# Supporting Information

## Chiral Ruthenium Lewis Acid Catalyzed Intramolecular Diels-Alder Reactions

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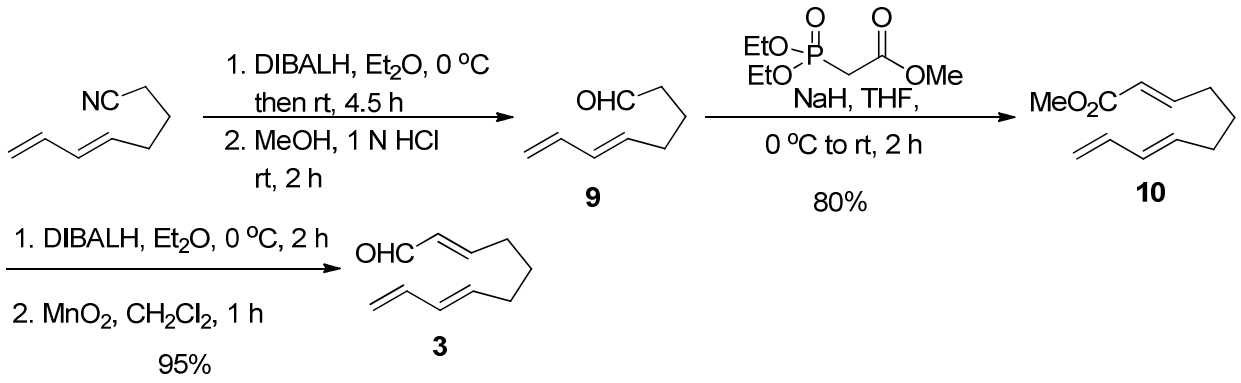
**General**

$^{1}$H-, $^{13}$C-, $^{31}$P-, $^{19}$F-NMR spectra were recorded on Bruker ARX-500, AMX-400 or ARX-300 FT spectrometers in the solvent indicated. $^{1}$H- and $^{13}$C-NMR chemical shifts (δ) are quoted in parts per million (ppm) relative to TMS. Coupling constants (*J*) are in hertz (Hz). $^{31}$P-NMR chemical shifts are referenced to $H_3PO_4$ as external standard. Infrared spectra were recorded on a Perkin–Elmer Spectrum One spectrophotometer using a diamond ATR Golden Gate sampling. Electron impact (EI) HRMS mass spectra were obtained using a *Finningan MAT 95* operating at 70eV. Electrospray ionization (ESI) HRMS analyses were measured on a VG analytical 7070E instrument. Optical rotations were measured on a Perkin Elmer 241 Polarimeter using a quartz cell ($l$ = 10 cm) with a Na high-pressure lamp ($\lambda$ = 589 nm, continuous). UV-Vis spectra were recorded on a JASCO V-650 spectrophotometer equipped with a stirrer and a temperature controller (25 ºC). CD spectra were recorded on a JASCO J-815 spectropolarimeter with a thermostated S3cell holder at 25°C in quartz cells with 1 cm light path. Three spectra were averaged, and the spectrum of solvent was subtracted for correction. The reactions were carried out under nitrogen atmosphere. Solvents were removed by using a rotary evaporator at a water-aspirator pressure followed by evacuation of the flask to approximate 0.20 mmHg to remove traces of solvents. All glassware and syringes were oven-dried and further dried by placing under vacuum and heating with a heat gun for *ca.* 5 minutes as necessary. F.c. was performed by using Brunschwig silica gel (60 Å/32-63 mesh) (Art. 7736). Thin layer chromatography was performed on pre-coated aluminium plates (Fluka silica $60F_{254}$), and visualized using UV light or aq. $KMnO_4$. Purification of THF, diethyl ether, toluene and dichloromethane was carried out using a Solvtek© purification system. Acetone was distilled from drierite before use. Dicyclopentadiene was cracked at 170 ºC and cyclopentadiene was traped at -78 $^{o}$C. It was either used immediately or stored under $N_2$ at -40 ºC. Commercial chemicals were used as supplied unless otherwise stated.

## 1. Synthesis of triene 3

**(*E*)-octa-5,7-dienenitrile** [1-3] was prepared according to the literature procedure.




### 1.1 (2*E*,7*E*)-methyl deca-2,7,9-trienoate (10)[3]

In a 50 mL round-bottom flask equipped with a magnetic stirring bar, under $N_2$, was charged with a solution of to a solution of (*E*)-octa-5,7-dienenitrile (2.78 g, 23 mmol, 1 eq) in dry $Et_2O$ (45 mL). Then, at 0 °C DIBALH (1.2 M in toluene, 28.75 mL, 34.50 mmol, 1.5 eq) was added dropwise. The solution was warmed to room temperature (r.t.) and stirred for 4.5 h. The solution was cooled to 0 °C, and then MeOH (17.20 mL) was added followed by 1 N HCl (87.20 mL). This two-phase mixture was stirred for 2 h at r.t.. The aq. phase was then extracted with $Et_2O$ (3 × 30 mL). The combined organic phases were washed with sat. $NaHCO_3$ (30 mL), dried (anh. $Na_2SO_4$). Volatiles were removed in vacuo to give crude aldehyde **9** ($R_f$ = 0.18, 6% $EtO_2$ in pentanes) which was used in the next step without purification. IR (neat): $\nu_{max}$ 2925*s*, 1726*m*, 1652*m*, 1603*m*, 1455*m*, 1134*s* $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz): δ 9.82 (t, *J* = 1.6 Hz, 1H), 6.35 (td, *J* = 16.9, 10.3 Hz, 1H), 6.11 (dd, *J* = 15.1, 10.3 Hz, 1H), 5.70 (q, *J* = 15.1, 7.4 Hz, 1H), 5.16 (d, *J* = 16.9 Hz, 1H), 5.04 (d, *J* = 16.9 Hz, 1H), 2.50 (dt, *J* = 7.4, 1.6 Hz, 2H), 2.18 (dd, *J* = 14.4, 7.4 Hz, 2H), 1.79 (quin, *J* = 7.4 Hz, 2H).

A 50 mL round-bottom flask equipped with a magnetic stirring bar was loaded with NaH (1.10 g of 60% suspension in mineral oil, 27.6 mmol, 1.2 eq), and it was washed with hexanes (3 × 10 mL) and the liquid phase was removed by syringe under $N_2$. Methyl diethylphosphonoacetate (4.65 mL, 25 mmol, 1.1 eq) was added to a suspension of NaH in THF (100 mL) at 0 °C and the resulting mixture was stirred for 60 min. A solution of crude dienal **9** (23 mmol, 1 eq) in THF (6.70 mL) was then added at 0 °C. After stirring for 2 h at r.t., the reaction mixture was quenched with water (to aid clarification, 100 mL of 1 N HCl was added as

well). The aq. and organic layers were then separated, the aq. layer was extracted with $Et_2O$ (3 × 30 mL), and the combined organic layers were dried (anh. $Na_2SO_4$). Volatiles were removed in vacuo. The crude mixture was chromatographed on silica gel ($R_f$ = 0.27, 5% $EtO_2$ in pentanes) to afford the ester **10** as colorless oil in a 80% yield (0.494 g, 2.74 mmol). IR (neat): $\nu_{max}$ 1722*s*, 1656*m*, 1603*w*, 1436*m*, 1269*s*, 1198*s*, 1174*s*, 1004*m*, 899*s* $cm^{-1}$; MS(ESI): *m/z* 180 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.00 (td, *J* = 15.6, 7.4 Hz, 1H), 6.35 (td, *J* = 16.8, 10.2 Hz, 1H), 6.10 (dd, *J* = 15.2, 10.2 Hz, 1H), 5.87 (d, *J* = 15.6 Hz, 1H), 5.71 (td, *J* = 15.2, 7.4 Hz, 1H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.02 (d, *J* = 10.2 Hz, 1H), 3.77 (s, 3H), 2.26 (q, *J* = 7.4 Hz, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.61 (quin, *J* = 7.4 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 167.2, 149.2, 137.1, 134.16, 131.7, 121.2, 115.3, 51.5, 31.9, 31.6, 21.5; HRMS (ESI-TOF) calcd for $C_{11}H_{16}OH$: 165.1273; found: 165.1266.

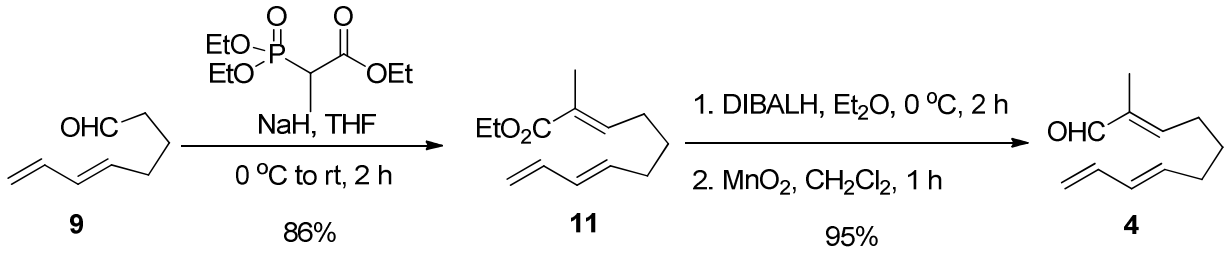
**1.2 (2*E*,7*E*)-deca-2,7,9-trienal (3)**[4]

The ester **10** (0.62 g, 3.44 mmol, 1 eq) was dissolved in dry $Et_2O$ (19 mL) and cooled to -78 $^oC$. To this solution, DIBALH (1.2 M in toluene, 6.30 mL, 7.60 mmol, 2.2 eq) was added dropwise. After 2 h, the reaction was quenched by addition of a sat. aq. solution of Rochelle's salt (50 mL) and the mixture was allowed to warm to r.t.. After 18 h, the clear phases were separated and the aq. phase was extracted with $Et_2O$ (3 × 20 mL). The combined organic extracts were dried (anh. $Na_2SO_4$) and evaporated to dryness. The crude product was used in further reaction. IR (neat): $\nu_{max}$ 3335*b*, 2925*m*, 1652*w*, 1603*w*, 1436*m*, 1001*s*, 895*s* $cm^{-1}$.

This crude alcohol was dissolved in $Et_2O$ (20 mL) and then $MnO_2$ (6 g, 68.8 mmol, 20 eq) was added. The reaction mixture was stirred at r.t. for 1 h. After removing $MnO_2$ by filtration, the crude aldehyde was purified on silica gel ($R_f$ = 0.08, 7% $EtO_2$ in pentanes) to give the trienal **3** as a pale yellow oil in 95% yield (0.49 g, 3.26 mmol). IR (neat): $\nu_{max}$ 1686*s*, 1652*w*, 1637*w*, 1603*w*, 1437*w*, 1121*m*, 1004*m*, 973*m*, 898*m* $cm^{-1}$; MS(EI): *m/z* (%) relative intensity 152 ($M^+$+2, 57), 150 ($M^+$, 52), 134 (100), 122 (20); $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.55 (d, *J* = 7.7 Hz, 1H), 6.89 (td, *J* = 15.2, 7.7 Hz, 1H), 6.35 (td, *J* = 17.0, 10.1 Hz, 1H), 6.15 (dd, *J* = 14.7, 7.6 Hz, 1H), 6.11 (dd, *J* = 15.2, 10.1 Hz, 1H), 5.71 (td, *J* = 15.2, 7.6 Hz, 1H), 5.15 (d, *J* = 17.0 Hz, 1H), 5.03 (d, *J* = 10.1 Hz, 1H), 2.39 (q, *J* = 7.4 Hz, 2H), 2.19 (q, *J* = 7.4 Hz, 2H), 1.67 (quin, *J*

= 7.4 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 194.1, 158.43, 137.0, 133.8, 133.2, 132.0, 115.5, 32.1, 31.9, 27.3; HRMS (ESI-TOF) calcd for $C_{10}H_{14}O$; 150.1045 found: 150.1042.

**2. Synthesis of triene 4**




**2.1 (2*E*,7*E*)-ethyl 2-methyldeca-2,7,9-trienoate (11)**

A 50 mL round-bottom flask equipped with a magnetic stirring bar was loaded with NaH (0.268 g of 60% suspension in mineral oil, 6.70 mmol, 1.5 eq), and it was washed with hexanes (3 × 15 mL) and the liquid phase was removed by syringe under $N_2$. Triethylphosphonopropionate (1.29 mL, 6.02 mmol, 1.35 eq) was added to a suspension of NaH in THF (10 mL) at 0 °C and the resulting mixture was stirred for 1 h at r.t.. A solution of crude dienal **9** (4.46 mmol, 1 eq) in THF (1.40 mL) was then added to the previous solution at 0 °C. The reaction mixture was slowly warmed to r.t. and stirred for 0.5 h. The reaction was quenched with sat. $NH_4Cl$. The aq. and organic layers were then separated, the aq. layer was extracted with $Et_2O$ (3 × 15 mL), and the combined organic layers were dried (anh. $Na_2SO_4$). Volatiles were removed in vacuo, the residue was chromatographed on silica gel ($R_f$ = 0.29, 3-5% $EtO_2$ in pentanes) to give a pale yellow oil of ester **11** in a 86% yield (0.806 g, 3.84 mmol). IR (neat): $\nu_{max}$ 1710*s*, 1651*m*, 1436*w*, 1252*s*, 1115*m*, 1004*m* cm$^{-1}$; MS(ESI): *m/z* 208 ($M^+$); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.73 (m, 1H), 6.29 (td, *J* = 17.0, 10.5 Hz, 1H), 6.04 (dd, *J* = 14.8, 10.5 Hz, 1H), 5.73-5.59 (m, 1H), 5.08 (d, *J* = 17.0 Hz, 1H), 4.96 (d, *J* = 10.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.17 (dd, *J* = 15.0, 7.4 Hz, 2H), 2.10 (dd, *J* = 14.5, 7.4 Hz, 2H), 1.81 (s, 3H), 1.54 (quin, *J* = 7.4 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 168.3, 141.8, 137.2, 134.5, 131.6, 128.1, 115.2, 60.5, 32.2, 28.1, 28.1, 14.4, 12.5; HRMS (ESI-TOF) calcd for $C_{13}H_{20}O_2$; 208.1463 found: 208.1462.

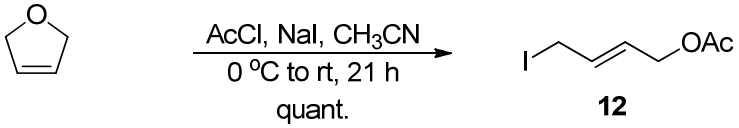
**2.2 (2*E*,7*E*)-ethyl 2-methyldeca-2,7,9-trienal (4)**[5]

The ester **11** (135 mg, 0.65 mmol, 1 eq) was dissolved in dry $Et_2O$ and cooled to -78 °C. To this solution, DIBALH (1.0 M in hexanes, 1.43 mL, 1.43 mmol, 2.2 eq) was added dropwise. After 2 h, the reaction was quenched by addition of a sat. aq. solution of Rochelle's salt (10 mL) and the mixture was allowed to warm to r.t.. After 18 h, the clear phases were separated and the aq. phase was extracted with $Et_2O$ (3 × 10 mL). The combined organic extracts were dried (anh. $Na_2SO_4$) and evaporated to dryness. The crude product was used in further reaction. IR (neat): $\nu_{max}$ 3306*s*, 2923*m*, 1651*w*, 1602*w*, 1438*m*, 1000*s*, 896*m* $cm^{-1}$.

This crude alcohol was dissolved in $CH_2Cl_2$ (10 mL) and then $MnO_2$ (5 g, 58 mmol, 15 eq) was added. The reaction mixture was stirred at r.t. for 1 h. After removing $MnO_2$ by filtration and purification by flash column chromatography (f.c.) on silica gel ($R_f$ = 0.31, 10% $EtO_2$ in pentanes), the pale yellow oil of aldehyde **4** was obtained in 95% yield (100 mg, 0.63 mmol). IR (neat): $\nu_{max}$ 1686*s*, 1646*m*, 1406*w*, 1234*w*, 1004*m* $cm^{-1}$; MS(ESI): *m/z* 164 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.40 (s, 1H), 6.48 (t, *J* = 7.0 Hz, 1H), 6.31 (td, *J* = 10.1, 5.3 Hz, 1H), 6.08 (t, *J* = 12.8 Hz, 1H), 5.68 (dt, *J* = 15.4, 6.4 Hz, 1H), 5.11 (d, *J* = 16.8 Hz, 1H), 4.99 (d, *J* = 10.1 Hz, 1H), 2.37 (q, *J* = 7.0 Hz, 2H), 2.10 (m, 2H), 1.74 (s, 3H), 1.62 (quin, *J* = 7.6 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 195.4, 154.4, 139.7, 137.0, 134.0, 131.9, 115.4, 32.1, 28.5, 27.9, 9.3; HRMS (ESI-TOF) calcd for $C_{11}H_{16}O$; 164.1201 found: 164.1199.

## 3. Synthesis of triene 5

**3.1 (*E*)-4-iodobut-2-enyl acetate (12)**

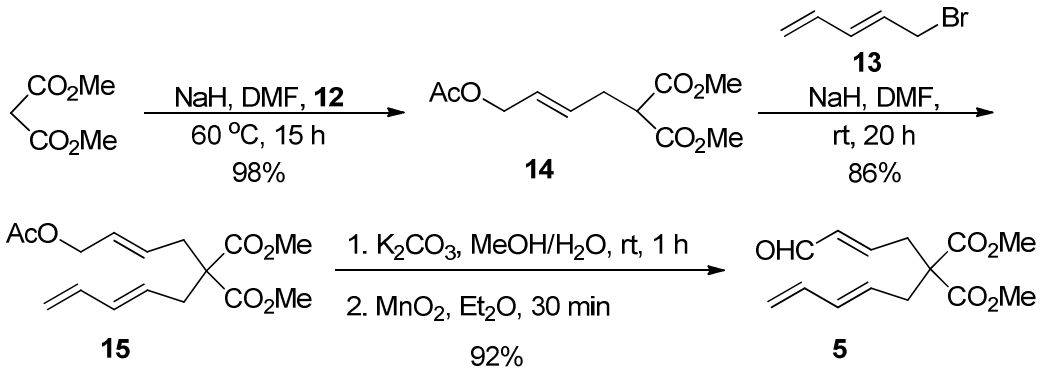



**12**

To an acetronitrile (18 mL) solution of 2,5-dihydrofuran (3 mL, 40 mmol, 1 eq) and NaI (7.2 g, 48 mmol, 1.2 eq) was added an acetronitrile (11 mL) solution of acetyl chloride (2.83 mL, 40 mmol, 1 eq) at 0 °C under $N_2$. The reaction was stirred under Neon light at r.t. for 21 h. Then it was quenched by the addition of sat. $Na_2SO_3$ (20 mL) and extracted with $Et_2O$ (3 × 30 mL). The combined organic layers were washed with water, brine (50 mL) and dried (anh. $Na_2SO_4$). Filtration followed by evaporation to dryness afforded a crude yellow liquid. A 9:1 ration of *E:Z*

isomer was observed by $^1$H NMR of olefinic protons. This crude product was used to further reaction. IR (neat): $\nu_{max}$ 1736*s*, 1432*w*, 1362*m*, 1221*s*, 1152*m*, 1024*m*, 963*m* cm$^{-1}$; MS(EI): *m/z* (%) relative intensity 127 (12), 113 (100), 71 (21), 54 (47), 53 (30); $^1$H NMR (300 MHz, $CDCl_3$): δ 6.04 (m, 1H), 5.82 (m, 1H), 4.58 (d, *J* = 5.9 Hz, 1H), 3.90 (d, *J* = 7.9 Hz, 1H), 2.11 (s, 3H); $^{13}$C NMR ($CDCl_3$, 75 MHz): δ 170.6, 131.9, 127.5, 63.7, 27.4, 20.9.

**(*E*)-5-bromopenta-1,3-diene** (**13**)[6] was prepared according to the literature procedure.




### 3.2 (*E*)-dimethyl 2-(4-acetoxybut-2-enyl)malonate (14)

To a suspension of NaH (60% suspension in mineral oil, 0.363 g, 9.0 mmol, 1.8 eq) in DMF (10 mL) at 0 °C dimethyl malonate (0.863 g, 10.0 mmol, 2 eq) was added. After 15 min, a solution of (*E*)-7-iodohepta-1,3-diene (**12**) (1.08 g, 5.0 mmol, 1.1 eq) in DMF (5 mL) was added dropwise to previous solution (turbid solution became to clear solution). The mixture was stirred for 15 h at 60 °C and then quenched with sat. $NH_4Cl$ (10 mL) and extracted with $Et_2O$ (3 × 30 mL). The organic layer was washed with water (20 mL), brine, and dried (anh. $Na_2SO_4$). Volatiles were removed in vacuo. The residue was purified by f.c. ($R_f$ = 0.32, 25% $EtO_2$ in pentanes) to give monoalkylated product **14** as a colorless oil (1.20 g, 4.90 mmol, 98 %). IR (neat): $\nu_{max}$ 1732s, 1437*m*, 1365*w*, 1226*s*, 1156*m*, 1026*m*, 970*m* cm$^{-1}$; MS(EI): *m/z* 244 ($M^+$); $^1$H NMR (400 MHz, $CDCl_3$): δ 5.69 (m, 2H), 4.49 (d, *J* = 5.1 Hz, 2H), 3.74 (s, 6H), 3.45 (t, *J* = 7.5 Hz, 1H), 2.65 (t, *J* = 6.6 Hz, 2H), 2.05 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 169.2 (3CO), 130.7, 127.3, 64.6, 52.6 ($2CH_3$), 51.3, 31.5, 21.0.

### 3.3 Dimethyl 2-((*E*)-4-acetoxybut-2-enyl)-2-((*E*)-penta-2,4-dienyl)malonate (15)

A solution of **14** (0.366 g, 1.50 mmol, 1 eq) in dry DMF (3 mL) was added to a suspension of NaH (72 mg of a 60% suspension in mineral oil, 1.80 mmol, 1.2 eq) in dry DMF

(3 mL) at r.t. under $N_2$. The mixture was stirred at r.t. for 15 min. Then solution of diene **13** (0.441 g, 3.00 mmol, 2.00 eq) in dry DMF (2 mL) was added dropwise and the reaction was stirred at r.t. for 20 h. Then the mixture was quenched with sat. $NH_4Cl$ (10 mL), extracted with $Et_2O$ (3 × 10 mL). Combined organic portions were washed with water (10 mL) and dried (anh. $Na_2SO_4$). The solvent was evaporated and the residue was chromatographed on silica gel ($R_f$ = 0.26, 35 % $EtO_2$ in pentanes) to afford dialkylated product **15** as a colorless viscous liquid in 86% yield (400 mg, 1.29 mmol) and. IR (neat): $\nu_{max}$ 1738*s*, 1449*m*, 1368*m*, 1235*s*, 1207*s*, 1032*m*, 1012*m*, 975*m* $cm^{-1}$; MS(ESI): *m/z* 333 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 6.26 (dt, *J* = 16.9, 10.5 Hz, 1H), 6.07 (dd, *J* = 15.1, 10.3 Hz, 1H), 5.61 (m, 2H), 5.47 (dt, *J* = 15.1, 7.6 Hz, 1H), 5.11 (d, *J* = 16.9 Hz, 1H), 5.01 (d, *J* = 10.5 Hz, 1H), 4.47 (d, *J* = 5.0 Hz, 2H), 3.70 (s, 6H), 2.61 (d, *J* = 7.7 Hz, 4H), 2.04 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 171.0 (2CO), 170.7, 136.5, 135.3, 129.3, 128.7, 127.5, 116.7, 64.6, 57.8, 52.5 ($2CH_3$), 36.1, 35.7, 21.0; HRMS (ESI-TOF) calcd for $C_{16}H_{22}O_6Na$; 333.1308 found: 333.1297.

### 3.4 Dimethyl 2-((*E*)-4-oxobut-2-enyl)-2-((*E*)-penta-2,4-dienyl)malonate (5)

A solution of **15** (0.314 g, 1.01 mmol, 1 eq) in MeOH (3.37 mL) was added to a solution of $K_2CO_3$ (0.307 g, 2.90 mmol, 2.2 eq) in a mixture of MeOH (14.40 mL) and $H_2O$ (3.37 mL) at r.t.. The mixture was stirred at r.t. for 1 h, and then MeOH was removed under reduced pressure. The residue was extracted with $CH_2Cl_2$ (3 × 15 mL). The combined organic layers were brine and dried (anh. $Na_2SO_4$). Volatiles were removed in vacuo and the residue was used in further step. IR (neat): $\nu_{max}$ 3442m, 1728*s*, 1437*m*, 1267*s*, 1203*s*, 1005*s* $cm^{-1}$; MS(ESI): *m/z* 286 ($M^+$ + $H_2O$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 6.28 (dt, *J* = 16.9, 10.3 Hz, 1H, $CH_2$=C*H*CH), 6.09 (dd, *J* = 15.1, 10.3 Hz, 1H), 5.72 (dt, *J* = 15.3, 5.6 Hz, 1H), 5.52 (sept, *J* = 7.6 Hz, 2H), 5.13 (d, *J* = 16.9 Hz, 1H), 5.03 (d, *J* = 10.3 Hz, 1H,), 4.08 (d, *J* = 5.3 Hz, 2H), 3.72 (s, 6H), 2.64 (dd, *J* = 9.9, 8.1 Hz, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 171.2 (2CO), 136.6, 135.2, 134.0, 127.6, 125.8, 116.7, 63.3, 58.0, 52.6 ($2CH_3$), 35.9, 35.6.

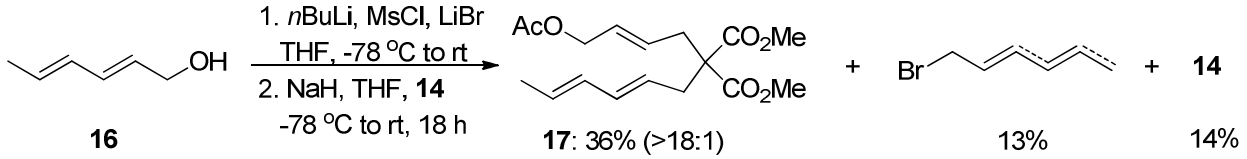
The crude alcohol (1.01 mmol, 1 eq) was dissolved in $Et_2O$ (10 mL) and then $MnO_2$ (1.74 g, 20 mmol, 20 eq) was added. The reaction mixture was stirred at r.t. for 1 h. After removing $MnO_2$ by filtration, the pure aldehyde **5** was obtained as pale yellow oil in 92% yield[9] (0.245 g, 0.92 mmol). IR (Neat): $\nu_{max}$ 1733*s*, 1692*m*, 1437*m*, 1205*s*, 1008*m* $cm^{-1}$; MS(ESI): *m/z* 266 ($M^+$);

$^1$H NMR (400 MHz, $CDCl_3$): δ 9.50 (d, *J* = 7.7 Hz, 1H), 6.73 (td, *J* = 15.1, 7.7 Hz, 1H), 6.27 (td, *J* = 16.8, 10.4 Hz, 1H), 6.11 (ddd, *J* = 15.1, 10.4, 9.3 Hz, 2H), 5.47 (td, *J* = 15.0, 7.6 Hz, 1H), 5.15 (d, *J* = 16.8 Hz, 1H), 5.06 (d, *J* = 10.1 Hz, 1H), 3.74 (s, 6H), 2.86 (dd, *J* = 7.5, 1.1 Hz, 2H), 2.70 (d, *J* = 7.6 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 193.5, 170.5 (2CO), 151.8, 136.2, 135.9 (2CH), 126.6, 117.4, 57.5, 52.9 ($2CH_3$), 36.8, 36.2; HRMS (ESI-TOF) calcd for $C_{14}H_{18}O_5$; 266.1154 found: 266.1154.

## 4. Synthesis of triene 6

**(2*E*,4*E*)-hexa-2,4-dien-1-ol (16)**[7] was prepared according to the literature procedure.

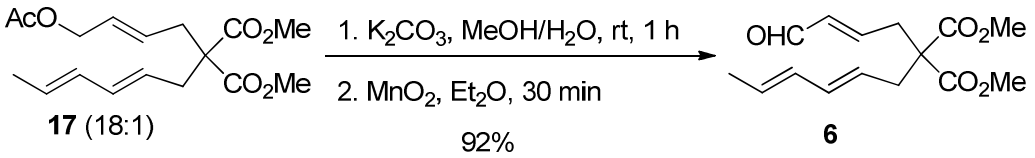
### 4.1 Dimethyl 2-((*Z*)-4-acetoxybut-2-enyl)-2-((2*E*,4*E*)-hexa-2,4-dienyl)malonate (17)[8]




THF (1.30 mL) was added under $N_2$ to a round bottom flask containing alcohol **16** (216 mg, 2.2 mmol, 1.1 eq) and a stirring bar. The reaction flask was then placed into a dry ice/acetone bath (-78 ºC). *n*-BuLi (1.60 M in hexanes, 1.44 mL, 2.3 mmol, 1.15 eq) was added dropwise over 5 min and the yellow solution was stirred for 15 min. Methanesulfonyl chloride (0.19 mL, 2.40 mmol, 1.20 eq) was then added dropwise causing the solution to become colorless. After 15 min a solution of LiBr (0.87 g in 2.3 mL of THF, 10 mmol, 5 eq) was added and the reaction was then allowed to warm to r.t.. In a separate 2 necks of round bottom flask, NaH (92 mg of 60% suspension in mineral oil, 2.3 mmol, 1.15 eq) was placed and washed with hexanes (3 × 5 mL), the liquid phase was removed by syringe and then dried under vacuum. THF (2.5 mL) was added to the previous flask under $N_2$ followed by the slow addition of a solution of dimethyl allylmalonate **14** (0.488 g, 2.0 mmol, 1 eq) in THF (2 mL). The reaction was stirred for 20 min at r.t. then placed into a dryice/acetone bath (-78 ºC). The solution containing the diene was then transferred via cannula to the flask containing the malonate anion and the reaction was allowed to warm to r.t. and was stirred for 15 h. Sat. $NH_4Cl$ (7 mL) was added and mixture was poured into a separating funnel and extracted with $Et_2O$ (3 × 10 mL). The combined organic layers were washed with brine (25 mL) and dried (anh. $MgSO_4$). Volatiles were removed in vacuo. The residue was purified by f.c. ($R_f$ = 0.20, 20% $Et_2O$ in pentanes) affording a colorless

oil in 36% yield (140 mg, 0.43 mmol) in a 18:1 ratio of **17** and its isomer which was determined by $^1$H NMR. Alkenyl bromide and starting material **14** were also obtained in 13% yield and 14% yield, respectively. IR (neat): $\nu_{max}$ 1730*s*, 1436*m*, 1380*w*, 1226*s*, 1200*s*, 1025*m*, 990*m*, 973*m* cm$^{-1}$; MS(ESI): *m/z* 324 ($M^+$); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.06-5.91 (m, 2H), 5.68-5.53 (m, 3H), 5.29 (m, 1H), 4.47 (d, *J* = 5.0 Hz, 2H), 3.69 (s, 6H), 2.60 (d, *J* = 6.3 Hz, 4H), 2.06 (s, 3H), 1.71 (d, *J* = 7.4 Hz, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): δ 171.0 (2CO), 170.6, 134.8, 131.0, 129.4, 129.4, 128.9, 123.8, 64.5, 57.5, 52.4 ($2CH_3$), 36.0, 35.5, 20.9, 18.0 ; HRMS (ESI-TOF) calcd for $C_{17}H_{24}O_6Na$; 347.1465 found: 347.1457.

