Supporting information

$Bi(OTf)_3$-catalysed intramolecular cyclisation of unsaturated acetals

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1. General experimental conditions

All commercially available chemicals were used without further purification. Moisture sensitive reactions were performed under nitrogen. CH_2Cl_2 and $MeNO_2$ were dried with 4 Å molecular sieves.

GC analysis were performed on an Agilent Technologies 6980N, with an Agilent Technologies HP5 (30 m x 250 µm) column. It is equipped with a FID detector and uses hydrogen as carrier gas.

GC-MS analysis were performed on an Agilent Technologies 7890N, equipped with a Mass Agilent technologies 5975C VL MSD detector using hydrogen as carrier gas. Equipped with a polar Agilent Technologies HP-Innowax (20 m x 180 µm) and an apolar Agilent Technologies DB-1MS UI (20 m x 180 µm) column.

High resolution mass spectra were determined on a GC-QTOF 7200 Accurate Mass.

^{1}H NMR spectra were obtained on Bruker 300 MHz and 500 MHz FT-NMR spectrometers. ^{13}C NMR spectra were recorded at 75 MHz and 126 MHz. Multiplicity is indicated as follows: s (singlet); bs (broad singlet); d (doublet); t (triplet); q (quartet); m (multiplet); dd (doublet of doublets), etc...

Flash chromatography was performed with a Teledyne Isco Combiflash Rf^{+} Lumen™ using RediSep Rf Gold columns.

Thin-layer chromatography (TLC) was performed on precoated glass-backed plates (Merck Kieselgel 60 F254), and components were visualized by observation under UV light or by treating the plates with $KMnO_4/H_2SO_4$ followed by heating.

2. Synthesis of the starting materials

Compounds **1a**-**1i** were obtained via a first allylation procedure **A**, followed by an alkylation procedure **B** (for **1a**, **1b**, **1d**-**1g**, **1i**), or **C** (for **1c, 1h**).

General procedure A for the allylation of malonates: A solution of NaOMe (2.472 kg, 13.72 mol, 30% wt in MeOH) and KI (12 g, 74 mmol) were added in MeOH (6 L) at 25 °C and treated dropwise with a solution of dimethyl malonate (1.95 kg, 14.76 mol). The reaction was stirred at 25 °C for 30 min. The corresponding allyl bromide or chloride (14.76 mol) was then added dropwise. After 18 hours at 25 °C, the solvent was removed under reduced pressure before adding an aqueous solution of HCl 10% until pH = 1. The organic layer was separated from the aqueous phase. The aqueous phase was extracted with methyl *t*-butyl ether (MTBE, 2 x 300 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by distillation.

Dimethyl 2-(3-methylbut-2-en-1-yl)malonate: allylation with 1-bromo-3-methylbut-2-ene (2.2 kg, 14.76 mol); distillation at 74 °C under 0.4 Torr. Yellowish liquid (2.1 kg, 10.49 mol, 71%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ [ppm] 5.11 – 4.99 (m, 1H), 3.74 (s, 6H), 3.37 (t, *J* = 7.7 Hz, 1H), 2.60 (t, *J* = 7.5 Hz, 2H), 1.69 (d, *J* = 1.4 Hz, 3H), 1.63 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ [ppm] 169.62 (2C), 135.14, 119.43, 52.50, 52.41, 51.90, 27.61, 25.77, 17.70. **FT-IR** λ max (NaCl): 955, 1733, 1240, 1147 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{10}H_{16}O_4$ [M^+] 200.1049, found 200.1046.

Dimethyl-2-methallyl malonate (Propanedioic acid, 2-(2-methyl-2-propen-1-yl)-, 1,3-dimethyl ester)**:** reaction on a 1.045 mol scale with methallyl chloride (18 h, 25 °C); distillation at 82 °C under 0.4 Torr as a colorless liquid (127 g, 0.683 mol, 65%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ [ppm] 4.78 (s, 1H), 4.71 (s, 1H), 3.73 (m, 6H), 3.61 (t, *J* = 7.8 Hz, 1H), 2.61 (d, *J* = 7.8 Hz, 2H), 1.73 (s, 3H). **^{13}C-NMR** (75 MHz, $CDCl_3$): δ 169.44 (2C), 141.55, 112.31, 52.52, 52.49, 50.26, 36.52, 22.21. **FT-IR** λ max (NaCl): 2955, 1733, 1651, 1226, 1149, 896 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_9H_{14}O_4$ [M^+] 186.0892, found 186.0887.

Dimethyl-2-cinnamyl malonate: reaction on a 1.309 mol with cinnamyl chloride (4 h, 25 °C); distillation at 141 °C under 0.5 Torr as a colorless liquid (177 g, 0.713 mol, 54%). **^{1}H-NMR** (300 MHz, $CDCl_3$): δ [ppm] 7.38 – 7.19 (m, 5H), 6.50 (d, *J* = 15.8, 1H), 6.16 (dt, *J* = 15.8, 7.2 Hz, 1H), 3.76 (s, 6H), 3.55 (t, *J* = 7.5 Hz, 1H), 2.83 (td, *J* = 7.3, 1.4 Hz, 2H). **^{13}C-NMR** (0 MHz, $CDCl_3$): δ [ppm] 169.26 (2C), 136.98, 132.93, 128.51, 127.43, 126.21, 125.35, 52.60 (2C), 51.74, 32.27. **FT-IR** λ max (NaCl): 3026, 2953, 1732, 1598, 1227, 1150, 744, 693 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{14}H_{16}O_4$ [M^+] 248.1049, found 248.1050.

General procedure B for the alkylation of allylated malonates: A solution of the allylated malonate (115 mmol) was added dropwise to a solution of NaOMe (23 mL, 121 mmol, 30% wt in MeOH) and KI (572 mg, 3.45 mmol) in MeOH (15 mL) at 25 °C. The mixture was stirred at 25 °C for 30 min. The corresponding bromoacetal (148 mmol) was then added dropwise. After 19 hours at reflux, the solvent was removed under reduced pressure before adding a saturated aqueous bicarbonate solution. The organic phase was extracted with MTBE (2 x 50 mL). The combined organic layers where dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by distillation.

Dimethyl 2-(2,2-dimethoxyethyl)-2-(3-methylbut-2-en-1-yl)malonate, 1a: alkylation of dimethyl 2-(3-methylbut-2-en-1-yl)malonate (100 g, 499 mmol) with 2-bromo-1,1-dimethoxyethane (100 g, 589 mmol). Distillation at 120 °C under 0.8 Torr. Colorless liquid (46.7 g, 162 mmol, 32%). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 4.99 – 4.89 (m, 1H), 4.45 (td, J = 5.6, 1.2 Hz, 1H), 3.74 – 3.67 (m, 6H), 3.30 (m, 6H), 2.66

(d, *J* = 7.5, 1.0 Hz, 2H), 2.20 (dd, *J* = 5.6, 1.2 Hz, 2H), 1.70 (s, 3H), 1.62 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.71 (2C), 136.01, 117.38, 101.99, 55.30, 53.56, 53.54, 52.36, 52.33, 35.89, 32.03, 26.02, 17.88. **FT-IR** λ max (NaCl): 2835, 1736, 1676, 1233, 1217, 1181, 852 cm^{-1}. **HRMS** (ESI$^+$) calcd. for $C_{13}H_{21}O_5^+$ [M^+-OMe] 257.1384, found 257.1363.

Dimethyl 2-(3,3-dimethoxypropyl)-2-(3-methylbut-2-en-1-yl)malonate, 1b: alkylation of dimethyl 2-(3-methylbut-2-en-1-yl)malonate (23 g, 115 mmol) with 3-bromo-1,1-dimethoxypropane (25 g, 137 mmol). Distillation at 110 °C under 0.4 Torr. Colorless liquid (16 g, 52.9 mmol, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.01 – 4.87 (m, 1H), 4.34 (t, *J* = 5.7 Hz, 1H), 3.71 (s, 6H), 3.29 (s, 6H), 2.61 (d, 2H), 1.97 – 1.84 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.56 – 1.41 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.85 (2C), 135.64, 117.47, 104.15, 57.26, 52.55, 52.52, 52.32, 52.29, 31.46, 27.50, 27.34, 25.97, 17.84. **FT-IR** λ max (NaCl): 3473, 2833, 1735, 1676, 1276, 1225, 852 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{15}H_{26}O_6$ [M^+] 302.1729, found 302.1693.

Dimethyl 2-(2,2-dimethoxyethyl)-2-(2-methylallyl)malonate, 1d: alkylation of dimethyl-2-methallyl malonate (23 g, 124 mmol) with 2-bromo-1,1-dimethoxyethane (25 g, 148 mmol). Distillation at 107 °C under 0.6 Torr. Colorless liquid (8 g, 29.2 mmol, 24%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.89 and 4.75 (m, 2H), 4.49 (t, *J* = 5.5 Hz, 1H), 3.71 (s, 6H), 3.29 (s, 6H), 2.76 (s, 2H), 2.21 (d, *J* = 5.5 Hz, 2H), 1.64 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.74 (2C), 140.28, 116.04, 101.87, 54.41, 53.58, 53.56, 52.40, 52.38, 41.22, 36.07, 23.00. **FT-IR** λ max (NaCl): 2832, 1727, 1285, 1178, 1104, 908 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{12}H_{29}O_5^+$ [M^+-OMe] 243.1227, found 243.1209

Diisopropyl 2-(2,2-dimethoxyethyl)-2-(3-methylbut-2-en-1-yl)malonate, 1e: alkylation of diisopropyl 2-(3-methylbut-2-en-1-yl)malonate (20 g, 78 mmol) with 2-bromo-1,1-dimethoxyethane (15.8 g, 94 mmol). Distillation at 120 °C under 0.4 Torr. Colorless liquid (11 g, 31.9 mmol, 41%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.11 – 4.87 (m, 3H), 4.45 – 4.34 (m, 1H), 3.34 – 3.22 (m, 6H), 2.63 (d, J = 7.2 Hz, 2H), 2.23 – 2.13 (m, 2H), 1.71 – 1.58 (m, 6H), 1.24 – 1.18 (m, 12H). **^{13}C NMR** (75 MHz, CDCl3) δ 170.70 (2C), 135.14, 117.85, 102.04, 68.54 (2C), 55.10, 53.23 (2C), 35.17, 31.29, 25.96, 21.54 (2C), 21.47 (2C), 18.03. **FT-IR** λ max (NaCl): 2832, 1726, 1285, 1178, 1104, 908 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{19}H_{29}O_5^+$ [M^+-OMe] 313.2010, found 313.1982.

Dimethyl 2-cinnamyl-2-(2,2-dimethoxyethyl)malonate, 1f: alkylation of dimethyl-2-cinnamyl malonate (30 g, 121 mmol) with 2-bromo-1,1-dimethoxyethane (24.5 g, 145 mmol). Distillation at 140 °C under 0.1 Torr. Colorless liquid (8.5 g, 25.3 mmol, 21%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.18 (m, 5H), 6.46 (d, *J* = 15.7, 1.4 Hz, 1H), 6.02 (dt, *J*= 15.7, 7.5 Hz, 1H), 4.52 (t, *J* = 5.3 Hz, 1H), 3.74 (s, 6H), 3.32 (s, 6H), 2.86 (dd, *J* = 7.5, 1.4 Hz, 2H), 2.27 (d, *J* = 5.4 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.35 (2C), 136.95, 134.26, 128.56, 128.50, 127.49, 126.28, 126.23, 123.68, 101.96, 55.64, 53.68 (2C), 52.48 (2C), 37.23, 36.24. **FT-IR** λ max (NaCl): 2833, 1731, 1598, 1178, 740, 693 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{18}H_{24}O_6$ [M^+] 336.1573, found 336.1568.

Dimethyl 2-cinnamyl-2-(3,3-dimethoxypropyl)malonate, 1g: alkylation of dimethyl-2-cinnamyl malonate (28 g, 113 mmol) with 3-bromo-1,1-dimethoxypropane (24.8 g, 135 mmol). Distillation at 167 °C under 0.1 Torr. Colorless liquid (18.2 g, 51.9 mmol, 46%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.04 (dt, *J* = 15.7, 7.5 Hz, 1H), 4.36 (t, *J* = 5.6 Hz, 1H), 3.74 (s, 6H), 3.31 (s, 6H), 2.81 (d, *J* = 7.5 Hz, 2H), 2.03 – 1.93 (m, 2H), 1.62 – 1.53 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.53 (2C), 137.03, 133.97, 128.48 (2C), 127.42, 126.22 (2C), 123.81, 104.08, 57.57, 52.66 (2C),

52.49 (2C), 36.76, 27.89, 27.31. **FT-IR** λ max (NaCl): 2831, 1730, 1598, 1194, 1053, 741, 693 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{19}H_{26}O_6$ [M^+] 350.1729, found 350.1738.

Dimethyl 2-(3,3-dimethoxypropyl)-2-(2-methylallyl)malonate, 1i: alkylation of dimethyl-2-methallyl malonate (21 g, 113 mmol) with 3-bromo-1,1-dimethoxypropane (24.6 g, 134 mmol). Distillation at 116 °C under 0.5 Torr. Colorless liquid (10 g, 34.7 mmol, 31%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.86 and 4.74 (m, 2H), 4.32 (t, *J* = 5.7 Hz, 1H), 3.72 (s, 6H), 3.29 (s, 6H), 2.70 (s, 2H), 2.01 – 1.88 (m, 2H), 1.64 (s, 3H), 1.58 – 1.41 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.86 (2C), 140.42, 115.68, 104.21, 56.70, 52.66 (2C), 52.40, 52.38, 40.60, 27.58, 27.46, 23.04. **FT-IR** λ max (NaCl): 2832, 1731, 1644, 1195, 1055, 896 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{14}H_{24}O_6$ [M^+] 288.1573, found 288.1564.

General procedure for the alkylation by but-3-ene-2-one and further acetalisation: The corresponding allylated malonate (499 mmol) and DBU (38 g, 250 mmol) were added in toluene (100 mL). But-3-ene-2-one (42 g, 599 mmol) was then added dropwise at 20 °C. After 30 minutes, the reaction was quenched with an aqueous solution of HCl 10% (50 mL) and extracted with MTBE (50 mL). The organic layer was washed with H_2O (50 mL), dried over magnesium sulfate and the solvent was removed under reduced pressure. The residue was purified by distillation. For the acetalisation, trimethoxymethane (11,78 g, 111 mmol) and PTSA.H_2O (127 mg, 667.67 μmol) were added in methanol (22 mL). The corresponding dialkylated malonate (111 mmol) was then added dropwise at 20 °C. After 3 hours, the reaction was quenched by adding sodium methanolate (300 mg, 5.55 mmol) in the mixture. Stirred for 5 minutes and then filtered off. The solvent was then removed under reduced pressure. The residue was purified by distillation.

Dimethyl 2-(3,3-dimethoxybutyl)-2-(3-methylbut-2-en-1-yl)malonate, 1c: Preparation of dimethyl 2-(3-methylbut-2-en-1-yl)-2-(3-oxobutyl)malonate, **6**: alkylation of dimethyl 2-(3-methylbut-2-en-1-yl)malonate (100 g, 499 mmol) with DBU (38 g, 250 mmol) and but-3-ene-2-one (42 g, 599 mmol). Distillation at 139 °C under 0.7 Torr. Colorless oil (117 g, 433 mmol, 87%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.99 – 4.85 (m, 1H), 3.69 (s, 6H), 2.58 (d, *J* = 7.5 Hz, 2H), 2.48 – 2.37 (m, 2H), 2.16 – 2.05 (m, 5H), 1.67 (s, 3H), 1.60 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.36, 207.34, 171.69, 135.97, 117.25, 56.91, 52.38, 52.36, 38.74, 32.28, 29.89, 26.47, 25.98, 17.85. **FT-IR** λ max (NaCl): 3470, 2863, 1730, 1677, 1199, 1093 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{14}H_{22}O_5$ [M^+] 270.1467, found 270.1472. Acetalisation of dimethyl 2-(3-methylbut-2-en-1-yl)-2-(3-oxobutyl)malonate, **6** (30 g, 111 mmol) with trimethoxymethane (11,78 g, 111 mmol) and PTSA.H_2O (127 mg, 667.67 μmol). Distillation at 120 °C under 0.5 Torr. Colorless liquid (23 g, 72.7 mmol, 66%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.99 – 4.86 (m, 1H), 3.68 (s, 6H), 3.12 (s, 6H), 2.58 (d, *J* = 7.5 Hz, 2H), 1.94 – 1.79 (m, 2H), 1.66 (s, 3H), 1.59 (s, 3H), 1.51 – 1.39 (m, 2H), 1.23 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.86 (2C), 135.55, 117.51, 101.31, 57.26, 52.29 (2C), 47.91 (2C), 31.34, 30.86, 27.04, 25.96, 20.76, 17.86. **FT-IR** λ max (NaCl): 2823, 1732, 1208, 1052, 850 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{15}H_{25}O_6^+$ [M^+-Me] 301.1646, found 301.1652.

Dimethyl 2-cinnamyl-2-(3,3-dimethoxybutyl)malonate, 1h: Preparation of dimethyl 2-cinnamyl-2-(3-oxobutyl)malonate**:** alkylation of dimethyl 2-cinnamylmalonate (30 g, 121 mmol) with DBU (4.6 g, 30 mmol) and but-3-ene-2-one (18.1 g, 258 mmol). Distillation at 186 °C under 0.1 Torr. Colorless oil (29 g, 91 mmol, 75%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 – 7.07 (m, 5H), 6.55 – 6.35 (m, 1H), 6.14 – 5.93 (m, 1H), 3.74 (s, 6H), 2.90 – 2.72 (m, 2H), 2.60 – 2.43 (m, 2H), 2.30 – 2.08 (m, 5H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 207.16, 171.36 (2C), 136.89, 134.16, 128.51 (2C), 127.52, 126.24 (2C), 123.54, 57.21, 52.55, 52.51, 38.68, 37.65, 29.93, 26.90. **FT-IR** λ max (NaCl): 3028, 1733, 1270, 1182, 748, 696 cm^{-1}. **HRMS** (ESI+)

calcd. for $C_{18}H_{22}O_5$ [M^+] 318.1467, found 318.1467. Acetalisation of dimethyl 2-cinnamyl-2-(3-oxobutyl)malonate (13 g, 40.8 mmol) with trimethoxymethane (4.33 g, 40.8 mmol) and PTSA.H_2O (78 mg, 408 μmol). Distillation at 157 °C under 0.11 Torr. Colorless oil (5.5 g, 15.09 mmol, 37%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.36 – 7.28 (m, 4H), 7.26 – 7.18 (m, 1H), 6.47 (dt, *J* = 15.7, 1.2 Hz, 1H), 6.03 (dt, *J* = 15.7, 7.5 Hz, 1H), 3.74 (s, 6H), 3.16 (s, 6H), 2.82 (dd, *J* = 7.5, 1.2 Hz, 2H), 2.03 – 1.90 (m, 2H), 1.63 – 1.48 (m, 2H), 1.26 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.54 (2C), 137.01, 133.97, 128.50 (2C), 127.43, 126.19 (2C), 123.86, 101.33, 57.55, 52.48 (2C), 48.03 (2C), 36.63, 30.79, 27.47, 20.85. **FT-IR** λ max (NaCl): 2829, 1731, 1598, 1210, 1051, 850, 742, 693 cm^{-1}. **HRMS** (ESI$^+$) calcd. for $C_{19}H_{23}O_5^+$ [M^+-Me] 349.1646, found 349.1638.

3. Cyclisation reactions

General cyclisation procedure with $Bi(OTf)_3$: compound **1** (20.8 mmol) was added to dichloromethane (100 mL) and bismuth(III) triflate ($Bi(OTf)_3$) (0.208 mmol) was then added and the mixture stirred at room temperature. The reaction was followed by GC using 1,4-dichlorobenzene as the internal standard. After complete consumption of the starting material, the reaction was quenched with neutral activated aluminum oxide (42.4 mg, 416 mmol). The solid was then filtered off and the solvent removed under reduced pressure. The oily residue was purified by flash-chromatography through silica-gel with cyclohexane as the eluent (unless stated) or by distillation.

