Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information for

Control of Selectivity in the Generation and Reactions of Oxonium Ylides

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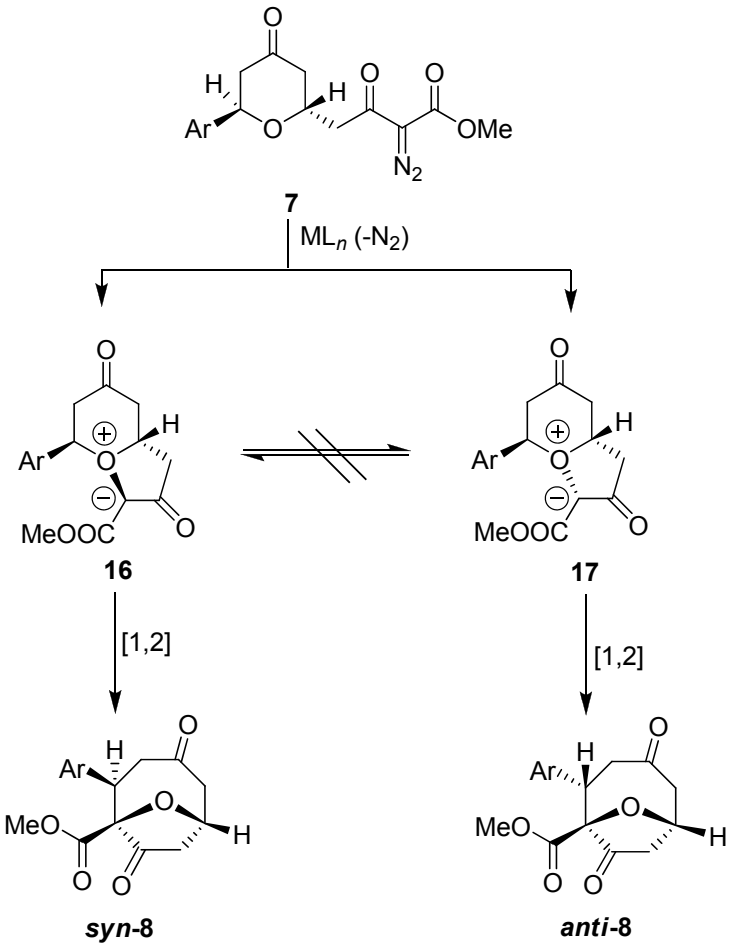
Explanation of the apparent isomerism. This may arise from two non-interconverting ylide intermediates formed from two conformational isomers (axial-equatorial and equatorial-axial for aryl and acetoacetate groups) of the metal carbene generated from **7** (Scheme 5). Accordingly, product stereochemistry (**8** and **9**) is determined by the two ylide intermediates (**16** and **17**) whose ratio is related to the ratio of conformational isomers of **7**. Consistent with related structures,[16] conformational isomers of the reactant diazo compound **7a**, whose ring is flattened from the ideal chair parameters, could not be resolved even at -95°C, but DFT calculations at the PBEPBE level with the LANL2-DZ basis set showed an energy difference of 0.7 kcal/mol favoring the conformer with the phenyl group in the equatorial position.



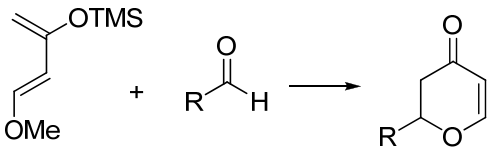
Scheme 5. Formation of non-interconverting ylide intermediates in the apparent isomerization that produces ***anti*-8** and ***syn*-8.**

General procedures and methods of analysis

General information. All reagents were obtained commercially unless otherwise noted. Reactions were performed using oven-dried or flame-dried glassware under an atmosphere of nitrogen. Air and moisture sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Dichloromethane (DCM) was passed through a solvent column prior to use. Toluene and 1,2-dichloroethane (DCE) were distilled over CaH_2 prior to use. Thin-layer chromatography (TLC) was performed on EM Science silica gel 60 F254 plates, and visualization of the developed plates was accomplished by ultraviolet light (254 nm) and/or by staining with iodine, butanolic ninhydrin, *p*-anisaldehyde, and phosphomolybdic acid (PMA) solution. Chromatographic purification of products was performed using forced-flow chromatography on silica gel (230 x 400 mesh). Compounds purified by chromatography on silica gel were typically applied to the absorbent bed using the indicated solvent conditions with a minimum amount of added dichloromethane as needed for solubility. Unless otherwise described, reactions were carried out at ambient temperature. Elevated temperatures were obtained using thermostat-controlled silicone oil baths. Low temperatures were obtained by ice bath or by mixing dry-ice with organic solvents. Zinc triflate was purchased from Aldrich and used as received. Methyl 3-(*tert*-butyldimethylsilyloxy)-2-diazo-3-butenoate was prepared by the method described by Davies.[1]

NMR spectra were measured on Bruker AV-400, Bruker DRX-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz), Bruker DRX-500 (^{1}H at 500 MHz, ^{13}C at 125 MHz), or Bruker AVIII-600 (^{1}H at 600 MHz, ^{13}C at 150 MHz). Data for ^{1}H NMR are recorded as follows relative to residual solvent peaks: (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dq = doublet of quartets, ddd= doublet of doublet of doublets, tdd triplet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, m = multiplet, comp = composite), coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported in terms of chemical shift (δ, ppm) relative to residual solvent peak. All spectra are recorded in $CDCl_3$ as solvent, unless otherwise described. Mass spectra (MS) and high resolution mass spectra (HRMS) were recorded by JEOL AccuTOF-CS (ESI positive, needle voltage 1800-2400eV, flow rate 50uL/min). IR spectra were recorded on a JASCO FT-IR-4100 instrument. Melting points were determined with a MEL-TEMP Digital melting point apparatus.

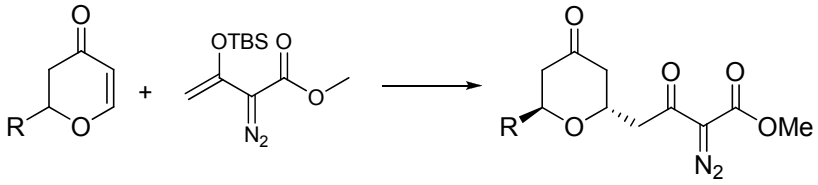
General procedures for the hetero-Diels-Alder (HDA) reaction



HDA reaction using $BF_3.Et_2O$ - Method A. To a cold solution (-78°C) of benzaldehyde (0.2 g, 1.88 mmoles) and Danishefsky's diene (0.4 mL, 2.26 mmoles) in dry DCM (19 mL) was added $BF_3.Et_2O$ (0.24 mL, 1.88 mmoles) dropwise, which produced an instant color change from colorless to yellow to dark brown. After 8 hours at – 78ºC, the reaction was quenched with $NaHCO_3$ (10 mL) followed by brine (10 mL), then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layer was dried over $MgSO_4$, filtered and evaporated under reduced pressure.

HDA reaction using $Rh_2(OAc)_4$ – Method B. Rhodium(II) acetate (5.8 mg, 0.013 mmoles) and 4-nitrobenzaldehyde (0.2g, 1.32 mmoles) were dissolved in 5 mL of DCM. The suspension was stirred for 20 minutes at RT, before adding Danishefsky's diene (0.5 mL, 2.65 mmoles). The solution was left to stir at room temperature for 24 hrs. After the reaction was complete judging by TLC analysis, TFA (1 mL) was added and the solution was stirred for a further 30 minutes. The reaction was later washed with saturated $NaHCO_3$ (10 mL) and brine then extracted into DCM (3 × 15 mL). The organic extracts were combined, dried over $MgSO_4$, filtered and evaporated to yield a yellow solid. Characterization of most of the HDA products can be found in the literature.[2]

General Procedure for the Mukaiyama-Michael reaction



To a flame-dried 25-mL round bottom flask under nitrogen was added zinc triflate (2.1 mg, 0.006 mmol), followed by 6-phenylpyranone (102 mg, 0.586 mmol) that was dissolved in dry DCM (2 mL). Methyl 3-(tert-butyldimethylsilyloxy)-2-diazo-3-butenoate (225 mg, 0.879 mmol)

was then added via syringe all at once. The orange solution was stirred at 40°C for 16 hour and then slowly cooled to room temperature. The Mukaiyama-Michael reactions were worked up using two methods, as shown below. For the synthesis of methyl 2-diazo-3-oxo-4-((2*S**,6*S**)-4-oxo-6-phenyltetrahyro-2*H*-pyran-2-yl)butanoate, method A using 4N HCl was followed.

Mukaiyama-Michael reaction work up using 4N HCl - Method A. After the reaction was complete judging by TLC analysis, the crude reaction mixture was concentrated under reduced pressure then dissolved in 10 mL of tetrahydrofuran (THF). To that was added 2.0 mL of 4N aqueous HCl solution dropwise. After 2hrs the reaction was quenched by slow addition of $NaHCO_3$ (15mL) until the reaction was neutralized. The resulting solution was extracted with DCM (3 × 15 mL) and the combined organic layer was dried over anhydrous $MgSO_4$ and then concentrated under reduced pressure.

Mukaiyama-Michael reaction work up using TBAF and AcOH - Method B. The calculation for the work-up below is based on the substrate 2-(4-methoxyphenyl)pyranone (292 mg, 1.43 mmoles). After the reaction was complete (TLC analysis), the crude reaction mixture was concentrated under reduced pressure then dissolved in 14 mL of tetrahydrofuran (THF) at 0°C. To that solution was added AcOH (0.6 mL) and TBAF (1M THF solution, 2mL, 2.1 mmoles). The resulting mixture was stirred at 0°C for 4 hrs. The reaction mixture was quenched with Et_3N, then diluted with saturated $NaHCO_3$ (15mL), and the aqueous layer was extracted with DCM (20mL x 3). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure after filtration.

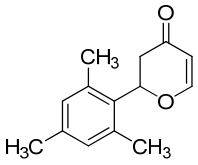
General Procedure for catalytic dinitrogen extrusion. The catalyst $Rh_2(pfb)_4$ (5 mg, 0.005 mmoles) was dissolved in anhydrous DCM (2 mL) and then transferred to a flame-dried two neck flask. Methyl 2-diazo-3-oxo-4-(4-oxo-6-phenyltetrahyro-2*H*-pyran-2-yl)butanoate (151 mg, 0.477 mmoles) was dissolved in anhydrous DCM (3 mL) and added dropwise to the reaction mixture via a syringe pump over two hours. Once the addition was complete, the reaction was left to stir at reflux (40°C) for an additional two hours. After the diazo starting material had been consumed judging by TLC analysis, the reaction was cooled to room temperature, the solvent

was evaporated, and the reaction was purified using column chromatography to yield a white powdery solid.

Characterization of all new compounds

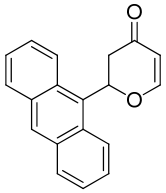
Characterization for HDA products.

2-Mesityl-2*H*-pyran-4(3H)-one



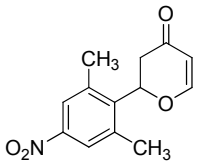
Prepared by method A. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (100% to 95% hexane): yellow solid (65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 6.0,0.6 Hz, 1H), 6.88 (s, 2H), 5.81 (dd, *J* = 16.0,3.8 Hz, 1H), 5.53 (dd, *J* = 6.0,1.2 Hz, 1H), 3.16 (dd, *J* = 17.2,16.0 Hz, 1H), 2.43 (ddd, *J* = 17.2,3.8,1.2 Hz, 1H), 2.38 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.45, 163.49, 138.26, 136.12, 130.41, 130.36, 107.12, 78.78, 40.36, 20.80, 20.56. HRMS (ESI+): expected mass 217.1223, found 217.1230. M.p. 72.0-73.0 °C.

2-(Anthracen-9-yl)-2*H*-pyran-4(3*H*)-one



Prepared by method A. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (100% to 95% hexane): orange solid (53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.36 (d, *J* = 8.8 Hz, 2H), 8.07 (dd, *J* = 8.4,0.8 Hz, 2H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.58-7.49 (comp, 4H), 6.94 (dd, *J* = 16.0,4.0 Hz, 1H), 5.74 (dd, *J* = 6.0,0.8 Hz, 1H), 3.69 (dd, *J* = 17.8, 16.0 Hz, 1H), 2.73 (ddd, *J* = 17.8,4.0,0.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.03, 163.36, 131.36, 129.65, 129.54, 129.04, 127.04, 126.43, 124.85, 123.50, 107.68, 78.11, 41.91. HRMS (ESI+): expected mass 275.1067, found 275.1075. M.p. 160.0-162.3 °C.

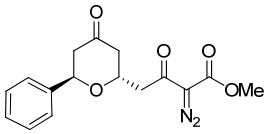
2-(2,6-Dimethyl-4-nitrophenyl)-2*H*-pyran-4(3*H*)-one



Prepared by method A. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (100% to 85% hexane); pale yellow solid (50% yield). The 2,6-dimethyl-4-nitro benzaldehyde was synthesized following literature procedures.[3] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.50 (d, *J* = 6.0 Hz, 1H), 5.87 (dd, *J* = 16.0,4.0 Hz, 1H), 5.58 (d, *J* = 6.0 Hz, 1H), 3.10 (dd, *J* = 17.5,16.0 Hz, 1H), 2.52 (s, 6H), 2.45 (ddd, *J* = 17.5,4.0,1.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.76, 162.67, 147.18, 140.07, 138.15, 124.11, 107.65, 77.95, 39.38, 20.95. HRMS (ESI+): expected mass 248.0917, found 248.0912. M.p. 120.1-122.3 °C.

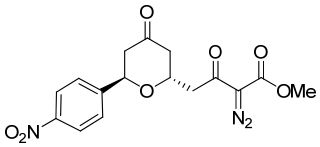
Data Characterization for Mukaiyama-Michael products

Methyl 2-diazo-3-oxo-4-((2*S,6*S**)-4-oxo-6-phenyltetrahyro-2*H*-pyran-2-yl)butanoate (7a)**



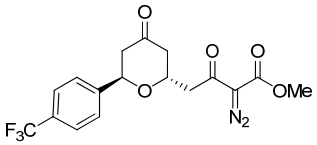
Followed method A for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 75% hexane): yellow solid (99% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (comp, 5H), 5.29 (t, *J* = 5.8 Hz, 1H), 4.60-4.53 (m, 1H), 3.79 (s, 3H), 3.31 (dd, *J* = 15.6,8.0 Hz, 1H), 3.05 (dd, *J* = 15.6,5.6 Hz, 1H), 2.87 (ddd, *J* = 14.8, 6.4, 1.2 Hz, 1H), 2.79 (ddd, *J* = 14.8, 5.2, 1.2 Hz, 1H), 2.65 (ddd, *J* = 14.8, 4.8,1.2 Hz, 1H), 2.45 (ddd, *J* = 14.8,7.2,1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.24, 188.90, 161.52, 139.61, 128.60, 128.14, 126.82, 74.05, 68.65, 52.26, 46.46, 46.06, 44.54. IR (cm^{-1}): 2959, 2925, 2854, 2143, 1708, 1664, 1646. HRMS (ESI+): expected mass 317.1132, found 317.1128. M.p. 71.0-73.1 °C.

Methyl 2-diazo-4-((2*S,6*S**)-6-(4-nitrophenyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-3-oxobutanoate (7b)**



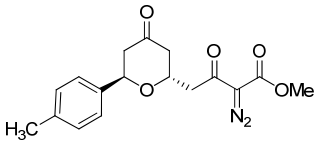
Followed method A for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 60% hexane): yellow solid (80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25-8.22 (comp, 2H), 7.58-7.55 (comp, 2H), 5.35 (dd, *J* = 6.6,5.4 Hz, 1H), 4.70-4.63 (m, 1H), 3.82 (s, 3H), 3.39 (dd, *J* = 16.0,8.2 Hz, 1H), 3.04 (dd, *J* = 16.0,5.2 Hz, 1H), 2.87 – 2.76 (comp, 2H), 2.69 (ddd, *J* = 14.8,5.2,1.2 Hz, 1H), 2.50 (ddd, *J* = 14.8,6.6,1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.90, 188.64, 161.54, 147.59, 146.91, 127.47, 123.86, 73.14, 69.34, 52.35, 46.25, 46.15, 44.17. IR (cm^{-1}): 2959, 2921, 2849, 2123, 1717, 1641, 1598, 1512, 1335, 1302. HRMS (ESI+): expected mass 362.0983, found 362.0984. M.p. 103.3-104.7 °C.

Methyl 2-diazo-3-oxo-4-((2*S,6*S**)-4-oxo-6-(4-(trifluoromethyl)phenyl)tetrahyro-2*H*-pyran-2-yl)butanoate (7c)**



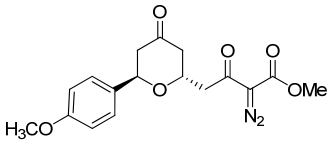
Followed method A for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 70% hexane): yellow solid (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 5.30 (t, *J* = 5.6 Hz, 1H), 4.61-4.54 (m, 1H), 3.77 (s, 3H), 3.32 (dd, *J* = 15.6,8.1 Hz, 1H), 3.02 (dd, *J* = 15.6,5.2 Hz, 1H), 2.80 (d, *J* = 5.6 Hz, 2H), 2.64 (dd, *J* = 14.8,4.6 Hz, 1H), 2.45 (dd, *J* = 14.8,7.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.32, 188.67, 161.46, 143.71, 130.20 (q, *J* = 32.6 Hz), 126.97, 125.50 (q, *J* = 3.7 Hz), 123.90 (q, *J* = 270.5 Hz), 73.37, 69.04, 52.20, 46.21, 46.04, 44.33. HRMS (ESI+): expected mass 385.1011 , found 385.1005. IR (cm^{-1}): 2964, 2921, 2854, 2128, 1717, 1641, 1622, 1316. HRMS (ESI+): expected mass 385.1011, found 385.1005. M.p. 64.5-65.5 °C.

Methyl 2-diazo-3-oxo-4-((2*S,6*S**)-4-oxo-6-*p*-tolyltetrahydro-2*H*-pyran-2-yl)butanoate (7d)**



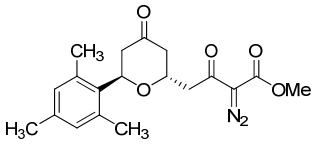
Followed method B for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 70% hexane): yellow oil (97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24-7.22 (comp, 2H), 7.17-7.15 (comp, 2H), 5.26 (t, *J* = 6.0 Hz, 1H), 4.55-4.48 (m, 1H), 3.79 (s, 3H), 3.29 (dd, *J* = 15.6,8.0 Hz, 1H), 3.03 (dd, *J* = 15.6,5.6 Hz, 1H), 2.86 (ddd, *J* = 14.8, 6.0, 1.4 Hz, 1H), 2.77 (ddd, *J* = 14.8, 5.6, 1.2 Hz, 1H), 2.62 (ddd, *J* = 14.8,7.6,1.2 Hz, 1H), 2.43 (ddd, *J* = 14.8,7.6,1.2 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.38, 188.88, 161.52, 137.88, 136.49, 129.21, 126.84, 73.96, 68.35, 52.22, 46.51, 45.89, 44.61, 21.07. IR (cm^{-1}): 2906, 2959, 2128, 2128, 1713, 1646, 1512. HRMS (ESI+): expected mass 331.1288, found 331.1279.

Methyl 2-diazo-4-((2*S,6*S**)-6-(4-methoxyphenyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-3-oxobutanoate (7e)**



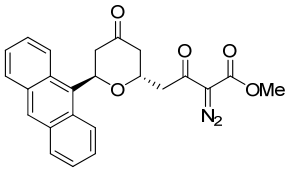
Followed method B for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 75% hexane); yellow oil (92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27-7.24 (comp, 2H), 6.89-6.85 (comp, 2H), 5.25 (t, *J* = 5.6 Hz, 1H), 4.50-4.44 (m, 1H), 3.78 (s, 6H), 3.27 (dd, *J* = 15.6,8.0 Hz, 1H), 3.02 (dd, *J* = 15.6,5.2 Hz, 1H), 2.85 (ddd, *J* = 14.8, 6.0, 1.2 Hz, 1H), 2.76 (ddd, *J* = 14.8, 5.2, 1.2 Hz, 1H), 2.60 (ddd, *J* = 14.8,4.4,1.2 Hz, 1H), 2.41 (ddd, *J* = 14.8,8.0,1.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.40, 188.87, 161.48, 159.33, 131.51, 128.27, 113.84, 73.75, 68.13, 55.20, 52.20, 46.55, 45.79, 44.67. IR (cm^{-1}): 3055, 2959, 2835, 2138, 1708, 1646, 1607, 1507, 1431. HRMS (ESI+): expected mass 347.1238, found 347.1242.

Methyl 2-diazo-4-((2*S,6*S**)-6-mesityl-4-oxotetrahydro-2*H*-pyran-2-yl)-3-oxobutanoate (10)**



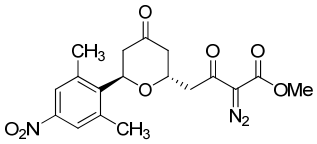
Followed method B for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 80% hexane): yellow solid (99% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.83 (s, 2H), 5.51 (dd, *J* = 12.0,3.6 Hz, 1H), 5.11 – 5.05 (m, 1H), 3.82 (s, 3H), 3.33 (dd, *J* = 15.0,8.4 Hz, 1H), 3.17 (dd, *J* = 15.0,6.0 Hz, 1H), 2.97 (dd, *J* = 15.0,12.0 Hz, 1H), 2.92 (dd, *J* = 15.0,6.6 Hz, 1H), 2.50 (ddd, *J* = 15.0,3.0,2.0 Hz, 1H), 2.46 – 2.39 (comp, 7H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.74, 188.77, 161.55, 137.37, 136.15, 132.67, 130.27, 70.64, 70.33, 52.25, 45.64, 45.48, 42.81, 20.73, 20.54. IR (cm^{-1}): 2973, 2359, 2339, 2137, 1713, 1652, 1612. HRMS (ESI+): expected mass 359.1601, found 359.1609. M.p. 83.7-86.5 °C.

Methyl 2-diazo-4-((2*S,6*S**)-6-(anthracen-9-yl)-4-oxotetrahydro-2*H*-pyran-2-yl)-3-oxobutanoate (12)**



Followed method B for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 80% hexane): white solid (90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 2H), 8.46 (s, 1H), 8.03-8.01 (comp, 2H), 7.56-7.52 (comp, 2H), 7.49-7.45 (comp, 2H), 6.68 (dd, *J* = 12.0,3.2 Hz, 1H), 5.40-5.34 (m, 1H), 3.80 (s, 3H), 3.65 (dd, *J* = 15.2,8.8 Hz, 1H), 3.48 (dd, *J* = 15.2, 12.0 Hz, 1H), 3.30 (dd, *J* = 15.2,5.6 Hz, 1H), 3.26 (dd, *J* = 15.2,7.2 Hz, 1H), 2.71-2.67 (comp, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.14, 188.76, 161.62, 131.69, 129.94, 129.50, 129.22, 129.08, 126.16, 124.85, 119.57, 71.70, 70.14, 52.27, 47.49, 46.00, 42.51. IR (cm^{-1}): 2361, 2149, 1714, 1694, 1633. HRMS (ESI+): expected mass 417.1445, found 417.1439. M.p. 157.5-158.5 °C.

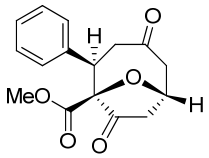
Methyl 2-diazo-4-((2*R,6*R**)-6-(2,6-dimethyl-4-nitrophenyl)-4-oxotetrahydro-2*H*-pyran-2-yl)-3-oxobutanoate (14)**



Followed method B for the work-up. Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 80% hexane): yellow solid (95% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (s, 2H), 5.61 (dd, *J* = 12.0,3.0 Hz, 1H), 5.12-5.08 (m, 1H), 3.82 (s, 3H), 3.31 (dd, *J* = 15.0, 9.0 Hz, 1H), 3.19 (dd, *J* = 15.0,5.5 Hz, 1H), 2.94 (dd, *J* = 15.0,6.5 Hz, 1H), 2.90 (dd, *J* = 15.0, 12.0 Hz, 1H), 2.57 (s, 6H), 2.55-2.52 (m, 1H), 2.45-2.41 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.04, 188.58, 161.57, 146.71, 142.52, 138.26, 124.03,70.96, 69.98, 52.33, 45.53, 44.40, 42.74, 20.96. IR (cm^{-1}): 2964, 2144, 1711, 1675, 1618, 1421, 1360, 1220. HRMS (ESI+): expected mass 390.1296, found 390.1301. M.p. 107.5-109.0 °C.

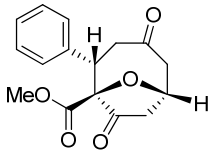
Data Characterization for Dinitrogen Extrusion Products

(1*S,2*R**,6*R**)-Methyl 4,8-dioxo-2-phenyl-9-oxabicyclo[4.2.1]nonane-1-carboxylate (*syn*-8a)**



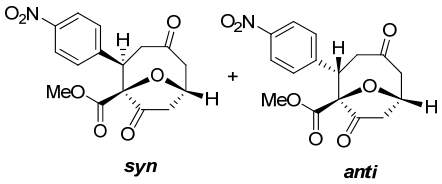
Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 65% hexane): white solid (77% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.27 (comp, 4H), 7.24-7.20 (m, 1H), 5.25-5.21 (m, 1H), 3.54 (dd, *J* = 9.6,6.4 Hz, 1H), 3.38 (dd, *J* = 13.0,6.4 Hz, 1H), 3.31 (s, 3H), 3.01-2.94 (comp, 2H), 2.69 (ddd, *J* = 11.6,6.4,1.6 Hz, 1H), 2.53-2.47 (comp, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.02, 206.63, 165.60, 140.09, 128.61, 128.01, 127.41, 89.87, 70.03, 52.65, 52.55, 48.80, 45.54, 40.75. IR (cm^{-1}): 1769, 1732, 1693, 1268, 1245, 2925. HRMS (ESI+): expected mass 289.1071, found 289.1069. M.p. 165.0-166.5 °C.

(1*S,2*S**,6*R**)-Methyl 4,8-dioxo-2-phenyl-9-oxabicyclo[4.2.1]nonane-1-carboxylate (*anti*-8a)**



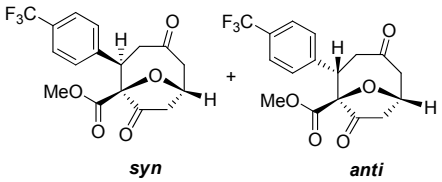
Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 65% hexane): white solid (77% combined yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.27 (comp, 3H), 7.21-7.19 (comp, 2H), 4.99 – 4.95 (m, 1H), 3.72 (dd, *J* = 12.0,4.0 Hz, 1H), 3.52 (s, 3H), 3.31 (dd, *J* = 16.0,6.6 Hz, 1H), 3.16 (dd, *J* = 18.8, 10.0 Hz, 1H), 3.03-2.96 (m, 1H), 2.87 (dd, *J* = 14.4, 4.0 Hz, 1H), 2.74-2.65 (comp, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.21, 206.07, 166.01, 136.61, 128.71, 128.31, 127.99, 86.62, 69.53, 52.66, 51.75, 48.01, 47.49, 43.99. IR (cm^{-1}): 1775, 1727, 1704, 1292, 1235, 2916, 2357, 1064, 1045. HRMS (ESI+): expected mass 289.1071, found 289.1065. M.p. 129.5-131.5 °C.

Methyl 2-(4-nitrophenyl)-4,8-dioxo-9-oxabicyclo[4.2.1]nonane-1-carboxylate (8b)



Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 60% hexane): yellow solid (94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.13 (comp, 4H), 7.55-7.46 (comp, 4H), 5.30-5.26 (m, 1H), 5.06 (ddt, *J* = 9.6,6.8,1.6 Hz, 1H), 3.96 (dd, *J* = 9.6,5.4 Hz, 1H), 3.70 (dd, *J* = 9.2,6.4 Hz, 1H), 3.62 (s, 3H), 3.42 – 3.37 (m, 1H), 3.39 (s, 3H), 3.24-3.14 (comp, 2H), 3.04 (ddd, *J* = 18.0,9.2,0.8 Hz, 1H), 2.99-2.86 (comp, 3H), 2.74-2.68 (comp, 3H), 2.58-2.52 (comp, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.50 and 206.44, 205.39 and 205.27, 166.11 and 165.34, 147.74 and 147.32, 147.15 and 144.39, 130.15 and 128.97, 123.90 and 123.25, 89.26 and 86.19, 70.39 and 70.32, 53.04 and 53.01, 52.51 and 51.98, 48.20 and 46.59, 45.88 and 44.97, 43.62 and 40.82. IR (cm^{-1}): 2959.23, 2915.84, 2858.95, 1769.37, 1736.58, 1707.66, 1607.38, 1507.10, 1345.11. HRMS (ESI+): expected mass 334.0921, found 334.0918.

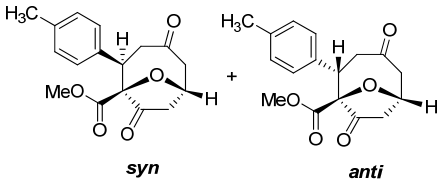
Methyl-4,8-dioxo-2-(4-(trifluoromethyl)phenyl)-9-oxabicyclo[4.2.1]nonane-1-carboxylate (8c)



syn *anti*

Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 60% hexane): yellow solid (92% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.53 (comp, 4H), 7.47-7.37 (comp, 4H), 5.26 – 5.23 (m, 1H), 5.02 (ddt, *J* = 10.0,6.5,1.6 Hz, 1H), 3.84 (dd, *J* = 10.0,5.7 Hz, 1H), 3.63 (dd, *J* = 9.3,6.5 Hz, 1H), 3.57 (s, 3H), 3.40-3.34 (m, 1H), 3.35 (s, 3H), 3.22 – 3.14 (comp, 2H), 3.01 (dd, *J* = 18.0,9.3 Hz, 1H), 2.95-2.88 (comp, 3H), 2.74-2.65 (comp, 3H), 2.56-2.50 (comp, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.48 and 206.66, 205.82 and 205.55, 166.05 and 165.47, 144.31 and 140.89, 129.71 and 129.70 (q, *J* = 32.5 Hz, 2C), 129.41 and 128.42, 125.65 and 125.16 (q, *J* = 3.7 Hz, 2C), 125.3 and 125.1 (q, *J* = 271 Hz, 2C), 89.52 and 86.31, 70.22 and 70.01, 52.88 and 52.54, 51.86 and 48.52, 47.05 and 46.78, 46.73 and 45.17, 43.87 and 40.81. IR (cm^{-1}): 2969, 2930, 1769, 1741, 1703, 1331. HRMS (ESI+): expected mass 357.0944, found 357.0951.

Methyl 4,8-dioxo-2-*p*-tolyl-9-oxabicyclo[4.2.1]nonane-1-carboxylate (8d)

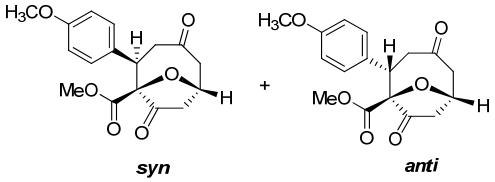


syn *anti*

Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 70% hexane): yellow solid (55% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22-7.20 (comp, 2H), 7.10-7.05 (comp, 6H), 5.24 – 5.20 (m, 1H), 5.00 – 4.96 (m, 1H), 3.86-3.78 (m, 1H), 3.70 (dd, *J* = 11.7,4.5 Hz, 1H), 3.55 (s, 3H), 3.52 (dd, *J* = 9.5,6.5 Hz, 1H), 3.40 – 3.30 (comp, 2H), 3.35 (s, 3H), 3.18 (dd, *J* = 19.0,10.0 Hz, 1H), 3.01-2.94 (comp, 3H), 2.89-2.86 (m, 1H), 2.74-2.65 (comp, 2H), 2.52-2.47 (comp, 2H), 2.31 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.20 and 207.13, 206.71 and 206.09, 166.05 and 165.70, 137.72 and 137.12, 136.94 and 133.44, 129.33 and 129.03, 128.55 and 127.97, 90.00 and 86.69, 70.01 and 69.46, 52.72 and 52.66, 52.60 and

51.73, 48.93 and 47.64, 47.60 and 45.28, 44.06 and 40.87, 21.08 and 21.03. IR (cm^{-1}): 2959, 2930, 1765, 1746, 1708. HRMS (ESI+): expected mass 303.1227, found 303.1231.

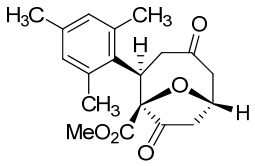
Methyl 2-(4-methoxyhenyl)-4,8-dioxo-9-oxabicyclo[4.2.1]nonane-1-carboxylate (8e)



syn *anti*

Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 60% hexane): yellow solid (22% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (comp, 4H), 7.12-7.11 (m, 1H), 6.84-6.82 (comp, 3H), 5.23-5.20 (m, 1H), 4.99-4.96 (m, 1H), 3.89–3.79 (m, 1H), 3.78 (s, 3H), 3.77 (s, 3H), 3.71-3.67 (m, 1H), 3.56 (s,3H), 3.54-3.50 (m, 1H), 3.37 (s, 3H), 3.39 – 3.30 (comp, 2H), 3.18 (dd, *J* = 19.0,10.0 Hz, 1H), 3.01-2.93 (comp, 3H), 2.87 (dd, *J* = 14.5,4.0 Hz, 1H), 2.73-2.63 (comp, 2H), 2.52-2.48 (comp, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.37 and 207.16, 206.73 and 206.13, 165.72 and 165.68, 159.17 and 158.83, 131.83 and 129.85, 129.28 and 128.46, 113.99 and 113.66, 90.05 and 86.68, 69.98 and 69.44, 55.18 and 55.15, 52.76 and 52.70, 52.57 and 51.72, 48.93 and 47.74, 47.25 and 44.95, 44.07 and 40.94. IR (cm^{-1}): 2954.41, 2920.66, 2834.85, 1769.37, 1741.41, 1707.66, 1607.38, 1507.10, 1254.47. HRMS (ESI+): expected mass 319.1176, found 319.1184.

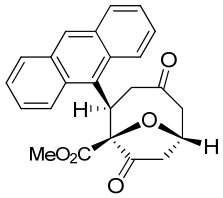
(1*S,2*R**,6*R**)-Methyl 2-mesityl-4,8-dioxo-9-oxabicyclo[4.2.1]nonane-1-carboxylate (*syn*-11)**



Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (100% to 70% hexane): pale yellow oil (42% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, *J* = 12.0 Hz, 2H), 5.24 – 5.21 (m, 1H), 3.92 (dd, *J* = 12.0,6.0 Hz, 1H), 3.41 (dd, *J* = 12.0,6.0 Hz, 1H), 3.39-3.34 (m, 1H), 3.20 (s, 3H), 2.90 (ddd, *J* = 17.5,9.0,0.5 Hz, 1H), 2.53 (s, 3H), 2.44 (s, 3H), 2.34-2.29 (comp, 3H), 2.21 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.71, 207.45, 165.69, 138.35, 136.54, 136.34, 133.01, 131.24, 129.20, 89.52, 70.23, 52.62, 52.27, 44.32, 41.67, 39.92, 21.34,

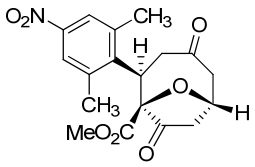
20.61, 20.52. IR (cm^{-1}): 2967.96, 2921.85, 1768.57, 1743.99, 1700.67, 1609.83, 1433.53, 1264.48. HRMS (ESI+): expected mass 331.1540, found 331.1549.

