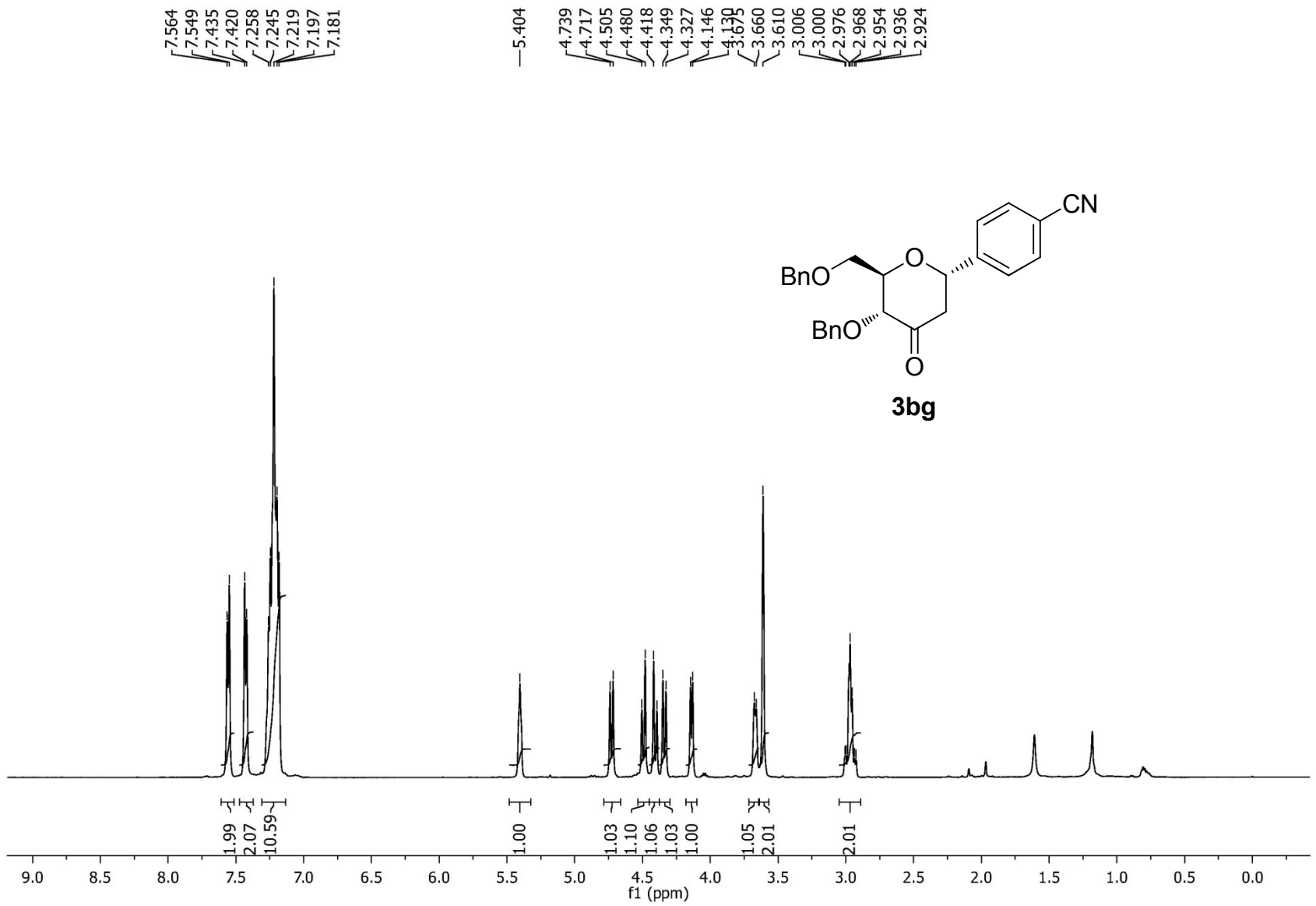

Figure S83: ^{1}H-NMR spectrum of compound 3bg in $CDCl_3$

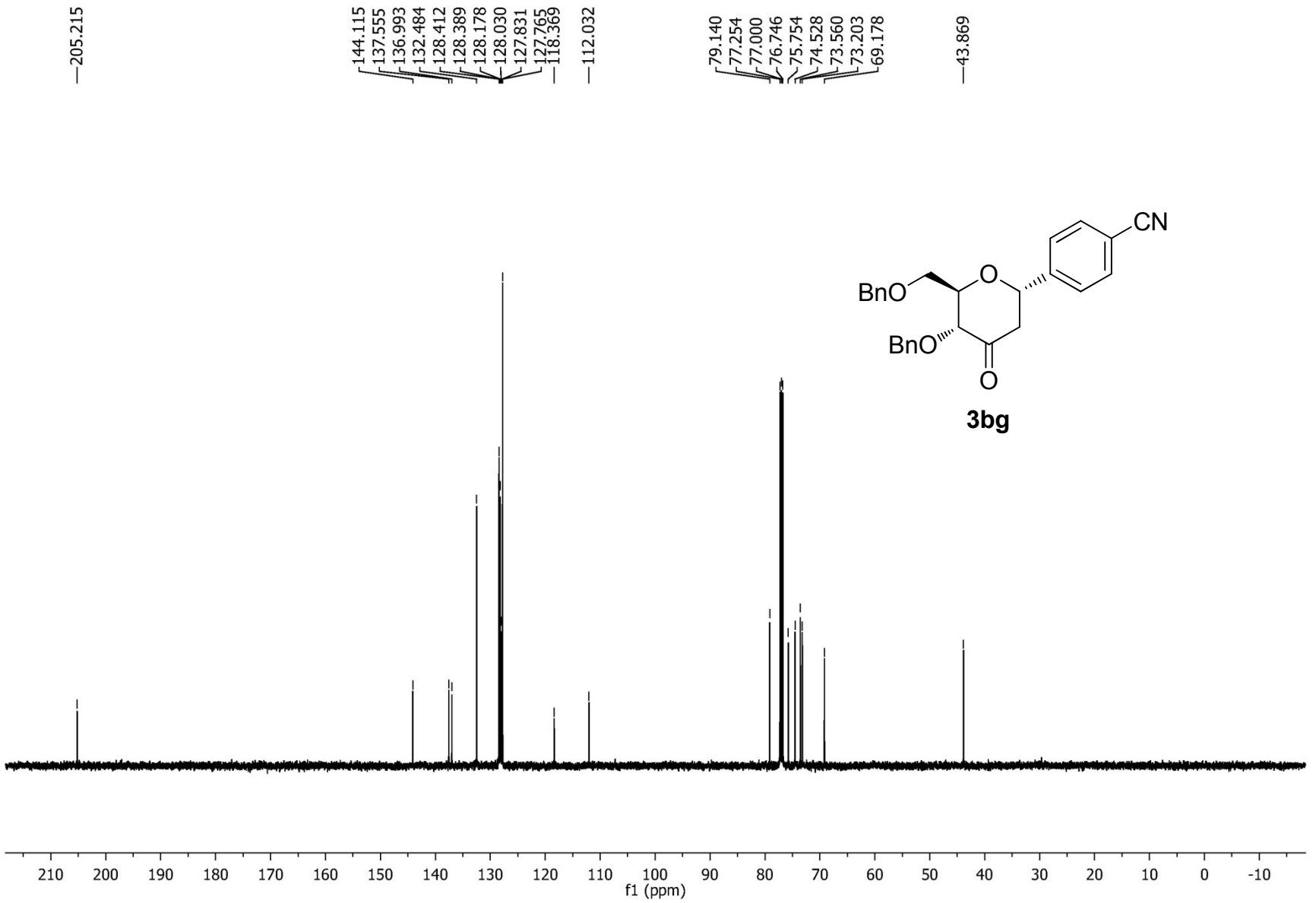

Figure S84: ^{13}C-NMR spectrum of compound 3bg in $CDCl_3$

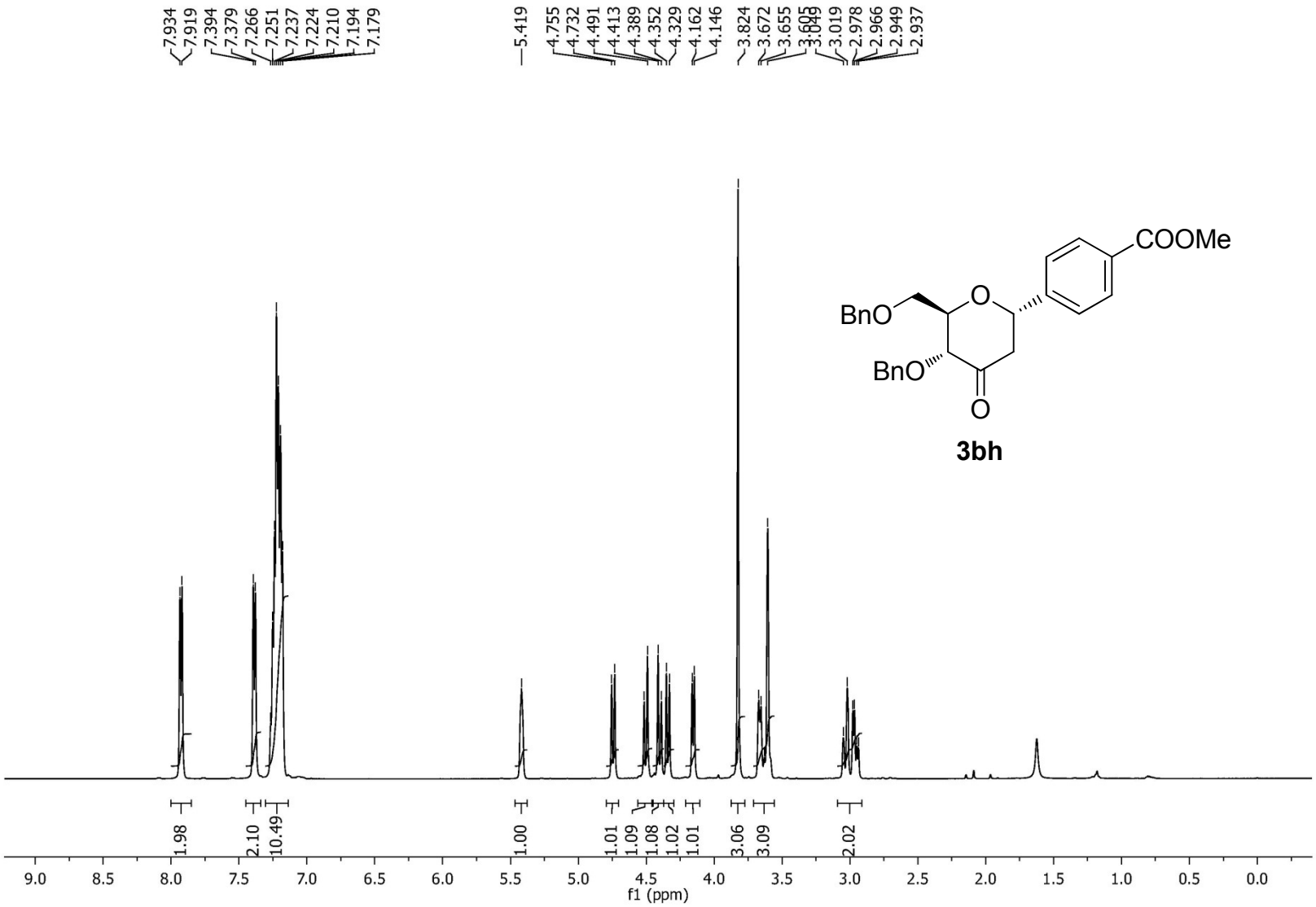

Figure S85: ^{1}H-NMR spectrum of compound 3bh in $CDCl_3$

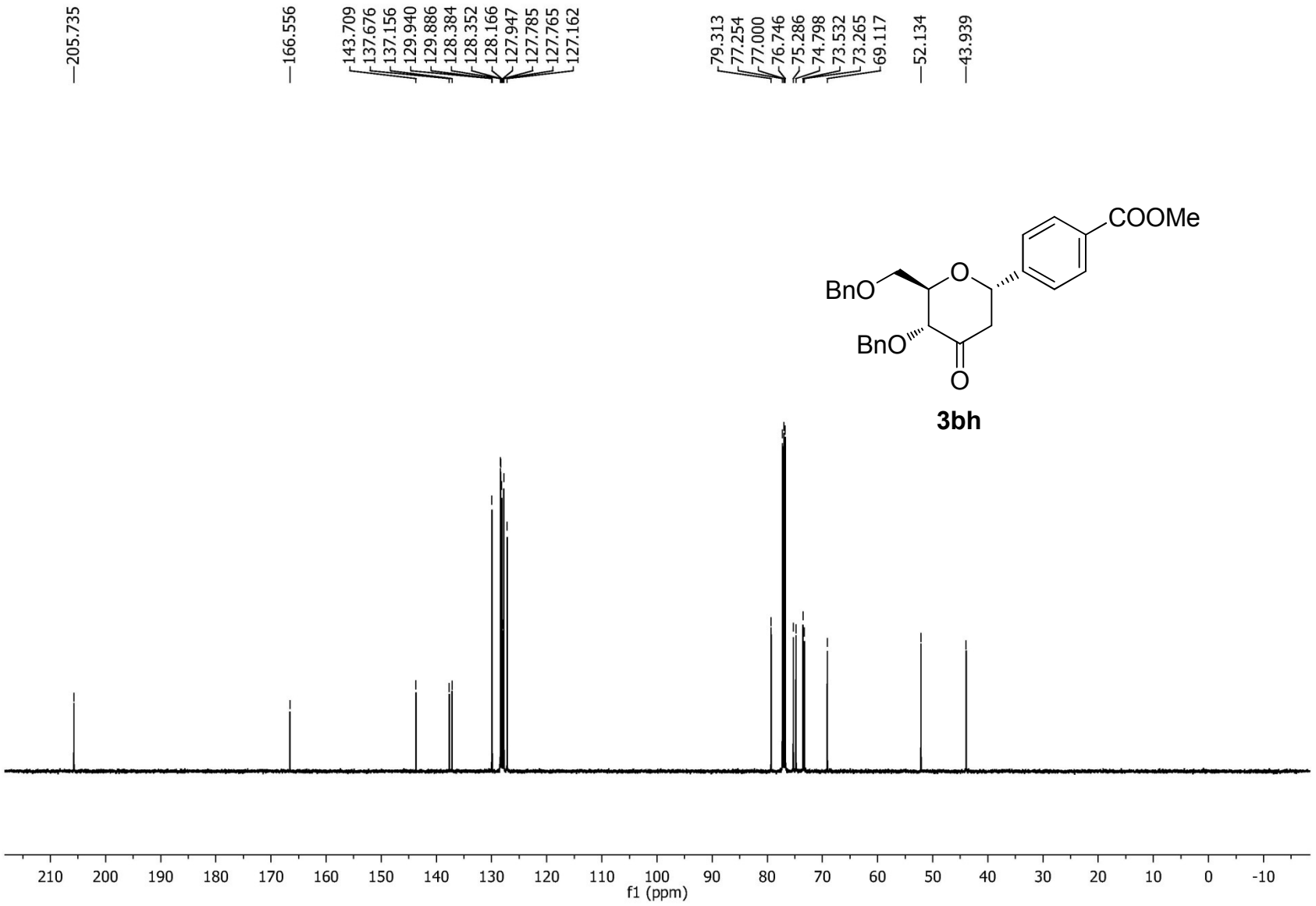

Figure S86: ^{13}C-NMR spectrum of compound 3bh in $CDCl_3$

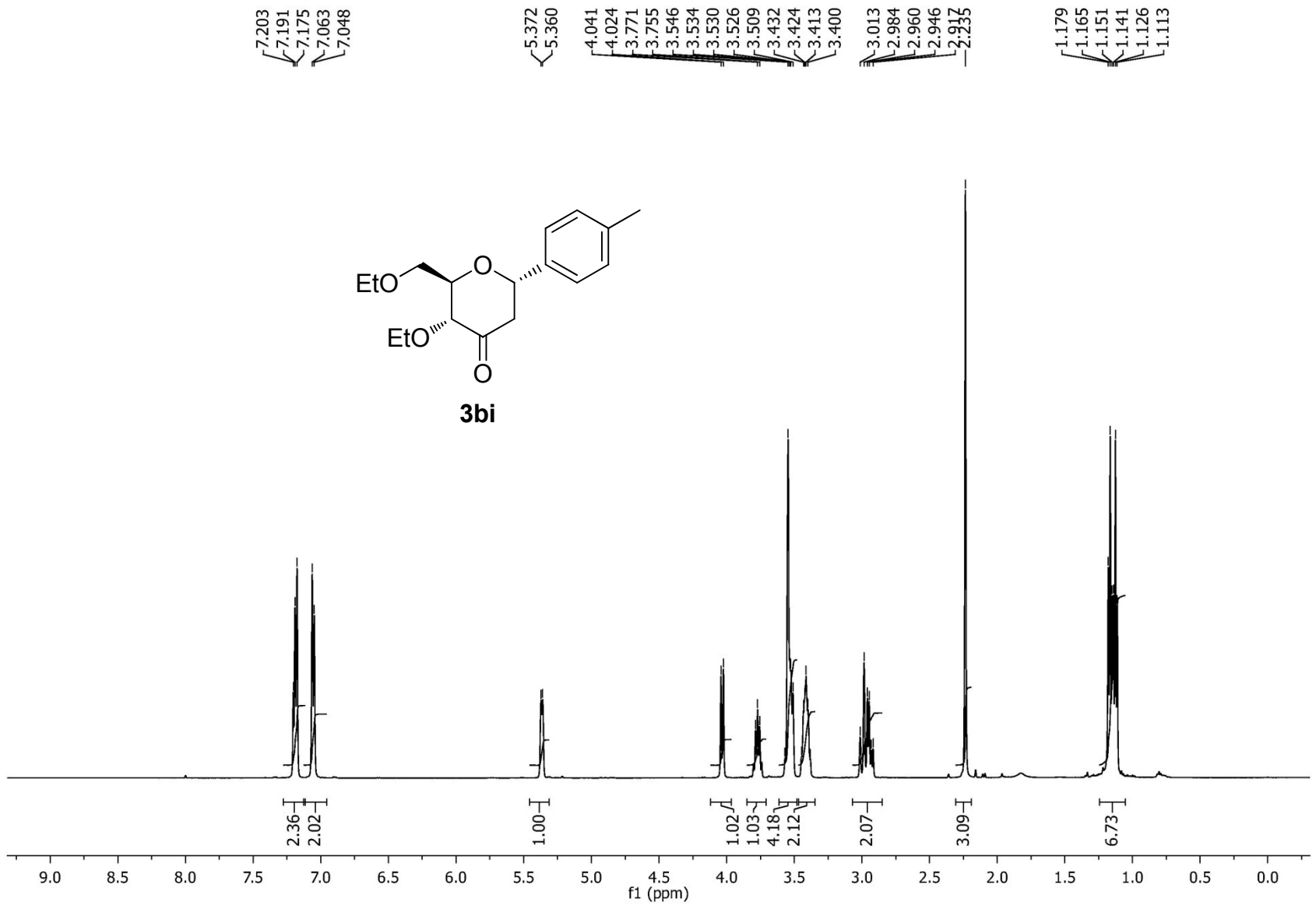

Figure S87: ^{1}H-NMR spectrum of compound 3bi in $CDCl_3$

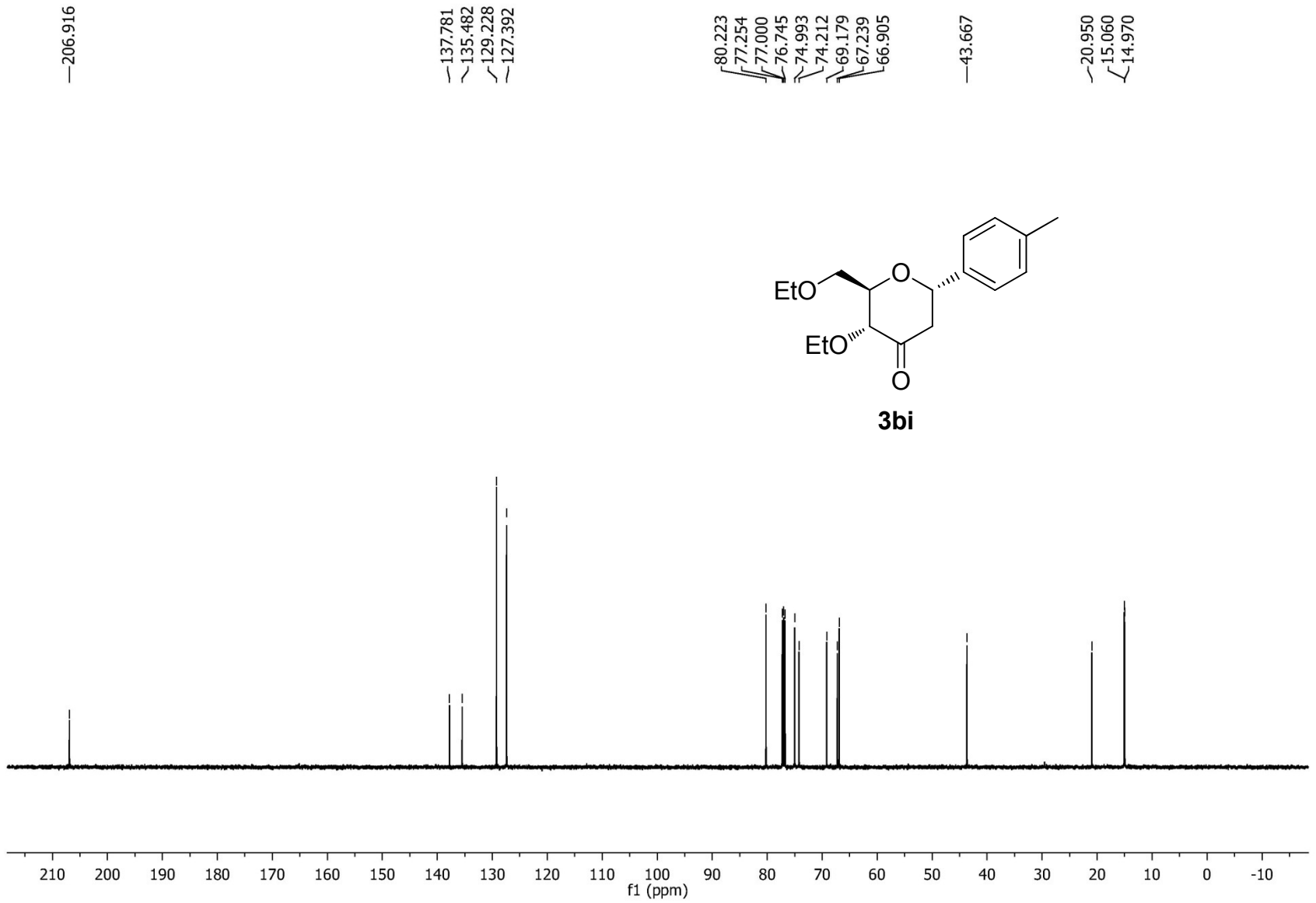

Figure S88: ^{13}C-NMR spectrum of compound 3bi in $CDCl_3$

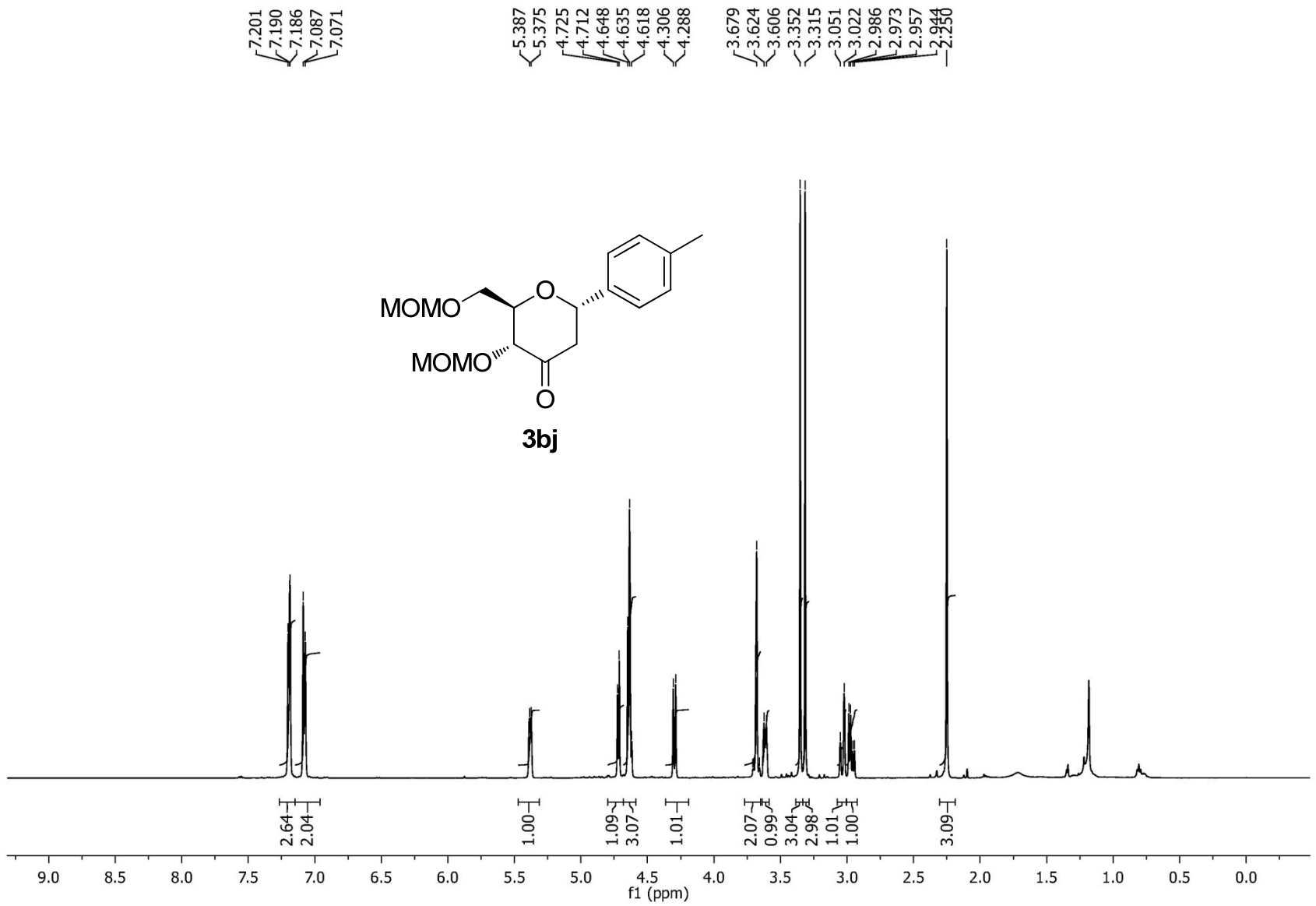

