Remote C-H Insertion of Vinyl Cations Leading to Cyclopentenones

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I) General Experimental Details

All reactions were performed under an atmosphere of nitrogen in flame-dried glassware. Solvents were removed in vacuo using a rotary evaporator attached to a dry vacuum pump, and further dried under reduced pressure on a high vacuum line. The cyclopentenone products were somewhat volatile and care was taken not to subject these compounds to high vacuum during concentration (vacuum pressures did not exceed 125 torr).

Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were dried via a solvent dispensing system. Diisopropylamine (iPr$_2$NH) was freshly distilled from CaH_2 prior to use. Tin(IV) chloride ($SnCl_4$) was distilled twice from P_2O_5 under inert atmosphere conditions and was stored in sealed tubes under an atmosphere of nitrogen as a 1M solution in CH_2Cl_2. All other commercially available reagents were used without further purification.

Flash column chromatography was performed on silica gel (230-400 mesh) as well as on a CombiFlash® R_f 150 system using RediSep® R_f Gold silica columns. TLC analysis was carried out using silica on glass plates. Visualization of TLC plates was achieved using ultraviolet light, ceric ammonium molybdate, or potassium permanganate.

^{1}H and ^{13}C NMR data was collected at room temperature on a 500 MHz spectrometer in $CDCl_3$. ^{1}H NMR chemical shifts are reported in ppm (δ units) downfield from tetramethylsilane, and ^{13}C NMR spectra are referenced to the CDCl signal at 77.0 ppm. IR data were collected on a Shimadzu IR Affinity-1 FTIR and the values are reported in wavenumbers. Exact mass analysis was performed on a Waters Xevo G2-XS QTof LCMS operated in positive ESI mode.

All α-diazo ketones used are known compounds that were prepared by reacting diazomethane with the corresponding acid chlorides in accordance with standard literature procedures : [*t*-butyl],[1] [*i*-propyl],[2] [*n*-propyl],[3] [*i*-butyl],[3] and [ethyl].[4]

II) Experimental Procedures and Compound Characterisation data

General Procedure A: Preparation of β-hydroxy-α-diazo ketones

A cold (–78 °C) solution of LDA (1.5 equiv) [prepared by addition of *n*-butyllithium in hexanes (1.5 equiv) to a solution of *i*Pr_2NH (1.7 equiv) in THF (3 mL per mmol of *n*-butyllithium)] was added dropwise over 30 min via cannula down the side of a chilled flask containing a cold (–78 °C) stirred solution of ketone (1 equiv) and α-diazo ketone (1.6 equiv) in THF (3 mL per mmol of ketone). The mixture was maintained at –78 °C until complete conversion was achieved as monitored by TLC. Saturated aqueous NH_4Cl solution (5 mL) was added quickly to the reaction mixture at –78 °C, the reaction flask was removed from the cold bath and an additional portion of saturated NH_4Cl (15 mL) was added. The mixture was extracted three times with EtOAc (15 mL), the organic layers were combined, washed with saturated aqueous $NaHCO_3$ (50 mL), brine (50 mL), and dried over anhydrous $CaCl_2$. The solvent was removed in vacuo to provide an oily residue that was subjected to flash silica gel chromatography to afford the desired β-hydroxy-α-diazo ketone.

1-Diazo-1-(1-hydroxycyclohexyl)-3,3-dimethylbutan-2-one (**1**): Prepared from cyclohexanone (75 μL, 0.73 mmol) and 1-diazo-3,3-dimethyl-2-butanone (147 mg, 1.17 mmol) following General Procedure A with the modification that 1M acetic acid in THF

(0.73 mL, 0.73 mmol) was used to quench the reaction in place of NH_4Cl. The oily yellow residue was purified by silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 10% EtOAc) to give 140 mg (86% yield) of the title compound as a yellow oil: R_f = 0.65 (hexanes/EtOAc 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.61 (s, 1H), 1.92 (dt, *J* = 12.8, 4.5 Hz, 2H), 1.76 (dtt, *J* = 14.2, 10.7, 3.7 Hz, 2H), 1.62-1.50 (m, 3H), 1.46 (ddt, *J* = 13.9, 9.1, 4.8 Hz, 2H), 1.37-1.24 (m, 1H), 1.22 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.0, 72.0, 68.3, 44.8, 36.0, 26.5, 25.4, 21.9; IR (film) 3449 (br), 2932, 2862, 2068, 1605, 1304, 1196. MS (ESI): Calculated for $[C_{12}H_{20}N_2O_2Na]^+$: 247.1422. Found: 247.1422.

1-Diazo-1-(1-hydroxycyclohexyl)-3-methylbutan-2-one (**3**): Prepared from cyclohexanone (130 μL, 1.3 mmol) and 1-diazo-3-methyl-2-butanone (248 mg, 2.21 mmol) following General Procedure A. The crude yellow oil material was purified using silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 10% EtOAc) to give 242 mg (88% yield) of the title compound as a yellow oil which solidified upon standing in freezer: R_f = 0.50 (3.7:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) 4.36 (s, 1H), 2.81 (hept, *J* = 6.8 Hz, 1H), 1.96-1.88 (m, 2H), 1.81 – 1.71 (m, 2H), 1.63 – 1.56 (m, 3H), 1.49 – 1.40 (m, 2H), 1.35-1.24 (m, 1H), 1.13 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 201.0, 71.1, 71.0, 36.4, 36.2, 25.3, 21.8, 18.5; IR (film) 3397 (br), 2934, 2860, 2070, 1620, 1248. MS (ESI): Calculated for $[C_{11}H_{18}N_2O_2Na]^+$: 233.1266. Found: 233.1263.

1-Diazo-1-(1-hydroxy-4,4-dimethylcyclohexyl)-3,3-dimethylbutan-2-one (**10**): Prepared from 4,4-dimethylcyclohexanone (125 mg, 0.99 mmol) and 1-diazo-3,3-dimethyl-2-butanone (204 mg, 1.62 mmol) following General Procedure A. The oily yellow residue was purified by silica gel flash column chromatography (12:1 hexanes/EtOAc) to give 217 mg (86% yield) of the title compound as a yellow oil which solidified upon standing in freezer: R_f = 0.64 (hexanes/EtOAc 3.7:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.50 (s, 1H), 1.93-1.85 (m, 2H), 1.71-1.59 (m, 4H), 1.22 (s, 9H), 1.21-1.15 (m, 2H), 0.95 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.7, 71.4, 68.2, 44.6, 34.4, 31.9, 30.7, 29.2, 26.4, 25.2; IR (film) 3439, 2953, 2928, 2068, 1599, 1306, 1200. MS (ESI): Calculated for $[C_{14}H_{24}N_2O_2Na]^+$: 275.1735. Found: 275.1737.

1-(4-(*tert*-Butyl)-1-hydroxycylcohexyl)-1-diazo-3,3-dimethylbutan-2-one (**12**): Prepared from 4-*tert*-butylcylochexanone (119 mg, 0.77 mmol) and 1-diazo-3,3-dimethyl-2-butanone (156 mg, 1.24 mmol) following General Procedure A with the modification that 0.2M acetic acid in THF (6.5 mL, 1.3 mmol) was used to quench the reaction in place of NH_4Cl. The crude solid was purified by silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 15% EtOAc) to give 115 mg (53% yield) of the pure major diastereomer as a yellow solid: R_f = 0.55 (hexanes/EtOAc 8:1); 1H NMR (500 MHz, $CDCl_3$): δ 4.56 (s, 1H), 2.09 (dp, J = 12.8, 4.3 Hz, 2H), 1.54-1.60(m, 2H), 1.52 (dq, J = 12.8, 3.3 Hz), 1.34 (td, J = 13.1, 4.3 Hz, 2 H), 1.19 (s, 9H), 0.97 (tt, J = 11.6, 3.5 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.8, 70.9, 68.6, 47.7, 44.7, 36.3, 32.4, 27.6, 26.5, 22.2; IR (film) 3503 (b), 2955, 2870, 2068, 1620, 1296. MS (ESI): Calculated for $[C_{16}H_{28}N_2O_2Na]^+$: 303.2048. Found: 303.2043.

1-Diazo-1-(1-hydroxycyclohexyl)butan-2-one (**14**): Prepared from cyclohexanone (170 μL, 1.6 mmol) and 1-diazo-2-butanone (275 mg, 2.80 mmol) following General Procedure A. The crude yellow oil was purified using silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 15% EtOAc) to give 284 mg (90% yield) of the title compound as a yellow oil: R_f = 0.26 (6:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.28 (s, 1H), 2.50 (q, J = 7.4 Hz, 2H), 1.97 – 1.90 (m, 2H), 1.81 – 1.70 (m, 2H), 1.63 – 1.54 (m, 3H), 1.50 – 1.42 (m, 2H), 1.35-1.24 (m, 1H), 1.14 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 197.3, 72.2, 70.9, 36.2, 32.0, 25.3, 21.8, 8.3; IR (film) 3441, 2931, 2854, 2067, 1626 cm^{-1}. MS (ESI): Calculated for $[C_{10}H_{16}N_2O_2Na]^+$: 219.1109. Found: 219.1119.

1-Diazo-1-(1-hydroxycyclohexyl)pentan-2-one (**16**): Prepard from cyclohexanone (170 μL, 1.7 mmol) and 1-diazo-2-pentanone (307 mg, 2.74 mmol) following General Procedure A. The crude yellow oil was purified using silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 10% EtOAc) to give 314 mg (88% yield) of the title compound as a yellow oil which solidified upon standing in freezer: R_f = 0.29 (6:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.33 (s, 1H), 2.44 (t, J = 7.4 Hz, 2H), 1.96-1.89 (m, 2H), 1.80 – 1.71 (m, 2H), 1.67 (h, J = 7.4 Hz, 2H), 1.62-1.55 (m, 3H), 1.49 – 1.41 (m, 2H), 1.34 – 1.24 (m, 1H), 0.95 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 196.9, 72.6, 71.9, 40.6, 36.2, 25.3, 21.8, 18.1, 13.6; IR (film) 3425, 2931, 2862, 2067, 1620 cm^{-1}. MS (ESI): Calculated for $[C_{11}H_{18}N_2O_2Na]^+$: 233.1266. Found: 233.1262.

1-Diazo-1-(1-hydroxycyclohexyl)-4-methylpentan-2-one (**18**): Prepared from cyclohexanone (0.10 mL, 0.10 mmol) and 1-diazo-4-methyl-2-pentanone (189 mg, 1.50 mmol) following Genearl Procedure A. The crude yellow oil was purified using silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 10% EtOA) to give 145 mg (65% yield) of the title compound as a yellow oil which solidified upon standing in freezer: R_f = 0.33 (6:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.39 (s, 1H), 2.32 (d, J = 7.1 Hz, 2H), 2.19-2.09 (m, 1H), 1.97-1.89 (m, 2H), 1.81-1.70 (m, 2H), 1.63-1.53 (m, 3H), 1.50-1.41 (m, 2H), 1.35 – 1.23 (m, 1H), 0.96 (d, J = 6.6 Hz, 6H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 196.8, 73.1, 71.0, 47.5, 36.2, 26.0, 25.3, 22.4, 21.8; IR (film) 3340, 2931, 2862, 2075, 1589 cm^{-1}. MS (ESI): Calculated for $[C_{12}H_{20}N_2O_2Na]^+$: 247.1422. Found: 247.1418

1-Diazo-1-(1-hydroxycylcobutyl)-3-methylbutan-2-one (**20**): Prepared from cyclobutanone (62 mg, 0.89 mmol) and 1-diazo-3-methyl-2-butanone (159 mg, 1.42 mmol) following General Procedure A with the modification that 1M acetic acid in THF (1.3 mL, 1.3 mmol) was used to quench the reaction in place of NH_4Cl. The crude material was purified by flash column chromatography (hexanes/EtOAc, gradient elution 0 to 15% EtOAc) to give 122 mg (75% yield) of title compound as a yellow oil: R_f = 0.25 (hexanes/EtOAc 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.07 (bs, 1H), 2.83 (hept, J = 6.8 Hz, 1H), 2.36 (dtdd, J = 9.6, 8.1, 3.6, 2.1 Hz, 2H), 2.22-2.17 (m, 2H), 1.95 (dtt, J = 11.4, 9.4, 4.6 Hz, 1H), 1.63 (dp, J = 11.3, 8.5 Hz, 1H), 1.12 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.5, 73.0, 36.5, 35.6, 18.5, 13.5; IR (film) 3435 (br), 2972, 2873,

2074, 1624, 1258. MS (ESI): Calculated for $[C_9H_{14}N_2O_2Na]^+$: 205.0953. Found 205.0956.

1-Diazo-1-(1-hydroxycyclopentyl)-3-methylbutan-2-one (**23**): Prepared from cyclopentanone (90 µl, 0.77 mmol) and 1-diazo-3-methyl-2-butanone (143 mg, 1.23 mmol) following General Procedure A. Purification of the crude material using silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 15% EtOAc) afforded 114 mg (75% yield) of the title comound as a yellow oil: R_f = 0.47 (5:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.04 (bs, 1H), 2.83 (hept, J = 6.8 Hz, 1H), 2.13-2.04 (m, 2H), 1.94-1.85 (m, 2H), 1.76-1.64 (m, 4H), 1.14 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.0, 79.4, 70.5, 39.2, 36.4, 23.0, 18.5; IR (film) 3437 (br), 2970, 2073, 1624, 1254. MS (ESI): Calculated for $[C_{10}H_{17}N_2O_2]^+$: 197.1290. Found: 197.1279.

1-Diazo-1-(1-hydroxycycloheptyl)-3-methylbutan-2-one (**26**): Prepared from cycloheptanone (0.16 mL, 1.4 mmol) and 1-diazo-3-methyl-2-butanone (155 mg, 1.38 mmol) following General Procedure A. The ketone starting material was never fully consumed, and the reaction was quenched after stirring at −78 °C for 1 h using 1M acetic acid in THF (2.1 mL, 2.1 mmol) in place of NH_4Cl. Unreacted cycloheptanone and 1-diazo-3-methyl-2-butanone were removed under reduced pressure over 12 h. The resulting oily residue was dissolved in 5 mL 4:1 hexanes/EtOAc and filtered through a plug of silica, which was then rinsed with 4:1 hexanes/EtOAc (5 mL × 3). The filtrate was concentrated *in vacuo* to give 175 mg (59% yield) of the title comound as a yellow

oil: R_f = 0.52 (hexanes/EtOAc 5:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.64 (s, 1H), 2.82 (hept, J = 6.8 Hz, 1H), 2.07 (ddd, J = 14.4, 9.9, 1.6 Hz, 2H), 1.83 (ddd, 14.4, 9.9, 1.6 Hz, 2H), 1.75-1.61 (m, 4H), 1.57-1.49 (m, 2H), 1.44-1.36 (m, 2H), 1.13 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.3, 74.9, 72.0, 40.1, 36.5, 29.1, 21.8, 18.5; IR (film) 3456 (br), 2928, 2860, 2068, 1616, 1246. MS (ESI): Calculated for $[C_{12}H_{21}N_2O_2]^+$: 225.1603. Found: 225.1598.

4-Diazo-5-hydroxy-2-methyl-5-propyloctan-3-one (29): Prepared from 4-heptanone (0.20 mL, 1.44 mmol) and 1-diazo-3-methyl-2-butanone (164 mg, 1.46 mmol) following General Procedure A with the modification that 0.2M acetic acid in THF (7 mL, 1.4 mmol) was used to quench the reaction in place of NH_4Cl. The resulting oily residue was purified by silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 15% EtOAc) to give 199 mg (61% yield) of the title compound as a yellow oil: R_f = 0.63 (5:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.80 (s, 1H), 2.82 (hept, J = 6.8 Hz, 1H), 1.59-1.70 (m, 4H), 1.25-1.46 (m, 4H), 1.12 (d, J = 6.8 Hz, 6H), 0.90 (t, J = 7.4 Hz, 6H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 201.3, 74.5, 69.2, 41.5, 36.5, 18.6, 17.0, 14.3. MS (ESI): Calculated for $[C_{12}H_{22}N_2O_2Na]^+$: 249.1579. Found: 249.1577.

4-Diazo-5-hydroxy-2,2-dimethyl-5-propylocan-3-one (31): Prepared from 4-heptanone (0.12 mL, 0.86 mmol) and 1-diazo-3,3-dimethyl-2-butanone (175 mg, 1.39 mmol) following General Procedure A with the modification that 0.2M acetic acid in THF (7 mL, 1.4 mmol) was used to quench the reaction in place of NH_4Cl. Unreacted 4-heptanone was removed under reduced pressure over 12 h. The resulting oily residue

was purified by silica gel flash column chromatography (hexanes/EtOAc, gradient elution 0 to 10% EtOAc) to give 73 mg (35% yield) of the title compound as a yellow oil: R_f = 0.66 (5:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.98 (s, 1H), 1.64 (dtd, J = 18.0, 14.0, 5.0 Hz, 4H), 1.26-1.46 (m, 4H), 1.22 (s, 9H), 0.91 (t, J = 7.4 Hz, 6H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 202.9, 75.2, 66.6, 44.8, 41.2, 26.5, 17.1, 14.3; IR (film) 3475 (br), 2963, 2870, 2068, 1605, 1466, 1312, 1204. MS (ESI): Calculated for $[C_{13}H_{24}N_2O_2Na]^+$: 263.1735. Found: 263.1732.

General Procedure B: Tin(IV) chloride-promoted cyclopentenone formation

A 1M solution of $SnCl_4$ in CH_2Cl_2 (1 equiv) was added quickly as a stream to a stirred –20 °C solution of diazo ketone (1 equiv) in CH_2Cl_2 (20 mL/mmol of diazo ketone). The bright yellow reaction mixture was stirred at –20 °C for 10 min during which gas evolved and the solution's color diminished. Saturated aqueous $NaHCO_3$ (20 mL) was added and the mixture was transferred to a separatory funnel with the aid of 10 mL CH_2Cl_2. The layers were separated, and the aqueous layer was extracted three times with Et_2O (10 mL). The organic layers were combined and washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum that did not exceed 125 mmHg. The residue was purified by silica gel flash column chromatorgraphy.

General Procedure C: Tris(pentafluorophenyl)borane-promoted cyclopentenone formation

A –15 °C solution of 0.1M diazo ketone (1 equiv) in CH_2Cl_2 was rapidly added to a stirred –15 °C solution of 0.1M tris(pentafluorophenyl)borane (1 equiv) in CH_2Cl_2. The

reaction mixture was stirred at –15 °C for 10 min during which gas evolved and the solution's color diminished. Saturated aqueous $NaHCO_3$ (20 mL) was added and the mixture was transferred to a separatory funnel with the aid of 10 mL CH_2Cl_2. The layers were separated, and the aqueous layer was extracted three times with Et_2O (10 mL). The organic layers were combined and washed with water and brine, dried over $MgSO_4$, and concentrated under vacuum that did not exceed 125 mmHg. The residue was purified by silica gel flash column chromatorgraphy.

