

Supporting Information

Ring Expansion of Cyclic 1,2-Diols to form Medium Sized Rings *via* Ruthenium Catalyzed Transfer Hydrogenative [4+2] Cycloaddition

Zachary A. Kasun, Liana M. Geary, and Michael J. Krische

University of Texas at Austin, Department of Chemistry and Biochemistry

Austin, TX 78712

mkrische@mail.utexas.edu

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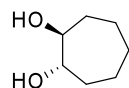
General Information: All reactions were run under an atmosphere of argon. Anhydrous solvents were distilled using solvent stills, and solvents were transferred by syringe. Sealed tubes (13×100 mm²) were purchased from Fisher Scientific (catalog number 14-959-35C) and were dried in an oven overnight and cooled under a stream of argon prior to use. Ru₃(CO)₁₂, racemic 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (*rac*-BINAP) and 1,3-bis(diphenylphosphino)-propane (dppp) were used without purification. All commercially available starting materials were used without purification, except *trans*-1,2-cyclohexanediol, which was recrystallized from boiling ethyl acetate, and isoprene, which was distilled, before use. Analytical thin-layer chromatography (TLC) was carried out using 0.25 mm commercial silica gel plates (Silicycle Siliaplate, F-254). Visualization was accomplished by dipping in a *p*-anisaldehyde solution and heating. Purification of reaction products was carried out by flash column chromatography using Silicycle silica gel (40-63 μm), according to the method described by Still.¹

Spectroscopy and Spectrometry: Infrared spectra were recorded on a Thermo Nicolet 380 spectrometer. Low-resolution mass spectra (LRMS) were obtained on a Thermo Scientific TSQ for chemical ionization (CI) or an Agilent Technologies 6530 Accurate Mass QToF/MS for electrospray ionization (ESI) and are reported as *m/z* (relative intensity). Accurate masses are reported for the molecular ion (M+H or M+Na) or a suitable fragment ion. Melting points were obtained on a Stuart SMP3 apparatus and are uncorrected. ¹H NMR spectra were recorded on a Varian DirectDrive (400 MHz) or Agilent MR (400 MHz) spectrometer at ambient temperature unless otherwise noted. Chemical shifts are reported in delta (δ) units, parts per million (ppm), relative to the center of the singlet at 7.26 ppm for deuteriochloroform. Data are reported as: multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin. = quintet, m = multiplet), integration and coupling constant(s) in Hz. ¹³C NMR spectra were recorded on a Varian DirectDrive (100 MHz) or Agilent MR (100 MHz) spectrometer and were routinely run with broadband decoupling. Chemical shifts are reported in ppm, with the residual solvent resonance employed as the internal standard (CDCl₃ at 77.16 ppm).

¹ Still, W.C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Synthesis of starting materials

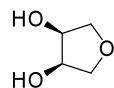
trans-1,2-heptanediol (**1c**)



To a round bottom flask charged with cycloheptene (1.5 mL, 12.85 mmol) was added a solution of H₂O₂ (30% w/w in H₂O, 14.5 mL) and formic acid (88% w/w in H₂O, 65 mL). The resulting solution was heated at 50 °C for 1 hour, was cooled to ambient temperature, and was allowed to stir overnight. The mixture was subjected to rotary evaporation under reduced pressure. To the residue was added NaOH (aq.) (10.0 M) until the solution was basic. The resulting mixture was extracted four times with ethyl acetate. The combined organic layers were dried (Na₂SO₄), filtered, and subjected to rotary evaporation under reduced pressure to afford a colorless solid (1.0 g, 7.6 mmol, 60% yield). ¹H NMR spectrum **1c** was identical in all respects to literature material.²

¹H NMR (400 MHz, CDCl₃): δ 3.44-3.40 (2H, m), 2.91 (2H, s), 1.91-1.83 (2H, m), 1.70-1.63 (2H, m), 1.56-1.44 (6H, m) ppm.

(3*R**,4*S**)-tetrahydrofuran-3,4-diol (**1e**)



To a round bottom flask charged with *meso*-erythritol (17.3 g, 14.2 mmol, 100 mol%) was added *p*-toluenesulfonic acid hydrate (1.35 g, 7.1 mmol, 5 mol%). The flask was fitted to a high vacuum distillation apparatus. The mixture was heated to 175 °C under vacuum. The diol was distilled (1.3 g, 12 mmol, 88% yield). ¹H and ¹³C NMR spectrum **1e** was identical in all respects to literature material.³

TLC (SiO₂): 0.02 (1:1, hexanes: ethyl acetate).

¹H NMR (400 MHz, CD₃CN): δ 4.13 (m, 2H), 3.81 (m, 2H), 3.62 (br s, 2H), 3.54 (m, 2H) ppm.

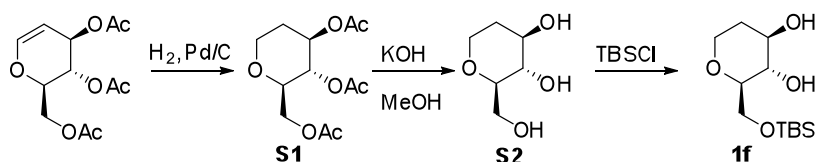
¹H NMR (400 MHz, CDCl₃): δ 4.27 (m, 2H), 3.92 (m, 2H), 3.73 (m, 2H), 2.92 (br s, 2H) ppm.

¹³C NMR (100 MHz, CD₃CN): δ 71.9, 69.1 ppm.

² Daiichi Pharmaceutical Co., Ltd. Antithrombic Diaminocyclohexane Derivatives. European Patent EP1577301 A1, Sep 21, 2005.

³ Arceo, E; Marsden, P.; Bergman, R. G; Ellman, J. A. *Chem. Commun.* **2009**, 3357.

(2*R*,3*S*,3*R*)-2-(((*tert*-Butyldimethylsilyl)oxy)methyl)tetrahydro-2*H*-pyran-3,4-diol (1f**)**



To a round bottom flask charged with tri-*O*-acetyl-D-glucal (4.00 g, 14.7 mmol, 100 mol%) and palladium on carbon (0.40 g, 10 mass%) was added ethyl acetate (12 mL, 1.2 M). The solution was sparged with nitrogen and a hydrogen balloon was attached to the flask. The reaction was allowed to stir at ambient temperature for 16 hours, at which point the reaction was filtered through celite with the aid of ethyl acetate. The reaction mixture was subjected to rotary evaporation under reduced pressure to give crude **S1** (4.01 g, 14.7 mmol, 99% yield). The ^1H NMR spectrum of **S1** was identical in all respects to literature material.⁴

^1H NMR (400 MHz, CDCl_3): δ 5.00-4.91 (m, 2H), 4.26-4.18 (m, 1H), 4.13-3.98 (m, 3H), 3.54-3.44 (m, 2H), 2.11-2.03 (m, 1H), 2.08 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.87-1.74 (m, 1H), 1.27-1.21 (m, 1H) ppm.

To a round bottom flask charged with crude **S1** (4.01 g, 14.7 mmol, 100 mol%) was added methanol (60 mL, 0.25 M). KOH (aq.) (10% w/w in H_2O , 40 mL) was added, and the reaction mixture was allowed to stir at ambient temperature for 16 hours. To the reaction mixture was added HCl (aq.) (2.0 M) until the solution was neutral. The volatiles were subjected to rotary evaporation under reduced pressure. The resulting solid was suspended in ethanol, filtered, and the volatiles were removed *in vacuo* to give crude **S2** (2.18 g, 14.7 mmol, 99% yield). The ^1H NMR spectrum of **S2** was identical in all respects to literature material.⁴

^1H NMR (400 MHz, CDCl_3): δ 3.98 (dd, 1H, $J = 1.9, 5.2$), 3.90-3.78 (m, 2H), 3.69-3.62 (m, 2H), 3.50 (dt, $J = 1.9, 12$ Hz, 1H), 3.24-3.19 (m, 1H), 2.01-1.94 (m, 1H), 1.75-1.63 (m, 2H) ppm.

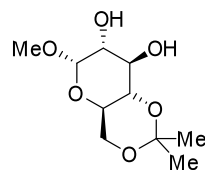
⁴ Shigetomi, K.; Shoji, K.; Mitsunashi, S.; Ubukata, M. *Phytochemistry* **2010**, 71, 312.

To a round bottom flask charged with crude triol **S2** (2.12 g, 14.7 mmol, 100 mol%) was added *N,N*-dimethylformamide (50 mL, 0.3M). Imidazole (2.00 g, 29.4 mmol, 200 mol%) and chlorodimethyl-*tert*butylsilane (2.43 g, 16.17 mmol, 110 mol%) were added to the solution. The solution was allowed to stir at ambient temperature for 12 hours. To the reaction was added water (100 mL), and the resulting solution was extracted three times with dichloromethane. The organic layers were combined and washed three times with water, and once with brine. The organic layer was dried (Na₂SO₄), filtered, and the volatiles were subjected to rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂, 1:24 methanol: dichloromethane) to give **1f** (2.7g, 10.3 mmol, 70% yield) as a solid. The ¹H NMR spectrum of **1f** was identical in all respects to literature material⁵

¹H NMR (400 MHz, CDCl₃): δ 3.96-3.91 (m, 2H), 3.73 (dd, 1H, *J* = 7, 10 Hz), 3.70-3.63 (m, 1H), 3.47 (dd, 1H, *J* = 1.8, 12 Hz), 3.43 (t, 1H, *J* = 9 Hz), 3.24-3.17 (m, 1H), 2.04-1.58 (br s, 2H), 1.96-1.90 (m, 1H), 1.73-1.62 (m, 1H), 0.90 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 77.8, 76.0, 72.9, 65.6, 65.5, 32.7, 25.8, 18.2, -5.53, -5.55 ppm.

(4a*R*,6*S*,7*R*,8*R*,8a*S*)-6-methoxy-2,2-dimethylhexahydropyrano[3,2-*d*][1,3]dioxine-7,8-diol (1g**)**



To a round bottom flask charged with α-methyl glucopyranoside (1.50 g, 7.72 mmol, 100 mol%) and *p*-toluenesulfonic acid hydrate (0.15 g, 0.77 mmol, 10 mol%) was added acetone (15 mL, 0.77M). A reflux condenser was fitted to the flask. Dimethoxypropane (1.5 mL, 11.58 mmol, 150 mol%) was added. *N,N*-dimethylformamide was added until the reaction became homogeneous (approximately 2 mL). The reaction mixture was refluxed for 15 hours, and it was cooled to ambient temperature. Triethylamine was added, and the mixture was filtered through celite with the aid of acetone. The volatiles were subjected to rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂, 1:20, methanol: dichloromethane) to give **1g** as a colorless solid (0.84 g, 3.55 mmol, 46% yield). The ¹H NMR spectrum of **1g** was identical in all respects to literature material.⁶

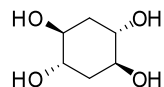
¹H NMR (400 MHz, CDCl₃): δ 4.72 (m, 1H), 3.87-3.67 (m, 4H), 3.63-3.45 (m, 3H), 3.40 (s, 3H), 1.48 (s, 3H), 1.41 (s, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 100.0, 99.9, 73.7, 73.2, 72.1, 63.5, 62.5, 55.6, 29.3, 19.3.

⁵ Kanai, M.; Hamashima, Y.; Shibasaki, M. *Tetrahedron Lett.* **2000**, *41*, 2405.

⁶ Khan, A. T.; Khan, M. M.; Adhikary, A. *Carbohydrate Research* **2011**, *346*, 673.

(1S*,2S*,4S*,5S*)-cyclohexane-1,2,4,5-tetraol (1h)



To a round bottom flask charged with a stirred solution of selenium dioxide (5.6 mg, 0.63 mmol, 2.5 mol%) in *tert*-butanol (7.5 mL, 0.08M) was added 1,4- cyclohexadiene (2.00 g, 25 mmol, 100 mol%). To the resulting mixture H₂O₂ (30% w/w in H₂O, 5.60 g, 50 mmol) was added dropwise over 20 min at room temperature. The mixture was allowed to stir for 24 hours at room temperature. NaHSO₃ (500 mg) was added to quench possibly unreacted H₂O₂. The solid precipitate was filtered and washed with ethanol. The volatiles were subjected to rotary evaporation under reduced pressure to give a syrup. The residue was dissolved in hot ethanol (50 mL), and the mixture was filtered and subjected to rotary evaporation under reduced pressure to give tetraol **1d**. Tetraol **1d** was further purified by recrystallizing from ethanol to give a colorless solid in 54% yield (1.89 g, 12.9 mmol). The ¹H NMR spectrum of **1d** was identical in all respects to literature material.⁷

¹H NMR (400 MHz, D₂O): δ 3.76 (m, 4H), 1.84 (m, 4H) ppm.

¹³C NMR (100 MHz, D₂O): δ 74.4, 38.3 ppm.

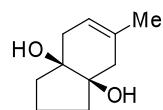
⁷ Maras, A.; Erden, M.; Secen, H.; Sutbeyaz, Y. *Carbohydrate Research* **1998**, 308, 435.

Preparation of cycloadduct-1,2-diols (3b, 3d-f, 3h, 3k):

Notwithstanding variation of ligand, the cycloadducts 3b, 3d-f, 3h, 3k were prepared using our previously described method.⁸ The ¹H and ¹³C NMR spectra are identical with those previously reported.

GENERAL PROCEDURE: To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added *diol* (0.3 mmol, 100 mol%), Ru₃(CO)₁₂ (3.8 mg, 0.006 mmol, 2 mol%), and a suitable ligand (0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Diene (0.9- 1.5 mmol, 300-500 mol%) was added via syringe. The reaction vessel was capped, and the reaction stirred at 130 °C for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography.

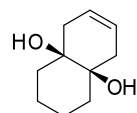
(3a*R**,7a*S**)-5-methyl-2,3,4,7-tetrahydro-1*H*-indene-3a,7a-diol (3b)



¹H NMR (400 MHz, CDCl₃): δ 5.26-5.23 (m, 1H), 2.31-2.09 (m, 6H), 1.90-1.54 (m, 10H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 131.2, 117.7, 78.7, 78.0, 40.1, 35.5, 35.1, 34.8, 23.1, 17.4 ppm.

(4a*R**,8a*S**)-1,2,3,4,5,8-hexahydronaphthalene-4a,8a-diol (3d)

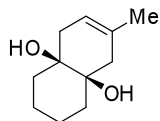


¹H NMR (400 MHz, CDCl₃): δ 5.55 (m, 2H), 2.38-2.16 (m, 6H), 1.66-1.56 (m, 4H), 1.52-1.34 (m, 4H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 123.8, 72.3, 36.6, 34.0, 22.0 ppm.

⁸ Geary, L. M.; Glasspoole, B. W.; Kim, M. M.; Krische, M. J. *J. Am. Chem. Soc.* **2012**, *135*, 3796.

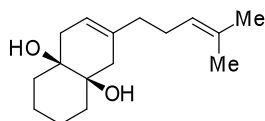
(4a*R,8a*S**)-6-methyl-1,2,3,4,5,8-hexahydronaphthalene-4a,8a-diol (3e)**



¹H NMR (400 MHz, CDCl₃): δ 5.27-5.23 (m, 1H), 2.34-2.03 (m, 6H), 1.71-1.61 (m, 7H), 1.51-1.37 (m, 4H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 131.0, 117.6, 72.5, 72.0, 41.5, 36.6, 34.0, 33.8, 23.1, 21.99, 21.96 ppm.

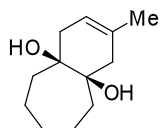
(4a*R,8a*S**)-6-(4-methylpent-3-en-1-yl)-1,2,3,4,5,8-hexahydronaphthalene-4a,8a-diol (3f)**



¹H NMR (400 MHz, CDCl₃): δ 5.27 (m, 1H), 5.09-5.03 (m, 1H), 2.34-1.92 (m, 10H), 1.73-1.62 (m, 7H), 1.60 (s, 3H), 1.49-1.36 (m, 4H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 134.7, 131.6, 124.0, 117.3, 72.6, 72.1, 39.7, 36.9, 36.7, 33.9, 33.7, 26.2, 25.7, 22.0, 21.9, 17.7 ppm.

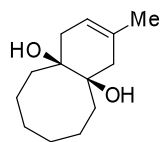
(4a*S,9a*R**)-2-methyl-1,4,6,7,8,9-hexahydro-4a*H*-benzo[7]annulene-4a,9a(5*H*)-diol (3h)**



¹H NMR (400 MHz, CDCl₃): δ 5.27 (s, 1H), 2.29-2.06 (m, 6H), 1.97-1.89 (m, 2H), 1.75-1.71 (m, 3H), 1.66 (s, 3H), 1.55-1.45 (m, 5H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 131.6, 118.1, 75.4, 74.9, 43.1, 38.3, 35.9, 35.7, 26.2, 23.1, 20.9 ppm.

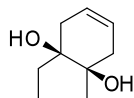
(4a*S,10a*R**)-2-methyl-1,4,5,6,7,8,9,10-octahydrobenzo[8]annulene-4a,10a-diol (3k)**



¹H NMR (400 MHz, CDCl₃): δ 5.29-2.25 (m, 1H), 2.32-2.04 (m, 6H), 1.98-1.90 (m, 2H), 1.86-1.75, (m, 2H), 1.69-1.41 (m, 12H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 131.6, 118.1, 75.1, 74.6, 44.8, 40.0, 35.82, 35.75, 28.0, 23.1 ppm.

(3aR*,7aS*)-2,3,4,7-tetrahydro-1H-indene-3a,7a-diol (3a)



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added *cis*-1,2-cyclopentanediol **1a** (30.6 mg, 0.3 mmol, 100 mol%), $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), 3,5-dimethylbenzoic acid (4.5 mg, 0.03 mmol, 10 mol%), and dppp (7.4 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Freshly condensed butadiene **2c** (0.13 mL, 1.5 mmol, 500 mol%) was added at -78 °C via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 7 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 2:3- 3:2, ethyl acetate: hexanes) to furnish cycloadduct **3a** (37.5 mg, 0.243 mmol, 81% yield) as a colorless solid.

TLC (SiO_2): Rf = 0.15 (2:3, ethyl acetate: hexanes).

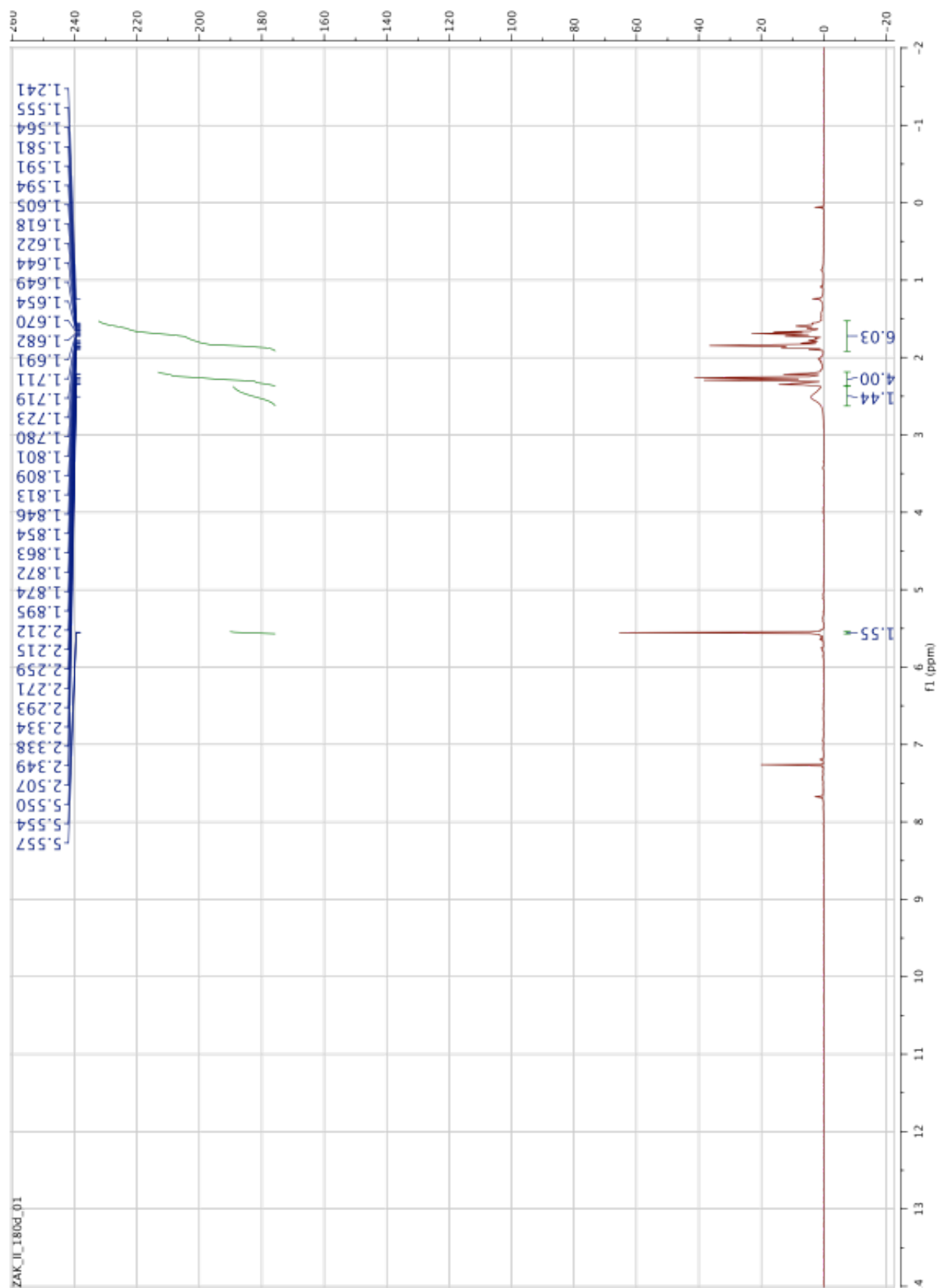
^1H NMR (400 MHz, CDCl_3): δ 5.55 (t, J = 1.4 Hz, 2H), 2.51 (s, 2H), 2.35-2.21 (m, 4H), 1.90-1.55 (m, 6H) ppm.

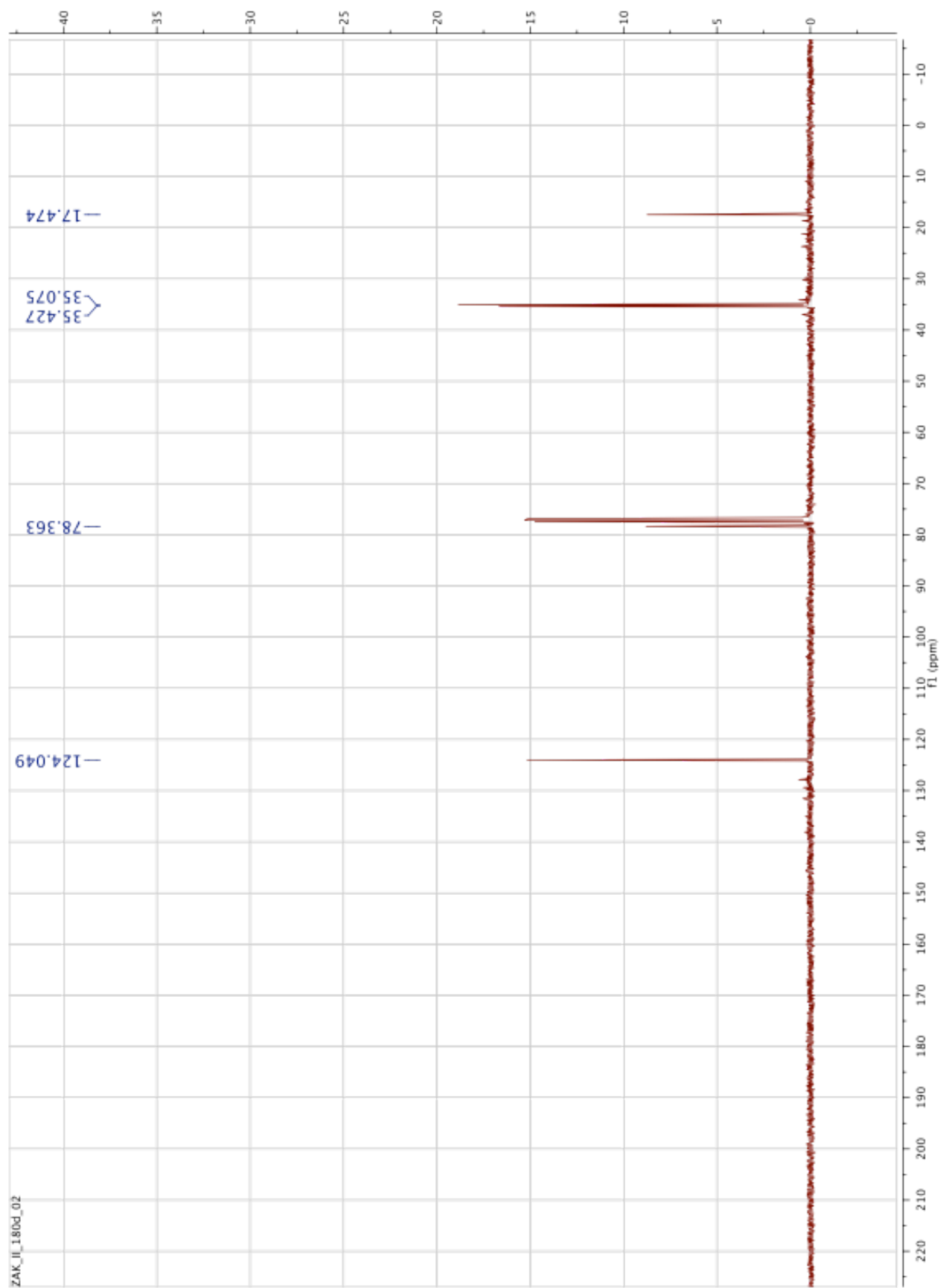
^{13}C NMR (100 MHz, CDCl_3): δ 124.0, 78.4, 35.4, 35.1, 17.5 ppm.

MP: 54-56 °C.

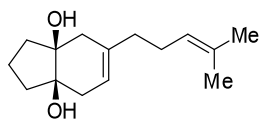
LRMS (ESI+): Calculated for $\text{C}_9\text{H}_{14}\text{NaO}_2^+$ ($\text{M}+\text{Na}^+$) 177.1; Found 177.1.

FTIR (neat): ν 3311, 3022, 2944, 2906, 1425, 1393, 1232, 1203, 1121, 1106, 1045, 993, 951, 923, 895, 849, 665 cm^{-1} .





(3aS*,7aR*)-5-(4-methylpent-3-en-1-yl)-2,3,3a,4,7,7a-hexahydro-1H-indene-3a,7a diol (3c)



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added *cis*-1,2-cyclopentanediol **1a** (30.6 mg, 0.3 mmol, 100 mol%), Ru₃(CO)₁₂ (3.8 mg, 0.006 mmol, 2 mol%), 3,5-dimethylbenzoic acid (4.5 mg, 0.03 mmol, 10 mol%), and dppp (7.4 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Myrcene **2c** (0.23mL, 1.2 mmol, 400 mol%) was added via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO₂: 1:4, ethyl acetate: hexanes) to furnish cycloadduct **3c** (64.6 mg, 0.273 mmol, 91% yield) as a colorless oil.

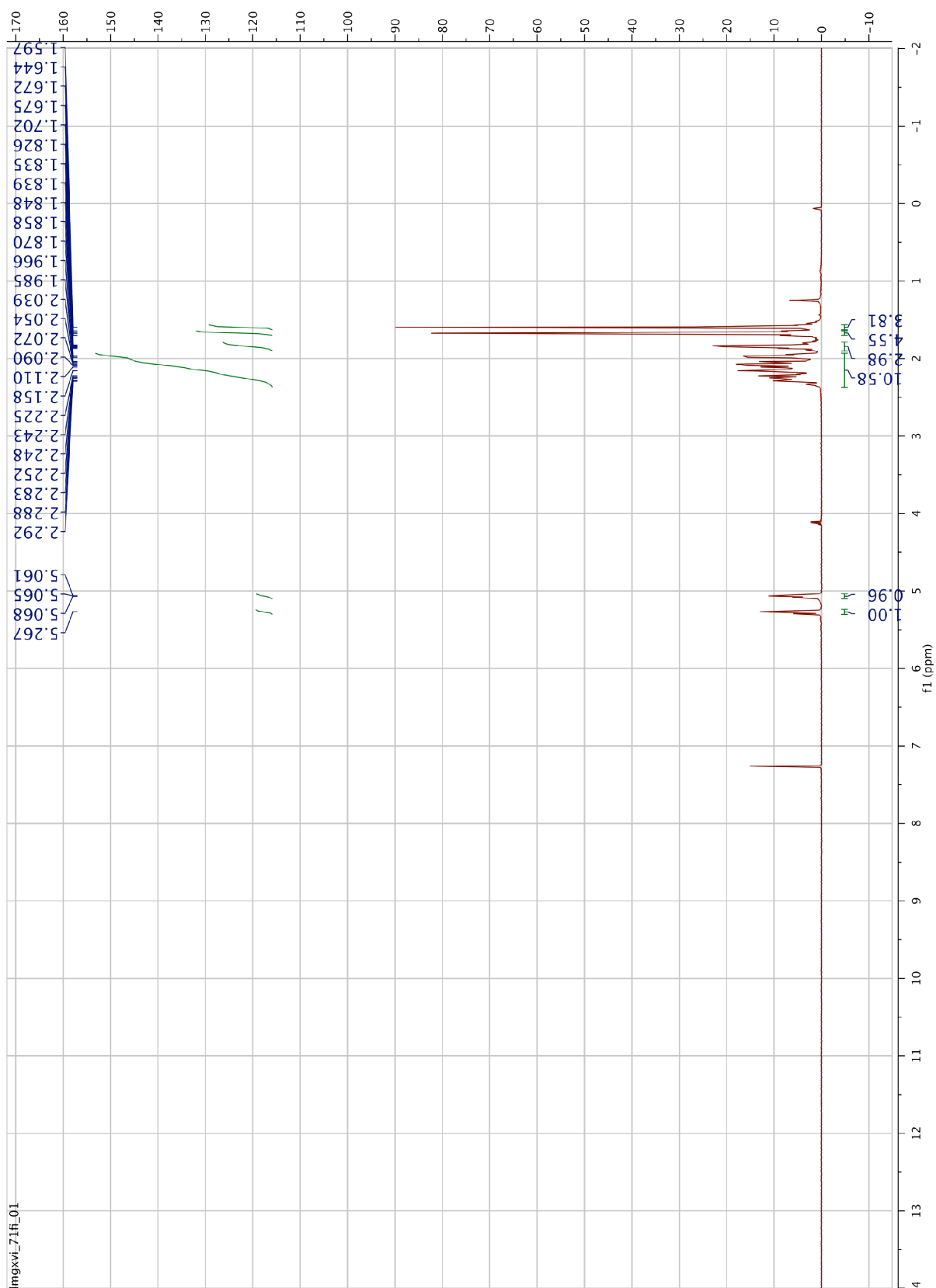
TLC (SiO₂): R_f = 0.30 (2:3, ethyl acetate: hexanes).

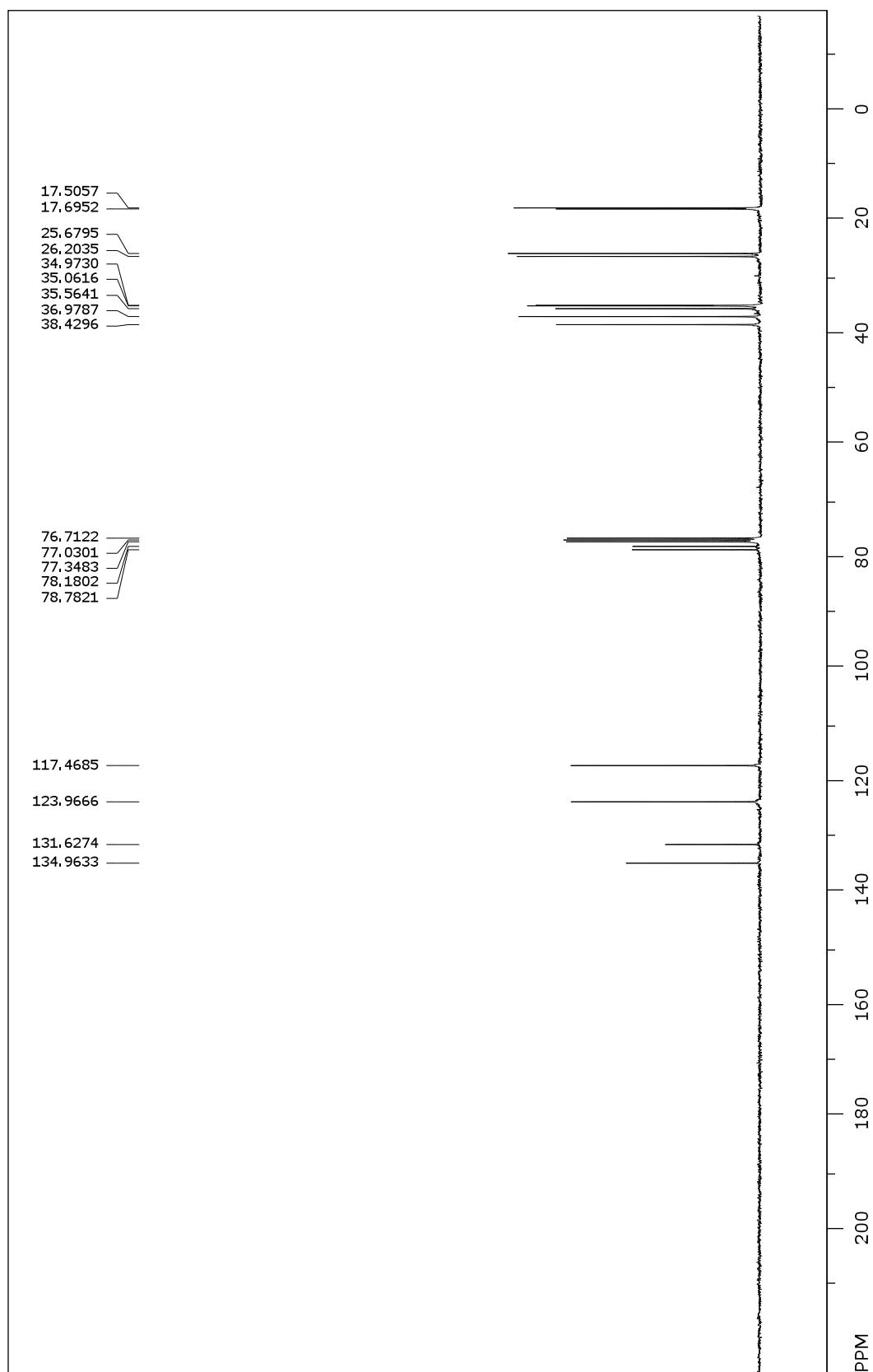
¹H NMR (400 MHz, CDCl₃): δ 5.25 (m, 1H), 5.06 (m, 1H), 2.32-1.93 (m, 10H), 1.89-1.79 (m, 3H), 1.71-1.63 (m, 4H), 1.59 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 135.0, 131.6, 124.0, 117.5, 78.8, 78.2, 38.4, 37.0, 35.6, 35.06, 34.97, 26.2, 25.7, 17.7, 17.5 ppm.

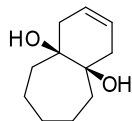
LRMS (CI⁺): Calculated for C₁₅H₂₃O⁺ (M-OH) 219; Found 219.

FTIR (neat): ν 3413, 2964, 2915, 1376, 1101, 951 cm⁻¹.





(4a*R*,9a*S*)-1,4,6,7,8,9-hexahydro-4a*H*-benzo[7]annulene-4a,9a(5*H*)-diol (3g**)**



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added *trans*-1,2-cycloheptanediol **1c** (39.1 mg, 0.3 mmol, 100 mol%), Ru₃(CO)₁₂ (3.8 mg, 0.006 mmol, 2 mol%), and *rac*-BINAP (11.2 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Freshly condensed butadiene **2a** (0.13 mL, 1.5 mmol, 500 mol%) was added at -78 °C via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO₂: 2:3- 3:2, ethyl acetate: hexanes) to furnish cycloadduct **3g** (45.0 mg, 0.247 mmol, 82% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.20 (3:7, ethyl acetate: hexanes).

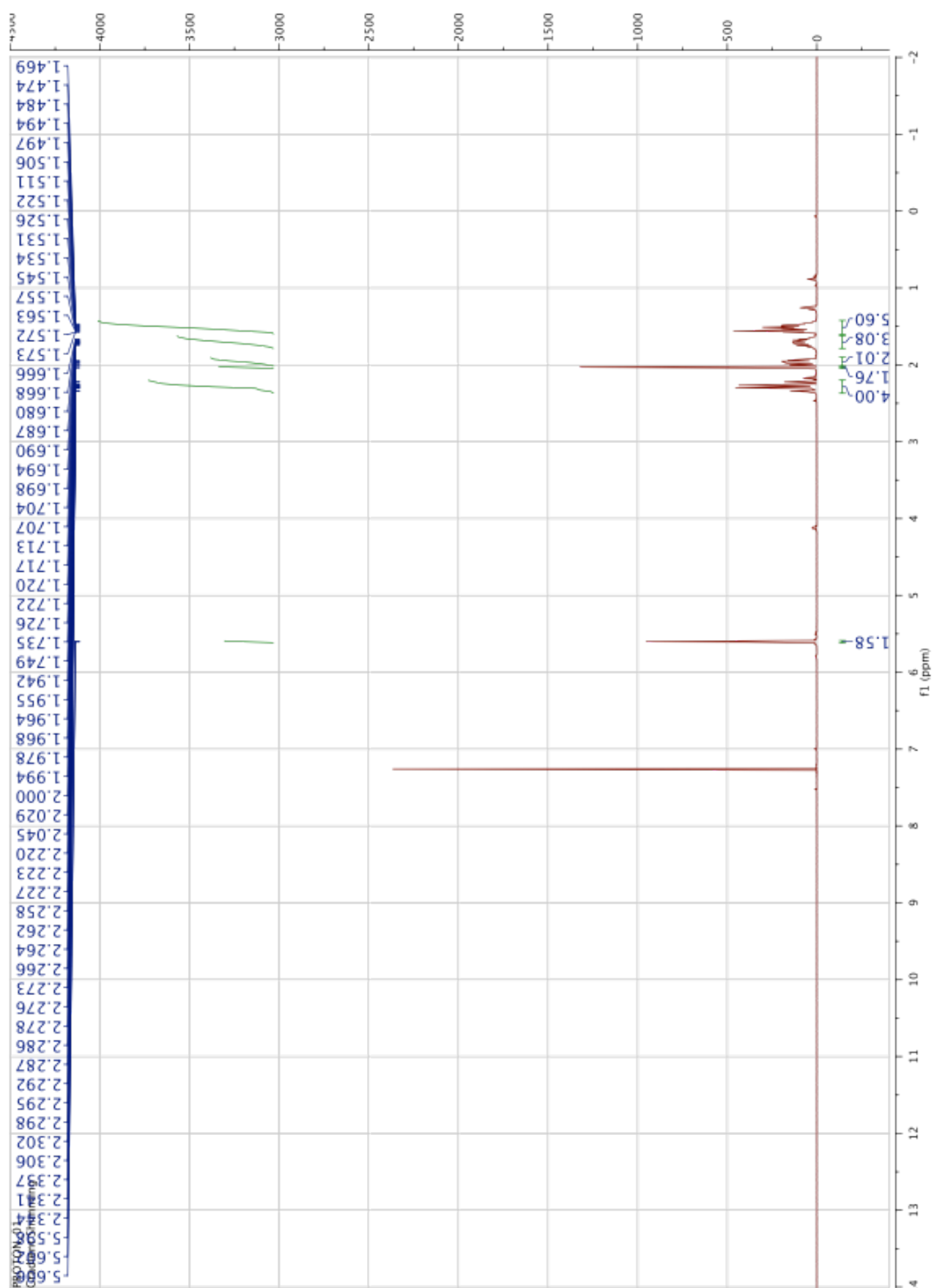
¹H NMR (400 MHz, CDCl₃): δ 5.59 (t, *J* = 1.5 Hz, 2H), 2.32-2.21 (m, 4H), 2.11 (s, 2H), 1.99-1.92 (m, 2H), 1.75-1.64 (m, 3H), 1.56-1.43 (m, 5H) ppm.

