Impact of Stereo- and Regiochemistry on Energetic Materials

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SUPPORTING INFORMATION

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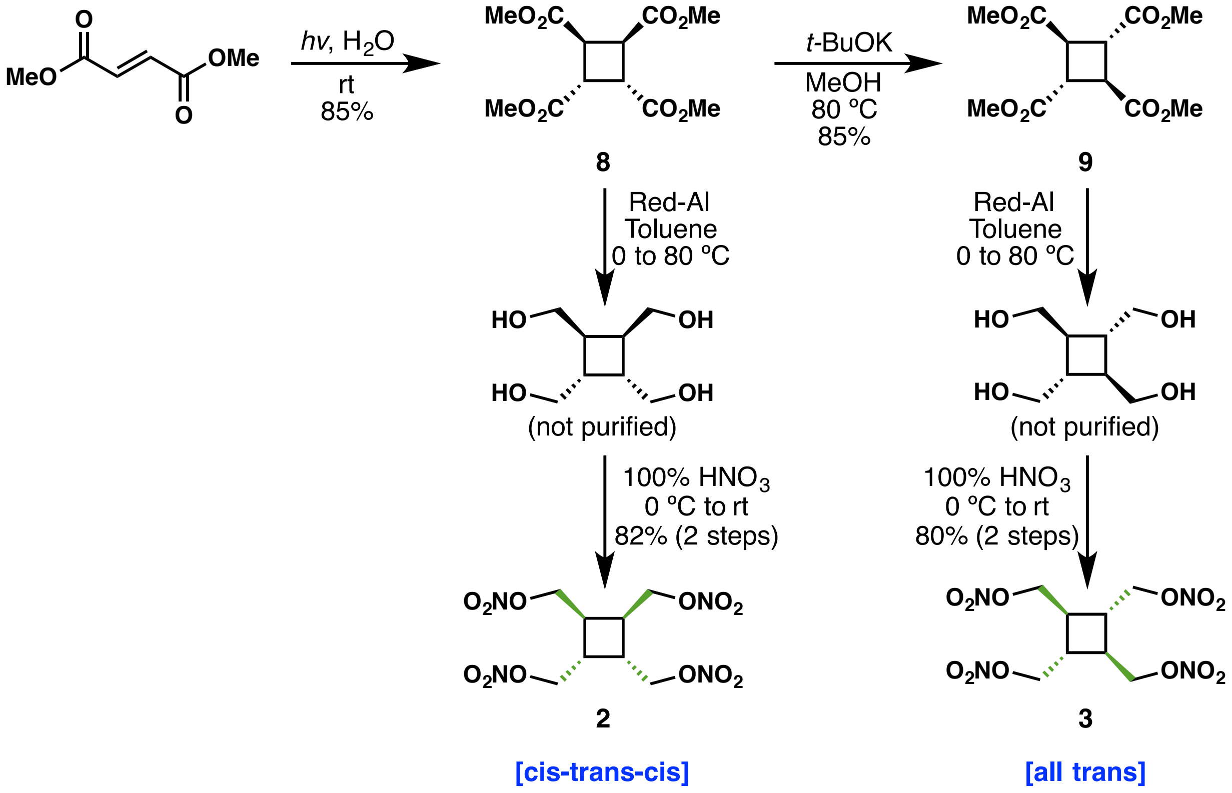
General Experimental

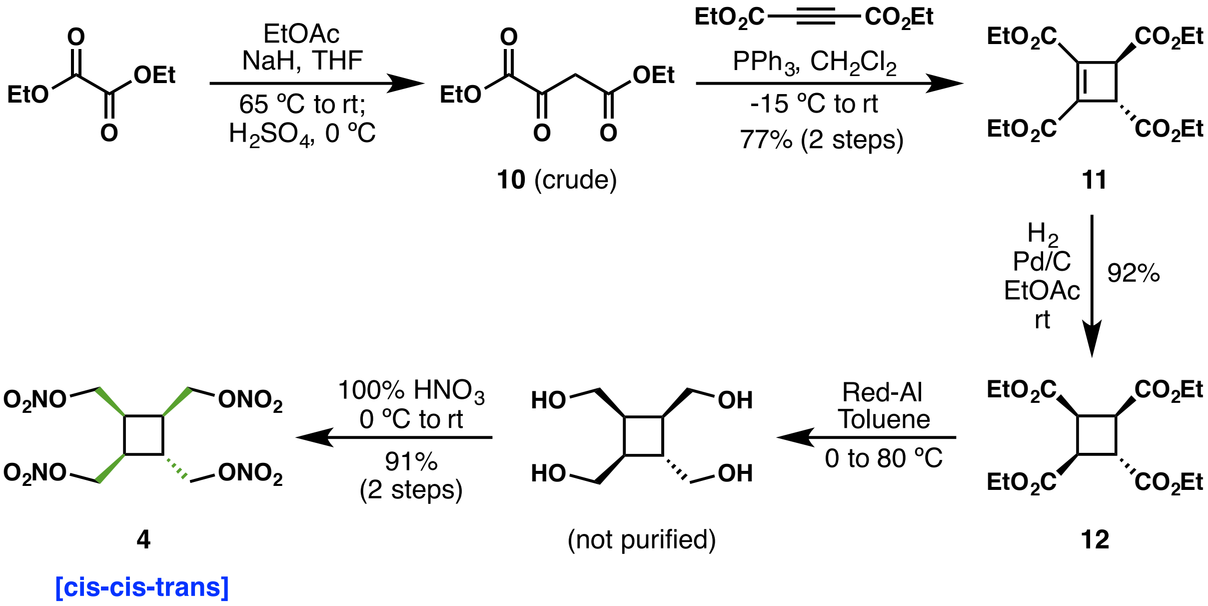
Tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF), toluene, acetonitrile (CH_3CN), and dichloromethane (CH_2Cl_2) were obtained by passing the previously degassed solvents through an activated alumina column. Reagents were purchased at the highest commercial quality grade and used without further purification, unless otherwise stated. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous material, unless otherwise stated. The reactions were monitored by GC/MS, ^{1}H NMR, and thin layer chromatography (TLC). TLC was performed using 0.25 mm E. Merck Silica plates (60F-254), using short-wave UV light as the visualizing agent, acidic ethanolic anisaldehyde, or $KMnO_4$ and heat as developing agents. NMR spectra were recorded on Bruker DRX-600 and Bruker 400 MHz Avance III HD Magnet instruments and are calibrated using residual undeuterated solvent ($CHCl_3$ at 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR; acetone-d_6 at 2.05 ppm ^{1}H NMR, 29.84 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Column chromatography was performed using E. Merck Silica (60, particle size 0.043–0.063 mm). High-resolution mass spectra (HRMS) were recorded on an Agilent LC/MSD TOF mass spectrometer by electrospray ionization time of flight reflectron experiments. Melting points were recorded on a Fisher-Johns 12-144 melting point apparatus and are uncorrected. Infrared spectra were measured with a Bruker Alpha-P FTIR instrument. Melting and decomposition temperatures of tetranitrates were measured at a heating rate of 5 °C/min using a TA Instruments Q10 DSC instrument. Single crystal x-ray diffraction studies for compounds **2-3** and **5-7** were performed with a SuperNova Dualflex diffractometer containing an EosS2 charge-couple device detector and a molybdenum Mo-$K\alpha$ (λ = 0.71073 Å) radiation source. CCDC numbers 1935553 (for **2**), 1935554 (for **3**), 1935555 (for **5**), 1935556 (for **6**), and 1935557 (for **7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

Overall Synthetic Routes

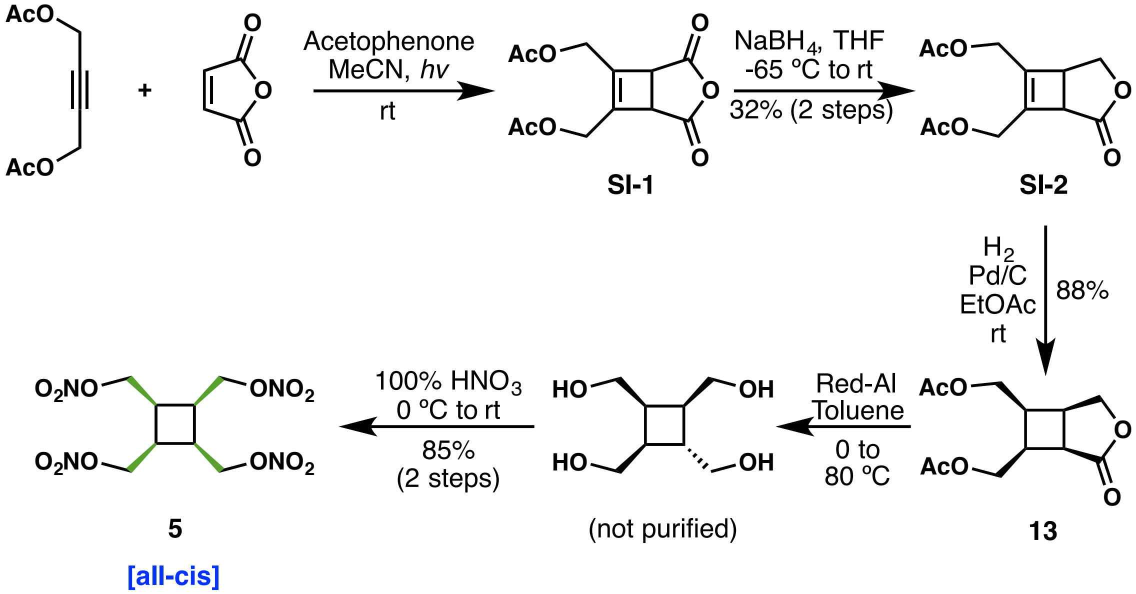
Scheme S1: Synthesis of Cis-Trans-Cis and All-Trans Tetranitrates



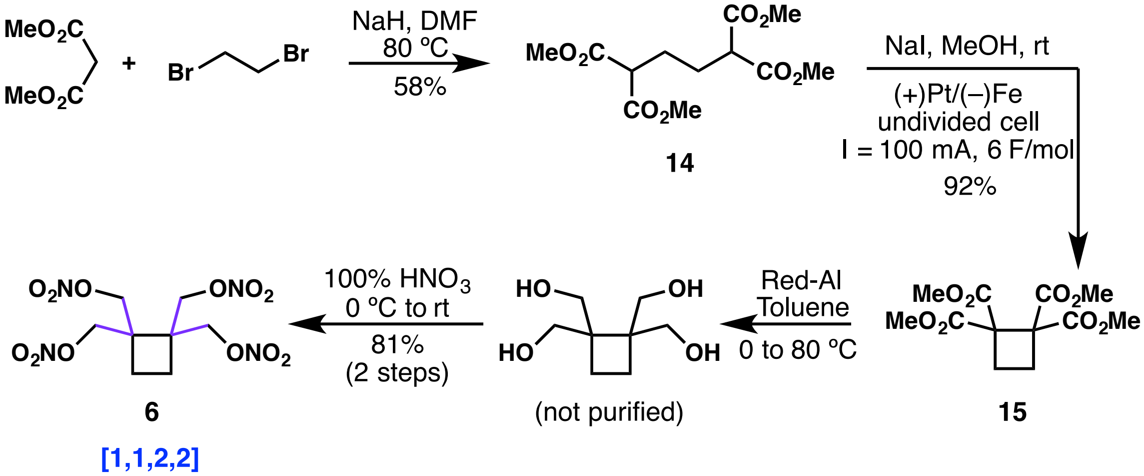
Scheme S2: Synthesis of Cis-Cis-Trans Tetranitrates



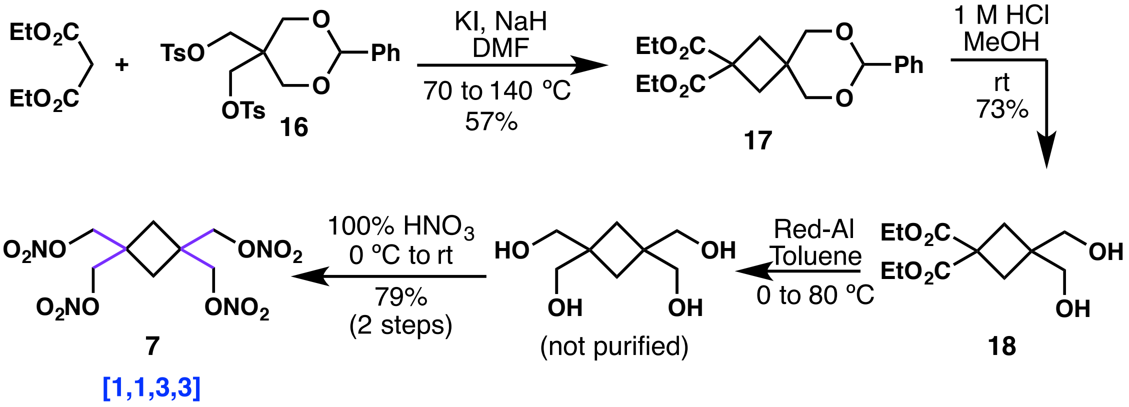
Scheme S3: Synthesis of All-Cis Tetranitrates



Scheme S4: Synthesis of 1,1,2,2 Tetranitrates

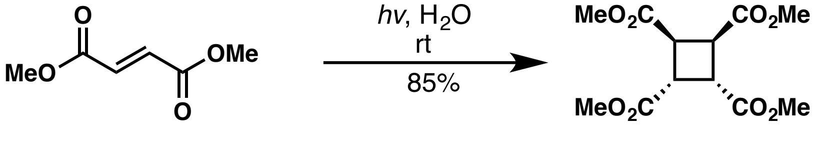


Scheme S5: Synthesis of 1,1,3,3 Tetranitrates



Synthetic Procedures and Characterization Data

Compound 8

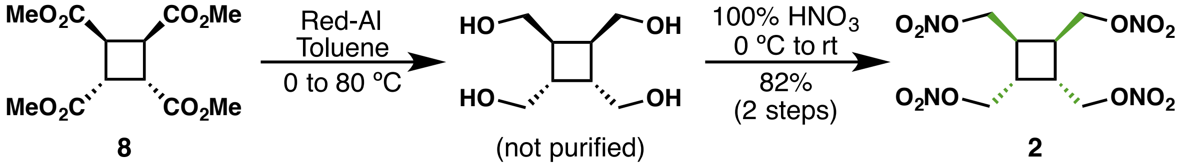


8

The following was modified from a previously reported procedure.[1] A 1 Liter photochemical reaction vessel (#7863) equipped with a quartz immersion well (#7874) was charged with dimethyl fumarate (80.0 g, 555 mmol) and H_2O (800 mL). The suspension was vigorously stirred and irradiated with a mercury lamp at room temperature for 72 hours or until complete consumption of starting matieral was observed by ^{1}H NMR. The resulting white solid was collected by filtration and washed with H_2O (2x 200 mL), followed by cold MeOH (1x 200 mL) and Et_2O (1x 200 mL). The solid was then azeotroped with toluene to ensure no residual H_2O remained to afford 68.0 g (85%) of the title compound **8**. This procedure was repeated multiple times in order to provide over 1.0 kilograms of compound **8**.

Physical State: white solid.
m.p.: 125–132 ºC.
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.76 (s, 4H), 3.69 (s, 12H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 171.4, 52.5, 40.9 ppm.
HRMS (ESI-TOF): calc'd for $C_{12}H_{17}O_8$ $[M+H]^+$: 289.0923, found: 289.0928.
TLC: $R_f = 0.31$ (2:1 hexanes/EtOAc).

Compound 2



Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

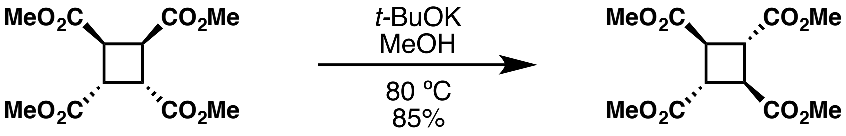
In a 250 mL three-neck round-bottom flask equipped with a reflux condenser and a mechanical stir bar was added 50 mL of toluene. A 60 wt.% solution of Red-Al in toluene (17.5 g, 16.9 mL, 52.1 mmol, 5.00 equiv.) was then added dropwise by means of a syringe over 30 minutes at room temperature. The flask was then immersed into an ice-water bath, and after 20 minutes, tetraester **8** (3 g, 10.4 mmol, 1.00 equiv.) was added in six-500 mg portions over the course of 1 hour. The ice-water bath was removed, and the reaction mixture was stirred for 1 hour at room temperature. The reaction mixture was then immersed in an oil bath, heated to 80 ºC and stirred for 16 hours. The heat was turned off, the reaction mixture was then cooled to room temperature, removed from the oil bath, placed in an ice-water bath, and cooled to 0 ºC.

With vigorous stirring, the reaction mixture was treated with 2.1 mL of H_2O, followed by 2.1 mL of a 15% NaOH solution, followed by 6.3 mL H_2O. After stirring for 1 hour, the solid that formed was collected by means of a Büchner funnel. The mother liquor was discarded, and the solid material was returned to the flask. 60 mL of MeOH was added, and the material was heated to reflux and stirred for 1 hour. After cooling the reaction to room temperature, the solid was collected by means of a Büchner funnel, and rinsed with two-20 mL portions of MeOH. The solid was discarded, and the mother liquor was concentrated *in vacuo* to afford 2.71 g of a white solid material. This solid was the presumed tetrol contaminated with aluminum salts, and was subjected to nitration conditions without further purification.

30 mL of 100% HNO_3 was poured into a three-neck 250 mL round-bottom flask and was cooled to 0 ºC in an ice-water bath. 2.71 g of the above solid material was added portionwise over 1 hour at a rate such that the internal temperature did not rise above 15 ºC. After complete addition of the solid, the reaction mixture was stirred for 1 hour at 0 ºC, the ice-water bath was removed, and the reaction mixture was stirred for an additional 3 hours at room temperature. The reaction mixture was poured onto crushed ice with stirring, and stirred for 2 hours during which time the ice melted and a white/yellow solid appeared. The solid was collected by Büchner funnel and was recrystallized from hot isopropanol to give tetranitrate **2** (3.04 g, 82%) as a white solid.

Physical State: white solid.
m.p.: 106.0–109.6 ºC.
T_{dec} (onset): 198.5 ºC.
T_{peak}: 222.5 ºC.
IR (neat): $\tilde{\nu}$ = 2987.18 (w), 2961.77 (w), 2888.82 (w), 1618.35 (s), 1274.06 (s) cm^{-1}.
^{1}H NMR (400 MHz, acetone-d_6): δ 4.85 (ABX, J_{AB} = 12 Hz, J_{AX} = 8Hz, J_{BX} = 8 Hz, 8 H), 3.01 (s, 4H) ppm.
^{13}C NMR (101 MHz, acetone-d_6): δ 73.0, 34.6 ppm.

Compound 9


8 **9**

The following was modified from a previously reported procedure.[2] Compound **8** (140.1 g, 486 mmol, 1 equiv.) was added to a round bottom flask and dispersed in anhydrous MeOH (1.6 L). *t*-BuOK (16.4 g, 146 mmol, 0.3 equiv.) was then added portionwise. The flask was connected to a reflux condenser and the suspension was heated to 80 ºC, at which point **8** fully dissolved into the solution, and the reaction was stirred at 80 ºC for 24 hours. The reaction was then allowed to cool to room temperature and cooled to -20 ºC until product had fully precipitated from the solution. Product was collected via filtration and washed several times with cold MeOH to afford 118.7 g (85%) of the title compound **9**. This procedure was repeated multiple times in order to provide over 1.0 kilograms of compound **9**.

Physical State: white solid

m.p.: 100–105 ºC.

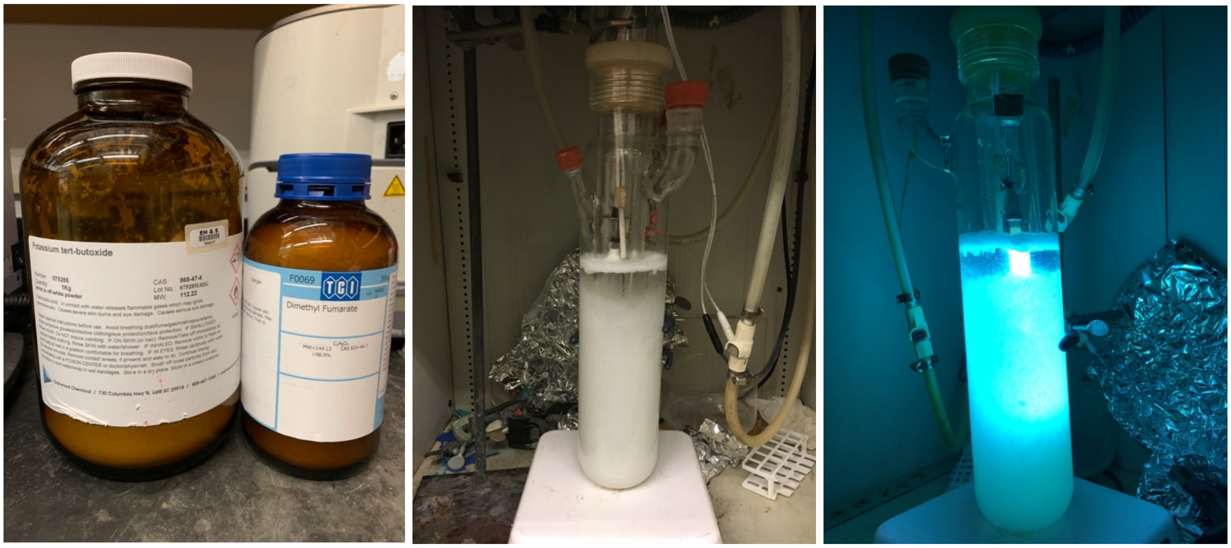
^{1}H NMR (600 MHz, CDCl$_3$): δ 3.75 (s, 12H), 3.48 (s, 4H) ppm.

^{13}C NMR (151 MHz, CDCl$_3$): δ 171.4, 52.7, 40.3 ppm.

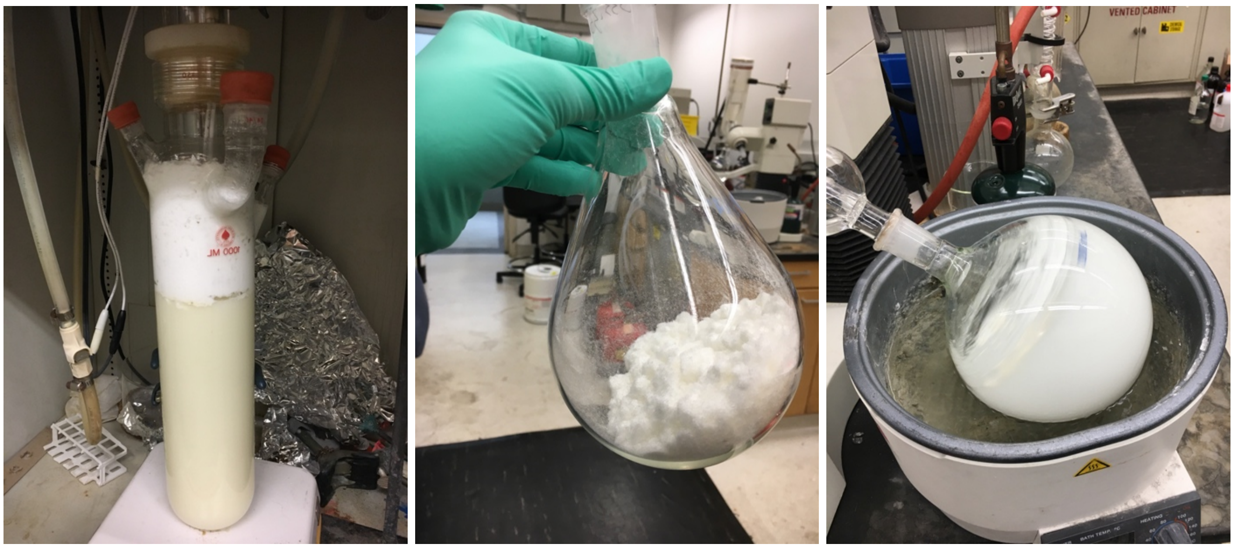
HRMS (ESI-TOF): calc'd for $C_{12}H_{17}O_8$ $[M+H]^+$: 289.0923, found: 289.0928 .

TLC: $R_f = 0.30$ (2:1 hexanes/EtOAc).

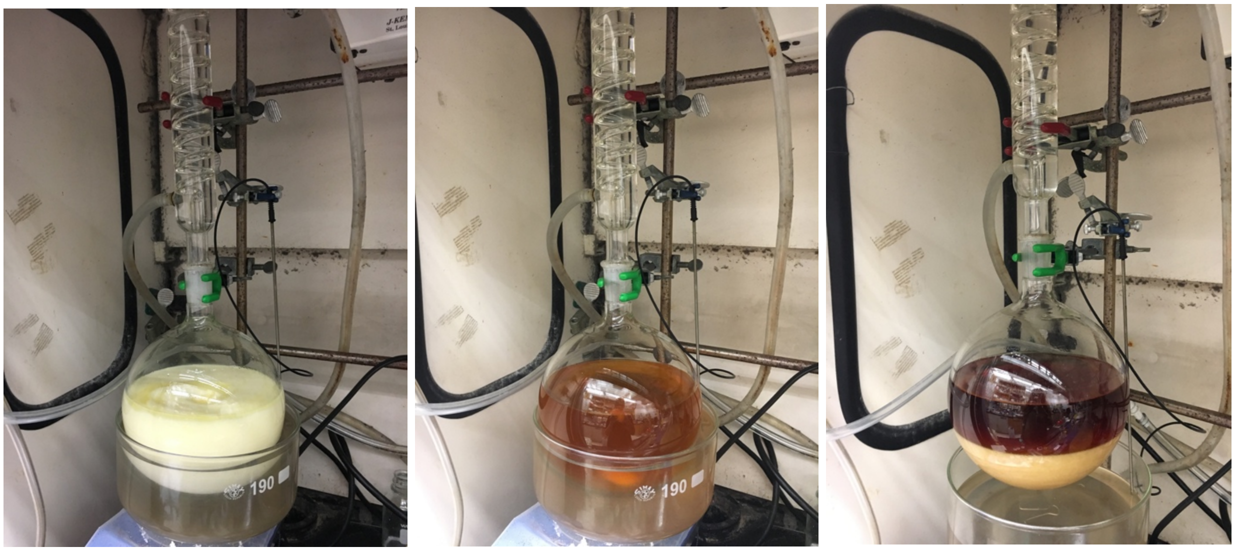
Graphical Supporting Information for the Synthesis of Compounds 8 and 9



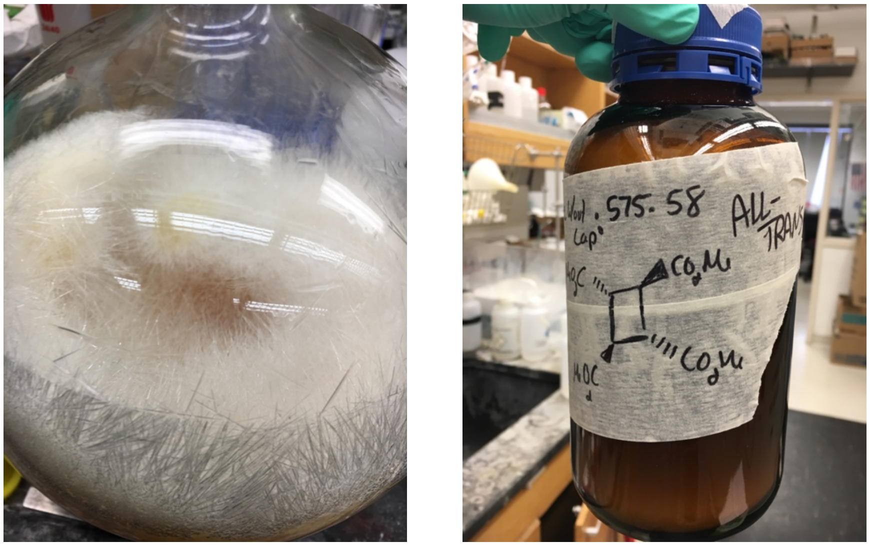
(Left) Reagents used for these reactions. From left to right: *t*-BuOK and Dimethyl Fumarate. **(Center)** Dimethyl fumarate dispersed in H_2O in a 1 L photochemical reaction vessel with quartz immersion well (containing a high pressure mercury lamp) submerged into the solution. No precaution was taken to exclude air from reactor. **(Right)** Irradiation of solution while stirring vigorously.



(Left) Appearance of reaction after dimerization was completed. **(Center)** Compound **8** after filtration. **(Right)** Azeotrop of **8** with Toluene.

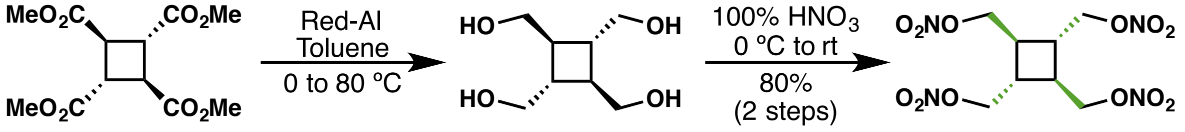


(Left) Dispersion of **8** and *t*-BuOK in MeOH before heat has been applied. **(Center)** Reaction mixture after reaching 80 ºC. **(Right)** Reaction mixture after full consumption of **8** and cooling to room temperature. Desired compound **9** has already begun to crash out of the solution.



(Left). Crystalization of **9** after cooling solution to -20 ºC. **(Right)** Isolated product **9**.

Compound 3



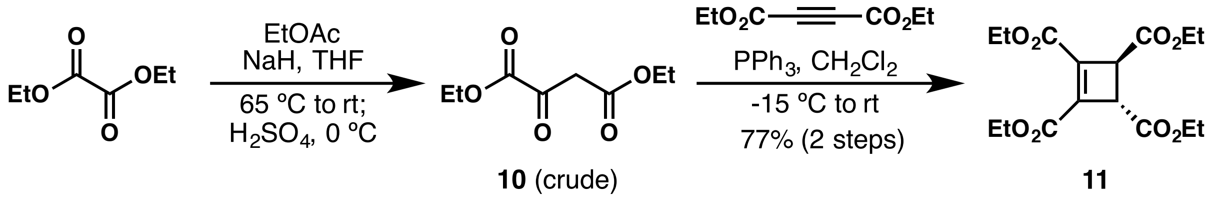
9 (not purified) **3**

Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

Compound **3** was prepared following the same procedure as that used to synthesize compound **2,** with a 60 wt.% solution of Red-Al in toluene (17.5 g, 16.9 mL, 52.1 mmol, 5.00 equiv.), tetraester **9** (3 g, 10.4 mmol, 1.00 equiv.), and toluene (50 mL). After workup, 2.89 g of the presumed tetrol contaminated with aluminum salts was obtained and subjected to the same nitration conditions as that to give compound **2** (using 30 mL 100% HNO_3) without further purification. Workup and recrystallization from hot isopropanol afforded tetranitrate **3** (2.97 g, 80%) as a white solid.

Physical State: white solid.
m.p.: 47.5–49.7 ºC.
T_{dec} (onset): 199.7 ºC.
T_{peak}: 223.8 ºC.
IR (neat): $\tilde{\nu}$ = 2964.39 (w), 2886.45 (w), 1611.76 (s), 1267.36 (s) cm^{-1}.
^{1}H NMR (400 MHz, acetone-d_6): δ 4.70 (s, 8 H), 2.61 (s, 4H) ppm.
^{13}C NMR (101 MHz, acetone-d_6): δ 75.0, 36.7 ppm.

Compound 11



10 (crude) **11**

10 was prepared according to a previously reported procedure.[3] To a flame dried round bottom flask was added NaH (60% oil dispersion, 720 mg, 18 mmol, 1.2 equiv.), which was then placed under argon and dispersed in THF (30 mL). The reaction was then heated to 65 ºC and diethyl oxylate (2.0 mL, 15 mmol, 1 equiv.) was added dropwise, followed by EtOAc (dropwise, 1.5 mL, 15 mmol, 1 equiv.). The reaction was stirred at 65 ºC for 1.5 hours before cooling to room temperature and stirring for an additional 1 hour. The reaction was cooled to 0 ºC and quenched by the careful addition of concentrated sulfuric acid until pH 3 was reached. The suspension was filtered through a pad of Celite and concentrated under reduced pressure. The resulting oil was then diluted with EtOAc, washed with H_2O (3x), dried with Na_2SO_4, filtered and concentrated to give 2.811 g (99%) of **10** as a red oil which was used without any additional purification.

Cyclization was performed according to a reported procedure.[4] **10** (1.76 g, 9.35 mmol, 1 equiv.) and triphenylphosphine (2.45 g, 9.35 mmol, 1 equiv.) were added to a round bottom flask, placed under argon, and dissolved in anhydrous DCM (19 mL). The reaction mixture was then cooled to -15 ºC and a solution of diethyl acetylenedicarboxylate (1.5 mL, 9.35 mmol, 1 equiv.) in DCM (9.5 mL) was added dropwise. The reaction was then allowed to gradually warm to room temperature and stirred for an additional 2 days until complete consumption of the starting material was observed. The reaction was concentrated and purified by column chromatography (silica, 97:3 hexanes/EtOAc to 23:2 hexanes:EtOAc) to afford compound **11** (2.46 g, 77%, 2 steps).

Physical State: pale yellow oil.

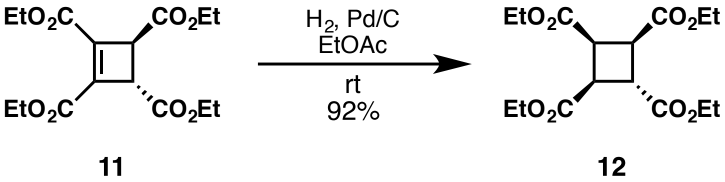
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.27 (ttd, J = 10.5, 6.9, 6.4, 3.2 Hz, 4H), 4.20 (q, J = 7.3 Hz, 4H), 3.81 (s, 2H), 1.31 (t, J = 7.1 Hz, 6H), 1.27 (t, J = 7.3 Hz, 6H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 169.1, 159.8, 141.5, 61.8, 61.7, 46.0, 14.2, 14.2 ppm.

HRMS (ESI-TOF): calc'd for $C_{16}H_{23}O_8$ $[M+H]^+$: 343.1393, found: 343.1398.

TLC: R_f = 0.25 (4:1 hexanes/EtOAc).

Compound 12



Compound **11** (1.0 g, 2.92 mmol, 1 equiv.) and 10% Pd/C (155.4 mg, 0.146 mmol, 5 mol%) were added to a round bottom flask and dissolved in EtOAc (29 mL). The solution was sparged with Argon for 20 minutes before exchanging for a balloon of H_2. The reaction was then stirred at room temperature under H_2 atmosphere overnight. Once starting material was fully consumed (monitored by ^{1}H NMR), the reaction was sparged with argon then filtered through a plug of Celite. After concentration, the filtrate was passed through a flash column (silica, 7:3 hexanes/EtOAc) to remove small amounts of residual Pd and afford 922.4 mg (92%) of compound **12**.

Physical State: pale yellow oil.

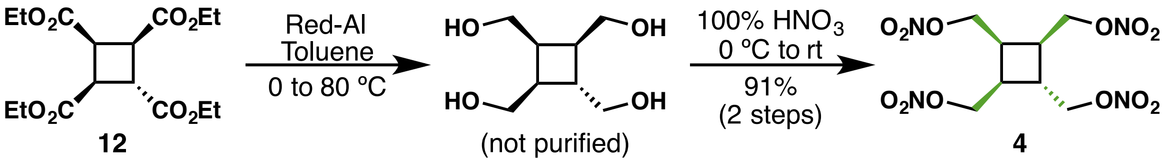
^{1}H NMR (600 MHz, $CDCl_3$): δ 4.20 (qd, *J* = 7.1, 1.6 Hz, 2H), 4.17 – 4.10 (m, 6H), 4.07 (t, *J* = 9.9 Hz, 1H), 3.60 (t, *J* = 9.1 Hz, 1H), 3.46 (td, *J* = 9.6, 1.7 Hz, 2H), 1.28 (td, *J* = 7.2, 1.6 Hz, 3H), 1.24 (dtd, *J* = 11.7, 7.1, 1.6 Hz, 9H) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 172.5, 171.1, 170.1, 61.4, 61.3, 61.3, 42.4, 42.4, 39.3, 14.3, 14.2, 14.2 ppm.

HRMS (ESI-TOF): calc'd for $C_{16}H_{25}O_8$ $[M+H]^+$: 345.1549, found: 345.1545.