### 4.2 Dimethyl 2-((2*E*,4*E*)-hexa-2,4-dienyl)-2-((*E*)-4-oxobut-2-enyl)malonate (6)



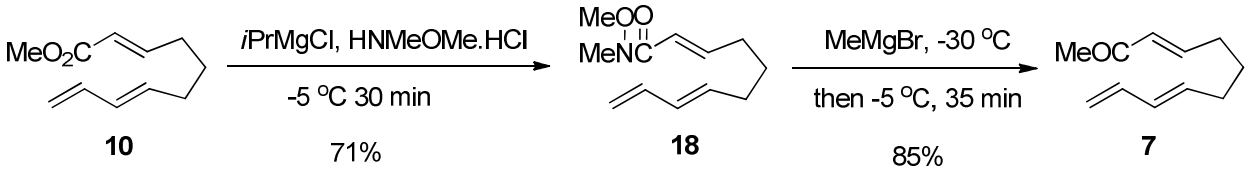

**17** (18:1) **6**

A solution of **17** (200 mg, 0.62 mmol, 1 eq) in MeOH (2.10 mL) was added to a solution of $K_2CO_3$ (0.186 g, 1.35 mmol, 2.2 eq) in a mixture of MeOH (8.60 mL) and $H_2O$ (2.10 mL) at r.t.. The mixture was stirred at r.t. for 30 min, and then MeOH was removed under reduced pressure. The residue was extracted with $CH_2Cl_2$ (3 × 10 mL). The combined organic layers were brine and dried (anh. $Na_2SO_4$). Volatiles were removed in vacuo and the residue was used in next step. IR (neat): $\nu_{max}$ 3456*br*, 1732*s*, 1437*m*, 1280*m*, 1200*s*, 991*m* cm$^{-1}$; MS(ESI): *m/z* 300 ($M^+$+$H_2O$); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.01 (quin, *J* = 6.0 Hz, 2H), 5.80-5.47 (m, 3H), 5.32 (dt, *J* = 11.0, 7.4 Hz, 1H), 4.08 (t, *J* = 5.3 Hz, 2H), 3.71 (s, 6H), 2.63 (d, *J* = 7.5 Hz, 4H), 1.73 (d, *J* = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 171.3 (2CO), 134.8, 133.8, 131.11, 129.0, 126.0, 124.0, 63.4, 58.1, 52.5 ($2CH_3$), 35.9, 35.5, 18.1.

This crude alcohol was dissolved in $Et_2O$ (6 mL) and then $MnO_2$ (1.08 g, 12.40 mmol, 20 eq) was added. The reaction mixture was stirred at r.t. for 30 min. After removing $MnO_2$ by filtration, give a trienal **6** as a colorless oil ($R_f$ = 0.18, 40% $Et_2O$ in pentanes) in 92% yield (0.160 g, 0.57 mmol).[9] IR (neat): $\nu_{max}$ 1733*s*, 1693*m*, 1436*m*, 1337*m*, 1226*s*, 1198*s*, 1152*s*, 990*m* cm$^{-1}$; MS(EI): *m/z* (%) relative intensity 280 ($M^+$); $^1$H NMR (400 MHz, $CDCl_3$): δ 9.50 (d, *J* = 7.9 Hz, 1H), 6.74 (dt, *J* = 11.5, 7.5 Hz, 1H), 6.13 (dd, *J* = 15.6, 7.9 Hz, 1H,), 6.09-5.95 (m, 2H), 5.65 (dq, *J* = 12.8, 6.6, 6.2 Hz, 1H), 5.30 (m, 1H), 3.74 (s, 6H), 2.86 (d, *J* = 7.5 Hz, 2H), 2.68 (d, *J* =

7.8 Hz, 2H), 1.74 (d, $J$ = 6.6 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 193.5, 170.6 (2CO), 152.0, 135.8, 135.5, 130.8, 129.7, 123.1, 57.6, 52.8 ($2CH_3$), 36.8, 36.2, 18.1; HRMS (ESI-TOF) calcd for $C_{15}H_{20}O_5$; 280.1311 found: 280.1311.

### 5. Synthesis of triene 7




**10** **18** **7**

#### 5.1 (2*E*,7*E*)-*N*-methoxy-*N*-methyldeca-2,7,9-trienamide (18)

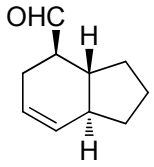
To a solution of ester **10** and *N,O*-dimethylhydroxyamine hydrochloride (0.585 g, 6 mmol, 2 eq) in THF (6 mL), a solution of *i*PrMgCl (2 M in THF, 6.75 mL, 13.5 mmol, 4.5 eq) was added dropwise at -5 °C. The mixture was stirred for 30 min, and then treated with sat. aq. $NH_4Cl$ (20 mL). The two layer mixture was separated and organic phase was dried (anh. $Na_2SO_4$). After removal of the solvent, purification by f.c. on silica gel ($R_f$ = 0.33, 50% EtOAc in pentanes) gave a colorless oil of Weinreb amide **18** in 71% yield (0.413 g, 1.96 mmol). IR (neat): $\nu_{max}$ 2933*w*, 1663*s*, 1633*s*, 1412*m*, 1379*s*, 1178*m*, 1002*s*, 979*s*, 952*m*, 898*m* cm$^{-1}$; MS(ESI): *m/z* 210 ($M^+$); $^1$H NMR (400 MHz, $CDCl_3$) δ 6.96 (td, $J$ = 15.3, 7.0 Hz, 1H), 6.40 (d, $J$ = 15.4 Hz, 1H), 6.31 (td, $J$ = 16.9, 10.3 Hz, 1H), 6.10-6.01 (m, 1H), 5.73-5.62 (m, 1H), 5.09 (d, $J$ = 16.9 Hz, 1H), 5.00-4.94 (m, 1H), 3.72-3.67 (m, 1H), 3.23 (s, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 167.0, 147.4, 137.2, 134.4, 131.6, 119.0, 115.1, 61.7, 32.4, 32.0, 31.9, 27.8; HRMS (ESI-TOF) calcd for $C_{12}H_{20}NO_2$: 210.1488; found: 210.1480.

#### 5.2 (3*E*,8*E*)-undeca-3,8,10-trien-2-one (7)

A solution of MeMgBr (1 M in THF, 3.9 mL, 3.94 mmol, 2.2 eq) was added dropwise to a solution of Weinreb amide **18** (0.38 g, 1.79 mmol, 1 eq) at -30 °C. The reaction mixture was stirred at -5 °C for 35 min, and then the mixture was treated with sat. $NH_4Cl$ (15 mL). The aq. phase was extracted with EtOAc (3 × 15 mL), and the organic layer was washed with brine (15 mL), and dried (anh. $Na_2SO_4$). After removal of the solvent, purification by f.c. on silica gel ($R_f$ = 0.19, 5% EtOAc in pentanes) gave a pale yellow oil of trienone **7** in 85% yield (0.25 g, 1.52 mmol); IR (neat): $\nu_{max}$ 2929*w*, 1698*m*, 1673*s*, 1626*m*, 1434*w*, 1360*m*, 1253*s*, 1003*s*, 978*s*, 952*m*,

898*m* $cm^{-1}$; MS(EI): *m/z* (%) relative intensity 164 ($M^+$, 8), 149 (8), 121 (99), 106 (20), 93 (24), 84 (90), 67 (100), 53 (38); $^1H$ NMR (400 MHz, $CDCl_3$): δ 6.80 (td, *J* = 15.8, 6.87 Hz, 1H), 6.31 (td, *J* = 16.9, 10.2 Hz, 1H), 6.08 (d, *J* = 15.8 Hz, 1H), 6.05 (d, *J* = 14.7 Hz, 1H), 5.67 (td, *J* = 15.2, 7.2 Hz, 1H,), 5.11 (d, *J* = 16.9 Hz, 1H), 4.98 (d, *J* = 10.2 Hz, 1H), 2.24 (m, 5H), 2.13 (q, *J* = 7.2 Hz, 2H), 1.59 (quin, *J* = 7.4 Hz, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$,): δ 198.6, 148.0, 137.0, 134.0, 131.7, 131.5, 115.3, 31.9, 31.8, 27.5, 26.9; HRMS (ESI-TOF) calcd for $C_{11}H_{16}ONa$: 165.1273; found: 165.1266.

### 6. (3a*R*,4*R*,7a*S*)-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (19)




**19**

*Racemic:*

In a 10 mL Schlenk tube equipped with a magnetic stirring bar, under $N_2$, to stirred a triene **3** (23 mg, 0.15 mmol, 1 eq) solution in dry $CH_2Cl_2$ (0.5 mL) at r.t. $AlEt_2Cl$ solution (1 M in hexanes, 0.075 mL, 0.075 mmol, 0.5 eq) was added dropwise. The yellow reaction mixture was stirred at r.t. for 30 min and quenched with water (1 mL) and $Et_2O$ (1 mL). The organic phase was extracted with $Et_2O$ (5 × 3 mL), brine and dried (anh. $Na_2SO_4$). The crude product was purified by f.c. to give the racemic adduct **19** in 65% yield (14 mg, 0.95 mmol).

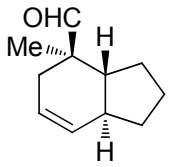
*Asymmetric:*

In a 50 mL Schlenk tube equipped with a magnetic stirring bar at r.t. and under $N_2$, Ru catalyst **1c** (73 mg, 0.05 mmol, 0.05 eq) was dissolved in dry $CH_2Cl_2$ (1.80 mL). To the stirring mixture, 2,6-lutidine (2.3 μL, 0.02 mmol, 0.02 eq) and a solution of triene **3** (150 mg, 1.00 mmol, 1 eq) in dry $CH_2Cl_2$ (1.50 mL) were carefully added, and the resulting orange solution was stirred at r.t. and under $N_2$ for 7 d. The reaction was then monitored by TLC. At the end of the reaction, $CH_2Cl_2$ was removed under vacuum pump and hexane (20 mL) was added, and the mixture was suspended and filtered through a Celite 545 plug to give recoverable catalyst on Cilite. Volatiles were removed in vacuo and the residue was purified by f.c. using a silica gel column ($R_f$ = 0.22, 5% $Et_2O$ in pentanes) to give a pale yellow oil of adduct **19** in 92% isolated

yield (138 mg, 0.92 mmol). Chiral GC (Hydrodex-β, $H_2$, 100 °C 30 min then heating 0.5 °C/min to 120 °C): $t_R$ of *endo* product (min) = 33.69 (7.84), 35.30 (92.16) and $t_R$ of starting material (min) = 47.69 (1.16) Calculated : 99% conv. and 84% ee. $[\alpha]^{23}_D$ = -93.5° (*c* = 1.05, $CHCl_3$); IR (neat): $\nu_{max}$ 2954*m*, 2870*m*, 1726*s*, 1639*w*, 1454*w*, 1437*w* $cm^{-1}$; MS(EI): *m/z* (%) relative intensity 150 ($M^+$+1, 9), 137 (10), 121 (98), 91 (84), 79 (100), 81 (58), 55 (34); $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.68 (dd, *J* = 2.7, 1.1 Hz, 1H), 5.86 (d, *J* = 9.85 Hz, 1H), 5.62 (dtd, *J* = 5.6, 4.0, 2.2 Hz, 1H), 2.49 (m, 1H), 2.37-2.20 (m, 2H), 2.00-1.84 (m, 3H), 1.80-1.71 (m, 2H), 1.43 (ddd, *J* = 22.7, 11.0, 6.2 Hz, 1H), 1.36-1.26 (m, 1H), 1.16 (quin, *J* = 11.0 Hz, 1H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 203.8, 130.0, 125.1, 52.6, 44.5, 44.0, 28.6, 27.5, 25.7, 22.3; HRMS (ESI-TOF) calcd for $C_{10}H_{14}O$-H; 149.0966 found: 149.0962. $^1H$ NMR and $[\alpha]^{23}_D$ are in accordance with Yamamoto's data.[4]

Using [Ru($\eta^5$-$C_5H_5$)((*S,S*)-BIPHOP-F)(acetone)][$SbF_6$] (**1b**), the reaction was run in the same scale at r.t. for 9 d to afford the corresponding adduct **19** in 82% yield with 72% ee.

### 7. (3a*R*,4*R*,7a*S*)-4-methyl-2,3,3a,4,5,7a-hexahydro-1*H*-indene-4-carbaldehyde (20)




**20**

*Racemic:*

In a 10 mL Schlenk tube equipped with a magnetic stirring bar, under $N_2$, a solution of triene **4** (20 mg, 0.12 mmol, 1 eq) was stirred in dry $CH_2Cl_2$ (2 mL) at r.t.. $AlEt_2Cl$ solution (1 M in hexanes, 0.12 mL, 0.12 mmol, 1 eq) was added dropwise. The yellow reaction mixture was stirred at -78 to 0 °C for overnight and quenched with water (2 mL) and $CH_2Cl_2$ (2 mL). The organic phase was extracted with $CH_2Cl_2$ (3 × 5 mL). The combined organic phases were brine and dried (anh. $Na_2SO_4$). A 99:1 mixture of *endo*:*exo* adducts **20** was obtained in 90% yield (18 mg, 0.11 mmol).

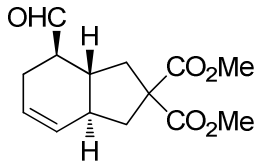
*Asymmetric:*

In a 50 mL Schlenk tube equipped with a magnetic stirring bar at r.t. and under $N_2$, Ru catalyst **1b** (70 mg, 0.05 mmol, 0.05 eq) was dissolved in dry $CH_2Cl_2$ (1.80 mL). To the stirring

mixture, 2,6-lutidine (2.3 μL, 0.02 mmol, 0.02 eq) and a solution of triene **4** (164 mg, 1.00 mmol, 1 eq) in dry $CH_2Cl_2$ (1.50 mL) was carefully added, and the resulting yellow solution was stirred at r.t. and under $N_2$ for 7 d. The reaction was then monitored by TLC. At the end of the reaction, $CH_2Cl_2$ was removed under vacuum pump and hexane (20 mL) was added, and the mixture was suspended and filtered through a Celite 545 plug to give recoverable catalyst on Cilite. Volatiles were removed in vacuo and the residue was purified by f.c. using a silica gel column ($R_f$ = 0.36, 10% $Et_2O$ in pentanes) to give a pale yellow oil of adduct in 82% isolated yield (135 mg, 0.82 mmol). Chiral GC (Hydrodex-β, $H_2$, 100 °C 30 min then heating 0.5 °C/min to 120 °C): $t_R$ of *exo* product (min) = 34.82 (15.56), 38.03 (0.79) and $t_R$ of *endo* product (min) = 40.85 (4.26), 41.52 (79.38). Calculated: 100% conv., a 16:84 ratio of *exo:endo* isomers and 92% ee for both isomers; IR (neat): $\nu_{max}$ 1726*s*, 1634*w*, 1456*m*, 691*m* $cm^{-1}$; MS(ESI): *m/z* 164 ($M^+$); $^1H$ NMR (500 MHz, $CDCl_3$): δ 9.49 (s, 1H), 5.85 (d, *J* = 9.9 Hz, 1H), 5.61 (tdd, *J* = 9.9, 4.6, 2.6 Hz, 1H), 2.45 (ddd, *J* = 18.0, 6.2, 2.7 Hz, 1H), 2.04-1.86 (m, 2H), 1.82-1.76 (dp, *J* = 18.0, 2.1 Hz, 1H), 1.76-1.68 (m, 2H), 1.64-1.50 (m, 2H), 1.35-1.11 (m, 2H), 1.03 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 205.6, 129.4, 124.3, 47.8, 46.4, 39.2, 33.4, 28.7, 23.7, 22.1, 12.5; HRMS (ESI-TOF) calcd for $C_{11}H_{16}O$; 164.1201 found: 164.1199. $^1H$ NMR is in accordance with Yamamoto's data.[5]

Using [Ru($\eta^5$-$C_8H_7$)((*S,S*)-BIPHOP-F)(acetone)][$SbF_6$] (**1c**), the reaction was run in the same scale at r.t. for 6 d to afford the corresponding adduct **20** in a 81:19 mixture of *endo:exo* isomers with 84% ee and 90% ee respectively (85% yield, 139 mg, 0.85 mmol).

8. **dimethyl (3a*R*,4*R*,7a*S*)-4-formyl-1,3,3a,4,5,7a-hexahydro-2*H*-indene-2,2-dicarboxylate (21)**




**21**

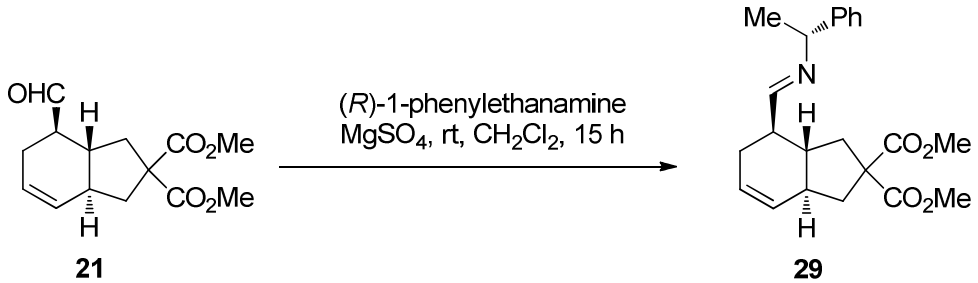
*Racemic:*

To a solution of triene **5** (20 mg, 0.07 mmol) in $CH_2Cl_2$ (1 mL), silica gel and 1 drops of conc. HCl were added, and then stirred at r.t. for overnight. After filtration, the *endo* adduct **21** was obtained in quantitative yield.

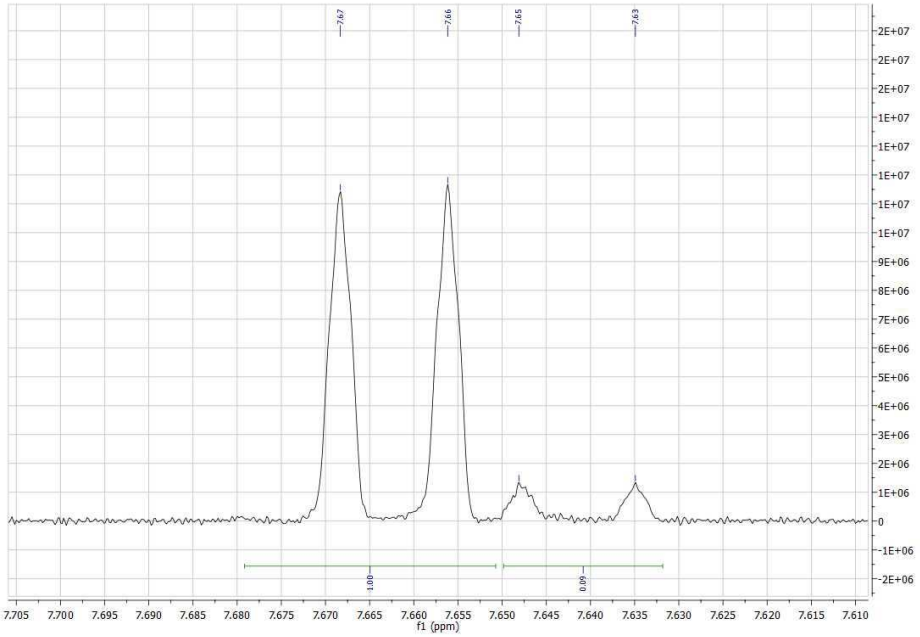
*Asymmetric:*

In a 20 mL Schlenk tube equipped with a magnetic stirring bar at r.t. and under $N_2$, Ru catalyst (**1c**) (14.6 mg, 0.010 mmol, 0.05 eq) was dissolved in dry $CH_2Cl_2$ (0.70 mL). To the stirring mixture, 2,6-lutidine (1.2 μL, 0.010 mmol, 0.05 eq) and a solution of triene **5** (56 mg, 0.2 mmol, 1 eq) in dry $CH_2Cl_2$ (0.70 mL) was carefully added, and the resulting orange solution was stirred at r.t. and under $N_2$ for 4 h. The reaction was then monitored by IR (peak at 1692 $cm^{-1}$ of α,β-unsaturated aldehyde was disappeared)[10]. At the end of the reaction, $CH_2Cl_2$ was removed under vacuum pump and hexane (10 mL) was added, and the mixture was suspended and filtered through a Celite 545 plug to give recoverable catalyst on Cilite. Volatiles were removed in vacuo and the residue was purified by f.c. using a silica gel column ($R_f$ = 0.26, 35% $Et_2O$ in pentanes) to give a pale yellow oil of *endo*-adduct in quantitative yield (56 mg, 0.2 mmol). $[\alpha]^{23}_D$ = -16.1° (*c* = 1.35, $CHCl_3$); IR (neat): $\nu_{max}$ 1731*s*, 1436*m*, 1266*m*, 905*s*, 728*s* $cm^{-1}$; MS(ESI): *m/z* 266 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.68 (d, *J* = 2.5 Hz, 1H), 5.81 (dd, *J* = 9.8, 1.7 Hz, 1H), 5.67 (ddd, *J* = 9.8, 6.3, 3.3 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 2.74 (dd, *J* = 13.0, 6.3 Hz, 1H), 2.66 (dd, *J* = 13.0, 6.7 Hz, 1H), 2.53 (dtd, *J* = 11.2, 8.5, 2.5 Hz, 1H), 2.31 (m, 2H), 2.17 (m, 1H), 1.87 (t, *J* = 12.7 Hz, 1H), 1.67 (m, 2H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 203.0, 173.0 (2CO), 128.3, 126.3, 58.7, 53.12 ($2CH_3$), 52.13, 43.8, 43.2, 38.2, 37.4, 25.8; HRMS (ESI-TOF) calcd for $C_{14}H_{18}O_5$; 266.1154 found: 266.1157.

To determine enantiomeric ratio, aldehyde adduct was changed to chiral imine derivative **29**. The 92:8 ratio of emine protons was shown to give 84% ee by $^1H$ NMR (500 MHz, $CDCl_3$) at 7.66 (d, *J* = 6 Hz) and 7.64 (d, *J* = 6.5 Hz).

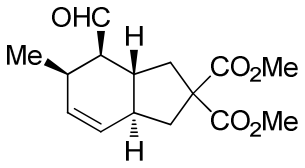



**21** **29**




Using [Ru($\eta^5$-$C_5H_5$)((*S,S*)-BIPHOP-F)(acetone)][$SbF_6$] (**1b**), the reaction was run in the same scale at r.t. for 5 h to afford the corresponding *endo*-adduct **21** in quantitative yield with 43% ee (28 mg, 0.10 mmol).

9. **dimethyl (3a*R*,4*R*,5*R*,7a*S*)-4-formyl-5-methyl-1,3,3a,4,5,7a-hexahydro-2*H*-indene-2,2-dicarboxylate (22)**




**22**

*Racemic:*

A solution of triene **6** (20 mg, 0.07 mmol) in $CH_2Cl_2$ (1 mL) was then put silica gel and stirred at r.t. overnight. After removal silica gel by filtration, the adduct **22** was obtained in quantitative yield.

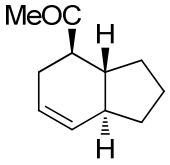
*Asymmetric:*

In a 20 mL Schlenk tube equipped with a magnetic stirring bar at r.t. and under $N_2$, Ru catalyst (**1c**) (7.3 mg, 0.005 mmol, 0.05 eq) was dissolved in dry $CH_2Cl_2$ (0.35 mL). To the stirring mixture, 2,6-lutidine (0.6 µL, 0.005 mmol, 0.05 eq) and a solution of triene **6** (freshly

prepared from the allylic alcohol by oxidation with $MnO_2$, 28 mg, 0.10 mmol, 1 eq) in dry $CH_2Cl_2$ (0.35 mL) was carefully added at r.t., and the resulting orange solution mixture was stirred under $N_2$ for 4 h. The reaction was then monitored by IR (peak at 1693 $cm^{-1}$ of α,β-unsaturated aldehyde was disappeared)[10]. At the end of the reaction, $CH_2Cl_2$ was removed under vacuum pump and hexane (10 mL) was added, and the mixture was suspended and filtered through a Celite 545 plug to give recoverable catalyst on Cilite. Volatiles were removed in vacuo and the residue was purified by f.c. using a silica gel column ($R_f$ = 0.17, 40% $Et_2O$ in pentanes) to give a pale yellow oil of adduct in quantitative yield; Chiral GC (CP-Chirasil-DexCB, $H_2$, 160 °C isothermal, 45 min): $t_R$ of *endo* product (min) = 30.35 (77.73), 32.67 (22.27) Calculated: 56% ee; IR (neat): $\nu_{max}$ 1726*s*, 1473*m*, 1435*m*, 1252*s*, 1197*m*, 1154*m*, 1091*m*, 912*m* $cm^{-1}$; MS(ESI): *m/z* 280 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.74 (d, *J* = 1.8 Hz, 1H), 5.75 (d, *J* = 9.8 Hz, 1H) 5.56 (ddd, *J* = 9.8, 4.0, 2.9 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 2.86 (m, 2H), 2.62 (ddd, *J* = 11.0, 6.3, 1.8 Hz, 1H), 2.57 (dd, *J* = 12.7, 6.5 Hz, 1H), 2.04 (m, 1H), 1.84 (ddd, *J* = 21.6, 11.0, 5.7 Hz, 1H), 1.74 (t, *J* = 12.7 Hz, 2H), 0.97 (d, *J* = 7.2 Hz, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 203.5, 173.1, 172.9, 133.2, 127.1, 58.7, 55.8, 52.9, 52.9, 44.4, 38.2, 37.8, 37.2, 31.6, 17.5; HRMS (ESI-TOF) calcd for $C_{15}H_{20}O_5$; 280.1311 found: 280.1310.

In the case of using [Ru($\eta^5$-$C_5H_5$)((*S,S*)-BIPHOP-F)(acetone)][$SbF_6$] (**1b**), the reaction was run in the same scale at r.t. for 5 h to afford the corresponding *endo*-adduct **22** in quantitative yield with 55% ee (28 mg, 0.10 mmol).

### 10. 1-[(3a,4,7a)-2,3,3a,4,5,7a-hexahydro-1*H*-inden-4-yl]ethanone (23)



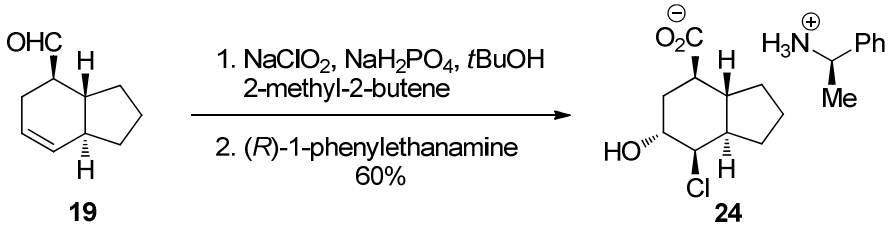

**23**

*Racemic:*

In a 10 mL round-bottom flask equipped with a magnetic stirring bar, under $N_2$, to stirred a triene **7** (30 mg, 0.18 mmol, 1 eq) solution in dry $CH_2Cl_2$ (0.2 mL) at -78 °C, $AlEt_2Cl$ solution (1 M in hexanes, 0.072 mL, 0.072 mmol, 0.4 eq) was added dropwise. The yellow reaction mixture was stirred at -78 °C to r.t. for 2 h and quenched with water (2 mL) and $Et_2O$ (2 mL).

