

Supporting Information

Tuning Donor Ability of Oxygen with Inverse α -Effect: Two Levels of Kinetic Control Open Access to Four Classes of Peroxygenated Heterocycles

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Experimental Section

Caution: Although we have encountered no difficulties in working with the peroxides described below, the proper precautions, such as the use of shields, fume hoods, and the avoidance of transition metal salts, heating and shaking, should be taken whenever possible.

^1H , ^{13}C , and ^{15}N NMR spectra were recorded on a 300 MHz (300.1 and 75.5 MHz, respectively) spectrometer in CDCl_3 solutions. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: ^1H (CDCl_3 $\delta = 7.26$ ppm), ^{13}C (CDCl_3 $\delta = 77.16$ ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), m (multiplet). Determinations of structures and stereochemistry of obtained compounds and assignments of ^1H and ^{13}C signals were made with the aid of 2D COSY, NOESY, HSQC, HMBC spectra. Structures of the new peroxides were established via the combination of ^1H and ^{13}C NMR spectroscopy. The NMR analysis was facilitated by 2D correlation spectroscopic techniques (COSY, NOESY, HSQC, and HMBC) that provided the reference NMR chemical shifts and structural frameworks for both diastereomers of the peroxides. Stereochemical analysis was performed based on established key ^1H and ^{13}C chemical shifts in combination with NOE data (See SI). The stereochemical and NMR assignments were further confirmed by X-ray single-crystal analysis for *cis*-**2a**, *trans*-**2a**, *cis*-**3a**, **5a**, **6a**, **7a** and *cis*-**3a** (See Fig. S1-7).

High resolution mass spectra (HRMS) were measured using electrospray ionization (ESI). The measurements were performed in a positive ion mode (interface capillary voltage 4500 V); the mass ratio was from m/z 50 to 3000 Da; external/internal calibration was done with Electrospray Calibrant Solution. A syringe injection was used for solutions in MeCN (flow rate 3 $\mu\text{L}/\text{min}$). Nitrogen was applied as a dry gas; interface temperature was set at 180 $^\circ\text{C}$.

The TLC analysis was carried out on silica gel chromatography plates Macherey-Nagel Alugram UV254; Sorbent: Silica 60, specific surface (BET) ~ 500 m^2/g , mean pore size 60 \AA , specific pore volume 0.75 mL/g , particle size 5–17 μm ; Binder: highly polymeric product, which is stable in almost all organic solvents and resistant towards aggressive visualization reagents. The melting points were determined on a Kofler hot-stage apparatus. Column chromatography was performed on silica gel (0.060-0.200 mm, 60 \AA , CAS 7631-86-9).

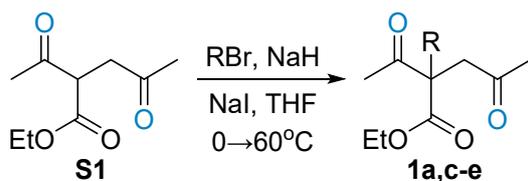
Hexane-2,5-dione, ethyl acetoacetate, chloroacetone, 1,4-diphenylbutane-1,4-dione, benzyl and alkyl halides, potassium *tert*-butoxide, 98% H_2SO_4 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$, NaI, NH_4Cl , $\text{Na}_2\text{S}_2\text{O}_3$, MgSO_4 , NaHCO_3 , tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), ethyl acetate (EA),

petroleum ether (PE) (40/70), acetonitrile (CH₃CN), chloroform (CHCl₃), diethyl ether (Et₂O), H₂O₂ (35% aqueous solution), were purchased from commercial suppliers. Solvents were purified by distillation prior to use.

A solution of H₂O₂ in Et₂O (9.27 M) was prepared by the extraction with Et₂O (3 × 100 mL) from a 35% aq. solution (100 mL) followed by drying over MgSO₄ and partial evaporation of Et₂O.

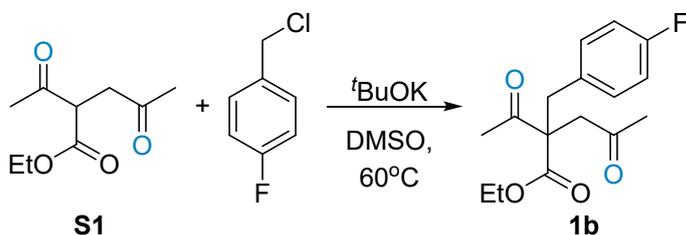
1,4 – Diketone **1i**¹, **1j**² **1k**³ and **1l**⁴ were synthesized according to a known procedures.

General procedure for the synthesis of 1,4-diketones **1a**, **c-e**



Ethyl 2-acetyl-4-oxopentanoate **S1** (1.866 g, 10.02 mmol) was added dropwise with stirring to a suspension of 60% NaH (0.441 g, 11.02 mmol; 1.1 mol NaH / 1.0 mol **S1**) in THF (20 mL) at 0 – 2°C. After 1 h alkylator (10.02 mmol, 1.0 mol RBr / 1.0 mol **S1**) and NaI (1.502 g, 10.02 mmol, 1.0 mol NaI / 1.0 mol **S1**) were added. The reaction mixture was stirred at 60°C for 72 h. Then Et₂O (50 mL) and saturated aqueous solution of NH₄Cl (50 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by Et₂O (3×50 mL). The combined organic phases were washed with saturated aqueous solution of Na₂S₂O₃ (3×50 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. 1,4-Diketones **1a**, **c-e** were isolated by chromatography on SiO₂ using PE : EA (from 10:1 to 2:1) mixture as the eluent.

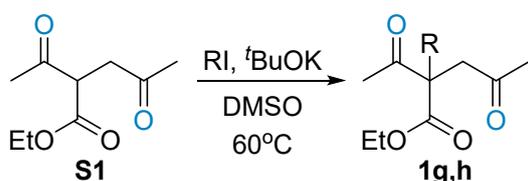
Procedure for the synthesis of 1,4-diketone **1b**⁵



Potassium *tert*-butoxide (2.693 g, 24.0 mmol) was added to a solution of ethyl 2-acetyl-4-oxopentanoate **S1** (3.724 g, 20.0 mmol) in DMSO (20 mL). After 20 min stirring at 20 – 25°C, 4-fluorobenzyl bromide (3.18 g, 22.0 mmol) was added. The resulting mixture was stirred for 48 h at 60°C. The mixture was quenched with H₂O (60 mL), and the product was extracted with Et₂O (3×50 mL). Combined organic layers were washed with H₂O (2×20 mL), dried over MgSO₄,

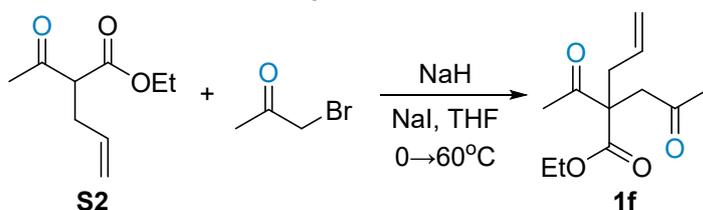
filtered and concentrated under reduced pressure. Cold petroleum ether was added to the crude product. The precipitated 1,4-diketone **1b** was filtered off.

General procedure for the synthesis of 1,4-diketones **1g, h** ⁵



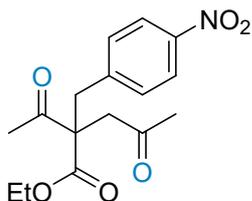
Potassium *tert*-butoxide (2.188 g, 19.5 mmol) was added to a solution of ethyl 2-acetyl-4-oxopentanoate **S1** (2.793 g, 15.0 mmol) in DMSO (15 mL). After 20 min stirring at 20 – 25°C, alkyl iodide (2.59 g, 15.0 mmol, 1.0 mol RI / 1.0 mol **S1**) was added. The resulting suspension was stirred for 48 h at 60°C. The mixture was quenched with H₂O (50 mL), and the product was extracted with Et₂O (3×40 mL). Combined organic layers were washed with H₂O (2×10 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. 1,4-Diketone **1g, h** were isolated by chromatography on SiO₂ using PE : EA (from 20:1 to 2:1) mixture as the eluent.

Procedure for the synthesis of 1,4-diketone **1f**



Ethyl 2-acetylpent-4-enoate **S2** (4.001 g, 23.50 mmol) was added dropwise with stirring to a suspension of 60% NaH (1.128 g, 28.20 mmol; 1.2 mol NaH / 1.0 mol **S2**) in THF (47 mL) at 0 – 2°C. After 30 min bromoacetone (3.863 g, 28.20 mmol, 1.2 mol bromoacetone / 1.0 mol **S2**) and NaI (3.522 g, 23.50 mmol, 1.0 mol NaI / 1.0 mol **S2**) were added. The reaction mixture was stirred at 60°C for 72 h. Then Et₂O (50 mL) and saturated aqueous solution of NH₄Cl (50 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by Et₂O (3×50 mL). The combined organic phases were washed with saturated aqueous solution of Na₂S₂O₃ (3×50 mL). The organic phase was dried over MgSO₄, filtered and concentrated under reduced pressure. 1,4-Diketone **1f** were isolated by chromatography on SiO₂ using PE : EA (from 20:1 to 5:1) mixture as the eluent.

Ethyl 2-acetyl-2-(4-nitrobenzyl)-4-oxopentanoate, 1a



Yield 85%. Yellowish crystals. Mp = 48 – 50 °C. R_f = 0.66 (TLC, PE : EA, 2 : 1).

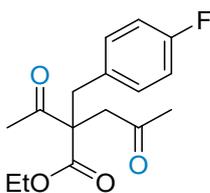
¹H NMR (300.13 MHz, CDCl₃), δ: 8.11 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.7 Hz, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.55 (d, *J* = 13.7 Hz, 1H), 3.32 (d, *J* = 13.7 Hz, 1H), 2.98 (d, *J* = 18.6 Hz, 1H), 2.89 (d, *J* = 18.5 Hz, 1H), 2.35 (s, 3H), 2.08 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75.48 MHz, CDCl₃), δ: 205.8, 204.1, 170.7, 147.3, 144.1, 130.8, 123.7, 62.1, 62.0, 46.3, 38.9, 30.0, 27.6, 14.0.

Anal. Calcd for C₁₆H₁₉NO₆: C, 59.81; H, 5.96. Found: C, 59.92; H, 6.05.

HRMS (ESI-TOF): *m/z* [M+Na]⁺: calculated for [C₁₆H₁₉NaNO₆]⁺: 344.1105; found: 344.1106.

Ethyl 2-acetyl-2-(4-fluorobenzyl)-4-oxopentanoate, 1b



Yield 64%. White crystals. Mp = 50 – 52 °C. R_f = 0.43 (TLC, PE : EA, 5 : 1).

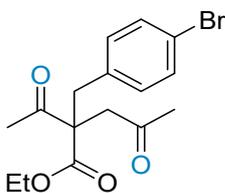
¹H NMR (300.13 MHz, CDCl₃), δ: 6.98 – 6.88 (m, 4H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.40 (d, *J* = 14.0 Hz, 1H), 3.17 (d, *J* = 14.0 Hz, 1H), 2.98 (d, *J* = 18.5 Hz, 1H), 2.90 (d, *J* = 18.5 Hz, 1H), 2.36 (s, 3H), 2.06 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75.48 MHz, CDCl₃), δ: 206.2, 205.0, 171.2, 162.1 (d, ¹*J*_{CF} = 246.0 Hz), 131.9 (d, ⁴*J*_{CF} = 3.4 Hz), 131.3 (d, ³*J*_{CF} = 8.0 Hz), 115.5 (d, ²*J*_{CF} = 21.3 Hz), 62.3, 61.8, 46.4, 38.7, 30.0, 27.7, 14.0.

Anal. Calcd for C₁₆H₁₉FO₄: C, 65.29; H, 6.51. Found: C, 65.36; H, 6.66.

HRMS (ESI-TOF): *m/z* [M+Na]⁺: calculated for [C₁₆H₁₉NaFO₄]⁺: 317.1160; found: 317.1152.

Ethyl 2-acetyl-2-(4-bromobenzyl)-4-oxopentanoate, 1c



Yield 51%. Yellowish oil. R_f = 0.62 (TLC, PE : EA, 2 : 1).

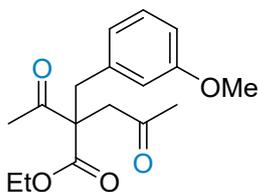
^1H NMR (300.13 MHz, CDCl_3), δ : 7.36 (d, $J = 8.3$ Hz, 2H), 6.83 (d, $J = 8.2$ Hz, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 3.38 (d, $J = 13.8$ Hz, 1H), 3.15 (d, $J = 13.8$ Hz, 1H), 2.97 (d, $J = 18.5$ Hz, 1H), 2.88 (d, $J = 18.5$ Hz, 1H), 2.34 (s, 3H), 2.06 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 206.1, 204.7, 171.0, 135.2, 131.7, 131.5, 121.3, 62.1, 61.8, 46.3, 38.8, 30.0, 27.6, 14.0.

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}_4$: C, 54.10; H, 5.39. Found: C, 54.24; H, 5.49.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{16}\text{H}_{20}\text{BrO}_4]^+$: 355.0539, 357.0520; found: 355.0532, 357.0514.

Ethyl 2-acetyl-2-(3-methoxybenzyl)-4-oxopentanoate, 1d



Yield 57%. Colorless oil. $R_f = 0.36$ (TLC, PE : EA, 5 : 1).

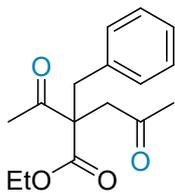
^1H NMR (300.13 MHz, CDCl_3), δ : 7.12 (t, $J = 7.9$ Hz, 1H), 6.76 – 6.68 (dd, $J = 8.5, 1.8$ Hz, 1H), 6.55 – 6.38 (m, 2H), 4.14 (q, $J = 7.1$ Hz, 2H), 3.70 (s, 3H), 3.38 (d, $J = 13.7$ Hz, 1H), 3.14 (d, $J = 13.7$ Hz, 1H), 3.04 – 2.80 (m, 2H), 2.33 (s, 3H), 2.02 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 206.1, 204.8, 171.0, 159.6, 137.5, 129.4, 122.0, 115.5, 112.3, 62.1, 61.6, 55.0, 46.3, 39.3, 29.8, 27.4, 13.9.

Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_5$: C, 66.65; H, 7.24. Found: C, 66.78; H, 7.35.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{17}\text{H}_{22}\text{NaO}_5]^+$: 329.1359; found: 329.1356.

Ethyl 2-acetyl-2-benzyl-4-oxopentanoate, 1e



Yield 66%. Yellowish oil. $R_f = 0.54$ (TLC, PE : EA, 5 : 1).

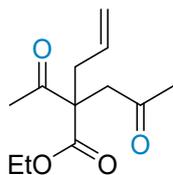
^1H NMR (300.13 MHz, CDCl_3), δ : 7.33 – 7.22 (m, 3H), 7.03 – 6.95 (m, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 3.46 (d, $J = 13.8$ Hz, 1H), 3.23 (d, $J = 13.8$ Hz, 1H), 3.01 (d, $J = 18.6$ Hz, 1H), 2.94 (d, $J = 18.5$ Hz, 1H), 2.40 (s, 3H), 2.08 (s, 3H), 1.25 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 206.2, 205.1, 171.2, 136.1, 129.8, 128.6, 127.3, 62.3, 61.7, 46.4, 39.5, 29.9, 27.6, 14.0.

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_4$: C, 69.55; H, 7.30. Found: C, 69.68; H, 7.45.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{20}\text{NaO}_4]^+$: 299.1254; found: 299.1257.

Ethyl 2-acetyl-2-(2-oxopropyl)pent-4-enoate, **1f**



Yield 35%. Colorless oil. $R_f = 0.72$ (TLC, PE : EA, 2 : 1).

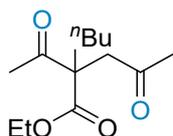
$^1\text{H NMR}$ (300.13 MHz, CDCl_3), δ : 5.59 – 5.49 (m, 1H), 5.12 – 4.94 (m, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 3.04 (s, 2H), 2.79 – 2.56 (m, 2H), 2.24 (s, 3H), 2.09 (s, 3H), 1.21 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (75.48 MHz, CDCl_3), δ : 205.8, 204.6, 171.2, 132.3, 119.6, 61.6, 61.0, 46.1, 38.0, 30.1, 27.2, 14.0.

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_4$: C, 63.70; H, 8.02. Found: C, 63.82; H, 8.09.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{12}\text{H}_{18}\text{NaO}_4]^+$: 249.1097; found: 249.1091.

Ethyl 2-acetyl-2-(2-oxopropyl)hexanoate, **1g**



Yield 63%. Yellow oil. $R_f = 0.63$ (TLC, PE : EA, 2 : 1).

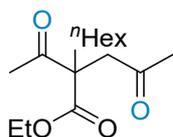
$^1\text{H NMR}$ (300.13 MHz, CDCl_3), δ : 4.16 (q, $J = 7.1$ Hz, 2H), 3.05 (s, 2H), 2.27 (s, 3H), 2.12 (s, 3H), 2.03 – 1.80 (m, 2H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.32 – 1.19 (m, 2H), 1.11 – 0.99 (m, 2H), 0.85 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (75.48 MHz, CDCl_3), δ : 206.0, 205.8, 172.0, 61.5, 61.3, 46.3, 34.0, 30.1, 27.4, 26.8, 23.0, 14.1, 13.9.

Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{O}_4$: C, 64.44; H, 9.15. Found: C, 64.57; H, 9.24.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{13}\text{H}_{22}\text{NaO}_4]^+$: 265.1410; found: 265.1408.

Ethyl 2-acetyl-2-(2-oxopropyl)octanoate, **1h**



Yield 51%. Yellow oil. $R_f = 0.70$ (TLC, PE : EA, 2 : 1).

$^1\text{H NMR}$ (300.13 MHz, CDCl_3), δ : 4.16 (q, $J = 7.1$ Hz, 2H), 3.06 (s, 2H), 2.28 (s, 3H), 2.13 (s, 3H), 2.00 – 1.80 (m, 2H), 1.31 – 1.18 (m, 9H), 1.12 – 1.00 (m, 2H), 0.84 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (75.48 MHz, CDCl_3), δ : 206.1, 206.0, 172.0, 61.5, 61.3, 46.3, 34.2, 31.6, 30.1, 29.5, 27.5, 24.6, 22.6, 14.1, 14.1.

Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_4$: C, 66.64; H, 9.69. Found: C, 66.75; H, 9.82.

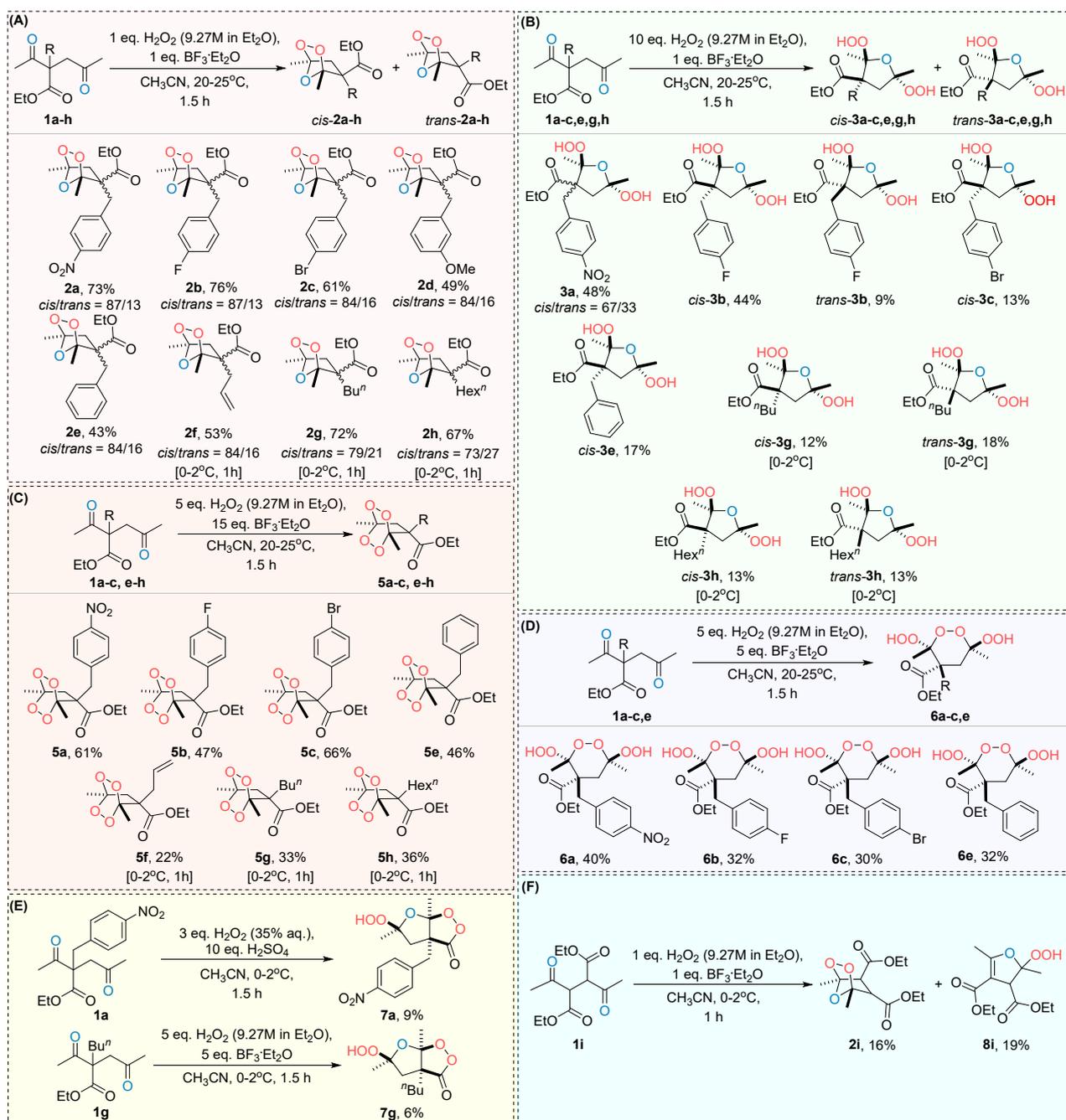
HRMS (ESI-TOF): m/z $[M+Na]^+$: calculated for $[C_{15}H_{26}NaO_4]^+$: 293.1723; found: 293.1726.

Procedure for peroxidation of 1a with ethereal solution of H₂O₂ and BF₃·Et₂O (Table 1, runs 1-17).

A 9.27 M ethereal solution of H₂O₂ (0.10 – 1.01 mL, 0.93 – 9.34 mmol; 1.0 – 10.0 mol H₂O₂ / 1.0 mol **1a**) and BF₃·Et₂O (0.12 – 2.35 mL, 0.93 – 18.67 mmol; 1.0 – 20.0 mol BF₃·Et₂O / 1.0 mol **1a**) were successively added with stirring to a solution of 1,4-diketone **1a** (0.300 g, 0.93 mmol) in CH₃CN (5 mL) at 20 – 25 °C (runs 1, 3 – 17) and at 0 – 2 °C (run 2). The reaction mixture was stirred at 20 – 25 °C for 1.5 h (runs 1, 3 – 17) and at 0 – 2 °C for 1.5 h (run 2). Then CHCl₃ (30 mL) and saturated aqueous solution of NaHCO₃ (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Peroxides *cis-2a*, *trans-2a*, *cis-3a*, *trans-3a*, **4a**, **5a**, **6a** were isolated by chromatography on SiO₂ using PE : EA mixture as the eluent with a gradient of EA from 9 to 33 vol. %.

Procedure for peroxidation of 1a with 35% aqueous solution of H₂O₂ and 98% H₂SO₄ (Table 2, runs 1-10).

A 35% aqueous solution of H₂O₂ (0.08 – 0.40 mL, 0.93 – 4.67 mmol; 1.0 – 5.0 mol H₂O₂ / 1.0 mol **1a**) and 98% H₂SO₄ (0.05 – 0.76 mL, 1.40 – 14.0 mmol; 1.0 – 15.0 mol H₂SO₄ / 1.0 mol **1a**) were successively added with stirring to a solution of 1,4-diketone **1a** (0.300 g, 0.93 mmol) in CH₃CN (5 mL) at 20 – 25 °C. The reaction mixture was stirred at 20 – 25 °C for 3 – 5 h. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Peroxides *cis-2a*, *trans-2a*, *cis-3a*, *trans-3a*, **4a**, **5a**, **6a**, **7a** were isolated by chromatography on SiO₂ using PE : EA mixture as the eluent with a gradient of EA from 9 to 33 vol. %.



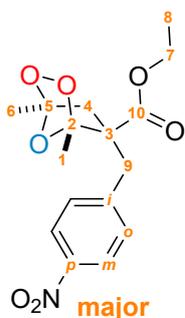
General procedure for the synthesis of ozonides *cis-2a-h*, *trans-2a-h*, **2i from 1,4-diketones **1a – i** and ethereal solution of H₂O₂ in the presence of BF₃·Et₂O.**

A 9.27 M ethereal solution of H₂O₂ (0.09 – 0.14 mL, 0.84 – 1.32 mmol; 1.0 mol H₂O₂ / 1.0 mol **1a-i**) and BF₃·Et₂O (0.11 – 0.17 mL, 0.84 – 1.32 mmol; 1.0 mol BF₃·Et₂O / 1.0 mol **1a-i**) were successively added with stirring to a solution of 1,4-diketone **1a-i** (0.300 g, 0.84 – 1.33 mmol) in CH₃CN (5 mL) at 20 – 25 °C in the case of benzyl substituents and at 0 – 2 °C in the case of alkyl, allyl substituents and ester group. The reaction mixture was stirred at 20 – 25 °C for 1.5 h in the case of benzyl substituents and at 0 – 2 °C for 1 h in the case of alkyl, allyl substituents and ester group. Then CHCl₃ (30 mL) and saturated aqueous solution of NaHCO₃ (10 mL) were added to

the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl_3 (2×30 mL). The combined organic phases were dried over MgSO_4 and filtered. The solvent was removed in vacuum of a water jet pump. Ozonides **cis-2a-h**, **trans-2a-h**, **2i** were isolated by chromatography on SiO_2 using PE : EA (20 : 1) mixture as the eluent.

Compounds: **cis-2a** + **trans-2a**: 0.232 g, 0.69 mmol, yield 73%; **cis-2b** + **trans-2b**: 0.243 g, 0.78 mmol, yield 76%; **cis-2c** + **trans-2c**: 0.193 g, 0.52 mmol, yield 61%; **cis-2d** + **trans-2d**: 0.155 g, 0.48 mmol, yield 49%; **cis-2e** + **trans-2e**: 0.138 g, 0.47 mmol, yield 43%; **cis-2f** + **trans-2f**: 0.171 g, 0.71 mmol, yield 53%; **cis-2g** + **trans-2g**: 0.231 g, 0.89 mmol, yield 72%; **cis-2h** + **trans-2h**: 0.215 g, 0.75 mmol, yield 67%; **2i**: 0.051 g, 0.19 mmol, yield 16%; **9j**: 0.173 g, 0.74 mmol, yield 54%; **9k**: 0.090 g, 0.41 mmol, yield 28%

Ethyl (1*S,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a**



White crystals. Mp = 100 – 102 °C. R_f = 0.50 (TLC, PE : EA, 2 : 1).

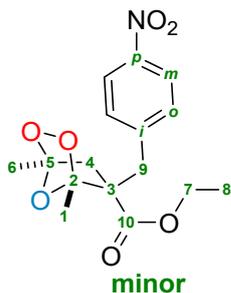
^1H NMR (300.13 MHz, CDCl_3), δ : 8.13 (d, J = 8.7 Hz, 2H, H^m), 7.22 (d, J = 8.7 Hz, 2H, H^o), 4.33 – 4.18 (m, 2H, H^7), 3.55 (d, J = 13.4 Hz, 1H, H^9), 2.79 (d, J = 13.2 Hz, 1H, H^4), 2.66 (d, J = 13.4 Hz, 1H, H^9), 1.84 (s, 3H, H^1), 1.74 (d, J = 13.2 Hz, 1H, H^4), 1.66 (s, 3H, H^6), 1.29 (t, J = 7.1 Hz, 3H, H^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 170.9 (C^{10}), 147.3 (C^p), 143.5 (C^i), 130.4 (C^o), 123.8 (C^m), 112.2 (C^2), 111.1 (C^5), 61.9 (C^7), 60.9 (C^3), 42.0 (C^4), 41.1 (C^9), 15.1 (C^6), 14.2 (C^8), 12.1 (C^1).

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{NO}_7$: C, 56.97; H, 5.68. Found: C, 57.09; H, 5.79.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{19}\text{NNaO}_7]^+$: 360.1054; found: 360.1049.

Ethyl (1*S,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a**



Slightly yellow crystals. Mp = 101 – 103 °C. R_f = 0.56 (TLC, PE : EA, 2 : 1).

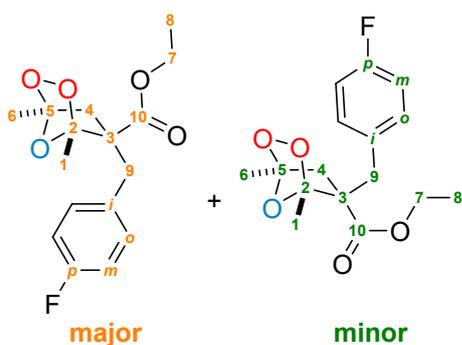
¹H NMR (300.13 MHz, CDCl₃), δ: 8.12 (d, *J* = 8.7 Hz, 2H, **H^m**), 7.33 (d, *J* = 8.7 Hz, 2H, **H^o**), 4.23 – 4.07 (m, 2H, **H⁷**), 3.45 (d, *J* = 14.3 Hz, 1H, **H⁹**), 3.35 (d, *J* = 14.3 Hz, 1H, **H⁹**), 2.66 (d, *J* = 12.8 Hz, 1H, **H⁴**), 2.11 (d, *J* = 12.8 Hz, 1H, **H⁴**), 1.69 (s, 3H, **H⁶**), 1.65 (s, 3H, **H¹**), 1.22 (t, *J* = 7.1 Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ: 171.6 (**C¹⁰**), 147.0 (**C^p**), 145.9 (**Cⁱ**), 130.3 (**C^o**), 123.7 (**C^m**), 112.3 (**C²**), 110.6 (**C⁵**), 62.0 (**C⁷**), 60.8 (**C³**), 43.2 (**C⁴**), 38.4 (**C⁹**), 15.0 (**C⁶**), 14.2 (**C⁸**), 13.2 (**C¹**).

Anal. Calcd for C₁₆H₁₉NO₇: C, 56.97; H, 5.68. Found: C, 57.06; H, 5.75.

HRMS (ESI-TOF): *m/z* [M+Na]⁺: calculated for [C₁₆H₁₉NNaO₇]⁺: 360.1054; found: 360.1062.

Ethyl 5-(4-fluorobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2b+*trans*-2b



White crystals. Ratio of *cis*-2b : *trans*-2b = 87 : 13. R_f = 0.45 (TLC, PE : EA, 5 : 1).

***cis*-2b (major):** ¹H NMR (300.13 MHz, CDCl₃), δ: 7.02 – 6.91 (m, 4H, **H^o**, **H^m**), 4.31 – 4.17 (m, 2H, **H⁷**), 3.43 (d, *J* = 13.4 Hz, 1H, **H⁹**), 2.75 (d, *J* = 13.2 Hz, 1H, **H⁴**), 2.51 (d, *J* = 13.4 Hz, 1H, **H⁹**), 1.83 (s, 3H, **H¹**), 1.78 (d, *J* = 13.2 Hz, 1H, **H⁴**), 1.66 (s, 3H, **H⁶**), 1.29 (t, *J* = 7.1 Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ: 171.3 (**C¹⁰**), 162.1 (d, ¹*J*_{CF} = 245.5 Hz, **C^p**), 131.4 (d, ⁴*J*_{CF} = 3.2 Hz, **Cⁱ**), 131.0 (d, ³*J*_{CF} = 7.9 Hz, **C^o**), 115.6 (d, ²*J*_{CF} = 21.3 Hz, **C^m**), 112.4 (**C²**), 111.1 (**C⁵**), 61.7 (**C⁷**), 61.2 (**C³**), 42.0 (**C⁴**), 40.6 (**C⁹**), 15.1 (**C⁶**), 14.2 (**C⁸**), 12.1 (**C¹**).

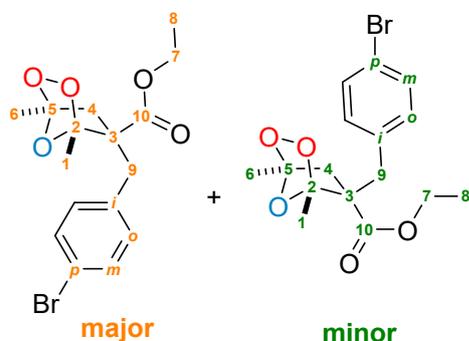
trans-2b (minor): ^1H NMR (300.13 MHz, CDCl_3), δ : 7.05 – 6.89 (m, 4H, \mathbf{H}^o , \mathbf{H}^m), 4.34 – 4.15 (m, 2H, \mathbf{H}^7), 3.31 (d, $J = 14.1$ Hz, 1H, \mathbf{H}^9), 3.21 (d, $J = 14.1$ Hz, 1H, \mathbf{H}^9), 2.62 (d, $J = 12.9$ Hz, 1H, \mathbf{H}^4), 2.12 (d, $J = 12.9$ Hz, 1H, \mathbf{H}^4), 1.67 (s, 3H, \mathbf{H}^6), 1.65 (s, 3H, \mathbf{H}^1), 1.23 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.3 (\mathbf{C}^{10}), 162.1 (d, $^1J_{\text{CF}} = 245.5$ Hz, \mathbf{C}^p), 131.4 (d, $^4J_{\text{CF}} = 3.2$ Hz, \mathbf{C}^i), 131.0 (d, $^3J_{\text{CF}} = 7.9$ Hz, \mathbf{C}^o), 115.6 (d, $^2J_{\text{CF}} = 21.3$ Hz, \mathbf{C}^m), 112.4 (\mathbf{C}^2), 111 (\mathbf{C}^5), 61.7 (\mathbf{C}^7), 61.2 (\mathbf{C}^3), 43.1 (\mathbf{C}^4), 37.8 (\mathbf{C}^9), 15.1 (\mathbf{C}^6), 14.1 (\mathbf{C}^8), 13.3 (\mathbf{C}^1).

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{FO}_5$: C, 61.93; H, 6.17. Found: C, 62.01; H, 6.28.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{19}\text{FNaO}_5]^+$: 333.1109; found: 333.1104.

Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c+*trans*-2c



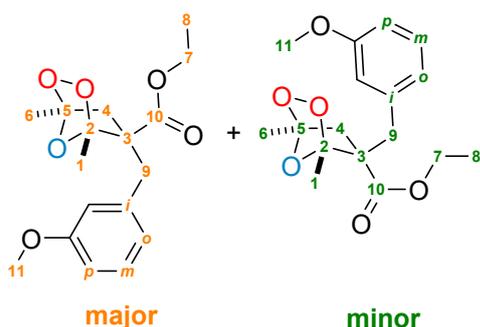
White crystals. Ratio of *cis*-2c : *trans*-2c = 84 : 16. $R_f = 0.43$ (TLC, PE : EA, 5 : 1).

***cis*-2c (major):** ^1H NMR (300.13 MHz, CDCl_3), δ : 7.39 (d, $J = 8.4$ Hz, 2H, \mathbf{H}^m), 6.91 (d, $J = 8.4$ Hz, 2H, \mathbf{H}^o), 4.31 – 4.16 (m, 2H, \mathbf{H}^7), 3.41 (d, $J = 13.4$ Hz, 1H, \mathbf{H}^9), 2.76 (d, $J = 13.2$ Hz, 1H, \mathbf{H}^4), 2.49 (d, $J = 13.4$ Hz, 1H, \mathbf{H}^9), 1.83 (s, 3H, \mathbf{H}^1), 1.75 (d, $J = 13.2$ Hz, 1H, \mathbf{H}^4), 1.66 (s, 3H, \mathbf{H}^6), 1.29 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8). ^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.2 (\mathbf{C}^{10}), 134.7 (\mathbf{C}^p), 131.8 (\mathbf{C}^o), 131.2 (\mathbf{C}^m), 121.2 (\mathbf{C}^i), 112.4 (\mathbf{C}^2), 111.1 (\mathbf{C}^5), 61.7 (\mathbf{C}^7), 61.0 (\mathbf{C}^3), 42.0 (\mathbf{C}^4), 40.8 (\mathbf{C}^9), 15.1 (\mathbf{C}^6), 14.2 (\mathbf{C}^8), 12.1 (\mathbf{C}^1).

***trans*-2c (minor):** ^1H NMR (300.13 MHz, CDCl_3), δ : 7.39 (d, $J = 8.4$ Hz, 2H, \mathbf{H}^m), 7.03 (d, $J = 8.4$ Hz, 2H, \mathbf{H}^o), 4.31 – 4.16 (m, 2H, \mathbf{H}^7), 3.30 (d, $J = 14.3$ Hz, 1H, \mathbf{H}^9), 3.18 (d, $J = 14.3$ Hz, 1H, \mathbf{H}^9), 2.62 (d, $J = 12.8$ Hz, 1H, \mathbf{H}^4), 2.10 (d, $J = 12.8$ Hz, 1H, \mathbf{H}^4), 1.67 (s, 3H, \mathbf{H}^6), 1.65 (s, 3H, \mathbf{H}^1), 1.23 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8). ^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.2 (\mathbf{C}^{10}), 134.7 (\mathbf{C}^p), 131.6 (\mathbf{C}^o), 131.1 (\mathbf{C}^m), 121.1 (\mathbf{C}^i), 112.4 (\mathbf{C}^2), 111.1 (\mathbf{C}^5), 61.7 (\mathbf{C}^7), 61.0 (\mathbf{C}^3), 43.1 (\mathbf{C}^4), 38.5 (\mathbf{C}^9), 15.1 (\mathbf{C}^6), 14.2 (\mathbf{C}^8), 13.3 (\mathbf{C}^1). Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{BrO}_5$: C, 51.77; H, 5.16. Found: C, 51.88; H, 5.27.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{16}\text{H}_{20}\text{BrO}_5]^+$: 371.0489, 373.0469; found: 371.0492, 373.0472.

Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d+*trans*-2d



Slightly yellow oil. Ratio of *cis*-2d : *trans*-2d = 84 : 16. R_f = 0.42 (TLC, PE : EA, 5 : 1).

***cis*-2d (major):** ^1H NMR (300.13 MHz, CDCl_3), δ : 7.24 – 7.14 (m, 1H), 6.80 – 6.74 (m, 1H), 6.64 – 6.55 (m, 2H), 4.32 – 4.17 (m, 2H, H^7), 3.76 (s, 3H, H^{11}), 3.45 (d, J = 13.4 Hz, 1H, H^9), 2.77 (d, J = 13.2 Hz, 1H, H^4), 2.50 (d, J = 13.4 Hz, 1H, H^9), 1.83 (s, 3H, H^1), 1.83 (d, J = 13.2 Hz, 1H, H^4), 1.65 (s, 3H, H^6), 1.30 (t, J = 7.1 Hz, 3H, H^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.4 (C^{10}), 159.8, 137.3, 121.9, 115.6, 112.4 (C^2), 112.1, 111.2 (C^5), 61.6 (C^7), 61.1 (C^3), 55.2 (C^{11}), 41.9 (C^4), 41.4 (C^9), 15.1 (C^6), 14.2 (C^8), 12.1 (C^1).

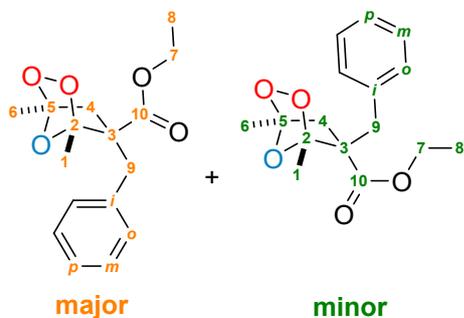
***trans*-2d (minor):** ^1H NMR (300.13 MHz, CDCl_3), δ : 7.24 – 7.14 (m, 1H), 6.80 – 6.74 (m, 1H), 6.64 – 6.55 (m, 2H), 4.32 – 4.17 (m, 2H, H^7), 3.76 (s, 3H, H^{11}), 3.33 (d, J = 14.0 Hz, 1H, H^9), 3.21 (d, J = 14.0 Hz, 1H, H^9), 2.64 (d, J = 12.9 Hz, 1H, H^4), 2.15 (d, J = 12.9 Hz, 1H, H^4), 1.67 (s, 3H, H^1), 1.66 (s, 3H, H^6), 1.23 (t, J = 7.1 Hz, 3H, H^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.4 (C^{10}), 159.8, 137.3, 121.8, 115.4, 112.4 (C^2), 112.0, 111.2 (C^5), 61.6 (C^7), 60.6 (C^3), 55.2 (C^{11}), 43.1 (C^4), 38.5 (C^9), 15.1 (C^6), 14.1 (C^8), 13.3 (C^1).

Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{O}_6$: C, 63.34; H, 6.88. Found: C, 63.45; H, 6.97.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{17}\text{H}_{23}\text{O}_6]^+$: 323.1489; found: 323.1489.

Ethyl-5-benzyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2e+*trans*-2e



Slightly yellow crystals. *cis*-2e : *trans*-2e = 84 : 16. R_f = 0.58 (TLC, PE : EA, 5 : 1).

cis-2e (major): ^1H NMR (300.13 MHz, CDCl_3), δ : 7.32 – 7.23 (m, 3H, \mathbf{H}^m , \mathbf{H}^p), 7.08 – 7.02 (m, 2H, \mathbf{H}^o), 4.34 – 4.18 (m, 2H, \mathbf{H}^7), 3.49 (d, $J = 13.4$ Hz, 1H, \mathbf{H}^9), 2.78 (d, $J = 13.2$ Hz, 1H, \mathbf{H}^4), 2.55 (d, $J = 13.4$ Hz, 1H, \mathbf{H}^9), 1.86 (s, 3H, \mathbf{H}^l), 1.84 (d, $J = 13.2$ Hz, 1H, \mathbf{H}^4), 1.68 (s, 3H, \mathbf{H}^6), 1.31 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.4 (\mathbf{C}^{10}), 135.7, 129.6, 128.7, 127.1, 112.5 (\mathbf{C}^2), 111.2 (\mathbf{C}^5), 61.6 (\mathbf{C}^7), 61.2 (\mathbf{C}^3), 41.9 (\mathbf{C}^4), 41.4 (\mathbf{C}^9), 15.1 (\mathbf{C}^6), 14.2 (\mathbf{C}^8), 12.1 (\mathbf{C}^1).

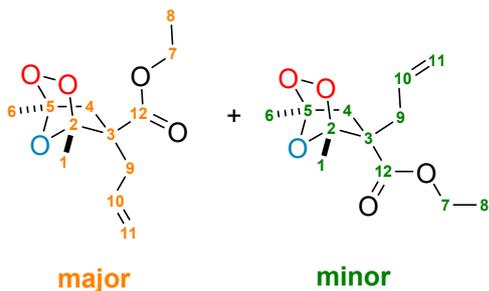
trans-2e (minor): ^1H NMR (300.13 MHz, CDCl_3), δ : 7.32 – 7.23 (m, 3H, \mathbf{H}^m , \mathbf{H}^p), 7.08 – 7.02 (m, 2H, \mathbf{H}^o), 4.34 – 4.18 (m, 2H, \mathbf{H}^7), 3.37 (d, $J = 14.4$ Hz, 1H, \mathbf{H}^9), 3.26 (d, $J = 14.4$ Hz, 1H, \mathbf{H}^9), 2.66 (d, $J = 12.9$ Hz, 1H, \mathbf{H}^4), 2.17 (d, $J = 12.9$ Hz, 1H, \mathbf{H}^4), 1.69 (s, 3H, \mathbf{H}^l), 1.68 (s, 3H, \mathbf{H}^6), 1.24 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.4 (\mathbf{C}^{10}), 135.7, 129.4, 128.5, 127.1, 112.5 (\mathbf{C}^2), 111.2 (\mathbf{C}^5), 61.6 (\mathbf{C}^7), 61.2 (\mathbf{C}^3), 43.1 (\mathbf{C}^4), 38.5 (\mathbf{C}^9), 15.1 (\mathbf{C}^6), 14.1 (\mathbf{C}^8), 12.1 (\mathbf{C}^1).

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5$: C, 65.74; H, 6.90. Found: C, 65.88; H, 7.02.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{16}\text{H}_{21}\text{O}_5]^+$: 293.1384; found: 293.1395.

Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis-2f*+*trans-2f*



Slightly yellow oil. Ratio of *cis-2f* : *trans-2f* = 84 : 16. $R_f = 0.60$ (TLC, PE : EA, 5 : 1).

cis-2f (major): ^1H NMR (300.13 MHz, CDCl_3), δ : 5.61 – 5.44 (m, 1H, \mathbf{H}^{11}), 5.14 – 5.00 (m, 2H, \mathbf{H}^{10}), 4.23 – 4.14 (m, 2H, \mathbf{H}^7), 2.91 (d, $J = 13.0$ Hz, 1H, \mathbf{H}^4), 2.74 – 2.60 (m, 1H, \mathbf{H}^9), 2.17 – 2.04 (m, 1H, \mathbf{H}^9), 1.75 (d, $J = 14.7$ Hz, 1H, \mathbf{H}^4), 1.73 (s, 3H, \mathbf{H}^l), 1.63 (s, 3H, \mathbf{H}^6), 1.26 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.0 (\mathbf{C}^{12}), 131.5 (\mathbf{C}^{10}), 119.2 (\mathbf{C}^{11}), 111.9 (\mathbf{C}^2), 110.9 (\mathbf{C}^5), 61.3 (\mathbf{C}^7), 59.7 (\mathbf{C}^3), 42.4 (\mathbf{C}^4), 40.4 (\mathbf{C}^9), 14.9 (\mathbf{C}^6), 14.2 (\mathbf{C}^8), 12.0 (\mathbf{C}^1).

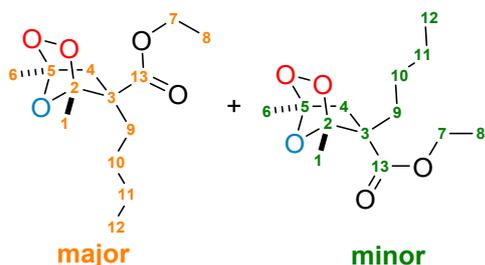
trans-2f (minor): ^1H NMR (300.13 MHz, CDCl_3), δ : 5.61 – 5.44 (m, 1H, \mathbf{H}^{11}), 5.14 – 5.00 (m, 2H, \mathbf{H}^{10}), 4.23 – 4.14 (m, 2H, \mathbf{H}^7), 2.74 – 2.60 (m, 2H, \mathbf{H}^4 , \mathbf{H}^9), 2.15 – 2.04 (m, 1H, \mathbf{H}^9), 1.95 (d, $J = 12.8$ Hz, 1H, \mathbf{H}^4), 1.65 (s, 3H, \mathbf{H}^6), 1.61 (s, 3H, \mathbf{H}^l), 1.26 (t, $J = 7.1$ Hz, 3H, \mathbf{H}^8).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.0 (\mathbf{C}^{12}), 133.9 (\mathbf{C}^{10}), 118.3 (\mathbf{C}^{11}), 112.1 (\mathbf{C}^2), 110.5 (\mathbf{C}^5), 61.5 (\mathbf{C}^7), 59.7 (\mathbf{C}^3), 42.8 (\mathbf{C}^4), 37.4 (\mathbf{C}^9), 14.9 (\mathbf{C}^6), 14.2 (\mathbf{C}^8), 13.0 (\mathbf{C}^1).

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_5$: C, 59.49; H, 7.49. Found: C, 59.60; H, 7.58.

HRMS (ESI-TOF): m/z $[M+H]^+$: calculated for $[C_{12}H_{19}O_5]^+$: 243.1227; found: 243.1231.

Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g+*trans*-2g



Slightly yellow oil. Ratio of *cis*-2g : *trans*-2g = 79 : 21. R_f = 0.44 (TLC, PE : EA, 10 : 1).

***cis*-2g (major):** 1H NMR (300.13 MHz, $CDCl_3$), δ : 4.30 – 4.14 (m, 2H, H^7), 2.98 (d, J = 12.7 Hz, 1H, H^4), 2.02 – 1.86 (m, 1H, H^9), 1.76 (s, 3H, H^1), 1.67 (s, 3H, H^6), 1.69 (m, 1H, H^4), 1.46 – 1.12 (m, 4H, H^9 , H^{10} , H^{11}), 1.28 (t, J = 7.1 Hz, 3H, H^7), 1.08 – 0.94 (m, 1H, H^{10}), 0.88 (t, J = 7.1 Hz, 3H, H^{12}).

^{13}C NMR (75.48 MHz, $CDCl_3$), δ : 171.7 (C^{13}), 112.5 (C^2), 110.9 (C^5), 61.3 (C^7), 60.6 (C^3), 43.2 (C^4), 35.8 (C^9), 26.1 (C^{11}), 22.9 (C^{10}), 15.2 (C^6), 14.3 (C^8), 14.0 (C^{12}), 12.2 (C^1).

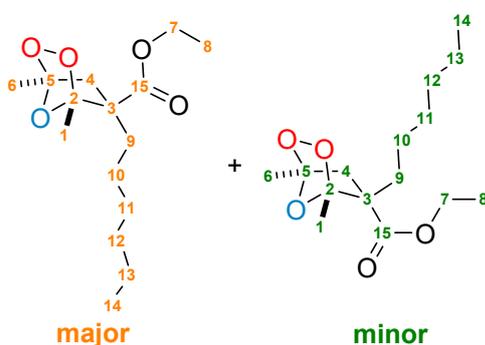
***trans*-2g (minor):** 1H NMR (300.13 MHz, $CDCl_3$), δ : 4.30 – 4.14 (m, 2H, H^7), 2.72 (d, J = 12.7 Hz, 1H, H^4), 2.02 – 1.86 (m, 3H, H^9 , H^4), 1.68 (s, 3H, H^6), 1.65 (s, 3H, H^1), 1.46 – 1.12 (m, 4H, H^{10} , H^{11}), 1.31 (t, J = 7.1 Hz, 3H, H^8), 0.88 (t, J = 7.1 Hz, 3H, H^{12}).

^{13}C NMR (75.48 MHz, $CDCl_3$), δ : 171.7 (C^{13}), 112.5 (C^2), 110.6 (C^5), 61.5 (C^7), 60.7 (C^3), 43.0 (C^4), 32.8 (C^9), 28.7 (C^{11}), 23.2 (C^{10}), 15.1 (C^6), 14.3 (C^8), 14.0 (C^{12}), 13.4 (C^1).

Anal. Calcd for $C_{13}H_{22}O_5$: C, 60.45; H, 8.58. Found: C, 60.57; H, 8.71.

HRMS (ESI-TOF): m/z $[M+H]^+$: calculated for $[C_{13}H_{23}O_5]^+$: 259.1540; found: 259.1546.

Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h+*trans*-2h



Slightly yellow oil. Ratio of *cis*-2h : *trans*-2h = 73 : 27. R_f = 0.68 (TLC, PE : EA, 5 : 1).

***cis*-2h (major):** 1H NMR (300.13 MHz, $CDCl_3$), δ : 4.25 – 4.12 (m, 2H, H^7), 2.95 (d, J = 12.7 Hz, 1H, H^4), 1.96 – 1.86 (m, 1H, H^9), 1.70 (s, 3H, H^1), 1.68 (m, 1H, H^4), 1.62 (s, 3H, H^6), 1.34 – 1.10

(m, 8H, H^9 , H^{10} , H^{11} , H^{12} , H^{13}), 1.26 (t, $J = 7.1$ Hz, 3H, H^7), 1.05 – 0.92 (m, 1H, H^{10}), 0.85 (t, $J = 7.1$ Hz, 3H, H^{14}).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.6 (C^{15}), 112.4 (C^2), 110.8 (C^5), 61.2 (C^7), 60.7 (C^3), 43.1 (C^4), 36.0, 31.6, 29.4, 23.8, 22.6, 15.1, 14.2, 14.1, 12.2.

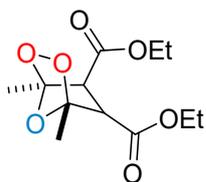
trans-2h (minor): ^1H NMR (300.13 MHz, CDCl_3), δ : 4.25 – 4.12 (m, 2H, H^7), 2.69 (d, $J = 12.7$ Hz, 1H, H^4), 1.97 – 1.76 (m, 3H, H^9 , H^4), 1.64 (s, 3H, H^6), 1.60 (s, 3H, H^1), 1.33 – 1.09 (m, 8H, H^{10} , H^{11} , H^{12} , H^{13}), 1.26 (t, $J = 7.1$ Hz, 3H, H^8), 0.85 (t, $J = 7.1$ Hz, 3H, H^{14}).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 172.5 (C^{15}), 112.4 (C^2), 110.5 (C^5), 61.4 (C^7), 60.6 (C^3), 43.0 (C^4), 33.1, 31.6, 29.7, 26.4, 22.6, 15.1, 14.2, 14.1, 13.1.

Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_5$: C, 62.91; H, 9.15. Found: C, 63.12; H, 9.28.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{15}\text{H}_{27}\text{O}_5]^+$: 287.1853; found: 287.1853.

Diethyl (1*S**,4*S**,5*S**)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5,6-dicarboxylate, 2i



Slightly yellow oil. $R_f = 0.56$ (TLC, PE : EA, 5 : 1).

^1H NMR (300.13 MHz, CDCl_3), δ : 4.30 – 4.14 (m, 4H), 3.79 (d, $J = 4.6$ Hz, 1H), 3.56 (d, $J = 4.6$ Hz, 1H), 1.87 (s, 3H), 1.68 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 169.7, 168.0, 111.1, 110.2, 61.9, 61.8, 55.1, 54.3, 14.6, 14.3, 14.3, 13.8.

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_7$: C, 52.55; H, 6.62. Found: C, 52.63; H, 6.71.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{12}\text{H}_{19}\text{O}_7]^+$: 275.1125; found: 275.1125.

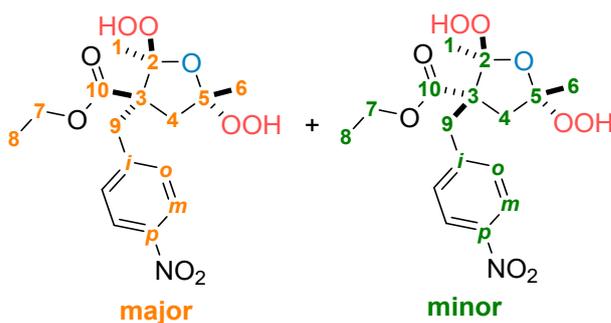
General procedure for the synthesis of dihydroperoxy-tetrahydrofurans *cis*-3a + *trans*-3a, *cis*-3b, *trans*-3b, *cis*-3c, *cis*-3e, *cis*-3g, *trans*-3g, *cis*-3h, *trans*-3h from 1,4-diketones 1a – c,e,g,h and ethereal solution of H_2O_2 in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

A 9.27 M ethereal solution of H_2O_2 (0.91 – 1.34 mL, 8.45 – 12.38 mmol; 10.0 mol H_2O_2 / 1.0 mol 1a-c,e,g,h) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.11 – 0.16 mL, 0.84 – 1.24 mmol; 1.0 mol $\text{BF}_3 \cdot \text{Et}_2\text{O}$ / 1.0 mol 1a-c,e,g,h) were successively added with stirring to a solution of 1,4-diketone 1a-c,e,g,h (0.300 g, 0.84 – 1.24 mmol) in CH_3CN (5 mL) at 20 – 25 °C in the case of benzyl substituents and at 0 – 2 °C in the case of alkyl and allyl substituents. The reaction mixture was stirred at 20 – 25 °C for

1.5 h in the case of benzyl substituents and at 0 – 2 °C for 1.5 h in the case of alkyl and allyl substituents. Then CHCl₃ (30 mL) and saturated aqueous solution of NaHCO₃ (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Dihydroperoxy-tetrahydrofurans *cis-3a* + *trans-3a*, *cis-3b*, *trans-3b*, *cis-3c*, *cis-3e*, *cis-3g*, *trans-3g*, *cis-3h*, *trans-3h* were isolated by chromatography on SiO₂ using PE : EA mixture as the eluent with a gradient of EA from 9 to 33 vol. %.

Compounds: *cis-3a* + *trans-3a*: 0.167 g, 0.45 mmol, yield 48%; *cis-3b*: 0.155 g, 0.45 mmol, yield 44%; *trans-3b*: 0.034 g, 0.10 mmol, yield 9%; *cis-3c*: 0.045 g, 0.11 mmol, yield 13%; *cis-3e*: 0.061 g, 0.19 mmol, yield 17%; *cis-3g*: 0.044 g, 0.15 mmol, yield 12%; *trans-3g*: 0.067 g, 0.23 mmol, yield 18%; *cis-3h*: 0.048 g, 0.15 mmol, yield 13%; *trans-3h*: 0.047 g, 0.15 mmol, yield 13%.

Ethyl 2,5-dihydroperoxy-2,5-dimethyl-3-(4-nitrobenzyl)tetrahydrofuran-3-carboxylate, *cis-3a*+*trans-3a*



Slightly yellow crystals. Ratio of *cis-3a* : *trans-3a* = 67 : 33. R_f = 0.31 (TLC, PE : EA, 2 : 1).

***cis-3a* (major):** ¹H NMR (300.13 MHz, CDCl₃), δ: 8.32 (s, 1H, **OOH**), 8.12 (d, *J* = 8.6 Hz, 2H, **H^m**), 7.95 (s, 1H, **OOH**), 7.32 (d, *J* = 8.6 Hz, 2H, **H^o**), 4.30 – 4.12 (m, 2H, **H⁷**), 3.48 (d, *J* = 12.7 Hz, 1H, **H⁹**), 3.14 (d, *J* = 12.7 Hz, 1H, **H⁹**), 2.72 (d, *J* = 15.0 Hz, 1H, **H⁴**), 2.02 (d, *J* = 15.0 Hz, 1H, **H⁴**), 1.78 (s, 3H, **H¹**), 1.71 (s, 3H, **H⁶**), 1.28 (t, *J* = 7.1 Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ: 170.2 (**C¹⁰**), 147.3 (**C^p**), 143.9 (**Cⁱ**), 131.3 (**C^o**), 123.7 (**C^m**), 115.8 (**C²**), 112.9 (**C⁵**), 61.9 (**C⁷**), 59.6 (**C³**), 38.9 (**C⁹**), 38.5 (**C⁴**), 23.7 (**C⁶**), 17.0 (**C¹**), 14.2 (**C⁸**).

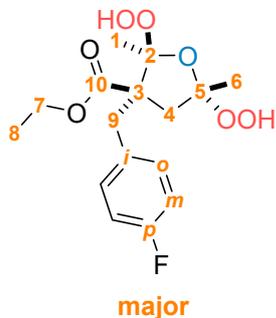
***trans-3a* (minor):** ¹H NMR (300.13 MHz, CDCl₃), δ: 8.72 (s, 2H, **OOH**), 8.15 (d, *J* = 8.6 Hz, 2H, **H^m**), 7.22 (d, *J* = 8.6 Hz, 2H, **H^o**), 4.30 – 4.12 (m, 2H, **H⁷**), 3.61 (d, *J* = 12.7 Hz, 1H, **H⁹**), 2.73 (d, *J* = 14.7 Hz, 1H, **H⁴**), 2.71 (d, *J* = 12.7 Hz, 1H, **H⁹**), 1.95 (d, *J* = 14.7 Hz, 1H, **H⁴**), 1.77 (s, 3H, **H¹**), 1.74 (s, 3H, **H⁶**), 1.27 (t, *J* = 7.1 Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ: 170.2 (**C¹⁰**), 147.3 (**C^p**), 143.4 (**Cⁱ**), 130.8 (**C^o**), 124.0 (**C^m**), 115.8 (**C²**), 112.0 (**C⁵**), 62.0 (**C⁷**), 61.0 (**C³**), 39.7 (**C⁹**), 38.4 (**C⁴**), 24.1 (**C⁶**), 16.5 (**C¹**), 14.2 (**C⁸**).

Anal. Calcd for C₁₆H₂₁NO₉: C, 51.75; H, 5.70. Found: C, 51.87; H, 5.83.

HRMS (ESI-TOF): m/z [M+Na]⁺: calculated for [C₁₆H₂₁NNaO₉]⁺: 394.1109; found: 394.1095.

Ethyl (2*S,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b**



White crystals. Mp = 109 – 111 °C. R_f = 0.45 (TLC, PE : EA, 2 : 1).

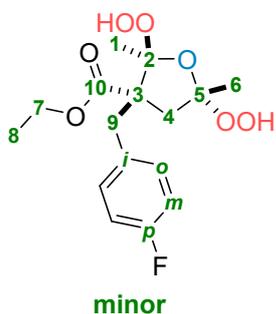
***cis*-3b (major):** ¹H NMR (300.13 MHz, CDCl₃), δ: 8.38 (br.s, 1H, **OOH**), 8.02 (s, 1H, **OOH**), 7.18 – 7.04 (m, 2H, **H^m**), 7.01 – 6.84 (m, 2H, **H^o**), 4.32 – 4.05 (m, 2H, **H⁷**), 3.36 (d, *J* = 13.0 Hz, 1H, **H⁹**), 2.97 (d, *J* = 13.0 Hz, 1H, **H⁹**), 2.67 (d, *J* = 15.0 Hz, 1H, **H⁴**), 2.11 (d, *J* = 15.0 Hz, 1H, **H⁴**), 1.77 (s, 3H, **H¹**), 1.70 (s, 3H, **H¹**), 1.27 (t, *J* = 7.1 Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ: 170.7 (**C¹⁰**), 162.1 (d, ¹*J*_{CF} = 245.4 Hz), 131.9 (d, ³*J*_{CF} = 8.0 Hz), 131.6 (d, ⁴*J*_{CF} = 3.3 Hz), 115.9 (**C²**), 115.4 (d, ²*J*_{CF} = 21.1 Hz), 112.9 (**C⁵**), 61.6 (**C⁷**), 59.8 (**C³**), 38.5 (**C⁴**), 38.4 (**C⁹**), 23.8 (**C¹**), 17.0 (**C⁶**), 14.1 (**C⁸**).

Anal. Calcd for C₁₆H₂₁FO₇: C, 55.81; H, 6.15. Found: C, 56.01; H, 6.33.

HRMS (ESI-TOF): m/z [M+Na]⁺: calculated for [C₁₆H₂₁FNaO₇]⁺: 367.1164; found: 367.1157.

Ethyl (2*S,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3b**



Colorless oil. R_f = 0.48 (TLC, PE : EA, 2 : 1).

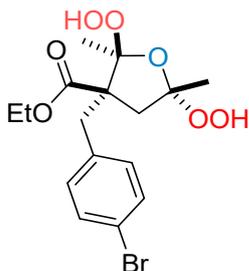
***trans*-3b (minor):** ¹H NMR (300.13 MHz, CDCl₃), δ: 8.95 (s, 2H, **OOH**), 7.06 – 6.88 (m, 4H, **H^{o,m}**), 4.30 – 4.03 (m, 2H, **H⁷**), 3.47 (d, *J* = 13.6 Hz, 1H, **H⁹**), 2.64 (d, *J* = 14.8 Hz, 1H, **H⁴**), 2.58 (d, *J* = 13.6 Hz, 1H, **H⁹**), 2.03 (d, *J* = 14.8 Hz, 1H, **H⁴**), 1.74 (s, 3H, **H¹**), 1.72 (s, 3H, **H⁶**), 1.25 (t, *J* = 7.1 Hz, 3H, **H⁸**).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 170.6 (C^{10}), 162.2 (d, $^1J_{\text{CF}} = 246.1$ Hz), 131.4 (d, $^3J_{\text{CF}} = 8.1$ Hz), 131.6 (d, $^4J_{\text{CF}} = 3.3$ Hz), 115.7 (d, $^2J_{\text{CF}} = 21.4$ Hz), 115.2 (C^2), 112.1 (C^5), 61.9 (C^7), 61.2 (C^3), 39.1 (C^9), 38.1 (C^4), 24.0 (C^6), 16.4 (C^1), 14.1 (C^8).

Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{FO}_7$: C, 55.81; H, 6.15. Found: C, 55.98; H, 6.29.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{21}\text{FNaO}_7]^+$: 367.1164; found: 367.1154.

Ethyl (2*S,3*S**,5*S**)-3-(4-bromobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3c**



White crystals. Mp = 137 – 139 °C. $R_f = 0.31$ (TLC, PE : EA, 2 : 1).

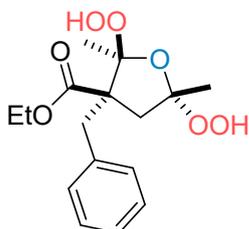
^1H NMR (300.13 MHz, CD_3OD), δ : 7.44 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.39 – 3.30 (m, 3H), 3.16 (d, $J = 12.9$ Hz, 1H), 2.63 (d, $J = 14.5$ Hz, 1H), 2.06 (d, $J = 14.5$ Hz, 1H), 1.75 (s, 3H), 1.66 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CD_3OD), δ : 172.3, 137.2, 133.3, 132.3, 121.8, 116.1, 113.1, 62.3, 60.9, 39.5, 39.3, 24.2, 17.3, 14.3.

Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{BrO}_7$: C, 47.42; H, 5.22. Found: C, 47.52; H, 5.32.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{21}\text{BrNaO}_7]^+$: 427.0363, 429.0343; found: 427.0372, 429.0356.

Ethyl (2*S,3*S**,5*R**)-3-benzyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3e**



Colorless oil. $R_f = 0.36$ (TLC, PE : EA, 2 : 1).

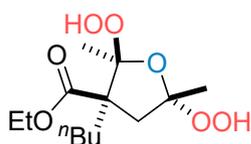
^1H NMR (300.13 MHz, CDCl_3), δ : 8.42 (br.s, 1H), 8.07 (br.s, 1H), 7.35 – 7.21 (m, 3H), 7.18 – 7.12 (m, 2H), 4.32 – 4.05 (m, 2H), 3.42 (d, $J = 12.9$ Hz, 1H), 3.02 (d, $J = 12.8$ Hz, 1H), 2.69 (d, $J = 14.9$ Hz, 1H), 2.19 (d, $J = 14.9$ Hz, 1H), 1.81 (s, 3H), 1.73 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 170.8, 136.0, 130.4, 128.5, 127.2, 115.9, 112.9, 61.6, 59.9, 39.2, 38.6, 23.8, 17.0, 14.1.

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_7$: C, 58.89; H, 6.80. Found: C, 59.00; H, 6.99.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{22}\text{NaO}_7]^+$: 349.1258; found: 349.1262.

Ethyl (2*S,3*S**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3g**



Colorless oil. R_f = 0.36 (TLC, PE : EA, 2 : 1).

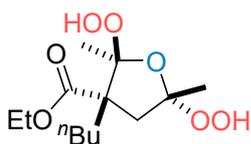
^1H NMR (300.13 MHz, CDCl_3), δ : 8.46 (br.s, 1H), 8.21 (br.s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 2.81 (d, J = 14.6 Hz, 1H), 2.13 (d, J = 14.6 Hz, 1H), 1.97 – 1.66 (m, 2H), 1.67 (s, 3H), 1.62 (s, 3H), 1.35 – 1.19 (m, 3H), 1.25 (t, J = 7.1 Hz, 3H), 0.97 – 0.79 (m, 1H), 0.86 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.5, 115.9, 112.7, 61.4, 59.0, 39.4, 33.4, 26.6, 23.9, 22.9, 17.1, 14.1, 14.0.

Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_7$: C, 53.41; H, 8.28. Found: C, 53.50; H, 8.35.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{13}\text{H}_{24}\text{NaO}_7]^+$: 315.1414; found: 315.1411.

Ethyl (2*S,3*R**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3g**



Colorless oil. R_f = 0.41 (TLC, PE : EA, 2 : 1).

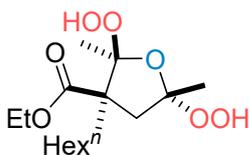
^1H NMR (300.13 MHz, CDCl_3), δ : 9.17 (br.s, 2H), 4.14 (q, J = 7.1 Hz, 2H), 2.79 (d, J = 14.4 Hz, 1H), 2.02 (d, J = 14.4 Hz, 1H), 2.02 – 1.86 (m, 1H), 1.60 (s, 3H), 1.56 (s, 3H), 1.43 – 1.16 (m, 4H), 1.23 (t, J = 7.1 Hz, 3H), 1.04 – 0.88 (m, 1H), 0.87 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.3, 115.2, 112.0, 61.6, 60.3, 39.2, 34.0, 26.2, 24.1, 22.9, 16.5, 14.1, 13.9.

Anal. Calcd for $\text{C}_{13}\text{H}_{24}\text{O}_7$: C, 53.41; H, 8.28. Found: C, 53.50; H, 8.38.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{13}\text{H}_{24}\text{NaO}_7]^+$: 315.1414; found: 315.1415.

Ethyl (2*S,3*S**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3h**



Colorless oil. $R_f = 0.51$ (TLC, PE : EA, 2 : 1).

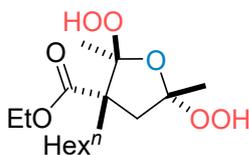
^1H NMR (300.13 MHz, CDCl_3), δ : 8.38 (br.s, 1H), 8.14 (br.s, 1H), 4.19 (q, $J = 7.1$ Hz, 2H), 2.85 (d, $J = 14.6$ Hz, 1H), 2.16 (d, $J = 14.6$ Hz, 1H), 2.02 – 1.86 (m, 1H), 1.83 – 1.69 (m, 1H), 1.70 (s, 3H), 1.65 (s, 3H), 1.39 – 1.20 (m, 7H), 1.29 (t, $J = 7.1$ Hz, 3H), 0.99 – 0.87 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.4, 116.0, 112.7, 61.4, 59.0, 39.4, 33.7, 31.6, 29.5, 24.4, 23.9, 22.6, 17.2, 14.2, 14.1.

Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_7$: C, 56.23; H, 8.81. Found: C, 56.31; H, 8.90.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{15}\text{H}_{28}\text{NaO}_7]^+$: 343.1727; found: 343.1718.

Ethyl (2*S,3*R**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3h**



Colorless oil. $R_f = 0.73$ (TLC, PE : EA, 2 : 1).

^1H NMR (300.13 MHz, CDCl_3), δ : 8.91 (br.s, 2H), 4.16 (q, $J = 7.1$ Hz, 2H), 2.83 (d, $J = 14.4$ Hz, 1H), 2.03 (d, $J = 14.4$ Hz, 1H), 2.02 – 1.86 (m, 1H), 1.83 – 1.69 (m, 1H), 1.62 (s, 3H), 1.58 (s, 3H), 1.43 – 1.16 (m, 7H), 1.25 (t, $J = 7.1$ Hz, 3H), 1.04 – 0.94 (m, 1H), 0.87 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.1, 115.3, 112.1, 61.6, 60.5, 39.3, 34.3, 31.6, 29.5, 24.12, 24.09, 22.6, 16.6, 14.2, 14.1.

Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{O}_7$: C, 56.23; H, 8.81. Found: C, 56.32; H, 8.93.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{15}\text{H}_{28}\text{NaO}_7]^+$: 343.1727; found: 343.1728.

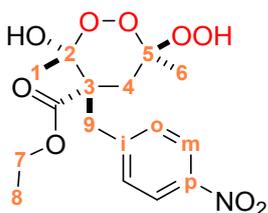
Procedure for the synthesis of hydroxy-hydroperoxy-1,2-dioxane 4a from 1,4-diketone 1a and ethereal solution of H_2O_2 in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

A 9.27 M ethereal solution of H_2O_2 (0.50 mL, 4.67 mmol; 5.0 mol H_2O_2 / 1.0 mol **1a**) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.35 mL, 2.80 mmol; 3.0 mol $\text{BF}_3 \cdot \text{Et}_2\text{O}$ / 1.0 mol **1a**) were successively added with stirring to a solution of 1,4-diketone **1a** (0.300 g, 0.93 mmol) in CH_3CN (5 mL) at 20 – 25 °C. The reaction mixture was stirred at 20 – 25 °C for 1.5 h. Then CHCl_3 (30 mL) and saturated aqueous solution

of NaHCO₃ (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Hydroxyhydroperoxy-1,2-dioxane **4a** were isolated by chromatography on SiO₂ using PE : EA mixture as the eluent with a gradient of EA from 9 to 33 vol. %.

Compound: **4a**: 0.063 g, 0.17 mmol, yield 18%.

Ethyl (3*R,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, **4a****



Colorless oil. $R_f = 0.22$ (TLC, PE : EA, 2 : 1).

¹H NMR (300.13 MHz, CDCl₃), δ : 8.59 (br. s, 1H, **OOH**), 8.11 (d, $J = 8.7$ Hz, 2H, **H^m**), 7.41 (d, $J = 8.7$ Hz, 2H, **H^o**), 4.17 (q, $J = 7.1$ Hz, 2H, **H⁷**), 3.59 (br. s, 1H, **OH**), 3.40 – 3.25 (m, 2H, **H⁹**), 2.39 (d, $J = 15.8$ Hz, 1H, **H⁴**), 1.74 (m, 3H, **H¹**), 1.60 (d, $J = 15.8$ Hz, 1H, **H⁴**), 1.51 (s, 3H, **H⁶**), 1.24 (t, $J = 7.1$ Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ : 172.0 (**C¹⁰**), 147.1 (**C^p**), 144.5 (**Cⁱ**), 131.6 (**C^o**), 123.5 (**C^m**), 106.6 (**C⁵**), 101.5 (**C²**), 61.8 (**C⁷**), 51.4 (**C³**), 38.6 (**C⁹**), 29.7 (**C⁴**), 21.4 (**C¹**), 21.2 (**C⁶**), 14.1 (**C¹**).

Anal. Calcd for C₁₆H₂₁NO₉: C, 51.75; H, 5.70. Found: C, 51.88; H, 5.82.

HRMS (ESI-TOF): m/z [M+Na]⁺: calculated for [C₁₆H₂₁NNaO₉]⁺: 394.1109; found: 394.1101.

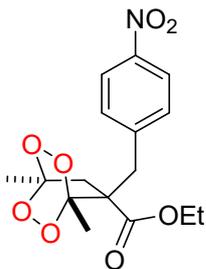
General procedure for the synthesis of tetraoxanes **5a–c, **e–h** from 1,4-diketones **1a–c**, **e–h** and ethereal solution of H₂O₂ in the presence of BF₃·Et₂O.**

A 9.27 M ethereal solution of H₂O₂ (0.46 – 0.72 mL, 4.22 – 6.63 mmol; 5.0 mol H₂O₂ / 1.0 mol **1a–c**, **e–h**) and BF₃·Et₂O (1.59 – 2.50 mL, 12.67 – 19.89 mmol; 15.0 mol BF₃·Et₂O / 1.0 mol **1a–c**, **e–h**) were successively added with stirring to a solution of 1,4-diketone **1a–c**, **e–h** (0.300 g, 0.84 – 1.33 mmol) in CH₃CN (5 mL) at 20 – 25 °C in the case of benzyl substituents and at 0 – 2 °C in the case of alkyl and allyl substituents. The reaction mixture was stirred at 20 – 25 °C for 1.5 h in the case of benzyl substituents and at 0 – 2 °C for 1 h in the case of alkyl and allyl substituents. Then CHCl₃ (30 mL) and saturated aqueous solution of NaHCO₃ (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was

removed in vacuum of a water jet pump. Tetraoxanes **5a–c**, **e–h** were isolated by chromatography on SiO₂ using PE : EA (20 : 1) mixture as the eluent.

Compounds: **5a**: 0.202 g, 0.57 mmol, yield 61%; **5b**: 0.157 g, 0.48 mmol, yield 47%; **5c**: 0.217 g, 0.56 mmol, yield 66%; **5e**: 0.155 g, 0.50 mmol, yield 46%; **5f**: 0.077 g, 0.30 mmol, yield 22%; **5g**: 0.114 g, 0.42 mmol, yield 33%; **5h**: 0.122 g, 0.40 mmol, yield 36%.

Ethyl (1*R,4*R**,7*S**)-1,4-dimethyl-7-(4-nitrobenzyl)-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5a**



White crystals. Mp = 89 – 91 °C. R_f = 0.52 (TLC, PE : EA, 2 : 1).

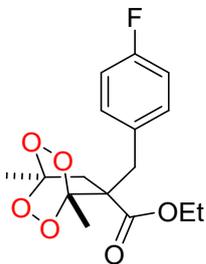
¹H NMR (300.13 MHz, CDCl₃), δ: 8.16 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.7 Hz, 2H), 4.20 – 4.29 (m, 2H), 3.49 (d, *J* = 13.2 Hz, 1H), 3.12 (d, *J* = 13.2 Hz, 1H), 2.85 (d, *J* = 13.8 Hz, 1H), 2.08 (d, *J* = 13.8 Hz, 1H), 1.67 (s, 3H), 1.39 (s, 3H), 1.31 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75.48 MHz, CDCl₃), δ: 170.9, 147.5, 143.1, 130.8, 123.9, 106.0, 103.3, 62.5, 52.4, 39.9, 36.8, 20.6, 17.7, 14.2.

Anal. Calcd for C₁₆H₁₉NO₈: C, 54.39; H, 5.42. Found: C, 54.51; H, 5.54.

HRMS (ESI-TOF): *m/z* [M+K]⁺: calculated for [C₁₆H₁₉NKO₈]⁺: 392.0742; found: 392.0732.

Ethyl (1*R,4*R**,7*S**)-7-(4-fluorobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5b**



White crystals. Mp = 54 – 56 °C. R_f = 0.63 (TLC, PE : EA, 5 : 1).

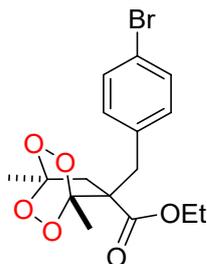
¹H NMR (300.13 MHz, CDCl₃), δ: 7.10 – 6.92 (m, 4H), 4.32 – 4.18 (m, 2H), 3.36 (d, *J* = 13.3 Hz, 1H), 2.96 (d, *J* = 13.3 Hz, 1H), 2.83 (d, *J* = 13.9 Hz, 1H), 2.10 (d, *J* = 13.9 Hz, 1H), 1.66 (s, 3H), 1.38 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.1, 162.1 (d, $^1J_{\text{CF}} = 246.1$ Hz), 131.3 (d, $^3J_{\text{CF}} = 8.0$ Hz), 130.9 (d, $^4J_{\text{CF}} = 3.3$ Hz), 115.5 (d, $^2J_{\text{CF}} = 21.4$ Hz), 106.2, 103.3, 62.0, 52.5, 39.2, 36.7, 20.5, 17.6, 14.0.

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{FO}_6$: C, 58.89; H, 5.87. Found: C, 58.97; H, 5.96.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{19}\text{FNaO}_6]^+$: 349.1058; found: 349.1055.

Ethyl (1*R,4*R**,7*S**)-7-(4-bromobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5c**



White crystals. Mp = 78 – 80 °C. $R_f = 0.83$ (TLC, PE : EA, 2 : 1).

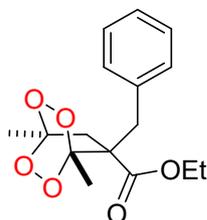
^1H NMR (300.13 MHz, CDCl_3), δ : 7.41 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 4.32 – 4.18 (m, 2H), 3.35 (d, $J = 13.3$ Hz, 1H), 2.94 (d, $J = 13.3$ Hz, 1H), 2.84 (d, $J = 13.8$ Hz, 1H), 2.07 (d, $J = 13.8$ Hz, 1H), 1.65 (s, 3H), 1.38 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.1, 134.3, 131.8, 131.6, 121.5, 106.2, 103.4, 62.2, 52.5, 39.5, 36.7, 20.6, 17.7, 14.2.

Anal. Calcd for $\text{C}_{16}\text{H}_{19}\text{O}_6$: C, 49.63; H, 4.95. Found: C, 49.75; H, 5.08.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{19}\text{BrNaO}_6]^+$: 409.0257, 411.0238; found: 409.0251, 411.0228.

Ethyl (1*R,4*R**,7*S**)-7-benzyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5e**



Slightly yellow oil. $R_f = 0.41$ (TLC, PE : EA, 5 : 1).

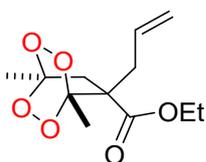
^1H NMR (300.13 MHz, CDCl_3), δ : 7.34 – 7.23 (m, 3H), 7.14 – 7.06 (m, 2H), 4.32 – 4.18 (m, 2H), 3.41 (d, $J = 13.2$ Hz, 1H), 2.98 (d, $J = 13.2$ Hz, 1H), 2.84 (d, $J = 13.9$ Hz, 1H), 2.14 (d, $J = 13.9$ Hz, 1H), 1.68 (s, 3H), 1.38 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.3, 135.3, 129.9, 128.7, 127.4, 106.4, 103.5, 62.0, 52.6, 40.1, 36.8, 20.6, 17.7, 14.1.

Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_6$: C, 62.33; H, 6.54. Found: C, 62.40; H, 6.59.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{16}\text{H}_{21}\text{O}_6]^+$: 309.1333; found: 309.1324.

Ethyl (1*R,4*R**,7*S**)-7-allyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5f**



Yellow oil. R_f = 0.55 (TLC, PE : EA, 5 : 1).

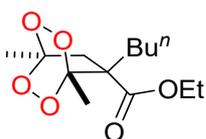
^1H NMR (300.13 MHz, CDCl_3), δ : 5.67 – 5.48 (m, 1H), 5.21 – 5.09 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.10 (d, J = 13.8 Hz, 1H), 2.73 – 2.62 (m, 1H), 2.53 – 2.43 (m, 1H), 2.04 (d, J = 13.8 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.1, 131.3, 120.0, 105.9, 103.4, 62.0, 51.3, 39.4, 37.2, 20.6, 17.6, 14.2.

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_6$: C, 55.81; H, 7.03. Found: C, 55.94; H, 7.15.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{12}\text{H}_{19}\text{O}_6]^+$: 259.1176; found: 259.1175.

Ethyl (1*R,4*R**,7*S**)-7-butyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5g**



Slightly yellow oil. R_f = 0.48 (TLC, PE : EA, 10 : 1)

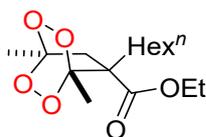
^1H NMR (300.13 MHz, CDCl_3), δ : 4.25 (q, J = 7.1, 2H), 3.21 (d, J = 13.5 Hz, 1H), 1.99 (d, J = 13.5 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.79 – 1.66 (m, 1H), 1.57 (s, 3H), 1.42 (s, 3H), 1.37 – 1.23 (m, 6H), 1.13 – 0.98 (m, 1H), 0.88 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.7, 106.5, 103.5, 61.8, 51.8, 37.8, 34.6, 25.8, 23.0, 20.7, 17.7, 14.2, 14.0.

Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{O}_6$: C, 56.92; H, 8.08. Found: C, 56.99; H, 8.15.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{13}\text{H}_{23}\text{O}_6]^+$: 275.1489; found: 275.1491.

Ethyl (1*R,4*R**,7*S**)-7-hexyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5h**



Slightly yellow oil. $R_f = 0.68$ (TLC, PE : EA, 5 : 1).

$^1\text{H NMR}$ (300.13 MHz, CDCl_3), δ : 4.25 (q, $J = 7.1$ Hz, 2H), 3.20 (d, $J = 13.5$ Hz, 1H), 1.98 (d, $J = 13.5$ Hz, 1H), 1.94 – 1.81 (m, 1H), 1.78 – 1.68 (m, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 1.36 – 1.18 (m, 10H), 1.12 – 0.98 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 3H).

$^{13}\text{C NMR}$ (75.48 MHz, CDCl_3), δ : 171.7, 106.5, 103.5, 61.8, 51.9, 37.8, 34.9, 31.7, 29.5, 23.6, 22.6, 20.7, 17.6, 14.2, 14.1.

Anal. Calcd for $\text{C}_{15}\text{H}_{26}\text{O}_6$: C, 59.58; H, 8.67. Found: C, 59.66; H, 8.75.

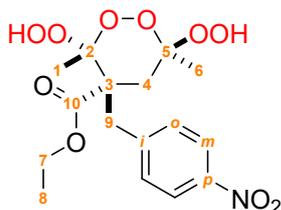
HRMS (ESI-TOF): m/z $[\text{M}+\text{K}]^+$: calculated for $[\text{C}_{15}\text{H}_{26}\text{KO}_6]^+$: 341.1361; found: 341.1360.

General procedure for the synthesis of dihydroperoxy-1,2-dioxane 6a–c,e from 1,4-diketones 1a–c,e and ethereal solution of H_2O_2 in the presence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$.

A 9.27 M ethereal solution of H_2O_2 (0.46 – 0.59 mL, 4.22 – 5.43 mmol; 5.0 mol H_2O_2 / 1.0 mol **1a–c,e**) and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (0.53 – 0.68 mL, 4.22 – 5.43 mmol; 5.0 mol $\text{BF}_3 \cdot \text{Et}_2\text{O}$ / 1.0 mol **1a–c,e**) were successively added with stirring to a solution of 1,4-diketone **1a–c,e** (0.300 g, 0.84 – 1.09 mmol) in CH_3CN (5 mL) at 20 – 25 °C. The reaction mixture was stirred at 20 – 25 °C for 1.5 h. Then CHCl_3 (30 mL) and saturated aqueous solution of NaHCO_3 (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl_3 (2×30 mL). The combined organic phases were dried over MgSO_4 and filtered. The solvent was removed in vacuum of a water jet pump. Dihydroperoxy-1,2-dioxanes **6a–c,e** were isolated by chromatography on SiO_2 using PE : EA mixture as the eluent with a gradient of EA from 9 to 33 vol. %.

Compounds: **6a**: 0.145 g, 0.37 mmol, yield 40%; **6b**: 0.119 g, 0.33 mmol, yield 32%; **6c**: 0.107 g, 0.25 mmol, yield 30%; **6e**: 0.119 g, 0.35 mmol, yield 32%.

Ethyl (3*R,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a**



White crystals. Mp = 129 – 131 °C. R_f = 0.22 (TLC, PE : EA, 2 : 1).

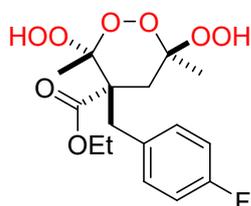
¹H NMR (300.13 MHz, CDCl₃), δ: 8.62 – 8.69 (m, 2H, **OOH**), 8.11 (d, *J* = 8.8 Hz, 2H, **H^m**), 7.39 (d, *J* = 8.6 Hz, 2H, **H^o**), 4.18 (q, *J* = 7.1 Hz, 2H, **H⁷**), 3.47 – 3.31 (m, 2H, **H⁹**), 2.39 (d, *J* = 15.7 Hz, 1H, **H⁴**), 1.80 (m, 3H, **H¹**), 1.60 (d, *J* = 15.6 Hz, 1H, **H⁴**), 1.52 (s, 3H, **H⁶**), 1.25 (t, *J* = 7.1 Hz, 3H, **H⁸**).

¹³C NMR (75.48 MHz, CDCl₃), δ: 170.7 (**C¹⁰**), 147.3 (**C^p**), 143.6 (**Cⁱ**), 131.7 (**C^o**), 123.5 (**C^m**), 108.9 (**C²**), 106.9 (**C⁵**), 62.1 (**C⁷**), 49.5 (**C³**), 38.8 (**C⁹**), 29.8 (**C⁴**), 21.2 (**C⁶**), 14.8 (**C¹**), 14.1 (**C⁸**).

Anal. Calcd for C₁₆H₂₁NO₁₀: C, 49.61; H, 5.46. Found: C, 49.70; H, 5.51.

HRMS (ESI-TOF): *m/z* [M+K]⁺: calculated for [C₁₆H₂₁NKO₁₀]⁺: 426.0797; found: 426.0806.

Ethyl (3*R,4*S**,6*R**)-4-(4-fluorobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6b**



White crystals. Mp = 128 – 130 °C. R_f = 0.73 (TLC, PE : EA, 2 : 1).

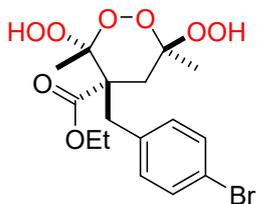
¹H NMR (300.13 MHz, CDCl₃), δ: 8.32 (br.s, 1H), 8.21 (br.s, 1H), 7.21 – 7.13 (m, 2H), 6.94 (t, *J* = 8.7 Hz, 2H), 4.27 – 4.02 (m, 2H), 3.34 – 3.10 (m, 2H), 2.34 (dd, *J* = 15.6, 1.7 Hz, 1H), 1.80 (s, 3H), 1.72 (d, *J* = 15.6 Hz, 1H), 1.52 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75.48 MHz, CDCl₃), δ: 171.1, 162.2 (d, ¹*J*_{CF} = 246.1 Hz), 133.3 (d, ⁴*J*_{CF} = 3.3 Hz), 132.3 (d, ³*J*_{CF} = 7.9 Hz), 115.5 (d, ²*J*_{CF} = 21.1 Hz), 109.1, 107.0, 61.8, 49.6, 38.2, 29.7, 21.3, 14.8, 14.1.

Anal. Calcd for C₁₆H₂₁FO₈: C, 53.33; H, 5.87. Found: C, 53.40; H, 5.96.

HRMS (ESI-TOF): *m/z* [M+Na]⁺: calculated for [C₁₆H₂₁FNao₈]⁺: 383.1113; found: 383.1111.

Ethyl (3*R,4*S**,6*R**)-4-(4-bromobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6c**



White crystals. Mp = 118 – 120 °C. R_f = 0.60 (TLC, PE : EA, 2 : 1).

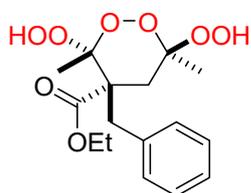
^1H NMR (300.13 MHz, CDCl_3), δ : 8.40 (br.s, 1H), 8.28 (br.s, 1H), 7.37 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 8.4 Hz, 2H), 4.22 – 4.08 (m, 2H), 3.30 – 3.11 (m, 2H), 2.35 (dd, J = 15.7, 1.7 Hz, 1H), 1.79 (s, 3H), 1.69 (d, J = 15.7 Hz, 1H), 1.51 (s, 3H), 1.24 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.0, 134.6, 132.5, 131.5, 121.3, 109.0, 106.9, 61.9, 49.5, 38.4, 29.7, 21.2, 14.8, 14.1.

Anal. Calcd for $\text{C}_{16}\text{H}_{21}\text{BrO}_8$: C, 45.62; H, 5.03. Found: C, 45.70; H, 5.12.

HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{21}\text{BrNaO}_8]^+$: 443.0312, 445.0292; found: 443.0314, 445.0293.

Ethyl (3*R,4*S**,6*R**)-4-benzyl-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6e**



Slightly yellow oil. R_f = 0.43 (TLC, PE : EA, 2 : 1).

^1H NMR (300.13 MHz, CDCl_3), δ : 8.25 (s, 1H), 8.16 (s, 1H), 7.38 – 7.13 (m, 5H), 4.28 – 4.05 (m, 2H), 3.39 – 3.16 (m, 2H), 2.34 (dd, J = 15.6, 1.7 Hz, 1H), 1.82 (s, 3H), 1.77 (d, J = 15.6 Hz, 1H), 1.52 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 171.3, 135.6, 130.7, 128.3, 127.1, 109.1, 107.0, 61.7, 49.6, 39.0, 29.8, 21.2, 14.8, 14.0.

Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_8$: C, 56.14; H, 6.48. Found: C, 56.22; H, 6.58.

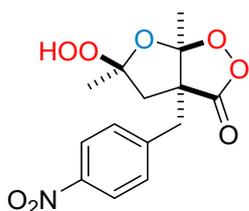
HRMS (ESI-TOF): m/z $[\text{M}+\text{Na}]^+$: calculated for $[\text{C}_{16}\text{H}_{22}\text{NaO}_8]^+$: 365.1207; found: 365.1198.

Procedure for the synthesis of peroxolactone 7a from 1,4-diketone 1a and 35% aqueous solution of H₂O₂ in the presence of 98% H₂SO₄.

A 35% aqueous solution of H₂O₂ (0.24 mL, 2.80 mmol; 3.0 mol H₂O₂ / 1.0 mol **1a**) and 98% H₂SO₄ (0.51 mL, 9.34 mmol; 10.0 mol H₂SO₄ / 1.0 mol **1a**) were successively added with stirring to a solution of 1,4-diketone **1a** (0.300 g, 0.93 mmol) in CH₃CN (5 mL) at 20 – 25 °C. The reaction mixture was stirred at 20 – 25 °C for 3 h. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Peroxide **7a** was isolated by chromatography on SiO₂ using PE : EA mixture as the eluent with a gradient of EA from 9 to 33 vol. %.

Compound: **7a**: 0.028 g, 0.09 mmol, yield 9%.

(3*aS*,5*R*,6*aS*)-5-hydroperoxy-5,6a-dimethyl-3a-(4-nitrobenzyl)tetrahydro-3H-furo[2,3-*c*][1,2]dioxol-3-one, 7a



Slightly yellow crystals. Mp = 146 – 148 °C. R_f = 0.28 (TLC, PE : EA, 2 : 1).

¹H NMR (300.13 MHz, CDCl₃), δ: 8.32– 8.17 (m, 1H), 8.18 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 3.12 (s, 2H), 2.56 (d, *J* = 14.0 Hz, 1H), 2.19 (d, *J* = 14.0 Hz, 1H), 1.63 (s, 3H), 1.61 (s, 3H).

¹³C NMR (75.48 MHz, CDCl₃), δ: 176.4, 147.7, 141.3, 131.0, 123.9, 118.8, 110.4, 57.7, 45.2, 37.0, 21.5, 19.6.

Anal. Calcd for C₁₄H₁₅NO₈: C, 51.70; H, 4.65. Found: C, 51.82; H, 4.77.

HRMS (ESI-TOF): *m/z* [M+NH₄]⁺: calculated for [C₁₄H₁₅NO₈NH₄]⁺: 343.1136; found: 343.1127.

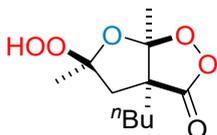
Procedure for the synthesis of peroxolactone 7g from 1,4-diketone 1g and ethereal solution of H₂O₂ in the presence of BF₃·Et₂O.

A 9.27 M ethereal solution of H₂O₂ (0.67 mL, 6.19 mmol; 5.0 mol H₂O₂ / 1.0 mol **1g**) and BF₃·Et₂O (0.78 mL, 6.19 mmol; 5.0 mol BF₃·Et₂O / 1.0 mol **1g**) were successively added with stirring to a solution of 1,4-diketone **1g** (0.300 g, 1.24 mmol) in CH₃CN (5 mL) at 0 – 2 °C. The reaction mixture was stirred at 0 – 2 °C for 1.5 h. Then CHCl₃ (30 mL) and saturated aqueous solution of NaHCO₃ (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over

MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Peroxide **7g** was by chromatography on SiO₂ using PE : EA mixture as the eluent with a gradient of EA from 9 to 17 vol. %.

Compound: **7g**: 0.019 g, 0.08 mmol, yield 6%.

(3aS,5R,6aS)-3a-butyl-5-hydroperoxy-5,6a-dimethyltetrahydro-3H-furo[2,3-c][1,2]dioxol-3-one, 7g



White crystals. Mp = 47 – 49 °C. R_f = 0.71 (TLC, PE : EA, 2 : 1).

¹H NMR (300.13 MHz, CDCl₃), δ: 8.12 (s, 1H), 2.65 (d, *J* = 14.1 Hz, 1H), 2.01 (d, *J* = 14.1 Hz, 1H), 1.80 – 1.63 (m, 2H), 1.58 (s, 3H), 1.55 (s, 3H), 1.45 – 1.20 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (75.48 MHz, CDCl₃), δ: 177.6, 119.0, 110.4, 57.6, 45.2, 31.3, 26.3, 23.0, 21.4, 19.3, 13.8.

Anal. Calcd for C₁₁H₁₈O₆: C, 53.65; H, 7.37. Found: C, 53.78; H, 7.50.

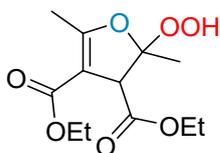
HRMS (ESI-TOF): *m/z* [M+NH₄]⁺: calculated for [C₁₁H₁₈O₆NH₄]⁺: 264.1442; found: 264.1447.

Procedure for the synthesis of peroxide 8i from 1,4-diketone 1i and ethereal solution of H₂O₂ in the presence BF₃·Et₂O.

A 9.27 M ethereal solution of H₂O₂ (0.13 mL, 1.16 mmol; 1.0 mol H₂O₂ / 1.0 mol **1i**) and BF₃·Et₂O (0.15 mL, 1.16 mmol; 1.0 mol BF₃·Et₂O / 1.0 mol **1i**) were successively added with stirring to a solution of 1,4-diketone **1i** (0.300 g, 1.16 mmol) in CH₃CN (5 mL) at 0 – 2 °C. The reaction mixture was stirred at 0 – 2 °C for 1 h. Then CHCl₃ (30 mL) and saturated aqueous solution of NaHCO₃ (10 mL) were added to the reaction mixture. The organic phase was separated; the aqueous phase was washed by CHCl₃ (2×30 mL). The combined organic phases were dried over MgSO₄ and filtered. The solvent was removed in vacuum of a water jet pump. Peroxide **8i** was isolated by chromatography on SiO₂ using PE : EA (20 : 1) mixture as the eluent.

Compound: **8i**: 0.061 g, 0.22 mmol, yield 19%.

Diethyl 2-hydroperoxy-2,3,5-trimethyl-2,3-dihydrofuran-3,4-dicarboxylate, 8i



Colorless oil. R_f = 0.31 (TLC, PE : EA, 2 : 1).

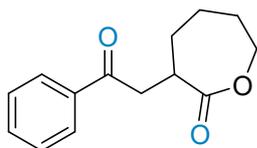
^1H NMR (300.13 MHz, CDCl_3), δ : 9.13 (br.s, 1H), 4.25 – 4.04 (m, 5H), 2.27 (s, 3H), 1.52, (s, 3H), 1.27 (t, $J = 7.1$ Hz, 3H), 1.21 (t, $J = 7.1$ Hz, 3H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 170.7, 168.1, 164.8, 114.3, 103.7, 61.5, 60.1, 54.9, 18.9, 14.3, 14.3, 14.0.

Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{O}_7$: C, 52.55; H, 6.62. Found: C, 52.69; H, 6.80.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{12}\text{H}_{19}\text{O}_7]^+$: 275.1125; found: 275.1123.

3-(2-Oxo-2-phenylethyl)oxepan-2-one, 9j



Colorless oil. $R_f = 0.45$ (TLC, PE : EA, 2 : 1).

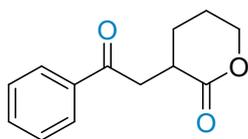
^1H NMR (300.13 MHz, CDCl_3), δ : 8.06 – 7.85 (m, 2H), 7.63 – 7.29 (m, 3H), 4.48 – 4.24 (m, 2H), 3.69 (dd, $J = 18.0, 7.2$ Hz, 1H), 3.52 – 3.25 (m, 1H), 2.96 (dd, $J = 18.0, 5.8$ Hz, 1H), 2.06 – 1.89 (m, 2H), 1.85 – 1.66 (m, 3H), 1.63 – 1.46 (m, 1H).

^{13}C NMR (75.48 MHz, CDCl_3), δ : 198.1, 177.2, 136.8, 133.3, 128.7, 128.2, 68.7, 41.7, 38.4, 30.0, 28.9, 28.3.

Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3$: C, 72.39; H, 6.94. Found: C, 72.54; H, 7.11.

HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{14}\text{H}_{17}\text{O}_3]^+$: 233.1172; found: 233.1180.

3-(2-oxo-2-phenylethyl)tetrahydro-2H-pyran-2-one, 9k ⁶



Colorless oil. $R_f = 0.45$ (TLC, PE : EA, 1 : 1).

^1H NMR (300.13 MHz, CDCl_3), δ : 8.04 – 7.86 (m, 2H), 7.64 – 7.39 (m, 3H), 4.43 (t, $J = 5.8$ Hz, 2H), 3.59 (dd, $J = 18.0, 4.1$ Hz, 1H), 3.27 (dd, $J = 18.0, 6.7$ Hz, 1H), 3.25 – 3.05 (m, 1H), 2.26 – 2.07 (m, 1H), 1.98 – 1.88 (m, 2H), 1.73 – 1.55 (m, 1H).

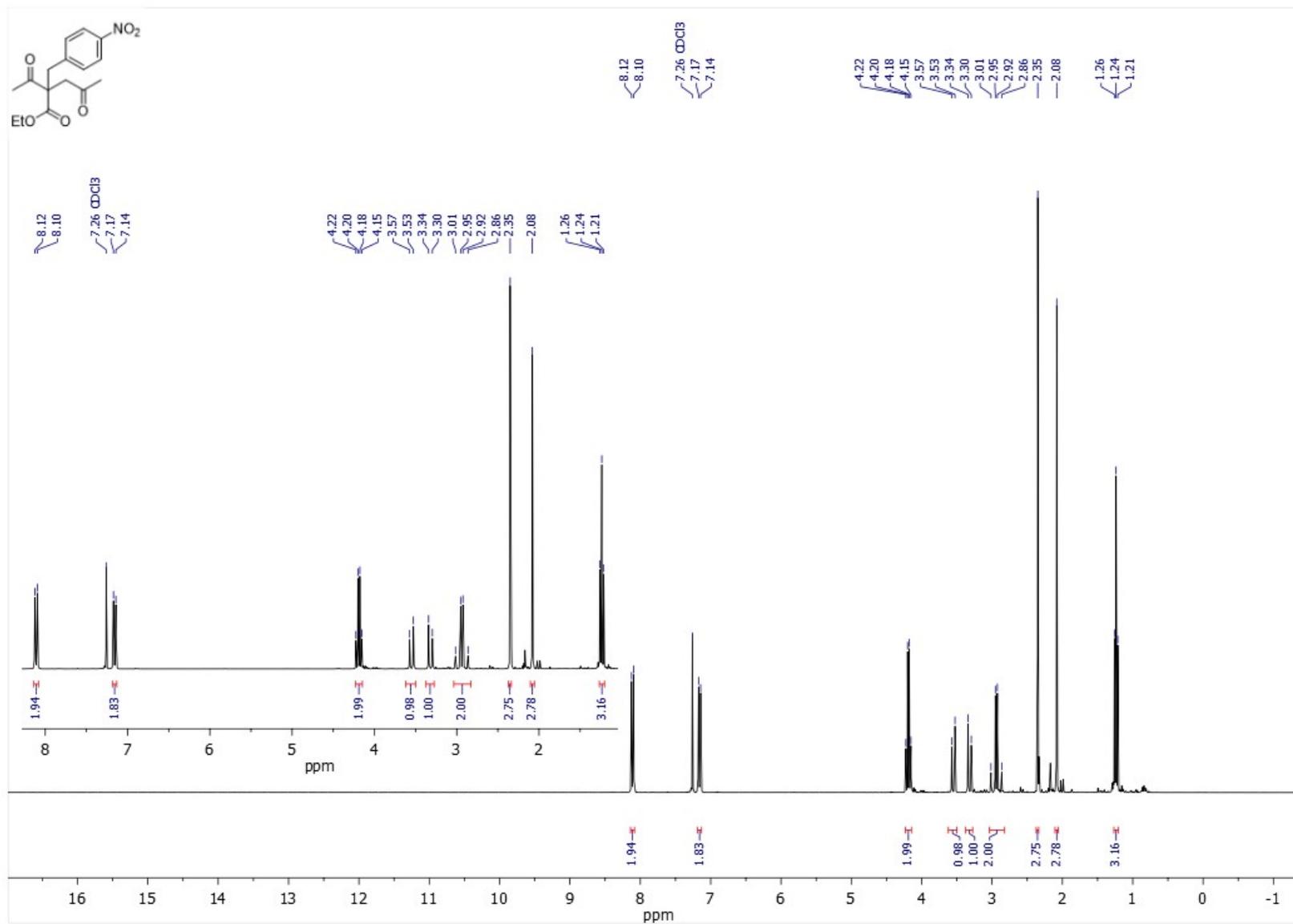
^{13}C NMR (75.48 MHz, CDCl_3), δ : 197.5, 174.2, 136.6, 133.5, 128.7, 128.2, 68.8, 40.2, 35.7, 25.2, 22.6.

Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3$: C, 71.54; H, 6.47. Found: C, 71.68; H, 6.60.

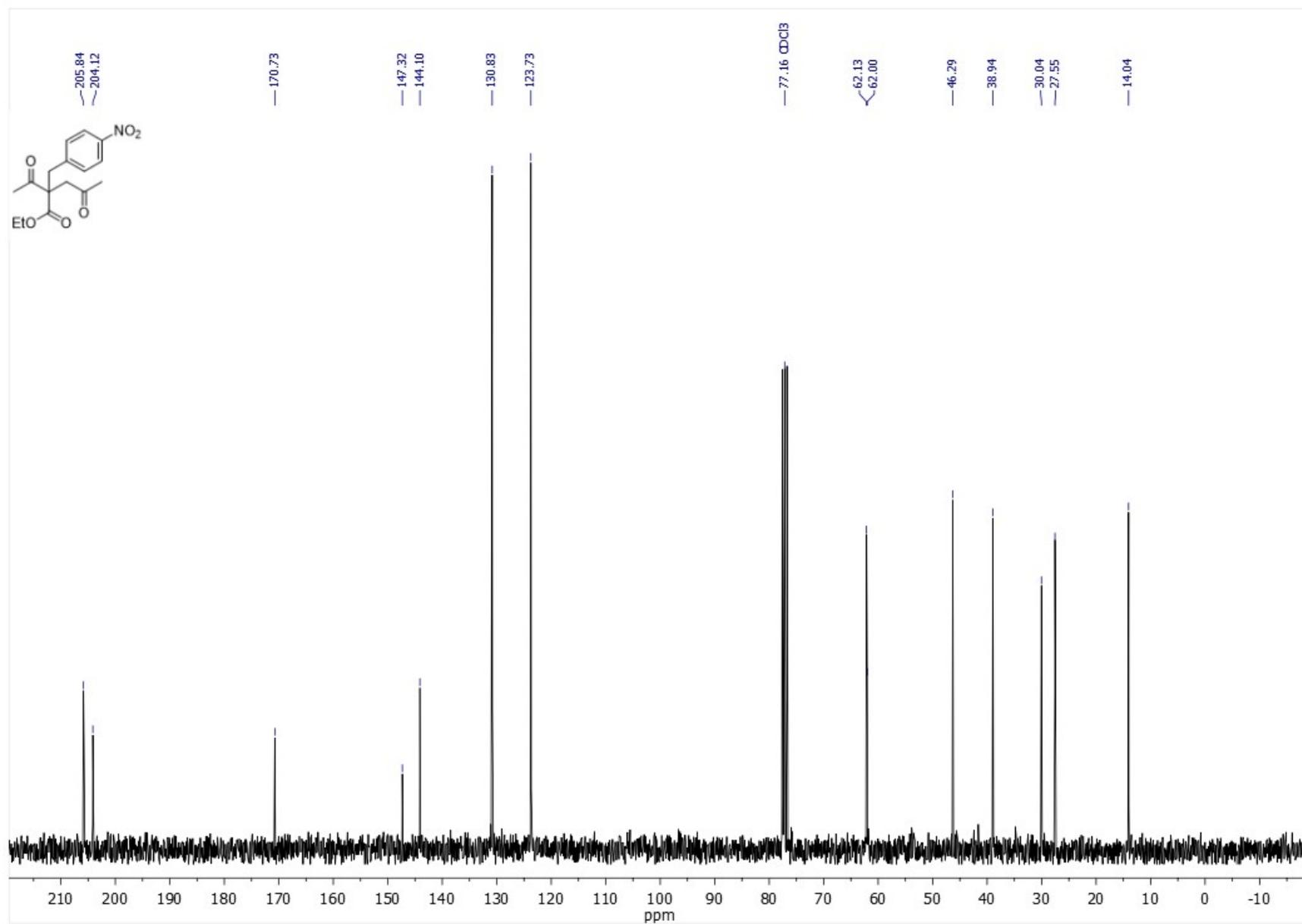
HRMS (ESI-TOF): m/z $[\text{M}+\text{H}]^+$: calculated for $[\text{C}_{13}\text{H}_{15}\text{O}_3]^+$: 219.1016; found: 219.1018.

NMR spectra of compounds 1a-h

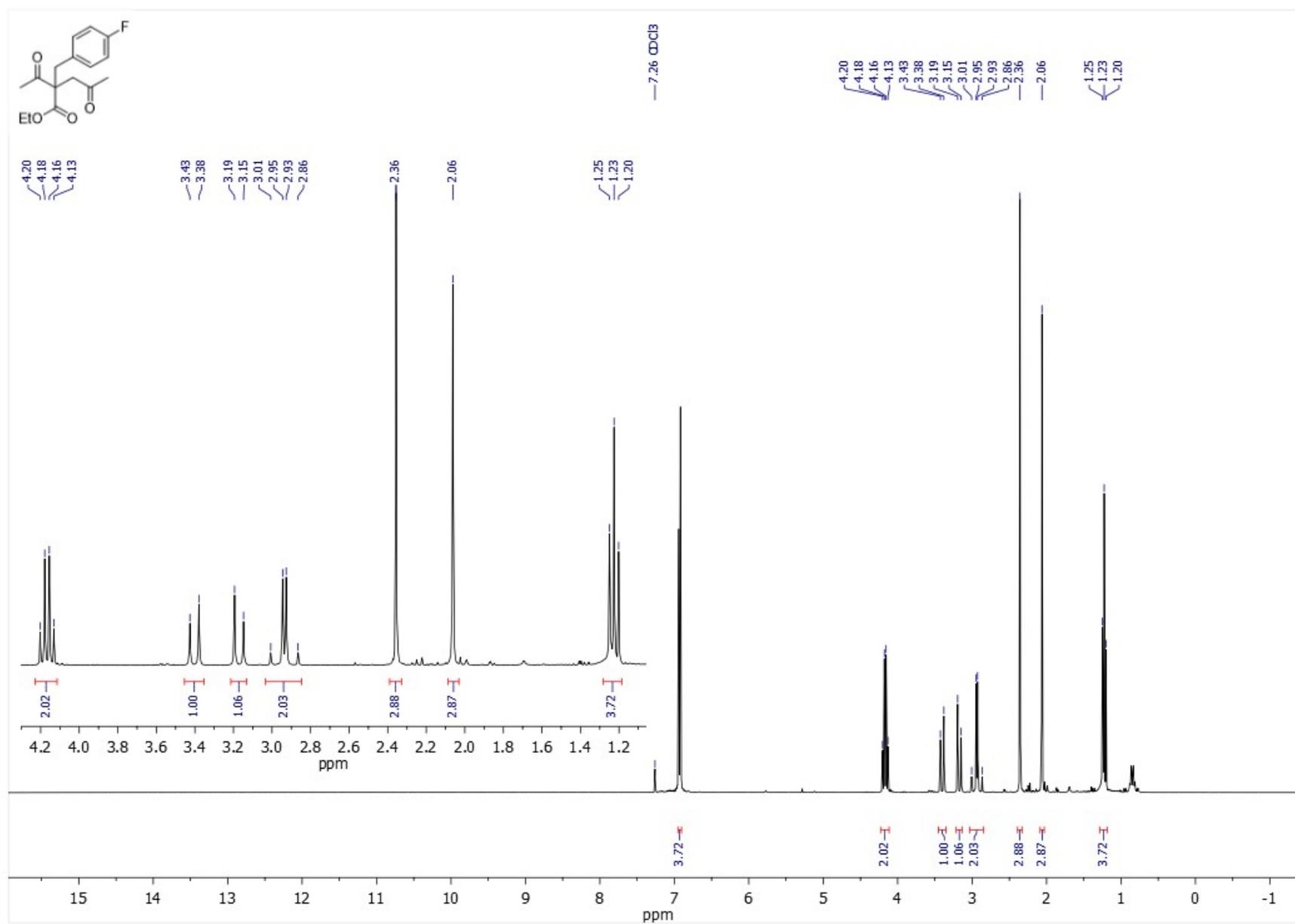
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(4-nitrobenzyl)-4-oxopentanoate, 1a



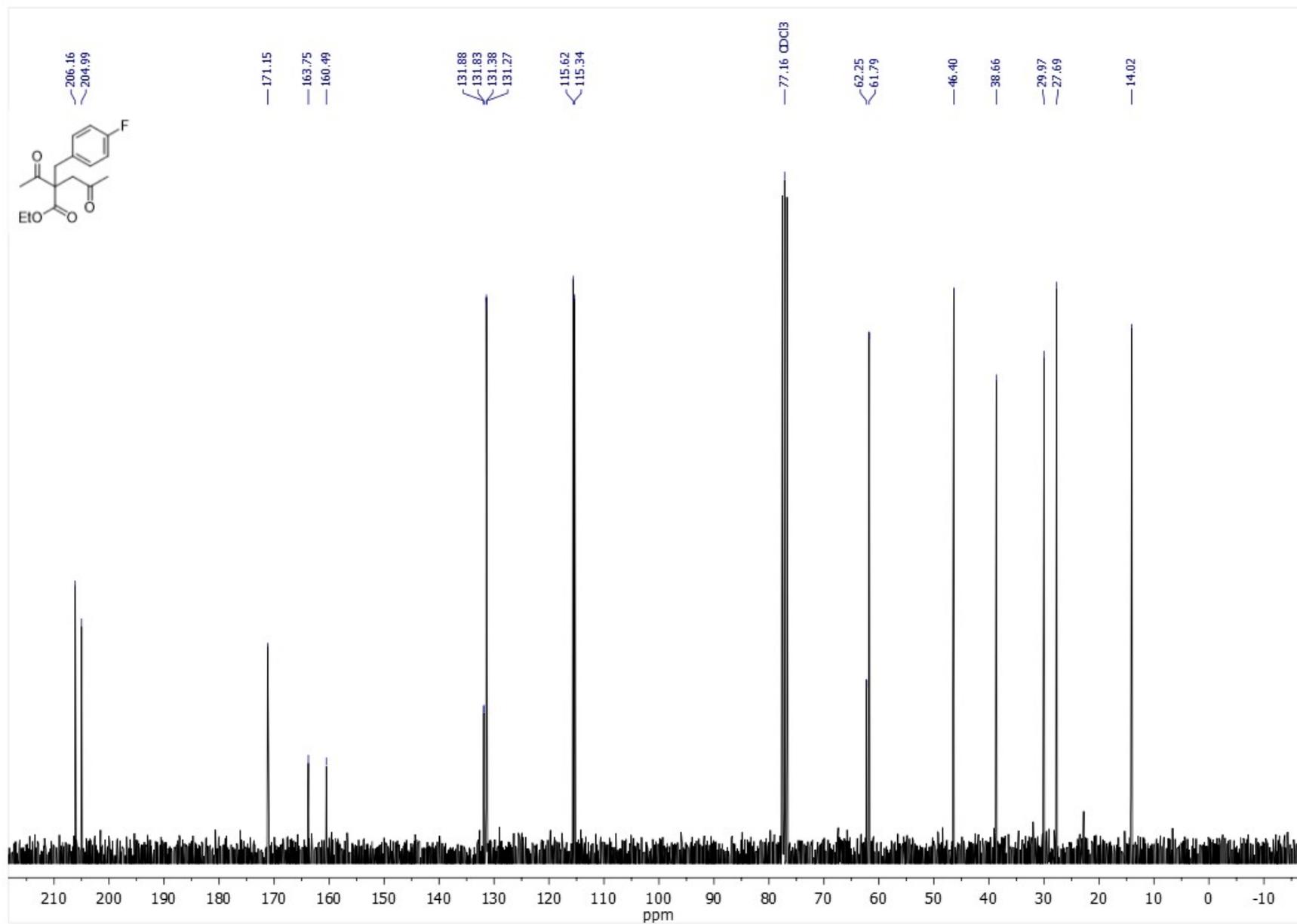
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(4-nitrobenzyl)-4-oxopentanoate, 1a



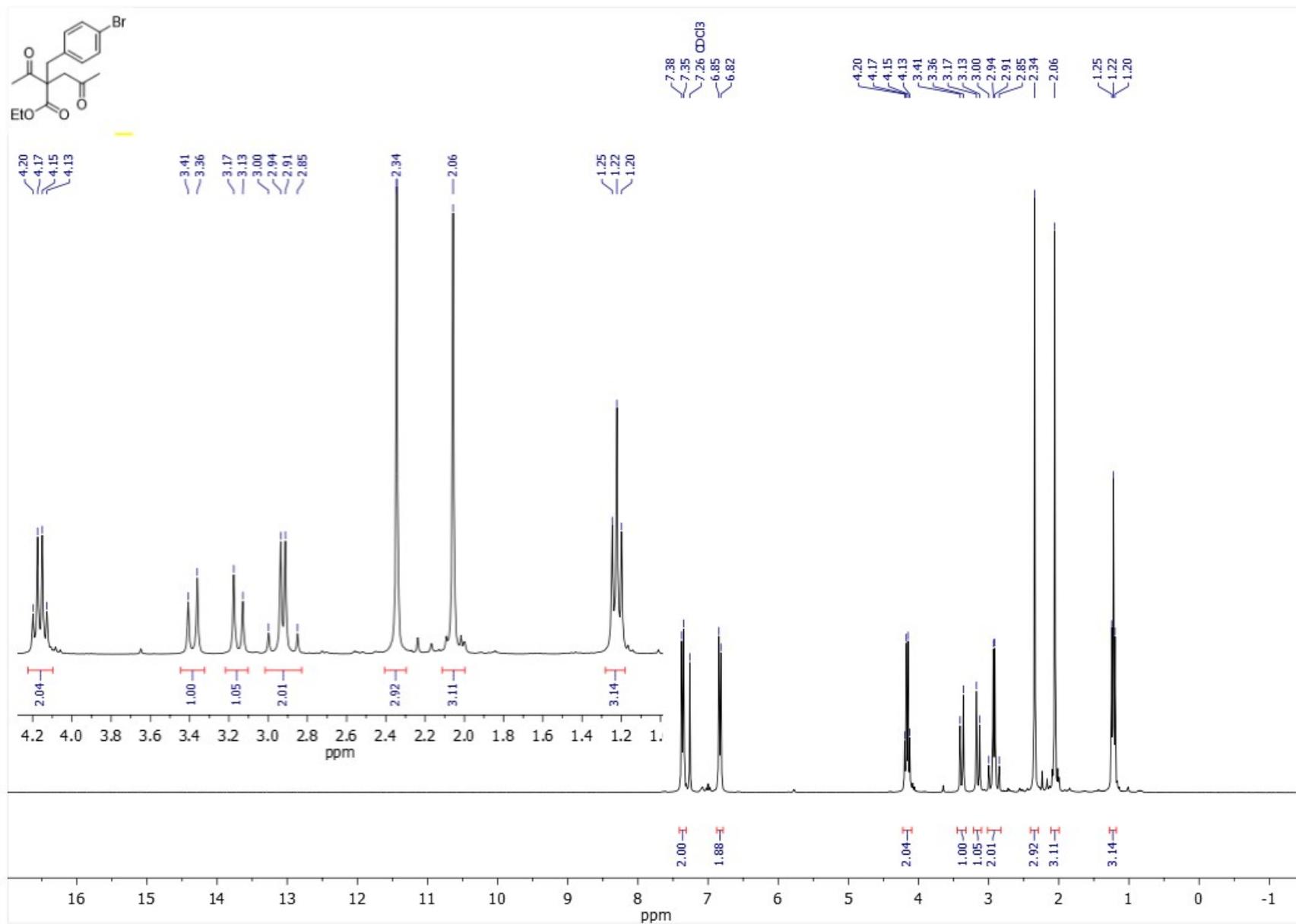
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(4-fluorobenzyl)-4-oxopentanoate, 1b



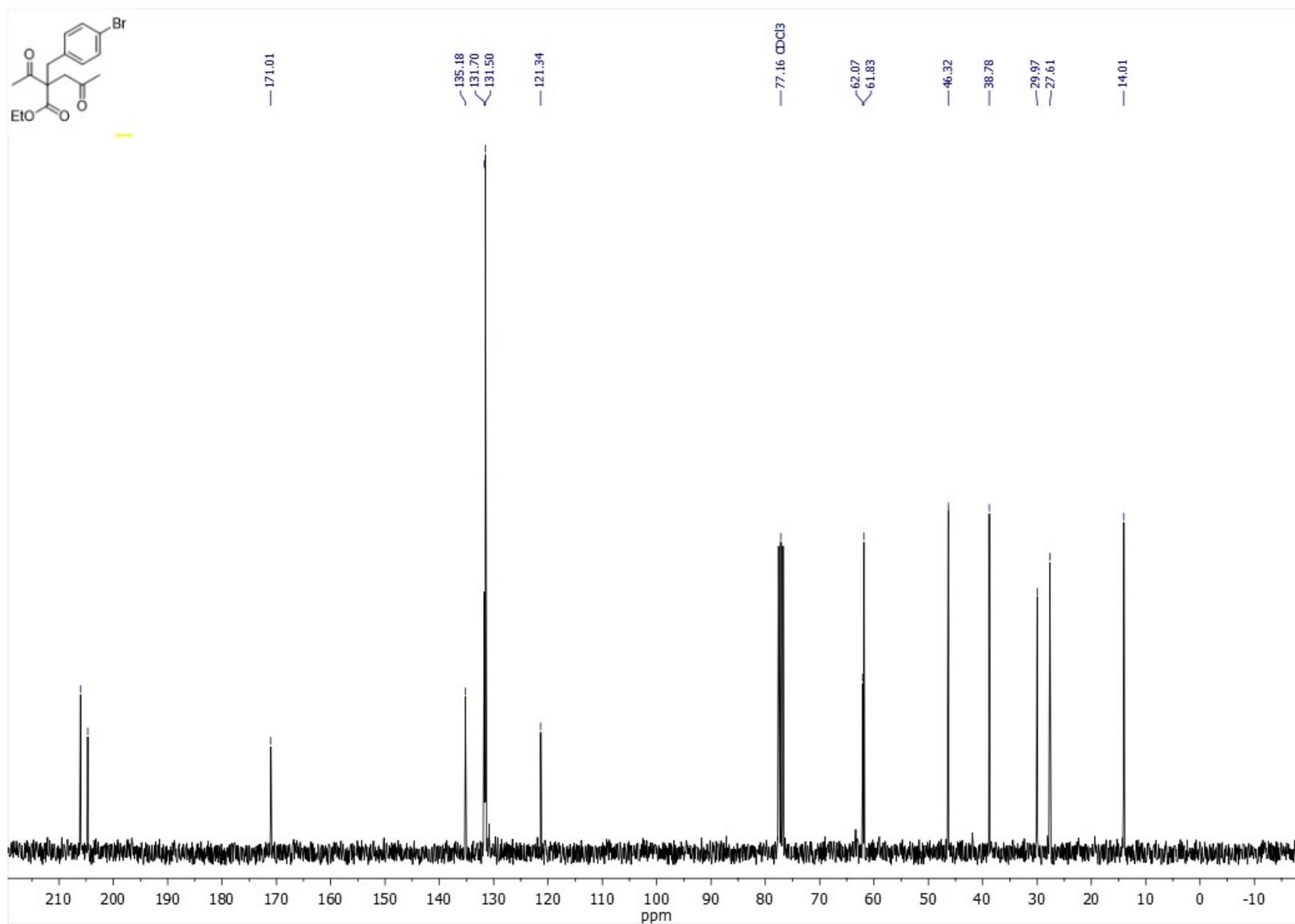
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(4-fluorobenzyl)-4-oxopentanoate, 1b



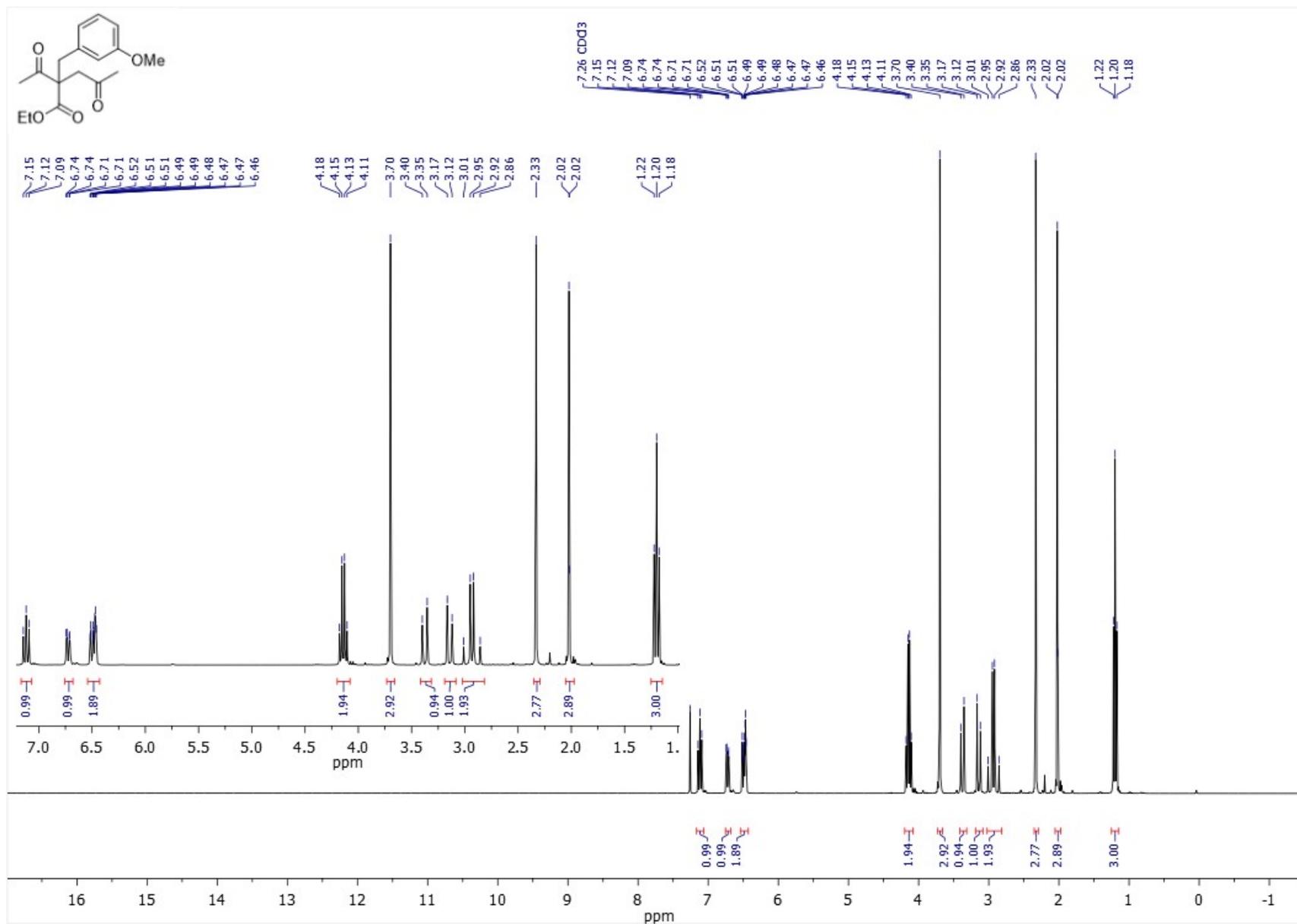
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(4-bromobenzyl)-4-oxopentanoate, 1c



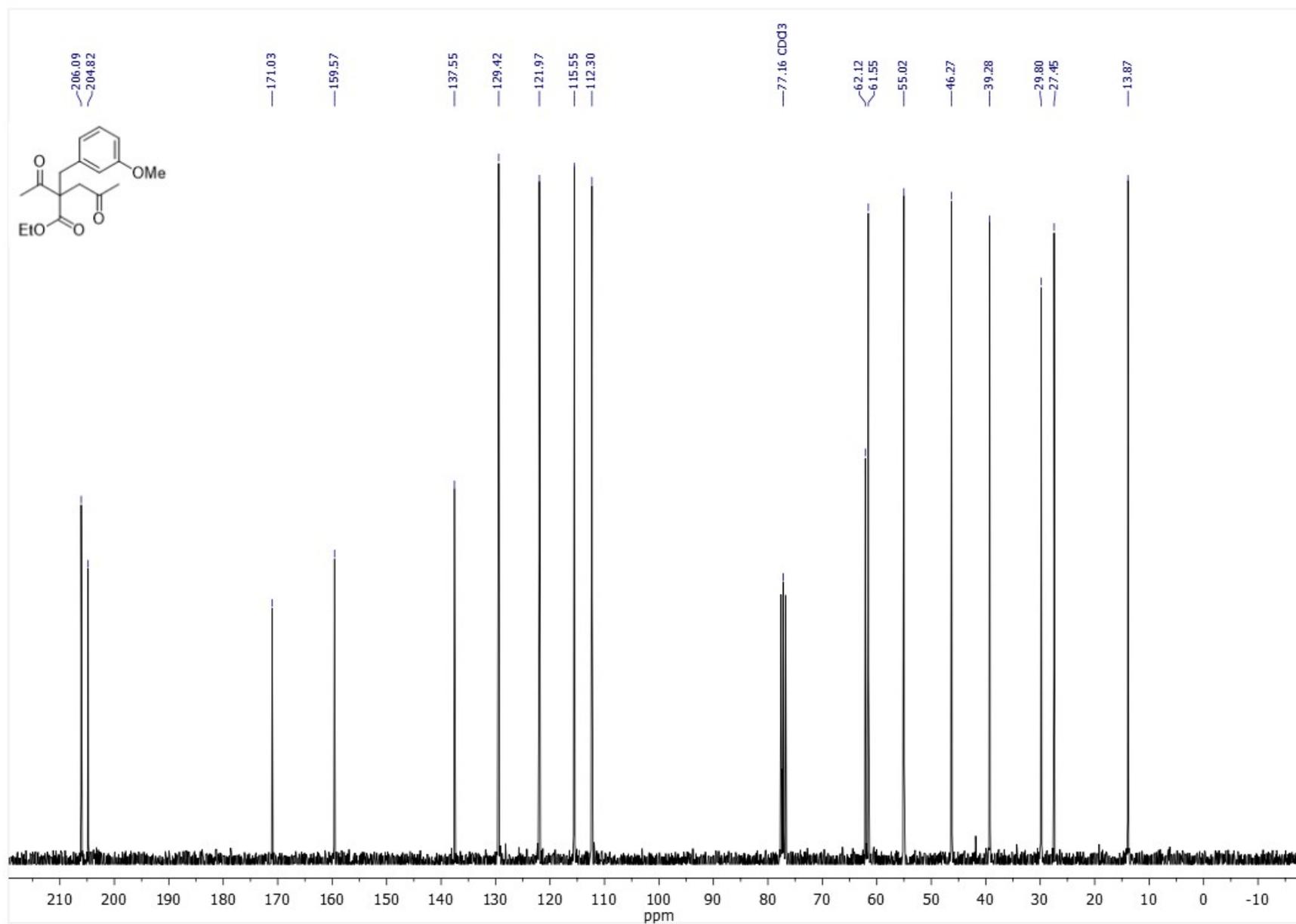
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(4-bromobenzyl)-4-oxopentanoate, 1c



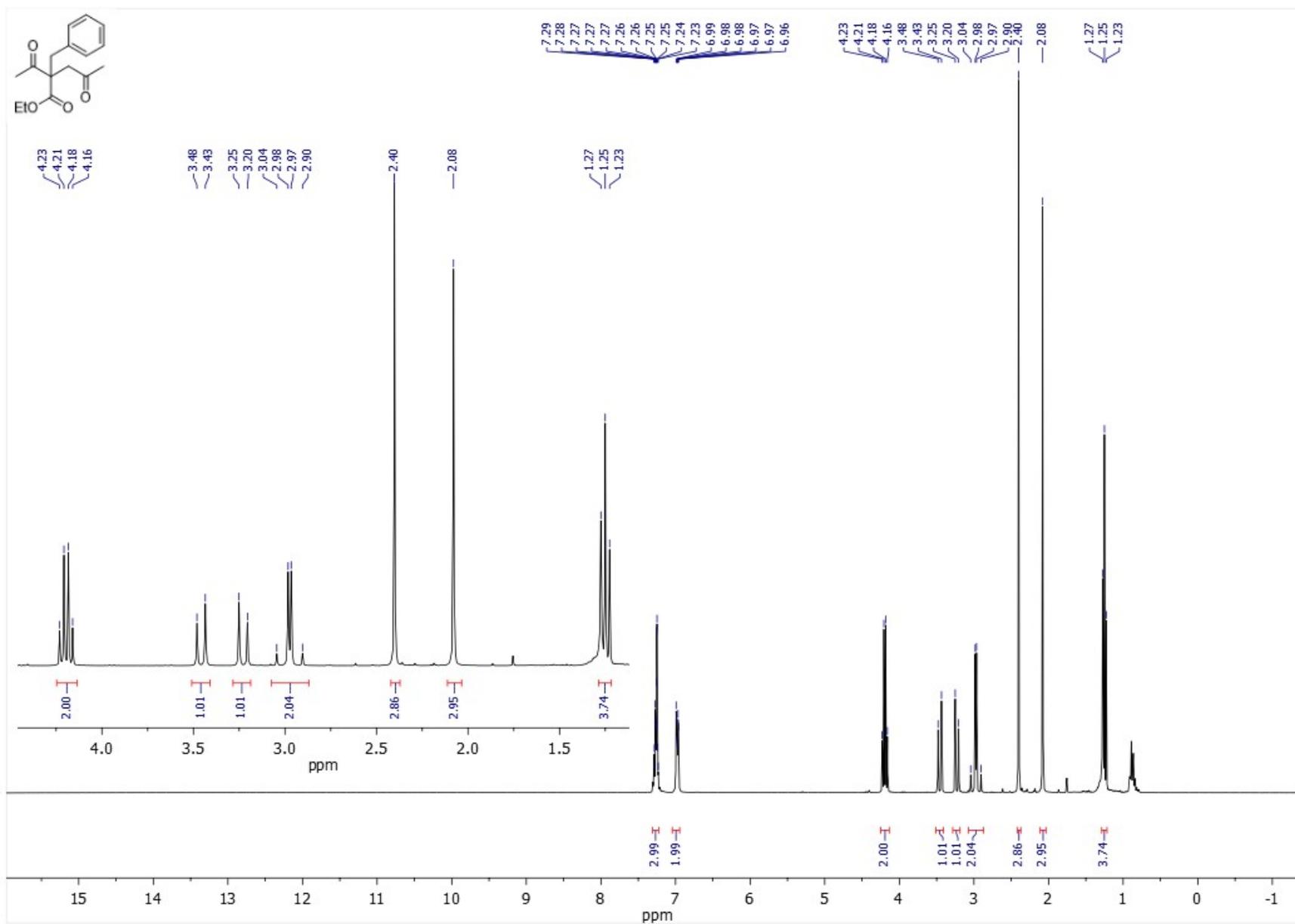
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(3-methoxybenzyl)-4-oxopentanoate, 1d



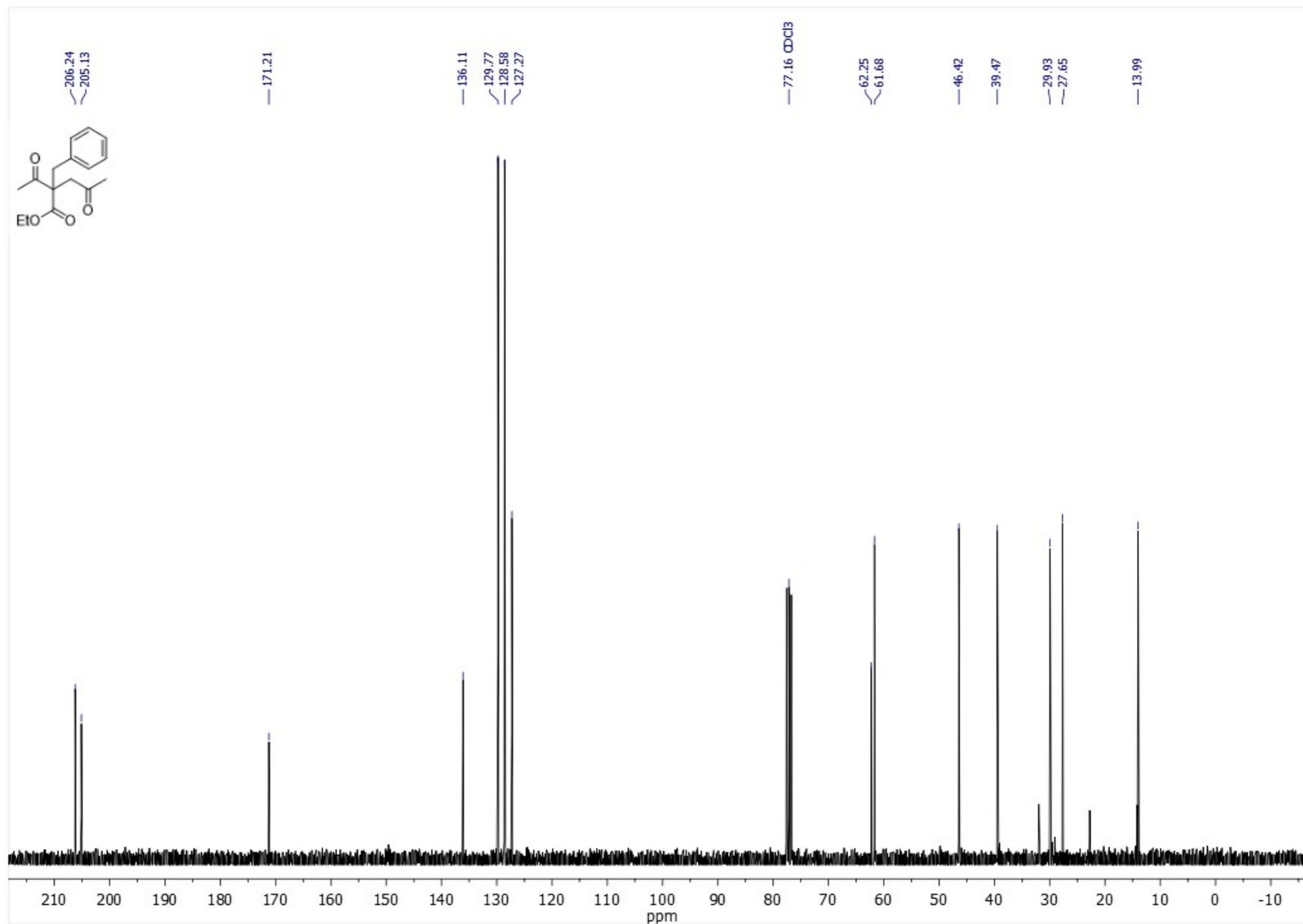
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(3-methoxybenzyl)-4-oxopentanoate, 1d



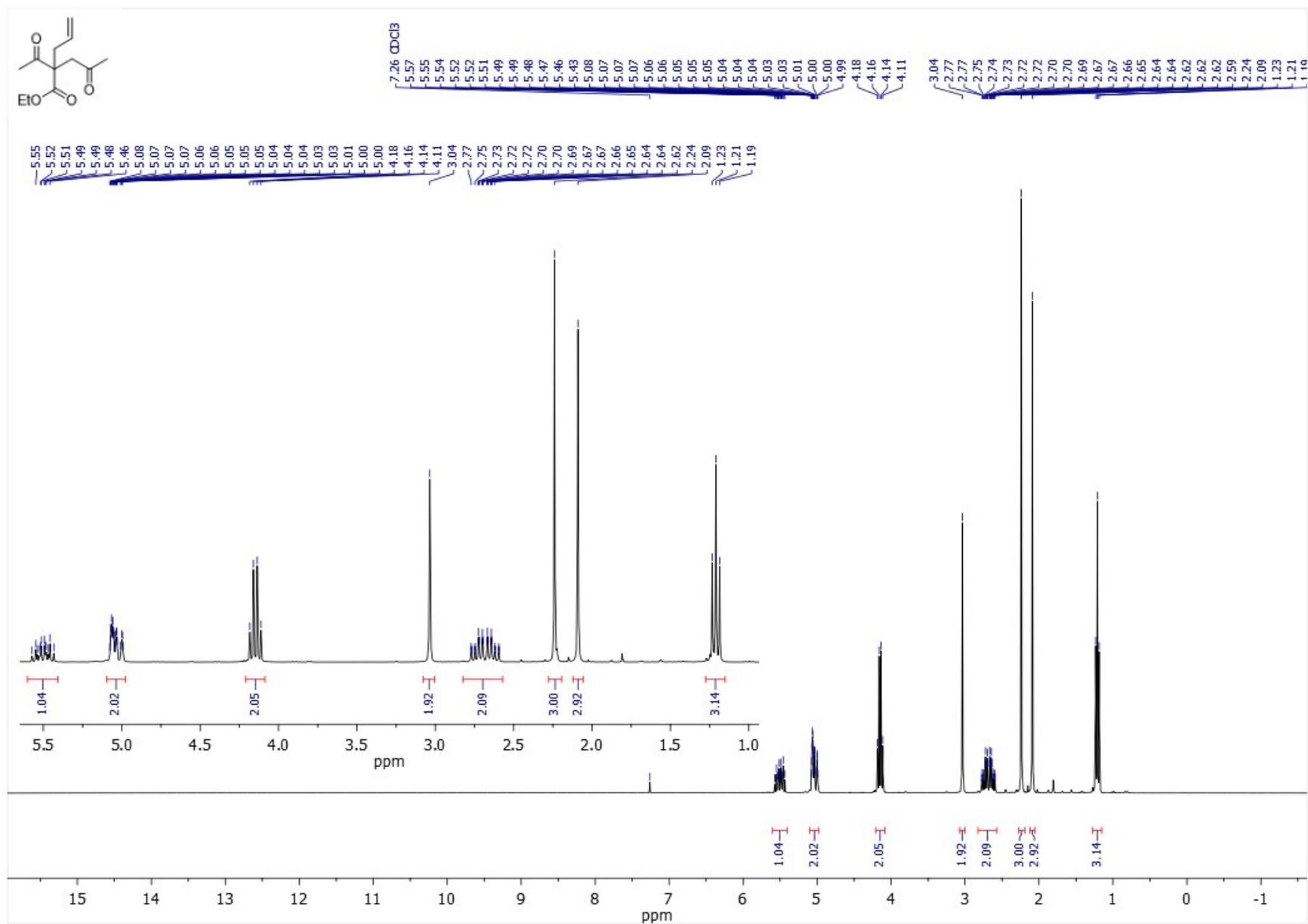
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-benzyl-4-oxopentanoate, 1e



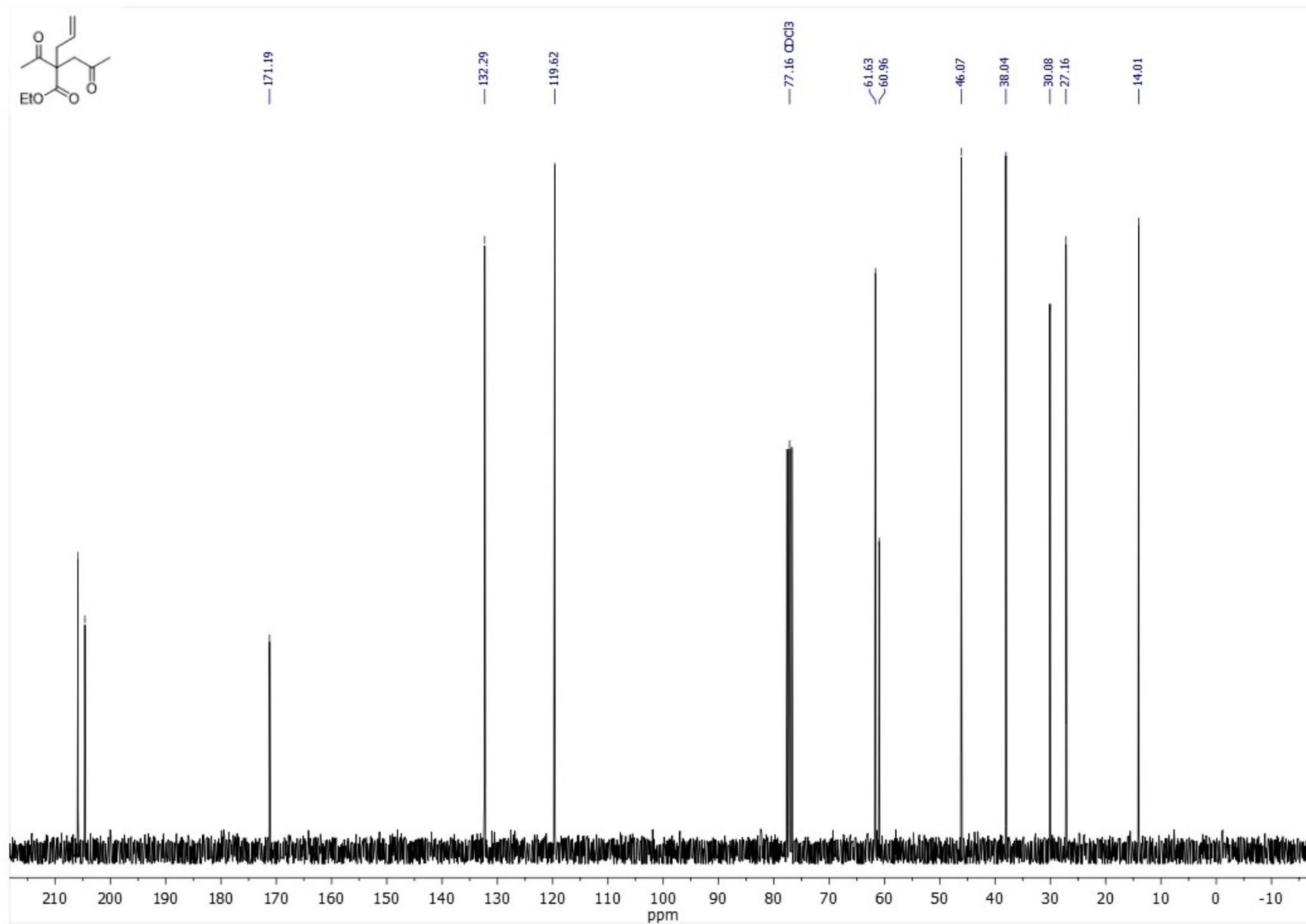
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-benzyl-4-oxopentanoate, 1e



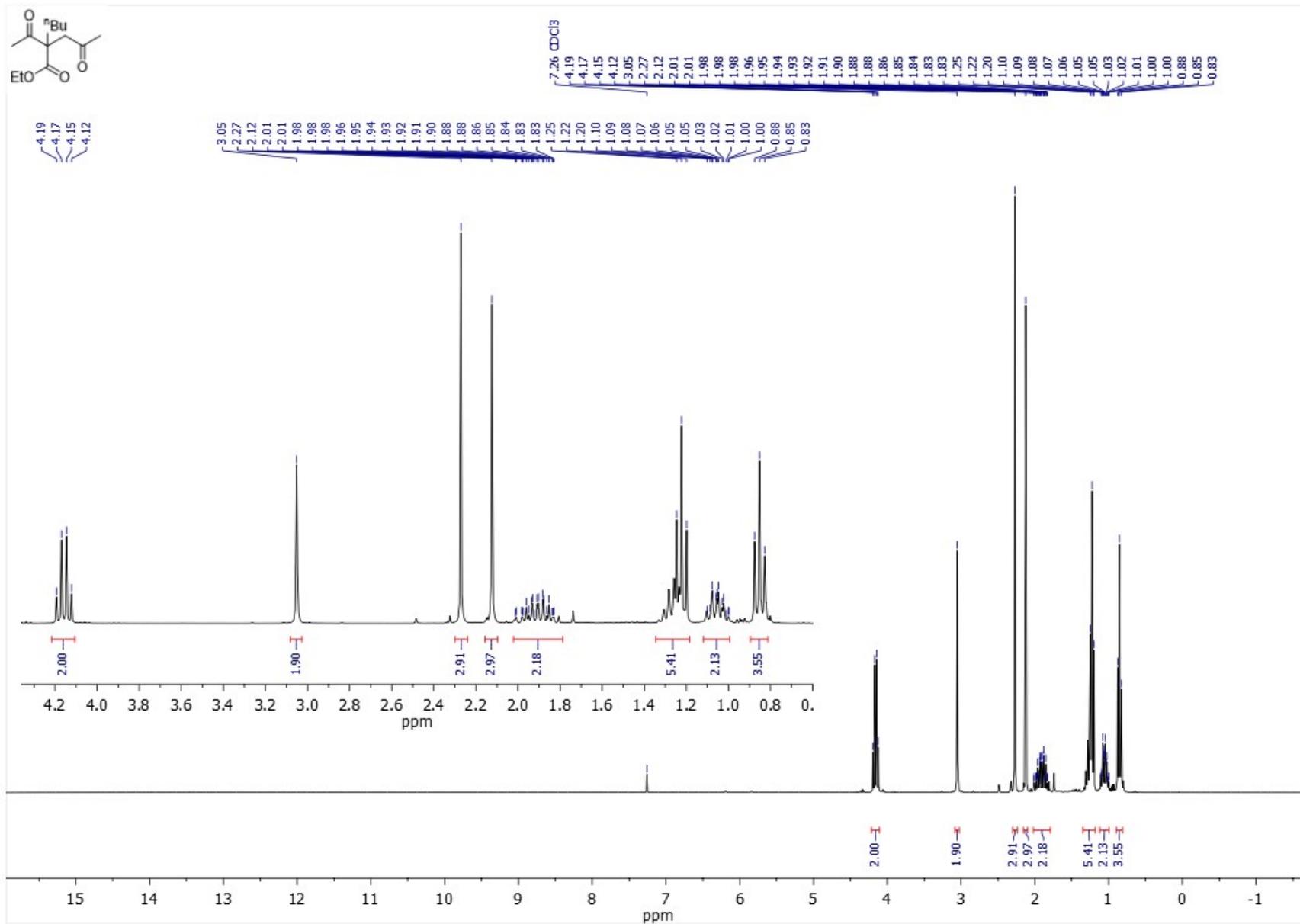
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(2-oxopropyl)pent-4-enoate, 1f



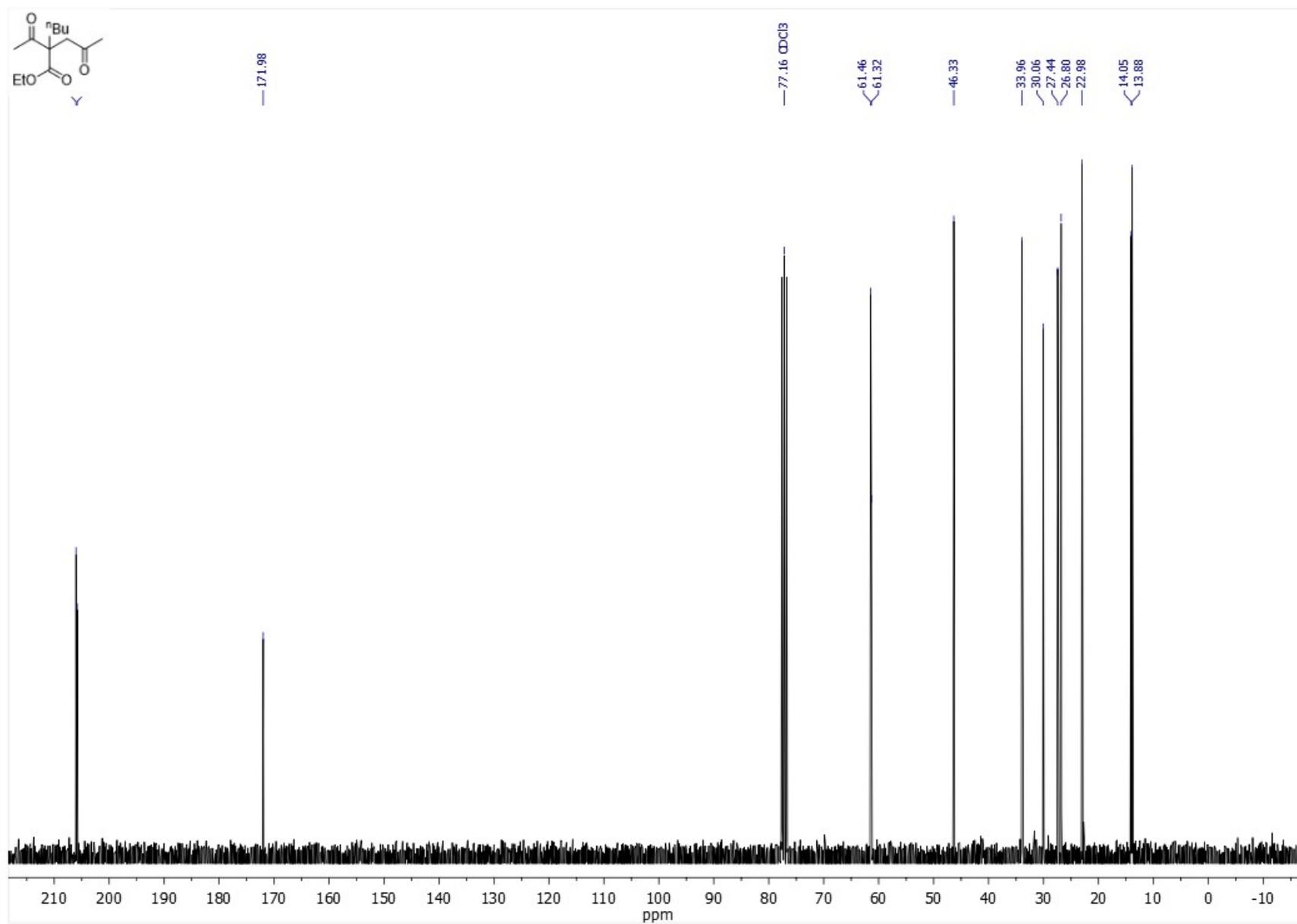
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(2-oxopropyl)pent-4-enoate, 1f



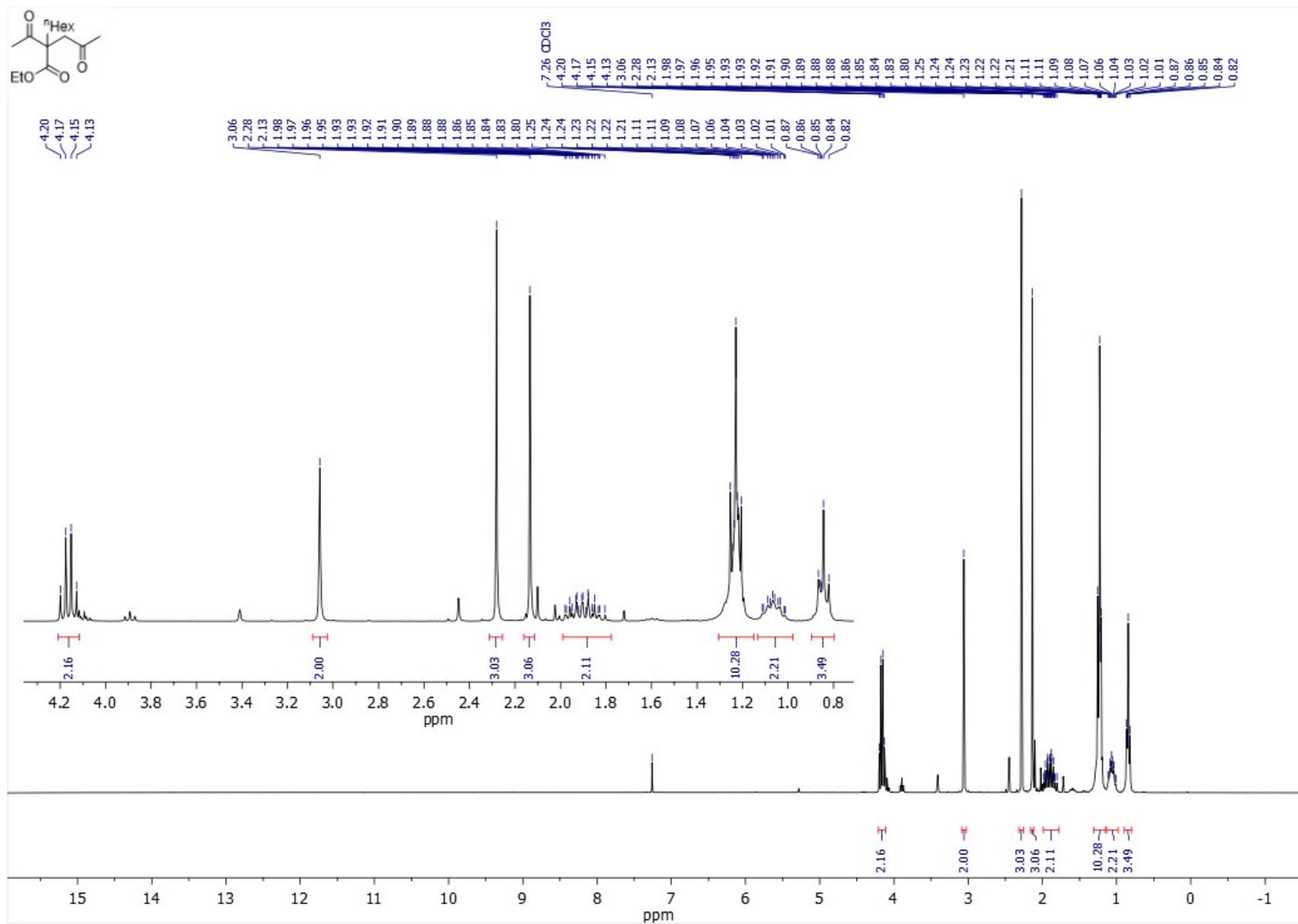
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(2-oxopropyl)hexanoate, 1g



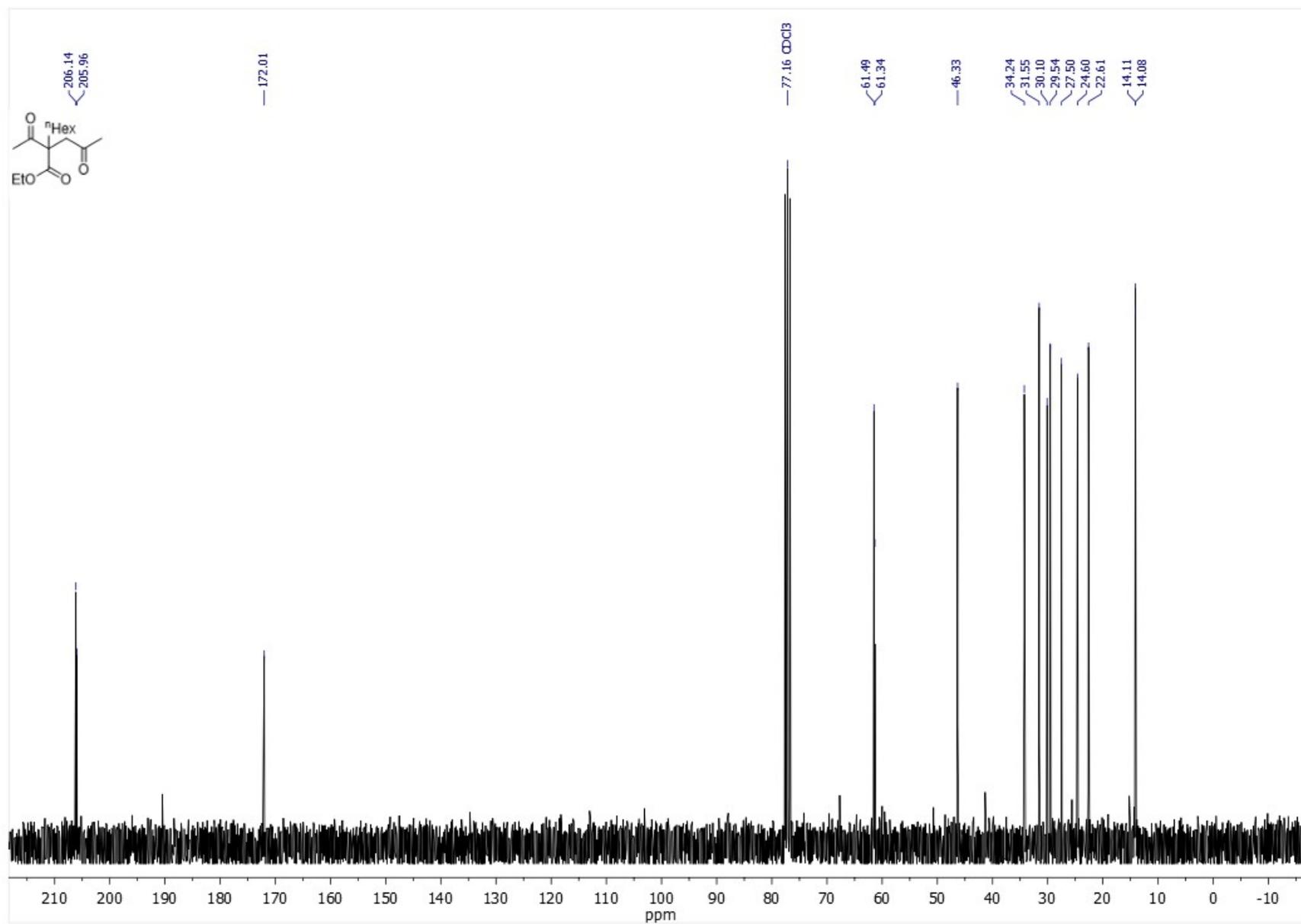
¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(2-oxopropyl)hexanoate, 1g