(1*S,2*R**,6*R**)-Methyl 2-(anthracen-9-yl)-4,8-dioxo-9-oxabicyclo[4.2.1]nonane-1-carboxylate (*syn*-13)**



Purified by preparative thin layer chromatography (gradient elution: hexane/ethyl acetate (70% hexane): yellow solid (45% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.04 (d, *J* = 9.0 Hz, 1H), 8.58 (d, *J* = 9.0 Hz, 1H), 8.39 (s, 1H), 7.99 (t, *J* = 7.2 Hz, 2H), 7.64-7.58 (comp, 2H), 7.50-7.44 (comp, 2H), 5.48 – 5.45 (m, 1H), 5.11 (dd, *J* = 12.0,5.7 Hz, 1H), 3.80 (t, *J* = 12.0 Hz, 1H), 3.61 (dd, *J* = 12.0,6.5 Hz, 1H), 3.07 (dd, *J* = 17.5,9.0 Hz, 1H), 2.70 (s, 3H), 2.60 (comp, 2H), 2.49 (ddd, *J* = 11.0,5.5,1.5 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.74, 207.62, 165.31, 131.68, 131.58, 131.36, 130.98, 129.49, 129.23, 129.08, 128.42, 126.92, 125.87, 125.59, 124.92, 124.91, 123.68, 89.43, 70.74, 52.67, 52.09, 46.23, 41.44, 40.17. IR (cm^{-1}): 2953, 2926, 2853, 1772, 1726, 1699, 1597. HRMS (ESI+): expected mass 389.1384, found 389.1391. M.p. 159.0-161.5 °C.

(1*S,2*R**,6*R**)-Methyl 2-(2,6-dimethyl-4-nitrophenyl)-4,8-dioxo-9-oxabicyclo[4.2.1]nonane-1-carboxylate (*syn*-15)**

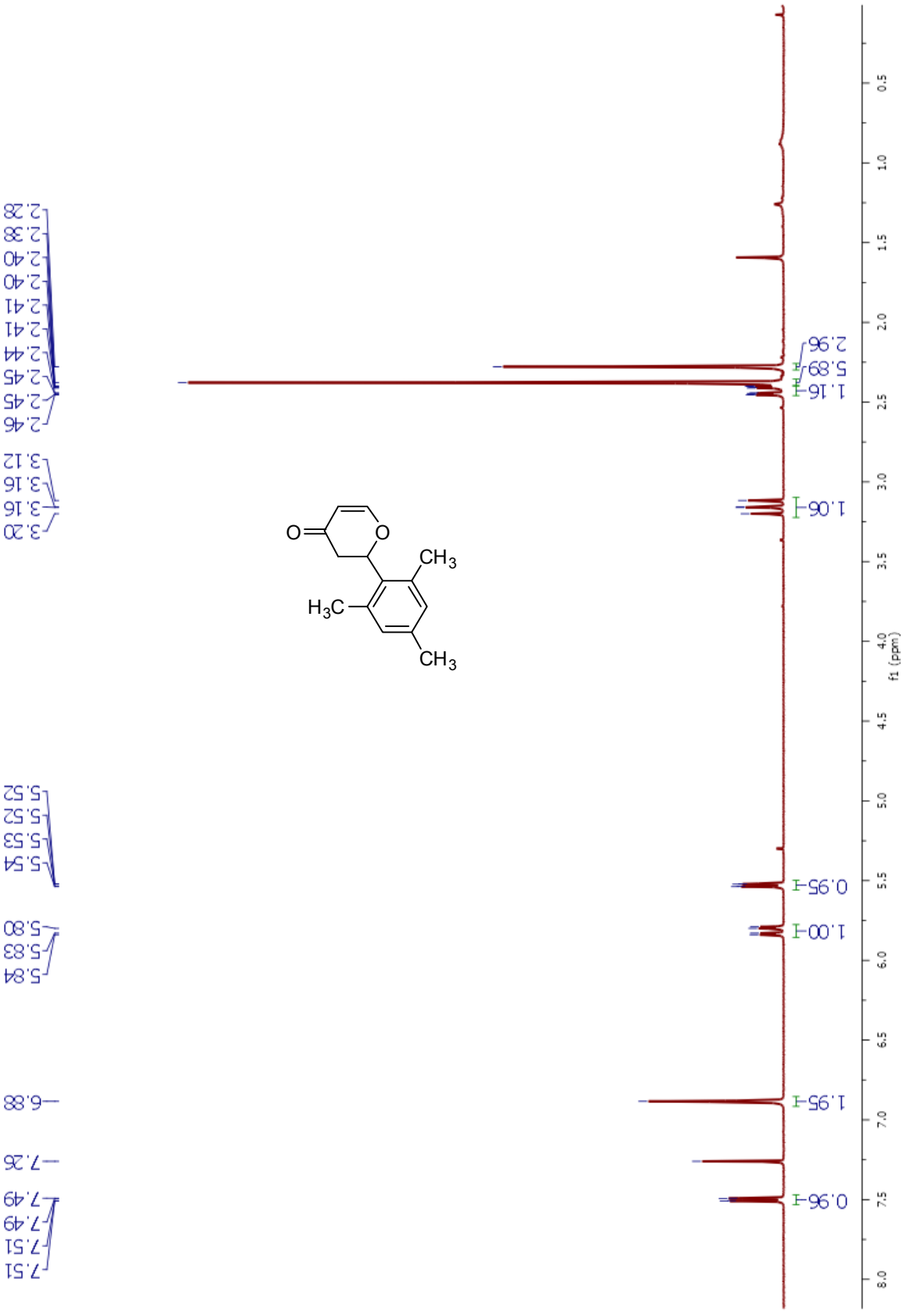


Purified by chromatography on silica gel (gradient elution: hexane/ethyl acetate (90% to 60% hexane): pale yellow solid (77% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 10.0,2.5 Hz, 2H), 5.28 – 5.25 (m, 1H), 4.00 (dd, *J* = 12.0,5.5 Hz, 1H), 3.42 (dd, *J* = 12.0,6.5 Hz, 1H), 3.32 – 3.28 (m, 1H), 3.26 (s, 3H), 2.95 (dd, *J* = 18.0,9.0 Hz, 1H), 2.66 (s, 3H), 2.59 (s, 3H), 2.51 – 2.44 (comp, 2H), 2.28 (ddd, *J* = 11.0,5.5,1.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.78, 206.48, 165.29, 146.18, 144.04, 140.52, 138.26, 124.96, 122.64, 88.81, 70.60, 52.65, 52.58, 43.40, 41.79,

39.73, 21.74, 20.80. IR (cm^{-1}): 2923, 2852, 2358, 1747, 1702, 1519, 1346, 1260, 1225. HRMS (ESI+): expected mass 362.1234, found 362.1241. M.p. 165.0-166.1 °C.

2. NMR spectra of new compounds

Content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2.41
2.44
2.45
2.45
2.46
3.12
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3.16
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CH3
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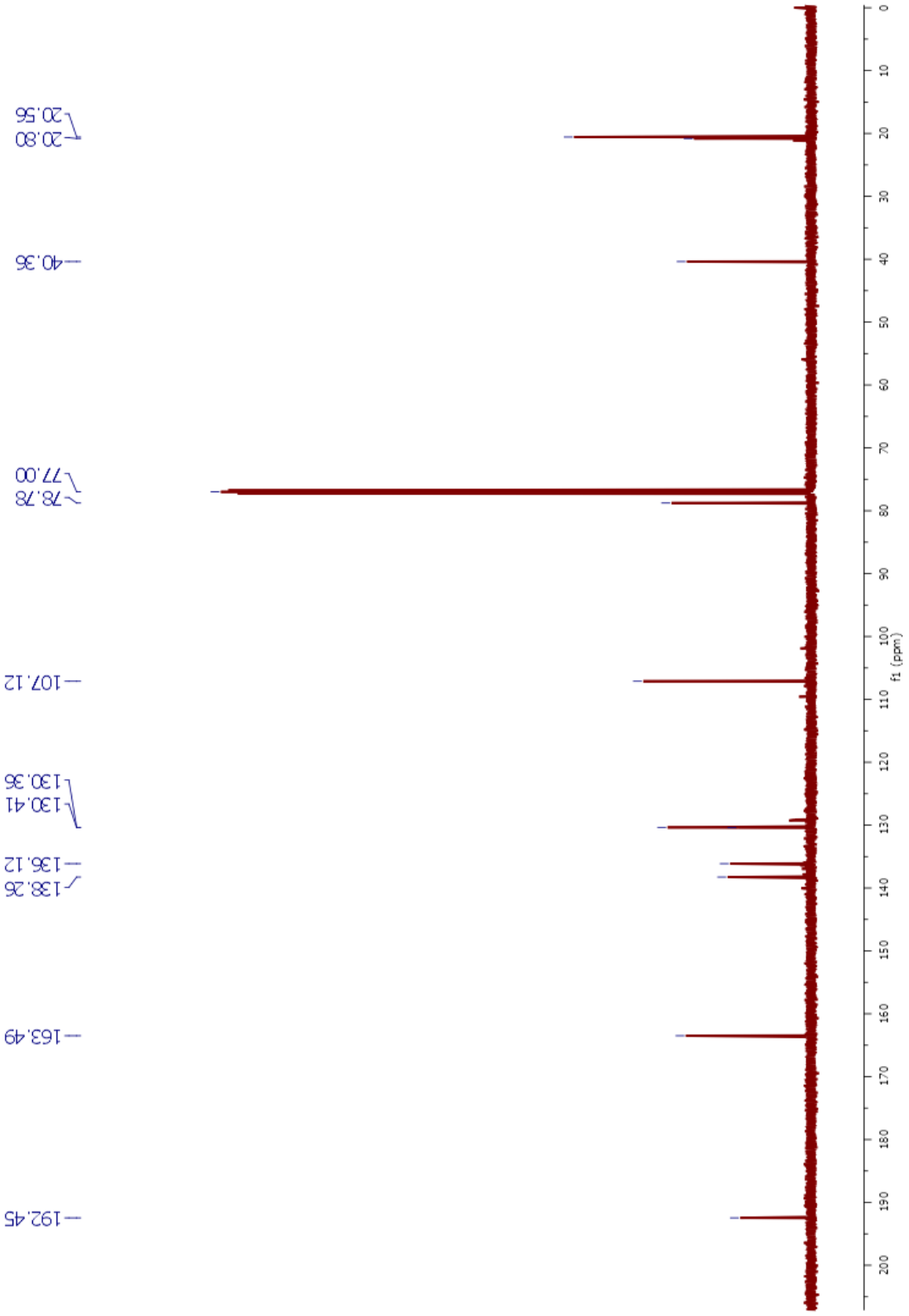
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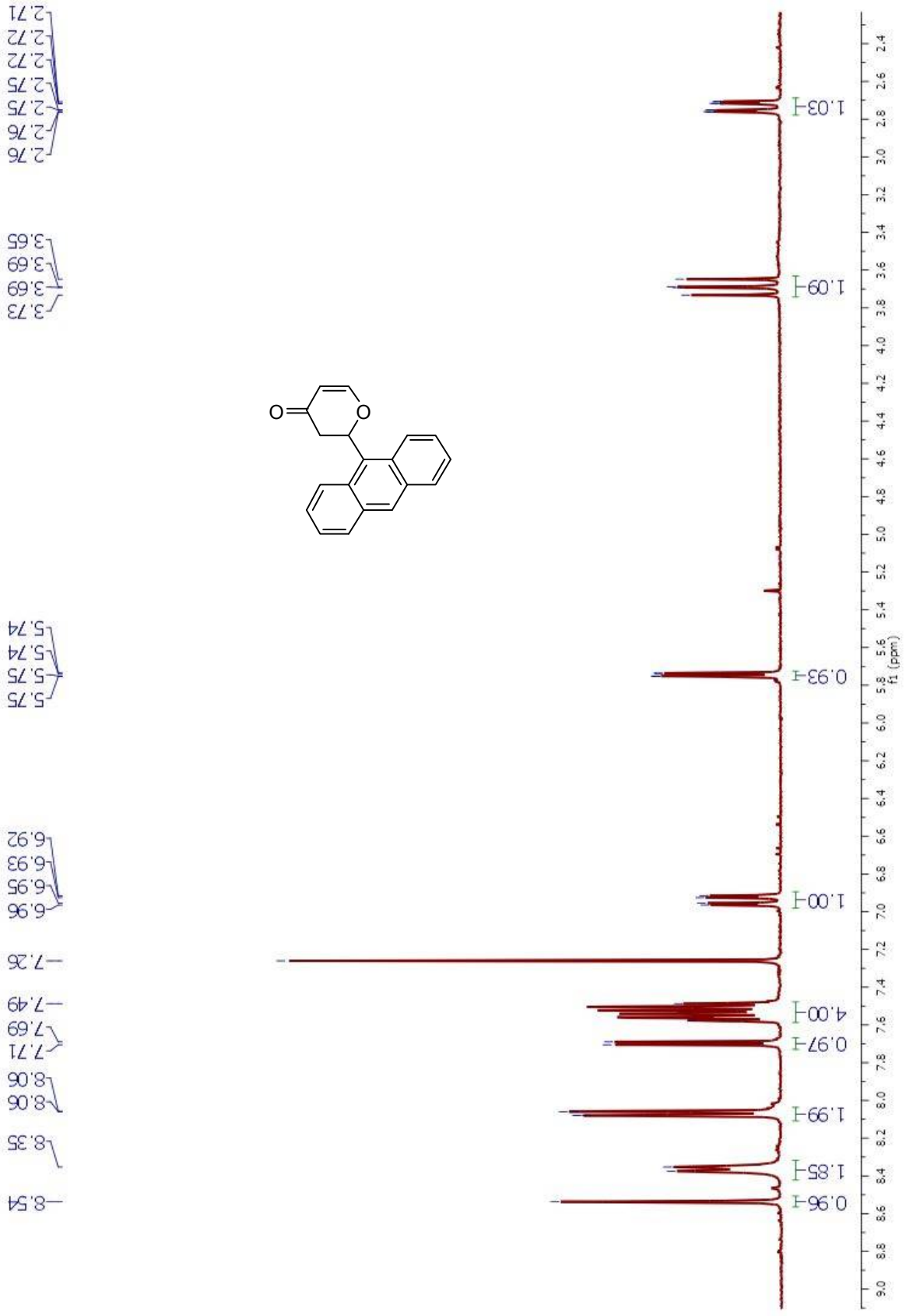
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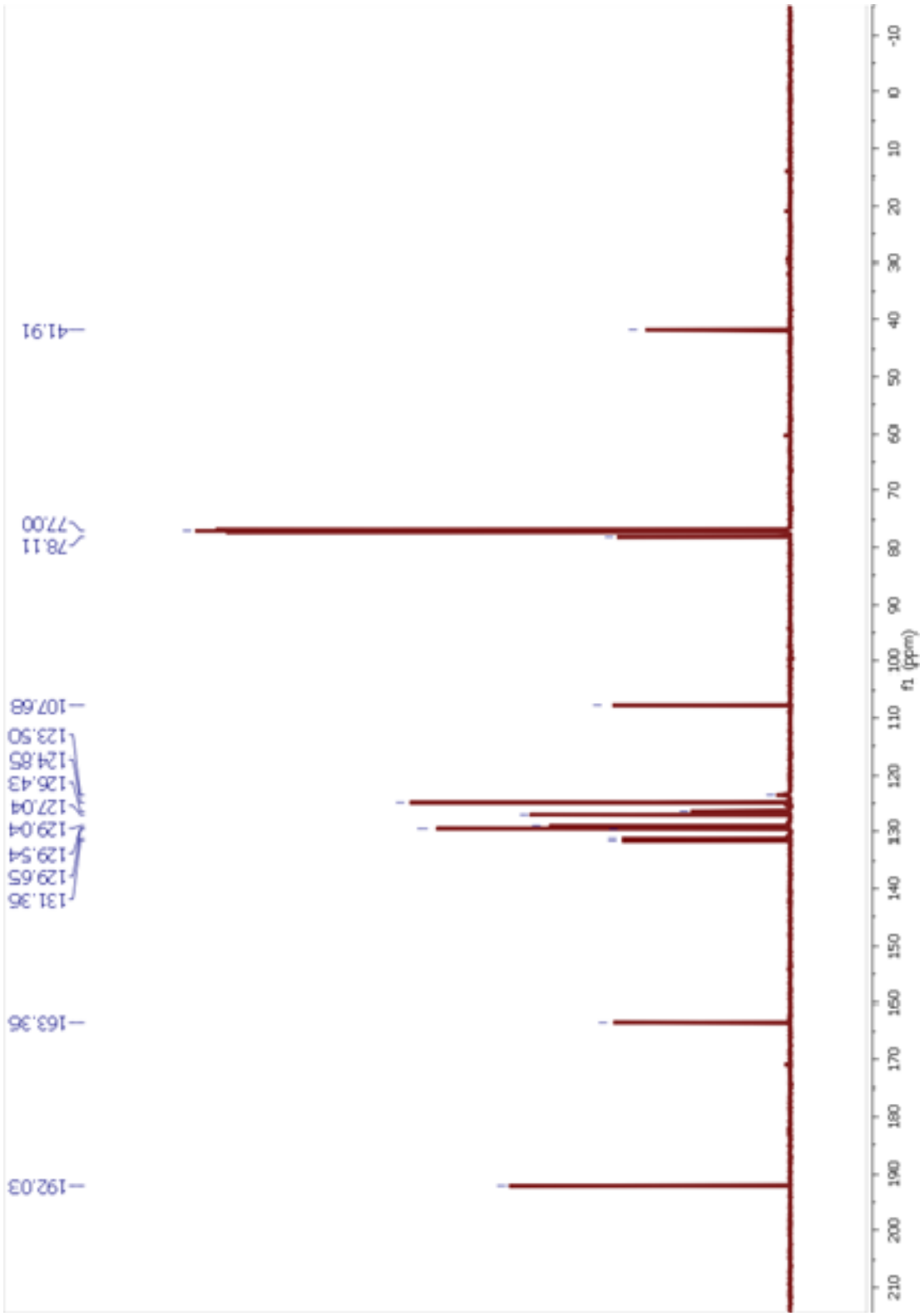
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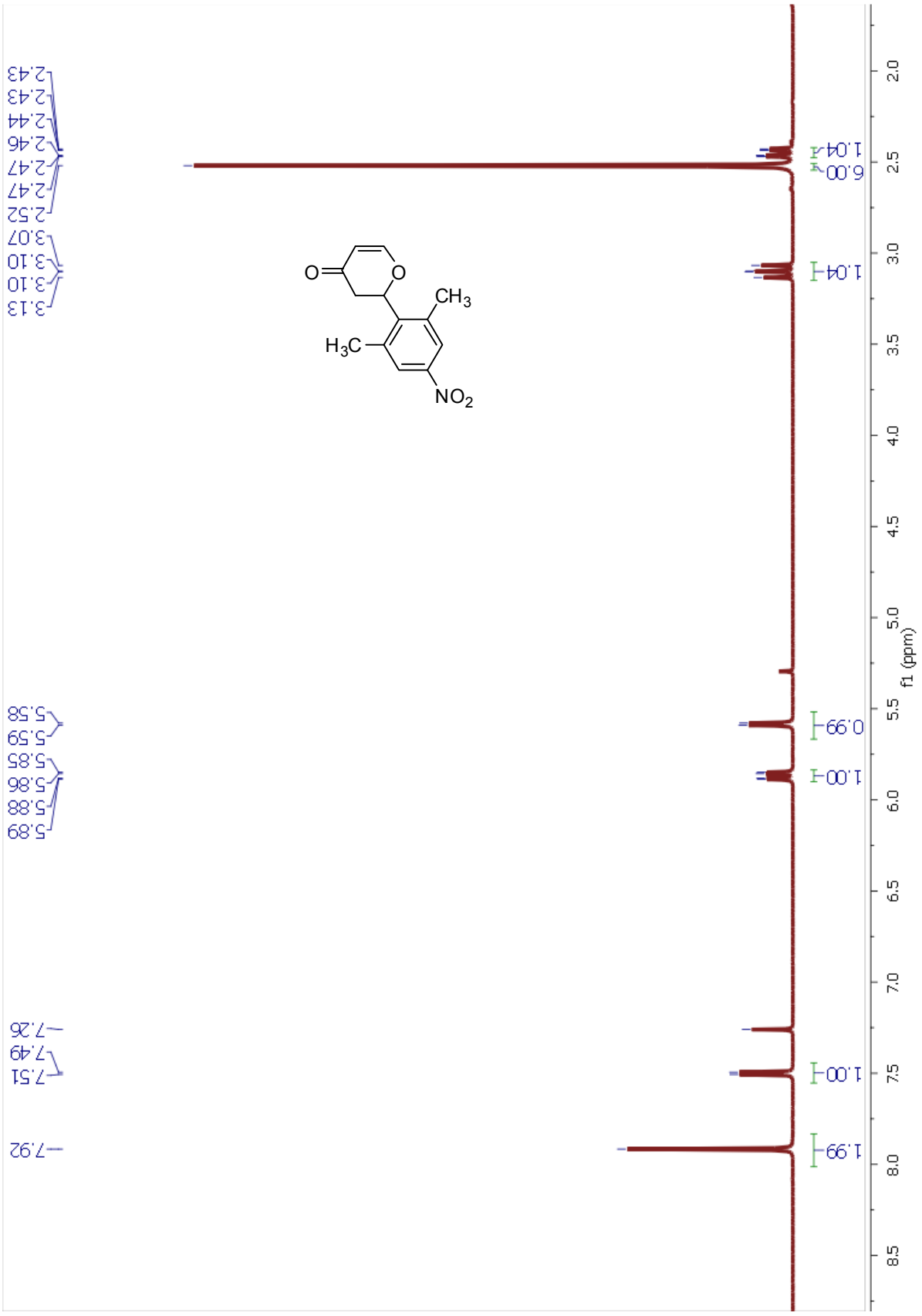
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1.00
1.00
1.99
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2.5
3.0
3.5
4.0
4.5
5.0
5.5
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6.5
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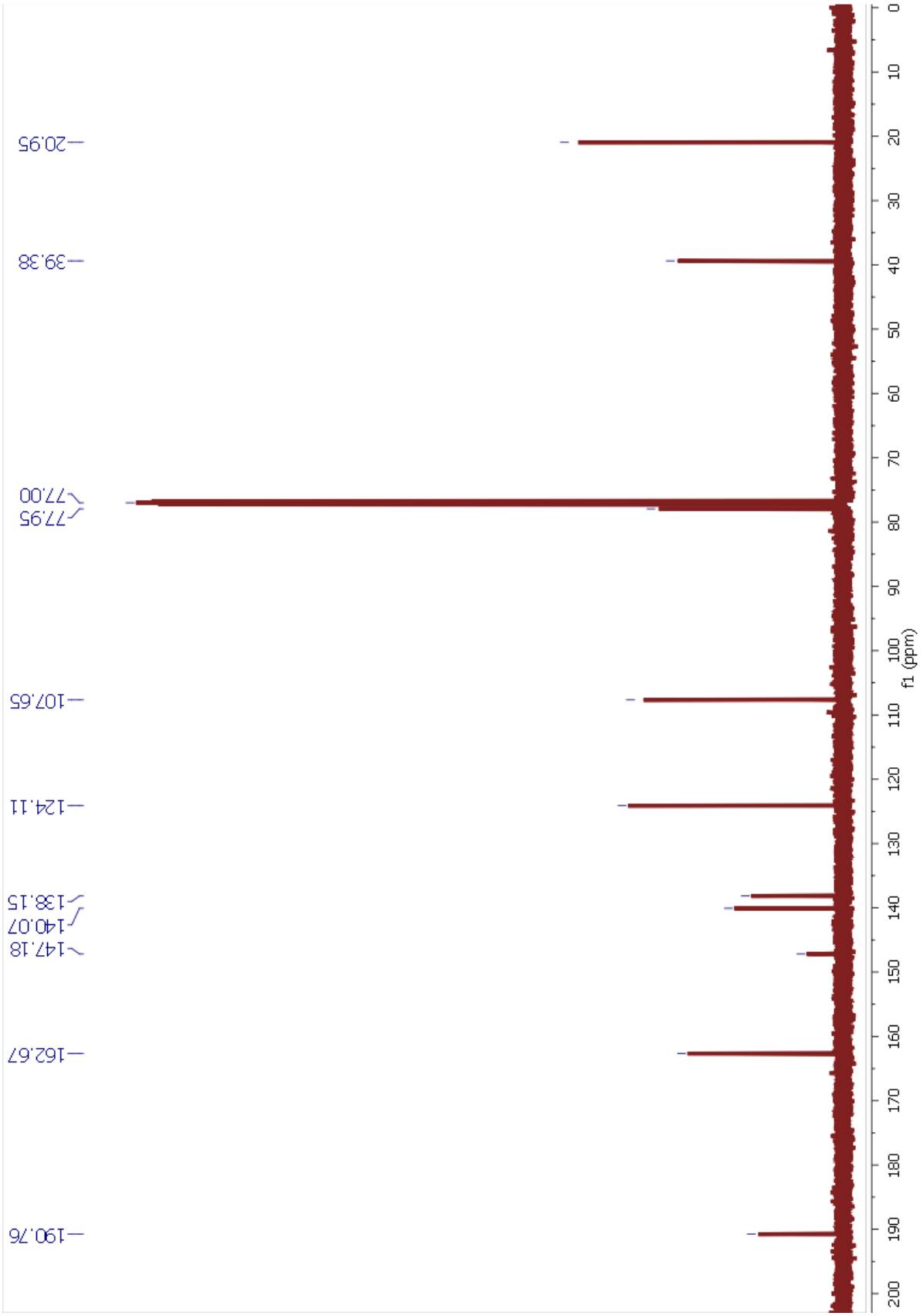
7.5
8.0
8.5
f1 (ppm)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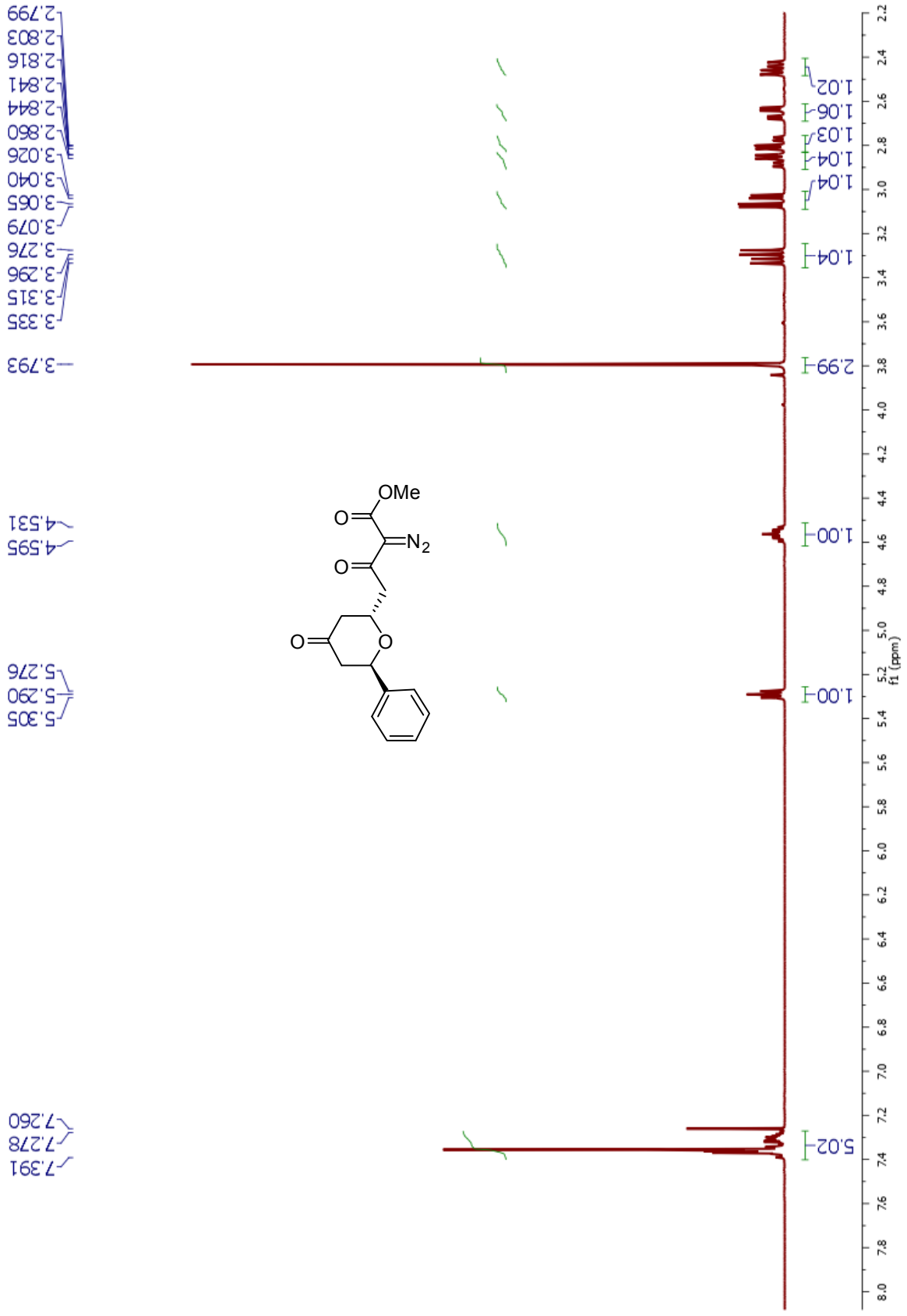
77.95
107.65
124.11
138.15
140.07
147.18
162.67
190.76
f1 (ppm)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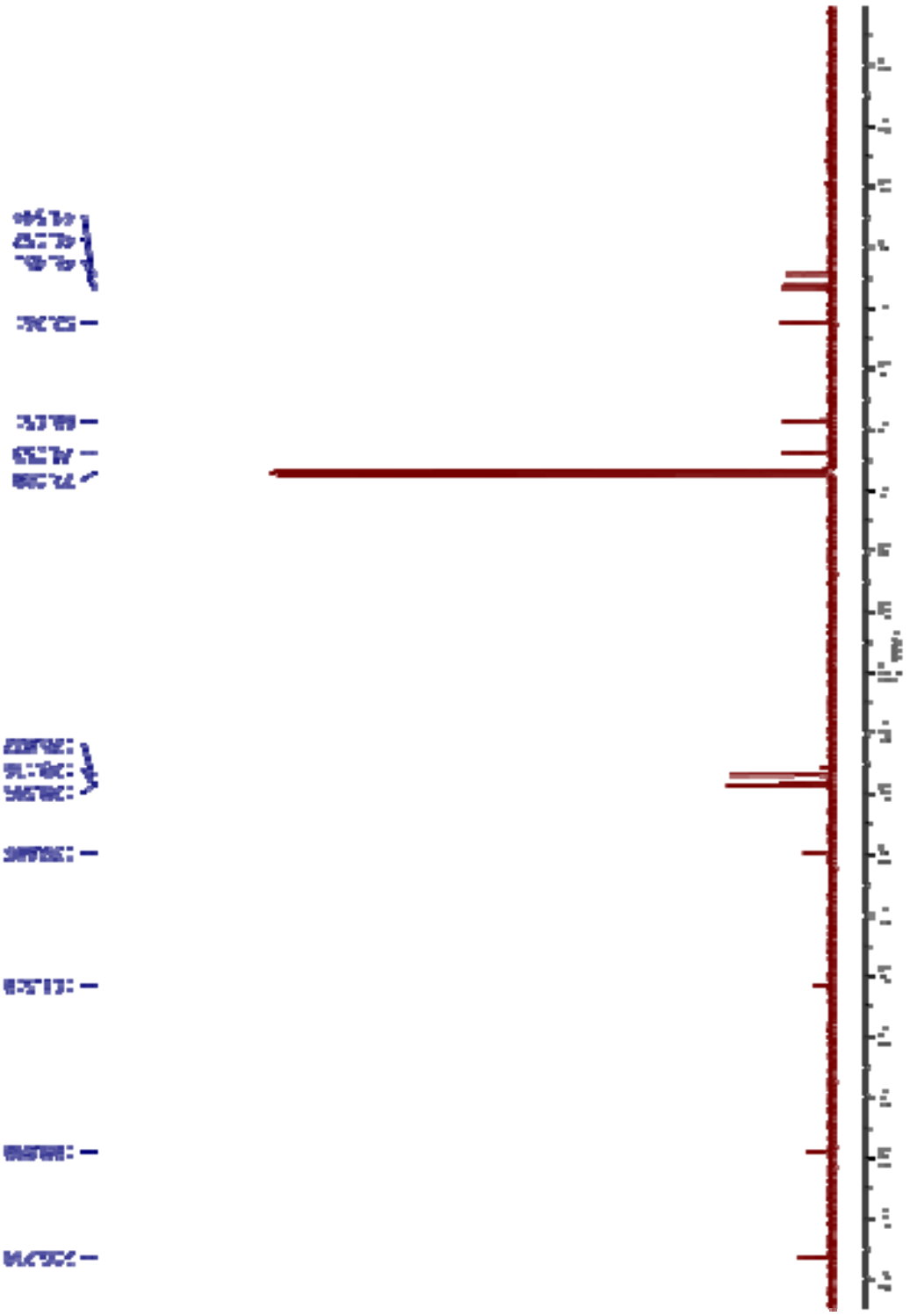
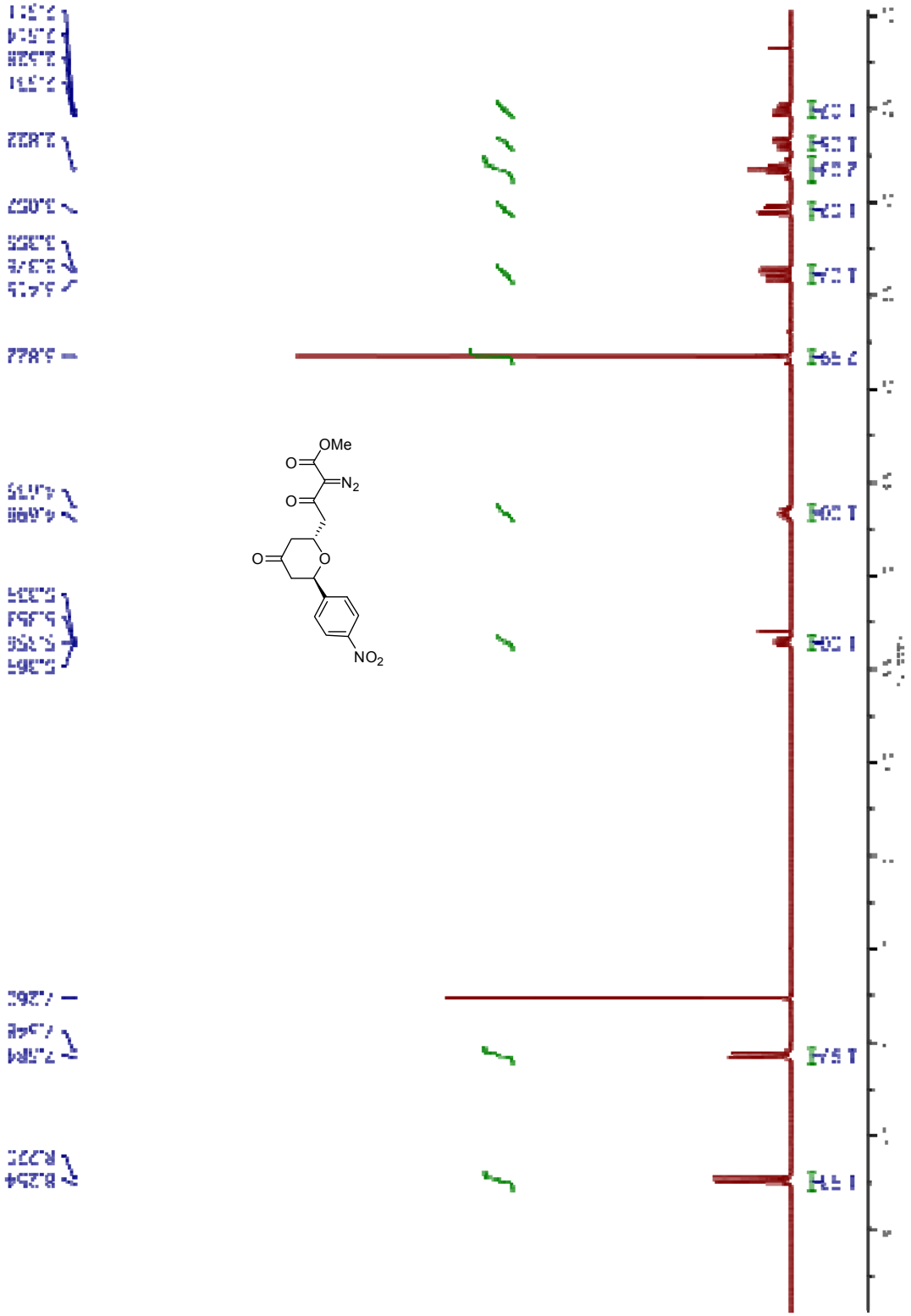
2.803
2.816
2.841
2.844
2.860
3.026
3.040
3.065
3.079
3.276
3.296
3.315
3.335
3.793
4.531
4.595
5.276
5.290
5.305
7.260
7.278
7.391
1.02
1.06
1.03
1.04
1.04
1.04
2.99
1.00
1.00
5.02
OMe
O
N2
O
O
O
f1 (ppm)