TLC: R_f = 0.45 (2:1 hexanes/EtOAc).

Compound 4



Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

Compound **4** was prepared following the same procedure as that used to synthesize compound **2**, with a 60 wt.% solution of Red-Al in toluene (9.79 g, 9.45 mL, 29.1 mmol, 5.00 equiv.), tetraester **12** (2 g, 5.81 mmol, 1.00 equiv.), and toluene (25 mL). After workup, 2.44 g of the presumed tetrol contaminated with aluminum salts was obtained and subjected to the same nitration conditions (using 20 mL 100% HNO_3) as that to make compound **2** without further purification. The nitration was quenched by pouring the reaction mixture onto crushed ice and subsequently stirring for 2 hours, during which time the ice melted. The quenched reaction mixture was transferred to a separatory funnel and was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic extracts were washed with a saturated solution of $NaHCO_3$ (50 mL), dried over magnesium sulfate, and filtered. Evaporation of the solvent in a well-ventilated fume hood afforded tetranitrate **4** (1.88 g, 91%) as a viscous light-yellow liquid.

Physical State: viscous light-yellow liquid.

T_{dec} (onset): 186.8 ºC.

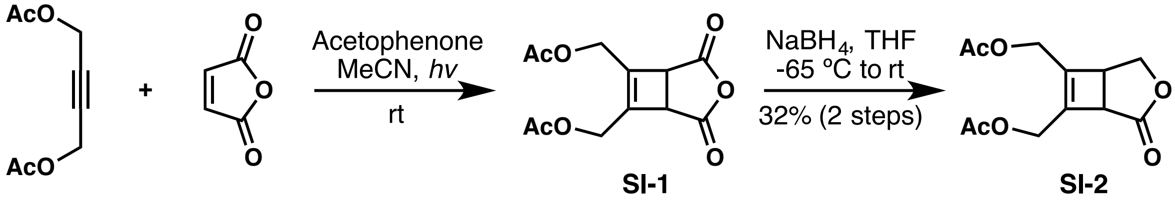
T_{peak}: 214.6 ºC.

IR (neat): $\tilde{\nu}$ = 2964.82 (w), 2987.15 (w), 1617.21 (s), 1270.62 (s) cm^{-1}.

^{1}H NMR (400 MHz, acetone-d$_6$): δ 5.00 (d, *J* = 8 Hz, 2 H), 4.81-4.71 (m, 6H), 3.11 (q, *J* = 8 Hz, 1 H), 3.00-2.88 (m, 3H) ppm.

^{13}C NMR (101 MHz, acetone-d$_6$): δ 75.1, 72.7, 71.2, 37.7, 34.8, 34.1 ppm.

Compound SI-2

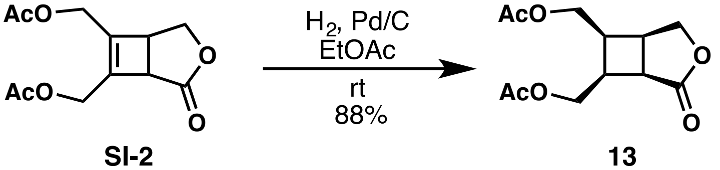


Maleic anhydride (1.96 g, 20 mmol, 1 equiv.), 2-butyne-1,4-diol diacetate (4.1 g, 24 mmol, 1.2 equiv.), and acetophenone (0.47 mL, 4 mmol, 0.2 equiv.) were equally separated into 4 separate pyrex culture tubes, dissolved in MeCN (4x 25mL) and sparged with Argon for 15 minutes. The reaction mixtures were then irradiated with a mercury lamp while stirring vigorously at room temperature. After 9 days, full consumption of maleic anhydride was observed by ^{1}H NMR. All 4 reactions were then combined and concentrated under reduced pressure to give compound **SI-1** which was then subsequently used without any additional purification.

$NaBH_4$ (780 mg, 20.6 mmol, 1.03 equiv.) was added to a flame dried round bottom flask, dispersed in THF (10 mL), and cooled to -65 ºC. A solution of **SI-1** in THF (20 mL) was then added dropwise. The reaction was allowed to gradually warm to room temperature and upon full consumption of **SI-1** (monitered by ^{1}H NMR), the reaction was quenched by the careful addition of 1 M HCl. The reaction was then extracted with EtOAc (3x). The organic layers were then combined, washed with brine, dried with Na_2SO_4, filtered, and concentrated. The crude residue was purified twice by column chromatography (silica, 33:17 hexanes/EtOAc) to afford 1.63 g (32%) of the title compound **SI-2**.

Physical State: pale yellow oil.
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.67 – 4.47 (m, 4H), 4.26 (dd, *J* = 10.0, 2.0 Hz, 1H), 4.19 (dd, *J* = 10.1, 7.1 Hz, 1H), 3.46 – 3.44 (m, 1H), 3.44 – 3.39 (m, 1H), 1.98 (d, *J* = 3.3 Hz, 6H).
^{13}C NMR (151 MHz, CDCl$_3$): δ 173.9, 170.4, 170.3, 142.9, 140.7, 67.3, 58.3, 58.2, 44.1, 39.8, 20.5, 20.5.
HRMS (ESI-TOF): calc’d for $C_{12}H_{15}O_6$ $[M+H]^+$: 255.0869, found 255.0877.
TLC: R_f = 0.25 (1:1 hexanes/EtOAc).

Compound 13



SI-2 **13**

Compound **SI-2** (1.59 g, 6.23 mmol, 1 equiv.) and 10% Pd/C (200 mg, 0.187 mmol, 3 mol%) were added to a round bottom flask and dissolved in EtOAc (60 mL). The solution was sparged with Argon for 20 minutes before exchanging for a balloon of H_2. The reaction was then stirred at room temperature under H_2 atmosphere overnight. Once starting material was fully consumed (monitered by ^{1}H NMR), the reaction was sparged with argon then filtered through a plug of Celite. After concentration, the crude residue was purified by column chromatography (silica, 1.7:1 hexanes/EtOAc) to afford 1.4 g (88%) of the title compound **13**.

Physical State: clear crystals.

m.p.: 37–40 ºC.

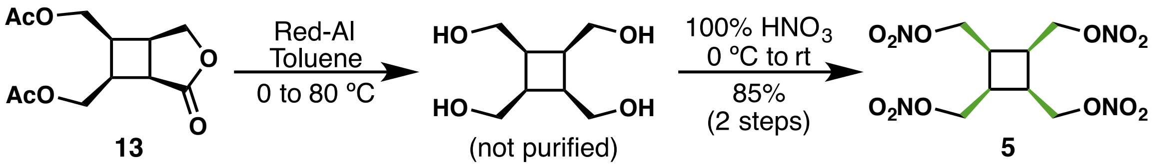
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.47 – 4.44 (m, 1H), 4.41 (dd, *J* = 11.8, 6.1 Hz, 1H), 4.36 – 4.32 (m, 1H), 4.28 (dd, *J* = 11.8, 8.9 Hz, 1H), 4.25 (dd, *J* = 12.1, 5.9 Hz, 1H), 4.18 (dd, *J* = 12.0, 7.0 Hz, 1H), 3.31 – 3.26 (m, 2H), 3.26 – 3.19 (m, 1H), 3.11 – 3.04 (m, 1H), 2.05 (s, 3H), 2.05 (s, 3H) ppm.

^{13}C NMR (151 MHz, CDCl$_3$): δ 177.2, 170.7, 170.6, 68.8, 61.5, 61.1, 38.6, 35.8, 34.8, 33.6, 21.0, 20.9 ppm.

HRMS (ESI-TOF): calc'd for $C_{12}H_{17}O_6$ $[M+H]^+$: 257.1025, found: 257.1022.

TLC: R_f = 0.25 (1:1 hexanes/EtOAc).

Compound 5



Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

Compound **5** was prepared following the same procedure as that used to synthesize compound **2**, with a 60 wt.% solution of Red-Al in toluene (6.58 g, 6.35 mL, 19.5 mmol, 5.00 equiv.), **13** (1 g, 3.90 mmol, 1.00 equiv.), and toluene (25 mL). After workup, 2.80 g of the presumed tetrol contaminated with aluminum salts was obtained and subjected to the same nitration conditions (using 20 mL 100% HNO_3) as that to make compound **2** without further purification. Workup and recrystallization from hot isopropanol afforded tetranitrate **5** (1.18 g, 85%) as a white solid.

Physical State: white solid.

m.p.: 100.8–102.7 ºC.

T_{dec} (onset): 194.3 ºC.

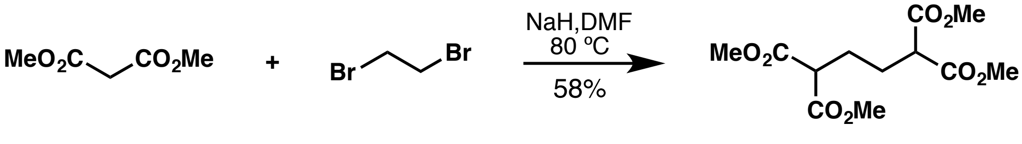
T_{peak}: 210.3 ºC.

IR (neat): $\tilde{\nu}$ = 3001.85 (w) 2973.70 (w), 2891.13 (w), 1646.65 (m), 1613.96 (s), 1479.41 (m), 1284.77 (s), 1270.28 (s) cm^{-1}.

^{1}H NMR (400 MHz, acetone-d$_6$): δ 4.96 (s, 8 H), 3.31 (s, 4H) ppm.

^{13}C NMR (101 MHz, acetone-d$_6$): δ 71.5, 34.3 ppm.

Compound 14

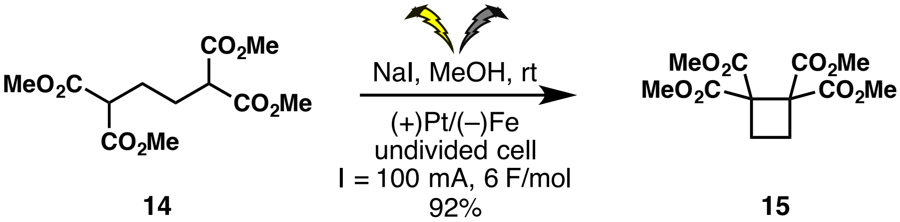


14

NaH (60% oil dispersion, 4.8 g, 120 mmol, 4 equiv.) was added to a flame dried 3 neck round bottom flask, placed under argon, dispersed in DMF (30 mL) and heated to 80 ºC. Dimethyl malonate (17.1 mL, 150 mmol, 5 equiv.) was then added slowly until no more gas evolution was observed. A solution of dibromoethane (2.6 mL, 30 mmol, 1 equiv.) in DMF (30 mL) was then added dropwise via an addition funnel over 1.5 hours. The reaction was allowed to stir at 80 ºC for 24 hours before cooling to room temperature and carefully being quenched with 0.5 M HCl. The reaction was then extracted with EtOAc (3x) and the organic layers were combined, dried with Na_2SO_4, filtered, and concentrated. The crude filtrate was then purified by column chromatography (silica, 17:3 hexanes/EtOAc to 4:1 hexanes/EtOAc) to afford the desired product that was recrystallized from MeOH to give 5.05 g (58%) of the title compound **14**.

Physical State: white solid.
m.p.: 58–62 ºC.
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.74 (s, 12H), 3.41 – 3.35 (m, 2H), 1.93 (d, J = 3.6 Hz, 4H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 169.4, 52.8, 51.4, 26.6 ppm.
HRMS (ESI-TOF): calc'd for $C_{12}H_{19}O_8$ $[M+H]^+$: 291.1080, found: 291.1082.
TLC: R_f = 0.27 (2:1 hexanes/EtOAc).

Compound 15

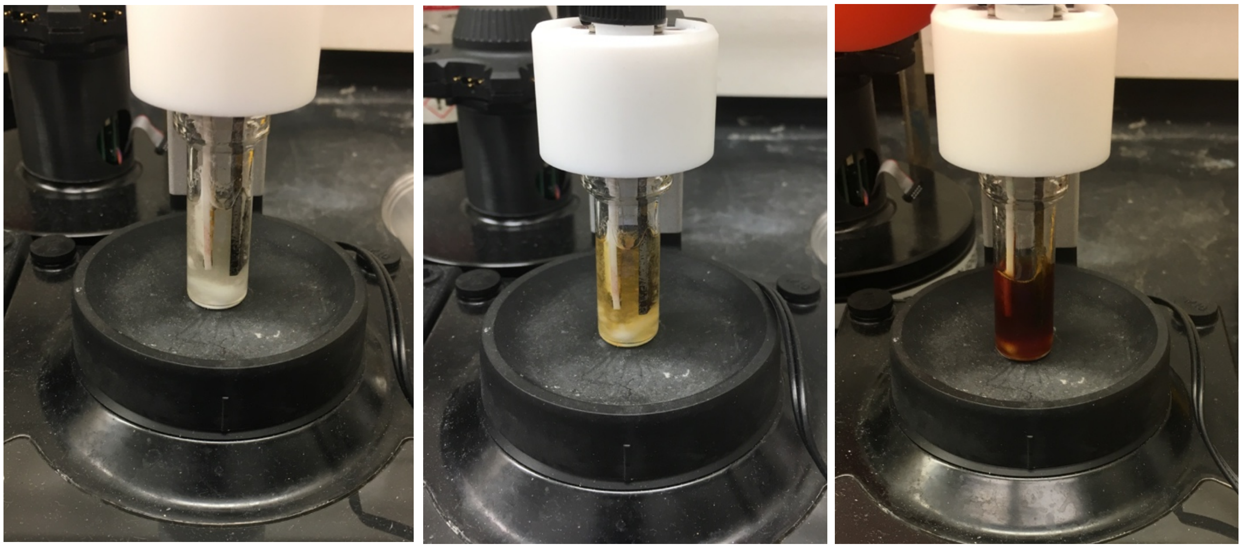


The following was modified from a previously reported procedure.[5] To a 20 mL ElectraSyn Vial was added compound **14** (1.5 g, 5.17 mmol, 1 equiv.) and NaI (519 mg, 3.46 mmol, 0.67 equiv.). The ElectraSyn vial cap, equipped with anode (Pt) and cathode (Fe), was inserted into the mixture. The vial was then evacuated and backfilled with Argon from a balloon (3x) and dissolved in anhydrous MeOH (17 mL). The reaction mixture was electrolyzed under a constant current of 100 mA until 6 F/mol had been passed through the solution. The reaction was then diluted with EtOAc and washed with sat. $Na_2S_2O_3$ (1x), H_2O (3x) and brine (1x). The organic layers were then dried with Na_2SO_4, filtered, concentrated, and purified by flash column chromatography (silica, 1:1 hexanes/EtOAc) to afford 1.364 g (92%) of the title compound **15**.

Physical State: white solid.
m.p.: 65–68 ºC.
^{1}H NMR (600 MHz, $CDCl_3$): δ 3.76 (s, 12H), 2.60 (s, 3H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 170.3, 58.6, 53.1, 26.0 ppm.
HRMS (ESI-TOF): calc'd for $C_{12}H_{17}O_8$ $[M+H]^+$: 289.0923, found: 289.0928.
TLC: R_f = 0.27 (2:1 hexanes/EtOAc).

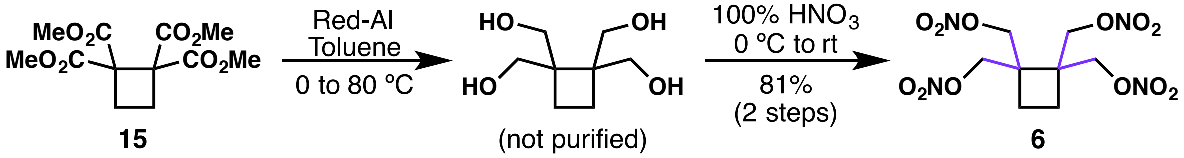
Graphical Supporting Information for Electrochemical Cyclization to Afford Compound 15

For detailed graphical information of the set-up and use of ElectraSyn see Reference 6.



(Left) Reaction vial containing **14**, NaI, and MeOH before beginning electrolysis. Compound **14** is not dissolved at this point. **(Center)** Reaction mixure after electrolysis began. Note that a color change can already be observed as I_2 is generated. **(Right)** Reaction mixture after completion of electrolysis.

Compound 6

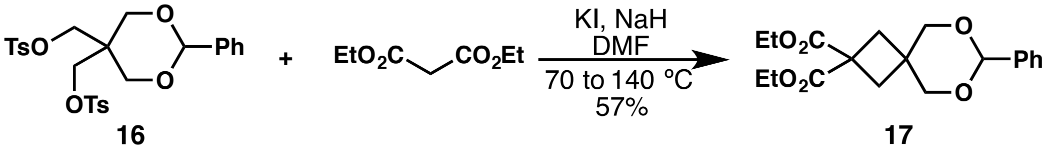


Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

Compound **6** was prepared following the same procedure as that used to synthesize compound **2**, with a 60 wt.% solution of Red-Al in toluene (5.84 g, 5.64 mL, 17.4 mmol, 5.00 equiv.), **15** (1 g, 3.47 mmol, 1.00 equiv.), and toluene (25 mL). After workup, 2.93 g of the presumed tetrol contaminated with aluminum salts was obtained and subjected to the same nitration conditions (using 20 mL 100% HNO_3) as that to give compound **2** without further purification. Workup and recrystallization from hot isopropanol afforded tetranitrate **6** (1.00 g, 81%) as a white solid.

Physical State: white solid.
m.p.: 85.9–86.7 ºC.
T_{dec} (onset): 192.8 ºC.
T_{peak}: 218.9 ºC.
IR (neat): $\tilde{\nu}$ = 3001.38 (w), 2975.13 (w), 2891.32 (w), 1614.62 (s), 1472.51 (w), 1270.24 (s) cm^{-1}.
^{1}H NMR (400 MHz, acetone-d_6): δ 4.87 (AB_q, J = 12 Hz, 8 H), 2.23 (s, 4H) ppm.
^{13}C NMR (101 MHz, acetone-d_6): δ 72.8, 44.1, 23.3 ppm.

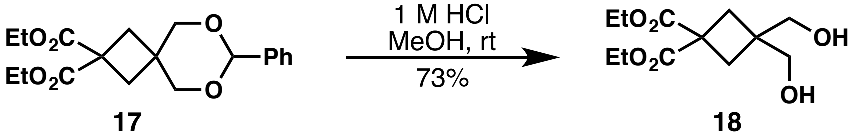
Compound 17



NaH (60% oil dispersion, 1.32 g, 33.1 mmol, 2 equiv.) was added to a flame dried 3 neck round bottom flask, placed under argon, dispersed in DMF (33 mL) and heated to 70 ºC. Diethyl malonate (5.13 mL, 33.8 mmol, 2.04 equiv.) was then added dropwise until no more gas evolution was observed. The reaction was stirred at 70 ºC for 30 minutes, then **16** (8.82 g, 16.55 mmol, 1 equiv., prepared in 2 steps from pentaerythritol[7]) and KI (274 mg, 1.66 mmol, 0.1 equiv.) were added in one portion and the reaction was stirred at 140 ºC overnight. The reaction was then allowed to cool to room temperature and quenched by the careful addition of saturated NH_4Cl. The aqueous phase was extracted with EtOAc (4x). The organic layers were then combined, washed with H_2O (2x), dried over Na_2SO_4, filtered, and concentrated. Crude filtrate was purified by column chromatography (silica, 23:2 hexanes/EtOAc) to afford 3.29 g (57%) of the title compound **17**.

Physical State: white solid.
m.p.: 75–77 ºC.
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.30 (m, 3H), 5.41 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 4H), 4.15 (d, *J* = 11.1 Hz, 2H), 3.75 (d, *J* = 11.0 Hz, 2H), 2.79 (s, 2H), 2.23 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 6H) ppm.
^{13}C NMR (151 MHz, $CDCl_3$): δ 171.8, 138.1, 129.1, 128.4, 126.2, 101.5, 75.4, 61.9, 47.3, 37.7, 31.8, 31.5, 14.2 ppm.
HRMS (ESI-TOF): calc'd for $C_{19}H_{25}O_6$ $[M+H]^+$: 349.1651, found: 349.1655.
TLC: R_f = 0.60 (2:1 hexanes/EtOAc).

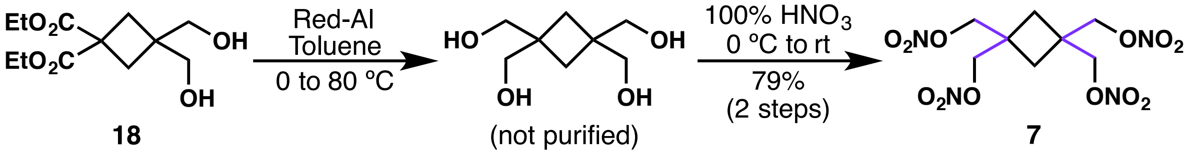
Compound 18



Compound **16** (2.0 g, 5.74 mmol) was added to a round bottom flask and dissolved in MeOH (140 mL). 1 M HCl (23 mL) was then added and the reaction was stirred at room temperature overnight. The reaction was concentrated to remove the MeOH and the remaining aqueous phase was extracted with EtOAc (3x). The organic layers were then combined, dried over Na_2SO_4, filtered, and concentrated. Crude filtrate was purified by column chromatography (silica, 3:1 hexanes/EtOAc to 1:3 hexanes:EtOAc) to afford 1.10 g (73%) of the title compound **18**.

Physical State: pale yellow oil.
^{1}H NMR (600 MHz, CDCl$_3$): δ 4.21 (q, *J* = 7.2 Hz, 4H), 3.72 (d, *J* = 1.9 Hz, 4H), 2.43 (d, *J* = 1.9 Hz, 4H), 2.28 (bs, 2H), 1.25 (t, *J* = 7.2 Hz, 6H) ppm.
^{13}C NMR (151 MHz, CDCl$_3$): δ 172.1, 68.9, 61.9, 47.2, 38.1, 32.8, 14.2 ppm.
HRMS (ESI-TOF): calc'd for $C_{12}H_{21}O_6$ $[M+H]^+$: 261.1338, found: 261.1336.
TLC: R_f = 0.45 (1:3 hexanes/EtOAc).

Compound 7



Caution! Although we did not experience any problems in performing the reaction described in this paper, proper laboratory precautions should be taken. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coat, ballistic face shield, ear plugs, and blast shields are necessary.

Compound **7** was prepared following the same procedure as that used to synthesize compound **2**, with a 60 wt.% solution of Red-Al in toluene (6.48 g, 6.25 mL, 19.2 mmol, 5.00 equiv.), **18** (1 g, 3.85 mmol, 1.00 equiv.), and toluene (25 mL). After workup, 2.88 g of the presumed tetrol contaminated with aluminum salts was obtained and subjected to the same nitration conditions (using 20 mL 100% HNO_3) as that to give compound **2** without further purification. Workup and recrystallization from hot isopropanol afforded tetranitrate **7** (1.08 g, 79%) as a white solid.

Physical State: white solid.

m.p.: 146.9–148.4 °C.

T_{dec} (onset): 196.2 °C.

T_{peak}: 214.1 °C.

IR (neat): $\tilde{\nu}$ = 3001.33 (w), 2973.63 (w), 2891.06 (w), 1646.00 (m), 1616.16 (s), 1470.24 (w), 1269.40 (s) cm^{-1}.

^{1}H NMR (400 MHz, acetone-d_6): δ 4.77 (s, 8 H), 2.37 (s, 4H) ppm.

^{13}C NMR (101 MHz, acetone-d_6): δ 76.0, 33.9, 31.3 ppm.

X-Ray Crystallographic Data

General Experimental Details

Single crystals of compounds (**2**), (**3**), (**5**), (**6**), and (**7**) were characterized with a SuperNova, Dualflex, EosS2 diffractometer using a Mo Kα (λ = 0.71073 Å) radiation source and an EosS2 charged coupled device (CCD) detector at 298 K. Tables S1, S7, S13, S19, and S25 list the data collection, and structure refinement details for the aformentioned compounds. The diffraction patters were measured using the program CrysAlis^{Pro}. The same program was used to refine the cell dimensions and for data reduction. The structures were solved with SHEL-XT using intrinsic phasing and was refined with SHEL-XL using least squares minimization. Empirical absorption corrections using spherical harmonics, implemented in the Scale3 ABSPACK scaling algorithm, were applied using CrysAlis^{Pro}. The hydrogen atoms were refined using a riding model approximation with parameters having values 1.2 or 1.5 U_{eq} of the attached C atoms [(**2**), (**3**), (**5**)] or they were refined independently including isotropic displacement parameters [(**6**), (**7**)].

The Cambridge Crystallographic Data Centre (CCDC) has assigned crystallographic information file deposition numbers: 1935553, 1935554, 1935555, 1935556, and 1935557 for compounds (**2**), (**3**), (**5**), (**6**), and (**7**), respectively.

Compound 2

CCDC 1935553

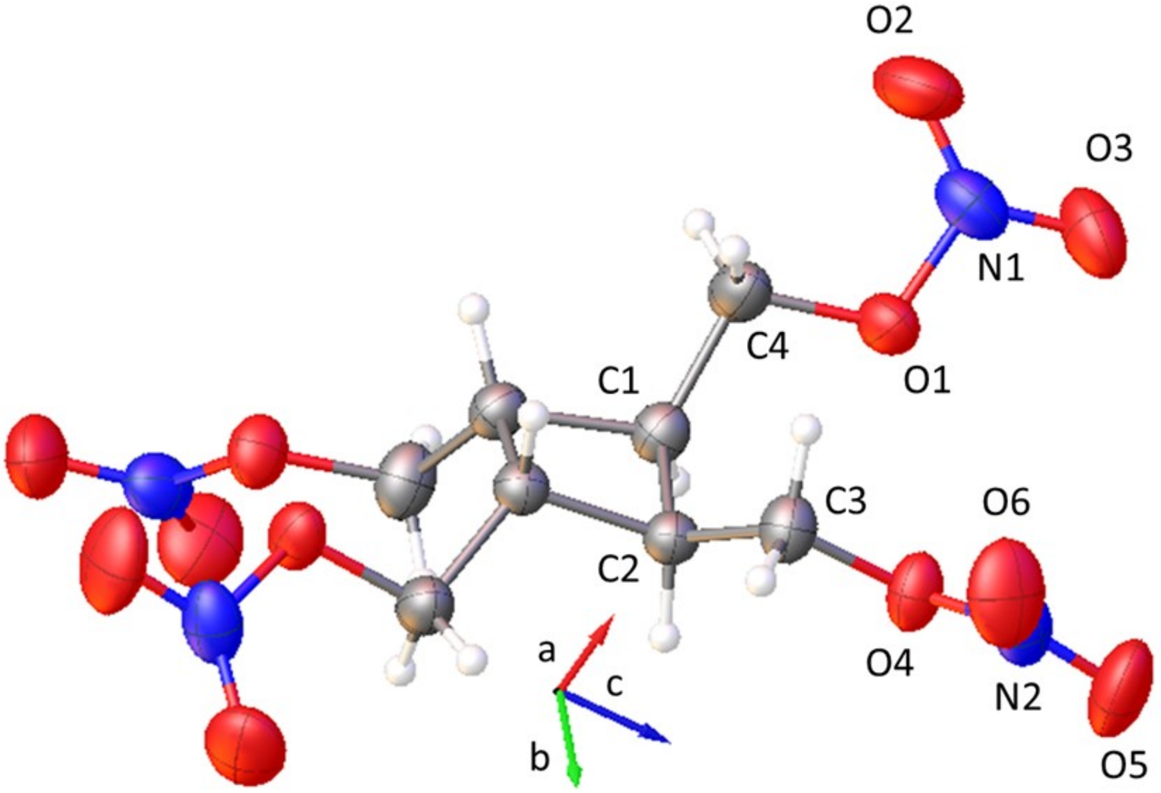


Figure S1. Molecular conformation and atom-numbering scheme for Compound **2**. Non-labeled atoms are generated by inversion (1 - x, -y, ½ - z). Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

Table S1. Crystal data and structure refinement for Compound **2**.

Empirical formula	$C_8H_{12}N_4O_{12}$
Formula weight	356.22
Temperature/K	298.00(10)
Crystal system	orthorhombic
Space group	Pbcn
a/Å	7.9408 (3)
b/Å	16.1350 (7)
c/Å	11.2323 (4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1439.14(10)
Z	4
ρ_{calc}g/cm^3	1.644
μ/mm^{-1}	0.158
F(000)	736.0
Crystal size/mm^3	0.35 × 0.3 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.05 to 52.738
Index ranges	$-9 \le h \le 9$, $-20 \le k \le 19$, $-14 \le l \le 12$
Reflections collected	6369
Independent reflections	1476 [R_{int} = 0.0201, R_{sigma} = 0.0152]
Data/restraints/parameters	1476/0/109
Goodness-of-fit on F^2	1.122
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.1016
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.1067
Largest diff. peak/hole / e Å^{-3}	0.29/-0.27

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times 10^3$) for **2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	5321.7(17)	5001.4(9)	3156.9(12)	32.5(3)
C2	5116.2(16)	5958.0(8)	3184.0(11)	28.6(3)
C3	6470.1(18)	6529.0(9)	3635.9(13)	36.3(4)
C4	7058(2)	4629(1)	3234.9(13)	41.5(4)
N1	8948.5(17)	4196.1(9)	4757.4(14)	46.3(4)
N2	7221.5(19)	7131.8(8)	5496.7(13)	47.4(4)
O1	7512.2(13)	4645.1(7)	4487.6(9)	41.1(3)
O2	9697.8(17)	3872.7(9)	3954.2(13)	68.7(4)
O3	9269.9(16)	4193.4(9)	5806.3(12)	63.0(4)
O4	6380.5(14)	6494.7(6)	4924.5(9)	41.2(3)
O5	7028(2)	7129.4(9)	6550.5(11)	72.5(5)
O6	8027(2)	7604.3(9)	4901.2(13)	69.4(5)

Table S3. Anisotropic Displacement Parameters ($Å^2\times 10^3$) for Compound **2**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	37.3(7)	29.8(7)	30.3(8)	1.7(6)	0.7(6)	-1.1(6)
C2	28.1(6)	28.3(7)	29.4(7)	-0.2(5)	0.5(5)	0.7(5)
C3	40.9(8)	36.3(8)	31.7(8)	1.6(6)	-2.8(6)	-6.4(6)
C4	50.4(9)	39.0(8)	35.0(8)	-0.9(6)	-2.2(7)	12.0(7)
N1	36.3(7)	43.9(8)	58.7(9)	10.8(7)	-4.6(7)	2.7(6)
N2	59.5(9)	32.7(7)	49.9(9)	-5.3(6)	-20.4(7)	2.0(7)
O1	41.5(6)	43.4(6)	38.5(6)	2.0(5)	-3.9(5)	11.1(5)
O2	55.5(8)	77.3(10)	73.4(10)	3.1(7)	5.1(7)	30.4(7)
O3	52.3(7)	80.4(10)	56.3(8)	15.5(7)	-17.7(6)	2.1(7)
O4	56.3(7)	34.4(6)	32.8(6)	-0.2(4)	-9.2(5)	-9.8(5)
O5	113.0(13)	64.0(9)	40.4(8)	-14.1(6)	-20.9(7)	3.5(8)
O6	85.2(10)	48.3(8)	74.8(10)	3.1(7)	-21.4(8)	-29.5(8)

Table S4. Bond Lengths for Compound **2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C1^1	1.562(3)	N1	O1	1.3847(17)
C1	C2	1.5524(19)	N1	O2	1.2001(19)
C1	C4	1.507(2)	N1	O3	1.2055(18)
C2	C2^1	1.548(3)	N2	O4	1.3841(16)
C2	C3	1.5041(19)	N2	O5	1.1936(19)
C3	O4	1.4503(17)	N2	O6	1.1990(19)
C4	O1	1.4528(18)			

^{1}1-X,+Y,1/2-Z

Table S5. Bond Angles for Compound **2**.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C2	C1	C1^1	89.09(7)	O2	N1	O1	118.12(14)
C4	C1	C1^1	110.75(13)	O2	N1	O3	128.92(15)
C4	C1	C2	119.44(12)	O3	N1	O1	112.96(14)
C2^1	C2	C1	89.61(7)	O5	N2	O4	113.32(15)
C3	C2	C1	122.72(11)	O5	N2	O6	128.60(15)
C3	C2	C2^1	114.85(11)	O6	N2	O4	118.08(14)
O4	C3	C2	106.16(11)	N1	O1	C4	114.01(11)
O1	C4	C1	106.04(11)	N2	O4	C3	114.29(11)

^{1}1-X,+Y,1/2-Z

Table S6. Torsion Angles for Compound **2**.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1^1	C1	C2	C2^1	-12.18(13)	C2	C3	O4	N2	-164.11(12)
C1^1	C1	C2	C3	-131.86(14)	C4	C1	C2	C2^1	101.27(14)
C1^1	C1	C4	O1	-178.87(9)	C4	C1	C2	C3	-18.41(19)
C1	C2	C3	O4	-78.32(15)	O2	N1	O1	C4	2.8(2)
C1	C4	O1	N1	169.33(12)	O3	N1	O1	C4	-177.57(13)
C2	C1	C4	O1	79.93(15)	O5	N2	O4	C3	174.64(14)
C2^1	C2	C3	O4	174.92(11)	O6	N2	O4	C3	-5.3(2)

^{1}1-X,+Y,1/2-Z

Compound 3

CCDC 1935554

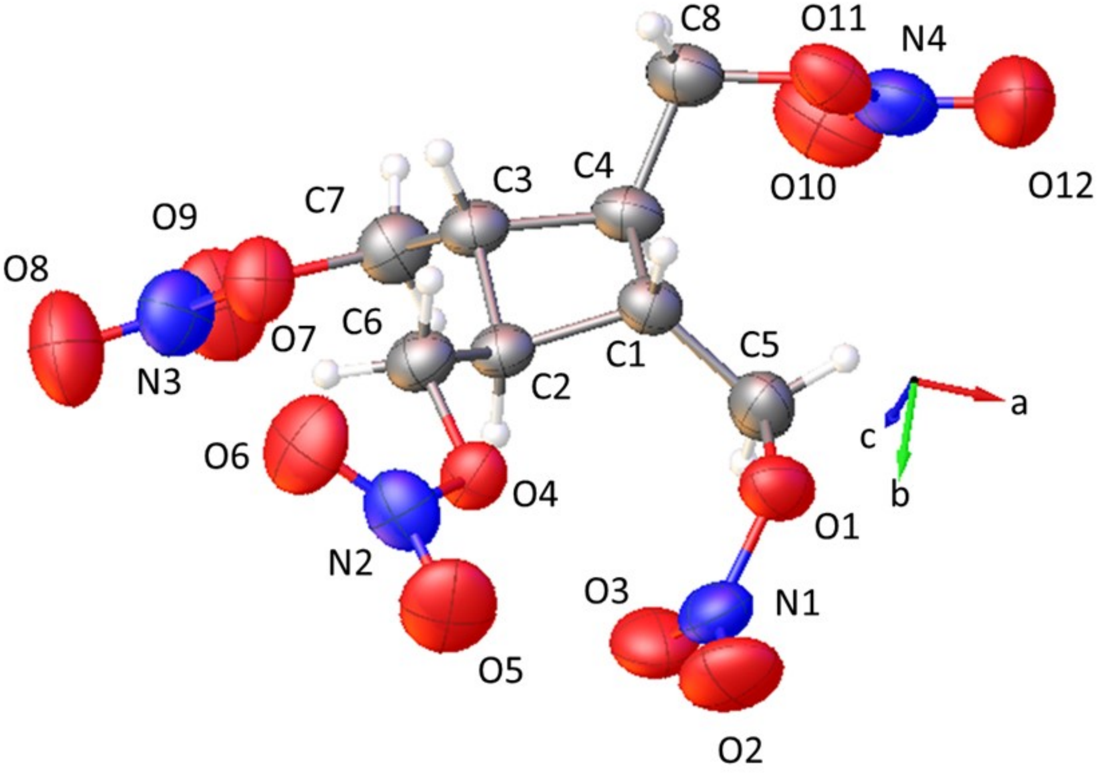


Figure S2. Molecular conformation and atom-numbering scheme for Compound **3**. Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

Table S7. Crystal data and structure refinement for Compound **3**.

