SUPPORTING INFORMATION

An Efficient Synthesis of Geminal-Dialkyl Dienes for Olefin Metathesis Polymerization

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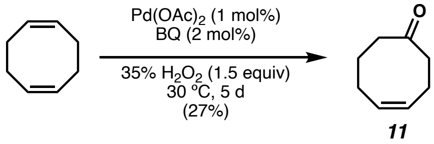
TABLE OF CONTENTS

General Considerations

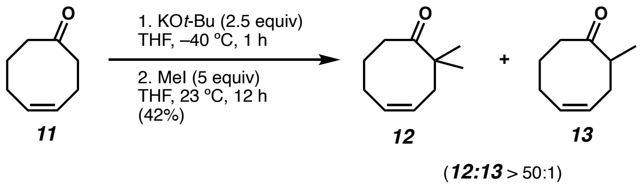
Unless otherwise stated, all reactions were performed under argon atmosphere using oven dried glassware. Anhydrous solvents were dried using activated alumina and stored in Schlenk flasks over activated 3 Å molecular sieves. All reagents were purchased from commercial suppliers ($TiCl_4$ was purchased from Acros Organics, all other reagents and solvents were purchased from Millipore Sigma) and used as received. $CDCl_3$ (99.8% D) was purchased from Cambridge Isotope Laboratories, Inc. and used as received. Methyl 9-decenoate was a donation from Elevance Renewable Sciences. The second generation Ru metathesis catalyst was received as a donation from Materia Inc. NMR spectra were collected using Varian 500 or 600 MHz spectrometers or a Bruker 400 MHz spectrometer. Mass spectrometry was performed at the Caltech Mass spectrometry facility. Differential Scanning Calorimetry was performed using a Mettler Toledo DSC 3+ Star System. Ethyl-(*E*)-hex-4-enoate, [i] and nona-1,8-dien-5-one [ii] were synthesized according to literature precedent.

Experimental Procedures



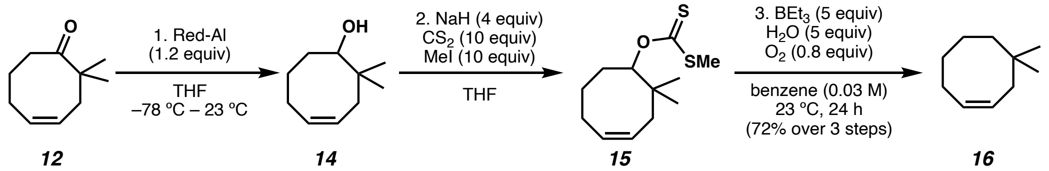
11

(*Z*)-cyclooct-4-en-1-one (11): According to a known procedure,[iii] a solution of hydrogen peroxide (35% in water, 5 mL, 60 mmol) was added to a mixture of palladium acetate (90 mg, 0.4 mmol), benzoquinone (87 mg, 0.8 mmol) and 1,5-cyclooctadiene (5.4 mL, 40 mmol). The mixture was stirred for 5 days at 30° C. The mixture was poured into Et_2O (100 mL) and water was added (100 mL) then the mixture was slowly basified with 1M NaOH solution while cooling with ice. The layers were separated and the aqueous layer was extracted with Et_2O (2 × 100 mL). The combined organic layers were twice washed with 1M NaOH and dried over Na_2SO_4. Distillation under reduced pressure afforded ketone **11** (1.36 g, 27% yield) as a colorless oil.
Spectral data matched those reported in the literature.[iv]



(*Z*)-2,2-dimethylcyclooct-4-en-1-one (12): To a stirred solution of KO*t*-Bu (5.61 g, 2.5 equiv) in THF (100 mL) was added ketone **11** (2.48 g, 20.0 mmol) in THF (20 mL). The solution was stirred for 1 hour at –40 ºC, and MeI (6.3 mL, 5.0 equiv) was added. The reaction mixture was slowly warmed to 23 ºC and stirring was continues for 20 hours. Water (50 mL) was then added and the aqueous phase was extracted by Et_2O (3 × 50 mL). GC analysis showed > 50:1 ratio of products **12** and **13**, and pure compound **12** can be isolated by column chromatography (SiO_2, 10:1 pentane/Et_2O) as a colorless liquid (1.29 g, 42%).

TLC (10:1 pentane/Et_2O): R_f= 0.4 ($KMnO_4$).
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.69 – 5.56 (m, 1H), 2.45 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.25 (d, *J* = 7.2 Hz, 1H), 2.15 – 2.07 (m, 1H), 1.64 – 1.54 (m, 1H), 1.06 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 217.5, 131.9, 129.2, 52.6, 37.8, 36.5, 27.3, 26.3, 23.7.
HRMS (FAB+, m/z): calc'd for $C_{10}H_{17}O$ $[M+H]^+$ 153.1279, found: 153.1276.



(*Z*)-4,4-dimethylcyclooct-1-ene (16): Ketone **12** (2.10 g, 13.8 mmol) in THF (50 mL) was added to a solution of Red-Al (16.6 mmol, 1.2 equiv) in THF (40 mL) dropwise at –78 °C under argon atmosphere. After stirring at the same temperature for 3 hours, the solution was quenched with 0.1 M HCl (100 mL), and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were then washed with saturated aqueous $NaHCO_3$ (50 mL) and brine (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was filtered through a plug of silica with Et_2O wash. The crude alcohol product **14** was obtained as a colorless oil (2.23 g), which was used in the next step without further purification.

To a suspension of NaH (60% in mineral oil, 2.24 g, 96 mmol, 4.0 equiv) in THF (100 mL) at 0 °C was added alcohol **14** (2.23 g, 14 mmol, 1.0 equiv) in THF (20 mL). The mixture was stirred for 30 min, at which point CS_2 (8.4 mL, 140 mmol, 10.0 equiv) was added. The mixture was stirred for an additional 30 min, at which point iodomethane (8.7 mL, 140 mmol, 10.0 equiv) was added. The reaction mixture was allowed to warm to room temperature for 3 hours before being quenched with MeOH (50 mL) and evaporated *in vacuo*. The residue was dissolved in EtOAc (100 mL), washed with water (50 mL) and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated. Column chromatography (SiO_2, hexanes) afforded crude xanthate **15** (4.42 g) as a yellow oil.

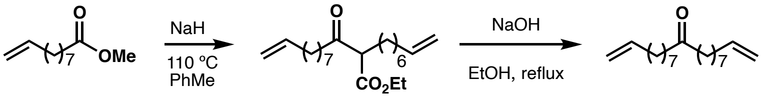
Then, methyl xanthate **15** (733 mg, 3 mmol, 1.0 equiv) was dissolved in a flame-dried 500 mL flask with benzene (100 mL), combined with H_2O (0.27 mL, 15 mmol, 5.0 equiv) and allowed to stir for 1 h. Argon gas was then bubbled through the solution for a period of 1 h, after which, a solution of BEt_3 (1.0 M in THF, 15 mL, 15 mmol, 5.0 equiv) was added via syringe pump over 1 h. On completion of BEt_3 addition, dry oxygen (54 mL, 2.4 mmol O_2, 0.8 equiv) was introduced

via syringe pump at a rate of 1.2 ml/hr through a stainless steel cannula positioned beneath the reaction surface. Upon completion of air addition, hydrogen peroxide (30 % in water, 50 mL) and sodium hydroxide (3.0 M in water, 50 mL) were introduced simultaneously into the reaction mixture (*Caution*: reaction is exothermic). After stirring for 10 min, the solution was diluted with brine (100 mL), and the aqueous layer was extracted with EtOAc (3 × 100 mL). Combined organic portions were dried over anhydrous sodium sulfate, filtered, and concentrated. Distillation under reduced pressure afforded **16** as a colorless oil (297 mg, 72%).
TLC (pentane): R_f= 0.9 ($KMnO_4$).

^{1}**H NMR** (400 MHz, $CDCl_3$) δ 5.85 – 5.48 (m, 2H), 2.17 – 2.04 (m, 2H), 1.92 (d, *J* = 8.2 Hz, 2H), 1.49 (dd, *J* = 6.0, 3.2 Hz, 4H), 1.33 – 1.23 (m, 2H), 0.89 (s, 6H).

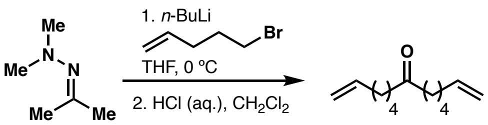
^{13}**C NMR** (126 MHz, $CDCl_3$) δ 131.4, 128.9, 39.7, 37.5, 36.1, 30.3, 29.0, 26.8, 23.5.

HRMS (EI+, m/z): calc'd for $C_{10}H_{18}$ $[M]^{+\bullet}$ 138.1409, found: 138.1408.



17 *18a* *18* (90%)

Nonadeca-1,18-dien-10-one (18): A 100 mL three-necked round bottom flask was fitted with a dropping funnel and two ground glass stoppers and charged with a magnetic stirbar, NaH (60 wt% in mineral oil, 3.7 g, 92 mmol, 1.2 equiv), and toluene (25 mL). This suspension was heated to 100 °C and a solution of methyl 9-decenoate (14.3 g, 80 mmol, 1 equiv) in toluene (10 mL) was added dropwise over the course of 30 min. The reaction mixture was then heated to 110 °C with stirring for 24 h, cooled to ambient temperature and quenched by the slow addition of MeOH. The solvent was removed *in vacuo* and the residue was suspended in EtOH (50 mL) and water (25 mL). NaOH (1.6 g, 1.0 equiv) was added and the reaction mixture was heated to reflux for 2 h. After cooling to ambient temperature, the reaction mixture was extracted with Et_2O (3 × 50 mL) and the combined organic layers were washed with water (3 × 50 mL), brine (30 mL), dried over anhydrous $MgSO_4$, filtered, and concentrated. Crystallization with MeOH afforded **18** as a white solid (10.2 g, 90% yield over two steps)
Spectral data matched those reported in the literature.[v]



25 *26* (90%)

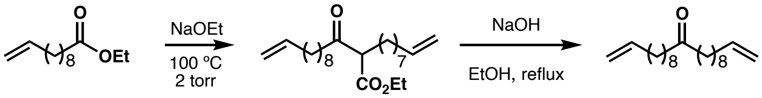
Trideca-1,12-dien-7-one (26): To a stirred solution of hydrazone **25** (4.0 g, 40 mmol, 1.0 equiv) in THF (80 mL) was added *n*-butyl lithium solution (16.8 mL, 2.5 M solution in hexanes, 42 mmol, 1.05 equiv). After stirring 30 minutes at 0 ºC, 5-bromo-1-pentene (4.8 mL, 40 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 1 hour at 23 ºC. Then the reaction mixture was cooled to 0 ºC again and *n*-butyl lithium solution (16.8 mL, 2.5 M solution in hexanes, 42 mmol, 1.05 equiv) was added. After stirring 30 minutes at 0 ºC, 5-bromo-1-pentene (4.8 mL, 40 mmol, 1.0 equiv) was added again and the reaction mixture was stirred for 2 hours at 23 ºC before quenched by saturated NH_4Cl solution (100 mL). The aqueous layer was extracted with Et_2O (2 × 100 mL) and the combined organic phases were washed with brine (100 mL), dried over anhydrous

$MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction mixture was dissolved in CH_2Cl_2 (40 mL), and HCl solution (16 mL, 3.0 M) was added. After 12 h, the phases were separated and the aqueous phase was extracted with CH_2Cl_2 (2 × 50 mL). The combined organic phases are washed with saturated $NaHCO_3$ solution (100 mL). Column chromatography (SiO_2, 10:1 hexanes/EtOAc) gave **26** as a colorless oil (7.0 g, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.66 (ddt, *J* = 16.9, 10.2, 6.5 Hz, 2H), 4.94 – 4.77 (m, 4H), 2.32 – 2.23 (m, 4H), 1.97 – 1.88 (m, 4H), 1.46 (dt, *J* = 15.2, 7.3 Hz, 4H), 1.30 – 1.20 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 211.2, 138.5, 114.6, 42.6, 33.6, 28.5, 23.3.

HRMS (EI+, m/z): calc'd for $C_{13}H_{22}O$ $[M]^{+\bullet}$ 194.1671, found: 194.1646.



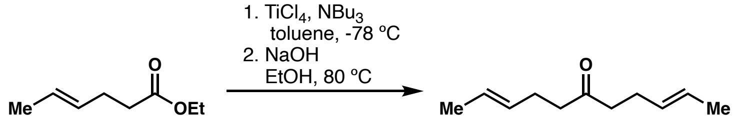
28 *29a* *29* (63%)

Henicosa-1,20-dien-11-one (29): A 500 mL flamed-dried round bottom flask charged with ethyl 10-undecenoate (21.0 g, 100 mmol, 1.0 equiv) and sodium ethoxide (3.4 g, 50 mmol, 0.5 equiv) was equipped with a reflux condenser and a vacuum adapter. The reaction was stirred at 100 ºC under a dynamic vacuum (2 torr) for 12 hours to remove the ethanol produced. After the reaction was cooled to 23 ºC, the crude β-keto ester **29a** was dissolved in ethanol (50 mL) and 2 M NaOH solution (20 mL, 1.0 equiv) was added. The reaction mixture was warmed to reflux for 2 hours and cooled to 23 ºC. A white solid precipitated and was collected by filtration and recrystallized from refluxing methanol, to give ketone **29** as a white solid (7.47 g, 63% yield over two steps).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 2H), 4.97 – 4.82 (m, 4H), 2.31 (t, *J* = 7.5 Hz, 4H), 2.01 – 1.91 (m, 4H), 1.49 (q, *J* = 7.0 Hz, 4H), 1.34 – 1.25 (m, 4H), 1.24 – 1.17 (m, 16H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 211.7, 139.2, 114.2, 42.8, 33.8, 29.4, 29.3, 29.3, 29.1, 28.9, 23.9.

HRMS (EI+, m/z): calc'd for $C_{21}H_{38}O$ $[M]^{+\bullet}$ 306.2923, found: 306.2927.



31

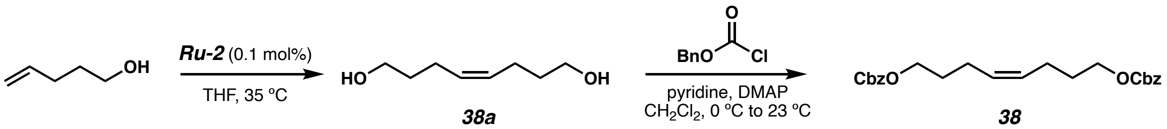
An oven-dried 500 mL three-necked round bottom flask was equipped with a magnetic stirbar and fitted with two rubber septa and a ground glass flow adaptor to introduce inert atmosphere. This flask was charged with (*E*)-hex-4-enoate (20 g, 140 mmol) and NBu_3 (17 mL, 140 mmol) via syringe. Anhydrous toluene (350 mL) was added by cannula, and the reaction mixture was cooled to –78 °C. $TiCl_4$ (18.4 mL, 168 mmol) was added dropwise via syringe over twenty minutes, causing the reaction mixture to become deep red in color. The reaction mixture was stirred with warming to ambient temperature for 10 h, and saturated aqueous $NaHCO_3$ was carefully added to quench the reaction. The organic layer was separated, the aqueous layer was extracted with Et_2O (3 × 25 mL), and the combined organic layers were washed with water (20 mL), brine (2 × 20 mL), dried over $MgSO_4$, and concentrated to a clear, yellow oil.

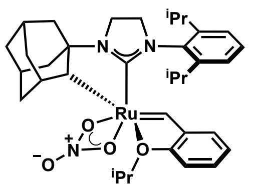
The yellow oil was dissolved in EtOH (200 mL) and water (50 mL) and NaOH pellets were added (3 g). The reaction mixture was heated to 85 °C and monitored by TLC (5% Et_2O in hexanes) until the starting material was fully consumed. The reaction mixture was concentrated and extracted with Et_2O (3 × 50 mL), and the combined organic layers were washed with water (3 × 25 mL) and brine (25 mL), dried over $MgSO_4$, filtered and concentrated. The product **31** was purified by column chromatography (SiO_2, 5% Et_2O in hexanes) to yield a clear, pale yellow oil (11 g, 60 mmol, 85 %)

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.49 – 5.34 (m, 4H), 2.43 (t, J = 7.4 Hz, 4H), 2.28 – 2.19 (m, 4H), 1.65 – 1.59 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.4, 129.7, 126.0, 42.8, 26.9, 18.0.

HRMS (EI+) calc'd for $C_{11}H_{18}O$ $[M]^{+\bullet}$ 166.1358; found 166.1346





Ru-2

(*Z*)-dibenzyl oct-4-ene-1,8-diyl bis(carbonate) (**38**): In a nitrogen-filled glovebox, 4-penten-1-ol (1.72 g, 20 mmol) was dissolved in 6 mL THF in a 20 mL vial equipped with a stir bar, and **Ru-2** (13.5 mg, 0.1 mol%) was added. The vial was placed on a 35 ºC stir plate without capping and stirring was continued for 4 hours. At that time the reaction progress was monitored by GC analysis to ensure full conversion, and the vial was brought outside the glovebox and the reaction mixture was quenched with a few drops of ethyl vinyl ether. Column chromatography (SiO_2, 2:1 hexanes/EtOAc) gave **38a** as a colorless oil (1.06 g, 74% yield).

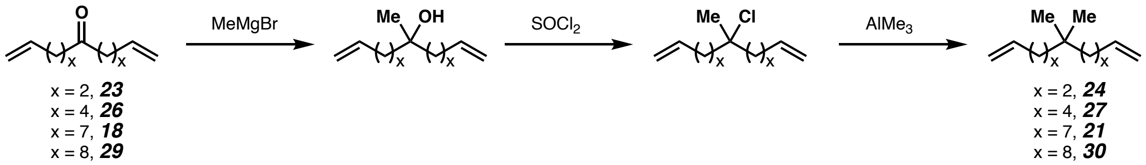
To the diol **38a** (1.06 g, 7.35 mmol, 1.0 equiv) in 30 mL CH_2Cl_2, pyridine (3.0 mL, 36.75 mmol, 5.0 equiv) and DMAP (180 mg, 1.47 mmol, 0.2 equiv) was added sequentially at 0 ºC. Then benzyl chloroformate (4.2 mL, 29.4 mmol, 4.0 equiv) was added dropwisely. The mixture was left to stir at 23 ºC for overnight before it was quenched with 1 M HCl (30 mL). The aqueous phase was extracted by Et_2O three times. The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressure. Column chromatography (SiO_2, 9:1 hexanes/EtOAc) gave **38** as a colorless oil (2.52 g, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 10H), 5.38 (ddd, J = 5.6, 4.4, 1.1 Hz, 2H), 5.15 (s, 4H), 4.13 (t, J = 6.6 Hz, 4H), 2.18 – 2.03 (m, 4H), 1.72 (dq, J = 8.2, 6.7 Hz, 4H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 155.3, 135.4, 129.5, 128.7, 128.6, 128.5, 69.6, 67.7, 28.6, 23.4.

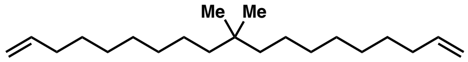
HRMS (FAB+, m/z): calc'd for $C_{24}H_{29}O_6$ [M+H]$^+$ 413.1964, found: 413.1961.

General Procedure A for *gem*-dimethylation of ketones:



In a flame-dried round-bottom flask, ketone (1.0 equiv) was dissolved in THF and the reaction mixture was cooled to 0 ºC. Methylmagnesium bromide solution (3.0 M solution in diethyl ether, 1.5 equiv) was added dropwise, and the reaction mixture was slowly warmed to 23 ºC. After 1 hour, the reaction mixture was cooled to 0 ºC, and quenched by saturated NH_4Cl solution. The aqueous phase was extracted with Et_2O twice, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure.

The crude tertiary alcohol was transferred into a Schlenk flask (with one side arm fitted with a glass stopcock) with dry CH_2Cl_2. The residual solvent was removed by connecting the side arm to vacuum. The flask was back-filled with argon and cooled to 0 ºC, and then $SOCl_2$ (2.5 equiv) was added slowly. A minimal amount of CH_2Cl_2 can be added to aid with stirring. The reaction mixture was stirred at 0 °C for 1 hour, and the reaction progress can be monitored by TLC (using Al_2O_3 plate). The side arm of the Schlenk flask was reconnected to vacuum and excess $SOCl_2$ was removed at 0 ºC. Then the crude tertiary chloride product was dissolved in CH_2Cl_2 (0.3 M) and the reaction mixture was cooled to –78 °C. Trimethylaluminum (2.0 M solution in hexanes, 2.0 equiv) was added dropwise. The reaction mixture was slowly warmed to 23 ºC and stirred for 4 hours and then quenched with aqueous HCl solution (1.0 M) at 0 ºC. The aqueous layer was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The *gem*-dimethylation products were purified by column chromatography (SiO_2, 100% hexanes) or distillation.



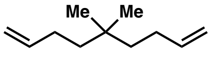
21

10,10-dimethylnonadeca-1,18-diene (**21**): Prepared according to General Procedure A from ketone **18** (10.2 g, 37 mmol) as a colorless liquid (9.1 g, 83% yield).

^{1}H NMR (600 MHz, CDCl$_3$) δ 5.82 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 2H), 5.00 (dq, *J* = 17.1, 1.7 Hz, 2H), 4.93 (ddt, *J* = 10.2, 2.4, 1.2 Hz, 2H), 2.07 – 2.00 (m, 4H), 1.42 – 1.09 (m, 24H), 0.81 (s, 6H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 139.3, 114.1, 42.0, 33.8, 32.6, 30.6, 29.6, 29.2, 29.0, 27.3, 24.0.

HRMS (EI+, m/z): calc'd for $C_{21}H_{40}$ [M]$^{+\bullet}$ 292.3130, found: 292.3144.



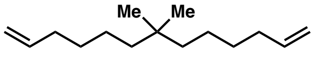
24

5,5-dimethylnona-1,8-diene (**24**): Prepared according to General Procedure A from ketone **23** (25 g, 181 mmol) as a colorless liquid (13 g, 58% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 2H), 4.99 (dq, *J* = 17.1, 1.7 Hz, 2H), 4.94 – 4.86 (m, 2H), 2.02 – 1.93 (m, 4H), 1.30 – 1.22 (m, 4H), 0.86 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 139.80, 113.77, 41.06, 32.65, 28.58, 27.08.

HRMS (EI+, m/z): calc'd for $C_{11}H_{20}$ $[M]^{+\bullet}$ 152.1565, found: 152.1561.



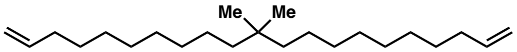
27

7,7-dimethyltrideca-1,12-diene (**27**): Prepared according to General Procedure A from ketone **26** (1.94 g, 10 mmol) as a colorless liquid (1.2 g, 58% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.75 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 2H), 4.98 – 4.81 (m, 4H), 2.03 – 1.94 (m, 4H), 1.32 – 1.23 (m, 4H), 1.19 – 1.05 (m, 8H), 0.75 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 139.3, 114.1, 41.8, 33.9, 32.7, 29.9, 27.3, 23.5.

HRMS (EI+, m/z): calc'd for $C_{15}H_{28}$ $[M]^{+\bullet}$ 208.2191, found: 208.2177.



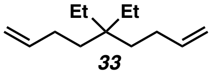
30

11,11-dimethylhenicosa-1,20-diene (**30**): Prepared according to General Procedure A from ketone **29** (7.47 g, 24.4 mmol) as a colorless liquid (5.66 g, 72% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.84 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 2H), 5.08 – 4.89 (m, 4H), 2.14 – 2.00 (m, 4H), 1.40 (q, *J* = 6.9 Hz, 4H), 1.35 – 1.12 (m, 24H), 0.84 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 139.4, 114.2, 42.1, 34.0, 32.7, 30.8, 29.8, 29.7, 29.3, 29.1, 27.5, 24.2.

HRMS (EI+, m/z): calc'd for $C_{23}H_{44}$ $[M]^{+\bullet}$ 320.3443, found: 320.3425.



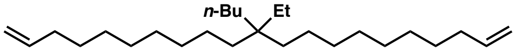
33

5,5-diethylnona-1,8-diene (**33**): Prepared according to modified General Procedure A from ketone **23** (276 mg, 2.0 mmol), EtMgBr, and AlEt$_3$ to afford **33** as a clear, colorless oil (230 mg, 63% yield).

^{1}H NMR (600 MHz, CDCl$_3$) δ 5.82 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 2H), 5.00 (dq, *J* = 17.1, 1.6 Hz, 2H), 4.91 (ddt, *J* = 10.0, 2.3, 1.2 Hz, 2H), 1.96 – 1.87 (m, 4H), 1.26 – 1.19 (m, 8H), 0.75 (t, *J* = 7.5, 1.0 Hz, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 139.9, 113.9, 37.3, 34.9, 28.0, 27.7, 7.6.

HRMS (EI+) calc'd for $C_{13}H_{24}$ $[M]^{+\bullet}$ 180.1878; found 180.1894.



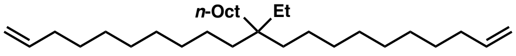
34

11-butyl-11-ethylhenicosa-1,20-diene (**34**): Prepared according to modified General Procedure A from ketone **29** (918 mg, 3 mmol) with *n*-butylmagnesium chloride solution (2.0 M solution in diethyl ether, 1.5 equiv) and triethylaluminum (2.0 equiv). **34** was obtained as a colorless liquid (680 mg, 60% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.74 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 2H), 4.96 – 4.82 (m, 4H), 2.01 – 1.92 (m, 4H), 1.35 – 1.25 (m, 4H), 1.25 – 1.11 (m, 24H), 1.07 – 0.99 (m, 8H), 0.82 (td, *J* = 7.2, 2.0 Hz, 3H), 0.64 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 139.4, 114.2, 37.5, 37.1, 36.2, 35.9, 33.9, 33.9, 33.5, 30.8, 30.3, 29.8, 29.7, 29.7, 29.3, 29.1, 28.7, 26.8, 25.4, 23.8, 23.3, 23.1, 14.4, 14.4, 7.7.

HRMS (EI+, m/z): calc'd for $C_{27}H_{52}$ $[M]^{+\bullet}$ 376.4069, found: 376.4120.



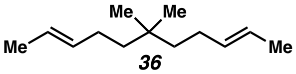
35

11-ethyl-11-octylhenicosa-1,20-diene (**35**): Prepared according to modified General Procedure A from ketone **29** (153 mg, 0.5 mmol) with *n*-octylmagnesium chloride solution (2.0 M solution in THF, 1.5 equiv) and triethylaluminum (2.0 equiv). **35** was obtained as a colorless liquid (154 mg, 71% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.74 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 2H), 4.99 – 4.80 (m, 4H), 2.04 – 1.90 (m, 4H), 1.34 – 1.26 (m, 4H), 1.25 – 1.10 (m, 34H), 1.05 – 1.00 (m, 6H), 0.83 – 0.78 (m, 3H), 0.64 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 139.4, 114.2, 37.5, 37.2, 36.2, 34.0, 33.8, 32.1, 30.8, 30.8, 30.5, 30.3, 30.3, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.3, 29.1, 28.7, 26.8, 23.1, 22.9, 14.3, 7.7.

HRMS (EI+, m/z): calc'd for $C_{31}H_{60}$ $[M]^{+\bullet}$ 432.4695, found: 432.4714.