Dimethyl 3-methoxy-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate, **2a:** acetal **1a** (6 g, 20.81 mmol) in dichloromethane with $Bi(OTf)_3$ (137 mg, 0.208 mmol) was stirred at room temperature for 10 minutes. After work-up, **2a** was obtained as a colorless oil with a GC ratio of 11/89. The oily residue was purified by flash-chromatography through silica-gel (3.2 g, 12.49 mmol, 60%). *Trans* Isomer: **^{1}H NMR** (500 MHz, $CDCl_3$): δ 4.91 – 4.70 (m, 2H), 3.75 – 3.68 (m, 7H), 3.33 – 3.21 (m, 3H), 2.68 – 2.58 (m, 2H), 2.28 – 2.21 (m, 1H), 1.98 – 1.88 (m, 1H), 1.82 – 1.73 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.52, 172.15, 144.61, 111.23, 83.64, 57.11, 57.08, 52.77, 52.75, 51.83, 38.57, 36.47, 20.54. Isomer *cis*: 173.34, 172.27, 143.20, 111.43, 82.27, 58.04, 56.25, 52.81, 52.69, 50.99, 38.14, 35.29, 22.44. **FT-IR** λ max (NaCl): 3083, 2827, 1735, 1649, 1257, 1103, 1086, 692 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{13}H_{20}O_5$ [M^+] 256.1311, found 256.1281.

Dimethyl 4-methoxy-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate, 2b : acetal **1b** (3 g, 9.92 mmol) in dichloromethane with $Bi(OTf)_3$ (65 mg, 0.099 mmol) was stirred at room temperature for 40 minutes. After work-up, **2b** was obtained as a colorless oil with a GC ratio of 70/30. The oily residue was purified by flash-chromatography through silica-gel (1.6 g, 5.9 mmol, 60%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.94 – 4.65 (m, 2H), 3.83 – 3.64 (m, 6H), 3.57 – 3.47 (m, 1H), 3.35 – 3.23 (m, 3H), 2.53 – 1.88 (m, 5H), 1.83 – 1.70 (m, 3H), 1.70 – 1.10 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ Isomer *cis*: 173.06, 172.22, 146.75, 111.29, 75.96, 57.08, 55.53, 53.14, 53.01, 44.66, 29.86, 25.60, 25.18, 22.54. Isomer *trans*: 172.82, 171.48, 146.75, 112.48, 80.28, 56.77, 55.37, 53.27, 53.11, 48.43, 36.68, 30.34, 27.58, 20.15. **FT-IR** λ max (NaCl): 3086, 2826, 1734, 1648, 1252, 1103, 1066, 692 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{14}H_{22}O_5$ [M^+] 270.1467, found 270.1445.

Dimethyl 4-methoxy-4-methyl-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate, 2c: acetal **1c** (3 g, 9.48 mmol) in dichloromethane with $Bi(OTf)_3$ (62.2 mg, 0.95 mmol) was stirred at room temperature for 24 hours. After work-up, **2c** was obtained as a colorless oil with a GC ratio of 70/30. The oily residue was purified by flash-chromatography through silica-gel (2.18 g, 7.67 mmol, 81%). *Cis* isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 4.87 – 4.67 (m, 2H), 3.76 (s, 3H), 3.71 (s, 3H), 3.12 (s, 3H), 2.41 – 2.28 (m, 1H), 2.18 – 2.10 (m, 1H), 2.10 – 1.85 (m, 4H), 1.75 (s, 3H), 1.20 (ddd, *J* = 15.5, 14.1, 3.8 Hz, 1H), 1.06 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.65, 171.91, 146.25, 113.65, 73.49, 55.05, 52.63, 52.48, 51.74, 48.28, 31.39, 30.36, 26.36, 22.44, 21.50. **FT-IR** λ max (NaCl): 3072, 2828, 1734, 1641, 1250, 1075, 696 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{15}H_{24}O_5$ [M^+] 284.1624, found 284.1621. The cyclisation to **2c** was run at a 300 g-scale with a yield of 69% after hexane crystallisation.

Dimethyl 5-methoxy-3-methylcyclohex-3-ene-1,1-dicarboxylate, 2d: acetal **1d** (2 g, 7.29 mmol) in dichloromethane with $Bi(OTf)_3$ (48 mg, 0.073 mmol) was stirred at room temperature for 10 minutes. After work-up, the oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10). Colorless oil (1.32 g, 5.45 mmol, 75%). The NMR ratio of isomers

for the olefin position was of 80/20. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.59 - 5.42 (m, 1H), 3.82 - 3.73 (m, 1H), 3.73 - 3.63 (m, 6H), 3.39 - 3.24 (m, 3H), 2.63 - 2.51 (m, 1H), 2.36 - 2.18 (m, 3H), 1.73 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ Major isomer: 171.70, 171.35, 135.67, 120.81, 72.83, 55.89, 52.69, 52.47, 52.29, 35.22, 31.60, 23.21. Minor isomer: 171.65, 171.08, 136.39, 117.86, 73.52, 56.12, 52.81, 52.76, 52.29, 35.96, 32.70, 23.71. **FT-IR** λ max (NaCl): 2822, 1738, 1683, 1259, 1083 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{12}H_{18}O_5$ [M^+] 242.1154, found 242.1150.

Diisopropyl 3-methoxy-4-(prop-1-en-2-yl)cyclopentane-1,1-dicarboxylate, 2e: acetal **1e** (2.5 g, 7.26 mmol) in dichloromethane with $Bi(OTf)_3$ (48 mg, 0.073 mmol) was stirred at room temperature for 10 minutes. After work-up, 2e was obtained as a colorless oil with a GC ratio of 10/90. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 95/5 (1.58 g, 5.06 mmol, 70%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.11 – 4.96 (m, 2H), 4.91 – 4.74 (m, 2H), 3.86 – 3.64 (m, 1H), 3.31 (s, 3H), 2.68 – 2.50 (m, 3H), 2.24 – 2.09 (m, 1H), 1.95 – 1.80 (m, 1H), 1.80 – 1.72 (m, 3H), 1.25 – 1.20 (m, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ *Trans* isomer: 171.68, 171.19, 144.72, 111.21, 83.53, 68.91, 68.78, 57.21, 56.98, 51.85, 38.27, 36.13, 21.48, 21.46, 20.42. *Cis* isomer: 172.46, 171.28, 143.43, 111.33, 82.31, 68.86, 68.63, 58.18, 56.21, 50.93, 37.73, 35.07, 22.47, 21.48 (2C), 21.46 (2C). **FT-IR** λ max (NaCl): 3085, 2825, 1728, 1651, 1264, 1103, 887 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{17}H_{28}O_5$ [M^+] 312.1937, found 312.1962.

Dimethyl 3-methoxy-4-(methoxy(phenyl)methyl)cyclopentane-1,1-dicarboxylate, 3f: acetal **1f** (3 g, 8.92 mmol) in dichloromethane with $Bi(OTf)_3$ (59 mg, 0.089 mmol) was stirred at room temperature for 20 minutes. After work-up, a colorless oil gave a GC ratio of isomers is of 59/26/11/4. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 98/2), (2.55 g, 7.6 mmol, 85%). For the major isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 – 7.10 (m, 5H), 4.29 – 4.08 (m, 1H), 3.81 – 3.59 (m, 7H), 3.40 – 3.07 (m, 6H), 2.59 – 2.40 (m, 2H), 2.40 – 2.22 (m, 2H), 2.21 – 2.05 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.60, 172.12, 140.64, 128.34 (2C), 127.55, 126.78 (2C), 83.55, 82.83, 58.01, 57.08, 56.68, 52.78, 52.69, 52.17, 38.71, 33.01. **FT-IR** λ max (NaCl): 3029, 2826, 1735, 1682, 1266, 1093, 765, 705 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{18}H_{24}O_6$ [M^+] 336.1573, found 336.1574.

Dimethyl 4-methoxy-3-(methoxy(phenyl)methyl)cyclohexane-1,1-dicarboxylate, 3g: acetal **1g** (3 g, 8.56 mmol) in dichloromethane with $Bi(OTf)_3$ (56 mg, 0.086 mmol) was stirred at room temperature for 20 minutes. After work-up, a colorless oil gave a GC ratio of isomers was of 47/30/18/5. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10), (2.72 g, 7.76 mmol, 91%). For the major isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 – 7.23 (m, 5H), 4.83 – 4.62 (m, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 3.32 (s, 3H), 3.29 (s, 3H), 2.65 (dt, *J* = 13.7, 3.3 Hz, 1H), 2.57 (dd, *J* = 10.6, 4.3 Hz, 1H), 2.34 (dq, *J* = 13.3, 3.3 Hz, 1H), 2.27 – 2.05 (m, 2H), 1.50 – 1.17 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.48, 171.16, 138.34, 127.90 (2C), 127.80 (2C), 127.30, 81.45, 77.99, 56.85, 54.90, 54.45, 52.64, 52.56, 43.84, 29.25, 29.08, 26.48. **FT-IR** λ max (NaCl): 3063, 3031, 2825, 1735, 1258, 1100, 769, 711 cm^{-1}. **HRMS (ESI^+)** calcd. for $C_{18}H_{23}O_6^+$ [M^+-Me] 335.1489, found 335.1486.

Dimethyl 4-methoxy-3-(methoxy(phenyl)methyl)-4-methylcyclohexane-1,1-dicarboxylate, 3h: acetal **1h** (2.5 g, 6.86 mmol) in dichloromethane with $Bi(OTf)_3$ (45 mg, 0.069 mmol) was stirred at room temperature for 20 minutes. After work-up, a colorless oil gave a GC ratio of isomers was of 25/10/5/60. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10), (2 g, 5.49 mmol, 80%). For the major isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.47 – 7.13 (m, 5H), 4.41 (d, *J* = 4.2 Hz, 1H), 3.70 (s, 3H), 3.56 (s, 3H), 3.22 (s, 3H), 3.19 (s, 3H),

2.45 – 2.32 (m, 1H), 2.19 – 2.02 (m, 2H), 1.99 – 1.86 (m, 2H), 1.78 – 1.68 (m, 1H), 1.19 (ddd, *J* = 15.8, 14.5, 4.0 Hz, 1H), 1.01 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.68, 171.72, 143.10, 128.11 (2C), 127.04 (3C), 82.12, 73.56, 56.99, 54.98, 52.48, 52.13, 50.68, 48.69, 31.07, 26.86, 26.23, 23.71. **FT-IR** λ max (NaCl): 3086, 3063, 3029, 2826, 1734, 1253, 1079, 765, 705 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{20}H_{28}O_6$ [M^+] 364.1886, found 364.1881.

Dimethyl 5-methoxy-3-methylcyclohept-3-ene-1,1-dicarboxylate, 2i: acetal **1i** (3 g, 10.4 mmol) in nitromethane with $Bi(OTf)_3$ (68 mg, 0.104 mmol) was stirred at room temperature for 23 hours. After work-up, the oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10) and **2i** was obtained as a colorless oil (500 mg, 1.95 mmol, 19%). The GC ratio of isomers for the olefin position was of 56/44. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.64 – 4.81 (m, 2H), 3.84 – 3.24 (m, 10H), 2.91 – 2.70 (m, 1H), 2.70 – 2.53 (m, 1H), 2.50 – 1.68 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ Major isomer: 172.29, 172.17, 140.72, 117.15, 79.21, 57.26, 56.06, 52.53 (2C), 42.69, 39.90, 28.19, 27.73. Minor isomer: ^{13}C NMR (75 MHz, Chloroform-*d*) δ 172.43, 171.26, 134.23, 130.67, 78.91, 56.18, 55.29, 52.27 (2C), 37.25, 31.85, 28.05, 26.62. **FT-IR** λ max (NaCl): Major isomer: 3077, 2825, 1735, 1647, (1282, 1246, 1197, 1164), 1097, 911 cm^{-1}. Minor isomer: 2822, 1734, 1073, (1241, 1205, 1175), 1090 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{12}H_{17}O_5^+$ [M^+-Me] 241.1071, found 241.1094.

Methyl 4-methoxy-6-methyl-8-oxo-7-oxabicyclo[4.2.1]nonane-1-carboxylate, 5i: acetal **1i** (3 g, 10.4 mmol) in nitromethane with $Bi(OTf)_3$ (68 mg, 0.104 mmol) was stirred at room temperature for 23 hours. After work-up, the oily residue was purified by flash-chromatography through silica-gel (ethyl acetate, 100%) and **5i** was obtained as a colorless oil (1.24 g, 5.12 mmol, 49%) with a GC isomer ratio of 60/40. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.50 – 3.36 (m, 1H), 3.29 (s, 3H), 2.64 (d, *J* = 13.1 Hz, 1H), 2.46 – 2.33 (m, 1H), 2.28 (d, *J* = 13.1 Hz, 1H), 2.12 – 1.87 (m, 4H), 1.80 – 1.62 (m, 1H), 1.53 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.13, 170.60, 83.72, 77.87, 56.40, 56.19, 53.07, 44.24, 42.07, 30.35, 29.51, 28.26. **FT-IR** λ max (NaCl): 2827, 1771, 1742, 1247, 1093 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{12}H_{18}O_5$ [M^+] 242.1154, found 242.1162.

General cyclisation procedure with $Fe(OTf)_3$: compound **1** (10.4 mmol) and methanol (20.8 mmol)) were added to nitromethane (104 mL). Iron(III) triflate ($Fe(OTf)_3$) (0.104 mmol) was then added and the mixture stirred at room temperature. The reaction was followed by GC using 1,4-dichlorobenzene as the internal standard. After complete consumption of the starting material, the reaction was quenched with neutral activated aluminum oxide (21.2 mg, 0.208 mmol). The solid was then filtered off and the solvent removed under reduced pressure. The oily residue was purified by flash-chromatography through silica-gel or by distillation.

Dimethyl 3-methoxy-4-(2-methoxypropan-2-yl)cyclopentane-1,1-dicarboxylate, 3a: acetal **1a** (3 g, 10.4 mmol) and methanol (667 mg, 20.81 mmol) in nitromethane with $Fe(OTf)_3$ (52 mg, 0.104 mmol) were stirred at room temperature for 10 minutes. After work-up, a colorless oil gave a GC ratio of isomers was of 60/40. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane, 100%), colorless oil (2.35 g, 8.15 mmol, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.78 – 3.70 (m, 7H), 3.24 – 3.16 (m, 6H), 2.72 (d, J = 14.6 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.33 – 2.25 (m, 1H), 2.15 – 2.06 (m, 2H), 1.24 – 1.11 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ *Cis* isomer: 173.44, 172.45, 82.40, 75.55, 57.88, 55.65, 52.74, 52.62, 52.56, 48.76, 38.03, 33.29, 23.70, 23.33. *Trans* isomer: 172.24, 172.04, 82.48, 74.69, 58.93, 56.27, 54.83, 52.58, 52.51, 49.15, 38.88, 33.97, 22.89, 22.74. **FT-IR** λ max (NaCl): 2829, 1736, 1244, 1093 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{13}H_{21}O_6^+$ [M^+-Me] 273.1333, found 273.1335.

Dimethyl 4-methoxy-3-(2-methoxypropan-2-yl)cyclohexane-1,1-dicarboxylate, 3b: acetal **1b** (3 g, 9.92 mmol) and methanol (636 mg, 19.84 mmol) in nitromethane with $Fe(OTf)_3$ (50 mg, 0.099 mmol) were stirred at room temperature for 1 hour. After work-up, a colorless oil gave a GC ratio of isomers was of 83/17. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10), colorless oil (1.52 g, 5 mmol, 51%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ *Cis* isomer: 3.74 (s, 3H), 3.71 (s, 3H), 3.52 (s, 1H), 3.26 (s, 3H), 3.19 (s, 3H), 2.26 – 2.18 (m, 1H), 2.16 – 1.90 (m, 4H), 1.71 – 1.66 (m, 1H), 1.39 – 1.30 (m, 1H), 1.18 (s, 6H). *Trans* isomer: 3.75 (s, 3H), 3.70 (s, 3H), 3.29 (s, 3H), 3.22 (s, 3H), 3.05 (td, J = 10.1, 4.2 Hz, 1H), 2.52 (dt, J = 14.0, 3.1 Hz, 1H), 2.39 (dq, J = 13.7, 3.6 Hz, 1H), 2.14 (dq, J = 13.3, 4.0 Hz, 1H), 1.92 – 1.81 (m, 1H), 1.75 (td, J = 13.7, 3.8 Hz, 1H), 1.49 – 1.37 (m, 1H), 1.33 (s, 3H), 1.23 – 1.19 (m, 1H), 1.12 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) *Cis* isomer: δ 173.43, 172.58, 77.21, 74.94, 56.48, 55.99, 53.34, 53.14, 49.43, 45.09, 27.49, 25.98, 25.65, 24.70, 23.37. *Trans* isomer: 172.70, 171.43, 80.04, 76.08, 55.58, 54.86, 52.72, 52.46, 48.63, 45.00, 30.87, 29.39, 27.40, 26.14, 23.04. **FT-IR** λ max (NaCl): 2828, 1734, 1248, 1084 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{14}H_{23}O_5^+$ [M^+-OMe] 271.1540, found 271.1583.

Diisopropyl 3-methoxy-4-(2-methoxypropan-2-yl)cyclopentane-1,1-dicarboxylate, 3e: acetal **1e** (3 g, 8.71 mmol) and methanol (558 mg, 17.42 mmol) in nitromethane with $Fe(OTf)_3$ (43.8 mg, 0.087 mmol) were stirred at room temperature for 10 minutes. After work-up, a colorless oil gave a GC ratio of isomers was of 65/35. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10), colorless oil (2.15 g, 6.24 mmol, 72%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.12 – 4.94 (m, 2H), 3.77 – 3.68 (m, 1H), 3.26 – 3.14 (m, 6H), 2.71 – 2.02 (m, 4H), 1.87 – 1.70 (m, 1H), 1.27 – 1.11 (m, 18H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ *Cis* isomer:171.39, 171.05, 82.58, 74.77, 68.70, 68.40, 59.02, 56.44, 54.61, 49.12, 38.50, 33.68, 23.02, 22.78, 21.52 (2C), 21.48 (2C). *Trans* isomer: 172.55, 171.44, 82.47, 75.63, 68.76, 68.50, 58.07, 55.66, 52.17, 48.78, 37.70, 33.07, 23.90, 23.39, 21.57 (2C), 21.52 (2C). **FT-IR** λ max (NaCl): 2827, 1729, 1261, 1105 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{17}H_{29}O_5$ [M^+-OMe] 313.2010, found 313.1972.

Dimethyl 3,5-dimethoxy-3-methylcycloheptane-1,1-dicarboxylate, 3i: acetal **1i** (3 g, 10.4 mmol) in nitromethane with $Fe(OTf)_3$ (52 mg, 0.104 mmol) was stirred at room temperature for 23 hours. After work-up, a colorless oil gave a GC ratio of isomers was of 84/16. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 90/10). Colorless oil (1.93 g, 6.69 mmol, 64%). Major isomer: **^{1}H NMR** (300 MHz, $CDCl_3$) δ 3.70 (s, 6H), 3.29 (s, 4H), 3.13 (s, 3H), 2.62 (ddd, *J* = 15.0, 7.4, 4.9 Hz, 1H), 2.54 (d, *J* = 15.3 Hz, 1H), 2.04 (d, *J* = 15.3 Hz, 1H), 2.01 – 1.89 (m, 3H), 1.86 – 1.68 (m, 2H), 1.19 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 173.21, 172.27, 77.75, 74.36, 56.01, 54.82, 52.73, 52.28, 48.83, 42.57, 41.23, 28.57, 28.54, 26.35. **FT-IR** λ max (NaCl): 2829, 1733, 1277, 1091 cm^{-1}. **HRMS** (ESI+) calcd. for $C_{13}H_{21}O_6^+$ [M^+-Me] 273.1333, found 273.1335.