Figure S89: ^{1}H-NMR spectrum of compound 3bj in $CDCl_3$

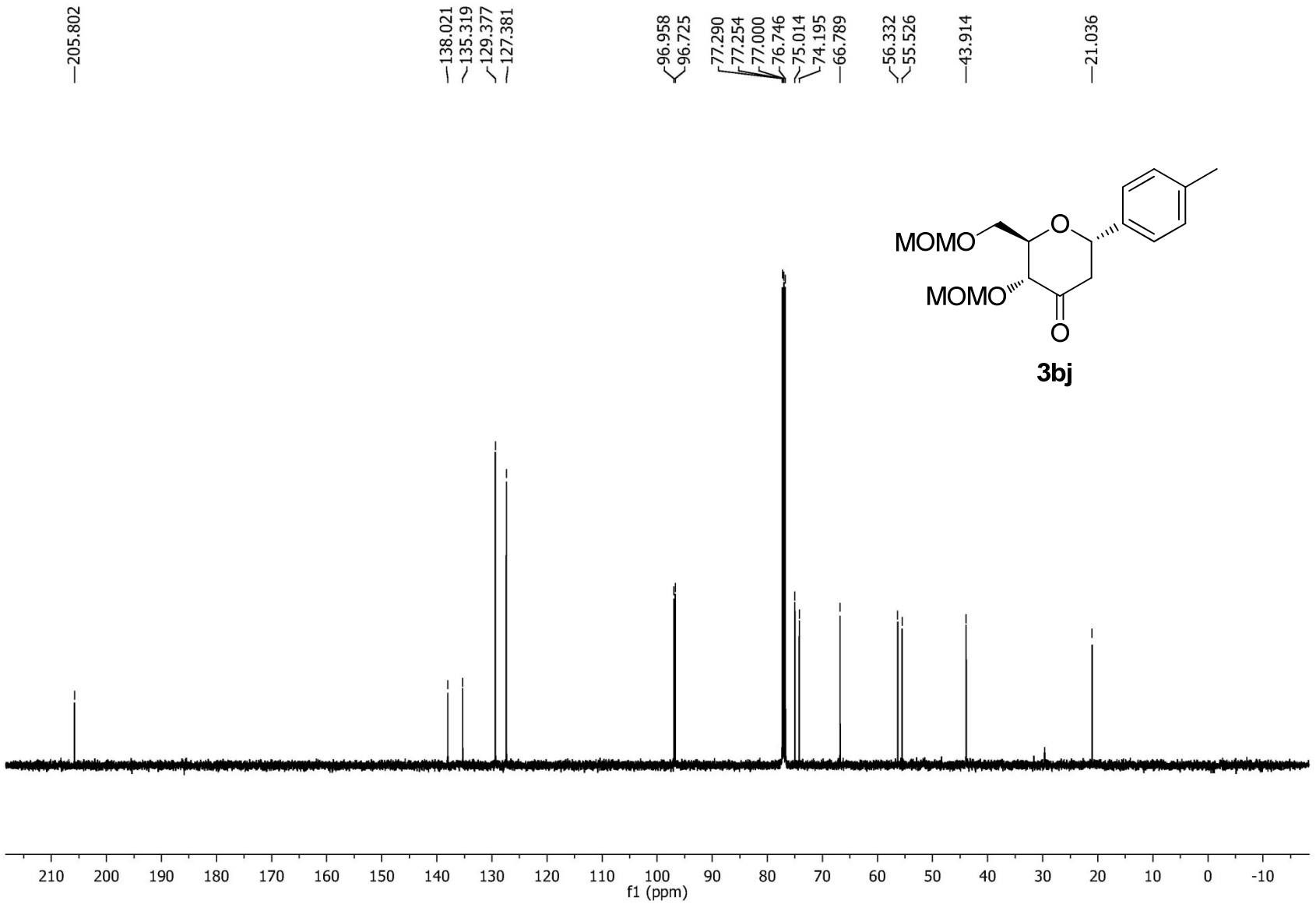

Figure S90: ^{13}C-NMR spectrum of compound 3bj in $CDCl_3$

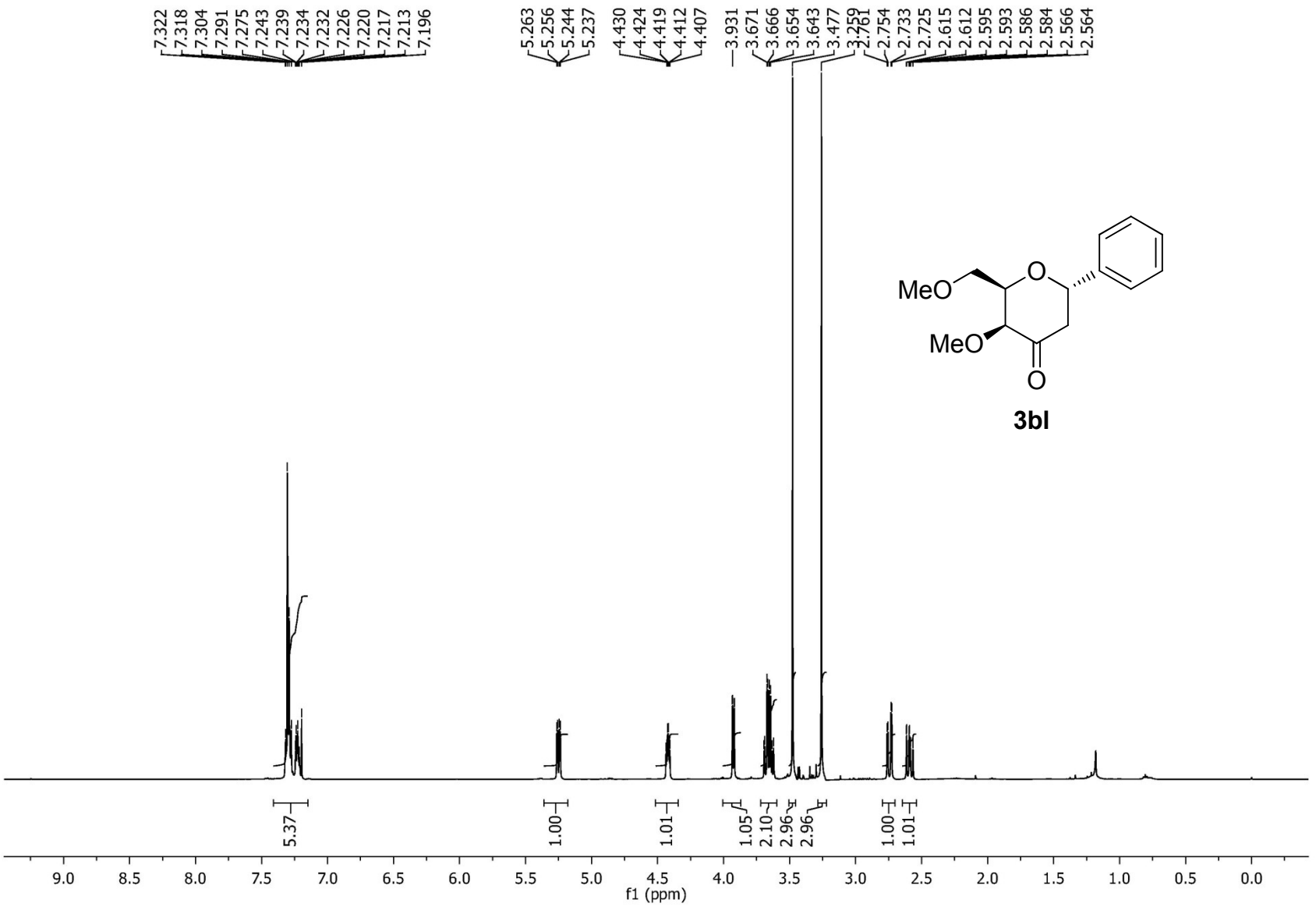

Figure S91: ^{1}H-NMR spectrum of compound 3bl in $CDCl_3$

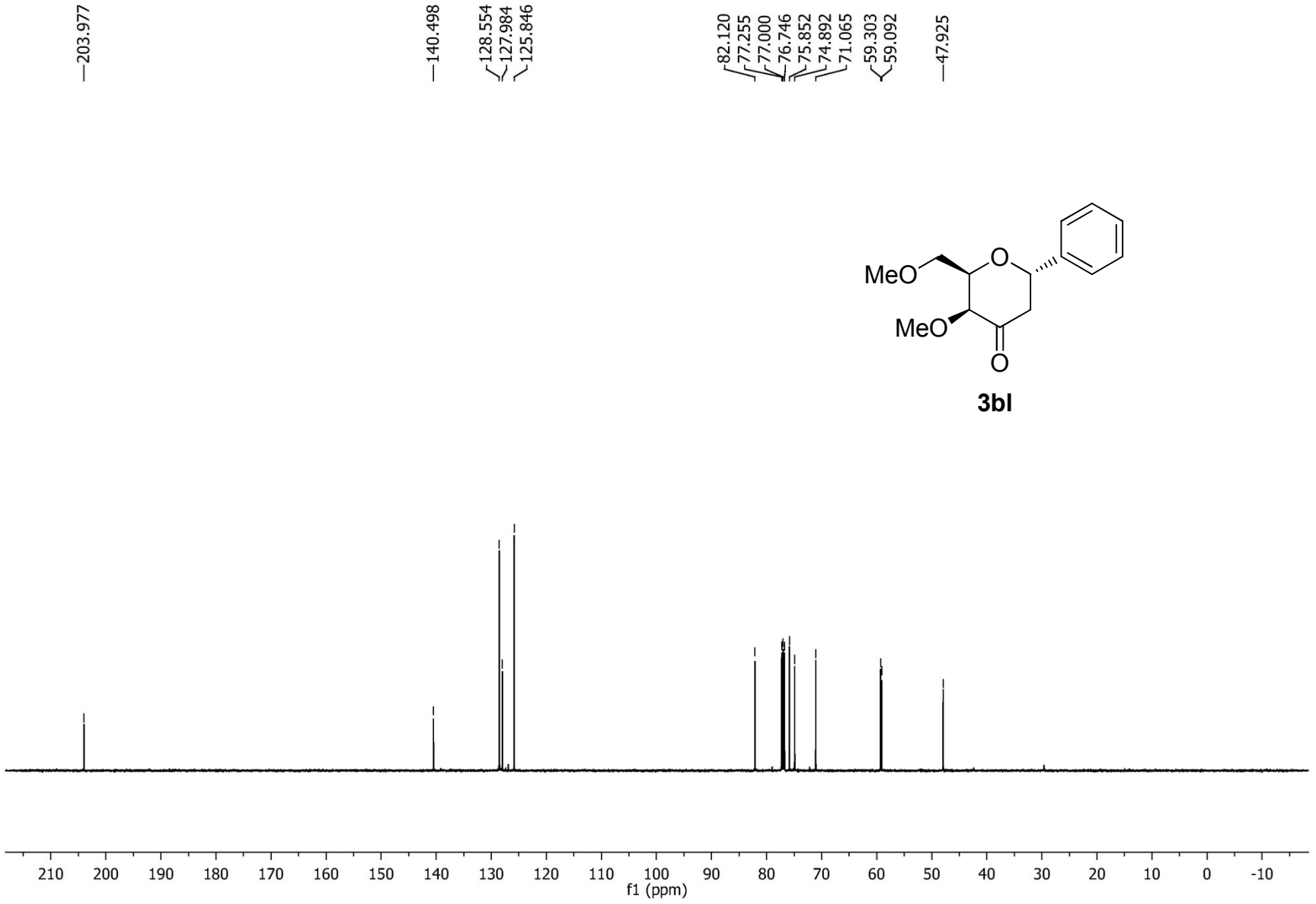

Figure S92: ^{13}C-NMR spectrum of compound 3bl in $CDCl_3$

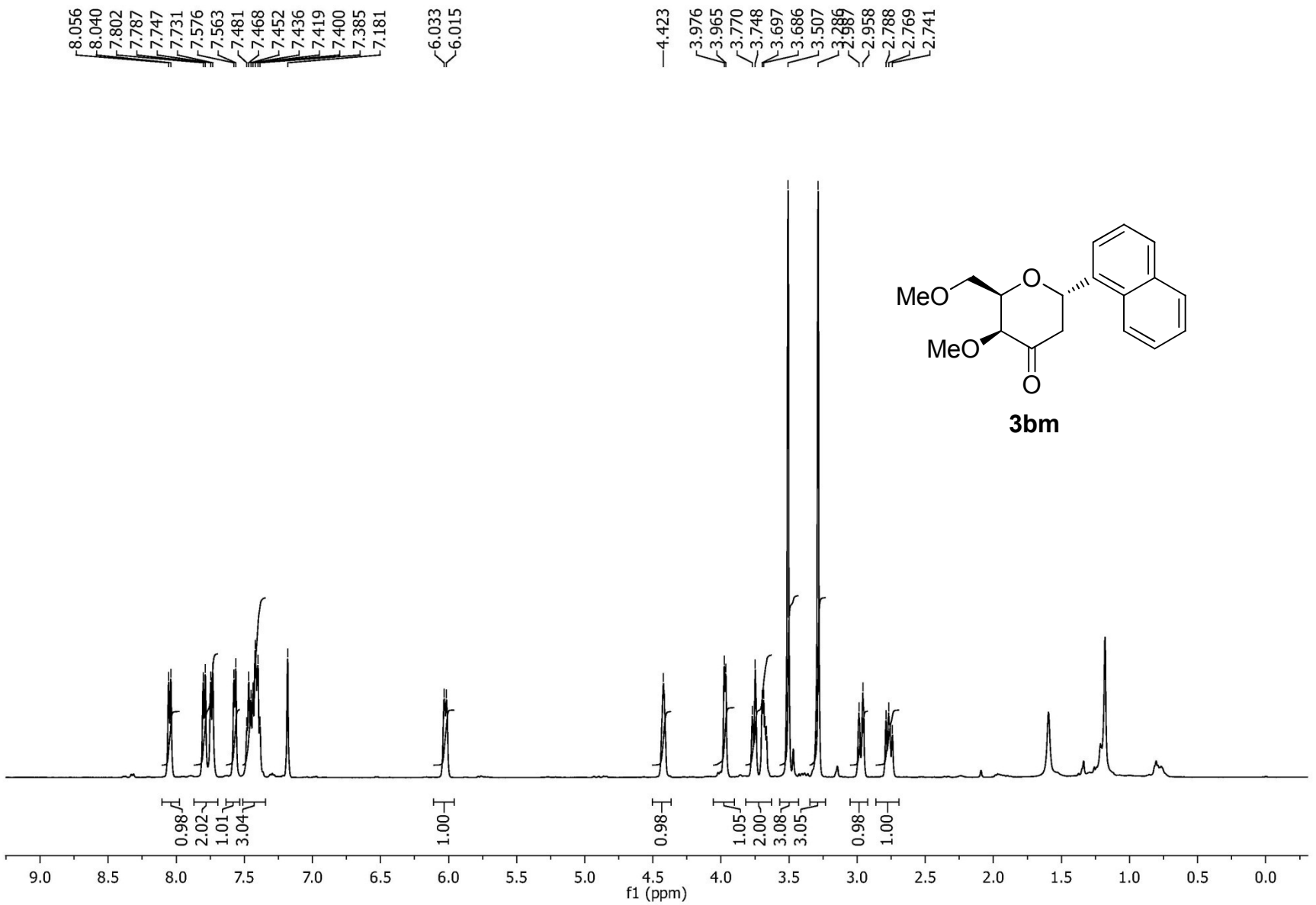

Figure S93: ^{1}H-NMR spectrum of compound 3bm in $CDCl_3$

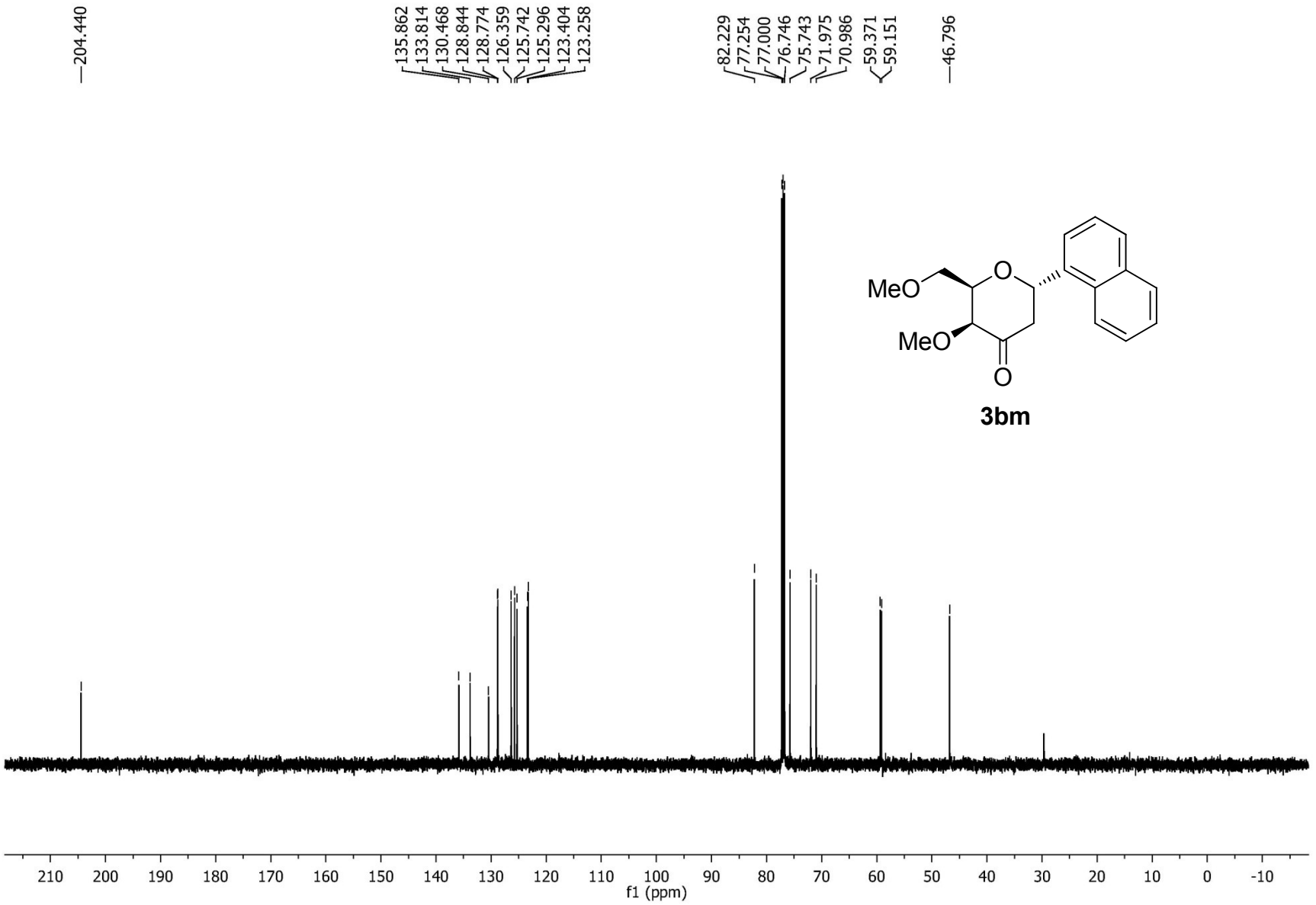

Figure S94: ^{13}C-NMR spectrum of compound 3bm in $CDCl_3$

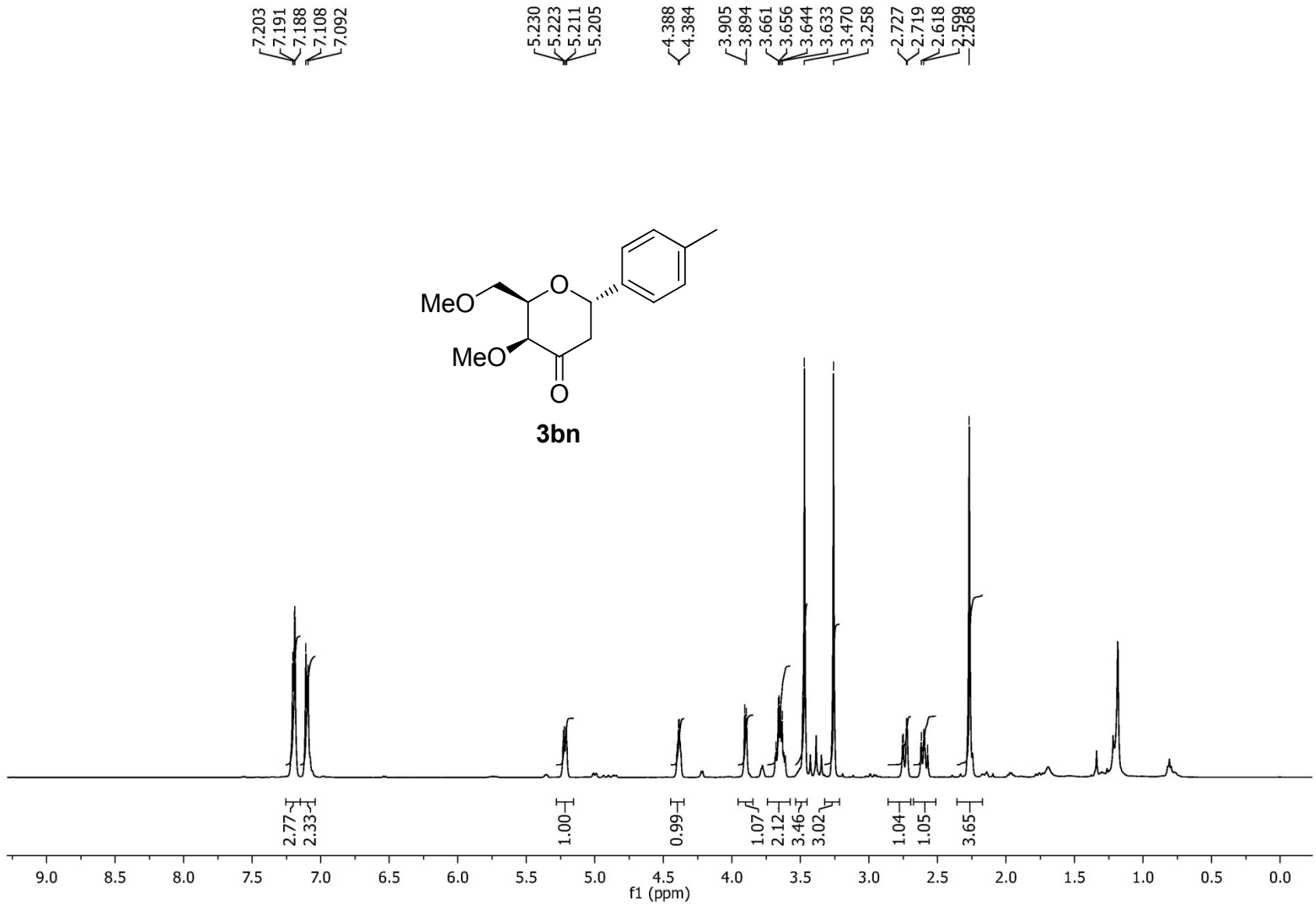

Figure S95: ^{1}H-NMR spectrum of compound 3bn in $CDCl_3$