¹H NMR (300.13 MHz, CDCl₃). Ethyl 2-acetyl-2-(2-oxopropyl)octanoate, 1h

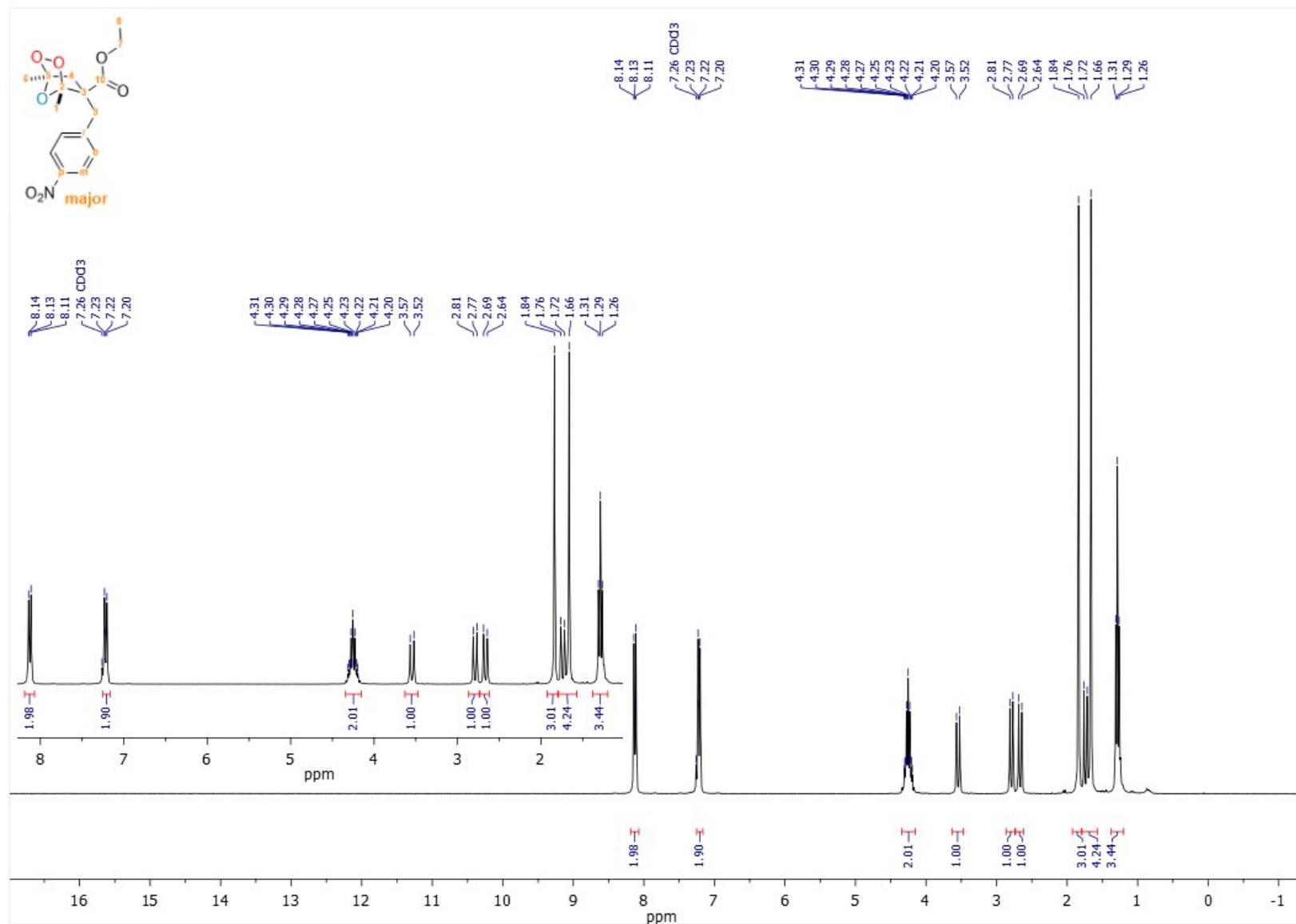


¹³C NMR (75.48 MHz, CDCl₃). Ethyl 2-acetyl-2-(2-oxopropyl)octanoate, 1h

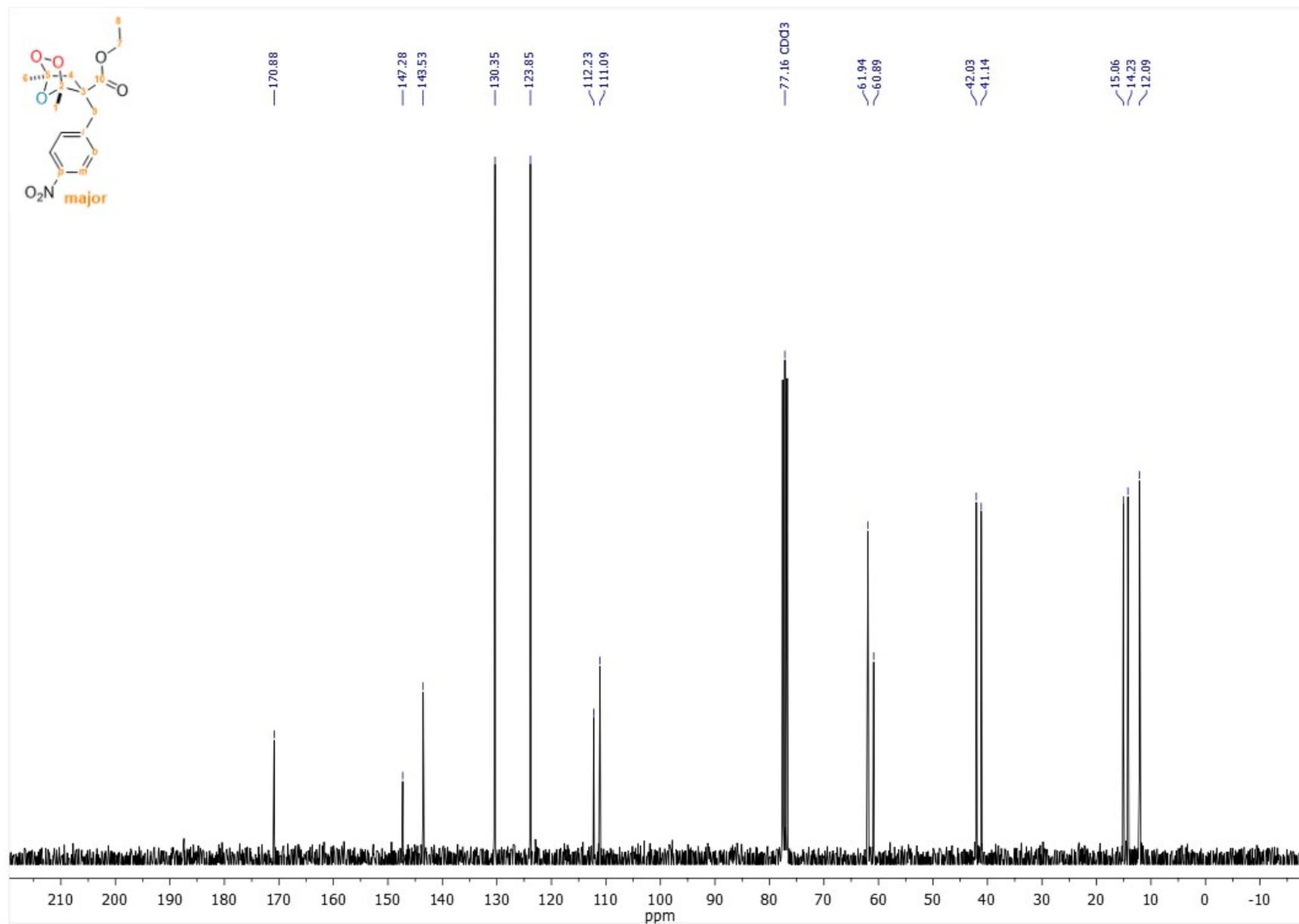


NMR spectra of peroxides *cis*-2a-h, *trans*-2a-h, 2i, *cis*-3a,b,c,e,g,h, *trans*-3a,b,g,h, 4a, 5a-c,e-h 6a-c,e, 7a,g, 8i

¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a

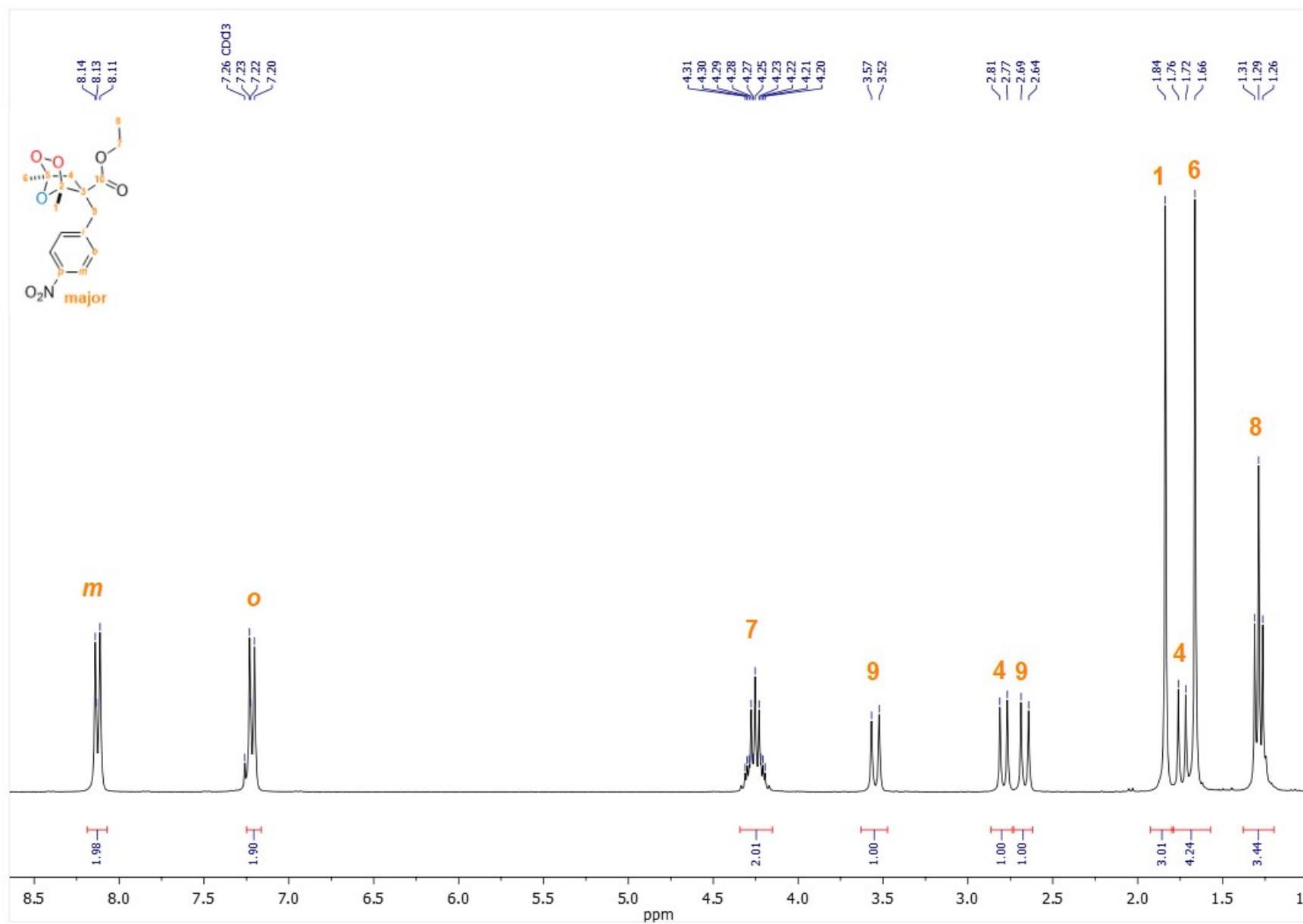


^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a

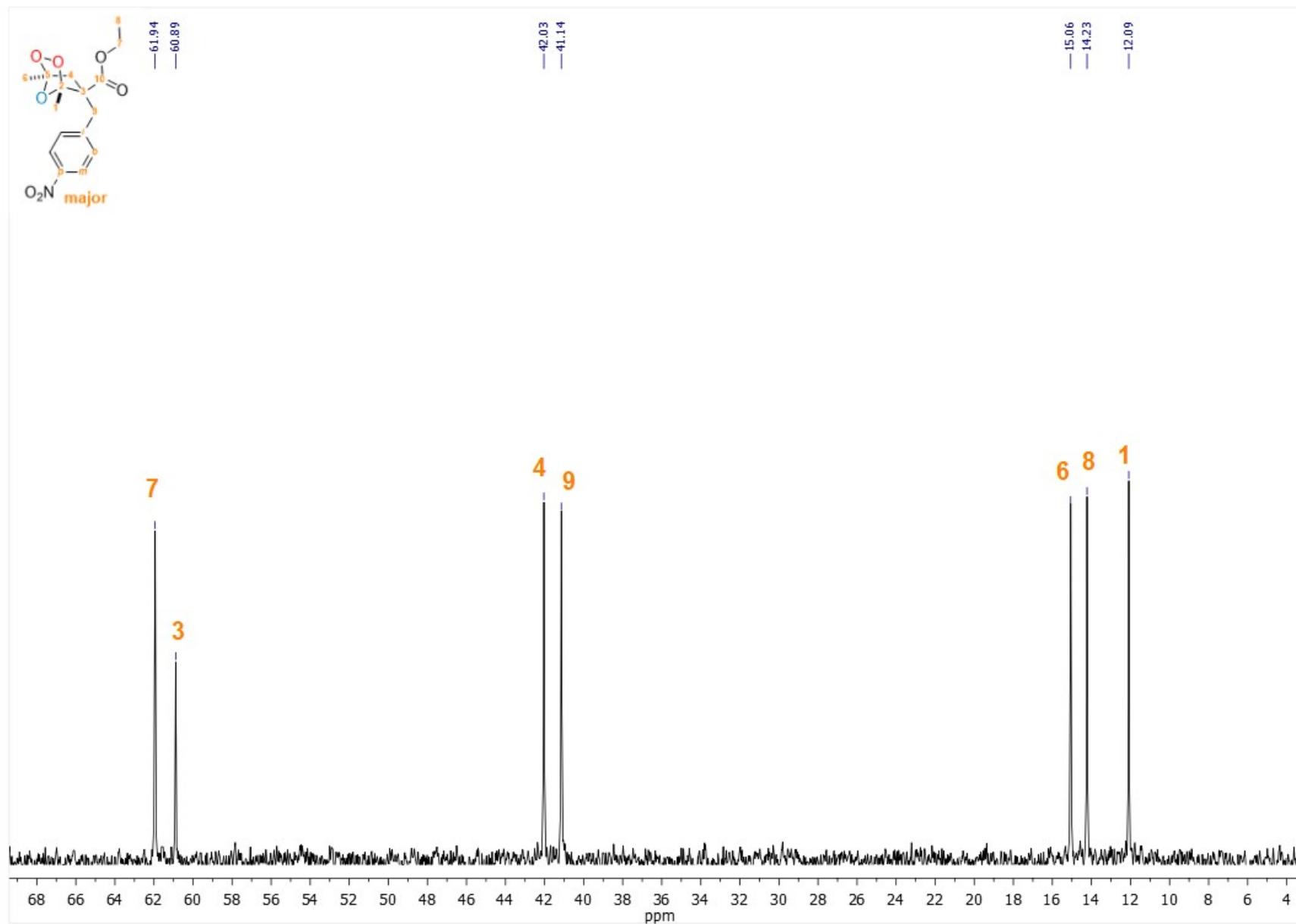


S51

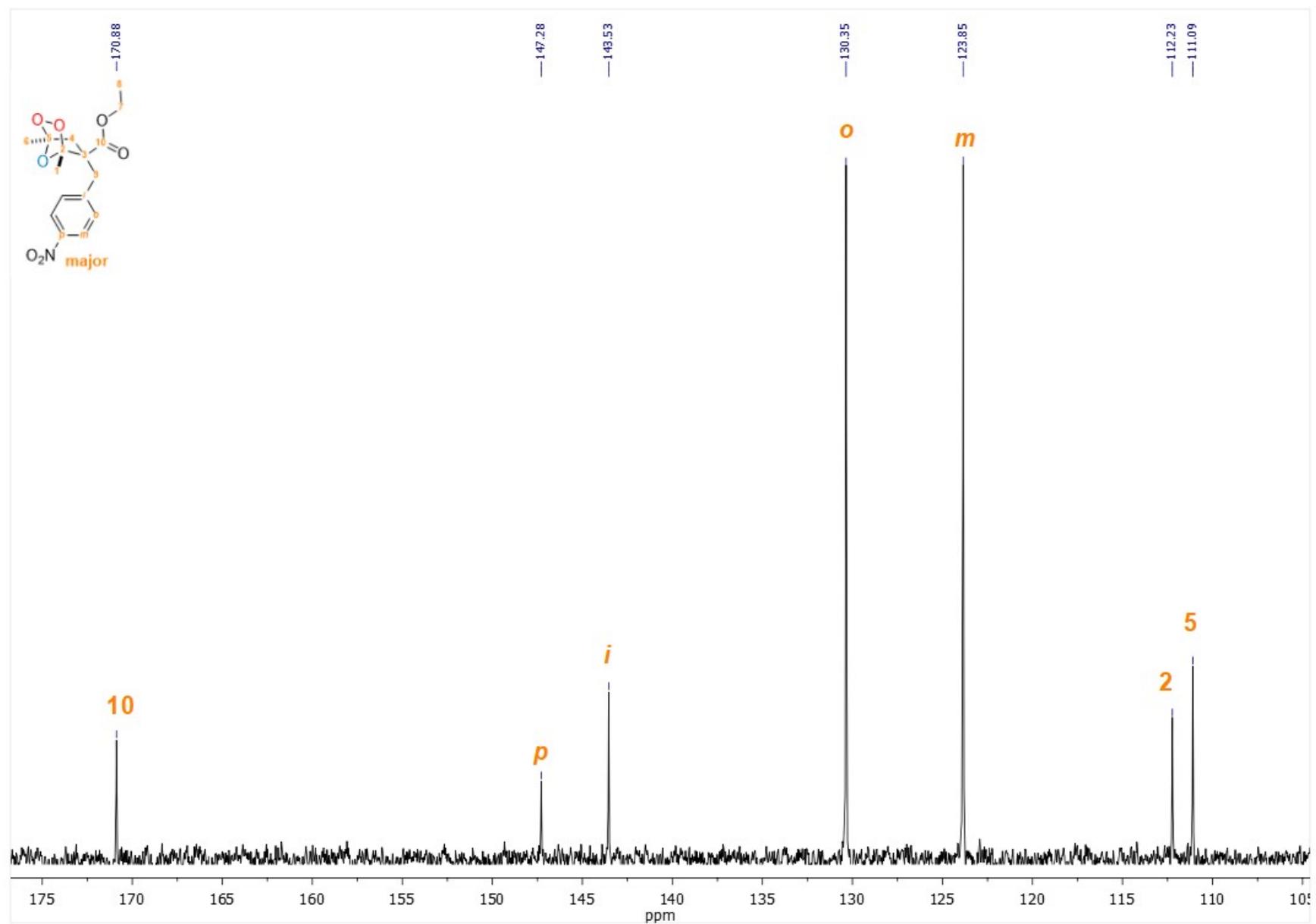
¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a



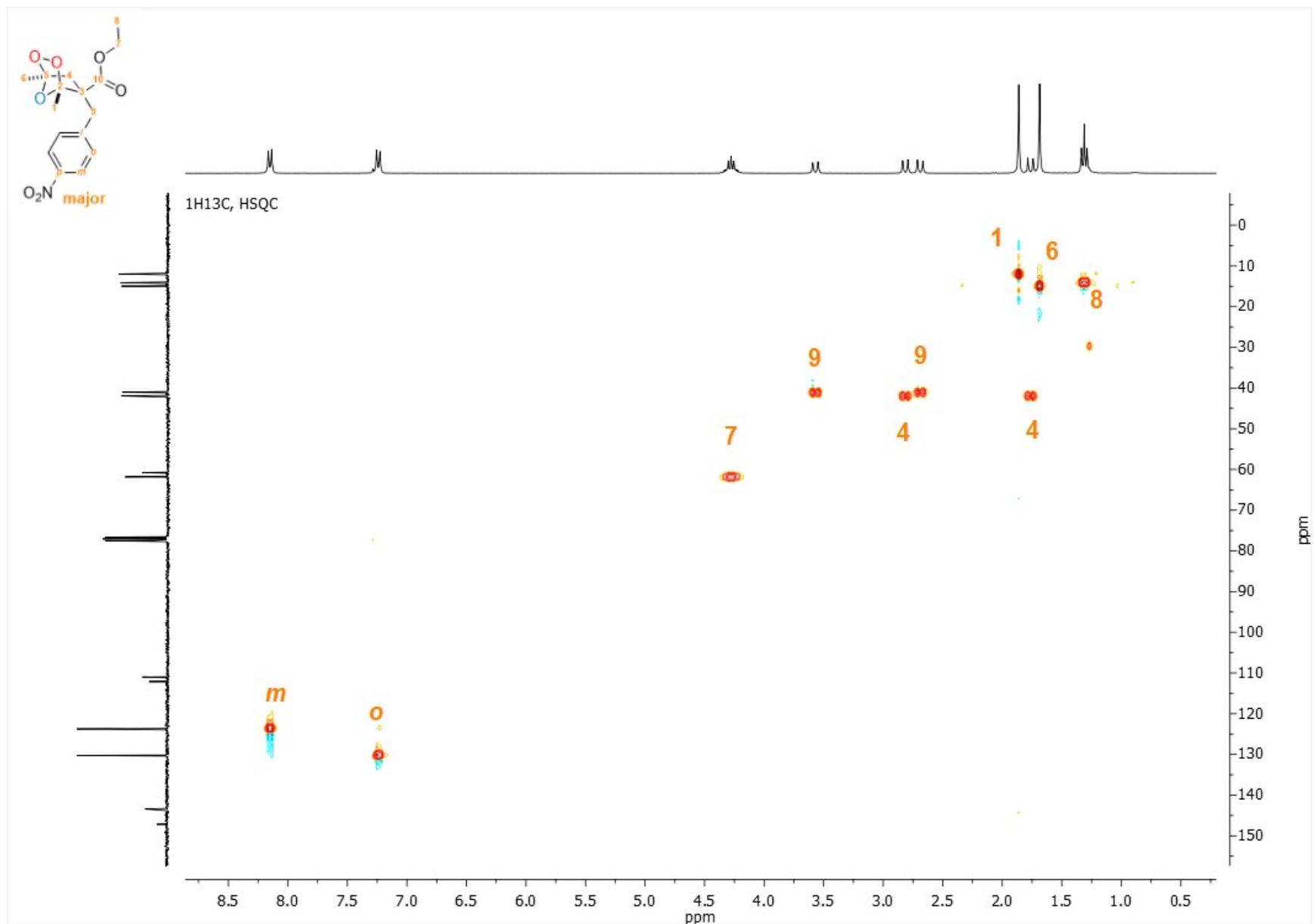
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a



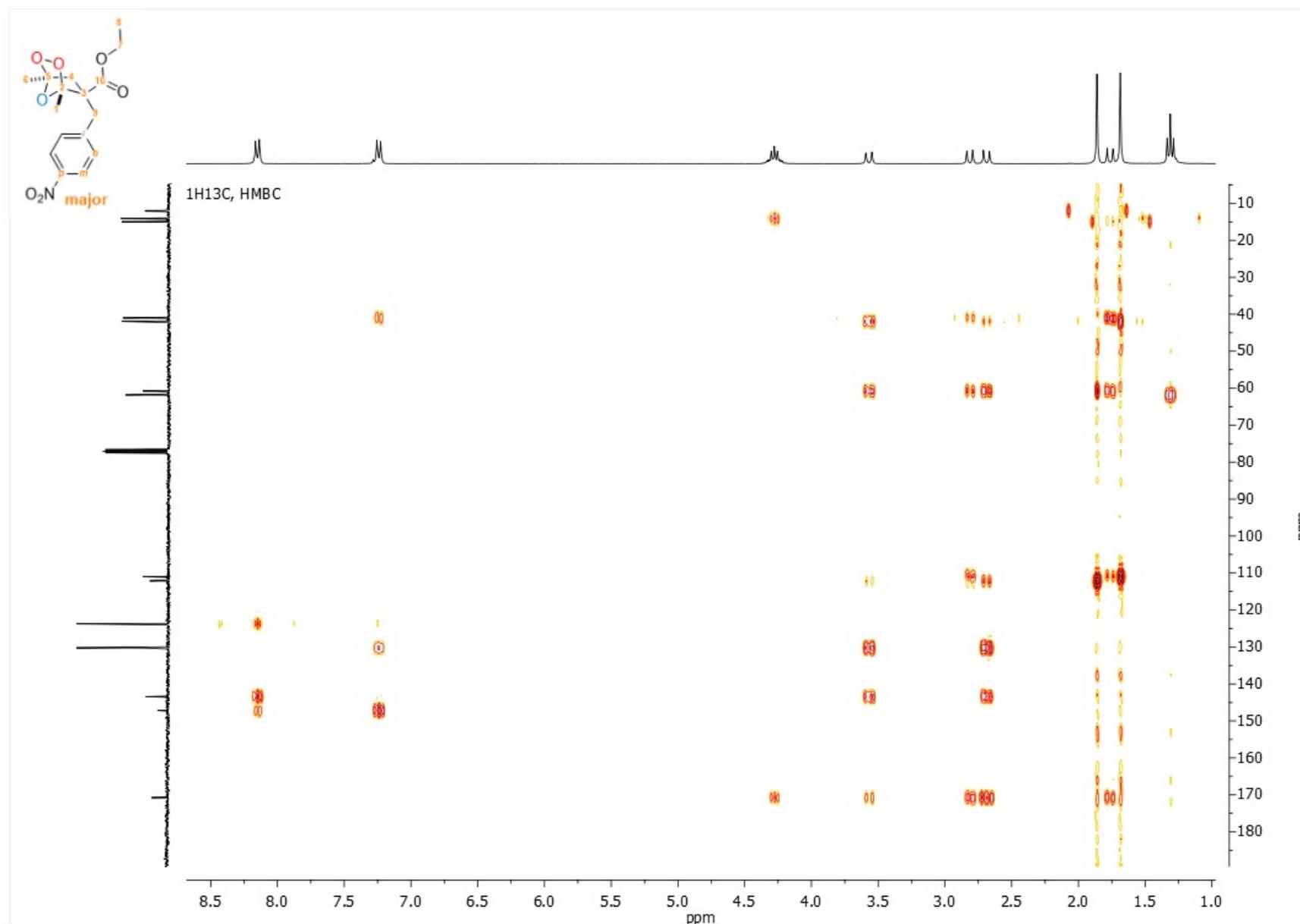
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a



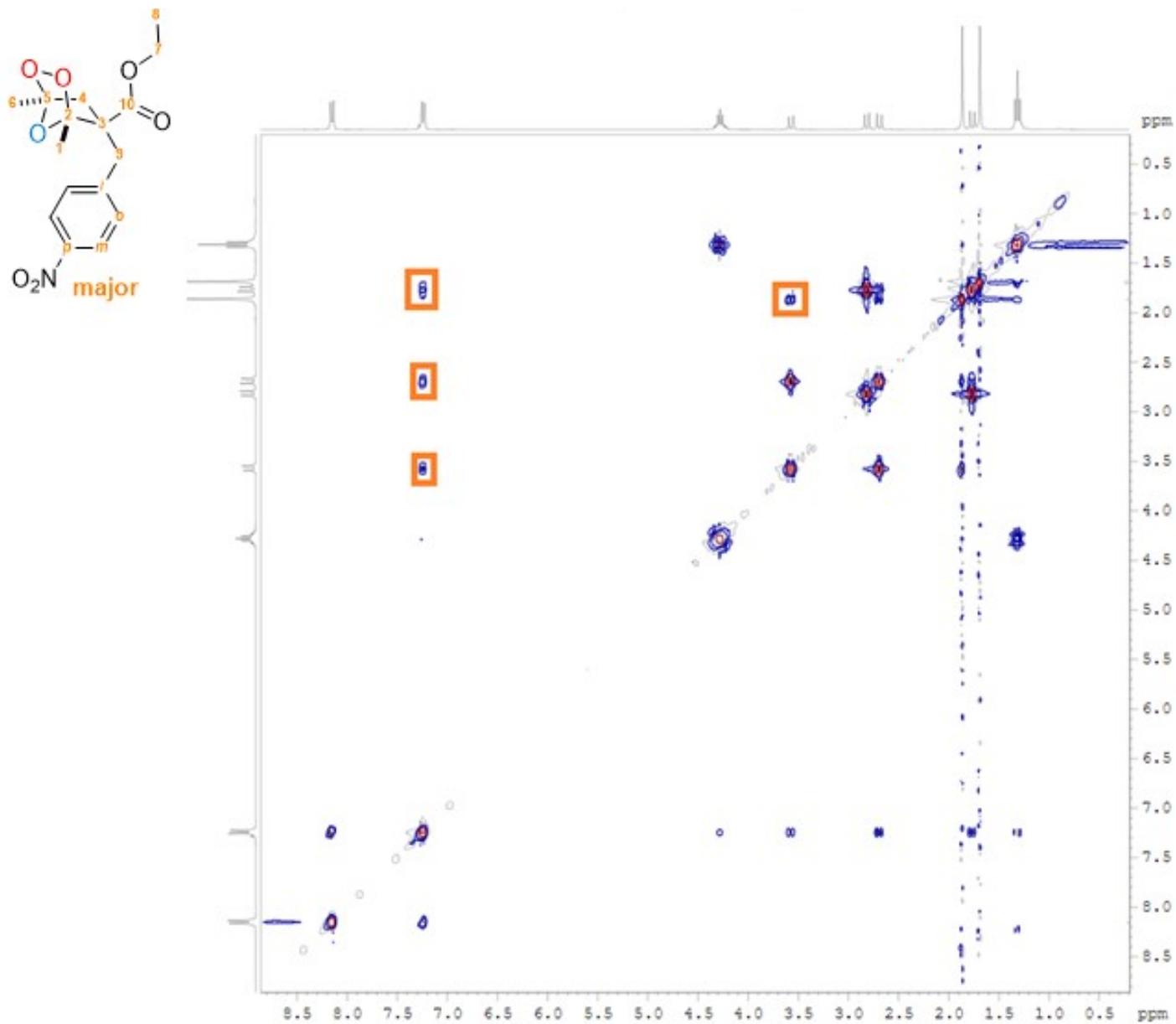
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a



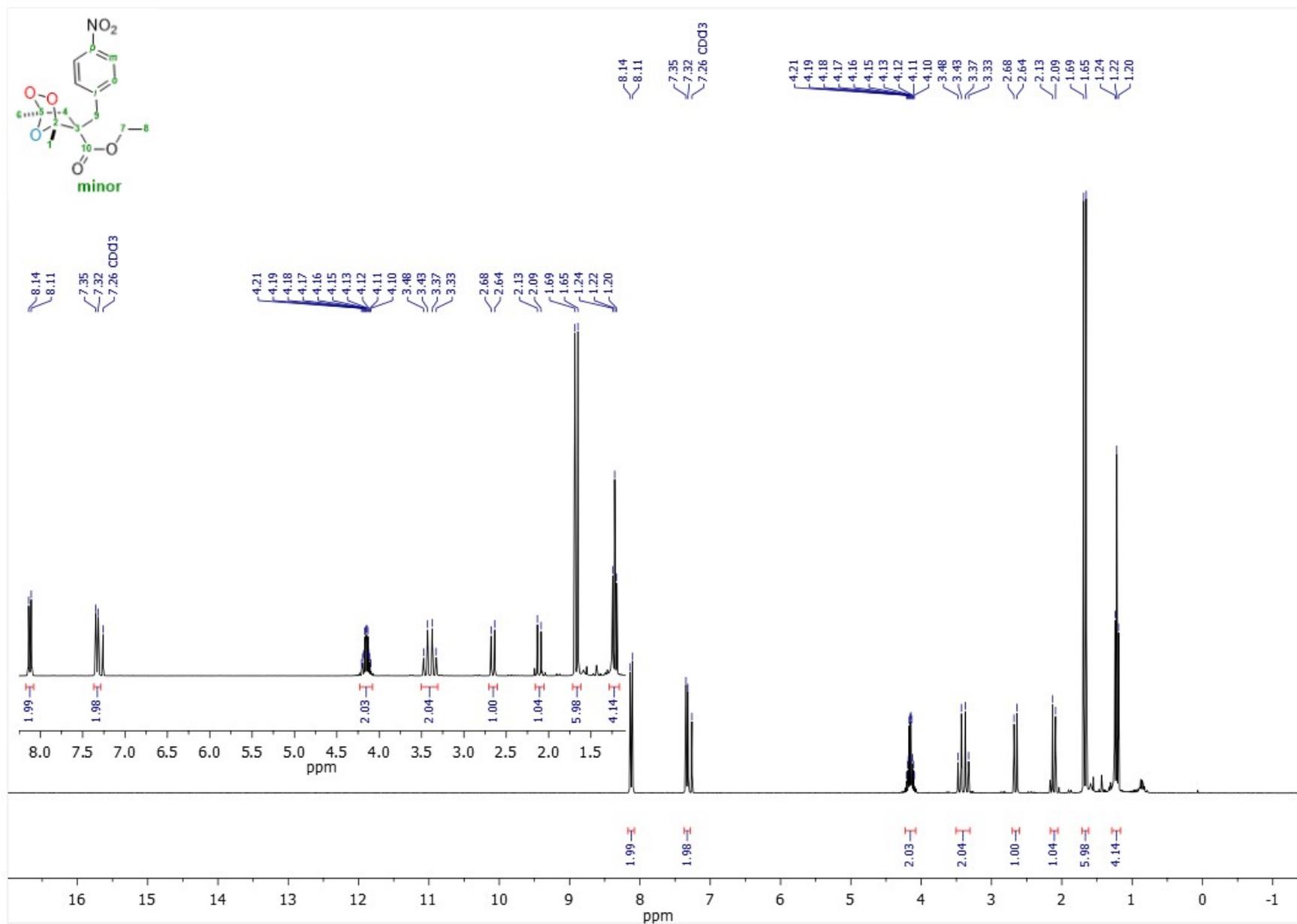
$^1\text{H} - ^{13}\text{C}$, HMBC. Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a



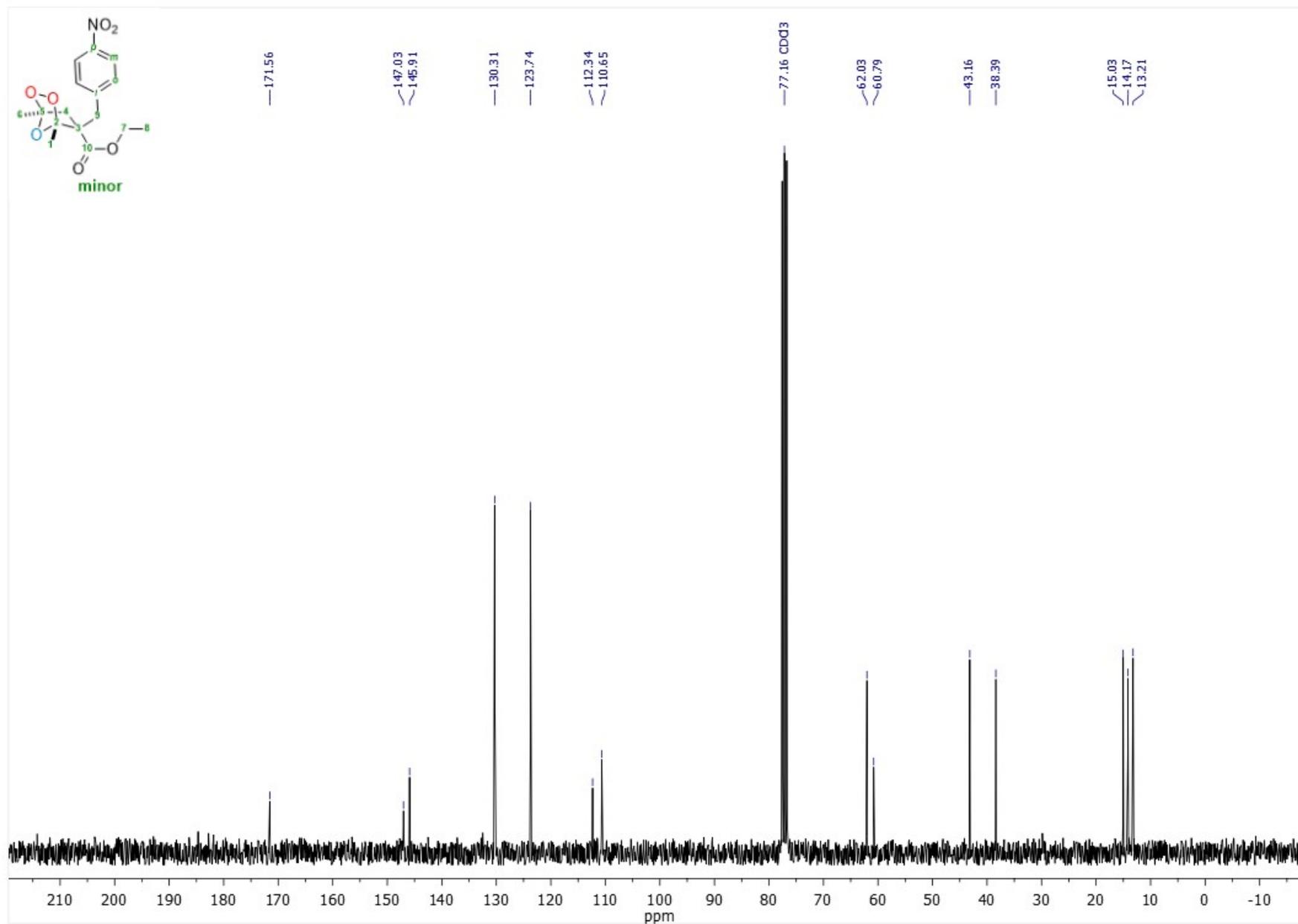
$^1\text{H} - ^1\text{H}$, NOESY. Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2a



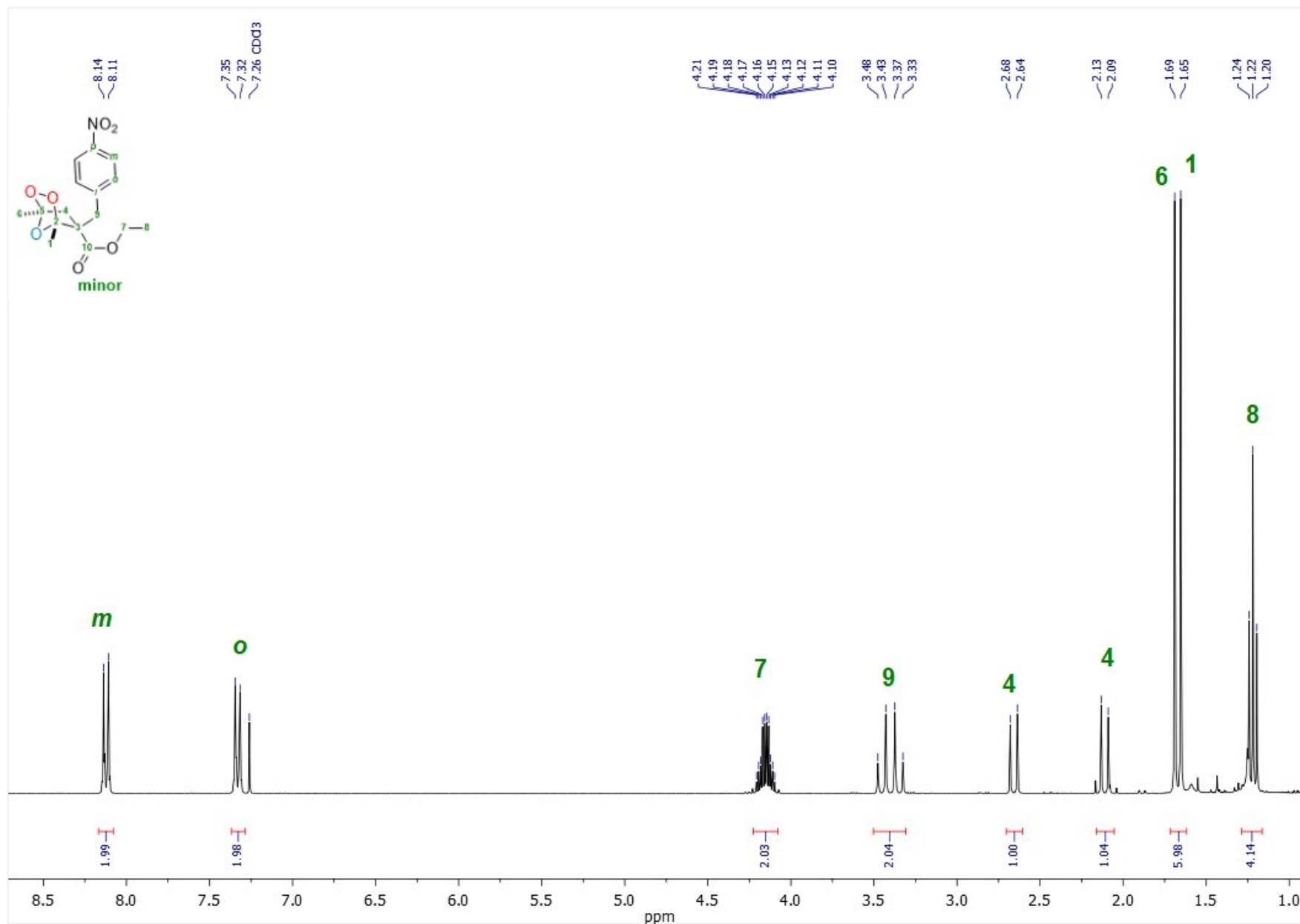
¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a

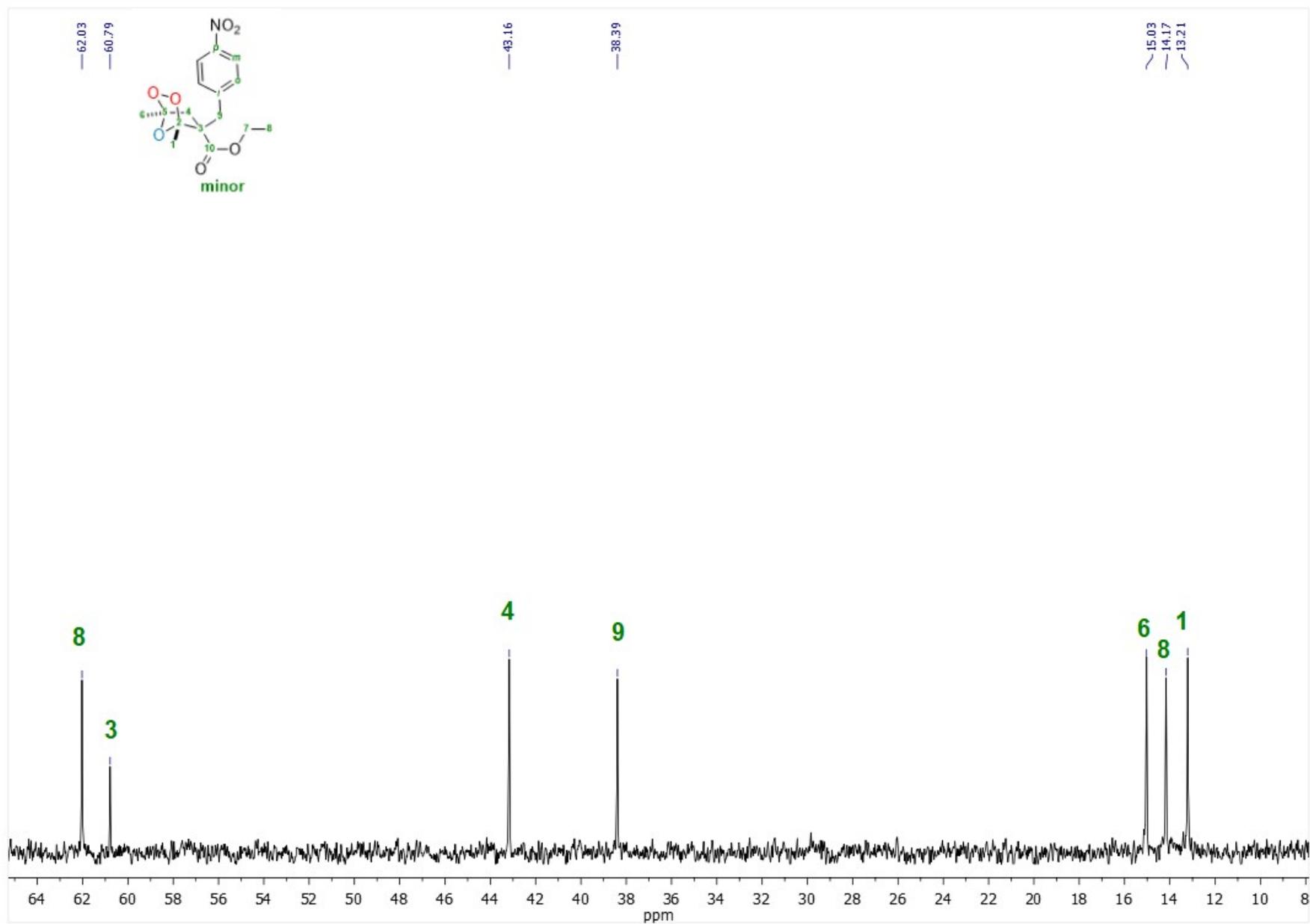


¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a

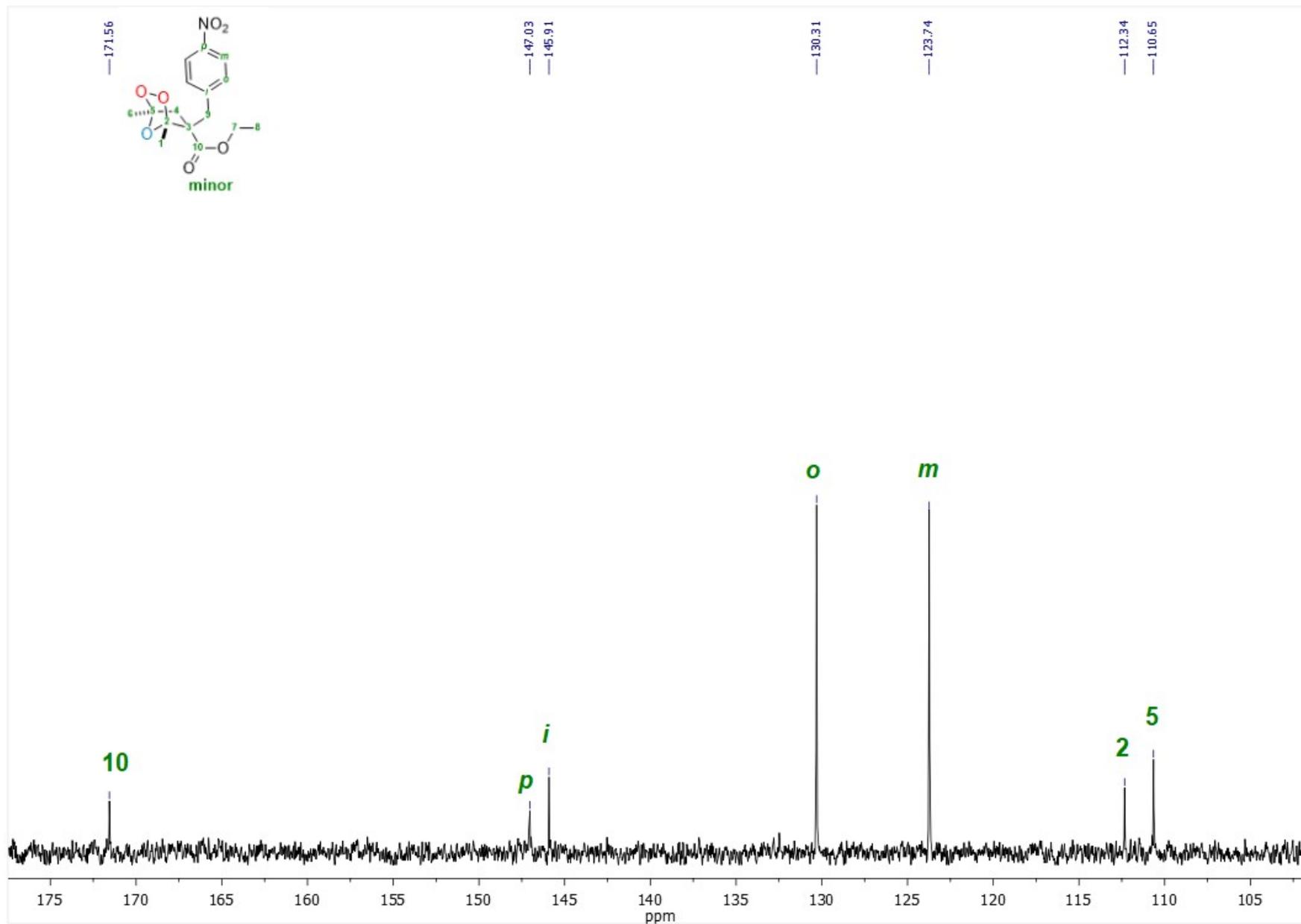


S61

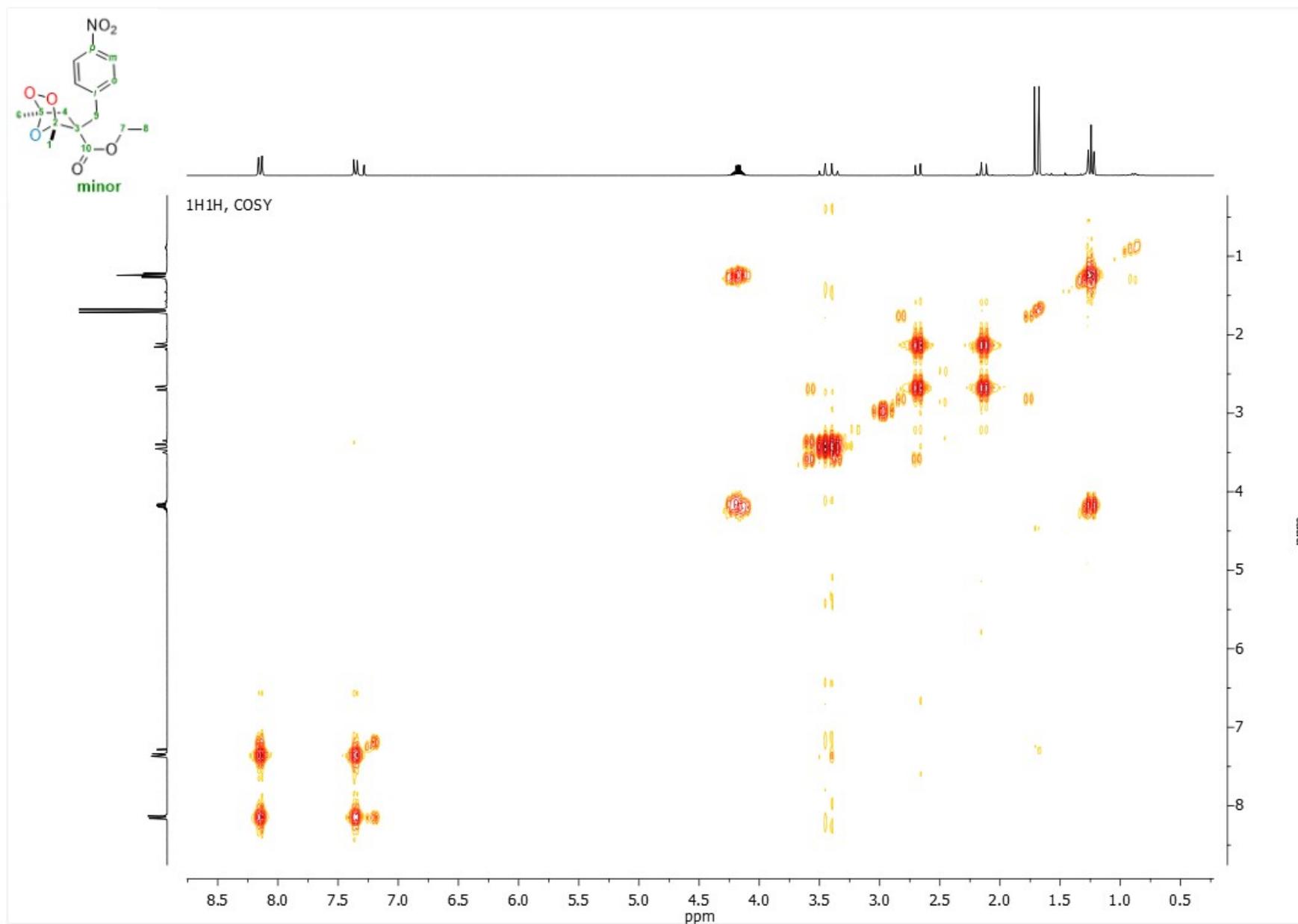
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



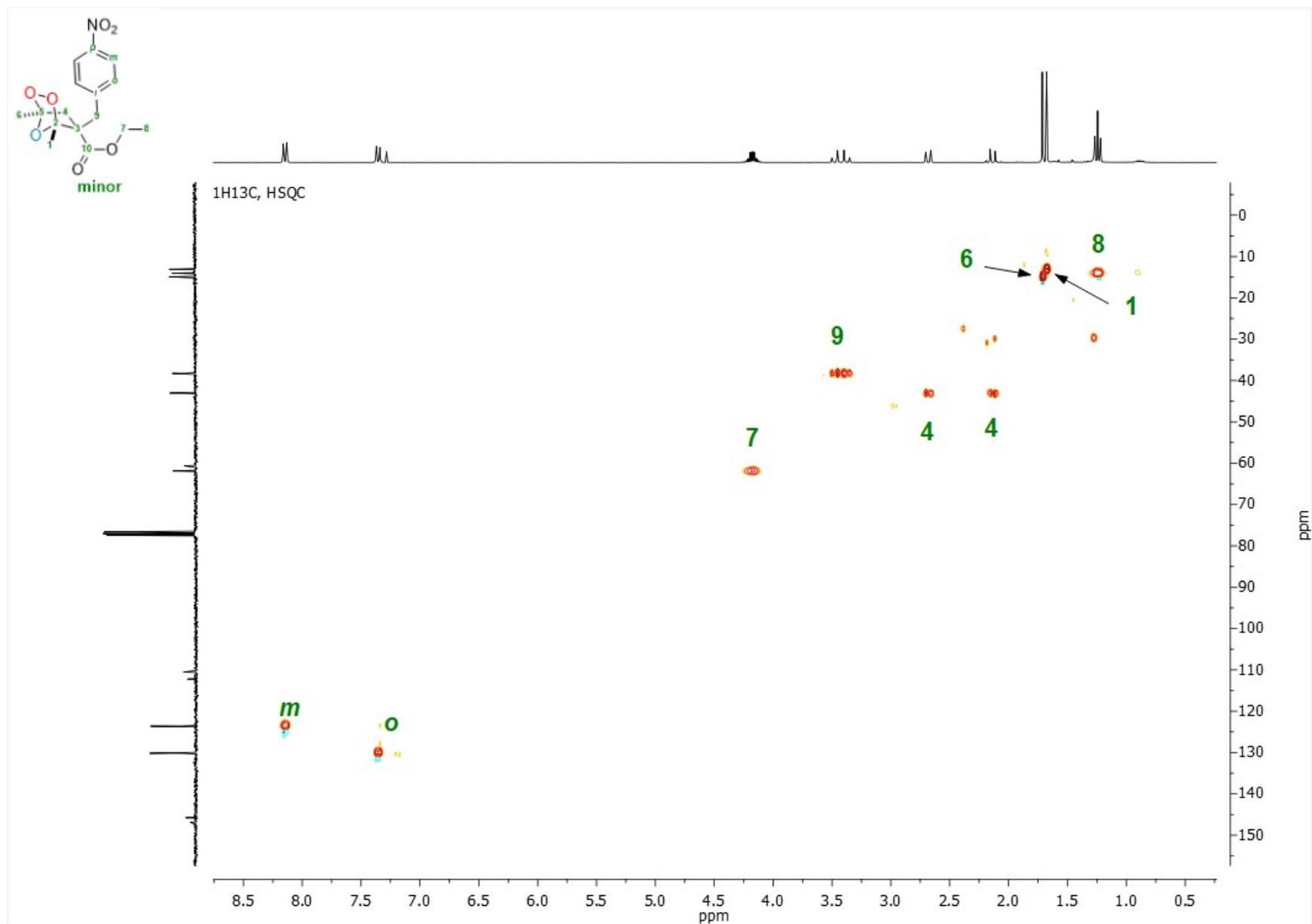
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



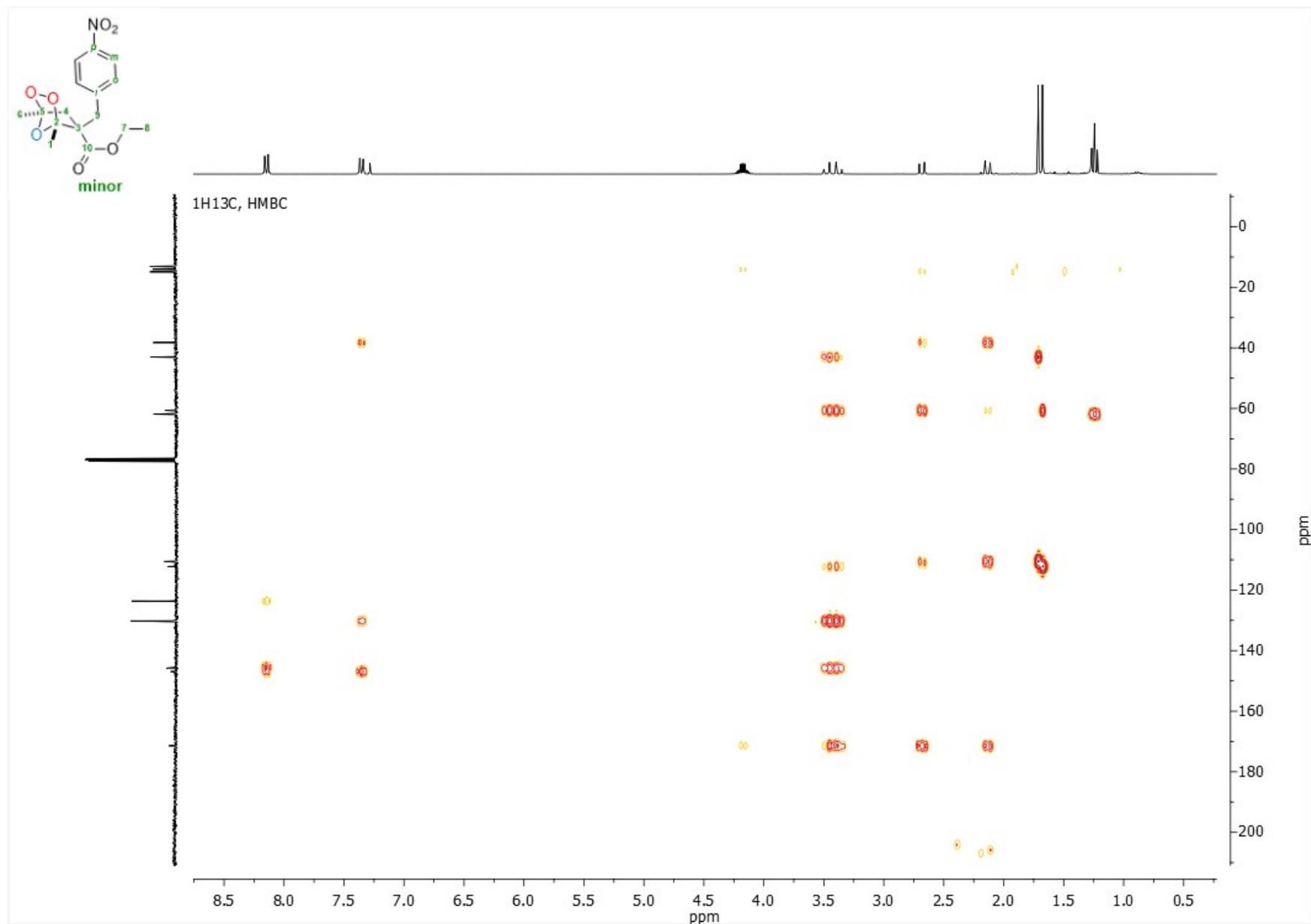
$^1\text{H} - ^1\text{H}$, COSY. Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



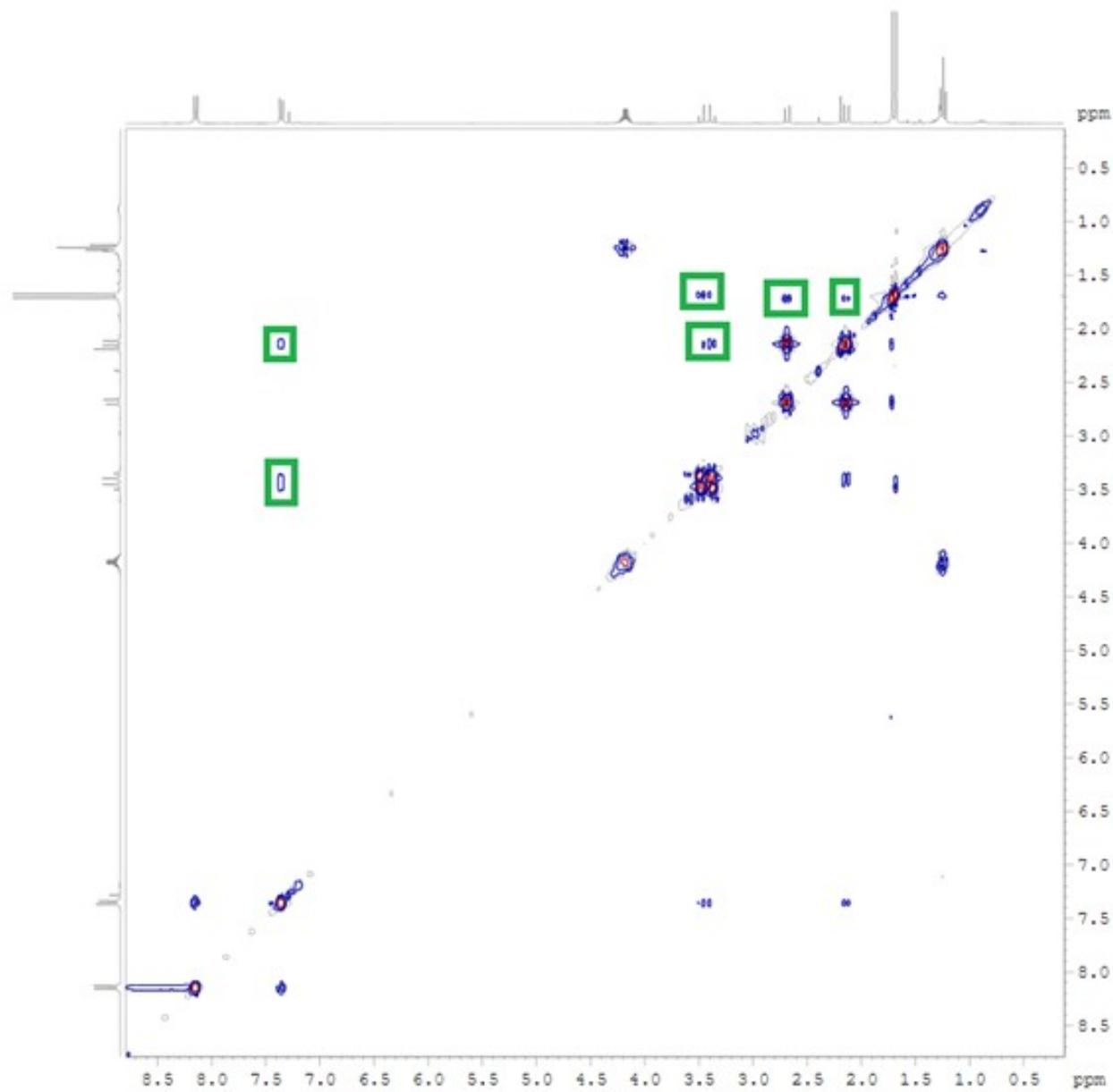
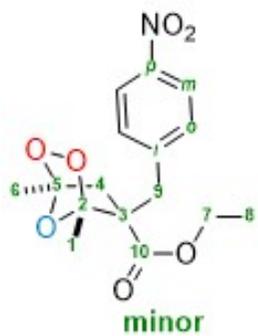
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



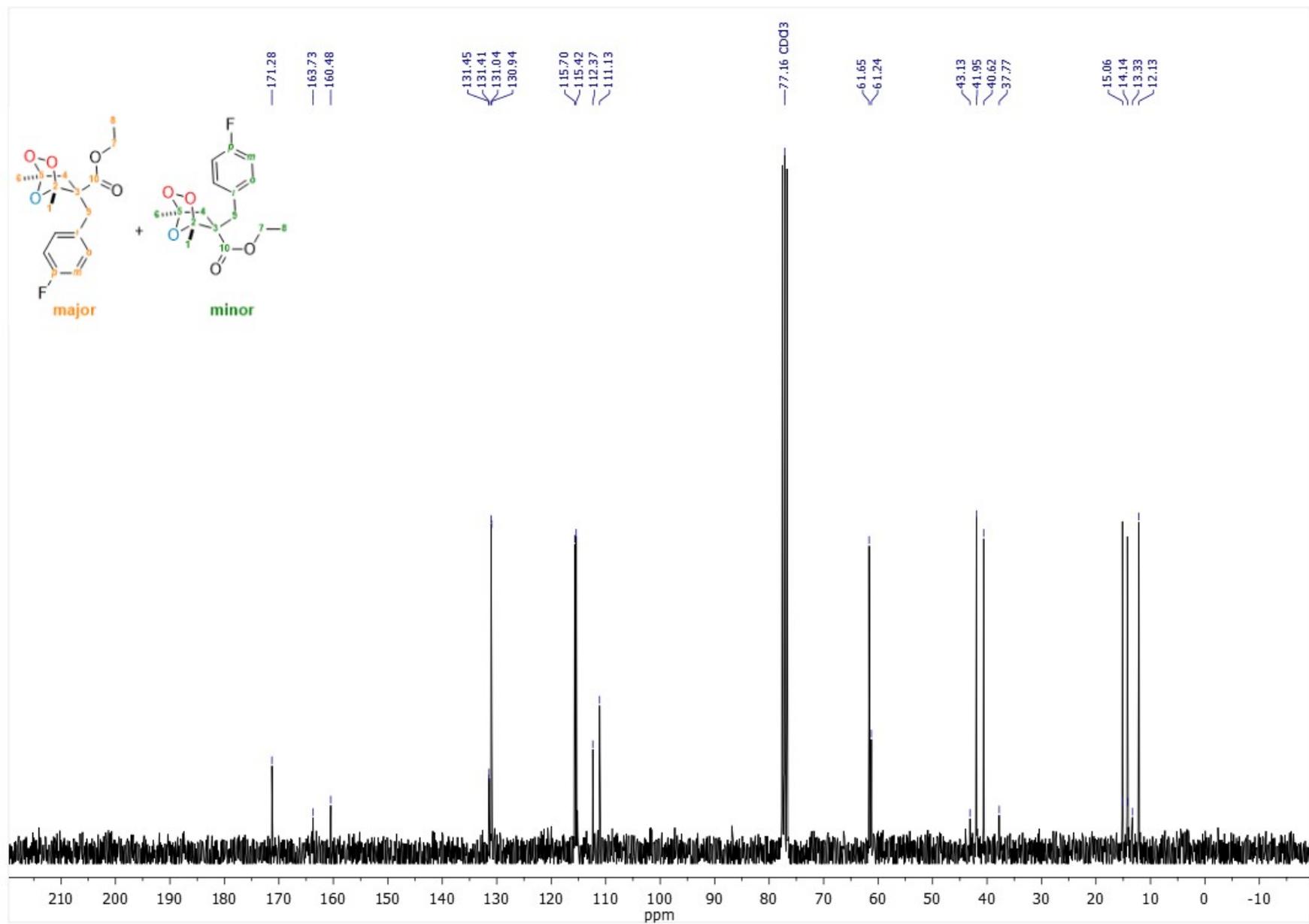
$^1\text{H} - ^{13}\text{C}$, HMBC. Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



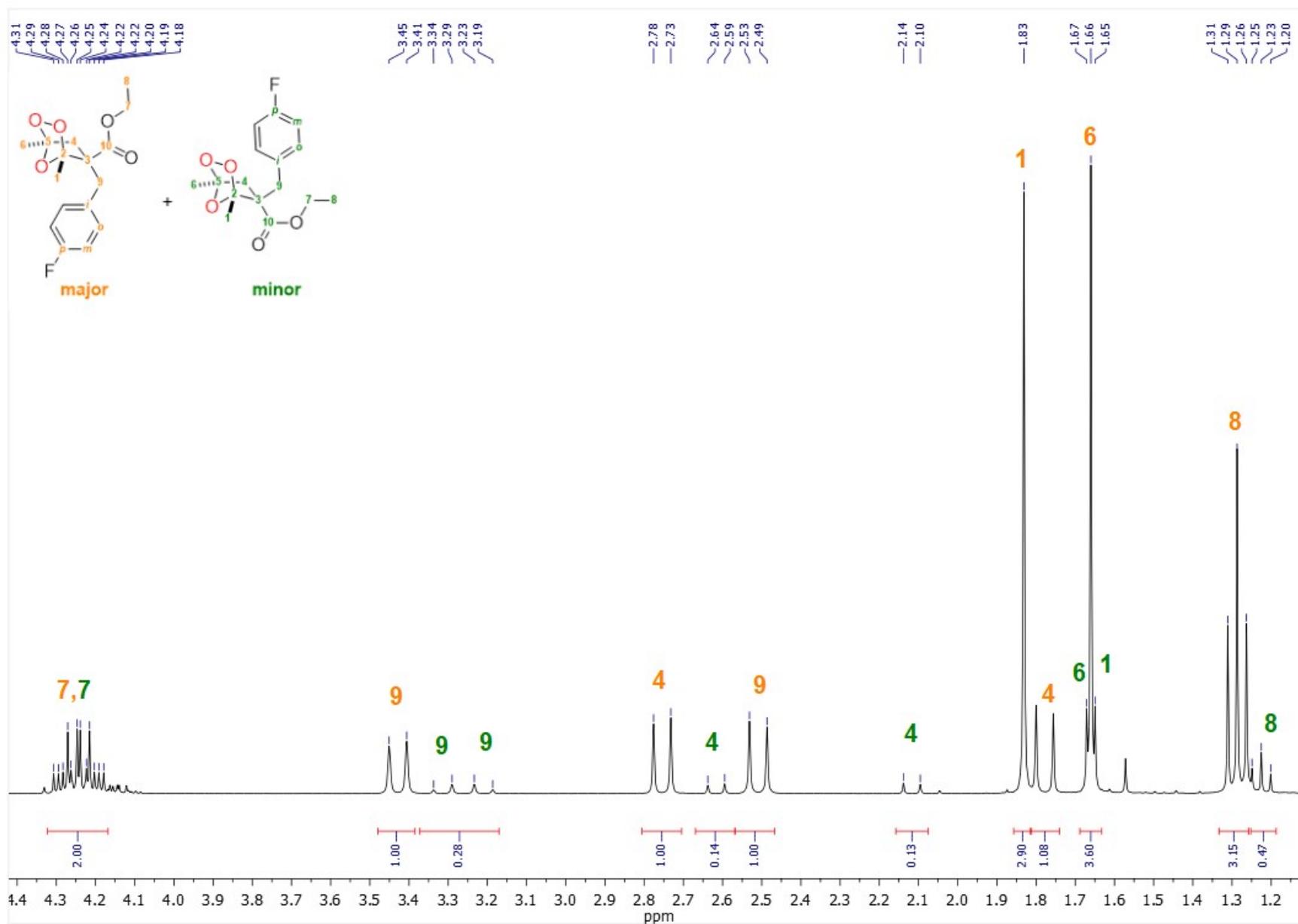
$^1\text{H} - ^1\text{H}$, NOESY. Ethyl (1*S**,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a



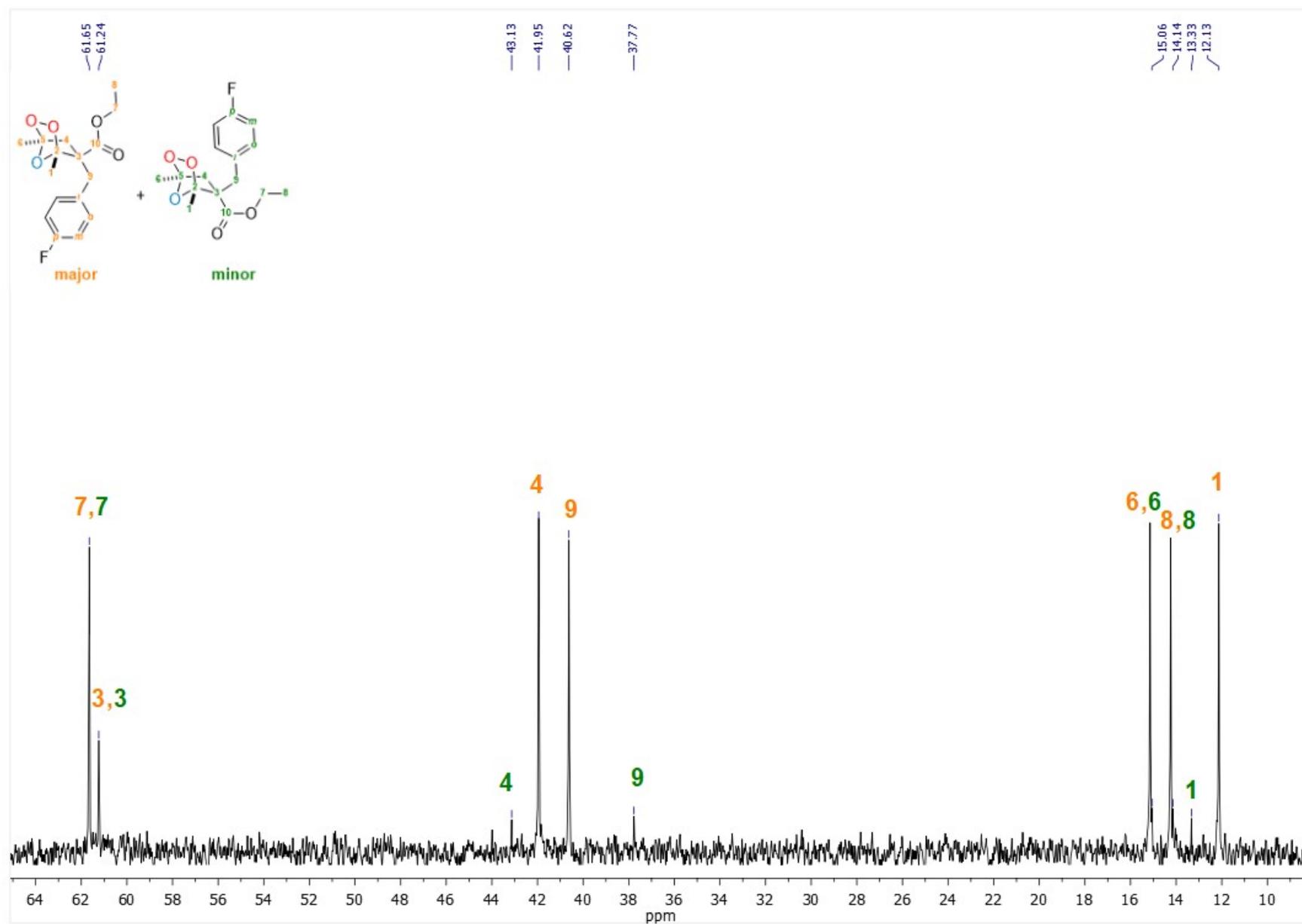
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl 5-(4-fluorobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2b + *trans*-2b



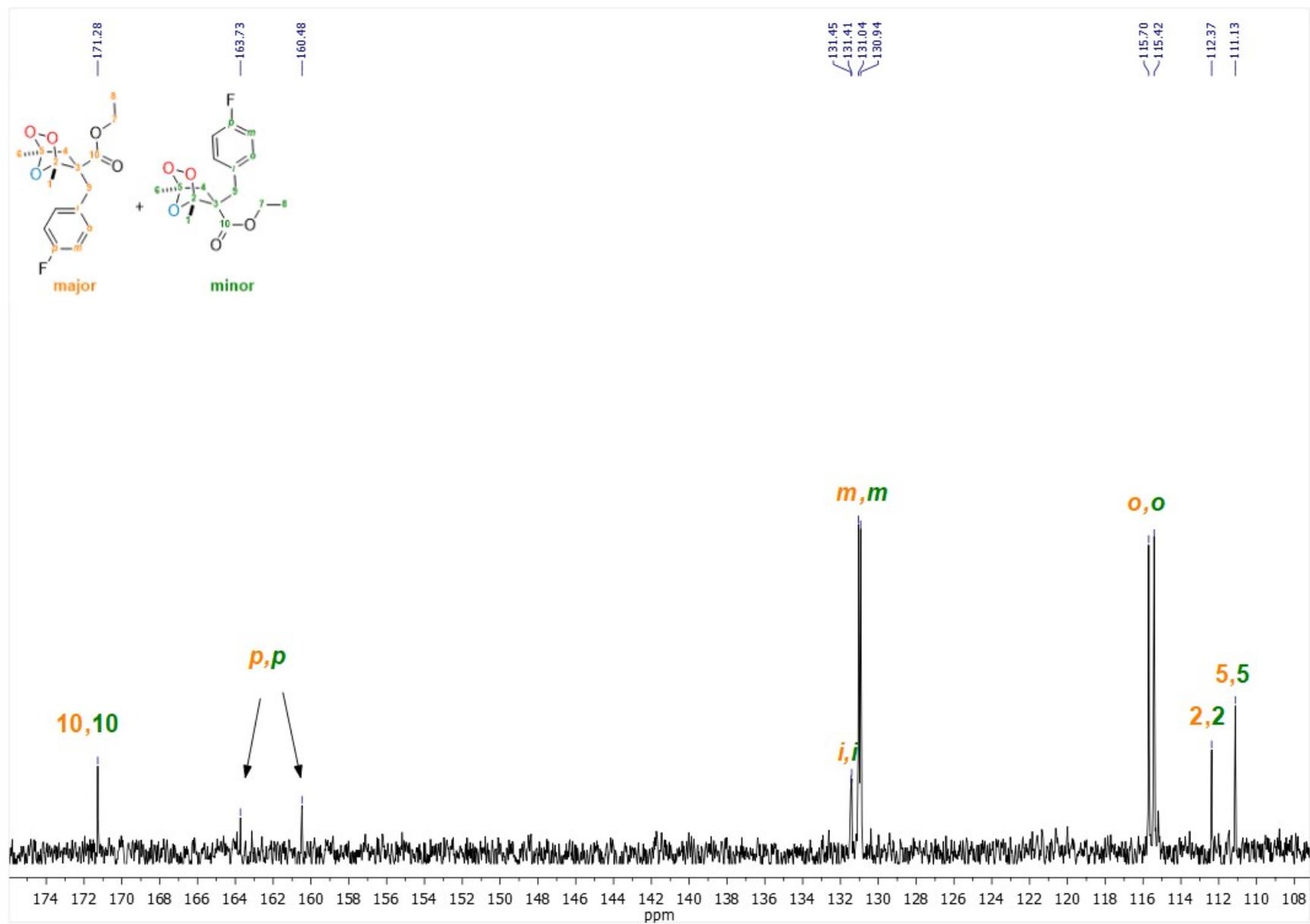
¹H NMR (300.13 MHz, CDCl₃). Ethyl 5-(4-fluorobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2b + *trans*-2b



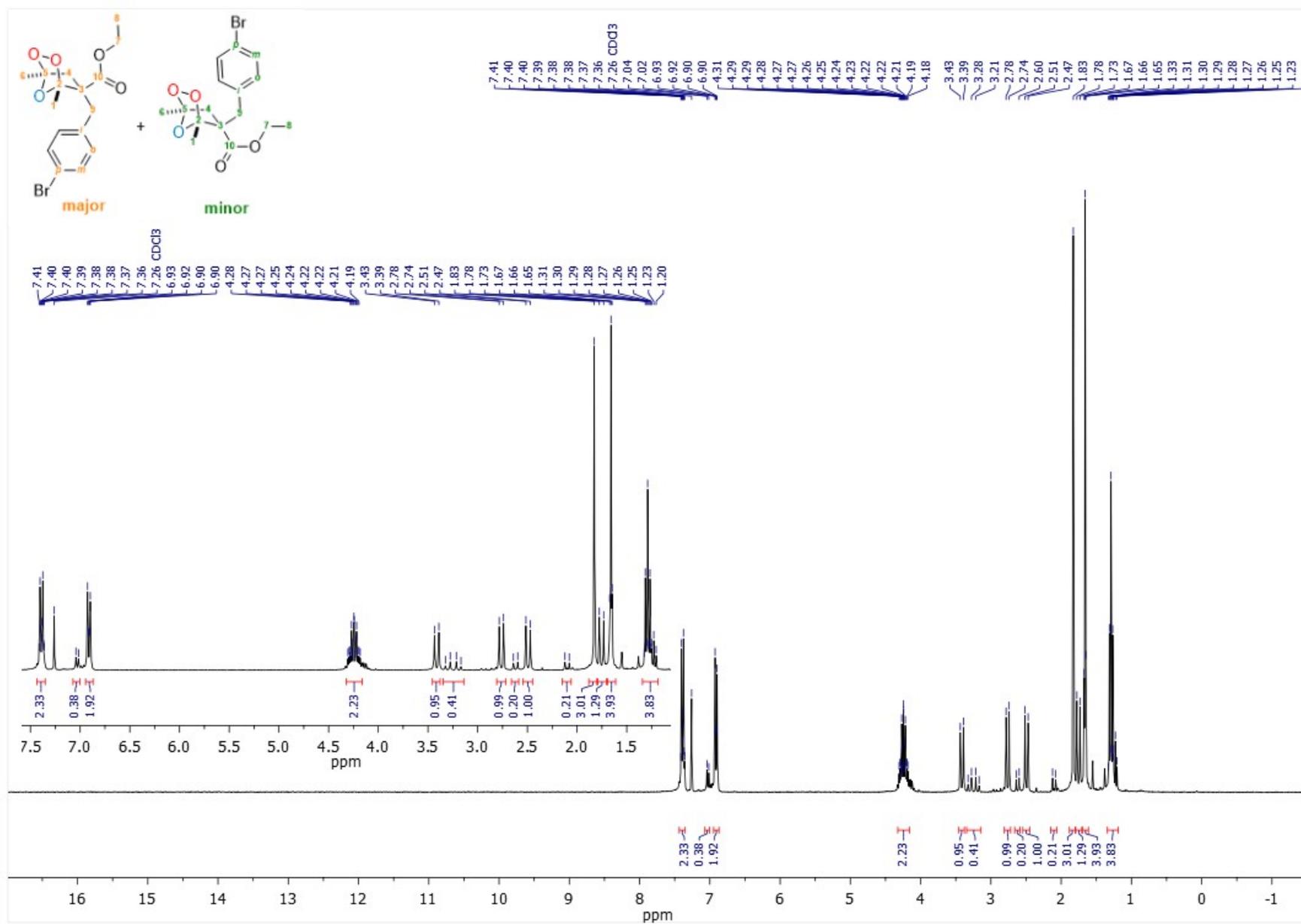
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl 5-(4-fluorobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2b + *trans*-2b



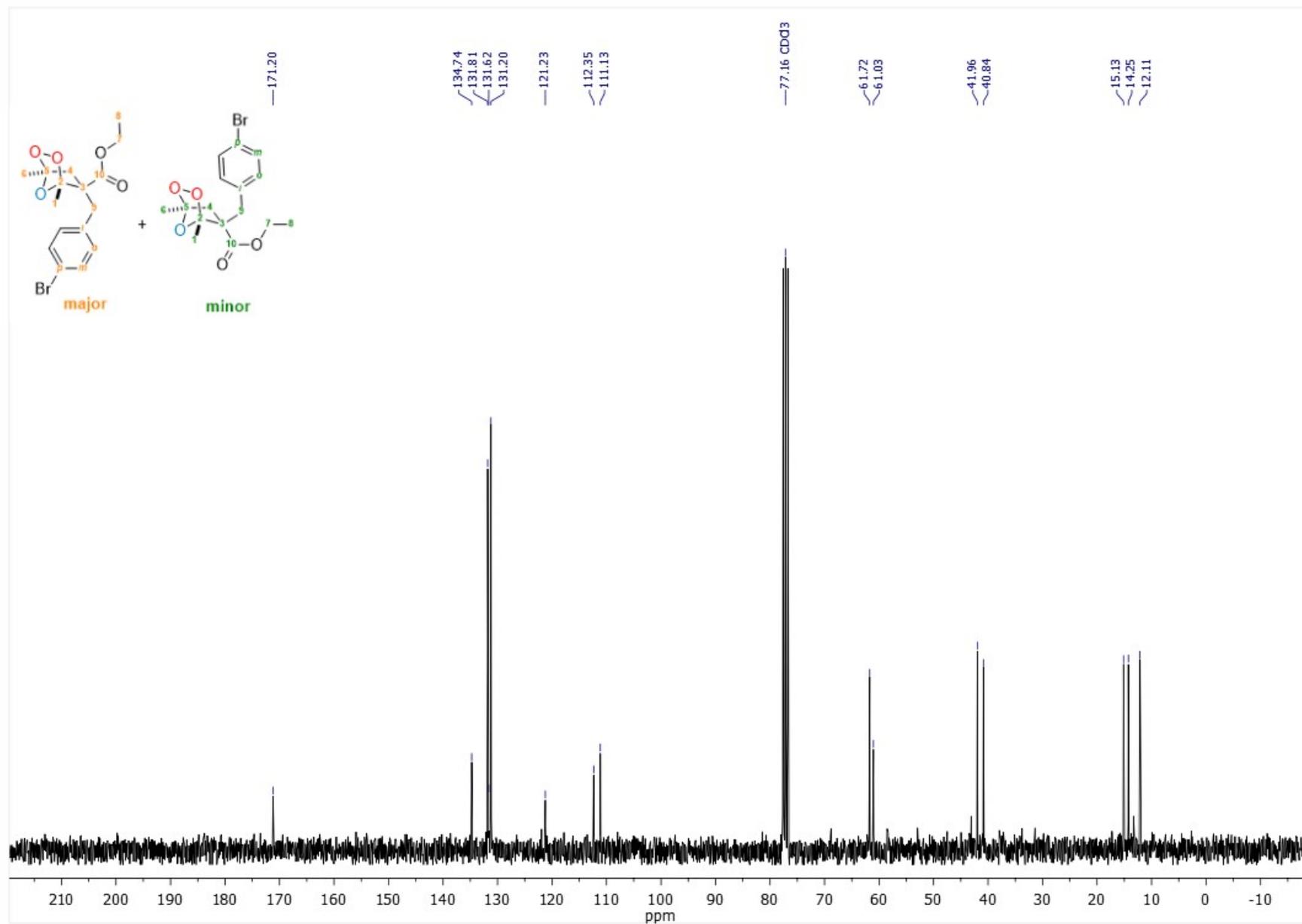
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl 5-(4-fluorobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2b + *trans*-2b



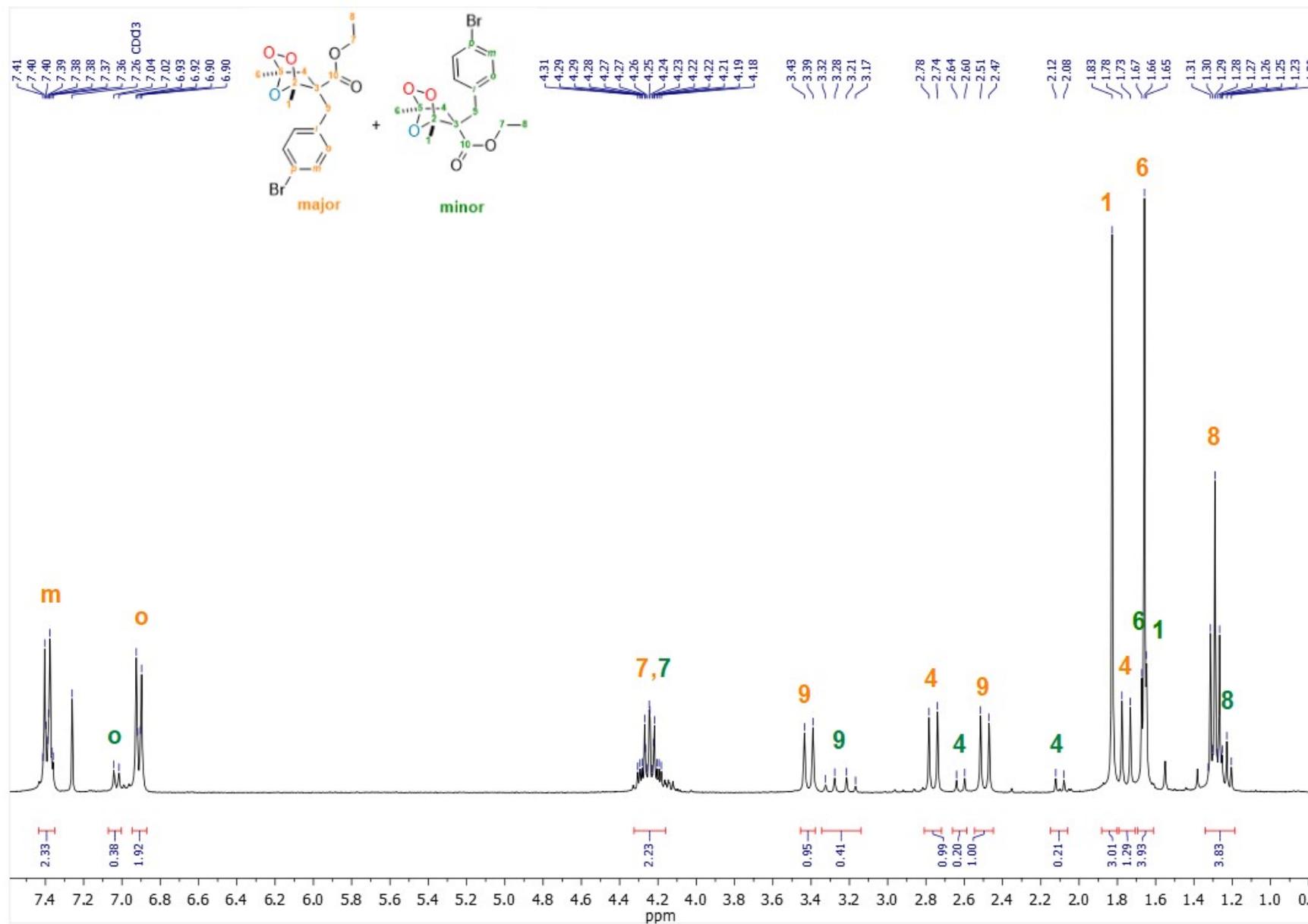
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c + *trans*-2c



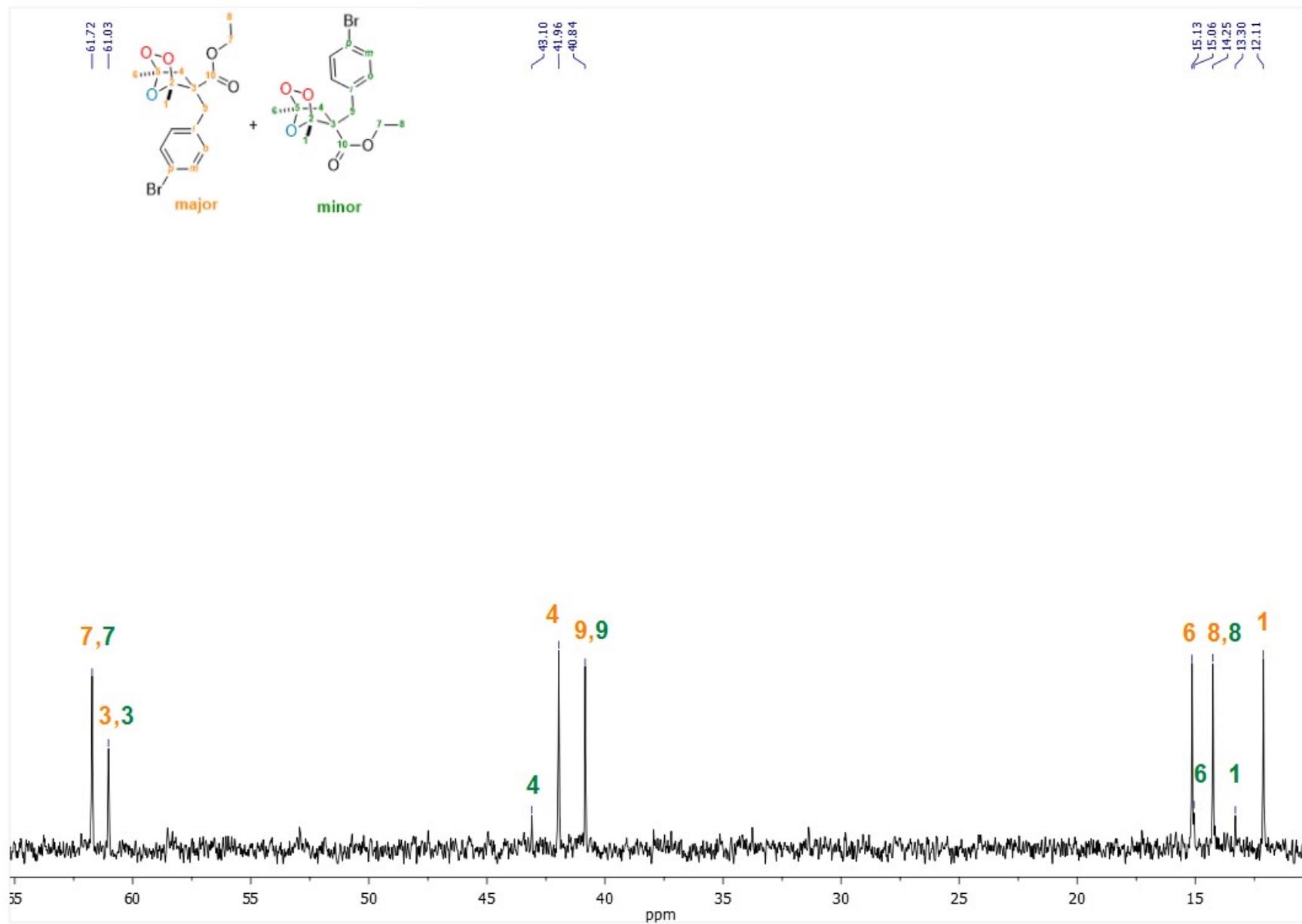
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c + *trans*-2c



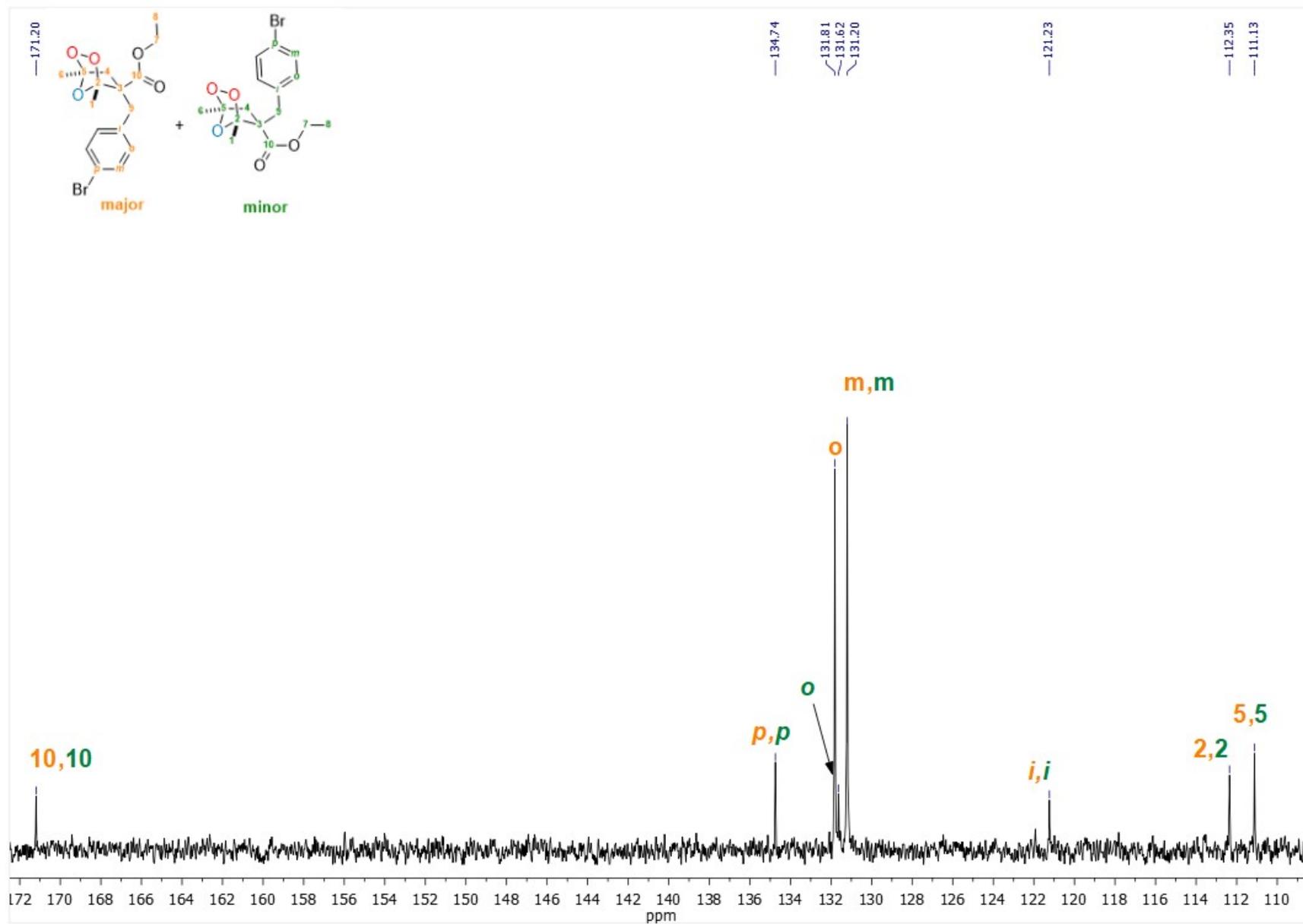
^1H NMR (300.13 MHz, CDCl_3). Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c + *trans*-2c



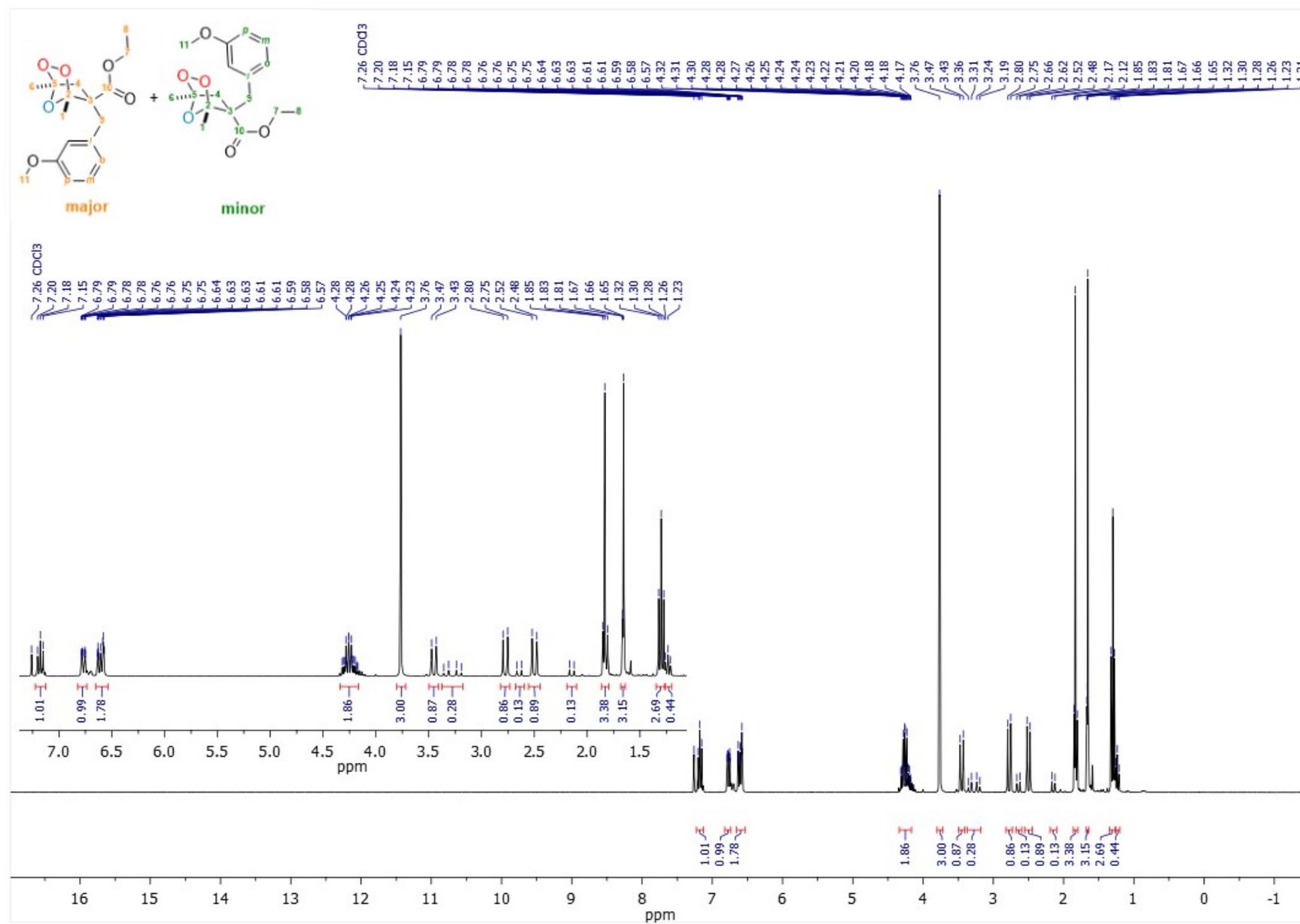
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c + *trans*-2c



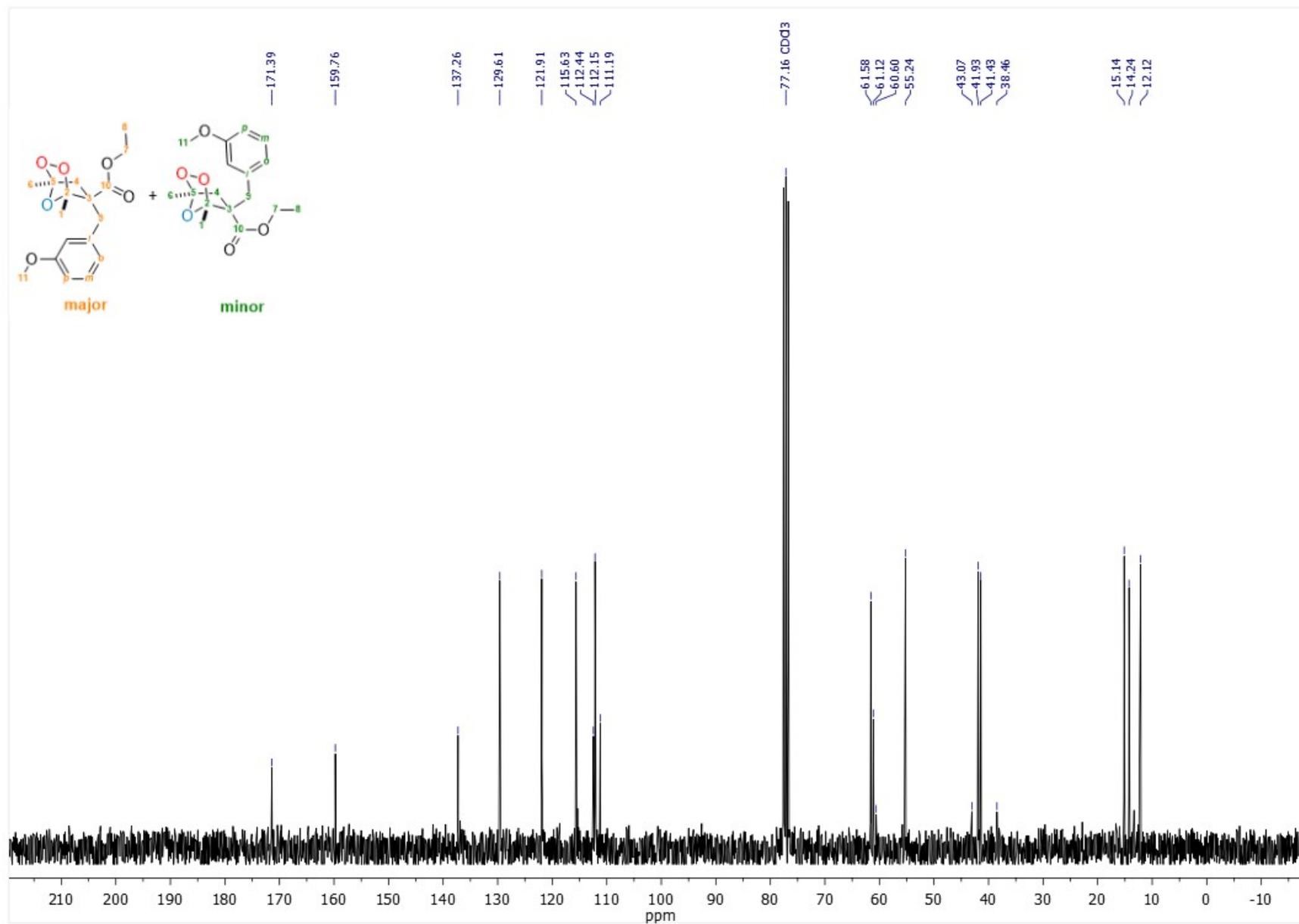
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c + *trans*-2c



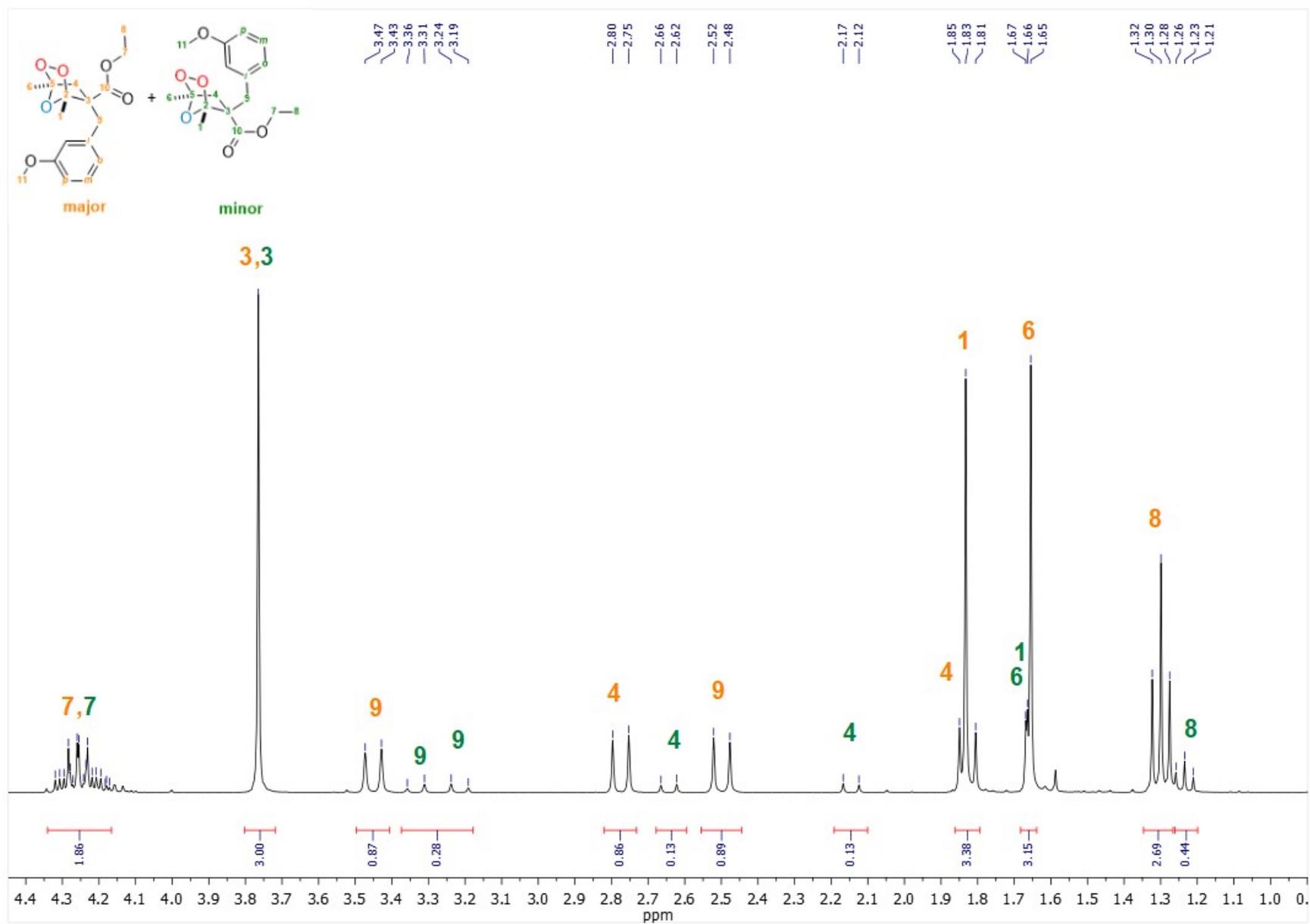
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d + *trans*-2d



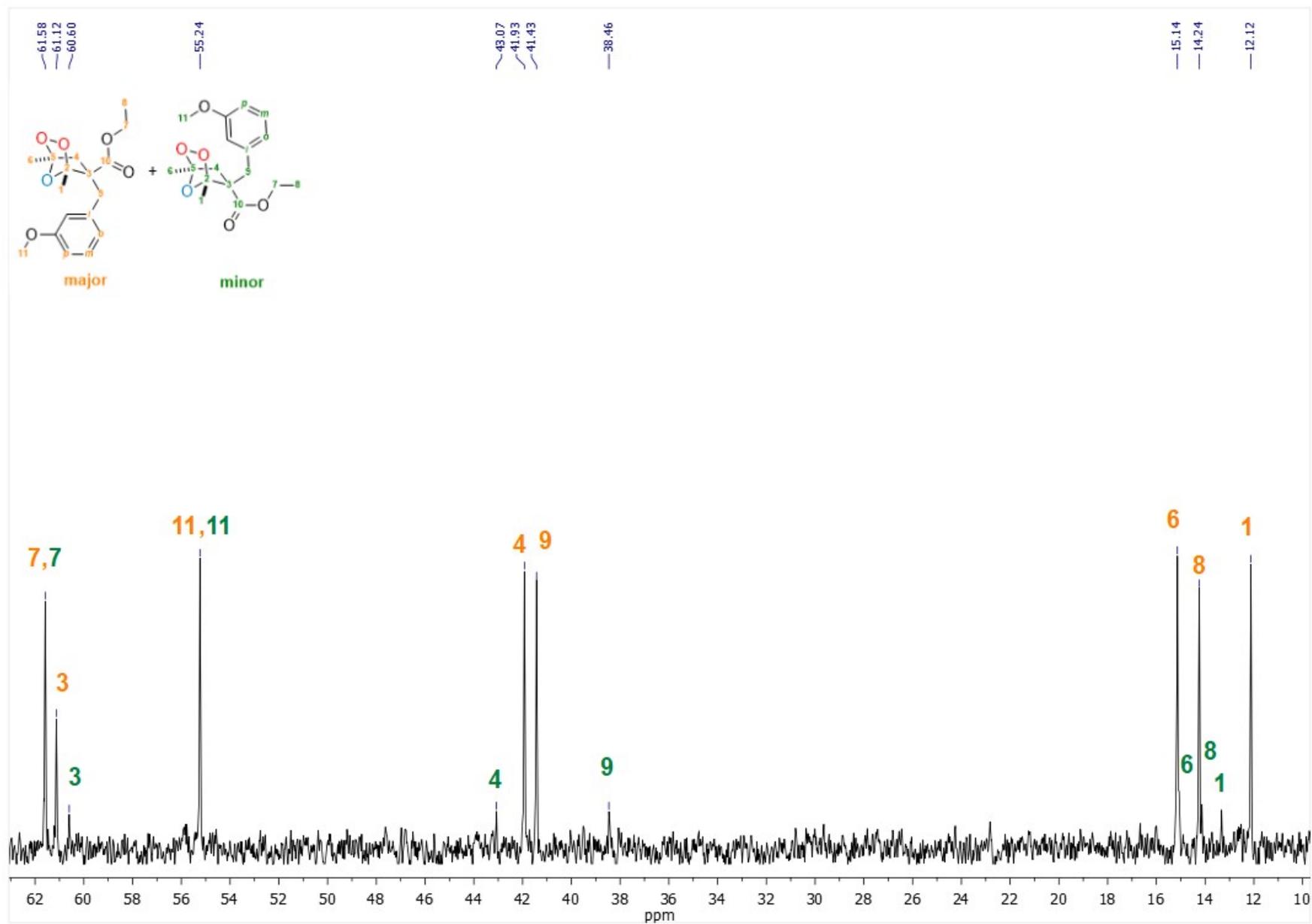
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d + *trans*-2d



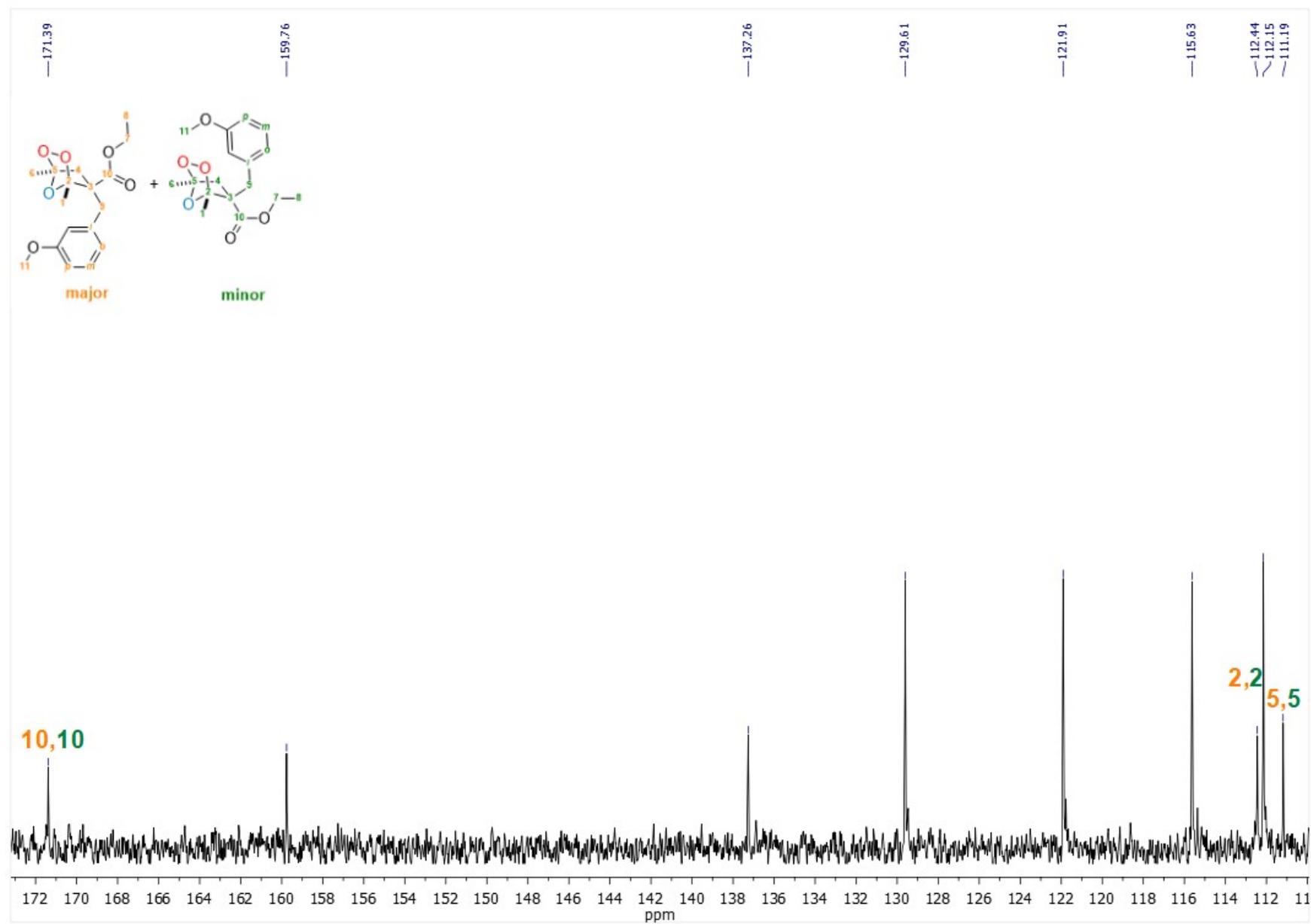
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d + *trans*-2d



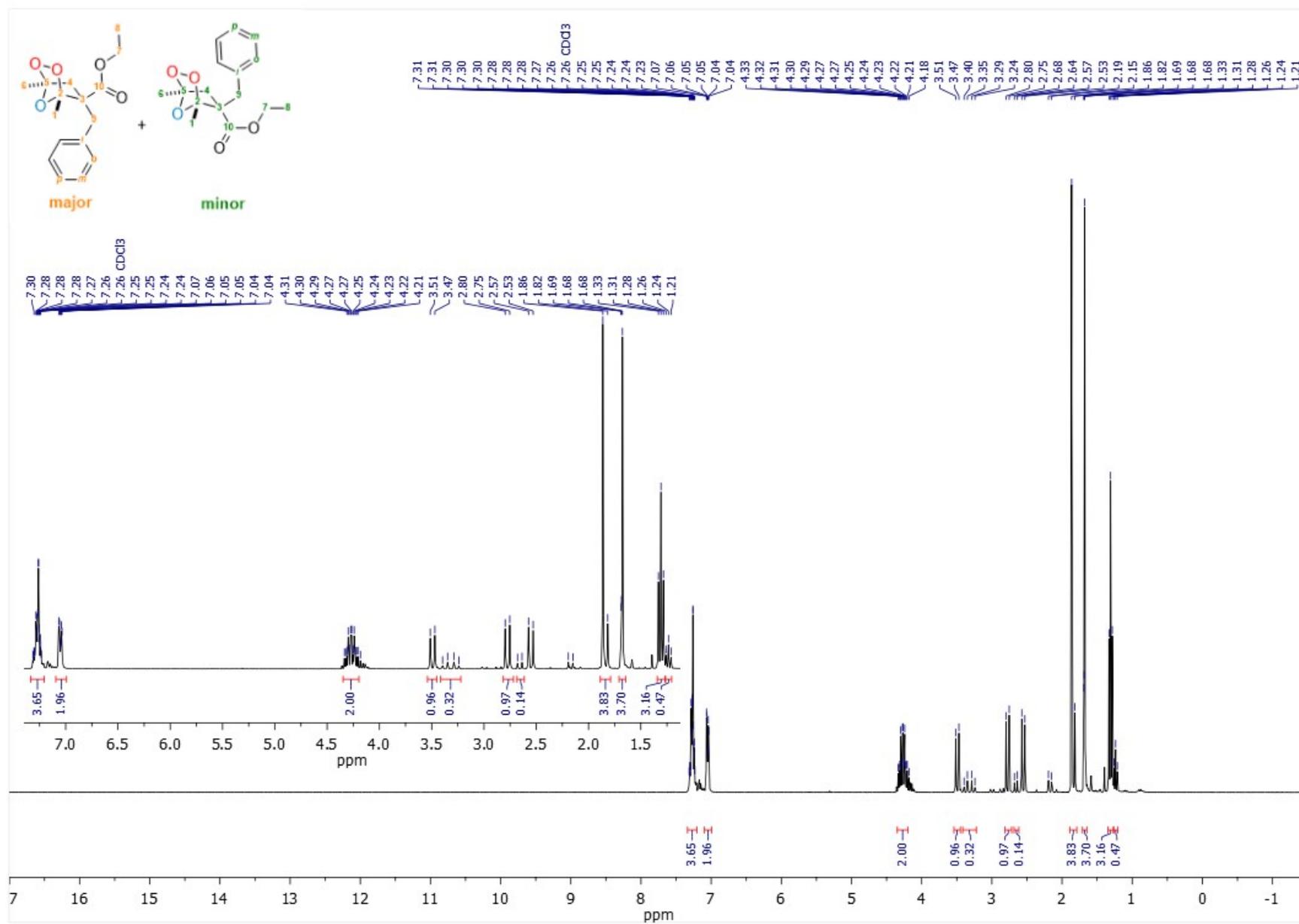
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d + *trans*-2d



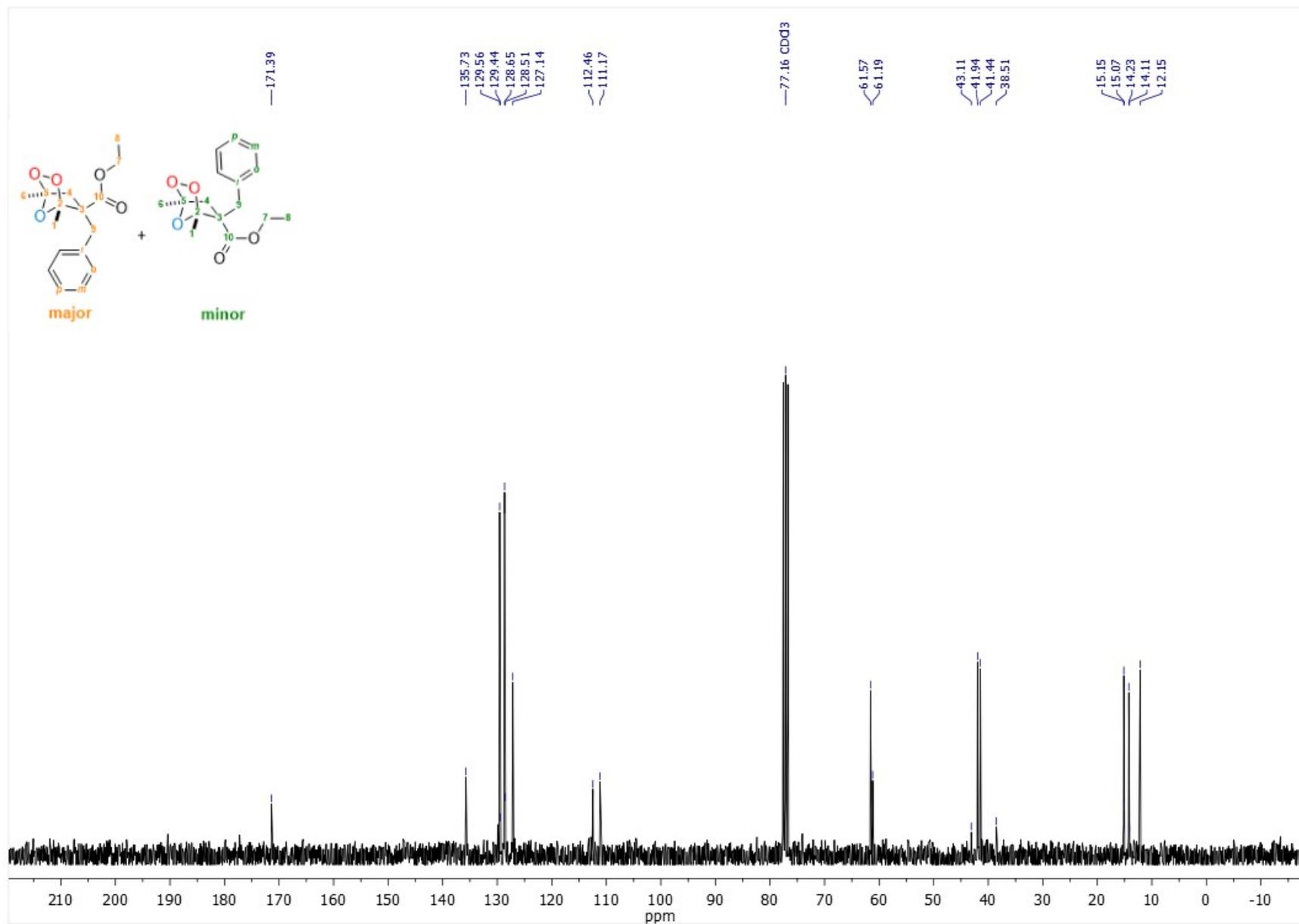
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d + *trans*-2d



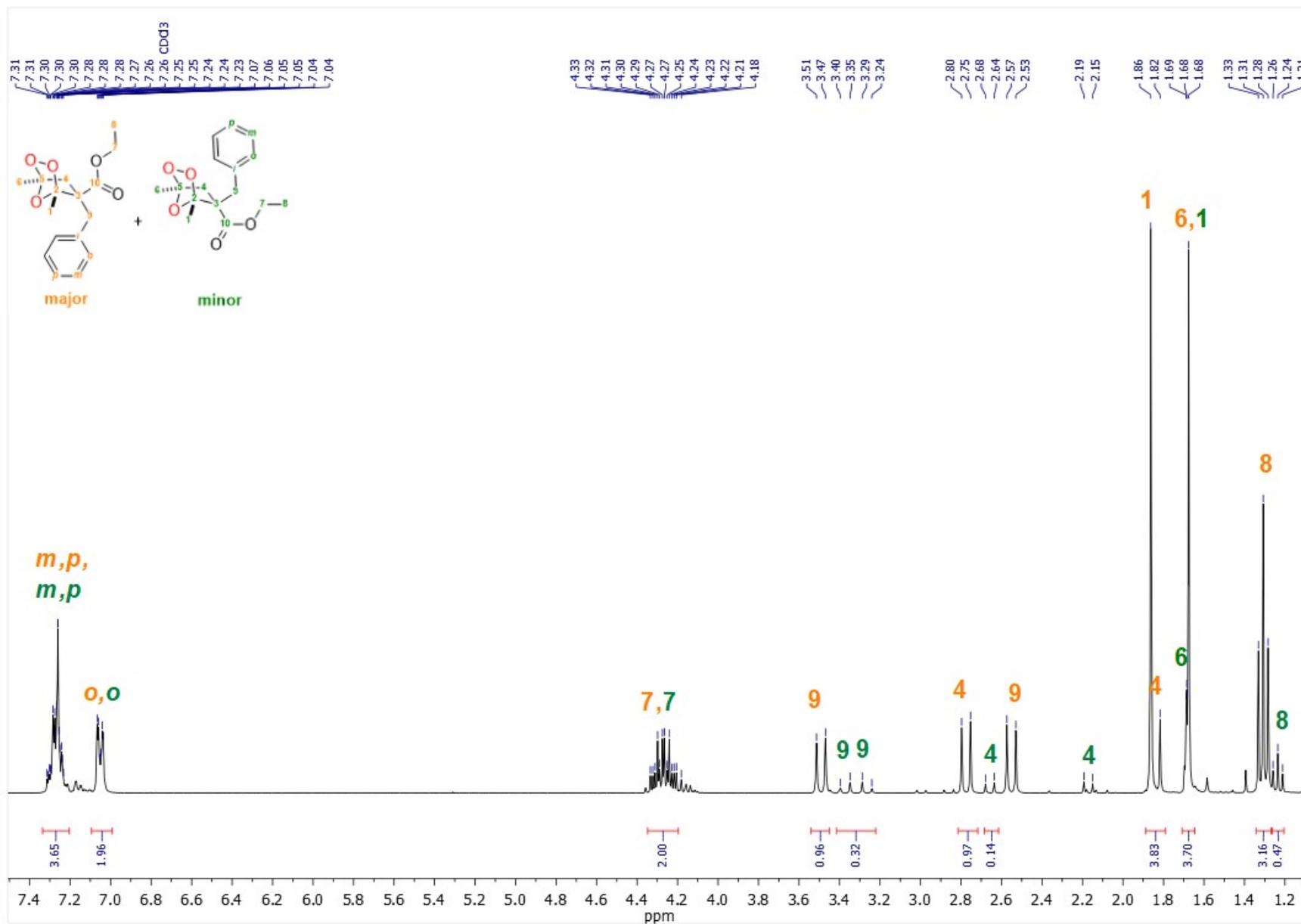
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2e + *trans*-2e



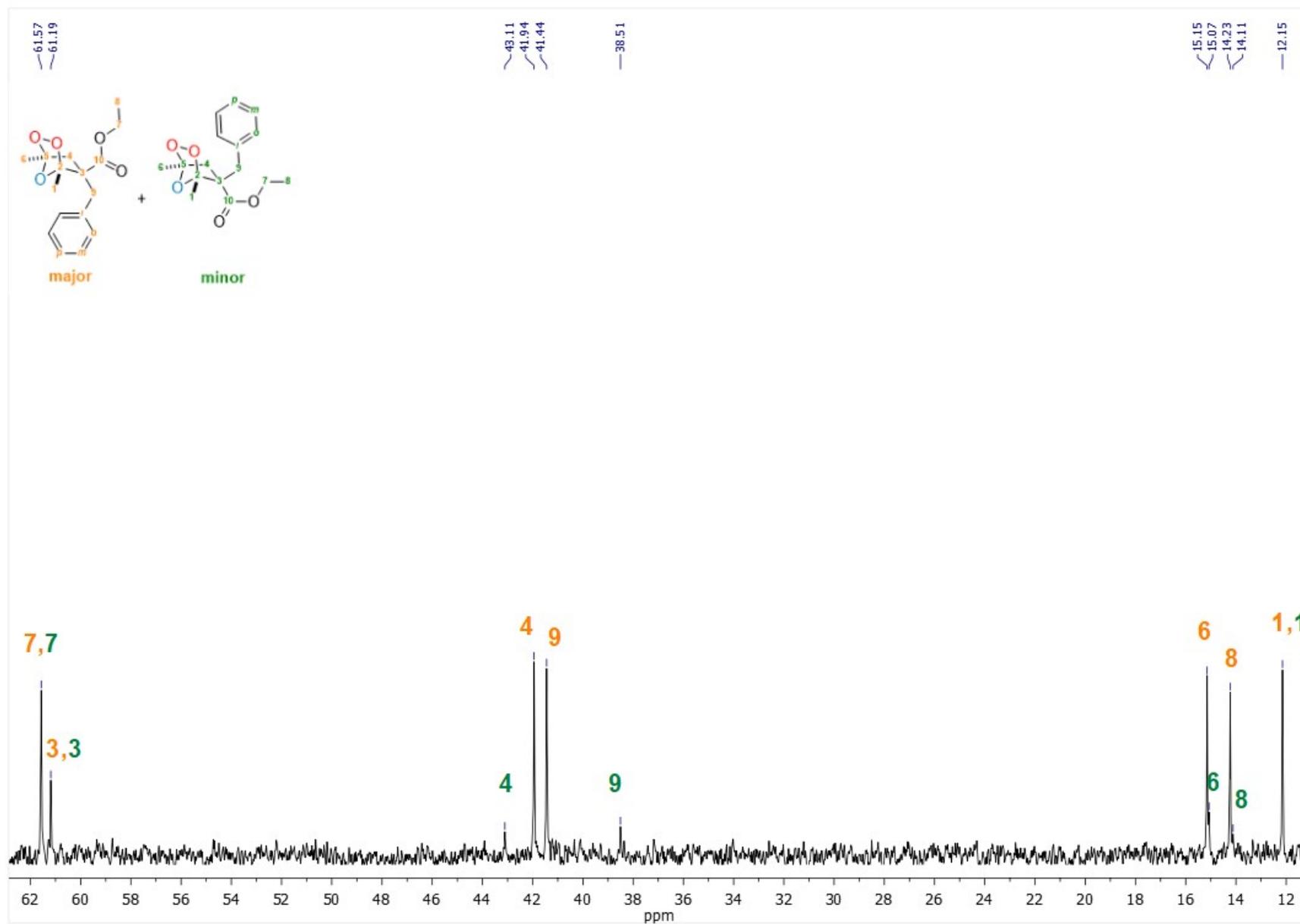
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2e + *trans*-2e



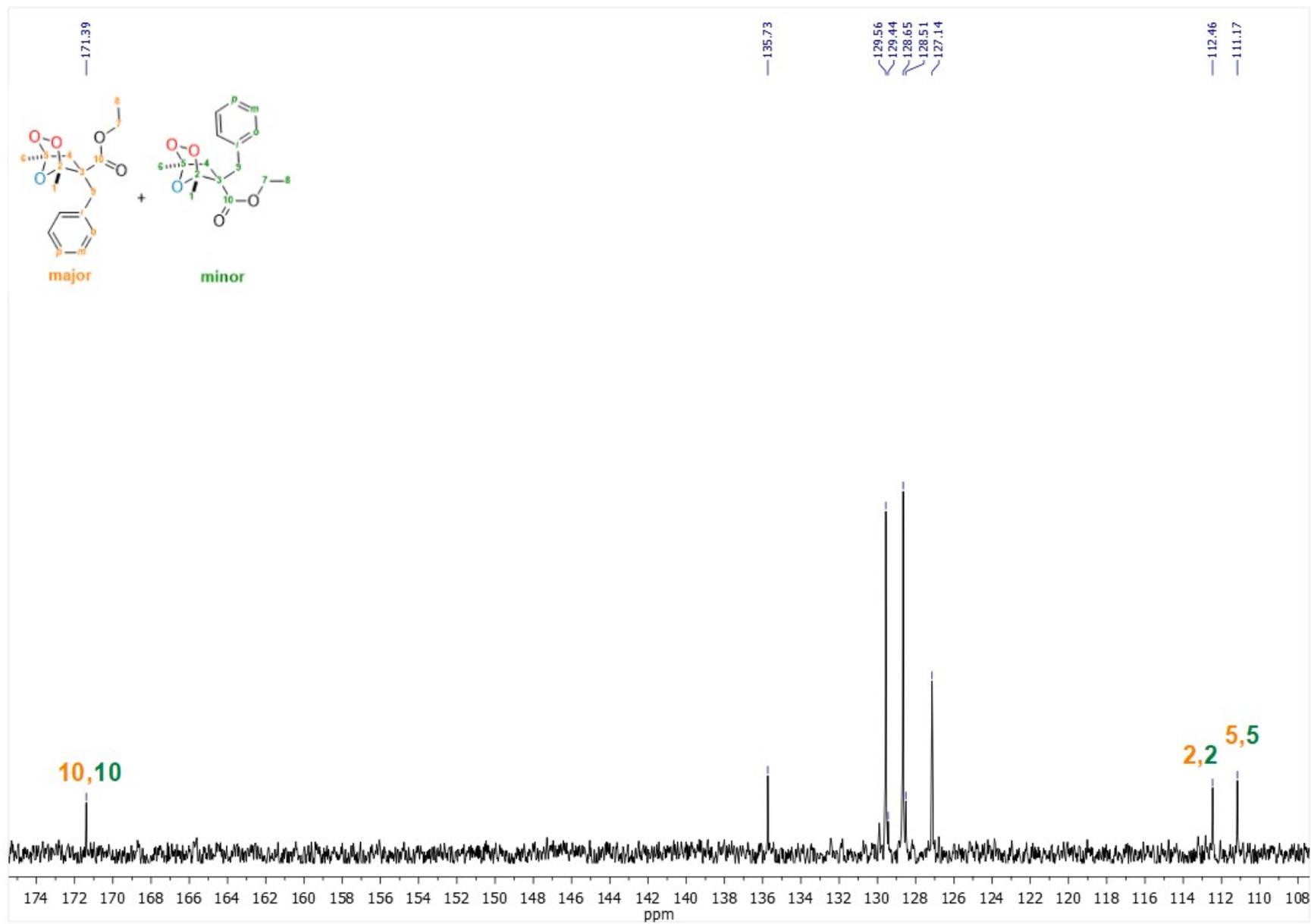
^1H NMR (300.13 MHz, CDCl_3). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2e + *trans*-2e



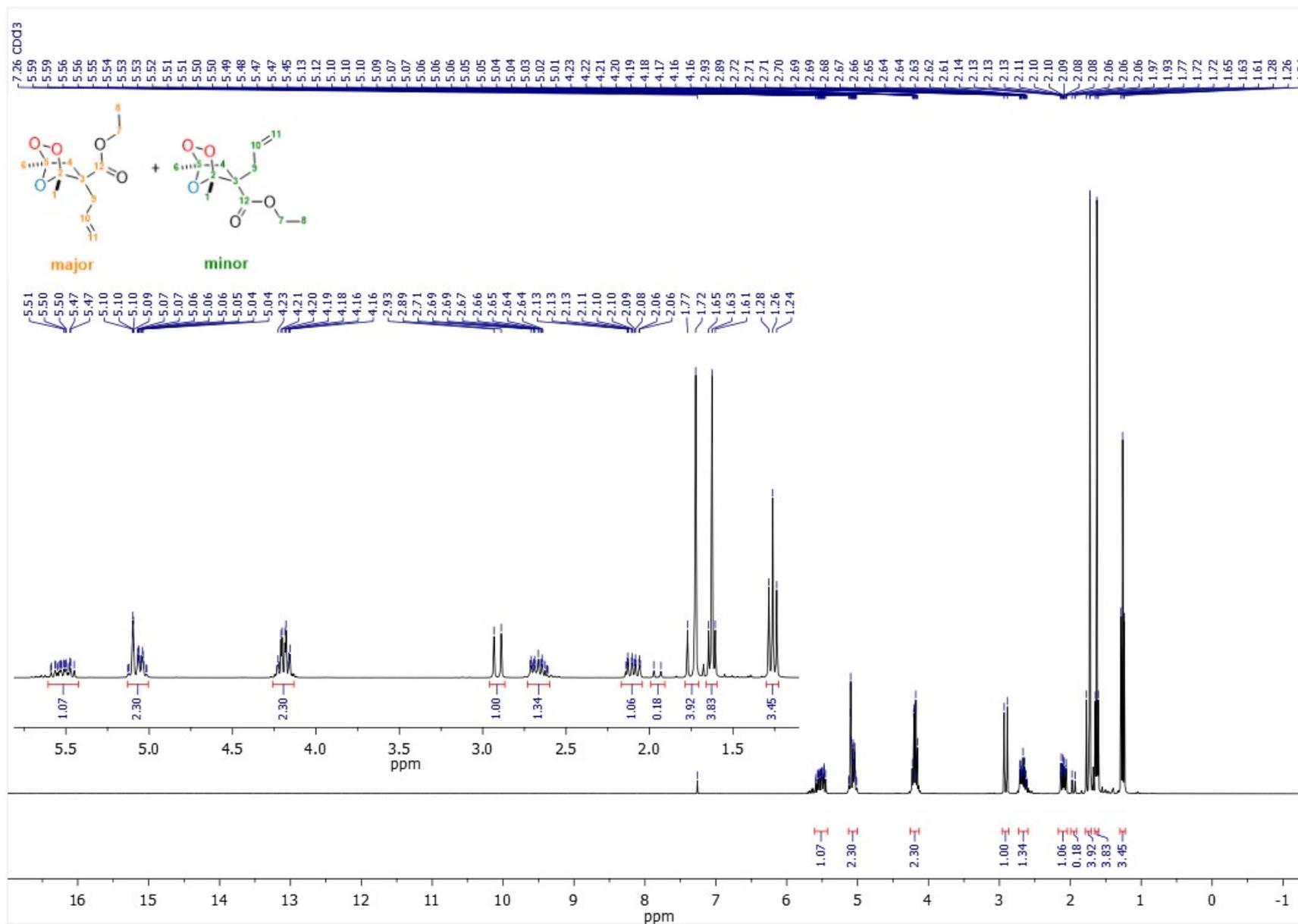
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2e + *trans*-2e



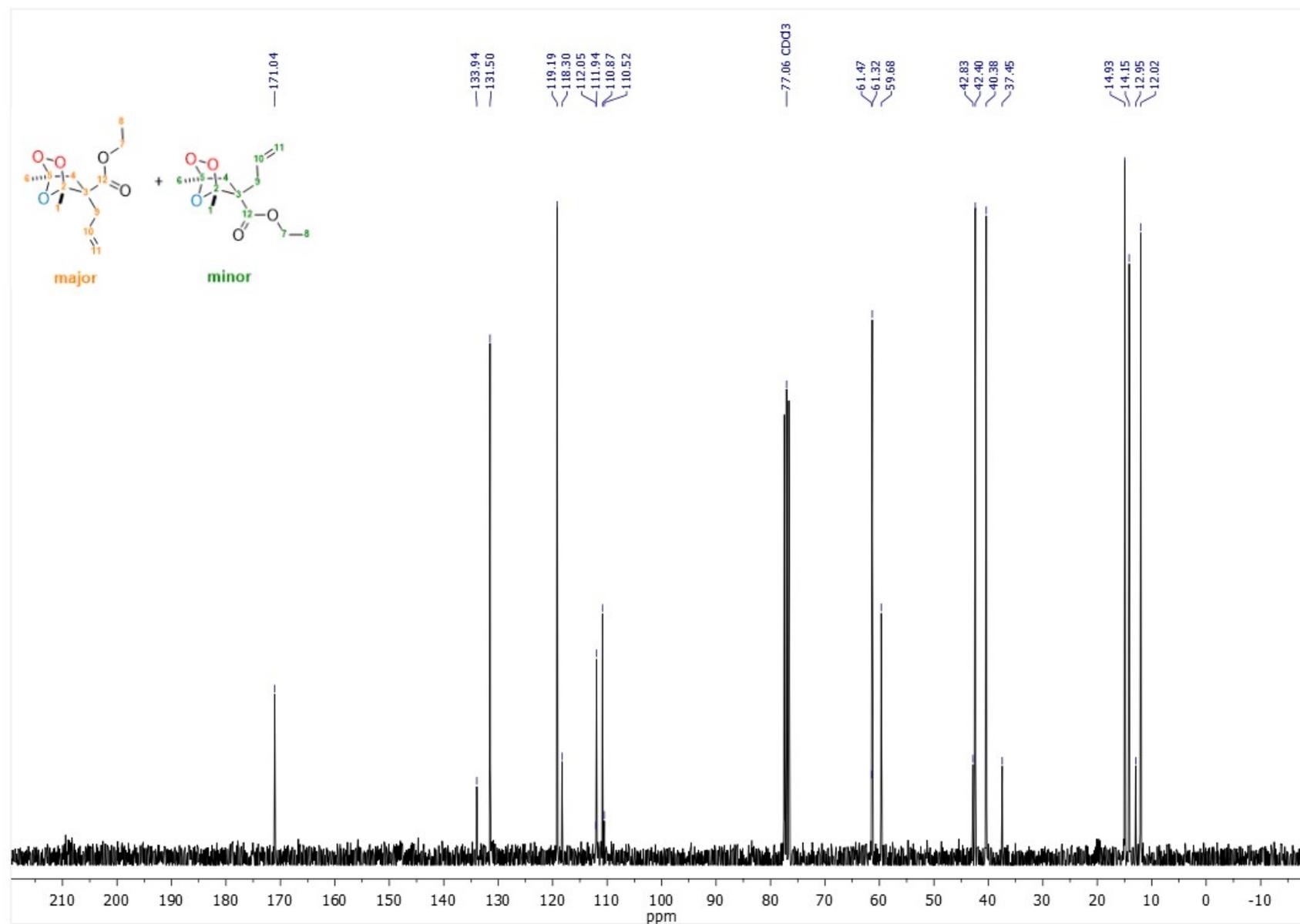
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2e + *trans*-2e



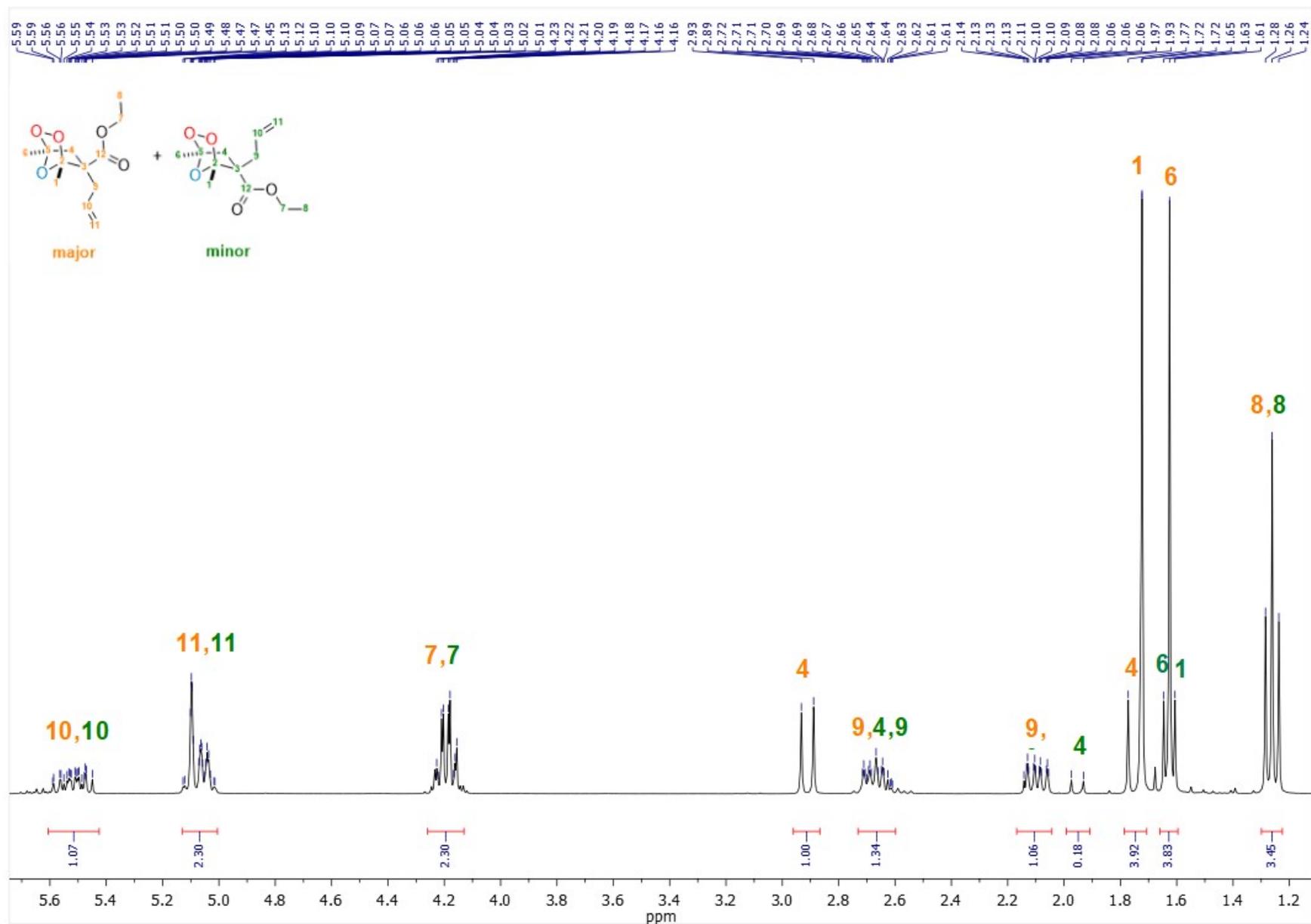
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2f + *trans*-2f



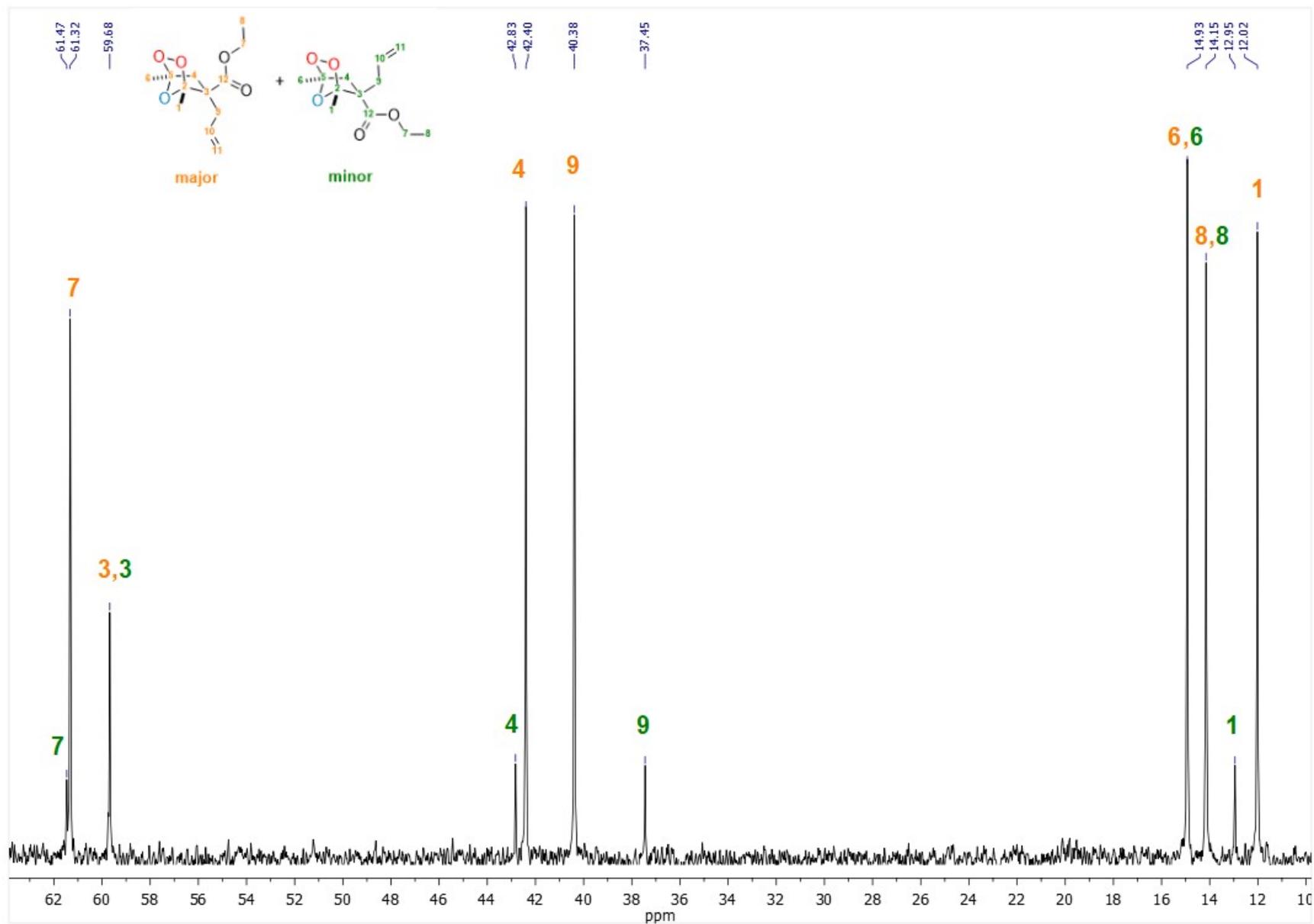
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2f + *trans*-2f



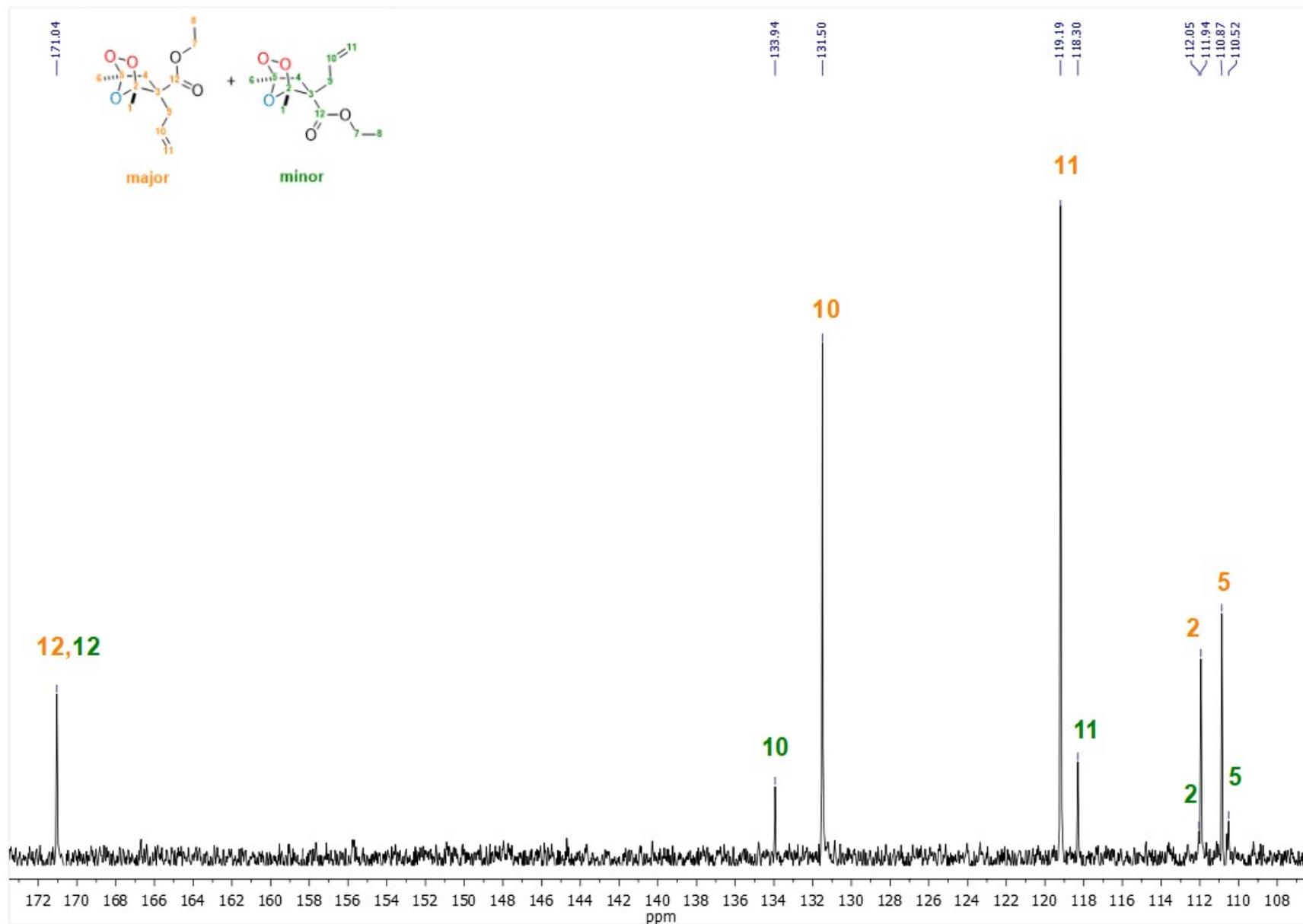
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2f + *trans*-2f



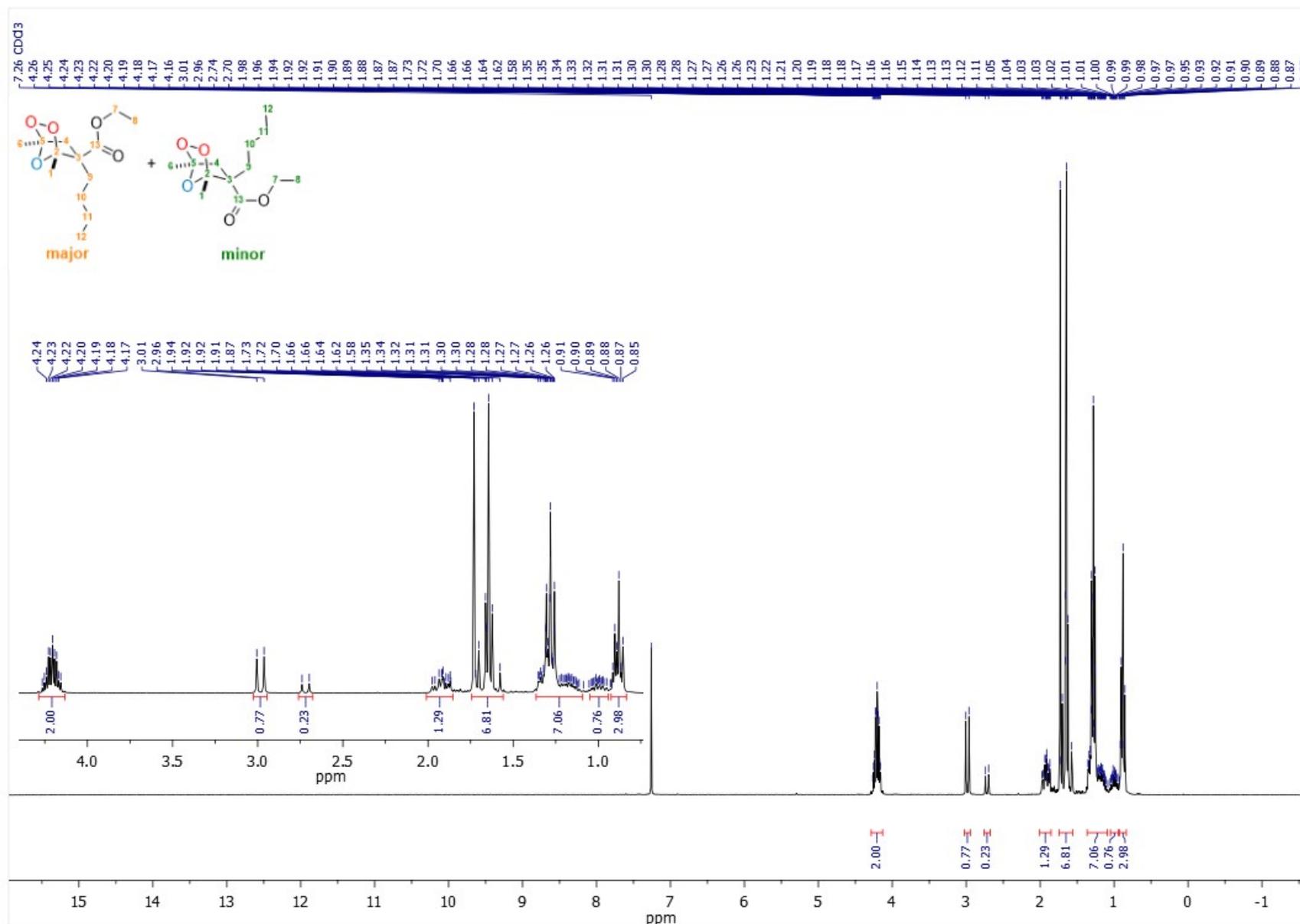
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2f + *trans*-2f



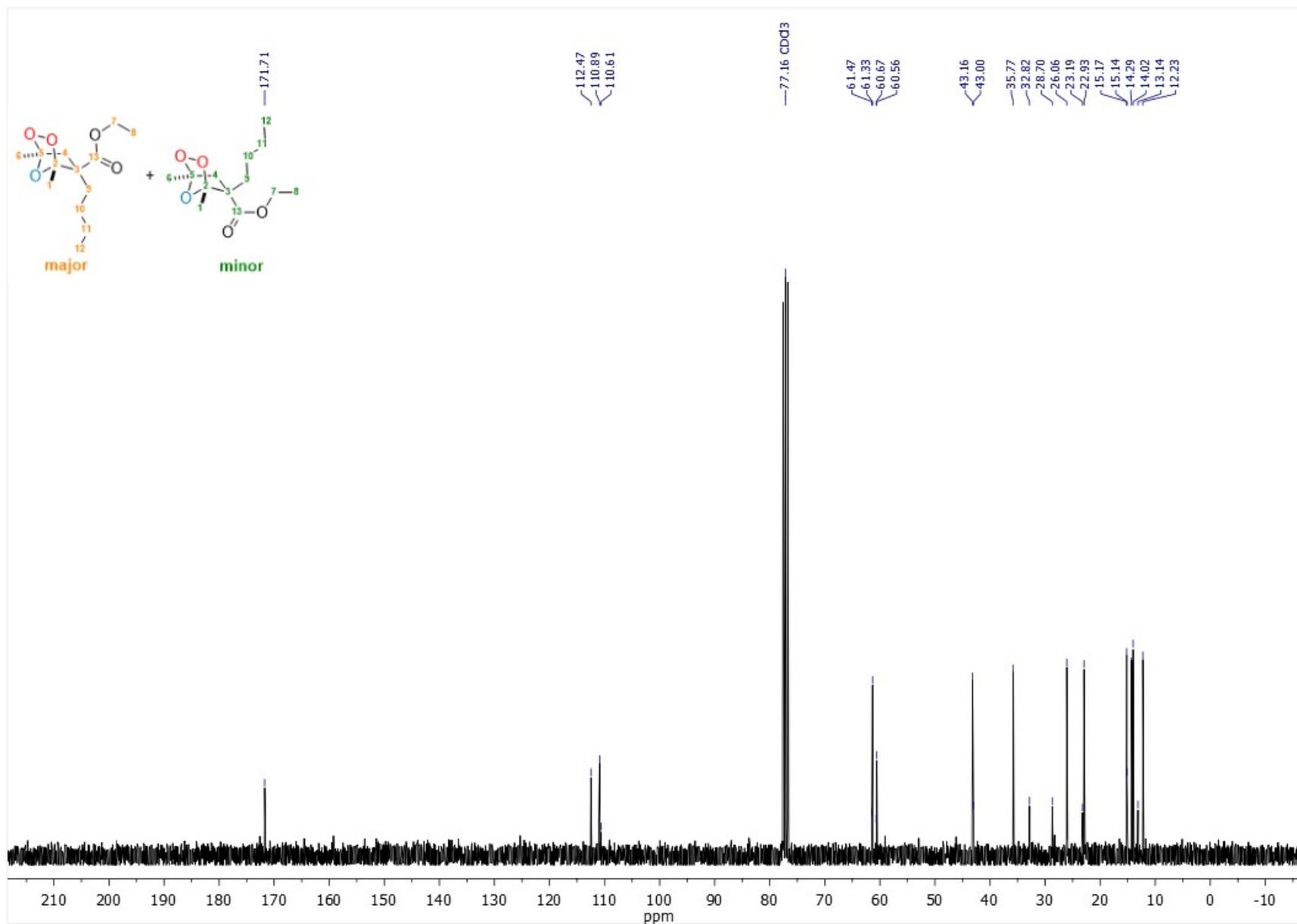
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2f + *trans*-2f



