

Intramolecular Bromonium Ion Assisted Epoxide Ring-Opening: Capture of the Oxonium Ion with an Added External Nucleophile

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SUPPORTING INFORMATION

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pS69-pS71	Copies of ¹³ C NMR resonances exhibiting bromine (2 , 3 , 4 , 6a , 7a , 6b , 8b , 6c , 7c , 8c , 6d , 7d , 8d , 6e , 7e , 8e , 6g , 12 , 13) and chlorine (6d , 7d)-induced isotopic shifts;
pS72-pS88	X-Ray crystallographic details for 6b , 6c , 7b , 7c , 7d and 8a-d .

General experimental

Reagents. *N*-Bromosuccinimide (NBS) was recrystallized from water. Pyridine was distilled from CaH₂ and stored over 4Å molecular sieves. All other reagents were obtained from commercial sources and used as received.

Solvents. All solvents were distilled under N₂. Toluene was distilled from sodium in the presence of benzophenone. THF was distilled from potassium in the presence of benzophenone. Et₂O was distilled from sodium in the presence of benzophenone. Alternatively, HPLC grade CH₂Cl₂, THF, Et₂O and toluene were dried by passing through a column of alumina beads. MeOH and EtOH were purchased and used as received. Extraction solvents and chromatography eluents were used as received. Petroleum ether 40-60°C and Et₂O were GPR grade. MeOH was AnalR, HiperSolv or GPR grade. EtOAc and CH₂Cl₂ were GPR or HiperSolv grade. EtOH was GPR grade.

Experimental Techniques. All reactions were carried out in oven-dried glassware under an inert atmosphere of N₂ unless otherwise stated. All reactions involving NBS were carried out in the absence of light. Reaction temperatures other than room temperature were recorded as bath temperatures. Brine refers to a saturated aqueous solution of NaCl. The term, *in vacuo*, refers to rotary evaporation. Chromatographed, refers to purification by column chromatography, which was performed on silica gel, particle size 33-70 µm. Analytical thin layer chromatography (tlc) was performed on Kieselgel 60 F₂₅₄ pre-coated plastic-backed plates which were visualized by ultraviolet light (254 and 350 nm) and/or chemical staining using a potassium permanganate dip.

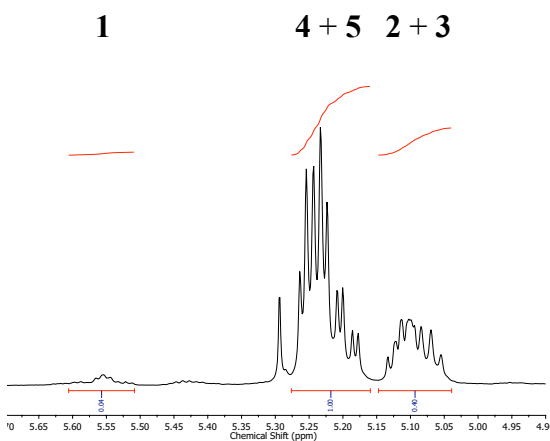
Characterization. Melting points are uncorrected. Fourier transform infra-red (IR) spectra were recorded neat using an ATR-IR spectrometer, or on samples prepared as thin films on sodium chloride plates either neat or as KBr disks as indicated in parentheses. ¹H NMR spectra were recorded at 400 MHz and at 500 MHz. ¹³C NMR spectra were recorded at 100 MHz and 125 MHz. Chemical shifts (δ) are quoted in parts per million

(ppm) and are referenced to the residual solvent peak. Coupling constants (J) are quoted in Hertz (Hz).

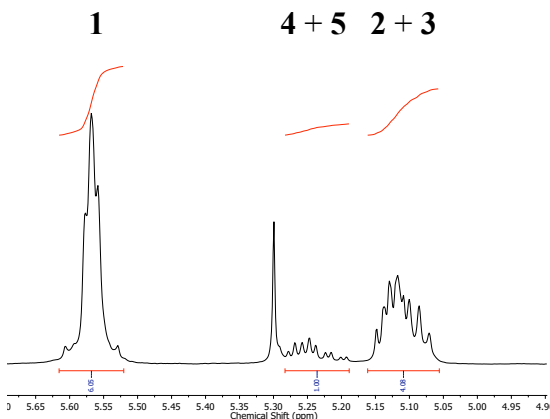
HPLC. Preparative HPLC was performed on a 25 cm x 21.2 mm LC-Si HPLC column with a particle size of 5 μm . All solvents for HPLC were HiperSolv grade and used as received.

Procedure for Dilution Studies Using 9-Oxabicyclo[6.1.0]non-4-ene (1), where Acetate was the Nucleophile (Table 1). To a solution of epoxyalkene **1** (50 mg, 0.4 mmol, 1.0 equiv) in CH₂Cl₂ (1.6 mL: 0.25 M; 16 mL: 0.025 M; 160 mL: 0.0025 M) was added *N*-bromosuccinimide (72 mg, 0.4 mmol, 1.0 equiv) in a single portion, along with 1 drop of tetramethylguanidine. Acetic acid (24 mg, 0.4 mmol, 1.0 equiv) was added and the reaction mixture was stirred at room temperature for 2.5 h. After this time the reaction mixture was washed with 10% w/w sodium sulfite (8 mL), dried over sodium sulfate and the solvent was removed *in vacuo*. The product distribution was estimated by ¹H NMR analysis of the crude mixture (below).

Table 1, Entry 1 (400 MHz, CDCl₃)

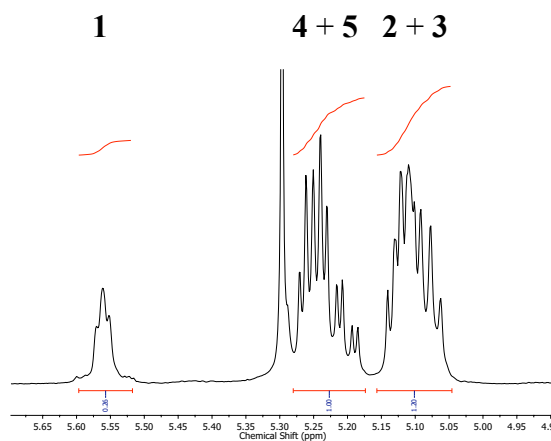


Conversion of **1** = 99%; Ratio of **2 + 3** : **4 + 5** = 30 : 70
Table 1, Entry 3 (400 MHz, CDCl₃)

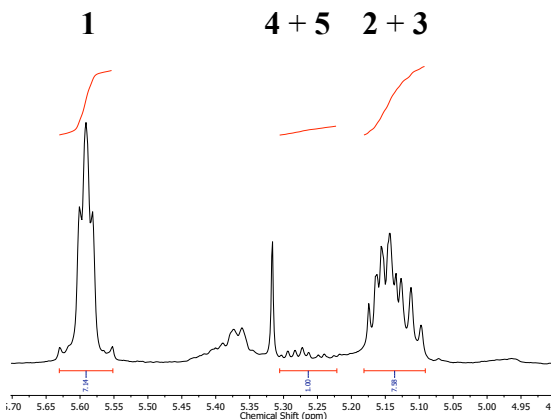


Conversion of **1** = 63%; Ratio of **2 + 3** : **4 + 5** = 80 : 20
 The ratio of **2 + 3** : **4 + 5** was determined by integration of the resonances at 5.04 – 5.14 vs 5.17 – 5.27 ppm, respectively.

Table 1, Entry 2 (400 MHz, CDCl₃)



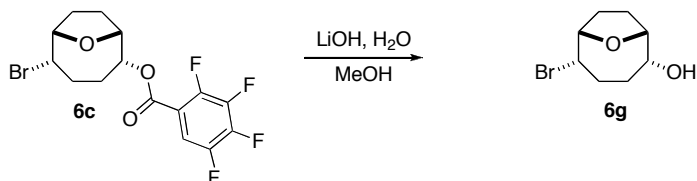
Conversion of **1** = 95%; Ratio of **2 + 3** : **4 + 5** = 55 : 45
Table 1, Entry 4 (400 MHz, CDCl₃)



Conversion of **1** = 72%; Ratio of **2 + 3** : **4 + 5** = 85 : 15

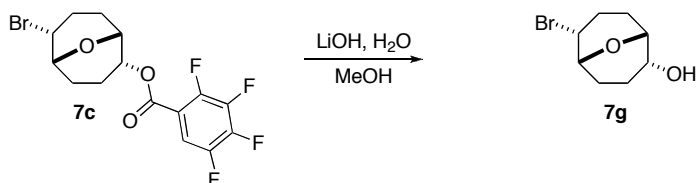
Saponification of tetrafluorobenzoates **6c and **7c** to provide alcohols **6g** and **7g**.**

Alcohol **6g:**



To a solution of tetrafluorobenzoate **6c** (390 mg, 1 mmol) in MeOH (40 mL) was added LiOH.H₂O (170 mg, 4 mmol) and H₂O (2 mL) at room temperature and stirred for 1 h. The solvent was evaporated *in vacuo*. Column chromatography with petrol:EtOAc (8:2) afforded alcohol **6g** (180 mg, 83%) as a colorless oil. Data for **6g** in main paper.

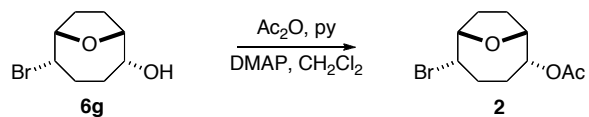
Alcohol **7g:**



To a solution of tetrafluorobenzoate **7c** (360 mg, 0.91 mmol) in MeOH (10 mL) were added H₂O (5 mL) and LiOH.H₂O (133 mg, 3.18 mmol) at 0 °C. The reaction mixture was stirred for 1 h and diluted with H₂O (50 mL). The mixture was extracted with EtOAc (3 × 50 mL), the organic layer dried over MgSO₄, and the solvent was evaporated *in vacuo*. Column chromatography afforded alcohol **7g** (190 mg, 95%) as a colorless oil. Data for **7g** in main paper.

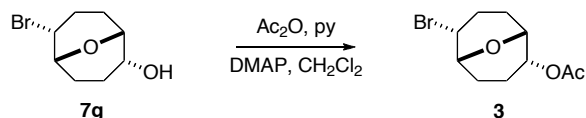
Procedures for the preparation of authentic samples from alcohols **6g** and **7g**.

Acetate **2**:



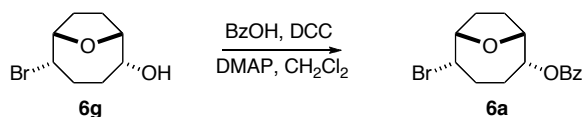
To a solution of alcohol **6g** (45 mg, 0.2 mmol) in CH₂Cl₂ (5 mL) at room temperature was added Ac₂O (0.04 mL, 0.4 mmol), pyridine (0.03 mL, 0.4 mmol) and DMAP (49 mg, 0.4 mmol) and stirred for 24 hours. The mixture was quenched with aqueous NH₄Cl (10 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The organic layer was dried over MgSO₄ and the solvent was evaporated *in vacuo*. Column chromatography with petrol:EtOAc (9:1) afforded acetate **2** (54 mg, 100%) as a colorless oil. Data for **2** in main paper.

Acetate **3**:



To a solution of alcohol **7g** (25 mg, 0.11 mmol) in CH₂Cl₂ (5 mL) at room temperature was added Ac₂O (0.02 mL, 0.22 mmol), pyridine (0.02 mL, 0.22 mmol) and DMAP (27 mg, 0.22 mmol) and stirred for 24 hours. The mixture was quenched with aqueous NH₄Cl (10 mL) and extracted with CH₂Cl₂ (3 × 20 mL). The organic layer was dried over MgSO₄ and the solvent was evaporated *in vacuo*. Column chromatography with petrol:EtOAc (9:1) afforded acetate **3** (29 mg, 98%) as a colorless oil. Data for **3** in main paper.

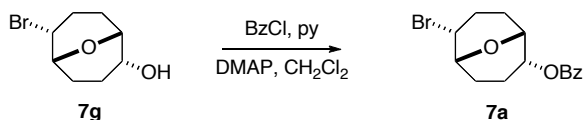
Benzoate **6a**:



To a solution of alcohol **6g** (81 mg, 0.37 mmol, 1.0 equiv) in CH₂Cl₂ (3.5 mL) at 0°C was added benzoic acid (49 mg, 0.40 mmol, 1.1 equiv), DMAP (9 mg, 0.07 mmol, 0.2 equiv) and DCC (83 mg, 0.40 mmol, 1.1 equiv). The white suspension was allowed to warm to room temperature and stirred for 4 h. Additional benzoic acid (49 mg, 0.40 mmol, 1.1

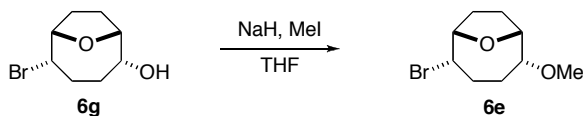
equiv) and DCC (83 mg, 0.40 mmol, 1.1 equiv) were added at room temperature and the reaction mixture was allowed to stir at room temperature for 16 h. The solvent was removed *in vacuo* and the mixture subjected to column chromatography with petrol:EtOAc (9:1) to afford benzoate **6a** (76 mg, 64%) as a colorless oil. Data for **6a** in main paper.

Benzoate **7a**:



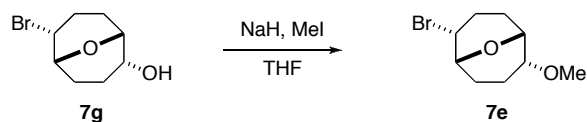
To a solution of alcohol **7g** (25 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) at room temperature was added BzCl (0.02 mL, 0.163 mmol), pyridine (0.013 mL, 0.163 mmol) and DMAP (20 mg, 0.163 mmol) and stirred for 48 h. It was quenched with aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (3×20 mL). The organic layer was dried over MgSO_4 and the solvent was evaporated *in vacuo*. Column chromatography with petrol:EtOAc (9:1) afforded benzoate **7a** (29 mg, 78%) as a colorless oil. Data for **7a** in main paper.

Methyl ether **6e**:



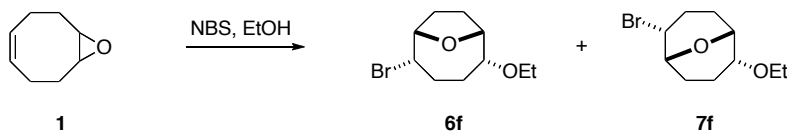
To a solution of alcohol **6g** (70 mg, 0.32 mmol) in THF (20 mL) was added MeI (0.05 mL, 0.81 mmol) and NaH (100 mg, 2.5 mmol) at 0 °C and stirred for 3 h during which time the reaction mixture was allowed to warm to room temperature. It was quenched with saturated aqueous NH_4Cl (10 mL) and extracted with EtOAc (3×20 mL). The combined organic layer was dried over MgSO_4 and the solvent was evaporated *in vacuo*. Column chromatography with petrol:EtOAc (9:1) afforded the methyl ether **6e** (17 mg, 23%) as a colorless oil. Data for **6e** in main paper. Alcohol **6g** (45 mg, 64%) was also recovered.

Methyl ether 7e:



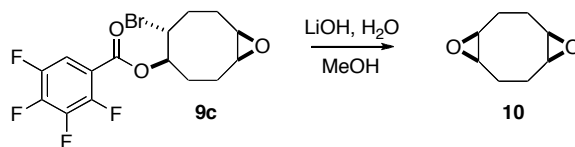
To a solution of alcohol **7g** (40 mg, 0.18 mmol) in THF (20 mL) was added MeI (0.04 mL, 0.64 mmol) and NaH (50 mg, 0.24 mmol) at 0 °C and stirred for 6 h during which time the reaction mixture was allowed to warm to room temperature. It was quenched with saturated aqueous NH₄Cl (10 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layer was dried over MgSO₄ and the solvent was evaporated *in vacuo*. Column chromatography with petrol:EtOAc (9:1) afforded methyl ether **7e** (42 mg, 99%) as a colorless oil. Data for **7e** in main paper.

(1*S,2*S**,5*R**,6*R**)-2-Bromo-5-ethoxy-9-oxabicyclo[4.2.1]nonane (6f) and (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-ethoxy-9-oxabicyclo[3.3.1]nonane (7f):**



NBS (316 mg, 1.77 mmol, 1.1 equiv) was added to a solution of epoxyalkene **1** (200 mg, 1.61 mmol, 1.0 equiv) in EtOH (6.5 mL) at room temperature. After stirring for 40 h, the reaction mixture was diluted with CH₂Cl₂ (50 mL) and washed with aqueous sodium sulfite (50 mL). The layers were separated and the aqueous extracted with CH₂Cl₂ (3 × 50 mL). The organics were combined, washed with brine (50 mL), dried over Na₂SO₄, filtered and the solvent was removed *in vacuo*. The mixture was purified by column chromatography eluting with petrol:EtOAc (9:1) to give an inseparable mixture of bicyclic ethers **6f** and **7f** (205 mg, 51 %, **6f** : **7f** = 1.0 : 3.2) as a colorless oil; *R_f* (PE : EtOAc 4 : 1) 0.61; IR (neat) 1105, 1065, 1044, 1034 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.64 – 4.56 (**6f**, m, 2H), 4.46 (**7f**, dt, *J* = 12.8, 5.6 Hz, 1H), 4.19 (**6f**, dt, *J* = 9.7, 5.1 Hz, 1H), 3.99 (**7f**, app t, *J* = 5.7 Hz, 1H), 3.92 (**7f**, app t, *J* = 5.4 Hz, 1H), 3.76 (**6f**, dt, *J* = 7.0, 4.6 Hz, 1H), 3.72 (**7f**, dt, *J* = 11.3, 5.8 Hz, 1H), 3.61 – 3.38 (**6f**, m, 2H and **7f**, m, 2H), 2.51 – 1.77 (**6f**, m, 8H and **7f**, m, 8H), 1.21 (**7f**, t, *J* = 7.2 Hz, 3H), 1.19 (**6f**, t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) **6f** – 82.6, 79.8, 78.4, 64.7, 54.7, 29.9, 29.2, 26.2, 25.3, 15.6; **7f** – 75.3, 70.0, 67.7, 64.0, 51.4, 31.4, 26.3, 25.2, 23.3, 15.7; MS (CI⁺, NH₃) *m/z* 268, 266 (M + NH₄⁺); HRMS (CI⁺, NH₃) *m/z* calcd for C₁₀H₂₁NO₂⁷⁹Br (M + NH₄⁺) 266.0756, found 266.0770.

Saponification of tetrafluorobenzoate **9c**

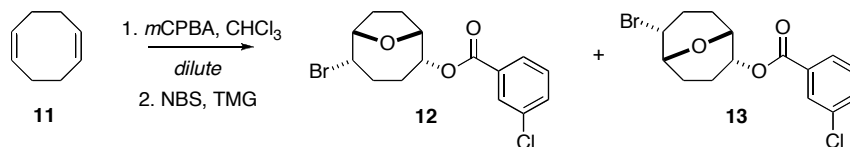


To a solution of tetrafluorobenzoate **9c** (150 mg, 0.38 mmol) in MeOH:H₂O (5 mL : 0.2 mL) was added LiOH (63 mg, 1.5 mmol) and stirred at ambient temperature for 1 h. The solvent was evaporated, the residue was dissolved in water (20 mL), extracted with EtOAc (3 × 20 mL), dried over MgSO₄ and the solvent was evaporated *in vacuo*. Purification by column chromatography eluting with petrol:EtOAc (7:3) afforded bisepoxide **10** (12 mg, 23%) as a colorless oil. R_f (petrol:EtOAc 7:3) 0.53, ¹H NMR (400 MHz, CDCl₃) δ 3.05 – 2.99 (m, 4H), 2.11 – 1.86 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 56.1, 22.0 (lit. δ 56.1, 22.0); MS (EI) *m/z* 158 (M+NH₄)⁺, 141 (M+H)⁺; HRMS (EI) *m/z* calcd for C₈H₁₃O₂ (M+H)⁺ 141.0916, found 141.0915.

Literature reference with characterizing data for **10**: Rudolph, J.; Reddy, K. L.; Chiang, J. P.; Sharpless, K. B. *J. Am. Chem. Soc.* **1997**, *119*, 6189–6190.

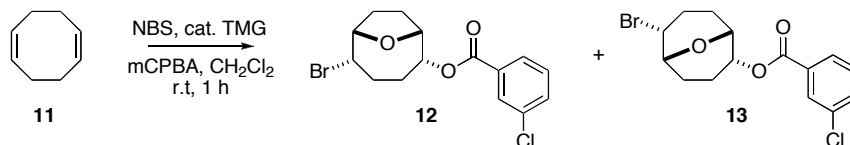
One-pot epoxidation-bromination of 1,5-cyclooctadiene **11**

Method A.



To a solution of diene **11** (200 mg, 1.85 mmol) in CHCl_3 (10 mL) at room temperature was added *m*-chloroperbenzoic acid (335 mg, 1.94 mmol) and stirred for 24 h. TLC showed complete conversion into epoxyalkene **1**. The reaction mixture was diluted with CHCl_3 (1 L), and NBS (395 mg, 2.22 mmol) and TMG (2 mg, 1 mol%) were added, and the mixture was stirred for 1 h at room temperature. The solvent was evaporated *in vacuo* and column chromatography was carried out with petrol:EtOAc (9:1) to afford chlorobenzoate ethers **12** and **13** (260 mg, 40%) as a colorless oil as a 1:1 mixture of inseparable products.

Method B.



To a solution of diene **11** (200 mg, 1.6 mmol) in CH_2Cl_2 (1 L) at room temperature was added NBS (574 mg, 3.23 mmol), TMG (2 mg, 1 mol%) and *m*CPBA (340 mg, 1.94 mmol) and stirred for 1 h. The mixture was washed with NaOH (10% w/w, 50 mL), the organic layer was dried over MgSO_4 and the solvent was evaporated *in vacuo*. Column chromatography eluting with petrol:EtOAc (90:10) afforded chlorobenzoate ethers **12** and **13** (280 mg, 50%) as a colorless oil as a 1:1 mixture of inseparable products.

The chlorobenzoates **12** and **13** were separated using HPLC on a 25 cm Supelcosil LC-Si column (ID 21.2 mm), eluting with *n*-Hexane-*i*PrOH (95:5), flow rate 9 mLmin^{-1} , detecting at 254 nm. R_t **12** 20.7 min; R_t **13** 18.9 min.

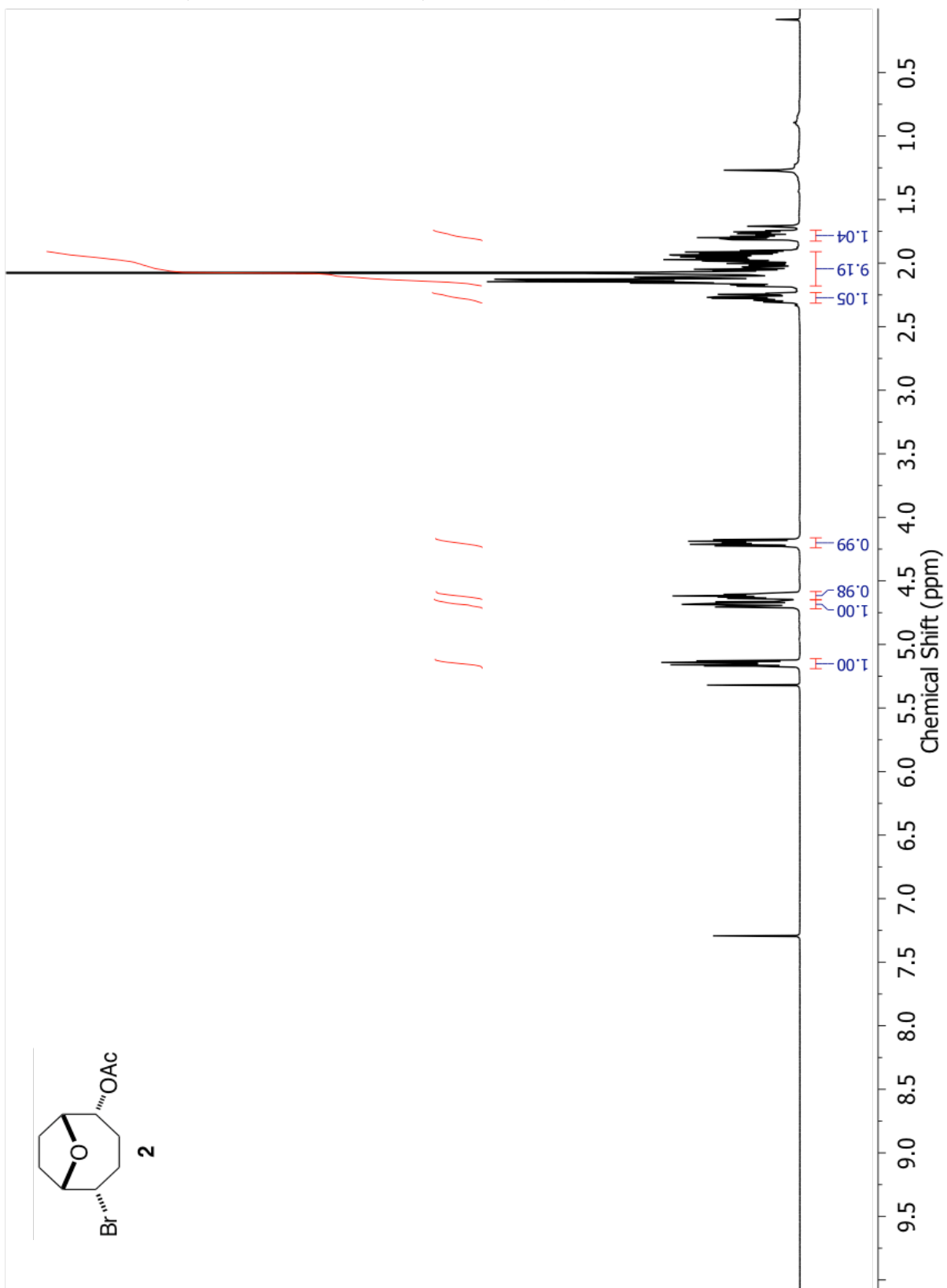
(1R*,2R*,5S*,6S*)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl 3-chlorobenzoate (12). Colorless oil: R_f (PE : EtOAc 9 : 1) 0.34; IR (neat) 1718 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (t, $J = 0.8\text{ Hz}$, 1H), 7.94 (dt, $J = 7.7, 1.2\text{ Hz}$), 7.60 – 7.57 (m, 1H), 7.43 (t,

$J = 7.9$ Hz), 5.44 – 5.40 (m, 1H), 4.84 – 4.80 (m, 1H), 4.69 – 4.66 (m, 1H), 4.28 – 4.23 (m, 1H), 2.38 – 1.91 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 134.7, 133.2, 131.8, 129.8, 129.6, 127.7, 82.9, 78.2, 74.4, 53.5, 29.8, 29.4, 26.4, 25.9; MS (Cl^+ , NH_3) m/z 380, 378, 376 ($\text{M} + \text{NH}_4$) $^+$; HRMS (Cl^+ , NH_3) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3^{35}\text{Cl}^{79}\text{Br}$ ($\text{M} + \text{NH}_4$) $^+$ 376.0315, found 376.0308.

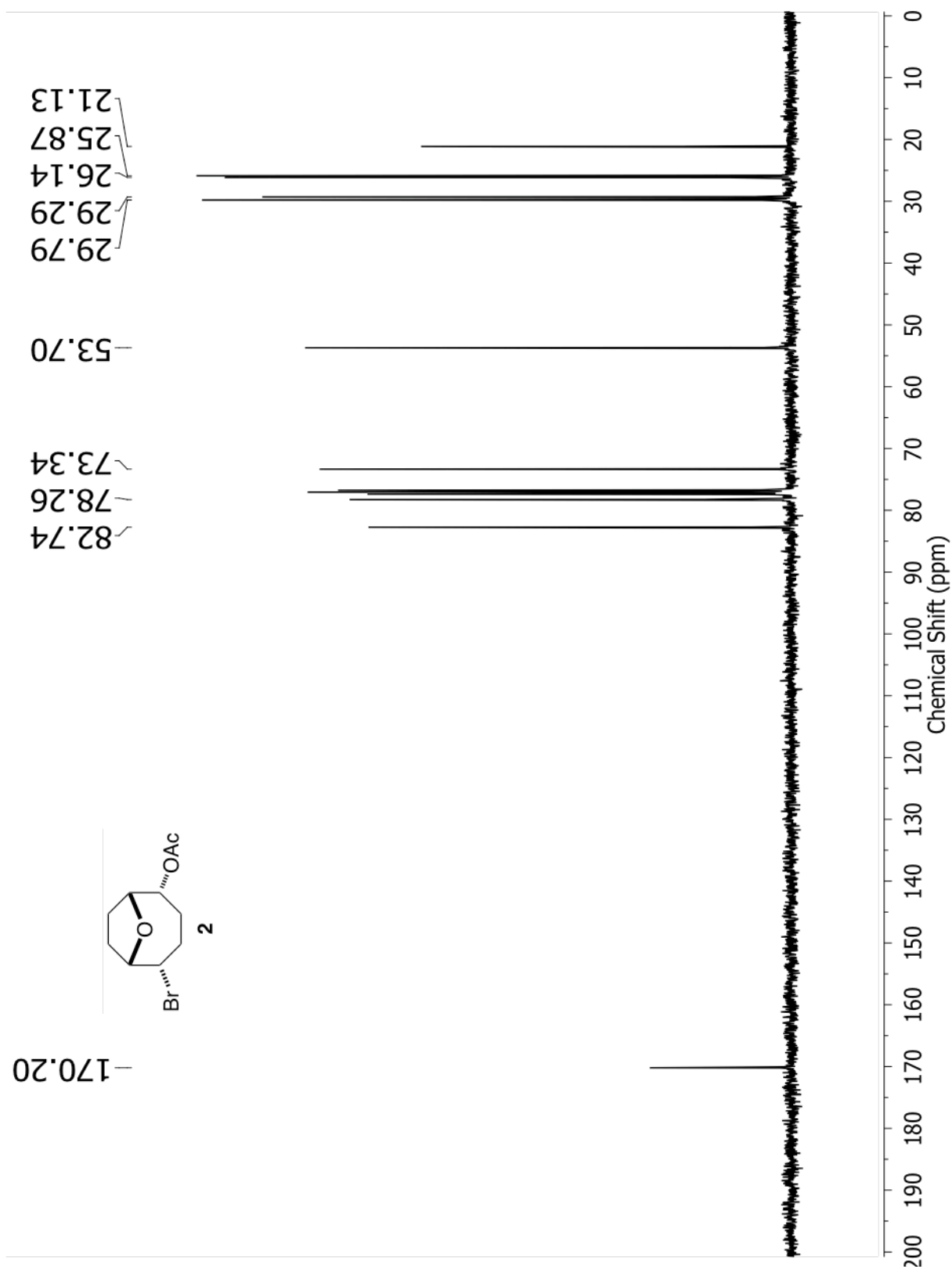
(1*R,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl 3-chlorobenzoate (13).**

White solid: m.p. 95-96 °C. R_f (PE : EtOAc 9 : 1) 0.34; IR (neat) 172 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.00 (t, $J = 0.8$ Hz, 1H), 7.93 (dt, $J = 7.8, 1.4$ Hz), 7.59 – 7.56 (m, 1H), 7.42 (t, $J = 7.9$ Hz), 5.42 – 5.36 (m, 1H), 4.50 (dt, $J = 11.7, 5.5$ Hz, 1H), 4.13 (t, $J = 5.4$ Hz, 1H), 4.02 (t, $J = 5.1$ Hz, 1H), 2.62 – 2.44 (m, 2H), 2.36 – 2.30 (m, 1H), 2.22 – 2.06 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.4, 134.6, 133.2, 131.8, 129.8, 129.6, 127.8, 71.4, 69.8, 66.5, 50.4, 31.1, 25.8, 25.15, 23.2; MS (Cl^+ , NH_3) m/z 380, 378, 376 ($\text{M} + \text{NH}_4$) $^+$; HRMS (Cl^+ , NH_3) m/z calcd for $\text{C}_{15}\text{H}_{20}\text{NO}_3^{35}\text{Cl}^{79}\text{Br}$ ($\text{M} + \text{NH}_4$) $^+$ 376.0315, found 376.0307.