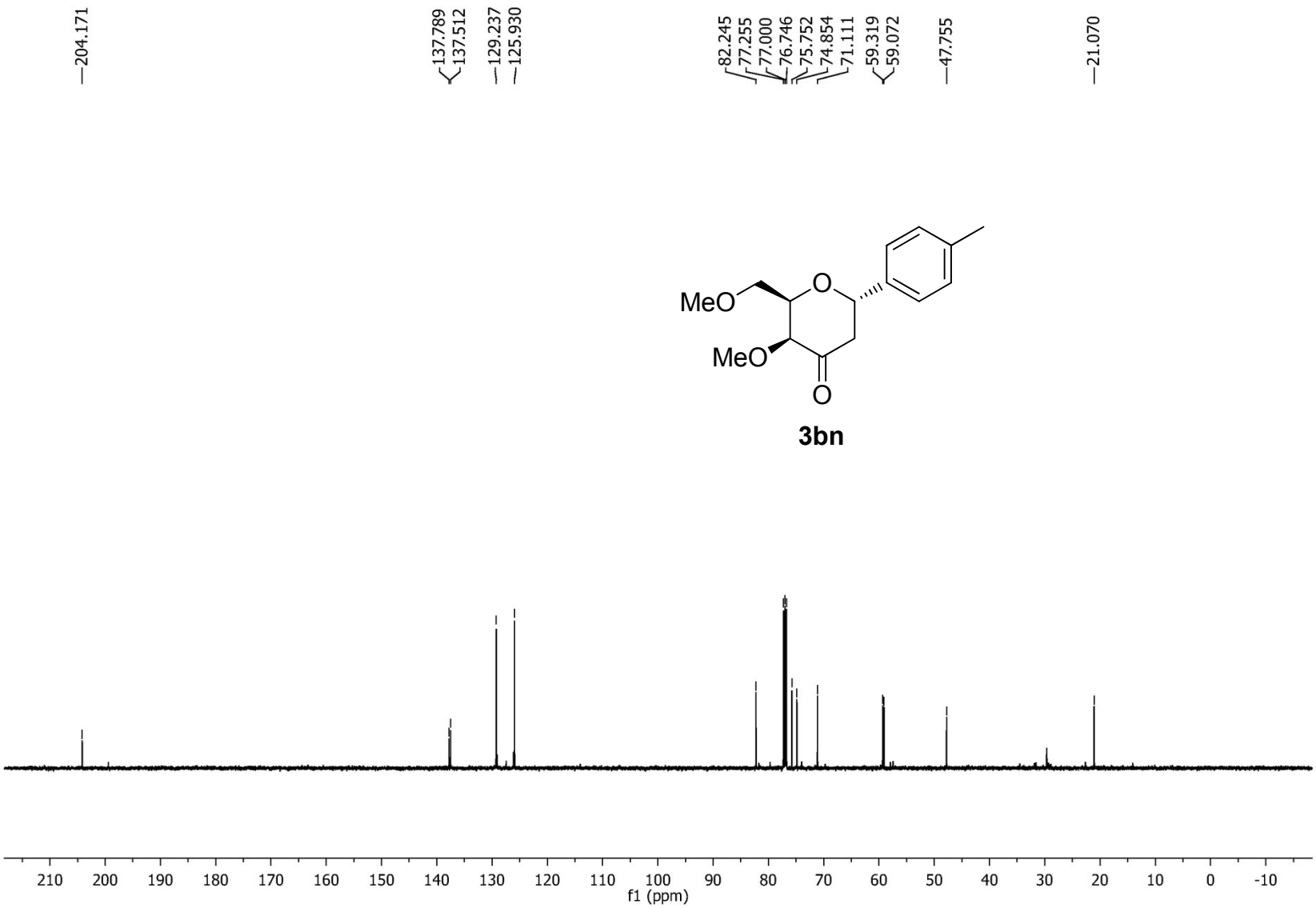

Figure S96: ^{13}C-NMR spectrum of compound 3bn in $CDCl_3$

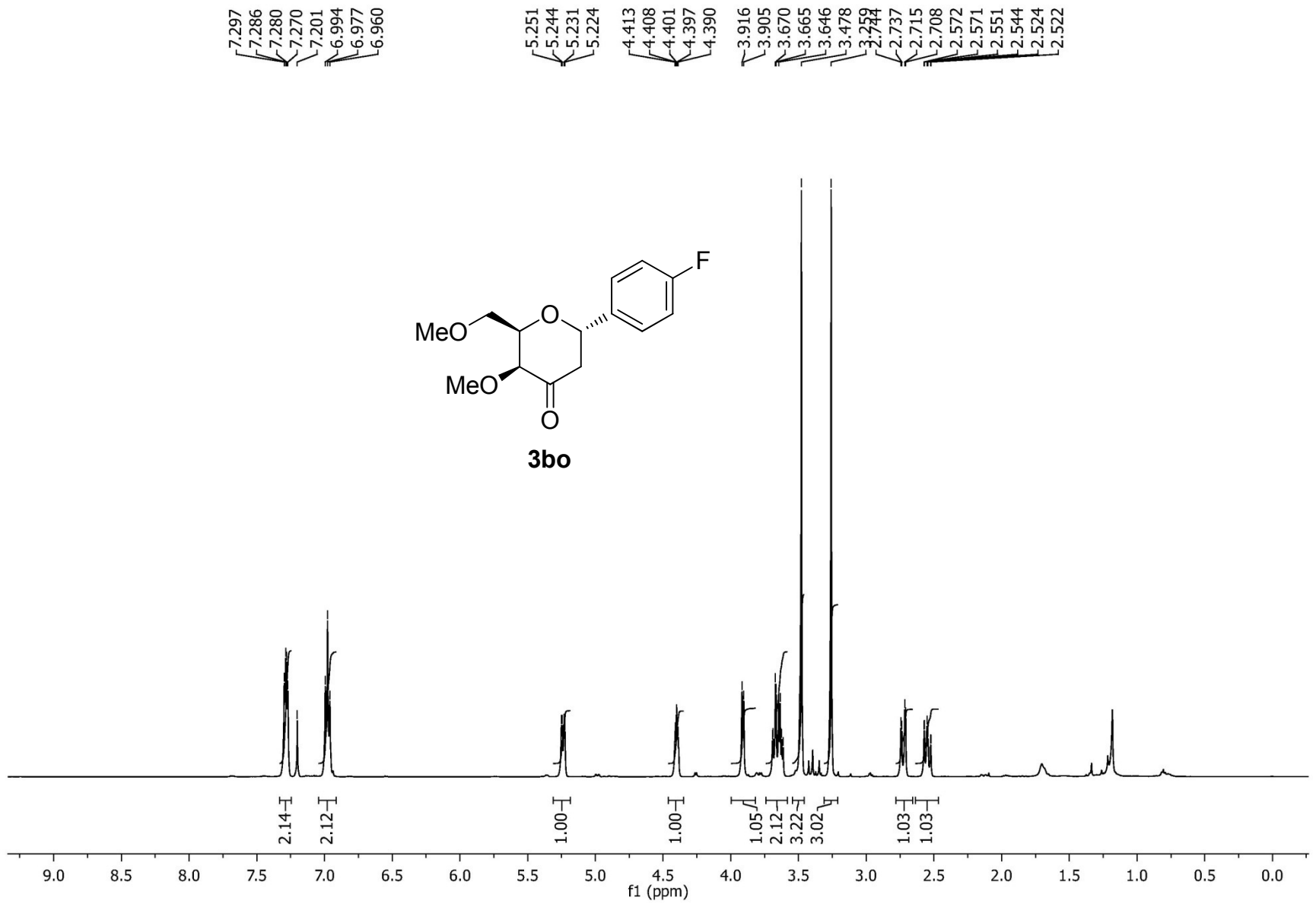

Figure S97: ^{1}H-NMR spectrum of compound 3bo in $CDCl_3$

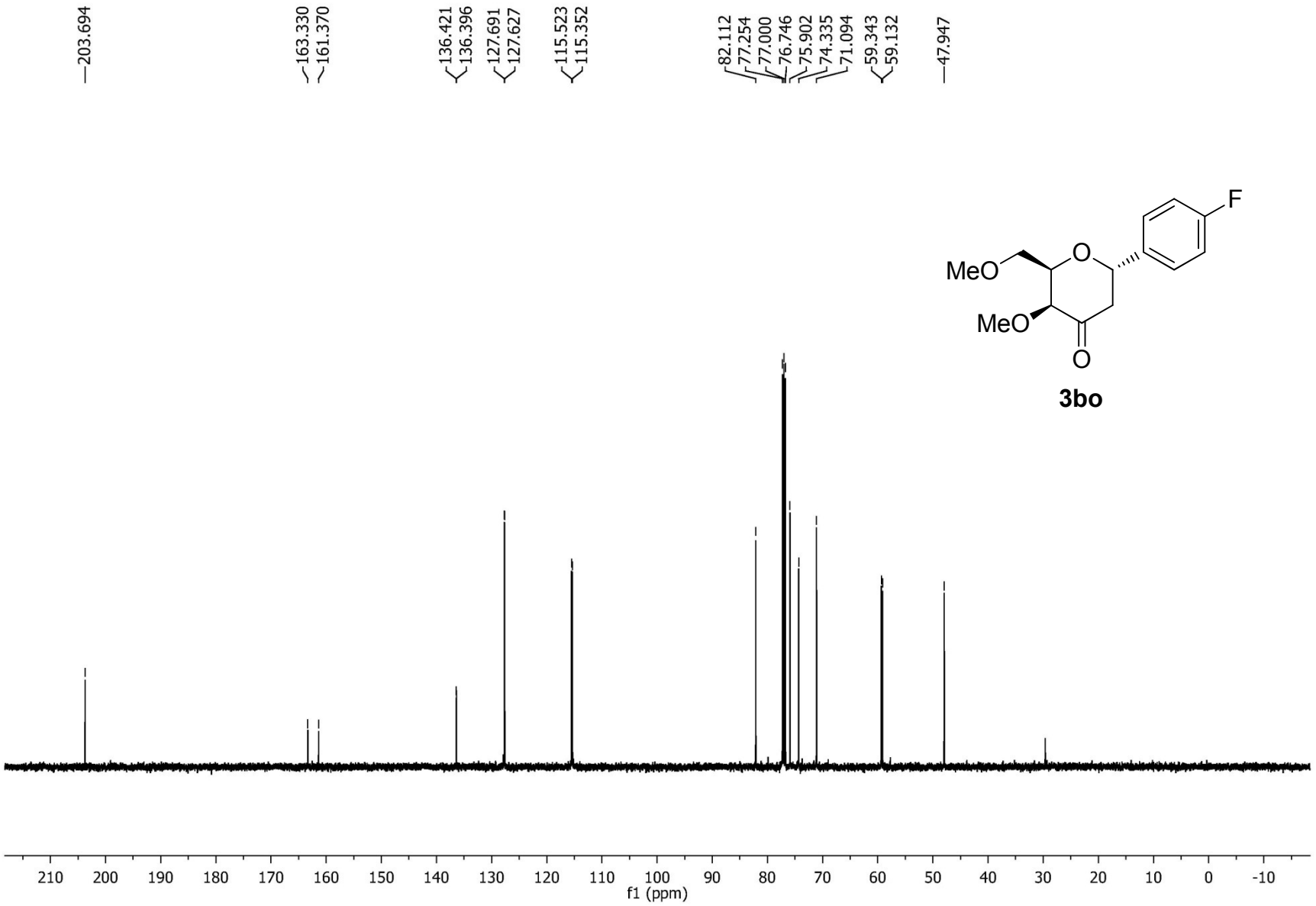

Figure S98: ^{13}C-NMR spectrum of compound 3bo in $CDCl_3$

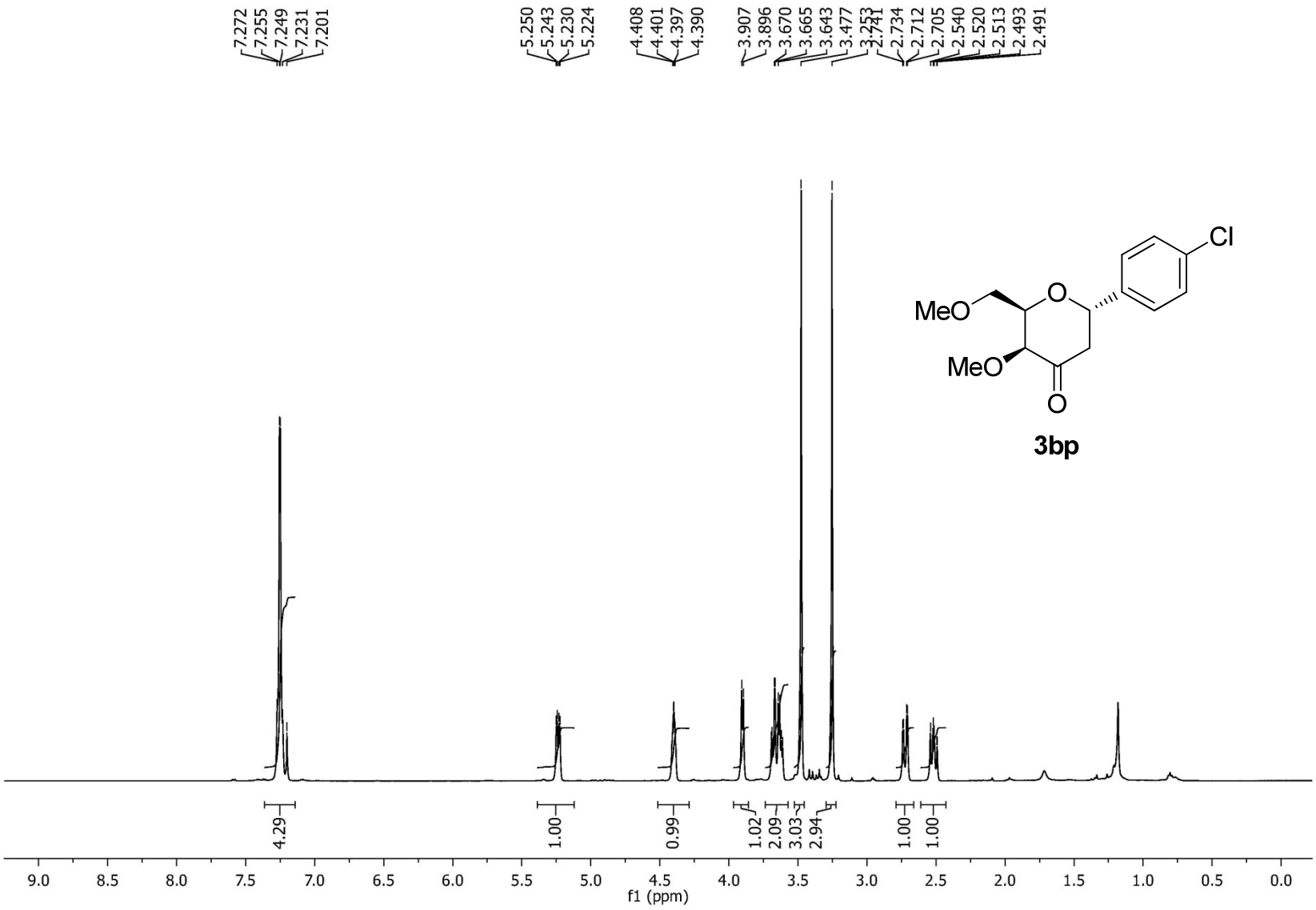

Figure S99: ^{1}H-NMR spectrum of compound 3bp in $CDCl_3$

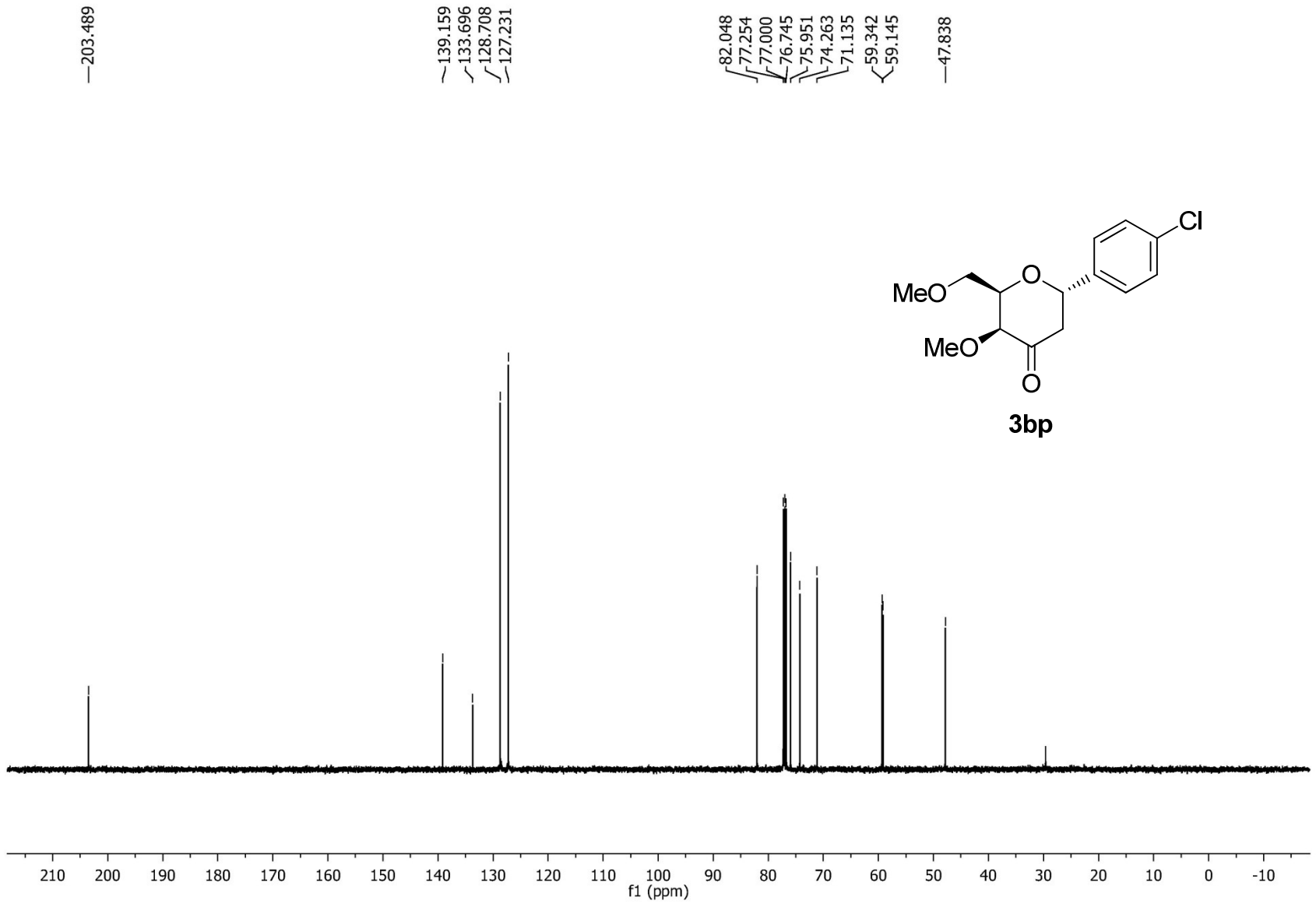

Figure S100: ^{13}C-NMR spectrum of compound 3bp in $CDCl_3$

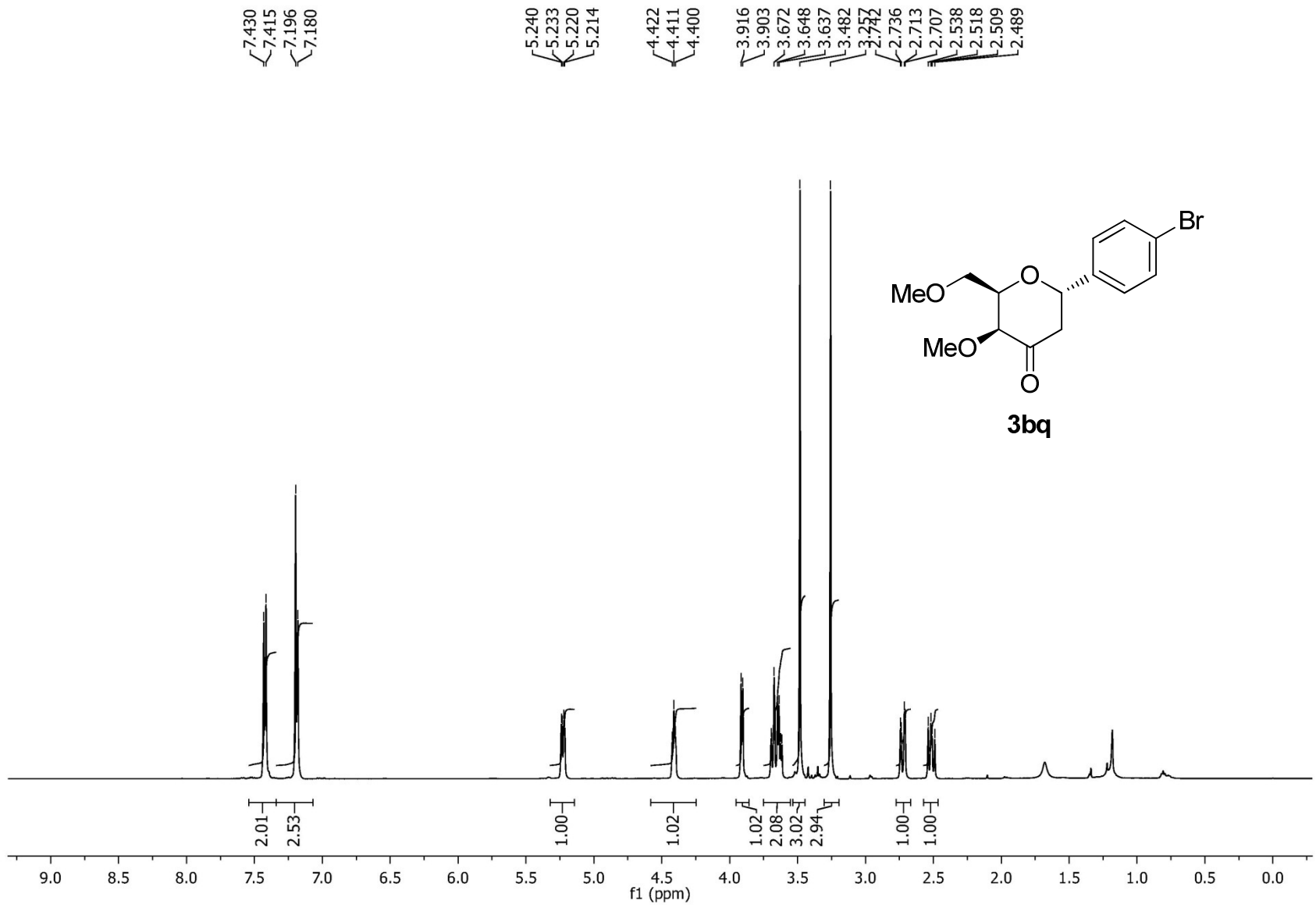

Figure S101: ^{1}H-NMR spectrum of compound 3bq in $CDCl_3$

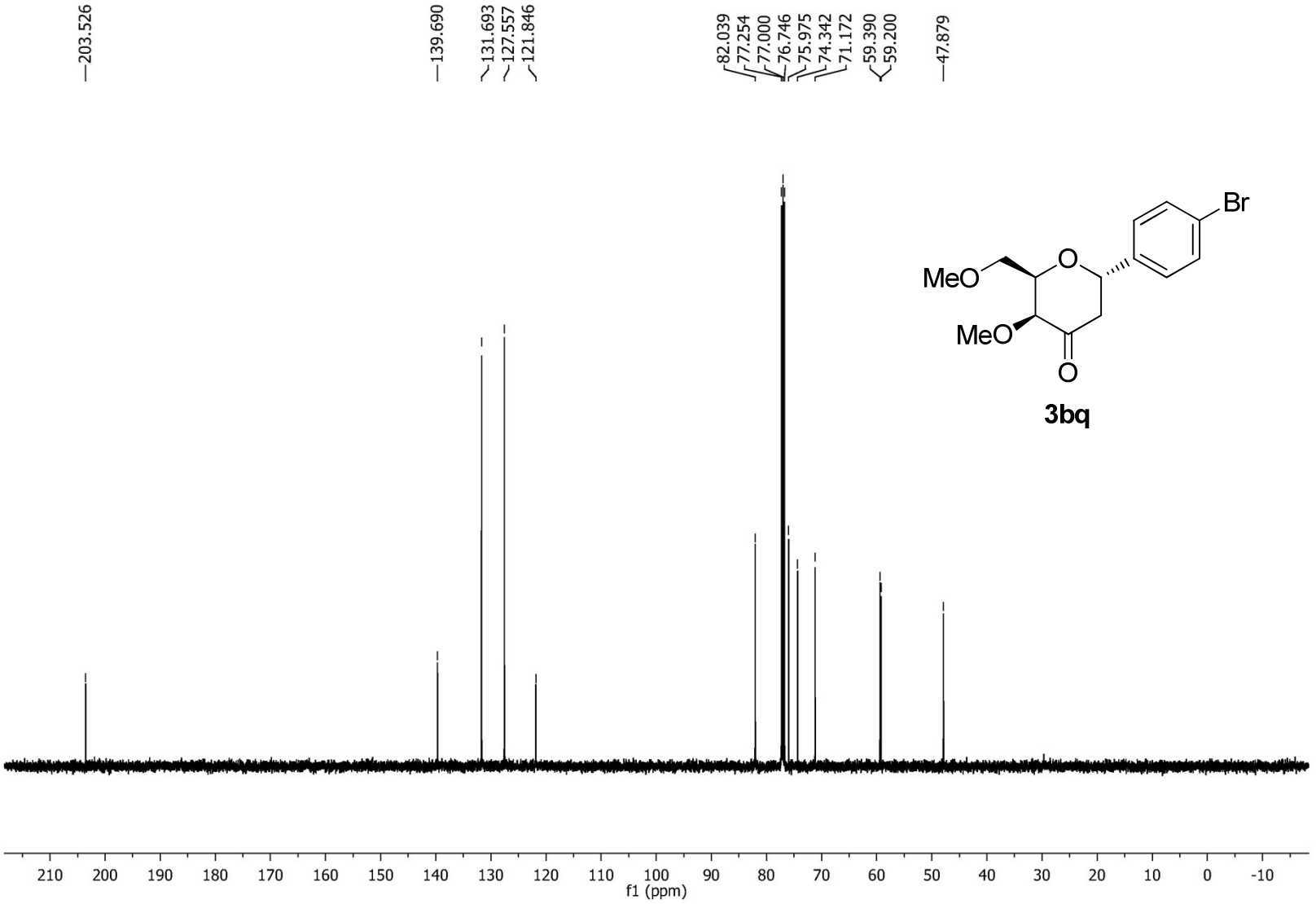