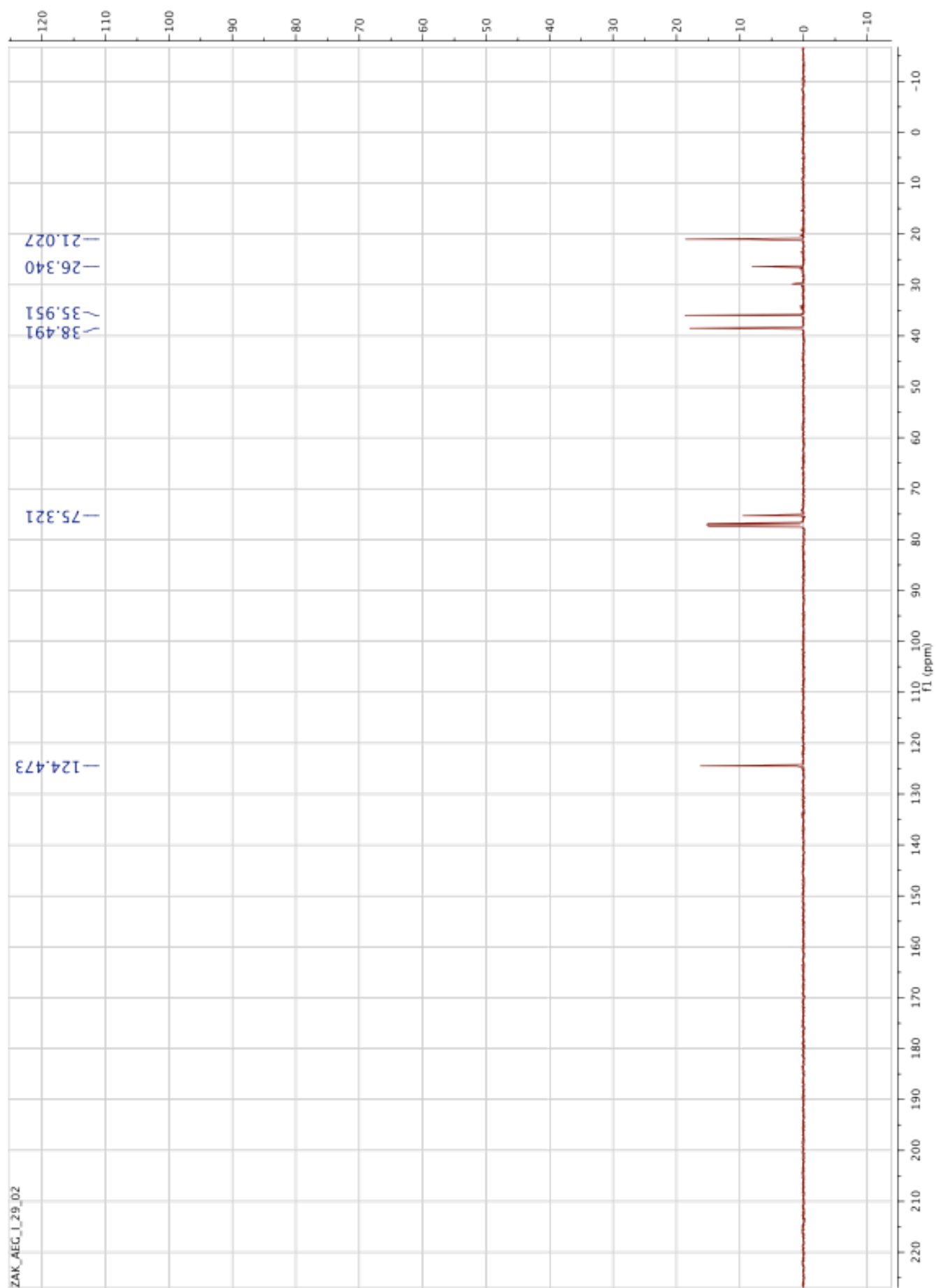
¹³C NMR (100 MHz, CDCl₃): δ 124.5, 75.3, 38.5, 36.0, 26.3, 21.0 ppm.

MP: 73 -76 °C.

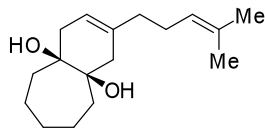
LRMS (+ESI): Calculated for C₁₁H₁₈NaO₂⁺ (*M*+Na⁺) 205.1; Found 205.1.

FTIR: (neat): ν 3399, 2916, 1408, 1049, 1202, 1112, 1079, 1049, 1034, 1009, 977, 884, 801, 662 cm⁻¹.





(4a*S,9a*R**)-2-(4-methylpent-3-en-1-yl)-1,4,6,7,8,9-hexahydro-4a*H*-benzo[7]annulene-4a,9a(5*H*)-diol (3i)**



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added *trans*-1,2-cycloheptanediol **1c** (39.1 mg, 0.30 mmol, 100 mol%), Ru₃(CO)₁₂ (3.8 mg, 0.006 mmol, 2 mol%), and dppp (7.4 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Myrcene **2c** (0.23mL, 1.2 mmol, 400 mol%) was added via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 18 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO₂: 1:4, ethyl acetate: hexanes) to furnish cycloadduct **3i** (52.0 mg, 0.197 mmol, 66% yield) as a colorless oil.

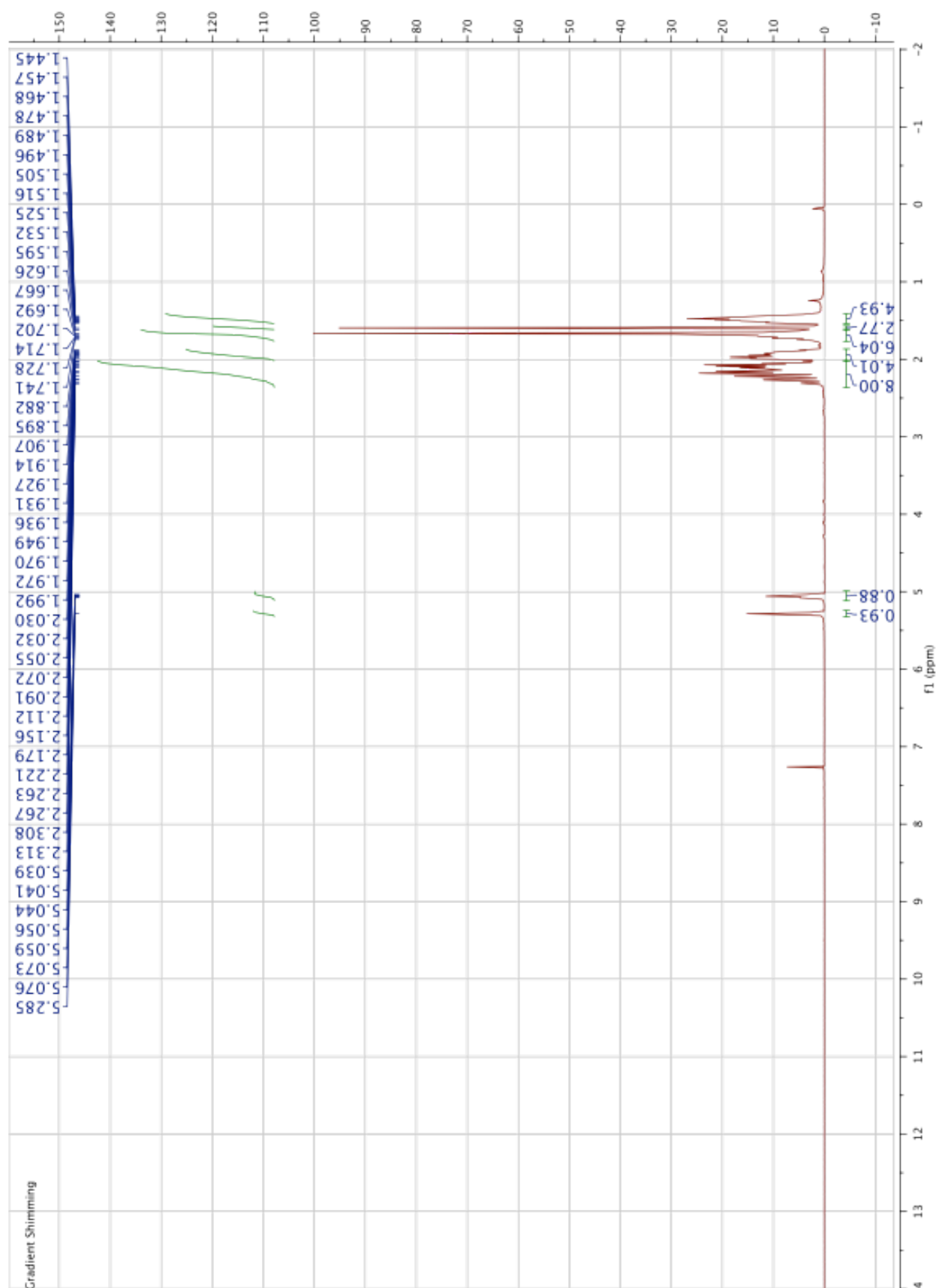
TLC (SiO₂): R_f = 0.26 (3:7, ethyl acetate: hexanes).

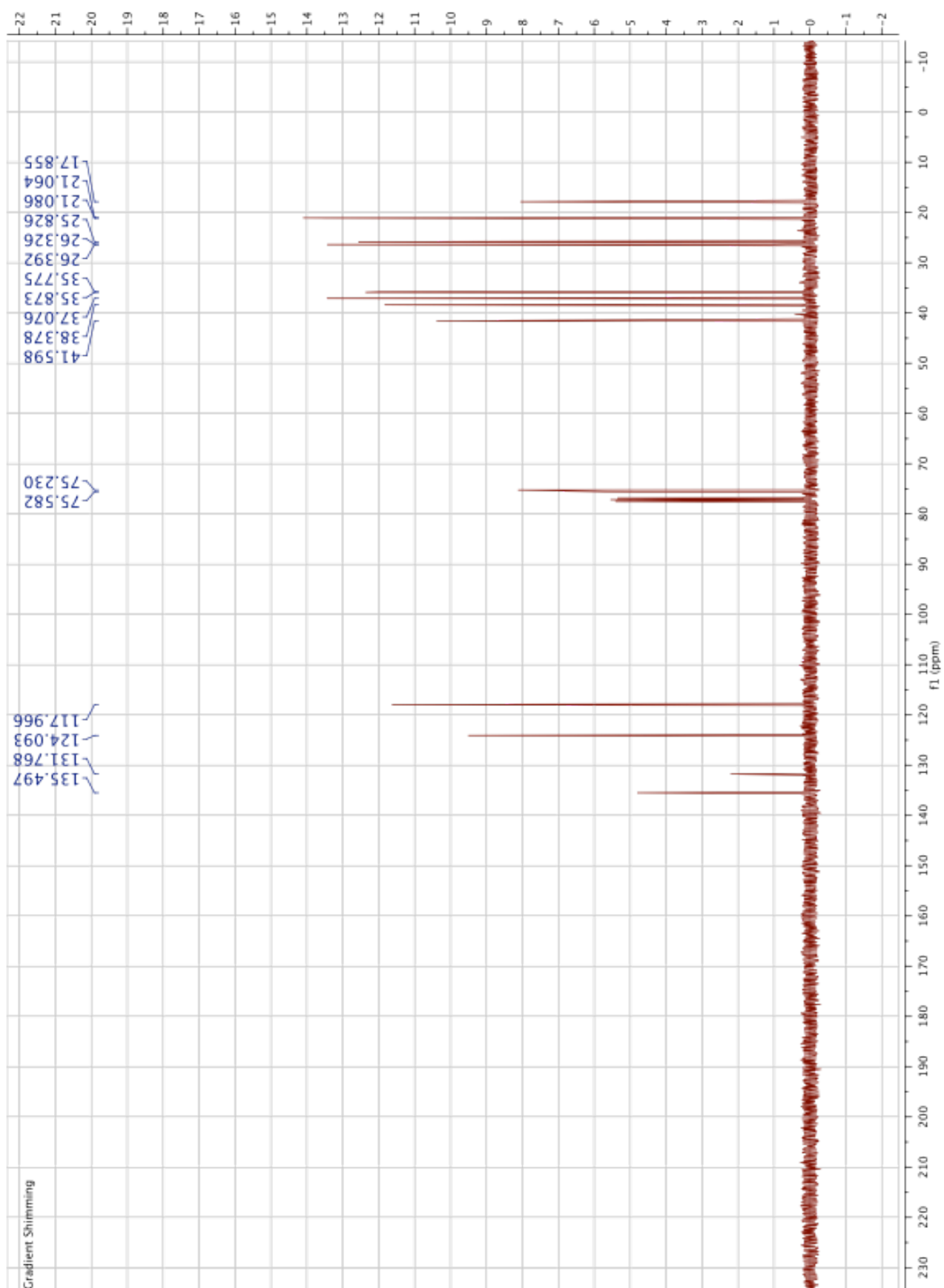
¹H NMR (400 MHz, CDCl₃): δ 5.23 (s, 1H), 5.07 (t, *J* = 6.8 Hz, 1H), 2.31-1.88 (m, 12H), 1.74-1.63 (m, 6H), 1.60 (s, 3H), 1.53-1.45 (m, 5H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 135.5, 131.8, 124.1, 118.0, 75.6, 75.2, 41.6, 38.4, 37.1, 35.9, 35.8, 26.4, 26.3, 25.8, 21.08, 21.06, 17.9 ppm.

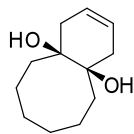
LRMS (+ESI): Calculated for C₁₇H₂₈NaO₂⁺ (*M*+Na⁺) 287.2; Found 287.2.

FTIR (neat): ν 3403, 2918, 2860, 1619, 1588, 1437, 1284, 1228, 1104, 1045, 1014, 864, 821, 780, 652 cm⁻¹.





(4aR*,10aS*)-1,4,5,6,7,8,9,10-octahydrobenzo[8]annulene-4a,10a-diol (3j)



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was *cis*-1,2-cyclooctanediol **1d** (43.2 mg, 0.30 mmol, 100 mol%), $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), and dppp (11.5 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Freshly condensed butadiene **2a** (0.13 mL, 1.5 mmol, 500 mol%) was added at -78 °C via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 3:7, ethyl acetate: hexanes) to furnish the cycloadduct **3j** (36.6 mg, 0.186 mmol, 62% yield) as a colorless solid.

TLC (SiO_2): R_f = 0.33 (2:3 ethyl acetate: hexanes).

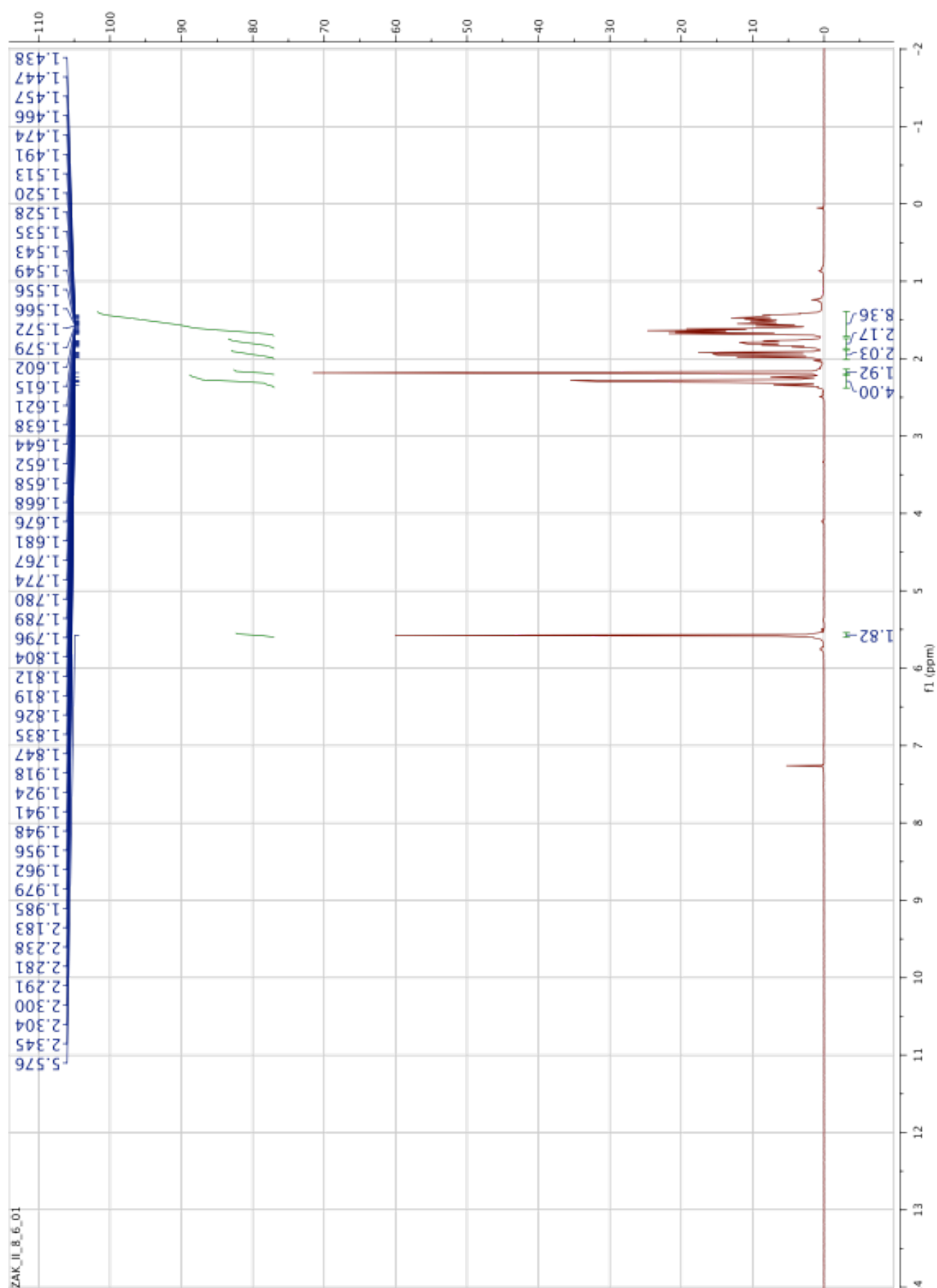
^1H NMR (400 MHz, CDCl_3): δ 5.58 (s, 2H), 2.35-2.24 (m, 4H), 2.18 (s, 2H), 1.95 (ddd, J =15.2, 9.4, 2.4 Hz, 2H), 1.85-1.77 (m, 2H), 1.68-1.44 (m, 8H) ppm.

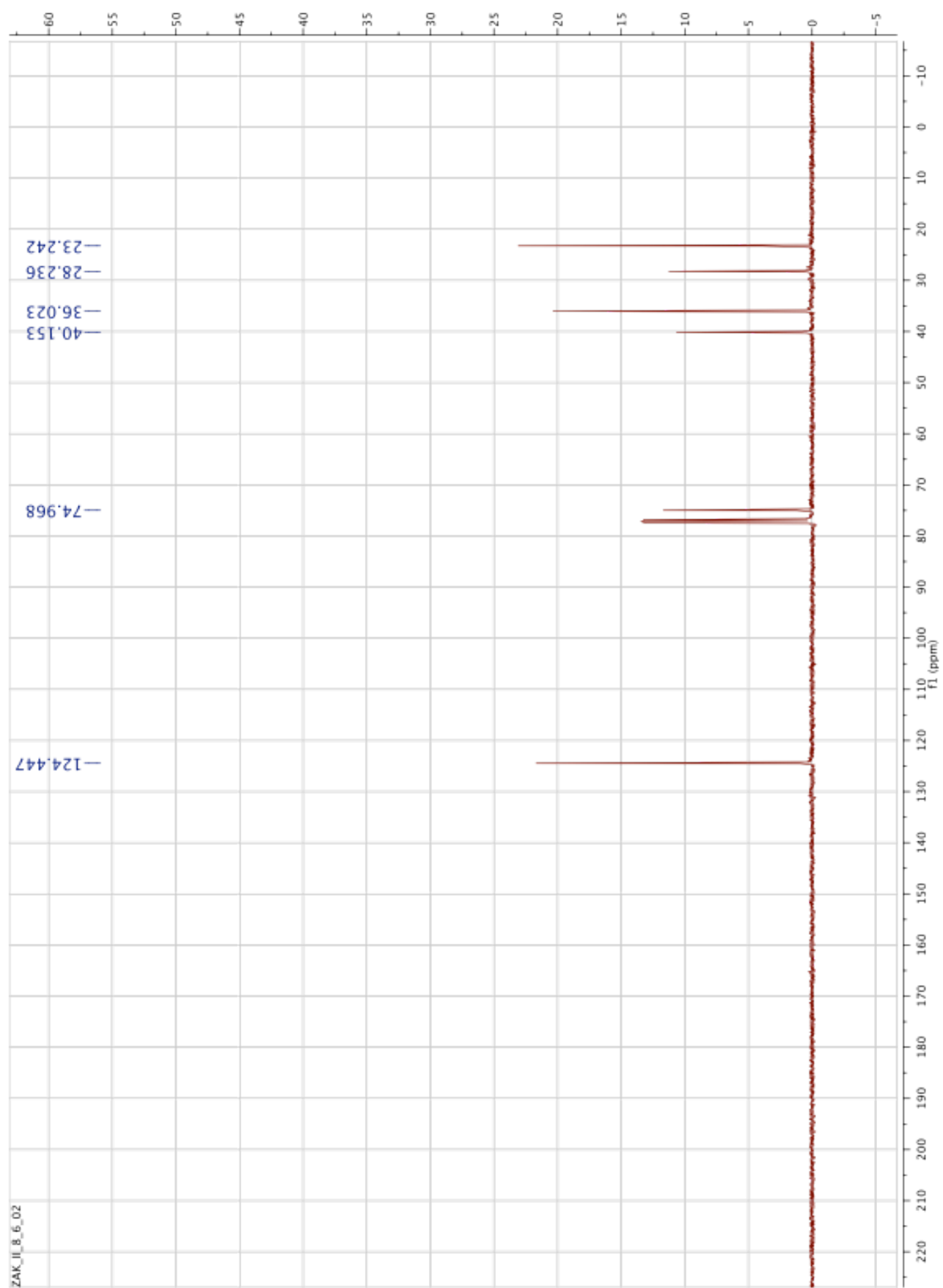
^{13}C NMR (100 MHz, CDCl_3): δ 124.4, 75.0, 40.2, 36.0, 28.2, 23.2 ppm.

MP: 103-104 °C.

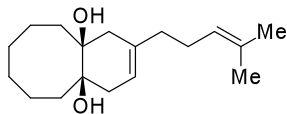
LRMS (+ESI): Calculated for $\text{C}_{12}\text{H}_{20}\text{NaO}_2^+$ ($M+\text{Na}^+$) 219.1; Found 219.1.

FTIR (neat): ν 3390, 3306, 3024, 2942, 2917, 2849, 1458, 1408, 1317, 1158, 1057, 1030, 995, 983, 964, 889, 855, 768, 749, 662 cm^{-1} .





(4a*R,10a*S**)-2-(4-methylpent-3-en-1-yl)-1,4,4a,5,6,7,8,9,10,10a-decahydrobenzo[8]annulene-4a,10a-diol (**3l**)**



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added *cis*-1,2-cyclooctanediol **1d** (39.1 mg, 0.30 mmol, 100 mol%), Ru₃(CO)₁₂ (3.8 mg, 0.006 mmol, 2 mol%), dppp (7.4 mg, 0.018 mmol, 6 mol%), and 3,5-dimethylbenzoic acid (4.5 mg, 0.03 mmol, 10 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Myrcene **2c** (0.23mL, 1.2 mmol, 400 mol%) was added via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO₂: 1:19, ethyl acetate: hexanes) to furnish cycloadduct **3l** (63.0 mg, 0.225 mmol, 75% yield) as a colorless oil.

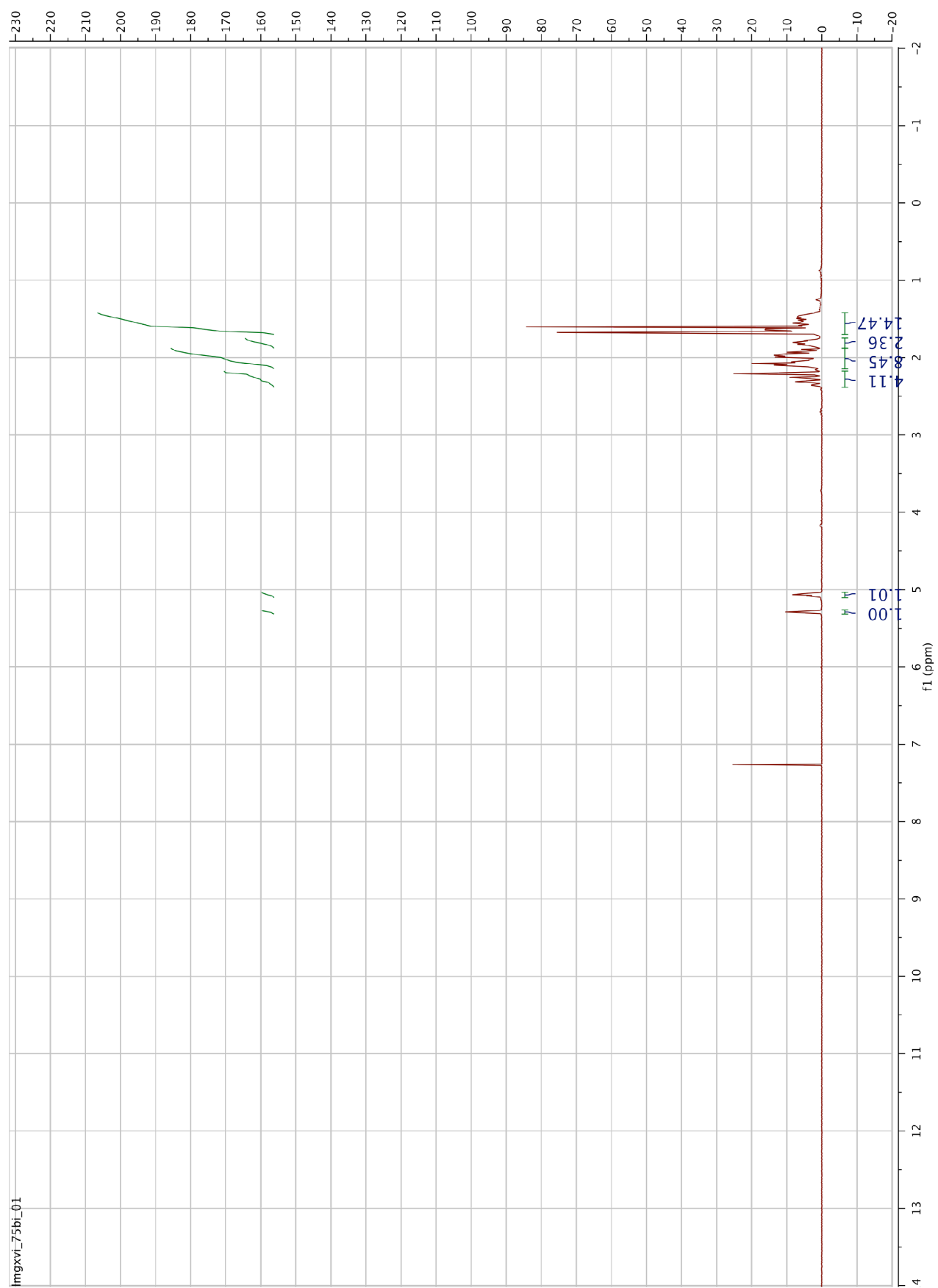
TLC (SiO₂): R_f = 0.48 (2:3, ethyl acetate: hexanes).

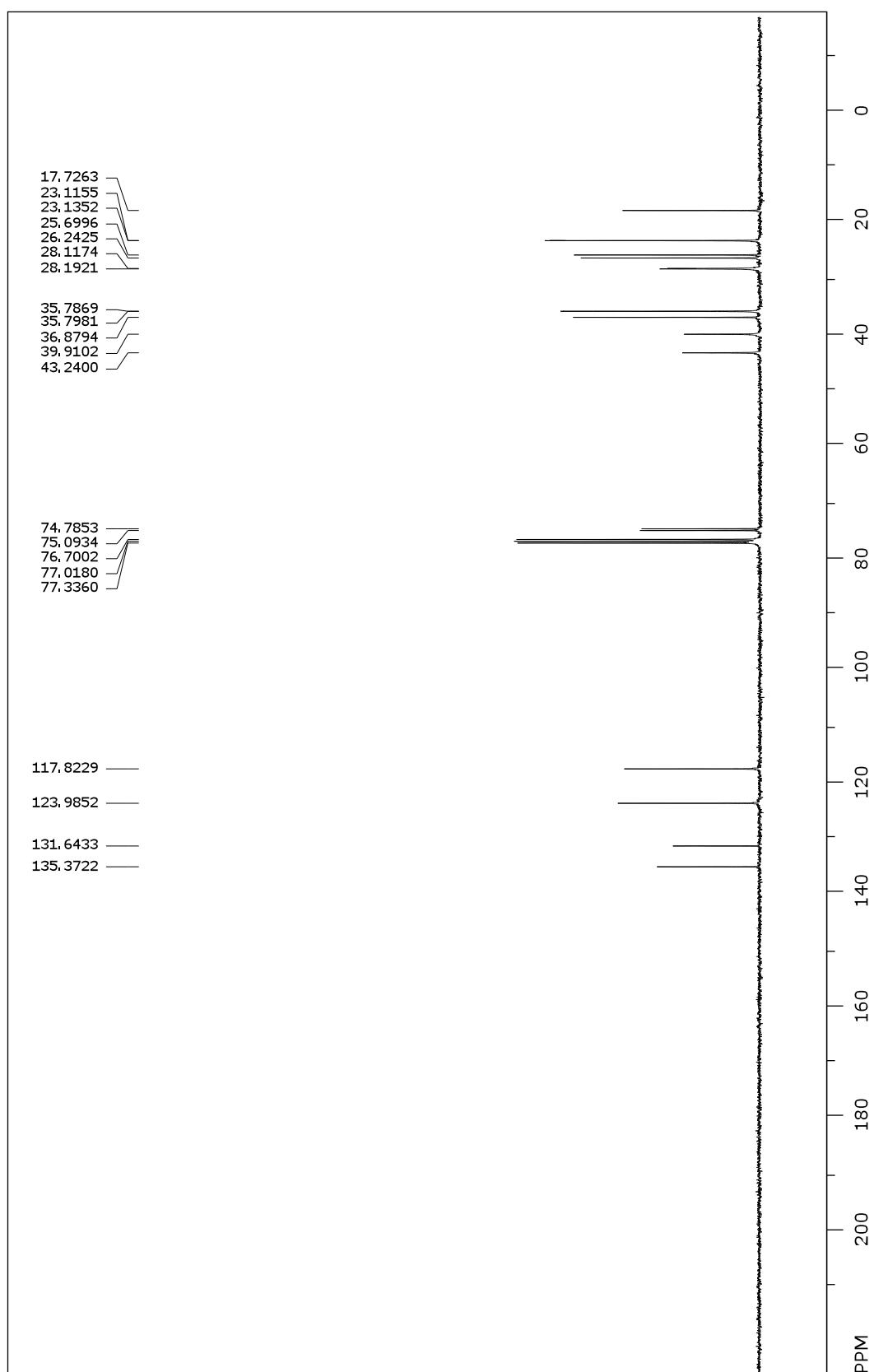
¹H NMR (400 MHz, CDCl₃): δ 5.28 (m, 1H), 5.06 (m, 1H), 2.37-2.24 (m, 2H), 2.20 (m, 2H), 2.16-2.04 (m, 4H), 2.00-1.88 (m, 4H), 1.87-1.76 (m, 2H), 1.70-1.40 (m, 8H), 1.67 (s, 3H), 1.60 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 135.4, 131.6, 124.0, 117.8, 75.1, 74.8, 43.2, 39.9, 36.9, 35.80, 35.79, 28.2, 28.1, 26.2, 25.7, 23.13, 23.12, 17.7 ppm.

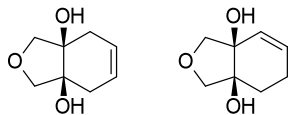
LRMS (ESI⁺): Calculated for C₁₈H₃₀NaO₂⁺ (M+Na) 301; Found 301.

FTIR (neat): ν 3413, 2925, 2855, 1683, 1449, 1378, 1045 cm⁻¹.





(3aR*,7aS*)-1,3,3a,4,7,7a-hexahydroisobenzofuran-3a-7a-diol (3m) and (3aS*,7aR*)-1,3,3a,4,5,7a-hexahydroisobenzofuran-3a-7a-diol (*iso*-3m)



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) and dppp (7.4 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Tetrahydrofuran diol **1e** (31.2 mg, 0.30 mmol, 100 mol%) was then added. Freshly condensed butadiene **2a** (0.13 mL, 1.5 mmol, 500 mol%) was added at $-78\text{ }^\circ\text{C}$ via syringe. The septum was replaced with a screw cap, and the reaction was heated to $130\text{ }^\circ\text{C}$. The reaction was allowed to stir for 4 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 1:1, ethyl acetate: hexanes) to furnish the cycloadduct **3m** (44.6 mg, 0.2856 mmol, 95% yield, 5.2:1 rr) as a colorless solid.

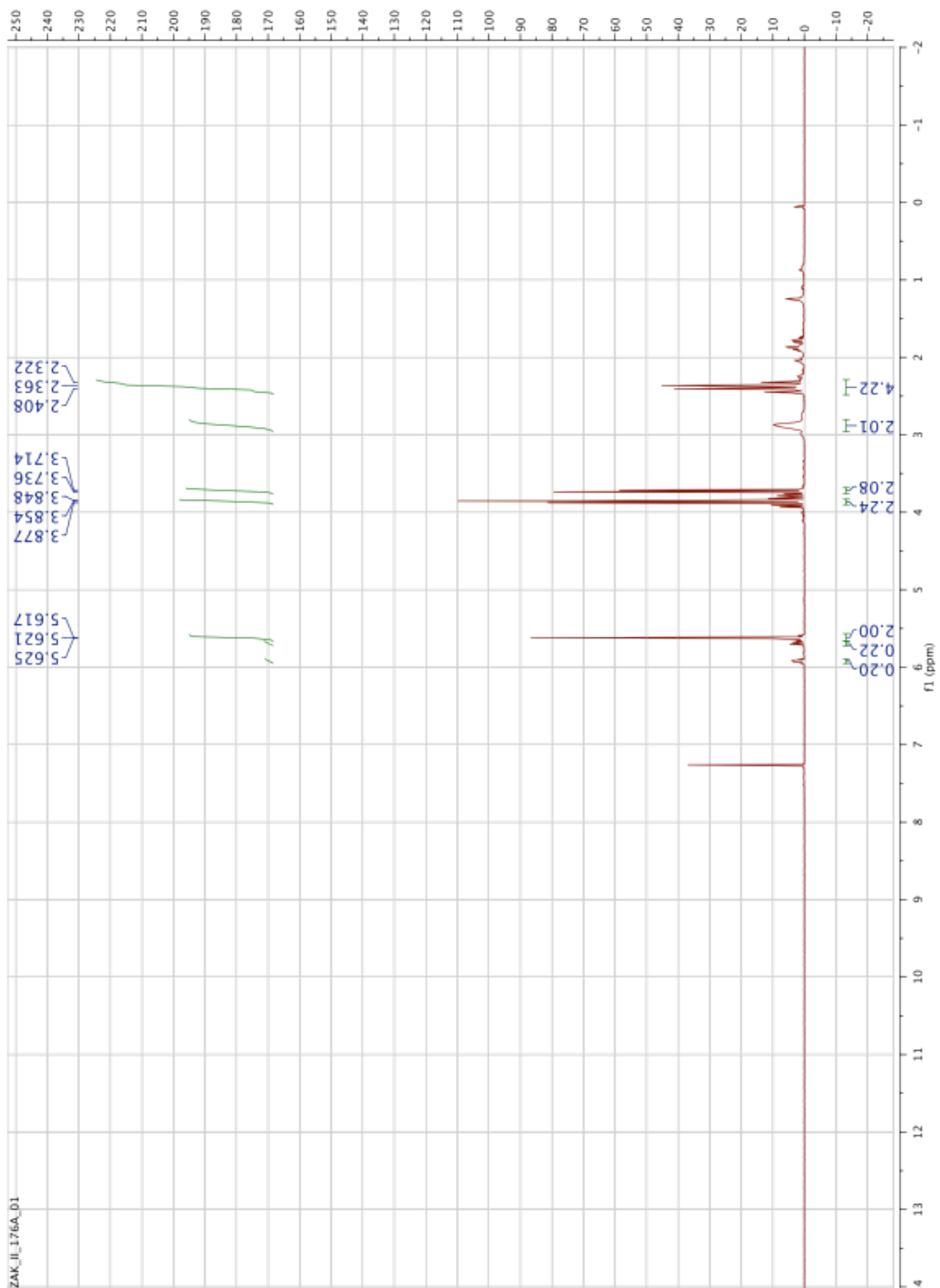
TLC (SiO_2): $R_f = 0.08$ (2:3, ethyl acetate: hexanes).