The organic phase was extracted with $Et_2O$ (5 × 3 mL). The combined organic layers were brine and dried (anh. $Na_2SO_4$). A >99:1 mixture of *endo*:*exo* adducts and complete conversion were determined by $^1H$ NMR. The crude reaction was purified with f.c. ($R_f$ = 0.31, 5% $Et_2O$ in pentanes) to give a colorless oil in 67% yield (20 mg, 0.12 mmol). Chiral GC (Hydrodex-β, $H_2$, 100 °C 30 min then heating 0.5 °C/min to 120 °C): $t_R$ of *endo* product (min) = 47.24, 49.04 and $t_R$ of starting material (min) = 61.01; IR (neat): $\nu_{max}$ 2924*s*, 2870*s*, 1708*s*, 1454*m*, 1377*w*, 1059*s* $cm^{-1}$; MS(EI): *m/z* (%) relative intensity 164 ($M^+$, 10), 146 (10), 121 (100), 93 (22), 91 (30), 79 (47), 77 (14), 67 (26), 55 (12); $^1H$ NMR (400 MHz, $CDCl_3$): δ 5.78 (d, *J* = 9.8 Hz, 1H), 5.53 (ddd, *J* = 9.8, 6.5, 2.9 Hz, 1H), 2.59 (dt, *J* = 10.7, 6.7 Hz, 1H), 2.29-2.13 (m, 2H), 2.12-2.08 (m, 3H), 1.90-1.60 (m, 3H), 1.42 (m, 1H), 1.36-1.10 (m, 4H); $^{13}C$ NMR (100 MHz, $CDCl_3$): δ 211.8, 129.9, 125.6, 53.3, 45.6, 44.4, 29.4, 29.3, 28.8, 28.2, 22.1. HRMS (ESI-TOF) calcd for $C_{11}H_{15}O$; 164.1201 found: 164.1200.

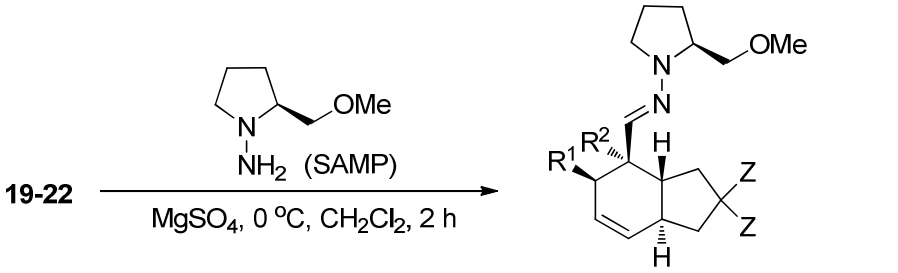
### 11. (1*R*)-1-phenylethanaminium (3a*S*,4*R*,6*R*,7*R*,7a*R*)-7-chloro-6-hydroxyoctahydro-1*H*-indene-4-carboxylate (24)




To solution of aldehyde **19** (80 mg, 0.53 mmol, 1 eq) in *t*BuOH (24 mL) was added 2-methyl-2-butene (7.3 mL, 68.9 mmol, 130 eq), followed by $NaH_2PO_4.2H_2O$ (3.12 g, 20.14 mmol, 38 eq) and $NaClO_2$ (0.527 g, 5.83 mmol, 11 eq) in water (19 mL). After 1 h, the reaction was quenched by the addition of sat. $NH_4Cl$ (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layers were washed with brine (15 mL), dried (anh. $MgSO_4$). Volatiles were removed in vacuo. The chiral amine was added to the crude oxidized product to afford white solid. Decantation by using syringe and recrystallization from warm ethanol, then cooling down to r.t. afforded white crystal of **24** in 60% yield (110 mg, 0.32 mmol); IR ($CHCl_3$): $\nu_{max}$ 3262*m*, 2931*m*, 1643*s*, 1530*s*, 1399*m*, 1258*m*, 1108*m* $cm^{-1}$; MS(ESI): *m/z* (%) relative intensity 217.3 ($M^-$) and 122.3 ($M^+$); $^1H$ NMR (400 MHz, $CDCl_3$): δ 7.51-7.37 (m, 5H), 5.10-4.80 (m, 4H), 4.43 (q,

$J$ = 6.8 Hz, 1H), 4.22 (br. s, 1H), 4.09 (d, $J$ = 2.4 Hz, 1H), 2.35 (td, $J$ = 12.0, 3.3 Hz, 1H), 2.10 (td, $J$ = 13.4, 2.6 Hz, 1H), 2.02 (br.s, 1H), 1.95-1.75 (m, 3H), 1.72-1.56 (m, 7H), 1.24 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 183.8, 140.9, 130.4 (2CH), 130.0, 127.7 (2CH), 72.5, 64.5, 52.4, 48.1, 44.2, 41.7, 32.5, 30.6, 27.7, 22.3, 21.5; Elemental analysis: C, 63.61; H, 7.71; N, 4.12; found C, 63.53; H, 7.78; N, 4.08.

### 12. Hydrazone derivatives 25-28




**25**: $R^1$ = H, $R^2$ = H, Z = H
**26**: $R^1$ = H, $R^2$ = Me, Z = H
**27**: $R^1$ = H, $R^2$ = H, Z = $CO_2Me$
**28**: $R^1$ = Me, $R^2$ = H, Z = $CO_2Me$

*General procedure:*

A solution of aldehyde (0.2 mmol, 1 eq) in $CH_2Cl_2$ (1 mL) and anhydride $MgSO_4$ were placed in the reaction flask and cooled to 0 °C. SAMP (29 μL, 0.22 mmol, 1.1 eq) was carefully added to the mixture. After stirring at 0 °C for 2 h, the reaction mixture was filtered through Celite plug. Volatiles were removed in vacuo. The residue was purified by f.c. to afford the hydrazone derivatives.

#### 12.1 (2*S*)-*N*-[(1*E*)-(3a*R*,4*R*,7a*S*)-2,3,3a,4,5,7a-hexahydro-1*H*-inden-4-ylmethylene]-2-(methoxymethyl)pyrrolidin-1-amine (25)

Obtained as a yellow liquid in 95% yield: $R_f$ = 0.26 (20% $Et_2O$ in pentanes); IR (neat): $\nu_{max}$ 3016*m*, 2951*s*, 2868*s*, 1638*w*, 1602*w*, 1455*m*, 1339*m*, 1196*m*, 1117*s* cm$^{-1}$; MS(ESI): *m/z* 263 ($M^+$+H); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.62 (d, $J$ = 6.46 Hz, 1H), 5.87 (d, $J$ = 9.80 Hz, 1H), 5.64 (ddd, $J$ = 9.59, 6.61, 2.72 Hz, 1H), 3.61 (dd, $J$ = 8.7, 3.3 Hz, 1H), 3.34-3.50 (m, 6H), 2.78 (q, $J$ = 8.4 Hz, 1H), 2.45 (tt, $J$ = 10.8, 6.3 Hz, 1H), 2.33 (dddd, $J$ = 18.2, 8.4, 4.2, 2.2 Hz, 1H),

2.22-2.08 (m, 1H), 2.05-1.64 (m, 9H), 1.44-1.14 (m, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 142.4, 129.9, 126.6, 74.8, 63.5, 59.3, 50.5, 47.7, 44.7, 43.5, 31.8, 29.5, 28.1, 26.6, 22.2, 22.1; HRMS (ESI-TOF) calcd for $C_{16}H_{27}N_2O$; 263.2117 found: 263.2119.

### 12.2 (2*S*)-2-(methoxymethyl)-*N*-{(1*E*)-[(3a*R*,4*R*,7a*S*)-4-methyl-2,3,3a,4,5,7a-hexahydro-1*H*-inden-4-yl]methylene}pyrrolidin-1-amine (26)

Obtained as a yellow liquid in 96% yield: $R_f$ = 0.33 (20% $EtO_2$ in pentane); IR (neat): $\nu_{max}$ 3014*m*, 2954*s*, 2870*s*, 1638*w*, 1603*w*, 1457*m*, 1340*m*, 1196*m*, 1119*s* cm$^{-1}$; MS(ESI): *m/z* 277.3 ($M^+$+H); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.71 (s, 1H of *exo*), 6.65 (s, 1H of *endo*), 5.83 (d, *J* = 9.9 Hz, 1H of *endo*), 5.64 (ddt, *J* = 9.7, 4.8, 2.5 Hz, 1H of *endo*), 5.56 (dtd, *J* = 7.2, 4.8, 2.3 Hz, 1H of *exo*), 5.43 (d, *J* = 10.1 Hz, 1H of *exo*), 3.65 (dt, *J* = 9.1, 3.1 Hz, 2H of *endo* and *exo*), 3.54-3.29 (m, 12H of *endo* and *exo*), 2.80-2.60 (m, 2H of *endo* and *exo*), 2.50-2.35 (m, 2H of *endo* and *exo*), 2.15-1.77 (m, 14H of *endo* and *exo*), 1.76-1.59 (m, 6H of *endo* and *exo*), 1.54-1.43 (m, 2H of *endo* and *exo*), 1.34-1.14 (m, 4H of *endo* and *exo*), 1.09 (d, *J* = 4.5 Hz, 3H of *exo*), 1.04 (s, 3H of *endo*); $^{13}$C NMR (100 MHz, $CDCl_3$): δ of *endo* 146.6, 128.8, 126.3, 74.7, 63.6, 59.3, 50.9, 50.2, 40.2, 38.8, 38.6, 29.3, 26.6, 24.1, 22.0, 21.9, 16.4; HRMS (ESI-TOF) calcd for $C_{17}H_{29}N_2O$; 277.2274 found: 277.2274.

### 12.3 Dimethyl (3a*R*,4*R*,7a*S*)-4-[(*E*)-{[(2*S*)-2-(methoxymethyl)pyrrolidin-1-yl]imino}methyl]-1,3,3a,4,5,7a-hexahydro-2*H*-indene-2,2-dicarboxylate (27)

Obtained as a yellow liquid in 86% yield: $R_f$ = 0.21 (40% $EtO_2$ in pentanes); IR (neat): $\nu_{max}$ 3019*w*, 2953*m*, 2919*m*, 1732*s*, 1601*w*, 1435*m*, 1251*s*, 1196*s*, 1159*s*, 1110*s* cm$^{-1}$; MS(ESI): *m/z* 378 ($M^+$+H); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.55 (d, *J* = 6.4 Hz, 1H), 5.81 (d, *J* = 9.9 Hz, 1H), 5.73–5.63 (m, 1H), 3.763 (s, 3H), 3.758 (s, 3H), 3.64–3.57 (m, 1H), 3.50–3.34 (m, 6H), 2.86–2.60 (m, 3H), 2.44 (m, 1H), 2.40–2.28 (m, 1H), 2.16 (m, 2H), 2.06–1.90 (m, 3H), 1.89–1.78 (m, 2H), 1.72 (t, *J* = 12.8 Hz, 1H), 1.62 (m, 1H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 173.2, 140.1, 127.9, 127.5, 77.4, 77.1, 76.8, 63.4, 59.2, 58.2, 52.8, 50.3, 46.7, 43.8, 43.0, 38.7, 37.9, 31.5, 26.6, 22.2; HRMS (ESI-TOF) calcd for $C_{20}H_{31}N_2O_5$; 379.2227 found: 379.2239.

### 12.4 Dimethyl (3a*R*,4*R*,5*R*,7a*S*)-4-[(*E*)-{[(2*S*)-2-(methoxymethyl)pyrrolidin-1-yl] imino}methyl]-5-methyl-1,3,3a,4,5,7a-hexahydro-2*H*-indene-2,2-dicarboxylate (28)

Obtained as a yellow liquid in 84% yield: $R_f$ = 0.19 (40% $EtO_2$ in pentanes); IR (neat): $\nu_{max}$ 3018*w*, 2954*m*, 2927*m*, 1733*s*, 1598*w*, 1435*m*, 1251*s*, 1196*s*, 1153*s*, 1114*s* $cm^{-1}$; MS(ESI): *m/z* 378 ($M^+$+H); $^1$H NMR (400 MHz, $CDCl_3$): δ 6.65 (d, *J* = 7.3 Hz, 1H), 5.76 (d, *J* = 9.9 Hz, 1H), 5.63-5.56 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.64-3.55 (m, 1H), 3.53-3.34 (m, 6H), 2.90-2.47 (m, 4H), 2.12 (m, 1H), 2.07-1.61 (m, 8H), 1.03 (d, *J* = 7.1 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ 173.3, 173.2, 139.3, 134.5, 126.6, 74.9, 63.2, 59.2, 58.5, 52.74, 52.71, 50.7, 46.6, 44.9, 41.5, 38.6, 37.8, 35.3, 26.7, 22.2, 17.0. HRMS (ESI-TOF) calcd for $C_{21}H_{33}N_2O_5$; 393.2383 found: 379.2402.

**References**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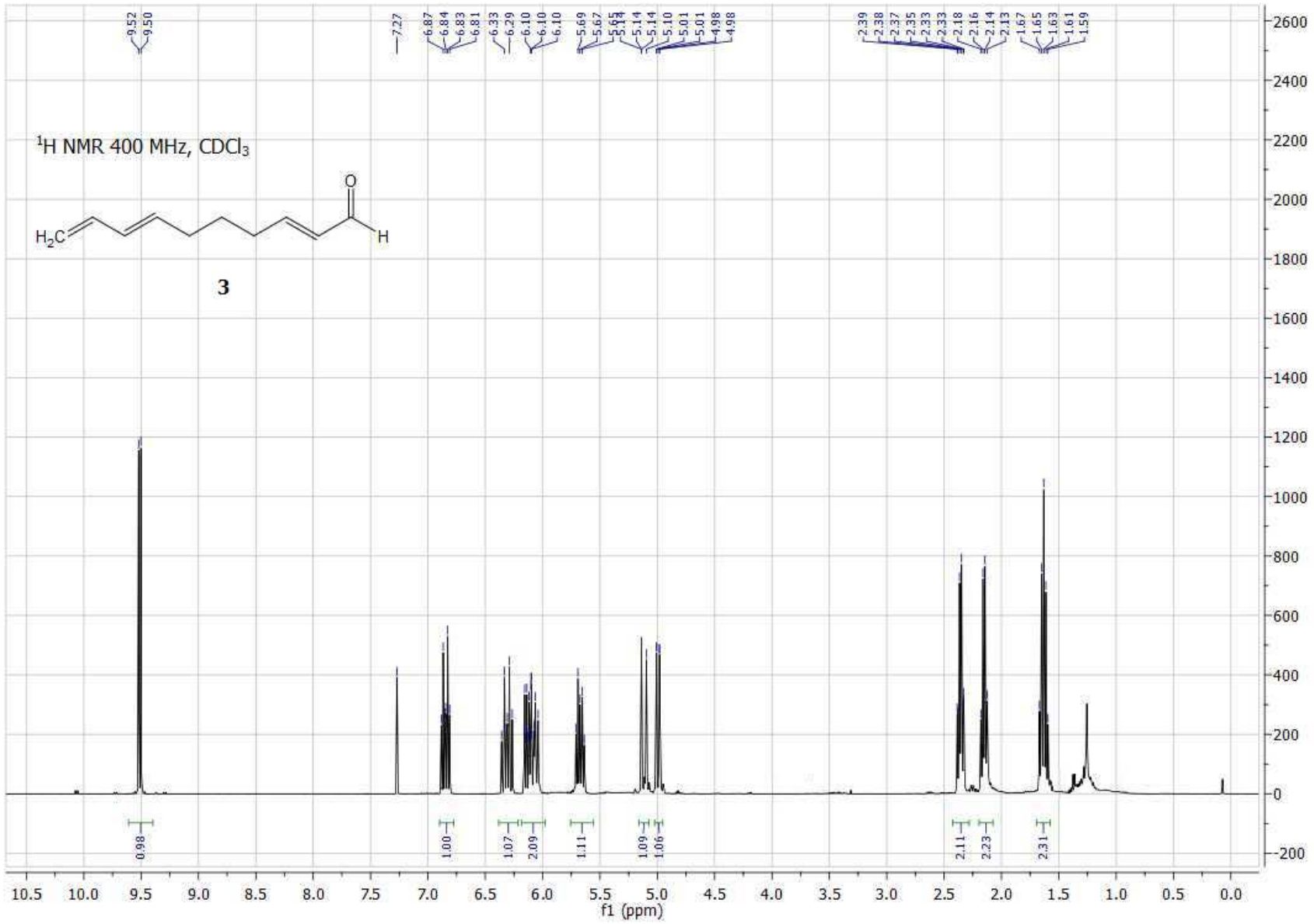
6. Nakanishi, H.; Miyazawa, N. *Japanese Kokai Tokkyo Koho* **2008**, 15.
7. Bross, H; Schneider, R; Hopf, H. *Tetrahedron Lett.* **1979**, *23*, 2129.
8. Wender, P. A.; Christy, J. P. *J. Chem. Am. Soc.* **2006**, *128*, 5354.
9. Trienes **5** and **6** cannot be purified by f.c. on silica gel because it undergoes IMDA reaction spontaneously. Therefore, the alcohol intermediate was stored and freshly oxidized to trienal **6** before do asymmetric IMDA reaction.
10. The IMDA reaction cannot follow by TLC because $R_f$ of starting material and adduct are similar.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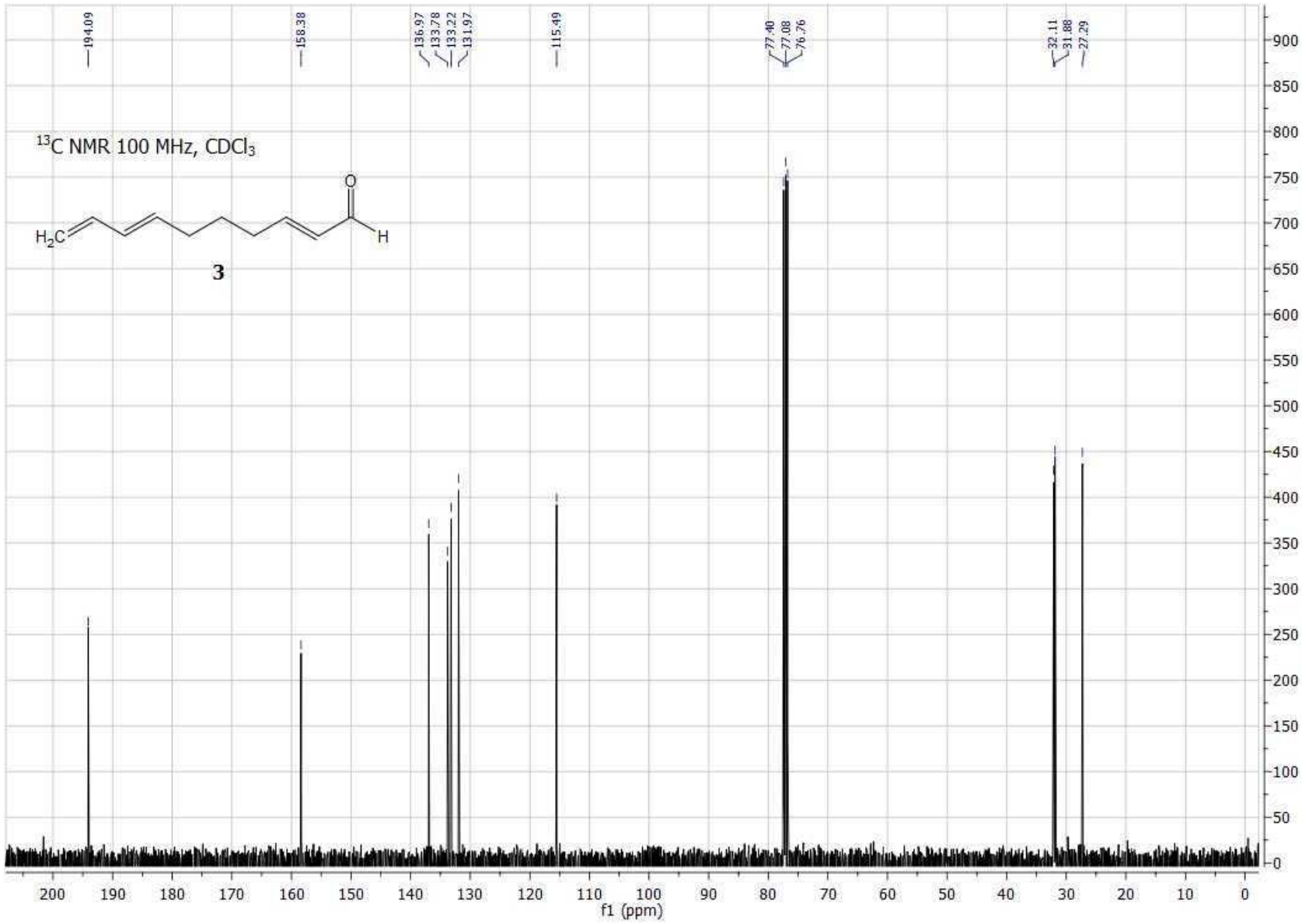
H
3
f1 (ppm)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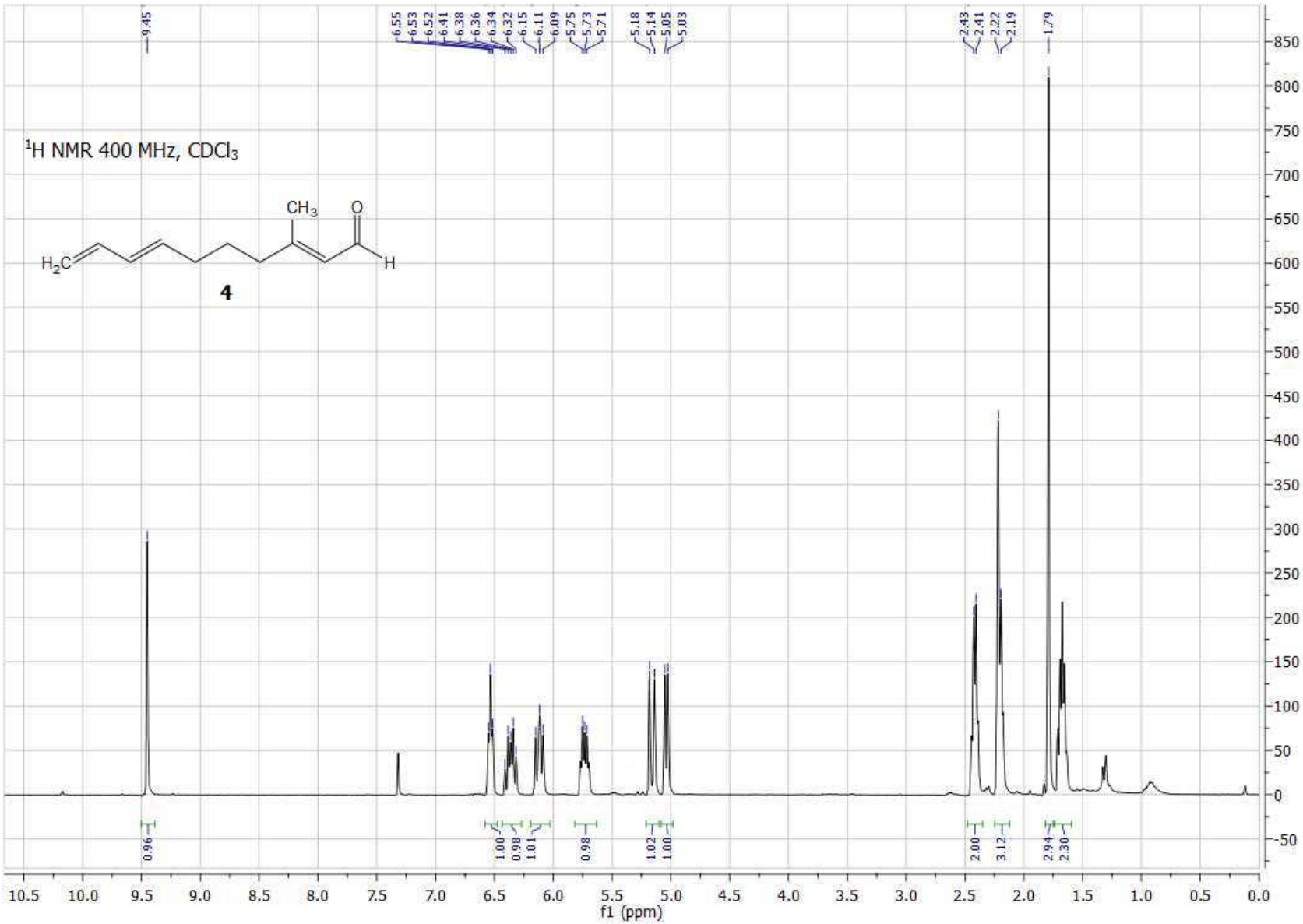
$H_2C$
O
H
3
f1 (ppm)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6.32
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6.11
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5.73
5.71
5.18
5.14
5.05
5.03
2.43
2.41
2.22
2.19
1.79
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$CH_3$
O
$H_2C$
H
4
0.96
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1.01
0.98
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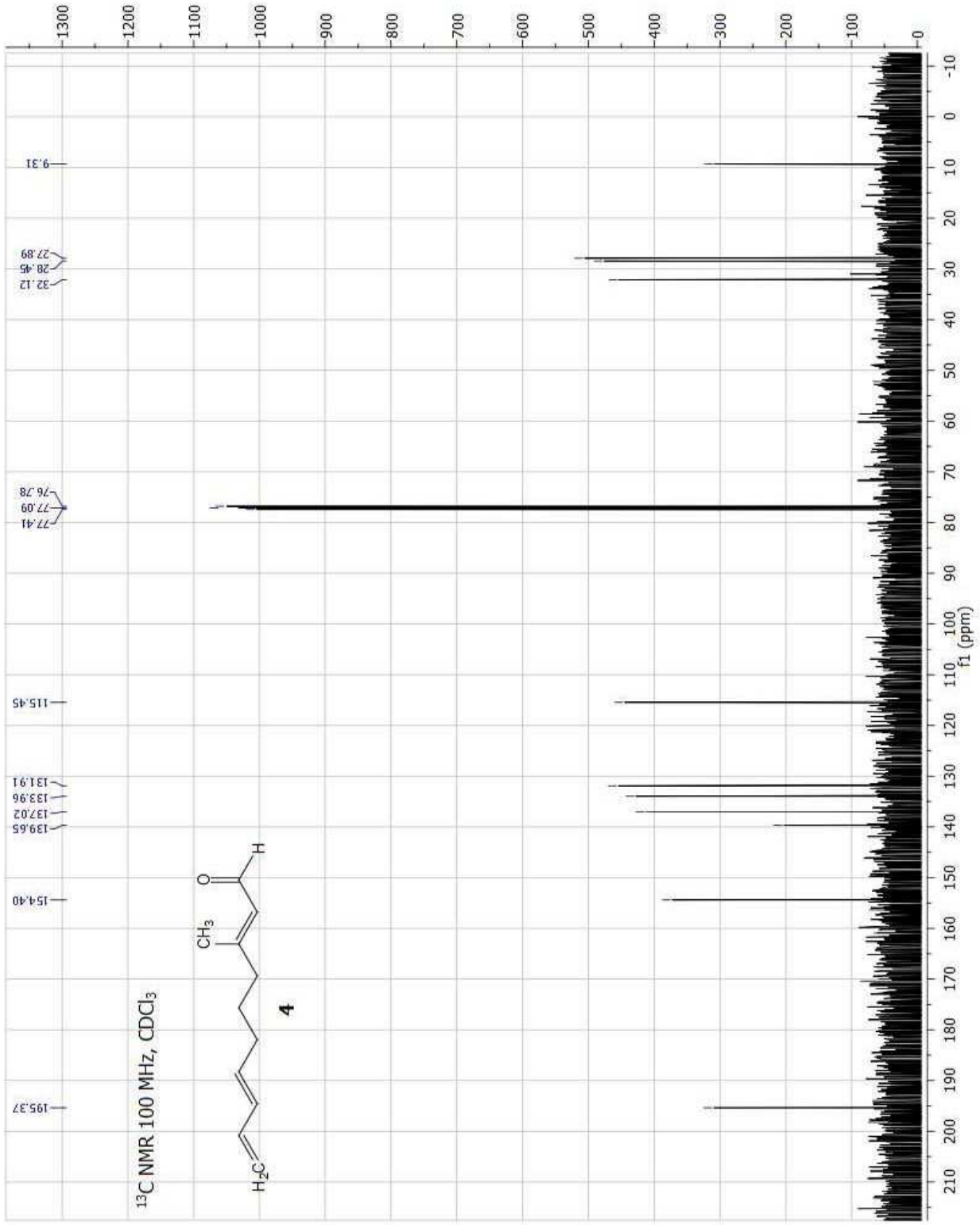
1.00
2.00
3.12
2.94
2.30
f1 (ppm)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131.91
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76.78
32.12
28.45
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f1 (ppm)
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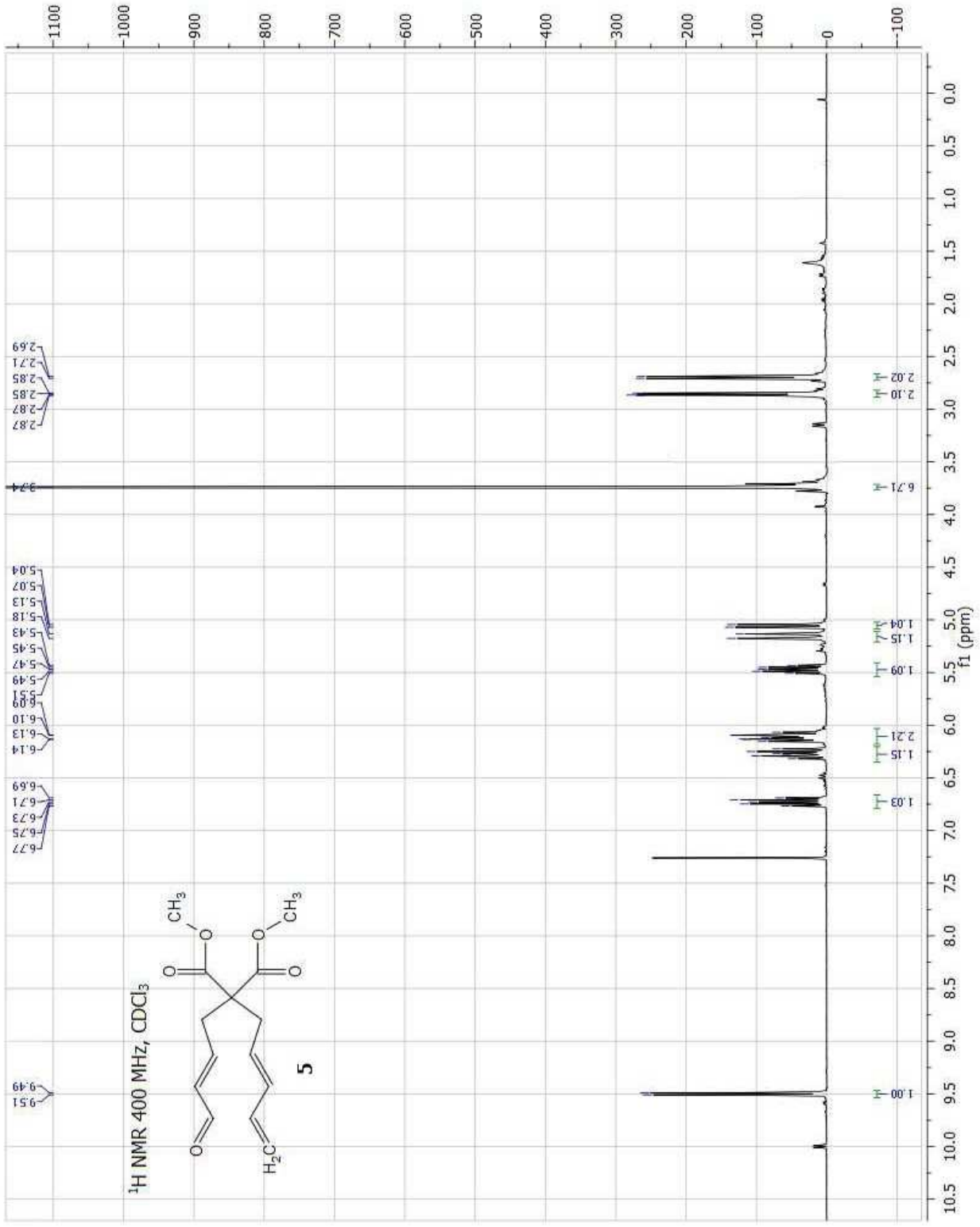
4
$H_2C$
$CH_3$
O
H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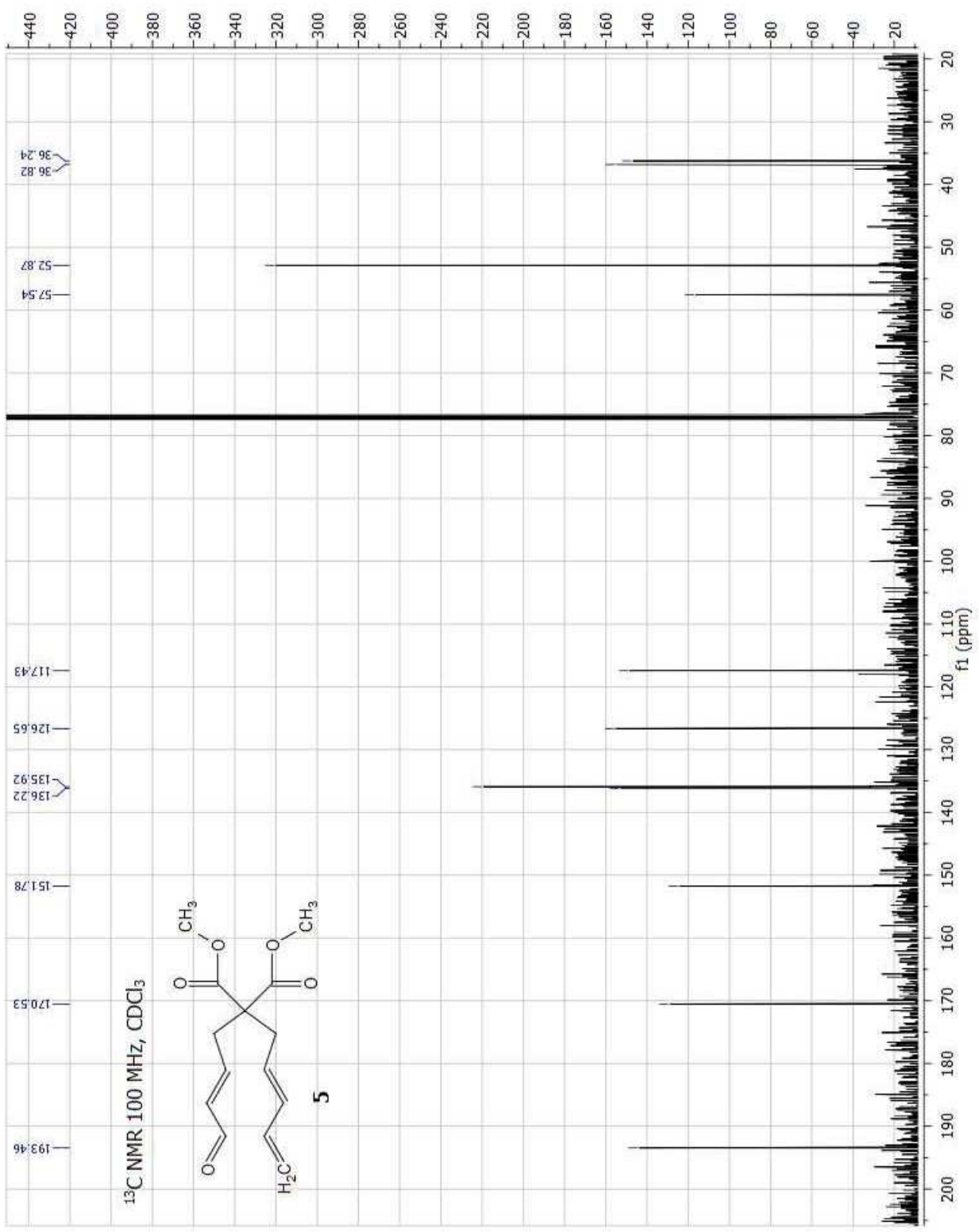
f1 (ppm)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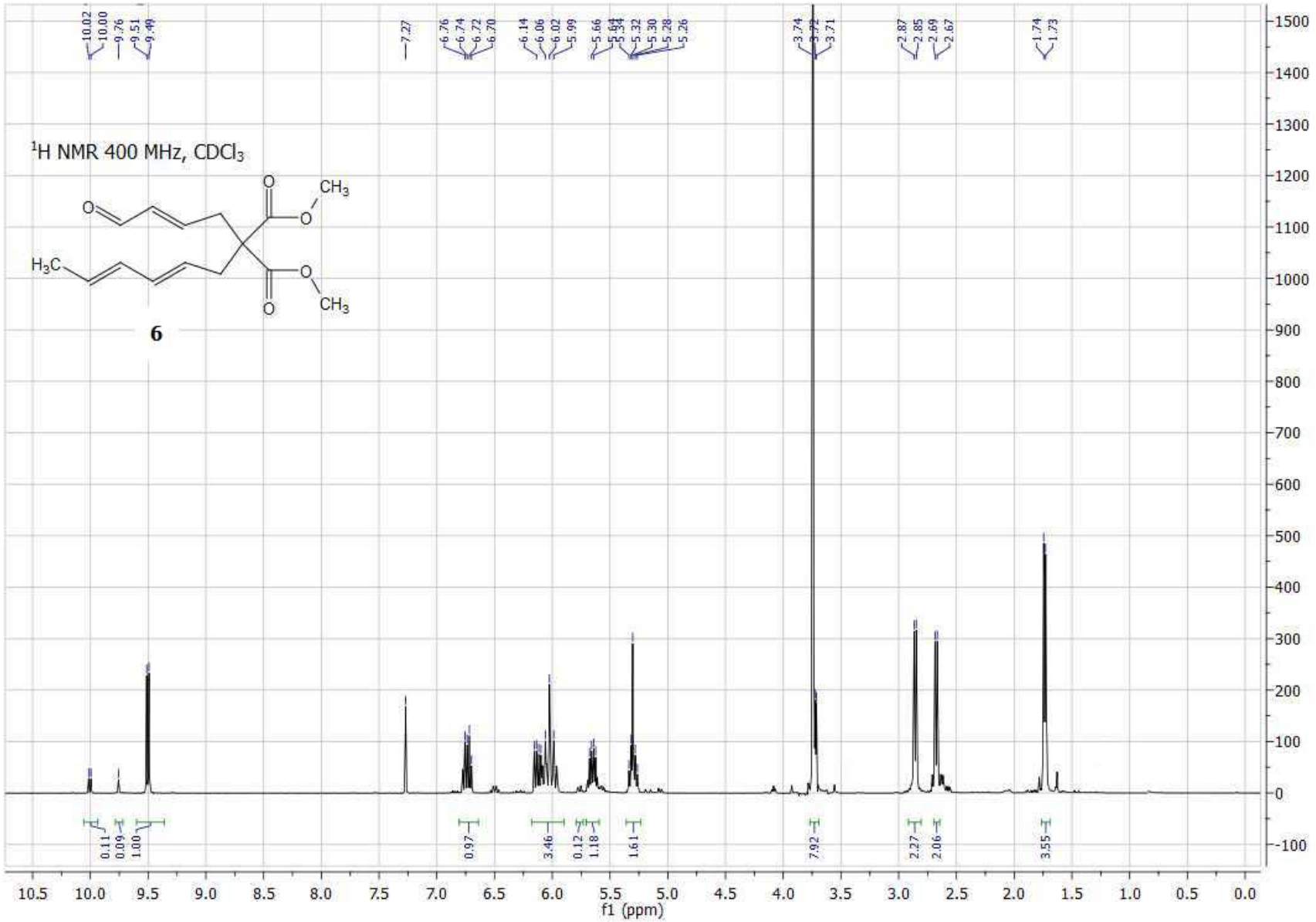
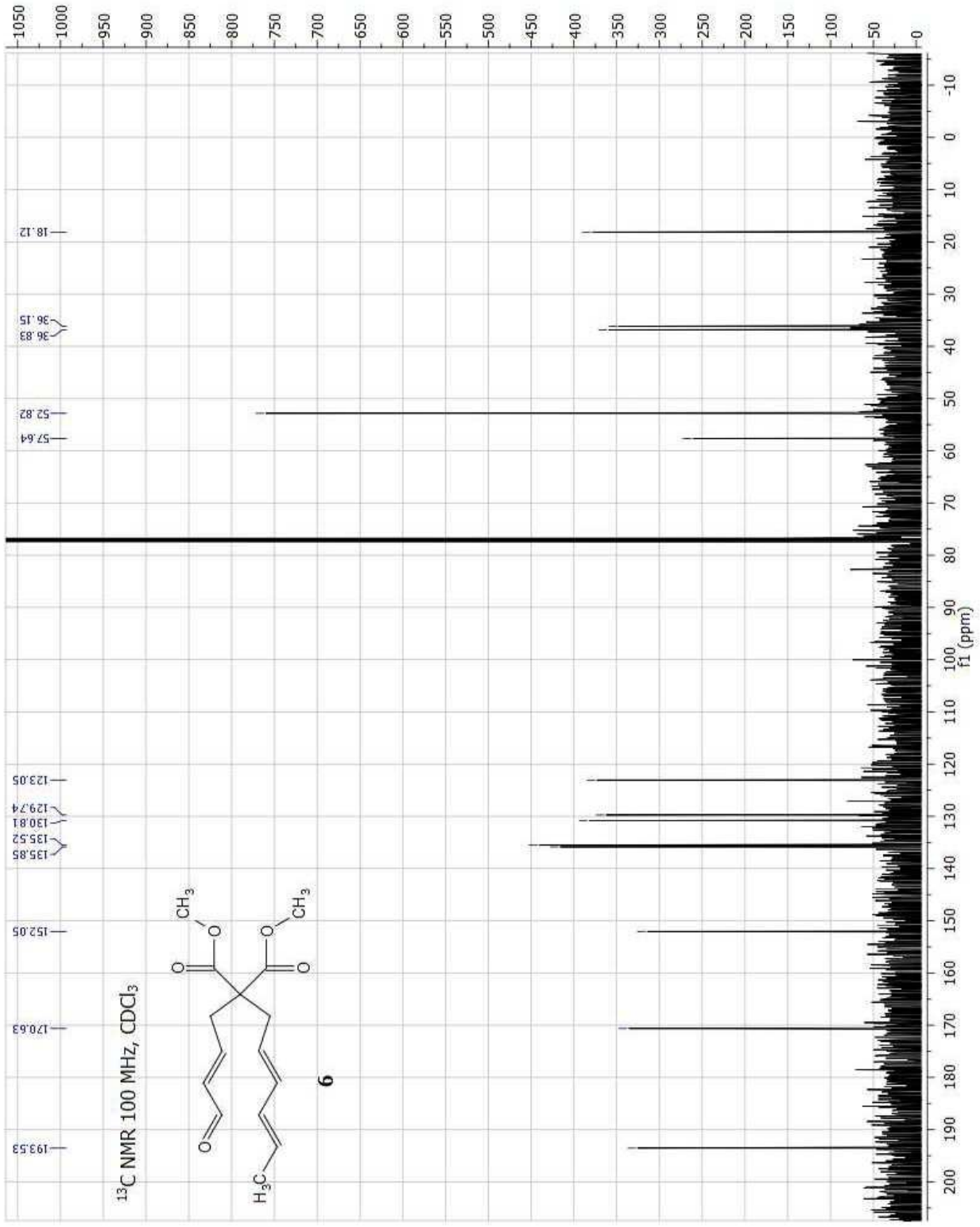
36.24
f1 (ppm)
5