Cyclisation of ketone 6 for comparison:

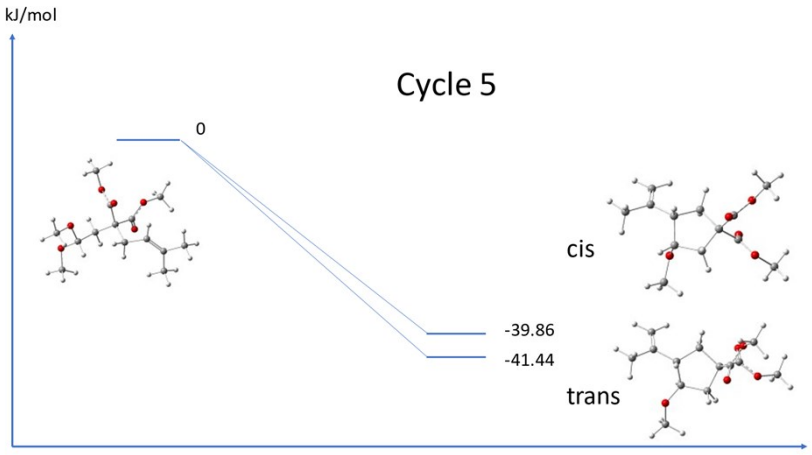
Dimethyl 4-hydroxy-4-methyl-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate, 7: ketone **6** (3 g, 11.1 mmol) in dichloromethane with $Bi(OTf)_3$ (73 mg, 0.111 mmol) was stirred at room temperature for 48 hours. After work-up, a colorless oil gave a NMR ratio of isomers was of 85/15. The oily residue was purified by flash-chromatography through silica-gel (cyclohexane/ethyl acetate, 80/20), colorless oil (700 mg, 2.59 mmol, 23%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 5.08 – 4.78 (m, 2H), 3.83 – 3.70 (m, 6H), 2.21 – 2.03 (m, 5H), 1.84 (s, 3H), 1.72 (dt, *J* = 14.4, 3.5 Hz, 1H), 1.58 – 1.46 (m, 2H), 1.15 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.50, 171.68, 146.85, 112.70, 69.20, 55.09, 52.69, 52.51, 48.89, 36.49, 32.05,

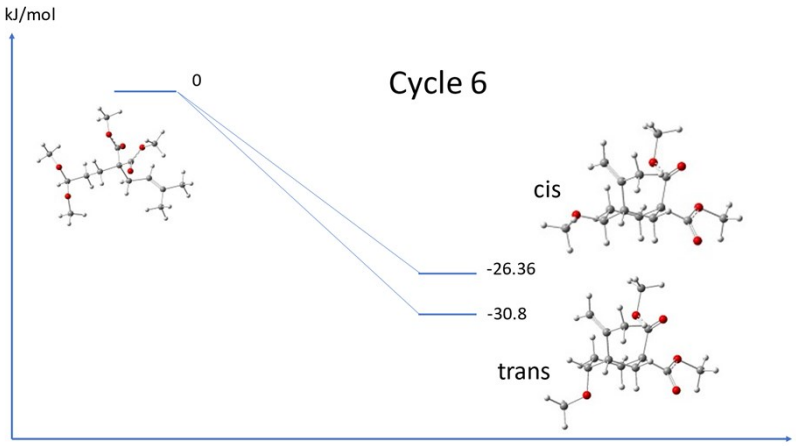
29.47, 26.41, 25.11. **FT-IR** λ max (NaCl): 3535, 3075, 2856, 1732, 1642, 1255, 1040, 900 cm^{-1}. **HRMS** (ESI^+) calcd. for $C_{14}H_{22}O_5$ [M^+] 270.1467, found 270.1467.

4. Theoretical calculations and kinetic data

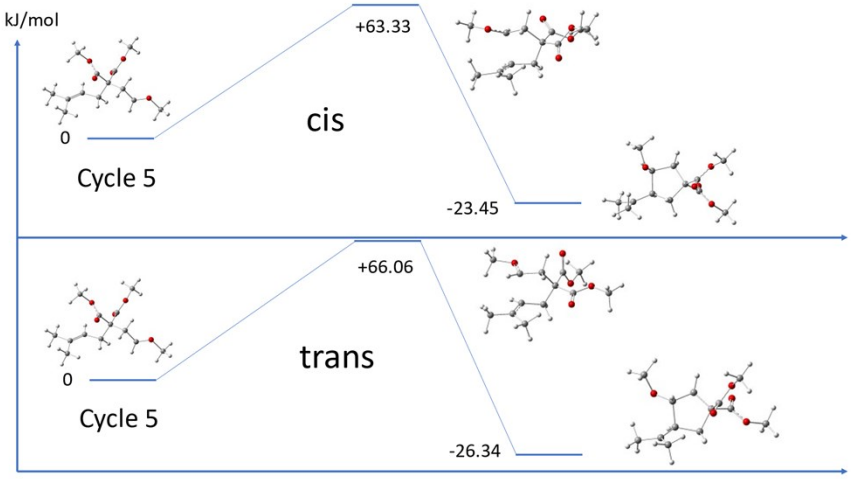
DFT calculation were carried out at ICN, University Côte d'Azur.

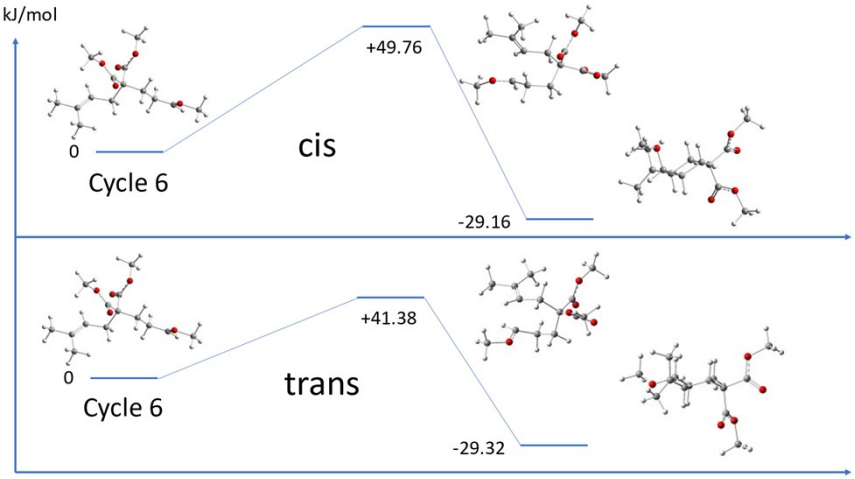
For the energies of **1a**, and **2a** in 5- and 6-membered rings:
Method Gaussian 16, B3LYP/6-31+**, solvent PCM dichloromethane.



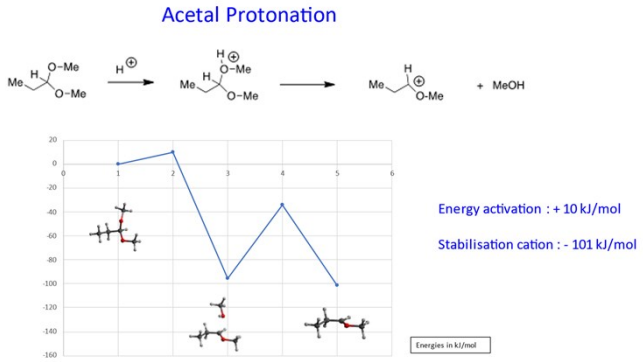


For the energies of the carbocation issued from **1a** and its cyclisation to 5- and 6-membered rings:

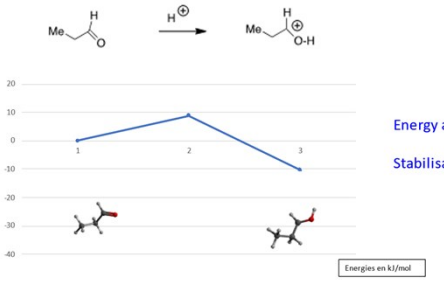




For the protonation of acetals and carbonyl groups, with GAUSSIAN 16. B3LYP 6-31+g(d,p), solvent PCM, nitromethane:



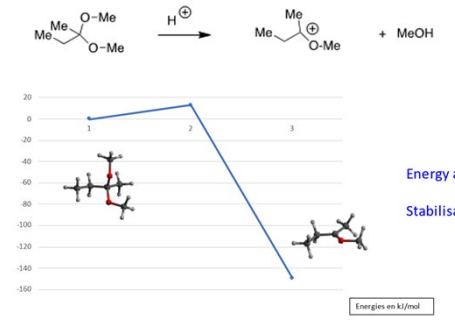
Aldehyde Protonation



Energy activation : + 9 kJ/mol

Stabilisation cation : - 11 kJ/mol

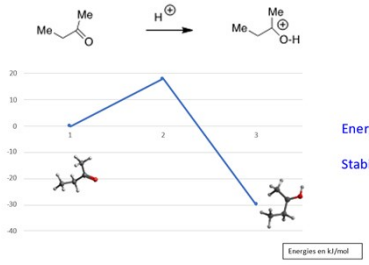
Ketal Protonation



Energy activation : + 13 kJ/mol

Stabilisation cation : - 150 kJ/mol

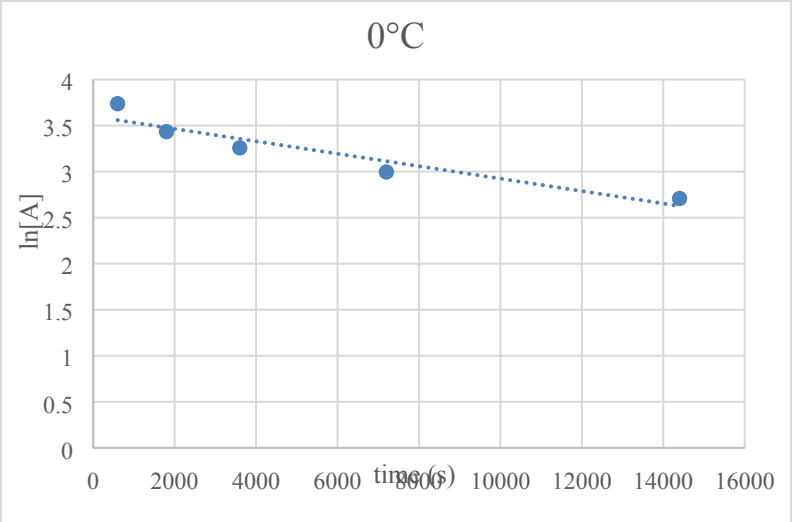
Ketone Protonation

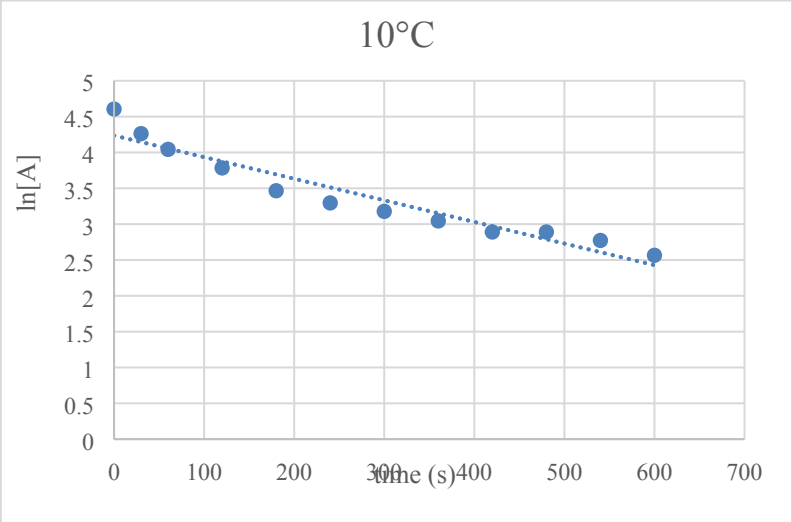


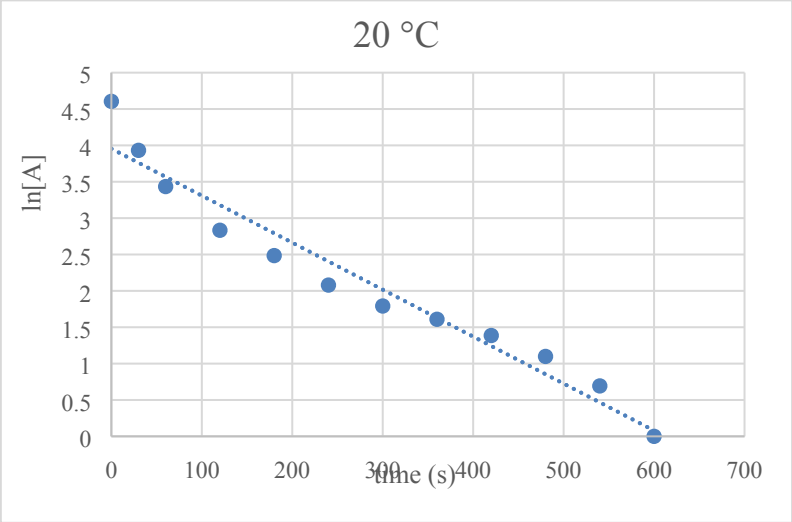
Energy activation : + 18 kJ/mol

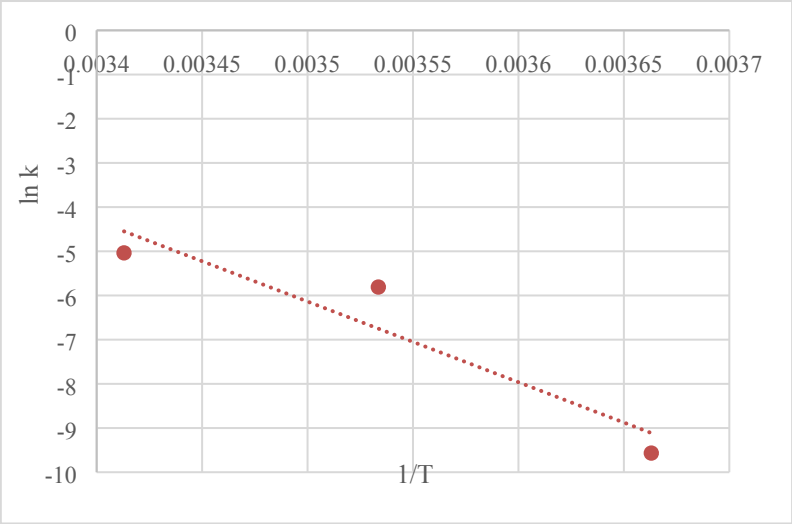
Stabilisation cation : - 30 kJ/mol

Kinetic data for the cyclisation of **1a**, at 0 °C, 10 °C and 20 °C, followed by the graph of ln k versus 1/T.


0°C
ln[A]
time (s)
4
3.5
3
2.5
2
1.5
1
0.5
0
0
2000
4000
6000
8000
10000
12000
14000
16000

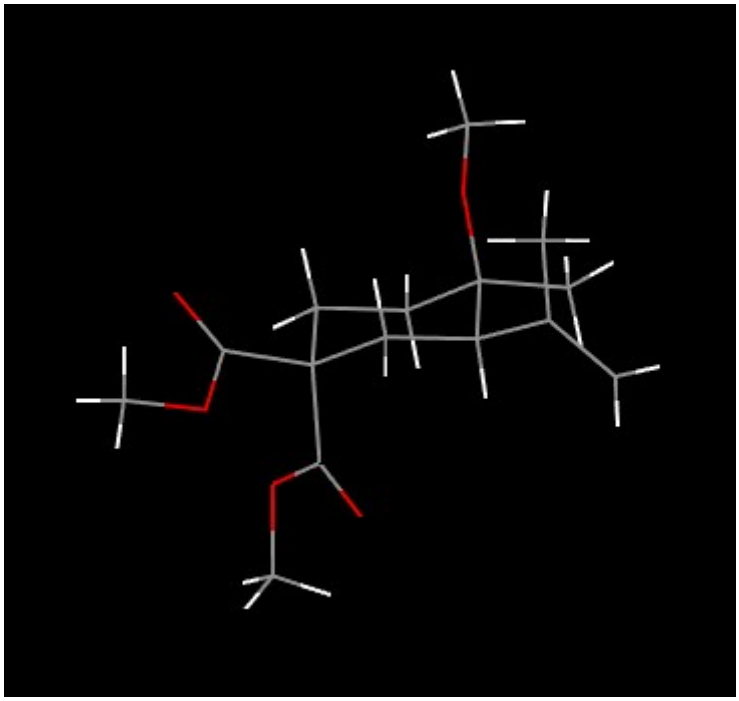

10°C
ln[A]
time (s)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
700


20 °C
ln[A]
time (s)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
100
200
300
400
500
600
700

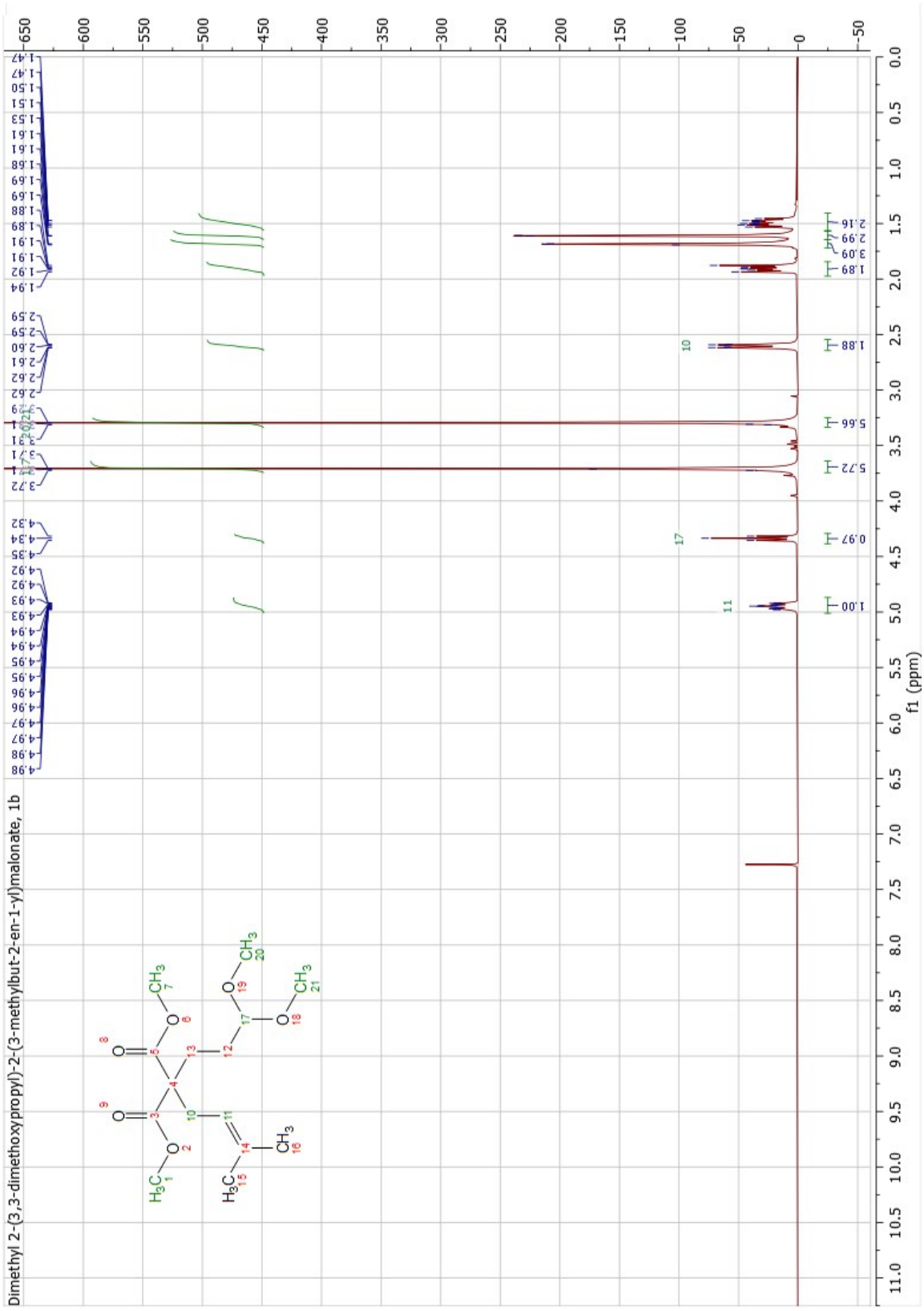

0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
ln k
0.0034
0.00345
0.0035
0.00355
0.0036
0.00365
0.0037
1/T