2,2-Dimethyl-2,3,5,6,7,8-hexahydroazulen-1(4*H*)-one (**2**): Prepared by subjecting diazo ketone **1** (0.14 mmol) to General Procedure B or C . The colorless oily residue was subjected to silica gel flash column chromatography (100% CH_2Cl_2) which gave the title compound as a colorless oil in 21 mg (83% yield) from procedure B and 22 mg (88% yield) from procedure C: R_f = 0.27 (100% CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42 (dd, J = 6.5, 5.8 Hz, 2H), 2.37 (s, 2H), 2.30, (t, J = 5.6, 2H), 1.76-1.81 (m, 2H), 1.67-1.62 (m, 2H), 1.51-1.55 (m, 2H), 1.08 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.2, 173.4, 139.4, 48.9, 43.1, 33.5, 31.3, 26.8, 26.4, 25.1, 23.8. MS (ESI): Calculated for $[C_{12}H_{19}O]^+$: 179.1436. Found: 179.1430.

2-Methyl-2,3,5,6,7,8-hexahydroazulen-1(4*H*)-one (**4**), **1-Chloro-1-cyclohexylidene-3-methylbutan-2-one** (**9**):[8] Prepared by subjecting diazo ketone **3** to General Procedure B (67.6 mg, 0.32 mmol) or General Procedure C (69.8 mg, 0.33 mmol). The crude brown oil was purified by flash silica gel column chromatography (hexanes/Et_2O, gradient elution 0 to 10% Et_2O) to give 2-Methyl-2,3,5,6,7,8-hexahydroazulen-1(4H)-one (**4**) as a

faint yellow oil in 36.6 mg (70% yield) from General Procedure B and 44.8 mg (82% yield) from General Procedure C; (R_f = 0.15 in 10:1 hexane/EtOAc) ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.74 (dd, *J* = 18.4, 6.6 Hz, 1H), 2.47 – 2.41 (m, 2H), 2.41-2.32 (m, 1H), 2.32-2.26 (m, 2H), 2.09 (d, *J* = 18.4 Hz, 1H), 1.82-1.75 (m, 2H), 1.65 (pent, *J* = 5.4 Hz, 2H), 1.53 (pent, *J* = 5.4 Hz, 2H), 1.15 (d, *J* = 7.7, 1.4 Hz, 3H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 211.5, 174.9, 140.9, 40.8, 39.9, 33.5, 31.2, 26.7, 26.3, 23.6, 16.6. MS (ESI): Calculated for $[C_{11}H_{16}ONa]^+$: 187.1099. Found: 187.1096.

In addition, General Procedure B gave 1-Chloro-1-cyclohexylidene-3-methylbutan-2-one (**9**) in 10% yield: R_f = 0.83 (100% CH_2Cl_2); ^{1}H and ^{13}C NMR data matched previously reported values.[8] MS (ESI): Calculated for $[C_{11}H_{18}ClO]^+$: 201.1046. Found 201.1046.

2,2,6,6-Tetramethyl-2,3,5,6,7,8-hexahydroazulen-1(4*H*)-one (**11**): Prepared by subjecting diazo ketone **10** to General Procedure C (85.6 mg, 0.34 mmol). The crude brown oil was purified by flash silica gel column chromatography (hexanes/Et_2O, gradient elution 0 to 10% Et_2O) to give 54.4 mg (78% yield) of the title compound as a faint yellow oil: R_f= 0.60 (3.7:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.4-2.34 (m, 2H), 2.33 (s, 2H), 2.26-2.20 (m, 2H), 1.55-1.50 (m, 2H), 1.45-1.40 (m, 2H), 1.07 (s, 6H), 0.98 (s, 6H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 213.8, 173.0, 139.3, 49.2, 43.4, 39.8, 39.0, 34.1, 29.3, 28.9, 25.6, 19.3. MS (ESI): Calculated for $[C_{14}H_{23}O]^+$: 207.1749. Found: 207.1757.

6-(*tert*-Butyl)-2,2-dimethyl-2,3,5,6,7,8-hexahydroazulen-1(4*H*)-one (**13**): Prepared by subjecting diazo ketone **12** to General Procedure B (48 mg, 0.17 mmol) or General Procedure C (46 mg, 0.16 mmol). The colorless oily residue was subjected to silica gel

flash column chromatography (hexanes/Et_2O, gradient elution 0 to 10% Et_2O) to give the title compound as a colorless oil in 16 mg (40% yield) from procedure B and 21 mg (56% yield) from procedure C. The yield of **13** could be further improved to 66% by following General Procedure C with the addition of 1 equiv $MgSO_4$ to the 0.1M solution of tris(pentafluorophenyl)borane: R_f = 0.21 (9:1 hexanes/Et_2O); ^1H NMR (500 MHz, $CDCl_3$): δ 2.64 (ddd, *J* = 16.0, 6.2, 3.5 Hz, 1H), 2.50 (ddd, *J* = 16.2, 5.7, 3.0 Hz, 1H), 2.30-2.39 (m, 1H), 2.35 (s, 2H), 1.88-2.02 (m, 3H), 1.16-1.28 (m, 2H), 1.08 (s, 3H), 1.07 (s, 3H), 0.89 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 213.3, 172.7, 138.8, 52.1, 48.7, 43.1, 34.0, 33.1, 27.9, 27.7, 27.2, 25.19, 25.15, 22.9. MS (ESI): Calculated for $[C_{16}H_{26}ONa]^+$: 257.1881. Found: 257.1884.

2,3,5,6,7,8-Hexahydroazulen-1(4H)-one (**15**): Prepared by subjecting diazo ketone **14** to General Procedure B (100 mg, 0.50 mmol) or C (64.1 mg, 0.33 mmol). The crude brown oil was purified by flash silica gel column chromatography (hexanes/Et_2O, gradient elution 0 to 25% Et_2O) to give the title compound as a faint yellow oil in 46.8 mg (62% yield) from procedure B and 35.1 mg (70% yield) from procedure C: R_f = 0.34 (3.7:1 hexane/EtOAc); ^1H NMR and ^{13}C NMR values match previously reported data.[5]

3-Methyl-2,3,5,6,7,8-hexahydroazulen-1(4H)-one (**17**): Prepared by subjecting diazo ketone **16** to General Procedure B (119 mg, 0.56 mmol) or C (77.5 mg, 0.37 mmol). The crude brown oil was purified by flash silica gel column chromatography (hexanes/Et_2O, gradient elution 0 to 10% Et_2O) to give the title compound as a faint yellow oil in 30.0 mg (32% yield) from procedure B and 33.8 mg (55% yield) from procedure C: R_f = 0.15

(5:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.70 (dddd, *J* = 18.5, 7.0, 7.0 7.0, 1.6 Hz, 1H), 2.61 (dd, *J* = 18.6, 6.5 Hz, 1H), 2.48 (dt, *J* = 16.0, 6.0, 6.0 Hz, 1 H), 2.41 (dt, *J* = 16.0, 6.0, 6.0 Hz, 1 H), 2.35-2.24 (m, 2H), 1.99 (dd, *J* = 18.5, 1.6 Hz, 1H), 1.85-1.73 (m, 2H), 1.66-1.60 (m, 2H), 1.54-1.48 (m, 2H), 1.15 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 208.0, 180.9, 141.8, 43.2, 37.1, 31.5, 31.2, 26.5, 26.4, 23.2, 19.1. MS (ESI): Calculated for $[C_{11}H_{16}ONa]^+$: 187.1099. Found: 187.1097.

1-(Cyclohept-1-en-1-yl)-3-methylbut-3-en-1-one (**19**): Prepared by subjecting diazo ketone **18** to General Procedure C (69.6 mg, 0.31 mmol). The crude brown oil was purified by flash silica gel column chromatography (hexanes/Et_2O, gradient elution 0 to 7% Et_2O) to give 43.4 mg (77% yield) of the title compound as a faint yellow oil: R_f = 0.74 (3.7:1 hexane/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11 (t, *J* = 6.7 Hz, 1H), 4.90 (s, 1H), 4.74 (s, 1H), 3.38 (s, 2H), 2.52-2.47 (m, 2H), 2.37-2.31 (m, 2H), 1.81-1.76 (m, 2H), 1.75 (s, 3H), 1.57-1.52 (m, 2H), 1.48-1.42 (m, 2H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 199.2, 146.0, 145.2, 140.8, 113.9, 46.4, 32.3, 29.1, 26.1, 25.8, 25.6, 22.8. MS (ESI): Calculated for $[C_{12}H_{18}ONa]^+$: 201.1255. Found: 201.1251.

2-Methyl-2,3,5,6,7,8-hexahydroazulen-1(4*H*)-one (**21**) and **1-Chloro-1-cyclobutylidene-3-methylbutan-2-one** (**22**)[6]: The title compounds were prepared by subjecting diazo ketone **20** (50 mg, 0.28 mmol) to General Procedure B. The oily residue was purified using silica gel flash column chromatography to afford 32 mg (68% yield) of vinyl chloride **22**; (100% CH_2Cl_2, R_f = 0.81) ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.39 (hept, *J* = 6.8 Hz, 1H), 2.78 (tt, *J* = 7.9, 2.4 Hz, 2H), 2.69 (tt, *J* = 7.8, 2.4 Hz, 2H), 1.92

(p, J = 7.8 Hz, 2H), 1.10 (d, J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, CDCl3): δ 202.8, 139.1, 136.0, 41.4, 38.0, 33.2, 20.2, 18.2. MS (ESI): Calculated for $[C_9H_{14}ClO]^+$: 173.0733. Found: 173.0730.

In addition, cyclopentenone **21** was observed as a minor product (<5%) in the crude reaction mixture. ^{1}H NMR matched previously reported values.[6]

2-Methyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-one (**24**)[7] and **1-Chloro-1-cyclopentylidene-3-methylbutan-2-one** (**25**): Prepared by subjecting diazo ketone **23** to General Procedure B (46 mg, 0.23 mmol) or General Procedure C (44 mg, 0.22 mmol). The yellow oily residue was purified by silica gel flash chromatography (4:1 pentane/CH_2Cl_2) to give cyclopentenone **24** as a colorless oil in 7 mg (21% yield; General Procedure B) or 20 mg (60% yield; General Procedure C): R_f = 0.41 (5:1 hexanes/EtOAc); ^{1}H NMR and ^{13}C NMR spectral data match previously reported data.[7]

In addition, General Procedure B provided 13 mg (30% yield) of vinyl chloride **25** as a yellow oil: R_f = 0.77 (5:1 hexanes/EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.41 (hept, J = 6.8 Hz, 1H), 2.76 (tt, J = 5.6, 1.2 Hz, 2H), 2.55 (tt, J = 5.6, 1.0 Hz, 2H), 1.79 (p, J = 5.6 Hz, 2H), 1.71 (p, J = 5.6 Hz, 2H), 1.10 (d, J = 6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.2, 161.3, 121.8, 36.6, 36.4, 35.3, 27.9, 25.0, 18.4. MS (ESI): Calculated for $[C_{10}H_{16}ClO]^+$: 187.0890. Found: 187.0887.

2-Methyl-2,3,4,5,6,7,8,9-octahydro-1*H*-cyclopenta[8]annulen-1-one (**27**) and **1-Chloro-1-cycloheptylidene-3-methylbutan-2-one** (**28**): Prepared by subjecting diazo ketone **26** to General Procedure B (66.3 mg, 0.296 mmol) or General Procedure C (43.2

mg, 0.193 mmol). The oily residue was purified by silica gel flash chromatography (hexanes/Et_2O, elution gradient 0 to 5% Et_2O) to give 2-Methyl-2,3,4,5,6,7,8,9-octahydro-1H-cyclopenta[8]annulen-1-one (**27**) as a colorless oil in 22.1 mg (42% yield, General Procedure B) and 22.9 mg (66% yield, General Procedure C): R_f = 0.78 (9:1 hexanes/Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.73 (dd, *J* = 18.3, 6.6 Hz, 1H), 2.49 (dd, *J* = 7.9, 5.0 Hz, 2H), 2.37 (pd, *J* = 7.4, 3.9 Hz, 1H), 2.33 (t, *J* = 6.5 Hz, 2H), 2.07 (d, *J* = 14.8 Hz, 1H), 1.75 (p, *J* = 6.7, 6.2 Hz, 2H), 1.53 (m, 2H), 1.44 (m, 4H), 1.15 (d, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.6, 173.4, 139.2, 39.9, 39.2, 30.2, 28.5, 27.2, 26.2, 25.7, 21.3, 16.8. MS (ESI): Calculated for $[C_{12}H_{19}O]^+$: 179.1436. Found: 179.1433.

In addition, General Procedure B returned 15.1 mg (24% yield) of 1-chloro-1-cycloheptylidene-3-methylbutan-2-one (**28**) as a yellow oil: R_f = 0.80 in (9:1 hexanes/Et_2O) ; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.33 (hept, *J* = 6.9 Hz, 1H), 2.51 (ddd, *J* = 13.2, 7.1, 5.1 Hz, 4H), 1.67 (dp, *J* = 16.6, 5.7 Hz, 4H), 1.57-1.48 (m, 4H), 1.11 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.0, 150.6, 124.7, 37.3, 34.7, 32.9, 29.2, 28.6, 27.8, 25.7, 18.2. MS (ESI): Calculated for $[C_{12}H_{20}ClO]^+$: 215.1203. Found: 215.1202.

5-Methyl-2,3-dipropylcyclopent-2-enone (**30**): Prepared by subjecting β-hydroxy-α-diazo ketone **29** (76 mg, 0.34 mmol) to General Procedure C. The oily residue was subjected to silica gel flash column chromatography (hexanes/Et_2O, gradient elution 0 to 10% Et_2O) to give the title compound as a colorless oil in 20 mg (33% yield): R_f = 0.24 (9:1 hexanes/Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.73 (dd, *J* = 18.3, 6.9 Hz, 1H), 2.38

(t, J = 7.7 Hz, 2H), 2.34 (pd, J = 7.0, 2.0 Hz, 1H), 2.14 (t, J = 7.6 Hz, 2H), 2.06 (d, J = 18.3 Hz, 1H), 1.56 (h, J = 7.4 Hz, 2H), 1.40 (hd, J = 7.5, 2.0 Hz, 2H), 1.15 (d, J = 7.4 Hz, 3H), 0.96 (t, J = 7.4 Hz, 3H), 0.88 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 212.4, 171.9, 139.1, 39.5, 38.1, 33.0, 25.1, 21.9, 20.8, 16.8, 14.2, 14.1. MS (ESI): Calculated for $[C_{12}H_{20}ONa]^+$: 203.1412. Found: 203.1405.

5,5-Dimethyl-2,3-dipropylcyclopent-2-enone (**32**): Prepared by subjecting β-hydroxy-α-diazo ketone **31** (52 mg, 0.22 mmol) to General Procedure C. The oily residue was subjected to silica gel flash column chromatography (hexanes/Et_2O, gradient elution 0 to 10% Et_2O) to give the title compound as a colorless oil in 26 mg (63% yield): R_f = 0.38 (9:1 hexanes/Et_2O); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (dd, J = 8.5, 7.5 Hz, 2H), 2.35 (s, 2H), 2.14 (dd, J = 9.0, 7.5 Hz, 2H), 1.55 (h, J = 7.5 Hz, 2H), 1.41 (h, J = 7.5 Hz, 2H), 1.07 (s, 6H), 0.95 (t, J = 7.5 Hz, 3H), 0.87 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 Mhz, $CDCl_3$) δ 214.0, 170.2, 137.6, 46.1, 42.6, 32.8, 25.2, 25.1, 21.8, 20.8, 14.1, 14.0. MS (ESI): Calculated for $[C_{13}H_{22}ONa]^+$: 217.1568. Found: 217.1569.

III) References

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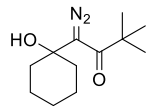
^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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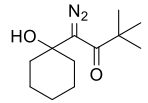

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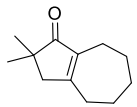