36

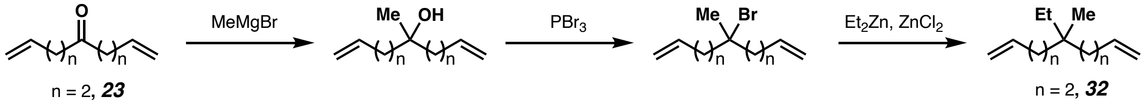
(2*E*,9*E*)-6,6-dimethylundeca-2,9-diene (36): Prepared according to general procedure A from ketone **31** (258 mg, 1.6 mmol) as a colorless liquid (230 mg, 82%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 5.49 – 5.39 (m, 4H), 1.96 – 1.89 (m, 4H), 1.66 (dt, *J* = 4.8, 1.3 Hz, 6H), 1.27 – 1.21 (m, 4H), 0.86 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 132.3, 124.2, 41.8, 32.6, 27.3, 27.1, 18.0.

HRMS (EI+) calc'd for $C_{13}H_{24}$ $[M]^{+\bullet}$ 180.1878; found 180.1865.

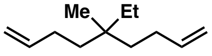
General Procedure B for *gem*-dialkylation of ketones:



In a flame-dried round-bottom flask, ketone (1.0 equiv) was dissolved in THF and the reaction mixture was cooled to 0 ºC. Methylmagnesium bromide solution (3.0 M solution in diethyl ether, 1.5 equiv) was added dropwise, and the reaction mixture was slowly warmed to 23 ºC. After 1 hour, the reaction mixture was cooled to 0 ºC, and quenched by saturated NH_4Cl solution. The aqueous phase was extracted with Et_2O twice, dried over anhydrous $MgSO_4$, filtered over a short silica plug, and concentrated under reduced pressure.

A 100 mL round bottom flask equipped with a magnetic stirbar was charged with the tertiary alcohol (1.0 equiv) and dissolved in anhydrous CH_2Cl_2 (1 M). This solution was cooled to 0 °C and PBr_3 (0.35 equiv) was added dropwise. The reaction mixture was stirred for 2 h at 0 °C, and then concentrated *in vacuo*. The flask was fitted with a short path distillation head and the residue was distilled under vacuum to afford the tertiary bromide as a clear, colorless oil.

A 250 mL round bottom flask equipped with a magnetic stirbar was charged with $ZnCl_2$ (0.1 equiv) and the tertiary bromide (1 equiv) and dissolved in anhydrous CH_2Cl_2 (0.5 M). This solution was cooled to –40 °C and the dialkylzinc reagent (1.0 equiv) was added dropwise via syringe. The reaction mixture was stirred with warming to ambient temperature for 12 h, and then quenched by the dropwise addition of MeOH. The reaction mixture was washed with 1 M HCl, the organic layer was separated, washed with brine, dried over $MgSO_4$, and concentrated *in vacuo*. The product was purified by distillation.



32

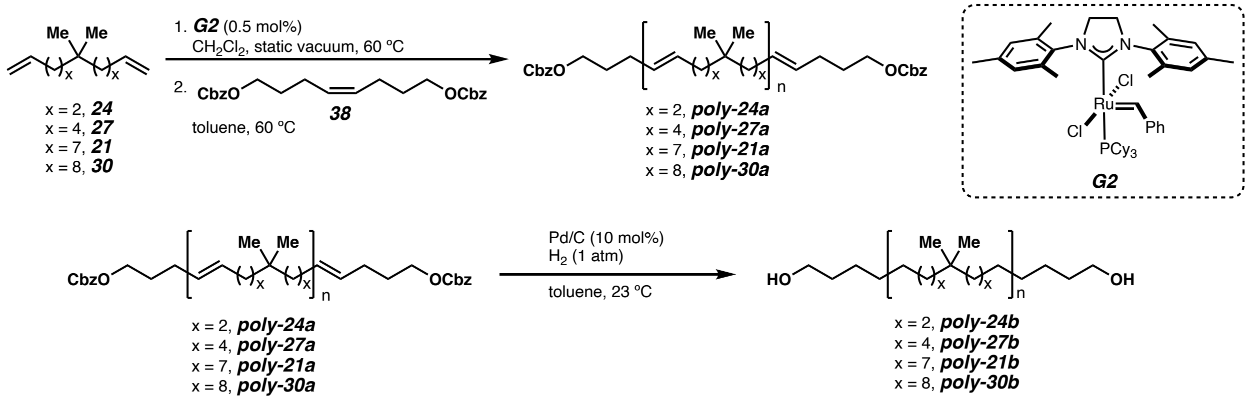
5-ethyl-5-methylnona-1,8-diene (32): Prepared according to general procedure B from ketone **23** (5.86 g, 42.5 mmol) and Et_2Zn to afford **32** as a clear, colorless oil (4.3 g, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.9, 10.1, 6.6 Hz, 2H), 4.97 (dt, *J* = 17.0, 1.8 Hz, 2H), 4.92 – 4.86 (m, 2H), 1.96 – 1.88 (m, 4H), 1.27 – 1.18 (overlapping m, 6H), 0.79 (s, 3H), 0.76 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 113.7, 38.1, 34.9, 31.4, 28.1, 24.4, 7.9.

HRMS (EI+) calc'd for $C_{12}H_{22}$ $[M]^{+\bullet}$ 166.1722; found 166.1700.

General Procedure C for ADMET Polymerization:



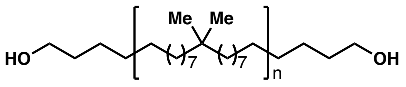
In a nitrogen-filled glovebox, monomer **30** (320 mg, 1 mmol) in 0.5 mL CH_2Cl_2 was transferred into a 50 mL Schlenk flask equipped with a stir bar, followed by Grubbs 2nd Generation Catalyst (4.2 mg, 0.5 mol%) in 0.5 mL CH_2Cl_2. The Schlenk tube was sealed and removed from the glovebox and placed under static vacuum after one freeze-pump-thaw cycle. Then the Schlenk flask was placed in to a 60 ºC oil bath for 12 hours. The valve was opened to dynamic vacuum and stirring was continued for 2 hours until the mixture turned viscous and became difficult to stir. The Schlenk tube was sealed and taken into the glovebox where the CTA **38** (20.6 mg, 0.05 mmol, 20:1 monomer: CTA ratio) in 2 mL toluene was added. The Schlenk tube was removed from the glovebox and the side arm was flame dried under vacuum and backfilled three times with argon. Then the Schlenk tube was opened to the argon line and placed in a 60 °C oil bath for 72 h. The reaction mixture was transferred into a flame-dried round bottom flask and the solvent was removed under reduced pressure to obtain crude polymer **poly-30a**.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.14 (m, 5H), 5.47 – 5.32 (m, 11H), 5.16 (s, 1H), 4.21 – 4.10 (m, 1H), 2.08 – 1.91 (m, 21H), 1.46 – 1.06 (m, 131H), 0.82 (s, 29H). ^{1}H NMR determined n = 22, M_n = 6800. GPC data: M_n = 5400; PDI (M_w/M_n) = 1.2.

The crude polymer **poly-30a** was dissolved in toluene (10 mL) and 10% palladium on carbon (100 mg, 0.1 equiv) was added in a round-bottom flask with a stir bar. The flask was sealed with a septum and back-filled with argon for three times, and then back-filled with H_2 using a balloon. The reaction was allowed to stir at 23 °C for 24 hours under an atmosphere of hydrogen (1 atm H_2 balloon). After that time the reaction mixture was filtered through a short pad of Celite (*caution: Palladium on carbon is highly flammable and the palladium waste must be collected separately and covered with water*). The filtered solution was concentrated upon heating under high vacuum to obtain the hydroxyl telechelic polymer **poly-30b** (286 mg, 97% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.65 (t, J = 6.6 Hz, 1H), 1.39 – 1.10 (m, 210H), 0.82 (s, 32H). ^{1}H NMR determined n = 21, M_n = 6300. GPC data: M_n = 7600; PDI (M_w/M_n) = 1.1.

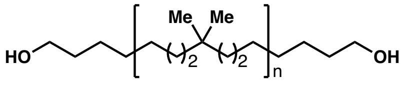
Table S1. Summary of Telechelic Polymer Samples Prepared.

Polymer	Monomer/CTA ratio	Yield (%)	n	M_n(NMR)(Da)
poly-21b	10:1	95	15	4200
poly-24b	22:1	55	16	2200
poly-27b	12:1	99	10	2000
poly-30b-1	8:1	99	10	3100
poly-30b-2	20:1	97	21	6300
poly-30b-3	50:1	96	58	17200
poly-30b-4	100:1	89	97	28700
poly-32b	22:1	56	22	3200
poly-34b	20:1	95	19	6800



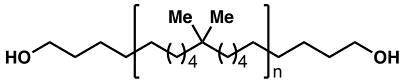
poly-21b

Telechelic polymer poly-21b: **^{1}H NMR** (400 MHz, CDCl$_3$) δ 3.57 (t, *J* = 6.6 Hz, 1H), 1.62 – 1.48 (m, 7H), 1.32 – 1.00 (m, 122H), 0.74 (s, 22H). ^{1}H NMR determined n = 15, M$_n$ = 4200. GPC data: M$_n$ =2800; PDI (M$_w$/M$_n$) = 1.44.



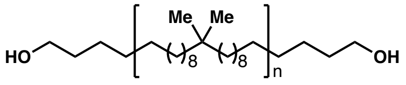
poly-24b

Telechelic polymer poly-24b: **^{1}H NMR** (600 MHz, CDCl$_3$) δ 3.63 (t, *J* = 6.7 Hz, 1H), 1.59 – 1.52 (m, 1H), 1.36 – 1.04 (m, 46H), 0.80 (s, 20H).^{1}H NMR determined n = 16, M$_n$ = 2200. GPC data: M$_n$ =4000; PDI (M$_w$/M$_n$) = 1.4.



poly-27b

Telechelic polymer poly-27b: **^{1}H NMR** (500 MHz, CDCl$_3$) δ 3.65 (t, *J* = 6.6 Hz, 1H), 1.43 – 1.09 (m, 58H), 0.82 (s, 13H).^{1}H NMR determined n = 10, M$_n$ = 2000. GPC data: M$_n$ = 3800; PDI (M$_w$/M$_n$) = 1.5.

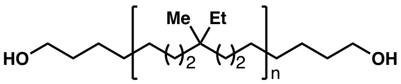


poly-30b

poly-30b-1: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.65 (dt, *J* = 6.5, 4.8 Hz, 1H), 1.41 – 1.17 (m, 94H), 0.82 (s, 15H). ^{1}H NMR determined n = 10, M$_n$ = 3100.

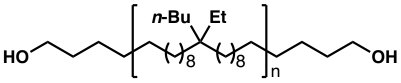
poly-30b-2: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.65 (t, *J* = 6.6 Hz, 1H), 1.34 – 1.11 (m, 208H), 0.82 (s, 32H). ^{1}H NMR determined n = 21, M$_n$ = 6300.
poly-30b-3: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.65 (dt, *J* = 6.7, 5.6 Hz, 1H), 1.32 – 1.12 (m, 571H), 0.82 (s, 88H). ^{1}H NMR determined n = 58, M$_n$ = 17200.

poly-30b-4: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.65 (dt, *J* = 6.6, 5.5 Hz, 1H), 1.35 – 1.11 (m, 943H), 0.82 (s, 146H). ^{1}H NMR determined n = 97, M$_n$ = 28700.



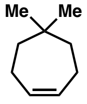
poly-32b

Telechelic polymer poly-32b: **^{1}H NMR** (600 MHz, CDCl$_3$) δ 3.63 (t, *J* = 6.7 Hz, 1H), 1.55 (q, *J* = 6.9 Hz, 2H), 1.38 – 1.05 (m, 83H), 0.78 – 0.68 (m, 34H). ^{1}H NMR determined n = 22, M$_n$ = 3200. GPC data: M$_n$ =6800; PDI (M$_w$/M$_n$) = 1.1.



poly-34b

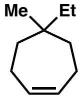
poly-34b: ^{1}H NMR (500 MHz, CDCl$_3$) δ 3.65 (q, *J* = 6.4 Hz, 1H), 1.34 – 1.19 (m, 265H), 1.14 – 1.09 (m, 56H), 0.92 – 0.87 (m, 29H), 0.72 (t, *J* = 7.5 Hz, 14H). ^{1}H NMR determined n = 19, M$_n$ = 6800.



37

5,5-dimethylcyclohept-1-ene (37): After the polymerization of **24**, the cyclic olefin was removed by vacuum distillation from the reaction mixture (23 °C, 100 mTorr).

^{1}H NMR (400 MHz, CDCl$_3$) δ 5.60 (ddd, *J* = 3.8, 2.9, 0.8 Hz, 2H), 2.06 – 1.94 (m, 4H), 1.40 – 1.32 (m, 4H), 0.87 (s, 6H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 131.5, 40.3, 33.7, 29.3, 24.4.
HRMS (EI+, m/z) calc'd for C_9H_{16} [M]$^{+•}$ 124.1252, found: 124.1264.

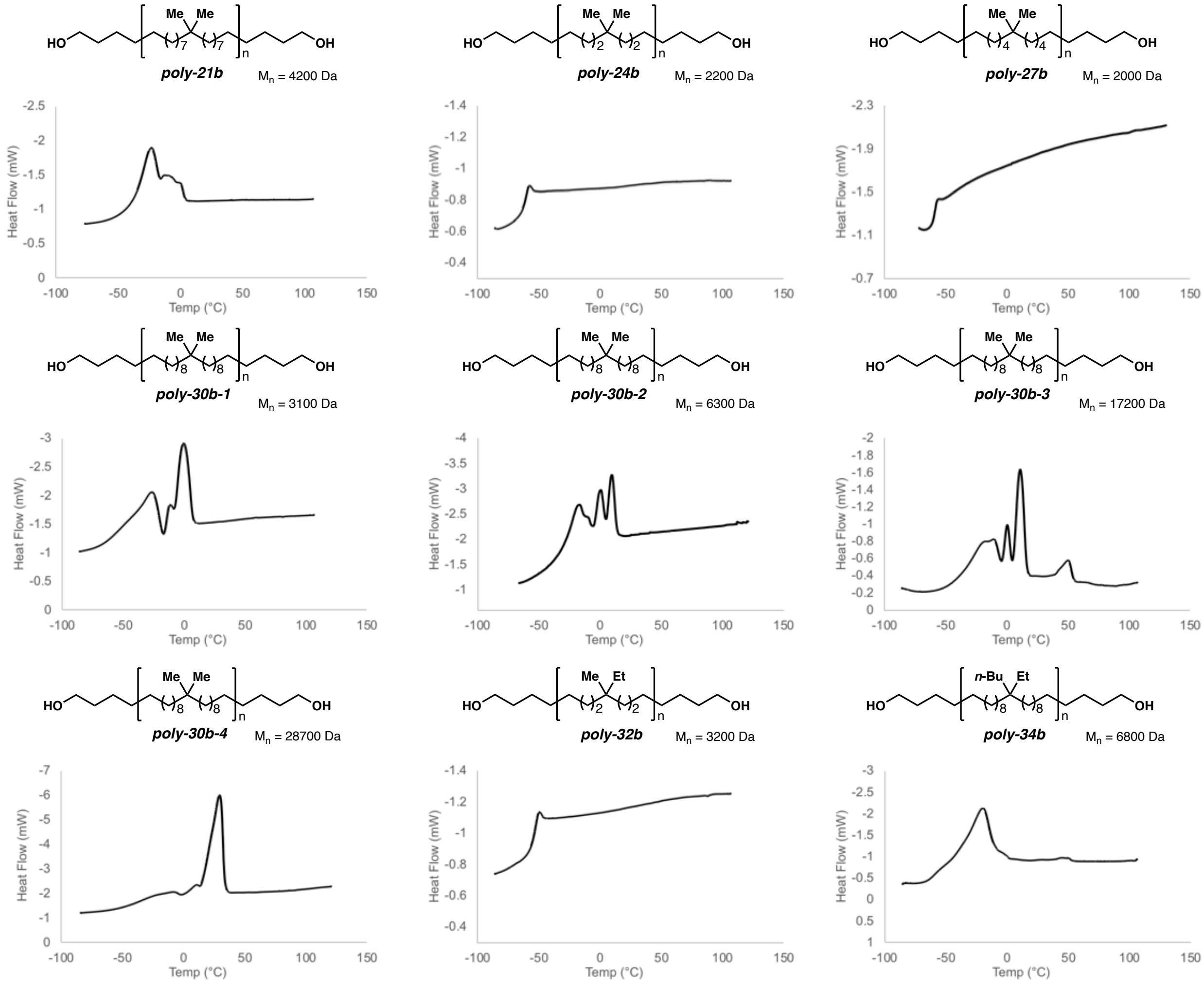


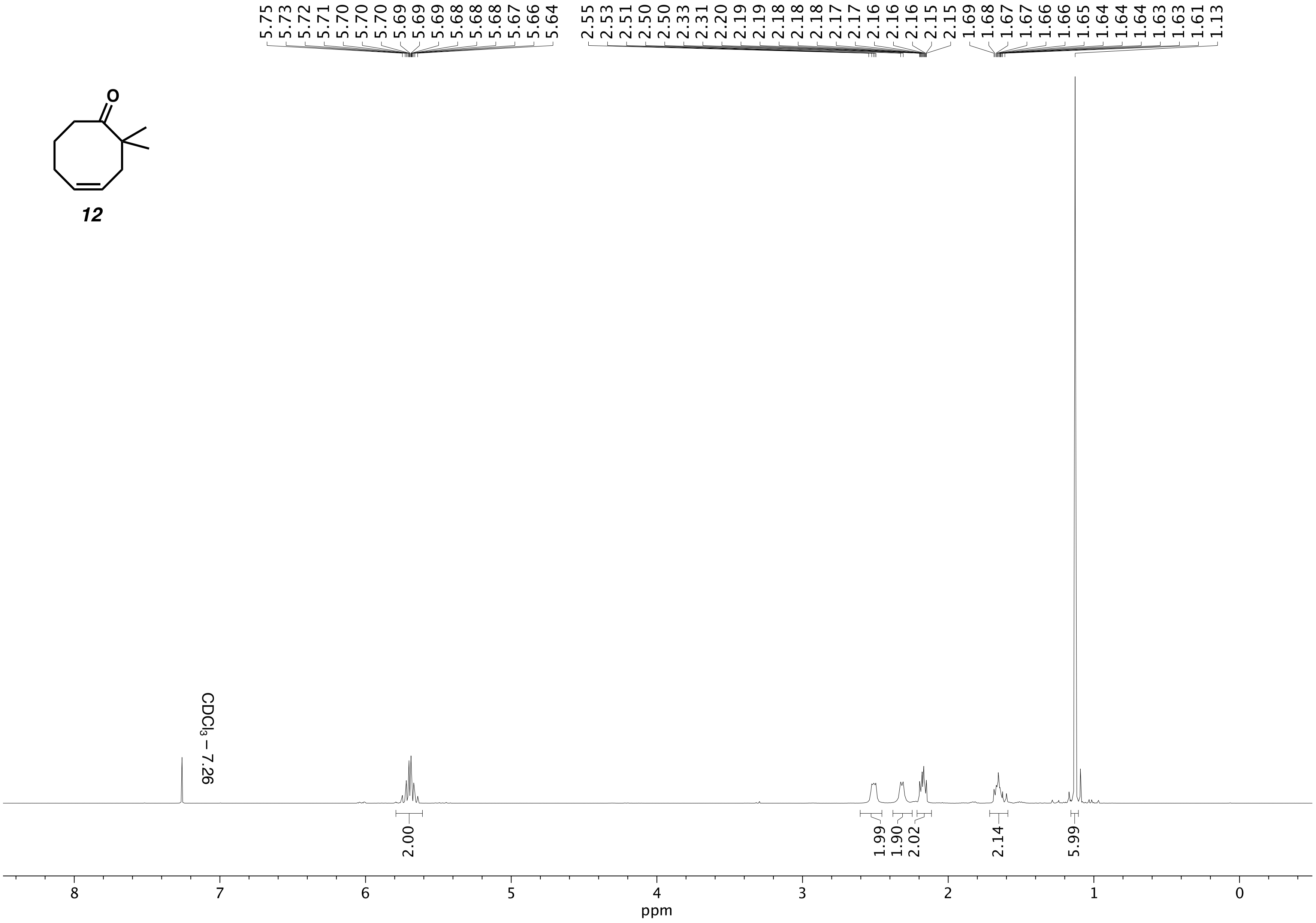
39

5-ethyl-5-methylcyclohept-1-ene (39): After the polymerization of **32**, the cyclic olefin was removed by vacuum distillation from the reaction mixture (23 °C, 100 mTorr).
^{1}H NMR (600 MHz, CDCl$_3$) δ 5.63 (t, *J* = 3.2 Hz, 2H), 2.09 – 2.01 (m, 4H), 1.49 – 1.33 (m, 4H), 1.29 (q, *J* = 7.5 Hz, 2H), 0.83 (s, 3H), 0.80 (t, *J* = 7.5 Hz, 3H).
^{13}C NMR (126 MHz, CDCl$_3$) δ 131.4, 38.3, 35.9, 33.6, 25.2, 24.1, 8.1.
HRMS (EI+, m/z) calc'd for $C_{10}H_{18}$ [M]$^{+•}$ 138.1409, found: 138.1413.

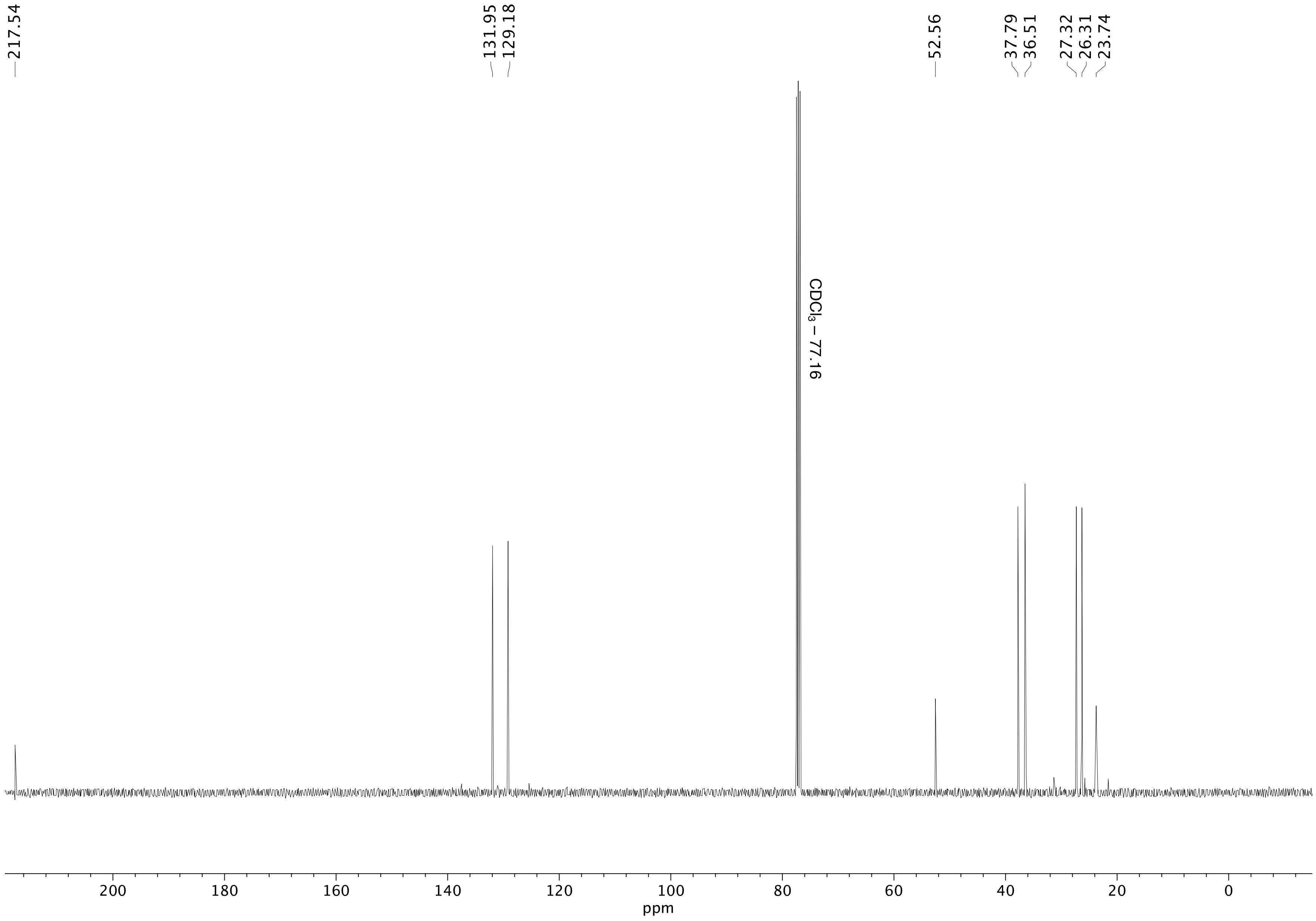
DSC was performed using a Mettler Toledo DSC 3+ Star System. Scan rates of 10 K/min for heating and 5K/min for cooling were used.

Figure S1. DSC Traces for Different Gem-*dimethyl Polymer Samples*

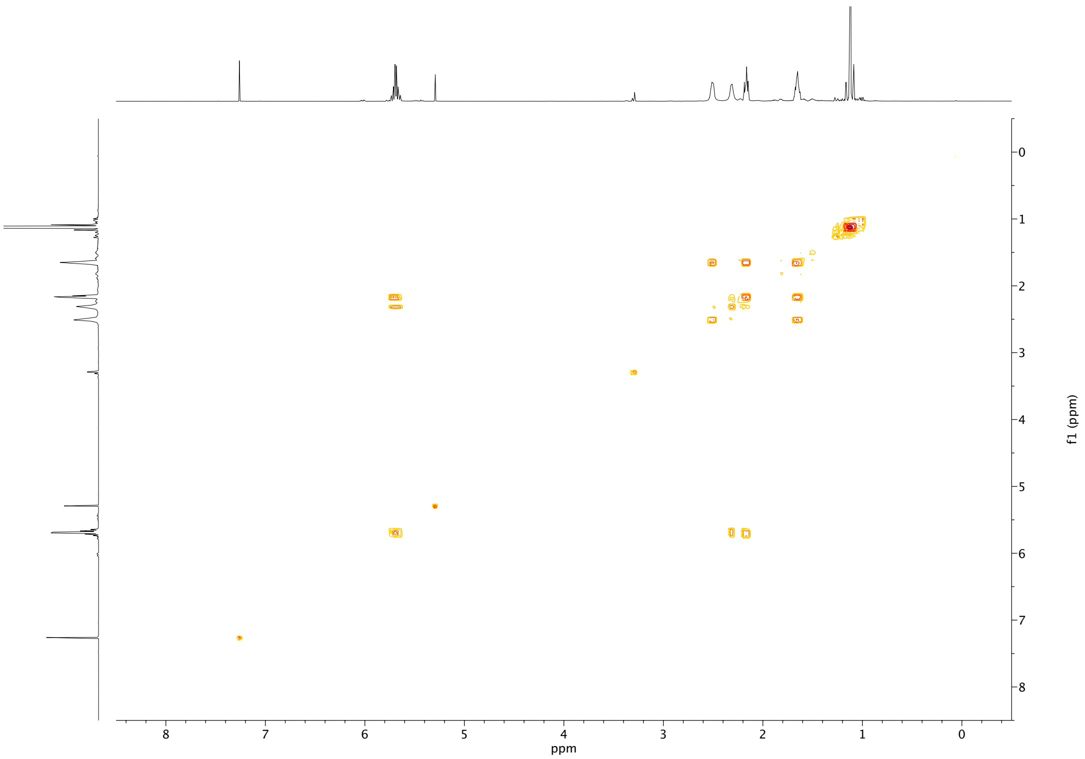




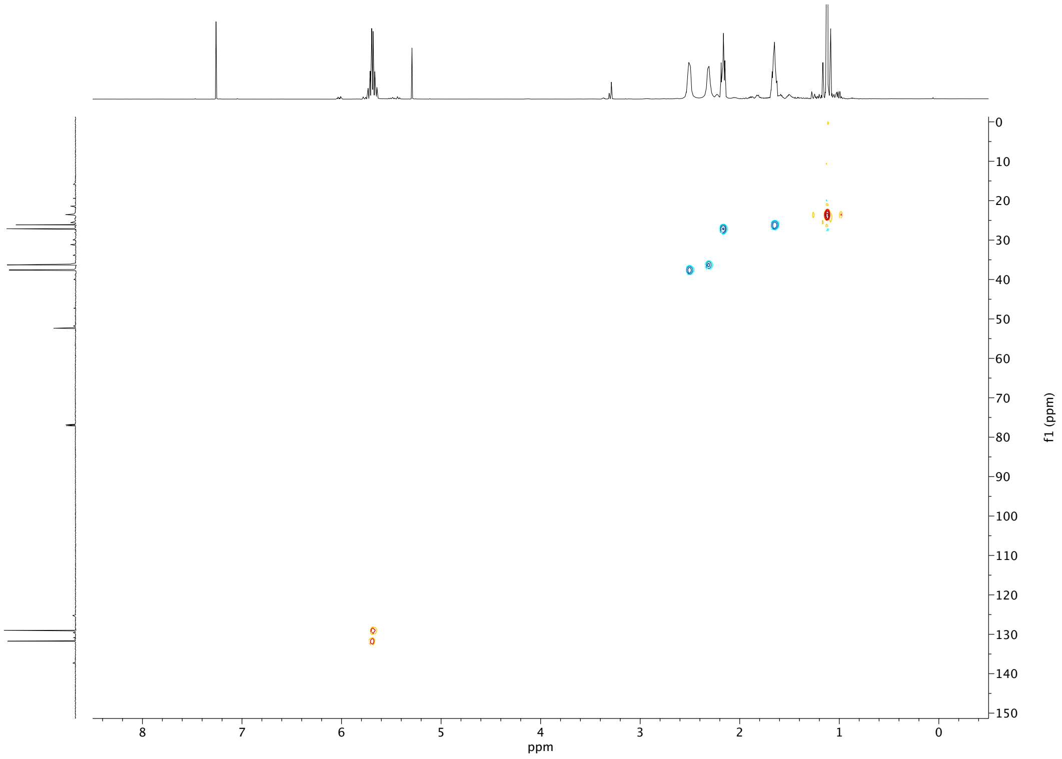
^{1}H NMR (400 MHz, $CDCl_3$) of compound **12**.