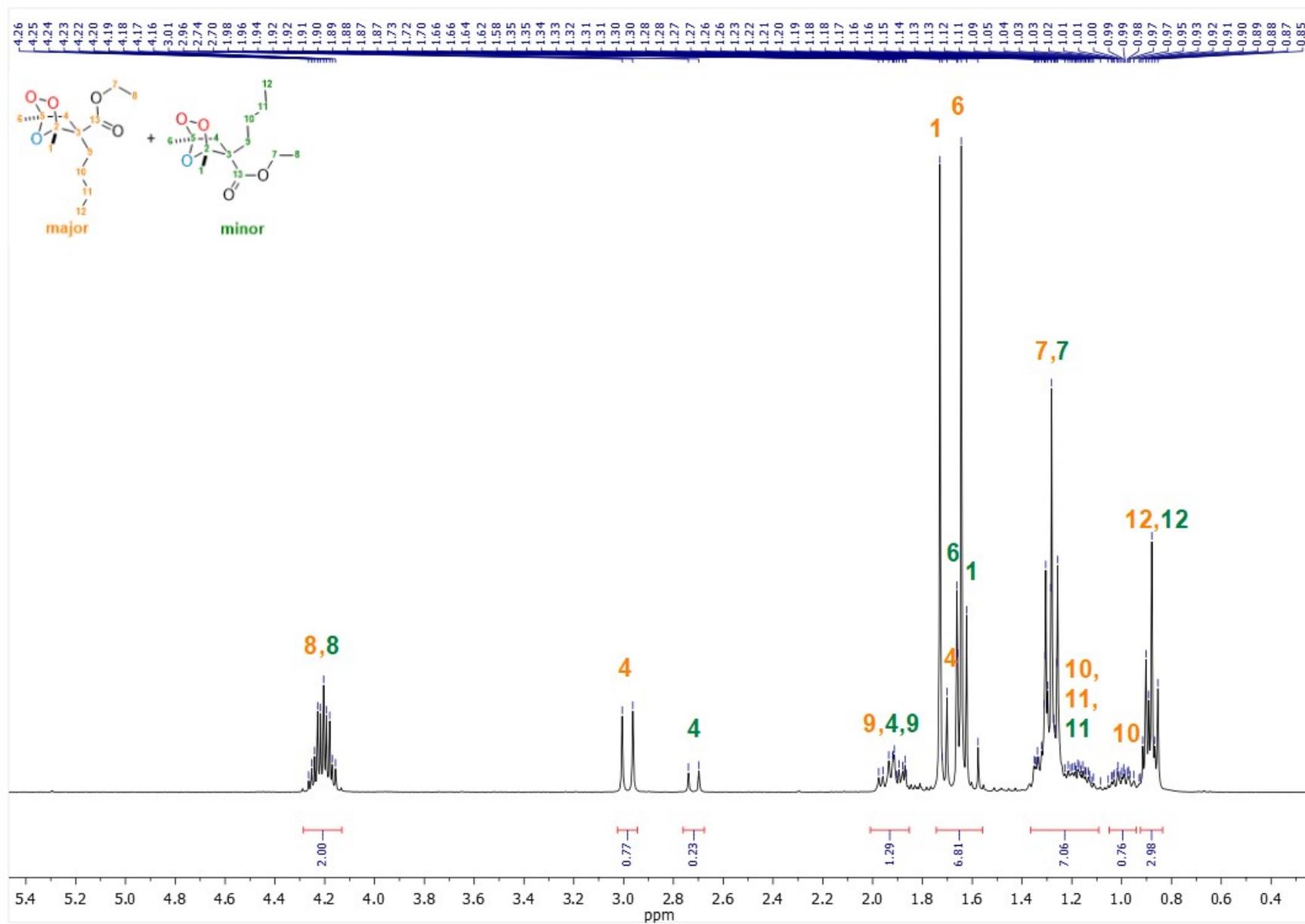
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



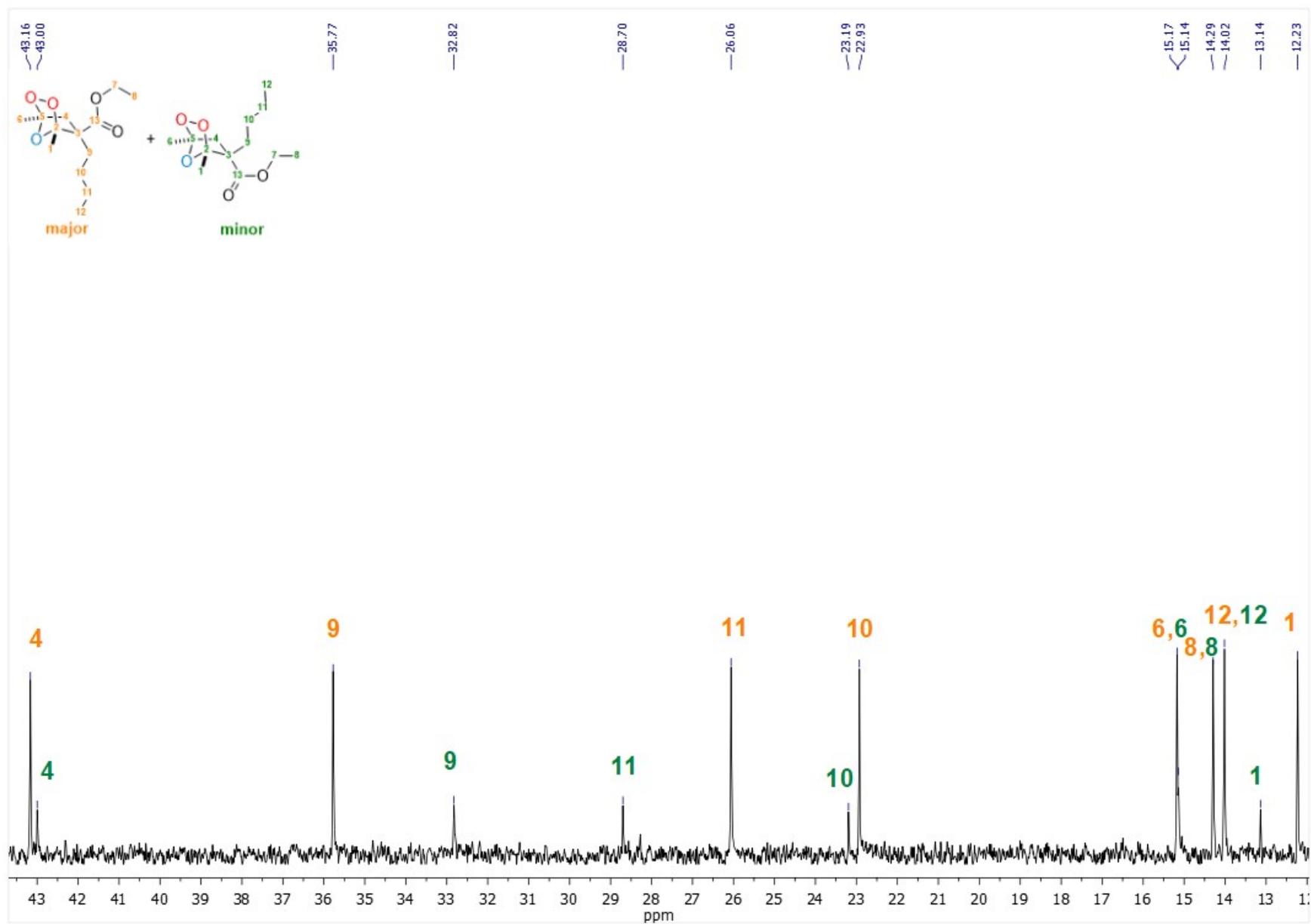
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



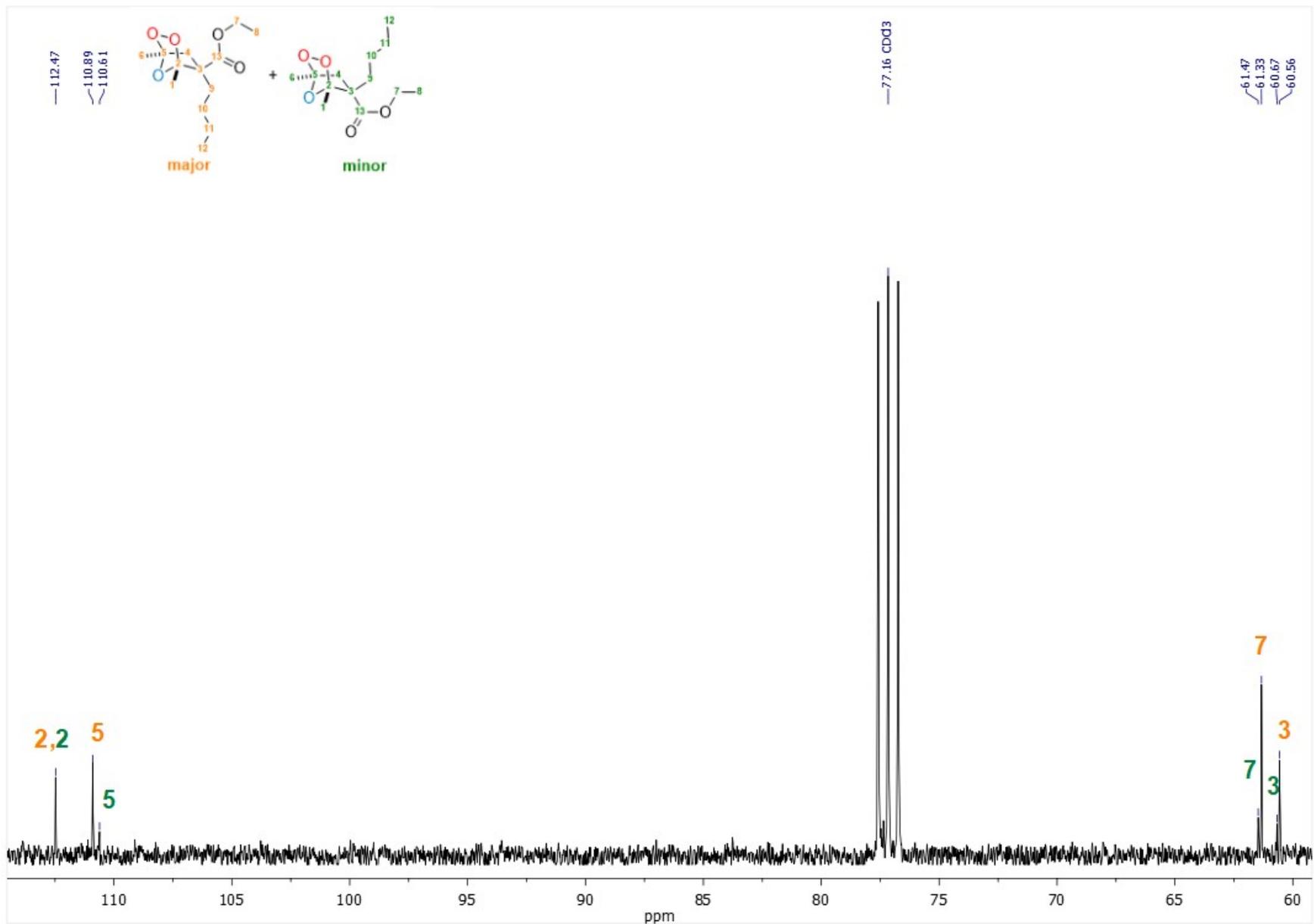
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



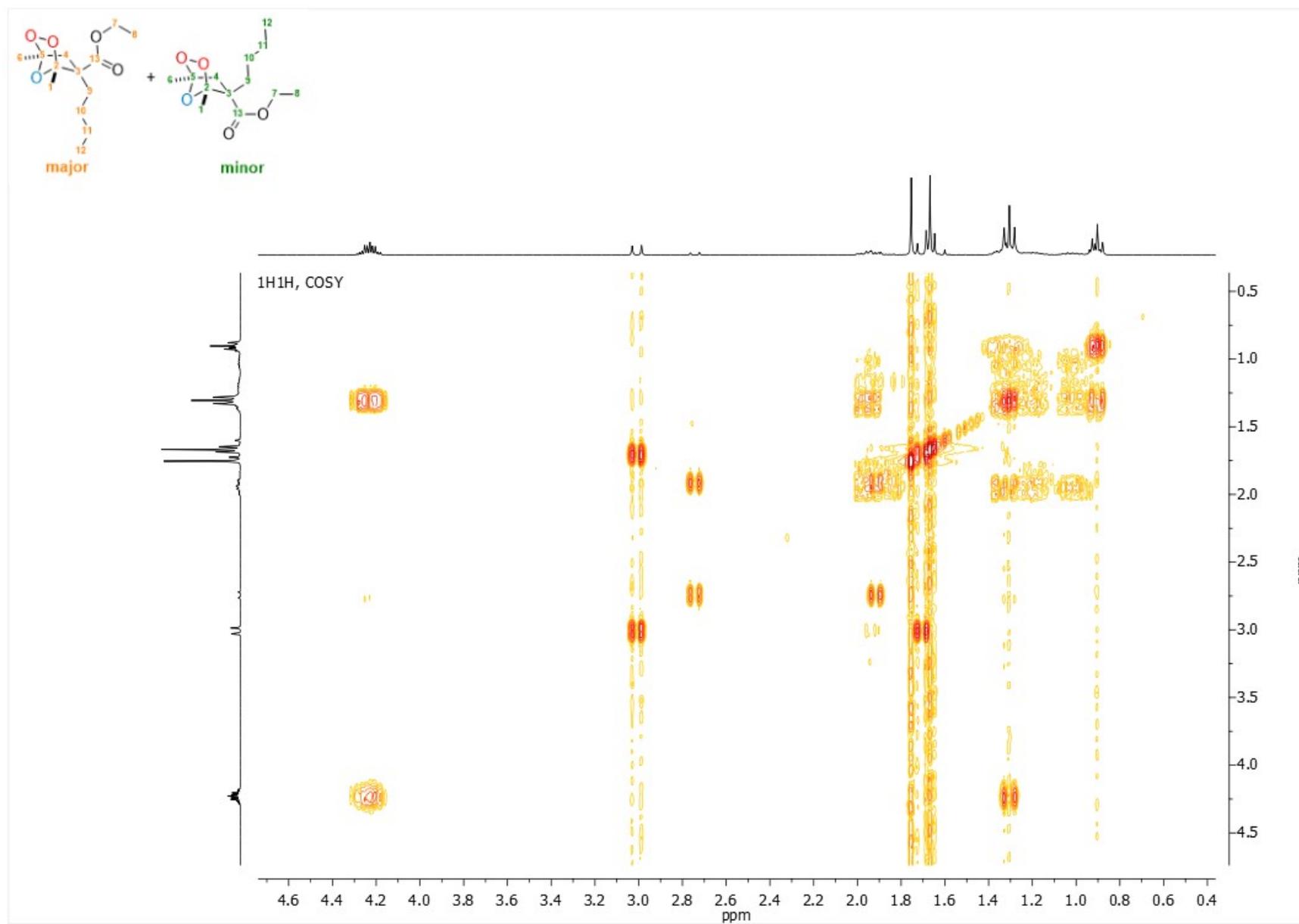
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



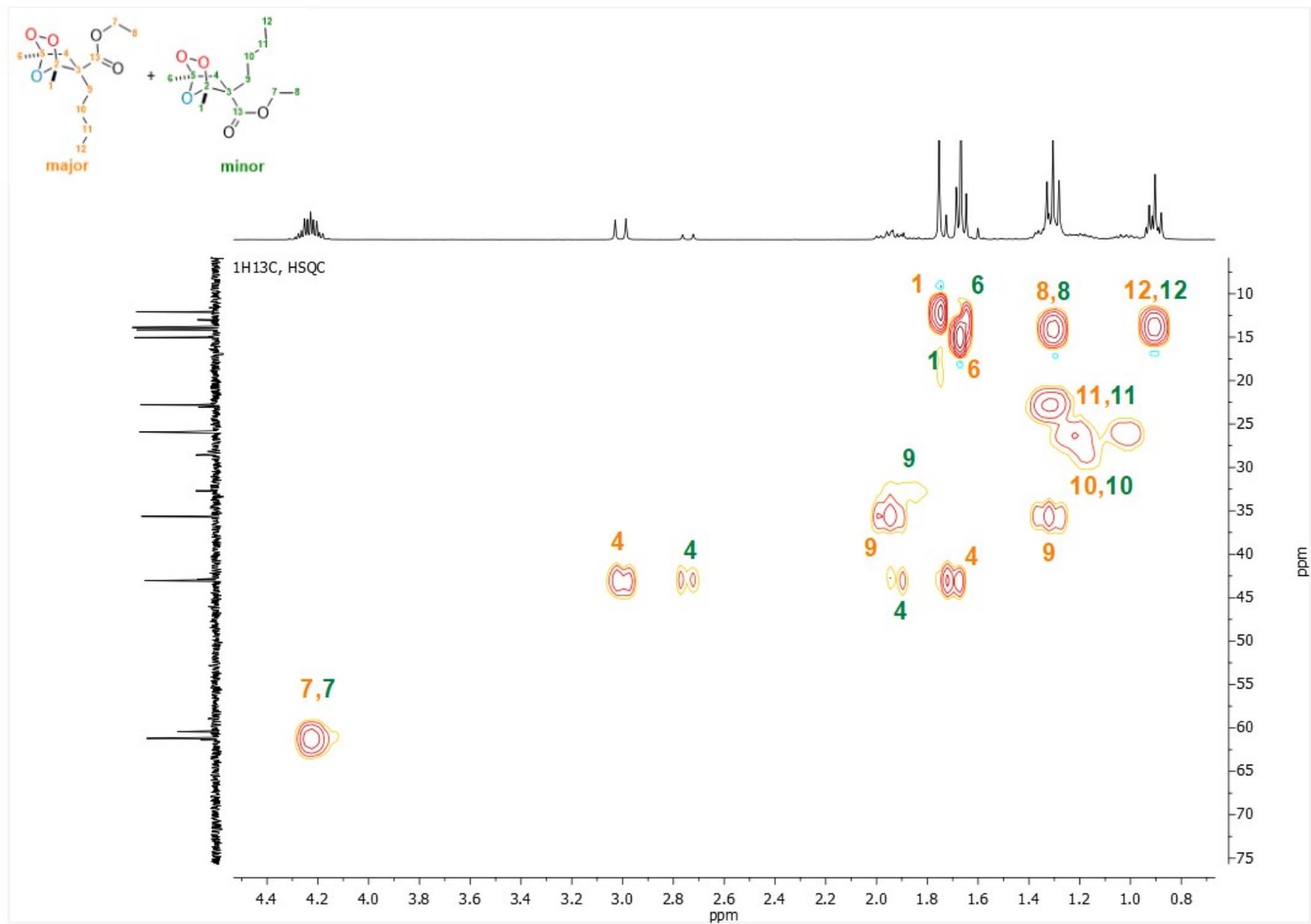
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



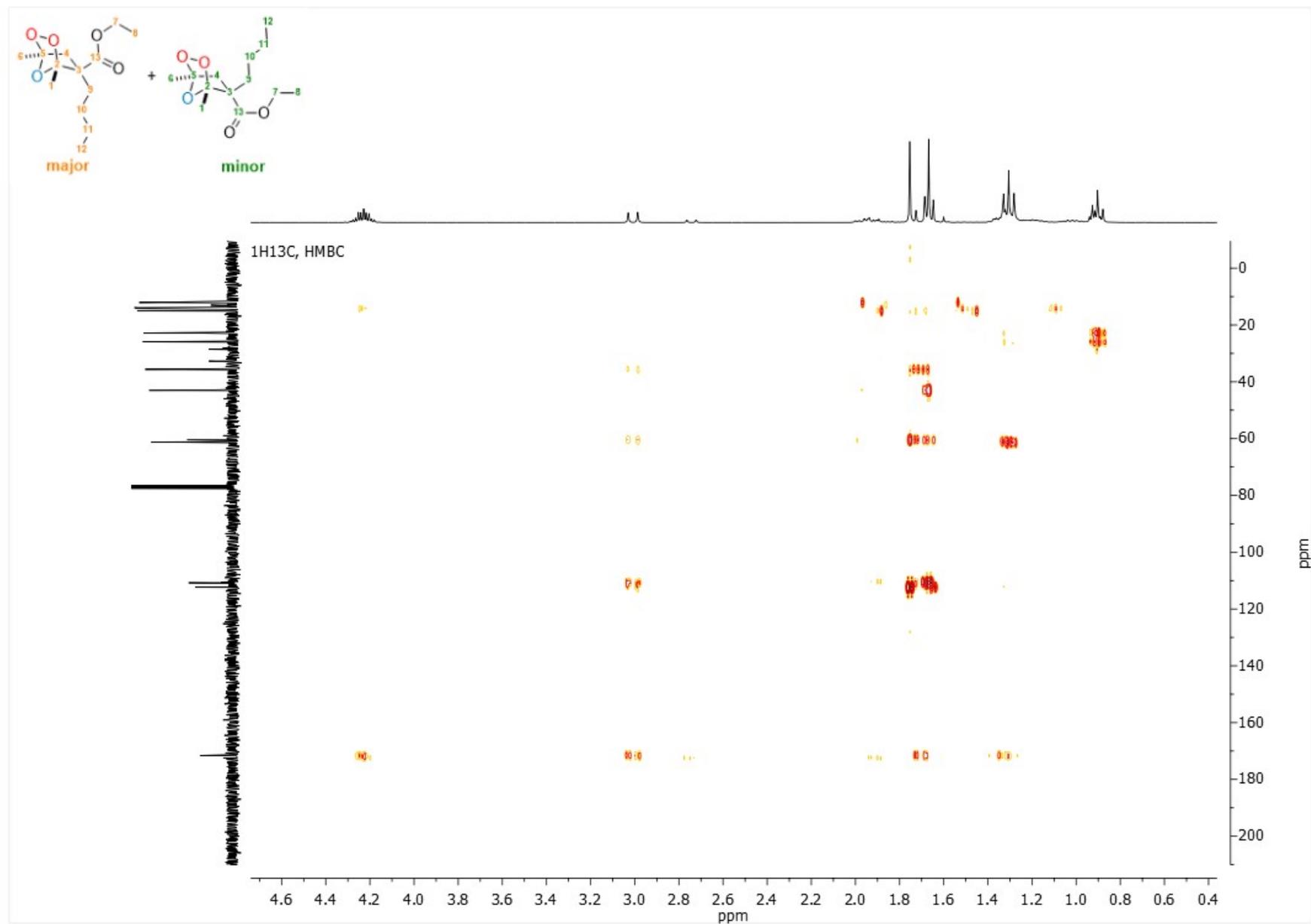
^1H - ^1H , COSY. Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



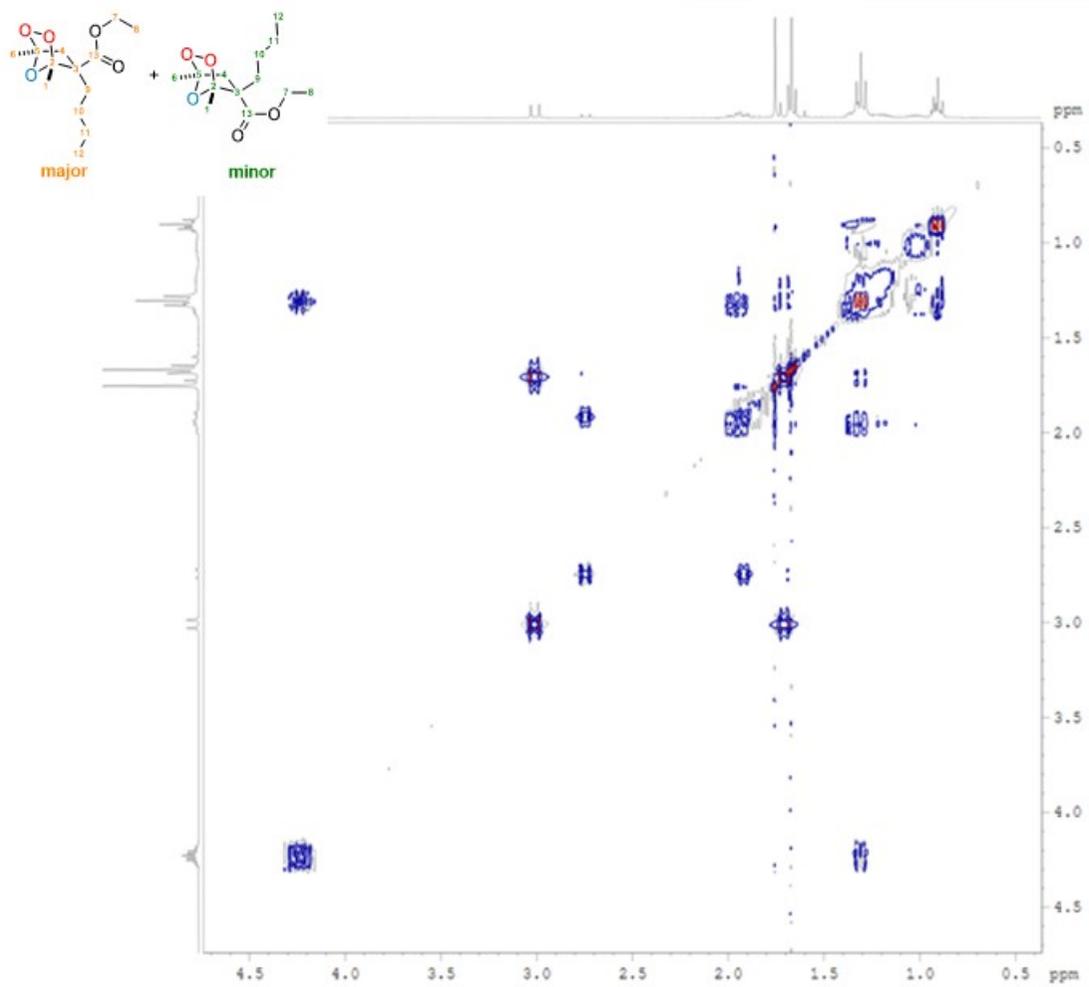
^1H - ^{13}C , HSQC. Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



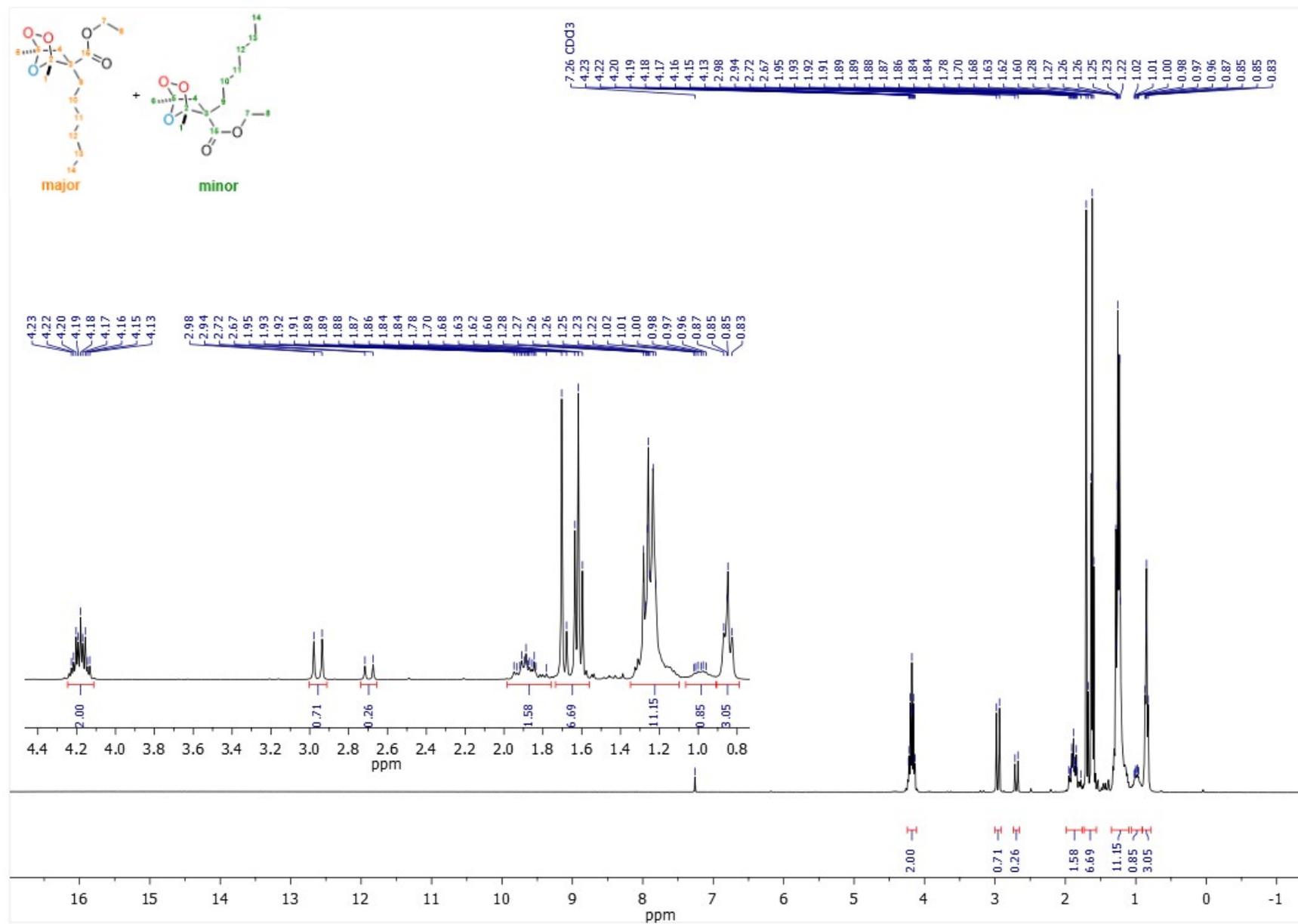
^1H - ^{13}C , HMBC. Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



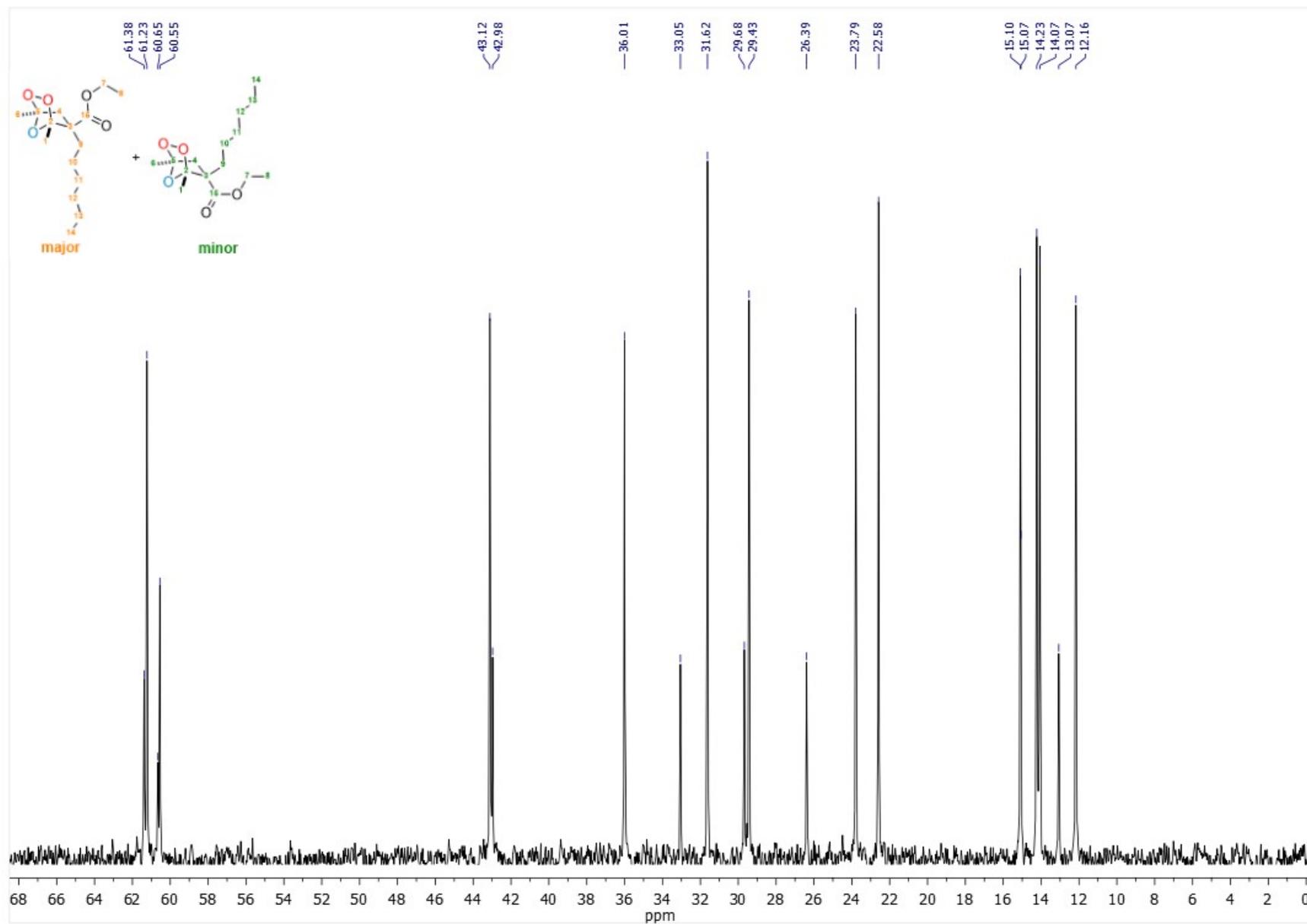
^1H - ^1H , NOESY. Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g + *trans*-2g



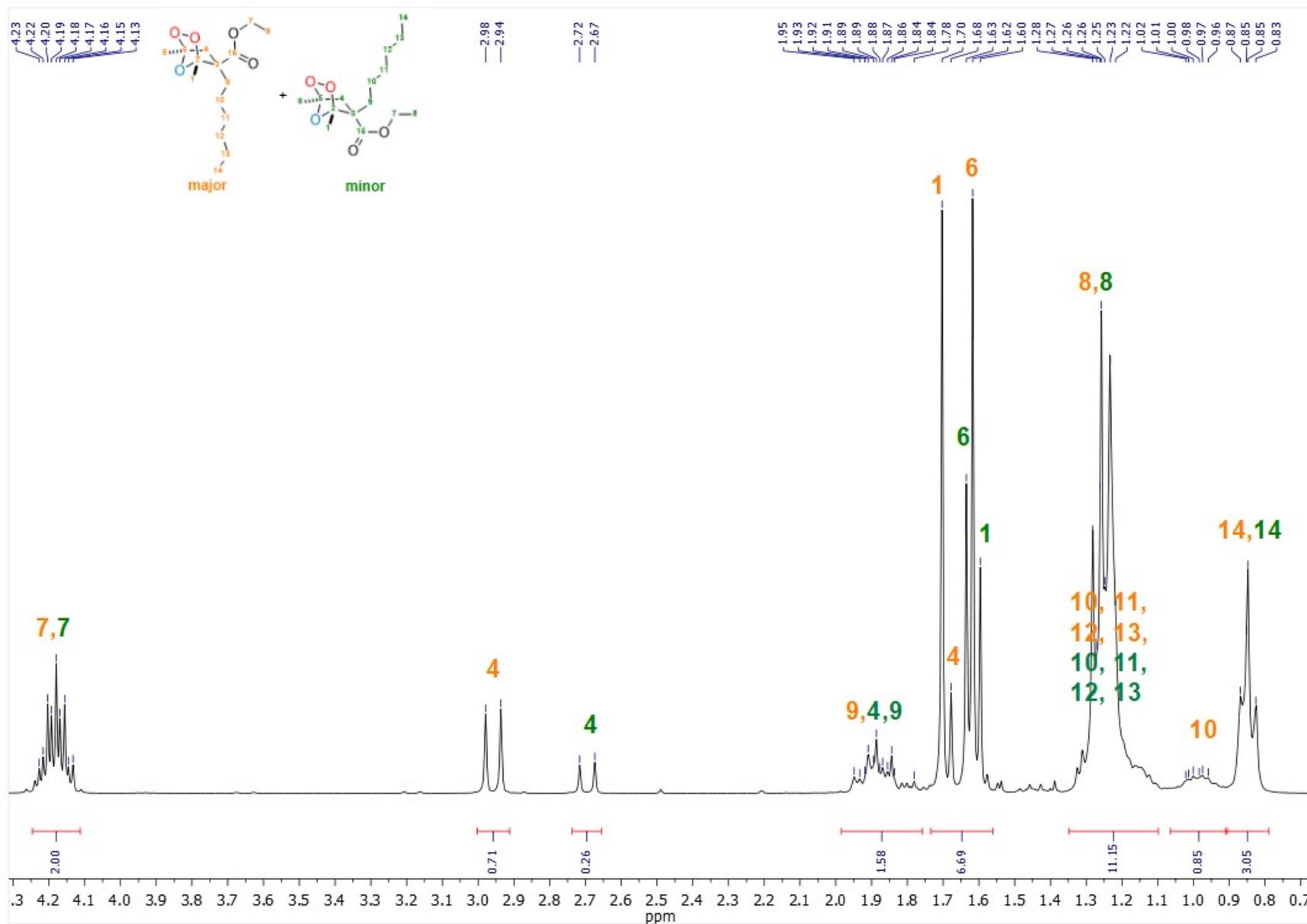
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h + *trans*-2h



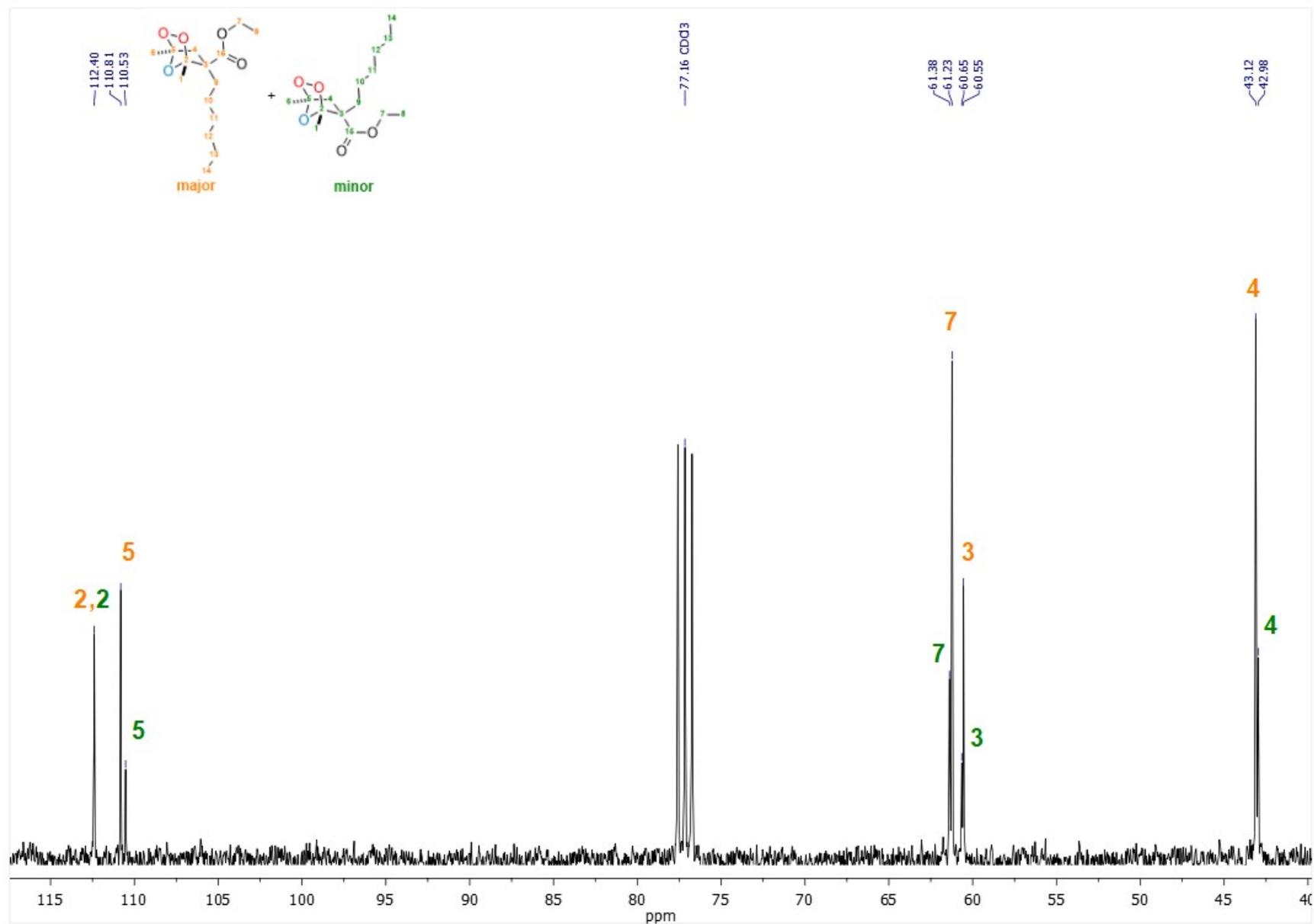
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h + *trans*-2h



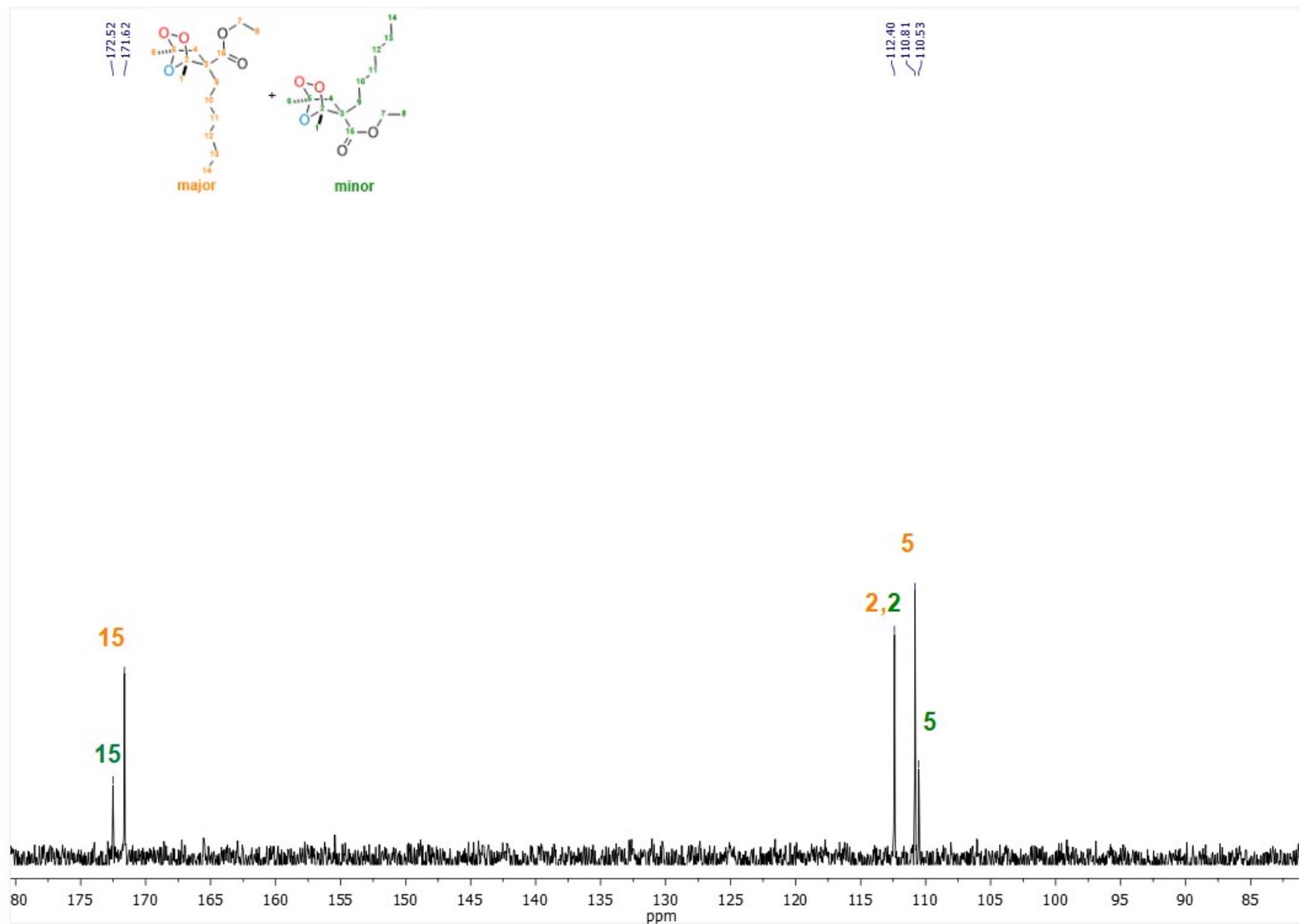
¹H NMR (300.13 MHz, CDCl₃). Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h + *trans*-2h



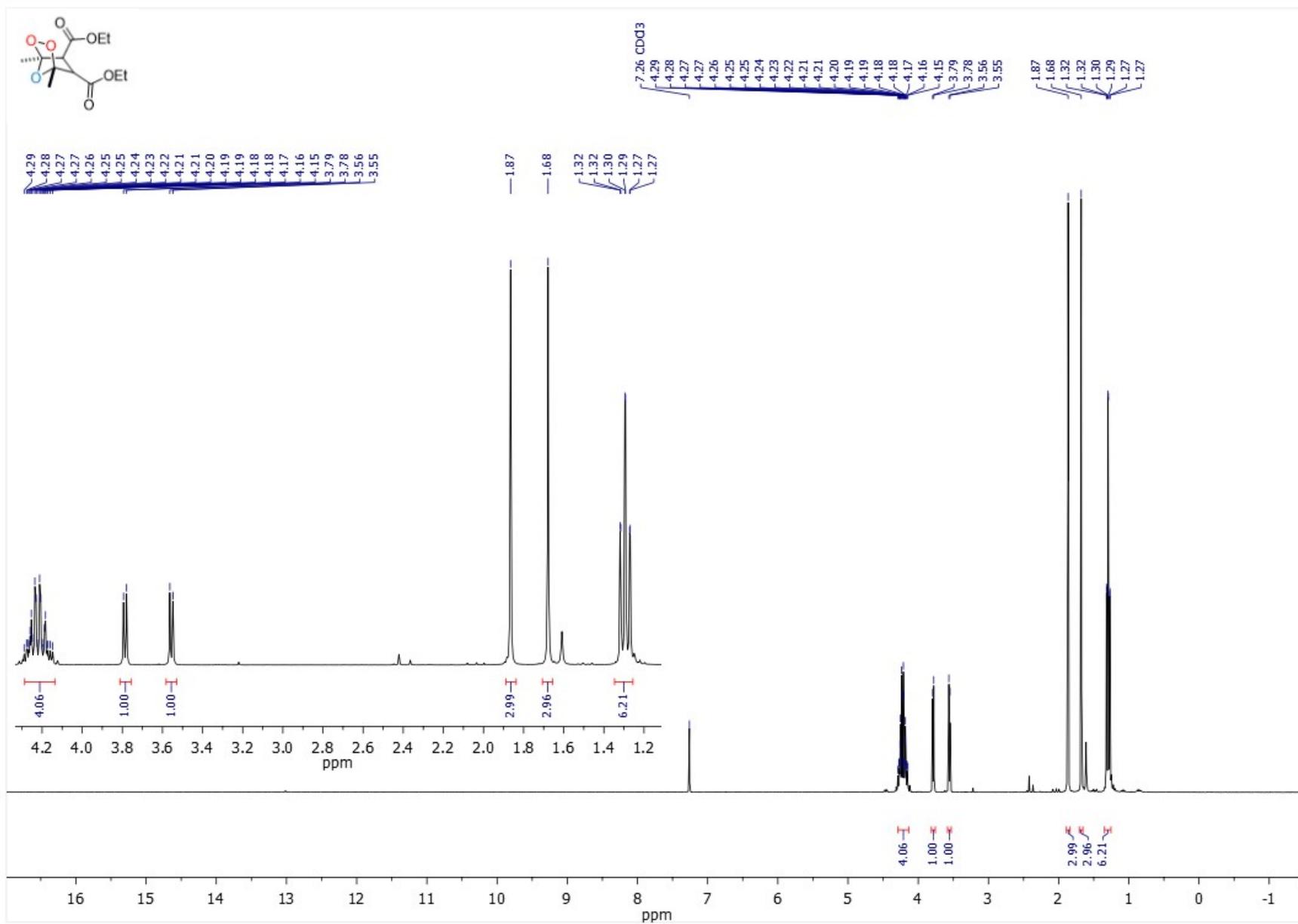
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h + *trans*-2h



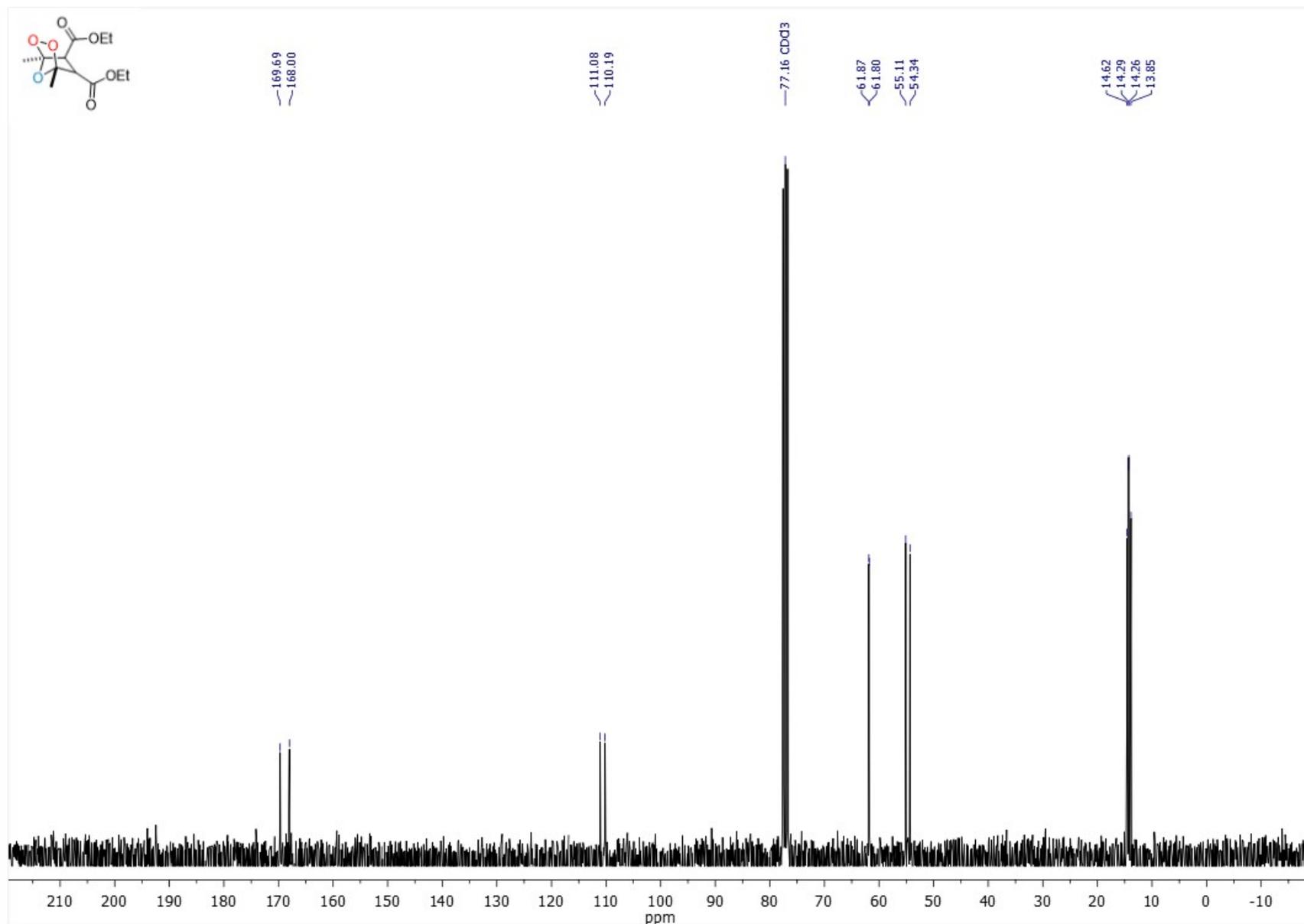
¹³C NMR (75.48 MHz, CDCl₃). Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h + *trans*-2h



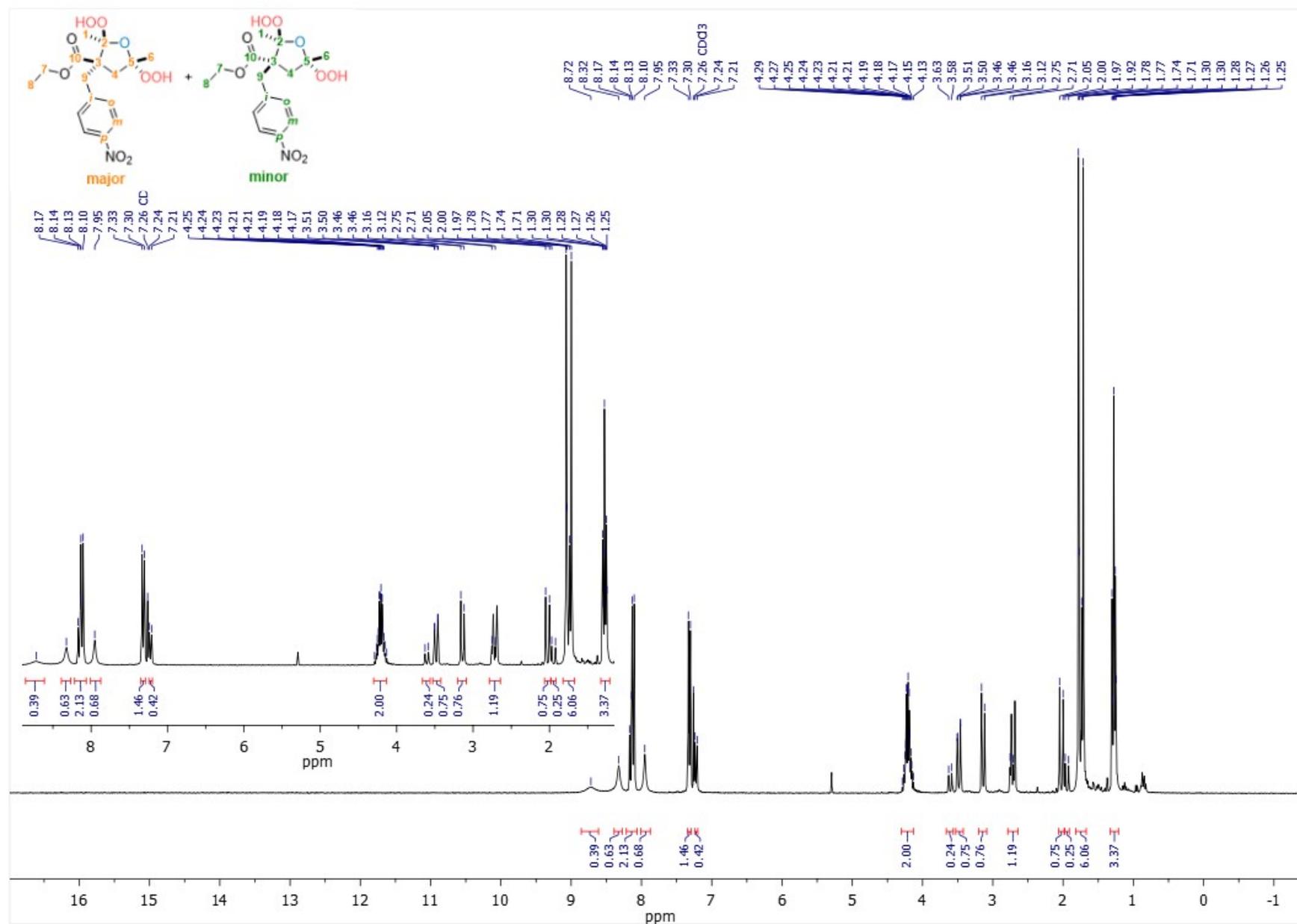
¹H NMR (300.13 MHz, CDCl₃). Diethyl (1*S**,4*S**,5*S**)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5,6-dicarboxylate, 2i



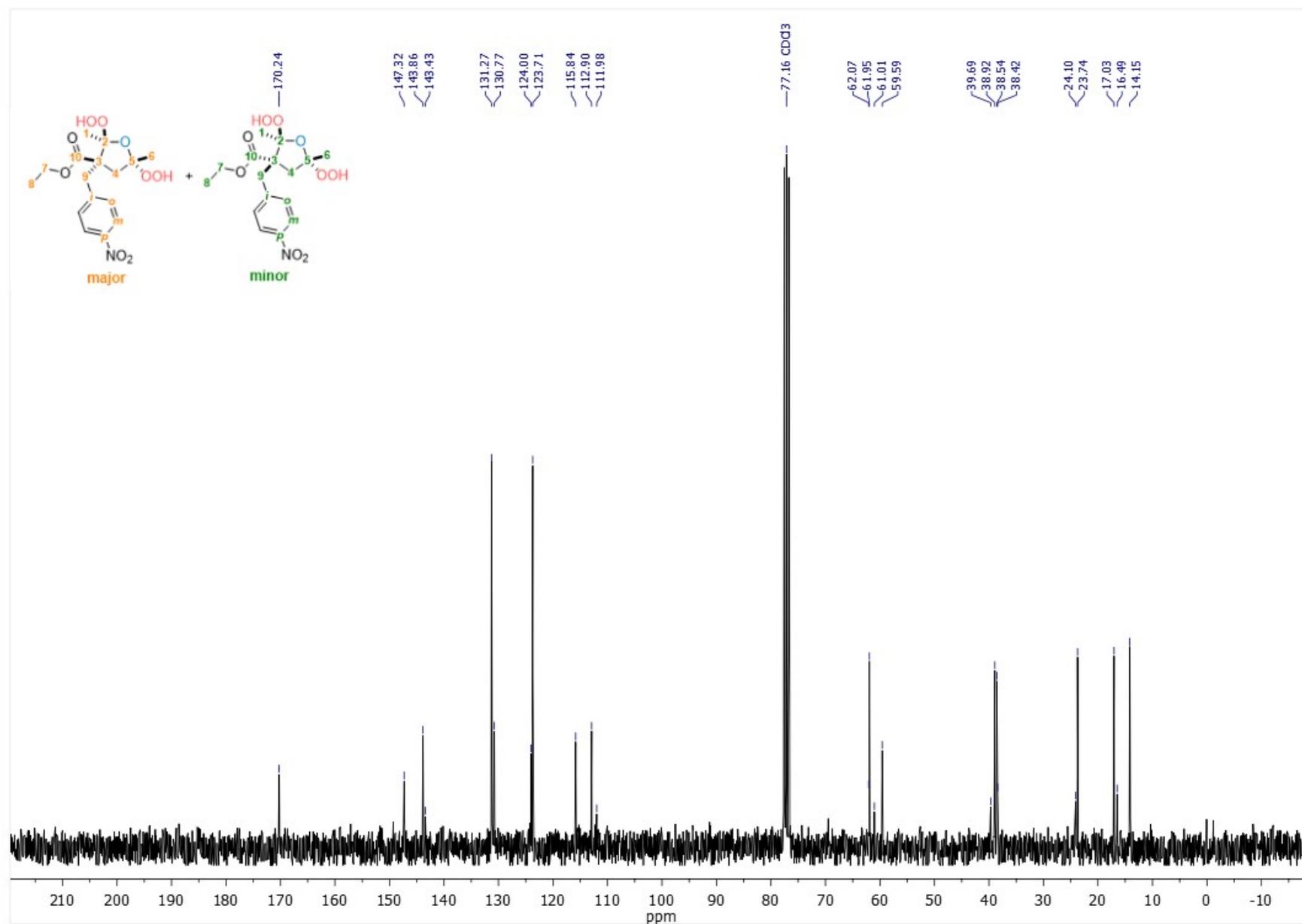
¹³C NMR (75.48 MHz, CDCl₃). Diethyl (1*S**,4*S**,5*S**)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5,6-dicarboxylate, 2i



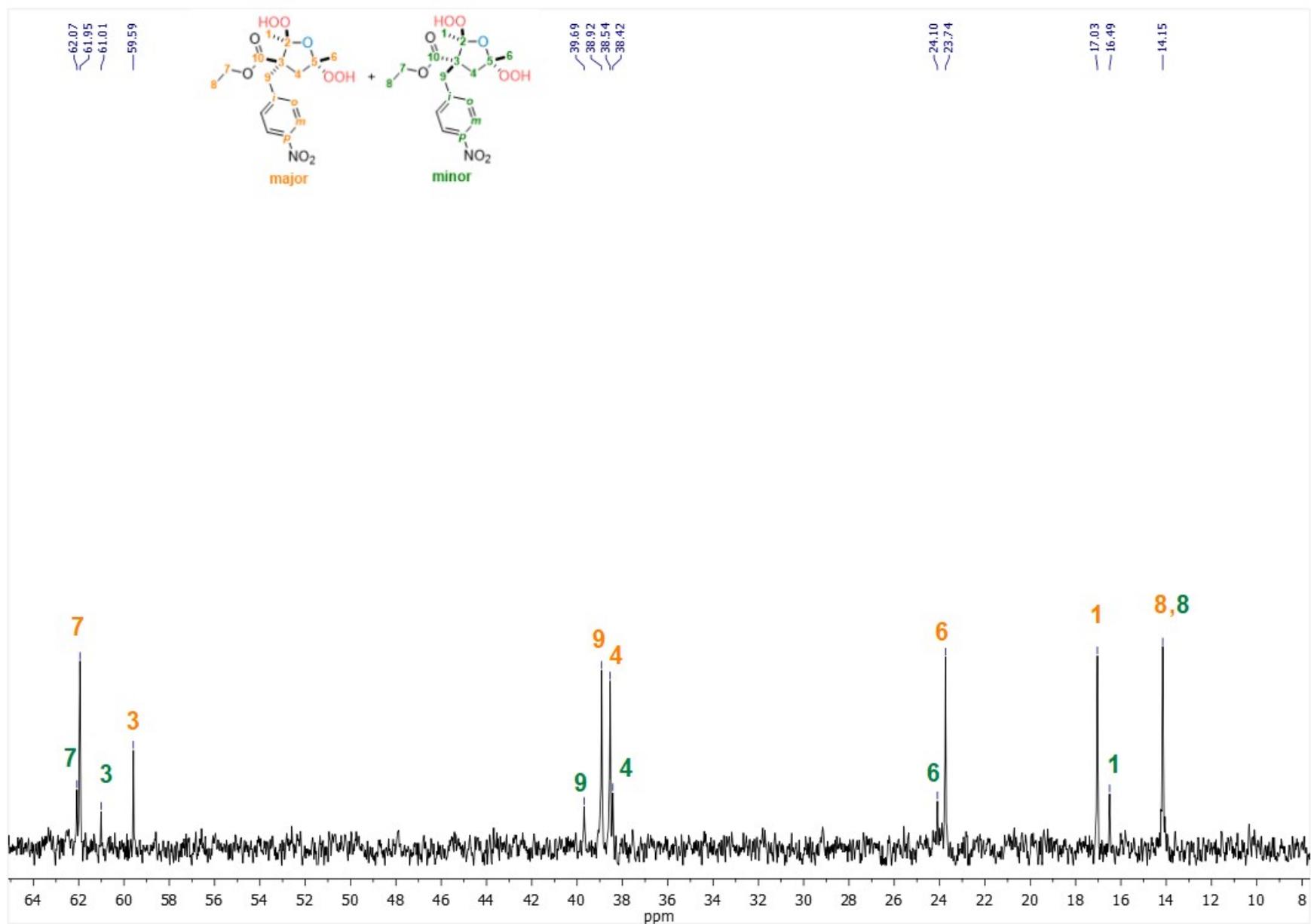
¹H NMR (300.13 MHz, CDCl₃). Ethyl 2,5-dihydroperoxy-2,5-dimethyl-3-(4-nitrobenzyl)tetrahydrofuran-3-carboxylate, *cis*-3a+*trans*-3a



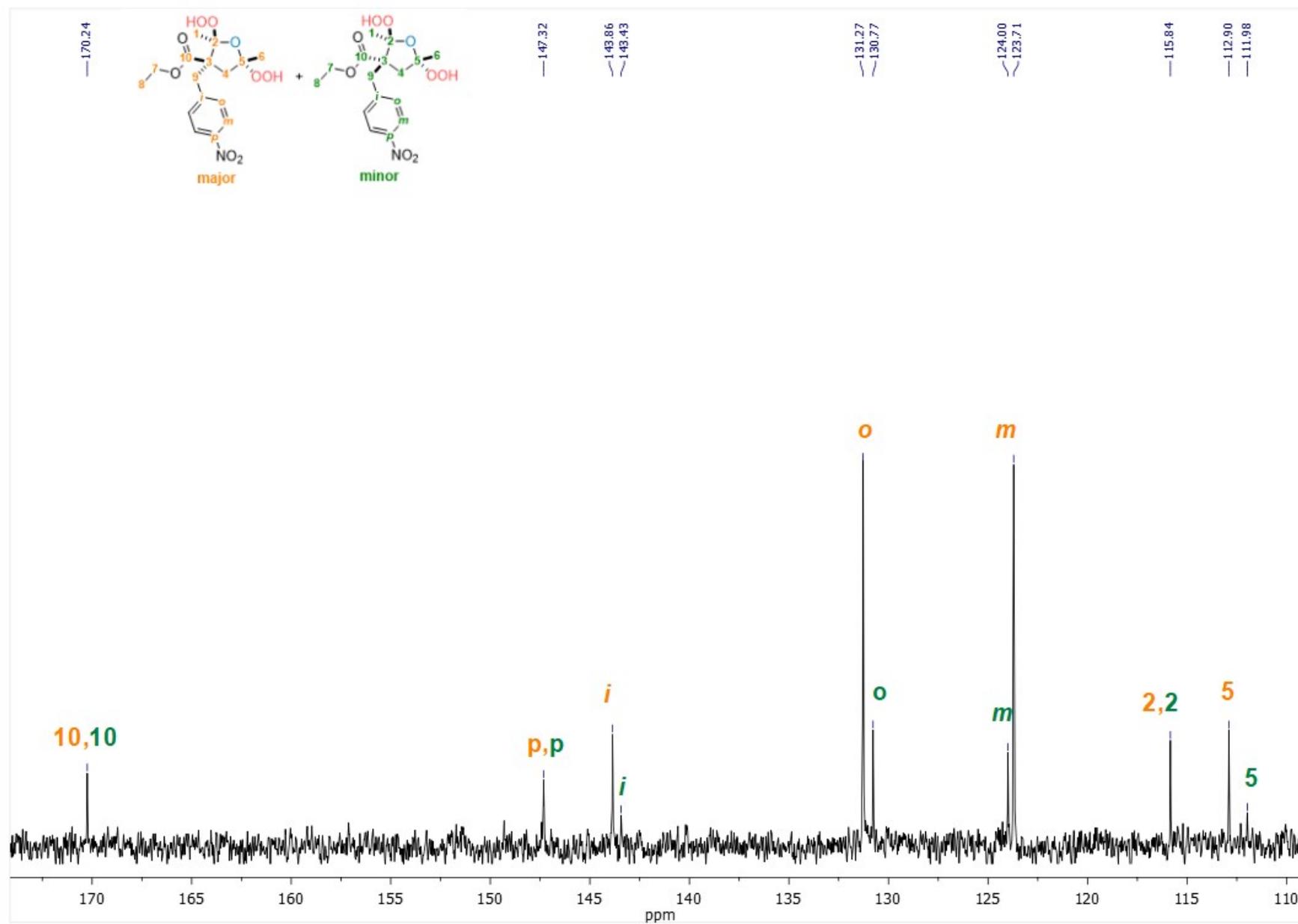
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl 2,5-dihydroperoxy-2,5-dimethyl-3-(4-nitrobenzyl)tetrahydrofuran-3-carboxylate, *cis*-3a+*trans*-3a



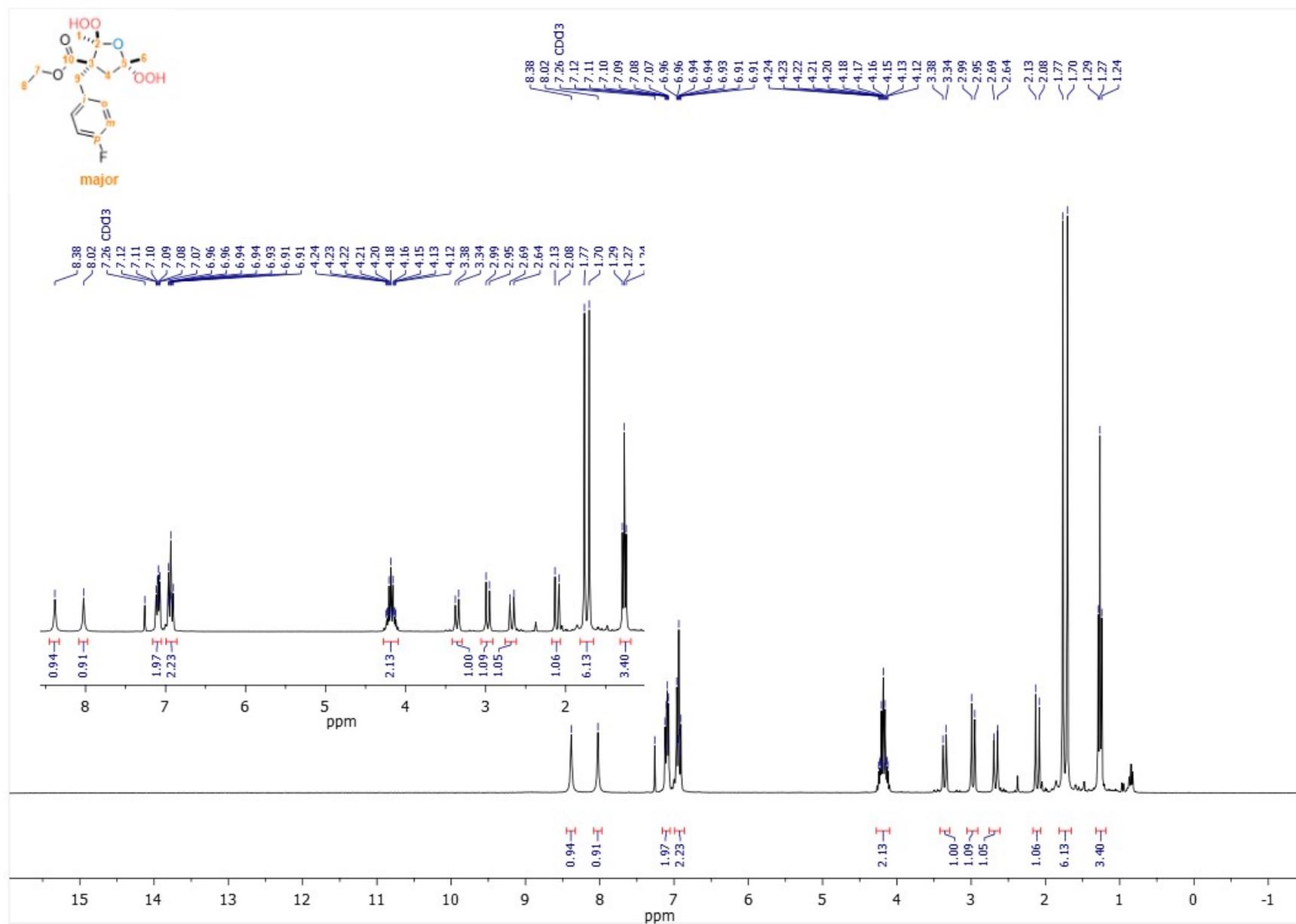
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl 2,5-dihydroperoxy-2,5-dimethyl-3-(4-nitrobenzyl)tetrahydrofuran-3-carboxylate, *cis*-3a+*trans*-3a



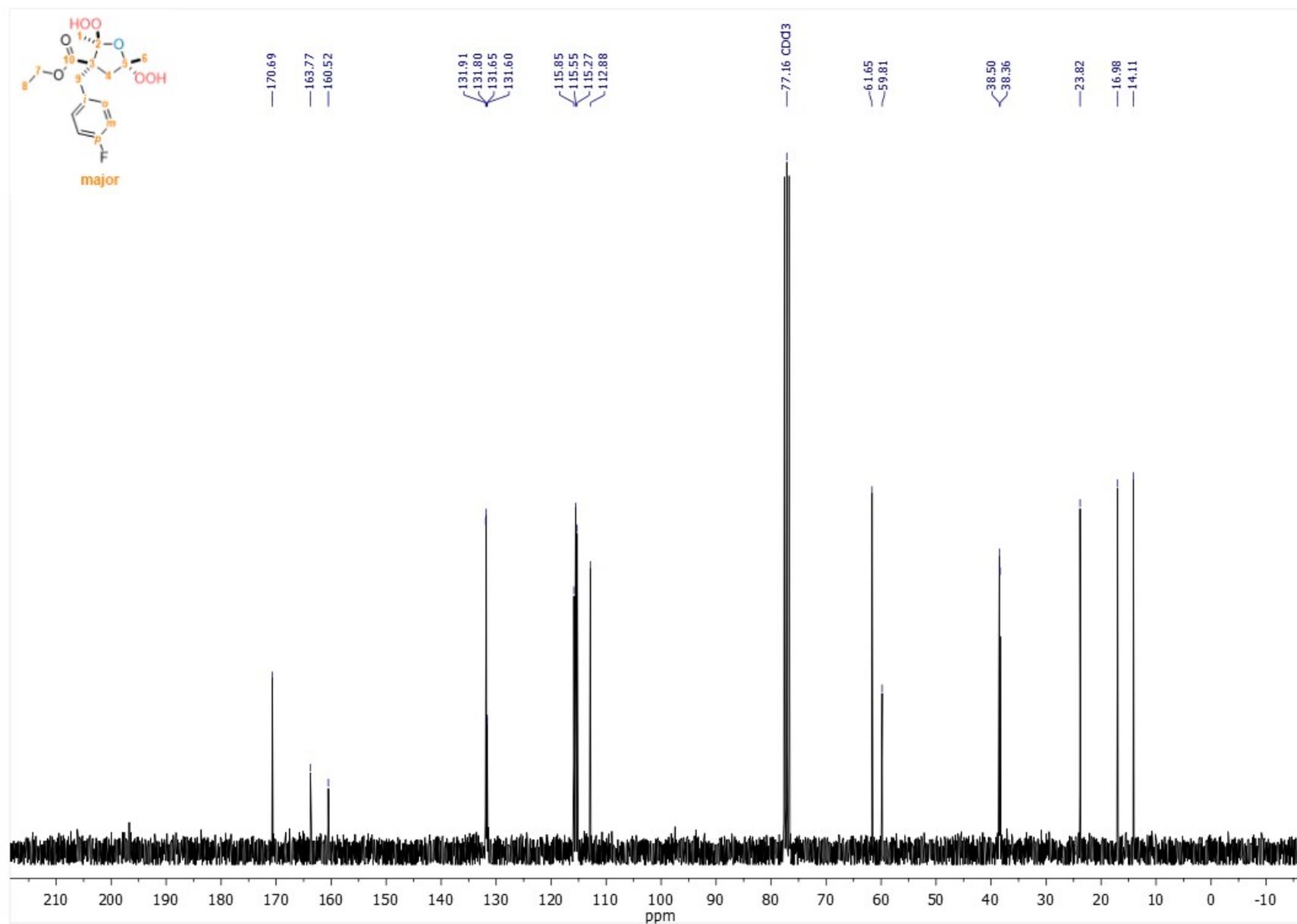
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl 2,5-dihydroperoxy-2,5-dimethyl-3-(4-nitrobenzyl)tetrahydrofuran-3-carboxylate, *cis*-3a+*trans*-3a



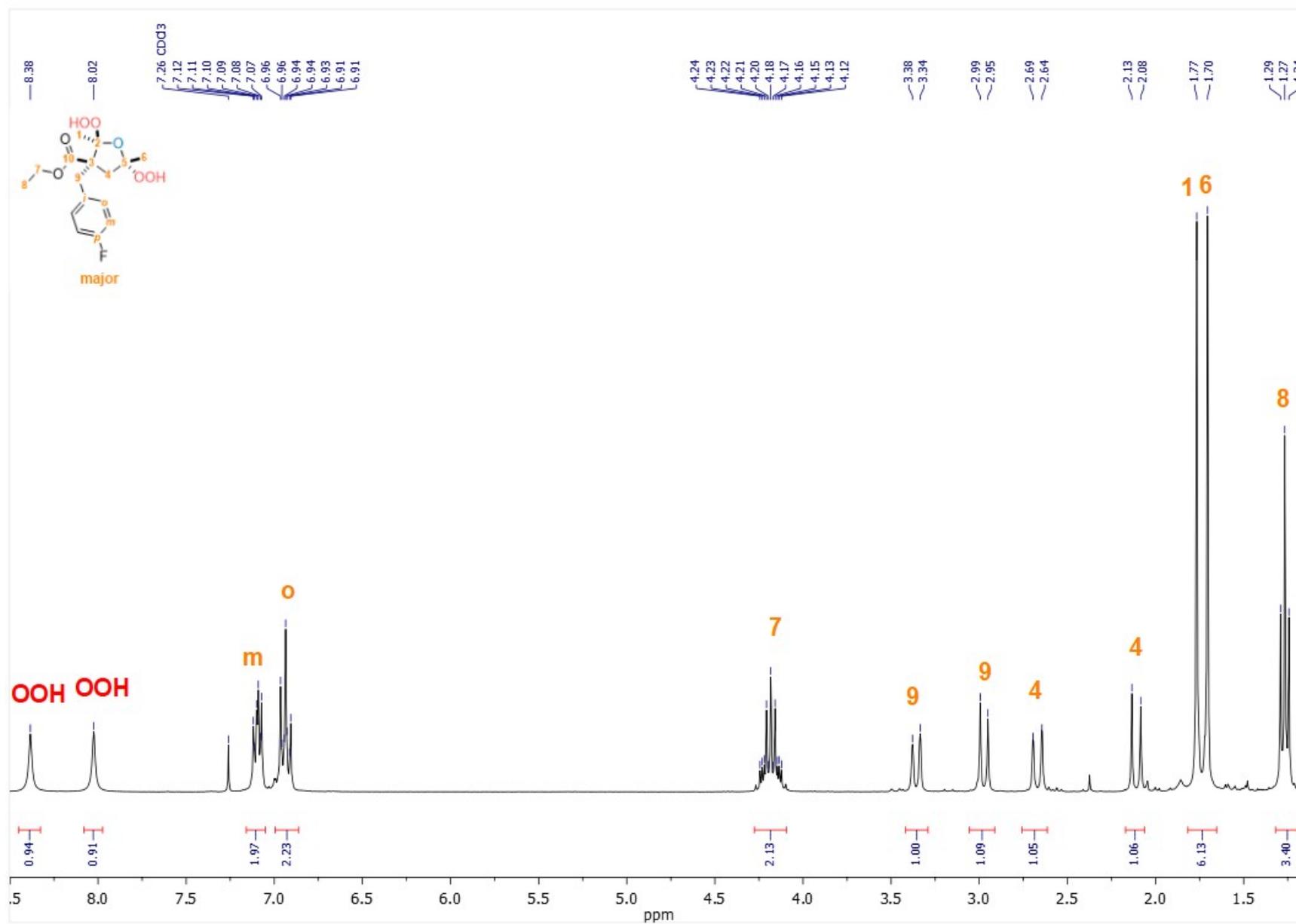
¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



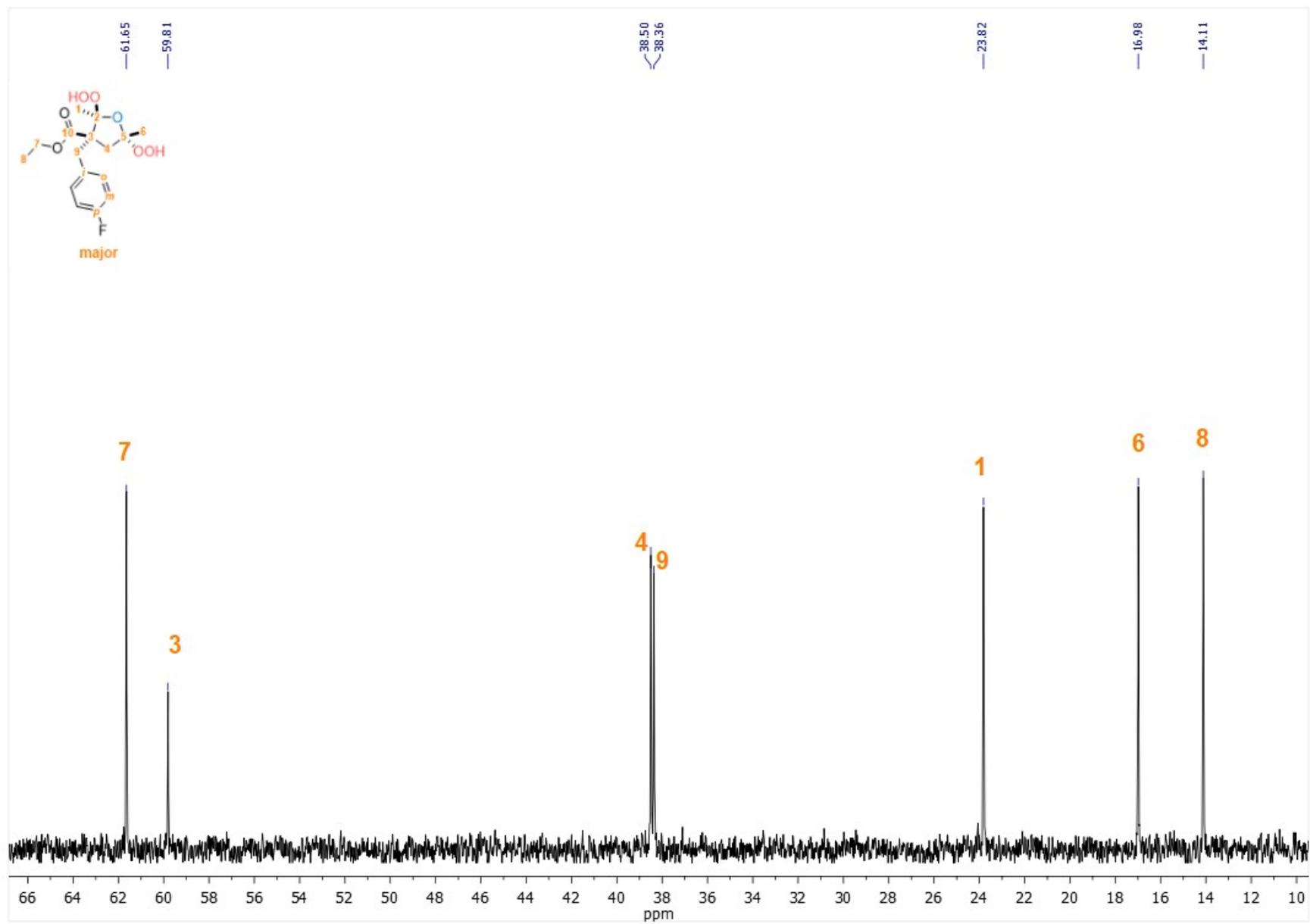
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



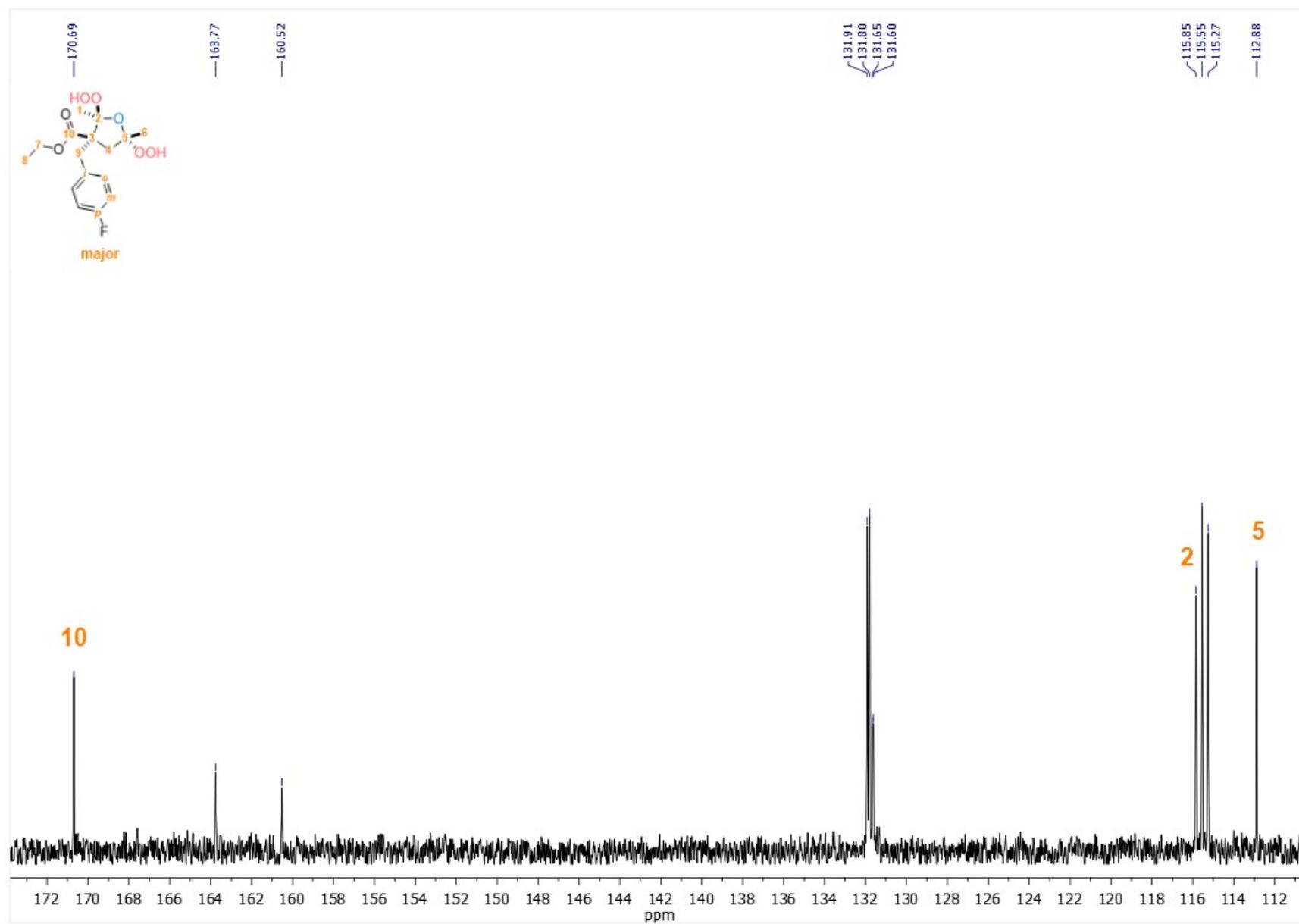
¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



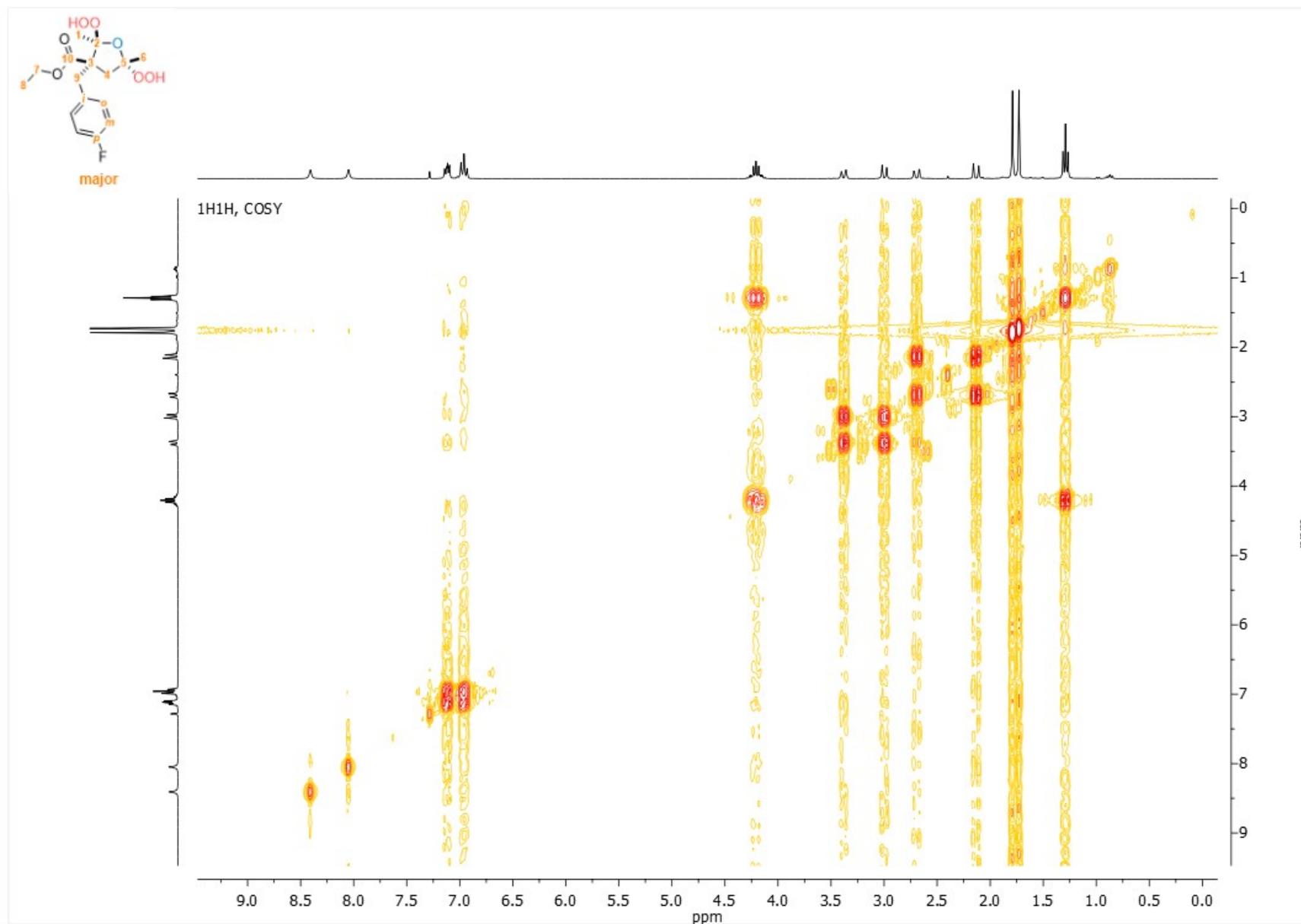
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



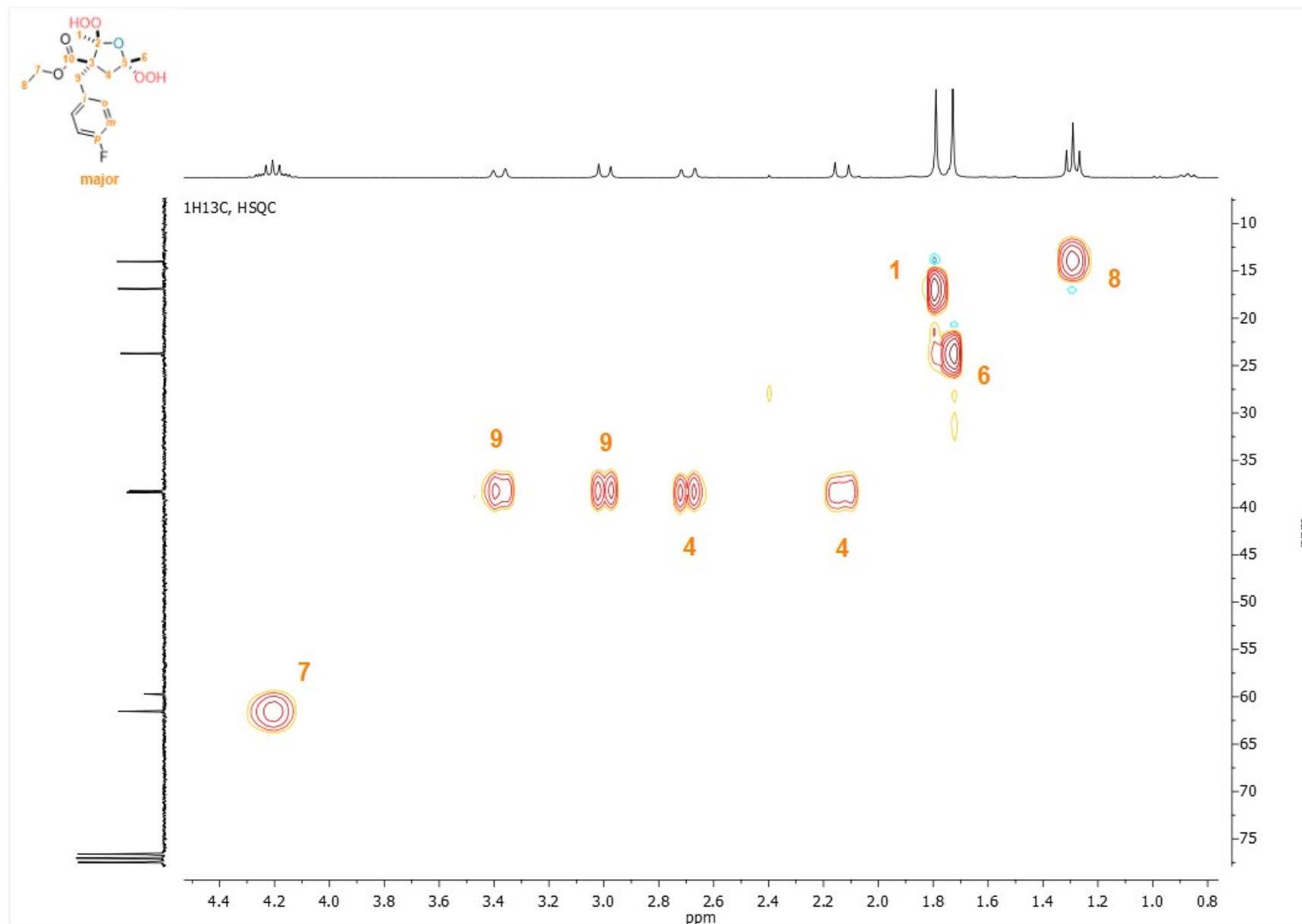
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



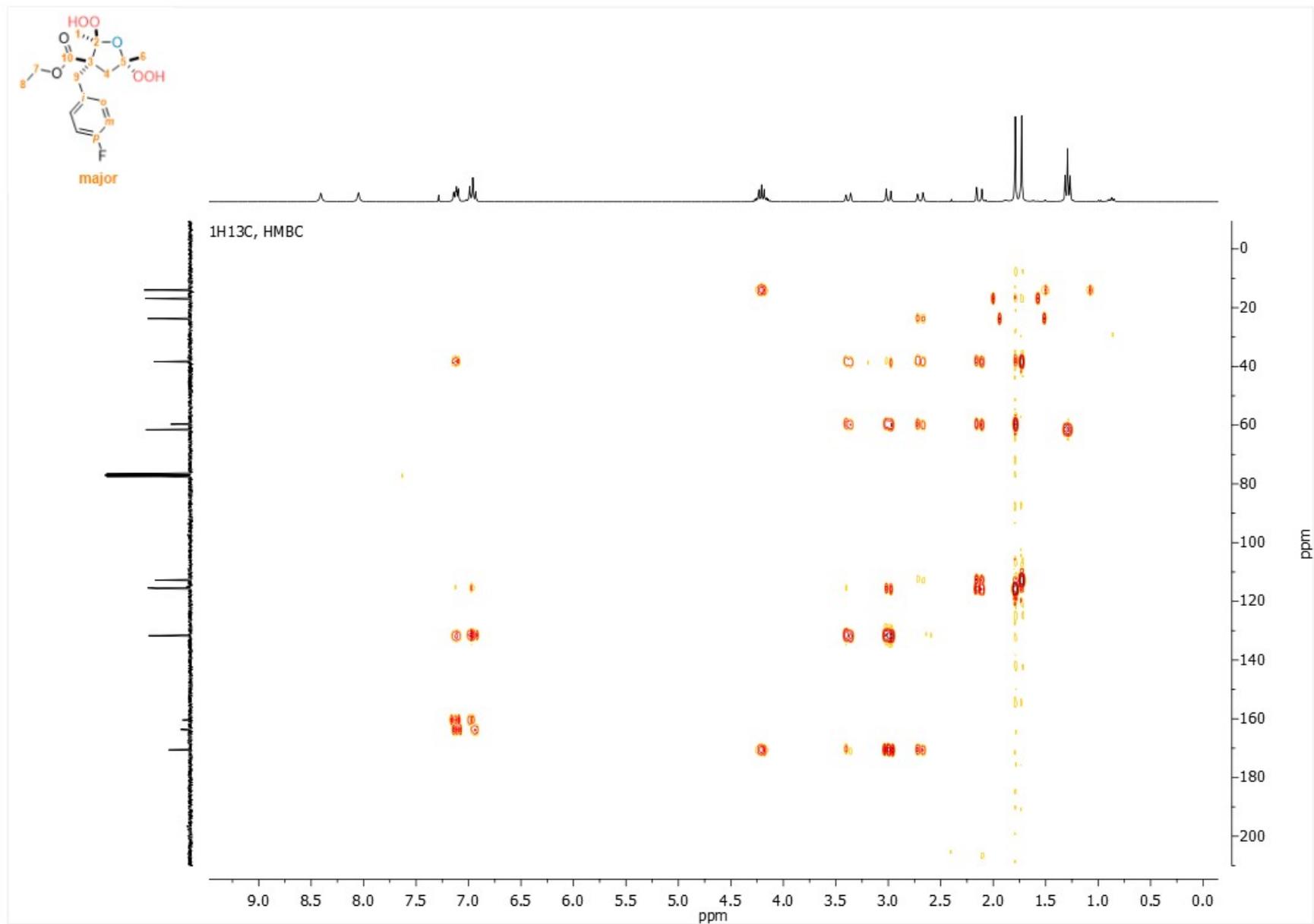
$^1\text{H} - ^1\text{H}$, COSY. Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



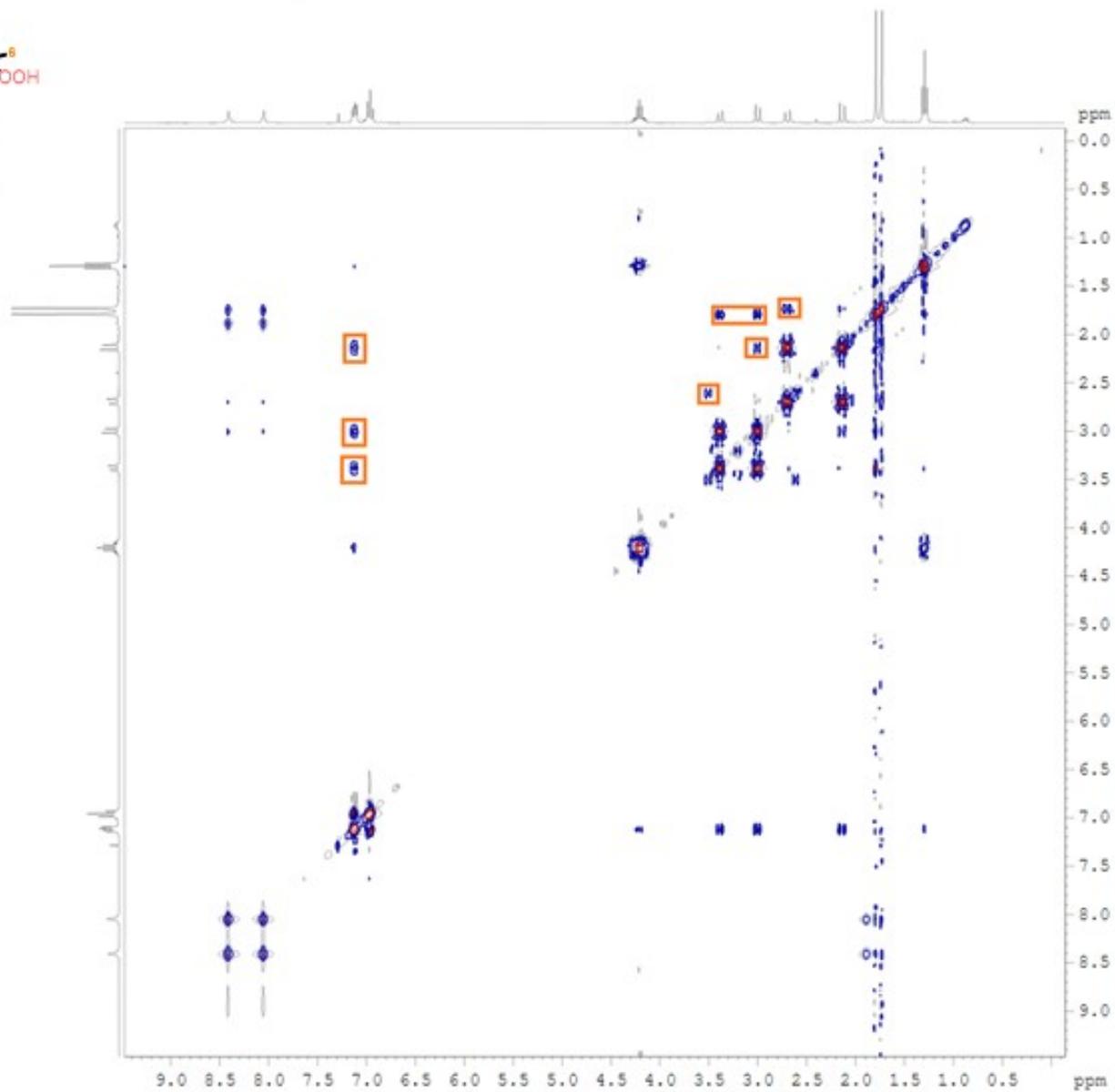
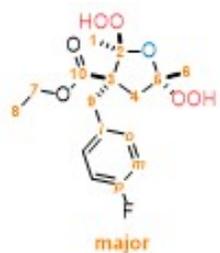
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



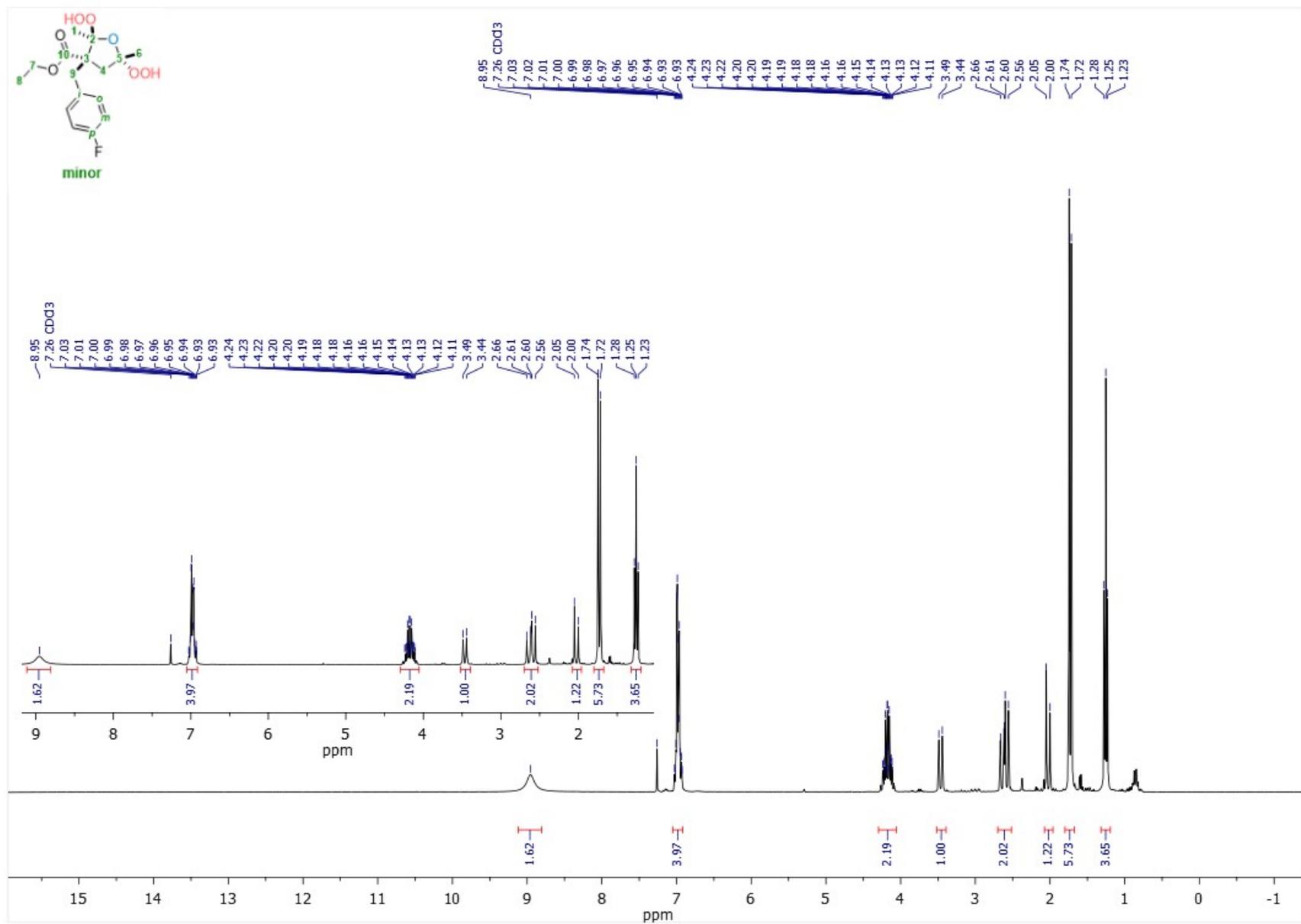
¹H – ¹³C, HMBC. Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



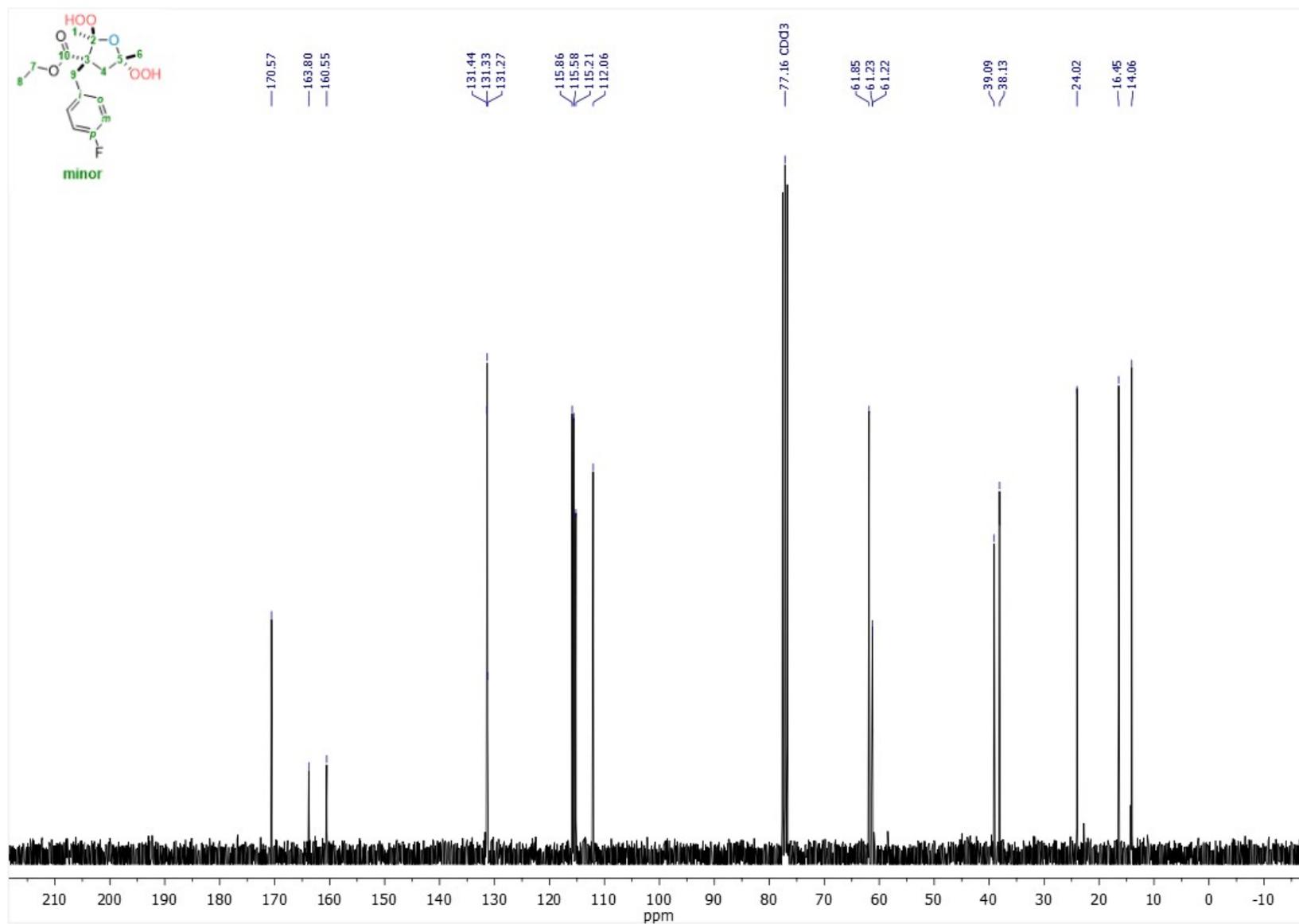
¹H – ¹H, NOESY. Ethyl (2*S,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b**



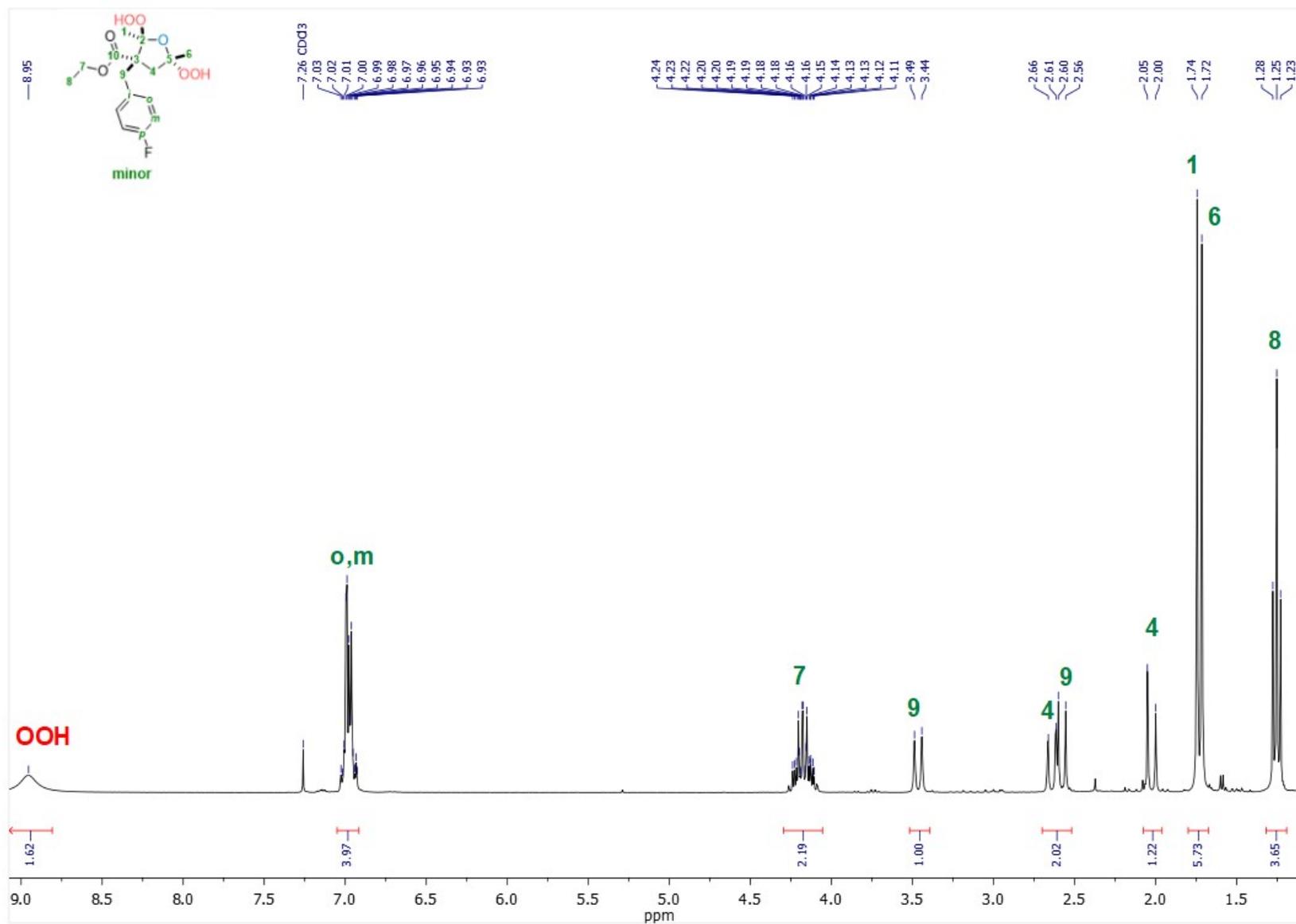
¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-**3b**



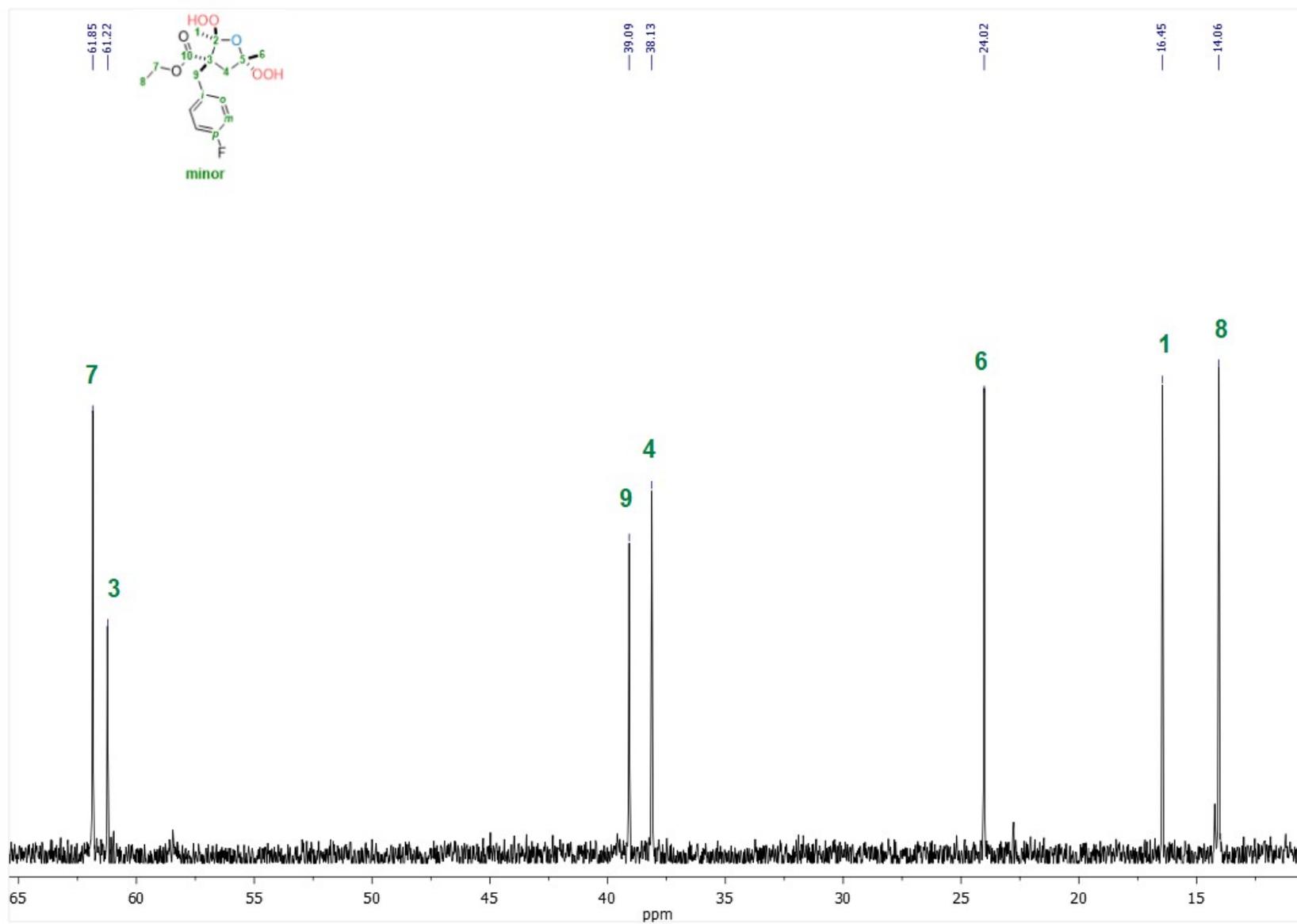
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-**3b**



^1H NMR (300.13 MHz, CDCl_3). Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-**3b**

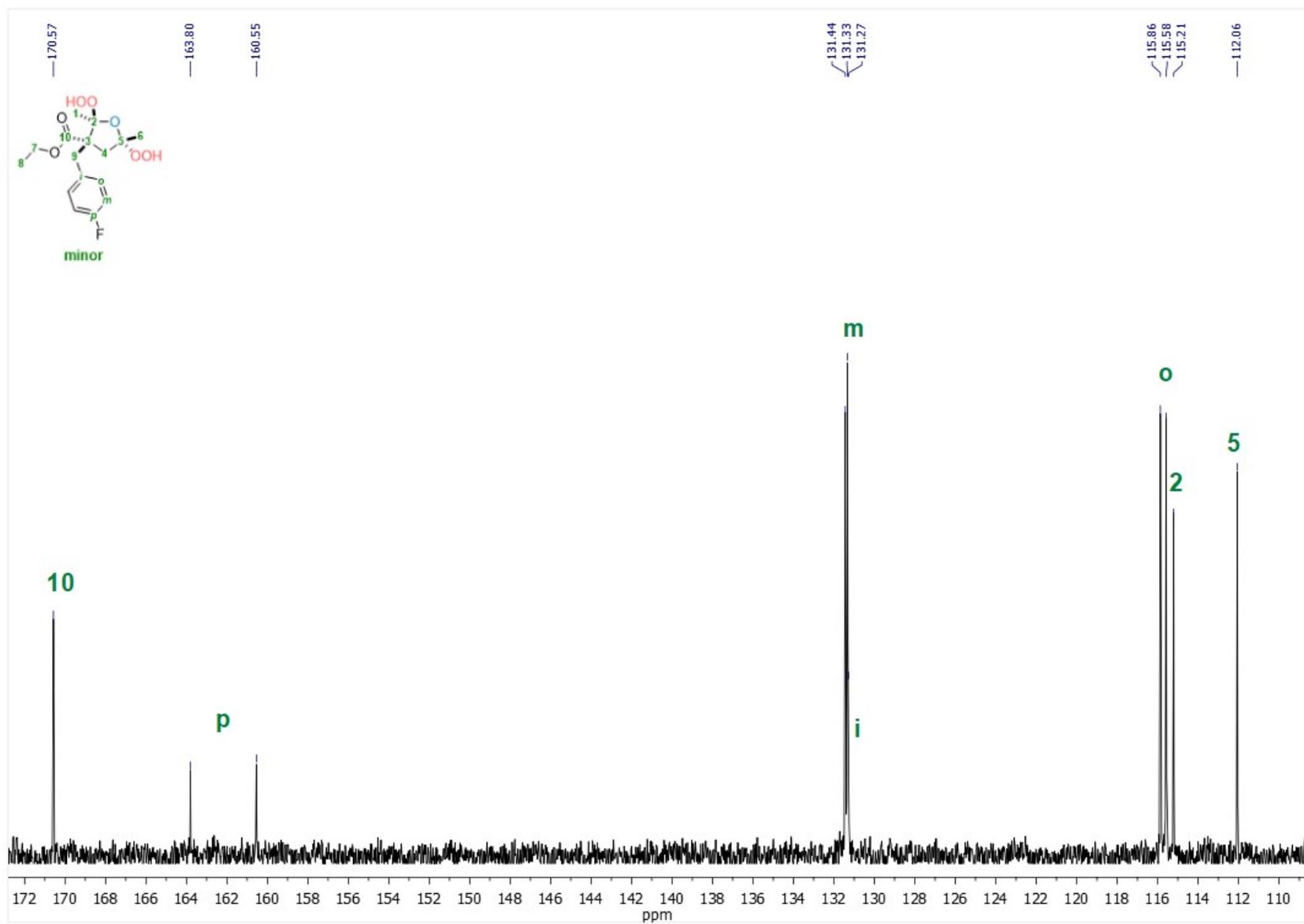


^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-**3b**

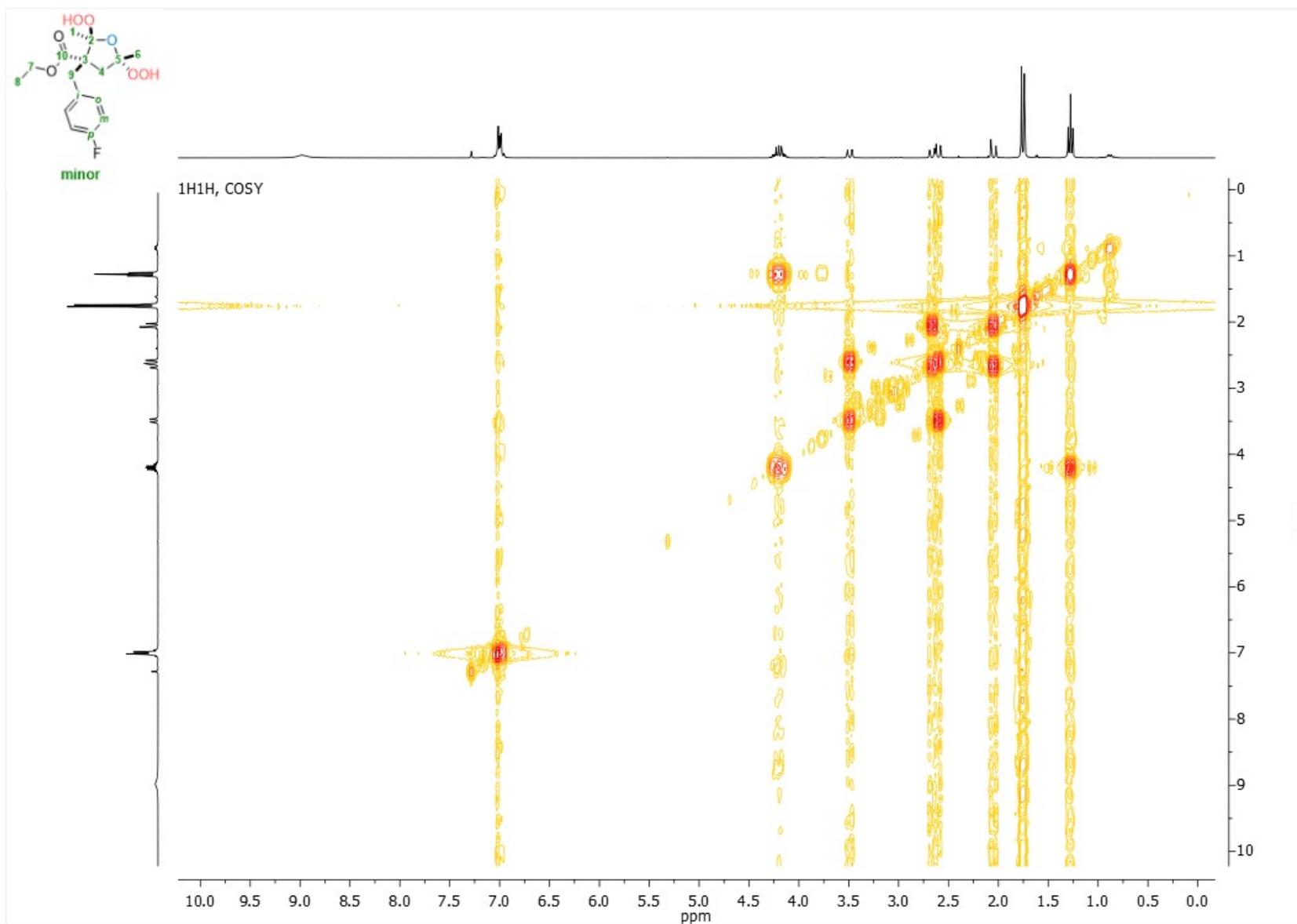


S126

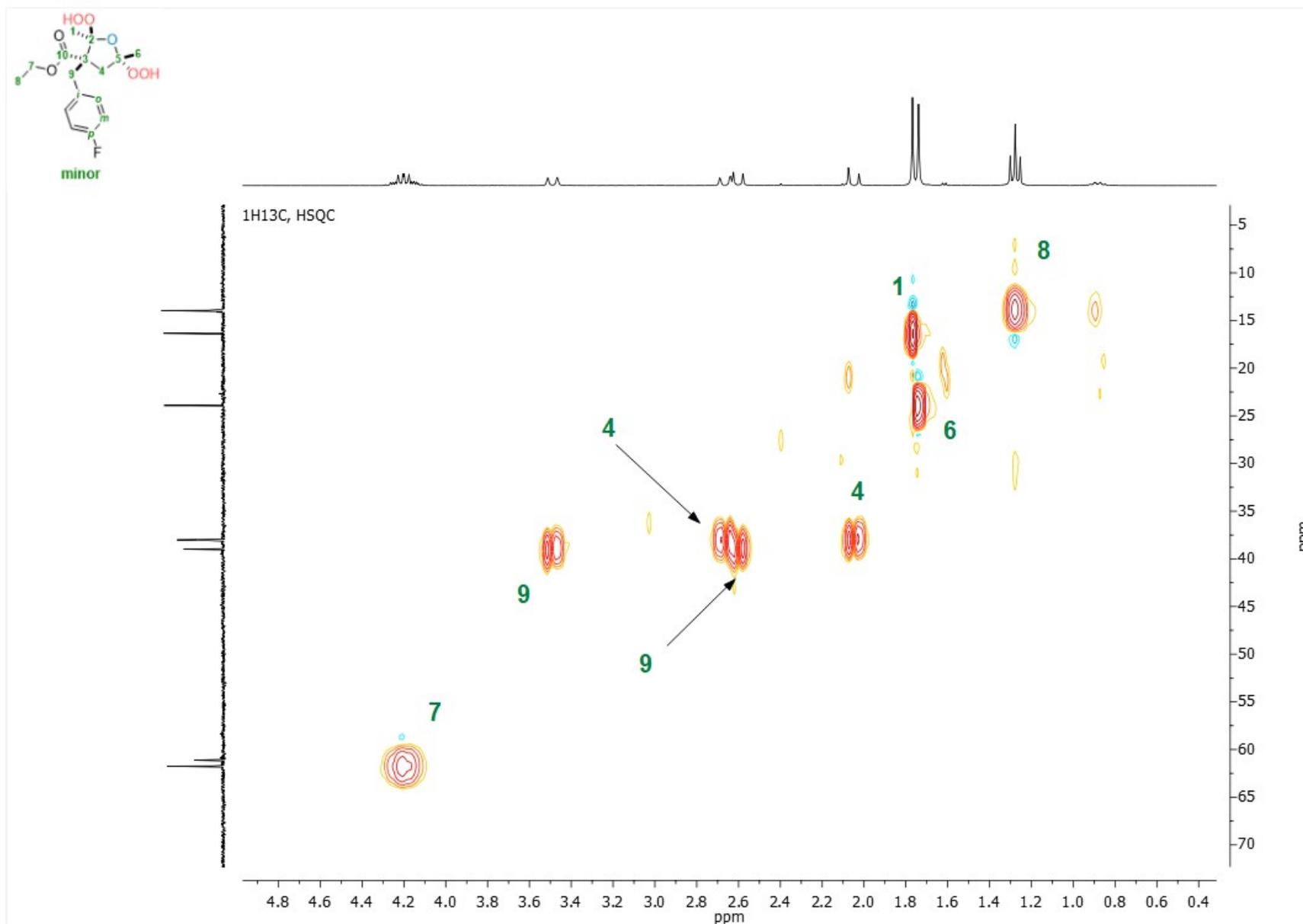
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-**3b**



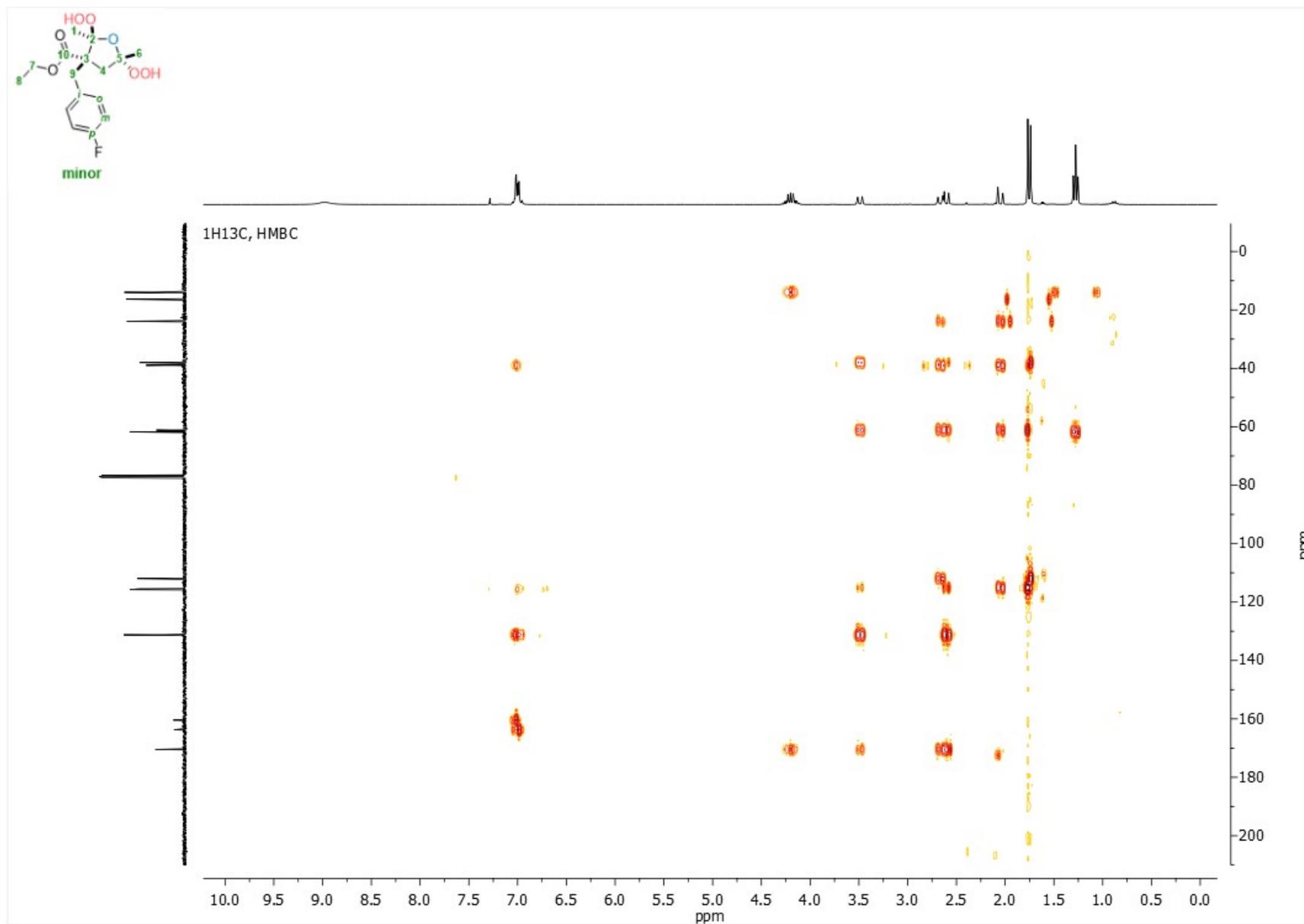
$^1\text{H} - ^1\text{H}$, COSY. Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3b



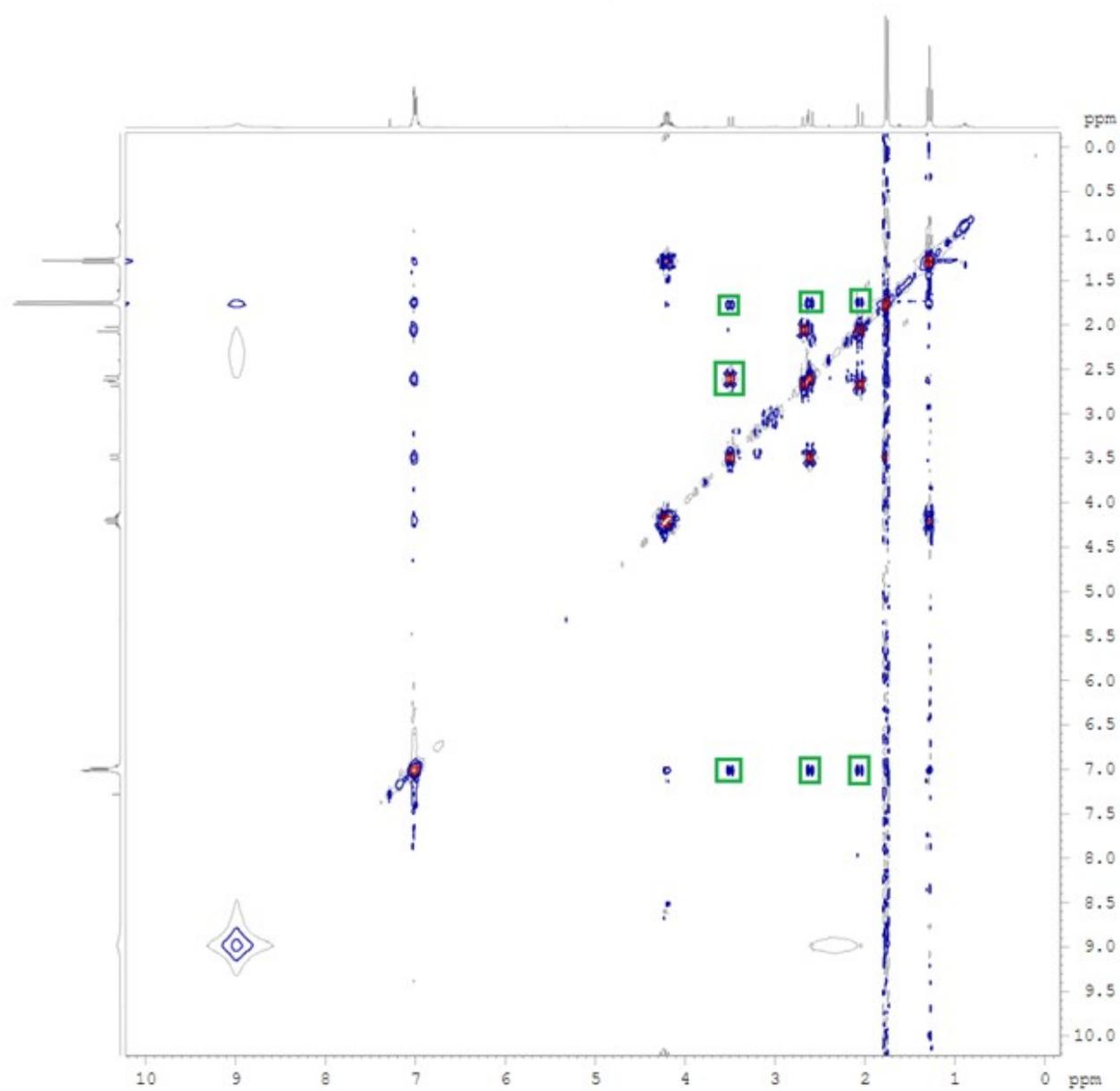
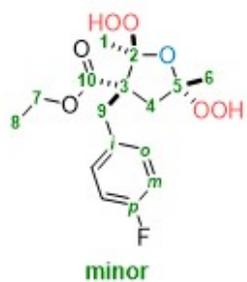
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3b



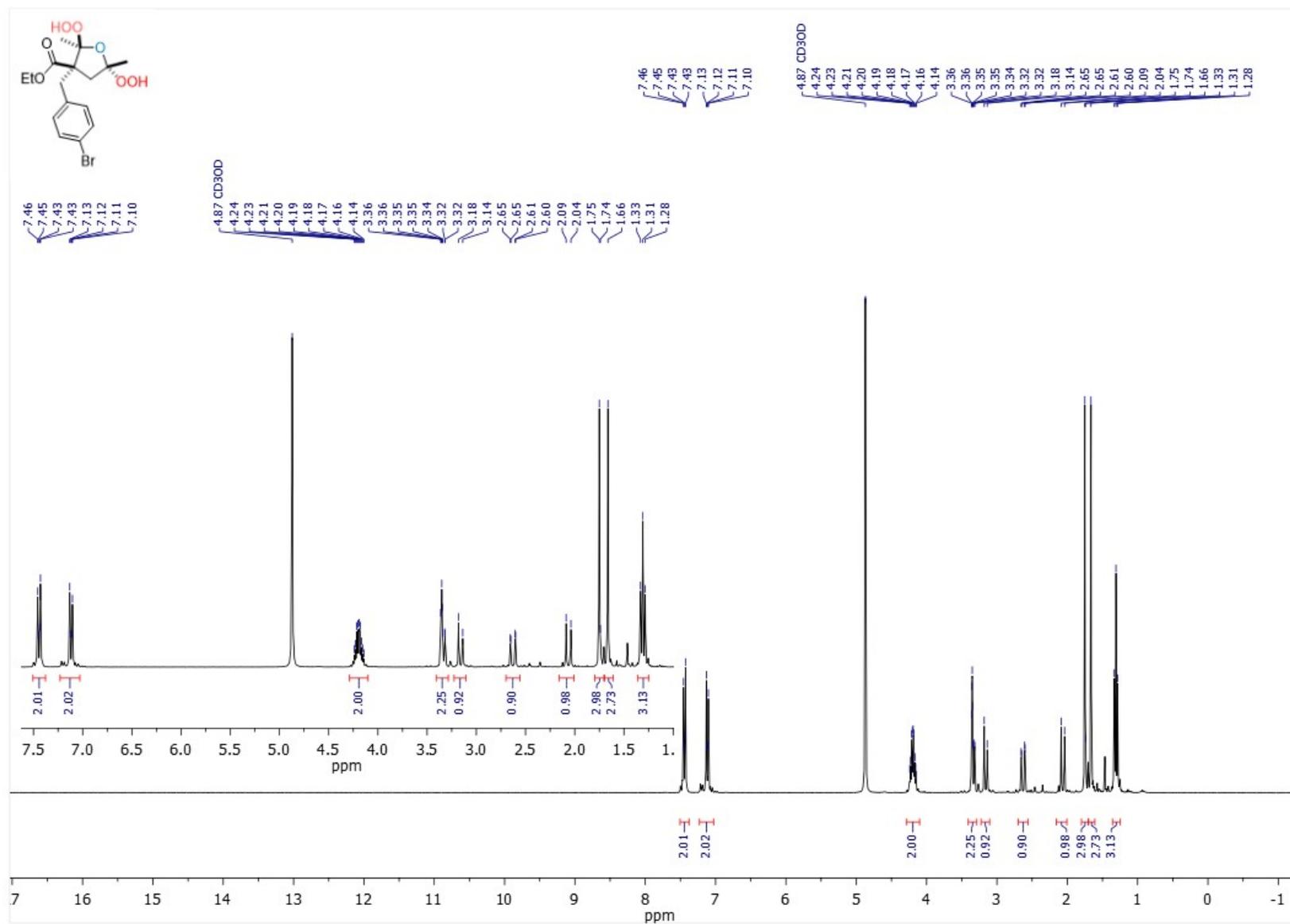
$^1\text{H} - ^{13}\text{C}$, HMBC. Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3b



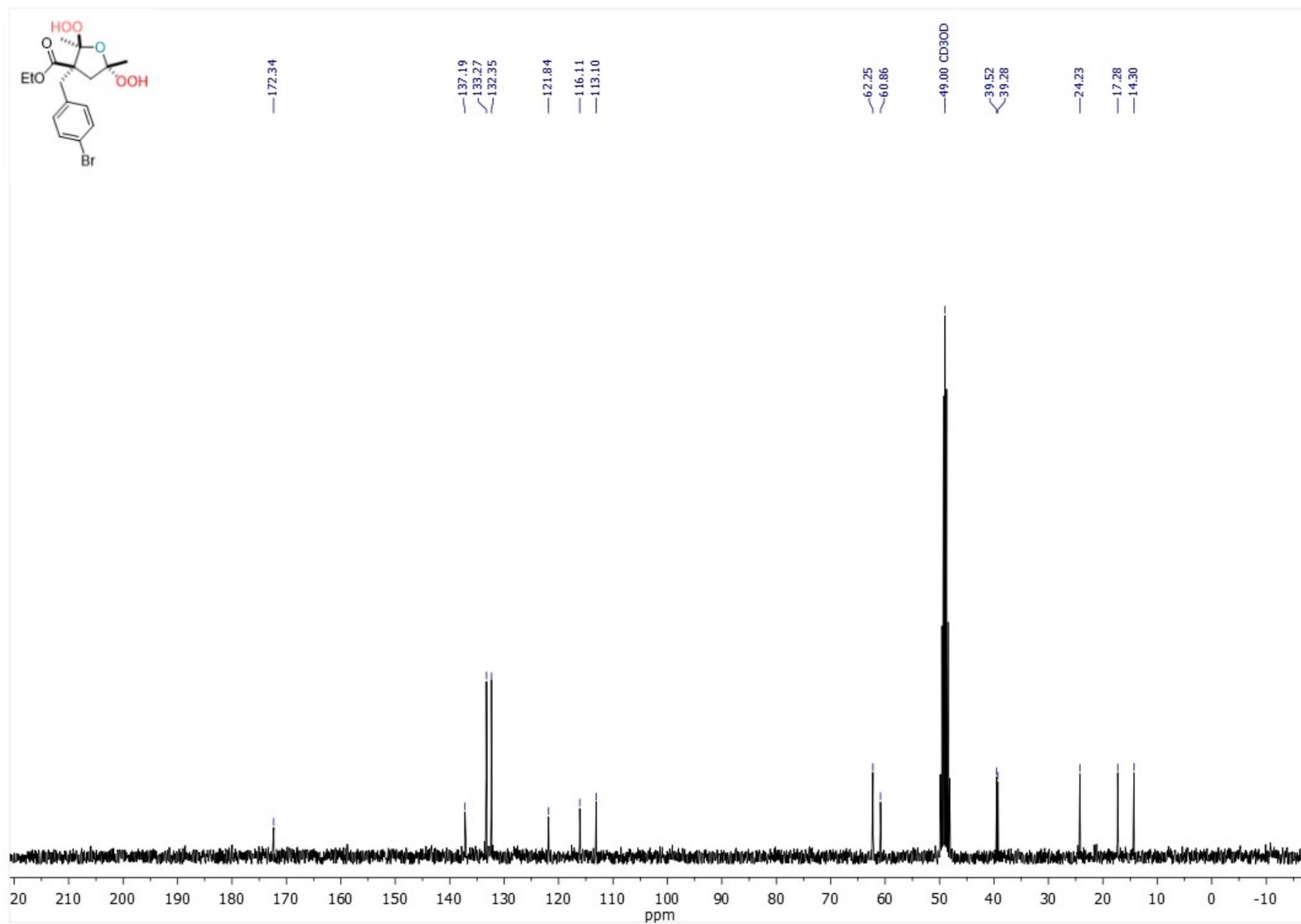
$^1\text{H} - ^1\text{H}$, NOESY. Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3b



¹H NMR (300.13 MHz, CD₃OD). Ethyl (2*S,3*S**,5*S**)-3-(4-bromobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-**3c****

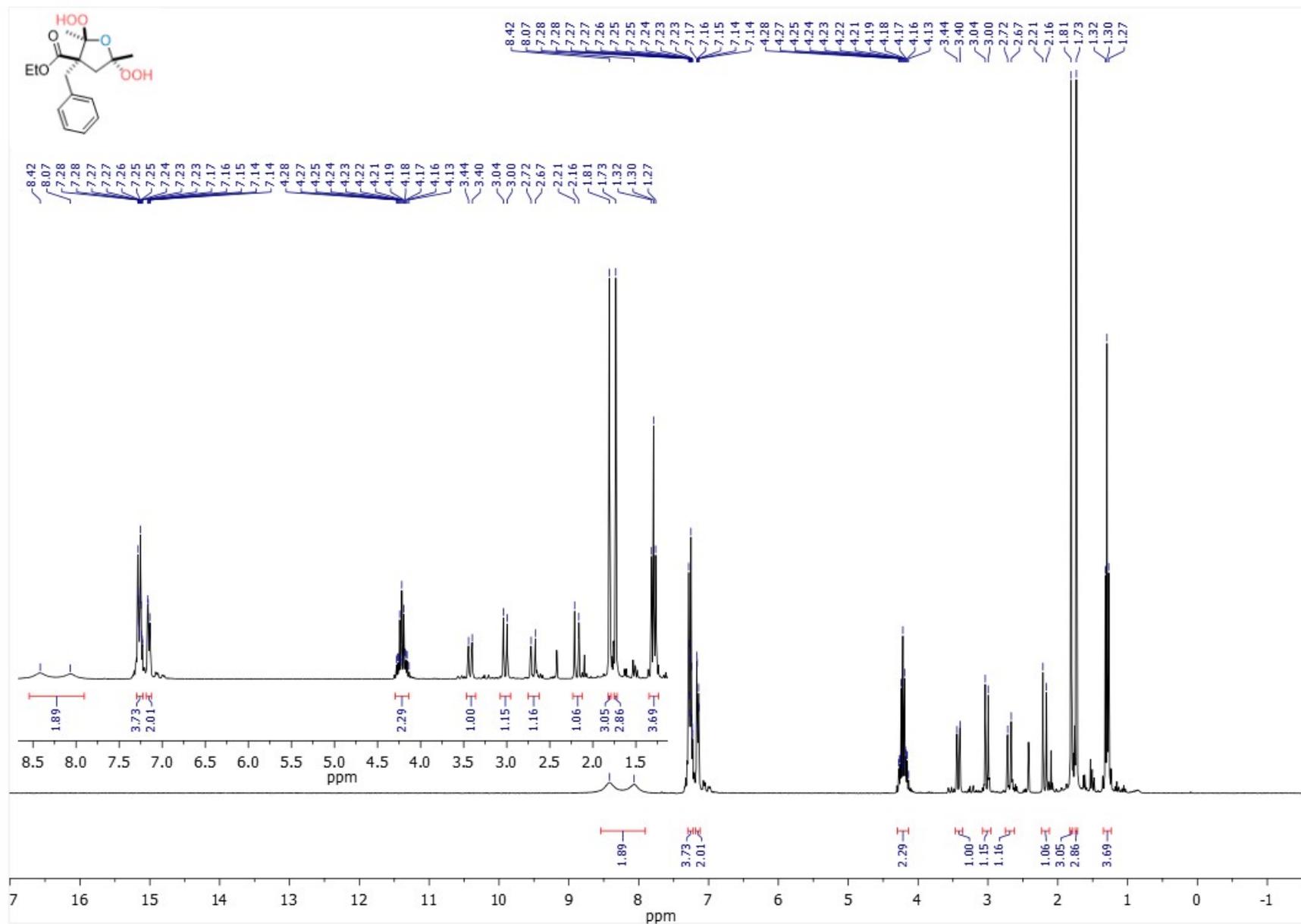


^{13}C NMR (75.48 MHz, CD_3OD). Ethyl (2*S**,3*S**,5*S**)-3-(4-bromobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3c

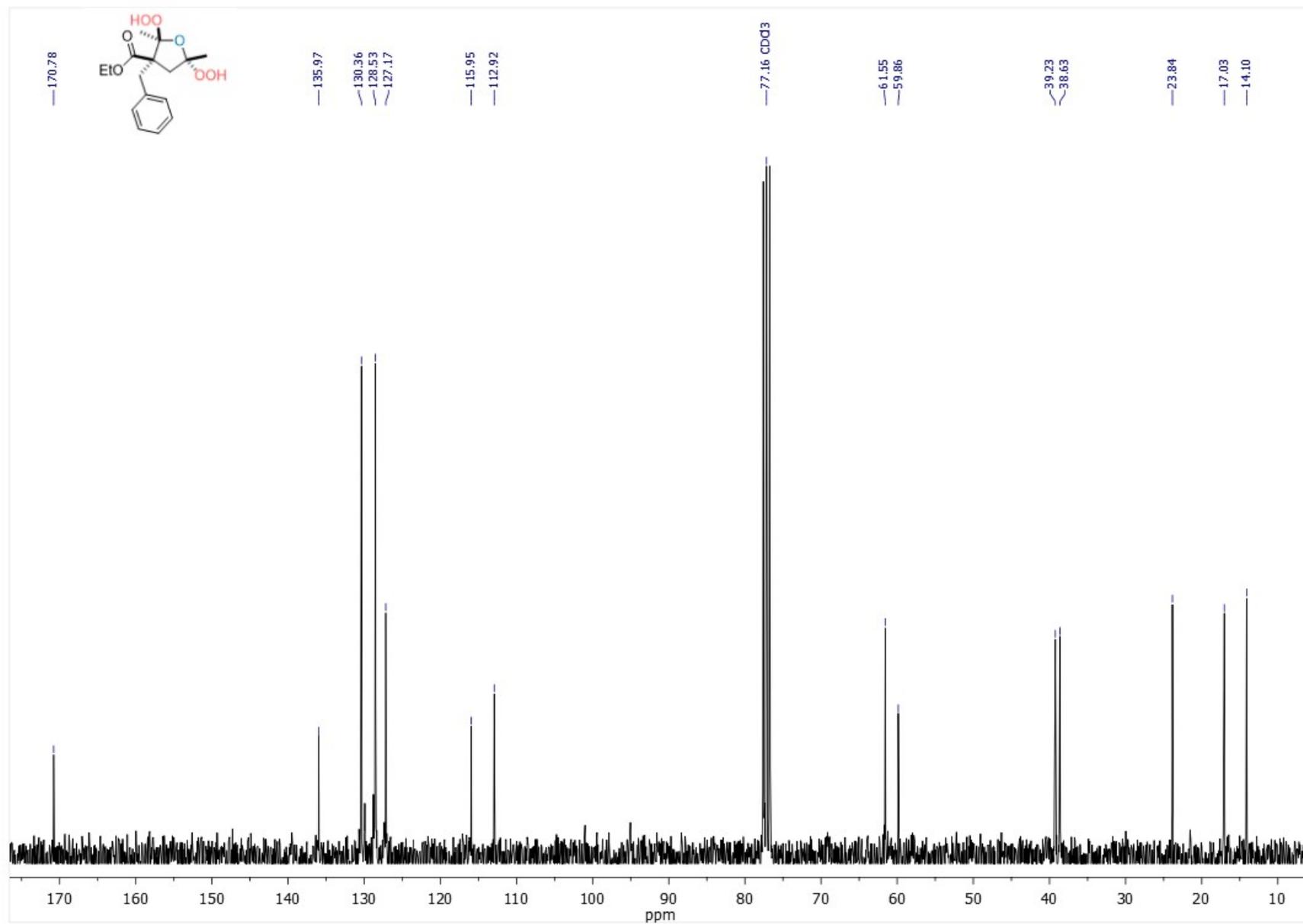


S133

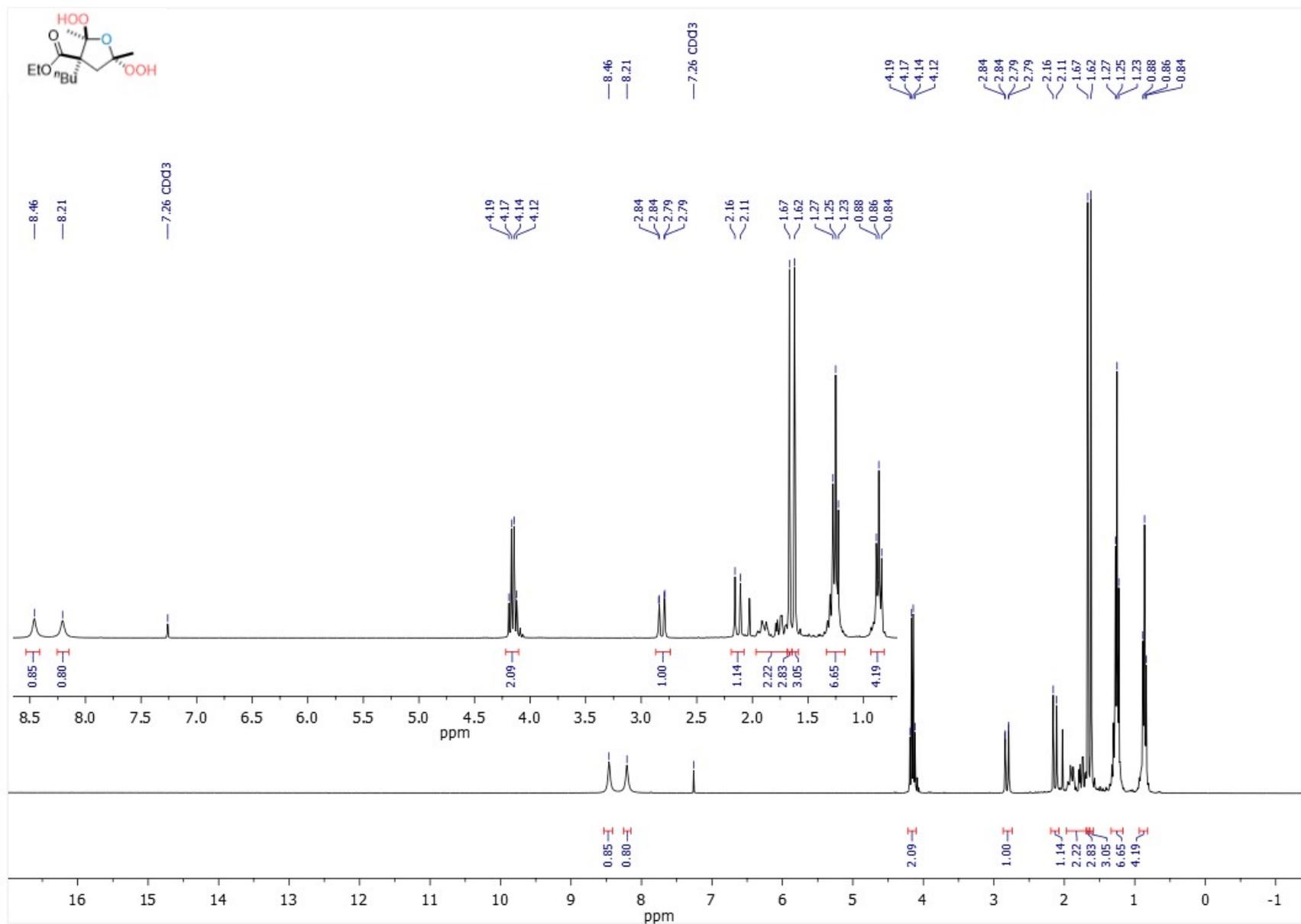
¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*S**,5*R**)-3-benzyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3e



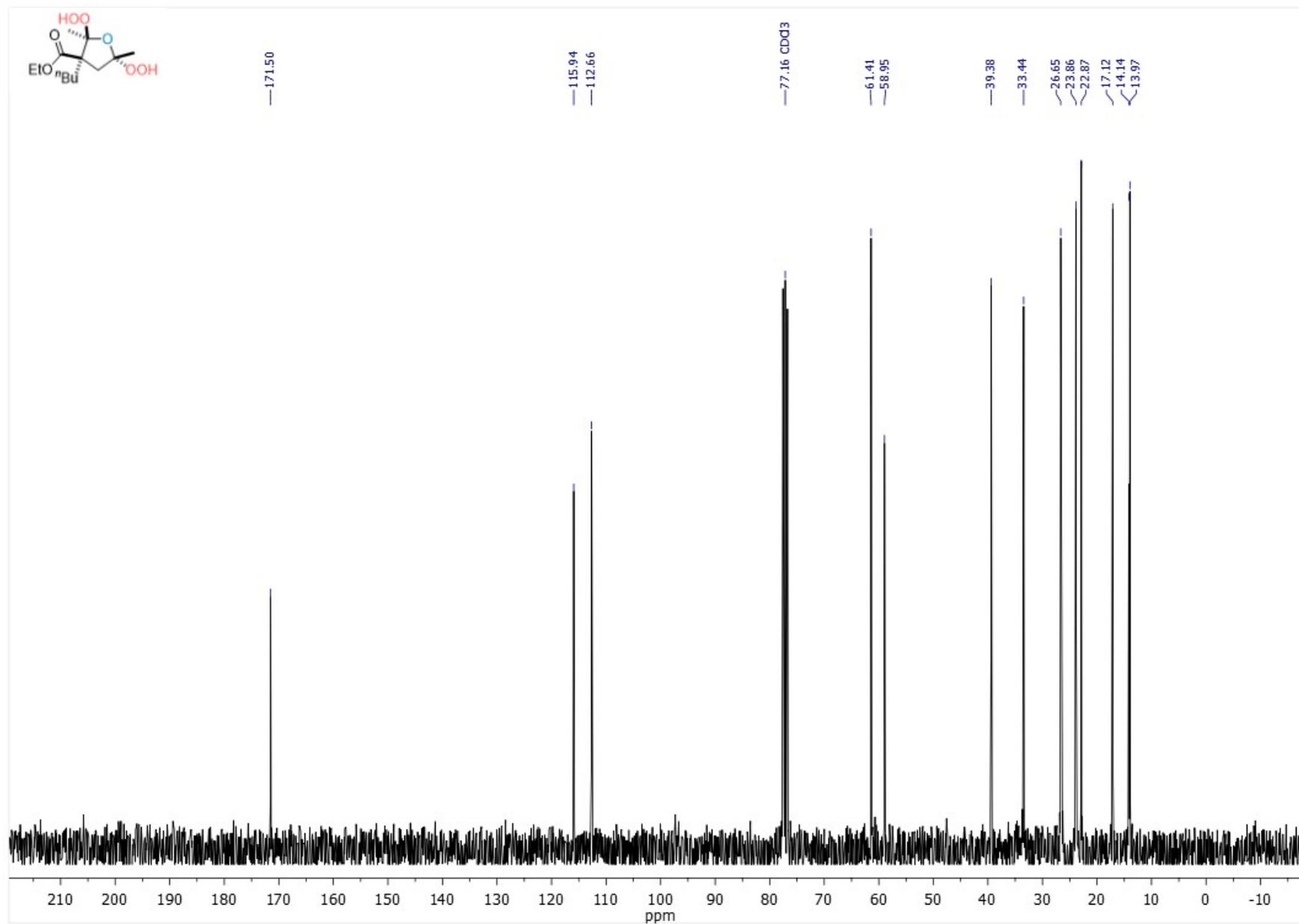
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*S**,5*R**)-3-benzyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3e



¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*S**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3g

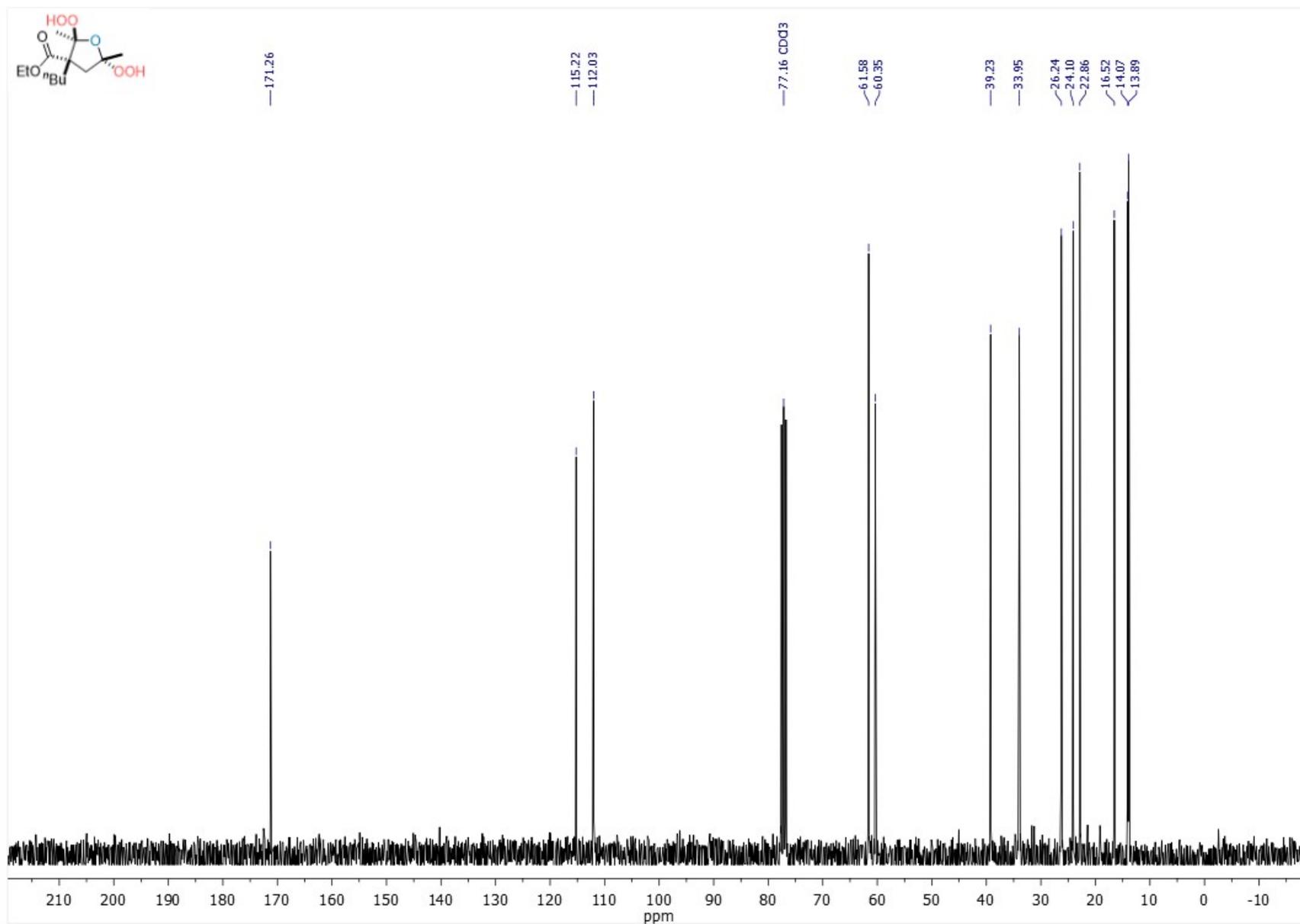


^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (2*S**,3*S**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3g