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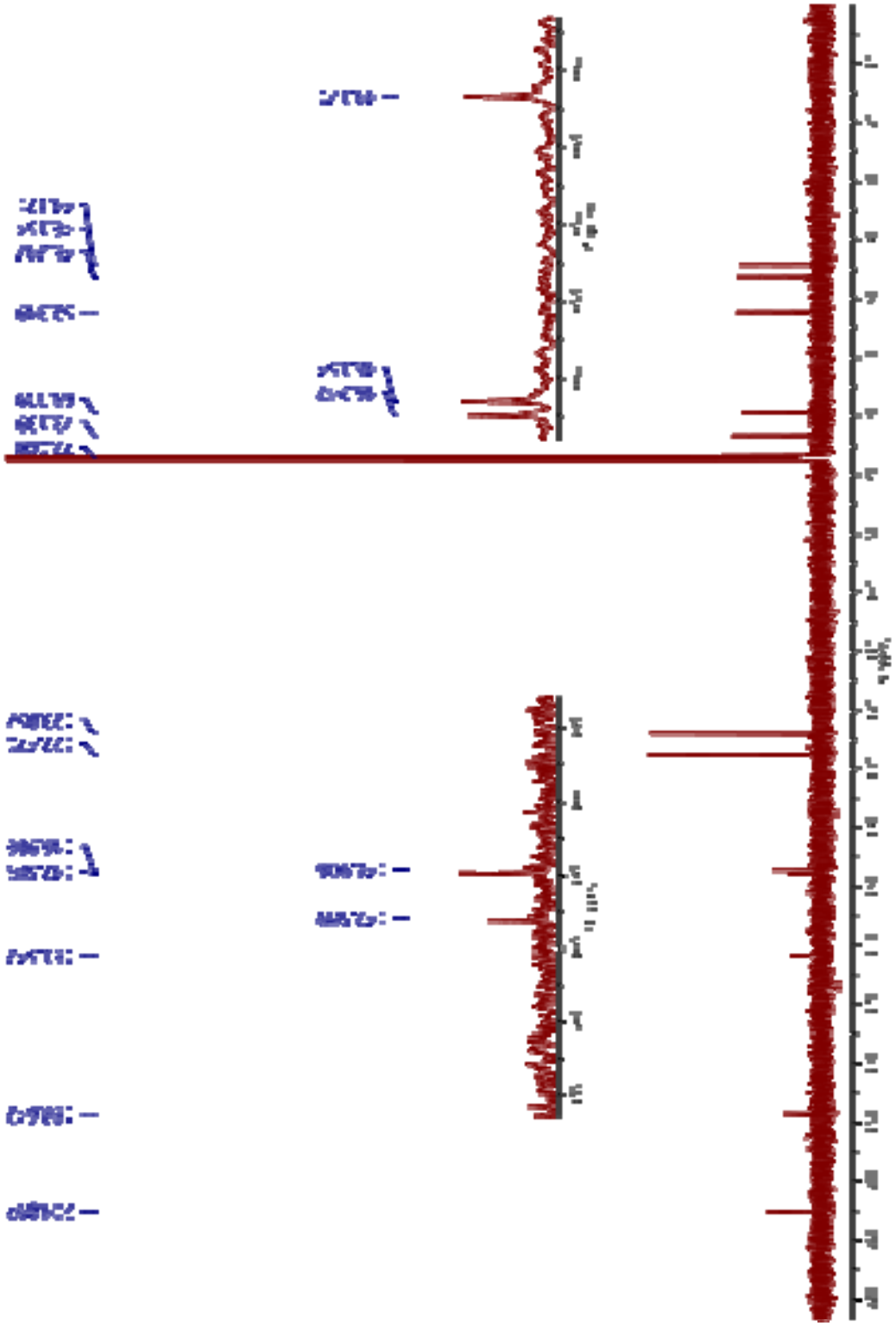
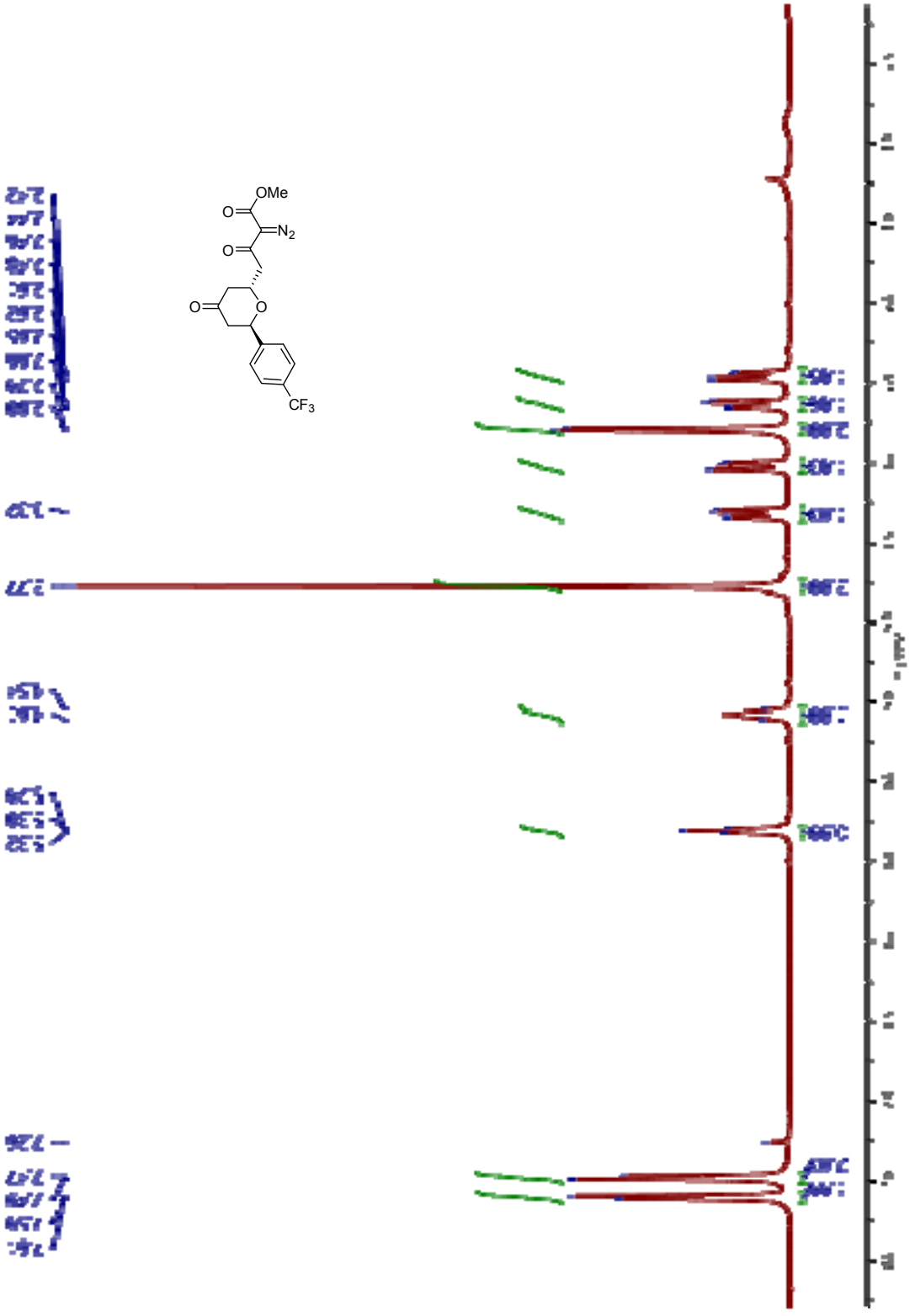
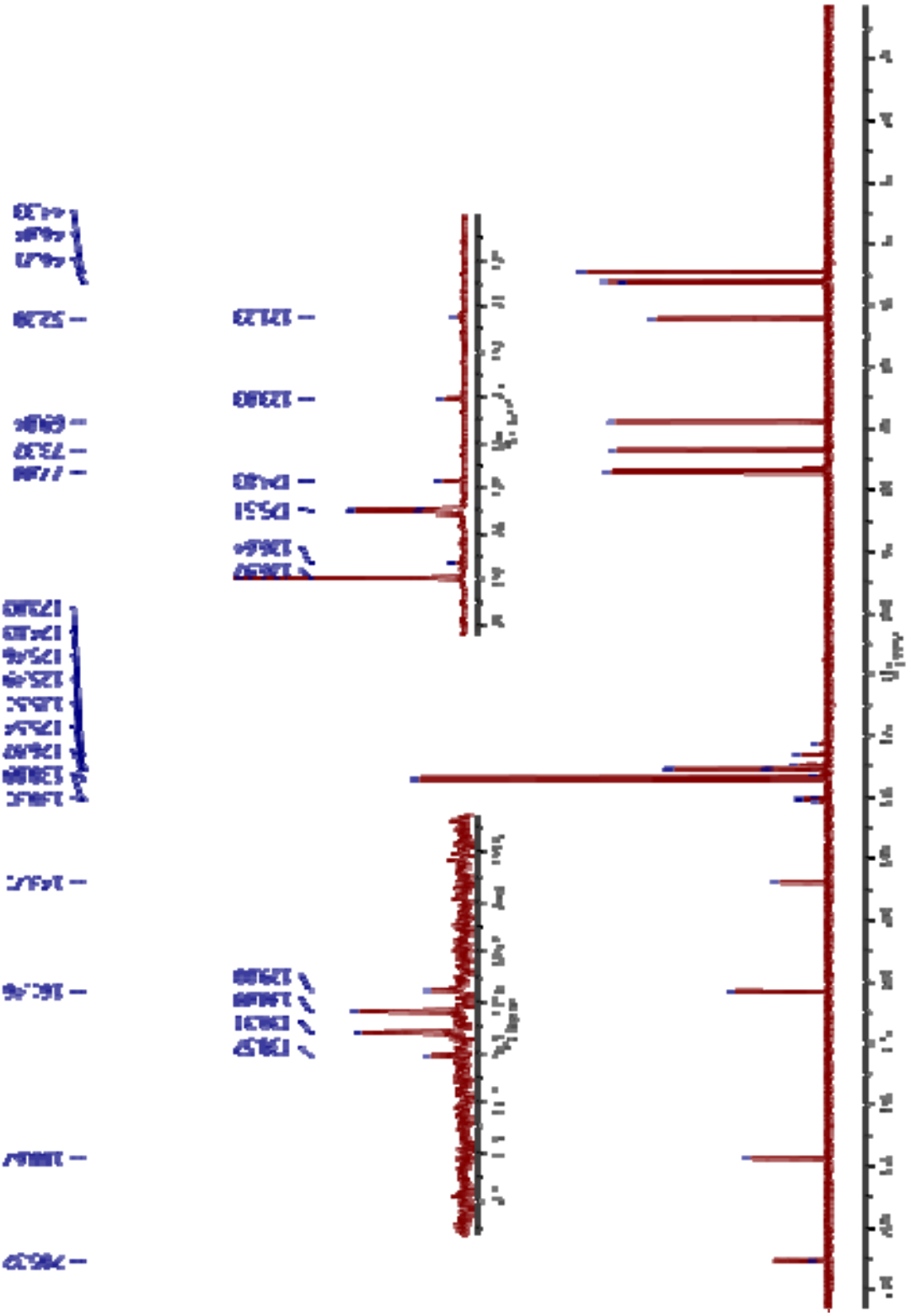
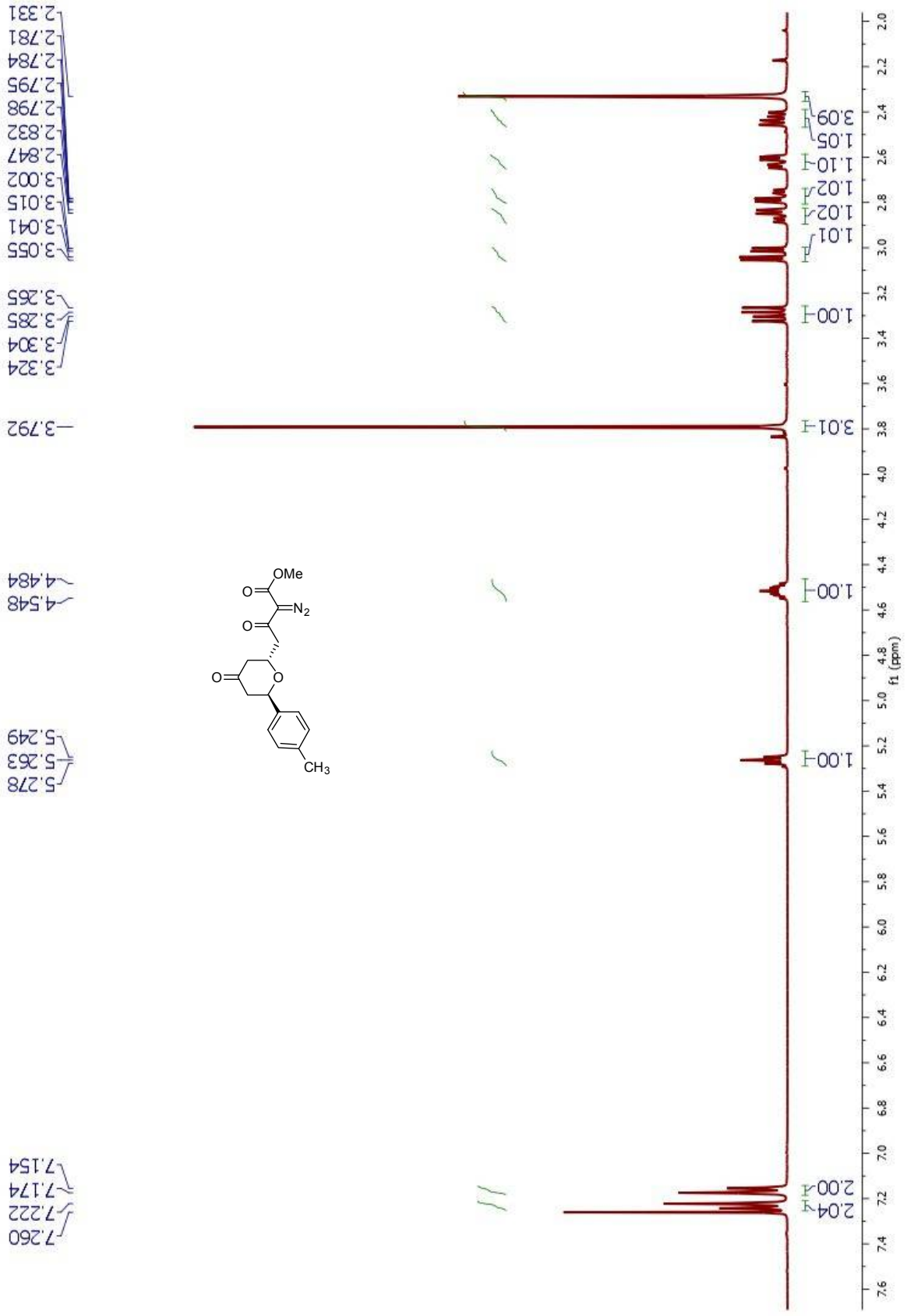
O
N2
O
O
O
NO2




OMe
O
N2
O
O
O
CF3

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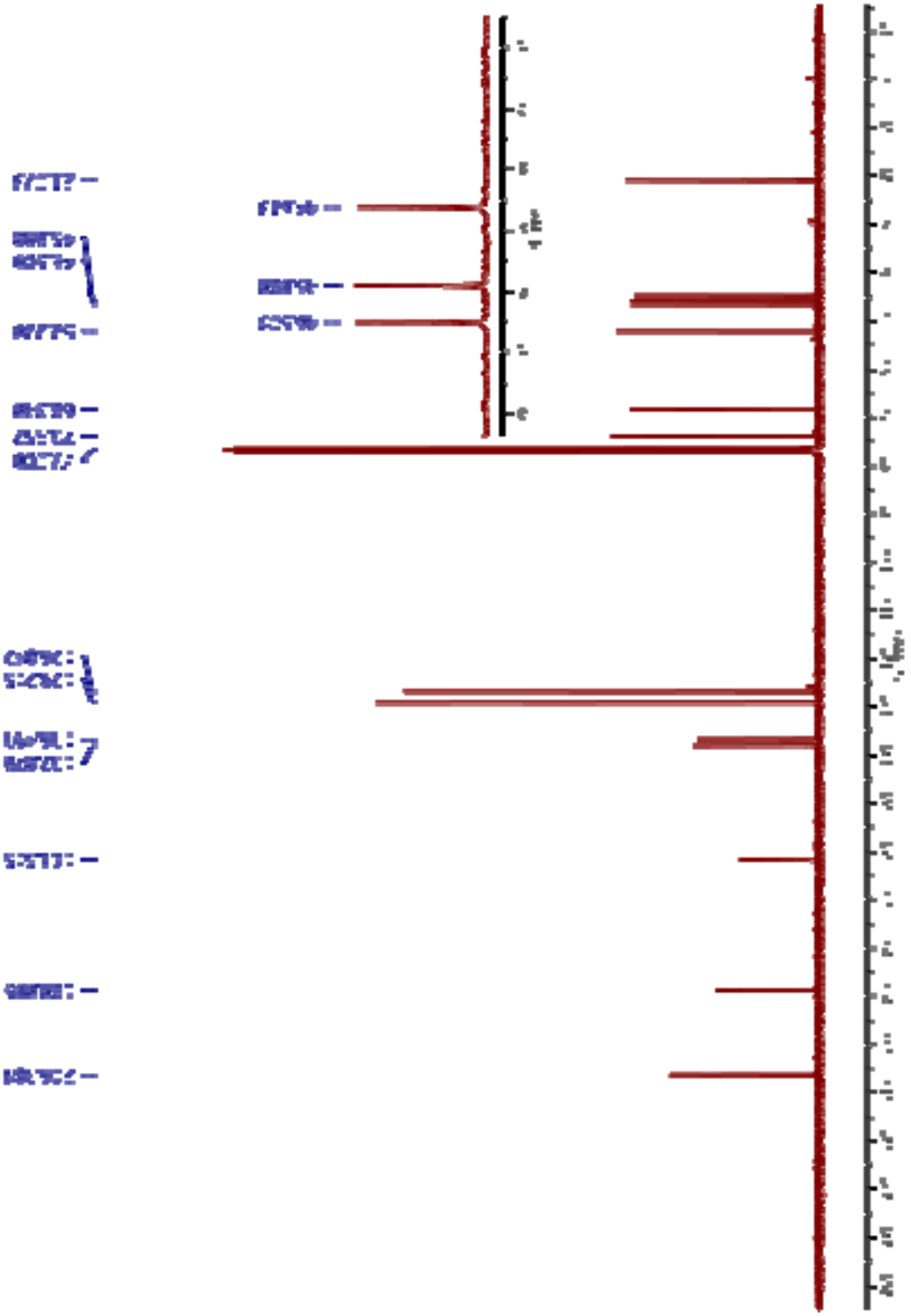
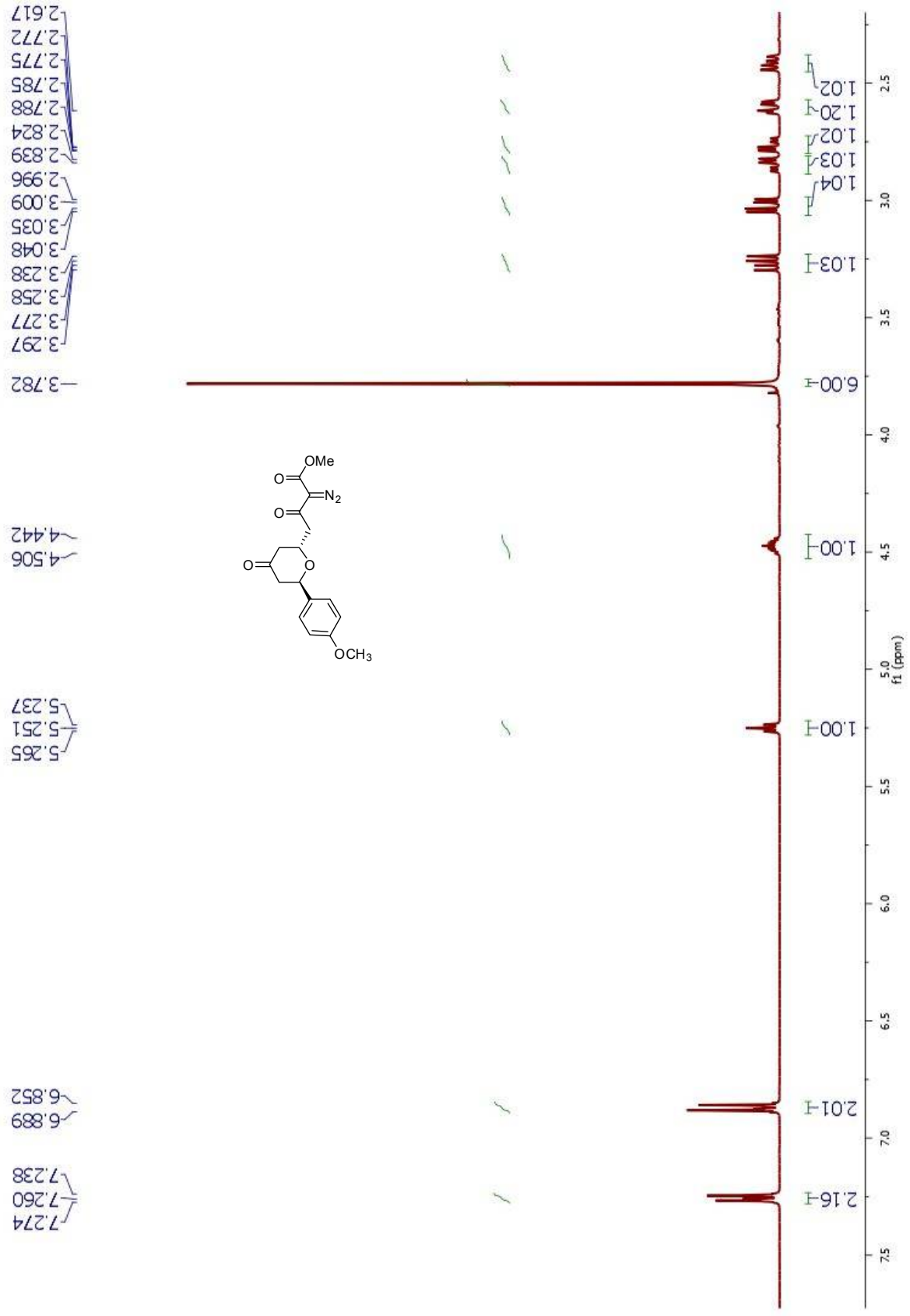
2.832
2.847
3.002
3.015
3.041
3.055
3.265
3.285
3.304
3.324
3.792
4.484
4.548
5.249
5.263
5.278
7.154
7.174
7.222
7.260
3.09
1.05
1.10
1.02
1.02
1.01
1.00
3.01
1.00
1.00
2.04
2.00
OMe
O
N2
O
O
O
CH3
f1 (ppm)

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2.775
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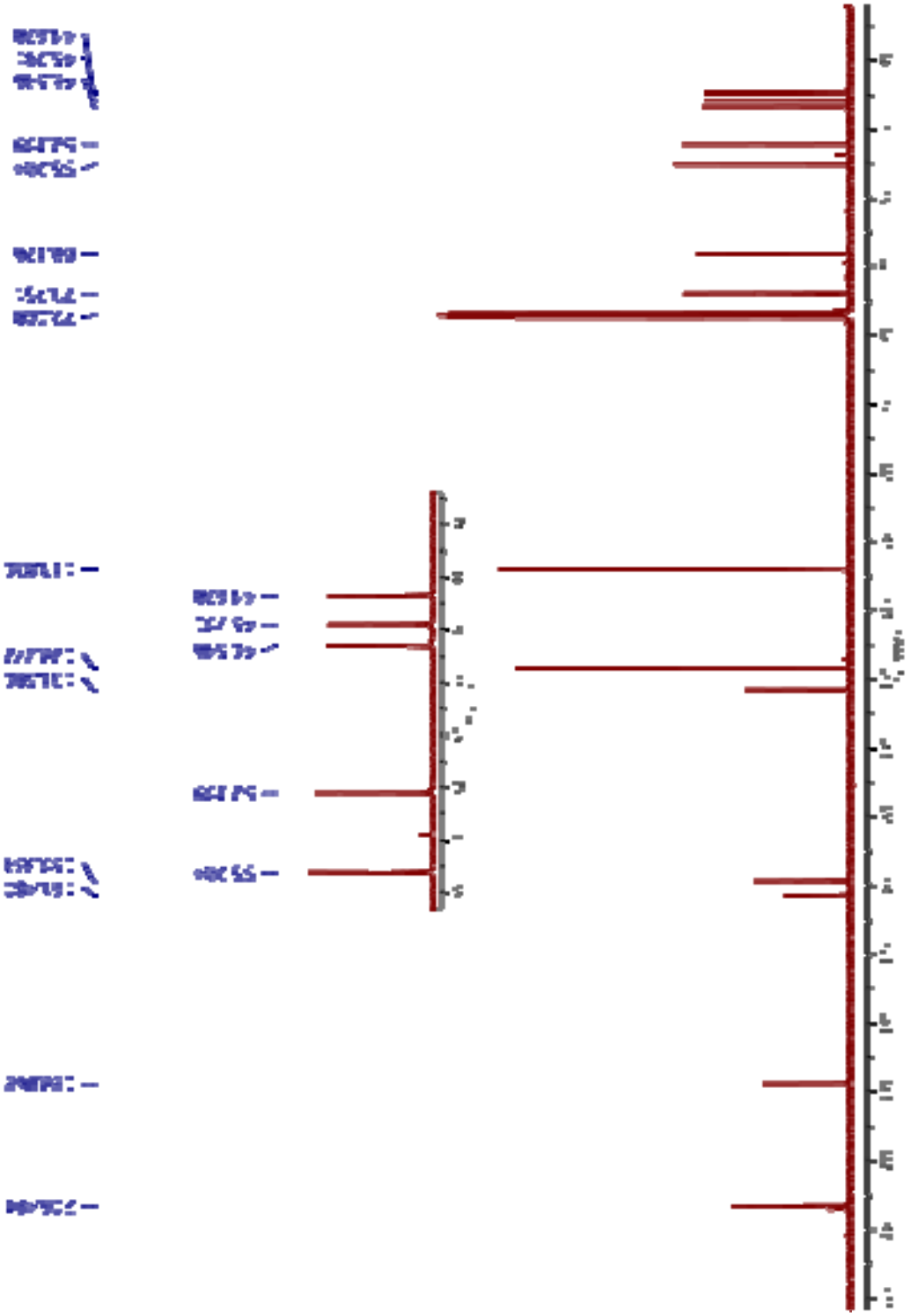
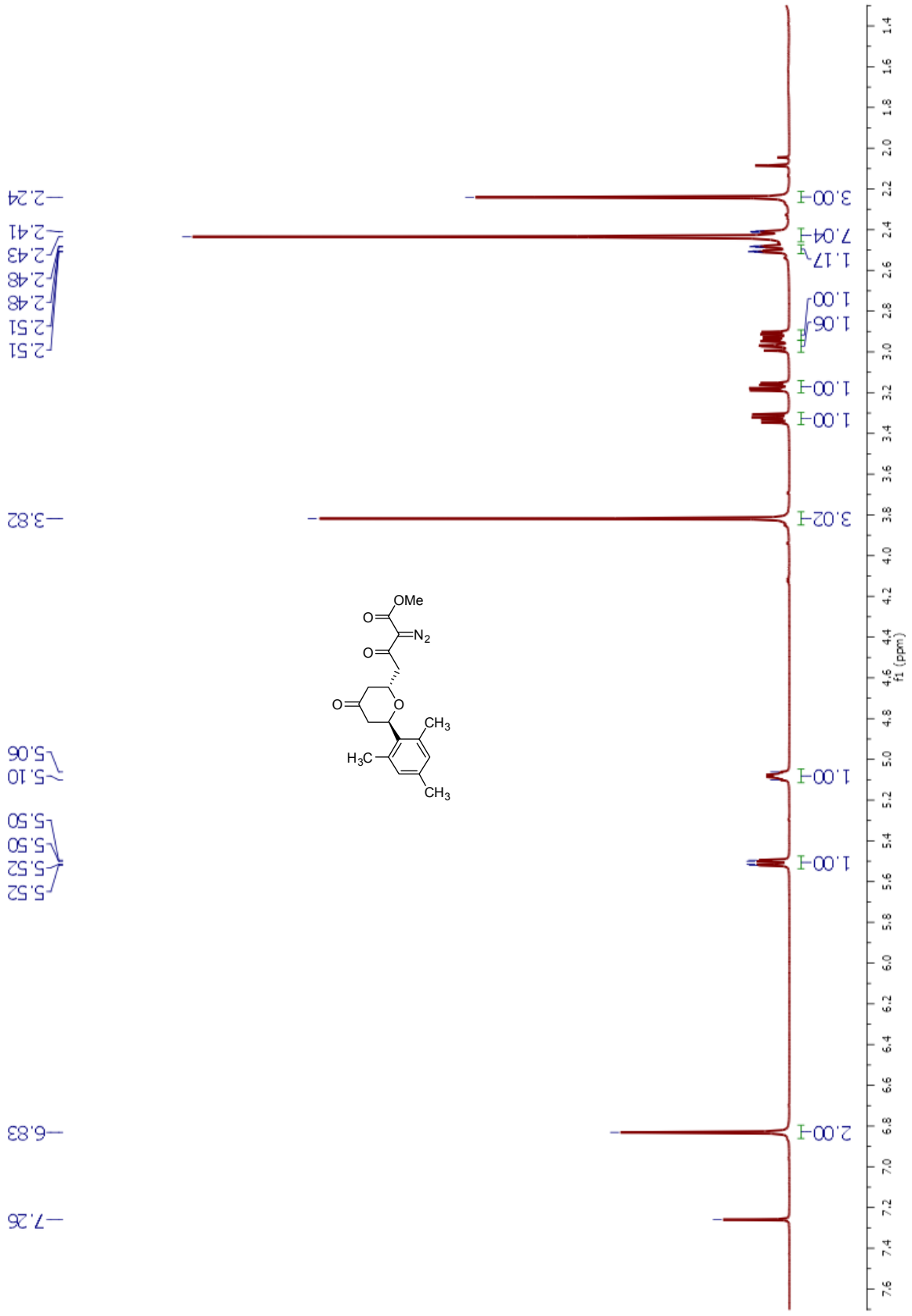
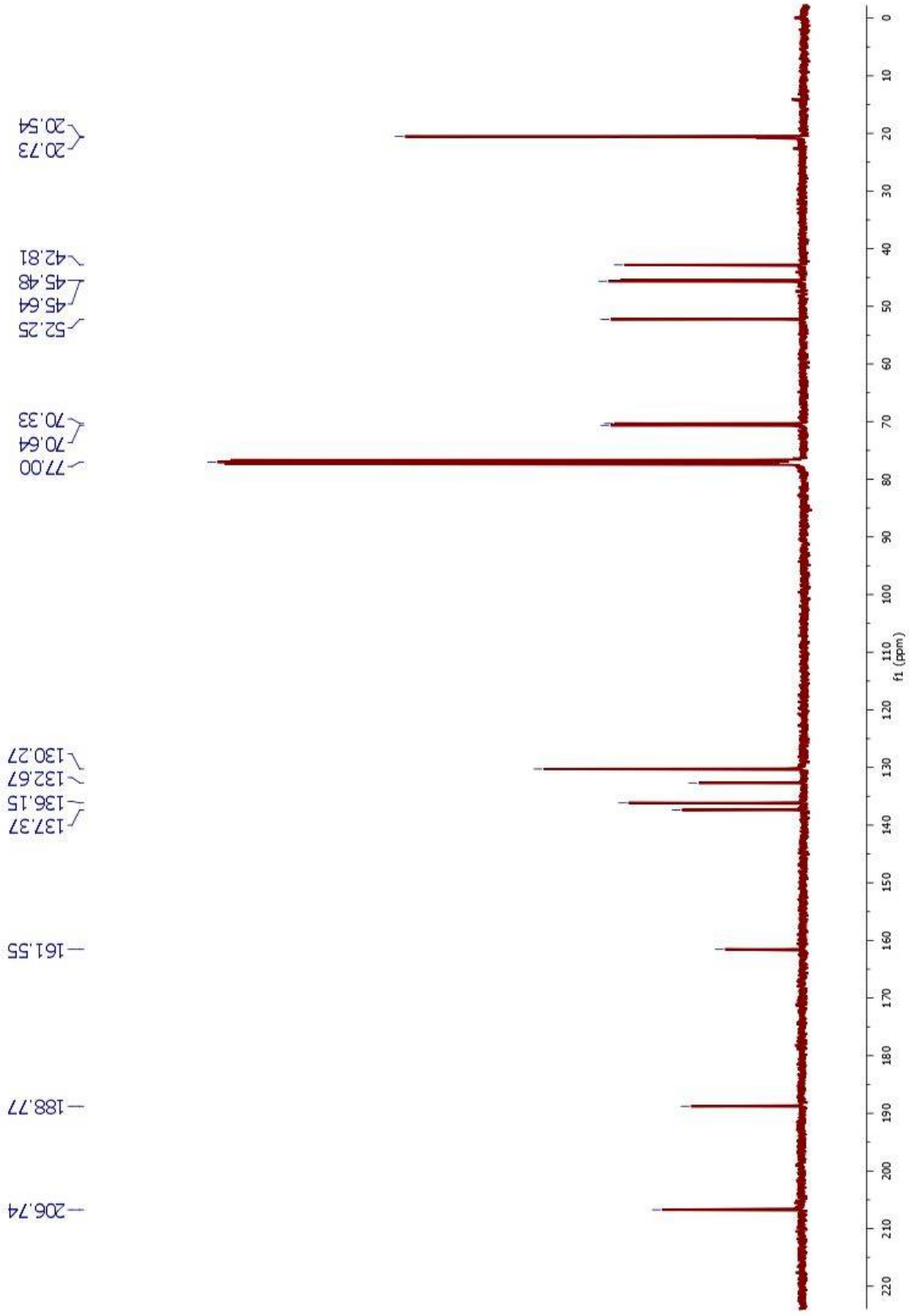
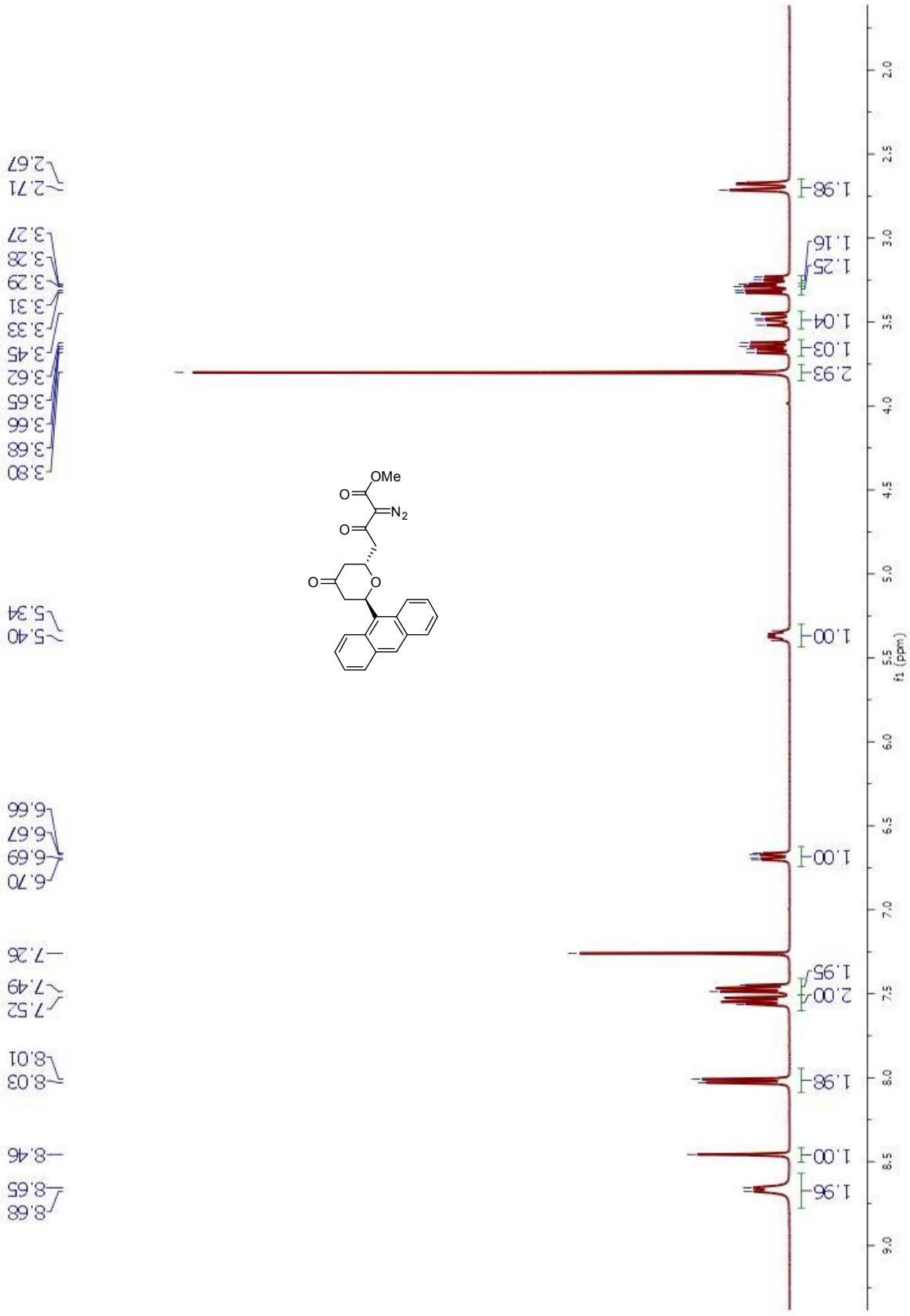
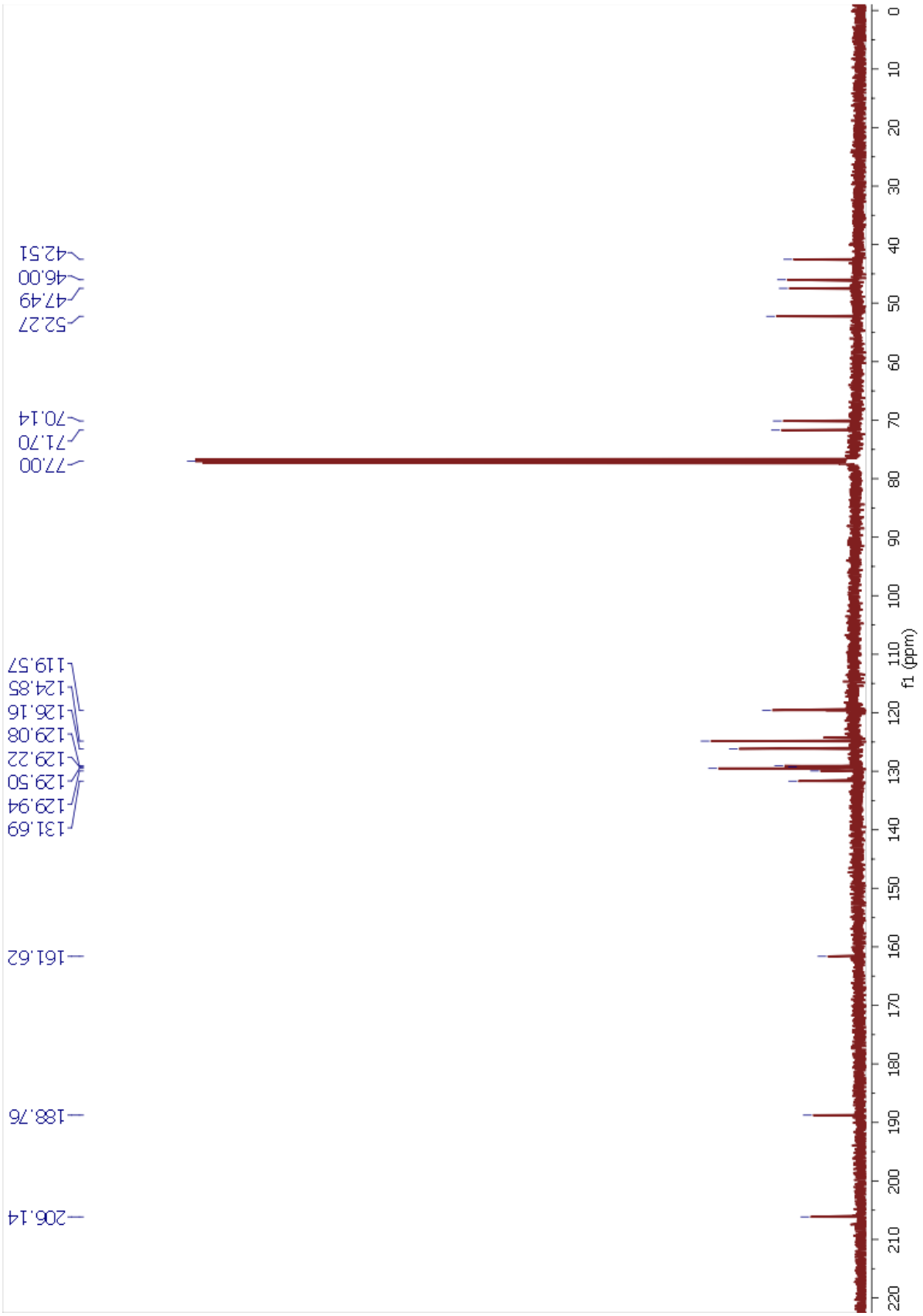
2.996
3.009
3.035
3.048
3.238
3.258
3.277
3.297
3.782
4.442
4.506
5.237
5.251
5.265
6.852
6.889
7.238
7.260
7.274
OMe
O
N2
O
O
O
OCH3
1.02
1.20
1.02
1.03
1.04
1.03
6.00
1.00
1.00
2.01
2.16
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
f1 (ppm)