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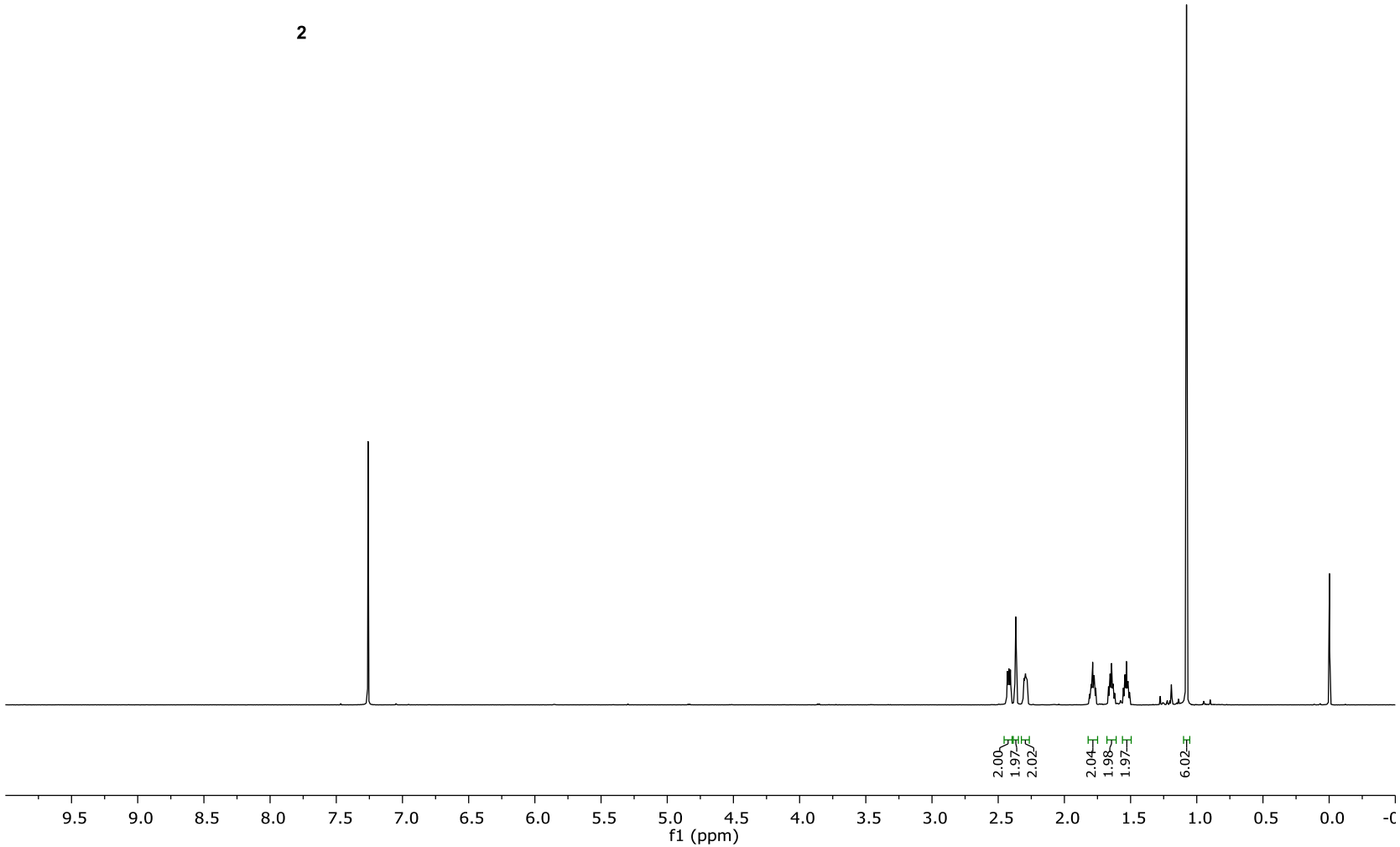
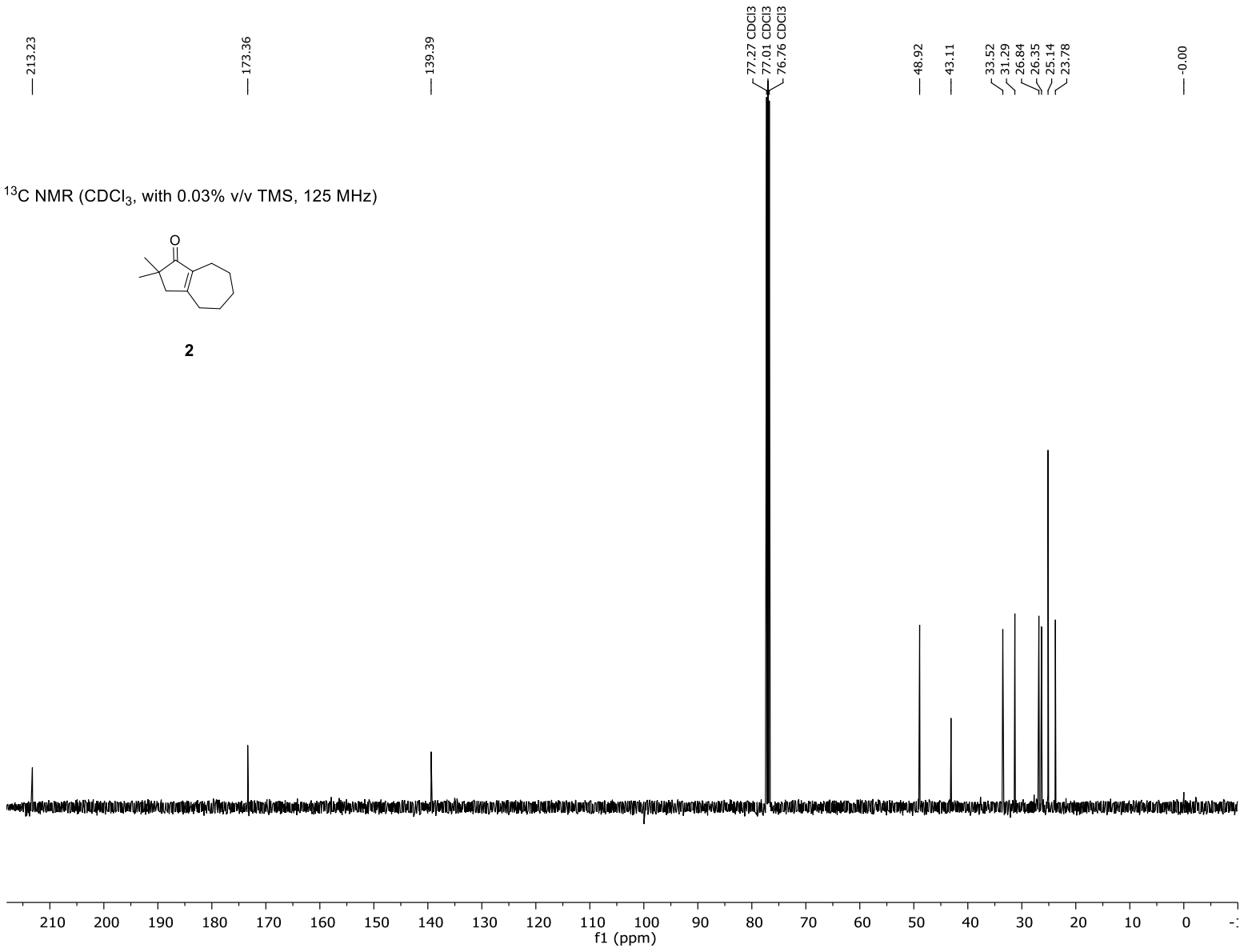
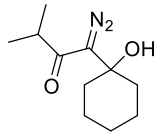



213.23
173.36
139.39
77.27 CDCl3
77.01 CDCl3
76.76 CDCl3
48.92
43.11
33.52
31.29
26.84
26.35
25.14
23.78
-0.00
13C NMR (CDCl3, with 0.03% v/v TMS, 125 MHz)
O
2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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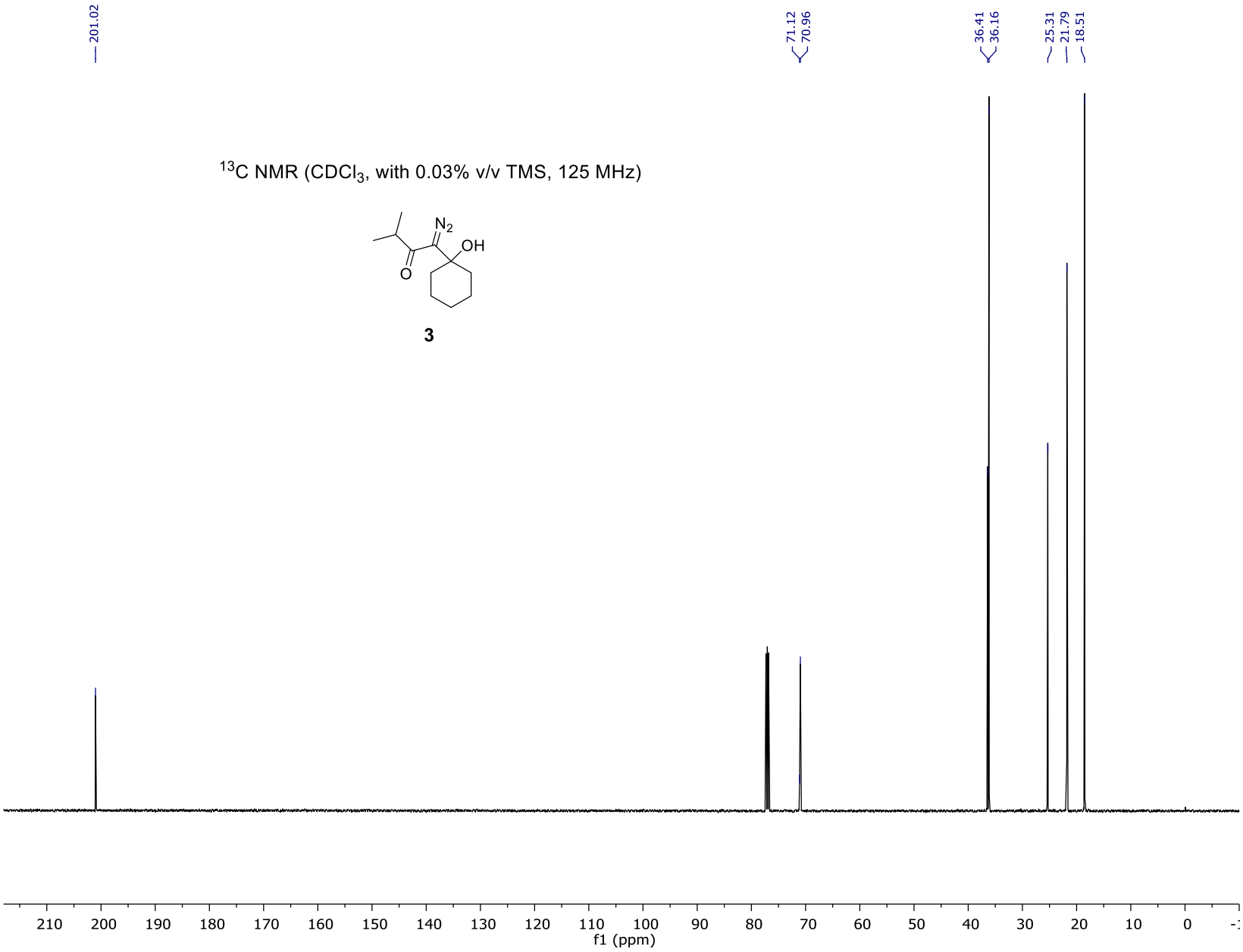
201.02
71.12
70.96
36.41
36.16
25.31
21.79
18.51
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N_2
OH
O
3
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f1 (ppm)

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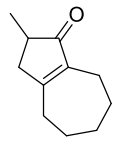

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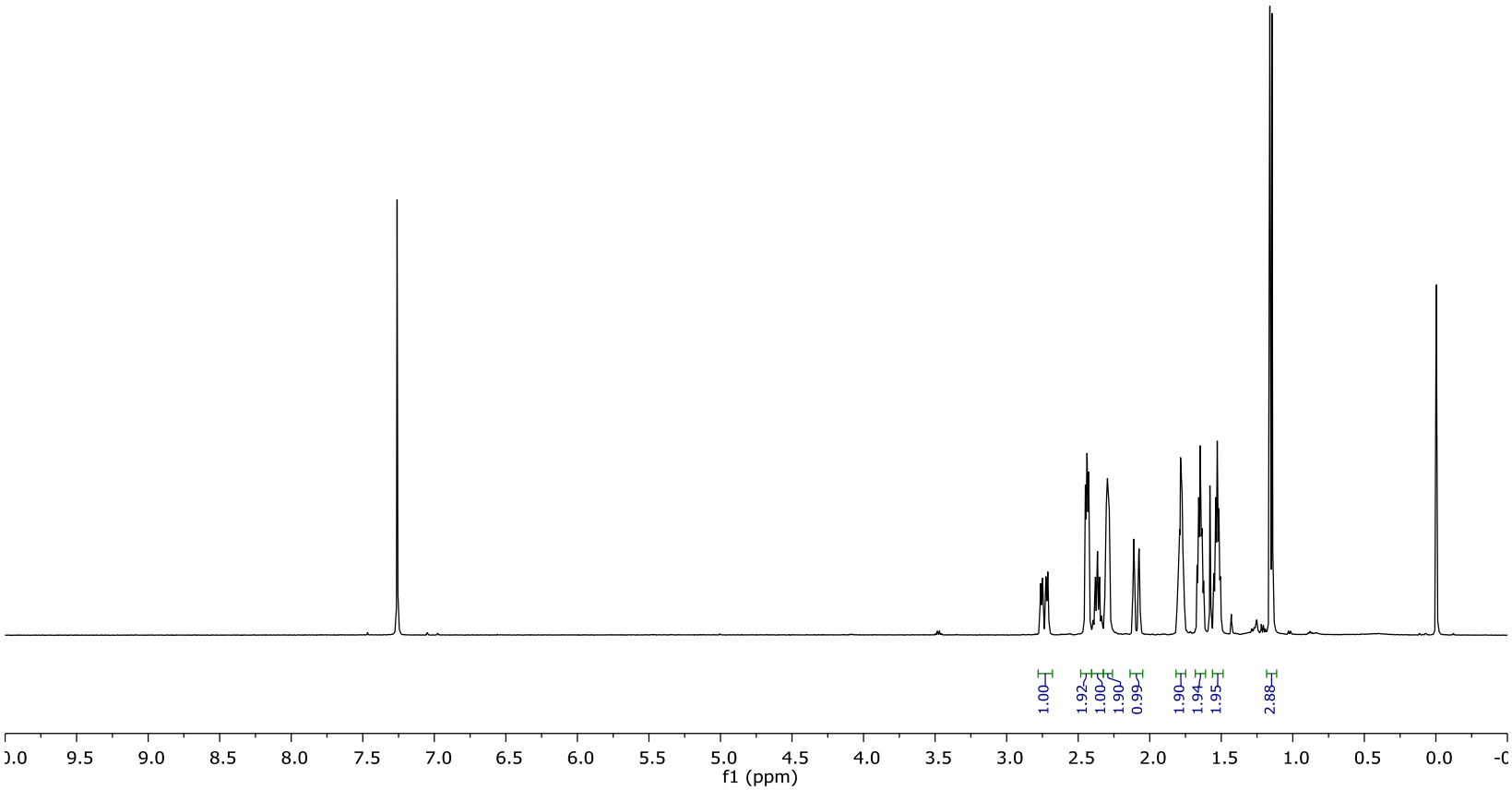

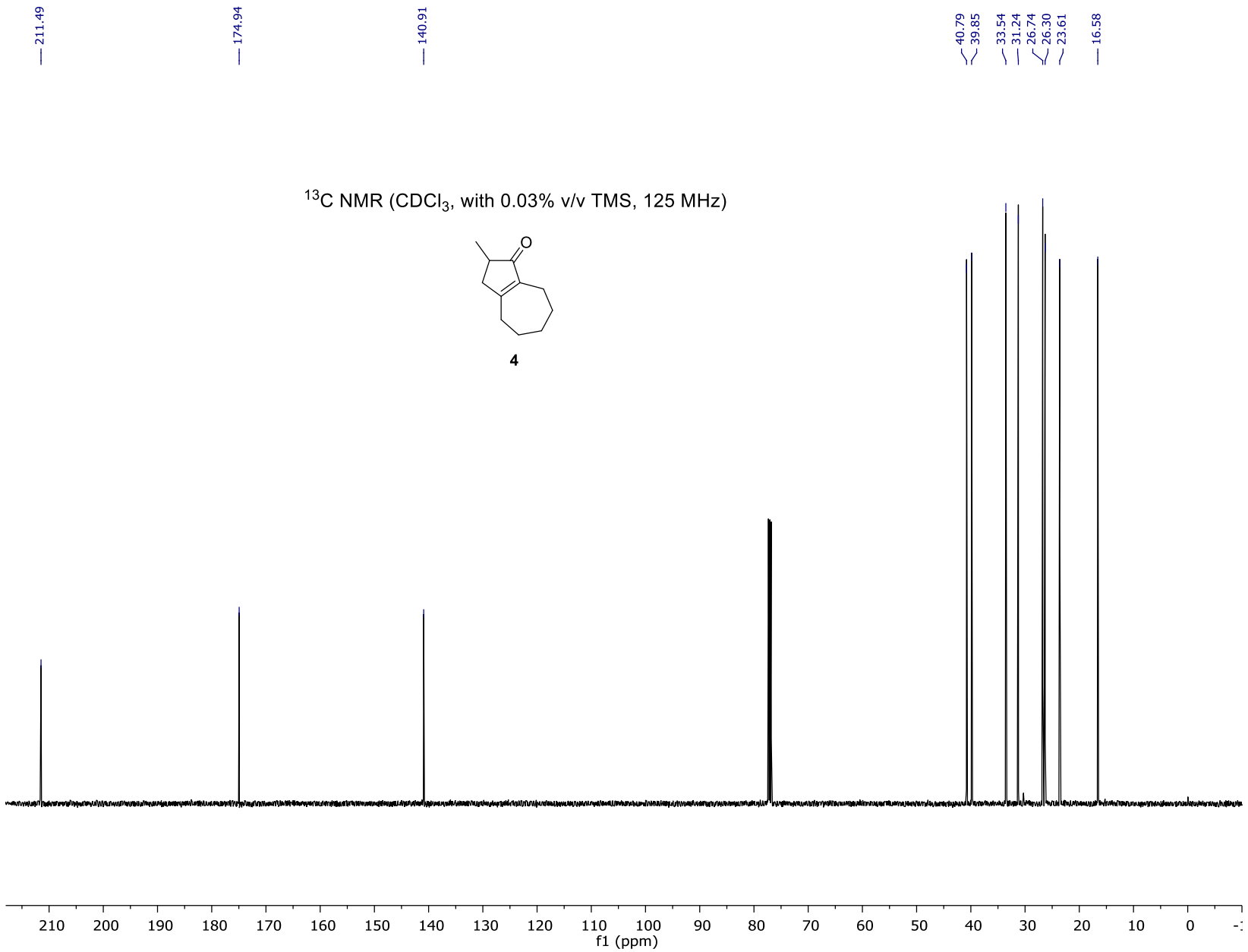
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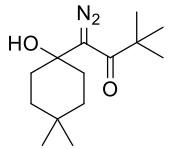
174.94
140.91
40.79
39.85
33.54
31.24
26.74
26.30
23.61
16.58
^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)
O
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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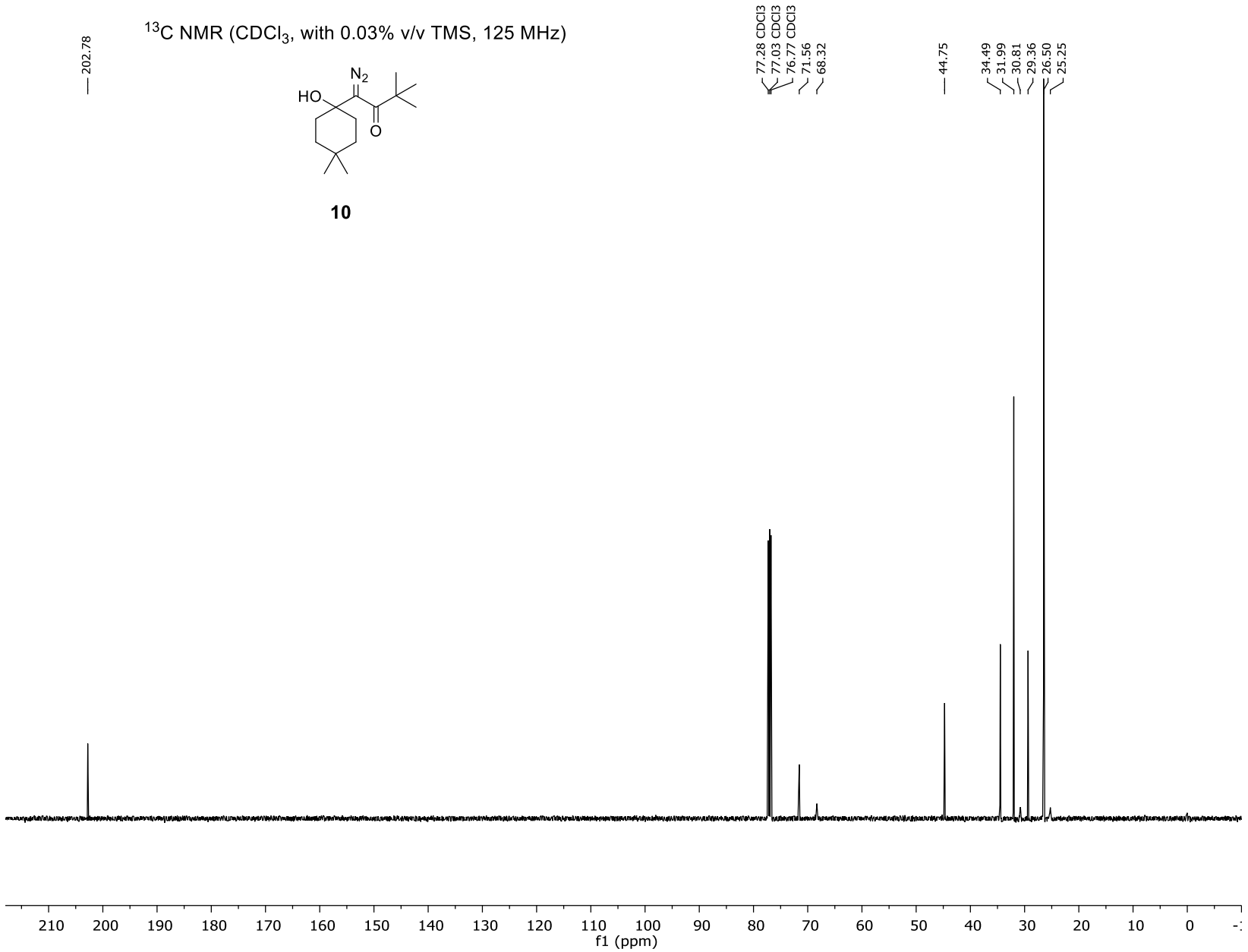
^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)
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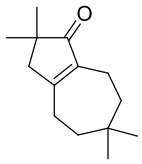
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
71.56
68.32
44.75
34.49
31.99
30.81
29.36
26.50
25.25
HO
N_2
O
10
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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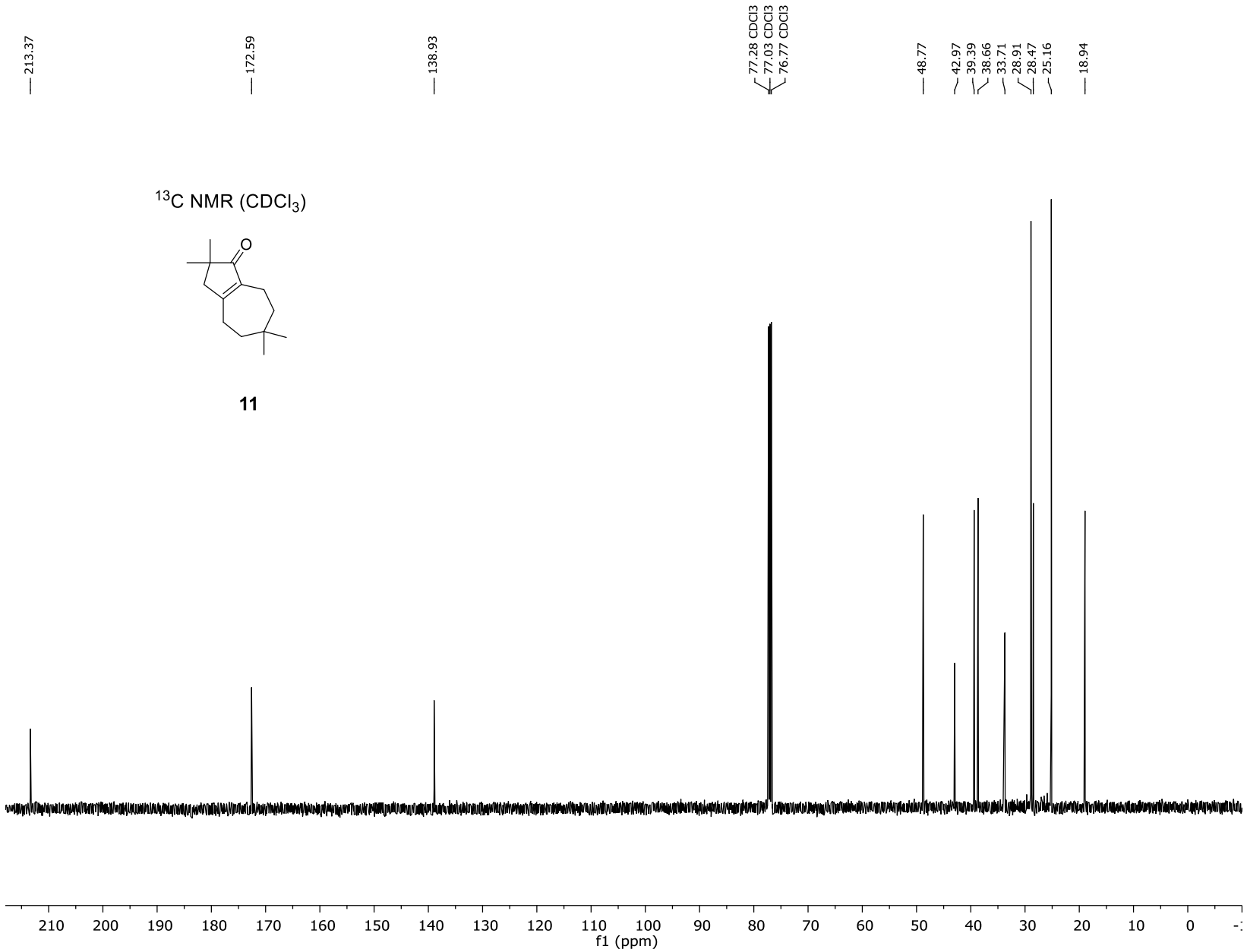
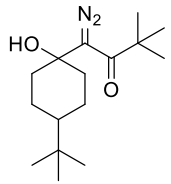