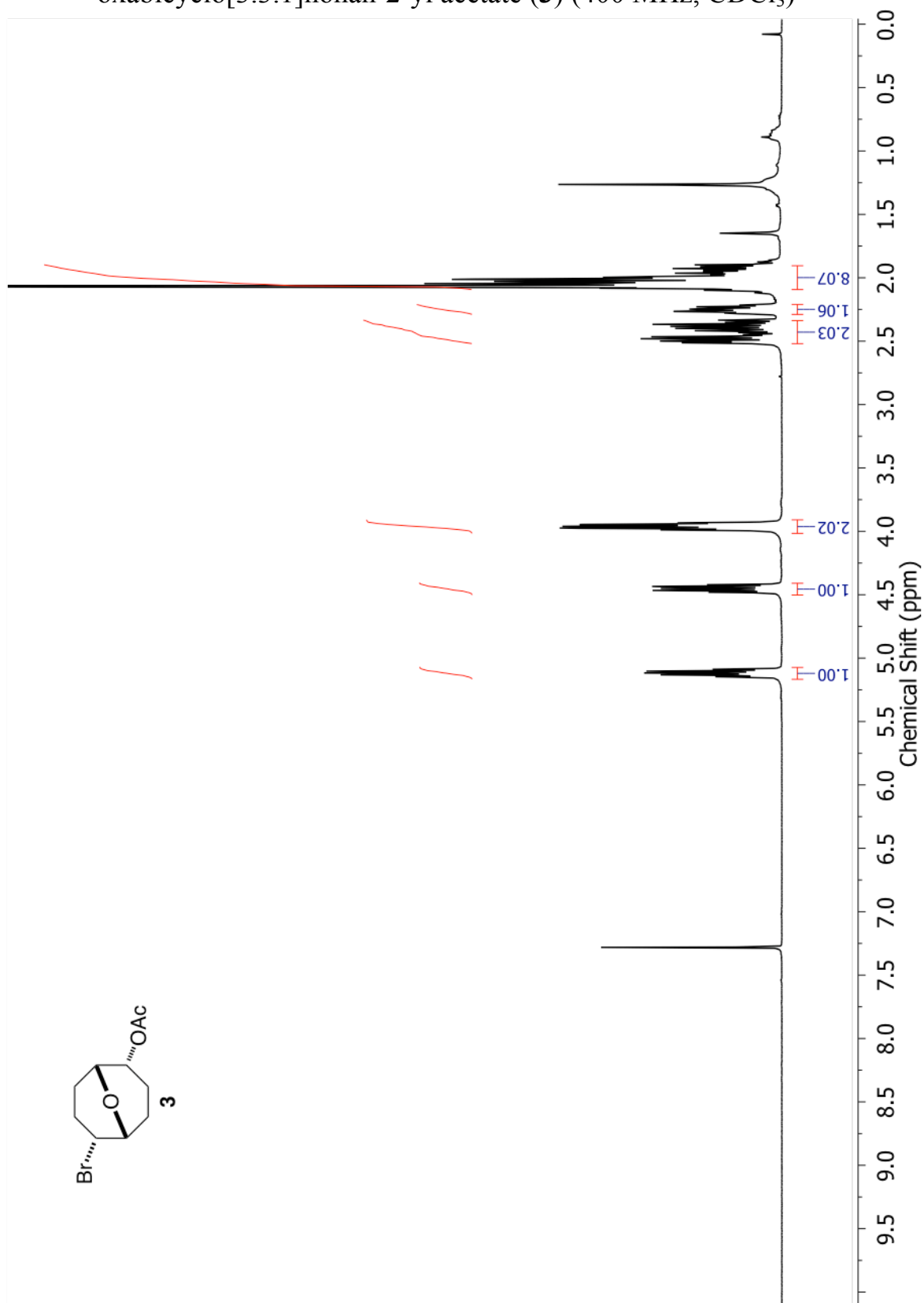
^1H NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl acetate (**2**) (400 MHz, CDCl_3)



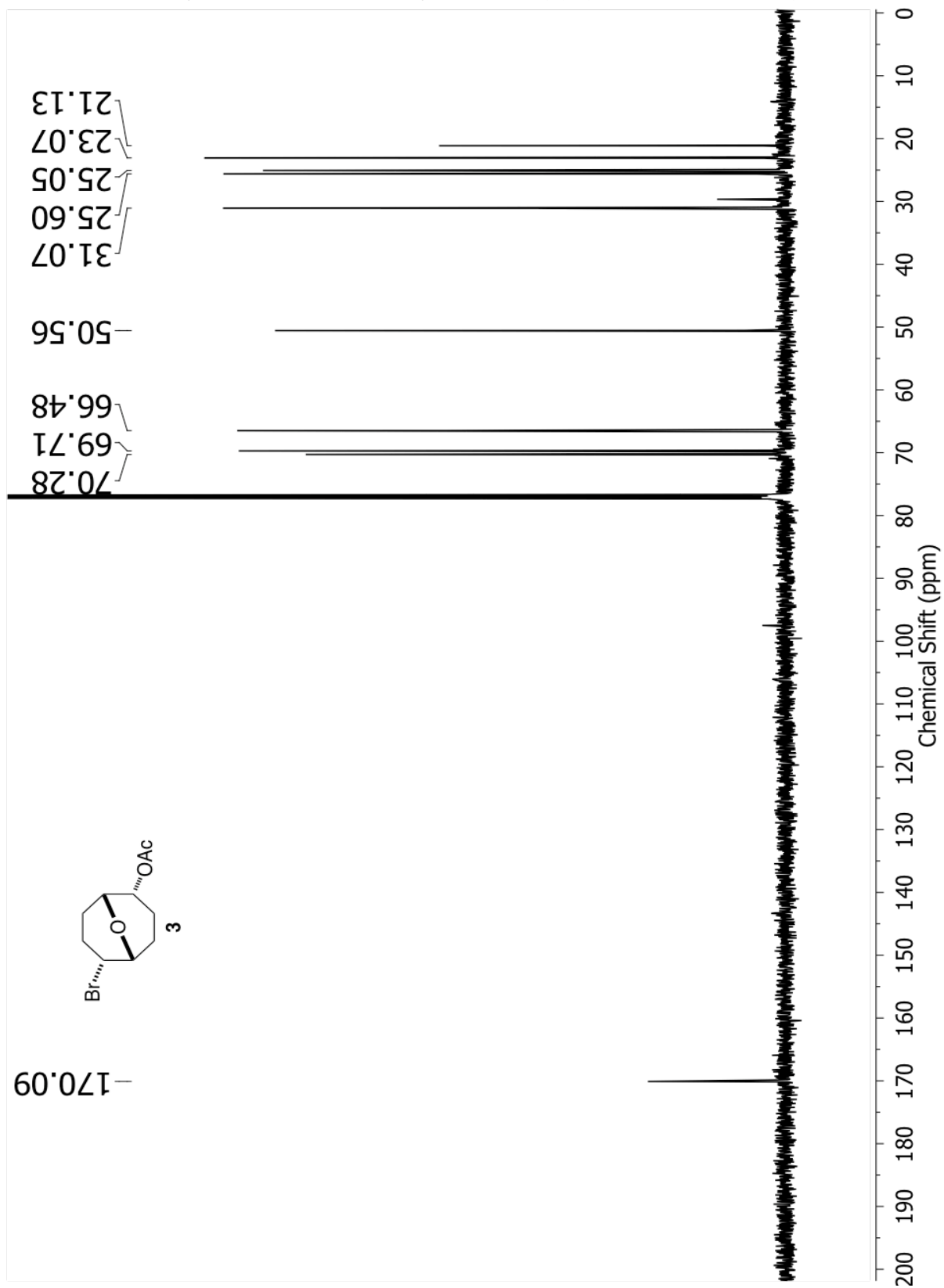
^{13}C NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl acetate (**2**) (100 MHz, CDCl_3)



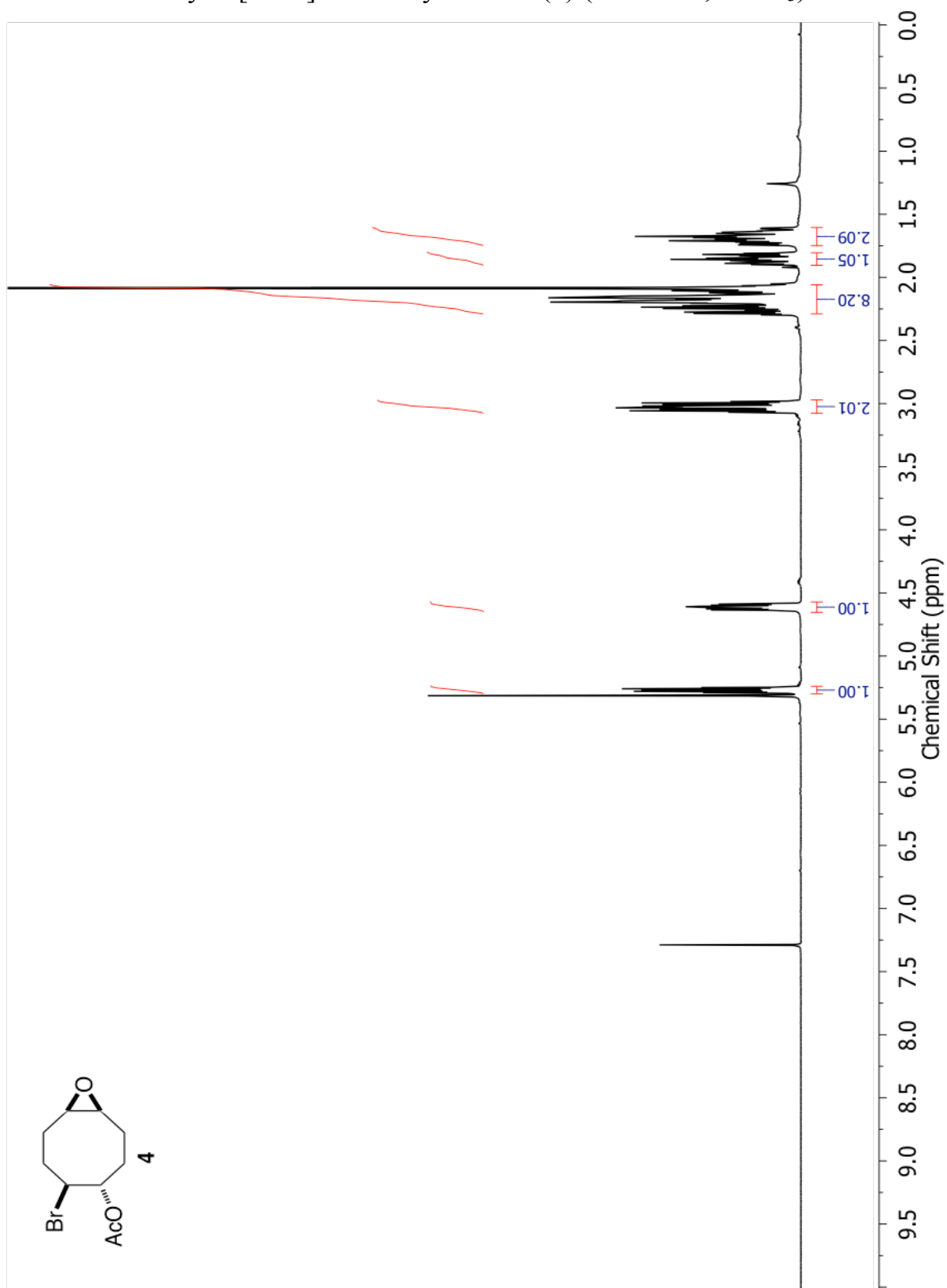
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl acetate (**3**) (400 MHz, CDCl_3)



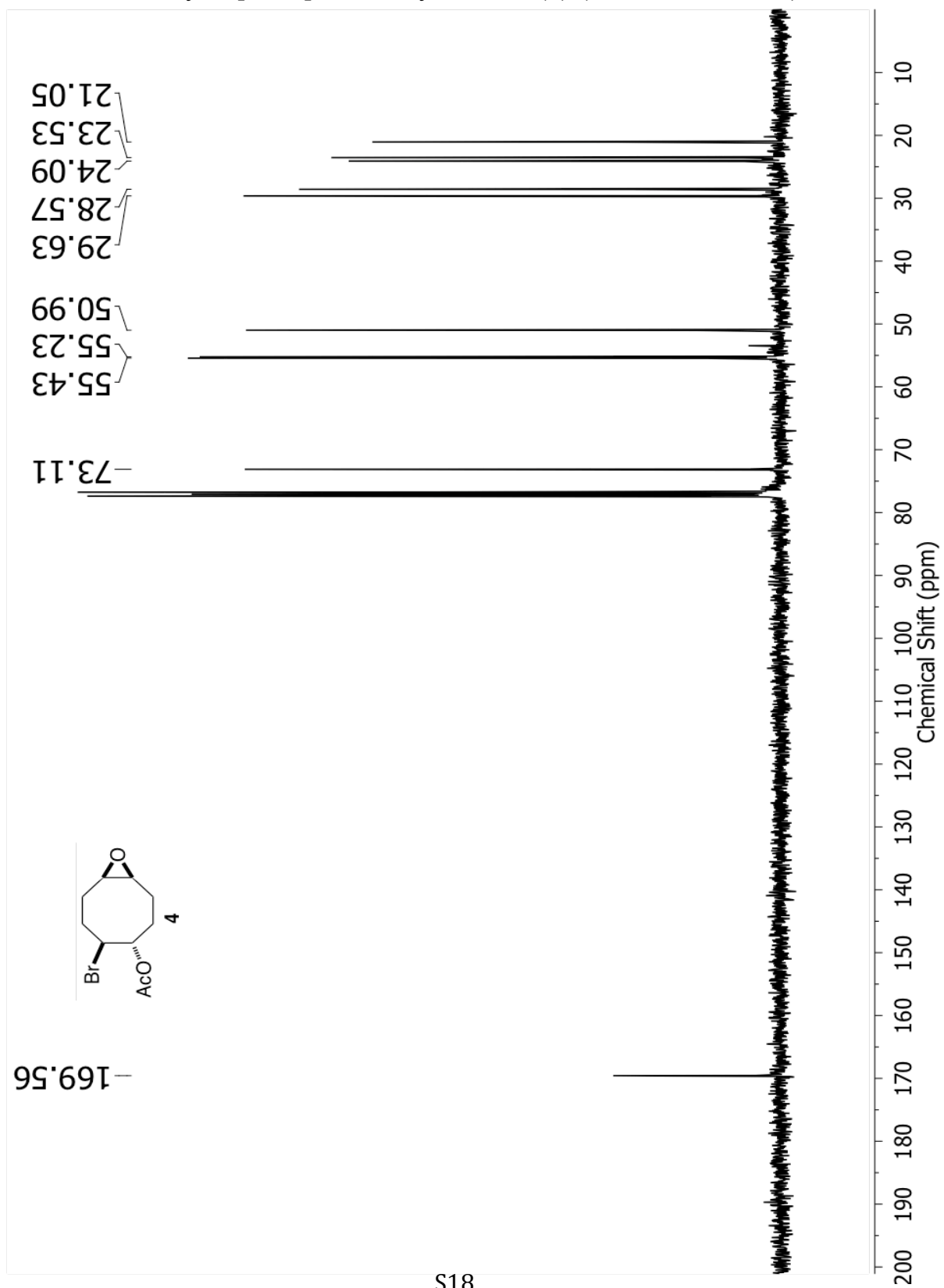
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl acetate (**3**) (125 MHz, CDCl_3)



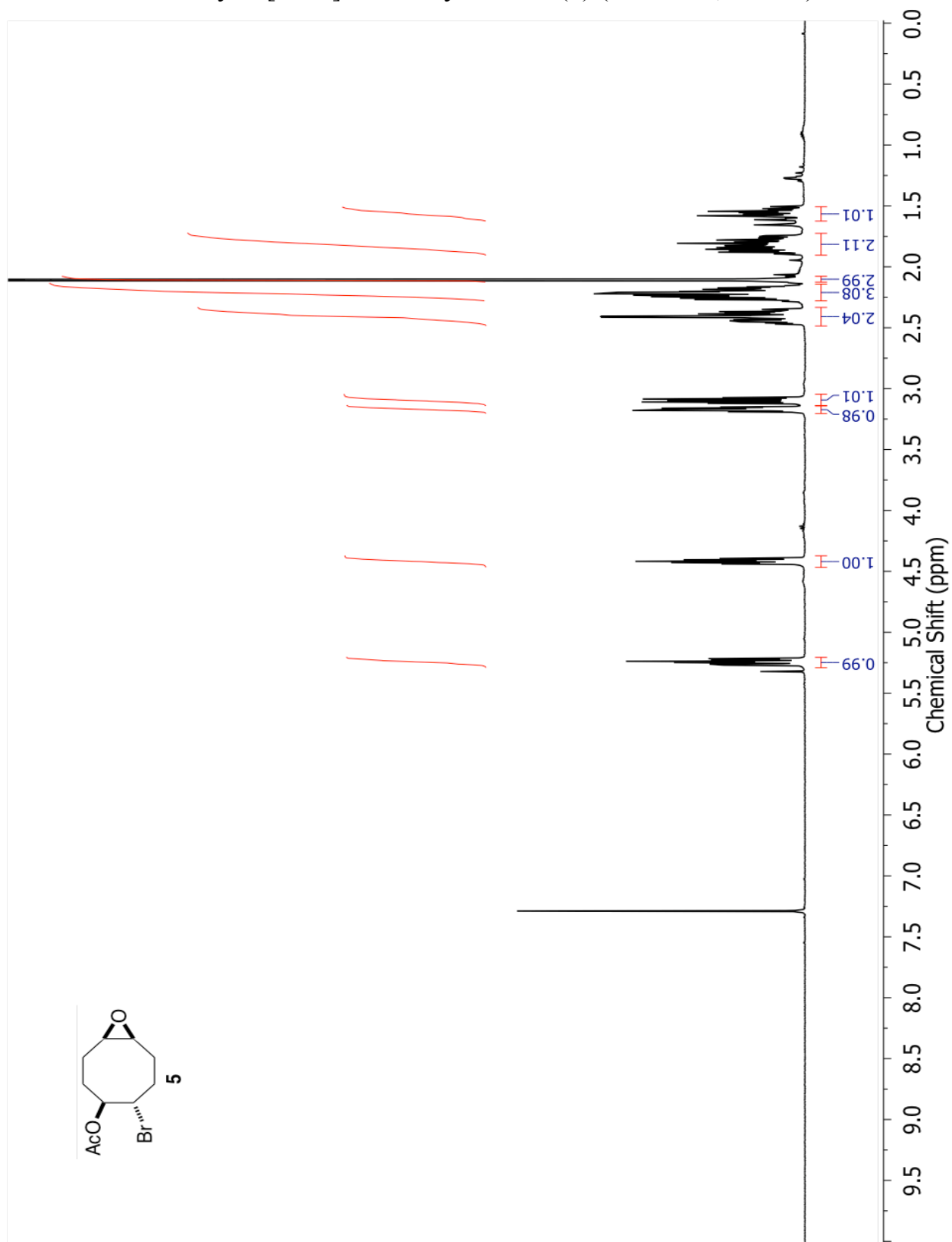
^1H NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl acetate (**4**) (400 MHz, CDCl_3)



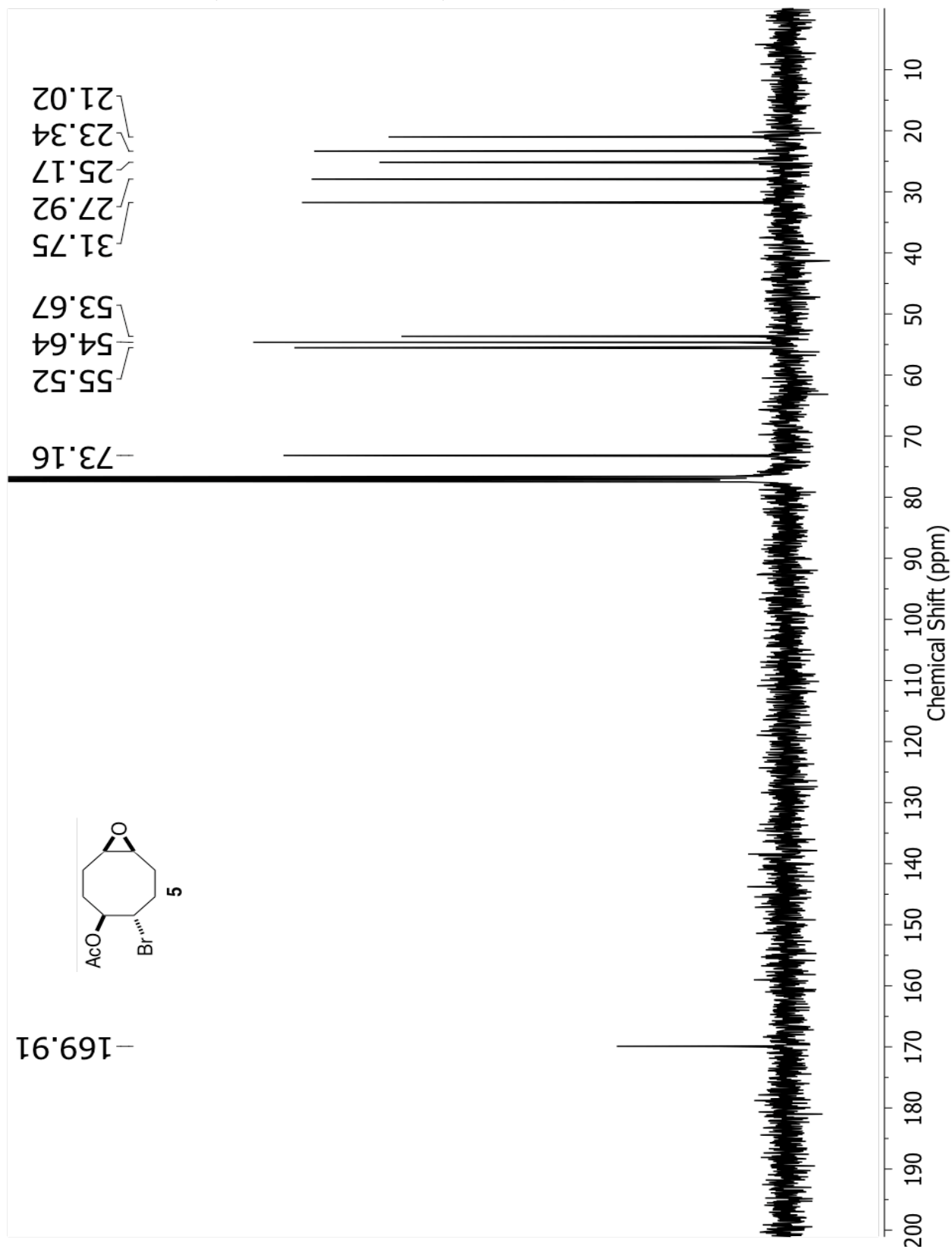
^{13}C NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl acetate (**4**) (100 MHz, CDCl_3)



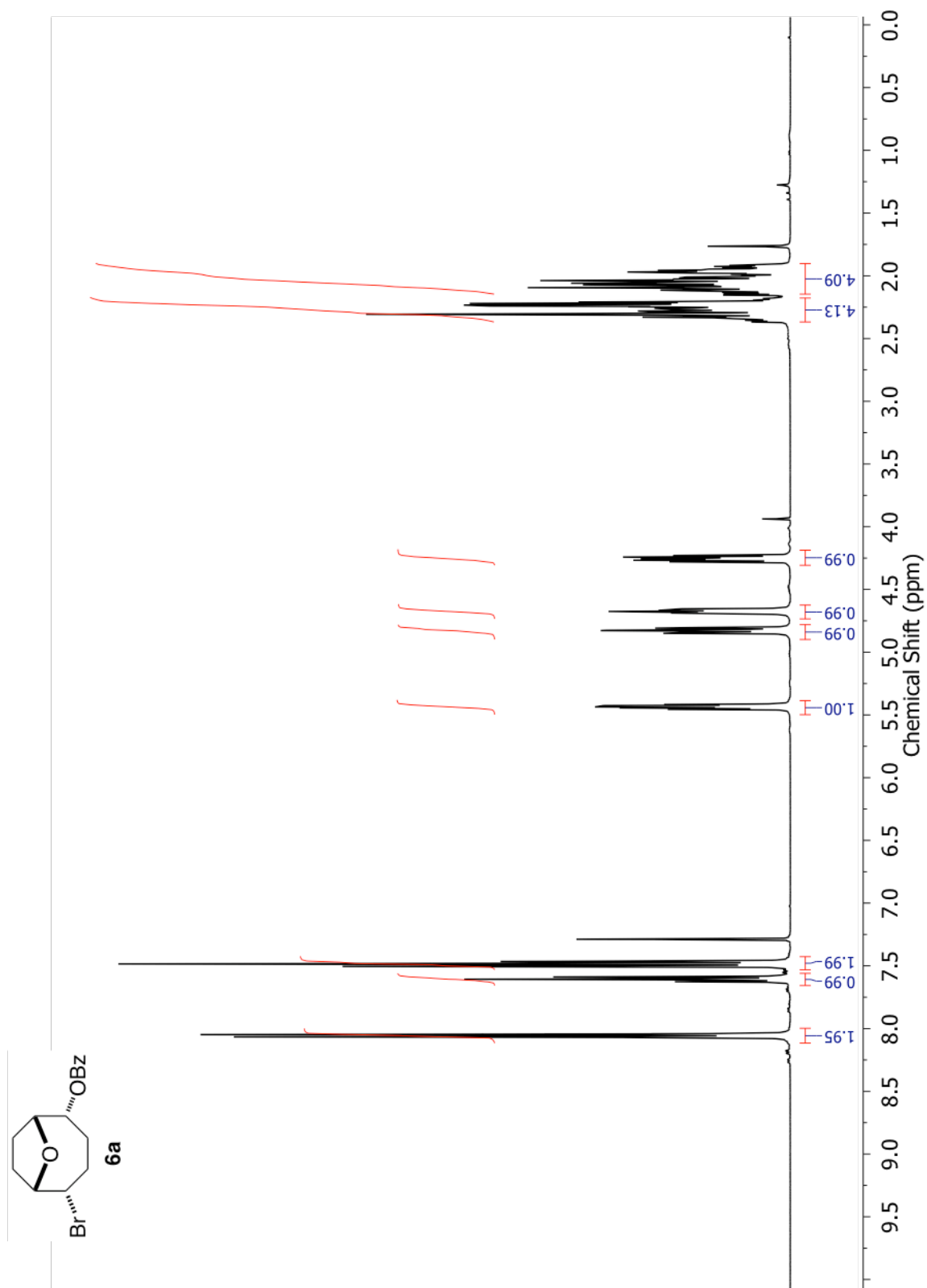
^1H NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl acetate (**5**) (400 MHz, CDCl_3)



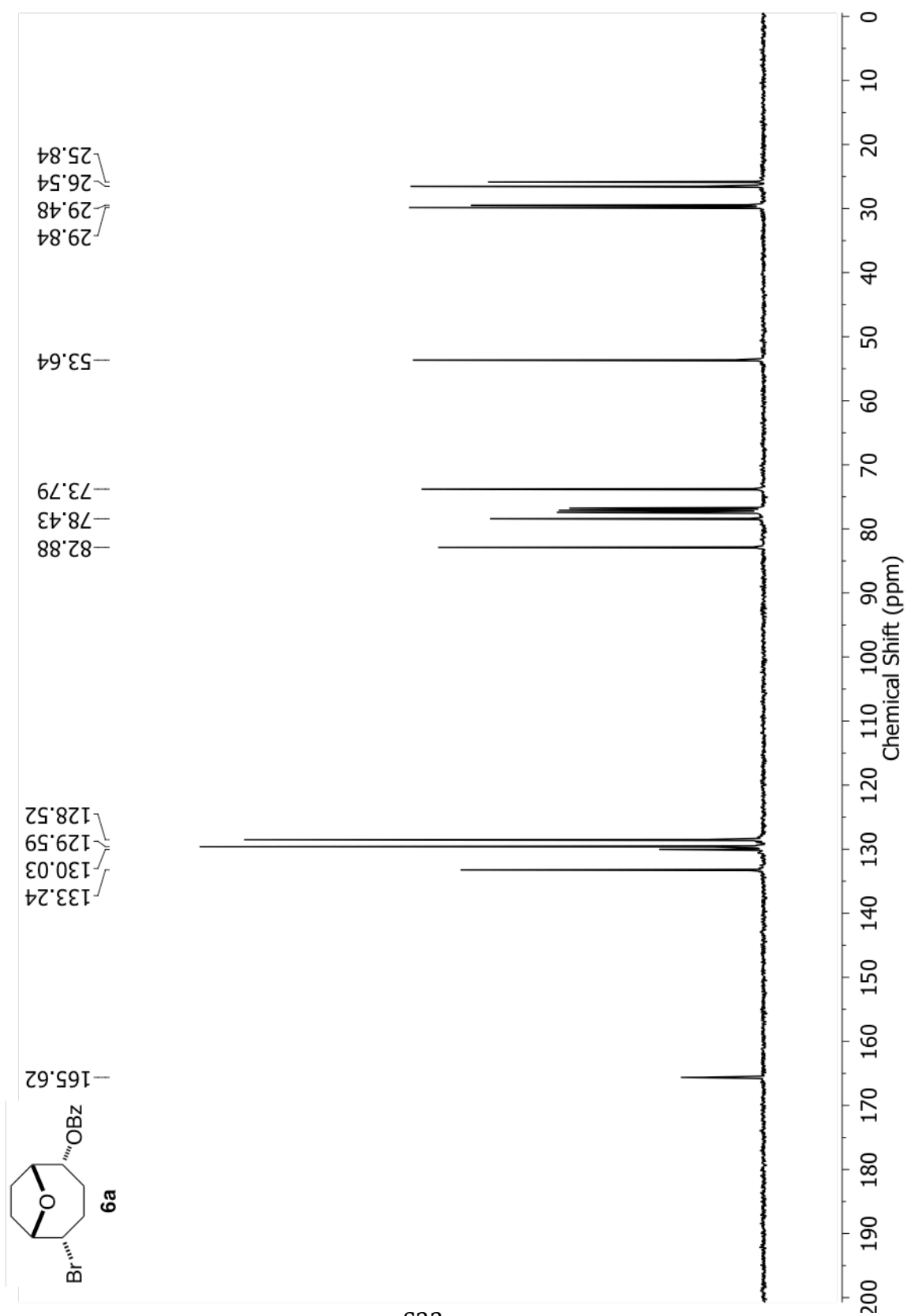
^{13}C NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl acetate (**5**) (100 MHz, CDCl_3)



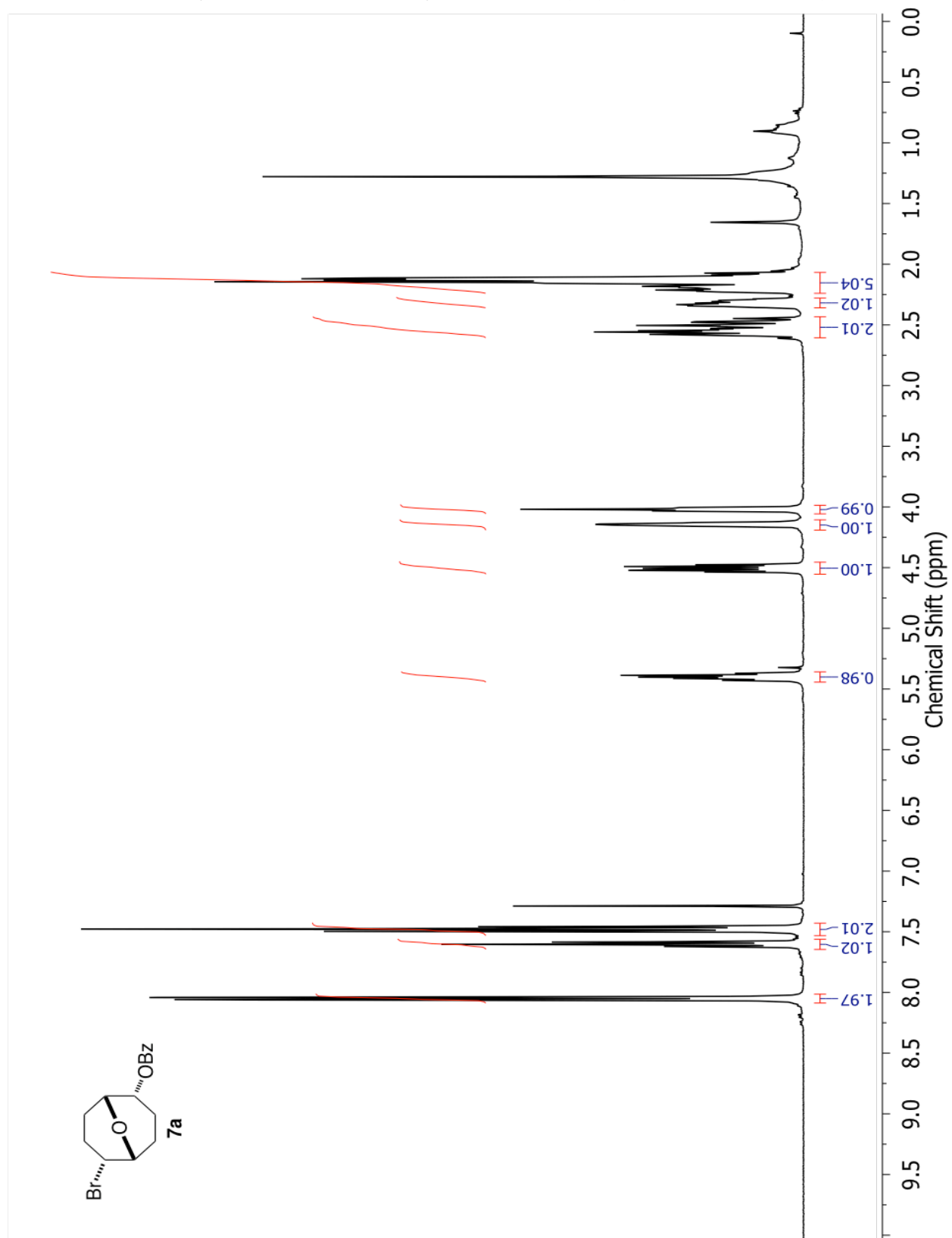
^1H NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl benzoate (**6a**) (400 MHz, CDCl_3)



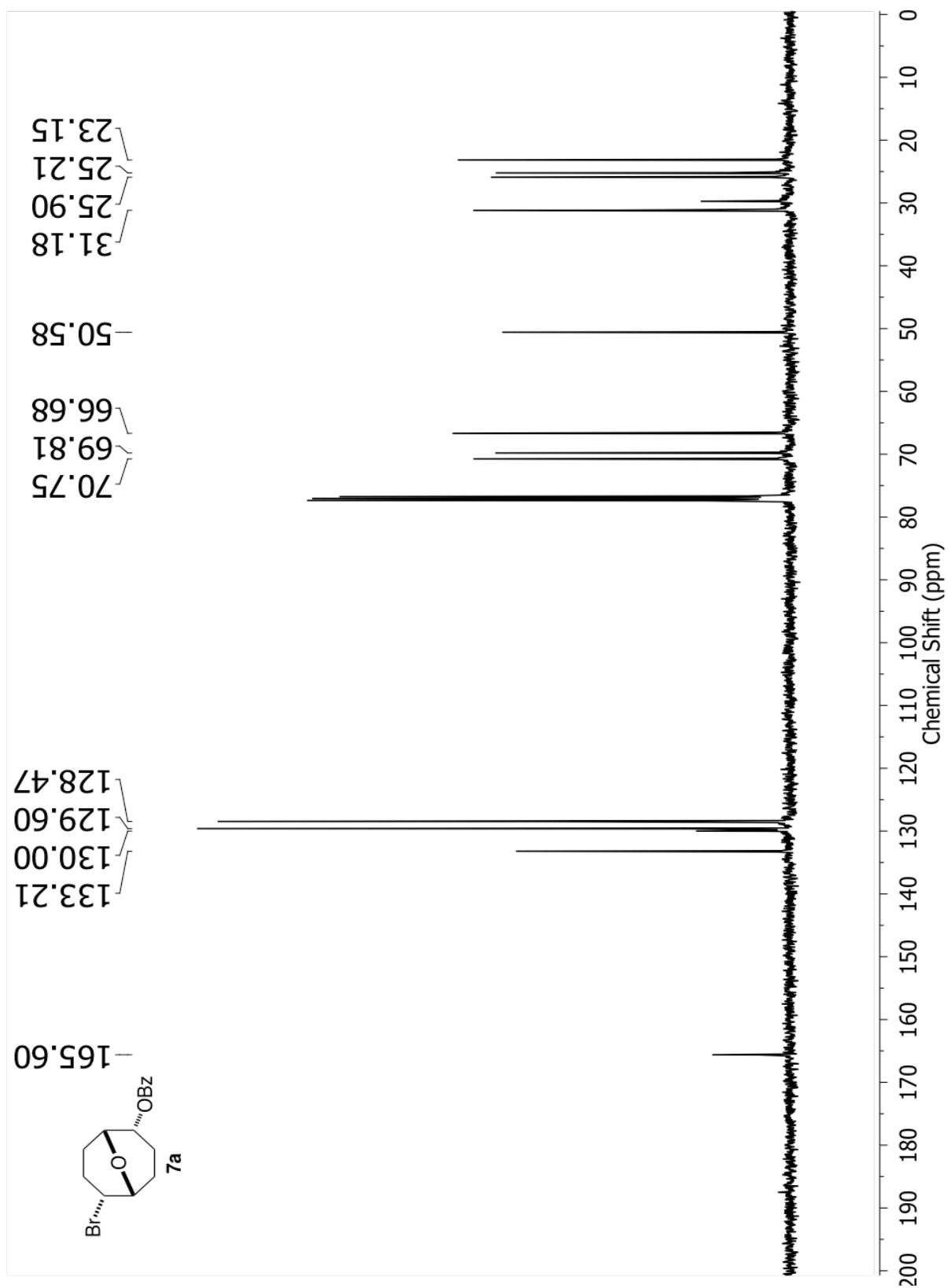
^{13}C NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl benzoate (**6a**) (100 MHz, CDCl_3)