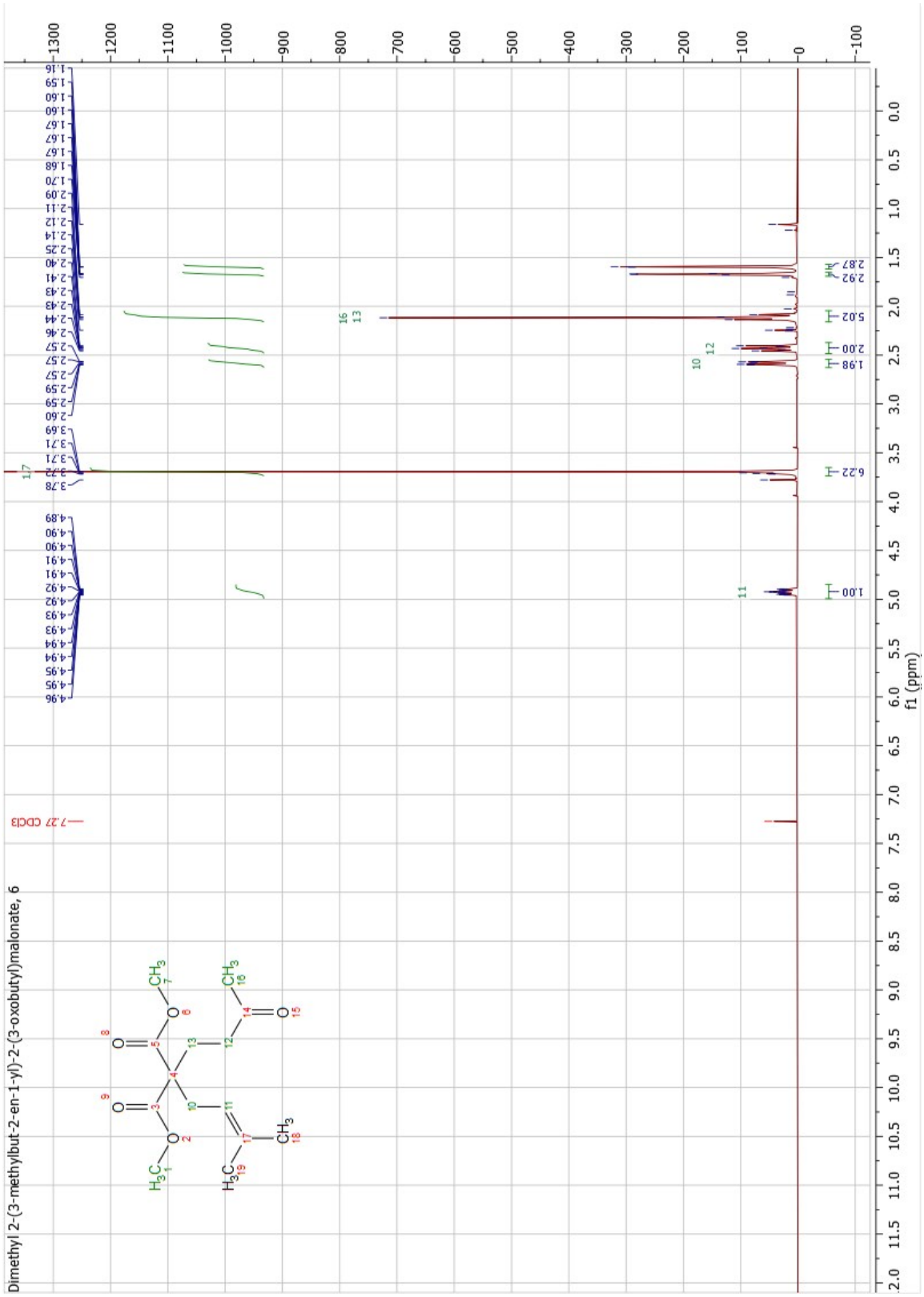
5. X-Ray analysis

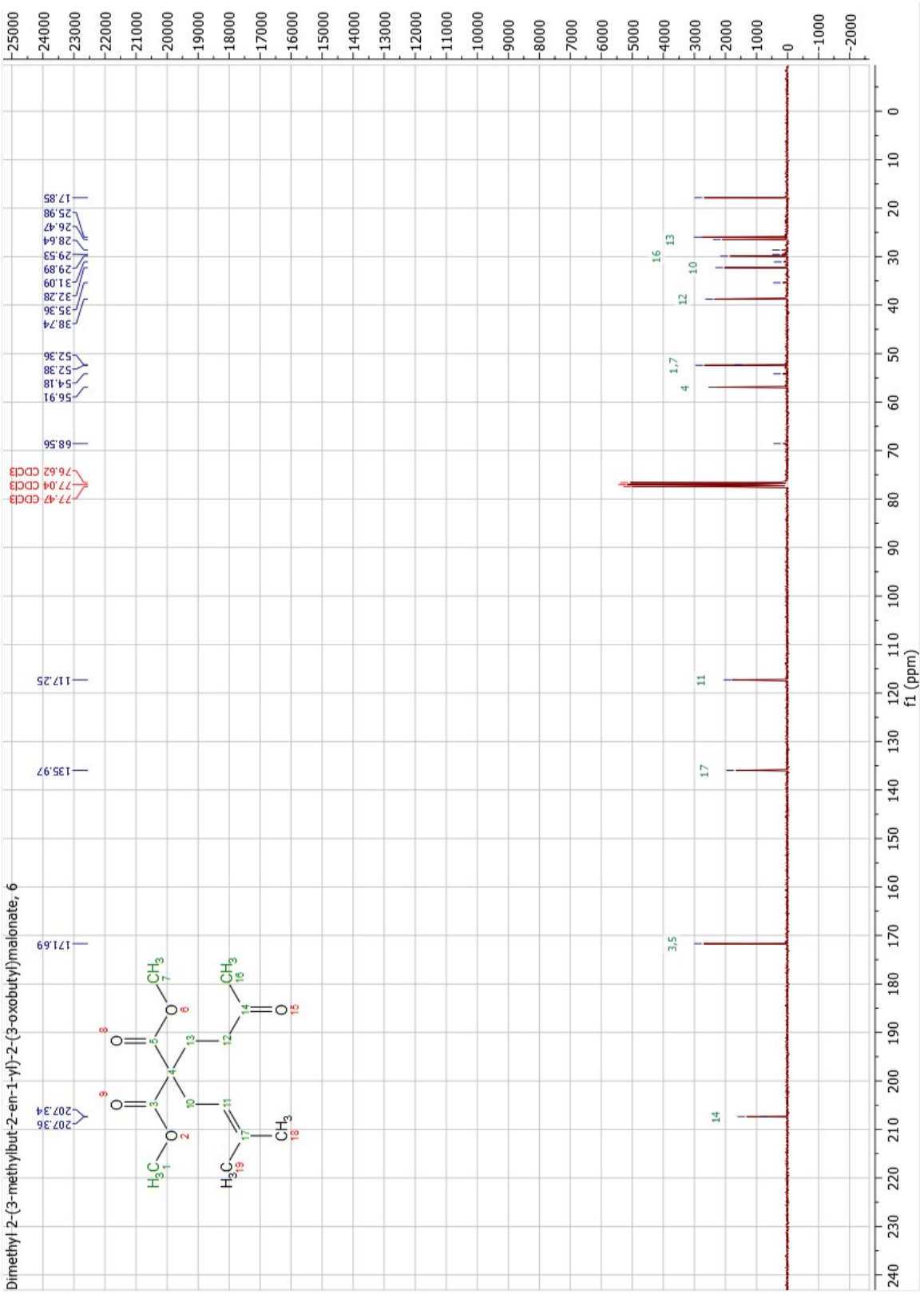
Compound **2c** was crystallized in hexane and an X-Ray analysis was carried out at Spectropôle University Aix-Marseille.

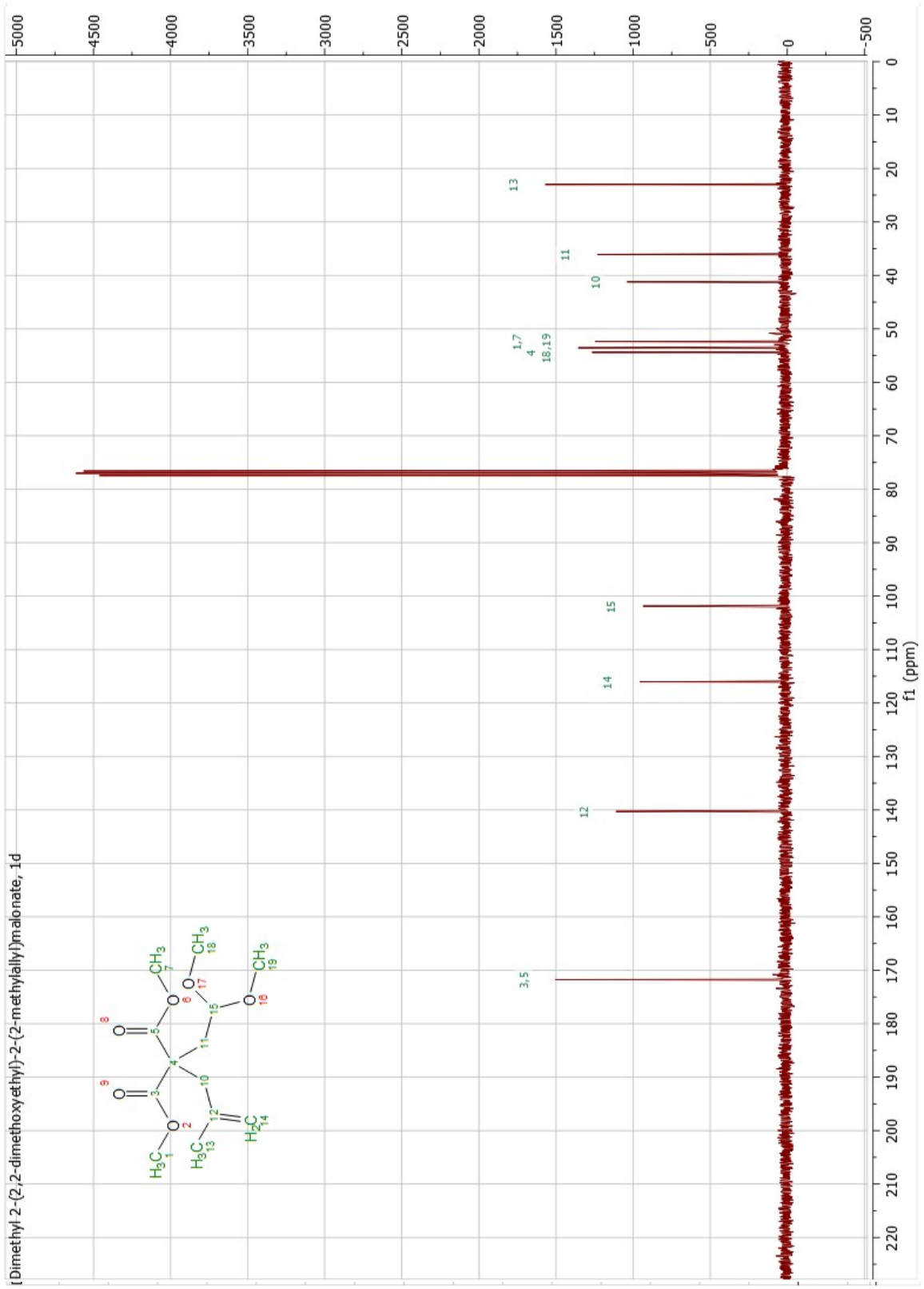


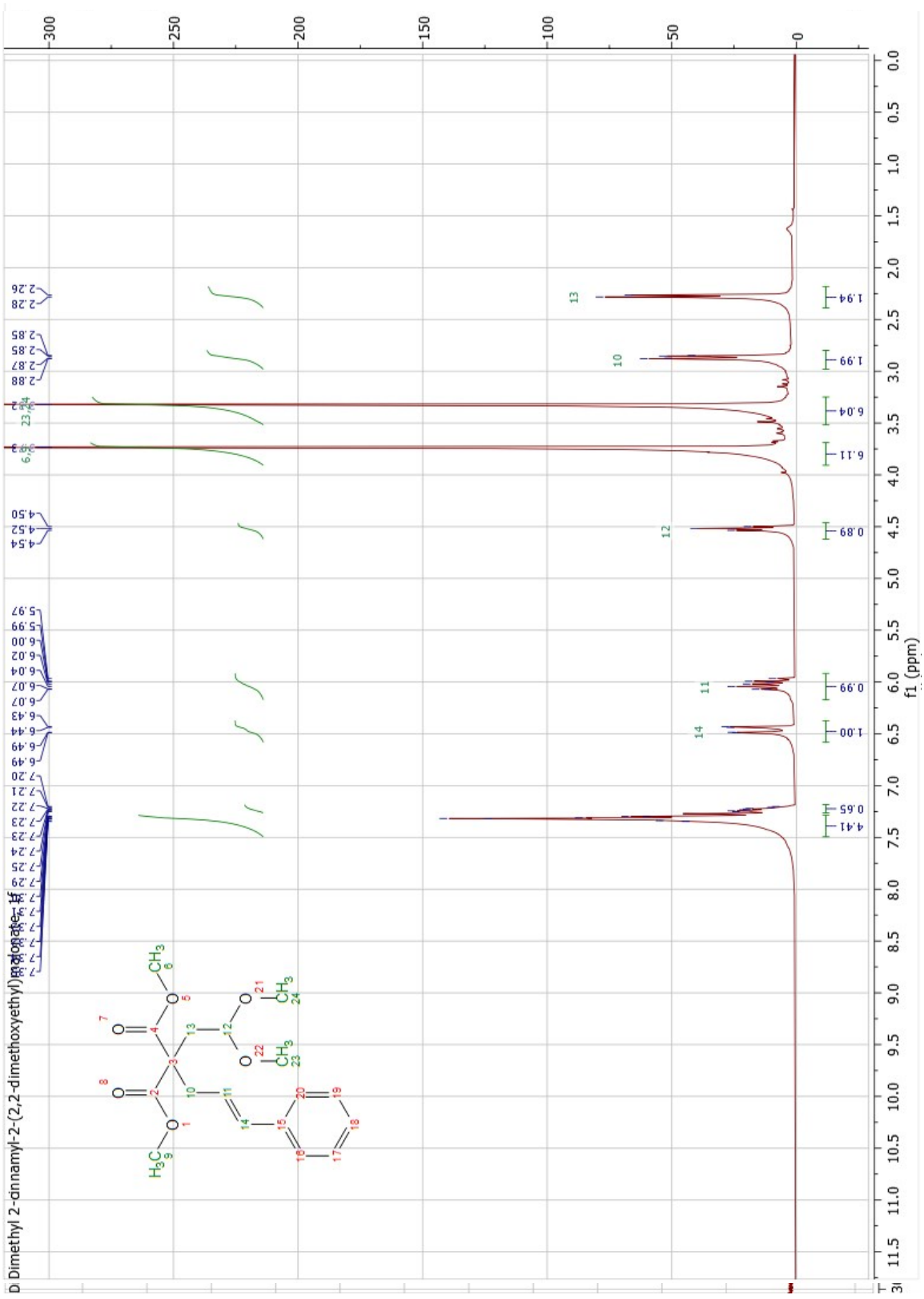
6. NMR Spectra

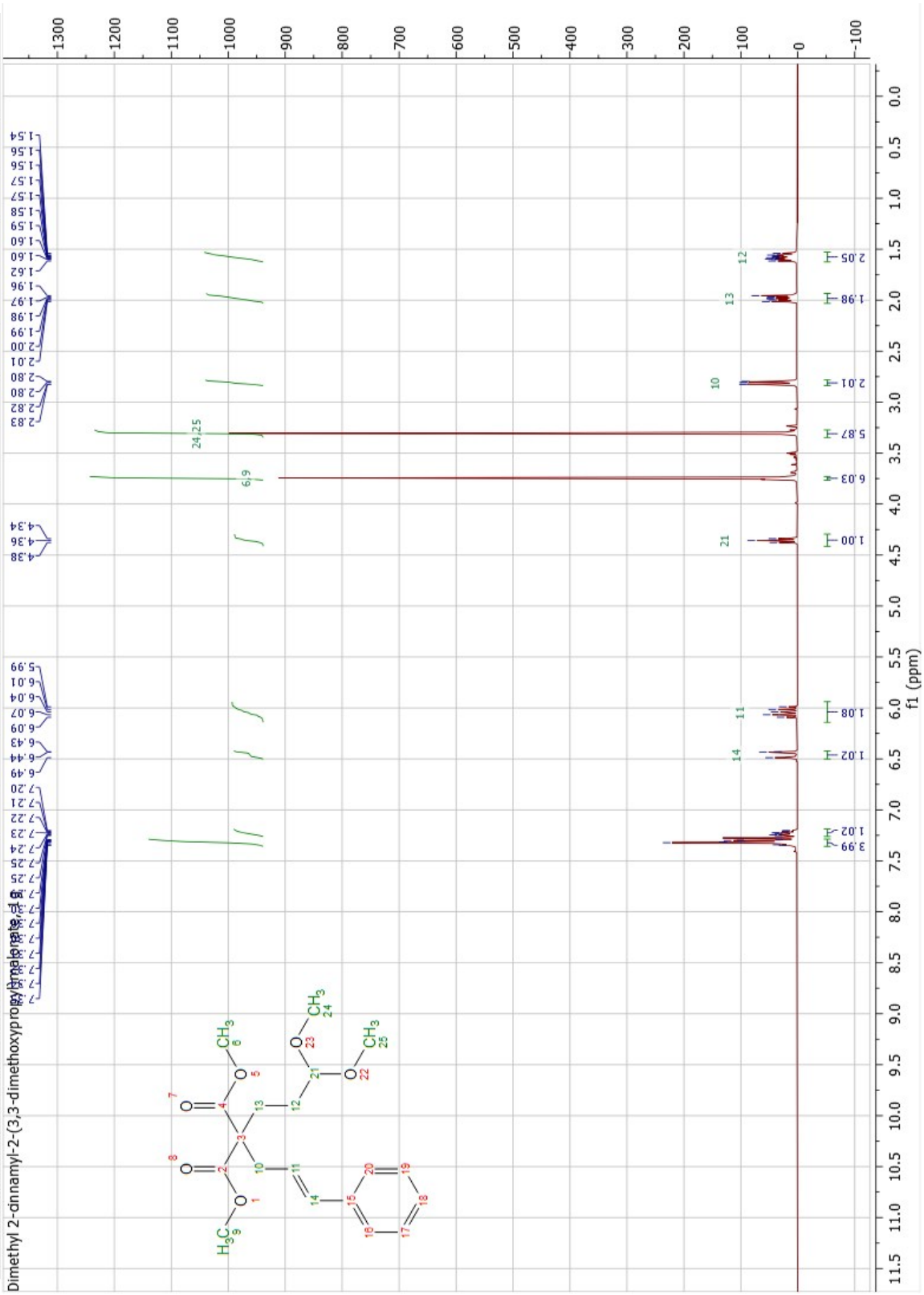


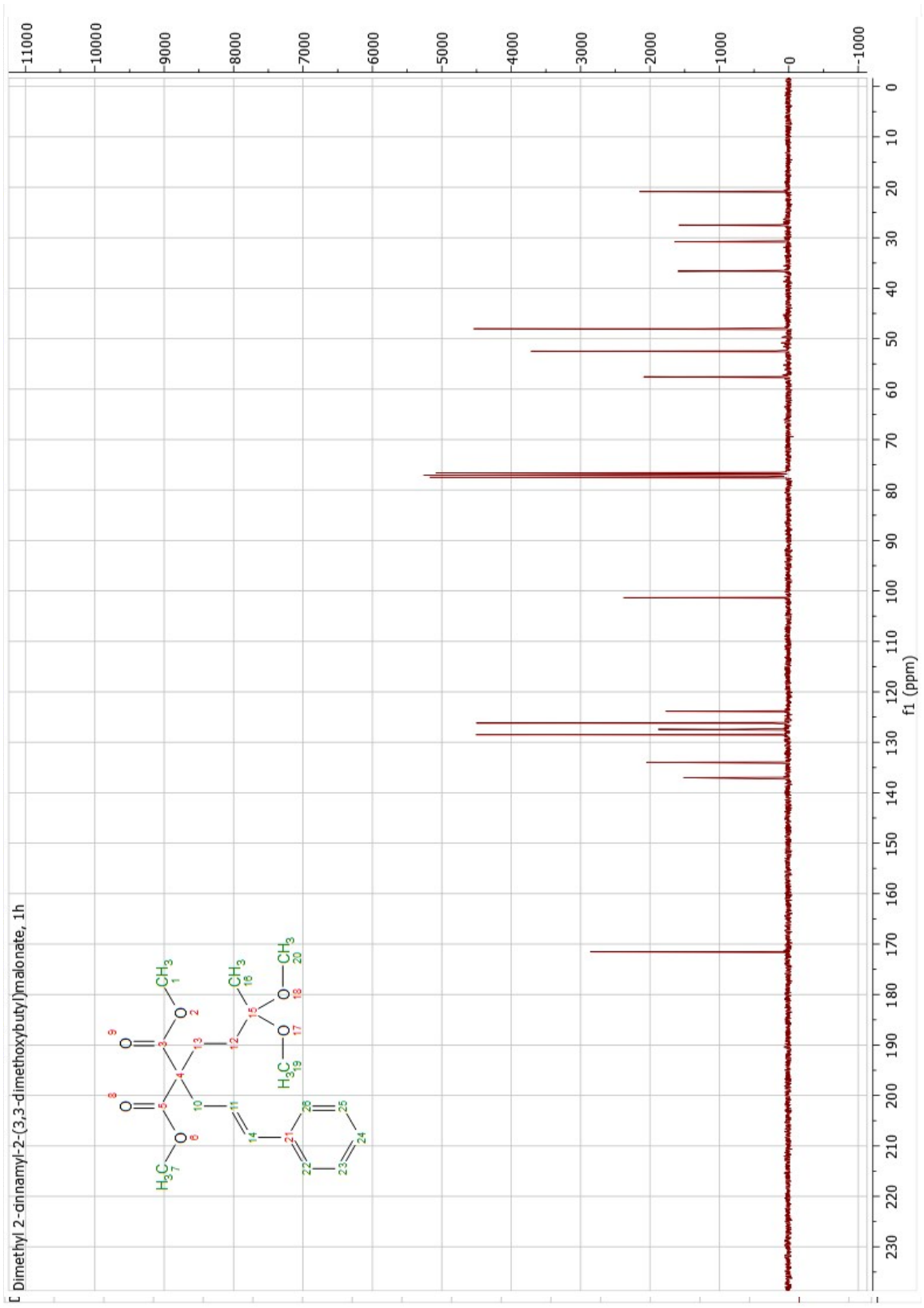

Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(3-oxobutyl)malonate, 6
7.27 CDCl3
f1 (ppm)