213.37
172.59
138.93
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
48.77
42.97
39.39
38.66
33.71
28.91
28.47
25.16
18.94
13C NMR (CDCl3)
O
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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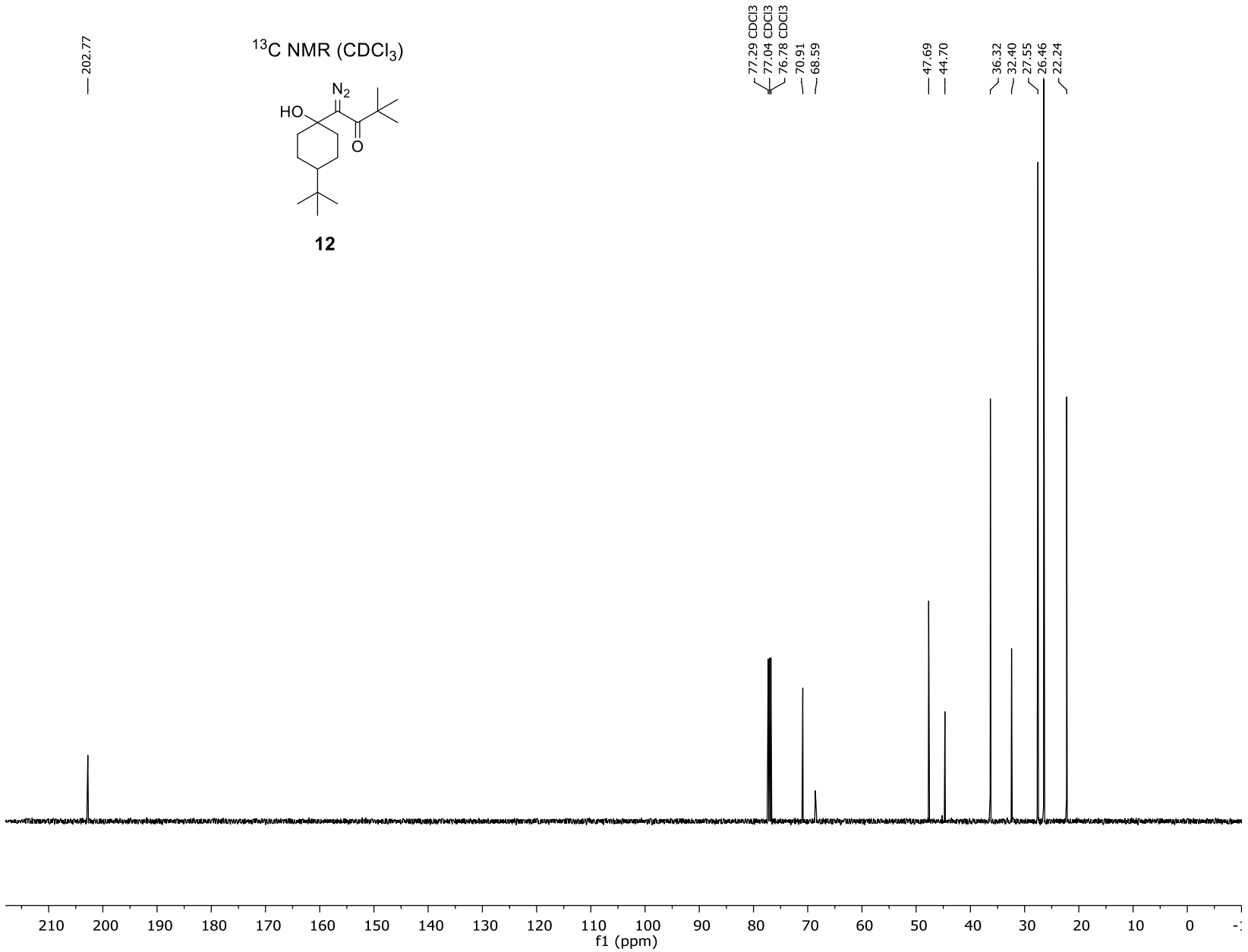
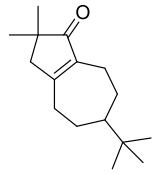


^{13}C NMR ($CDCl_3$)

12

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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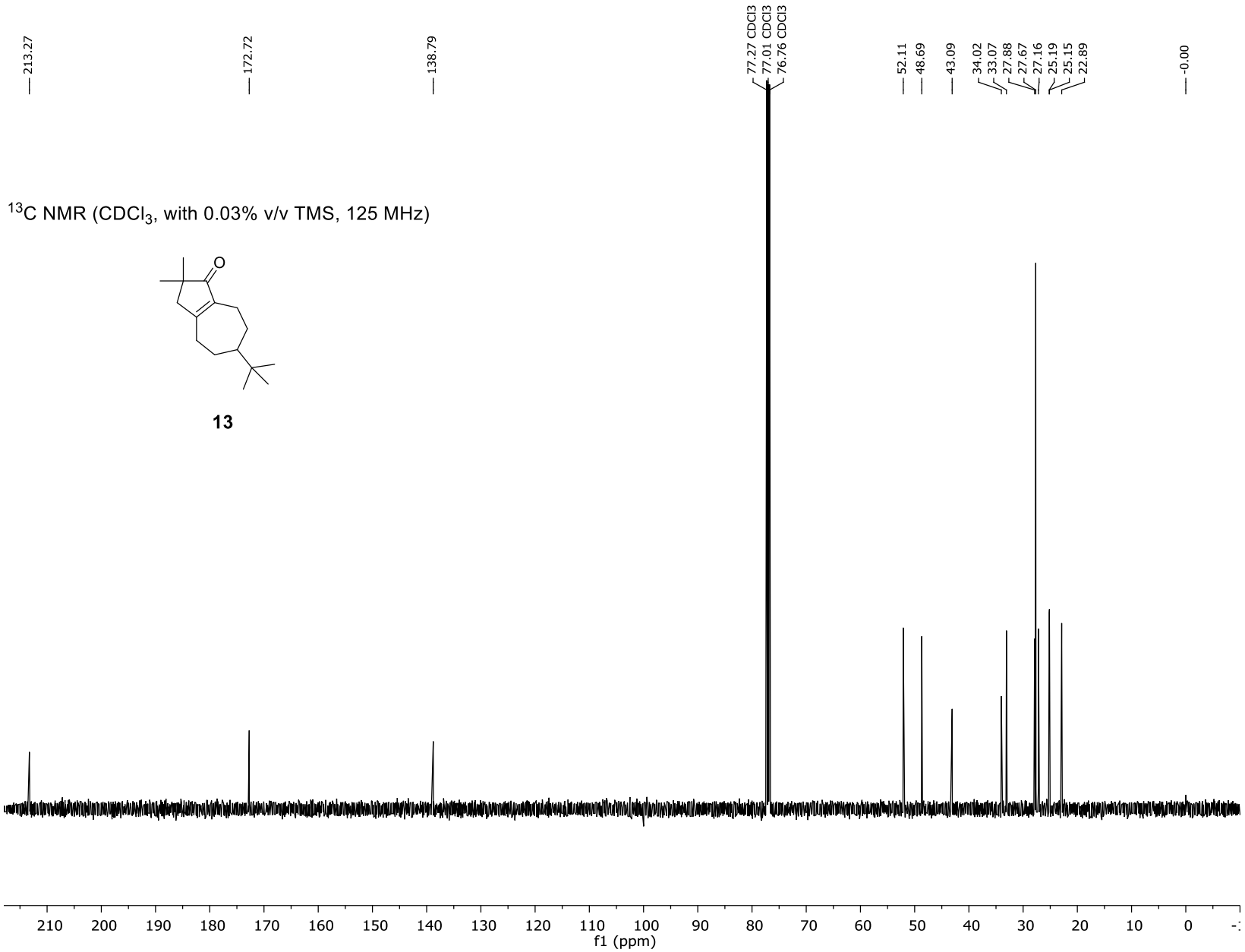
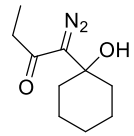

213.27
172.72
138.79
77.27 CDCl3
77.01 CDCl3
76.76 CDCl3
52.11
48.69
43.09
34.02
33.07
27.88
27.67
27.16
25.19
25.15
22.89
0.00
13C NMR (CDCl3, with 0.03% v/v TMS, 125 MHz)
O
13
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



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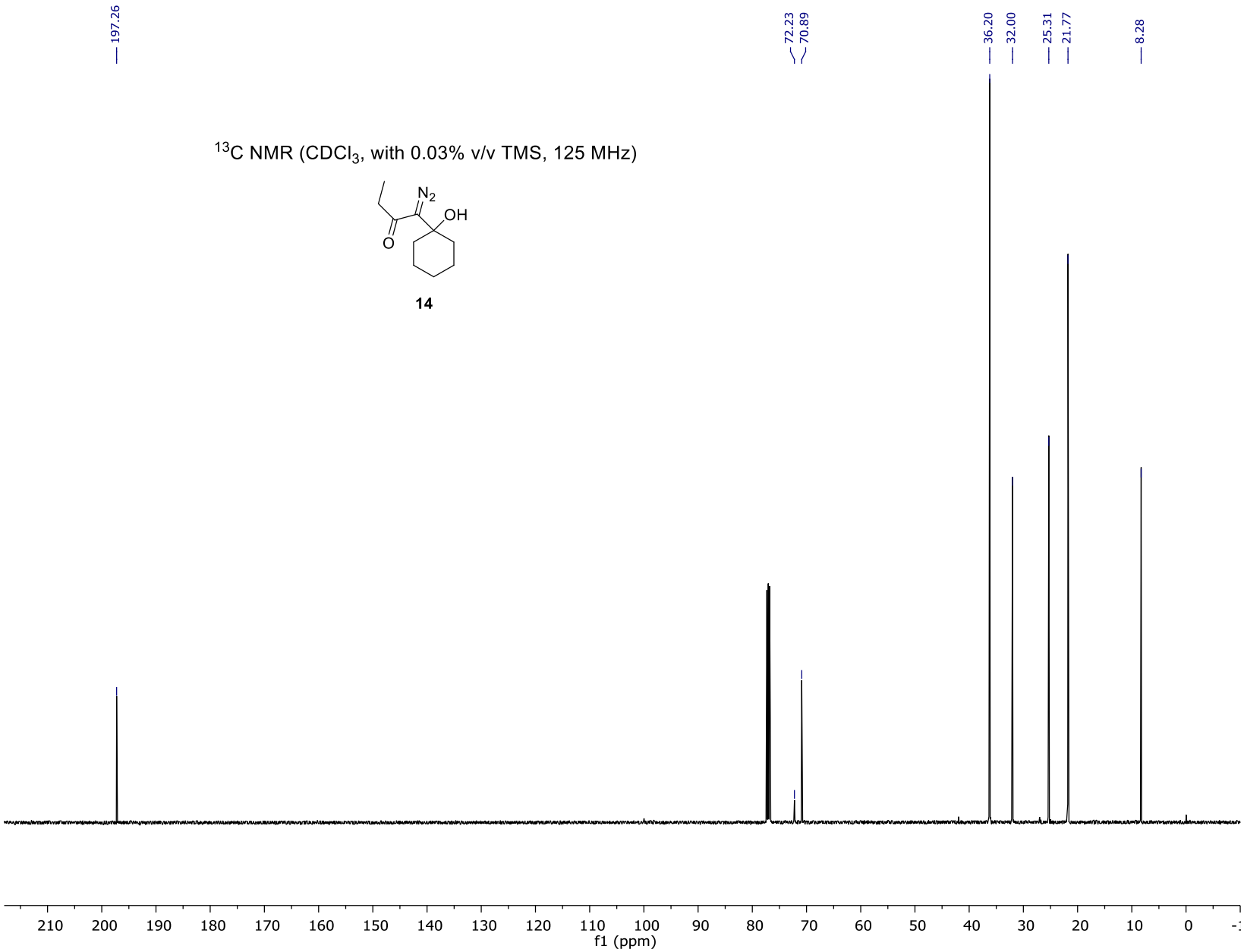
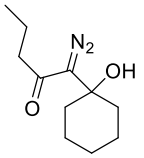
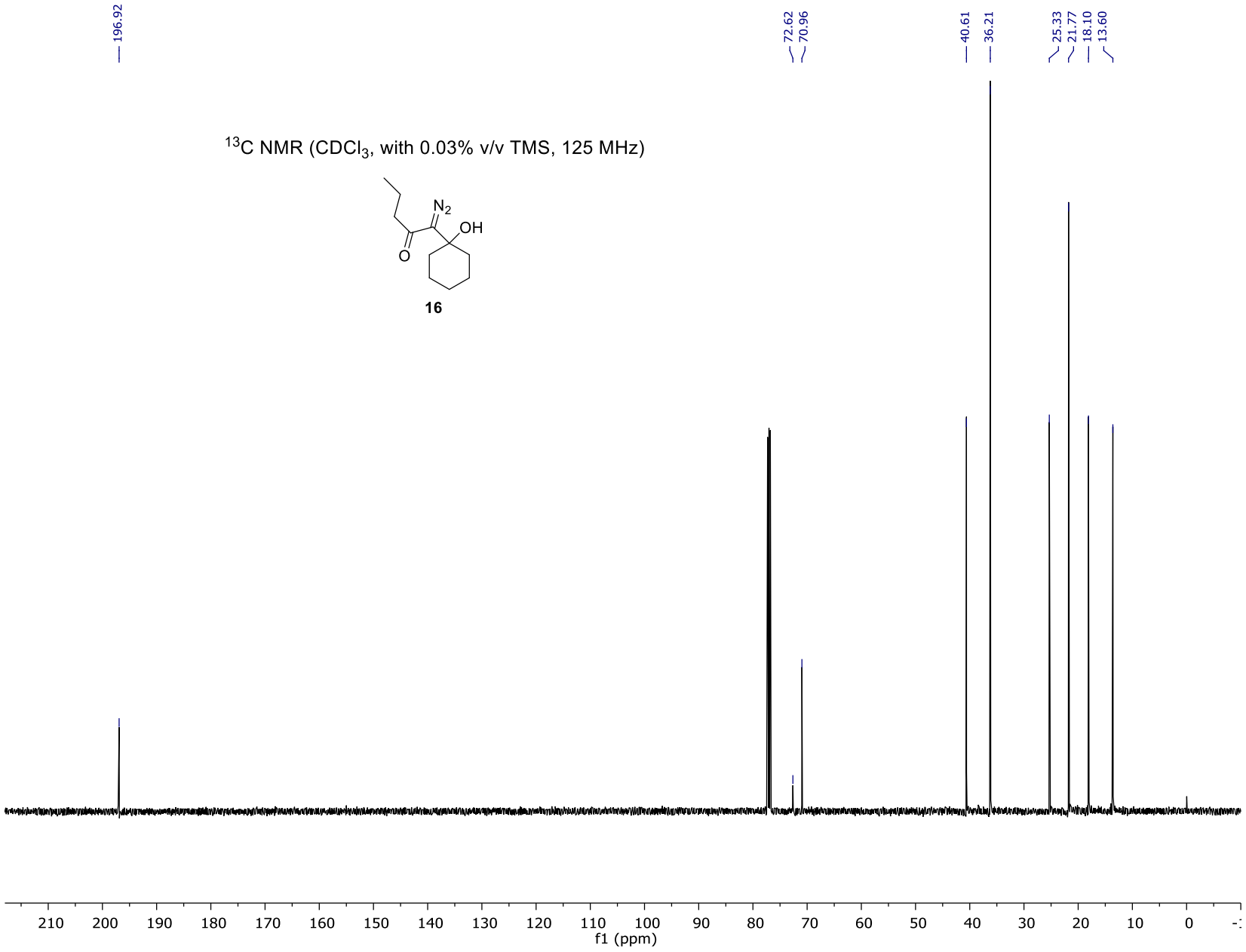