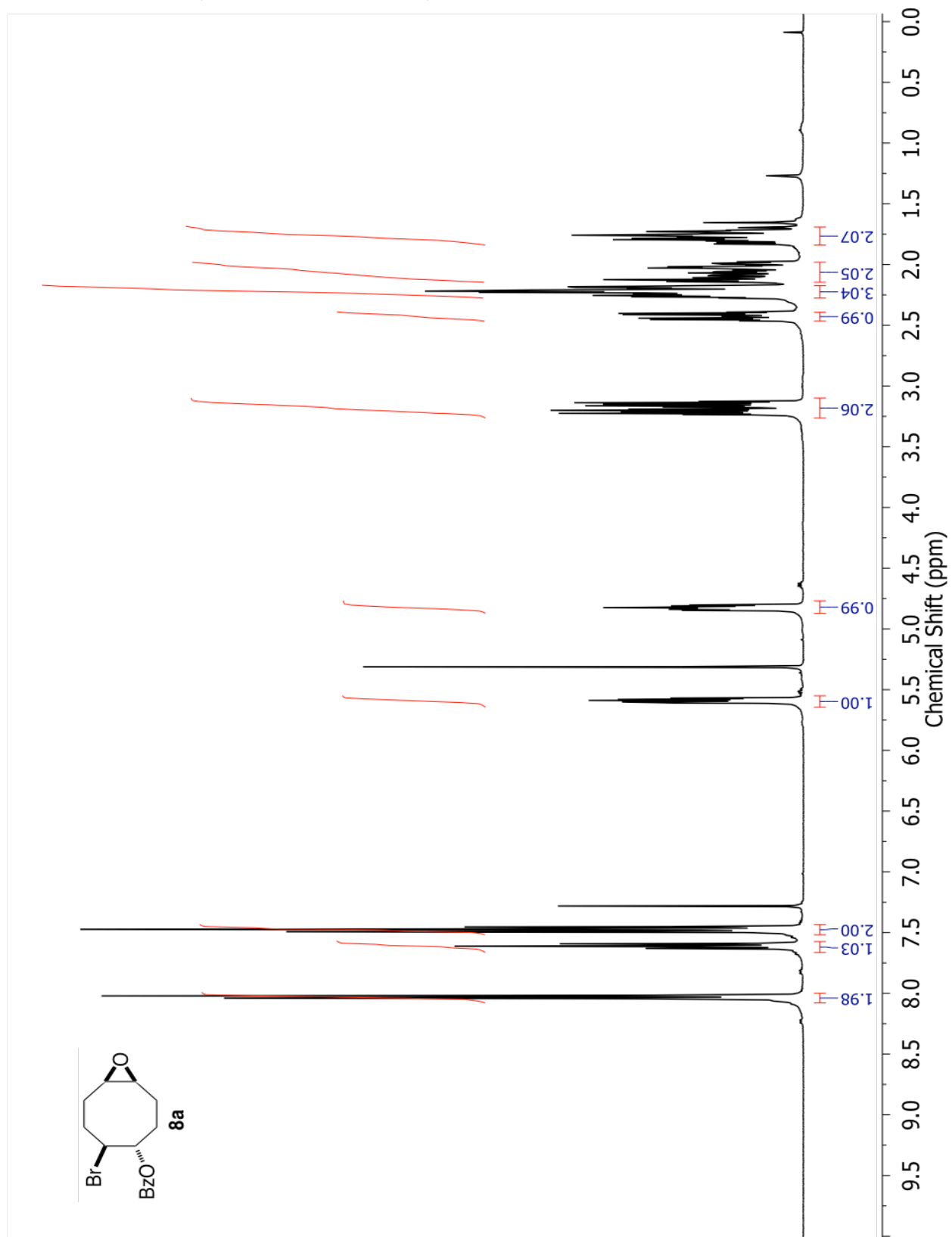
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl benzoate (**7a**) (400 MHz, CDCl_3)



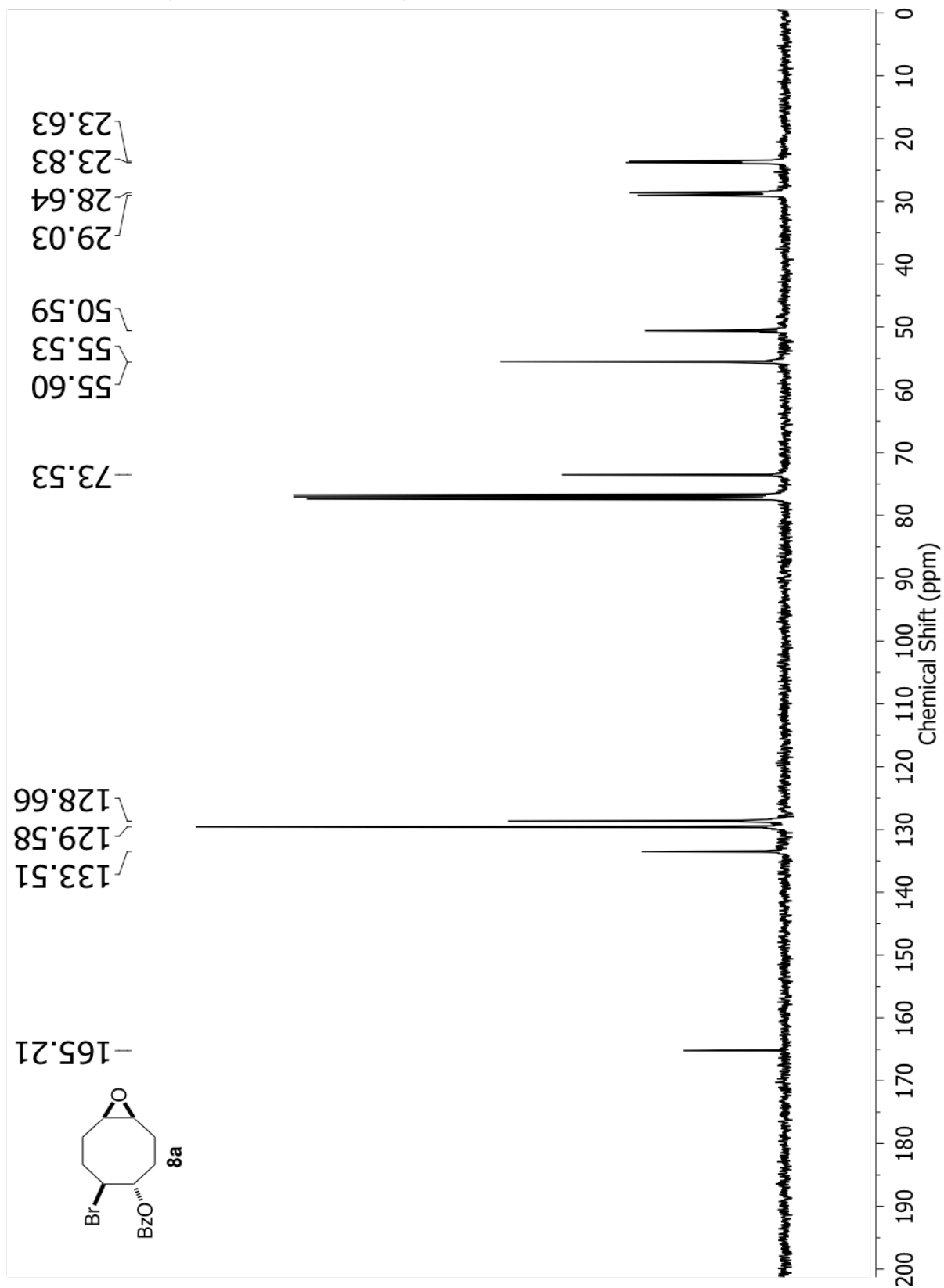
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl benzoate (**7a**) (100 MHz, CDCl_3)



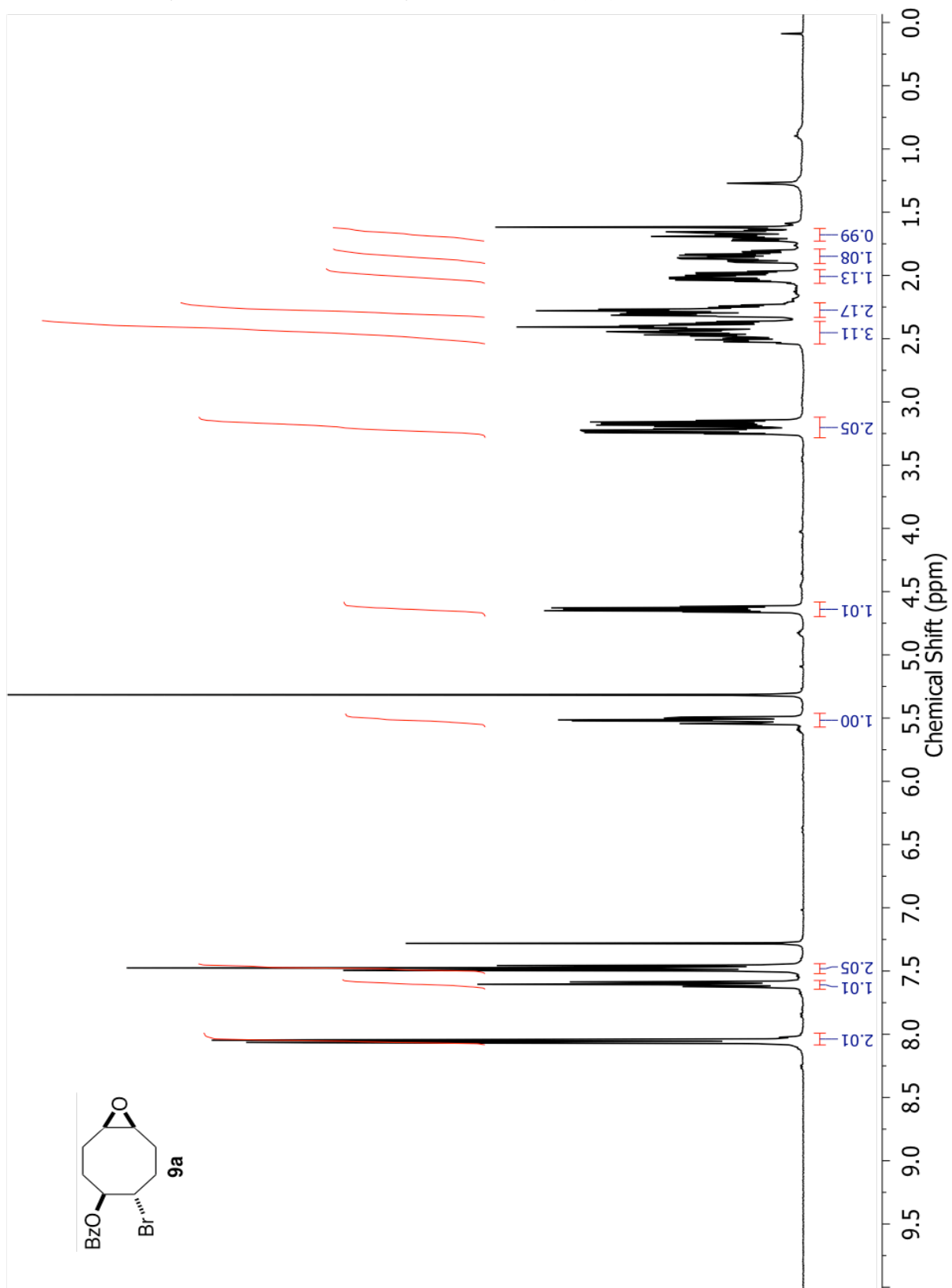
^1H NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl benzoate (**8a**) (400 MHz, CDCl_3)



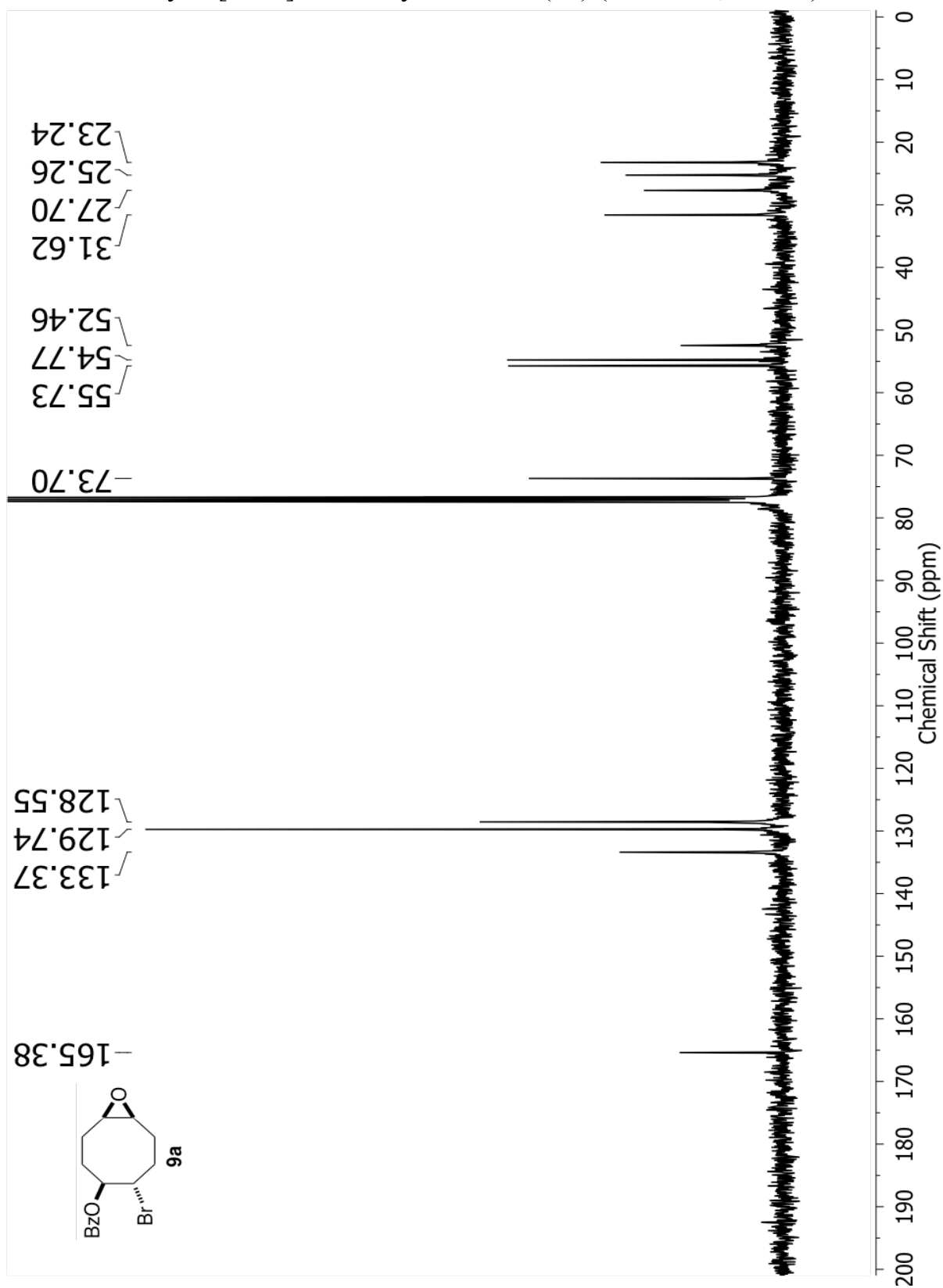
^{13}C NMR Spectrum of Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl benzoate (**8a**) (100 MHz, CDCl_3)



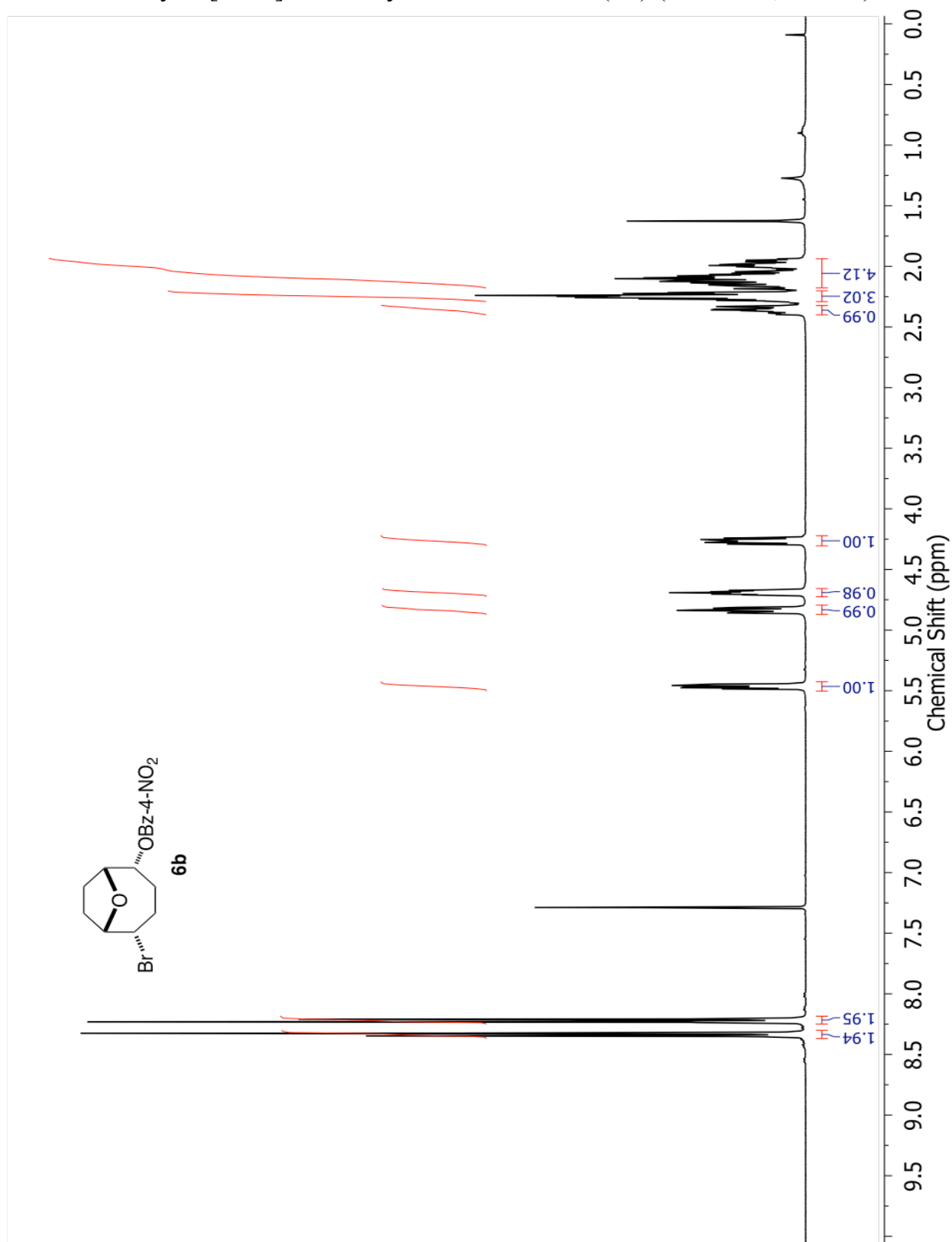
^1H NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl benzoate (**9a**) (400 MHz, CDCl_3)



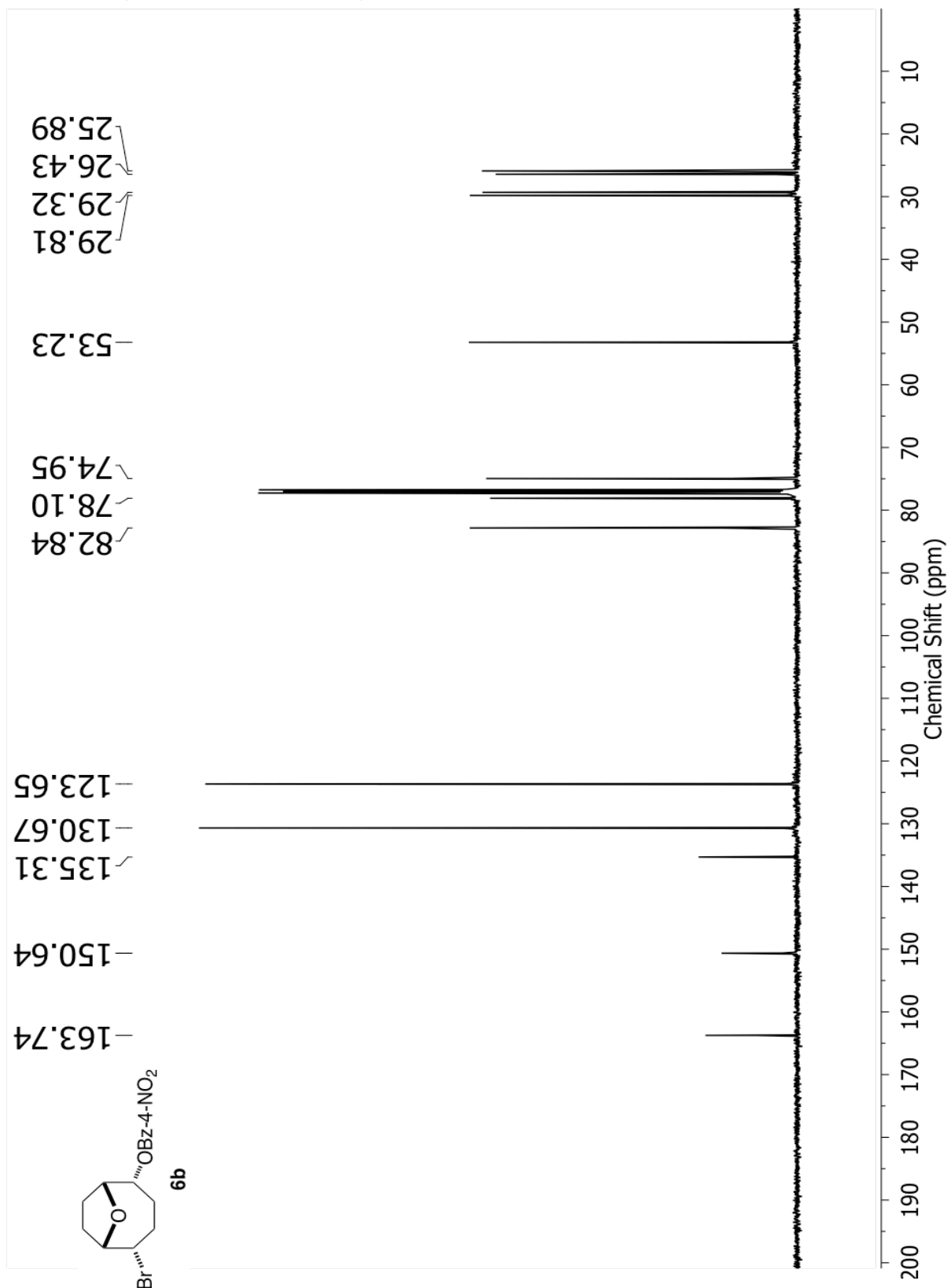
^{13}C NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl benzoate (**9a**) (100 MHz, CDCl_3)



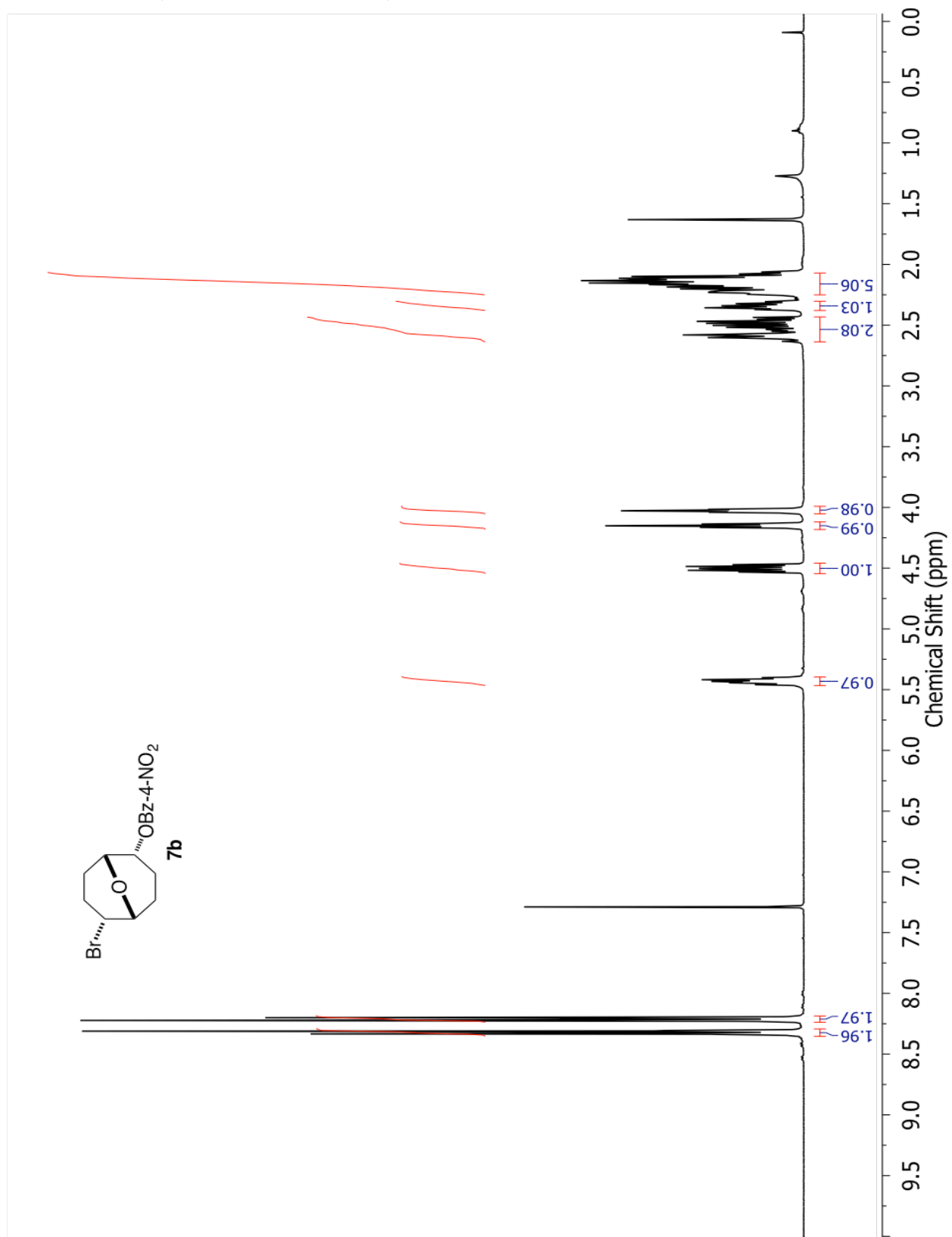
^1H NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl 4-nitrobenzoate (**6b**) (400 MHz, CDCl_3)



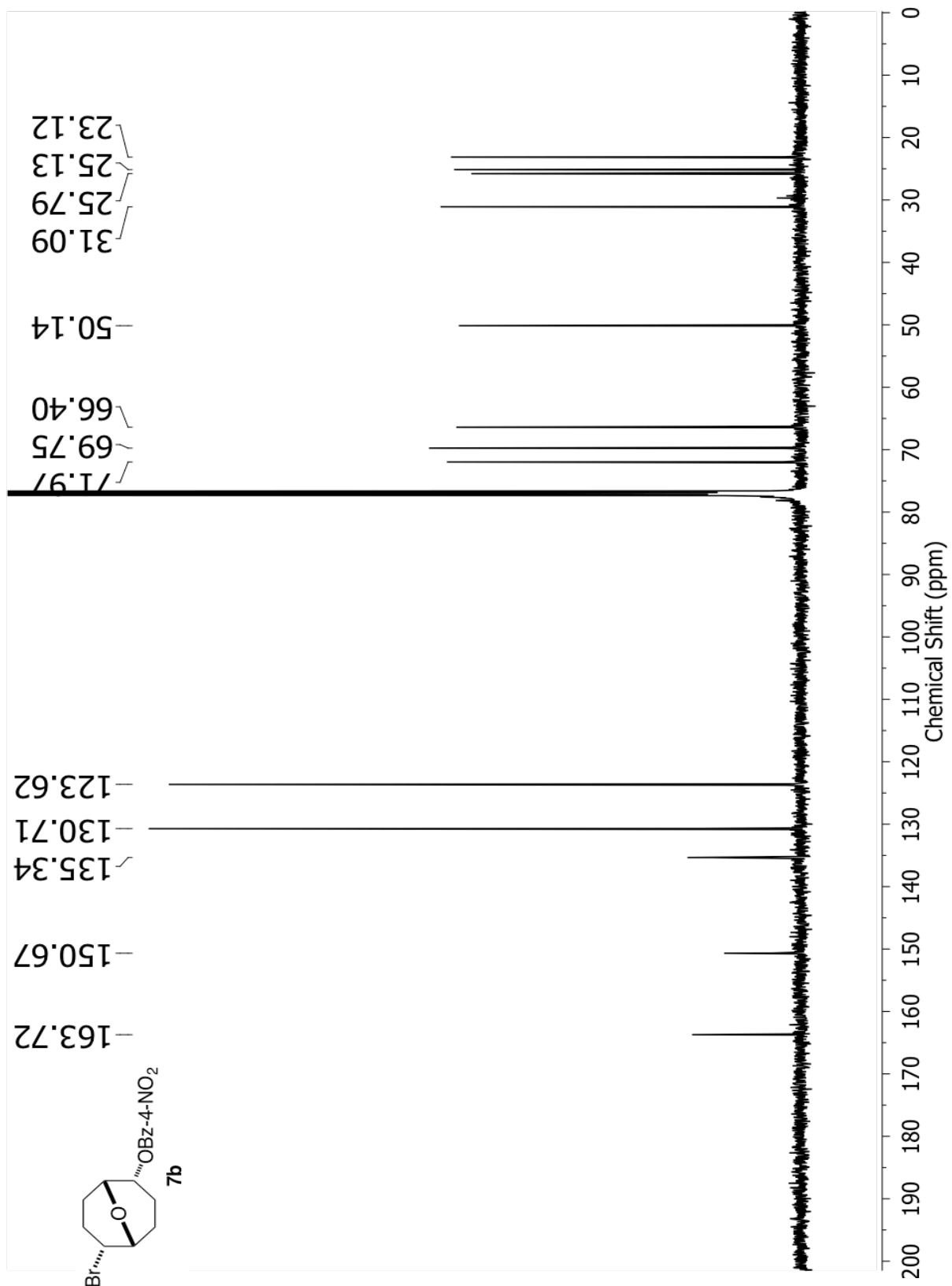
^{13}C NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl 4-nitrobenzoate (**6b**) (125 MHz, CDCl_3)



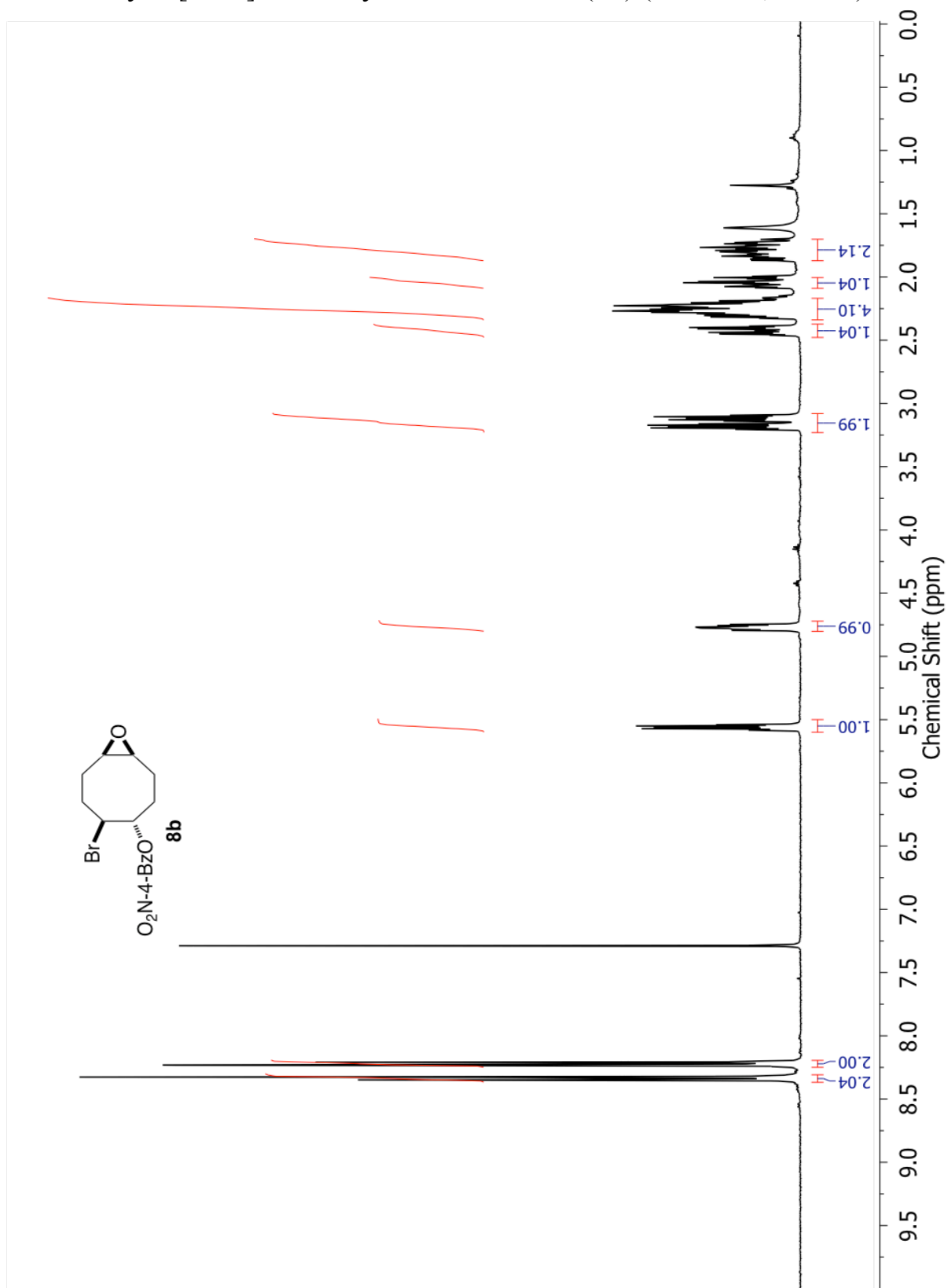
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl 4-nitrobenzoate (**7b**) (400 MHz, CDCl_3)