Figure S102: ^{13}C-NMR spectrum of compound 3bq in $CDCl_3$

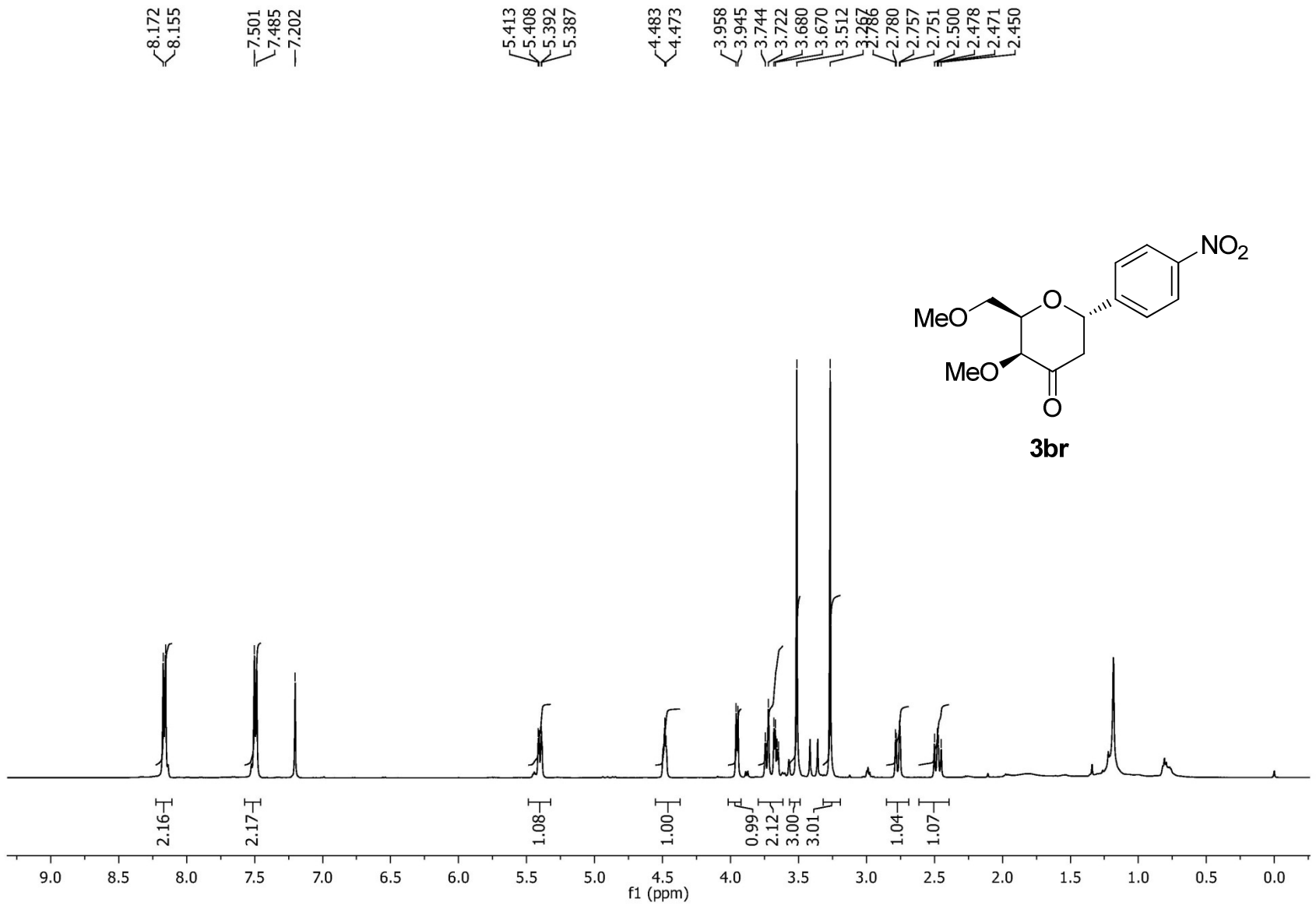

Figure S103: ^{1}H-NMR spectrum of compound 3br in $CDCl_3$

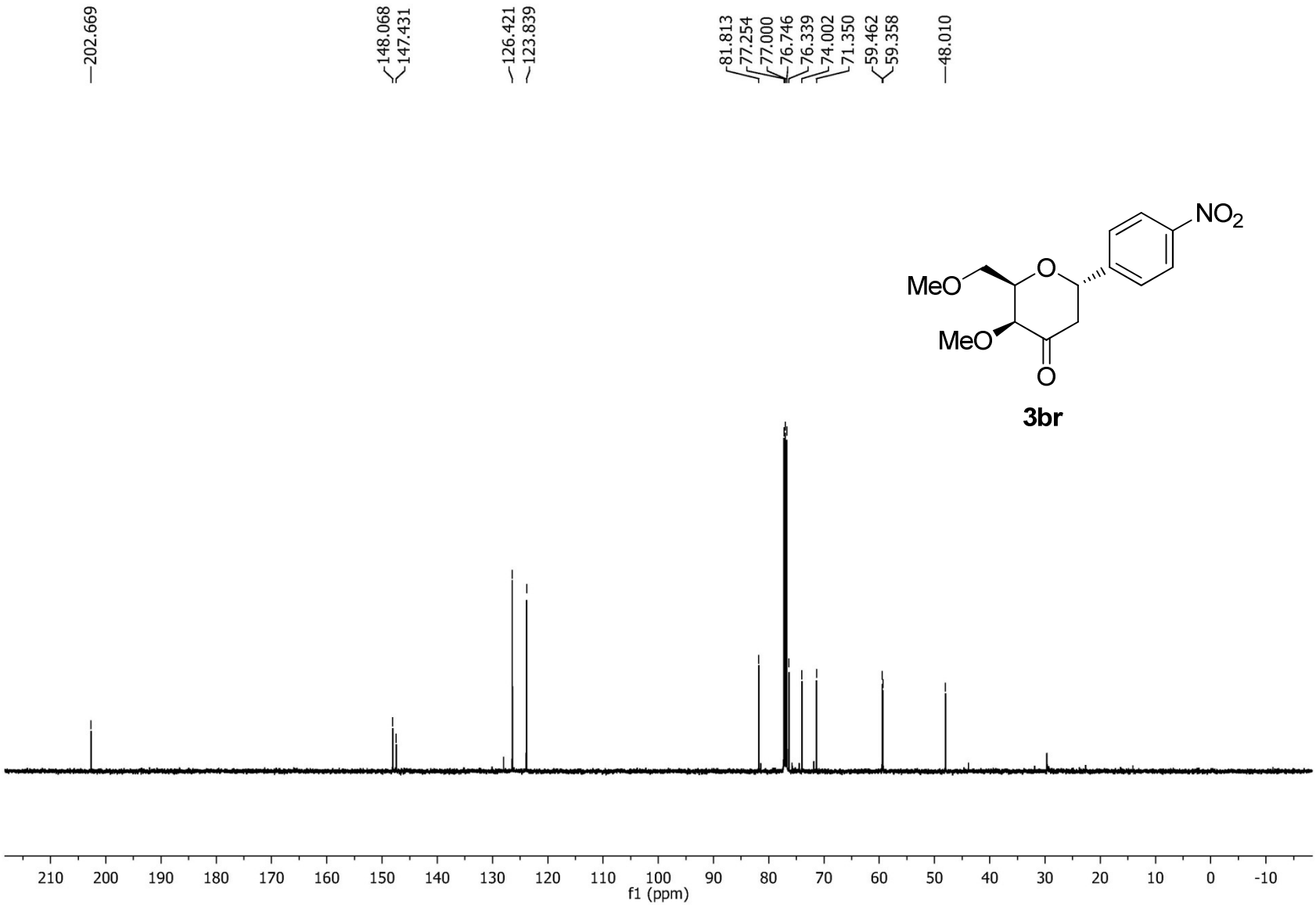

Figure S104: ^{13}C-NMR spectrum of compound 3br in $CDCl_3$

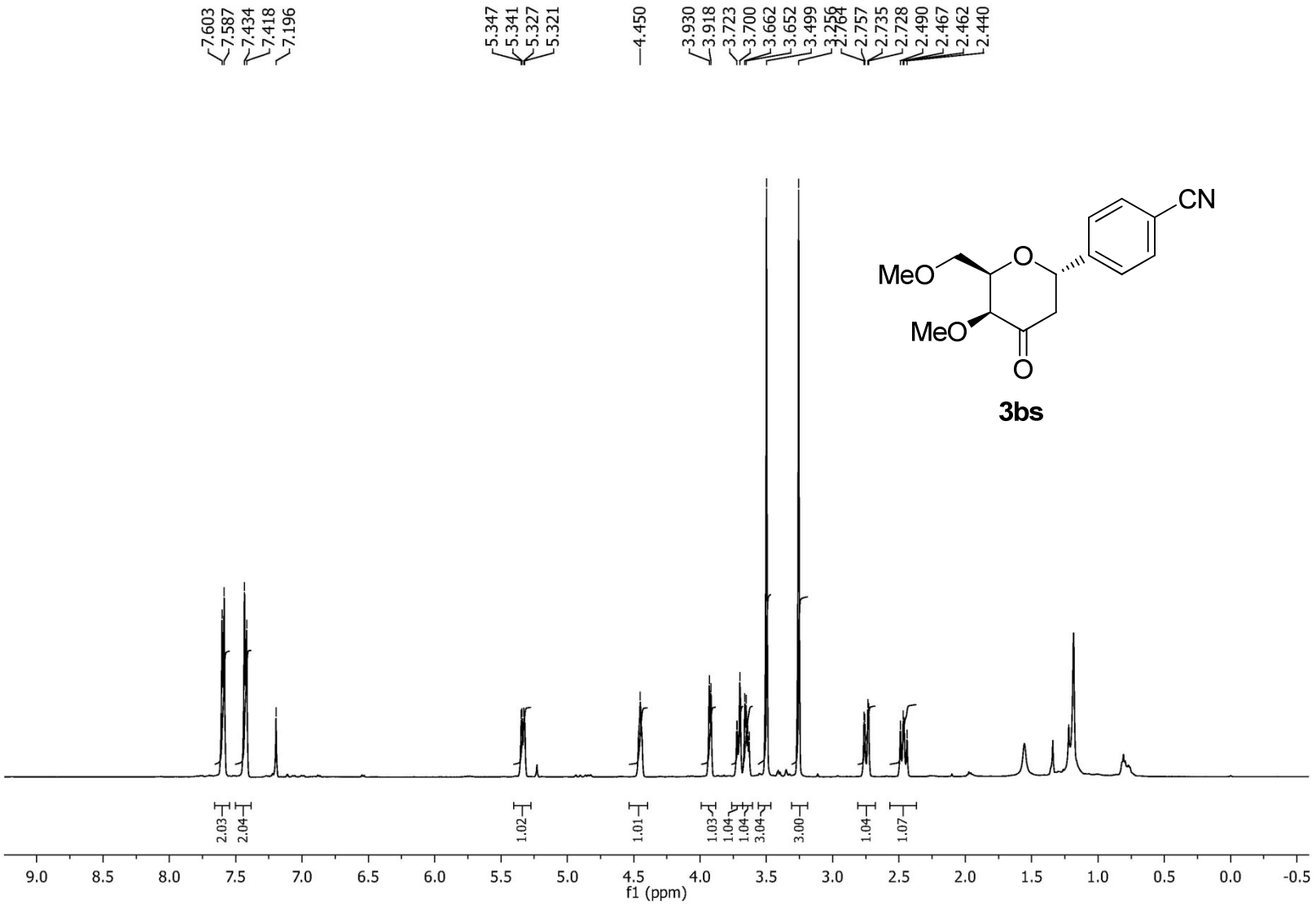

Figure S105: ^{1}H-NMR spectrum of compound 3bs in $CDCl_3$

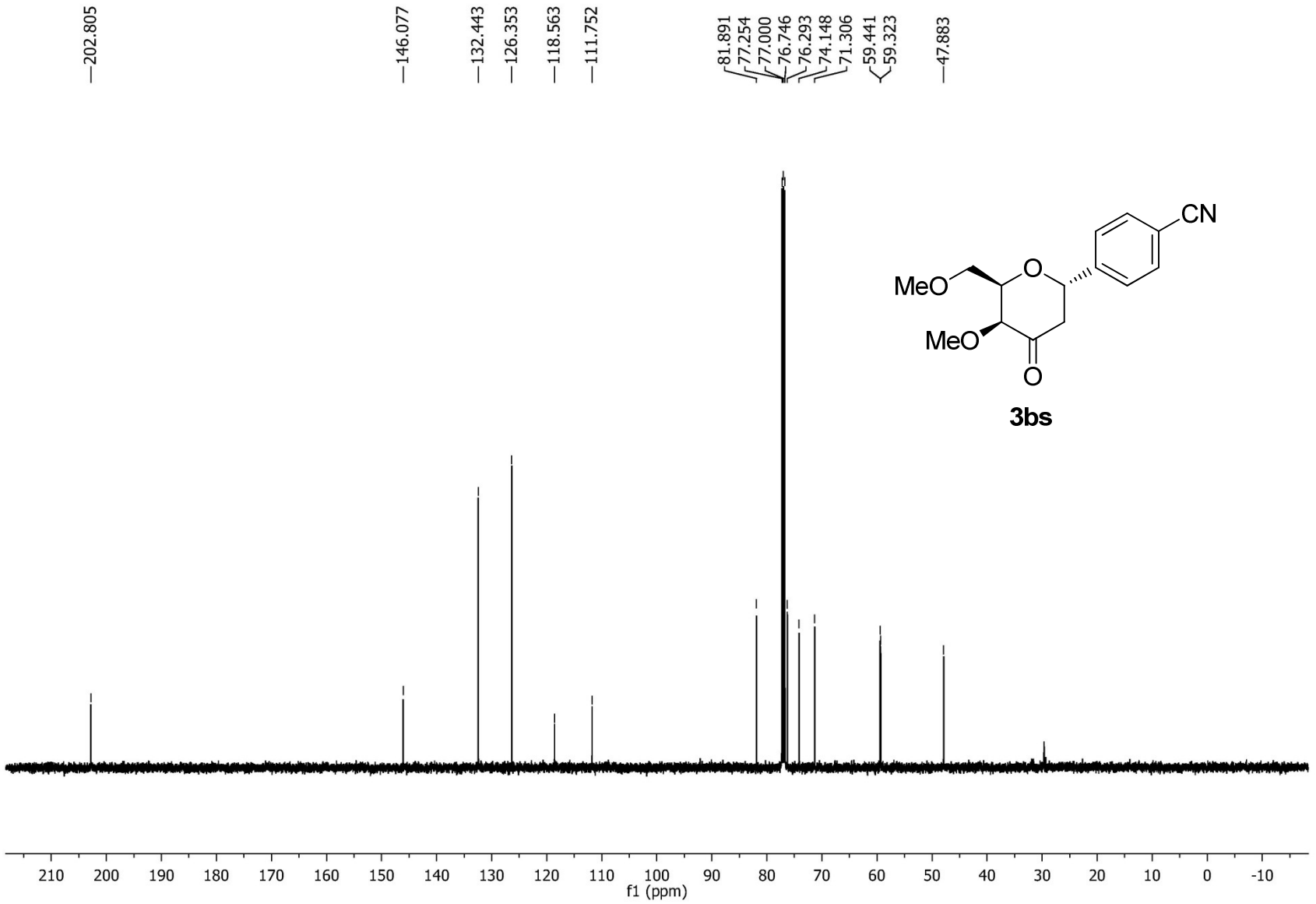

Figure S106: ^{13}C-NMR spectrum of compound 3bs in $CDCl_3$

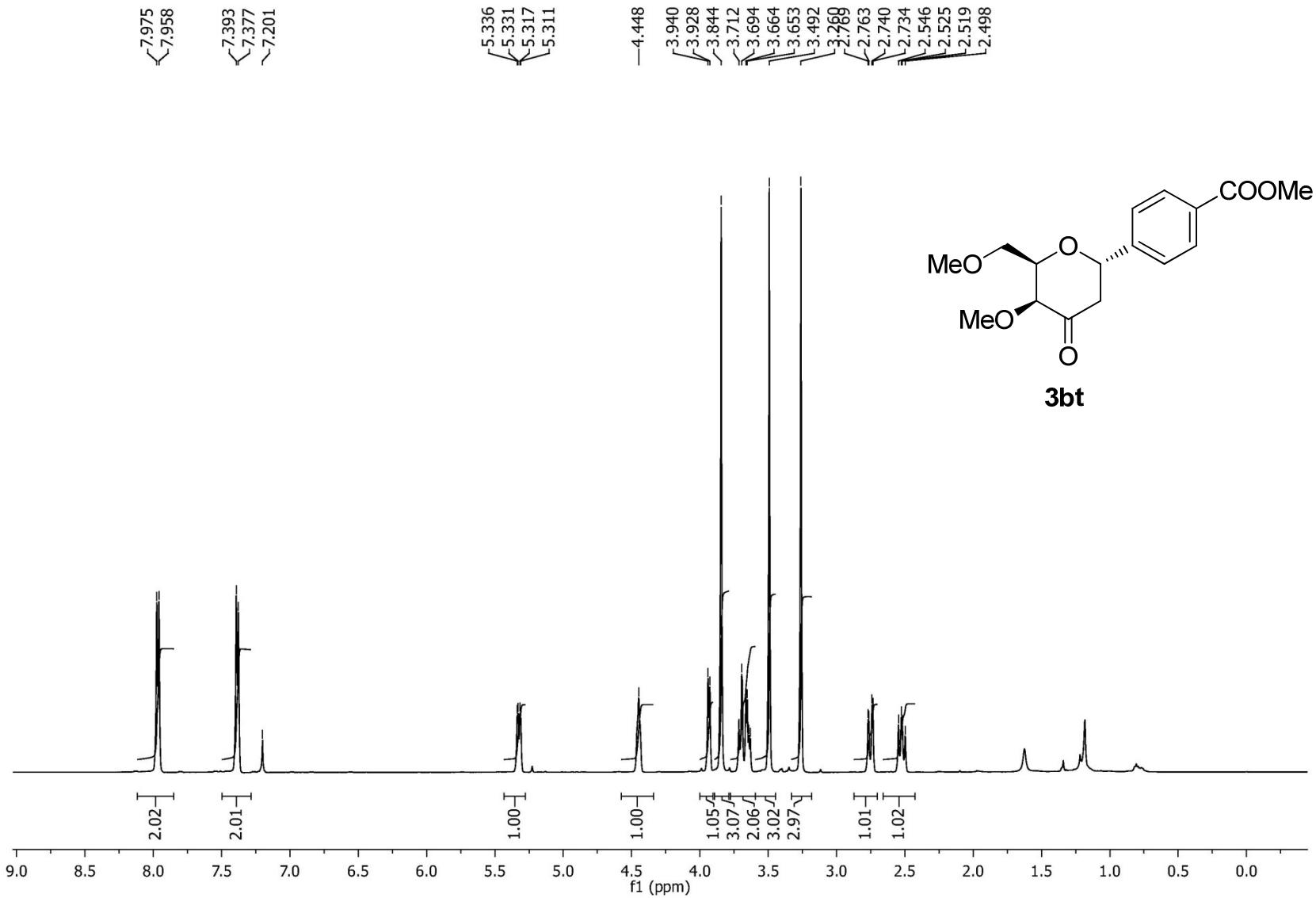

Figure S107: ^{1}H-NMR spectrum of compound 3bt in $CDCl_3$

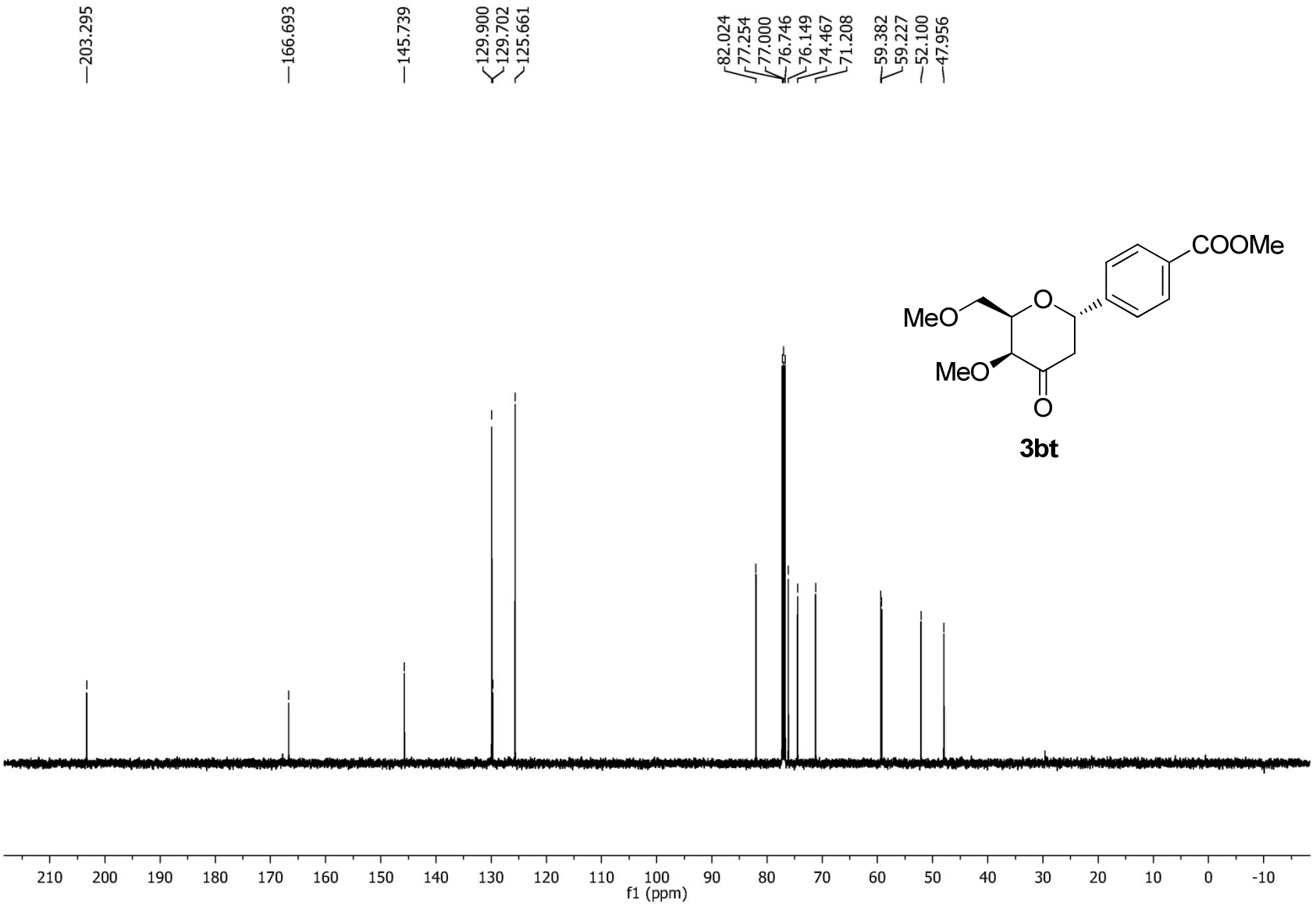

Figure S108: ^{13}C-NMR spectrum of compound 3bt in $CDCl_3$.