197.26
72.23
70.89
36.20
32.00
25.31
21.77
8.28
^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)
N_2
OH
O
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

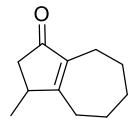
^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



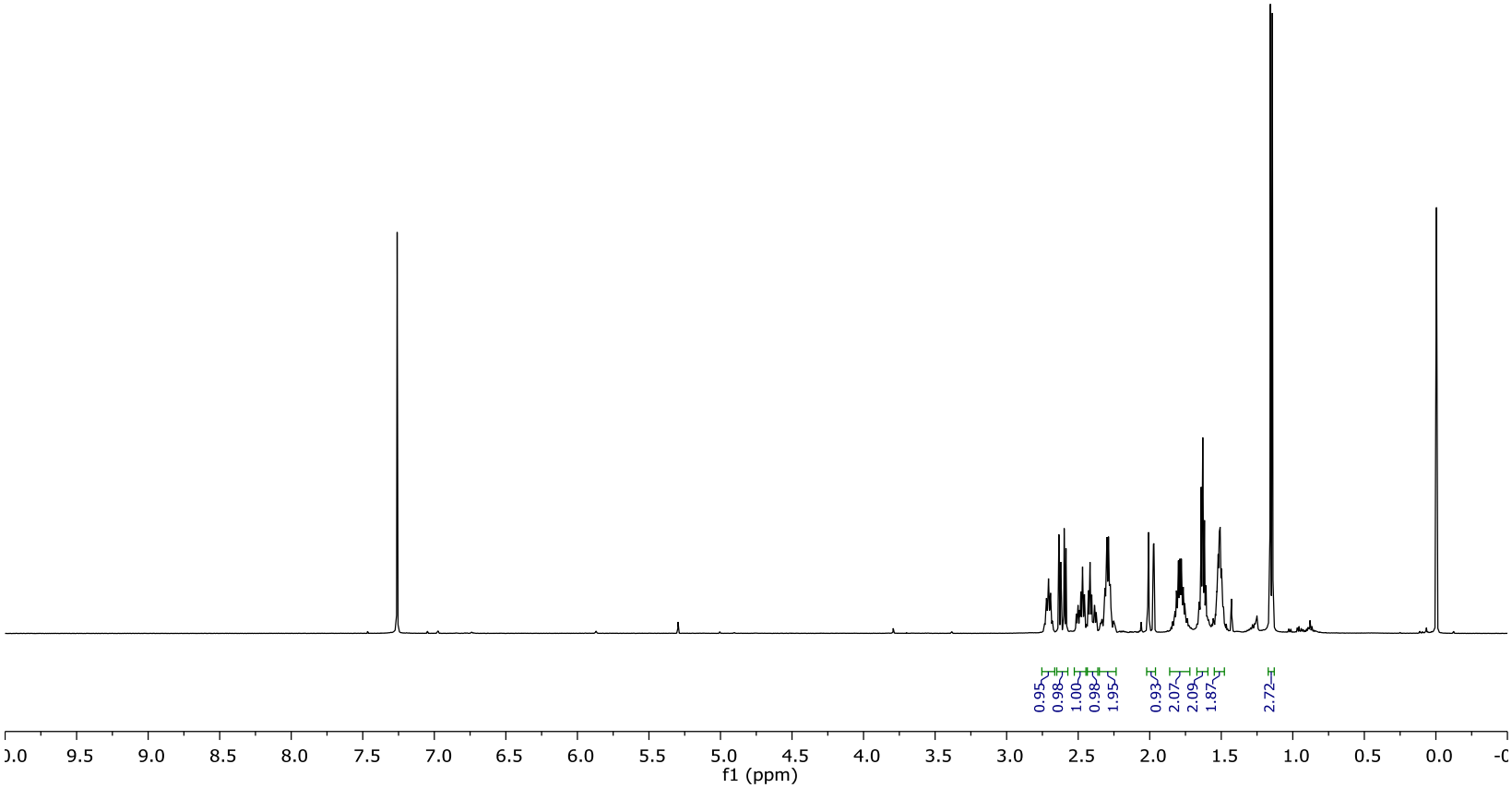
16


196.92
72.62
70.96
40.61
36.21
25.33
21.77
18.10
13.60
^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)
N_2
OH
O
16
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

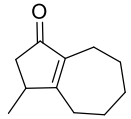


17



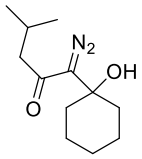
208.05
180.89
141.79
43.21
37.10
31.49
31.19
26.59
26.41
23.17
19.06

^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)

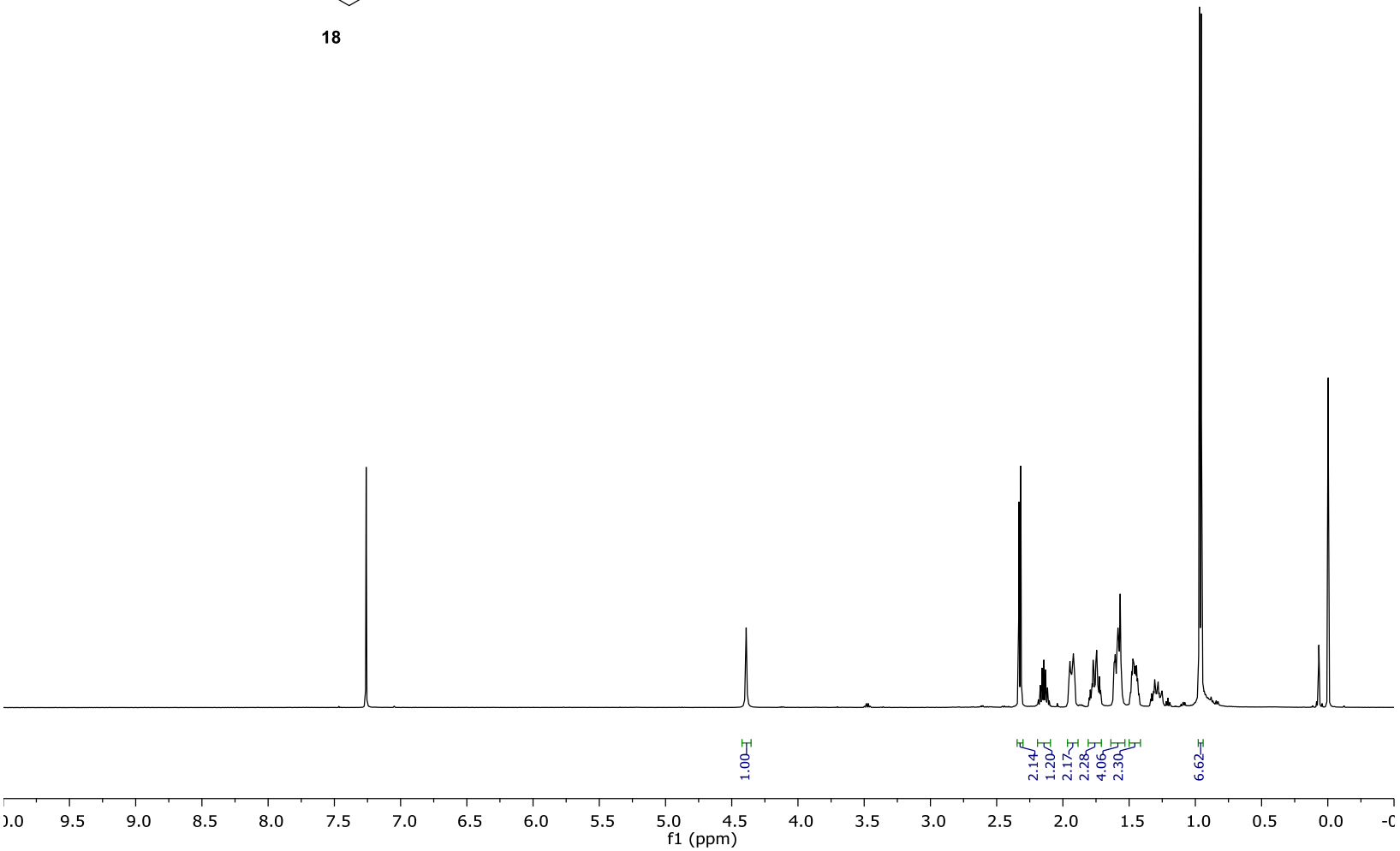


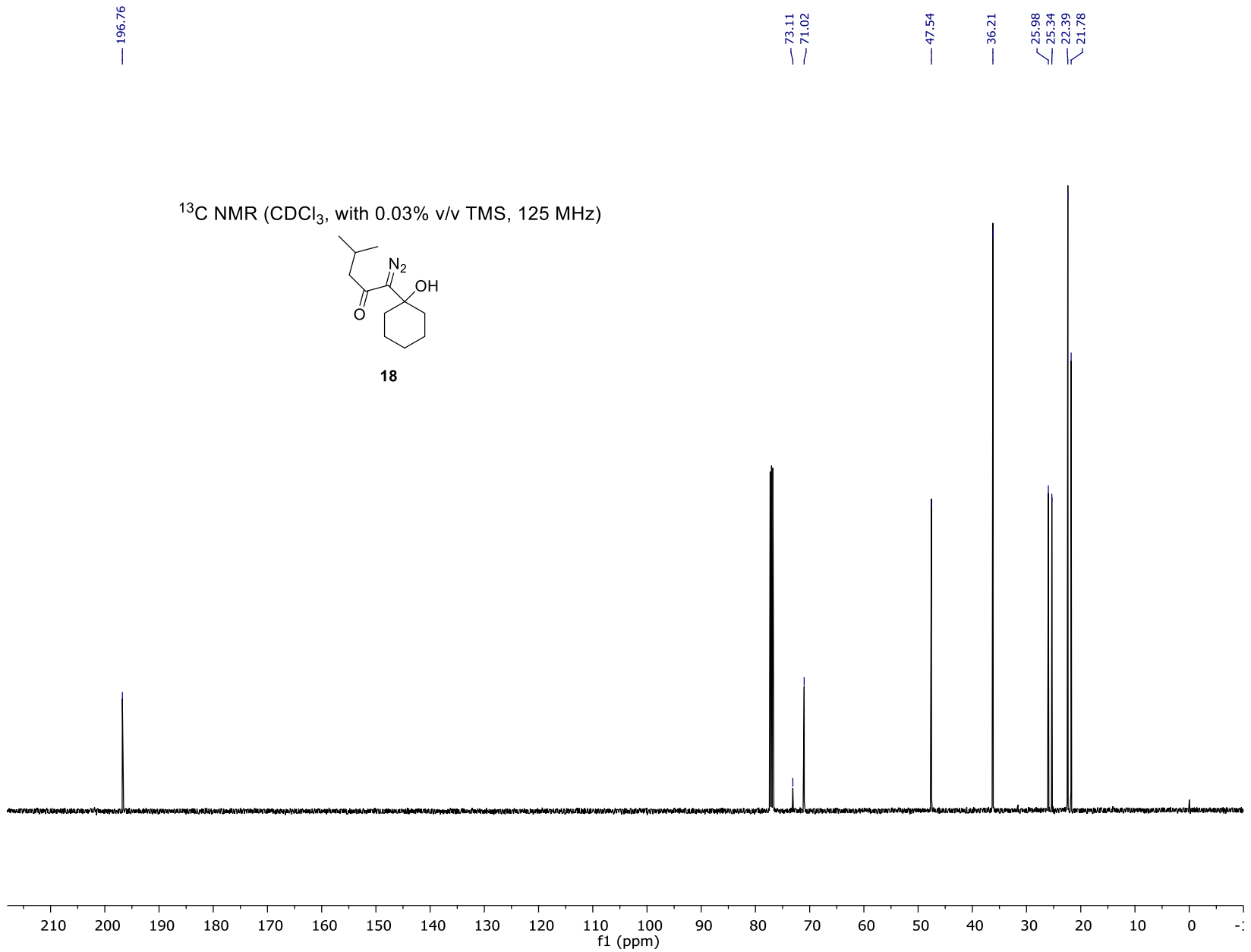
17

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

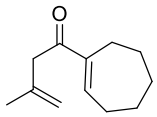


18

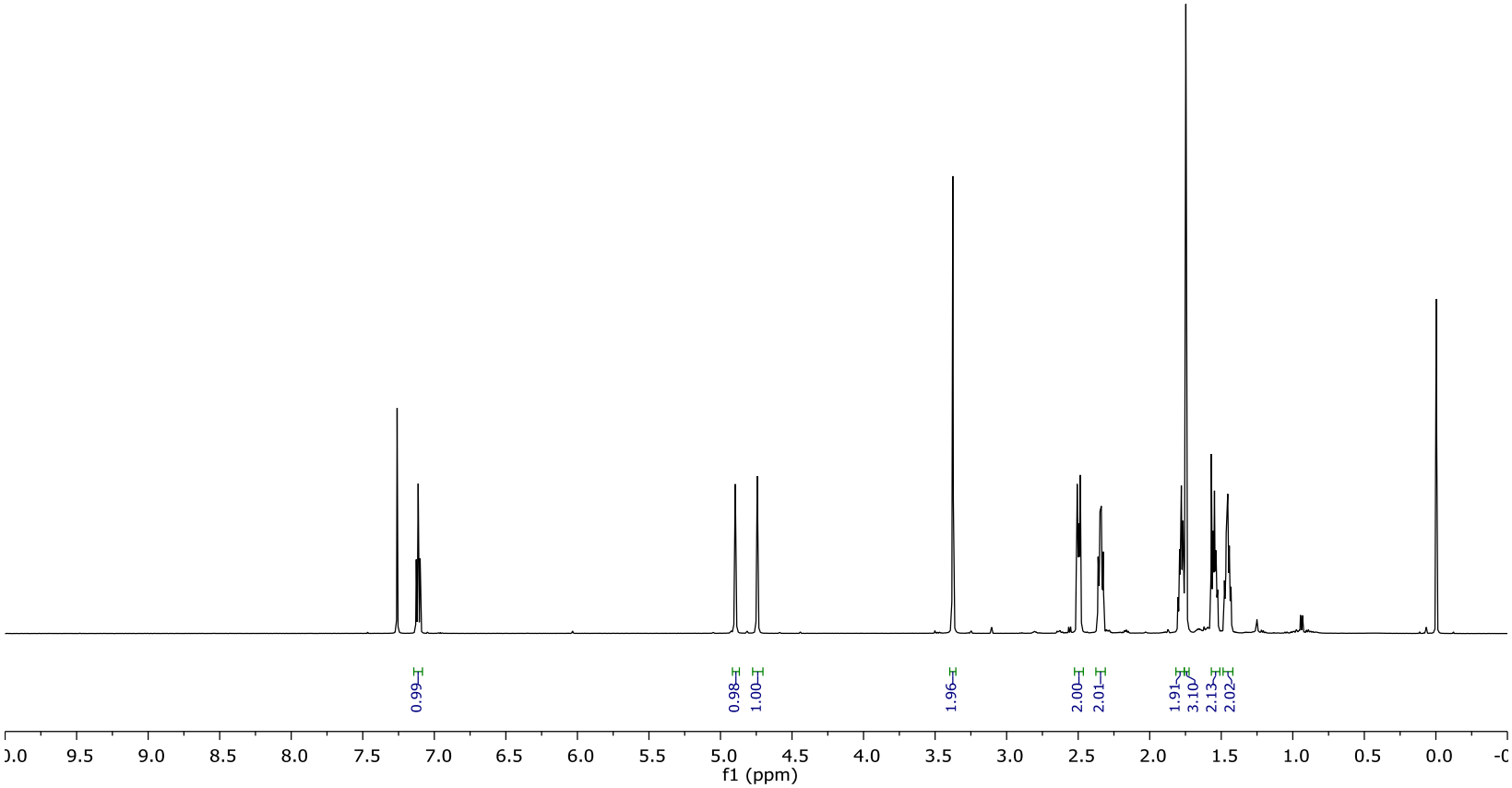


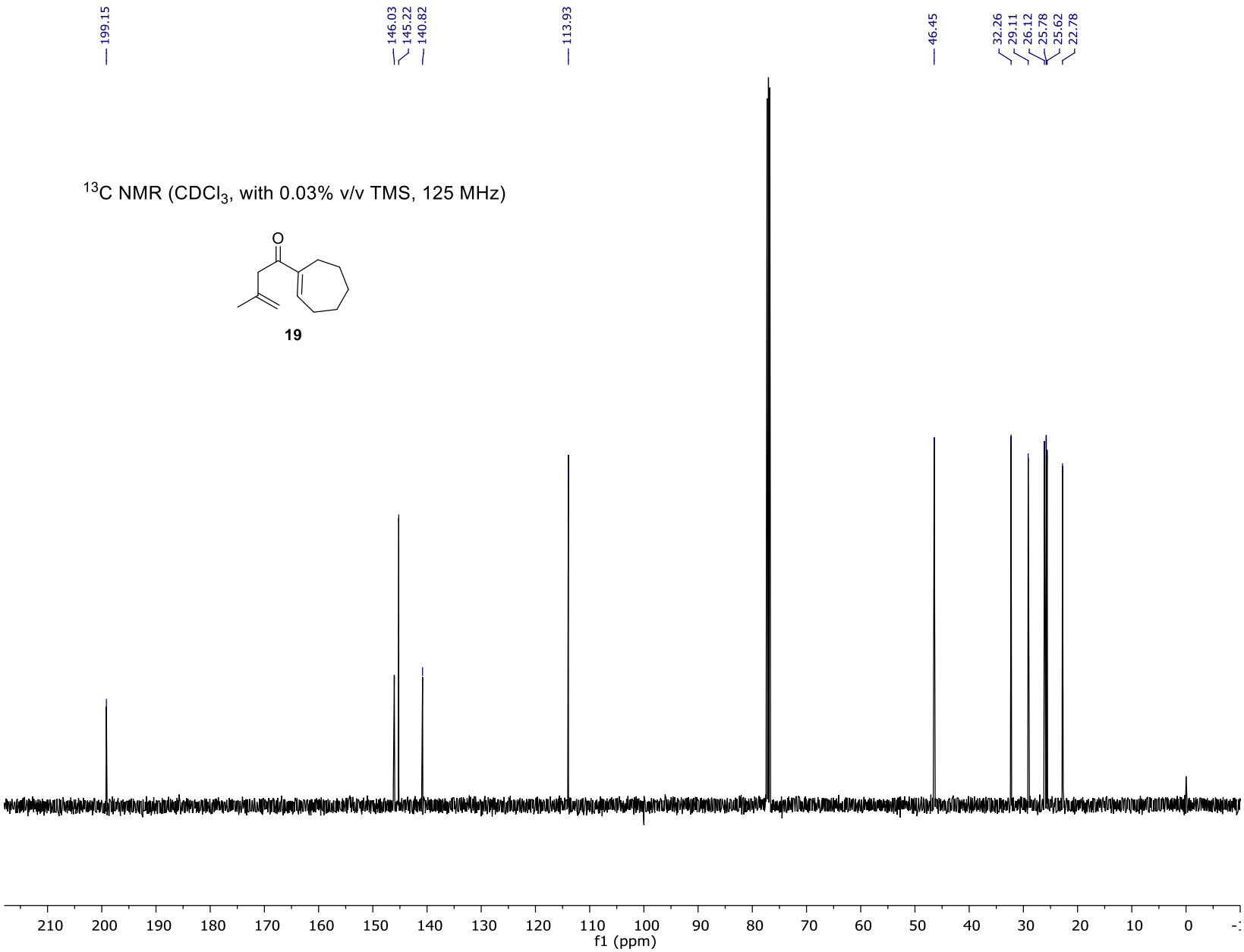

196.76
73.11
71.02
47.54
36.21
25.98
25.34
22.39
21.78
^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)
N_2
OH
O
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