Empirical formula	$C_8H_{12}N_4O_{12}$
Formula weight	356.22
Temperature/K	298.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	7.6027(4)
b/Å	9.8312(4)
c/Å	9.8783(4)
α/°	90
β/°	93.581(5)
γ/°	90
Volume/$Å^3$	736.90(6)
Z	2
$\rho_{calc}g/cm^3$	1.605
μ/mm^{-1}	0.154
F(000)	368.0
Crystal size/mm^3	0.32 × 0.23 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.132 to 50.7
Index ranges	$-9 \leq h \leq 8, -11 \leq k \leq 11, -11 \leq l \leq 11$
Reflections collected	5945
Independent reflections	2668 [$R_{int} = 0.0200$, $R_{sigma} = 0.0290$]
Data/restraints/parameters	2668/1/217
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	$R_1 = 0.0399$, $wR_2 = 0.0725$
Final R indexes [all data]	$R_1 = 0.0472$, $wR_2 = 0.0757$
Largest diff. peak/hole / e $Å^{-3}$	0.12/-0.12
Flack parameter	-0.1(5)

Table S8. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **3**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	6350(4)	6329(3)	1561(3)	58.0(7)
O2	6114(5)	8510(3)	1580(4)	86.7(10)
O3	5505(4)	7410(3)	3386(3)	73.7(8)
O4	2297(3)	7007(2)	1382(2)	45.9(6)
O5	1991(4)	8992(3)	462(3)	87.2(10)
O6	-227(4)	7612(3)	309(3)	78.5(10)
O7	-170(3)	3841(3)	4275(2)	58.2(7)
O8	-2234(4)	4383(4)	5591(3)	98.6(12)
O9	-99(5)	3111(4)	6408(3)	92.1(11)
O10	6261(4)	1581(2)	1662(3)	61.8(7)
O11	6848(5)	947(4)	3789(4)	92.9(12)
O12	8898(5)	1026(4)	2384(5)	112.6(14)
N1	5965(4)	7513(3)	2248(4)	56.9(9)
N2	1246(5)	7936(4)	654(3)	57.7(8)
N3	-882(5)	3756(4)	5541(3)	67.3(10)
N4	7403(6)	1152(4)	2712(5)	72.3(10)
C1	4424(4)	4388(3)	1963(3)	40.1(8)
C2	2720(4)	4945(3)	2543(3)	37.2(7)
C3	2196(4)	3467(3)	2881(3)	40.9(8)
C4	4136(5)	3034(4)	2715(3)	43.7(8)
C5	6170(5)	5065(4)	2299(4)	53.8(9)
C6	1438(5)	5721(4)	1631(3)	45.4(9)
C7	1535(5)	3177(4)	4251(3)	49.7(9)
C8	4436(5)	1712(4)	1996(4)	52.3(9)

Table S9. Anisotropic Displacement Parameters (Å^2×10^3) for Compound **3**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	67.4(19)	42.9(15)	65.4(15)	-1.9(13)	16.9(13)	-6.3(13)
O2	107(3)	42.1(17)	110(2)	13.0(17)	-2.4(19)	-14.0(17)
O3	81(2)	75(2)	63.3(18)	-21.6(16)	-4.5(15)	-4.8(17)
O4	45.2(14)	39.1(13)	52.8(13)	12.7(10)	-2.3(11)	2.4(11)
O5	100(2)	53.8(18)	109(2)	37.9(19)	10.0(18)	1.4(19)
O6	63.5(19)	89(2)	79.8(19)	28.0(17)	-22.0(16)	8.1(17)
O7	55.2(16)	74.4(19)	45.3(13)	15.7(13)	6.1(11)	4.6(15)
O8	73(2)	137(3)	87(2)	11(2)	24.9(18)	20(2)
O9	108(3)	110(3)	60.9(17)	39(2)	24.4(18)	12(2)
O10	82(2)	40.3(16)	64.2(16)	2.5(12)	16.6(15)	9.1(14)
O11	129(3)	81(2)	67(2)	7.8(17)	-6(2)	27(2)
O12	70(3)	92(3)	177(4)	-23(3)	12(3)	3(2)
N1	52(2)	49(2)	68(2)	-6.1(19)	-8.0(17)	-8.4(17)
N2	66(2)	55(2)	52.3(18)	15.3(16)	3.1(16)	13.8(19)
N3	70(3)	77(3)	56(2)	9.2(19)	17.3(19)	-5(2)
N4	81(3)	44(2)	91(3)	-9(2)	-2(3)	5(2)
C1	47(2)	36.0(18)	36.6(16)	0.3(14)	2.1(14)	1.6(16)
C2	42(2)	35.3(17)	33.5(16)	-0.5(13)	-4.2(13)	-3.6(16)
C3	49(2)	37.8(18)	35.6(16)	0.1(14)	-4.2(14)	-4.5(16)
C4	55(2)	32.9(17)	42.0(17)	-1.3(15)	-2.0(15)	1.3(17)
C5	48(2)	44(2)	70(2)	2.9(19)	4.6(17)	5.0(19)
C6	46(2)	42.1(19)	46.9(19)	2.0(15)	-6.9(16)	-3.4(17)
C7	57(2)	48(2)	44.3(18)	10.7(16)	1.5(16)	-1.8(19)
C8	62(3)	40(2)	54(2)	-1.0(16)	-2.2(18)	2.6(19)

Table S10. Bond Lengths for Compound **3**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N1	1.389(4)	O10	N4	1.376(5)
O1	C5	1.452(4)	O10	C8	1.452(4)
O2	N1	1.191(4)	O11	N4	1.185(5)
O3	N1	1.202(4)	O12	N4	1.208(5)
O4	N2	1.386(3)	C1	C2	1.549(5)
O4	C6	1.450(4)	C1	C4	1.547(5)
O5	N2	1.203(4)	C1	C5	1.503(5)
O6	N2	1.193(4)	C2	C3	1.548(4)
O7	N3	1.395(4)	C2	C6	1.495(4)
O7	C7	1.453(4)	C3	C4	1.554(5)
O8	N3	1.203(4)	C3	C7	1.501(4)
O9	N3	1.194(4)	C4	C8	1.505(5)

Table S11. Bond Angles for Compound **3**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	O1	C5	116.3(3)	C4	C1	C2	88.8(2)
N2	O4	C6	114.3(3)	C5	C1	C2	120.6(3)
N3	O7	C7	112.6(3)	C5	C1	C4	115.1(3)
N4	O10	C8	115.0(3)	C3	C2	C1	88.9(2)
O2	N1	O1	112.9(3)	C6	C2	C1	119.1(3)
O2	N1	O3	129.1(4)	C6	C2	C3	116.2(3)
O3	N1	O1	118.0(3)	C2	C3	C4	88.6(2)
O5	N2	O4	112.9(3)	C7	C3	C2	118.5(3)
O6	N2	O4	118.2(3)	C7	C3	C4	114.6(3)
O6	N2	O5	128.9(3)	C1	C4	C3	88.8(2)
O8	N3	O7	112.7(3)	C8	C4	C1	119.1(3)
O9	N3	O7	118.1(4)	C8	C4	C3	117.3(3)
O9	N3	O8	129.2(4)	O1	C5	C1	112.2(3)
O11	N4	O10	119.0(4)	O4	C6	C2	105.3(2)
O11	N4	O12	128.1(5)	O7	C7	C3	106.2(3)
O12	N4	O10	112.9(5)	O10	C8	C4	111.1(3)

Table S12. Torsion Angles for Compound **3**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	O1	C5	C1	97.1(3)	C4	C1	C5	O1	-179.9(3)
N2	O4	C6	C2	-174.1(3)	C4	C3	C7	O7	171.2(3)
N3	O7	C7	C3	-174.8(3)	C5	O1	N1	O2	-179.0(3)
N4	O10	C8	C4	80.7(4)	C5	O1	N1	O3	-0.5(4)
C1	C2	C3	C4	16.6(2)	C5	C1	C2	C3	-135.4(3)
C1	C2	C3	C7	134.1(3)	C5	C1	C2	C6	104.9(3)
C1	C2	C6	O4	-70.7(3)	C5	C1	C4	C3	140.2(3)
C1	C4	C8	O10	62.8(4)	C5	C1	C4	C8	-98.9(4)
C2	C1	C4	C3	16.6(2)	C6	O4	N2	O5	-180.0(3)
C2	C1	C4	C8	137.5(3)	C6	O4	N2	O6	0.2(4)
C2	C1	C5	O1	-75.4(4)	C6	C2	C3	C4	138.8(3)
C2	C3	C4	C1	-16.6(2)	C6	C2	C3	C7	-103.7(4)
C2	C3	C4	C8	-139.1(3)	C7	O7	N3	O8	175.2(4)
C2	C3	C7	O7	68.5(4)	C7	O7	N3	O9	-4.1(5)
C3	C2	C6	O4	-175.1(3)	C7	C3	C4	C1	-137.6(3)
C3	C4	C8	O10	167.8(3)	C7	C3	C4	C8	100.0(4)
C4	C1	C2	C3	-16.7(2)	C8	O10	N4	O11	-1.2(5)
C4	C1	C2	C6	-136.4(3)	C8	O10	N4	O12	178.4(3)

Compound 5

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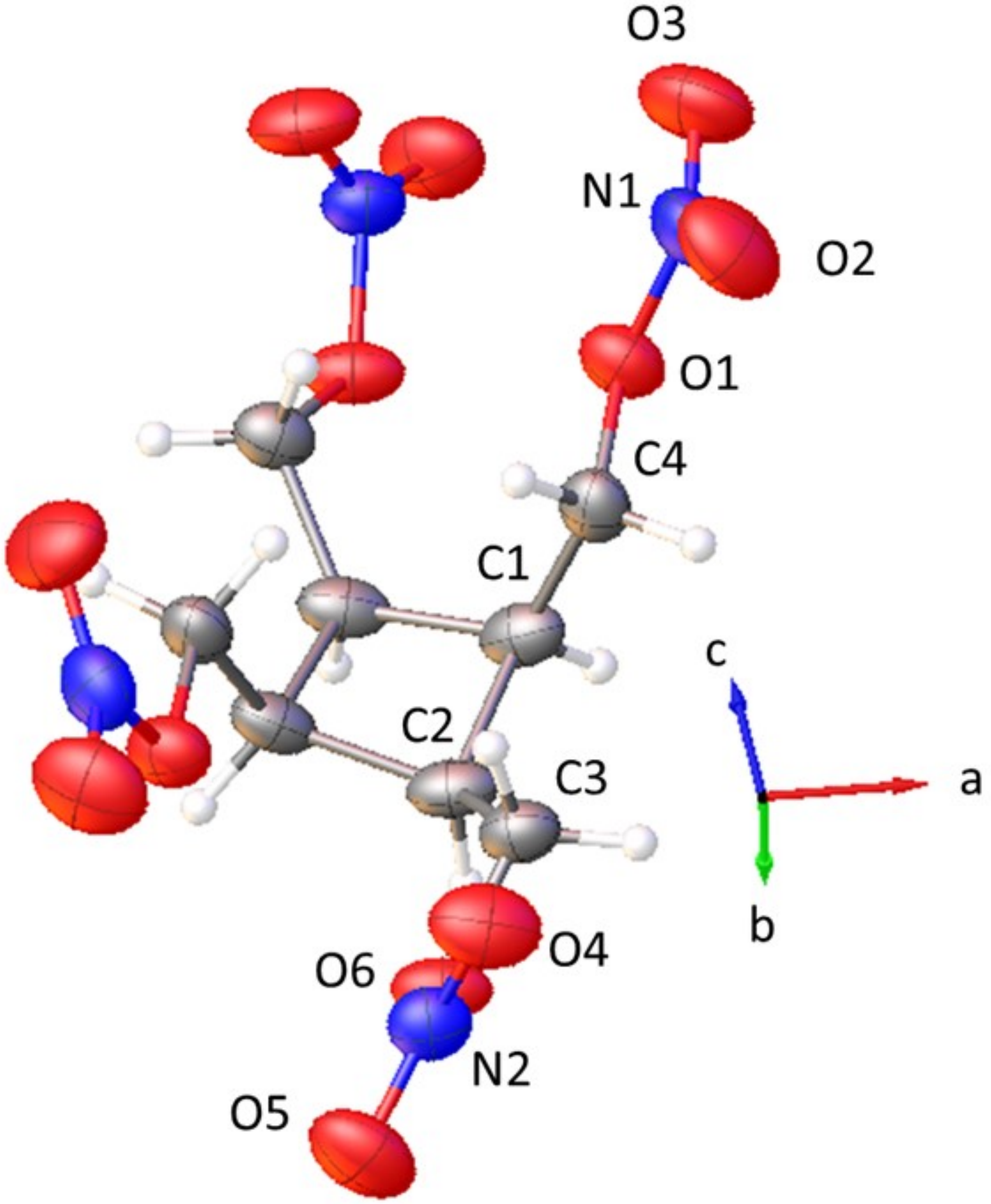

Figure S3. Molecular conformation and atom-numbering scheme for Compound **5**. Non-labeled atoms are generated by inversion (1 - x, y, 3/2 - z). Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

Table **S13**. Crystal data and structure refinement for Compound **5**.

Empirical formula	$C_8H_{12}N_4O_{12}$
Formula weight	356.22
Temperature/K	298.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	12.8079(4)
b/Å	9.3371(3)
c/Å	12.0047(4)
α/°	90
β/°	95.751(3)
γ/°	90
Volume/Å^3	1428.40(8)
Z	4
ρ_{calc}g/cm^3	1.656
μ/mm^{-1}	0.159
F(000)	736.0
Crystal size/mm^3	0.32 × 0.23 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.408 to 52.742
Index ranges	$-16 \leq h \leq 15$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$
Reflections collected	5975
Independent reflections	1460 [$R_{int} = 0.0173$, $R_{sigma} = 0.0140$]
Data/restraints/parameters	1460/0/110
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	$R_1 = 0.0337$, $wR_2 = 0.0880$
Final R indexes [all data]	$R_1 = 0.0364$, $wR_2 = 0.0901$
Largest diff. peak/hole / e Å^{-3}	0.25/-0.13

Table S14. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **5**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	5844.8(11)	8130.9(14)	7801.9(10)	37.3(3)
C2	5190.2(11)	8386.8(13)	6652(1)	37.3(3)
C3	5438.9(11)	7538.0(14)	5642.8(10)	36.7(3)
C4	6337.9(10)	6662.5(15)	7908.9(10)	37.2(3)
N1	7209.9(9)	5202.3(14)	9340.8(11)	46.7(3)
N2	4534.0(9)	7270.0(13)	3811.2(9)	40.2(3)
O1	6727.8(7)	6513.5(11)	9083.5(8)	43.2(3)
O2	7333.4(10)	4401.5(14)	8586.4(11)	67.9(4)
O3	7439.9(11)	5039.2(14)	10325.7(9)	69.8(4)
O4	4767.9(8)	8162(1)	4717.1(7)	42.5(3)
O5	3968.8(10)	7829.7(14)	3077.5(9)	62.4(4)
O6	4903.9(10)	6086.3(12)	3841.9(9)	57.1(3)

Table S15. Anisotropic Displacement Parameters (Å^2×10^3) for Compound **5**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	48.9(8)	33.3(7)	28.0(6)	0.4(5)	-3.6(5)	-13.0(6)
C2	58.6(8)	25.0(6)	27.1(6)	2.0(5)	-1.6(5)	-6.1(5)
C3	45.8(7)	34.9(7)	28.6(6)	2.4(5)	-0.1(5)	-5.0(6)
C4	34.4(6)	47.0(8)	29.2(6)	-2.9(5)	-2.0(5)	-1.8(6)
N1	36.6(6)	51.4(7)	49.9(7)	3.9(6)	-6.6(5)	2.8(5)
N2	49.5(7)	40.2(6)	30.6(6)	-4.0(5)	2.6(5)	-1.2(5)
O1	46.9(6)	45.5(6)	34.8(5)	-1.7(4)	-7.3(4)	4.3(4)
O2	69.0(8)	66.8(8)	66.2(8)	-11.0(6)	-1.4(6)	28.3(6)
O3	82.1(9)	70.0(8)	51.2(7)	12.0(6)	-22.9(6)	3.3(7)
O4	69.4(7)	29.8(5)	26.6(5)	-0.4(4)	-2.7(4)	1.0(4)
O5	70.4(8)	72.1(8)	40.4(6)	-5.3(5)	-16.3(5)	15.6(6)
O6	86.5(8)	39.8(6)	43.9(6)	-9.5(5)	0.7(5)	9.2(6)

Table S16. Bond Lengths for Compound **5**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C1	C2[1]	1.5552(19)	N1	O1	1.3918(15)
C1	C2	1.5600(17)	N1	O2	1.1970(16)
C1	C4	1.5097(19)	N1	O3	1.1993(16)
C2	C1[1]	1.5552(19)	N2	O4	1.3787(14)
C2	C3	1.5082(18)	N2	O5	1.2021(15)
C3	O4	1.4566(15)	N2	O6	1.2016(16)
C4	O1	1.4546(15)			

[1] 1-X,+Y,3/2-Z

Table S17. Bond Angles for Compound **5**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C2[1]	C1	C2	86.81(10)	O2	N1	O1	118.09(12)
C4	C1	C2[1]	118.08(11)	O2	N1	O3	128.95(14)
C4	C1	C2	113.43(10)	O3	N1	O1	112.96(12)
C1[1]	C2	C1	90.50(10)	O5	N2	O4	112.50(12)
C3	C2	C1	119.49(12)	O6	N2	O4	118.53(11)
C3	C2	C1[1]	121.03(11)	O6	N2	O5	128.97(12)
O4	C3	C2	104.28(11)	N1	O1	C4	113.62(10)
O1	C4	C1	105.63(10)	N2	O4	C3	115.15(10)

[1] 1-X,+Y,3/2-Z

Table S18. Torsion Angles for Compound **5**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C1	C2	C3	O4	-173.82(10)	C2	C3	O4	N2	-155.71(11)
C1[1]	C2	C3	O4	75.58(14)	C4	C1	C2	C1[1]	101.83(11)
C1	C4	O1	N1	179.72(10)	C4	C1	C2	C3	-24.83(17)
C2[1]	C1	C2	C1[1]	-17.48(13)	O2	N1	O1	C4	6.02(17)
C2[1]	C1	C2	C3	-144.14(10)	O3	N1	O1	C4	-173.46(12)
C2	C1	C4	O1	-168.92(10)	O5	N2	O4	C3	179.15(12)
C2[1]	C1	C4	O1	-69.58(13)	O6	N2	O4	C3	-1.21(17)

[1] 1-X,+Y,3/2-Z

Compound 6

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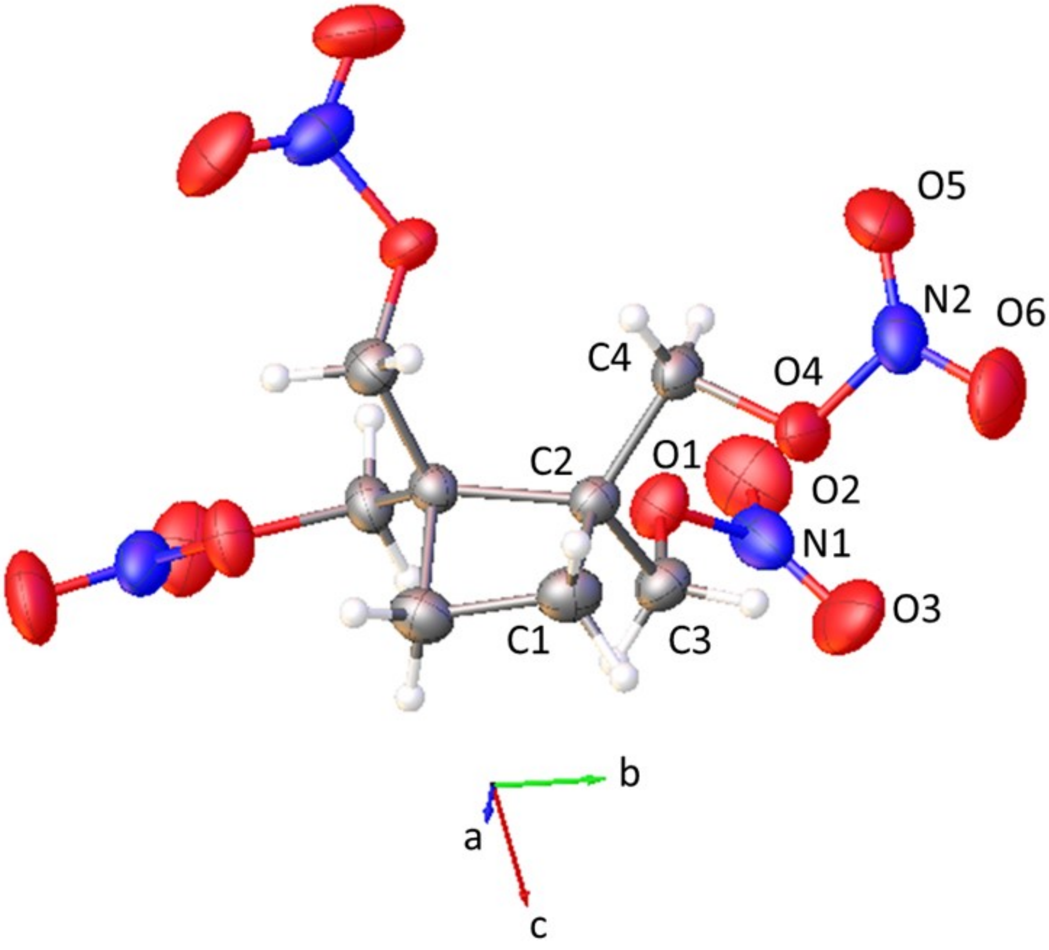


Figure S4. Molecular conformation and atom-numbering scheme for Compound **6**. Non-labeled atoms are generated by inversion (1 - x, 1 - y, z). Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

Table S19. Crystal data and structure refinement for Compound **6**.

Empirical formula	$C_8H_{12}N_4O_{12}$
Formula weight	356.22
Temperature/K	296(3)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	26.9938(19)
b/Å	17.3049(9)
c/Å	6.0736(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2837.1(3)
Z	8
ρ_{calc}g/cm^3	1.668
μ/mm^{-1}	0.160
F(000)	1472.0
Crystal size/mm^3	0.3 × 0.18 × 0.03
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.592 to 52.732
Index ranges	$-33 \leq h \leq 18$, $-21 \leq k \leq 18$, $-7 \leq l \leq 5$
Reflections collected	2501
Independent reflections	1248 [R_{int} = 0.0139, R_{sigma} = 0.0214]
Data/restraints/parameters	1248/1/133
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0303, wR_2 = 0.0716
Final R indexes [all data]	R_1 = 0.0326, wR_2 = 0.0731
Largest diff. peak/hole / e Å^{-3}	0.14/-0.14
Flack parameter	-0.6(8)

Table S20. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **6**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
C1	5029.1(10)	4560.1(13)	11460(4)	36.4(5)
C2	4943.4(7)	4549(1)	8939(4)	26.9(5)
C3	4403.4(9)	4345.0(12)	8513(4)	33.0(5)
C4	5282.7(9)	4009.5(11)	7663(4)	30.8(5)
N1	3904.0(8)	4065.4(12)	5333(5)	44.3(5)
N2	5446.9(8)	2648.7(10)	7940(5)	43.4(6)
O1	4297.8(6)	4496.2(8)	6218(3)	37.1(4)
O2	3806.9(9)	4250.5(13)	3484(4)	64.5(6)
O3	3726.2(8)	3570.3(12)	6459(4)	66.6(6)
O4	5177.3(7)	3270.3(7)	8727(3)	42.3(5)
O5	5719.1(8)	2742.3(10)	6437(5)	61.7(6)
O6	5361.5(8)	2069.3(9)	8964(5)	68.2(7)

Table S21. Anisotropic Displacement Parameters (Å^2×10^3) for Compound **6**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
C1	34.2(13)	43.2(11)	31.7(13)	4.7(10)	0.5(12)	2.8(10)
C2	24.4(10)	26.9(9)	29.3(11)	3.1(9)	0.4(10)	0.6(7)
C3	27.2(11)	34.7(10)	37.0(14)	2.8(10)	2.2(11)	-3.1(9)
C4	28.5(12)	25.8(9)	38.2(14)	4.1(9)	2.5(12)	1.2(8)
N1	27.9(10)	50.6(11)	54.3(15)	-17.9(11)	-2.3(11)	-1.9(9)
N2	34.0(11)	31.0(9)	65.4(16)	-3.6(10)	-4.0(12)	3.2(7)
O1	32.6(8)	39.0(7)	39.8(10)	2.2(7)	-8.3(8)	-8.7(6)
O2	53.0(13)	84.0(13)	56.6(14)	-9.7(11)	-24.4(12)	2.1(10)
O3	55.9(13)	72.2(12)	71.8(15)	-12.8(12)	7.3(13)	-34.6(11)
O4	45.9(9)	27.2(6)	53.7(12)	4.2(7)	12.5(10)	5.0(6)
O5	51.0(12)	47.8(9)	86.3(17)	-10.3(11)	23.8(14)	5.9(8)
O6	74.4(14)	27.4(8)	103.0(19)	13.4(10)	4.6(15)	4.7(8)

Table S22. Bond Lengths for Compound **6**.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**

C1	C1[1]	1.531(5)	N1	O1	1.405(3)
C1	C2	1.549(3)	N1	O2	1.197(4)
C2	C2[1]	1.591(3)	N1	O3	1.197(3)
C2	C3	1.522(3)	N2	O4	1.384(3)
C2	C4	1.520(3)	N2	O5	1.183(3)
C3	O1	1.447(3)	N2	O6	1.202(3)
C4	O4	1.461(2)			

[1] 1-X,1-Y,+Z

Table S23. Bond Angles for Compound **6**.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
C1[1]	C1	C2	89.83(11)	O2	N1	O1	112.5(2)
C1	C2	C2[1]	87.66(11)	O2	N1	O3	129.8(2)
C3	C2	C1	108.28(19)	O3	N1	O1	117.7(3)
C3	C2	C2[1]	114.31(19)	O5	N2	O4	119.1(2)
C4	C2	C1	114.92(19)	O5	N2	O6	129.2(2)
C4	C2	C2[1]	119.14(18)	O6	N2	O4	111.7(2)
C4	C2	C3	110.38(19)	N1	O1	C3	114.93(19)
O1	C3	C2	108.07(19)	N2	O4	C4	115.18(19)
O4	C4	C2	101.25(18)				

[1] 1-X,1-Y,+Z

Table S24. Torsion Angles for Compound **6**.

A	**B**	**C**	**D**	**Angle/°**	**A**	**B**	**C**	**D**	**Angle/°**
C1[1]	C1	C2	C2[1]	16.8(2)	C2	C4	O4	N2	-178.44(18)
C1[1]	C1	C2	C3	-98.1(2)	C3	C2	C4	O4	-65.4(2)
C1[1]	C1	C2	C4	138.0(2)	C4	C2	C3	O1	-65.5(2)
C1	C2	C3	O1	167.88(17)	O2	N1	O1	C3	174.8(2)
C1	C2	C4	O4	57.4(2)	O3	N1	O1	C3	-7.0(3)
C2[1]	C2	C3	O1	72.03(17)	O5	N2	O4	C4	-3.5(3)
C2[1]	C2	C4	O4	159.36(15)	O6	N2	O4	C4	176.3(2)
C2	C3	O1	N1	155.07(17)					

[1] 1-X,1-Y,+Z

Compound 7

CCDC 1935557

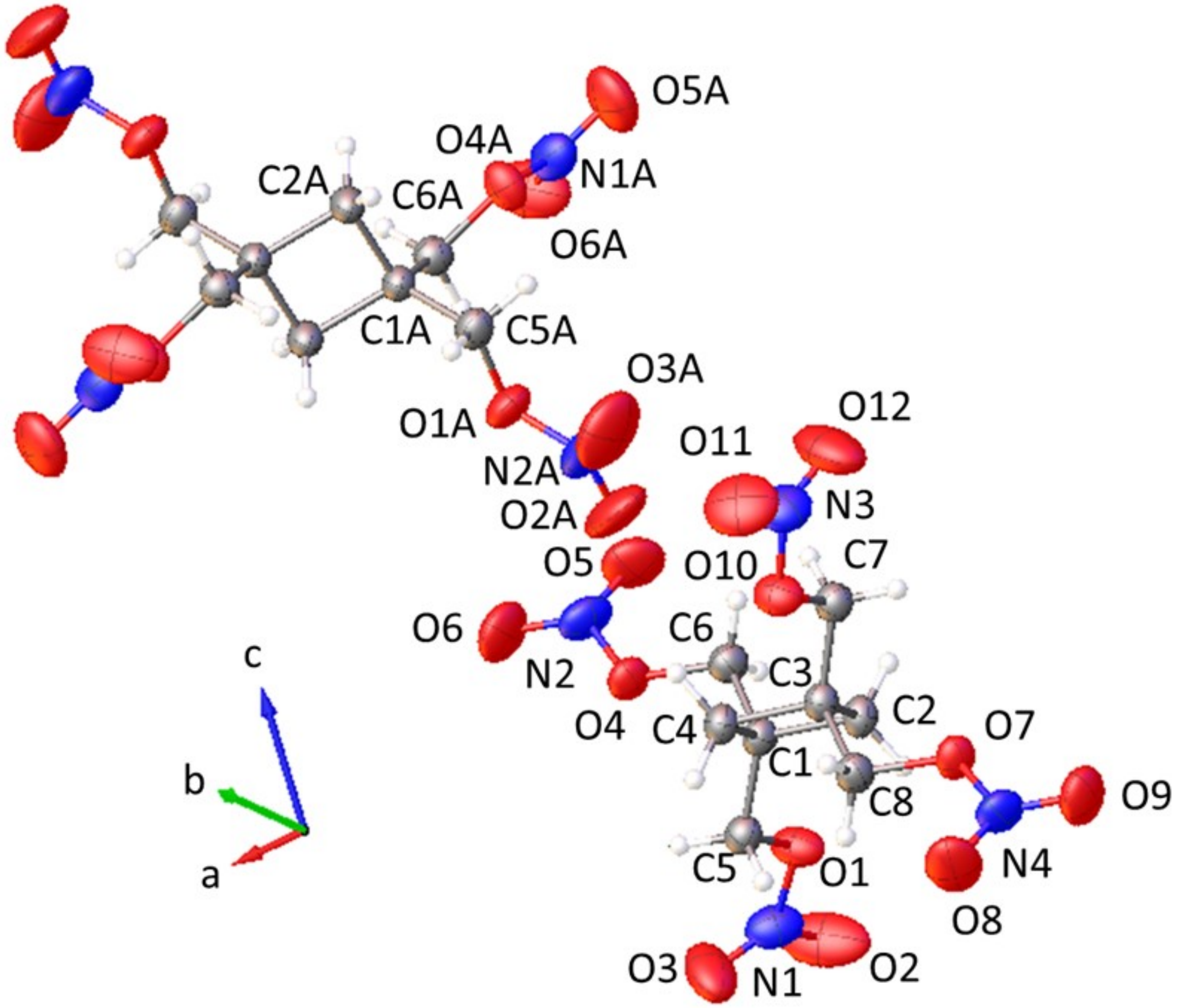


Figure S5. Molecular conformation and atom-numbering scheme for Compound **7**. Non-labeled atoms are generated by inversion (two - x, 1 - y, 2 – z). Non-hydrogen atoms are shown as 50% probability displacement ellipsoids.

Table S25. Crystal data and structure refinement for Compound **7**.

Empirical formula	$C_8H_{12}N_4O_{12}$
Formula weight	356.22
Temperature/K	298.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	6.2457(2)
b/Å	23.7522(7)
c/Å	15.0056(4)
α/°	90
β/°	93.400(3)
γ/°	90
Volume/Å^3	2222.15(11)
Z	6
ρ_{calc}g/cm^3	1.597
μ/mm^{-1}	0.153
F(000)	1104.0
Crystal size/mm^3	0.35 × 0.24 × 0.23
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.214 to 52.74
Index ranges	$-7 \leq h \leq 7$, $-29 \leq k \leq 29$, $-18 \leq l \leq 18$
Reflections collected	18585
Independent reflections	4544 [R_{int} = 0.0235, R_{sigma} = 0.0192]
Data/restraints/parameters	4544/0/397
Goodness-of-fit on F^2	1.041
Final R indexes [I>=2σ (I)]	R_1 = 0.0421, wR_2 = 0.0937
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1005
Largest diff. peak/hole / e Å^{-3}	0.20/-0.33

Table S26. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **7**. U$_{eq}$ is defined as 1/3 of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	6723(2)	2096.2(5)	4268.1(8)	45.9(3)
O2	7714(4)	1302.9(6)	3722.7(13)	98.0(7)
O3	9700(3)	2024.1(8)	3538.4(14)	85.9(6)
O4	8507.6(18)	2861.3(5)	6123.8(7)	42.3(3)
O5	8145(3)	2408.8(8)	7394.9(10)	73.8(5)
O6	11143(3)	2817.0(8)	7119(1)	79.4(5)
O7	532.5(17)	3669.8(5)	3569.6(7)	39.3(3)
O8	701(3)	4176.5(8)	2339.6(10)	77.2(5)
O9	-2210(2)	3743.2(7)	2633.9(10)	70.5(5)
O10	2514(2)	4453.5(5)	5396.6(8)	44.4(3)
O11	1747(3)	5261.6(7)	5946.2(12)	85.4(5)
O12	212(3)	4530.0(8)	6450.4(14)	91.8(6)
N1	8206(3)	1784.0(7)	3808(1)	51.4(4)
N2	9309(3)	2678.5(8)	6957.3(10)	54.0(4)
N3	1375(3)	4770.3(7)	5988.1(12)	55.5(4)
N4	-378(3)	3883.1(7)	2774.9(10)	48.8(4)
C1	5782(2)	2948.2(6)	4981.7(10)	29.9(3)
C2	3331(3)	2946.1(7)	4731.0(12)	33.2(4)
C3	3324(2)	3599.5(6)	4688.3(10)	29.5(3)
C4	5782(2)	3602.2(7)	4919.8(12)	32.3(3)
C5	7167(3)	2693.6(7)	4294.9(11)	33.6(4)
C6	6277(3)	2714.6(8)	5908.2(11)	35.9(4)
C7	2019(3)	3857.3(7)	5402.2(12)	34.9(4)
C8	2749(3)	3839.5(8)	3770.8(11)	36.4(4)
O1A	7576(2)	4333.0(6)	8340.3(8)	52.4(3)
O2A	6342(4)	3916.2(10)	7141.1(11)	103.6(7)
O3A	4966(4)	4718.4(11)	7491.2(13)	111.5(8)
O4A	6355.2(18)	4121.0(5)	10466.9(8)	43.6(3)
O5A	3886(3)	3632.5(7)	11047.3(12)	80.2(5)
O6A	6856(3)	3223.4(6)	10789.7(12)	83.3(6)
N1A	6151(4)	4330.6(11)	7592.7(12)	72.9(6)
N2A	5664(3)	3611.5(7)	10790.6(10)	50.5(4)
C1A	8803(2)	4688.7(6)	9746(1)	30.2(3)
C2A	8815(3)	5184.7(8)	10420.0(12)	35.6(4)
C5A	7241(3)	4789.9(8)	8954.3(11)	37.9(4)
C6A	8512(3)	4114.6(7)	10151.5(12)	35.9(4)

Table S27. Anisotropic Displacement Parameters (Å^2×10^3) for Compound **7**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O1	61.1(8)	30.8(6)	47.7(7)	-1.5(5)	19.4(6)	2.3(5)
O2	170(2)	31.2(9)	99.4(14)	0.1(9)	61.1(13)	12(1)
O3	50.3(9)	90.0(13)	119.9(15)	-45.2(11)	26.1(9)	-3.0(9)
O4	40.8(6)	54.6(8)	30.3(6)	7.8(5)	-8.5(5)	0.5(5)
O5	89.4(12)	94.8(13)	36.6(8)	21.3(8)	-1.2(8)	4.2(10)
O6	62.5(10)	117.4(15)	54.4(9)	1.2(9)	-29.5(8)	0.4(9)
O7	36.8(6)	47.2(7)	32.8(6)	10.2(5)	-7.0(5)	-1.5(5)
O8	75.3(10)	113.5(14)	42.0(8)	36.3(9)	-2.5(7)	-15.3(10)
O9	52.9(9)	102.6(13)	52.9(9)	12.7(8)	-22.0(7)	-9.2(8)
O10	55.7(7)	30.6(6)	48.1(7)	-3.4(5)	12.1(6)	1.6(5)
O11	125.3(15)	35.6(9)	96.4(13)	-10.6(8)	17.2(11)	13.6(9)
O12	101.8(14)	76.2(12)	103.9(14)	-24.7(11)	60.7(12)	-6.4(10)
N1	69.1(11)	42.2(10)	42.9(9)	-1.1(7)	4.1(8)	17.2(8)
N2	64.5(11)	66.3(11)	29.9(8)	1.7(8)	-9.6(8)	11.6(9)
N3	62.8(11)	45.7(10)	58.2(11)	-10.9(8)	6.1(9)	12.2(8)
N4	51.5(9)	64.7(11)	29.3(8)	8.0(7)	-5.7(7)	2.0(8)
C1	30.1(8)	28.9(8)	30.3(8)	0.9(6)	-1.7(6)	-0.2(6)
C2	31.5(8)	29.6(8)	38.0(9)	0.3(7)	-2.3(7)	-2.2(6)
C3	29.4(7)	27.5(8)	31.3(8)	1.3(6)	-1.0(6)	-1.1(6)
C4	30.8(8)	30.5(9)	35.2(9)	-1.0(7)	-2.1(7)	-2.7(6)
C5	36.1(9)	31.9(8)	32.4(9)	0.1(7)	-0.2(7)	-2.2(7)
C6	36.5(9)	38.5(10)	32.4(9)	2.3(7)	0.2(7)	0.6(7)
C7	35.8(9)	33.5(9)	35.4(9)	0.7(7)	1.8(7)	-2.1(7)
C8	34.6(8)	40.6(10)	33.9(9)	3.9(7)	-0.1(7)	-1.6(7)
O1A	59.3(8)	64.1(9)	32.7(6)	-11.7(6)	-6.6(6)	-7.8(7)
O2A	140.7(18)	125.0(17)	44.5(9)	-32.0(11)	0.7(10)	-55.5(14)
O3A	115.5(17)	137(2)	74.9(13)	12.7(13)	-53.6(12)	0.4(15)
O4A	39.4(6)	36.1(7)	55.9(8)	12.6(6)	7.3(5)	-4.1(5)
O5A	59.8(10)	84.8(12)	97.4(13)	26.5(10)	16.0(9)	-26.4(8)
O6A	123.6(15)	31.6(8)	98.5(13)	6.3(8)	39.4(11)	2.8(9)
N1A	82.9(15)	100.7(17)	33.4(9)	-0.3(11)	-9.2(9)	-37.4(13)
N2A	65.5(11)	41.4(10)	44.5(9)	3.5(7)	2.8(8)	-17.7(8)
C1A	28.0(7)	32.5(8)	30.1(8)	-4.0(6)	1.0(6)	-3.5(6)
C2A	30.4(8)	39.3(10)	37.3(9)	-9.4(8)	4.5(7)	-4.0(7)
C5A	39.0(9)	40.1(10)	34.1(9)	2.4(8)	-2.1(7)	-4.9(7)
C6A	36.2(9)	36.3(9)	35.0(9)	-0.4(7)	2.4(7)	1.7(7)

Table S28. Bond Lengths for Compound **7**.