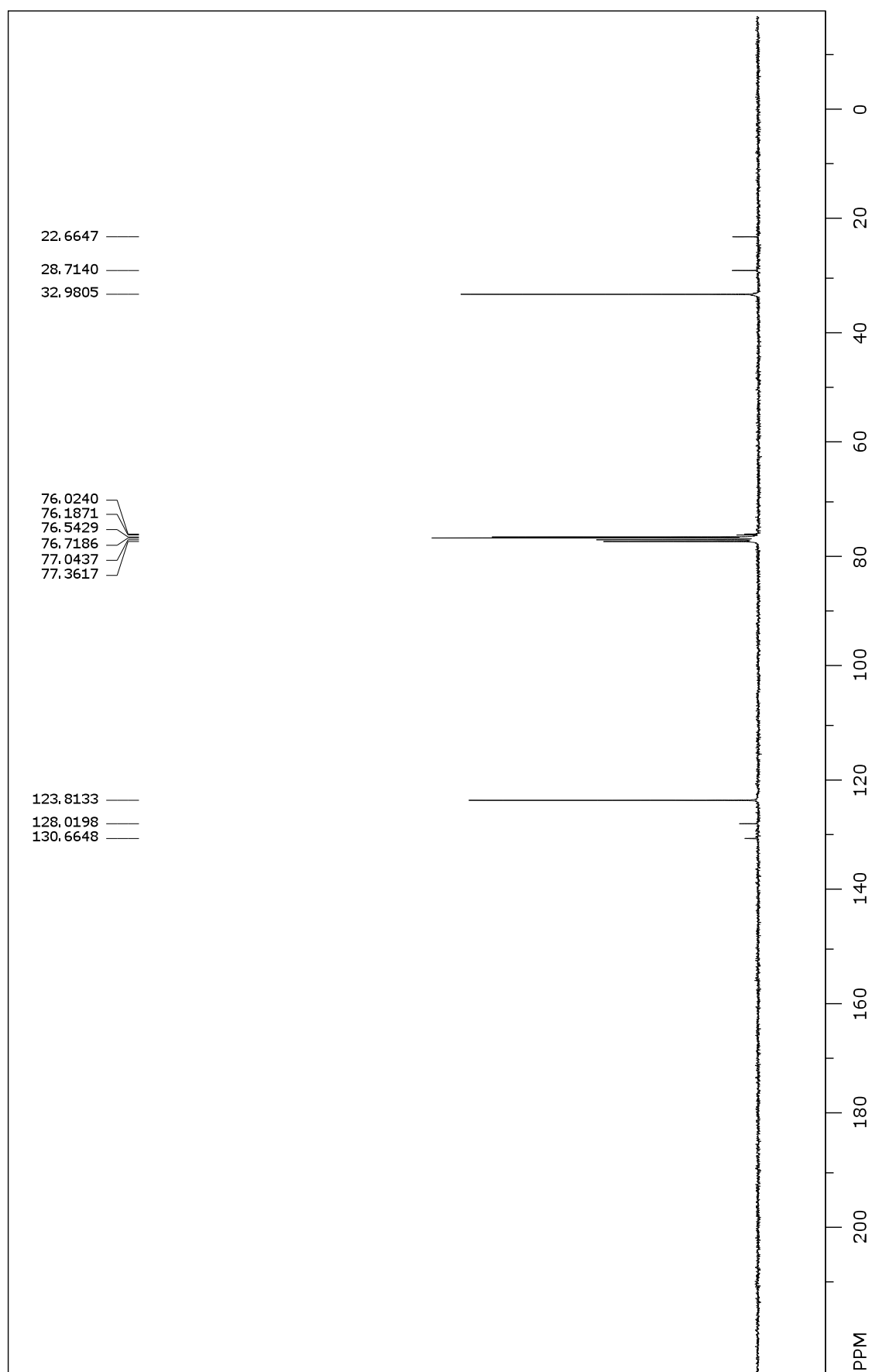
^1H NMR (400 MHz, CDCl_3 , major isomer): δ 5.60 (m, 2H), 3.85 (d, 2H, $J = 9\text{ Hz}$), 3.70 (d, 2H, $J = 9\text{ Hz}$), 3.21 (br, 2H), 2.45-2.28 (m, 4H) ppm.

^{13}C NMR (100 MHz, CDCl_3 , major isomer): δ 123.8, 76.7, 76.5, 33.0 ppm.

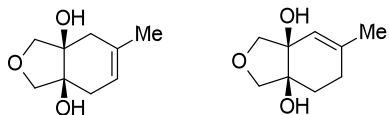
LRMS (CI^+): Calculated for $\text{C}_8\text{H}_{11}\text{O}_2$ (M-OH) 139; Found 139.

FTIR (neat): ν 3350, 2886, 1110, 1029, 1010 cm^{-1} .





(3aR*,7aS*)-5-methyl-1,3,3a,4,7,7a-hexahydroisobenzofuran-3a-7a-diol (3n**) and (3aS*,7aR*)-5-methyl-1,3,3a,4,5,7a-hexahydroisobenzofuran-3a-7a-diol (*iso*-**3n**)**



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) and dppp (7.4 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Tetrahydrofuran diol **1e** (31.2 mg, 0.30 mmol, 100 mol%) was then added. Freshly distilled isoprene **2b** (0.15 mL, 1.5 mmol, 500 mol%) was added via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 8 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 1:1, ethyl acetate: hexanes) to furnish the cycloadduct **3n** (34.6 mg, 0.203 mmol, 75% yield, 14:1 rr) as a colorless solid.

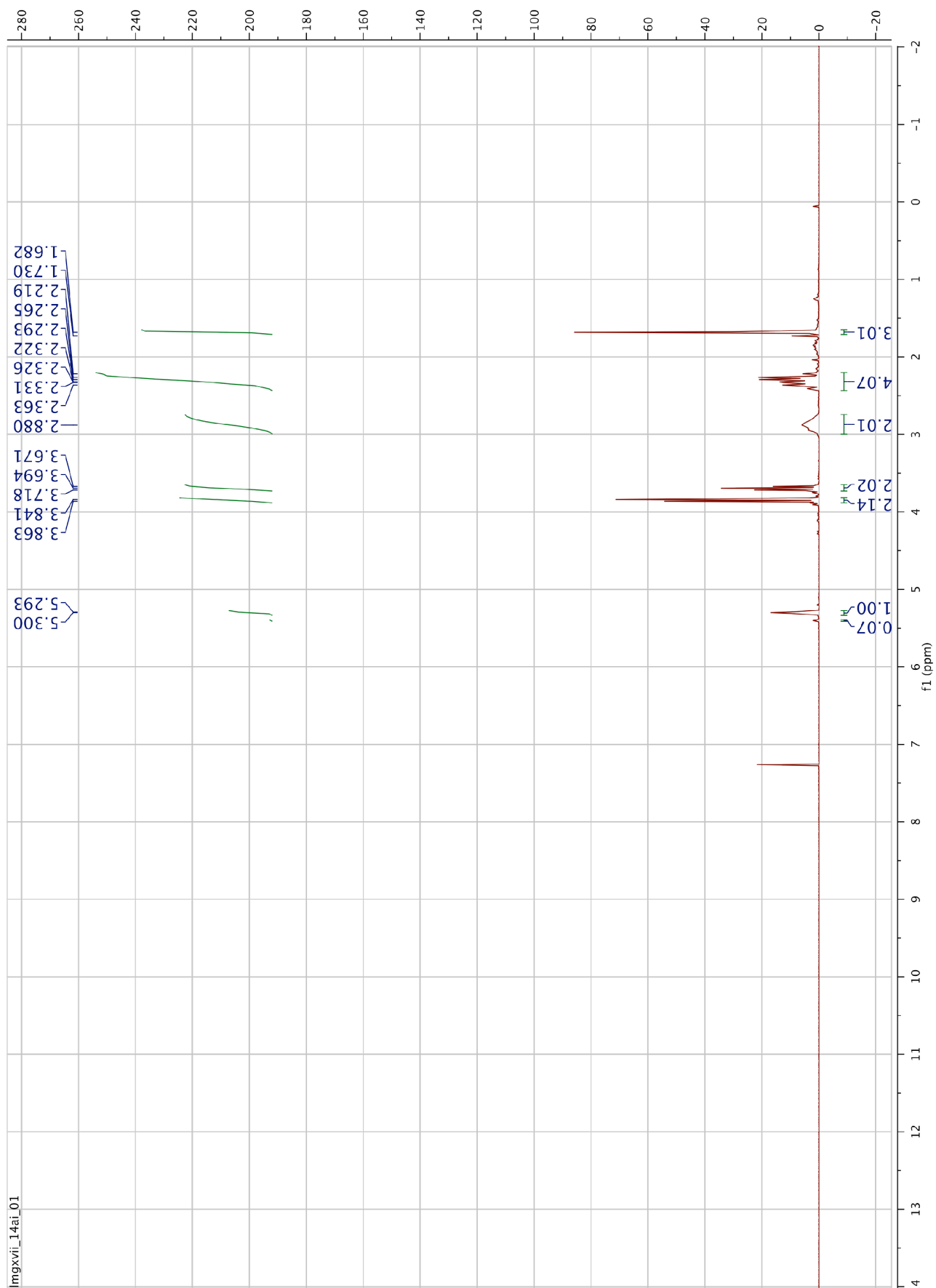
TLC (SiO_2): R_f = 0.14 (2:3, ethyl acetate: hexanes).

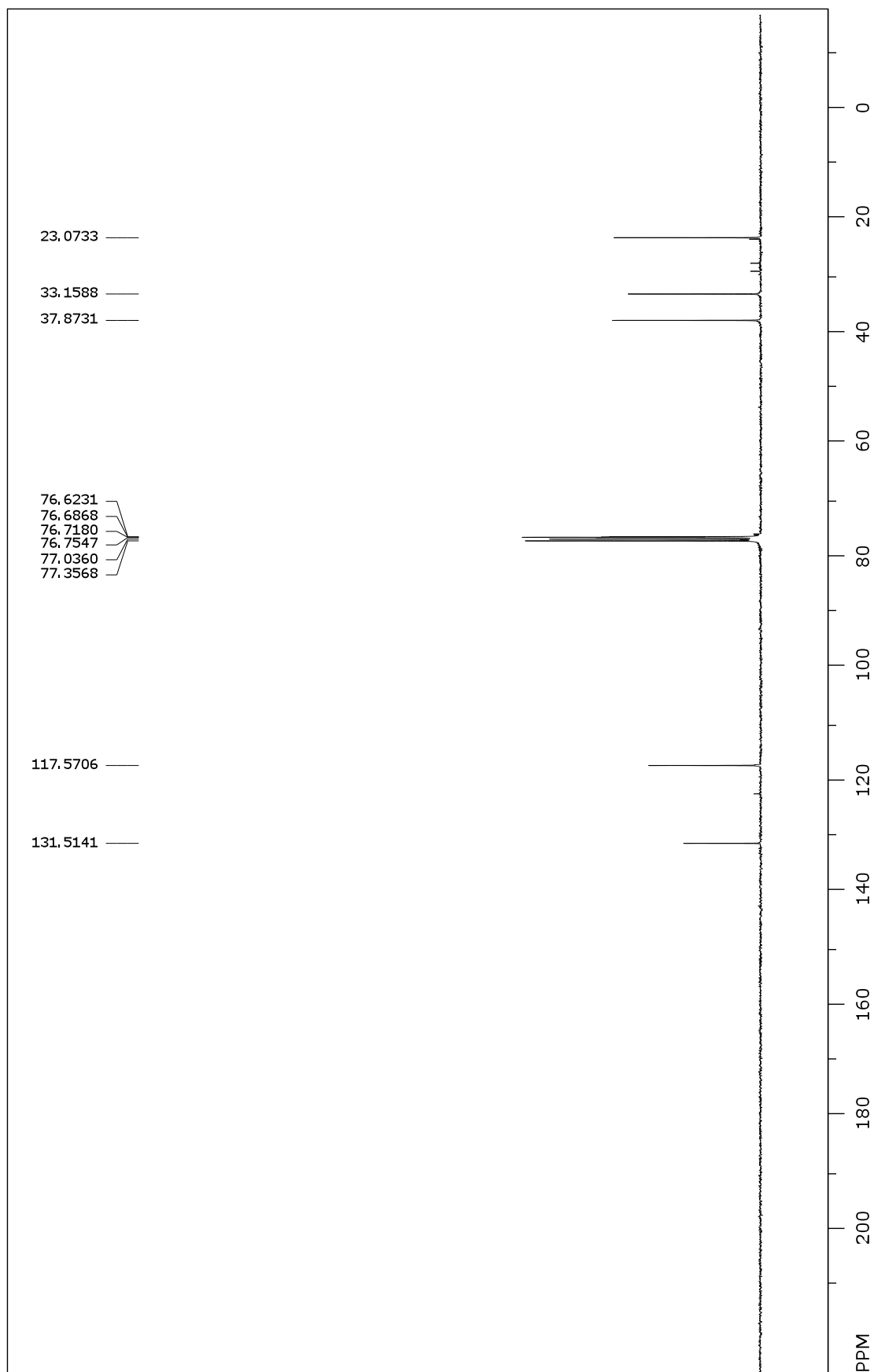
^1H NMR (400 MHz, CDCl_3 , major isomer): δ 5.30 (m, 1H), 3.85 (m, 2H), 3.69 (m, 2H), 2.88 (br, 2H), 2.44-2.19 (m, 4H), 1.69 (m, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3 , major isomer): δ 131.5, 117.8, 76.8, 76.7, 76.6, 37.9, 33.2, 23.1 ppm.

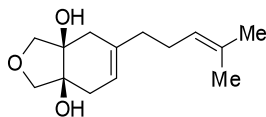
LRMS (CI^+): Calculated for $\text{C}_{19}\text{H}_{14}\text{NaO}_3$ ($M+\text{Na}$) 193; Found 193.

FTIR (neat): ν 3350, 2886, 1110, 1029, 1010 cm^{-1} .





(3a*R,7a*S**)-5-(4-methylpent-3-en-1-yl)-1,3,3a,4,7,7a-hexahydroisobenzofuran-3a,7a-diol (3o)**



To an oven dried pressure tube equipped with a stir bar and sealed with a septum under argon was added $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%) and dppp (7.4 mg, 0.018 mmol, 6 mol%). The vessel was purged with argon, and toluene (0.15 mL, 2.0 M) was added via syringe. Tetrahydrofuran diol **1e** (31.2 mg, 0.30 mmol, 100 mol%) was then added. Myrcene **2c** (0.23 mL, 1.2 mmol, 400 mol%) was added via syringe. The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 1:19, Ethyl acetate: hexanes) to furnish the cycloadduct **3o** (63.7 mg, 0.267 mmol, 89% yield) as a colorless oil.

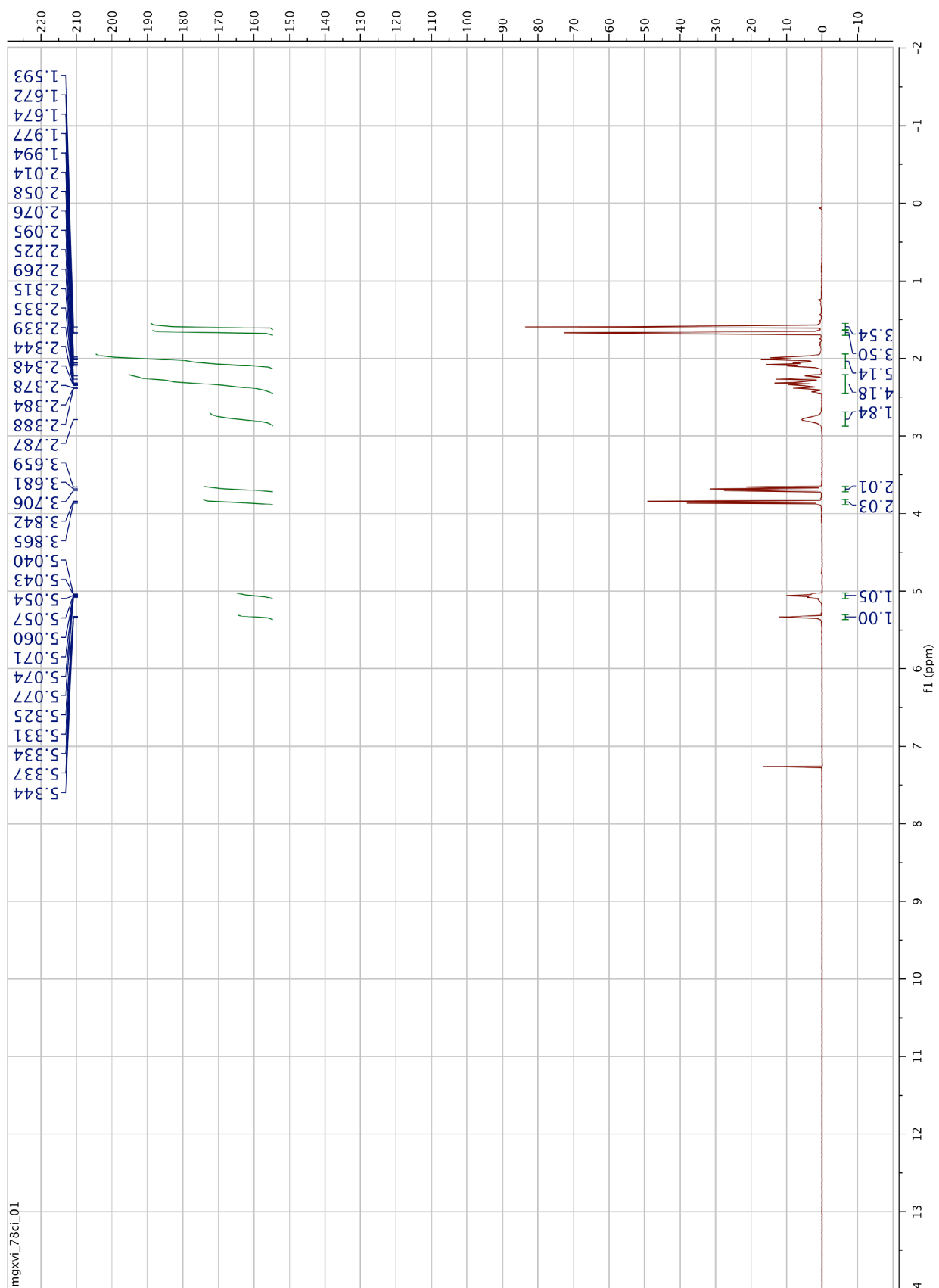
TLC (SiO_2): R_f = 0.25 (1:1, ethyl acetate: hexanes).

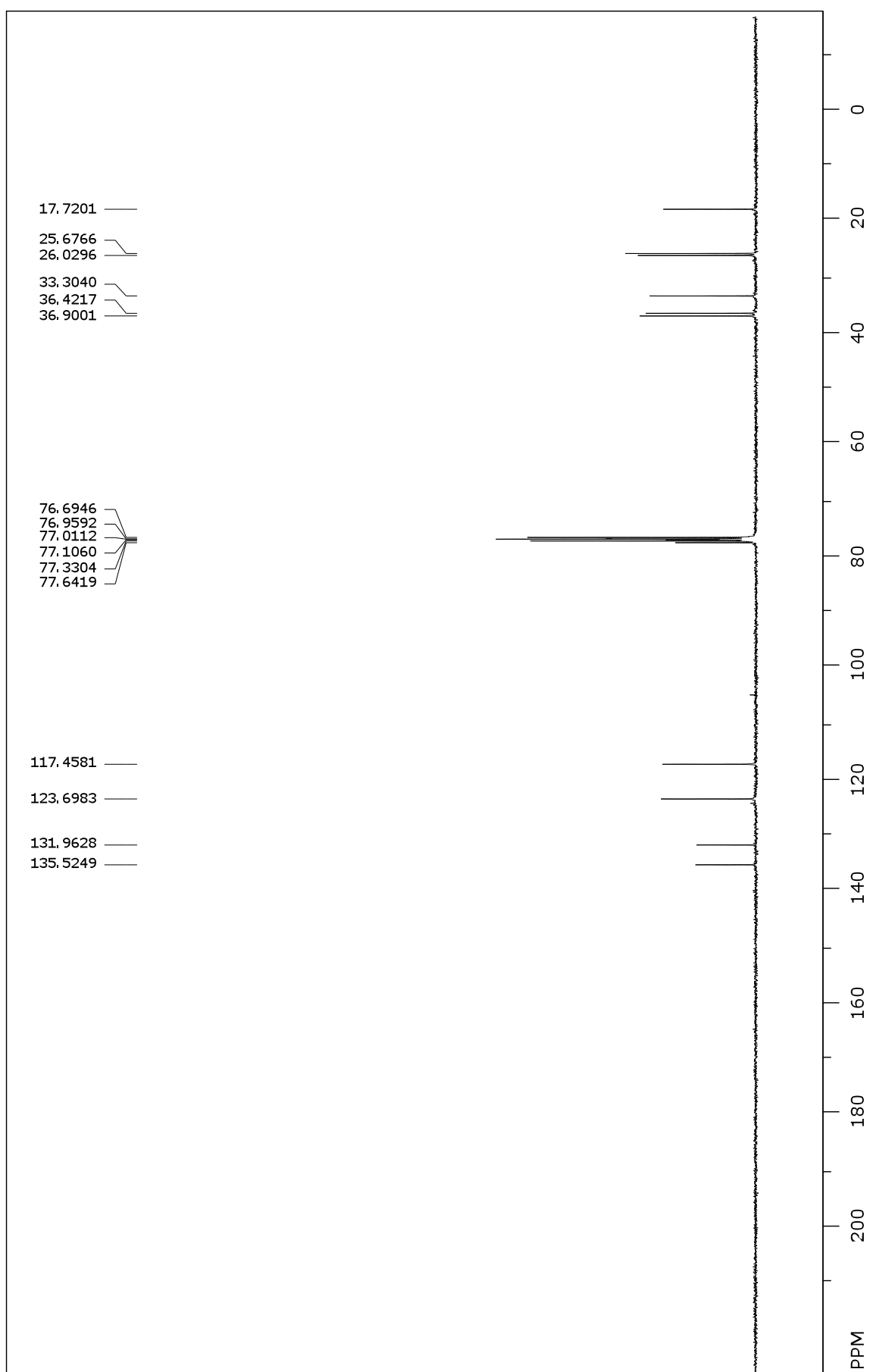
^1H NMR (400 MHz, CDCl_3): δ 5.33 (m, 1H), 5.06 (m, 1H), 3.85 (d, 2H, J = 9 Hz), 3.68 (t, 2H, J = 9Hz), 2.78 (br s, 2H), 2.44-2.20 (m, 4H), 2.12-1.97 (m, 5H), 1.67 (m, 3H), 1.59 (s, 3H) ppm.

^{13}C NMR (100 MHz, CDCl_3): δ 135.5, 132.0, 123.7, 117.5, 77.6, 77.1, 77.01, 77.96, 36.9, 36.4, 33.3, 26.0, 25.7, 17.7 ppm.

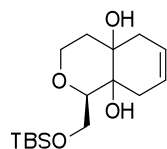
LRMS (CI^+): Calculated for $\text{C}_{14}\text{H}_{22}\text{NaO}_3$ ($M+\text{Na}$) 261; Found 261.

FTIR (neat): ν 3385, 2914, 1376, 1099, 1033, 901 cm^{-1} .





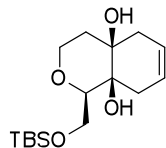
1-(((*tert*-butyldimethylsilyloxy)methyl)-3,4,4a,5,8,8a-hexahydro-1*H*-isochromene-4a,8a-diol (3p)



To an oven dried sealed tube equipped with a stir bar and sealed with a septum under argon was added $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), dppp (7.4 mg, 0.018 mmol, 6 mol%) and diol **1f** (78.7 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.15 mL, 2.0 M) was added via syringe, followed by freshly condensed butadiene **2a** (0.13 mL, 1.5 mmol, 500 mol%) at -78°C . The septum was replaced with a screw cap and the reaction was heated to 130°C . The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 1:19, ethyl acetate: hexanes) to furnish cycloadducts **3p** (90.7 mg, 0.288 mmol, 96% yield, 1:1 dr) as a colorless oil.

The two diastereomers could be separated via column chromatography and were characterized separately.

(1*R*,4*aR*,8*aS*)-1-(((*tert*-butyldimethylsilyloxy)methyl)-3,4,4*a*,5,8,8*a*-hexahydro-1*H*-isochromene-4*a*,8*a*-diol (3p)



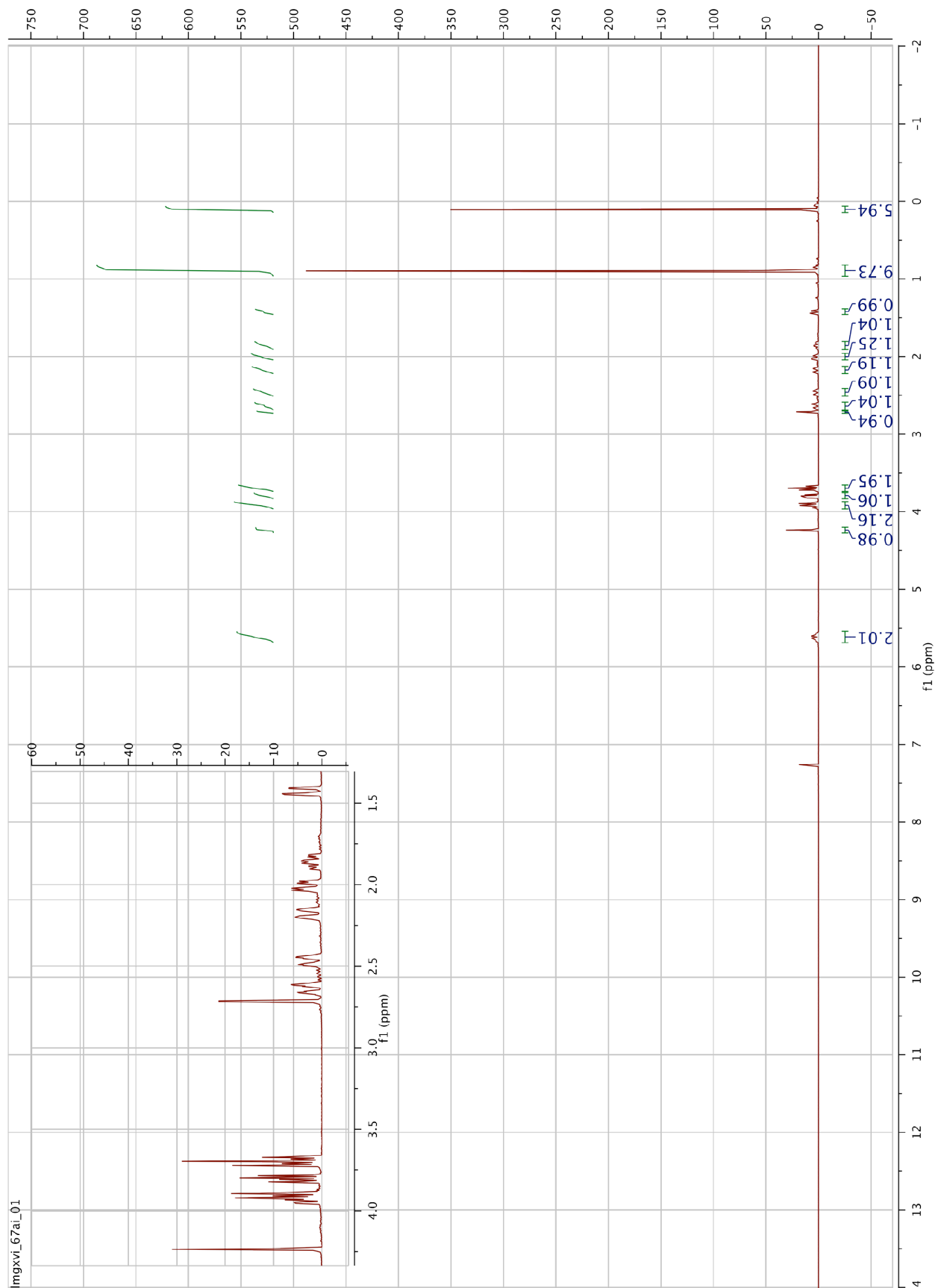
TLC (SiO₂): R_f = 0.28 (2:3, ethyl acetate: hexanes).

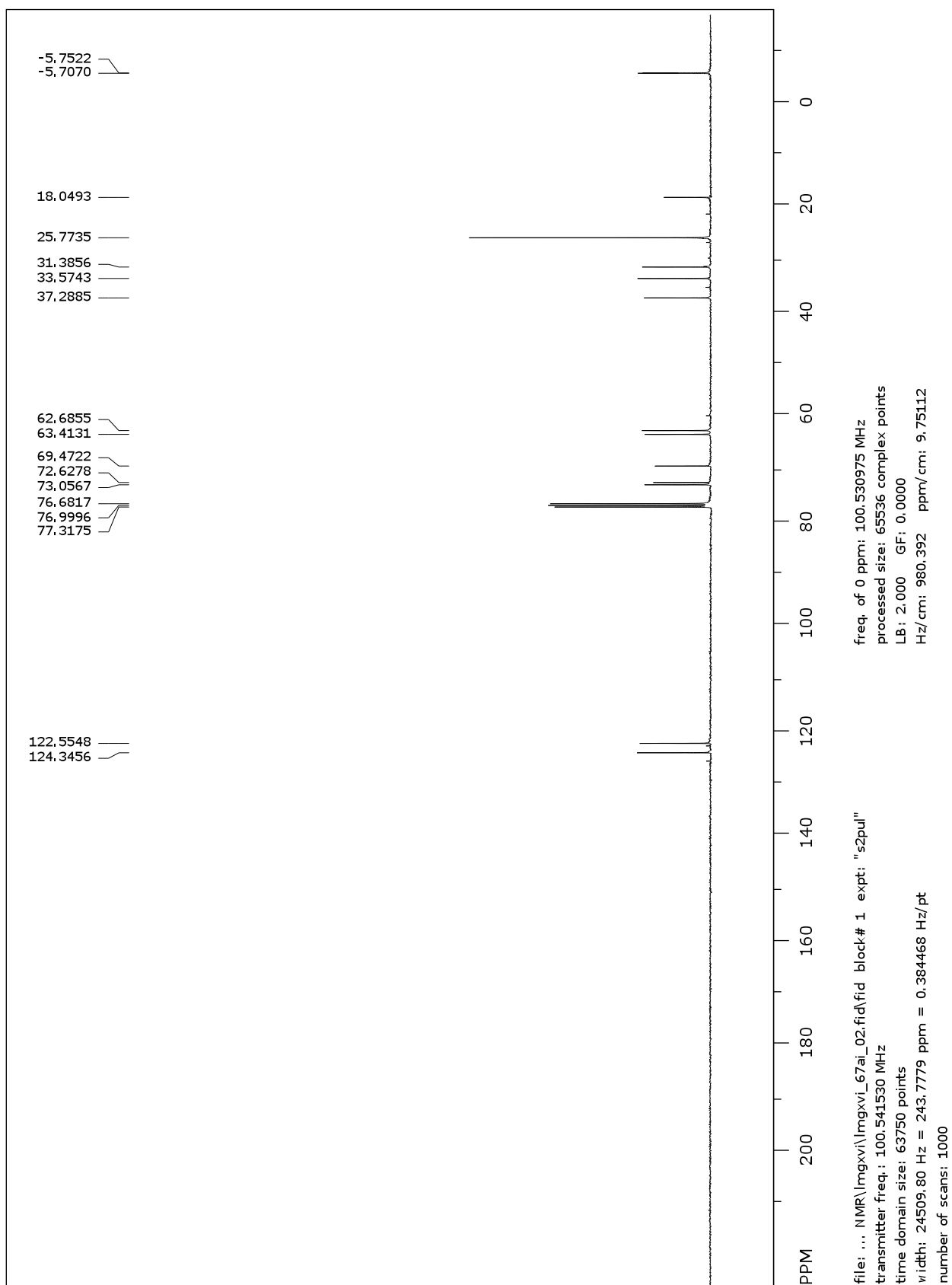
¹H NMR (400 MHz, CDCl₃): δ 5.67-5.56 (m, 2H), 4.24 (br s, 1H), 3.96-3.88 (m, 2H), 3.81 (dd, 1H, *J* = 5.5, 9.8 Hz), 3.73-3.66 (m, 2H), 2.71 (d, 1H, *J* = 2.5 Hz), 2.64 (m, 1H), 2.46 (m, 1H), 2.18 (m, 1H), 2.01 (m, 1H), 1.86 (m, 1H), 1.43 (m, 1H), 0.90 (s, 9H), 0.11 (s, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 124.3, 122.6, 73.1, 72.6, 69.5, 63.4, 62.7, 37.3, 33.6, 25.8, 18.0, -5.71, -5.75 ppm.

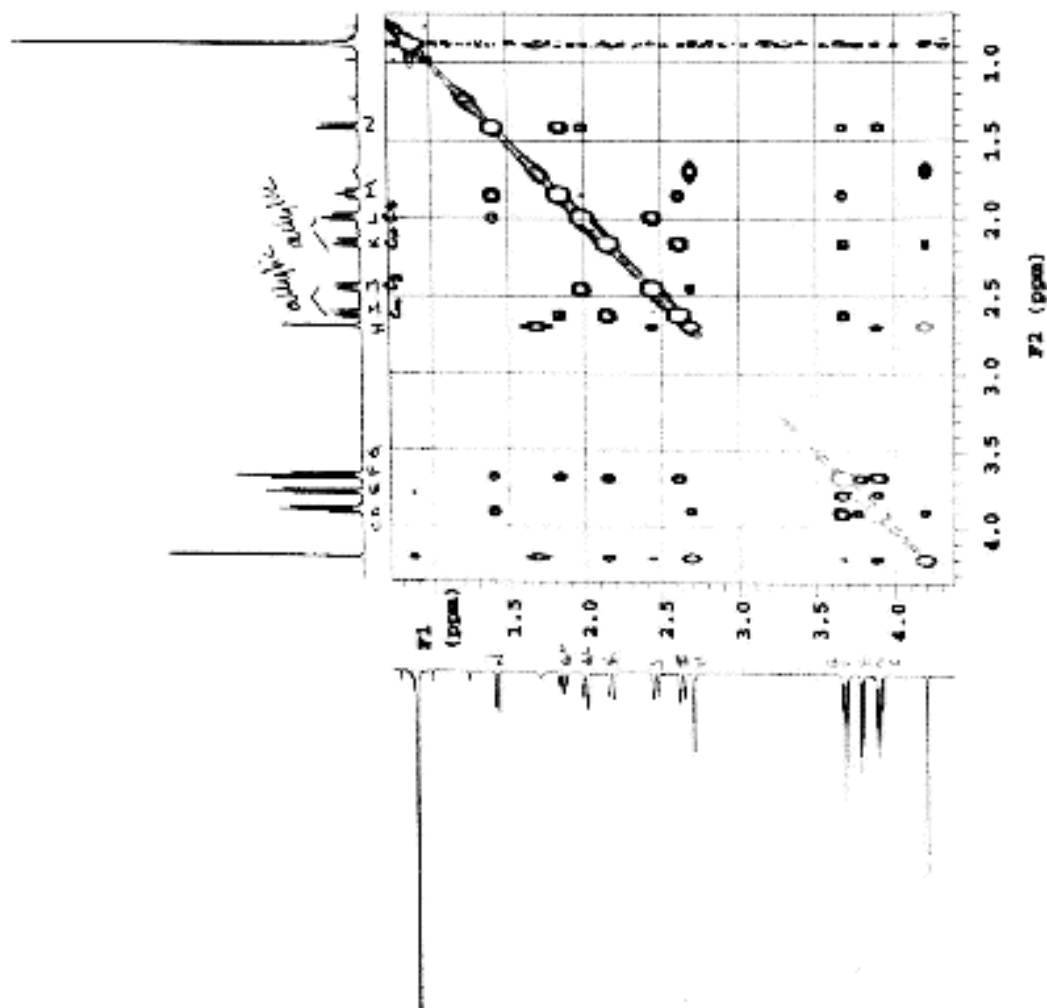
LRMS (CI⁺): Calculated for C₁₆H₂₉O₃Si⁺ (M-OH) 297; Found 297.

FTIR (neat): ν 3467, 2928, 1253, 1093, 833, 777, 661 cm⁻¹.



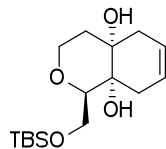


NOESY spectrum for **3p**- *syn, syn*



100001_0704
 Sample Name:
 Data Collected on:
 Instrument: spect
 Sample directory:
 Sample directory:
 File: 100001_0704
 Pulse sequence: NOESY
 Solvent: cdcl3
 Data collected on: Mar 5 2014

(1*R*,4*aS*,8*aR*)-1-(((*tert*-butyldimethylsilyloxy)methyl)-3,4,4*a*,5,8,8*a*-hexahydro-1*H*-isochromene-4*a*,8*a*-diol (3p)



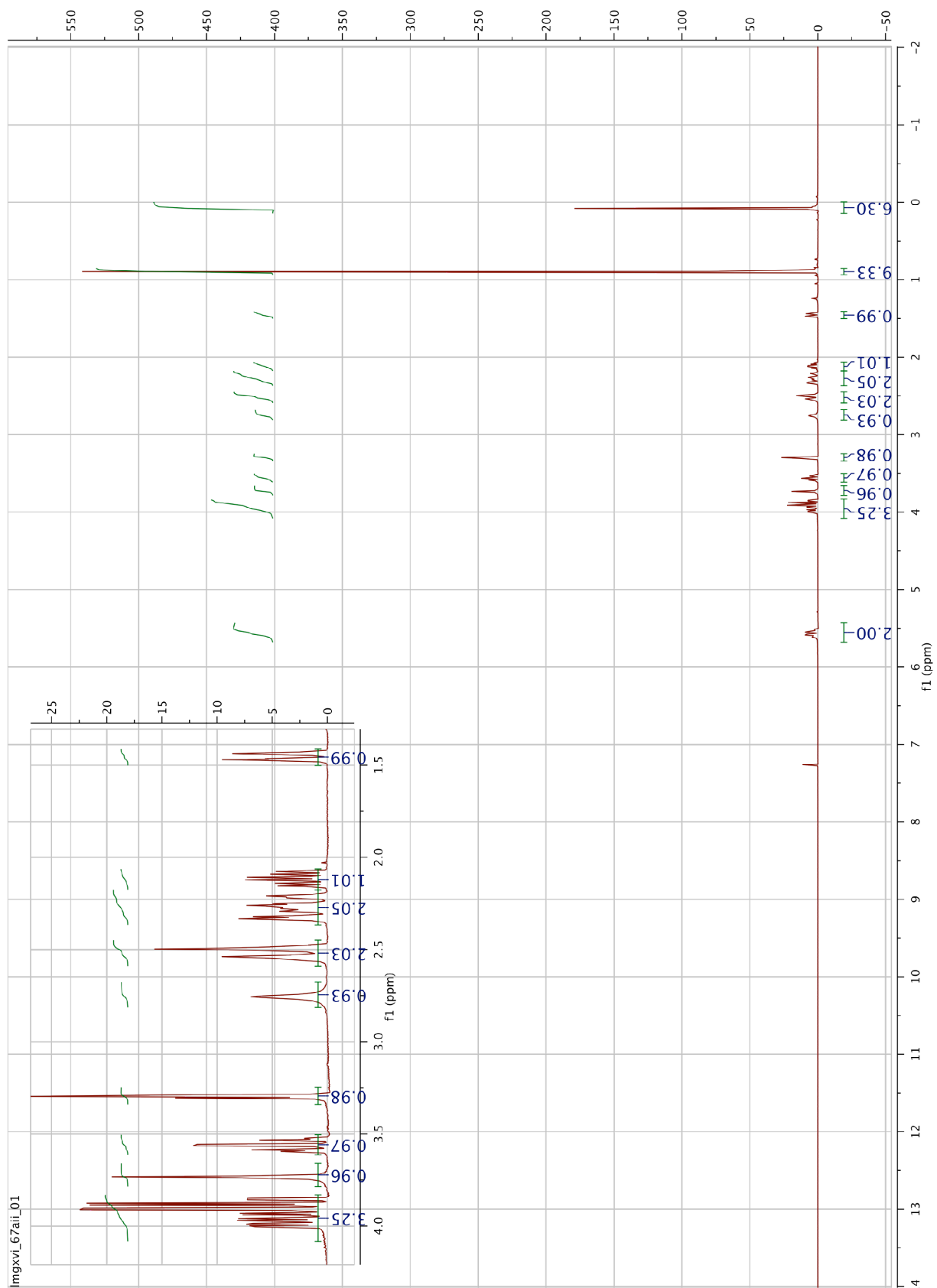
TLC (SiO₂): R_f = 0.10 (2:3, ethyl acetate: hexanes).