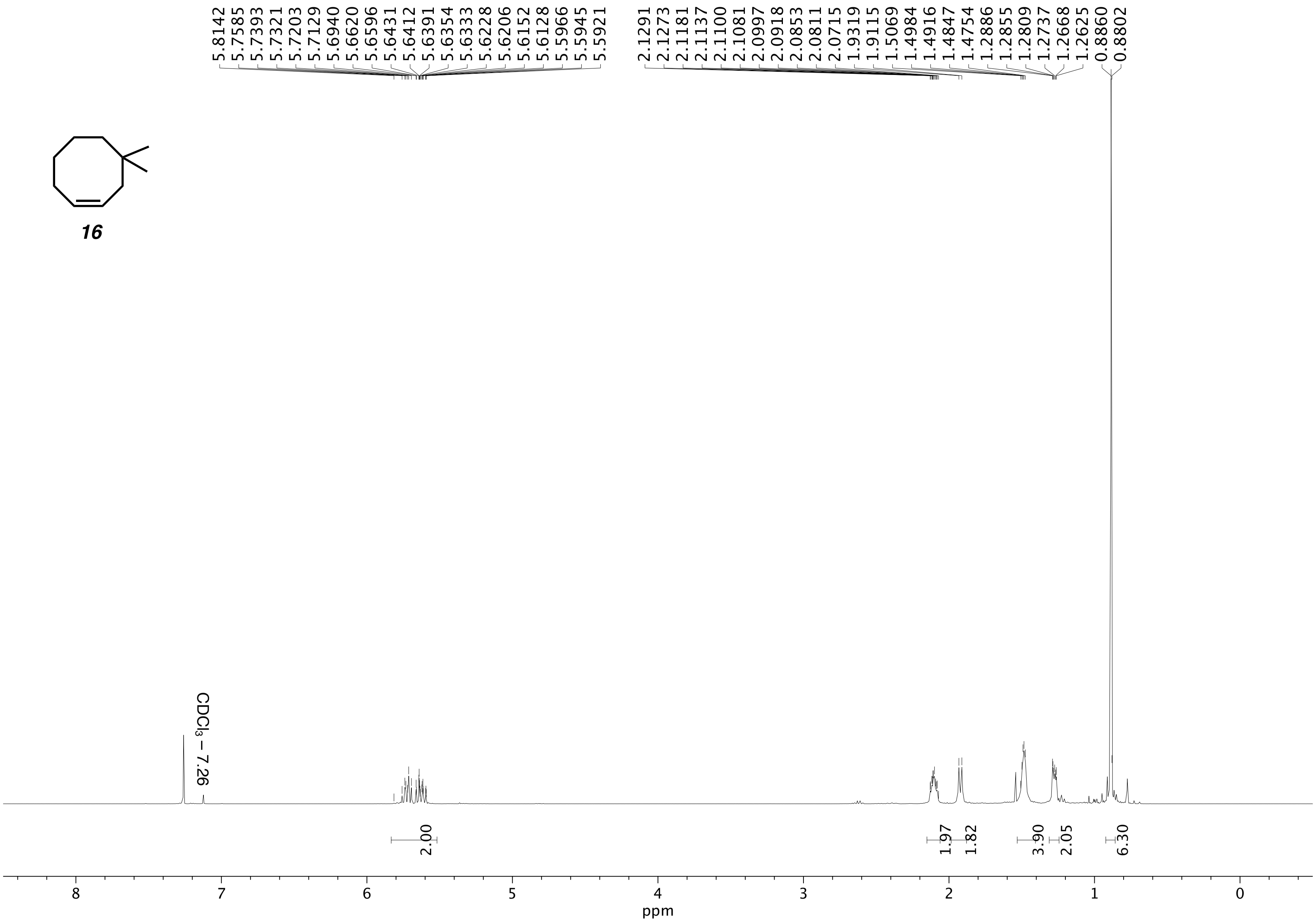
^{13}C NMR (101 MHz, CDCl$_3$) of compound **12**.



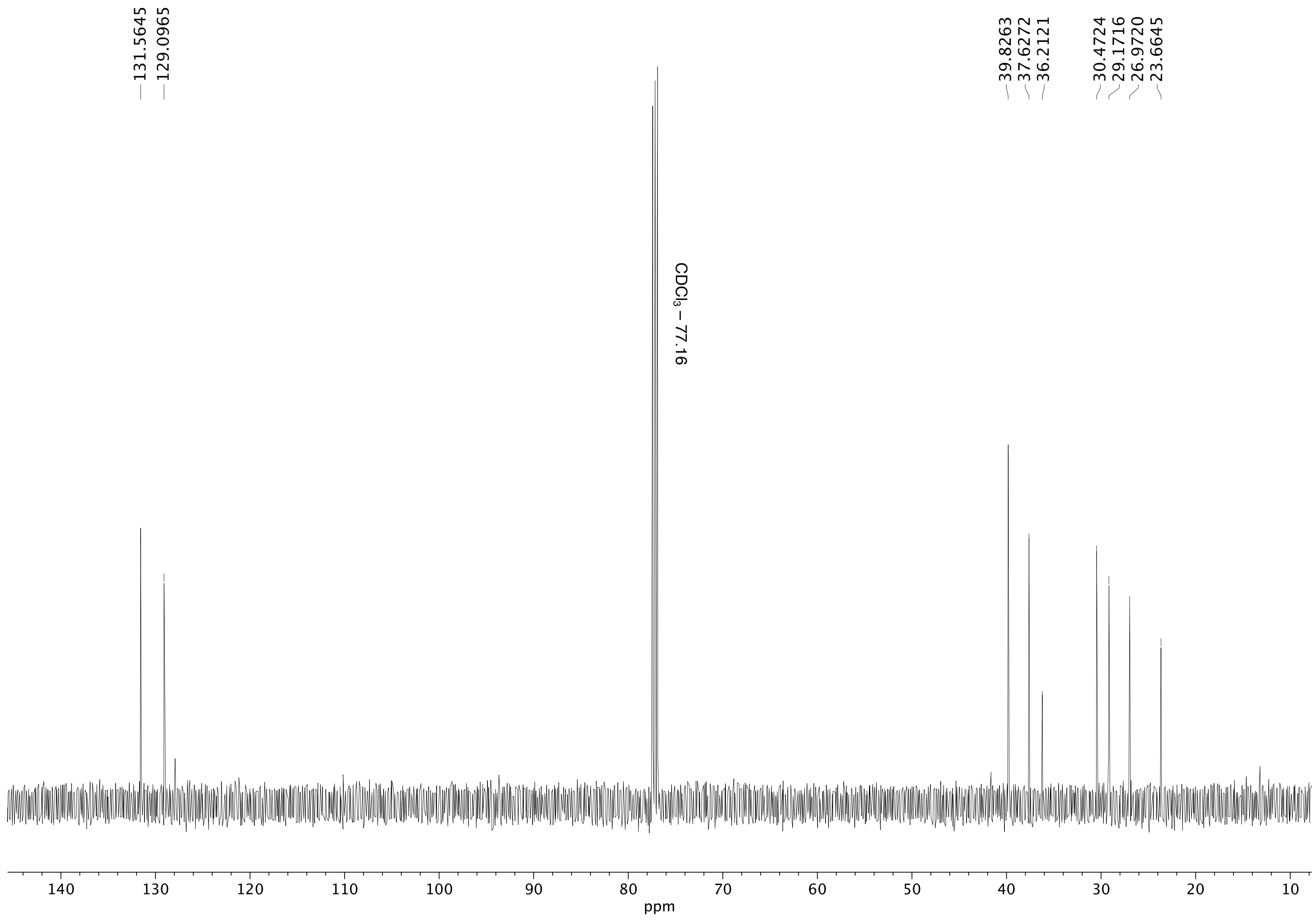
^{1}H–^{1}H COSY NMR (400 MHz, $CDCl_3$) of compound **12**.



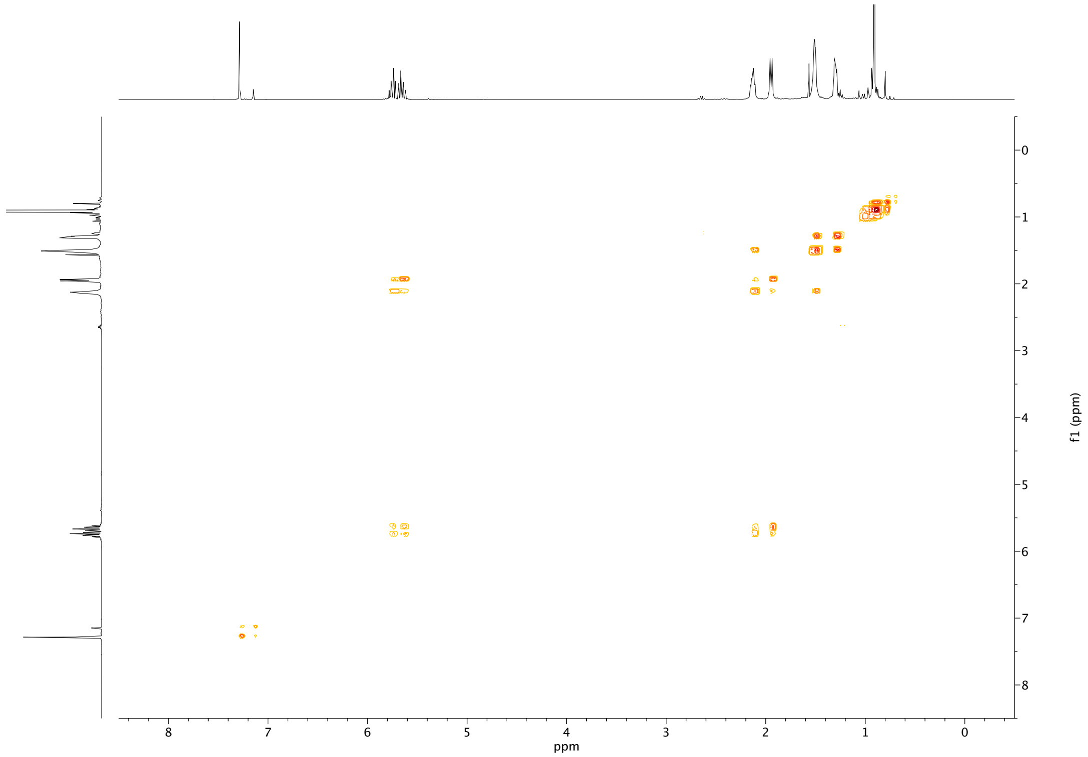
^{1}H–^{13}C HSQC NMR (400 MHz, $CDCl_3$) of compound **12**.



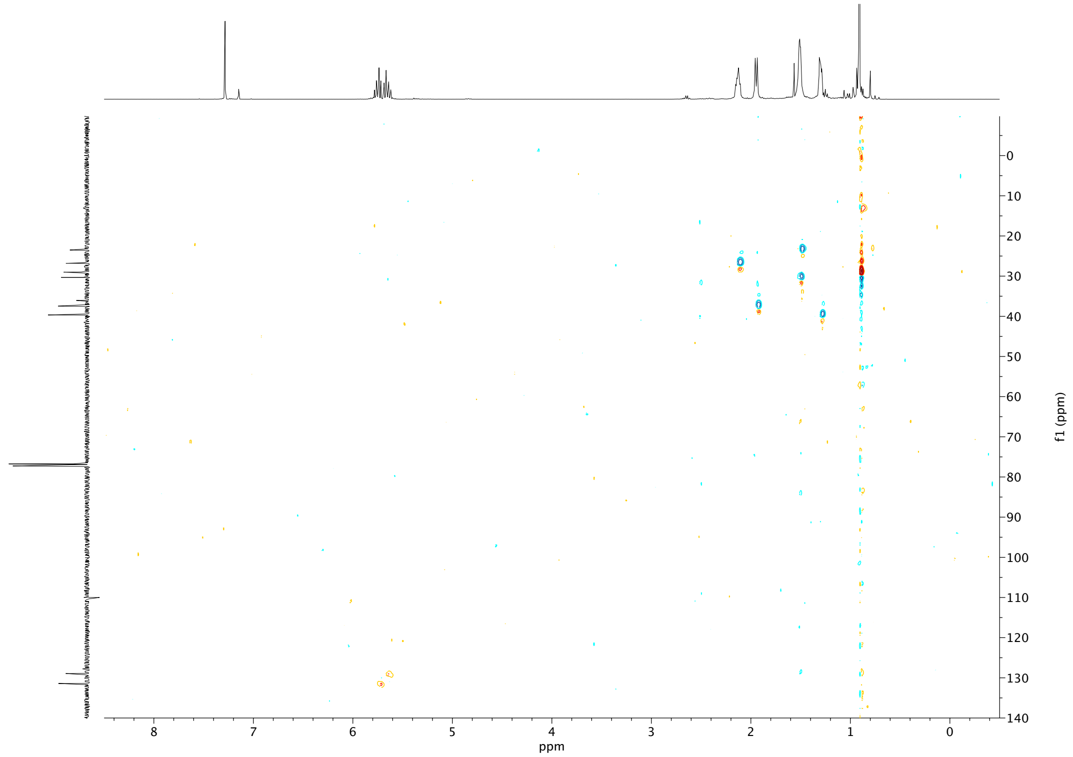
^{1}H NMR (400 MHz, CDCl$_3$) of compound **16**.



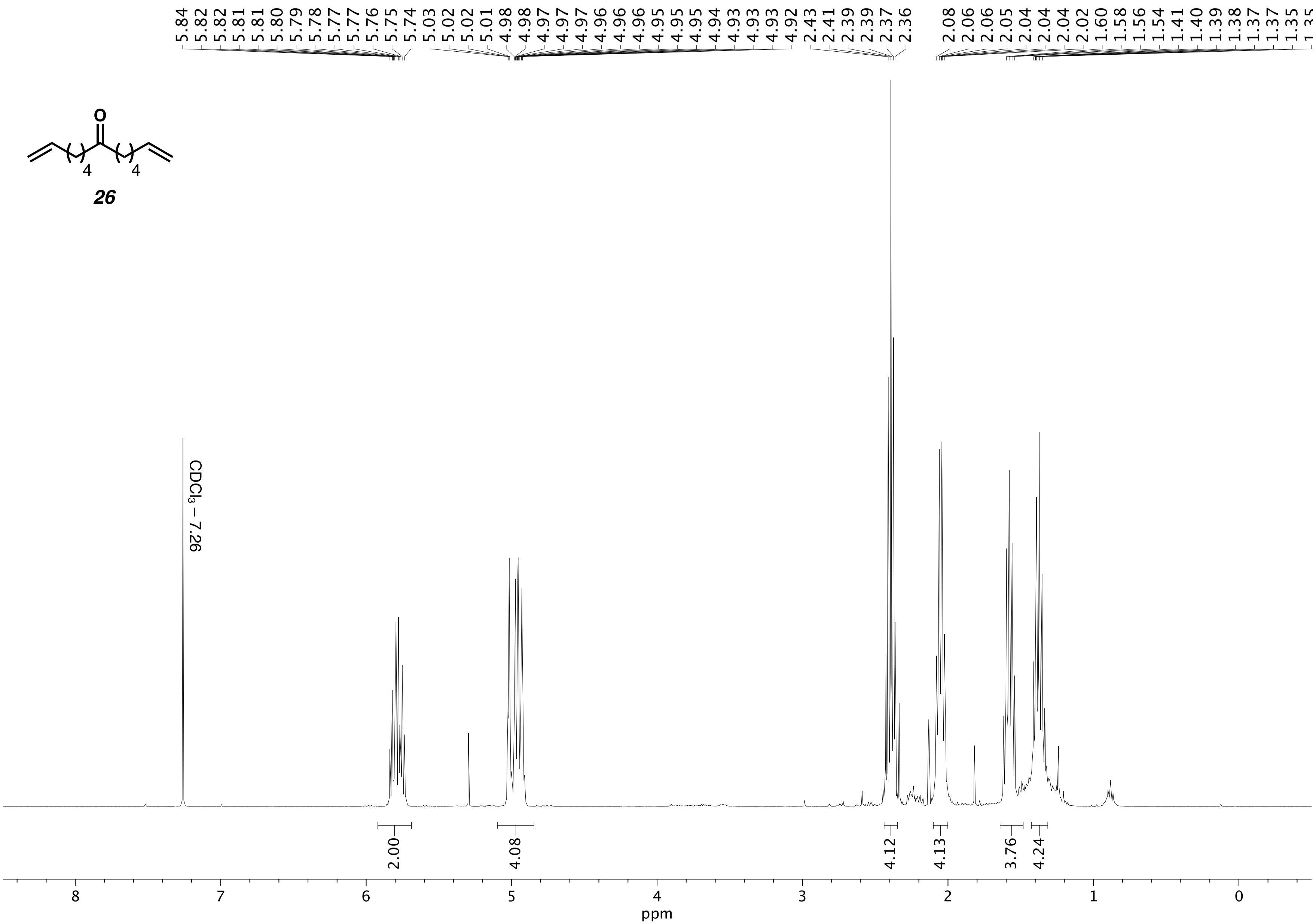
^{13}C NMR (101 MHz, CDCl$_3$) of compound **16**.



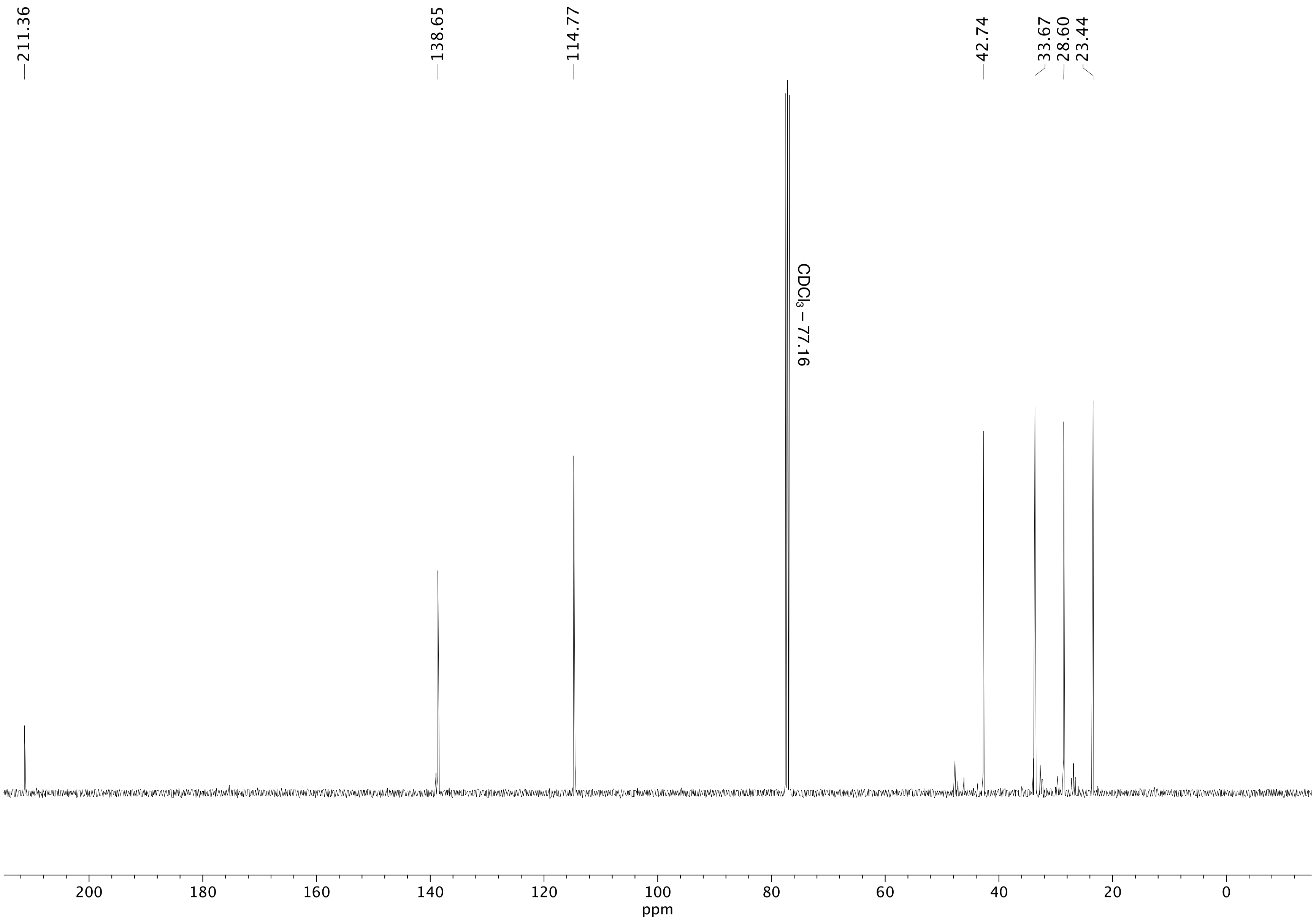
^1H–^1H COSY NMR (400 MHz, $CDCl_3$) of compound **16**.



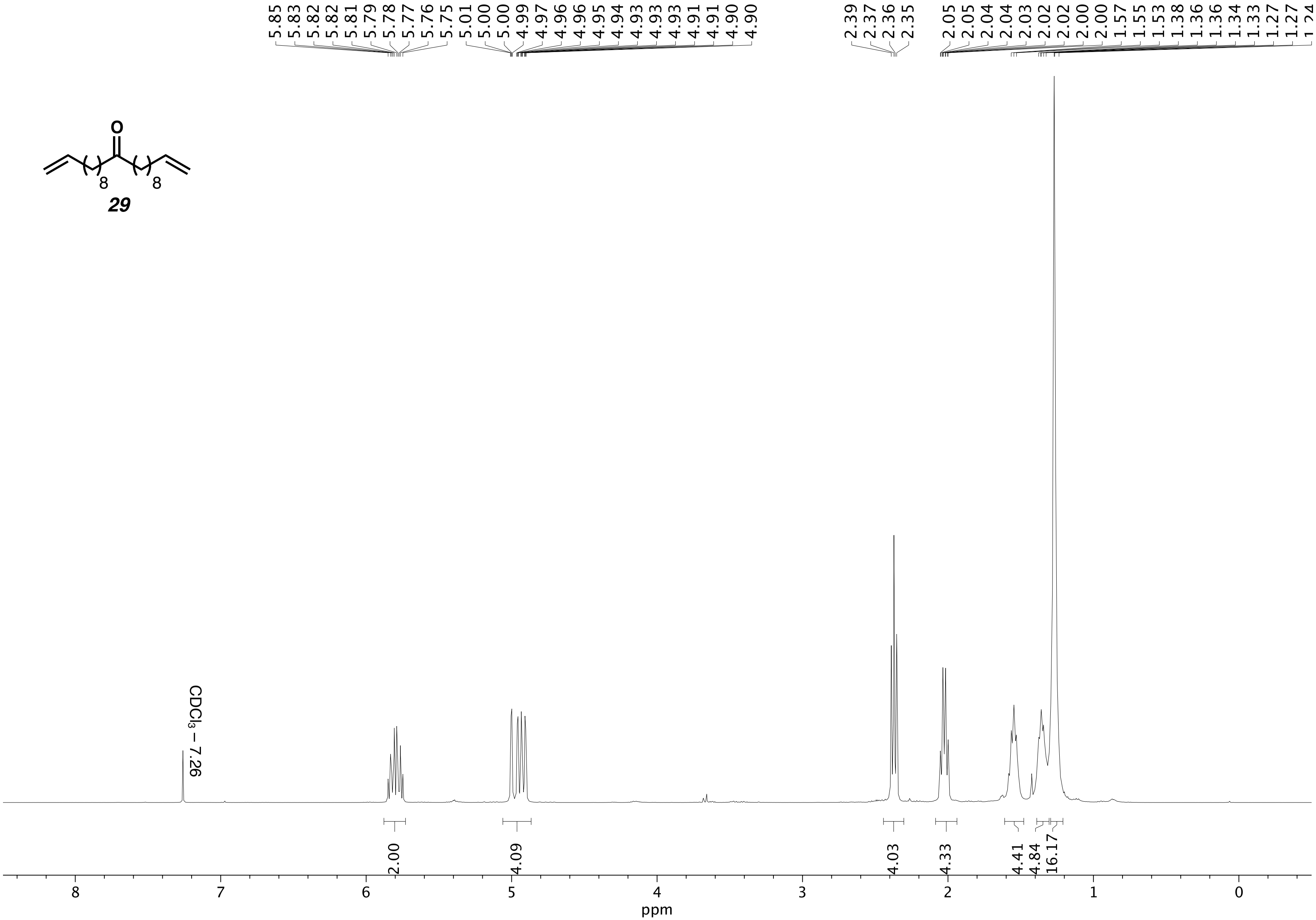
^1H–^{13}C HSQC NMR (400 MHz, $CDCl_3$) of compound **16**.