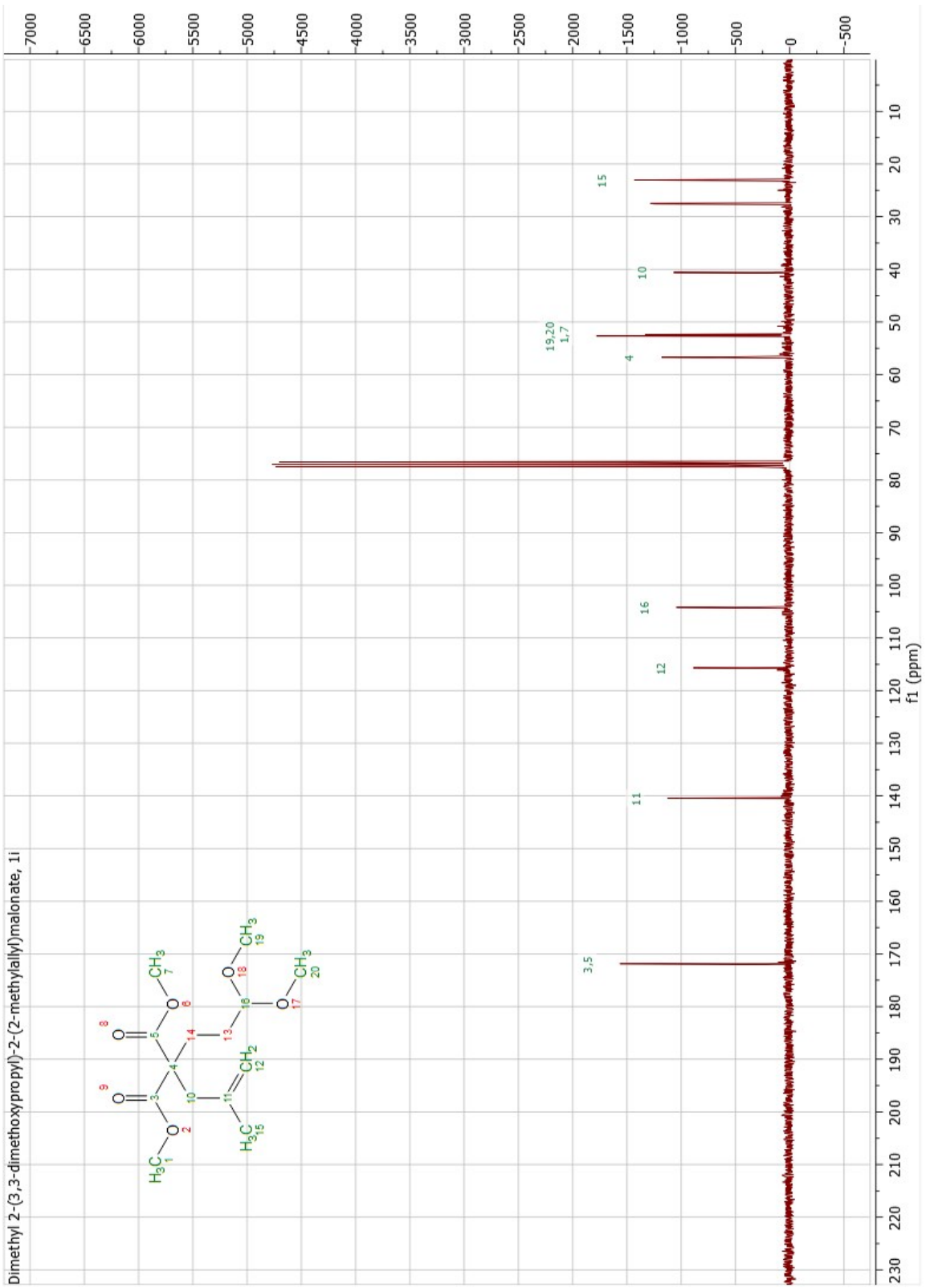

Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(3-oxobutyl)malonate, 6
f1 (ppm)
207.36
207.34
171.69
135.97
117.25
77.47 CDCl3
77.04 CDCl3
76.62 CDCl3
68.56
56.91
54.18
52.38
52.36
38.74
35.36
32.28
31.09
29.89
29.53
28.64
26.47
25.98
17.85
3,5
4
1,7
16
13
10
12
11
17
14

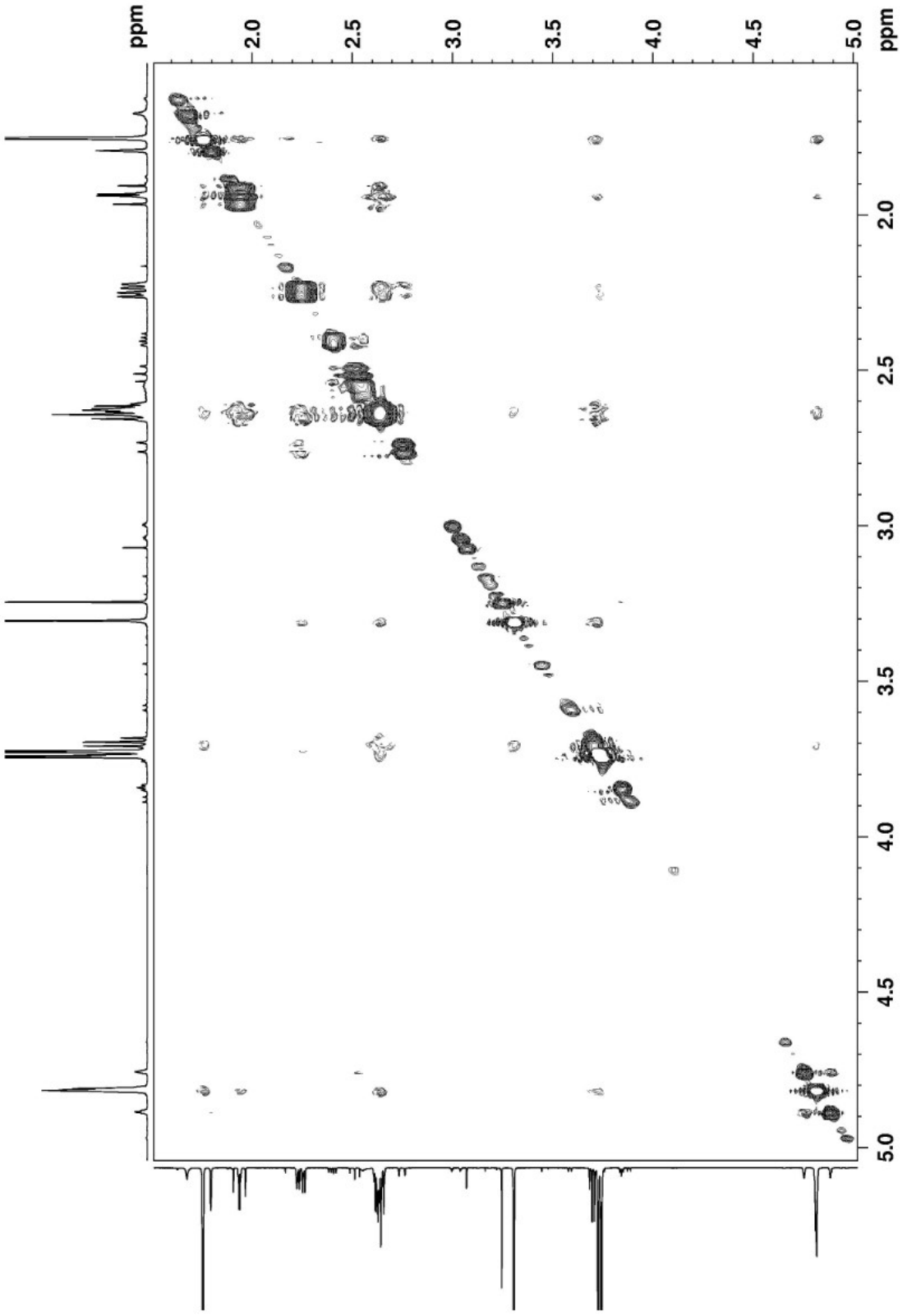

[Dimethyl 2-(2,2-dimethoxyethyl)-2-(2-methylallyl)malonate, 1d
f1 (ppm)
3,5
12
14
15
1,7
4
18,19
13
11
10

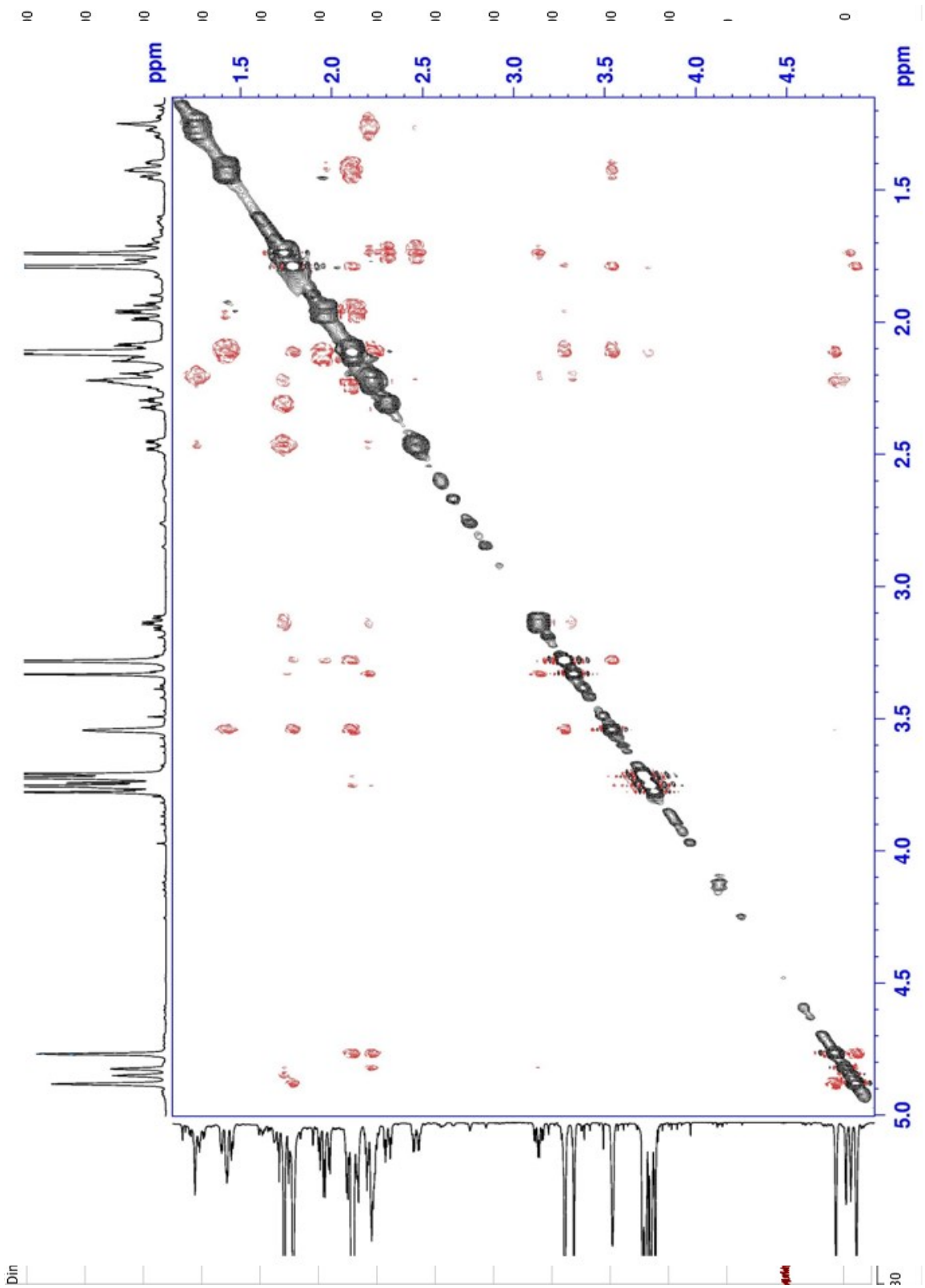

Dimethyl 2-cinnamyl-2-(2,2-dimethoxyethyl)malonate_1H
f1 (ppm)

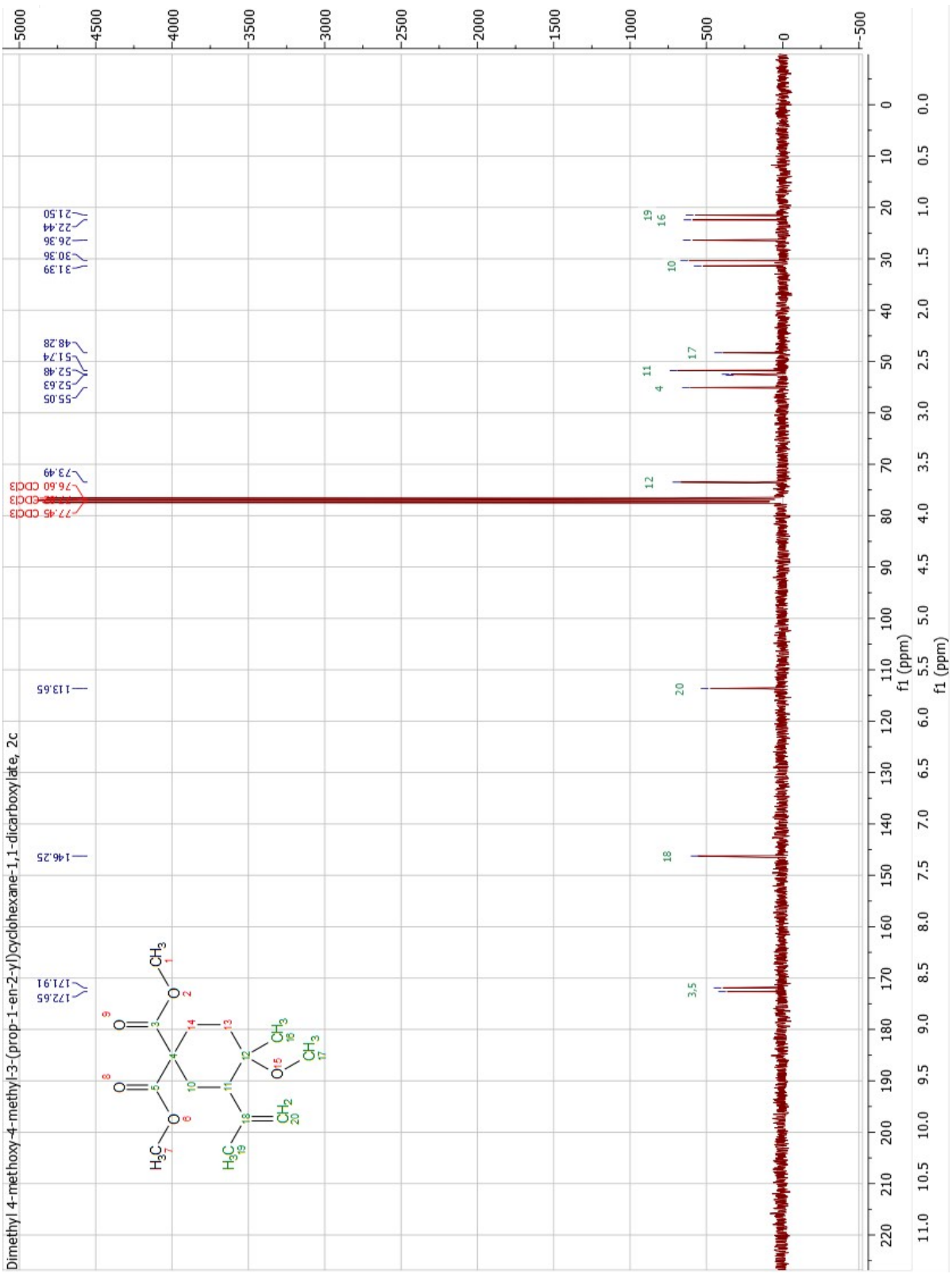

Dimethyl 2-cinnamyl-2-(3,3-dimethoxypropyl)malonate
f1 (ppm)

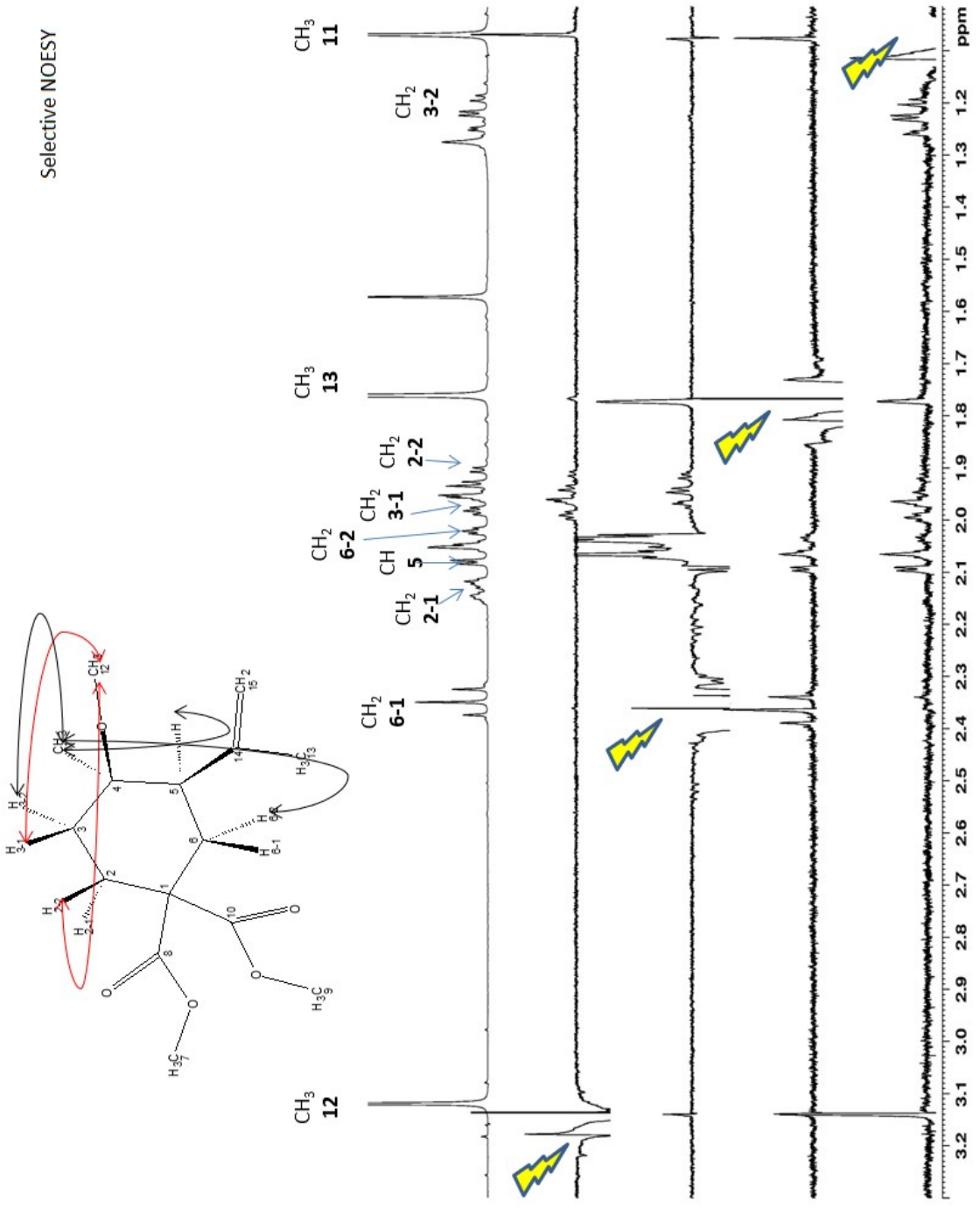

Dimethyl 2-cinnamyl-2-(3,3-dimethoxybutyl)malonate, 1h
f1 (ppm)