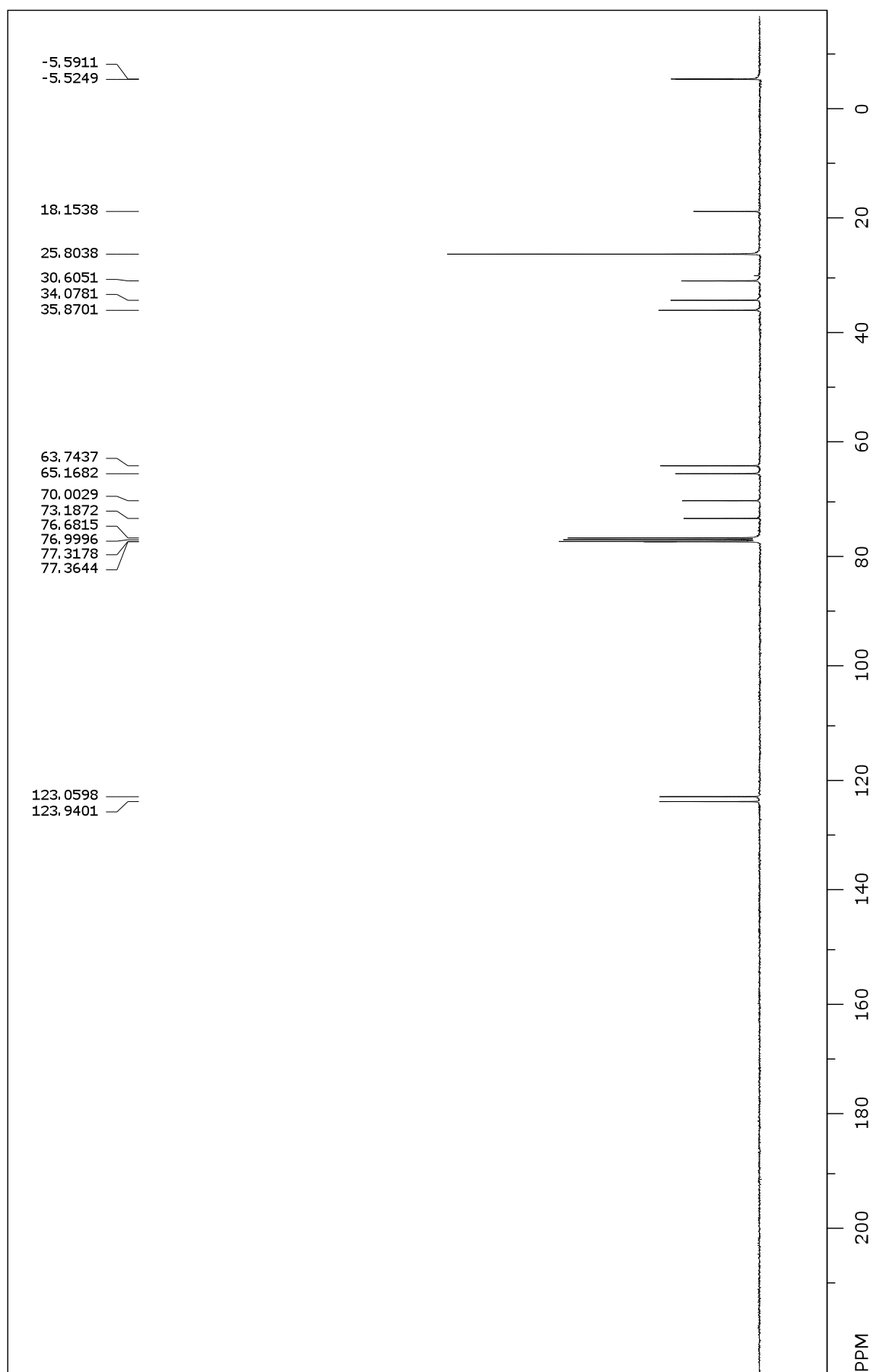
¹H NMR (400 MHz, CDCl₃): δ 5.63-5.50 (m, 2H), 3.98 (ddd, 1H, *J* = 1.8, 5.5, 12 Hz), 3.92 (dd, 1H, *J* = 3.5, 11 Hz), 3.86 (dd, 1H, *J* = 3.5, 11 Hz), 3.74 (br s, 1H), 3.56 (ddd, 1H, *J* = 2.8, 12, 12 Hz), 3.30 (dd, 1H, *J* = 3.6, 4 Hz), 2.77 (br s, 1H), 2.58-2.46 (m, 2H), 2.35-2.18 (m, 2H), 2.11 (ddd, 1H, *J* = 5.6, 6, 12 Hz), 1.45 (m, 1H), 0.89 (s, 9H), 0.082 (s, 3H), 0.077 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 123.9, 123.1, 77.4, 73.2, 70.0, 65.2, 63.7, 35.9, 34.1, 30.6, 25.8, 18.2, -5.52, -5.59 ppm.

LRMS (CI⁺): Calculated for C₁₆H₂₉O₃Si⁺ (M-OH) 297; Found 297.

FTIR (neat): ν 3467, 2928, 1472, 1101, 837, 777, 667 cm⁻¹.



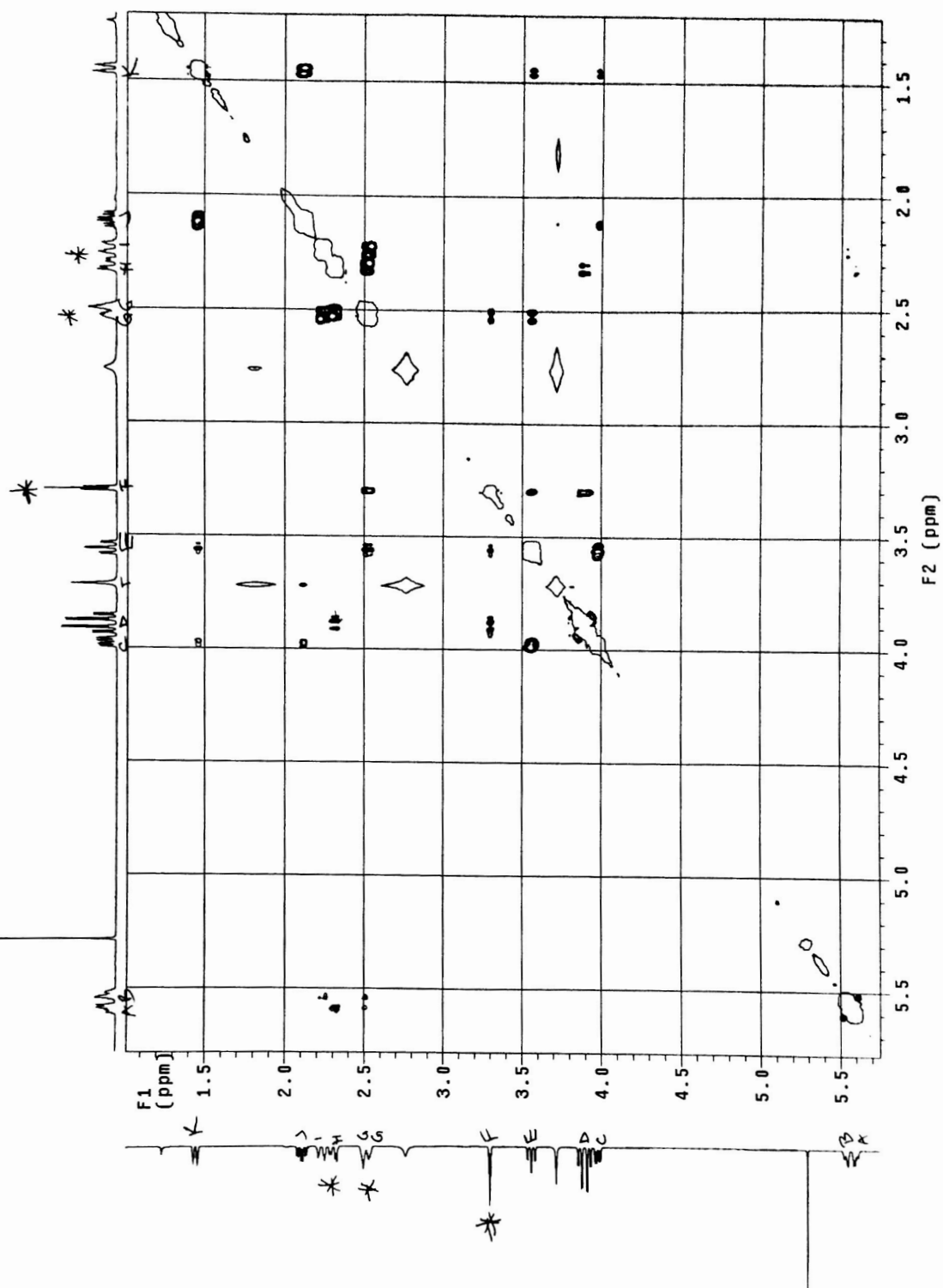


NOESY spectrum of **3p-anti, syn**

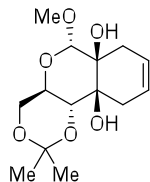
1mxvl_67bil_noesy

File: Noesy

Pulse Sequence: NOESY



(4a*S*,6*S*,10*bR*)-6-methoxy-2,2-dimethyl-4,4a,6,6a,7,10,10a,10b-octahydro-[1,3]-dioxino[5,4-*c*]isochromene-6a,10a-diol (3q**)**



To an oven dried sealed tube equipped with a stir bar and sealed with a septum under argon was added $\text{Ru}_3(\text{CO})_{12}$ (3.8 mg, 0.006 mmol, 2 mol%), dppp (7.4 mg, 0.018 mmol, 6 mol%), 3,5-dimethylbenzoic acid (4.5 mg, 0.03 mmol, 10 mol%) and diol **1g** (70.3 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon and toluene (0.30 mL, 1.0 M) was added via syringe, followed by freshly condensed butadiene **2a** (0.13 mL, 1.5 mmol, 500 mol%) at -78°C . The septum was replaced with a screw cap, and the reaction was heated to 140°C . The reaction was allowed to stir for 48 hours. The volatiles were removed via rotary evaporation under reduced pressure, and the residue was subjected to flash column chromatography (SiO_2 : 1:19, ethyl acetate: hexanes) to provide the cycloadducts **3q** as colorless solid in 3.2:1 dr (41.8 mg, 0.1460 mmol, 48% yield).

The two diastereomers could be separated via column chromatography and the characterization of the major diastereomer is given below (stereochemistry and the ring junction was determined by X-ray crystallography).

TLC (SiO_2): Rf = 0.27 (2:3, ethyl acetate: hexanes).

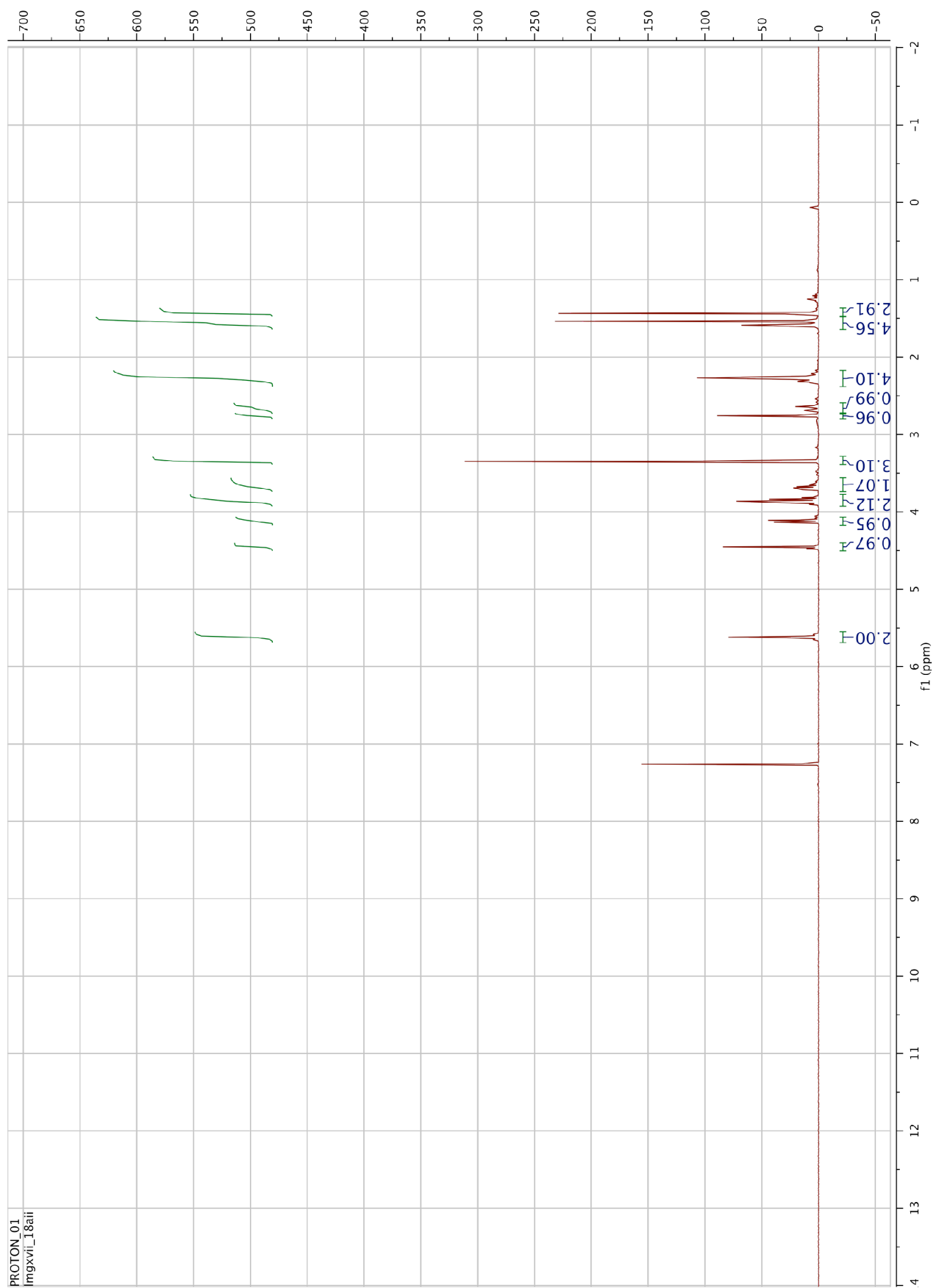
^1H NMR (400 MHz, CDCl_3): δ 5.61 (m, 2H), 4.44 (br s, 1H), 4.11 (d, 1H, $J = 9$ Hz), 3.89-3.79 (m, 2H), 3.71-3.63 (m, 1H), 3.34 (s, 3H), 2.79 (br s, 1H), 2.69-2.61 (m, 1H), 2.33-2.22 (m, 4H), 1.53 (s, 3H), 1.43 (s, 3H) ppm.

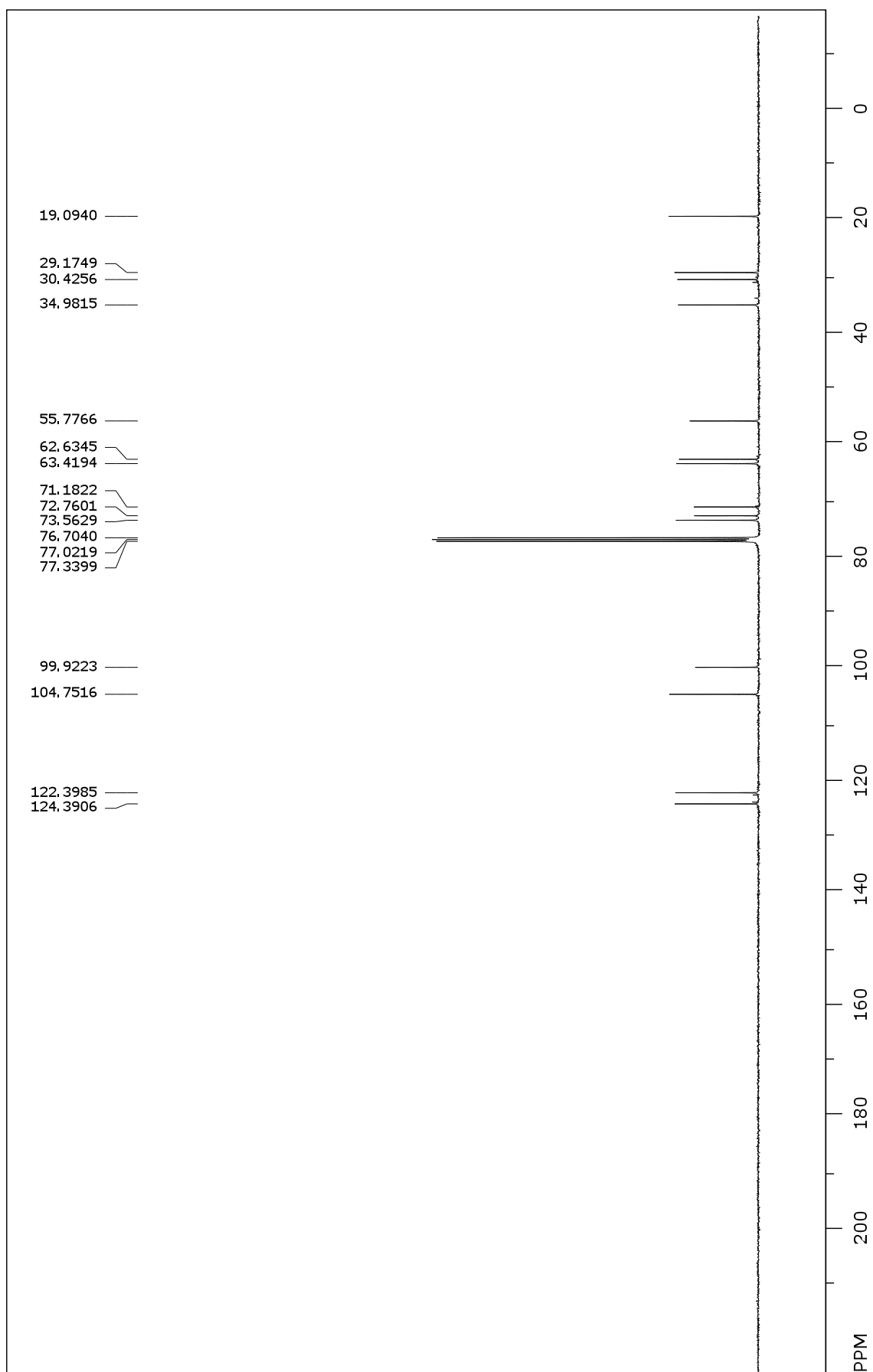
^{13}C NMR (100 MHz, CDCl_3): δ 124.4, 122.4, 104.8, 99.9, 73.6, 72.8, 71.8, 63.4, 62.6, 55.8, 35.0, 30.4, 29.2, 19.1 ppm.

LRMS (ESI⁺): Calculated for $\text{C}_{15}\text{H}_{22}\text{NaO}_5^+$ ($\text{M}+\text{Na}^+$) 309; Found 309.

FTIR (neat): 3458, 2931, 1379, 1083, 1003, 973, 862, 656 cm^{-1} .

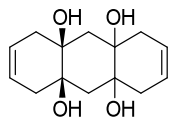
MP: 162-165 $^\circ\text{C}$.





(4aR*,8aS*,9aS*,10aR*)-1,4,5,8-tetrahydroanthracene-4a,8a,9a,10a(9H,10H)-tetraol

and (4aR*,8aR*,9aS*,10aS*)-1,4,5,8-tetrahydroanthracene-4a,8a,9a,10a(9H,10H)-tetraol (3r)



To an oven dried pressure tube sealed equipped with a stir bar with a septum under an argon atmosphere was added $\text{Ru}_3(\text{CO})_{12}$ (7.6 mg, 0.012 mmol, 4 mol%), dppp (14.8 mg, 0.036 mmol, 12 mol%) and tetraol **1d** (44.5 mg, 0.3 mmol, 100 mol%). The pressure tube was purged with argon, and toluene (0.30 mL, 1.0 M) and *N,N*-dimethylacetamide (0.30 mL, 1.0 M) was added via syringe, followed by freshly condensed butadiene **2a** (0.26 mL, 3.0 mmol, 1000 mol%). The septum was replaced with a screw cap, and the reaction was heated to 130 °C. The reaction was allowed to stir for 48 hours. The volatiles were removed *in vacuo*, and the residue was subjected to flash column chromatography (SiO_2 : 3:47, methanol: dichloromethane) to provide the cycloadduct **3r** (71.4 mg, 0.283 mmol, 92% yield, 1.4:1 dr) as a colorless solid. The ^1H NMR spectrum of **3r** was identical in all respects to literature material.⁹

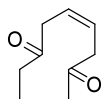
^1H NMR (400 MHz, acetone- d_6): δ 5.49 (m, 1.75 H), 5.45 (m, 1.30 H), 2.85-2.78 (m, 8H), 2.32-2.62 (m, 4H) ppm.

⁹ Geary, L. M.; Chen, T. Y.; Montgomery, P.; Krische, M. J., *J. Am. Chem. Soc.* **2014**, In Press. DOI: 10.1021/ja502659t

Preparation and Spectroscopic Data for 1,6 -Diones **4a-4r**

Yields in Table 2 are reported as an average of two yields. The higher of the two yields is reported herein for compounds **4a-4o**.

(Z)-cyclonon-7-ene-1,5-dione (4a)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3a** (15.4 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2 hours. The volatiles were removed via rotary evaporation under reduced pressure. The crude products were subjected to flash column chromatography (SiO₂: 2:3, ethyl acetate: hexanes) to furnish cyclononene **4a** (15.2 mg, 0.10 mmol, 99% yield) as a colorless oil.

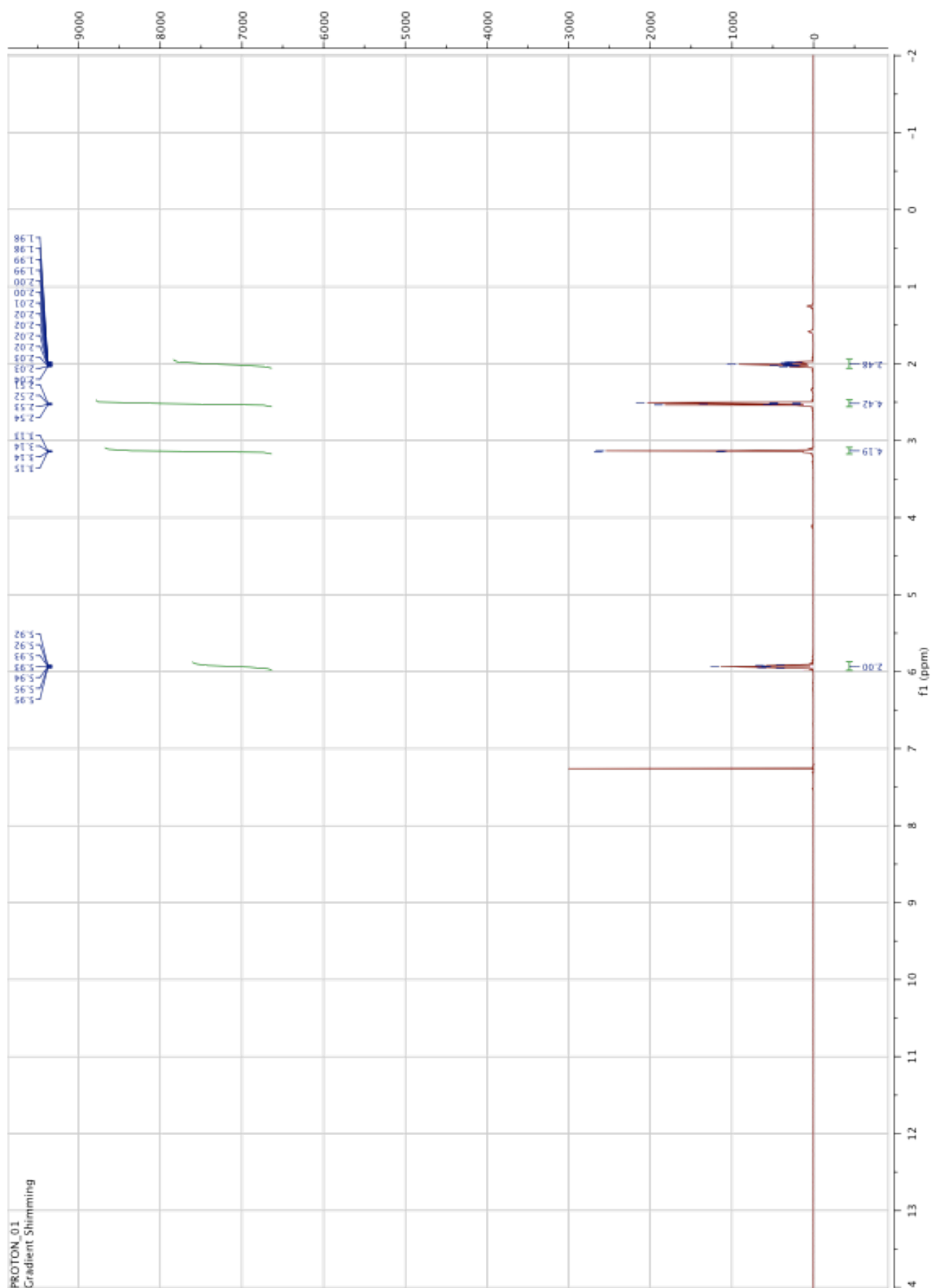
TLC (SiO₂): R_f = 0.33 (2:3, ethyl acetate: hexanes).

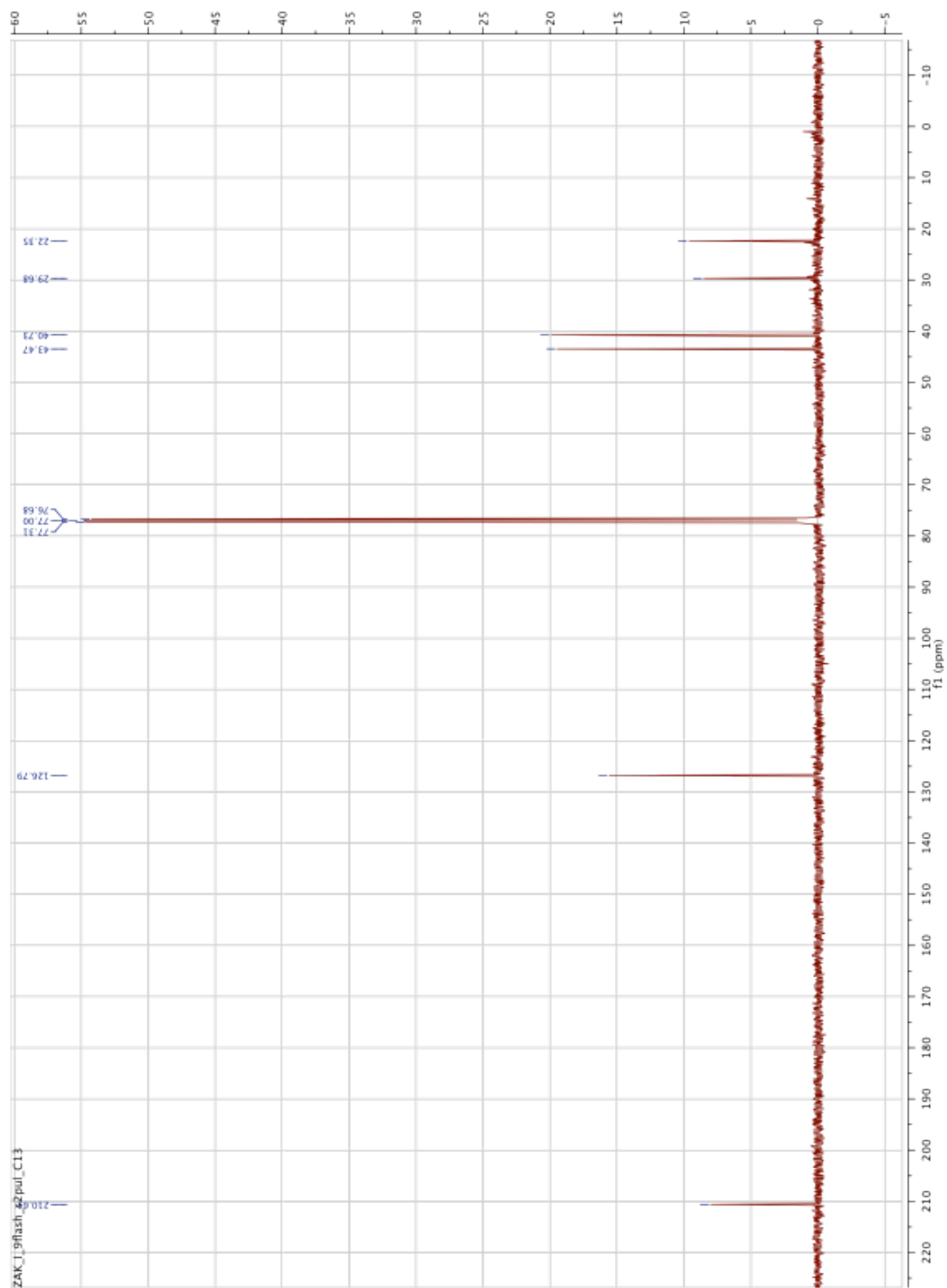
¹H NMR (400 MHz, CDCl₃): δ 5.93 (ddd, *J* = 6.8, 5.2, 1.6 Hz, 2H), 3.14 (dd, *J* = 5.2, 1.6 Hz, 4H), 2.53-2.51 (m, 4H), 2.04-1.98 (m, 2H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 210.6, 126.8, 43.5, 40.7, 29.7, 22.4 ppm.

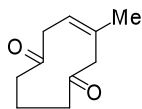
LRMS (ESI⁺): Calculated for C₉H₁₂NaO₂⁺ (*M*+Na⁺) 175.1; Found 175.1.

FTIR (neat): ν 2957, 2921, 2853, 2361, 2343, 1463, 1377, 1260, 1017, 800, 720 cm⁻¹.





(Z)-7-methylcyclonon-7-ene-1,5-dione (4b**)**



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3b** (16.9 mg, 0.1 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2.5 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 2:3, ethyl acetate: hexanes) to furnish cyclononene **4b** (14.5 mg, 0.087 mmol, 87% yield) as a colorless oil.

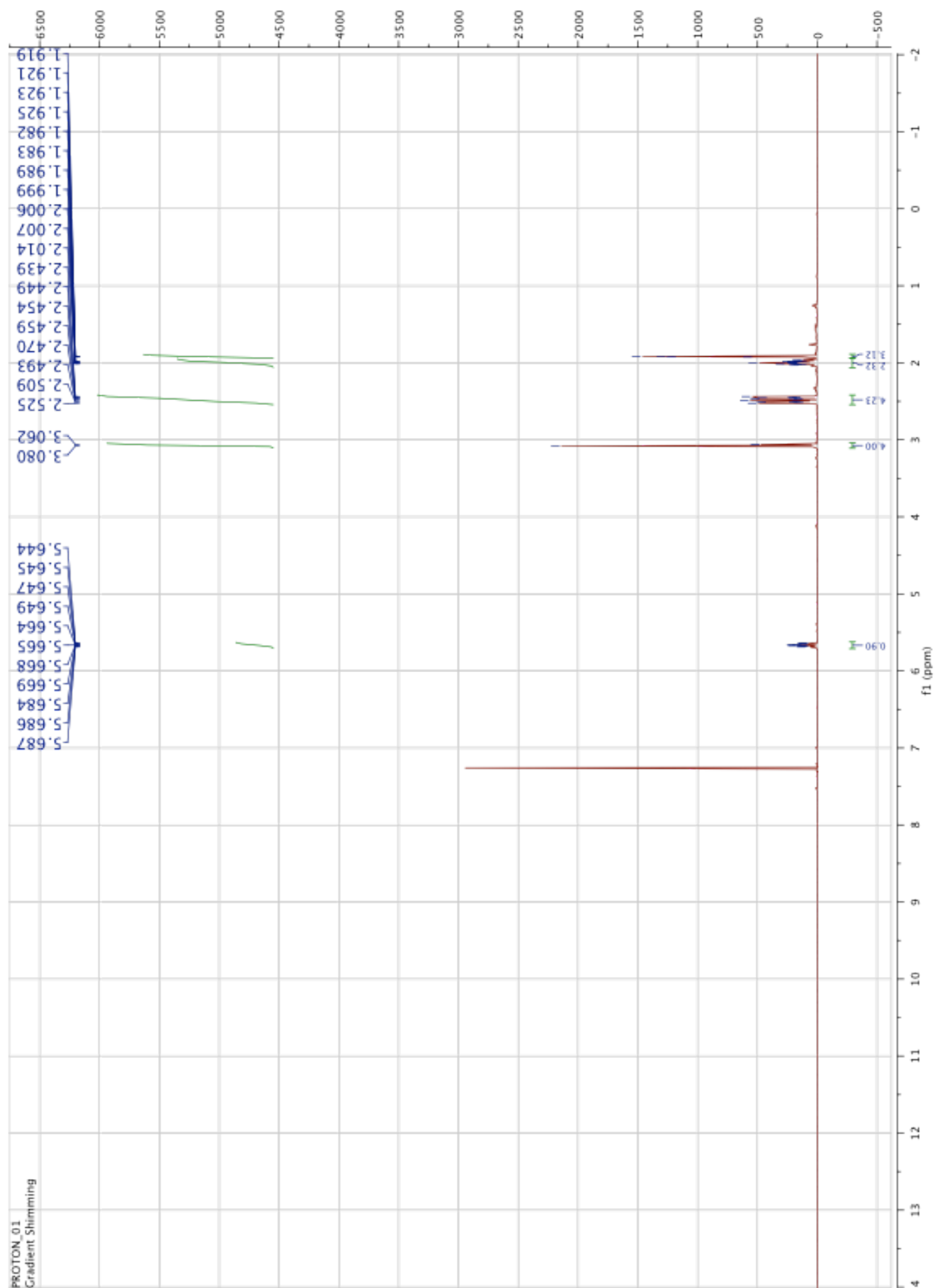
TLC (SiO₂): R_f = 0.21 (3:7, ethyl acetate: hexanes).

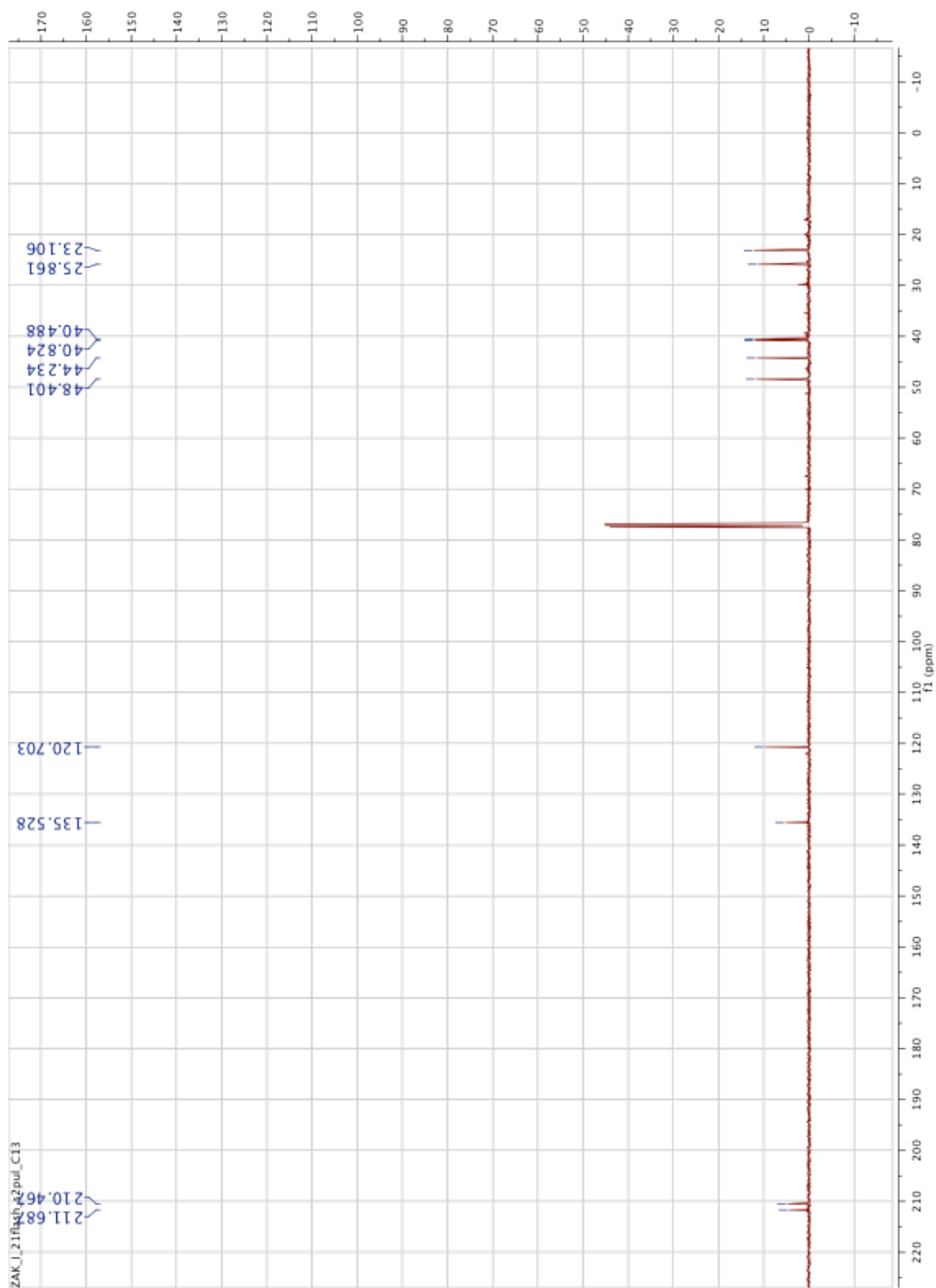
¹H NMR (400 MHz, CDCl₃): δ 5.67 (t, *J* = 8.0 Hz, 1H), 3.08 (s, 2H), 3.07 (d, *J* = 7.2 Hz, 2H), 2.51 (t, *J* = 6.4 Hz, 2H), 2.45 (t, *J* = 6.4 Hz, 2H), 2.03-1.96 (m, 2H), 1.93-1.92 (m, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 211.7, 210.5, 135.5, 120.7, 48.4, 44.2, 40.8, 40.5, 25.9, 23.1 ppm.