$^1$H NMR 400 MHz, $CDCl_3$



**6**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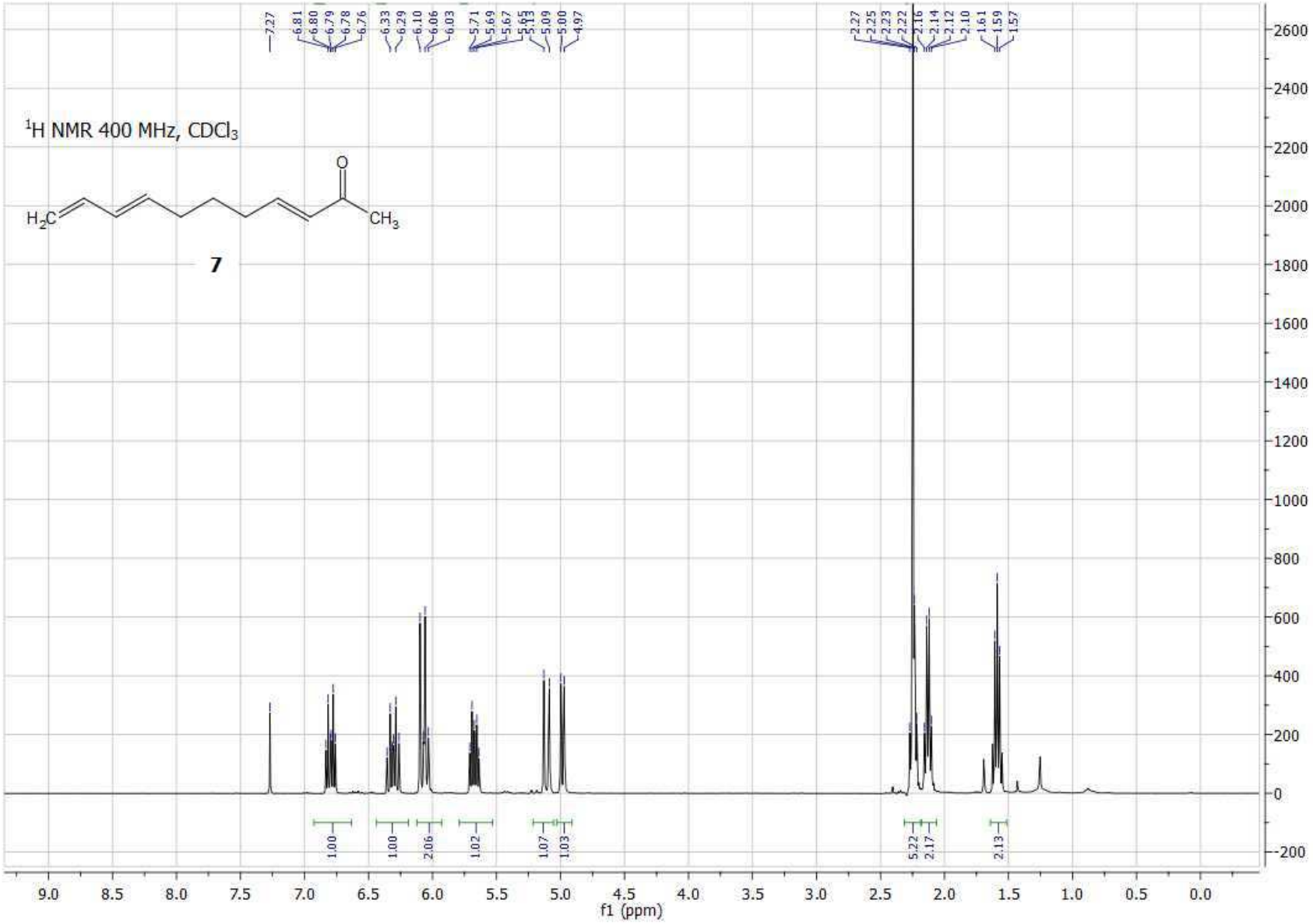
f1 (ppm)
6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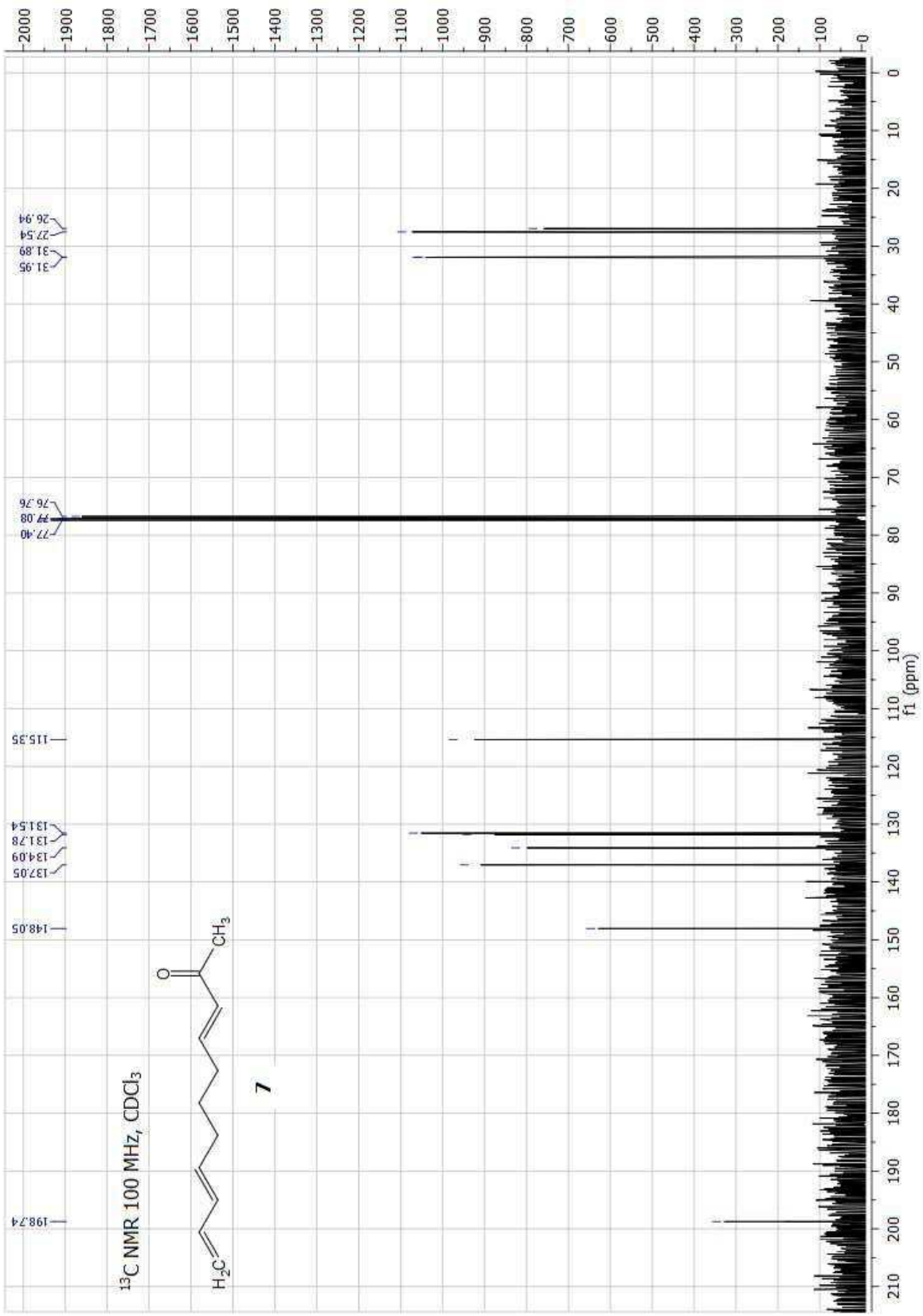
O
$CH_3$
7
f1 (ppm)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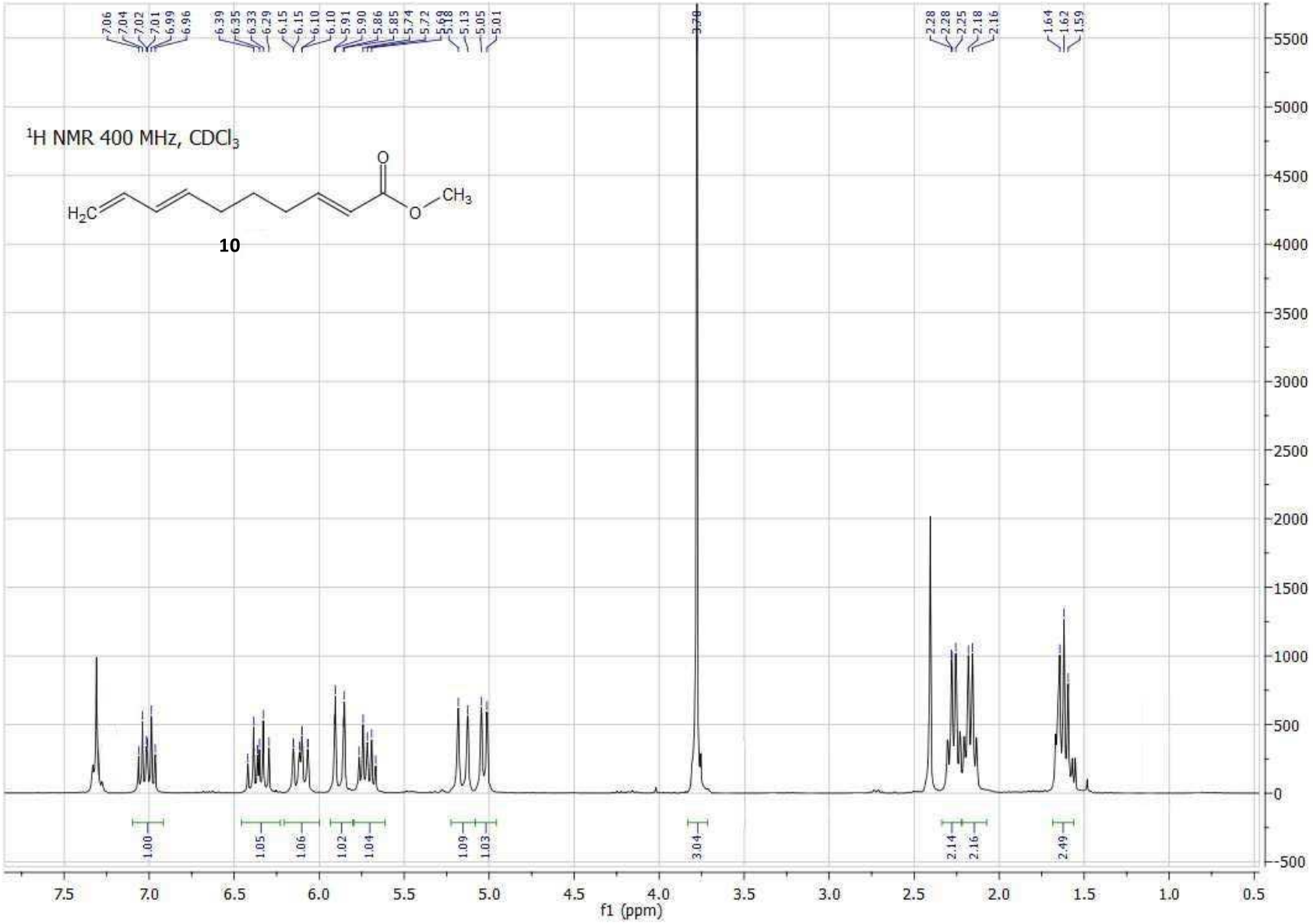
27.54
26.94
f1 (ppm)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5.85
5.74
5.72
5.68
5.18
5.13
5.05
5.01
3.78
2.28
2.28
2.25
2.18
2.16
1.64
1.62
1.59
1H NMR 400 MHz, CDCl3
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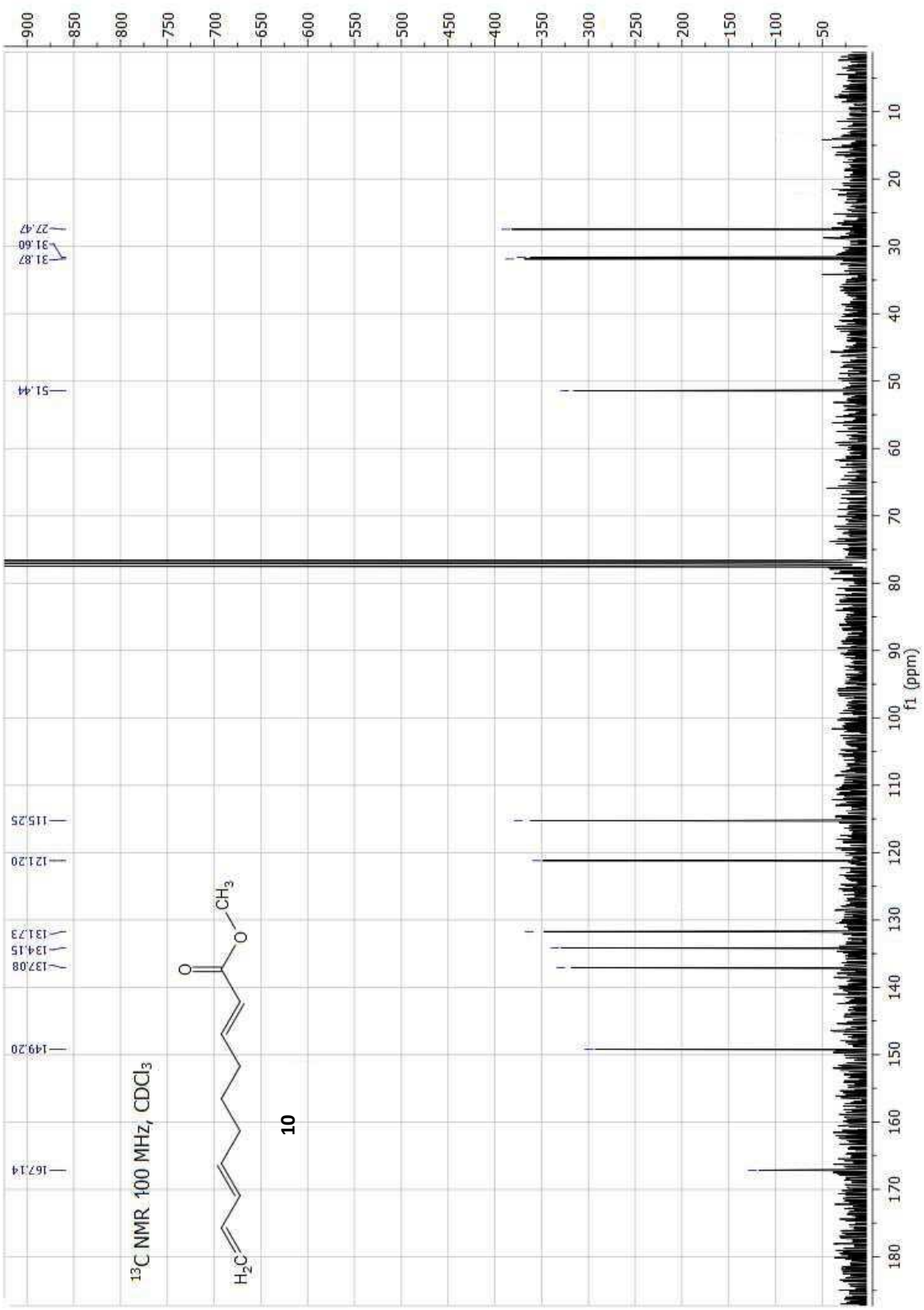
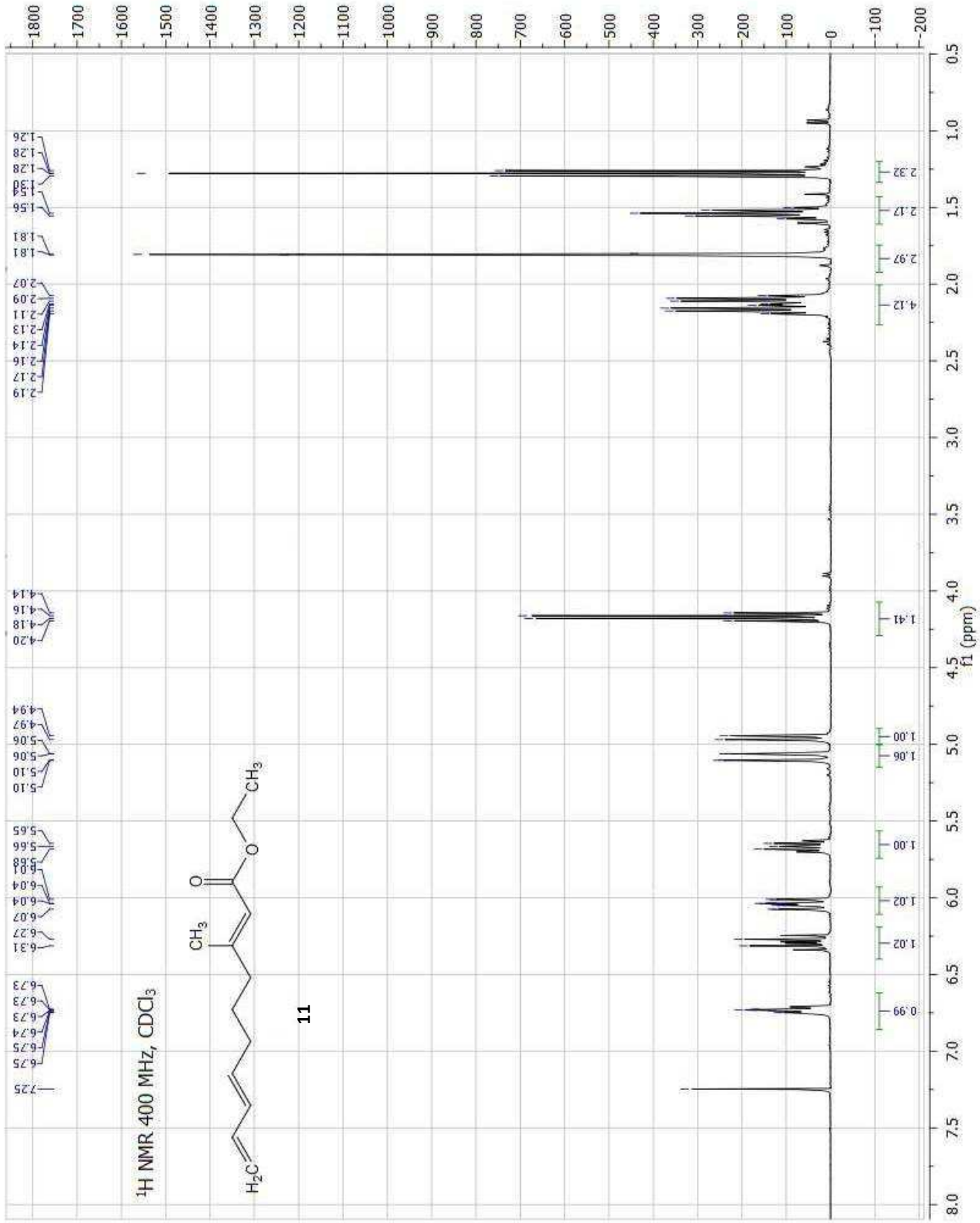
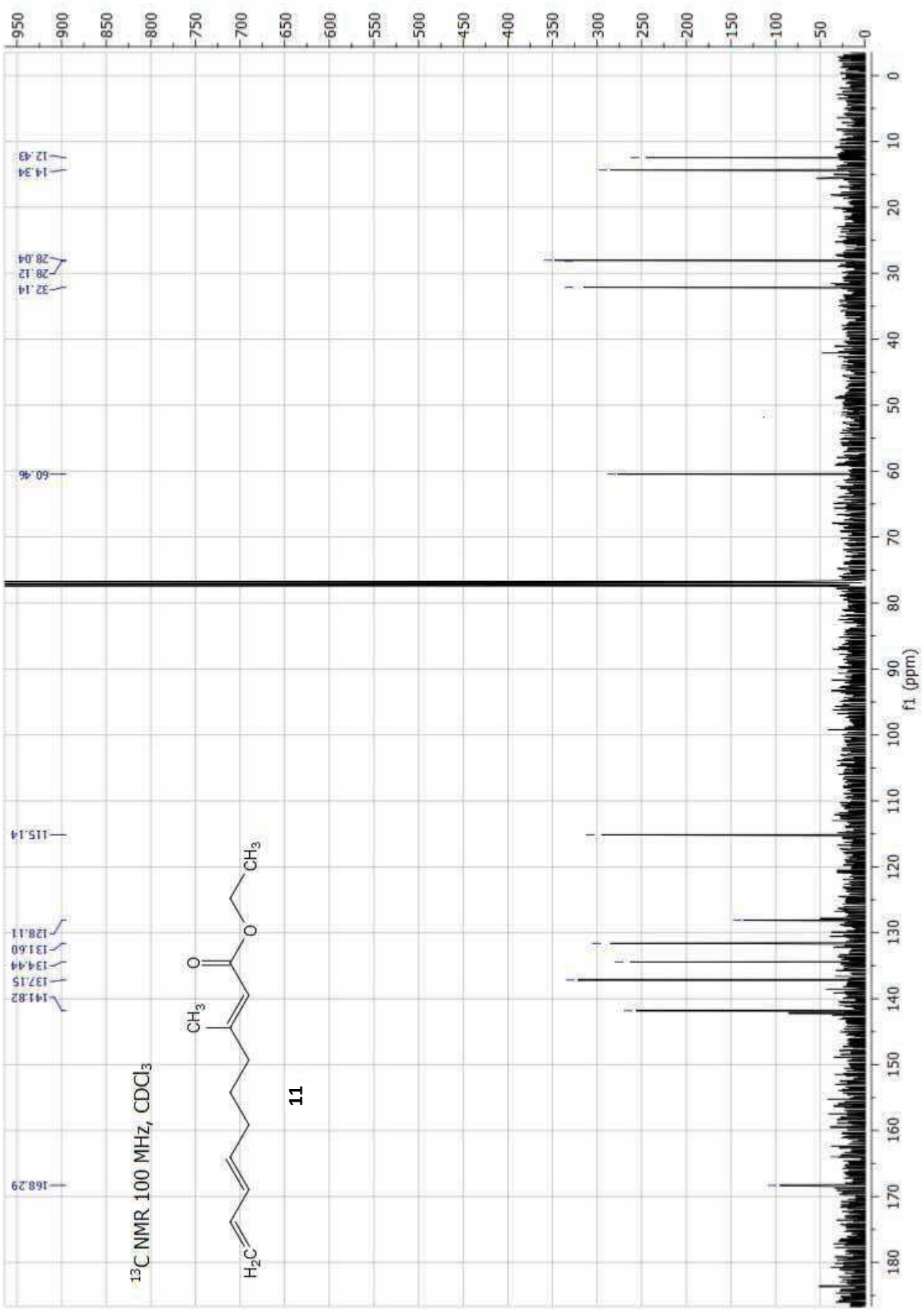
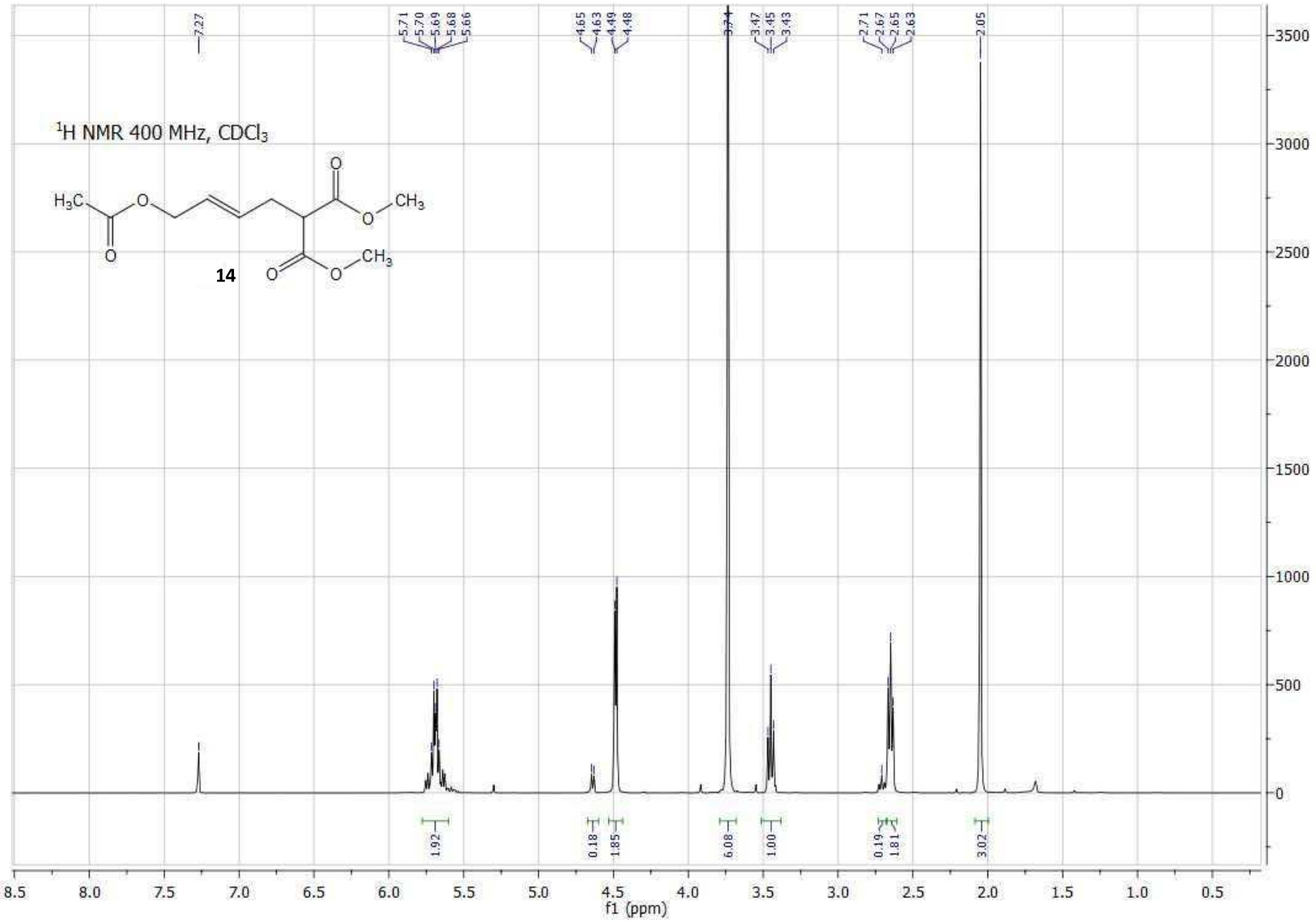
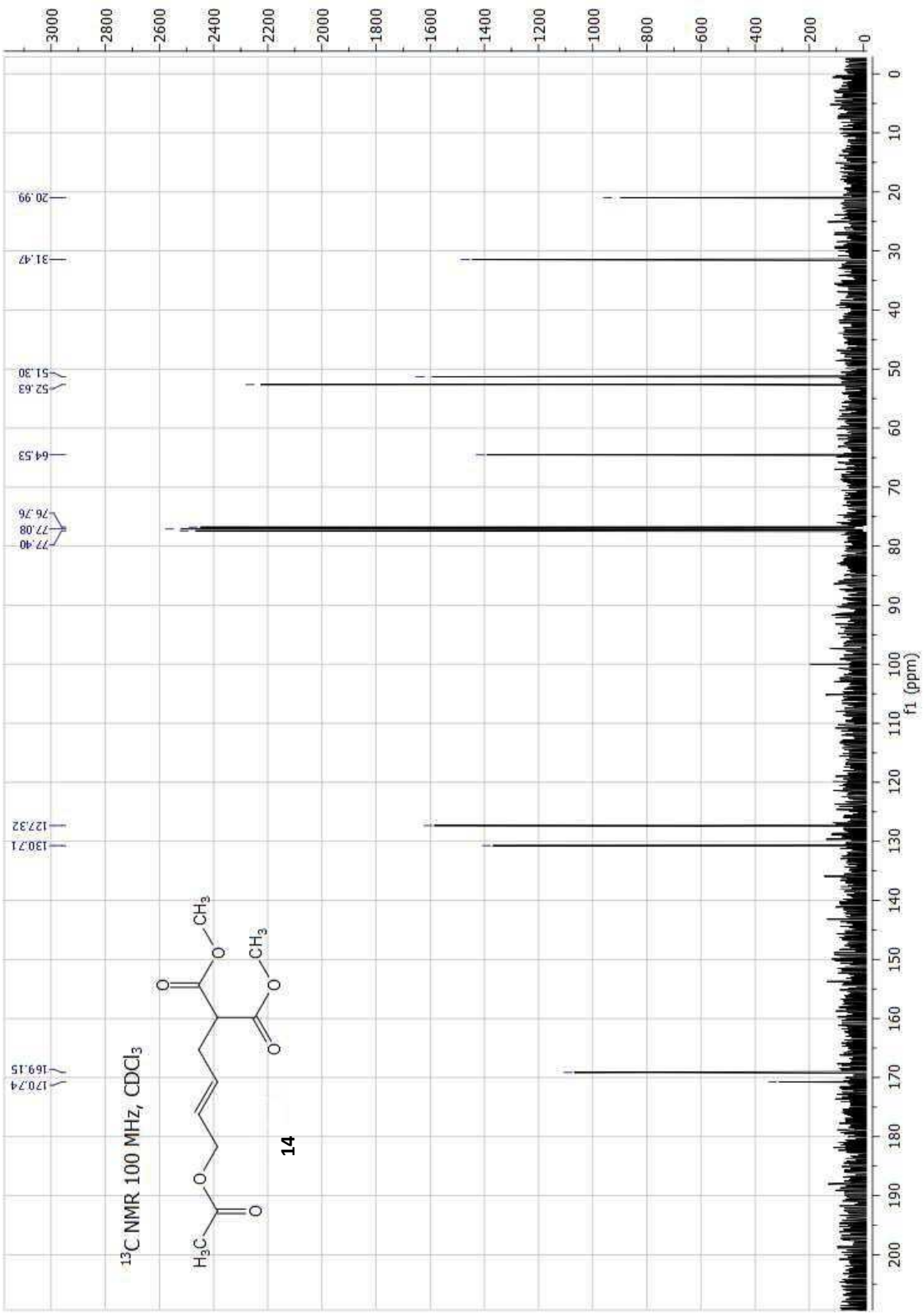
O
CH3
10
1.00
1.05
1.06
1.02
1.04
1.09
1.03
3.04
2.14
2.16
2.49
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