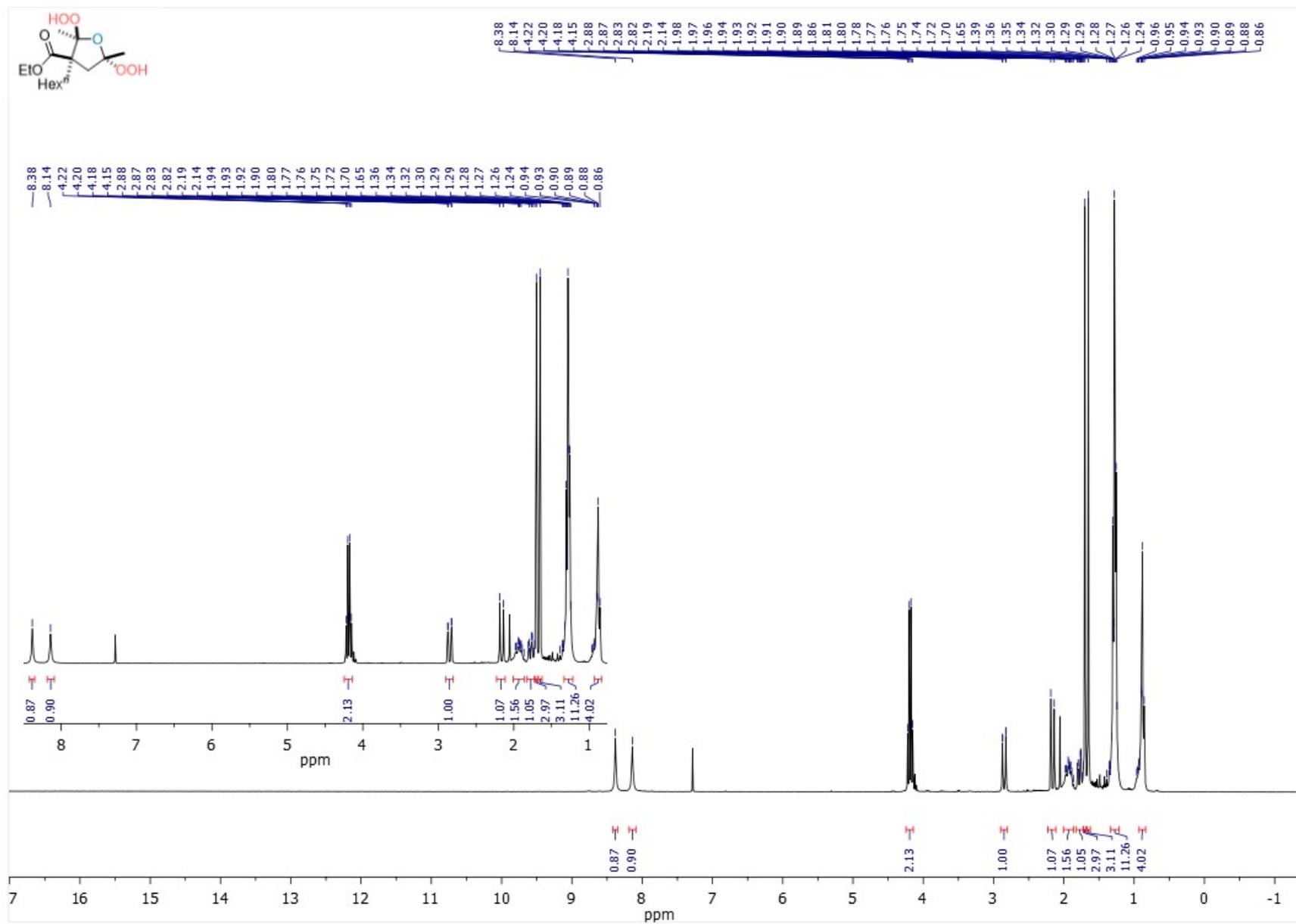


S137

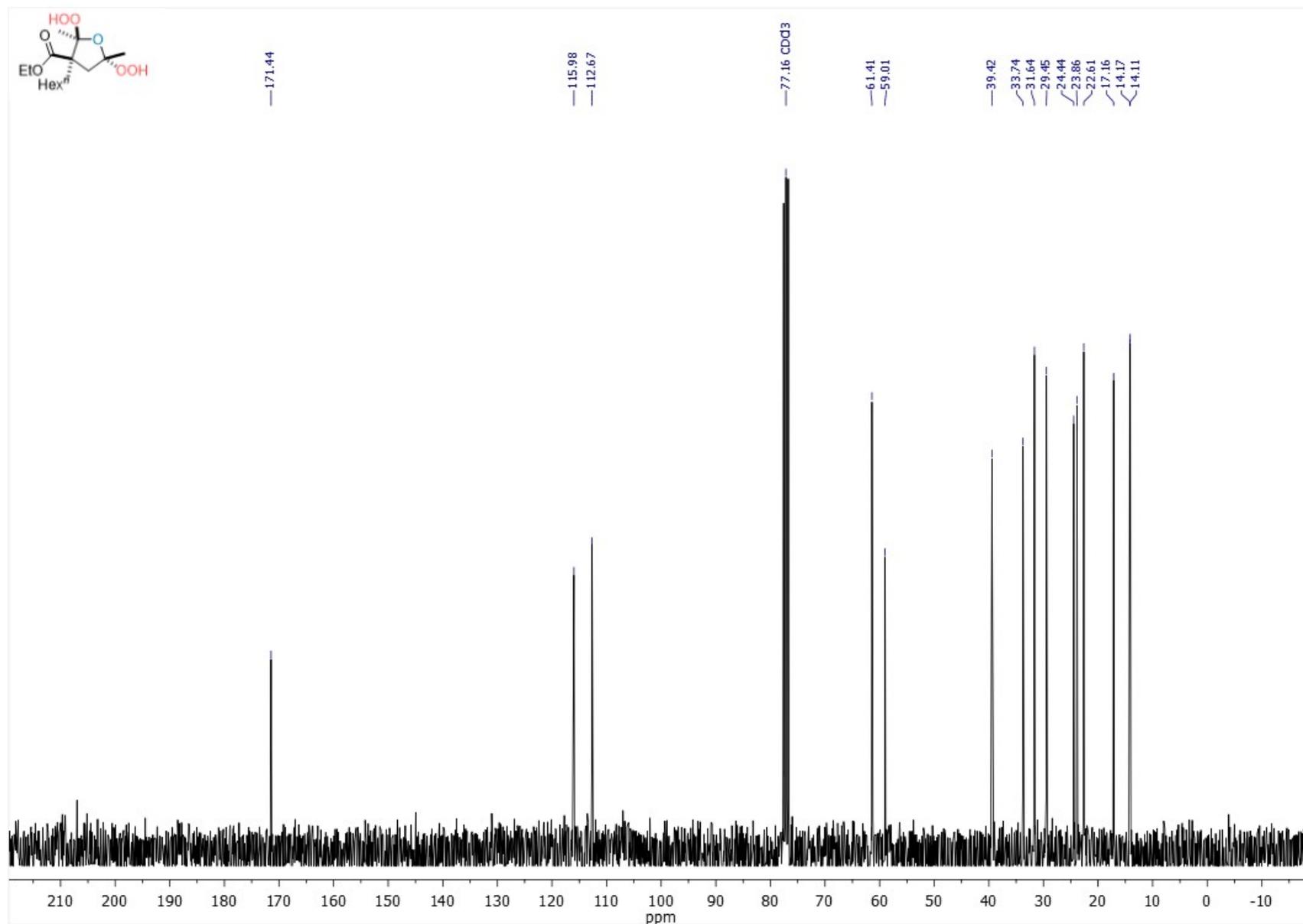
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (2*S**,3*R**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3g



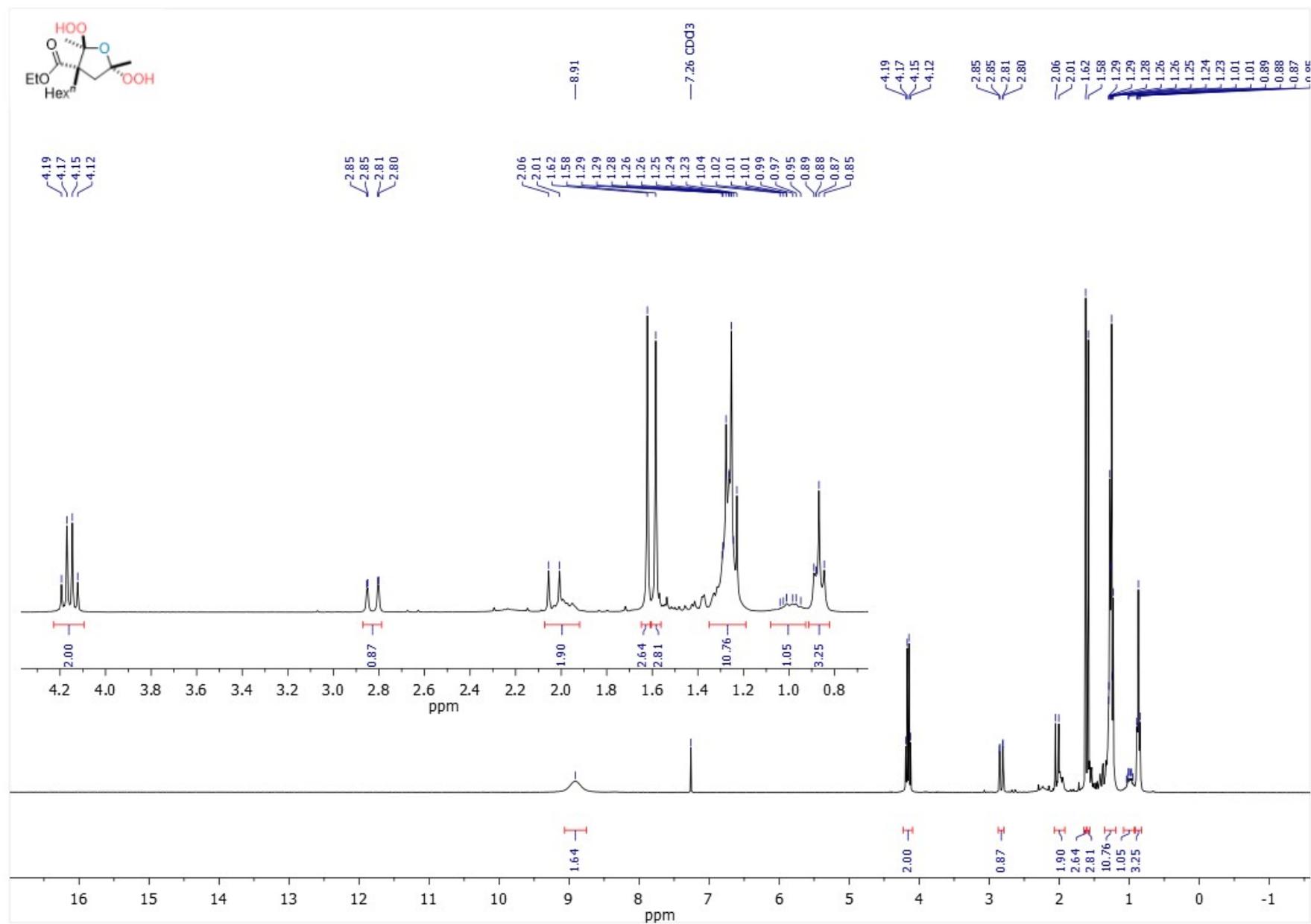
¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*S**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3h



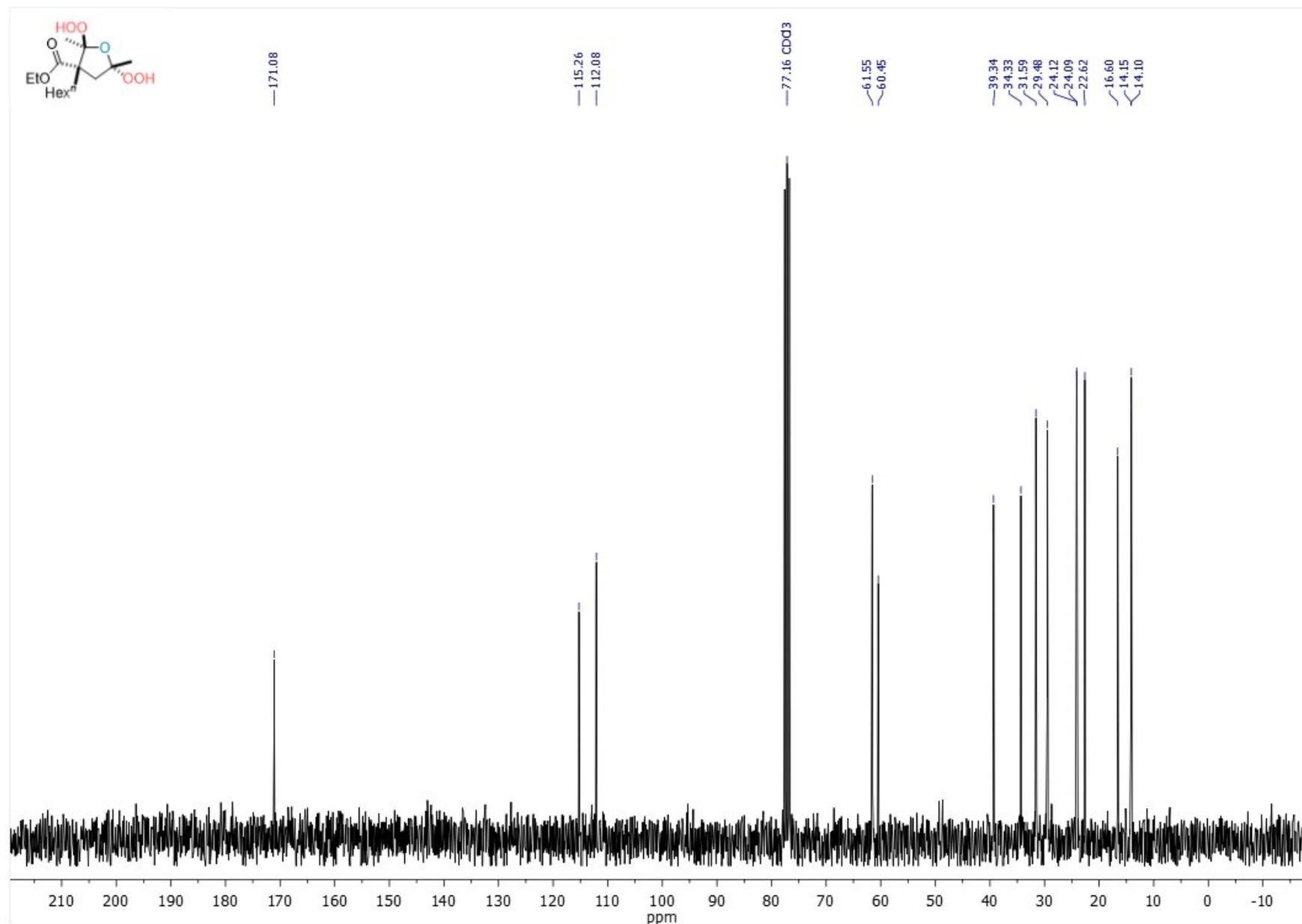
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (2*S**,3*S**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3h



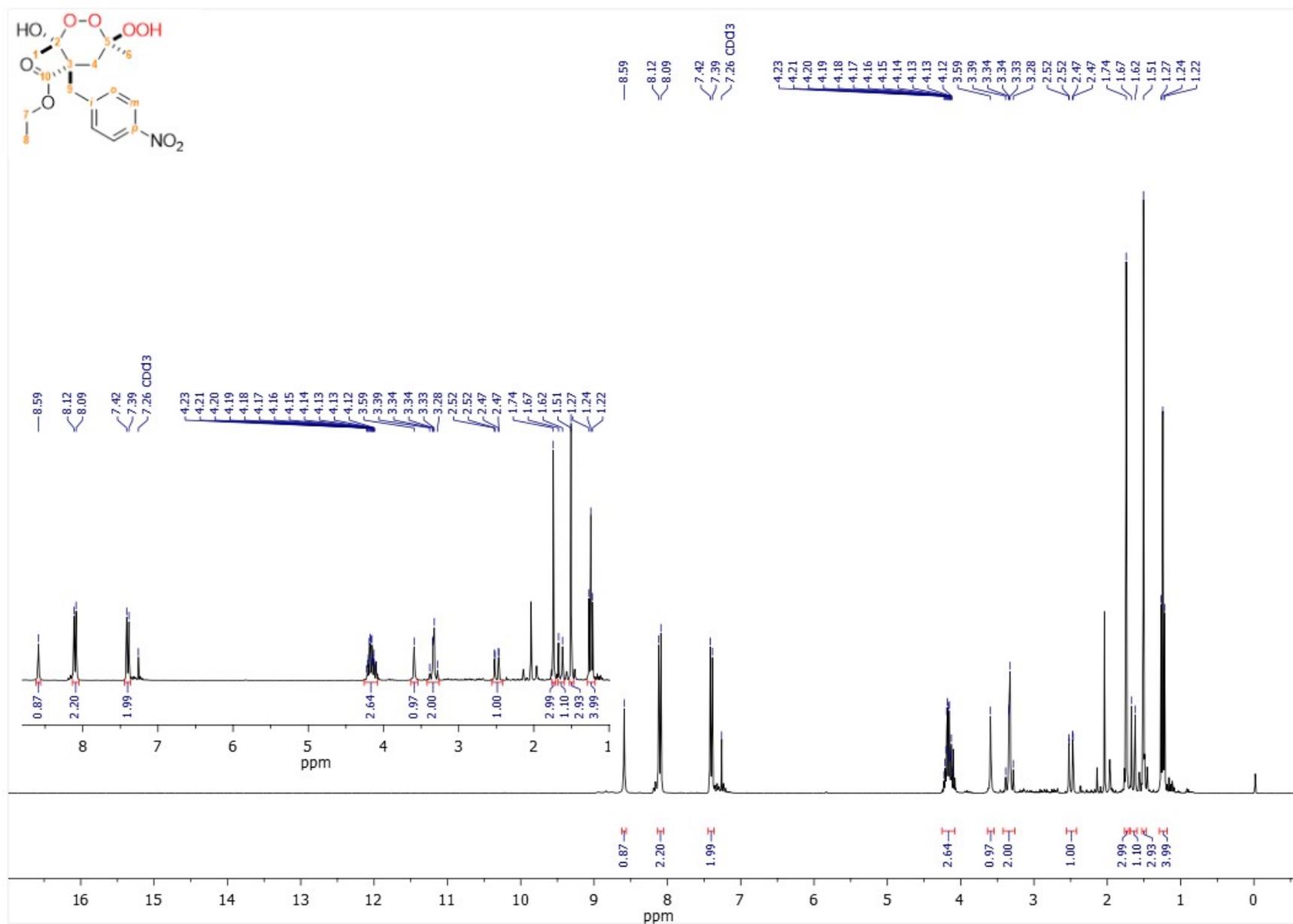
¹H NMR (300.13 MHz, CDCl₃). Ethyl (2*S**,3*R**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3h



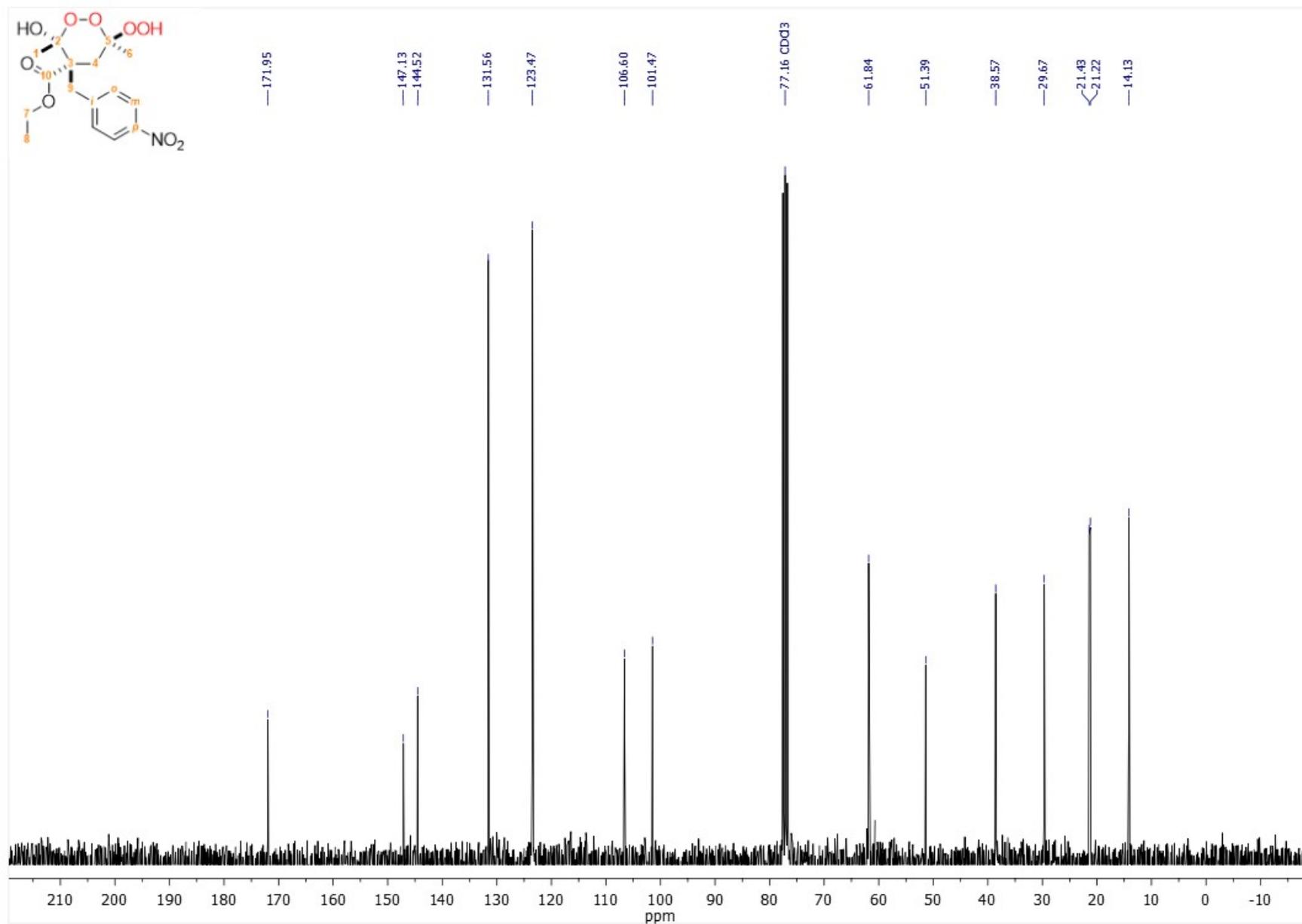
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (2*S**,3*R**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3h



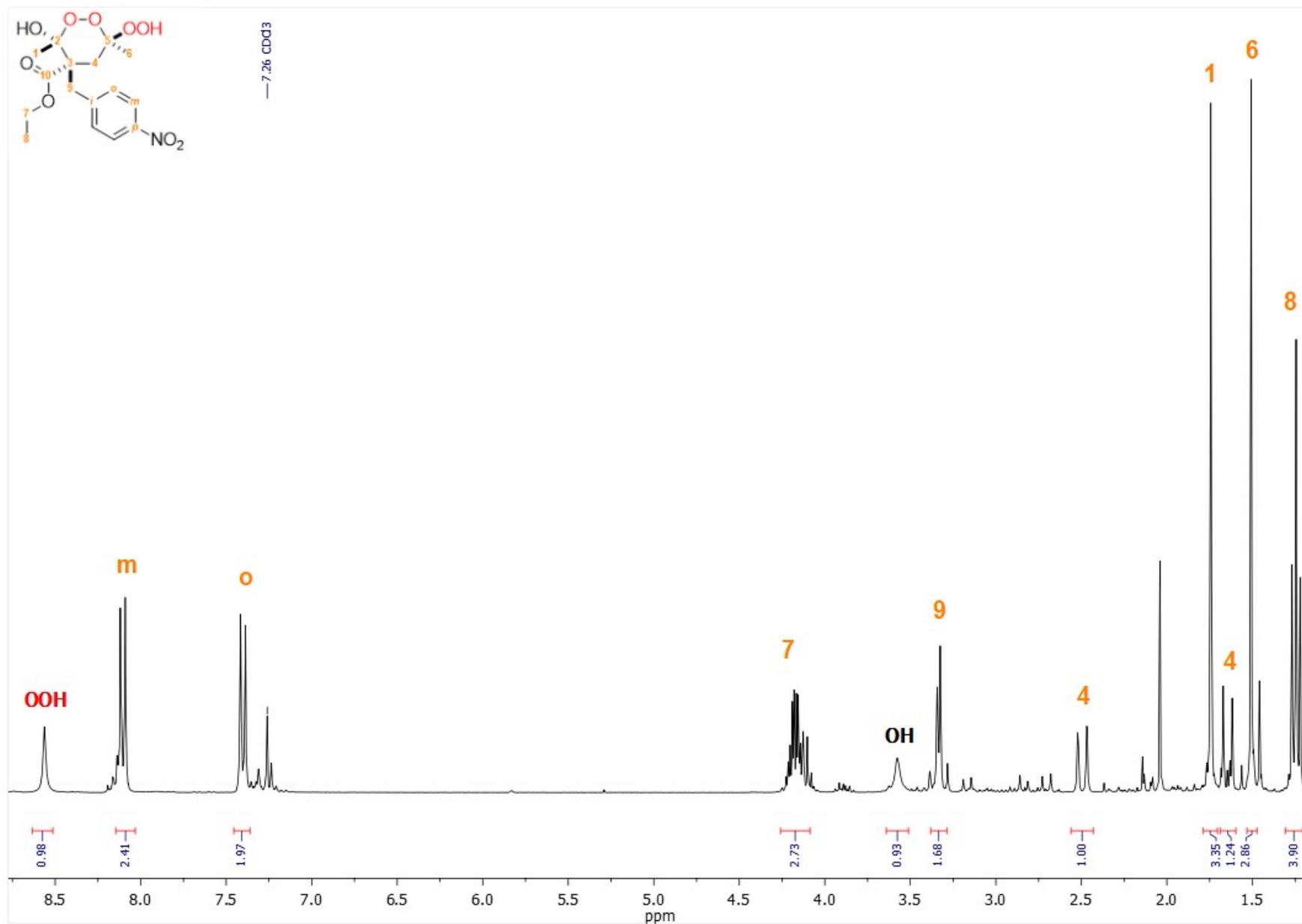
¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-3-hydroperoxy-6-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a



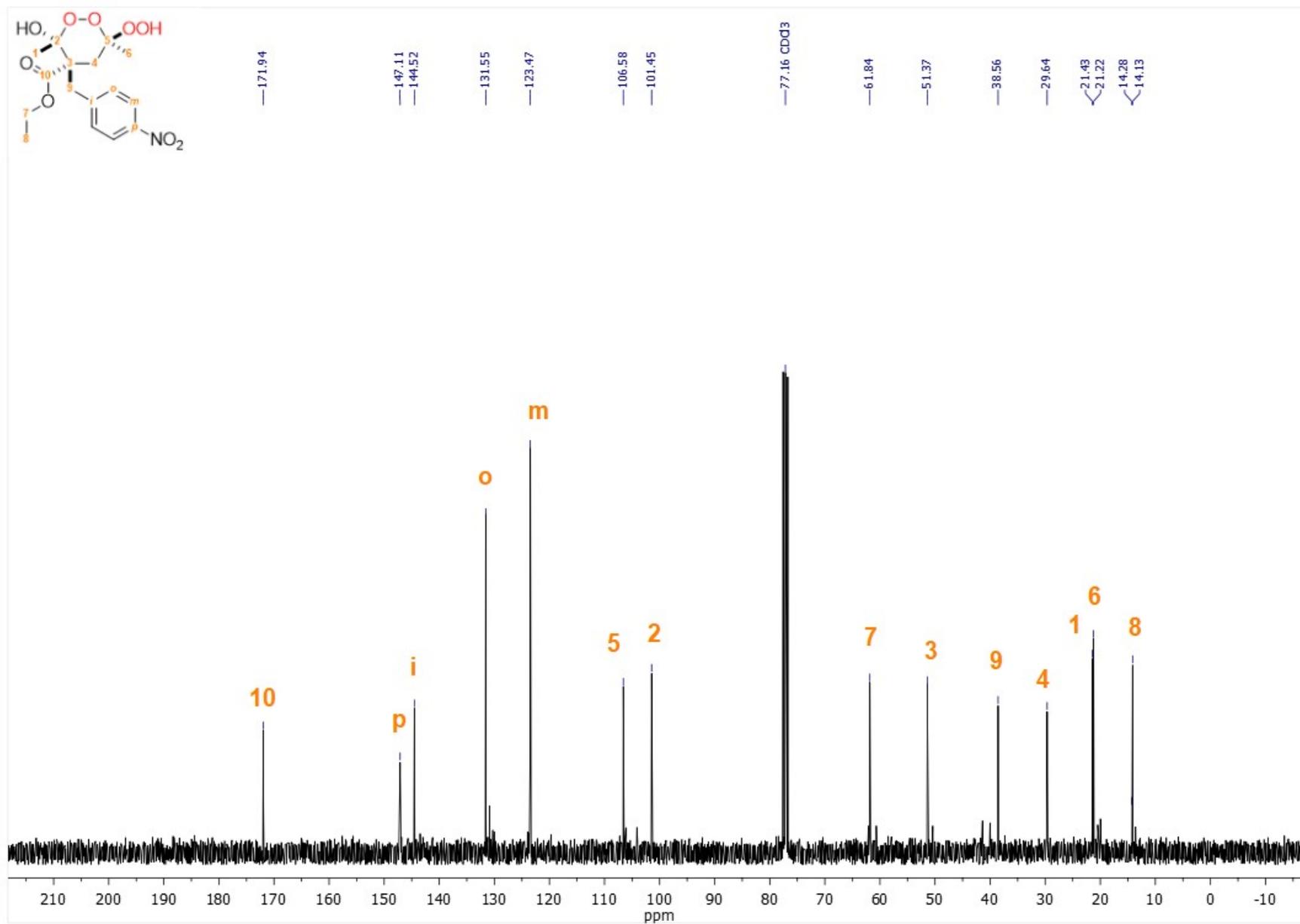
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-3-hydroperoxy-6-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a



¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a

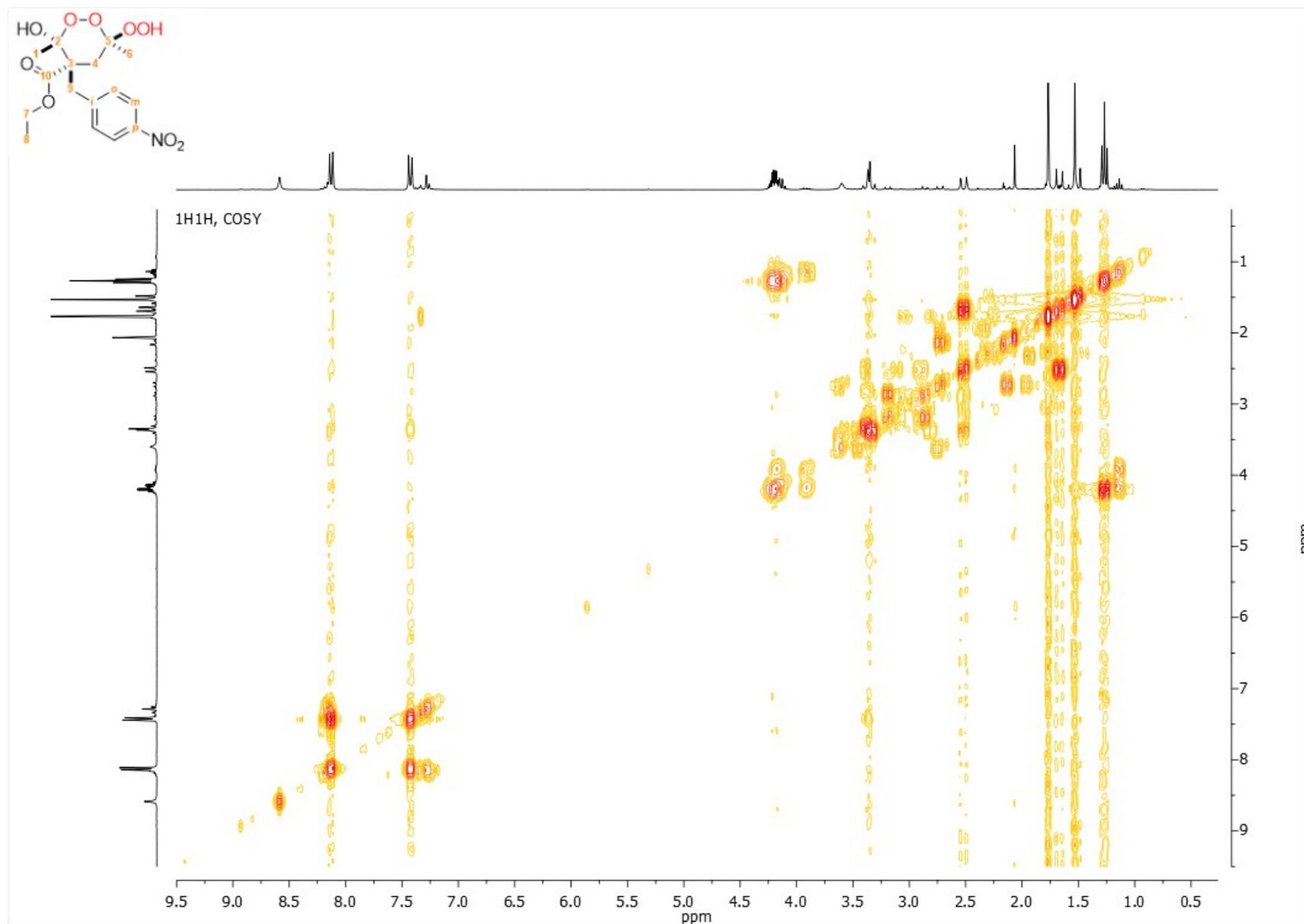


^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (3*R**,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a

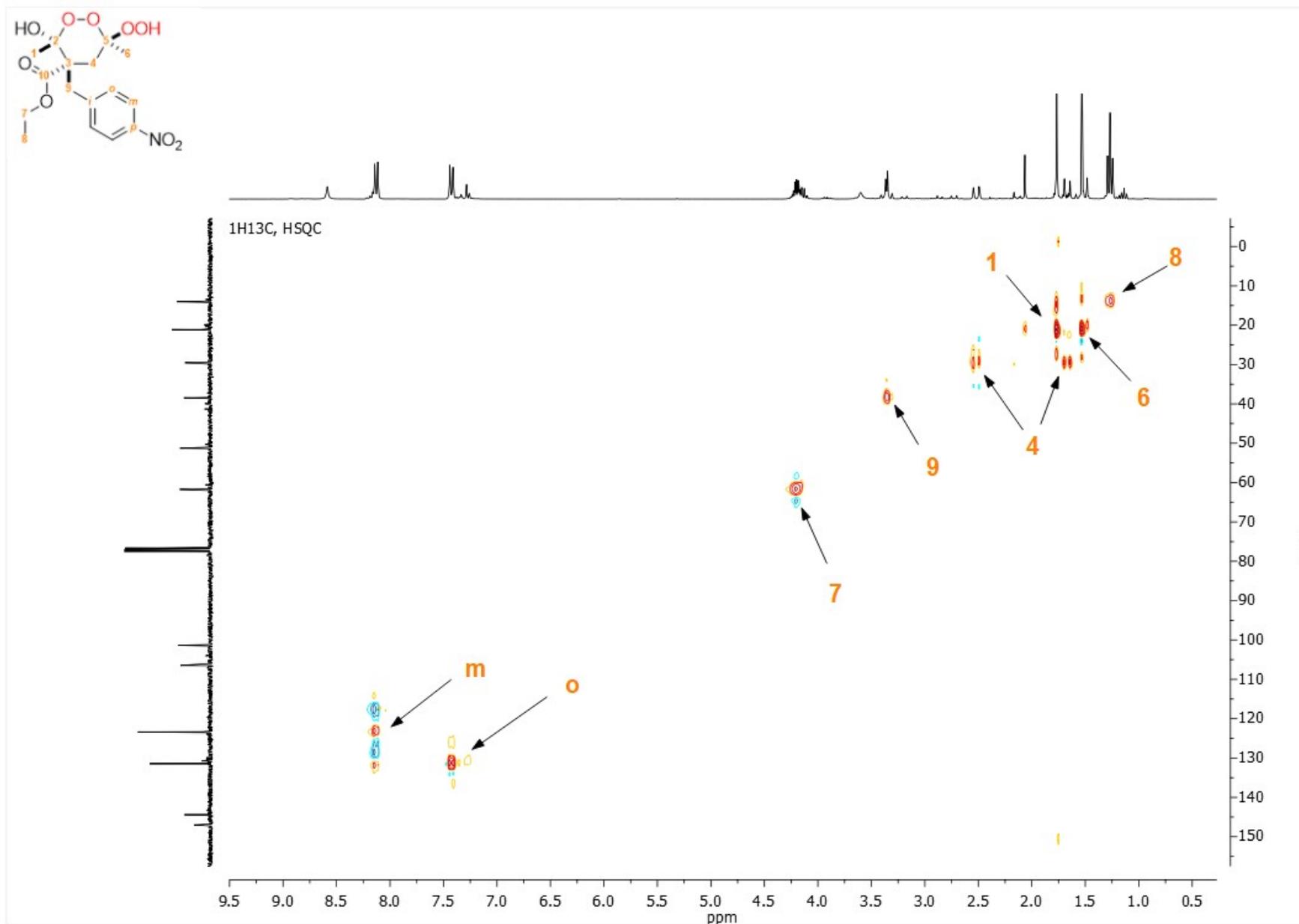


S147

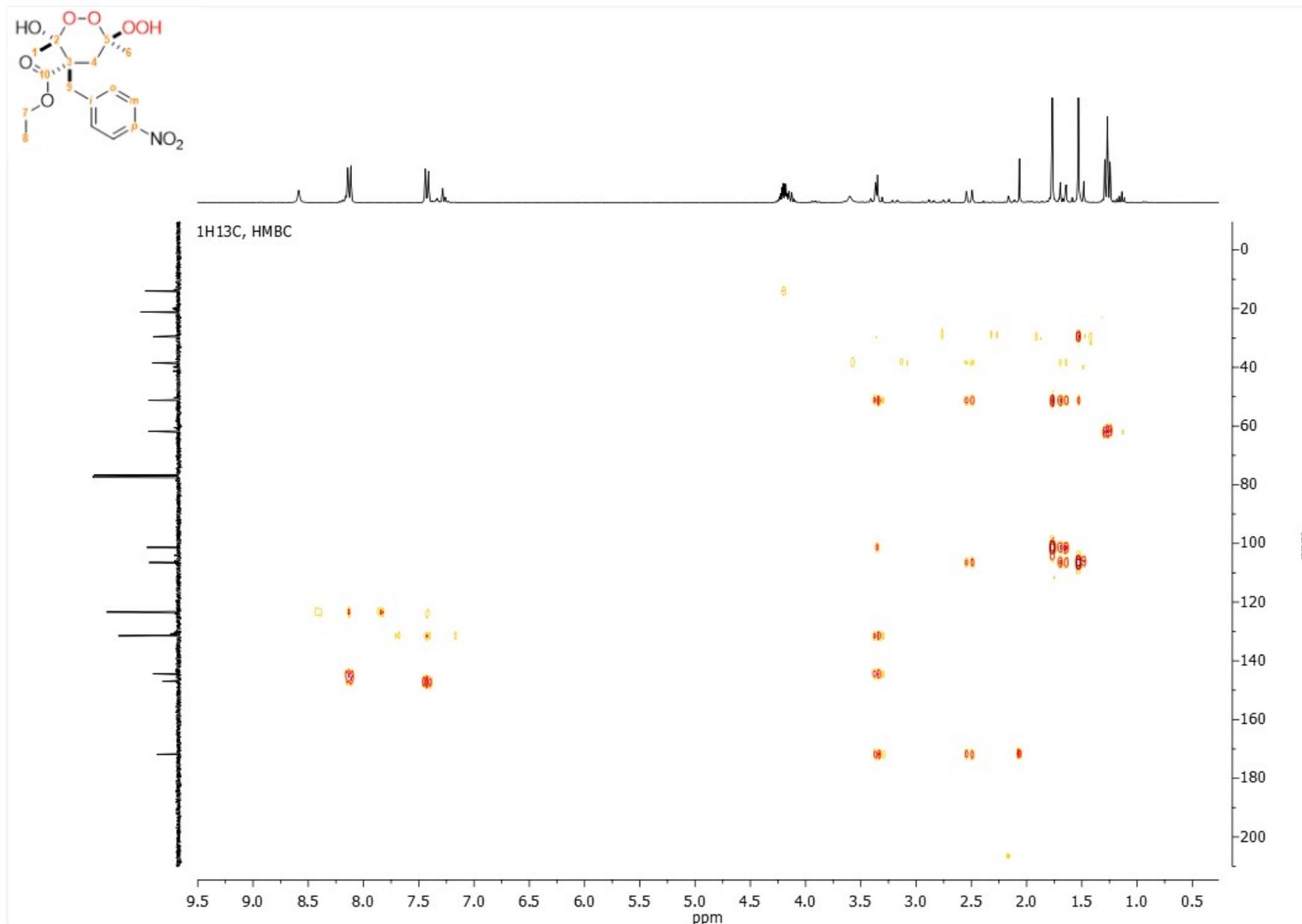
¹H – ¹H, COSY. Ethyl (3*R,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a**



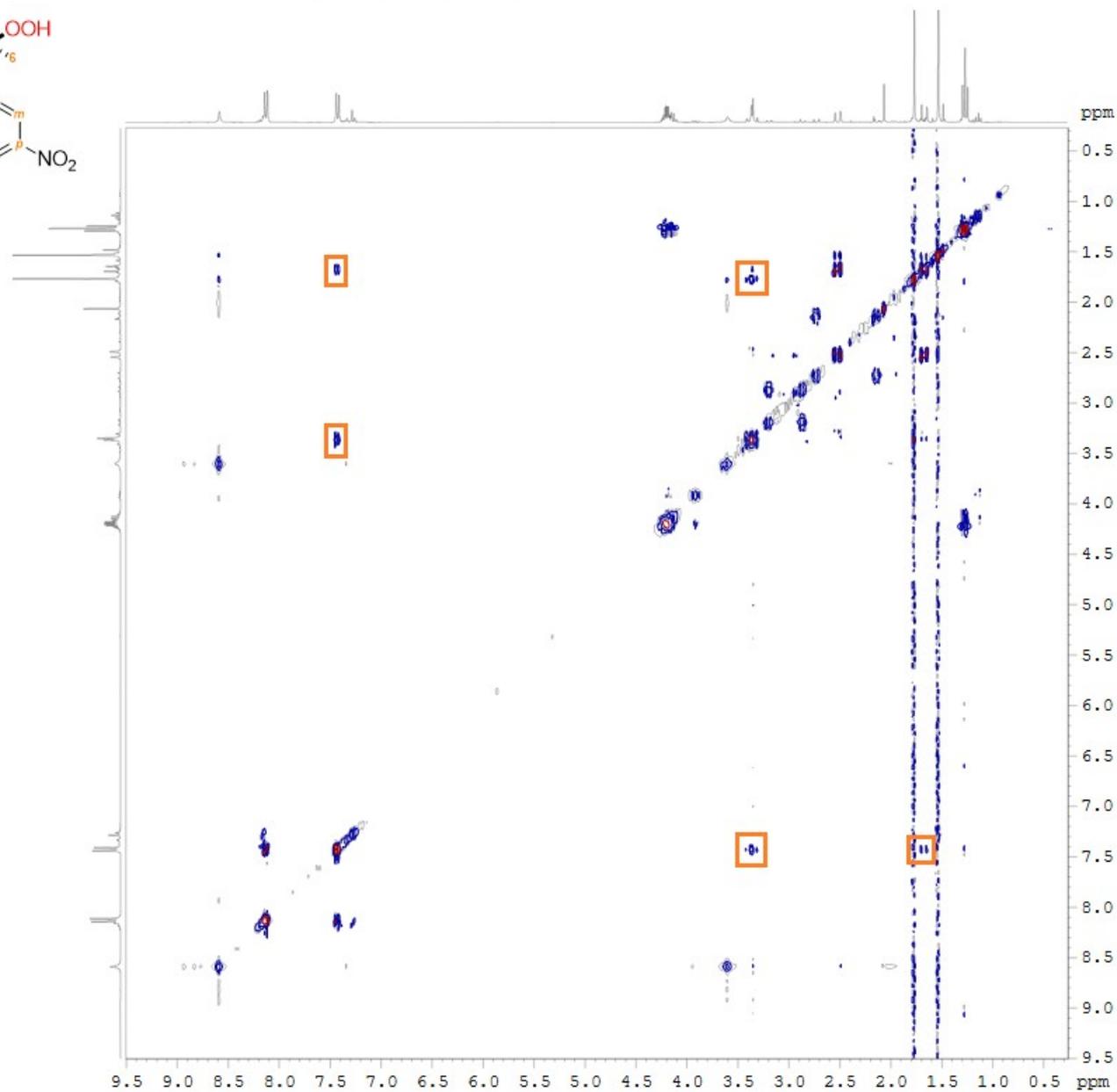
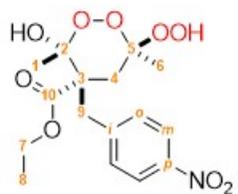
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (3*R**,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a



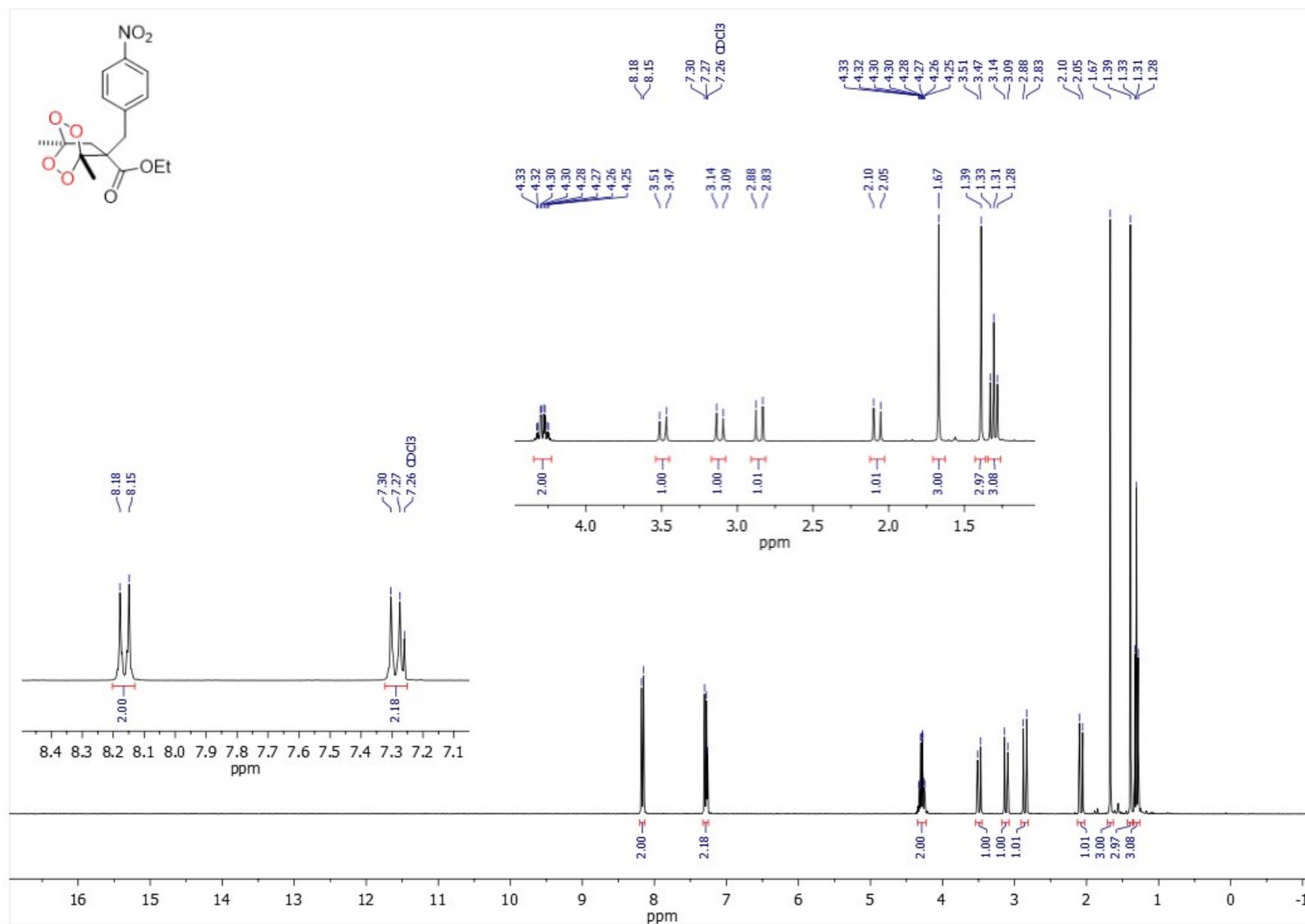
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (3*R**,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a



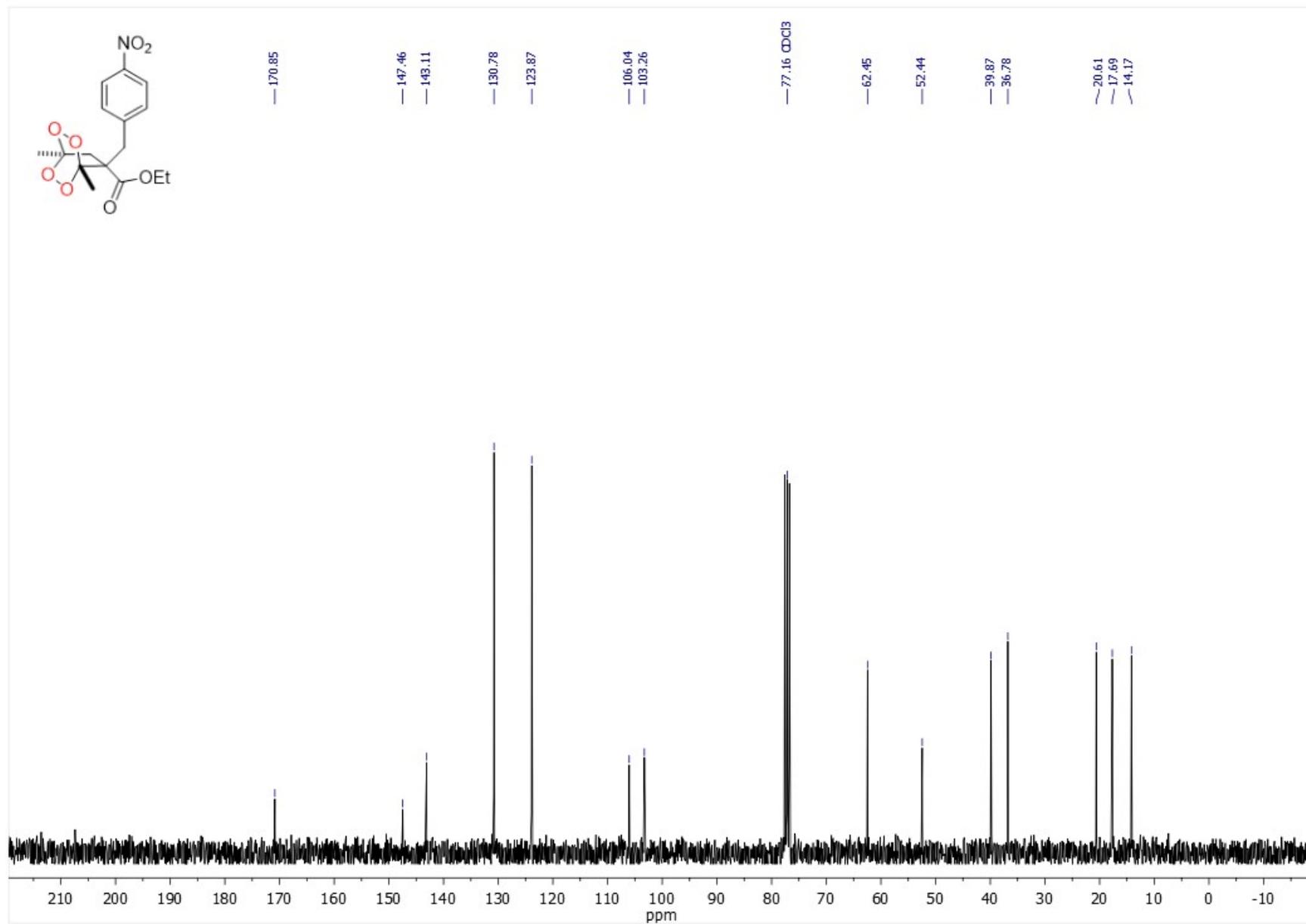
$^1\text{H} - ^1\text{H}$, NOESY. Ethyl (3*R**,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a



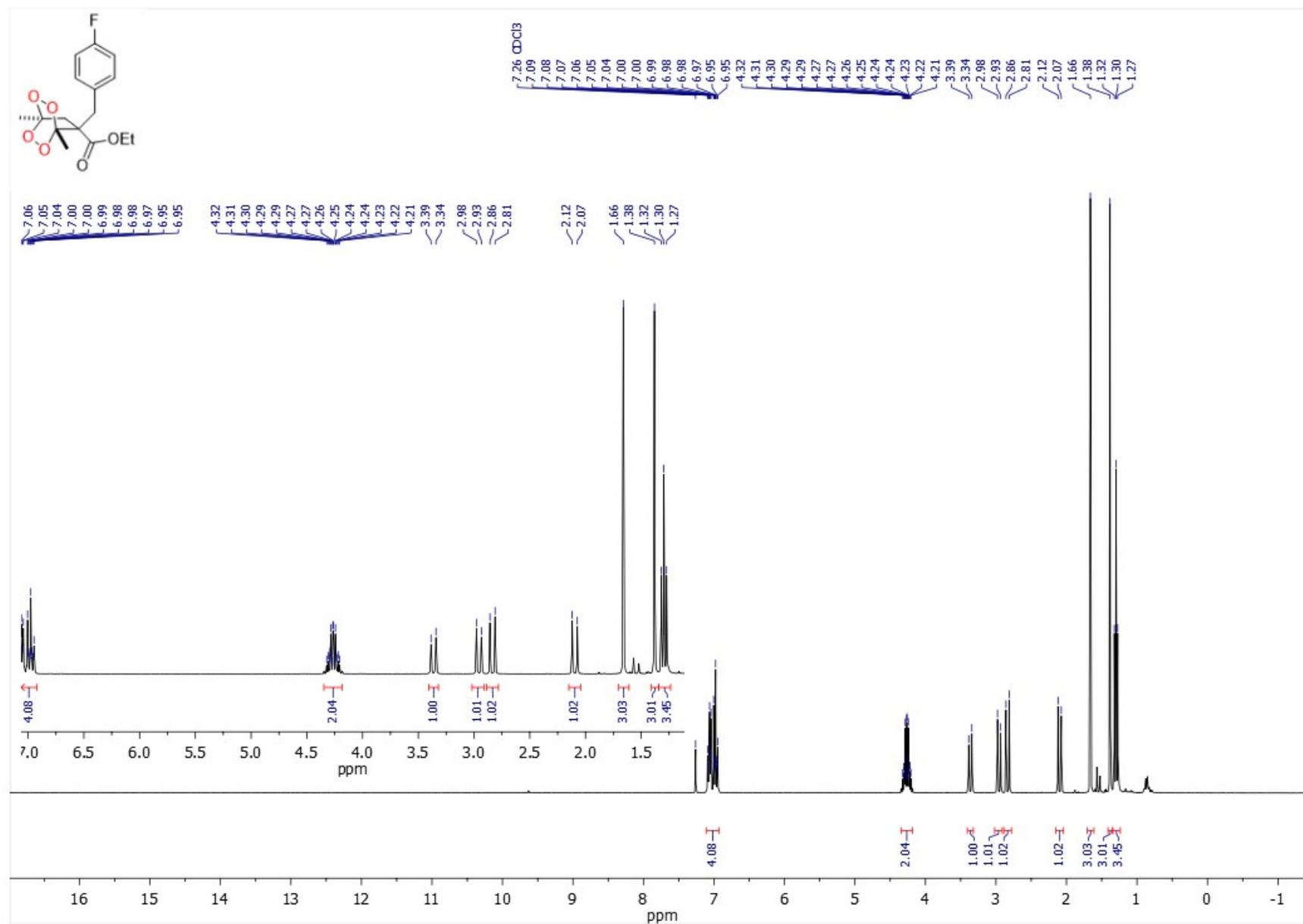
¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-1,4-dimethyl-7-(4-nitrobenzyl)-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5a



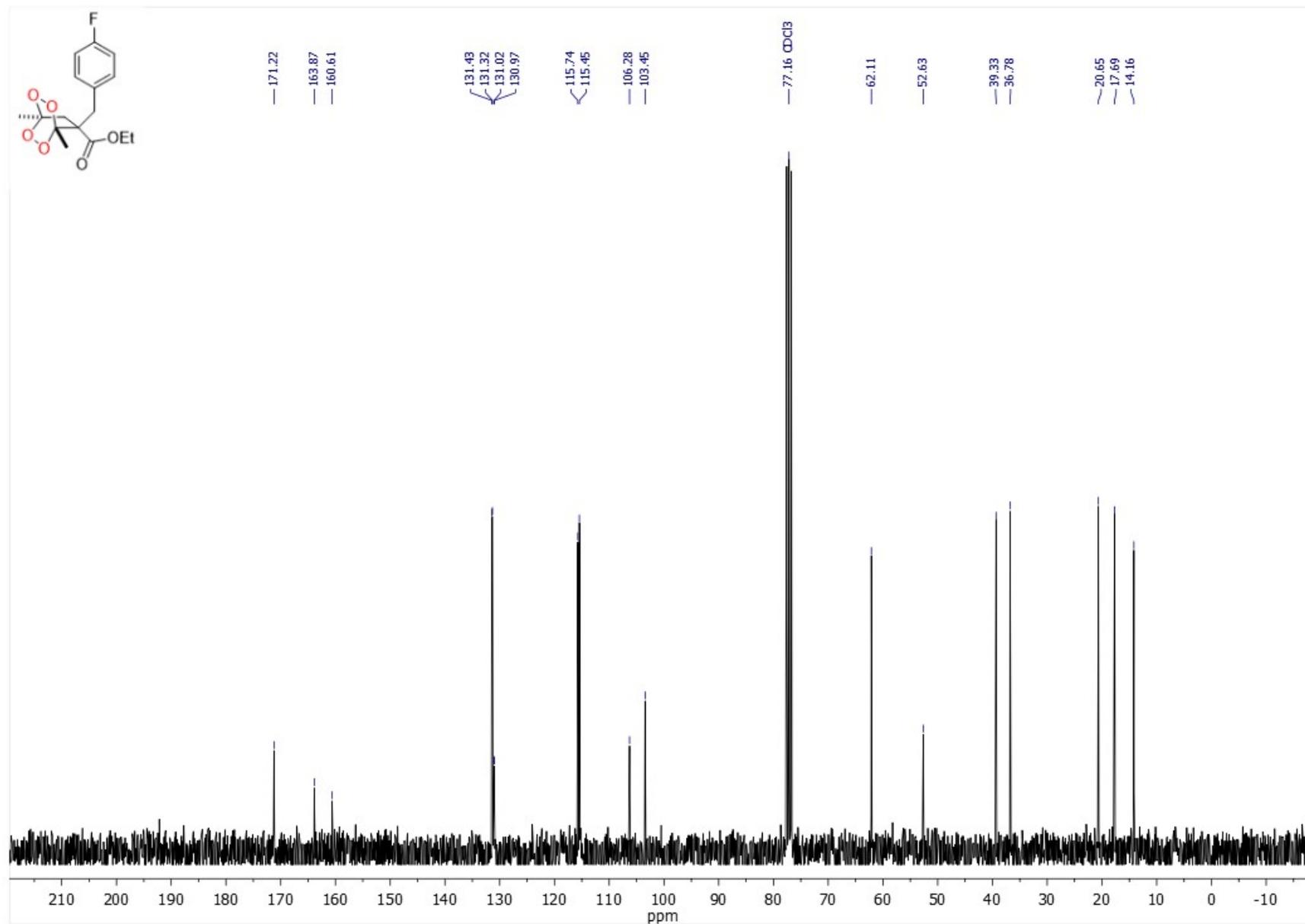
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-1,4-dimethyl-7-(4-nitrobenzyl)-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5a



¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-(4-fluorobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5b

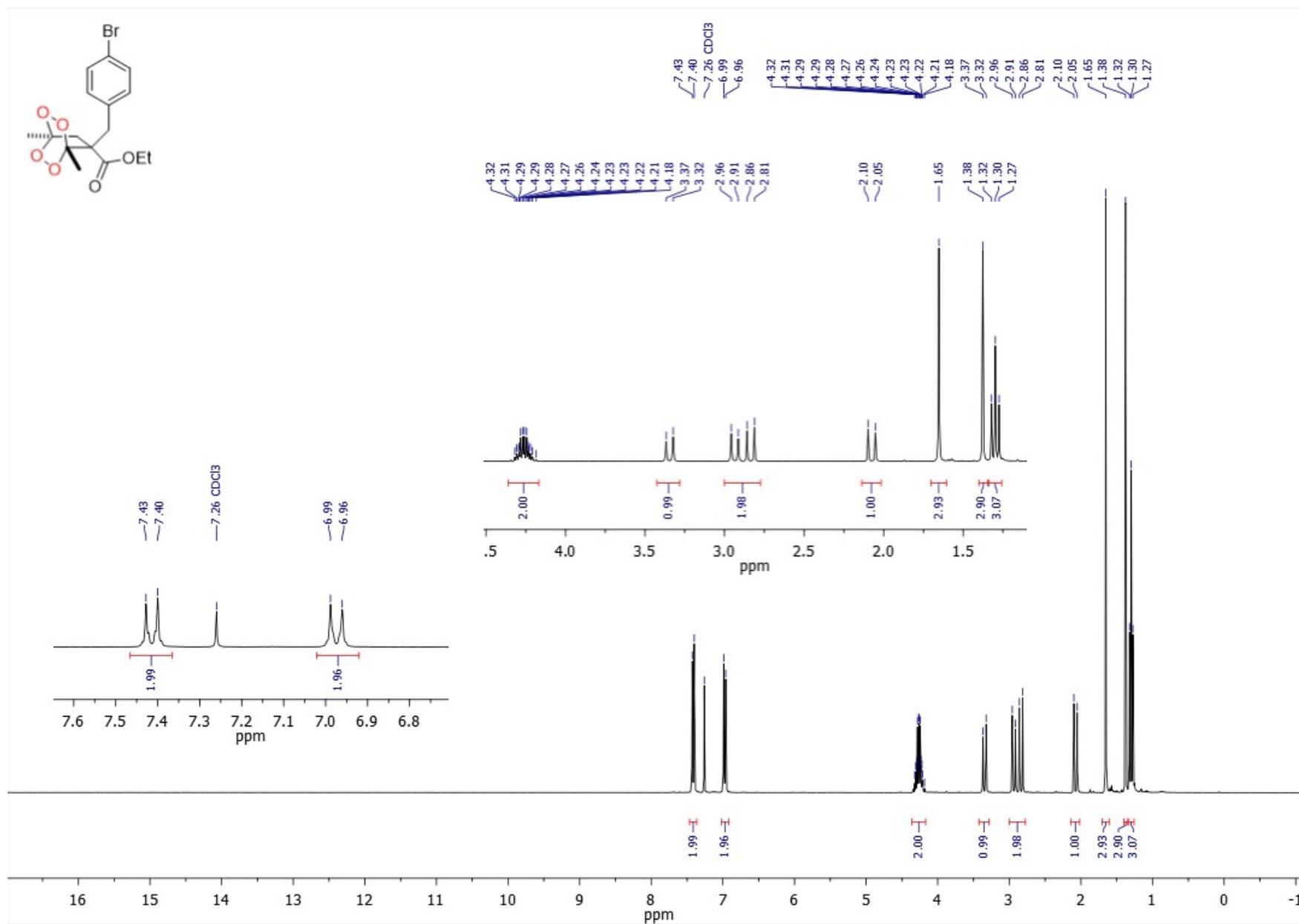


¹³C NMR (75.48 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-(4-fluorobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5b

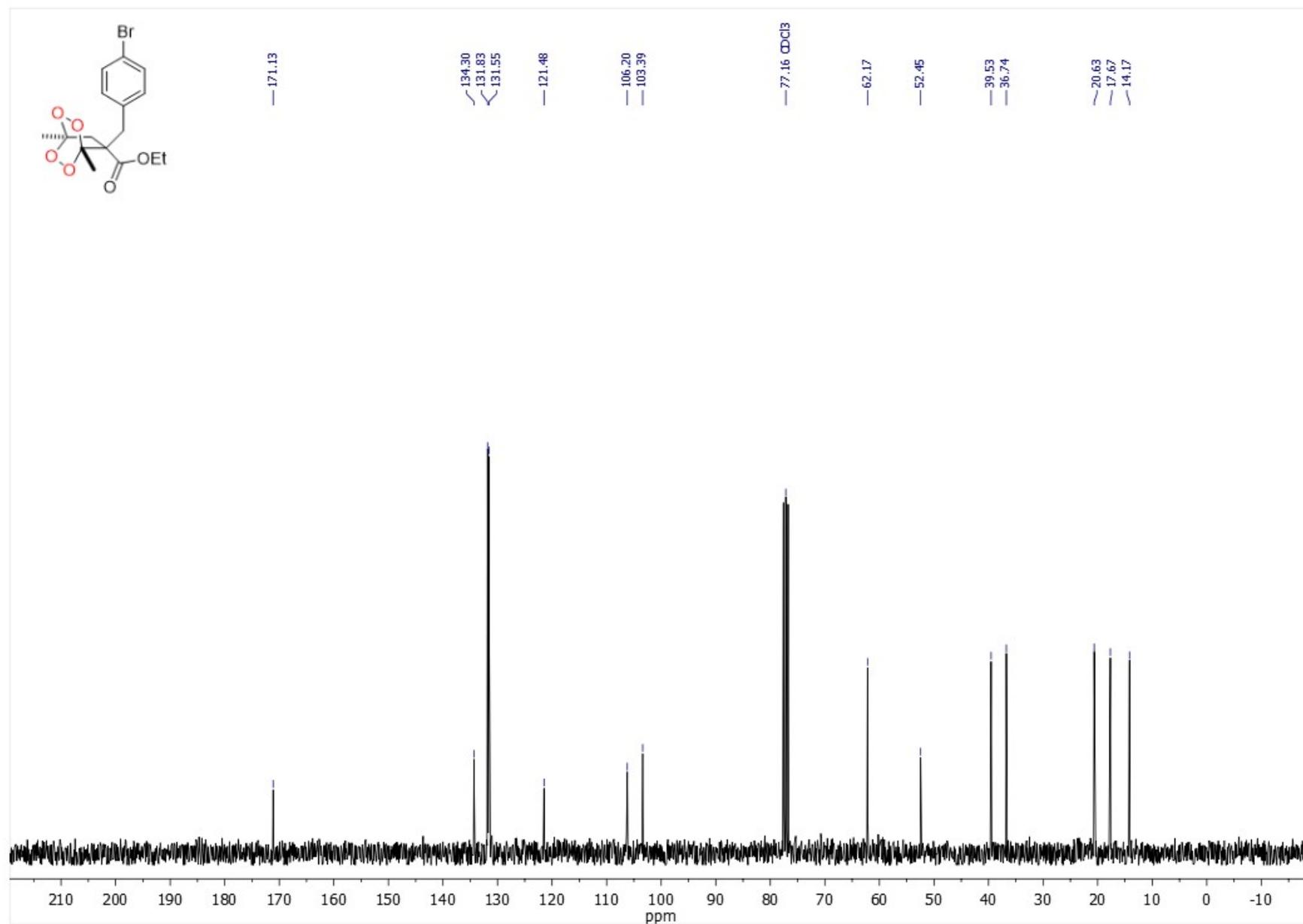


S155

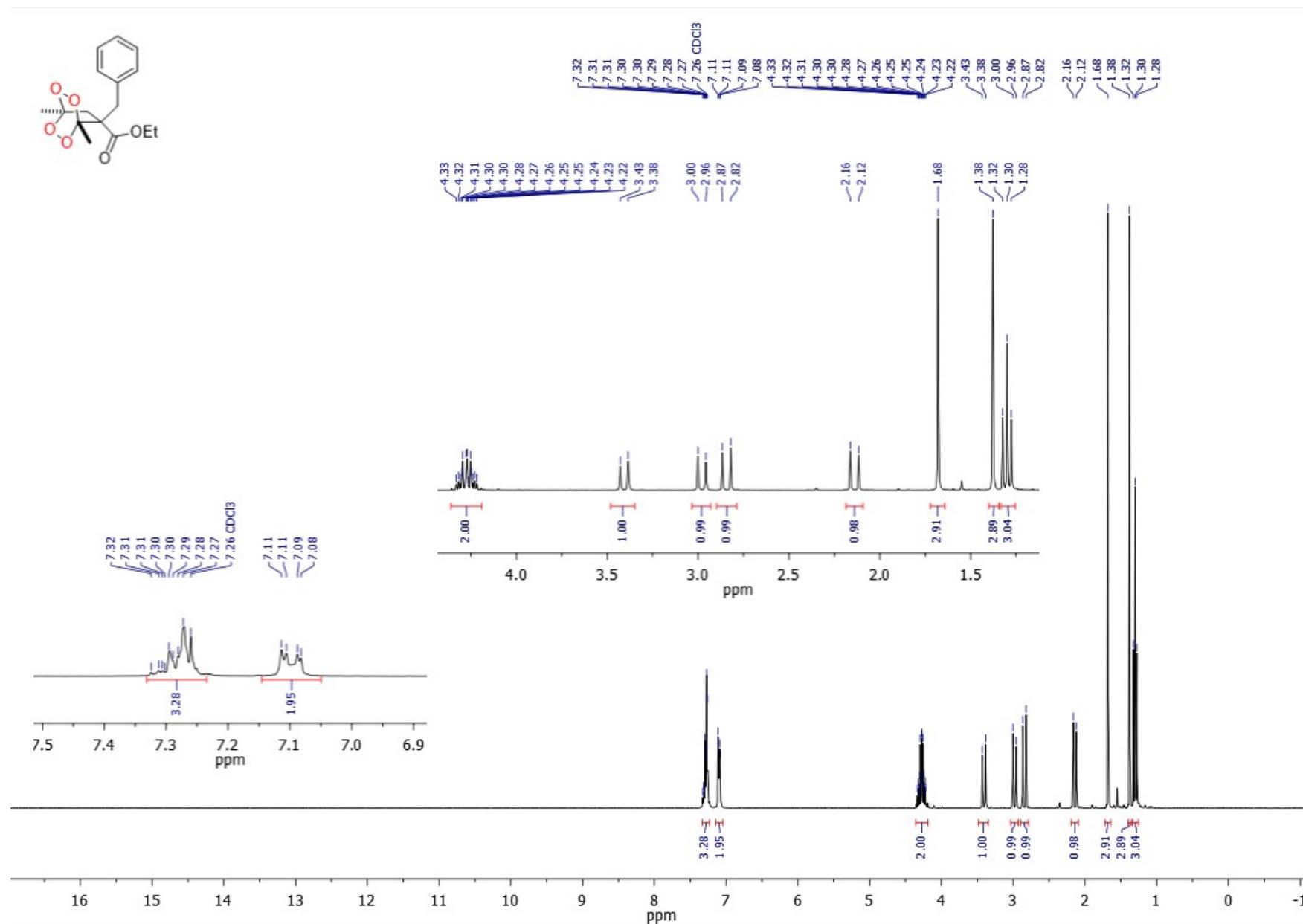
¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-(4-bromobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5c



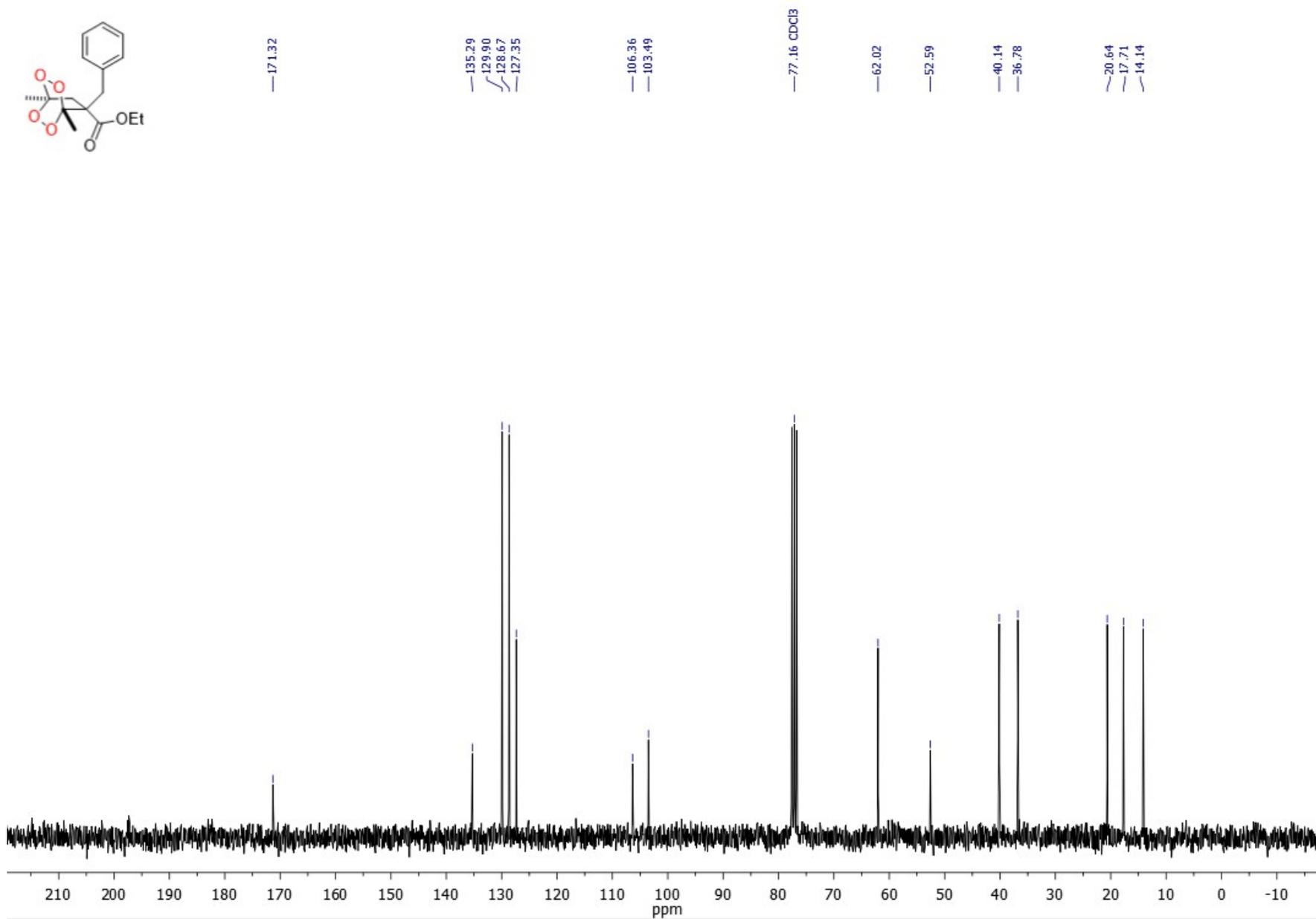
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-(4-bromobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, **5c**



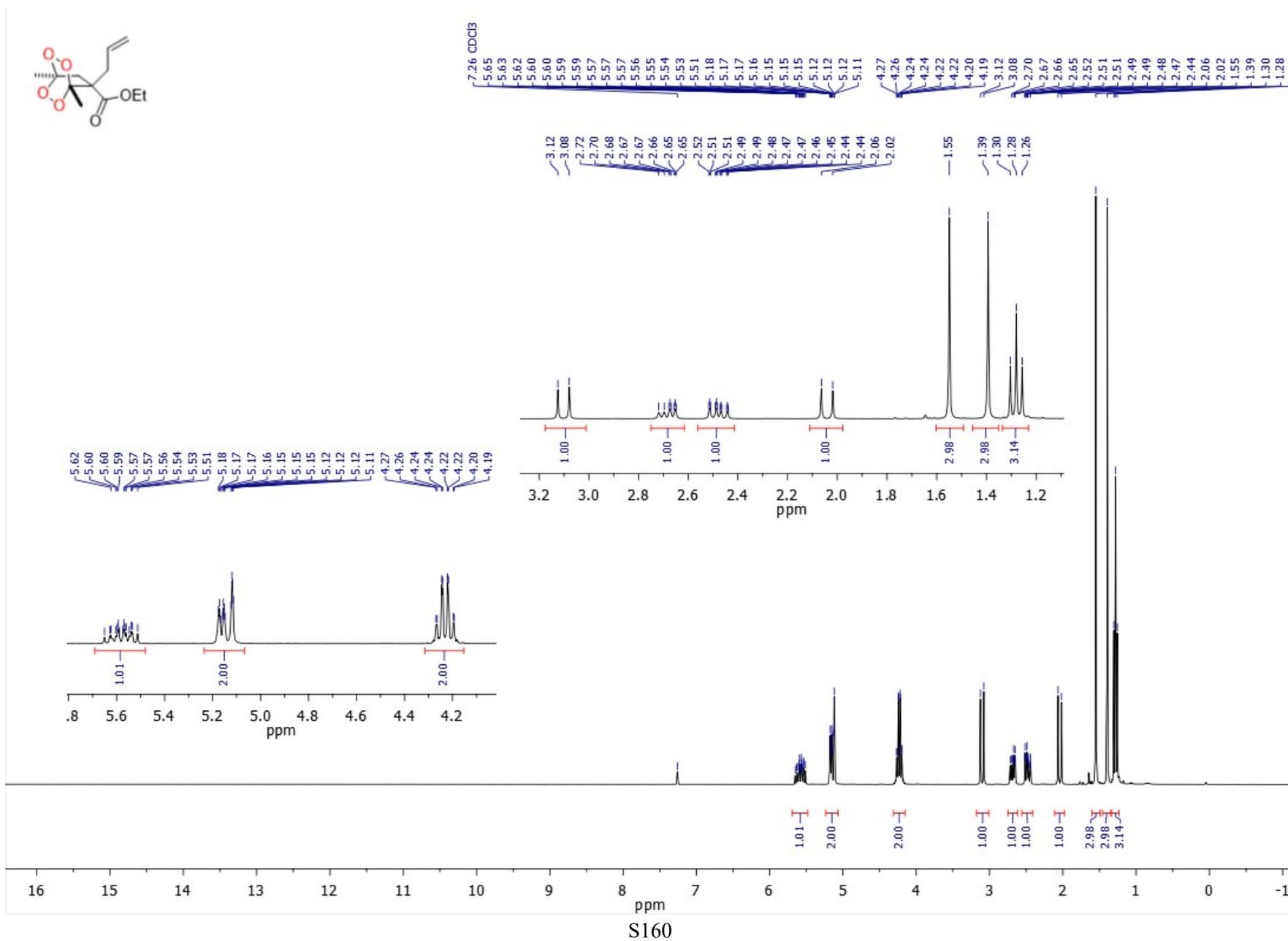
¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-benzyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5e



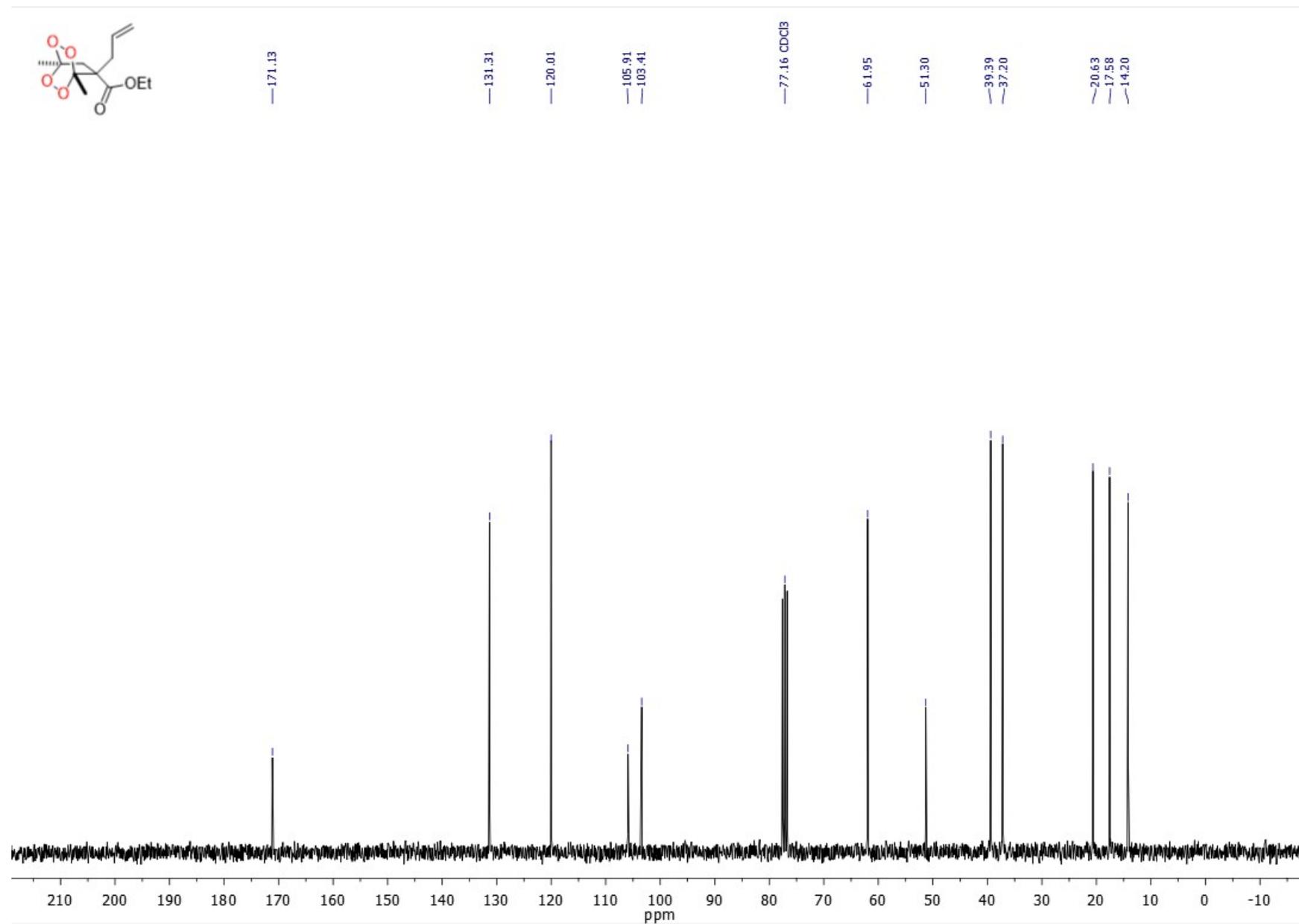
^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (1*R**,4*R**,7*S**)-7-benzyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, **5e**



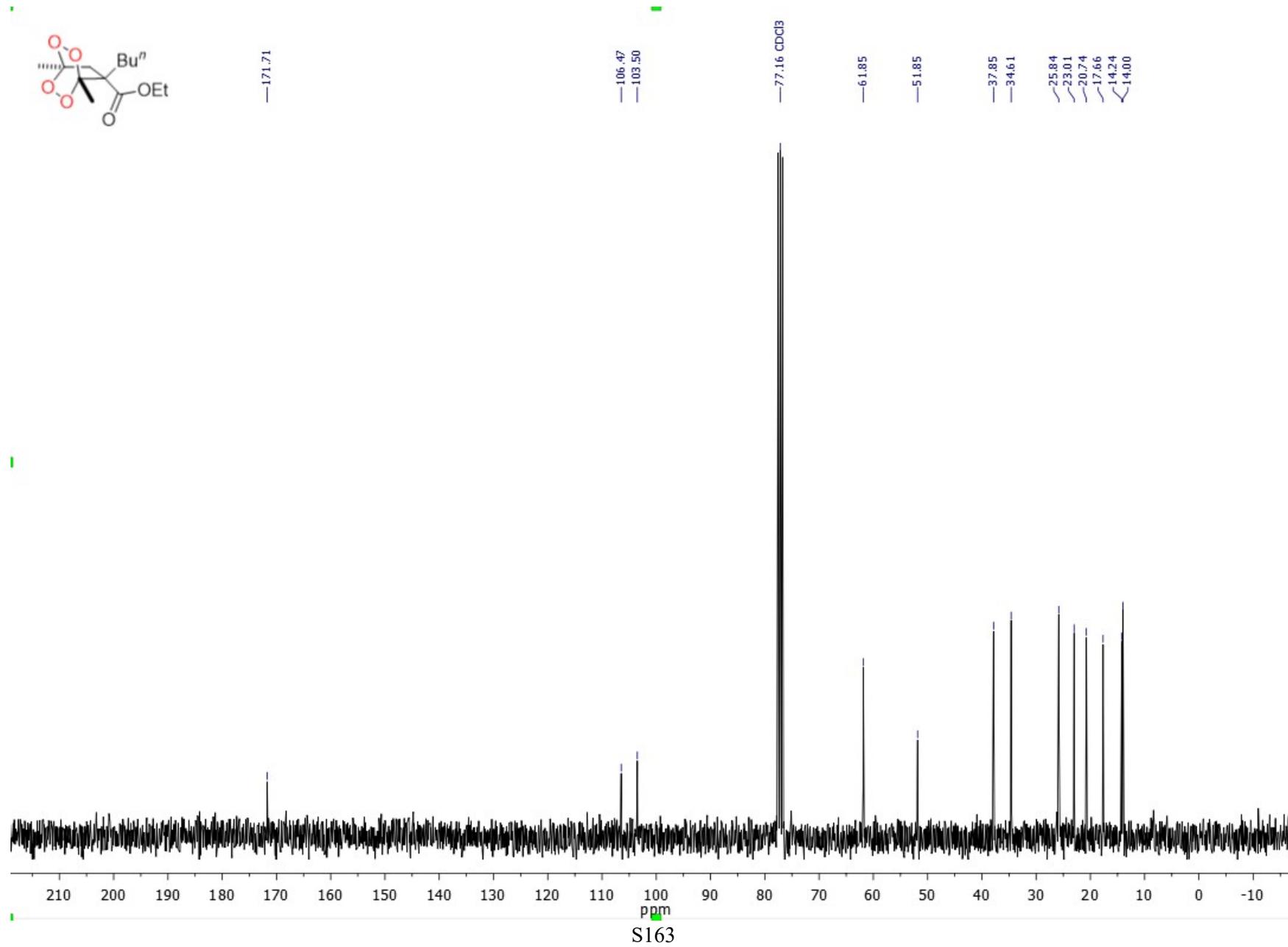
¹H NMR (300.13 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-allyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5f



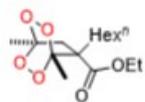
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-allyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5f



¹³C NMR (75.48 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-butyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5g



¹³C NMR (75.48 MHz, CDCl₃). Ethyl (1*R**,4*R**,7*S**)-7-hexyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5h



—171.70

—106.45

—103.49

—77.16 CDCl₃

—61.83

—51.87

—37.84

—34.88

—31.65

—29.54

—23.61

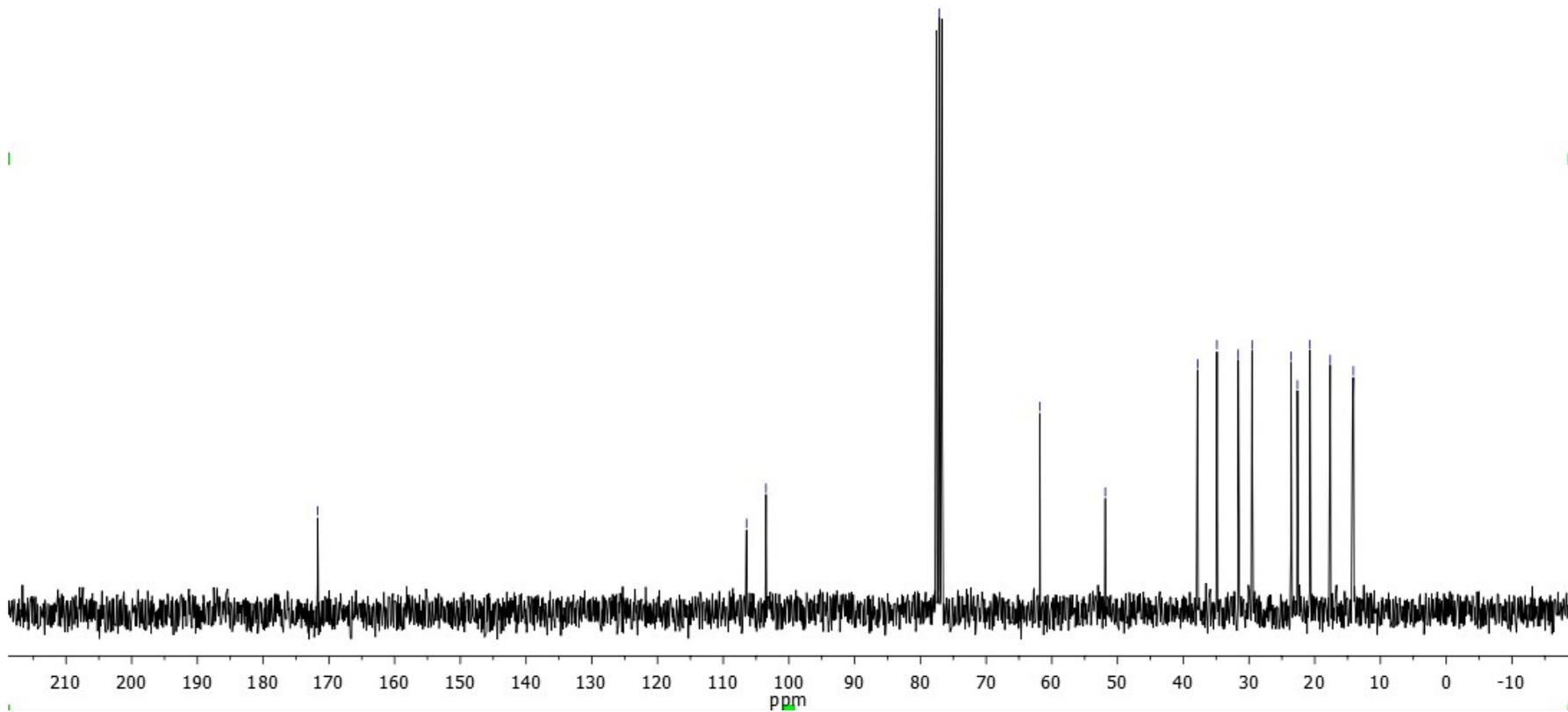
—22.64

—20.73

—17.65

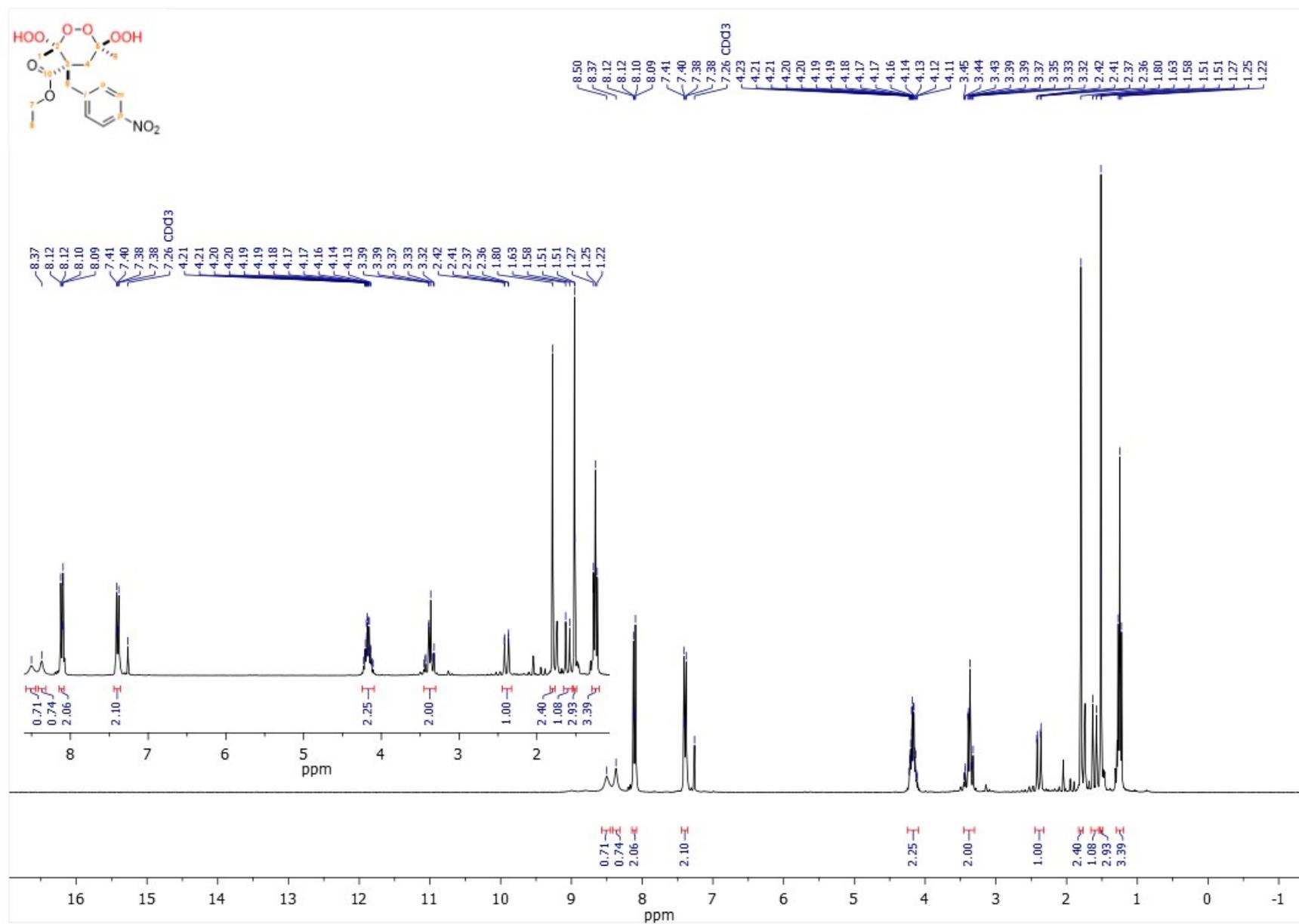
—14.74

—14.13

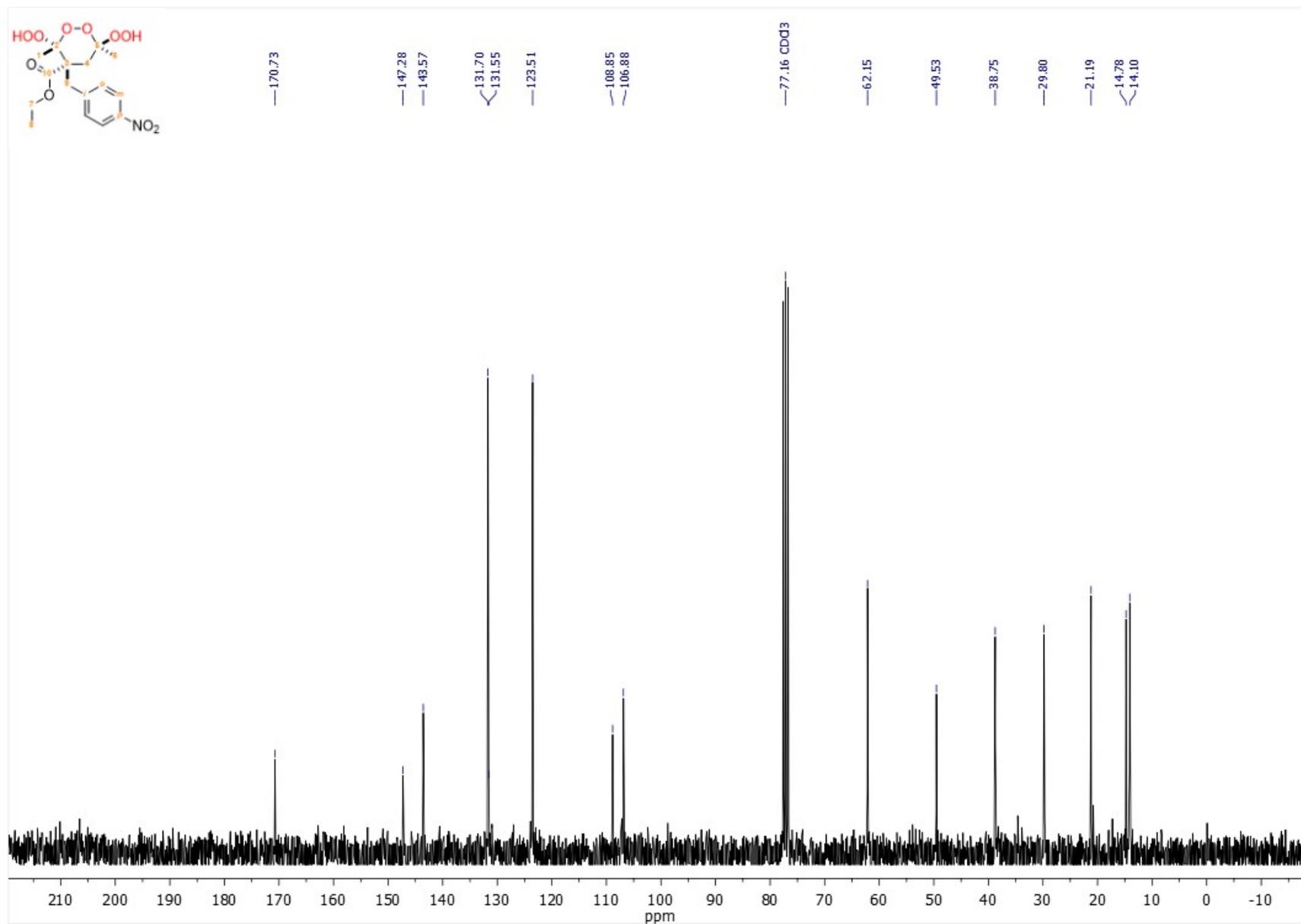


S165

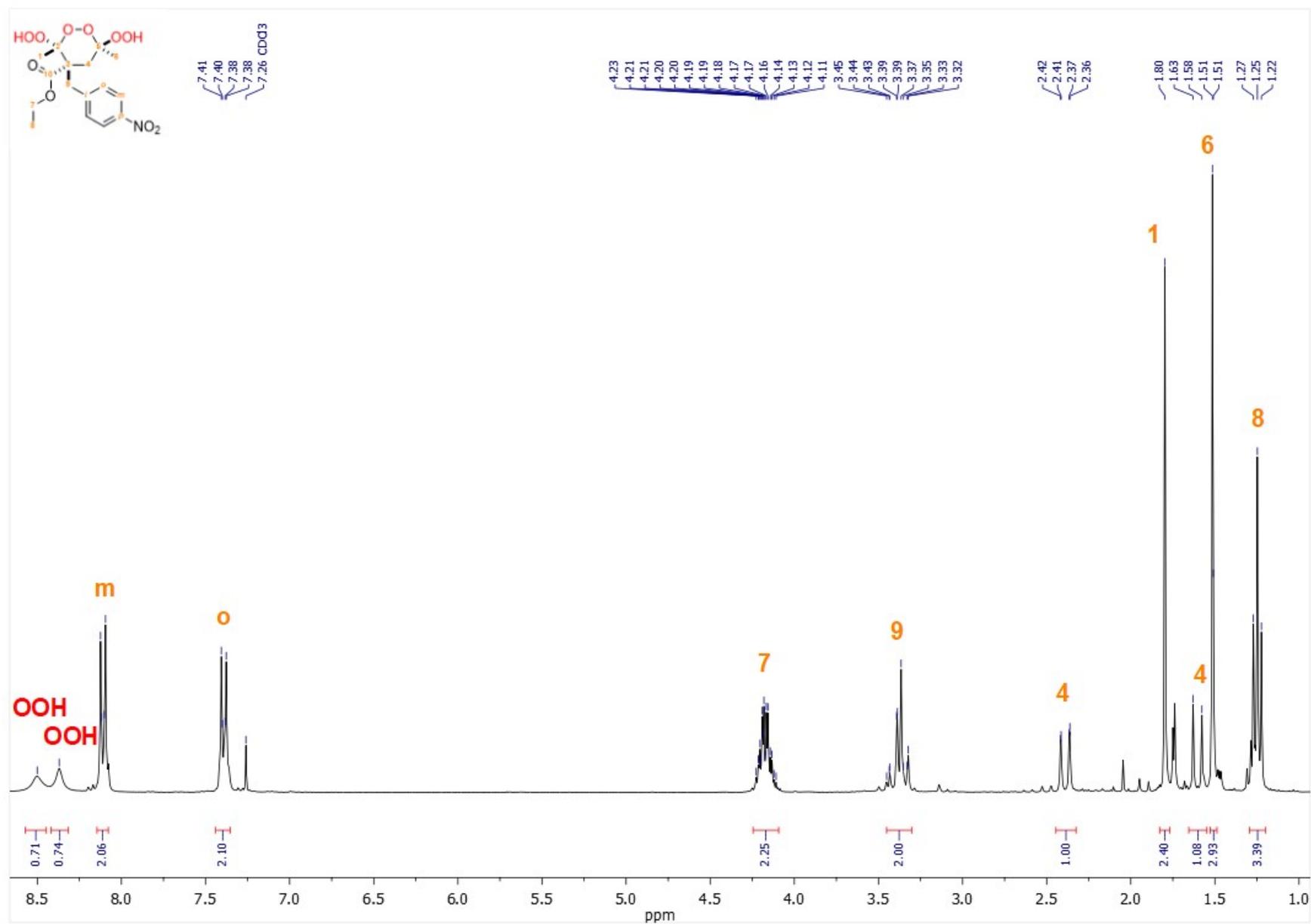
¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



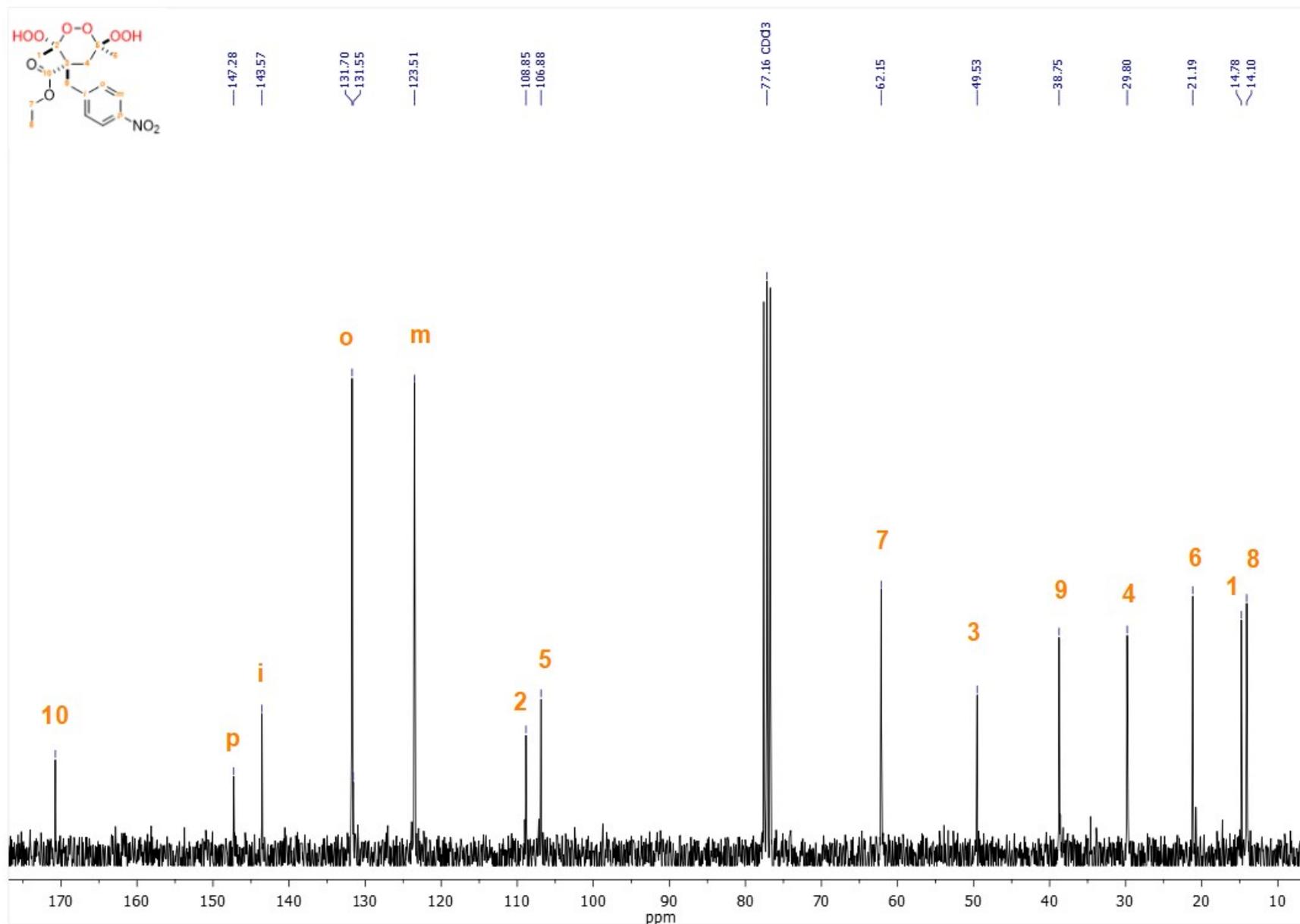
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



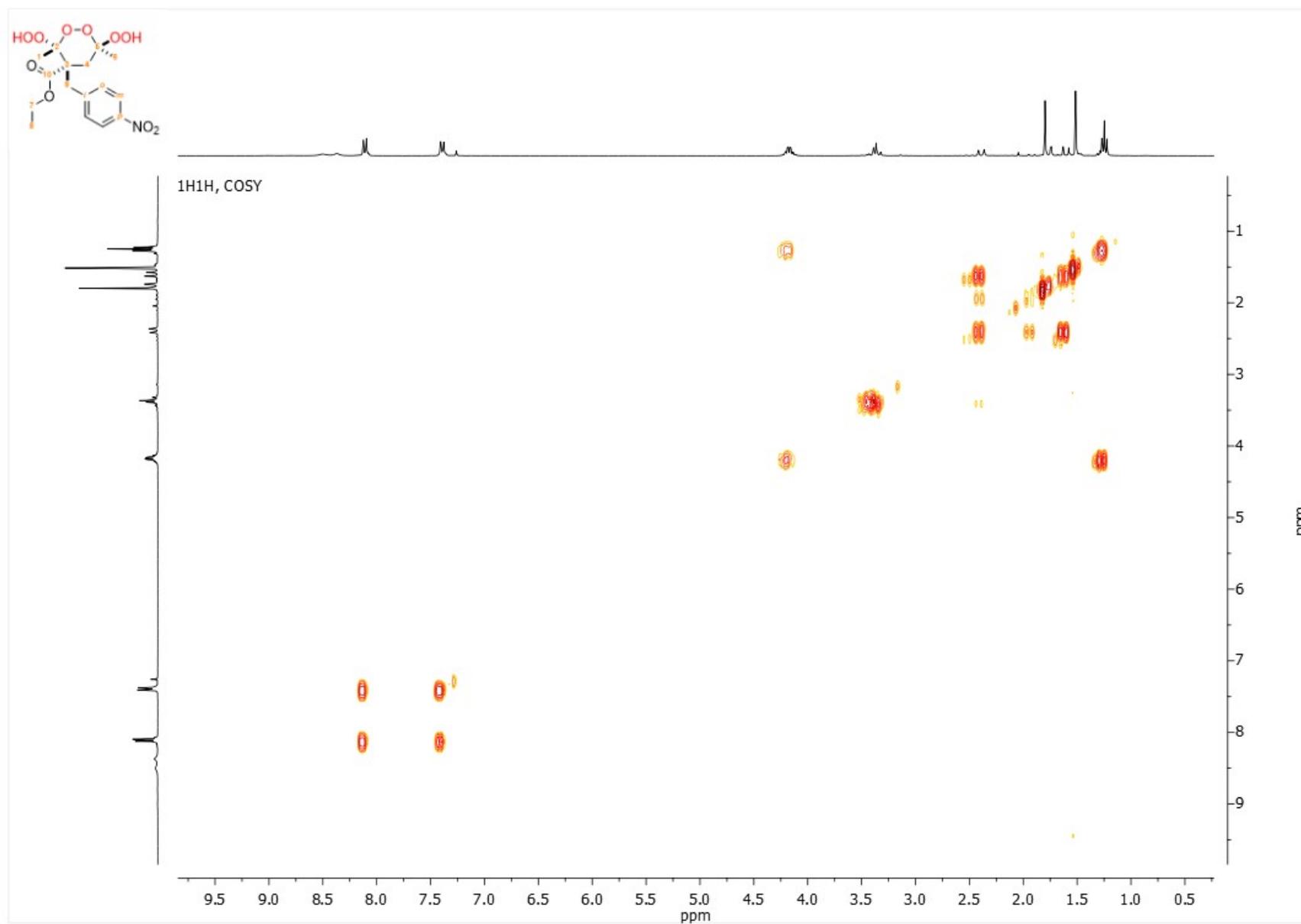
¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



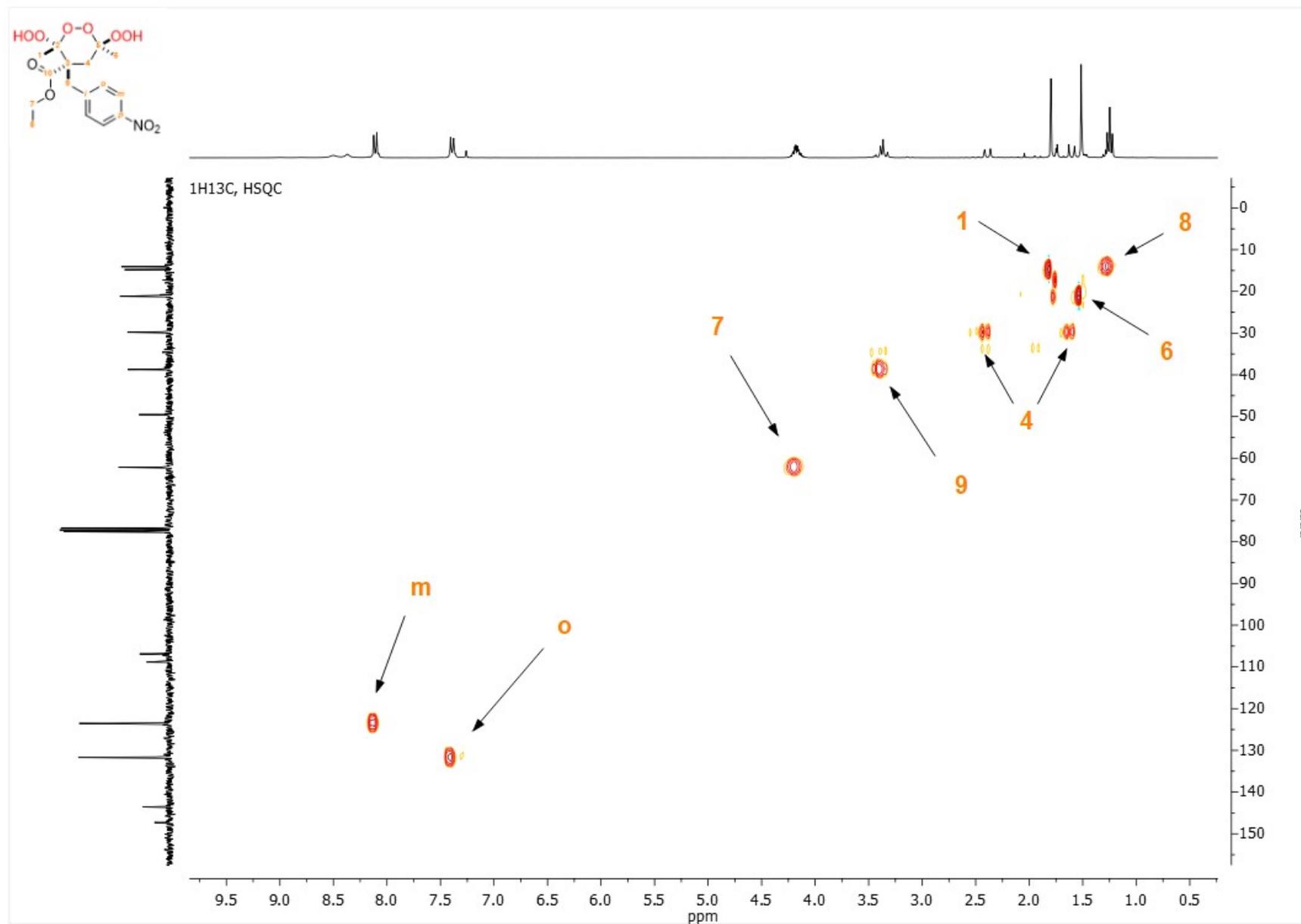
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



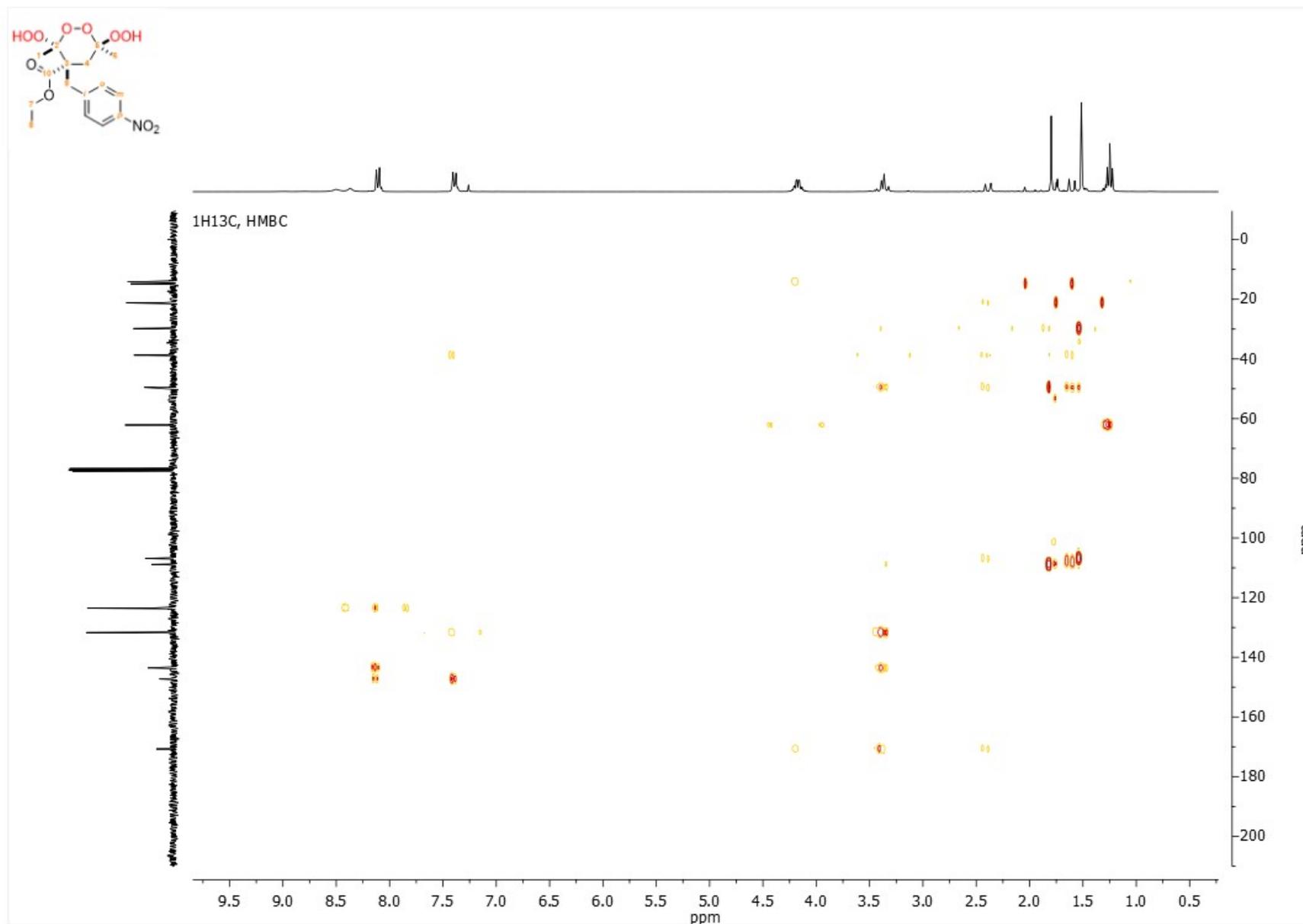
$^1\text{H} - ^1\text{H}$, COSY. Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



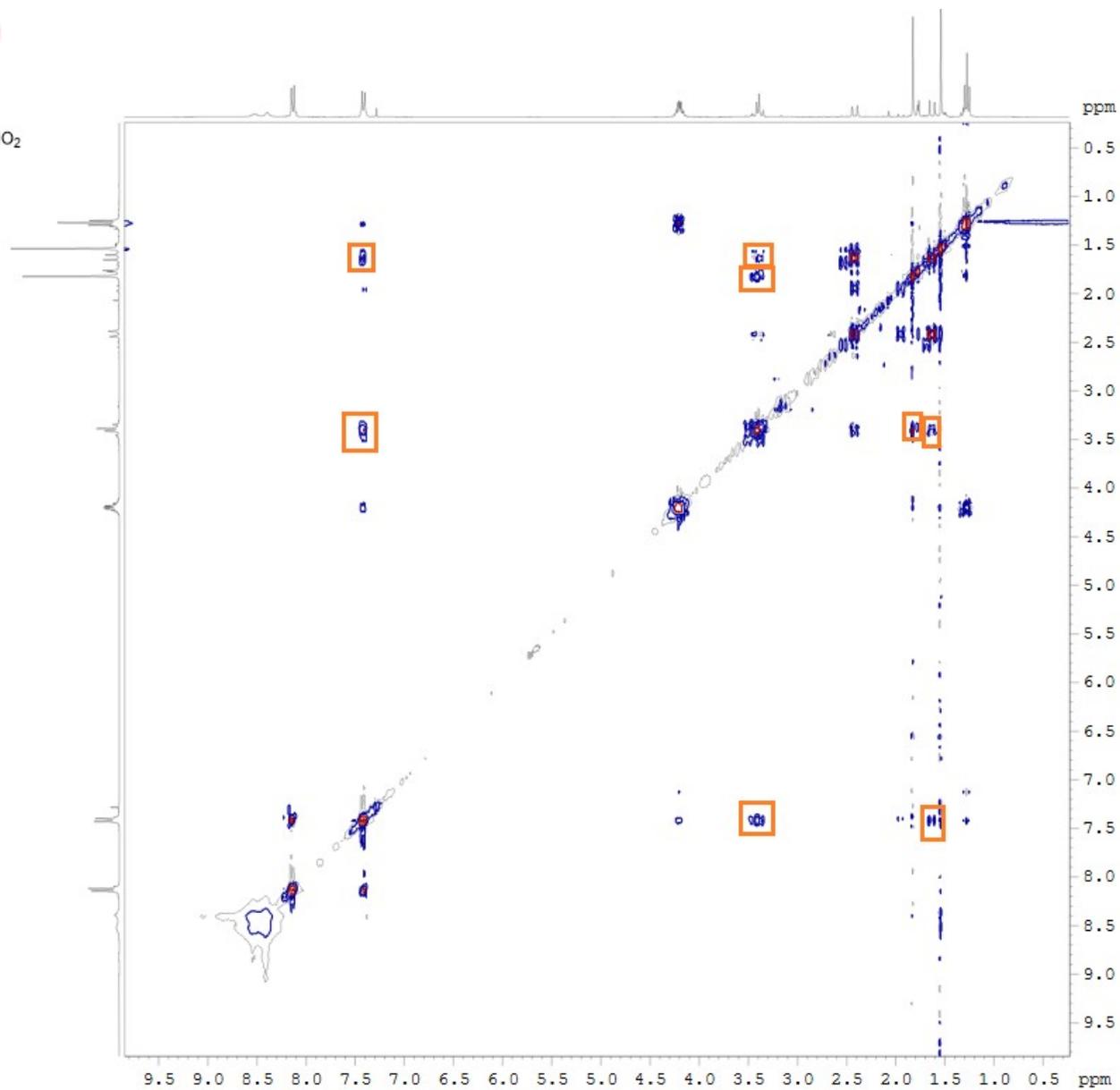
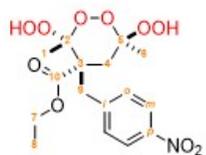
$^1\text{H} - ^{13}\text{C}$, HSQC. Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



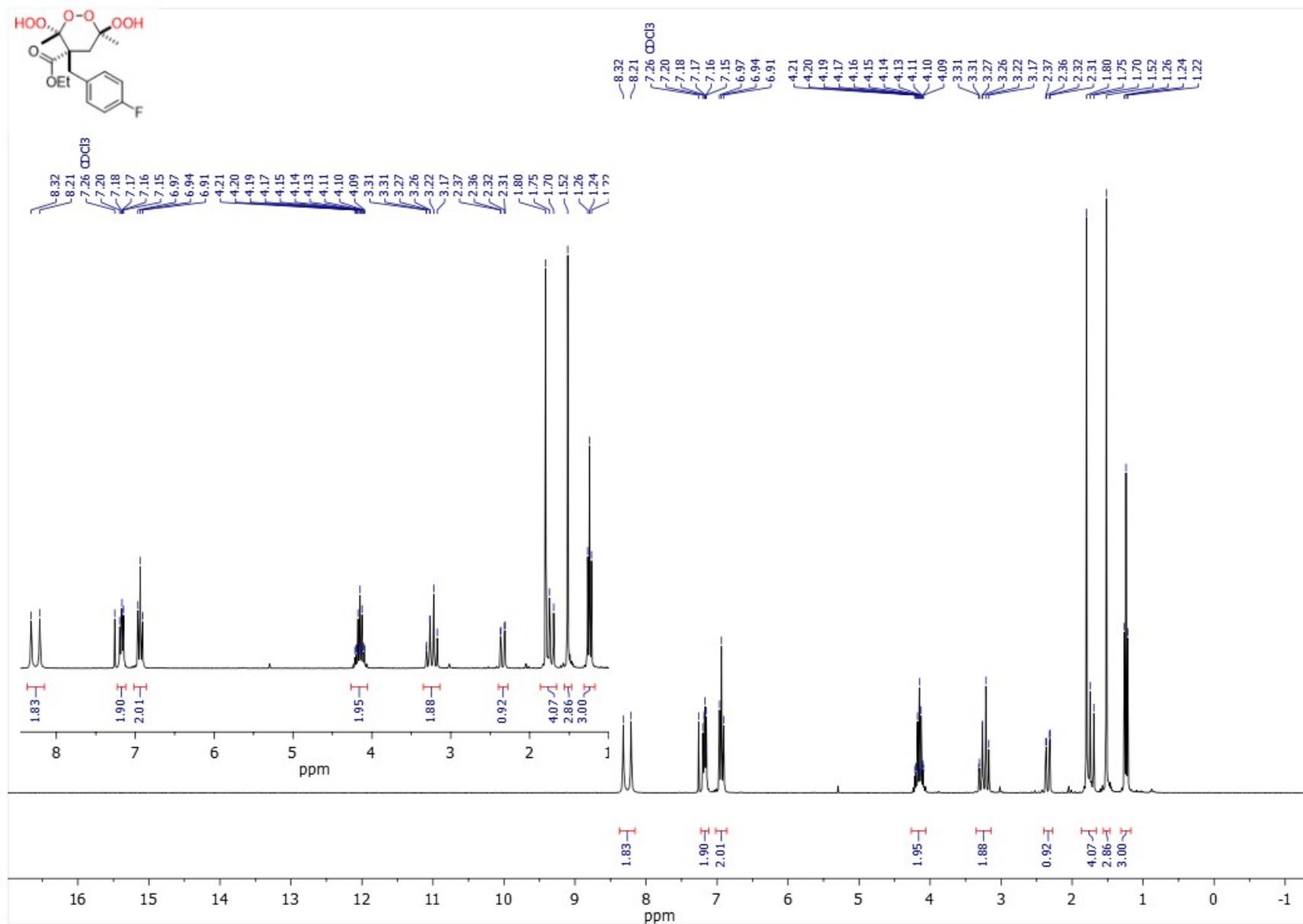
$^1\text{H} - ^{13}\text{C}$, HMBC. Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



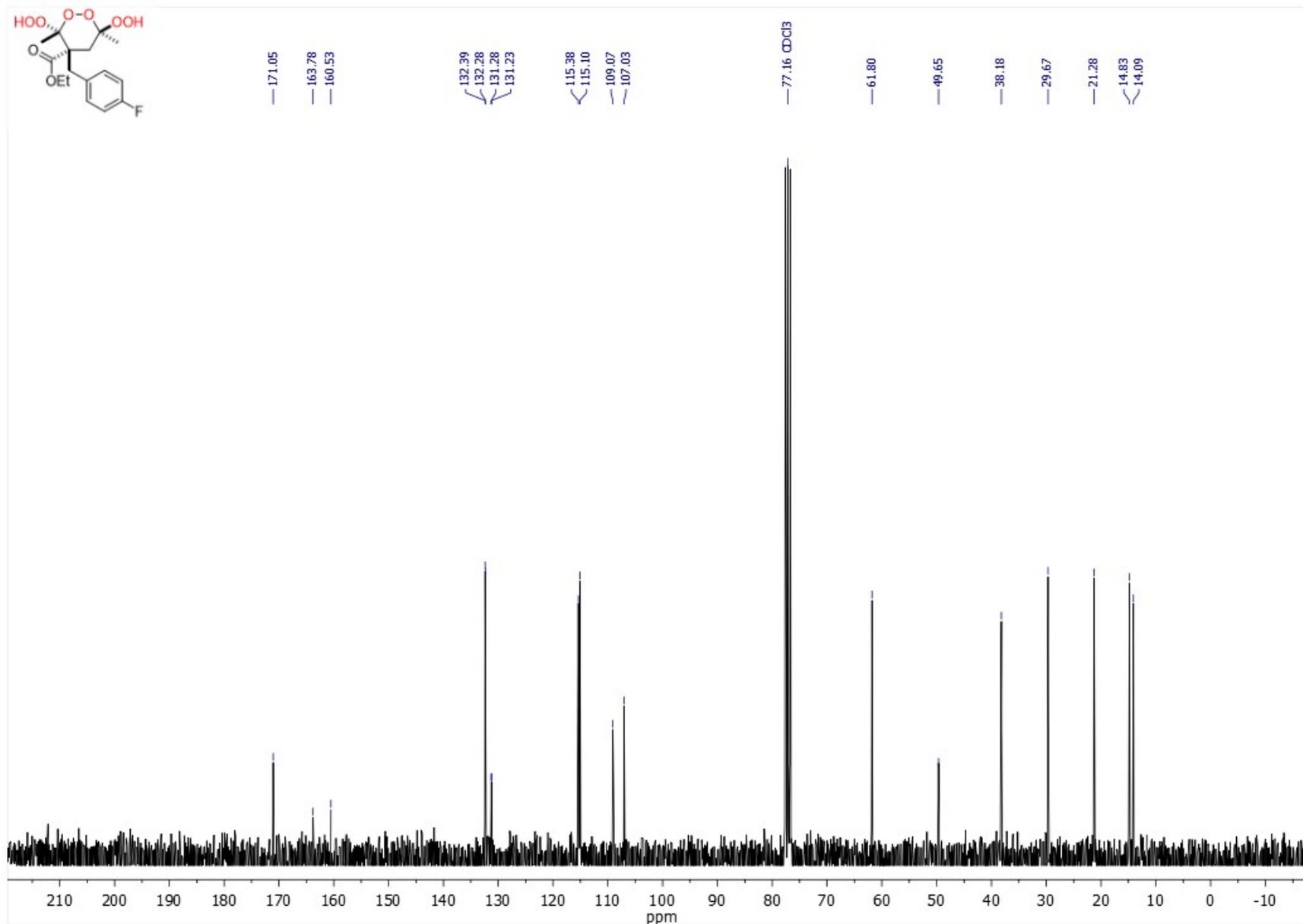
$^1\text{H} - ^1\text{H}$, NOESY. Ethyl (3*R**,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a



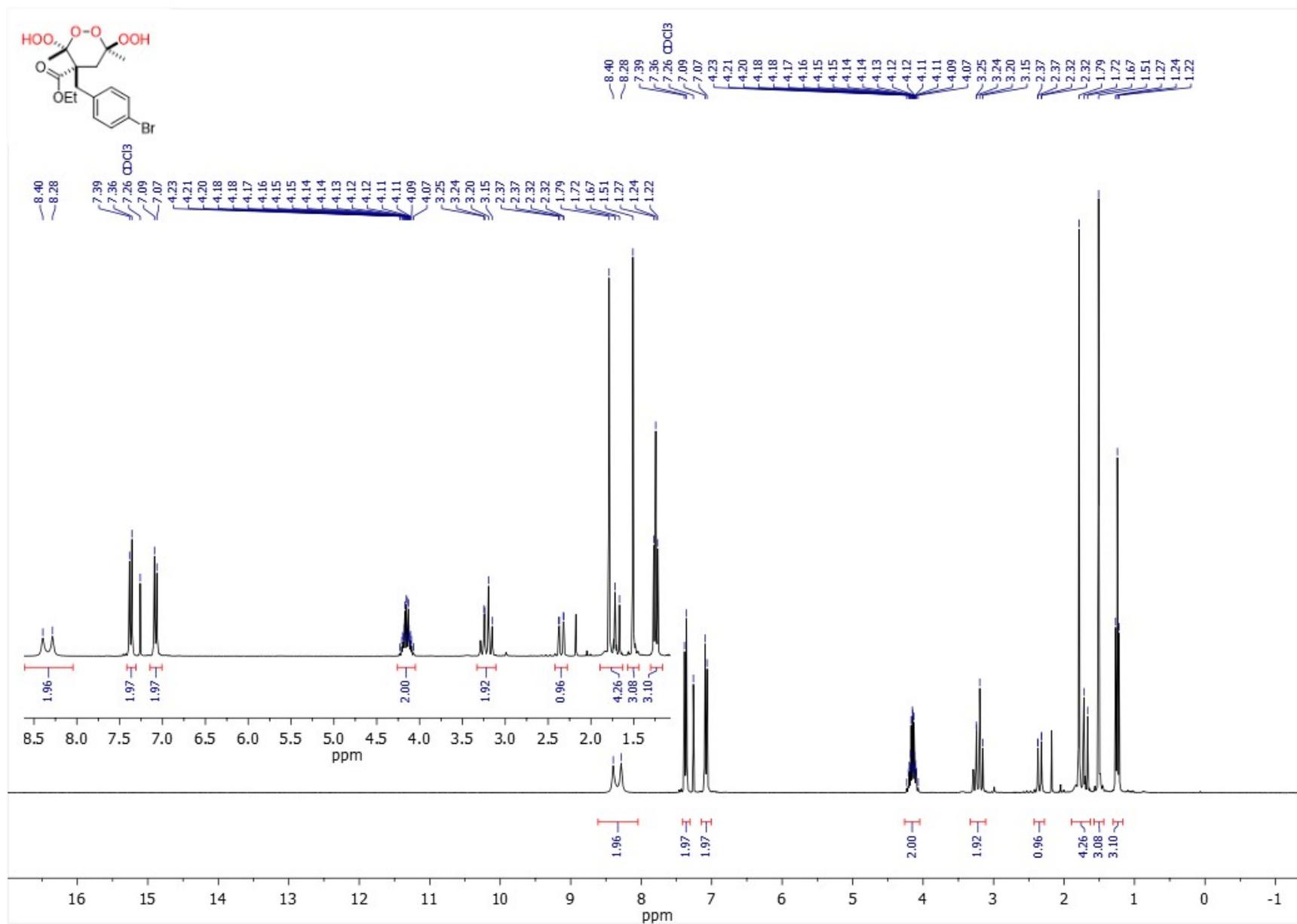
¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-4-(4-fluorobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6b



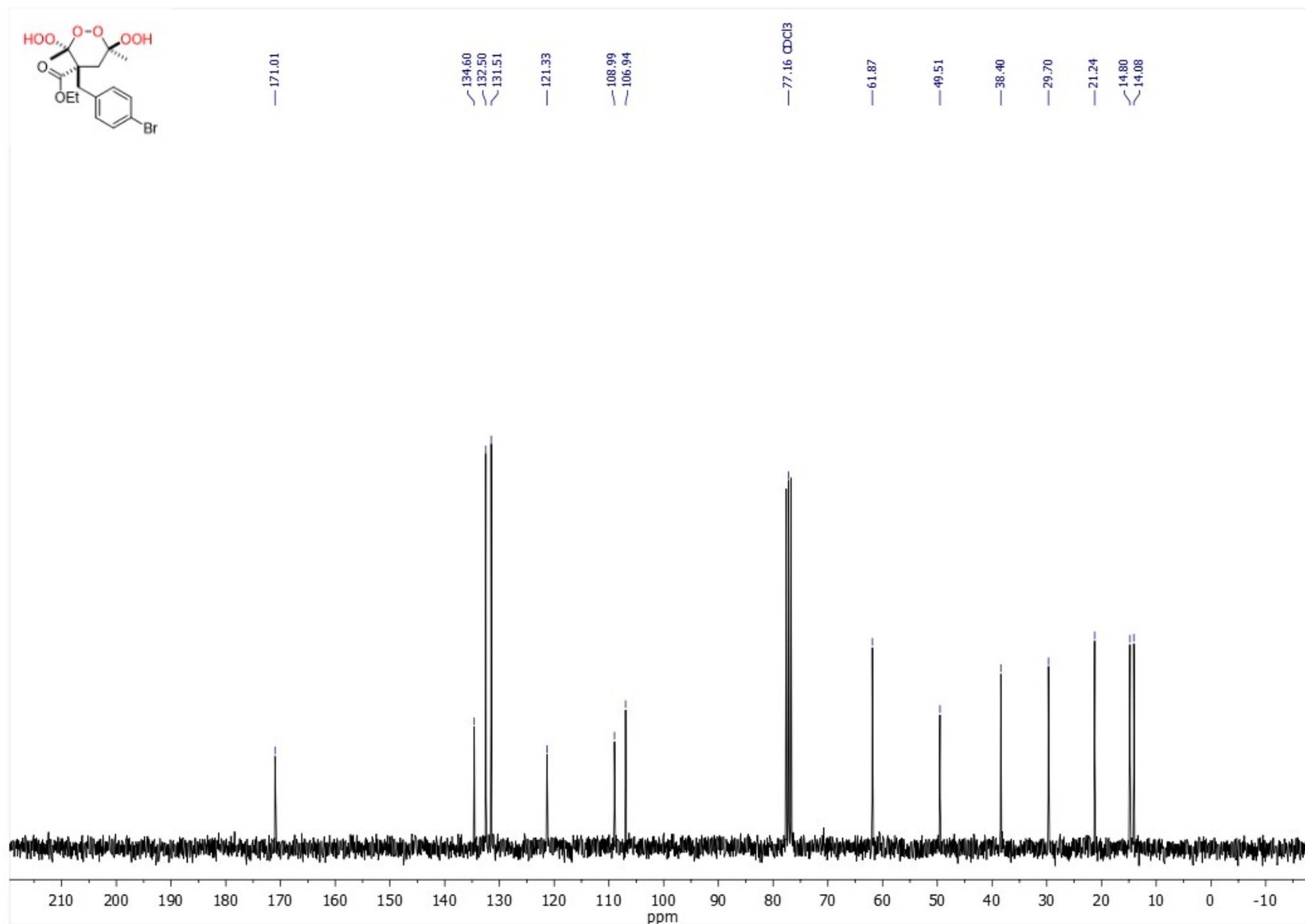
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-4-(4-fluorobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6b



¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-4-(4-bromobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6c

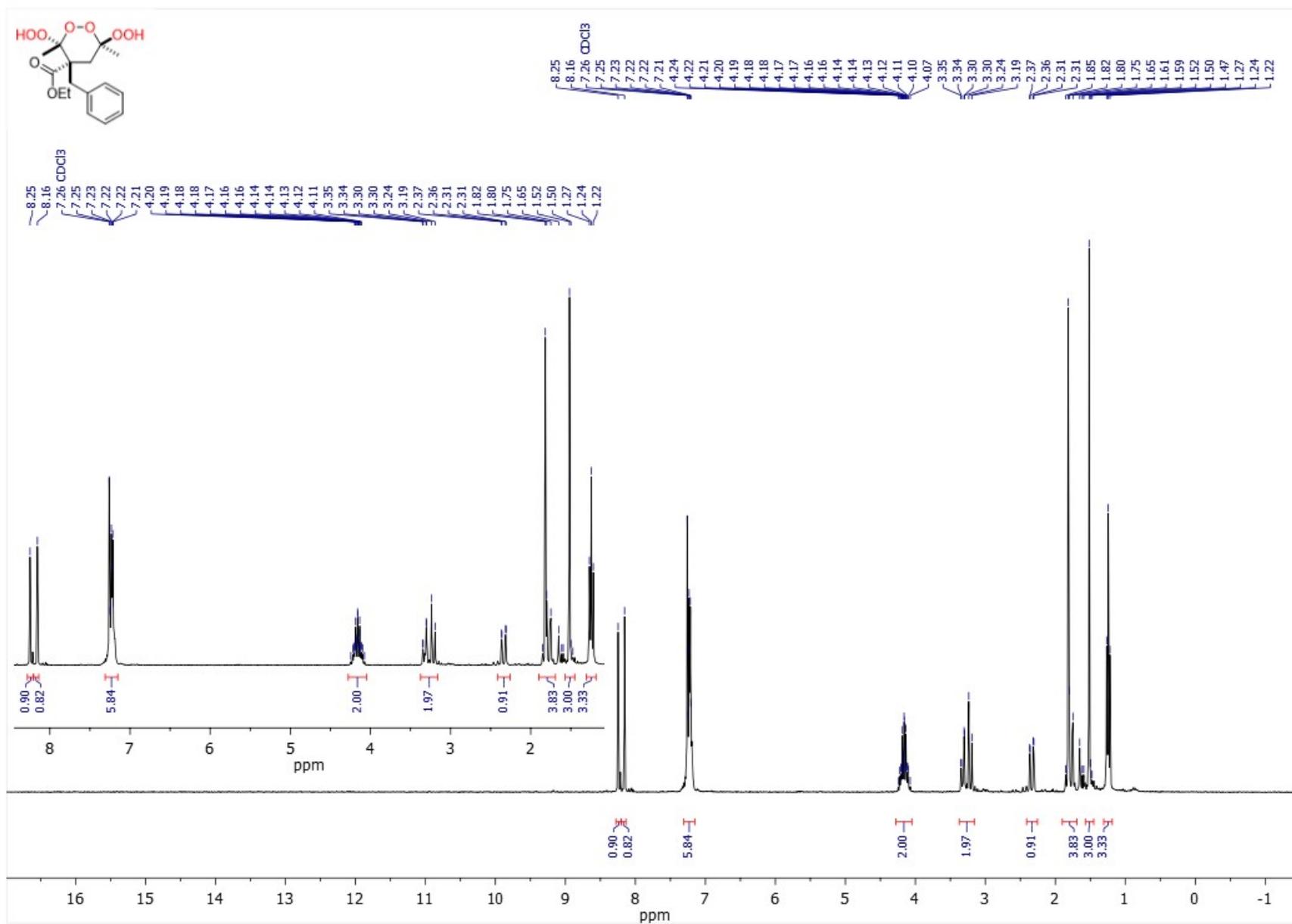


^{13}C NMR (75.48 MHz, CDCl_3). Ethyl (3*R**,4*S**,6*R**)-4-(4-bromobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, **6c**

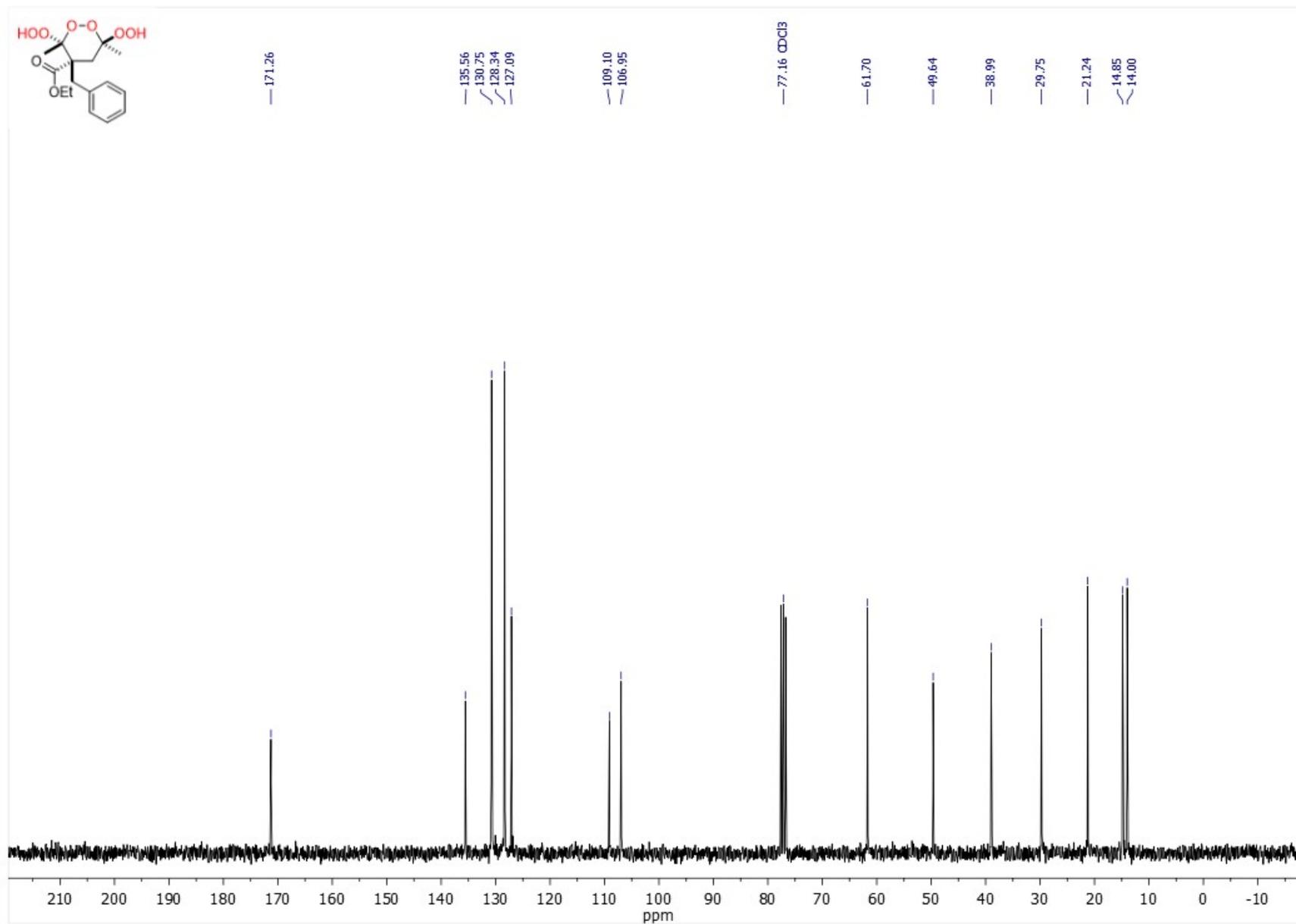


S177

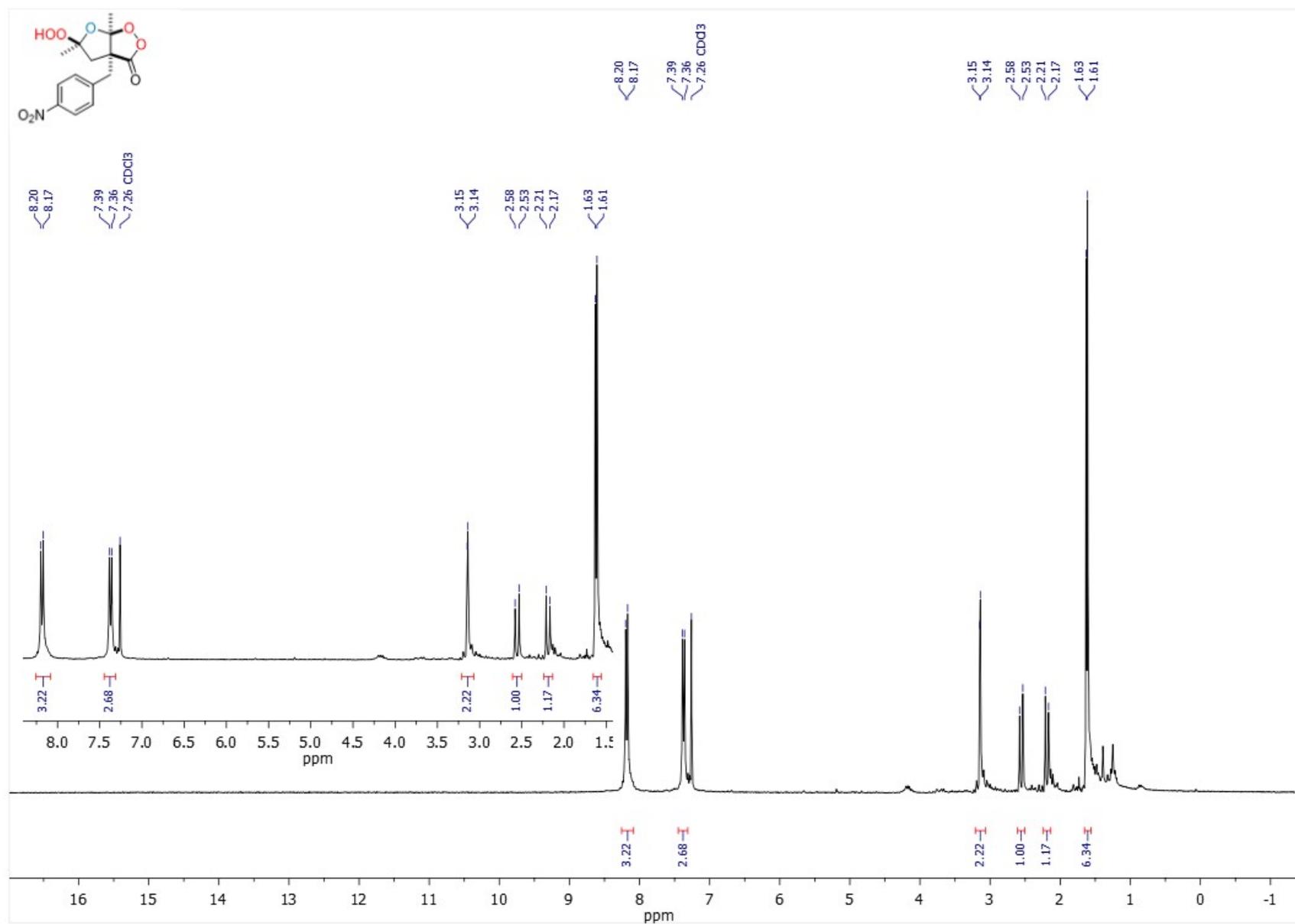
¹H NMR (300.13 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-4-benzyl-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6e



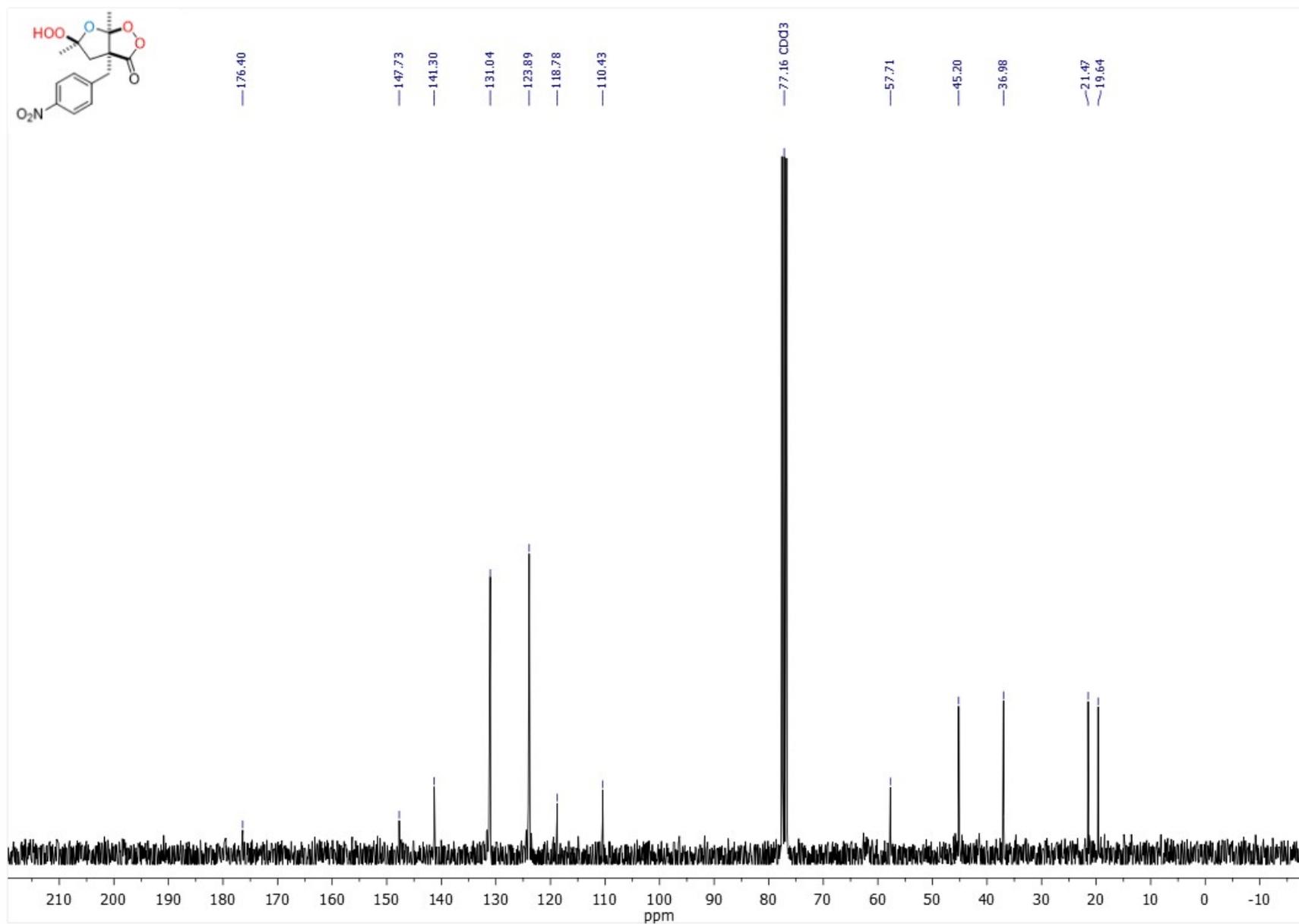
¹³C NMR (75.48 MHz, CDCl₃). Ethyl (3*R**,4*S**,6*R**)-4-benzyl-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6e



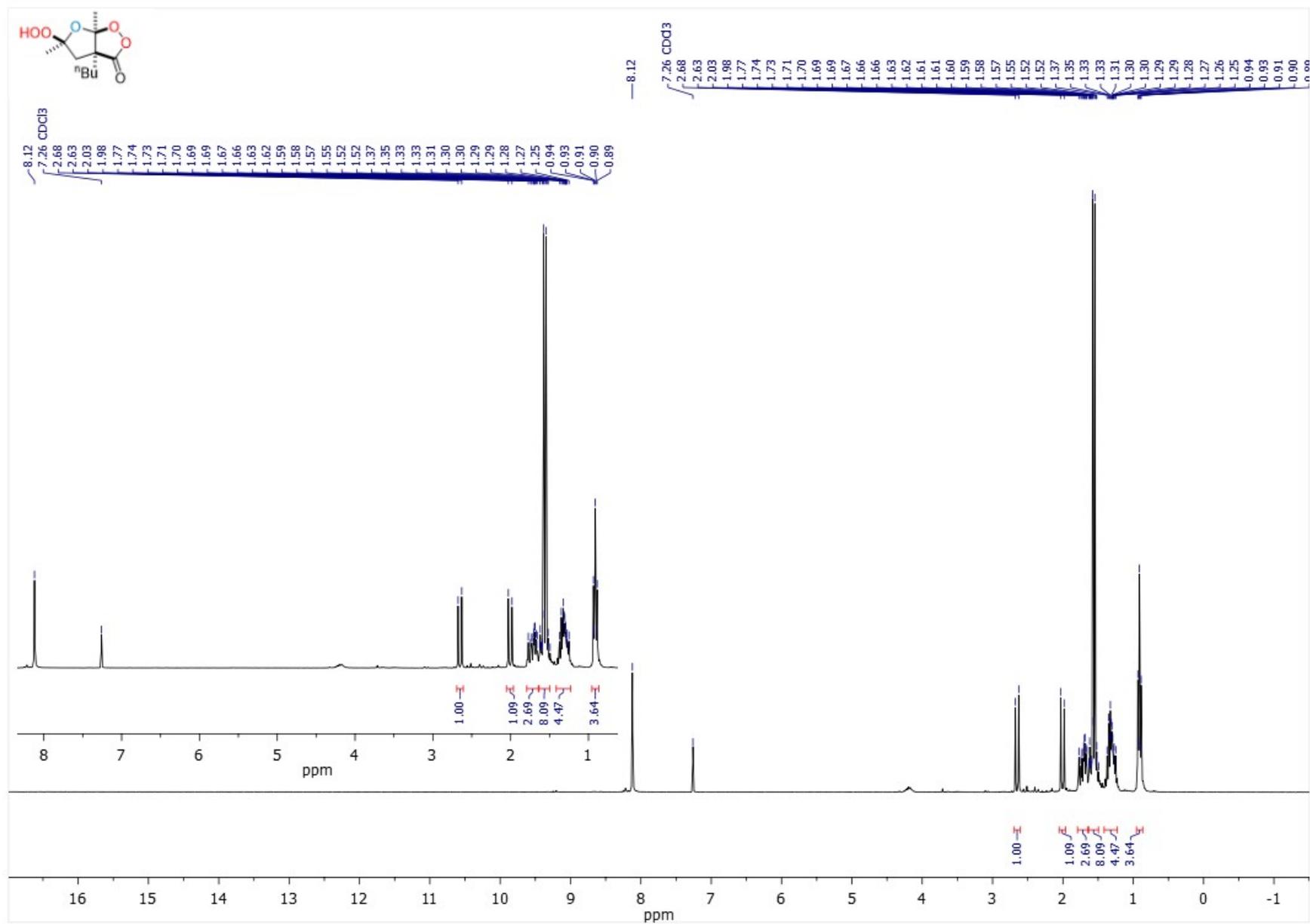
^1H NMR (300.13 MHz, CDCl_3). (3*aS*,5*R*,6*aS*)-5-hydroperoxy-5,6a-dimethyl-3a-(4-nitrobenzyl)tetrahydro-3H-furo[2,3-c][1,2]dioxol-3-one, 7a



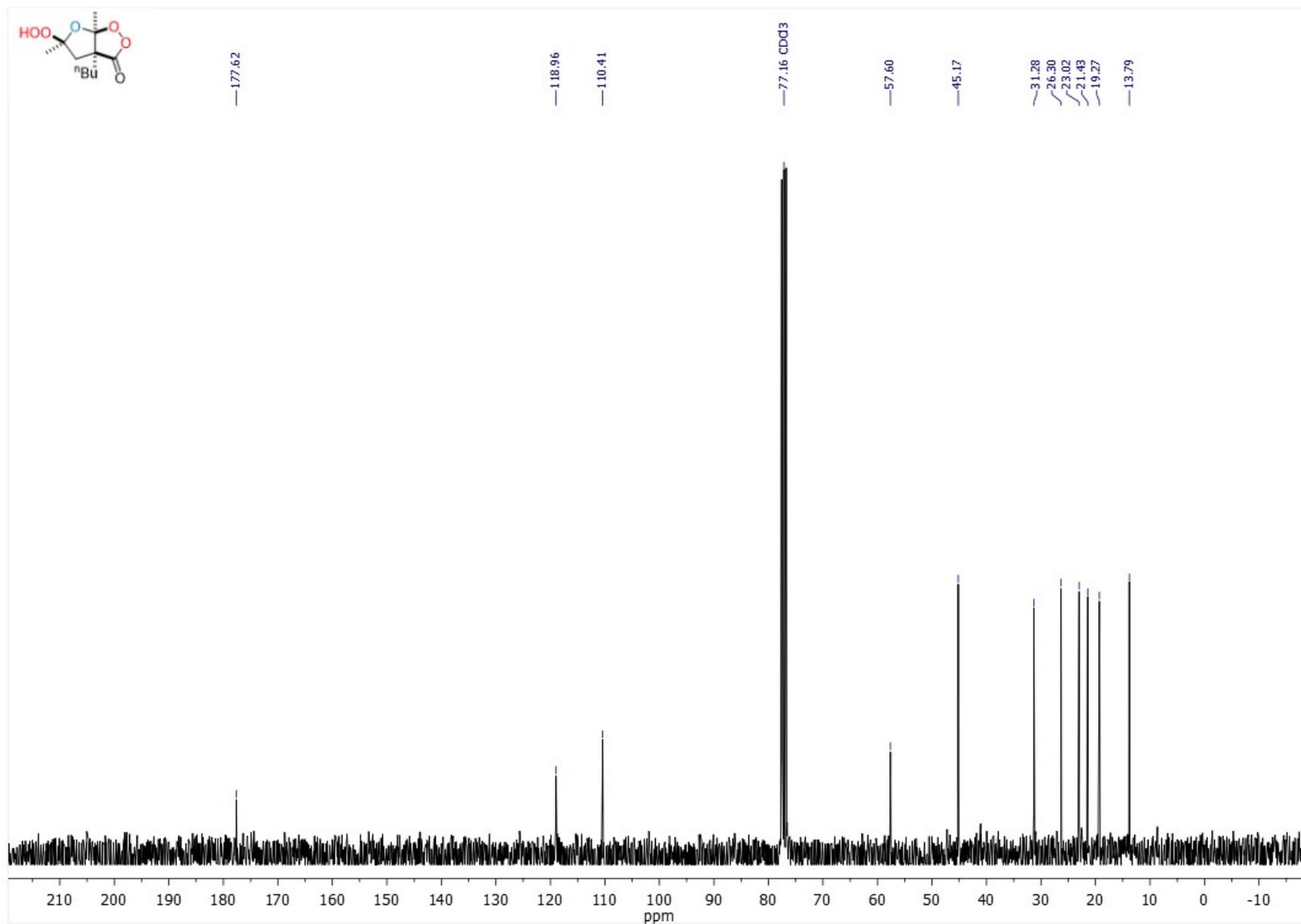
^{13}C NMR (75.48 MHz, CDCl_3). (3*aS*,5*R*,6*aS*)-5-hydroperoxy-5,6a-dimethyl-3a-(4-nitrobenzyl)tetrahydro-3H-furo[2,3-c][1,2]dioxol-3-one, 7a



¹H NMR (300.13 MHz, CDCl₃). (3*aS*,5*R*,6*aS*)-3*a*-butyl-5-hydroperoxy-5,6*a*-dimethyltetrahydro-3H-furo[2,3-*c*][1,2]dioxol-3-one, 7g