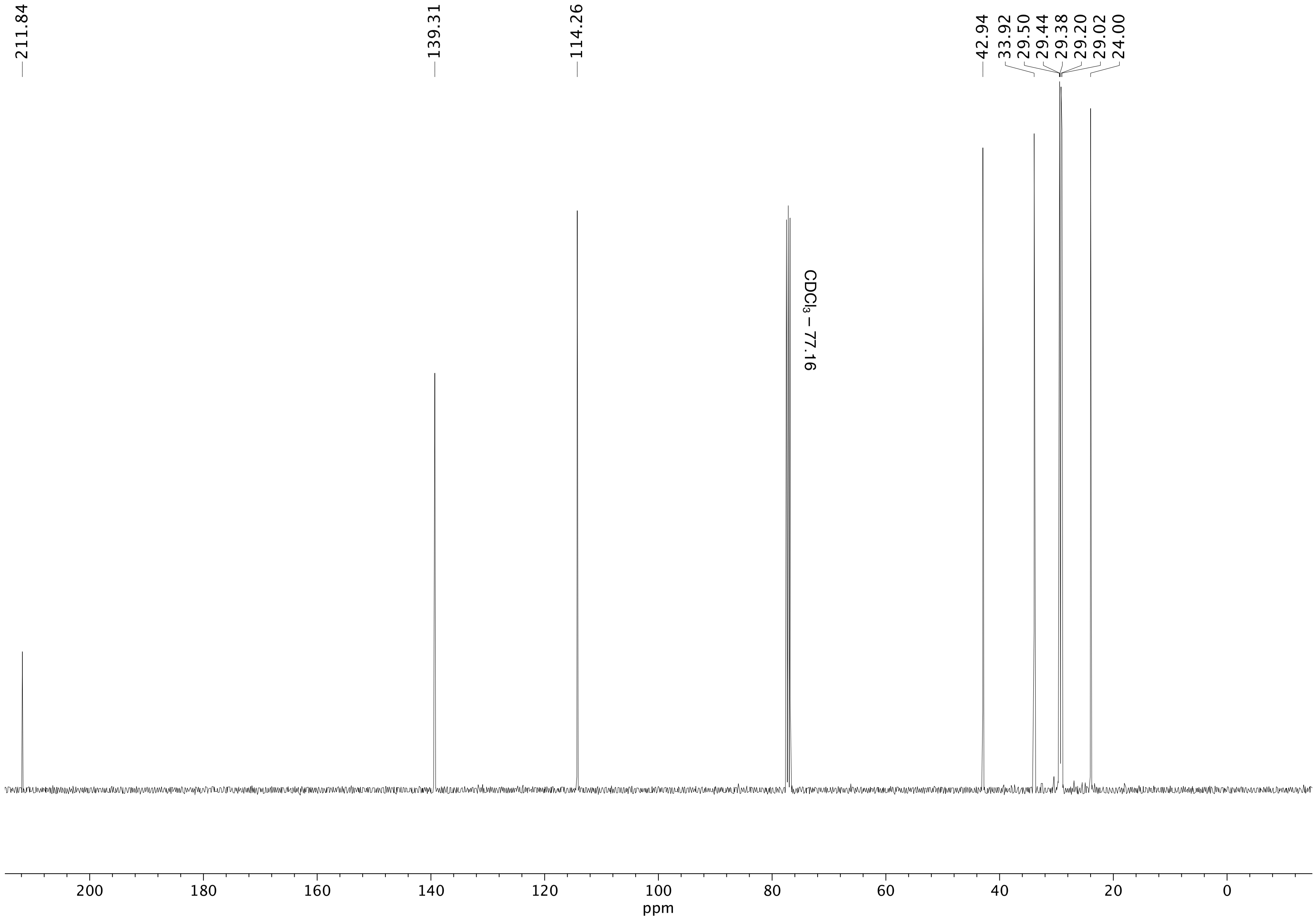
^{1}H NMR (400 MHz, CDCl$_3$) of compound **26**.



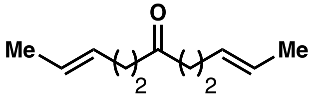
^{13}C NMR (101 MHz, CDCl$_3$) of compound **26**.



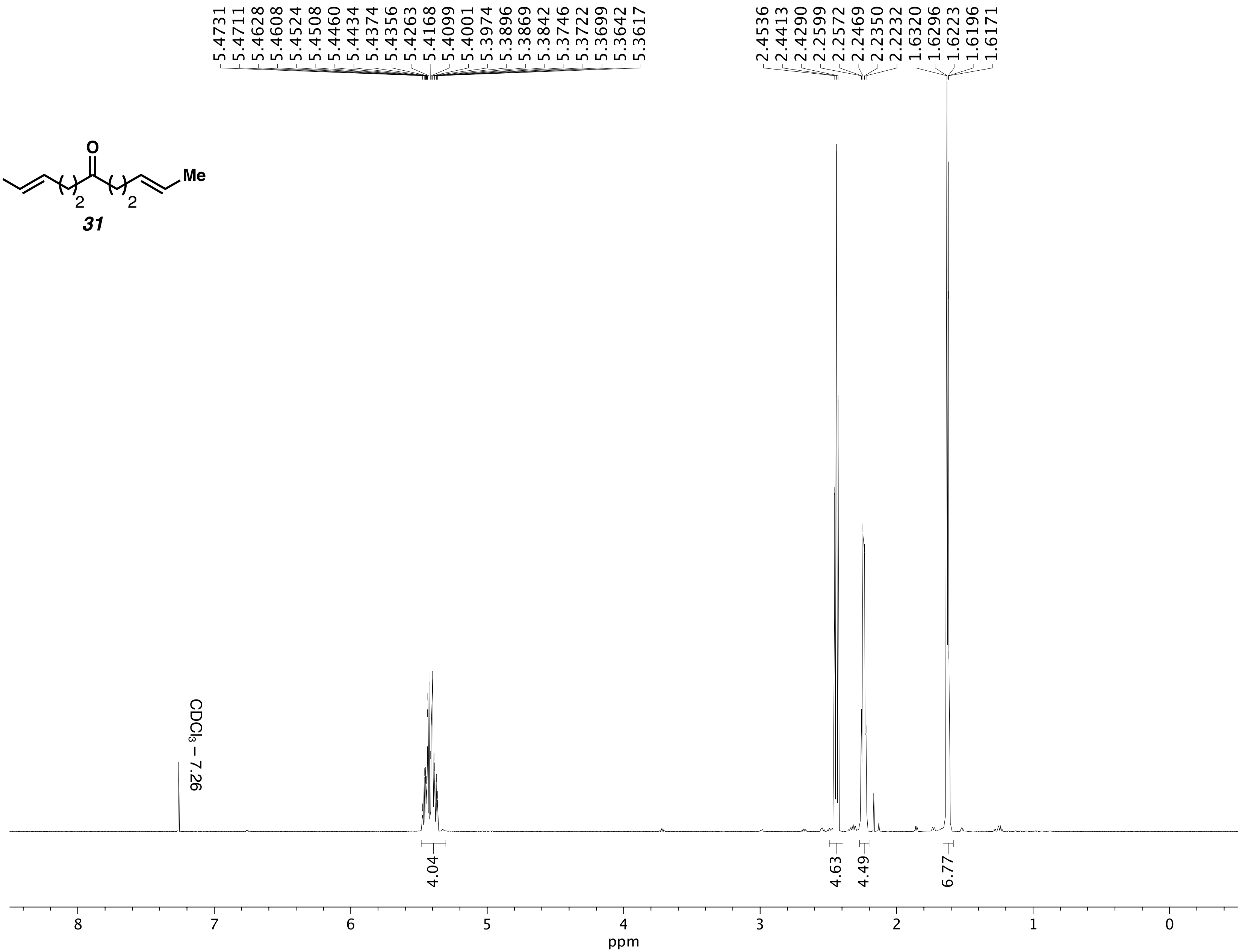
^{1}H NMR (400 MHz, $CDCl_3$) of compound **29**.



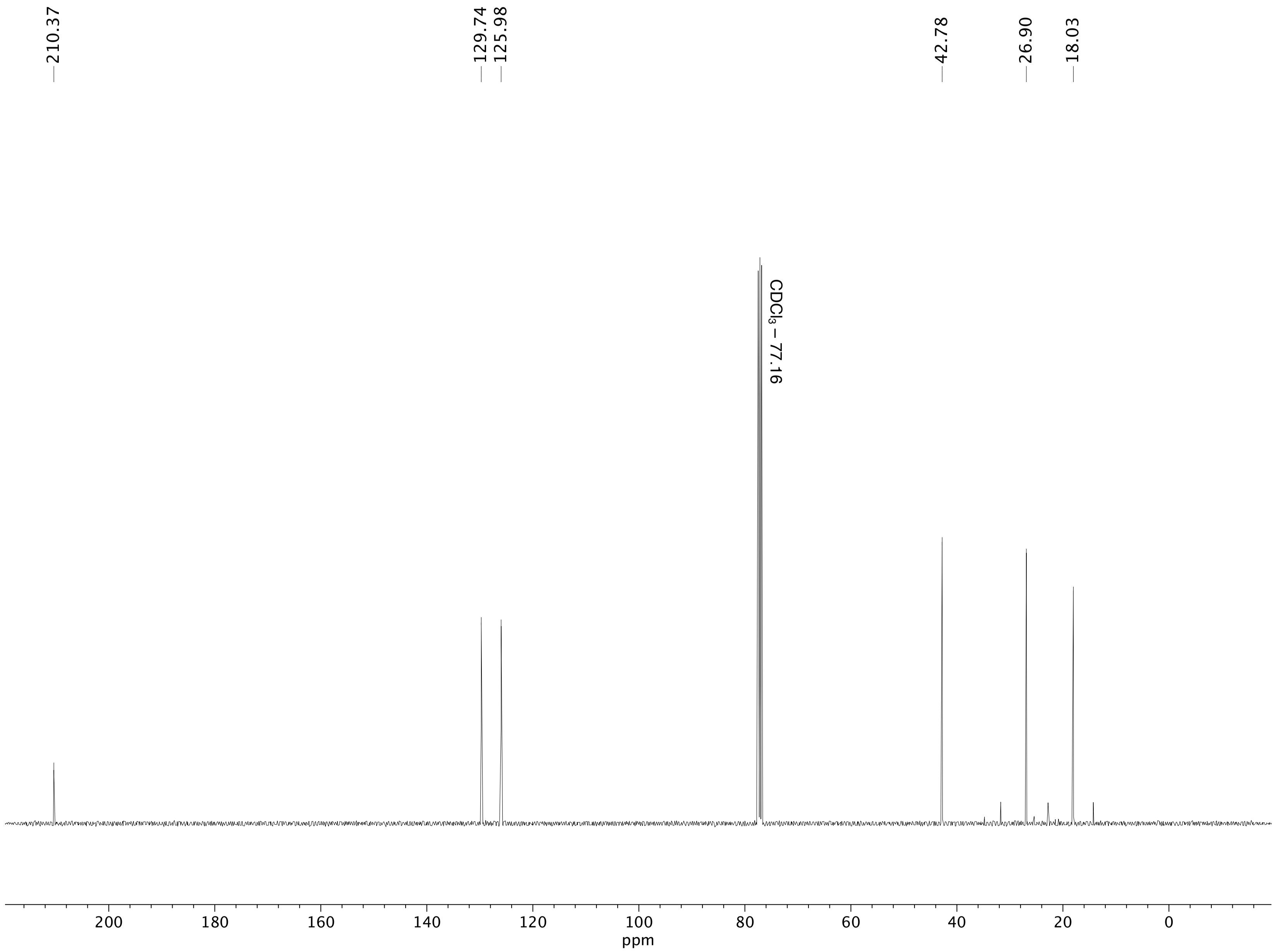
^{13}C NMR (101 MHz, CDCl$_3$) of compound **29**.



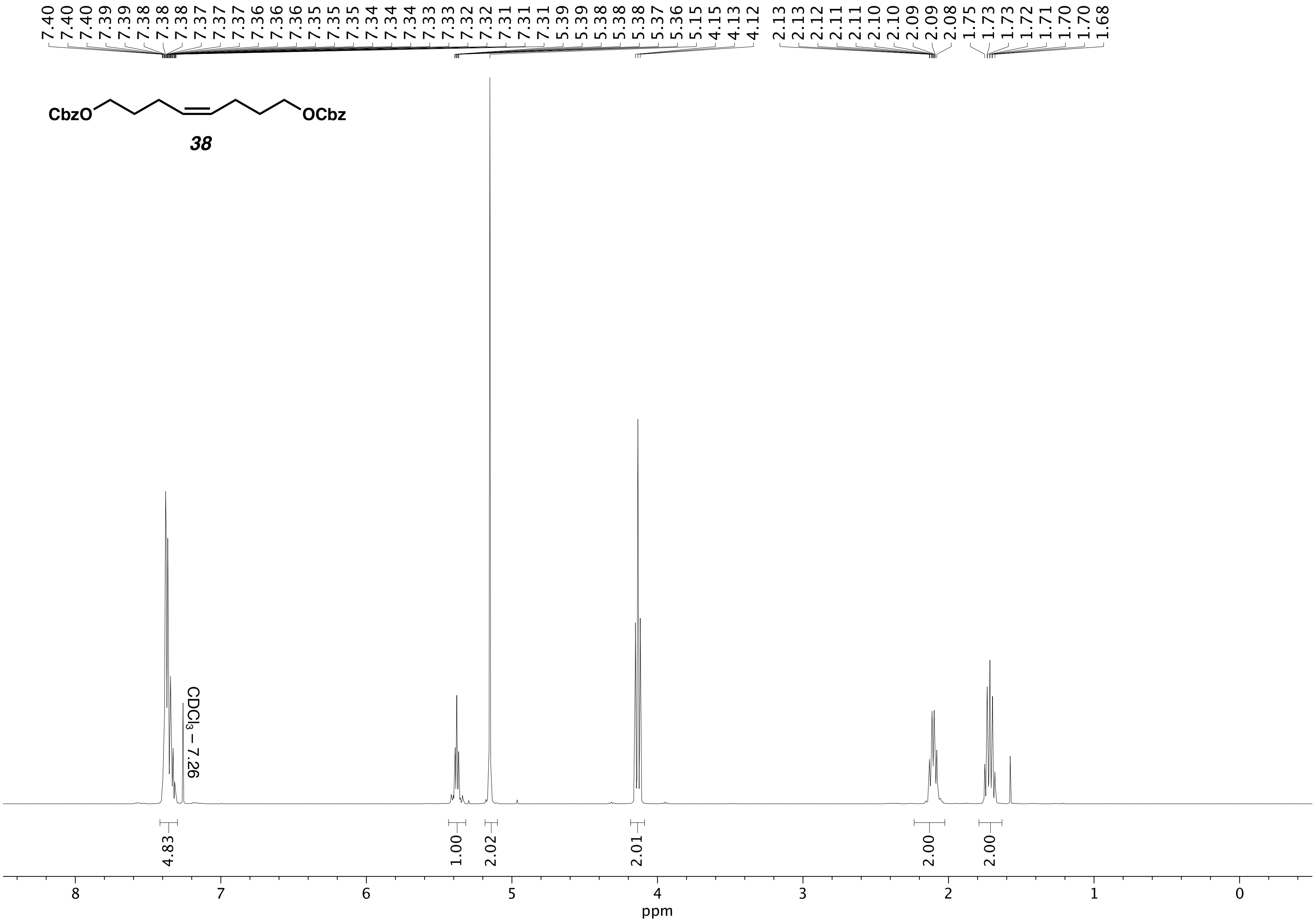
31



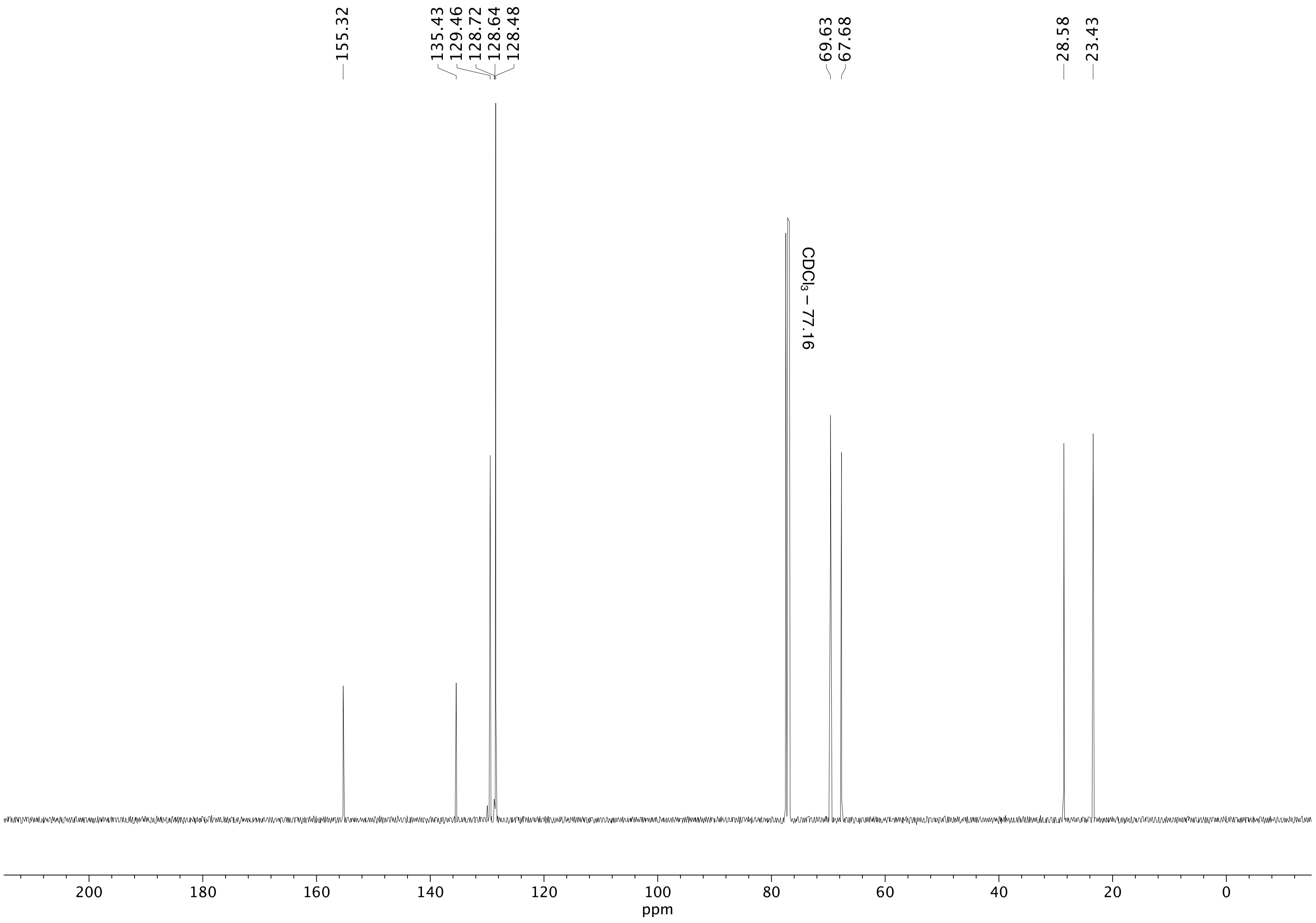
^{1}H NMR (600 MHz, CDCl$_3$) of compound **31**.



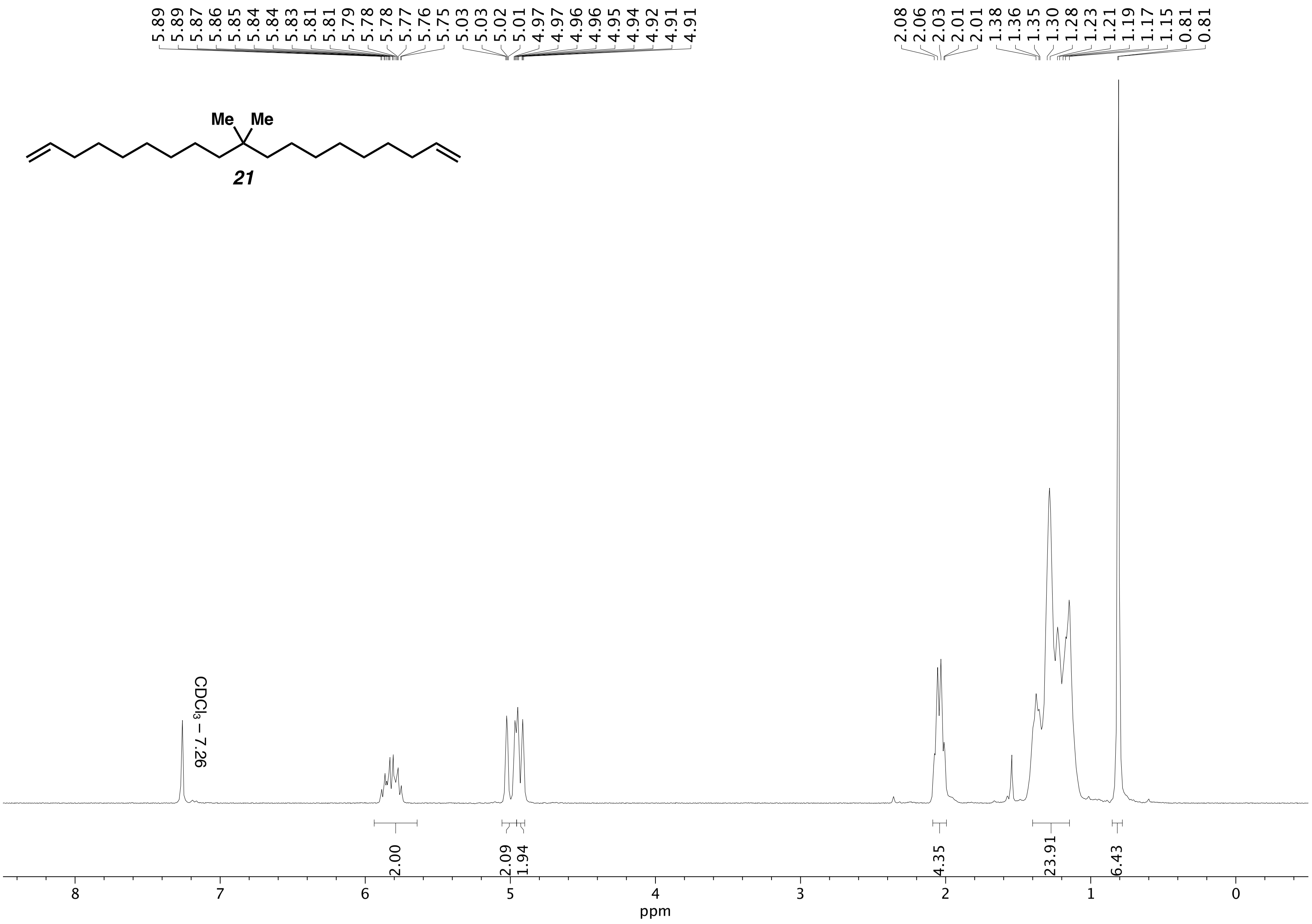
^{13}C NMR (101 MHz, CDCl$_3$) of compound **31**.



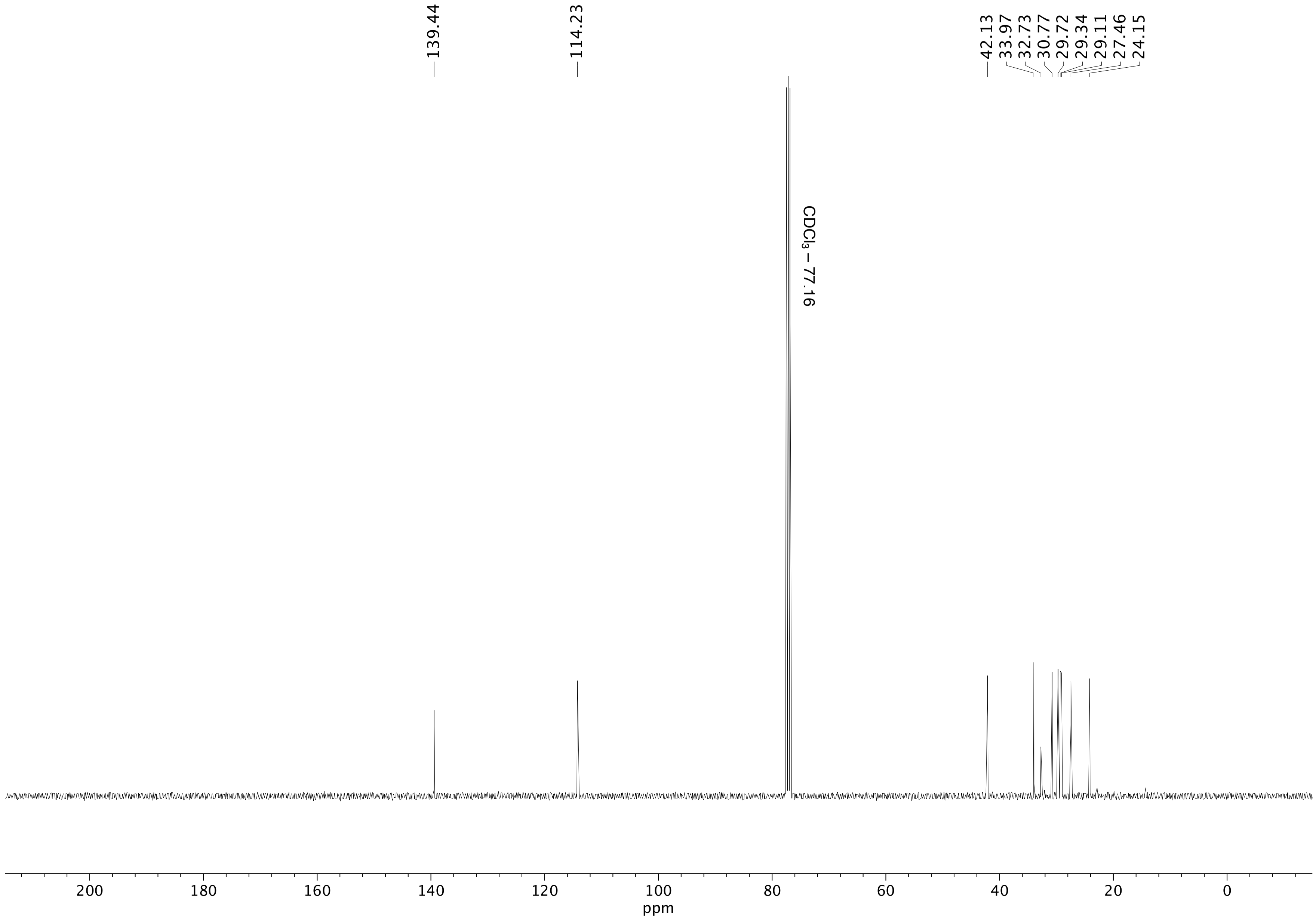
^{1}H NMR (600 MHz, $CDCl_3$) of compound **38**.