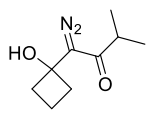


19

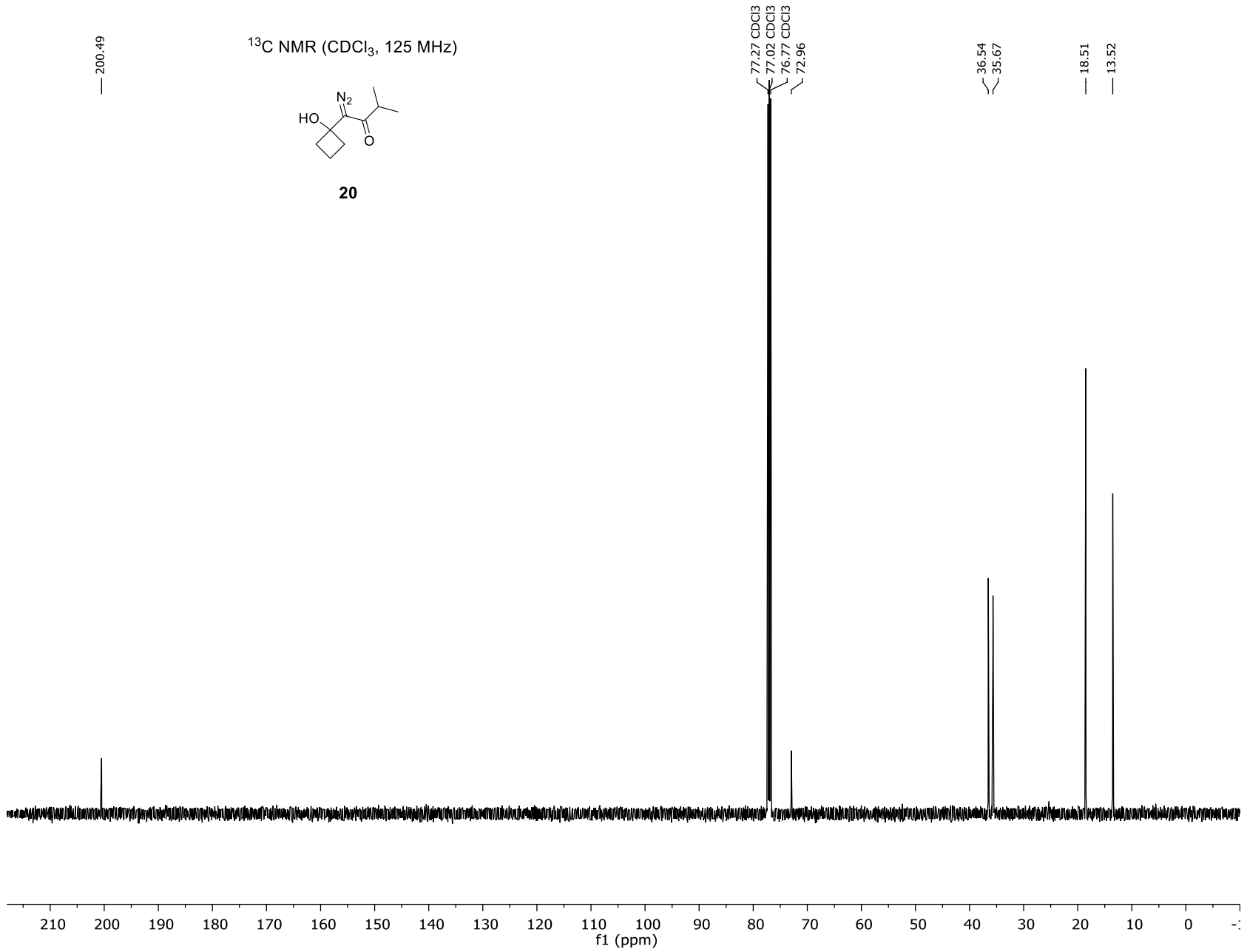



199.15
146.03
145.22
140.82
113.93
46.45
32.26
29.11
26.12
25.78
25.62
22.78
^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)
O
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

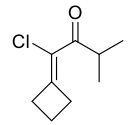
^{1}H NMR ($CDCl_3$, 500 MHz)



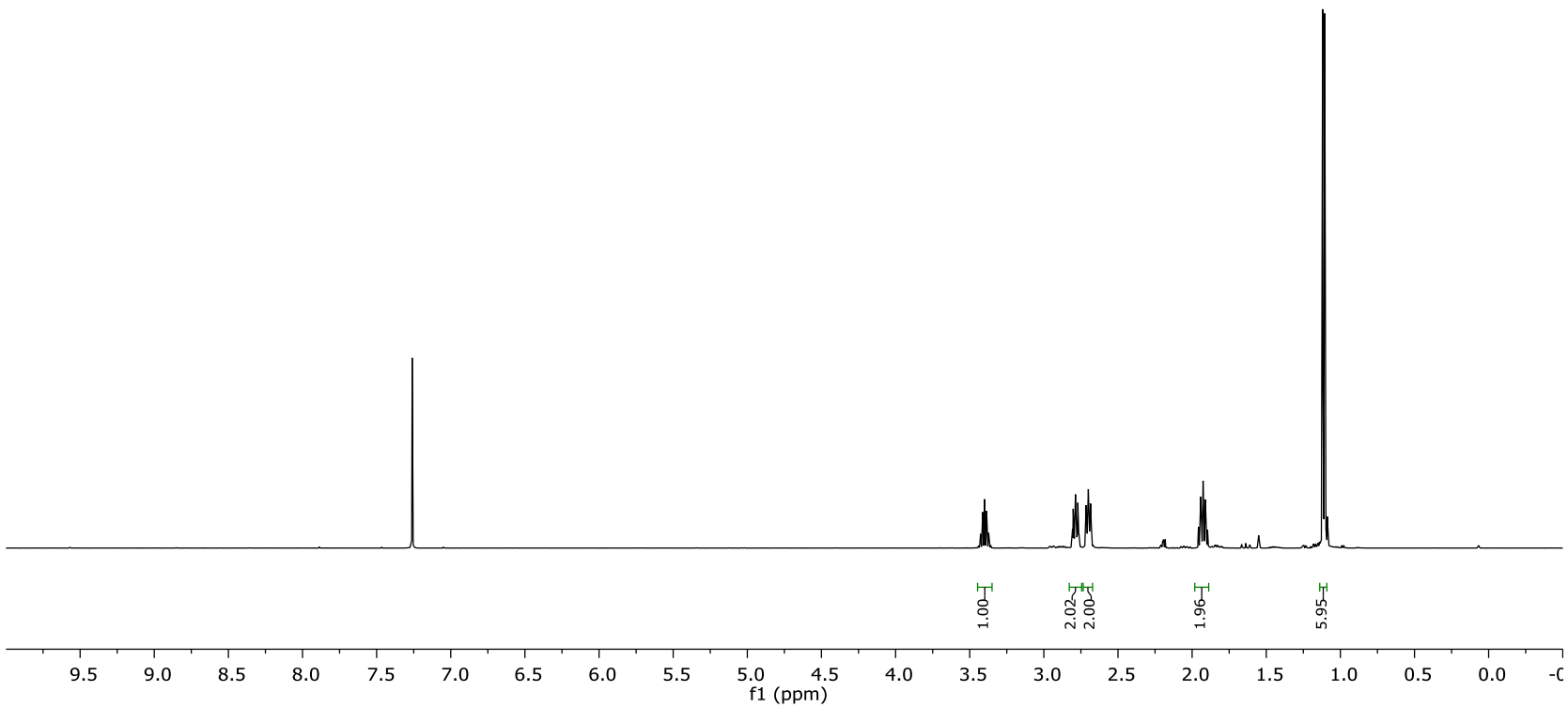
20

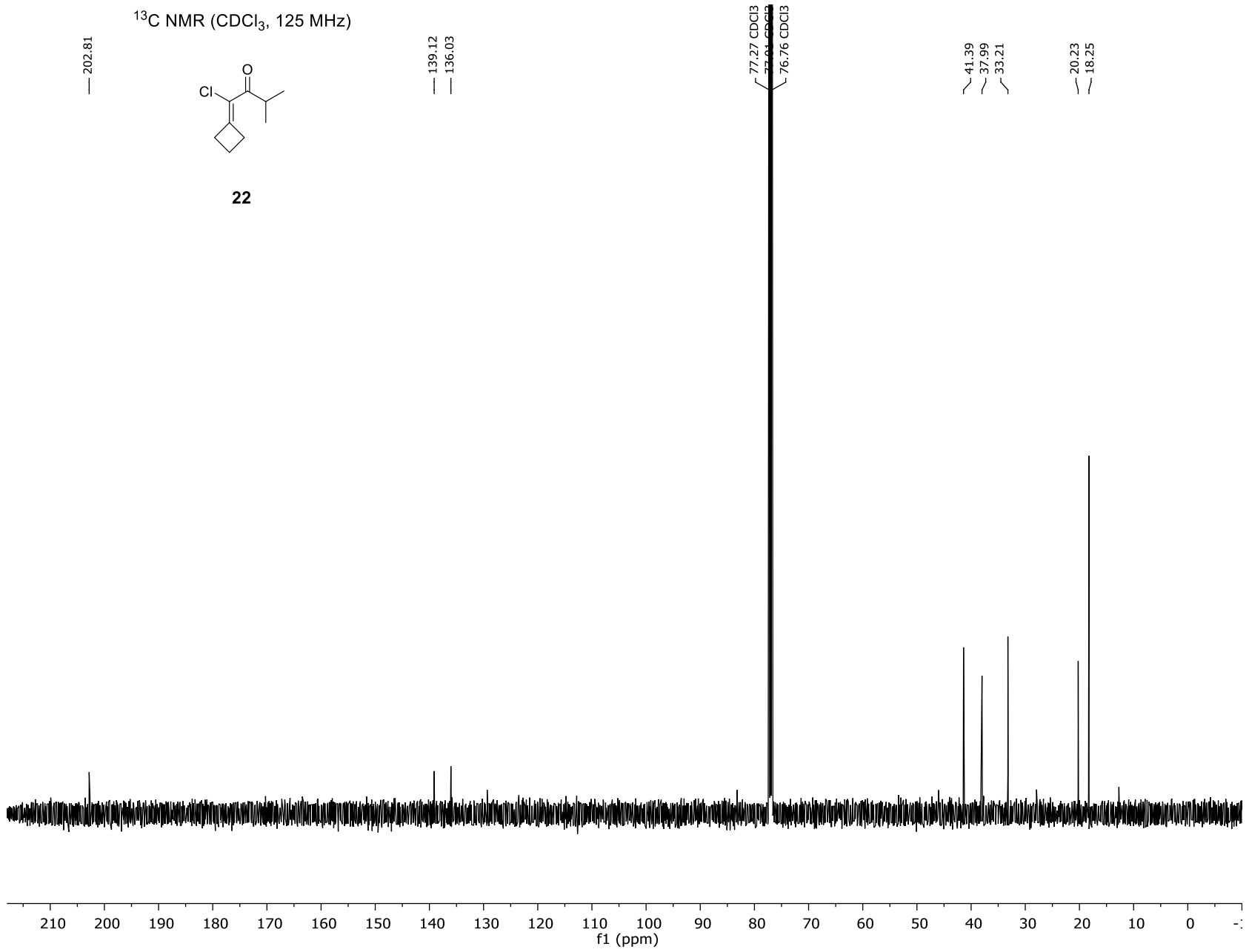

^{13}C NMR ($CDCl_3$, 125 MHz)
200.49
77.27 CDCl3
77.02 CDCl3
76.77 CDCl3
72.96
36.54
35.67
18.51
13.52
HO
N_2
O
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, 500 MHz)

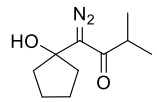


22



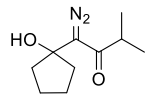

^{13}C NMR ($CDCl_3$, 125 MHz)
202.81
139.12
136.03
77.27 CDCl3
76.76 CDCl3
41.39
37.99
33.21
20.23
18.25
Cl
O
22
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



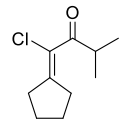
23

^{13}C NMR ($CDCl_3$, 125 MHz)