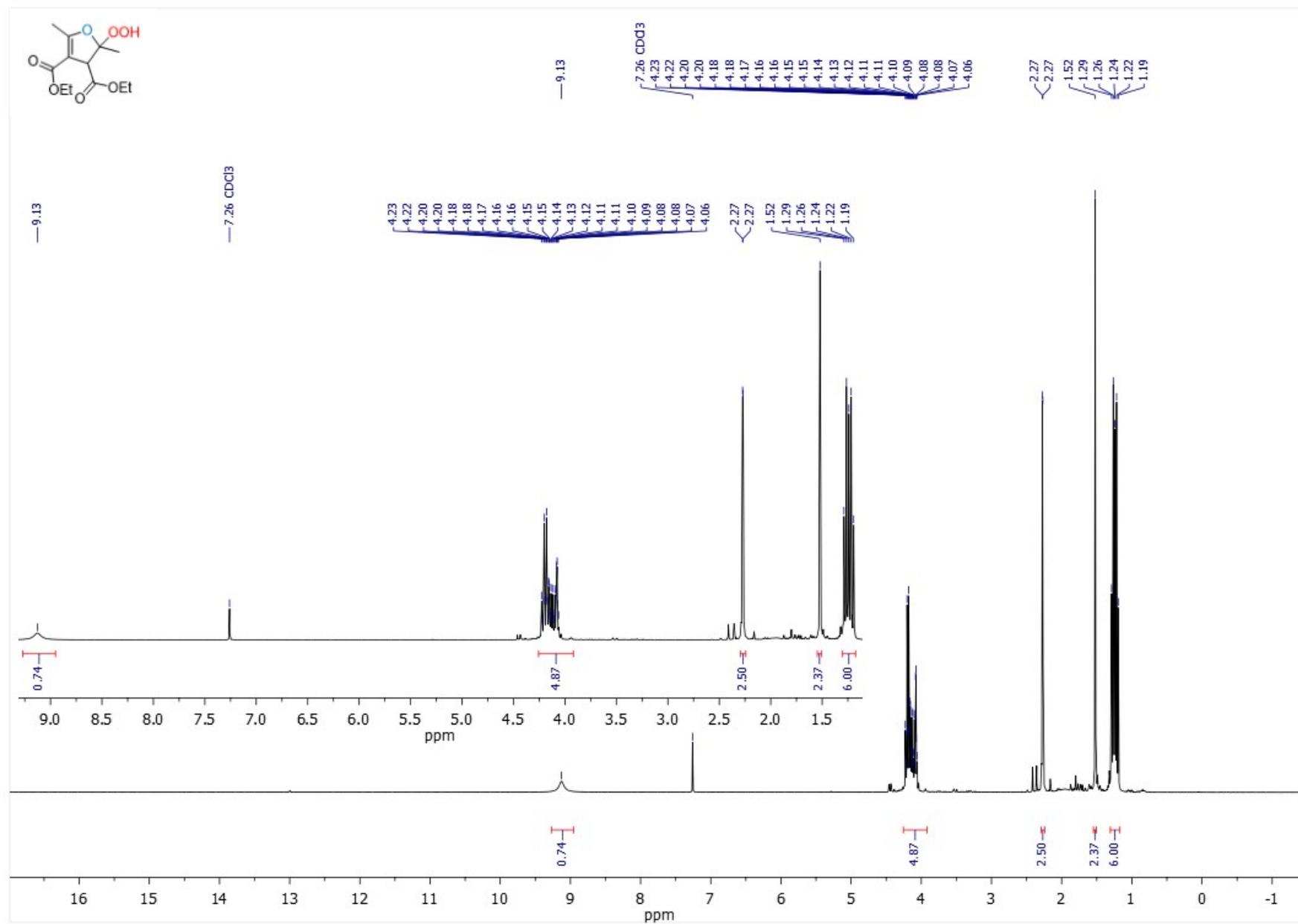


¹³C NMR (75.48 MHz, CDCl₃). (3*aS*,5*R*,6*aS*)-3*a*-butyl-5-hydroperoxy-5,6*a*-dimethyltetrahydro-3H-furo[2,3-*c*][1,2]dioxol-3-one, 7g

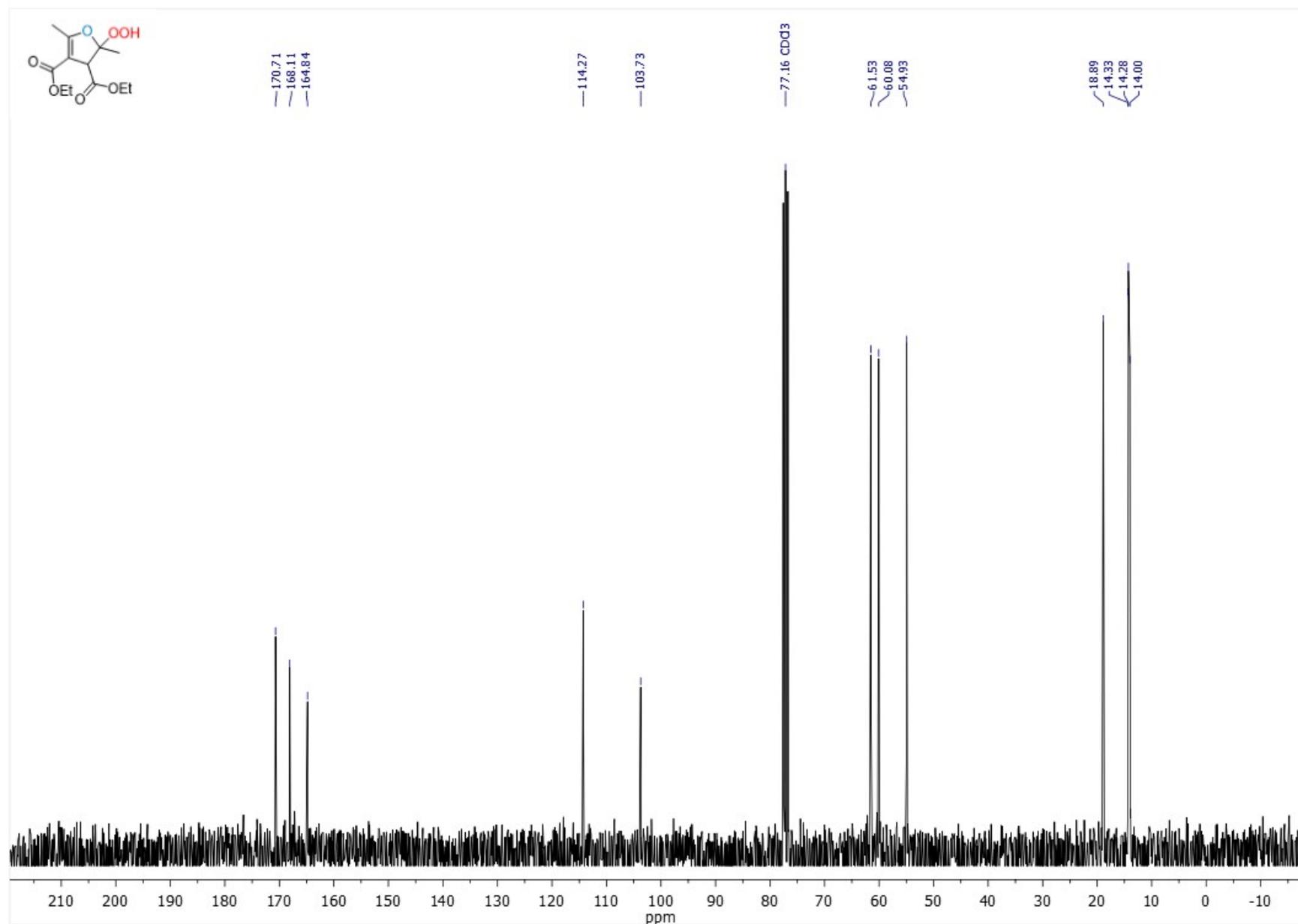


S183

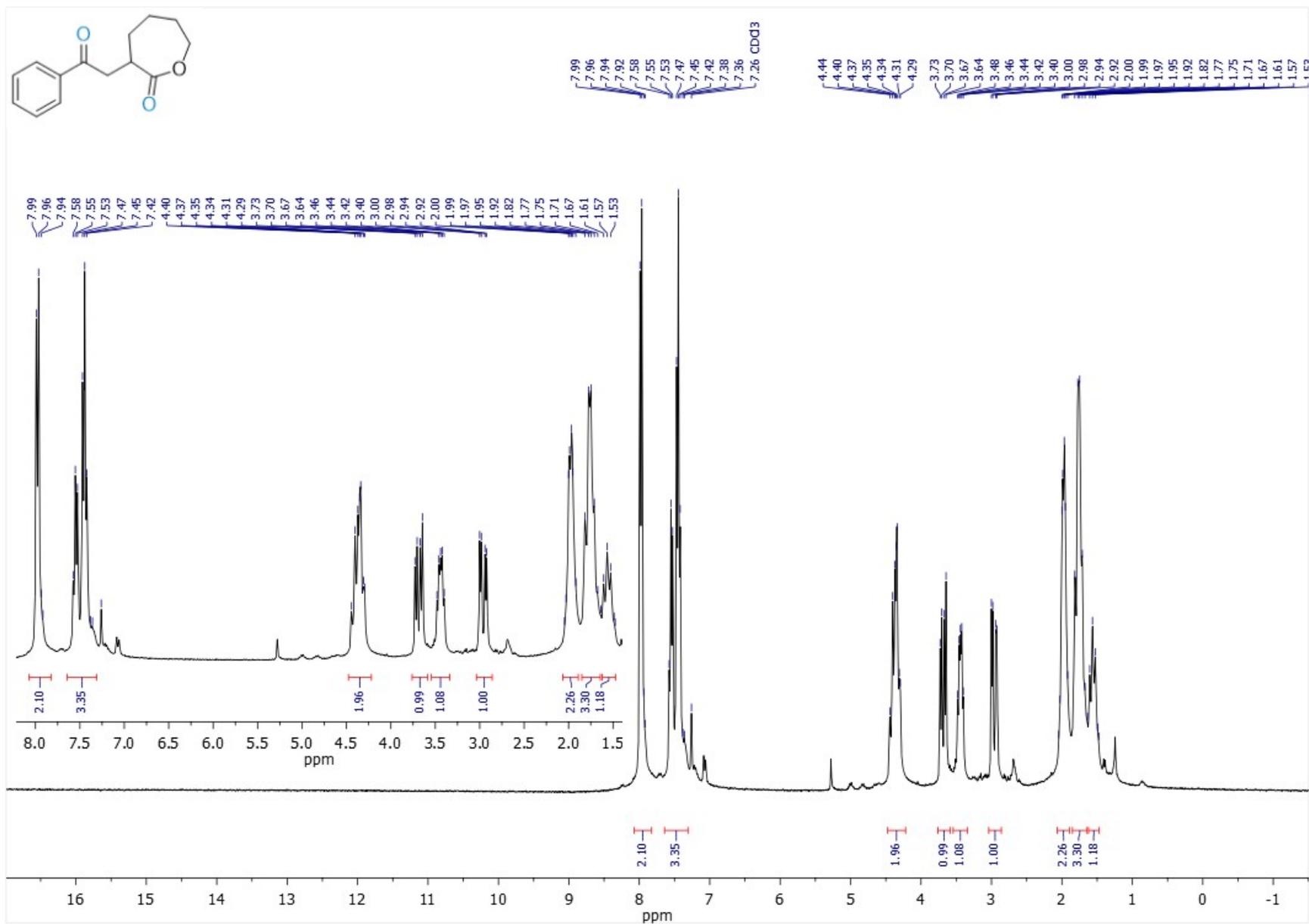
¹H NMR (300.13 MHz, CDCl₃). Diethyl 2-hydroperoxy-2,3,5-trimethyl-2,3-dihydrofuran-3,4-dicarboxylate, 8i



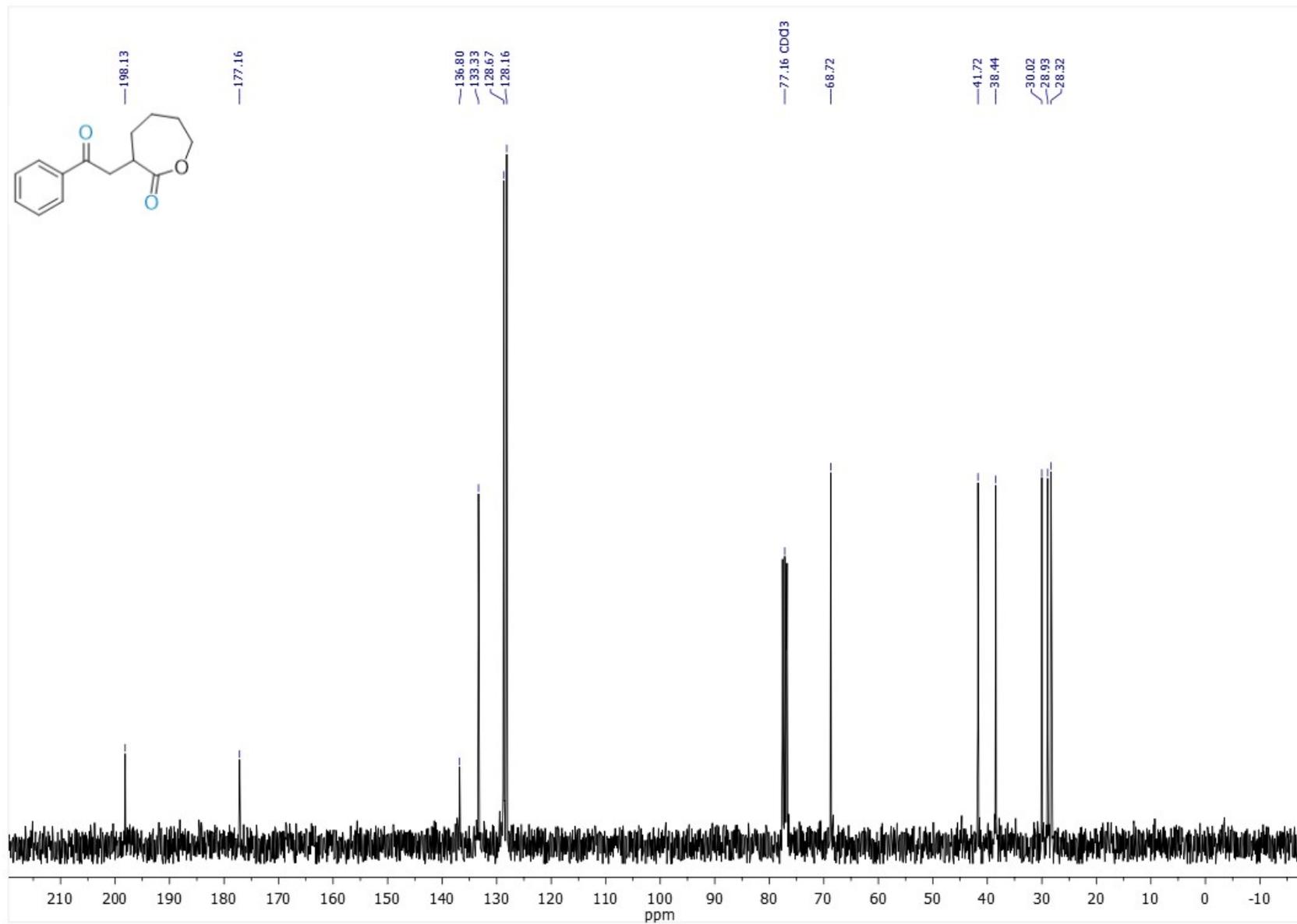
¹³C NMR (75.48 MHz, CDCl₃). Diethyl 2-hydroperoxy-2,3,5-trimethyl-2,3-dihydrofuran-3,4-dicarboxylate, 8i



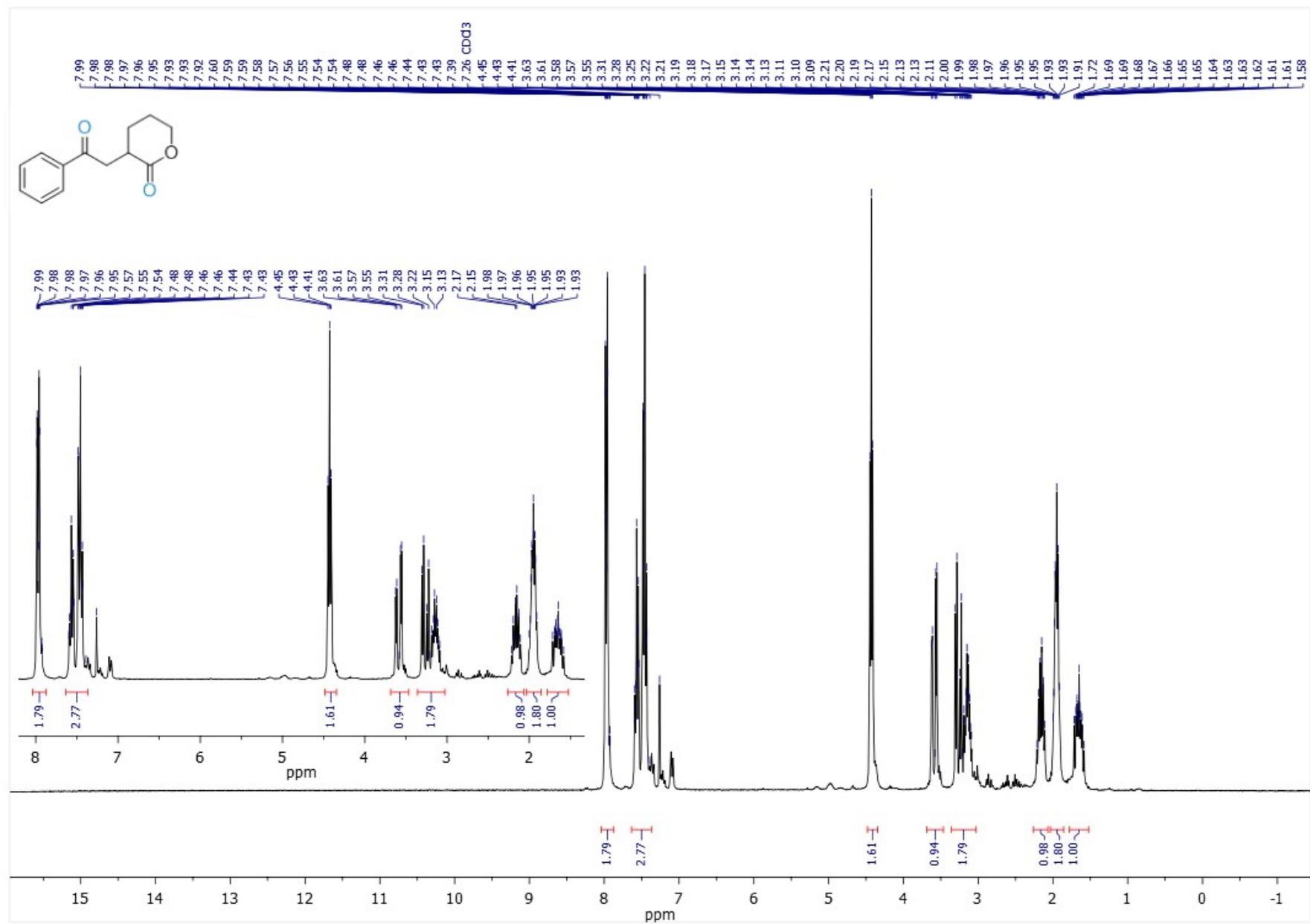
¹H NMR (300.13 MHz, CDCl₃). 3-(2-Oxo-2-phenylethyl)oxepan-2-one, 9j



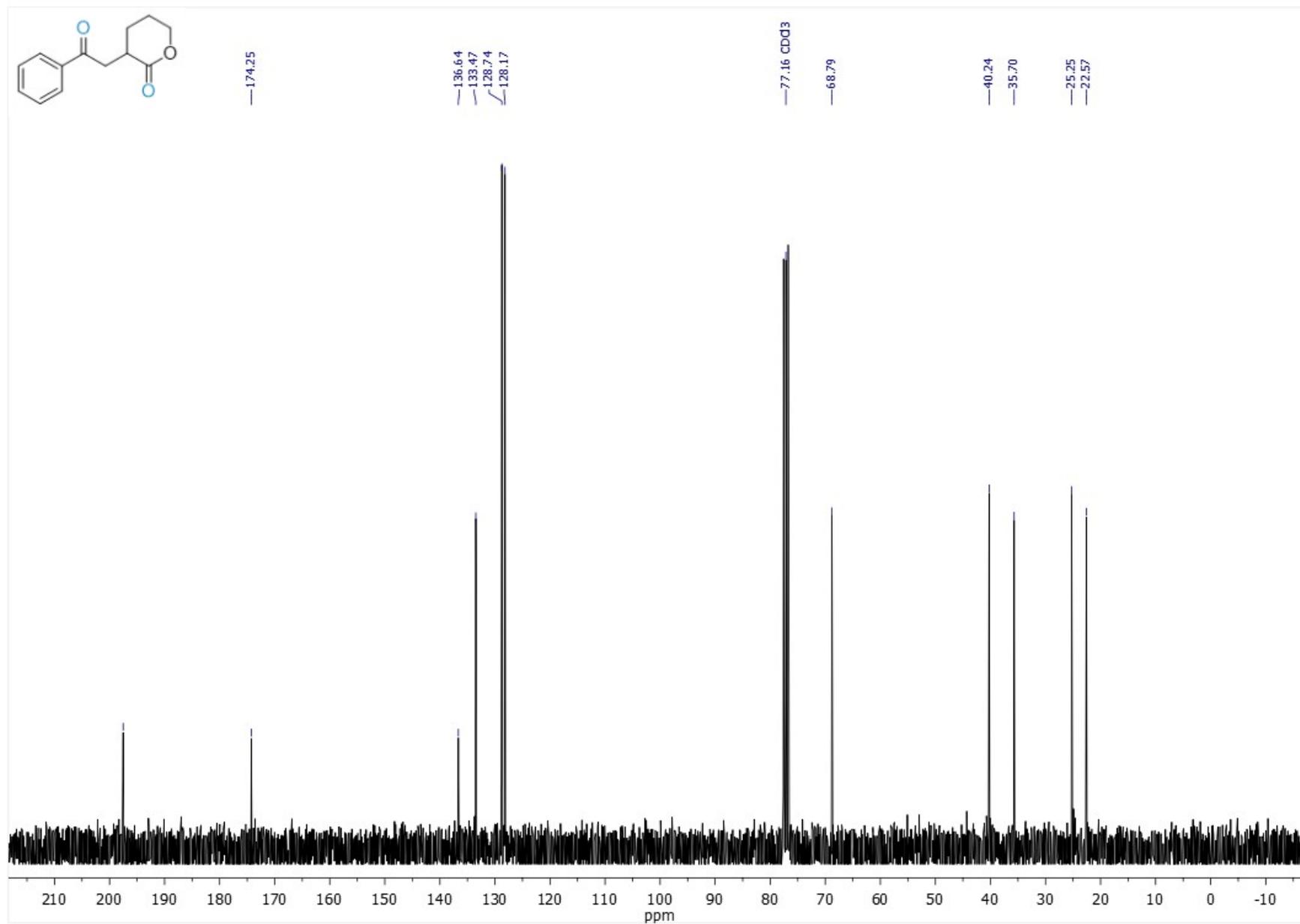
¹³C NMR (75.48 MHz, CDCl₃). 3-(2-Oxo-2-phenylethyl)oxepan-2-one, 9j



¹H NMR (300.13 MHz, CDCl₃). 3-(2-oxo-2-phenylethyl)tetrahydro-2H-pyran-2-one, 9k

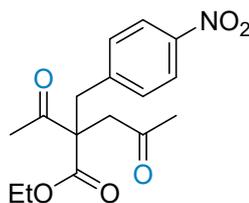


¹³C NMR (75.48 MHz, CDCl₃). 3-(2-oxo-2-phenylethyl)tetrahydro-2H-pyran-2-one, 9k



HRMS spectra of compounds 1a-h

Ethyl 2-acetyl-2-(4-nitrobenzyl)-4-oxopentanoate, 1a



Display Report

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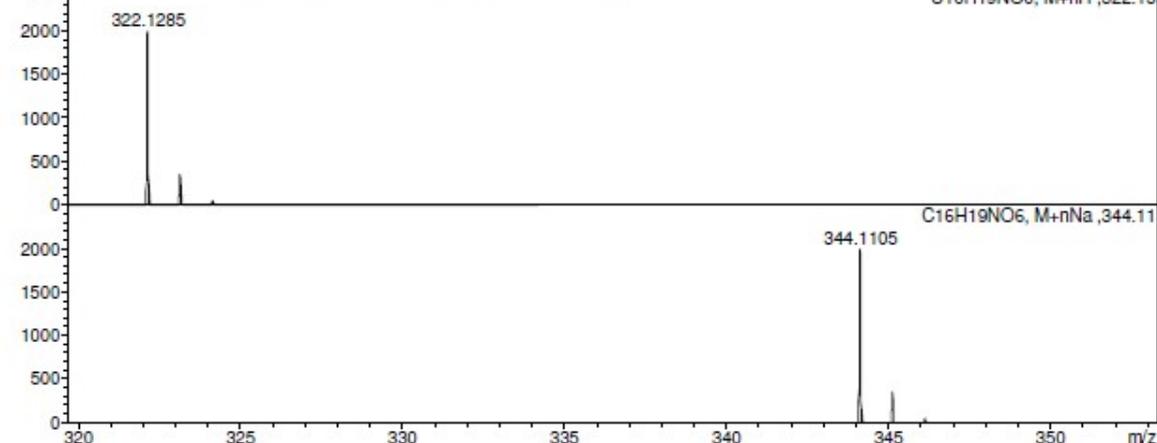
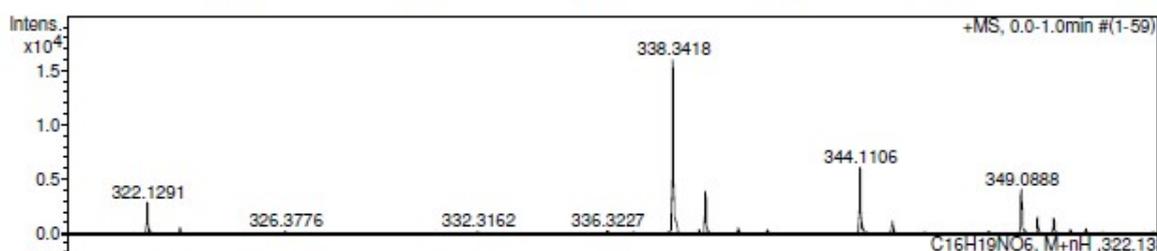
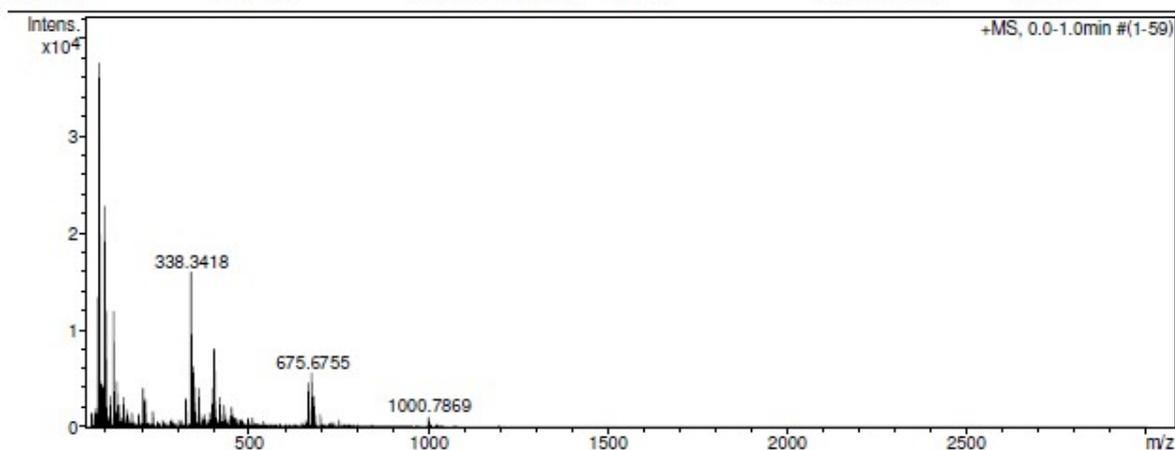
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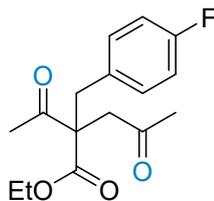
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

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Ethyl 2-acetyl-2-(4-fluorobenzyl)-4-oxopentanoate, 1b



Display Report

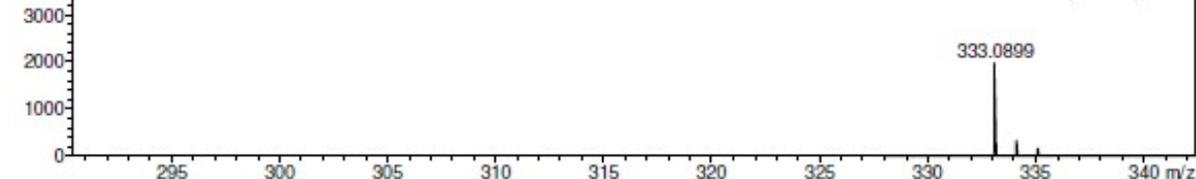
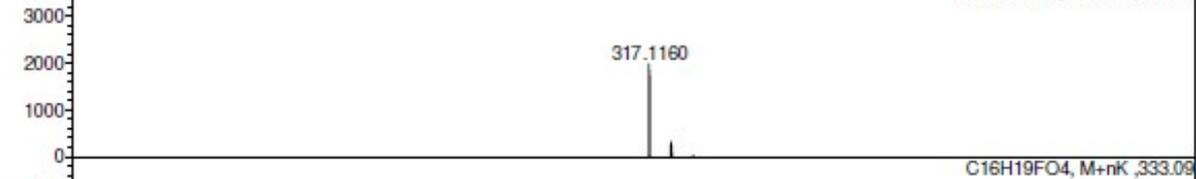
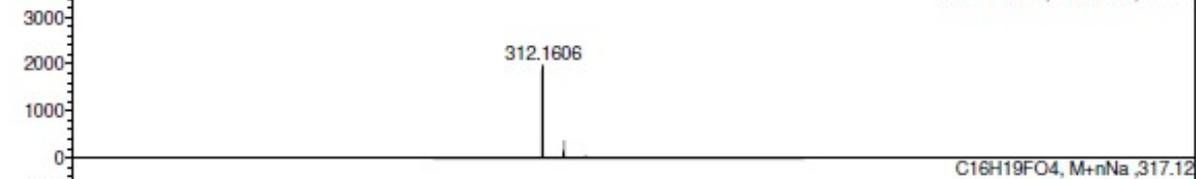
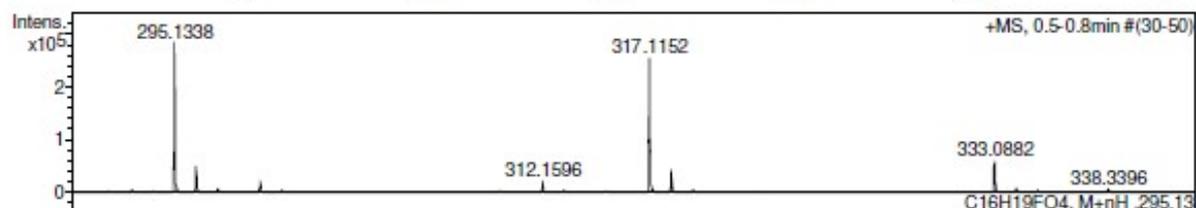
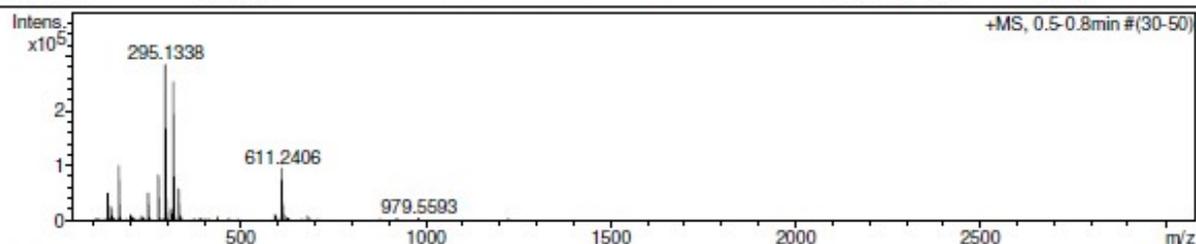
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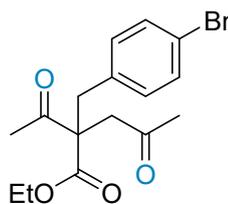
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Ethyl 2-acetyl-2-(4-bromobenzyl)-4-oxopentanoate, 1c



Display Report

Analysis Info

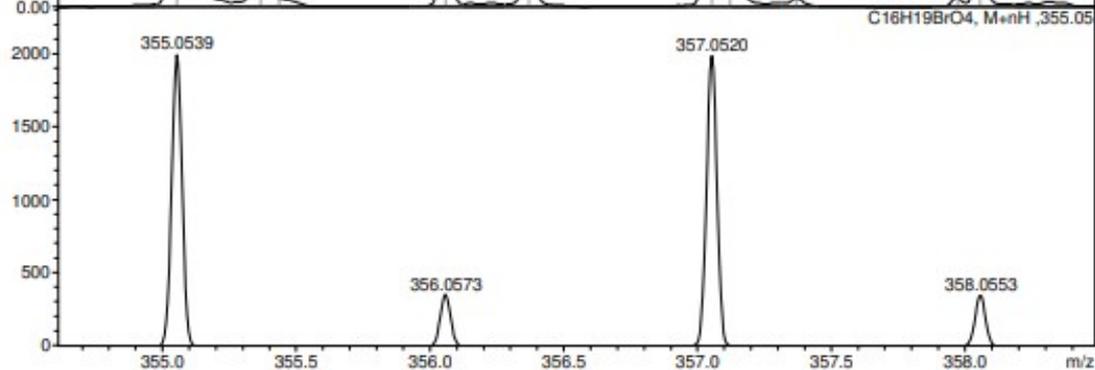
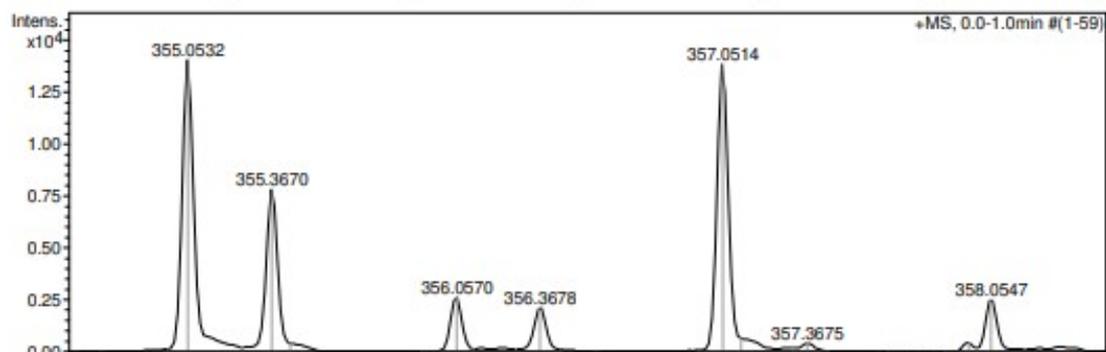
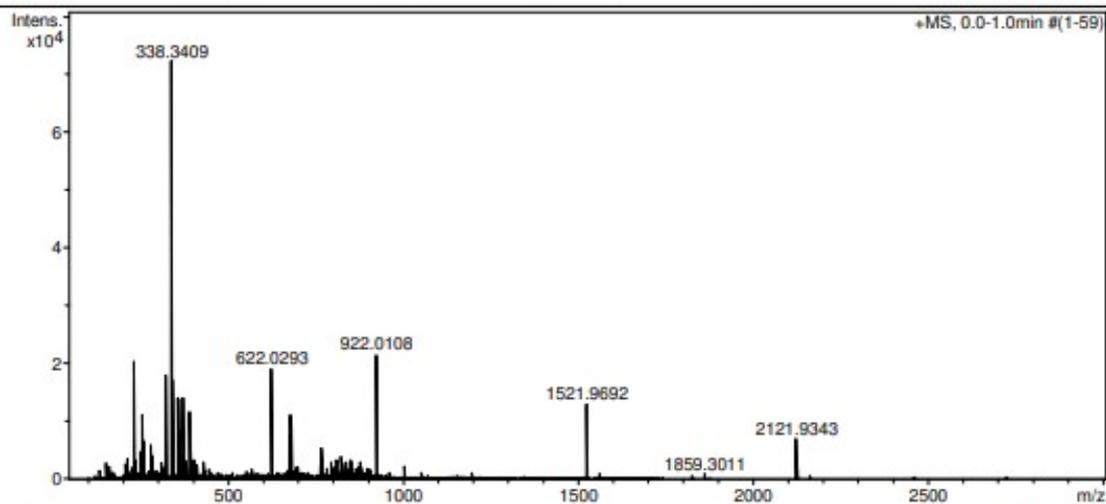
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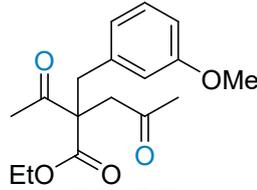
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Ethyl 2-acetyl-2-(3-methoxybenzyl)-4-oxopentanoate, 1d



Display Report

Analysis Info

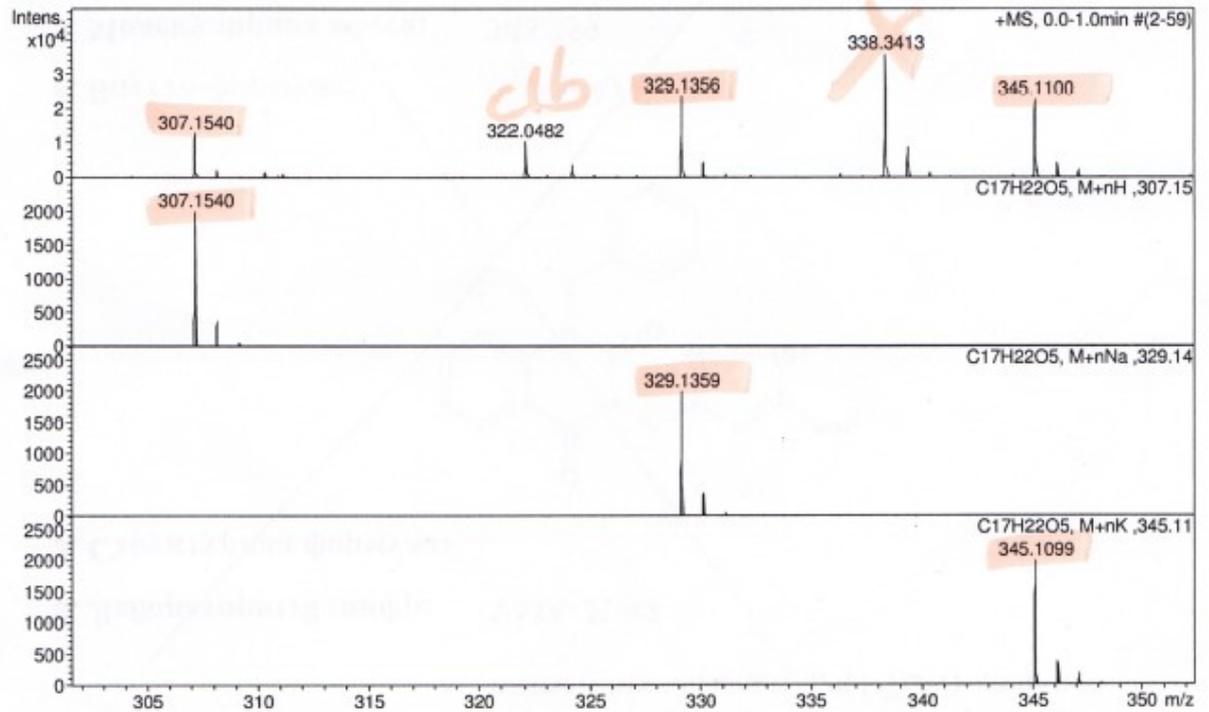
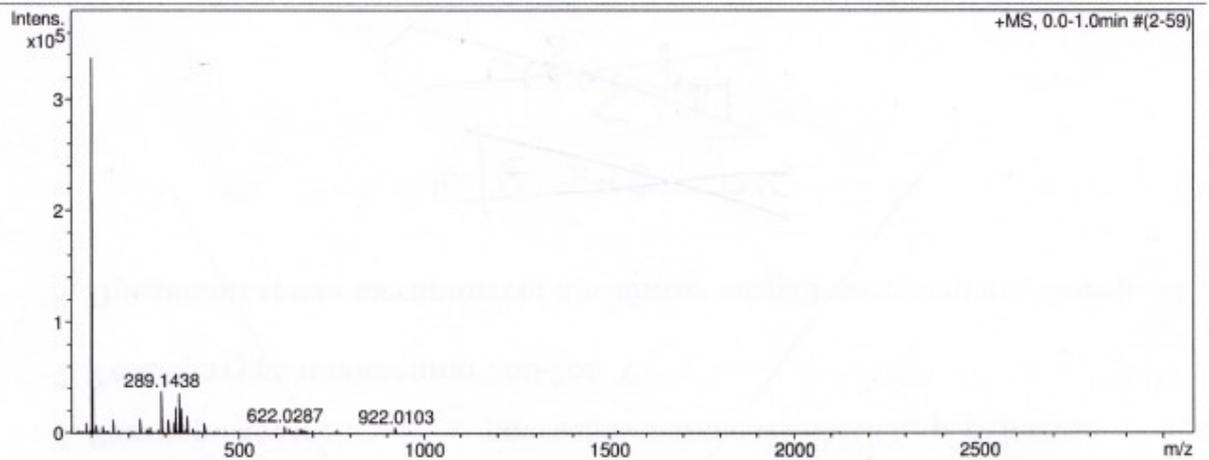
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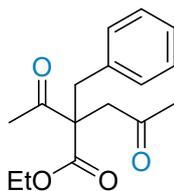
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Acquisition Parameter

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Ethyl 2-acetyl-2-benzyl-4-oxopentanoate, 1e



Display Report

Analysis Info

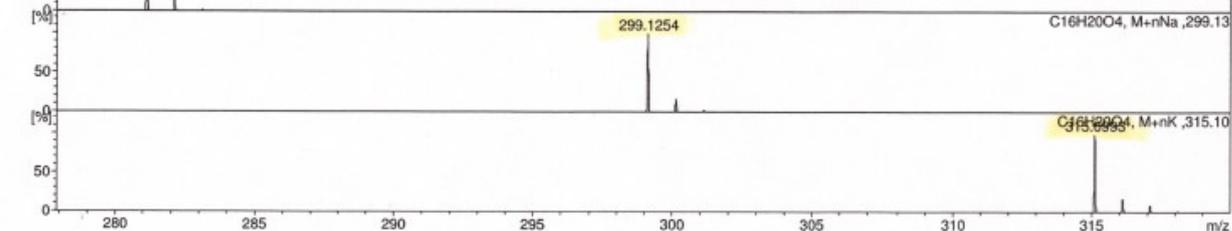
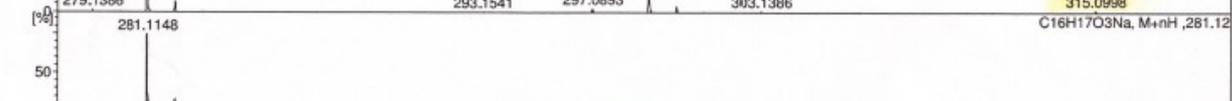
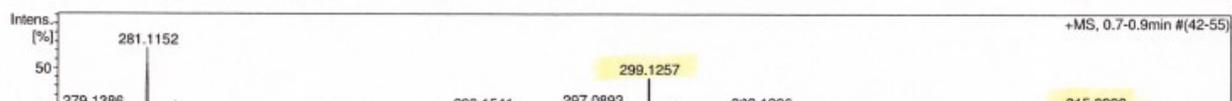
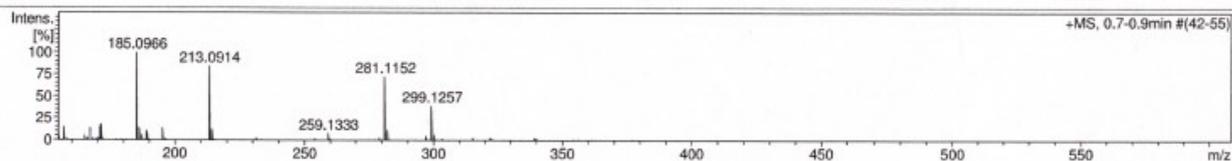
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Acquisition Date 15.03.2022 11:20:36

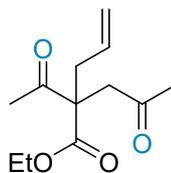
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	1600 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl 2-acetyl-2-(2-oxopropyl)pent-4-enoate, 1f



Display Report

Analysis Info

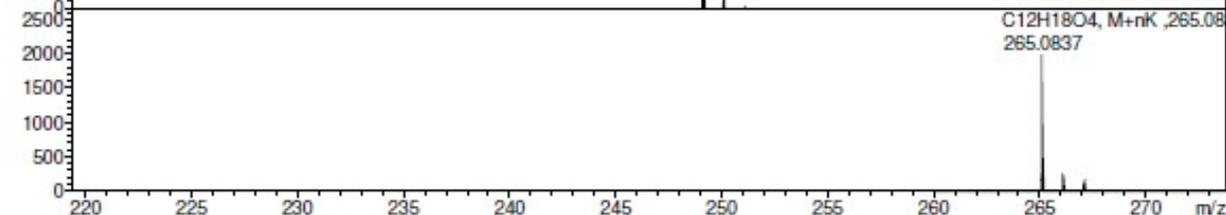
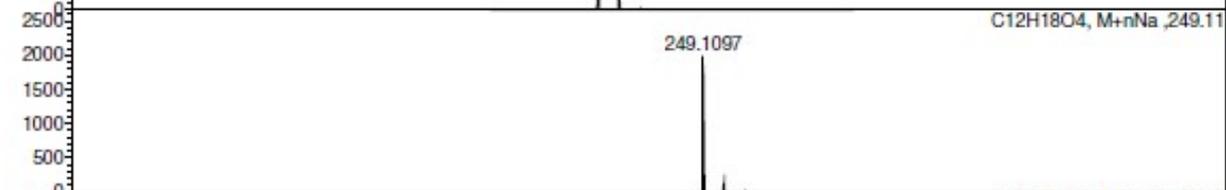
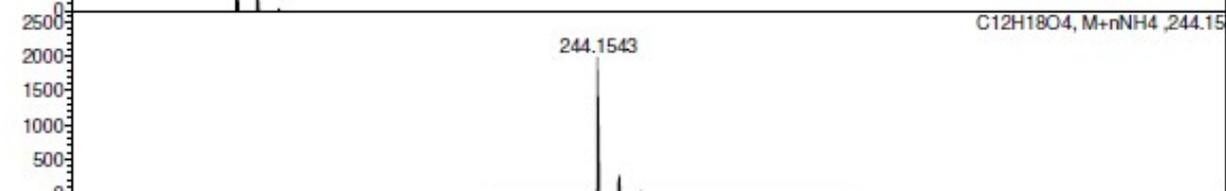
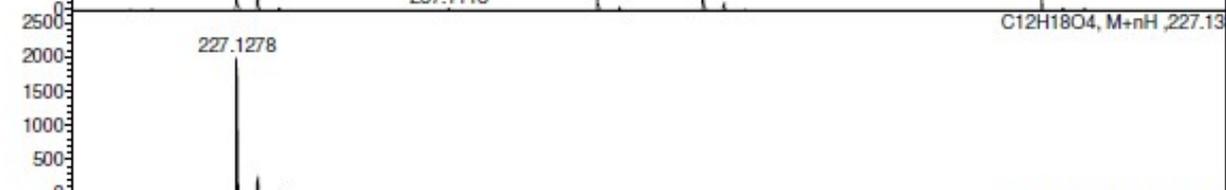
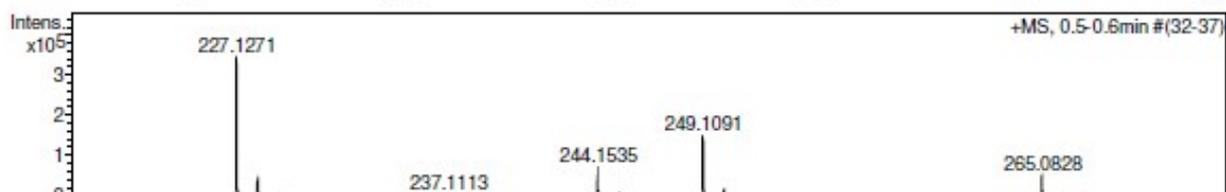
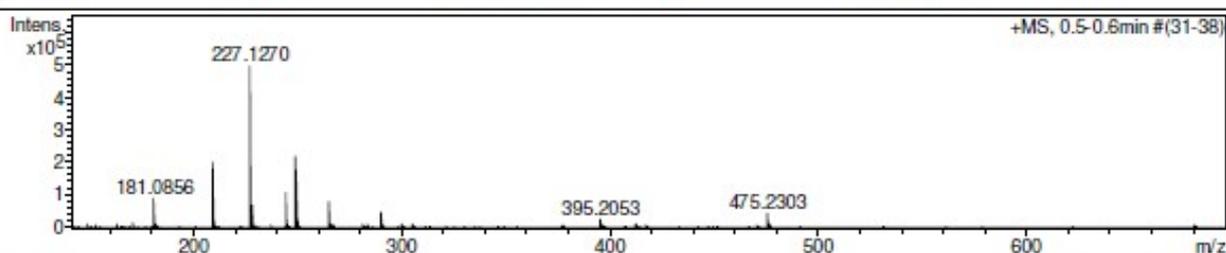
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Comment C12H18O4 mH 227.1277 calibrant added CH3CN

Acquisition Date 18.04.2024 18:11:26

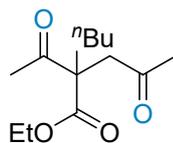
Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl 2-acetyl-2-(2-oxopropyl)hexanoate, 1g



Display Report

Analysis Info

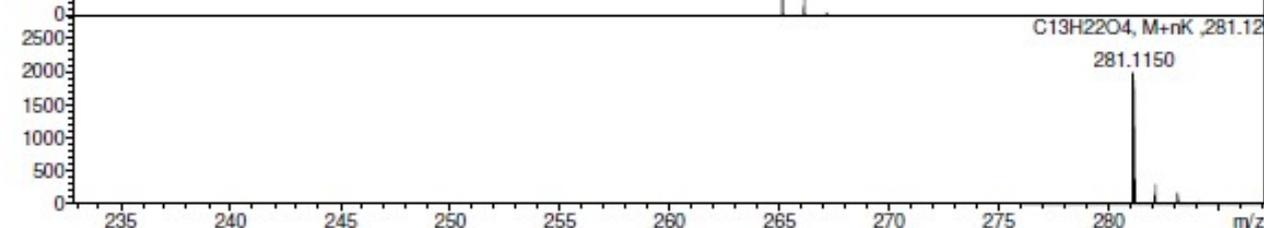
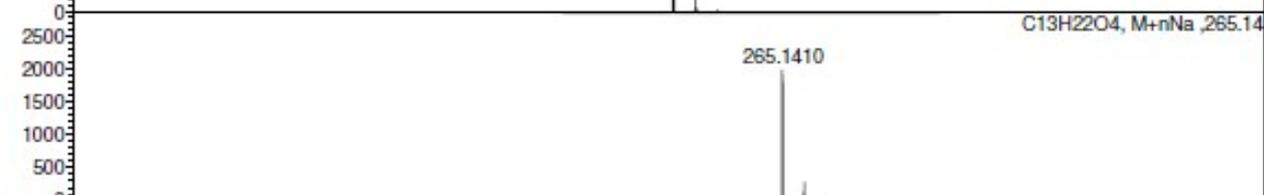
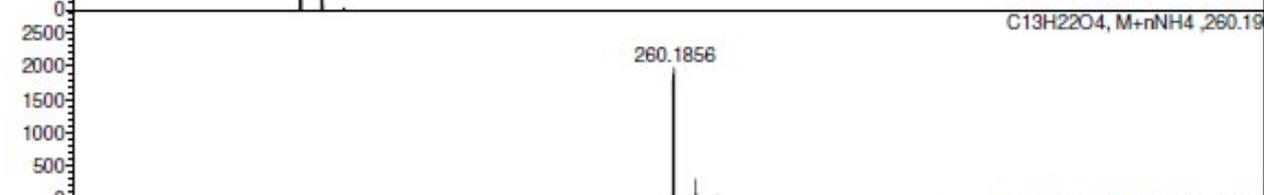
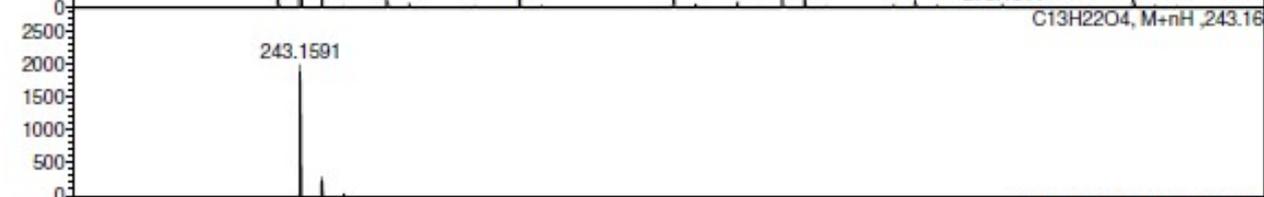
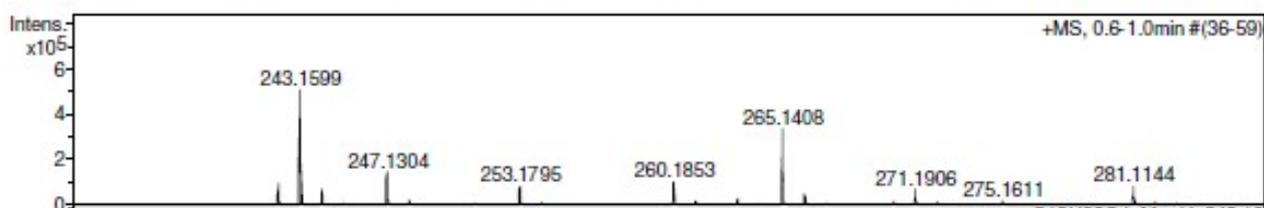
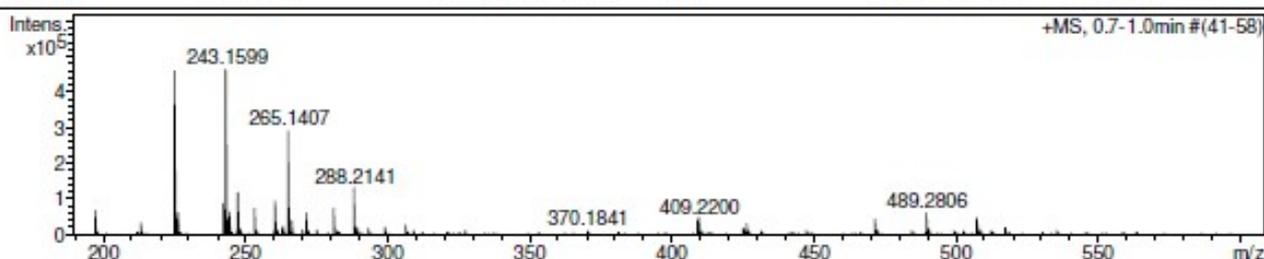
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 Sample Name /IYAR S-314
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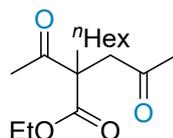
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl 2-acetyl-2-(2-oxopropyl)octanoate, 1h



Display Report

Analysis Info

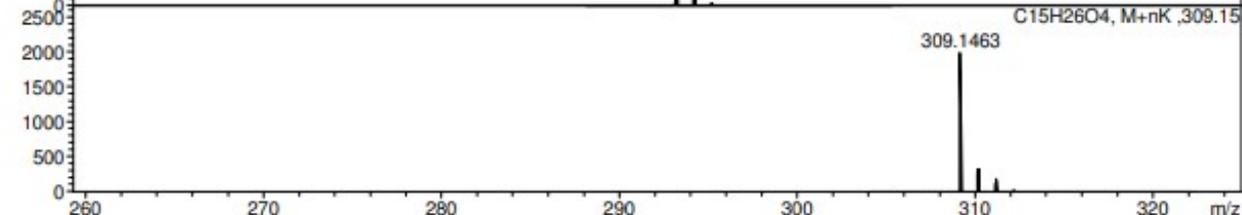
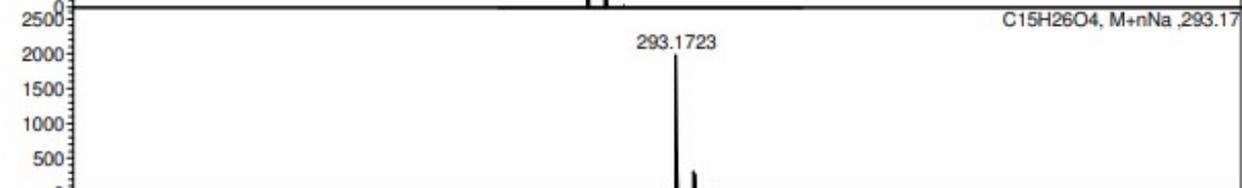
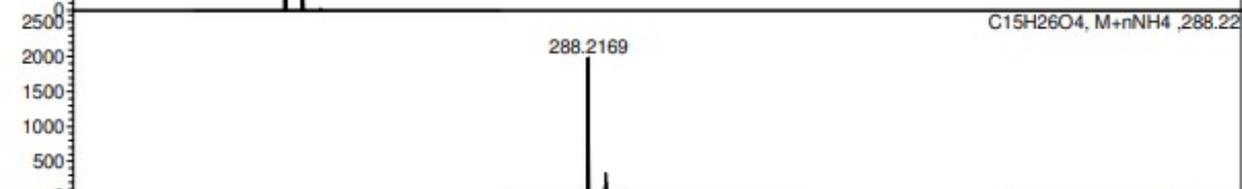
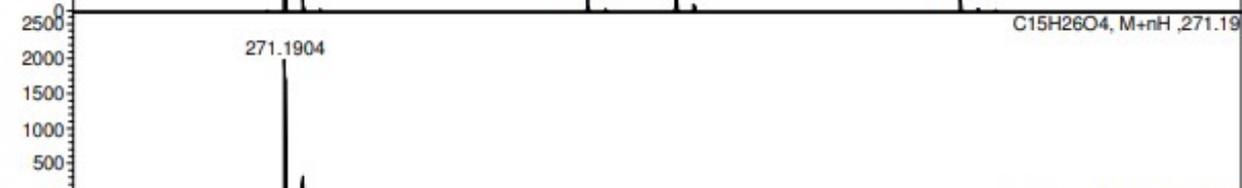
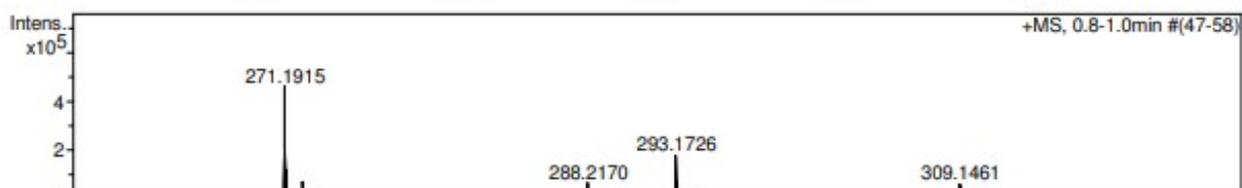
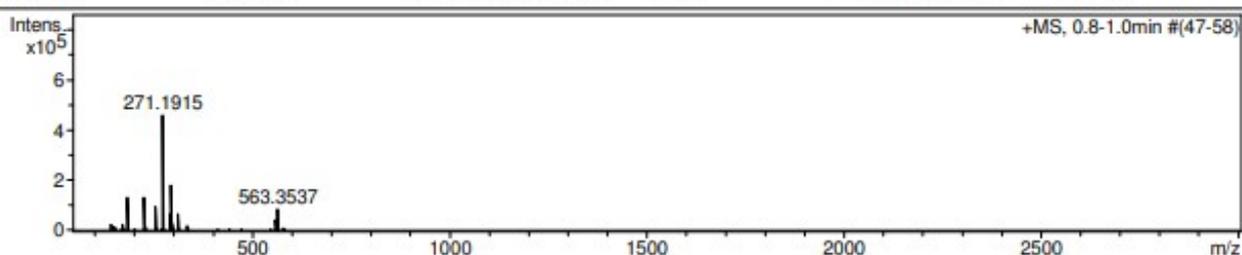
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Acquisition Date 18.04.2024 17:39:53

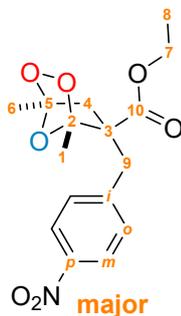
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



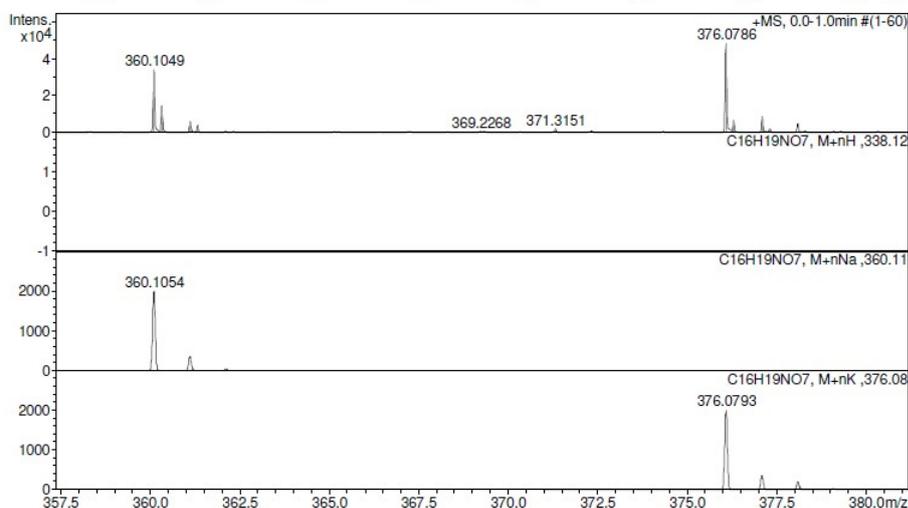
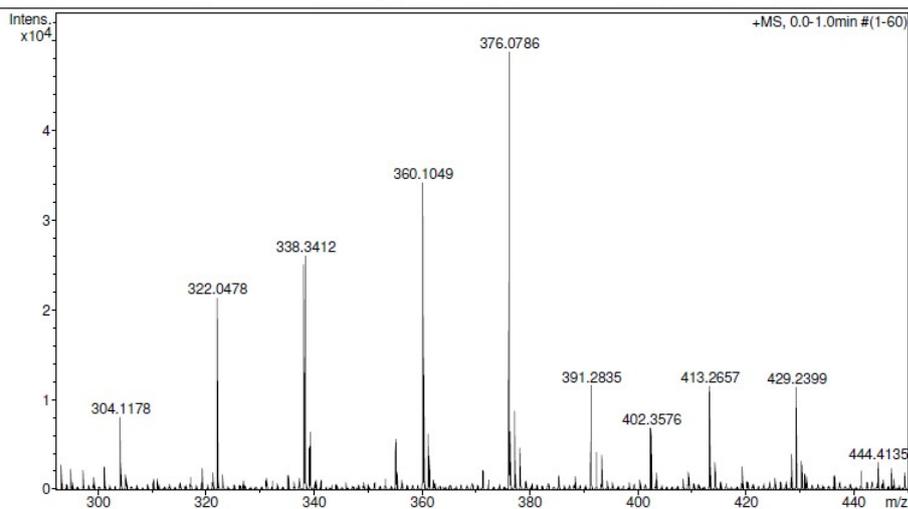
**HRMS spectra of peroxides *cis*-2a-h, *trans*-2a-h, 2i, *cis*-3a,b,c,e,g,h,
trans-3a,c,e,g,h, 4a, 5a-h, 6a-c,e, 7a,g, 8i, , 9j, 9k
 Ethyl (1*S**,4*R**,5*R**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-
 carboxylate, *cis*-2a**



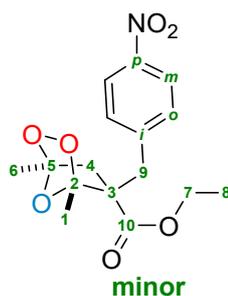
Display Report

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Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN Rd1312_2	Instrument / Ser#	micrOTOF 10248
Comment	CH3CN 100%, dil. 200, calibrant added		

Acquisition Parameter			
Source Type	ESI	Ion Polarity	Positive
Focus	Not active	Set Nebulizer	0.4 Bar
Scan Begin	50 m/z	Set Dry Heater	180 °C
Scan End	3000 m/z	Set Capillary	4500 V
		Set End Plate Offset	-500 V
		Set Dry Gas	4.0 l/min
		Set Divert Valve	Waste



Ethyl (1*S,4*R**,5*S**)-1,4-dimethyl-5-(4-nitrobenzyl)-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *trans*-2a**



Display Report

Analysis Info

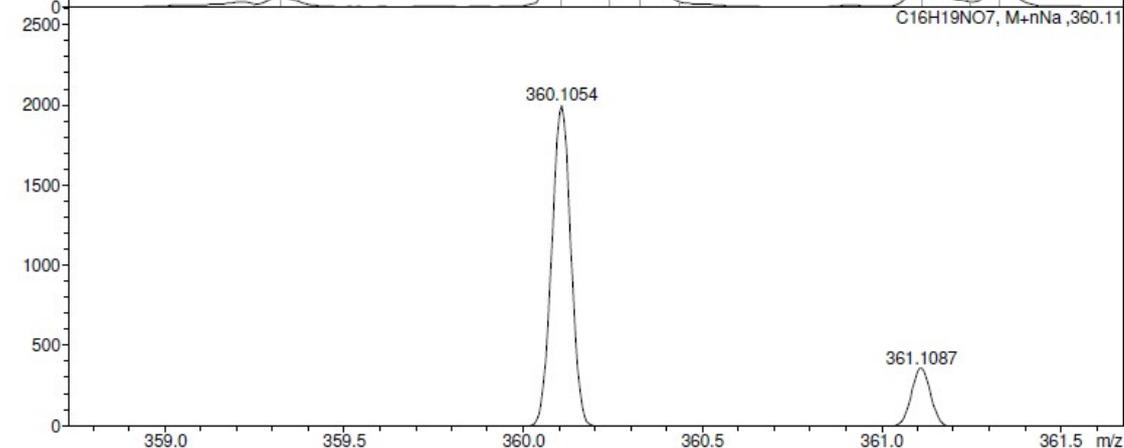
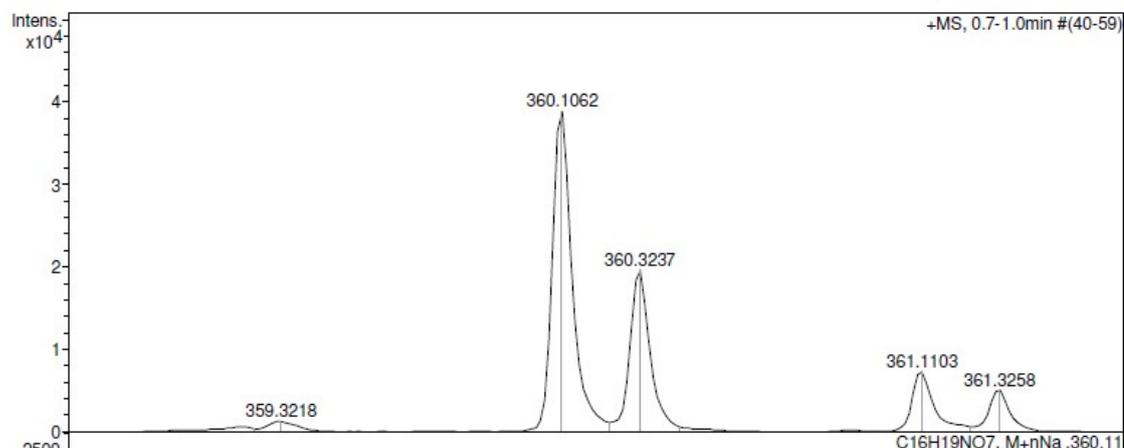
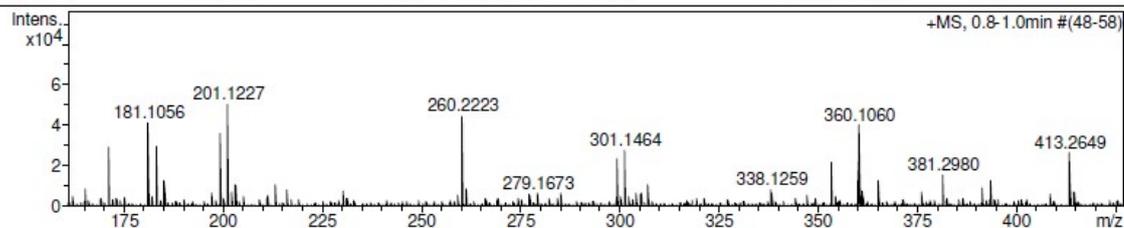
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Acquisition Date 25.01.2024 14:25:17

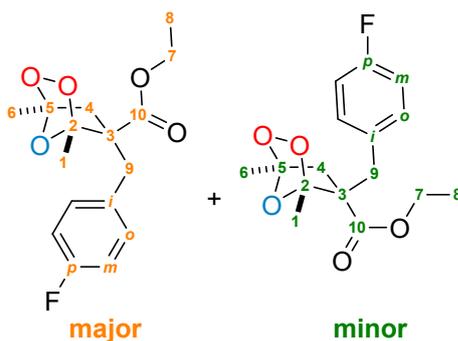
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl 5-(4-fluorobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2b+*trans*-2b



Display Report

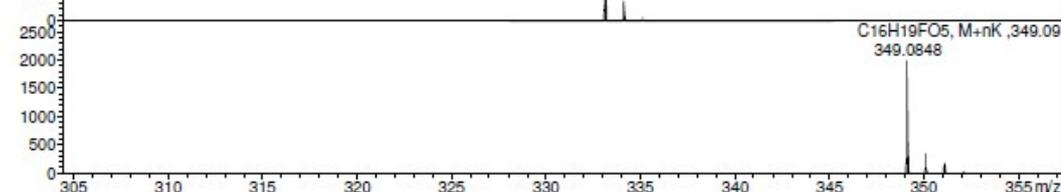
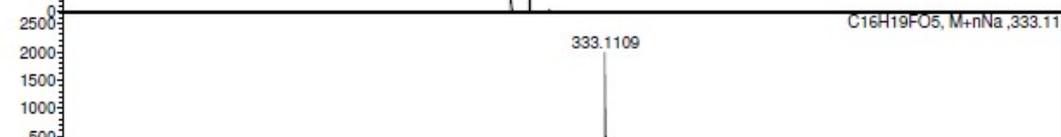
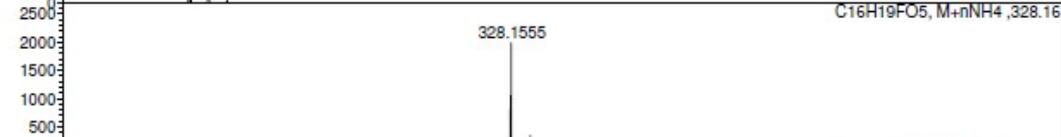
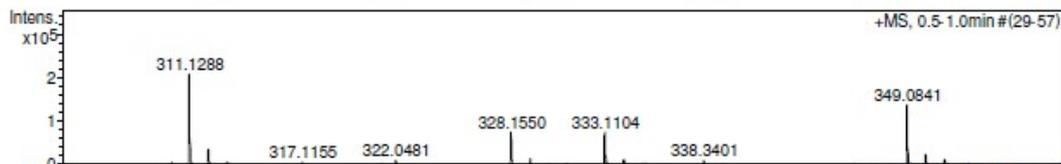
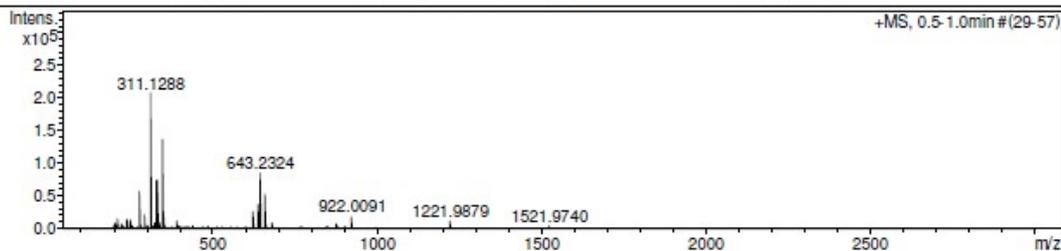
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 Sample Name /YAR BL-1618
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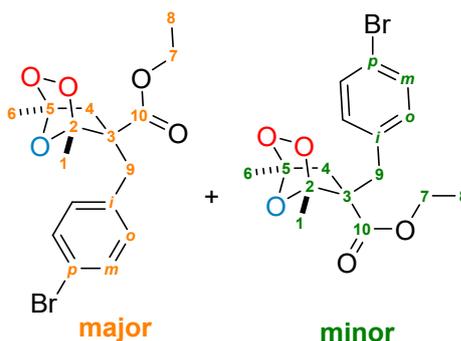
Acquisition Date 23.04.2024 16:17:36
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl-5-(4-bromobenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2c+*trans*-2c



Display Report

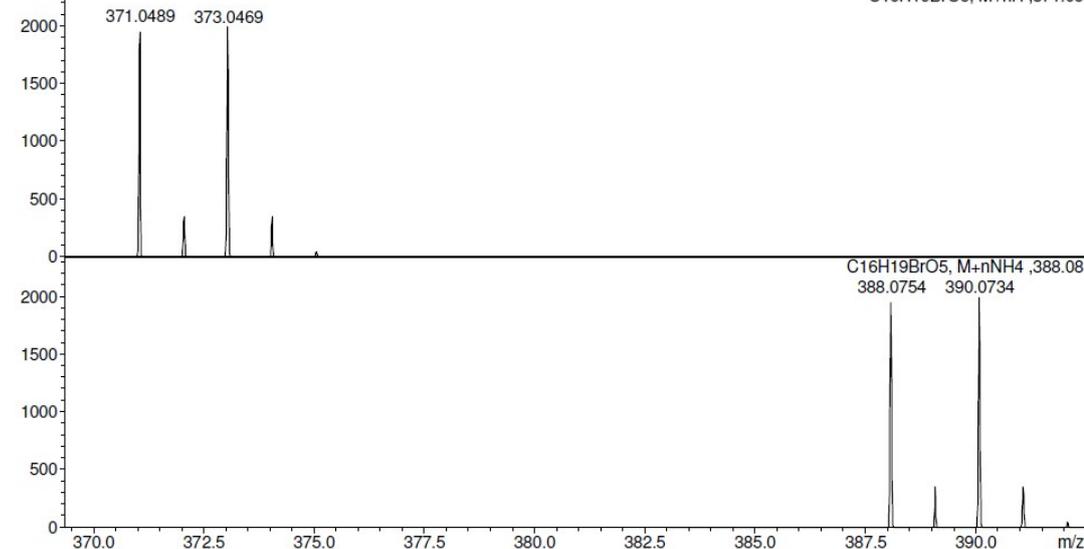
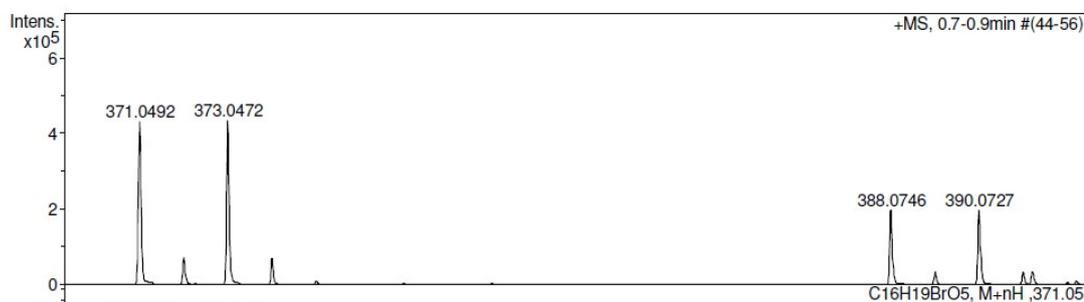
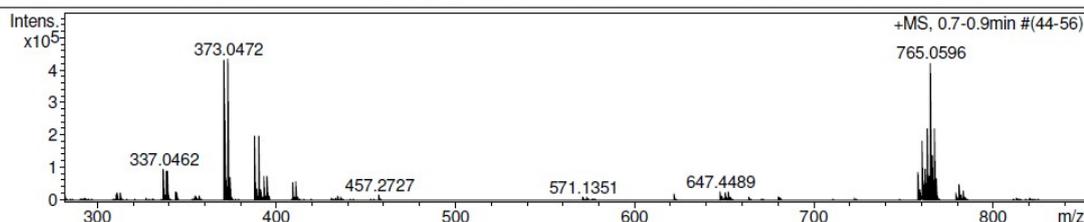
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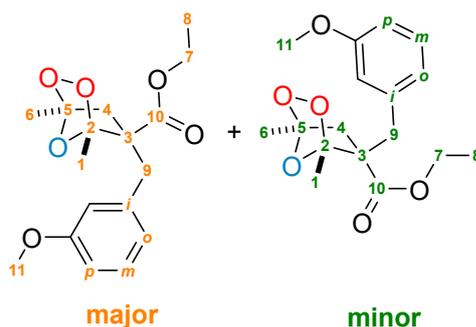
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 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl-5-(4-methoxybenzyl)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2d+*trans*-2d



Display Report

Analysis Info

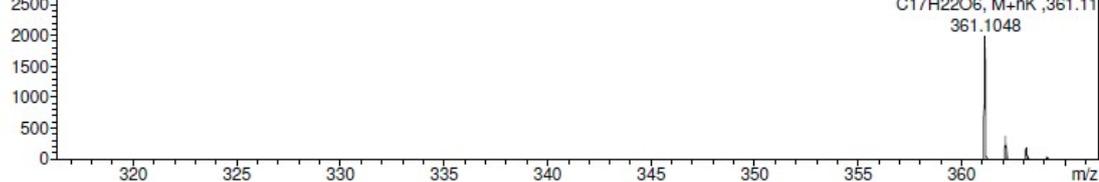
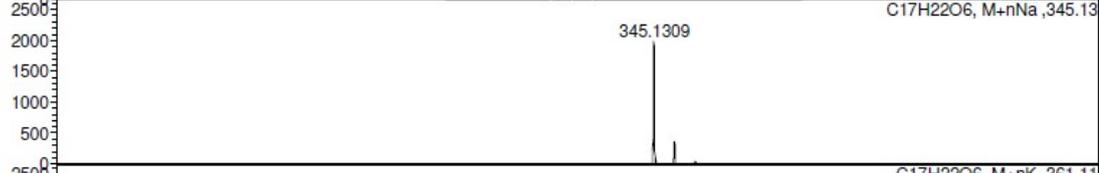
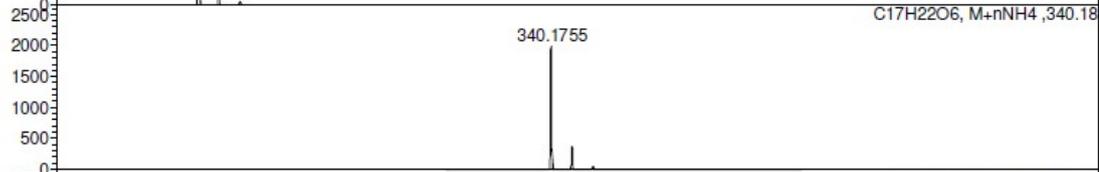
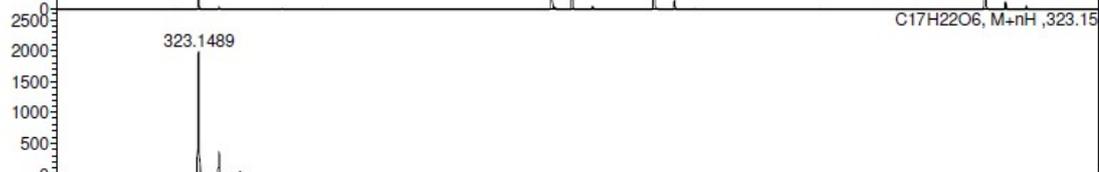
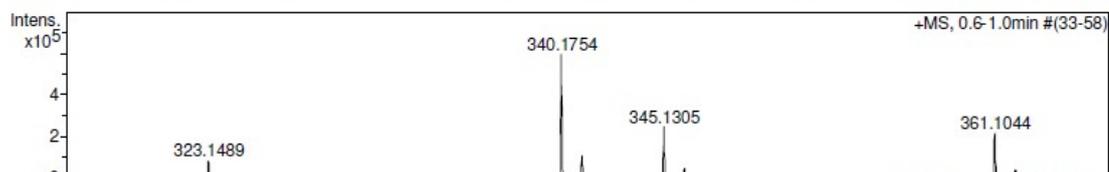
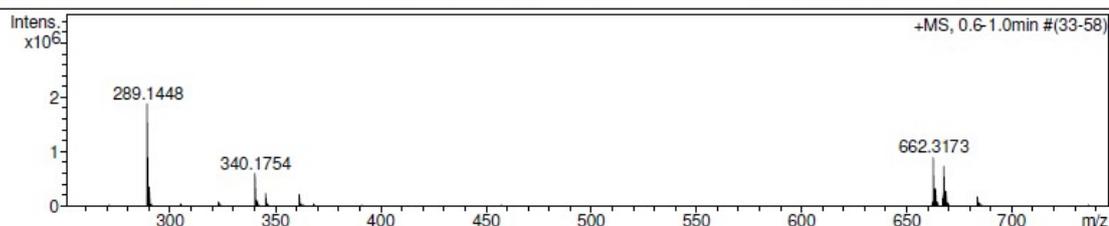
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Acquisition Date 22.12.2023 12:26:22

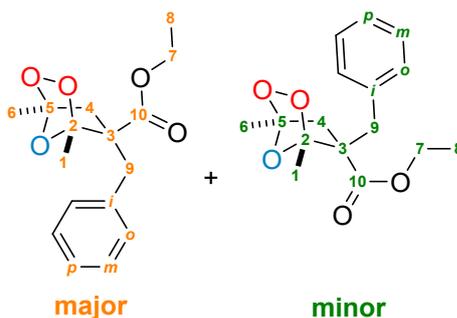
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl-5-benzyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis-2e+trans-2e*



Display Report

Analysis Info

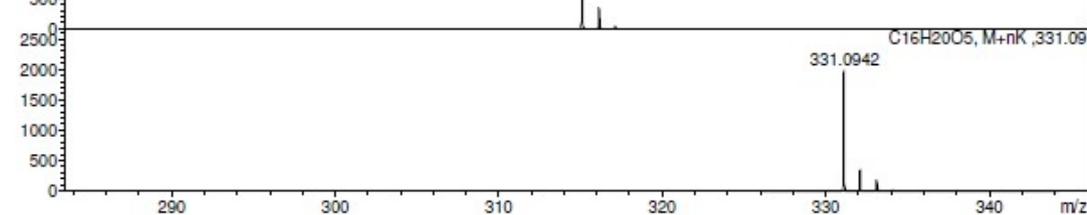
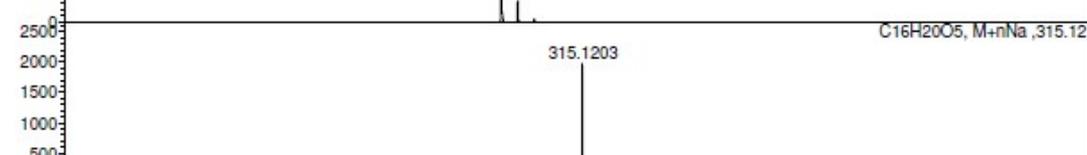
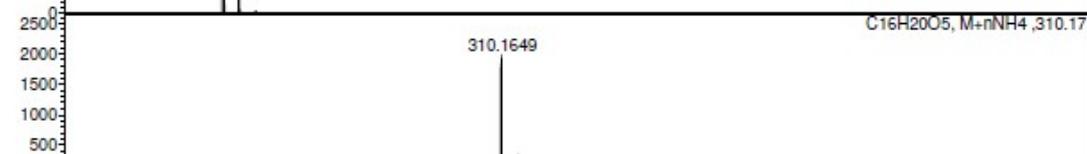
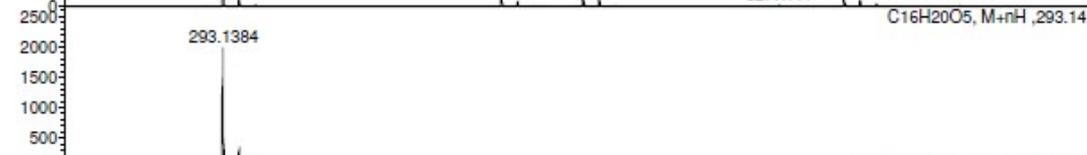
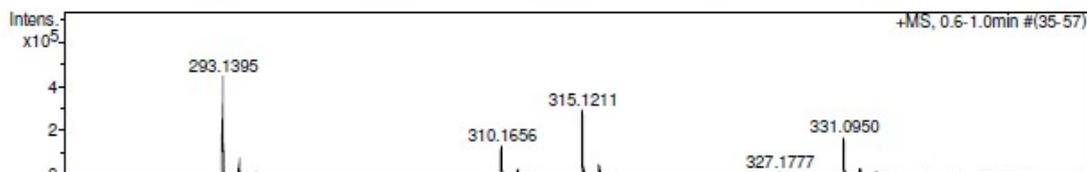
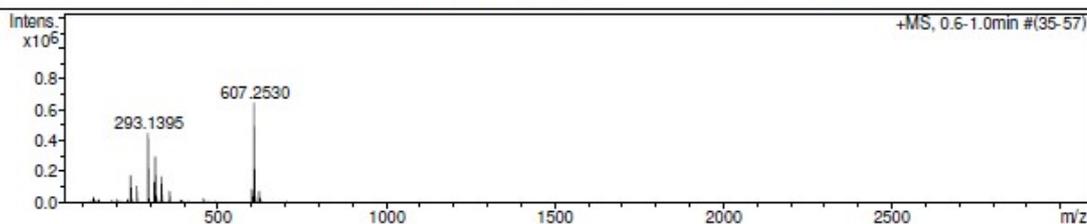
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Acquisition Date 22.12.2023 12:18:53

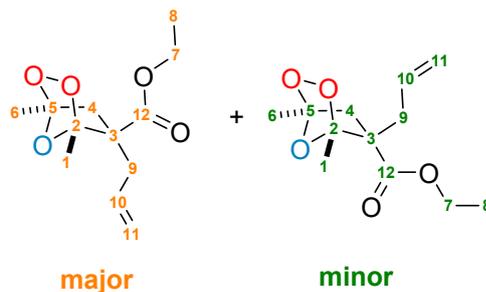
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl-5-allyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2f+*trans*-2f



Display Report

Analysis Info

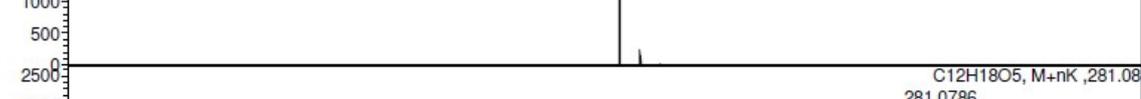
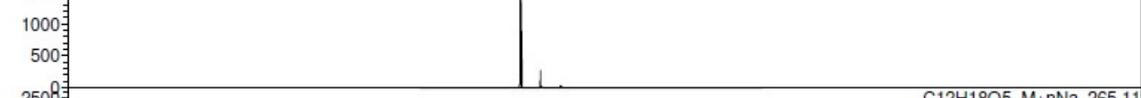
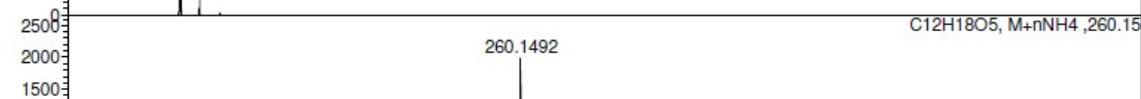
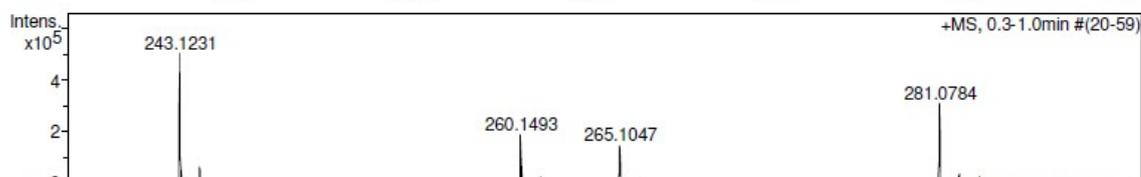
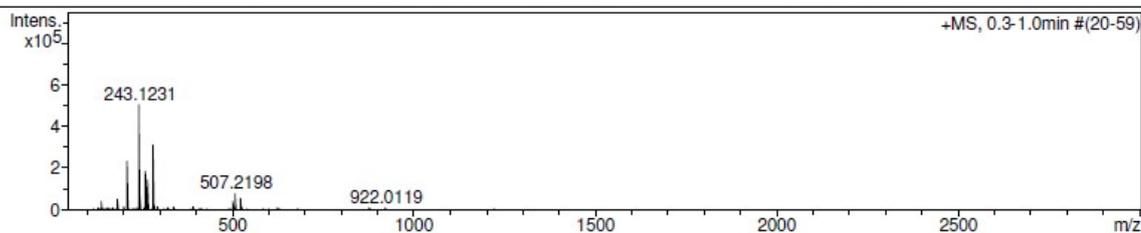
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 Comment C12H18O5 mH243.1227 calibrant added CH3CN

Acquisition Date 05.03.2024 13:09:04

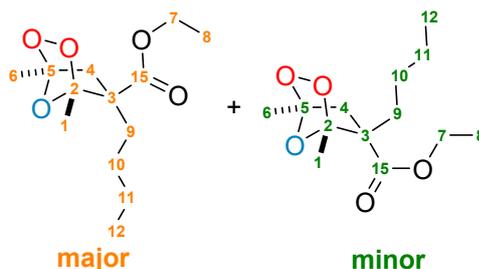
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl-5-butyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2g+*trans*-2g



Display Report

Analysis Info

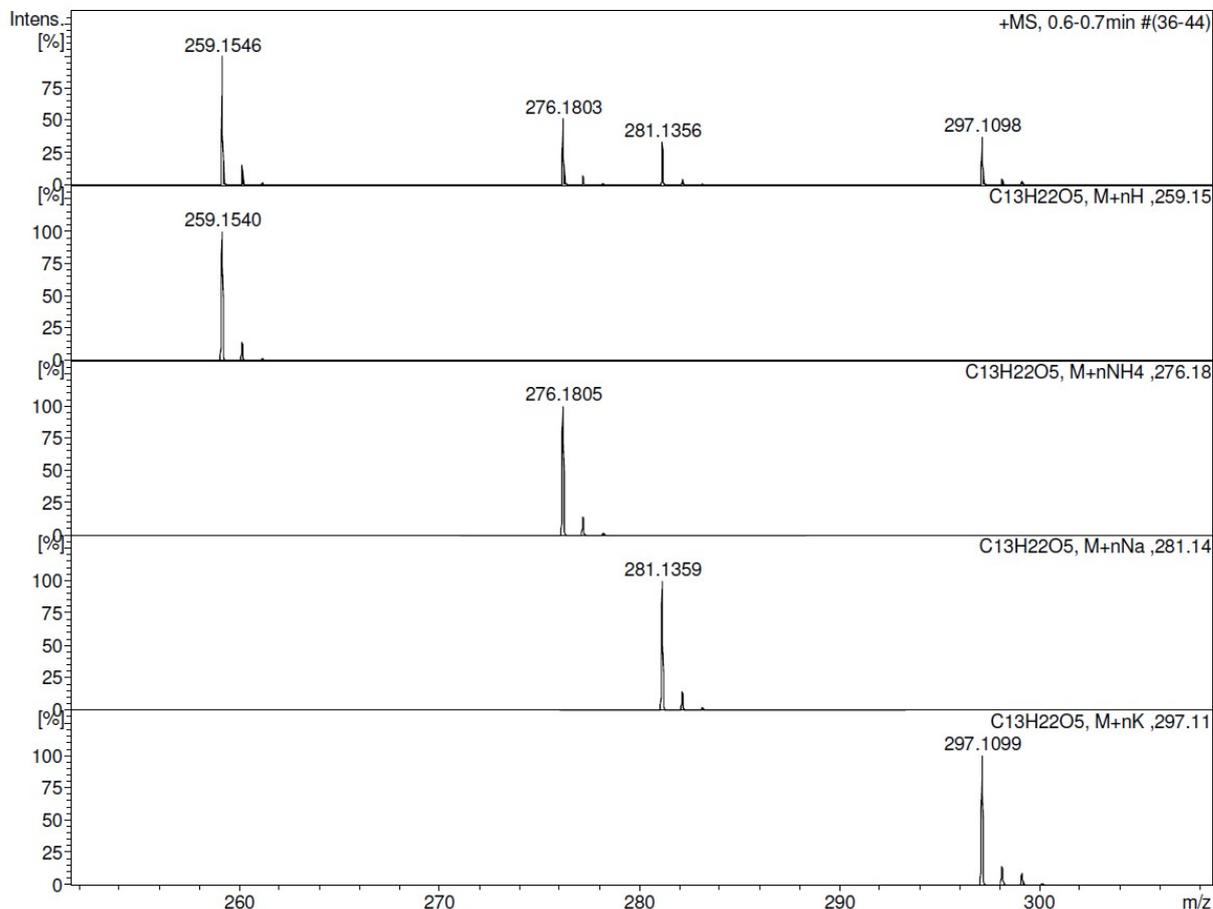
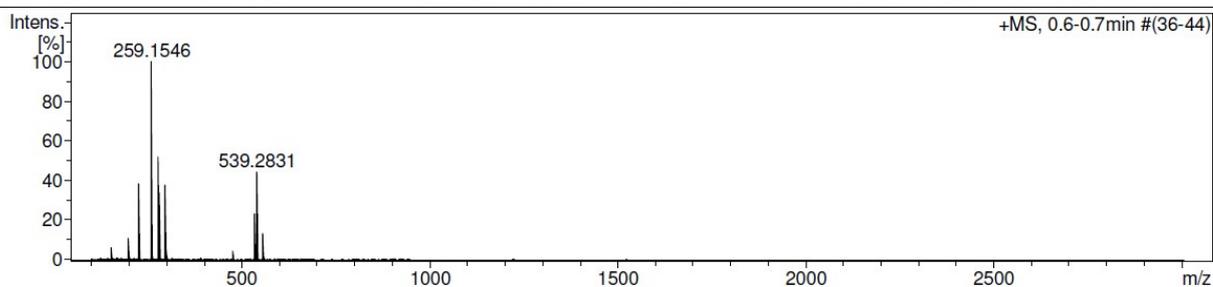
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 Sample Name /IYAR BL-1612
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Acquisition Date 28.03.2024 13:30:16

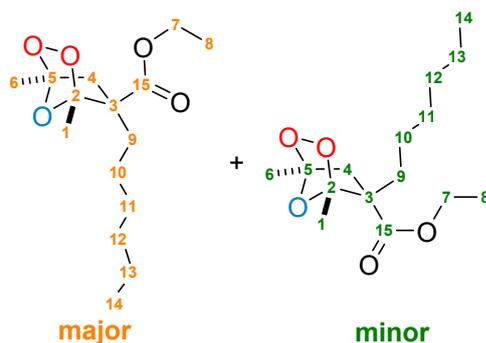
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl-5-hexyl-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5-carboxylate, *cis*-2h+*trans*-2h



Display Report

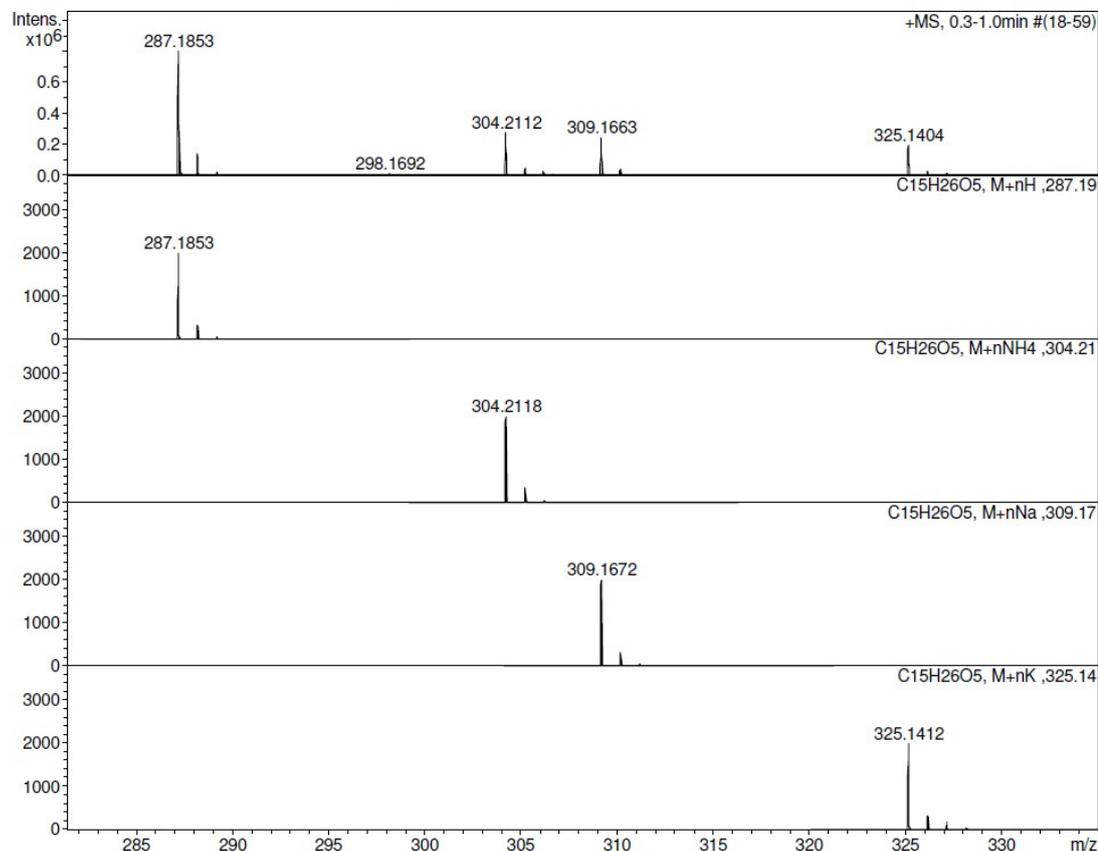
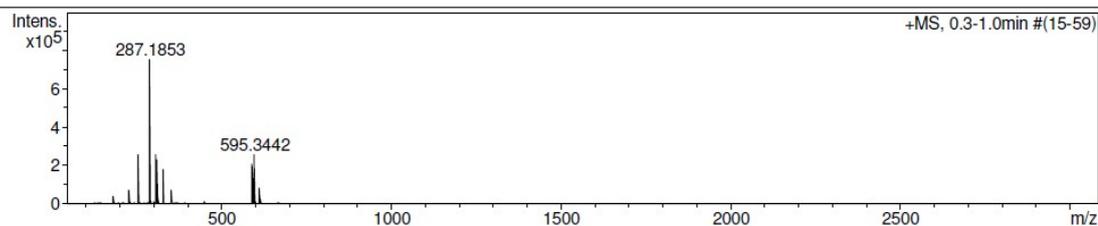
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Analysis Name D:\Data\Kolotyrkina\2024\Belyakova\0307005.d
 Method tune_low.m
 Sample Name /IYAR BL-1602
 Comment C15H26O5 mH 287.1853 calibrant added CH3CN

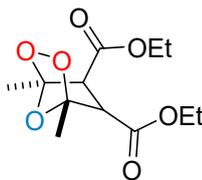
Acquisition Date 07.03.2024 12:48:25
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Diethyl (1*S**,4*S**,5*S**)-1,4-dimethyl-2,3,7-trioxabicyclo[2.2.1]heptane-5,6-dicarboxylate, 2i



Display Report

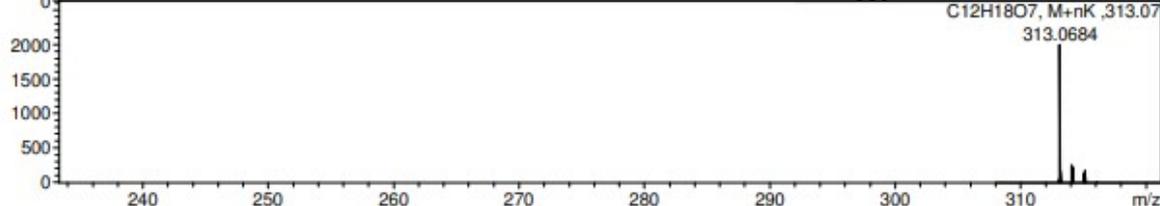
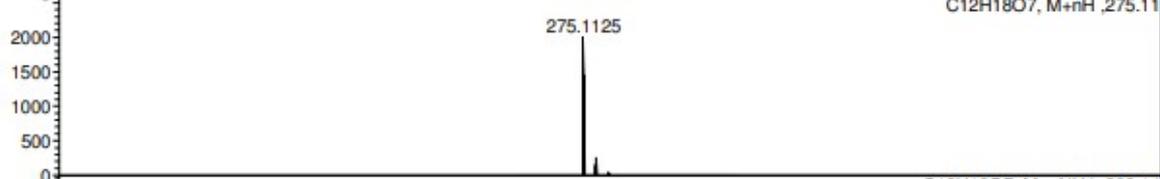
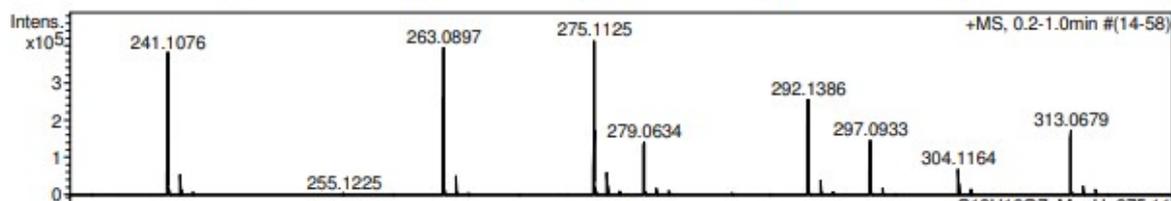
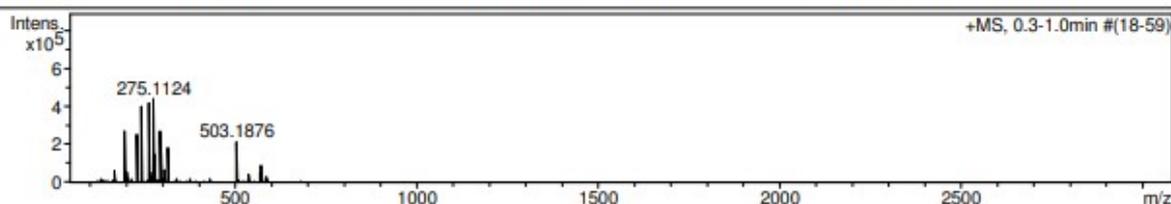
Analysis Info

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 Method tune_low.m
 Sample Name /YAR BL-1642_1
 Comment C12H18O7 mH275.1125 clb added, CH3CN

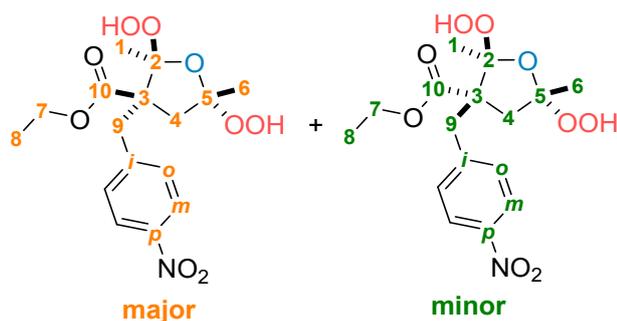
Acquisition Date 04.07.2024 13:13:41
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



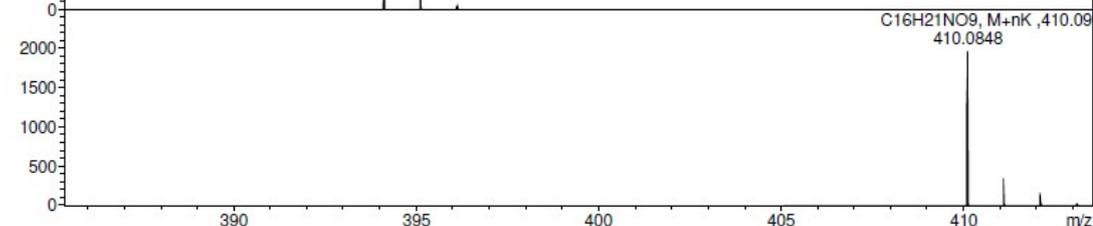
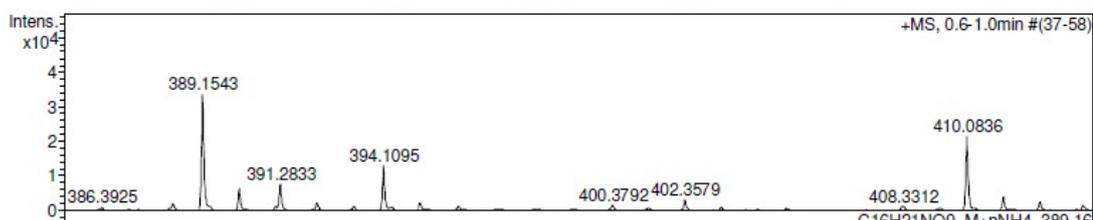
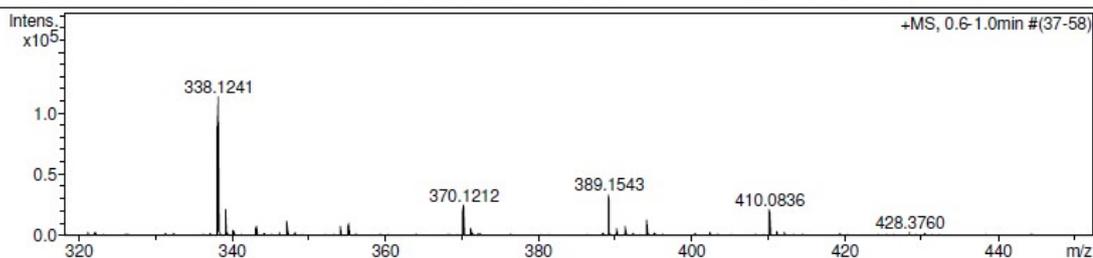
Ethyl 2,5-dihydroperoxy-2,5-dimethyl-3-(4-nitrobenzyl)tetrahydrofuran-3-carboxylate, *cis*-**3a**+*trans*-**3a**



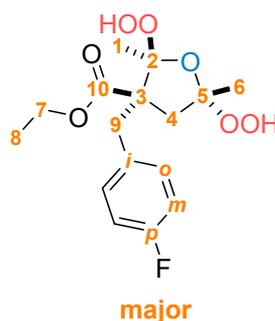
Display Report

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\Kolotyrykina\2023\Belyakova\0831017.d	Acquisition Date	31.08.2023 13:24:26
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/TERN BL-1527	Instrument / Ser#	micrOTOF 10248
Comment	C16H21NO9 mH372.1289 clb added CH3CN		

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



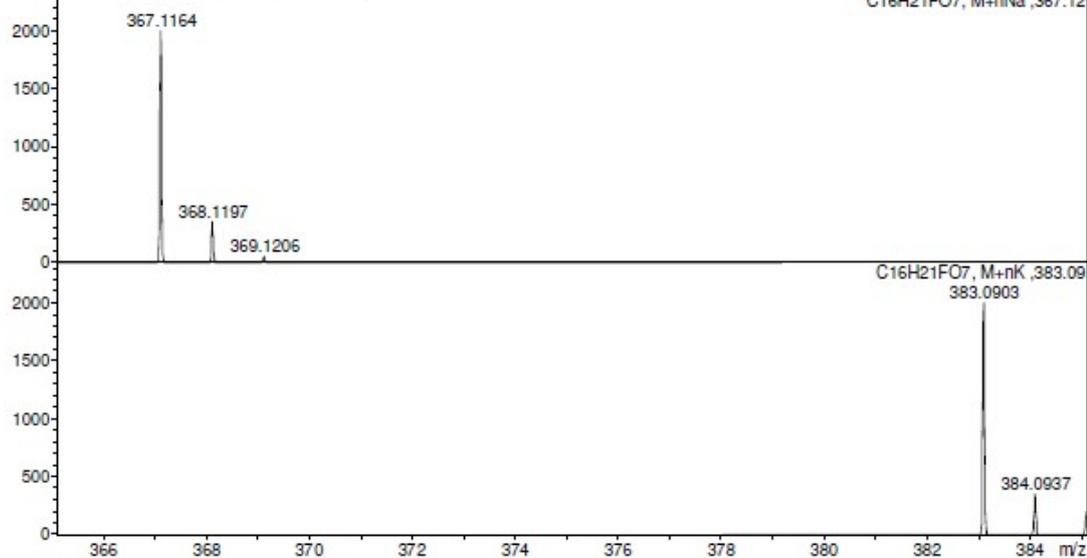
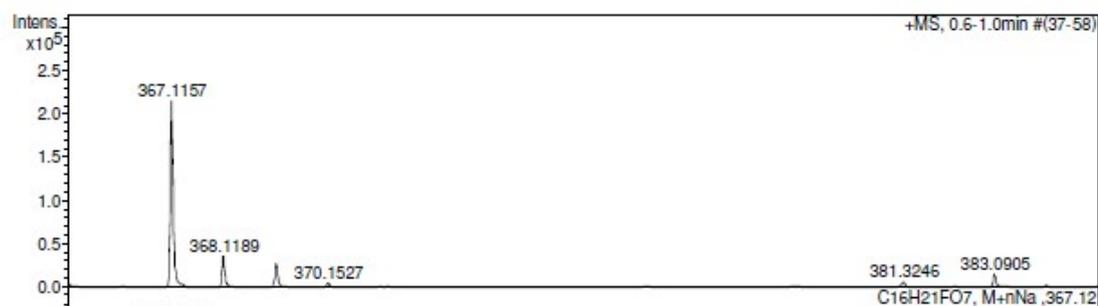
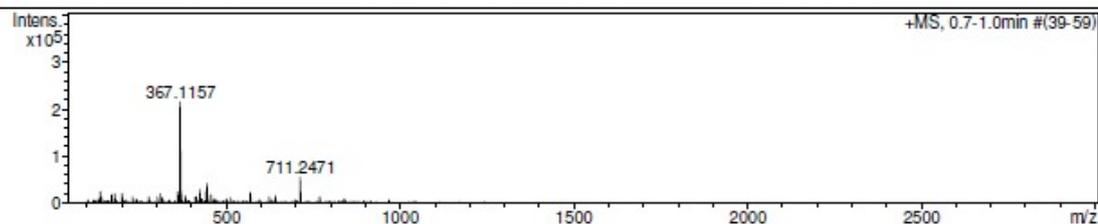
Ethyl (2*S**,3*S**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3b



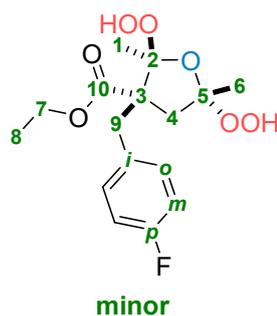
Display Report

Analysis Info		Acquisition Date	
Analysis Name	D:\Data\Kolotyrykina\2024\Belyakova\0507016.d	Acquisition Date	07.05.2024 13:21:25
Method	tune_low.m	Operator	BDAL@DE
Sample Name	/IYAR BL-1621_2	Instrument / Ser#	microTOF 10248
Comment	C16H21FO7 mH345.1344 calibrant added CH3CN		

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S**,3*R**,5*S**)-3-(4-fluorobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3b



Display Report

Analysis Info

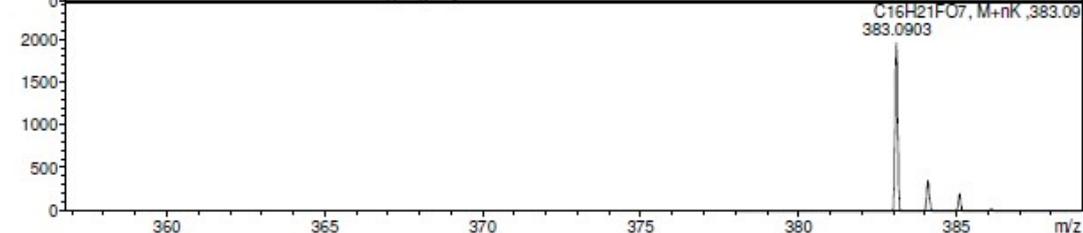
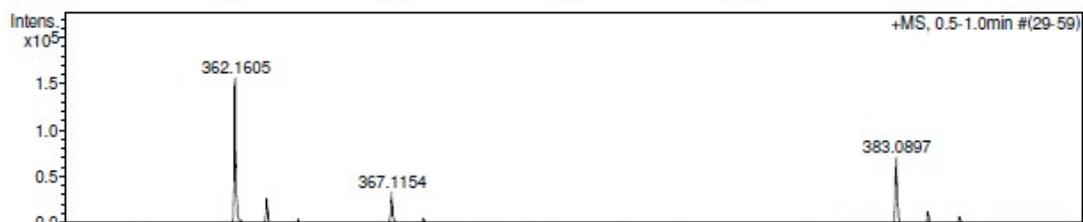
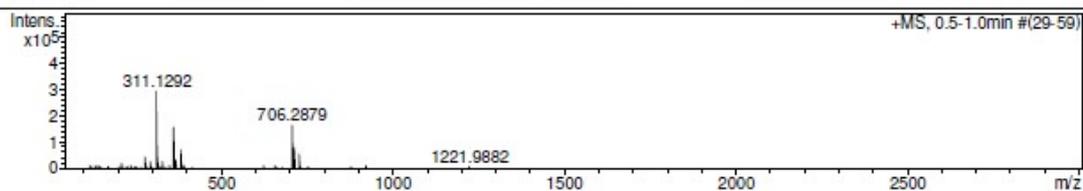
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Acquisition Date 08.05.2024 12:45:41

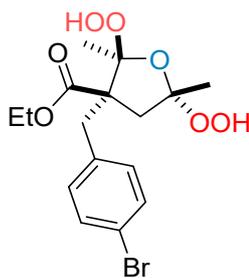
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S,3*S**,5*S**)-3-(4-bromobenzyl)-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3c**



Display Report

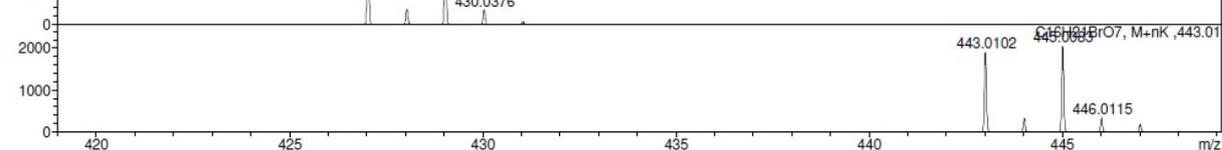
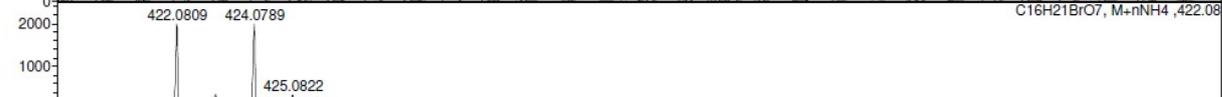
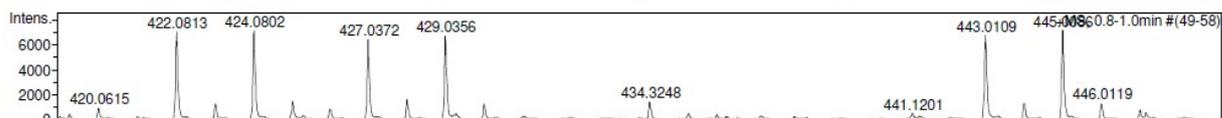
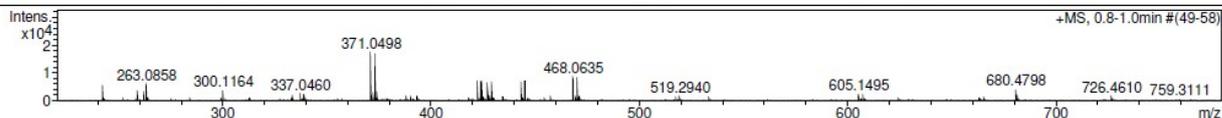
Analysis Info

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 Method tune_low.m
 Sample Name /IYAR BL-1578
 Comment C16H21BrO7 mH405.0554 calibrant added CH3CN

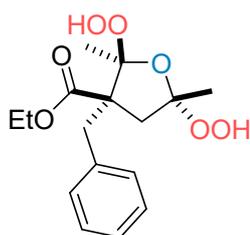
Acquisition Date 25.01.2024 14:37:22
 Operator BDAL@DE
 Instrument / Ser# microTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S,3*S**,5*R**)-3-benzyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3e**



Display Report

Analysis Info

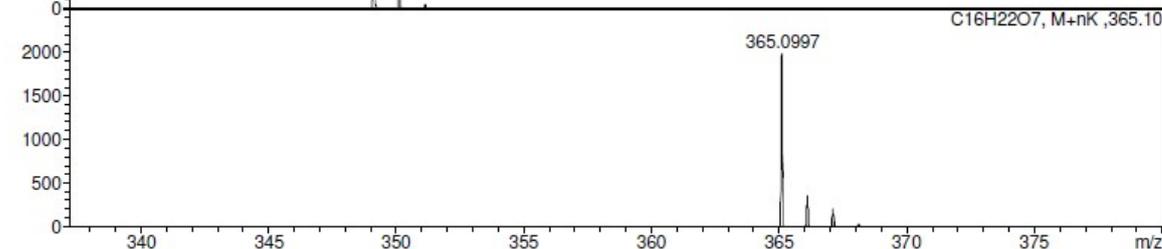
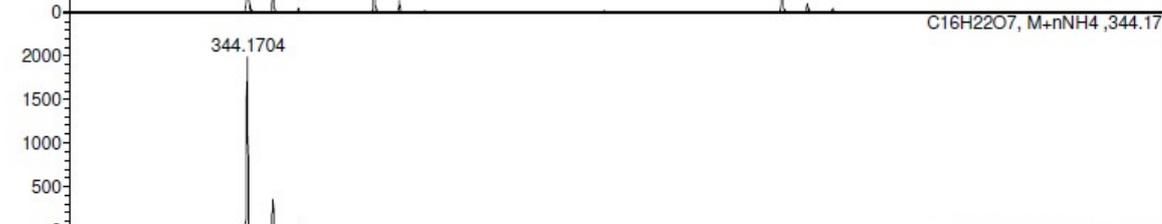
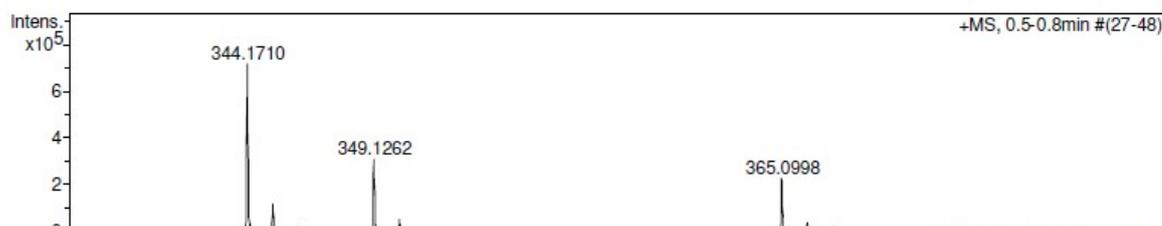
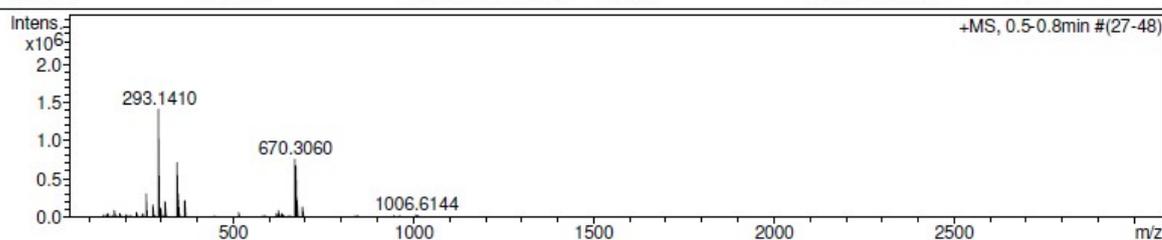
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 Sample Name /IYAR BL-1582
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Acquisition Date 25.01.2024 14:12:05

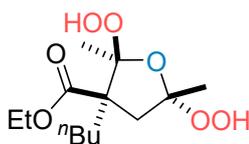
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S,3*S**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3g**



Display Report

Analysis Info

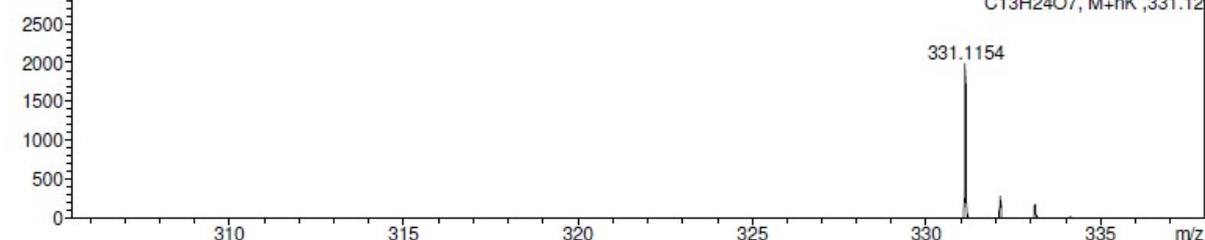
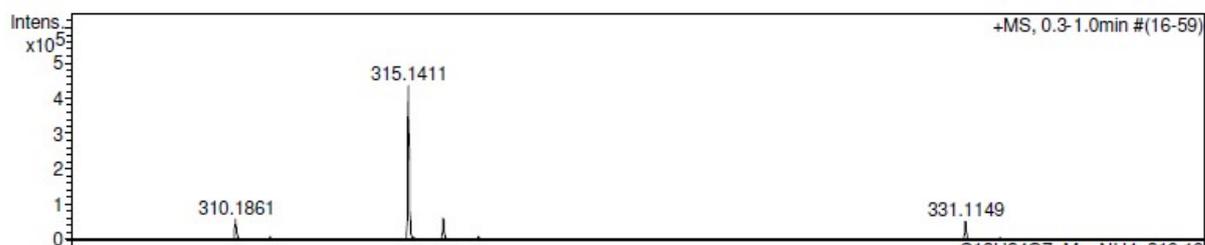
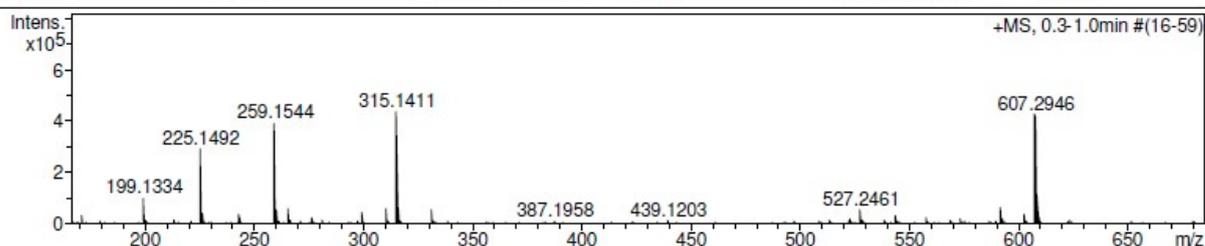
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Acquisition Date 04.04.2024 12:44:31

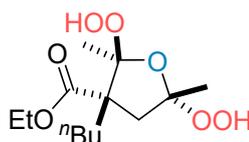
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S,3*R**,5*S**)-3-butyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3g**



Display Report

Analysis Info

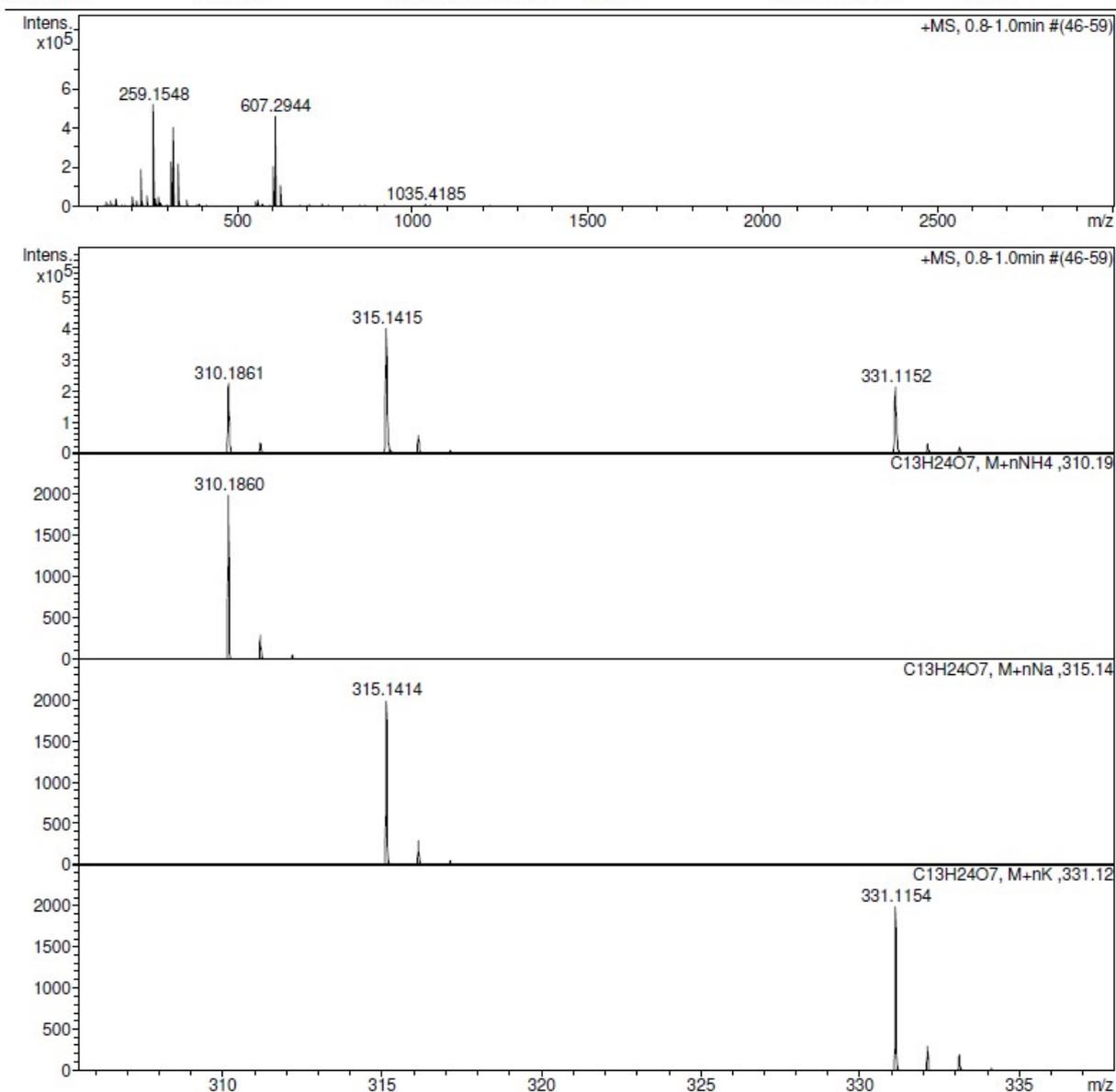
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Acquisition Date 04.04.2024 12:39:14

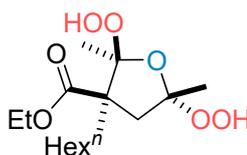
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S,3*S**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *cis*-3h**



Display Report

Analysis Info

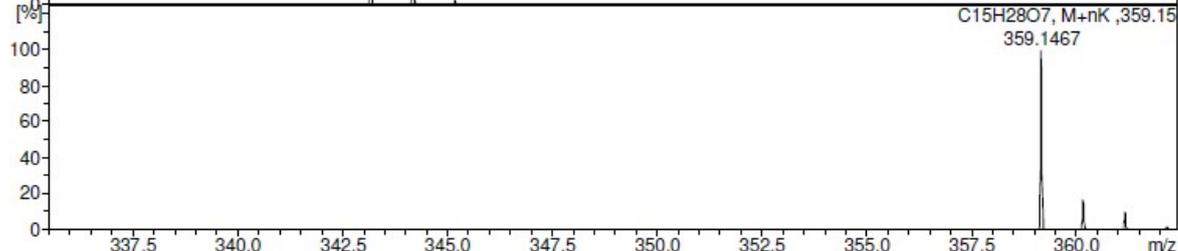
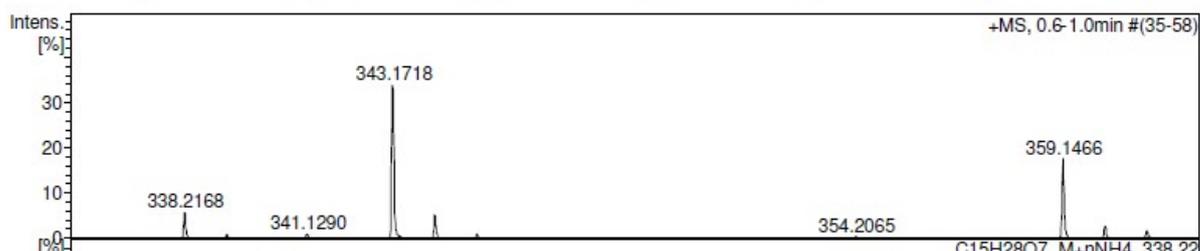
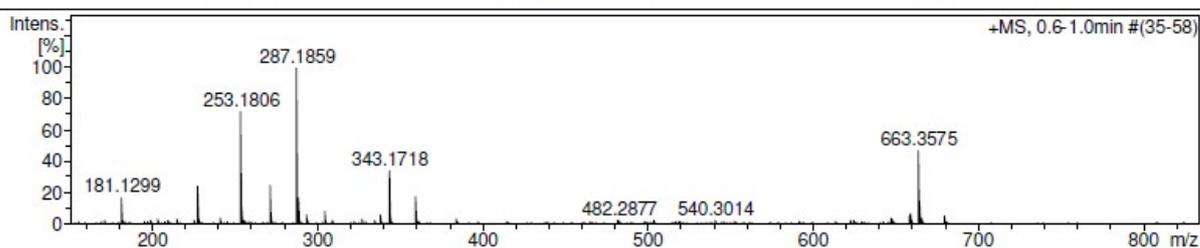
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Acquisition Date 09.04.2024 13:44:04

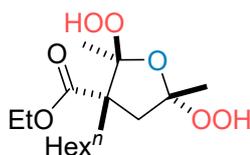
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (2*S,3*R**,5*S**)-3-hexyl-2,5-dihydroperoxy-2,5-dimethyltetrahydrofuran-3-carboxylate, *trans*-3h**



Display Report

Analysis Info

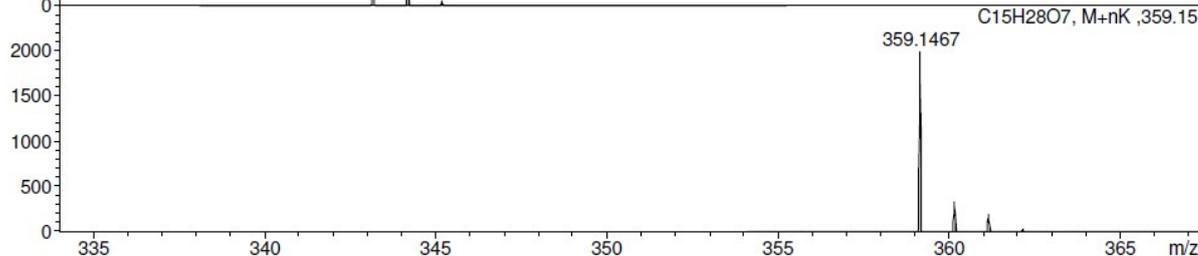
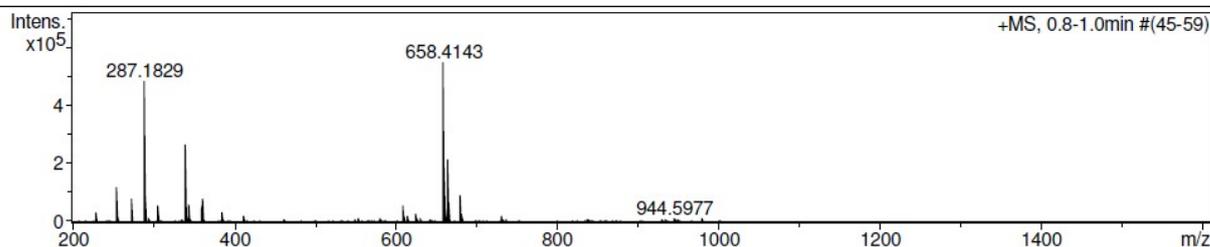
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Acquisition Date 09.04.2024 13:39:07

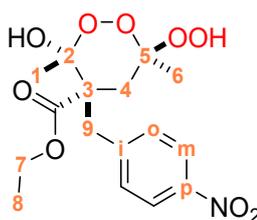
Operator BDAL@DE
 Instrument / Ser# microTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (3*R,4*S**,6*R**)-6-hydroperoxy-3-hydroxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 4a**



Display Report

Analysis Info

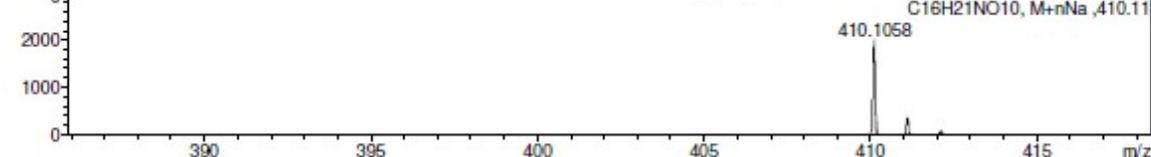
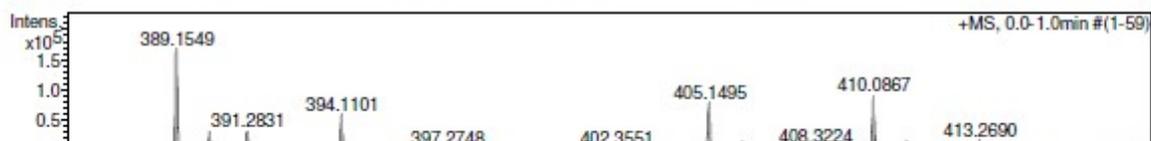
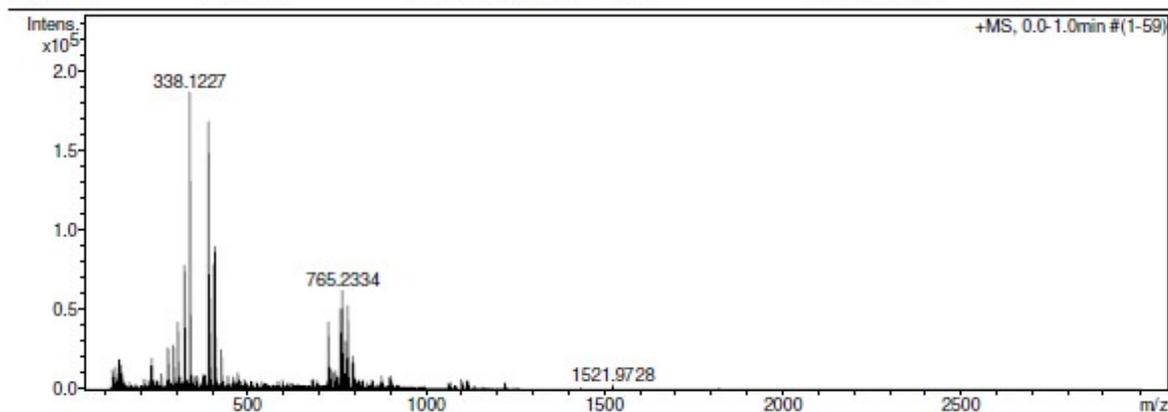
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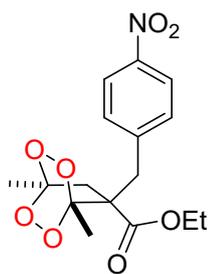
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (1*R,4*R**,7*S**)-1,4-dimethyl-7-(4-nitrobenzyl)-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5a**



Display Report

Analysis Info

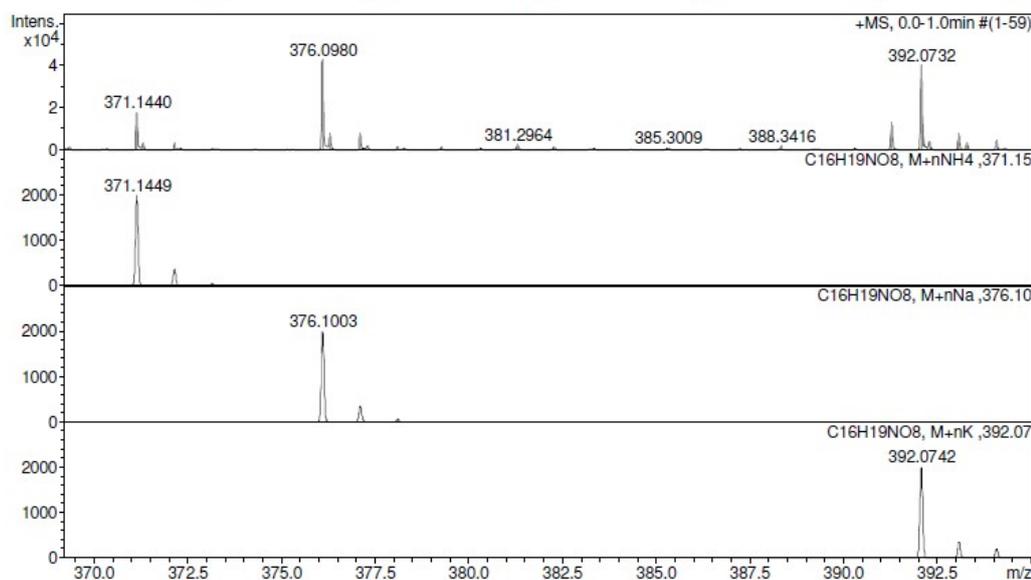
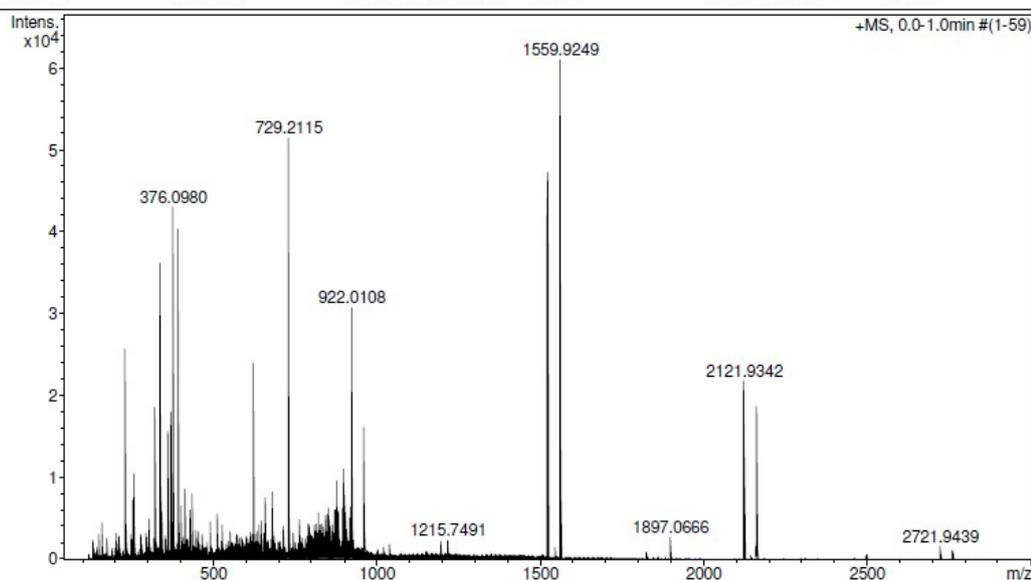
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 Method tune_low.m
 Sample Name /TERN Rd1314
 Comment CH3CN 100%, dil. 20, calibrant added

Acquisition Date 14.02.2022 17:49:17

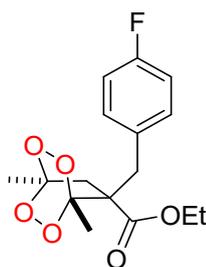
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



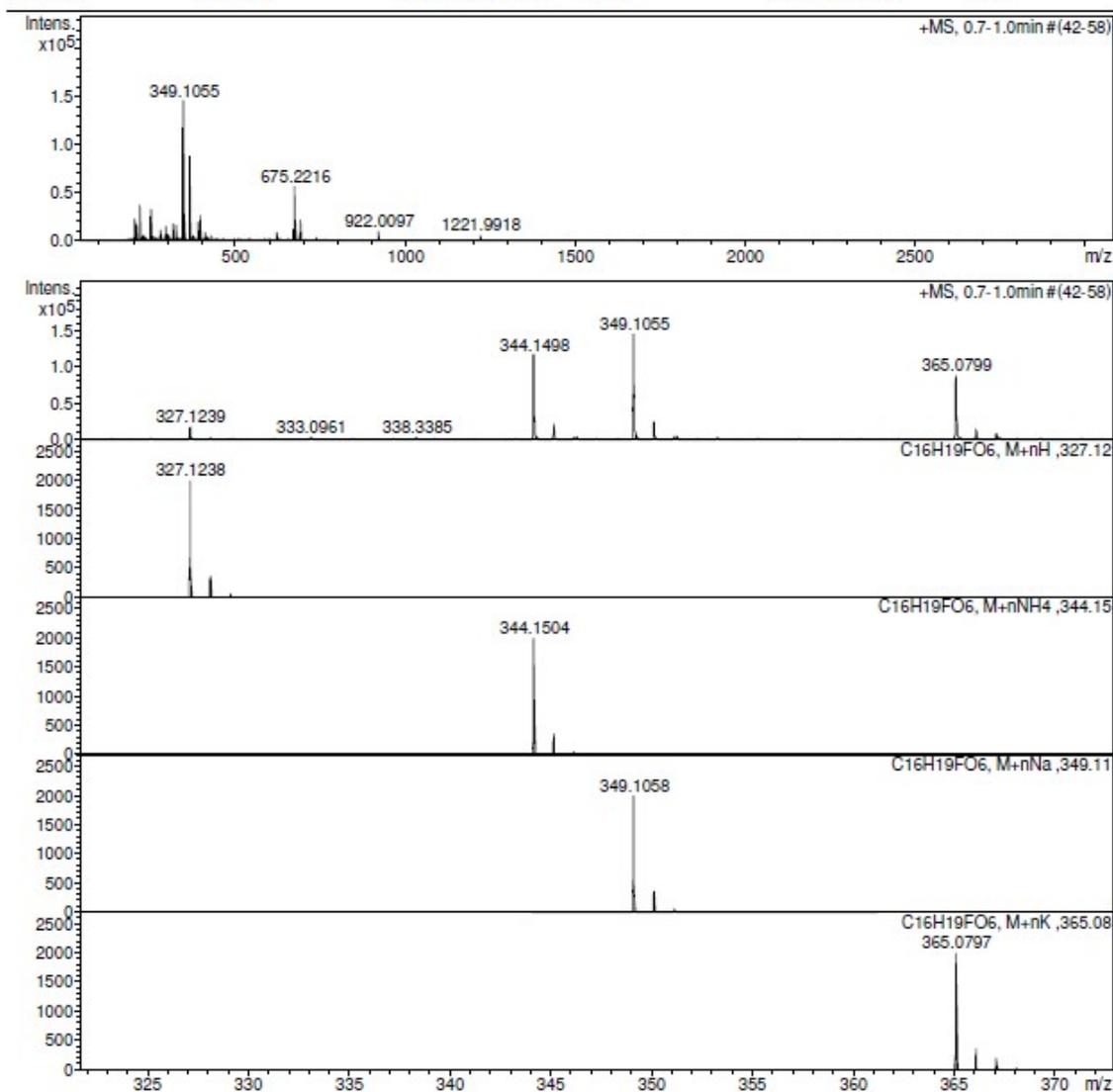
Ethyl (1*R,4*R**,7*S**)-7-(4-fluorobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5b**



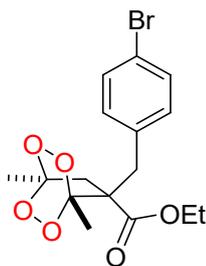
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Method	tune_low.m	Instrument / Ser#	micrOTOF 10248
Sample Name	/IYAR BL-1619		
Comment	C16H19FO6 mH327.1238 calibrant added CH3CN		

Acquisition Parameter					
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (1*R**,4*R**,7*S**)-7-(4-bromobenzyl)-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5c



Display Report

Analysis Info

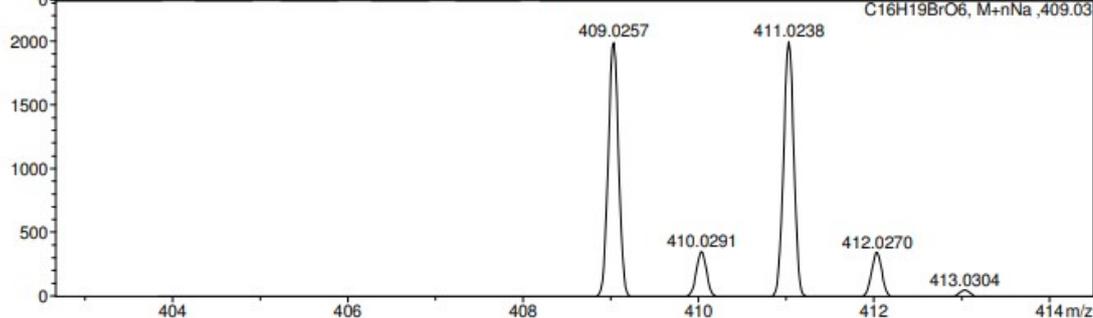
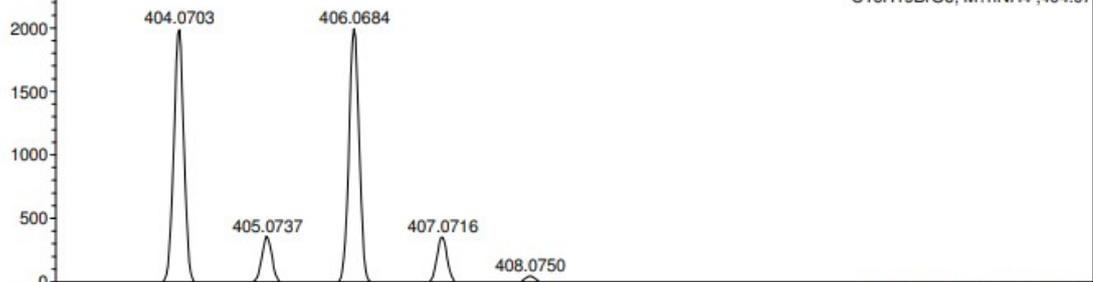
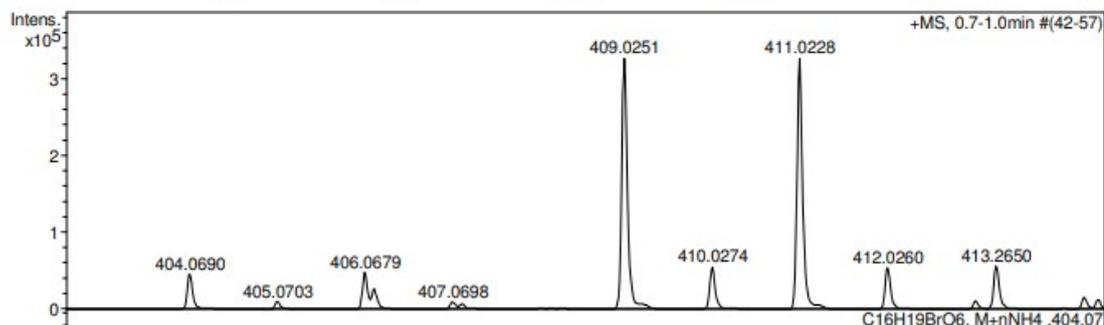
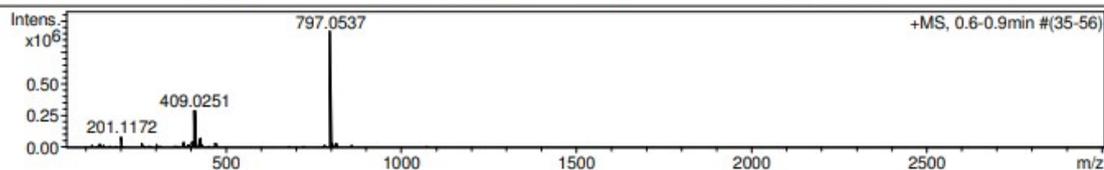
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Acquisition Date 13.12.2023 12:08:13

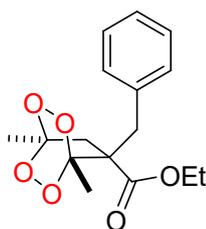
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (1*R,4*R**,7*S**)-7-benzyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5e**



Display Report

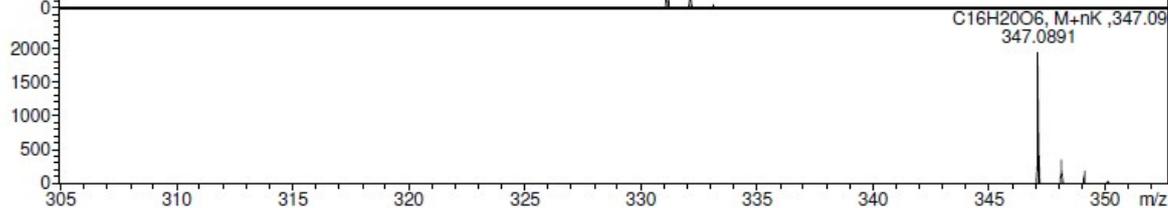
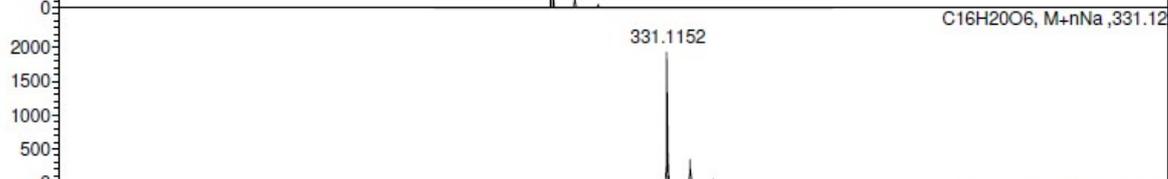
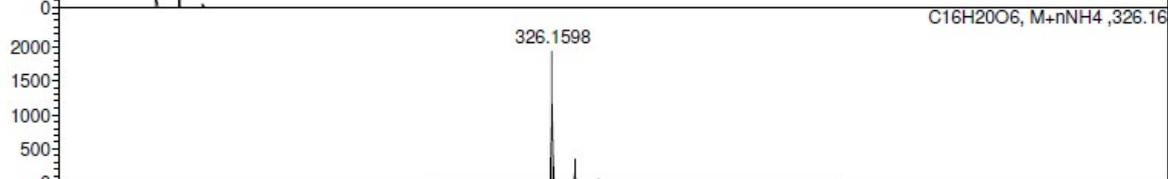
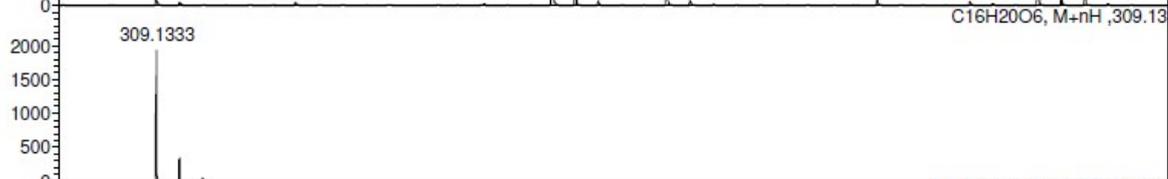
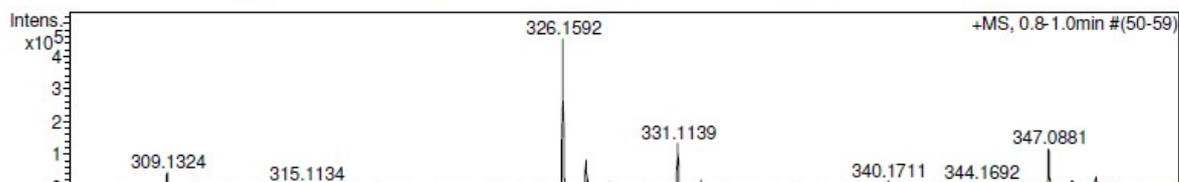
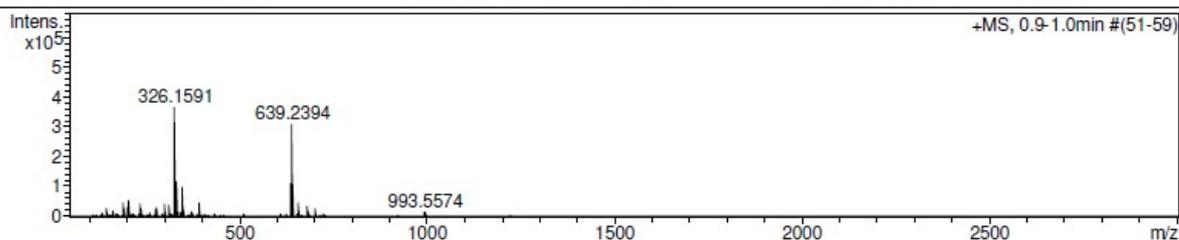
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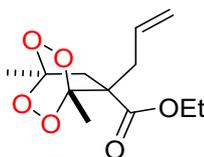
Acquisition Date 14.12.2023 12:19:00
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (1*R,4*R**,7*S**)-7-allyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5f**



Display Report

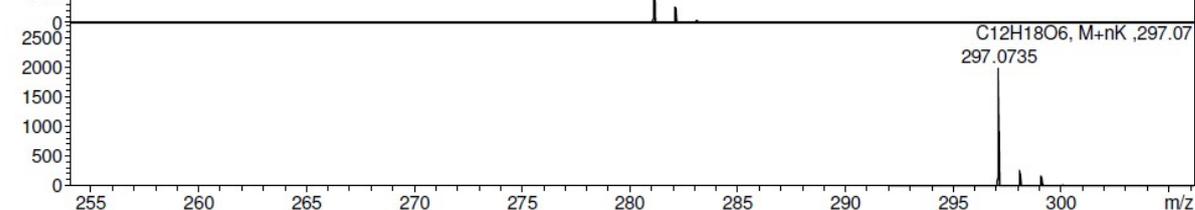
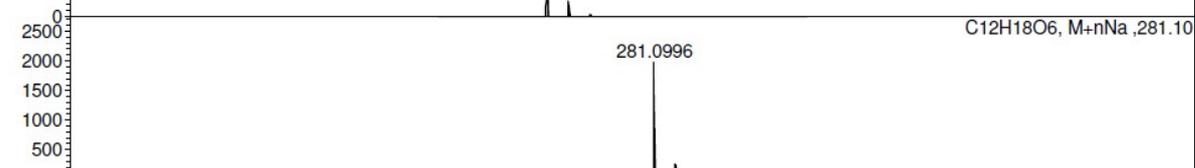
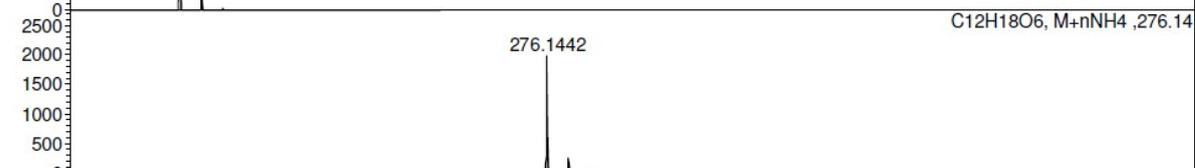
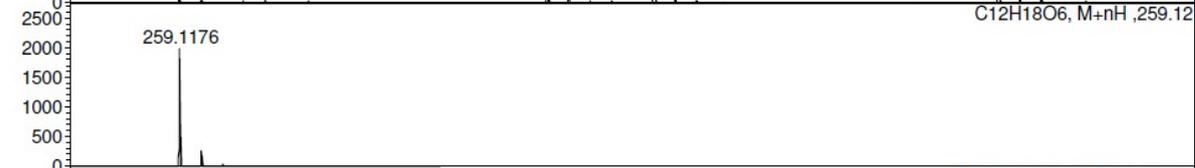
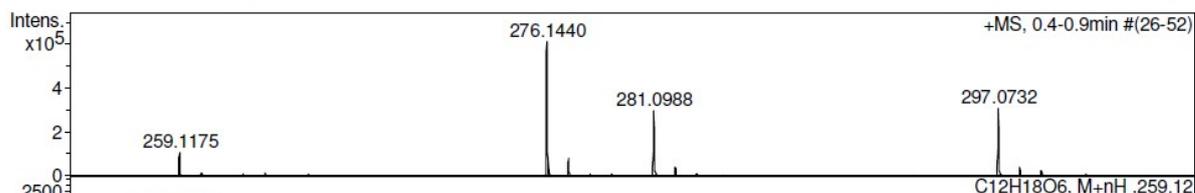
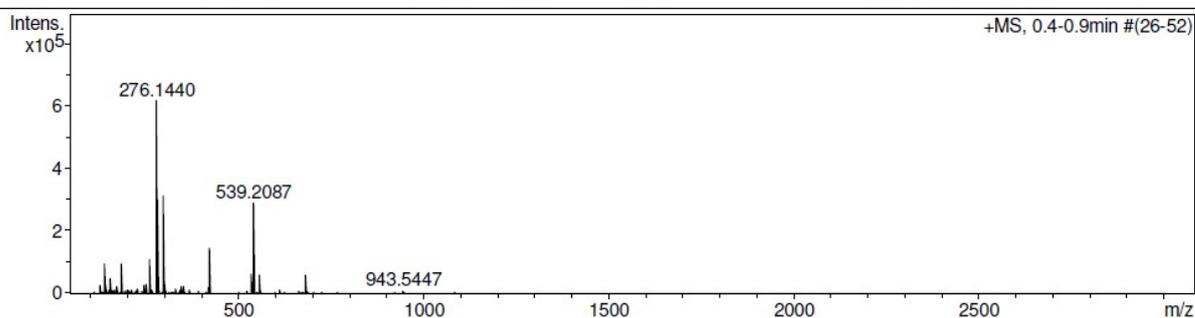
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Method tune_low.m
Sample Name /IYAR BL-1607_1
Comment C12H18O6 mH259.1176 calibrant added CH3CN

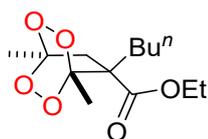
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Operator BDAL@DE
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (1*R,4*R**,7*S**)-7-butyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5g**