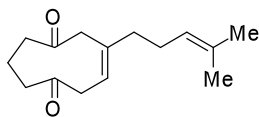
LRMS (CI⁺): Calculated for C₁₀H₁₅O₂⁺ (M+H⁺) 167; Found 167.

FTIR (neat): ν 2929, 1698, 1437, 1320, 1204, 1150, 833 cm⁻¹.





(Z)-7-(4-Methylpent-3-en-1-yl)cyclonon-7-ene-1,5-dione (4c)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (85.8mg, 0.26 mmol, 120 mol%) and diol **3c** (52.5 mg, 0.22 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2.5 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:9, ethyl acetate: hexanes) to furnish cyclononene **4c** (48.5 mg, 0.205 mmol, 93% yield) as a colorless oil.

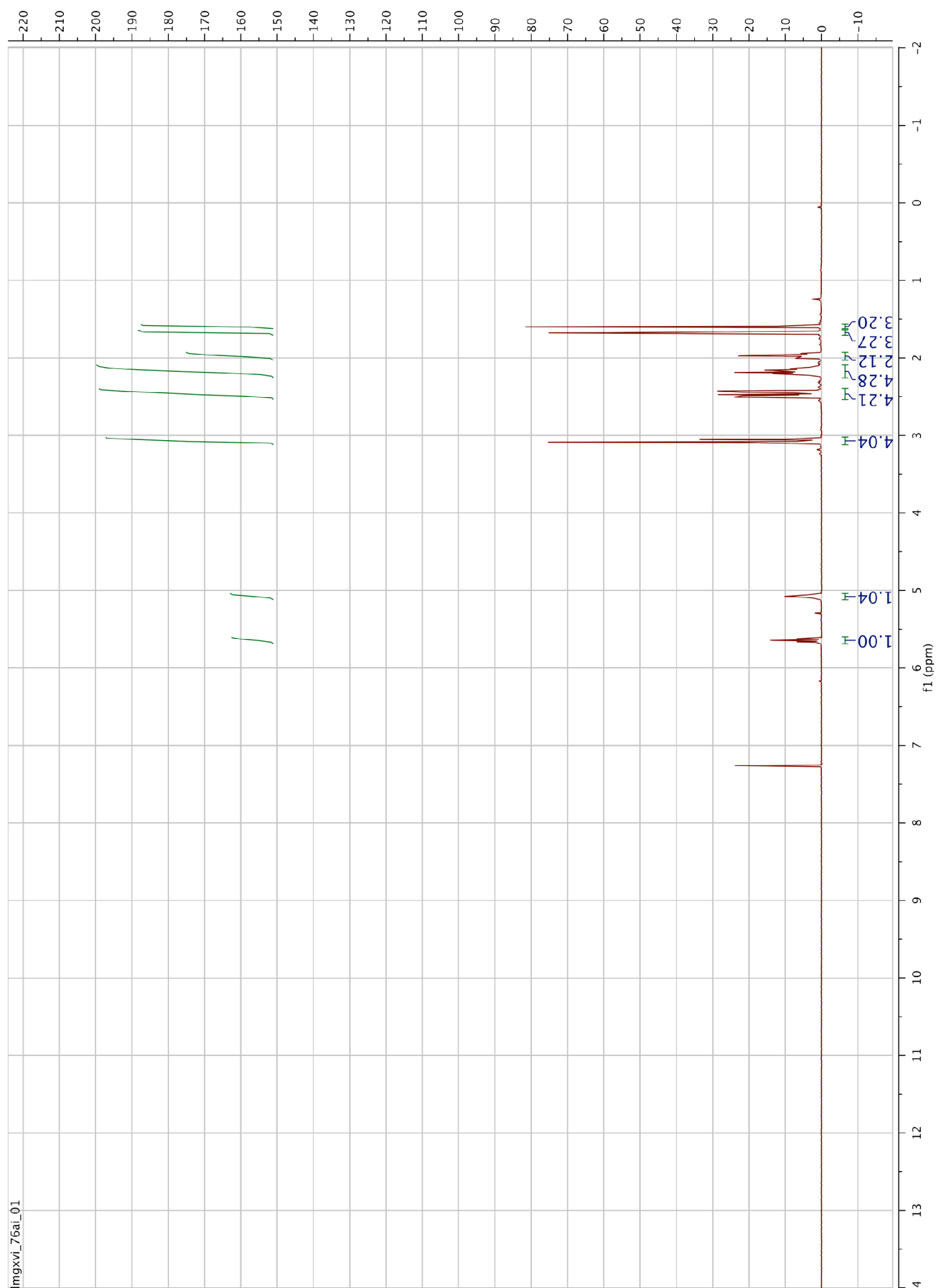
TLC (SiO₂): R_f = 0.40 (2:3, ethyl acetate: hexanes).

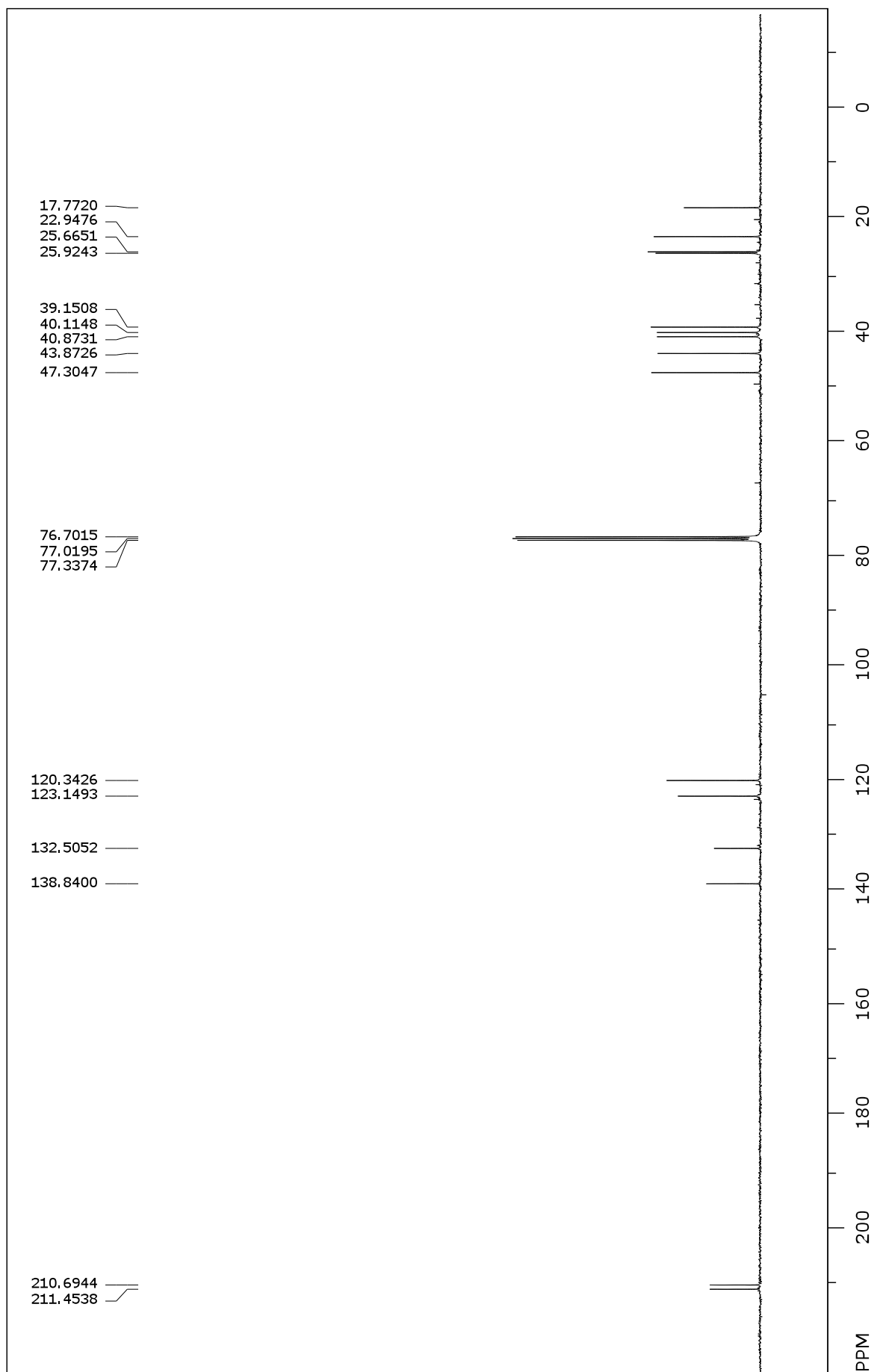
¹H NMR (400 MHz, CDCl₃): δ 5.64 (t, 1H, *J* = 7 Hz), 5.07 (m, 1H), 3.07 (m, 4H), 2.51-2.41 (m, 4H), 2.24-2.10 (m, 4H), 2.01-1.93 (m, 2H), 1.68 (s, 3H), 1.60 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 211.5, 210.7, 138.8, 132.5, 123.2, 120.3, 47.3, 43.9, 40.9, 40.1, 39.2, 25.9, 25.7, 22.9, 17.8 ppm.

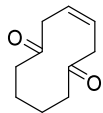
LRMS (CI⁺): Calculated for C₁₅H₂₃O₂ (M+H) 235; Found 235.

FTIR (neat): ν 2930, 1699, 1437, 1145, 1070 cm⁻¹.





(Z)-cyclodec-3-ene-1,6-dione (4d)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3d** (16.8 mg, 0.1000 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 3 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 3:7, ethyl acetate: hexanes) to furnish cyclodecene **4d** (15.0 mg, 0.902 mmol, 90% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.31 (hexanes:ethyl acetate = 7:3).

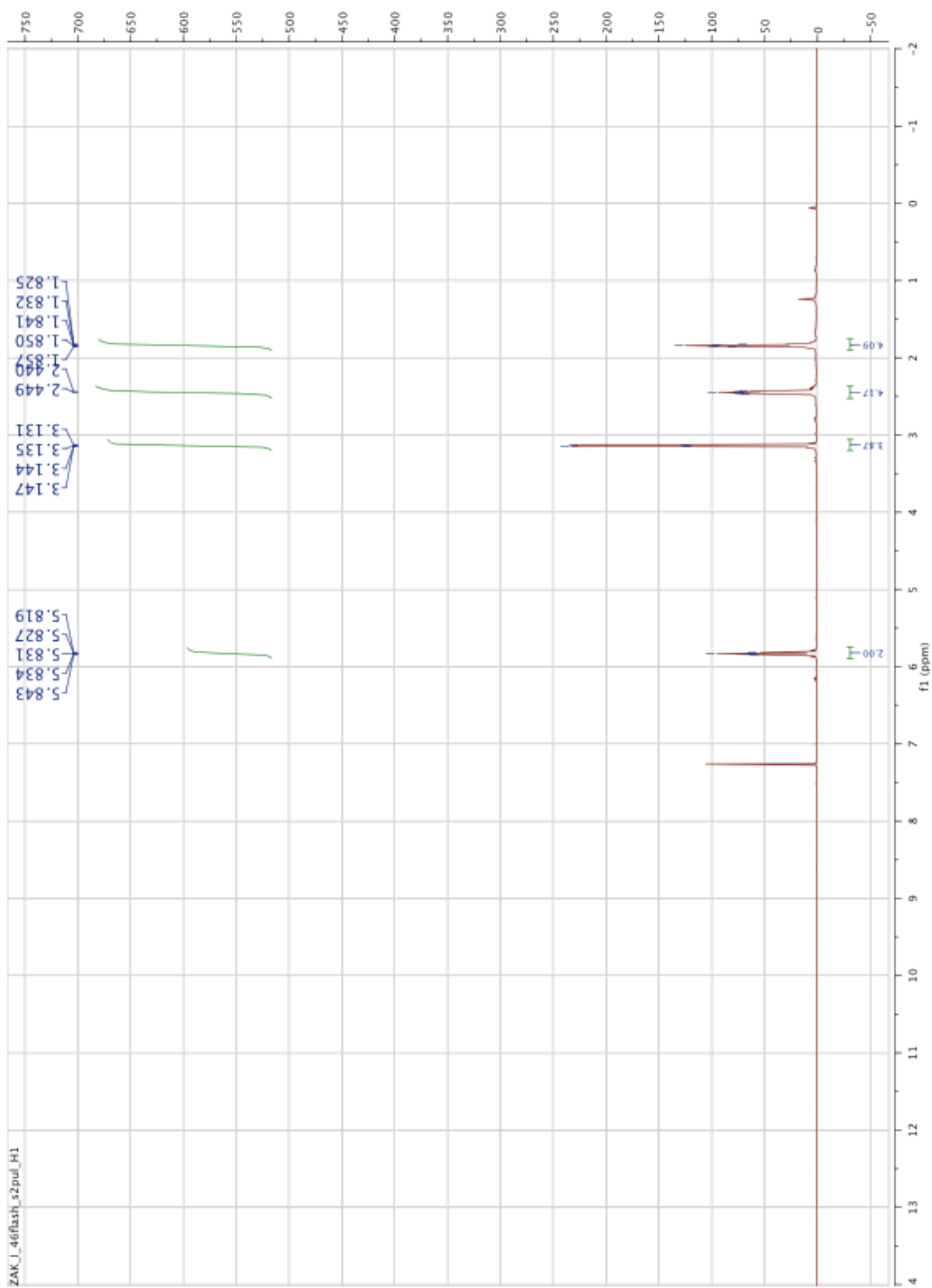
¹H NMR (400 MHz, CDCl₃): δ 5.83 (ddd, *J* = 6.2, 4.8, 1.2 Hz, 4H), 3.14 (dd, *J* = 5.0, 1.2 Hz, 4H), 2.47-2.44 (m, 4H), 1.86-1.83 (m, 4H) ppm.

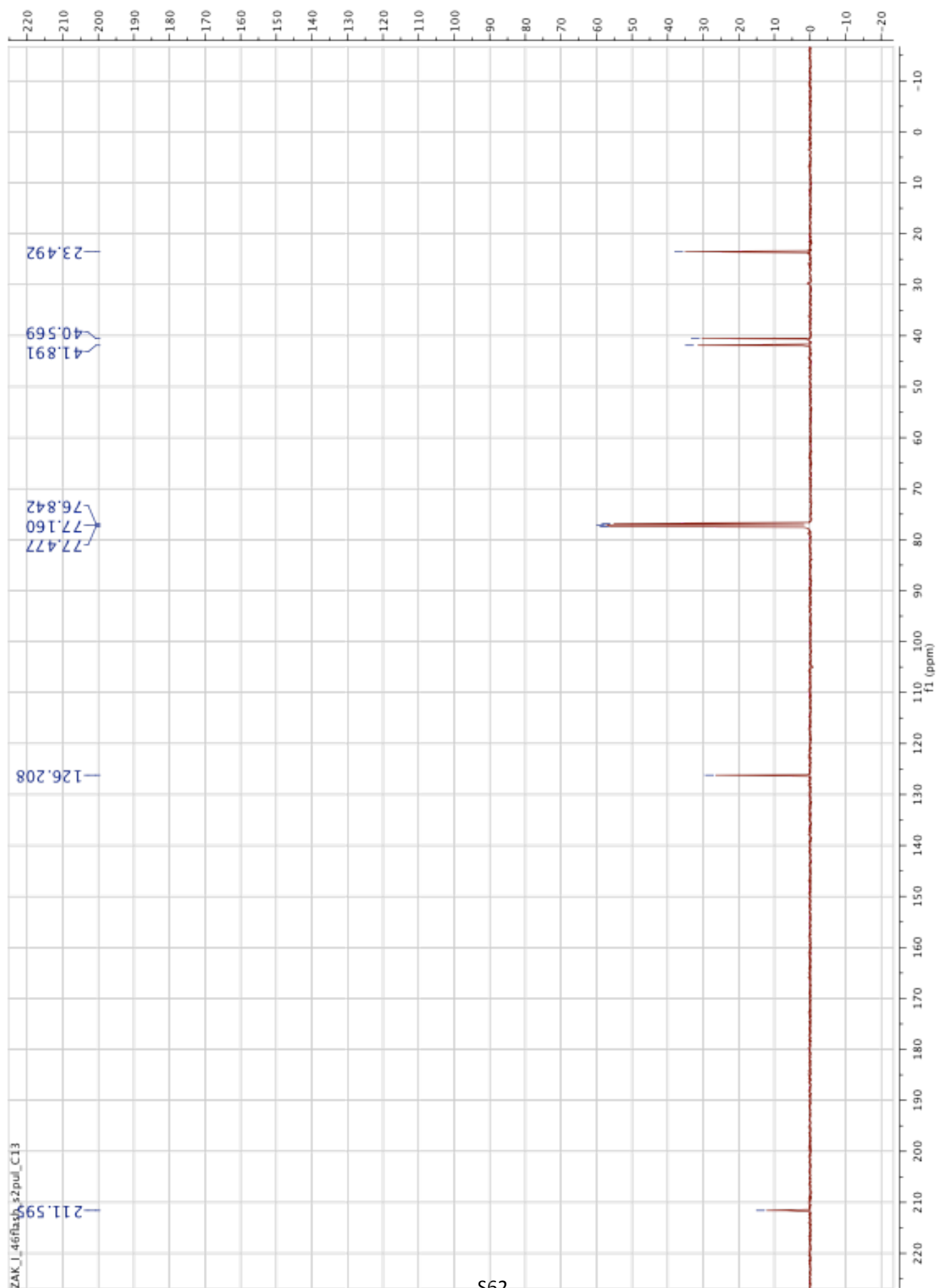
¹³C NMR (100 MHz, CDCl₃): δ 211.6, 126.3, 41.9, 40.6, 23.5 ppm.

MP: 83-85 °C.

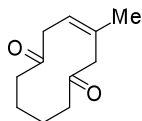
LRMS (ESI+): Calculated for C₁₀H₁₄NaO₂⁺ (*M*+Na⁺) 189.1; Found 189.1.

FTIR (neat): ν 2937, 2359, 1690, 1426, 1330, 1304, 1217, 1197, 1150, 988, 804, 699, 673 cm⁻¹.





(Z)-3-methylcyclodec-3-ene-1,6-dione (4e)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3e** (18.2 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 3:7, ethyl acetate: hexanes) to furnish cyclodecene **4e** (18.0 mg, 0.12 mmol, 99% yield) as a colorless oil.

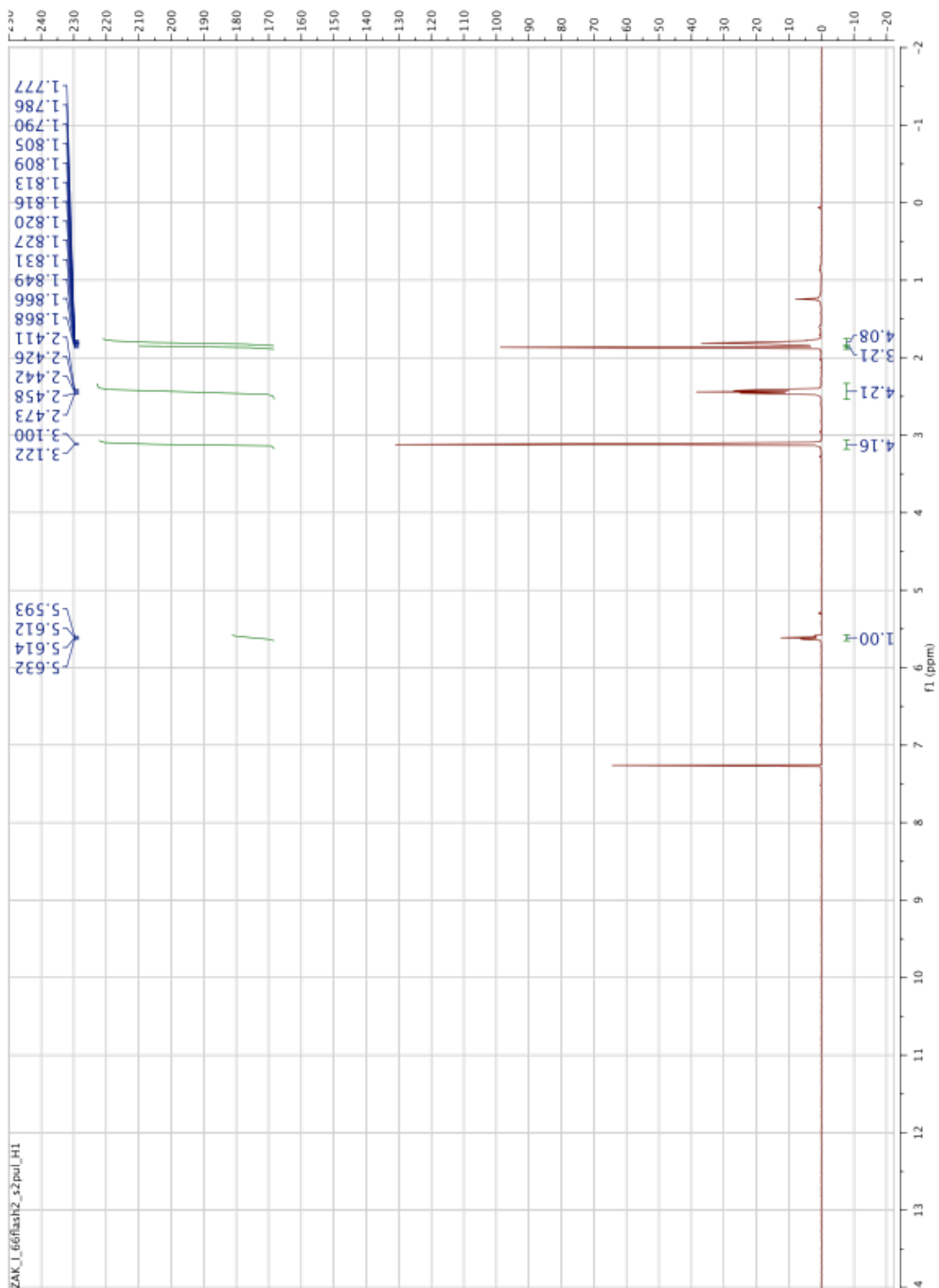
TLC (SiO₂): R_f = 0.37 (3:7, ethyl acetate: hexanes).

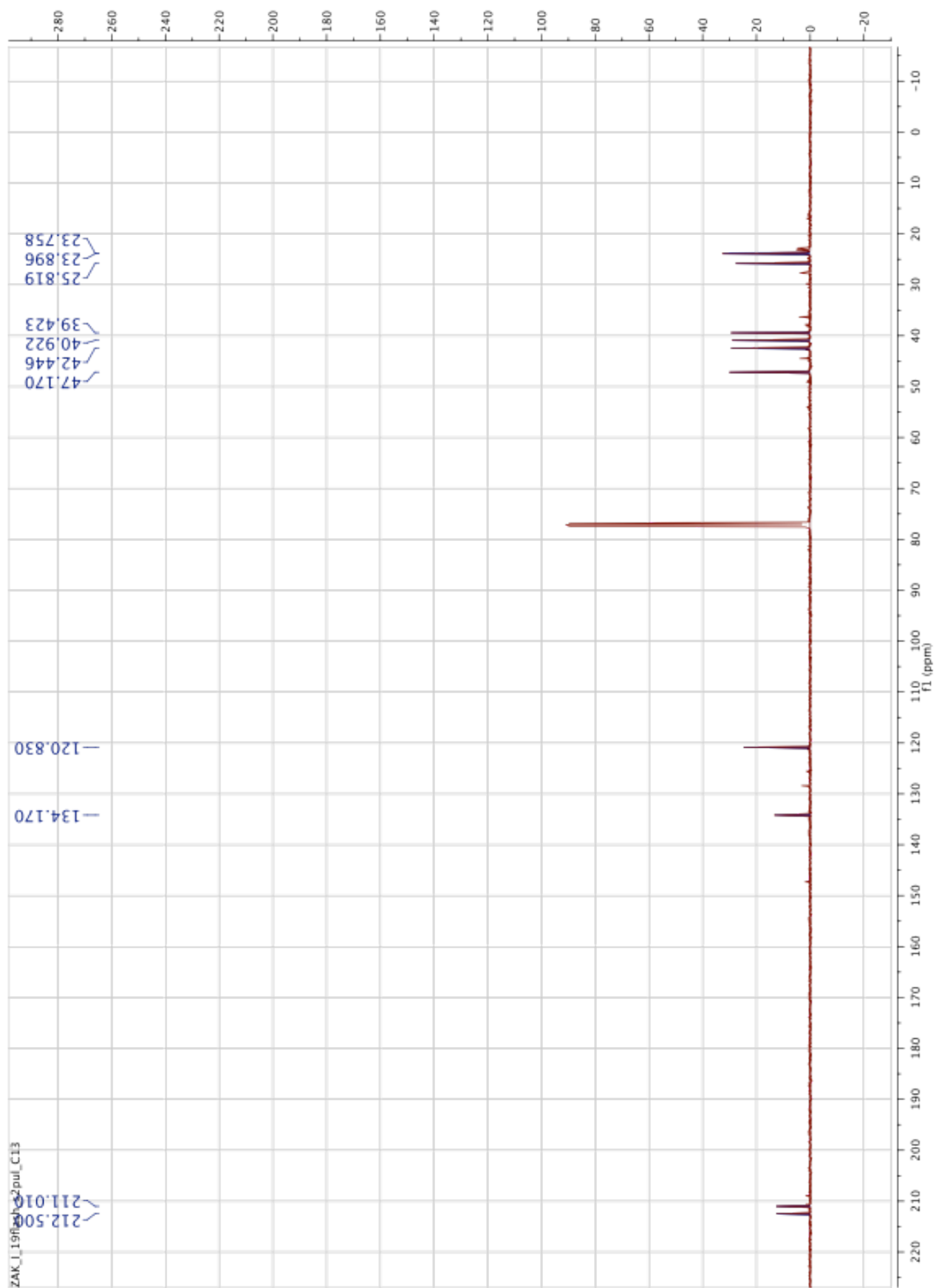
¹H NMR (400 MHz, CDCl₃): δ 5.61 (t, *J* = 7.8 Hz, 1H), 3.12(s, 2H), 3.11 (d, 8.8 Hz, 2H), 2.47-2.41 (m, 4H), 1.87 (s, 3H), 1.77-1.87 (m, 4H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 212.5, 211.0, 134.2, 120.8, 47.2, 42.4, 40.9, 39.4, 25.8, 23.9, 23.8 ppm.

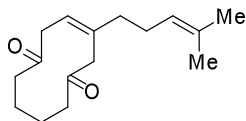
LRMS (CI⁺): Calculated for C₁₁H₁₇O₂⁺ (M+H⁺) 181; Found 181.

FTIR (neat): ν 2930, 1698, 1434, 1329, 1112, 849 cm⁻¹.





(Z)-3-(4-methylpent-3-en-1-yl)cyclodec-3-ene-1,6-dione (4f)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3f** (25.0 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 4 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:4-3:7, ethyl acetate: hexanes) to furnish cyclodecene **4f** (24.8 mg, 0.10 mmol, 99% yield) as a colorless oil.

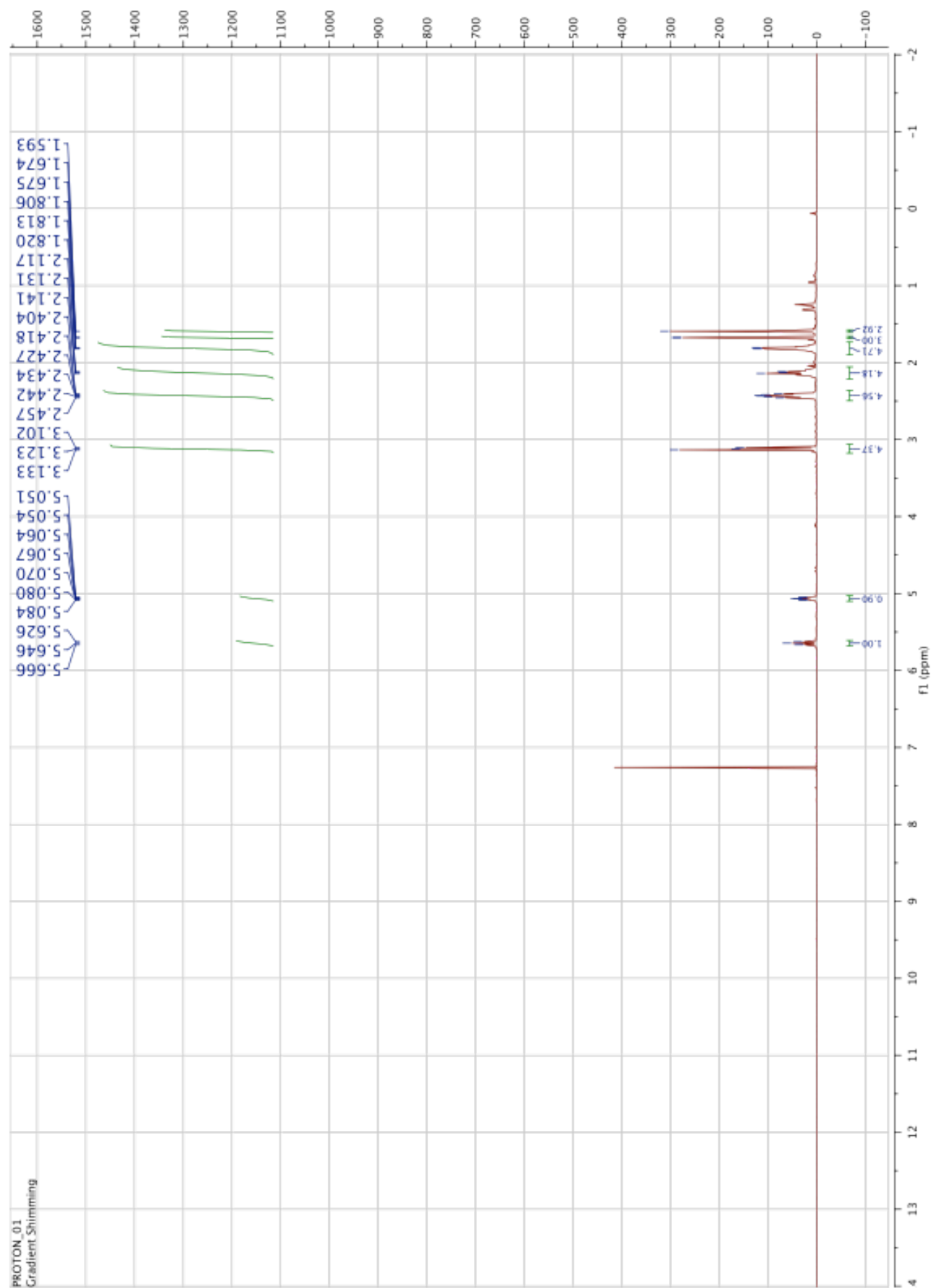
TLC (SiO₂): R_f = 0.40 (3:7, ethyl acetate: hexanes).

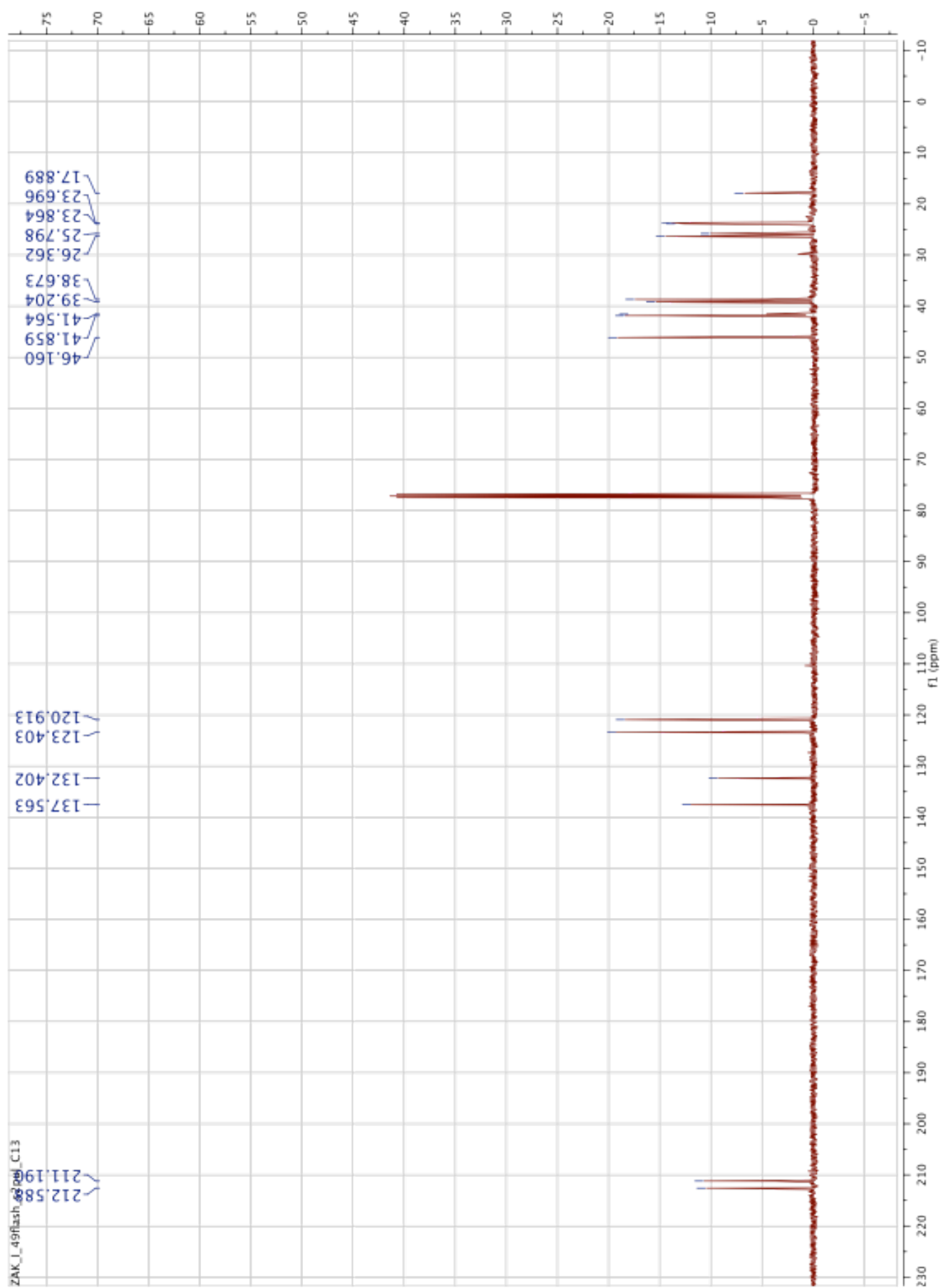
¹H NMR (400 MHz, CDCl₃): δ 5.65 (t, *J* = 8.1 Hz, 1H), 5.08-5.05 (m, 1H), 3.13 (s, 2H), 3.11 (d, *J* = 8.3 Hz, 2H), 2.46-2.40 (m, 4H), 2.18-2.09 (m, 4H) 1.85-1.79 (m, 4H), 1.67 (s, 3H), 1.59 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 212.6, 211.2, 137.6, 132.4, 123.4, 120.9, 46.2, 41.9, 41.6, 39.2, 38.7, 26.4, 25.8, 23.9, 23.7, 17.9 ppm.

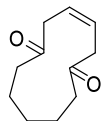
LRMS (CI⁺): Calculated for C₁₆H₂₅O₂⁺ (M+H⁺) 249; Found 249.

FTIR (neat): ν 2929, 2360, 1700, 1439, 1364, 1302, 1218, 1105, 668 cm⁻¹.





(Z)-cycloundec-3-ene-1,6-dione (4g)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3f** (18.2 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 3:7, ethyl acetate: hexanes) to furnish cycloundecene **4g** (18.0 mg, 0.10 mmol, 99% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.29 (3:7 ethyl acetate: hexanes).

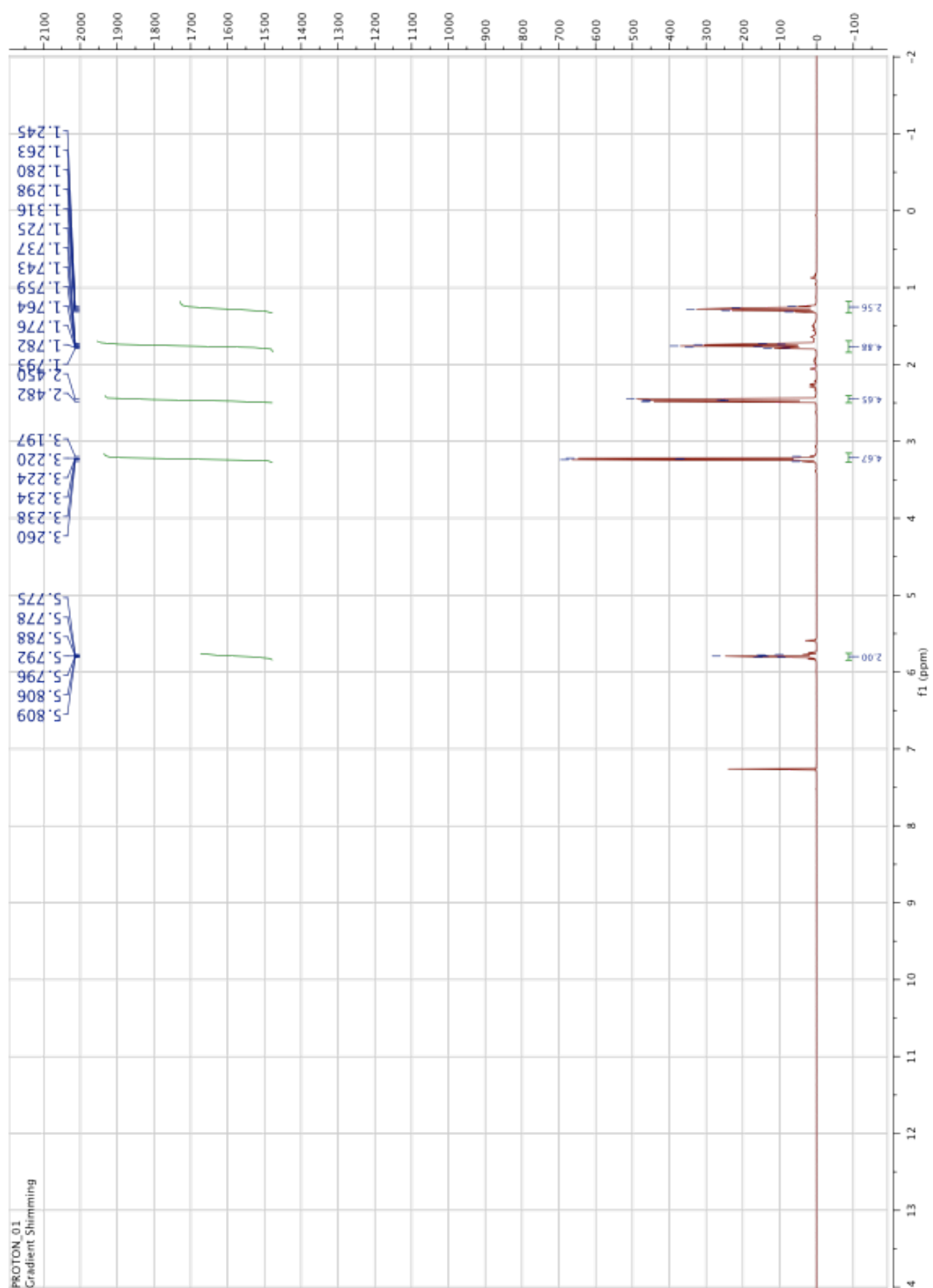
¹H NMR (400 MHz, CDCl₃): δ 5.79 (ddd, *J* = 7.0, 5.4, 1.2 Hz), 3.23 (dd, *J* = 5.6, 1.5 Hz, 4H), 2.49-2.45 (m, 4H), 1.79-1.73 (m, 4H), 1.28 (quin., *J* = 7.1 Hz, 2H) ppm.