Atom	Atom	Length/Å
O1	N1	1.4002(19)
O1	C5	1.4457(19)
O2	N1	1.188(2)
O3	N1	1.185(2)
O4	N2	1.3891(18)
O4	C6	1.454(2)
O5	N2	1.195(2)
O6	N2	1.203(2)
O7	N4	1.3862(17)
O7	C8	1.4564(19)
O8	N4	1.191(2)
O9	N4	1.198(2)
O10	N3	1.391(2)
O10	C7	1.450(2)
O11	N3	1.192(2)
O12	N3	1.181(2)
C1	C2	1.554(2)
C1	C4	1.556(2)
C1	C5	1.511(2)
C1	C6	1.512(2)
C2	C3	1.553(2)
C3	C4	1.554(2)
C3	C7	1.514(2)
C3	C8	1.513(2)
O1A	N1A	1.390(2)
O1A	C5A	1.447(2)
O2A	N1A	1.205(3)
O3A	N1A	1.186(3)
O4A	N2A	1.3827(19)
O4A	C6A	1.454(2)
O5A	N2A	1.198(2)
O6A	N2A	1.185(2)
C1A	C2A	1.552(2)
C1A	C2A[1]	1.552(2)
C1A	C5A	1.511(2)
C1A	C6A	1.509(2)
C2A	C1A[1]	1.552(2)

[1] 2-X,1-Y,2-Z

Table S29. Bond Angles for Compound **7**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	O1	C5	113.71(13)	C7	C3	C8	112.51(13)
N2	O4	C6	114.52(13)	C8	C3	C2	114.44(14)
N4	O7	C8	114.43(12)	C8	C3	C4	112.32(13)
N3	O10	C7	114.06(14)	C3	C4	C1	90.32(11)
O2	N1	O1	112.82(18)	O1	C5	C1	107.17(13)
O3	N1	O1	118.08(16)	O4	C6	C1	104.94(13)
O3	N1	O2	129.06(19)	O10	C7	C3	105.50(13)
O5	N2	O4	117.64(16)	O7	C8	C3	104.81(13)
O5	N2	O6	129.74(17)	N1A	O1A	C5A	114.03(16)
O6	N2	O4	112.60(17)	N2A	O4A	C6A	114.82(13)
O11	N3	O10	112.80(18)	O2A	N1A	O1A	112.2(2)
O12	N3	O10	117.96(17)	O3A	N1A	O1A	117.7(2)
O12	N3	O11	129.24(19)	O3A	N1A	O2A	130.1(2)
O8	N4	O7	117.96(15)	O5A	N2A	O4A	113.02(17)
O8	N4	O9	129.12(16)	O6A	N2A	O4A	118.11(17)
O9	N4	O7	112.92(15)	O6A	N2A	O5A	128.87(18)
C2	C1	C4	89.57(11)	C2A	C1A	C2A[1]	89.42(12)
C5	C1	C2	115.42(13)	C5A	C1A	C2A	111.69(14)
C5	C1	C4	110.90(13)	C5A	C1A	C2A[1]	115.04(14)
C5	C1	C6	112.72(13)	C6A	C1A	C2A	114.78(14)
C6	C1	C2	111.49(13)	C6A	C1A	C2A[1]	112.28(13)
C6	C1	C4	114.86(14)	C6A	C1A	C5A	111.92(13)
C3	C2	C1	90.40(11)	C1A	C2A	C1A[1]	90.57(12)
C2	C3	C4	89.69(11)	O1A	C5A	C1A	105.69(13)
C7	C3	C2	112.04(13)	O4A	C6A	C1A	104.95(12)
C7	C3	C4	113.99(13)				

[1] 2-X,1-Y,2-Z

Table S30. Torsion Angles for Compound **7**.

A	B	C	D	Angle/°
N1	O1	C5	C1	-166.92(13)
N2	O4	C6	C1	-179.40(13)
N3	O10	C7	C3	177.15(13)
N4	O7	C8	C3	175.52(13)
C1	C2	C3	C4	1.08(13)
C1	C2	C3	C7	-114.80(14)
C1	C2	C3	C8	115.58(14)
C2	C1	C4	C3	1.08(13)
C2	C1	C5	O1	-68.16(17)
C2	C1	C6	O4	-167.31(13)
C2	C3	C4	C1	-1.08(13)
C2	C3	C7	O10	168.74(12)
C2	C3	C8	O7	64.88(17)
C4	C1	C2	C3	-1.08(13)
C4	C1	C5	O1	-168.09(12)
C4	C1	C6	O4	-67.32(17)
C4	C3	C7	O10	68.73(16)
C4	C3	C8	O7	165.26(13)
C5	O1	N1	O2	-173.64(17)
C5	O1	N1	O3	4.2(2)
C5	C1	C2	C3	-114.12(14)
C5	C1	C4	C3	118.25(13)
C5	C1	C6	O4	61.01(17)
C6	O4	N2	O5	2.4(2)
C6	O4	N2	O6	-178.63(16)
C6	C1	C2	C3	115.59(14)
C6	C1	C4	C3	-112.51(14)
C6	C1	C5	O1	61.53(17)
C7	O10	N3	O11	-177.23(16)
C7	O10	N3	O12	2.8(2)
C7	C3	C4	C1	113.02(14)
C7	C3	C8	O7	-64.51(17)
C8	O7	N4	O8	0.1(2)
C8	O7	N4	O9	-178.97(16)
C8	C3	C4	C1	-117.51(14)
C8	C3	C7	O10	-60.65(16)
N1A	O1A	C5A	C1A	175.30(14)
N2A	O4A	C6A	C1A	174.04(13)
C2A[1]	C1A	C2A	C1A[1]	0.000(1)
C2A[1]	C1A	C5A	O1A	73.52(17)
C2A	C1A	C5A	O1A	173.53(13)
C2A[1]	C1A	C6A	O4A	166.03(13)
C2A	C1A	C6A	O4A	65.82(16)
C5A	O1A	N1A	O2A	-173.32(17)
C5A	O1A	N1A	O3A	6.6(3)
C5A	C1A	C2A	C1A[1]	-116.84(16)
C5A	C1A	C6A	O4A	-62.83(17)
C6A	O4A	N2A	O5A	179.76(16)
C6A	O4A	N2A	O6A	0.4(2)
C6A	C1A	C2A	C1A[1]	114.39(15)
C6A	C1A	C5A	O1A	-56.21(18)

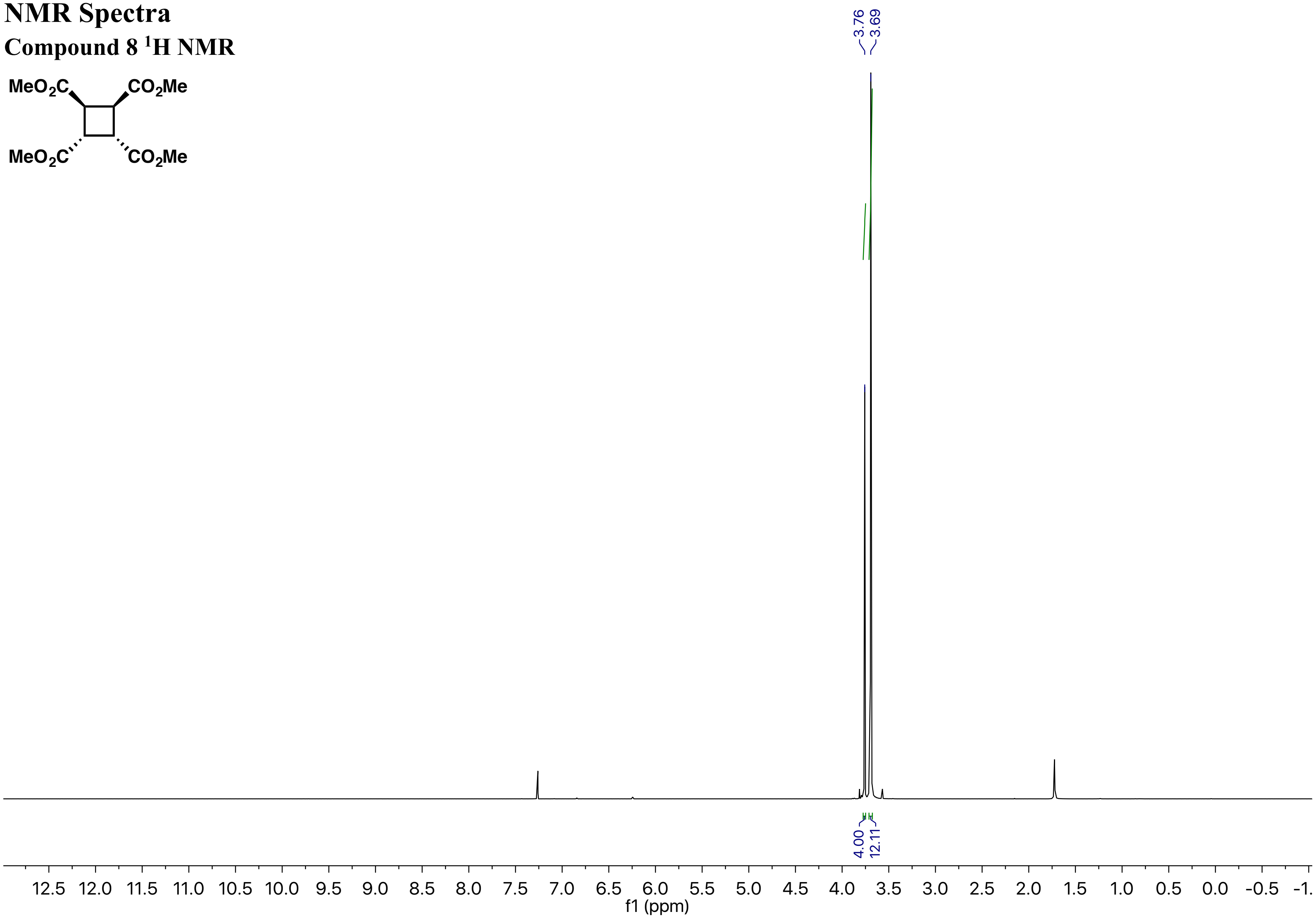
[1] 2-X,1-Y,2-Z

Special Details

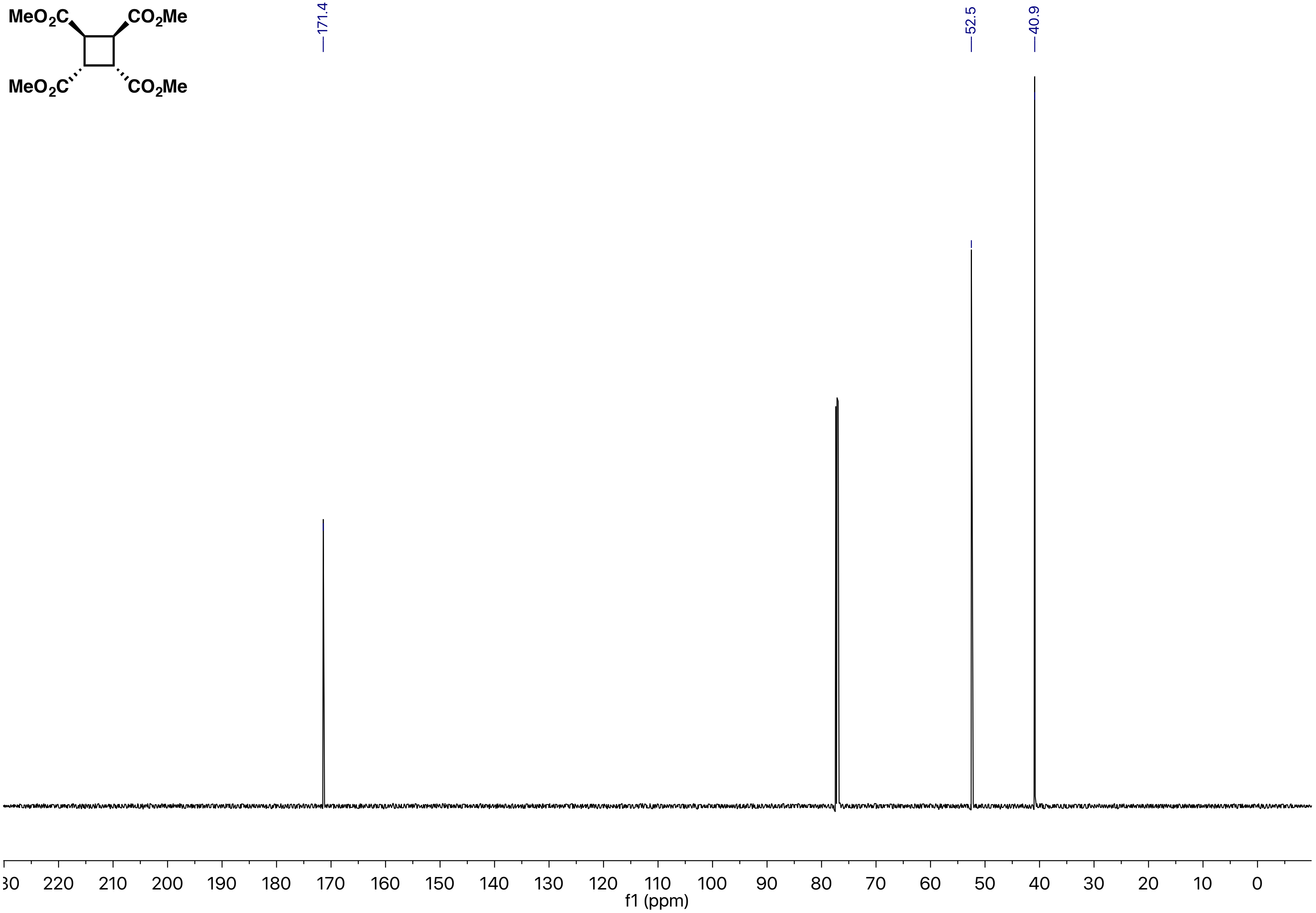
Geometry. All experimental estimated standard deviations (esds) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances and angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

NMR Spectra

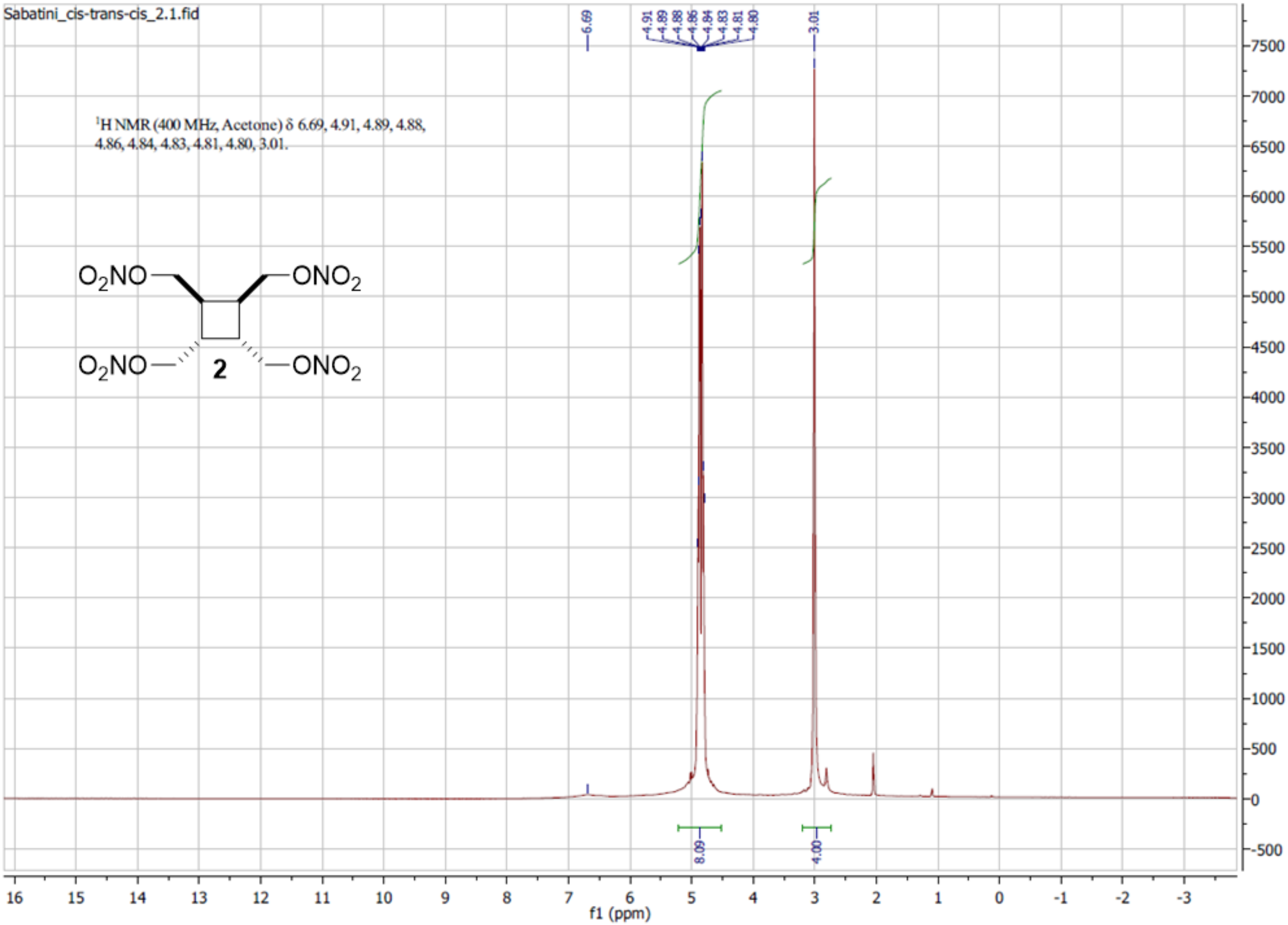
Compound 8 ^{1}H NMR



Compound 8 ^{13}C NMR

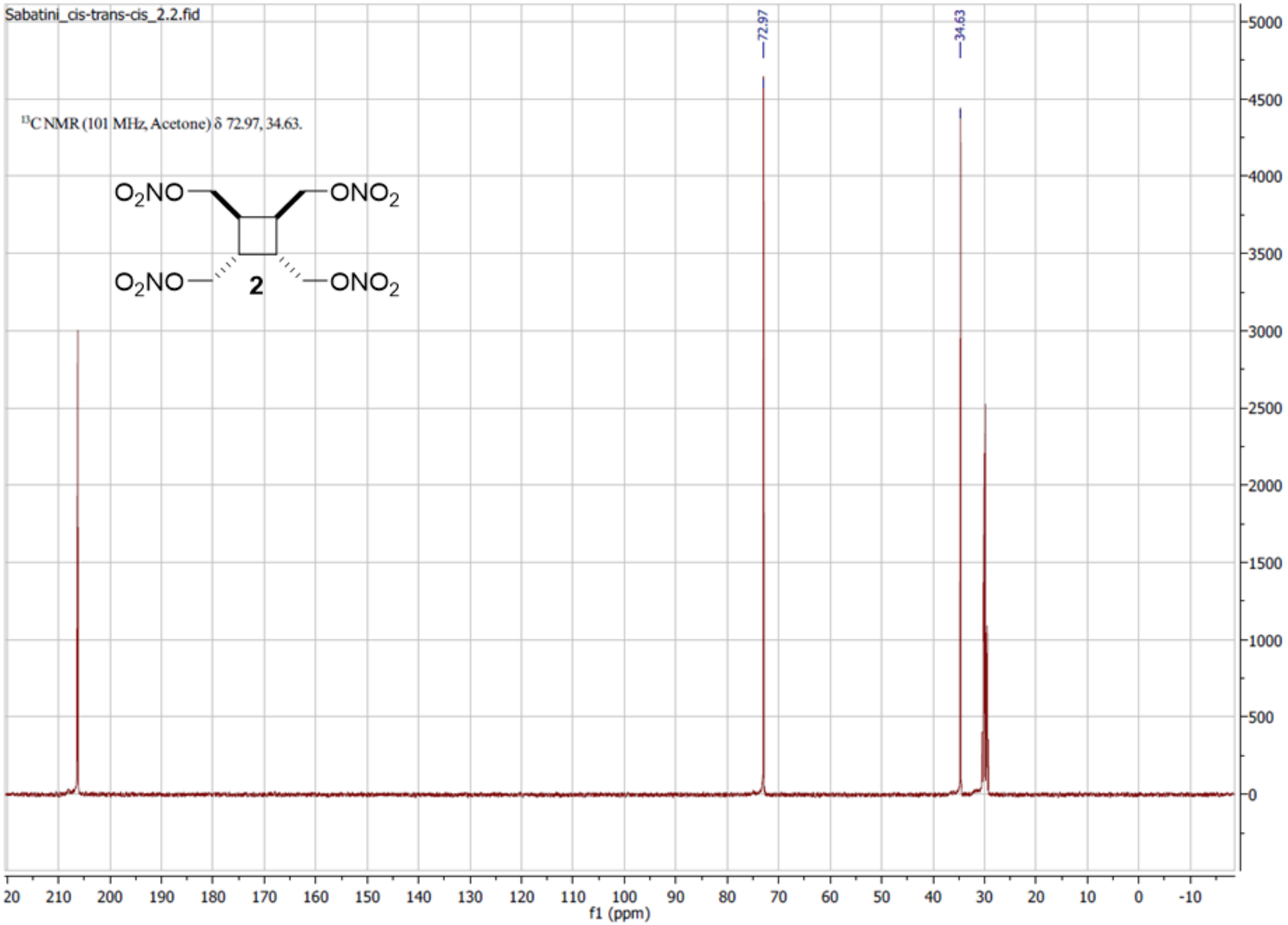


Compound 2 ^{1}H NMR

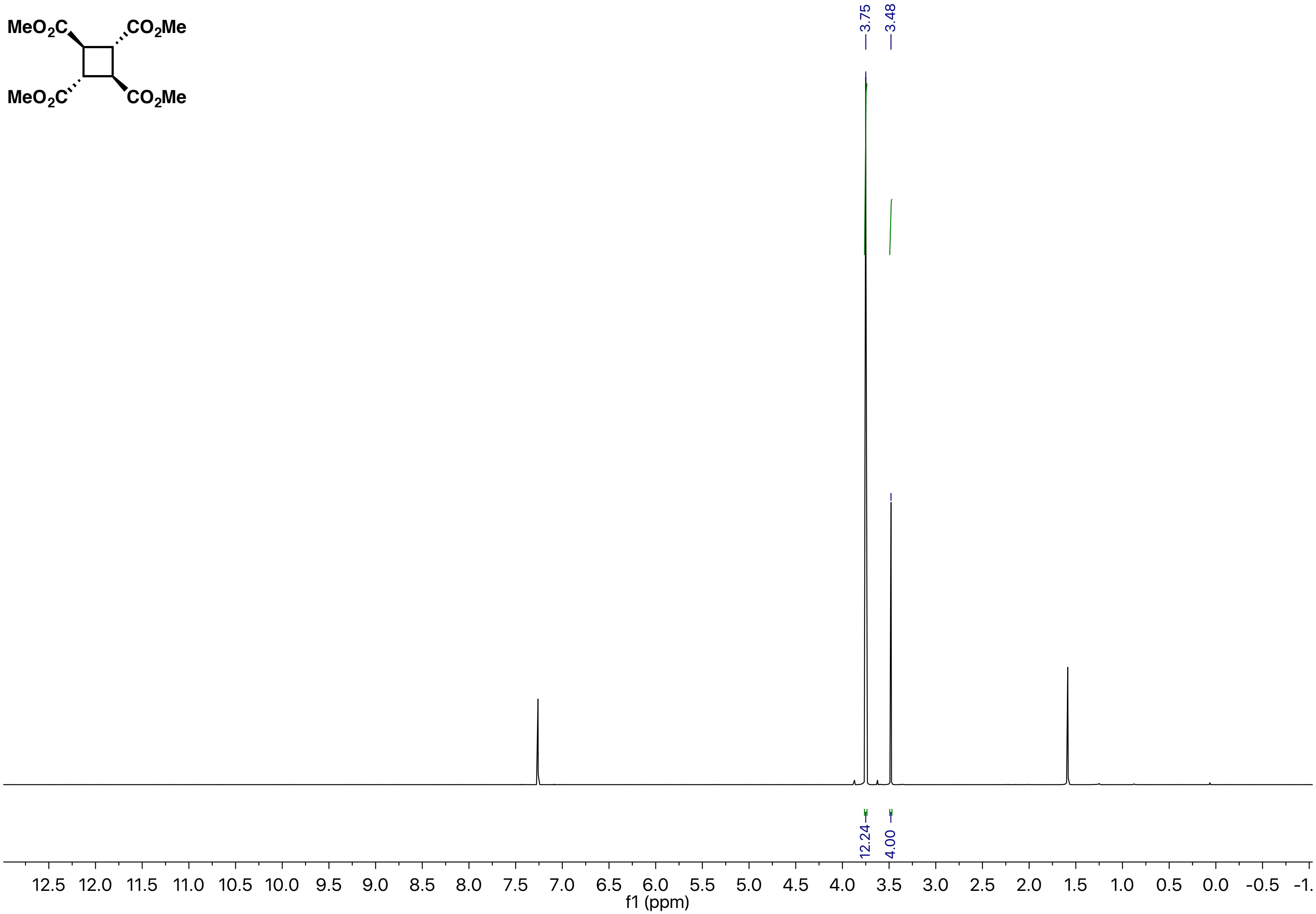


^{1}H NMR (400 MHz, Acetone) δ 6.69, 4.91, 4.89, 4.88, 4.86, 4.84, 4.83, 4.81, 4.80, 3.01.