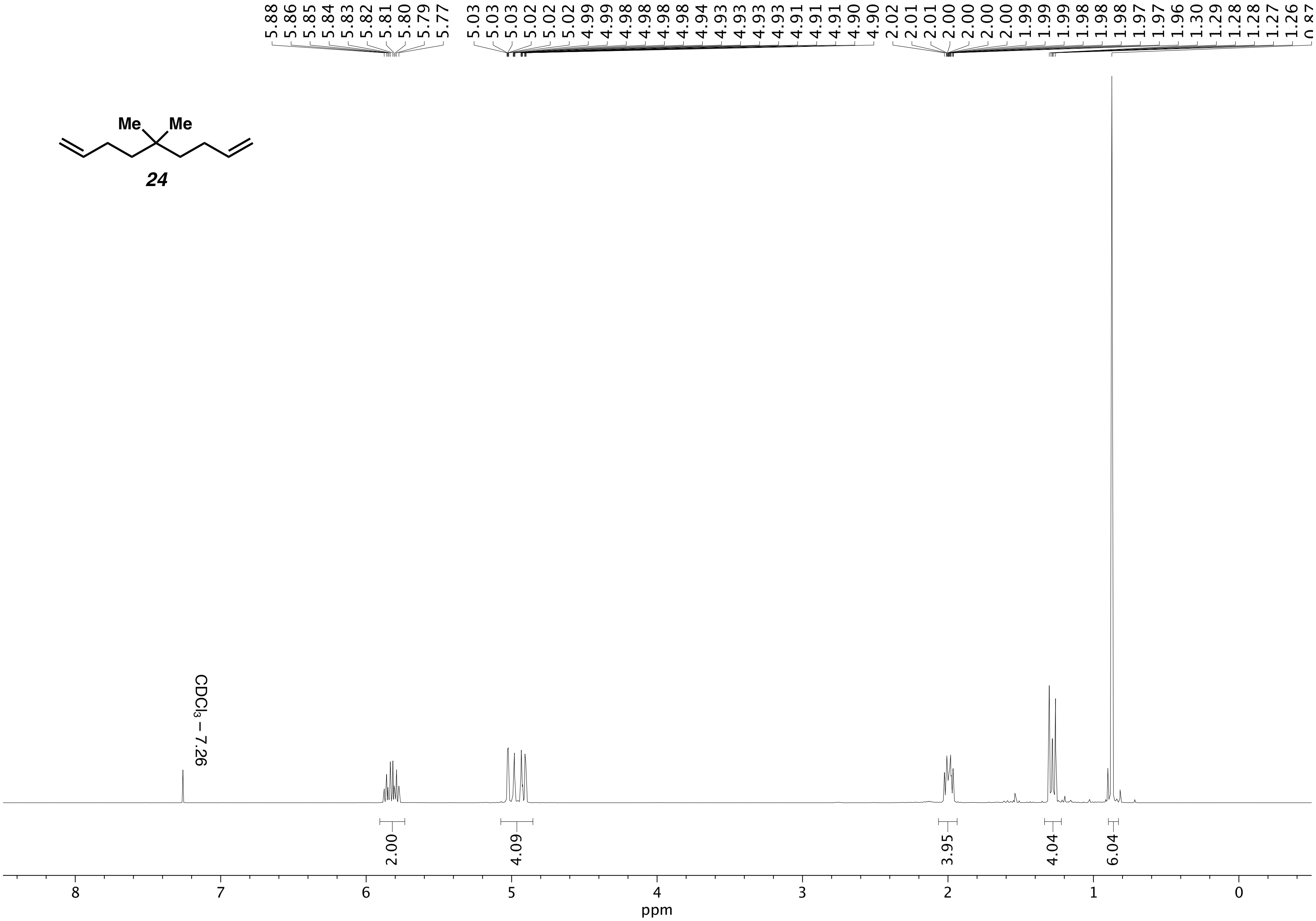
^{13}C NMR (101 MHz, CDCl$_3$) of compound **38**.



^{1}H NMR (600 MHz, $CDCl_3$) of compound **21**.

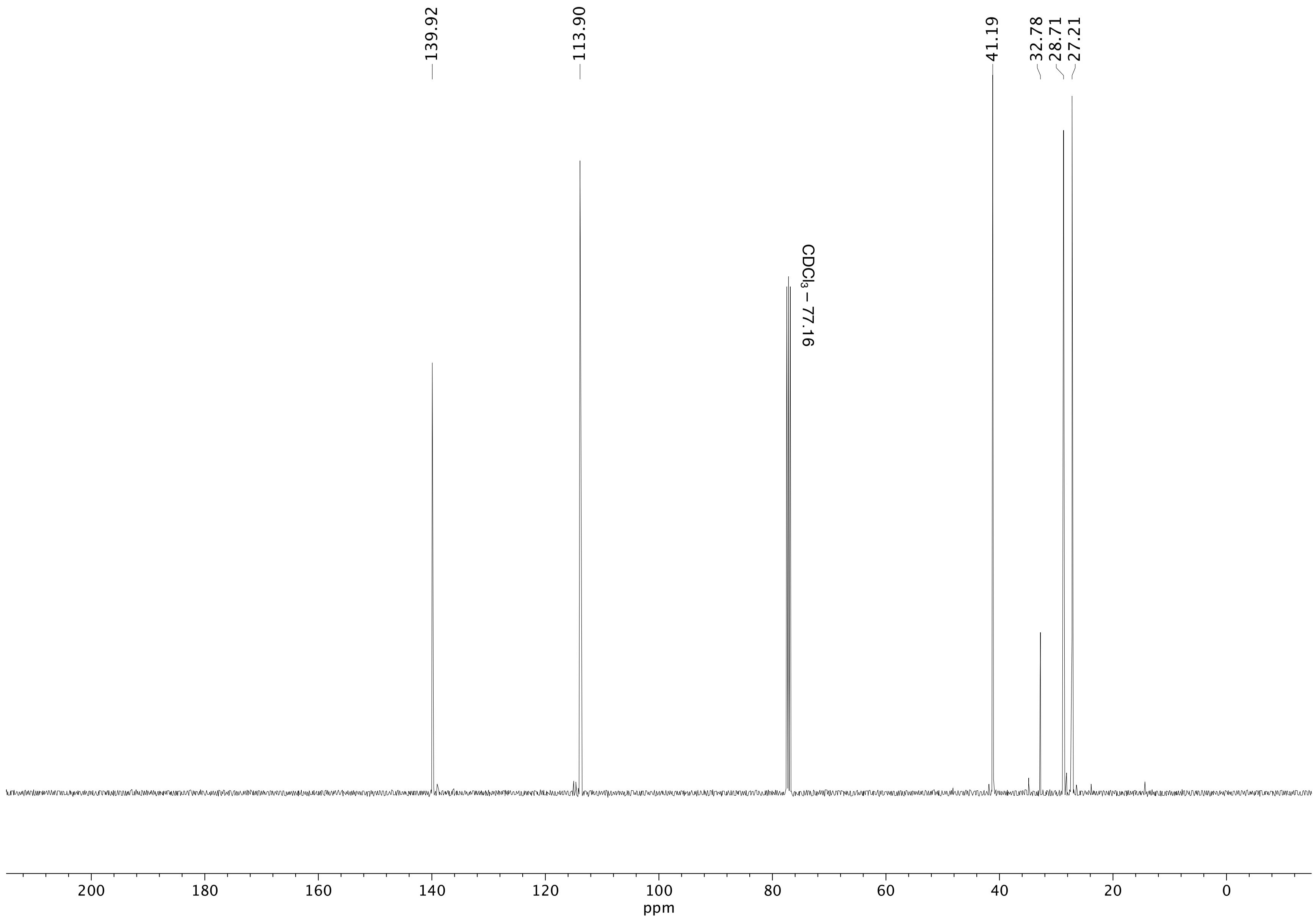


^{13}C NMR (101 MHz, CDCl$_3$) of compound **21**.

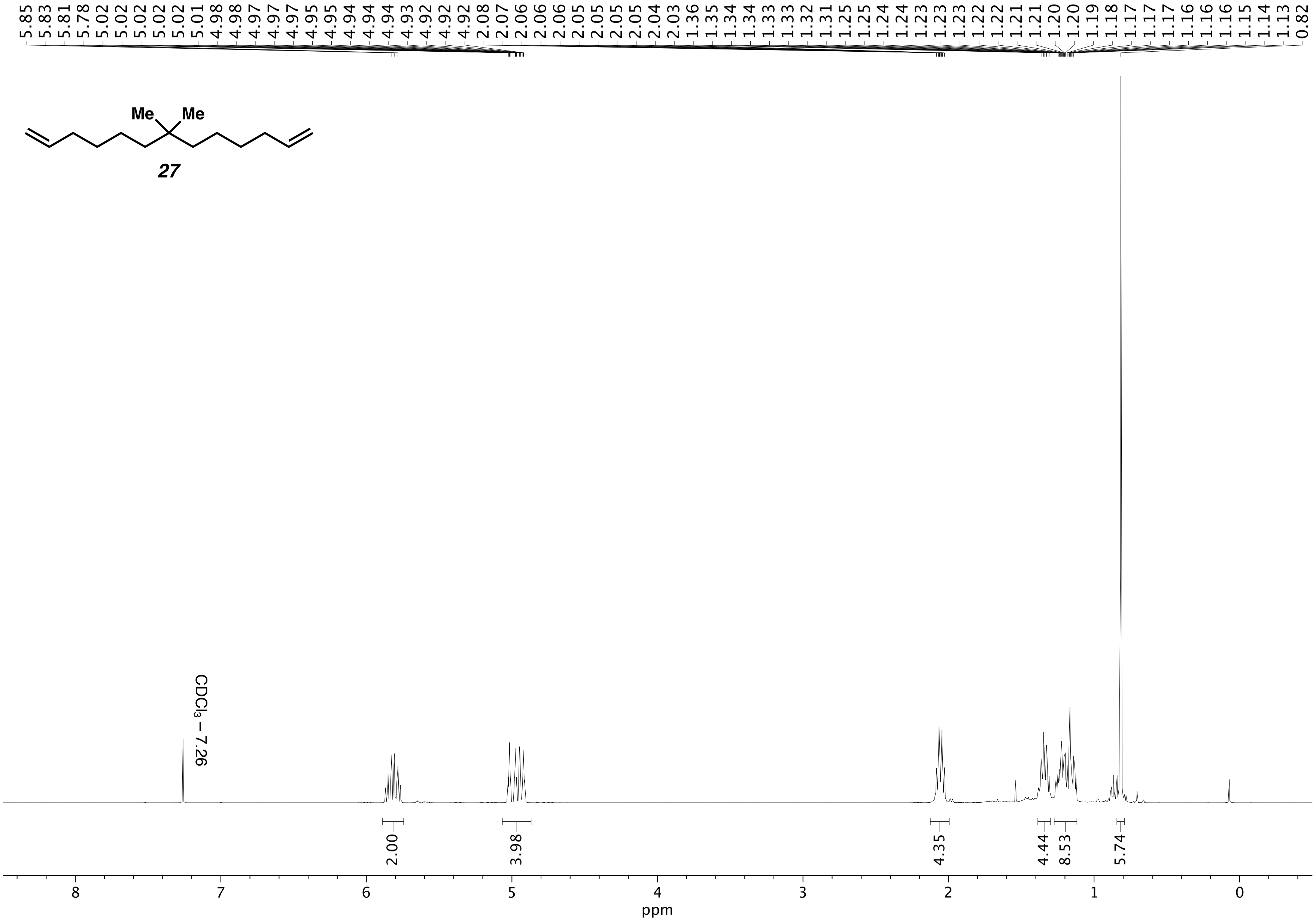


24

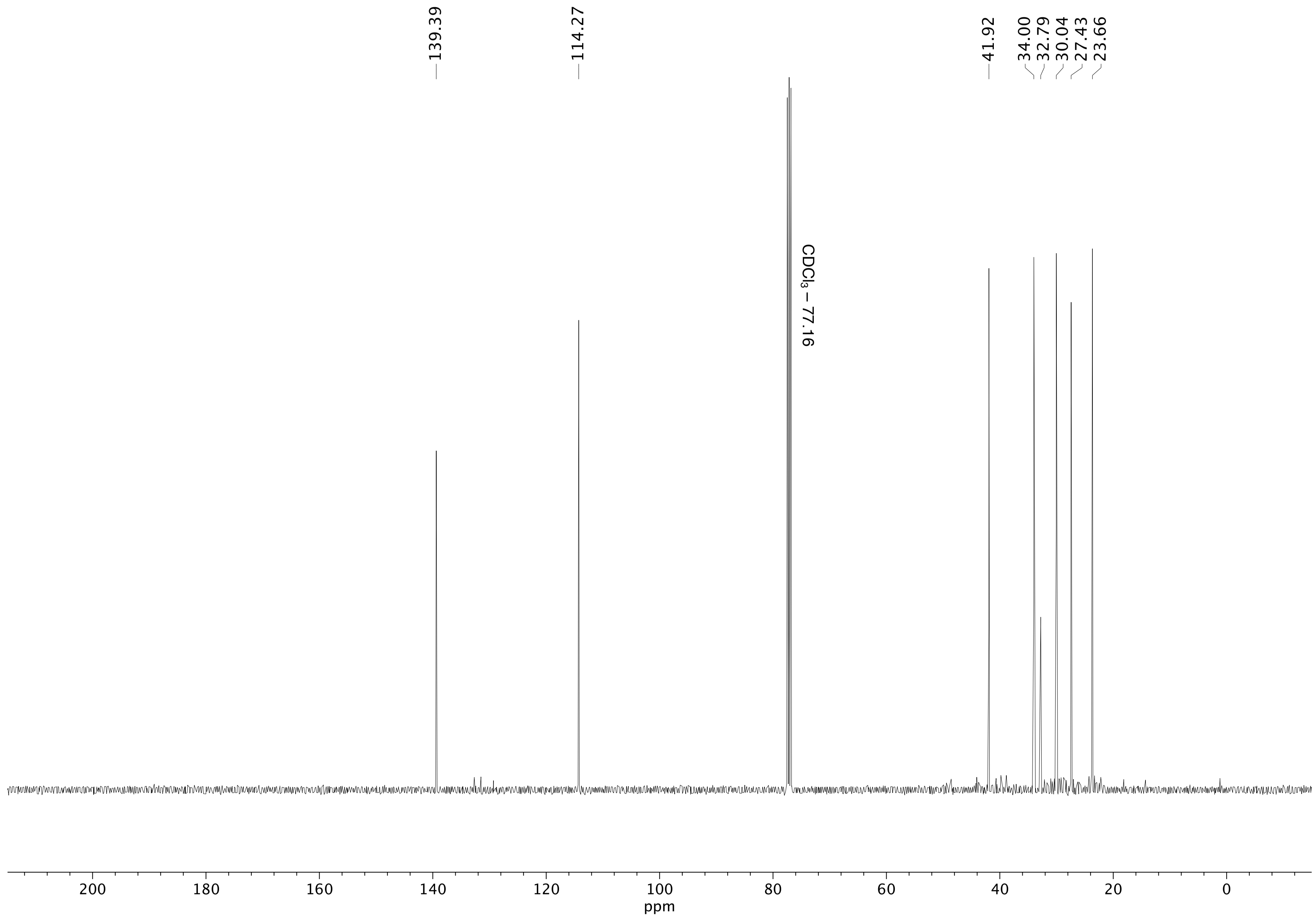
^{1}H NMR (400 MHz, $CDCl_3$) of compound **24**.



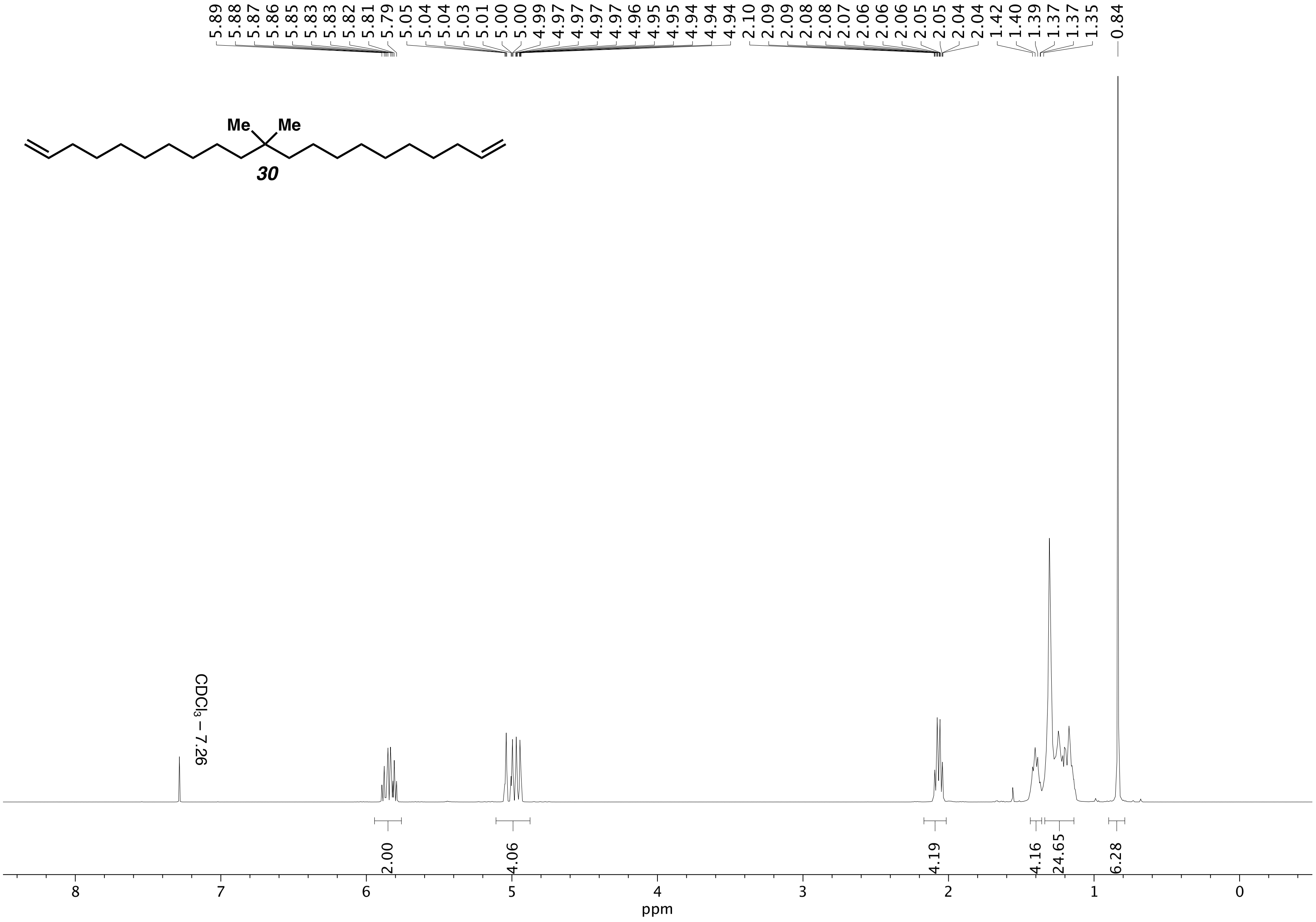
^{13}C NMR (101 MHz, CDCl$_3$) of compound **24**.



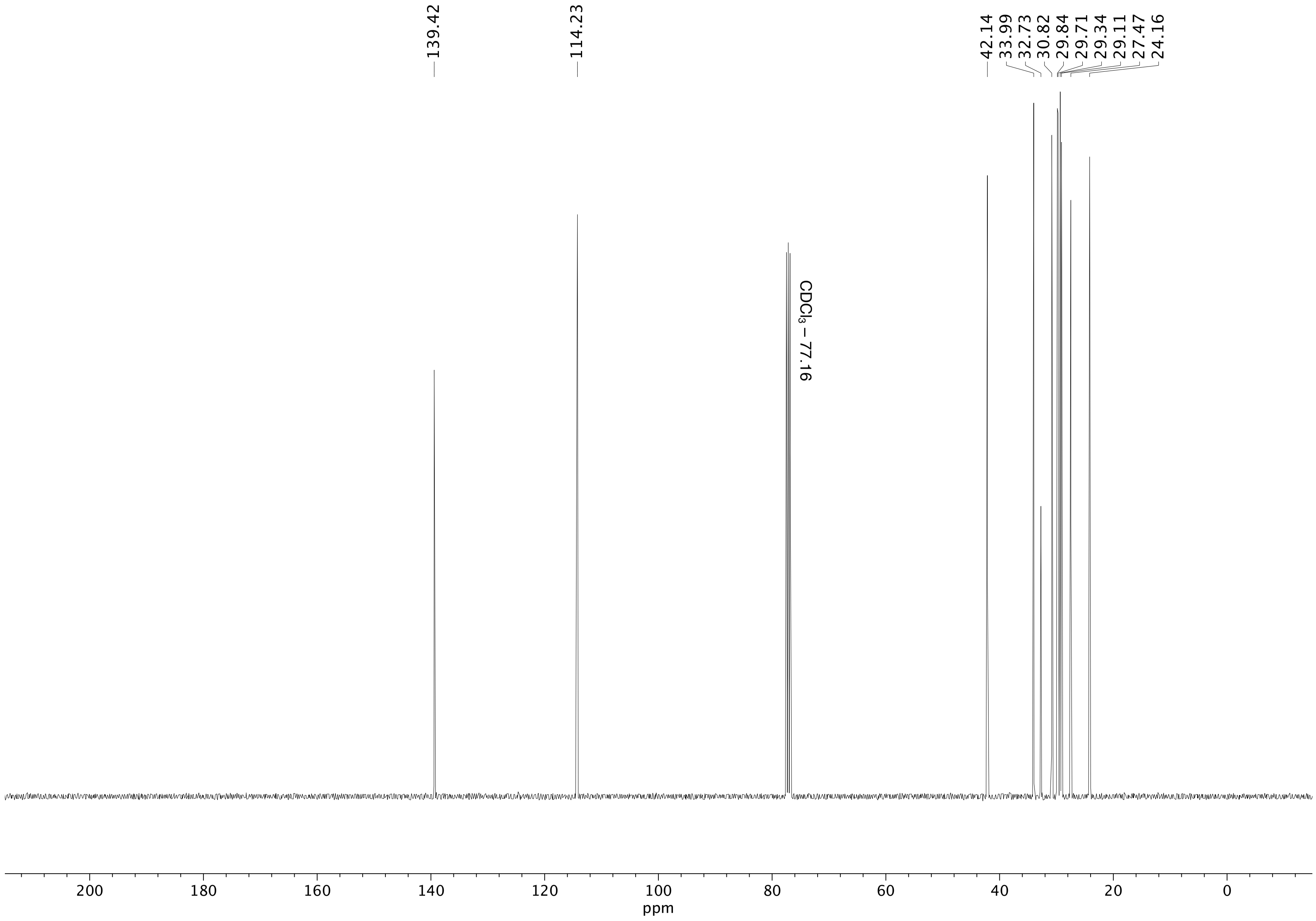
^{1}H NMR (400 MHz, $CDCl_3$) of compound **27**.



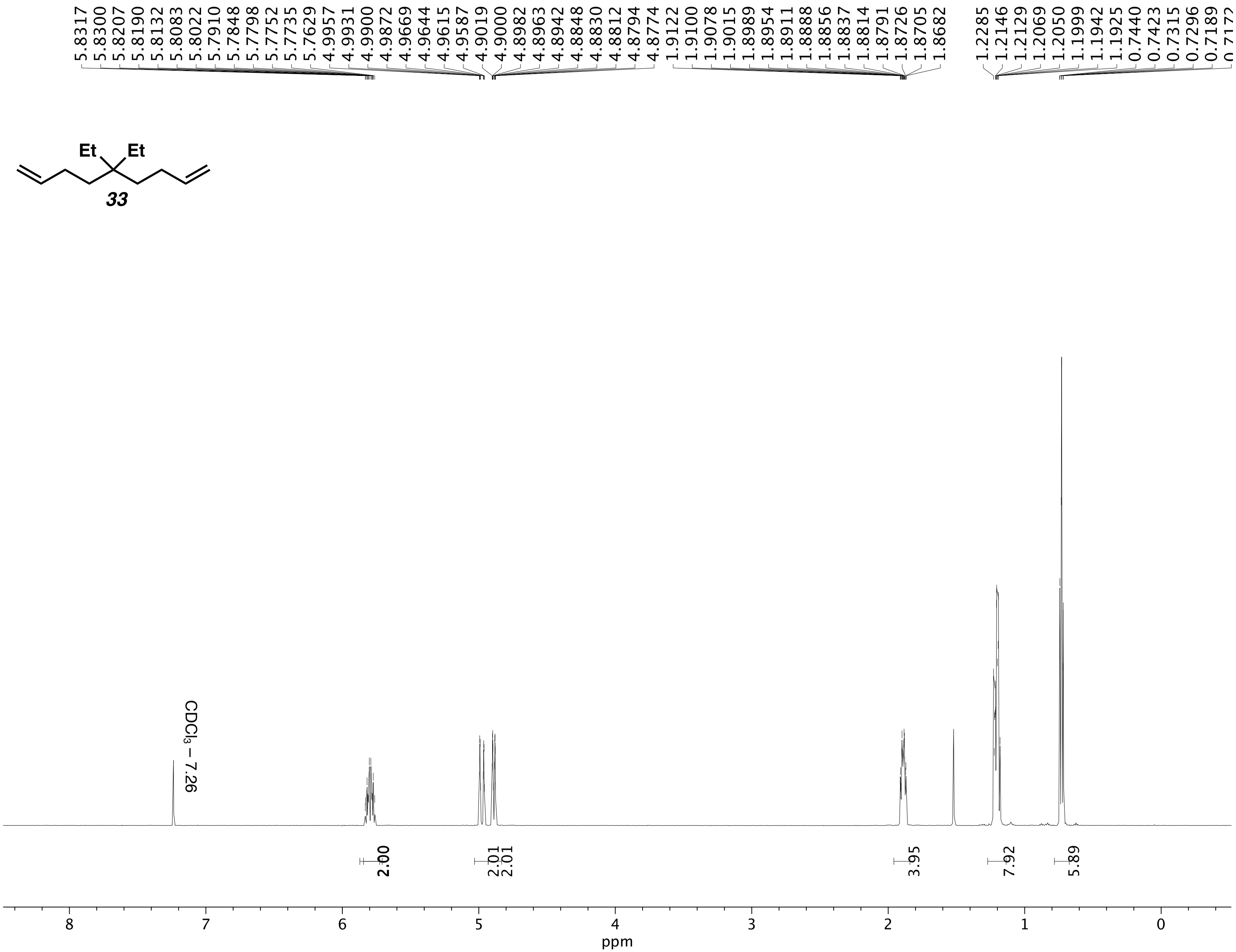
^{13}C NMR (101 MHz, CDCl$_3$) of compound **27**.