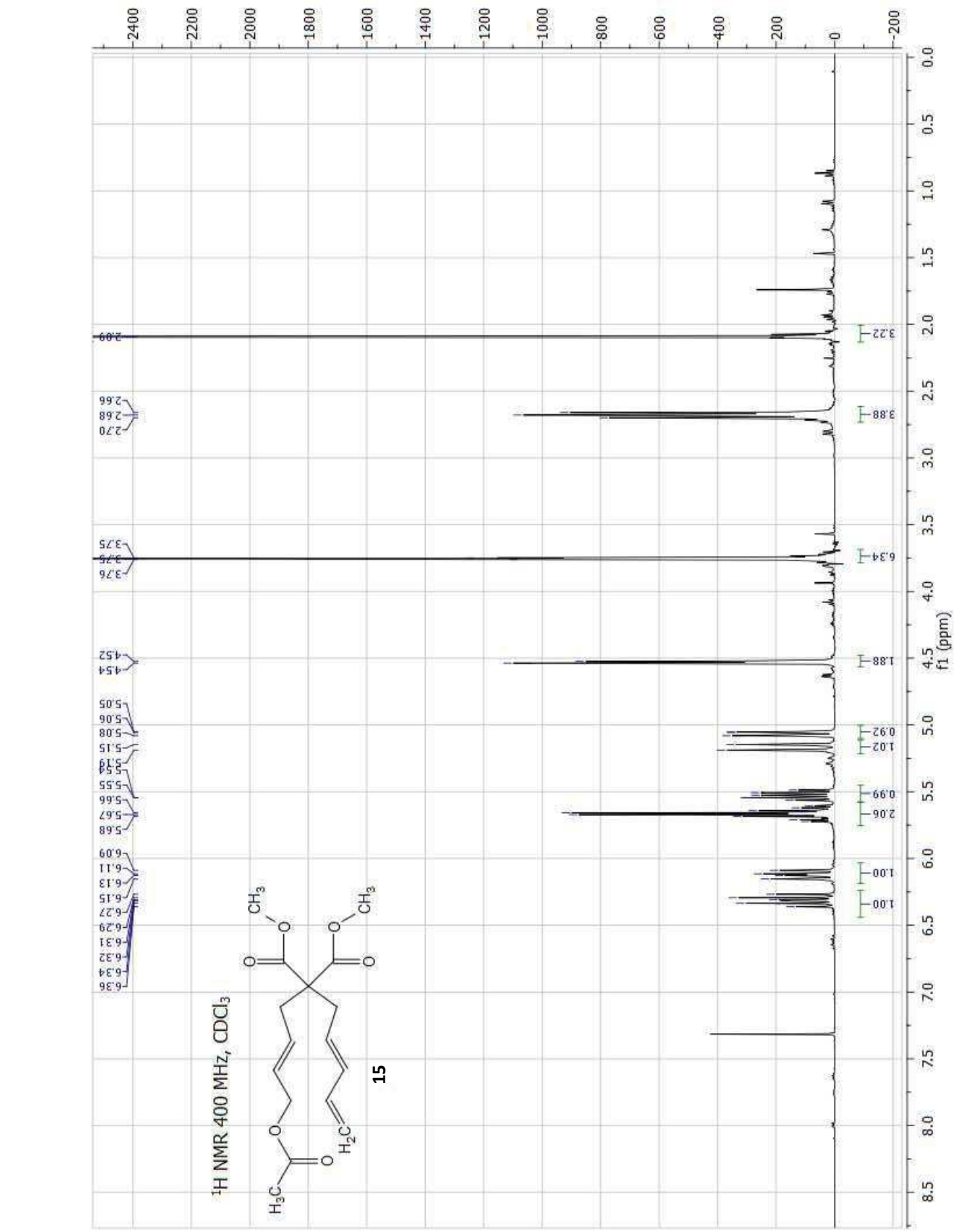

$^{13}$C NMR 100 MHz, $CDCl_3$
10
167.14
149.20
137.08
134.15
131.73
121.20
115.25
51.44
31.87
31.60
27.47
f1 (ppm)

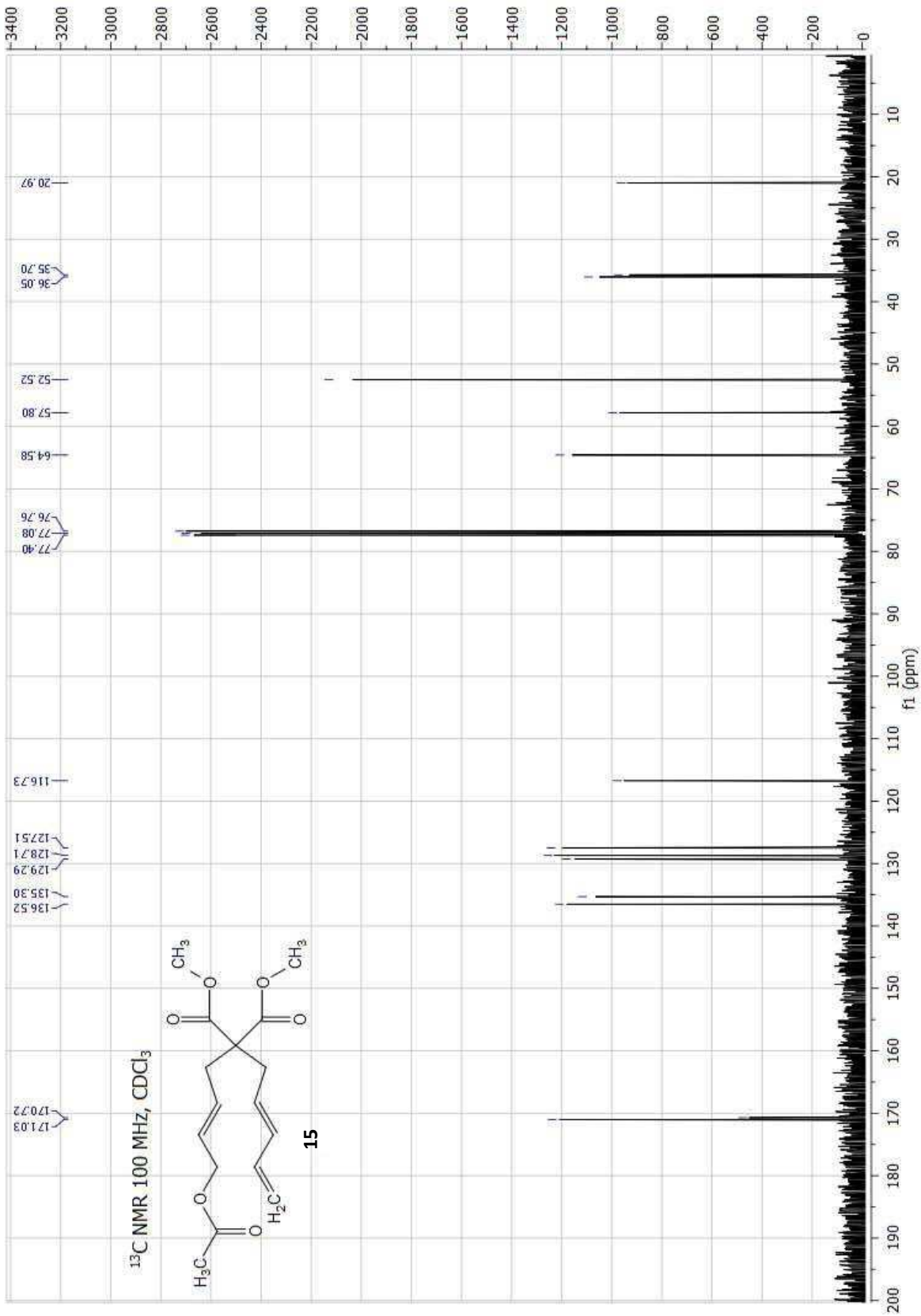

$^1$H NMR 400 MHz, $CDCl_3$
11
$CH_3$
O
O
$CH_3$
$H_2C$
f1 (ppm)

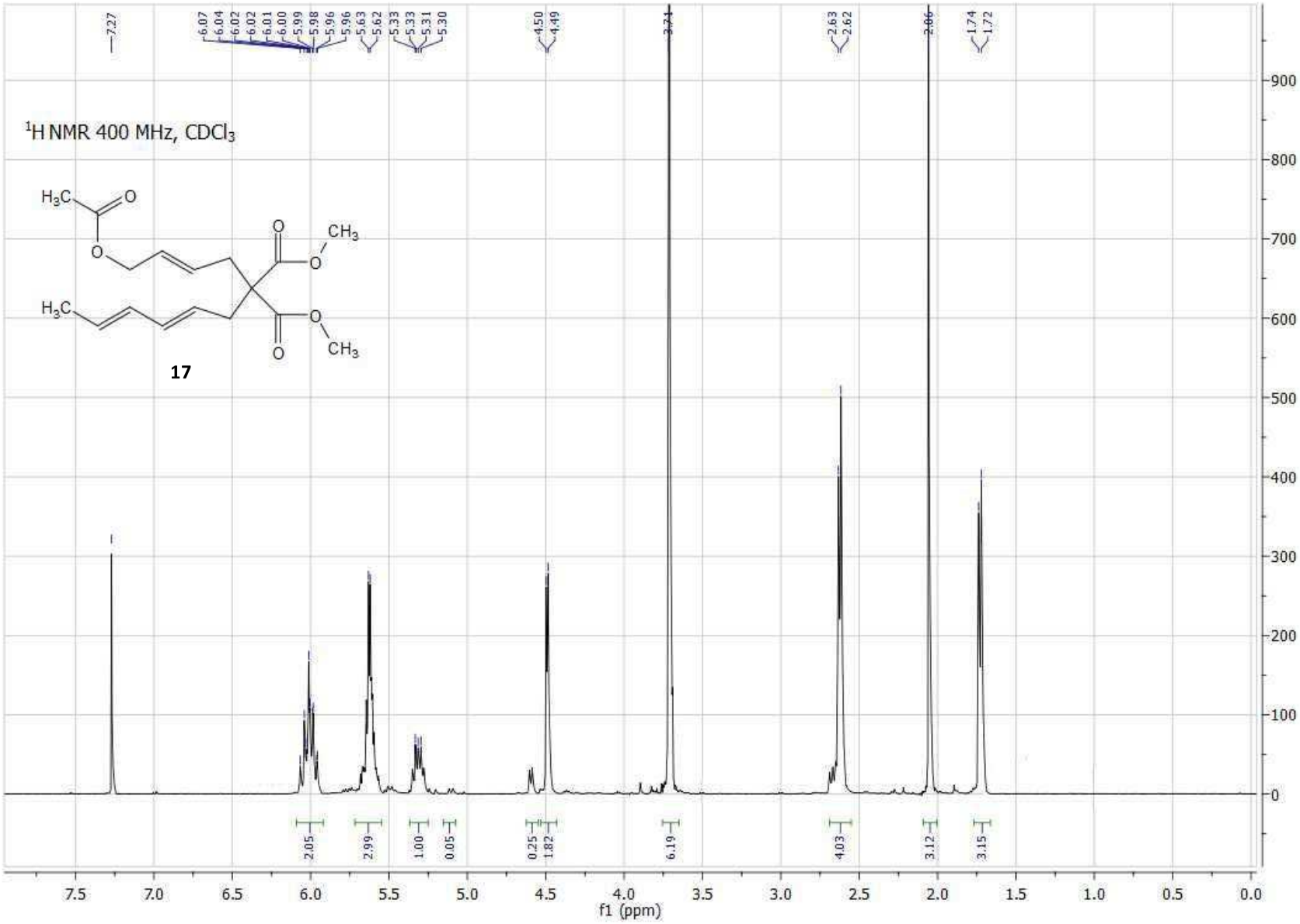

$^{13}$C NMR 100 MHz, $CDCl_3$
11
f1 (ppm)
168.29
141.82
137.15
134.44
131.60
128.11
115.14
60.46
32.14
28.12
28.04
14.34
12.43

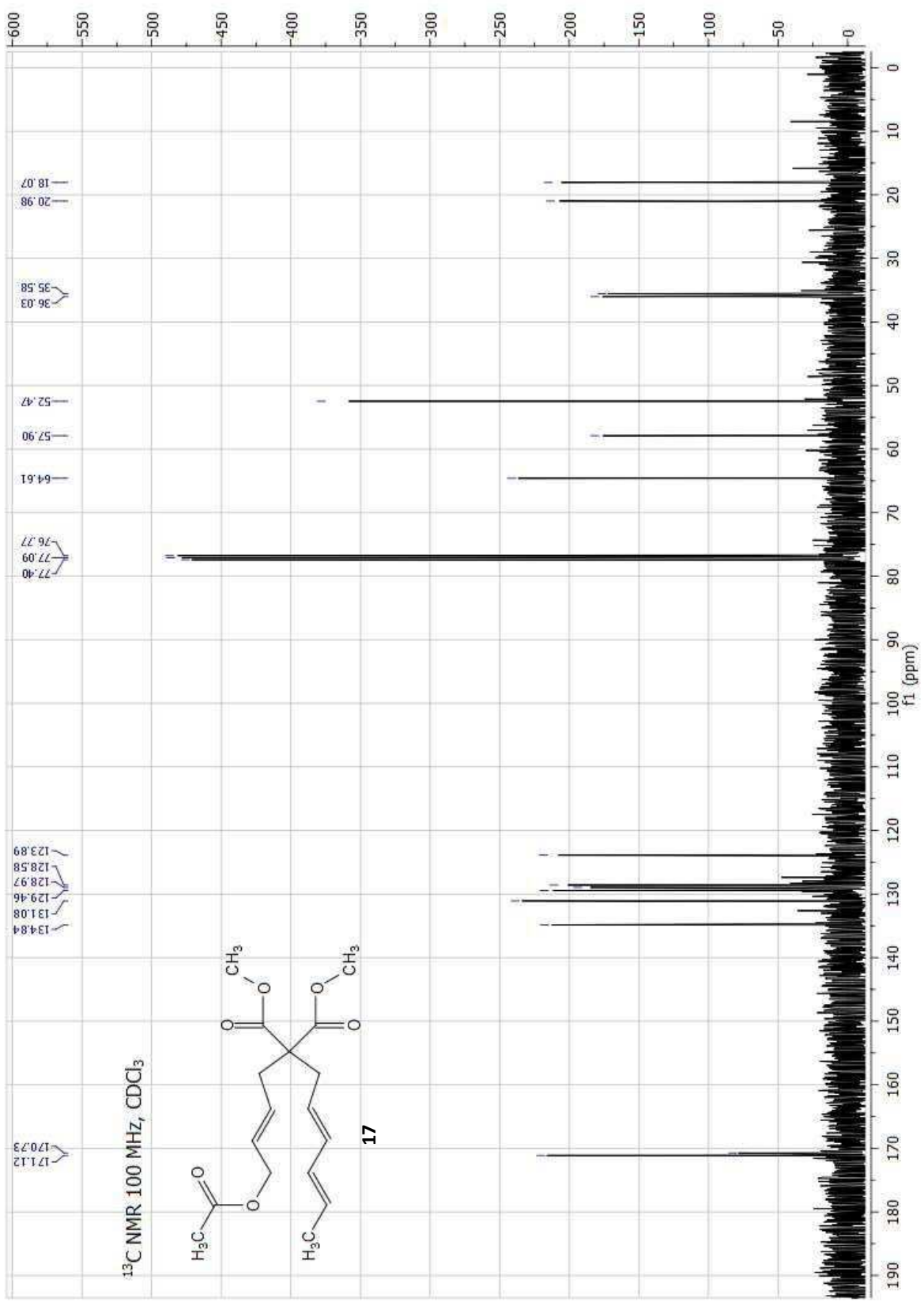

$^1$H NMR 400 MHz, $CDCl_3$
14
7.27
5.71
5.70
5.69
5.68
5.66
4.65
4.63
4.49
4.48
3.47
3.45
3.43
2.71
2.67
2.65
2.63
2.05
1.92
0.18
1.85
6.08
1.00
0.19
1.81
3.02
f1 (ppm)