Display Report

Analysis Info

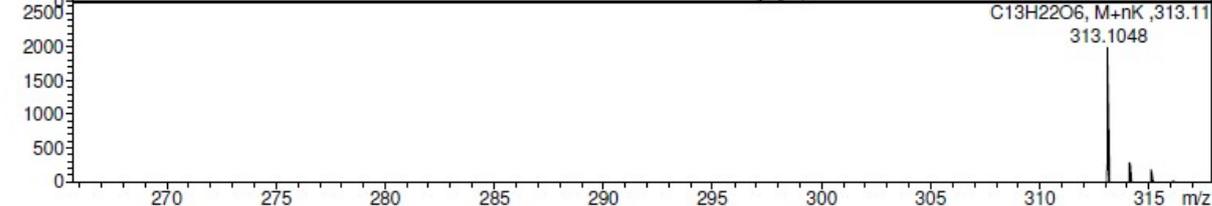
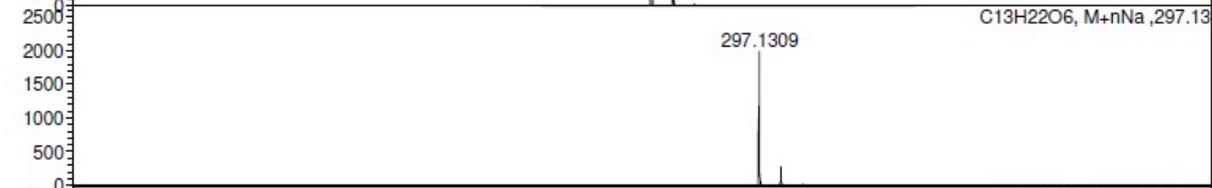
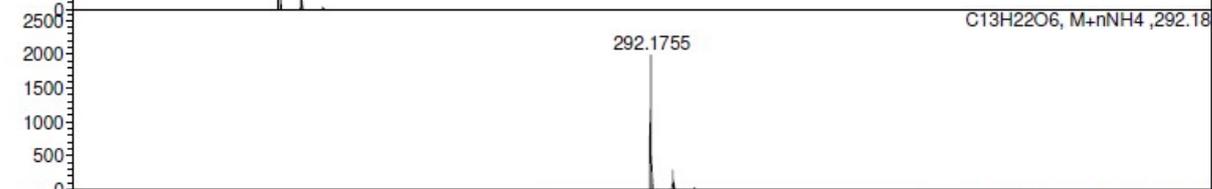
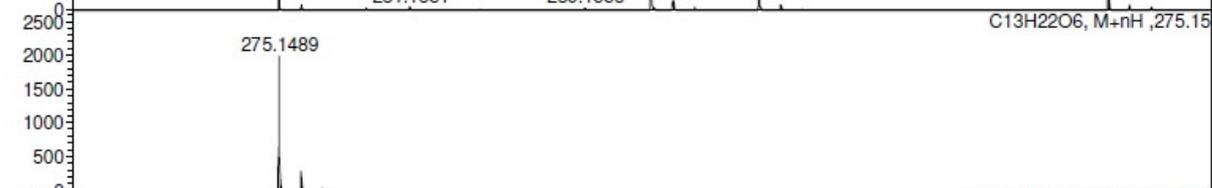
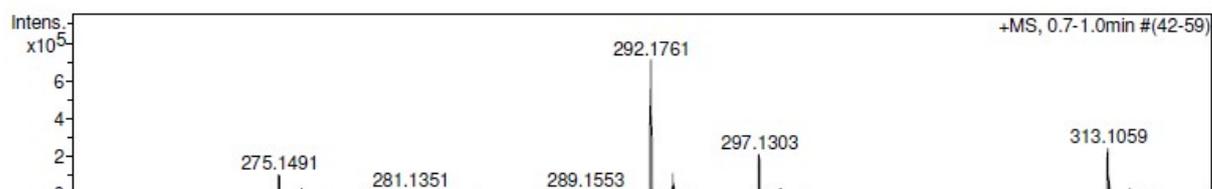
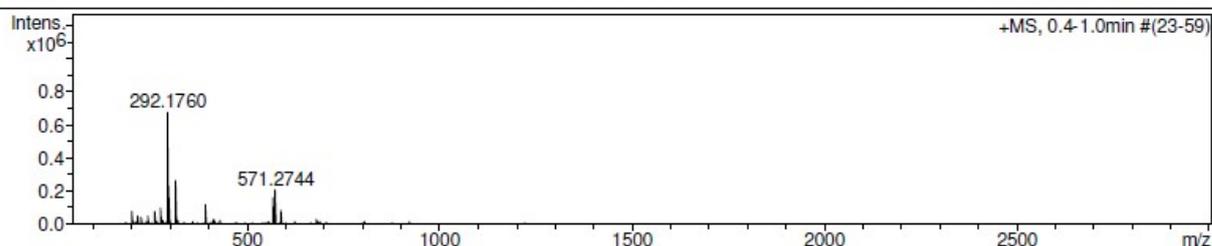
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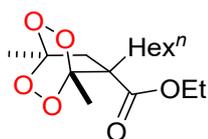
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (1*R,4*R**,7*S**)-7-hexyl-1,4-dimethyl-2,3,5,6-tetraoxabicyclo[2.2.2]octane-7-carboxylate, 5h**



Display Report

Analysis Info

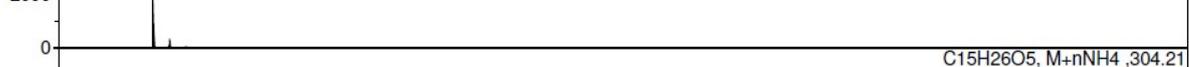
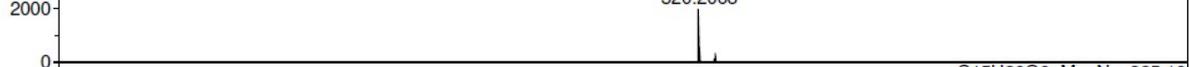
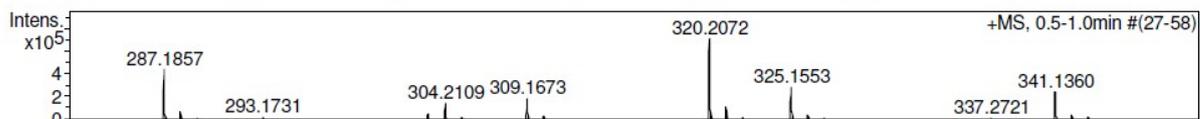
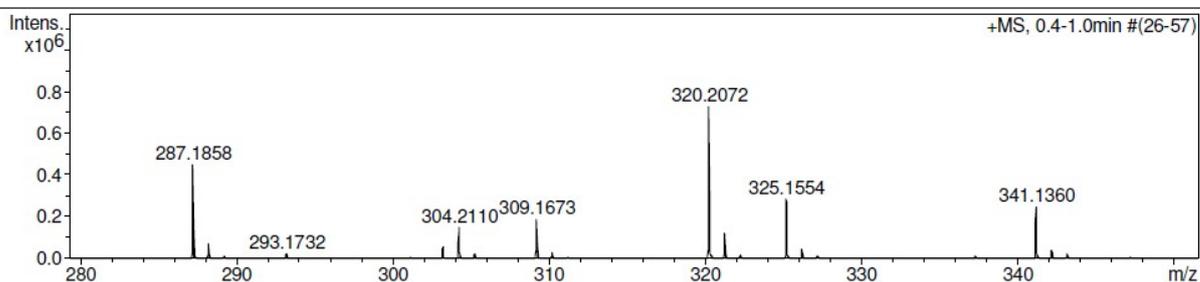
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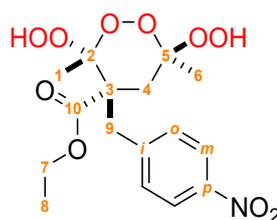
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (3*R,4*S**,6*R**)-3,6-dihydroperoxy-3,6-dimethyl-4-(4-nitrobenzyl)-1,2-dioxane-4-carboxylate, 6a**



Display Report

Analysis Info

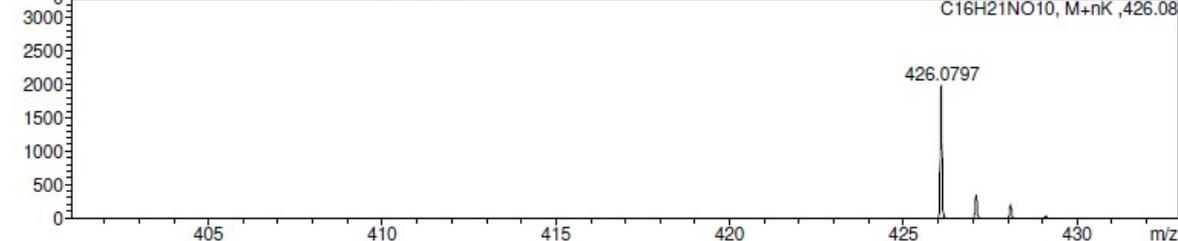
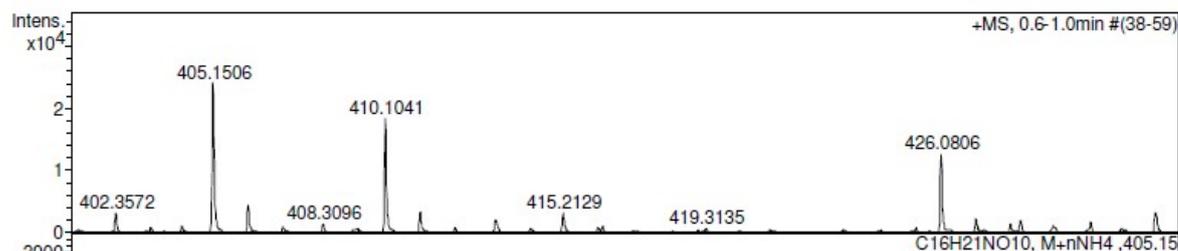
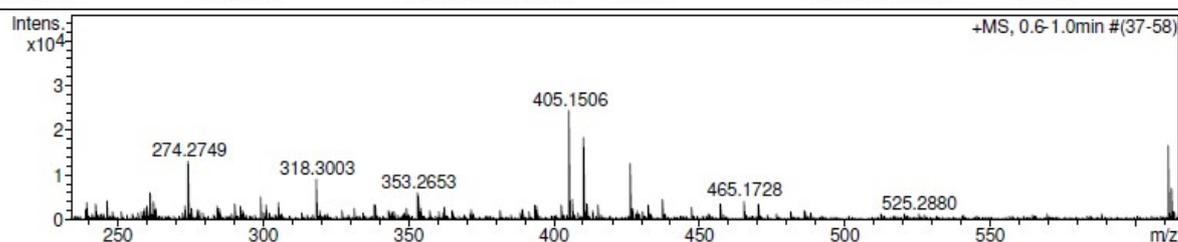
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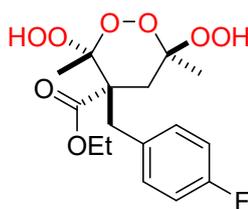
Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (3*R,4*S**,6*R**)-4-(4-fluorobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6b**



Display Report

Analysis Info

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 Sample Name /IYAR BL-1620
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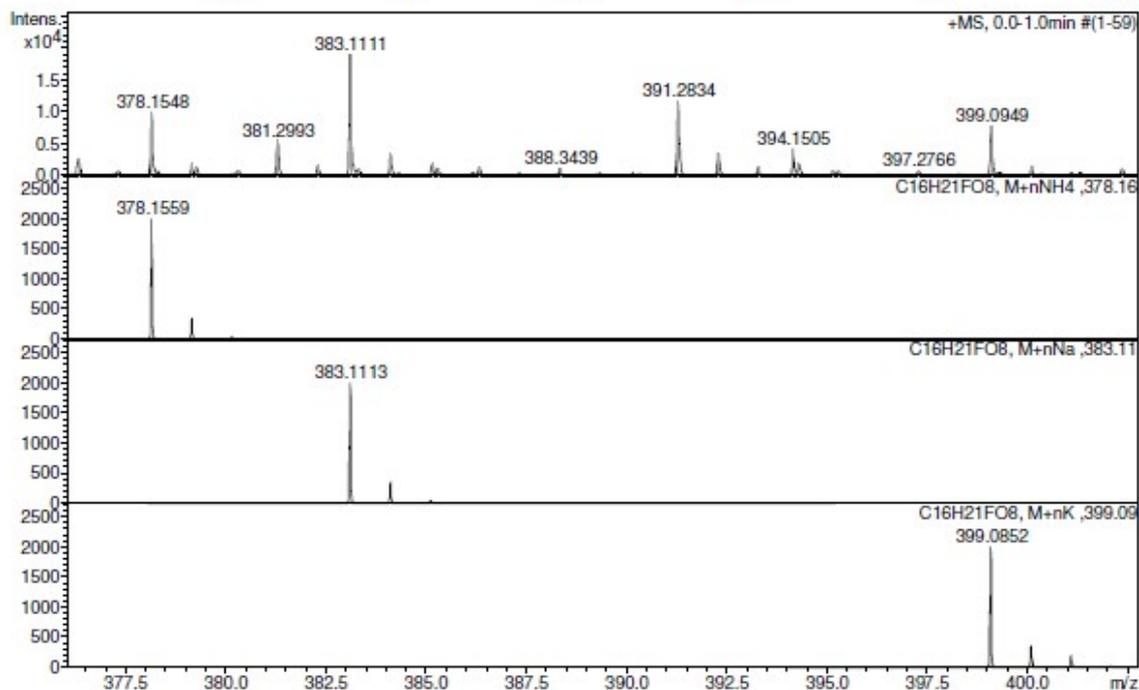
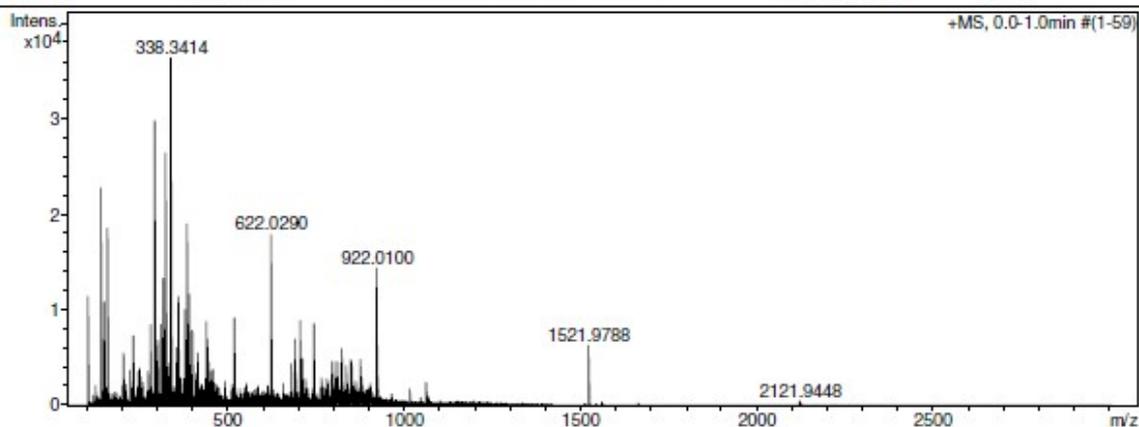
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Operator BDAL@DE

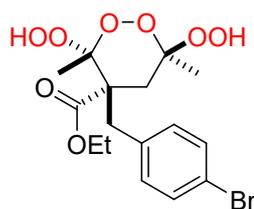
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (3*R,4*S**,6*R**)-4-(4-bromobenzyl)-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6c**



Display Report

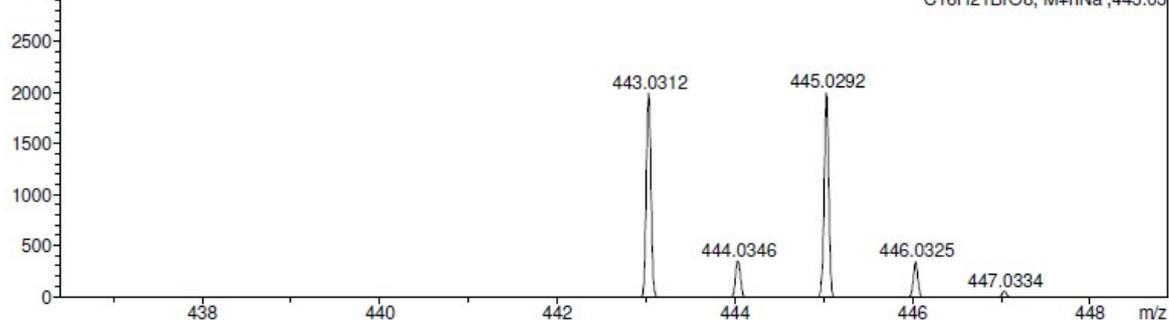
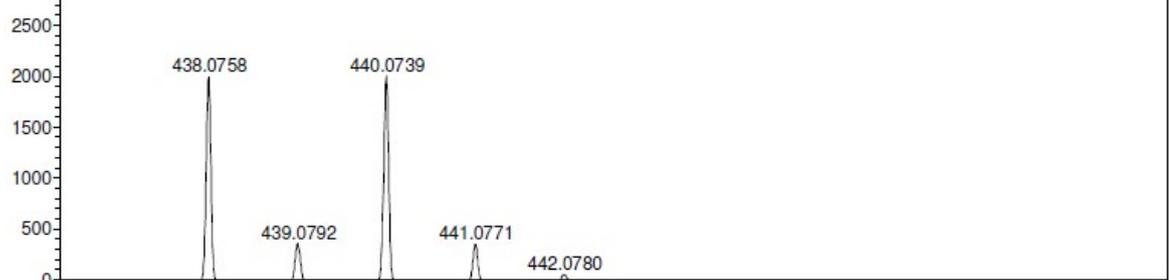
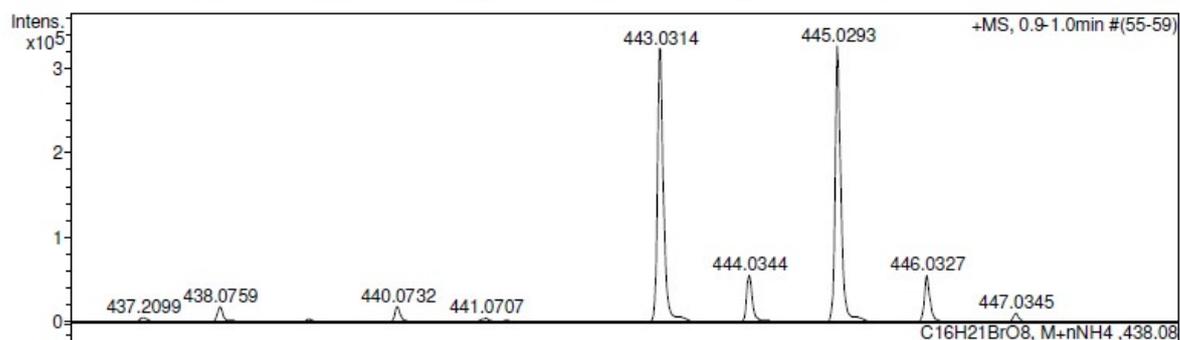
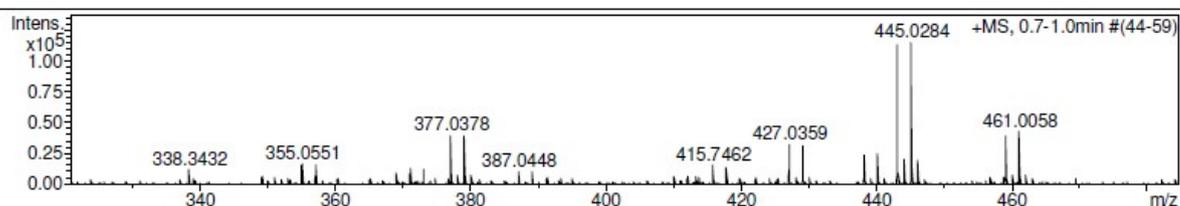
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 Sample Name /IYAR BL-1583
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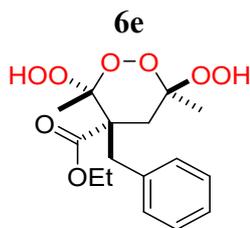
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 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



Ethyl (3*R,4*S**,6*R**)-4-benzyl-3,6-dihydroperoxy-3,6-dimethyl-1,2-dioxane-4-carboxylate, 6e**



Display Report

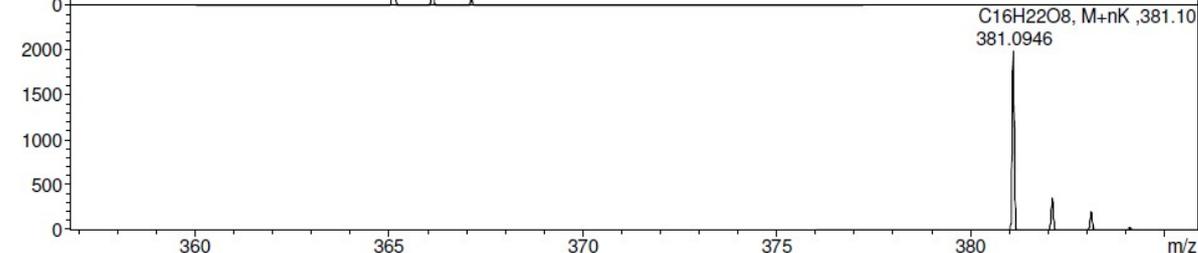
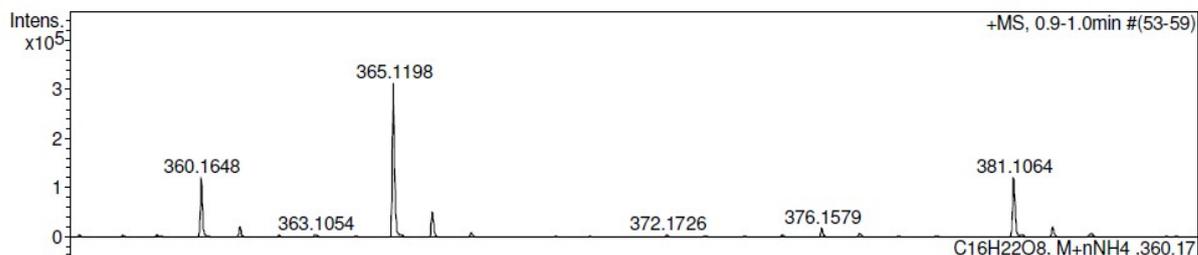
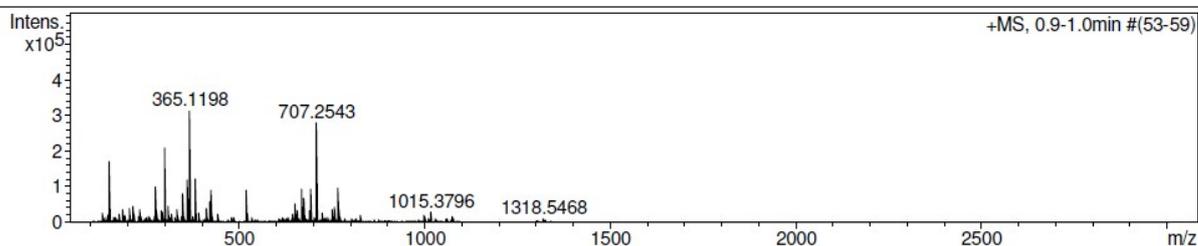
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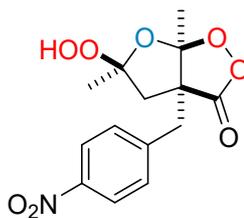
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 Operator BDAL@DE
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Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(3*a*S,5*R*,6*a*S)-5-hydroperoxy-5,6*a*-dimethyl-3*a*-(4-nitrobenzyl)tetrahydro-3H-furo[2,3-*c*][1,2]dioxol-3-one, 7*a*



Display Report

Analysis Info

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 Sample Name /IYAR AS-30
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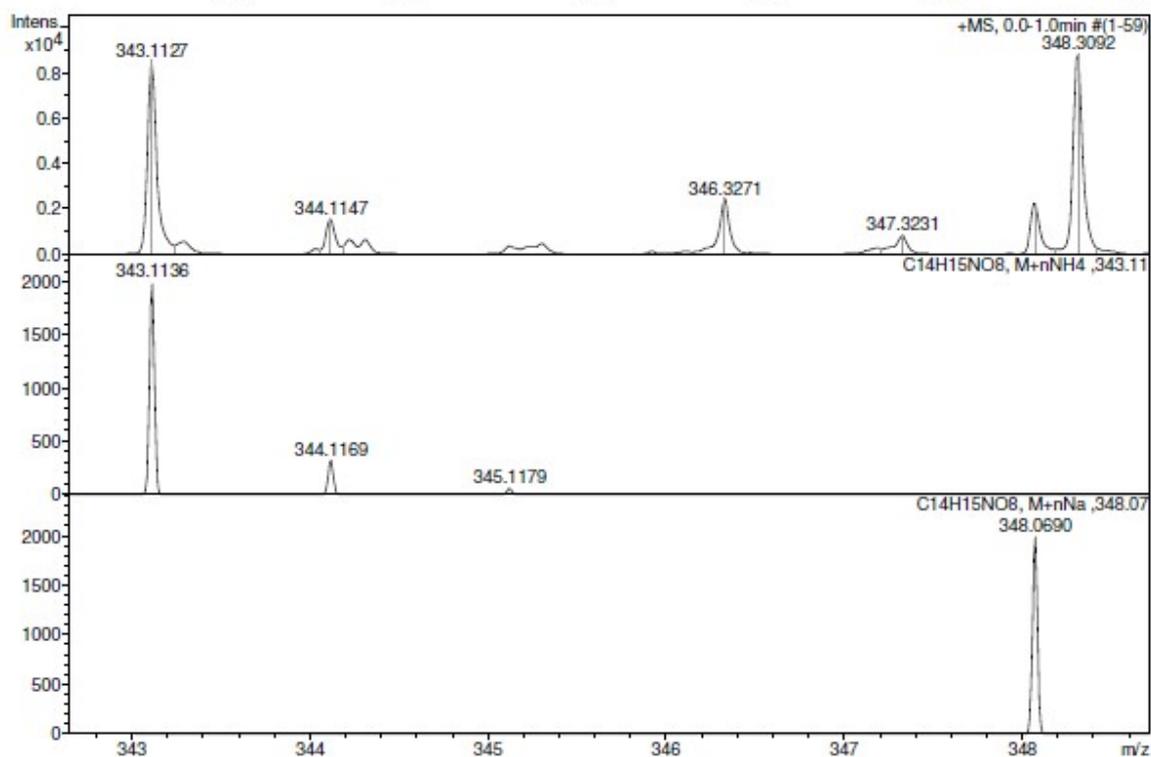
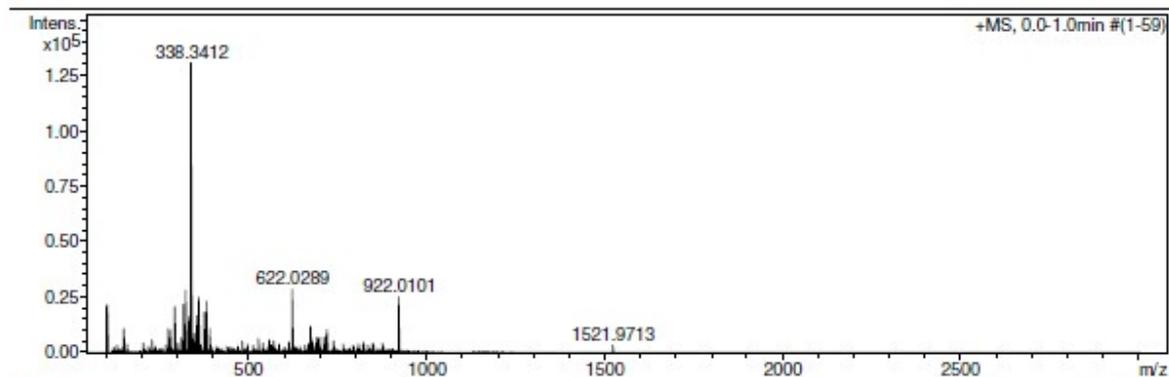
Acquisition Date 07.06.2024 17:55:13

Operator BDAL@DE

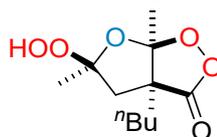
Instrument / Ser# micrOTOF 10248

Acquisition Parameter

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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



(3*aS*,5*R*,6*aS*)-3*a*-butyl-5-hydroperoxy-5,6*a*-dimethyltetrahydro-3*H*-furo[2,3-*c*][1,2]dioxol-3-one, 7*g*



Display Report

Analysis Info

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Method tune_low.m
Sample Name //YAR BL-1614
Comment CH3CN 100 %, dil. 200, calibrant added

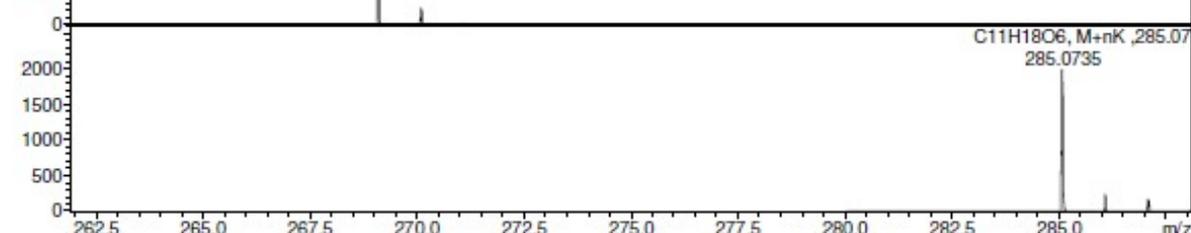
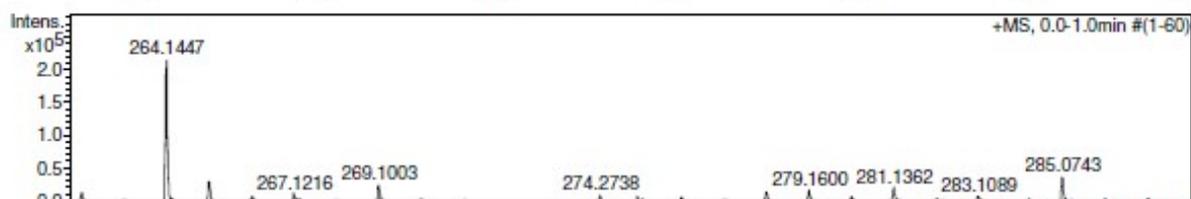
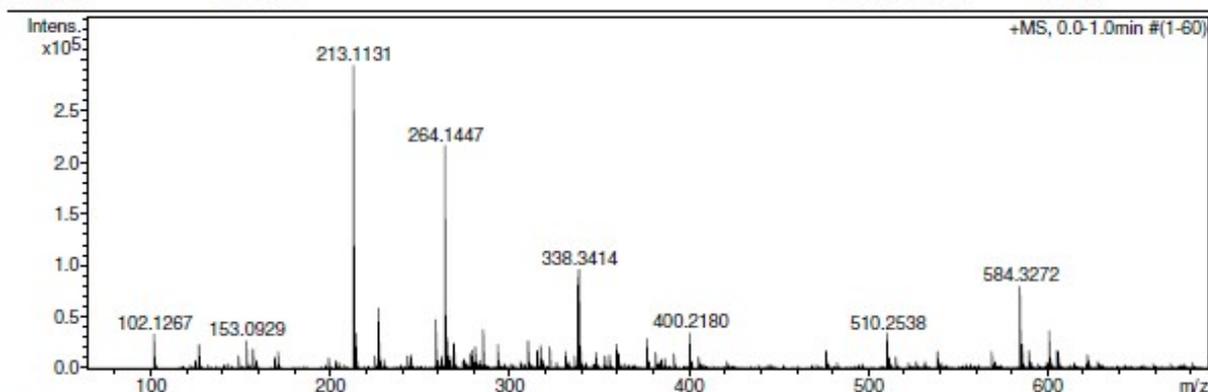
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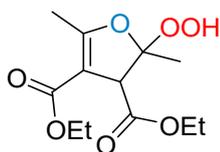
Operator BDAL@DE

Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
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Display Report

Analysis Info

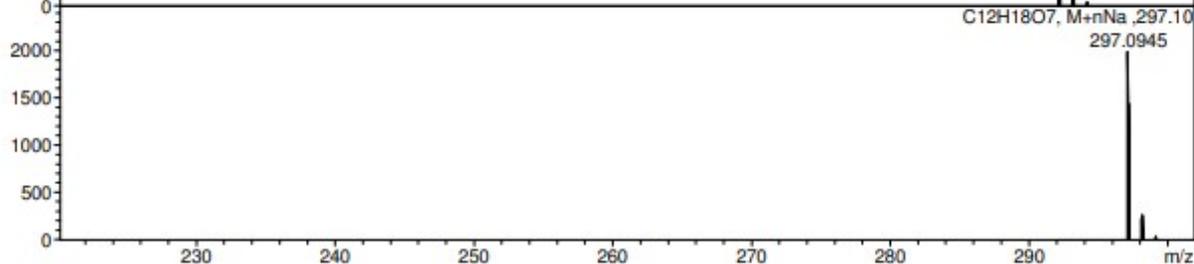
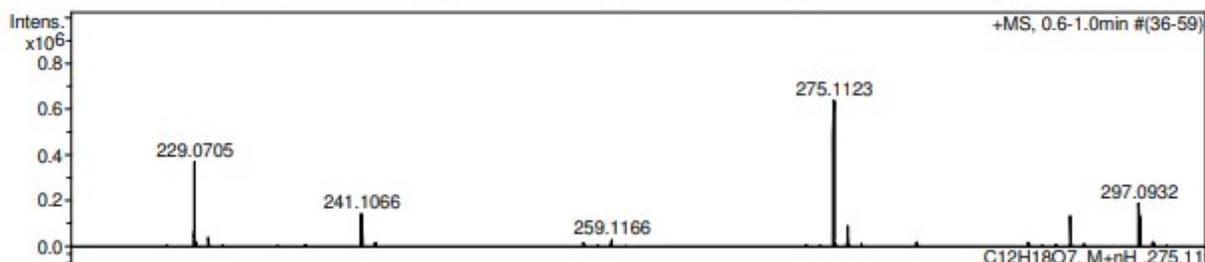
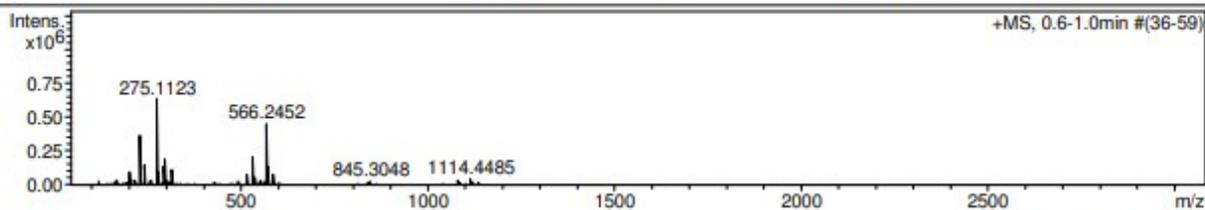
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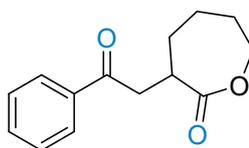
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Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste





Display Report

Analysis Info

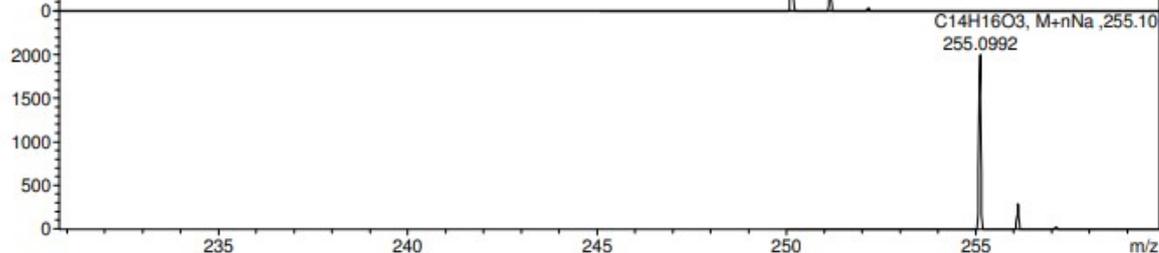
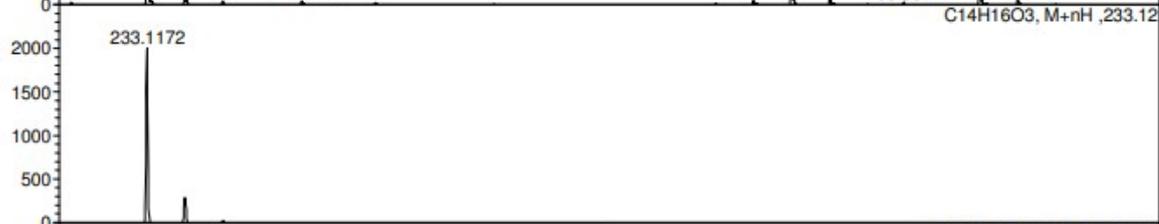
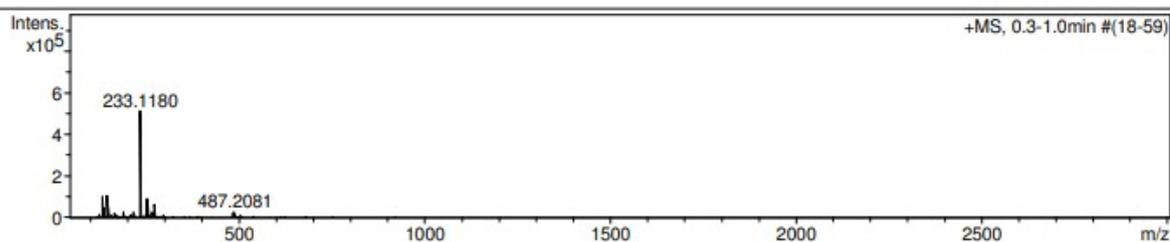
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 Sample Name /IYAR BL-1706
 Comment C14H16O3 clb added CH3CN

Acquisition Date 27.11.2024 18:55:39

Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

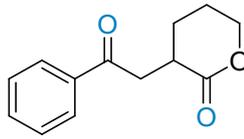
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Focus	Not active			Set Dry Heater	180 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



3-(2-oxo-2-phenylethyl)tetrahydro-2H-pyran-2-one, 9k

S232



Display Report

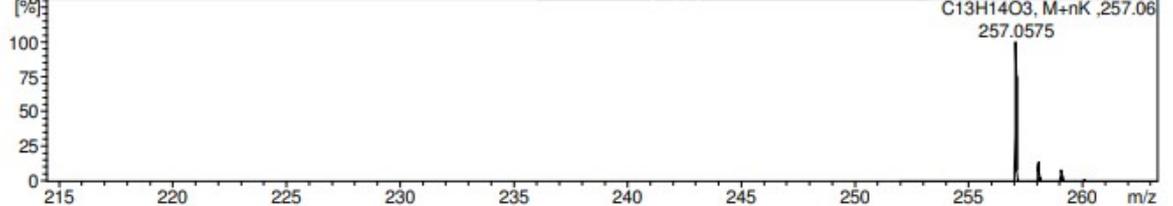
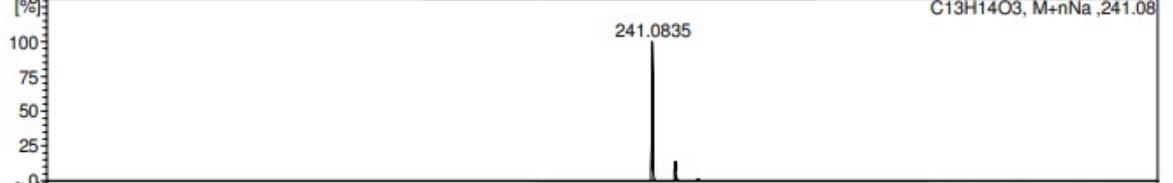
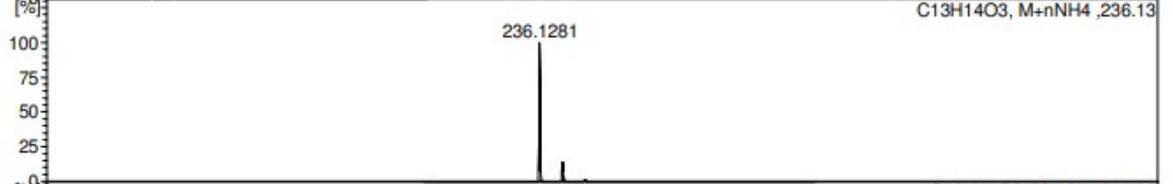
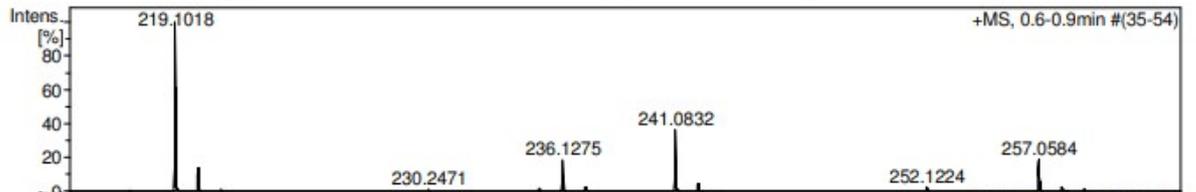
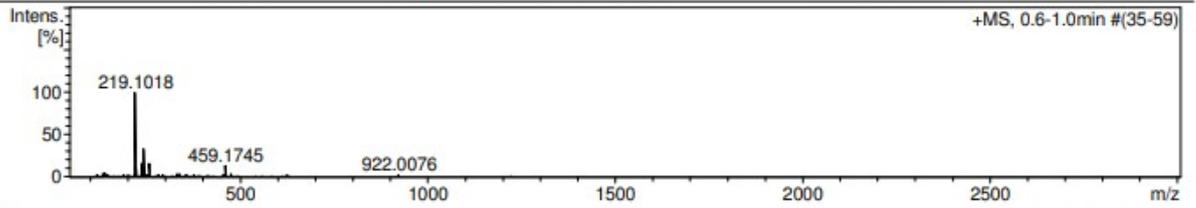
Analysis Info

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 Method tune_low.m
 Sample Name /IYAR BL-1711
 Comment C13H14O3 clb added CH3CN

Acquisition Date 09.12.2024 16:06:50
 Operator BDAL@DE
 Instrument / Ser# micrOTOF 10248

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



X-Ray data of *cis-2a*, *trans-2a*, *cis-3a*, *5a*, *6a*, *7a* and *cis-3c*

X-Ray data of *cis-2a*

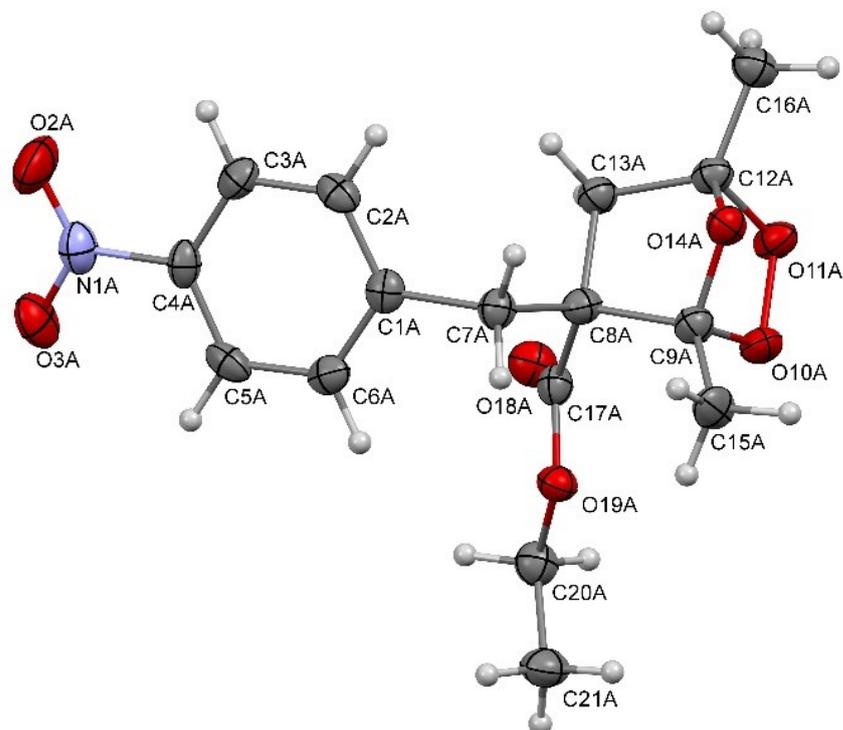


Figure S1. Molecular structure of *cis-2a* presented in thermal ellipsoids (50% probability).

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω -scan technique), using monochromatized Cu K_{α} -radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.⁷ The structure was solved by direct methods using SHELXT⁸ and refined on F^2 using SHELXL-2018⁹ in the OLEX2 program.¹⁰ All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. The Mercury program suite¹¹ was used for molecular graphics.

Table S1. Crystal data and structure refinement for *cis-2a*

Identification code	<i>cis-2a</i>	
Empirical formula	C ₁₆ H ₁₉ NO ₇	
Formula weight	337.32	
Temperature	99.9(3) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	Pna2 ₁	
Unit cell dimensions	a = 15.4118(6) Å	a = 90°.
	b = 8.0417(2) Å	b = 90°.
	c = 26.1942(9) Å	c = 90°.
Volume	3246.43(19) Å ³	
Z	8	
Density (calculated)	1.380 g/cm ³	
Absorption coefficient	0.925 mm ⁻¹	
F(000)	1424	
Crystal size	0.35 x 0.03 x 0.02 mm ³	
Theta range for data collection	5.742 to 77.807°.	

Index ranges	-19<=h<=19, -8<=k<=10, -33<=l<=31
Reflections collected	23073
Independent reflections	6205 [R(int) = 0.0400]
Observed reflections	5514
Completeness to theta = 67.684°	99.8 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.597
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6205 / 1 / 439
Goodness-of-fit on F ²	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0677, wR2 = 0.1756
R indices (all data)	R1 = 0.0738, wR2 = 0.1812
Absolute structure parameter	0.13(13)
Largest diff. peak and hole	0.730 and -0.293 e.Å ⁻³

Table S2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for *cis*-2a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(19A)	5526(2)	3591(3)	5873(1)	27(1)
O(14B)	7093(2)	8663(4)	3928(1)	25(1)
O(11A)	4376(2)	7863(5)	5239(1)	31(1)
O(10B)	7753(2)	7336(4)	4571(1)	29(1)
O(19B)	8014(2)	3682(4)	4129(1)	28(1)
O(10A)	5212(2)	7143(4)	5410(2)	33(1)
O(14A)	4622(2)	8572(4)	6053(1)	28(1)
O(18B)	6756(2)	3586(4)	4552(2)	38(1)
O(18A)	4222(2)	3432(4)	5493(1)	34(1)
O(11B)	6923(2)	8062(4)	4758(1)	32(1)
O(2B)	4981(3)	-1532(4)	2925(2)	41(1)
O(3A)	2519(3)	-1581(4)	7080(2)	42(1)
O(3B)	4061(3)	170(5)	2589(2)	57(1)
C(5A)	3686(3)	908(6)	6896(2)	30(1)
N(1A)	2281(3)	-169(5)	7197(2)	36(1)
C(1A)	3919(3)	3862(6)	6825(2)	26(1)
C(6A)	4213(3)	2240(6)	6778(2)	28(1)
N(1B)	4745(3)	-138(5)	2809(2)	35(1)
O(2A)	1603(3)	120(6)	7411(2)	59(1)
C(9B)	7618(3)	7252(5)	4028(2)	25(1)
C(15B)	8486(3)	7333(6)	3766(2)	32(1)
C(4A)	2855(3)	1216(6)	7069(2)	27(1)
C(5B)	4989(3)	2874(6)	2887(2)	28(1)
C(2A)	3080(3)	4136(5)	7003(2)	28(1)
C(20A)	5789(3)	2144(6)	5573(2)	32(1)
C(8B)	6987(3)	5768(5)	3921(2)	23(1)
C(17A)	4717(3)	4131(5)	5781(2)	26(1)
C(13A)	3625(3)	6460(5)	5914(2)	28(1)
C(4B)	5305(3)	1283(6)	2947(2)	28(1)
C(12B)	6432(3)	8238(5)	4291(2)	25(1)
C(8A)	4498(3)	5684(5)	6089(2)	26(1)
C(6B)	5533(3)	4191(5)	3023(2)	27(1)
C(3A)	2540(3)	2823(6)	7123(2)	30(1)
C(7B)	6969(3)	5326(5)	3346(2)	27(1)
C(1B)	6361(3)	3903(5)	3203(2)	23(1)
C(2B)	6659(3)	2282(6)	3251(2)	28(1)
C(7A)	4516(3)	5278(5)	6669(2)	26(1)
C(17B)	7219(3)	4232(5)	4245(2)	26(1)
C(13B)	6123(3)	6539(5)	4114(2)	27(1)
C(12A)	3926(3)	8137(6)	5716(2)	27(1)
C(9A)	5125(3)	7142(6)	5957(2)	27(1)

C(16A)	3286(3)	9508(6)	5645(2)	32(1)
C(3B)	6137(3)	942(5)	3126(2)	28(1)
C(16B)	5784(3)	9589(6)	4365(2)	30(1)
C(21B)	9185(3)	1764(7)	4251(3)	42(1)
C(20B)	8292(3)	2225(6)	4420(2)	30(1)
C(15A)	6013(3)	7243(7)	6188(3)	36(1)
C(21A)	6714(3)	1755(6)	5717(2)	37(1)

Table S3. Bond lengths [Å] and angles [°] for *cis*-2a.

O(19A)-C(20A)	1.461(6)
O(19A)-C(17A)	1.341(5)
O(14B)-C(9B)	1.418(5)
O(14B)-C(12B)	1.436(5)
O(11A)-O(10A)	1.482(5)
O(11A)-C(12A)	1.447(6)
O(10B)-O(11B)	1.489(5)
O(10B)-C(9B)	1.440(6)
O(19B)-C(17B)	1.337(5)
O(19B)-C(20B)	1.462(5)
O(10A)-C(9A)	1.440(6)
O(14A)-C(12A)	1.432(5)
O(14A)-C(9A)	1.409(6)
O(18B)-C(17B)	1.194(6)
O(18A)-C(17A)	1.212(6)
O(11B)-C(12B)	1.446(6)
O(2B)-N(1B)	1.217(6)
O(3A)-N(1A)	1.231(6)
O(3B)-N(1B)	1.226(6)
C(5A)-H(5A)	0.9500
C(5A)-C(6A)	1.380(7)
C(5A)-C(4A)	1.380(7)
N(1A)-O(2A)	1.210(6)
N(1A)-C(4A)	1.460(6)
C(1A)-C(6A)	1.387(7)
C(1A)-C(2A)	1.391(6)
C(1A)-C(7A)	1.521(6)
C(6A)-H(6A)	0.9500
N(1B)-C(4B)	1.477(6)
C(9B)-C(15B)	1.504(7)
C(9B)-C(8B)	1.565(6)
C(15B)-H(15D)	0.9800
C(15B)-H(15E)	0.9800
C(15B)-H(15F)	0.9800
C(4A)-C(3A)	1.388(7)
C(5B)-H(5B)	0.9500
C(5B)-C(4B)	1.378(7)
C(5B)-C(6B)	1.398(7)
C(2A)-H(2A)	0.9500
C(2A)-C(3A)	1.380(7)
C(20A)-H(20A)	0.9900
C(20A)-H(20B)	0.9900
C(20A)-C(21A)	1.507(7)
C(8B)-C(7B)	1.545(6)
C(8B)-C(17B)	1.542(6)
C(8B)-C(13B)	1.554(6)
C(17A)-C(8A)	1.525(6)
C(13A)-H(13A)	0.9900
C(13A)-H(13B)	0.9900
C(13A)-C(8A)	1.553(6)
C(13A)-C(12A)	1.518(6)

C(4B)-C(3B)	1.392(7)
C(12B)-C(13B)	1.519(6)
C(12B)-C(16B)	1.488(6)
C(8A)-C(7A)	1.553(6)
C(8A)-C(9A)	1.558(6)
C(6B)-H(6B)	0.9500
C(6B)-C(1B)	1.379(7)
C(3A)-H(3A)	0.9500
C(7B)-H(7C)	0.9900
C(7B)-H(7D)	0.9900
C(7B)-C(1B)	1.526(6)
C(1B)-C(2B)	1.388(6)
C(2B)-H(2B)	0.9500
C(2B)-C(3B)	1.385(7)
C(7A)-H(7A)	0.9900
C(7A)-H(7B)	0.9900
C(13B)-H(13C)	0.9900
C(13B)-H(13D)	0.9900
C(12A)-C(16A)	1.491(6)
C(9A)-C(15A)	1.498(7)
C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800
C(16A)-H(16C)	0.9800
C(3B)-H(3B)	0.9500
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
C(21B)-H(21D)	0.9800
C(21B)-H(21E)	0.9800
C(21B)-H(21F)	0.9800
C(21B)-C(20B)	1.492(7)
C(20B)-H(20C)	0.9900
C(20B)-H(20D)	0.9900
C(15A)-H(15A)	0.9800
C(15A)-H(15B)	0.9800
C(15A)-H(15C)	0.9800
C(21A)-H(21A)	0.9800
C(21A)-H(21B)	0.9800
C(21A)-H(21C)	0.9800
C(17A)-O(19A)-C(20A)	114.8(4)
C(9B)-O(14B)-C(12B)	95.3(3)
C(12A)-O(11A)-O(10A)	102.3(3)
C(9B)-O(10B)-O(11B)	102.7(3)
C(17B)-O(19B)-C(20B)	114.5(4)
C(9A)-O(10A)-O(11A)	102.8(3)
C(9A)-O(14A)-C(12A)	95.9(3)
C(12B)-O(11B)-O(10B)	102.1(3)
C(6A)-C(5A)-H(5A)	120.6
C(6A)-C(5A)-C(4A)	118.8(4)
C(4A)-C(5A)-H(5A)	120.6
O(3A)-N(1A)-C(4A)	117.8(4)
O(2A)-N(1A)-O(3A)	123.3(4)
O(2A)-N(1A)-C(4A)	118.9(4)
C(6A)-C(1A)-C(2A)	118.9(4)
C(6A)-C(1A)-C(7A)	118.8(4)
C(2A)-C(1A)-C(7A)	122.3(4)
C(5A)-C(6A)-C(1A)	121.1(5)
C(5A)-C(6A)-H(6A)	119.4
C(1A)-C(6A)-H(6A)	119.4
O(2B)-N(1B)-O(3B)	124.1(4)
O(2B)-N(1B)-C(4B)	118.5(4)
O(3B)-N(1B)-C(4B)	117.4(4)

O(14B)-C(9B)-O(10B)	103.2(4)
O(14B)-C(9B)-C(15B)	112.9(4)
O(14B)-C(9B)-C(8B)	102.8(3)
O(10B)-C(9B)-C(15B)	108.6(4)
O(10B)-C(9B)-C(8B)	107.6(4)
C(15B)-C(9B)-C(8B)	120.3(4)
C(9B)-C(15B)-H(15D)	109.5
C(9B)-C(15B)-H(15E)	109.5
C(9B)-C(15B)-H(15F)	109.5
H(15D)-C(15B)-H(15E)	109.5
H(15D)-C(15B)-H(15F)	109.5
H(15E)-C(15B)-H(15F)	109.5
C(5A)-C(4A)-N(1A)	120.0(4)
C(5A)-C(4A)-C(3A)	121.6(4)
C(3A)-C(4A)-N(1A)	118.4(4)
C(4B)-C(5B)-H(5B)	121.2
C(4B)-C(5B)-C(6B)	117.6(4)
C(6B)-C(5B)-H(5B)	121.2
C(1A)-C(2A)-H(2A)	119.5
C(3A)-C(2A)-C(1A)	121.0(4)
C(3A)-C(2A)-H(2A)	119.5
O(19A)-C(20A)-H(20A)	110.3
O(19A)-C(20A)-H(20B)	110.3
O(19A)-C(20A)-C(21A)	107.1(4)
H(20A)-C(20A)-H(20B)	108.6
C(21A)-C(20A)-H(20A)	110.3
C(21A)-C(20A)-H(20B)	110.3
C(7B)-C(8B)-C(9B)	111.2(4)
C(7B)-C(8B)-C(13B)	113.2(4)
C(17B)-C(8B)-C(9B)	111.6(3)
C(17B)-C(8B)-C(7B)	110.9(3)
C(17B)-C(8B)-C(13B)	109.8(4)
C(13B)-C(8B)-C(9B)	99.8(3)
O(19A)-C(17A)-C(8A)	112.1(4)
O(18A)-C(17A)-O(19A)	123.1(4)
O(18A)-C(17A)-C(8A)	124.8(4)
H(13A)-C(13A)-H(13B)	109.4
C(8A)-C(13A)-H(13A)	111.6
C(8A)-C(13A)-H(13B)	111.6
C(12A)-C(13A)-H(13A)	111.6
C(12A)-C(13A)-H(13B)	111.6
C(12A)-C(13A)-C(8A)	101.1(3)
C(5B)-C(4B)-N(1B)	118.9(4)
C(5B)-C(4B)-C(3B)	123.1(4)
C(3B)-C(4B)-N(1B)	117.9(4)
O(14B)-C(12B)-O(11B)	102.3(3)
O(14B)-C(12B)-C(13B)	103.5(3)
O(14B)-C(12B)-C(16B)	112.9(4)
O(11B)-C(12B)-C(13B)	109.5(4)
O(11B)-C(12B)-C(16B)	108.2(4)
C(16B)-C(12B)-C(13B)	119.1(4)
C(17A)-C(8A)-C(13A)	111.4(4)
C(17A)-C(8A)-C(7A)	109.9(4)
C(17A)-C(8A)-C(9A)	111.2(4)
C(13A)-C(8A)-C(9A)	99.8(3)
C(7A)-C(8A)-C(13A)	112.9(4)
C(7A)-C(8A)-C(9A)	111.3(4)
C(5B)-C(6B)-H(6B)	119.5
C(1B)-C(6B)-C(5B)	121.0(4)
C(1B)-C(6B)-H(6B)	119.5
C(4A)-C(3A)-H(3A)	120.7
C(2A)-C(3A)-C(4A)	118.6(4)

C(2A)-C(3A)-H(3A)	120.7
C(8B)-C(7B)-H(7C)	108.5
C(8B)-C(7B)-H(7D)	108.5
H(7C)-C(7B)-H(7D)	107.5
C(1B)-C(7B)-C(8B)	115.0(4)
C(1B)-C(7B)-H(7C)	108.5
C(1B)-C(7B)-H(7D)	108.5
C(6B)-C(1B)-C(7B)	121.7(4)
C(6B)-C(1B)-C(2B)	119.7(4)
C(2B)-C(1B)-C(7B)	118.6(4)
C(1B)-C(2B)-H(2B)	119.4
C(3B)-C(2B)-C(1B)	121.1(4)
C(3B)-C(2B)-H(2B)	119.4
C(1A)-C(7A)-C(8A)	114.1(4)
C(1A)-C(7A)-H(7A)	108.7
C(1A)-C(7A)-H(7B)	108.7
C(8A)-C(7A)-H(7A)	108.7
C(8A)-C(7A)-H(7B)	108.7
H(7A)-C(7A)-H(7B)	107.6
O(19B)-C(17B)-C(8B)	110.6(4)
O(18B)-C(17B)-O(19B)	123.9(4)
O(18B)-C(17B)-C(8B)	125.5(4)
C(8B)-C(13B)-H(13C)	111.6
C(8B)-C(13B)-H(13D)	111.6
C(12B)-C(13B)-C(8B)	101.0(3)
C(12B)-C(13B)-H(13C)	111.6
C(12B)-C(13B)-H(13D)	111.6
H(13C)-C(13B)-H(13D)	109.4
O(11A)-C(12A)-C(13A)	107.9(4)
O(11A)-C(12A)-C(16A)	108.7(4)
O(14A)-C(12A)-O(11A)	102.2(3)
O(14A)-C(12A)-C(13A)	103.7(4)
O(14A)-C(12A)-C(16A)	113.1(4)
C(16A)-C(12A)-C(13A)	119.8(4)
O(10A)-C(9A)-C(8A)	106.2(4)
O(10A)-C(9A)-C(15A)	108.4(4)
O(14A)-C(9A)-O(10A)	103.2(4)
O(14A)-C(9A)-C(8A)	103.5(4)
O(14A)-C(9A)-C(15A)	112.7(4)
C(15A)-C(9A)-C(8A)	121.2(4)
C(12A)-C(16A)-H(16A)	109.5
C(12A)-C(16A)-H(16B)	109.5
C(12A)-C(16A)-H(16C)	109.5
H(16A)-C(16A)-H(16B)	109.5
H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5
C(4B)-C(3B)-H(3B)	121.2
C(2B)-C(3B)-C(4B)	117.5(4)
C(2B)-C(3B)-H(3B)	121.2
C(12B)-C(16B)-H(16D)	109.5
C(12B)-C(16B)-H(16E)	109.5
C(12B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5
H(21D)-C(21B)-H(21E)	109.5
H(21D)-C(21B)-H(21F)	109.5
H(21E)-C(21B)-H(21F)	109.5
C(20B)-C(21B)-H(21D)	109.5
C(20B)-C(21B)-H(21E)	109.5
C(20B)-C(21B)-H(21F)	109.5
O(19B)-C(20B)-C(21B)	108.4(4)

O(19B)-C(20B)-H(20C)	110.0
O(19B)-C(20B)-H(20D)	110.0
C(21B)-C(20B)-H(20C)	110.0
C(21B)-C(20B)-H(20D)	110.0
H(20C)-C(20B)-H(20D)	108.4
C(9A)-C(15A)-H(15A)	109.5
C(9A)-C(15A)-H(15B)	109.5
C(9A)-C(15A)-H(15C)	109.5
H(15A)-C(15A)-H(15B)	109.5
H(15A)-C(15A)-H(15C)	109.5
H(15B)-C(15A)-H(15C)	109.5
C(20A)-C(21A)-H(21A)	109.5
C(20A)-C(21A)-H(21B)	109.5
C(20A)-C(21A)-H(21C)	109.5
H(21A)-C(21A)-H(21B)	109.5
H(21A)-C(21A)-H(21C)	109.5
H(21B)-C(21A)-H(21C)	109.5

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *cis*-2a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(19A)	26(2)	23(1)	31(2)	-1(1)	0(1)	3(1)
O(14B)	25(2)	26(1)	24(2)	3(1)	3(1)	-2(1)
O(11A)	23(2)	46(2)	23(2)	5(1)	1(1)	4(1)
O(10B)	26(2)	33(2)	27(2)	0(1)	-7(1)	3(1)
O(19B)	27(2)	24(1)	33(2)	4(1)	-3(1)	4(1)
O(10A)	21(2)	39(2)	38(2)	6(2)	3(2)	3(1)
O(14A)	24(2)	26(2)	34(2)	0(1)	-3(1)	-3(1)
O(18B)	38(2)	35(2)	41(2)	12(2)	12(2)	4(2)
O(18A)	35(2)	33(2)	35(2)	-6(1)	-5(1)	-1(1)
O(11B)	31(2)	34(2)	32(2)	-2(2)	-2(1)	1(1)
O(2B)	51(2)	24(2)	47(2)	2(1)	8(2)	-4(2)
O(3A)	50(2)	23(2)	53(2)	1(2)	-9(2)	-9(1)
O(3B)	44(2)	41(2)	85(3)	0(2)	-22(2)	-14(2)
C(5A)	40(3)	25(2)	24(2)	0(2)	-6(2)	9(2)
N(1A)	40(2)	31(2)	37(2)	4(2)	-3(2)	-10(2)
C(1A)	29(2)	28(2)	19(2)	-2(2)	-3(2)	-4(2)
C(6A)	26(2)	37(2)	21(2)	1(2)	0(2)	4(2)
N(1B)	38(2)	32(2)	37(2)	0(2)	2(2)	-8(2)
O(2A)	50(2)	48(2)	78(3)	1(2)	27(2)	-17(2)
C(9B)	21(2)	28(2)	27(2)	3(2)	-4(2)	1(2)
C(15B)	23(2)	32(2)	39(3)	-1(2)	3(2)	-4(2)
C(4A)	31(2)	27(2)	23(2)	3(2)	-4(2)	-11(2)
C(5B)	23(2)	37(2)	24(2)	6(2)	0(2)	4(2)
C(2A)	37(2)	24(2)	22(2)	-2(2)	-2(2)	5(2)
C(20A)	33(3)	30(2)	33(3)	-2(2)	-1(2)	-1(2)
C(8B)	22(2)	27(2)	20(2)	1(2)	-2(2)	2(2)
C(17A)	29(2)	23(2)	26(2)	1(2)	2(2)	-3(2)
C(13A)	23(2)	27(2)	32(2)	0(2)	-1(2)	0(2)
C(4B)	34(2)	27(2)	23(2)	-6(2)	5(2)	-8(2)
C(12B)	24(2)	21(2)	29(2)	-1(2)	5(2)	-1(2)
C(8A)	22(2)	26(2)	29(2)	-4(2)	1(2)	1(2)
C(6B)	32(2)	25(2)	25(2)	5(2)	1(2)	5(2)
C(3A)	28(2)	37(2)	24(2)	0(2)	4(2)	-3(2)
C(7B)	32(2)	24(2)	25(2)	3(2)	2(2)	-3(2)
C(1B)	28(2)	22(2)	20(2)	-1(2)	4(2)	-1(2)
C(2B)	26(2)	33(2)	25(2)	0(2)	-2(2)	3(2)
C(7A)	28(2)	26(2)	26(2)	-1(2)	0(2)	-2(2)
C(17B)	26(2)	26(2)	27(2)	-1(2)	-3(2)	-1(2)

C(13B)	26(2)	25(2)	30(2)	1(2)	3(2)	-1(2)
C(12A)	22(2)	32(2)	26(2)	0(2)	-2(2)	2(2)
C(9A)	23(2)	27(2)	31(2)	1(2)	-2(2)	-1(2)
C(16A)	30(2)	31(2)	36(2)	-1(2)	-4(2)	3(2)
C(3B)	40(3)	18(2)	25(2)	5(2)	3(2)	6(2)
C(16B)	29(2)	26(2)	35(2)	-1(2)	6(2)	0(2)
C(21B)	36(3)	32(2)	60(3)	5(2)	1(2)	4(2)
C(20B)	32(2)	30(2)	28(2)	0(2)	-6(2)	6(2)
C(15A)	22(2)	30(2)	55(3)	4(2)	-6(2)	-8(2)
C(21A)	32(2)	32(2)	47(3)	-3(2)	1(2)	7(2)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for *cis*-2a.

	x	y	z	U(eq)
H(5A)	3891	-200	6860	35
H(6A)	4788	2042	6662	34
H(15D)	8402	7325	3395	47
H(15E)	8836	6370	3867	47
H(15F)	8786	8358	3866	47
H(5B)	4421	3068	2759	34
H(2A)	2875	5243	7041	33
H(20A)	5748	2391	5204	38
H(20B)	5409	1184	5650	38
H(13A)	3349	5791	5641	33
H(13B)	3215	6582	6202	33
H(6B)	5330	5302	2992	33
H(3A)	1966	3016	7241	36
H(7C)	6795	6328	3152	32
H(7D)	7565	5028	3238	32
H(2B)	7231	2089	3373	33
H(7A)	5118	4988	6767	32
H(7B)	4350	6289	6861	32
H(13C)	5690	6631	3837	32
H(13D)	5874	5887	4400	32
H(16A)	3591	10521	5540	49
H(16B)	2981	9711	5967	49
H(16C)	2867	9193	5381	49
H(3B)	6339	-169	3160	33
H(16D)	6086	10635	4438	45
H(16E)	5403	9309	4652	45
H(16F)	5436	9714	4055	45
H(21D)	9192	1624	3880	64
H(21E)	9357	719	4415	64
H(21F)	9592	2645	4348	64
H(20C)	7889	1288	4360	36
H(20D)	8292	2483	4790	36
H(15A)	6323	6199	6126	54
H(15B)	5963	7431	6556	54
H(15C)	6333	8165	6032	54
H(21A)	6939	881	5493	56
H(21B)	6735	1374	6072	56
H(21C)	7069	2758	5680	56

Table S6. Torsion angles [$^\circ$] for *cis*-2a.

O(19A)-C(17A)-C(8A)-C(13A)	170.5(4)
O(19A)-C(17A)-C(8A)-C(7A)	-63.6(5)

O(19A)-C(17A)-C(8A)-C(9A)	60.2(5)
O(14B)-C(9B)-C(8B)-C(7B)	84.5(4)
O(14B)-C(9B)-C(8B)-C(17B)	-151.1(3)
O(14B)-C(9B)-C(8B)-C(13B)	-35.2(4)
O(14B)-C(12B)-C(13B)-C(8B)	35.8(4)
O(11A)-O(10A)-C(9A)-O(14A)	-33.3(4)
O(11A)-O(10A)-C(9A)-C(8A)	75.2(4)
O(11A)-O(10A)-C(9A)-C(15A)	-153.1(3)
O(10B)-O(11B)-C(12B)-O(14B)	-35.3(4)
O(10B)-O(11B)-C(12B)-C(13B)	74.0(4)
O(10B)-O(11B)-C(12B)-C(16B)	-154.7(3)
O(10B)-C(9B)-C(8B)-C(7B)	-166.9(4)
O(10B)-C(9B)-C(8B)-C(17B)	-42.6(5)
O(10B)-C(9B)-C(8B)-C(13B)	73.3(4)
O(10A)-O(11A)-C(12A)-O(14A)	34.5(4)
O(10A)-O(11A)-C(12A)-C(13A)	-74.4(4)
O(10A)-O(11A)-C(12A)-C(16A)	154.2(3)
O(18A)-C(17A)-C(8A)-C(13A)	-10.7(6)
O(18A)-C(17A)-C(8A)-C(7A)	115.3(5)
O(18A)-C(17A)-C(8A)-C(9A)	-121.0(5)
O(11B)-O(10B)-C(9B)-O(14B)	33.4(4)
O(11B)-O(10B)-C(9B)-C(15B)	153.4(3)
O(11B)-O(10B)-C(9B)-C(8B)	-74.9(4)
O(11B)-C(12B)-C(13B)-C(8B)	-72.7(4)
O(2B)-N(1B)-C(4B)-C(5B)	-170.3(4)
O(2B)-N(1B)-C(4B)-C(3B)	10.4(7)
O(3A)-N(1A)-C(4A)-C(5A)	-9.7(7)
O(3A)-N(1A)-C(4A)-C(3A)	170.0(4)
O(3B)-N(1B)-C(4B)-C(5B)	8.8(7)
O(3B)-N(1B)-C(4B)-C(3B)	-170.5(5)
C(5A)-C(4A)-C(3A)-C(2A)	-0.3(7)
N(1A)-C(4A)-C(3A)-C(2A)	-180.0(4)
C(1A)-C(2A)-C(3A)-C(4A)	0.7(7)
C(6A)-C(5A)-C(4A)-N(1A)	179.9(5)
C(6A)-C(5A)-C(4A)-C(3A)	0.2(7)
C(6A)-C(1A)-C(2A)-C(3A)	-1.0(7)
C(6A)-C(1A)-C(7A)-C(8A)	84.2(5)
N(1B)-C(4B)-C(3B)-C(2B)	179.7(4)
O(2A)-N(1A)-C(4A)-C(5A)	170.1(5)
O(2A)-N(1A)-C(4A)-C(3A)	-10.2(7)
C(9B)-O(14B)-C(12B)-O(11B)	55.3(4)
C(9B)-O(14B)-C(12B)-C(13B)	-58.5(4)
C(9B)-O(14B)-C(12B)-C(16B)	171.4(4)
C(9B)-O(10B)-O(11B)-C(12B)	1.5(4)
C(9B)-C(8B)-C(7B)-C(1B)	-179.2(4)
C(9B)-C(8B)-C(17B)-O(19B)	-62.2(5)
C(9B)-C(8B)-C(17B)-O(18B)	119.2(5)
C(9B)-C(8B)-C(13B)-C(12B)	-0.6(4)
C(15B)-C(9B)-C(8B)-C(7B)	-42.0(5)
C(15B)-C(9B)-C(8B)-C(17B)	82.4(5)
C(15B)-C(9B)-C(8B)-C(13B)	-161.7(4)
C(4A)-C(5A)-C(6A)-C(1A)	-0.6(8)
C(5B)-C(4B)-C(3B)-C(2B)	0.5(7)
C(5B)-C(6B)-C(1B)-C(7B)	179.2(5)
C(5B)-C(6B)-C(1B)-C(2B)	-0.2(7)
C(2A)-C(1A)-C(6A)-C(5A)	1.0(7)
C(2A)-C(1A)-C(7A)-C(8A)	-94.3(5)
C(20A)-O(19A)-C(17A)-O(18A)	3.6(6)
C(20A)-O(19A)-C(17A)-C(8A)	-177.6(4)
C(8B)-C(7B)-C(1B)-C(6B)	96.5(5)
C(8B)-C(7B)-C(1B)-C(2B)	-84.1(5)
C(17A)-O(19A)-C(20A)-C(21A)	178.5(4)

C(17A)-C(8A)-C(7A)-C(1A)	-56.3(5)
C(17A)-C(8A)-C(9A)-O(10A)	43.6(5)
C(17A)-C(8A)-C(9A)-O(14A)	151.9(4)
C(17A)-C(8A)-C(9A)-C(15A)	-80.5(6)
C(13A)-C(8A)-C(7A)-C(1A)	68.8(5)
C(13A)-C(8A)-C(9A)-O(10A)	-74.0(4)
C(13A)-C(8A)-C(9A)-O(14A)	34.3(4)
C(13A)-C(8A)-C(9A)-C(15A)	161.9(5)
C(4B)-C(5B)-C(6B)-C(1B)	0.9(7)
C(12B)-O(14B)-C(9B)-O(10B)	-54.5(4)
C(12B)-O(14B)-C(9B)-C(15B)	-171.6(4)
C(12B)-O(14B)-C(9B)-C(8B)	57.3(4)
C(8A)-C(13A)-C(12A)-O(11A)	72.6(4)
C(8A)-C(13A)-C(12A)-O(14A)	-35.3(4)
C(8A)-C(13A)-C(12A)-C(16A)	-162.4(4)
C(6B)-C(5B)-C(4B)-N(1B)	179.7(4)
C(6B)-C(5B)-C(4B)-C(3B)	-1.1(7)
C(6B)-C(1B)-C(2B)-C(3B)	-0.5(8)
C(7B)-C(8B)-C(17B)-O(19B)	62.3(5)
C(7B)-C(8B)-C(17B)-O(18B)	-116.3(5)
C(7B)-C(8B)-C(13B)-C(12B)	-118.8(4)
C(7B)-C(1B)-C(2B)-C(3B)	-179.8(4)
C(1B)-C(2B)-C(3B)-C(4B)	0.3(8)
C(7A)-C(1A)-C(6A)-C(5A)	-177.6(4)
C(7A)-C(1A)-C(2A)-C(3A)	177.5(4)
C(7A)-C(8A)-C(9A)-O(10A)	166.6(3)
C(7A)-C(8A)-C(9A)-O(14A)	-85.1(4)
C(7A)-C(8A)-C(9A)-C(15A)	42.5(6)
C(17B)-O(19B)-C(20B)-C(21B)	-179.8(4)
C(17B)-C(8B)-C(7B)-C(1B)	56.0(5)
C(17B)-C(8B)-C(13B)-C(12B)	116.7(4)
C(13B)-C(8B)-C(7B)-C(1B)	-67.9(5)
C(13B)-C(8B)-C(17B)-O(19B)	-171.9(3)
C(13B)-C(8B)-C(17B)-O(18B)	9.6(6)
C(12A)-O(11A)-O(10A)-C(9A)	-1.1(4)
C(12A)-O(14A)-C(9A)-O(10A)	54.2(4)
C(12A)-O(14A)-C(9A)-C(8A)	-56.4(4)
C(12A)-O(14A)-C(9A)-C(15A)	170.9(4)
C(12A)-C(13A)-C(8A)-C(17A)	-116.6(4)
C(12A)-C(13A)-C(8A)-C(7A)	119.1(4)
C(12A)-C(13A)-C(8A)-C(9A)	0.9(4)
C(9A)-O(14A)-C(12A)-O(11A)	-54.6(4)
C(9A)-O(14A)-C(12A)-C(13A)	57.4(4)
C(9A)-O(14A)-C(12A)-C(16A)	-171.3(4)
C(9A)-C(8A)-C(7A)-C(1A)	-179.9(4)
C(16B)-C(12B)-C(13B)-C(8B)	162.1(4)
C(20B)-O(19B)-C(17B)-O(18B)	-1.6(6)
C(20B)-O(19B)-C(17B)-C(8B)	179.8(4)

X-Ray data of *trans-2a*

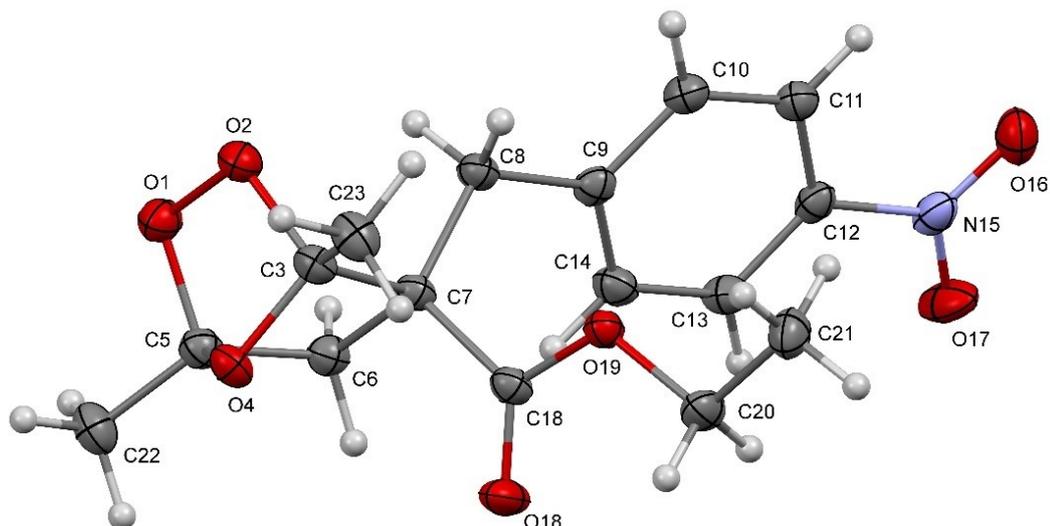


Figure S2. Molecular structure of **trans-2a** presented in thermal ellipsoids (50% probability).

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω -scan technique), using monochromatized Cu K_{α} -radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.⁷ The structure was solved by direct methods using SHELXT⁸ and refined on F^2 using SHELXL-2018⁹ in the OLEX2 program.¹⁰ All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. The Mercury program suite¹¹ was used for molecular graphics.

Table S7. Crystal data and structure refinement for **trans-2a**

Identification code	<i>trans-2a</i>	
Empirical formula	C ₁₆ H ₁₉ NO ₇	
Formula weight	337.32	
Temperature	99.99(10) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.81567(11) Å	a = 77.6093(19)°
	b = 8.70518(17) Å	b = 89.4484(15)°
	c = 12.2530(3) Å	g = 78.8430(14)°
Volume	798.41(3) Å ³	
Z	2	
Density (calculated)	1.403 g/cm ³	
Absorption coefficient	0.940 mm ⁻¹	
F(000)	356	
Crystal size	0.25 x 0.19 x 0.13 mm ³	
Theta range for data collection	3.695 to 79.712°	
Index ranges	-9 ≤ h ≤ 8, -11 ≤ k ≤ 11, -15 ≤ l ≤ 15	
Reflections collected	21228	
Independent reflections	3442 [R(int) = 0.0275]	
Observed reflections	3335	
Completeness to theta = 67.684°	99.9 %	
Absorption correction	Gaussian	

Max. and min. transmission	1.000 and 0.598
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3442 / 0 / 220
Goodness-of-fit on F ²	1.040
Final R indices [I>2sigma(I)]	R1 = 0.0401, wR2 = 0.0994
R indices (all data)	R1 = 0.0409, wR2 = 0.1000
Largest diff. peak and hole	0.318 and -0.273 e.Å ⁻³

Table S8. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for *trans*-2a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1A)	9567(1)	11608(2)	8542(1)	42(1)
O(2A)	9905(1)	9923(2)	7781(1)	58(1)
O(3A)	8544(1)	1452(2)	10132(1)	29(1)
O(4A)	7728(1)	2142(2)	9486(1)	32(1)
O(5A)	7897(1)	2882(2)	10408(1)	32(1)
O(6A)	8365(1)	6419(2)	10947(1)	28(1)
O(7A)	7986(1)	6584(2)	9457(1)	34(1)
N(1A)	9686(1)	10205(2)	8363(1)	36(1)
C(1A)	9560(1)	8801(2)	8866(1)	29(1)
C(2A)	9619(1)	7198(2)	8579(1)	31(1)
C(3A)	9492(1)	5883(2)	9058(1)	30(1)
C(4A)	9313(1)	6160(2)	9810(1)	27(1)
C(5A)	9268(1)	7793(2)	10084(1)	30(1)
C(6A)	9388(1)	9124(2)	9613(1)	30(1)
C(7A)	9163(1)	4742(2)	10331(1)	29(1)
C(8A)	8583(1)	4341(2)	10027(1)	26(1)
C(9A)	8409(1)	3562(2)	9068(1)	28(1)
C(10A)	8205(1)	1886(2)	9268(1)	27(1)
C(11A)	8139(1)	515(2)	8589(1)	32(1)
C(12A)	8448(1)	2888(2)	10591(1)	28(1)
C(13A)	8681(1)	2783(2)	11593(1)	35(1)
C(14A)	8273(1)	5891(2)	10094(1)	27(1)
C(15A)	8068(1)	7865(2)	11072(1)	31(1)
C(16A)	8203(1)	8254(3)	12060(1)	40(1)
O(1B)	5079(1)	-4784(2)	2867(1)	60(1)
O(2B)	5412(1)	-6495(2)	3949(1)	44(1)
O(3B)	6419(1)	3675(2)	6565(1)	28(1)
O(4B)	7250(1)	3084(2)	6800(1)	32(1)
O(5B)	7063(1)	2343(2)	7536(1)	32(1)
O(6B)	6621(1)	-1308(2)	7584(1)	30(1)
O(7B)	7049(1)	-1378(2)	6535(1)	38(1)
N(1B)	5299(1)	-5081(2)	3658(1)	38(1)
C(1B)	5435(1)	-3686(2)	4288(1)	29(1)
C(2B)	5611(1)	-4024(2)	5202(1)	31(1)
C(3B)	5740(1)	-2705(2)	5795(1)	30(1)
C(4B)	5698(1)	-1064(2)	5484(1)	27(1)
C(5B)	5516(1)	-774(2)	4559(1)	29(1)
C(6B)	5382(1)	-2078(2)	3949(1)	30(1)
C(7B)	5839(1)	347(2)	6154(1)	29(1)
C(8B)	6416(1)	776(2)	6452(1)	26(1)
C(9B)	6608(1)	1568(2)	5684(1)	28(1)
C(10B)	6783(1)	3272(2)	6078(1)	27(1)
C(11B)	6859(1)	4629(2)	5466(1)	32(1)
C(12B)	6518(1)	2261(2)	7135(1)	28(1)
C(13B)	6258(1)	2339(3)	7875(1)	35(1)
C(14B)	6737(1)	-736(2)	6846(1)	28(1)
C(15B)	6911(1)	-2779(2)	7993(1)	33(1)
C(16B)	6740(1)	-3230(3)	8809(2)	42(1)

Table S9. Bond lengths [Å] and angles [°] for *trans*-2a.

O(1A)-N(1A)	1.228(2)
O(2A)-N(1A)	1.227(3)
O(3A)-C(10A)	1.435(2)
O(3A)-C(12A)	1.418(2)
O(4A)-O(5A)	1.4899(17)
O(4A)-C(10A)	1.445(2)
O(5A)-C(12A)	1.445(2)
O(6A)-C(14A)	1.338(2)
O(6A)-C(15A)	1.460(2)
O(7A)-C(14A)	1.207(2)
N(1A)-C(1A)	1.464(2)
C(1A)-C(2A)	1.388(3)
C(1A)-C(6A)	1.383(3)
C(2A)-H(2A)	0.9500
C(2A)-C(3A)	1.388(3)
C(3A)-H(3A)	0.9500
C(3A)-C(4A)	1.394(3)
C(4A)-C(5A)	1.396(2)
C(4A)-C(7A)	1.516(2)
C(5A)-H(5A)	0.9500
C(5A)-C(6A)	1.383(3)
C(6A)-H(6A)	0.9500
C(7A)-H(7A)	0.9900
C(7A)-H(7B)	0.9900
C(7A)-C(8A)	1.551(2)
C(8A)-C(9A)	1.552(2)
C(8A)-C(12A)	1.562(2)
C(8A)-C(14A)	1.527(2)
C(9A)-H(9A)	0.9900
C(9A)-H(9B)	0.9900
C(9A)-C(10A)	1.522(2)
C(10A)-C(11A)	1.497(2)
C(11A)-H(11A)	0.9800
C(11A)-H(11B)	0.9800
C(11A)-H(11C)	0.9800
C(12A)-C(13A)	1.500(2)
C(13A)-H(13A)	0.9800
C(13A)-H(13B)	0.9800
C(13A)-H(13C)	0.9800
C(15A)-H(15A)	0.9900
C(15A)-H(15B)	0.9900
C(15A)-C(16A)	1.495(3)
C(16A)-H(16A)	0.9800
C(16A)-H(16B)	0.9800
C(16A)-H(16C)	0.9800
O(1B)-N(1B)	1.221(3)
O(2B)-N(1B)	1.231(2)
O(3B)-C(10B)	1.438(2)
O(3B)-C(12B)	1.417(2)
O(4B)-O(5B)	1.4902(18)
O(4B)-C(10B)	1.446(2)
O(5B)-C(12B)	1.441(2)
O(6B)-C(14B)	1.343(2)
O(6B)-C(15B)	1.466(2)
O(7B)-C(14B)	1.202(2)
N(1B)-C(1B)	1.463(2)
C(1B)-C(2B)	1.383(3)
C(1B)-C(6B)	1.389(3)

C(2B)-H(2B)	0.9500
C(2B)-C(3B)	1.381(3)
C(3B)-H(3B)	0.9500
C(3B)-C(4B)	1.399(3)
C(4B)-C(5B)	1.392(3)
C(4B)-C(7B)	1.511(2)
C(5B)-H(5B)	0.9500
C(5B)-C(6B)	1.389(3)
C(6B)-H(6B)	0.9500
C(7B)-H(7C)	0.9900
C(7B)-H(7D)	0.9900
C(7B)-C(8B)	1.548(2)
C(8B)-C(9B)	1.559(2)
C(8B)-C(12B)	1.565(2)
C(8B)-C(14B)	1.523(2)
C(9B)-H(9C)	0.9900
C(9B)-H(9D)	0.9900
C(9B)-C(10B)	1.522(2)
C(10B)-C(11B)	1.494(2)
C(11B)-H(11D)	0.9800
C(11B)-H(11E)	0.9800
C(11B)-H(11F)	0.9800
C(12B)-C(13B)	1.501(2)
C(13B)-H(13D)	0.9800
C(13B)-H(13E)	0.9800
C(13B)-H(13F)	0.9800
C(15B)-H(15C)	0.9900
C(15B)-H(15D)	0.9900
C(15B)-C(16B)	1.501(3)
C(16B)-H(16D)	0.9800
C(16B)-H(16E)	0.9800
C(16B)-H(16F)	0.9800
C(12A)-O(3A)-C(10A)	95.89(13)
C(10A)-O(4A)-O(5A)	102.62(11)
C(12A)-O(5A)-O(4A)	102.48(11)
C(14A)-O(6A)-C(15A)	115.06(14)
O(1A)-N(1A)-C(1A)	118.44(17)
O(2A)-N(1A)-O(1A)	123.17(18)
O(2A)-N(1A)-C(1A)	118.39(17)
C(2A)-C(1A)-N(1A)	119.03(17)
C(6A)-C(1A)-N(1A)	118.58(17)
C(6A)-C(1A)-C(2A)	122.39(17)
C(1A)-C(2A)-H(2A)	120.9
C(1A)-C(2A)-C(3A)	118.19(17)
C(3A)-C(2A)-H(2A)	120.9
C(2A)-C(3A)-H(3A)	119.5
C(2A)-C(3A)-C(4A)	121.04(17)
C(4A)-C(3A)-H(3A)	119.5
C(3A)-C(4A)-C(5A)	118.85(17)
C(3A)-C(4A)-C(7A)	121.78(16)
C(5A)-C(4A)-C(7A)	119.37(16)
C(4A)-C(5A)-H(5A)	119.4
C(6A)-C(5A)-C(4A)	121.17(17)
C(6A)-C(5A)-H(5A)	119.4
C(1A)-C(6A)-C(5A)	118.36(16)
C(1A)-C(6A)-H(6A)	120.8
C(5A)-C(6A)-H(6A)	120.8
C(4A)-C(7A)-H(7A)	108.9
C(4A)-C(7A)-H(7B)	108.9
C(4A)-C(7A)-C(8A)	113.53(14)
H(7A)-C(7A)-H(7B)	107.7
C(8A)-C(7A)-H(7A)	108.9

C(8A)-C(7A)-H(7B)	108.9
C(7A)-C(8A)-C(9A)	112.81(14)
C(7A)-C(8A)-C(12A)	111.49(14)
C(9A)-C(8A)-C(12A)	99.74(13)
C(14A)-C(8A)-C(7A)	110.19(14)
C(14A)-C(8A)-C(9A)	111.49(14)
C(14A)-C(8A)-C(12A)	110.75(14)
C(8A)-C(9A)-H(9A)	111.5
C(8A)-C(9A)-H(9B)	111.5
H(9A)-C(9A)-H(9B)	109.3
C(10A)-C(9A)-C(8A)	101.42(14)
C(10A)-C(9A)-H(9A)	111.5
C(10A)-C(9A)-H(9B)	111.5
O(3A)-C(10A)-O(4A)	101.98(13)
O(3A)-C(10A)-C(9A)	103.14(14)
O(3A)-C(10A)-C(11A)	112.94(14)
O(4A)-C(10A)-C(9A)	108.77(14)
O(4A)-C(10A)-C(11A)	109.01(14)
C(11A)-C(10A)-C(9A)	119.49(15)
C(10A)-C(11A)-H(11A)	109.5
C(10A)-C(11A)-H(11B)	109.5
C(10A)-C(11A)-H(11C)	109.5
H(11A)-C(11A)-H(11B)	109.5
H(11A)-C(11A)-H(11C)	109.5
H(11B)-C(11A)-H(11C)	109.5
O(3A)-C(12A)-O(5A)	103.12(13)
O(3A)-C(12A)-C(8A)	103.20(13)
O(3A)-C(12A)-C(13A)	112.52(15)
O(5A)-C(12A)-C(8A)	106.62(13)
O(5A)-C(12A)-C(13A)	108.69(14)
C(13A)-C(12A)-C(8A)	121.10(15)
C(12A)-C(13A)-H(13A)	109.5
C(12A)-C(13A)-H(13B)	109.5
C(12A)-C(13A)-H(13C)	109.5
H(13A)-C(13A)-H(13B)	109.5
H(13A)-C(13A)-H(13C)	109.5
H(13B)-C(13A)-H(13C)	109.5
O(6A)-C(14A)-C(8A)	111.77(14)
O(7A)-C(14A)-O(6A)	123.55(16)
O(7A)-C(14A)-C(8A)	124.67(16)
O(6A)-C(15A)-H(15A)	110.1
O(6A)-C(15A)-H(15B)	110.1
O(6A)-C(15A)-C(16A)	108.15(15)
H(15A)-C(15A)-H(15B)	108.4
C(16A)-C(15A)-H(15A)	110.1
C(16A)-C(15A)-H(15B)	110.1
C(15A)-C(16A)-H(16A)	109.5
C(15A)-C(16A)-H(16B)	109.5
C(15A)-C(16A)-H(16C)	109.5
H(16A)-C(16A)-H(16B)	109.5
H(16A)-C(16A)-H(16C)	109.5
H(16B)-C(16A)-H(16C)	109.5
C(12B)-O(3B)-C(10B)	95.86(12)
C(10B)-O(4B)-O(5B)	102.32(11)
C(12B)-O(5B)-O(4B)	102.85(11)
C(14B)-O(6B)-C(15B)	114.47(14)
O(1B)-N(1B)-O(2B)	123.24(18)
O(1B)-N(1B)-C(1B)	118.31(17)
O(2B)-N(1B)-C(1B)	118.45(17)
C(2B)-C(1B)-N(1B)	118.46(17)
C(2B)-C(1B)-C(6B)	122.42(17)
C(6B)-C(1B)-N(1B)	119.12(17)

C(1B)-C(2B)-H(2B)	120.8
C(3B)-C(2B)-C(1B)	118.33(17)
C(3B)-C(2B)-H(2B)	120.8
C(2B)-C(3B)-H(3B)	119.4
C(2B)-C(3B)-C(4B)	121.26(17)
C(4B)-C(3B)-H(3B)	119.4
C(3B)-C(4B)-C(7B)	119.77(16)
C(5B)-C(4B)-C(3B)	118.73(17)
C(5B)-C(4B)-C(7B)	121.49(16)
C(4B)-C(5B)-H(5B)	119.4
C(6B)-C(5B)-C(4B)	121.14(17)
C(6B)-C(5B)-H(5B)	119.4
C(1B)-C(6B)-H(6B)	120.9
C(5B)-C(6B)-C(1B)	118.10(17)
C(5B)-C(6B)-H(6B)	120.9
C(4B)-C(7B)-H(7C)	108.6
C(4B)-C(7B)-H(7D)	108.6
C(4B)-C(7B)-C(8B)	114.48(14)
H(7C)-C(7B)-H(7D)	107.6
C(8B)-C(7B)-H(7C)	108.6
C(8B)-C(7B)-H(7D)	108.6
C(7B)-C(8B)-C(9B)	113.20(14)
C(7B)-C(8B)-C(12B)	110.26(14)
C(9B)-C(8B)-C(12B)	99.38(13)
C(14B)-C(8B)-C(7B)	111.25(14)
C(14B)-C(8B)-C(9B)	110.64(14)
C(14B)-C(8B)-C(12B)	111.58(14)
C(8B)-C(9B)-H(9C)	111.5
C(8B)-C(9B)-H(9D)	111.5
H(9C)-C(9B)-H(9D)	109.3
C(10B)-C(9B)-C(8B)	101.56(14)
C(10B)-C(9B)-H(9C)	111.5
C(10B)-C(9B)-H(9D)	111.5
O(3B)-C(10B)-O(4B)	102.00(13)
O(3B)-C(10B)-C(9B)	103.14(14)
O(3B)-C(10B)-C(11B)	113.63(14)
O(4B)-C(10B)-C(9B)	108.83(14)
O(4B)-C(10B)-C(11B)	108.39(14)
C(11B)-C(10B)-C(9B)	119.41(15)
C(10B)-C(11B)-H(11D)	109.5
C(10B)-C(11B)-H(11E)	109.5
C(10B)-C(11B)-H(11F)	109.5
H(11D)-C(11B)-H(11E)	109.5
H(11D)-C(11B)-H(11F)	109.5
H(11E)-C(11B)-H(11F)	109.5
O(3B)-C(12B)-O(5B)	102.93(13)
O(3B)-C(12B)-C(8B)	103.31(13)
O(3B)-C(12B)-C(13B)	112.79(14)
O(5B)-C(12B)-C(8B)	107.00(14)
O(5B)-C(12B)-C(13B)	108.69(14)
C(13B)-C(12B)-C(8B)	120.59(15)
C(12B)-C(13B)-H(13D)	109.5
C(12B)-C(13B)-H(13E)	109.5
C(12B)-C(13B)-H(13F)	109.5
H(13D)-C(13B)-H(13E)	109.5
H(13D)-C(13B)-H(13F)	109.5
H(13E)-C(13B)-H(13F)	109.5
O(6B)-C(14B)-C(8B)	111.52(15)
O(7B)-C(14B)-O(6B)	123.31(16)
O(7B)-C(14B)-C(8B)	125.15(17)
O(6B)-C(15B)-H(15C)	110.2
O(6B)-C(15B)-H(15D)	110.2

O(6B)-C(15B)-C(16B)	107.37(15)
H(15C)-C(15B)-H(15D)	108.5
C(16B)-C(15B)-H(15C)	110.2
C(16B)-C(15B)-H(15D)	110.2
C(15B)-C(16B)-H(16D)	109.5
C(15B)-C(16B)-H(16E)	109.5
C(15B)-C(16B)-H(16F)	109.5
H(16D)-C(16B)-H(16E)	109.5
H(16D)-C(16B)-H(16F)	109.5
H(16E)-C(16B)-H(16F)	109.5

Table S10. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *trans*-2a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1A)	46(1)	26(1)	51(1)	7(1)	6(1)	-1(1)
O(2A)	78(1)	45(1)	64(1)	10(1)	42(1)	-4(1)
O(3A)	32(1)	26(1)	26(1)	2(1)	6(1)	1(1)
O(4A)	28(1)	40(1)	29(1)	-4(1)	9(1)	-4(1)
O(5A)	32(1)	36(1)	31(1)	-4(1)	13(1)	-4(1)
O(6A)	29(1)	26(1)	30(1)	-1(1)	9(1)	2(1)
O(7A)	33(1)	32(1)	34(1)	3(1)	4(1)	6(1)
N(1A)	34(1)	34(1)	39(1)	6(1)	8(1)	-3(1)
C(1A)	24(1)	27(1)	35(1)	4(1)	5(1)	-2(1)
C(2A)	26(1)	33(1)	34(1)	0(1)	10(1)	1(1)
C(3A)	26(1)	26(1)	37(1)	-1(1)	10(1)	2(1)
C(4A)	19(1)	27(1)	32(1)	2(1)	5(1)	0(1)
C(5A)	25(1)	31(1)	34(1)	-4(1)	10(1)	-2(1)
C(6A)	26(1)	23(1)	38(1)	-4(1)	6(1)	0(1)
C(7A)	25(1)	28(1)	32(1)	3(1)	6(1)	1(1)
C(8A)	25(1)	27(1)	27(1)	2(1)	8(1)	-1(1)
C(9A)	29(1)	27(1)	27(1)	1(1)	8(1)	0(1)
C(10A)	27(1)	28(1)	26(1)	1(1)	6(1)	0(1)
C(11A)	35(1)	30(1)	30(1)	-3(1)	6(1)	-1(1)
C(12A)	30(1)	26(1)	28(1)	1(1)	10(1)	-1(1)
C(13A)	46(1)	31(1)	28(1)	4(1)	10(1)	-2(1)
C(14A)	25(1)	25(1)	30(1)	2(1)	7(1)	-2(1)
C(15A)	30(1)	27(1)	38(1)	0(1)	13(1)	2(1)
C(16A)	48(1)	35(1)	38(1)	-5(1)	13(1)	4(1)
O(1B)	78(1)	48(1)	43(1)	-14(1)	-2(1)	0(1)
O(2B)	47(1)	28(1)	61(1)	-8(1)	22(1)	-1(1)
O(3B)	29(1)	24(1)	32(1)	0(1)	11(1)	3(1)
O(4B)	26(1)	36(1)	32(1)	1(1)	6(1)	-1(1)
O(5B)	31(1)	35(1)	29(1)	0(1)	4(1)	-2(1)
O(6B)	30(1)	27(1)	31(1)	3(1)	7(1)	3(1)
O(7B)	39(1)	34(1)	48(1)	6(1)	21(1)	11(1)
N(1B)	34(1)	34(1)	45(1)	-8(1)	12(1)	-1(1)
C(1B)	24(1)	27(1)	37(1)	-4(1)	8(1)	1(1)
C(2B)	25(1)	25(1)	42(1)	4(1)	7(1)	0(1)
C(3B)	26(1)	31(1)	32(1)	4(1)	5(1)	-1(1)
C(4B)	21(1)	27(1)	32(1)	-1(1)	6(1)	0(1)
C(5B)	24(1)	27(1)	33(1)	2(1)	6(1)	3(1)
C(6B)	25(1)	33(1)	31(1)	2(1)	5(1)	2(1)
C(7B)	26(1)	27(1)	32(1)	-2(1)	8(1)	2(1)
C(8B)	27(1)	24(1)	27(1)	-1(1)	7(1)	1(1)
C(9B)	29(1)	26(1)	29(1)	0(1)	8(1)	1(1)
C(10B)	24(1)	27(1)	29(1)	-1(1)	8(1)	2(1)
C(11B)	33(1)	27(1)	39(1)	2(1)	14(1)	1(1)
C(12B)	29(1)	25(1)	28(1)	0(1)	6(1)	1(1)
C(13B)	45(1)	31(1)	31(1)	-2(1)	15(1)	1(1)

C(14B)	25(1)	26(1)	31(1)	-1(1)	5(1)	-1(1)
C(15B)	31(1)	29(1)	37(1)	5(1)	7(1)	3(1)
C(16B)	50(1)	34(1)	42(1)	8(1)	14(1)	5(1)

Table S11. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for *trans*-2a.

	x	y	z	U(eq)
H(2A)	9743	7006	8068	37
H(3A)	9528	4777	8871	35
H(5A)	9152	7993	10602	35
H(6A)	9352	10232	9798	35
H(7A)	9263	5026	10982	34
H(7B)	9356	3737	10254	34
H(9A)	8138	4233	8655	33
H(9B)	8699	3432	8804	33
H(11A)	8462	328	8442	48
H(11B)	7873	825	8039	48
H(11C)	8037	-504	8841	48
H(13A)	8530	1849	11836	53
H(13B)	8615	3817	11877	53
H(13C)	9051	2615	11722	53
H(15A)	7697	7625	10842	37
H(15B)	8148	8826	10734	37
H(16A)	7997	9193	12161	60
H(16B)	8567	8541	12275	60
H(16C)	8135	7282	12391	60
H(2B)	5642	-5135	5417	38
H(3B)	5859	-2916	6426	36
H(5B)	5484	336	4341	34
H(6B)	5256	-1875	3318	36
H(7C)	5730	57	6697	34
H(7D)	5645	1348	5881	34
H(9C)	6895	926	5572	34
H(9D)	6330	1657	5114	34
H(11D)	6546	4770	4970	48
H(11E)	7143	4340	5219	48
H(11F)	6938	5668	5808	48
H(13D)	6383	3306	8259	52
H(13E)	6333	1326	8240	52
H(13F)	5887	2438	7608	52
H(15C)	7282	-2535	8171	40
H(15D)	6845	-3710	7556	40
H(16D)	6372	-3467	8624	62
H(16E)	6809	-2302	9237	62
H(16F)	6927	-4215	9098	62

Table S12. Torsion angles [$^\circ$] for *trans*-2a.

O(1A)-N(1A)-C(1A)-C(2A)	170.01(17)
O(1A)-N(1A)-C(1A)-C(6A)	-10.1(3)
O(2A)-N(1A)-C(1A)-C(2A)	-9.8(3)
O(2A)-N(1A)-C(1A)-C(6A)	170.11(19)
O(4A)-O(5A)-C(12A)-O(3A)	-32.77(14)
O(4A)-O(5A)-C(12A)-C(8A)	75.55(14)
O(4A)-O(5A)-C(12A)-C(13A)	-152.37(13)
O(5A)-O(4A)-C(10A)-O(3A)	35.25(15)
O(5A)-O(4A)-C(10A)-C(9A)	-73.27(15)

O(5A)-O(4A)-C(10A)-C(11A)	154.89(13)
N(1A)-C(1A)-C(2A)-C(3A)	-179.31(16)
N(1A)-C(1A)-C(6A)-C(5A)	179.82(16)
C(1A)-C(2A)-C(3A)-C(4A)	-0.3(3)
C(2A)-C(1A)-C(6A)-C(5A)	-0.3(3)
C(2A)-C(3A)-C(4A)-C(5A)	-0.7(3)
C(2A)-C(3A)-C(4A)-C(7A)	178.76(16)
C(3A)-C(4A)-C(5A)-C(6A)	1.2(3)
C(3A)-C(4A)-C(7A)-C(8A)	-94.97(19)
C(4A)-C(5A)-C(6A)-C(1A)	-0.7(3)
C(4A)-C(7A)-C(8A)-C(9A)	69.43(19)
C(4A)-C(7A)-C(8A)-C(12A)	-179.29(14)
C(4A)-C(7A)-C(8A)-C(14A)	-55.9(2)
C(5A)-C(4A)-C(7A)-C(8A)	84.5(2)
C(6A)-C(1A)-C(2A)-C(3A)	0.8(3)
C(7A)-C(4A)-C(5A)-C(6A)	-178.25(16)
C(7A)-C(8A)-C(9A)-C(10A)	119.42(15)
C(7A)-C(8A)-C(12A)-O(3A)	-85.06(16)
C(7A)-C(8A)-C(12A)-O(5A)	166.68(14)
C(7A)-C(8A)-C(12A)-C(13A)	41.9(2)
C(7A)-C(8A)-C(14A)-O(6A)	-63.61(18)
C(7A)-C(8A)-C(14A)-O(7A)	115.10(19)
C(8A)-C(9A)-C(10A)-O(3A)	-35.65(16)
C(8A)-C(9A)-C(10A)-O(4A)	72.08(16)
C(8A)-C(9A)-C(10A)-C(11A)	-161.94(15)
C(9A)-C(8A)-C(12A)-O(3A)	34.31(15)
C(9A)-C(8A)-C(12A)-O(5A)	-73.95(15)
C(9A)-C(8A)-C(12A)-C(13A)	161.25(16)
C(9A)-C(8A)-C(14A)-O(6A)	170.33(13)
C(9A)-C(8A)-C(14A)-O(7A)	-11.0(2)
C(10A)-O(3A)-C(12A)-O(5A)	54.13(14)
C(10A)-O(3A)-C(12A)-C(8A)	-56.75(15)
C(10A)-O(3A)-C(12A)-C(13A)	171.06(15)
C(10A)-O(4A)-O(5A)-C(12A)	-1.84(15)
C(12A)-O(3A)-C(10A)-O(4A)	-55.04(14)
C(12A)-O(3A)-C(10A)-C(9A)	57.75(15)
C(12A)-O(3A)-C(10A)-C(11A)	-171.88(15)
C(12A)-C(8A)-C(9A)-C(10A)	1.02(16)
C(12A)-C(8A)-C(14A)-O(6A)	60.23(18)
C(12A)-C(8A)-C(14A)-O(7A)	-121.07(19)
C(14A)-O(6A)-C(15A)-C(16A)	178.14(15)
C(14A)-C(8A)-C(9A)-C(10A)	-115.97(15)
C(14A)-C(8A)-C(12A)-O(3A)	151.86(14)
C(14A)-C(8A)-C(12A)-O(5A)	43.60(18)
C(14A)-C(8A)-C(12A)-C(13A)	-81.2(2)
C(15A)-O(6A)-C(14A)-O(7A)	3.4(2)
C(15A)-O(6A)-C(14A)-C(8A)	-177.89(13)
O(1B)-N(1B)-C(1B)-C(2B)	170.18(19)
O(1B)-N(1B)-C(1B)-C(6B)	-9.5(3)
O(2B)-N(1B)-C(1B)-C(2B)	-10.1(3)
O(2B)-N(1B)-C(1B)-C(6B)	170.27(17)
O(4B)-O(5B)-C(12B)-O(3B)	-33.10(15)
O(4B)-O(5B)-C(12B)-C(8B)	75.39(15)
O(4B)-O(5B)-C(12B)-C(13B)	-152.92(14)
O(5B)-O(4B)-C(10B)-O(3B)	35.02(14)
O(5B)-O(4B)-C(10B)-C(9B)	-73.52(15)
O(5B)-O(4B)-C(10B)-C(11B)	155.18(13)
N(1B)-C(1B)-C(2B)-C(3B)	179.97(16)
N(1B)-C(1B)-C(6B)-C(5B)	-179.63(16)
C(1B)-C(2B)-C(3B)-C(4B)	-0.4(3)
C(2B)-C(1B)-C(6B)-C(5B)	0.7(3)
C(2B)-C(3B)-C(4B)-C(5B)	0.8(3)

C(2B)-C(3B)-C(4B)-C(7B)	179.56(16)
C(3B)-C(4B)-C(5B)-C(6B)	-0.4(3)
C(3B)-C(4B)-C(7B)-C(8B)	84.5(2)
C(4B)-C(5B)-C(6B)-C(1B)	-0.3(3)
C(4B)-C(7B)-C(8B)-C(9B)	69.11(19)
C(4B)-C(7B)-C(8B)-C(12B)	179.43(14)
C(4B)-C(7B)-C(8B)-C(14B)	-56.2(2)
C(5B)-C(4B)-C(7B)-C(8B)	-96.79(19)
C(6B)-C(1B)-C(2B)-C(3B)	-0.4(3)
C(7B)-C(4B)-C(5B)-C(6B)	-179.17(16)
C(7B)-C(8B)-C(9B)-C(10B)	117.77(15)
C(7B)-C(8B)-C(12B)-O(3B)	-84.55(16)
C(7B)-C(8B)-C(12B)-O(5B)	167.22(14)
C(7B)-C(8B)-C(12B)-C(13B)	42.5(2)
C(7B)-C(8B)-C(14B)-O(6B)	-61.27(19)
C(7B)-C(8B)-C(14B)-O(7B)	117.1(2)
C(8B)-C(9B)-C(10B)-O(3B)	-35.50(16)
C(8B)-C(9B)-C(10B)-O(4B)	72.27(16)
C(8B)-C(9B)-C(10B)-C(11B)	-162.65(15)
C(9B)-C(8B)-C(12B)-O(3B)	34.57(15)
C(9B)-C(8B)-C(12B)-O(5B)	-73.66(15)
C(9B)-C(8B)-C(12B)-C(13B)	161.60(15)
C(9B)-C(8B)-C(14B)-O(6B)	171.98(13)
C(9B)-C(8B)-C(14B)-O(7B)	-9.6(2)
C(10B)-O(3B)-C(12B)-O(5B)	54.27(14)
C(10B)-O(3B)-C(12B)-C(8B)	-56.99(14)
C(10B)-O(3B)-C(12B)-C(13B)	171.20(15)
C(10B)-O(4B)-O(5B)-C(12B)	-1.53(15)
C(12B)-O(3B)-C(10B)-O(4B)	-55.08(14)
C(12B)-O(3B)-C(10B)-C(9B)	57.77(15)
C(12B)-O(3B)-C(10B)-C(11B)	-171.50(15)
C(12B)-C(8B)-C(9B)-C(10B)	0.85(15)
C(12B)-C(8B)-C(14B)-O(6B)	62.33(19)
C(12B)-C(8B)-C(14B)-O(7B)	-119.3(2)
C(14B)-O(6B)-C(15B)-C(16B)	179.18(15)
C(14B)-C(8B)-C(9B)-C(10B)	-116.58(15)
C(14B)-C(8B)-C(12B)-O(3B)	151.29(14)
C(14B)-C(8B)-C(12B)-O(5B)	43.06(18)
C(14B)-C(8B)-C(12B)-C(13B)	-81.7(2)
C(15B)-O(6B)-C(14B)-O(7B)	0.8(2)
C(15B)-O(6B)-C(14B)-C(8B)	179.23(14)

X-Ray data of *cis-3a*

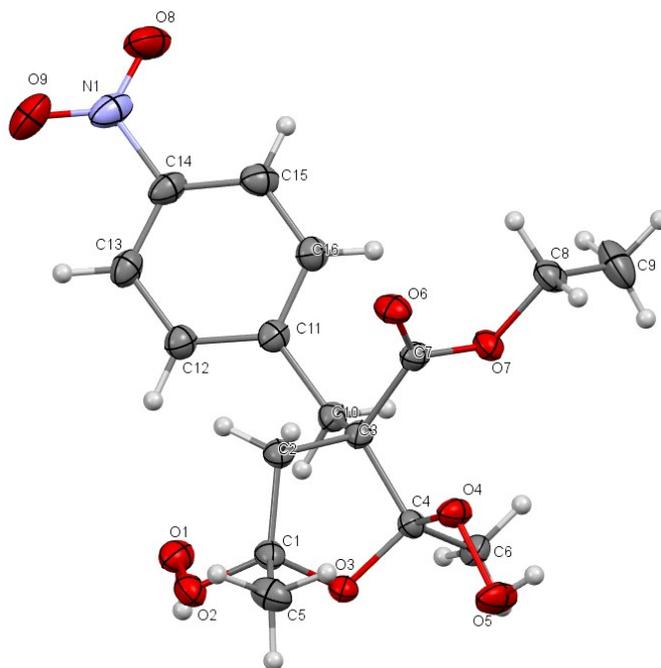


Figure S3. Molecular structure of *cis-3a* presented in thermal ellipsoids (50% probability).

The single-crystal X-ray data were collected using a Bruker D8 Venture Photon II four-circle diffractometer (Bruker, Billerica, MA, USA) in ω -scan mode (Cu K α radiation, $\lambda = 1.54178$ Å). The raw data were indexed and integrated with the APEX3 program suite (Bruker AXS Inc., Madison, WI, USA, 2016). The experimental intensities were corrected for absorption effects using SADABS.¹² The crystal structure was solved using direct methods⁸ and refined via full-matrix least-squares on F²⁹ using the OLEX2 structural data visualization and analysis program suite.¹⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. The C–H hydrogen atoms were placed in the calculated positions and refined using a riding model with dependent isotropic thermal parameters, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl and hydroxyl groups and with $U_{iso}(H) = 1.2U_{eq}(C)$ for other hydrogen atoms. In the refinement of the structure *cis-3a* some SHELX restraints and constrains were used (DFIX, SIMU, ISOR, SADI, EADP).

Table S13. Crystal data and structure refinement for *cis-3a*.

Identification code	<i>cis-3a</i>
Empirical formula	C ₁₆ H ₂₁ NO ₉
Formula weight	371.34
Temperature	100(2) K
Wavelength	1.54178 E
Crystal system	Monoclinic
Space group	P21/c
Unit cell dimensions	a = 7.2471(9) E $\alpha = 90^\circ$. b = 7.9047(10) E $\beta = 91.709(5)^\circ$. c = 30.181(4) E $\gamma = 90^\circ$.
Volume	1728.2(4) E ³
Z	4
Density (calculated)	1.427 Mg/m ³
Absorption coefficient	1.009 mm ⁻¹
F(000)	784
Crystal size	0.230 x 0.140 x 0.080 mm ³
Theta range for data collection	2.929 to 67.726°.
Index ranges	-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -36 ≤ l ≤ 35
Reflections collected	13715

Independent reflections 3117 [R(int) = 0.0305]
 Completeness to theta = 67.679° 99.5 %
 Absorption correction Semi-empirical from equivalents
 Max. and min. transmission 0.7530 and 0.6889
 Refinement method Full-matrix least-squares on F2
 Data / restraints / parameters 3117 / 0 / 301
 Goodness-of-fit on F2 1.059
 Final R indices [I>2sigma(I)] R1 = 0.0346, wR2 = 0.0861
 R indices (all data) R1 = 0.0359, wR2 = 0.0870
 Extinction coefficient 0.0022(3)
 Largest diff. peak and hole 0.304 and -0.200 e.E-3

Table S14. Bond lengths [Å] and angles [°] for *cis*-3a.

O(1)-O(2)	1.4637(15)
O(1)-H(1)	0.93(2)
O(2)-C(1)	1.4090(16)
O(3)-C(4)	1.4147(15)
O(3)-C(1)	1.4430(15)
O(4)-C(4)	1.4208(16)
O(4)-O(5)	1.4723(13)
O(5)-H(5)	0.93(2)
O(6)-C(7)	1.2048(16)
O(7)-C(7)	1.3342(16)
O(7)-C(8)	1.4581(16)
O(8)-N(1)	1.2306(19)
O(9)-N(1)	1.2251(18)
N(1)-C(14)	1.4730(18)
C(1)-C(5)	1.519(2)
C(1)-C(2)	1.5361(18)
C(2)-C(3)	1.5344(18)
C(2)-H(2A)	0.965(17)
C(2)-H(2B)	0.985(16)
C(3)-C(7)	1.5283(17)
C(3)-C(10)	1.5522(17)
C(3)-C(4)	1.5656(17)
C(4)-C(6)	1.5012(19)
C(5)-H(5A)	1.00(2)
C(5)-H(5B)	1.00(2)
C(5)-H(5C)	0.98(2)
C(6)-H(6A)	0.983(19)
C(6)-H(6B)	0.982(19)
C(6)-H(6C)	0.969(19)
C(8)-C(9)	1.495(2)
C(8)-H(8A)	1.000(18)
C(8)-H(8B)	0.995(18)
C(9)-H(9A)	1.02(2)
C(9)-H(9B)	0.97(2)
C(9)-H(9C)	0.94(2)
C(10)-C(11)	1.5140(18)
C(10)-H(10A)	0.971(16)
C(10)-H(10B)	0.976(17)
C(11)-C(16)	1.394(2)
C(11)-C(12)	1.397(2)
C(12)-C(13)	1.390(2)
C(12)-H(12)	0.988(17)
C(13)-C(14)	1.380(2)
C(13)-H(13)	0.966(17)
C(14)-C(15)	1.385(2)
C(15)-C(16)	1.384(2)
C(15)-H(15)	0.938(19)
C(16)-H(16)	0.923(17)

O(2)-O(1)-H(1)	97.0(13)
C(1)-O(2)-O(1)	109.70(9)
C(4)-O(3)-C(1)	109.73(9)
C(4)-O(4)-O(5)	107.52(9)
O(4)-O(5)-H(5)	95.7(14)
C(7)-O(7)-C(8)	116.98(10)
O(9)-N(1)-O(8)	123.79(13)
O(9)-N(1)-C(14)	118.39(14)
O(8)-N(1)-C(14)	117.81(14)
O(2)-C(1)-O(3)	107.67(10)
O(2)-C(1)-C(5)	102.38(11)
O(3)-C(1)-C(5)	110.45(11)
O(2)-C(1)-C(2)	115.69(11)
O(3)-C(1)-C(2)	105.17(10)
C(5)-C(1)-C(2)	115.35(11)
C(3)-C(2)-C(1)	106.33(10)
C(3)-C(2)-H(2A)	110.3(9)
C(1)-C(2)-H(2A)	107.9(10)
C(3)-C(2)-H(2B)	111.6(9)
C(1)-C(2)-H(2B)	110.6(9)
H(2A)-C(2)-H(2B)	110.0(13)
C(7)-C(3)-C(2)	111.50(10)
C(7)-C(3)-C(10)	109.19(10)
C(2)-C(3)-C(10)	113.53(10)
C(7)-C(3)-C(4)	111.60(10)
C(2)-C(3)-C(4)	100.81(10)
C(10)-C(3)-C(4)	110.01(10)
O(3)-C(4)-O(4)	110.51(10)
O(3)-C(4)-C(6)	108.45(11)
O(4)-C(4)-C(6)	113.11(11)
O(3)-C(4)-C(3)	103.81(10)
O(4)-C(4)-C(3)	100.82(10)
C(6)-C(4)-C(3)	119.56(11)
C(1)-C(5)-H(5A)	109.6(11)
C(1)-C(5)-H(5B)	107.4(11)
H(5A)-C(5)-H(5B)	109.2(15)
C(1)-C(5)-H(5C)	108.0(11)
H(5A)-C(5)-H(5C)	111.2(16)
H(5B)-C(5)-H(5C)	111.5(16)
C(4)-C(6)-H(6A)	110.8(10)
C(4)-C(6)-H(6B)	109.6(11)
H(6A)-C(6)-H(6B)	108.6(15)
C(4)-C(6)-H(6C)	108.4(11)
H(6A)-C(6)-H(6C)	109.6(15)
H(6B)-C(6)-H(6C)	109.9(14)
O(6)-C(7)-O(7)	124.37(12)
O(6)-C(7)-C(3)	124.57(12)
O(7)-C(7)-C(3)	111.02(11)
O(7)-C(8)-C(9)	106.92(12)
O(7)-C(8)-H(8A)	108.0(10)
C(9)-C(8)-H(8A)	113.1(10)
O(7)-C(8)-H(8B)	106.3(10)
C(9)-C(8)-H(8B)	112.9(10)
H(8A)-C(8)-H(8B)	109.3(14)
C(8)-C(9)-H(9A)	108.8(13)
C(8)-C(9)-H(9B)	109.1(14)
H(9A)-C(9)-H(9B)	106.9(19)
C(8)-C(9)-H(9C)	109.8(14)
H(9A)-C(9)-H(9C)	112.3(19)
H(9B)-C(9)-H(9C)	110(2)
C(11)-C(10)-C(3)	113.79(10)

C(11)-C(10)-H(10A)	107.8(9)
C(3)-C(10)-H(10A)	109.4(9)
C(11)-C(10)-H(10B)	110.0(9)
C(3)-C(10)-H(10B)	107.5(9)
H(10A)-C(10)-H(10B)	108.2(13)
C(16)-C(11)-C(12)	118.68(13)
C(16)-C(11)-C(10)	120.27(12)
C(12)-C(11)-C(10)	121.01(12)
C(13)-C(12)-C(11)	121.16(14)
C(13)-C(12)-H(12)	119.8(10)
C(11)-C(12)-H(12)	119.1(10)
C(14)-C(13)-C(12)	118.19(13)
C(14)-C(13)-H(13)	121.2(10)
C(12)-C(13)-H(13)	120.5(10)
C(13)-C(14)-C(15)	122.32(13)
C(13)-C(14)-N(1)	118.75(13)
C(15)-C(14)-N(1)	118.91(14)
C(16)-C(15)-C(14)	118.60(14)
C(16)-C(15)-H(15)	120.2(11)
C(14)-C(15)-H(15)	121.2(11)
C(15)-C(16)-C(11)	121.02(14)
C(15)-C(16)-H(16)	120.5(11)
C(11)-C(16)-H(16)	118.4(11)

Table S15. Torsion angles [$^{\circ}$] for *cis*-3a.

O(1)-O(2)-C(1)-O(3)	-65.25(12)
O(1)-O(2)-C(1)-C(5)	178.30(10)
O(1)-O(2)-C(1)-C(2)	52.01(14)
C(4)-O(3)-C(1)-O(2)	145.99(10)
C(4)-O(3)-C(1)-C(5)	-102.97(12)
C(4)-O(3)-C(1)-C(2)	22.09(13)
O(2)-C(1)-C(2)-C(3)	-116.24(12)
O(3)-C(1)-C(2)-C(3)	2.41(13)
C(5)-C(1)-C(2)-C(3)	124.35(12)
C(1)-C(2)-C(3)-C(7)	-141.21(11)
C(1)-C(2)-C(3)-C(10)	94.95(12)
C(1)-C(2)-C(3)-C(4)	-22.64(12)
C(1)-O(3)-C(4)-O(4)	70.28(12)
C(1)-O(3)-C(4)-C(6)	-165.21(10)
C(1)-O(3)-C(4)-C(3)	-37.07(12)
O(5)-O(4)-C(4)-O(3)	62.26(12)
O(5)-O(4)-C(4)-C(6)	-59.54(13)
O(5)-O(4)-C(4)-C(3)	171.59(9)
C(7)-C(3)-C(4)-O(3)	154.29(10)
C(2)-C(3)-C(4)-O(3)	35.80(12)
C(10)-C(3)-C(4)-O(3)	-84.34(12)
C(7)-C(3)-C(4)-O(4)	39.81(13)
C(2)-C(3)-C(4)-O(4)	-78.68(11)
C(10)-C(3)-C(4)-O(4)	161.18(10)
C(7)-C(3)-C(4)-C(6)	-84.78(14)
C(2)-C(3)-C(4)-C(6)	156.73(12)
C(10)-C(3)-C(4)-C(6)	36.59(15)
C(8)-O(7)-C(7)-O(6)	5.74(18)
C(8)-O(7)-C(7)-C(3)	-176.63(10)
C(2)-C(3)-C(7)-O(6)	-7.93(18)
C(10)-C(3)-C(7)-O(6)	118.33(14)
C(4)-C(3)-C(7)-O(6)	-119.83(14)
C(2)-C(3)-C(7)-O(7)	174.45(10)
C(10)-C(3)-C(7)-O(7)	-59.30(13)
C(4)-C(3)-C(7)-O(7)	62.55(14)
C(7)-O(7)-C(8)-C(9)	-169.06(13)

C(7)-C(3)-C(10)-C(11)	-62.60(14)
C(2)-C(3)-C(10)-C(11)	62.49(15)
C(4)-C(3)-C(10)-C(11)	174.60(11)
C(3)-C(10)-C(11)-C(16)	92.94(15)
C(3)-C(10)-C(11)-C(12)	-89.15(15)
C(16)-C(11)-C(12)-C(13)	-0.8(2)
C(10)-C(11)-C(12)-C(13)	-178.75(12)
C(11)-C(12)-C(13)-C(14)	1.3(2)
C(12)-C(13)-C(14)-C(15)	-0.5(2)
C(12)-C(13)-C(14)-N(1)	177.94(13)
O(9)-N(1)-C(14)-C(13)	7.8(2)
O(8)-N(1)-C(14)-C(13)	-171.03(14)
O(9)-N(1)-C(14)-C(15)	-173.77(14)
O(8)-N(1)-C(14)-C(15)	7.4(2)
C(13)-C(14)-C(15)-C(16)	-0.9(2)
N(1)-C(14)-C(15)-C(16)	-179.29(13)
C(14)-C(15)-C(16)-C(11)	1.4(2)
C(12)-C(11)-C(16)-C(15)	-0.6(2)
C(10)-C(11)-C(16)-C(15)	177.36(12)

Table S16. Hydrogen bonds for *cis*-3a [E and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1)...O(6)#1	0.93(2)	1.89(2)	2.8126(14)	172(2)
O(5)-H(5)...O(3)#2	0.93(2)	1.86(2)	2.7909(14)	178(2)

#1 x,y-1,z #2 -x,y+1/2,-z+1/2

X-Ray data of **5a**

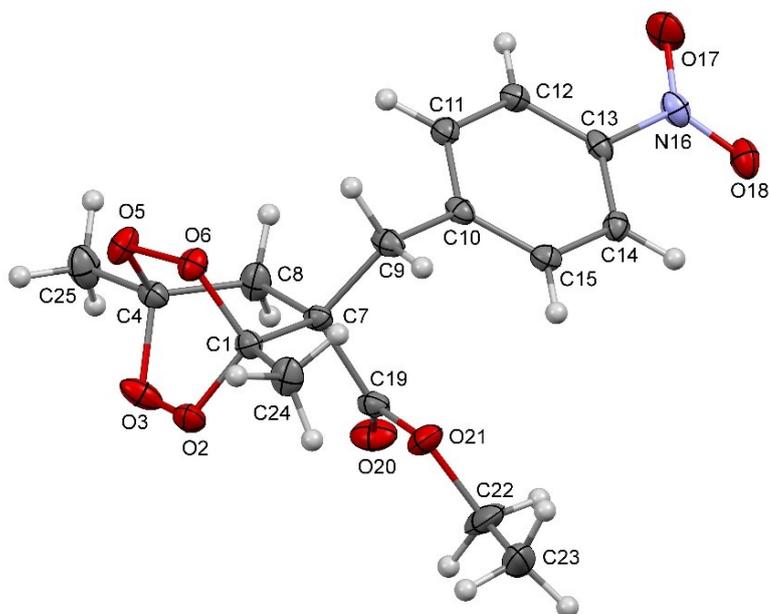


Figure S4. Molecular structure of **5a** presented in thermal ellipsoids (50% probability).

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω -scan technique), using monochromatized Cu K_{α} -radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.⁷ The structure was solved by direct methods using SHELXT⁸ and refined on F^2 using SHELXL-2018⁹ in the OLEX2 program.¹⁰ All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. The Mercury program suite¹¹ was used for molecular graphics.

Atoms O3 and O5 are disordered over two positions with the contribution of the main component of 0.64(2).

Table S17. Crystal data and structure refinement for **5a**

Identification code	5a	
Empirical formula	C ₁₆ H ₁₉ NO ₈	
Formula weight	353.32	
Temperature	99.97(18) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	I a	
Unit cell dimensions	a = 6.83692(6) Å	a = 90°.
	b = 21.3655(2) Å	b = 91.5169(8)°.
	c = 11.21195(9) Å	g = 90°.
Volume	1637.20(2) Å ³	
Z	4	
Density (calculated)	1.433 g/cm ³	
Absorption coefficient	0.991 mm ⁻¹	
F(000)	744	
Crystal size	0.59 x 0.45 x 0.23 mm ³	
Theta range for data collection	4.138 to 77.754°.	
Index ranges	-8 ≤ h ≤ 8, -26 ≤ k ≤ 26, -12 ≤ l ≤ 14	
Reflections collected	20824	
Independent reflections	3079 [R(int) = 0.0327]	
Observed reflections	3069	
	S259	

Completeness to theta = 67.684°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.66074
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3079 / 6 / 237
Goodness-of-fit on F ²	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0251, wR2 = 0.0661
R indices (all data)	R1 = 0.0251, wR2 = 0.0661
Absolute structure parameter	0.03(7)
Extinction coefficient	0.0018(2)
Largest diff. peak and hole	0.161 and -0.166 e.Å ⁻³

Table S18. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(2)	5092(2)	7611(1)	3159(1)	22(1)
O(3)	6931(9)	7715(4)	3863(5)	26(1)
O(3A)	6688(17)	7878(5)	3945(10)	26(1)
O(5)	4907(9)	8079(4)	5357(7)	23(1)
O(5A)	4718(16)	7952(5)	5569(11)	23(1)
O(6)	3083(2)	7817(1)	4760(1)	20(1)
O(17)	4441(2)	4229(1)	8921(1)	35(1)
O(18)	4290(2)	3702(1)	7273(1)	26(1)
O(20)	6754(2)	6083(1)	3600(1)	31(1)
O(21)	3676(2)	6111(1)	2863(1)	25(1)
N(16)	4252(2)	4193(1)	7835(1)	21(1)
C(1)	3597(3)	7365(1)	3882(2)	18(1)
C(4)	6471(3)	7671(1)	5116(2)	19(1)
C(7)	4375(2)	6766(1)	4524(2)	16(1)
C(8)	6082(3)	6989(1)	5342(2)	25(1)
C(9)	2711(3)	6466(1)	5245(2)	20(1)
C(10)	3266(2)	5875(1)	5916(2)	17(1)
C(11)	3866(2)	5893(1)	7116(2)	19(1)
C(12)	4213(2)	5344(1)	7751(2)	18(1)
C(13)	3966(2)	4779(1)	7162(2)	18(1)
C(14)	3429(2)	4742(1)	5969(2)	18(1)
C(15)	3073(2)	5294(1)	5352(2)	18(1)
C(19)	5113(3)	6288(1)	3616(2)	20(1)
C(22)	4163(4)	5635(1)	1989(2)	38(1)
C(23)	2512(4)	5612(1)	1086(2)	41(1)
C(24)	1802(3)	7325(1)	3070(2)	25(1)
C(25)	8196(3)	7941(1)	5807(2)	30(1)

Table S19. Bond lengths [\AA] and angles [$^\circ$] for 5a.

O(2)-O(3)	1.484(6)
O(2)-O(3A)	1.498(12)
O(2)-C(1)	1.422(2)
O(3)-C(4)	1.450(6)
O(3A)-C(4)	1.397(12)
O(5)-O(6)	1.508(6)
O(5)-C(4)	1.412(6)
O(5A)-O(6)	1.450(12)
O(5A)-C(4)	1.445(12)
O(6)-C(1)	1.429(2)
O(17)-N(16)	1.223(2)
O(18)-N(16)	1.224(2)
O(20)-C(19)	1.205(2)

O(21)-C(19)	1.333(2)
O(21)-C(22)	1.457(2)
N(16)-C(13)	1.472(2)
C(1)-C(7)	1.555(2)
C(1)-C(24)	1.511(3)
C(4)-C(8)	1.505(2)
C(4)-C(25)	1.508(3)
C(7)-C(8)	1.541(3)
C(7)-C(9)	1.551(2)
C(7)-C(19)	1.536(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(9)-C(10)	1.513(2)
C(10)-C(11)	1.396(2)
C(10)-C(15)	1.397(2)
C(11)-H(11)	0.9500
C(11)-C(12)	1.389(2)
C(12)-H(12)	0.9500
C(12)-C(13)	1.385(2)
C(13)-C(14)	1.380(2)
C(14)-H(14)	0.9500
C(14)-C(15)	1.387(2)
C(15)-H(15)	0.9500
C(22)-H(22A)	0.9900
C(22)-H(22B)	0.9900
C(22)-C(23)	1.497(3)
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
C(1)-O(2)-O(3)	111.3(3)
C(1)-O(2)-O(3A)	109.2(5)
C(4)-O(3)-O(2)	107.7(4)
C(4)-O(3A)-O(2)	109.8(8)
C(4)-O(5)-O(6)	107.9(4)
C(4)-O(5A)-O(6)	109.3(8)
C(1)-O(6)-O(5)	110.0(3)
C(1)-O(6)-O(5A)	111.5(5)
C(19)-O(21)-C(22)	116.50(16)
O(17)-N(16)-O(18)	124.25(15)
O(17)-N(16)-C(13)	117.76(15)
O(18)-N(16)-C(13)	117.99(14)
O(2)-C(1)-O(6)	109.66(13)
O(2)-C(1)-C(7)	109.03(13)
O(2)-C(1)-C(24)	105.15(14)
O(6)-C(1)-C(7)	108.95(13)
O(6)-C(1)-C(24)	104.00(14)
C(24)-C(1)-C(7)	119.69(14)
O(3)-C(4)-C(8)	105.6(4)
O(3)-C(4)-C(25)	106.7(3)
O(3A)-C(4)-O(5A)	108.0(6)
O(3A)-C(4)-C(8)	119.3(5)
O(3A)-C(4)-C(25)	105.1(5)
O(5)-C(4)-O(3)	109.2(3)
O(5)-C(4)-C(8)	115.4(4)

O(5)-C(4)-C(25)	104.6(3)
O(5A)-C(4)-C(8)	101.0(4)
O(5A)-C(4)-C(25)	107.8(5)
C(8)-C(4)-C(25)	115.01(16)
C(8)-C(7)-C(1)	105.37(14)
C(8)-C(7)-C(9)	111.88(15)
C(9)-C(7)-C(1)	109.53(13)
C(19)-C(7)-C(1)	110.75(13)
C(19)-C(7)-C(8)	110.06(15)
C(19)-C(7)-C(9)	109.22(14)
C(4)-C(8)-C(7)	109.54(15)
C(4)-C(8)-H(8A)	109.8
C(4)-C(8)-H(8B)	109.8
C(7)-C(8)-H(8A)	109.8
C(7)-C(8)-H(8B)	109.8
H(8A)-C(8)-H(8B)	108.2
C(7)-C(9)-H(9A)	108.5
C(7)-C(9)-H(9B)	108.5
H(9A)-C(9)-H(9B)	107.5
C(10)-C(9)-C(7)	115.18(14)
C(10)-C(9)-H(9A)	108.5
C(10)-C(9)-H(9B)	108.5
C(11)-C(10)-C(9)	121.31(16)
C(11)-C(10)-C(15)	118.81(16)
C(15)-C(10)-C(9)	119.77(16)
C(10)-C(11)-H(11)	119.6
C(12)-C(11)-C(10)	120.87(16)
C(12)-C(11)-H(11)	119.6
C(11)-C(12)-H(12)	120.8
C(13)-C(12)-C(11)	118.35(16)
C(13)-C(12)-H(12)	120.8
C(12)-C(13)-N(16)	119.00(15)
C(14)-C(13)-N(16)	118.46(16)
C(14)-C(13)-C(12)	122.54(16)
C(13)-C(14)-H(14)	120.9
C(13)-C(14)-C(15)	118.27(16)
C(15)-C(14)-H(14)	120.9
C(10)-C(15)-H(15)	119.4
C(14)-C(15)-C(10)	121.13(17)
C(14)-C(15)-H(15)	119.4
O(20)-C(19)-O(21)	124.00(17)
O(20)-C(19)-C(7)	124.94(18)
O(21)-C(19)-C(7)	111.02(14)
O(21)-C(22)-H(22A)	110.3
O(21)-C(22)-H(22B)	110.3
O(21)-C(22)-C(23)	107.28(19)
H(22A)-C(22)-H(22B)	108.5
C(23)-C(22)-H(22A)	110.3
C(23)-C(22)-H(22B)	110.3
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(1)-C(24)-H(24A)	109.5
C(1)-C(24)-H(24B)	109.5
C(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(4)-C(25)-H(25A)	109.5

C(4)-C(25)-H(25B)	109.5
C(4)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5

Table S20. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 5a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(2)	27(1)	23(1)	16(1)	4(1)	0(1)	-2(1)
O(3)	15(2)	41(3)	21(1)	13(2)	1(1)	2(2)
O(3A)	15(2)	41(3)	21(1)	13(2)	1(1)	2(2)
O(5)	24(1)	17(2)	27(2)	-5(2)	-7(1)	4(1)
O(5A)	24(1)	17(2)	27(2)	-5(2)	-7(1)	4(1)
O(6)	18(1)	18(1)	24(1)	-2(1)	-1(1)	3(1)
O(17)	50(1)	30(1)	24(1)	11(1)	-8(1)	-3(1)
O(18)	26(1)	16(1)	36(1)	5(1)	2(1)	1(1)
O(20)	30(1)	36(1)	26(1)	1(1)	5(1)	16(1)
O(21)	36(1)	21(1)	18(1)	-5(1)	-3(1)	6(1)
N(16)	19(1)	20(1)	25(1)	7(1)	-2(1)	-1(1)
C(1)	23(1)	14(1)	17(1)	3(1)	1(1)	2(1)
C(4)	20(1)	20(1)	18(1)	3(1)	2(1)	0(1)
C(7)	20(1)	16(1)	13(1)	2(1)	0(1)	2(1)
C(8)	30(1)	19(1)	25(1)	3(1)	-10(1)	-1(1)
C(9)	22(1)	19(1)	20(1)	5(1)	6(1)	6(1)
C(10)	15(1)	18(1)	18(1)	4(1)	4(1)	2(1)
C(11)	20(1)	17(1)	20(1)	0(1)	4(1)	0(1)
C(12)	18(1)	21(1)	16(1)	2(1)	1(1)	-1(1)
C(13)	13(1)	18(1)	22(1)	5(1)	2(1)	0(1)
C(14)	15(1)	16(1)	22(1)	-1(1)	2(1)	-1(1)
C(15)	16(1)	21(1)	17(1)	1(1)	2(1)	-1(1)
C(19)	26(1)	18(1)	15(1)	4(1)	4(1)	5(1)
C(22)	72(2)	22(1)	19(1)	-7(1)	1(1)	12(1)
C(23)	71(2)	31(1)	22(1)	-4(1)	3(1)	-20(1)
C(24)	28(1)	20(1)	25(1)	5(1)	-9(1)	3(1)
C(25)	27(1)	29(1)	34(1)	6(1)	-8(1)	-7(1)

Table S21. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 5a.

	x	y	z	U(eq)
H(8A)	5750	6926	6187	30
H(8B)	7270	6741	5181	30
H(9A)	2245	6778	5825	24
H(9B)	1604	6369	4688	24
H(11)	4039	6285	7502	23
H(12)	4609	5356	8569	22
H(14)	3307	4348	5580	21
H(15)	2691	5278	4531	22
H(22A)	4328	5223	2382	45
H(22B)	5400	5744	1599	45
H(23A)	2508	5995	607	62
H(23B)	1269	5575	1495	62
H(23C)	2679	5249	563	62
H(24A)	780	7087	3466	37
H(24B)	2138	7115	2326	37

H(24C)	1323	7748	2892	37
H(25A)	8331	8386	5614	45
H(25B)	9390	7718	5593	45
H(25C)	7989	7894	6664	45

Table S22. Torsion angles [°] for 5a.

O(2)-O(3)-C(4)-O(5)	-53.1(5)
O(2)-O(3)-C(4)-C(8)	71.6(5)
O(2)-O(3)-C(4)-C(25)	-165.6(4)
O(2)-O(3A)-C(4)-O(5A)	-67.9(8)
O(2)-O(3A)-C(4)-C(8)	46.4(8)
O(2)-O(3A)-C(4)-C(25)	177.3(5)
O(2)-C(1)-C(7)-C(8)	63.54(17)
O(2)-C(1)-C(7)-C(9)	-175.96(14)
O(2)-C(1)-C(7)-C(19)	-55.44(18)
O(3)-O(2)-C(1)-O(6)	65.0(4)
O(3)-O(2)-C(1)-C(7)	-54.2(4)
O(3)-O(2)-C(1)-C(24)	176.3(4)
O(3)-C(4)-C(8)-C(7)	-59.1(3)
O(3A)-O(2)-C(1)-O(6)	48.8(5)
O(3A)-O(2)-C(1)-C(7)	-70.4(5)
O(3A)-O(2)-C(1)-C(24)	160.1(4)
O(3A)-C(4)-C(8)-C(7)	-50.1(6)
O(5)-O(6)-C(1)-O(2)	-47.5(4)
O(5)-O(6)-C(1)-C(7)	71.7(4)
O(5)-O(6)-C(1)-C(24)	-159.6(4)
O(5)-C(4)-C(8)-C(7)	61.7(4)
O(5A)-O(6)-C(1)-O(2)	-63.3(5)
O(5A)-O(6)-C(1)-C(7)	55.9(5)
O(5A)-O(6)-C(1)-C(24)	-175.4(5)
O(5A)-C(4)-C(8)-C(7)	67.9(5)
O(6)-O(5)-C(4)-O(3)	69.9(5)
O(6)-O(5)-C(4)-C(8)	-48.9(6)
O(6)-O(5)-C(4)-C(25)	-176.3(4)
O(6)-O(5A)-C(4)-O(3A)	54.0(8)
O(6)-O(5A)-C(4)-C(8)	-71.9(6)
O(6)-O(5A)-C(4)-C(25)	167.1(5)
O(6)-C(1)-C(7)-C(8)	-56.10(17)
O(6)-C(1)-C(7)-C(9)	64.39(17)
O(6)-C(1)-C(7)-C(19)	-175.08(14)
O(17)-N(16)-C(13)-C(12)	9.5(2)
O(17)-N(16)-C(13)-C(14)	-169.45(16)
O(18)-N(16)-C(13)-C(12)	-170.28(15)
O(18)-N(16)-C(13)-C(14)	10.7(2)
N(16)-C(13)-C(14)-C(15)	177.05(14)
C(1)-O(2)-O(3)-C(4)	-13.2(7)
C(1)-O(2)-O(3A)-C(4)	14.6(8)
C(1)-C(7)-C(8)-C(4)	-5.80(19)
C(1)-C(7)-C(9)-C(10)	179.85(14)
C(1)-C(7)-C(19)-O(20)	121.10(19)
C(1)-C(7)-C(19)-O(21)	-60.92(18)
C(4)-O(5)-O(6)-C(1)	-17.0(6)
C(4)-O(5A)-O(6)-C(1)	10.0(8)
C(7)-C(9)-C(10)-C(11)	95.12(19)
C(7)-C(9)-C(10)-C(15)	-88.6(2)
C(8)-C(7)-C(9)-C(10)	-63.70(19)
C(8)-C(7)-C(19)-O(20)	5.0(2)
C(8)-C(7)-C(19)-O(21)	-177.03(14)
C(9)-C(7)-C(8)-C(4)	-124.74(16)
C(9)-C(7)-C(19)-O(20)	-118.20(19)

C(9)-C(7)-C(19)-O(21)	59.78(18)
C(9)-C(10)-C(11)-C(12)	174.47(15)
C(9)-C(10)-C(15)-C(14)	-175.10(15)
C(10)-C(11)-C(12)-C(13)	0.6(2)
C(11)-C(10)-C(15)-C(14)	1.2(2)
C(11)-C(12)-C(13)-N(16)	-177.60(14)
C(11)-C(12)-C(13)-C(14)	1.3(2)
C(12)-C(13)-C(14)-C(15)	-1.9(2)
C(13)-C(14)-C(15)-C(10)	0.6(2)
C(15)-C(10)-C(11)-C(12)	-1.8(2)
C(19)-O(21)-C(22)-C(23)	-167.79(16)
C(19)-C(7)-C(8)-C(4)	113.64(17)
C(19)-C(7)-C(9)-C(10)	58.4(2)
C(22)-O(21)-C(19)-O(20)	0.8(3)
C(22)-O(21)-C(19)-C(7)	-177.21(15)
C(24)-C(1)-C(7)-C(8)	-175.46(15)
C(24)-C(1)-C(7)-C(9)	-55.0(2)
C(24)-C(1)-C(7)-C(19)	65.6(2)
C(25)-C(4)-C(8)-C(7)	-176.43(15)

X-Ray data of **6a**

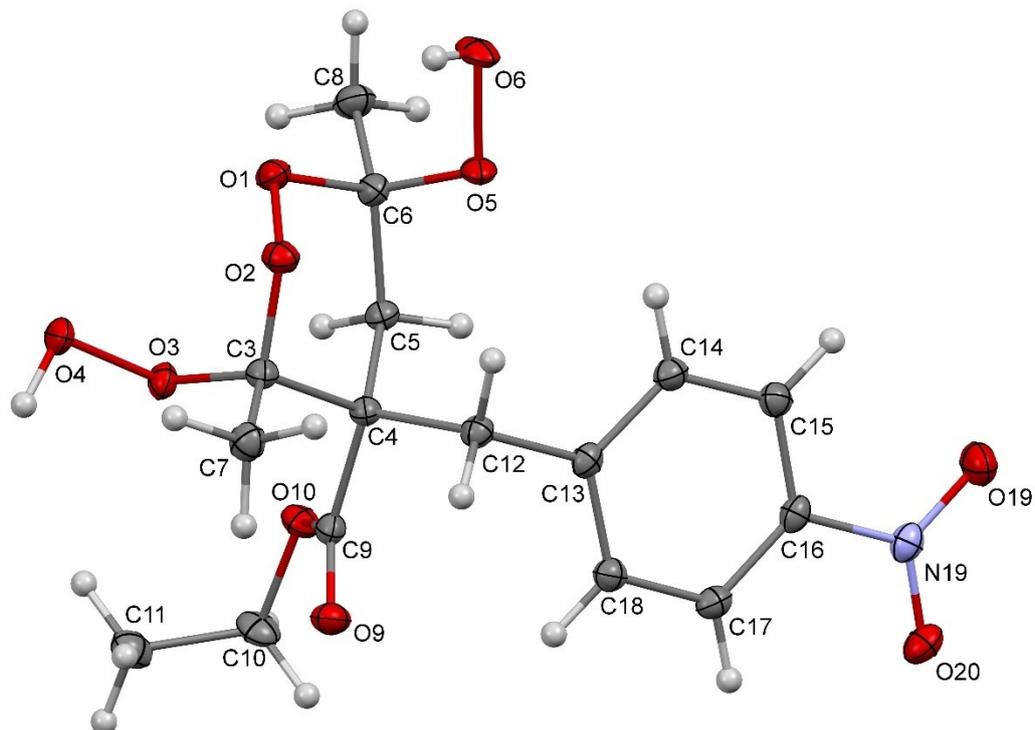


Figure S5. Molecular structure of **6a** presented in thermal ellipsoids (50% probability).

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω -scan technique), using monochromatized Cu K_{α} -radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.⁷ The structure was solved by direct methods using SHELXT⁸ and refined on F^2 using SHELXL-2018⁹ in the OLEX2 program.¹⁰ All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. The Mercury program suite¹¹ was used for molecular graphics.

Table S23. Crystal data and structure refinement for **6a**

Identification code	6a	
Empirical formula	C ₁₆ H ₂₁ NO ₁₀	
Formula weight	387.34	
Temperature	99.96(13) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 2 ₁ /n	
Unit cell dimensions	a = 6.27451(5) Å	a = 90°.
	b = 8.24052(7) Å	b = 92.3352(7)°.
	c = 33.9220(3) Å	g = 90°.
Volume	1752.49(3) Å ³	
Z	4	
Density (calculated)	1.468 g/cm ³	
Absorption coefficient	1.065 mm ⁻¹	
F(000)	816	
Crystal size	0.19 x 0.1 x 0.04 mm ³	
Theta range for data collection	2.607 to 77.807°.	

Index ranges	-6<=h<=7, -10<=k<=10, -42<=l<=42
Reflections collected	21207
Independent reflections	3681 [R(int) = 0.0202]
Observed reflections	3496
Completeness to theta = 67.684°	99.9 %
Absorption correction	Gaussian
Max. and min. transmission	1.000 and 0.691
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3681 / 0 / 255
Goodness-of-fit on F2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0288, wR2 = 0.0752
R indices (all data)	R1 = 0.0301, wR2 = 0.0761
Largest diff. peak and hole	0.282 and -0.220 e.Å ⁻³

Table S24. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6a. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^i tensor.

	x	y	z	U(eq)
O(1)	4451(1)	3310(1)	2809(1)	18(1)
O(2)	2469(1)	2450(1)	2890(1)	17(1)
O(3)	4682(1)	286(1)	3098(1)	17(1)
O(4)	4408(1)	-426(1)	2705(1)	20(1)
O(5)	3409(1)	5420(1)	3219(1)	18(1)
O(6)	3023(1)	6453(1)	2876(1)	24(1)
O(9)	3021(1)	-267(1)	4007(1)	20(1)
O(10)	6366(1)	622(1)	3935(1)	17(1)
O(19)	2820(1)	7972(1)	5173(1)	26(1)
O(20)	2831(1)	5743(1)	5512(1)	21(1)
N(19)	2737(1)	6487(1)	5198(1)	18(1)
C(3)	2861(2)	1228(1)	3181(1)	15(1)
C(4)	3536(2)	2044(1)	3585(1)	14(1)
C(5)	5345(2)	3266(1)	3514(1)	15(1)
C(6)	5055(2)	4289(1)	3140(1)	16(1)
C(7)	808(2)	254(1)	3166(1)	19(1)
C(8)	7112(2)	5087(1)	3020(1)	23(1)
C(9)	4267(2)	671(1)	3867(1)	15(1)
C(10)	7161(2)	-732(1)	4177(1)	21(1)
C(11)	7283(2)	-2244(1)	3930(1)	23(1)
C(12)	1533(2)	2847(1)	3759(1)	15(1)
C(13)	1962(1)	3788(1)	4138(1)	15(1)
C(14)	2150(2)	5475(1)	4130(1)	16(1)
C(15)	2419(2)	6371(1)	4475(1)	17(1)
C(16)	2504(2)	5544(1)	4831(1)	16(1)
C(17)	2347(2)	3867(1)	4852(1)	16(1)
C(18)	2073(2)	2995(1)	4504(1)	16(1)

Table S25. Bond lengths [\AA] and angles [$^\circ$] for 6a.

O(1)-O(2)	1.4672(10)
O(1)-C(6)	1.4222(12)
O(2)-C(3)	1.4248(11)
O(3)-O(4)	1.4590(9)
O(3)-C(3)	1.4188(12)
O(4)-H(4)	0.910(18)
O(5)-O(6)	1.4567(9)
O(5)-C(6)	1.4246(12)
O(6)-H(6)	0.843(19)

O(9)-C(9)	1.2109(13)
O(10)-C(9)	1.3288(12)
O(10)-C(10)	1.4603(12)
O(19)-N(19)	1.2273(12)
O(20)-N(19)	1.2281(11)
N(19)-C(16)	1.4710(12)
C(3)-C(4)	1.5695(13)
C(3)-C(7)	1.5173(14)
C(4)-C(5)	1.5443(13)
C(4)-C(9)	1.5382(13)
C(4)-C(12)	1.5571(13)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(5)-C(6)	1.5280(13)
C(6)-C(8)	1.5195(14)
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(10)-C(11)	1.5062(15)
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(12)-C(13)	1.5154(13)
C(13)-C(14)	1.3957(14)
C(13)-C(18)	1.4020(13)
C(14)-H(14)	0.9500
C(14)-C(15)	1.3872(14)
C(15)-H(15)	0.9500
C(15)-C(16)	1.3856(14)
C(16)-C(17)	1.3881(15)
C(17)-H(17)	0.9500
C(17)-C(18)	1.3872(14)
C(18)-H(18)	0.9500
C(6)-O(1)-O(2)	109.07(6)
C(3)-O(2)-O(1)	110.33(7)
C(3)-O(3)-O(4)	109.62(7)
O(3)-O(4)-H(4)	100.4(10)
C(6)-O(5)-O(6)	109.21(7)
O(5)-O(6)-H(6)	103.0(12)
C(9)-O(10)-C(10)	115.81(8)
O(19)-N(19)-O(20)	123.90(9)
O(19)-N(19)-C(16)	118.06(8)
O(20)-N(19)-C(16)	118.04(9)
O(2)-C(3)-C(4)	109.65(8)
O(2)-C(3)-C(7)	103.24(8)
O(3)-C(3)-O(2)	111.50(7)
O(3)-C(3)-C(4)	102.53(7)
O(3)-C(3)-C(7)	113.17(8)
C(7)-C(3)-C(4)	116.96(8)
C(5)-C(4)-C(3)	108.47(7)
C(5)-C(4)-C(12)	113.05(8)
C(9)-C(4)-C(3)	106.88(7)
C(9)-C(4)-C(5)	111.95(8)
C(9)-C(4)-C(12)	107.63(8)
C(12)-C(4)-C(3)	108.63(8)

C(4)-C(5)-H(5A)	108.5
C(4)-C(5)-H(5B)	108.5
H(5A)-C(5)-H(5B)	107.5
C(6)-C(5)-C(4)	115.20(8)
C(6)-C(5)-H(5A)	108.5
C(6)-C(5)-H(5B)	108.5
O(1)-C(6)-O(5)	110.39(8)
O(1)-C(6)-C(5)	111.24(8)
O(1)-C(6)-C(8)	103.56(8)
O(5)-C(6)-C(5)	105.48(7)
O(5)-C(6)-C(8)	113.48(8)
C(8)-C(6)-C(5)	112.83(8)
C(3)-C(7)-H(7A)	109.5
C(3)-C(7)-H(7B)	109.5
C(3)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(6)-C(8)-H(8A)	109.5
C(6)-C(8)-H(8B)	109.5
C(6)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
O(9)-C(9)-O(10)	124.24(9)
O(9)-C(9)-C(4)	122.19(9)
O(10)-C(9)-C(4)	113.58(8)
O(10)-C(10)-H(10A)	109.7
O(10)-C(10)-H(10B)	109.7
O(10)-C(10)-C(11)	110.05(8)
H(10A)-C(10)-H(10B)	108.2
C(11)-C(10)-H(10A)	109.7
C(11)-C(10)-H(10B)	109.7
C(10)-C(11)-H(11A)	109.5
C(10)-C(11)-H(11B)	109.5
C(10)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(4)-C(12)-H(12A)	108.6
C(4)-C(12)-H(12B)	108.6
H(12A)-C(12)-H(12B)	107.5
C(13)-C(12)-C(4)	114.83(8)
C(13)-C(12)-H(12A)	108.6
C(13)-C(12)-H(12B)	108.6
C(14)-C(13)-C(12)	120.41(9)
C(14)-C(13)-C(18)	118.64(9)
C(18)-C(13)-C(12)	120.88(9)
C(13)-C(14)-H(14)	119.3
C(15)-C(14)-C(13)	121.45(9)
C(15)-C(14)-H(14)	119.3
C(14)-C(15)-H(15)	120.9
C(16)-C(15)-C(14)	118.19(9)
C(16)-C(15)-H(15)	120.9
C(15)-C(16)-N(19)	118.55(9)
C(15)-C(16)-C(17)	122.29(9)
C(17)-C(16)-N(19)	119.15(9)
C(16)-C(17)-H(17)	120.7
C(18)-C(17)-C(16)	118.56(9)
C(18)-C(17)-H(17)	120.7
C(13)-C(18)-H(18)	119.6
C(17)-C(18)-C(13)	120.86(9)

Table S26. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6a. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
O(1)	25(1)	17(1)	13(1)	0(1)	3(1)	-4(1)
O(2)	20(1)	16(1)	15(1)	2(1)	-2(1)	-2(1)
O(3)	20(1)	18(1)	12(1)	-4(1)	0(1)	3(1)
O(4)	29(1)	17(1)	13(1)	-4(1)	2(1)	0(1)
O(5)	27(1)	15(1)	12(1)	4(1)	-1(1)	4(1)
O(6)	41(1)	14(1)	15(1)	6(1)	-8(1)	-1(1)
O(9)	23(1)	18(1)	21(1)	6(1)	4(1)	1(1)
O(10)	19(1)	15(1)	18(1)	3(1)	-4(1)	2(1)
O(19)	36(1)	19(1)	23(1)	-5(1)	0(1)	0(1)
O(20)	21(1)	29(1)	14(1)	0(1)	0(1)	1(1)
N(19)	15(1)	22(1)	17(1)	-2(1)	1(1)	1(1)
C(3)	19(1)	14(1)	13(1)	1(1)	1(1)	1(1)
C(4)	16(1)	13(1)	12(1)	1(1)	1(1)	1(1)
C(5)	16(1)	15(1)	13(1)	1(1)	1(1)	0(1)
C(6)	21(1)	15(1)	13(1)	0(1)	1(1)	0(1)
C(7)	20(1)	20(1)	18(1)	-3(1)	1(1)	-3(1)
C(8)	27(1)	22(1)	19(1)	2(1)	5(1)	-6(1)
C(9)	19(1)	14(1)	13(1)	-1(1)	1(1)	2(1)
C(10)	24(1)	18(1)	22(1)	6(1)	-6(1)	3(1)
C(11)	22(1)	18(1)	30(1)	3(1)	2(1)	3(1)
C(12)	15(1)	16(1)	14(1)	0(1)	0(1)	1(1)
C(13)	11(1)	18(1)	15(1)	0(1)	1(1)	2(1)
C(14)	16(1)	18(1)	15(1)	2(1)	2(1)	2(1)
C(15)	16(1)	16(1)	18(1)	1(1)	2(1)	1(1)
C(16)	13(1)	20(1)	14(1)	-2(1)	1(1)	1(1)
C(17)	14(1)	20(1)	14(1)	3(1)	1(1)	1(1)
C(18)	14(1)	16(1)	17(1)	1(1)	2(1)	1(1)

Table S27. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for 6a.

	x	y	z	U(eq)
H(4)	4030(30)	-1460(20)	2769(5)	42(4)
H(6)	2240(30)	5870(20)	2725(5)	42(4)
H(5A)	5476	4006	3744	18
H(5B)	6703	2660	3502	18
H(7A)	-406	986	3196	29
H(7B)	849	-543	3381	29
H(7C)	653	-311	2913	29
H(8A)	8140	4248	2951	34
H(8B)	7706	5738	3239	34
H(8C)	6817	5789	2791	34
H(10A)	6198	-919	4397	26
H(10B)	8595	-466	4292	26
H(11A)	8245	-2058	3714	35
H(11B)	5858	-2516	3821	35
H(11C)	7827	-3143	4094	35
H(12A)	887	3592	3559	18
H(12B)	474	1988	3809	18
H(14)	2093	6022	3883	20
H(15)	2542	7519	4467	20

H(17)	2425	3327	5099	19
H(18)	1958	1847	4513	19

Table S28. Torsion angles [°] for 6a.

O(1)-O(2)-C(3)-O(3)	-46.96(9)
O(1)-O(2)-C(3)-C(4)	65.88(9)
O(1)-O(2)-C(3)-C(7)	-168.77(7)
O(2)-O(1)-C(6)-O(5)	-58.74(9)
O(2)-O(1)-C(6)-C(5)	58.00(9)
O(2)-O(1)-C(6)-C(8)	179.45(7)
O(2)-C(3)-C(4)-C(5)	-50.48(10)
O(2)-C(3)-C(4)-C(9)	-171.37(7)
O(2)-C(3)-C(4)-C(12)	72.76(9)
O(3)-C(3)-C(4)-C(5)	68.07(9)
O(3)-C(3)-C(4)-C(9)	-52.81(9)
O(3)-C(3)-C(4)-C(12)	-168.69(7)
O(4)-O(3)-C(3)-O(2)	-56.62(9)
O(4)-O(3)-C(3)-C(4)	-173.86(7)
O(4)-O(3)-C(3)-C(7)	59.25(9)
O(6)-O(5)-C(6)-O(1)	-59.74(9)
O(6)-O(5)-C(6)-C(5)	180.00(7)
O(6)-O(5)-C(6)-C(8)	56.00(10)
O(19)-N(19)-C(16)-C(15)	0.86(13)
O(19)-N(19)-C(16)-C(17)	-178.23(9)
O(20)-N(19)-C(16)-C(15)	-179.34(9)
O(20)-N(19)-C(16)-C(17)	1.57(13)
N(19)-C(16)-C(17)-C(18)	178.36(8)
C(3)-C(4)-C(5)-C(6)	41.48(10)
C(3)-C(4)-C(9)-O(9)	-72.84(11)
C(3)-C(4)-C(9)-O(10)	106.84(9)
C(3)-C(4)-C(12)-C(13)	-176.00(8)
C(4)-C(5)-C(6)-O(1)	-47.04(11)
C(4)-C(5)-C(6)-O(5)	72.66(10)
C(4)-C(5)-C(6)-C(8)	-162.92(8)
C(4)-C(12)-C(13)-C(14)	99.83(10)
C(4)-C(12)-C(13)-C(18)	-83.36(11)
C(5)-C(4)-C(9)-O(9)	168.52(9)
C(5)-C(4)-C(9)-O(10)	-11.80(11)
C(5)-C(4)-C(12)-C(13)	-55.55(11)
C(6)-O(1)-O(2)-C(3)	-70.63(9)
C(7)-C(3)-C(4)-C(5)	-167.52(8)
C(7)-C(3)-C(4)-C(9)	71.60(10)
C(7)-C(3)-C(4)-C(12)	-44.27(11)
C(9)-O(10)-C(10)-C(11)	79.85(11)
C(9)-C(4)-C(5)-C(6)	159.17(8)
C(9)-C(4)-C(12)-C(13)	68.62(10)
C(10)-O(10)-C(9)-O(9)	4.02(14)
C(10)-O(10)-C(9)-C(4)	-175.65(8)
C(12)-C(4)-C(5)-C(6)	-79.06(10)
C(12)-C(4)-C(9)-O(9)	43.69(12)
C(12)-C(4)-C(9)-O(10)	-136.63(8)
C(12)-C(13)-C(14)-C(15)	176.21(9)
C(12)-C(13)-C(18)-C(17)	-176.38(8)
C(13)-C(14)-C(15)-C(16)	0.18(14)
C(14)-C(13)-C(18)-C(17)	0.49(14)
C(14)-C(15)-C(16)-N(19)	-178.54(8)
C(14)-C(15)-C(16)-C(17)	0.52(14)
C(15)-C(16)-C(17)-C(18)	-0.70(15)
C(16)-C(17)-C(18)-C(13)	0.17(14)
C(18)-C(13)-C(14)-C(15)	-0.67(14)

Table S29. Hydrogen bonds for 6a [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	$\angle(\text{DHA})$
O(4)-H(4)...O(6)#1	0.910(18)	1.875(18)	2.7824(11)	174.7(16)
O(6)-H(6)...O(4)#2	0.843(19)	2.055(19)	2.8921(11)	171.7(16)

Symmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$ #2 $-x+1/2, y+1/2, -z+1/2$

X-Ray data of 7a

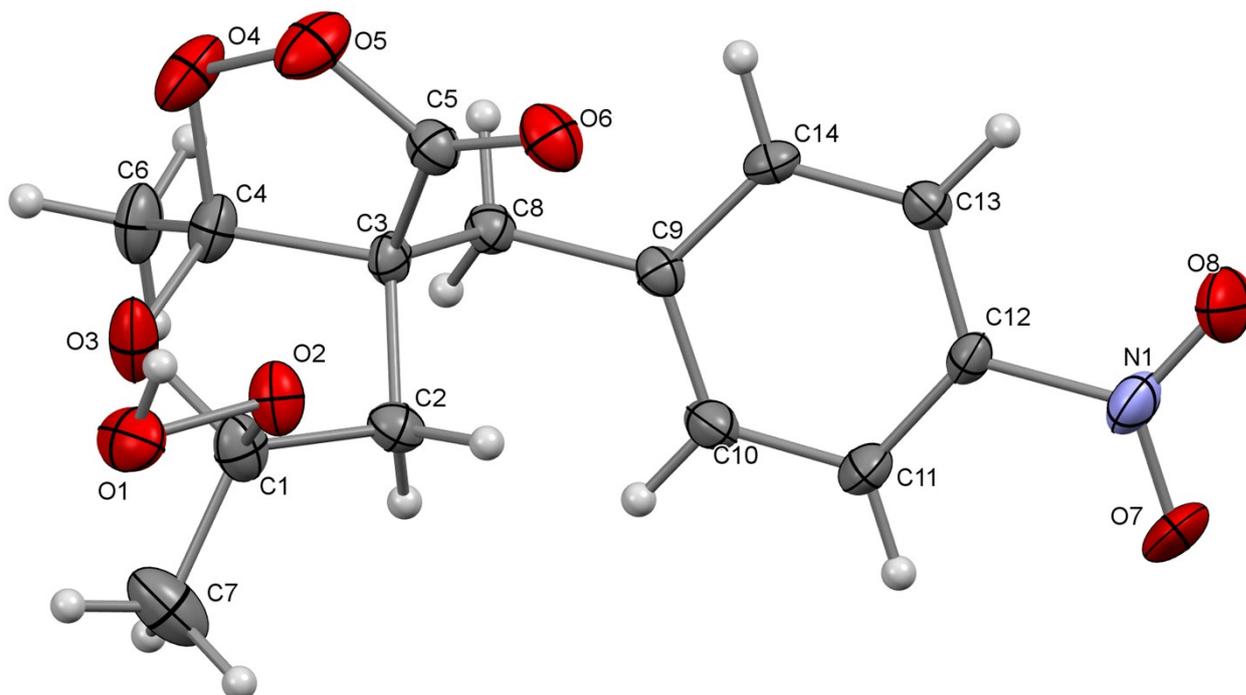


Figure S6. Molecular structure of **7a** presented in thermal ellipsoids (50% probability).