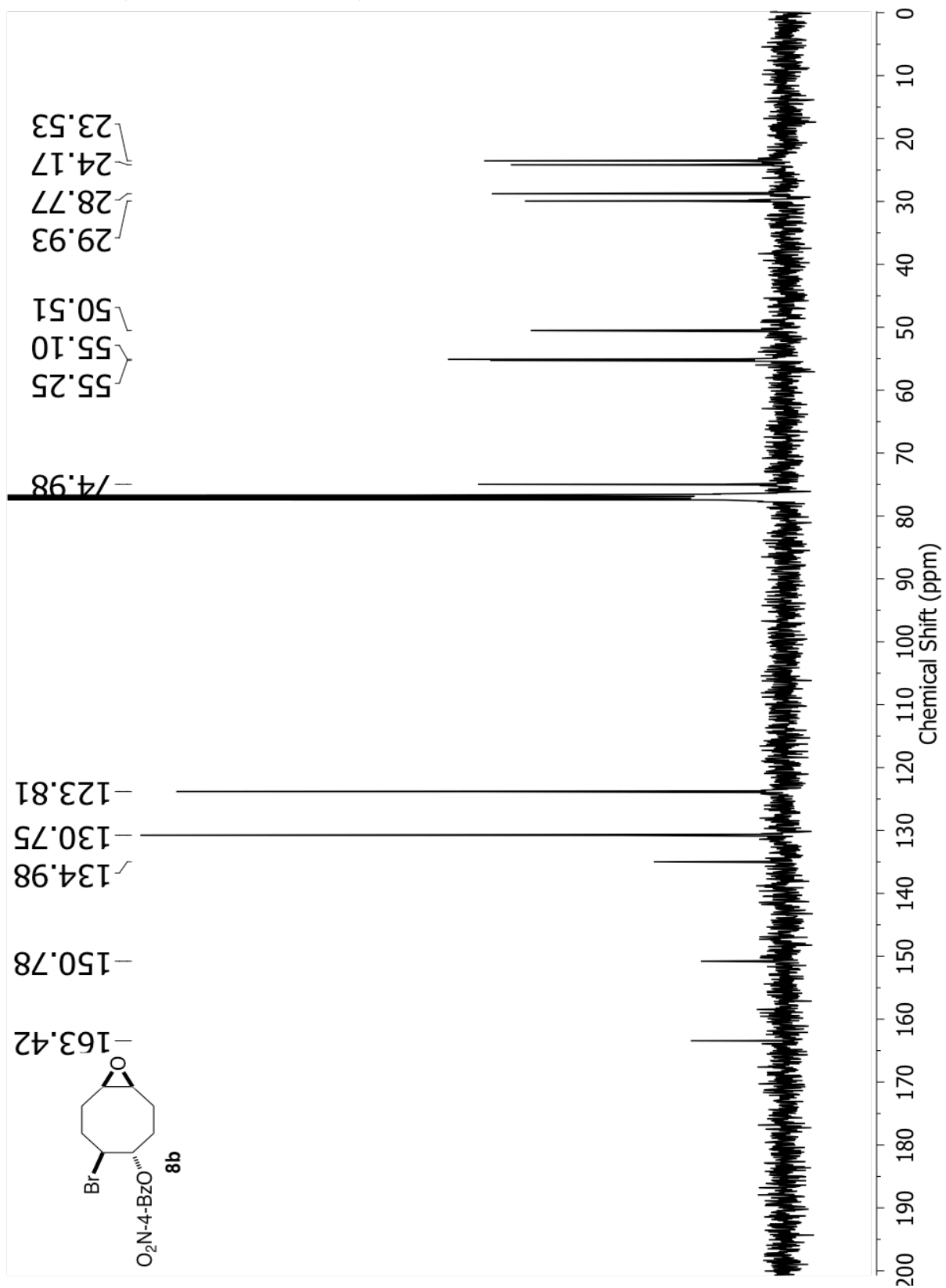
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl 4-nitrobenzoate (**7b**) (125 MHz, CDCl_3)



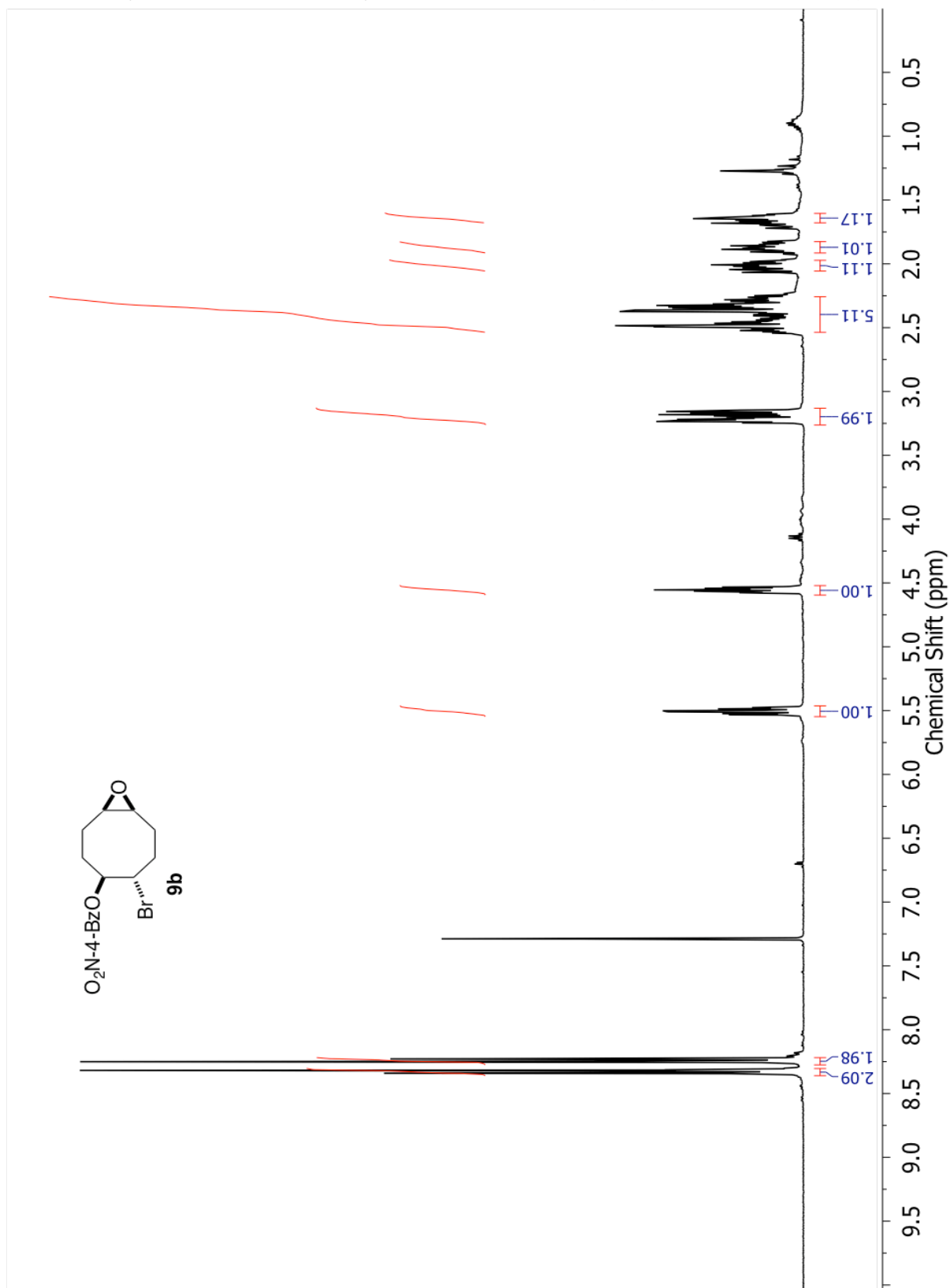
^1H NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 4-nitrobenzoate (**8b**) (400 MHz, CDCl_3)



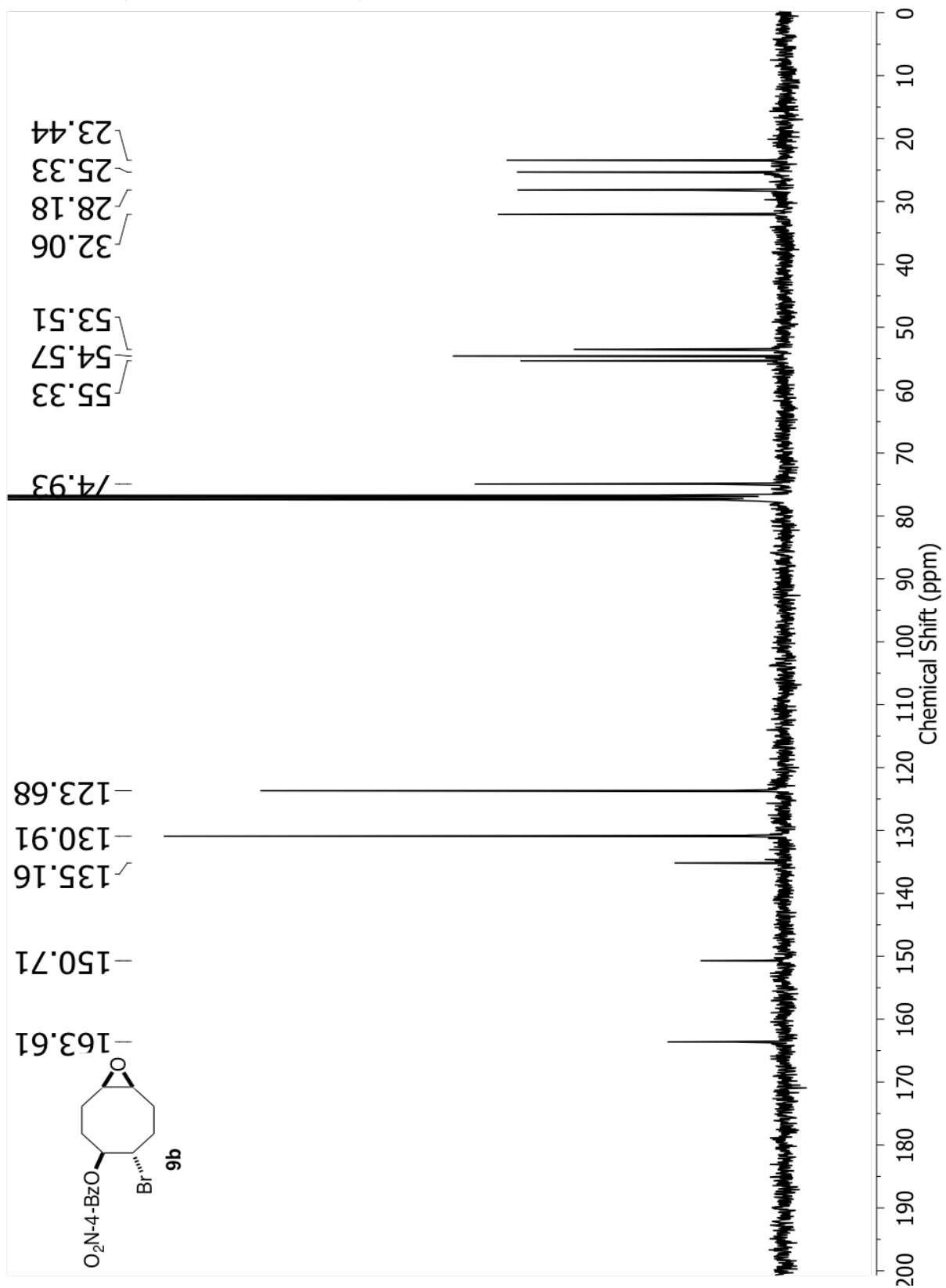
^{13}C NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 4-nitrobenzoate (**8b**) (100 MHz, CDCl_3)



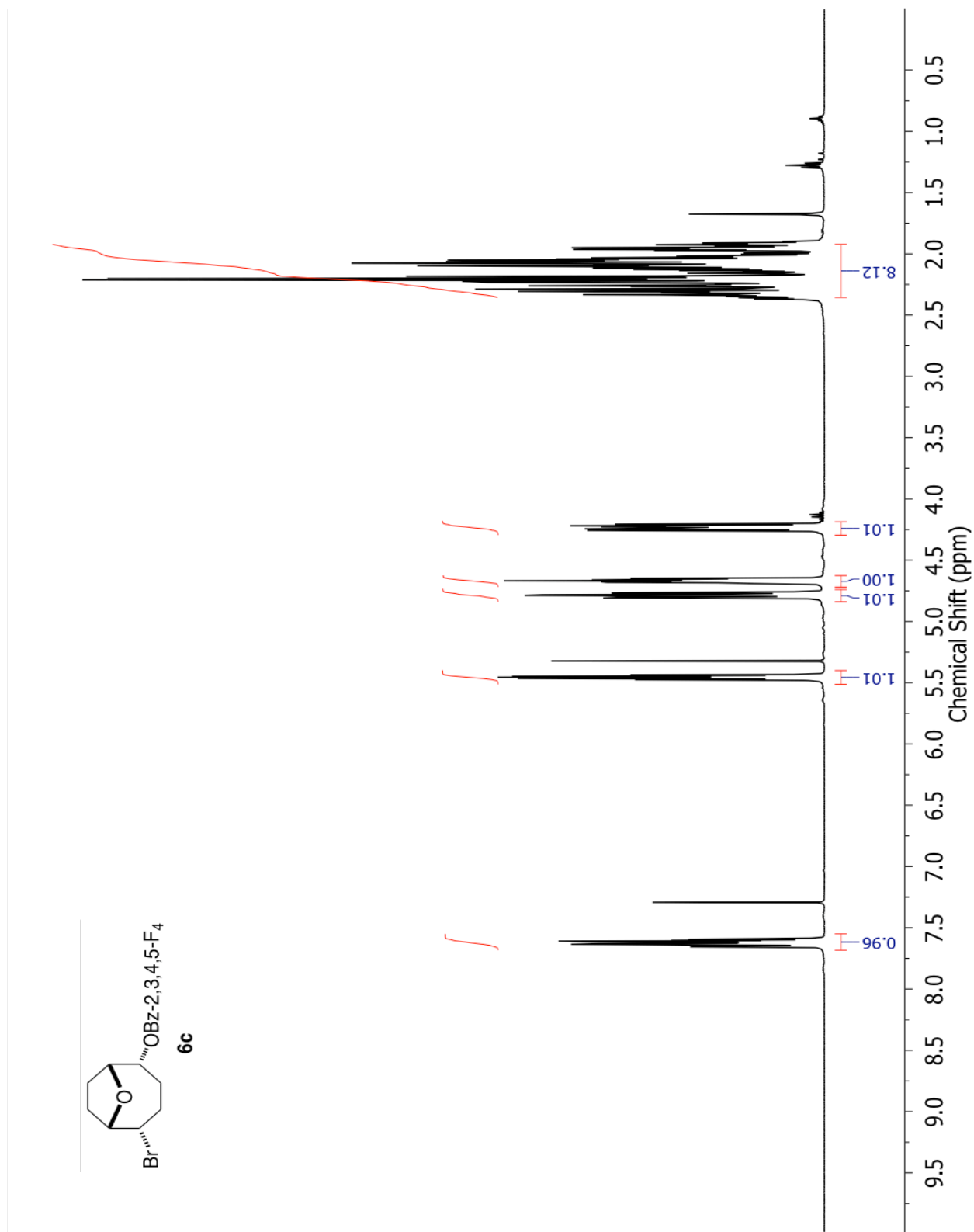
^1H NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 4-nitrobenzoate (**9b**) (400 MHz, CDCl_3)



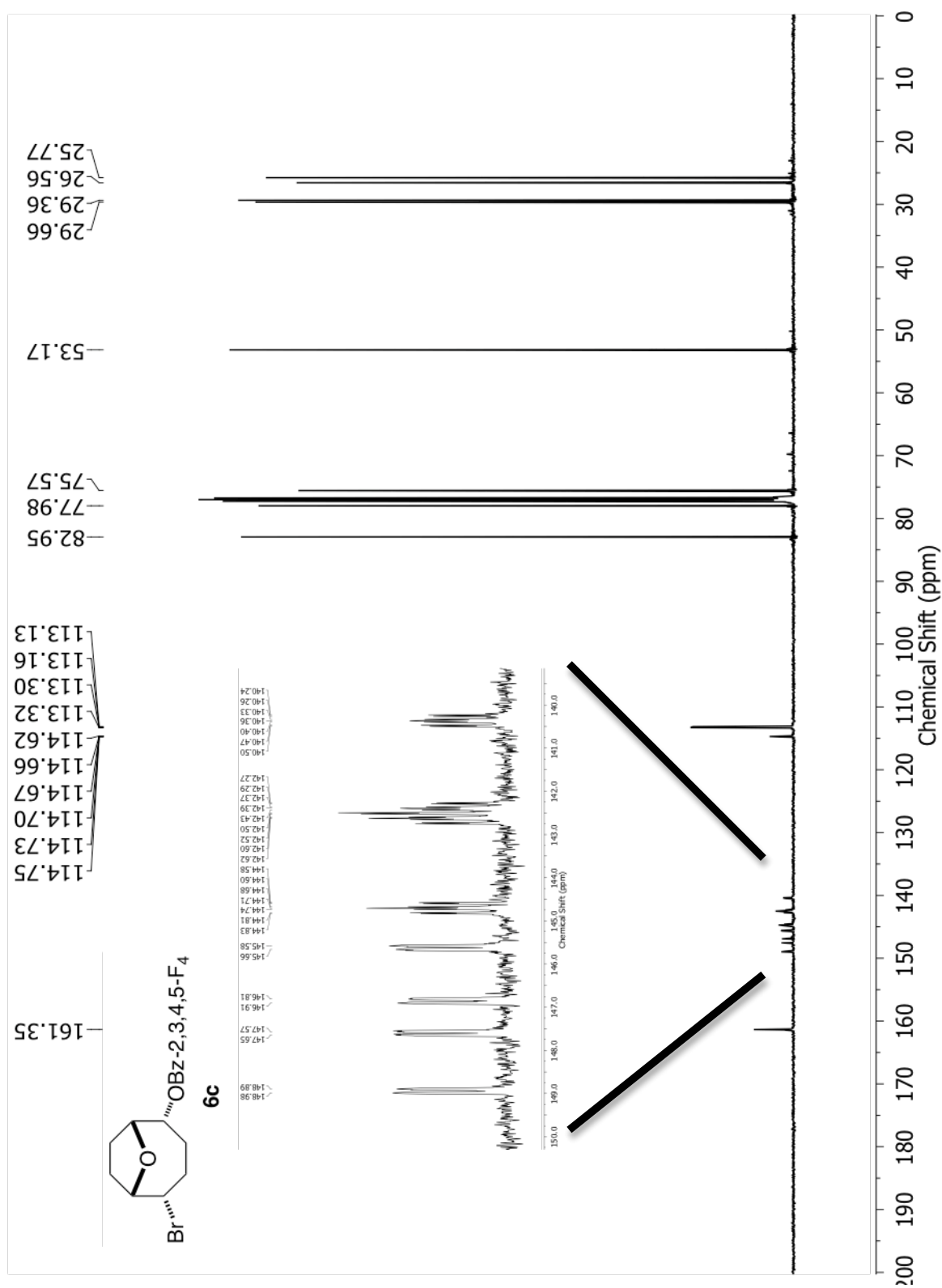
^{13}C NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 4-nitrobenzoate (**9b**) (100 MHz, CDCl_3)



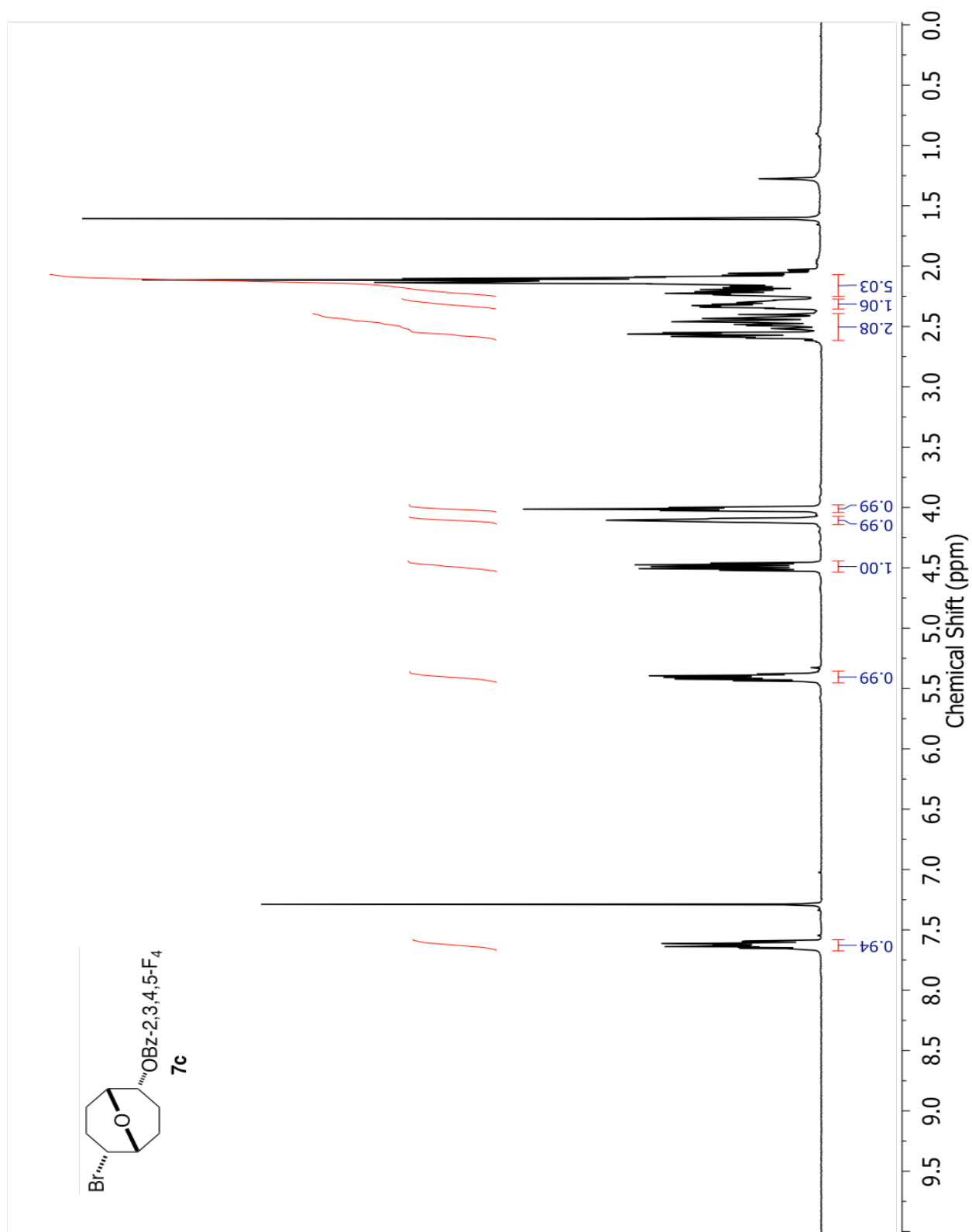
^1H NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl 2,3,4,5-tetrafluorobenzoate (**6c**) (400 MHz, CDCl_3)



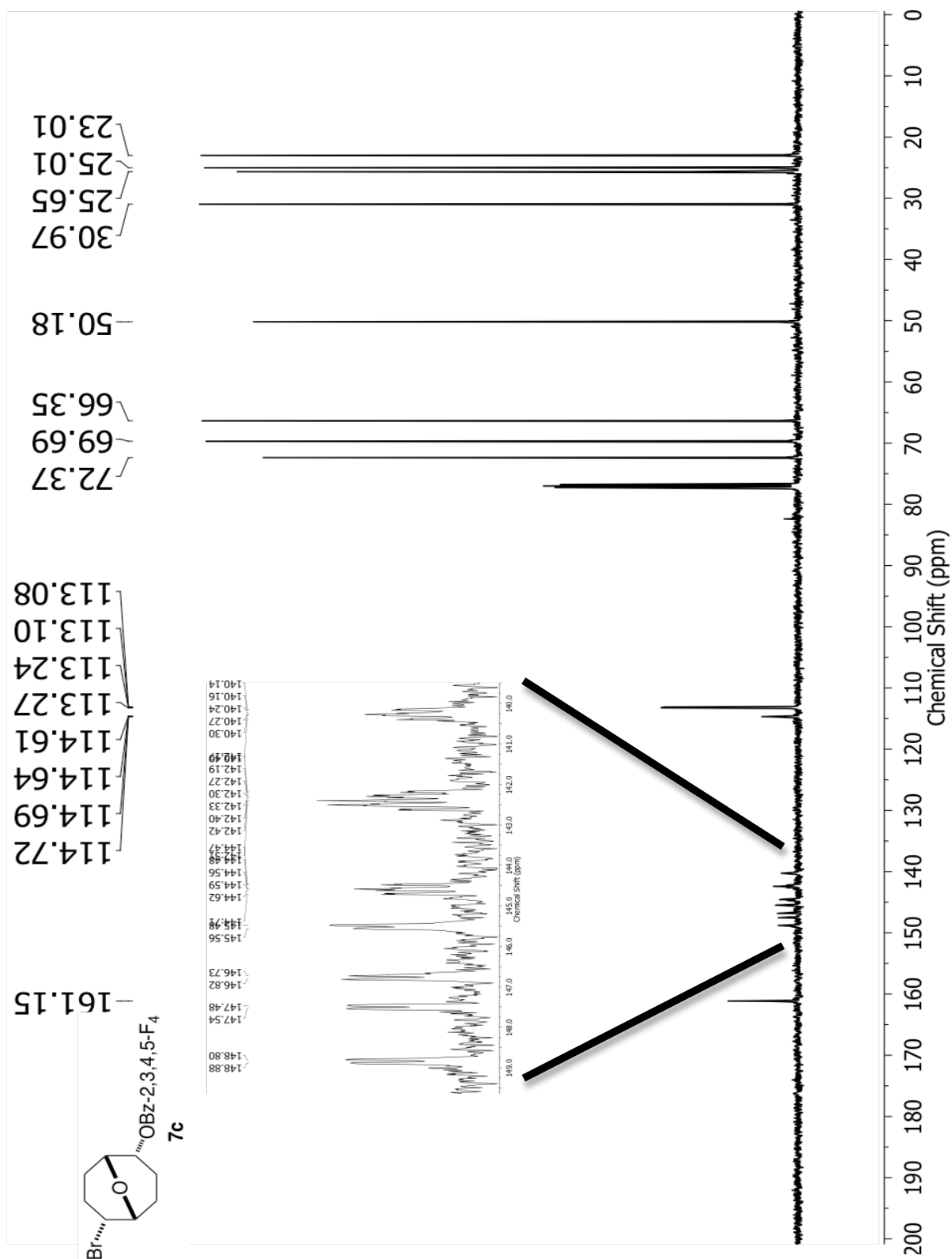
^{13}C NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-yl 2,3,4,5-tetrafluorobenzoate (**6c**) (125 MHz, CDCl_3)



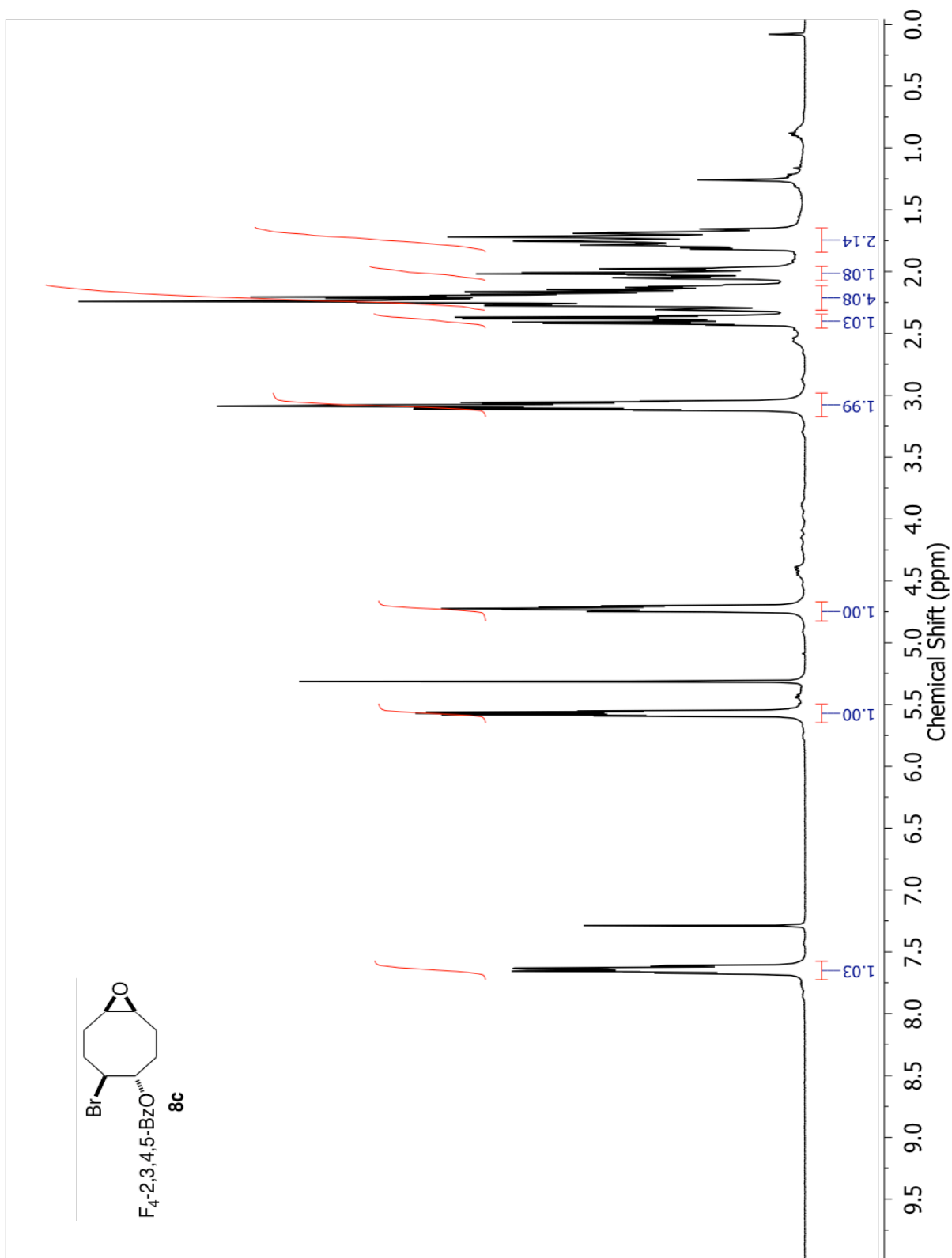
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl 2,3,4,5-tetrafluorobenzoate (**7c**) (400 MHz, CDCl_3)



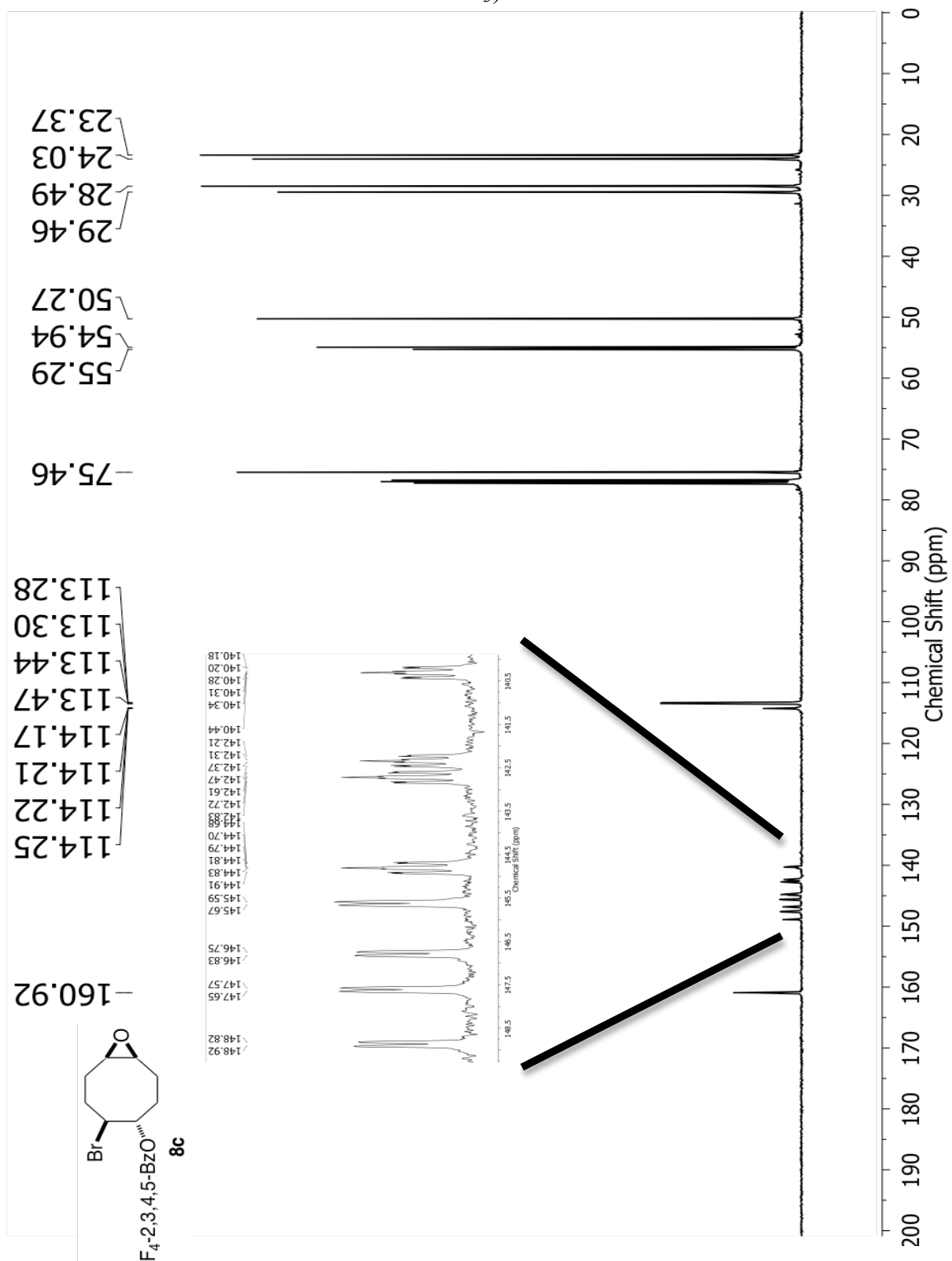
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-yl 2,3,4,5-tetrafluorobenzoate (**7c**) (125 MHz, CDCl_3)



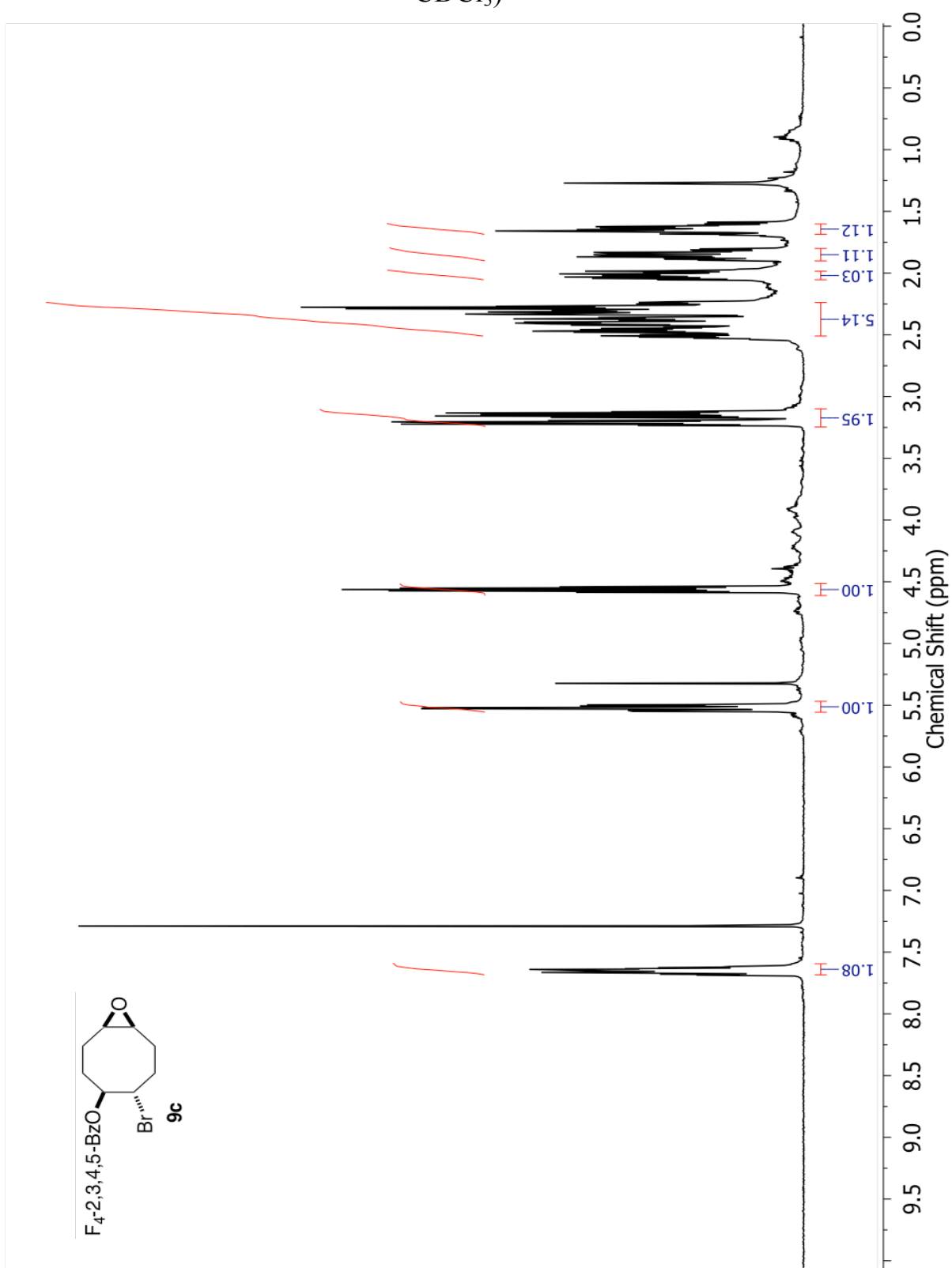
^1H NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 2,3,4,5-tetrafluorobenzoate (**8c**) (400 MHz, CDCl_3)