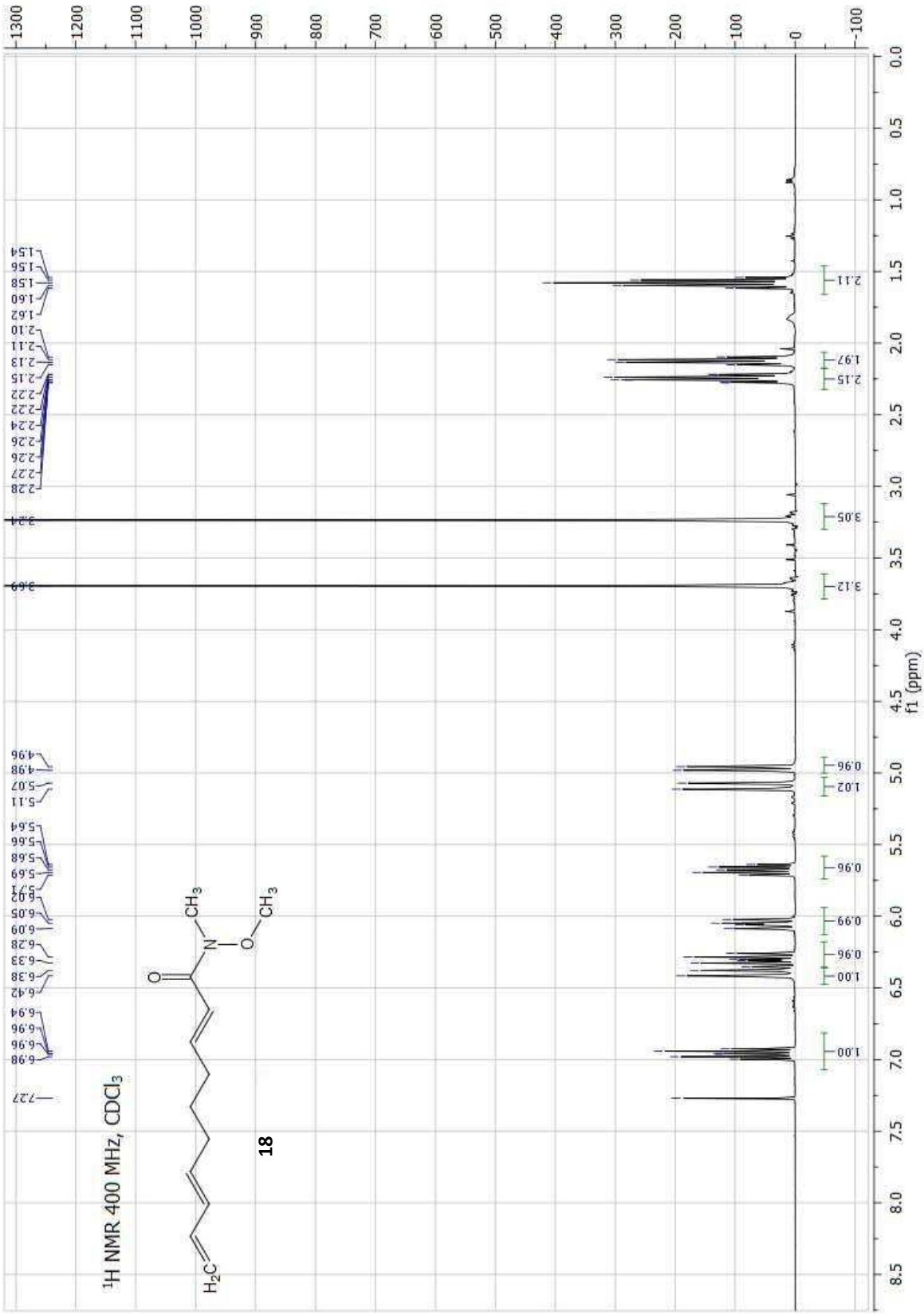

$^{13}$C NMR 100 MHz, $CDCl_3$
14
f1 (ppm)
20.99
31.47
51.30
52.63
64.53
76.76
77.08
77.40
127.32
130.71
169.15
170.74

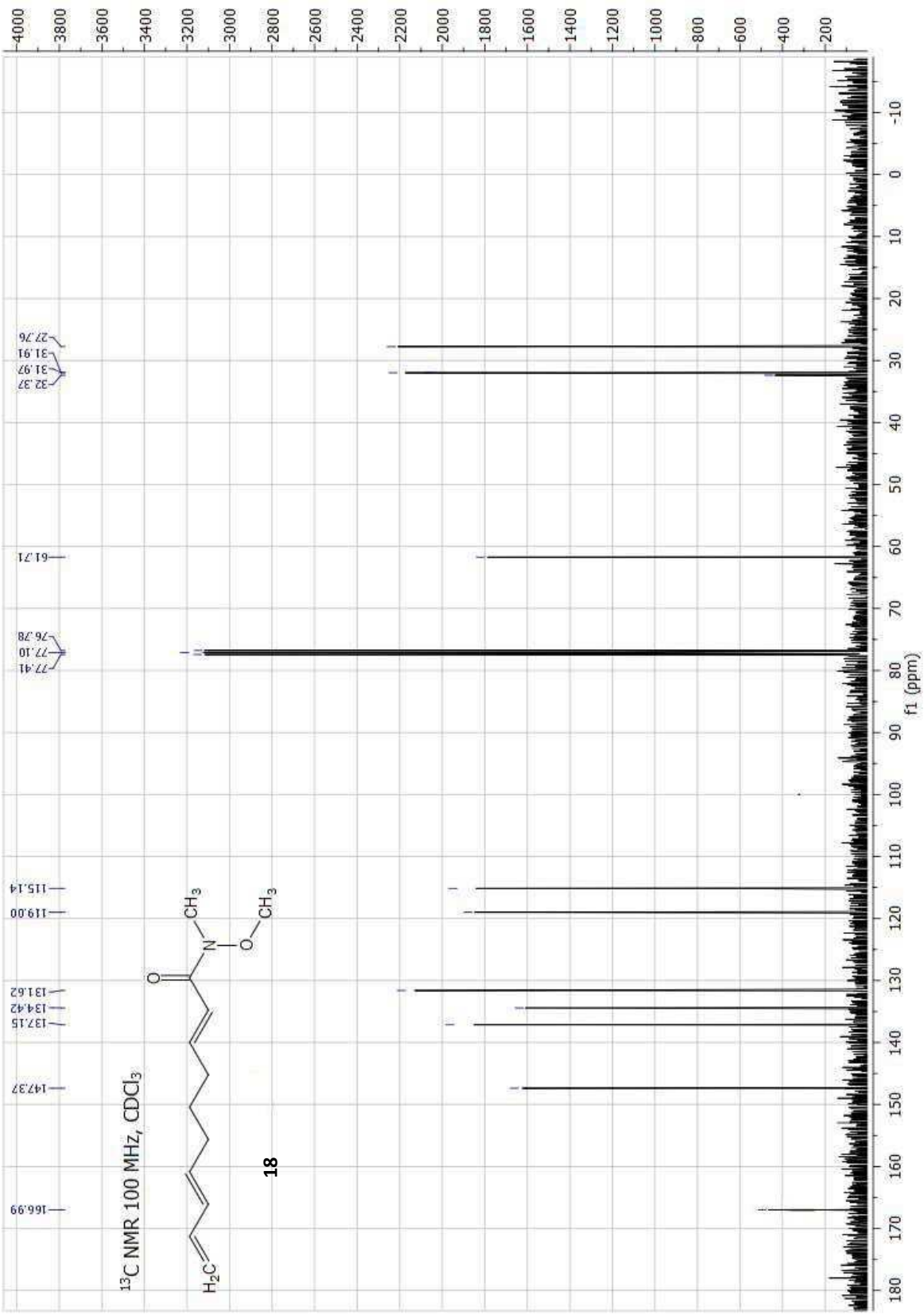

$^1$H NMR 400 MHz, $CDCl_3$
15
f1 (ppm)

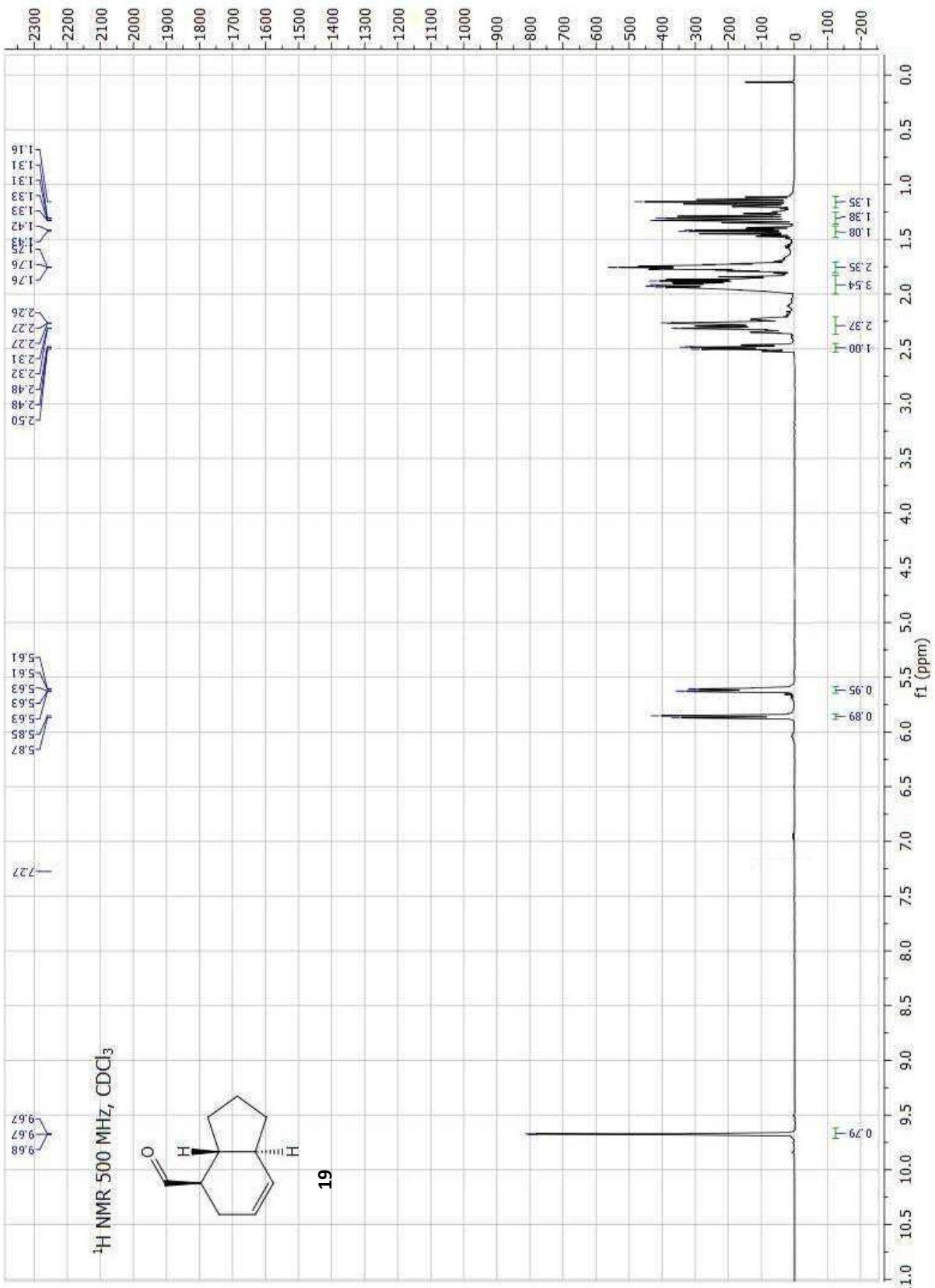

$^{13}$C NMR 100 MHz, $CDCl_3$
15
f1 (ppm)

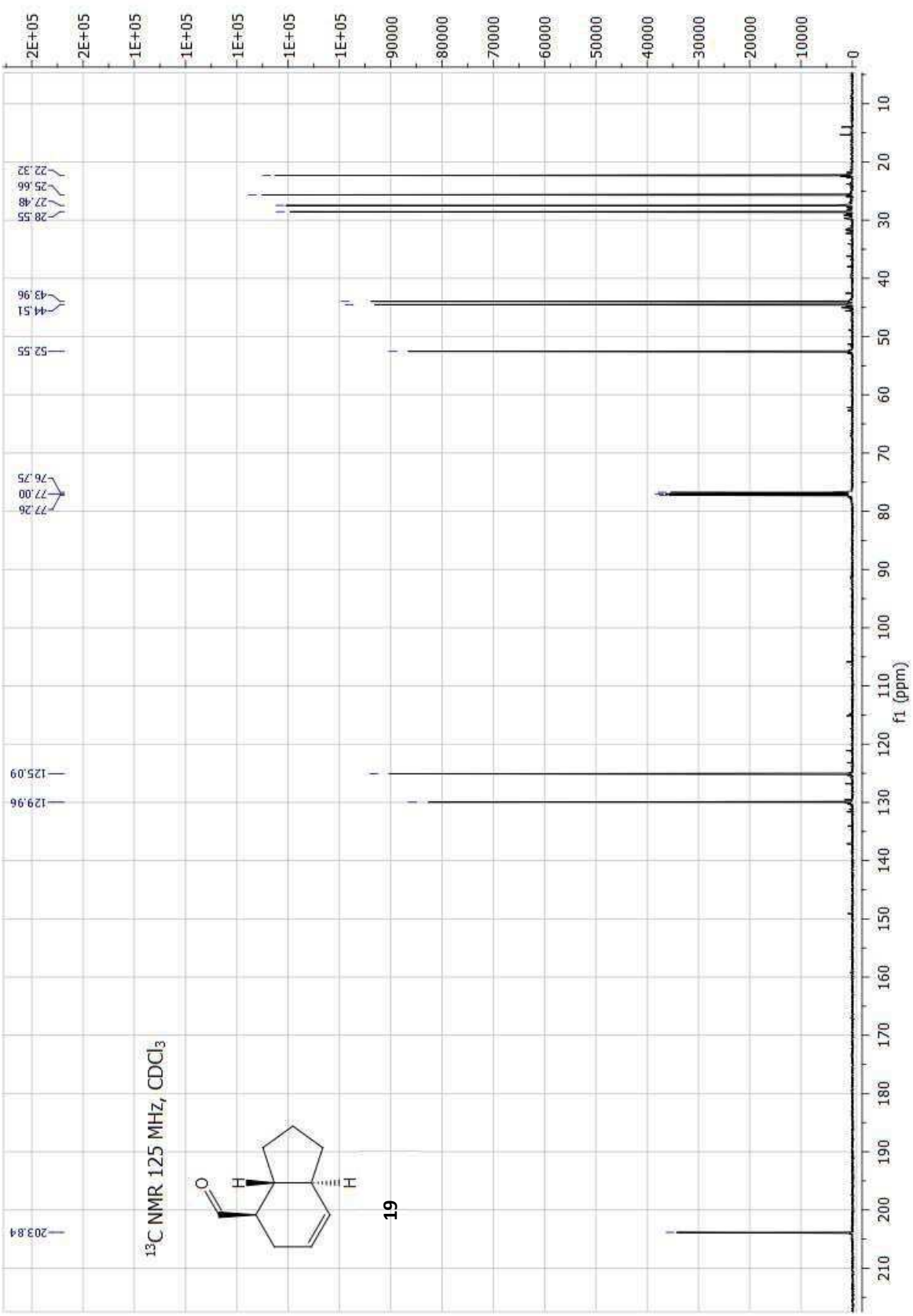

7.27
6.07
6.04
6.02
6.02
6.01
6.00
5.99
5.98
5.96
5.96
5.63
5.62
5.33
5.33
5.31
5.30
4.50
4.49
3.71
2.63
2.62
2.06
1.74
1.72
$^1$H NMR 400 MHz, $CDCl_3$
$H_3C$
O
O
O
$CH_3$
O
$H_3C$
O
O
$CH_3$
17
2.05
2.99
1.00
0.05
0.25
1.82
6.19
4.03
3.12
3.15
f1 (ppm)

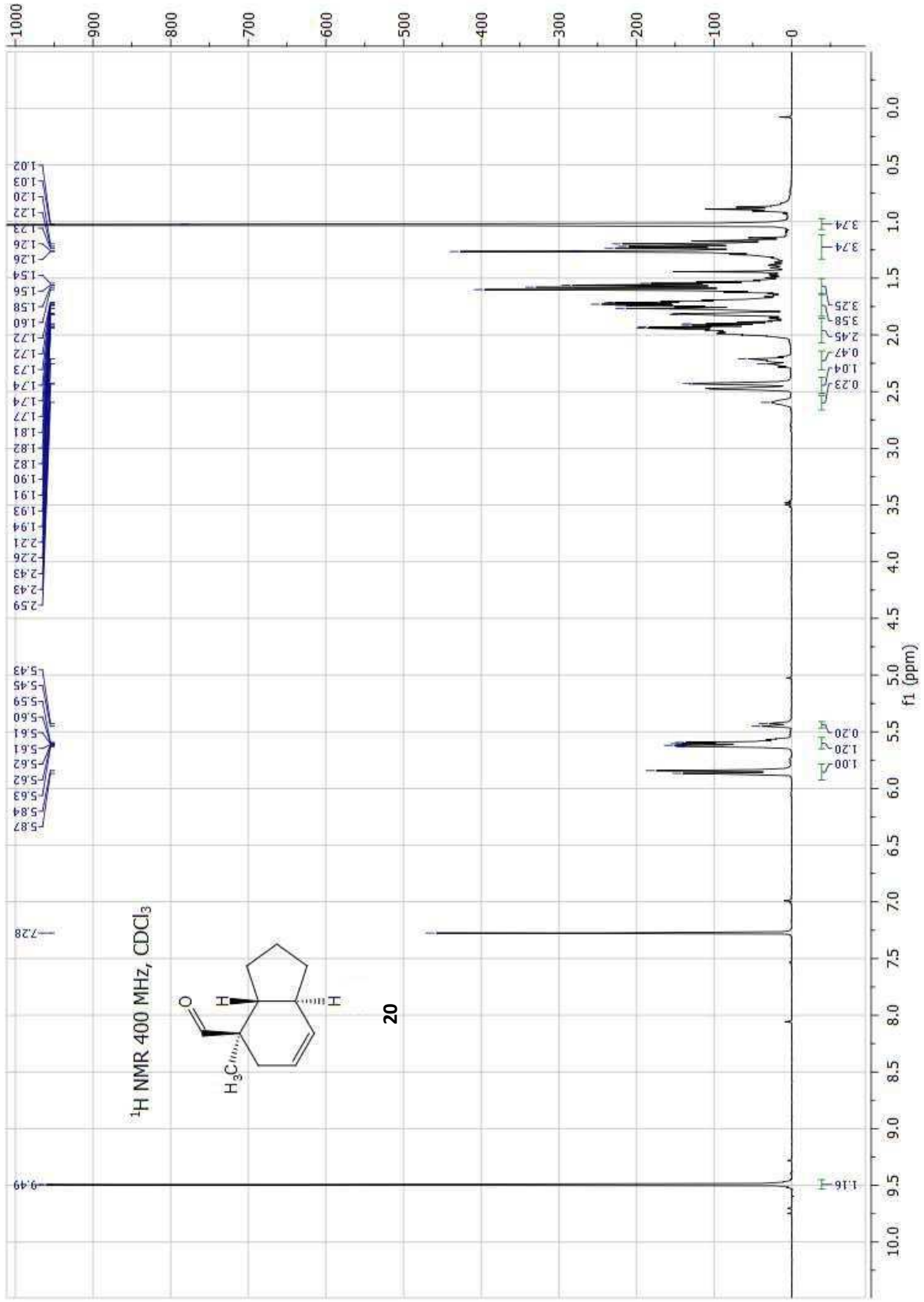

$^{13}$C NMR 100 MHz, $CDCl_3$
170.73
171.12
134.84
131.08
129.46
128.97
128.58
123.89
77.40
77.09
76.77
64.61
57.90
52.47
36.03
35.58
20.98
18.07
f1 (ppm)
17

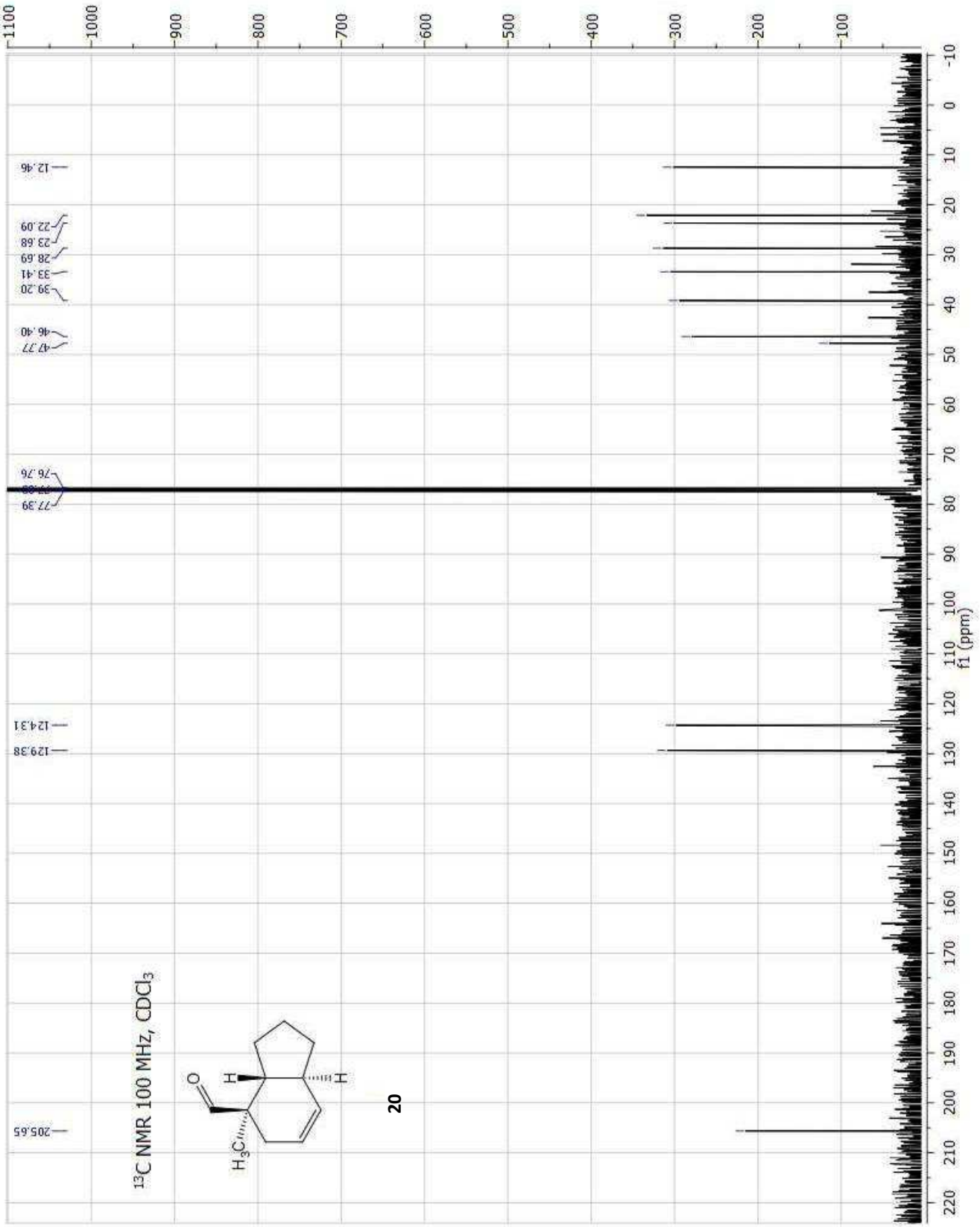

1H NMR 400 MHz, CDCl3
18
f1 (ppm)


$^{13}$C NMR 100 MHz, $CDCl_3$
18
f1 (ppm)

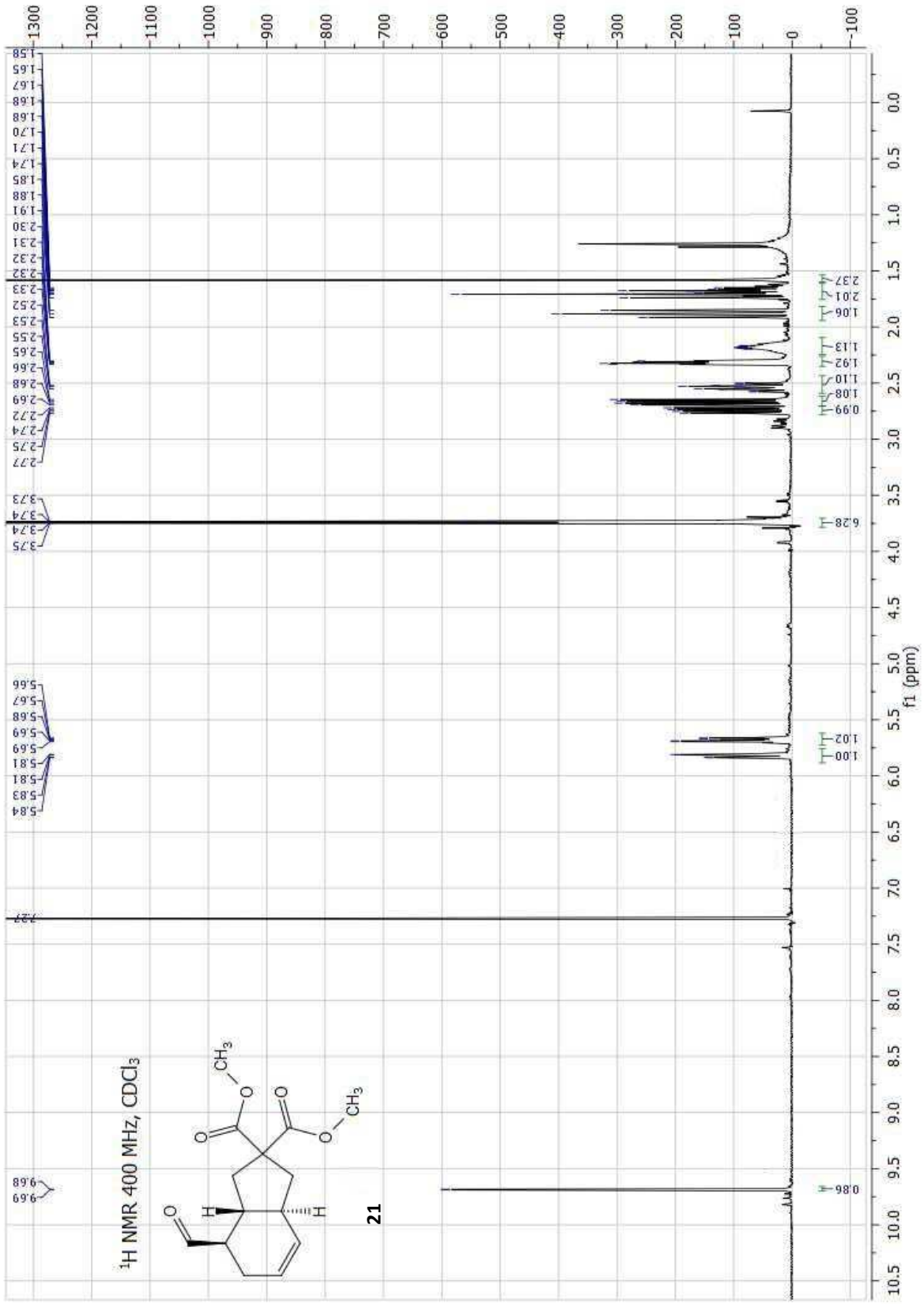

$^1$H NMR 500 MHz, $CDCl_3$
19
f1 (ppm)