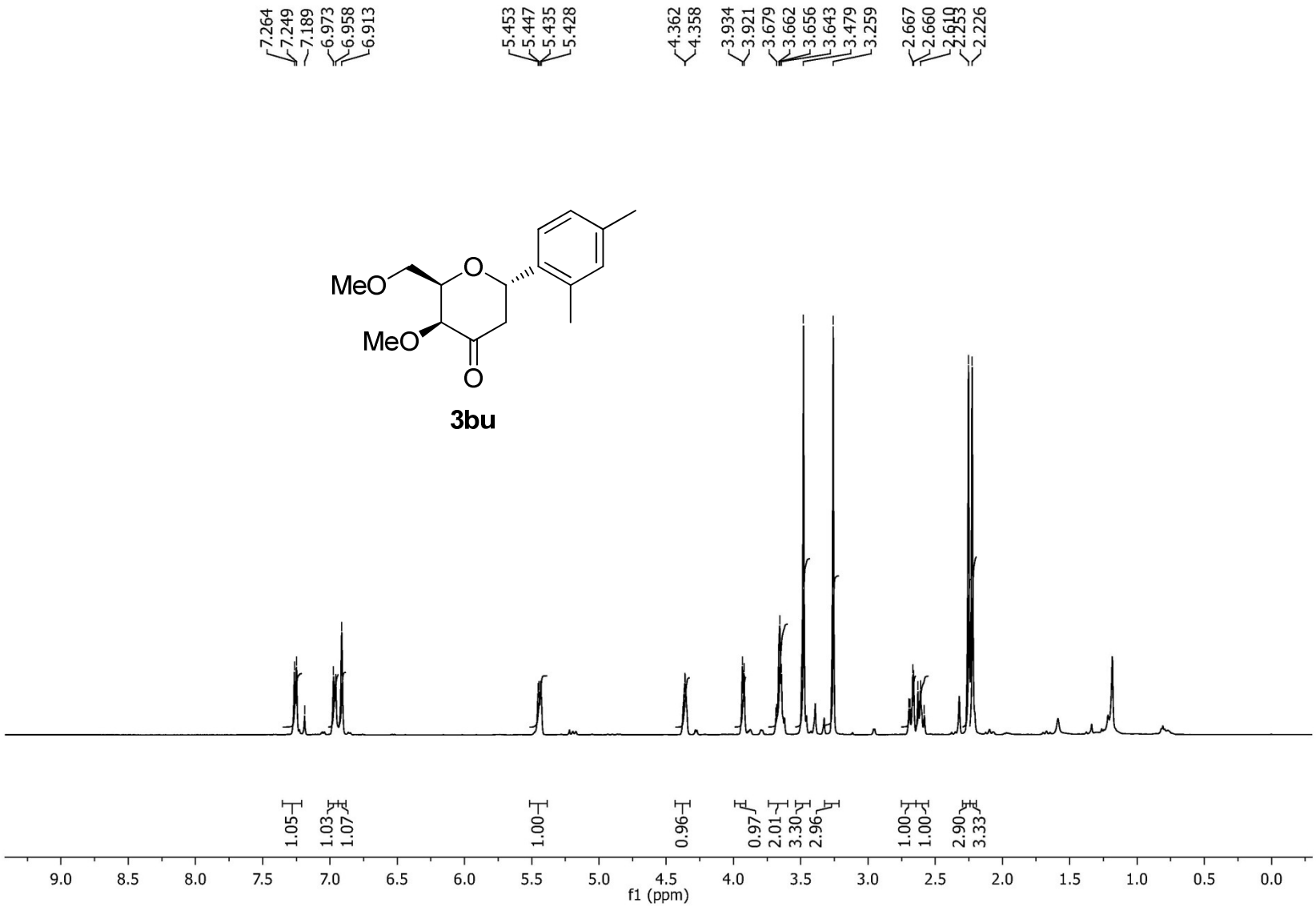

Figure S109: ^{1}H-NMR spectrum of compound 3bu in $CDCl_3$

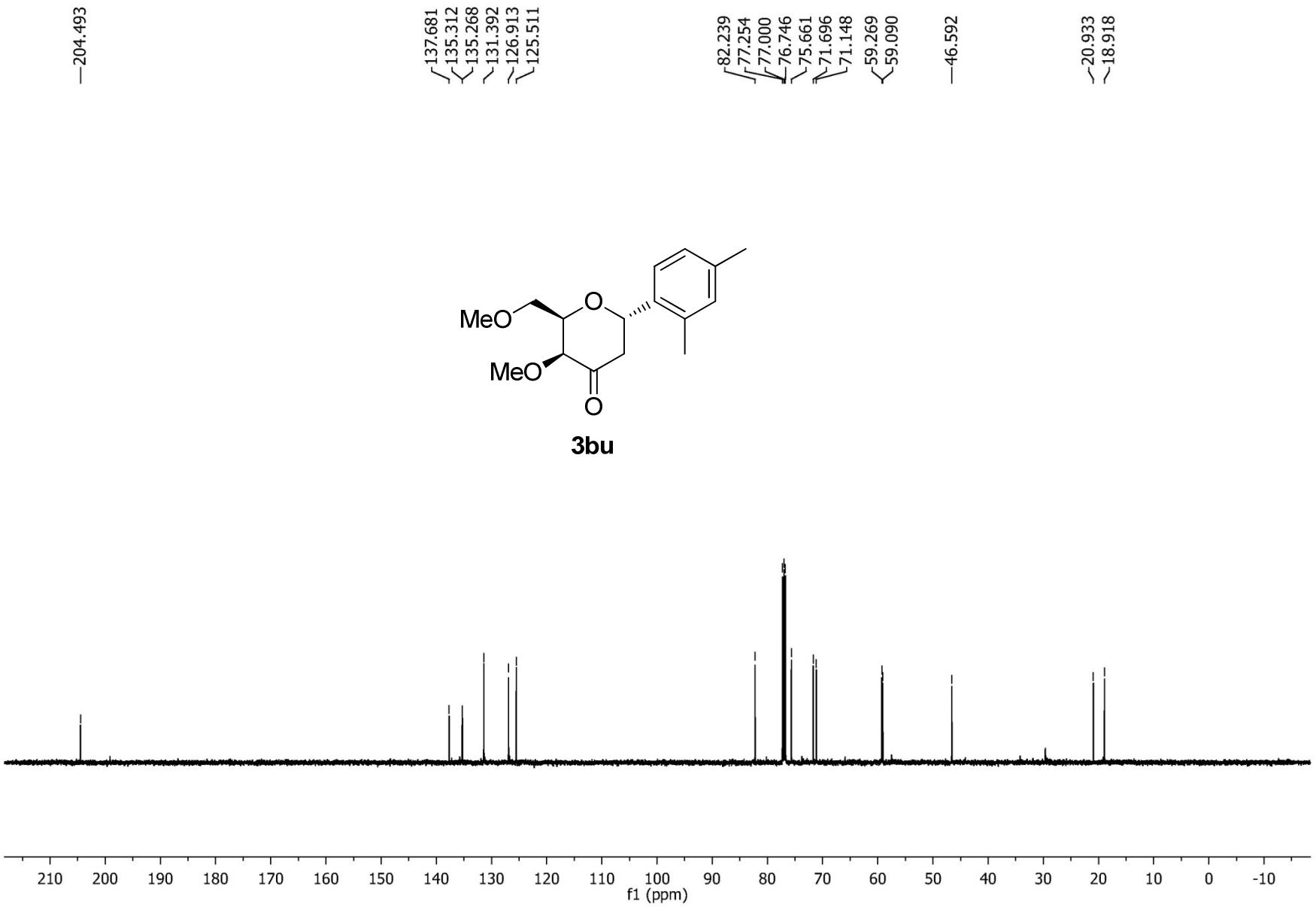

Figure S110: ^{13}C-NMR spectrum of compound 3bu in $CDCl_3$

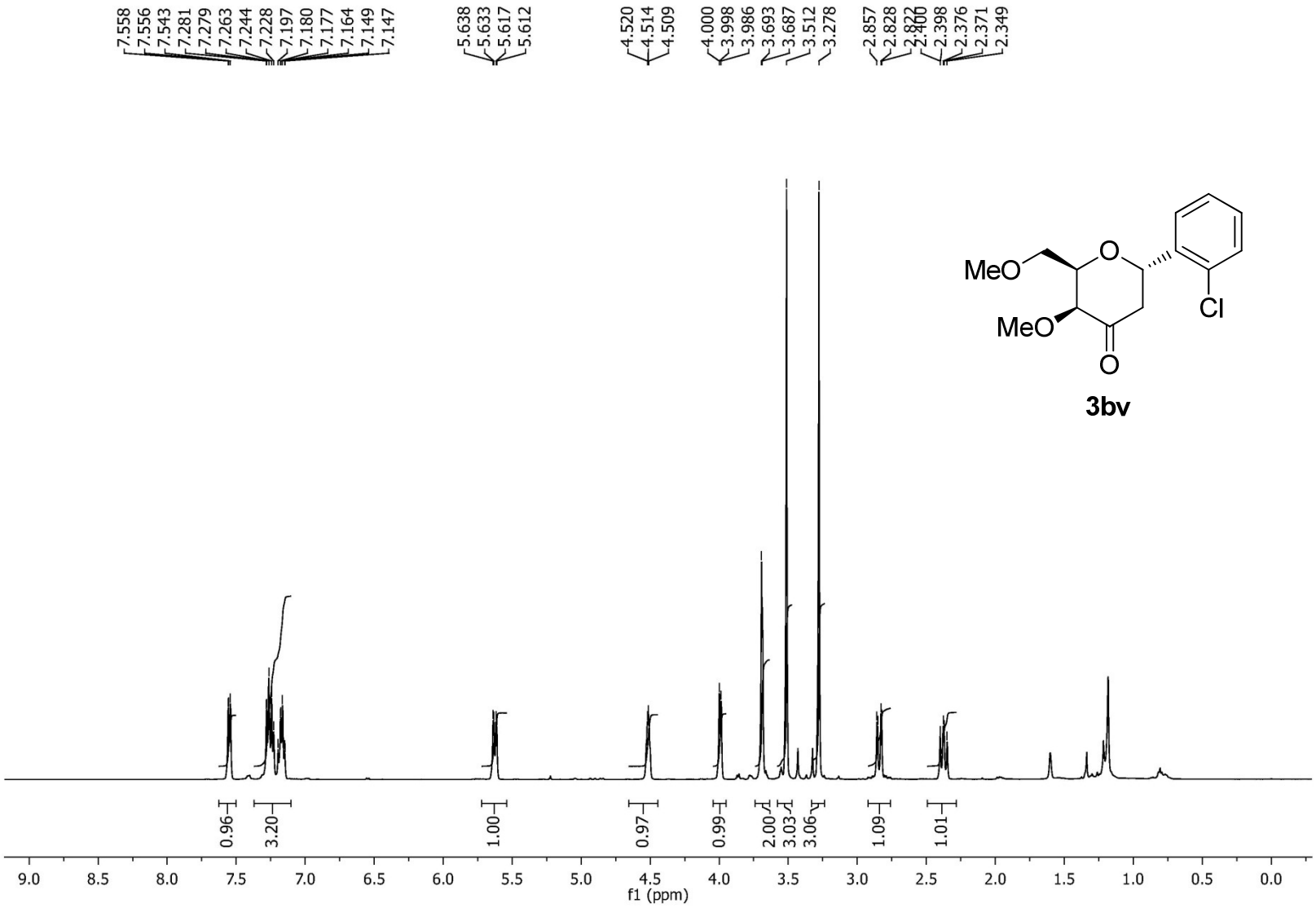

Figure S111: ^{1}H-NMR spectrum of compound 3bv in $CDCl_3$

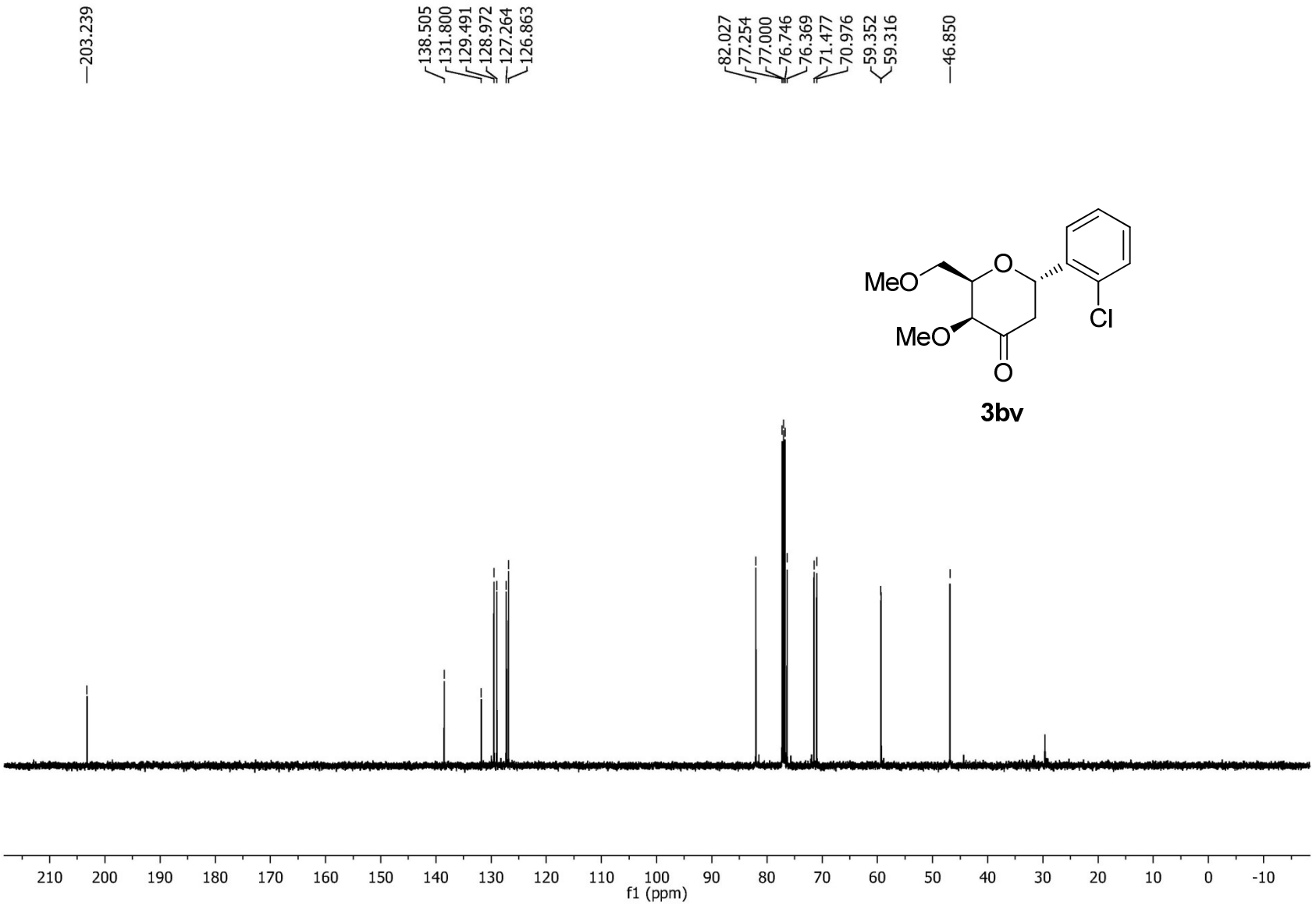

Figure S112: ^{13}C-NMR spectrum of compound 3bv in $CDCl_3$

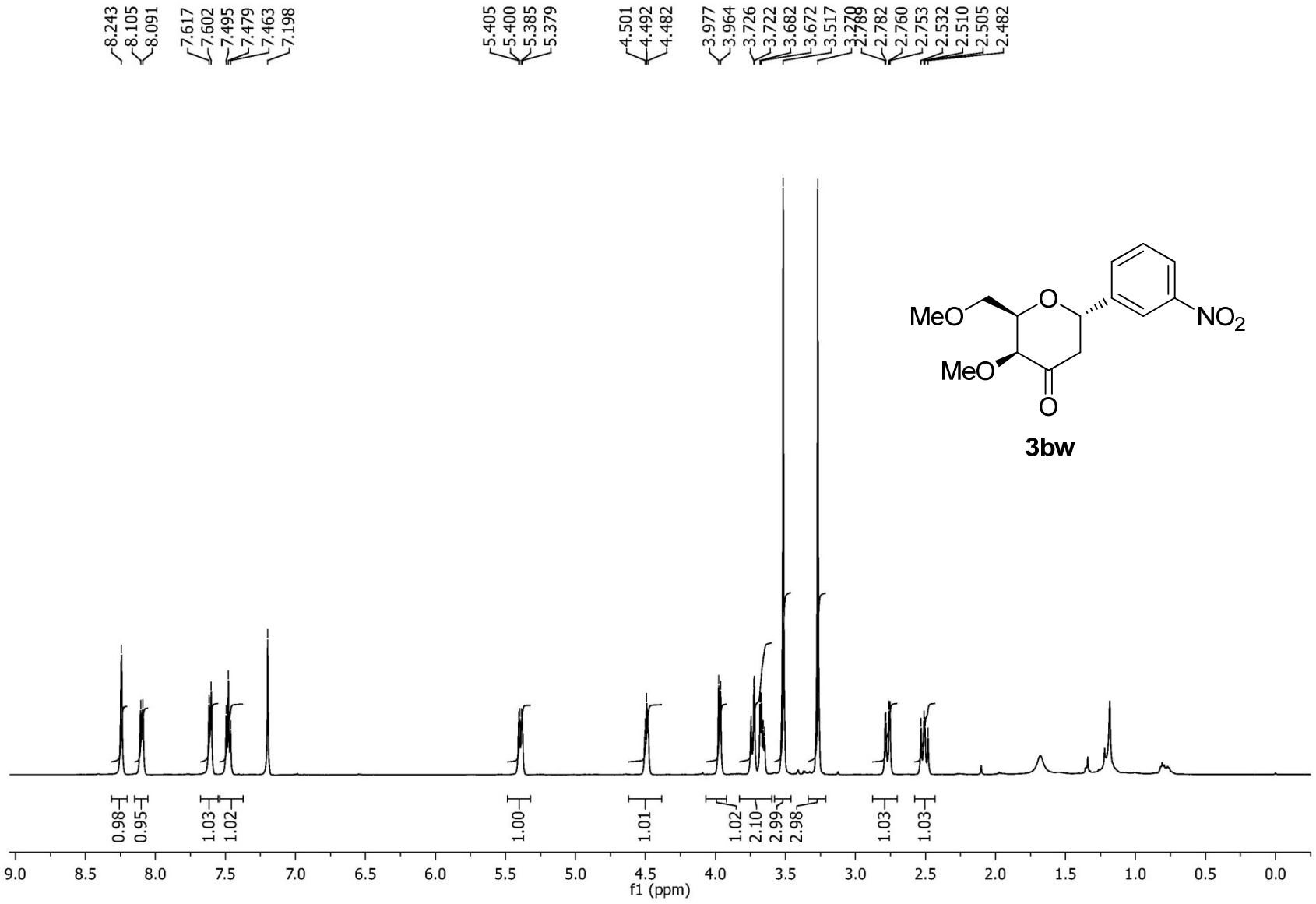

Figure S113: ^{1}H-NMR spectrum of compound 3bw in $CDCl_3$

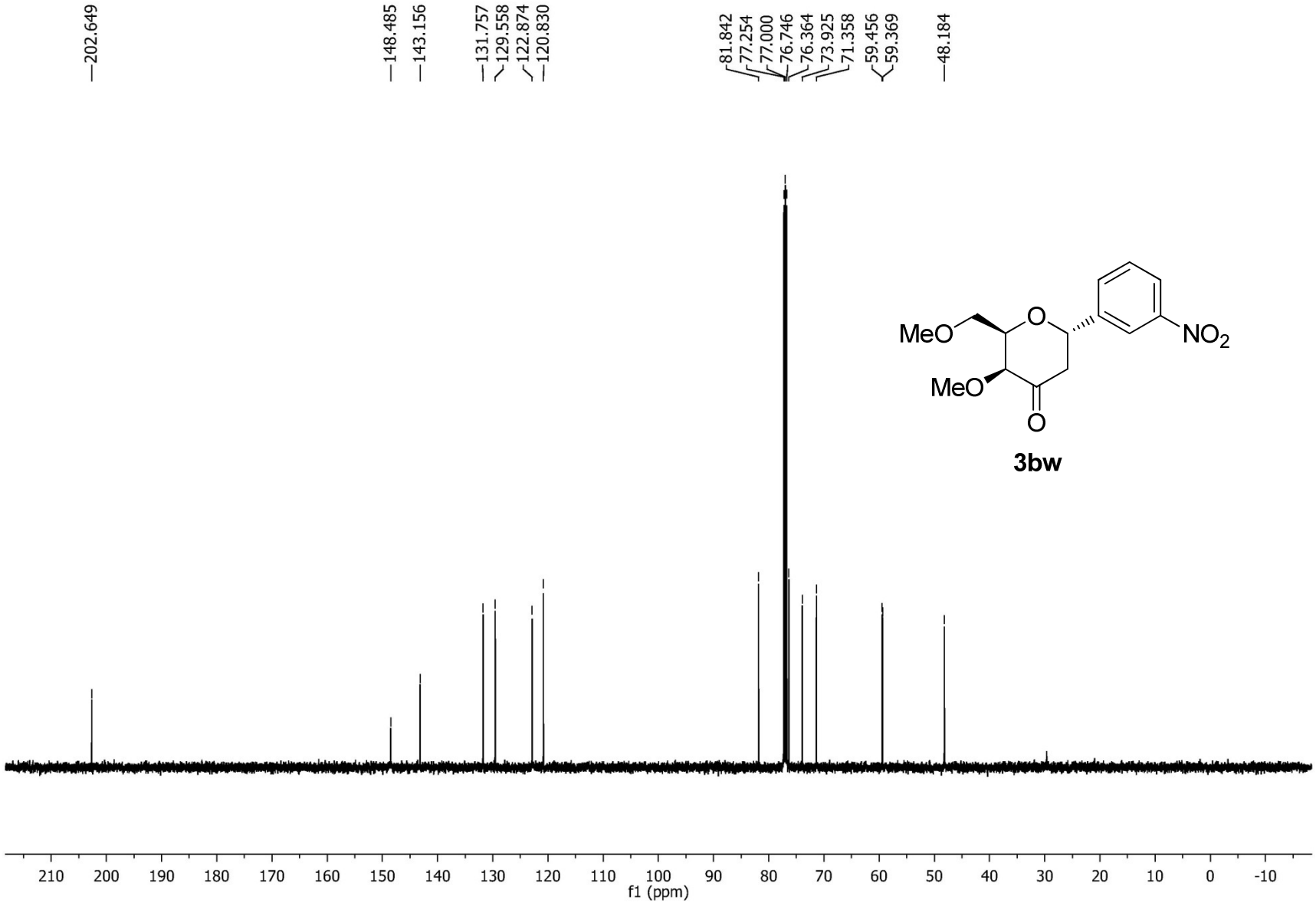

Figure S114: ^{13}C-NMR spectrum of compound 3bw in $CDCl_3$

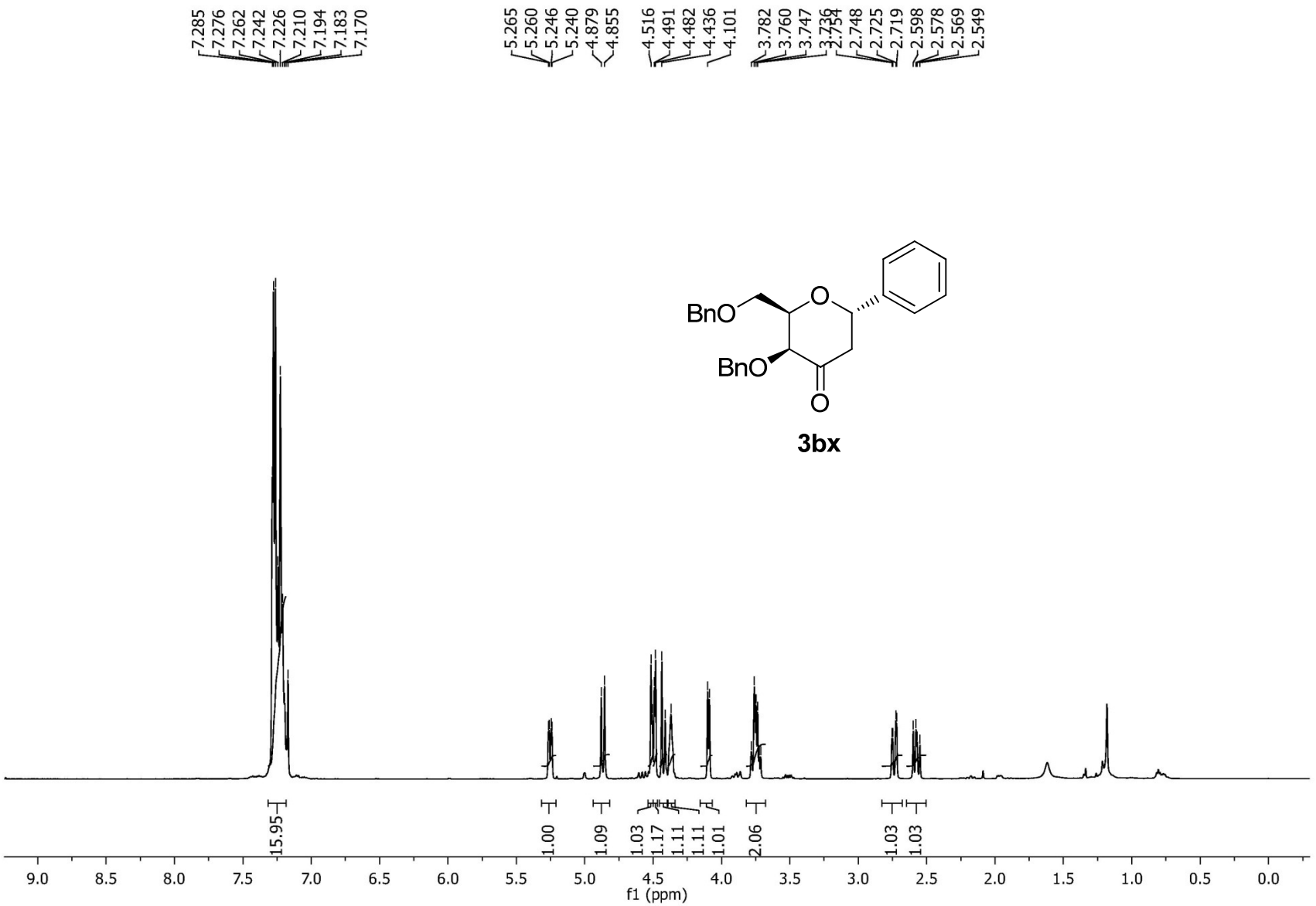

Figure S115: ^{1}H-NMR spectrum of compound 3bx in $CDCl_3$

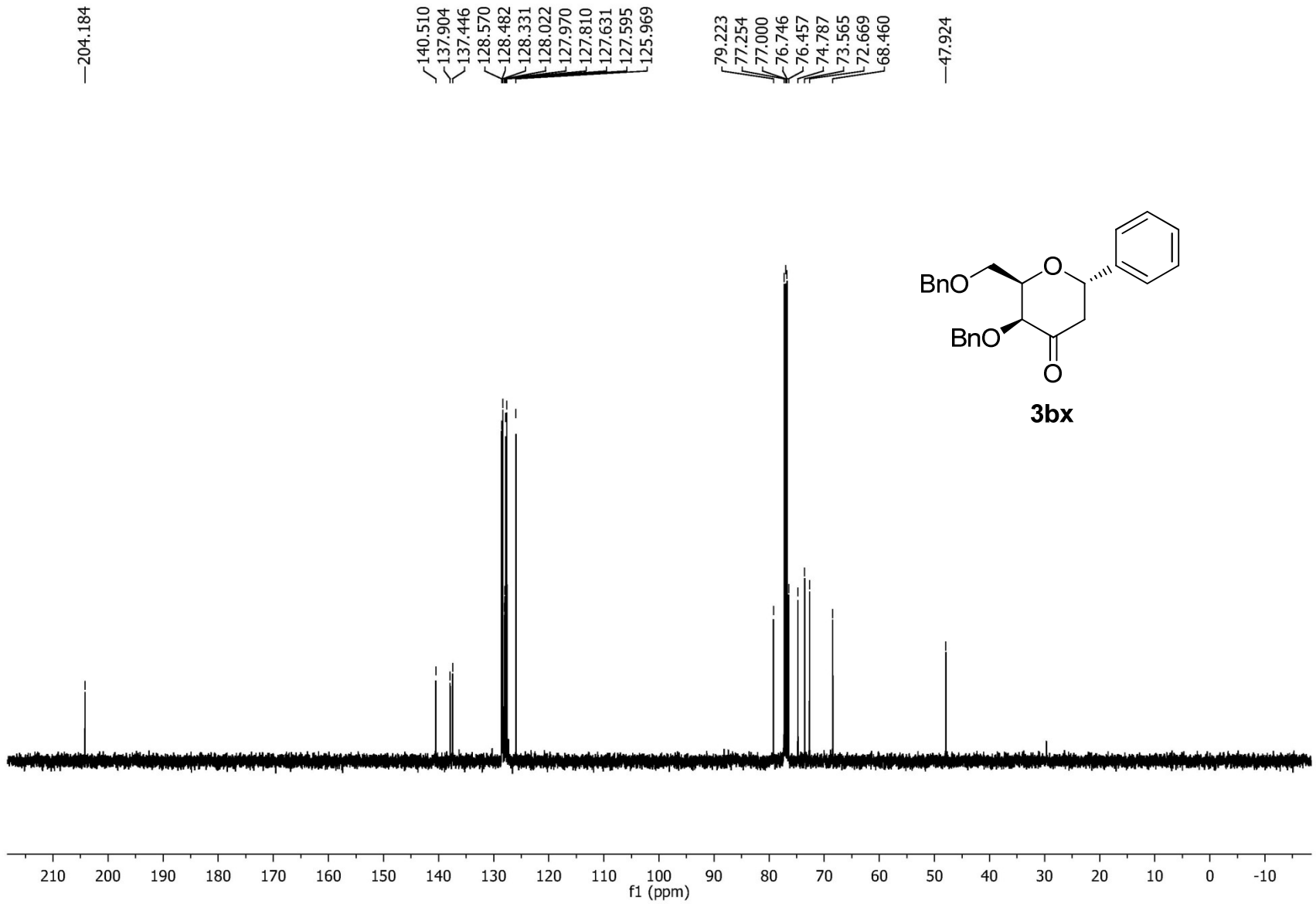

Figure S116: ^{13}C-NMR spectrum of compound 3bx in $CDCl_3$

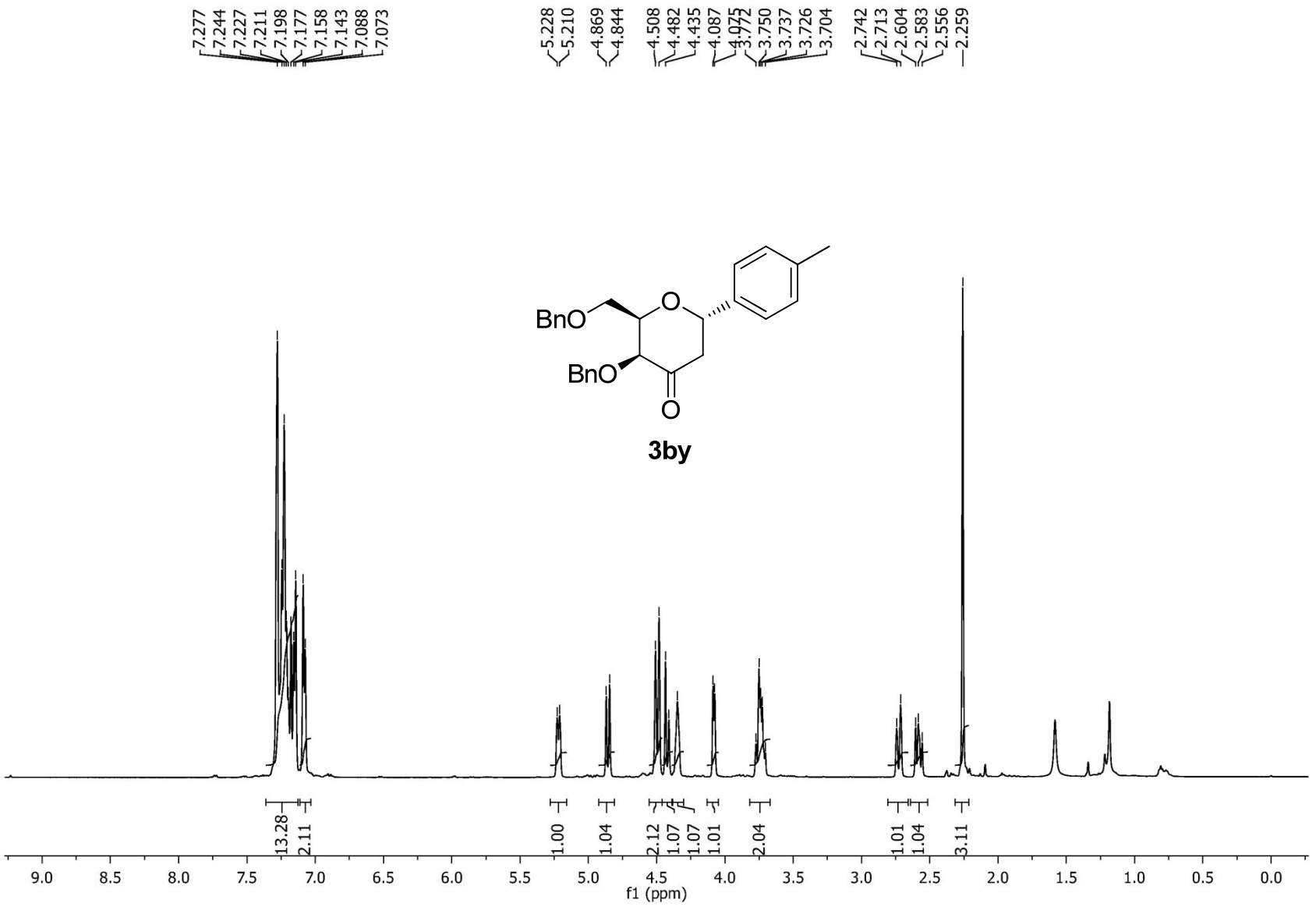

Figure S117: ^{1}H-NMR spectrum of compound 3by in $CDCl_3$