The single-crystal X-ray data were collected using a Bruker D8 Venture Photon II four-circle diffractometer (Bruker, Billerica, MA, USA) in ω -scan mode (Cu K α radiation, $\lambda = 1.54178$ Å). The raw data were indexed and integrated with the APEX3 program suite (Bruker AXS Inc., Madison, WI, USA, 2016). The experimental intensities were corrected for absorption effects using SADABS.¹² The crystal structure was solved using direct methods⁸ and refined via full-matrix least-squares on F²⁹ using the OLEX2 structural data visualization and analysis program suite.¹⁰ All non-hydrogen atoms were refined with anisotropic thermal parameters. The C–H hydrogen atoms were placed in the calculated positions and refined using a riding model with dependent isotropic thermal parameters, with $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl and hydroxyl groups and with $U_{iso}(H) = 1.2U_{eq}(C)$ for other hydrogen atoms. In the refinement of the structure **7a** some SHELX restraints and constrains were used (DFIX, SIMU, ISOR, SADI, EADP).

Table 30. Crystal data and structure refinement for **7a**.

Identification code	7a	
Empirical formula	C ₁₆ H ₁₉ N O ₉	
Formula weight	369.32	
Temperature	100(2) K	
Wavelength	1.54178 E	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 37.699(5) E	$\alpha = 90^\circ$.
	b = 7.8969(12) E	$\beta = 91.505(8)^\circ$.
	c = 11.6321(18) E	$\gamma = 90^\circ$.
Volume	3461.7(9) E ³	
Z	8	
Density (calculated)	1.417 Mg/m ³	
Absorption coefficient	1.008 mm ⁻¹	
F(000)	1552	
Crystal size	0.200 x 0.080 x 0.015 mm ³	
Theta range for data collection	2.345 to 66.570°.	
Index ranges	-44 ≤ h ≤ 44, -9 ≤ k ≤ 9, -12 ≤ l ≤ 13	
Reflections collected	2939	
Independent reflections	2939 [R(int) = ?]	

Completeness to theta = 66.570°	96.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7528 and 0.3977
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	2939 / 51 / 287
Goodness-of-fit on F2	1.131
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0686, wR2 = 0.1472
R indices (all data)	R1 = 0.0937, wR2 = 0.1570
Extinction coefficient	0.00041(6)
Largest diff. peak and hole	0.299 and -0.291 e.E-3

Table 31. Bond lengths [Å] and angles [°] for 7a.

O(1)-O(2)	1.477(12)
O(1)-H(1)	0.84(2)
O(1')-O(2)	1.468(11)
O(1')-H(1')	0.84(2)
O(2)-C(1)	1.423(5)
O(3)-C(4)	1.405(5)
O(3)-C(1)	1.440(5)
O(4)-C(4)	1.443(5)
O(4)-O(5)	1.475(4)
O(5)-C(5)	1.370(5)
O(6)-C(5)	1.197(5)
O(7)-N(1)	1.22(2)
O(7')-N(1)	1.29(4)
O(8)-N(1)	1.215(5)
N(1)-C(12)	1.470(5)
C(1)-C(7)	1.496(6)
C(1)-C(2)	1.520(6)
C(2)-C(3)	1.530(6)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(5)	1.505(5)
C(3)-C(4)	1.537(5)
C(3)-C(8)	1.554(5)
C(4)-C(6)	1.507(5)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-C(9)	1.498(5)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(14)	1.401(5)
C(9)-C(10)	1.401(6)
C(10)-C(11)	1.375(6)
C(10)-H(10)	0.9500
C(11)-C(12)	1.378(6)
C(11)-H(11)	0.9500
C(12)-C(13)	1.371(6)
C(13)-C(14)	1.387(6)
C(13)-H(13)	0.9500
C(14)-H(14)	0.9500
O(1S)-C(1S)	1.216(13)
O(2S)-C(1S)	1.38(8)
O(2S)-C(3S)	1.49(8)
C(1S)-C(2S)	1.49(4)
C(2S)-H(2SA)	0.9800
C(2S)-H(2SB)	0.9800

C(2S)-H(2SC)	0.9800
C(3S)-C(4S)	1.49(4)
C(3S)-H(3SA)	0.9900
C(3S)-H(3SB)	0.9900
C(4S)-H(4SA)	0.9800
C(4S)-H(4SB)	0.9800
C(4S)-H(4SC)	0.9800
O(2)-O(1)-H(1)	84(10)
O(2)-O(1')-H(1')	103(10)
C(1)-O(2)-O(1')	114.1(8)
C(1)-O(2)-O(1)	102.6(9)
C(4)-O(3)-C(1)	112.2(3)
C(4)-O(4)-O(5)	107.7(3)
C(5)-O(5)-O(4)	107.1(3)
O(8)-N(1)-O(7)	122.9(11)
O(8)-N(1)-O(7')	122(2)
O(8)-N(1)-C(12)	119.0(4)
O(7)-N(1)-C(12)	117.5(11)
O(7')-N(1)-C(12)	117(2)
O(2)-C(1)-O(3)	110.6(3)
O(2)-C(1)-C(7)	113.1(3)
O(3)-C(1)-C(7)	107.6(4)
O(2)-C(1)-C(2)	103.5(3)
O(3)-C(1)-C(2)	105.3(3)
C(7)-C(1)-C(2)	116.4(4)
C(1)-C(2)-C(3)	103.7(3)
C(1)-C(2)-H(2A)	111.0
C(3)-C(2)-H(2A)	111.0
C(1)-C(2)-H(2B)	111.0
C(3)-C(2)-H(2B)	111.0
H(2A)-C(2)-H(2B)	109.0
C(5)-C(3)-C(2)	110.2(3)
C(5)-C(3)-C(4)	102.5(3)
C(2)-C(3)-C(4)	103.3(3)
C(5)-C(3)-C(8)	111.3(3)
C(2)-C(3)-C(8)	114.0(3)
C(4)-C(3)-C(8)	114.8(3)
O(3)-C(4)-O(4)	110.8(3)
O(3)-C(4)-C(6)	109.4(3)
O(4)-C(4)-C(6)	104.5(4)
O(3)-C(4)-C(3)	106.9(3)
O(4)-C(4)-C(3)	104.2(3)
C(6)-C(4)-C(3)	120.8(3)
O(6)-C(5)-O(5)	118.5(4)
O(6)-C(5)-C(3)	130.3(4)
O(5)-C(5)-C(3)	111.2(3)
C(4)-C(6)-H(6A)	109.5
C(4)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(4)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(1)-C(7)-H(7A)	109.5
C(1)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(1)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(9)-C(8)-C(3)	113.2(3)
C(9)-C(8)-H(8A)	108.9
C(3)-C(8)-H(8A)	108.9

C(9)-C(8)-H(8B)	108.9
C(3)-C(8)-H(8B)	108.9
H(8A)-C(8)-H(8B)	107.8
C(14)-C(9)-C(10)	117.8(4)
C(14)-C(9)-C(8)	121.6(4)
C(10)-C(9)-C(8)	120.6(3)
C(11)-C(10)-C(9)	121.7(4)
C(11)-C(10)-H(10)	119.1
C(9)-C(10)-H(10)	119.1
C(10)-C(11)-C(12)	118.1(4)
C(10)-C(11)-H(11)	120.9
C(12)-C(11)-H(11)	120.9
C(13)-C(12)-C(11)	122.8(4)
C(13)-C(12)-N(1)	117.8(4)
C(11)-C(12)-N(1)	119.3(4)
C(12)-C(13)-C(14)	118.4(4)
C(12)-C(13)-H(13)	120.8
C(14)-C(13)-H(13)	120.8
C(13)-C(14)-C(9)	121.1(4)
C(13)-C(14)-H(14)	119.5
C(9)-C(14)-H(14)	119.5
C(1S)-O(2S)-C(3S)	113(2)
O(1S)-C(1S)-O(2S)	123(3)
O(1S)-C(1S)-C(2S)	126.6(17)
O(2S)-C(1S)-C(2S)	110(3)
C(1S)-C(2S)-H(2SA)	109.5
C(1S)-C(2S)-H(2SB)	109.5
H(2SA)-C(2S)-H(2SB)	109.5
C(1S)-C(2S)-H(2SC)	109.5
H(2SA)-C(2S)-H(2SC)	109.5
H(2SB)-C(2S)-H(2SC)	109.5
O(2S)-C(3S)-C(4S)	106(3)
O(2S)-C(3S)-H(3SA)	110.6
C(4S)-C(3S)-H(3SA)	110.6
O(2S)-C(3S)-H(3SB)	110.6
C(4S)-C(3S)-H(3SB)	110.6
H(3SA)-C(3S)-H(3SB)	108.7
C(3S)-C(4S)-H(4SA)	109.5
C(3S)-C(4S)-H(4SB)	109.5
H(4SA)-C(4S)-H(4SB)	109.5
C(3S)-C(4S)-H(4SC)	109.5
H(4SA)-C(4S)-H(4SC)	109.5
H(4SB)-C(4S)-H(4SC)	109.5

Table 32. Torsion angles [°] for 7a.

C(4)-O(4)-O(5)-C(5)	21.8(4)
O(1')-O(2)-C(1)-O(3)	60.0(9)
O(1)-O(2)-C(1)-O(3)	75.3(10)
O(1')-O(2)-C(1)-C(7)	-60.9(9)
O(1)-O(2)-C(1)-C(7)	-45.6(10)
O(1')-O(2)-C(1)-C(2)	172.3(8)
O(1)-O(2)-C(1)-C(2)	-172.4(9)
C(4)-O(3)-C(1)-O(2)	95.8(4)
C(4)-O(3)-C(1)-C(7)	-140.2(4)
C(4)-O(3)-C(1)-C(2)	-15.4(4)
O(2)-C(1)-C(2)-C(3)	-88.9(4)
O(3)-C(1)-C(2)-C(3)	27.3(4)
C(7)-C(1)-C(2)-C(3)	146.4(4)
C(1)-C(2)-C(3)-C(5)	80.3(4)
C(1)-C(2)-C(3)-C(4)	-28.6(4)
C(1)-C(2)-C(3)-C(8)	-153.8(3)

C(1)-O(3)-C(4)-O(4)	-116.1(4)
C(1)-O(3)-C(4)-C(6)	129.2(4)
C(1)-O(3)-C(4)-C(3)	-3.2(4)
O(5)-O(4)-C(4)-O(3)	86.9(4)
O(5)-O(4)-C(4)-C(6)	-155.4(3)
O(5)-O(4)-C(4)-C(3)	-27.7(4)
C(5)-C(3)-C(4)-O(3)	-94.4(4)
C(2)-C(3)-C(4)-O(3)	20.2(4)
C(8)-C(3)-C(4)-O(3)	144.8(3)
C(5)-C(3)-C(4)-O(4)	22.9(4)
C(2)-C(3)-C(4)-O(4)	137.5(3)
C(8)-C(3)-C(4)-O(4)	-97.8(4)
C(5)-C(3)-C(4)-C(6)	139.8(4)
C(2)-C(3)-C(4)-C(6)	-105.7(4)
C(8)-C(3)-C(4)-C(6)	19.0(6)
O(4)-O(5)-C(5)-O(6)	175.0(4)
O(4)-O(5)-C(5)-C(3)	-6.2(4)
C(2)-C(3)-C(5)-O(6)	58.8(6)
C(4)-C(3)-C(5)-O(6)	168.2(4)
C(8)-C(3)-C(5)-O(6)	-68.6(6)
C(2)-C(3)-C(5)-O(5)	-119.8(4)
C(4)-C(3)-C(5)-O(5)	-10.4(4)
C(8)-C(3)-C(5)-O(5)	112.7(4)
C(5)-C(3)-C(8)-C(9)	68.8(4)
C(2)-C(3)-C(8)-C(9)	-56.5(4)
C(4)-C(3)-C(8)-C(9)	-175.4(3)
C(3)-C(8)-C(9)-C(14)	-91.4(4)
C(3)-C(8)-C(9)-C(10)	87.2(4)
C(14)-C(9)-C(10)-C(11)	2.0(6)
C(8)-C(9)-C(10)-C(11)	-176.6(4)
C(9)-C(10)-C(11)-C(12)	-0.2(6)
C(10)-C(11)-C(12)-C(13)	-2.2(6)
C(10)-C(11)-C(12)-N(1)	179.0(4)
O(8)-N(1)-C(12)-C(13)	1.3(6)
O(7)-N(1)-C(12)-C(13)	-170(2)
O(7')-N(1)-C(12)-C(13)	165(2)
O(8)-N(1)-C(12)-C(11)	-179.8(4)
O(7)-N(1)-C(12)-C(11)	8(2)
O(7')-N(1)-C(12)-C(11)	-16(2)
C(11)-C(12)-C(13)-C(14)	2.5(6)
N(1)-C(12)-C(13)-C(14)	-178.7(3)
C(12)-C(13)-C(14)-C(9)	-0.5(6)
C(10)-C(9)-C(14)-C(13)	-1.7(6)
C(8)-C(9)-C(14)-C(13)	176.9(4)
C(3S)-O(2S)-C(1S)-O(1S)	-12(5)
C(3S)-O(2S)-C(1S)-C(2S)	175(3)
C(1S)-O(2S)-C(3S)-C(4S)	177(3)

Table 33. Hydrogen bonds for 7a [E and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)
O(1 ^{^a})-H(1 ^{^a})...O(1S ^{^a})	0.84(2)	1.99(12)	2.668(15)
O(1 ^{^b})-H(1 ^{^b})...O(1 ^{^b})#1	0.84(2)	2.40(7)	3.19(4)

#1 -x+1,-y+1,-z+1

X-Ray data of *cis-3c*

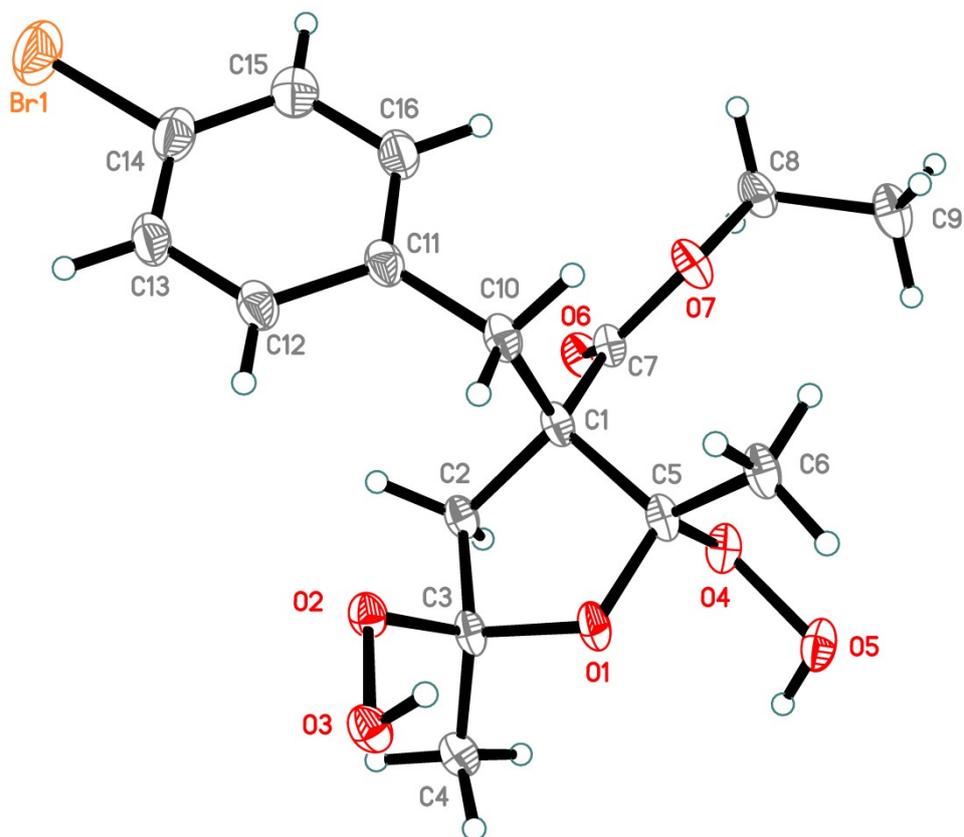


Figure S7. Molecular structure of **cis-3c** presented in thermal ellipsoids (50% probability).

X-ray diffraction data were collected at 100K on a four-circle Rigaku Synergy S diffractometer equipped with a HyPix6000HE area-detector (kappa geometry, shutterless ω -scan technique), using monochromatized Cu K_{α} -radiation. The intensity data were integrated and corrected for absorption and decay by the CrysAlisPro program.⁷ The structure was solved by direct methods using SHELXT⁸ and refined on F^2 using SHELXL-2018⁹ in the OLEX2 program.¹⁰ All non-hydrogen atoms were refined with individual anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters. A rotating group model was applied for methyl groups. The Mercury program suite¹¹ was used for molecular graphics.

Table S34. Crystal data and structure refinement for **cis-3c**.

Identification code	<i>cis-3c</i>	
Empirical formula	C ₁₆ H ₂₁ Br O ₇	
Formula weight	405.24	
Temperature	100.00(10) K	
Wavelength	1.54184 Å	
Crystal system	Trigonal	
Space group	R -3	
Unit cell dimensions	a = 36.0080(3) Å	$\alpha = 90^\circ$.
	b = 36.0080(3) Å	$\beta = 90^\circ$.
	c = 7.27389(6) Å	$\gamma = 120^\circ$.
Volume	8167.62(14) Å ³	
Z	18	
Density (calculated)	1.483 g/cm ³	
Absorption coefficient	3.390 mm ⁻¹	
F(000)	3744	
Crystal size	0.07 x 0.02 x 0.02 mm ³	
Theta range for data collection	6.248 to 80.594°.	

Index ranges	-46<=h<=46, -45<=k<=42, -6<=l<=9
Reflections collected	24685
Independent reflections	3941 [R(int) = 0.0384]
Observed reflections	3713
Completeness to theta = 67.684°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.50440
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3941 / 0 / 229
Goodness-of-fit on F ²	1.063
Final R indices [I>2sigma(I)]	R1 = 0.0274, wR2 = 0.0693
R indices (all data)	R1 = 0.0289, wR2 = 0.0703
Extinction coefficient	0.000049(8)
Largest diff. peak and hole	0.424 and -0.394 e.Å ⁻³

Table S35. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for *cis*-3c. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	3170(1)	5520(1)	3475(1)	44(1)
O(1)	4071(1)	4105(1)	10052(1)	19(1)
O(2)	3734(1)	3984(1)	7218(1)	18(1)
O(3)	3589(1)	3526(1)	7358(1)	20(1)
O(4)	4590(1)	4716(1)	11575(1)	21(1)
O(5)	4717(1)	4459(1)	12688(1)	24(1)
O(6)	4636(1)	5510(1)	9684(1)	22(1)
O(7)	4163(1)	5278(1)	12027(1)	23(1)
C(1)	4071(1)	4760(1)	9826(2)	17(1)
C(2)	4244(1)	4685(1)	8022(2)	18(1)
C(3)	4139(1)	4219(1)	8147(2)	17(1)
C(4)	4476(1)	4133(1)	7376(2)	22(1)
C(5)	4142(1)	4458(1)	11148(2)	18(1)
C(6)	3872(1)	4295(1)	12869(2)	22(1)
C(7)	4328(1)	5226(1)	10467(2)	18(1)
C(8)	4387(1)	5689(1)	12983(2)	23(1)
C(9)	4471(1)	5604(1)	14919(2)	27(1)
C(10)	3586(1)	4612(1)	9707(2)	20(1)
C(11)	3476(1)	4832(1)	8208(2)	21(1)
C(12)	3313(1)	4626(1)	6525(2)	24(1)
C(13)	3217(1)	4827(1)	5120(2)	27(1)
C(14)	3287(1)	5236(1)	5408(2)	30(1)
C(15)	3441(1)	5447(1)	7067(2)	31(1)
C(16)	3534(1)	5242(1)	8466(2)	26(1)

Table S36. Bond lengths [Å] and angles [°] for *cis*-3c.

Br(1)-C(14)	1.9052(15)
O(1)-C(3)	1.4312(14)
O(1)-C(5)	1.4104(15)
O(2)-O(3)	1.4634(12)
O(2)-C(3)	1.4353(14)
O(3)-H(3)	0.89(2)
O(4)-O(5)	1.4655(13)
O(4)-C(5)	1.4348(15)
O(5)-H(5)	0.86(3)
O(6)-C(7)	1.2092(16)
O(7)-C(7)	1.3372(15)
O(7)-C(8)	1.4598(15)
C(1)-C(2)	1.5339(16)
C(1)-C(5)	1.5670(17)

C(1)-C(7)	1.5283(17)
C(1)-C(10)	1.5518(17)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(2)-C(3)	1.5262(17)
C(3)-C(4)	1.5054(17)
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-C(6)	1.5120(16)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(8)-C(9)	1.5037(19)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(10)-C(11)	1.5118(18)
C(11)-C(12)	1.3997(18)
C(11)-C(16)	1.397(2)
C(12)-H(12)	0.9500
C(12)-C(13)	1.392(2)
C(13)-H(13)	0.9500
C(13)-C(14)	1.379(2)
C(14)-C(15)	1.386(2)
C(15)-H(15)	0.9500
C(15)-C(16)	1.393(2)
C(16)-H(16)	0.9500
C(5)-O(1)-C(3)	111.15(9)
C(3)-O(2)-O(3)	108.52(8)
O(2)-O(3)-H(3)	100.3(14)
C(5)-O(4)-O(5)	108.30(9)
O(4)-O(5)-H(5)	99.3(15)
C(7)-O(7)-C(8)	119.16(10)
C(2)-C(1)-C(5)	100.31(10)
C(2)-C(1)-C(10)	112.18(10)
C(7)-C(1)-C(2)	112.28(10)
C(7)-C(1)-C(5)	110.86(10)
C(7)-C(1)-C(10)	110.79(10)
C(10)-C(1)-C(5)	109.99(10)
C(1)-C(2)-H(2A)	110.9
C(1)-C(2)-H(2B)	110.9
H(2A)-C(2)-H(2B)	108.9
C(3)-C(2)-C(1)	104.19(9)
C(3)-C(2)-H(2A)	110.9
C(3)-C(2)-H(2B)	110.9
O(1)-C(3)-O(2)	108.02(9)
O(1)-C(3)-C(2)	106.57(9)
O(1)-C(3)-C(4)	109.97(10)
O(2)-C(3)-C(2)	103.95(10)
O(2)-C(3)-C(4)	112.88(10)
C(4)-C(3)-C(2)	114.97(10)
C(3)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4B)	109.5
C(3)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5

O(1)-C(5)-O(4)	110.29(10)
O(1)-C(5)-C(1)	105.09(9)
O(1)-C(5)-C(6)	109.01(10)
O(4)-C(5)-C(1)	101.71(9)
O(4)-C(5)-C(6)	111.54(10)
C(6)-C(5)-C(1)	118.77(11)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
O(6)-C(7)-O(7)	124.37(11)
O(6)-C(7)-C(1)	125.50(11)
O(7)-C(7)-C(1)	110.13(10)
O(7)-C(8)-H(8A)	110.2
O(7)-C(8)-H(8B)	110.2
O(7)-C(8)-C(9)	107.74(11)
H(8A)-C(8)-H(8B)	108.5
C(9)-C(8)-H(8A)	110.2
C(9)-C(8)-H(8B)	110.2
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(1)-C(10)-H(10A)	108.8
C(1)-C(10)-H(10B)	108.8
H(10A)-C(10)-H(10B)	107.7
C(11)-C(10)-C(1)	113.80(10)
C(11)-C(10)-H(10A)	108.8
C(11)-C(10)-H(10B)	108.8
C(12)-C(11)-C(10)	120.27(12)
C(16)-C(11)-C(10)	121.17(11)
C(16)-C(11)-C(12)	118.56(13)
C(11)-C(12)-H(12)	119.5
C(13)-C(12)-C(11)	120.97(13)
C(13)-C(12)-H(12)	119.5
C(12)-C(13)-H(13)	120.6
C(14)-C(13)-C(12)	118.90(13)
C(14)-C(13)-H(13)	120.6
C(13)-C(14)-Br(1)	119.29(11)
C(13)-C(14)-C(15)	121.82(14)
C(15)-C(14)-Br(1)	118.88(12)
C(14)-C(15)-H(15)	120.6
C(14)-C(15)-C(16)	118.75(14)
C(16)-C(15)-H(15)	120.6
C(11)-C(16)-H(16)	119.5
C(15)-C(16)-C(11)	120.97(13)
C(15)-C(16)-H(16)	119.5

Table S37. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for *cis*-3c. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	50(1)	59(1)	28(1)	9(1)	-4(1)	32(1)
O(1)	24(1)	18(1)	10(1)	0(1)	0(1)	7(1)
O(2)	19(1)	14(1)	16(1)	-1(1)	-2(1)	5(1)
O(3)	23(1)	14(1)	18(1)	-1(1)	1(1)	5(1)

O(4)	18(1)	22(1)	16(1)	2(1)	-2(1)	6(1)
O(5)	24(1)	32(1)	16(1)	6(1)	0(1)	13(1)
O(6)	22(1)	19(1)	19(1)	0(1)	3(1)	6(1)
O(7)	25(1)	20(1)	16(1)	-5(1)	3(1)	5(1)
C(1)	18(1)	18(1)	11(1)	-1(1)	1(1)	6(1)
C(2)	19(1)	18(1)	12(1)	0(1)	2(1)	6(1)
C(3)	18(1)	18(1)	10(1)	0(1)	0(1)	5(1)
C(4)	23(1)	23(1)	18(1)	-2(1)	1(1)	11(1)
C(5)	18(1)	19(1)	12(1)	-2(1)	0(1)	5(1)
C(6)	23(1)	24(1)	12(1)	1(1)	3(1)	7(1)
C(7)	20(1)	21(1)	12(1)	-1(1)	-1(1)	9(1)
C(8)	29(1)	18(1)	18(1)	-4(1)	0(1)	8(1)
C(9)	27(1)	25(1)	18(1)	-3(1)	-1(1)	6(1)
C(10)	18(1)	23(1)	14(1)	-2(1)	2(1)	6(1)
C(11)	17(1)	27(1)	15(1)	-2(1)	2(1)	9(1)
C(12)	18(1)	31(1)	18(1)	-4(1)	1(1)	10(1)
C(13)	23(1)	42(1)	17(1)	-4(1)	-1(1)	16(1)
C(14)	28(1)	42(1)	21(1)	5(1)	0(1)	19(1)
C(15)	35(1)	34(1)	28(1)	-1(1)	-3(1)	19(1)
C(16)	28(1)	30(1)	20(1)	-4(1)	-3(1)	14(1)

Table S38. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for *cis*-3c.

	x	y	z	U(eq)
H(3)	3432(7)	3460(7)	8390(30)	37(5)
H(5)	4883(8)	4432(7)	11910(30)	40(6)
H(2A)	4100	4728	6949	21
H(2B)	4557	4881	7918	21
H(4A)	4752	4324	7963	33
H(4B)	4501	4184	6047	33
H(4C)	4395	3834	7615	33
H(6A)	3921	4538	13639	33
H(6B)	3953	4111	13553	33
H(6C)	3569	4129	12531	33
H(8A)	4209	5828	12990	28
H(8B)	4661	5883	12355	28
H(9A)	4657	5478	14898	40
H(9B)	4198	5405	15514	40
H(9C)	4611	5874	15608	40
H(10A)	3424	4299	9490	24
H(10B)	3492	4668	10903	24
H(12)	3266	4345	6340	28
H(13)	3107	4686	3980	33
H(15)	3482	5727	7247	38
H(16)	3638	5383	9611	31

Table S39. Torsion angles [$^\circ$] for *cis*-3c.

Br(1)-C(14)-C(15)-C(16)	-178.76(11)
O(3)-O(2)-C(3)-O(1)	-63.51(11)
O(3)-O(2)-C(3)-C(2)	-176.45(8)
O(3)-O(2)-C(3)-C(4)	58.31(12)
O(5)-O(4)-C(5)-O(1)	-63.84(11)
O(5)-O(4)-C(5)-C(1)	-174.94(9)
O(5)-O(4)-C(5)-C(6)	57.45(12)
C(1)-C(2)-C(3)-O(1)	-19.94(12)
C(1)-C(2)-C(3)-O(2)	94.04(10)
C(1)-C(2)-C(3)-C(4)	-142.06(10)

C(1)-C(10)-C(11)-C(12)	99.53(14)
C(1)-C(10)-C(11)-C(16)	-80.68(15)
C(2)-C(1)-C(5)-O(1)	-34.51(11)
C(2)-C(1)-C(5)-O(4)	80.50(10)
C(2)-C(1)-C(5)-C(6)	-156.71(10)
C(2)-C(1)-C(7)-O(6)	-0.44(18)
C(2)-C(1)-C(7)-O(7)	179.19(10)
C(2)-C(1)-C(10)-C(11)	-58.66(14)
C(3)-O(1)-C(5)-O(4)	-84.98(11)
C(3)-O(1)-C(5)-C(1)	23.91(12)
C(3)-O(1)-C(5)-C(6)	152.23(10)
C(5)-O(1)-C(3)-O(2)	-113.93(10)
C(5)-O(1)-C(3)-C(2)	-2.75(13)
C(5)-O(1)-C(3)-C(4)	122.48(11)
C(5)-C(1)-C(2)-C(3)	32.19(11)
C(5)-C(1)-C(7)-O(6)	110.86(14)
C(5)-C(1)-C(7)-O(7)	-69.52(13)
C(5)-C(1)-C(10)-C(11)	-169.40(10)
C(7)-O(7)-C(8)-C(9)	-124.32(12)
C(7)-C(1)-C(2)-C(3)	149.94(10)
C(7)-C(1)-C(5)-O(1)	-153.31(10)
C(7)-C(1)-C(5)-O(4)	-38.30(12)
C(7)-C(1)-C(5)-C(6)	84.49(13)
C(7)-C(1)-C(10)-C(11)	67.69(13)
C(8)-O(7)-C(7)-O(6)	-6.73(19)
C(8)-O(7)-C(7)-C(1)	173.64(11)
C(10)-C(1)-C(2)-C(3)	-84.52(12)
C(10)-C(1)-C(5)-O(1)	83.82(11)
C(10)-C(1)-C(5)-O(4)	-161.17(9)
C(10)-C(1)-C(5)-C(6)	-38.38(14)
C(10)-C(1)-C(7)-O(6)	-126.73(13)
C(10)-C(1)-C(7)-O(7)	52.89(13)
C(10)-C(11)-C(12)-C(13)	-178.85(12)
C(10)-C(11)-C(16)-C(15)	178.67(13)
C(11)-C(12)-C(13)-C(14)	0.0(2)
C(12)-C(11)-C(16)-C(15)	-1.5(2)
C(12)-C(13)-C(14)-Br(1)	178.58(10)
C(12)-C(13)-C(14)-C(15)	-1.2(2)
C(13)-C(14)-C(15)-C(16)	1.0(2)
C(14)-C(15)-C(16)-C(11)	0.4(2)
C(16)-C(11)-C(12)-C(13)	1.36(19)

Table S40. Hydrogen bonds for *cis*-3c [\AA and $^\circ$].

D-H...A	d(D-H)	d(H...A)	d(D...A)	\angle (DHA)
O(3)-H(3)...O(3)#1	0.89(2)	1.93(2)	2.8184(8)	173(2)
O(5)-H(5)...O(6)#2	0.86(3)	2.01(3)	2.8585(14)	168(2)

Symmetry transformations used to generate equivalent atoms:

#1 $-y+2/3, x-y+1/3, z+1/3$ #2 $-x+1, -y+1, -z+2$

CCDC 2476564, 2476599, 2476570, 2476575, 2476565, 2476566, 2476572 contains the supplementary crystallographic data for *cis*-2a, *trans*-2a, *cis*-3a, *cis*-3c, 5a, 6a and 7a. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures>.

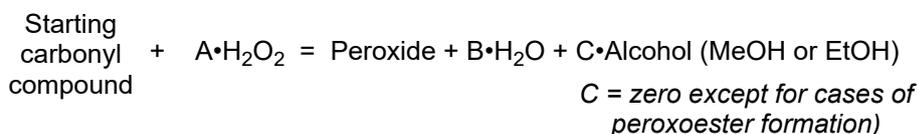
Computational details

DFT calculations were performed to elucidate the underlying principles governing the selectivity in the formation of specific peroxide structures. Computational modeling of the peroxidation of di- and tricarbonyl compounds is particularly challenging due to the vast number of possible product structures, reaction intermediates, and corresponding transition states—each with multiple accessible conformations.^{13, 14} Moreover, the present case is complicated by the complex nature of reaction medium, which includes MeCN, Et₂O, and sometimes significant amounts of BF₃•Et₂O and H₂O₂, which can also affect the solvation effects. MeCN was assumed as the main solvent and its characteristics were used for implicit solvation modeling during DFT calculations. The transition states of ring closures with the proton loss demand explicit introduction of hydrogen bond acceptor.¹³ Taking into account that oxygen of Et₂O is a better hydrogen bond acceptor than the nitrogen of MeCN (judging on higher basicity of ethers compared to nitriles) we decided to use Me₂O as model hydrogen bond acceptor for cyclization transition states with proton loss. The use of Me₂O as a simplified computational model instead of Et₂O allowed us to reduce the computational cost and conformation number.

Calculations of all structures, except for the simplest, such as H₂O and H₂O₂, were started from the initial conformational search employing GOAT algorithm in Orca^{15, 16} 6.0.1 program on GFN2-xTB^{17, 18} / ALPB(acetonitrile) semi-empirical level of theory. Next, at least 15 lowest energy conformers were optimized in the same program on DFT level (ω B97X-3c¹⁹ / CPCM(acetonitrile)) with vibrational analysis in order to get thermochemistry data and confirm the absence of imaginary vibration modes (or the presence of only one imaginary vibration mode corresponding to the reaction coordinate for transition states). The composite range-separated hybrid DFT method ω B97X-3c¹⁹ was used as fast and robust way to get preliminary thermochemical parameters and identify the conformer with lowest free energy. Finally, the lowest found conformer was reoptimized in Gaussian 16 A.03²⁰ on M06-2X^{21, 22}/6-311++G(d,p) level of theory, SMD solvation model²³ for MeCN medium, and D3 version of Grimme's dispersion correction with the original D3 damping function.²⁴ An alternative way to determine the most stable conformer was to perform single point electronic energy calculations on the final level of theory (M06-2X^{21, 22}-D3²⁴/6-311++G(d,p)/SMD(MeCN)) for geometries generated by GOAT algorithm (GFN2-xTB^{17, 18}/ALPB(acetonitrile)) followed by re-optimization and vibrational calculation for the conformer with the lowest EE. All calculations were performed for 1 atm. and 298.15 K.

In previous works on the construction of cyclic peroxides from di- and tricarbonyl compounds,^{13, 25, 26} it was enough to calculate the peroxide scaffolds without specific substituents

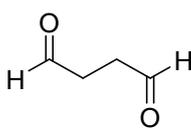
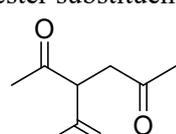
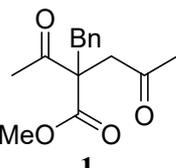
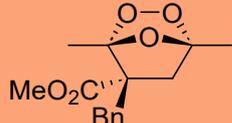
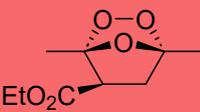
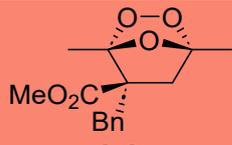
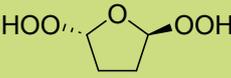
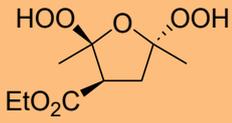
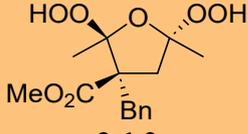
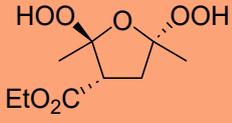
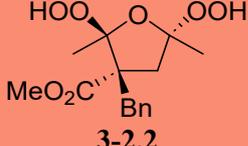
to identify the most thermodynamically favored structure. The case of the present work turned out to be the most complicated: many peroxide structures showed close free energy values and strong effect of substituents on relative peroxide stability was revealed (Table S1). For the calculations of relative free energies in Table S1 and below following stoichiometric equations were used:

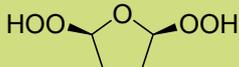
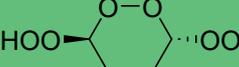
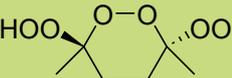
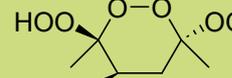
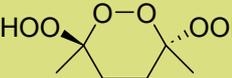
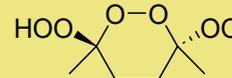
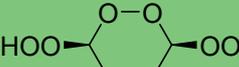
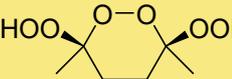
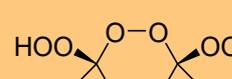


$$G_{\text{Rel}}(\text{Peroxide}) = G(\text{Peroxide}) + \text{B} \cdot G(\text{H}_2\text{O}) + \text{C} \cdot G(\text{Alcohol}) - G(\text{Starting carbonyl compound}) - \text{A} \cdot G(\text{H}_2\text{O}_2)$$

Where G is free energy value from DFT calculation

Table S1. Relative free energies (kcal/mol) of different peroxide structures calculated on M06-2X (D3) / 6-311++G(d,p) / SMD(MeCN) level of theory. Deep green color stands for thermodynamically most stable structures (most negative free energy values), red color stands for least stable structures.

	No substituents  S1	Only methyl and ester substituents  S8	All substituents  1 Methyl 2-acetyl-2-benzyl-4-oxopentanoate
Ozonide CO ₂ R-endo	 S2 -0.7	 S9 0.7	 2-1 -2.2
Ozonide CO ₂ R-exo		 S10 0.7	 2-2 -0.7
Tetrahydrofuran <i>vic-OOH-CO₂R-cis</i> <i>OOH-OOH-trans</i>	 S3 -9.5	 S11 -3.4	 3-1.2 -3.7
Tetrahydrofuran <i>vic-OOH-CO₂R-trans</i> <i>OOH-OOH-trans</i>		 S12 -2.2	 3-2.2 -1

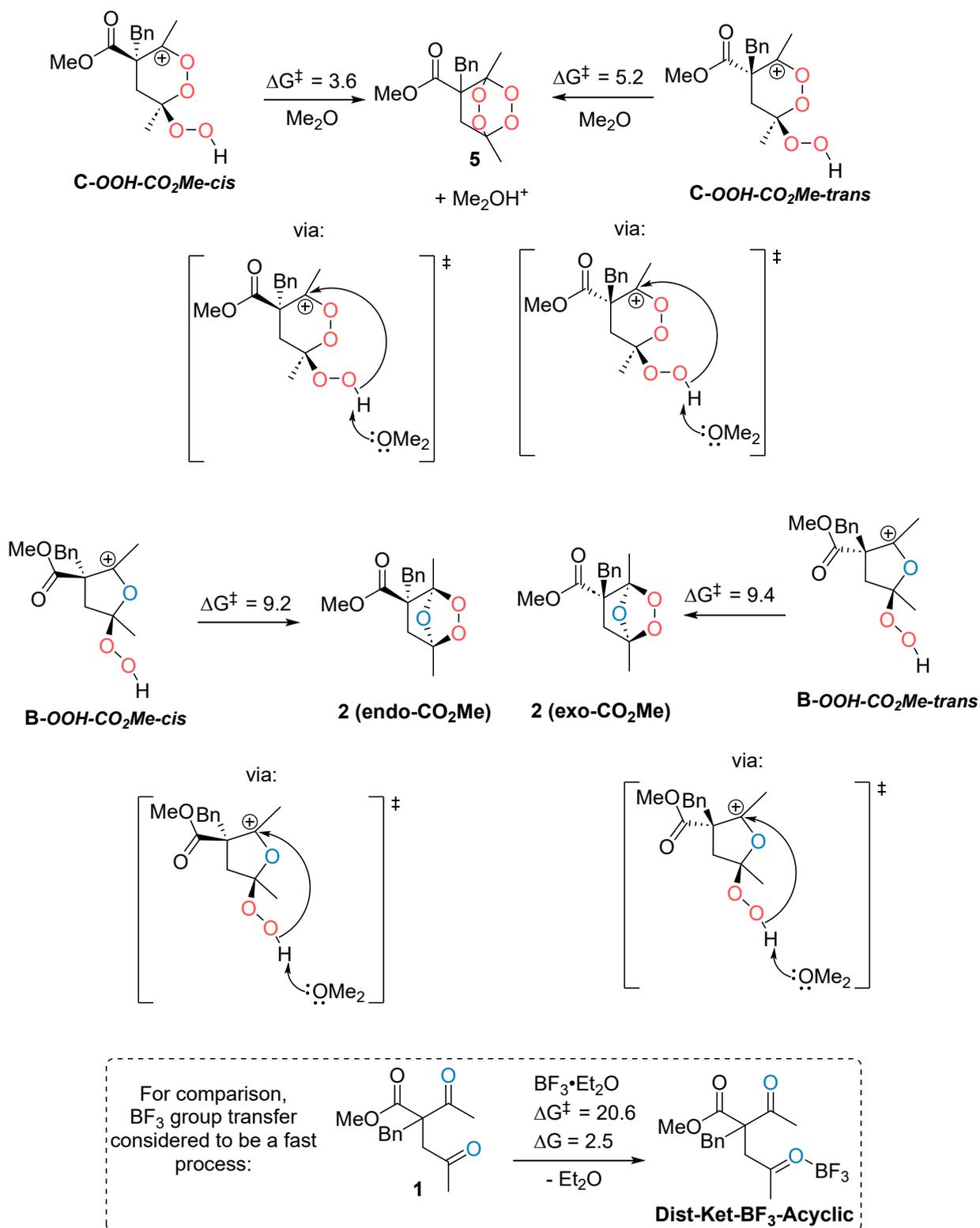
Tetrahydrofuran <i>vic-OOH-CO₂R-trans</i> <i>OOH-OOH-cis</i>	 S4 -9	 S13 -2.3	 3-2.1 -3.2
Tetrahydrofuran <i>vic-OOH-CO₂R-cis</i> <i>OOH-OOH-cis</i>		 S14 -2.3	 3-1.1 -4.4
Triperoxide <i>vic-OOH-CO₂R-cis</i> <i>OOH-OOH-trans</i>	 S5 -17.1	 S15 -9.7	 6-1.2 -9.3
Triperoxide <i>vic-OOH-CO₂R-trans</i> <i>OOH-OOH-trans</i>		 S16 -8.4	 6-2.2 -6.9
Triperoxide <i>vic-OOH-CO₂R-cis</i> <i>OOH-OOH-cis</i>	 S6 -15	 S17 -6.2	 6-1.1 -4
Triperoxide <i>vic-OOH-CO₂R-trans</i> <i>OOH-OOH-cis</i>		 S18 -6.6	 6-2.1 -5.4
Peroxolactone <i>OOH-OOC-cis</i>	-	 S20 -5.7	 7-1 -7.3
Peroxolactone <i>OOH-OOC-trans</i>		 S21 -3.8	 7-2 -5.9

tetraoxane	 S7 -7	 S22 -4	 5 -6.7
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As can be seen from color map of Table S1, different orders of peroxides by stability are characteristic for non-substituted peroxide scaffolds, peroxides with methyl and ester substituents, and peroxides with all substituents of a typical substrate of the present work (methyl ester group was used as model instead of ethyl ester group in order to reduce the number of similar conformations and computational cost). Thus, fully substituted model structure was used for further calculations. To reduce the computational cost and number of possible similar conformations, ester group $-\text{CO}_2\text{Me}$ was used instead of $-\text{CO}_2\text{Et}$ for all calculations.

Due to multiple possible reaction pathways and conformational diversity of both intermediates and transition states we found it unpractical to go for complete computational modeling of peroxidation mechanism but instead focused on some key intermediates and mechanistic steps. As our previous studies have shown, peroxocarbenium ions are the most plausible unstable intermediates being the products of rate-limiting mechanistic steps.^{1,12,13}

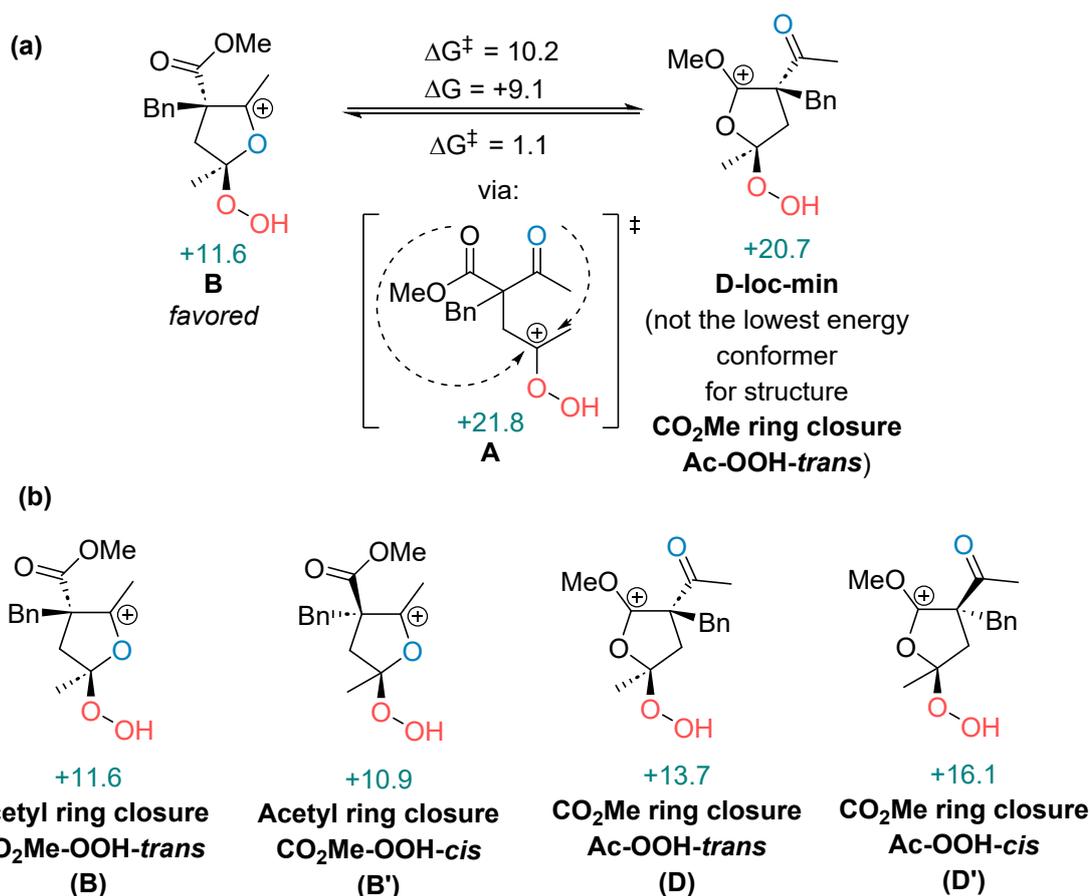
To check the correctness of the hypothesis of peroxocarbenium ion formation as the rate-limiting step we have calculated activation barriers of peroxide ring closures for the main cyclic products, ozonides **2** and tetraoxane **5** (Scheme S1). Me_2O was used as model hydrogen bond acceptor instead of Et_2O present in real reaction medium to reduce the number of similar conformations and computational cost in order to identify the global energy minima faster.



Scheme S1. Calculated activation barriers (kcal/mol, M06-2X(D3)/6-311++G(d,p)/SMD(MeCN)) for cyclizations of carbocations to cyclic peroxides. Calculated activation barrier for BF_3 group transfer is given for comparison as an example of fast process at room temperature for $\text{BF}_3 \cdot \text{Et}_2\text{O}$ catalyzed processes.

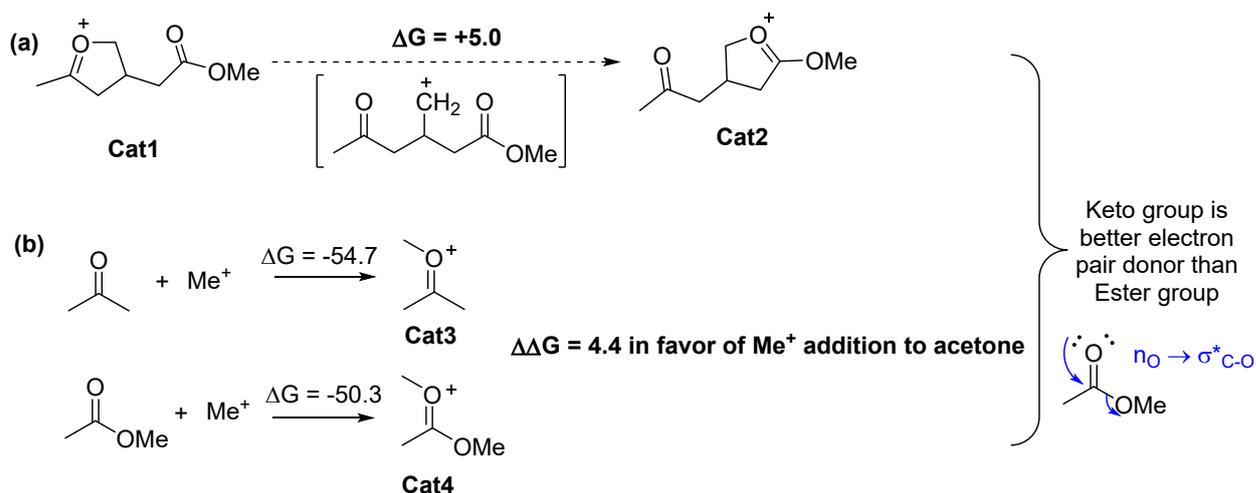
Expectedly, less stable peroxocarbenium ions demonstrate lower activation energies for the cyclizations to tetraoxane **5** compared to activation energies for oxonium ions cyclizations to ozonides **2**. Nevertheless, all these activation energies are much less than 20 kcal/mol. Taking into account that activation barrier calculated for BF₃ group transfer from BF₃•Et₂O to the starting diketone **1** (known to be fast) on the same level of theory is about 20.6 kcal/mol, these peroxide ring closures can also be considered as fast processes.

Thus, peroxide ring closures that follow the formation of oxonium or peroxocarbenium ions are not rate limiting, so we can suppose that the formation of corresponding cations determines the rate of overall process. We started with the examination of peroxocarbenium ion **A** (Scheme S2), as based on our previous results, the formation of peroxocarbenium ions^{13, 25, 26} can be the rate-limiting step in peroxidation of ketones. It is interesting to note that geometry optimization peroxocarbenium ion **A** led to the more stable cyclic oxocarbenium ion **B** (Scheme S2). Moreover, we found that certain peroxocarbenium ion **A** conformation is actually a transition state connecting two oxocarbenium ions (**B** and **D**, where **B** is thermodynamically favored, Scheme S2, a). This finding demonstrate clearly that peroxocarbenium ions are thermodynamically disfavored compared to oxocarbenium ions and processes leading to peroxocarbenium ions are expected to be rate-limiting. In summary, there are 4 cyclized structures for the discussed cationic intermediate, free energy values for the most stable conformers are given below (Scheme S2, b).



Scheme S2. Possible structures of monoperoxidated cationic intermediate. Peroxocarbenium ion **A** as a transition state connecting oxocarbenium ions **B** and **D**. Free energies are given in kcal/mol (M06-2X (D3) / 6-311++G(d,p) / SMD(MeCN)).

At first glance it is not clear and even confusing why oxocarbenium ions **D** and **D'** stabilized by two alkoxy electron-donating substituents are less favorable than oxocarbenium ions **B** and **B'** stabilized by only one electron-donating alkoxy substituent. Thus, we decided to check the generality of this phenomenon. First, a structure similar to the carbocation under study was used, but simplified as much as possible to exclude the influence of substituents (Scheme S2, a). The calculation predicts that the structure resulting from the addition of a ketone oxygen atom to the carbocationic center (left) is favored by about 5 kcal/mol compared to the analogous structure involving an ester oxygen atom (right), despite the fact that in the latter case the cationic center can be stabilized by two lone pairs of oxygen atoms. To exclude the influence of valence angles, which are affected by the presence of a five-membered ring, the model calculation of the thermochemistry of the addition of a methyl cation to acetone and methyl acetate was carried out (Scheme S3, b). The addition of the cation to the oxygen atom of the ketone is also more advantageous according to the calculation in this case.



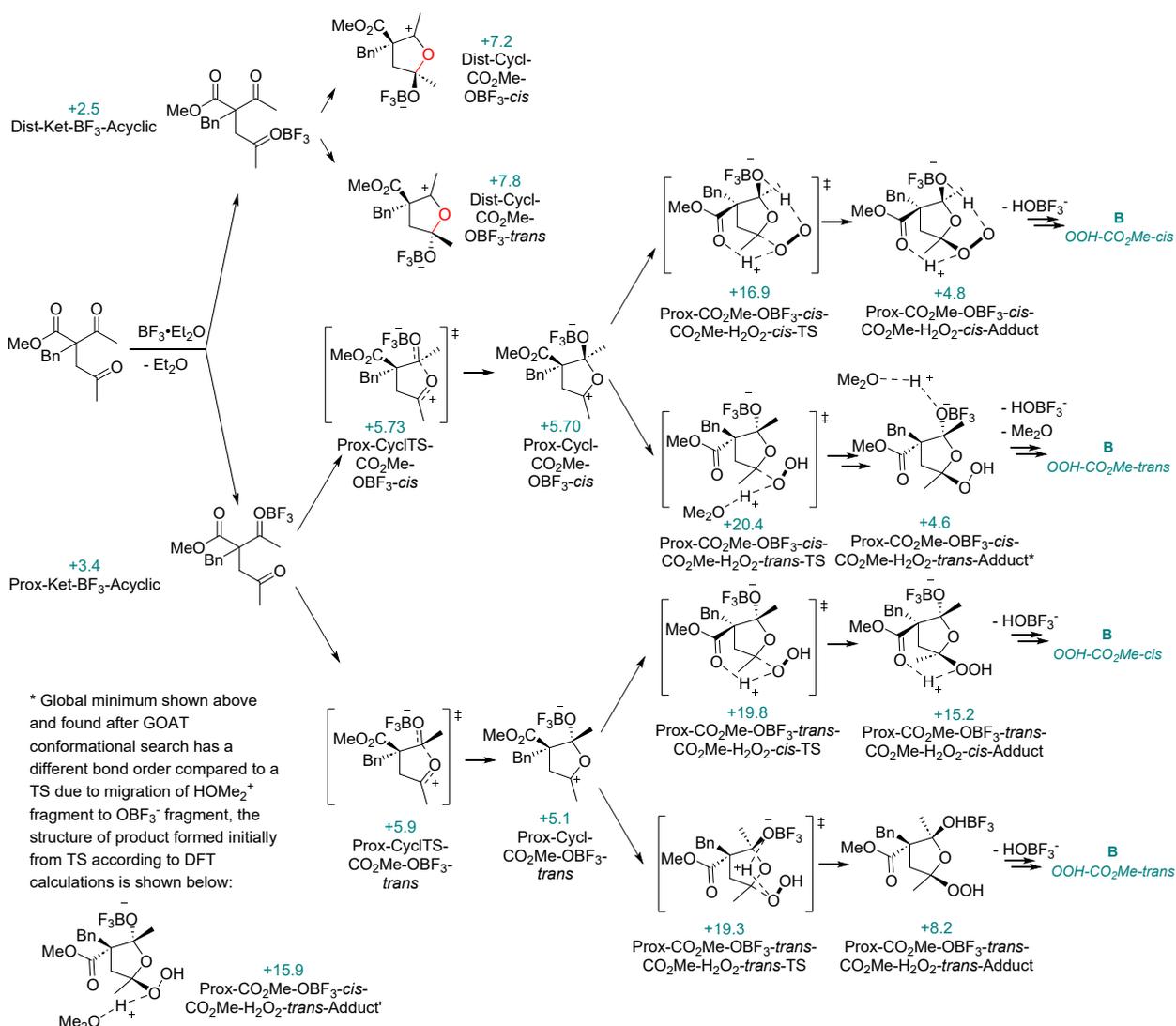
Scheme S3. Comparison of ketone and ester groups as electron pair donors for carbocations.

Free energies are given in kcal/mol (M06-2X (D3) / 6-311++G(d,p) / SMD(MeCN)).

To explain this paradox, we have to remember that when a cation is added to an ester, the stabilizing stereoelectronic effect $n_{\text{O}} \rightarrow \sigma^*_{\text{C-O}}$ characteristic to esters is disrupted. This effect can compensate the +M effect of alkoxy group in an ester. The fact that ketones can be better electron pair donors than esters is in agreement with experimental data on relatively higher basicity of ketones with respect to structurally similar esters (acetone – methyl acetate, acetophenone – methyl benzoate, etc.).²⁷⁻³⁰ Previously, this fact was explained so that -I effect of alkoxy group overcomes the π -donation (+M effect) of the same group.²⁹ However, explanation by stereoelectronic effect $n_{\text{O}} \rightarrow \sigma^*_{\text{C-O}}$ seems more exact, because in other cases, where such stereoelectronic effect is not involved, +M effect of alkoxy groups is always much stronger than their -I effect.

Returning back to the key intermediate **B** we wondered whether it can be formed avoiding the intermediate formation of unstable peroxocarbenium structures, such as **A**. Indeed, it was found that after BF_3 addition to a keto group (either one proximate relative to $-\text{CO}_2\text{Me}$ fragment, adduct Prox-Ket- BF_3 -Acyclic, or one distal relative to $-\text{CO}_2\text{Me}$ fragment, adduct Dist-Ket- BF_3 -Acyclic) cyclic oxocarbenium ions (Prox-Cycl- $\text{CO}_2\text{Me-OBF}_3$ -*trans*, Prox-Cycl- $\text{CO}_2\text{Me-OBF}_3$ -*cis*, Dist-Cycl- $\text{CO}_2\text{Me-OBF}_3$ -*trans*, Dist-Cycl- $\text{CO}_2\text{Me-OBF}_3$ -*cis*) can form and activation barriers for such cyclizations are very small, as shown on example of Prox-Ket- BF_3 -Acyclic cyclization (Scheme S4). Following steps were modelled only for Prox-Ket- BF_3 -Acyclic branch, as free energies for the corresponding cyclic oxocarbenium ions were slightly lower, however, reaction can also proceed via Dist-Ket- BF_3 -Acyclic to the same final cyclic peroxide by analogous steps. Cyclic peroxocarbenium ions (Prox-Cycl- $\text{CO}_2\text{Me-OBF}_3$ -*trans*, Prox-Cycl- $\text{CO}_2\text{Me-OBF}_3$ -*cis*) can react with H_2O_2 to form hydroperoxide intermediates that give intermediate **B** after HOBF_3^- elimination.

The relative free energy of peroxidation transition states relative to starting compounds is 16.9-20.4 kcal/mol, which makes these pathways easily kinetically accessible at room temperature.



Scheme S4. Comparison of ketone and ester groups as electron pair donors for carbocations. Free energies are given in kcal/mol (M06-2X (D3) / 6-311++G(d,p) / SMD(MeCN)). Given free energies are related to starting compounds and correspond to the lowest found conformers of intermediates of transition states. The transformations between conformers are considered as fast processes and are not shown.

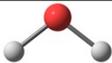
The summary of thermochemical calculations for the following steps leading to the final peroxides detected in reaction mixture is presented in Scheme S5.

fragments is favored. However, we cannot exclude the role of kinetic control in our discovered peroxidation process in addition to the thermodynamic control. The influence of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ amount on peroxidation selectivity evidences the probable importance of kinetic control, despite the fact that it can also influence peroxidation thermodynamically by quenching H_2O . According to our knowledge, higher activation barriers are typical for peroxidation of esters³¹⁻³³ compared to peroxidation of ketones and thus demand highly acidic conditions to proceed. Therefore, we can explain why peroxyesters **7** are formed only in the presents of several equivalents of acid catalyst ($\text{BF}_3 \cdot \text{Et}_2\text{O}$ or H_2SO_4). Speaking of other peroxide structures, ozonides **2** and dihydroperoxy tetrahydrofurans **3** can be produced avoiding thermodynamically unfavored peroxocarbenium ions **A** and **C**, and these products were successfully synthesized employing only 1 equivalent of $\text{BF}_3 \cdot \text{Et}_2\text{O}$. In contrast, products **5**, **4** and **6** demand the formation of peroxocarbenium ions **A** and **C** and are formed when higher concentrations of acid catalyst are present. A plausible obstacle to the formation of products **5**, **4** and **6**, which is responsible for the need for large quantities of acid catalyst is the nature of monoperoxidated cationic intermediate (see Scheme S2): the formation of **C** demands unfavored ring opening in **B**, whereas cyclization of **A** to **B** is spontaneous and favorable.

XYZ data for main mechanistic scheme (and Scheme S5)

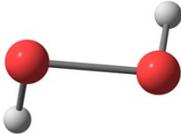
XYZ data of intermediates and transition states for the transformation of starting model carbonyl compound **1** to cations **A/B** are presented in separate section “XYZ data for Scheme S4” below. Details for cations **A**, **D** are presented in separate section “XYZ data for Scheme S2”.

Water

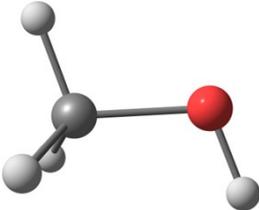
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O 0.00000000 0.00000000 0.11788400 H 0.00000000 0.76092100 -0.47153400 H 0.00000000 -0.76092100 -0.47153400		

Hydrogen peroxide

$\text{H}-\text{O}-\text{O}-\text{H}$	Multiplicity = 1 Charge = 0
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		Imaginary vib. modes: no
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-151.547223	-151.51615	-151.541869
<pre>O 0.00000000 0.71067600 -0.06343800 H 0.75559200 0.91665500 0.50750100 O 0.00000000 -0.71067600 -0.06343800 H -0.75559200 -0.91665500 0.50750100</pre>		

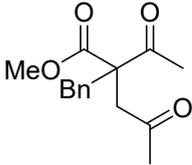
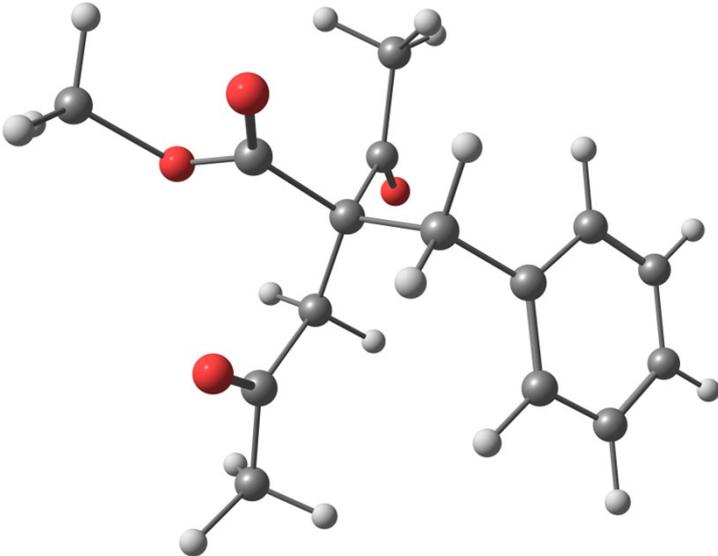
Methanol

CH ₃ OH		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-115.710389	-115.654422	-115.681448
<pre>C 0.66561000 -0.01964200 -0.00000200 H 1.01871900 -0.54854200 -0.89081000 H 1.01872200 -0.54853600 0.89080900 H 1.09128000 0.98403600 -0.00000600 O -0.74803500 0.12337200 -0.00000100 H -1.13809800 -0.75607800 0.00002200</pre>		

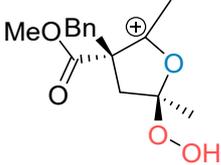
HOBF₃⁻

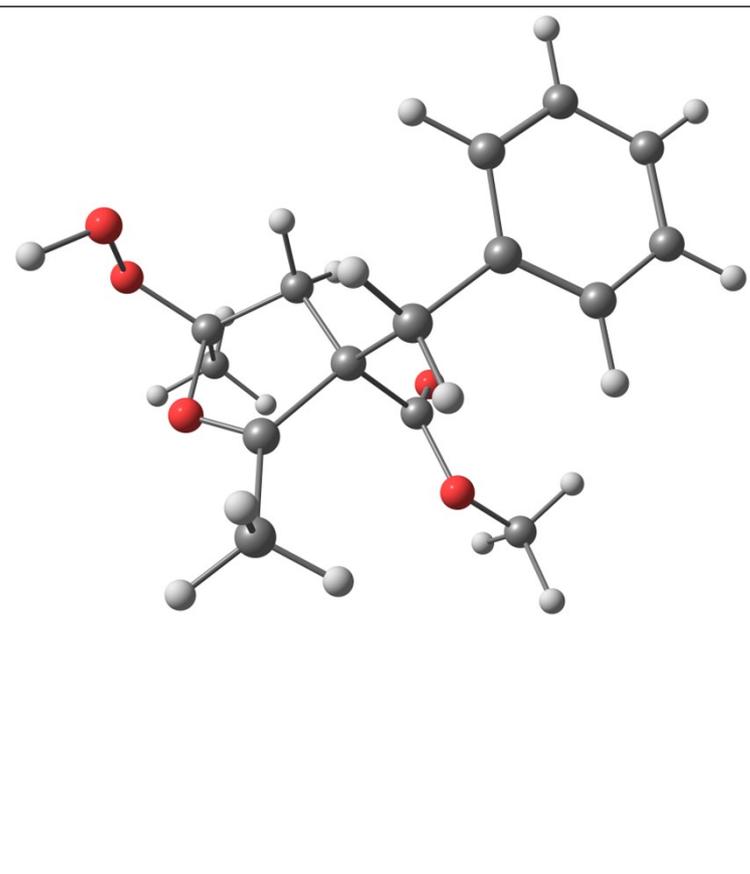
HOBF ₃ ⁻		Multiplicity = 1 Charge = -1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-400.595533	-400.563974	-400.597826
<pre>F -0.31594400 -0.76738100 1.14325400 F -0.82145500 1.16470600 0.00000000 F -0.31594500 -0.76738100 -1.14325400 O 1.37815900 0.44152100 -0.00000100 H 1.96798700 -0.31667200 0.00000100 B 0.01736800 0.02300300 0.00000000</pre>		

Model starting carbonyl compound (methyl 2-acetyl-2-benzyl-4-oxopentanoate) 1

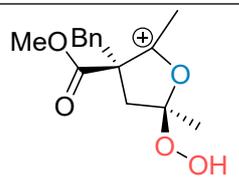
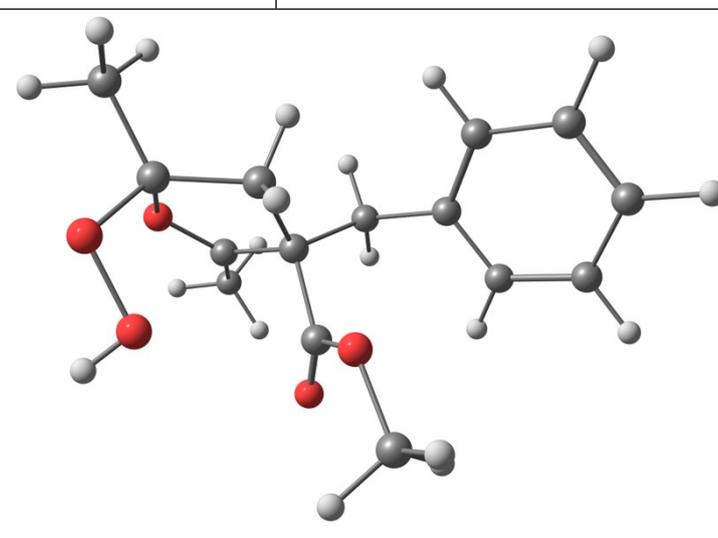
		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no	
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<pre> H -4.55948000 0.27640800 -0.83535200 C -4.33839200 -0.41999900 -0.02594700 H -4.94358100 -0.19086800 0.84745600 O -2.97540900 -0.26854200 0.39405200 H -4.52000800 -1.44305700 -0.35686800 C -2.04944700 -0.49240900 -0.54042300 O -2.30628100 -0.84982000 -1.66044200 C -0.64160000 -0.32400600 0.03234700 C -0.54476100 0.92496200 0.90887600 H 0.47217300 1.04295500 1.28886900 H -1.17970500 0.81982300 1.79455800 C -0.97218500 2.20490200 0.22452500 O -1.60217000 2.19804400 -0.81211500 C -0.57951600 3.47781300 0.91970500 H -0.80379300 3.41093400 1.98696600 H -1.08887000 4.33108800 0.47448500 H 0.50361800 3.60448000 0.82336500 C -0.35389700 -1.57279500 0.89831000 O 0.16370100 -1.45795600 1.98323600 </pre>			

Oxocarbenium ion B (OOH-CO₂Me-trans) (local minimum near TS A)

		Multiplicity = 1 Charge = 1 Imaginary vib. modes: no	
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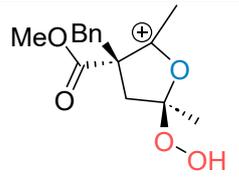
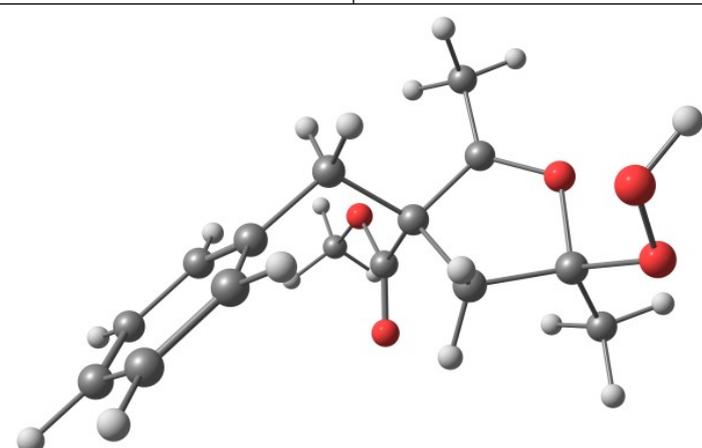
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C 1.20788300 -3.46149300 -0.56946000	
H 2.15475900 -3.08016100 -0.95150100	
O 0.50516400 -2.40836200 0.12351300	
C 0.20248000 -1.34040100 -0.59316600	
O 0.43234300 -1.20195300 -1.76102700	
C -0.43862600 -0.23710600 0.28925700	
C -0.97990700 0.91503300 -0.56648000	
H -0.50313400 0.95560000 -1.54324800	
H -0.83362600 1.85976800 -0.04774200	
C -2.47200900 0.64489300 -0.72164700	
C -2.92678500 -0.01462000 -1.99422000	
H -2.75990400 0.68122400 -2.81754500	
H -3.98482400 -0.26948500 -1.93241500	
H -2.33917600 -0.91611200 -2.17289000	
C -1.68600900 -0.77741000 0.93569700	
C -1.76180300 -1.66374000 2.09618900	
H -2.76149700 -2.07683200 2.21066600	
H -1.52370800 -1.03200600 2.96527000	
H -0.99391900 -2.43524200 2.04288300	
O -3.31728400 1.70092500 -0.48772200	
O -2.74588700 -0.34303700 0.41889100	
H 0.59451800 -3.83882400 -1.38680900	
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H 0.79063300 -0.65982200 2.02889600	
H 0.13708100 0.98677400 1.95999700	
C 1.88890100 0.66348600 0.74873100	
C 2.93161800 -0.23926300 0.52253000	
C 2.05375900 1.99708600 0.36776000	
C 4.11111600 0.18017300 -0.08615100	
H 2.82630100 -1.27289600 0.83853100	
C 3.23288300 2.41771400 -0.24081000	
H 1.25968300 2.71165600 0.55913800	
C 4.26222500 1.50910000 -0.47343600	
H 4.91367700 -0.52982700 -0.25064500	
H 3.34901400 3.45667600 -0.52775400	
H 5.18115700 1.83718900 -0.94563200	
O -2.93919100 2.37276700 0.70606900	
H -3.70613200 2.19442400 1.27699400	

Oxocarbenium ion B (OOH-CO₂Me-cis (Z)) (global minimum according to GOAT search)

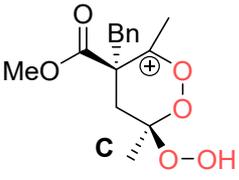
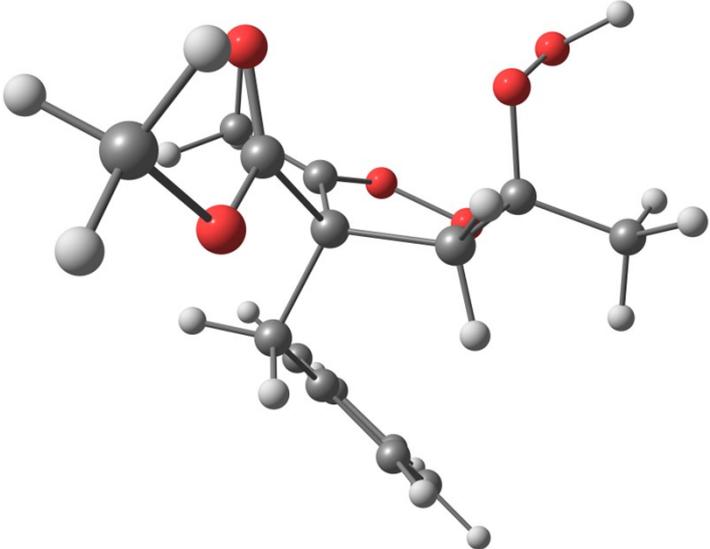
 <p style="text-align: center;">B (OOH-CO₂Me-cis)</p>		<p>Multiplicity = 1</p> <p>Charge = 1</p> <p>Imaginary vib. modes: no</p>																									
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)																									
-958.802610	-958.459114	-958.527499																									
<table border="1"> <tr><td>H 0.26152000 3.31984500 -1.67965600</td></tr> <tr><td>C 1.07132200 2.60704700 -1.52425500</td></tr> <tr><td>H 1.57255100 2.38581400 -2.46245200</td></tr> <tr><td>O 0.53496700 1.35092700 -1.07056400</td></tr> <tr><td>C -0.08734800 1.37478400 0.08914800</td></tr> <tr><td>O -0.24858300 2.35591000 0.76806500</td></tr> <tr><td>C -0.50608000 -0.04020400 0.52845100</td></tr> <tr><td>C -0.88593700 -0.98583000 -0.62102100</td></tr> <tr><td>H -0.51892400 -1.98996000 -0.41164700</td></tr> <tr><td>H -0.50477800 -0.66235500 -1.58625300</td></tr> <tr><td>C -2.40985800 -1.03397600 -0.64014800</td></tr> <tr><td>C -3.05910200 -2.37523000 -0.81664800</td></tr> <tr><td>H -2.75640300 -2.77857800 -1.78405300</td></tr> <tr><td>H -4.14430900 -2.28069700 -0.77856400</td></tr> <tr><td>H -2.71414400 -3.04504300 -0.02908700</td></tr> <tr><td>C -1.79020000 0.04123700 1.31190500</td></tr> <tr><td>O -3.03586700 -0.15915800 -1.49981400</td></tr> <tr><td>O -2.76325500 -0.52992400 0.75326300</td></tr> <tr><td>C -1.96920100 0.61937900 2.64162200</td></tr> <tr><td>H -3.02327900 0.75962400 2.87120400</td></tr> <tr><td>H -1.39134700 1.53934900 2.73107200</td></tr> <tr><td>H -1.53585500 -0.10713300 3.34509000</td></tr> <tr><td>C 0.62139000 -0.58791300 1.46800300</td></tr> <tr><td>H 0.29699100 -1.56865500 1.82400200</td></tr> <tr><td>H 0.70470700 0.08325800 2.32568000</td></tr> </table>		H 0.26152000 3.31984500 -1.67965600	C 1.07132200 2.60704700 -1.52425500	H 1.57255100 2.38581400 -2.46245200	O 0.53496700 1.35092700 -1.07056400	C -0.08734800 1.37478400 0.08914800	O -0.24858300 2.35591000 0.76806500	C -0.50608000 -0.04020400 0.52845100	C -0.88593700 -0.98583000 -0.62102100	H -0.51892400 -1.98996000 -0.41164700	H -0.50477800 -0.66235500 -1.58625300	C -2.40985800 -1.03397600 -0.64014800	C -3.05910200 -2.37523000 -0.81664800	H -2.75640300 -2.77857800 -1.78405300	H -4.14430900 -2.28069700 -0.77856400	H -2.71414400 -3.04504300 -0.02908700	C -1.79020000 0.04123700 1.31190500	O -3.03586700 -0.15915800 -1.49981400	O -2.76325500 -0.52992400 0.75326300	C -1.96920100 0.61937900 2.64162200	H -3.02327900 0.75962400 2.87120400	H -1.39134700 1.53934900 2.73107200	H -1.53585500 -0.10713300 3.34509000	C 0.62139000 -0.58791300 1.46800300	H 0.29699100 -1.56865500 1.82400200	H 0.70470700 0.08325800 2.32568000	
H 0.26152000 3.31984500 -1.67965600																											
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H 0.29699100 -1.56865500 1.82400200																											
H 0.70470700 0.08325800 2.32568000																											

C	1.95348100	-0.68855900	0.76697600
C	2.31997200	-1.84737200	0.08080300
C	2.83151900	0.39849200	0.77971100
C	3.53510600	-1.91196300	-0.59686700
H	1.65660400	-2.70635400	0.08375200
C	4.04475700	0.33674200	0.10261100
H	2.56236100	1.29809300	1.32677900
C	4.39676900	-0.81855900	-0.59244200
H	3.80941000	-2.81847800	-1.12440700
H	4.71669600	1.18739100	0.12133400
H	5.34257100	-0.86927300	-1.11968900
H	1.77930800	2.99507600	-0.79186600
O	-2.40584700	1.11259900	-1.39345300
H	-3.16454000	1.68680900	-1.18831000

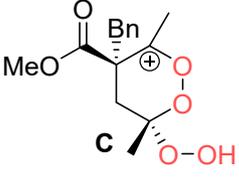
Oxocarbenium ion B (OOH-CO₂Me-trans (E)) (global minimum according to GOAT search)

 <p style="text-align: center;">B (OOH-CO₂Me-trans)</p>		Multiplicity = 1 Charge = 1 Imaginary vib. modes: no																																																																																																																																																												
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)																																																																																																																																																												
-958.800012	-958.456563	-958.525869																																																																																																																																																												
<table border="1"> <tbody> <tr><td>H</td><td>1.09478400</td><td>4.36792400</td><td>-0.23271000</td></tr> <tr><td>C</td><td>0.98883800</td><td>3.58971700</td><td>0.51767200</td></tr> <tr><td>H</td><td>1.96319000</td><td>3.28532800</td><td>0.89921900</td></tr> <tr><td>O</td><td>0.36604200</td><td>2.48076300</td><td>-0.16470700</td></tr> <tr><td>C</td><td>0.15086700</td><td>1.39776800</td><td>0.56157200</td></tr> <tr><td>O</td><td>0.40658000</td><td>1.28381400</td><td>1.72672400</td></tr> <tr><td>C</td><td>-0.42774600</td><td>0.24692400</td><td>-0.30230800</td></tr> <tr><td>C</td><td>-0.91415200</td><td>-0.91416500</td><td>0.57360500</td></tr> <tr><td>H</td><td>-0.42413800</td><td>-0.92487900</td><td>1.54457800</td></tr> <tr><td>H</td><td>-0.73806300</td><td>-1.85875300</td><td>0.06331000</td></tr> <tr><td>C</td><td>-2.41291400</td><td>-0.69568200</td><td>0.74261300</td></tr> <tr><td>C</td><td>-2.87637500</td><td>-0.01183800</td><td>1.99944800</td></tr> <tr><td>H</td><td>-2.66567000</td><td>-0.66898900</td><td>2.84419000</td></tr> <tr><td>H</td><td>-3.94562900</td><td>0.19347700</td><td>1.94650300</td></tr> <tr><td>H</td><td>-2.32822600</td><td>0.92133100</td><td>2.13668600</td></tr> <tr><td>C</td><td>-1.69976900</td><td>0.70945600</td><td>-0.96130300</td></tr> <tr><td>C</td><td>-1.81598400</td><td>1.54463000</td><td>-2.15515800</td></tr> <tr><td>H</td><td>-2.82678600</td><td>1.92933700</td><td>-2.27108000</td></tr> <tr><td>H</td><td>-1.58026800</td><td>0.87582300</td><td>-2.99741100</td></tr> <tr><td>H</td><td>-1.06450000</td><td>2.33344000</td><td>-2.15259400</td></tr> <tr><td>O</td><td>-3.22180200</td><td>-1.78858500</td><td>0.55461500</td></tr> <tr><td>O</td><td>-2.73748500</td><td>0.24485600</td><td>-0.42585400</td></tr> <tr><td>H</td><td>0.35088200</td><td>3.92485300</td><td>1.33463900</td></tr> <tr><td>C</td><td>0.63011600</td><td>-0.14895900</td><td>-1.37488700</td></tr> <tr><td>H</td><td>0.82250400</td><td>0.71372600</td><td>-2.01508000</td></tr> <tr><td>H</td><td>0.18929400</td><td>-0.94208700</td><td>-1.98300500</td></tr> <tr><td>C</td><td>1.91494100</td><td>-0.62264300</td><td>-0.73977900</td></tr> <tr><td>C</td><td>2.92242200</td><td>0.29161500</td><td>-0.42014800</td></tr> <tr><td>C</td><td>2.10844300</td><td>-1.97379200</td><td>-0.44463500</td></tr> <tr><td>C</td><td>4.09615200</td><td>-0.13544700</td><td>0.19386300</td></tr> <tr><td>H</td><td>2.79548400</td><td>1.34197500</td><td>-0.66659500</td></tr> <tr><td>C</td><td>3.28214100</td><td>-2.40252300</td><td>0.16894300</td></tr> <tr><td>H</td><td>1.34029900</td><td>-2.69426200</td><td>-0.70651800</td></tr> <tr><td>C</td><td>4.27676200</td><td>-1.48356700</td><td>0.49289500</td></tr> <tr><td>H</td><td>4.87175400</td><td>0.58359600</td><td>0.43163900</td></tr> <tr><td>H</td><td>3.42116100</td><td>-3.45507200</td><td>0.38824600</td></tr> <tr><td>H</td><td>5.19189600</td><td>-1.81738600</td><td>0.96843800</td></tr> <tr><td>O</td><td>-2.83789200</td><td>-2.48535300</td><td>-0.62272300</td></tr> <tr><td>H</td><td>-3.61395300</td><td>-2.34229400</td><td>-1.19127300</td></tr> </tbody> </table>		H	1.09478400	4.36792400	-0.23271000	C	0.98883800	3.58971700	0.51767200	H	1.96319000	3.28532800	0.89921900	O	0.36604200	2.48076300	-0.16470700	C	0.15086700	1.39776800	0.56157200	O	0.40658000	1.28381400	1.72672400	C	-0.42774600	0.24692400	-0.30230800	C	-0.91415200	-0.91416500	0.57360500	H	-0.42413800	-0.92487900	1.54457800	H	-0.73806300	-1.85875300	0.06331000	C	-2.41291400	-0.69568200	0.74261300	C	-2.87637500	-0.01183800	1.99944800	H	-2.66567000	-0.66898900	2.84419000	H	-3.94562900	0.19347700	1.94650300	H	-2.32822600	0.92133100	2.13668600	C	-1.69976900	0.70945600	-0.96130300	C	-1.81598400	1.54463000	-2.15515800	H	-2.82678600	1.92933700	-2.27108000	H	-1.58026800	0.87582300	-2.99741100	H	-1.06450000	2.33344000	-2.15259400	O	-3.22180200	-1.78858500	0.55461500	O	-2.73748500	0.24485600	-0.42585400	H	0.35088200	3.92485300	1.33463900	C	0.63011600	-0.14895900	-1.37488700	H	0.82250400	0.71372600	-2.01508000	H	0.18929400	-0.94208700	-1.98300500	C	1.91494100	-0.62264300	-0.73977900	C	2.92242200	0.29161500	-0.42014800	C	2.10844300	-1.97379200	-0.44463500	C	4.09615200	-0.13544700	0.19386300	H	2.79548400	1.34197500	-0.66659500	C	3.28214100	-2.40252300	0.16894300	H	1.34029900	-2.69426200	-0.70651800	C	4.27676200	-1.48356700	0.49289500	H	4.87175400	0.58359600	0.43163900	H	3.42116100	-3.45507200	0.38824600	H	5.19189600	-1.81738600	0.96843800	O	-2.83789200	-2.48535300	-0.62272300	H	-3.61395300	-2.34229400	-1.19127300	
H	1.09478400	4.36792400	-0.23271000																																																																																																																																																											
C	0.98883800	3.58971700	0.51767200																																																																																																																																																											
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C	0.15086700	1.39776800	0.56157200																																																																																																																																																											
O	0.40658000	1.28381400	1.72672400																																																																																																																																																											
C	-0.42774600	0.24692400	-0.30230800																																																																																																																																																											
C	-0.91415200	-0.91416500	0.57360500																																																																																																																																																											
H	-0.42413800	-0.92487900	1.54457800																																																																																																																																																											
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C	-2.41291400	-0.69568200	0.74261300																																																																																																																																																											
C	-2.87637500	-0.01183800	1.99944800																																																																																																																																																											
H	-2.66567000	-0.66898900	2.84419000																																																																																																																																																											
H	-3.94562900	0.19347700	1.94650300																																																																																																																																																											
H	-2.32822600	0.92133100	2.13668600																																																																																																																																																											
C	-1.69976900	0.70945600	-0.96130300																																																																																																																																																											
C	-1.81598400	1.54463000	-2.15515800																																																																																																																																																											
H	-2.82678600	1.92933700	-2.27108000																																																																																																																																																											
H	-1.58026800	0.87582300	-2.99741100																																																																																																																																																											
H	-1.06450000	2.33344000	-2.15259400																																																																																																																																																											
O	-3.22180200	-1.78858500	0.55461500																																																																																																																																																											
O	-2.73748500	0.24485600	-0.42585400																																																																																																																																																											
H	0.35088200	3.92485300	1.33463900																																																																																																																																																											
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H	2.79548400	1.34197500	-0.66659500																																																																																																																																																											
C	3.28214100	-2.40252300	0.16894300																																																																																																																																																											
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H	-3.61395300	-2.34229400	-1.19127300																																																																																																																																																											

Peroxacarbenium ion C Z (CO₂Me-OOH-cis)

		Multiplicity = 1 Charge = 1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1033.910086	-1033.561545	-1033.631665
<pre> H 3.81768600 -3.11066300 -1.88765600 C 3.85068500 -2.37521700 -1.08898200 H 4.20667400 -2.82673200 -0.16384900 O 2.48914900 -1.92918500 -0.92317400 C 2.28863100 -1.01521500 0.00614200 O 3.13851100 -0.55736900 0.72230600 C 0.83127200 -0.53123300 -0.01480500 C 0.68097000 0.46834800 -1.19111900 H -0.05975000 0.10076700 -1.89849000 H 1.62486100 0.58290900 -1.72619700 C 0.22864700 1.82773500 -0.70198900 C -0.39636500 2.70640800 -1.75567300 H 0.34036000 2.85514000 -2.54757000 H -0.68931700 3.66698800 -1.33472100 H -1.27150500 2.20976600 -2.17580500 C 0.48621700 0.04926200 1.31259300 O 1.34750000 2.36614500 -0.05242500 O -0.33963400 1.00614100 1.43666100 C 0.95098300 -0.47385500 2.60657900 H 1.18263900 -1.53619200 2.52790900 H 0.21959800 -0.26939400 3.38752200 H 1.88124600 0.06171400 2.83571100 O -0.83563300 1.63995000 0.26476000 O 1.01504100 3.60107700 0.55710100 H 1.45406300 4.24166000 -0.02763000 H 4.48270400 -1.53206200 -1.36646200 C -0.15790000 -1.76516100 -0.16664100 H 0.11623600 -2.20662900 -1.12509400 H 0.07131400 -2.48182100 0.62427500 C -1.62024000 -1.40038700 -0.15008800 C -2.31358800 -1.31685600 1.06053100 C -2.30506700 -1.14223500 -1.34039900 C -3.65462100 -0.94773700 1.08552200 H -1.80260900 -1.55278500 1.99033300 C -3.64682000 -0.77283400 -1.31761800 H -1.79031700 -1.24687400 -2.29023700 C -4.32138000 -0.66597700 -0.10425000 H -4.17921800 -0.88651200 2.03204900 H -4.16644100 -0.57563500 -2.24833600 H -5.36623500 -0.37798200 -0.08641400 </pre>		

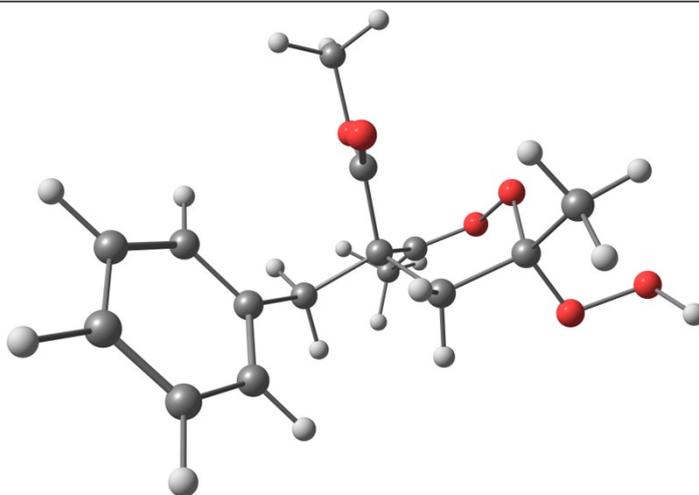
Peroxacarbenium ion C E (CO₂Me-OOH-trans)