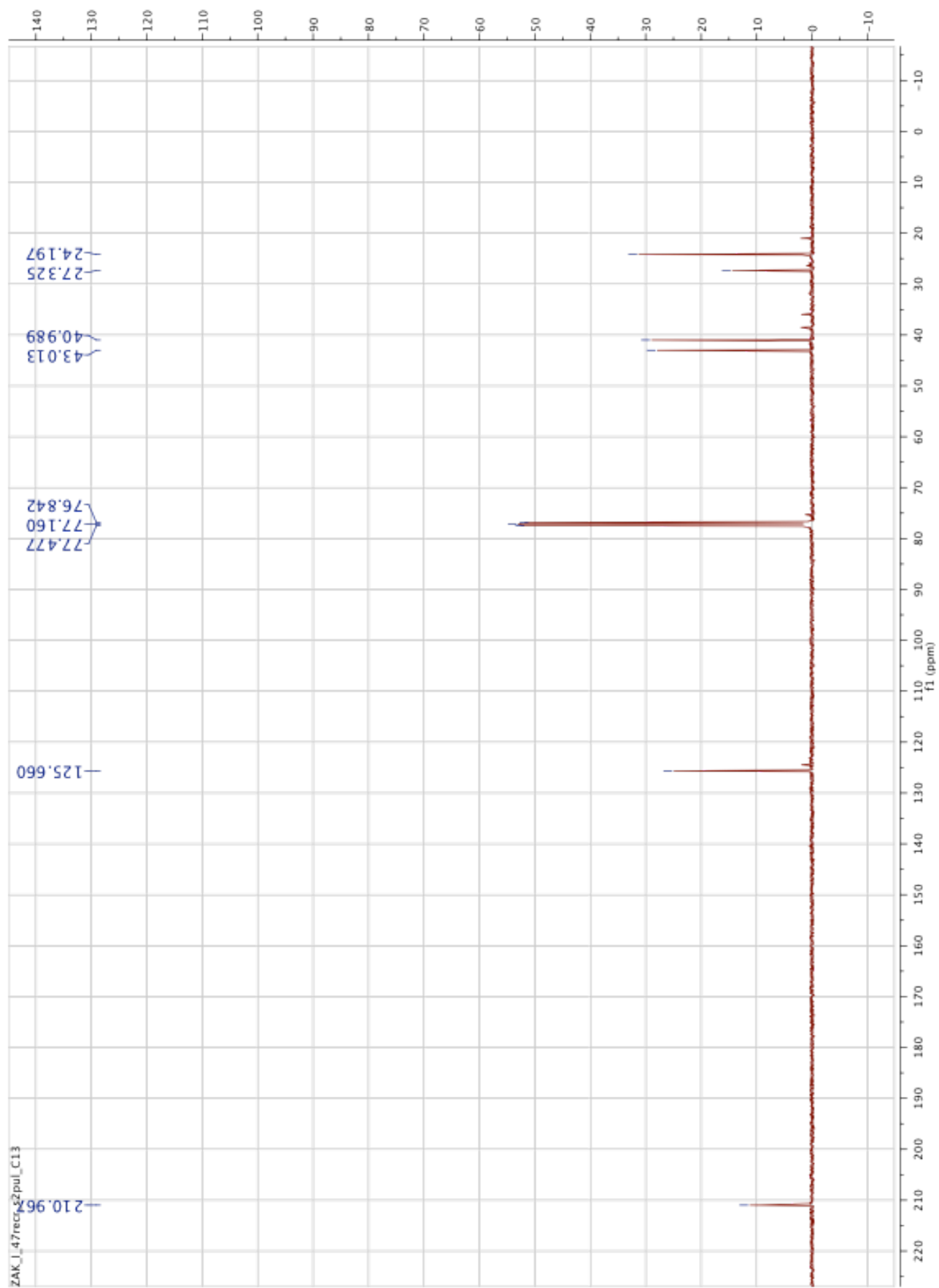
¹³C NMR (100 MHz, CDCl₃): δ 211.0, 125.7, 43.0, 41.0, 27.3, 24.2 ppm.

MP: 77-79 °C.

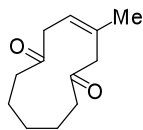
LRMS (ESI+): Calculated for C₁₁H₁₆NaO₂⁺ (*M*+Na⁺) 203.1; Found 203.1.

FTIR (neat): ν 2916, 2361, 1697, 1466, 1310, 1250, 1127, 704 cm⁻¹.





(Z)-3-methylcycloundec-3-ene-1,6-dione (4h)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3h** (19.6 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 3 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 3:7, ethyl acetate: hexanes) to furnish cycloundecene **4h** (18.0 mg, 0.093 mmol, 93% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.31 (3:7 ethyl acetate: hexanes).

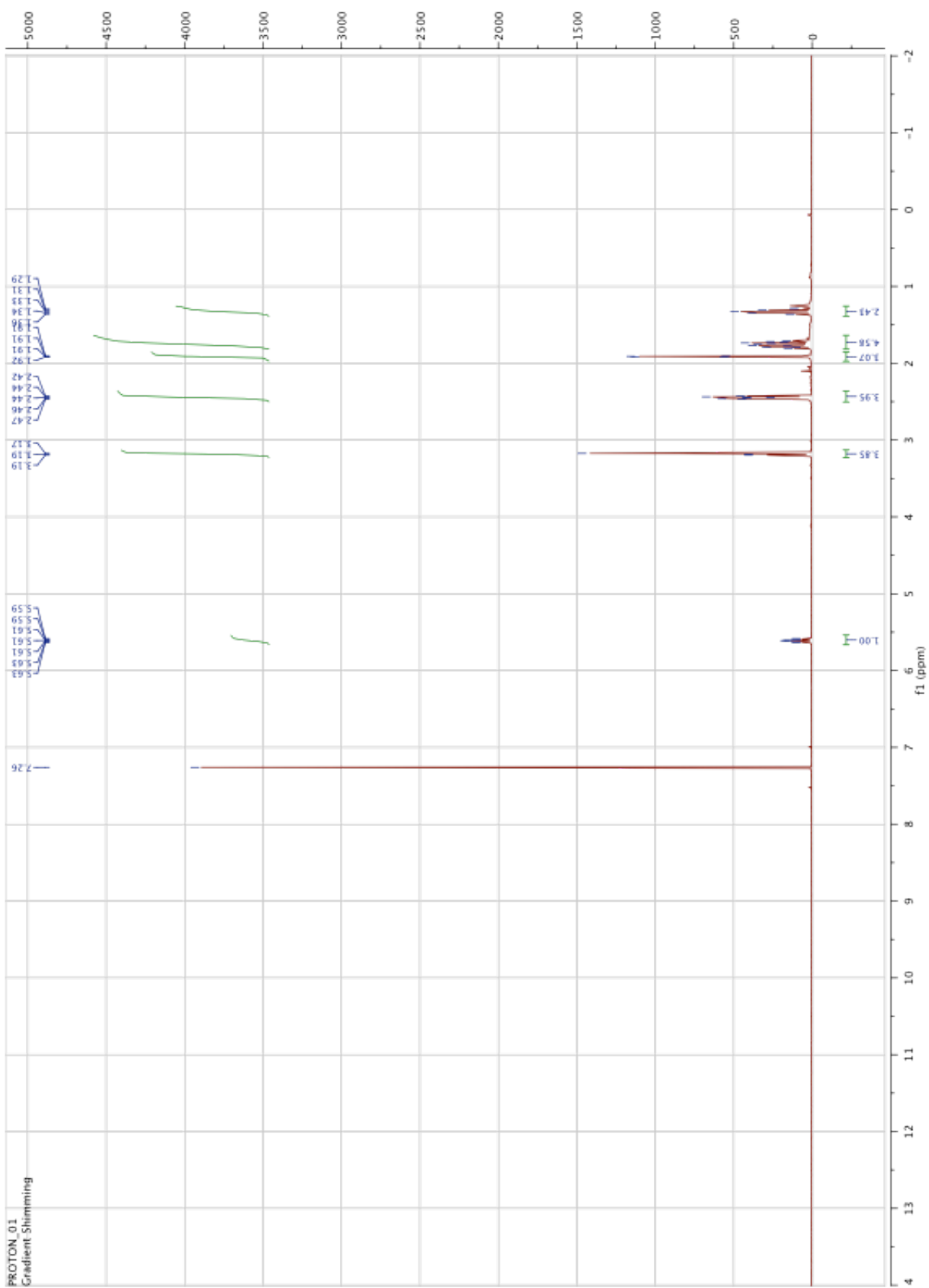
¹H NMR (400 MHz, CDCl₃): δ 5.61 (t, *J* = 8.1 Hz, 1H), 3.19-3.17 (m, 4H), 2.47-2.41 (m, 4H), 1.92-1.90 (m, 3H), 1.80-1.70 (m, 4H), 1.33 (quin, *J* = 6.9 Hz, 2H) ppm.

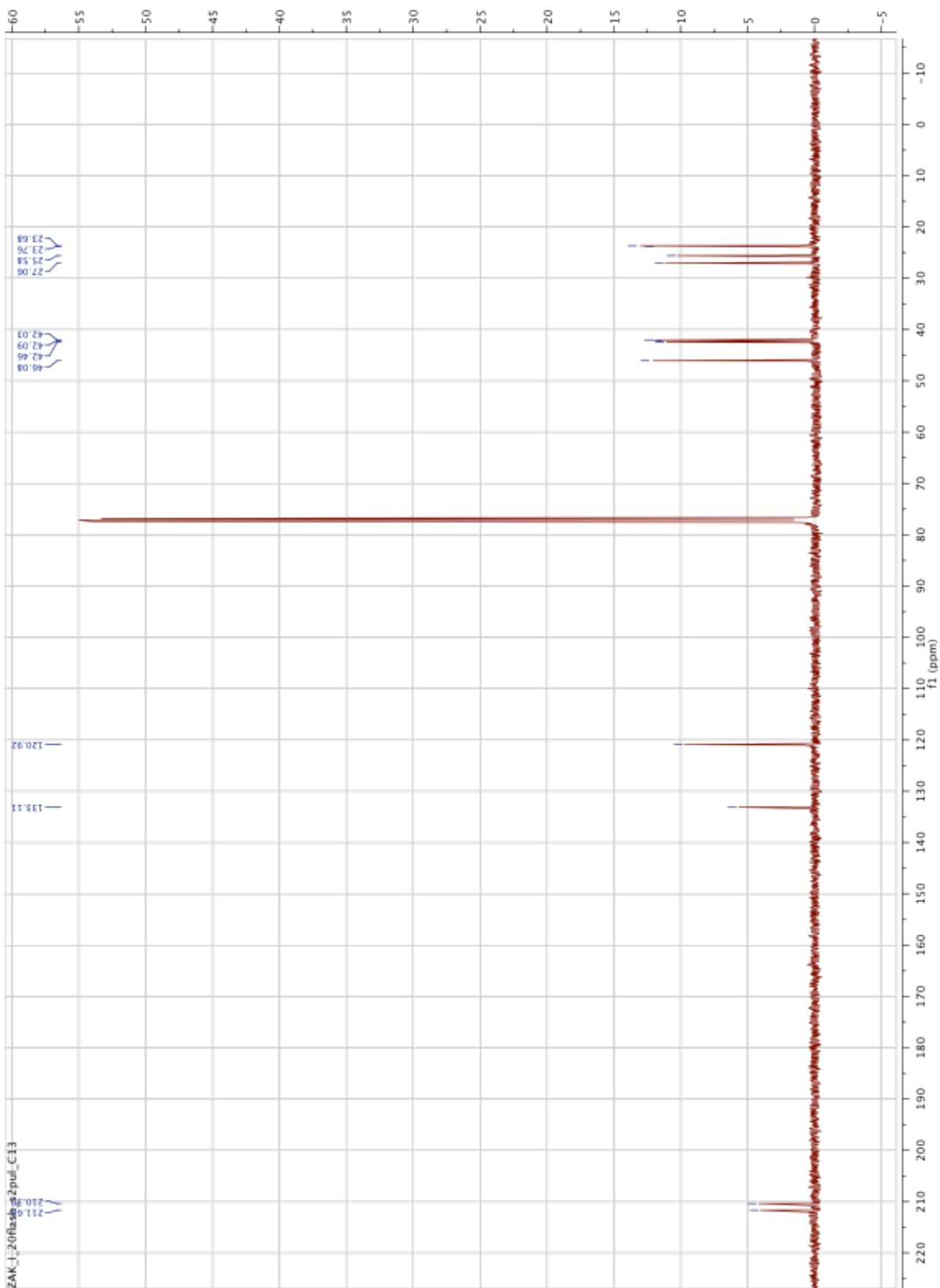
¹³C NMR (100 MHz, CDCl₃): δ 211.7, 210.4, 133.1, 120.9, 46.1, 42.5, 42.1, 42.0, 27.1, 25.6, 23.8, 23.7 ppm.

MP: 69-70 °C.

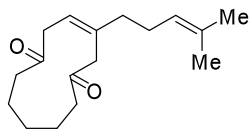
LRMS (CI⁺): Calculated for C₁₂H₁₉O₂⁺ (M+H⁺) 195; Found 195.

FTIR (neat): ν 2916, 1697, 1465, 1430, 1329, 1309, 1249, 1138, 1015, 984, 880 cm⁻¹.





(Z)-3-(4-methylpent-3-en-1-yl)cycloundec-3-ene-1,6-dione (4i)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3i** (26.4, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 4 hours. The volatiles were removed via rotary evaporation under reduced pressure. (SiO₂: 1:4- 3:7 ethyl acetate: hexanes) to furnish the cycloundecene **4i** (18.7 mg, 0.071 mmol, 71% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.38 (3:7, ethyl acetate, hexanes).

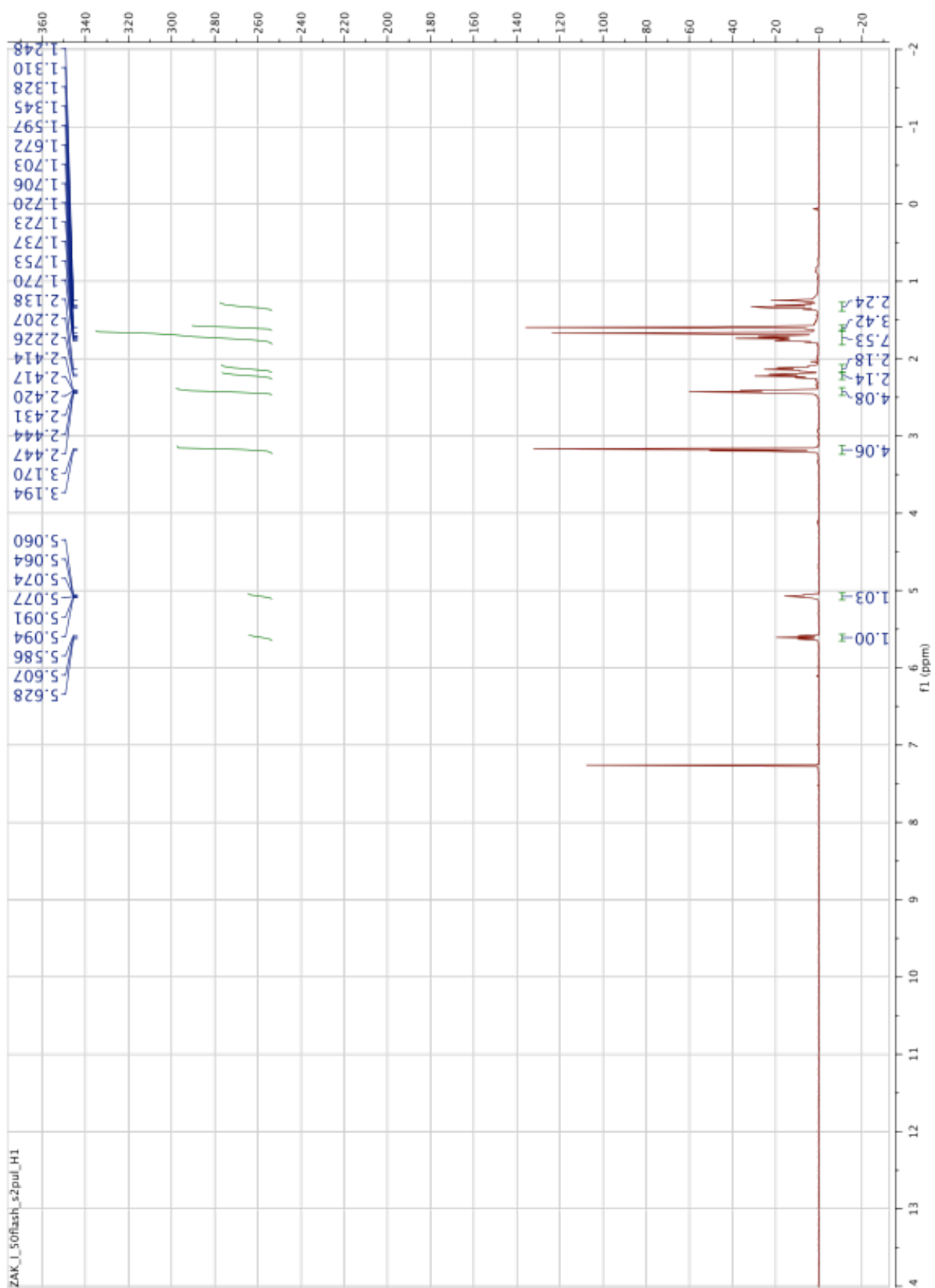
¹H NMR (400 MHz, CDCl₃): δ 5.61 (t, *J* = 8.3Hz, 1H) 5.09-5.06 (m, 1H), 3.18 (d, *J* = 9.6 Hz, 2H), 3.17 (s, 2H), 2.45-2.41 (m, 4H), 2.24- 2.10, (m, 4H), 1.79-1.67 (m, 7H), 1.60 (s, 3H), 1.33 (quin., *J* = 6.6 Hz, 2H) ppm.

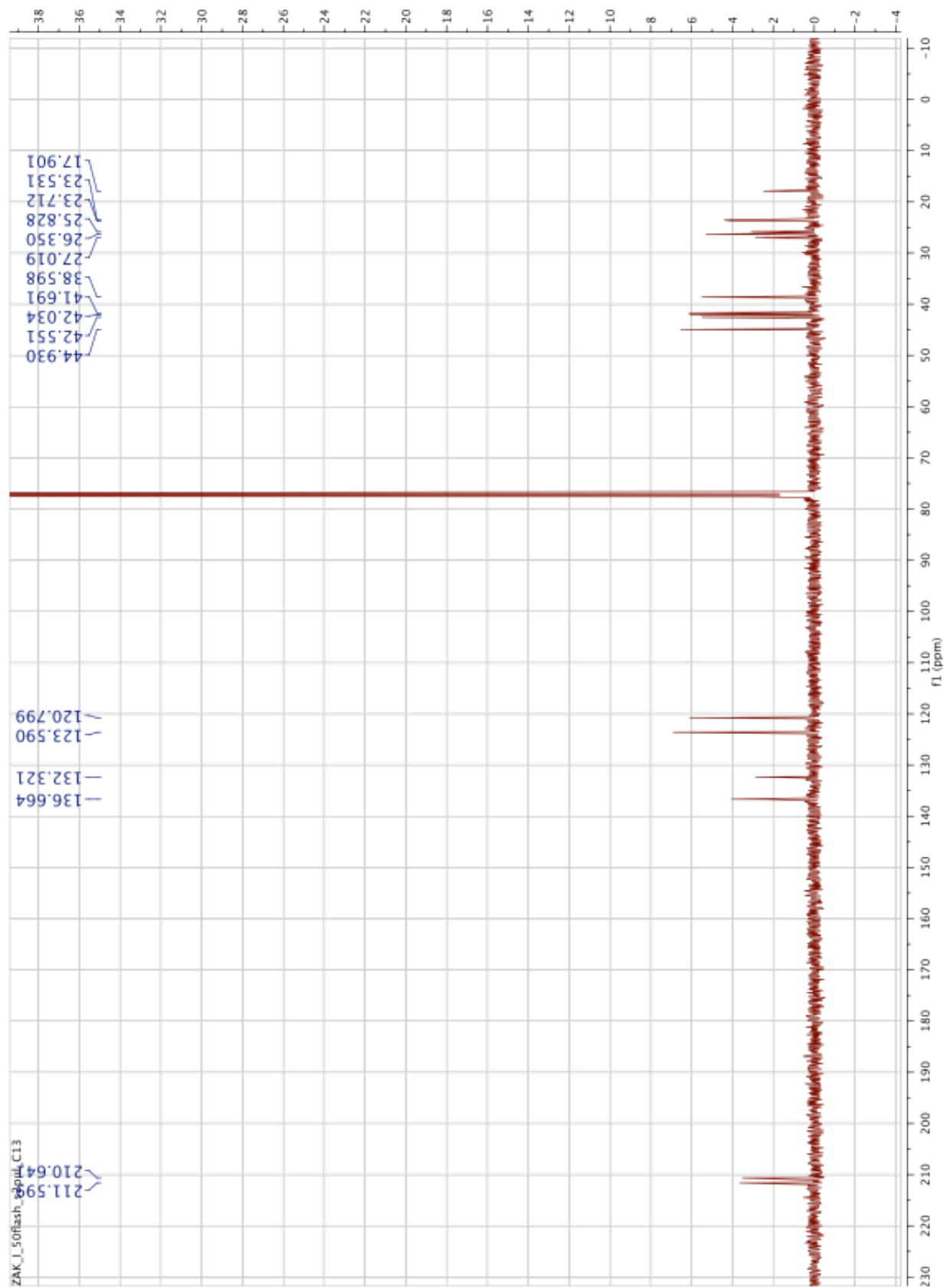
¹³C NMR (100 MHz, CDCl₃): δ 211.6, 210.6, 136.7, 132.3, 123.6, 120.8, 44.9, 42.5, 42.0, 41.7, 38.6, 27.0, 26.3, 25.8, 23.7, 23.5, 17.9 ppm.

MP: 53-55 °C.

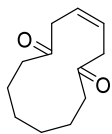
LRMS (CI⁺): Calculated for C₁₇H₂₇O₂⁺ (M+H⁺) 263; Found 263.

FTIR (neat): ν 2921, 2361, 1699, 1432, 1327, 1164, 1101, 1020, 986, 768 cm⁻¹.





(Z)-cyclododec-3-ene-1,6-dione (4j)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3j** (19.6 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 3:7, ethyl acetate: hexanes) to furnish the cyclododecene **4j** (19.4 mg, 0.10 mmol, 99% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.30 (3:7, ethyl acetates: hexanes).

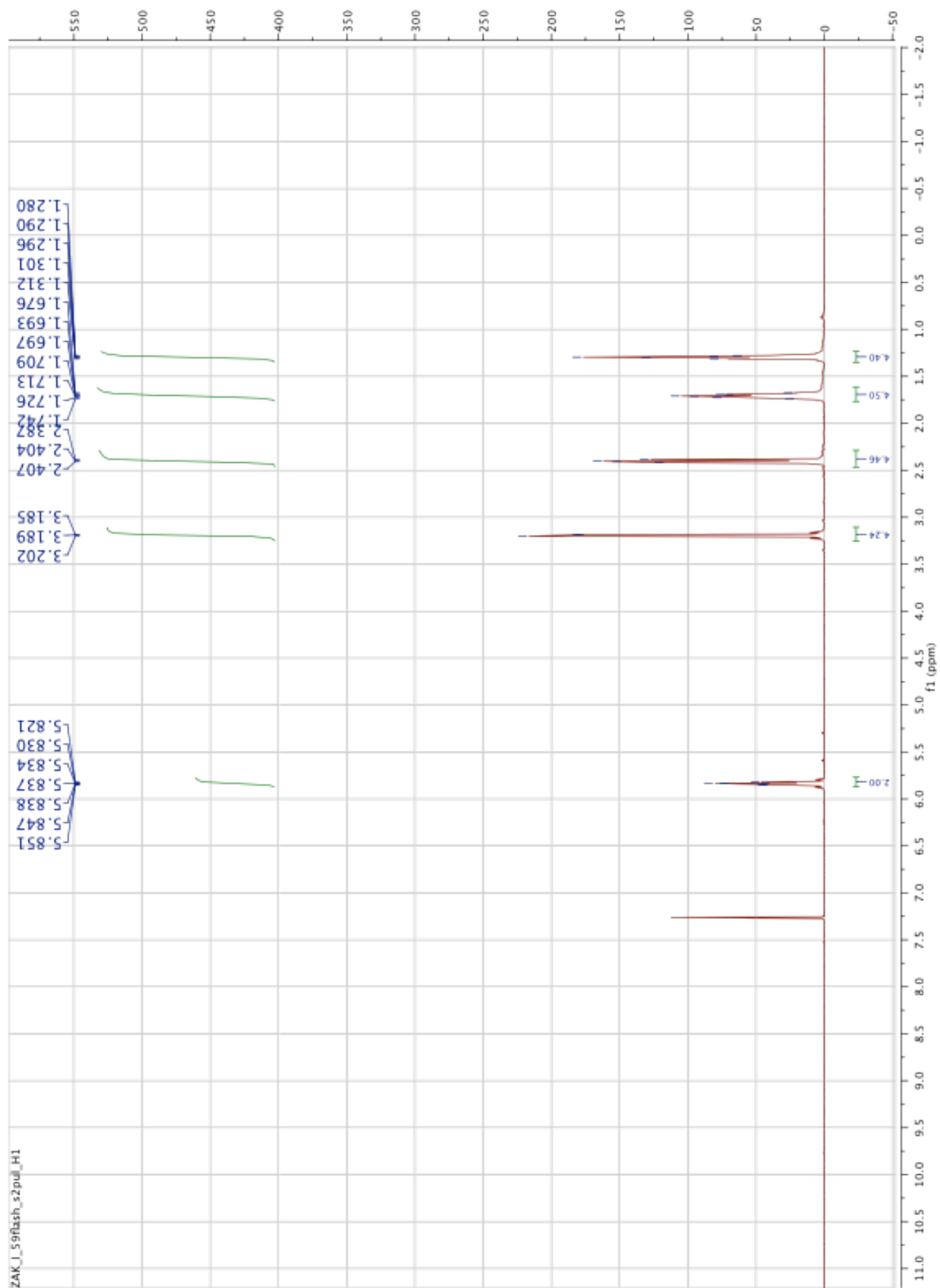
¹H NMR (400 MHz, CDCl₃): δ 5.88-5.79 (m, 2H), 3.21-3.18 (m, 4H), 2.41 (t, *J* = 6.4 Hz, 4H), 1.74-1.68 (m, 4H), 1.31-1.28 (m, 4H) ppm.

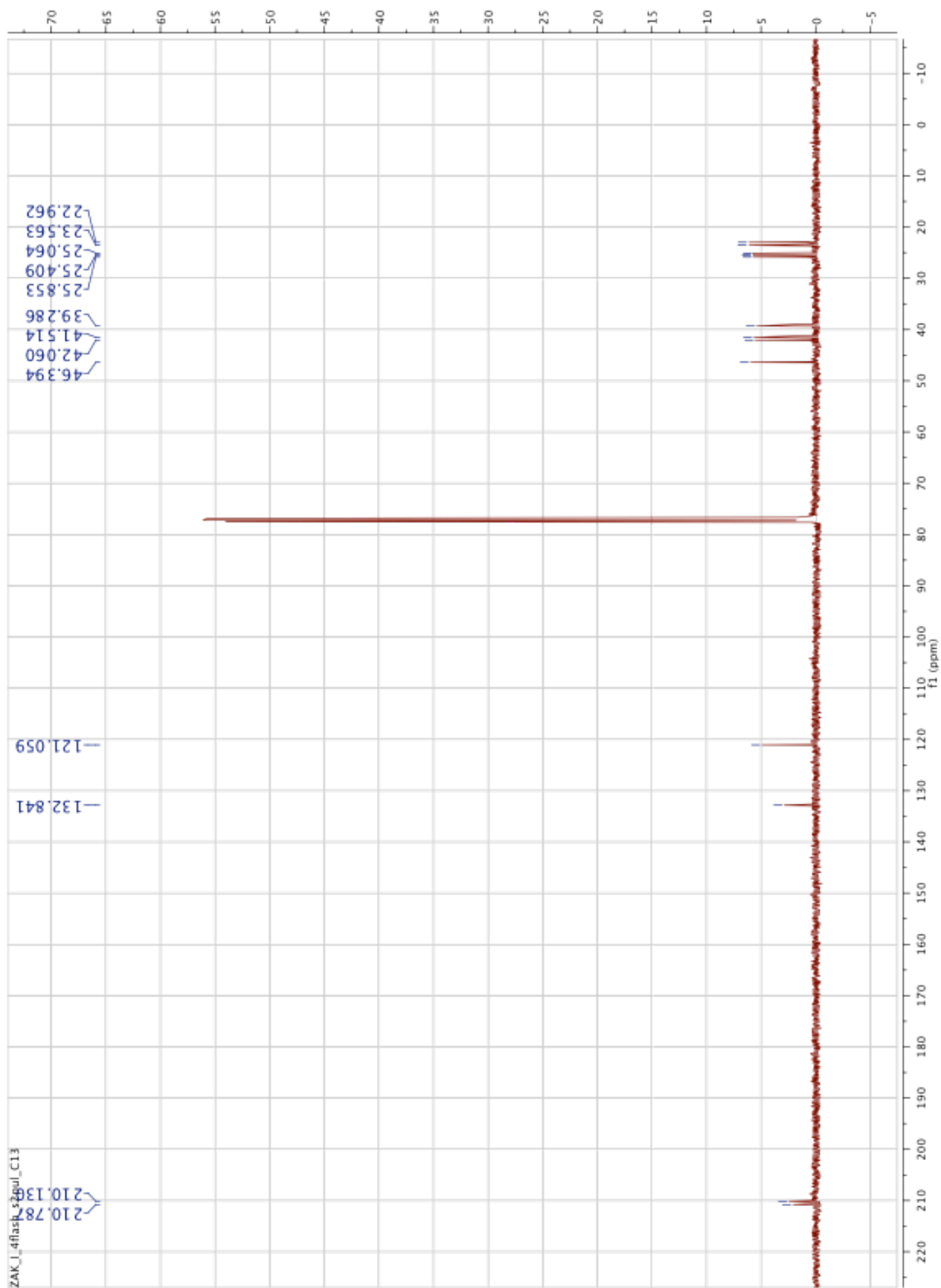
¹³C NMR (100 MHz, CDCl₃): δ 210.8, 210.1, 132.8, 121.1, 46.4, 42.1, 41.5, 39.3, 25.9, 25.4, 25.1, 23.6, 23.0 ppm.

MP: 58-61 °C.

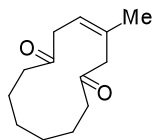
LRMS (CI⁺): Calculated for C₁₂H₁₉O₂⁺ (M+H⁺) 195; Found 195.

FTIR (neat): ν 3031, 2909, 1696, 1416, 1333, 1098, 820, 736, 694 cm⁻¹.





(Z)-3-methyl-3-cyclododecene-1,6-dione (4k)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (38.7mg, 0.12 mmol, 120 mol%) and diol **3k** (21.0 mg, 0.10 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 2.5 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:4, ethyl acetate: hexanes) to furnish the cyclododecene **4k** (17.1 mg, 0.082 mmol, 82% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.43 (3:7, ethyl acetate: hexanes).

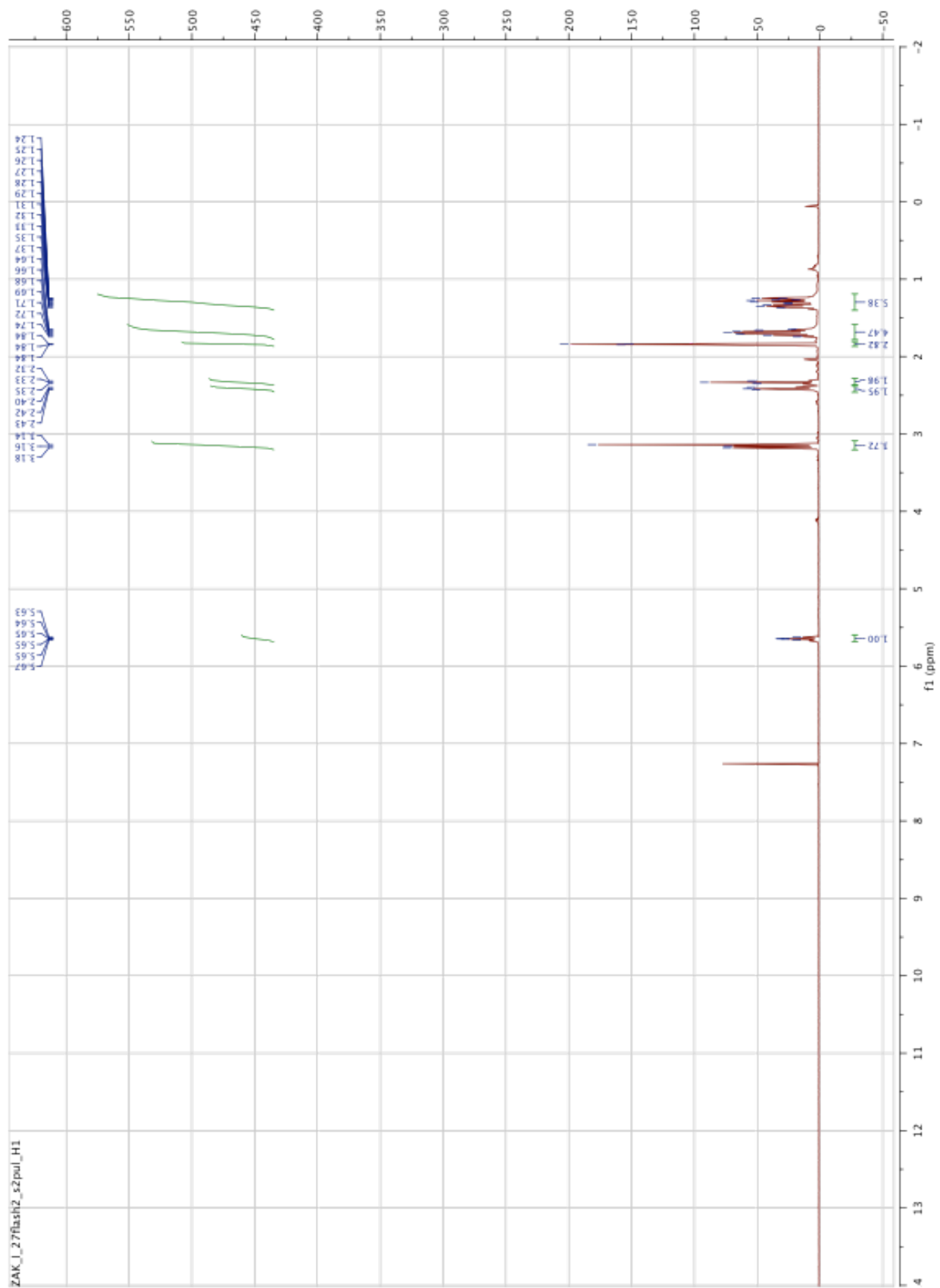
¹H NMR (400 MHz, CDCl₃): δ 5.65 (t, *J* = 8.4 Hz, 1H), 3.17 (d, *J* = 8.0 Hz, 2H), 3.14 (s, 2H), 2.42 (t, *J* = 6.4 Hz, 2H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.84 (m, 3H), 1.69 (sep, *J* = 6.4 Hz, 4H), 1.37-1.24 (m, 4H) ppm.

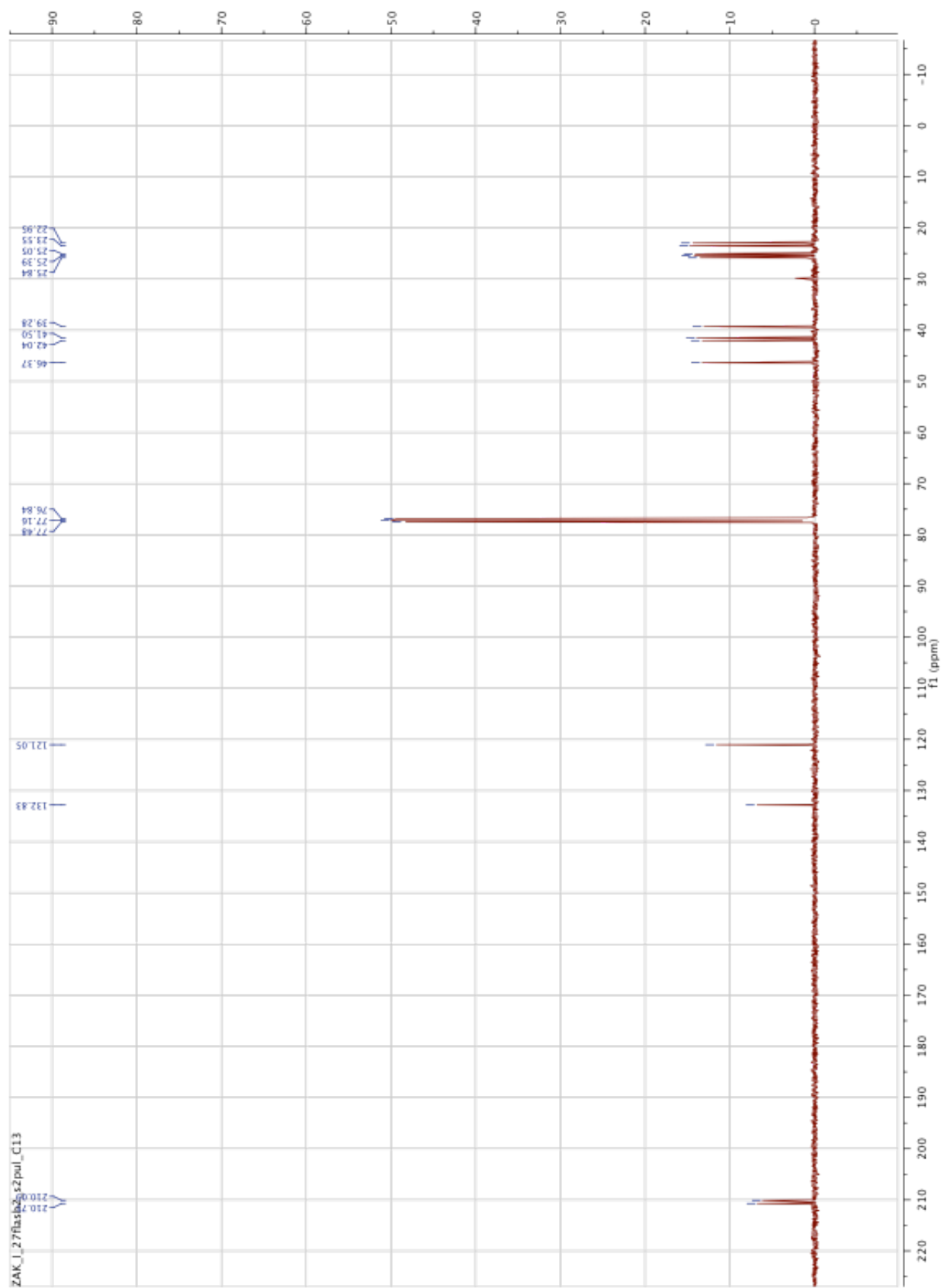
¹³C NMR (100 MHz, CDCl₃): δ 210.8, 210.1, 132.8, 121.1, 46.4, 42.0, 41.5, 39.3, 25.8, 25.4, 25.1, 23.6, 23.0 ppm.