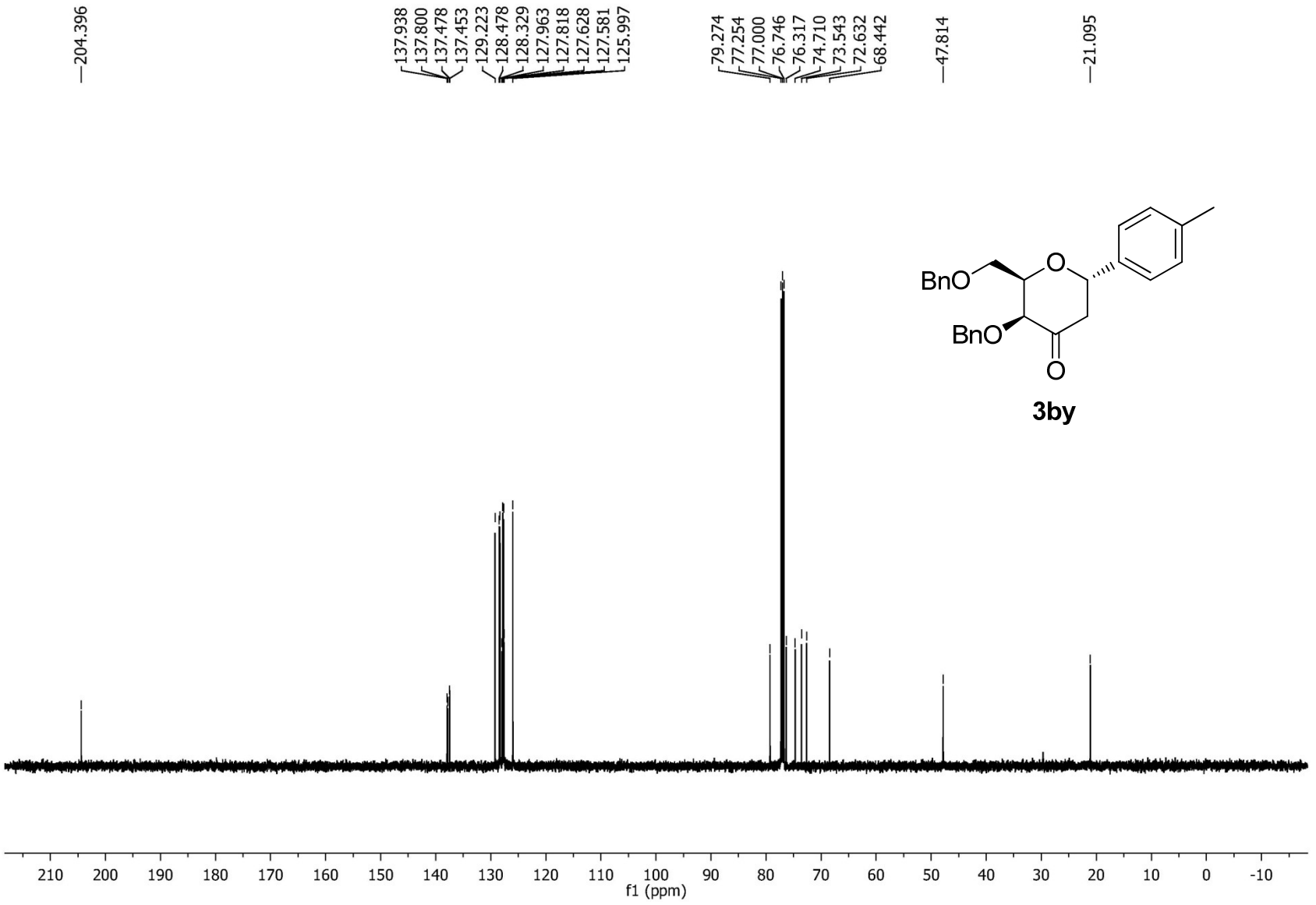

Figure S118: ^{13}C-NMR spectrum of compound 3by in $CDCl_3$

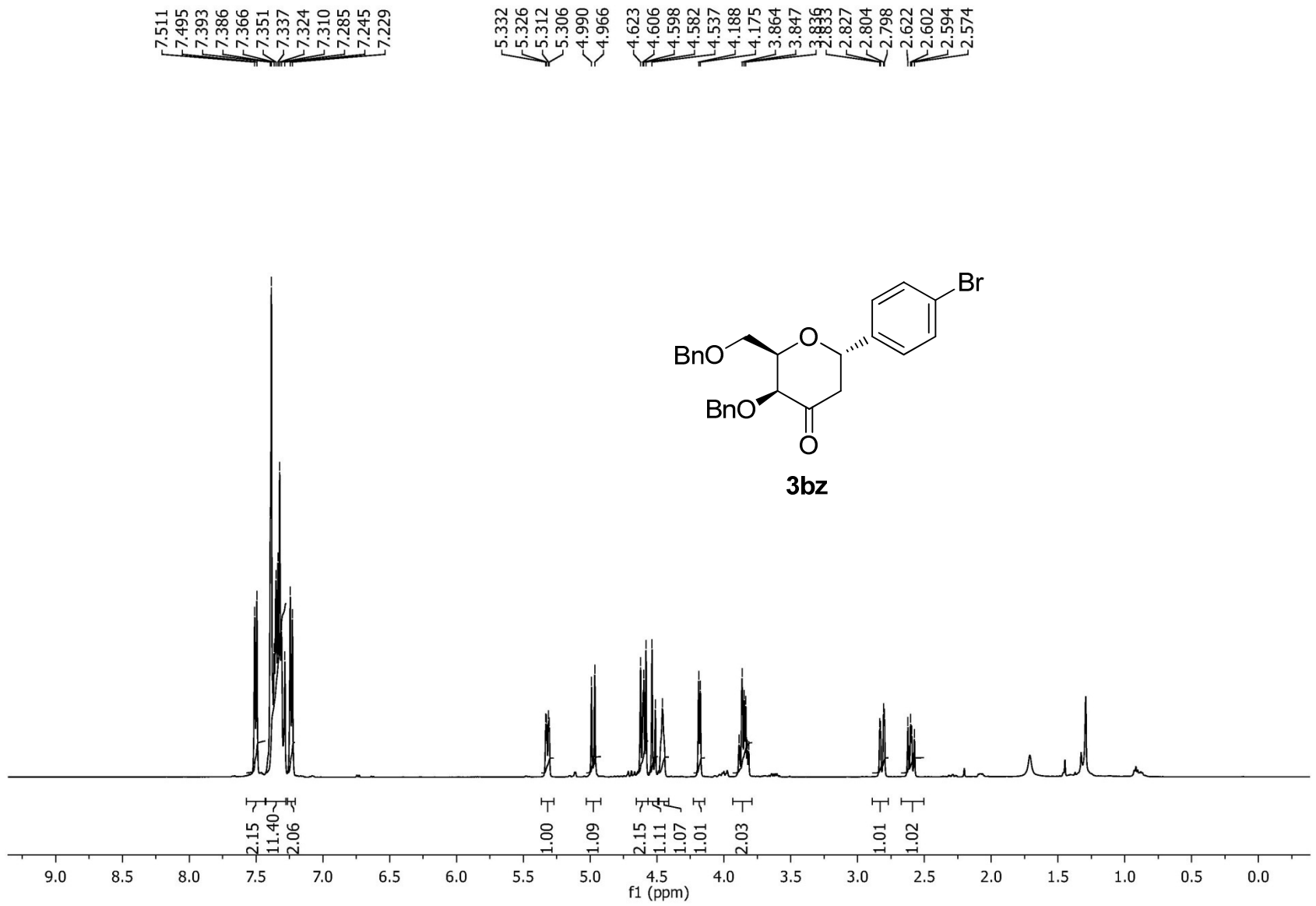

Figure S119: ^{1}H-NMR spectrum of compound 3bz in $CDCl_3$

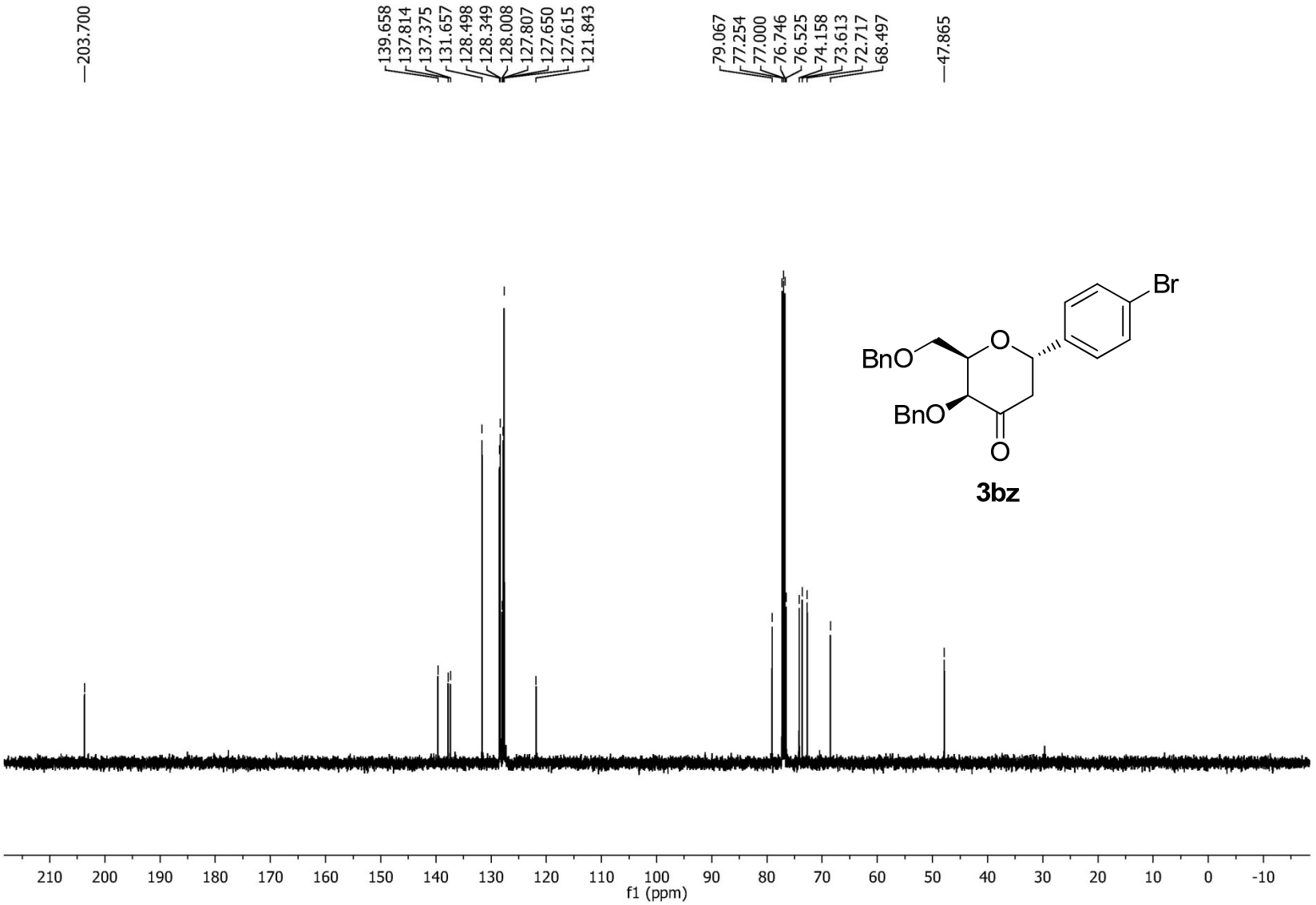

Figure S120: ^{13}C-NMR spectrum of compound 3bz in $CDCl_3$

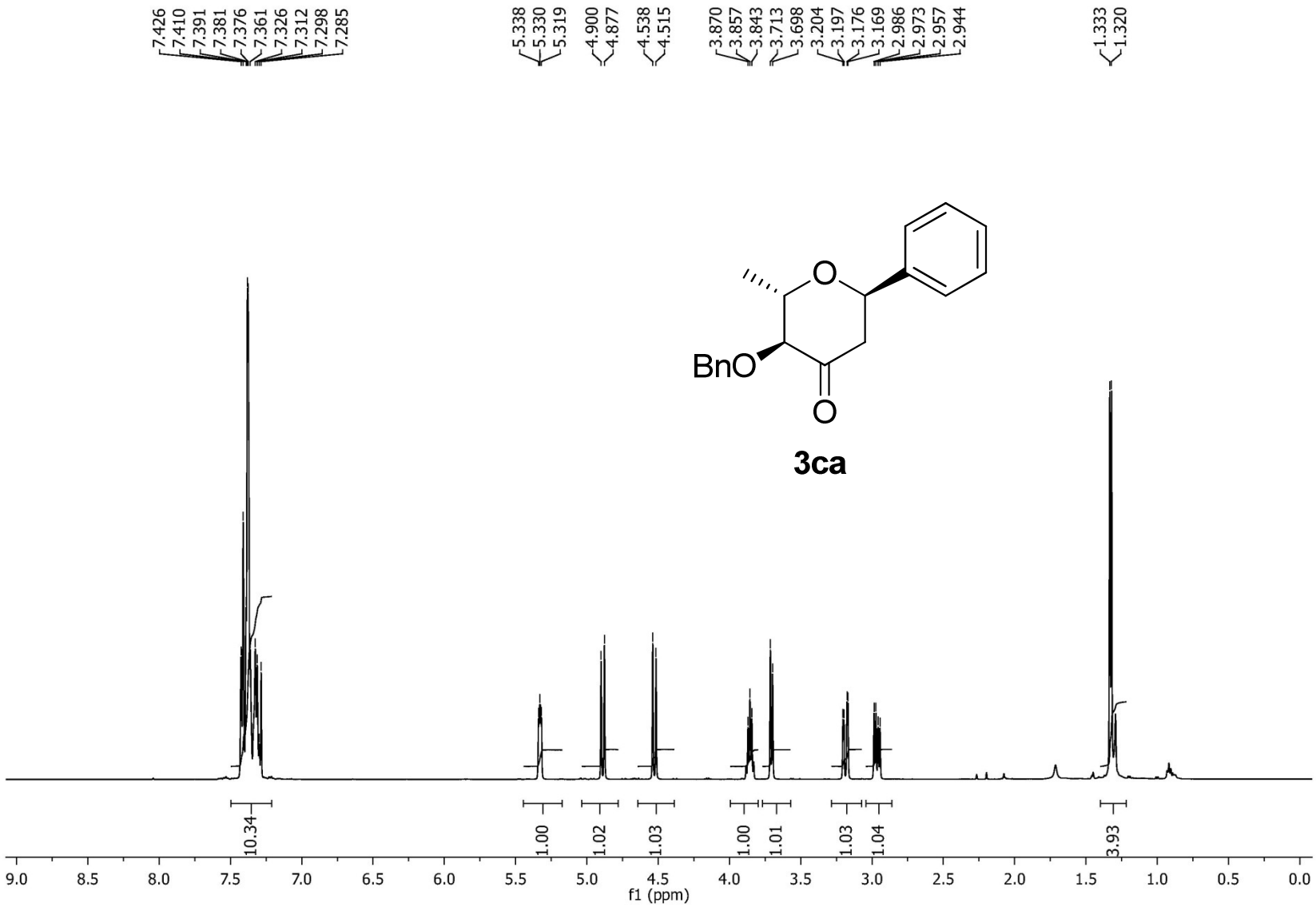

Figure S121: ^{1}H-NMR spectrum of compound 3ca in $CDCl_3$

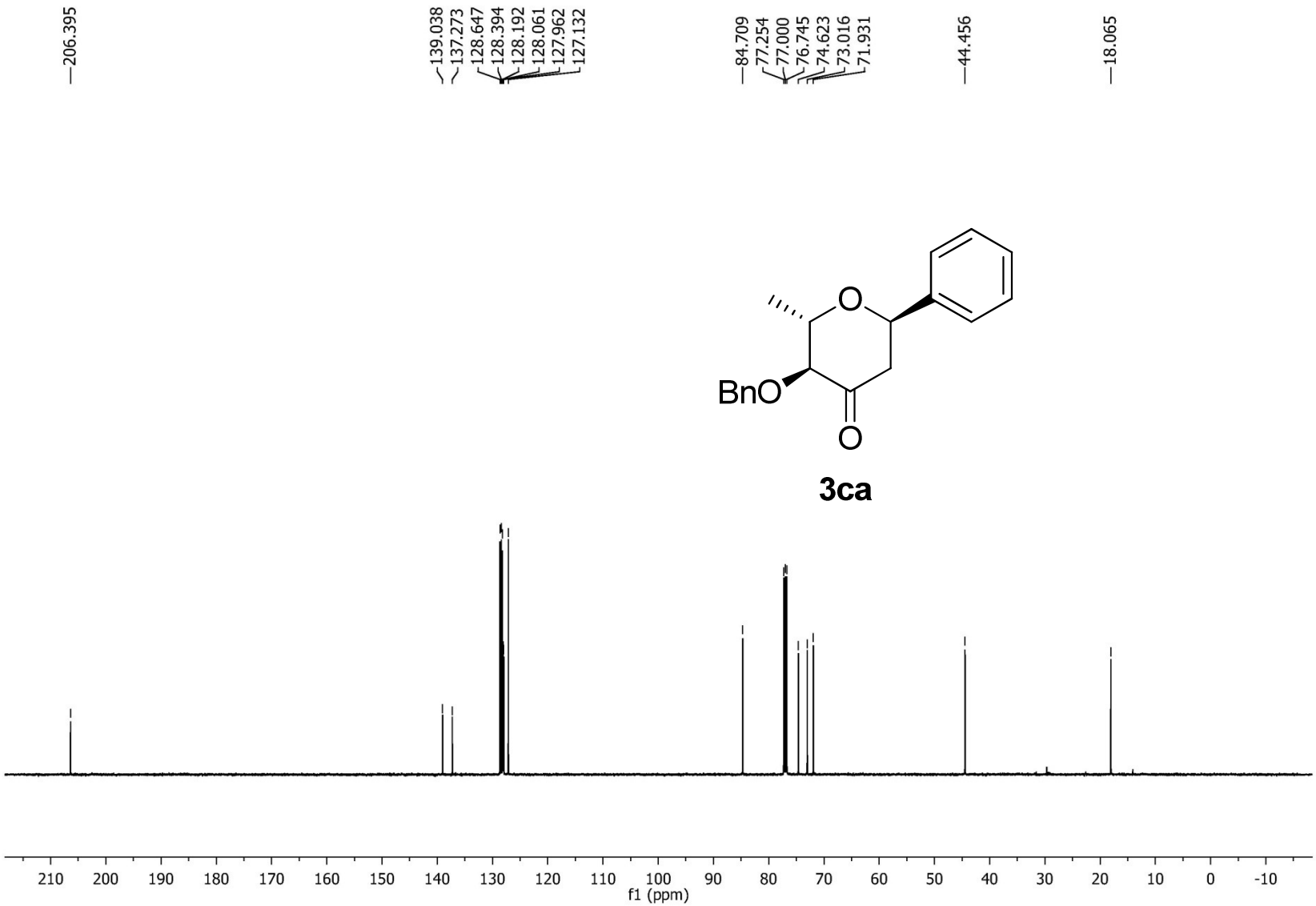

Figure S122: ^{13}C-NMR spectrum of compound 3ca in $CDCl_3$

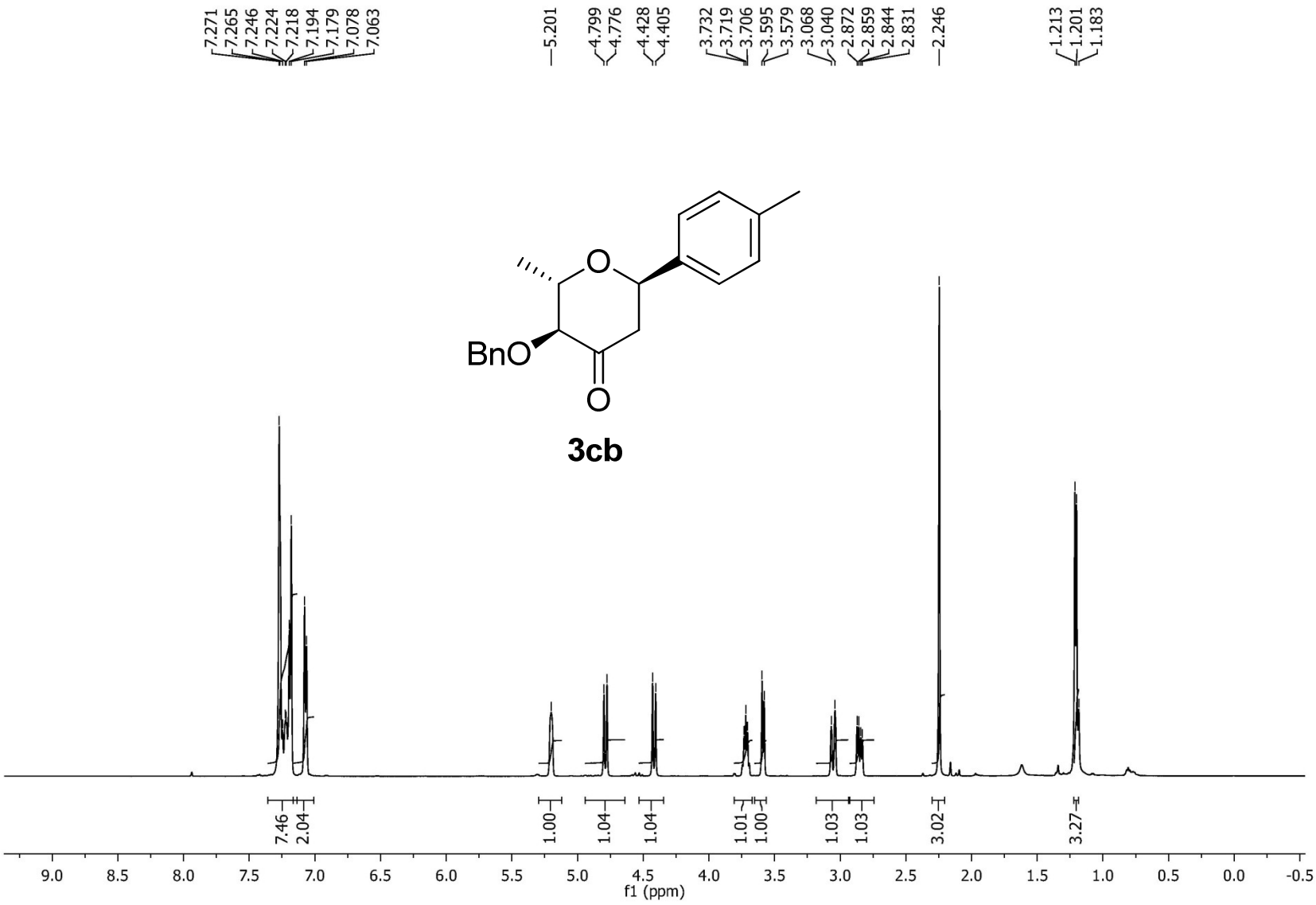

Figure S123: ^{1}H-NMR spectrum of compound 3cb in $CDCl_3$

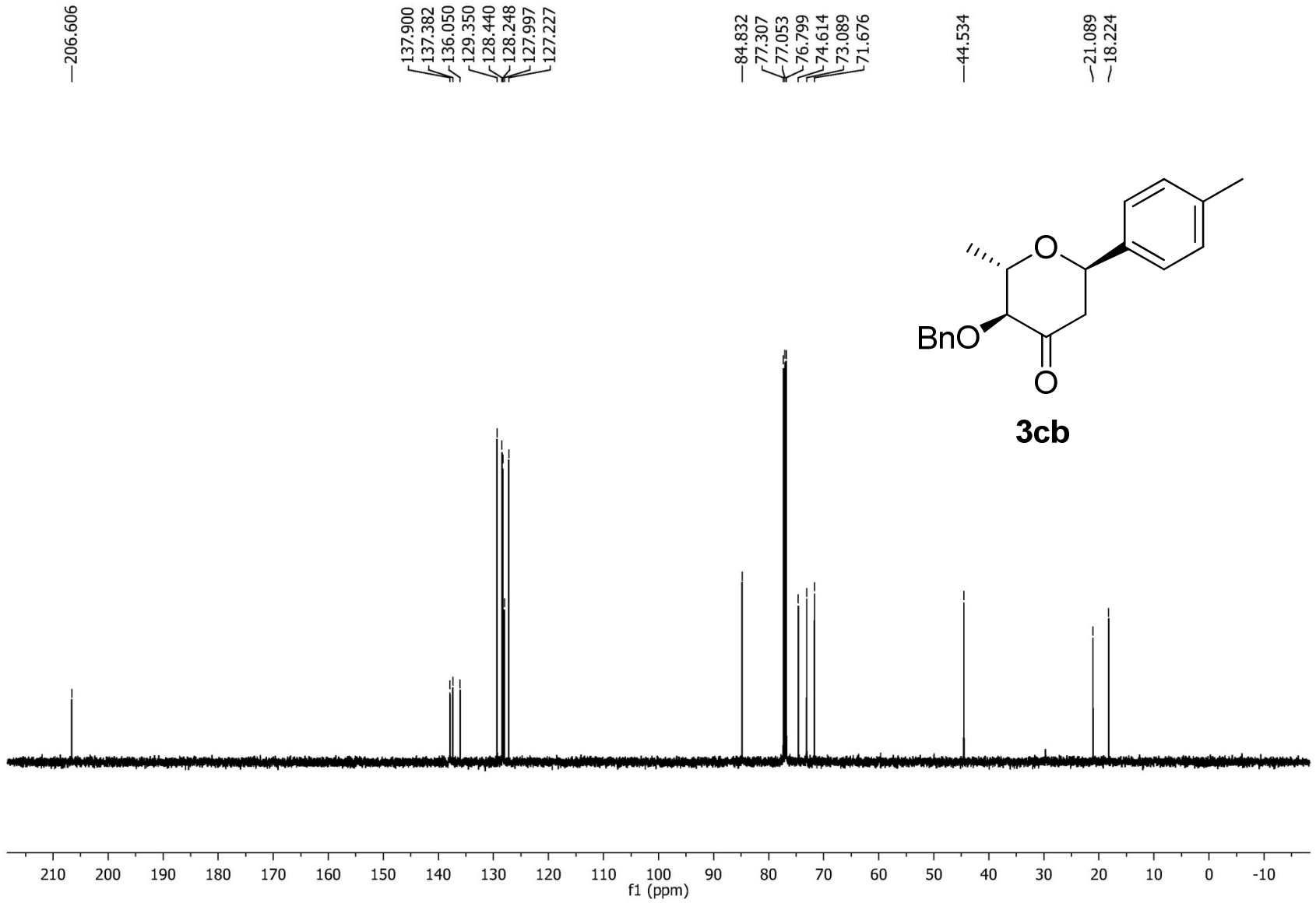

Figure S124: ^{13}C-NMR spectrum of compound 3cb in $CDCl_3$

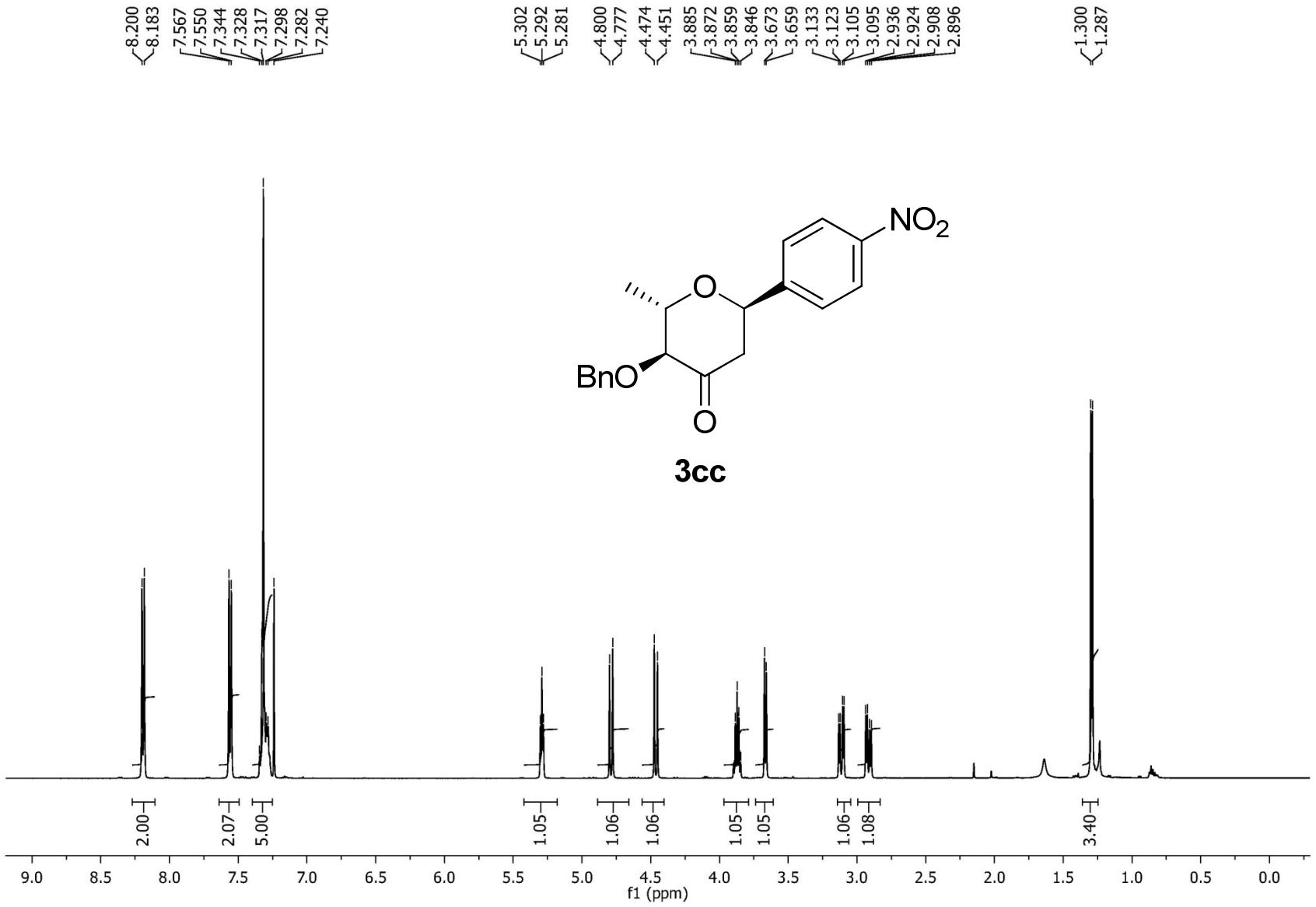

Figure S125: ^{1}H-NMR spectrum of compound 3cc in $CDCl_3$

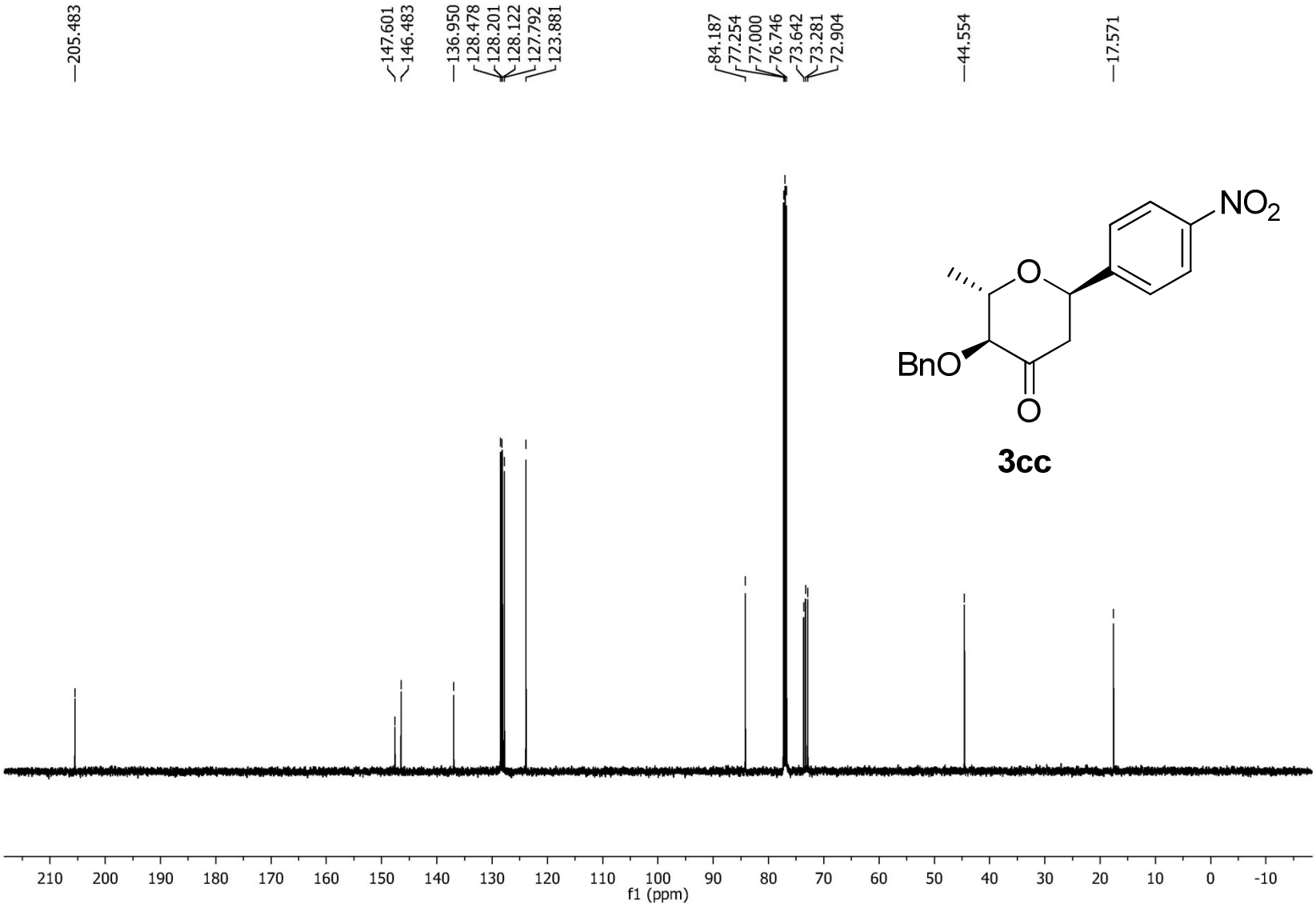

Figure S126: ^{13}C-NMR spectrum of compound 3cc in $CDCl_3$.