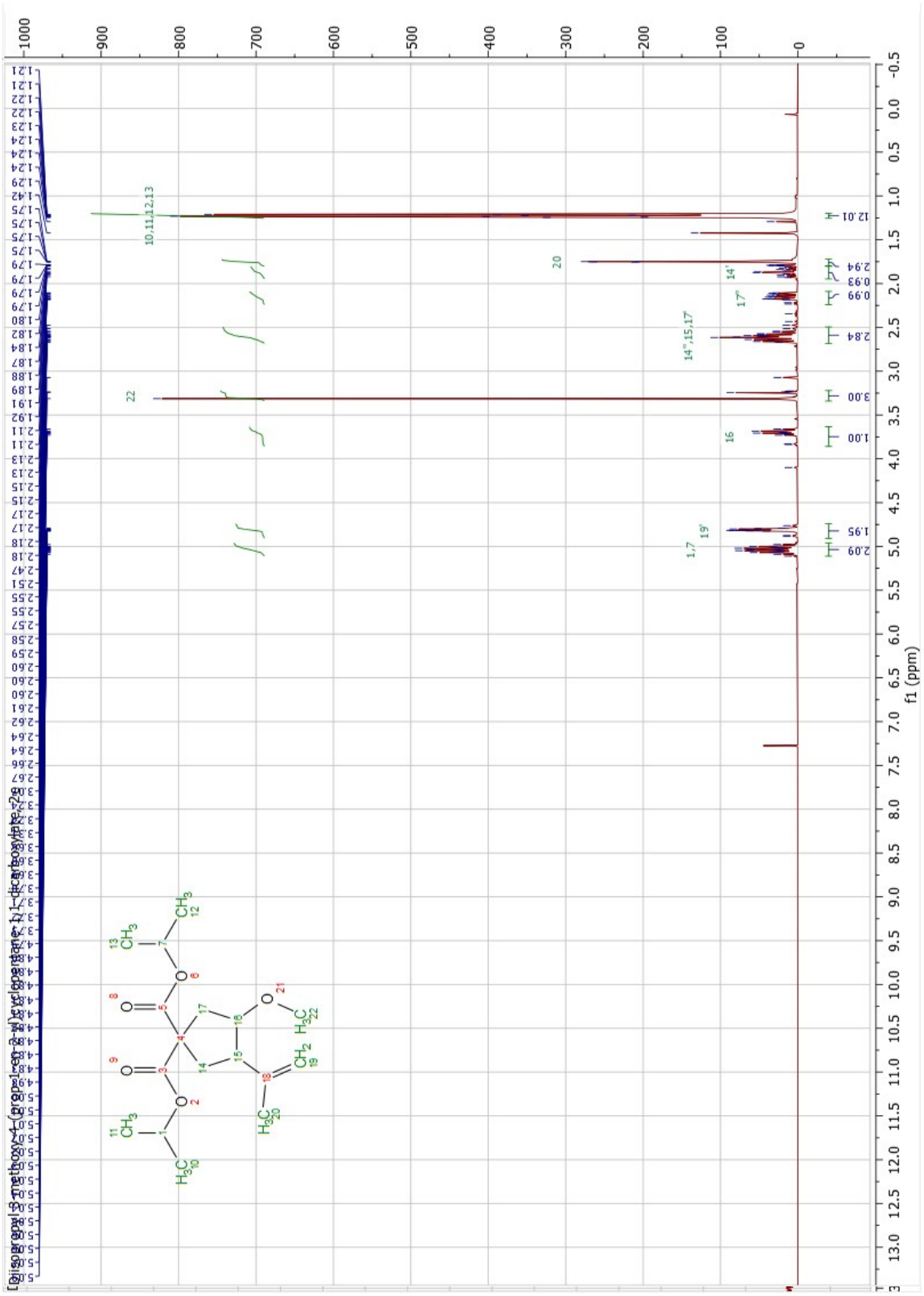

Dimethyl 2-(3,3-dimethoxypropyl)-2-(2-methylallyl)malonate, 1i
f1 (ppm)
3,5
11
16
12
15
10
19,20
1,7
4

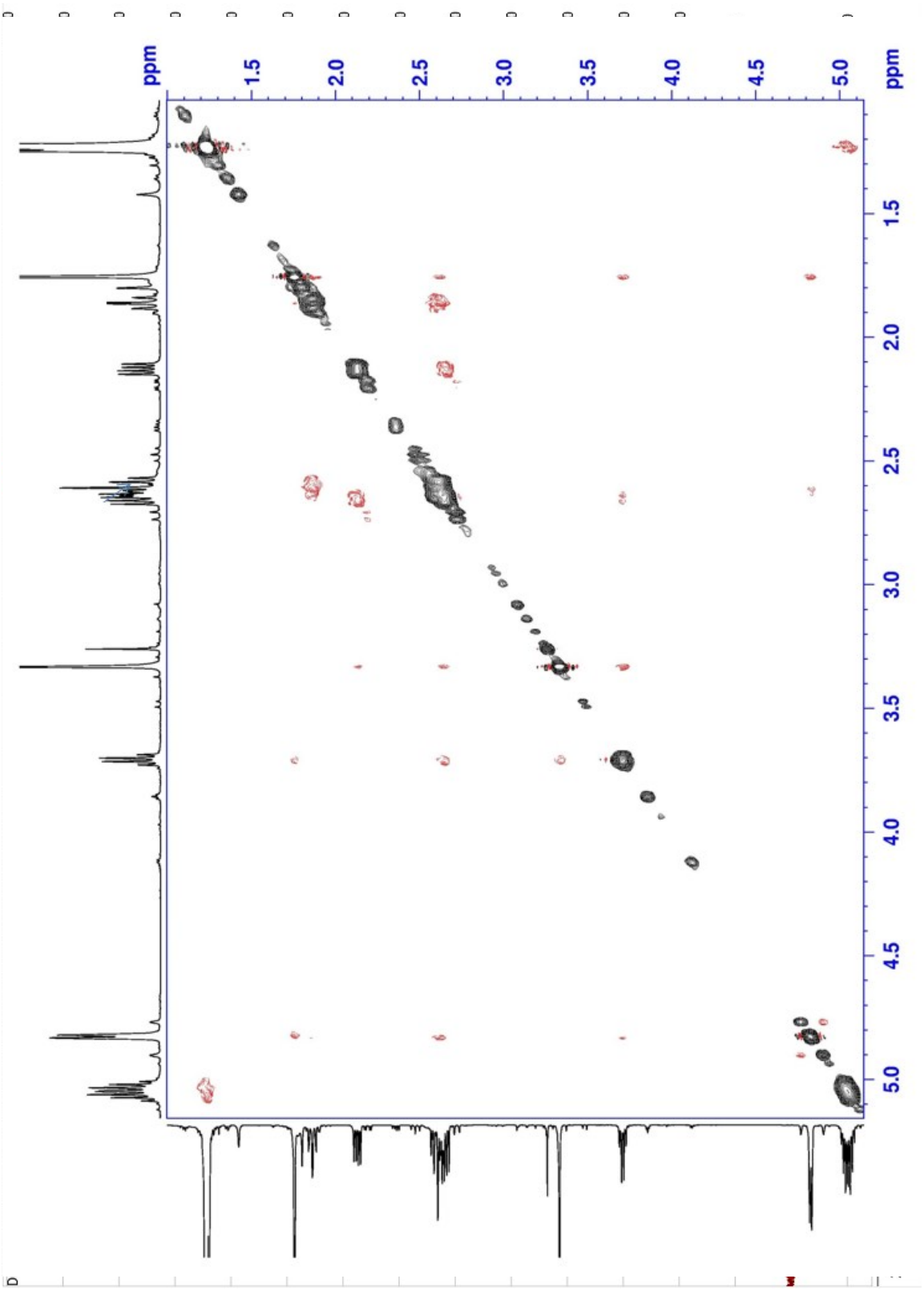

ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ppm
2.0
2.5
3.0
3.5
4.0
4.5
5.0

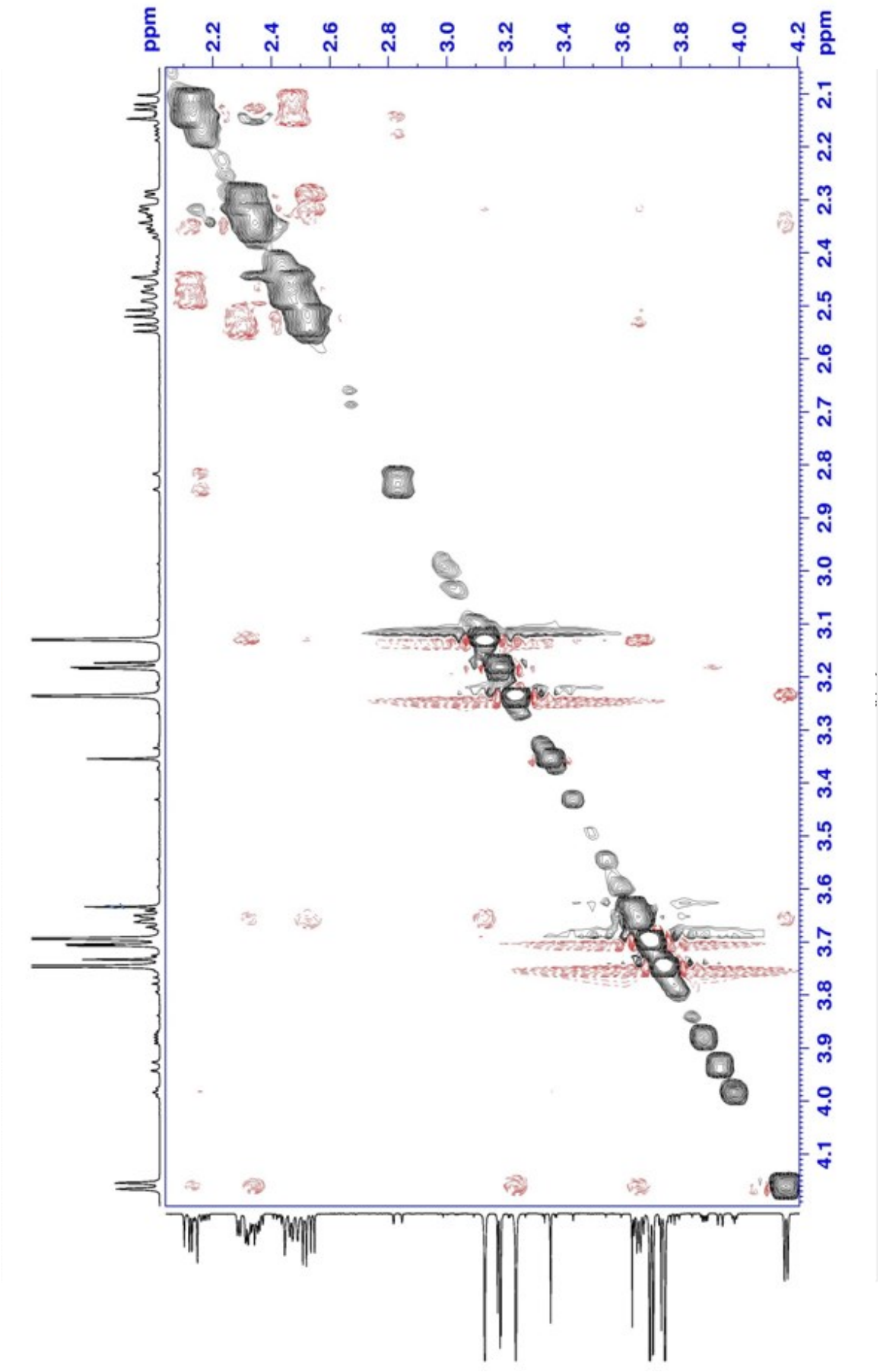

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

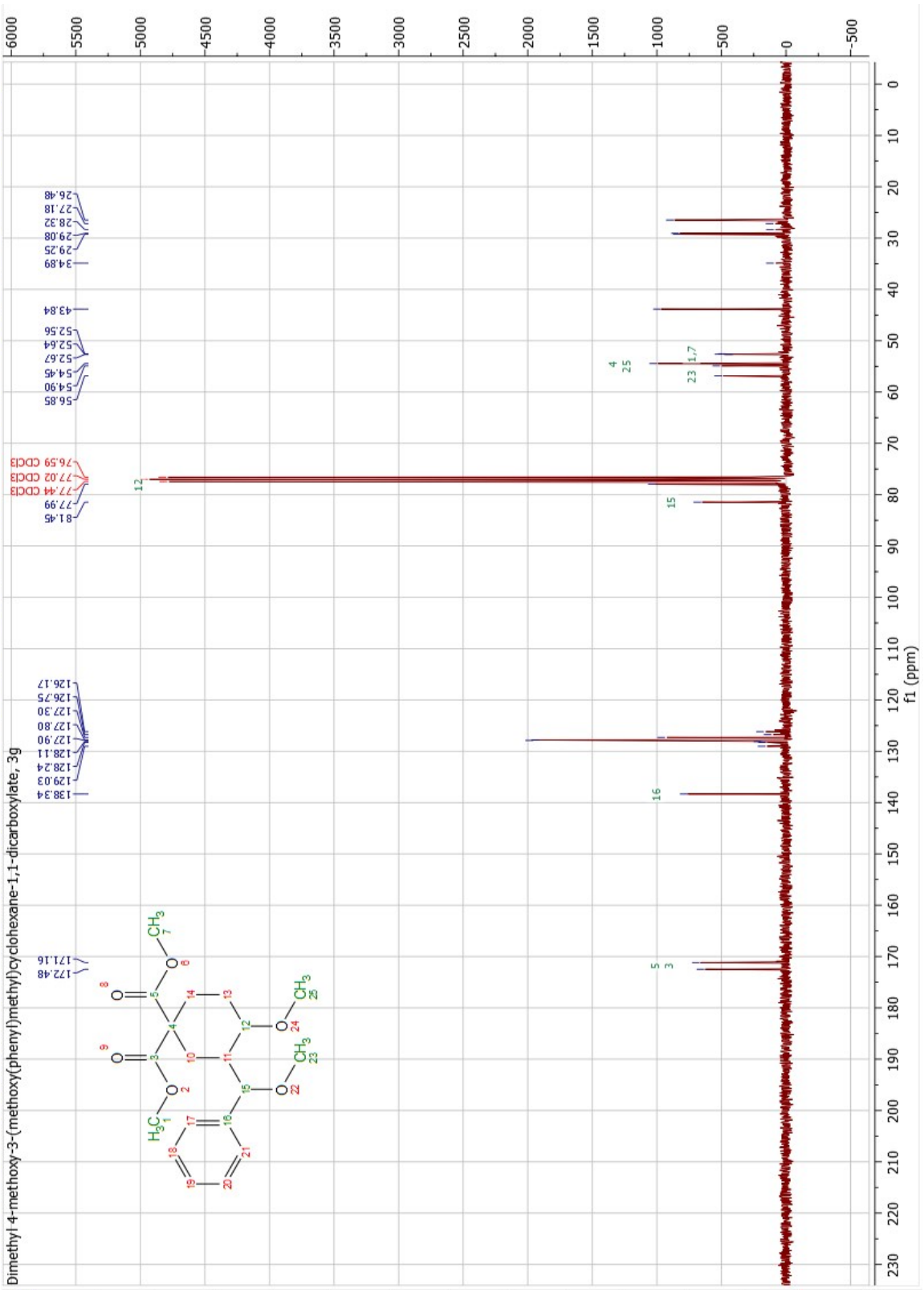

Dimethyl 4-methoxy-4-methyl-3-(prop-1-en-2-yl)cyclohexane-1,1-dicarboxylate, 2c
f1 (ppm)

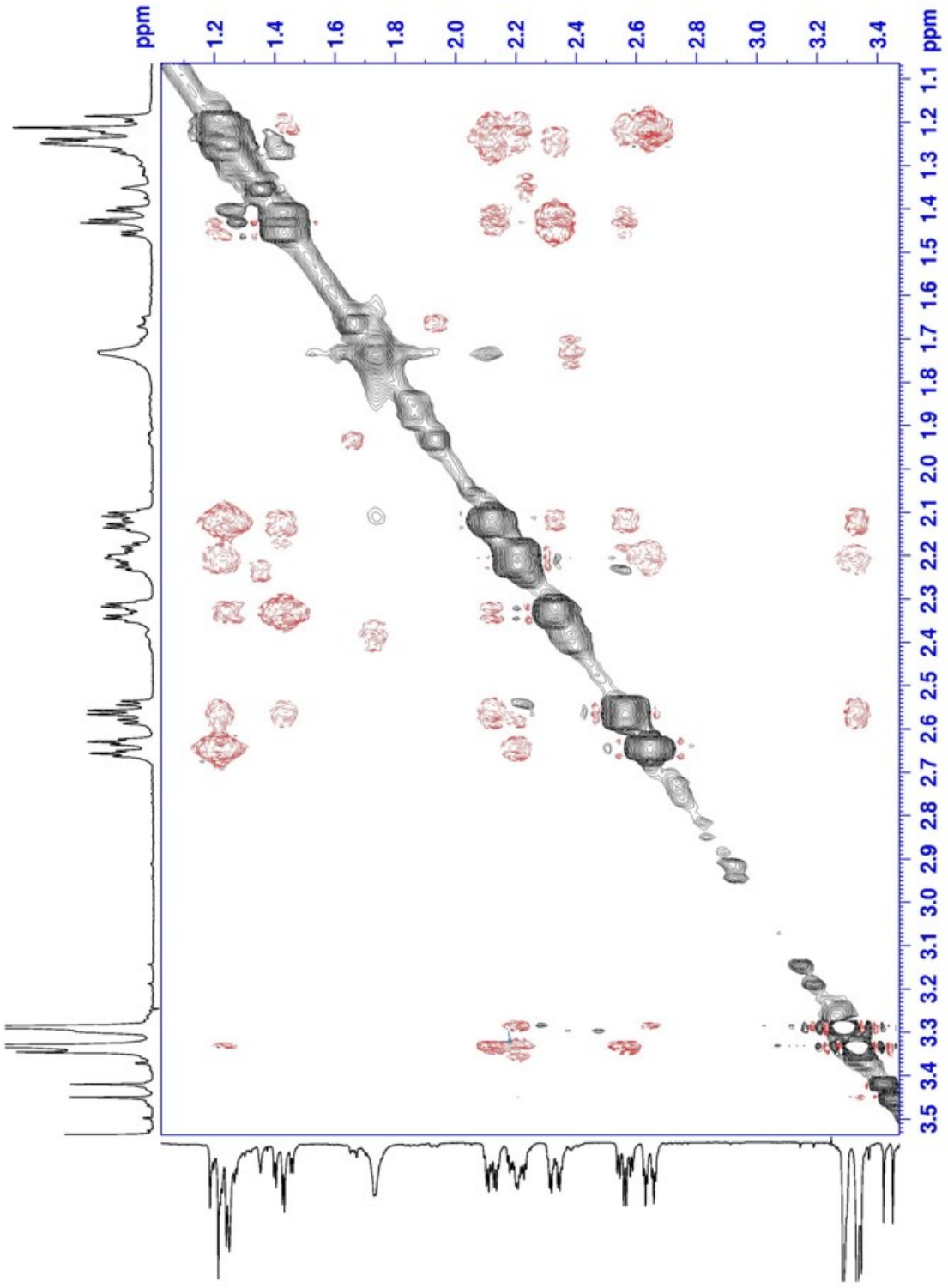

Selective NOESY
CH3 12
CH2 6-1
CH2 2-1
CH 5
CH2 6-2
CH2 3-1
CH2 2-2
CH3 13
CH2 3-2
CH3 11
ppm