MP: 77-78 °C.

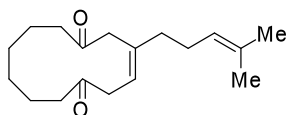
LRMS (CI⁺): Calculated for C₁₃H₂₁O₂⁺ (M+H⁺) 209; Found 209.

FTIR (neat): ν 2929, 2861, 2359, 1698, 1421, 1354, 1328, 1184, 1053 cm⁻¹.





(Z)-3-(4-Methylpent-3-en-1-yl)cyclododec-3-ene-1,6-dione (4I)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (79.2 mg, 0.246 mmol, 120 mol%) and diol **3I** (57.0 mg, 0.205 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 3 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:4, ethyl acetate: hexanes) to furnish the cyclododecene **4I** (39.7 mg, 0.151 mmol, 70% yield) as a colorless solid.

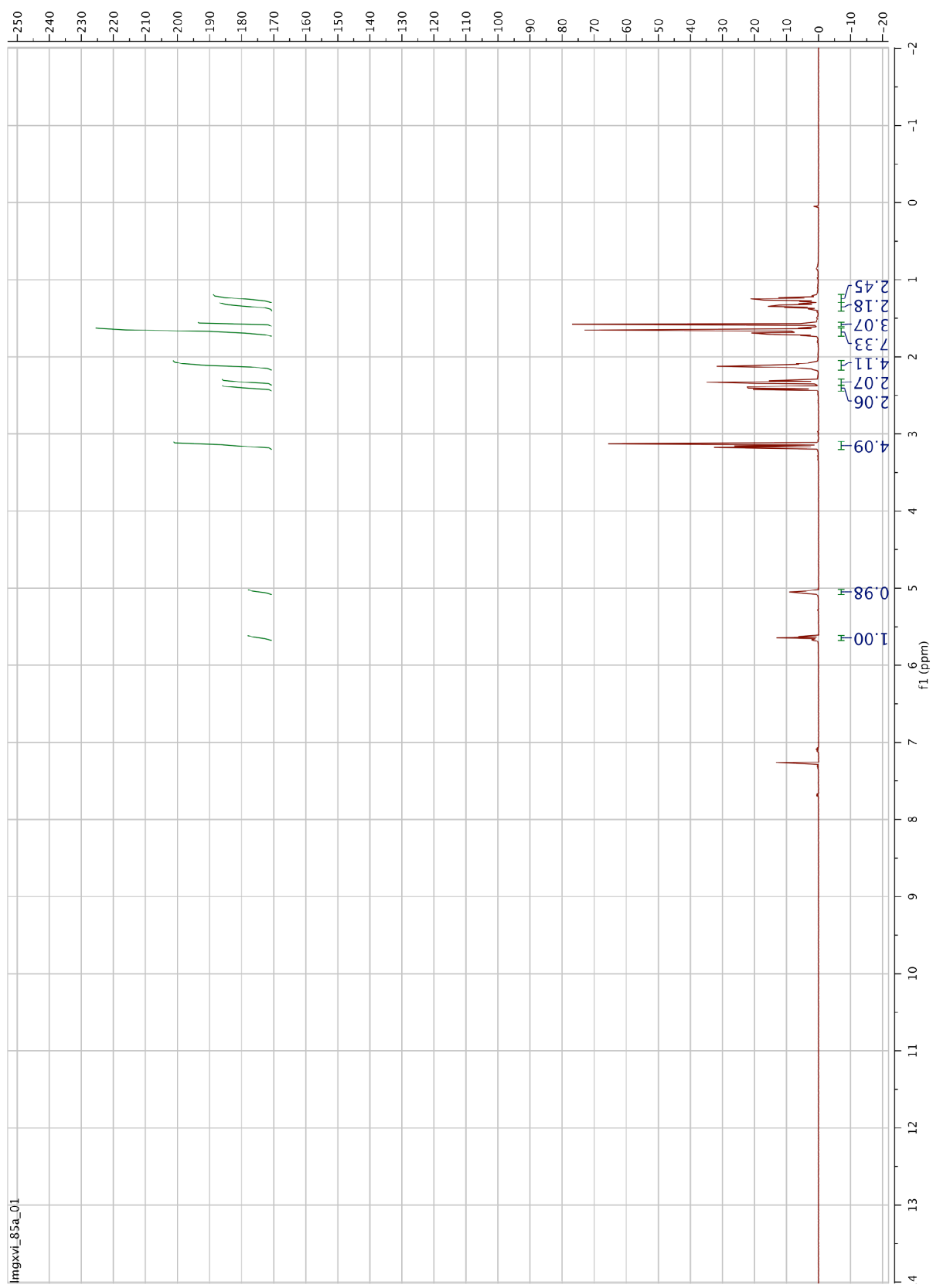
TLC (SiO₂): R_f = 0.34 (1:4, ethyl acetate: hexanes).

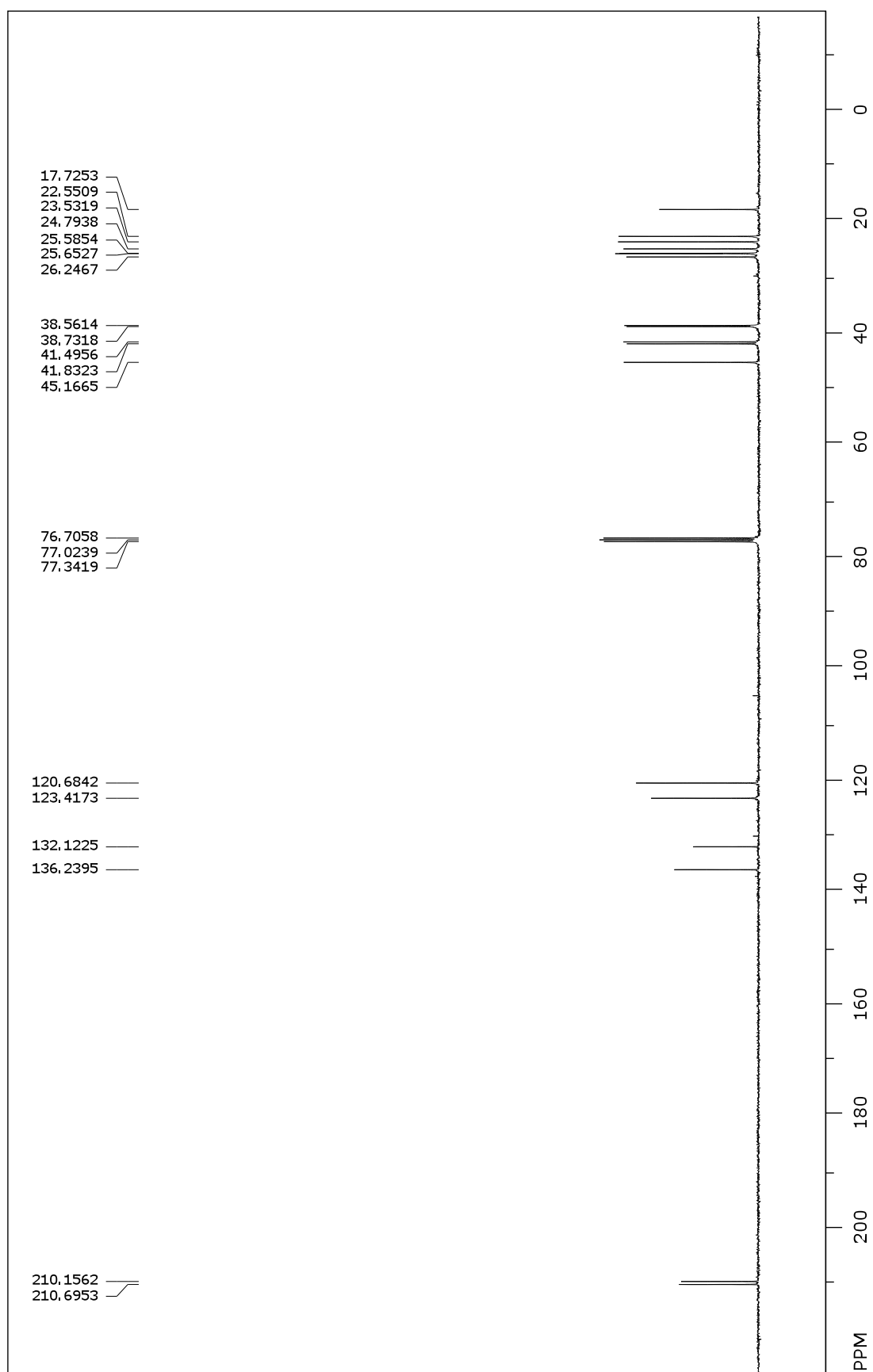
¹H NMR (400 MHz, CDCl₃): δ 5.65 (t, 1H, *J* = 8 Hz), 5.05 (m, 1H), 3.17 (d, 1H, *J* = 8 Hz), 3.13 (s, 2H), 2.40 (m, 2H), 2.33 (t, 2H, *J* = 7 Hz), 2.12 (m, 4H), 1.74-1.62 (m, 4H), 1.65 (s, 3H), 1.58 (s, 3H), 1.34 (m, 2H), 1.25 (m, 2H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 210.7, 210.2, 136.2, 132.1, 123.4, 120.7, 45.2, 41.8, 41.5, 38.7, 38.6, 26.2, 25.7, 25.6, 24.8, 23.5, 22.6, 17.7 ppm.

LRMS (CI⁺): Calculated for C₁₈H₂₉O₂ (M+H) 277; Found 277.

FTIR (neat): ν 2913, 1705, 1365, 1100 cm⁻¹.

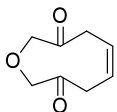




(Z)-7,9-dihydrooxonine-3,8(2H,4H)-dione (4m) and (Z)-4,5-dihydrooxonine-3,8(2H,9H)-dione (iso-4m)

To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (99.0 mg, 0.307 mmol, 120 mol%) and diols **3m** and *iso-3m* (57.0 mg, 0.205 mmol, 100 mol%, 5.2:1 mixture). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 3 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:9, ethyl acetate: hexanes) to furnish the diones **4m** (32.1 mg, 0.208, 81% yield) and *iso-4m* (6.8 mg, 0.044, 11% yield) as a colorless solid and a colorless oil, respectively.

(Z)-7,9-dihydrooxonine-3,8(2H,4H)-dione (4m)



TLC (SiO₂): R_f = 0.38 (2:3, ethyl acetate: hexanes).

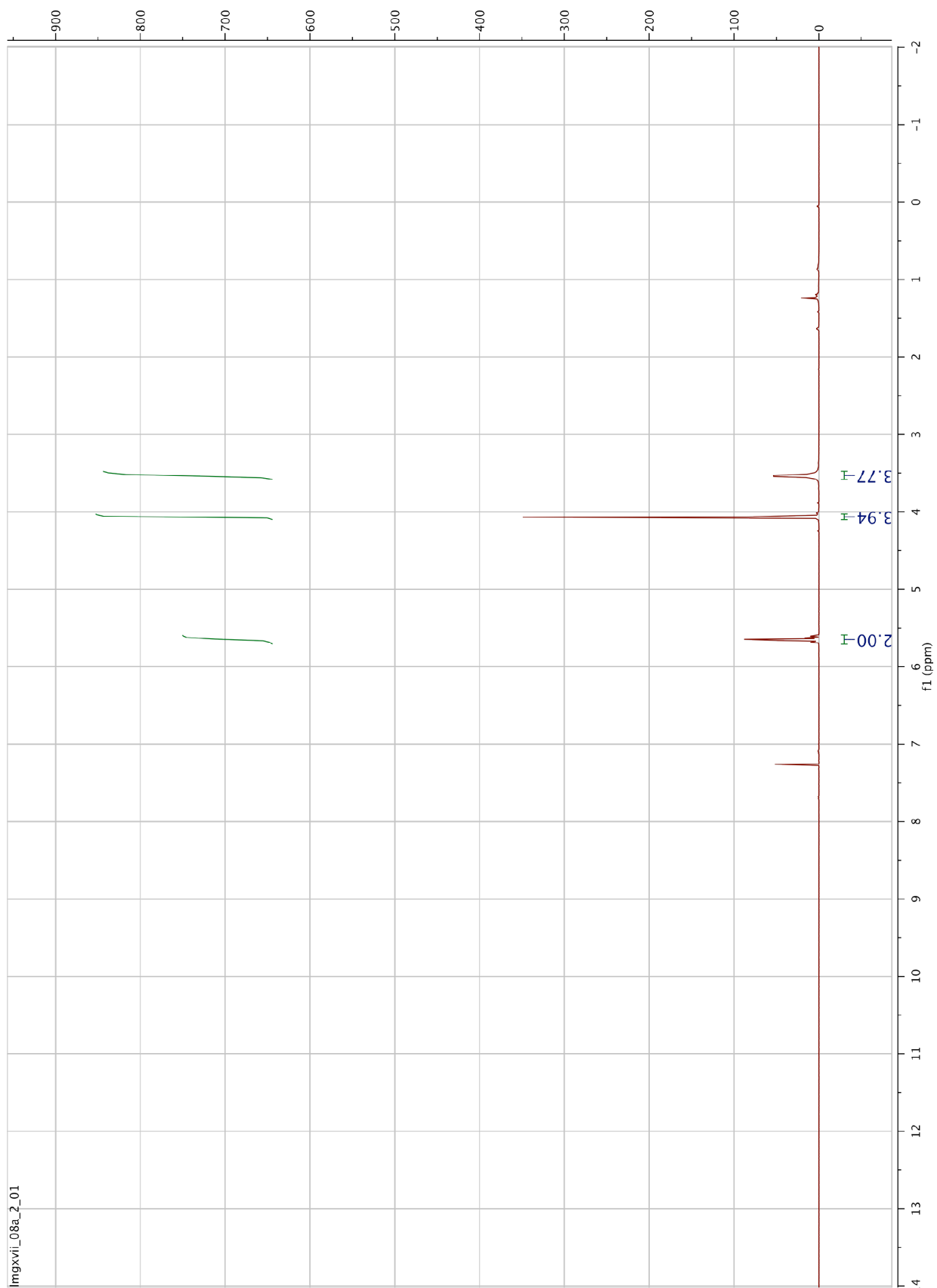
¹H NMR (400 MHz, CDCl₃): δ 5.68-5.59 (m, 2H), 4.06 (s, 4H), 3.60-3.45 (m, 4H) ppm.

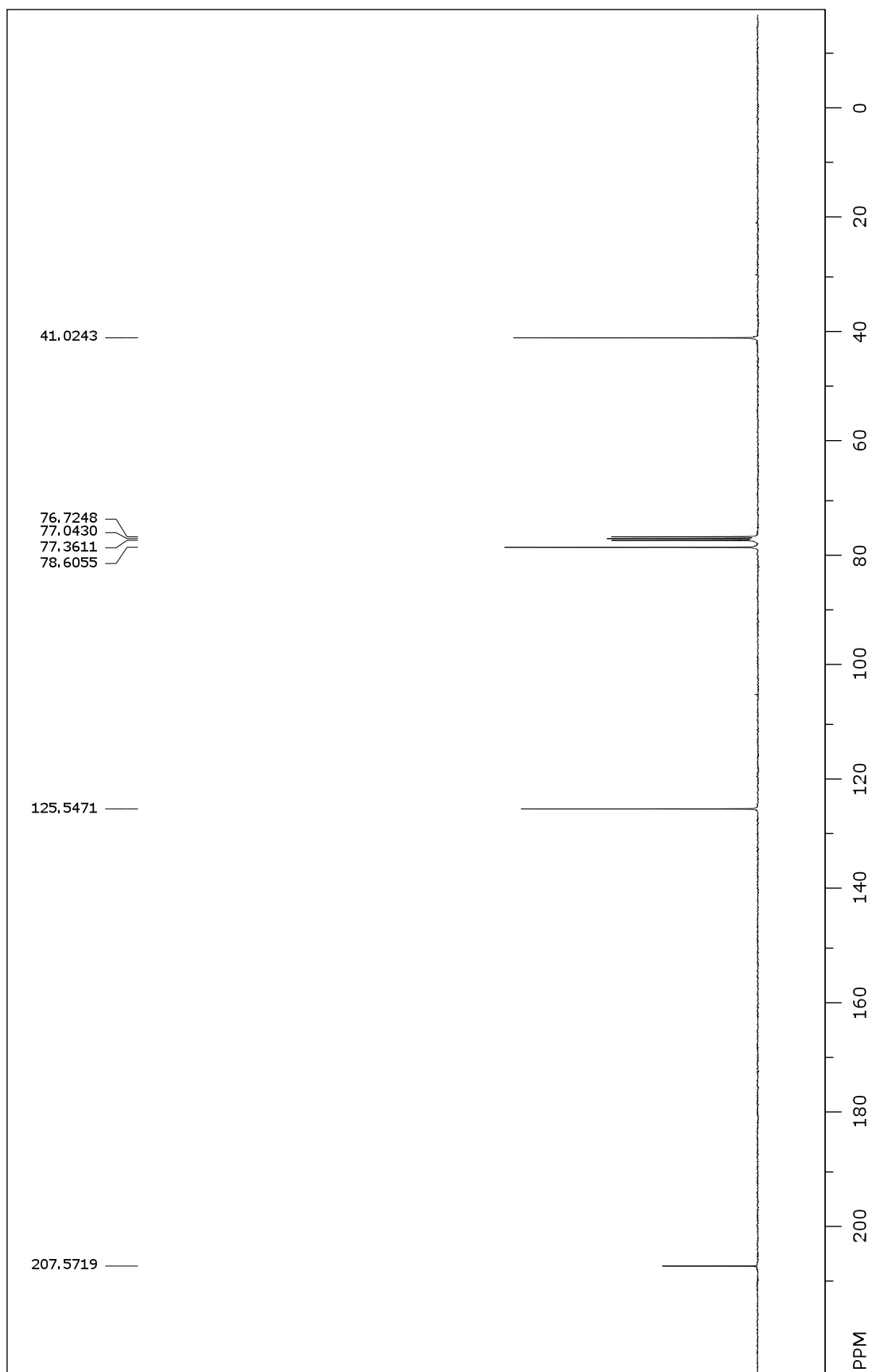
¹³C NMR (100 MHz, CDCl₃): δ 207.6, 125.5, 78.6, 41.0 ppm.

MP: 63-65 °C.

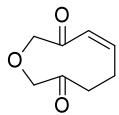
LRMS (CI⁺): Calculated for C₈H₂₁O₃ (M+H) 155; Found 155.

FTIR (neat): ν 2903, 2359, 1703, 1273, 1166, 1123, 1025, 825, 721 cm⁻¹.





(Z)-4,5-dihydrooxonine-3,8(2H,9H)-dione (iso-4m)



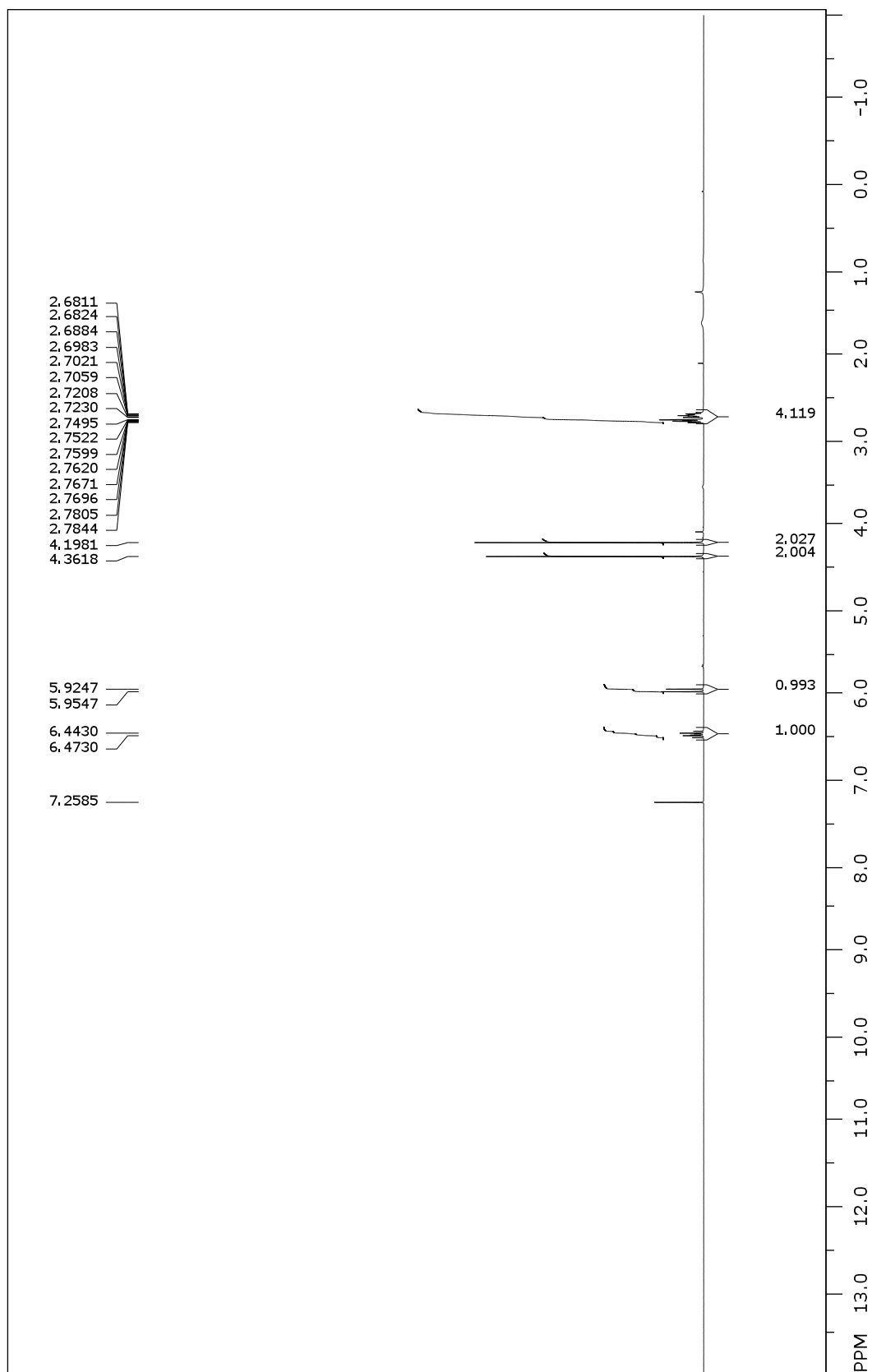
TLC (SiO₂): R_f = 0.26 (2:3 Ethyl acetate: hexanes).

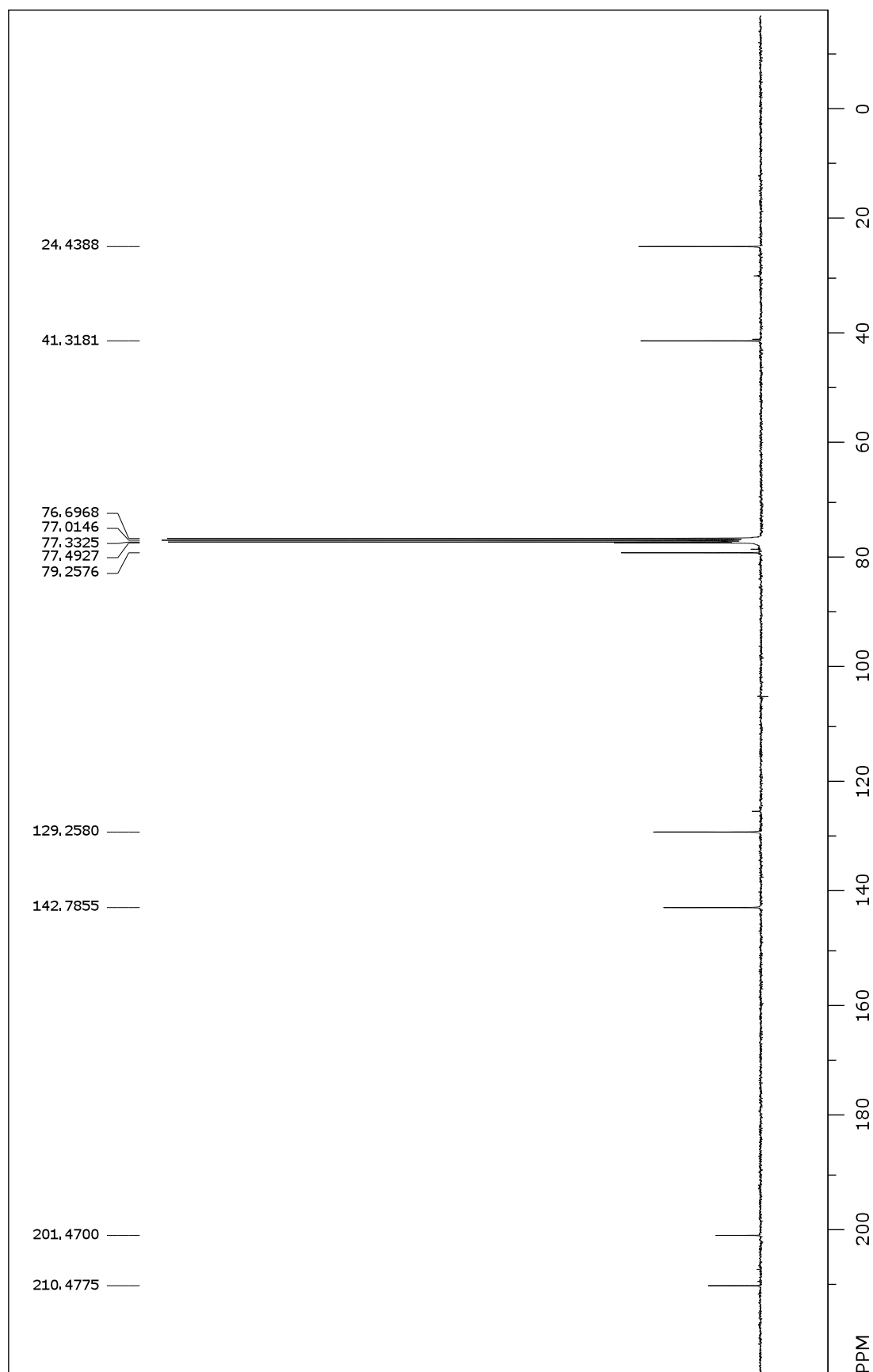
¹H NMR (400 MHz, CDCl₃): δ 6.46 (ddd, 1H, *J* = 2.5, 9, 12 Hz), 5.94 (d, 1H, *J* = 12 Hz), 4.36 (s, 2H), 4.20 (s, 2H), 2.80-2.65 (m, 4H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 210.5, 201.5, 142.8, 129.3, 79.3, 77.5, 41.3, 24.4 ppm.

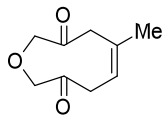
LRMS (CI+): Calculated for C₈H₂₁O₃ (M+H) 155; Found 155.

FTIR (neat): ν 2925, 2359, 1710, 1140, 1101, 958, 822 cm⁻¹.





(Z)-5-methyl-7,9-Dihydrooxonine-3,8(2H,4H)-dione (4n)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (63.8 mg, 0.198 mmol, 120 mol%) and diol **3n** (28.0 mg, 0.165 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 3 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:9, ethyl acetate: hexanes) to furnish dione **4n** (25.4 mg, 0.151 mmol, 90% yield) as a colorless oil.

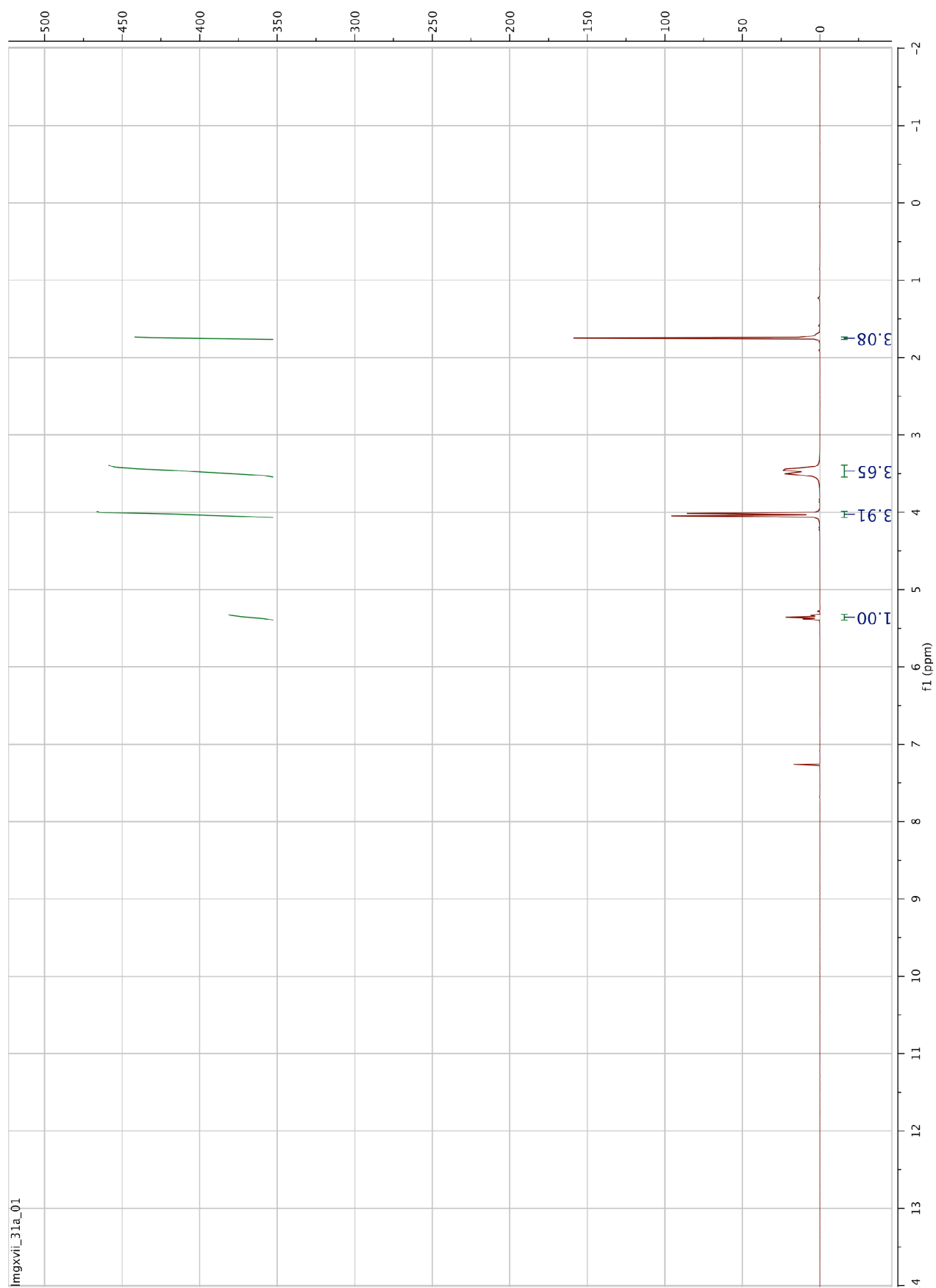
TLC (SiO₂): R_f = 0.44 (2:3, ethyl acetate: hexanes).

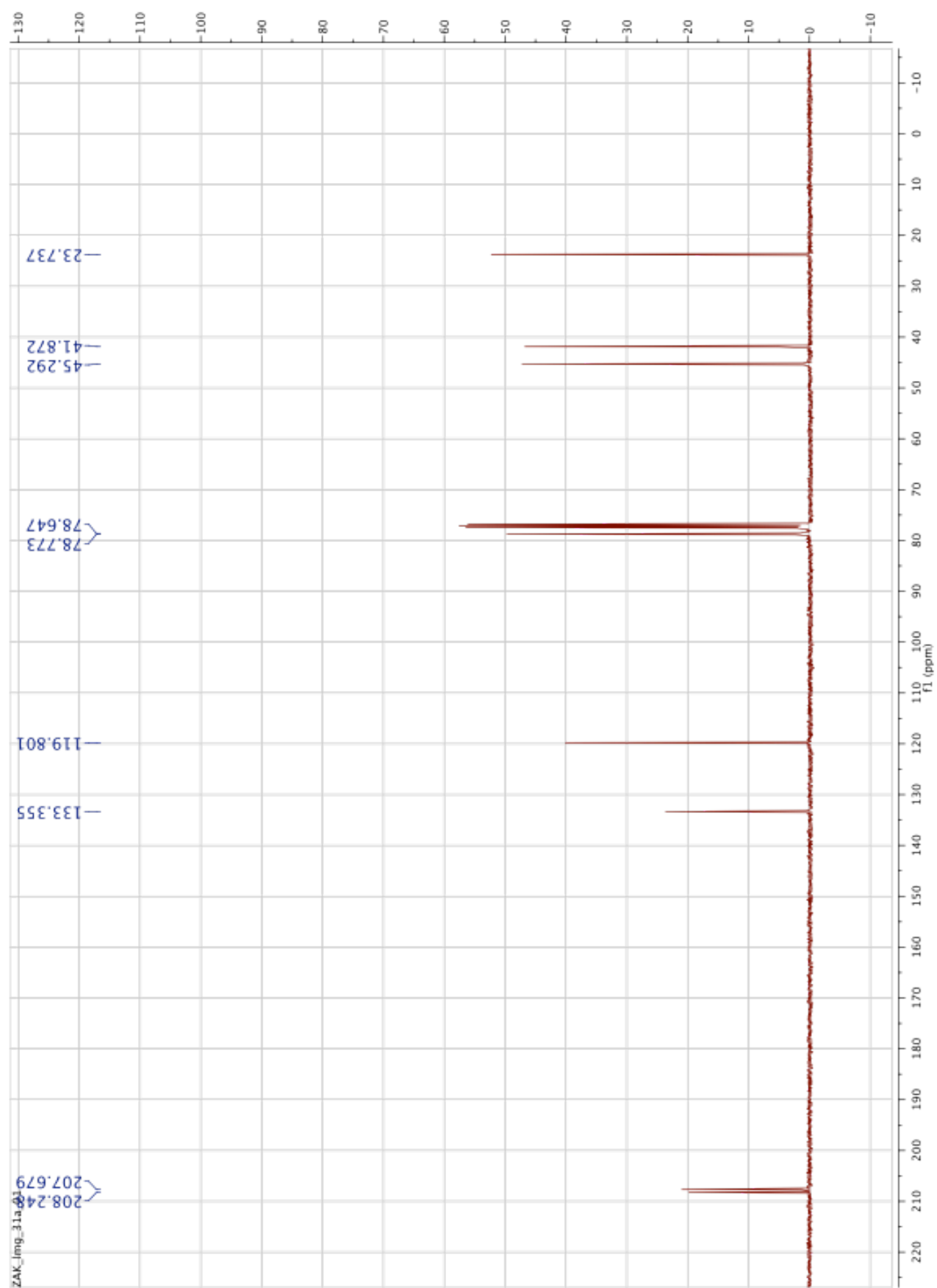
¹H NMR (400 MHz, CDCl₃): δ 5.36 (m, 1H), 4.03 (m, 4H), 3.60-3.38 (m, 4H), 1.75 (m, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 208.2, 207.7, 133.4, 119.8, 78.8, 78.6, 45.3, 41.9, 23.7 ppm.

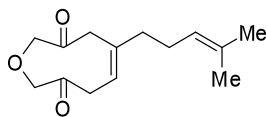
LRMS (CI⁺): Calculated for C₉H₁₃O₃ (M+H) 169; Found 169.

FTIR (neat): ν 2923, 2360, 1708, 1412, 1271, 1136, 1104, 862, 763 cm⁻¹.





(Z)-5-(4-methylpent-3-en-1-yl)-7,9-dihydrooxonine-3,8(2H,4H)-dione (4o)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (97.3 mg, 0.300 mmol, 120 mol%) and diol **3o** (60.0 mg, 0.25 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 1 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 1:9, ethyl acetate: hexanes) to furnish dione **4o** (43.5 mg, 0.183, 73% yield) as a colorless oil.