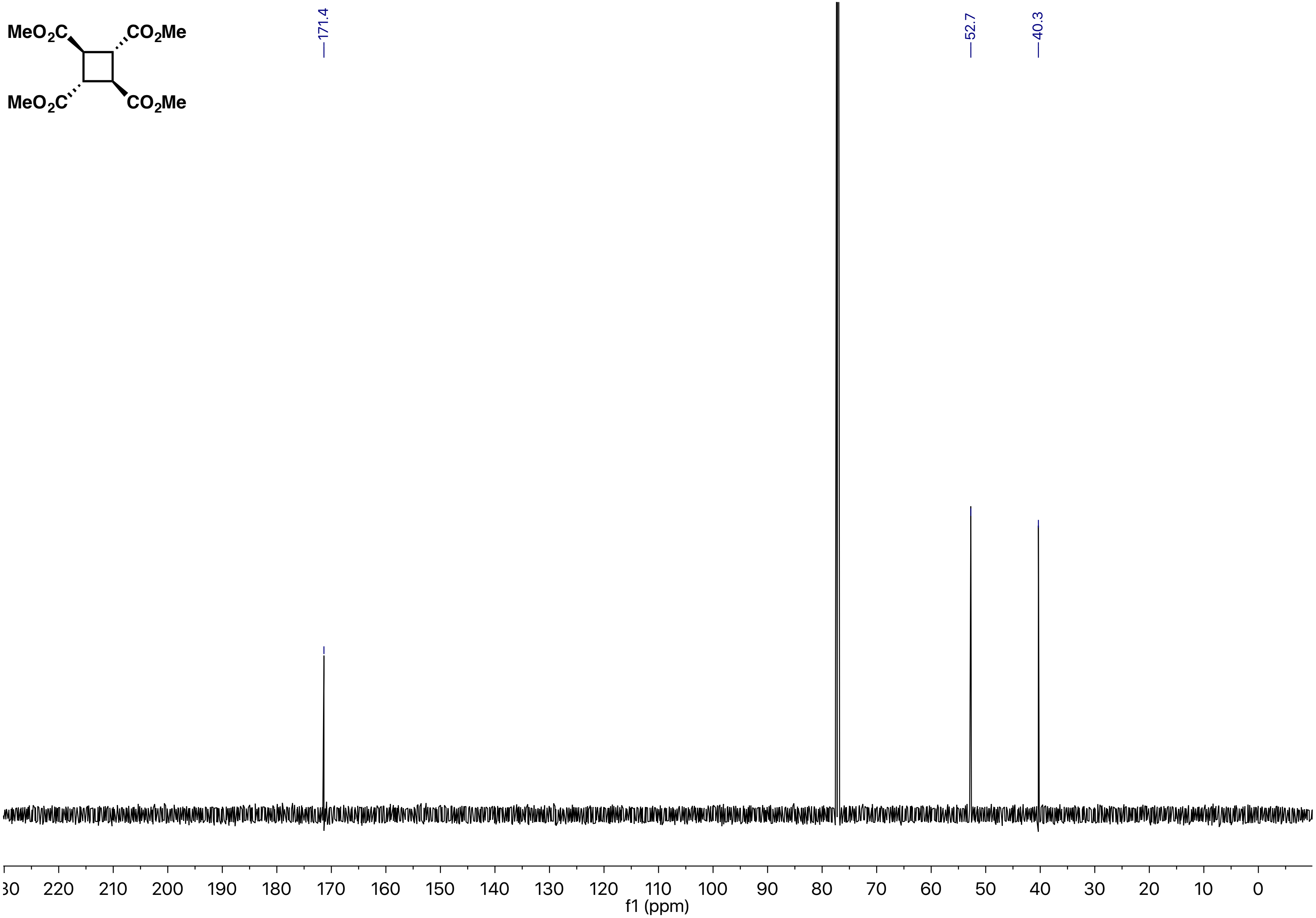
Compound 2 ^{13}C NMR



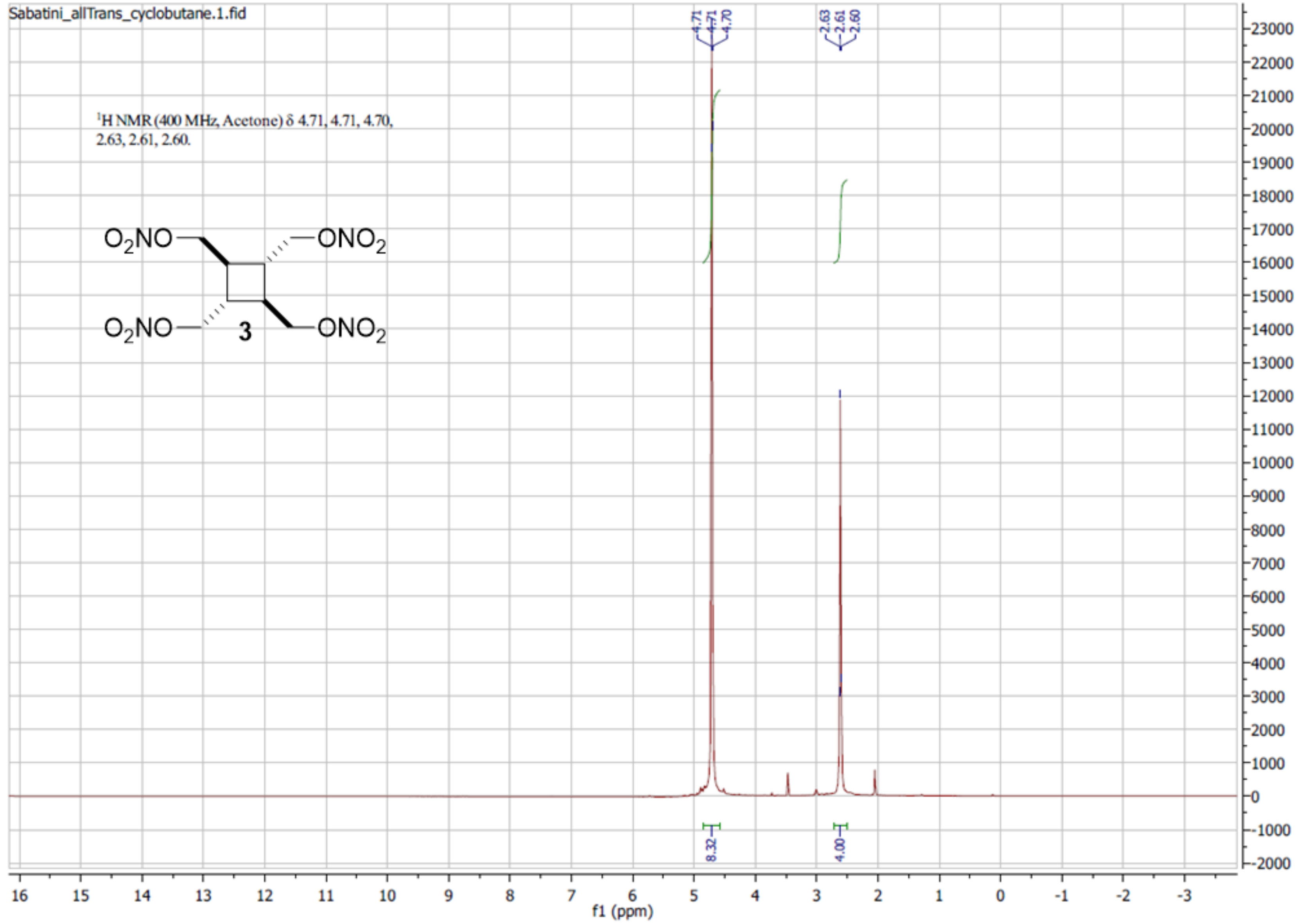
Compound 9 ^{1}H NMR



Compound 9 ^{13}C NMR

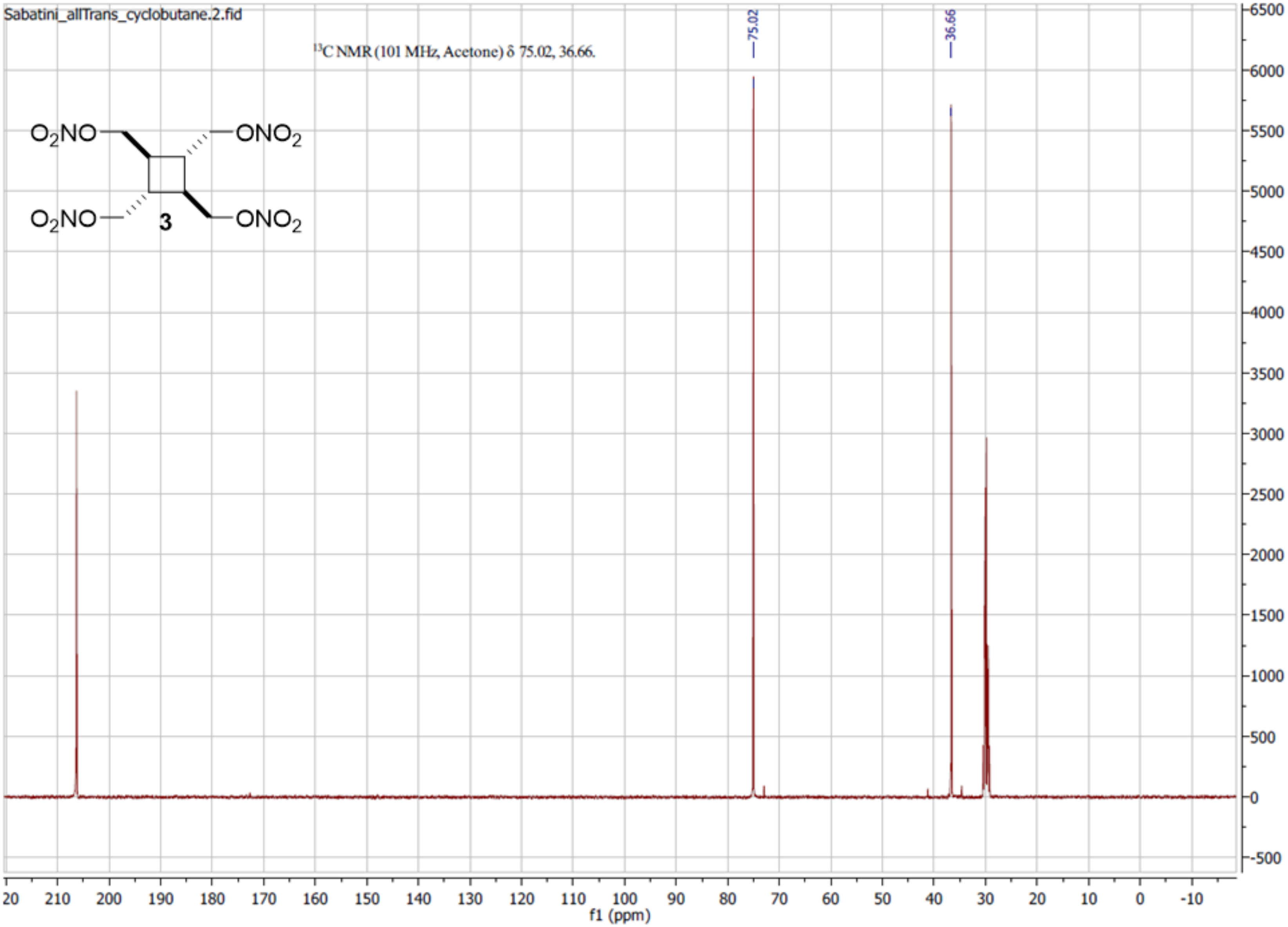


Compound 3 ^{1}H NMR

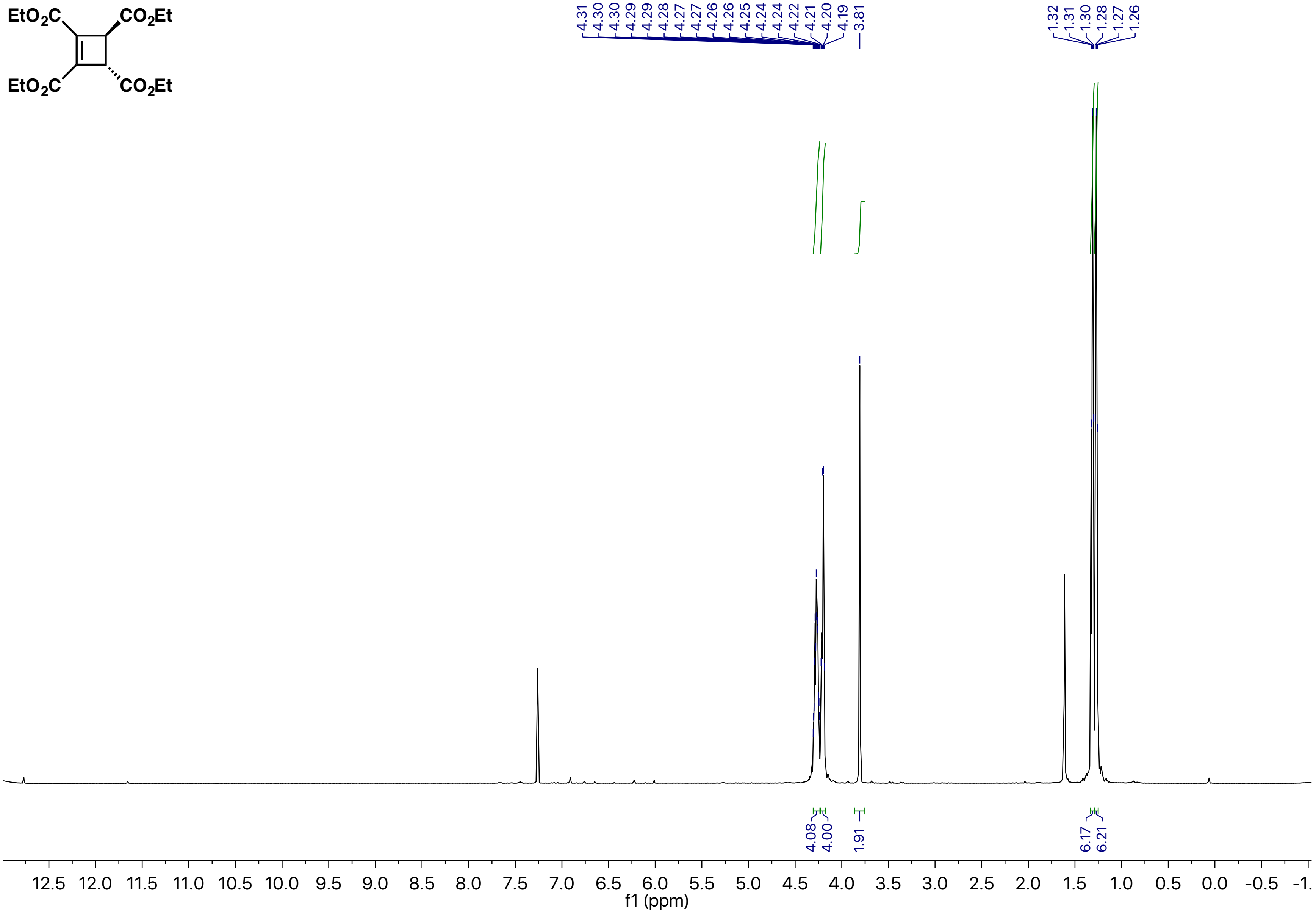


^{1}H NMR (400 MHz, Acetone) δ 4.71, 4.71, 4.70, 2.63, 2.61, 2.60.

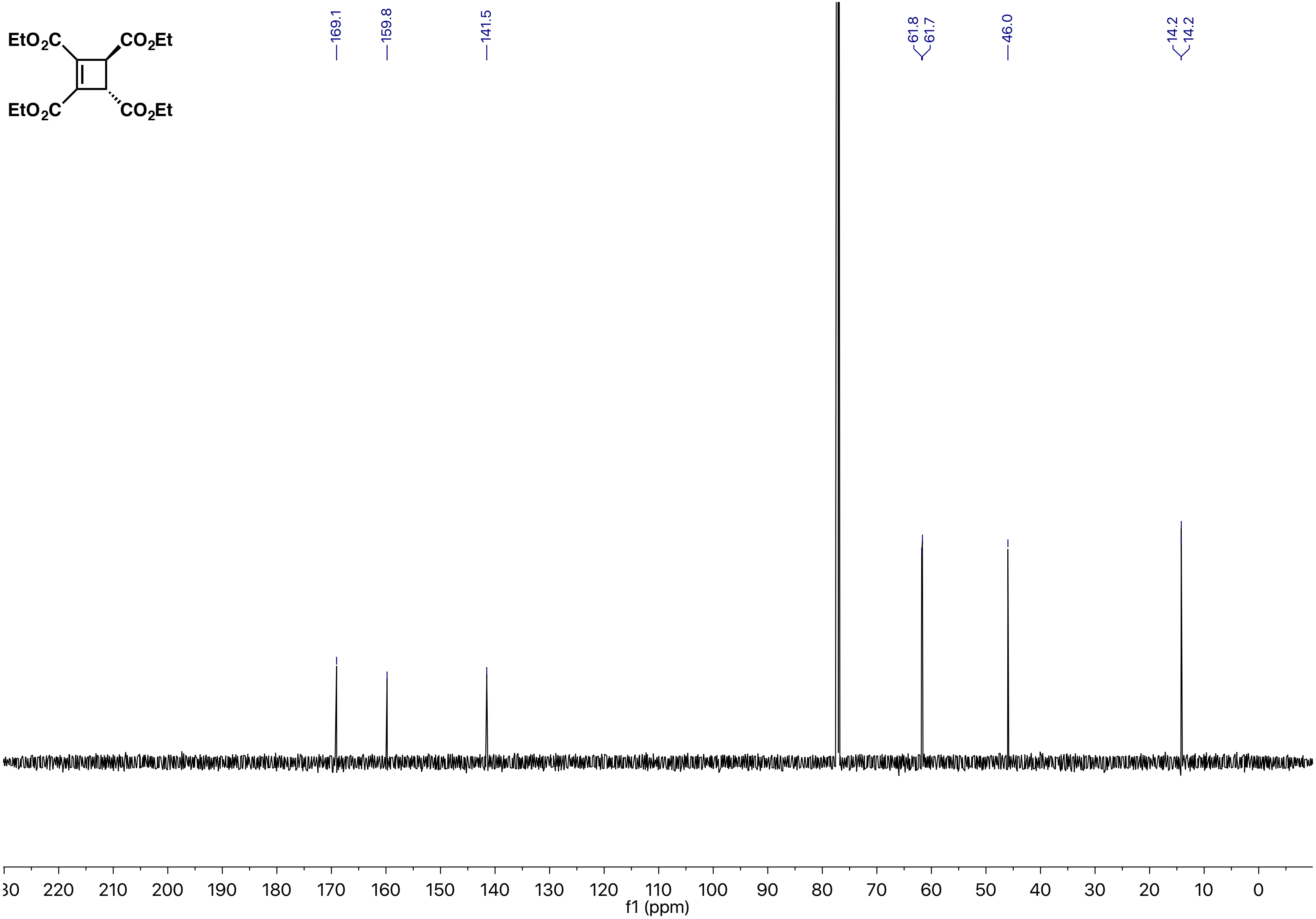
Compound 3 ^{13}C NMR



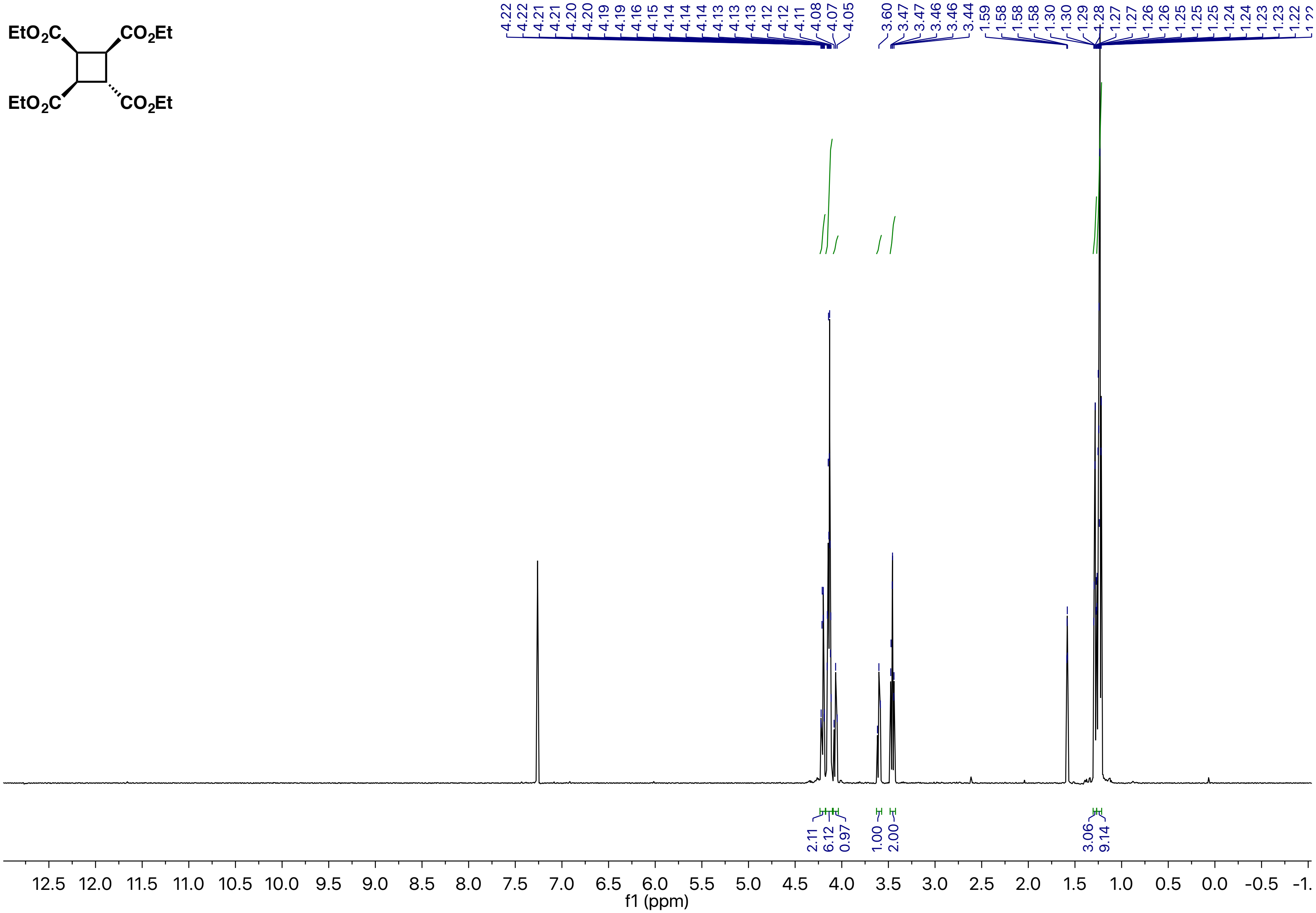
Compound 11 ^1H NMR



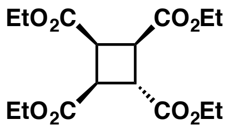
Compound 11 ^{13}C NMR

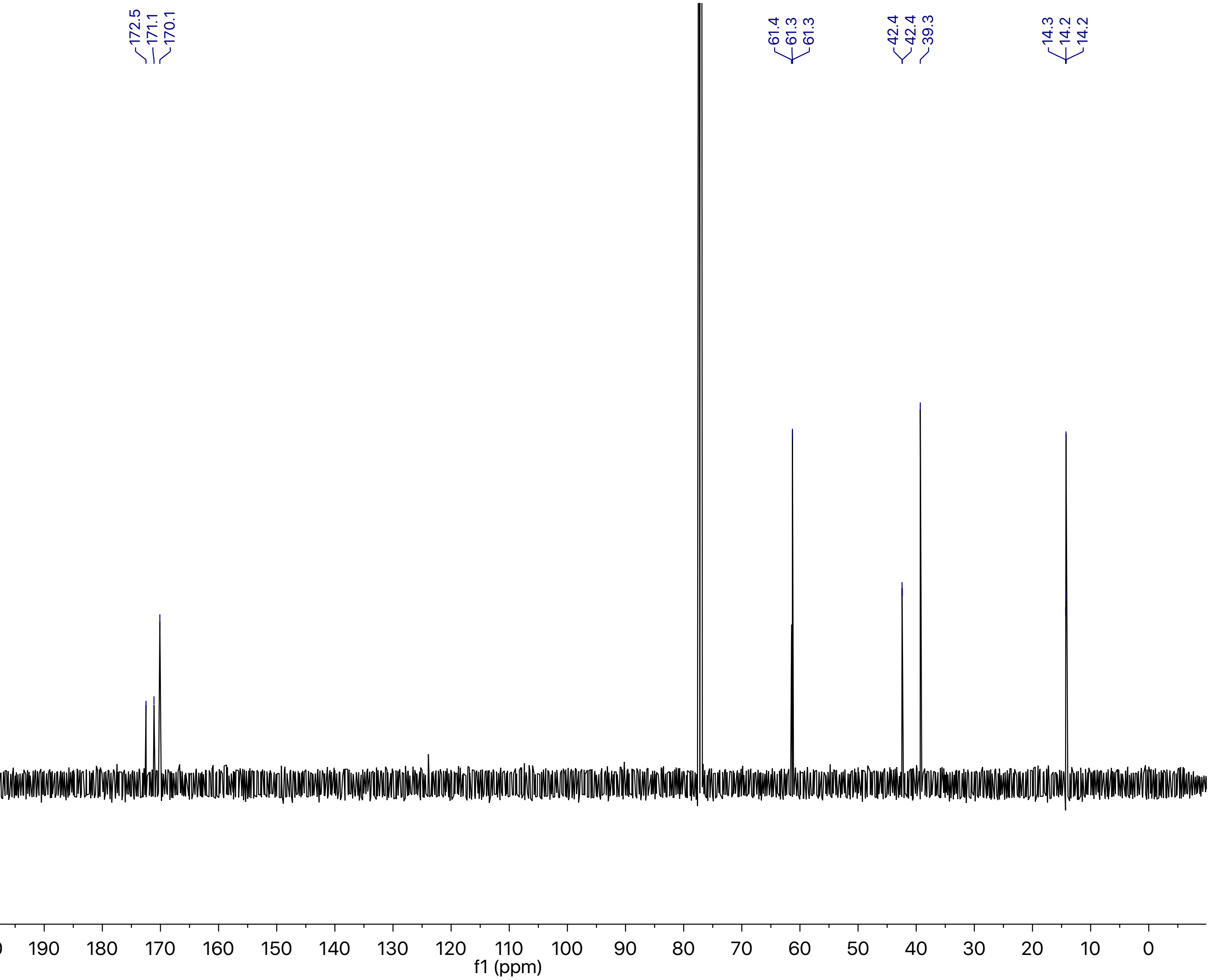


Compound 12 ^{1}H NMR

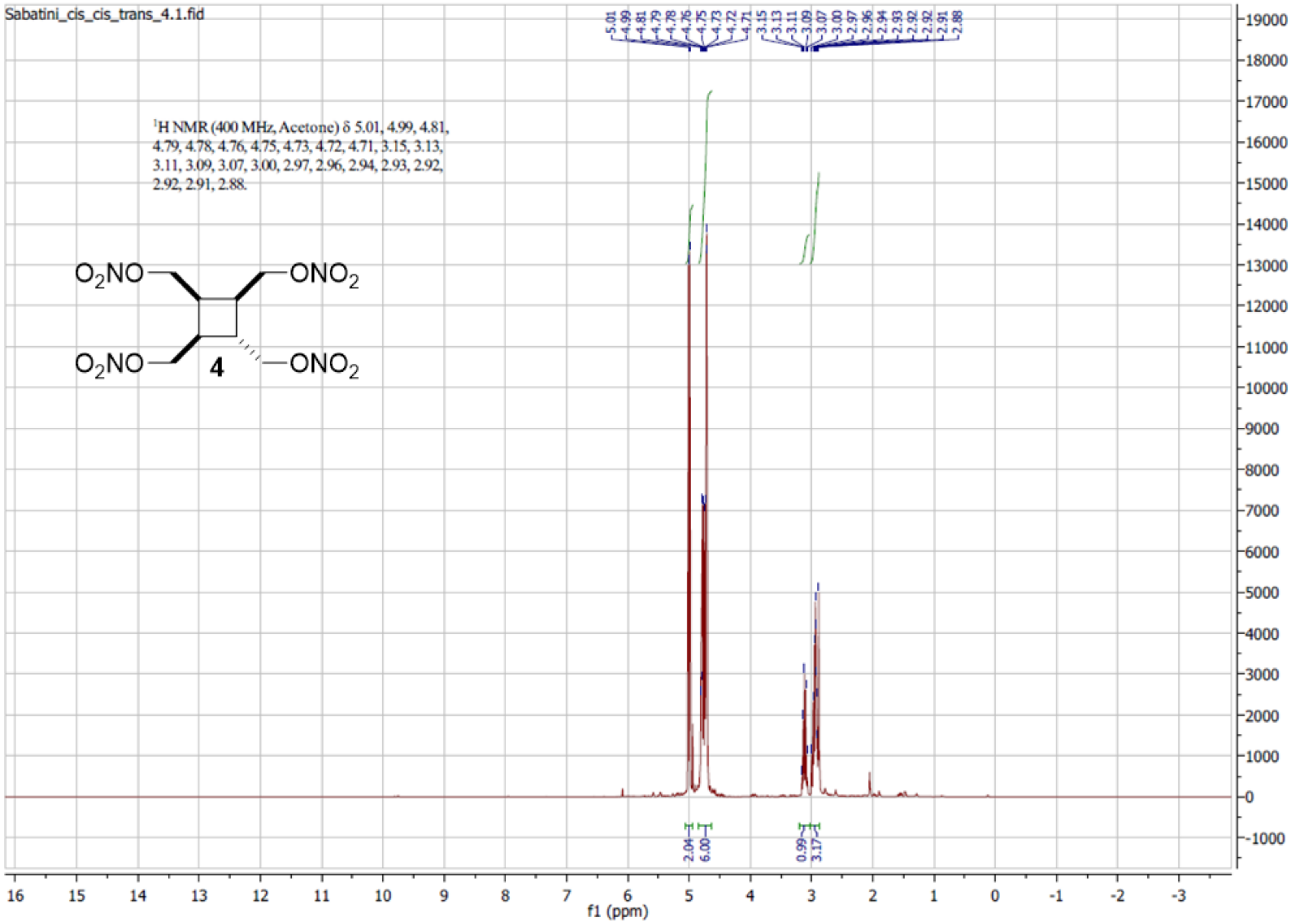


Compound 12 ^{13}C NMR



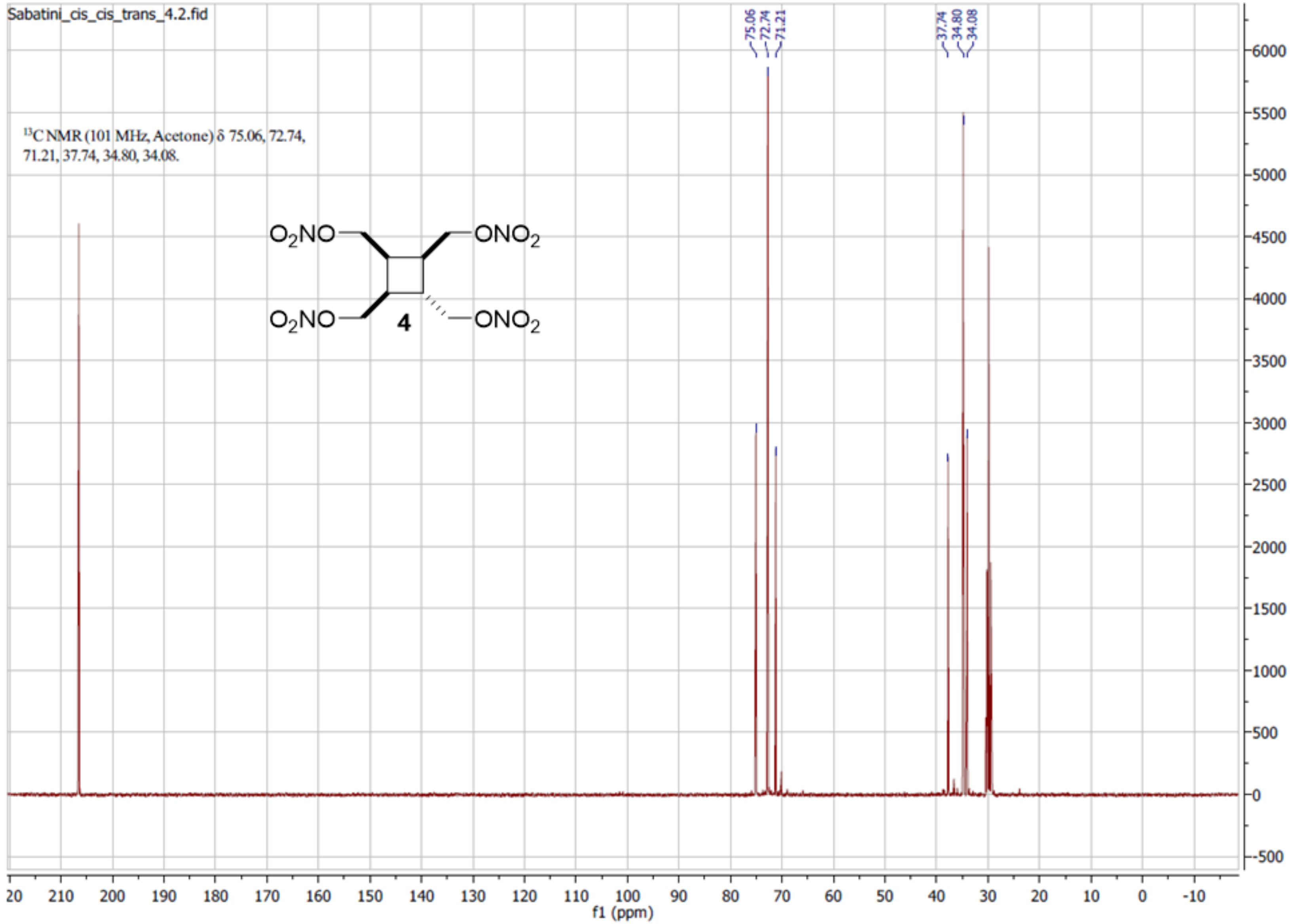


Compound 4 ^{1}H NMR



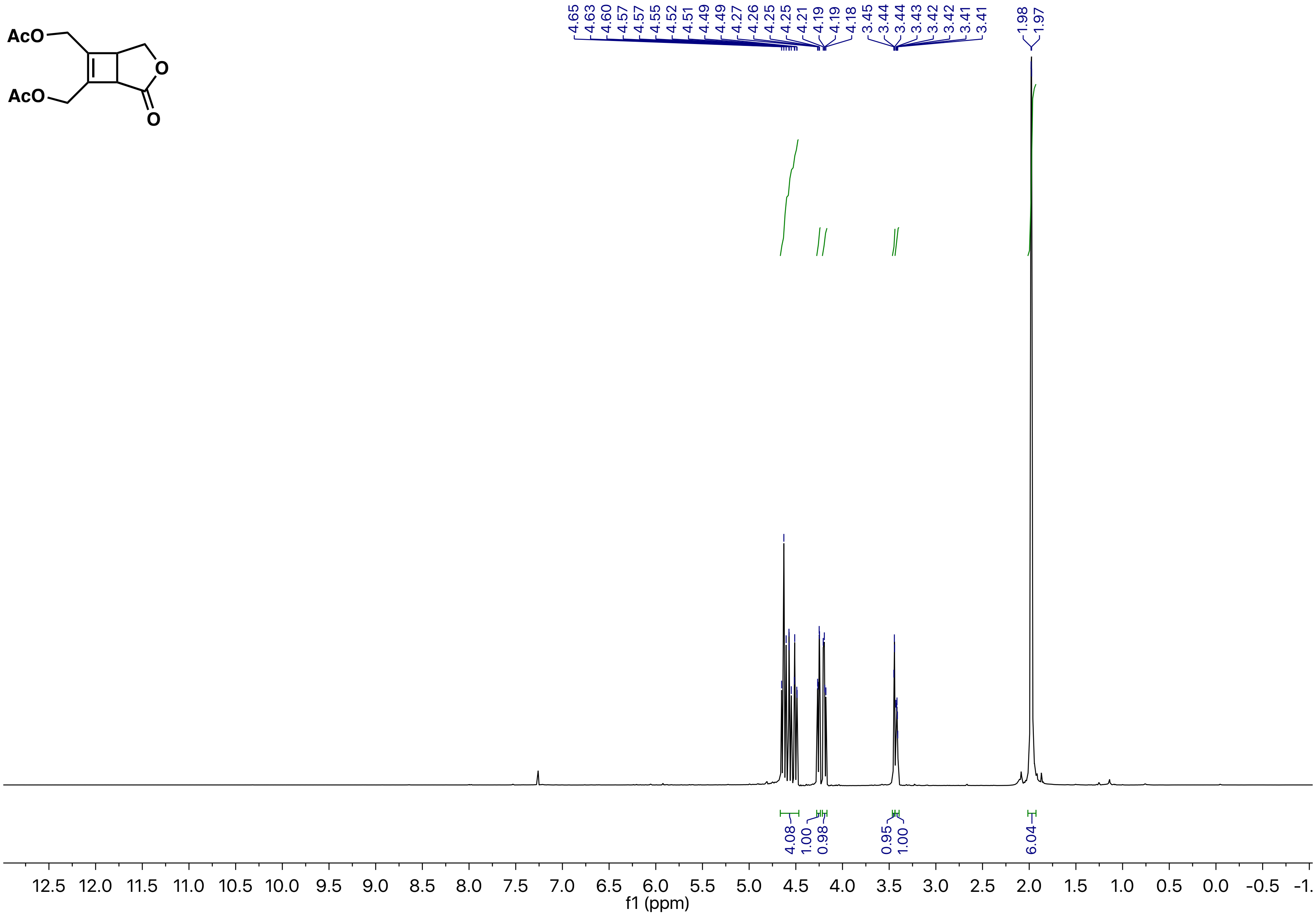
^{1}H NMR (400 MHz, Acetone) δ 5.01, 4.99, 4.81, 4.79, 4.78, 4.76, 4.75, 4.73, 4.72, 4.71, 3.15, 3.13, 3.11, 3.09, 3.07, 3.00, 2.97, 2.96, 2.94, 2.93, 2.92, 2.92, 2.91, 2.88.

Compound 4 ^{13}C NMR

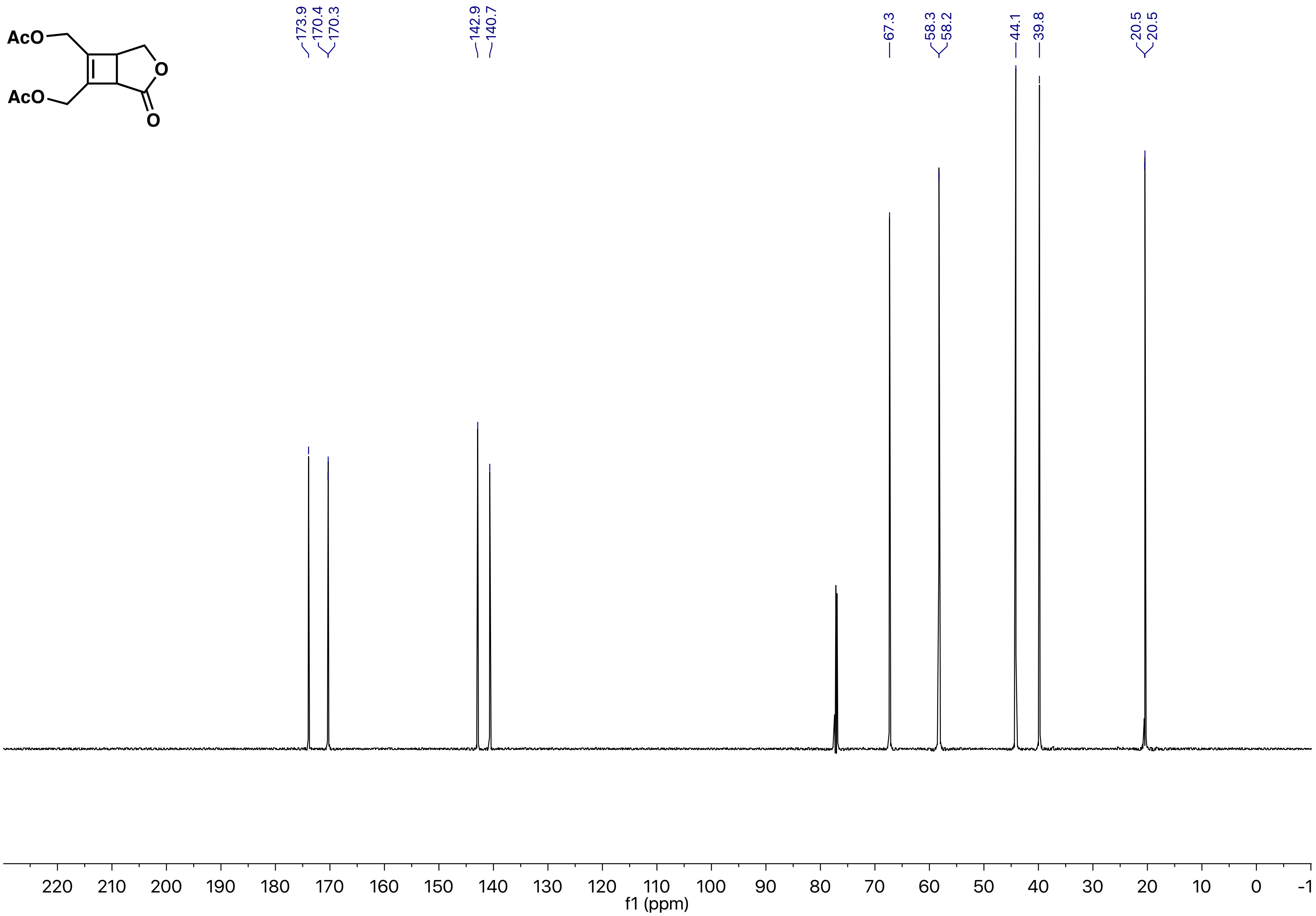


^{13}C NMR (101 MHz, Acetone) δ 75.06, 72.74, 71.21, 37.74, 34.80, 34.08.