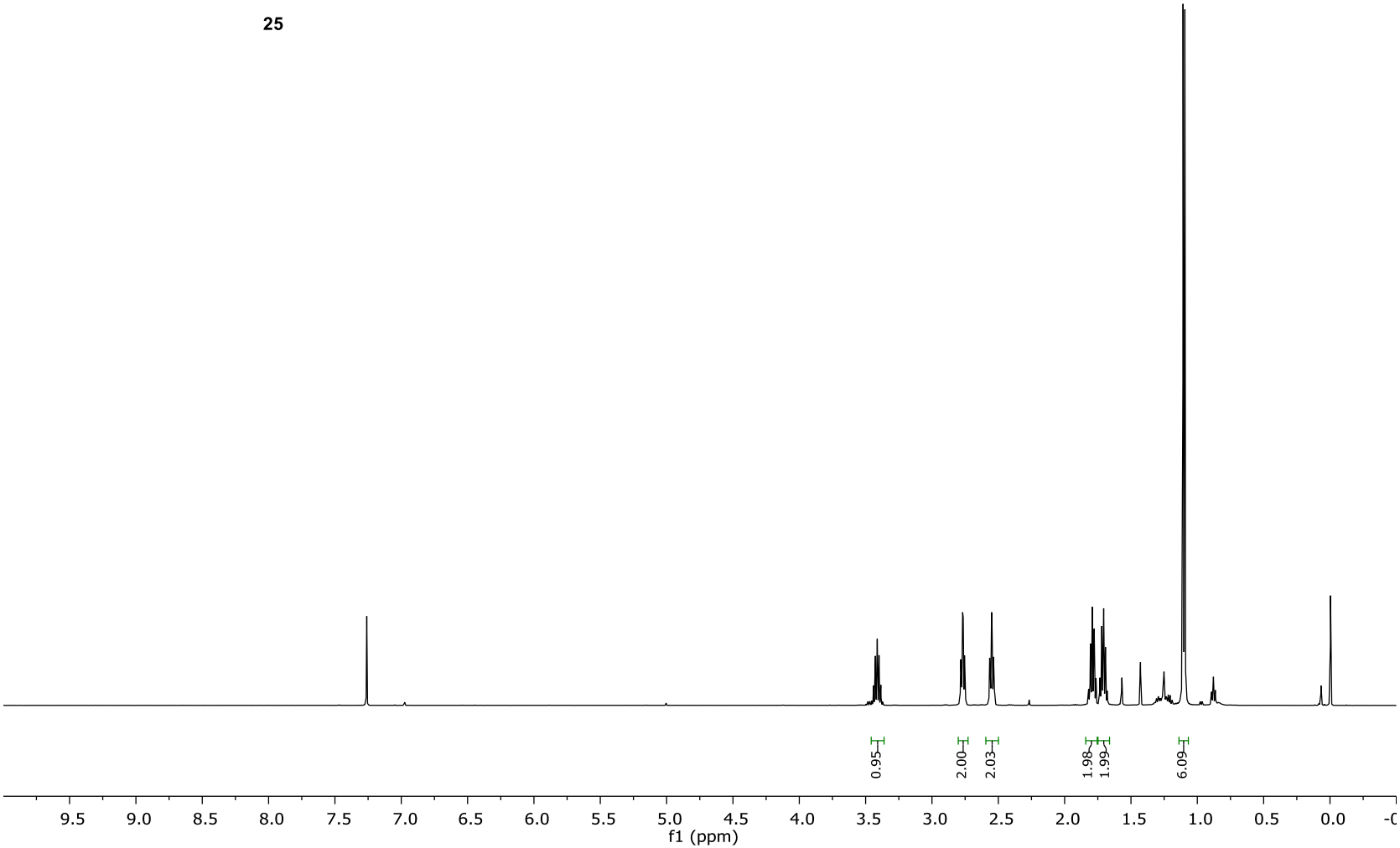


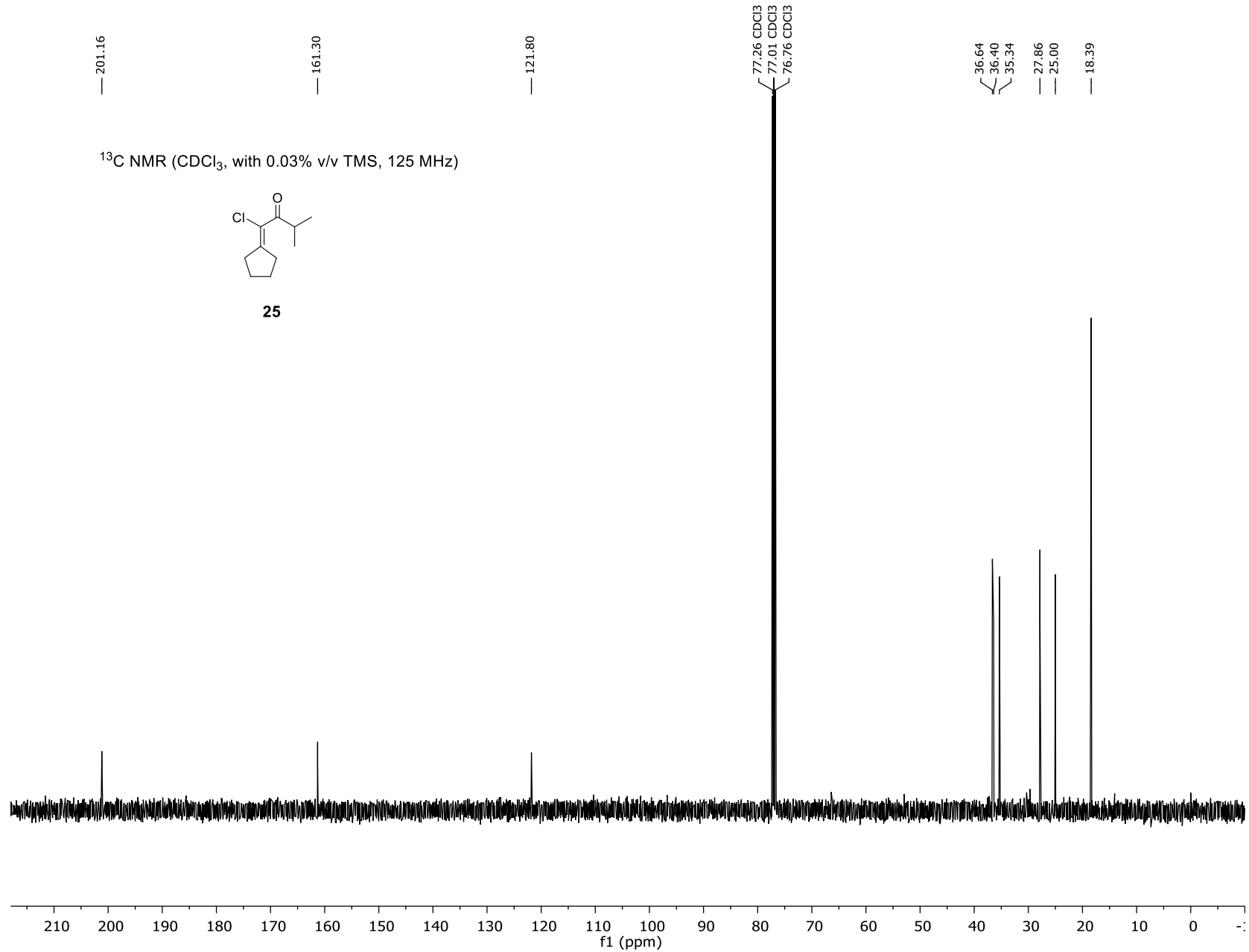
23

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

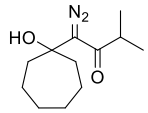


25



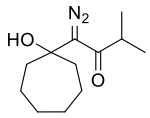

201.16
161.30
121.80
77.26 CDCl3
77.01 CDCl3
76.76 CDCl3
36.64
36.40
35.34
27.86
25.00
18.39
13C NMR (CDCl3, with 0.03% v/v TMS, 125 MHz)
Cl
O
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



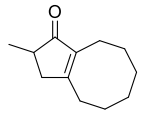
26

^{13}C NMR ($CDCl_3$, with 0.03% v/v TMS, 125 MHz)

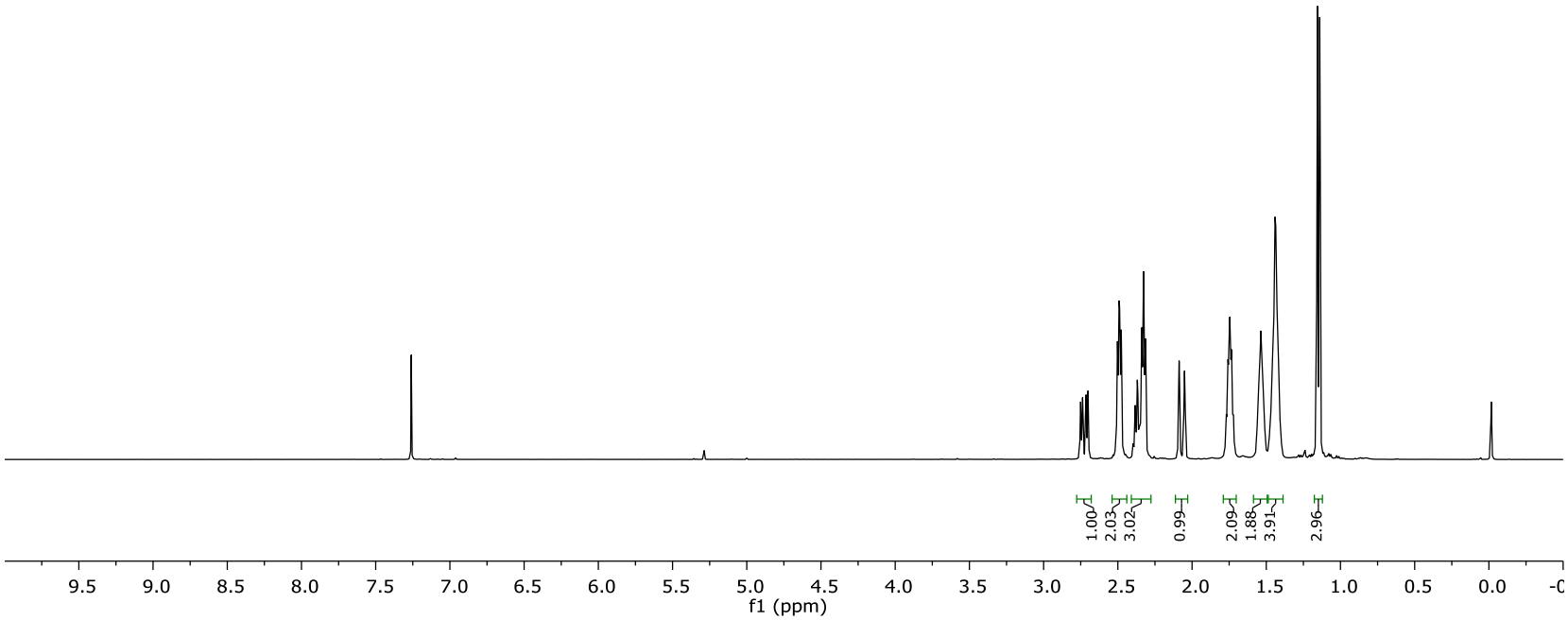


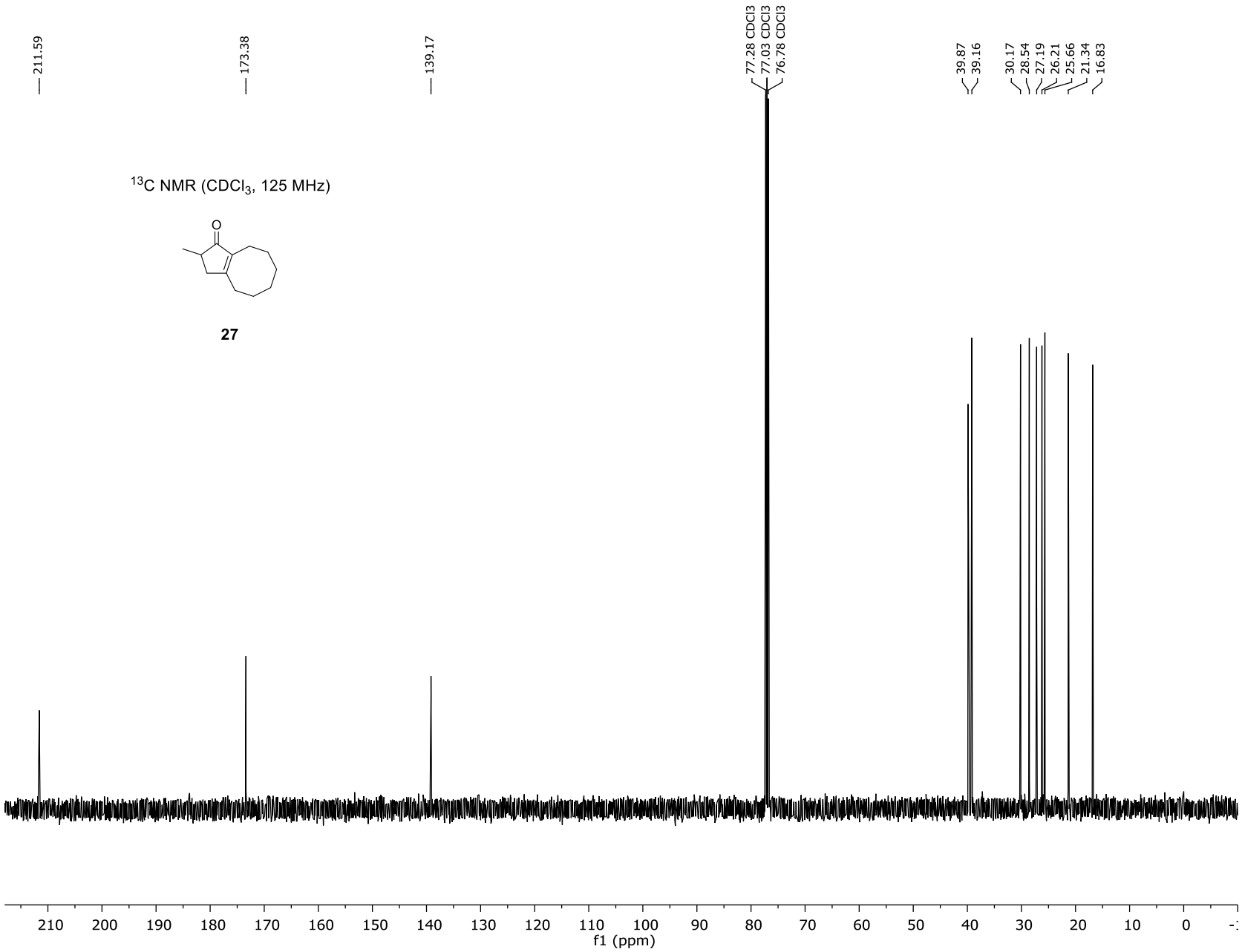
26

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

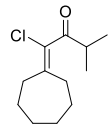


27

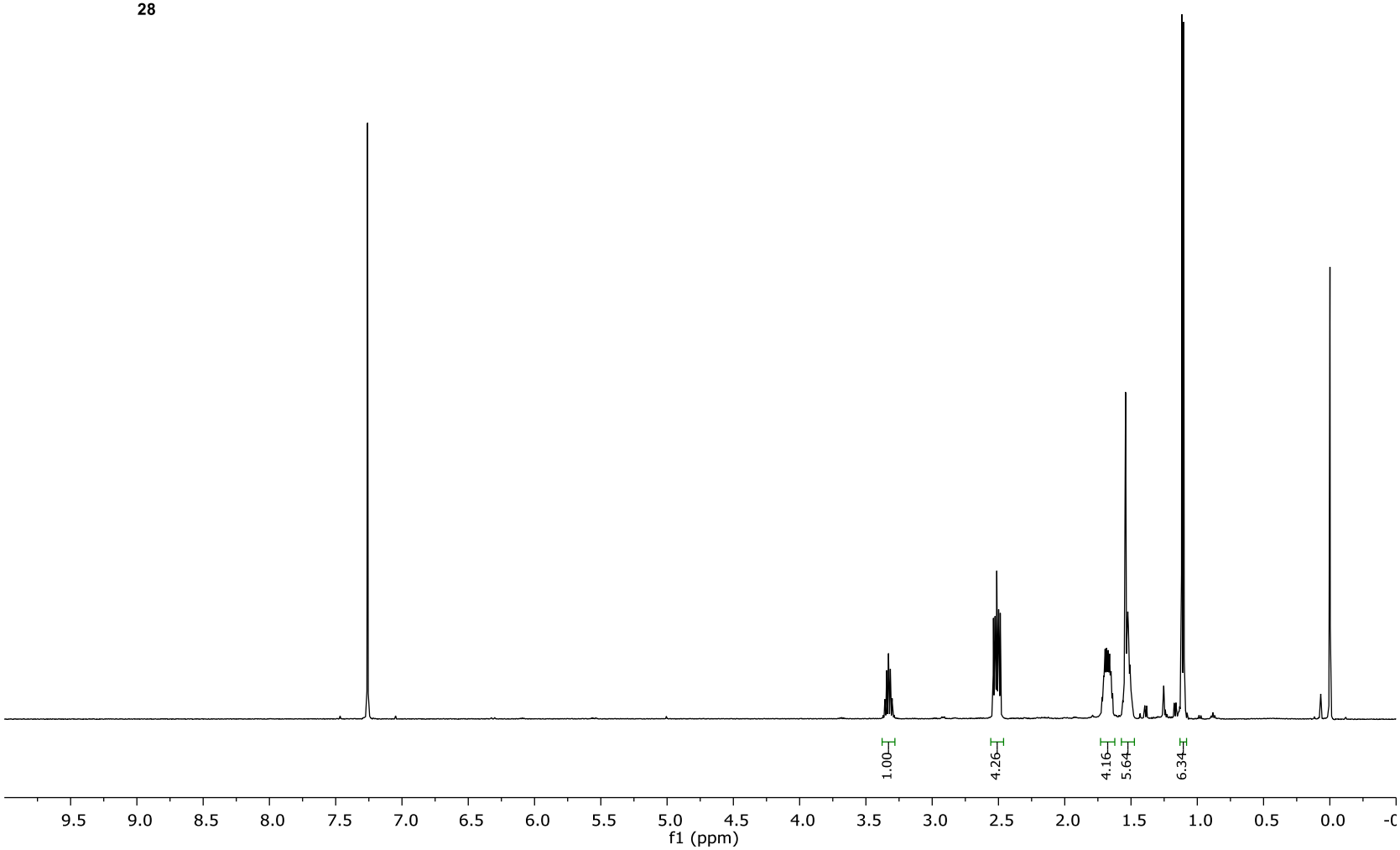


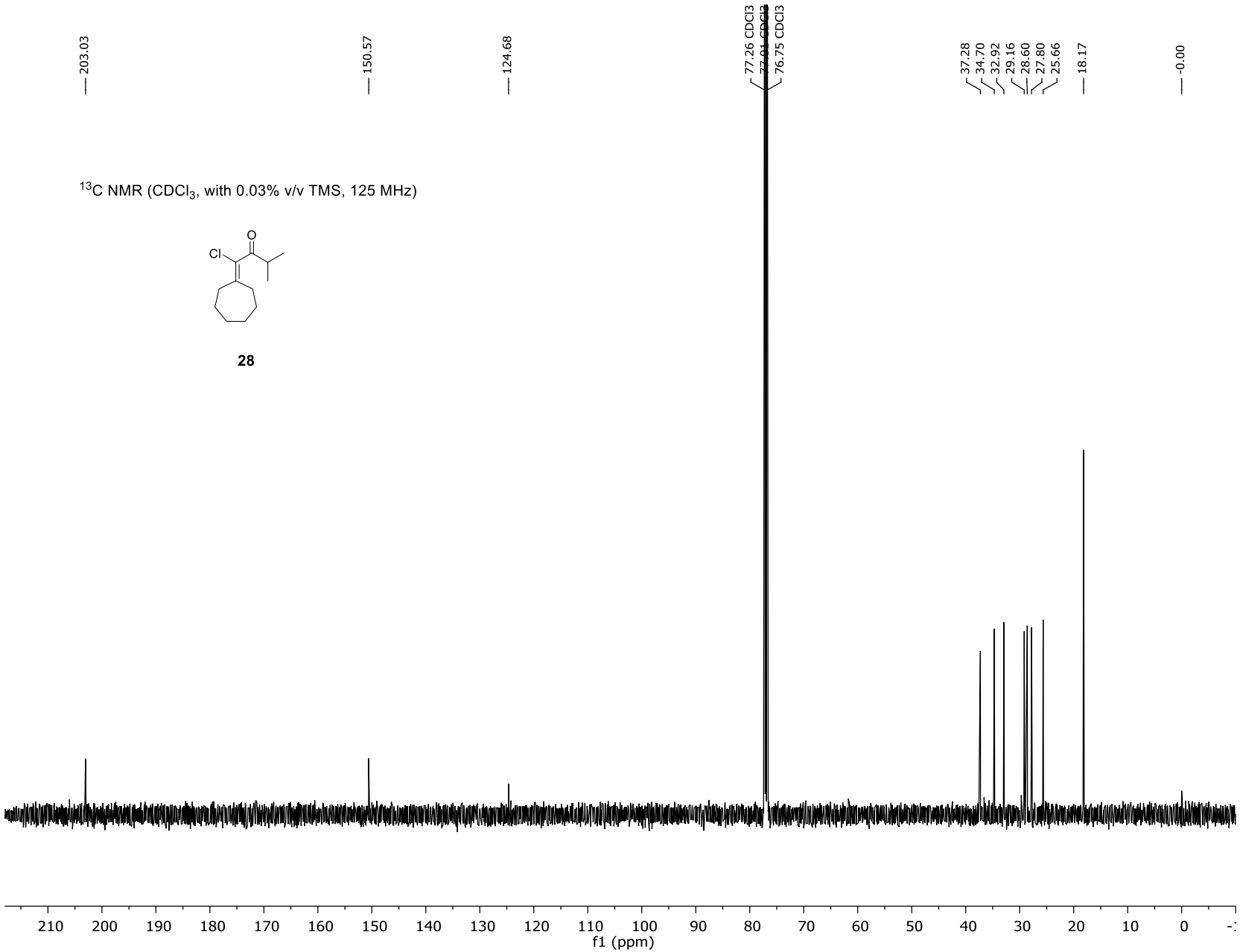

211.59
173.38
139.17
77.28 CDCl3
77.03 CDCl3
76.78 CDCl3
39.87
39.16
30.17
28.54
27.19
26.21
25.66
21.34
16.83
13C NMR (CDCl3, 125 MHz)
O
27
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