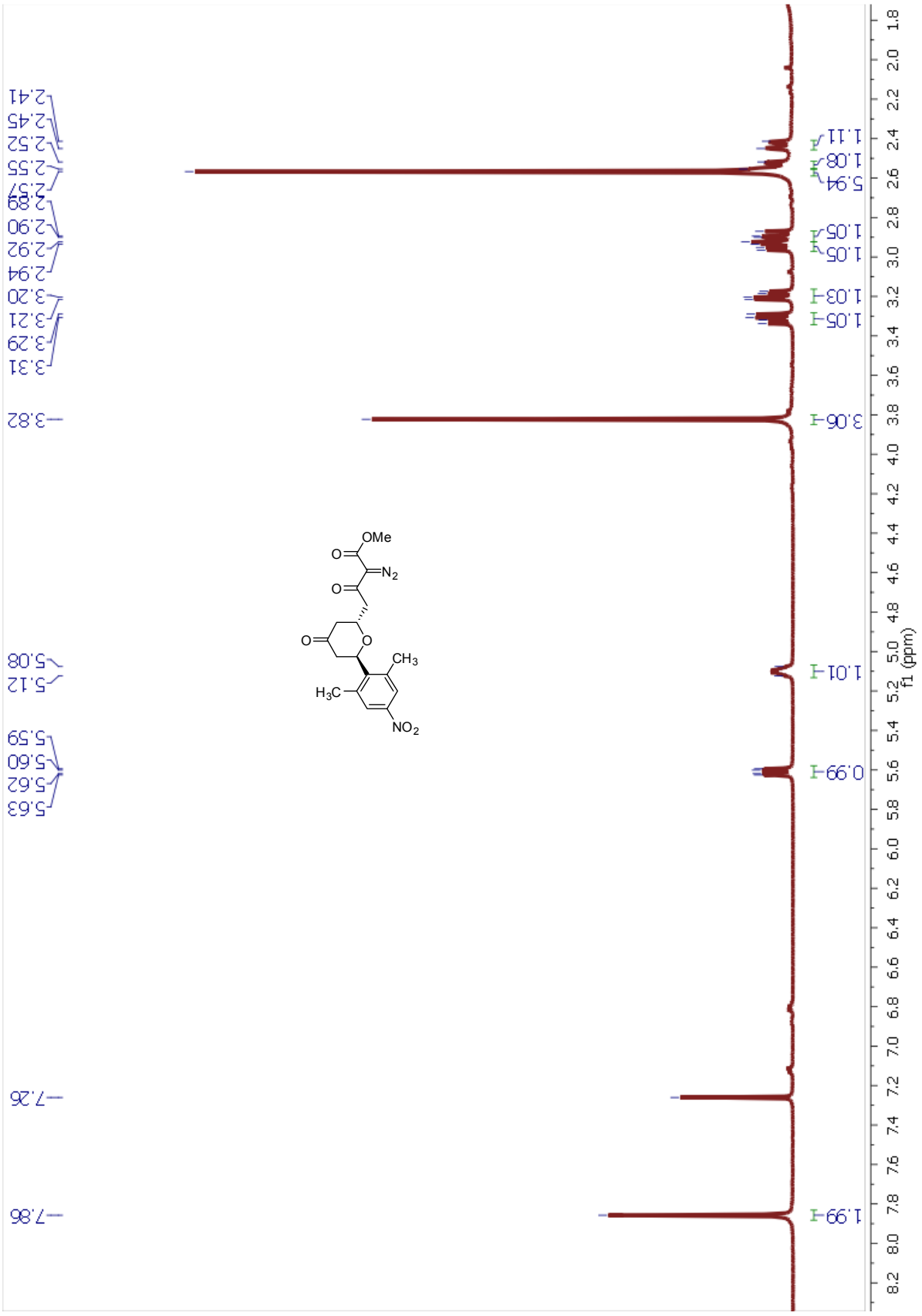


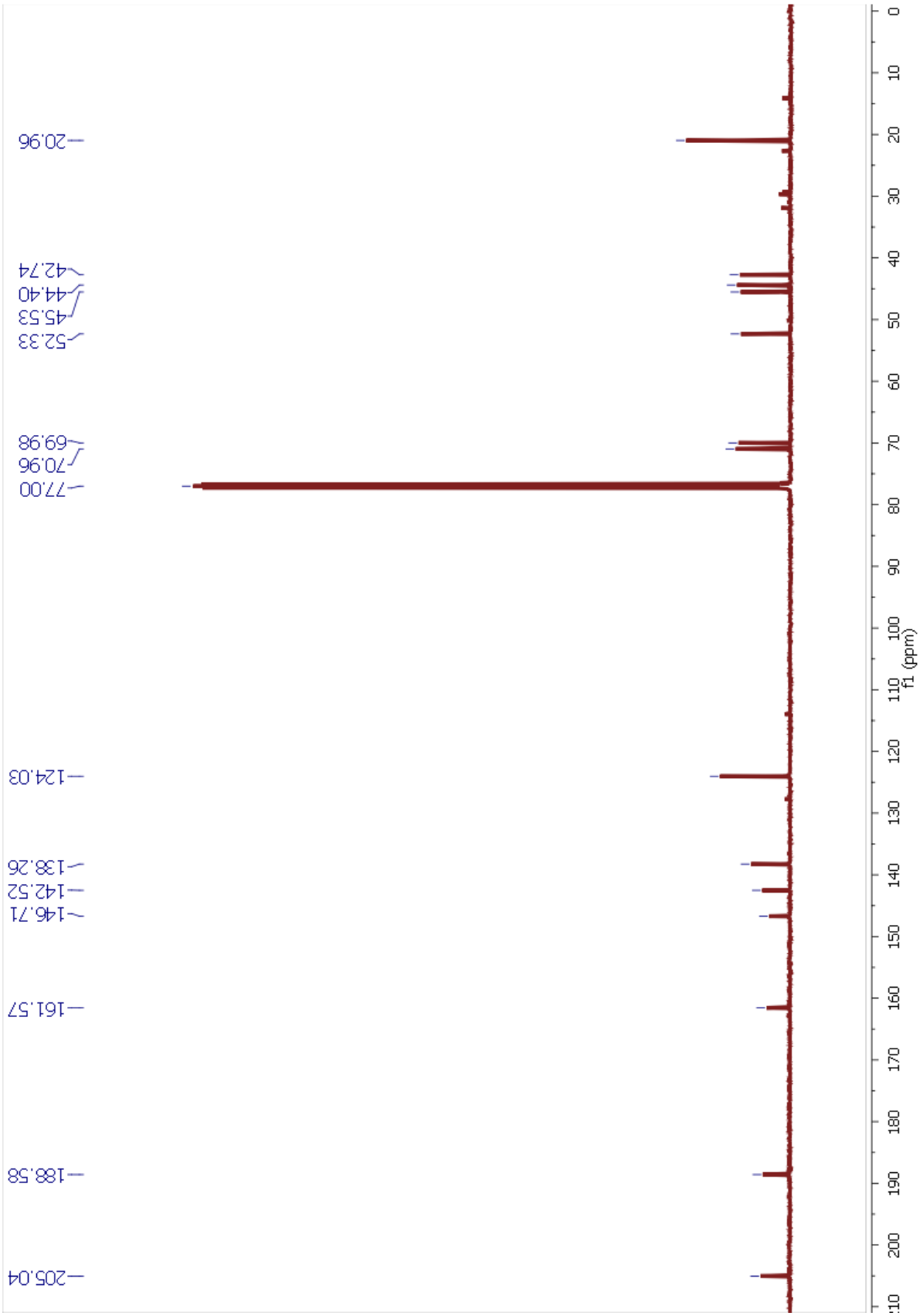

2.24
2.41
2.43
2.48
2.48
2.51
2.51
3.82
5.06
5.10
5.50
5.50
5.52
5.52
6.83
7.26
3.00
7.04
1.17
1.00
1.06
1.00
1.00
3.02
1.00
1.00
2.00
OMe
O
N2
O
O
O
CH3
H3C
CH3
f1 (ppm)

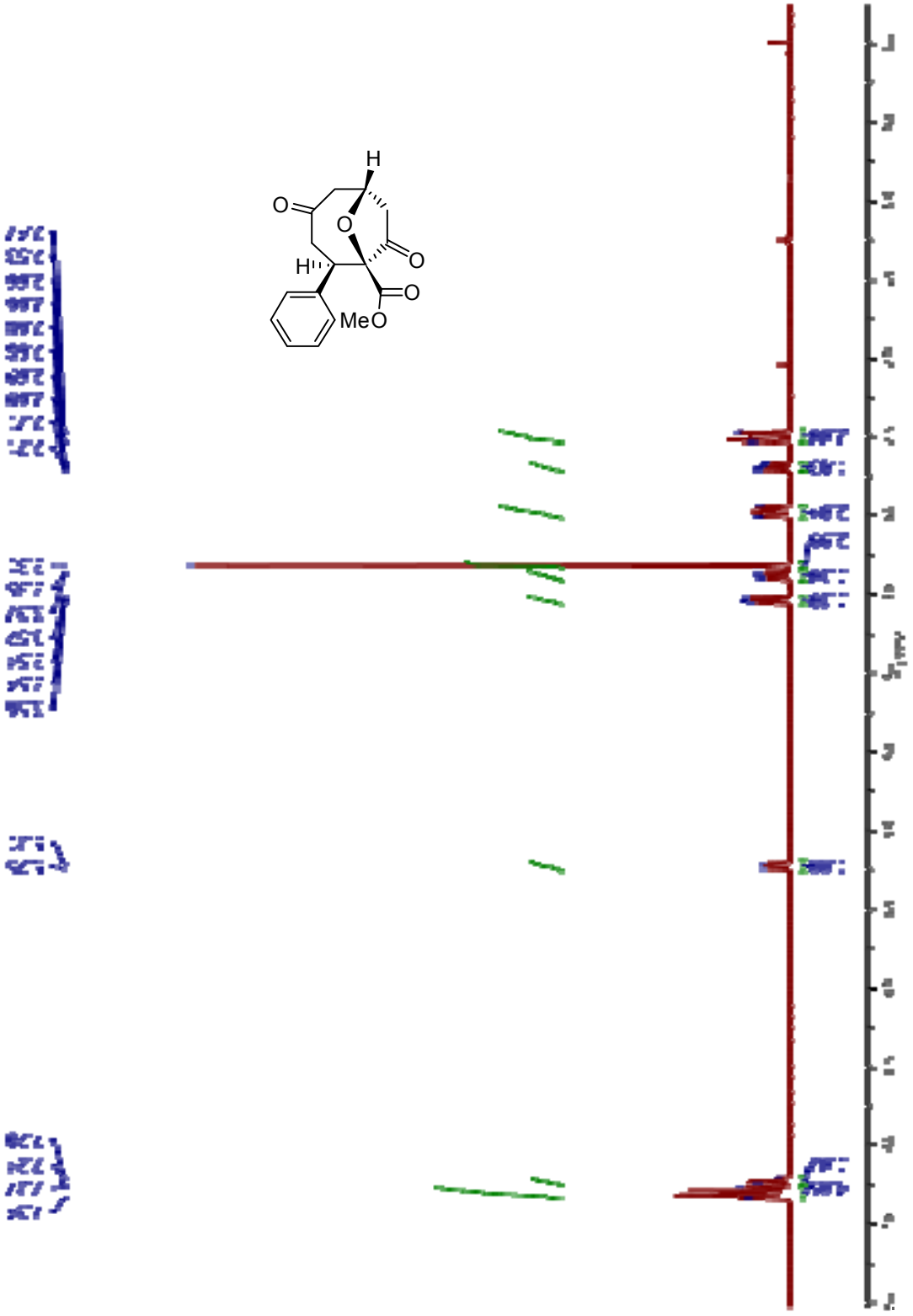

20.54
20.73
42.81
45.48
45.64
52.25
70.33
70.64
77.00
130.27
132.67
136.15
137.37
161.55
188.77
206.74
f1 (ppm)

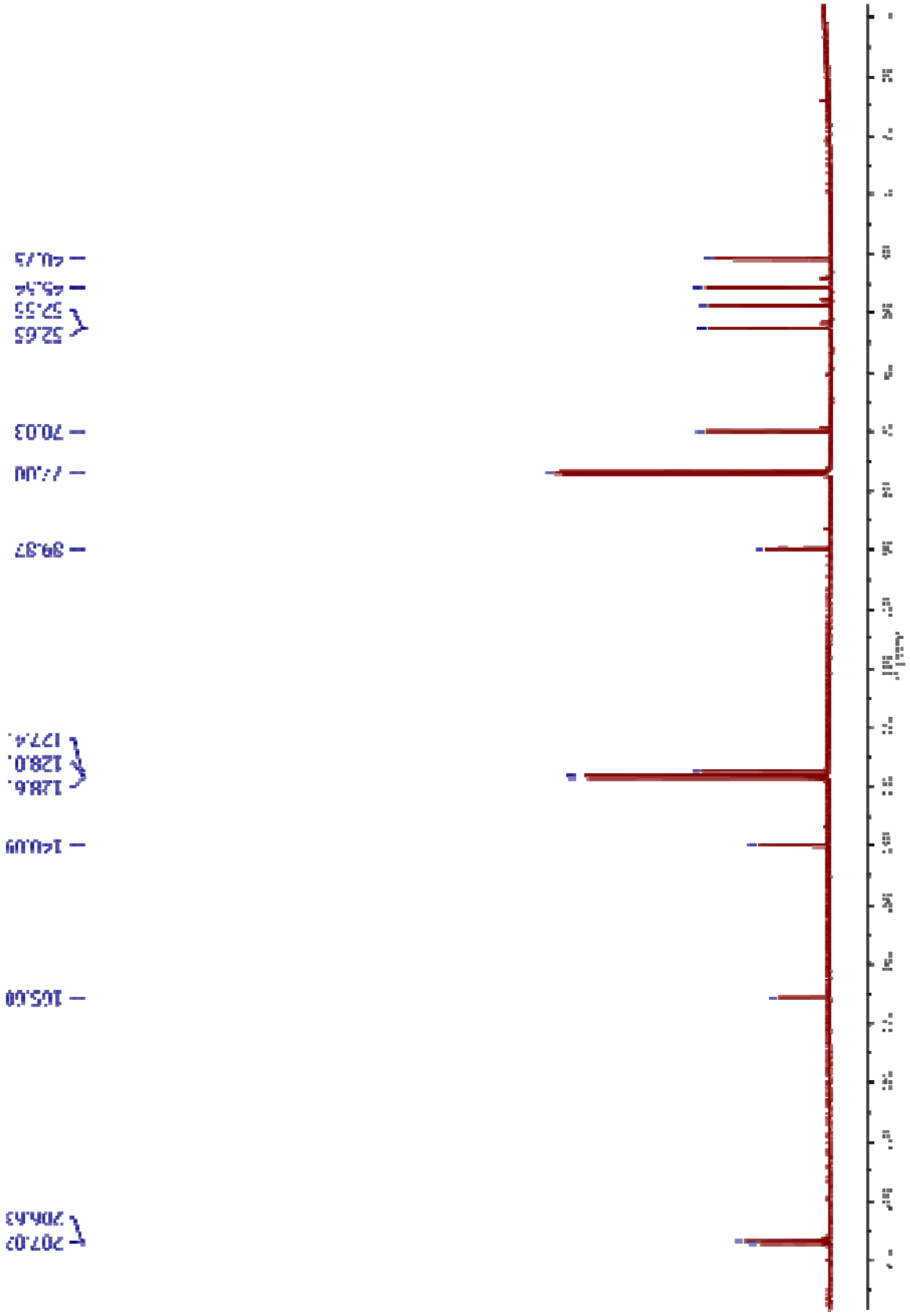

OMe
O
N2
O
O
O
2.67
2.71
3.27
3.28
3.29
3.31
3.33
3.45
3.62
3.65
3.66
3.68
3.80
5.34
5.40
6.66
6.67
6.69
6.70
7.26
7.49
7.52
8.01
8.03
8.46
8.65
8.68
1.98
1.16
1.25
1.04
1.03
2.93
1.00
1.00
1.95
2.00
1.98
1.00
1.96
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)

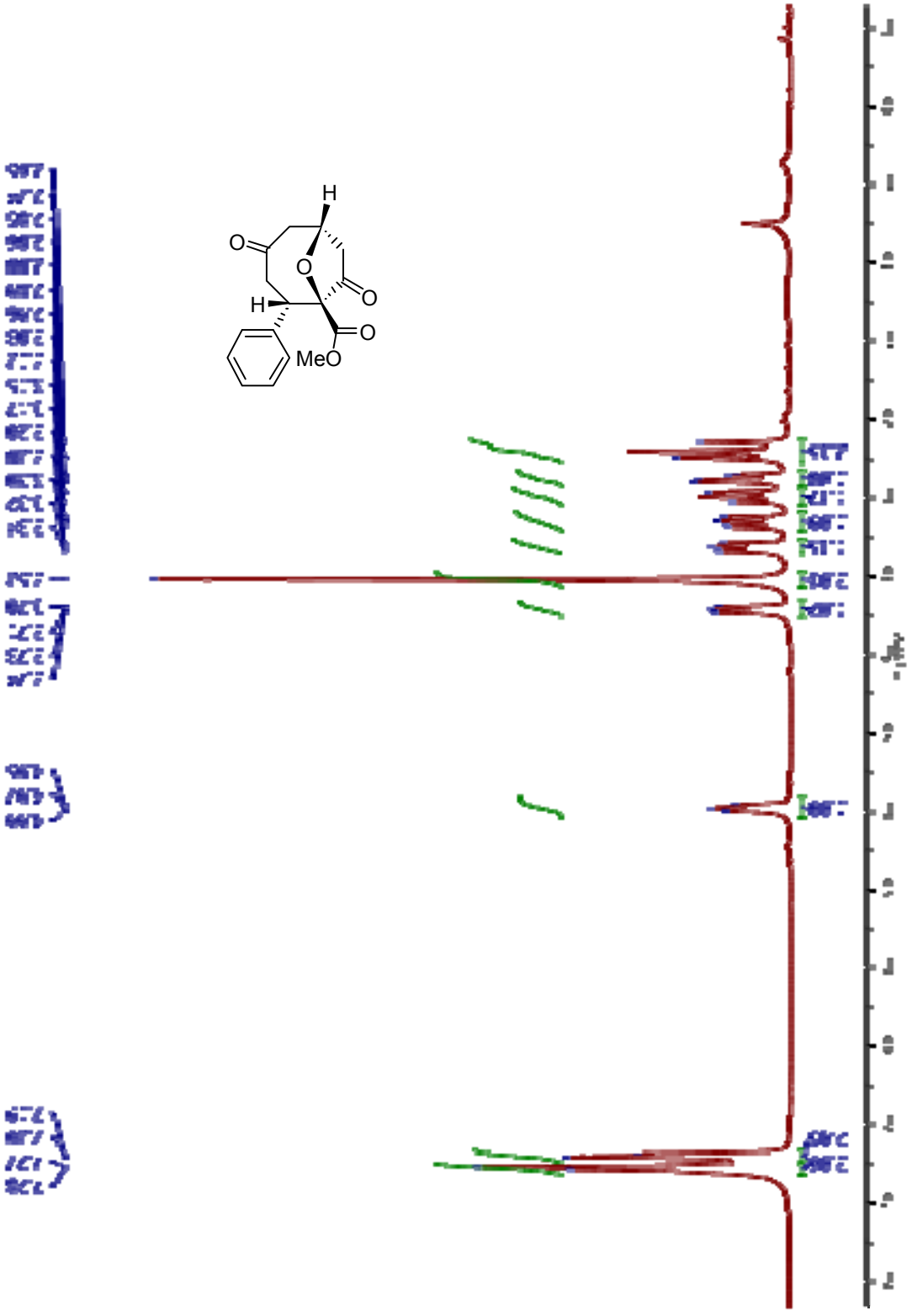

42.51
46.00
47.49
52.27
70.14
71.70
77.00
119.57
124.85
126.16
129.08
129.22
129.50
129.94
131.69
161.62
188.76
206.14
f1 (ppm)

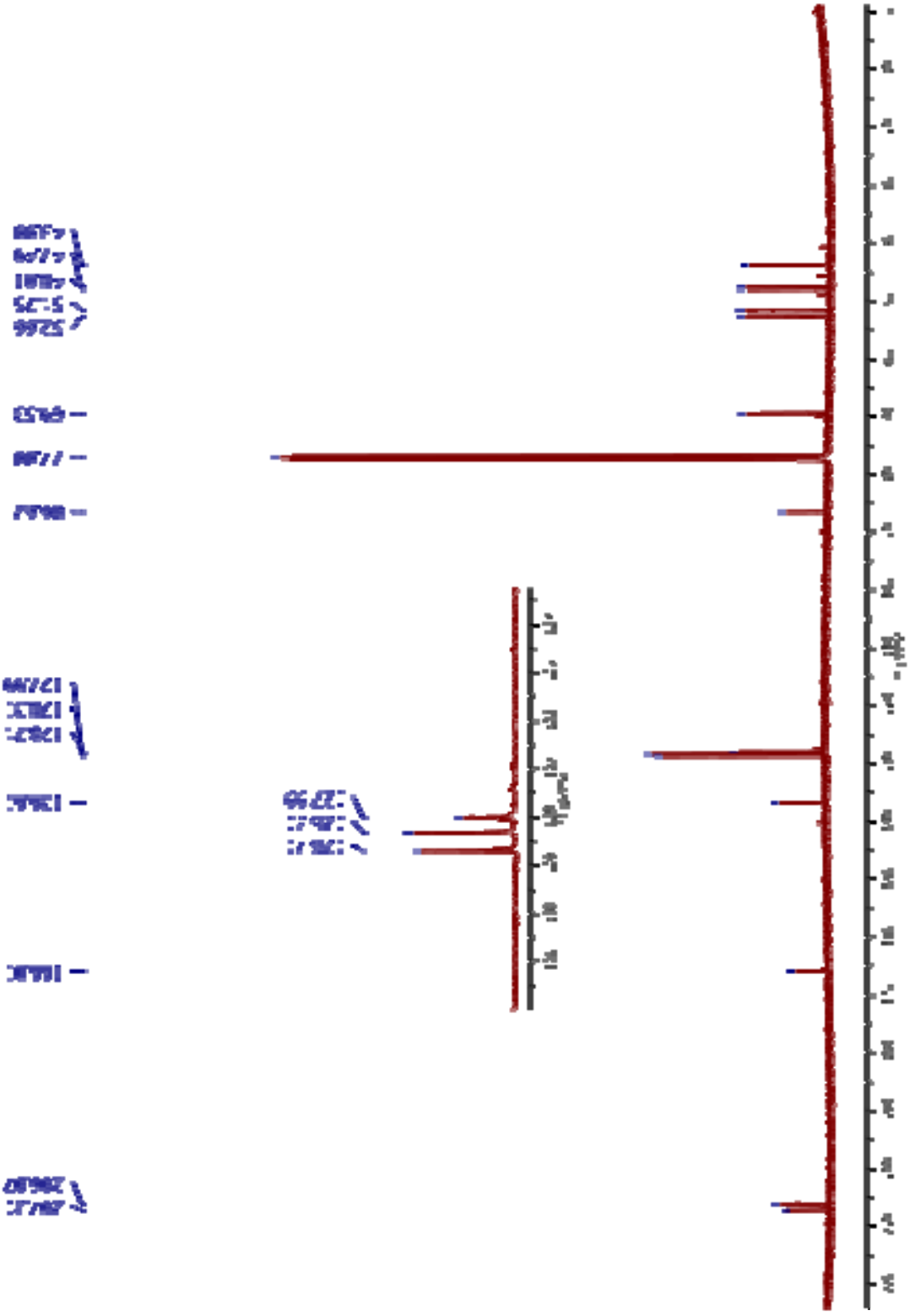

2.41
2.45
2.52
2.55
2.57
2.89
2.90
2.92
2.94
3.20
3.21
3.29
3.31
3.82
5.08
5.12
5.59
5.60
5.62
5.63
7.26
7.86
1.11
1.08
5.94
1.05
1.05
1.03
1.05
3.06
1.01
0.99
1.99
OMe
O
N2
O
O
O
CH3
H3C
NO2
f1 (ppm)

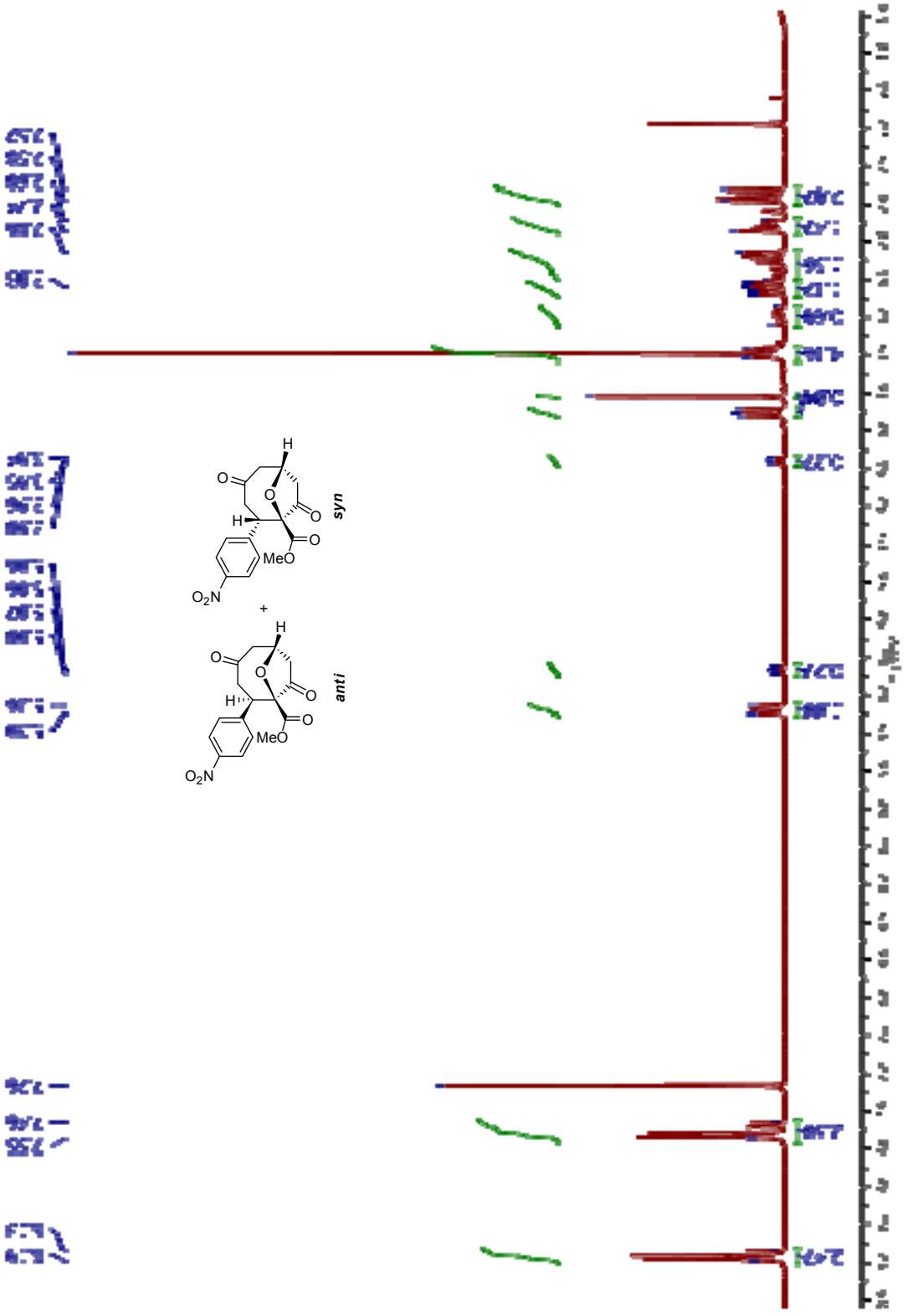

20.96
42.74
44.40
45.53
52.33
69.98
70.96
77.00
124.03
138.26
142.52
146.71
161.57
188.58
205.04
f1 (ppm)