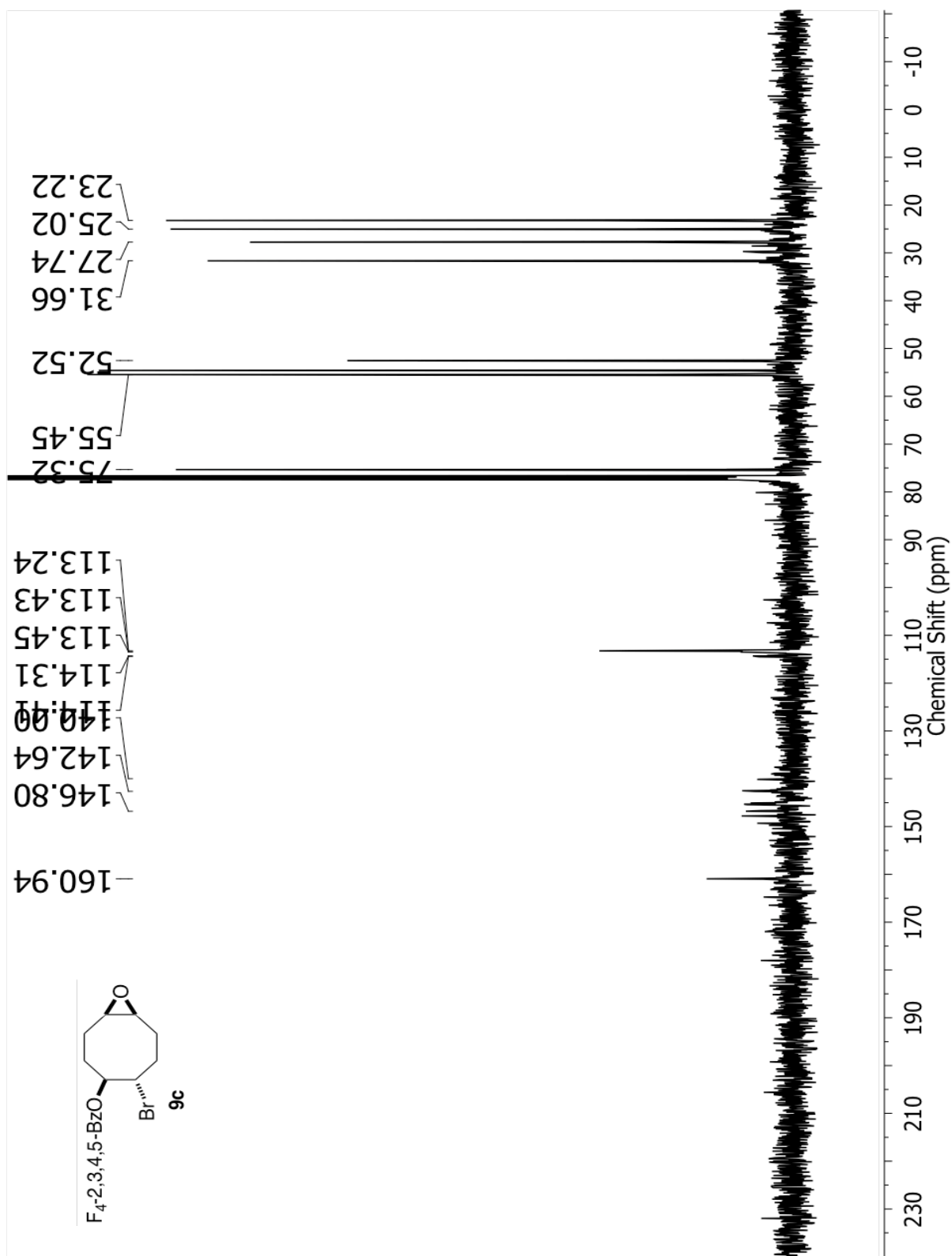
^{13}C NMR Spectrum of (1*S**,4*S**,5*S**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 2,3,4,5-tetrafluorobenzoate (**8c**) (125 MHz, CDCl_3)



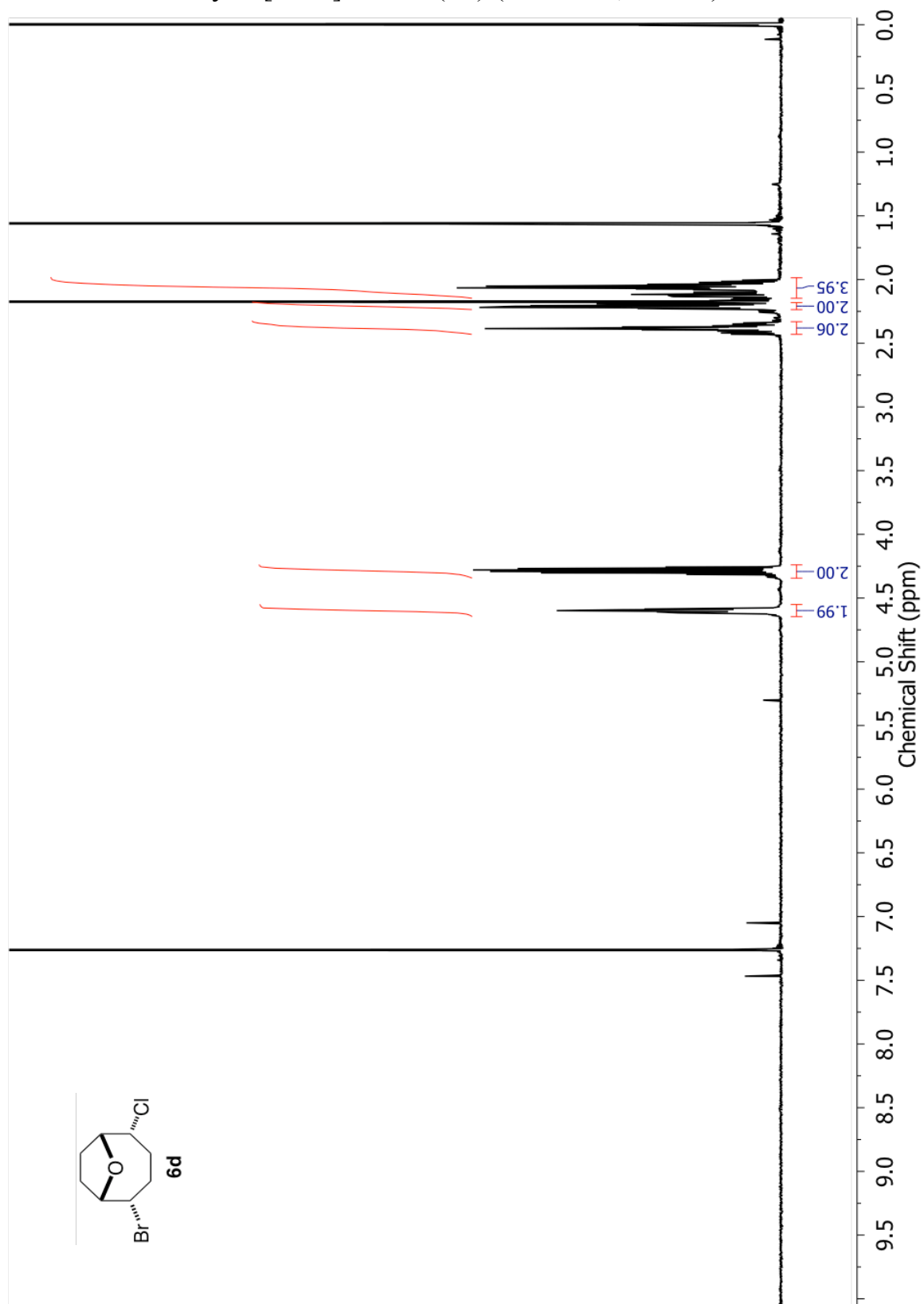
^1H NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 2,3,4,5-tetrafluorobenzoate (**9c**) (400 MHz, CDCl_3)



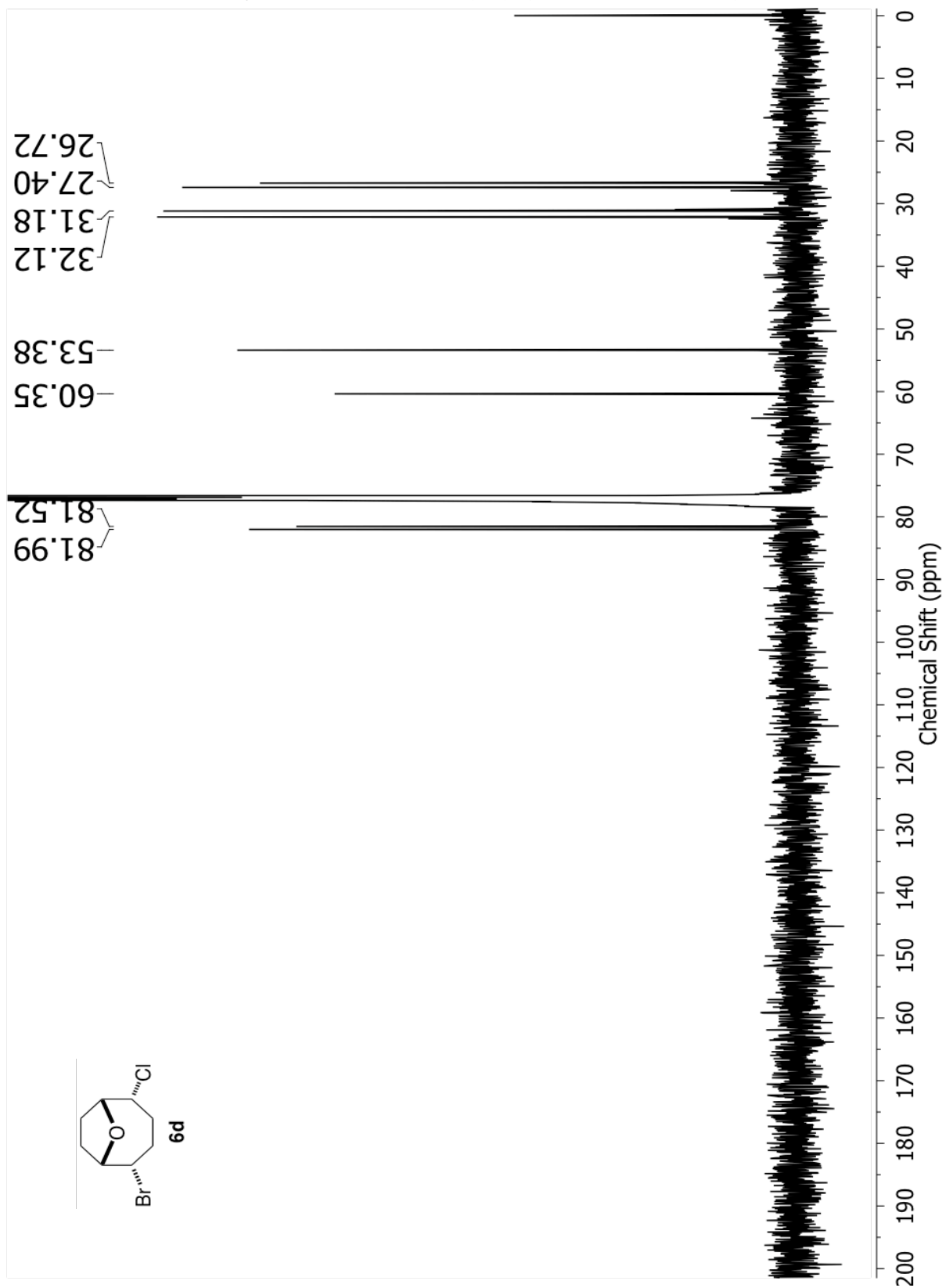
^{13}C NMR Spectrum of (1*S**,4*R**,5*R**,8*R**)-5-Bromo-9-oxabicyclo[6.1.0]nonan-4-yl 2,3,4,5-tetrafluorobenzoate (**9c**) (100 MHz, CDCl_3)



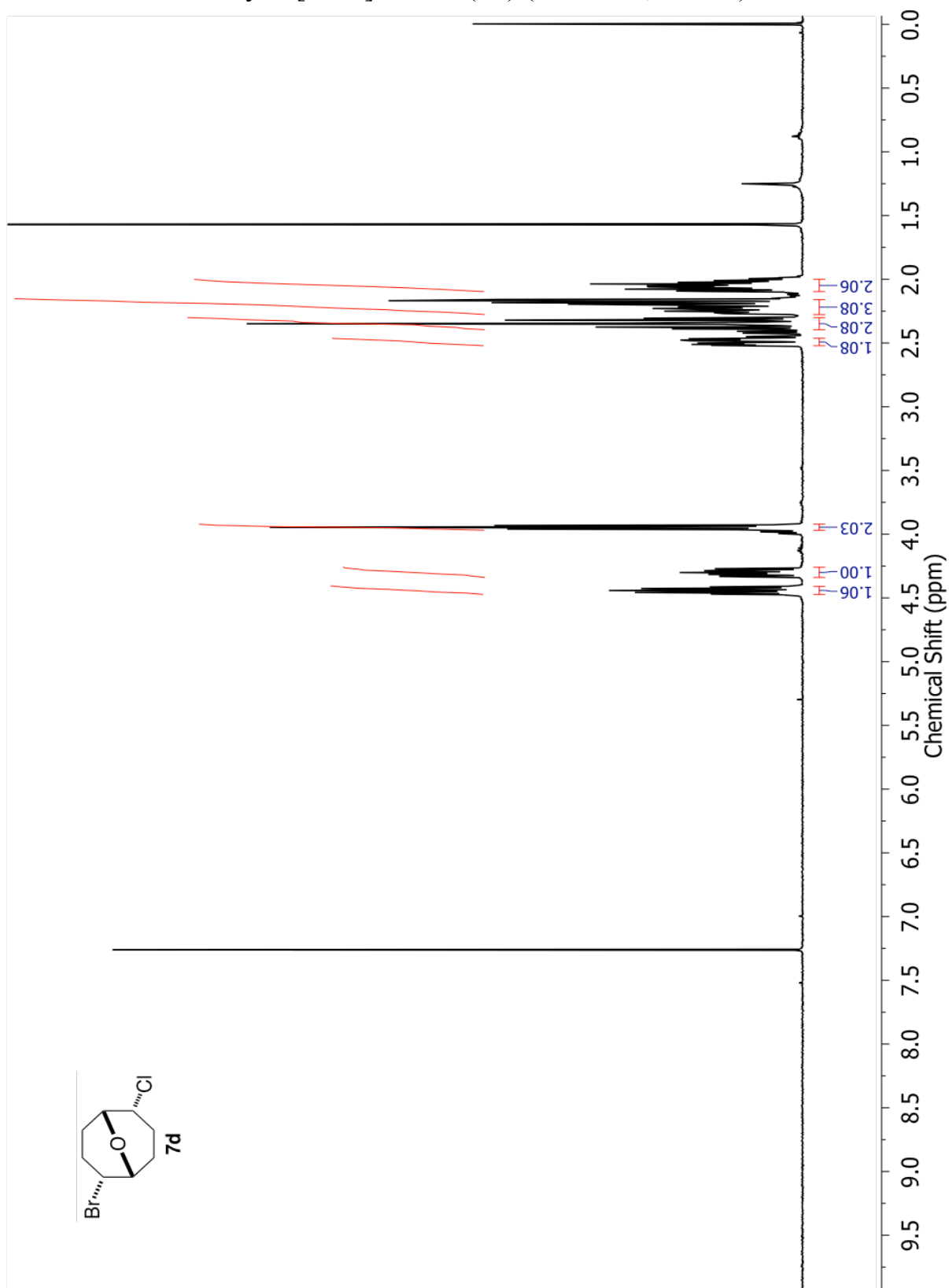
^1H NMR Spectrum of (1*S**,2*S**,5*R**,6*R**)-2-Bromo-5-chloro-9-oxabicyclo[4.2.1]nonane (**6d**) (500 MHz, CDCl_3)



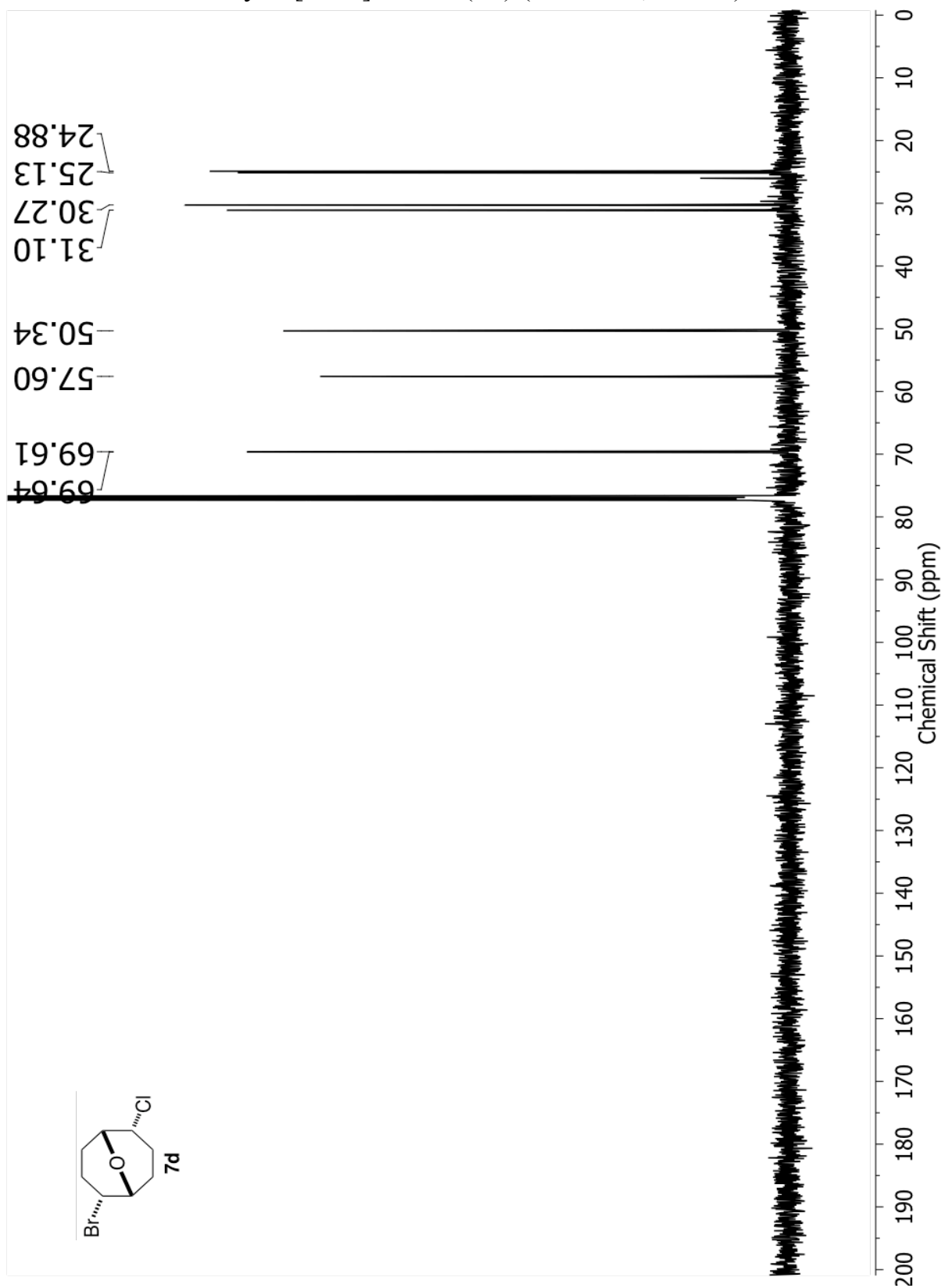
^{13}C NMR Spectrum of (1*S**,2*S**,5*R**,6*R**)-2-Bromo-5-chloro-9-oxabicyclo[4.2.1]nonane (**6d**) (125 MHz, CDCl_3)



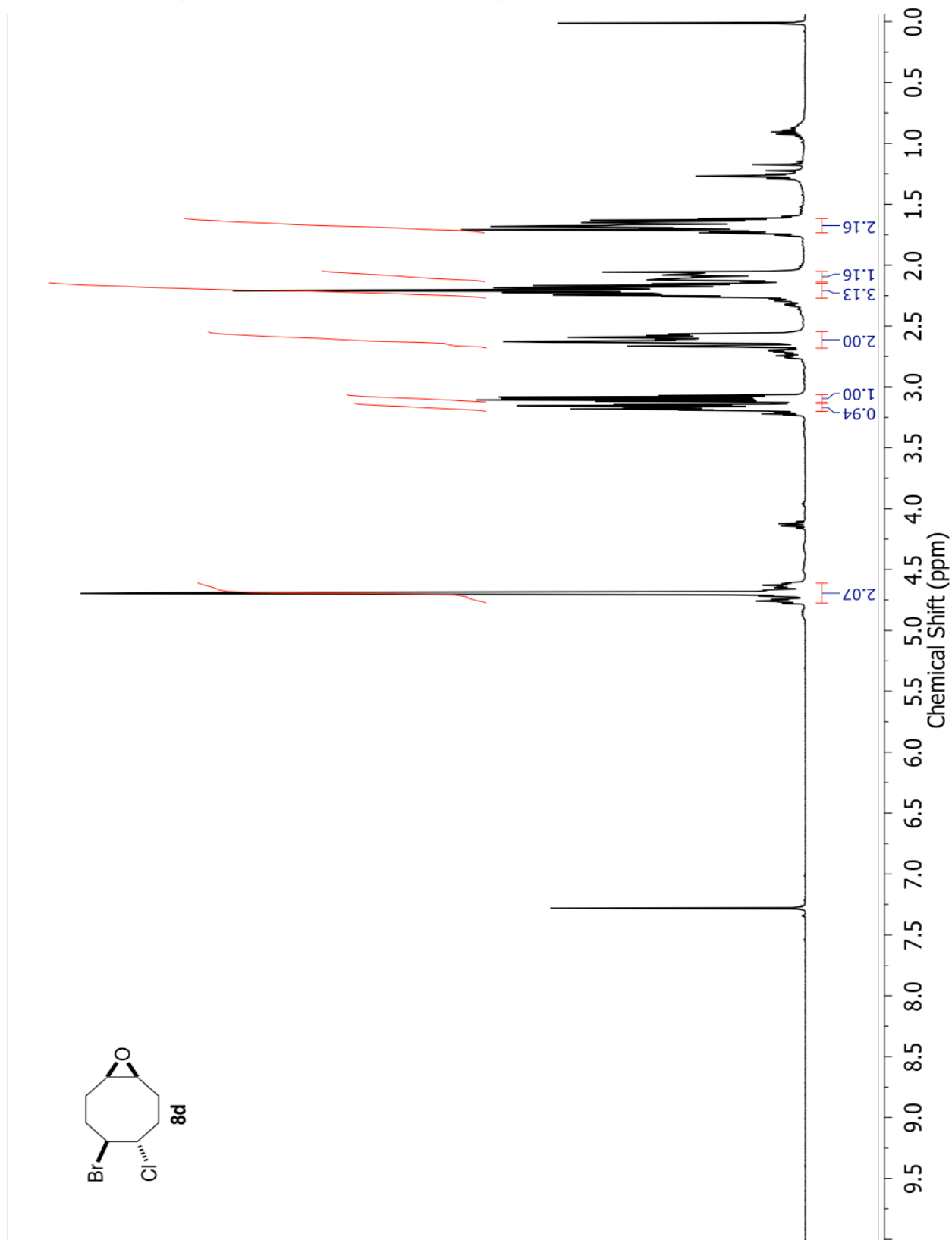
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-chloro-9-oxabicyclo[3.3.1]nonane (**7d**) (400 MHz, CDCl_3)



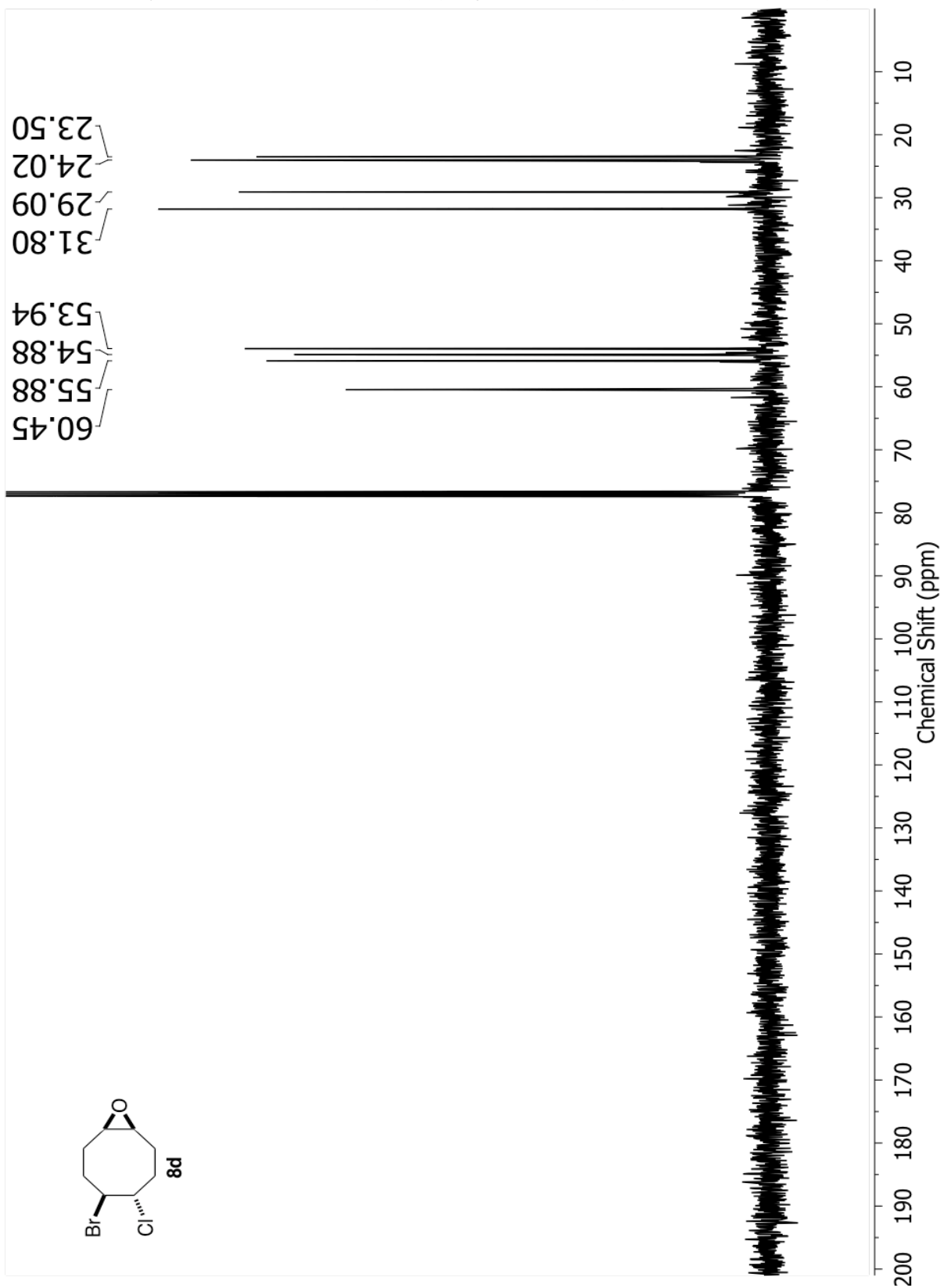
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-chloro-9-oxabicyclo[3.3.1]nonane (**7d**) (125 MHz, CDCl_3)



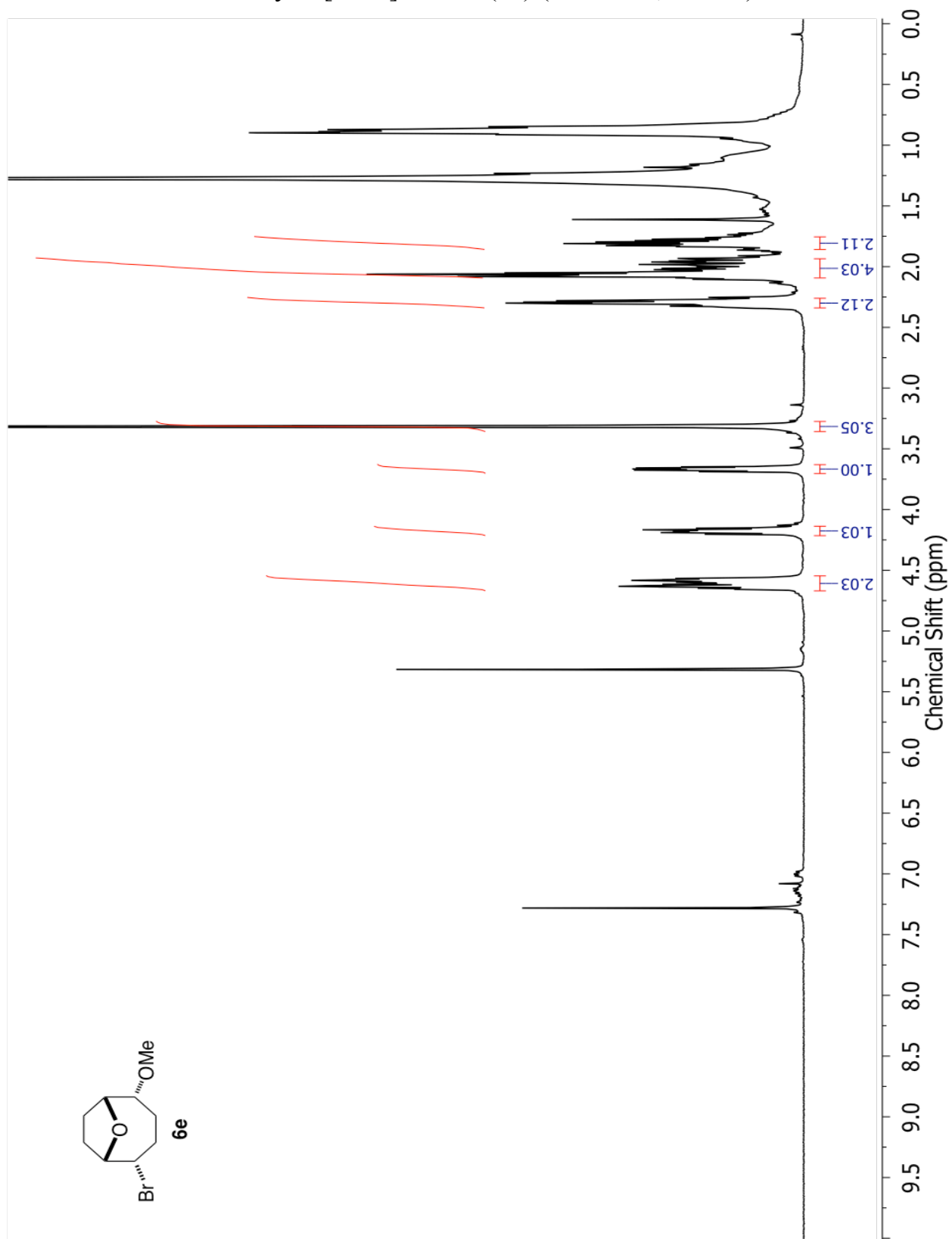
^1H NMR Spectrum of (1*R**,4*S**,5*S**,8*S**)-4-Bromo-5-chloro-9-oxabicyclo[6.1.0]nonane (**8d**) (major isomer) (400 MHz, CDCl_3).