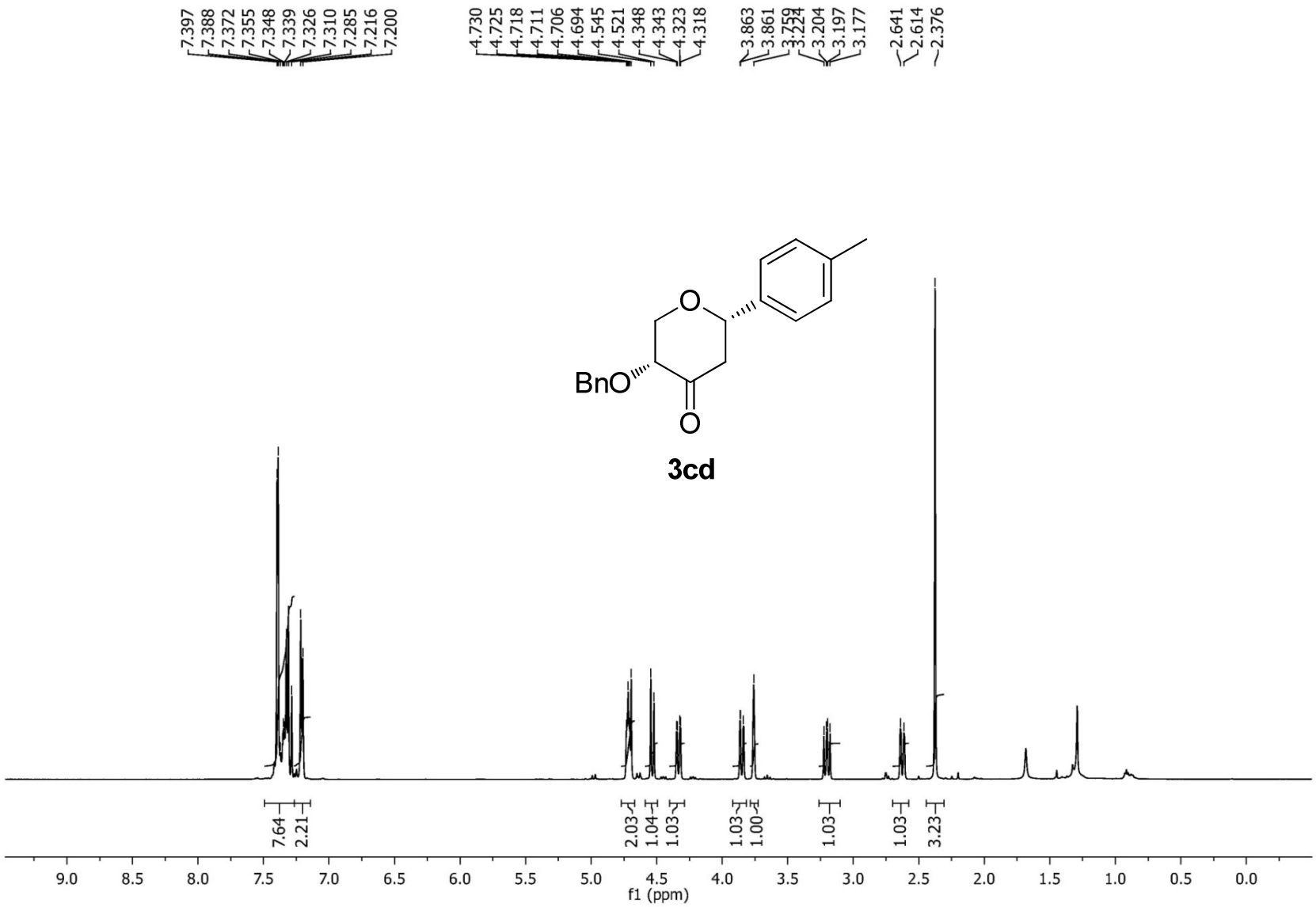

Figure S127: ^{1}H-NMR spectrum of compound 3cd in $CDCl_3$

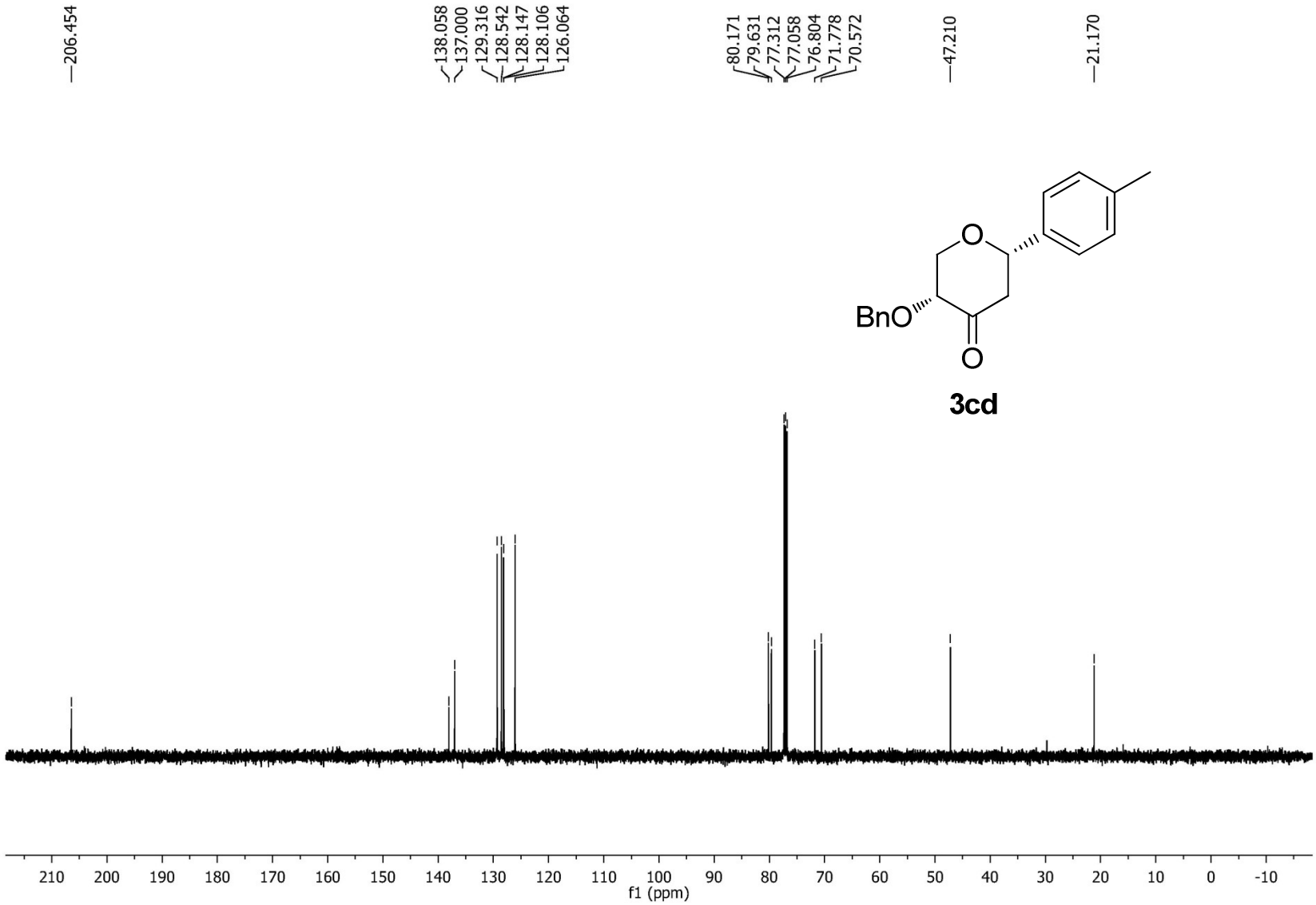

Figure S128: ^{13}C-NMR spectrum of compound 3cd in $CDCl_3$

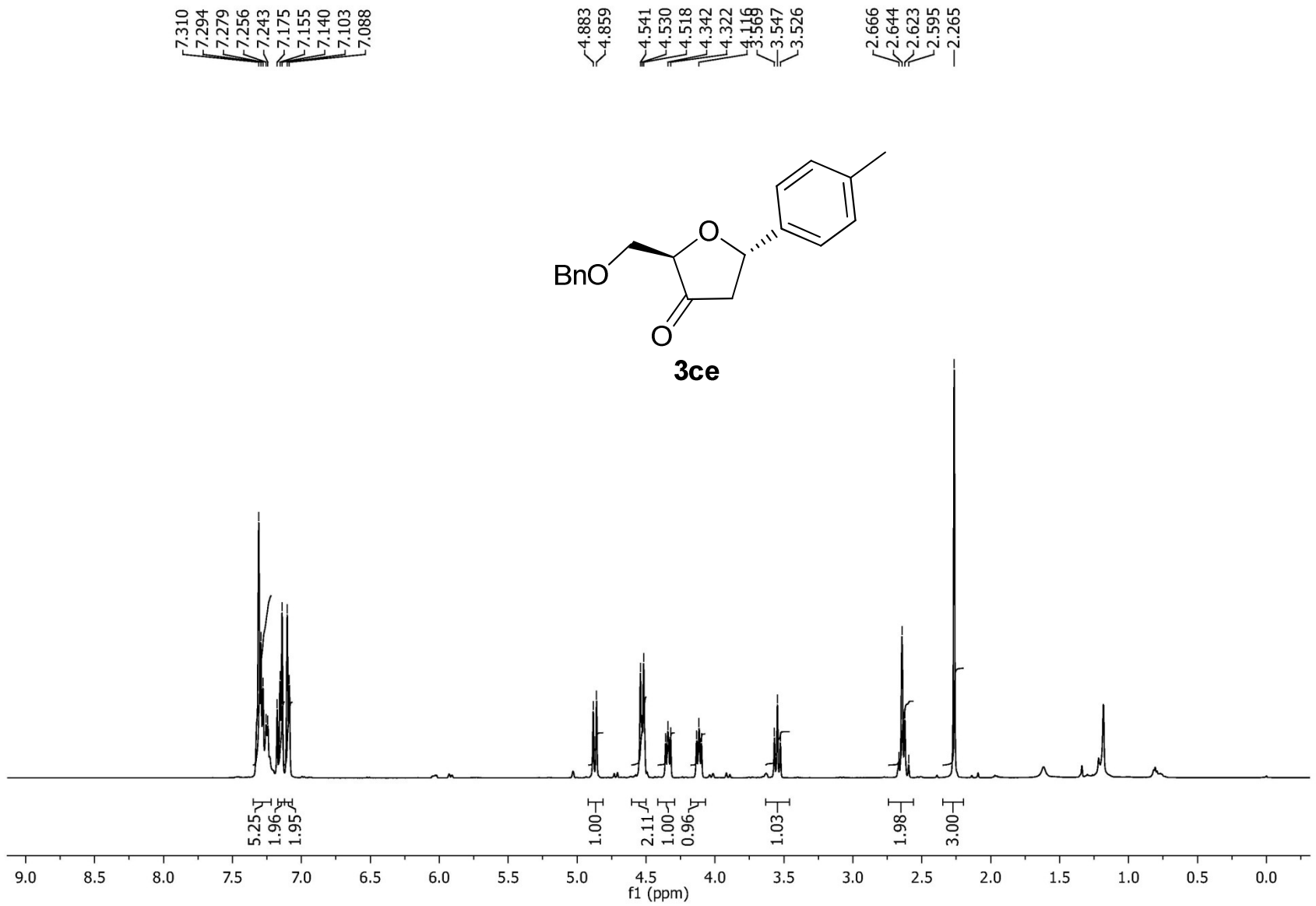

Figure S129: ^{1}H-NMR spectrum of compound 3ce in $CDCl_3$

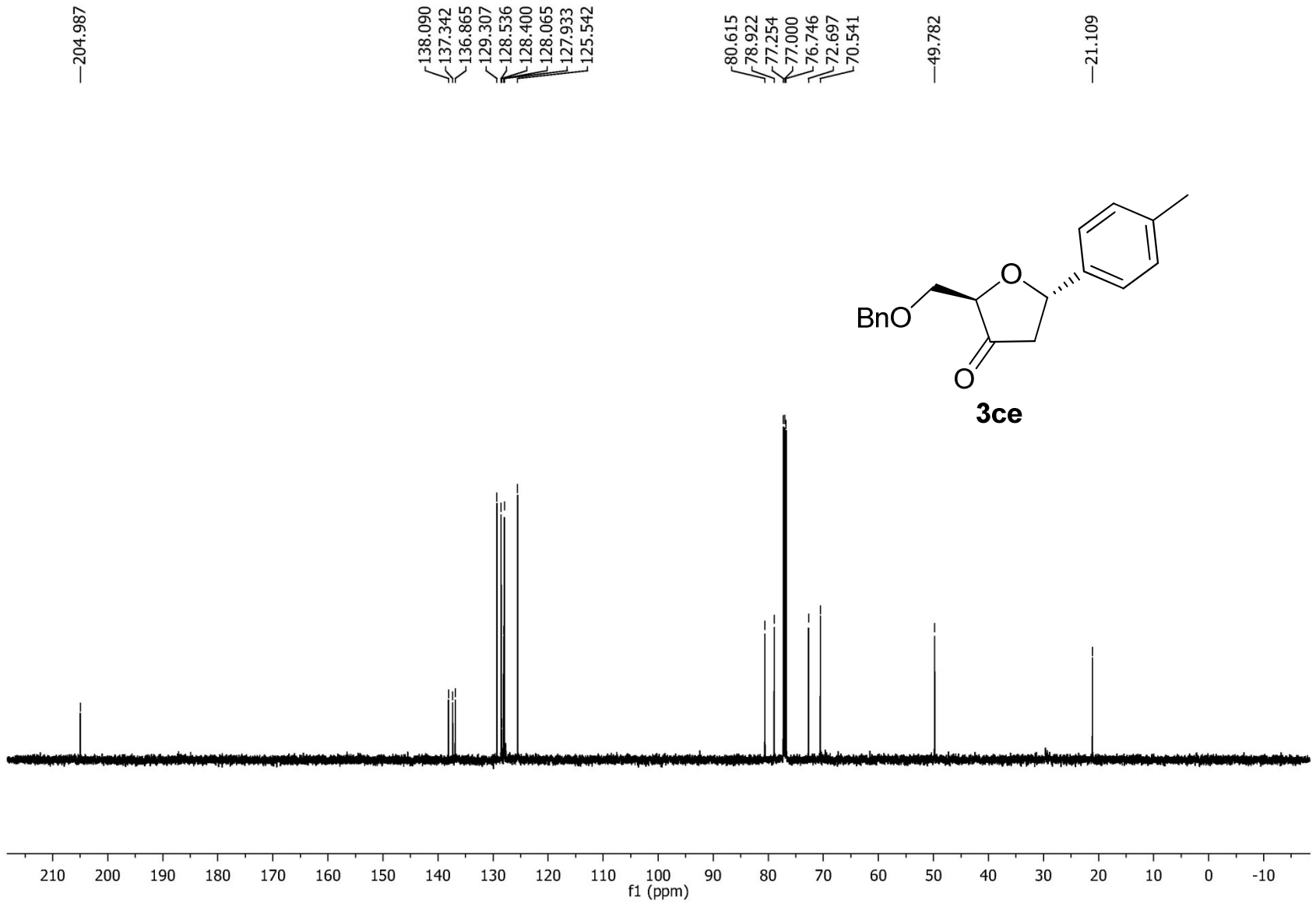

Figure S130: ^{13}C-NMR spectrum of compound 3ce in $CDCl_3$.