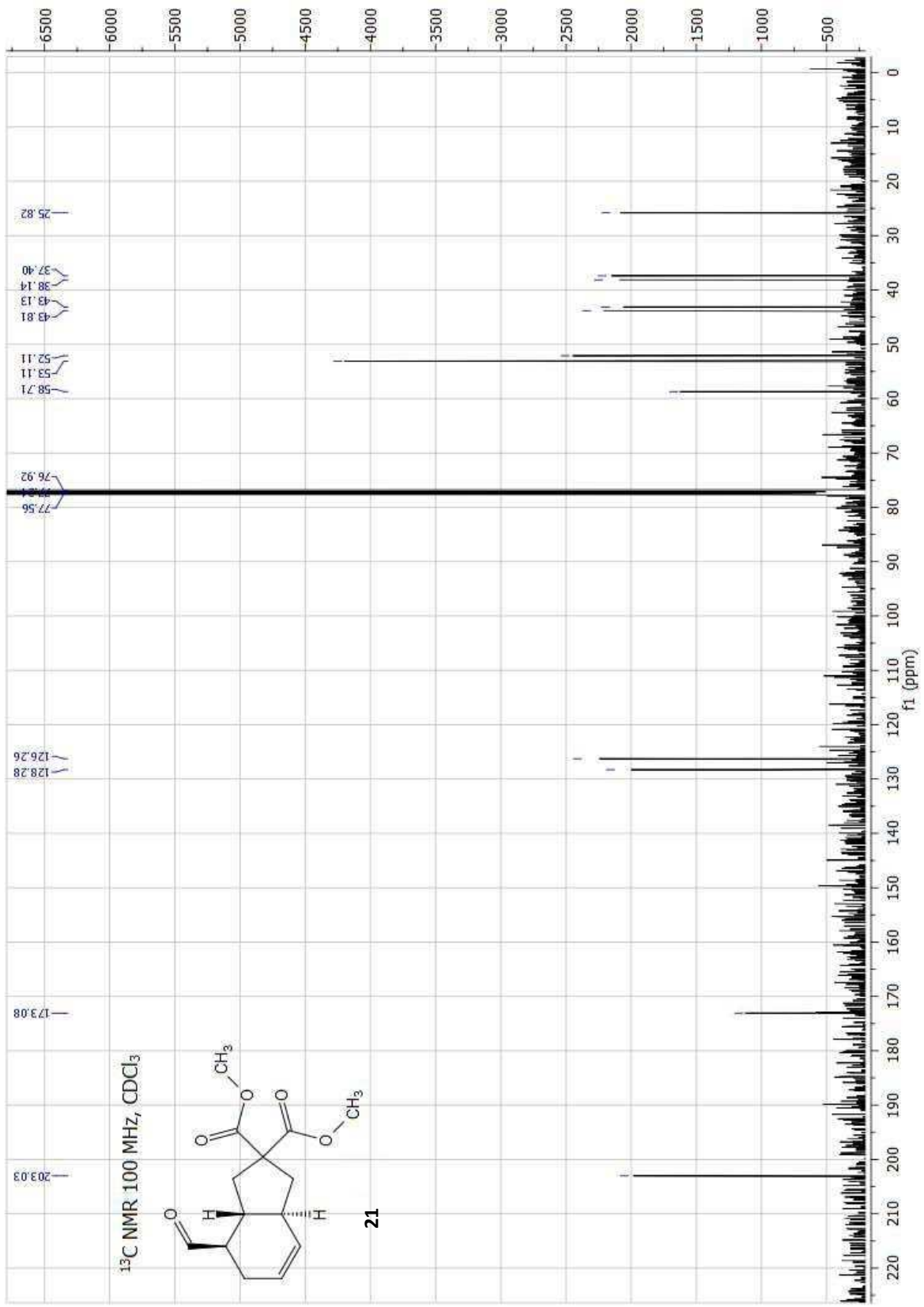

$^{13}$C NMR 125 MHz, $CDCl_3$
19
f1 (ppm)
203.84
129.96
125.09
77.26
77.00
76.75
52.55
44.51
43.96
28.55
27.48
25.66
22.32

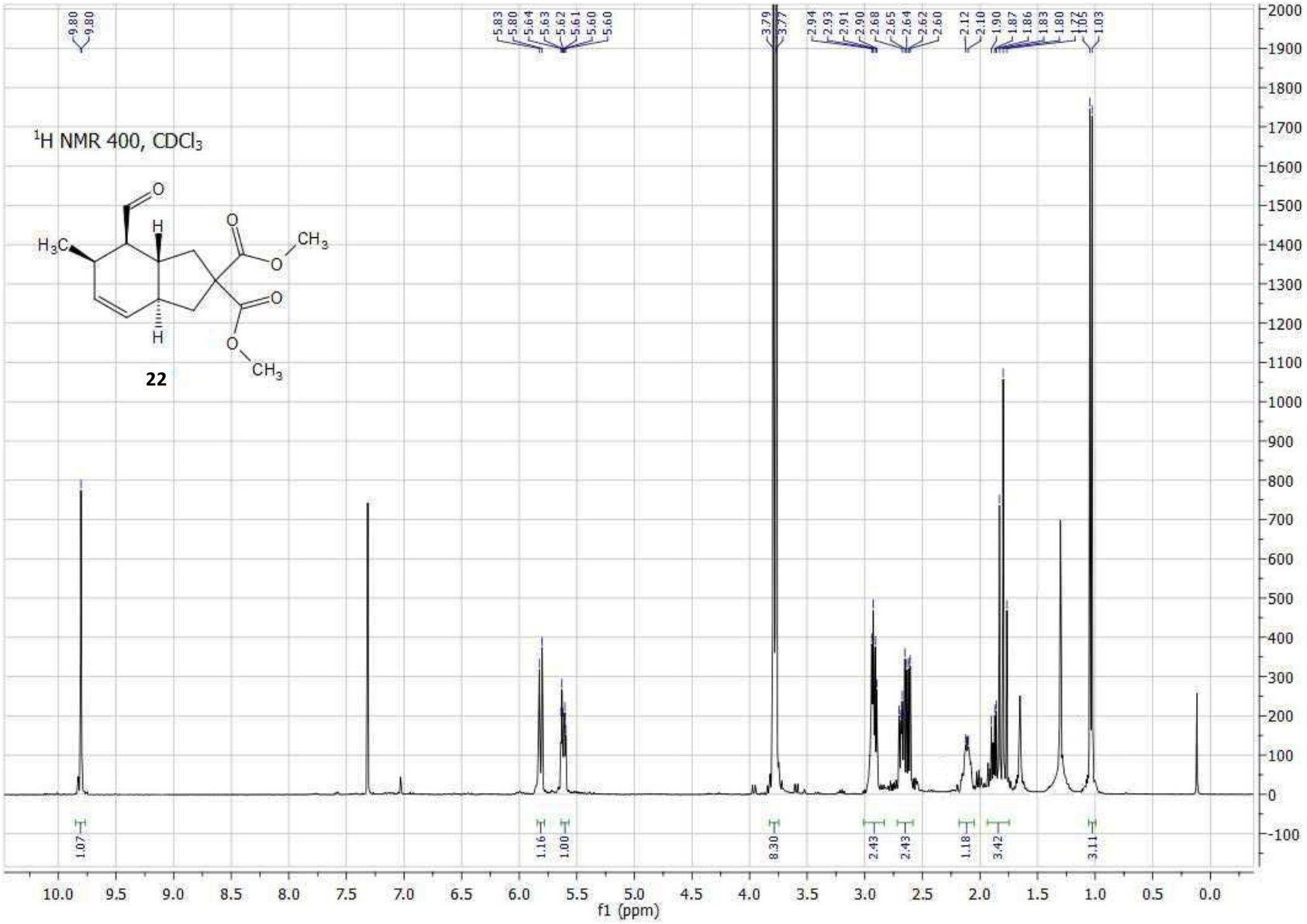

$^1$H NMR 400 MHz, $CDCl_3$
20
f1 (ppm)

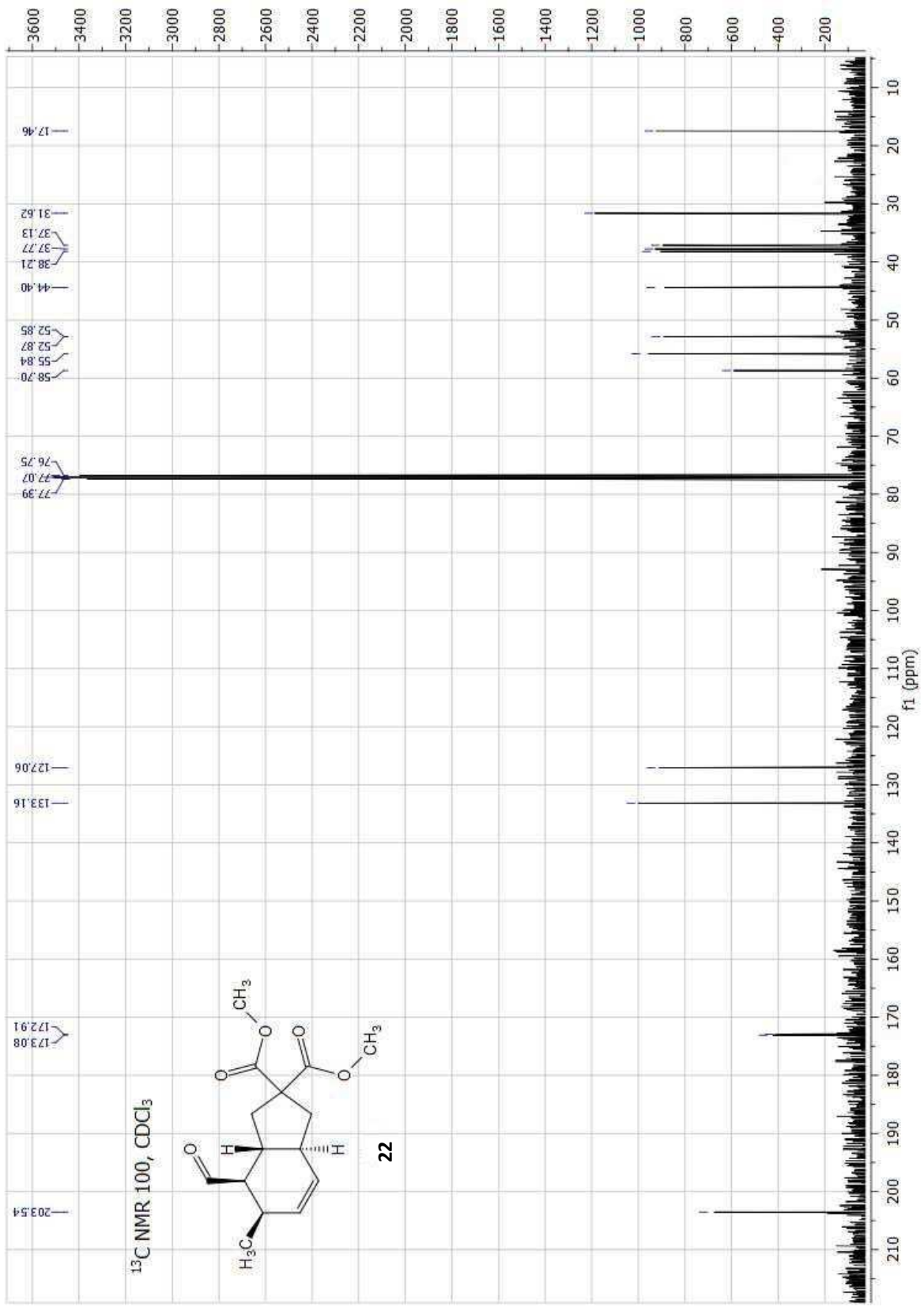

205.65
129.38
124.31
77.39
76.76
47.77
46.40
39.20
33.41
28.69
23.68
22.09
12.46
$^{13}$C NMR 100 MHz, $CDCl_3$
O
H
H
$H_3C$
f1 (ppm)

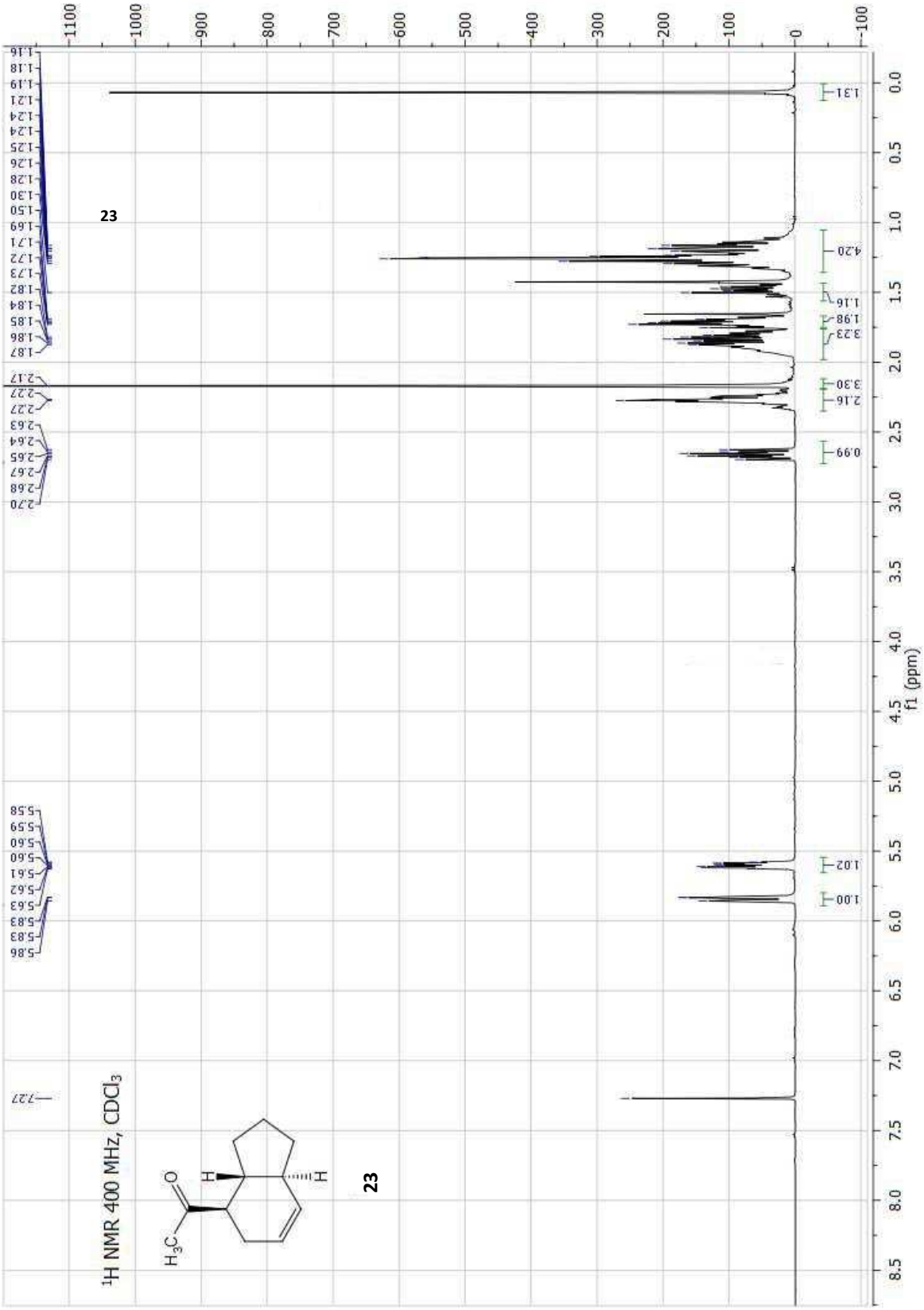
**20**

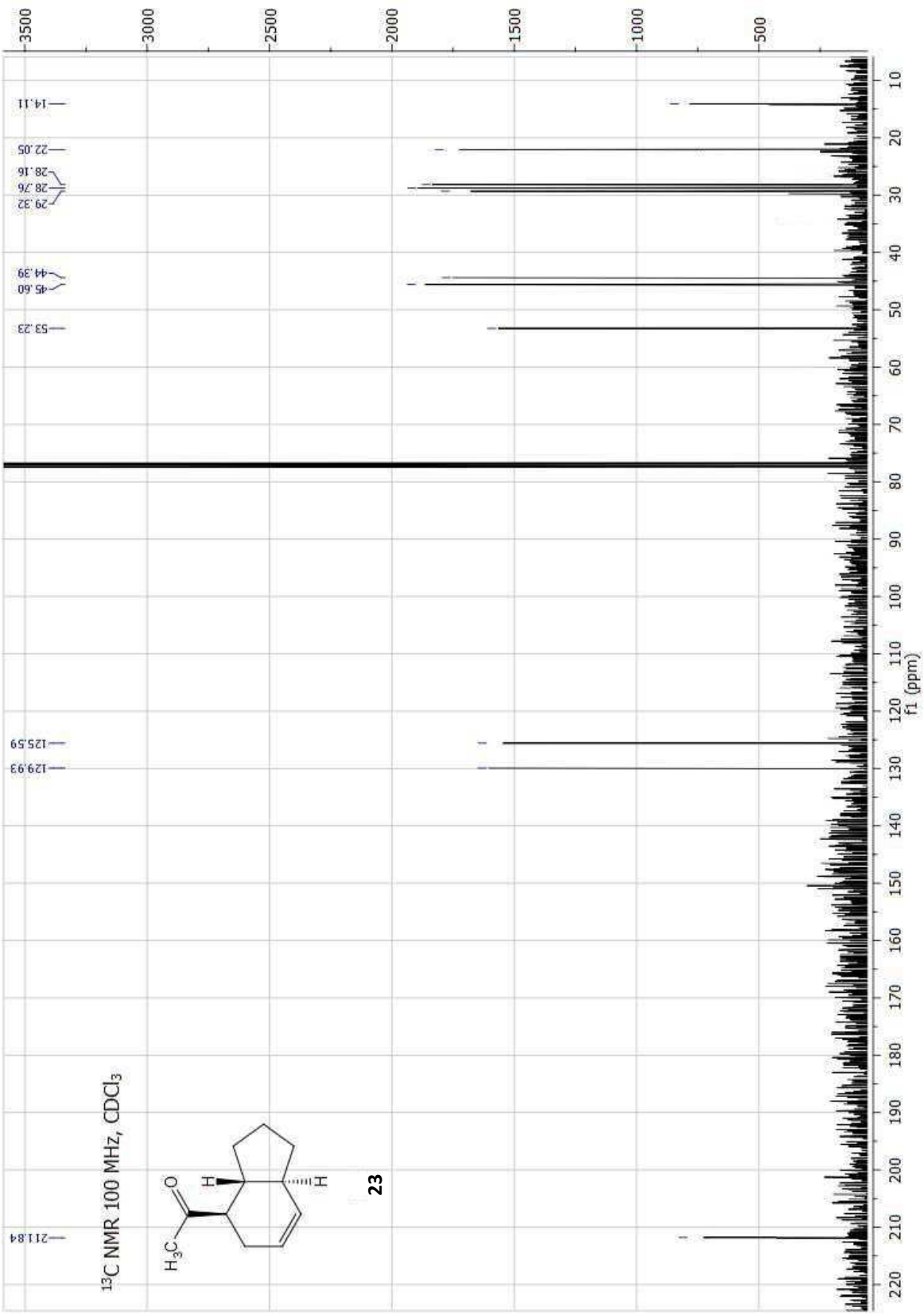

$^1$H NMR 400 MHz, $CDCl_3$
21
f1 (ppm)

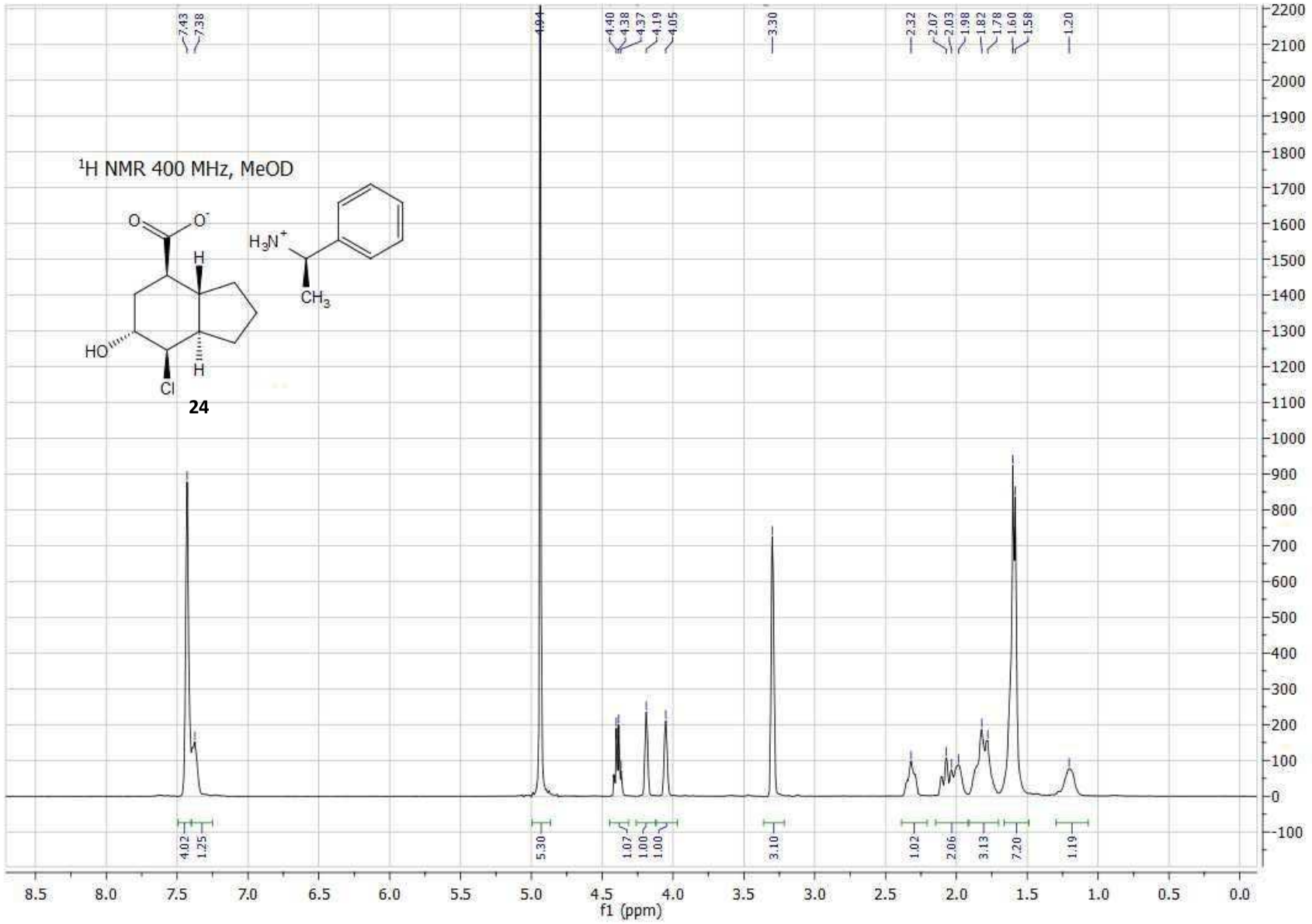

$^{13}$C NMR 100 MHz, $CDCl_3$
203.03
173.08
128.28
126.26
77.56
76.92
58.71
53.11
52.11
43.81
43.13
38.14
37.40
25.82
f1 (ppm)
21

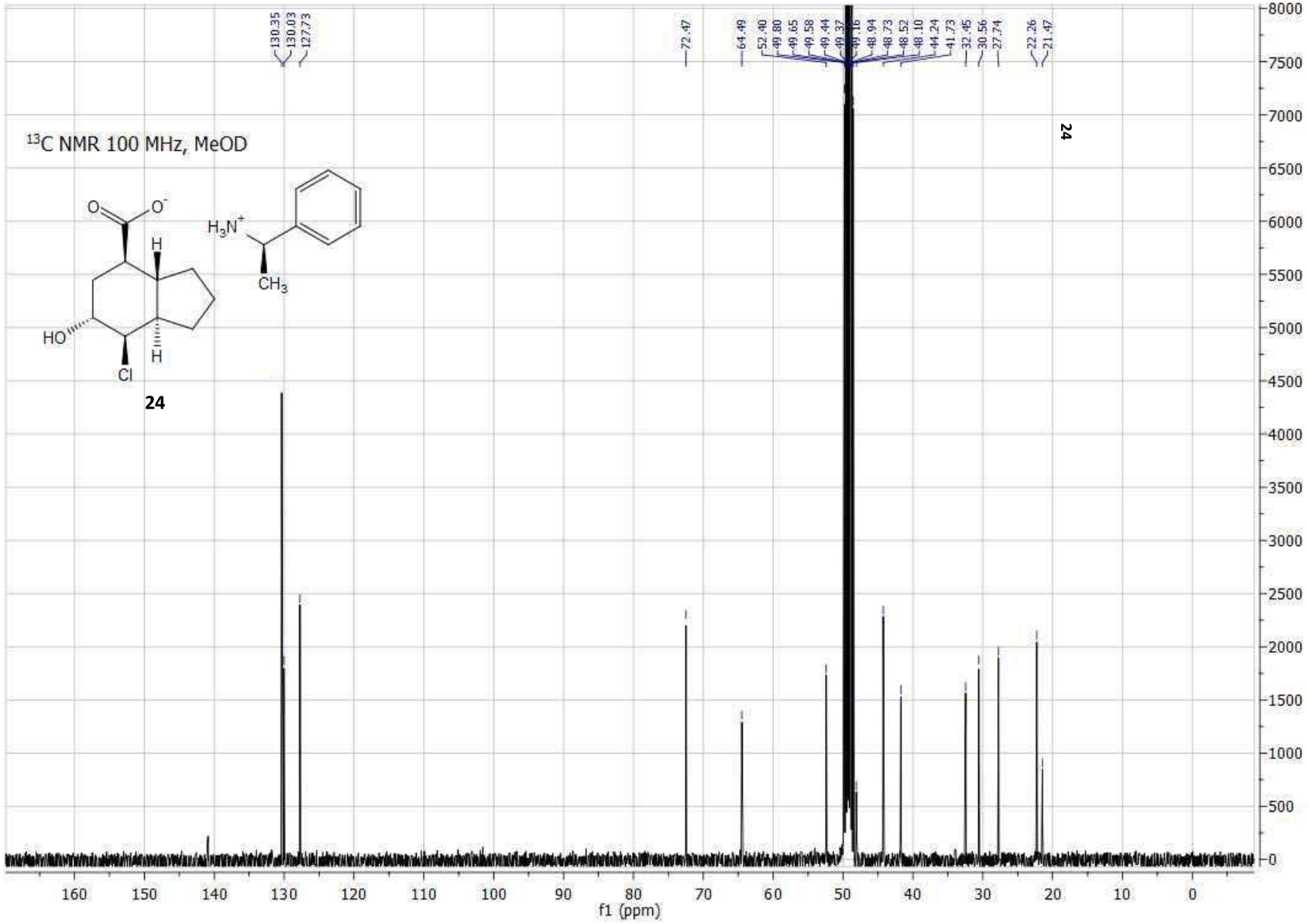

$^1$H NMR 400, CDCl$_3$
22
f1 (ppm)

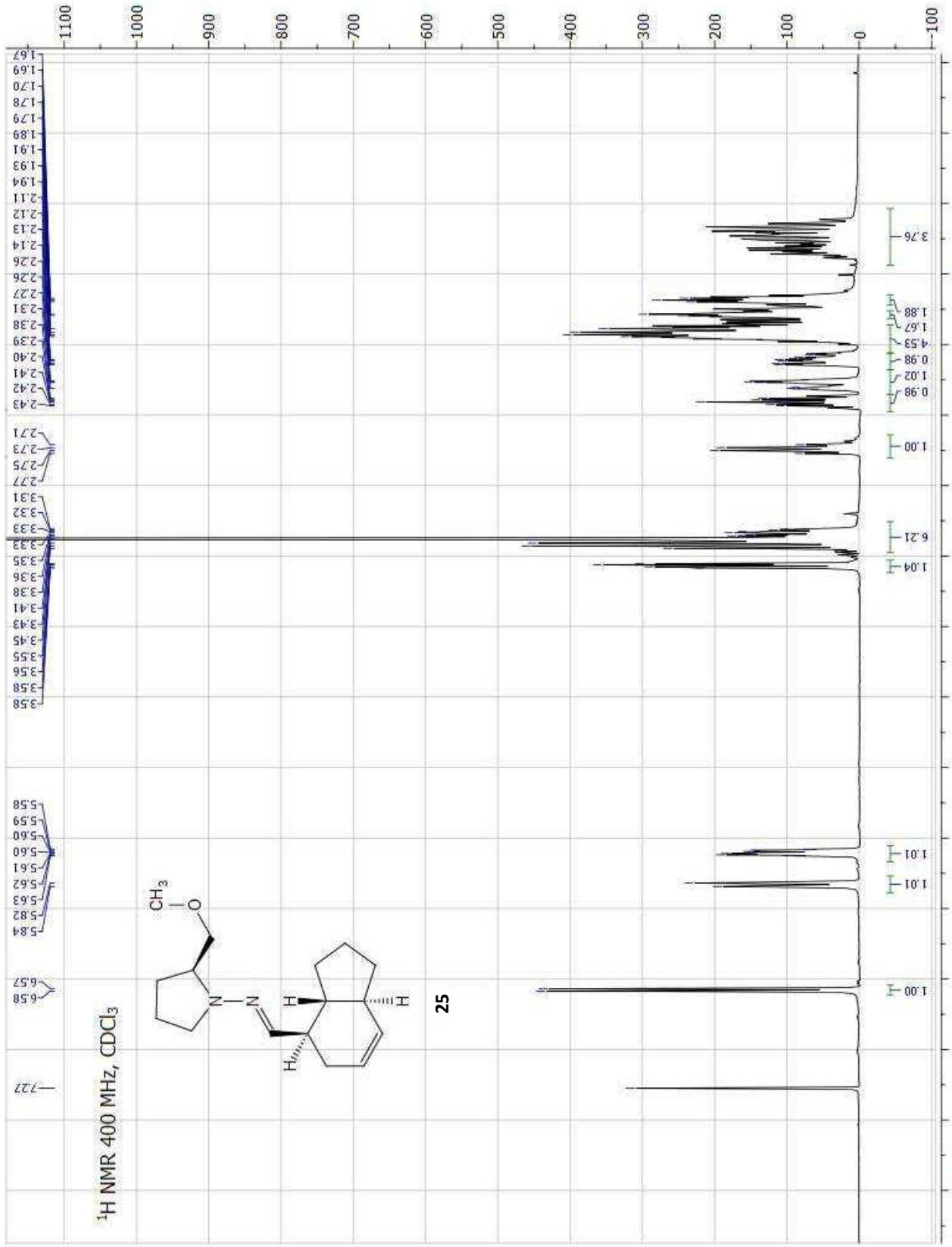

$^{13}$C NMR 100, $CDCl_3$
22
f1 (ppm)