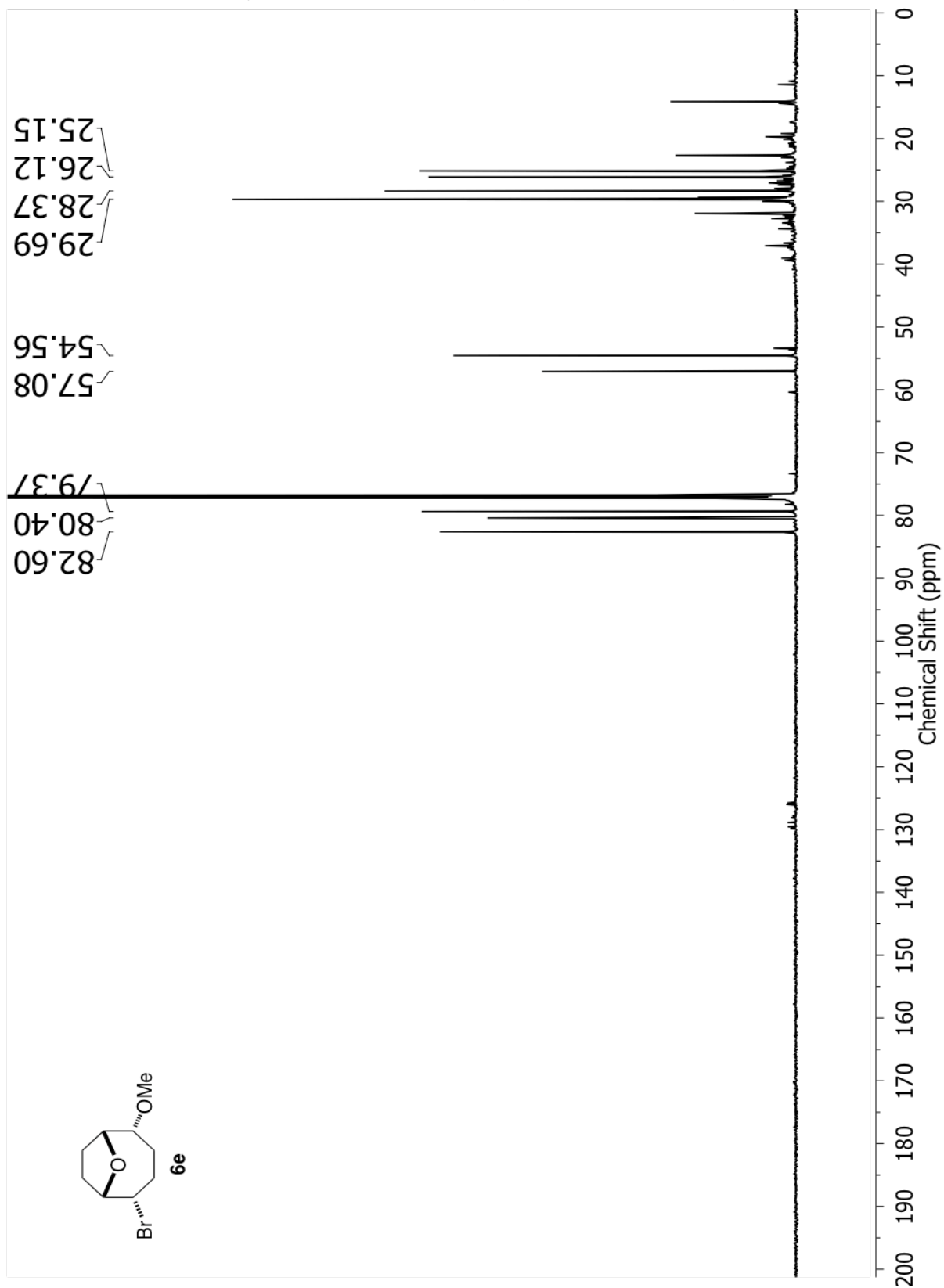
^{13}C NMR Spectrum of (1*R**,4*S**,5*S**,8*S**)-4-Bromo-5-chloro-9-oxabicyclo[6.1.0]nonane (**8d**) (major isomer) (100 MHz, CDCl_3)



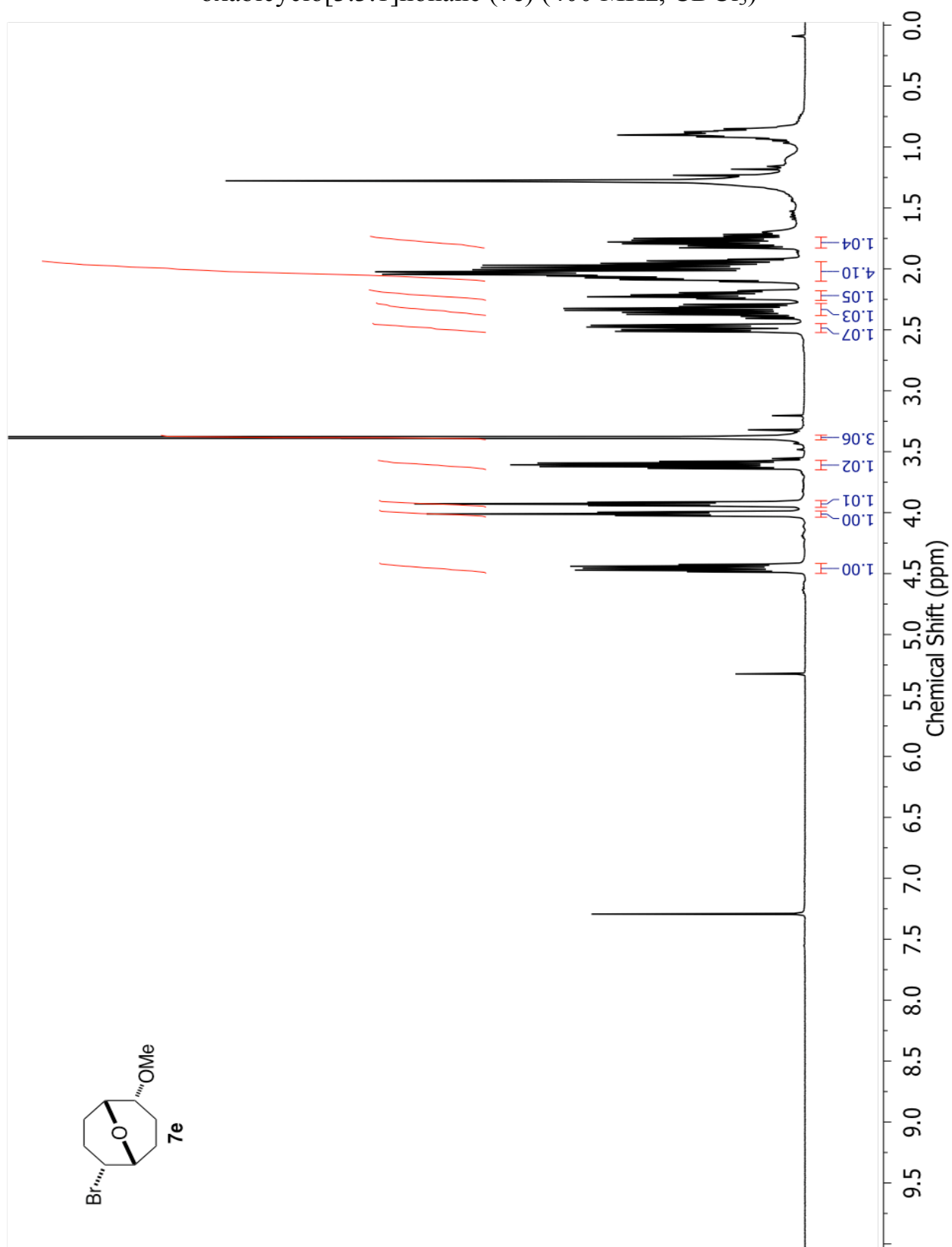
^1H NMR Spectrum of (1*S**,2*S**,5*R**,6*R**)-2-Bromo-5-methoxy-9-oxabicyclo[4.2.1]nonane (**6e**) (400 MHz, CDCl_3)



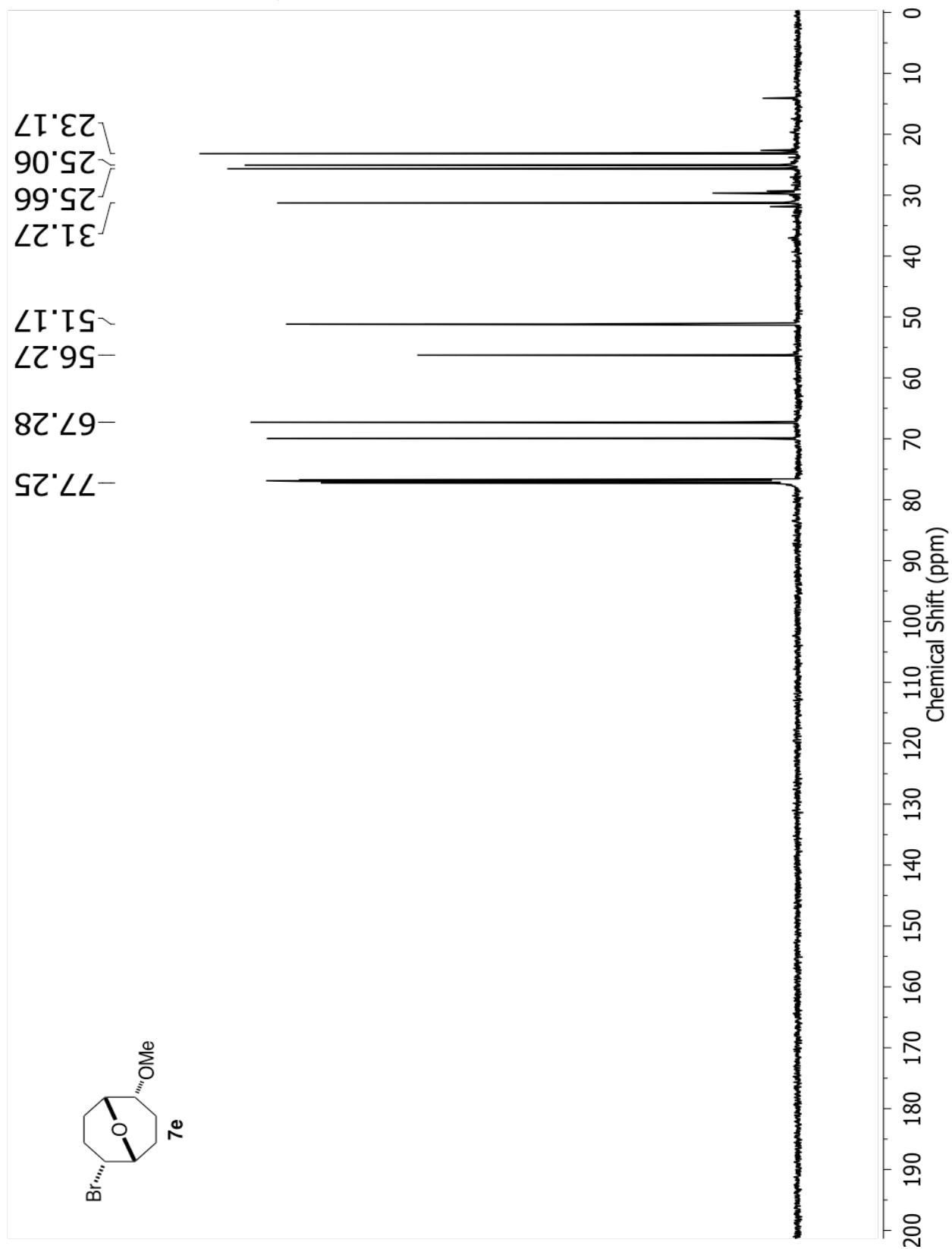
^{13}C NMR Spectrum of (1*S**,2*S**,5*R**,6*R**)-2-Bromo-5-methoxy-9-oxabicyclo[4.2.1]nonane (**6e**) (125 MHz, CDCl_3)



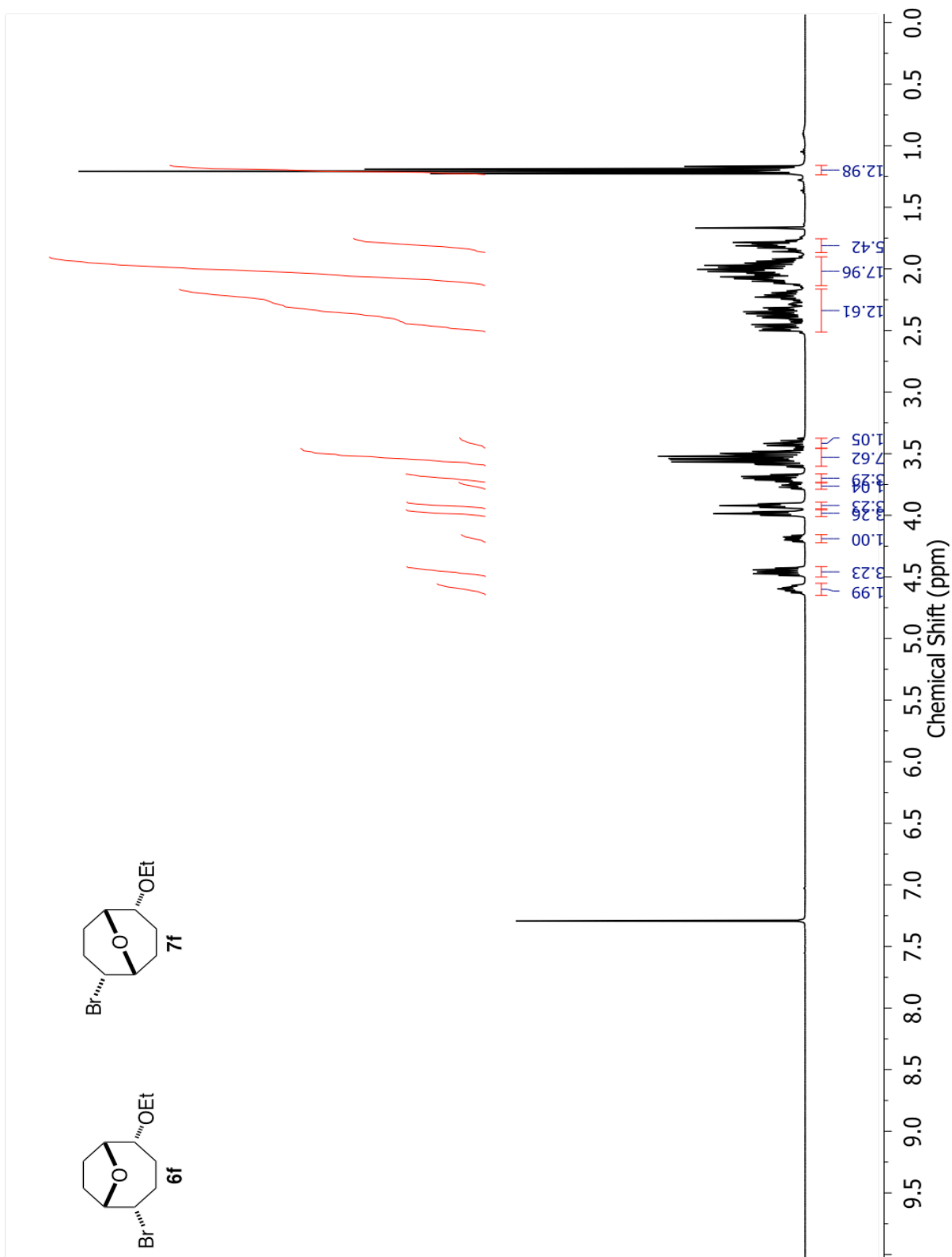
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-methoxy-9-oxabicyclo[3.3.1]nonane (**7e**) (400 MHz, CDCl_3)



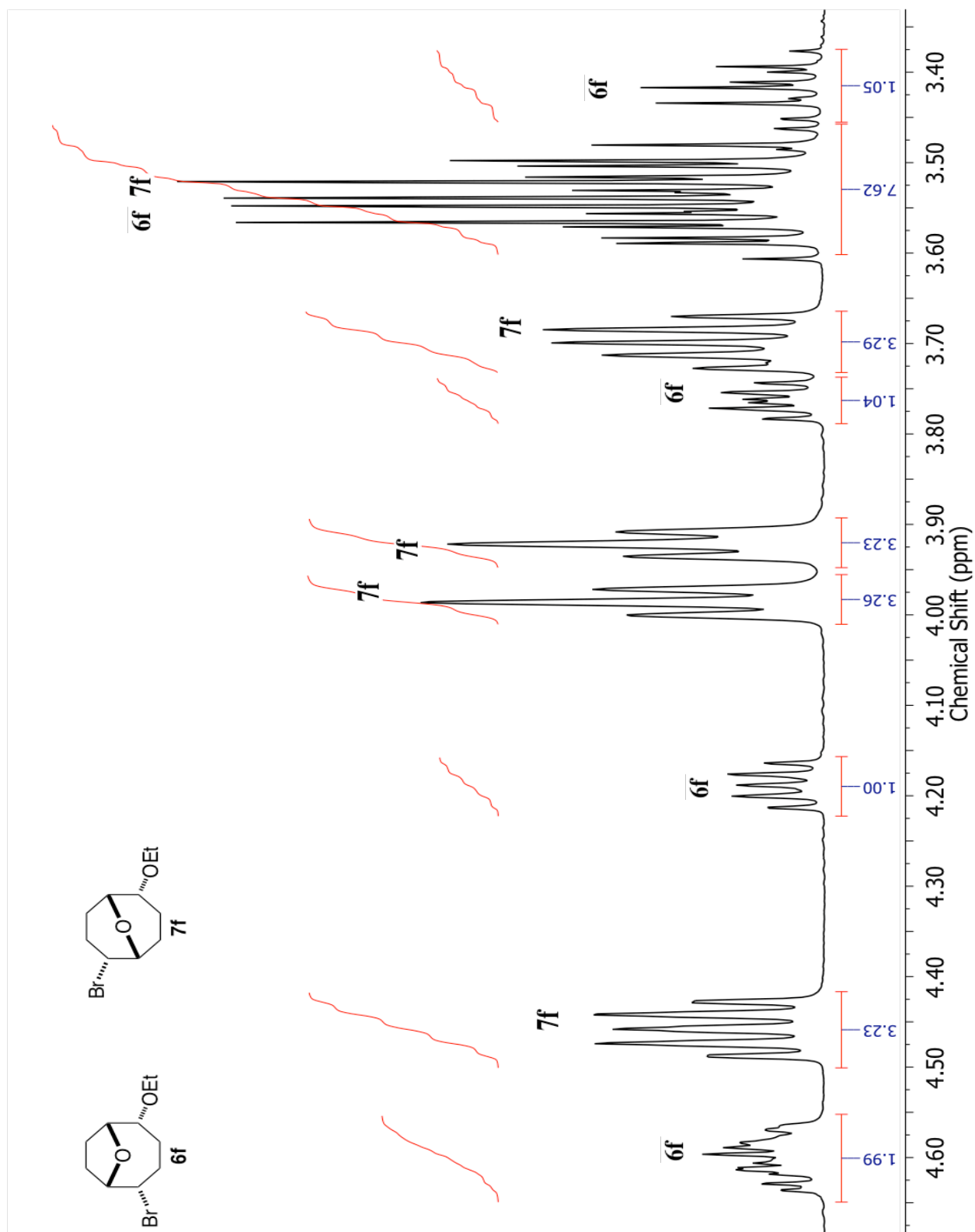
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-methoxy-9-oxabicyclo[3.3.1]nonane (**7e**) (125 MHz, CDCl_3)



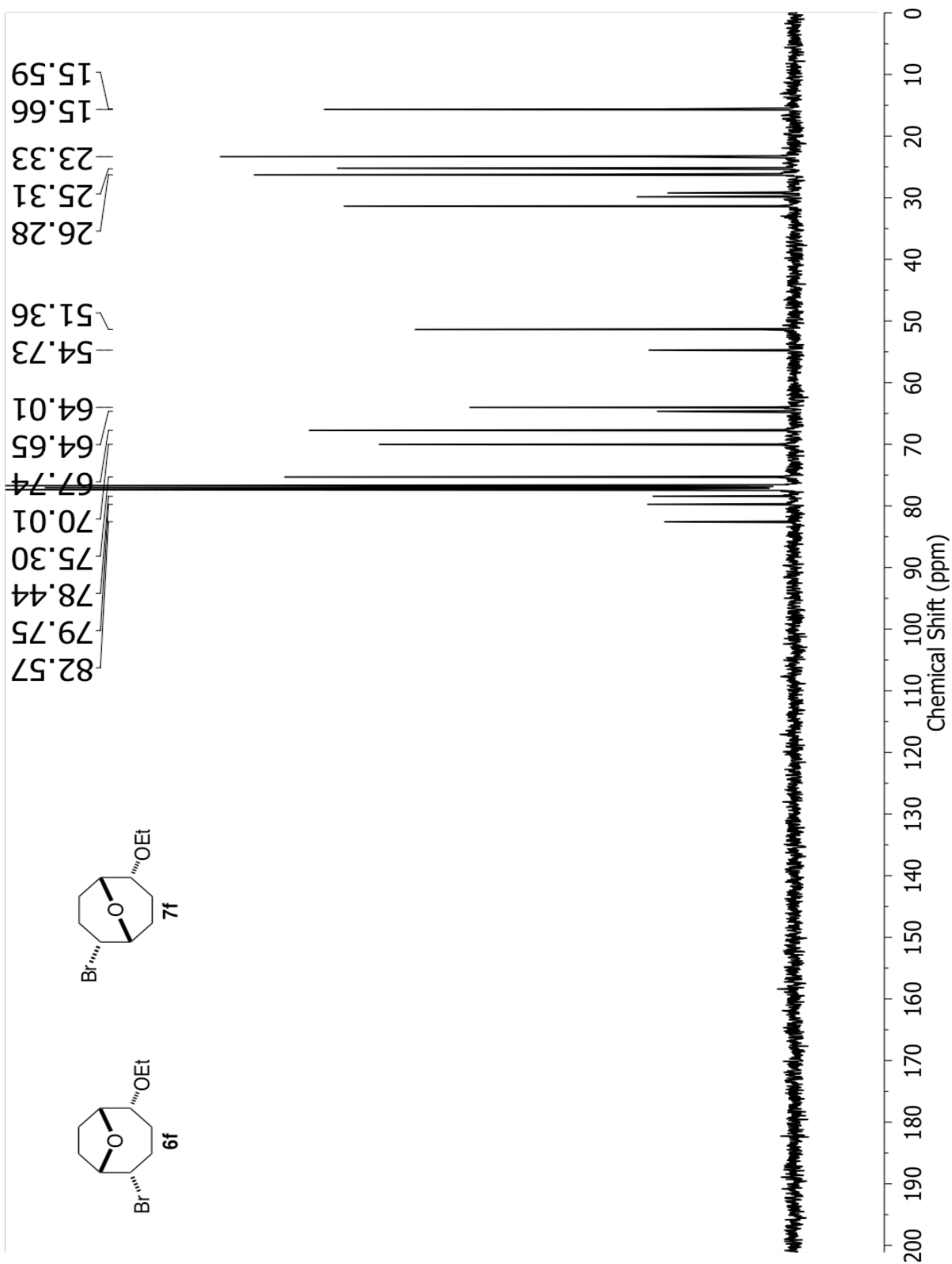
^1H NMR Spectrum of (1*S**,2*S**,5*R**,6*R**)-2-Bromo-5-ethoxy-9-oxabicyclo[4.2.1]nonane (**6f**) and (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-ethoxy-9-oxabicyclo[3.3.1]nonane (**7f**) (400 MHz, CDCl_3)



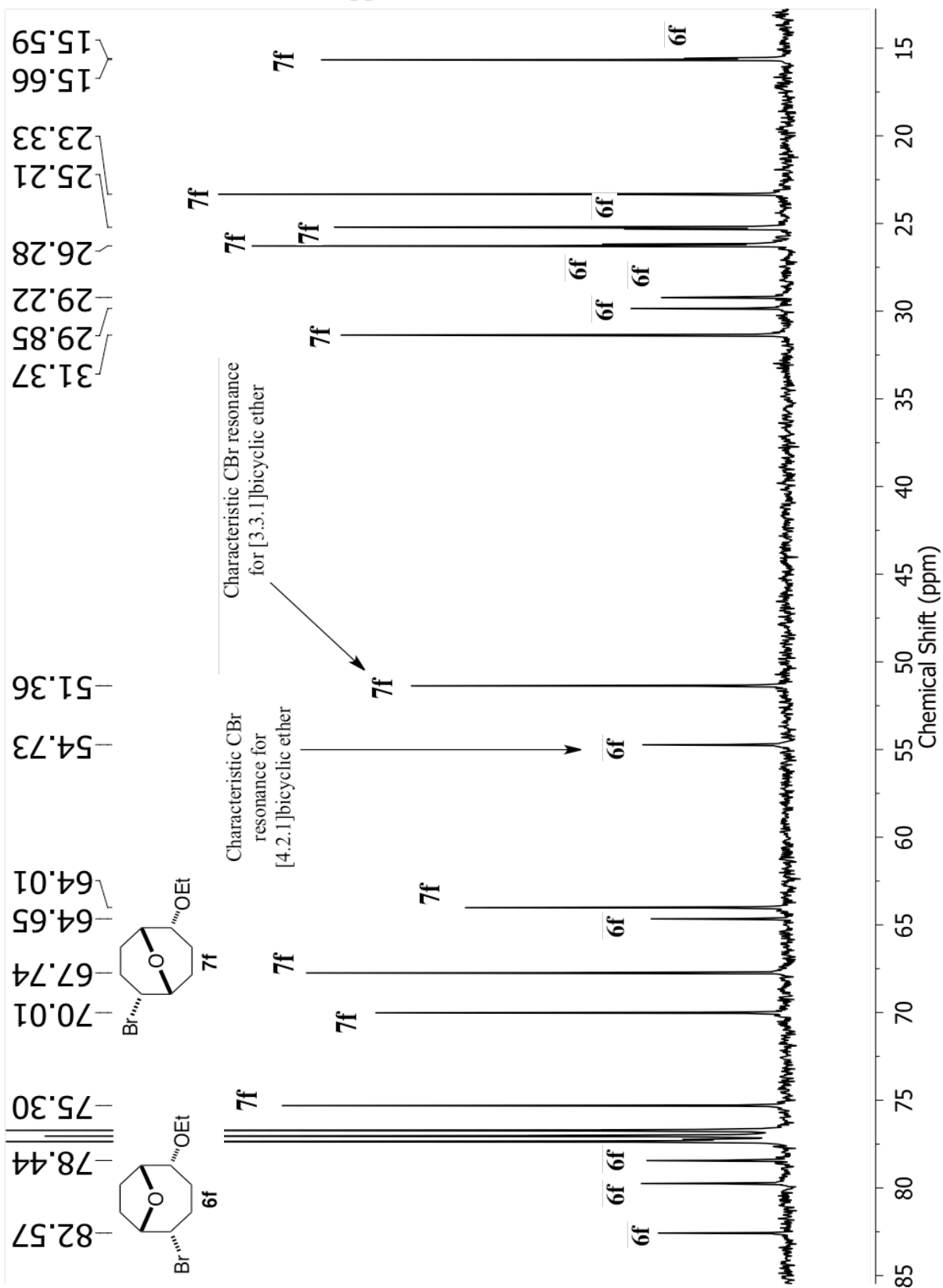
Expansion of ^1H NMR Spectrum of **6f** and **7f** in the region of 3.30-4.70 ppm
(400 MHz, CDCl_3) - Ratio of **6f** : **7f** = 1 : 3.2 as determined by integration
of the resonances at 4.20 and 3.92 ppm respectively



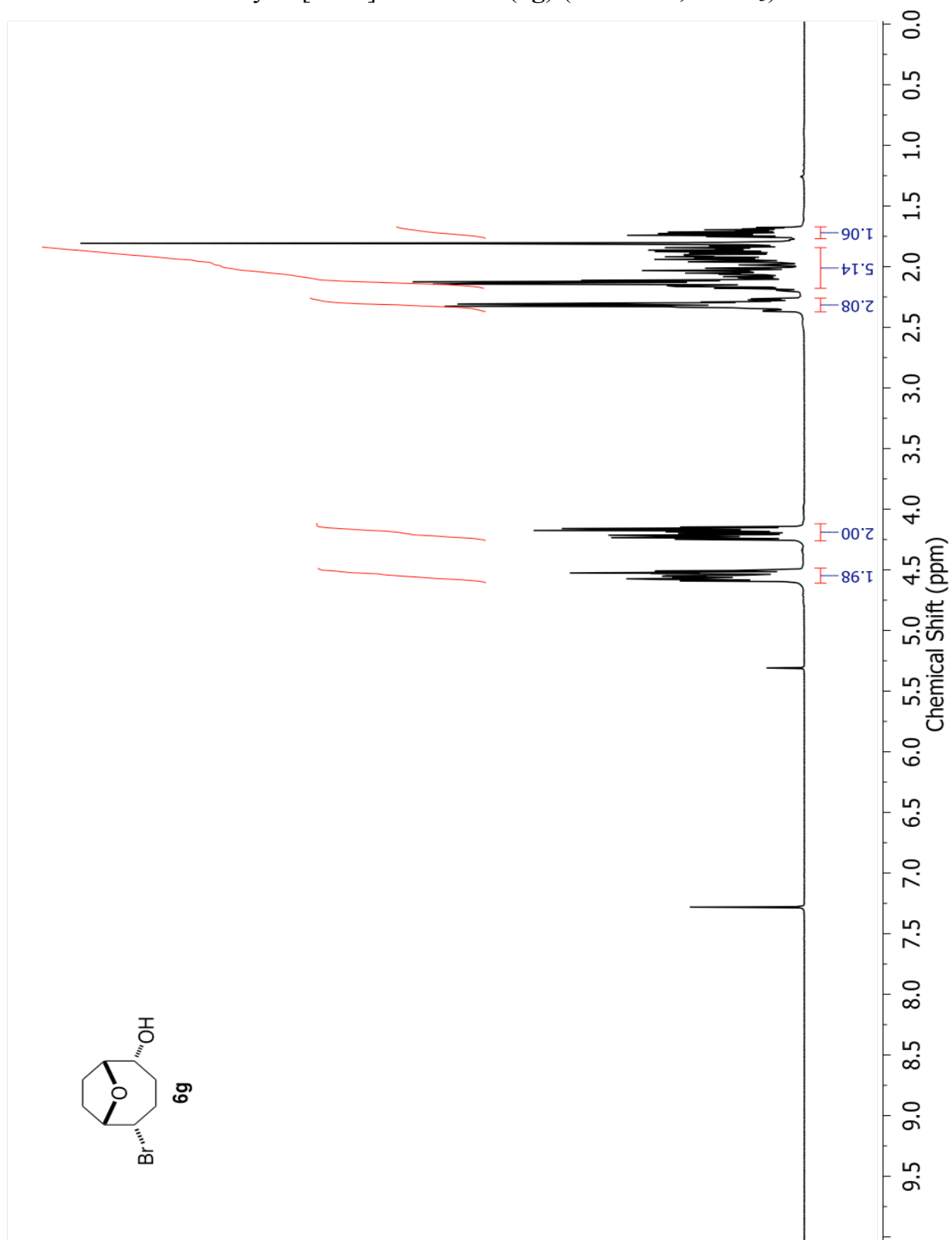
^{13}C NMR Spectrum of (1*S**,2*S**,5*R**,6*R**)-2-Bromo-5-ethoxy-9-oxabicyclo[4.2.1]nonane (**6f**) and (1*R**,2*R**,5*R**,6*R**)-2-Bromo-6-ethoxy-9-oxabicyclo[3.3.1]nonane (**7f**) (100 MHz, CDCl_3)



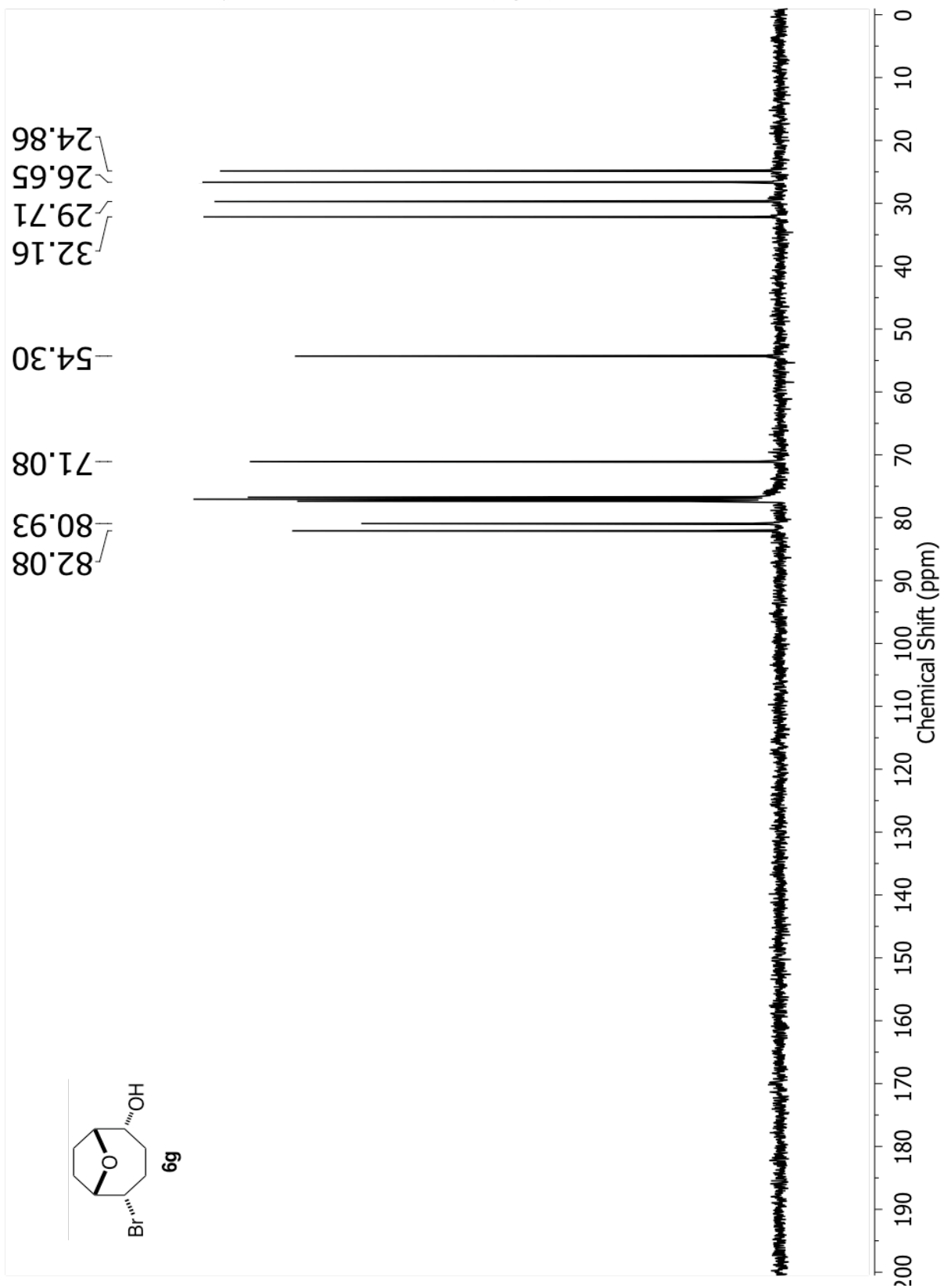
Expansion of ^{13}C NMR Spectrum of **6f** and **7f** in the region of 12-85 ppm (100 MHz, CDCl_3)



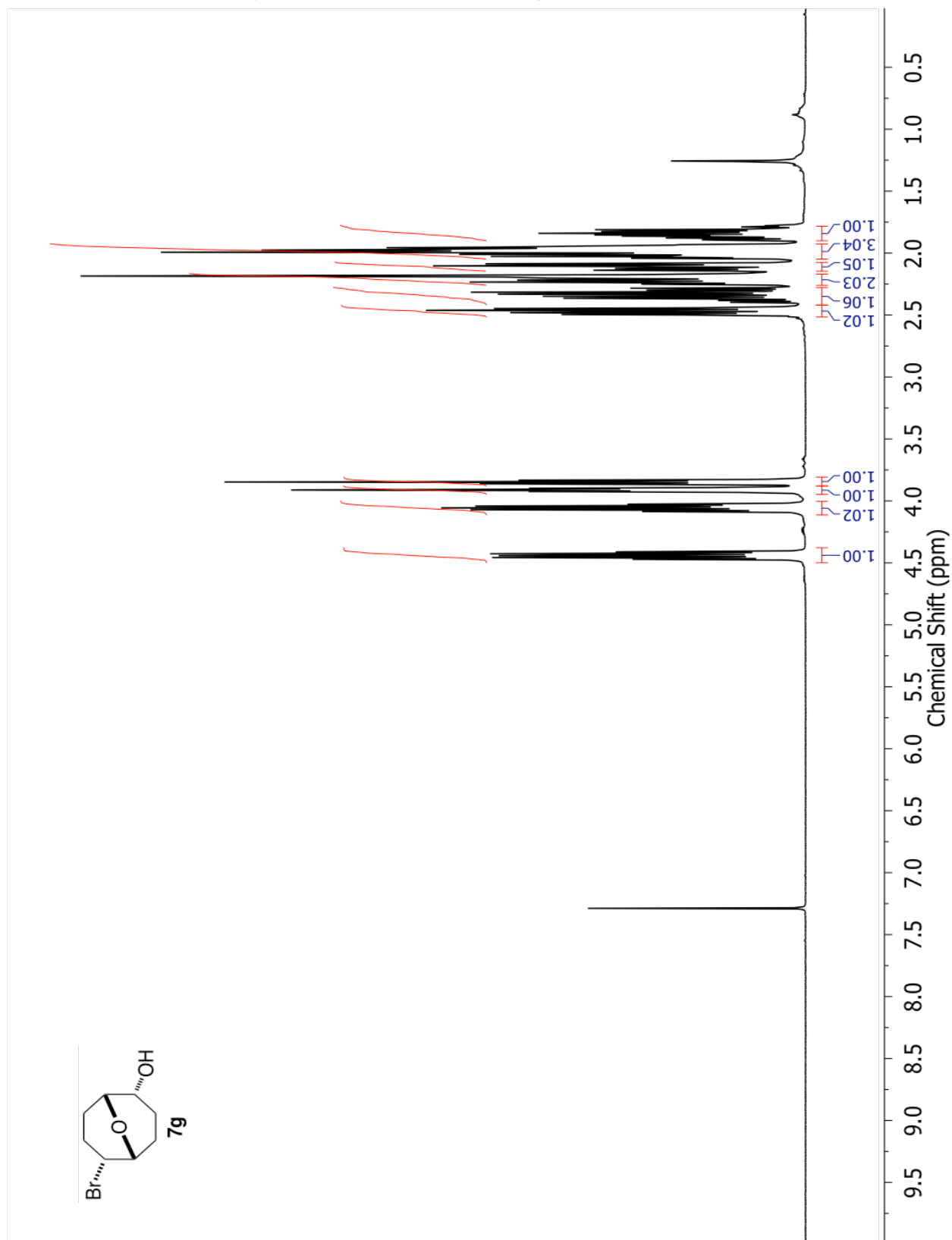
^1H NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-ol (**6g**) (400 MHz, CDCl_3)