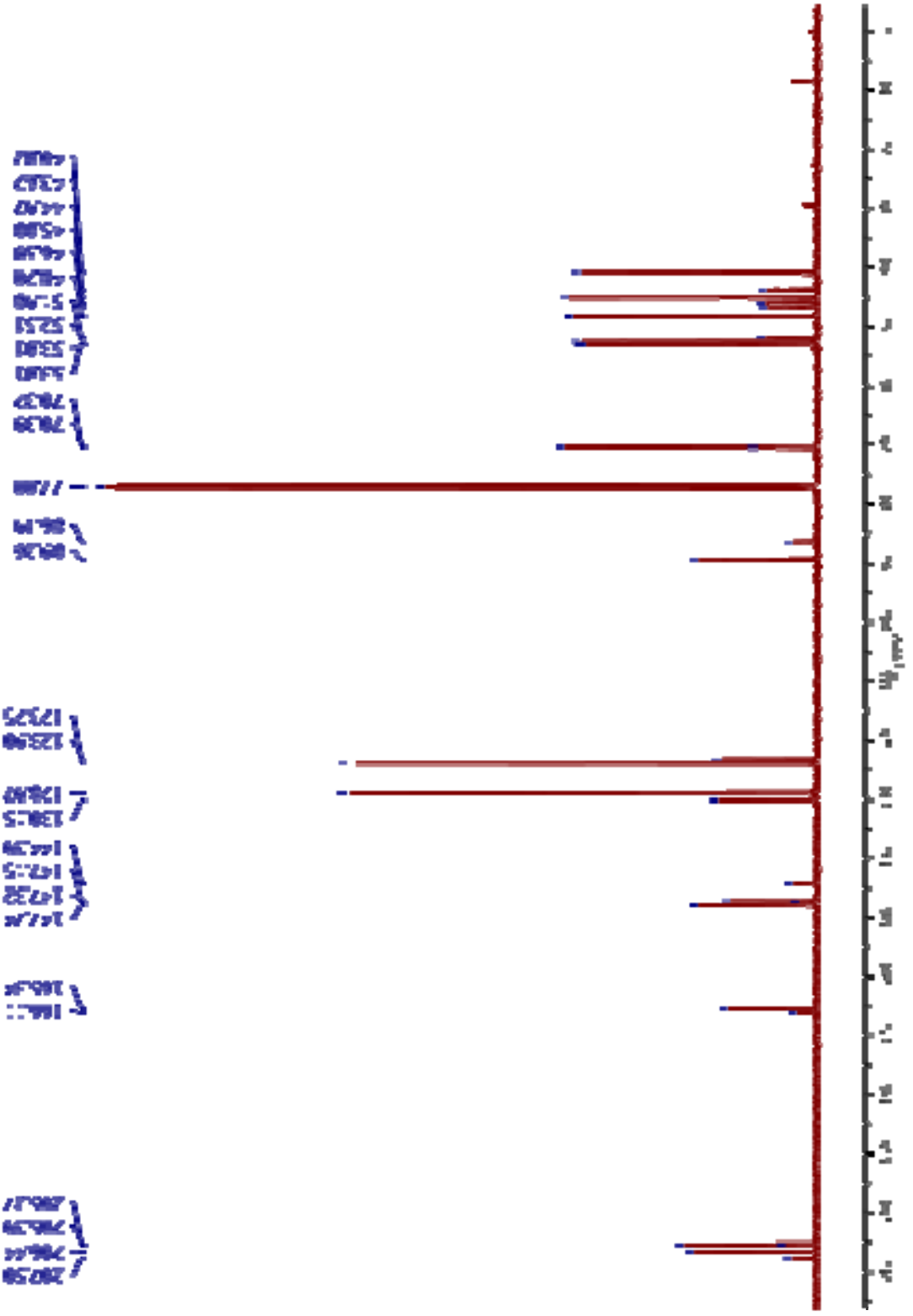

H
O
O
O
H
O
MeO

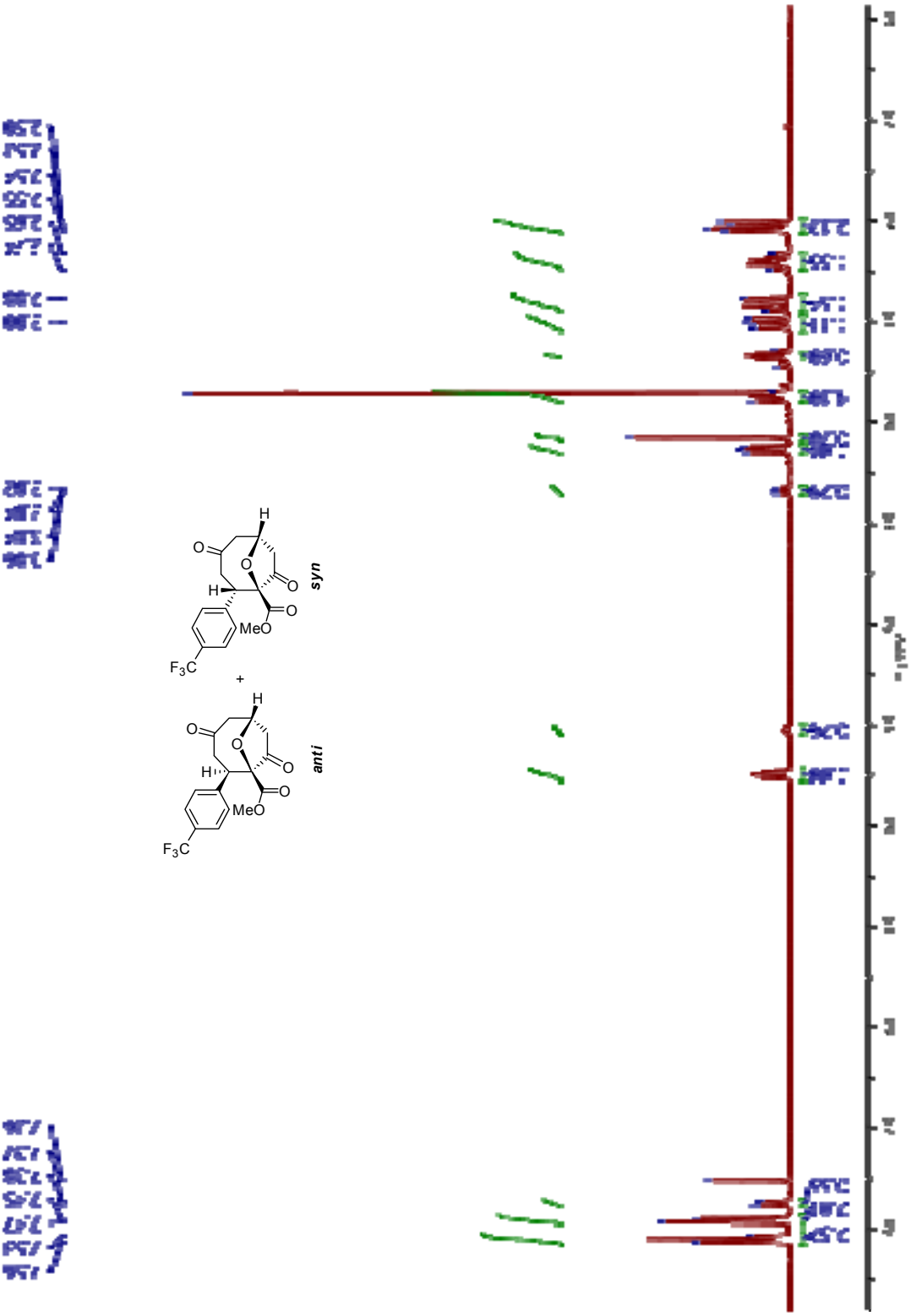

207.02
204.43
105.00
128.60
128.01
127.44
89.87
77.00
70.03
52.65
52.55
45.34
40.75