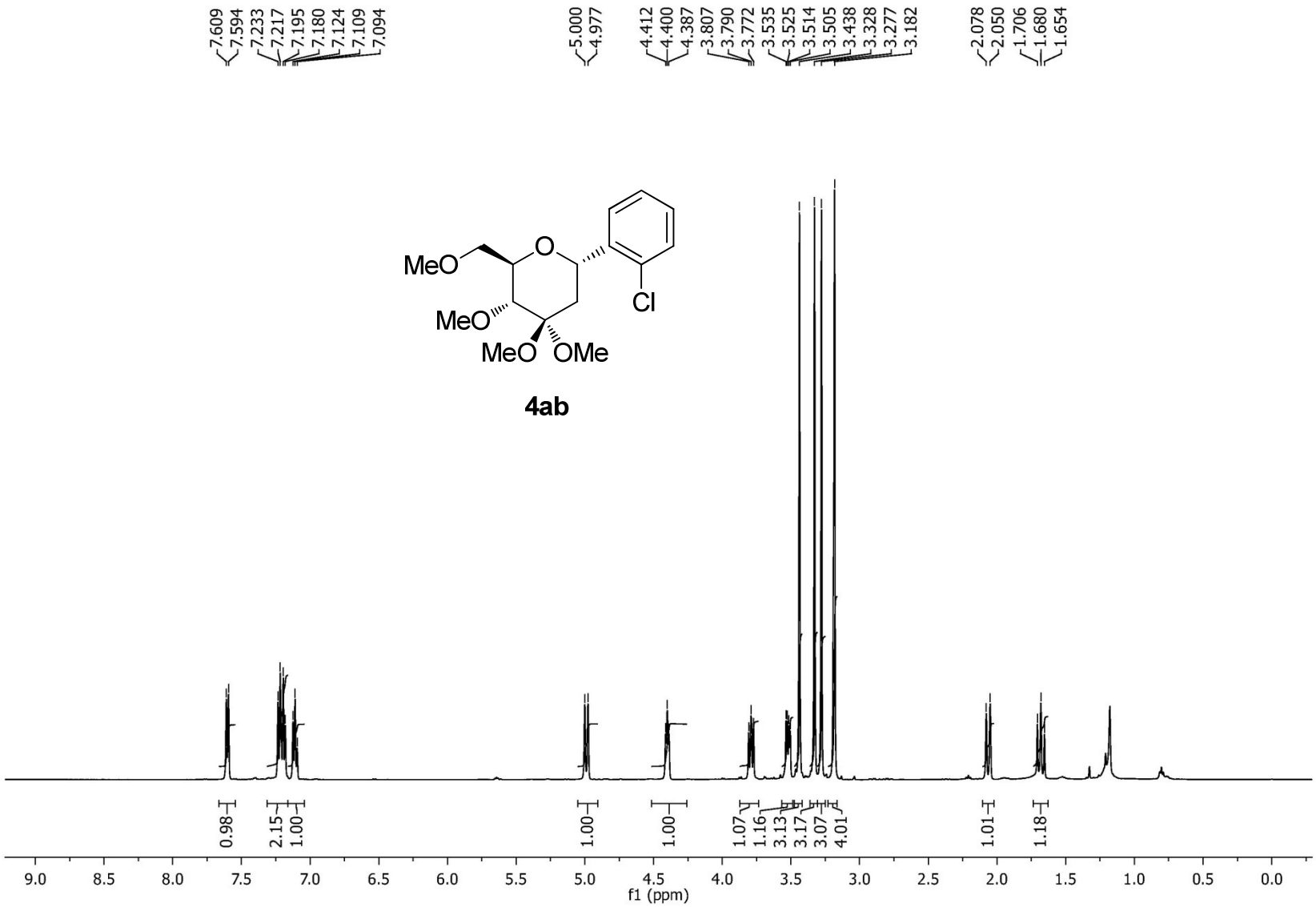

Figure S131: ^{1}H-NMR spectrum of compound 4ab in $CDCl_3$

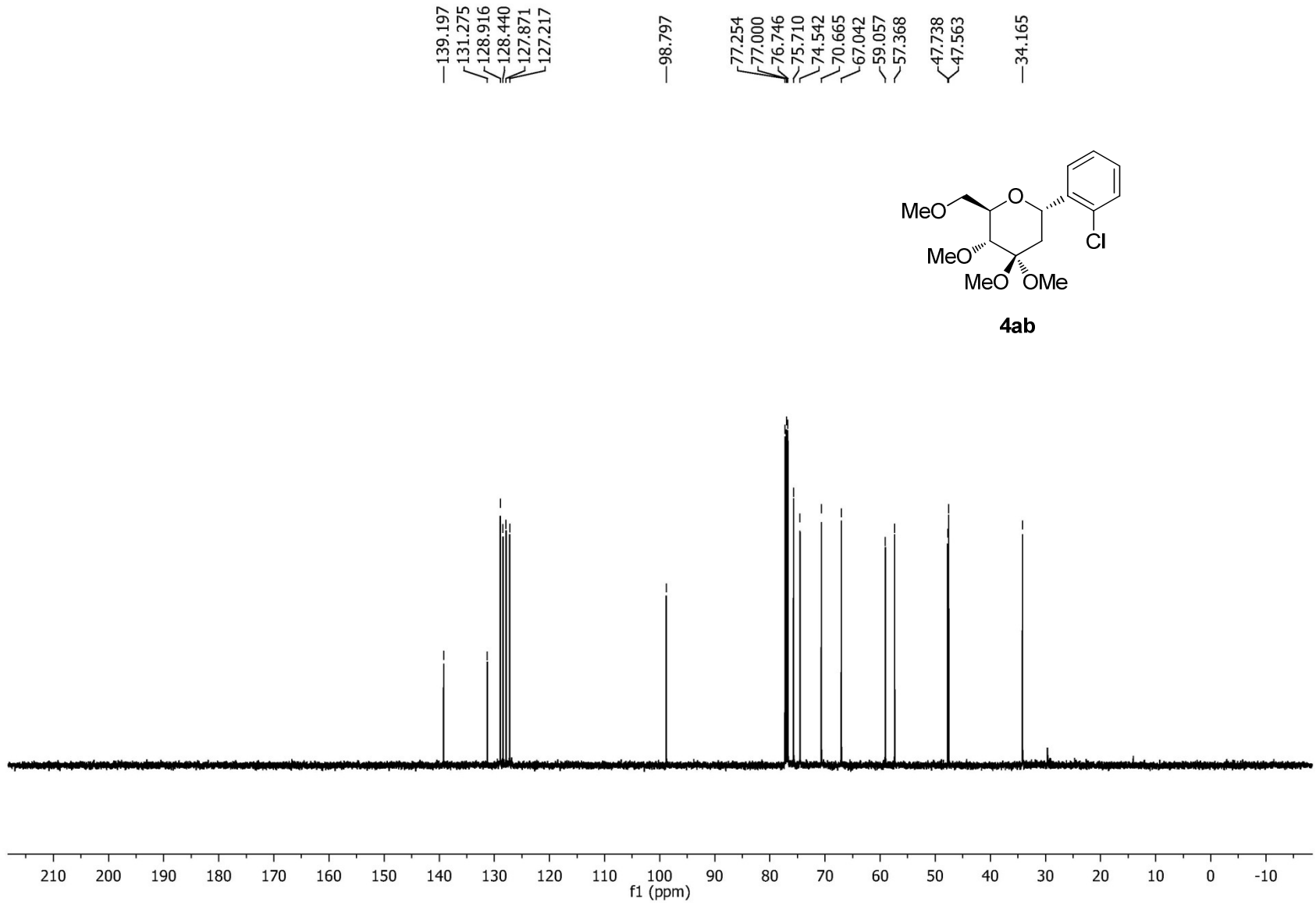

Figure S132: ^{13}C-NMR spectrum of compound 4ab in $CDCl_3$

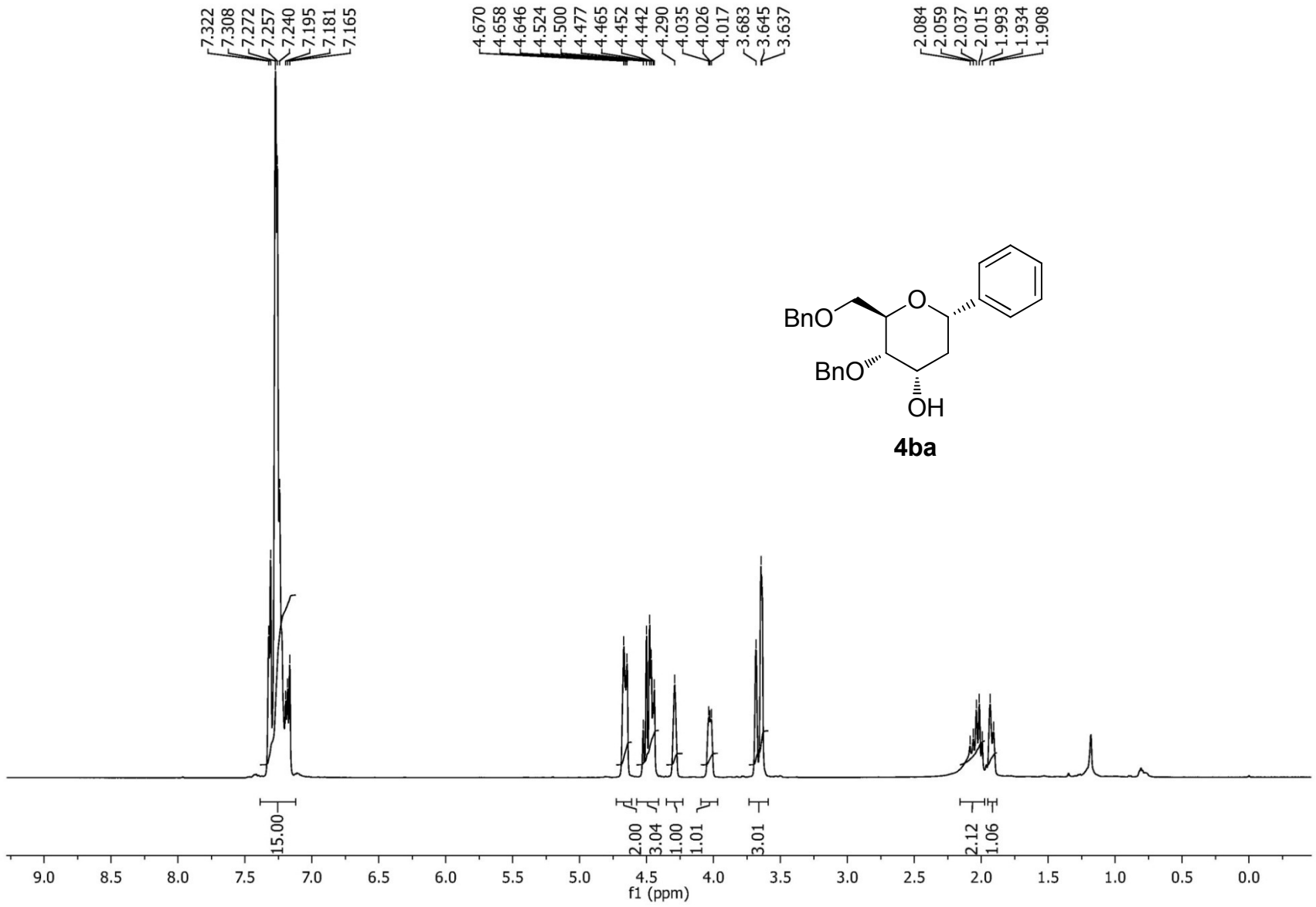

Figure S133: ^{1}H-NMR spectrum of compound 4ba in $CDCl_3$

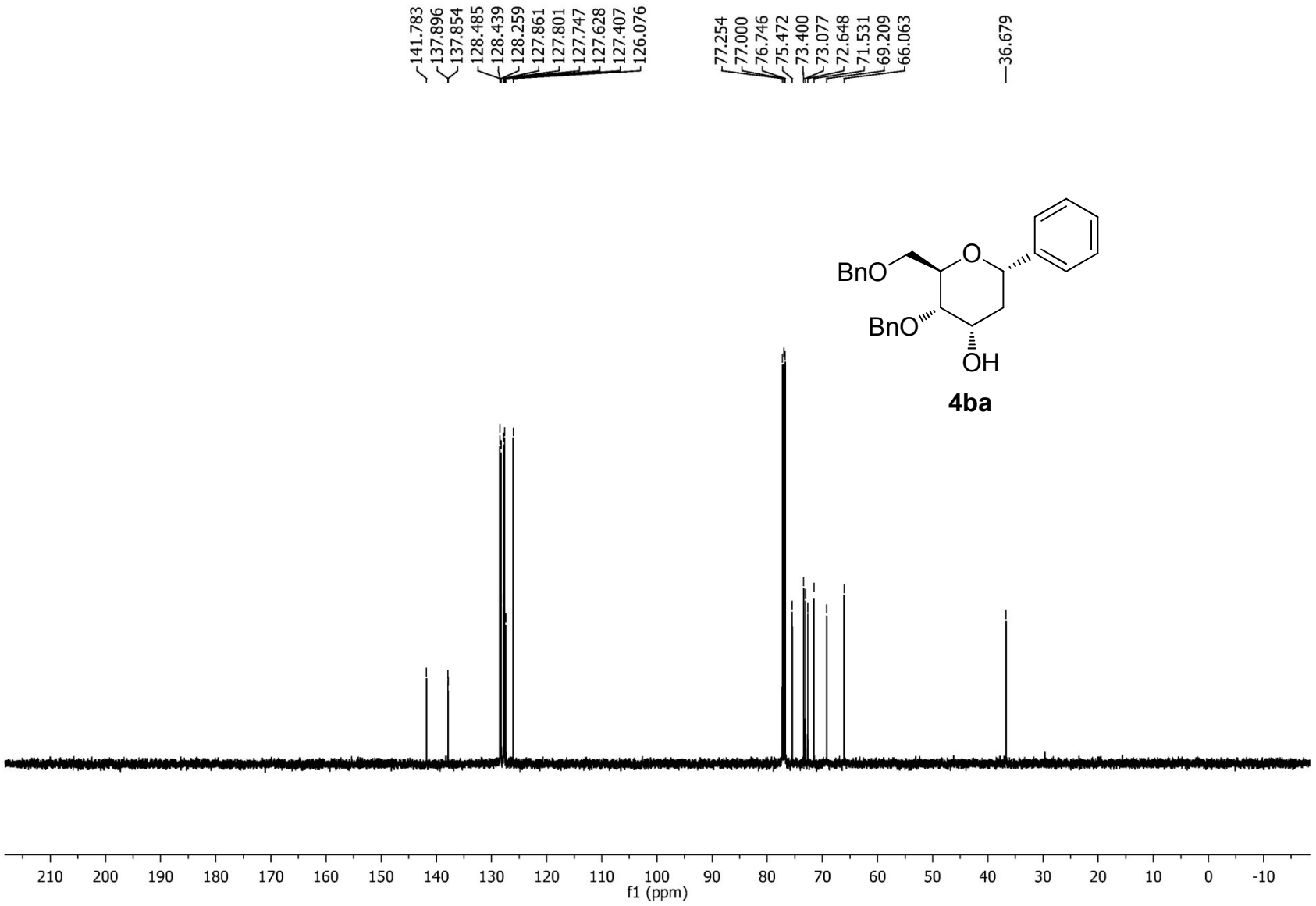

Figure S134: ^{13}C-NMR spectrum of compound 4ba in $CDCl_3$

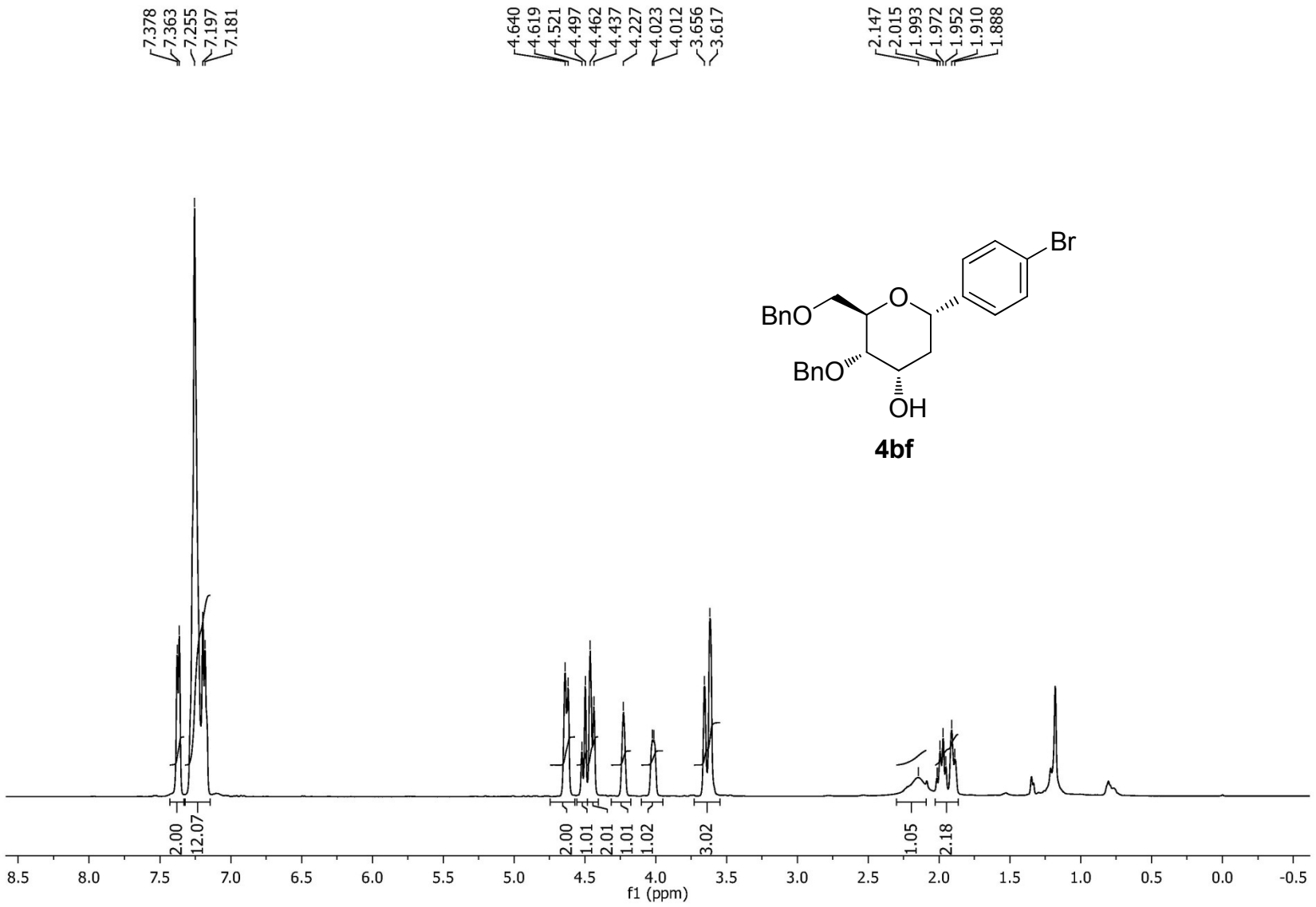

Figure S135: ^{1}H-NMR spectrum of compound 4bf in $CDCl_3$

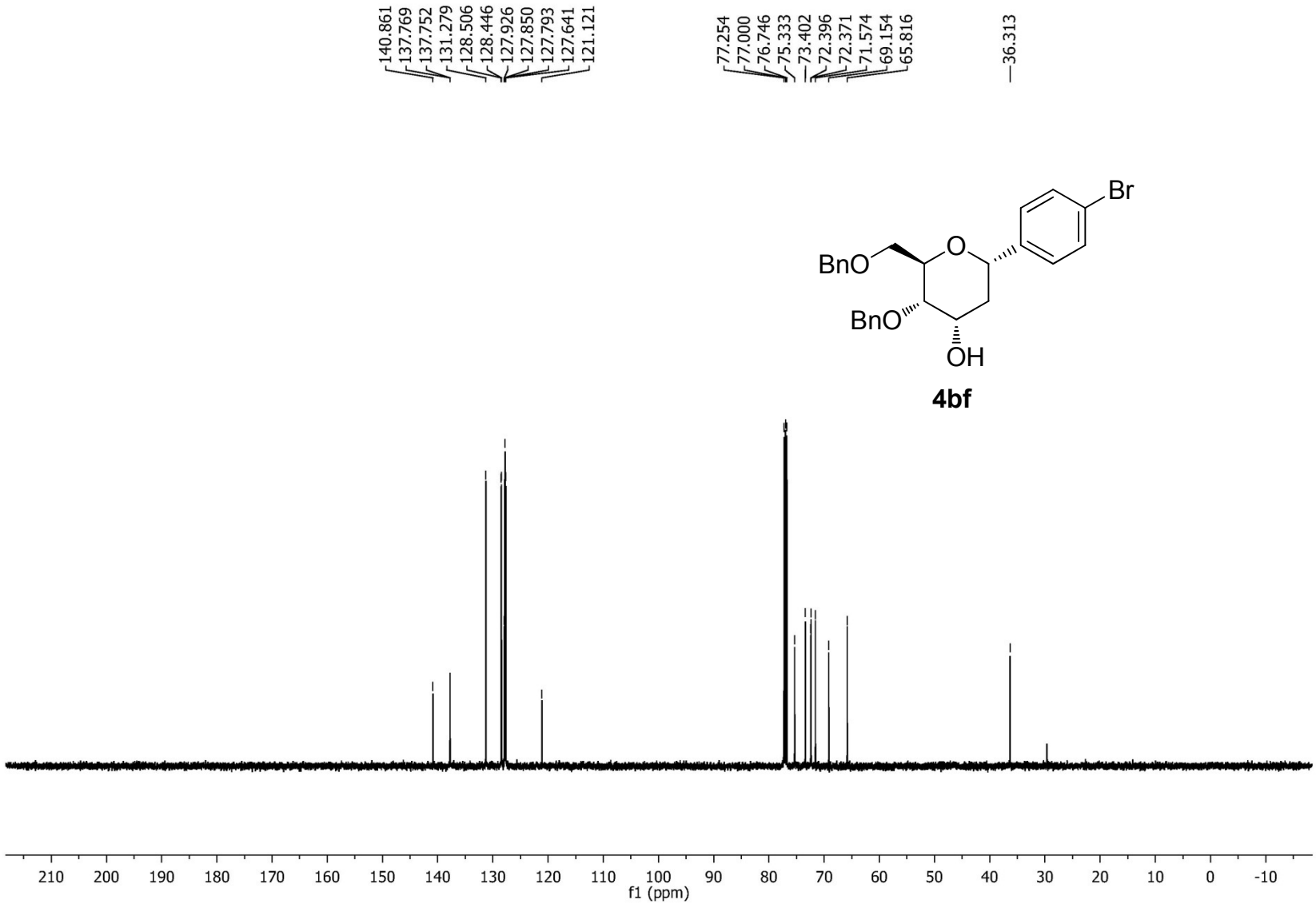

Figure S136: ^{13}C-NMR spectrum of compound 4bf in $CDCl_3$

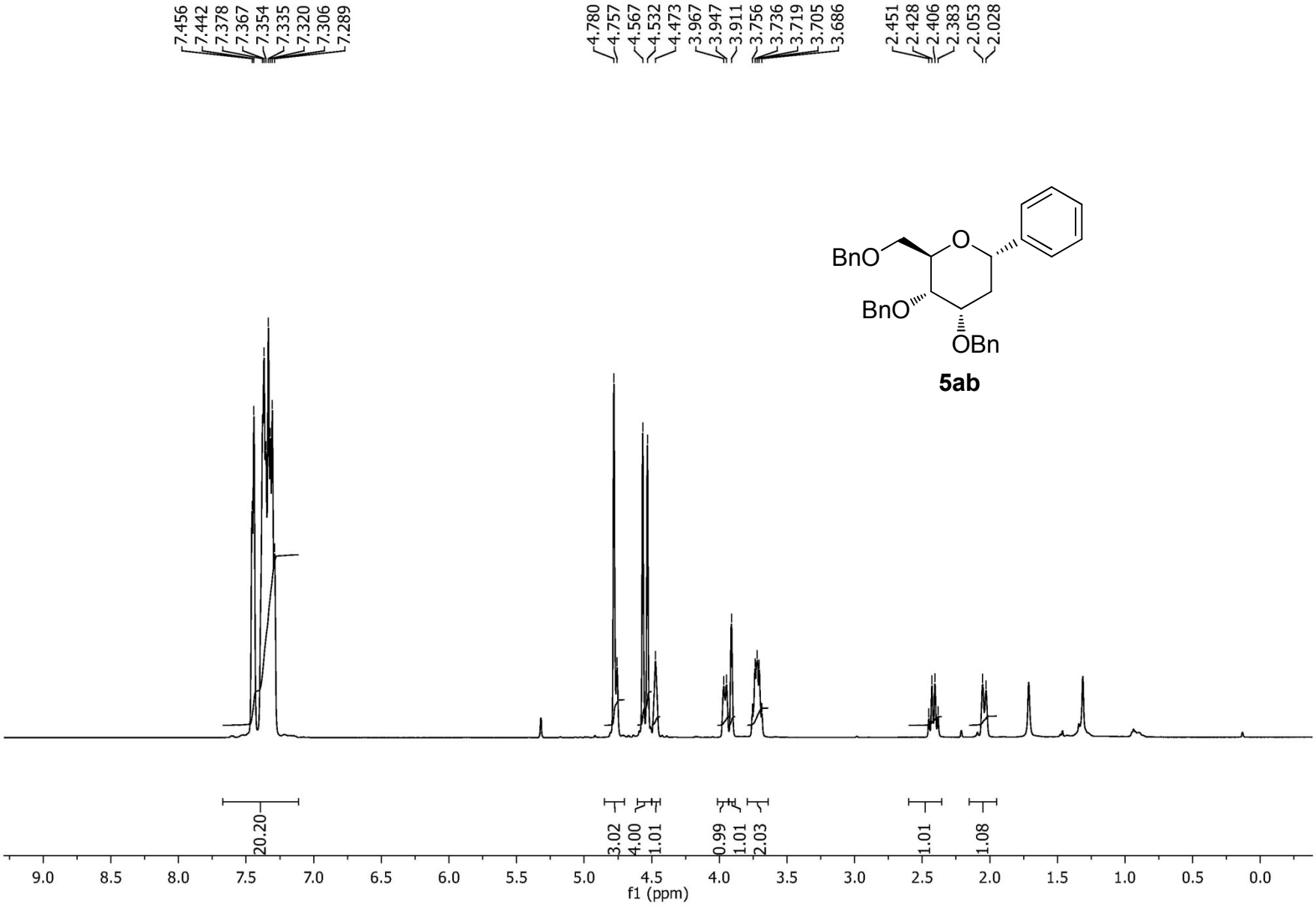

Figure S137: ^{1}H-NMR spectrum of compound 5ab in $CDCl_3$

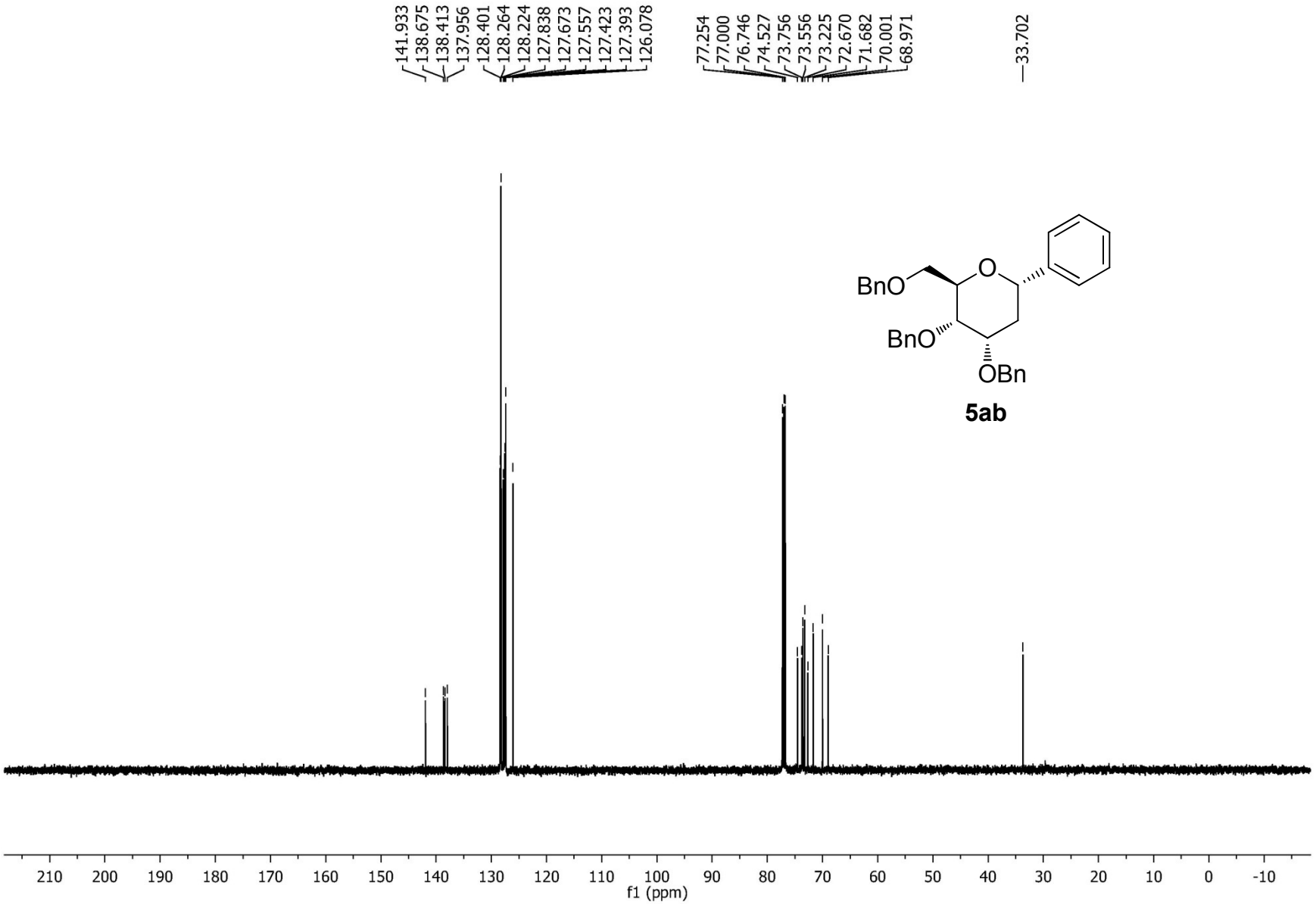

Figure S138: ^{13}C-NMR spectrum of compound 5ab in $CDCl_3$

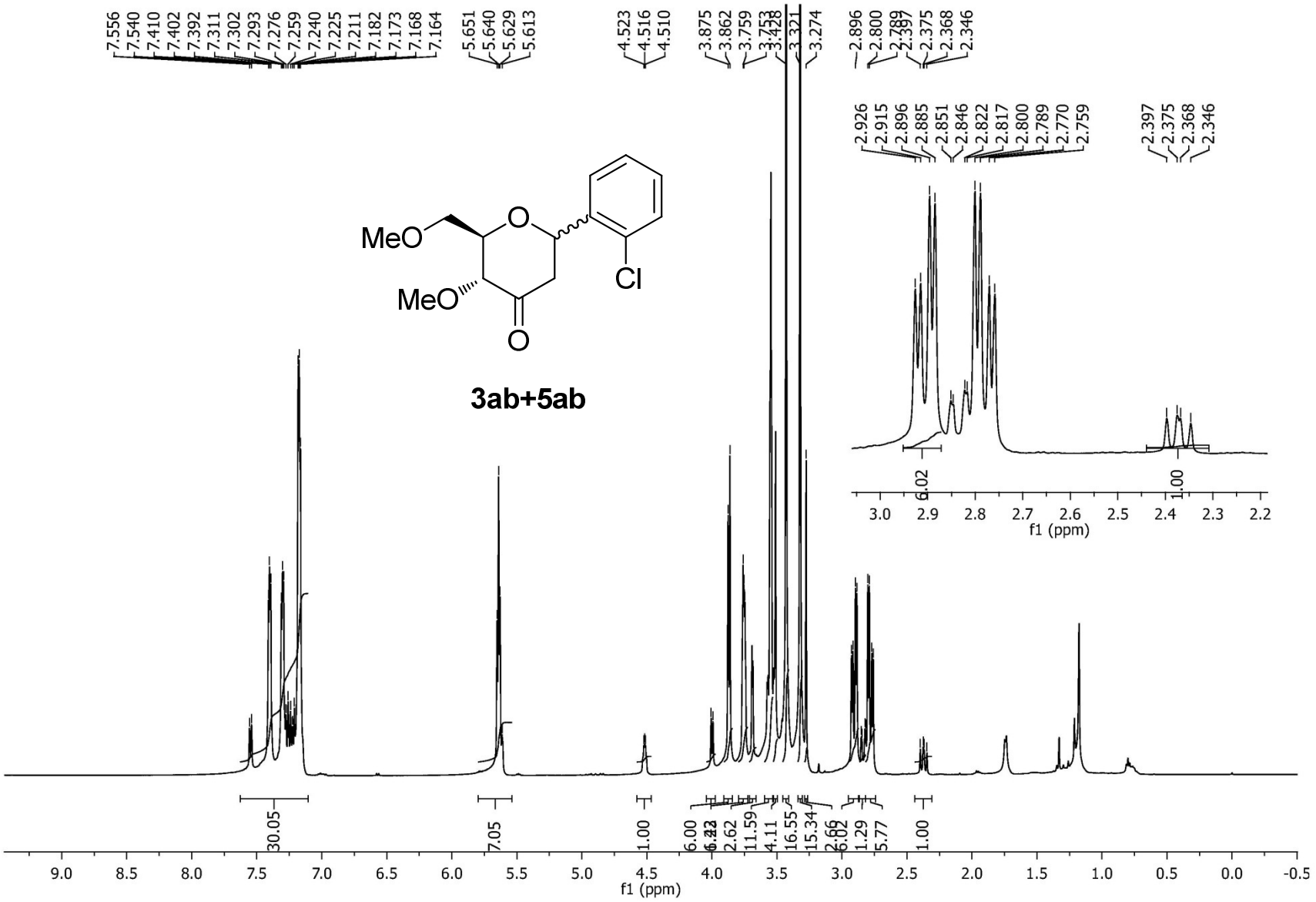

Figure S139: ^{1}H-NMR spectrum of compound 3ab+5ab in $CDCl_3$

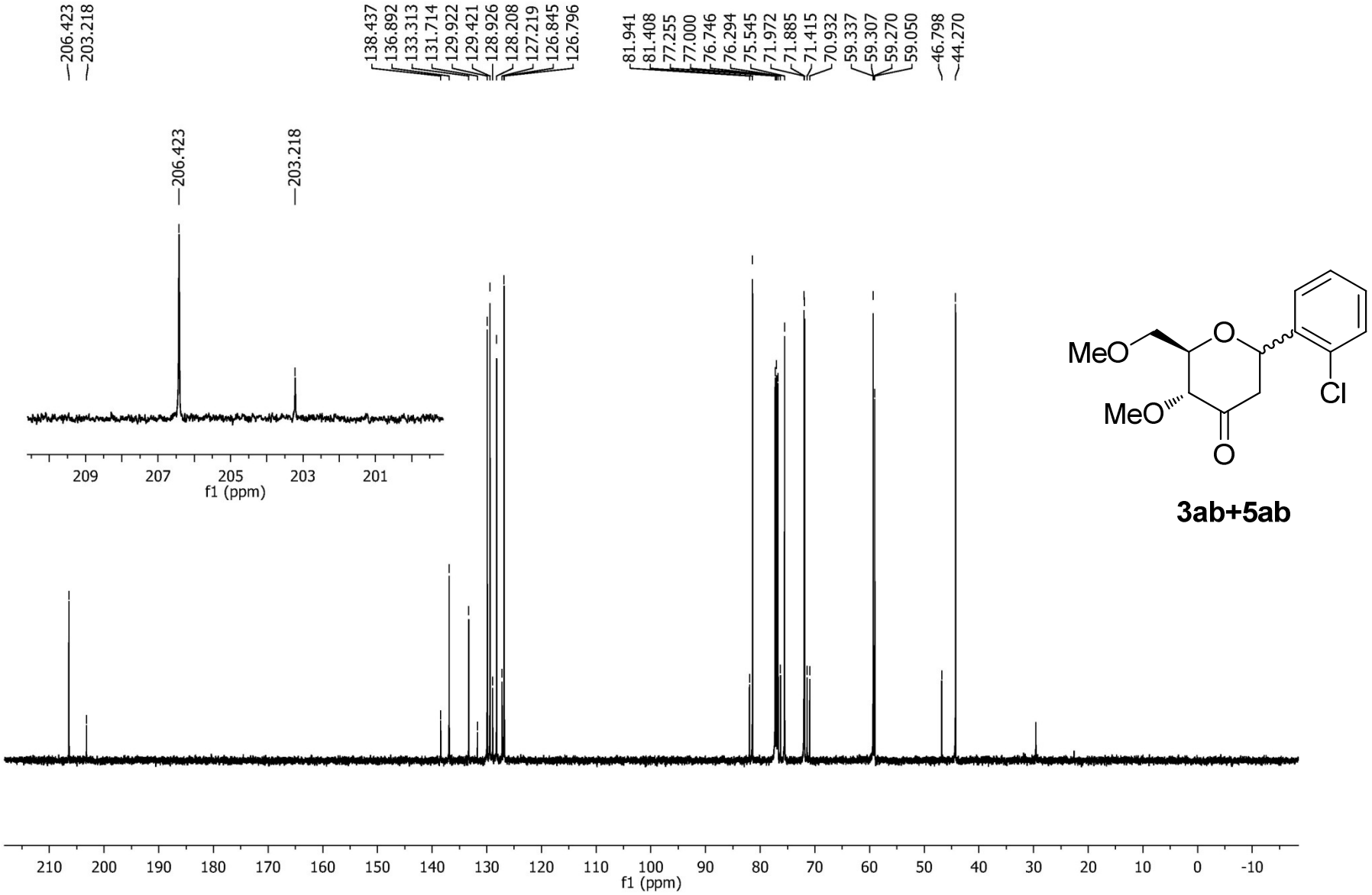

Figure S140: ^{13}C-NMR spectrum of compound 3ab+5ab in $CDCl_3$