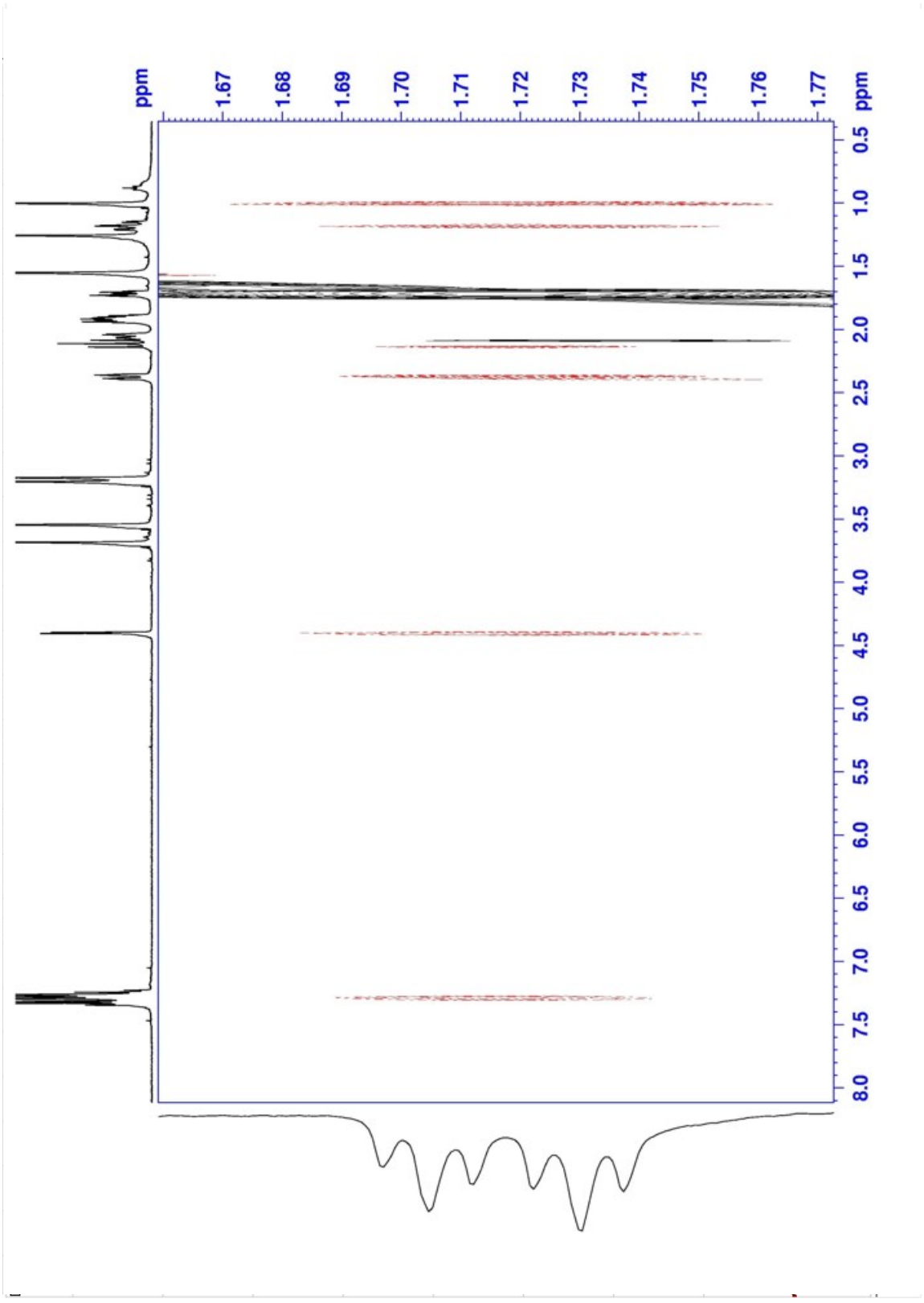

f1 (ppm)
10,11,12,13
20
22
14",15,17'
16
19'
14'
17'
12.01
2.94
0.99
0.93
2.84
3.00
1.00
1.95
2.09

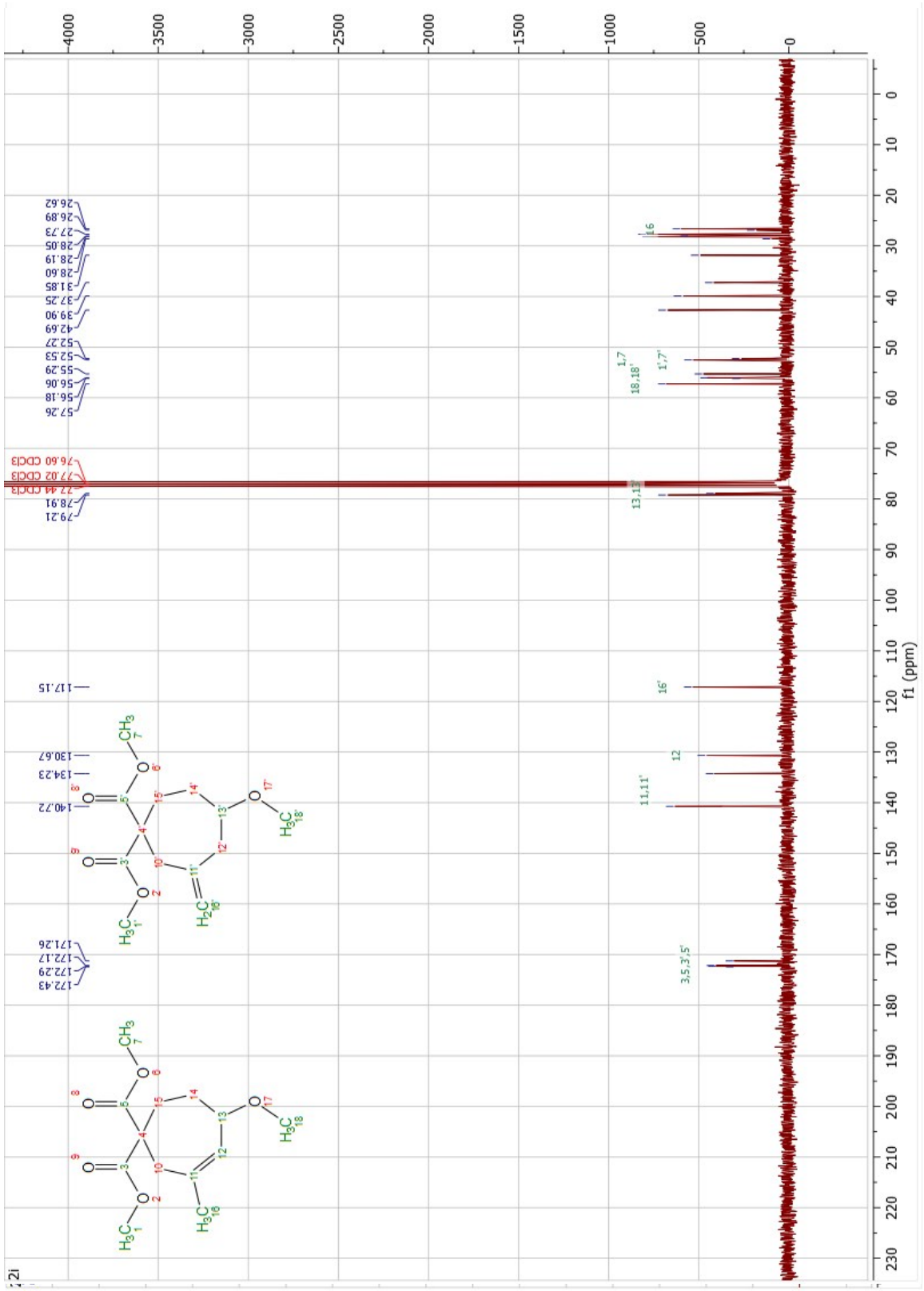

ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
ppm
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

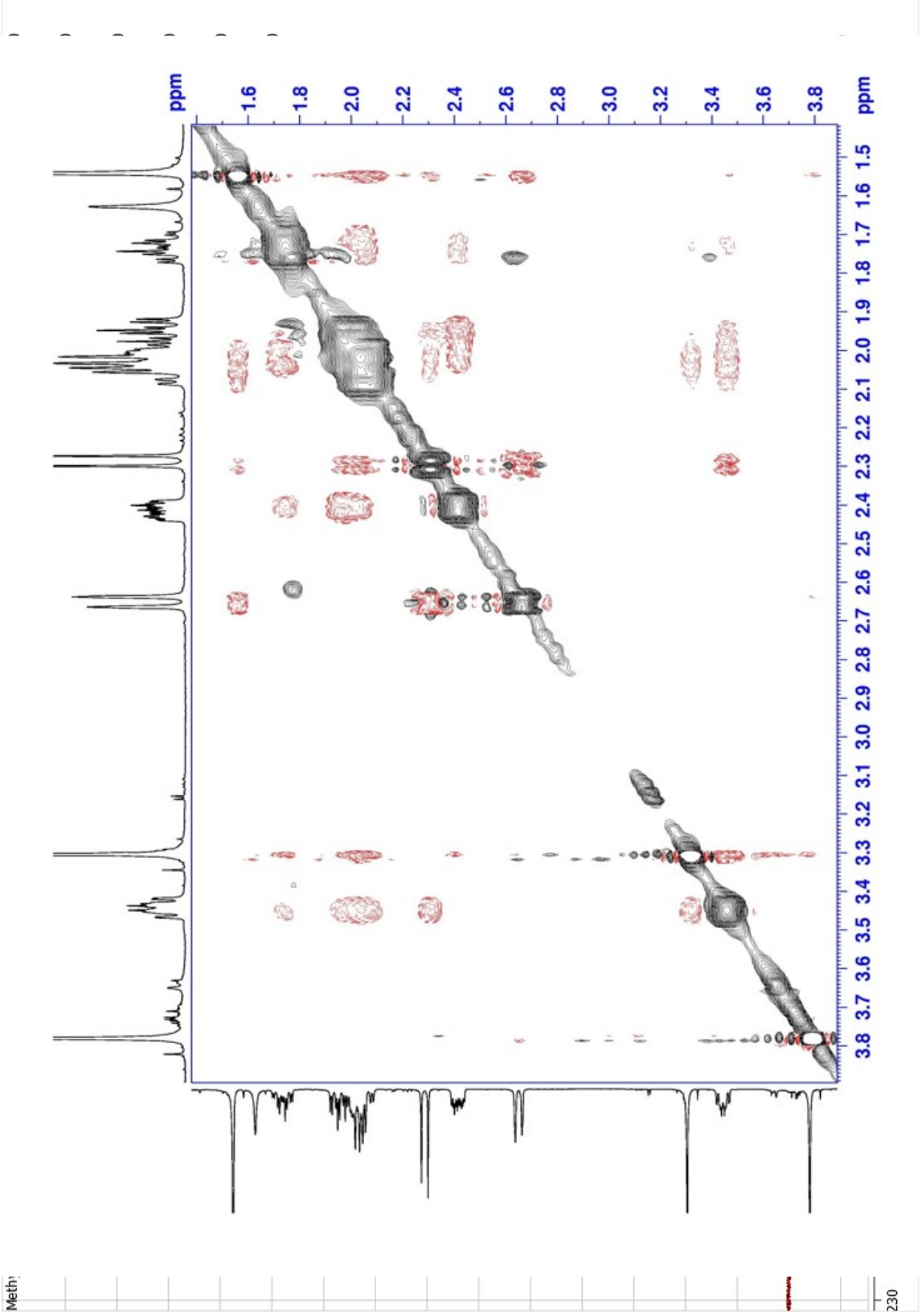

ppm
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
4.0
4.2
ppm
2.1
2.2
2.3
2.4
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
3.5
3.6
3.7
3.8
3.9
4.0
4.1

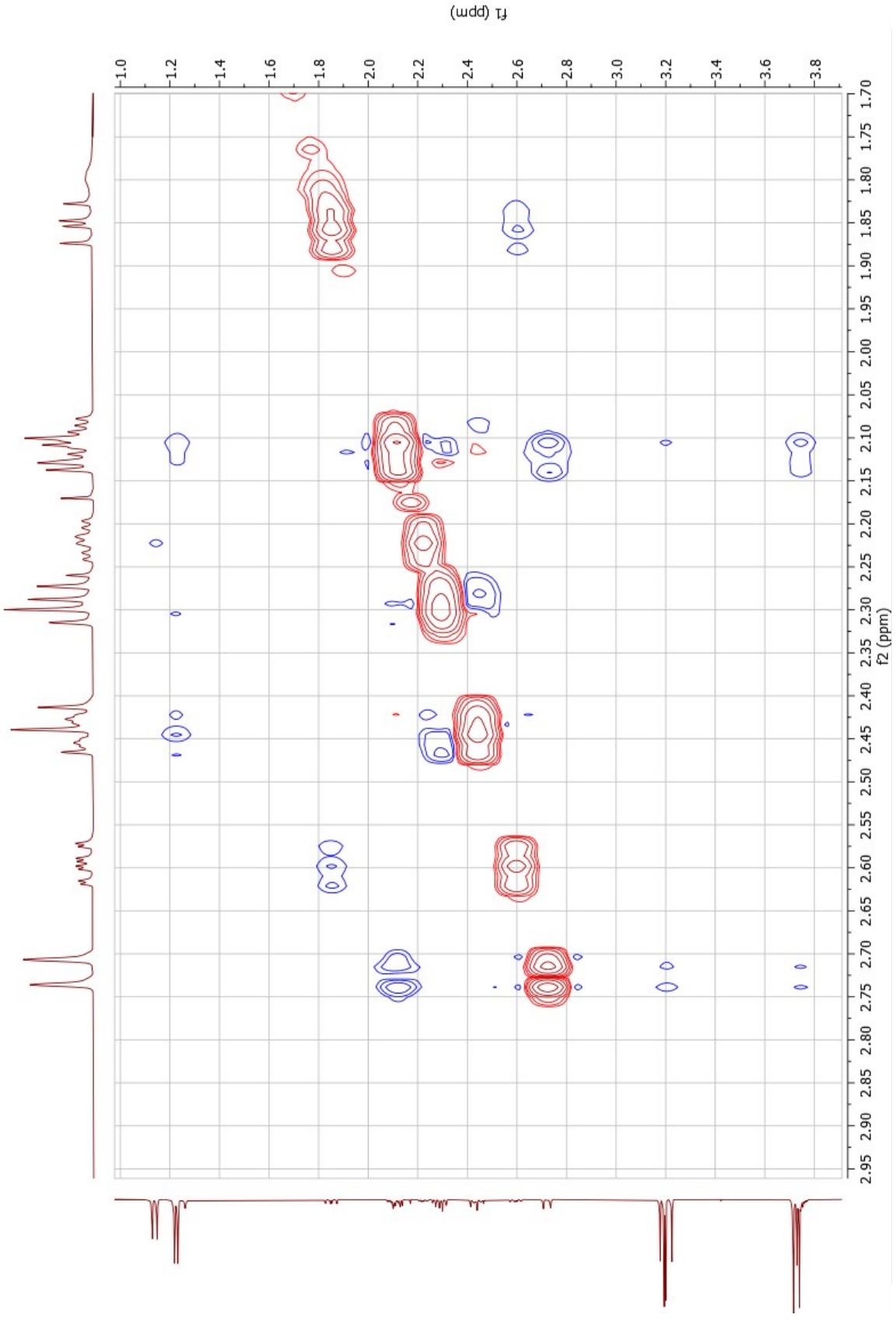

Dimethyl 4-methoxy-3-(methoxy(phenyl)methyl)cyclohexane-1,1-dicarboxylate, 3g
f1 (ppm)

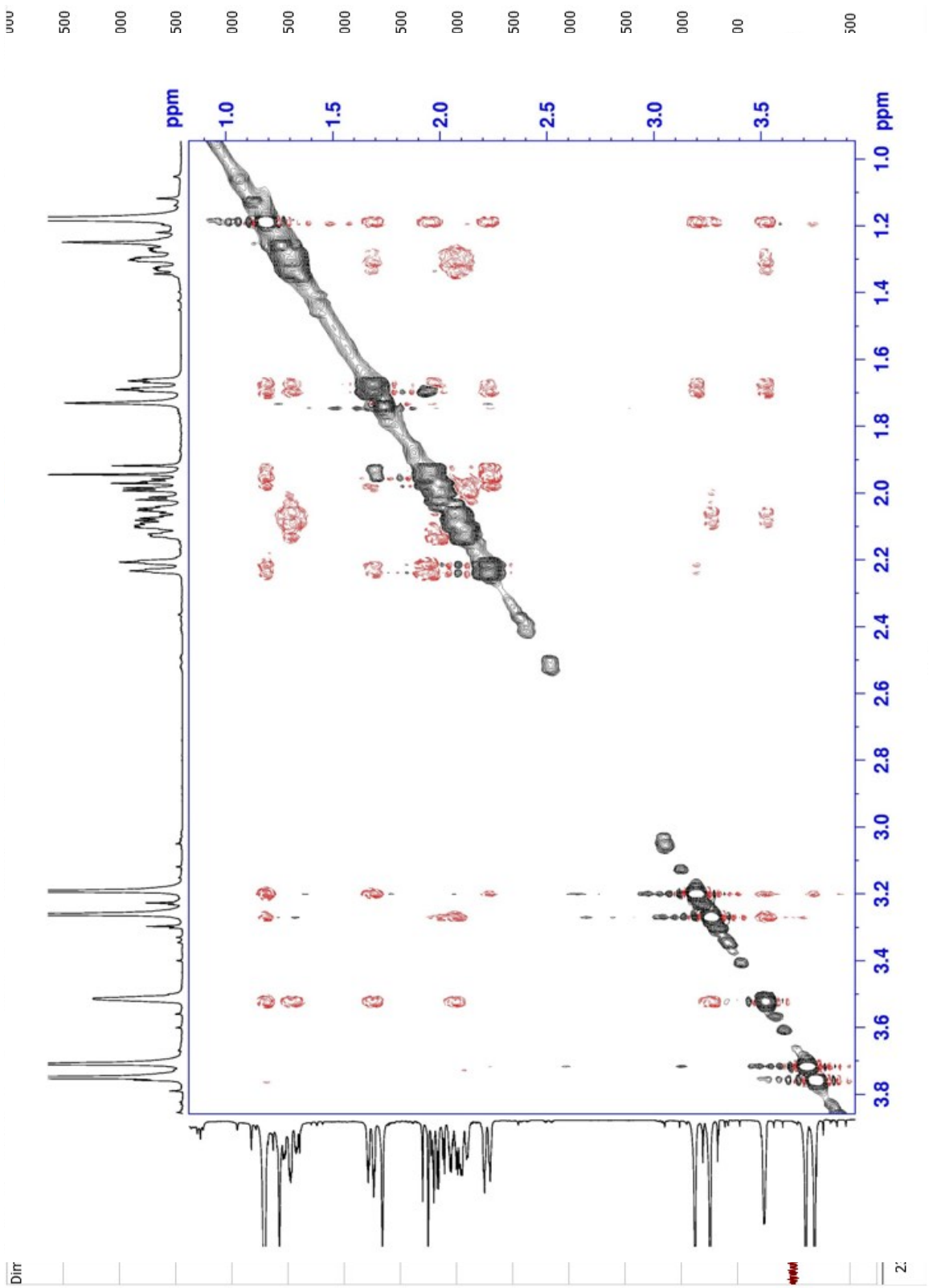

ppm
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
ppm
1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4 3.5