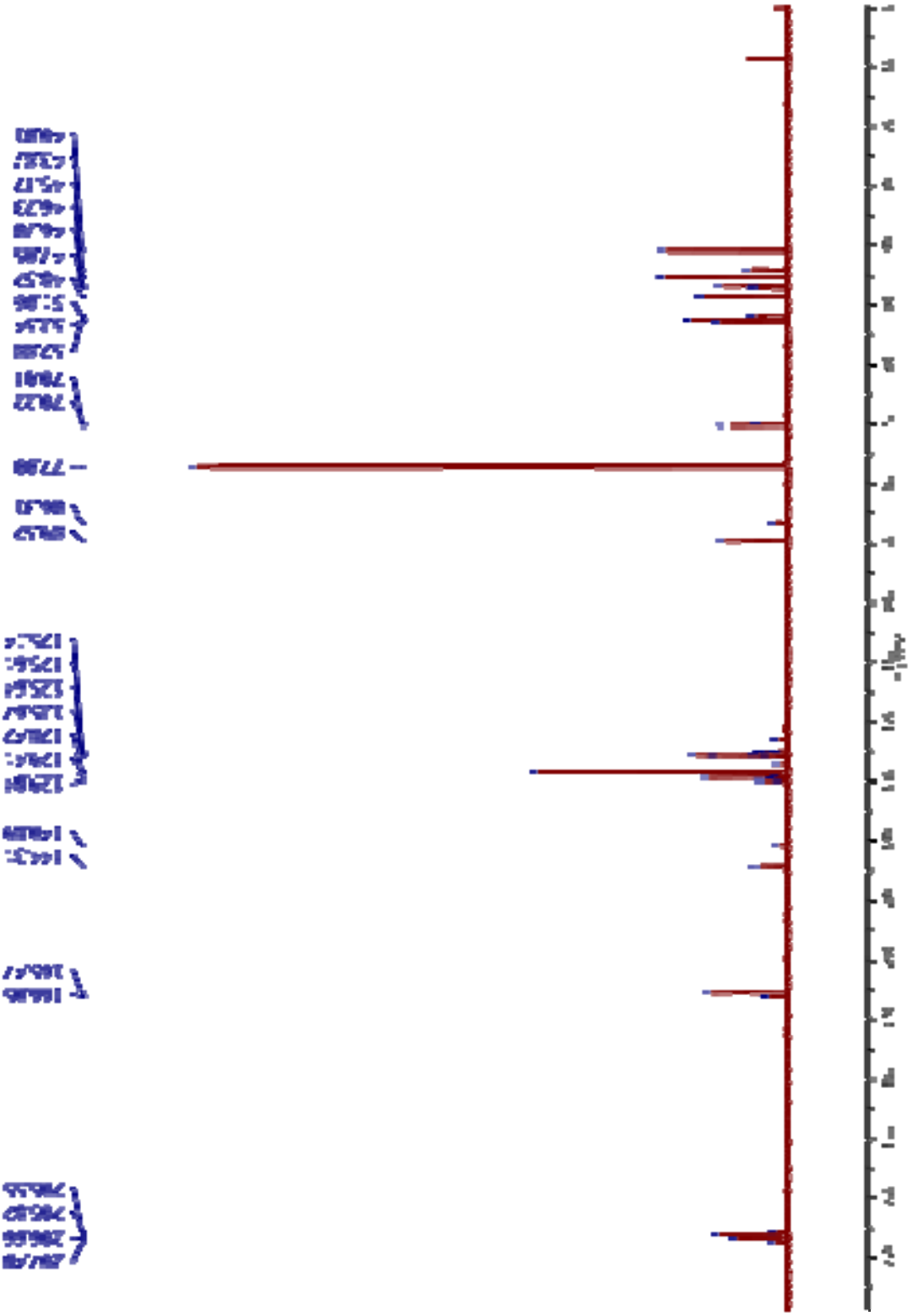

H
O
O
H
O
O
MeO

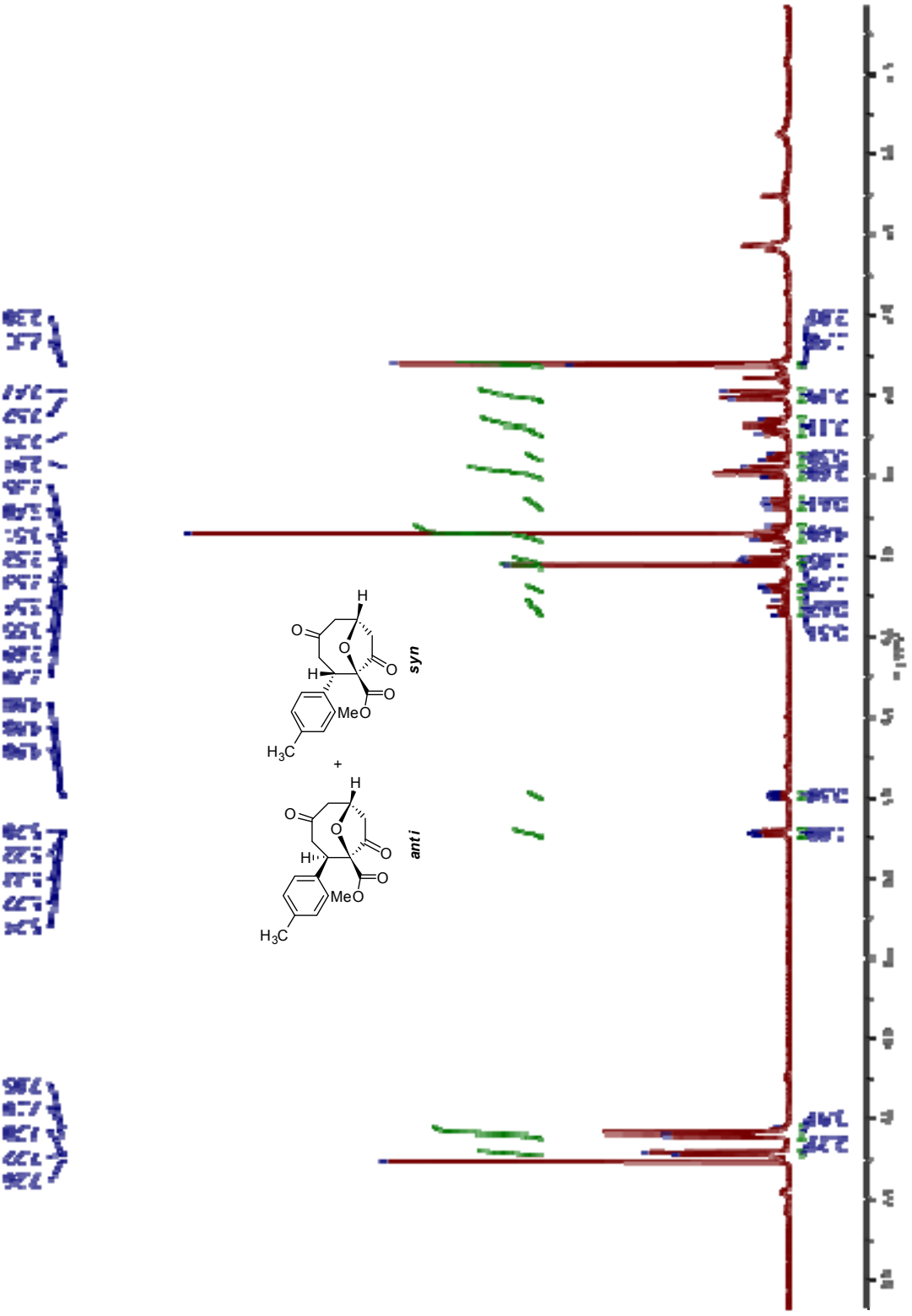


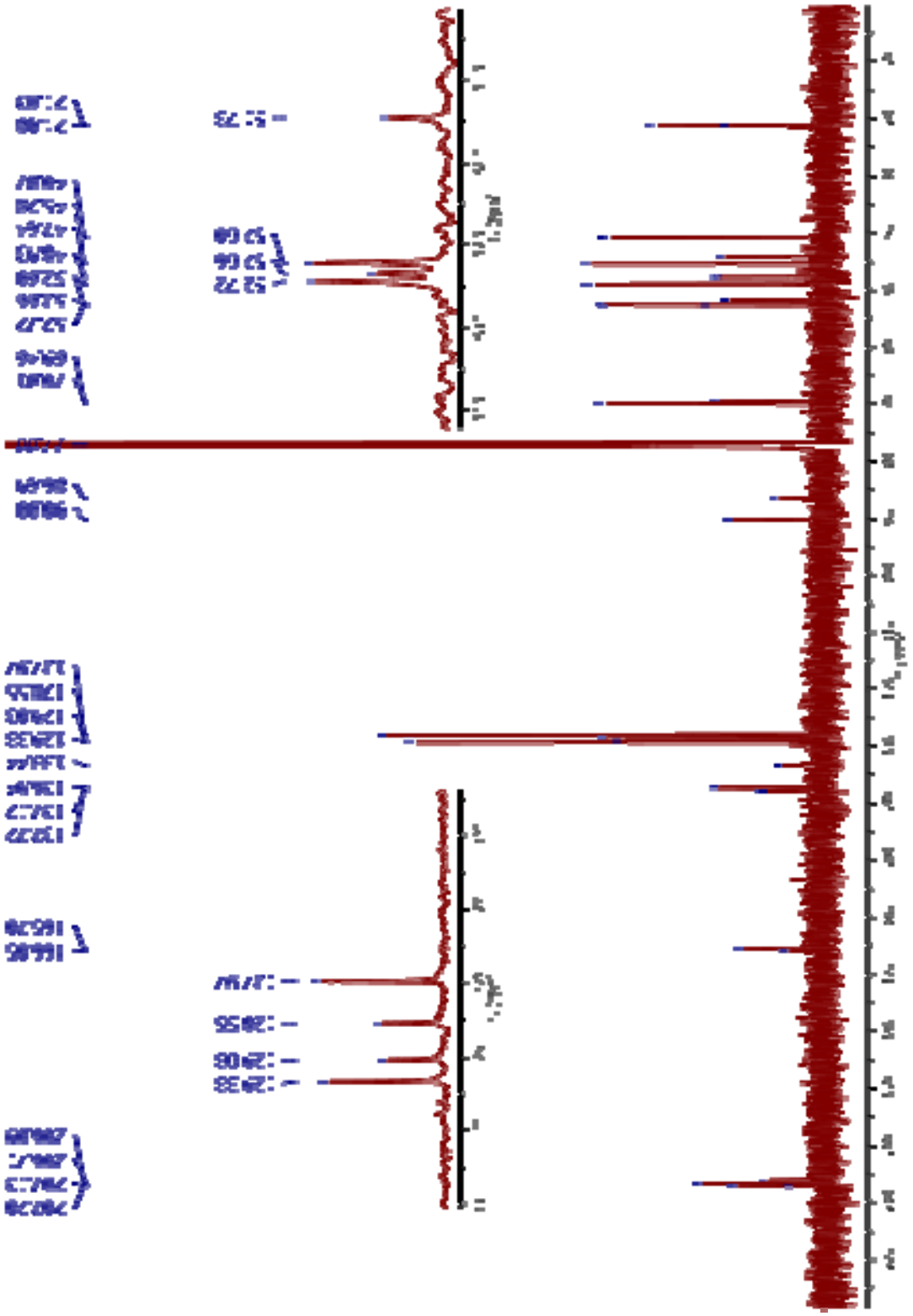

syn
anti
MeO
O2N

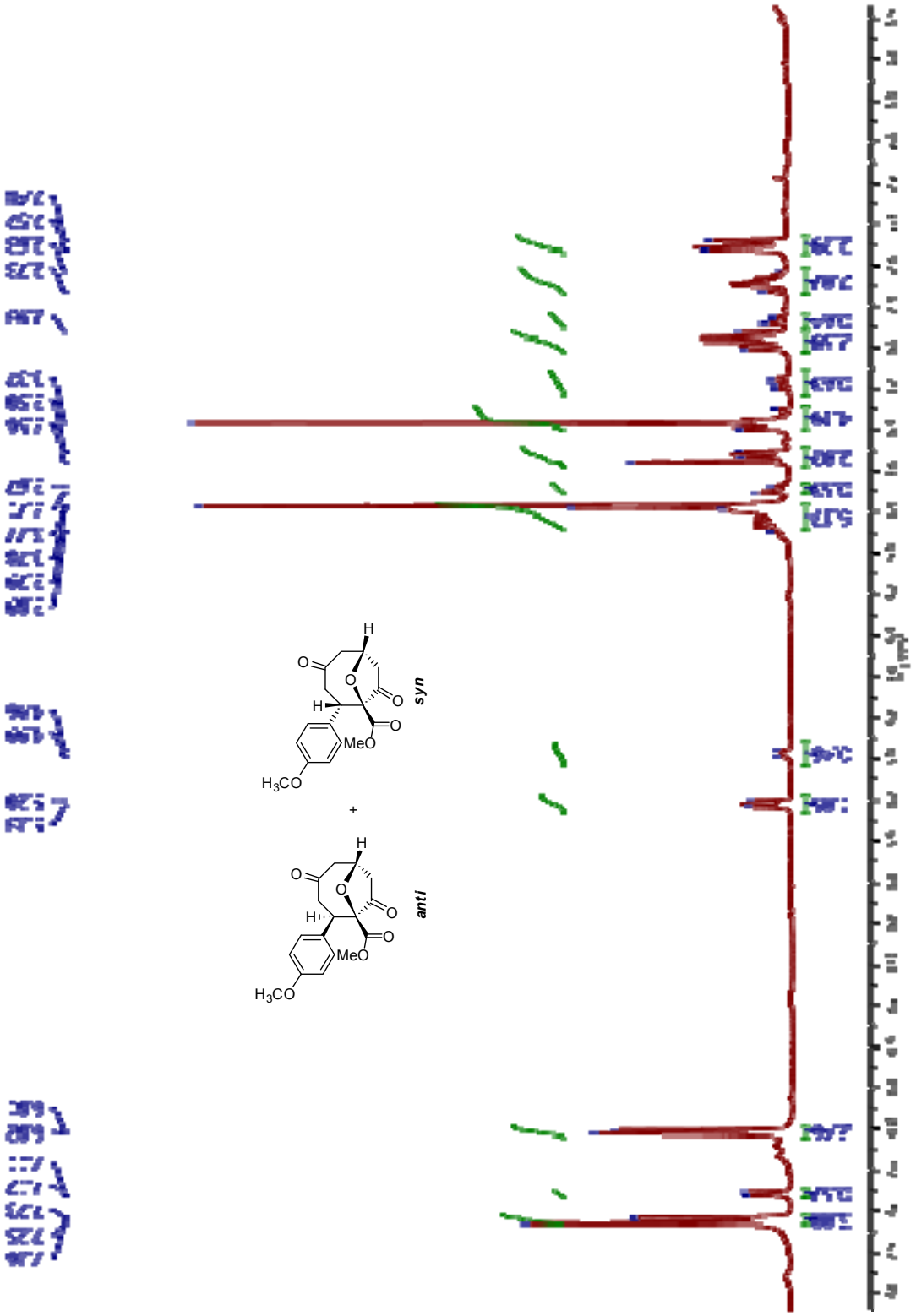


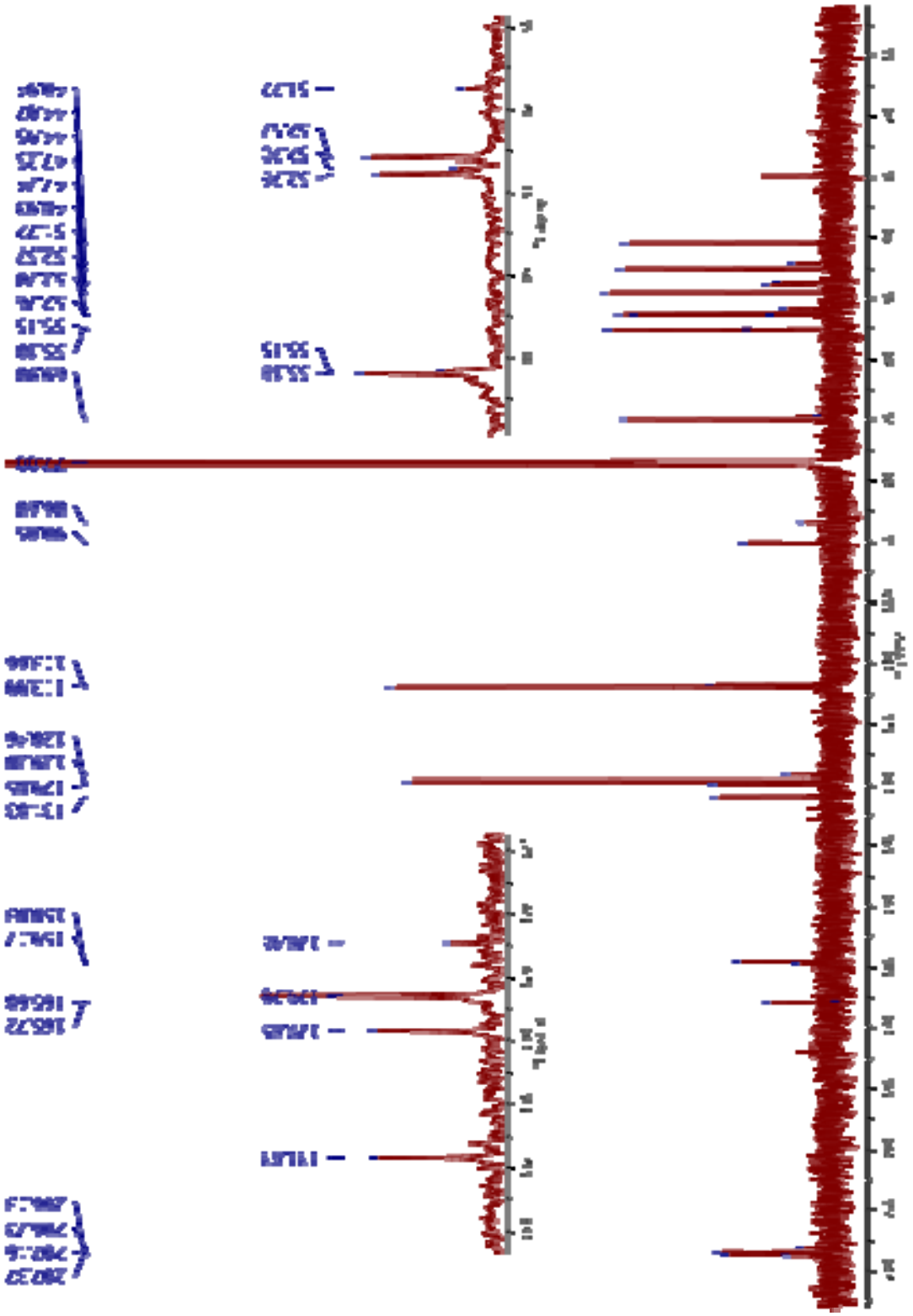

H
O
O
O
H
O
MeO
F3C
syn
+
H
O
O
O
H
O
MeO
F3C
anti

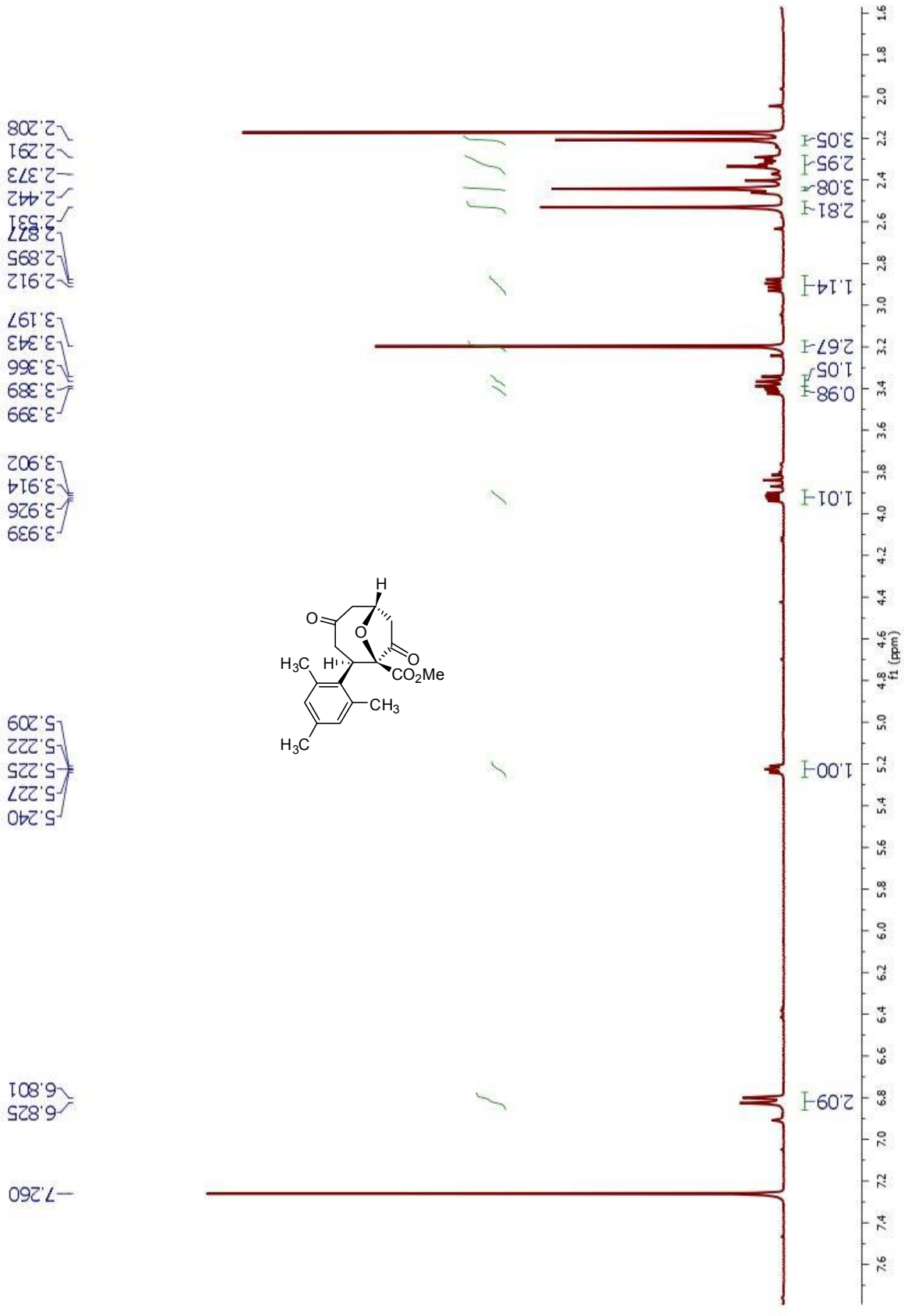


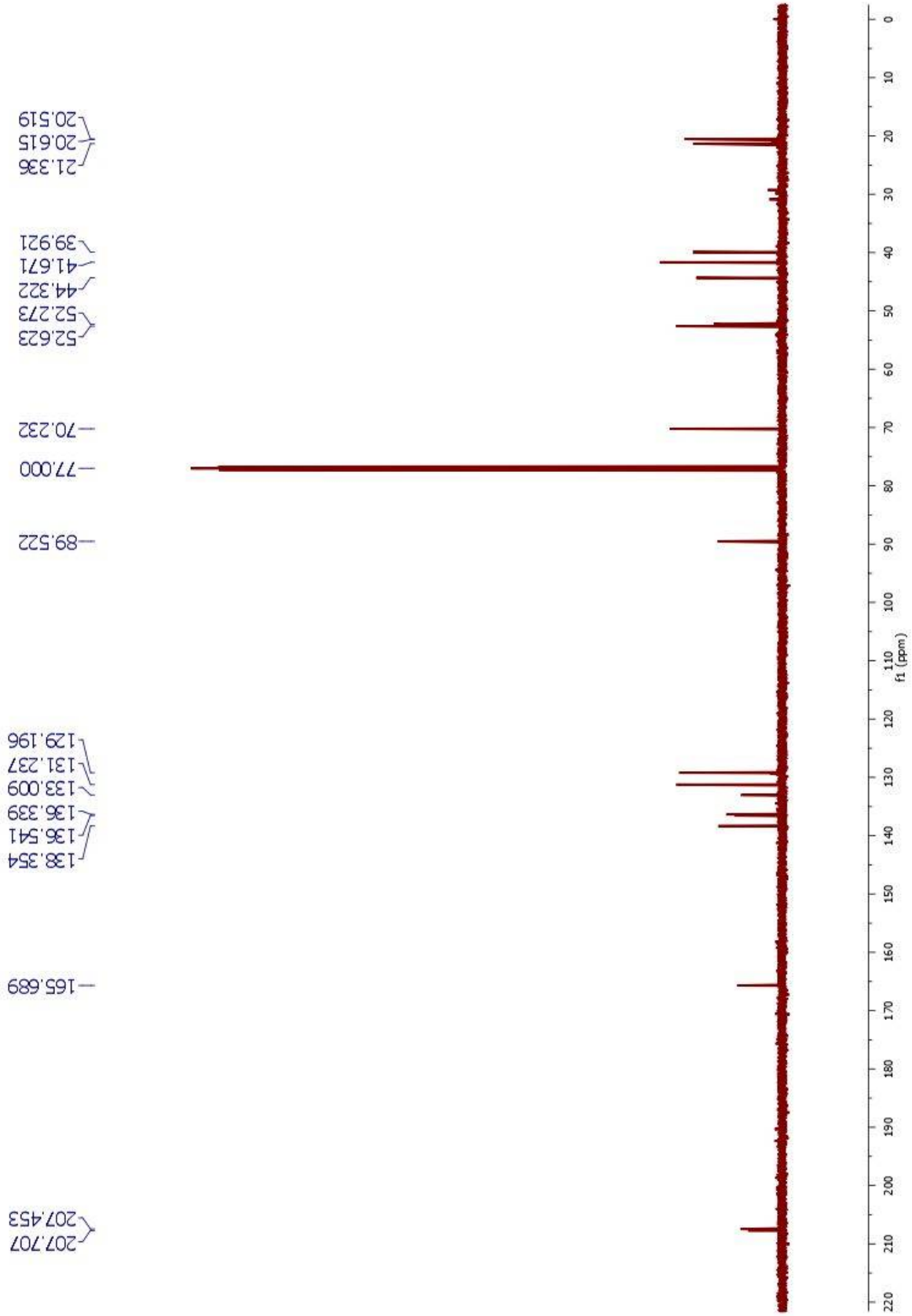

H
O
O
O
H
O
MeO
H3C
syn
+
H
O
O
O
H
O
MeO
H3C
anti

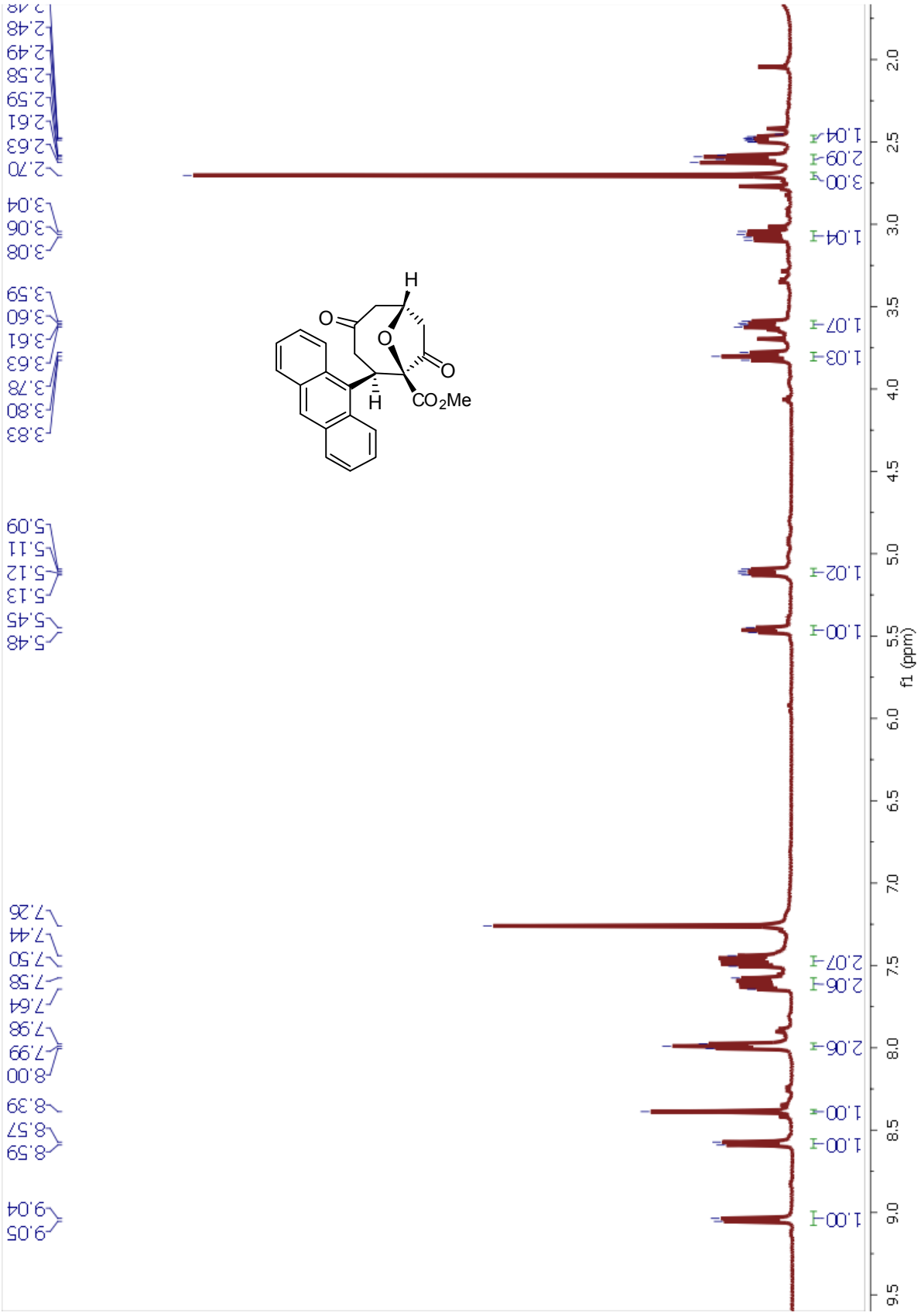


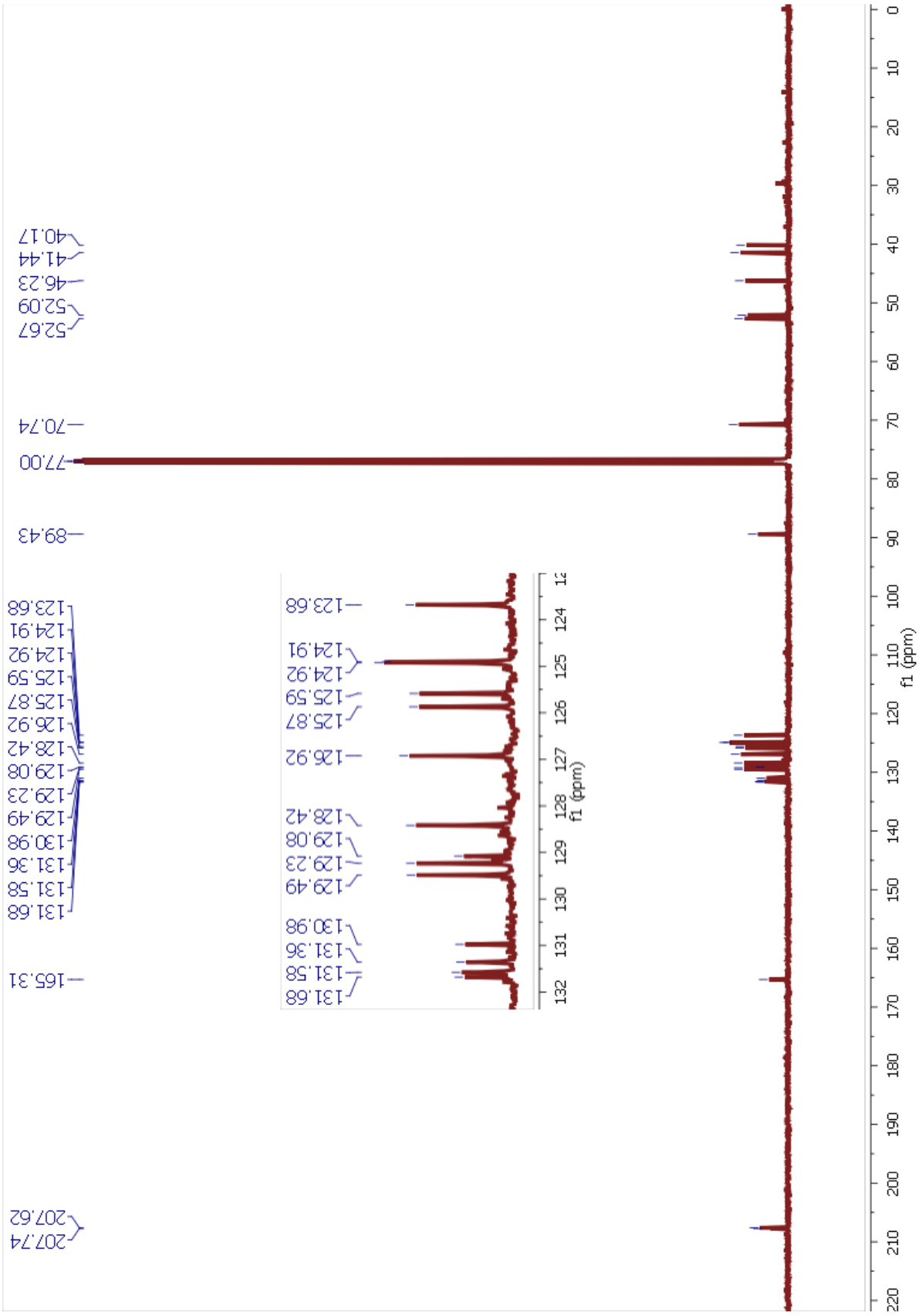

H
O
O
O
O
H
MeO
H3CO
syn
+
H
O
O
O
O
H
MeO
H3CO
anti

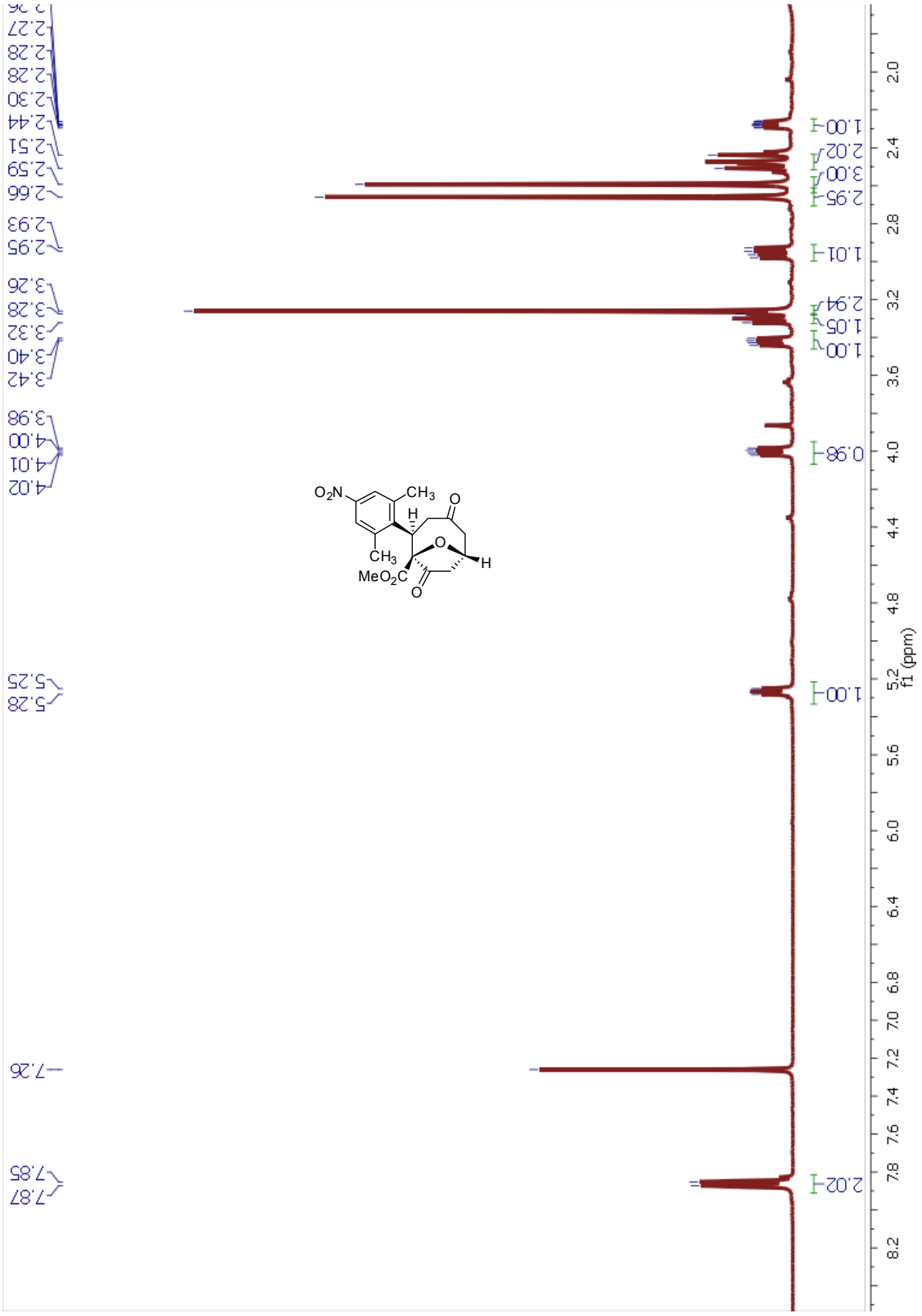


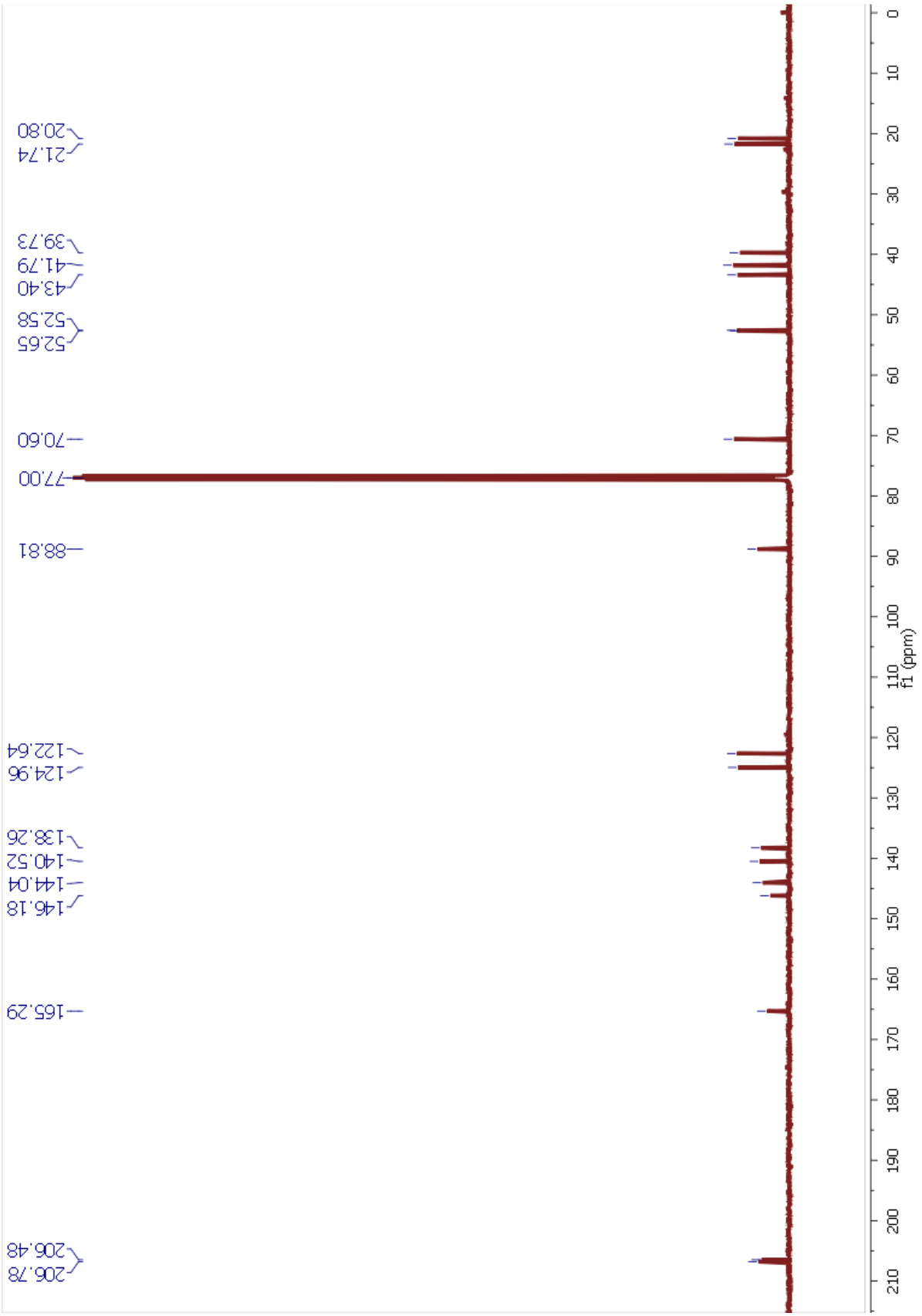

7.260
6.825
6.801
5.240
5.227
5.225
5.222
5.209
3.939
3.926
3.914
3.902
3.399
3.389
3.366
3.343
3.197
2.912
2.895
2.827
2.531
2.442
2.373
2.291
2.208
3.05
2.95
3.08
2.81
1.14
2.67
1.05
0.98
1.01
1.00
2.09
f1 (ppm)


207.707
207.453
165.689
138.354
136.541
136.339
133.009
131.237
129.196
89.522
77.000
70.232
52.623
52.273
44.322
41.671
39.921
21.336
20.615
20.519
f1 (ppm)


2.48
2.49
2.58
2.59
2.61
2.63
2.70
3.04
3.06
3.08
3.59
3.60
3.61
3.63
3.78
3.80
3.83
5.09
5.11
5.12
5.13
5.45
5.48
7.26
7.44
7.50
7.58
7.64
7.98
7.99
8.00
8.39
8.57
8.59
9.04
9.05
1.04
2.09
3.00
1.04
1.07
1.03
1.02
1.00
2.07
2.06
2.06
1.00
1.00
1.00
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
f1 (ppm)
H
O
O
O
H
CO2Me


207.74
207.62
165.31
131.68
131.58
131.36
130.98
129.49
129.23
129.08
128.42
126.92
125.87
125.59
124.92
124.91
123.68
89.43
77.00
70.74
52.67
52.09
46.23
41.44
40.17
f1 (ppm)

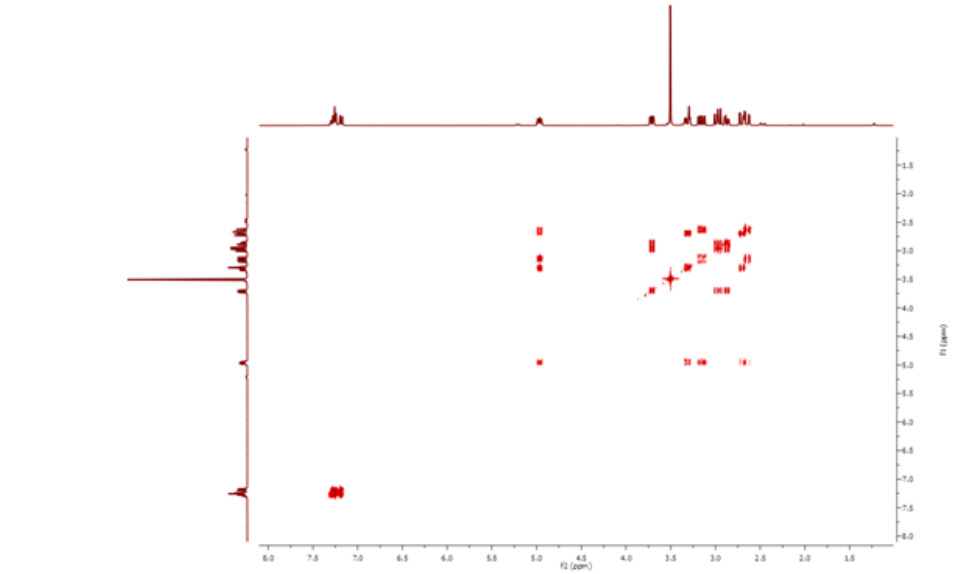

2.27
2.28
2.28
2.30
2.44
2.51
2.59
2.66
2.93
2.95
3.26
3.28
3.32
3.40
3.42
3.98
4.00
4.01
4.02
5.25
5.28
7.26
7.85
7.87
1.00
2.02
3.00
2.95
1.01
2.94
1.05
1.00
0.98
1.00
2.02
2.0
2.4
2.8
3.2
3.6
4.0
4.4
4.8
5.2
5.6
6.0
6.4
6.8
7.0
7.2
7.4
7.6
7.8
8.2
f1 (ppm)
O2N
CH3
H
O
O
H
CH3
MeO2C
O

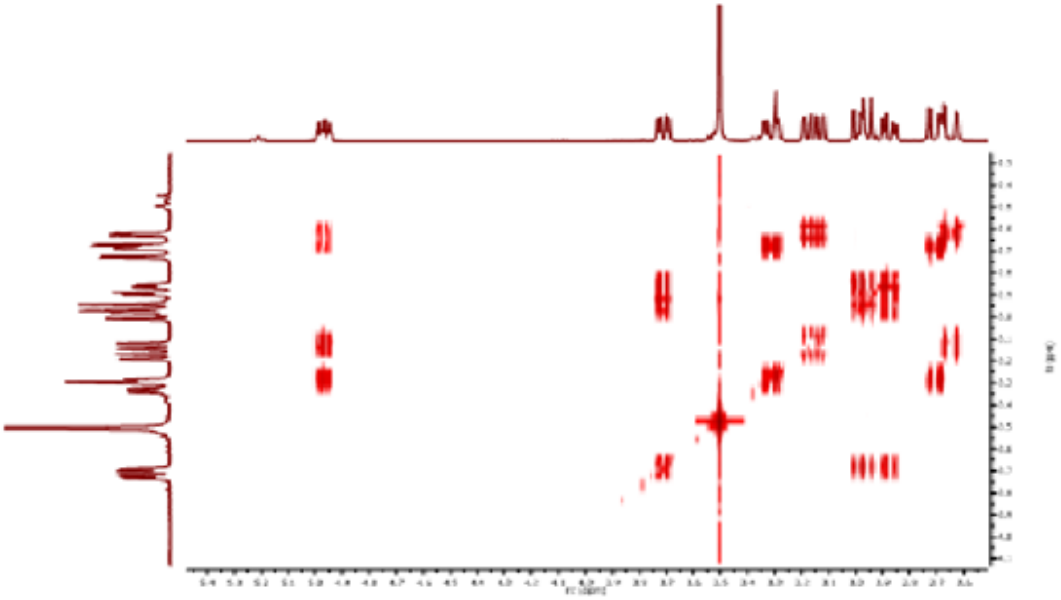

20.80
21.74
39.73
41.79
43.40
52.58
52.65
70.60
77.00
88.81
122.64
124.96
138.26
140.52
144.04
146.18
165.29
206.48
206.78
f1 (ppm)

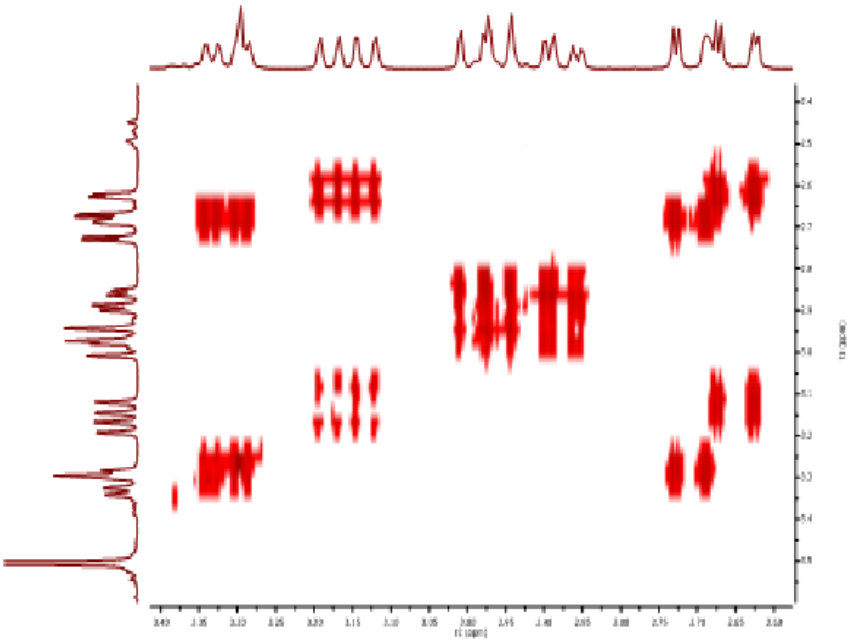
3. 2D spectra and NOE experiments

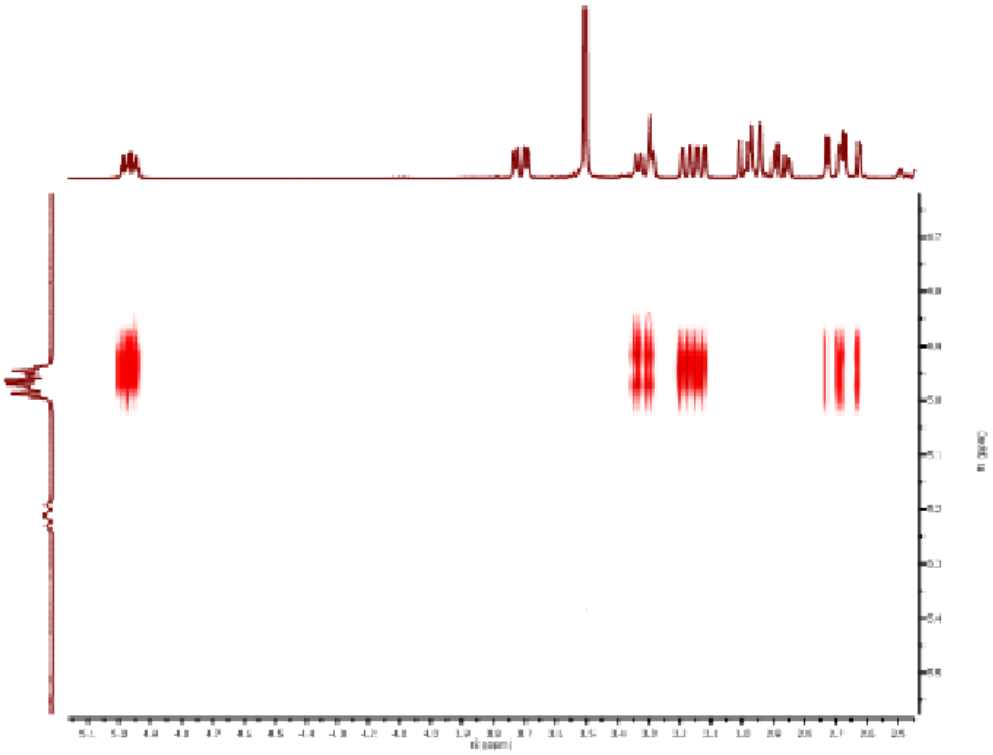
2D NMR spectra for the minor product (1*S**,2*S**,6*R**)-Methyl 4,8-dioxo-2-phenyl-9-oxabicyclo[4.2.1]nonane-1-carboxylate (*anti*-8a)

COSY

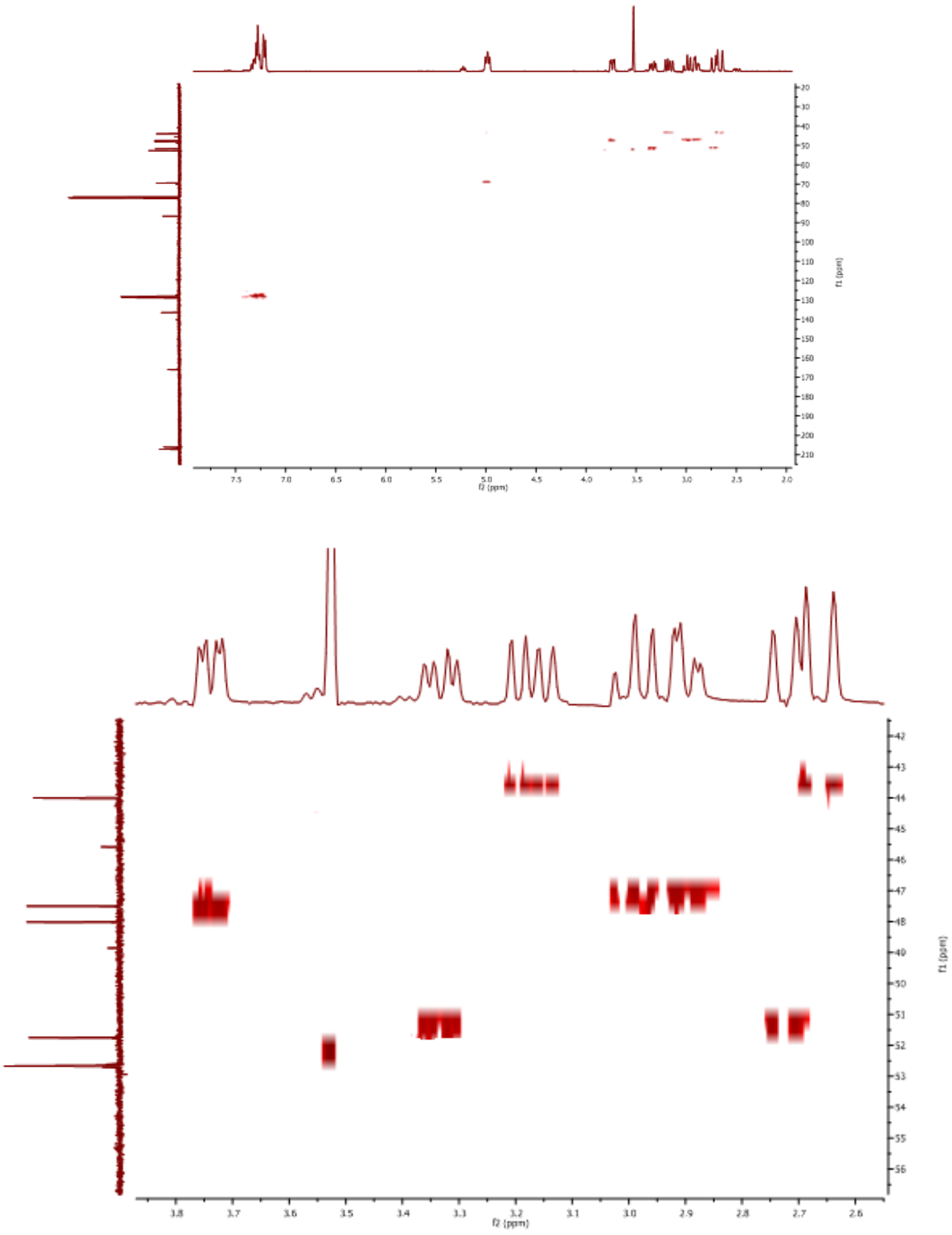




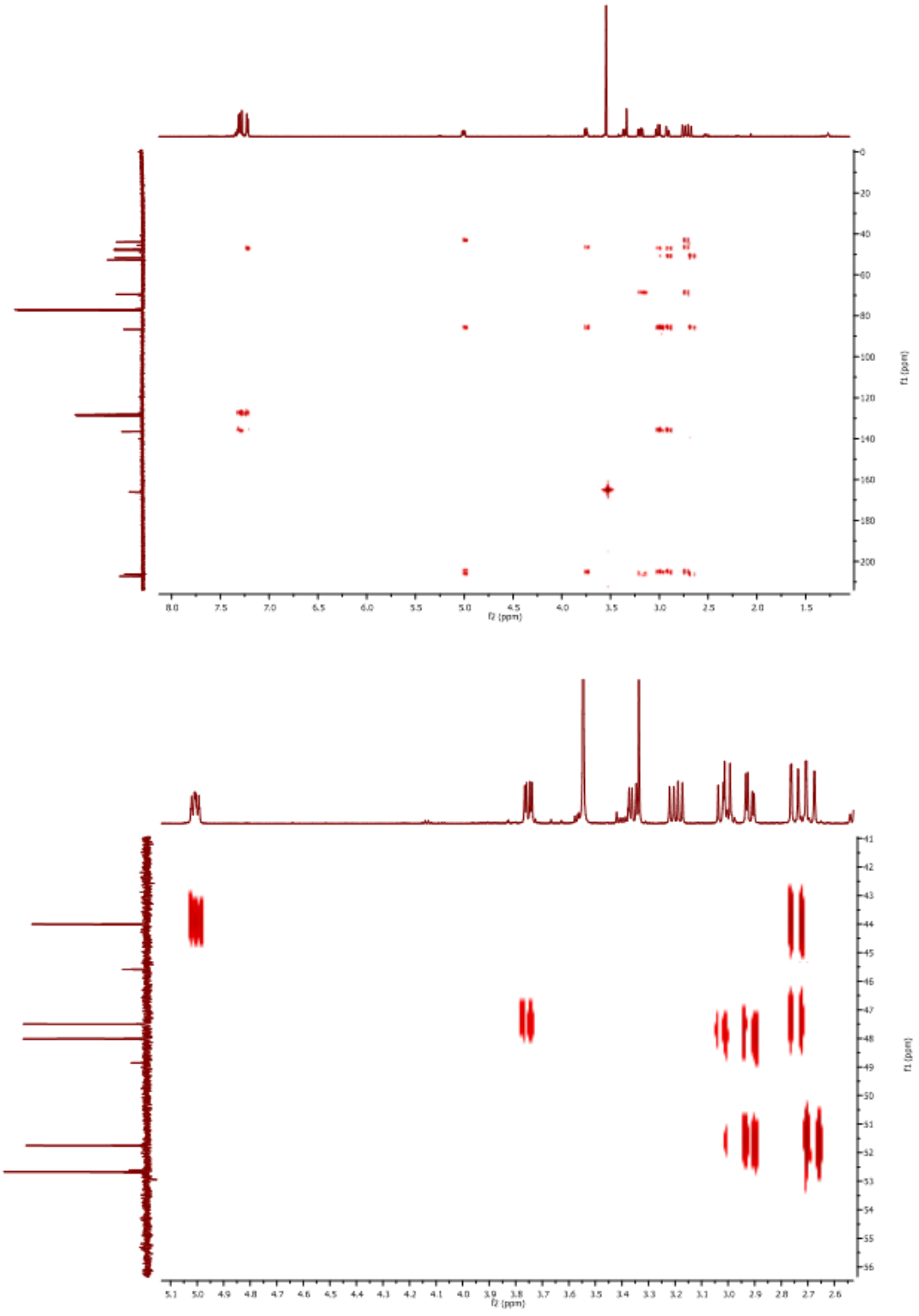


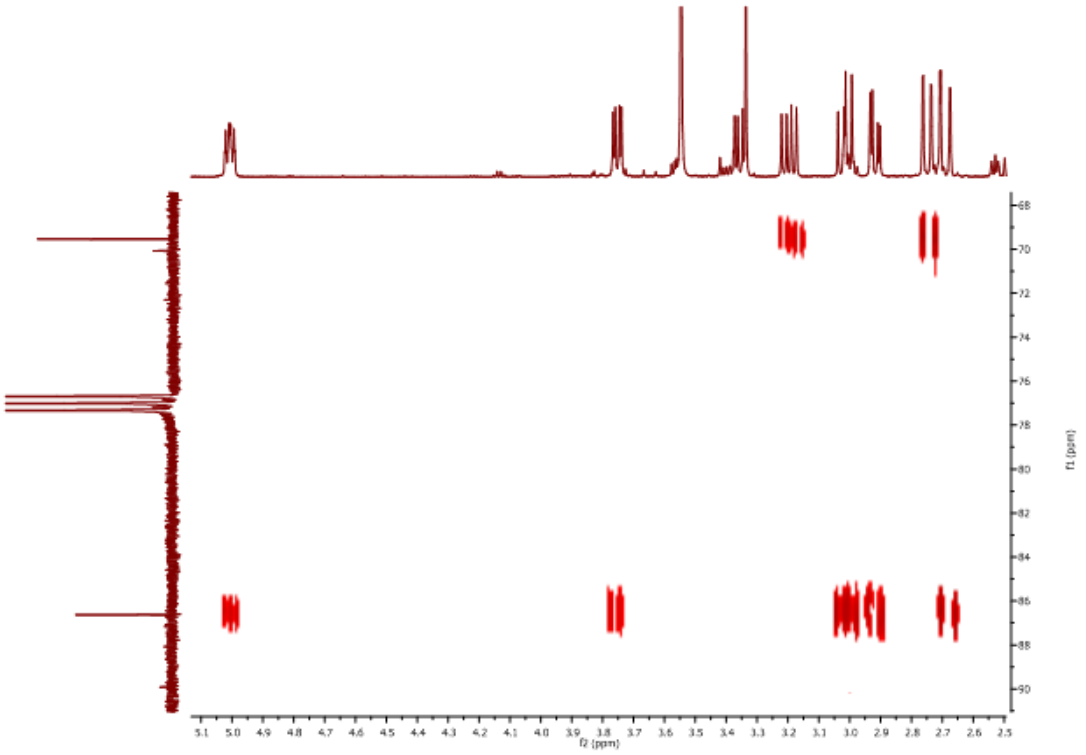


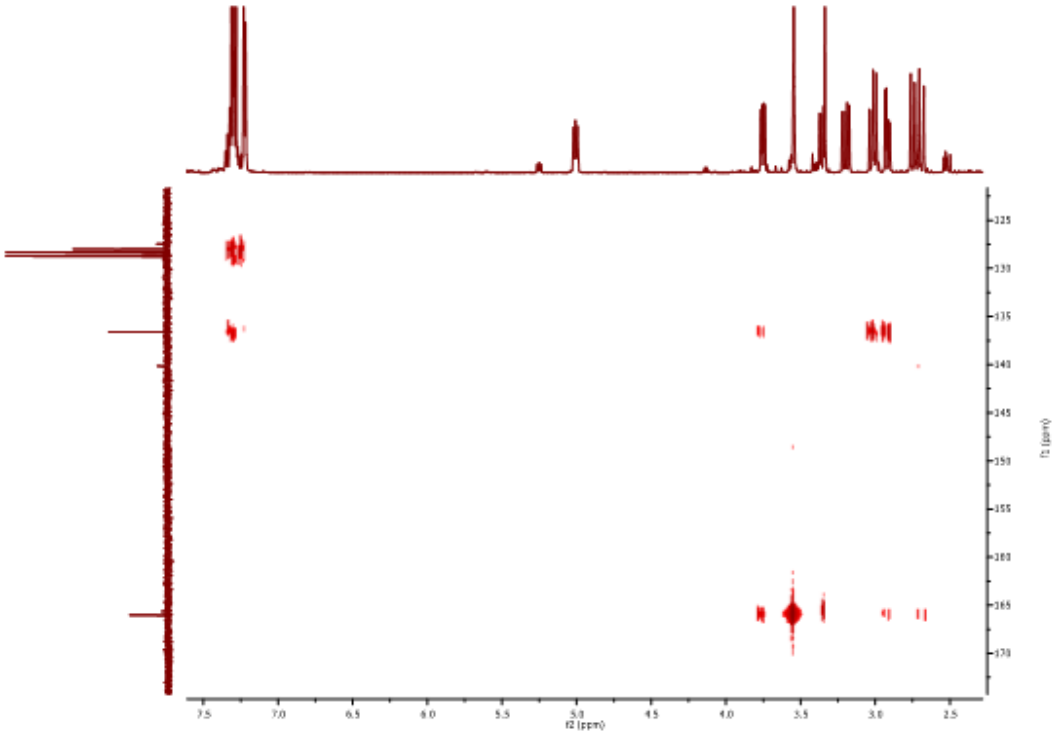
HSQC

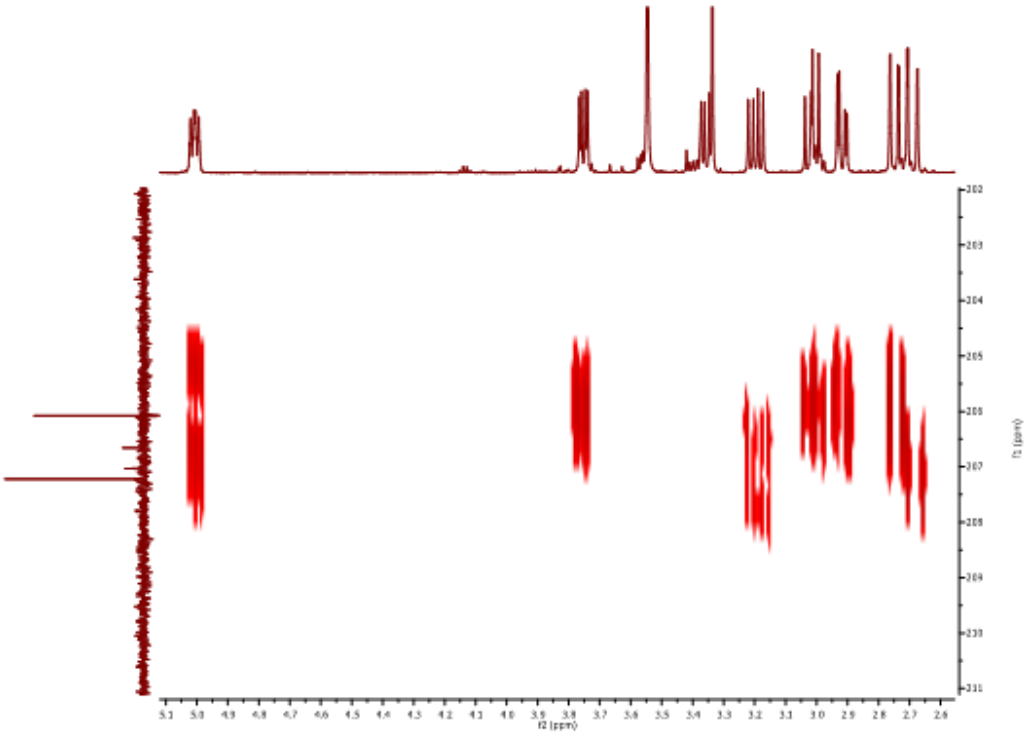


HMBC

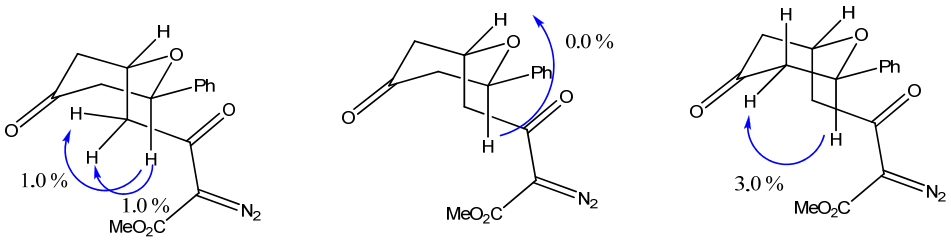



f2 (ppm)
f1 (ppm)

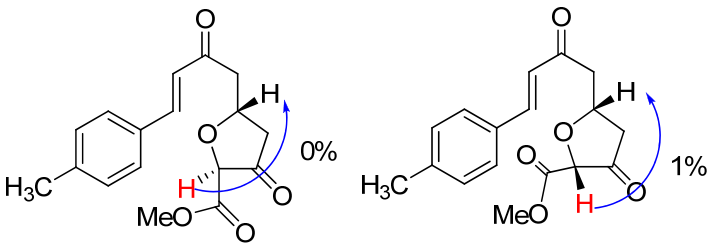

f2 (ppm)
f1 (ppm)



NOE experiments for Mukaiyama-Michael product: Methyl 2-diazo-3-oxo-4-((2*S,6*S**)-4-oxo-6-phenyltetrahyro-2*H*-pyran-2-yl)butanoate (7a)**



NOE experiments for the elimination products: *trans*-9 (major) vs. *cis*-9 (minor)



Major (***trans*-9**) Minor (***cis*-9**)

4. Crystal Structure Data

Compound name : Major product (*syn*-8)
Chemical formula : $C_{16}H_{16}O_5$
Final R_1 [I>2σ(I)] : 3.59 %

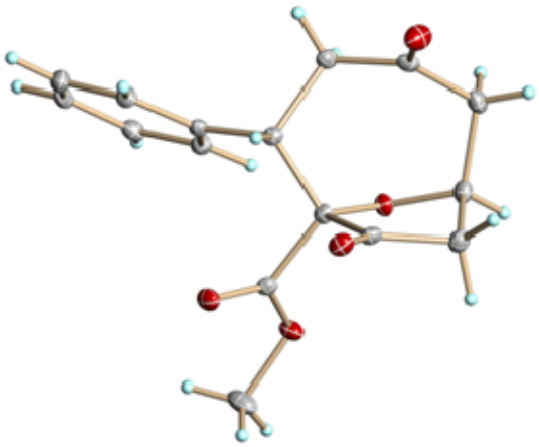


Figure 1. A view of UM#1906 showing the anisotropic atomic displacement ellipsoids for the non-hydrogen atoms are shown at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.