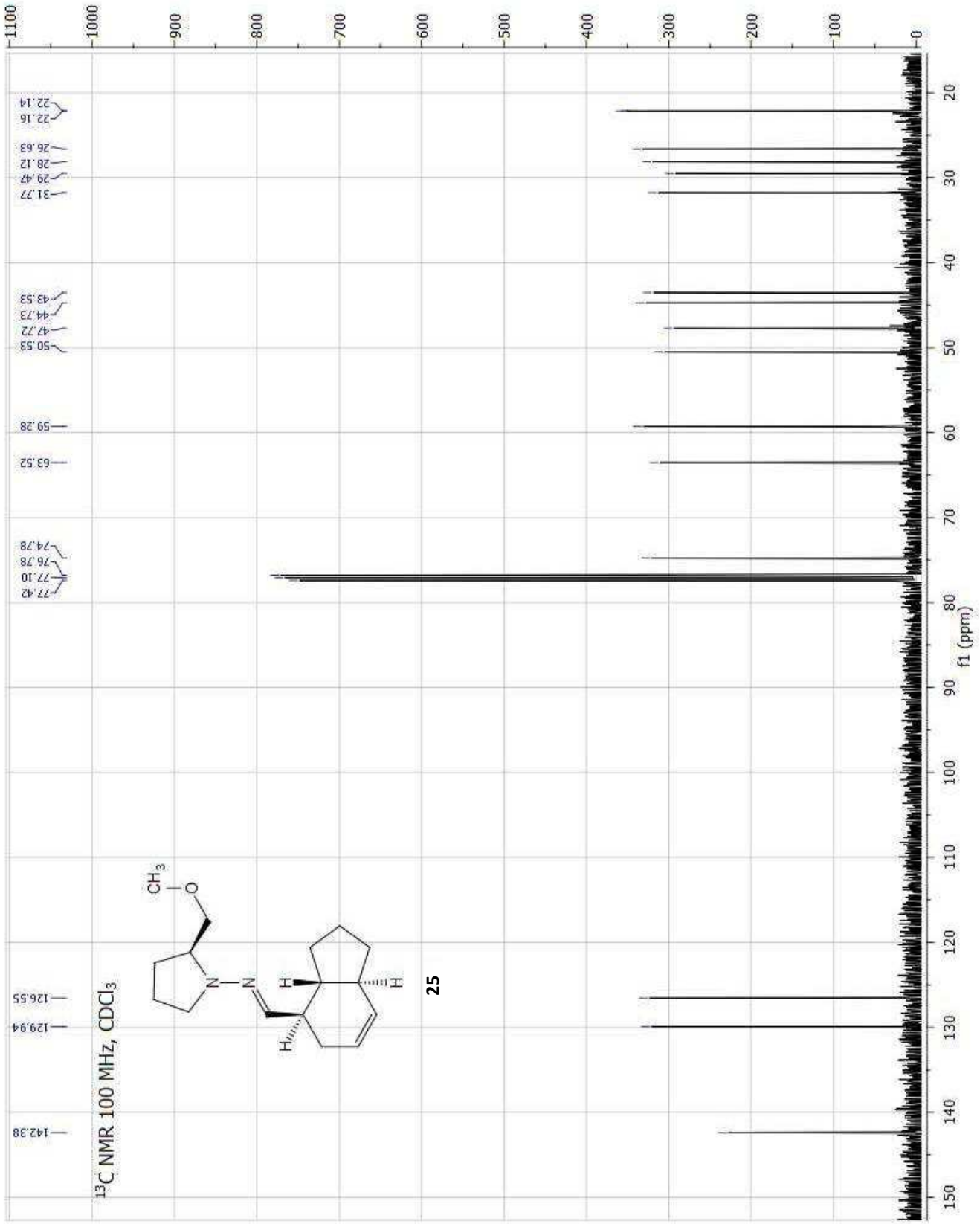

23
23
$^1$H NMR 400 MHz, $CDCl_3$
f1 (ppm)

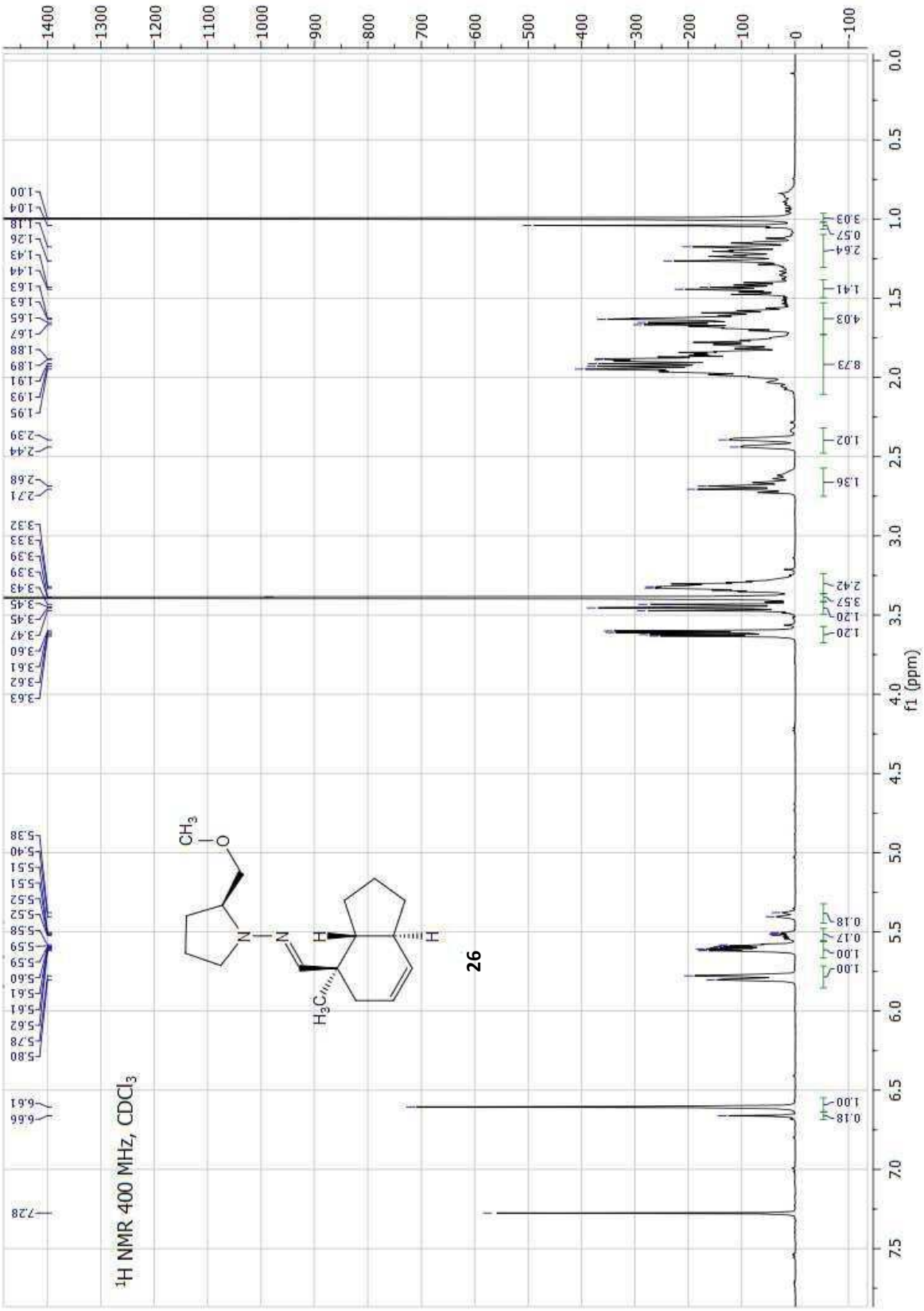

$^{13}$C NMR 100 MHz, $CDCl_3$
23
211.84
129.93
125.59
53.23
45.60
44.39
29.32
28.76
28.16
22.05
14.11
f1 (ppm)

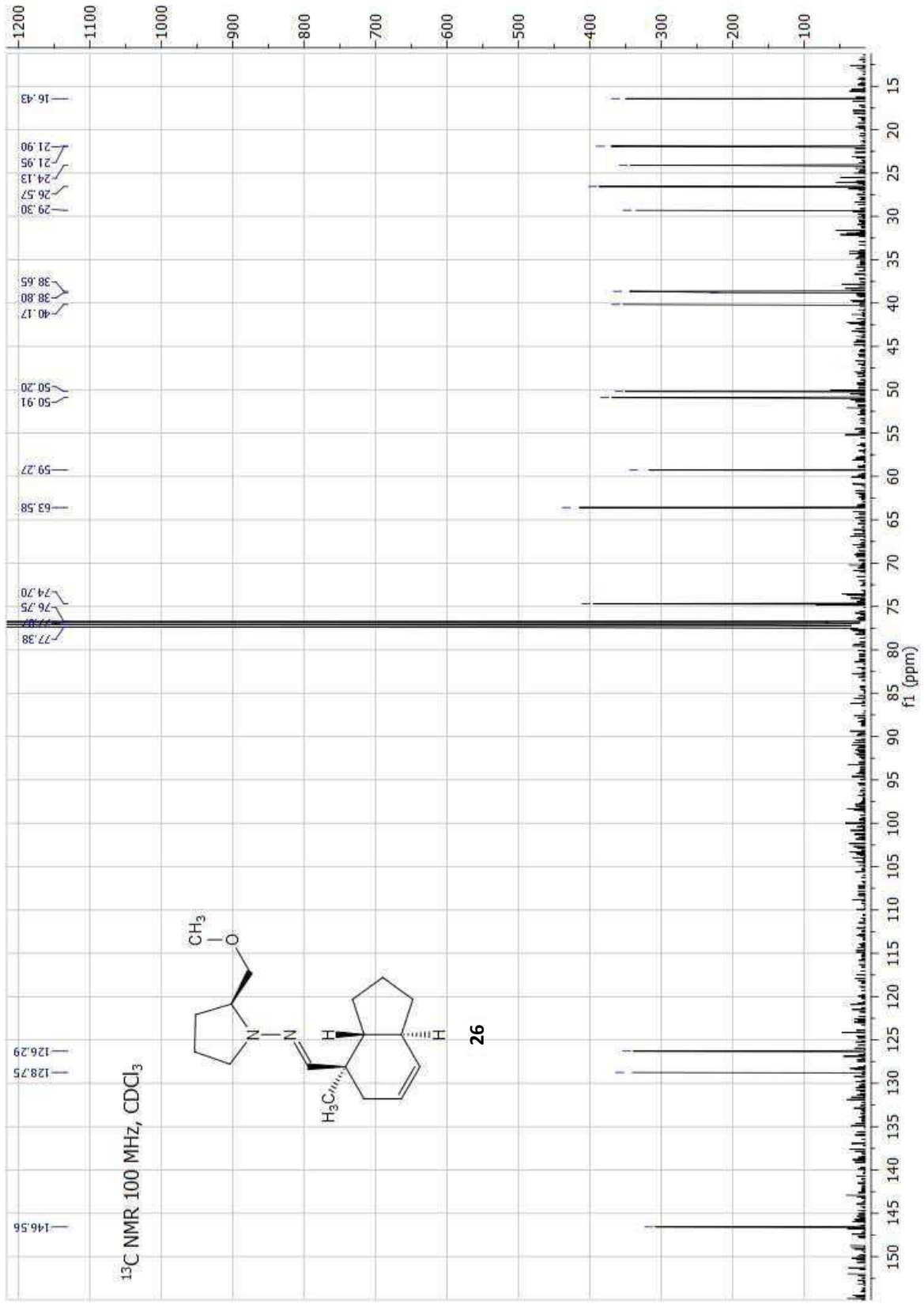

$^1$H NMR 400 MHz, MeOD
O
O
H
HO
H
Cl
$H_3N^+$
$CH_3$
24
7.43
7.38
4.94
4.40
4.38
4.37
4.19
4.05
3.30
2.32
2.07
2.03
1.98
1.82
1.78
1.60
1.58
1.20
4.02
1.25
5.30
1.07
1.00
1.00
3.10
1.02
2.06
3.13
7.20
1.19
f1 (ppm)

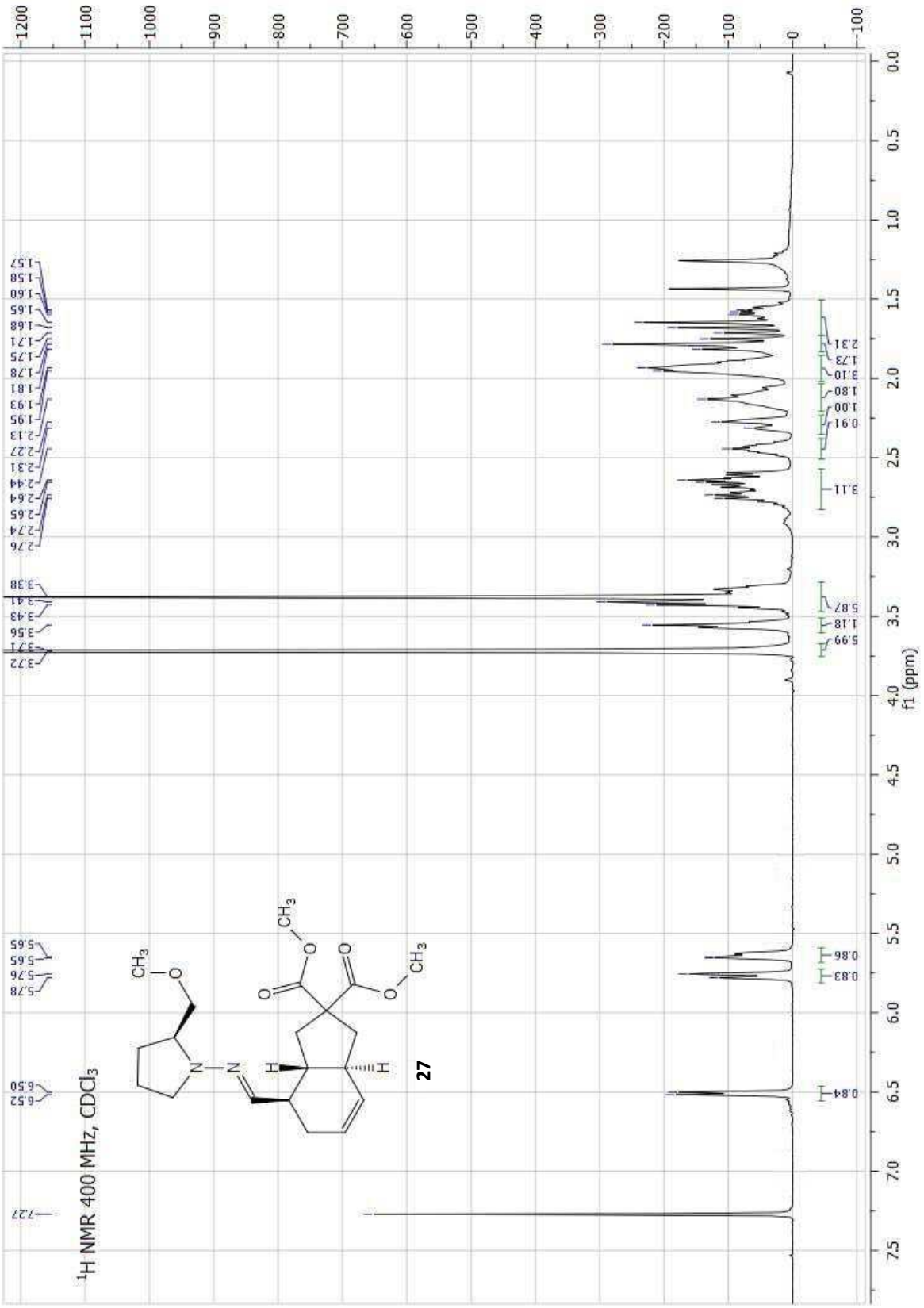

$^{13}$C NMR 100 MHz, MeOD
24
24
130.35
130.03
127.73
72.47
64.49
52.40
49.80
49.65
49.58
49.44
49.37
49.16
48.94
48.73
48.52
48.10
44.24
41.73
32.45
30.56
27.74
22.26
21.47
f1 (ppm)

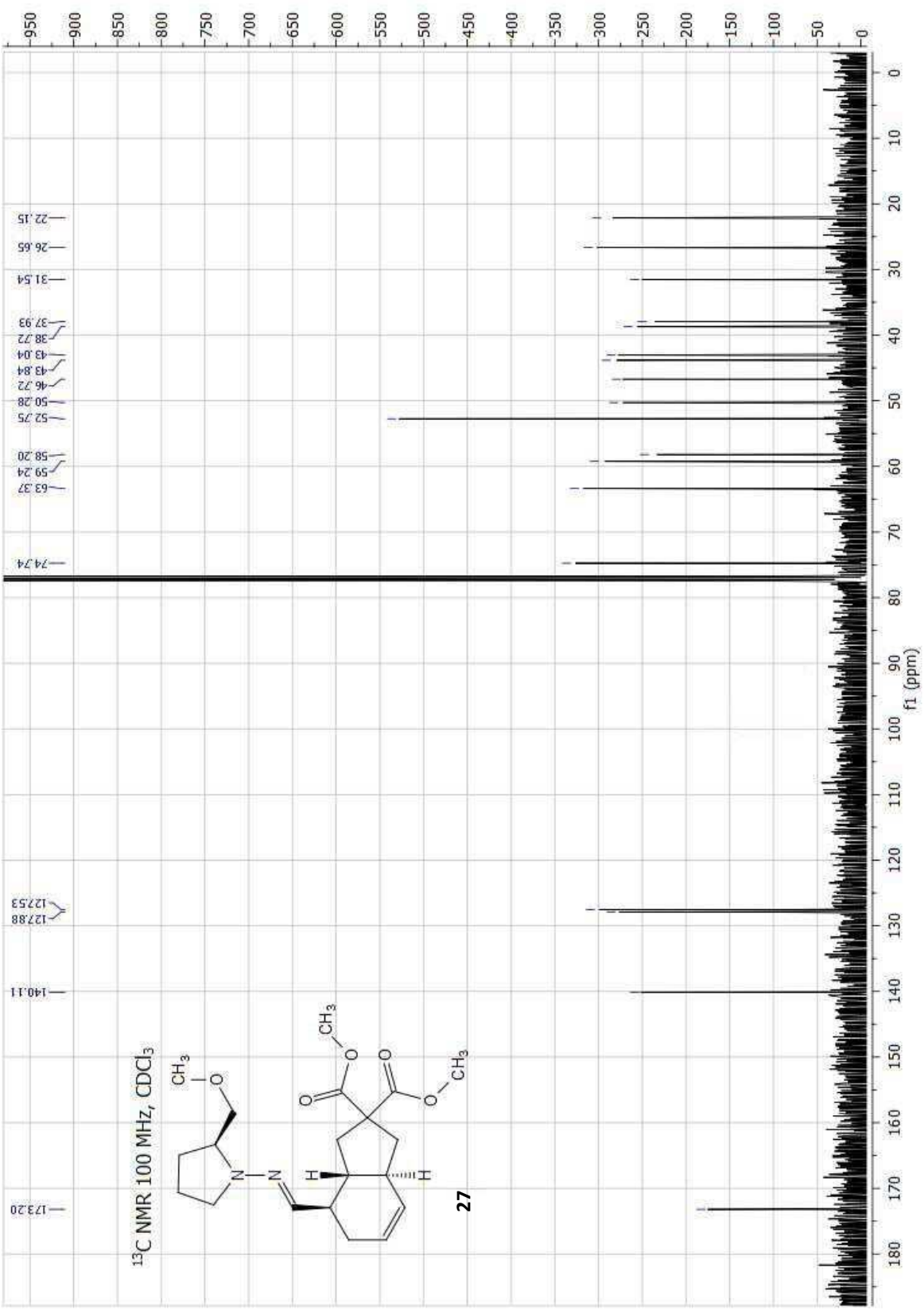

$^1$H NMR 400 MHz, $CDCl_3$
f1 (ppm)
25

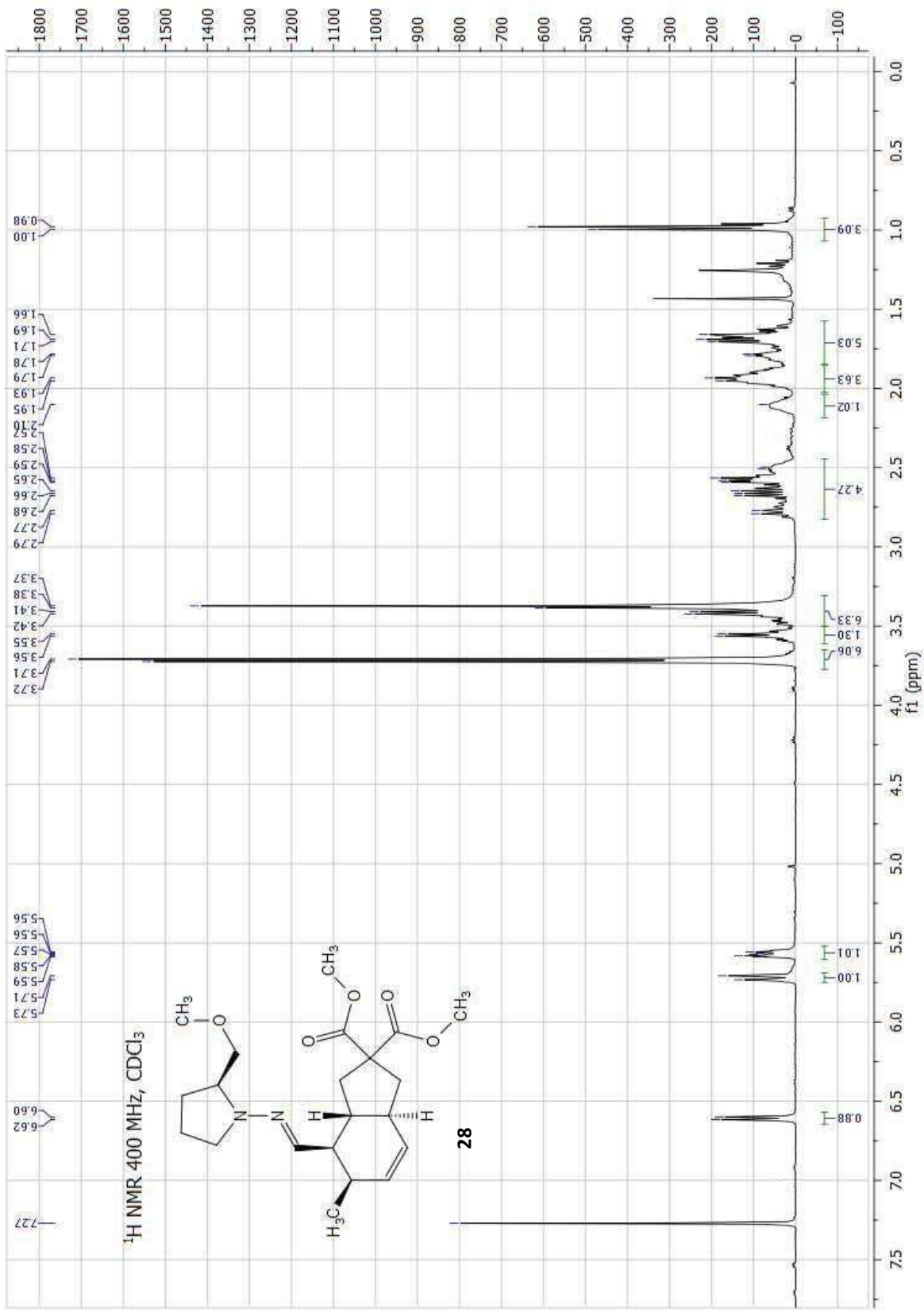

$^{13}$C NMR 100 MHz, $CDCl_3$
142.38
129.94
126.55
77.42
77.10
76.78
74.78
63.52
59.28
50.53
47.72
44.73
43.53
31.77
29.47
28.12
26.63
22.16
22.14
f1 (ppm)
25

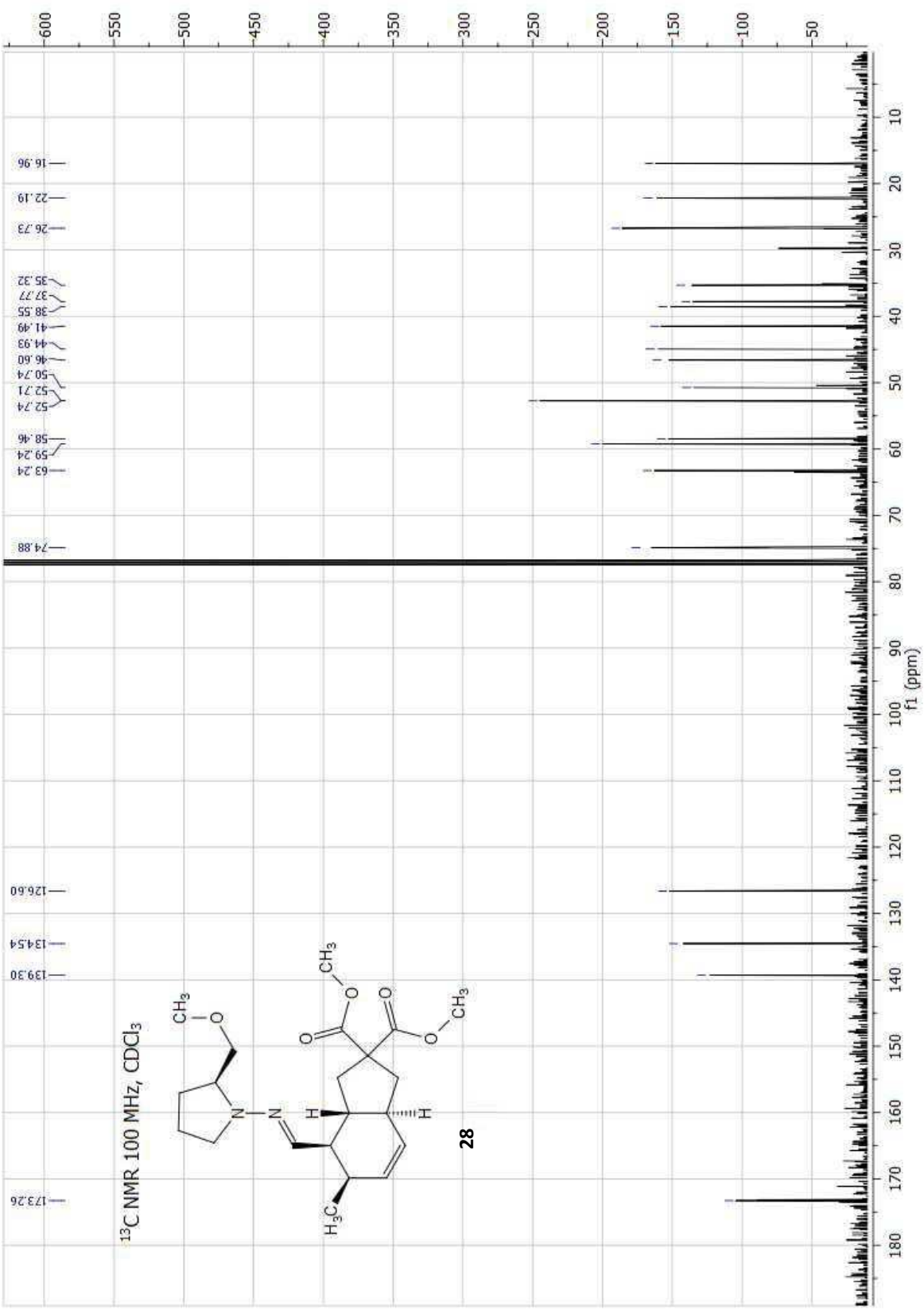

$^1$H NMR 400 MHz, $CDCl_3$
f1 (ppm)
26

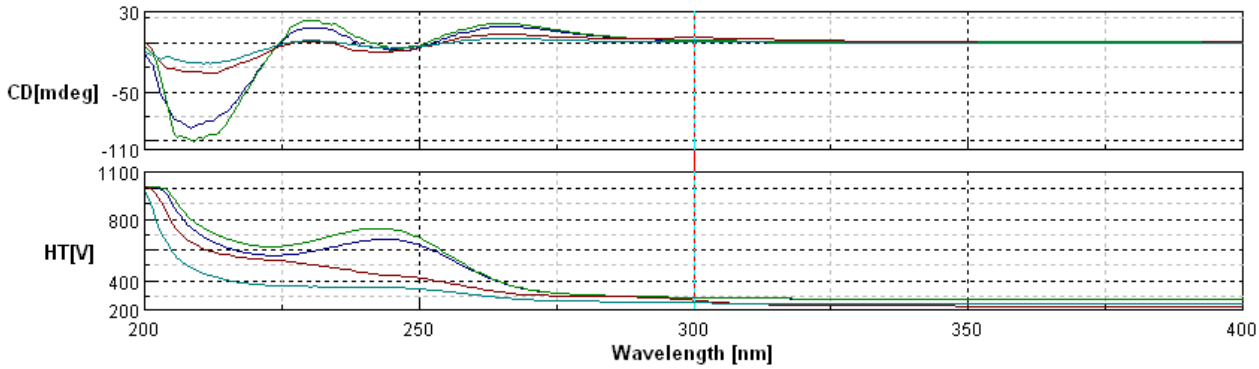

$^{13}$C NMR 100 MHz, $CDCl_3$
16.43
21.90
21.95
24.13
26.57
29.30
38.65
38.80
40.17
50.20
50.91
59.27
63.58
74.70
76.75
77.38
126.29
128.75
146.56
f1 (ppm)
26


$^1$H NMR 400 MHz, $CDCl_3$
f1 (ppm)
27


$^{13}$C NMR 100 MHz, $CDCl_3$
22.15
26.65
31.54
37.93
38.72
43.04
43.84
46.72
50.28
52.75
58.20
59.24
63.37
74.74
127.53
127.88
140.11
173.20
f1 (ppm)
27


$^1$H NMR 400 MHz, CDCl$_3$
28
f1 (ppm)


$^{13}$C NMR 100 MHz, $CDCl_3$
28
f1 (ppm)




**25** 0.00023 M in pentanes

**26** 0.00025 M in pentanes

**27** 0.00024 M in pentanes

**28** 0.00025 M in pentanes