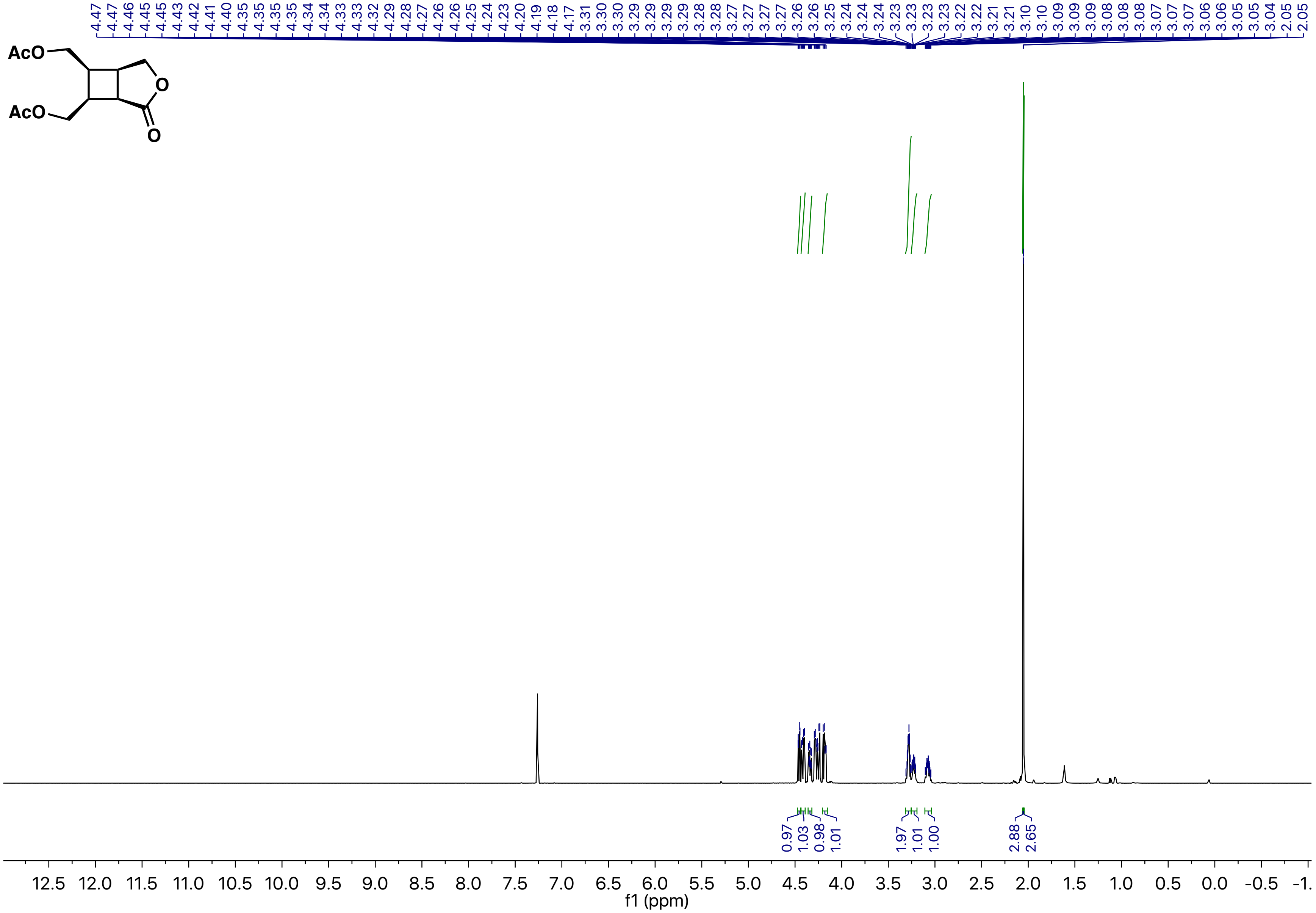
Compound SI-2 ^{1}H NMR



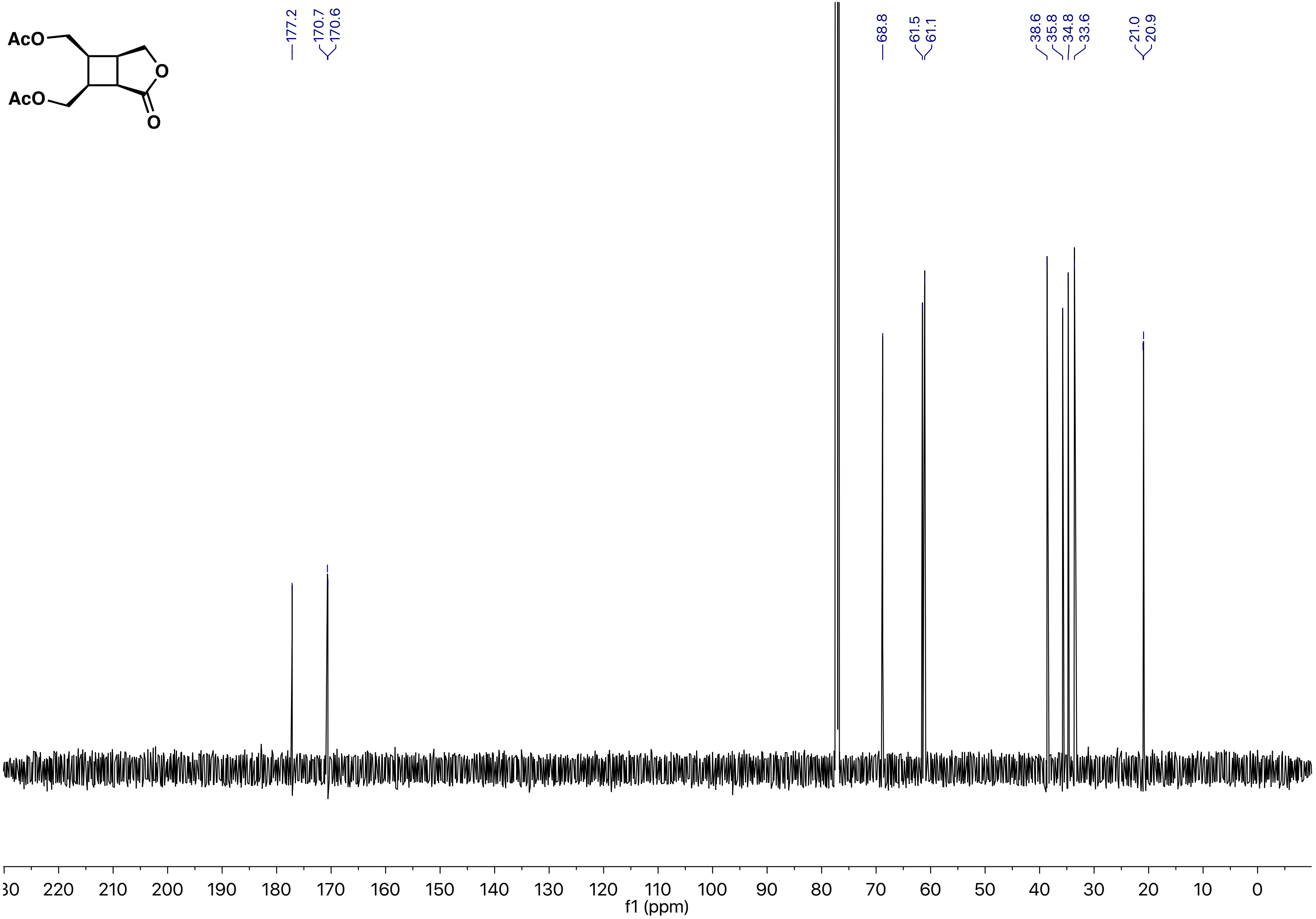
Compound SI-2 ^{13}C NMR



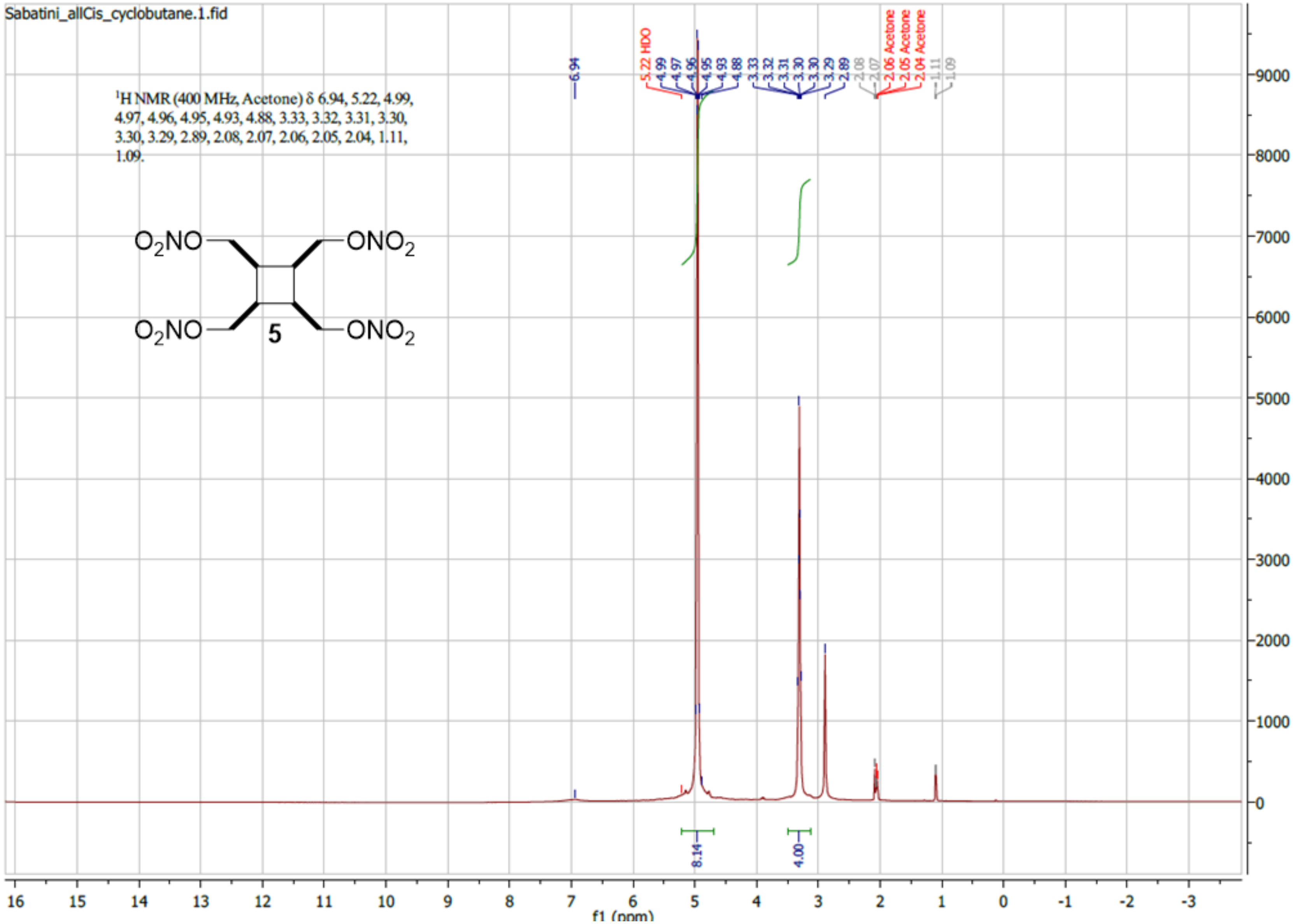
Compound 13 ^{1}H NMR



Compound 13 ^{13}C NMR

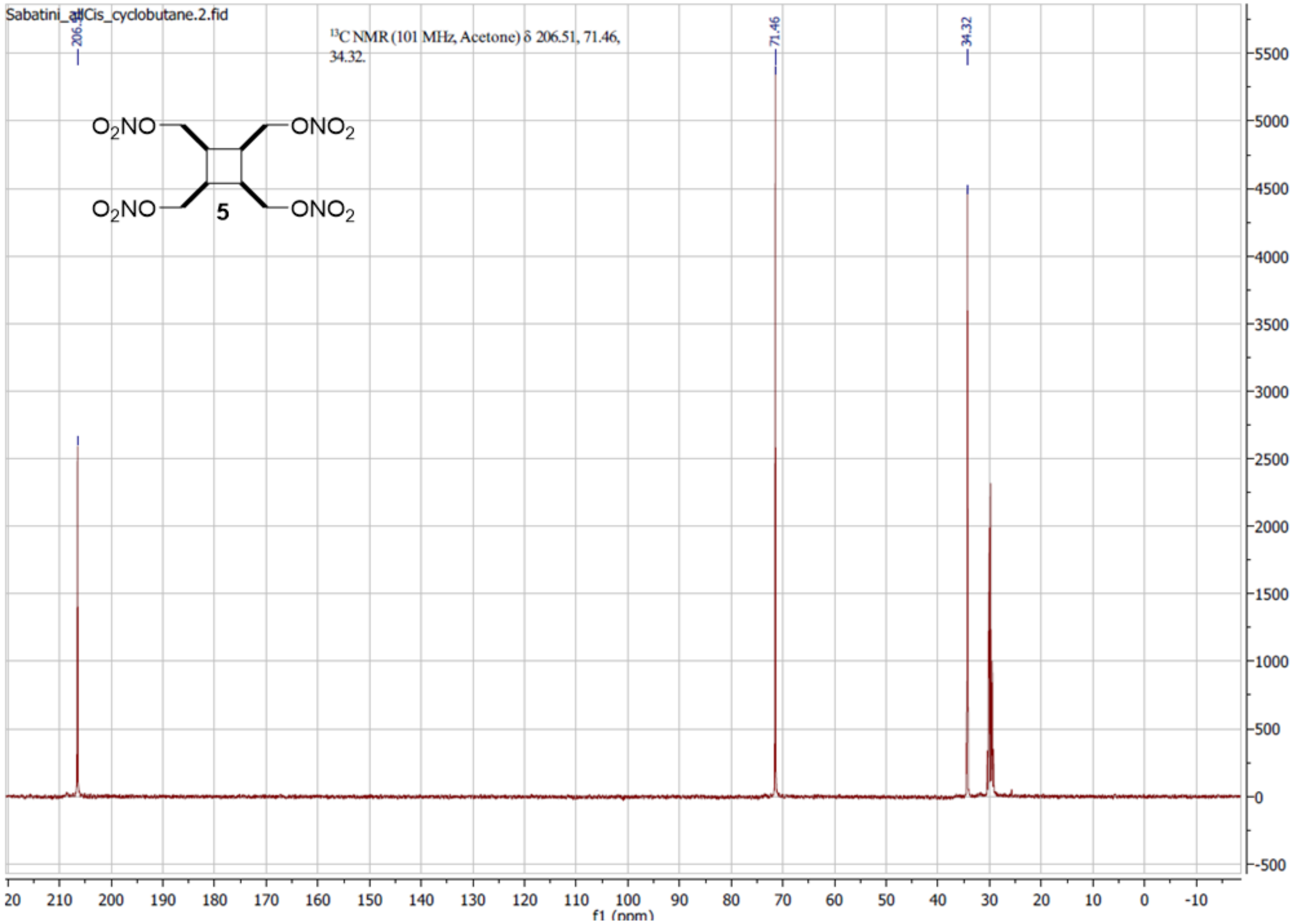


Compound 5 ^{1}H NMR



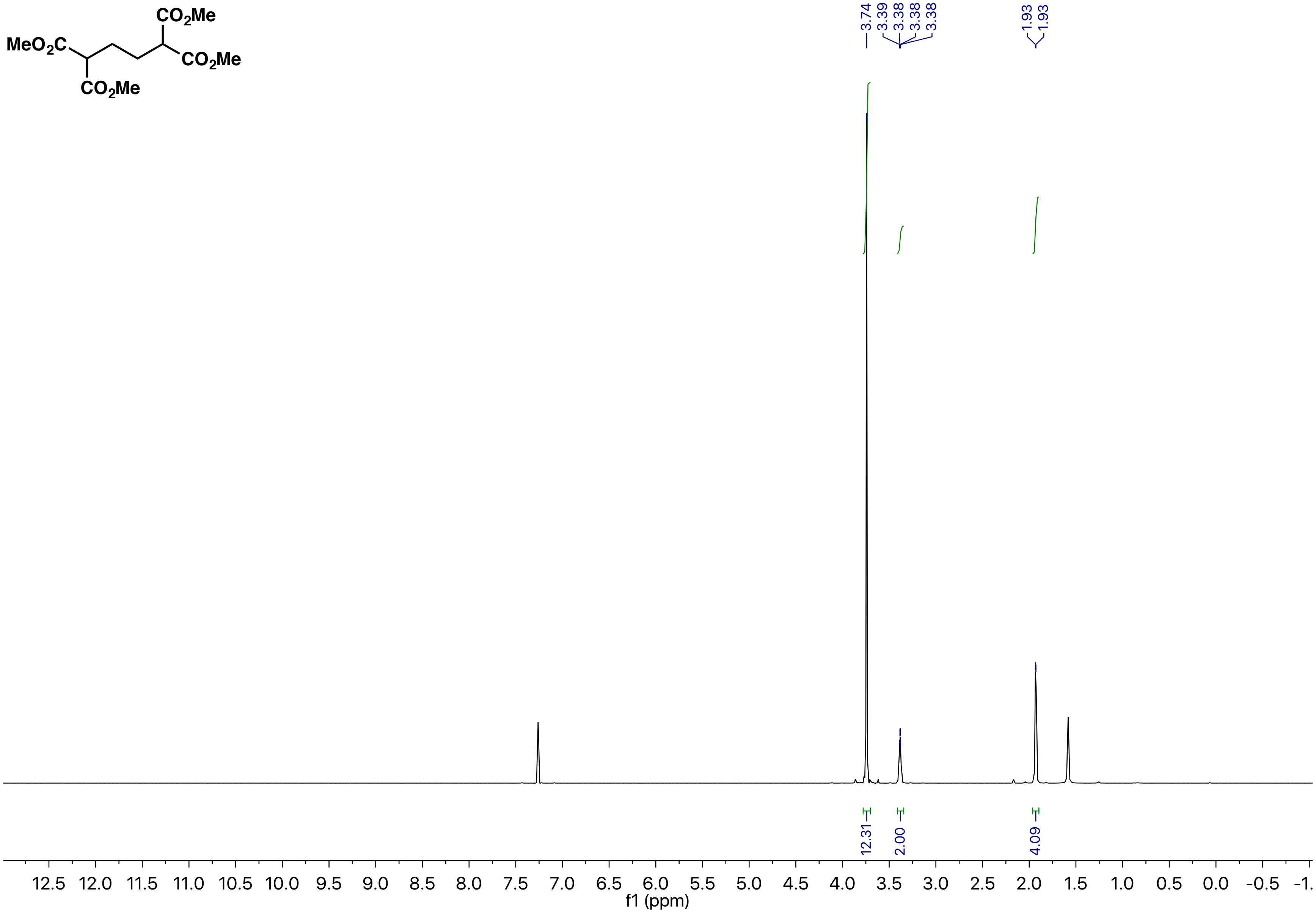
^{1}H NMR (400 MHz, Acetone) δ 6.94, 5.22, 4.99, 4.97, 4.96, 4.95, 4.93, 4.88, 3.33, 3.32, 3.31, 3.30, 3.30, 3.29, 2.89, 2.08, 2.07, 2.06, 2.05, 2.04, 1.11, 1.09.

Compound 5 ^{13}C NMR

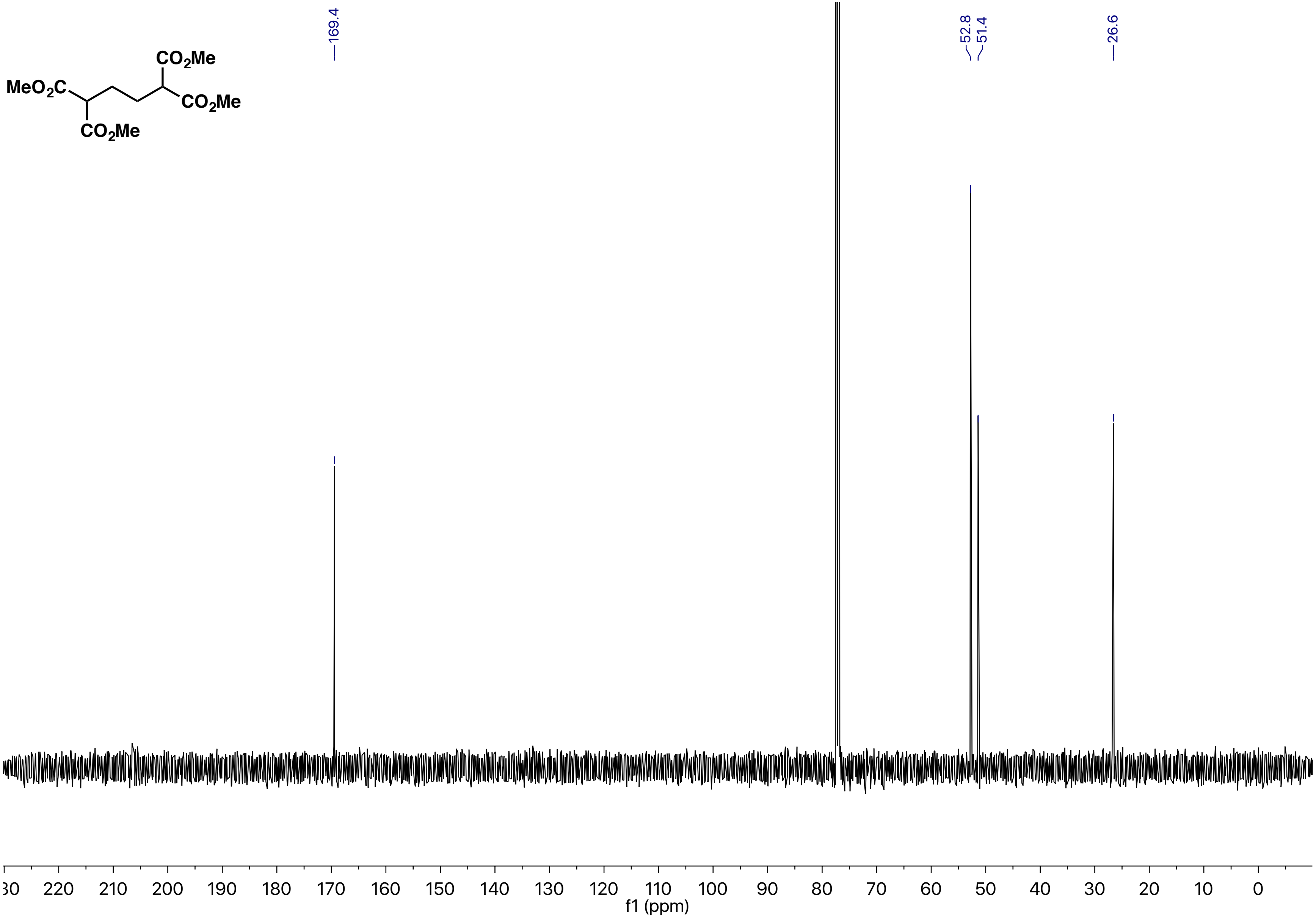


^{13}C NMR (101 MHz, Acetone) δ 206.51, 71.46, 34.32.

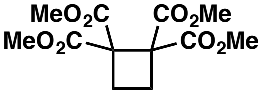
Compound 14 ^{1}H NMR

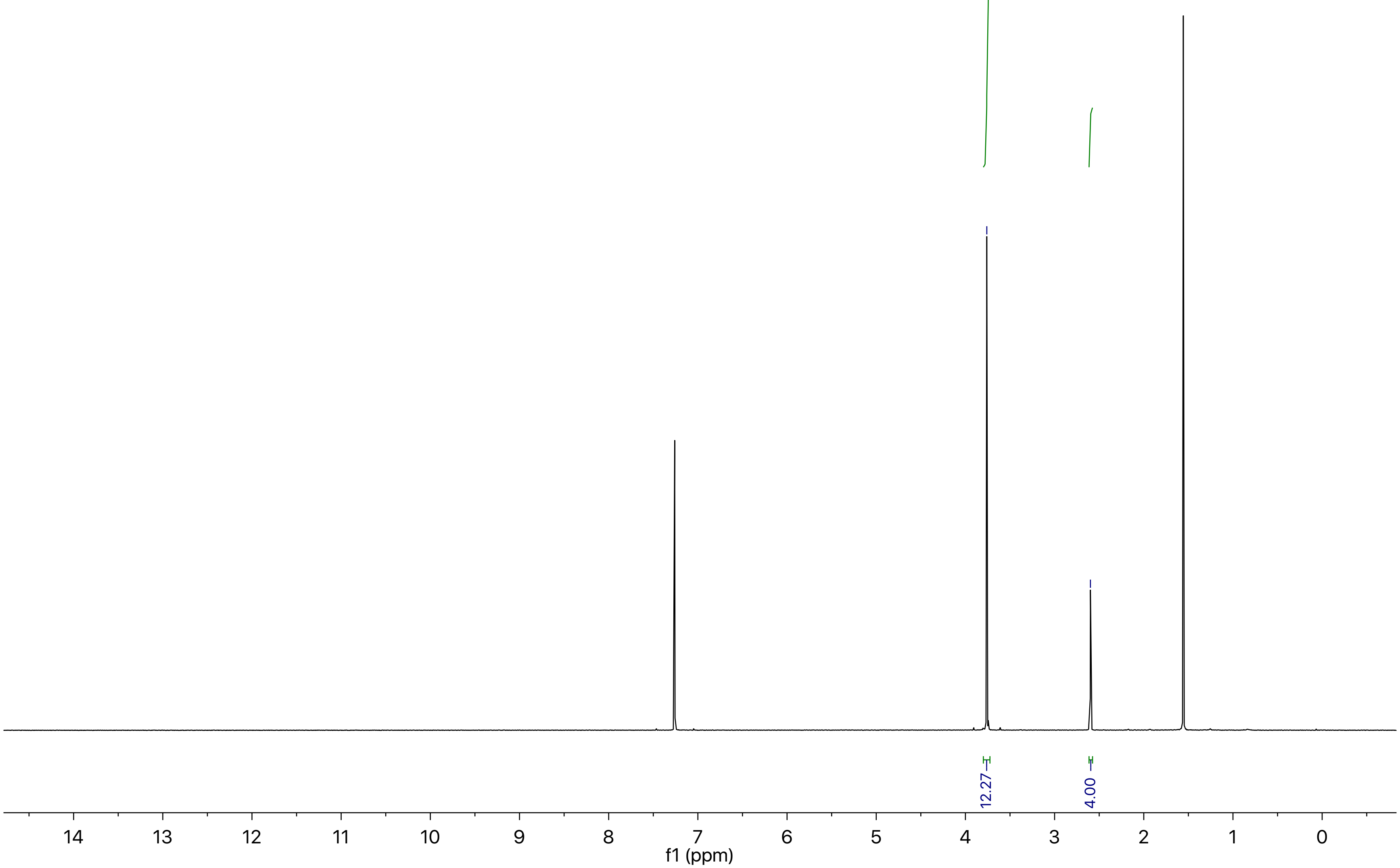


Compound 14 ^{13}C NMR

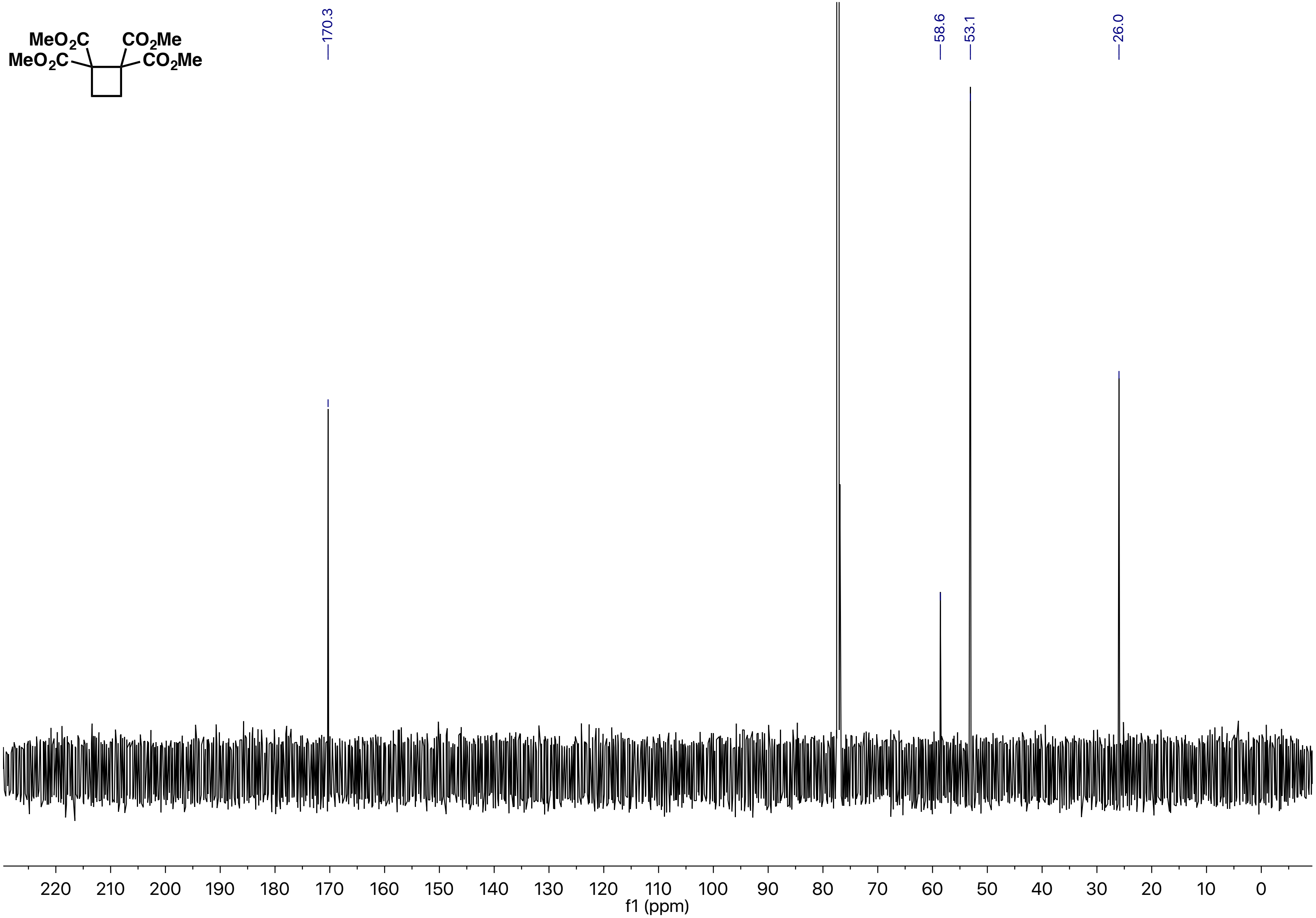


Compound 15 ^{1}H NMR

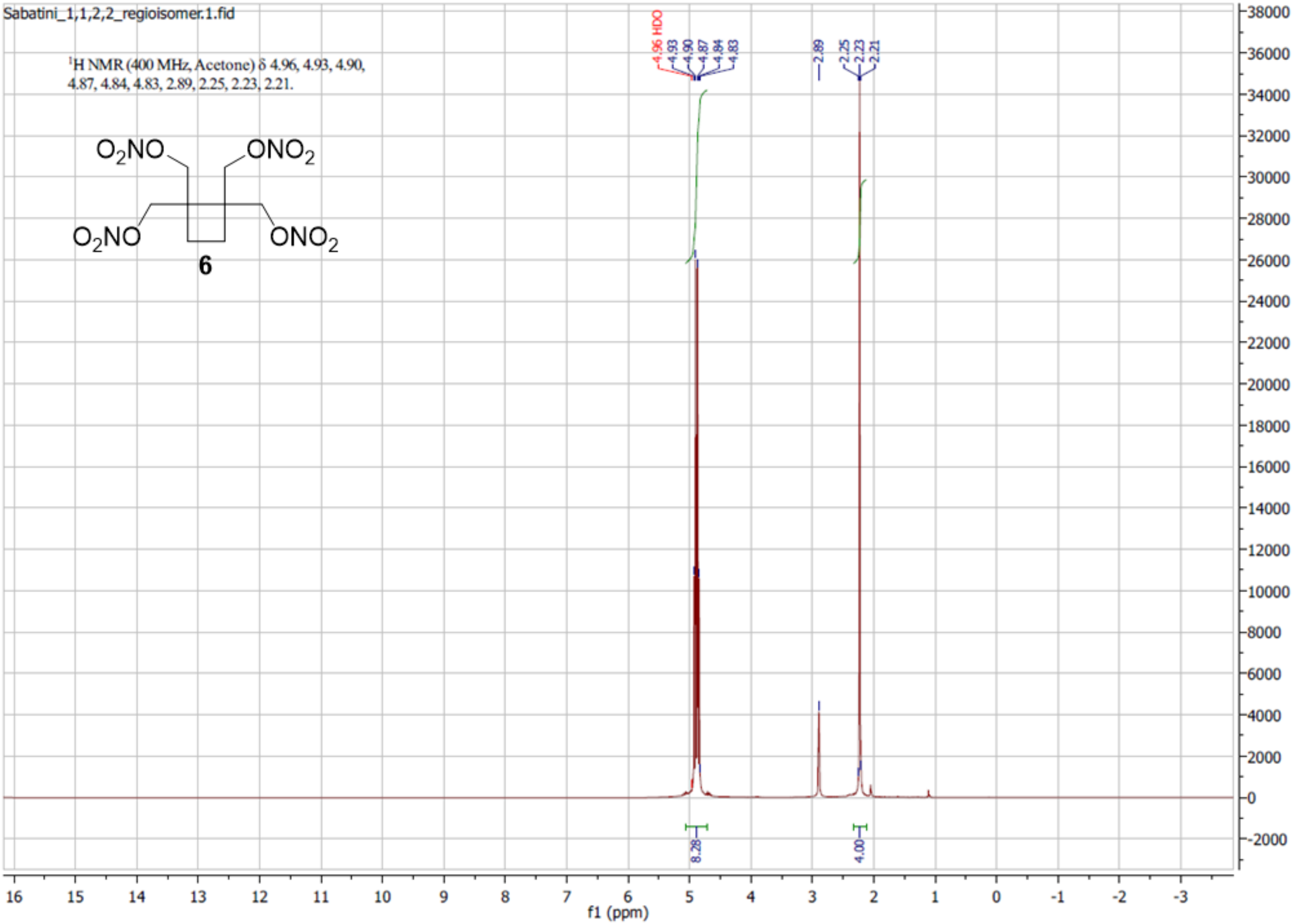




Compound 15 ^{13}C NMR



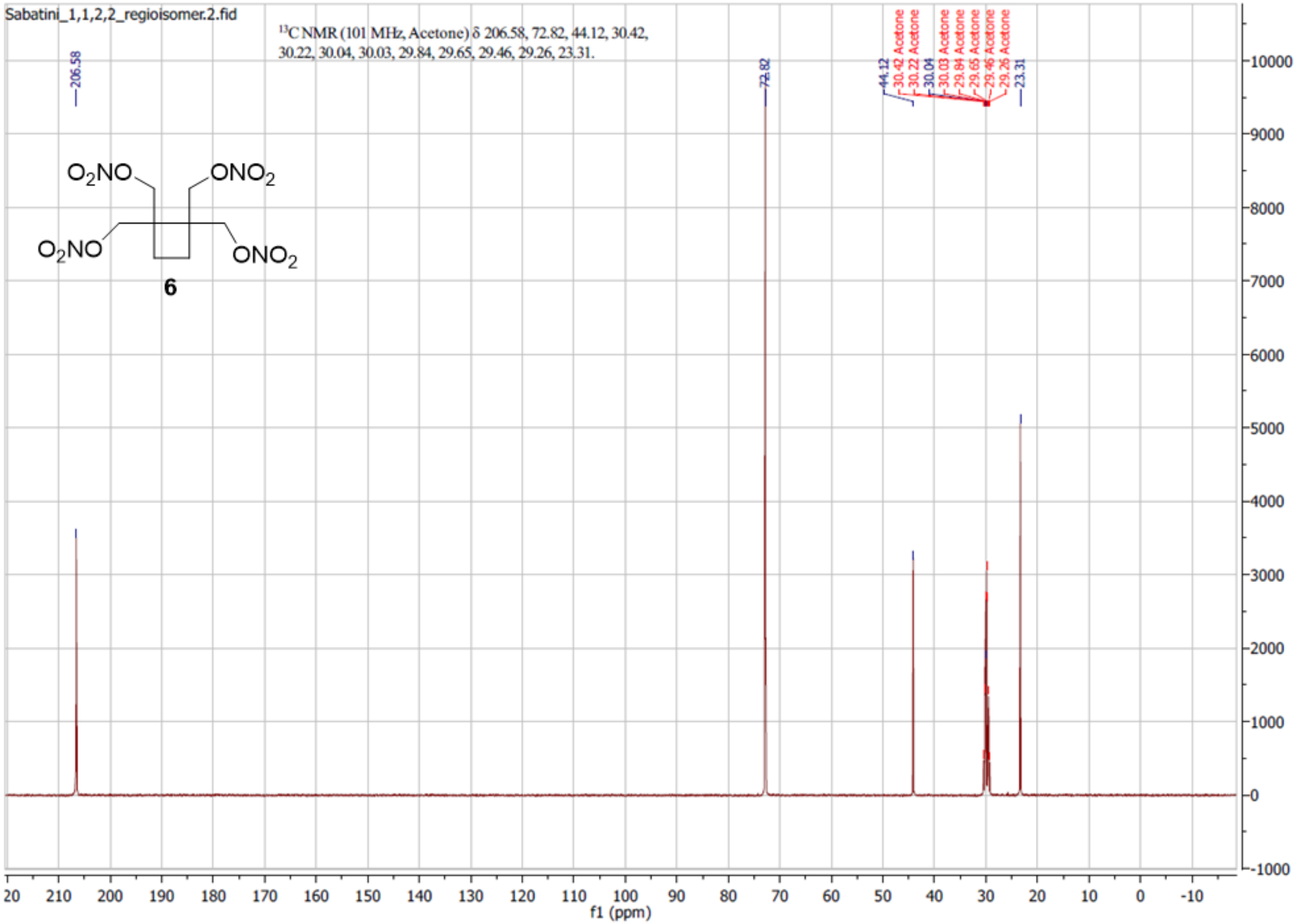
Compound 6 ^{1}H NMR



^{1}H NMR (400 MHz, Acetone) δ 4.96, 4.93, 4.90, 4.87, 4.84, 4.83, 2.89, 2.25, 2.23, 2.21.