A colorless needle of $C_{16}H_{16}O_5$, approximate dimensions 0.05×0.095×0.53 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 120(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoK α fine-focus sealed tube (λ= 0.71073 Å) . The detector was placed at a distance of 5.0000 cm from the crystal.

A total of 1830 frames were collected with a scan width of -0.3° an exposure time of 60 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 33.5 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 6300 reflections to a maximum θ angle of 27.50°, of which 6300 were independent (completeness = 99.7%, R_{int} = 0.00%, R_{sig} = 2.54%) and 5367 were greater than 2σ(I). The final cell dimensions of a = 10.3115(11) Å, b = 11.0094(12) Å, c = 13.2743(14) Å, α = 89.6028(14)°, β = 67.7337(13)°, γ = 80.3302(14)°, V = 1372.1(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 8296 reflections with 2.2 < θ < 28.3° using Apex2 software. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.945 and 0.995.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group *P-1* with Z = 4 for the formula unit $C_{16}H_{16}O_5$.

The final anisotropic full-matrix least-squares refinement on F^2 with 498 variables converged at R_1 = 3.59 % for the observed data and wR_2 = 7.79 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.354 $\bar{e}/Å^3$ and the largest hole was -0.227 $\bar{e}/Å^3$. On the basis of the final model, the calculated density was 1.396 g/cm^3 and F(000), 608 $\bar{e}$.

Comments:

- Data quality: very good
- Twinning: non-merohedral twinning in about 1:1 ratio by 180 deg. rotation around 001 axis in real space
- Disorder: none
- H-atoms: all refined
- Residual density: in the middle of the bonds
- Structure quality: very good
- Strong data set, no disorder, R_1 4% maximum. Publishable quality.

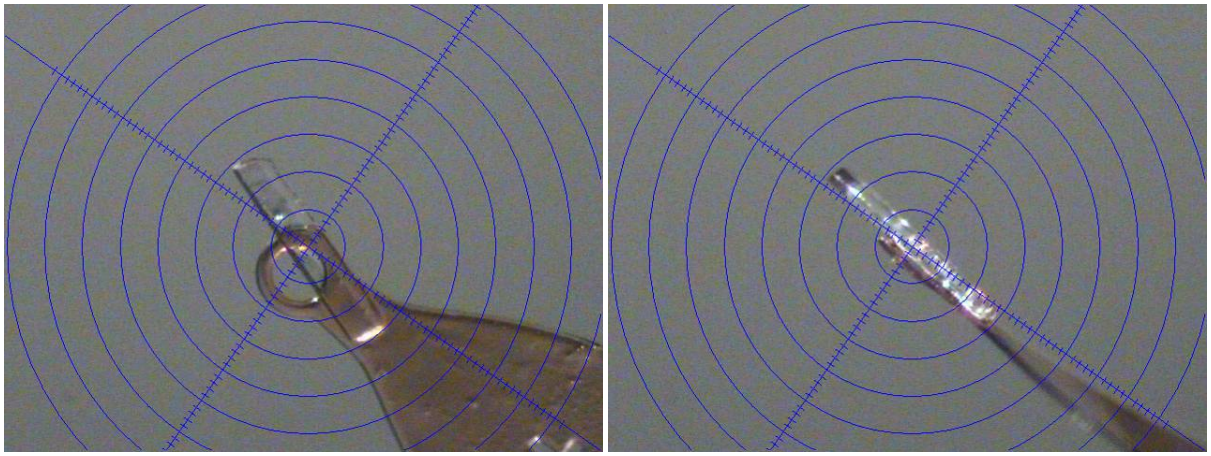


Table 1. Crystal data and structure refinement for UM#1906.

X-ray lab book No.	1906	
Crystal ID	Doyle/DeanaJaber Diazo Decomp-Major product @ 120K	
Empirical formula	C16 H16 O5	
Formula weight	288.29	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal size	0.53×0.095×0.05 mm^3	
Crystal habit	colorless needle	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.3115(11) Å	α = 89.6028(14)°
	b = 11.0094(12) Å	β = 67.7337(13)°
	c = 13.2743(14) Å	γ = 80.3302(14)°
Volume	1372.1(3) Å^3	
Z	4	

Density, ρ_{calc}		1.396 g/cm^3
Absorption coefficient, μ		0.104 mm^{-1}
F(000)		608 $\bar{e}$
Diffractometer		Bruker Smart Apex II CCD area detector
Radiation source		fine-focus sealed tube, MoKα
Detector distance		5.000 cm
Data collection method		ω scans
Total frames		1830
Frame size		1024 pixels
Frame width		-0.3°
Exposure per frame		60 sec
Total measurement time		33.5 hours
θ range for data collection		1.88 to 27.50°
Index ranges		$-12 \le h \le 13$, $-14 \le k \le 14$, $0 \le l \le 17$
Reflections collected		6300
Independent reflections		6300
Observed reflection, I>2σ(I)		5367
Coverage of independent reflections		99.7 %
Variation in check reflections		0 %
Absorption correction		Semi-empirical from equivalents SADABS (Sheldrick, 1996)
Max. and min. transmission		0.995 and 0.945
Structure solution technique		direct
Structure solution program		SHELXS-97 (Sheldrick, 1990)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 1997)
Function minimized		$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters		6300 / 0 / 498
Goodness-of-fit on F^2		1.000
Δ/σ_{max}		0.000
Final R indices:	R_1, I>2σ(I)	0.0359
	wR_2, all data	0.0779
	R_{int}	0.0000
	R_{sig}	0.0254
Weighting scheme		$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.562P]$, $P = [\max(F_o^2, 0) + 2F_o^2]/3$
Largest diff. peak and hole		0.354 and -0.227 $\bar{e}$/Å^3

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates and equivalent* isotropic atomic displacement parameters (Å^2) for UM#1906.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C1A	0.22635(16)	0.32619(14)	0.25043(12)	0.0206(3)
C2A	0.10385(16)	0.32845(15)	0.22948(13)	0.0231(3)
C3A	0.05685(16)	0.42586(16)	0.17739(13)	0.0248(3)
C4A	0.13135(17)	0.52299(15)	0.14907(13)	0.0256(3)
C5A	0.25254(16)	0.52239(14)	0.17139(13)	0.0212(3)
C6A	0.30221(15)	0.42319(13)	0.22102(12)	0.0176(3)
C7A	0.44285(15)	0.41846(13)	0.23378(12)	0.0171(3)
C8A	0.55910(16)	0.33459(15)	0.13711(13)	0.0213(3)
C9A	0.70306(16)	0.30808(15)	0.14566(12)	0.0218(3)
O9A	0.79052(12)	0.37467(12)	0.10687(10)	0.0323(3)
C10A	0.73173(17)	0.19566(15)	0.20587(14)	0.0235(3)
C11A	0.63514(16)	0.21148(14)	0.32752(13)	0.0221(3)

O11A	0.48554(10)	0.24223(9)	0.34222(9)	0.0196(2)
C12A	0.65908(17)	0.31795(15)	0.38644(14)	0.0235(3)
C13A	0.55991(16)	0.42593(14)	0.37052(12)	0.0190(3)
O13A	0.56593(12)	0.53390(10)	0.37454(9)	0.0239(2)
C14A	0.44513(15)	0.37263(12)	0.34424(12)	0.0172(3)
C15A	0.30217(15)	0.41986(13)	0.43701(12)	0.0186(3)
O15A	0.24458(12)	0.52596(10)	0.44725(9)	0.0255(2)
O16A	0.25329(12)	0.33268(10)	0.50378(9)	0.0235(2)
C16A	0.1223(2)	0.37689(18)	0.59645(16)	0.0351(4)
C1B	0.75571(16)	0.17931(14)	0.59334(13)	0.0189(3)
C2B	0.87838(16)	0.17725(14)	0.50000(13)	0.0221(3)
C3B	0.92517(16)	0.07956(15)	0.42193(13)	0.0227(3)
C4B	0.84949(17)	-0.01639(15)	0.43792(13)	0.0236(3)
C5B	0.72800(16)	-0.01621(14)	0.53176(12)	0.0200(3)
C6B	0.67989(15)	0.08222(13)	0.61008(12)	0.0169(3)
C7B	0.54159(15)	0.08455(13)	0.70790(12)	0.0165(3)
C8B	0.41969(16)	0.16512(15)	0.68290(13)	0.0209(3)
C9B	0.28052(16)	0.19378(15)	0.78089(13)	0.0221(3)
O9B	0.19379(12)	0.12532(11)	0.80412(10)	0.0312(3)
C10B	0.25798(17)	0.30945(15)	0.85096(14)	0.0236(3)
C11B	0.35803(15)	0.29395(14)	0.91300(13)	0.0203(3)
O11B	0.50630(10)	0.26108(9)	0.83760(9)	0.0186(2)
C12B	0.33458(17)	0.18785(14)	0.98812(13)	0.0213(3)
C13B	0.42953(14)	0.07910(13)	0.91426(11)	0.0163(3)
O13B	0.42212(11)	-0.02891(9)	0.92336(9)	0.0203(2)
C14B	0.54361(14)	0.13076(13)	0.81785(11)	0.0157(3)
C15B	0.68689(14)	0.08060(13)	0.82595(11)	0.0162(3)
O15B	0.74416(11)	-0.02539(9)	0.80080(9)	0.0209(2)
O16B	0.73513(11)	0.16505(9)	0.86709(9)	0.0210(2)
C16B	0.86695(17)	0.11881(17)	0.88156(15)	0.0278(4)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic atomic displacement parameters* ($Å^2$) for UM#1906.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1A	0.0239(8)	0.0183(7)	0.0202(7)	-0.0005(6)	-0.0089(6)	-0.0041(6)
C2A	0.0197(7)	0.0237(8)	0.0242(8)	-0.0041(6)	-0.0053(6)	-0.0064(6)
C3A	0.0168(7)	0.0329(9)	0.0227(8)	-0.0054(7)	-0.0075(6)	0.0007(6)
C4A	0.0249(8)	0.0273(8)	0.0234(8)	0.0021(7)	-0.0101(6)	0.0008(6)
C5A	0.0231(7)	0.0189(7)	0.0210(7)	0.0027(6)	-0.0076(6)	-0.0038(6)
C6A	0.0185(7)	0.0184(7)	0.0154(7)	-0.0026(5)	-0.0067(6)	-0.0015(5)
C7A	0.0205(7)	0.0153(7)	0.0173(7)	0.0012(5)	-0.0082(6)	-0.0056(5)
C8A	0.0210(7)	0.0256(8)	0.0187(7)	-0.0018(6)	-0.0088(6)	-0.0046(6)
C9A	0.0207(7)	0.0264(8)	0.0169(7)	-0.0056(6)	-0.0054(6)	-0.0046(6)
O9A	0.0274(6)	0.0427(7)	0.0315(6)	0.0075(5)	-0.0123(5)	-0.0162(5)
C10A	0.0195(7)	0.0223(8)	0.0283(8)	-0.0043(7)	-0.0098(6)	-0.0010(6)
C11A	0.0223(7)	0.0178(7)	0.0276(8)	0.0027(6)	-0.0118(6)	-0.0018(6)
O11A	0.0200(5)	0.0128(5)	0.0254(5)	0.0010(4)	-0.0082(4)	-0.0020(4)
C12A	0.0254(8)	0.0243(8)	0.0245(8)	0.0010(6)	-0.0138(7)	-0.0037(6)
C13A	0.0240(7)	0.0204(7)	0.0142(7)	0.0007(5)	-0.0084(6)	-0.0057(6)
O13A	0.0332(6)	0.0186(5)	0.0244(6)	0.0005(4)	-0.0141(5)	-0.0091(4)
C14A	0.0222(7)	0.0111(6)	0.0195(7)	0.0008(5)	-0.0090(6)	-0.0037(5)
C15A	0.0233(7)	0.0173(7)	0.0168(7)	-0.0006(5)	-0.0091(6)	-0.0047(6)

O15A	0.0306(6)	0.0167(5)	0.0252(6)	-0.0008(4)	-0.0080(5)	-0.0001(4)
O16A	0.0263(6)	0.0178(5)	0.0201(5)	0.0006(4)	-0.0018(4)	-0.0039(4)
C16A	0.0352(10)	0.0267(9)	0.0283(9)	-0.0001(7)	0.0044(8)	-0.0049(8)
C1B	0.0206(7)	0.0159(7)	0.0200(7)	0.0009(6)	-0.0082(6)	-0.0013(5)
C2B	0.0211(7)	0.0200(7)	0.0256(8)	0.0077(6)	-0.0093(6)	-0.0042(6)
C3B	0.0181(7)	0.0249(8)	0.0201(7)	0.0052(6)	-0.0041(6)	0.0016(6)
C4B	0.0269(8)	0.0212(8)	0.0192(7)	-0.0014(6)	-0.0076(6)	0.0021(6)
C5B	0.0234(7)	0.0171(7)	0.0201(7)	0.0017(6)	-0.0096(6)	-0.0026(6)
C6B	0.0186(7)	0.0166(7)	0.0157(7)	0.0025(5)	-0.0075(5)	-0.0017(5)
C7B	0.0176(7)	0.0150(7)	0.0170(7)	0.0017(5)	-0.0063(6)	-0.0043(5)
C8B	0.0220(7)	0.0233(8)	0.0192(7)	0.0023(6)	-0.0105(6)	-0.0030(6)
C9B	0.0185(7)	0.0262(8)	0.0240(8)	0.0033(6)	-0.0120(6)	-0.0011(6)
O9B	0.0229(6)	0.0367(7)	0.0369(7)	0.0015(5)	-0.0125(5)	-0.0104(5)
C10B	0.0191(7)	0.0216(8)	0.0269(8)	0.0021(7)	-0.0070(6)	0.0001(6)
C11B	0.0183(7)	0.0172(7)	0.0224(7)	-0.0030(6)	-0.0052(6)	-0.0016(5)
O11B	0.0166(5)	0.0137(5)	0.0236(5)	-0.0008(4)	-0.0056(4)	-0.0021(4)
C12B	0.0208(7)	0.0222(8)	0.0183(7)	-0.0018(6)	-0.0054(6)	-0.0015(6)
C13B	0.0166(6)	0.0202(7)	0.0148(7)	0.0009(5)	-0.0085(5)	-0.0044(5)
O13B	0.0233(5)	0.0189(5)	0.0204(5)	0.0030(4)	-0.0086(4)	-0.0075(4)
C14B	0.0168(7)	0.0136(6)	0.0167(7)	0.0001(5)	-0.0061(5)	-0.0031(5)
C15B	0.0174(7)	0.0176(7)	0.0127(6)	0.0016(5)	-0.0038(5)	-0.0051(5)
O15B	0.0212(5)	0.0183(5)	0.0212(5)	0.0001(4)	-0.0071(4)	-0.0002(4)
O16B	0.0187(5)	0.0213(5)	0.0253(6)	-0.0009(4)	-0.0102(4)	-0.0053(4)
C16B	0.0197(8)	0.0337(9)	0.0329(9)	-0.0028(8)	-0.0135(7)	-0.0045(7)

* The anisotropic atomic displacement factor exponent takes the form:$-2\pi^2$ [$h^2a^{*2}U_{11}$ +... + 2hka*b*U_{12}]

Table 4. Hydrogen atom coordinates and isotropic atomic displacement parameters (Å^2) for UM#1906.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H1A	0.2612(19)	0.2561(17)	0.2840(15)	0.026(5)
H2A	0.0540(19)	0.2605(16)	0.2497(15)	0.027(5)
H3A	-0.027(2)	0.4264(17)	0.1620(15)	0.030(5)
H4A	0.100(2)	0.5921(18)	0.1124(16)	0.032(5)
H5A	0.3014(18)	0.5917(16)	0.1536(14)	0.024(4)
H7A	0.4636(16)	0.5008(15)	0.2304(13)	0.014(4)
H8A	0.5252(18)	0.2558(16)	0.1366(15)	0.025(3)
H8B	0.5689(18)	0.3734(16)	0.0710(15)	0.025(3)
H10A	0.8335(19)	0.1817(16)	0.1959(14)	0.025(3)
H10B	0.7126(18)	0.1247(17)	0.1729(15)	0.025(3)
H11A	0.6451(18)	0.1326(16)	0.3624(15)	0.025(4)
H12A	0.625(2)	0.3082(17)	0.4661(16)	0.032(4)
H12B	0.757(2)	0.3350(17)	0.3586(15)	0.032(4)
H16A	0.136(2)	0.440(2)	0.6374(17)	0.040(3)
H16B	0.099(2)	0.305(2)	0.6394(17)	0.040(3)
H16C	0.048(2)	0.4117(19)	0.5728(17)	0.040(3)
H1B	0.7235(18)	0.2463(16)	0.6444(14)	0.021(4)
H2B	0.9319(19)	0.2444(17)	0.4890(15)	0.029(5)
H3B	1.0141(19)	0.0769(16)	0.3563(15)	0.025(5)
H4B	0.8782(19)	-0.0849(17)	0.3842(15)	0.027(5)
H5B	0.6777(19)	-0.0857(17)	0.5412(15)	0.029(5)
H7B	0.5236(17)	0.0018(15)	0.7187(13)	0.016(4)
H8C	0.4046(19)	0.1212(17)	0.6253(15)	0.028(3)
H8D	0.4496(19)	0.2411(17)	0.6556(15)	0.028(3)

H10C	0.2769(19)	0.3763(17)	0.8047(15)	0.025(3)
H10D	0.1607(19)	0.3261(16)	0.9036(15)	0.025(3)
H11B	0.3524(18)	0.3729(16)	0.9486(14)	0.022(4)
H12C	0.2373(19)	0.1752(16)	1.0226(14)	0.023(3)
H12D	0.3718(18)	0.1969(16)	1.0446(15)	0.023(3)
H16D	0.941(2)	0.0859(18)	0.8126(18)	0.040(3)
H16E	0.892(2)	0.1892(19)	0.9091(17)	0.040(3)
H16F	0.850(2)	0.0550(19)	0.9367(17)	0.040(3)

Table 5. Bond lengths (Å) and angles (°) for UM#1906.

C1A-C2A	1.389(2)	C1A-C6A	1.396(2)	C1A-H1A	0.973(18)
C2A-C3A	1.390(2)	C2A-H2A	0.959(18)	C3A-C4A	1.388(2)
C3A-H3A	0.963(19)	C4A-C5A	1.388(2)	C4A-H4A	0.977(19)
C5A-C6A	1.395(2)	C5A-H5A	0.963(17)	C6A-C7A	1.515(2)
C7A-C8A	1.554(2)	C7A-C14A	1.555(2)	C7A-H7A	0.962(16)
C8A-C9A	1.511(2)	C8A-H8A	0.990(18)	C8A-H8B	0.951(18)
C9A-O9A	1.2170(19)	C9A-C10A	1.517(2)	C10A-C11A	1.535(2)
C10A-H10A	0.991(18)	C10A-H10B	0.981(19)	C11A-O11A	1.4593(18)
C11A-C12A	1.517(2)	C11A-H11A	0.990(18)	O11A-C14A	1.4235(16)
C12A-C13A	1.502(2)	C12A-H12A	0.99(2)	C12A-H12B	0.982(19)
C13A-O13A	1.2032(18)	C13A-C14A	1.554(2)	C14A-C15A	1.528(2)
C15A-O15A	1.2015(18)	C15A-O16A	1.3316(17)	O16A-C16A	1.450(2)
C16A-H16A	0.94(2)	C16A-H16B	0.98(2)	C16A-H16C	0.96(2)
C1B-C2B	1.392(2)	C1B-C6B	1.396(2)	C1B-H1B	0.931(18)
C2B-C3B	1.388(2)	C2B-H2B	0.974(18)	C3B-C4B	1.385(2)
C3B-H3B	0.993(18)	C4B-C5B	1.392(2)	C4B-H4B	0.969(19)
C5B-C6B	1.395(2)	C5B-H5B	0.976(18)	C6B-C7B	1.5183(19)
C7B-C8B	1.554(2)	C7B-C14B	1.558(2)	C7B-H7B	0.959(16)
C8B-C9B	1.513(2)	C8B-H8C	0.98(2)	C8B-H8D	0.961(19)
C9B-O9B	1.2155(19)	C9B-C10B	1.515(2)	C10B-C11B	1.534(2)
C10B-H10C	0.953(18)	C10B-H10D	0.968(18)	C11B-O11B	1.4594(17)
C11B-C12B	1.521(2)	C11B-H11B	0.975(18)	O11B-C14B	1.4207(16)
C12B-C13B	1.499(2)	C12B-H12C	0.966(18)	C12B-H12D	0.976(19)
C13B-O13B	1.2067(17)	C13B-C14B	1.5553(19)	C14B-C15B	1.5313(19)
C15B-O15B	1.2026(17)	C15B-O16B	1.3336(17)	O16B-C16B	1.4518(19)
C16B-H16D	0.97(2)	C16B-H16E	0.97(2)	C16B-H16F	1.00(2)

C2A-C1A-C6A	120.16(15)	C2A-C1A-H1A	120.3(11)	C6A-C1A-H1A	119.5(11)
C1A-C2A-C3A	120.55(15)	C1A-C2A-H2A	118.8(11)	C3A-C2A-H2A	120.7(11)
C4A-C3A-C2A	119.35(15)	C4A-C3A-H3A	120.4(11)	C2A-C3A-H3A	120.3(11)
C3A-C4A-C5A	120.41(15)	C3A-C4A-H4A	120.3(11)	C5A-C4A-H4A	119.3(11)
C4A-C5A-C6A	120.39(14)	C4A-C5A-H5A	119.6(10)	C6A-C5A-H5A	120.0(10)
C5A-C6A-C1A	119.10(14)	C5A-C6A-C7A	119.29(13)	C1A-C6A-C7A	121.44(13)
C6A-C7A-C8A	107.42(12)	C6A-C7A-C14A	114.90(12)	C8A-C7A-C14A	110.42(12)
C6A-C7A-H7A	108.6(9)	C8A-C7A-H7A	109.8(10)	C14A-C7A-H7A	105.7(10)
C9A-C8A-C7A	113.75(12)	C9A-C8A-H8A	108.9(10)	C7A-C8A-H8A	106.8(10)
C9A-C8A-H8B	108.7(11)	C7A-C8A-H8B	108.8(11)	H8A-C8A-H8B	109.8(15)
O9A-C9A-C8A	121.31(15)	O9A-C9A-C10A	122.05(15)	C8A-C9A-C10A	116.63(13)
C9A-C10A-C11A	111.75(13)	C9A-C10A-H10A	108.3(10)	C11A-C10A-H10A	110.8(10)
C9A-C10A-H10B	107.6(11)	C11A-C10A-H10B	108.8(11)	H10A-C10A-H10B	109.5(15)
O11A-C11A-C12A	104.56(12)	O11A-C11A-C10A	110.79(13)	C12A-C11A-C10A	112.79(13)
O11A-C11A-H11A	105.8(10)	C12A-C11A-H11A	112.4(11)	C10A-C11A-H11A	110.1(10)
C14A-O11A-C11A	109.51(11)	C13A-C12A-C11A	102.82(12)	C13A-C12A-H12A	106.2(11)
C11A-C12A-H12A	111.2(11)	C13A-C12A-H12B	109.8(11)	C11A-C12A-H12B	115.7(11)
H12A-C12A-H12B	110.5(15)	O13A-C13A-C12A	128.28(14)	O13A-C13A-C14A	124.80(13)
C12A-C13A-C14A	106.90(12)	O11A-C14A-C15A	111.72(11)	O11A-C14A-C13A	104.75(11)
C15A-C14A-C13A	106.84(12)	O11A-C14A-C7A	113.17(12)	C15A-C14A-C7A	110.41(12)
C13A-C14A-C7A	109.60(11)	O15A-C15A-O16A	125.26(14)	O15A-C15A-C14A	121.76(13)
O16A-C15A-C14A	112.96(12)	C15A-O16A-C16A	114.05(12)	O16A-C16A-H16A	109.8(13)

O16A-C16A-H16B	106.2(12)	H16A-C16A-H16B	111.4(18)	O16A-C16A-H16C	110.8(13)
H16A-C16A-H16C	107.5(18)	H16B-C16A-H16C	111.3(17)	C2B-C1B-C6B	120.33(14)
C2B-C1B-H1B	119.8(10)	C6B-C1B-H1B	119.9(10)	C3B-C2B-C1B	120.29(14)
C3B-C2B-H2B	119.5(11)	C1B-C2B-H2B	120.2(11)	C4B-C3B-C2B	119.49(14)
C4B-C3B-H3B	120.1(10)	C2B-C3B-H3B	120.3(10)	C3B-C4B-C5B	120.69(15)
C3B-C4B-H4B	121.4(11)	C5B-C4B-H4B	117.9(11)	C4B-C5B-C6B	120.05(14)
C4B-C5B-H5B	118.8(11)	C6B-C5B-H5B	121.1(11)	C5B-C6B-C1B	119.15(14)
C5B-C6B-C7B	119.03(13)	C1B-C6B-C7B	121.72(13)	C6B-C7B-C8B	108.16(12)
C6B-C7B-C14B	114.57(12)	C8B-C7B-C14B	110.65(12)	C6B-C7B-H7B	108.7(10)
C8B-C7B-H7B	109.6(10)	C14B-C7B-H7B	105.0(10)	C9B-C8B-C7B	113.56(12)
C9B-C8B-H8C	109.0(10)	C7B-C8B-H8C	108.3(11)	C9B-C8B-H8D	109.3(11)
C7B-C8B-H8D	108.5(11)	H8C-C8B-H8D	108.1(15)	O9B-C9B-C8B	121.69(15)
O9B-C9B-C10B	121.85(15)	C8B-C9B-C10B	116.41(13)	C9B-C10B-C11B	111.02(12)
C9B-C10B-H10C	108.4(11)	C11B-C10B-H10C	109.3(11)	C9B-C10B-H10D	109.4(11)
C11B-C10B-H10D	108.5(11)	H10C-C10B-H10D	110.3(15)	O11B-C11B-C12B	104.49(11)
O11B-C11B-C10B	110.75(12)	C12B-C11B-C10B	112.21(13)	O11B-C11B-H11B	104.7(10)
C12B-C11B-H11B	114.6(10)	C10B-C11B-H11B	109.7(10)	C14B-O11B-C11B	109.46(10)
C13B-C12B-C11B	102.67(12)	C13B-C12B-H12C	112.1(11)	C11B-C12B-H12C	115.7(10)
C13B-C12B-H12D	106.3(10)	C11B-C12B-H12D	110.9(10)	H12C-C12B-H12D	108.6(14)
O13B-C13B-C12B	128.67(13)	O13B-C13B-C14B	124.43(13)	C12B-C13B-C14B	106.89(12)
O11B-C14B-C15B	111.85(11)	O11B-C14B-C13B	104.85(11)	C15B-C14B-C13B	105.96(11)
O11B-C14B-C7B	113.47(11)	C15B-C14B-C7B	110.72(11)	C13B-C14B-C7B	109.53(11)
O15B-C15B-O16B	125.27(13)	O15B-C15B-C14B	121.94(13)	O16B-C15B-C14B	112.74(12)
C15B-O16B-C16B	114.22(12)	O16B-C16B-H16D	110.3(12)	O16B-C16B-H16E	105.9(12)
H16D-C16B-H16E	110.2(17)	O16B-C16B-H16F	108.9(12)	H16D-C16B-H16F	111.5(16)
H16E-C16B-H16F	109.8(17)				

Table 6. Torsion angles (°) in UM#1906 compared for molecules A and B.

Angle	A	B
C6 - C1 - C2 - C3	1.2(2)	1.0(2)
C1 - C2 - C3 - C4	-1.8(2)	-0.5(2)
C2 - C3 - C4 - C5	0.7(2)	-0.6(2)
C3 - C4 - C5 - C6	1.0(2)	1.1(2)
C4 - C5 - C6 - C1	-1.6(2)	-0.5(2)
C4 - C5 - C6 - C7	173.67(14)	175.83(13)
C2 - C1 - C6 - C5	0.6(2)	-0.5(2)
C2 - C1 - C6 - C7	-174.65(14)	-176.75(14)
C5 - C6 - C7 - C8	-96.87(16)	-95.75(15)
C1 - C6 - C7 - C8	78.33(17)	80.51(17)
C5 - C6 - C7 - C14	139.84(14)	140.34(14)
C1 - C6 - C7 - C14	-44.95(19)	-43.41(19)
C6 - C7 - C8 - C9	-173.00(13)	-169.83(13)
C14 - C7 - C8 - C9	-47.00(17)	-43.59(17)
C7 - C8 - C9 - O9	-90.04(18)	-88.13(18)
C7 - C8 - C9 - C10	89.29(17)	89.41(17)
O9 - C9 - C10 - C11	113.11(17)	107.94(17)
C8 - C9 - C10 - C11	-66.22(18)	-69.60(17)
C9 - C10 - C11 - O11	54.44(17)	56.28(17)
C9 - C10 - C11 - C12	-62.38(17)	-60.05(17)
C12 - C11 - O11 - C14	33.33(15)	33.45(15)
C10 - C11 - O11 - C14	-88.45(14)	-87.57(14)
O11 - C11 - C12 - C13	-32.55(15)	-32.87(15)
C10 - C11 - C12 - C13	87.91(15)	87.17(14)
C11 - C12 - C13 - O13	-157.51(16)	-157.40(15)
C11 - C12 - C13 - C14	21.19(16)	21.58(15)
C11 - O11 - C14 - C15	-134.58(12)	-133.57(12)

C11 - O11 - C14 - C13	-19.29(14)	-19.19(14)
C11 - O11 - C14 - C7	100.05(14)	100.30(13)
O13 - C13 - C14 - O11	176.63(14)	176.56(13)
C12 - C13 - C14 - O11	-2.13(15)	-2.48(14)
O13 - C13 - C14 - C15	-64.72(18)	-65.00(17)
C12 - C13 - C14 - C15	116.52(13)	115.97(12)
O13 - C13 - C14 - C7	54.92(19)	54.46(18)
C12 - C13 - C14 - C7	-123.84(13)	-124.57(12)
C6 - C7 - C14 - O11	89.18(15)	86.99(14)
C8 - C7 - C14 - O11	-32.49(16)	-35.60(15)
C6 - C7 - C14 - C15	-36.88(16)	-39.74(16)
C8 - C7 - C14 - C15	-158.55(12)	-162.32(11)
C6 - C7 - C14 - C13	-154.31(12)	-156.23(12)
C8 - C7 - C14 - C13	84.02(14)	81.18(14)
O11 - C14 - C15 - O15	-174.18(13)	-172.05(12)
C13 - C14 - C15 - O15	71.81(17)	74.25(16)
C7 - C14 - C15 - O15	-47.30(19)	-44.43(18)
O11 - C14 - C15 - O16	7.28(17)	10.44(16)
C13 - C14 - C15 - O16	-106.73(13)	-103.26(13)
C7 - C14 - C15 - O16	134.16(13)	138.06(12)
O15 - C15 - O16 - C16	-2.2(2)	-0.6(2)
C14 - C15 - O16 - C16	176.27(14)	176.77(12)

Compound name : Minor product (*anti*-8)
Chemical formula : $C_{16}H_{16}O_5$
Final R_1 [I>2σ(I)] : 2.83 %

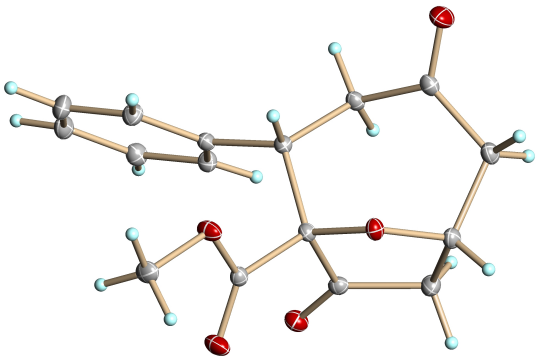


Figure 1. A view showing the anisotropic atomic displacement ellipsoids for the non-hydrogen atoms at the 30% probability level. Hydrogen atoms are displayed with an arbitrarily small radius.

A colorless prism of $C_{16}H_{16}O_5$, approximate dimensions 0.365×0.46×0.51 mm^3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 150(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoK α fine-focus sealed tube (λ= 0.71073 Å) . The detector was placed at a distance of 5.000 cm from the crystal.

A total of 3030 frames were collected with a scan width of -0.30° an exposure time of 5 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 9.3 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Orthorhombic unit cell yielded a total of 17271 reflections to a maximum θ angle of 30.00°, of which 4018 were independent (completeness = 100.0%, R_{int} = 1.74%, R_{sig} = 1.47%) and 3955 were greater than 2σ(I). The final cell dimensions of a = 8.4520(9) Å, b = 9.9029(11) Å, c = 16.5155(18) Å, α = 90°, β = 90°, λ = 90°, V = 1382.3(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 12995 reflections with 2.4 < θ < 32.2° using Apex2 software. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.886 and 0.963.