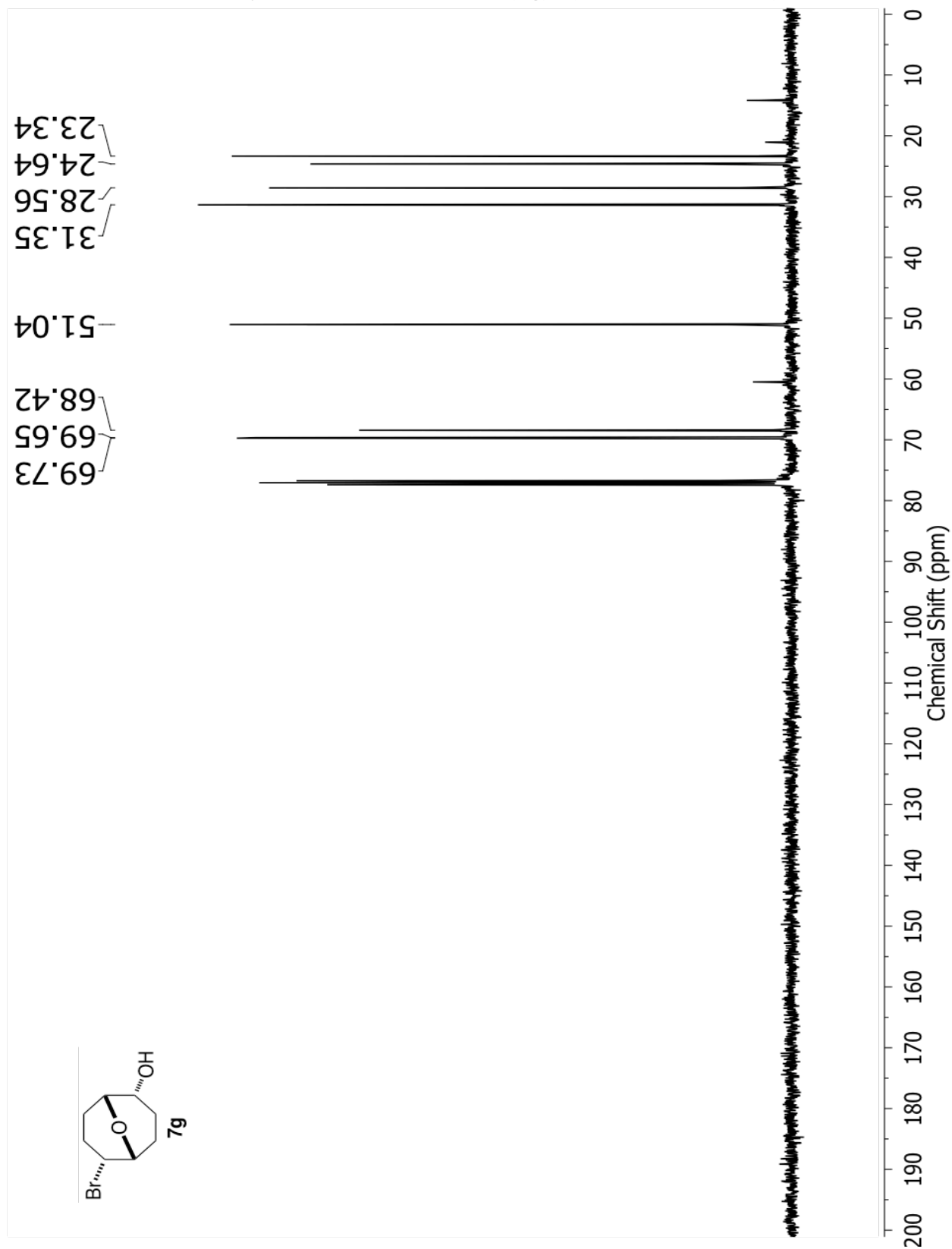
^{13}C NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]nonan-2-ol (**6g**) (100 MHz, CDCl_3)



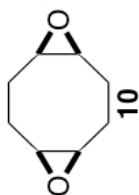
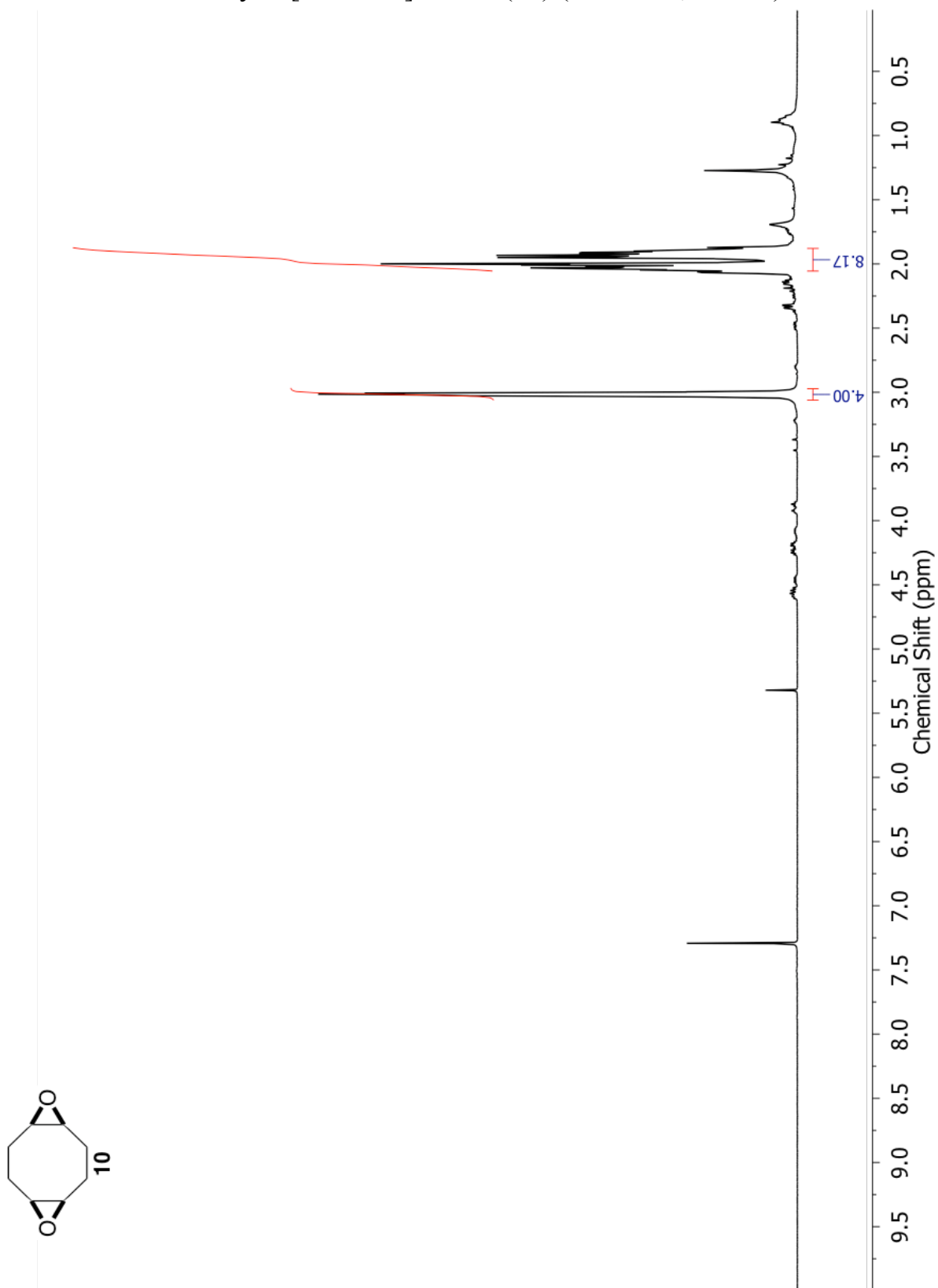
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-ol (**7g**) (400 MHz, CDCl_3)



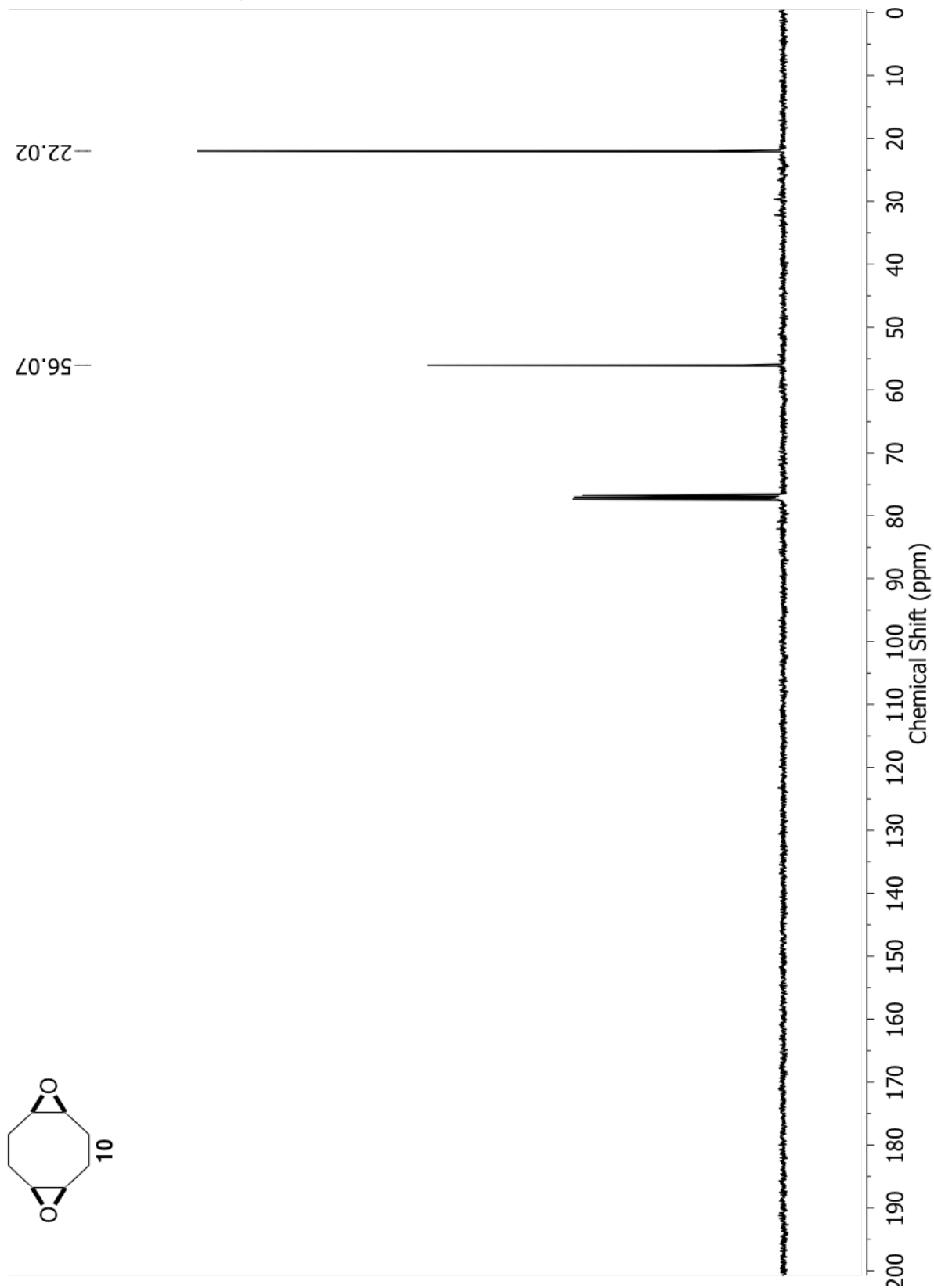
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]nonan-2-ol (**7g**) (100 MHz, CDCl_3)



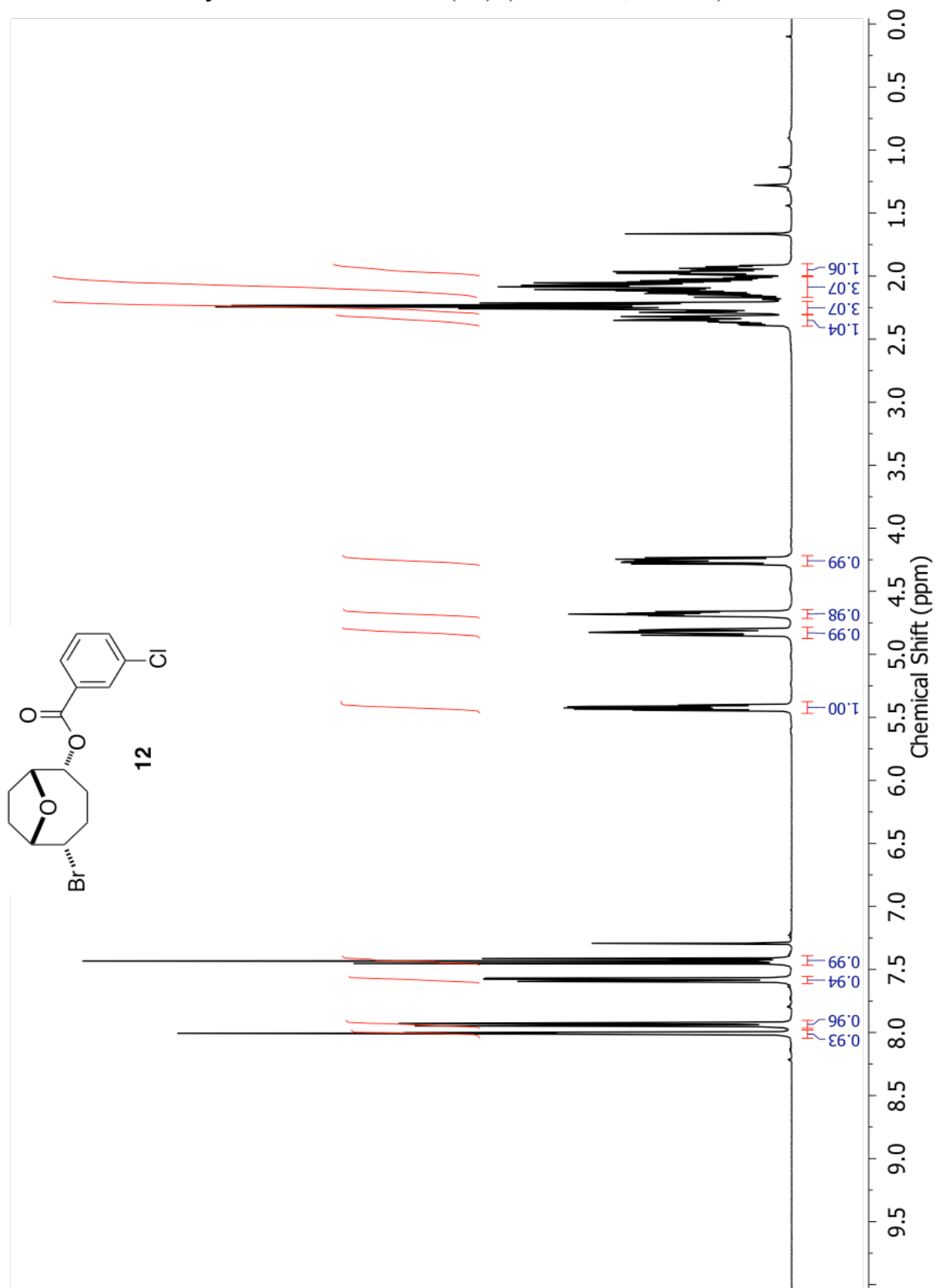
^1H NMR Spectrum of (1*R**,4*S**,6*R**,9*S**)-5,10-Dioxatricyclo[7.1.0.0^{4,6}]decane (**10**) (400 MHz, CDCl_3)



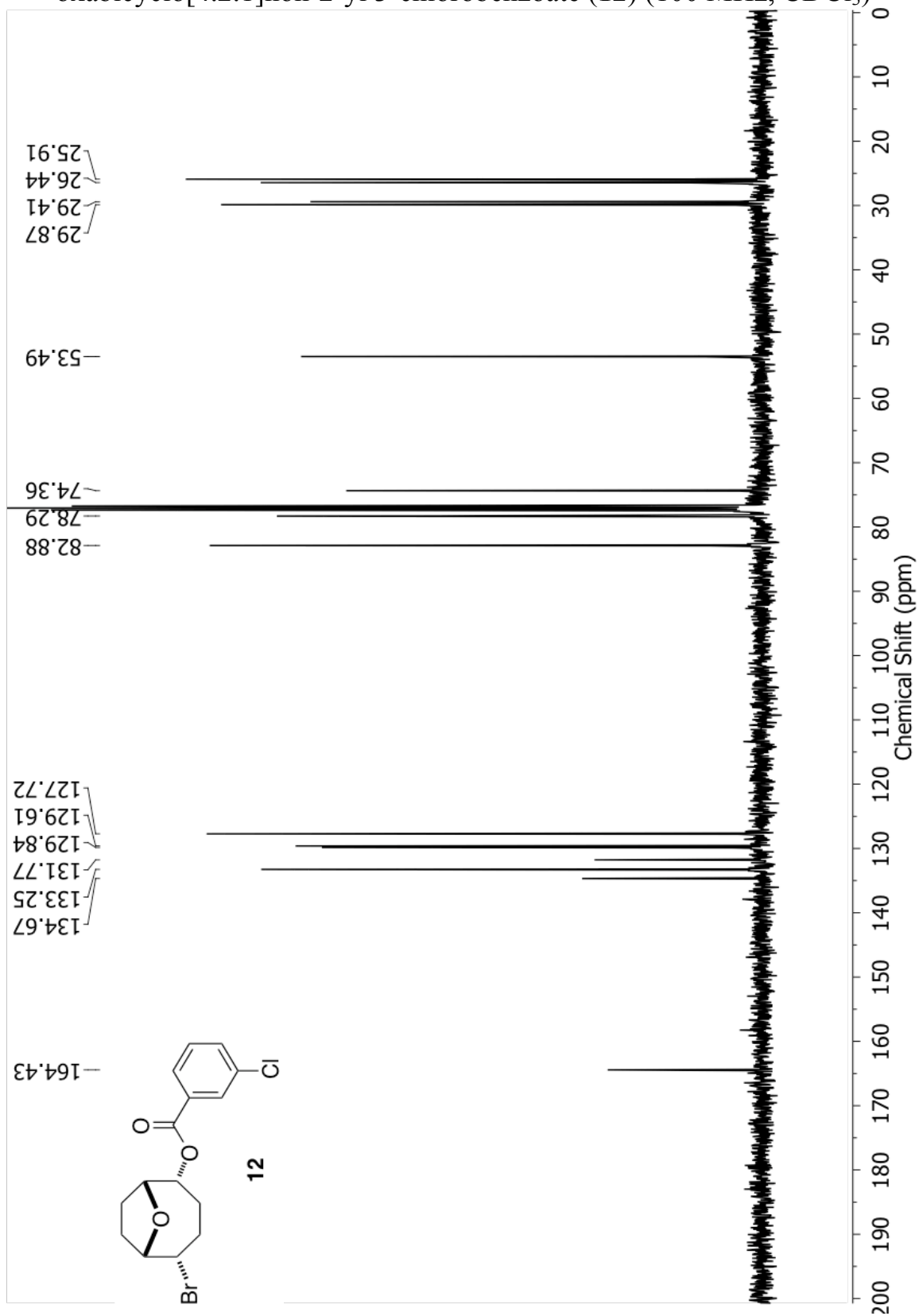
^{13}C NMR Spectrum of (1*R**,4*S**,6*R**,9*S**)-5,10-Dioxatricyclo[7.1.0.0^{4,6}]decane (**10**) (100 MHz, CDCl_3)



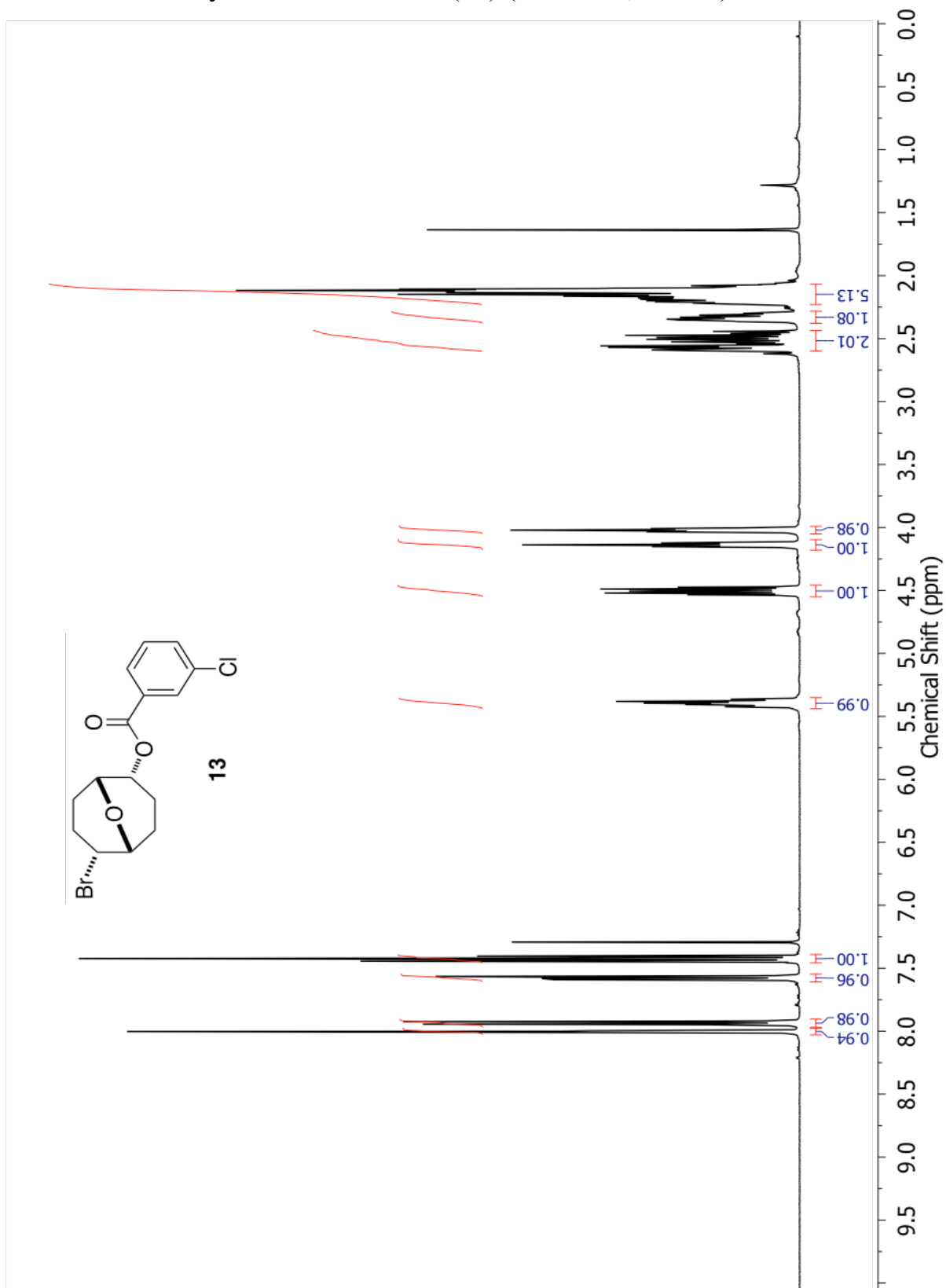
^1H NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]non-2-yl 3-chlorobenzoate (**12**) (400 MHz, CDCl_3)



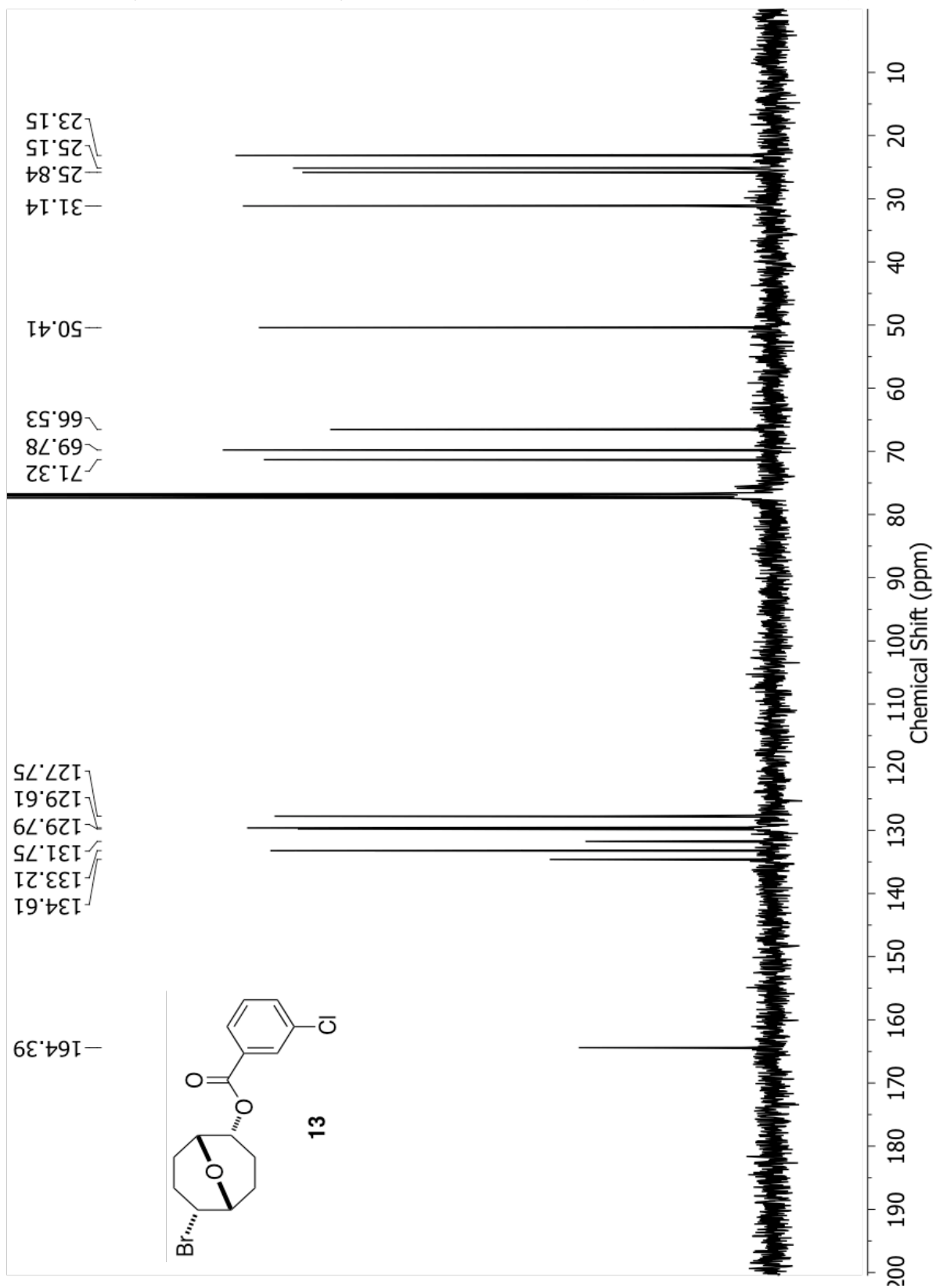
^{13}C NMR Spectrum of (1*R**,2*R**,5*S**,6*S**)-5-Bromo-9-oxabicyclo[4.2.1]non-2-yl 3-chlorobenzoate (**12**) (100 MHz, CDCl_3)



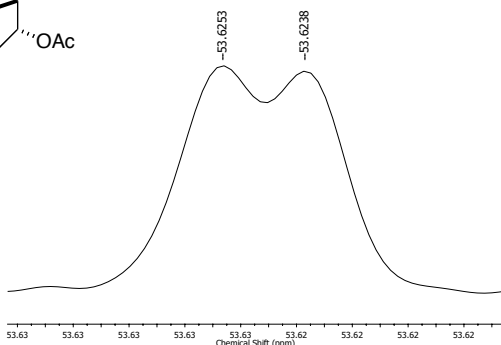
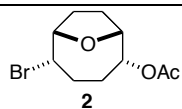
^1H NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]non-2-yl 3-chlorobenzoate (**13**) (400 MHz, CDCl_3)



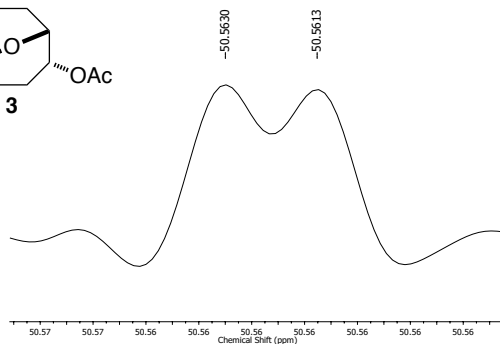
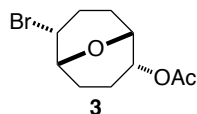
^{13}C NMR Spectrum of (1*R**,2*R**,5*R**,6*R**)-6-Bromo-9-oxabicyclo[3.3.1]non-2-yl 3-chlorobenzoate (**13**) (100 MHz, CDCl_3)



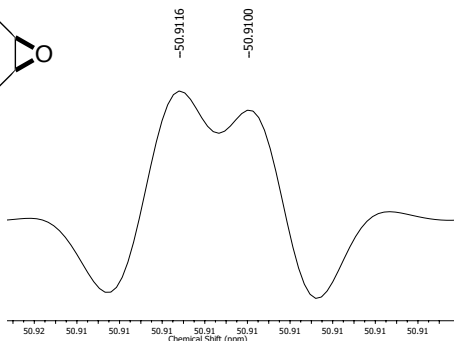
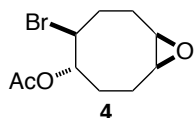
Bromine and chlorine-induced isotopic shifts in ^{13}C NMR spectra^a



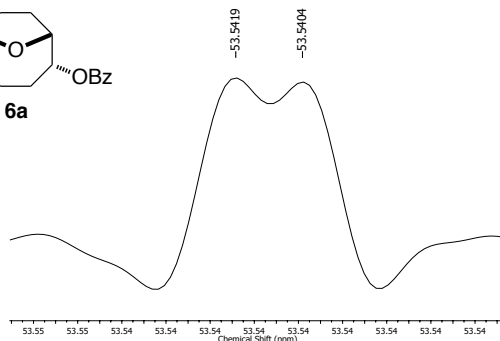
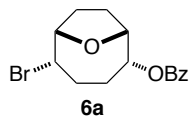
δ 53.6 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.5 ppb



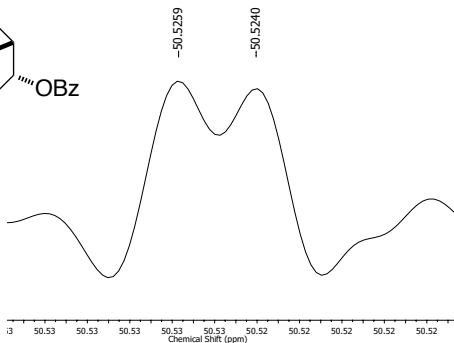
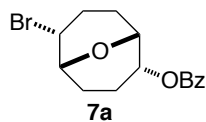
δ 50.6 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.7 ppb



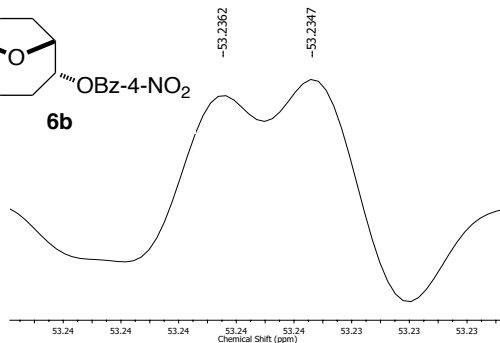
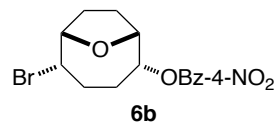
δ 50.9 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.6 ppb



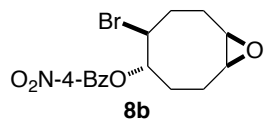
δ 53.5 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.5 ppb



δ 50.5 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.9 ppb




δ 53.2 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.5 ppb




6c

7c


8c




6d



7d

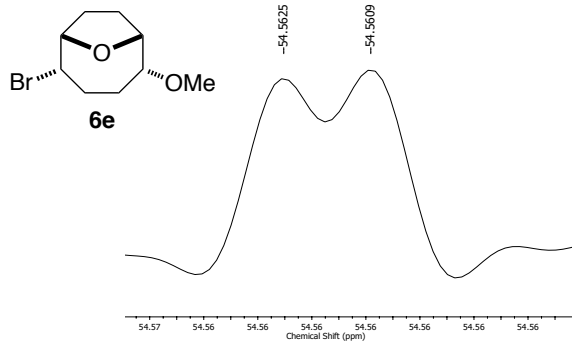


7d

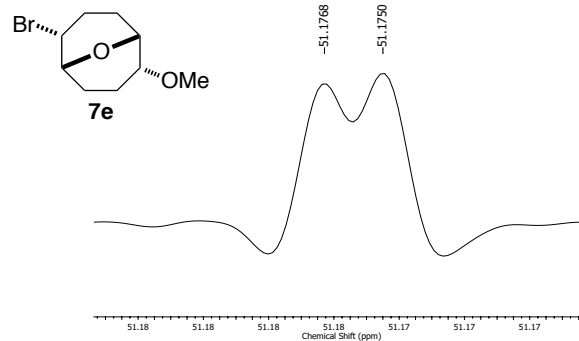


8d

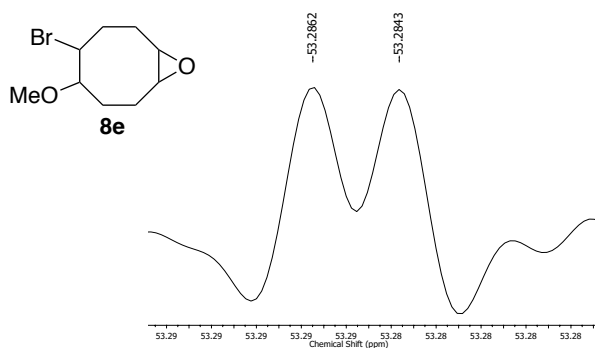
S70



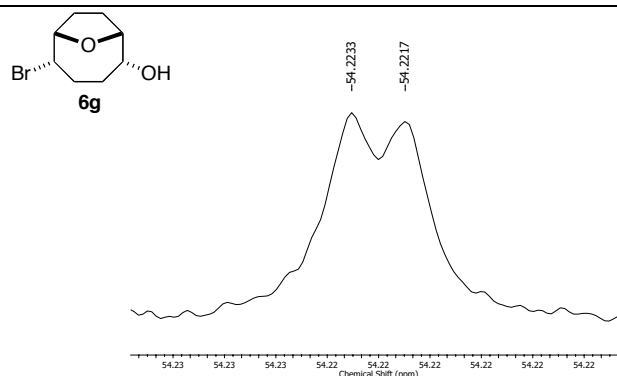
δ 54.6 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.6 ppb



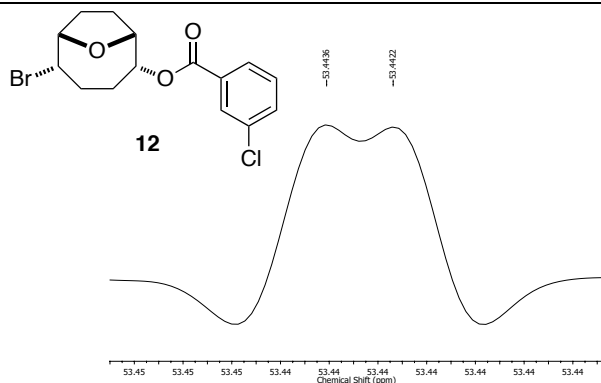
δ 51.2 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.8 ppb



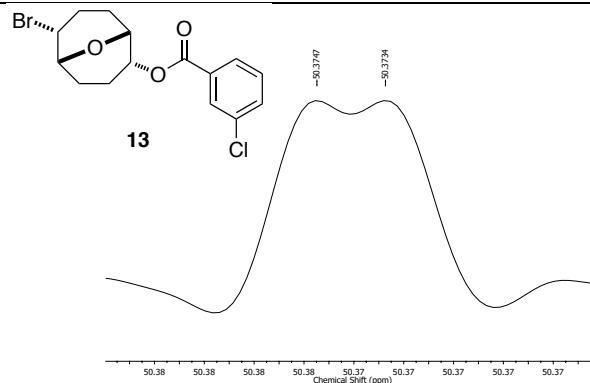
δ 53.3 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.9 ppb



δ 54.2 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.6 ppb



δ 53.4 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.4 ppb



δ 50.4 (CBr) ppm; $\Delta\delta$ ($C^{79}\text{Br}, C^{81}\text{Br}$) = 1.3 ppb

^a Satisfactory observation of the bromine and chlorine induced isotopic shifts in ¹³C spectra requires a very high digital resolution in the processed data. This was achieved by making narrow scans of the relevant regions of the ¹³C spectrum using a sweep width of 30-40ppm and relying on the digital filters of Bruker Avance spectrometers to eliminate folded signals. Usually 128K data points were collected in the time domain and zero-filled to give a spectrum of 256K data points. The final digital resolution was in the range 0.014 to 0.017 Hz/point. Data was resolution-enhanced by appropriate use of a Gaussian window function. All of the reported data was recorded at a nominal temperature of 298K.