		Multiplicity = 1 Charge = 1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1033.915243	-1033.566967	-1033.636391

```

H -0.59670600 3.07603900 -2.38533300
C 0.01057100 3.36296300 -1.52748800
H 1.06750400 3.36544800 -1.79104200
O -0.21582700 2.43763600 -0.44191200
C 0.07011900 1.16600200 -0.68222900
O 0.49639900 0.72293200 -1.70770100
C -0.18306200 0.31335000 0.58330800
C -0.60376800 -1.11292100 0.17303400
H -0.63580200 -1.74121500 1.06505100
H 0.14985700 -1.50775600 -0.50747800
C -1.97480800 -1.10765200 -0.51135900
C -1.98567700 -1.54954000 -1.95561200
H -1.69790400 -2.60279500 -1.97917800
H -1.25357500 -0.97255500 -2.51969700
H -2.97355400 -1.42770900 -2.39670700
C -1.35902300 0.91430200 1.28508100
O -2.46788700 0.26653500 -0.58640000
C -1.36586300 1.53957300 2.60303800
H -2.35571500 1.89869300 2.87371000
H -0.62943200 2.35205300 2.59471600
H -1.00252800 0.79437800 3.32196800
O -2.49815500 0.83219500 0.72040700
O -2.80259800 -1.83886700 0.34274500
O -4.11297100 -1.91924200 -0.19132000
H -4.15370900 -2.84362000 -0.48953200
C 1.08356900 0.31964200 1.47903700
H 0.85048400 -0.26595900 2.37144200
H 1.28831600 1.34680800 1.78866700
H -0.29355800 4.33357900 -1.14672400
C 2.30307900 -0.25229000 0.79613800
C 2.58041300 -1.61916500 0.86224700
C 3.17420100 0.58278600 0.09390300
C 3.70167600 -2.14427200 0.22599100
H 1.91728500 -2.27280400 1.42040600
C 4.29609800 0.06061000 -0.54266600
H 2.97381200 1.64962100 0.04991000
C 4.56011700 -1.30538500 -0.48027000
H 3.90732400 -3.20694700 0.28661600
H 4.96528300 0.72057500 -1.08287900
H 5.43507900 -1.71336500 -0.97339700

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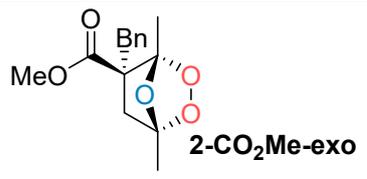
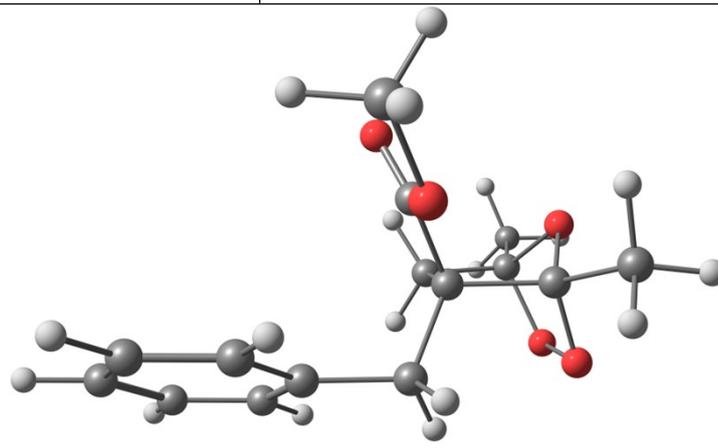


Ozonide 2 (CO₂Me-endo)

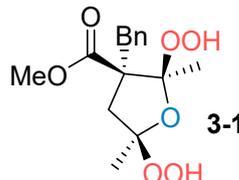
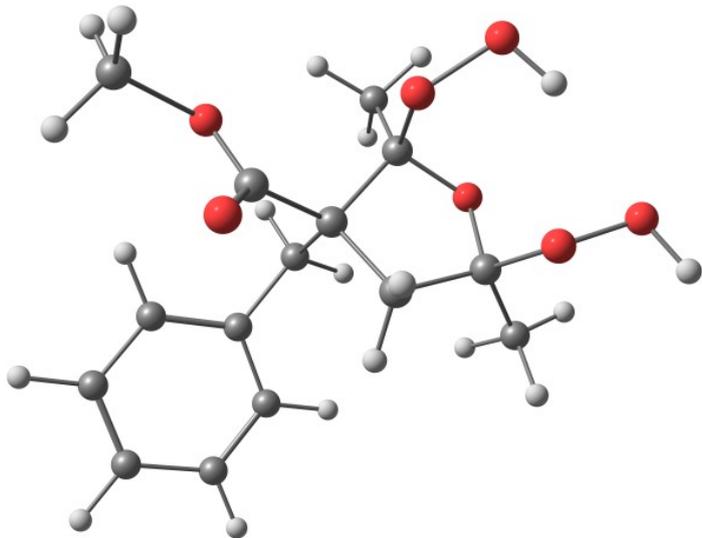
<p>2-CO₂Me-endo</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-958.389656	-958.058080	-958.123401
<pre> H -0.45051700 3.80953600 -1.32827400 C 0.28856300 3.58258000 -0.55962500 H 1.27626800 3.49109300 -1.01283200 O -0.05983600 2.36730700 0.11905000 C -0.11321200 1.26813800 -0.63660000 O 0.11619800 1.26912100 -1.81828900 C -0.47335400 0.04581100 0.19773700 C -0.71974900 -1.20035100 -0.68495300 H -0.15964300 -2.06301800 -0.32259500 H -0.49264900 -1.03207300 -1.73550000 C -2.20977100 -1.43103100 -0.45626600 C -2.81091200 -2.74900900 -0.83383300 H -2.70070500 -2.90642100 -1.90794500 H -3.86838300 -2.76875800 -0.56899900 H -2.28361700 -3.54596200 -0.30804000 C -1.90240800 0.22299800 0.81036300 O -2.72772000 0.76626500 -0.24035700 O -2.93798400 -0.36856800 -1.11163300 O -2.38028800 -1.09552600 0.90909500 C -2.10746000 1.01283000 2.06770100 H -3.16854900 1.00850300 2.31892800 H -1.76624300 2.03818200 1.93068900 H -1.54366600 0.55570800 2.88145400 C 0.58953000 -0.18263800 1.29561500 </pre>		

H	0.25957000	-1.02957000	1.90289500
H	0.63084800	0.69961600	1.93794200
C	1.96110400	-0.45943900	0.72725700
C	2.79008800	0.59628500	0.33316200
C	2.42212500	-1.76777900	0.56233800
C	4.04090600	0.34999900	-0.22500200
H	2.45855100	1.62083500	0.47581500
C	3.67399300	-2.01795500	0.00477600
H	1.79937800	-2.59661200	0.88391200
C	4.48509400	-0.95953400	-0.39475200
H	4.67104900	1.18097400	-0.52181700
H	4.01651700	-3.04004500	-0.11244800
H	5.46009100	-1.15253400	-0.82764300
H	0.29152700	4.35632400	0.20402100

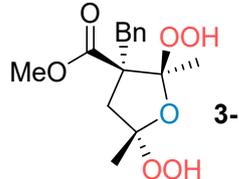
Ozonide 2 (CO₂Me-exo)

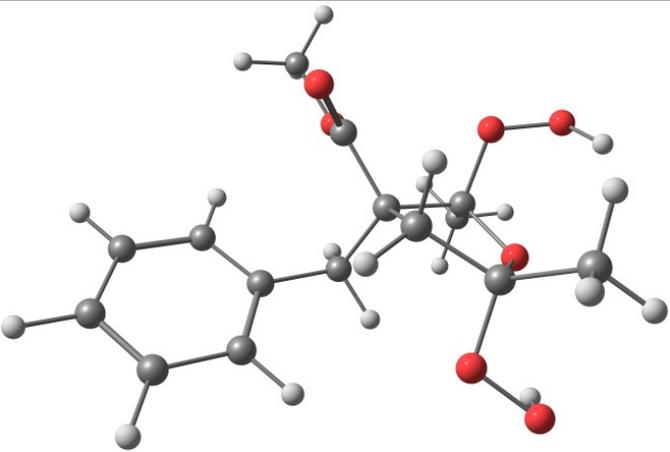
		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-958.387410	-958.055643	-958.121004
<pre> H 1.34147400 4.07833500 -0.11540600 C 1.04322700 3.37711100 0.66003200 H 1.91175000 3.05237300 1.23443300 O 0.46047100 2.26149300 -0.02781900 C 0.04068100 1.25284000 0.73594800 O 0.11166800 1.26513500 1.93859900 C -0.51991700 0.11009000 -0.10796800 C -0.93922000 -1.08181400 0.78674500 H -0.70806600 -0.89787400 1.83496300 H -0.49653700 -2.02508300 0.47319200 C -2.45115400 -1.10291800 0.57437700 C -3.31498200 -1.83223900 1.55526000 H -3.03683900 -2.88730600 1.57225300 H -4.36467400 -1.73628900 1.27620600 H -3.15722200 -1.41310800 2.54976900 C -1.92935900 0.51544000 -0.66610300 C -2.15504600 1.85526300 -1.30203900 H -2.02191000 2.64491900 -0.56310500 H -3.17274000 1.89064100 -1.69161900 H -1.44559700 2.01200900 -2.11525700 O -2.31752700 -0.50631000 -1.60101300 O -2.69974100 -1.61269000 -0.75396400 O -2.78646200 0.26426900 0.42188400 H 0.31080200 3.83517000 1.32539300 C 0.47229900 -0.25603700 -1.23371700 H 0.53801100 0.57828900 -1.93591800 H 0.05681500 -1.11291300 -1.76583200 C 1.85246900 -0.60022300 -0.71671800 C 2.16671700 -1.91129800 -0.34465800 C 2.84256700 0.38044700 -0.59217700 C 3.42400500 -2.23009800 0.16144100 H 1.42583000 -2.69441100 -0.46822100 C 4.10120400 0.06476900 -0.08646000 H 2.63043400 1.39660200 -0.90631100 C 4.39392100 -1.24048100 0.29962200 H 3.64757800 -3.25372400 0.44071800 H 4.85541400 0.83926100 -0.00083400 H 5.37374100 -1.48717900 0.69256800 </pre>		

Dihydroperoxy tetrahydrofuran 3-1.1 (vic-OOH-CO₂Me-cis, OOH-OOH-cis)

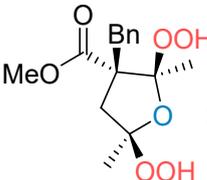
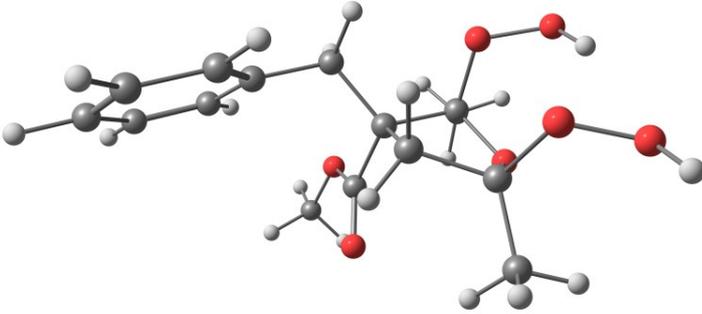
 <p>3-1.1 (vic-OOH-CO₂Me-cis, OOH-OOH-cis)</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1109.960966	-1109.595626	-1109.668681
<pre> H 2.24999800 3.41559700 -0.94291300 C 1.28353100 3.67333700 -0.50822700 H 1.40593900 4.41064200 0.28111400 O 0.70042100 2.52303500 0.12149600 C 0.47575100 1.47404500 -0.67034800 O 0.73924100 1.46126900 -1.84505800 C -0.10690400 0.30264600 0.10836700 C -0.51359400 -0.84920000 -0.82510900 H 0.26234000 -1.60720400 -0.91821000 H -0.74430100 -0.46948300 -1.81956000 C -1.78367100 -1.43089100 -0.18513600 C -1.69146600 -2.86144700 0.28856400 H -2.59568100 -3.14970400 0.82469600 H -0.83662200 -2.95591100 0.96049100 H -1.54321000 -3.52392800 -0.56656600 C -1.47760100 0.64964100 0.75588600 O -2.13140700 1.38847200 -0.28665300 O -2.79245900 -1.25840900 -1.18852600 O -2.09232100 -0.60107400 0.91849900 C -1.52400100 1.38849700 2.06907800 H -0.98174300 2.32988300 1.98662500 H -1.08661000 0.78281100 2.86260400 H -2.56644600 1.59128300 2.31734300 O -3.52202900 1.44308100 -0.03845900 H -3.81968300 0.58591500 -0.38728200 O -4.04865200 -1.68320100 -0.67186400 H -4.21081000 -2.50416100 -1.16313400 H 0.61946200 4.05379900 -1.28463800 C 0.89207000 -0.14362500 1.20763600 H 1.04489100 0.68786200 1.89797800 H 0.42587900 -0.96133400 1.76403100 C 2.22523300 -0.59376100 0.66013600 C 3.21981900 0.34015800 0.35278300 C 2.49080100 -1.94821700 0.44363600 C 4.44249400 -0.06833100 -0.17227100 H 3.04174700 1.39519500 0.53913100 C 3.71383600 -2.36097100 -0.07912200 H 1.73322500 -2.68472200 0.69404000 C 4.69175000 -1.42091600 -0.39290200 H 5.20297700 0.66946100 -0.40234200 H 3.90321500 -3.41671900 -0.23781900 H 5.64479100 -1.74046100 -0.79889100 </pre>		

Dihydroperoxy tetrahydrofuran 3-1.2 (vic-OOH-CO₂Me-cis, OOH-OOH-trans)

 <p>3-1.2 (vic-OOH-CO₂Me-cis, OOH-OOH-trans)</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1109.960428	-1109.594982	-1109.667672

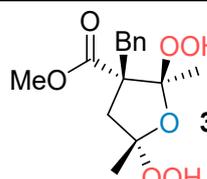
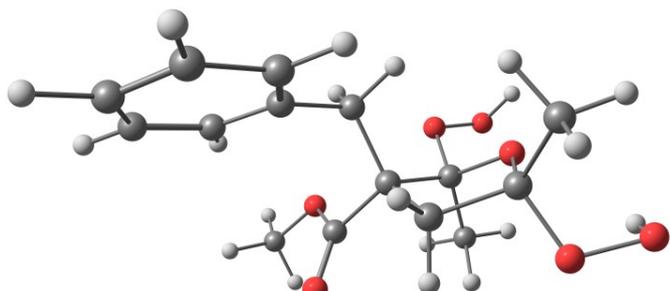
<pre> H 1.15595600 4.45915400 0.75316300 C 1.11106900 3.81584300 -0.12188400 H 0.49129400 4.26905000 -0.89590200 O 0.51988900 2.58806600 0.32845000 C 0.37053000 1.63848900 -0.59441200 O 0.71246200 1.76495200 -1.74179800 C -0.24081800 0.37470900 -0.00254300 C -0.54015900 -0.65859600 -1.09575600 H 0.29806400 -1.32197900 -1.30686900 H -0.82079900 -0.15677900 -2.02066500 C -1.73775800 -1.43581500 -0.55610700 C -2.76882200 -1.84579600 -1.58129500 H -3.15309900 -0.95361600 -2.07957200 H -3.59398300 -2.37456500 -1.10525900 H -2.30493600 -2.49398300 -2.32752800 C -1.67158100 0.63111700 0.54996900 O -2.22699900 1.53160500 -0.41642600 C -1.82883300 1.15356500 1.95671900 H -1.42190000 0.43709700 2.66975700 H -2.88788000 1.29474900 2.17002200 H -1.30879200 2.10617500 2.05949100 O -3.60369200 1.72656300 -0.15573800 H -4.00386100 0.91903500 -0.51941500 O -2.33865200 -0.60504400 0.43684600 O -1.17723600 -2.56150000 0.11405800 O -2.20550300 -3.27320400 0.78190700 H -2.34769200 -2.73653000 1.57910900 H 2.11284200 3.63128400 -0.51139100 C 0.68472200 -0.16369100 1.12055100 H 0.77535800 0.60487300 1.88975400 H 0.20126200 -1.03455500 1.56751000 C 2.05988200 -0.54192500 0.62497300 C 2.35262300 -1.86032500 0.26625500 C 3.06432800 0.42358800 0.50661200 C 3.61527000 -2.20578400 -0.20862200 H 1.58337900 -2.62007700 0.36574800 C 4.32670600 0.08225200 0.02901100 H 2.86151700 1.44834400 0.80381200 C 4.60474100 -1.23372000 -0.33277500 H 3.82637700 -3.23447100 -0.47868100 H 5.09483900 0.84304000 -0.05413900 H 5.58849200 -1.50121000 -0.70152700 </pre>	
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Dihydroperoxy tetrahydrofurane 3-2.1 (vic-OOH-CO₂Me-trans, OOH-OOH-cis)

 <p>3-2.1 (vic-OOH-CO₂Me-trans, OOH-OOH-cis)</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
<p>Electronic Energy (EE)</p>	<p>EE + Thermal Enthalpy Correction (H)</p>	<p>EE + Thermal Free Energy Correction (G)</p>
<p>-1109.959466</p>	<p>-1109.593977</p>	<p>-1109.666804</p>
<pre> H 2.16795400 3.92959500 0.30100600 C 1.73447900 3.19733600 0.97757000 H 2.51245200 2.72875800 1.58149500 O 1.10490400 2.21858500 0.13890100 C 0.51707900 1.20123400 0.76319600 O 0.48147900 1.09196900 1.96296000 C -0.09114500 0.20213100 -0.22342800 C -0.58385600 -1.04372500 0.53577300 H 0.01836200 -1.26310900 1.41481700 H -0.57646000 -1.90732400 -0.12926200 C -2.03638100 -0.71681200 0.92360600 C -2.34575400 -0.66759000 2.39994800 H -1.65055500 0.01974500 2.88135100 H -2.22232300 -1.66231000 2.83311300 H -3.36583400 -0.32084400 2.56585700 C -1.44812500 0.78269700 -0.72341600 O -1.77416500 -0.07291100 -1.82700500 O -2.80821100 -1.72195300 0.25007100 O -2.32520300 0.54295400 0.34776100 C -1.54223400 2.23466700 -1.12064700 </pre>		

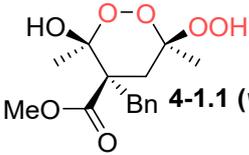
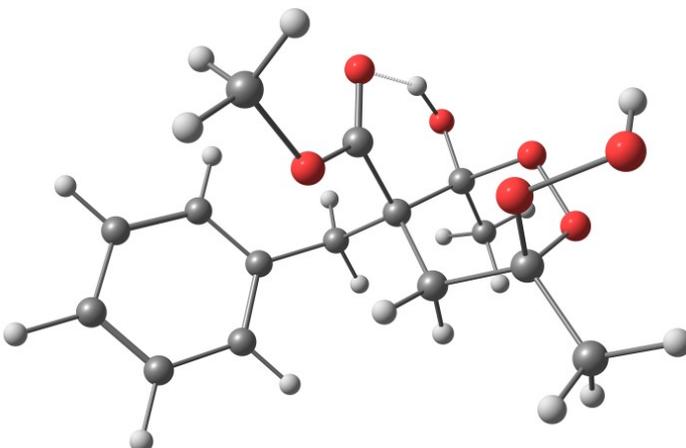
H	-1.39249100	2.88129200	-0.25586200
H	-2.53525100	2.41797000	-1.53199500
H	-0.78990000	2.46353600	-1.87613900
O	-3.14612500	0.06408000	-2.14140300
H	-3.56089900	-0.52878000	-1.49229800
O	-4.19365200	-1.46380000	0.44707300
H	-4.45624600	-2.17066900	1.05784900
C	0.91614500	-0.10526600	-1.35286600
H	0.46751400	-0.85660000	-2.00346600
H	1.07808900	0.80001500	-1.94124900
C	2.23748900	-0.61907000	-0.82166700
C	2.39266000	-1.96993600	-0.49386300
C	3.32383500	0.24071500	-0.63368700
C	3.59304400	-2.44559600	0.02597600
H	1.56919900	-2.65755800	-0.65759700
C	4.52707800	-0.23264300	-0.11499600
H	3.22893000	1.28697100	-0.90385100
C	4.66348100	-1.57617700	0.22268200
H	3.69398900	-3.49688500	0.27178200
H	5.35913900	0.44950800	0.02011400
H	5.59948200	-1.94560800	0.62605600
H	0.99585900	3.66913800	1.62635000

Dihydroperoxy tetrahydrofuran 3-2.2 (vic-OOH-CO₂Me-trans, OOH-OOH-trans)

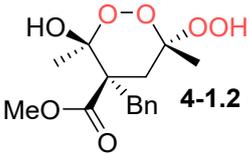
 <p>3-2.2 (vic-OOH-CO₂Me-trans, OOH-OOH-trans)</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>																																																																																																																																																																				
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)																																																																																																																																																																				
-1109.954886	-1109.589549	-1109.663291																																																																																																																																																																				
<table border="1"> <tbody> <tr><td>H</td><td>-1.44998300</td><td>4.38466400</td><td>-0.03286000</td></tr> <tr><td>C</td><td>-1.33398500</td><td>3.61521800</td><td>-0.79179400</td></tr> <tr><td>H</td><td>-2.30585300</td><td>3.32301800</td><td>-1.19111700</td></tr> <tr><td>O</td><td>-0.71592600</td><td>2.50359900</td><td>-0.12677500</td></tr> <tr><td>C</td><td>-0.49354200</td><td>1.42508200</td><td>-0.87578800</td></tr> <tr><td>O</td><td>-0.78626100</td><td>1.35342900</td><td>-2.04217700</td></tr> <tr><td>C</td><td>0.16040600</td><td>0.31376300</td><td>-0.06679000</td></tr> <tr><td>C</td><td>0.49334200</td><td>-0.90142200</td><td>-0.94251000</td></tr> <tr><td>H</td><td>0.67536100</td><td>-0.59304400</td><td>-1.97239600</td></tr> <tr><td>H</td><td>-0.30473700</td><td>-1.64164000</td><td>-0.94830500</td></tr> <tr><td>C</td><td>1.78716300</td><td>-1.46939600</td><td>-0.34164900</td></tr> <tr><td>C</td><td>1.67396900</td><td>-2.82597100</td><td>0.31432100</td></tr> <tr><td>H</td><td>1.40782000</td><td>-3.57229100</td><td>-0.43643100</td></tr> <tr><td>H</td><td>0.89123600</td><td>-2.79197800</td><td>1.07370500</td></tr> <tr><td>H</td><td>2.61637700</td><td>-3.10466400</td><td>0.78475500</td></tr> <tr><td>C</td><td>1.58607600</td><td>0.72300500</td><td>0.41612300</td></tr> <tr><td>O</td><td>1.46417500</td><td>1.32754000</td><td>1.67890500</td></tr> <tr><td>C</td><td>2.35218900</td><td>1.59090300</td><td>-0.56747200</td></tr> <tr><td>H</td><td>3.39612500</td><td>1.65632800</td><td>-0.26336200</td></tr> <tr><td>H</td><td>1.92549000</td><td>2.59569600</td><td>-0.59531100</td></tr> <tr><td>H</td><td>2.30760700</td><td>1.15332800</td><td>-1.56629400</td></tr> <tr><td>O</td><td>2.75610600</td><td>1.65118200</td><td>2.16791600</td></tr> <tr><td>H</td><td>3.02747200</td><td>0.82209300</td><td>2.59467800</td></tr> <tr><td>O</td><td>2.23697000</td><td>-0.52802300</td><td>0.61505600</td></tr> <tr><td>O</td><td>2.70467200</td><td>-1.48206800</td><td>-1.43724400</td></tr> <tr><td>O</td><td>3.97670800</td><td>-1.90955700</td><td>-0.98162200</td></tr> <tr><td>H</td><td>4.32198300</td><td>-1.11178400</td><td>-0.54797300</td></tr> <tr><td>C</td><td>-0.74568800</td><td>-0.06120400</td><td>1.13830800</td></tr> <tr><td>H</td><td>-0.85576000</td><td>0.81520600</td><td>1.77664500</td></tr> <tr><td>H</td><td>-0.22923800</td><td>-0.83122200</td><td>1.71575700</td></tr> <tr><td>C</td><td>-2.10856800</td><td>-0.56128300</td><td>0.72208300</td></tr> <tr><td>C</td><td>-2.36862000</td><td>-1.93046500</td><td>0.61948800</td></tr> <tr><td>C</td><td>-3.13891300</td><td>0.33767800</td><td>0.42750500</td></tr> <tr><td>C</td><td>-3.62007900</td><td>-2.39208200</td><td>0.21943500</td></tr> <tr><td>H</td><td>-1.58261200</td><td>-2.63970600</td><td>0.86133600</td></tr> <tr><td>C</td><td>-4.39046100</td><td>-0.11987200</td><td>0.02456700</td></tr> <tr><td>H</td><td>-2.96571400</td><td>1.40476900</td><td>0.52965000</td></tr> <tr><td>C</td><td>-4.63362900</td><td>-1.48699700</td><td>-0.08423700</td></tr> <tr><td>H</td><td>-3.80356500</td><td>-3.45836600</td><td>0.14828200</td></tr> <tr><td>H</td><td>-5.17794400</td><td>0.59179800</td><td>-0.19695300</td></tr> <tr><td>H</td><td>-5.60875200</td><td>-1.84413100</td><td>-0.39541900</td></tr> </tbody> </table>		H	-1.44998300	4.38466400	-0.03286000	C	-1.33398500	3.61521800	-0.79179400	H	-2.30585300	3.32301800	-1.19111700	O	-0.71592600	2.50359900	-0.12677500	C	-0.49354200	1.42508200	-0.87578800	O	-0.78626100	1.35342900	-2.04217700	C	0.16040600	0.31376300	-0.06679000	C	0.49334200	-0.90142200	-0.94251000	H	0.67536100	-0.59304400	-1.97239600	H	-0.30473700	-1.64164000	-0.94830500	C	1.78716300	-1.46939600	-0.34164900	C	1.67396900	-2.82597100	0.31432100	H	1.40782000	-3.57229100	-0.43643100	H	0.89123600	-2.79197800	1.07370500	H	2.61637700	-3.10466400	0.78475500	C	1.58607600	0.72300500	0.41612300	O	1.46417500	1.32754000	1.67890500	C	2.35218900	1.59090300	-0.56747200	H	3.39612500	1.65632800	-0.26336200	H	1.92549000	2.59569600	-0.59531100	H	2.30760700	1.15332800	-1.56629400	O	2.75610600	1.65118200	2.16791600	H	3.02747200	0.82209300	2.59467800	O	2.23697000	-0.52802300	0.61505600	O	2.70467200	-1.48206800	-1.43724400	O	3.97670800	-1.90955700	-0.98162200	H	4.32198300	-1.11178400	-0.54797300	C	-0.74568800	-0.06120400	1.13830800	H	-0.85576000	0.81520600	1.77664500	H	-0.22923800	-0.83122200	1.71575700	C	-2.10856800	-0.56128300	0.72208300	C	-2.36862000	-1.93046500	0.61948800	C	-3.13891300	0.33767800	0.42750500	C	-3.62007900	-2.39208200	0.21943500	H	-1.58261200	-2.63970600	0.86133600	C	-4.39046100	-0.11987200	0.02456700	H	-2.96571400	1.40476900	0.52965000	C	-4.63362900	-1.48699700	-0.08423700	H	-3.80356500	-3.45836600	0.14828200	H	-5.17794400	0.59179800	-0.19695300	H	-5.60875200	-1.84413100	-0.39541900	
H	-1.44998300	4.38466400	-0.03286000																																																																																																																																																																			
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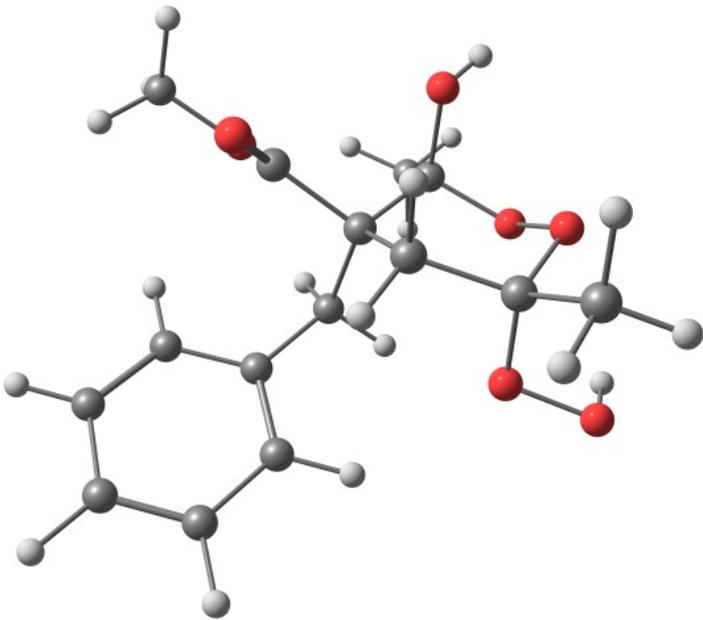
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Hydroxy hydroperoxyl dioxane 4-1.1 (vic-OH-CO₂Me-cis, OH-OOH-cis)

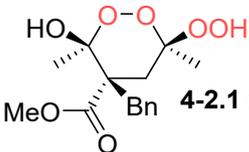
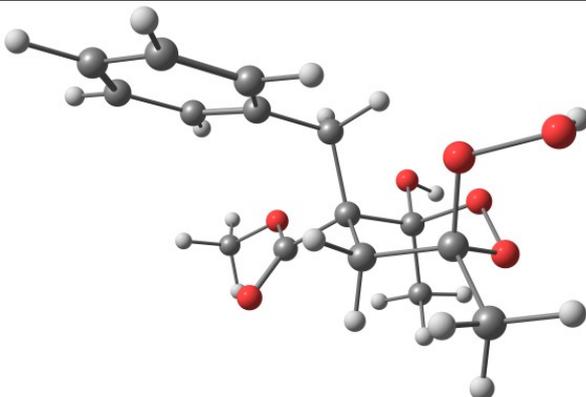
 <p>4-1.1 (vic-OH-CO₂Me-cis, OH-OOH-cis)</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1109.964874	-1109.598999	-1109.669601
<pre> H -1.76065300 -2.66508900 1.87305800 C -1.22774000 -1.78701400 2.22881900 H -1.89975600 -1.12962700 2.78121600 O -0.74511700 -1.12643400 1.05072500 C -0.09948400 0.00910000 1.23465800 O 0.09494900 0.47580600 2.34016700 C 0.27264100 0.69812900 -0.08457800 C 0.67577700 -0.34882100 -1.13955700 H 0.70556900 0.12720600 -2.12139700 H -0.05783800 -1.15304400 -1.18601000 C 2.05831400 -0.94222600 -0.88362000 C 2.59814400 -1.73368400 -2.05377800 H 1.89802500 -2.53765900 -2.28637900 H 3.57007900 -2.15922200 -1.80708900 H 2.69701000 -1.08562500 -2.92543400 C 1.47087500 1.67628100 0.13019900 O 1.91826100 -1.72565900 0.29213300 O 2.62324900 0.85653200 0.47417500 C 1.79598700 2.54898400 -1.06838300 H 1.01388200 3.29726300 -1.19584600 H 1.90281600 1.98043500 -1.99020100 H 2.73667800 3.06039600 -0.85719000 O 3.18054200 -2.23295000 0.68441200 H 3.54998800 -1.49636000 1.19862500 O 3.01198900 0.08583800 -0.65536700 H -0.38961200 -2.07946500 2.86199500 C -0.96673600 1.51966000 -0.55414700 H -0.73814300 1.89584800 -1.55351400 H -1.07169600 2.37856200 0.11417500 C -2.26516200 0.75314500 -0.59389500 C -2.62022600 0.00317700 -1.71661900 C -3.12224200 0.75862200 0.50952000 C -3.79575300 -0.74355900 -1.72906700 H -1.97106900 0.00521600 -2.58688800 C -4.29755800 0.01360000 0.50166400 H -2.86074400 1.34795900 1.38424200 C -4.63522700 -0.74443400 -0.61762600 H -4.05787000 -1.32162200 -2.60824500 H -4.95099500 0.02705700 1.36701900 H -5.55051100 -1.32537700 -0.62656700 O 1.31927400 2.51283100 1.21800500 H 0.96001700 1.97968600 1.94890700 </pre>		

Hydroxy hydroperoxyl dioxane 4-1.2 (vic-OH-CO₂Me-cis, OH-OOH-trans)

 <p>4-1.2 (vic-OH-CO₂Me-cis, OH-OOH-trans)</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1109.963665	-1109.597883	-1109.669391

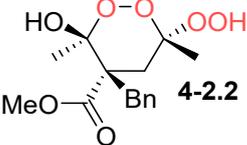
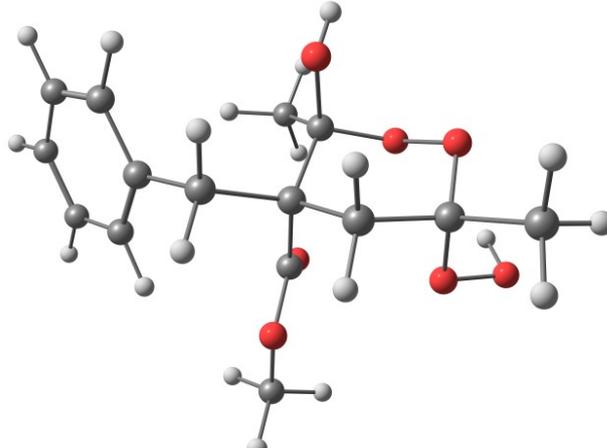
<pre> H -2.97938200 2.92866600 0.87760200 C -2.11244400 3.46598500 0.49150500 H -2.40727800 4.13437800 -0.31361700 O -1.17782300 2.54603200 -0.09075700 C -0.69002100 1.61116900 0.72565300 O -1.00275900 1.52760200 1.88565200 C 0.25763600 0.64662600 0.00390200 C 0.76856900 -0.35185600 1.05918400 H -0.01229400 -1.06872500 1.31789600 H 1.01412600 0.19752100 1.96763200 C 2.03290000 -1.10545400 0.66949300 C 2.68623500 -1.80018800 1.84575000 H 2.95865600 -1.06564600 2.60379100 H 3.57757600 -2.33752000 1.52506300 H 1.97243600 -2.50581500 2.27440600 C 1.48189000 1.43380200 -0.55203900 C 1.27985600 2.21985500 -1.83710500 H 2.20017700 2.77017700 -2.04771700 H 0.45880500 2.92367400 -1.72125100 H 1.07528500 1.55796500 -2.67811100 O 2.49895400 0.49646800 -0.94227800 O 1.64873300 -2.01579500 -0.35060800 O 2.77710800 -2.74254100 -0.80367800 H 3.15492600 -2.14660800 -1.47075900 O 3.01419000 -0.21403100 0.17413900 H -1.63731900 4.02663000 1.29680900 C -0.52426400 -0.02563900 -1.15879900 H -0.84947700 0.75512600 -1.84738200 H 0.16612200 -0.68209500 -1.68997800 C -1.73873900 -0.80422700 -0.70710400 C -1.66046400 -2.17309800 -0.43554600 C -2.97147400 -0.16221700 -0.55064500 C -2.78184800 -2.88061900 -0.00995200 H -0.71166700 -2.68389400 -0.56159000 C -4.09374100 -0.86599000 -0.12134900 H -3.05673000 0.89564900 -0.78095100 C -4.00141200 -2.22813200 0.15271800 H -2.70276200 -3.94300000 0.19254100 H -5.04146300 -0.35124600 -0.00873700 H -4.87506500 -2.77845300 0.48321400 O 1.92299900 2.23961900 0.49603600 H 2.64803800 2.79427300 0.17909800 </pre>	
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Hydroxy hydroperoxyl dioxane 4-2.1 (vic-OH-CO₂Me-trans, OH-OOH- cis)

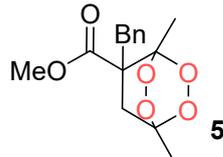
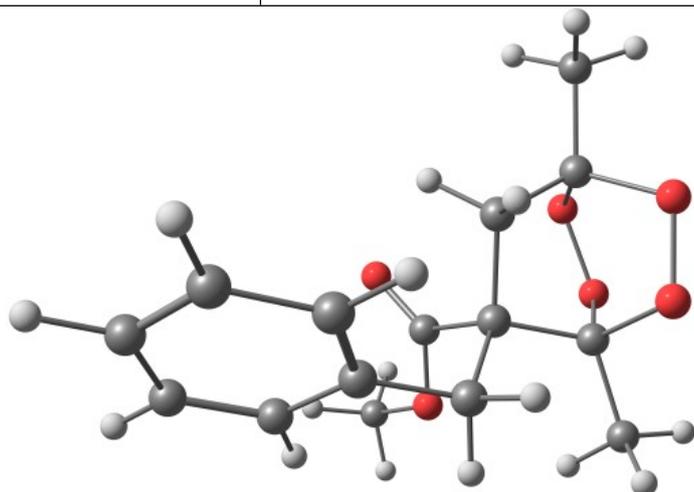
 <p>4-2.1 (vic-OH-CO₂Me-trans, OH-OOH-cis)</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
<p>Electronic Energy (EE)</p>	<p>EE + Thermal Enthalpy Correction (H)</p>	<p>EE + Thermal Free Energy Correction (G)</p>
<p>-1109.960799</p>	<p>-1109.595044</p>	<p>-1109.666537</p>
<pre> H 3.00240400 2.88841100 0.88054200 C 2.15650700 3.42745900 0.45217200 H 1.67014200 4.02309100 1.22550600 O 1.22114200 2.50669900 -0.12646500 C 0.70397600 1.60350500 0.70280300 O 0.98112400 1.55131200 1.87539400 C -0.25198100 0.64312500 -0.01170600 C -0.79023200 -0.34164600 1.04558000 H -1.02326900 0.20655500 1.95859300 H -0.02229100 -1.07093200 1.30875900 C -2.06439000 -1.08132100 0.65268000 C -2.76498000 -1.71040500 1.83852500 H -3.04916100 -0.93676800 2.55240500 H -2.07698700 -2.40553900 2.32275900 H -3.65456700 -2.24862700 1.51472000 C -1.45690600 1.43375500 -0.59948600 O -1.67294200 -2.04107400 -0.31662600 O -2.43962200 0.45738700 -1.03310100 C -2.08208900 2.42079900 0.37155500 H -2.98095200 2.84552000 -0.08274600 H -1.37497100 3.22931700 0.57011900 H -2.35961500 1.95138800 1.31450200 </pre>		

O	-2.80376500	-2.76455300	-0.76910600
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O	-3.01464700	-0.18916200	0.09132400
C	0.52687100	-0.05738200	-1.16147900
H	0.83107700	0.70944400	-1.87249900
H	-0.16532400	-0.73323400	-1.66403600
C	1.74600500	-0.81750100	-0.69244100
C	2.98184500	-0.17316600	-0.57083200
C	1.66947700	-2.17571700	-0.36914400
C	4.10650800	-0.86233000	-0.12411900
H	3.06737500	0.87432200	-0.84321600
C	2.79290600	-2.86882200	0.07436700
H	0.71950100	-2.69033000	-0.47051100
C	4.01467700	-2.21274700	0.20315000
H	5.05602600	-0.34546100	-0.03942700
H	2.71394300	-3.92288200	0.31667900
H	4.89011500	-2.75159100	0.54758200
H	2.48576800	4.06406400	-0.36522600
O	-1.08824100	2.03850700	-1.78801800
H	-1.77711400	2.66972000	-2.03399400

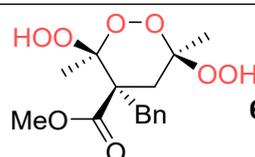
Hydroxy hydroperoxyl dioxane 4-2.2 (vic-OH-CO₂Me-trans, OH-OOH-trans)

 <p>4-2.2 (vic-OH-CO₂Me-trans, OH-OOH-trans)</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>																																																																																																																																																																								
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)																																																																																																																																																																								
-1109.960271	-1109.594651	-1109.666131																																																																																																																																																																								
<table border="1"> <tr><td>H</td><td>-0.67087400</td><td>3.71675600</td><td>0.44951700</td></tr> <tr><td>C</td><td>0.26260300</td><td>3.52831900</td><td>-0.08279800</td></tr> <tr><td>H</td><td>0.35191600</td><td>4.19539300</td><td>-0.93667900</td></tr> <tr><td>O</td><td>0.27223000</td><td>2.20191600</td><td>-0.62263000</td></tr> <tr><td>C</td><td>0.17777500</td><td>1.20920900</td><td>0.26855800</td></tr> <tr><td>O</td><td>0.04901800</td><td>1.40844300</td><td>1.44819900</td></tr> <tr><td>C</td><td>0.20684400</td><td>-0.14819000</td><td>-0.44079800</td></tr> <tr><td>C</td><td>1.46329400</td><td>-0.23219600</td><td>-1.33983500</td></tr> <tr><td>H</td><td>1.52698300</td><td>0.65051500</td><td>-1.97596700</td></tr> <tr><td>H</td><td>1.37521200</td><td>-1.11203900</td><td>-1.97910000</td></tr> <tr><td>C</td><td>2.75057000</td><td>-0.38425500</td><td>-0.54677700</td></tr> <tr><td>C</td><td>3.96275300</td><td>-0.69292300</td><td>-1.39635200</td></tr> <tr><td>H</td><td>4.08719500</td><td>0.10292000</td><td>-2.13239700</td></tr> <tr><td>H</td><td>3.82090400</td><td>-1.64041700</td><td>-1.91713300</td></tr> <tr><td>H</td><td>4.85439300</td><td>-0.75225700</td><td>-0.77255500</td></tr> <tr><td>C</td><td>0.28881800</td><td>-1.32169900</td><td>0.57621800</td></tr> <tr><td>C</td><td>-0.68655200</td><td>-1.36356400</td><td>1.74428500</td></tr> <tr><td>H</td><td>-1.71159200</td><td>-1.26699400</td><td>1.39212600</td></tr> <tr><td>H</td><td>-0.47784400</td><td>-0.57475900</td><td>2.46012700</td></tr> <tr><td>H</td><td>-0.57546500</td><td>-2.33399300</td><td>2.23600100</td></tr> <tr><td>O</td><td>1.56124500</td><td>-1.25545100</td><td>1.25471300</td></tr> <tr><td>O</td><td>2.87804100</td><td>0.84130800</td><td>0.16207600</td></tr> <tr><td>O</td><td>3.95554700</td><td>0.76757200</td><td>1.07508800</td></tr> <tr><td>H</td><td>3.54261200</td><td>0.34390600</td><td>1.84556300</td></tr> <tr><td>O</td><td>2.64699100</td><td>-1.46514700</td><td>0.36094700</td></tr> <tr><td>C</td><td>-1.01005100</td><td>-0.24662000</td><td>-1.40573700</td></tr> <tr><td>H</td><td>-0.91777600</td><td>-1.19474400</td><td>-1.93621100</td></tr> <tr><td>H</td><td>-0.88446600</td><td>0.55363600</td><td>-2.13981300</td></tr> <tr><td>C</td><td>-2.38717200</td><td>-0.15259500</td><td>-0.79362000</td></tr> <tr><td>C</td><td>-2.88106300</td><td>1.05574600</td><td>-0.29260900</td></tr> <tr><td>C</td><td>-3.20116600</td><td>-1.28590400</td><td>-0.72255200</td></tr> <tr><td>C</td><td>-4.14172400</td><td>1.12085600</td><td>0.29463800</td></tr> <tr><td>H</td><td>-2.28473300</td><td>1.95969100</td><td>-0.36951100</td></tr> <tr><td>C</td><td>-4.46522500</td><td>-1.22379100</td><td>-0.14244600</td></tr> <tr><td>H</td><td>-2.83209900</td><td>-2.22805400</td><td>-1.11579300</td></tr> <tr><td>C</td><td>-4.93622700</td><td>-0.02035400</td><td>0.37640800</td></tr> <tr><td>H</td><td>-4.50661600</td><td>2.06603200</td><td>0.68092200</td></tr> <tr><td>H</td><td>-5.08105700</td><td>-2.11504100</td><td>-0.09507500</td></tr> <tr><td>H</td><td>-5.91863100</td><td>0.03070800</td><td>0.83191500</td></tr> <tr><td>H</td><td>1.10570800</td><td>3.66393600</td><td>0.59552500</td></tr> <tr><td>O</td><td>0.20841000</td><td>-2.48296200</td><td>-0.19156200</td></tr> <tr><td>H</td><td>0.20351600</td><td>-3.24286500</td><td>0.40438600</td></tr> </table>		H	-0.67087400	3.71675600	0.44951700	C	0.26260300	3.52831900	-0.08279800	H	0.35191600	4.19539300	-0.93667900	O	0.27223000	2.20191600	-0.62263000	C	0.17777500	1.20920900	0.26855800	O	0.04901800	1.40844300	1.44819900	C	0.20684400	-0.14819000	-0.44079800	C	1.46329400	-0.23219600	-1.33983500	H	1.52698300	0.65051500	-1.97596700	H	1.37521200	-1.11203900	-1.97910000	C	2.75057000	-0.38425500	-0.54677700	C	3.96275300	-0.69292300	-1.39635200	H	4.08719500	0.10292000	-2.13239700	H	3.82090400	-1.64041700	-1.91713300	H	4.85439300	-0.75225700	-0.77255500	C	0.28881800	-1.32169900	0.57621800	C	-0.68655200	-1.36356400	1.74428500	H	-1.71159200	-1.26699400	1.39212600	H	-0.47784400	-0.57475900	2.46012700	H	-0.57546500	-2.33399300	2.23600100	O	1.56124500	-1.25545100	1.25471300	O	2.87804100	0.84130800	0.16207600	O	3.95554700	0.76757200	1.07508800	H	3.54261200	0.34390600	1.84556300	O	2.64699100	-1.46514700	0.36094700	C	-1.01005100	-0.24662000	-1.40573700	H	-0.91777600	-1.19474400	-1.93621100	H	-0.88446600	0.55363600	-2.13981300	C	-2.38717200	-0.15259500	-0.79362000	C	-2.88106300	1.05574600	-0.29260900	C	-3.20116600	-1.28590400	-0.72255200	C	-4.14172400	1.12085600	0.29463800	H	-2.28473300	1.95969100	-0.36951100	C	-4.46522500	-1.22379100	-0.14244600	H	-2.83209900	-2.22805400	-1.11579300	C	-4.93622700	-0.02035400	0.37640800	H	-4.50661600	2.06603200	0.68092200	H	-5.08105700	-2.11504100	-0.09507500	H	-5.91863100	0.03070800	0.83191500	H	1.10570800	3.66393600	0.59552500	O	0.20841000	-2.48296200	-0.19156200	H	0.20351600	-3.24286500	0.40438600	
H	-0.67087400	3.71675600	0.44951700																																																																																																																																																																							
C	0.26260300	3.52831900	-0.08279800																																																																																																																																																																							
H	0.35191600	4.19539300	-0.93667900																																																																																																																																																																							
O	0.27223000	2.20191600	-0.62263000																																																																																																																																																																							
C	0.17777500	1.20920900	0.26855800																																																																																																																																																																							
O	0.04901800	1.40844300	1.44819900																																																																																																																																																																							
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H	1.52698300	0.65051500	-1.97596700																																																																																																																																																																							
H	1.37521200	-1.11203900	-1.97910000																																																																																																																																																																							
C	2.75057000	-0.38425500	-0.54677700																																																																																																																																																																							
C	3.96275300	-0.69292300	-1.39635200																																																																																																																																																																							
H	4.08719500	0.10292000	-2.13239700																																																																																																																																																																							
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C	0.28881800	-1.32169900	0.57621800																																																																																																																																																																							
C	-0.68655200	-1.36356400	1.74428500																																																																																																																																																																							
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H	-0.47784400	-0.57475900	2.46012700																																																																																																																																																																							
H	-0.57546500	-2.33399300	2.23600100																																																																																																																																																																							
O	1.56124500	-1.25545100	1.25471300																																																																																																																																																																							
O	2.87804100	0.84130800	0.16207600																																																																																																																																																																							
O	3.95554700	0.76757200	1.07508800																																																																																																																																																																							
H	3.54261200	0.34390600	1.84556300																																																																																																																																																																							
O	2.64699100	-1.46514700	0.36094700																																																																																																																																																																							
C	-1.01005100	-0.24662000	-1.40573700																																																																																																																																																																							
H	-0.91777600	-1.19474400	-1.93621100																																																																																																																																																																							
H	-0.88446600	0.55363600	-2.13981300																																																																																																																																																																							
C	-2.38717200	-0.15259500	-0.79362000																																																																																																																																																																							
C	-2.88106300	1.05574600	-0.29260900																																																																																																																																																																							
C	-3.20116600	-1.28590400	-0.72255200																																																																																																																																																																							
C	-4.14172400	1.12085600	0.29463800																																																																																																																																																																							
H	-2.28473300	1.95969100	-0.36951100																																																																																																																																																																							
C	-4.46522500	-1.22379100	-0.14244600																																																																																																																																																																							
H	-2.83209900	-2.22805400	-1.11579300																																																																																																																																																																							
C	-4.93622700	-0.02035400	0.37640800																																																																																																																																																																							
H	-4.50661600	2.06603200	0.68092200																																																																																																																																																																							
H	-5.08105700	-2.11504100	-0.09507500																																																																																																																																																																							
H	-5.91863100	0.03070800	0.83191500																																																																																																																																																																							
H	1.10570800	3.66393600	0.59552500																																																																																																																																																																							
O	0.20841000	-2.48296200	-0.19156200																																																																																																																																																																							
H	0.20351600	-3.24286500	0.40438600																																																																																																																																																																							

Tetraoxane 5

		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1033.516192	-1033.179680	-1033.246470
<pre> H -0.22952600 3.63823800 -1.76371300 C 0.48251500 3.50532300 -0.94911400 H 1.47769800 3.31897900 -1.35418200 O 0.07730300 2.41229300 -0.11096000 C 0.00475800 1.21838800 -0.70014100 O 0.26228400 1.04223300 -1.86196800 C -0.37932200 0.11799700 0.29591200 C -0.60146300 -1.21145300 -0.44877900 H -0.28277500 -2.05826400 0.16049300 H -0.05974700 -1.22732900 -1.39312300 C -2.09327000 -1.34406200 -0.70816300 C -2.49730900 -2.37495600 -1.72596900 H -2.16071000 -2.05194600 -2.71220700 H -3.58140500 -2.49298800 -1.73278900 H -2.02082100 -3.32544700 -1.48272200 C -1.75402800 0.42820500 0.95033900 O -2.59736000 -0.07842800 -1.17134000 C -2.23044400 -0.79539200 1.53730300 C -1.82344200 1.45062700 2.05672700 H -1.34335100 2.37805500 1.75414600 H -1.32364900 1.05624100 2.94267900 H -2.87192600 1.63071500 2.29615100 O -2.67502300 0.82046400 -0.04331600 O -2.76393100 -1.63852400 0.49894100 C 0.72693900 0.00564300 1.37200000 H 0.81522200 0.96145600 1.89178500 H 0.40441800 -0.74744800 2.09517800 C 2.06692100 -0.37636900 0.78874700 C 2.47359700 -1.71153500 0.73051200 C 2.91909100 0.60650000 0.27568300 C 3.69652100 -2.05894000 0.16163200 H 1.83136300 -2.48303500 1.14309000 C 4.14139600 0.26281500 -0.29437300 H 2.62815200 1.65164700 0.33354100 C 4.53200400 -1.07282000 -0.35618700 H 3.99794400 -3.09991200 0.12752700 H 4.79076800 1.03844300 -0.68471000 H 5.48473500 -1.34203300 -0.79787900 H 0.49152300 4.38128000 -0.30549900 </pre>		

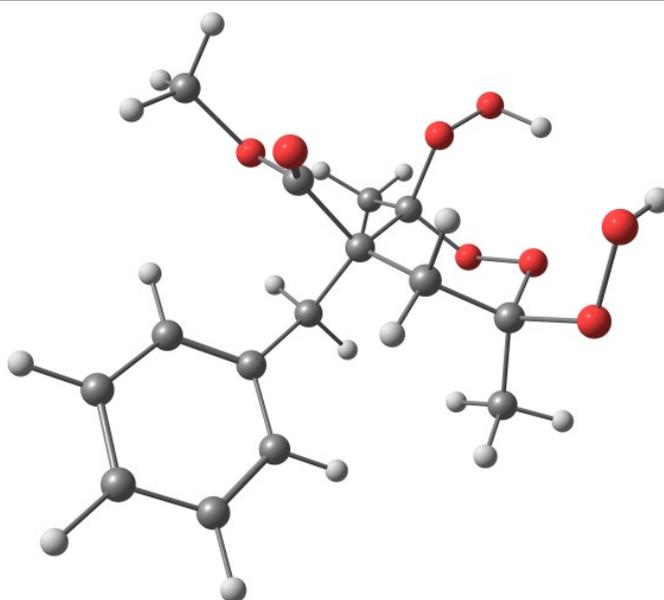
Dihydroperoxy dioxane 6-1.1 (vic-OOH-CO₂Me-cis, OOH-OOH-cis)

		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1185.080548	-1184.710005	-1184.784107

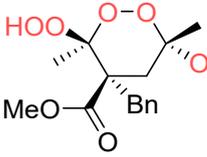
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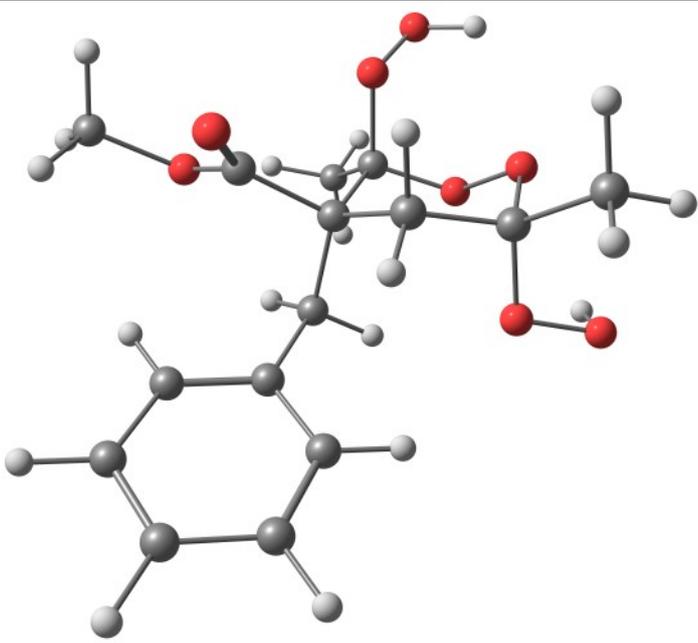
H -1.26086000 4.53634000 0.26099200
C -1.11901900 3.70243000 0.94366900
H -0.41344600 3.96942500 1.73054900
O -0.58810400 2.63421300 0.14453500
C -0.34394800 1.49074400 0.78364900
O -0.55327200 1.33704200 1.95864900
C 0.18018600 0.39879500 -0.16354500
C 0.47484700 -0.84537600 0.70361100
H -0.45615600 -1.37081800 0.92472300
H 0.88963600 -0.49987100 1.64667000
C 1.47196800 -1.84690500 0.12866200
C 0.93942200 -2.85171200 -0.86948100
H 1.73683500 -3.54566300 -1.14007200
H 0.59550300 -2.34394700 -1.76929800
H 0.10742700 -3.40326100 -0.43068600
C 1.50690500 0.86482500 -0.83299700
O 2.25710500 1.36081000 0.25978300
O 2.03961600 -2.65469400 1.13888800
O 2.16300600 -0.26022400 -1.41334400
C 1.42406300 1.84344100 -1.98660800
H 0.97036700 1.36914700 -2.85677900
H 2.43624100 2.15229900 -2.24508600
H 0.83575700 2.71246500 -1.70159000
O 3.58585900 1.63534900 -0.13632800
H 4.01679400 0.77446100 -0.00105100
O 2.59286100 -1.87210300 2.18556800
H 3.50600500 -1.73748700 1.88548700
O 2.61104200 -1.15139900 -0.41091200
H -2.07056800 3.40464600 1.38563200
C -0.89526400 0.16439000 -1.26347900
H -0.50124100 -0.55431300 -1.98414400
H -1.05086800 1.10544000 -1.79268100
C -2.22317700 -0.32047000 -0.72957600
C -3.15367300 0.58393900 -0.20784000
C -2.55247400 -1.67776600 -0.75009900
C -4.37197400 0.14045100 0.29924800
H -2.93282800 1.64702500 -0.21227800
C -3.77155100 -2.12510200 -0.24712400
H -1.84906500 -2.38778000 -1.17135100
C -4.68307400 -1.21693300 0.28463700
H -5.08129300 0.85700600 0.69807000
H -4.00975500 -3.18255000 -0.27449400
H -5.63282700 -1.56302400 0.67630700

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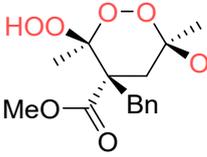


Dihydroperoxy dioxane 6-1.2 (vic-OOH-CO₂Me-cis, OOH-OOH-trans)

 <p>6-1.2 (vic-OOH-CO₂Me-cis, OOH-OOH-trans)</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1185.088436	-1184.717878	-1184.792471

H -0.91506700 4.19301400 1.27889400	
C -1.49645300 3.74525100 0.47291800	
H -2.45732000 3.40048600 0.85659700	
O -0.77450900 2.64842400 -0.10817200	
C -0.49562500 1.63371000 0.70811600	
O -0.81192700 1.61706900 1.86954100	
C 0.21511500 0.48218100 -0.01646000	
O 0.50827600 -0.60097400 1.04007500	
H -0.40494400 -1.13999600 1.29609700	
H 0.85888500 -0.11661500 1.95066600	
C 1.58632600 -1.60378600 0.65192200	
C 2.09925400 -2.40120800 1.83169700	
H 1.25964700 -2.93393900 2.28151800	
H 2.53021100 -1.72774200 2.57283700	
H 2.85297900 -3.11815400 1.50986200	
C 1.57205000 0.96459100 -0.61379600	
O 2.17882900 1.63157500 0.47863100	
C 1.54058300 1.80412800 -1.87483900	
O 0.87886100 2.65697200 -1.74242000	
H 1.19723000 1.20810300 -2.72010600	
H 2.55250200 2.15124100 -2.07998500	
O 3.51475500 1.97456300 0.16874500	
H 3.99668800 1.17410300 0.43664800	
O 2.35425300 -0.16078800 -0.99795100	
O 1.01536000 -2.42178500 -0.35436200	
O 1.95929900 -3.38050400 -0.79766000	
H 2.42362000 -2.90465800 -1.50530200	
O 2.72787100 -0.93547100 0.13277100	
H -1.64224300 4.45978600 -0.33319600	
C -0.70821600 -0.00741400 -1.16888700	
H -0.85713100 0.82060700 -1.86262100	
H -0.18580400 -0.80562800 -1.69782600	
C -2.05951700 -0.49389800 -0.69809900	
C -3.11972500 0.40476000 -0.54302500	
C -2.27956600 -1.84334600 -0.40810400	
C -4.36414300 -0.03067000 -0.09477600	
H -2.97505800 1.45228000 -0.78987200	
C -3.52396000 -2.28245800 0.03648900	
H -1.46713600 -2.55141800 -0.53438600	
C -4.56888800 -1.37626200 0.19923600	
H -5.17499200 0.68054800 0.01680300	
H -3.67742100 -3.33372100 0.25356400	
H -5.53801700 -1.71756600 0.54510100	

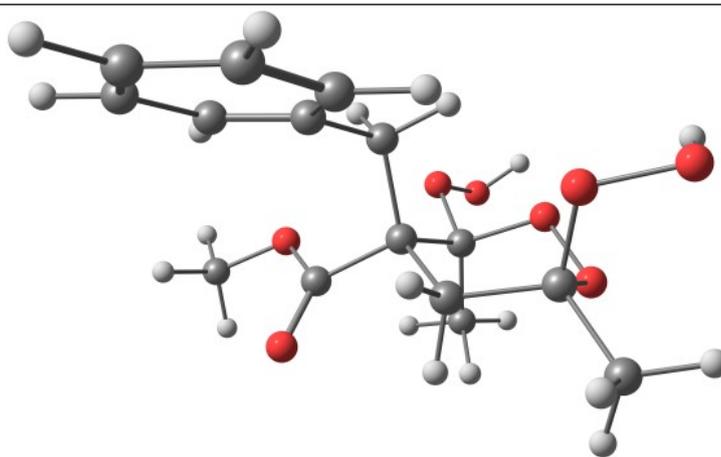
Dihydroperoxy dioxane 6-2.1 (vic-OOH-CO₂Me-trans, OOH-OOH-cis)

 <p>6-2.1 (vic-OOH-CO₂Me-trans, OOH-OOH-cis)</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1185.082926	-1184.712304	-1184.786367

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H 1.71117400 4.40451700 0.01562000
C 1.57976000 3.64216500 0.77921000
H 2.54660600 3.25570700 1.10385100
O 0.81195000 2.60056900 0.15844500
C 0.55086500 1.53907400 0.91586100
O 0.91595600 1.43627500 2.05980000
C -0.23751300 0.46882200 0.15280900
H -0.49629000 -0.70070900 1.12688000
H -0.74981400 -0.30099000 2.10837100
H 0.41590300 -1.28494400 1.25720500
C -1.63222500 -1.64098100 0.73374200
C -2.11540500 -2.49079700 1.88955600
H -2.90658900 -3.16402200 1.56301000
H -2.49000200 -1.84936800 2.68781300
H -1.27475100 -3.07510500 2.26748900
C -1.62476900 1.03142000 -0.27578500
O -1.42771700 1.79897300 -1.43184500
O -1.13346400 -2.41750600 -0.34244000
O -2.40258400 -0.07534500 -0.77157300
C -2.35207000 1.78555600 0.82199200
H -2.32440700 1.23623300 1.76196300
H -3.39089600 1.94634100 0.54004800
H -1.86941600 2.75504700 0.96376200
O -2.64013700 2.43532600 -1.80422700
H -3.04847900 1.77784700 -2.39054900
O -2.13159000 -3.31313400 -0.79852800
H -2.60701600 -2.77851400 -1.45480800
O -2.77604600 -0.91059500 0.30918100
C 0.58627200 0.04642300 -1.09909800
H 0.69795000 0.91806900 -1.74277200
H 0.00624500 -0.70333800 -1.63776800
C 1.95663300 -0.49729900 -0.76574700
C 3.04680800 0.36751800 -0.62424700
C 2.16760200 -1.86885000 -0.59652300
C 4.31065300 -0.12287800 -0.30599300
H 2.90853400 1.43299700 -0.78116500
C 3.43095600 -2.36289800 -0.28214100
H 1.33227100 -2.55120300 -0.71551100
C 4.50587400 -1.49047700 -0.13095900
H 5.14394300 0.56337500 -0.20348800
H 3.57582700 -3.43039700 -0.15822600
H 5.49003300 -1.87420900 0.11302900
H 1.03902700 4.04891700 1.63427100

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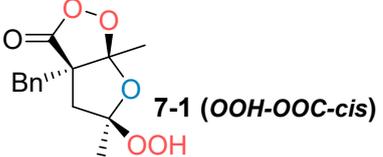
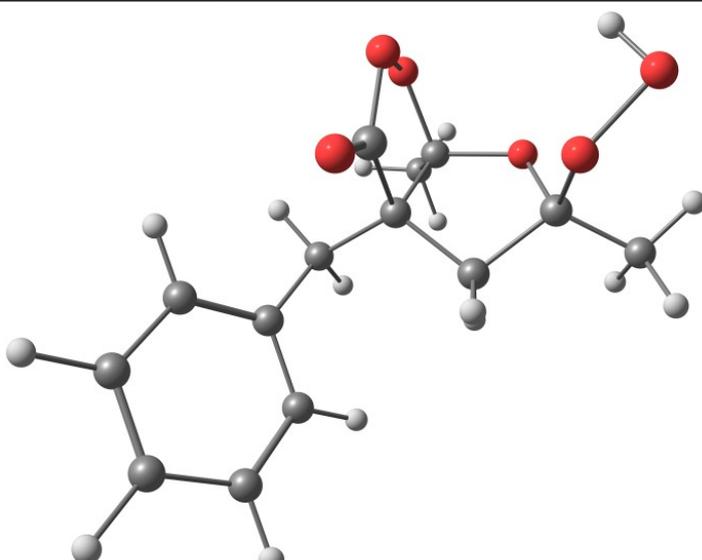


Dihydroperoxy dioxane 6-2.2 (vic-OOH-CO₂Me-trans, OOH-OOH-trans)

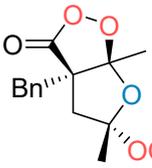
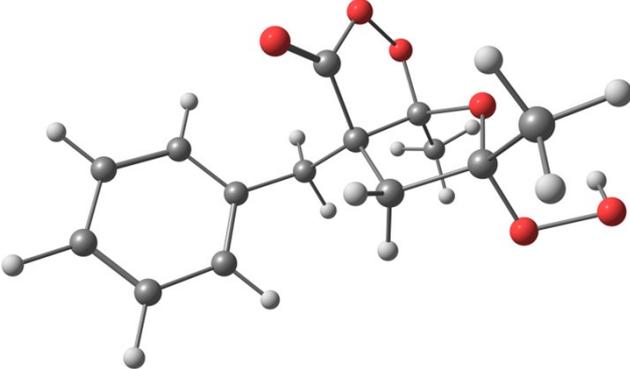
<p>6-2.2 (vic-OOH-CO₂Me-trans, OOH-OOH-trans)</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1185.084938	-1184.714503	-1184.788666
<pre> H 0.90606200 3.85568300 0.80176500 C 0.07321100 3.72414700 0.11029400 H -0.87074800 3.83345900 0.64579300 O 0.14832600 2.43475100 -0.51155700 C 0.08746600 1.38650900 0.31338400 O -0.05192000 1.49603200 1.50298000 C 0.17721300 0.07607900 -0.47529100 C 1.44206100 0.08590700 -1.36673800 H 1.49534200 1.02143500 -1.92336300 H 1.37243500 -0.73347400 -2.08354800 C 2.72935100 -0.11407900 -0.58518000 C 3.94159300 -0.36706500 -1.45152400 H 3.80210700 -1.28197500 -2.02824700 H 4.83419100 -0.45984400 -0.83368600 H 4.06025300 0.47202900 -2.13890700 C 0.28597100 -1.12301400 0.50860000 O 0.23933400 -2.24316100 -0.36319800 C -0.70377400 -1.24015300 1.66044600 H -0.28752500 -0.77649600 2.55189600 H -0.87882900 -2.29816200 1.85406200 H -1.64614100 -0.75024100 1.43175900 </pre>		

O	0.55595800	-3.42516900	0.34225200
H	1.52743400	-3.42613100	0.31418400
O	1.55134300	-1.08942000	1.17144100
O	2.84927600	1.05408600	0.20833600
O	3.94819100	0.93597200	1.09128600
H	3.54908500	0.49318100	1.85816300
O	2.62262400	-1.25916500	0.25132100
C	-1.03072300	-0.01992100	-1.45450600
H	-0.89585700	-0.92551000	-2.04705100
H	-0.93793000	0.83102000	-2.13404200
C	-2.40757500	-0.02577300	-0.83772200
C	-2.97975700	1.14783100	-0.33905200
C	-3.13040300	-1.21712700	-0.74345600
C	-4.23236700	1.12478600	0.26831100
H	-2.44715600	2.08981100	-0.43100000
C	-4.38579800	-1.24316300	-0.14264200
H	-2.69590400	-2.13261300	-1.13265800
C	-4.93672300	-0.07249600	0.37312600
H	-4.66085000	2.04317600	0.65381000
H	-4.93235600	-2.17720300	-0.07506600
H	-5.91258500	-0.09057400	0.84492600
H	0.13543100	4.44620700	-0.69999200

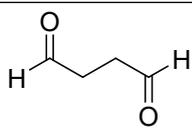
Peroxolactone 7-1 (OOH-OOC-cis)

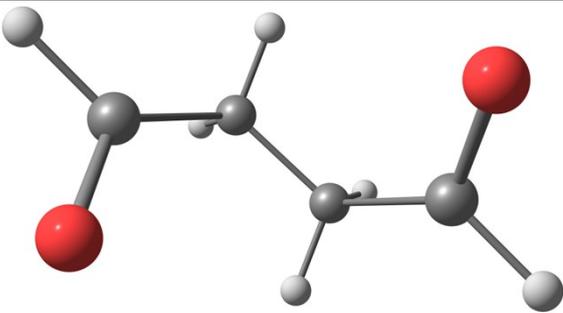
 <p>7-1 (OOH-OOC-cis)</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-994.234736	-993.928286	-993.991985
<pre> C 0.20335200 -0.81297100 -1.10229700 O -0.48785400 -0.46141500 -2.00743500 O 0.21774200 -0.36458300 0.35009100 C 0.50800000 1.13380400 0.43526800 H 0.30952100 1.49022800 1.44839700 H -0.06390400 1.72933100 -0.27646100 C 2.00835900 1.19222100 0.16477900 C 1.52771200 -1.00648500 0.84016300 O 1.74930800 -2.09845700 -0.05148300 C 1.61101200 -1.57800600 2.23276800 H 2.61760500 -1.96897400 2.39297900 H 0.88399000 -2.37627900 2.37645100 H 1.42751300 -0.77855700 2.95248200 O 1.17348200 -1.74922400 -1.30917900 O 2.53157600 -0.02151800 0.68034900 C 2.75709600 2.35782700 0.75817200 H 2.35175800 3.28912100 0.35879000 H 3.81699900 2.29176600 0.51393600 H 2.63677200 2.35010000 1.84198600 O 2.10214100 1.16022400 -1.26064700 O 3.45638400 1.00983500 -1.64359800 H 3.60700700 0.05758100 -1.52146400 C -1.04006800 -0.84877700 1.09572300 H -0.90671300 -0.57667600 2.14590700 H -1.08657600 -1.93967800 1.03615800 C -2.32780500 -0.25472900 0.57719400 C -3.11852900 -0.95866500 -0.33249500 C -2.74944600 1.00864700 0.99925700 C -4.30169000 -0.41034600 -0.81918300 H -2.80223200 -1.94357500 -0.66161300 C -3.93020200 1.56223900 0.51172000 H -2.15227900 1.55830300 1.72029200 C -4.70861100 0.85428300 -0.40101900 H -4.90573700 -0.97079600 -1.52393000 H -4.24538600 2.54310500 0.84968500 H -5.63016900 1.28268300 -0.77852400 </pre>		

Peroxolactone 7-2 (OOH-OOC-trans)

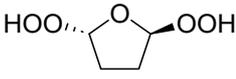
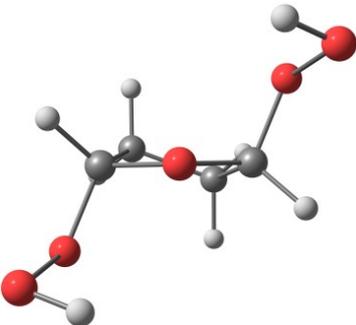
 7-1 (OOH-OOC-trans)		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-994.232410	-993.925820	-993.989704
<pre> C -0.10369500 1.29269600 0.95846100 O -0.82033100 1.14542300 1.90048800 C 0.17796500 0.36836000 -0.21489400 C 0.56905900 -1.02469100 0.26994600 H 0.39463600 -1.75644700 -0.52089500 H 0.01768800 -1.32951000 1.15926300 C 2.07955200 -0.90587400 0.54578600 C 1.49556700 0.98311600 -0.69782100 O 1.38812300 2.35955000 -0.37296500 C 1.87951200 0.89669100 -2.15200100 H 2.85847500 1.36030900 -2.28826600 H 1.14668700 1.39831300 -2.78359900 H 1.94462900 -0.15559600 -2.43589700 O 0.63729100 2.43047800 0.83915800 O 2.46975500 0.40252600 0.15237200 C 2.50756400 -1.13114900 1.97609600 H 1.94893000 -0.45369400 2.62510300 H 3.57346700 -0.93960300 2.09294200 H 2.28773600 -2.16060100 2.26401500 O 2.66790100 -1.84164800 -0.35422100 O 4.07913200 -1.77450900 -0.24896800 H 4.29207200 -0.98994200 -0.78117900 C -0.96590400 0.42771000 -1.24452400 H -0.65108400 -0.17856900 -2.09761700 H -1.07769400 1.45987900 -1.58899300 C -2.28516800 -0.07993500 -0.71444700 C -2.58966700 -1.44279200 -0.74953300 C -3.21880600 0.80534500 -0.17214600 C -3.79811300 -1.91272000 -0.24209200 H -1.87901700 -2.13842200 -1.18474700 C -4.42902800 0.33934600 0.33349700 H -2.99306700 1.86708400 -0.14616800 C -4.72028800 -1.02232500 0.30256100 H -4.02184800 -2.97302300 -0.27842600 H -5.14480800 1.03937200 0.74969600 H -5.66306800 -1.38677500 0.69452700 </pre>		

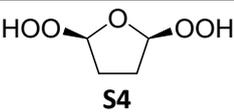
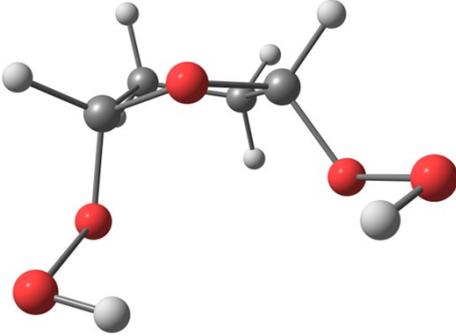
XYZ data for Table S1

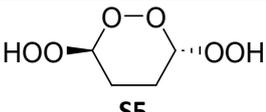
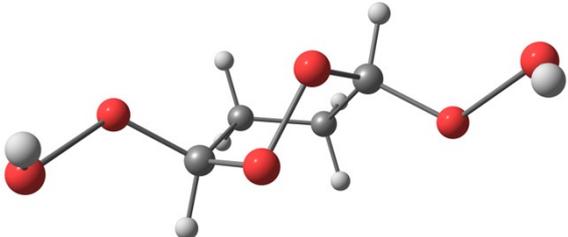
 S1		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-306.437239	-306.334871	-306.372779

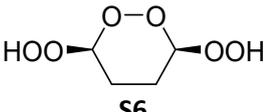
<pre> C 0.57873300 0.98026100 -0.48929300 H 1.17068400 1.89904500 -0.40710700 H 0.23446900 0.93750500 -1.52755000 C 1.53123400 -0.16087000 -0.28256400 H 2.33395300 -0.24986800 -1.03708900 C -0.57863500 0.98024200 0.48938600 H -1.17067400 1.89896600 0.40705900 H -0.23439900 0.93765200 1.52765000 C -1.53109200 -0.16093800 0.28269400 H -2.33355100 -0.25021600 1.03746300 O -1.47521800 -0.93766800 -0.63998100 O 1.47497700 -0.93798900 0.63976100 </pre>	
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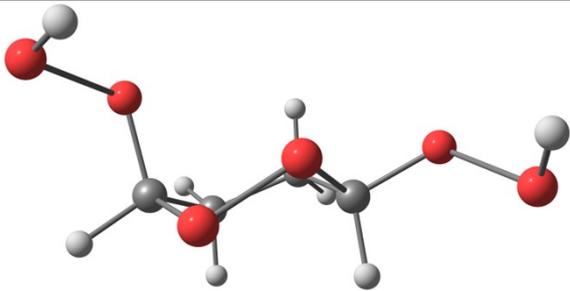
 <p style="text-align: center;">S2</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-381.565449	-381.455239	-381.489931
<pre> C 1.24550300 -0.77548700 -0.36036700 H 2.06431300 -1.18968200 0.22770900 H 1.25931600 -1.21265900 -1.35739800 O -1.15273600 0.72656500 -0.57600900 O -1.15204500 -0.72723000 -0.57632100 O -0.19273400 -0.00015300 1.28444700 C -0.08724000 1.03684000 0.33336700 H -0.28308000 2.01506800 0.76425300 C -0.08646500 -1.03693300 0.33330800 H -0.28180200 -2.01533900 0.76402000 C 1.24485000 0.77632900 -0.36049700 H 2.06346500 1.19135400 0.22724900 H 1.25802200 1.21329900 -1.35763100 </pre>		

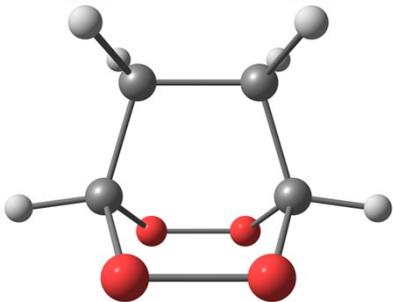
 <p style="text-align: center;">S3</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-533.145985	-533.001768	-533.045810
<pre> C 0.44510400 1.52610000 -0.62326800 H 1.25186400 2.25650700 -0.58720600 H -0.14141800 1.68896400 -1.52800700 O -2.15458700 0.10115200 -0.15355600 O -2.67013000 -1.22008100 -0.16291400 H -2.10752500 -1.66172600 -0.82018000 O 0.00043300 -0.70094500 0.00245600 O 2.15542800 0.10205200 0.15152700 O 2.67102100 -1.21915700 0.16195000 H 2.11019500 -1.65955000 0.82157700 C 0.97975400 0.10450100 -0.63081800 H 1.19951200 -0.32590300 -1.60799100 C -0.44647400 1.52670100 0.62294600 H 0.14017800 1.69015700 1.52751900 H -1.25315800 2.25714700 0.58636300 C -0.98074000 0.10506500 0.63168900 H -1.20282900 -0.32397400 1.60892500 </pre>		

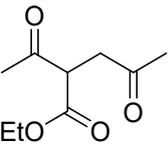
 S4		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-533.145289	-533.000960	-533.044910
<pre> C -1.20625000 1.61483300 0.03571000 H -1.98113200 1.82539100 -0.69956900 H -1.34497200 2.26994300 0.89646600 O 1.69343900 -0.12643200 -0.63495700 O 2.53905000 -0.99898400 0.09919500 H 1.94044900 -1.72435500 0.34159800 O 0.04593200 -0.09555600 1.00026400 O -1.55557100 -0.62071300 -0.60477300 O -1.61208200 -1.97358800 -0.18539300 H -0.68018000 -2.24558300 -0.21583300 C -1.25124600 0.17814700 0.52189000 H -1.95398200 -0.04499200 1.32408900 C 0.21819200 1.72468400 -0.52026900 H 0.25006000 1.45517100 -1.57733800 H 0.64968600 2.71584800 -0.39822200 C 0.99440600 0.68088600 0.28342000 H 1.70332700 1.07947400 1.00960600 </pre>		

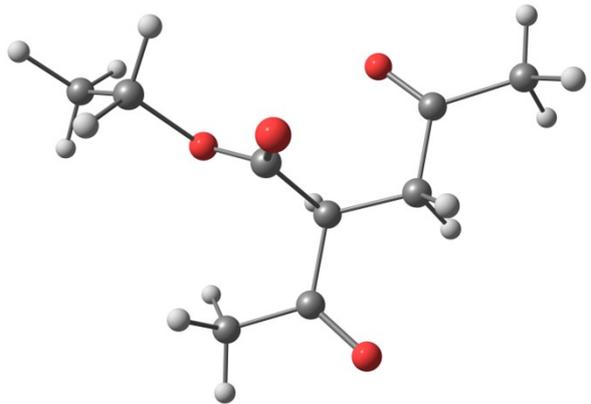
 S5		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-608.277565	-608.128221	-608.173828
<pre> C 0.74019400 1.60015600 -0.18648000 H 1.24811400 2.48093300 0.20284300 H 0.85541500 1.58950200 -1.27318900 O -2.40297500 -0.03924600 0.48110100 O 2.40301800 -0.03921100 -0.48106100 O -0.43171900 -0.69063900 -0.56807800 O -3.16163800 -1.06645600 -0.13739200 H -2.67646700 -1.86911500 0.11409800 O 3.16164600 -1.06645500 0.13739800 H 2.67648200 -1.86911300 -0.11410200 O 0.43172900 -0.69066200 0.56802900 C 1.38078800 0.34748700 0.39590500 H 1.78163100 0.48353700 1.40362100 C -0.74022900 1.60015500 0.18647800 H -0.85544900 1.58950500 1.27318800 H -1.24816600 2.48092200 -0.20284700 C -1.38081100 0.34747500 -0.39590000 H -1.78169400 0.48353500 -1.40360000 </pre>		

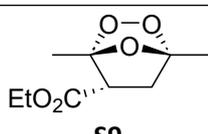
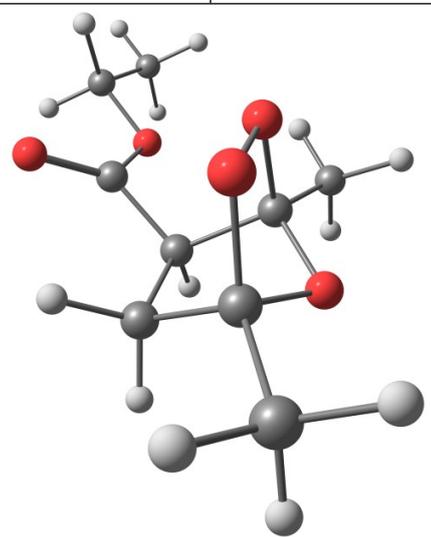
 S6		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-608.273764	-608.124492	-608.170535

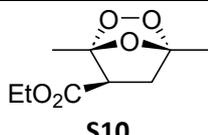
<pre> C 0.79173600 1.67650700 0.30368800 H 0.58168100 2.09548200 1.29044000 H 1.45712500 2.36405300 -0.21897500 O -2.36157500 0.01900200 -0.62656700 O 2.05506700 -0.04318400 -0.69485800 O -0.43469100 -0.84487600 0.14013400 O -3.21623200 -0.85463000 0.09814700 H -2.90275300 -1.73215000 -0.17353000 O 2.85383700 -1.19359400 -0.47878300 H 2.21443900 -1.91810300 -0.57306500 O 0.63651400 -0.63500600 1.05286800 C 1.50871100 0.35740800 0.53055000 H 2.28672900 0.41974000 1.29586500 C -1.26382700 0.32794900 0.16399400 H -1.56577700 0.51929800 1.19819900 C -0.51729500 1.47977600 -0.46711700 H -1.12544200 2.38388000 -0.41834800 H -0.32532000 1.23626400 -1.51479700 </pre>	
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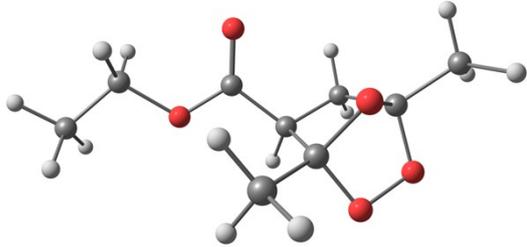
 <p style="text-align: center;">S7</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-456.693759	-456.579409	-456.614778
<pre> C 0.77015100 1.39936900 0.00016300 H 1.18199600 1.88396500 0.88532300 H 1.18233700 1.88450200 -0.88454100 O 0.72672200 -0.72772500 -1.15179800 O -0.72658900 -0.72787400 1.15179100 O -0.72674900 -0.72810900 -1.15154800 O 0.72688000 -0.72801800 1.15152900 C 1.19820900 -0.05220600 -0.00011700 H 2.27813100 -0.20311800 -0.00019000 C -1.19820100 -0.05241200 0.00010800 H -2.27809400 -0.20354000 0.00017900 C -0.77040500 1.39923800 -0.00013000 H -1.18267200 1.88427800 0.88458400 H -1.18232100 1.88378900 -0.88528300 </pre>		

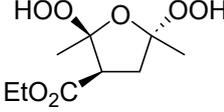
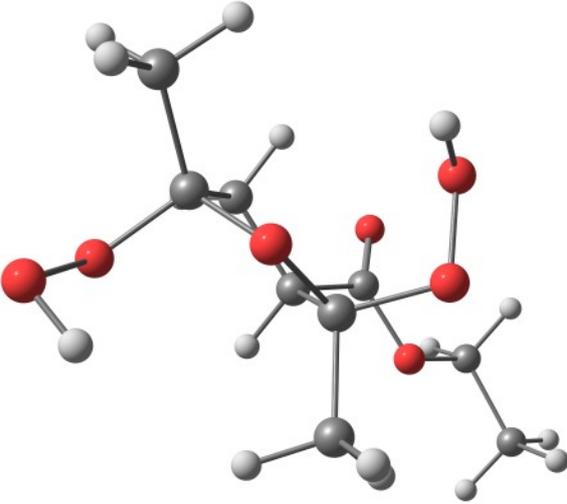
 <p style="text-align: center;">S8</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-652.243093	-652.004218	-652.065220

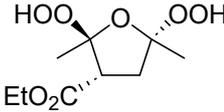
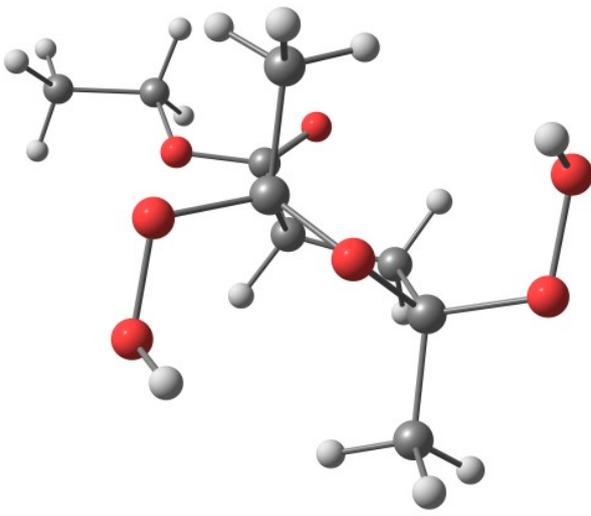
<pre> H -2.18448300 -2.15617300 -0.82082500 C -2.62191600 -1.22799300 -0.44843700 H -2.95124700 -0.63106000 -1.30140800 O -1.59855400 -0.49217200 0.25716200 C -3.74486500 -1.48470200 0.52634200 H -4.53925800 -2.03985000 0.02364100 H -4.16010300 -0.54484500 0.89550800 H -3.39420800 -2.07489200 1.37513000 C -0.52157100 -0.15575700 -0.44477300 O -0.35829000 -0.43675800 -1.60660000 C 0.46100900 0.67337600 0.36561700 H 0.26508800 0.47210500 1.42326700 C 1.89272900 0.32761000 0.00063000 H 2.59171200 0.95252500 0.56268500 H 2.08513300 0.53263400 -1.05707000 C 2.22734500 -1.12410200 0.26575900 O 1.39101500 -1.90292700 0.67211800 C 3.64800900 -1.53549300 -0.00077400 H 3.92142500 -1.27443600 -1.02642500 H 3.77224000 -2.60510600 0.16075100 H 4.31454700 -0.97876100 0.66395700 C 0.15626500 2.16254600 0.14806100 O 1.02879200 2.92633800 -0.19035400 C -1.26011900 2.60894700 0.38202500 H -1.88445400 2.25833500 -0.44704900 H -1.30292200 3.69611500 0.42348700 H -1.65849400 2.17097400 1.29904500 </pre>	
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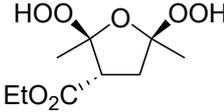
 <p style="text-align: center;">S9</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-727.370402	-727.124825	-727.180104
<pre> H -3.16045600 -0.76662100 1.31531400 C -3.35359700 -0.54424200 0.26427500 H -3.65574200 -1.46568700 -0.23701400 O -2.12637300 -0.07769100 -0.33785400 C -4.37972000 0.55015300 0.09991800 H -5.32410600 0.22918400 0.54391600 H -4.55070400 0.76701400 -0.95630300 H -4.05551800 1.46416200 0.60151300 C -1.07483500 -0.89436300 -0.26463000 O -1.11280000 -1.98460500 0.24649600 C 0.14089600 -0.26422700 -0.90659800 C 1.41290300 -1.13232900 -0.84812900 H 1.84140600 -1.28932700 -1.83771300 H 1.24814600 -2.09076100 -0.35927900 C 2.32617200 -0.23137200 -0.01923800 C 3.79964800 -0.49467000 -0.00459100 H 3.98921900 -1.48735700 0.40694000 H 4.30934200 0.25460300 0.60165800 H 4.17843200 -0.46237200 -1.02690600 C 0.61607500 0.99315500 -0.12823200 O 0.66108100 0.62952100 1.26450200 O 1.82839000 -0.22280000 1.33955800 O 1.98267000 1.07060200 -0.45650000 H -0.12251500 0.02912300 -1.92428600 C -0.10662900 2.29511800 -0.28914400 H 0.43212600 3.07643500 0.24784800 H -1.11972900 2.21247500 0.10243100 H -0.15912500 2.54558000 -1.34951900 </pre>		

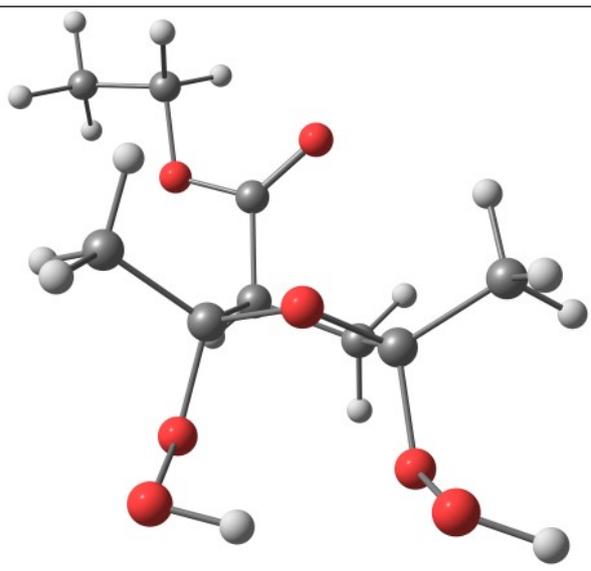
 <p style="text-align: center;">S10</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
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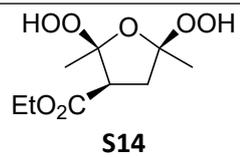
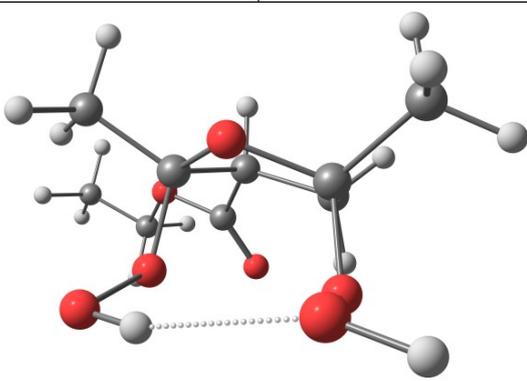
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-727.370489	-727.124832	-727.180112
H 3.70026900 -1.52641500 -0.06916900 C 3.50122800 -0.49186900 0.21652400 H 3.36899800 -0.44970200 1.29961700 O 2.26940300 -0.07233000 -0.41050600 C 4.58802200 0.44294700 -0.25480700 H 5.53612800 0.15424400 0.20314800 H 4.36480700 1.47251300 0.03181700 H 4.69908100 0.39363600 -1.33969500 C 1.17386800 -0.76113800 -0.09179200 O 1.17611000 -1.71810900 0.64191800 C -0.05395900 -0.15664800 -0.73406300 H 0.23039000 0.30993400 -1.67551700 C -1.23918800 -1.13565000 -0.84707400 H -0.99715100 -2.09911600 -0.39800000 H -1.58384700 -1.27708500 -1.86980000 C -2.29173600 -0.41980100 0.00126300 C -3.47909400 -1.18791300 0.49175800 H -4.04641900 -1.56673500 -0.35990200 H -4.11789800 -0.54605700 1.09894700 H -3.13442600 -2.03457200 1.08672700 C -0.68264400 0.92055800 0.19461600 C 0.19931600 1.88878400 0.92236000 H 0.79684400 2.45559700 0.20720600 H 0.87152300 1.34757800 1.59085100 H -0.41728600 2.57172600 1.50711700 O -1.62075400 1.64821600 -0.62140600 O -2.74000000 0.73919200 -0.73307600 O -1.53049600 0.17788400 1.03481400		

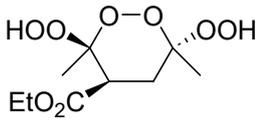
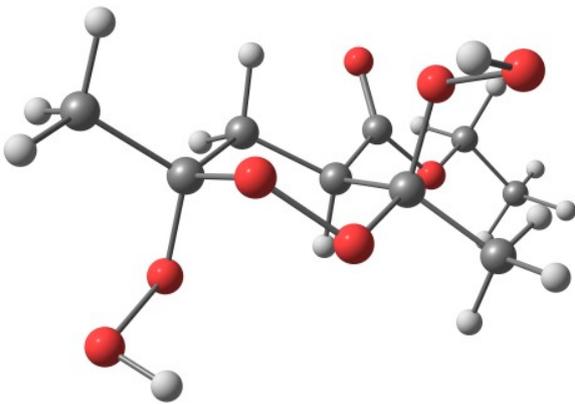
 S11		Multiplicity = 1
		Charge = 0
		Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-878.944577	-878.665312	-878.728531
H -3.86510200 -0.91638000 0.51553800 C -3.78240400 -0.28226400 -0.36925600 H -4.04088000 -0.87578300 -1.24839300 O -2.41140700 0.15134300 -0.49444900 C -4.63665800 0.95671800 -0.25514700 H -5.68467000 0.66610600 -0.15904600 H -4.53186000 1.58320800 -1.14312300 H -4.35692800 1.53969400 0.62456300 C -1.48655200 -0.80411900 -0.56682600 O -1.73757700 -1.98221400 -0.58585800 C -0.10095100 -0.21255000 -0.68218500 C 1.02125100 -1.24185700 -0.69577200 H 1.23261800 -1.64019900 -1.68748500 H 0.80015100 -2.06510500 -0.01704000 C 2.19814100 -0.44208500 -0.15488600 C 3.28009300 -1.22552100 0.54598900 H 2.84678100 -1.76130800 1.39213000 H 4.06394300 -0.56028800 0.90668500 H 3.71138600 -1.94803200 -0.14917300 C 0.27387300 0.75952400 0.47095000 O -0.43385900 0.52635500 1.67347900 H -0.09089100 0.37095100 -1.60662700 C 0.04159700 2.22372200 0.17321800 H 0.36669000 2.82975500 1.02030900 H -1.01650500 2.40217500 -0.02201800 H 0.61995400 2.49951400 -0.71028800 O -0.28894400 -0.83360800 2.04591300 H 0.57109900 -0.83680300 2.49871800 O 1.64632100 0.50570600 0.73954900 O 2.69454400 0.26084500 -1.29856900 O 3.69867300 1.17458000 -0.89353500 H 3.18186300 1.89903000 -0.50349900		

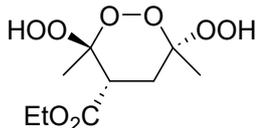
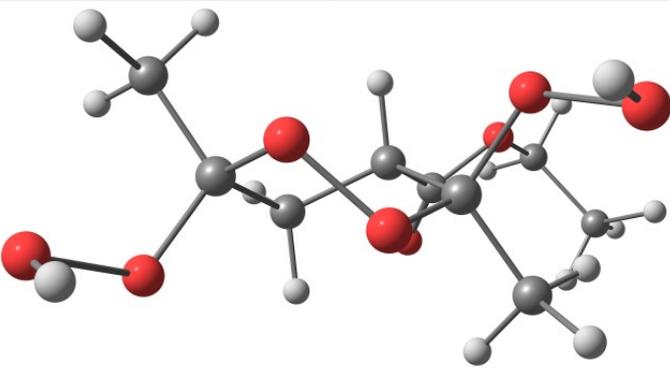
 <p style="text-align: center;">S12</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-878.942453	-878.663129	-878.726558
<pre> H 3.97149700 -1.34236900 -0.99413200 C 3.75199200 -0.68672000 -0.14942600 H 3.68734700 -1.29474200 0.75533200 O 2.46806800 -0.06398200 -0.37383000 C 4.77044500 0.41843400 -0.01303400 H 5.75613700 -0.01839400 0.15906000 H 4.52726700 1.06735100 0.83057500 H 4.81313900 1.02110600 -0.92226700 C 1.42208700 -0.87936000 -0.49197400 O 1.50256800 -2.08224400 -0.46375300 C 0.14052900 -0.09680000 -0.64471700 C -1.07389900 -0.94096800 -0.99789600 H -1.04692800 -1.88569100 -0.45466900 H -1.16161900 -1.13892400 -2.06530300 C -2.23503700 -0.08706900 -0.48945400 C -2.85916800 0.81957100 -1.52780300 H -2.07148500 1.40293600 -2.00894800 H -3.56979600 1.49749200 -1.05203200 C -3.36969800 0.22665600 -2.28821200 H -0.29091100 0.58895000 0.67581700 O 0.21258700 1.90068700 0.82660200 H 0.30412000 0.68951200 -1.38362000 C 0.12454800 -0.12750400 1.94403600 H 1.20716400 -0.08353300 2.07827100 H -0.18537900 -1.17280500 1.88397100 H -0.36382700 0.34126300 2.79950100 O -0.17065000 2.69728800 -0.27889300 H -1.09765800 2.90724800 -0.07562300 O -1.70371600 0.67920800 0.59007700 O -3.32091600 -0.83778900 0.02360400 O -2.87365200 -1.69095000 1.06179000 H -2.81809400 -1.08605500 1.82002900 </pre>		

 <p style="text-align: center;">S13</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-878.942958	-878.663620	-878.726811

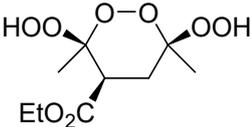
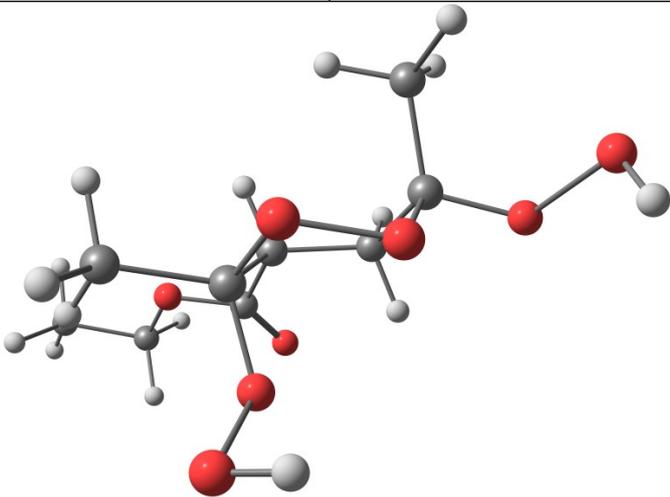
<pre> H 4.11225300 -1.47502400 -0.08386800 C 3.89561400 -0.46687900 0.27386300 H 3.68281800 -0.51497100 1.34383700 O 2.71325500 0.01501100 -0.40345300 C 5.01565900 0.49556700 -0.03566200 H 4.77408500 1.49889900 0.32060100 H 5.20590200 0.53692200 -1.10980300 H 5.92682000 0.16107600 0.46415500 C 1.60066200 -0.69360800 -0.23309300 O 1.54503000 -1.71870700 0.40020500 C 0.41341200 -0.03217000 -0.89933800 C -0.70209200 -1.03204400 -1.22789700 H -0.32861700 -2.05046300 -1.31615100 H -1.20337200 -0.75518500 -2.15468300 C -1.68654000 -0.91630400 -0.04825400 C -1.94689500 -2.18339500 0.72854600 H -2.43419200 -2.91616600 0.08231100 H -2.57890700 -1.98093600 1.59328600 H -0.99222800 -2.58552600 1.06889100 C -0.28127700 0.90067200 0.11727300 O -1.02816100 1.77502500 -0.74015400 O -2.88168000 -0.39401900 -0.64359900 O -1.14850000 0.05558000 0.82568100 H 0.75681400 0.53993400 -1.76014700 C 0.56690500 1.67757500 1.09271000 H -0.07883800 2.31083400 1.70156500 H 1.27702900 2.30141500 0.54883300 H 1.11261600 0.99807100 1.75023100 O -2.02259400 2.43928100 0.01575300 H -2.72883700 1.77212200 0.05493500 O -3.83094200 -0.11821600 0.38132700 H -4.52730300 -0.76911100 0.20103200 </pre>	
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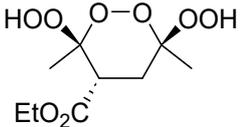
 <p style="text-align: center;">S14</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-878.942357	-878.663019	-878.726777
<pre> H 3.67366400 -0.01801600 -1.47779300 C 3.84544500 -0.35114400 -0.45256900 H 4.17040400 -1.39296800 -0.47473800 O 2.59521100 -0.27678500 0.26747000 C 4.83295800 0.53294800 0.26891600 H 5.79328200 0.49866900 -0.24933400 H 4.98169900 0.19185800 1.29525500 H 4.48632800 1.56810600 0.28594700 C 1.57473000 -0.96911500 -0.23553900 O 1.65671100 -1.66742400 -1.21365700 C 0.32348300 -0.77072000 0.59408000 C -0.87836400 -1.59299100 0.11998100 H -0.99727700 -2.51322600 0.68901600 H -0.78129500 -1.84399700 -0.93629700 C -2.08174900 -0.65873500 0.33053400 C -3.18598000 -1.18066200 1.21704200 H -3.63716500 -2.06364900 0.76047200 H -3.94896300 -0.41705100 1.36913000 H -2.76473700 -1.45769100 2.18445600 C -0.21314700 0.67538200 0.56019100 O -0.08111800 1.04377900 -0.81767400 O -2.54681600 -0.38470800 -0.99762000 O -1.56966200 0.53303700 0.89371900 H 0.57431700 -0.99174700 1.63395900 C 0.41614000 1.69073800 1.47913200 H -0.09367000 2.64805800 1.36631200 H 1.47021200 1.80922500 1.22995600 H 0.32499400 1.35570000 2.51317000 O -0.86173200 2.19381900 -1.07953800 H -1.75130200 1.81624500 -1.18866400 O -3.56122200 0.61233300 -0.93738900 H -4.35255800 0.12386300 -1.21395600 </pre>		

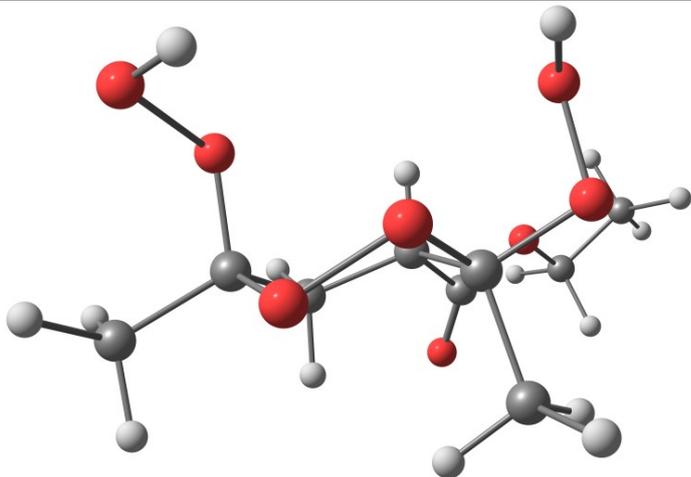
 <p style="text-align: center;">S15</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-954.072858	-953.788554	-953.854557
<pre> H 4.10517000 -0.17943100 -1.00555400 C 3.94956300 -0.80807500 -0.12688000 H 4.04050200 -1.85396900 -0.42581300 O 2.60654400 -0.58805600 0.36074700 C 4.89707200 -0.45639500 0.99363500 H 5.92445300 -0.61402200 0.65956500 H 4.71672500 -1.08673600 1.86650600 H 4.78448900 0.59037100 1.28278900 C 1.61625600 -0.80887500 -0.50026400 O 1.78285400 -1.21206200 -1.62318700 C 0.26004200 -0.51297200 0.11820700 C -0.84843500 -1.17863800 -0.69584900 H -0.78247800 -2.26402900 -0.60345900 H -0.74550400 -0.92113100 -1.75019300 C -2.22444800 -0.71800700 -0.24192400 C -3.34289500 -1.12951600 -1.17232500 H -3.17797400 -0.69944500 -2.16064400 H -4.30410600 -0.79395800 -0.78546700 H -3.34362300 -2.21773900 -1.25452500 C 0.00280100 1.00261100 0.25099900 O 0.14454800 1.49916900 -1.06316200 H 0.27103300 -0.89820500 1.13986700 C 0.86489500 1.72589800 1.26466000 H 0.49641900 2.74190400 1.39929900 H 1.89363700 1.75980500 0.90888900 H 0.83547700 1.19906600 2.21862300 O -0.12688900 2.88782900 -1.08684900 H -1.08558800 2.90819700 -1.24275900 O -1.32472200 1.21506800 0.71713800 O -2.36802100 -1.24097600 1.06654600 O -3.59539600 -0.81515800 1.62822500 H -3.35618000 0.03491600 2.03176800 O -2.28411400 0.70396500 -0.20201400 </pre>		

 <p style="text-align: center;">S16</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-954.072997	-953.788494	-953.852476
<pre> H 4.43080300 -0.69147200 -1.51970600 C 3.90359500 -0.96212800 -0.60648800 H 3.90272600 -2.04710000 -0.50023200 O 2.54625700 -0.51587800 -0.83353600 C 4.50278800 -0.27674900 0.60271100 H 3.95890700 -0.53601200 1.51287000 H 4.49029400 0.80764800 0.47449400 H 5.54064300 -0.59695500 0.71920200 C 1.59262300 -1.06767800 -0.08824300 O 1.78003400 -1.94742500 0.71403500 C 0.23806800 -0.45223700 -0.37996600 C -0.89129800 -1.28885300 0.21233100 H -0.81113900 -1.30186600 1.30124800 H -0.83828400 -2.31619200 -0.14672700 C -2.22746700 -0.67061300 -0.20001500 C -2.79820000 -1.21716900 -1.49111200 H -3.64577800 -0.62162200 -1.82755800 H -3.12314500 -2.24506200 -1.32399100 O -2.02397600 -1.20775700 -2.26021700 </pre>		

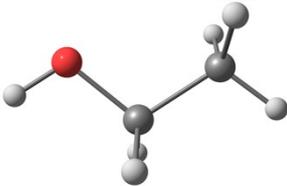
C	0.13872400	0.98449500	0.18722300
O	0.49459400	1.81402700	-0.89901800
H	0.13102800	-0.38656900	-1.46620300
C	0.94912300	1.24171700	1.44099000
H	0.66828000	2.19549800	1.88483700
H	2.01021600	1.26832500	1.18817600
H	0.76604400	0.44435700	2.16338300
O	0.51114200	3.16777300	-0.48137300
H	-0.41591500	3.43446200	-0.59284200
O	-1.20470300	1.24580500	0.57209600
O	-3.07014100	-0.87723600	0.91747900
O	-4.38019300	-0.42258000	0.62325800
H	-4.33507100	0.51715800	0.86296800
O	-2.07116300	0.72781900	-0.42972800

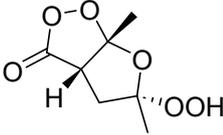
 <p style="text-align: center;">S17</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-954.067237	-953.782874	-953.849000
<pre> H 3.99229700 -0.45176900 -1.27013600 C 3.94539000 -0.90352900 -0.27752900 H 4.01301800 -1.98766600 -0.38398600 O 2.66463100 -0.58099500 0.31074500 C 5.01072000 -0.35810200 0.64145500 H 5.99486100 -0.58665100 0.22766500 H 4.93815600 -0.81144300 1.63188100 H 4.92055100 0.72549000 0.73989500 C 1.58456500 -0.94478500 -0.37535000 O 1.62423000 -1.55726600 -1.41154700 C 0.30394900 -0.51351000 0.32444500 C -0.89410900 -1.23646500 -0.29645200 H -0.84847600 -2.29918300 -0.05293400 H -0.86992400 -1.12504200 -1.38134100 C -2.20110000 -0.64845400 0.20948900 C -2.52784600 -0.95400400 1.65539300 H -2.70760200 -2.02611400 1.75455500 H -3.41480000 -0.40727900 1.97074000 H -1.69500400 -0.67903100 2.30185900 C 0.12149900 1.02073900 0.29372800 O 0.24275600 1.35428200 -1.07283500 O -3.17051900 -1.11664600 -0.69212900 O -1.17580200 1.35970200 0.77390100 H 0.40822100 -0.78063300 1.37887300 C 1.05153000 1.81014000 1.19234900 H 0.73294900 2.85124500 1.22082900 H 2.06791400 1.75322900 0.80729900 H 1.02838400 1.39696600 2.20127700 O 0.03550800 2.74249300 -1.25115400 H -0.92482300 2.79144900 -1.38905800 O -4.47099900 -0.73691700 -0.26662700 H -4.60748700 0.09958800 -0.73977800 O -2.17428300 0.77343100 -0.04320600 </pre>		

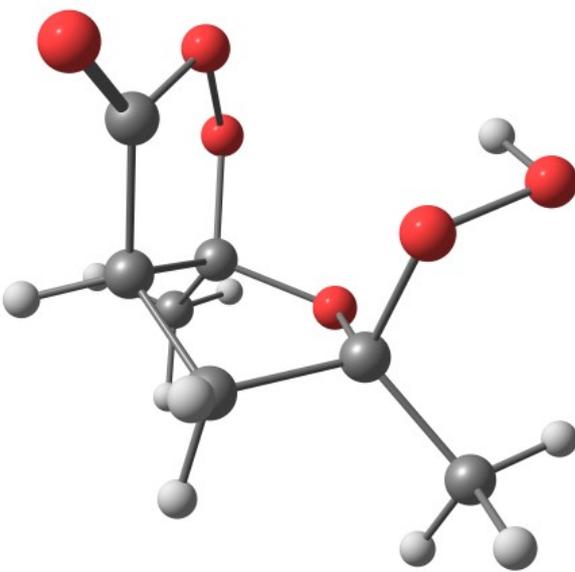
 <p style="text-align: center;">S18</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-954.068330	-953.783960	-953.849500

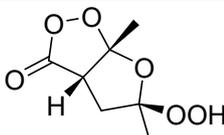
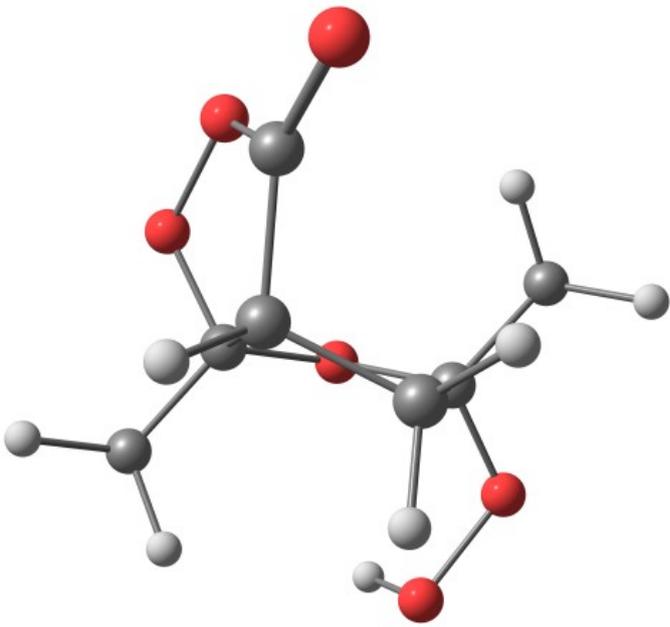
<pre> H 3.95500500 -1.71916500 -0.85570300 C 3.87870200 -0.77224800 -0.31780700 H 4.03636500 -0.96236400 0.74571200 O 2.54363300 -0.25011900 -0.49612100 C 4.83963900 0.26010400 -0.85450400 H 4.65752100 0.44481400 -1.91493000 H 5.86255700 -0.10316000 -0.73741600 H 4.74163000 1.20095700 -0.30958400 C 1.54519400 -1.00780900 -0.05649000 O 1.69721700 -2.09689800 0.44086600 C 0.20237700 -0.33019500 -0.25006400 C -0.92555100 -1.36400500 -0.22481000 H -0.83140100 -2.00886400 0.65036800 H -0.87169000 -1.99723600 -1.11218000 C -2.29080800 -0.69913800 -0.16087700 C -3.42314800 -1.65370900 0.14328500 H -3.43819400 -2.43069800 -0.62275800 H -4.37598400 -1.12616600 0.14434700 H -3.26378800 -2.11877700 1.11668500 C -0.02696400 0.74261700 0.83281200 O 0.78656100 1.87530700 0.67800800 O -2.43571700 -0.04168200 -1.40602400 O -1.35682900 1.26914800 0.66518800 H 0.21897100 0.18999800 -1.20727000 C 0.20929600 0.28641500 2.25649700 H -0.06233800 1.09157000 2.94001700 H 1.26129200 0.03314100 2.39943900 H -0.39763100 -0.59102600 2.47896400 O 0.71044300 2.38532300 -0.64384500 H -0.02531500 3.01535700 -0.58100600 O -3.64158500 0.69919300 -1.42726700 H -3.37666400 1.53942600 -1.01840700 O -2.32157000 0.25597900 0.89862700 </pre>	
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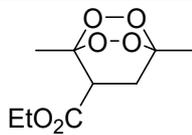
Ethanol

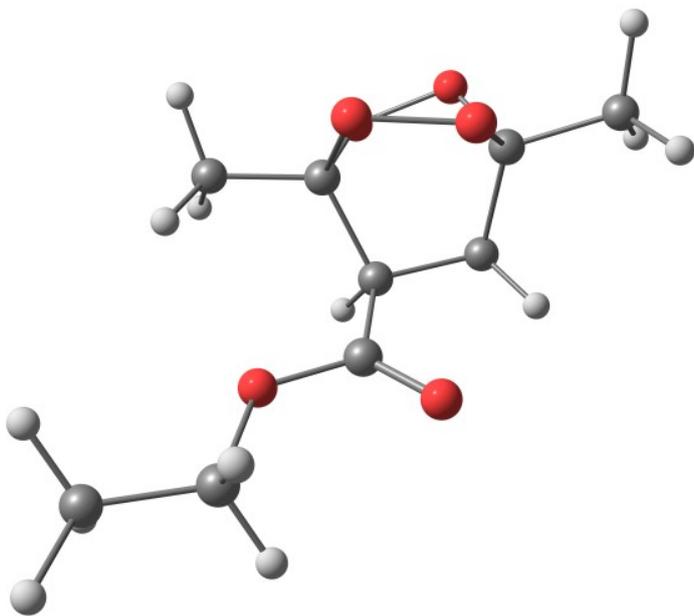
		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-155.020217	-154.934651	-154.965478
<pre> C 0.08123900 0.54710600 -0.00000200 H 0.14307100 1.18847100 -0.88618400 H 0.14308400 1.18846300 0.88618600 C -1.22048100 -0.22220700 0.00000400 H -2.06762000 0.46743000 -0.00015000 H -1.29080100 -0.85570800 0.88730200 H -1.29065700 -0.85591600 -0.88715800 O 1.15186600 -0.39630900 -0.00000700 H 1.98345400 0.08834000 0.00004300 </pre>		

 <p style="text-align: center;">S20</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-723.907300	-723.716643	-723.766621

<pre> C 1.43964200 -1.08140800 0.40629600 O 1.64443800 -2.14979200 0.89454000 C 0.92561500 0.19163000 1.03526400 C -0.47886300 0.01552100 1.61013900 H -0.71698900 0.84317200 2.27867600 H -0.62012000 -0.92835400 2.13602700 C -1.33942900 0.11635700 0.35342400 C 0.71991100 1.09867800 -0.17578300 O 1.50423100 0.50528500 -1.21688000 H 1.65996400 0.57176700 1.74463800 C 1.14868000 2.54044100 -0.08620800 H 0.94187700 3.04383800 -1.03259900 H 2.21240100 2.60634700 0.14046700 H 0.57503100 3.02619400 0.70446300 O 1.64908300 -0.88478600 -0.92590700 O -0.65791000 1.02924100 -0.49006000 C -2.76643800 0.56202900 0.53602000 H -3.27783200 0.59871600 -0.42555100 H -2.78122900 1.55368900 0.98928300 H -3.28239300 -0.14069600 1.19243400 O -1.24987700 -1.19154200 -0.21863100 O -1.82604000 -1.18631800 -1.51103100 H -1.11681400 -0.81085300 -2.05899100 </pre>	
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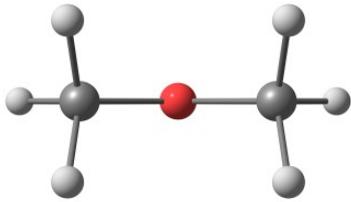
 <p style="text-align: center;">S21</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-723.904469	-723.713861	-723.763679
<pre> C 1.93956000 -0.54259400 0.39182000 O 2.52387300 -1.51867500 0.75156000 C 0.75759400 0.16808000 1.00959800 C -0.44219100 -0.75263300 1.18999100 H -1.12933900 -0.32195600 1.91646700 H -0.16308600 -1.75681100 1.50813100 C -1.08994100 -0.76122700 -0.20398500 C -0.81505700 -1.99740500 -1.03277000 H 0.26263300 -2.15448800 -1.11127000 H -1.22626000 -1.86913600 -2.03495500 H -1.26131900 -2.87318700 -0.55979000 C 0.34961400 1.11286100 -0.11417800 O 1.53565300 1.28012000 -0.89055000 H 1.07803800 0.68153000 1.91649300 C -0.13333200 2.49662300 0.23632200 H -0.41456100 3.02926300 -0.67413100 H 0.64582400 3.04847700 0.76183500 H -1.00768600 2.40928900 0.88294600 O 2.28504800 0.07136300 -0.77364800 O -0.60374500 0.40054000 -0.87367800 O -2.50288100 -0.68026000 -0.16337300 O -2.89914100 0.48520200 0.53677300 H -2.89218800 1.15847600 -0.16318400 </pre>		

 <p style="text-align: center;">S22</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
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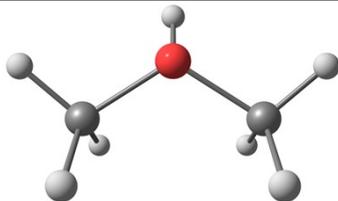
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-802.497197	-802.246687	-802.303530
<pre> H -3.22893500 -1.09287700 1.23205900 C -3.44901500 -0.74806800 0.22025500 H -3.67724700 -1.61548700 -0.40187600 O -2.26902200 -0.10381000 -0.31071500 C -4.56282000 0.26990600 0.20073700 H -5.47428600 -0.18580900 0.59250600 H -4.75778900 0.61263300 -0.81726700 H -4.31269100 1.13132200 0.82319400 C -1.15534600 -0.83286100 -0.34951600 O -1.10002100 -1.98158500 0.00677100 C 0.00557400 -0.03879300 -0.93125100 C 1.27362300 -0.88987000 -1.09058200 H 1.76956800 -0.68980200 -2.04041700 H 1.04014000 -1.95137400 -1.02163800 C 2.20891100 -0.51113800 0.04529000 C 3.37430800 -1.43351800 0.27606600 H 3.00178600 -2.39439700 0.63406700 H 4.05064700 -1.00719800 1.01763400 H 3.90345900 -1.58712600 -0.66521000 C 0.40848000 1.15030000 -0.03722800 O 1.45120500 -0.48283200 1.26902500 O 1.64704200 1.65794500 -0.56299800 H -0.32588100 0.37022200 -1.88747300 C -0.51976500 2.33524000 0.03050400 H -0.08239700 3.09295200 0.68106200 H -1.49213000 2.03186400 0.41152100 H -0.64308700 2.74587500 -0.97282700 O 0.63943800 0.71277400 1.28173800 O 2.72200100 0.78901000 -0.15519500 </pre>		

Data for column 3 of Table S1 can be found above (see XYZ data for main mechanistic scheme (and Scheme S5)).

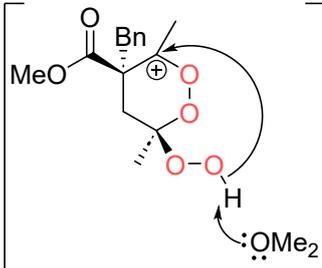
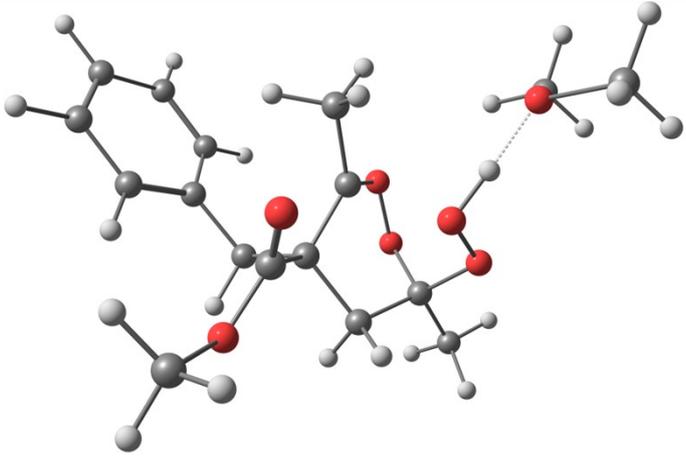
XYZ data for Scheme S1

Me ₂ O		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-154.998615	-154.913190	-154.943842
<pre> O 0.00000000 0.59585500 0.00000000 C 1.16570500 -0.19731800 0.00000000 H 1.20891200 -0.83629300 -0.89138100 H 1.20887900 -0.83634300 0.89134700 C -1.16570500 -0.19731800 0.00000000 H -1.20891500 -0.83629000 0.89138400 H -1.20887700 -0.83634700 -0.89134400 H -2.02553100 0.47312600 -0.00004100 H 2.02553100 0.47312600 0.00003600 </pre>		

Me ₂ OH ⁺	Multiplicity = 1 Charge = +1
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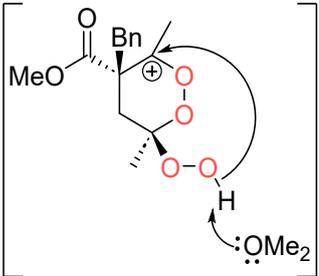
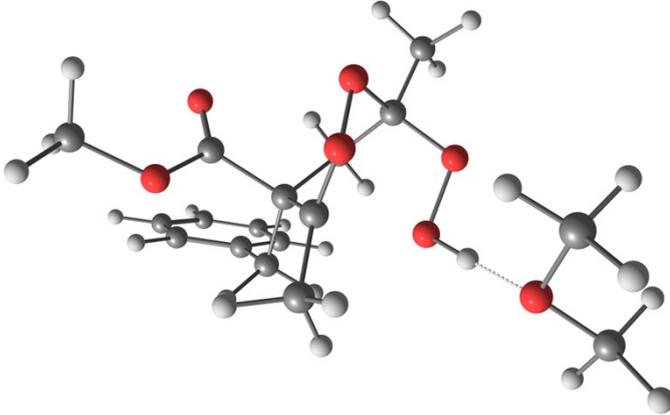
		Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-155.410845	-155.311540	-155.343201
<pre> O -0.00000500 0.52305600 -0.12581000 C -1.24433300 -0.25115100 0.02388200 H -2.05603500 0.46074000 -0.09429600 H -1.24094000 -0.71993600 1.00557400 C 1.24432600 -0.25116100 0.02387800 H 1.23161900 -0.97783100 -0.78328900 H 1.23962900 -0.72222900 1.00447300 H 2.05601100 0.46124300 -0.09138300 H -1.23019800 -0.97974800 -0.78152800 H -0.00000400 1.30718800 0.46037500 </pre>		

Transition state for cyclization of C-OOH-CO₂Me-cis to 5

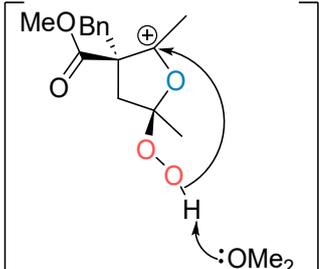
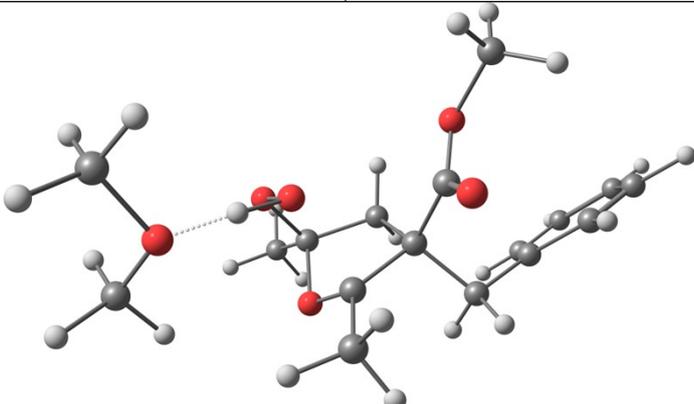
		<p>Multiplicity = 1 Charge = +1 Imaginary vib. modes: 1</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1188.921957	-1188.487563	-1188.569762
<pre> H -2.69763100 2.59093100 -2.57609700 C -2.00654300 3.24385400 -2.04297400 H -1.17517300 3.51873600 -2.69152400 O -1.51200200 2.57820800 -0.86578500 C -0.85794600 1.44317300 -1.07064200 O -0.65281800 0.96550400 -2.15375200 C -0.38437600 0.88228100 0.27125500 O 0.60052900 1.90168600 0.91205300 H 0.08253000 2.45768500 1.69377500 H 0.97913600 2.60812100 0.17258400 C 1.77477800 1.16872100 1.53144700 C 2.50380900 1.91087300 2.62029000 H 1.84365900 2.03494900 3.47910500 H 2.78341700 2.89405700 2.24003000 H 3.39580900 1.35831000 2.91640800 C 0.29681700 -0.45220700 0.11666300 O 2.72727100 0.78522500 0.57306100 O 0.88595500 -0.95895600 1.15605100 C 0.02150900 -1.48502900 -0.90843100 H 0.48751000 -2.42752600 -0.62312700 H 0.38748700 -1.14097100 -1.87519200 H -1.06239600 -1.60329800 -1.00060900 O 1.25307200 -0.02539400 2.17898100 O 2.03698200 0.42715000 -0.63112400 H 2.61754800 -0.37460400 -0.95097300 H -2.51951800 4.13051500 -1.68103900 C -1.60526100 0.66072000 1.23886000 H -1.20638200 0.40585000 2.22174900 H -2.08062000 1.63970700 1.31761100 C -2.59533200 -0.38286200 0.78623200 C -3.49179000 -0.11436000 -0.25211200 C -2.60023800 -1.64931900 1.37457800 C -4.35924900 -1.10193300 -0.70887300 H -3.52369300 0.87445900 -0.70026700 C -3.47036400 -2.63730600 0.92125500 H -1.91889400 -1.86235600 2.19284700 C -4.34614200 -2.36758000 -0.12668300 H -5.04925000 -0.88101300 -1.51519900 H -3.46421600 -3.61586400 1.38762100 H -5.02252700 -3.13632600 -0.48233100 </pre>		

O	3.39022000	-1.53775000	-1.32659600
C	4.39556300	-1.32830500	-2.31928700
H	3.96236600	-0.69342900	-3.09080100
H	4.68671700	-2.28895500	-2.74995300
H	5.26701600	-0.83885700	-1.87582300
H	4.12227600	-3.33145600	-0.60684800
C	3.84743900	-2.34069400	-0.23786900
H	4.70917900	-1.87031700	0.24367000
H	3.02700600	-2.43053200	0.47312600

Transition state for cyclization of C-OOH-CO2Me-trans to 5

		<p>Multiplicity = 1</p> <p>Charge = +1</p> <p>Imaginary vib. modes: 1</p>																																																																																																																																																																																																				
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)																																																																																																																																																																																																				
-1188.923642	-1188.489195	-1188.57196																																																																																																																																																																																																				
<table border="1"> <tbody> <tr><td>H</td><td>-2.94934900</td><td>3.38916000</td><td>-0.39580900</td></tr> <tr><td>C</td><td>-1.88850900</td><td>3.63590500</td><td>-0.42757900</td></tr> <tr><td>H</td><td>-1.66674100</td><td>4.27039400</td><td>-1.28095500</td></tr> <tr><td>O</td><td>-1.11534600</td><td>2.43501300</td><td>-0.63140000</td></tr> <tr><td>C</td><td>-1.22346500</td><td>1.50041700</td><td>0.30282300</td></tr> <tr><td>O</td><td>-1.89852600</td><td>1.58489300</td><td>1.28716400</td></tr> <tr><td>C</td><td>-0.39271700</td><td>0.24670300</td><td>-0.08622900</td></tr> <tr><td>C</td><td>-0.18628600</td><td>-0.63996200</td><td>1.15588300</td></tr> <tr><td>H</td><td>-0.18453700</td><td>-1.69290200</td><td>0.87742800</td></tr> <tr><td>H</td><td>-0.99294700</td><td>-0.45902500</td><td>1.86456200</td></tr> <tr><td>C</td><td>1.14031900</td><td>-0.29863700</td><td>1.80818000</td></tr> <tr><td>C</td><td>1.24060400</td><td>-0.56152900</td><td>3.28612200</td></tr> <tr><td>H</td><td>0.93961300</td><td>-1.59302200</td><td>3.47305300</td></tr> <tr><td>H</td><td>0.56360900</td><td>0.10810900</td><td>3.81800500</td></tr> <tr><td>H</td><td>2.26346600</td><td>-0.40250600</td><td>3.62840300</td></tr> <tr><td>C</td><td>0.94477900</td><td>0.78110700</td><td>-0.55148100</td></tr> <tr><td>O</td><td>1.33634700</td><td>1.14665600</td><td>1.67219500</td></tr> <tr><td>C</td><td>1.33393000</td><td>1.02298200</td><td>-1.95311300</td></tr> <tr><td>H</td><td>2.35303300</td><td>1.40234000</td><td>-2.01172700</td></tr> <tr><td>H</td><td>0.63614700</td><td>1.76139000</td><td>-2.36217000</td></tr> <tr><td>H</td><td>1.22450100</td><td>0.10369100</td><td>-2.53125900</td></tr> <tr><td>O</td><td>1.68498800</td><td>1.40532000</td><td>0.30653100</td></tr> <tr><td>O</td><td>2.21067700</td><td>-0.95695300</td><td>1.18123900</td></tr> <tr><td>O</td><td>1.91725900</td><td>-1.05863300</td><td>-0.21905100</td></tr> <tr><td>C</td><td>-1.12095200</td><td>-0.49549300</td><td>-1.23483600</td></tr> <tr><td>H</td><td>-0.50418200</td><td>-1.35617800</td><td>-1.50479500</td></tr> <tr><td>H</td><td>-1.18730400</td><td>0.16518700</td><td>-2.10157400</td></tr> <tr><td>H</td><td>-1.58335100</td><td>4.11693300</td><td>0.50108900</td></tr> <tr><td>C</td><td>-2.50671400</td><td>-0.94690500</td><td>-0.83875200</td></tr> <tr><td>C</td><td>-3.59312500</td><td>-0.08051300</td><td>-0.98606700</td></tr> <tr><td>C</td><td>-2.72553600</td><td>-2.22180000</td><td>-0.31341000</td></tr> <tr><td>C</td><td>-4.87083000</td><td>-0.47364300</td><td>-0.60039500</td></tr> <tr><td>H</td><td>-3.43978900</td><td>0.90609400</td><td>-1.41537500</td></tr> <tr><td>C</td><td>-4.00360400</td><td>-2.61800100</td><td>0.07241200</td></tr> <tr><td>H</td><td>-1.89312200</td><td>-2.91131500</td><td>-0.21569200</td></tr> <tr><td>C</td><td>-5.07774900</td><td>-1.74325500</td><td>-0.06606000</td></tr> <tr><td>H</td><td>-5.70435300</td><td>0.20867700</td><td>-0.72230400</td></tr> <tr><td>H</td><td>-4.15981500</td><td>-3.61200700</td><td>0.47597400</td></tr> <tr><td>H</td><td>-6.07308400</td><td>-2.05203800</td><td>0.23250600</td></tr> <tr><td>H</td><td>2.86954000</td><td>-0.93960900</td><td>-0.61795700</td></tr> <tr><td>O</td><td>4.20160800</td><td>-0.70516900</td><td>-1.13868300</td></tr> <tr><td>C</td><td>4.97783400</td><td>0.23885600</td><td>-0.40028100</td></tr> <tr><td>H</td><td>5.80895100</td><td>0.58914600</td><td>-1.01667600</td></tr> <tr><td>H</td><td>4.32804700</td><td>1.07758500</td><td>-0.15286300</td></tr> <tr><td>H</td><td>5.36067000</td><td>-0.21981400</td><td>0.51547300</td></tr> <tr><td>C</td><td>4.94168000</td><td>-1.87416500</td><td>-1.49340100</td></tr> <tr><td>H</td><td>5.77227700</td><td>-1.59566800</td><td>-2.14586300</td></tr> <tr><td>H</td><td>5.32269200</td><td>-2.36641800</td><td>-0.59442600</td></tr> <tr><td>H</td><td>4.26201700</td><td>-2.53960500</td><td>-2.02389300</td></tr> </tbody> </table>		H	-2.94934900	3.38916000	-0.39580900	C	-1.88850900	3.63590500	-0.42757900	H	-1.66674100	4.27039400	-1.28095500	O	-1.11534600	2.43501300	-0.63140000	C	-1.22346500	1.50041700	0.30282300	O	-1.89852600	1.58489300	1.28716400	C	-0.39271700	0.24670300	-0.08622900	C	-0.18628600	-0.63996200	1.15588300	H	-0.18453700	-1.69290200	0.87742800	H	-0.99294700	-0.45902500	1.86456200	C	1.14031900	-0.29863700	1.80818000	C	1.24060400	-0.56152900	3.28612200	H	0.93961300	-1.59302200	3.47305300	H	0.56360900	0.10810900	3.81800500	H	2.26346600	-0.40250600	3.62840300	C	0.94477900	0.78110700	-0.55148100	O	1.33634700	1.14665600	1.67219500	C	1.33393000	1.02298200	-1.95311300	H	2.35303300	1.40234000	-2.01172700	H	0.63614700	1.76139000	-2.36217000	H	1.22450100	0.10369100	-2.53125900	O	1.68498800	1.40532000	0.30653100	O	2.21067700	-0.95695300	1.18123900	O	1.91725900	-1.05863300	-0.21905100	C	-1.12095200	-0.49549300	-1.23483600	H	-0.50418200	-1.35617800	-1.50479500	H	-1.18730400	0.16518700	-2.10157400	H	-1.58335100	4.11693300	0.50108900	C	-2.50671400	-0.94690500	-0.83875200	C	-3.59312500	-0.08051300	-0.98606700	C	-2.72553600	-2.22180000	-0.31341000	C	-4.87083000	-0.47364300	-0.60039500	H	-3.43978900	0.90609400	-1.41537500	C	-4.00360400	-2.61800100	0.07241200	H	-1.89312200	-2.91131500	-0.21569200	C	-5.07774900	-1.74325500	-0.06606000	H	-5.70435300	0.20867700	-0.72230400	H	-4.15981500	-3.61200700	0.47597400	H	-6.07308400	-2.05203800	0.23250600	H	2.86954000	-0.93960900	-0.61795700	O	4.20160800	-0.70516900	-1.13868300	C	4.97783400	0.23885600	-0.40028100	H	5.80895100	0.58914600	-1.01667600	H	4.32804700	1.07758500	-0.15286300	H	5.36067000	-0.21981400	0.51547300	C	4.94168000	-1.87416500	-1.49340100	H	5.77227700	-1.59566800	-2.14586300	H	5.32269200	-2.36641800	-0.59442600	H	4.26201700	-2.53960500	-2.02389300	
H	-2.94934900	3.38916000	-0.39580900																																																																																																																																																																																																			
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C	1.24060400	-0.56152900	3.28612200																																																																																																																																																																																																			
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C	1.33393000	1.02298200	-1.95311300																																																																																																																																																																																																			
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O	1.68498800	1.40532000	0.30653100																																																																																																																																																																																																			
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H	-1.18730400	0.16518700	-2.10157400																																																																																																																																																																																																			
H	-1.58335100	4.11693300	0.50108900																																																																																																																																																																																																			
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Transition state for cyclization of B-OOH-CO₂Me-cis to 2 (endo-CO₂Me)

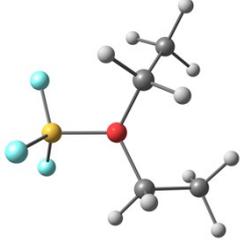
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H -1.71520800 -2.75275800 -2.61631300 C -1.31677100 -2.81336900 -1.60734200 H -2.05859700 -3.23135300 -0.92646900 O -1.01591300 -1.45780900 -1.23076200 C -0.53108800 -1.29096400 -0.01314400 O -0.30989600 -2.18922300 0.75957000 C -0.34405400 0.18008100 0.35052900 C -0.23967200 1.16390200 -0.83580000 H -0.93301500 1.99611200 -0.72089500 H -0.40067800 0.69728200 -1.80411800 C 1.18458800 1.69235200 -0.72928800 C 1.50209800 3.04855200 -1.26972500 H 0.85751200 3.78238700 -0.78576600 H 1.30240700 3.05662600 -2.34213100 H 2.54893600 3.29277500 -1.08783000 C 1.00362400 0.41099100 1.01734800 O 1.47234600 1.58761400 0.69671500 C 1.50215200 -0.21596300 2.25326500 H 0.90111900 0.18933400 3.07649500 H 2.54718100 0.04270200 2.41977400 H 1.34921200 -1.29312000 2.22363700 C -1.45614700 0.56471000 1.37687200 H -1.28049100 1.59749400 1.68772100 H -1.35703000 -0.08228600 2.25126300 C -2.83773400 0.42257100 0.78459700 C -3.48827200 1.51485900 0.20758800 C -3.47879700 -0.82015000 0.78884400 C -4.74696100 1.36554200 -0.37015900 H -3.01268700 2.49028300 0.22083100 C -4.73479400 -0.97184000 0.21066700 H -2.99421200 -1.67258000 1.25622600 C -5.37025300 0.12107600 -0.37520900 H -5.24112500 2.22352000 -0.81176400 H -5.22006900 -1.94125800 0.22377100 H -6.35016500 0.00443800 -0.82386900 H -0.40874200 -3.41566400 -1.58889700 H 2.95561700 -0.61531700 -0.18810100 O 2.12996300 0.76688100 -1.25909200 O 1.95210900 -0.41947700 -0.50325000 O 4.24871900 -0.76582000 0.24800400 C 5.04994800 -1.68984900 -0.49620900 H 5.34590900 -1.24496900 -1.44956800 H 5.93450000 -1.94864400 0.08859400 H 4.44326400 -2.57782300 -0.66615800 C 4.92210400 0.46782600 0.52127900 H 5.78920100 0.27019300 1.15443700 H 5.23745500 0.93857000 -0.41324400 H 4.22124900 1.11475600 1.04822400		

Transition state for cyclization of B-OOH-CO₂Me-trans to 2 (exo-CO₂Me)

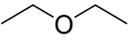
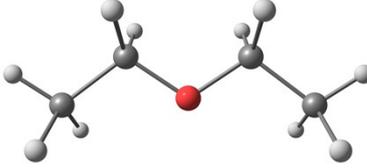
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<pre> H 2.05960100 3.96500400 0.07807800 C 2.39162000 3.22020700 -0.64472400 H 2.42061400 3.64287900 -1.64525700 O 1.44016300 2.14056900 -0.70938300 C 1.26921800 1.44627300 0.40582900 O 1.80841200 1.68629300 1.45036000 C 0.31143100 0.25307400 0.17031200 C 0.00527600 -0.46639800 1.49912500 H 0.62090400 -0.08975400 2.31319200 H 0.12719400 -1.54511200 1.41904300 C -1.46501000 -0.14644500 1.75910300 C -1.95009600 -0.00716200 3.16474500 H -1.37873100 0.77936000 3.65802000 H -1.78091400 -0.94800900 3.69036200 H -3.01250100 0.23747200 3.17762300 C -1.05347700 0.85557700 -0.13328000 C -1.46645100 1.59411800 -1.33960800 H -2.55052800 1.70022500 -1.36630800 H -1.09564600 1.10236900 -2.23852600 H -1.01694100 2.59118200 -1.28468600 O -1.91849000 -0.95665000 -0.28479900 O -1.70210200 1.07007200 0.97714800 H 3.37026500 2.83184700 -0.36181800 C 0.90596900 -0.62869900 -0.95433400 H 0.84341000 -0.08836700 -1.90014300 H 0.29384900 -1.52745800 -1.02823400 C 2.34767900 -0.99825600 -0.68114100 C 2.66492800 -2.08695300 0.13565000 C 3.38931600 -0.24329200 -1.22836300 C 3.99162300 -2.40199600 0.41568900 H 1.86964000 -2.70239200 0.54303000 C 4.71713200 -0.55675500 -0.94947900 H 3.15946000 0.58838600 -1.88669700 C 5.02148000 -1.63341400 -0.12111500 H 4.22045400 -3.25232400 1.04816400 H 5.51289600 0.03699100 -1.38511700 H 6.05475600 -1.87915500 0.09587600 H -2.85619400 -0.80654400 -0.75269100 O -2.31000000 -1.05784000 1.07343000 O -4.11878600 -0.52112800 -1.28364500 C -4.78931800 -1.59433400 -1.95038500 H -5.59695300 -1.18908100 -2.56324200 H -4.05518500 -2.08943000 -2.58399400 H -5.19150400 -2.29835000 -1.21731600 C -4.97153700 0.20586400 -0.39394100 H -5.76379900 0.69001100 -0.96849600 H -5.40455100 -0.46994400 0.34800700 H -4.36188500 0.96120200 0.10175000 </pre>		

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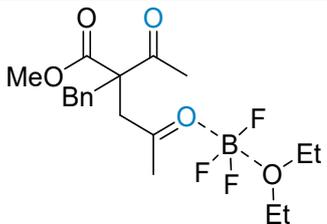
	Multiplicity = 1 Charge = 0 Imaginary vib. modes: no	
Electronic Energy (EE)	EE + Thermal Enthalpy	EE + Thermal Free Energy

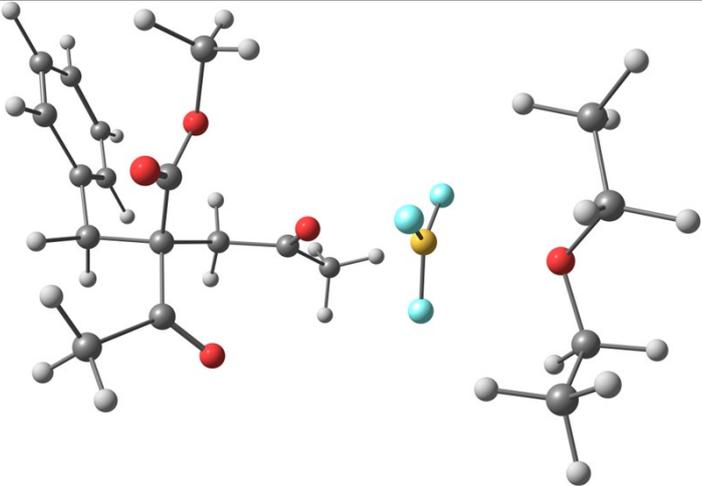
	Correction (H)	Correction (G)
		Imaginary vib. modes: no
-558.224257	-558.060053	-558.107783
C 0.86448800 1.11643700 0.69184000 H 1.62961700 0.74452100 1.37139000 H 0.06599600 1.57087800 1.27664700 C 1.42236500 2.05094000 -0.35091200 H 1.84535700 2.92353700 0.15204100 H 2.21118900 1.56438300 -0.92714300 H 0.63710200 2.38780600 -1.02885000 C 0.94073600 -1.34237400 0.34280600 H 0.98317100 -1.42781100 1.42966200 H 0.27728300 -2.10577400 -0.05752400 C 2.30165400 -1.39263200 -0.30446000 H 2.73953700 -2.37213700 -0.10077200 H 2.21872200 -1.26685300 -1.38536700 H 2.97344200 -0.63258100 0.09829700 O 0.28222800 -0.06647900 0.03543100 B -1.26429800 -0.10110500 -0.08081500 F -1.55761800 -1.03499300 -1.05268000 F -1.76241800 -0.46738300 1.15871500 F -1.64587600 1.17539500 -0.43752400		

Diethyl ether

	Multiplicity = 1
	Charge = 0
	Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy
	Correction (H)
	EE + Thermal Free Energy
	Correction (G)
-233.6178098	-233.47291
O 0.00000400 -0.27308000 -0.00078600 C 1.17636900 0.51482300 0.00127400 H 1.18496200 1.16204800 0.88912300 H 1.18558200 1.16587000 -0.88378700 C -1.17637800 0.51482900 -0.00120000 H -1.18577700 1.16269700 -0.88858300 H -1.18476500 1.16521500 0.88433600 C 2.37804400 -0.40406100 -0.00032000 H 3.29959500 0.18230600 0.00184600 H 2.37506600 -1.03895800 -0.88923300 H 2.37382600 -1.04352000 0.88532200 C -2.37804100 -0.40406400 0.00080900 H -3.29959600 0.18230000 -0.00000600 H -2.37418400 -1.03965000 0.88922800 H -2.37470500 -1.04283300 -0.88533200	

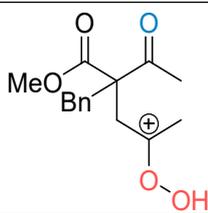
Transition state for BF₃ group transfer from BF₃•Et₂O to starting carbonyl compound 1

	Multiplicity = 1
	Charge = 0
	Imaginary vib. modes: 1
Electronic Energy (EE)	EE + Thermal Enthalpy
	Correction (H)
	EE + Thermal Free Energy
	Correction (G)
-1441.466971	-1440.977502
	-1441.078899

<pre> B 2.85752300 -0.29417800 0.46658100 O 5.20731600 -0.57040100 0.32789500 F 3.07079200 0.90900000 0.99508300 F 2.78572600 -0.44055500 -0.85277100 F 2.77623800 -1.35859600 1.25973300 C 5.93912500 0.64952100 0.41641800 C 5.64984200 -1.42938100 -0.71883200 H 7.00226100 0.41299400 0.54722500 H 5.58611600 1.13505800 1.32701200 C 5.74059300 1.56345300 -0.78139600 H 5.33819900 -1.02868500 -1.68963900 H 6.74620900 -1.46778600 -0.70342500 C 5.06735700 -2.80996900 -0.50466700 H 6.17038100 1.14069500 -1.69174600 H 4.67791900 1.75384100 -0.94912500 H 6.23483300 2.51923500 -0.59049300 H 3.97839700 -2.79269000 -0.57284200 H 5.44694300 -3.48959400 -1.27100900 H 5.35161400 -3.19806100 0.47597700 H -0.46081400 -2.41160900 -1.69302900 C -1.50526200 -2.38598500 -1.37962600 H -2.15436100 -2.36708300 -2.25577500 O -1.74376900 -1.23774700 -0.55701200 H -1.73532200 -3.24695700 -0.75691600 C -1.53800100 -0.05654900 -1.13151800 O -1.18801900 0.07110900 -2.27921000 C -1.87762900 1.09446900 -0.18289900 C -1.51966700 0.75004400 1.26010500 H -2.08742400 -0.12087700 1.60237600 H -1.78166600 1.58014000 1.92044500 C -0.06089700 0.41279700 1.45139200 O 0.62005200 0.03362300 0.51536200 C 0.48351800 0.55403600 2.84008000 H 1.42082100 0.01306600 2.95492600 H -0.25149800 0.21115200 3.57114200 H 0.65392900 1.62052800 3.02201500 C -1.10480400 2.36934800 -0.59970300 O -0.29839900 2.85188400 0.16142900 C -1.44429000 3.05113600 -1.89830200 H -1.77094100 2.35402500 -2.66585300 H -0.57740900 3.61872900 -2.23569000 H -2.25923200 3.75506100 -1.69752200 C -3.40146400 1.42046100 -0.32371100 H -3.60552800 2.26946000 0.33515200 H -3.59196500 1.74135100 -1.34950000 C -4.32740200 0.27725800 0.01019700 C -4.78988200 0.08132600 1.31279100 C -4.73069700 -0.61429500 -0.98736700 C -5.62425600 -0.99217600 1.61666400 H -4.49582500 0.77624100 2.09336000 C -5.56344300 -1.68781000 -0.68853800 H -4.38632500 -0.46422900 -2.00706400 C -6.01020800 -1.88150800 0.61728700 H -5.97605000 -1.13018300 2.63297900 H -5.86736800 -2.37020000 -1.47451200 H -6.66094700 -2.71616400 0.85225500 </pre>	
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XYZ data for Scheme S2

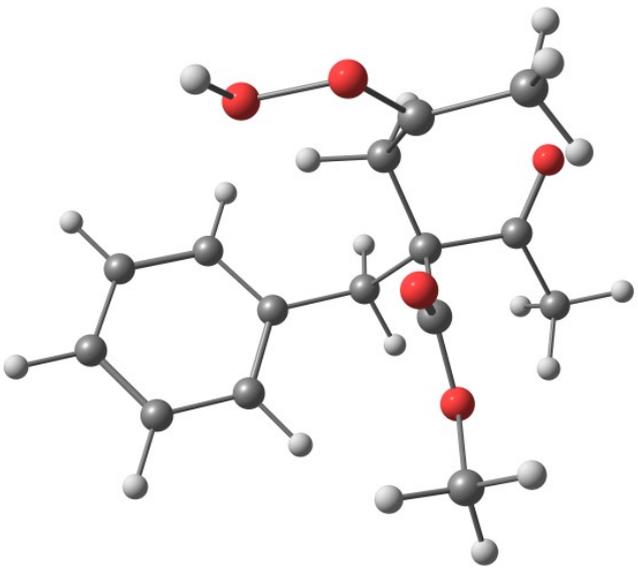
Peroxacarbenium ion A, a transition state between oxacarbenium ions B and D-loc-min

	<p>Multiplicity = 1 Charge = +1 Imaginary vib. modes: 1</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-958.781362	-958.439944	-958.510156

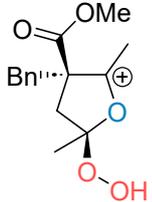
<pre> H 0.48313400 -4.11562800 -1.60829400 C 0.26213000 -3.09382800 -1.90382900 H 1.13643600 -2.62517700 -2.35573200 O -0.08408400 -2.40771100 -0.68442700 C -0.37184300 -1.12334100 -0.80154700 O -0.38388400 -0.52402300 -1.84858600 C -0.64366800 -0.43986400 0.54319700 C -0.87218200 1.04343400 0.28584400 H 0.01533900 1.49014300 -0.17868300 H -1.00411000 1.58205500 1.23358800 C -2.00635000 1.43206300 -0.57623500 C -3.07099000 0.61609400 -1.19442000 H -3.21518300 0.93545800 -2.22889100 H -3.99365900 0.82432000 -0.63986800 H -2.86255600 -0.44636000 -1.14932900 C -1.85106100 -1.02575800 1.32385900 C -1.77075800 -2.41464900 1.88244400 H -2.77566800 -2.75663500 2.12456900 H -1.18288400 -2.37010800 2.80537800 H -1.27500000 -3.10678300 1.20465500 O -2.15980100 2.66921700 -0.85950400 O -2.79887600 -0.30554600 1.53336400 H -0.57846800 -3.06686300 -2.59656000 C 0.61597600 -0.62051300 1.45568200 H 0.74551700 -1.68701400 1.64106400 H 0.39577000 -0.13427300 2.40968600 C 1.87982100 -0.04763500 0.86151400 C 2.67820700 -0.81494300 0.00829800 C 2.26468900 1.26546200 1.14437200 C 3.82812200 -0.27516100 -0.56165300 H 2.40938500 -1.84642900 -0.19763500 C 3.41499900 1.80638700 0.57703900 H 1.65928500 1.86495400 1.81751300 C 4.19691500 1.03810400 -0.28184100 H 4.43968500 -0.88408700 -1.21783100 H 3.70166800 2.82586500 0.80905400 H 5.09360100 1.45765800 -0.72340300 O -1.20657900 3.52001700 -0.27012000 H -1.45053800 4.36815300 -0.69144300 </pre>	
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Oxocarbenium ion D-loc-min (formed from TS above, not the lowest energy conformer)

	<p>Multiplicity = 1 Charge = +1 Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-958.782932	-958.440095	-958.511972

<pre> H 0.35984500 -3.19962600 2.78251800 C 0.46805000 -2.12328600 2.68573400 H -0.41947900 -1.60932800 3.05402900 O 0.61376600 -1.88070600 1.26848600 C 0.75121700 -0.63131400 0.89947400 O 0.79341600 0.30577100 1.67084300 C 0.84169800 -0.41673400 -0.61125200 C 0.78038600 1.10267200 -0.84458500 H -0.25201000 1.42256300 -0.93244500 H 1.30687900 1.34664100 -1.77463500 C 1.45780700 1.90909900 0.20293400 C 2.90359100 1.85639600 0.49665600 H 3.14256700 2.43704200 1.38577900 H 3.40861100 2.28479200 -0.37756500 H 3.23877800 0.82657100 0.60074900 C 2.15571600 -1.01689200 -1.20032300 C 2.33267300 -2.50756400 -1.21759700 H 3.39260000 -2.73390200 -1.32180500 H 1.80522600 -2.89295500 -2.09691600 H 1.91573600 -2.99461700 -0.33858600 O 0.89665200 2.91779900 0.75592000 O 2.96786000 -0.27550000 -1.69596900 H 1.35578400 -1.77442200 3.21145200 C -0.35426600 -1.12993600 -1.32202600 H -0.25334400 -2.20298500 -1.15536100 H -0.24471000 -0.94459200 -2.39385600 C -1.71694800 -0.67314700 -0.85301500 C -2.32252400 -1.25732400 0.26413400 C -2.39971800 0.34155300 -1.53011300 C -3.56584200 -0.81677400 0.70980500 H -1.83103200 -2.07733700 0.77645100 C -3.64352000 0.78268900 -1.08727700 H -1.95334600 0.78564200 -2.41483300 C -4.22640500 0.20937500 0.03979300 H -4.02171400 -1.28323300 1.57583600 H -4.15811800 1.57036800 -1.62580500 H -5.19517900 0.55104500 0.38593100 O -0.47750700 3.05611700 0.46719500 H -0.72207700 3.72761700 1.13321700 </pre>	
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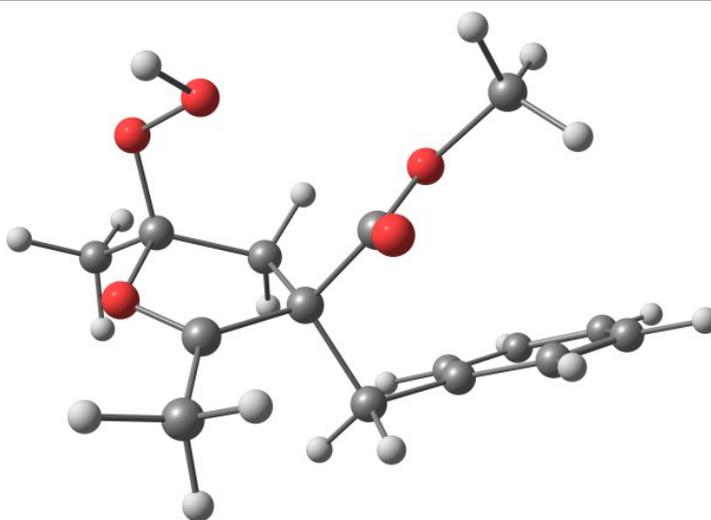
Acetyl ring closure CO₂Me-OOH-*cis* (B')

		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-958.80261	-958.459114	-958.527499

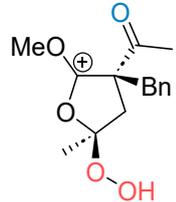
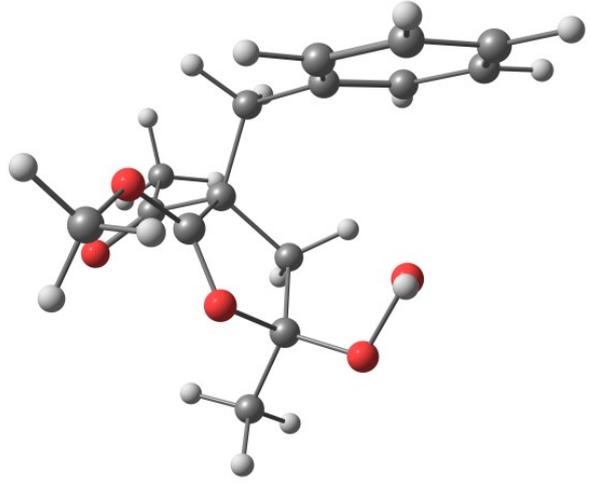
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H 0.26152000 3.31984500 -1.67965600
C 1.07132200 2.60704700 -1.52425500
H 1.57255100 2.38581400 -2.46245200
O 0.53496700 1.35092700 -1.07056400
C -0.08734800 1.37478400 0.08914800
O -0.24858300 2.35591000 0.76806500
C -0.50608000 -0.04020400 0.52845100
C -0.88593700 -0.98583000 -0.62102100
H -0.51892400 -1.98996000 -0.41164700
H -0.50477800 -0.66235500 -1.58625300
C -2.40985800 -1.03397600 -0.64014800
C -3.05910200 -2.37523000 -0.81664800
H -2.75640300 -2.77857800 -1.78405300
H -4.14430900 -2.28069700 -0.77856400
H -2.71414400 -3.04504300 -0.02908700
C -1.79020000 0.04123700 1.31190500
O -3.03586700 -0.15915800 -1.49981400
C -2.76325500 -0.52992400 0.75326300
C -1.96920100 0.61937900 2.64162200
H -3.02327900 0.75962400 2.87120400
H -1.39134700 1.53934900 2.73107200
H -1.53585500 -0.10713300 3.34509000
C 0.62139000 -0.58791300 1.46800300
H 0.29699100 -1.56865500 1.82400200
H 0.70470700 0.08325800 2.32568000
C 1.95348100 -0.68855900 0.76697600
C 2.31997200 -1.84737200 0.08080300
C 2.83151900 0.39849200 0.77971100
C 3.53510600 -1.91196300 -0.59686700
H 1.65660400 -2.70635400 0.08375200
C 4.04475700 0.33674200 0.10261100
H 2.56236100 1.29809300 1.32677900
C 4.39676900 -0.81855900 -0.59244200
H 3.80941000 -2.81847800 -1.12440700
H 4.71669600 1.18739100 0.12133400
H 5.34257100 -0.86927300 -1.11968900
H 1.77930800 2.99507600 -0.79186600
O -2.40584700 1.11259900 -1.39345300
H -3.16454000 1.68680900 -1.18831000

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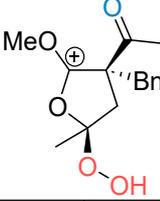
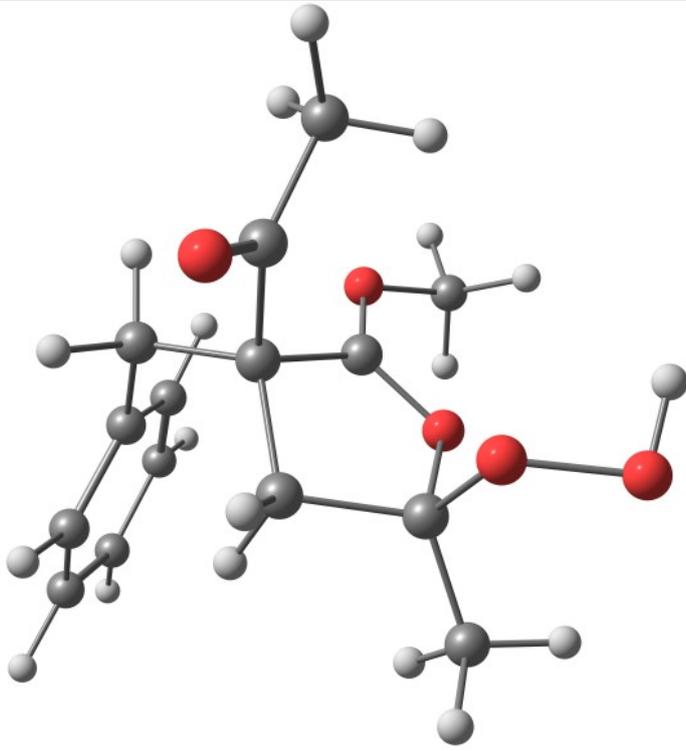


CO₂Me ring closure Ac-OOH-trans (D)

		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-958.797623	-958.453919	-958.523152
<pre> H 1.89348300 1.15447600 3.16920100 C 0.96416700 0.59165800 3.22613200 H 0.93286900 -0.03863900 4.10806500 O 0.91545400 -0.34586400 2.10184500 C 0.94401900 0.10613300 0.92415300 O 1.04614300 1.34822300 0.68755300 C 0.90465400 -0.79239900 -0.27386300 C 0.76280700 0.23210800 -1.42434000 H -0.24137100 0.20371600 -1.84168200 H 1.48264900 0.05015200 -2.22175000 C 1.02757000 1.61458500 -0.81024800 C 2.33554300 2.26988200 -1.15701900 H 3.15433200 1.58913700 -0.92034200 H 2.45450900 3.19951200 -0.60022900 H 2.34435700 2.47448600 -2.22837600 C 2.31818500 -1.42976400 -0.35262900 C 2.49252200 -2.57938000 -1.29246200 H 1.97696000 -2.39525800 -2.23754500 H 2.04449800 -3.46876900 -0.83839000 H 3.55425000 -2.75242600 -1.45863500 O 0.03953500 2.55285100 -0.99579500 O 3.20980800 -0.96182200 0.31439900 H 0.09371100 1.24340700 3.16983500 C -0.21596300 -1.85524900 -0.16919900 </pre>		

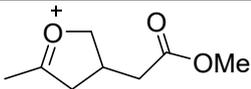
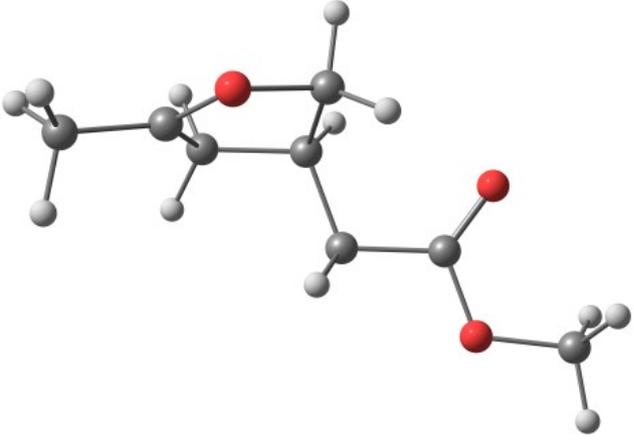
H	-0.00931200	-2.48383000	0.70150000
H	-0.14697500	-2.48235500	-1.05924500
C	-1.59490300	-1.24449300	-0.08123000
C	-2.37050100	-1.10020400	-1.23349900
C	-2.10071600	-0.77270800	1.13374300
C	-3.60945700	-0.46907700	-1.18231500
H	-1.99573500	-1.48228500	-2.17808800
C	-3.33683200	-0.13396200	1.18609900
H	-1.54067500	-0.92124900	2.05127600
C	-4.08991200	0.02818100	0.02605400
H	-4.19730800	-0.36258100	-2.08704100
H	-3.71508600	0.22708800	2.13588400
H	-5.05228700	0.52551800	0.06678900
O	-1.22939200	1.97320100	-0.72816100
H	-1.47234800	2.39531200	0.11377600

CO₂Me ring closure Ac-OOH-cis (D')

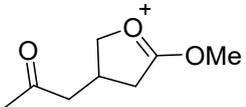
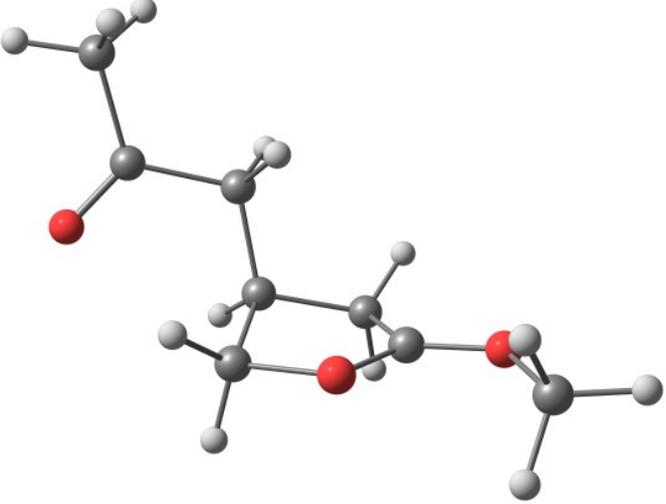
		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no																																																																																																																																																											
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)																																																																																																																																																											
-958.794015	-958.450373	-958.519221																																																																																																																																																											
<table border="1"> <tbody> <tr><td>H</td><td>-0.01798200</td><td>-1.49566300</td><td>3.72904800</td></tr> <tr><td>C</td><td>0.34889500</td><td>-0.66076200</td><td>3.14219700</td></tr> <tr><td>H</td><td>-0.26243200</td><td>0.22827700</td><td>3.28596000</td></tr> <tr><td>O</td><td>0.20535800</td><td>-1.09943500</td><td>1.75090900</td></tr> <tr><td>C</td><td>0.56889700</td><td>-0.32841300</td><td>0.81950400</td></tr> <tr><td>O</td><td>1.07006700</td><td>0.81802500</td><td>1.06433400</td></tr> <tr><td>C</td><td>0.44225800</td><td>-0.67940800</td><td>-0.62957800</td></tr> <tr><td>C</td><td>0.65511500</td><td>0.69828800</td><td>-1.27103900</td></tr> <tr><td>H</td><td>-0.29316300</td><td>1.21791200</td><td>-1.40318900</td></tr> <tr><td>H</td><td>1.16850400</td><td>0.63026200</td><td>-2.22832200</td></tr> <tr><td>C</td><td>1.48563400</td><td>1.46831400</td><td>-0.25351700</td></tr> <tr><td>C</td><td>1.23483200</td><td>2.93813600</td><td>-0.10877500</td></tr> <tr><td>H</td><td>0.17231300</td><td>3.10295500</td><td>0.07047300</td></tr> <tr><td>H</td><td>1.51679600</td><td>3.42009300</td><td>-1.04711700</td></tr> <tr><td>H</td><td>1.81815000</td><td>3.35851900</td><td>0.70773600</td></tr> <tr><td>C</td><td>1.55692100</td><td>-1.69265400</td><td>-1.07090300</td></tr> <tr><td>C</td><td>2.04870600</td><td>-2.69000100</td><td>-0.07006400</td></tr> <tr><td>H</td><td>2.68921600</td><td>-3.41689800</td><td>-0.56521500</td></tr> <tr><td>H</td><td>1.21149000</td><td>-3.19201700</td><td>0.42039900</td></tr> <tr><td>H</td><td>2.62276800</td><td>-2.16436300</td><td>0.70170300</td></tr> <tr><td>O</td><td>2.80004600</td><td>1.08772000</td><td>-0.45717700</td></tr> <tr><td>O</td><td>1.92257000</td><td>-1.64842700</td><td>-2.21321500</td></tr> <tr><td>H</td><td>1.40122500</td><td>-0.46464200</td><td>3.33828300</td></tr> <tr><td>C</td><td>-0.91028100</td><td>-1.37774700</td><td>-0.95735400</td></tr> <tr><td>H</td><td>-0.92223000</td><td>-2.35234600</td><td>-0.46300200</td></tr> <tr><td>H</td><td>-0.90177600</td><td>-1.54889900</td><td>-2.03602900</td></tr> <tr><td>C</td><td>-2.13291900</td><td>-0.58034200</td><td>-0.56818200</td></tr> <tr><td>C</td><td>-2.70203000</td><td>0.32404300</td><td>-1.46937800</td></tr> <tr><td>C</td><td>-2.71963600</td><td>-0.73419600</td><td>0.69153700</td></tr> <tr><td>C</td><td>-3.81860800</td><td>1.07454100</td><td>-1.11341300</td></tr> <tr><td>H</td><td>-2.27184400</td><td>0.43078100</td><td>-2.46037700</td></tr> <tr><td>C</td><td>-3.83573900</td><td>0.01724300</td><td>1.04987700</td></tr> <tr><td>H</td><td>-2.31683100</td><td>-1.46146400</td><td>1.38858400</td></tr> <tr><td>C</td><td>-4.38409800</td><td>0.92762700</td><td>0.15057700</td></tr> <tr><td>H</td><td>-4.24961300</td><td>1.76894800</td><td>-1.82562800</td></tr> <tr><td>H</td><td>-4.28231700</td><td>-0.11746500</td><td>2.02849400</td></tr> <tr><td>H</td><td>-5.25519500</td><td>1.51001800</td><td>0.42822000</td></tr> <tr><td>O</td><td>3.65497800</td><td>1.75344700</td><td>0.45920100</td></tr> <tr><td>H</td><td>3.92108500</td><td>1.02733100</td><td>1.04862200</td></tr> </tbody> </table>	H	-0.01798200	-1.49566300	3.72904800	C	0.34889500	-0.66076200	3.14219700	H	-0.26243200	0.22827700	3.28596000	O	0.20535800	-1.09943500	1.75090900	C	0.56889700	-0.32841300	0.81950400	O	1.07006700	0.81802500	1.06433400	C	0.44225800	-0.67940800	-0.62957800	C	0.65511500	0.69828800	-1.27103900	H	-0.29316300	1.21791200	-1.40318900	H	1.16850400	0.63026200	-2.22832200	C	1.48563400	1.46831400	-0.25351700	C	1.23483200	2.93813600	-0.10877500	H	0.17231300	3.10295500	0.07047300	H	1.51679600	3.42009300	-1.04711700	H	1.81815000	3.35851900	0.70773600	C	1.55692100	-1.69265400	-1.07090300	C	2.04870600	-2.69000100	-0.07006400	H	2.68921600	-3.41689800	-0.56521500	H	1.21149000	-3.19201700	0.42039900	H	2.62276800	-2.16436300	0.70170300	O	2.80004600	1.08772000	-0.45717700	O	1.92257000	-1.64842700	-2.21321500	H	1.40122500	-0.46464200	3.33828300	C	-0.91028100	-1.37774700	-0.95735400	H	-0.92223000	-2.35234600	-0.46300200	H	-0.90177600	-1.54889900	-2.03602900	C	-2.13291900	-0.58034200	-0.56818200	C	-2.70203000	0.32404300	-1.46937800	C	-2.71963600	-0.73419600	0.69153700	C	-3.81860800	1.07454100	-1.11341300	H	-2.27184400	0.43078100	-2.46037700	C	-3.83573900	0.01724300	1.04987700	H	-2.31683100	-1.46146400	1.38858400	C	-4.38409800	0.92762700	0.15057700	H	-4.24961300	1.76894800	-1.82562800	H	-4.28231700	-0.11746500	2.02849400	H	-5.25519500	1.51001800	0.42822000	O	3.65497800	1.75344700	0.45920100	H	3.92108500	1.02733100	1.04862200	
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H	3.92108500	1.02733100	1.04862200																																																																																																																																																										

XYZ data for Scheme S3

Cat1

		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-538.121749	-537.903289	-537.953998
<pre> C -0.54918600 -0.69740000 0.34469800 H -0.25049200 -1.15983400 -0.60249400 H -0.68855600 -1.51177600 1.06079700 C -1.88287500 -0.02363300 0.14223200 C 0.50655900 0.27893600 0.84964900 C 1.85380400 -0.42112500 1.08709600 H 0.15917400 0.77095000 1.75588000 C 2.60372400 -0.14711900 -0.15632500 H 2.43518400 0.04907200 1.89256800 H 1.80429900 -1.49065400 1.29774200 O 2.09242000 0.77588500 -0.84892800 O -2.10724100 1.14267000 0.35853200 C 0.87562000 1.32992700 -0.19662400 H 1.18677000 2.28441700 0.22470800 H 0.15653400 1.47560700 -0.99815300 C -4.11279000 -0.34133900 -0.52622500 H -4.07544200 0.45080900 -1.27431600 H -4.71383200 -1.17266700 -0.88535000 H -4.52220000 0.04845400 0.40583900 O -2.79987700 -0.87888000 -0.30560500 C 3.82193900 -0.81532000 -0.61119500 H 4.51807100 -0.88234600 0.22869600 H 3.54130700 -1.84348000 -0.87040900 H 4.26600500 -0.31350800 -1.46734000 </pre>		

Cat2

		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-538.113775	-537.895094	-537.945995
<pre> C -3.57838600 -1.36639000 -0.20461900 H -3.66966100 -1.88099200 0.75452000 H -3.13680300 -2.07422800 -0.91302900 H -4.55725300 -1.05335300 -0.56446500 C -1.34283400 -0.43245700 0.62608300 H -0.86269300 -1.30526200 0.16536400 H -1.57227700 -0.72503100 1.65638800 C -2.66085700 -0.18403900 -0.07886600 C -0.42674600 0.78464400 0.61609300 C 0.88160600 0.51780000 1.37848800 H -0.94512200 1.64933400 1.02515600 C 1.78117400 0.08305800 0.28584300 H 1.31577000 1.43412600 1.79501400 H 0.82313600 -0.23084000 2.16823200 O 1.37227400 0.37305800 -0.88630600 O 2.88079400 -0.51589700 0.46556500 C 3.70113500 -0.85486200 -0.69838300 H 3.97242500 0.06437200 -1.21377800 H 4.57273300 -1.34871600 -0.28290900 H 3.13427600 -1.52376500 -1.34279100 O -2.94346600 0.90991500 -0.51920600 C 0.08427800 1.11135900 -0.78944500 H 0.33739800 2.16067600 -0.92997100 H -0.52497300 0.74239500 -1.60931100 </pre>		

Methyl cation

<chem>CH3+</chem>		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-39.594521	-39.558869	-39.580049
C 0.00000000 0.00000000 0.00000000 H 0.00000000 1.08772500 0.00000000 H -0.94199700 -0.54386200 0.00000000 H 0.94199700 -0.54386200 0.00000000		

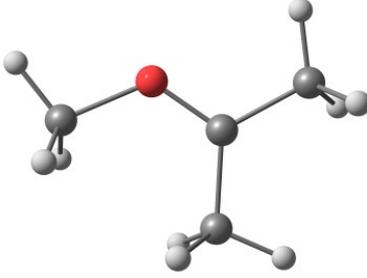
Acetone

<chem>CC(=O)C</chem>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-193.1298211	-193.039696	-193.074343
C -0.00000200 0.18324400 0.00001000 C 1.27879500 -0.61150100 -0.00253800 H 1.37262000 -1.12903700 0.95703800 H 1.24334300 -1.37848000 -0.78013400 H 2.13763800 0.04125900 -0.15167400 C -1.27876900 -0.61154500 0.00253500 H -2.13764900 0.04119900 0.15153700 H -1.37249000 -1.12916200 -0.95700800 H -1.24335400 -1.37843800 0.78021200 O -0.00003200 1.39643300 -0.00000100		

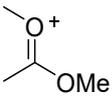
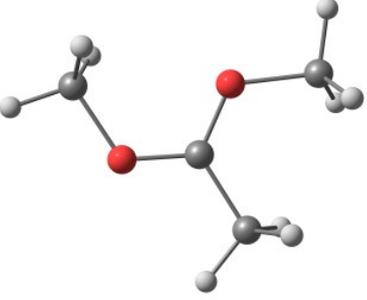
Methyl acetate

<chem>CC(=O)OC</chem>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-268.361988	-268.264639	-268.302218
C 0.46163400 0.17069100 -0.00009300 C 1.79494600 -0.51328000 0.00005000 H 1.87815400 -1.14909100 0.88342800 H 1.87725000 -1.15170600 -0.88150400 H 2.58962400 0.22888000 -0.00138400 O 0.28376000 1.36452300 -0.00001300 O -0.54427400 -0.71185100 -0.00013800 C -1.86758200 -0.16171700 0.00008600 H -2.02655600 0.44584900 -0.89132300 H -2.54181600 -1.01464100 -0.00022600 H -2.02653200 0.44516800 0.89196700		

Cat3

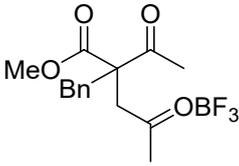
		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-232.836274	-232.703461	-232.74156
<pre> C -0.46025500 -0.00792600 0.00000100 C -0.34398300 1.45821000 0.00000000 H 0.22511000 1.77468300 -0.88137900 H -1.32818000 1.91793400 0.00000000 H 0.22511100 1.77468400 0.88137800 C -1.76285600 -0.68347400 0.00000000 H -2.31880000 -0.33401400 0.87675800 H -2.31879900 -0.33401300 -0.87675800 H -1.66237500 -1.76563600 -0.00000100 C 1.91014900 -0.21035100 0.00000000 H 2.04917500 0.38533100 0.90043100 H 2.55823300 -1.08018900 -0.00000100 H 2.04917400 0.38533200 -0.90043000 O 0.55787700 -0.75785900 0.00000000 </pre>		

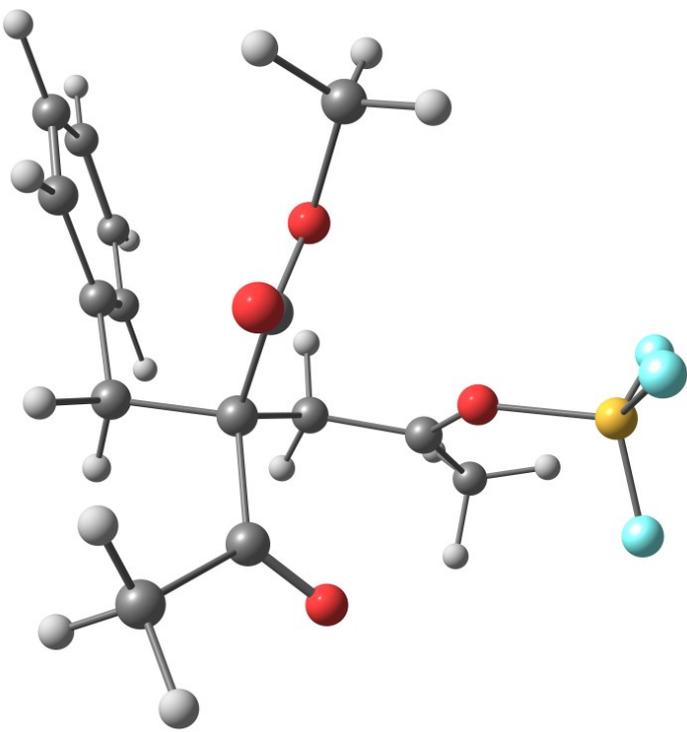
Cat4

		Multiplicity = 1 Charge = +1 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-308.06302	-307.922592	-307.962383
<pre> C -0.00093100 0.40486200 0.00000300 C 0.83406400 1.61807700 -0.00000100 H 1.47798200 1.60752700 -0.88385600 H 0.20059200 2.50023300 -0.00049600 H 1.47705600 1.60798300 0.88456600 C 1.89851600 -1.02106700 -0.00005900 H 2.32825700 -0.58855300 0.90084800 H 1.99588800 -2.10137700 0.00034500 H 2.32787700 -0.58923500 -0.90147700 O 0.45798100 -0.78432900 0.00010800 O -1.26719700 0.54260100 -0.00005900 C -2.12321800 -0.63881300 0.00000000 H -1.92586100 -1.21953900 0.89854000 H -3.13265500 -0.24206200 0.00007800 H -1.92599200 -1.21950600 -0.89859300 </pre>		

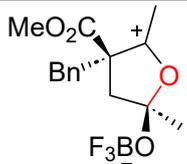
XYZ data for Scheme S4

Dist-Ket-BF₃-Acyclic

+2.5 Dist-Ket-BF ₃ -Acyclic		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy	EE + Thermal Free Energy

	Correction (H)	Correction (G)
-1207.861027	-1207.517608	-1207.596868
B 3.44458100 -0.98899800 -0.13522400 F 4.31297900 -0.12897200 0.51117500 F 3.57832300 -0.93848800 -1.50518700 F 3.52861300 -2.28100500 0.35202200 H 0.44753800 -1.82930800 -2.69446300 C -0.55136000 -1.80514000 -2.25763700 H -1.26496300 -1.41000400 -2.98098600 O -0.54782600 -0.99653900 -1.07176600 H -0.84901100 -2.79882000 -1.93308300 C -0.23237700 0.28155400 -1.23814800 O 0.04222100 0.77193500 -2.30471500 C -0.32254700 1.06050900 0.07652200 C 0.07950000 0.20798100 1.27989500 H -0.53400800 -0.69982100 1.33788600 H -0.08234600 0.75868200 2.20885400 C 1.48838800 -0.27168200 1.24917100 O 2.00163900 -0.48424900 0.12944300 C 2.18494200 -0.51858000 2.52909900 H 3.04542400 -1.17372700 2.42867300 H 1.46828300 -0.90927900 3.25367800 H 2.51088900 0.46354400 2.89349500 C 0.62584800 2.28471700 0.02015100 O 1.60068100 2.29904100 0.73746700 C 0.27609500 3.45250600 -0.85466100 H -0.17208700 3.13734300 -1.79490400 H 1.17124300 4.04741800 -1.03049800 H -0.45388400 4.06667900 -0.31640500 C -1.78614400 1.58483600 0.23658900 H -1.80332100 2.21380600 1.13110500 H -2.01735900 2.21697000 -0.62295800 C -2.82887200 0.49998800 0.34952900 C -3.18752800 -0.02258100 1.59354200 C -3.44346300 -0.00904900 -0.79735900 C -4.12937900 -1.04443800 1.68947800 H -2.72733900 0.37616400 2.49241500 C -4.38376700 -1.03015100 -0.70599200 H -3.18168300 0.39994900 -1.76954200 C -4.72633900 -1.55347800 0.53930900 H -4.39889400 -1.43920900 2.66266000 H -4.85200800 -1.41468200 -1.60517600 H -5.46030000 -2.34797800 0.61291800		

Dist-Cycl-CO₂Me-OBf₃-cis

 <p>+7.2 Dist-Cycl- CO₂Me- OBf₃-cis</p>	Multiplicity = 1 Charge = 0 Imaginary vib. modes: no	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.860021	-1207.515338	-1207.589422

<pre> B 2.61383600 -1.73223900 -0.01911000 F 2.57512000 -0.38724600 0.43635100 F 3.05564500 -1.73869100 -1.35174900 F 3.49494000 -2.47020300 0.77153700 H 2.81697000 4.07007400 0.91697600 C 2.67727100 3.48913700 0.00950300 H 2.39206200 4.13541200 -0.81998700 O 1.61216300 2.56611300 0.30369300 H 3.58473100 2.93830800 -0.23706600 C 1.27563600 1.73635300 -0.67098300 O 1.76679000 1.73299300 -1.76649900 C 0.10673900 0.82134500 -0.28958700 C 0.15406800 -0.50231700 -1.06879400 H 1.05041100 -0.55082100 -1.68216000 H -0.71057100 -0.60546900 -1.72129000 C 0.15498400 -1.65457700 -0.05444700 O 1.28478800 -2.34886800 0.09281700 C -1.05281400 -2.55004500 -0.06823300 H -1.97230600 -1.96459900 -0.01025700 H -1.00046300 -3.25329700 0.76340500 H -1.04547300 -3.10535500 -1.00881700 C 0.11317100 0.39204700 1.15684500 O 0.00174000 -0.83751300 1.31870200 C 0.19792200 1.25090000 2.35297500 H -0.29636700 0.76398300 3.19299200 H -0.19524500 2.24822600 2.16984800 H 1.26695400 1.34585700 2.58040600 C -1.19760600 1.65732000 -0.56357000 H -1.18134000 2.54871200 0.06742700 H -1.13166800 1.97691200 -1.60584400 C -2.46725500 0.87145700 -0.34640400 C -3.12619200 0.28285800 -1.42849600 C -2.99000100 0.69222600 0.93760200 C -4.26826200 -0.48837400 -1.23128300 H -2.74005100 0.43134600 -2.43206900 C -4.12861800 -0.08273000 1.13858600 H -2.51610000 1.17312000 1.78825800 C -4.76656800 -0.68086500 0.05448100 H -4.76693000 -0.93903200 -2.08188600 H -4.52031500 -0.21288700 2.14097900 H -5.65352700 -1.28424000 0.21050900 </pre>	
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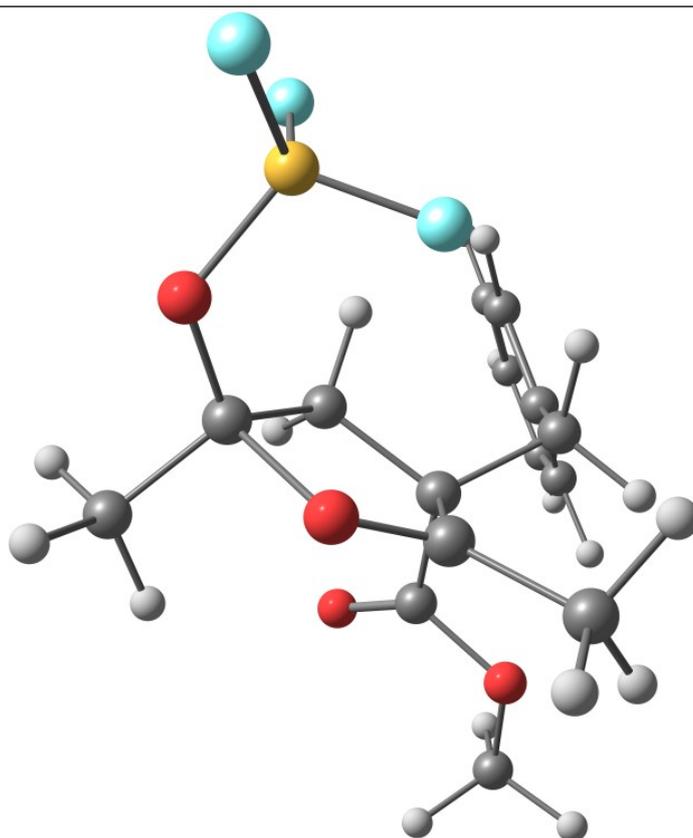
Dist-Cycl-CO₂Me-OBF₃-trans

	<p style="color: cyan;">+7.8</p> <p>Dist-Cycl- CO₂Me- OBF₃-trans</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.856718	-1207.512292	-1207.588429

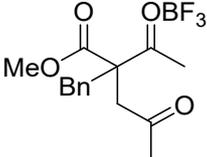
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B 3.16881800 1.24469100 -0.17999200
F 2.41725200 0.86052200 -1.31360400
F 4.51686700 1.36191800 -0.51687400
F 2.68695800 2.48051800 0.28328500
H -2.41091500 -3.88716400 0.88847000
C -2.82143200 -3.22283900 0.12863100
H -3.18252300 -3.79101000 -0.72406700
O -1.78198300 -2.36993700 -0.39015000
H -3.62028300 -2.61441000 0.55278200
C -1.19793700 -1.56463500 0.48468000
O -1.45789300 -1.52551600 1.65510700
C -0.15926000 -0.64503800 -0.20305900
C 0.61422900 0.17857400 0.83246200
H 0.07291100 0.23137500 1.77543700
H 0.76698500 1.18809000 0.46098400
C 1.96892800 -0.49737400 1.06849400
O 3.06468600 0.22074300 0.87806000
C 2.06719600 -1.38644400 2.27562100
H 2.99839200 -1.95253400 2.24577100
H 1.21524800 -2.06548400 2.33152900
H 2.06409000 -0.74568700 3.16010700
C 0.90610800 -1.52464200 -0.82232400
O 1.96399100 -1.57430600 -0.17683800
C 0.78367700 -2.23867100 -2.10298500
H 1.55462700 -3.00063200 -2.19713700
H 0.93467700 -1.47388600 -2.87829200
H -0.21716900 -2.64607800 -2.23550500
C -0.88062400 0.20954400 -1.28343200
H -0.11898700 0.82797300 -1.76251500
H -1.30988700 -0.45604700 -2.03410700
C -1.96051300 1.07595400 -0.68049300
C -1.67983300 2.37829100 -0.26047200
C -3.25601000 0.57757700 -0.51339900
C -2.66914700 3.16139900 0.32822200
H -0.68366500 2.78458200 -0.40573400
C -4.24593100 1.35870800 0.07574300
H -3.49689200 -0.42280000 -0.86064700
C -3.95321100 2.65166100 0.50214800
H -2.43723600 4.17181100 0.64551100
H -5.24695800 0.95970200 0.19475100
H -4.72405200 3.26184500 0.95890500

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Prox-Ket-BF₃-Acyclic

<p style="text-align: center;">+3.4 Prox-Ket-BF₃-Acyclic</p> 		<p>Multiplicity = 1 Charge = 0 Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.860576	-1207.516991	-1207.595401

<pre> H 1.70216600 2.91180400 -2.91415800 C 1.67423300 2.88452200 -1.82819000 H 2.68269200 2.81152300 -1.42015500 O 0.92277100 1.70638400 -1.48977300 H 1.17598200 3.77108800 -1.43573700 C 0.77460100 1.45795800 -0.19478800 O 1.21591600 2.15341900 0.68216900 C 0.01843300 0.14930300 0.05197300 C 0.00257400 -0.13585000 1.55683300 H 1.01135100 -0.09919400 1.96934800 H -0.39086300 -1.13950200 1.74898800 C -0.89000600 0.85078600 2.27720300 O -1.72849500 1.46939300 1.65177300 C -0.69529100 1.00016700 3.75196100 H 0.25600200 1.51661500 3.91623800 H -0.61534500 0.01625500 4.22001500 H -1.50822700 1.57391900 4.19326300 C -1.41510300 0.20649100 -0.44887000 C -1.93649600 1.27674300 -1.32949500 H -1.56850300 1.06164900 -2.34086500 H -1.55227500 2.25009300 -1.03141100 H -3.02312500 1.28280600 -1.33972400 C 0.71241200 -1.00607700 -0.74896000 H 0.19309100 -1.92922200 -0.48700700 H 0.57324200 -0.82383400 -1.81659500 C 2.18447400 -1.13033800 -0.43453100 C 3.14237200 -0.48066100 -1.21786200 C 2.61187000 -1.89894600 0.65204200 C 4.49706200 -0.58358100 -0.91131000 H 2.82719000 0.09753800 -2.08021200 C 3.96494700 -2.00348600 0.95943600 H 1.87719900 -2.42420300 1.25421200 C 4.91114600 -1.34094300 0.18079900 H 5.22848300 -0.07709700 -1.53104100 H 4.28051200 -2.60616200 1.80359600 H 5.96566300 -1.42271500 0.41858700 B -3.53906900 -1.12274500 -0.61088200 F -3.57319400 -1.06951300 -1.99227500 F -4.36167000 -0.17798700 -0.02887900 F -3.77706000 -2.39103200 -0.13023100 O -2.07968400 -0.81511800 -0.17015900 </pre>	
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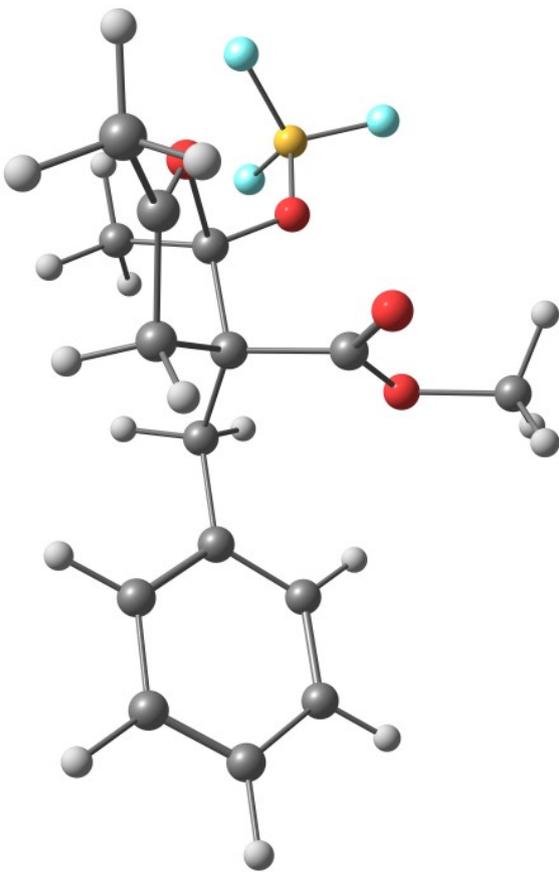
Prox-CyclTS-CO₂Me-OBF₃-cis

<p style="text-align: center;">+5.73 Prox-CyclTS- CO₂Me- OBF₃-cis</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: 1</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.858809	-1207.515912	-1207.591752

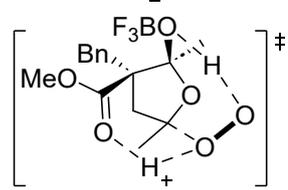
<pre> H -0.46879700 -3.52675900 1.88777000 C -0.40697200 -2.49227700 2.21509400 H -1.30224100 -2.21302600 2.77141400 O -0.31235400 -1.71106700 1.01347100 H 0.47922100 -2.33886000 2.83100500 C -0.23550700 -0.40125400 1.17461800 O -0.23315300 0.15289300 2.24534100 C -0.13995100 0.35506600 -0.15764100 C -0.53607300 1.81212800 0.09487000 H -1.42795500 1.90254300 0.71409400 H -0.73380300 2.33589300 -0.84755000 C 0.64785800 2.48256800 0.73008600 O 1.73872400 1.96430600 0.53061700 C 0.47560800 3.72098700 1.53028200 H 1.43634300 4.16682700 1.77877900 H -0.06446700 3.45303300 2.44412700 H -0.15332200 4.42358800 0.97807200 C 1.32869700 0.32785000 -0.59807900 C 1.70596800 0.93505600 -1.90863300 H 1.55070000 0.17166600 -2.67751100 H 2.75815200 1.21417800 -1.90457400 H 1.08695300 1.79983600 -2.14041600 C -0.99623800 -0.31083300 -1.27071500 H -0.85054900 0.26523100 -2.18672100 H -0.62626400 -1.32306600 -1.44303600 C -2.47188200 -0.34138600 -0.93572900 C -3.28178200 0.75888100 -1.23363200 C -3.05615800 -1.45960500 -0.33461200 C -4.63747400 0.75205700 -0.91977800 H -2.84763400 1.62417300 -1.72457200 C -4.41348300 -1.46952200 -0.02151100 H -2.44762700 -2.33067600 -0.11984400 C -5.20672900 -0.36199200 -0.30735500 H -5.25011700 1.61360600 -1.16055800 H -4.85132200 -2.34716500 0.44074200 H -6.26323900 -0.37030000 -0.06458500 B 3.46416700 -0.93709300 -0.46834500 F 4.27295500 0.18622400 -0.34767100 F 3.44642500 -1.40325900 -1.77882600 F 3.84702700 -1.93312100 0.41499300 O 2.04455500 -0.57240700 -0.06129900 </pre>	
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Prox-Cycl-CO₂Me-OBF₃-cis

<p>+5.70 Prox-Cycl- CO₂Me- OBF₃-cis</p>	<p>Multiplicity = 1 Charge = 0 Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.860566	-1207.516486	-1207.591798

<pre> H -0.67988800 -3.51050900 1.81817800 C -0.49956900 -2.49681600 2.16641000 H -1.31059300 -2.16581800 2.81543300 O -0.45258200 -1.68431000 0.98344300 H 0.45133100 -2.43835500 2.69628800 C -0.24556100 -0.39467800 1.16966100 O -0.10650000 0.12462000 2.25123400 C -0.17133300 0.39728200 -0.14107300 C -0.49031800 1.86018300 0.18592600 H -1.31497900 2.01485700 0.87969600 H -0.69603400 2.43447400 -0.72720500 C 0.79543900 2.37482000 0.72147500 O 1.79040200 1.70459200 0.37674300 C 0.93590800 3.57129700 1.56021100 H 1.97900600 3.83313900 1.72006000 H 0.44080600 3.35459600 2.51356900 H 0.38159400 4.39035800 1.09433300 C 1.33604400 0.43421200 -0.53120200 C 1.64673600 0.89628300 -1.93369700 H 1.41523800 0.08575800 -2.62592900 H 2.70592800 1.13831900 -2.01383700 H 1.05225500 1.77180700 -2.19694600 C -1.04036500 -0.20451800 -1.26062600 H -0.90273600 0.40952200 -2.15298200 H -0.67928400 -1.21040300 -1.48365000 C -2.51435800 -0.24113300 -0.91517300 C -3.30460400 0.89895300 -1.09116500 C -3.11813100 -1.40343700 -0.42807200 C -4.65804900 0.88689200 -0.76614700 H -2.85928300 1.80090500 -1.49934300 C -4.47304500 -1.41965100 -0.10567500 H -2.52415500 -2.30214900 -0.30716300 C -5.24564500 -0.27282100 -0.26678000 H -5.25456600 1.78062000 -0.91115800 H -4.92520900 -2.33182200 0.26745100 H -6.30021700 -0.28552200 -0.01583300 B 3.37127400 -0.96837500 -0.47669600 F 4.22503600 0.14320400 -0.39475700 F 3.37522200 -1.45843900 -1.79289600 F 3.79824900 -1.96883000 0.40026200 O 2.00105100 -0.60646900 -0.05959600 </pre>	
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Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-cis-TS

 <p style="text-align: center;">+16.9</p> <p style="text-align: center;">Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-cis-TS</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: 1</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1359.415502	-1359.038032	-1359.115801

<pre> H -0.65865100 -3.85538300 1.18872300 C -0.51891100 -2.88196600 1.65021800 H -1.32416900 -2.66761600 2.35241000 O -0.55591100 -1.93561900 0.56338600 H 0.44746600 -2.82607500 2.15057300 C -0.38446700 -0.67805100 0.87053300 O -0.22925900 -0.29401800 2.01977000 C -0.37893000 0.24210200 -0.35378000 C -0.60303700 1.70872800 0.05494000 H -1.16210400 1.86161400 0.97774100 H -1.12719400 2.24783700 -0.74023500 O 1.58560200 1.62968500 -0.65926000 C 1.02945600 3.75821800 0.22346200 H 0.41008700 4.17985900 1.01269400 H 0.76213400 4.22438600 -0.72960500 H 2.08600600 3.93463000 0.42321700 C 1.11358000 0.22950300 -0.90057300 C 1.27859700 -0.01064600 -2.38096100 H 0.95026000 -1.01963500 -2.63001100 H 2.32852100 0.10123900 -2.64942900 H 0.69061200 0.71340000 -2.94459400 C -1.43417000 -0.23174900 -1.38242800 H -1.37402200 0.43328400 -2.24521700 H -1.18831800 -1.24106400 -1.71325600 C -2.84722400 -0.19706100 -0.83335700 C -3.42132700 -1.32391500 -0.23565300 C -3.61430100 0.96897600 -0.92575200 C -4.71348300 -1.27671800 0.28163800 H -2.86042800 -2.25021500 -0.18789600 C -4.90496300 1.01983700 -0.40673100 H -3.20679800 1.84153900 -1.42568000 C -5.45650100 -0.10203500 0.20626200 H -5.14141100 -2.16275400 0.73715700 H -5.48228700 1.93372700 -0.49053200 H -6.46241100 -0.06530200 0.60871600 B 3.15279300 -1.19063400 -0.47805700 F 2.93875000 -2.22789400 -1.39220300 F 3.69899700 -1.69459300 0.71033800 F 4.03131700 -0.24518400 -1.03345200 O 1.88113600 -0.55444400 -0.07737900 C 0.76629200 2.30647300 0.08193200 H 0.64062600 1.01199700 2.09826300 O 2.55733900 1.28557500 1.93594900 H 2.56006400 0.56280700 1.27194800 O 1.24394400 1.78304100 1.85061400 </pre>	
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Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-cis-Adduct

<p style="color: red; text-align: center;">+4.8</p> <p style="text-align: center;">Prox-CO₂Me-OBF₃-cis- CO₂Me-H₂O₂-cis-Adduct</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1359.43542	-1359.057471	-1359.135138

<pre> H -2.51874200 0.18847100 3.25239300 C -1.72423500 -0.43842200 2.85851000 H -0.84134800 -0.39348700 3.49528200 O -1.41232500 0.11655900 1.56229100 H -2.06270200 -1.46779200 2.74537900 C -0.49396100 -0.48147100 0.86733700 O 0.10727700 -1.47300500 1.28054800 C -0.30194100 0.08383200 -0.53965300 C -0.36546900 1.61573300 -0.51044300 H -1.13803800 2.01388600 0.14303900 H -0.51348600 1.99682300 -1.52290400 O 1.88004800 1.03559100 -0.71004600 C 1.51379500 3.37478000 -0.37550500 H 1.44120800 3.54062300 -1.45080400 H 2.54751900 3.50913800 -0.05980800 H 0.88069800 4.09669700 0.14310400 C 1.16731300 -0.11838200 -1.07860400 C 1.29429900 -0.31403100 -2.57116400 H 0.81209000 0.51664400 -3.08899900 H 0.84413500 -1.25541000 -2.88512400 H 2.35480100 -0.31792700 -2.82218400 C -1.35770200 -0.60181100 -1.45093600 H -1.26813500 -0.14870400 -2.43909800 H -1.10346000 -1.66180400 -1.54103200 C -2.77801500 -0.46209000 -0.95957800 C -3.37161000 -1.48222600 -0.21395300 C -3.50724400 0.70067500 -1.21546200 C -4.66313800 -1.33728100 0.28486200 H -2.81382600 -2.39409700 -0.01848000 C -4.79944400 0.84849600 -0.71908800 H -3.06020800 1.49334100 -1.80759100 C -5.37874300 -0.16851900 0.03658400 H -5.11102800 -2.13743800 0.86349300 H -5.35540900 1.75622900 -0.92542400 H -6.38523500 -0.05367400 0.42264200 B 3.27980700 -1.34297600 -0.08792900 F 3.48627100 -0.56985600 1.06177300 F 4.00177000 -0.87440700 -1.15769900 F 3.51517100 -2.67575800 0.18437100 O 1.77981400 -1.27586500 -0.43773000 C 1.04159100 1.98081000 -0.05599800 H 1.16298100 -1.56300100 0.36121600 O 2.36813300 1.87631000 1.84685600 H 2.81060000 1.05281600 1.57437200 O 1.05663600 1.69830900 1.34092100 </pre>	
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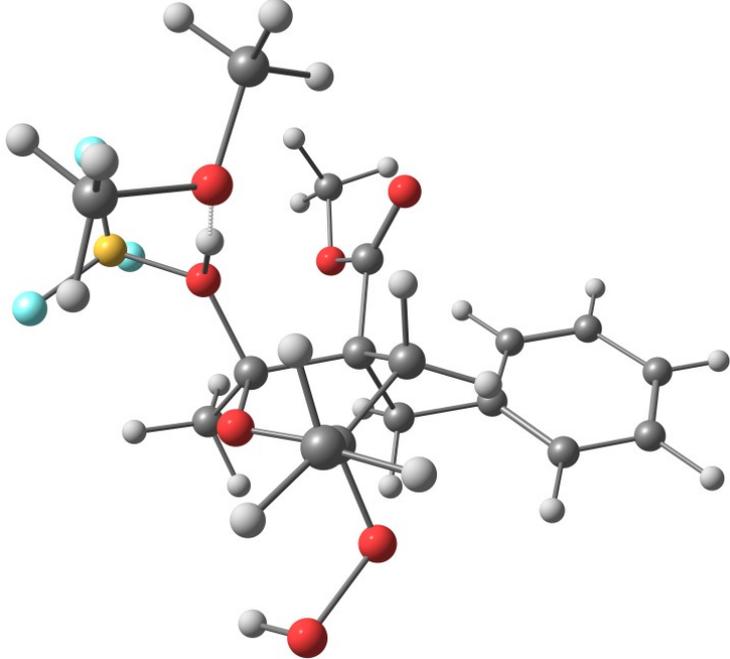
Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-trans-TS

<p>Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-trans-TS +20.4</p>		<p>Multiplicity = 1 Charge = 0 Imaginary vib. modes: 1</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1514.424494	-1513.960292	-1514.054017

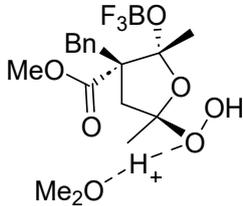
<pre> H 2.09623600 4.18415800 -0.77554400 C 2.76535000 3.43037200 -0.35895100 H 3.43805500 3.06263400 -1.13426500 O 2.00828800 2.34258700 0.19067300 H 3.33260600 3.84325700 0.47126500 C 1.23547600 1.67775700 -0.66548200 O 1.11222700 1.97231100 -1.82573200 C 0.51562900 0.52702900 0.02872500 C -0.28548000 -0.30026300 -0.98396200 H 0.16957400 -0.25062200 -1.97822600 H -1.33384600 -0.01623000 -1.08843600 O 0.88325200 -1.82273200 0.30390700 C -0.49401900 -2.90309200 -1.29467600 H -0.50876700 -3.78987900 -0.66122500 H 0.28627900 -3.02625400 -2.05295400 H -1.45201300 -2.75705500 -1.79166500 C 1.59721200 -0.50201900 0.50107400 C 2.01182000 -0.46776700 1.95233300 H 1.14600900 -0.58830900 2.60292300 H 2.49446300 0.48705300 2.16327700 H 2.71645600 -1.27502700 2.14939700 C -0.33839800 1.08359900 1.19578600 H -0.77265700 0.24741300 1.74335800 H 0.32665500 1.61752700 1.87686100 C -1.44605800 2.00367600 0.73847300 C -1.18454800 3.33048800 0.38195700 C -2.76039200 1.53875700 0.65874100 C -2.20900600 4.16341600 -0.05826900 H -0.17511900 3.72230300 0.46350900 C -3.78878500 2.36860500 0.21880000 H -2.98089400 0.51897500 0.95839400 C -3.51430900 3.68358800 -0.14527000 H -1.98855000 5.19039400 -0.32709300 H -4.80278600 1.98724900 0.16463000 H -4.31209200 4.33326200 -0.48670900 B 3.91898000 -1.07095000 -0.19128300 F 4.68039600 -0.31077500 0.72344200 F 4.57617200 -1.07696100 -1.43298900 F 3.82974300 -2.39146800 0.29643100 O 2.60403000 -0.48061000 -0.41197900 C -0.11457200 -1.70536800 -0.50418900 O -1.51510200 -2.88215700 1.52568700 H -1.30129300 -2.49979500 2.39233200 O -1.62746800 -1.72682300 0.72122500 C -4.25413800 -3.50460100 -0.27929200 H -4.80388500 -3.44586100 0.66436500 H -4.92567700 -3.81732200 -1.08227000 H -3.43288500 -4.21442900 -0.18928300 C -4.66815600 -1.21208700 -0.77458200 H -5.19027100 -1.02198100 0.16790200 H -4.14761700 -0.31478600 -1.10600400 H -5.38481700 -1.52305800 -1.53834300 H -2.49984700 -1.90240800 0.19081800 O -3.68657400 -2.23459400 -0.60251400 </pre>	
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Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-trans-Adduct

<p style="text-align: center; color: cyan;">+4.6</p> <p style="text-align: center;">Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-trans-Adduct</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1514.453383	-1513.987722	-1514.079298

<pre> H 0.68655400 -3.68811000 0.57976600 C -0.23275800 -3.64436100 -0.00553400 H -0.14979200 -4.26921000 -0.89096200 O -0.44189500 -2.31012700 -0.48987800 H -1.07809800 -3.96053500 0.60664600 C -0.52270500 -1.35695600 0.43253500 O -0.50815300 -1.56572600 1.61911300 C -0.60722800 0.02133000 -0.21332800 C -0.63685700 1.13920600 0.83570000 H -0.09698700 0.83966900 1.73520200 H -1.64383500 1.43543500 1.12638200 O 1.07532100 1.64855600 -0.67826300 C 0.81677800 3.25121300 1.09398300 H 1.41853700 3.95749600 0.52319900 H 1.45604300 2.70637000 1.78722300 H 0.06320200 3.79935900 1.66255300 C 0.75408500 0.30514200 -0.94318200 C 0.80627100 0.03240000 -2.42560400 H 0.08100400 0.67649300 -2.92270000 H 0.57172000 -1.01029000 -2.63559200 H 1.79979500 0.26899500 -2.80600900 C -1.81896600 0.05573200 -1.18283500 H -1.83498400 1.02477300 -1.68089900 H -1.67724000 -0.71375700 -1.94280600 C -3.13702200 -0.16878600 -0.47808900 C -3.92237500 0.91594800 -0.07870700 C -3.59548700 -1.46189700 -0.20740000 C -5.12984200 0.71667400 0.58547100 H -3.58467800 1.92477900 -0.29631800 C -4.80135000 -1.66467400 0.45834100 H -3.01264300 -2.31787900 -0.53336600 C -5.57086400 -0.57536400 0.85936500 H -5.72728700 1.57064600 0.88453300 H -5.14298900 -2.67446600 0.65648500 H -6.51147900 -0.73276000 1.37487700 B 2.96132200 -1.22642400 -0.87409000 F 3.75007200 -0.32588600 -1.57739400 F 2.49811200 -2.24257700 -1.68566200 F 3.63582400 -1.71668200 0.23991200 O 1.76875000 -0.48659300 -0.25772500 C 0.12177000 2.27892000 0.17147000 O -0.19711700 3.94185800 -1.41814400 H 0.18748600 3.43496200 -2.15229800 O -0.83919400 2.93669900 -0.65301800 C 2.50891200 -0.45954900 2.96515100 H 2.60482000 0.11143600 3.89042300 H 1.56816900 -1.00829100 2.95750700 H 3.35126200 -1.14569900 2.85401200 C 3.68425000 1.19335100 1.68709100 H 3.83424300 1.83988000 2.55379500 H 4.52755800 0.50781900 1.57632300 H 3.56491800 1.79606400 0.78713400 H 2.05081400 -0.06848500 0.70502000 O 2.47123000 0.45080200 1.85942200 </pre>	
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Prox-CO₂Me-OBF₃-cis-CO₂Me-H₂O₂-trans-Adduct'

 <p style="text-align: center;">+15.9 Prox-CO₂Me-OBF₃-<i>cis</i>- CO₂Me-H₂O₂-<i>trans</i>-Adduct'</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1514.435231	-1513.968684	-1514.061303

H 1.77063000	4.34998800	-0.92117500	
C 2.50825100	3.66727900	-0.49759100	
H 3.18353200	3.32141300	-1.28070200	
O 1.85593100	2.55014100	0.12080600	
H 3.06756800	4.15807300	0.29493500	
C 1.10264100	1.79491900	-0.68022000	
O 0.93309200	2.03403200	-1.84879200	
C 0.47578100	0.63637900	0.07676800	
C -0.25624200	-0.30647600	-0.88568000	
H 0.25715500	-0.33935300	-1.84523700	
H -1.29839100	-0.03296900	-1.06433800	
O 0.89168200	-1.58207400	0.72495400	
C 0.02420200	-2.86502200	-1.11557200	
H 0.04245400	-3.78591400	-0.53167100	
H 0.96986400	-2.76560100	-1.65059800	
H -0.78906500	-2.90250100	-1.84469800	
C 1.59115100	-0.31907000	0.60864100	
C 2.17300700	-0.01725200	1.97435200	
H 1.38877900	-0.01359100	2.73078000	
H 2.67045800	0.95197300	1.95974600	
H 2.90024900	-0.78782300	2.23123200	
C -0.41482100	1.17032300	1.22518000	
H -0.74396600	0.32062900	1.82714900	
H 0.19913300	1.80877300	1.86352000	
C -1.62026800	1.94199800	0.74661100	
C -1.50065100	3.26532900	0.31078700	
C -2.88111900	1.34231000	0.72081300	
C -2.61180000	3.96525400	-0.15063400	
H -0.53334500	3.75854900	0.34544700	
C -3.99624700	2.03932600	0.26191800	
H -2.98797000	0.32136600	1.07517300	
C -3.86327500	3.35307000	-0.17903400	
H -2.50171400	4.99175700	-0.48206500	
H -4.96756600	1.55631100	0.25174400	
H -4.72904400	3.89949100	-0.53545800	
B 3.84155900	-0.97526900	-0.23895400	
F 4.71273100	-0.10662600	0.47001400	
F 4.38217600	-1.17899100	-1.52744800	
F 3.82204900	-2.21401000	0.44455800	
O 2.52639700	-0.40379700	-0.40706500	
C -0.13024300	-1.66773100	-0.21112800	
O -1.30948500	-2.89844700	1.44760700	
H -0.75599700	-2.54445900	2.16666400	
O -1.38467000	-1.79400700	0.56408200	
C -3.68768600	-3.86334600	-0.40440500	
H -4.10971000	-3.88812900	0.59938500	
H -4.39587800	-4.22340000	-1.14645200	
H -2.75057800	-4.41171800	-0.46262000	
C -4.50934600	-1.56260200	-0.69137000	
H -4.85596100	-1.49714100	0.33962100	
H -4.14788800	-0.60746500	-1.06312700	
H -5.27753400	-1.96878300	-1.34522100	
H -2.55685800	-2.13786900	-0.21898800	
O -3.37904100	-2.48169100	-0.75646900	

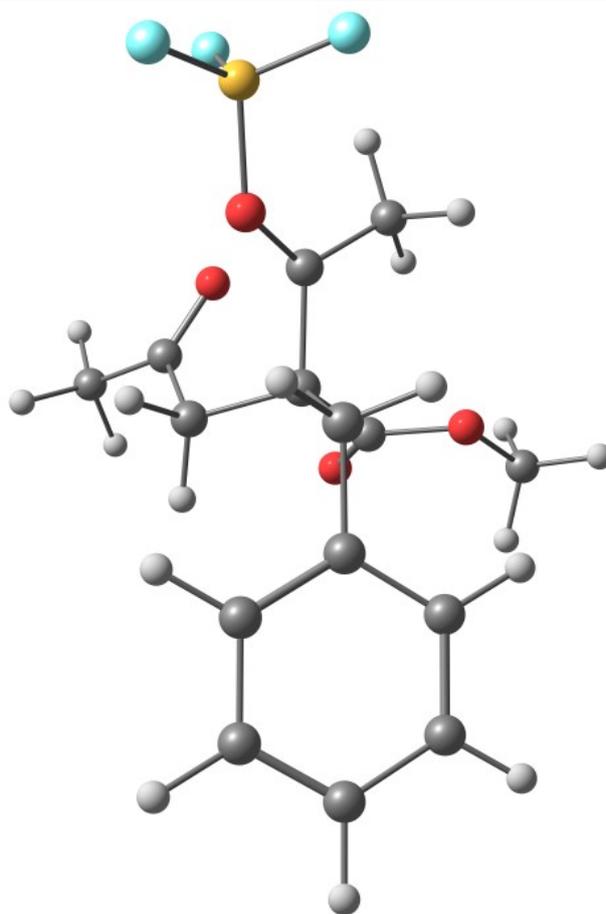
Prox-CyclITS-CO₂Me-OBF₃-trans

<p style="text-align: center;">+5.9 Prox-CyclITS- CO₂Me-OBF₃- trans</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: 1</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.858717	-1207.515937	-1207.591412

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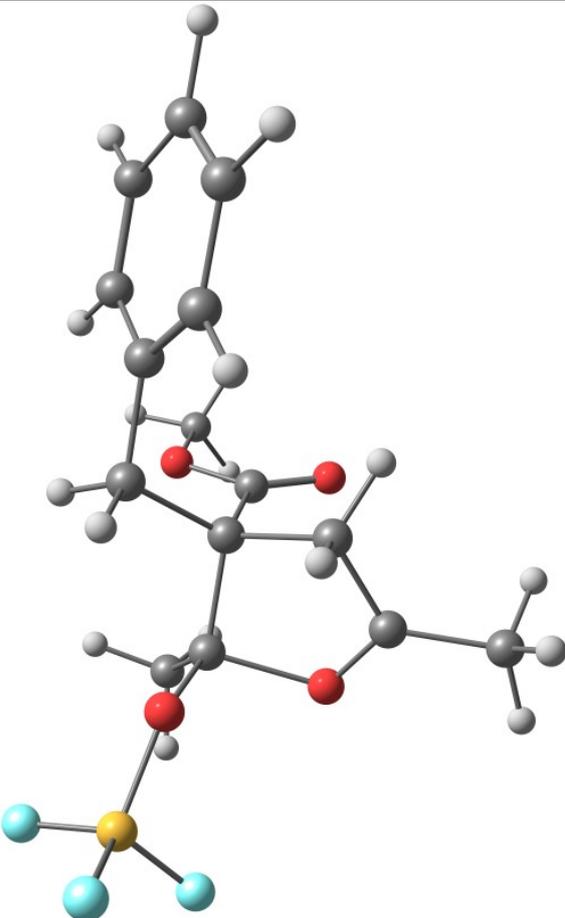
H -1.07845600  3.82655800 -1.39257000
C -1.69300100  2.98029200 -1.70047500
H -2.65469000  3.01052200 -1.18771200
O -1.01788200  1.74676300 -1.40215600
H -1.83386400  2.98353100 -2.77800200
C -0.76171700  1.51428200 -0.12270900
O -1.04167300  2.27136000  0.77163400
C -0.06564700  0.16606600  0.08872200
C -0.05713300  -0.13911800  1.58912700
H  0.23745500 -1.17857200  1.77205500
H -1.02228700  0.02678500  2.06651100
C  1.00732300  0.73949700  2.18116500
O  1.85079500  1.17148500  1.40270000
C  1.02499500  1.03944900  3.63364600
H  1.93914400  1.55558500  3.91870800
H  0.90615300  0.10899000  4.19424700
H  0.15281600  1.66323400  3.85449200
C  1.41000300  0.25906100 -0.32510400
C  1.91548100  1.31516700 -1.24811000
H  1.59506100  1.04224600 -2.25933800
H  3.00216600  1.35622500 -1.22109000
H  1.50309000  2.29084100 -0.99937000
C -0.74633400 -0.94598600 -0.75507700
H -0.61807700 -0.71451200 -1.81425900
H -0.21941100 -1.87708400 -0.54237800
C -2.21435900 -1.10026300 -0.42784300
C -2.61410900 -1.90084500  0.64648200
C -3.19497800 -0.44685500 -1.17901000
C -3.96006700 -2.03242000  0.97403600
H -1.86301000 -2.43099600  1.22382000
C -4.54315100 -0.57772500 -0.85343000
H -2.90234600  0.15872900 -2.03001500
C -4.92888900 -1.36596200  0.22699400
H -4.25247900 -2.65941300  1.80885600
H -5.29175900 -0.06720800 -1.44891900
H -5.97805800 -1.46849200  0.47998100
B  3.43371000 -1.14763300 -0.66361000
F  3.48923000 -1.01504700 -2.04756100
F  3.67742900 -2.45522100 -0.27443000
F  4.30765200 -0.26352900 -0.04114800
O  2.01759800 -0.85366600 -0.20082800

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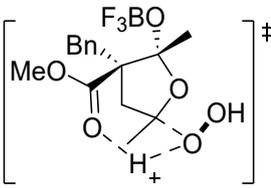


Prox-Cycl-CO₂Me-OBF₃-trans

<p>+5.1 Prox-Cycl- CO₂Me-OBF₃- trans</p>		Multiplicity = 1 Charge = 0 Imaginary vib. modes: no
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1207.86038	-1207.516505	-1207.592812

<pre> H -1.04677500 3.82979500 -1.43523200 C -1.73621700 3.01499200 -1.65699600 H -2.64890400 3.12636400 -1.07112600 O -1.11725300 1.75144300 -1.36164100 H -1.96514900 2.98682700 -2.71891600 C -0.75228000 1.55819300 -0.10498100 O -0.88570100 2.37584900 0.77298100 C -0.09903900 0.19125300 0.11279700 C -0.08211700 -0.07755800 1.62228900 H 0.15897800 -1.12749500 1.83192400 H -0.99516400 0.18140000 2.15569400 C 1.07813600 0.72523600 2.08514500 O 1.88961300 1.00911500 1.17611000 C 1.30535300 1.15683000 3.46840000 H 2.27641600 1.63005900 3.59121800 H 1.19531200 0.28799900 4.12337400 H 0.49902700 1.85200100 3.72725400 C 1.42253600 0.31014600 -0.20527900 C 1.86564000 1.28408500 -1.26490700 H 1.48857800 0.93929900 -2.22960800 H 2.95297500 1.32569800 -1.30068900 H 1.48015200 2.28437000 -1.06658600 C -0.76478900 -0.91561800 -0.72406900 H -0.64419000 -0.67995800 -1.78323400 H -0.22692500 -1.84166600 -0.51925500 C -2.22986000 -1.09077100 -0.38735100 C -2.60815300 -1.87836000 0.70447000 C -3.22891400 -0.47178800 -1.14340100 C -3.94909500 -2.02940700 1.04488300 H -1.84430400 -2.38576800 1.28575000 C -4.57215900 -0.62338800 -0.80648800 H -2.95367700 0.12508800 -2.00601700 C -4.93591000 -1.39718700 0.29197400 H -4.22315500 -2.64570300 1.89384100 H -5.33446200 -0.13942700 -1.40684800 H -5.98122200 -1.51514000 0.55409300 B 3.34691800 -1.18195300 -0.66177200 F 3.43257800 -1.06502500 -2.05859800 F 3.62594500 -2.49725000 -0.28063700 F 4.26537100 -0.30210900 -0.06622000 O 1.97385000 -0.89696600 -0.19827500 </pre>	
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Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-cis-TS

 <p style="text-align: center; color: cyan;">+19.8</p> <p style="text-align: center;">Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-cis-TS</p>		<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: 1</p>
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1359.408891	-1359.032331	-1359.111204

<pre> H 2.72597300 3.12313300 -1.26581900 C 2.00233400 2.82763400 -2.02459800 H 1.23196200 3.59029300 -2.13483200 O 1.39278700 1.57369900 -1.64969700 H 2.49388700 2.63371000 -2.97354600 C 0.74196500 1.54108900 -0.52018400 O 0.63718300 2.53202900 0.19542400 C 0.10257100 0.19071100 -0.21721300 C -0.20669600 0.07445300 1.28508700 H 0.45581500 0.64087300 1.94022900 H -0.17543700 -0.96761500 1.60358900 O -2.25150100 0.43481300 0.25086900 C -2.47233700 0.22300600 2.60058100 H -3.40517800 0.78579400 2.55648500 H -1.92052900 0.45993800 3.50852500 H -2.70200100 -0.84579500 2.58193100 C -1.34478400 0.17016400 -0.89586700 C -1.61362400 1.25763700 -1.91626800 H -2.65804200 1.17974500 -2.21949700 H -0.98014800 1.09667200 -2.78973200 H -1.43925600 2.25825800 -1.51555400 C 0.98708800 -0.96210300 -0.73978400 H 0.45534400 -1.88897500 -0.52584400 H 1.08333000 -0.87544400 -1.82286900 C 2.35441300 -1.00759100 -0.08877100 C 3.46654500 -0.40466700 -0.68510100 C 2.53380600 -1.67465800 1.12794300 C 4.71514100 -0.44187900 -0.06899700 H 3.35871700 0.08483200 -1.64626000 C 3.77954000 -1.71040700 1.74792600 H 1.69477000 -2.18778000 1.58661200 C 4.87414500 -1.08715800 1.15407500 H 5.56539700 0.02805100 -0.55066200 H 3.89646700 -2.23456500 2.68985600 H 5.84583900 -1.11668400 1.63382900 B -2.24467900 -2.15889200 -0.72994600 F -3.64114300 -2.02339300 -0.60141400 F -1.69596100 -2.30647900 0.56668400 F -1.96590400 -3.31301400 -1.48036600 O -1.66623100 -1.02820200 -1.44332800 C -1.64177000 0.49797400 1.39971800 H -0.51354000 2.51058800 1.13922900 O -2.37372000 3.04518500 1.05640700 H -2.76842400 3.51098300 1.81355800 O -1.35908000 2.29612400 1.68096000 </pre>	
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Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-cis-Adduct

<p style="color: cyan; font-weight: bold;">+15.2</p> <p>Prox-CO₂Me-OBF₃-<i>trans</i>- CO₂Me-H₂O₂-<i>cis</i>-Adduct</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy Correction (H)	EE + Thermal Free Energy Correction (G)
-1359.417808	-1359.039938	-1359.118539

<pre> H -1.20888500 2.13705300 3.41963100 C -2.01576800 1.55268400 2.98084600 H -2.49941300 0.92670000 3.72327300 O -1.45121200 0.61335500 2.01987700 H -2.73514400 2.19034300 2.47057500 C -0.81778900 1.05750600 1.00910100 O -0.69938700 2.31273500 0.87581400 C -0.22295600 0.03566400 0.07434700 C -0.02085500 0.60197600 -1.34270900 H -0.84930400 1.20846100 -1.71365200 H 0.12488800 -0.23208100 -2.02787800 O 1.91999500 1.00994700 -0.06561700 C 2.19449100 1.35204700 -2.44601900 H 2.52488900 0.32074000 -2.57857100 H 3.06579800 1.98679300 -2.28477800 H 1.65881400 1.67950100 -3.33848700 C 1.29251200 -0.16340300 0.49854100 C 1.56648500 -0.15643400 1.98910900 H 1.03205100 -0.97934400 2.46640300 H 1.26073600 0.78881100 2.44350000 H 2.63507600 -0.28299400 2.16020800 C -1.02832000 -1.27663900 0.12353700 H -0.51045400 -1.96818800 -0.53992200 H -0.97993300 -1.68715900 1.13437400 C -2.47138100 -1.13025300 -0.31195500 C -3.50671800 -1.07951000 0.62530000 C -2.79744200 -1.06240200 -1.67054800 C -4.83168800 -0.94187600 0.21810500 H -3.27521000 -1.16130100 1.68184600 C -4.11987300 -0.92112100 -2.08039900 H -2.01179800 -1.13711800 -2.41522400 C -5.14158900 -0.85464300 -1.13598100 H -5.62141700 -0.90875700 0.96035000 H -4.35276300 -0.87262500 -3.13822900 H -6.17238100 -0.74807200 -1.45431200 B 2.95782100 -1.96956700 0.14231600 F 3.22026000 -2.84300200 -0.92903000 F 2.84777100 -2.73218800 1.32974200 F 4.04235000 -1.07936800 0.29345000 O 1.71571500 -1.28045600 -0.16498800 C 1.28211800 1.40068100 -1.25226800 H -0.10389300 2.60091300 0.06732400 O 1.91145200 3.59896500 -0.63234200 H 2.25166300 3.16498400 0.17374300 O 0.83053300 2.77376900 -1.01315400 </pre>	
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Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-trans-TS

<p style="text-align: center; color: cyan;">+19.3</p> <p style="text-align: center;">Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-trans-TS</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: 1</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy	EE + Thermal Free Energy
	Correction (H)	Correction (G)
-1359.411314	-1359.033804	-1359.111954

<pre> H 1.72857400 3.72529400 1.65591300 C 2.36898000 3.22502400 0.92901800 H 2.69412700 3.92406800 0.16283400 O 1.62923500 2.20764800 0.23594800 H 3.22901800 2.78239200 1.43244700 C 1.14380500 1.22440500 0.98250700 O 1.27210500 1.16444200 2.17972500 C 0.38509200 0.19076500 0.14605800 C 0.12930200 -1.05330600 1.01845400 H 0.89029700 -1.20650700 1.78136200 H 0.07212000 -1.96212600 0.41602200 O -1.66250600 0.43681800 1.25706900 C -1.44398700 -1.04003100 3.11958900 H -2.47341000 -0.81694300 3.39785900 H -0.76902700 -0.39501200 3.68713000 H -1.20276700 -2.08100500 3.33320800 C -1.07270800 0.70972900 -0.06267800 C -1.27591500 2.17500900 -0.35209100 H -2.33991300 2.38917900 -0.44379500 H -0.77267500 2.43724100 -1.28316700 H -0.86989200 2.77839800 0.45969100 C 1.10906200 -0.10217100 -1.18134600 H 0.52833900 -0.85973400 -1.70870800 H 1.11145700 0.80527100 -1.78844000 C 2.52684900 -0.59547000 -0.97973000 C 2.77784100 -1.94861500 -0.73020300 C 3.61311000 0.28316800 -1.03697700 C 4.07500100 -2.40824900 -0.52040300 H 1.95322400 -2.65399000 -0.71572600 C 4.91230600 -0.17429600 -0.83036500 H 3.44029500 1.33127700 -1.25457800 C 5.14700700 -1.52046300 -0.56439900 H 4.24824400 -3.46171200 -0.33095000 H 5.74170100 0.52223700 -0.88341900 H 6.15808800 -1.87732600 -0.40428500 B -2.98571200 0.13829900 -1.59586400 F -3.91141500 0.53017500 -0.58220200 F -3.41661500 -1.07220400 -2.14434900 F -2.90890800 1.13152100 -2.56114600 O -1.68380800 -0.15535600 -0.97037100 C -1.20362500 -0.74657100 1.68241100 H -2.04178500 -1.58802100 -0.08042300 O -3.56436800 -1.60105100 1.12729800 H -3.71543300 -0.69975000 0.76115600 O -2.20344400 -1.85296500 0.87725600 </pre>	
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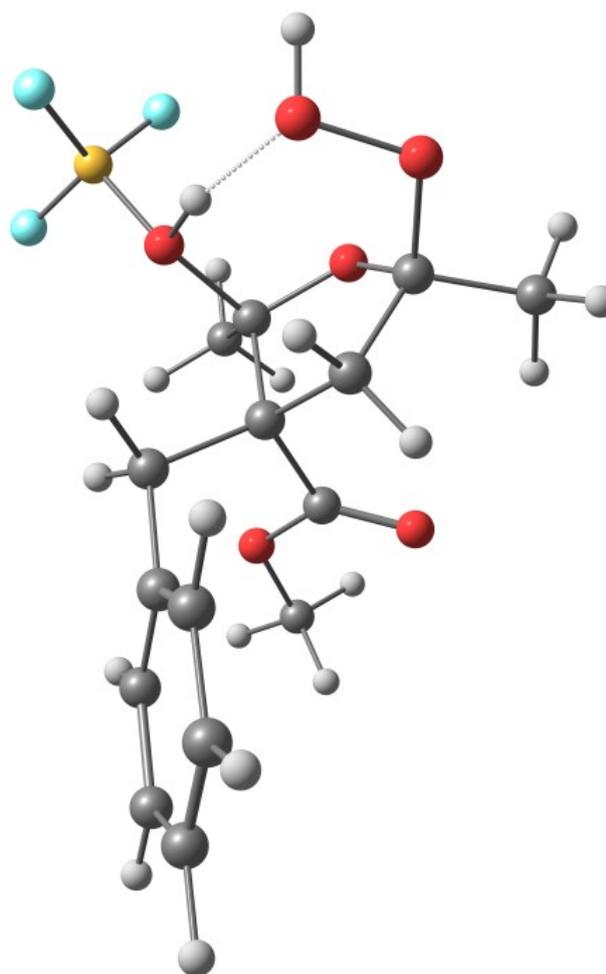
Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-trans-Adduct

<p style="text-align: center; color: blue;">+8.2</p> <p style="text-align: center;">Prox-CO₂Me-OBF₃-trans-CO₂Me-H₂O₂-trans-Adduct</p>	<p>Multiplicity = 1</p> <p>Charge = 0</p> <p>Imaginary vib. modes: no</p>	
Electronic Energy (EE)	EE + Thermal Enthalpy	EE + Thermal Free Energy
	Correction (H)	Correction (G)
-1359.429704	-1359.050339	-1359.129668

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H -3.24449100 -0.34028500 2.90389400
C -2.30063900 -0.82531900 3.15509700
H -1.81349400 -0.29176200 3.97156600
O -1.44353900 -0.85640500 2.00331300
H -2.46601300 -1.86506600 3.42533500
C -1.12344300 0.31976800 1.47823300
O -1.48856300 1.37461100 1.93068500
C -0.26141700 0.16266500 0.21801100
C -0.07983400 1.52860100 -0.46107800
H -0.93702500 2.18209100 -0.31540200
H 0.07085900 1.39597100 -1.53316800
O 1.78535100 1.07722000 0.92429100
C 0.97550900 3.33148500 1.07665100
H 0.28104600 3.05478000 1.86821700
H 0.55479100 4.15855800 0.50391700
H 1.92929600 3.63278400 1.51227300
C 1.20311100 -0.15372900 0.65160300
C 1.43073500 -1.10575700 1.79603900
H 0.95841700 -2.06694800 1.59696300
H 1.00028500 -0.67371300 2.69863500
H 2.49961300 -1.24158400 1.95430100
C -0.88254500 -0.92092600 -0.69303900
H -0.32088600 -0.93680100 -1.62795500
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C -2.34371600 -0.66017000 -0.99280100
C -2.71143400 0.26560200 -1.97445200
C -3.35276900 -1.33108700 -0.29626600
C -4.05219400 0.52936400 -2.23914500
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C -4.69539500 -1.07110100 -0.56093200
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H -5.46428600 -1.60456600 -0.01317000
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