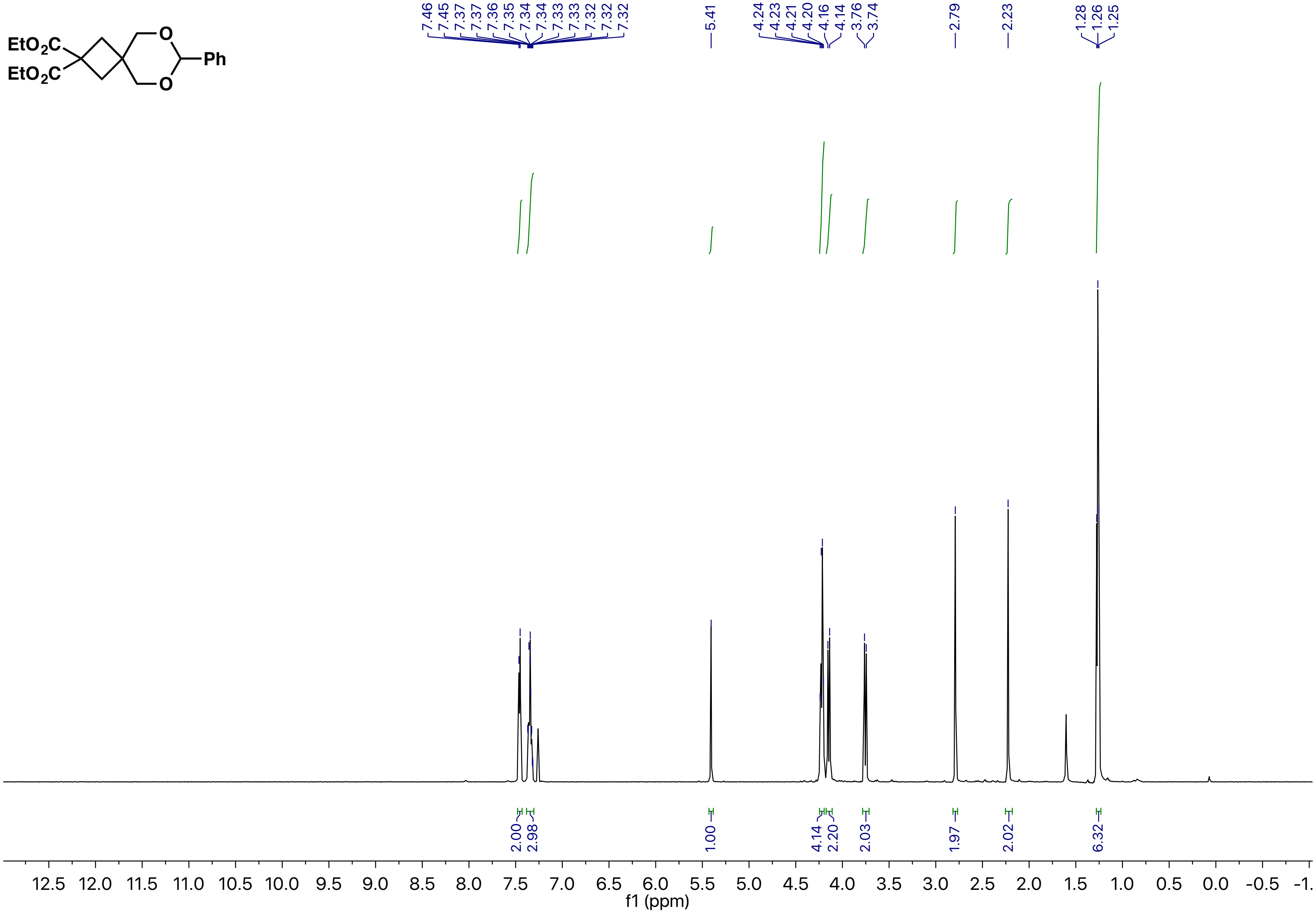
6

Compound 6 ^{13}C NMR

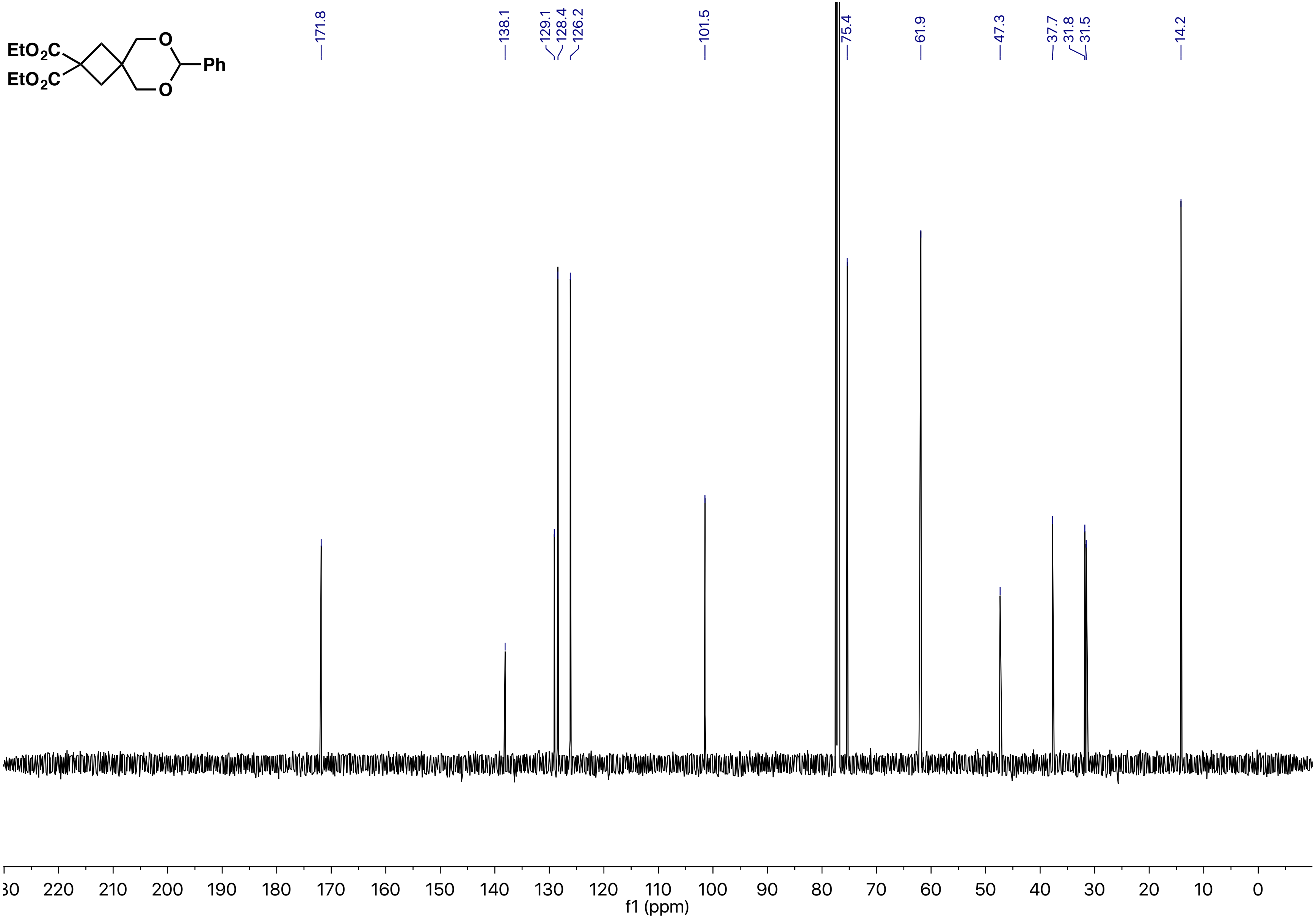


^{13}C NMR (101 MHz, Acetone) δ 206.58, 72.82, 44.12, 30.42, 30.22, 30.04, 30.03, 29.84, 29.65, 29.46, 29.26, 23.31.

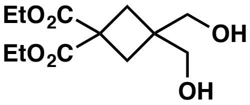
Compound 17 ^{1}H NMR

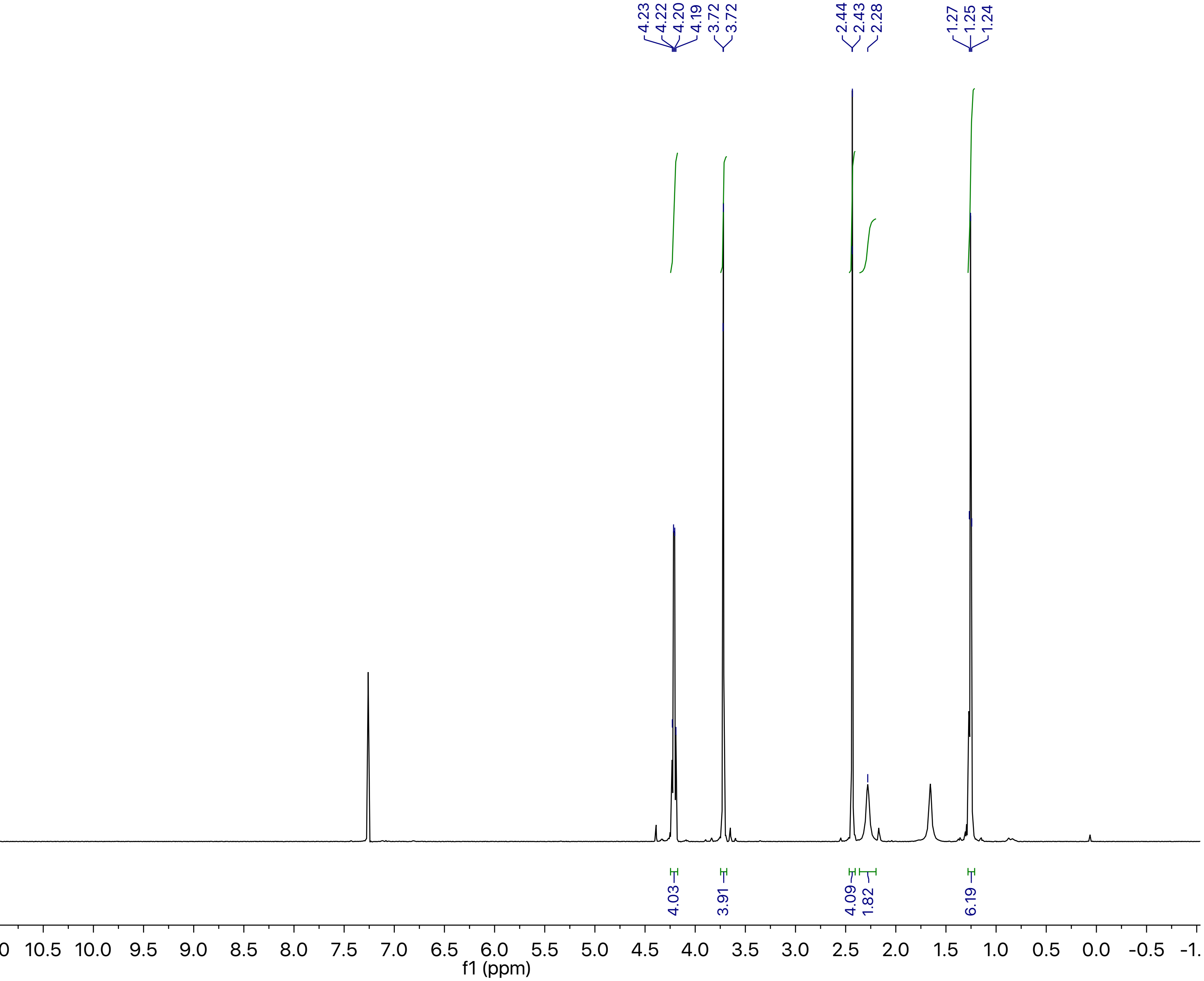


Compound 17 ^{13}C NMR

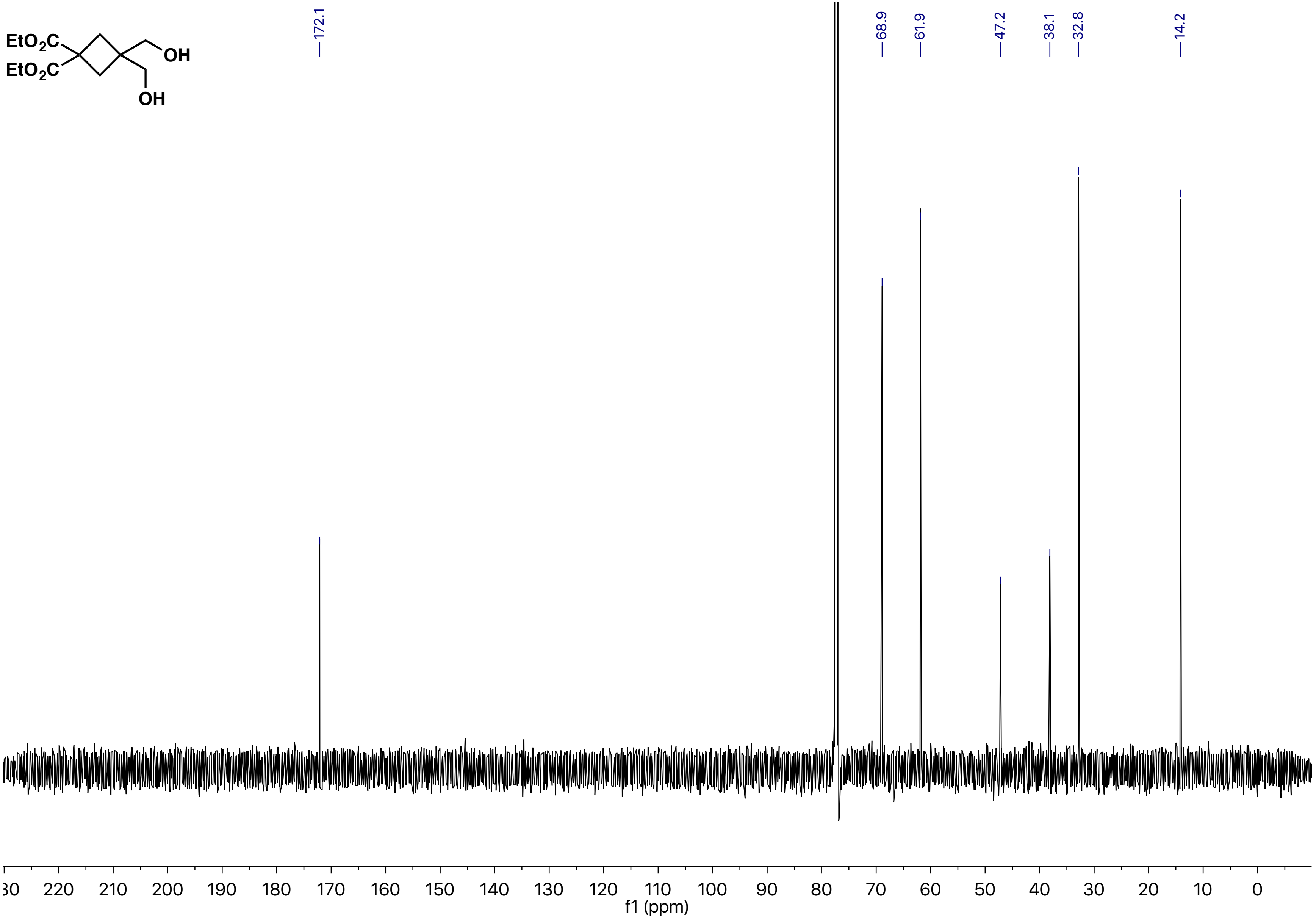


Compound 18 ^{1}H NMR

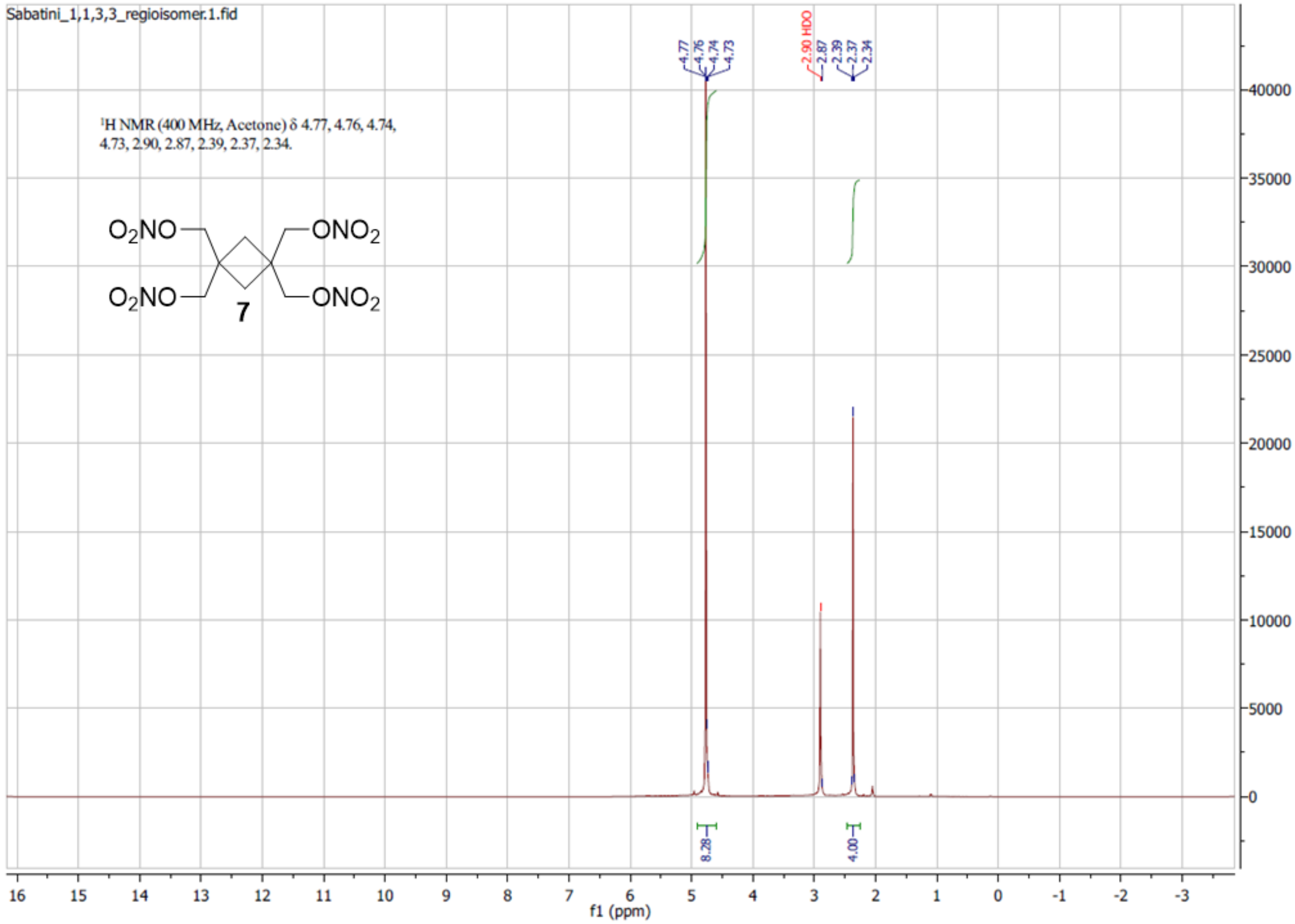




Compound 18 ^{13}C NMR

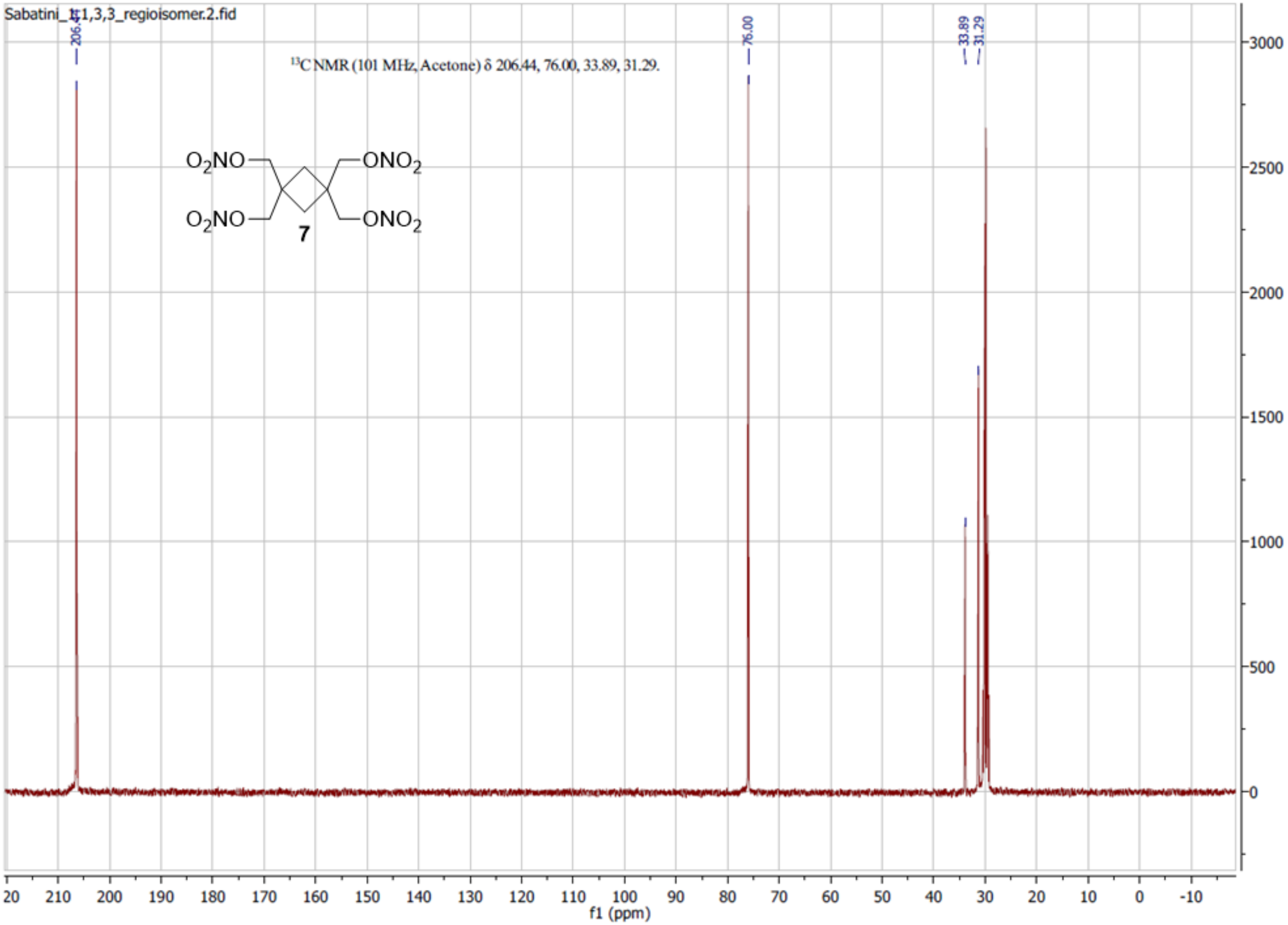


Compound 7 ^{1}H NMR



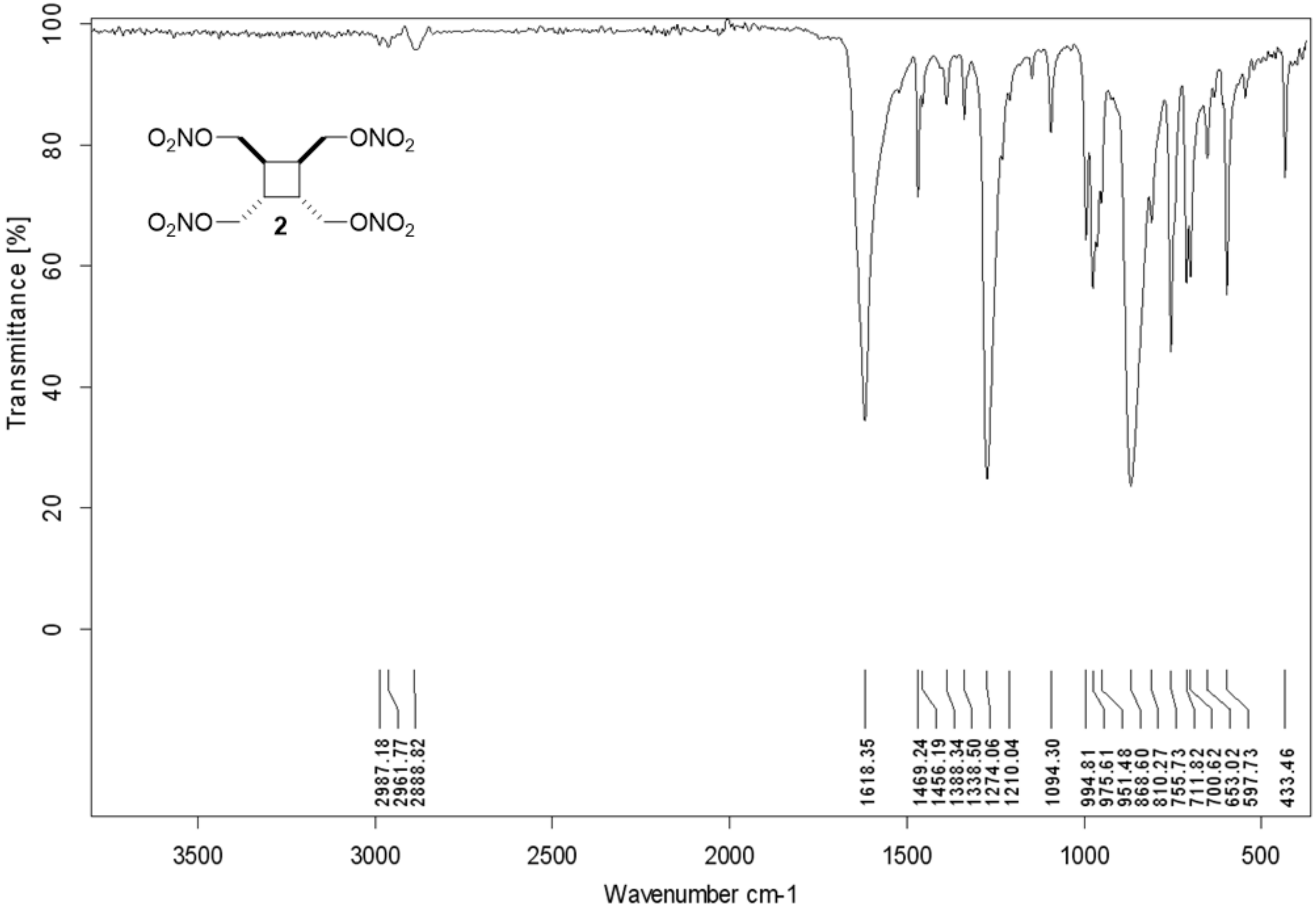
^{1}H NMR (400 MHz, Acetone) δ 4.77, 4.76, 4.74, 4.73, 2.90, 2.87, 2.39, 2.37, 2.34.

Compound 7 ^{13}C NMR

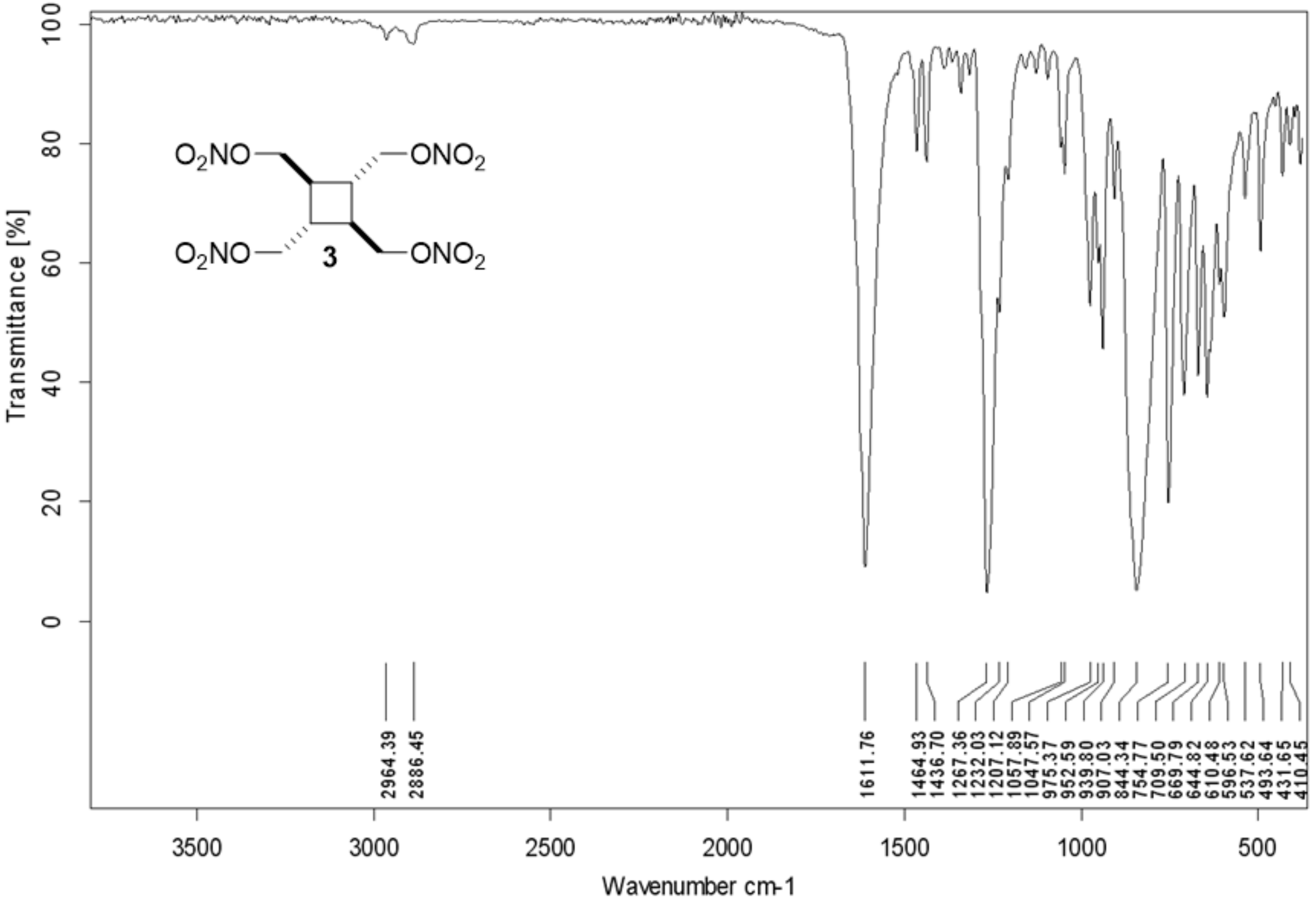


IR Spectra of Tetranitrates 2-7

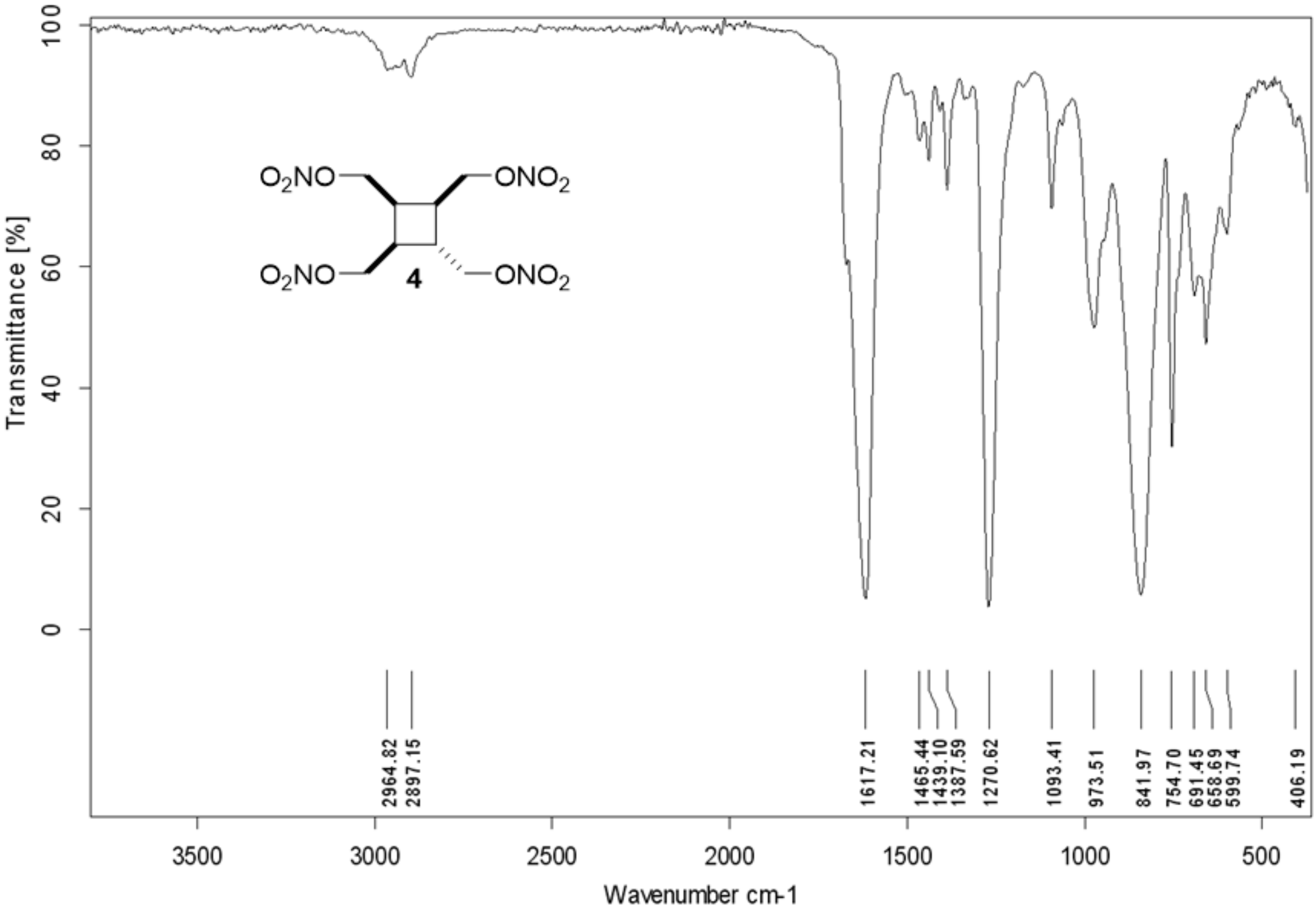
Compound 2



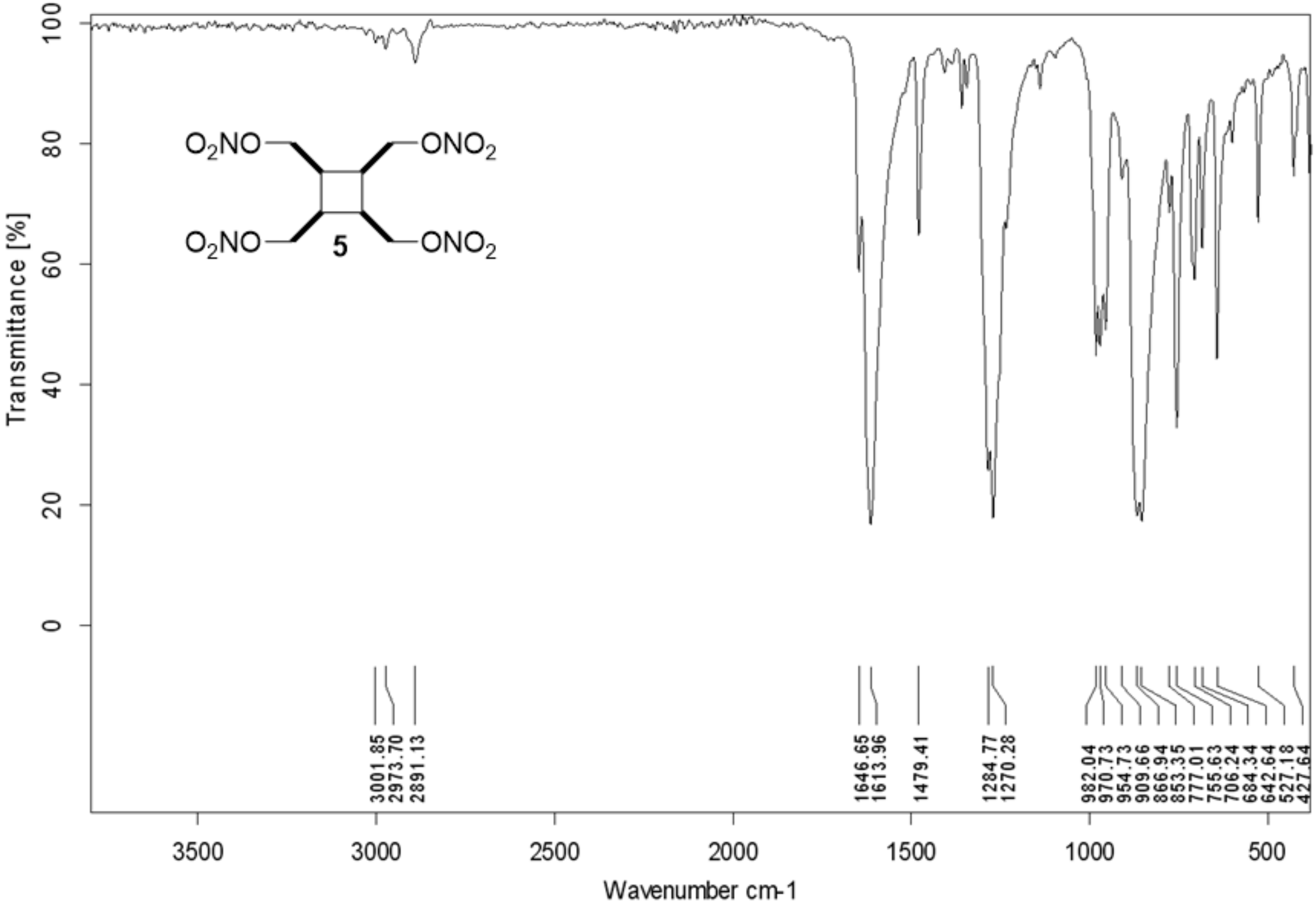
Compound 3


O$_2$NO
ONO$_2$
O$_2$NO
ONO$_2$
3
Transmittance [%]
100
80
60
40
20
0
2964.39
2886.45
1611.76
1464.93
1436.70
1267.36
1232.03
1207.12
1057.89
1047.57
975.37
952.59
939.80
907.03
844.34
754.77
709.50
669.79
644.82
610.48
596.53
537.62
493.64
431.65
410.45
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