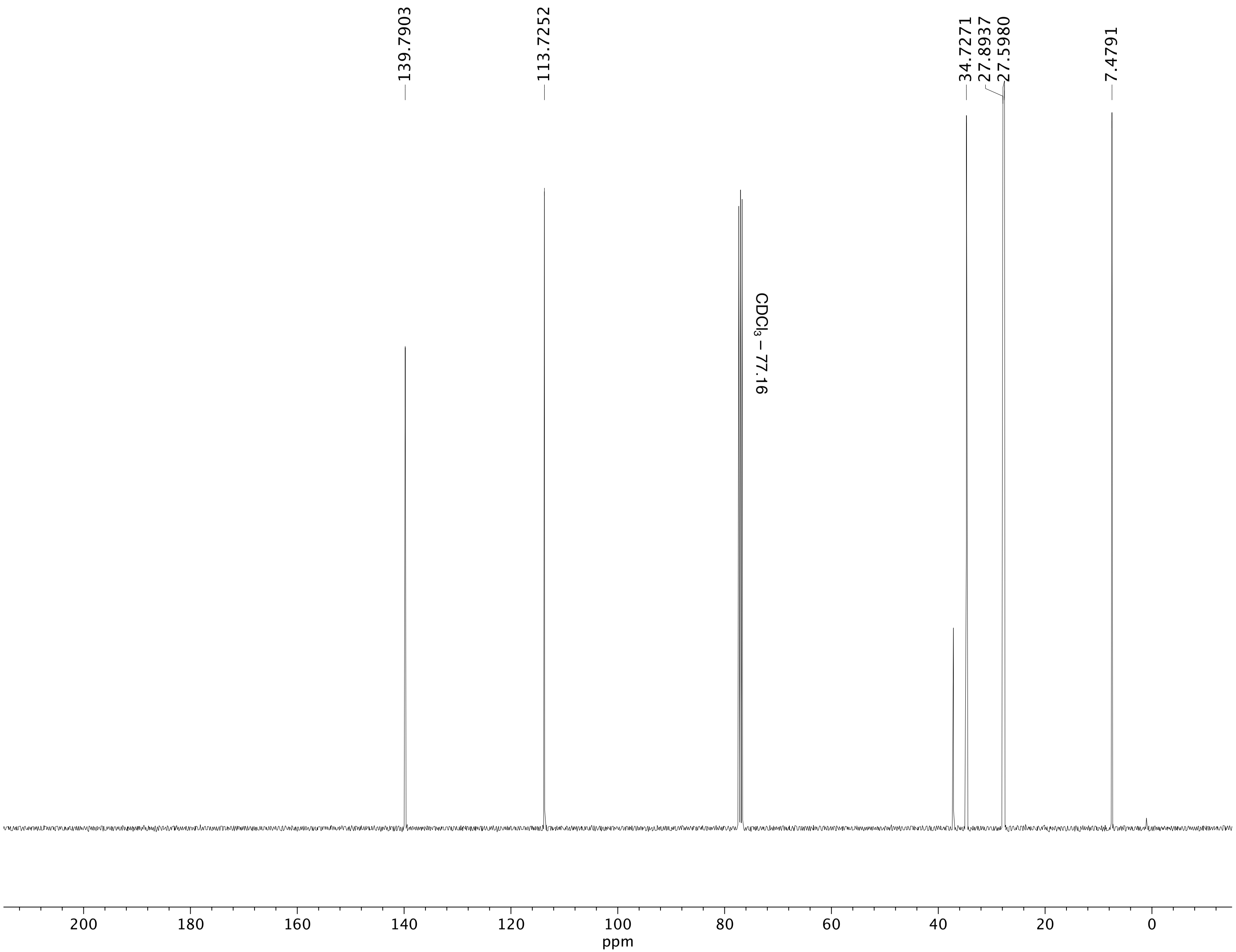
^{1}H NMR (400 MHz, $CDCl_3$) of compound **30**.



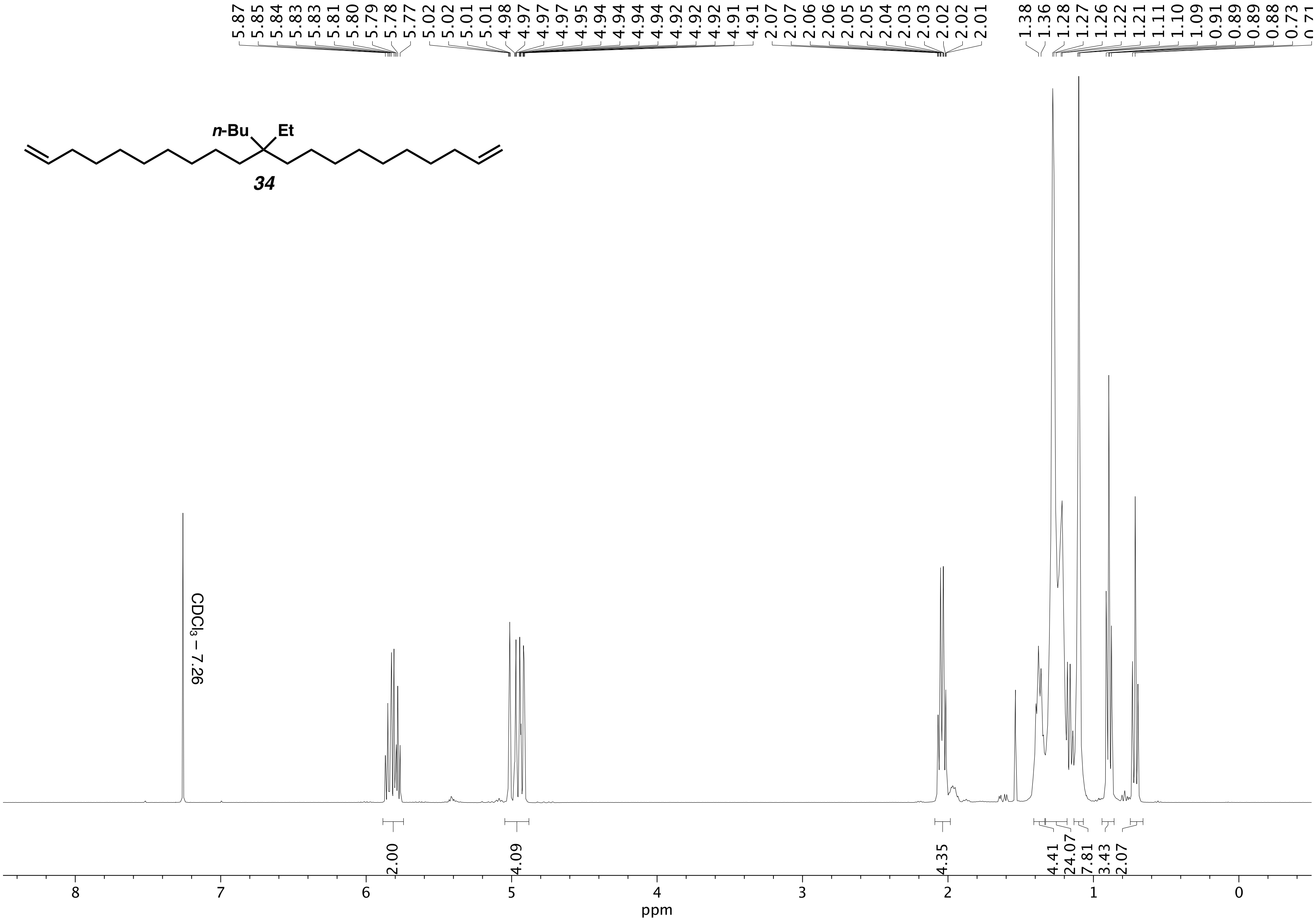
^{13}C NMR (101 MHz, CDCl$_3$) of compound **30**.



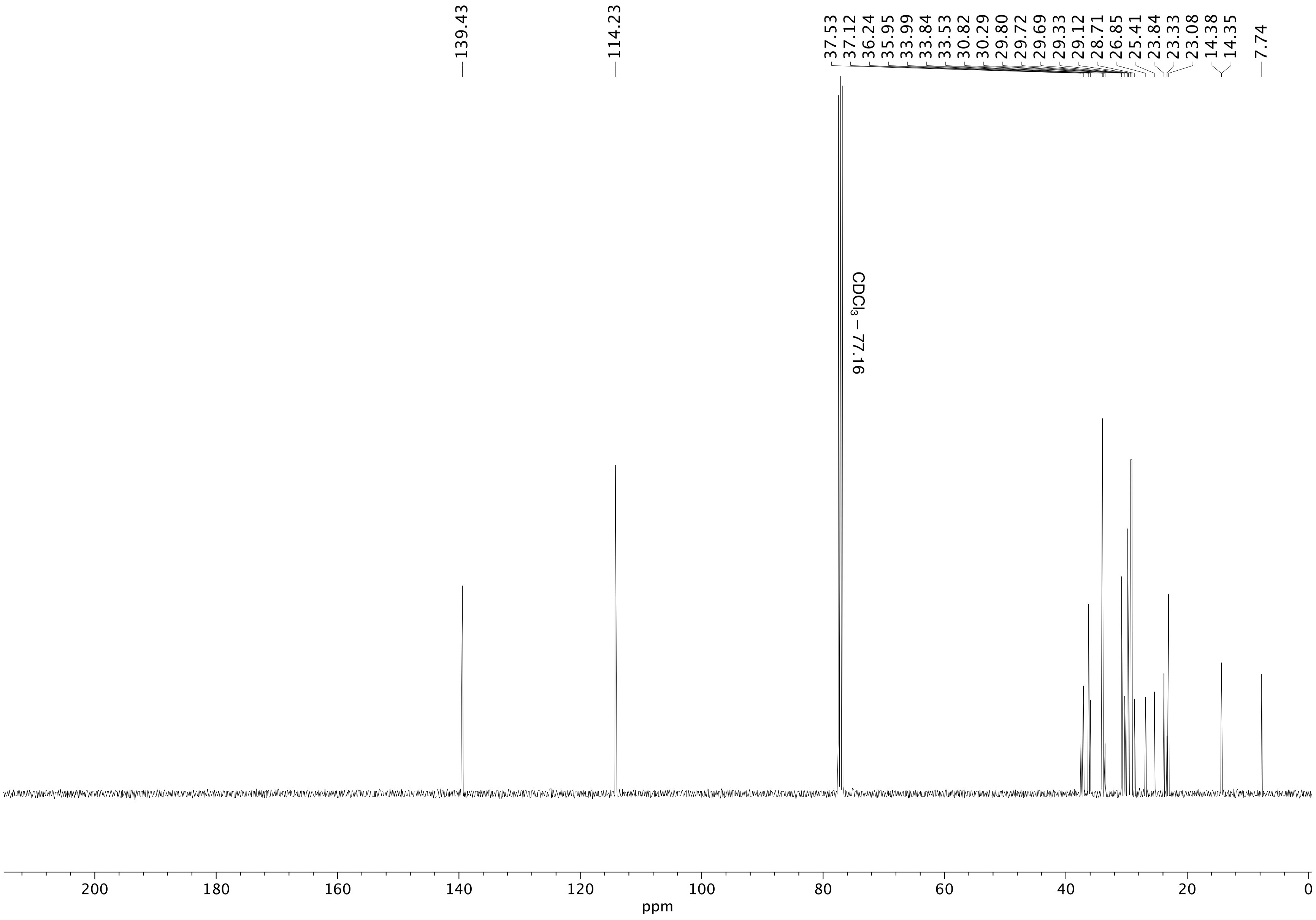
^{1}H NMR (600 MHz, CDCl$_3$) of compound **33**.



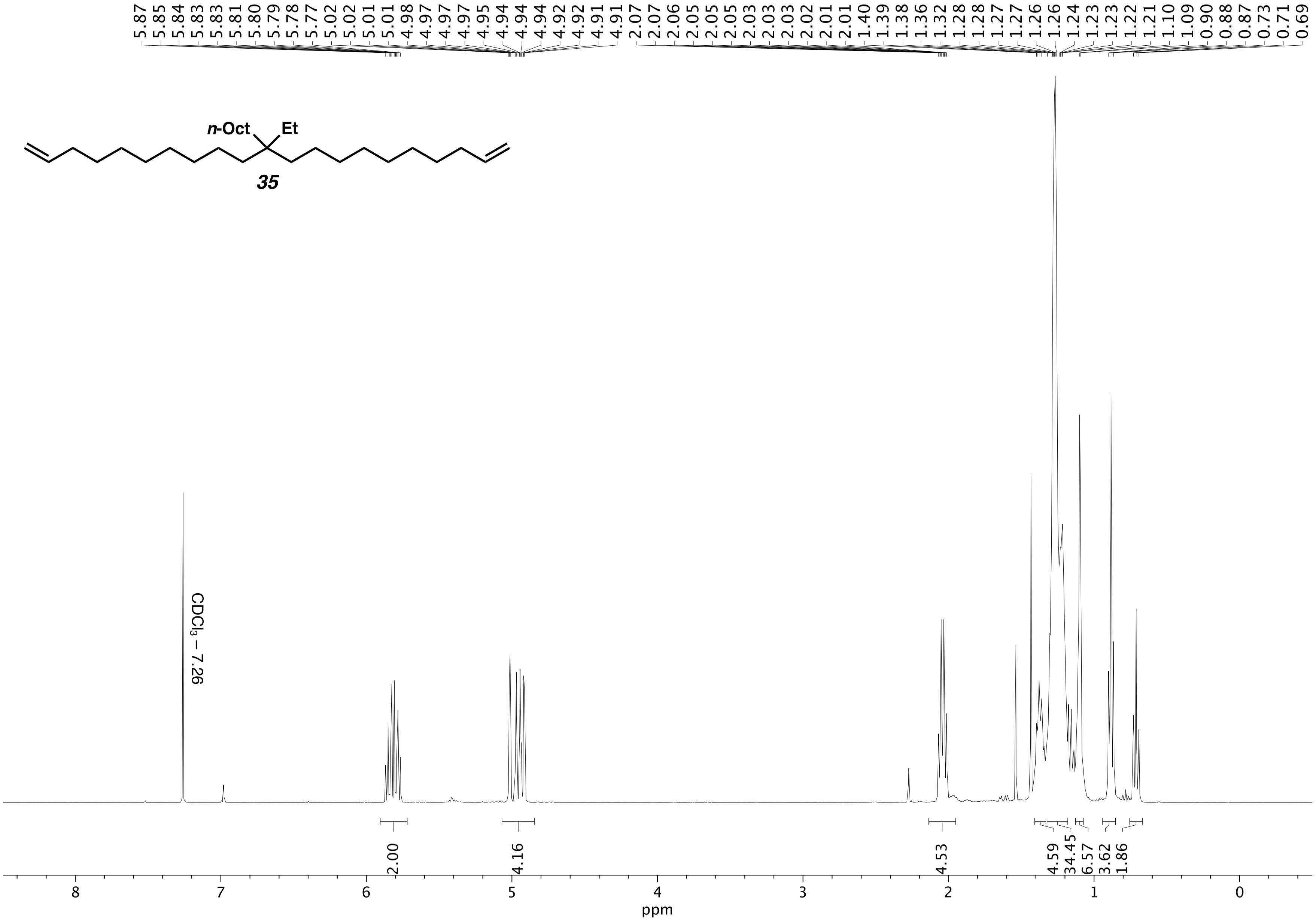
^{13}C NMR (101 MHz, CDCl$_3$) of compound **33**.



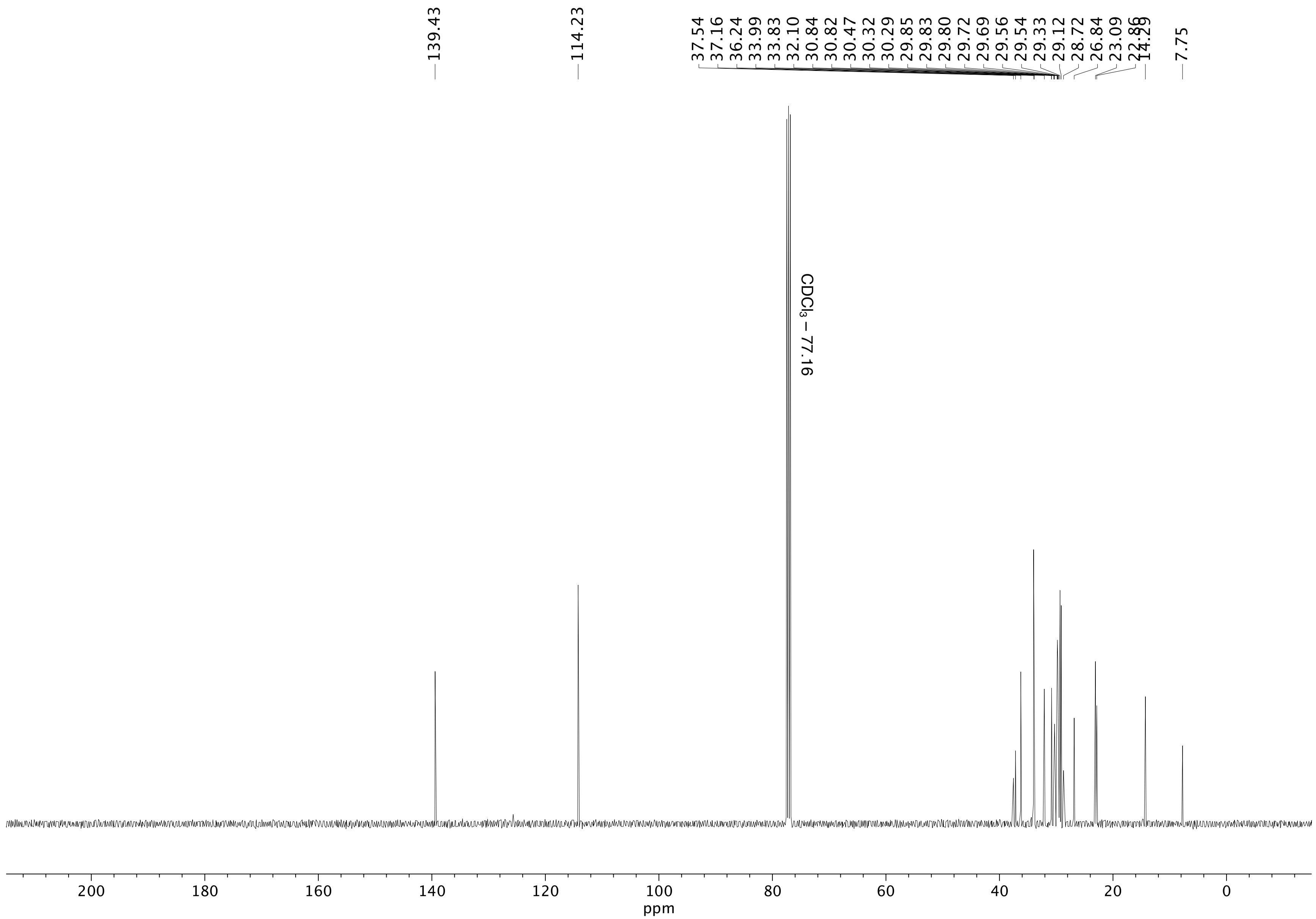
^{1}H NMR (400 MHz, CDCl$_3$) of compound **34**.



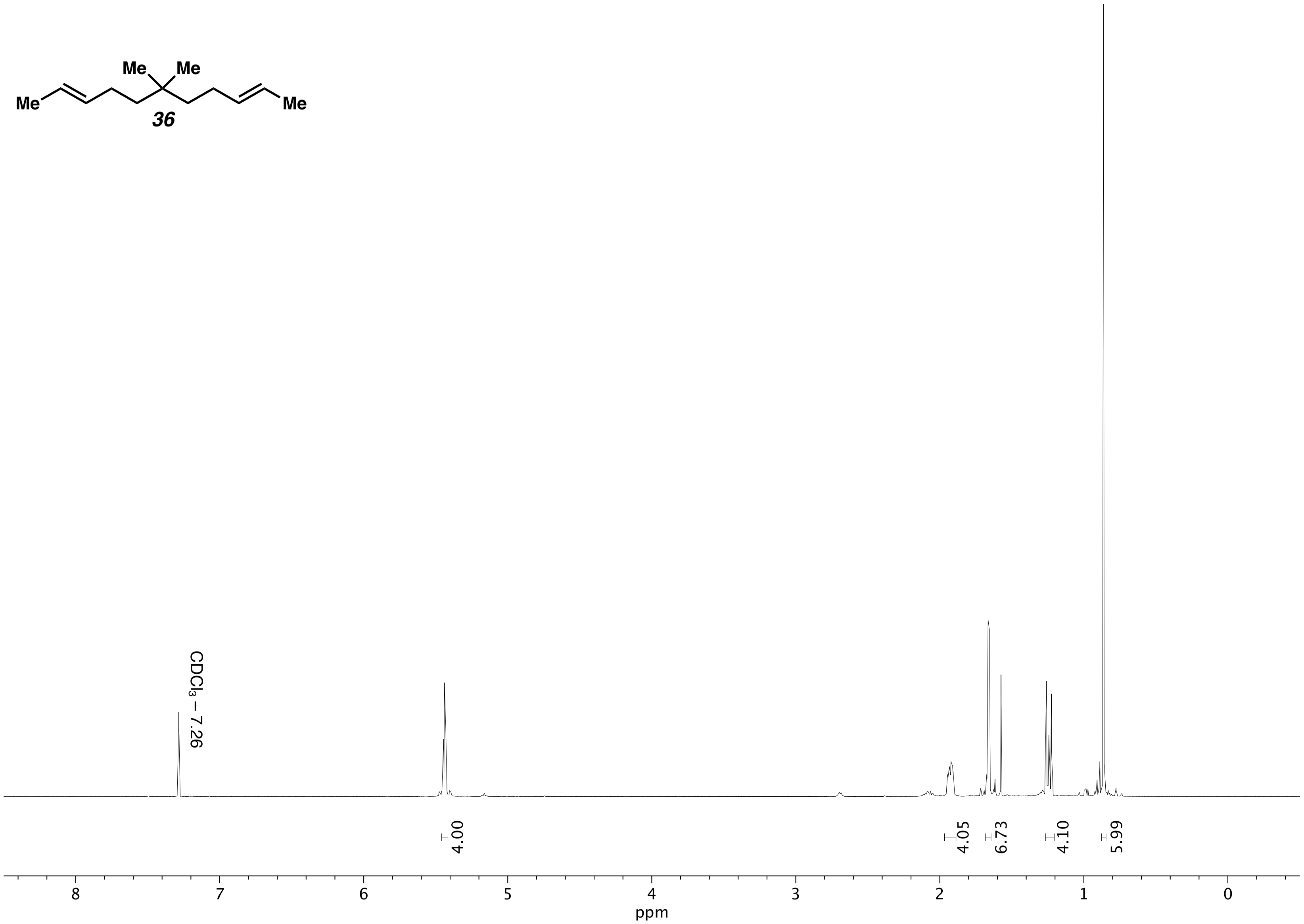
^{13}C NMR (101 MHz, CDCl$_3$) of compound **34**.



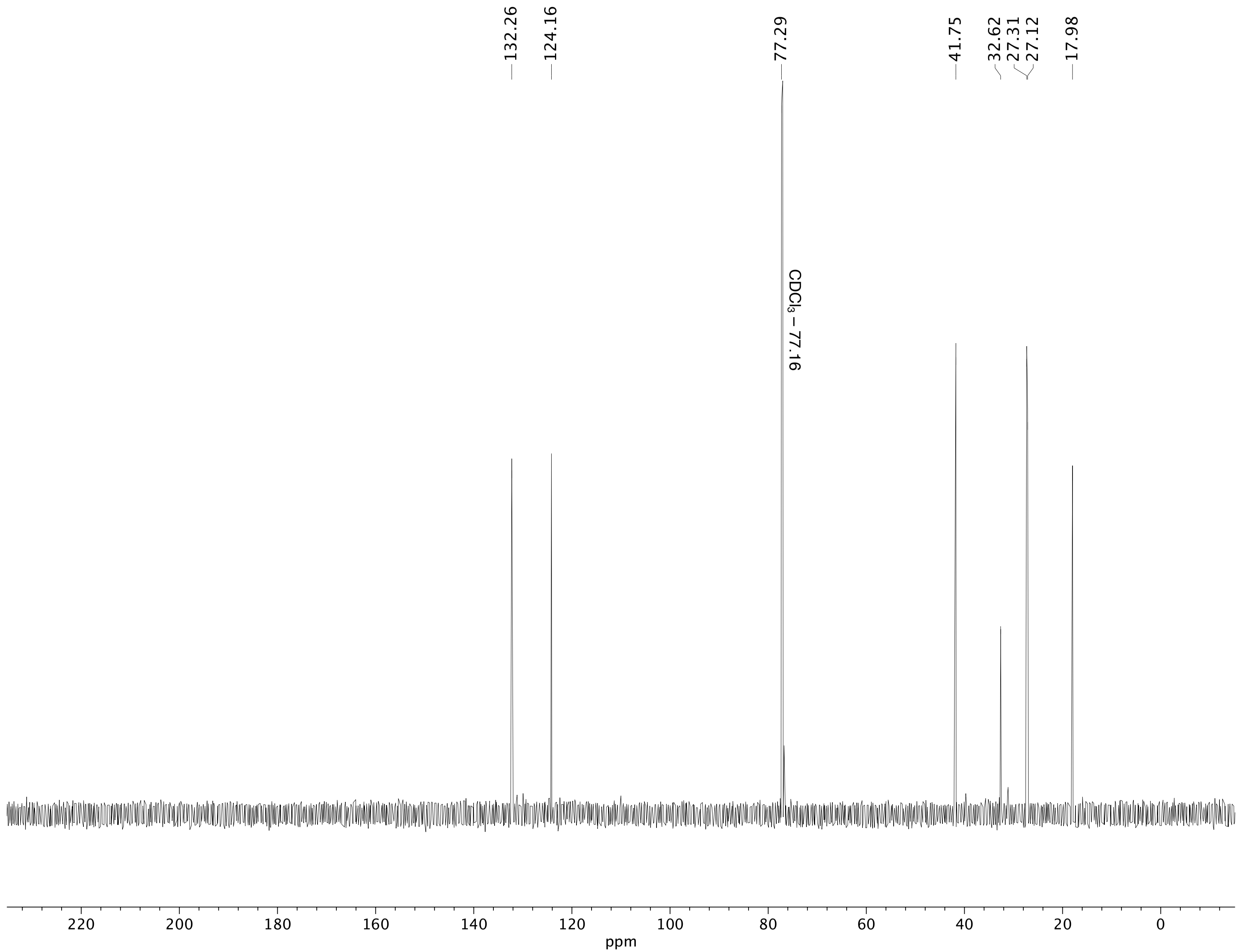
^{1}H NMR (400 MHz, $CDCl_3$) of compound **35**.



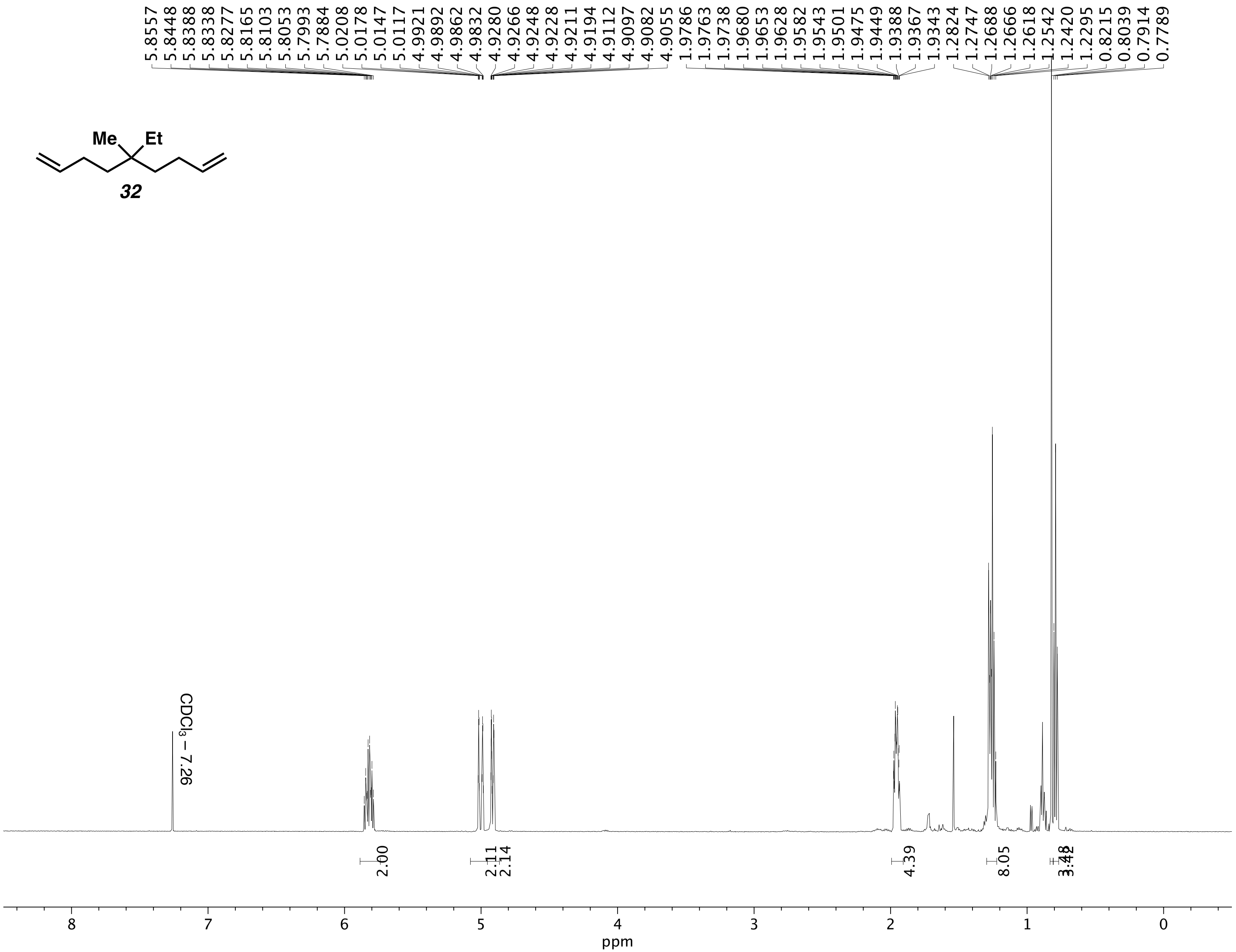
^{13}C NMR (101 MHz, $CDCl_3$) of compound **35**.