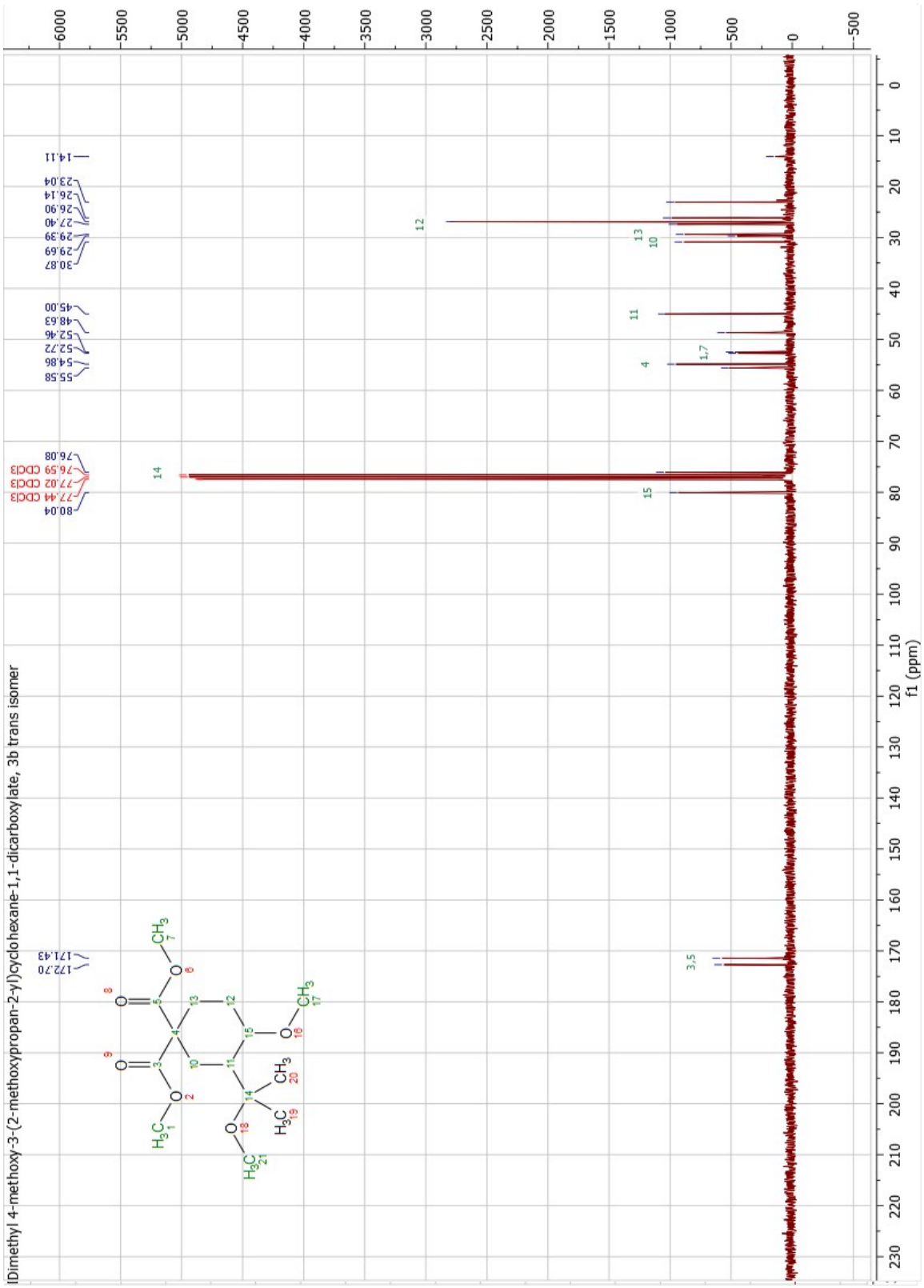

ppm
1.67
1.68
1.69
1.70
1.71
1.72
1.73
1.74
1.75
1.76
1.77
ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0

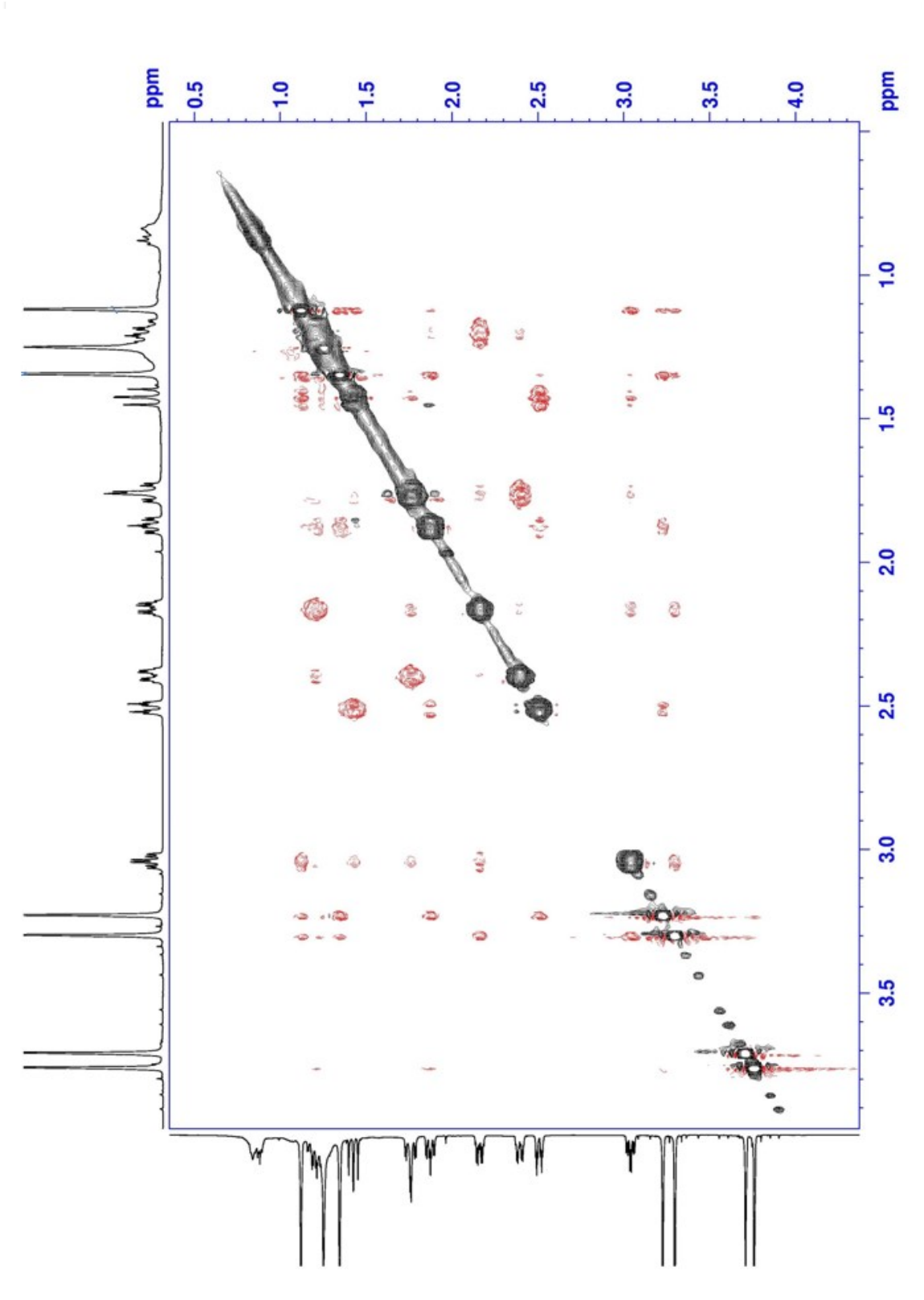

f1 (ppm)
CDCl3
CH3
H3C
H2C

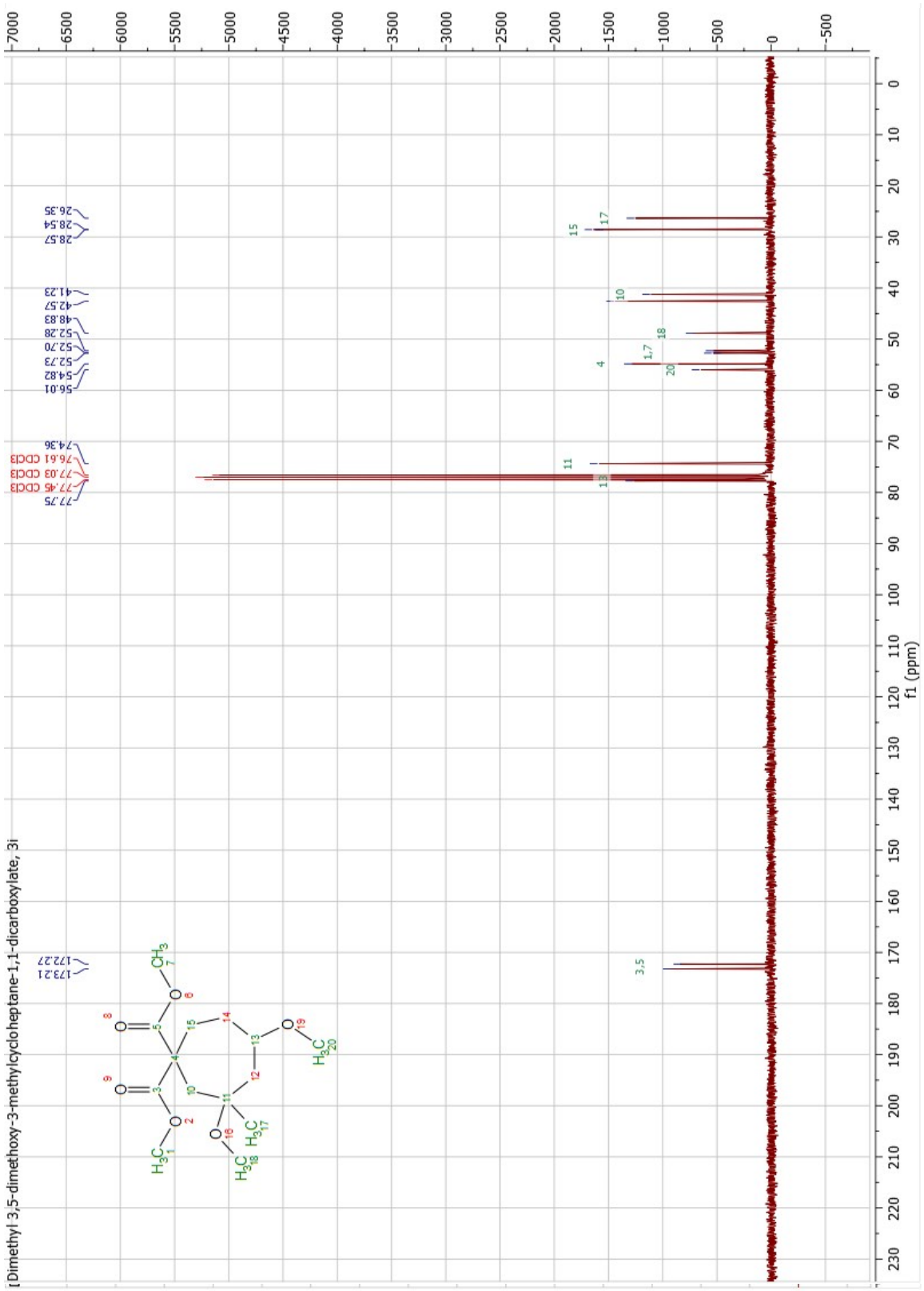

ppm
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
ppm
1.5 1.6 1.7 1.8 1.9 2.0 2.1 2.2 2.3 2.4 2.5 2.6 2.7 2.8 2.9 3.0 3.1 3.2 3.3 3.4 3.5 3.6 3.7 3.8
230

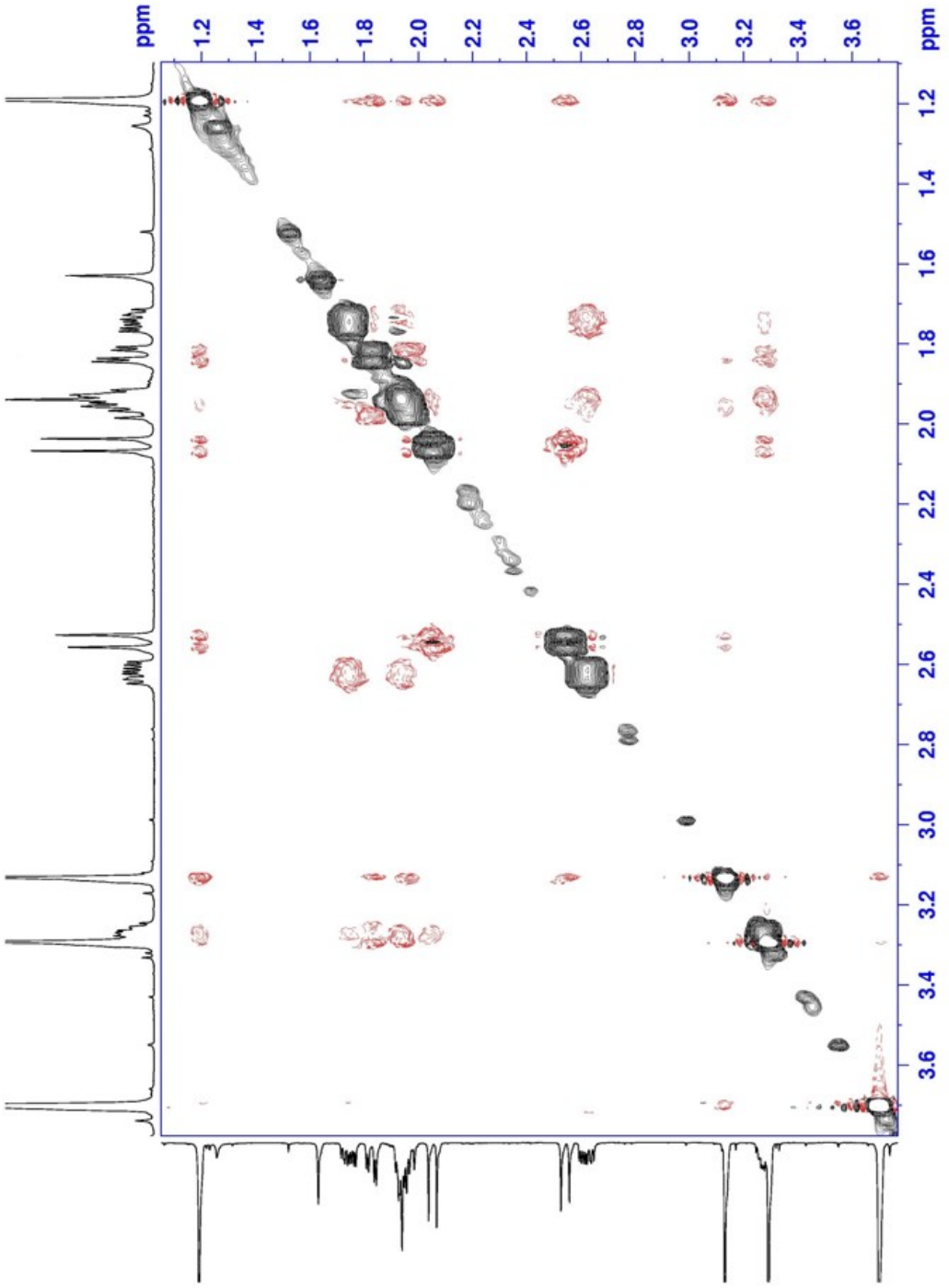

f1 (ppm)
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
f2 (ppm)
2.95
2.90
2.85
2.80
2.75
2.70
2.65
2.60
2.55
2.50
2.45
2.40
2.35
2.30
2.25
2.20
2.15
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70

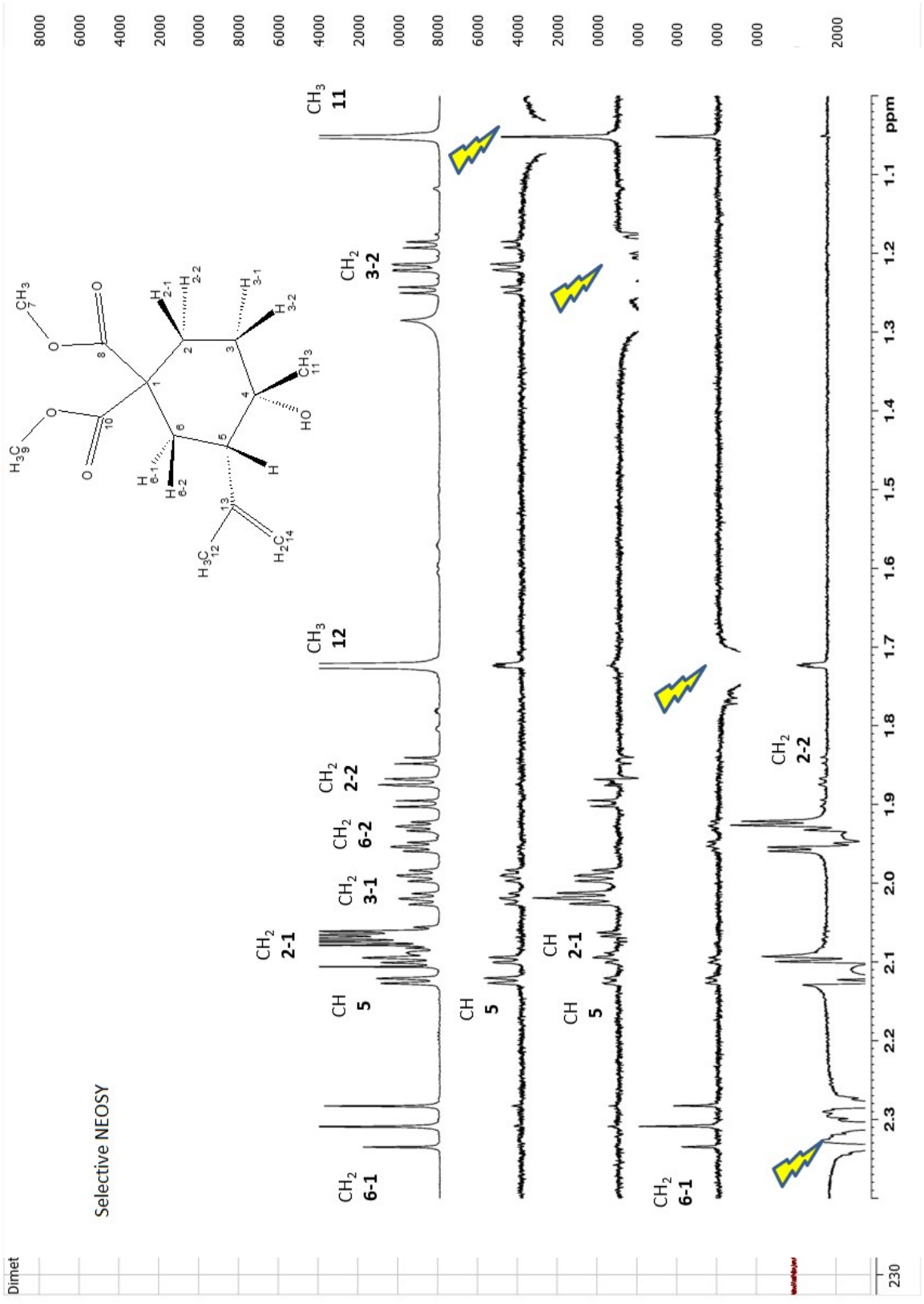

ppm
1.0
1.5
2.0
2.5
3.0
3.5
ppm
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8


Dimethyl 4-methoxy-3-(2-methoxypropan-2-yl)cyclohexane-1,1-dicarboxylate, 3b trans isomer
f1 (ppm)


ppm
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
ppm
1.0
1.5
2.0
2.5
3.0
3.5


[Dimethyl 3,5-dimethoxy-3-methylcycloheptane-1,1-dicarboxylate, 3i
f1 (ppm)
173.21
172.27
77.75
77.45 CDCl3
77.03 CDCl3
76.61 CDCl3
74.36
56.01
54.82
52.73
52.70
52.28
48.83
42.57
41.23
28.57
28.54
26.35
3.5


ppm
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
ppm


Selective NEOSY
Dimet
230
ppm
CH3 11
CH2 3-2
CH3 12
CH2 2-2
CH2 6-2
CH2 3-1
CH2 2-1
CH 5
CH2 6-1
CH2 2-1
CH 5
CH 5
CH2 6-1
CH2 2-2

45