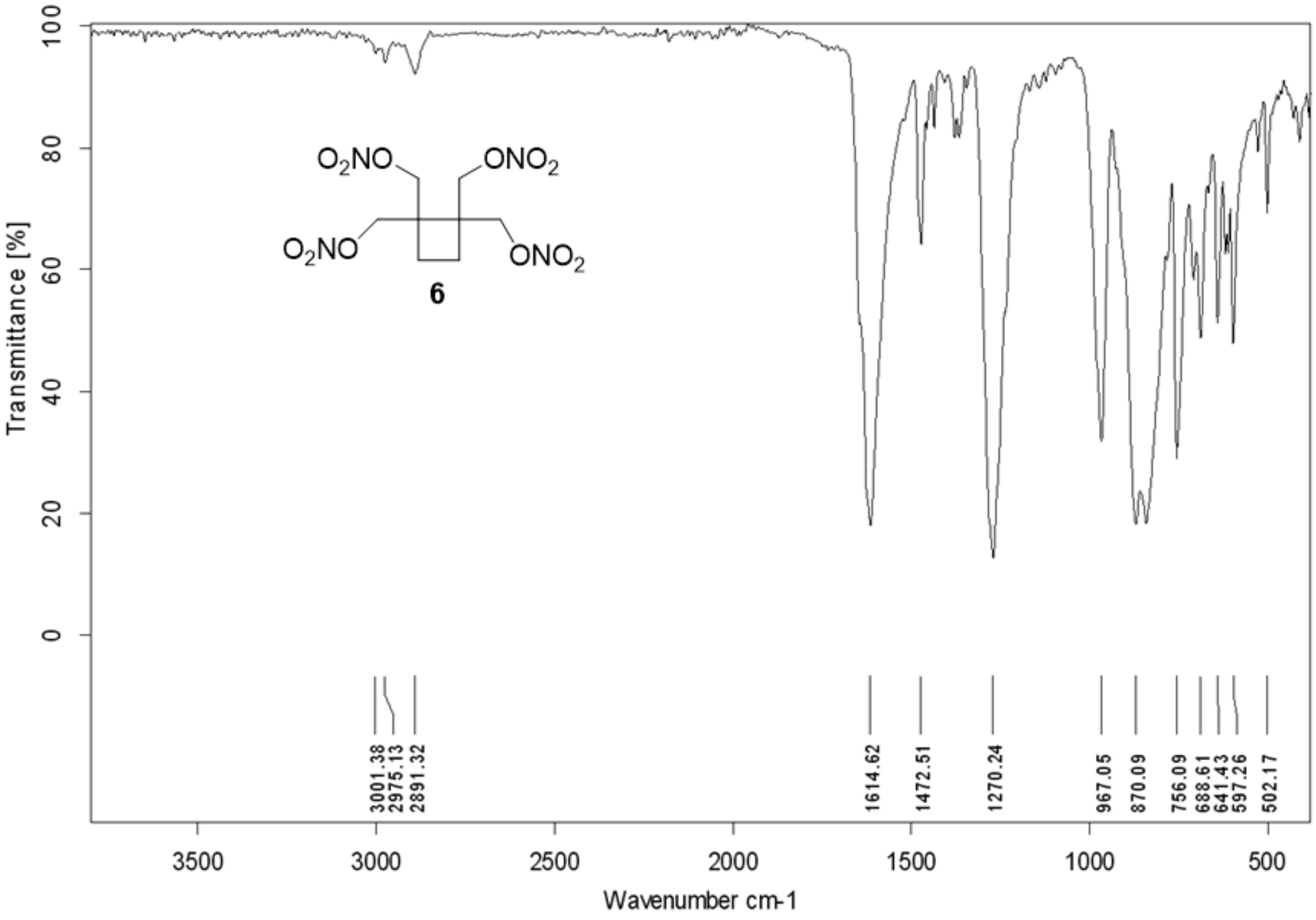
Compound 4


O2NO
ONO2
O2NO
ONO2
4
Transmittance [%]
100
80
60
40
20
0
2964.82
2897.15
1617.21
1465.44
1439.10
1387.59
1270.62
1093.41
973.51
841.97
754.70
691.45
658.69
599.74
406.19
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Compound 5

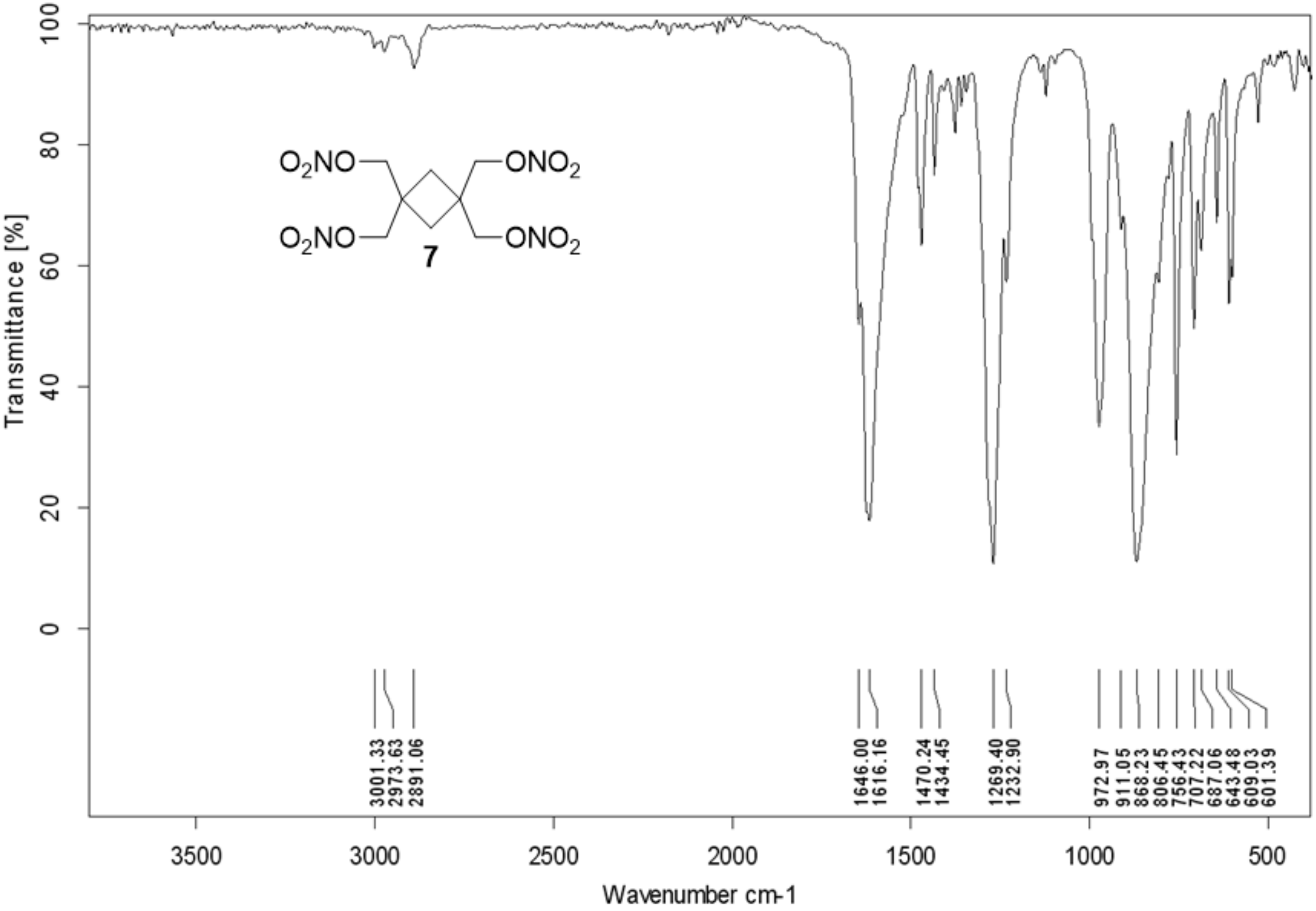

O$_2$NO
ONO$_2$
O$_2$NO
ONO$_2$
5
Transmittance [%]
100
80
60
40
20
0
3001.85
2973.70
2891.13
1646.65
1613.96
1479.41
1284.77
1270.28
982.04
970.73
954.73
909.66
866.94
853.35
777.01
755.63
706.24
684.34
642.64
527.18
427.64
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Compound 6



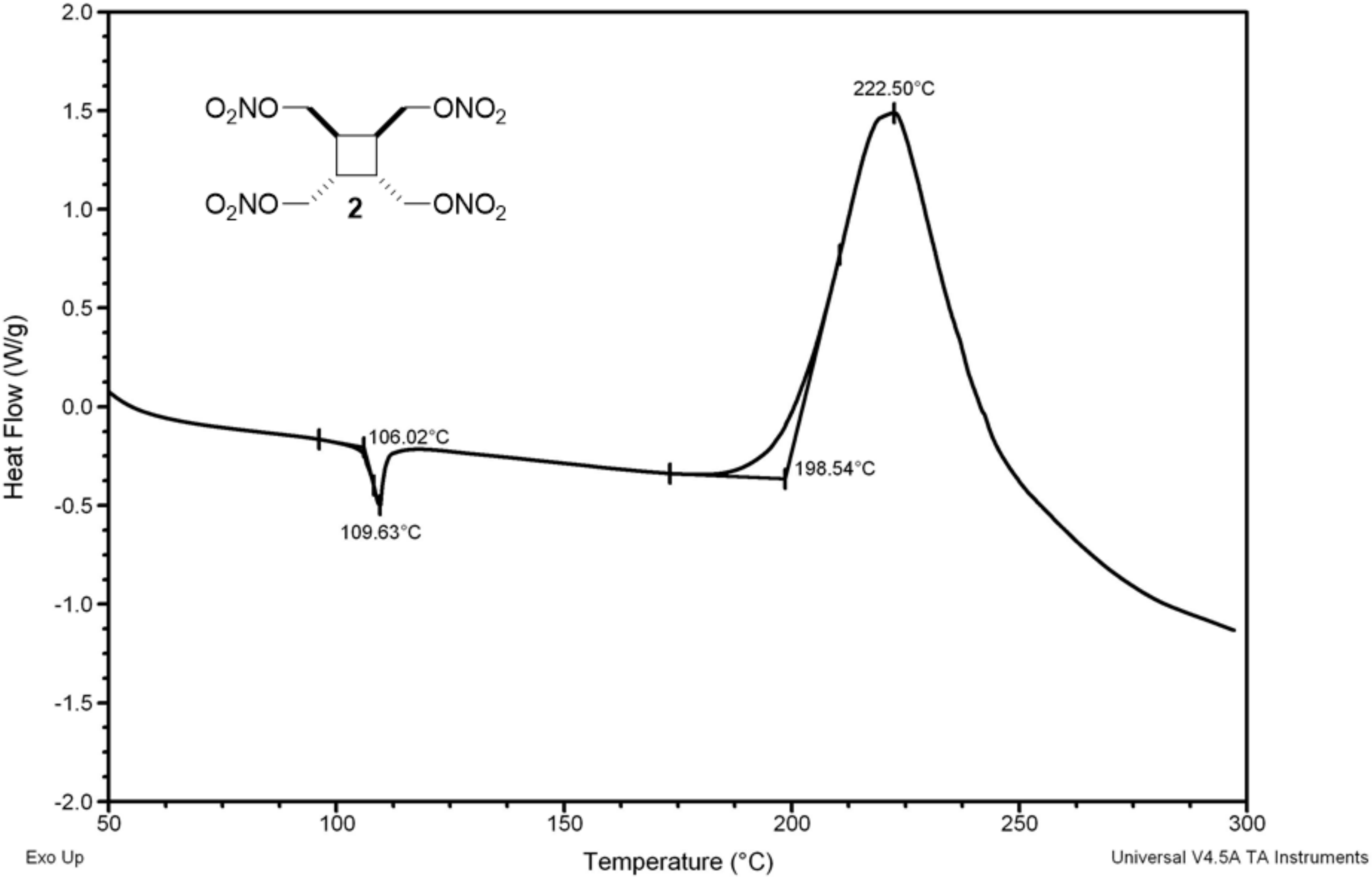
100
80
60
40
20
0
Transmittance [%]
O_2NO
ONO_2
O_2NO
ONO_2
6
3001.38
2975.13
2891.32
1614.62
1472.51
1270.24
967.05
870.09
756.09
688.61
641.43
597.26
502.17
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

Compound 7

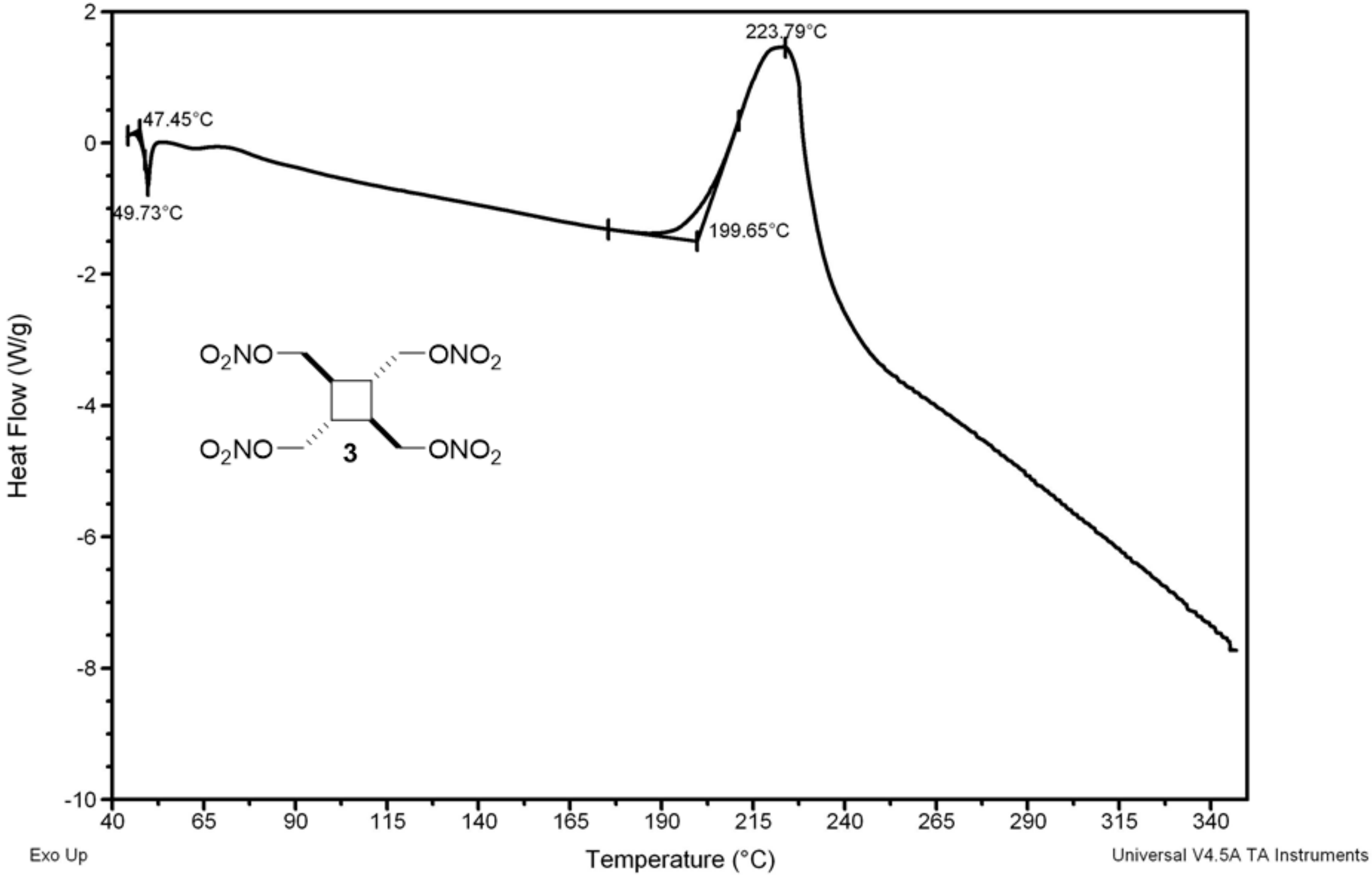

O2NO
ONO2
O2NO
ONO2
7
Transmittance [%]
0
20
40
60
80
100
3001.33
2973.63
2891.06
1646.00
1616.16
1470.24
1434.45
1269.40
1232.90
972.97
911.05
868.23
806.45
756.43
707.22
687.06
643.48
609.03
601.39
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

DSC Traces of Tetranitrates 2-7

Compound 2

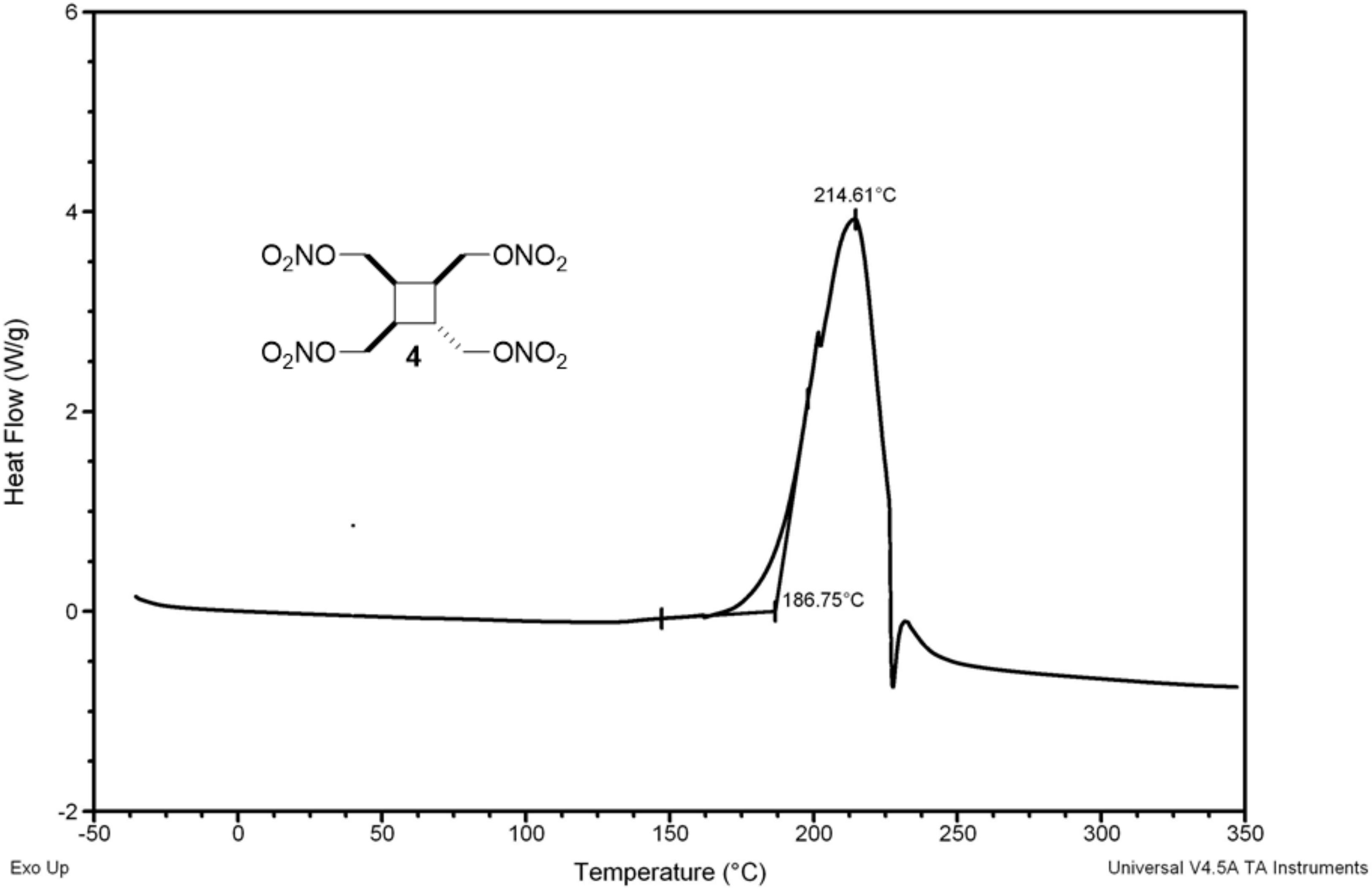


Compound 3



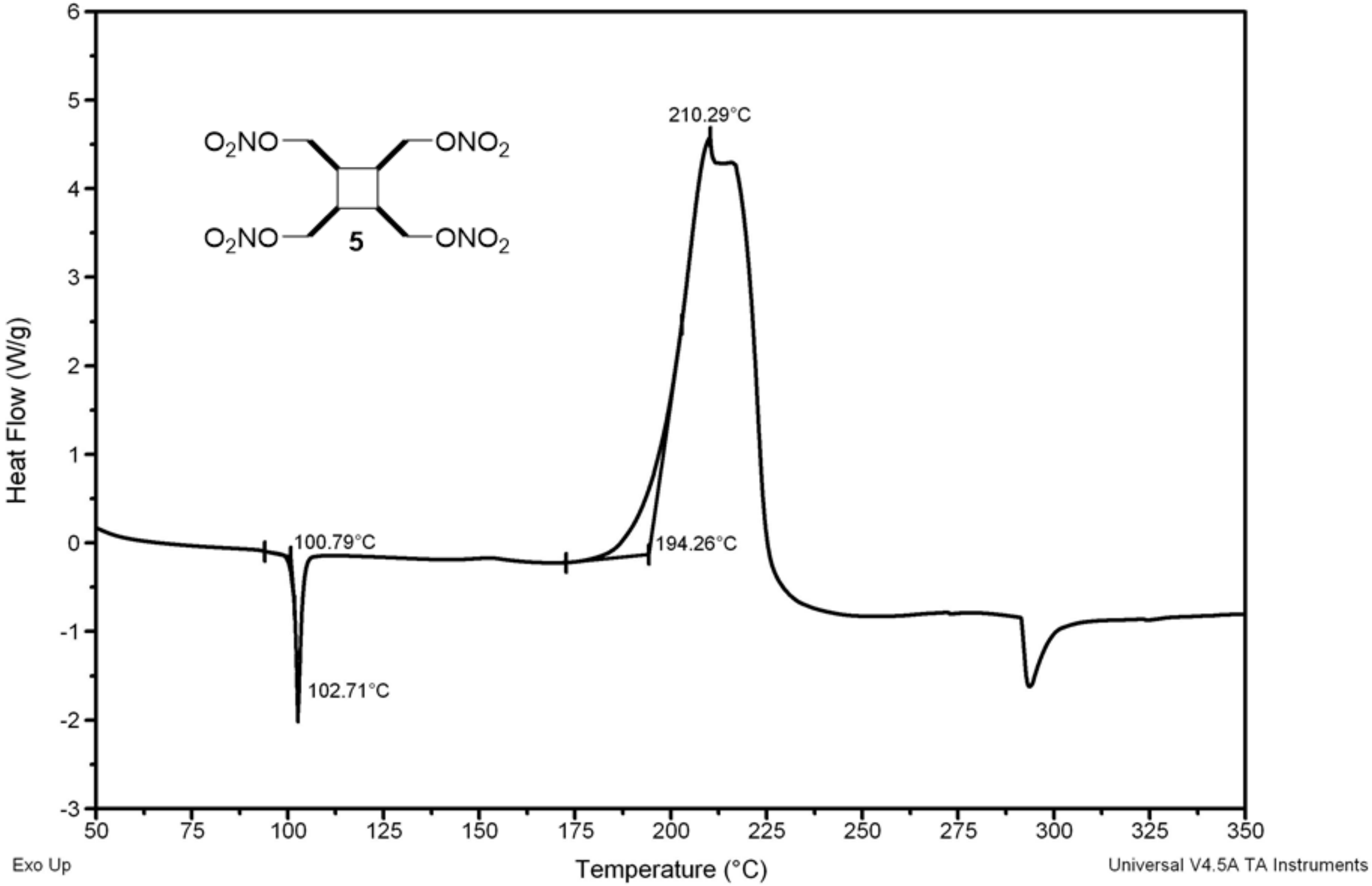
Heat Flow (W/g)
2
0
-2
-4
-6
-8
-10
40
65
90
115
140
165
190
215
240
265
290
315
340
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
47.45°C
49.73°C
223.79°C
199.65°C
O2NO
ONO2
O2NO
ONO2
3

Compound 4



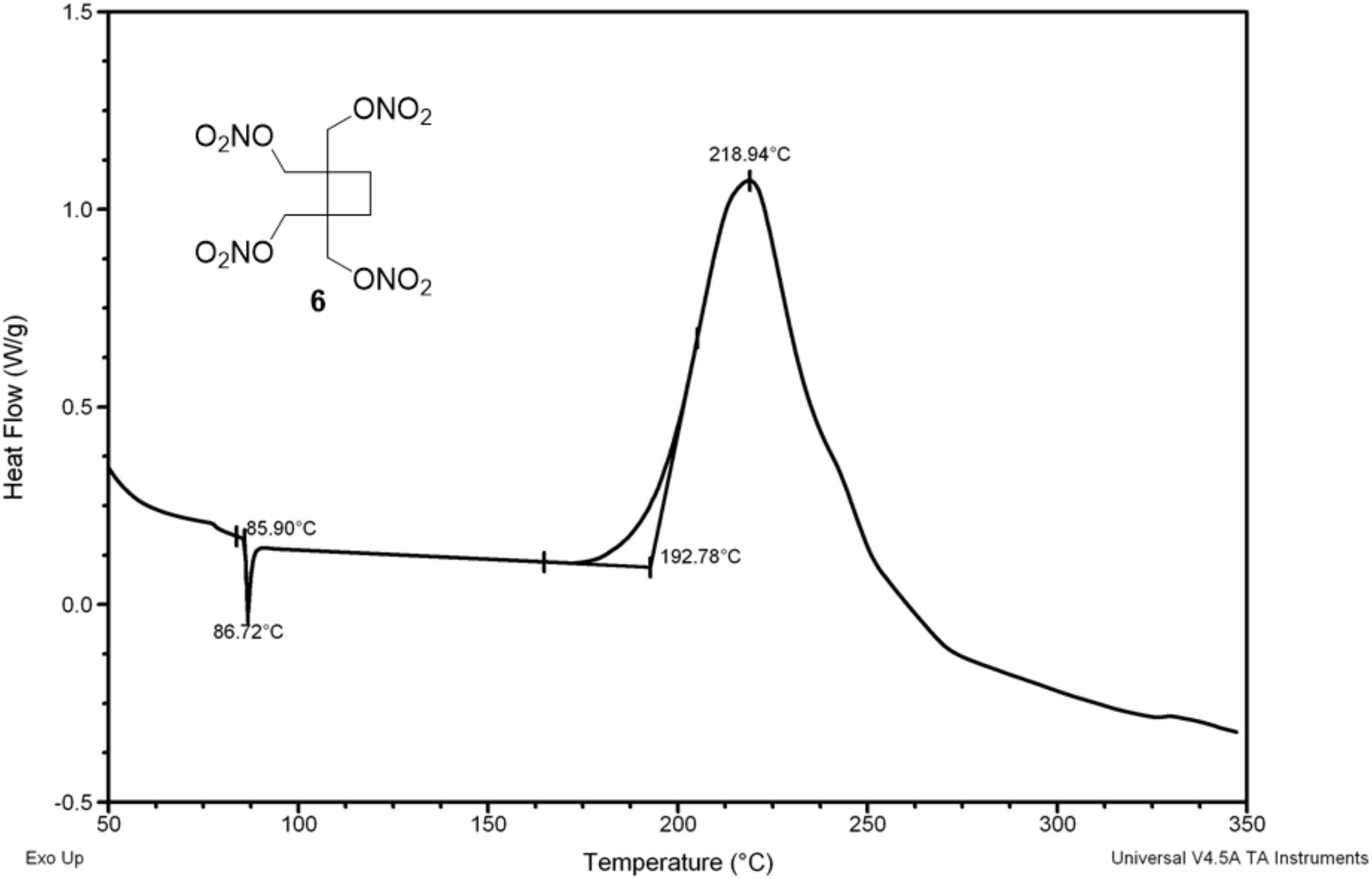
214.61°C
186.75°C
O2NO
ONO2
O2NO
ONO2
4
Heat Flow (W/g)
6
4
2
0
-2
-50
0
50
100
150
200
250
300
350
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

Compound 5

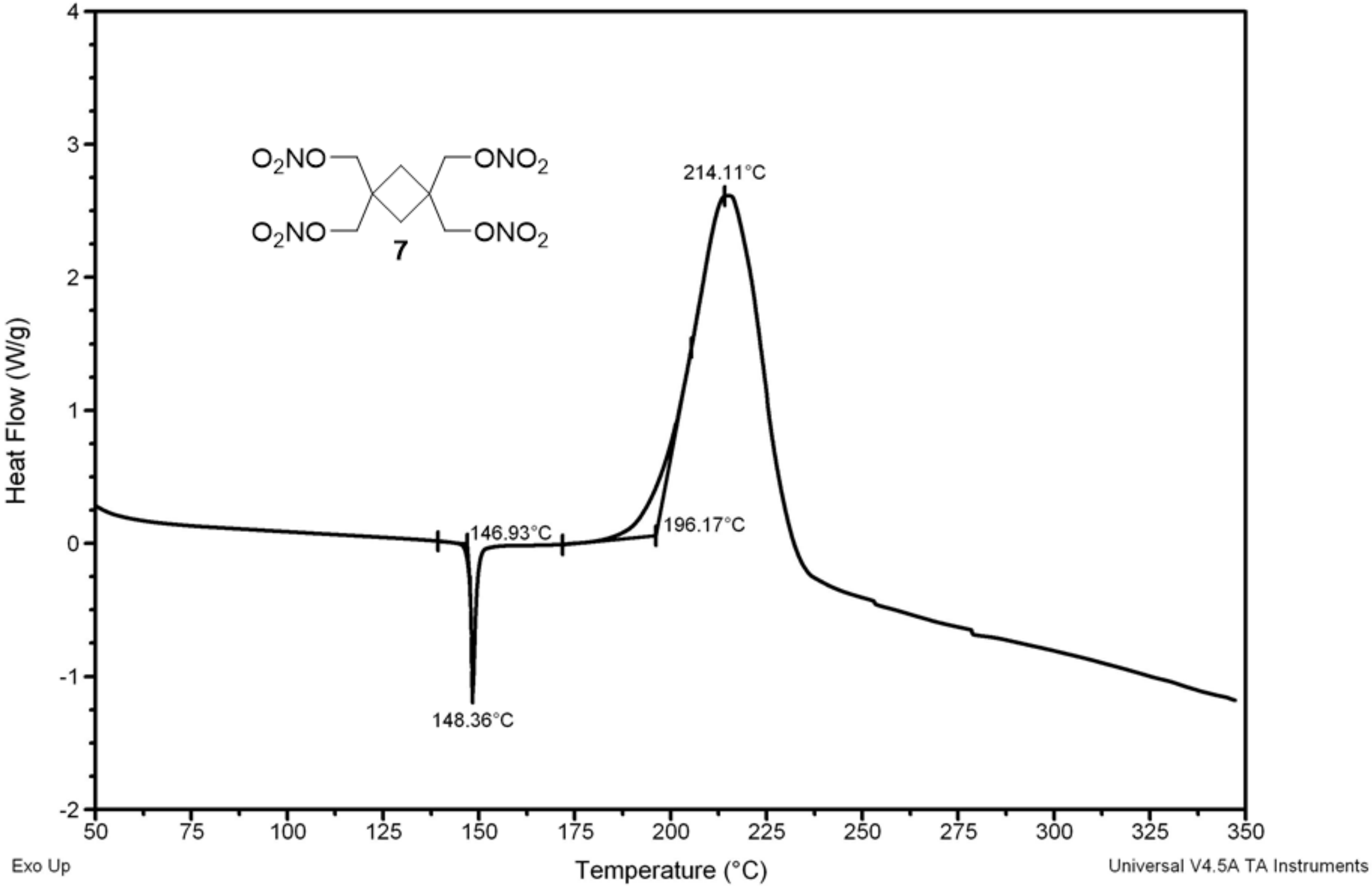


O2NO
ONO2
O2NO
ONO2
5
210.29°C
100.79°C
102.71°C
194.26°C
Heat Flow (W/g)
6
5
4
3
2
1
0
-1
-2
-3
50
75
100
125
150
175
200
225
250
275
300
325
350
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

Compound 6


1.5
1.0
0.5
0.0
-0.5
Heat Flow (W/g)
50
100
150
200
250
300
350
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments
218.94°C
192.78°C
85.90°C
86.72°C
ONO2
O2NO
O2NO
ONO2
6

Compound 7



O_2NO
ONO_2
O_2NO
ONO_2
7
214.11°C
146.93°C
196.17°C
148.36°C
Heat Flow (W/g)
4
3
2
1
0
-1
-2
50
75
100
125
150
175
200
225
250
275
300
325
350
Temperature (°C)
Exo Up
Universal V4.5A TA Instruments

References:

1. Lai, M. C.; Chang, C. W.; Ong, C. W. Cyclobutanetetracarboxylate Compound and Preparation Method Thereof. US Patent US20060089505A1, 2006
2. Suzuki, H.; Tamura, T. Cage-Shaped Cyclobutanoic Dianhydrides and Process for Production Thereof. European Patent EP1813592A1, 2005.
3. Barr, K. J.; Scott, M. E.; Thompson, C. F.; Anthony, N.; Cammarano, C. M.; Bakshi, R. K.; Mohanty, S. K.; Korapala, C. S.; Latthe, P. R.; Kambam, V. N.; Sarkar, S. K.; Thatai, J. T. Pyrrolidine derived beta 3 adrenegic receptor agonists. US Patent US9486448B2, 2016
4. Yavari, I.; Nourmohammadian, F. Stereoselective Synthesis of Tetraalkyl Cyclobutene-1,2,3,4-tetracarboxylates. Synthesis of Tetraalkyl (*Z*,*Z*)-Buta-1,3-diene-1,2,3,4-tetracarboxylates. *J. Chem. Research* **1999**, 512–513
5. Elinson, M. I.; Fedukovich, S. K.; Ugrak, B. I.; Nikishin, G. I. Electrochemical Oxidation of Tetramethyl Esters of α,α,ω,ω-Alcanetetracarboxylic Acids. *Russ. Chem. Bull.* **1992**, *41*, 1827–1833
6. Li, C.; Kawamata, Y.; Nakamura, H.; Vantourout, J. C.; Liu, Z.; Hou, Q.; Bao, D.; Starr, J. T.; Chen, J.; Yan, M.; Baran, P. S. Electrochemically Enabled, Nickel-Catalyzed Amination. *Angew. Chem. Int. Ed.* **2017**, *56*, 13088–13093
7. Pecquet, P.; Huet, F.; Legraverend, M.; Bisagni, E. Synthesis of New Carbocyclic Analogues of Oxetanocin A and Oxetanocin G. *Heterocycles* **1992**, *34*, 739–745.