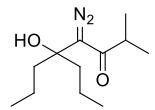


28

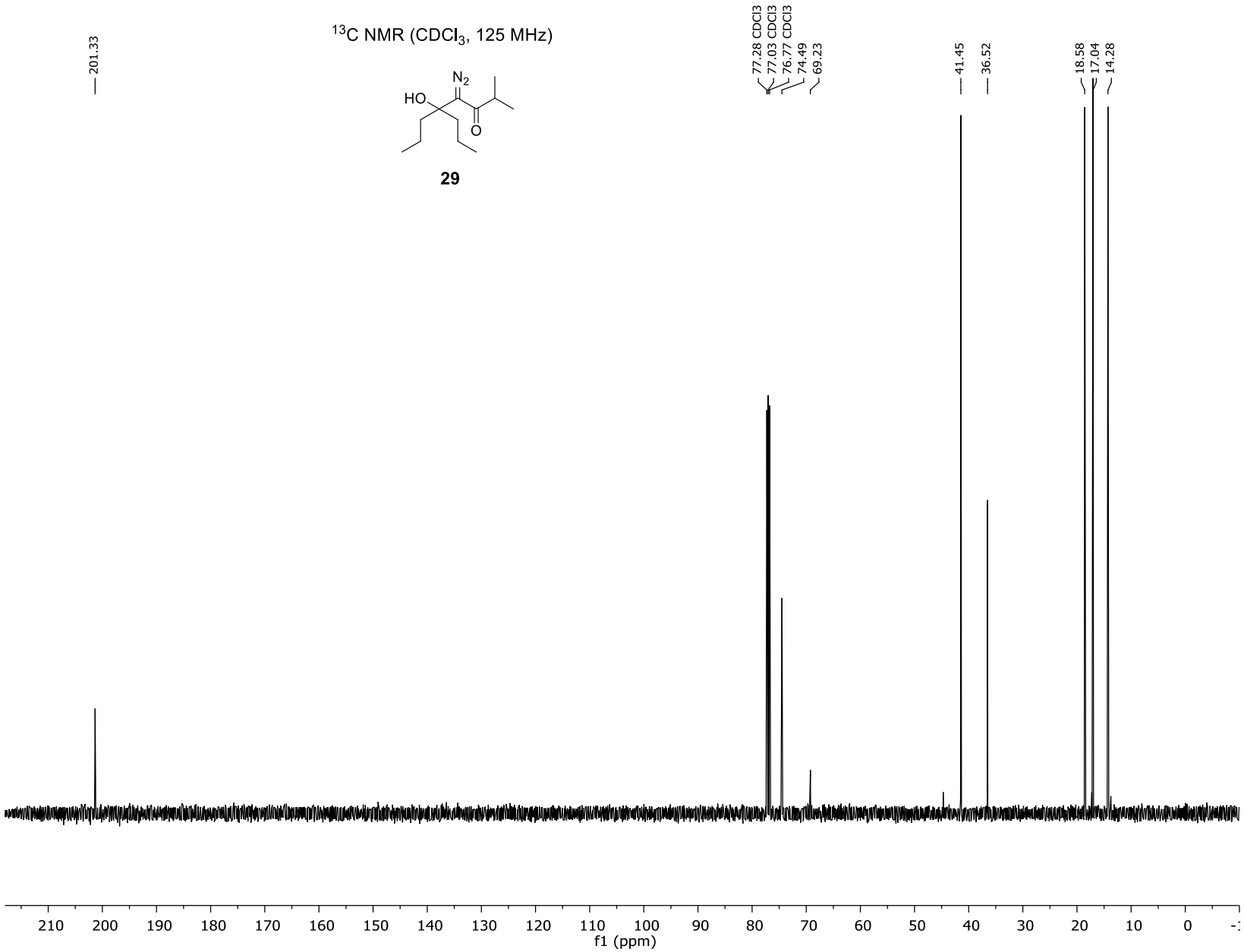



203.03
150.57
124.68
77.26 CDCl3
77.01 CDCl3
76.75 CDCl3
37.28
34.70
32.92
29.16
28.60
27.80
25.66
18.17
-0.00
13C NMR (CDCl3, with 0.03% v/v TMS, 125 MHz)
O
Cl
28
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

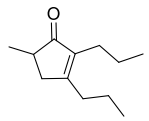
^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



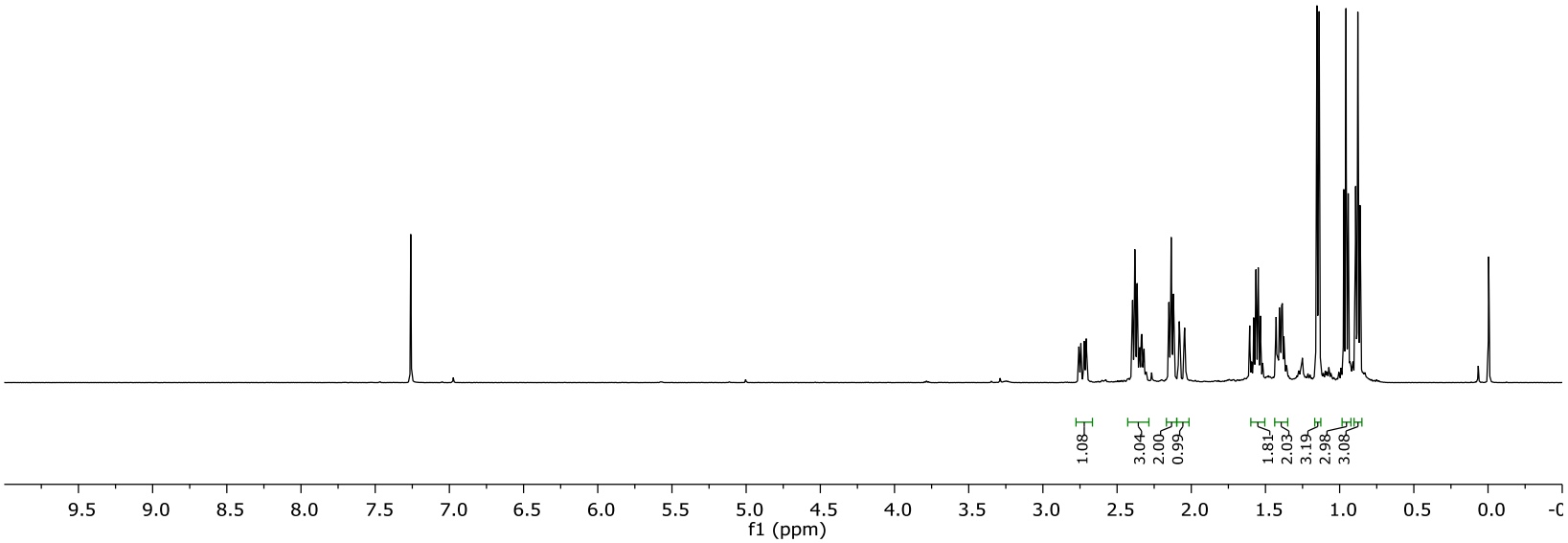
29

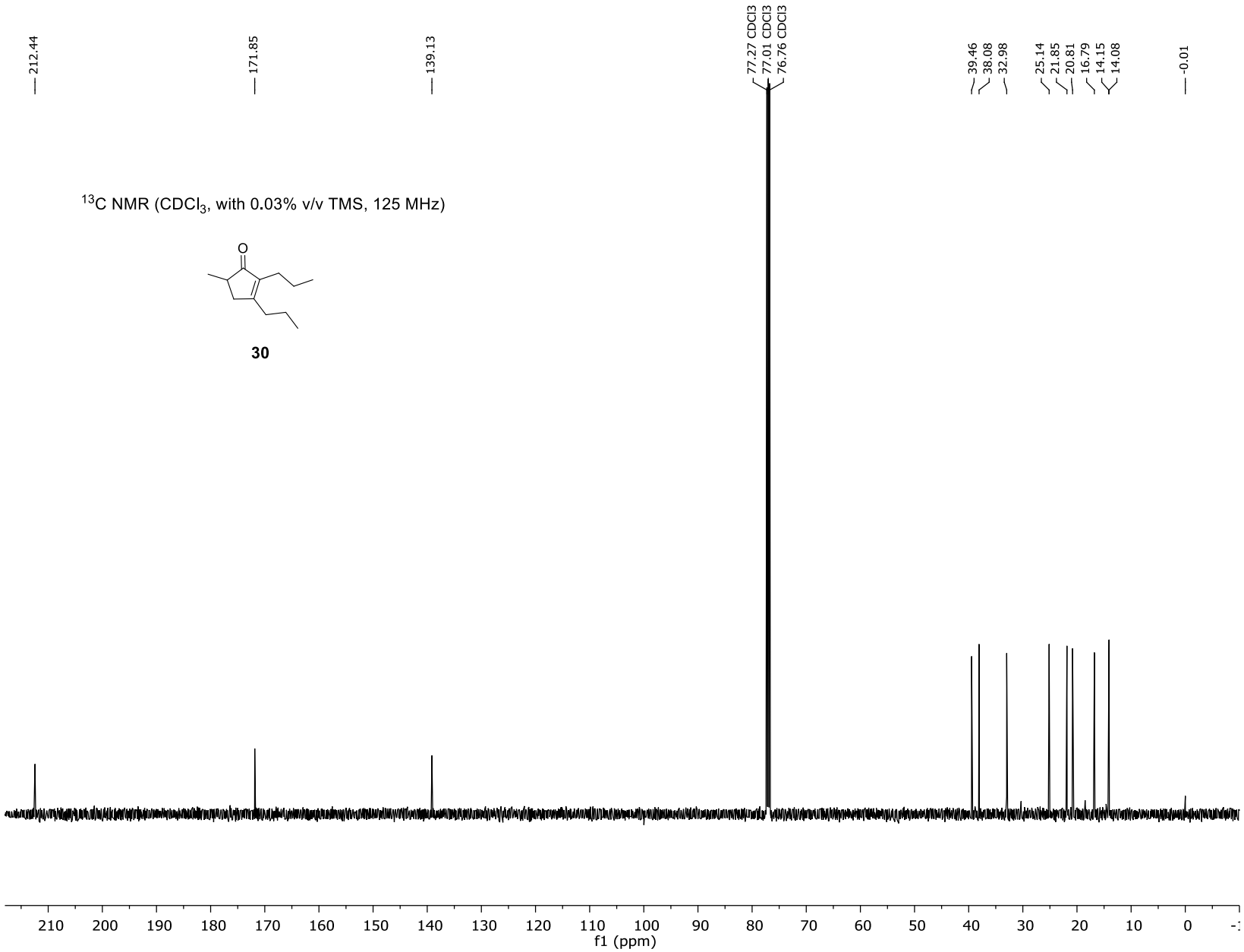

^{13}C NMR ($CDCl_3$, 125 MHz)
29
201.33
77.28 CDCl3
77.03 CDCl3
76.77 CDCl3
74.49
69.23
41.45
36.52
18.58
17.04
14.28
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)

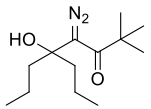


30

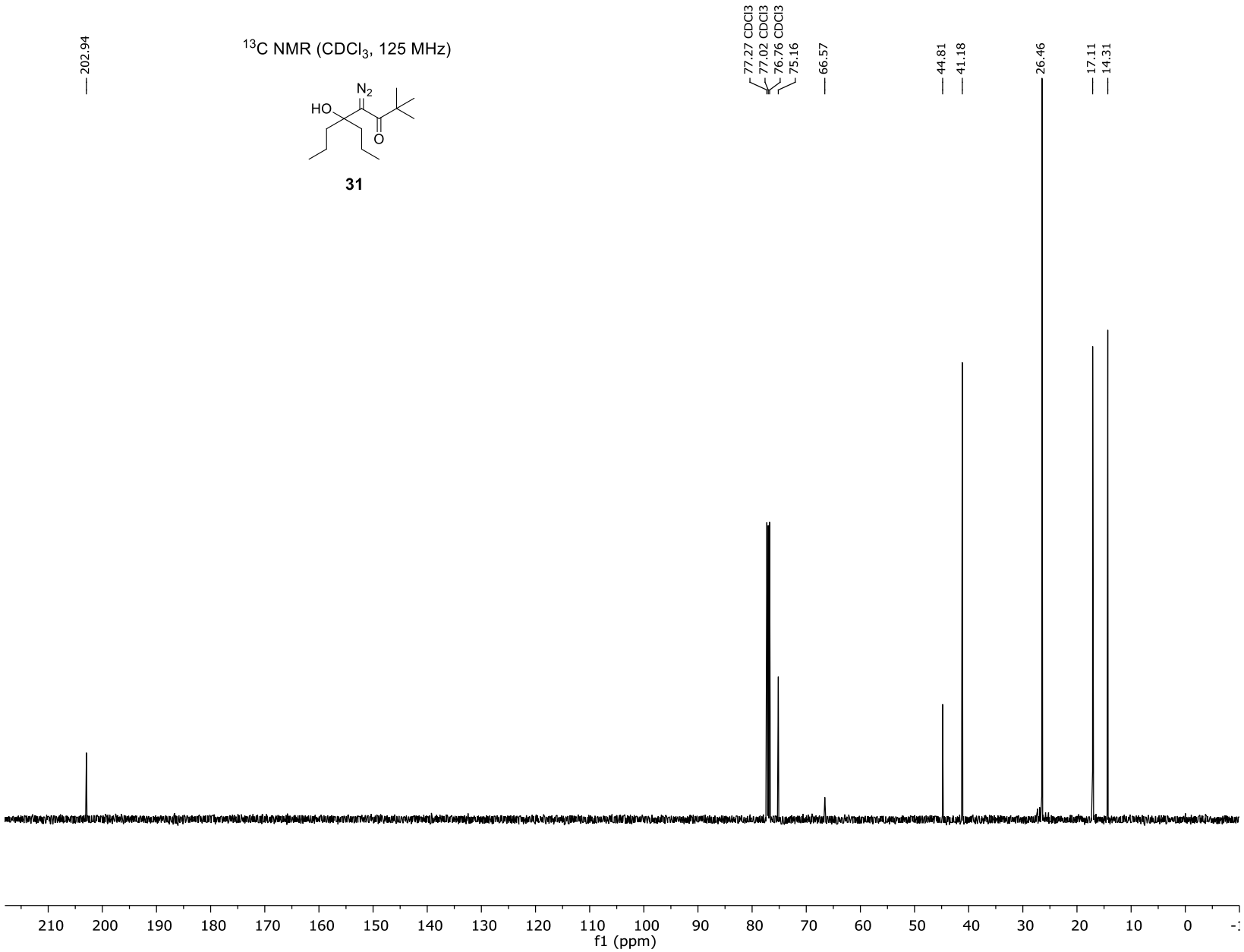



212.44
171.85
139.13
77.27 CDCl3
77.01 CDCl3
76.76 CDCl3
39.46
38.08
32.98
25.14
21.85
20.81
16.79
14.15
14.08
-0.01
13C NMR (CDCl3, with 0.03% v/v TMS, 125 MHz)
O
30
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

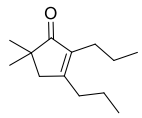
^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



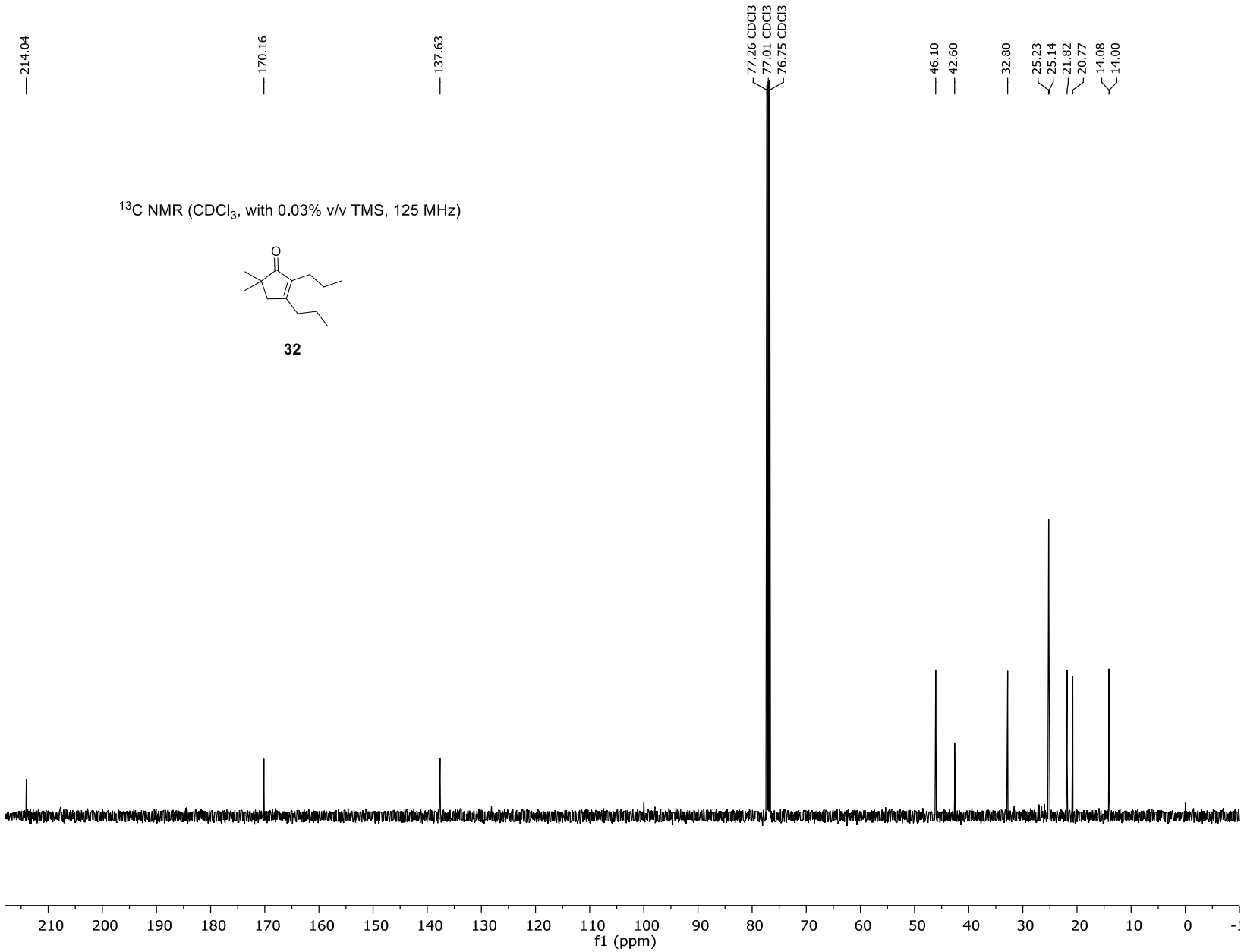
31


202.94
^{13}C NMR ($CDCl_3$, 125 MHz)
N_2
HO
O
31
77.27 CDCl3
77.02 CDCl3
76.76 CDCl3
75.16
66.57
44.81
41.18
26.46
17.11
14.31
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

^{1}H NMR ($CDCl_3$, with 0.03% v/v TMS, 500 MHz)



32


214.04
170.16
137.63
77.26 CDCl3
77.01 CDCl3
76.75 CDCl3
46.10
42.60
32.80
25.23
25.14
21.82
20.77
14.08
14.00
13C NMR (CDCl3, with 0.03% v/v TMS, 125 MHz)
O
32
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)