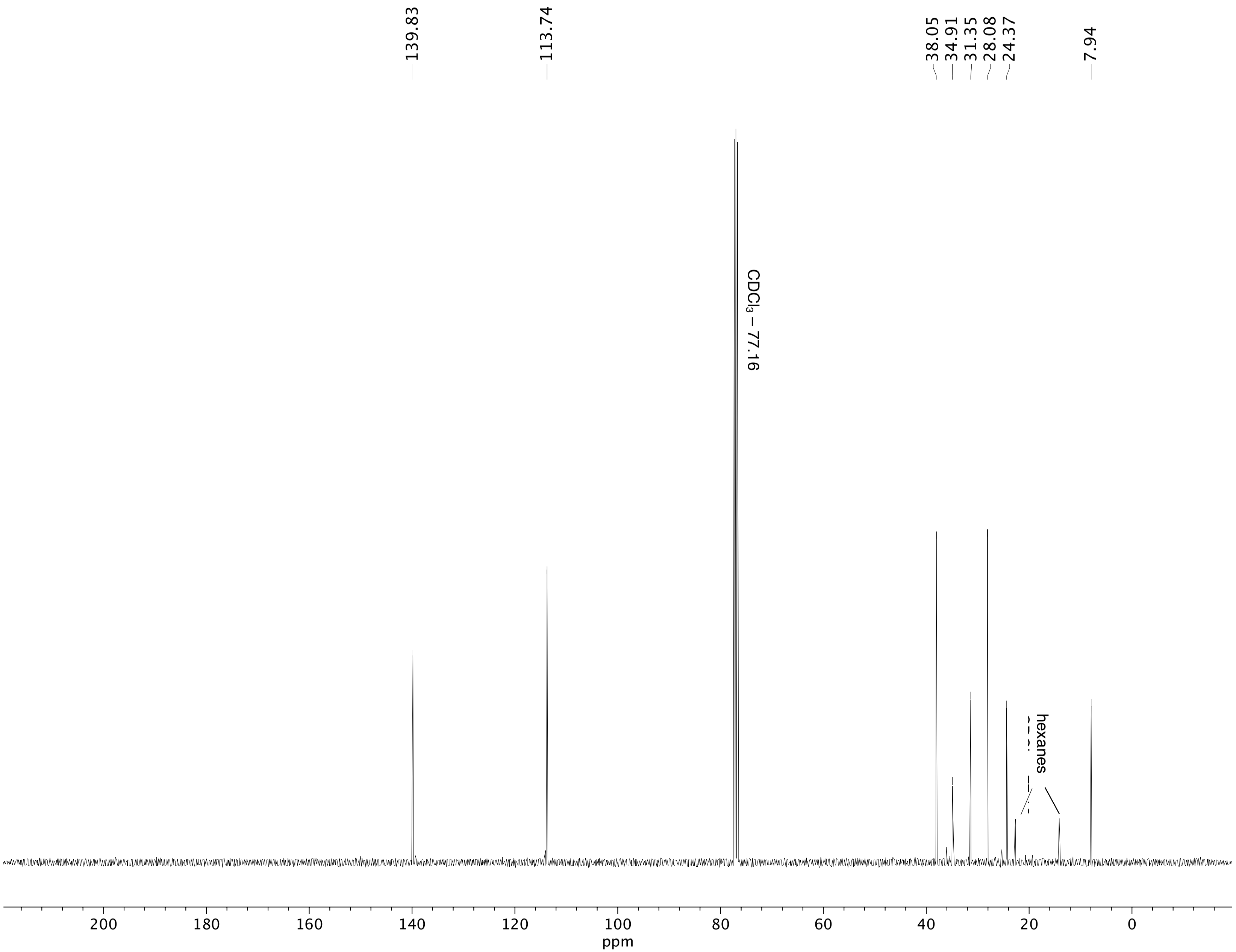
^{1}H NMR (500 MHz, CDCl$_3$) of compound **36**.



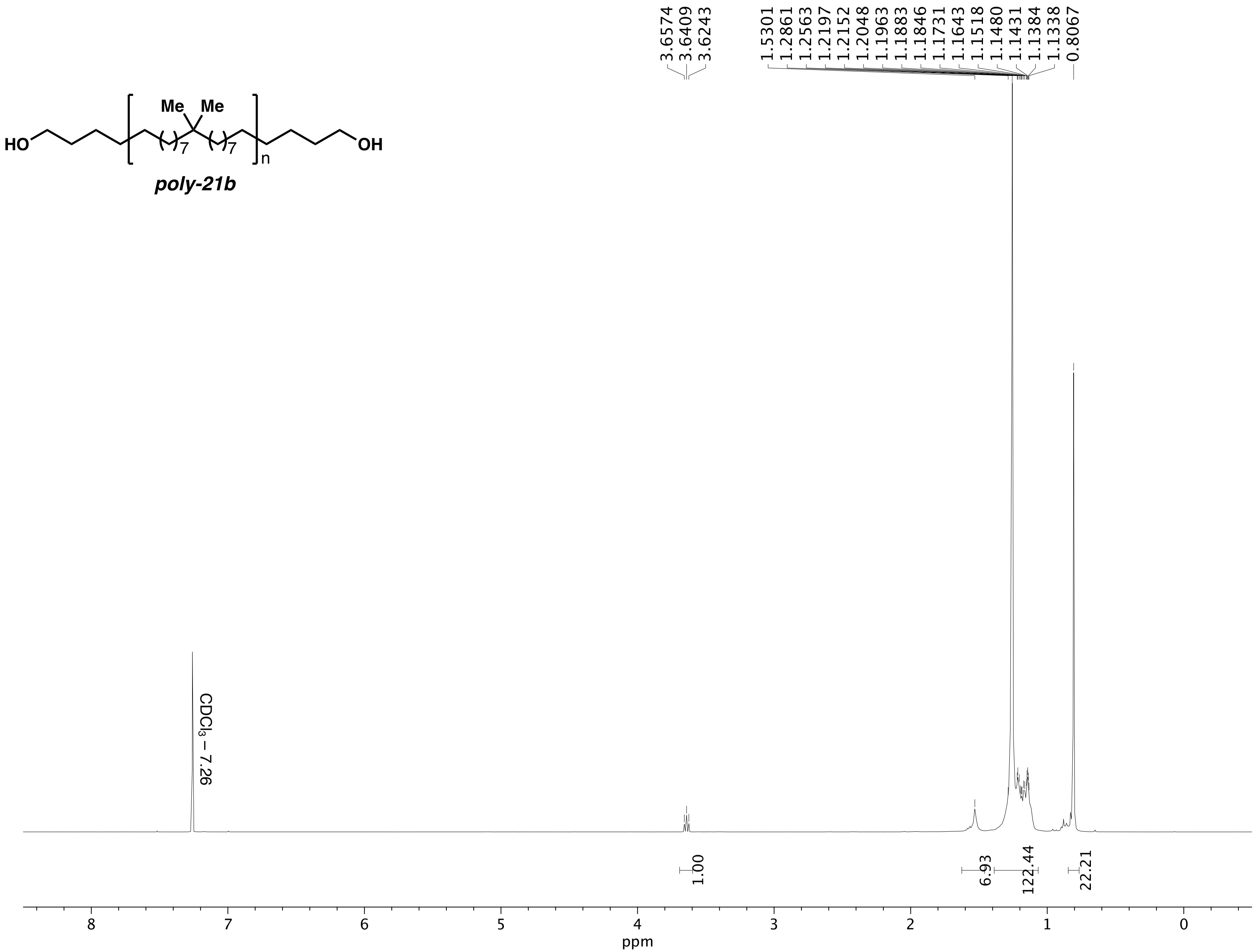
^{13}C NMR (101 MHz, CDCl$_3$) of compound **36**.



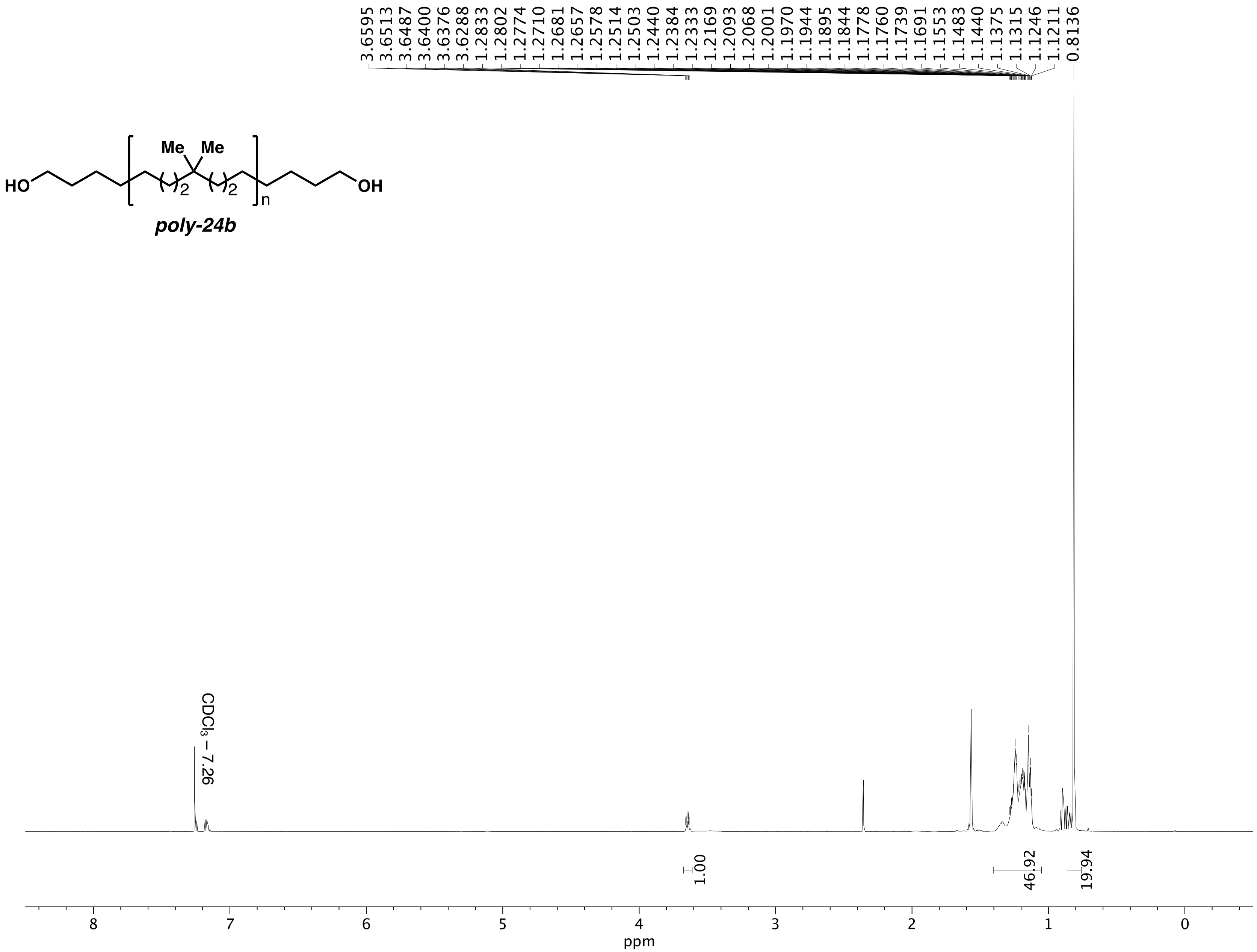
^{1}H NMR (600 MHz, $CDCl_3$) of compound **32**.



^{13}C NMR (101 MHz, CDCl$_3$) of compound **32**.

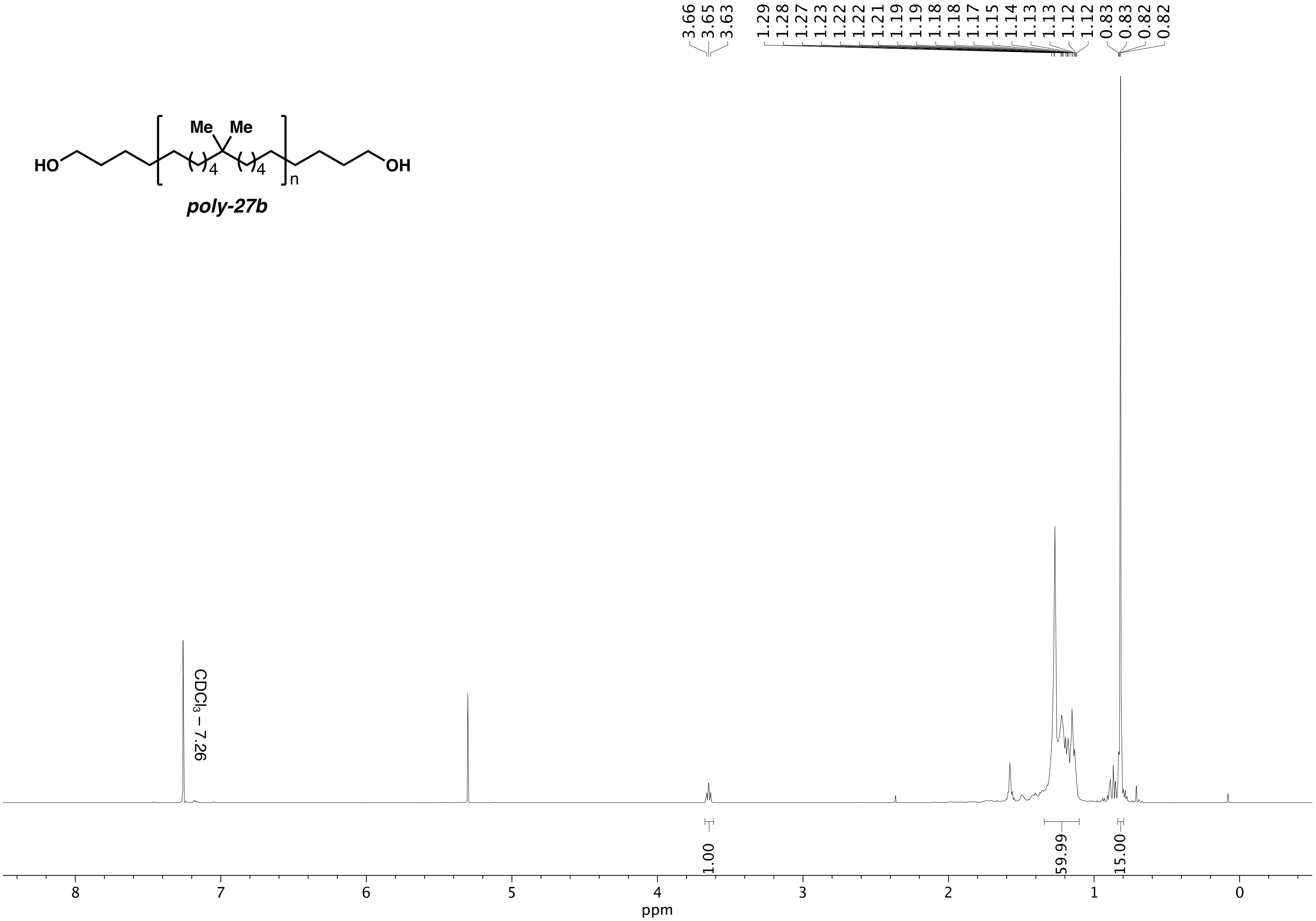


^{1}H NMR (400 MHz, $CDCl_3$) of compound **poly-21b**.

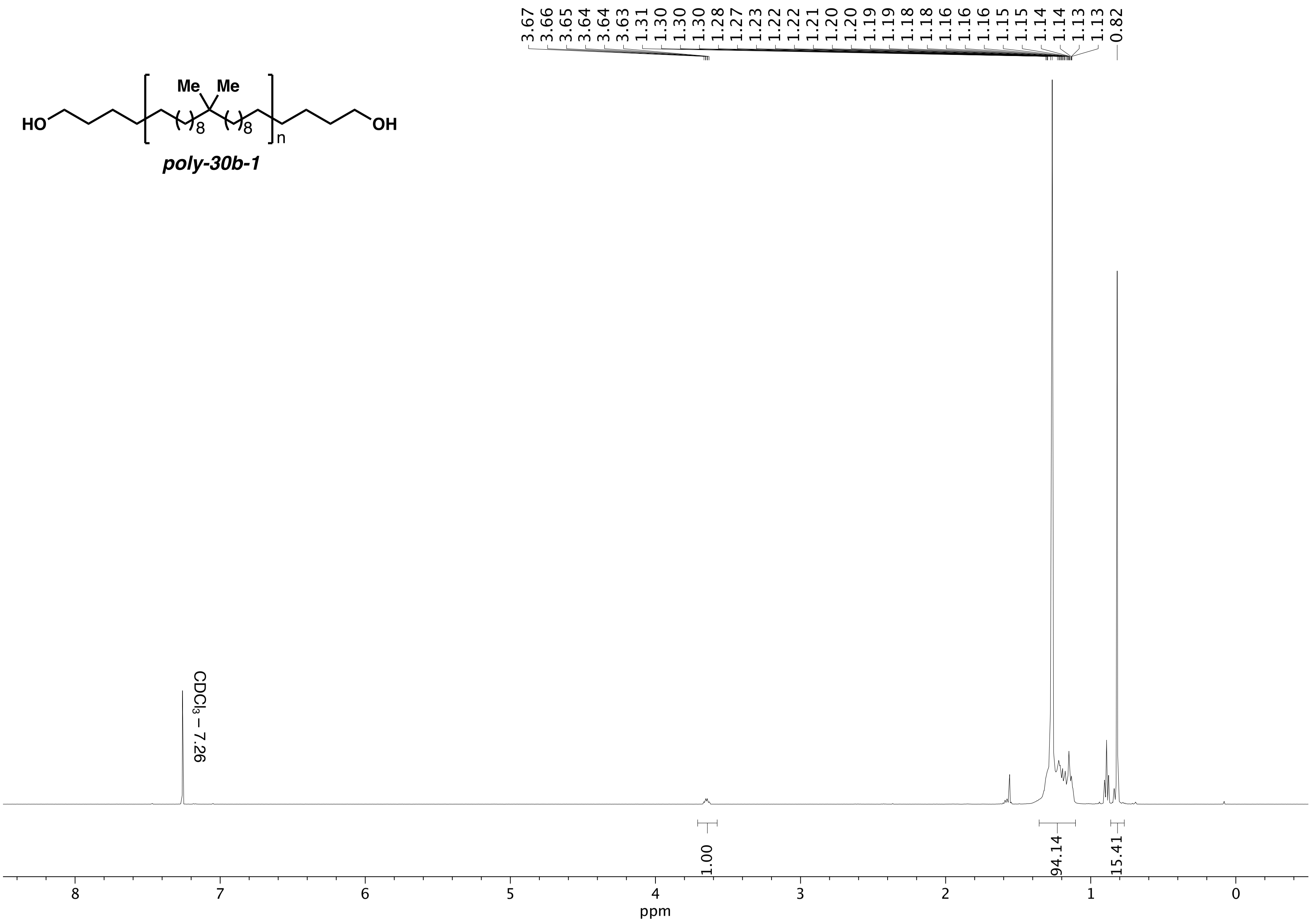


^{1}H NMR (600 MHz, $CDCl_3$) of compound **poly-24b**.

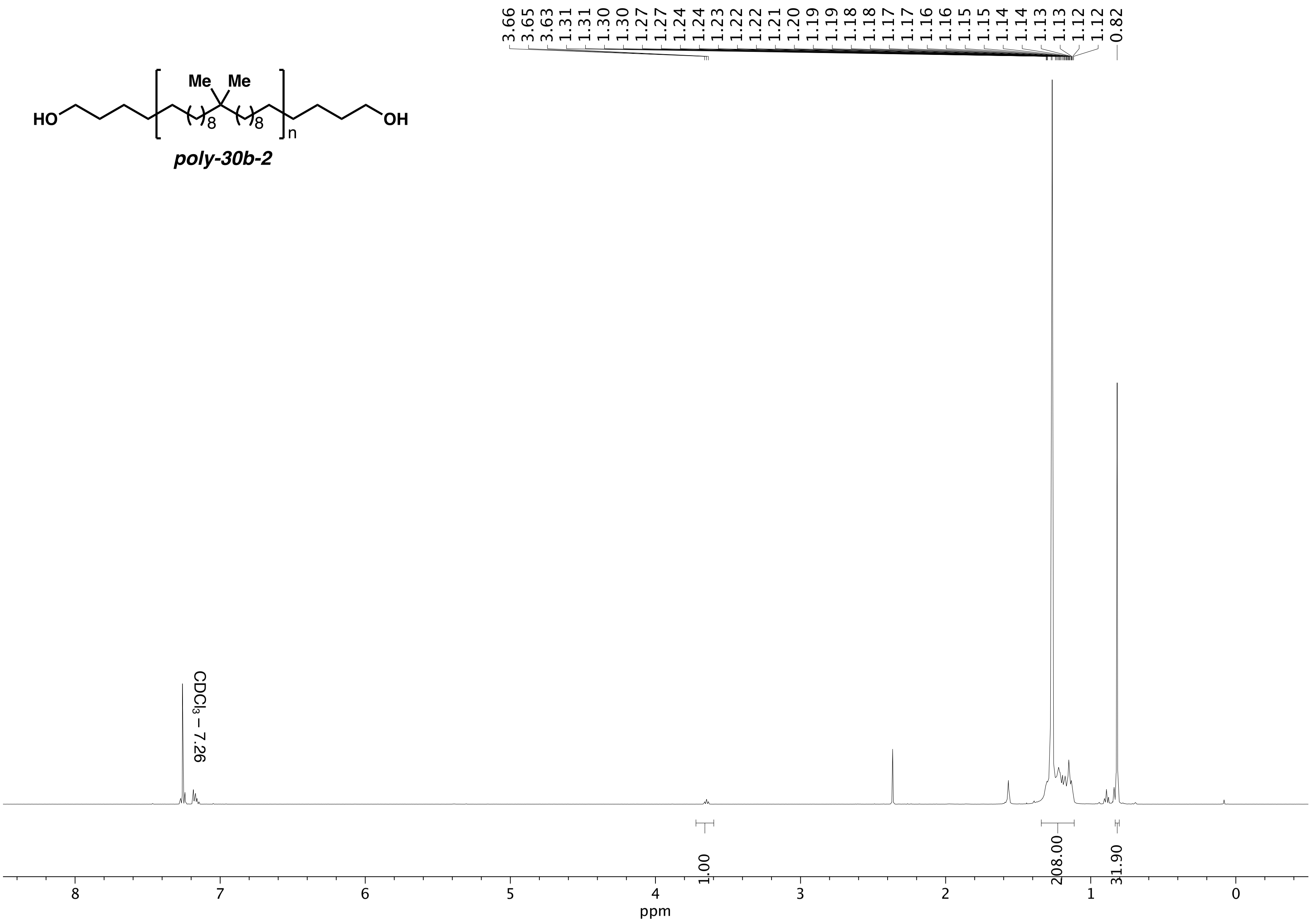
poly-27b



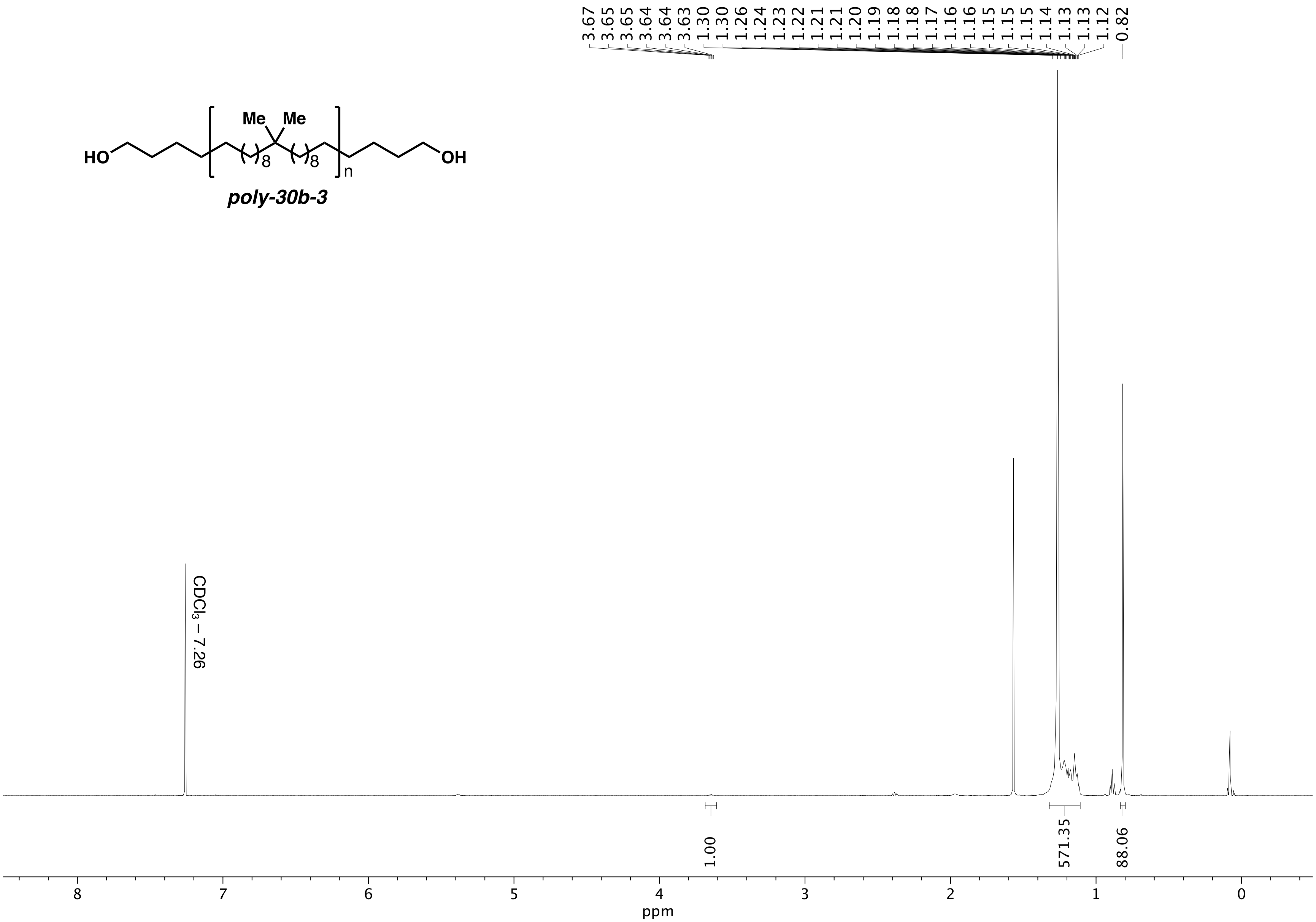
^{1}H NMR (500 MHz, CDCl$_3$) of compound **poly-27b**.