X-Ray Crystallography

Table 1. Crystal Data, Data Collection and Refinement Parameters for compounds **6b**, **6c**, **7b**, **7c**, **7d**, **8a**, **8b**, **8c** and **8d**.

data	6b	6c	7b
formula	C ₁₅ H ₁₆ BrNO ₅	C ₁₅ H ₁₃ BrF ₄ O ₃	C ₁₅ H ₁₆ BrNO ₅
formula weight	370.20	397.16	370.20
colour, habit	colorless platy needles	colorless blocks	colorless blocky needles
crystal size / mm	0.30 · 0.12 · 0.02	0.25 · 0.24 · 0.14	0.31 · 0.31 · 0.12
temperature / K	173	173	173
crystal system	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	(no. 2)	<i>P</i> 2 ₁ / <i>n</i> (no. 14)
<i>a</i> / Å	13.6954(4)	6.57204(16)	11.91851(14)
<i>b</i> / Å	6.38506(18)	10.0357(4)	6.03915(9)
<i>c</i> / Å	17.6341(6)	11.8115(4)	21.2100(3)
α / deg	—	95.809(3)	—
β / deg	104.081(3)	94.674(2)	97.2047(12)
γ / deg	—	105.721(3)	—
<i>V</i> / Å ³	1495.70(8)	741.20(4)	1514.59(4)
<i>Z</i>	4	2	4
<i>D_c</i> / g cm ⁻³	1.644	1.780	1.623
radiation used	Cu-K α	Cu-K α	Cu-K α
μ / mm ⁻¹	3.972	4.334	3.922
2 θ max / deg	128	143	143
no. of unique reflns			
measured	2399	2857	2841
obs, $ F_o > 4\sigma(F_o)$	1949	2711	2272
no. of variables	199	209	200
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [d]	0.0476, 0.1183	0.0270, 0.0675	0.0363, 0.0899

Table 1. Continued...

data	7c	7d	8a
formula	C ₁₅ H ₁₃ BrF ₄ O ₃	C ₈ H ₁₂ BrClO	C ₁₅ H ₁₇ BrO ₃
formula weight	397.16	239.54	325.20
colour, habit	colorless needles	colorless blocks	colorless blocky needles
crystal size / mm	0.28 · 0.26 · 0.12	0.30 · 0.15 · 0.13	0.26 · 0.18 · 0.16
temperature / K	293	173	173
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)	<i>C</i> 2/ <i>c</i> (no. 15)	<i>P</i> 2 ₁ / <i>m</i> (no. 11)
<i>a</i> / Å	11.0594(6)	13.0338(5)	11.17740(11)
<i>b</i> / Å	6.8012(3)	9.1341(4)	7.41636(11)
<i>c</i> / Å	20.1769(9)	7.5874(3)	17.15108(17)
α / deg	—	—	—
β / deg	92.102(4)	93.620(3)	101.722(1)
γ / deg	—	—	—
<i>V</i> / Å ³	1516.63(13)	901.49(6)	1392.10(3)
<i>Z</i>	4	4 [a]	4 [b]
<i>D_c</i> / g cm ⁻³	1.739	1.765	1.552
radiation used	Cu-K α	Mo-K α	Cu-K α
μ / mm ⁻¹	4.236	4.796	4.043
2 θ max / deg	143	65	143
no. of unique reflns			
measured	2846	1504	2904
obs, $ F_o > 4\sigma(F_o)$	1761	1124	2480
no. of variables	208	60	344
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [d]	0.0627, 0.2129	0.0303, 0.0920	0.0488, 0.1012

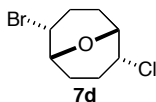
Table 1. Continued...

data	8b	8c	8d
formula	C ₁₅ H ₁₆ BrNO ₅	C ₁₅ H ₁₃ BrF ₄ O ₃	C ₈ H ₁₂ BrClO
formula weight	370.20	397.16	239.54
colour, habit	colorless blocky needles	colorless plates	colorless blocky needles
crystal size / mm	0.35 · 0.25 · 0.14	0.26 · 0.18 · 0.04	0.44 · 0.11 · 0.10
temperature / K	173	293	173
crystal system	monoclinic	orthorhombic	orthorhombic
space group	<i>P</i> 2 ₁ / <i>n</i> (no. 14)	<i>Pbca</i> (no. 61)	<i>Pnma</i> (no. 62)
<i>a</i> / Å	7.07940(12)	7.08444(10)	12.6909(4)
<i>b</i> / Å	31.7774(3)	13.3213(2)	8.7610(4)
<i>c</i> / Å	7.32126(12)	31.0102(4)	8.0814(2)
α / deg	—	—	—
β / deg	117.338(2)	—	—
γ / deg	—	—	—
<i>V</i> / Å ³	1463.08(5)	2926.57(7)	898.53(5)
<i>Z</i>	4	8	4 [c]
<i>D_c</i> / g cm ⁻³	1.681	1.803	1.771
radiation used	Cu-K α	Cu-K α	Mo-K α
μ / mm ⁻¹	4.060	4.390	4.812
2 θ max / deg	142	145	64
no. of unique reflns			
measured	2809	2897	1589
obs, $ F_o > 4\sigma(F_o)$	2761	2480	1073
no. of variables	200	209	95
<i>R</i> ₁ (obs), <i>wR</i> ₂ (all) [d]	0.0282, 0.0654	0.0313, 0.0887	0.0319, 0.0817

[a] The molecule has crystallographically *C*₂ symmetry. [b] There are two crystallographically independent *C*_S symmetric molecules in the asymmetric unit. [c] The molecule has crystallographically *C*_S symmetry. [d] $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table 1 provides a summary of the crystallographic data for compounds **6b**, **6c**, **7b**, **7c**, **7d**, **8a**, **8b**, **8c** and **8d**. Data were collected using Oxford Diffraction PX Ultra (**6b**, **6c**, **7b**, **7c**, **8a**, **8b** and **8c**) and Xcalibur 3 (**7d** and **8d**) diffractometers, and the structures were refined based on *F*² using the SHELXTL and SHELX-97 program systems.^[1] CCDC 784175 to 784183.

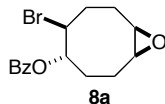
The X-ray crystal structure of **7d**



The structure of **7d** has crystallographic C_2 symmetry about an axis that passes through O(1) and bisects the C(1)–O(1)–C(1A) angle, and is thus inherently disordered; the mixed chloro/bromo species is incompatible with C_2 symmetry unless there is a perfectly 50:50 distribution of the positions of the halogen atoms. Unfortunately, the same asymmetric unit would arise from a 50:50 mixture of the dichloro and dibromo species as well as from a 50:50 mixture of different orientations of the same mixed halogen species. (An infinite number of combinations of all three species are also possible provided they involve equal amounts of the two dihalogen species and equal amounts of the two orientations of the mixed halogen species.) So, the assignment of the structure as being solely the mixed halogen species (and the decision to fix the relative occupancies of the two halogens as exactly 50:50) relies upon data other than the crystal structure.

This situation was modelled by including a 50% occupancy chlorine atom and a 50% occupancy bromine atom bound to C(2). Initially these two atoms were placed at the same coordinates, *ca.* 1.88 Å away from C(2). When they failed to move into sensible positions of their own accord, a pair of C–halogen distance constraints were applied [C(2)–Cl 1.75 Å and C(2)–Br 1.95 Å]. After the atoms moved into these new positions, the restraints were removed and the atoms settled into positions with C(2)–Cl and C(2)–Br bond lengths of 1.799(9) and 1.942(4) Å respectively. Both 50% occupancy halogen atoms were refined anisotropically.

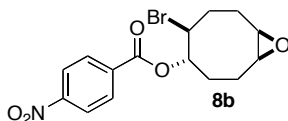
The X-ray crystal structure of **8a**



The structure of **8a** was found to contain two independent molecules (**8a-I** and **8a-II**), both of which are severely disordered across a mirror plane that passes through the epoxide oxygen atom O(1) and “bisects” the C(4)–C(5) bond.

(Unfortunately, use of the equivalent space group without the mirror plane, $P2_1$, does not remove the disorder.) As this bond is not perpendicular to the mirror plane in either independent molecule, the C(4) and C(5) atoms are inherently disordered, and the disorder takes the form of a swapping of the substitution positions of the bromide and benzoate substituents (*i.e.* the enantiomeric species). As a result, these substituents are also disordered, meaning that only the O(1), C(1), C(2) and C(3) atoms remain ordered. For all of the other non-hydrogen atoms two unique orientations were identified, of *ca.* 43 and 7% occupancy for molecule **8a-I**, and of *ca.* 40 and 10% occupancy for molecule **8a-II** (see Figs S8 and S9 respectively). In each case, operation of the mirror plane generates two other overlapping orientations of the same occupancies. For both independent molecules, the equivalent bond lengths and angles of the two unique orientations were restrained to be the same, the aryl rings were treated as optimized rigid bodies, the carboxylate groups were restrained to be flat, and the thermal parameters of chemically equivalent adjacent atoms were restrained to be similar. The non-hydrogen atoms of the major occupancy orientations were refined anisotropically, whilst those of the minor occupancy orientations were refined isotropically.

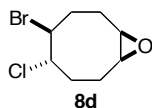
The X-ray crystal structure of **8b**



The three largest residual electron density peaks in the final refinement of the structure of **8b** fit to a possible flipping disorder of C(4) and C(5) across a non-existent mirror plane that would pass through the epoxide oxygen atom O(1) and “bisect” the C(4)–C(5) bond. The result would be a swapping of the substitution pattern (*i.e.* the enantiomeric species). However, the low electron densities of these peaks, (*ca.* 0.74, 0.49 and 0.39 eÅ⁻³), the lack of high thermal parameters for the atoms already present that would be involved in this disorder (and therefore be of less than full occupancy), and the low final *R*-factor (0.0282) without accounting for

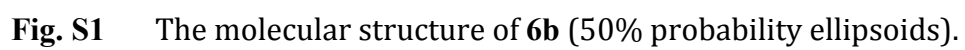
this possible disorder, all suggest that the occupancy of this potential second orientation could only be very small, and so it was not modelled.

The X-ray crystal structure of **8d**



The structure of **8d** was found to be severely disordered across a mirror plane that passes through the epoxide oxygen atom O(1) and “bisects” the C(4)–C(5) bond. (Unfortunately, use of the equivalent space group without the mirror plane, *Pna2₁*, does not remove the disorder.) As this bond is not perpendicular to the mirror plane, the C(4) and C(5) atoms are inherently disordered, and so are the halogen substituents. The result is that only the O(1), C(1), C(2) and C(3) atoms remain ordered. For all of the other non-hydrogen atoms three unique orientations were identified, of *ca.* 36, 8 and 6% occupancy (see Fig. S13). (The mirror plane generates three more overlapping orientations of the same occupancies.) The equivalent bond lengths and angles of the three unique orientations were restrained to be the same, and the thermal parameters of chemically equivalent adjacent atoms were restrained to be similar. Only the bromine and chlorine atoms of the major occupancy orientation were refined anisotropically; all of the other partial occupancy atoms were refined isotropically.

- [1] SHELXTL PC version 5.1, Bruker AXS, Madison, WI, 1997; SHELX-97, G. Sheldrick, Institut Anorg. Chemie, Tammannstr. 4, D37077 Göttingen, Germany, 1998.



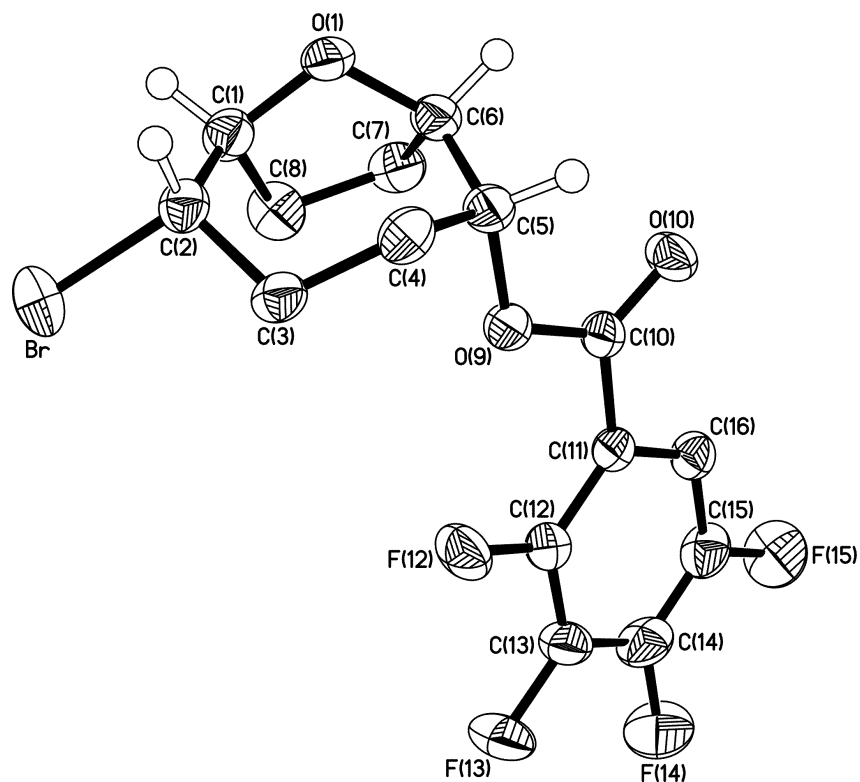


Fig. S2 The molecular structure of **6c** (50% probability ellipsoids).

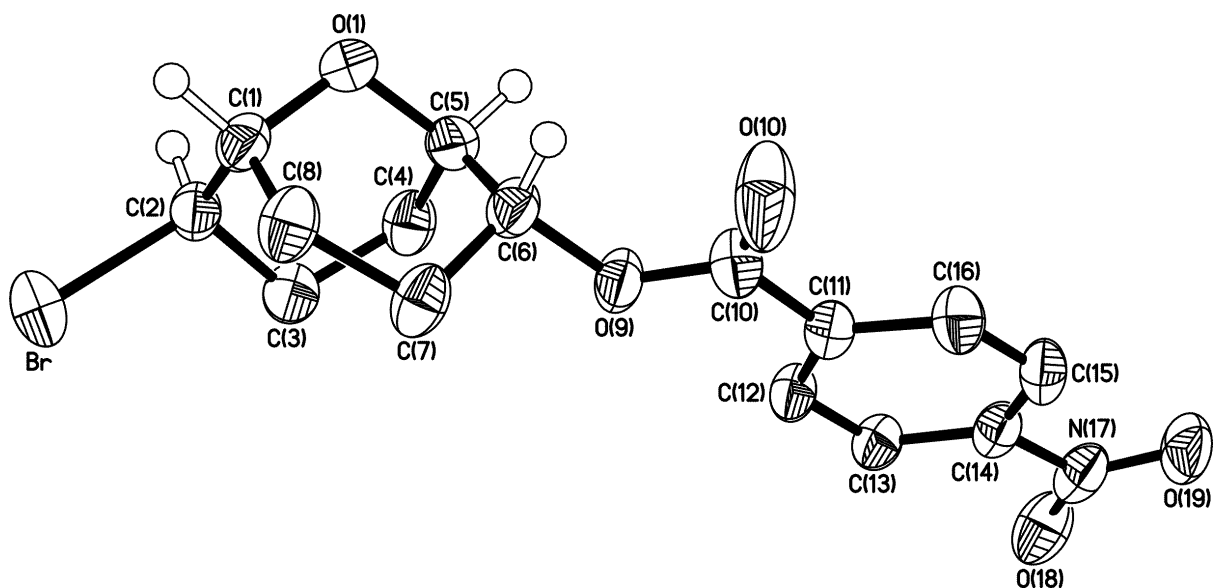


Fig. S3 The molecular structure of **7b** (50% probability ellipsoids).

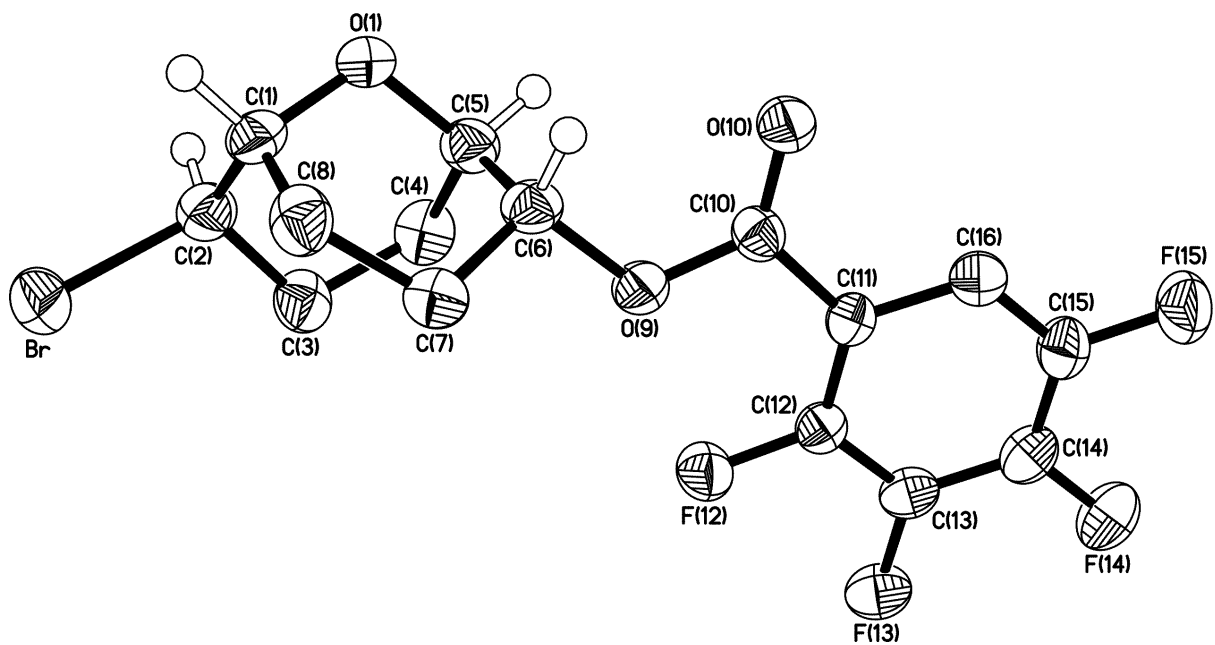


Fig. S4 The molecular structure of **7c** (30% probability ellipsoids).

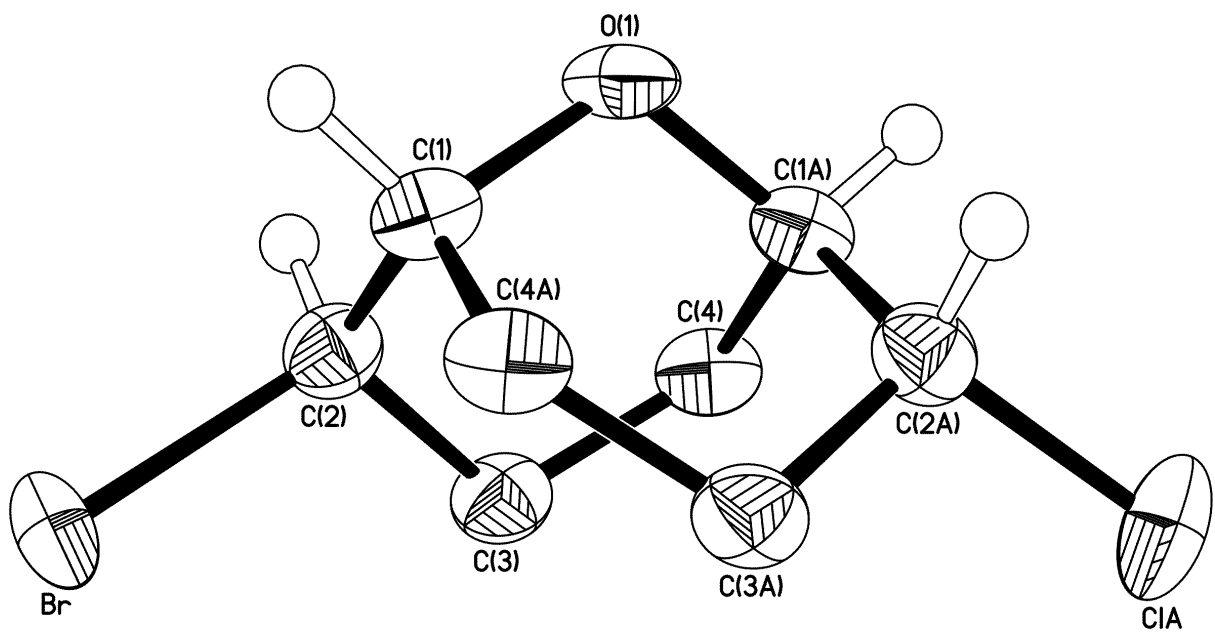
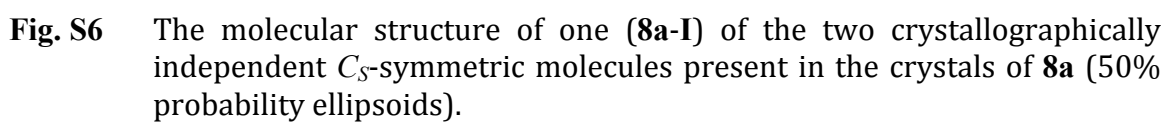


Fig. S5 The molecular structure of the C_2 -symmetric species **7d** (50% probability ellipsoids).



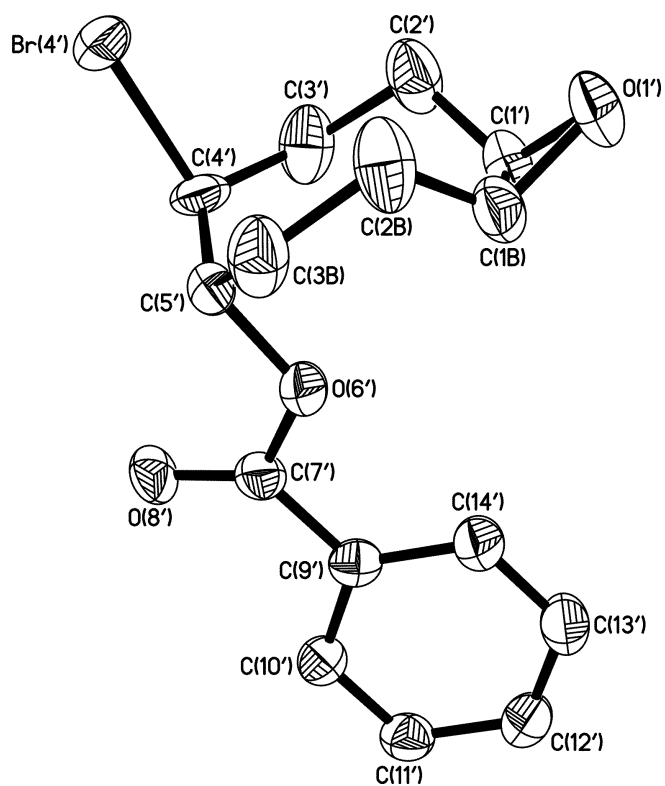


Fig. S7 The molecular structure of one (**8a-II**) of the two crystallographically independent C_s -symmetric molecules present in the crystals of **8a** (50% probability ellipsoids).

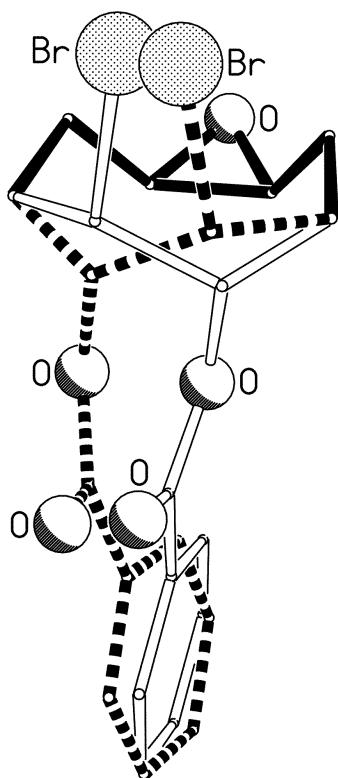


Fig. S8 The molecular structure of **8a-I** showing the two unique disordered orientations (two more are generated by the operation of the mirror plane). The major (*ca.* 43%) occupancy orientation is shown with open bonds and the minor (*ca.* 7%) occupancy orientation with dark dashed bonds, whilst the ordered parts of the structure have been drawn with dark bonds.

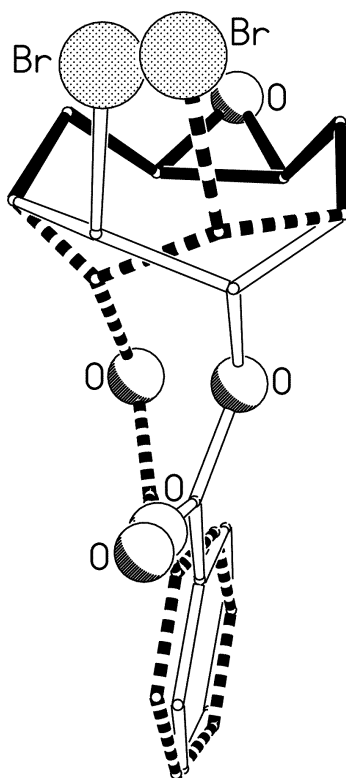


Fig. S9 The molecular structure of **8a-II** showing the two unique disordered orientations (two more are generated by the operation of the mirror plane). The major (*ca.* 40%) occupancy orientation is shown with open bonds and the minor (*ca.* 10%) occupancy orientation with dark dashed bonds, whilst the ordered parts of the structure have been drawn with dark bonds.

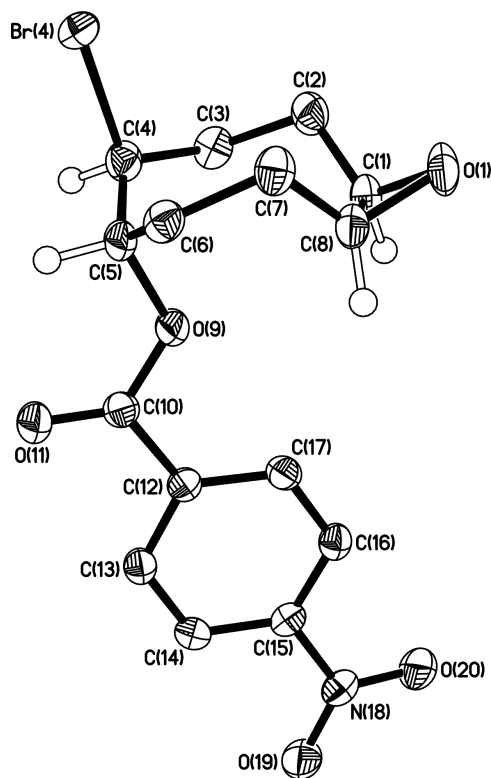


Fig. S10 The molecular structure of **8b** (50% probability ellipsoids).

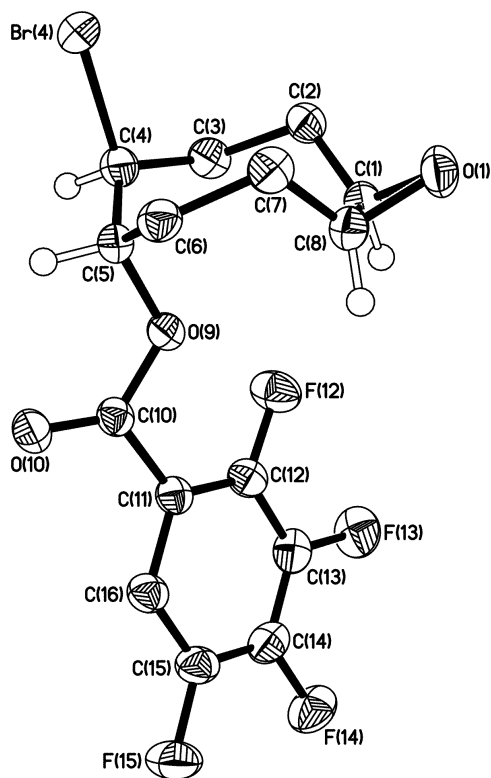


Fig. S11 The molecular structure of **8c** (30% probability ellipsoids).

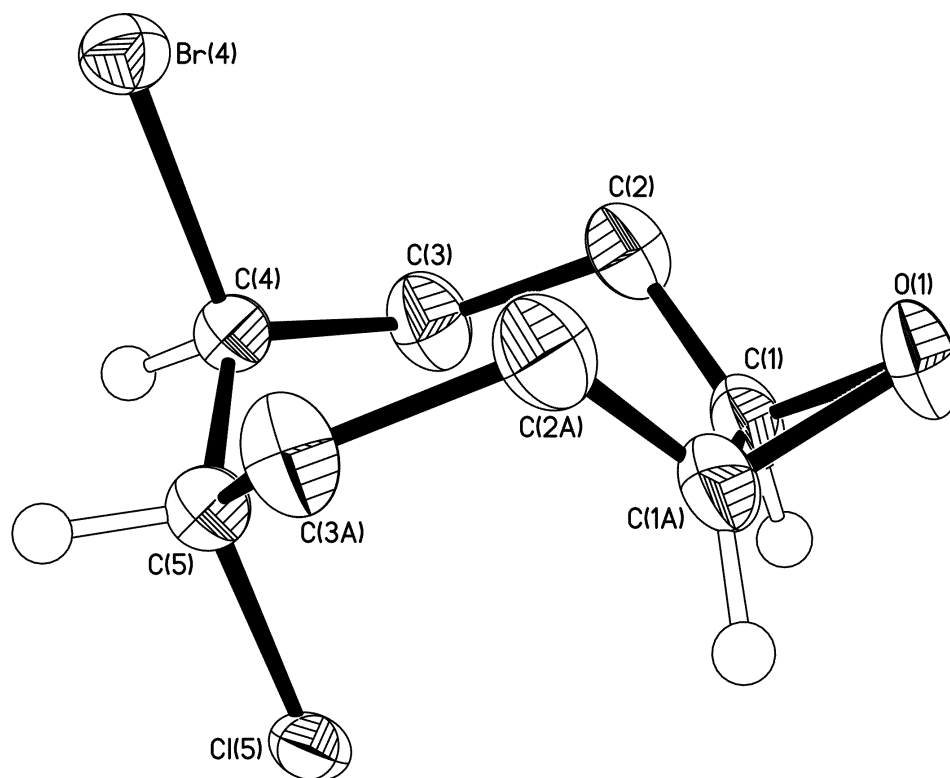


Fig. S12 The molecular structure of the C_s -symmetric species **8d** (50% probability ellipsoids).

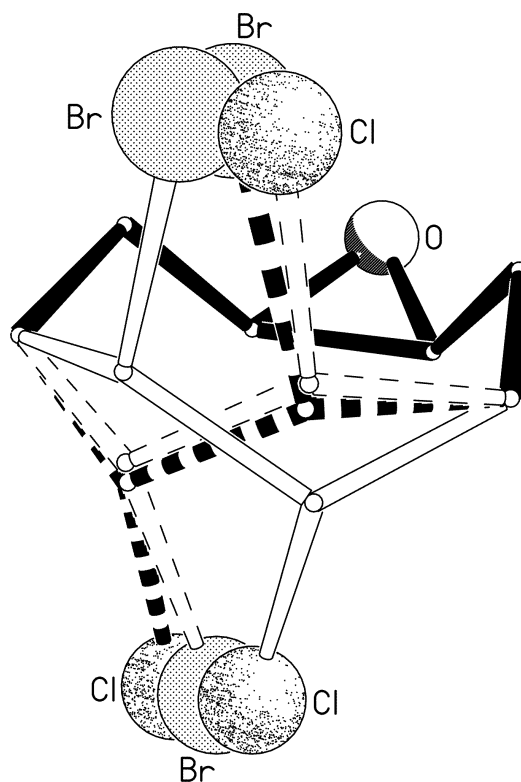


Fig. S13 The molecular structure of **8d** showing the three unique disordered orientations (three more are generated by the operation of the mirror plane). The major (*ca.* 36%) occupancy orientation is shown with open bonds, the intermediate (*ca.* 8%) occupancy orientation with dark dashed bonds, and the minor (*ca.* 6%) occupancy orientation with open dashed bonds, whilst the ordered parts of the structure have been drawn with dark bonds.