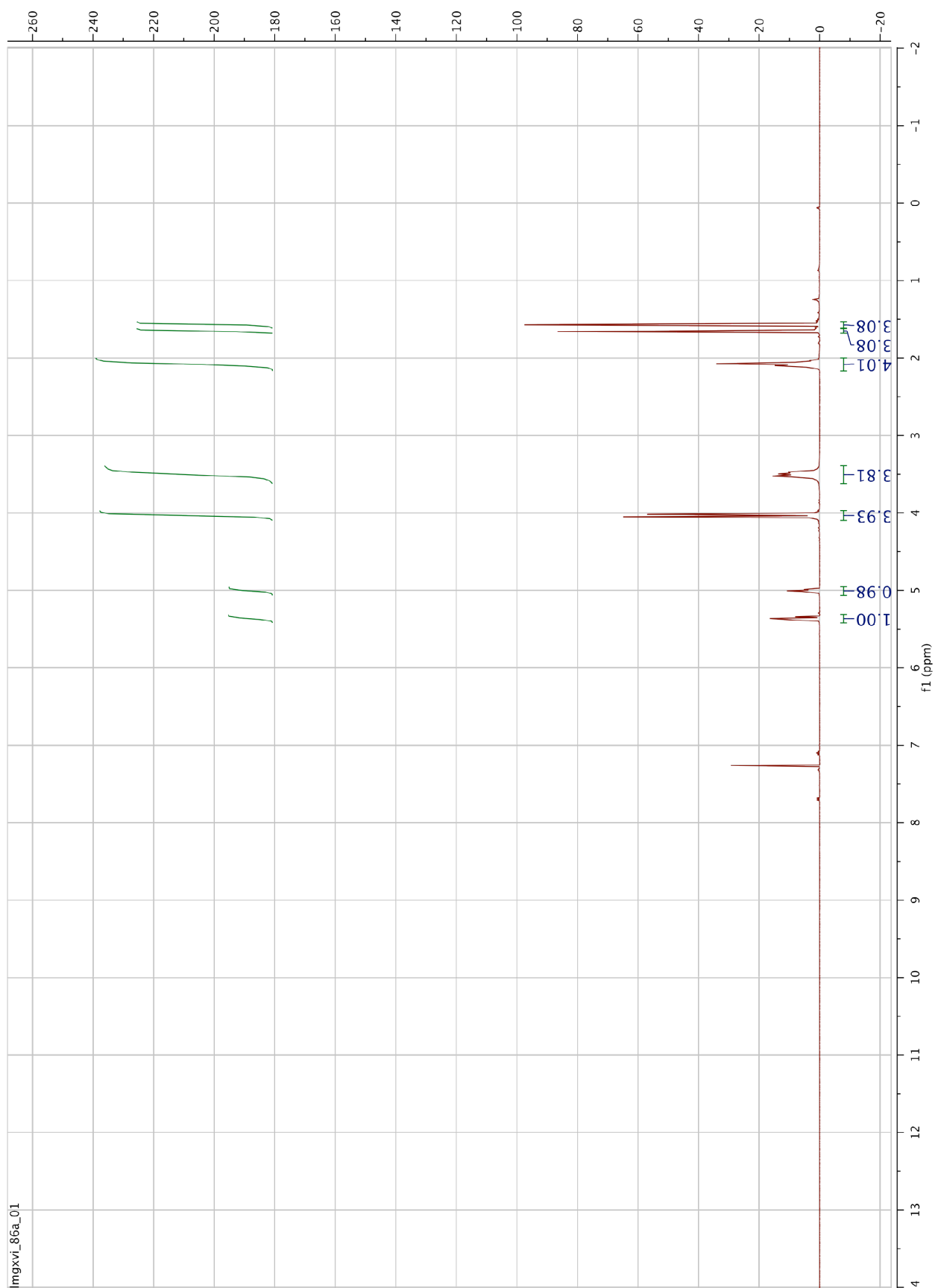
TLC (SiO₂): R_f = 0.55 (2:3, ethyl acetate: hexanes).

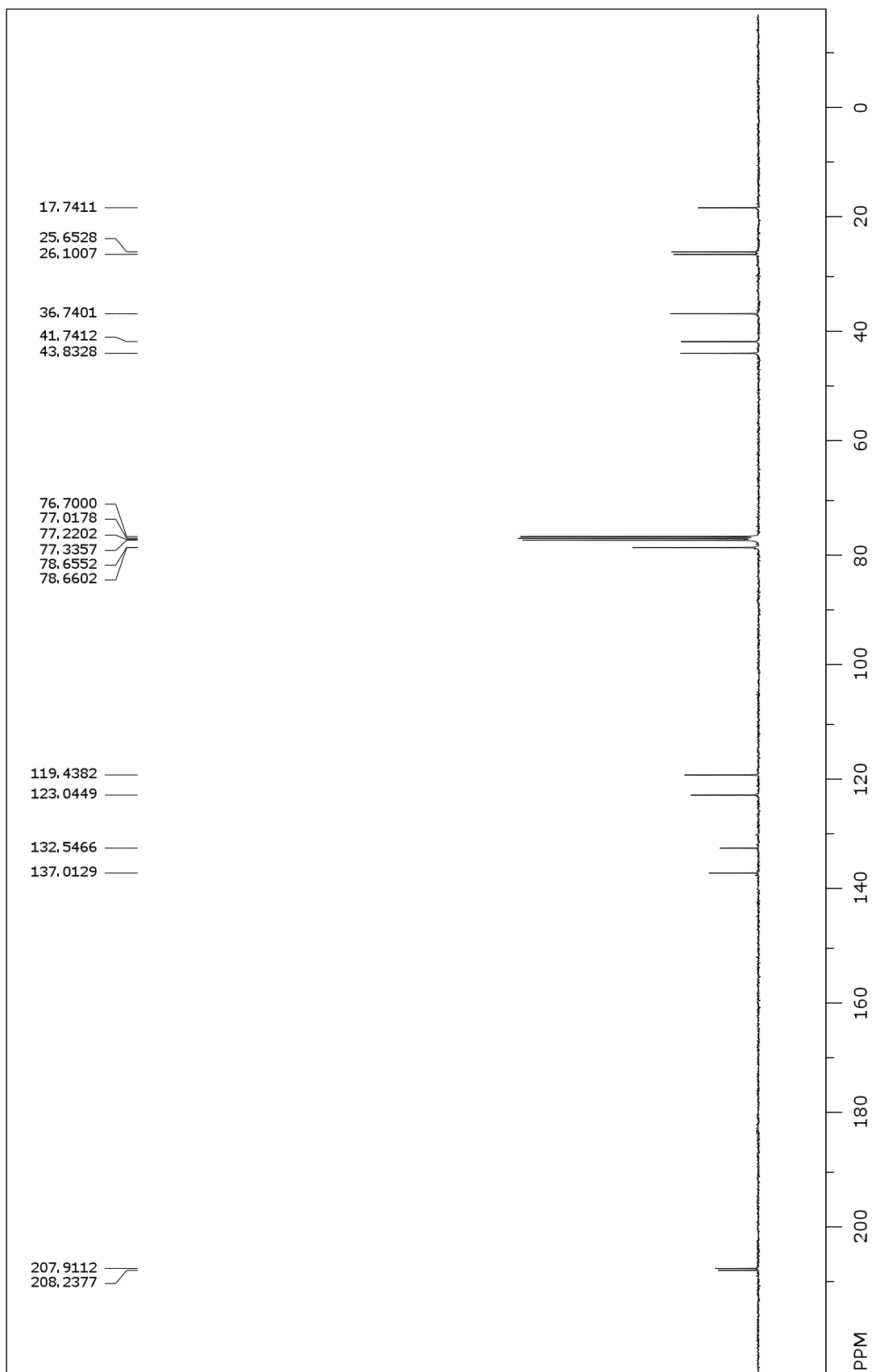
¹H NMR (400 MHz, CDCl₃): δ 5.36 (t, 1H, *J* = 8 Hz), 5.01 (m, 1H), 4.05 (s, 2H), 4.02 (s, 2H), 3.49 (m, 4H), 2.07 (m, 4H), 1.66 (s, 3H), 1.57 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃): δ 208.2, 207.9, 137.0, 132.5, 123.0, 119.4, 78.66, 78.65, 43.8, 41.7, 36.7, 26.1, 25.7, 17.7 ppm.

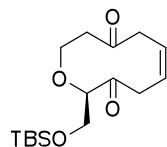
LRMS (CI⁺): Calculated for C₁₄H₂₁O₂ (M+H) 237; Found 237.

FTIR (neat): ν 2929, 1710, 1442, 1135 cm⁻¹.





(*R,Z*)-2-(((*tert*-butyldimethylsilyl)oxy)methyl)-9,10-dihydro-2*H*-oxecine-3,8(4*H*,7*H*)-dione (4p)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (52.2 mg, 0.162 mmol, 120 mol%) and diol **3p** (42.7 mg, 0.135 mmol, 100 mol%, 1:1 dr). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 4 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 3:17, ethyl acetate: hexanes) to furnish dione **4p** (38.6 mg, 0.123 mmol, 90% yield) as a colorless oil.

TLC (SiO₂): R_f = 0.42 (1:3, ethyl acetate: hexanes).

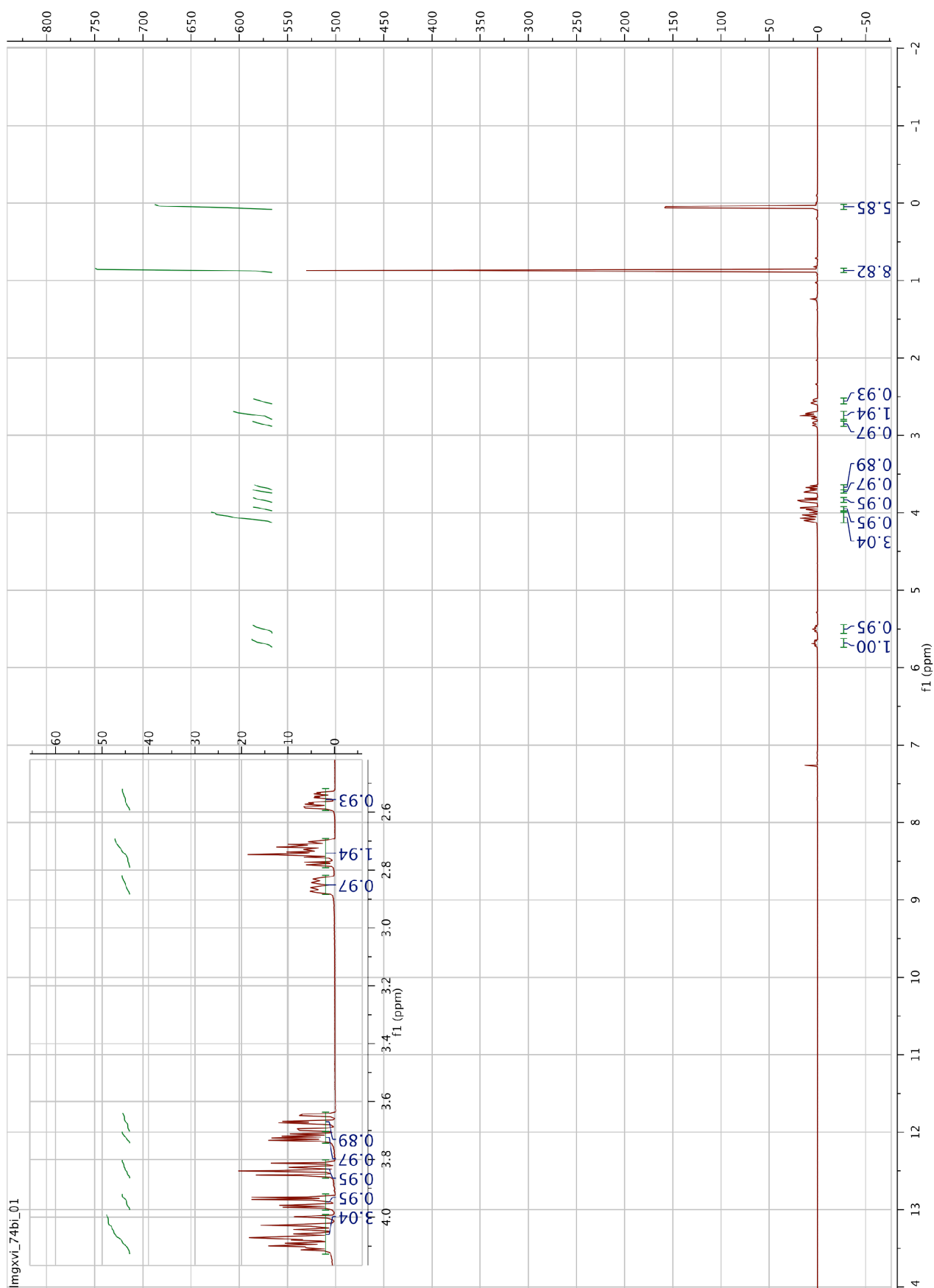
¹H NMR (400 MHz, CDCl₃): δ 5.69 (m, 1H), 5.50 (ddt, 1H, *J* = 1.5, 5.8, 10.6 Hz), 4.12-3.99 (m, 3H), 3.95 (dd, 1H, *J* = 3, 11 Hz), 3.84 (dd, 1H, *J* = 5.6, 11 Hz), 3.73 (dd, 1H, *J* = 3, 6 Hz), 3.68 (dt, 1H, *J* = 2, 10.5 Hz), 2.87 (m, 1H), 2.79-2.70 (m, 2H), 2.56 (ddd, 1H, *J* = 2.2, 5.4, 14 Hz), 0.88 (s, 9H), 0.07 (s, 3H), 0.05 (s, 3H) ppm.

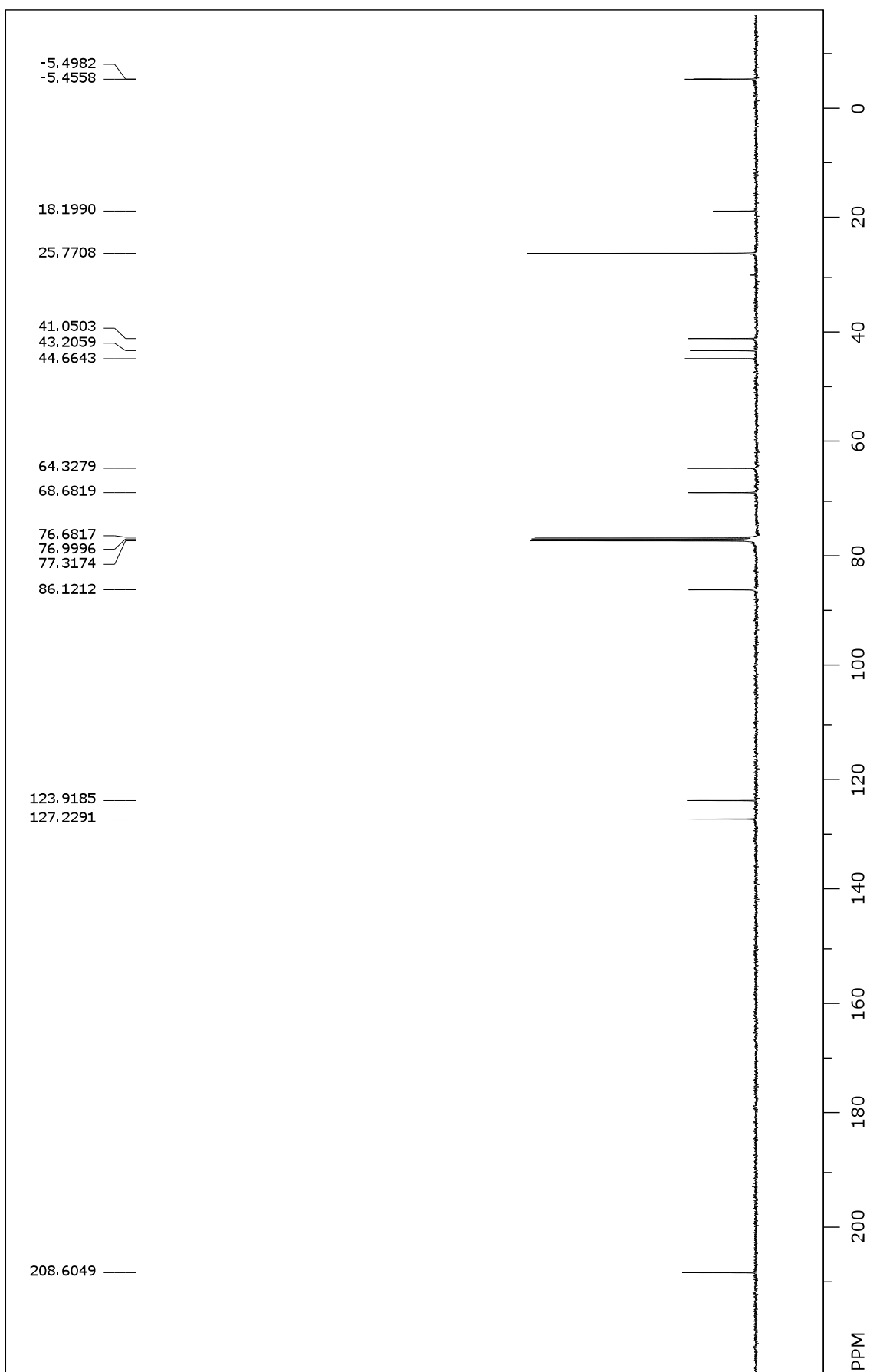
¹³C NMR (100 MHz, CDCl₃): δ 208.6, 127.2, 123.9, 86.1, 68.7, 64.3, 44.7, 43.2, 41.1, 25.8, 18.2, -5.45, -5.50 ppm.

LRMS (CI⁺): Calculated for C₁₆H₂₉O₄Si (M+H) 313; Found 313.

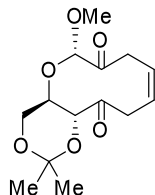
FTIR (neat): ν 2927, 2855, 1708, 1254, 1101, 883, 777 cm⁻¹.

[α]_D²⁸ +145 (c = 1.78, CH₂Cl₂).





(4a*R*,6*S*,12a*R*,*Z*)-6-Methoxy-2,2-dimethyl-4,4a,11,12a-tetrahydro[1,3]dioxino[5,4-*b*] oxecine-7,12(6*H*,8*H*)-dione (4q)



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxyiodobenzene (49.0 mg, 0.152 mmol, 120 mol%) and diol **3q** (29.0 mg, 0.101 mmol, 100 mol%, 3.2:1 dr). The vial was purged with argon, and dichloromethane was added (1.0 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 5 hours. The volatiles were removed via rotary evaporation under reduced pressure. The residue was subjected to flash column chromatography (SiO₂: 2:3, ethyl acetate: hexanes) to furnish dione **4q** (22.1 mg, 0.077 mmol, 77% yield) as a colorless oil.

TLC (SiO₂): R_f = 0.25 (2:3, ethyl acetate: hexanes).

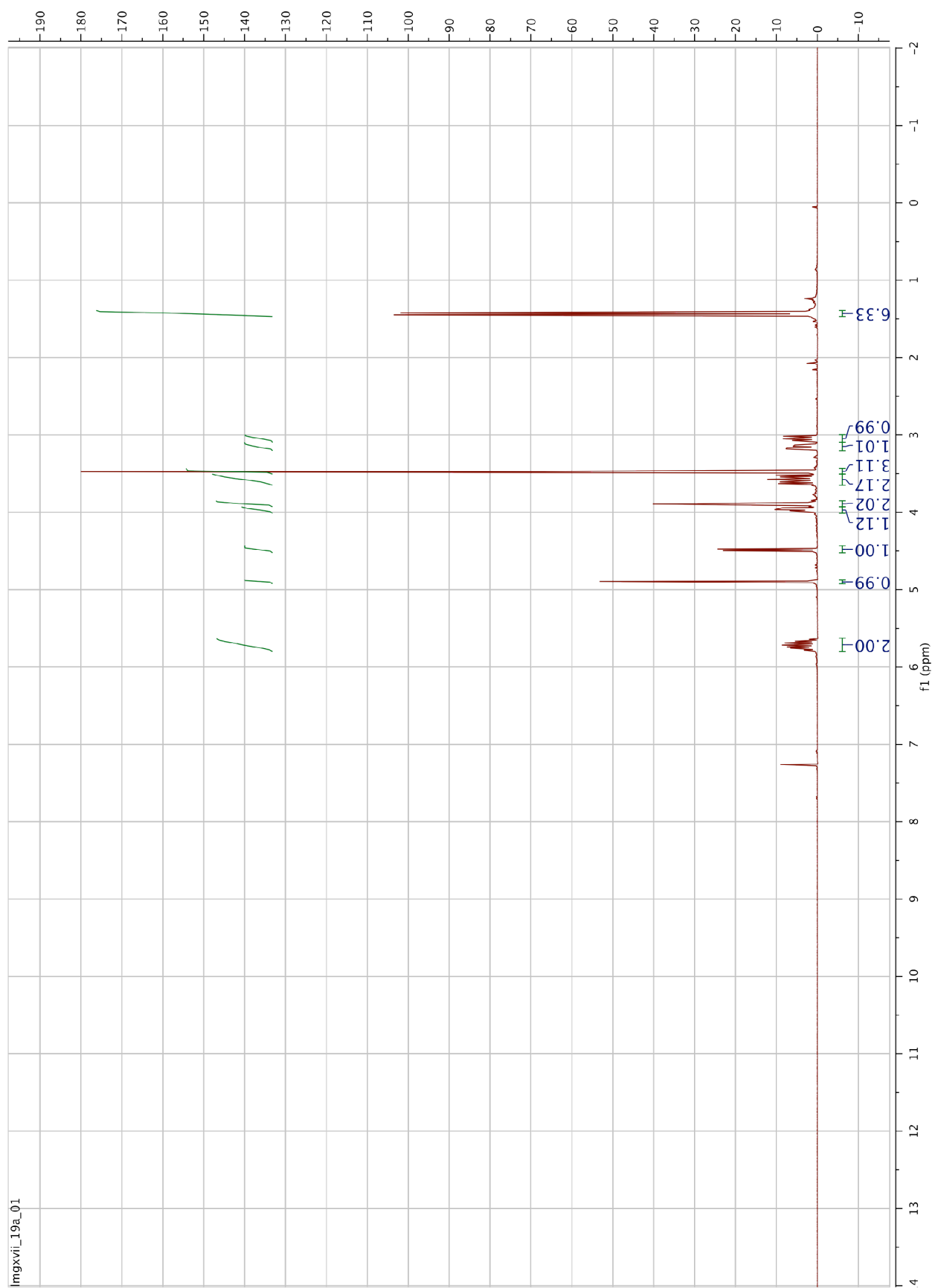
¹H NMR (400 MHz, CDCl₃): δ 5.79-5.63 (m, 2H), 4.89 (s, 1H), 4.48 (d, 1H, *J* = 9 Hz), 3.99-3.93 (m, 1H), 3.92-3.84 (m, 2H), 3.65-3.50 (m, 2H), 3.47 (s, 3H), 3.15 (m, 1H), 3.04 (m, 1H), 1.45 (s, 3H), 1.42 (s, 3H) ppm.

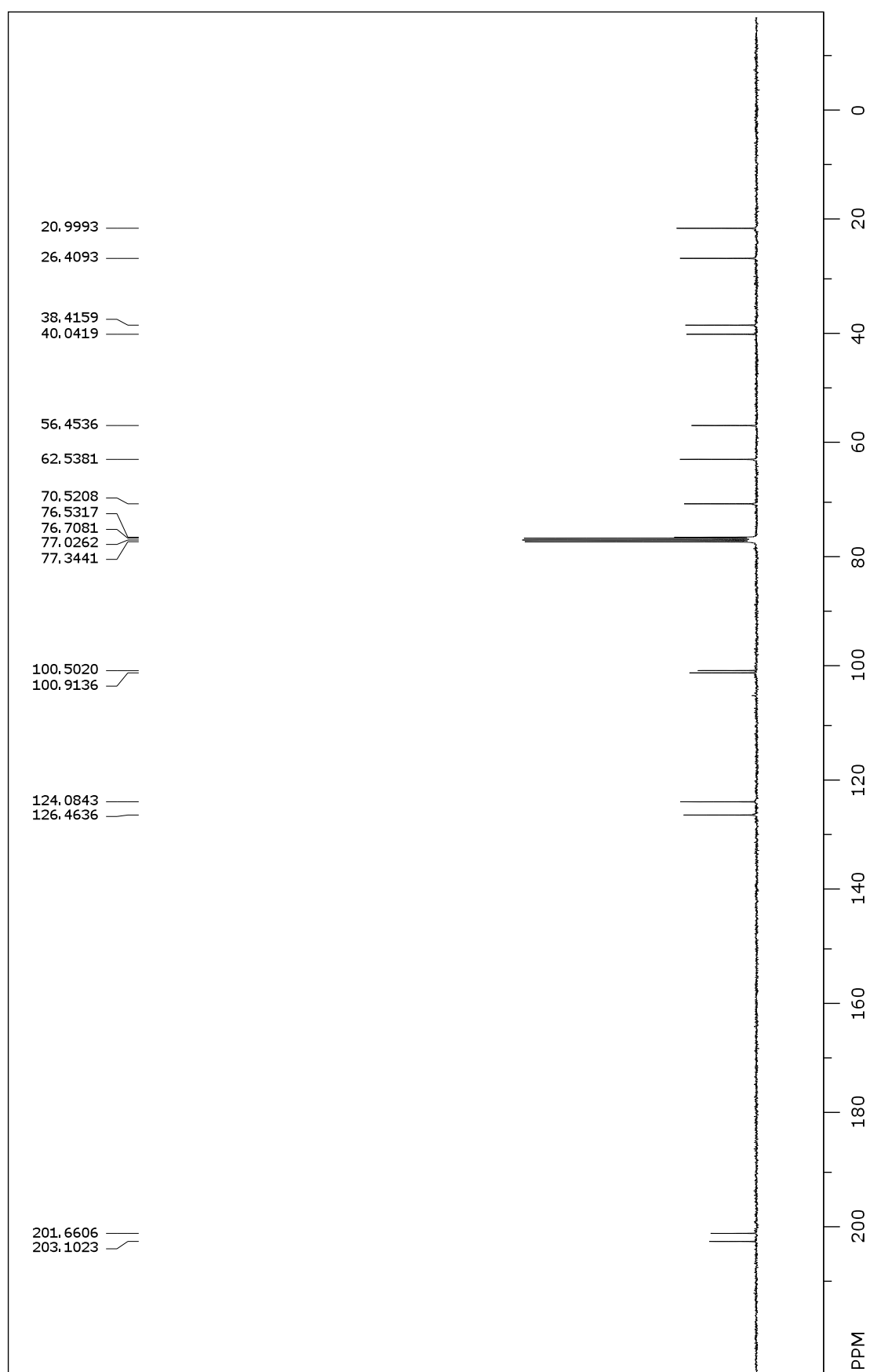
¹³C NMR (100 MHz, CDCl₃): δ 203.1, 201.7, 126.5, 124.1, 100.9, 100.5, 76.5, 70.5, 62.5, 56.5, 40.0, 38.4, 26.4, 21.0 ppm.

LRMS (CI⁺): Calculated for C₁₄H₂₀NaO₆ (M+Na) 307; Found 307.

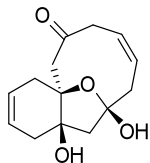
FTIR (neat): ν 2939, 1724, 1377, 1190, 1079, 859, 734 cm⁻¹.

[α]_D²⁷ -28 (*c* = 0.74, CH₂Cl₂).





(4a*S,11*R**,12a*R**,*Z*)-11,12a-dihydroxy-1,7,10,11,12,12a-hexahydro-4*H*-4a,11-epoxybenzo[10]annulen-6(5*H*)-one (4r)**



To an oven dried 2-dram vial equipped with a stir bar was added diacetoxiodobenzene (15.3 mg, 0.0476 mmol, 120 mol%) and diol **3r** (10.1 mg, 0.040 mmol, 100 mol%). The vial was purged with argon, and dichloromethane was added (0.4 mL, 0.1M). The reaction was allowed to stir at ambient temperature for 3 hours. The volatiles were removed via rotary evaporation under reduced pressure. The crude products were subjected to flash column chromatography (SiO₂: 2:3- 3:2, ethyl acetate: hexanes) to furnish compound **4r** (10.0 mg, 0.040 mmol, 99% yield) as a colorless solid.

TLC (SiO₂): R_f = 0.34 (2:3, ethyl acetate: hexanes)

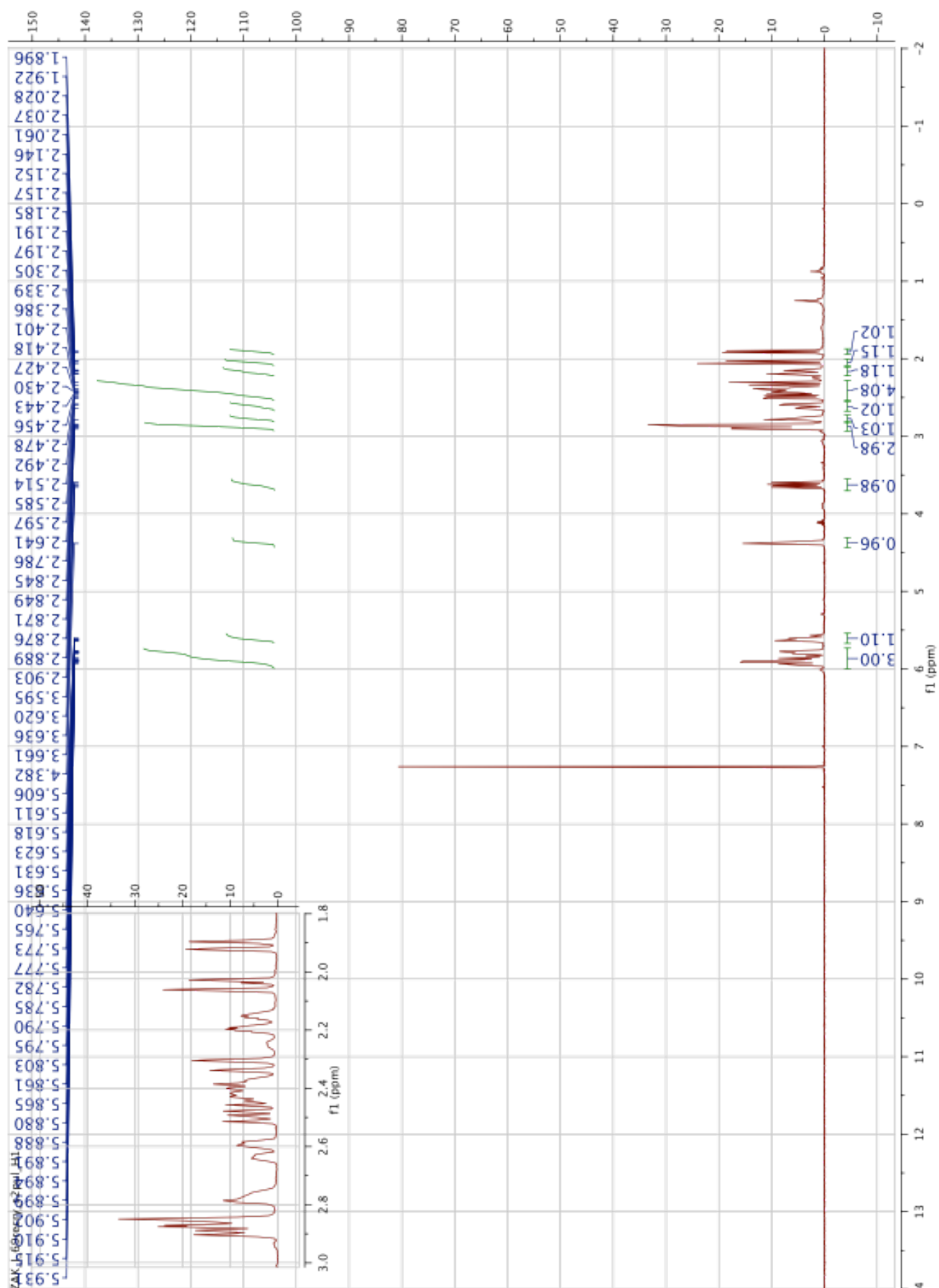
¹H NMR (400 MHz, CDCl₃): δ 5.96-5.84 (m, 2H), 5.80-5.77 (m, 1H), 5.64-5.61 (m, 1H), 4.39-4.35 (m, 1H, OH), 3.63 (dd, *J* = 16.4, 10.0 Hz, 1H), 2.91-2.84 (m, 3H), 2.80-2.75 (m, 1H, OH) 2.66-2.57 (m, 1H) 2.52-2.39 (m, 3H), 2.32 (d, *J* = 13.6 Hz, 1H), 2.21-2.13 (m, 1H), 2.07-2.02 (m, 1H), 1.91 (d, *J* = 10.4 Hz, 1H) ppm.

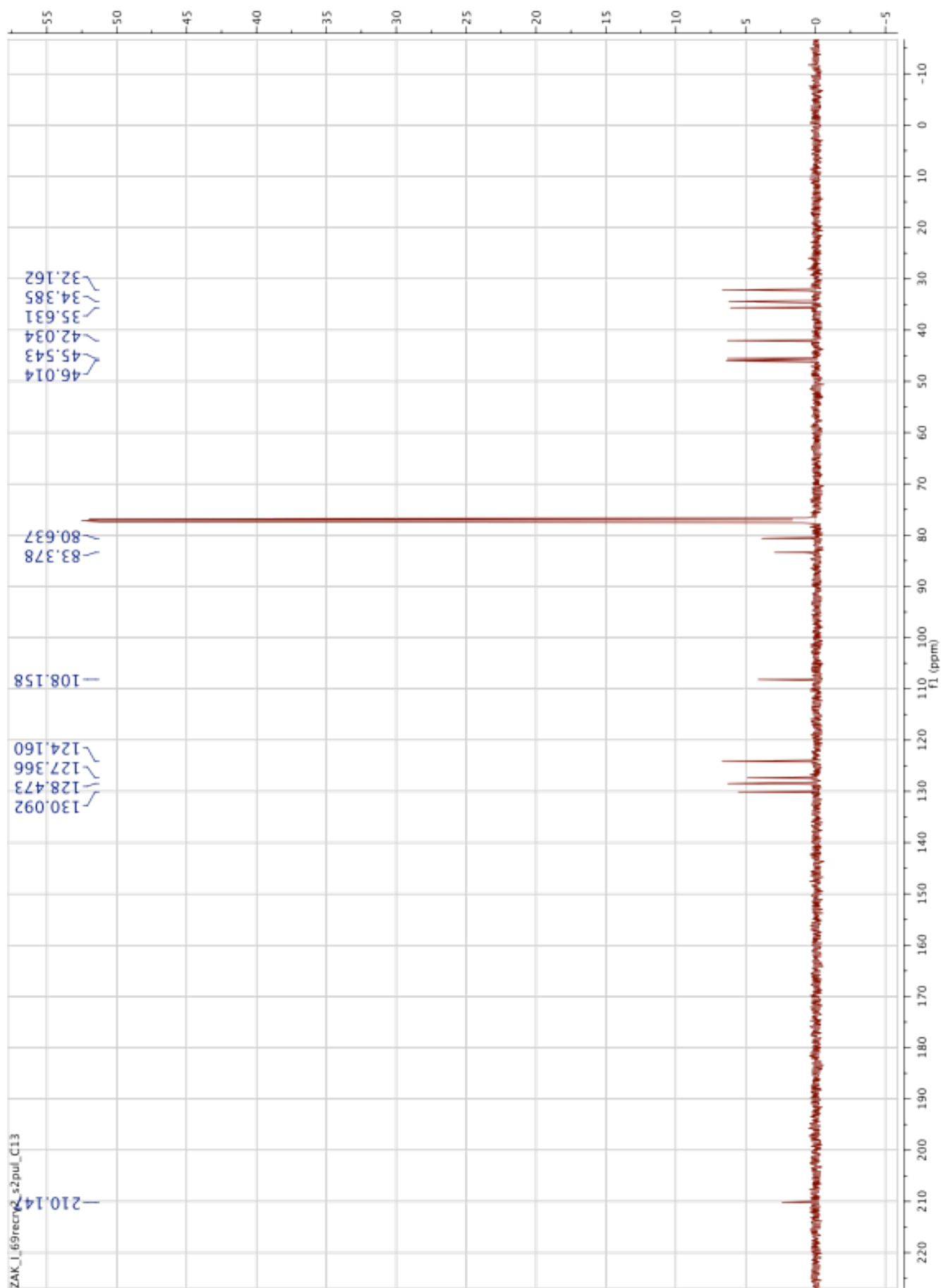
¹³C NMR (100 MHz, CDCl₃): δ 210.1, 130.1, 128.5, 127.4, 124.2, 108.2, 83.4, 80.6, 46.0, 45.5, 42.0, 35.6, 34.4, 32.3 ppm.

MP: 121-124 °C.

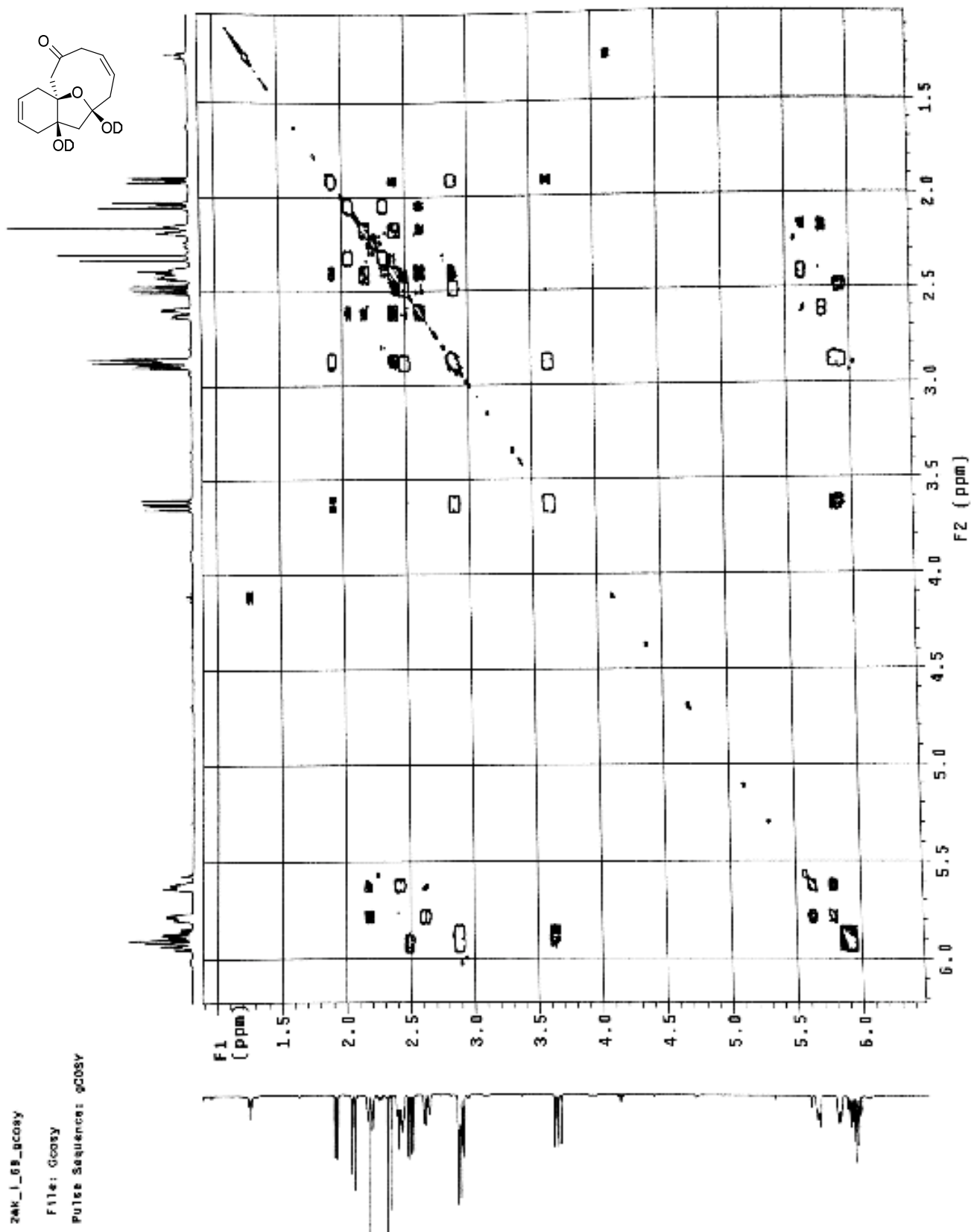
LRMS (+ESI): Calculated for C₁₄H₁₈NaO₄ (M+Na) 273.1; Found 273.1.

FTIR (neat): ν 3395, 2921, 2519, 1698, 1440, 1263, 1061, 958, 802, 667 cm⁻¹.





gCOSY spectrum of **4r-d₂**



gHMQC spectrum of $4r-d_2$