^{1}H NMR (500 MHz, CDCl$_3$) of compound **poly-30b-1**.

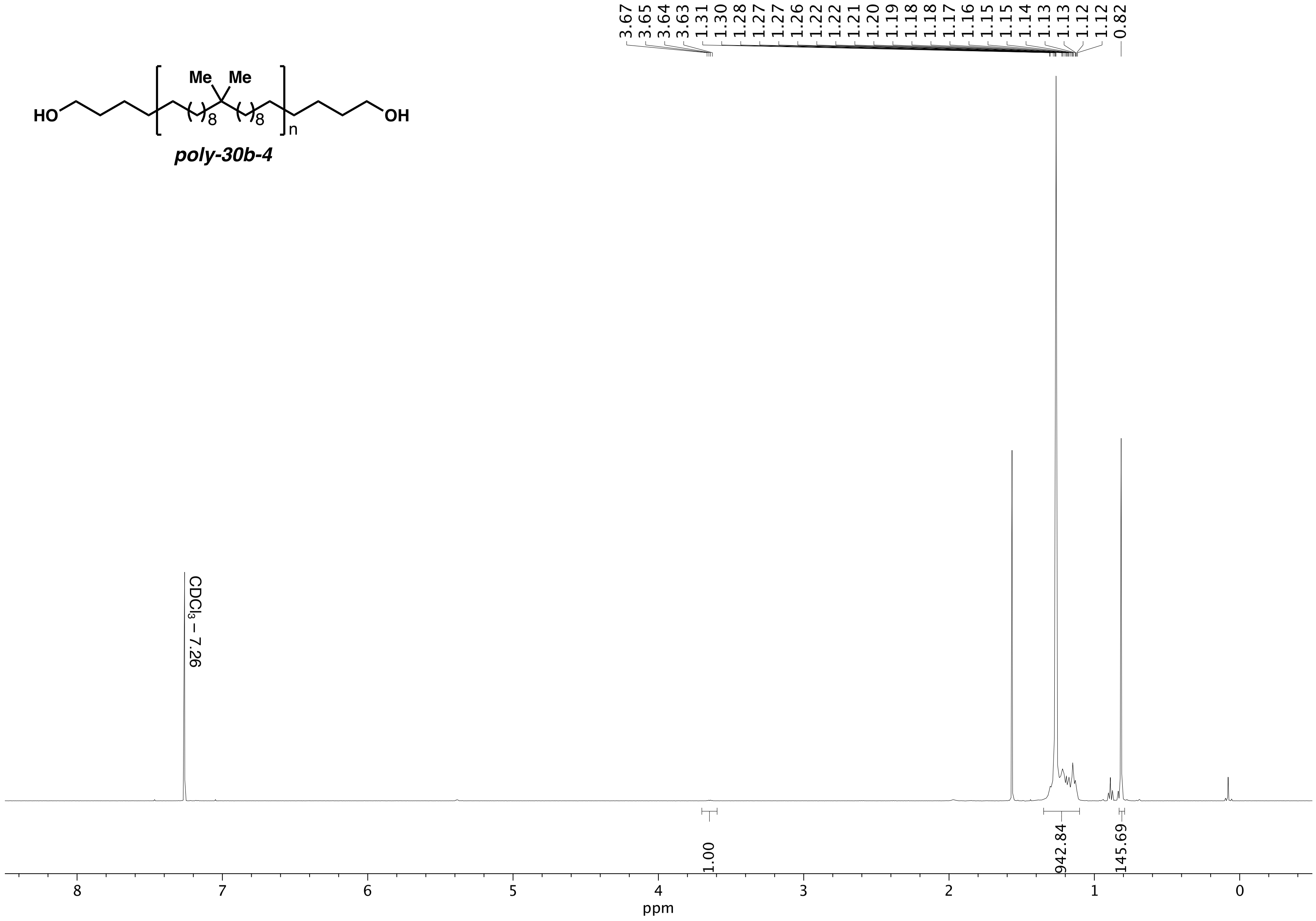


^{1}H NMR (500 MHz, CDCl$_3$) of compound **poly-30b-2**.

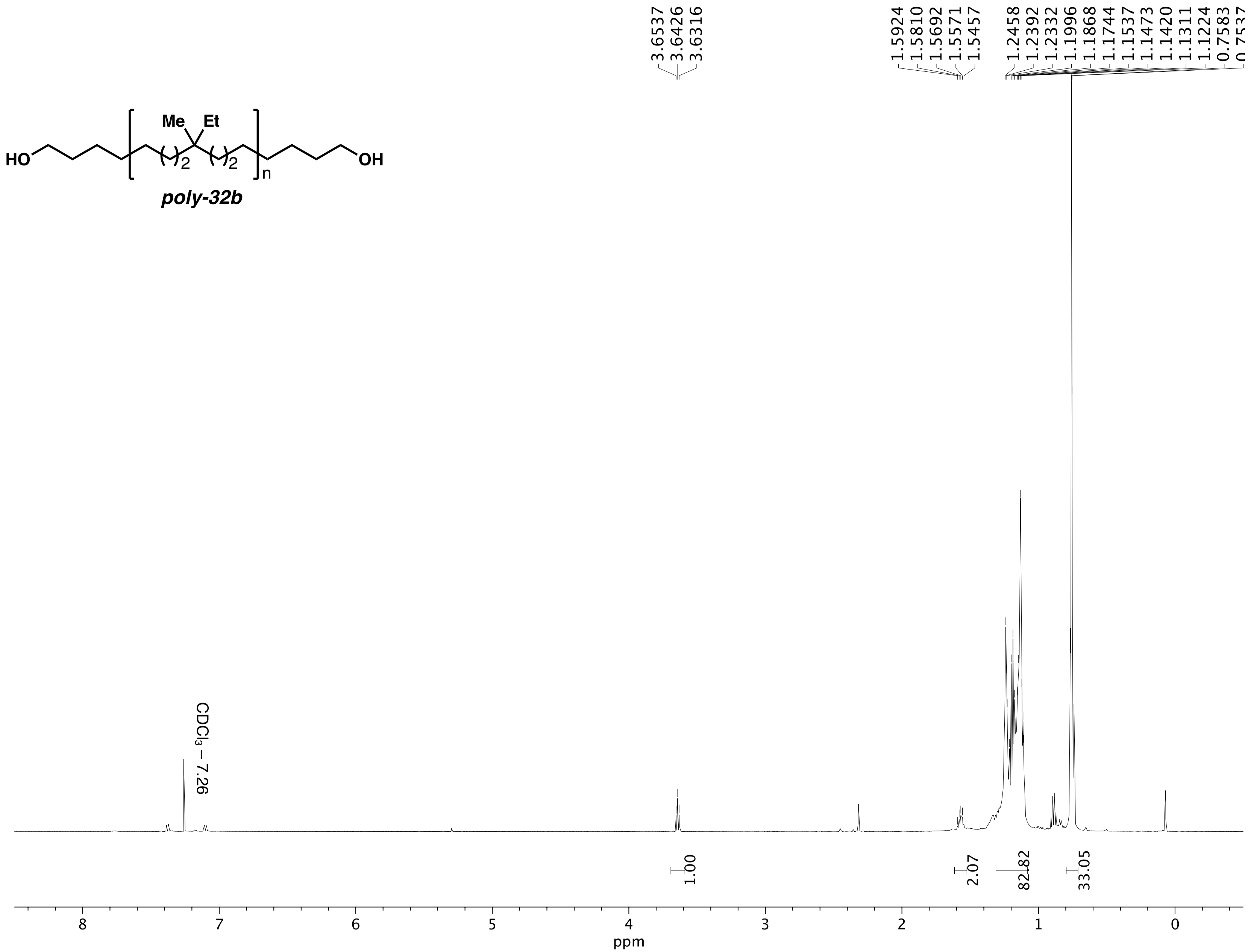


^{1}H NMR (500 MHz, CDCl$_3$) of compound **poly-30b-3**.

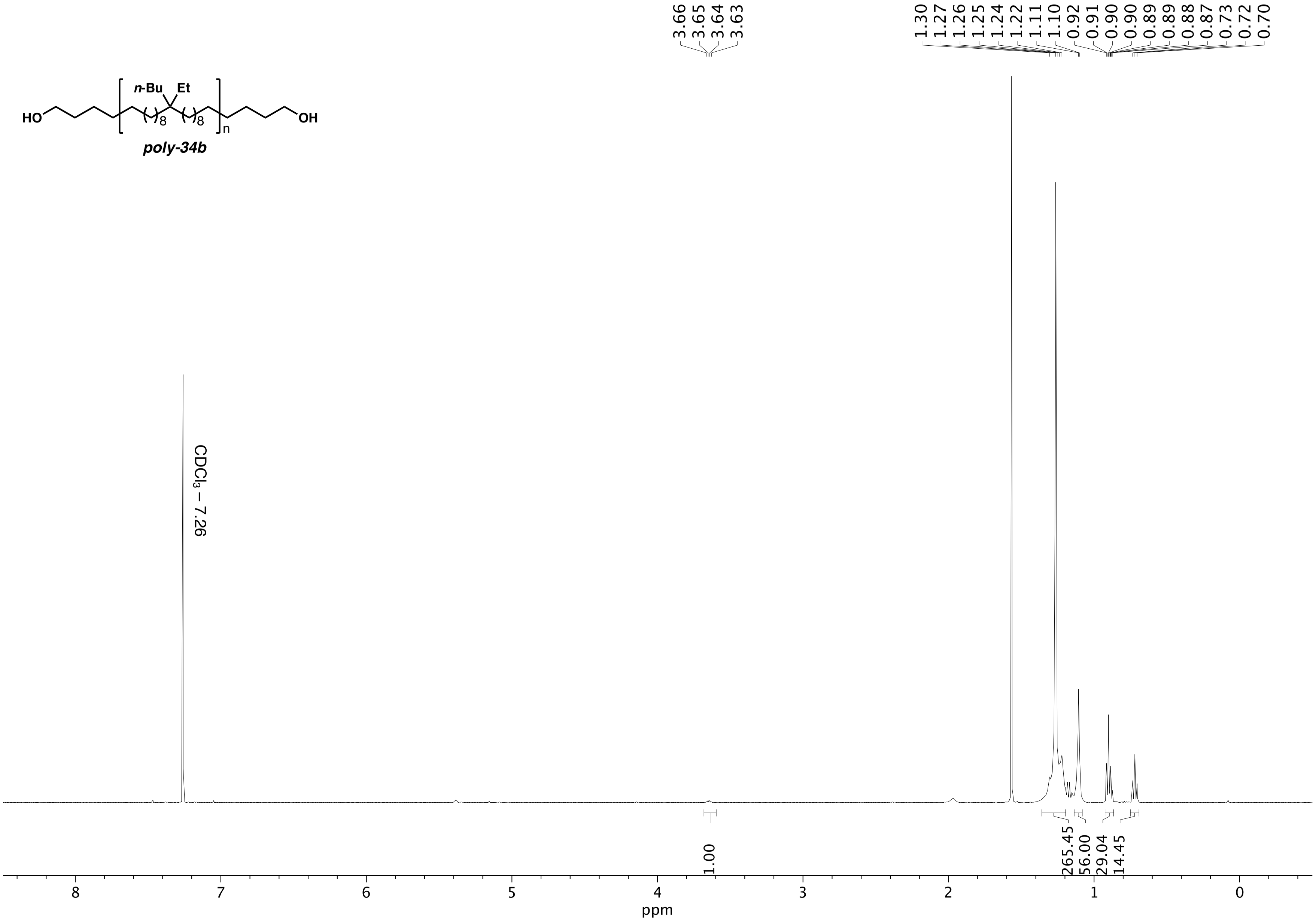
poly-30b-4



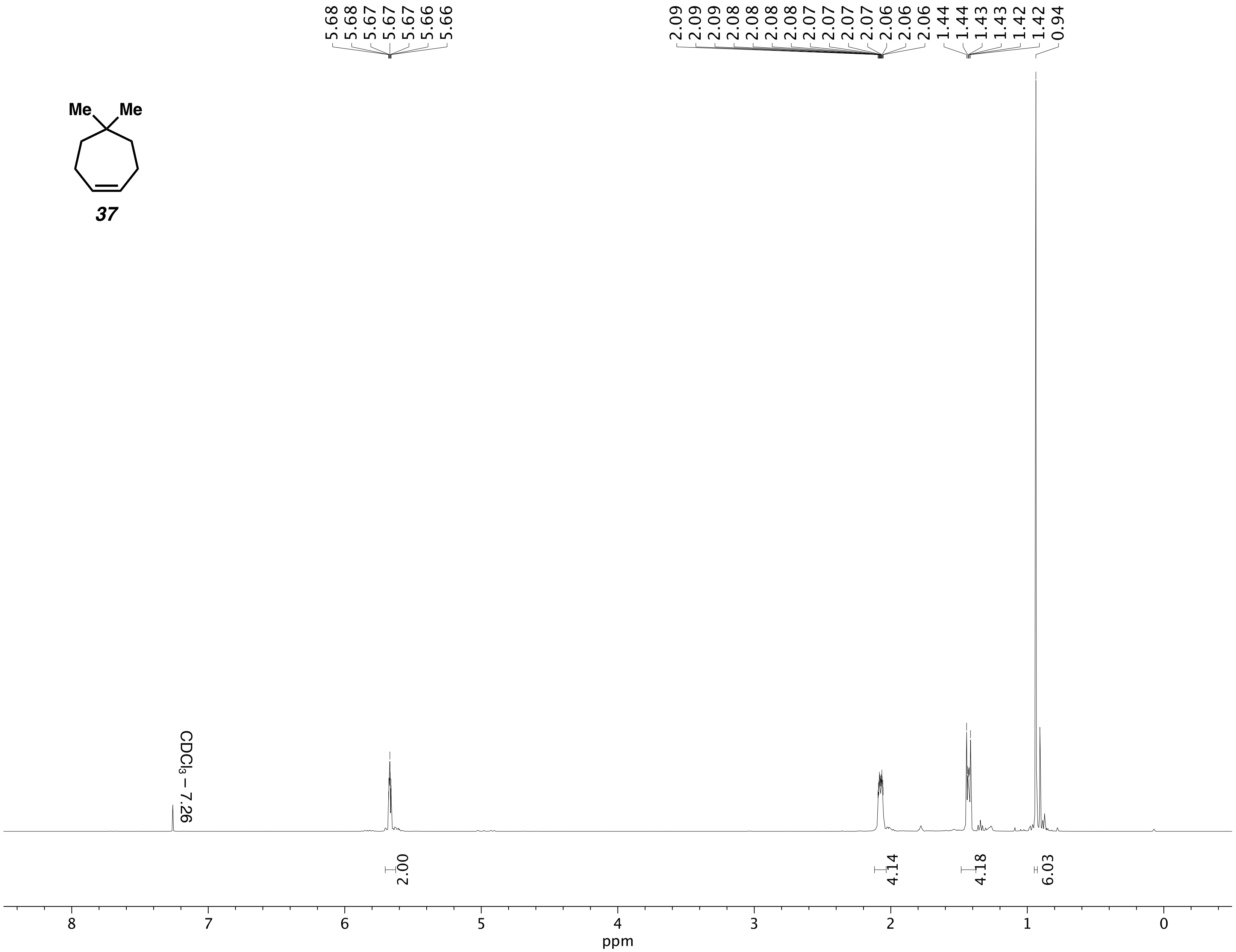
^{1}H NMR (500 MHz, $CDCl_3$) of compound **poly-30b-4**.



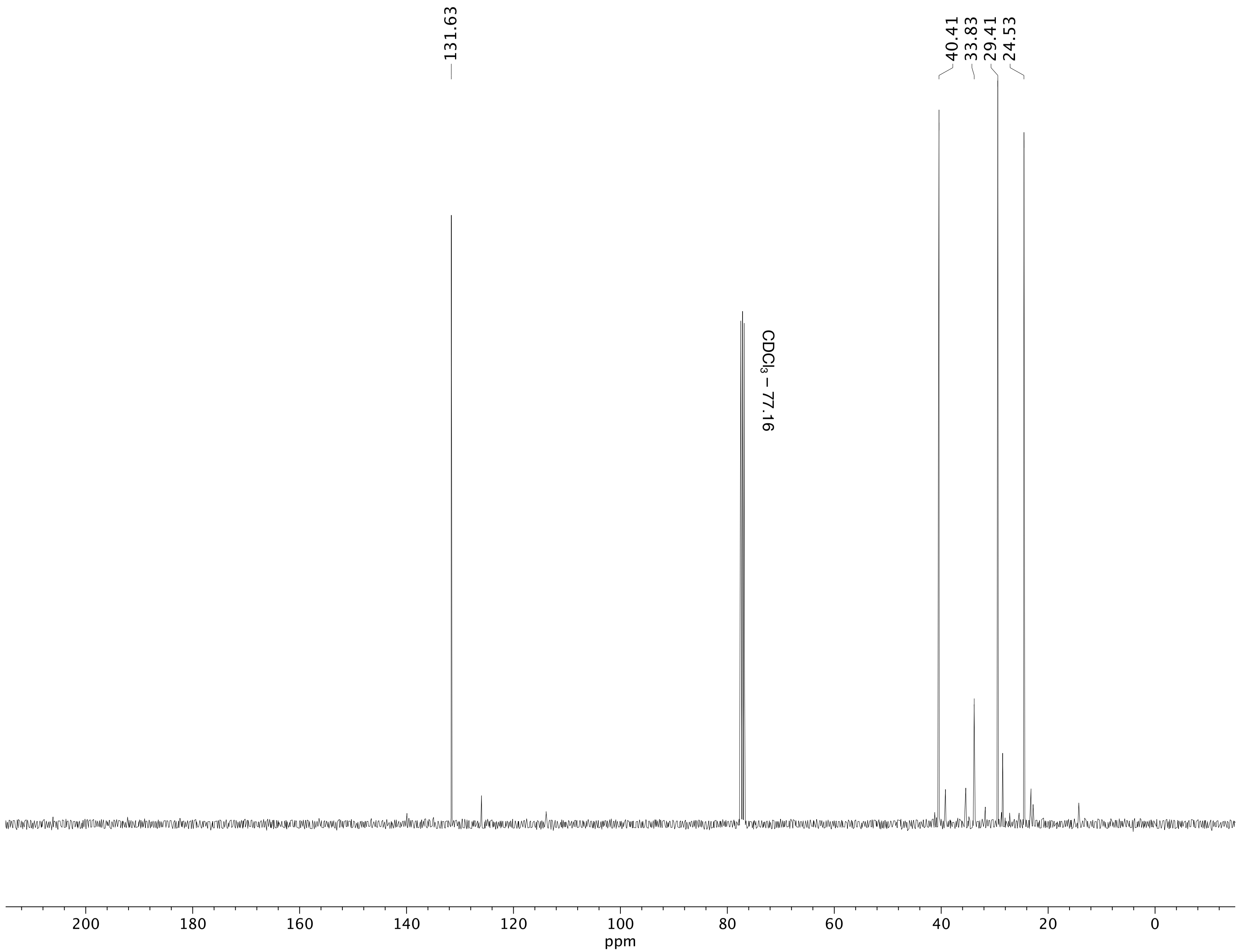
^{1}H NMR (500 MHz, CDCl$_3$) of compound **poly-32b**.



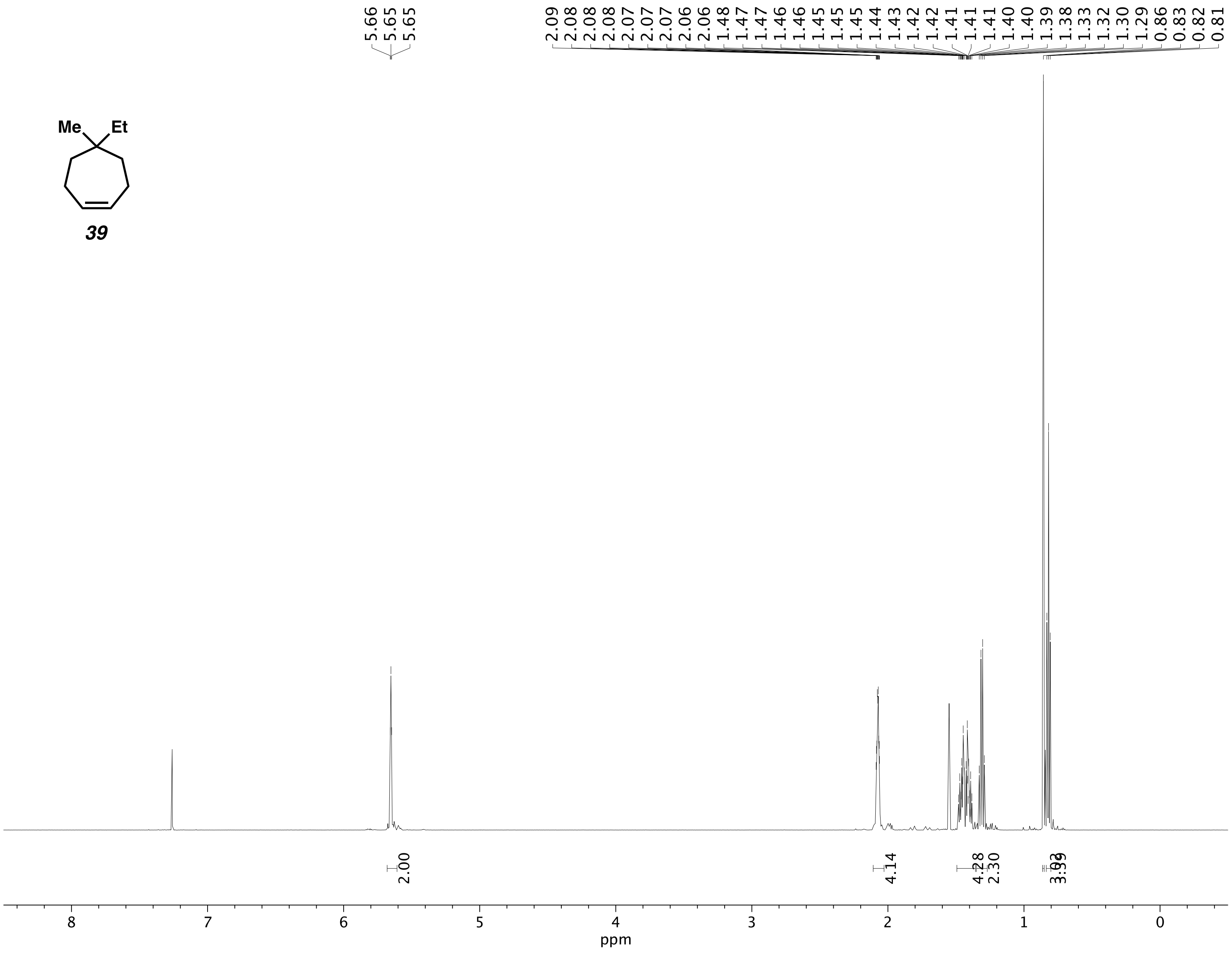
^{1}H NMR (500 MHz, $CDCl_3$) of compound **poly-34b**.



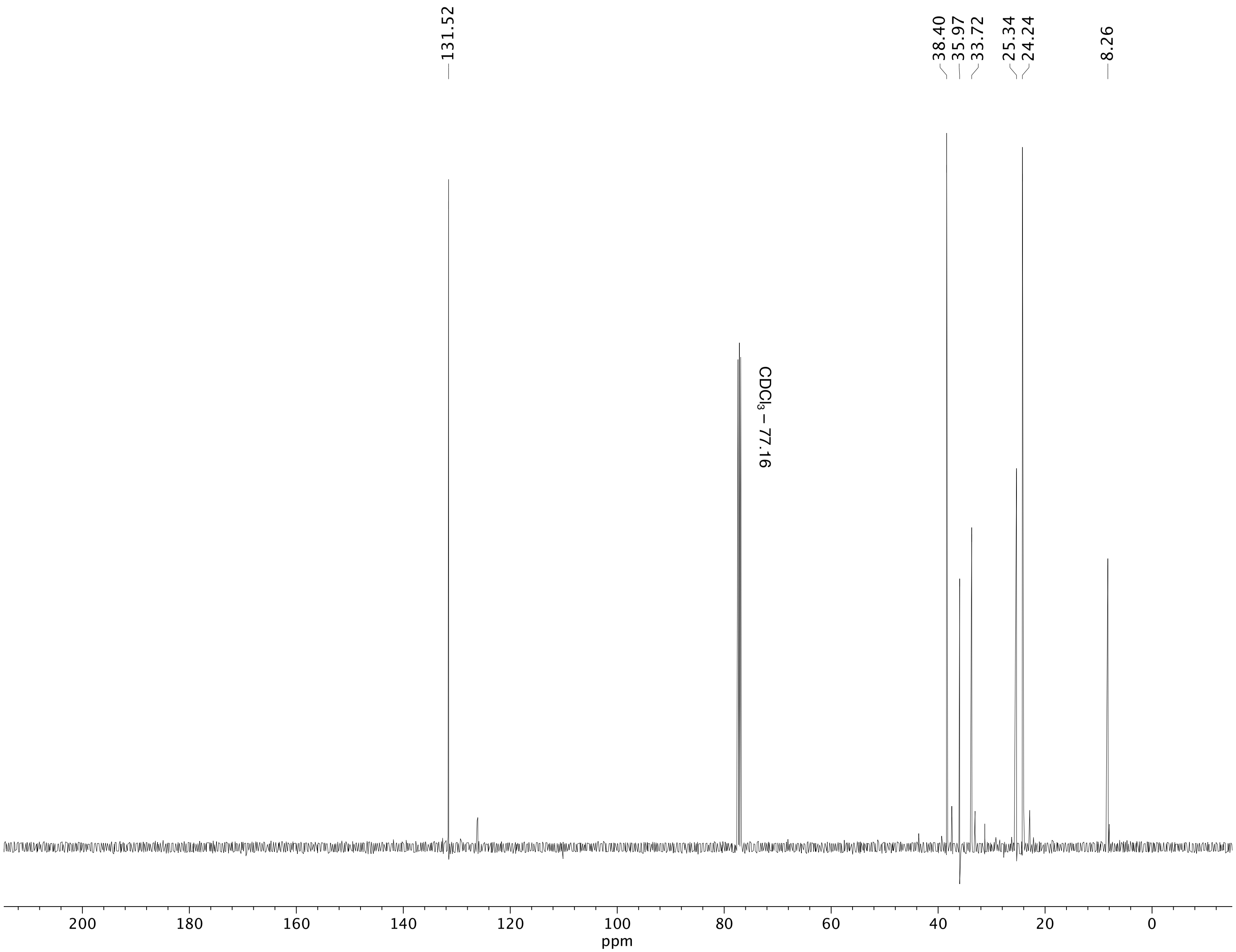
^{1}H NMR (400 MHz, $CDCl_3$) of compound **37**.



^{13}C NMR (101 MHz, CDCl$_3$) of compound **37**.



^{1}H NMR (600 MHz, CDCl$_3$) of compound **39**.



^{13}C NMR (101 MHz, CDCl$_3$) of compound **39**.

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