The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group $P2_12_12_1$ with Z = 4 for the formula unit $C_{16}H_{16}O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 249 variables converged at R_1 = 2.83 % for the observed data and wR_2 = 6.71 % for all data. The goodness-of-fit was 1.001. The largest peak on the final difference map was 0.279 $ē/Å^3$ and the largest hole

was -0.131 ē/Å^3. On the basis of the final model, the calculated density was 1.385 g/cm^3 and F(000), 608 ē.

Comments:

- H-atoms: all refined
- Residual density: in the middle of the
- Absolute configuration: not established

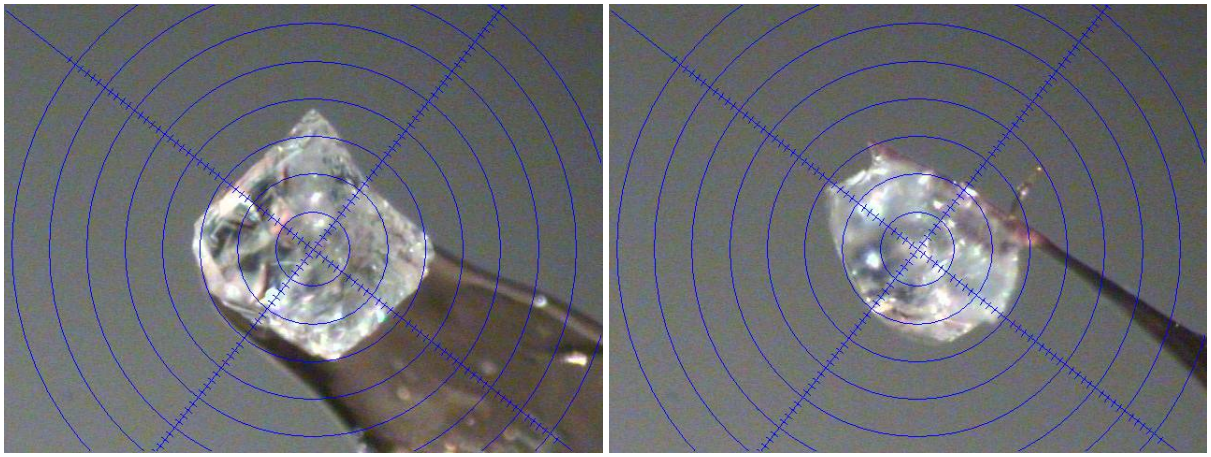


Table 1. Crystal data and structure refinement for UM#1972.

X-ray lab book No.	1972
Crystal ID	Doyle/Jaber Phenyl-Mirror product 150K
Empirical formula	$C_{16}H_{16}O_5$
Formula weight	288.29
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal size	0.51×0.46×0.365 mm^3
Crystal habit	colorless prism
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 8.4520(9) Å α = 90°
	b = 9.9029(11) Å β = 90°
	c = 16.5155(18) Å γ = 90°
Volume	1382.3(3) Å^3
Z	4
Density, ρ_{calc}	1.385 g/cm^3
Absorption coefficient, μ	0.103 mm^{-1}
F(000)	608 ē
Diffractometer	Bruker Smart Apex II CCD area detector
Radiation source	fine-focus sealed tube, MoKα
Detector distance	5.000 cm
Data collection method	ω and φ scans
Total frames	3030
Frame size	512 pixels
Frame width	-0.30°
Exposure per frame	5 sec
Total measurement time	9.3 hours

θ range for data collection		2.40 to 30.00°
Index ranges		$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-23 \leq l \leq 23$
Reflections collected		17271
Independent reflections		4018
Observed reflection, I>2σ(I)		3955
Coverage of independent reflections		100.0 %
Variation in check reflections		0 %
Absorption correction		Semi-empirical from equivalents SADABS (Sheldrick, 1996)
Max. and min. transmission		0.963 and 0.886
Structure solution technique		direct
Structure solution program		SHELXS-97 (Sheldrick, 1990)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 1997)
Function minimized		$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters		4018 / 0 / 249
Goodness-of-fit on F^2		1.001
Δ/σ_{max}		0.001
Final R indices:	R_1, I>2σ(I)	0.0283
	wR_2, all data	0.0671
	R_{int}	0.0174
	R_{sig}	0.0147
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+ (0.03P)^2 + 0.3615P]$, $P = [\max(F_o^2, 0) + 2F_o^2]/3$
Absolute structure parameter		-0.1(5)
Largest diff. peak and hole		0.279 and -0.131 $\bar{e}/Å^3$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates and equivalent* isotropic atomic displacement parameters ($Å^2$) for UM#1972.

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
C1	0.63633(13)	0.34498(11)	0.12104(6)	0.02255(19)
C2	0.50744(13)	0.40226(11)	0.16110(7)	0.0265(2)
C3	0.47345(13)	0.36522(11)	0.24027(7)	0.0253(2)
C4	0.56858(12)	0.27075(11)	0.27916(7)	0.02292(19)
C5	0.69707(12)	0.21306(10)	0.23912(6)	0.01947(18)
C6	0.73282(11)	0.24987(10)	0.15942(6)	0.01721(16)
C7	0.86764(11)	0.18466(9)	0.11182(6)	0.01645(16)
C8	0.86164(11)	0.02867(9)	0.12065(6)	0.01841(17)
C9	0.96906(12)	-0.04768(9)	0.06277(6)	0.01963(17)
O9	0.91467(10)	-0.10121(9)	0.00272(5)	0.03078(18)
C10	1.14397(12)	-0.06139(10)	0.08107(6)	0.02168(18)
C11	1.22046(11)	0.06390(10)	0.11875(6)	0.01985(17)
O11	1.15204(8)	0.18456(7)	0.08136(4)	0.01903(14)
C12	1.19917(13)	0.08142(11)	0.20999(6)	0.02264(19)
C13	1.08724(11)	0.19942(10)	0.21929(6)	0.01819(17)
O13	1.04734(9)	0.25237(8)	0.28150(4)	0.02343(15)
C14	1.03392(11)	0.24102(9)	0.13351(5)	0.01601(16)
C15	1.04838(11)	0.39433(9)	0.12199(6)	0.01749(17)
O15	1.10301(11)	0.46903(8)	0.17182(5)	0.02799(17)
O16	0.99901(9)	0.43324(7)	0.04917(4)	0.02421(15)
C16	1.01805(13)	0.57755(11)	0.03409(7)	0.0249(2)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Hydrogen atom coordinates and isotropic atomic displacement parameters (Å^2) for UM#1972.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H1	0.6588(18)	0.3682(15)	0.0667(9)	0.027(4)
H2	0.4400(18)	0.4682(15)	0.1337(9)	0.031(4)
H3	0.3851(18)	0.4029(15)	0.2652(9)	0.029(3)
H4	0.5471(17)	0.2455(15)	0.3343(9)	0.030(4)
H5	0.7570(17)	0.1476(14)	0.2639(8)	0.021(3)
H7	0.8560(15)	0.2051(13)	0.0562(7)	0.015(3)
H8A	0.8851(16)	0.0003(14)	0.1741(8)	0.021(2)
H8B	0.7556(17)	0.0034(14)	0.1080(8)	0.021(2)
H10A	1.1910(18)	-0.0848(16)	0.0318(9)	0.034(3)
H10B	1.1598(19)	-0.1351(16)	0.1159(10)	0.034(3)
H11	1.3320(17)	0.0626(15)	0.1039(8)	0.022(3)
H12A	1.1550(19)	0.0071(16)	0.2369(9)	0.034(3)
H12B	1.3027(18)	0.1031(16)	0.2358(9)	0.034(3)
H16A	0.9537(18)	0.6268(15)	0.0727(9)	0.030(2)
H16B	0.9819(18)	0.5928(15)	-0.0202(9)	0.030(2)
H16C	1.1252(19)	0.5994(16)	0.0386(9)	0.030(2)

Table 4. Anisotropic atomic displacement parameters* (Å^2) for UM#1972.

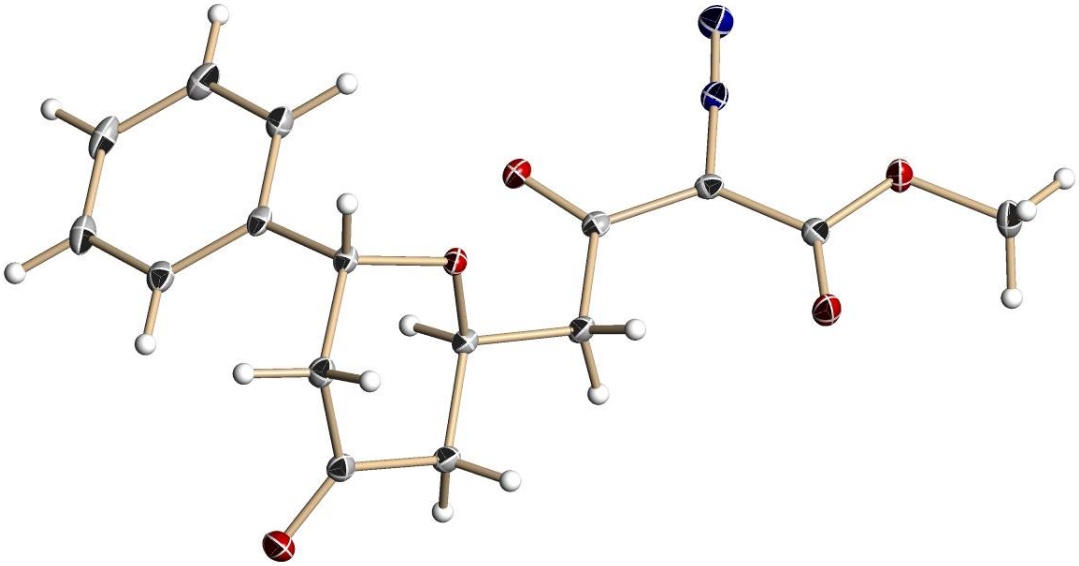
Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0231(5)	0.0239(4)	0.0206(4)	0.0011(4)	-0.0017(4)	0.0030(4)
C2	0.0226(5)	0.0254(5)	0.0316(5)	0.0006(4)	-0.0027(4)	0.0071(4)
C3	0.0190(5)	0.0251(5)	0.0317(5)	-0.0046(4)	0.0038(4)	0.0032(4)
C4	0.0216(5)	0.0232(5)	0.0239(5)	-0.0008(4)	0.0049(4)	-0.0008(4)
C5	0.0193(4)	0.0183(4)	0.0208(4)	0.0015(3)	0.0013(3)	0.0010(3)
C6	0.0166(4)	0.0158(4)	0.0192(4)	-0.0021(3)	-0.0001(3)	-0.0006(3)
C7	0.0170(4)	0.0156(4)	0.0168(4)	-0.0004(3)	0.0002(3)	0.0000(3)
C8	0.0182(4)	0.0153(4)	0.0217(4)	-0.0017(3)	0.0019(3)	-0.0019(3)
C9	0.0230(4)	0.0143(4)	0.0216(4)	-0.0001(3)	0.0025(3)	-0.0011(3)
O9	0.0309(4)	0.0323(4)	0.0291(4)	-0.0116(3)	-0.0025(3)	0.0008(3)
C10	0.0217(4)	0.0185(4)	0.0249(4)	-0.0035(4)	0.0021(4)	0.0022(4)
C11	0.0173(4)	0.0188(4)	0.0235(4)	-0.0017(4)	0.0014(3)	0.0021(3)
O11	0.0194(3)	0.0179(3)	0.0198(3)	0.0000(3)	0.0045(3)	0.0018(3)
C12	0.0231(5)	0.0225(5)	0.0223(4)	-0.0005(4)	-0.0037(4)	0.0040(4)
C13	0.0176(4)	0.0177(4)	0.0193(4)	0.0005(3)	-0.0009(3)	-0.0026(3)
O13	0.0277(4)	0.0237(3)	0.0188(3)	-0.0020(3)	0.0013(3)	-0.0021(3)
C14	0.0174(4)	0.0149(4)	0.0157(4)	-0.0014(3)	0.0012(3)	0.0002(3)
C15	0.0155(4)	0.0167(4)	0.0203(4)	-0.0004(3)	0.0020(3)	0.0007(3)
O15	0.0392(4)	0.0189(3)	0.0259(4)	-0.0018(3)	-0.0074(3)	-0.0045(3)
O16	0.0335(4)	0.0175(3)	0.0217(3)	0.0023(3)	-0.0050(3)	-0.0054(3)
C16	0.0279(5)	0.0174(4)	0.0294(5)	0.0046(4)	-0.0034(4)	-0.0037(4)

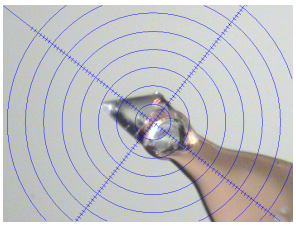
* The anisotropic atomic displacement factor exponent takes the form:$-2\pi^2$ [$h^2a^{*2}U_{11}$ +... + 2hka*b*U_{12}]

Table 5. Bond lengths (Å), valence and torsion angles (°) for UM#1972.

C1-C2	1.3951(15)	C1-C6	1.3979(14)	C1-H1	0.945(14)
C2-C3	1.3880(16)	C2-H2	0.978(15)	C3-C4	1.3907(15)
C3-H3	0.931(15)	C4-C5	1.3940(14)	C4-H4	0.962(15)
C5-C6	1.3988(13)	C5-H5	0.919(14)	C6-C7	1.5276(13)
C7-C8	1.5525(13)	C7-C14	1.5540(13)	C7-H7	0.946(12)
C8-C9	1.5198(13)	C8-H8A	0.948(14)	C8-H8B	0.954(14)
C9-O9	1.2147(13)	C9-C10	1.5151(15)	C10-C11	1.5313(14)
C10-H10A	0.934(15)	C10-H10B	0.939(16)	C11-O11	1.4641(12)
C11-C12	1.5275(14)	C11-H11	0.974(14)	O11-C14	1.4321(11)
C12-C13	1.5114(14)	C12-H12A	0.937(16)	C12-H12B	0.997(16)
C13-O13	1.2018(12)	C13-C14	1.5427(13)	C14-C15	1.5349(13)
C15-O15	1.1991(12)	C15-O16	1.3300(12)	O16-C16	1.4596(12)
C16-H16A	0.969(15)	C16-H16B	0.959(15)	C16-H16C	0.934(16)
C2-C1-C6	120.96(10)	C2-C1-H1	120.5(9)	C6-C1-H1	118.5(9)
C3-C2-C1	120.06(10)	C3-C2-H2	119.5(9)	C1-C2-H2	120.5(9)
C2-C3-C4	119.55(10)	C2-C3-H3	118.5(9)	C4-C3-H3	121.9(9)
C3-C4-C5	120.46(10)	C3-C4-H4	120.2(9)	C5-C4-H4	119.3(9)
C4-C5-C6	120.52(9)	C4-C5-H5	120.5(9)	C6-C5-H5	118.9(9)
C1-C6-C5	118.44(9)	C1-C6-C7	119.12(9)	C5-C6-C7	122.36(9)
C6-C7-C8	110.36(8)	C6-C7-C14	113.84(7)	C8-C7-C14	111.42(7)
C6-C7-H7	109.3(8)	C8-C7-H7	107.5(8)	C14-C7-H7	104.0(8)
C9-C8-C7	114.61(8)	C9-C8-H8A	108.3(8)	C7-C8-H8A	112.1(8)
C9-C8-H8B	107.1(8)	C7-C8-H8B	105.7(9)	H8A-C8-H8B	108.8(12)
O9-C9-C10	119.54(9)	O9-C9-C8	120.30(10)	C10-C9-C8	120.13(8)
C9-C10-C11	114.86(8)	C9-C10-H10A	105.3(9)	C11-C10-H10A	112.0(10)
C9-C10-H10B	109.3(10)	C11-C10-H10B	108.7(10)	H10A-C10-H10B	106.3(14)
O11-C11-C12	106.07(8)	O11-C11-C10	108.85(8)	C12-C11-C10	116.31(9)
O11-C11-H11	106.6(8)	C12-C11-H11	111.4(8)	C10-C11-H11	107.2(8)
C14-O11-C11	109.90(7)	C13-C12-C11	105.18(8)	C13-C12-H12A	108.0(10)
C11-C12-H12A	115.1(9)	C13-C12-H12B	109.8(9)	C11-C12-H12B	110.0(9)
H12A-C12-H12B	108.5(13)	O13-C13-C12	126.86(9)	O13-C13-C14	125.92(9)
C12-C13-C14	107.22(8)	O11-C14-C15	104.84(7)	O11-C14-C13	104.14(7)
C15-C14-C13	110.77(7)	O11-C14-C7	110.59(7)	C15-C14-C7	113.50(8)
C13-C14-C7	112.33(7)	O15-C15-O16	124.24(9)	O15-C15-C14	123.77(9)
O16-C15-C14	111.94(8)	C15-O16-C16	113.79(8)	O16-C16-H16A	108.6(9)
O16-C16-H16B	106.2(9)	H16A-C16-H16B	110.9(13)	O16-C16-H16C	108.7(10)
H16A-C16-H16C	112.0(13)	H16B-C16-H16C	110.3(13)		
C6-C1-C2-C3	0.09(17)	C1-C2-C3-C4	-0.05(17)	C2-C3-C4-C5	-0.18(16)
C3-C4-C5-C6	0.38(16)	C2-C1-C6-C5	0.11(15)	C2-C1-C6-C7	176.98(9)
C4-C5-C6-C1	-0.34(15)	C4-C5-C6-C7	-177.11(9)	C1-C6-C7-C8	-129.84(9)
C5-C6-C7-C8	46.91(12)	C1-C6-C7-C14	104.01(10)	C5-C6-C7-C14	-79.24(11)
C6-C7-C8-C9	168.33(8)	C14-C7-C8-C9	-64.18(10)	C7-C8-C9-O9	-101.74(11)
C7-C8-C9-C10	80.26(11)	O9-C9-C10-C11	143.90(10)	C8-C9-C10-C11	-38.08(13)
C9-C10-C11-O11	-37.79(11)	C9-C10-C11-C12	81.89(11)	C12-C11-O11-C14	-25.74(10)
C10-C11-O11-C14	100.12(9)	O11-C11-C12-C13	11.76(10)	C10-C11-C12-C13	-109.41(10)
C11-C12-C13-O13	-174.76(10)	C11-C12-C13-C14	4.74(10)	C11-O11-C14-C15	144.60(7)
C11-O11-C14-C13	28.17(9)	C11-O11-C14-C7	-92.71(9)	O13-C13-C14-O11	159.74(9)
C12-C13-C14-O11	-19.77(10)	O13-C13-C14-C15	47.52(12)	C12-C13-C14-C15	-131.98(8)
O13-C13-C14-C7	-80.56(12)	C12-C13-C14-C7	99.94(9)	C6-C7-C14-O11	-174.56(7)
C8-C7-C14-O11	59.86(10)	C6-C7-C14-C15	-57.07(10)	C8-C7-C14-C15	177.35(8)
C6-C7-C14-C13	69.56(10)	C8-C7-C14-C13	-56.02(10)	O11-C14-C15-O15	-107.58(10)
C13-C14-C15-O15	4.18(13)	C7-C14-C15-O15	131.63(10)	O11-C14-C15-O16	69.94(10)
C13-C14-C15-O16	-178.30(8)	C7-C14-C15-O16	-50.85(10)	O15-C15-O16-C16	0.41(14)
C14-C15-O16-C16	-177.09(8)				

Compound name : Diazoacetoacetate substituted tetrahydro-4-pyranones (7)
Chemical formula : $C_{16}H_{16}N_2O_5$





A colorless prism-like specimen of $C_{16}H_{16}N_2O_5$, approximate dimensions 0.17 mm x 0.27 mm x 0.42 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Smart Apex2 system equipped with a graphite monochromator and a MoK_α fine-focus sealed tube (λ = 0.71073 Å).

A total of 1819 frames were collected. The total exposure time was 12.12 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 21973 reflections to a maximum θ angle of 27.50° (0.77 Å resolution), of which 7204 were independent (average redundancy 3.050, completeness = 99.8%, R_{int} = 1.54%, R_{sig} = 1.67%) and 6391 (88.71%) were greater than $2\sigma(F^2)$. The final cell constants of a = 11.0436(6) Å, b = 11.2585(6) Å, c = 13.4333(8) Å, α = 90.2150(9)°, β = 107.0708(8)°, γ = 100.0912(9)°, volume = 1569.23(15) $Å^3$, are based upon the refinement of the XYZ-centroids of 9928 reflections above 20 σ(I) with 4.719° < 2θ < 62.22°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9589 and 0.9831.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with Z = 4 for the formula unit, $C_{16}H_{16}N_2O_5$. The final anisotropic full-matrix least-squares refinement on F^2 with 441 variables converged at R1 = 3.36%, for the observed data and wR2 = 6.86% for all data. The goodness-of-fit was 0.999. The largest peak in the final difference electron density synthesis was 0.317 $e^-/Å^3$ and the largest hole was -0.176 e^-

/Å^3 with an RMS deviation of 0.037 e$^-$/Å^3. On the basis of the final model, the calculated density was 1.339 g/cm^3 and F(000), 664 e$^-$.

Table 1. Sample and crystal data for UM2037.

Identification code	UM2037	
Chemical formula	$C_{16}H_{16}N_2O_5$	
Formula weight	316.31	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.17 x 0.27 x 0.42 mm	
Crystal habit	colorless prism	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.0436(6) Å	α = 90.2150(9)°
	b = 11.2585(6) Å	β = 107.0708(8)°
	c = 13.4333(8) Å	γ = 100.0912(9)°
Volume	1569.23(15) Å^3	
Z	4	
Density (calculated)	1.339 Mg/cm^3	
Absorption coefficient	0.101 mm^{-1}	
F(000)	664	

Table 2. Data collection and structure refinement for UM2037.

Diffractometer	Bruker Smart Apex2	
Radiation source	fine-focus sealed tube, MoK_α	
Theta range for data collection	1.84 to 27.50°	
Index ranges	-14<=h<=14, -14<=k<=14, -17<=l<=17	
Reflections collected	21973	
Independent reflections	7204 [R(int) = 0.0154]	
Coverage of independent reflections	99.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9831 and 0.9589	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-97 (Sheldrick, 2008)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7204 / 0 / 441	
Goodness-of-fit on F^2	0.999	
Δ/σ_{max}	0.001	
Final R indices	6391 data; I>2σ(I)	R1 = 0.0336, wR2 = 0.0669
	all data	R1 = 0.0384, wR2 = 0.0686
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+0.8850P]$	

	where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	0.317 and -0.176 eÅ^{-3}

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for UM2037.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
C1A	0.63677(12)	0.91830(10)	0.88520(10)	0.0281(3)
O1A	0.70214(8)	0.02580(7)	0.85019(6)	0.02442(17)
C2A	0.80256(10)	0.09042(10)	0.92376(9)	0.0201(2)
O2A	0.84318(8)	0.06132(7)	0.01196(6)	0.02699(18)
C3A	0.85396(10)	0.20131(10)	0.88219(8)	0.0191(2)
N1A	0.79766(9)	0.21486(8)	0.78055(7)	0.02033(19)
N2A	0.75407(10)	0.22894(10)	0.69674(8)	0.0295(2)
C4A	0.95445(10)	0.30337(10)	0.93352(8)	0.0185(2)
O4A	0.98302(7)	0.38903(7)	0.88349(6)	0.02148(16)
C5A	0.01742(10)	0.30035(10)	0.04962(8)	0.0213(2)
C6A	0.14488(10)	0.38752(9)	0.08798(8)	0.0180(2)
O6A	0.23501(7)	0.33741(6)	0.04993(6)	0.01818(15)
C7A	0.19043(10)	0.40233(10)	0.20753(8)	0.0206(2)
C8A	0.32838(11)	0.46780(10)	0.24864(8)	0.0214(2)
O8A	0.36400(8)	0.54369(8)	0.32071(7)	0.03083(19)
C9A	0.41851(10)	0.42832(10)	0.19519(9)	0.0214(2)
C10A	0.35990(10)	0.41451(9)	0.07619(8)	0.0186(2)
C11A	0.35336(10)	0.53267(10)	0.02145(9)	0.0193(2)
C12A	0.40644(11)	0.64593(10)	0.07273(10)	0.0234(2)
C13A	0.40139(11)	0.75086(11)	0.01757(11)	0.0290(3)
C14A	0.34182(11)	0.74336(11)	0.91120(11)	0.0310(3)
C15A	0.28762(12)	0.63084(12)	0.85923(10)	0.0302(3)
C16A	0.29382(11)	0.52653(11)	0.91399(9)	0.0246(2)
C1B	0.60971(13)	0.29628(14)	0.44380(12)	0.0427(4)
O1B	0.53563(8)	0.20437(8)	0.48829(7)	0.0305(2)
C2B	0.40972(11)	0.17290(10)	0.43467(9)	0.0224(2)
O2B	0.35850(8)	0.21379(7)	0.35347(6)	0.02729(18)
C3B	0.34546(10)	0.08181(10)	0.48840(8)	0.0206(2)
N1B	0.41943(9)	0.05070(9)	0.57930(7)	0.0232(2)
N2B	0.47720(10)	0.02317(11)	0.65548(8)	0.0341(3)
C4B	0.21054(11)	0.02008(10)	0.46215(8)	0.0201(2)
O4B	0.17907(8)	0.94029(7)	0.51577(6)	0.02546(18)
C5B	0.11542(11)	0.06405(10)	0.37077(9)	0.0228(2)
C6B	0.98577(10)	0.97971(9)	0.33529(8)	0.0192(2)
O6B	0.00583(7)	0.87695(7)	0.28322(6)	0.02043(16)

	x/a	y/b	z/c	U(eq)
C7B	0.88369(10)	0.04150(10)	0.26156(9)	0.0212(2)
C8B	0.76370(11)	0.95232(10)	0.20470(8)	0.0215(2)
O8B	0.65590(8)	0.97453(8)	0.18897(7)	0.02835(19)
C9B	0.78819(11)	0.83605(10)	0.16571(9)	0.0233(2)
C10B	0.89216(10)	0.78502(10)	0.24772(9)	0.0208(2)
C11B	0.85209(11)	0.72764(9)	0.33854(9)	0.0208(2)
C12B	0.72517(11)	0.70239(10)	0.34070(9)	0.0245(2)
C13B	0.69297(12)	0.64093(11)	0.42215(10)	0.0291(3)
C14B	0.78782(13)	0.60537(11)	0.50256(10)	0.0311(3)
C15B	0.91541(13)	0.63174(11)	0.50214(10)	0.0326(3)
C16B	0.94718(12)	0.69218(11)	0.42076(10)	0.0283(3)

Table 4. Bond lengths (Å) for UM2037.

C1A-O1A	1.4507(13)	C1A-H1A1	0.98	C1B-O1B	1.4465(14)	C1B-H1B1	0.98
C1A-H1A2	0.98	C1A-H1A3	0.98	C1B-H1B2	0.98	C1B-H1B3	0.98
O1A-C2A	1.3432(13)	C2A-O2A	1.2061(13)	O1B-C2B	1.3473(14)	C2B-O2B	1.2061(14)
C2A-C3A	1.4614(15)	C3A-N1A	1.3455(14)	C2B-C3B	1.4586(15)	C3B-N1B	1.3411(14)
C3A-C4A	1.4579(15)	N1A-N2A	1.1109(13)	C3B-C4B	1.4677(15)	N1B-N2B	1.1130(14)
C4A-O4A	1.2264(13)	C4A-C5A	1.5129(15)	C4B-O4B	1.2202(13)	C4B-C5B	1.5117(15)
C5A-C6A	1.5153(14)	C5A-H5A1	0.99	C5B-C6B	1.5160(15)	C5B-H5B1	0.99
C5A-H5A2	0.99	C6A-O6A	1.4365(12)	C5B-H5B2	0.99	C6B-O6B	1.4323(13)
C6A-C7A	1.5343(15)	C6A-H6A	1.0	C6B-C7B	1.5363(15)	C6B-H6B	1.0
O6A-C10A	1.4397(12)	C7A-C8A	1.5096(15)	O6B-C10B	1.4367(13)	C7B-C8B	1.5104(15)
C7A-H7A1	0.99	C7A-H7A2	0.99	C7B-H7B1	0.99	C7B-H7B2	0.99
C8A-O8A	1.2144(14)	C8A-C9A	1.5087(15)	C8B-O8B	1.2171(14)	C8B-C9B	1.5044(16)
C9A-C10A	1.5343(15)	C9A-H9A1	0.99	C9B-C10B	1.5347(15)	C9B-H9B1	0.99
C9A-H9A2	0.99	C10A-C11A	1.5249(14)	C9B-H9B2	0.99	C10B-C11B	1.5245(15)
C10A-H10A	1.0	C11A-C12A	1.3923(15)	C10B-H10B	1.0	C11B-C12B	1.3894(16)
C11A-C16A	1.3954(16)	C12A-C13A	1.3975(16)	C11B-C16B	1.3969(16)	C12B-C13B	1.3965(16)
C12A-H12A	0.95	C13A-C14A	1.3819(19)	C12B-H12B	0.95	C13B-C14B	1.3822(19)
C13A-H13A	0.95	C14A-C15A	1.3902(19)	C13B-H13B	0.95	C14B-C15B	1.3899(19)
C14A-H14A	0.95	C15A-C16A	1.3893(16)	C14B-H14B	0.95	C15B-C16B	1.3886(17)
C15A-H15A	0.95	C16A-H16A	0.95	C15B-H15B	0.95	C16B-H16B	0.95

Table 5. Bond angles (°) for UM2037.

O1A-C1A-H1A1	109.5	O1A-C1A-H1A2	109.5
H1A1-C1A-H1A2	109.5	O1A-C1A-H1A3	109.5
H1A1-C1A-H1A3	109.5	H1A2-C1A-H1A3	109.5
C2A-O1A-C1A	115.19(9)	O2A-C2A-O1A	124.55(10)
O2A-C2A-C3A	125.03(10)	O1A-C2A-C3A	110.42(9)
N1A-C3A-C4A	113.57(9)	N1A-C3A-C2A	115.72(9)

C4A-C3A-C2A	130.67(10)	N2A-N1A-C3A	177.88(12)
O4A-C4A-C3A	120.20(10)	O4A-C4A-C5A	122.25(10)
C3A-C4A-C5A	117.52(9)	C4A-C5A-C6A	112.65(9)
C4A-C5A-H5A1	109.1	C6A-C5A-H5A1	109.1
C4A-C5A-H5A2	109.1	C6A-C5A-H5A2	109.1
H5A1-C5A-H5A2	107.8	O6A-C6A-C5A	106.42(8)
O6A-C6A-C7A	110.82(8)	C5A-C6A-C7A	110.80(8)
O6A-C6A-H6A	109.6	C5A-C6A-H6A	109.6
C7A-C6A-H6A	109.6	C6A-O6A-C10A	112.58(8)
C8A-C7A-C6A	111.85(9)	C8A-C7A-H7A1	109.2
C6A-C7A-H7A1	109.2	C8A-C7A-H7A2	109.2
C6A-C7A-H7A2	109.2	H7A1-C7A-H7A2	107.9
O8A-C8A-C9A	123.00(10)	O8A-C8A-C7A	122.45(10)
C9A-C8A-C7A	114.52(9)	C8A-C9A-C10A	112.26(9)
C8A-C9A-H9A1	109.2	C10A-C9A-H9A1	109.2
C8A-C9A-H9A2	109.2	C10A-C9A-H9A2	109.2
H9A1-C9A-H9A2	107.9	O6A-C10A-C11A	111.12(8)
O6A-C10A-C9A	109.46(8)	C11A-C10A-C9A	115.25(9)
O6A-C10A-H10A	106.9	C11A-C10A-H10A	106.9
C9A-C10A-H10A	106.9	C12A-C11A-C16A	118.45(10)
C12A-C11A-C10A	123.38(10)	C16A-C11A-C10A	118.15(10)
C11A-C12A-C13A	120.71(11)	C11A-C12A-H12A	119.6
C13A-C12A-H12A	119.6	C14A-C13A-C12A	120.18(11)
C14A-C13A-H13A	119.9	C12A-C13A-H13A	119.9
C13A-C14A-C15A	119.65(11)	C13A-C14A-H14A	120.2
C15A-C14A-H14A	120.2	C16A-C15A-C14A	120.11(12)
C16A-C15A-H15A	119.9	C14A-C15A-H15A	119.9
C15A-C16A-C11A	120.90(11)	C15A-C16A-H16A	119.6
C11A-C16A-H16A	119.6	O1B-C1B-H1B1	109.5
O1B-C1B-H1B2	109.5	H1B1-C1B-H1B2	109.5
O1B-C1B-H1B3	109.5	H1B1-C1B-H1B3	109.5
H1B2-C1B-H1B3	109.5	C2B-O1B-C1B	115.52(9)
O2B-C2B-O1B	124.53(10)	O2B-C2B-C3B	125.25(10)
O1B-C2B-C3B	110.22(9)	N1B-C3B-C2B	115.78(10)
N1B-C3B-C4B	113.19(9)	C2B-C3B-C4B	130.99(10)
N2B-N1B-C3B	177.67(12)	O4B-C4B-C3B	119.83(10)
O4B-C4B-C5B	123.11(10)	C3B-C4B-C5B	117.00(9)
C4B-C5B-C6B	113.18(9)	C4B-C5B-H5B1	108.9
C6B-C5B-H5B1	108.9	C4B-C5B-H5B2	108.9
C6B-C5B-H5B2	108.9	H5B1-C5B-H5B2	107.8
O6B-C6B-C5B	105.87(9)	O6B-C6B-C7B	110.95(9)
C5B-C6B-C7B	111.04(9)	O6B-C6B-H6B	109.6
C5B-C6B-H6B	109.6	C7B-C6B-H6B	109.6
C6B-O6B-C10B	113.09(8)	C8B-C7B-C6B	112.16(9)

C8B-C7B-H7B1	109.2	C6B-C7B-H7B1	109.2
C8B-C7B-H7B2	109.2	C6B-C7B-H7B2	109.2
H7B1-C7B-H7B2	107.9	O8B-C8B-C9B	122.74(10)
O8B-C8B-C7B	122.49(10)	C9B-C8B-C7B	114.73(9)
C8B-C9B-C10B	112.12(9)	C8B-C9B-H9B1	109.2
C10B-C9B-H9B1	109.2	C8B-C9B-H9B2	109.2
C10B-C9B-H9B2	109.2	H9B1-C9B-H9B2	107.9
O6B-C10B-C11B	111.74(9)	O6B-C10B-C9B	109.06(9)
C11B-C10B-C9B	116.11(9)	O6B-C10B-H10B	106.4
C11B-C10B-H10B	106.4	C9B-C10B-H10B	106.4
C12B-C11B-C16B	118.47(11)	C12B-C11B-C10B	123.39(10)
C16B-C11B-C10B	118.02(10)	C11B-C12B-C13B	120.81(11)
C11B-C12B-H12B	119.6	C13B-C12B-H12B	119.6
C14B-C13B-C12B	120.14(11)	C14B-C13B-H13B	119.9
C12B-C13B-H13B	119.9	C13B-C14B-C15B	119.61(11)
C13B-C14B-H14B	120.2	C15B-C14B-H14B	120.2
C16B-C15B-C14B	120.18(12)	C16B-C15B-H15B	119.9
C14B-C15B-H15B	119.9	C15B-C16B-C11B	120.78(12)
C15B-C16B-H16B	119.6	C11B-C16B-H16B	119.6

Table 6. Torsion angles (°) for UM2037.

C1A-O1A-C2A-O2A	3.90(16)	C1A-O1A-C2A-C3A	-175.25(9)
O2A-C2A-C3A-N1A	177.79(11)	O1A-C2A-C3A-N1A	-3.06(13)
O2A-C2A-C3A-C4A	-4.61(19)	O1A-C2A-C3A-C4A	174.54(10)
C4A-C3A-N1A-N2A	12.(3)	C2A-C3A-N1A-N2A	-170.(3)
N1A-C3A-C4A-O4A	-2.11(15)	C2A-C3A-C4A-O4A	-179.75(11)
N1A-C3A-C4A-C5A	176.05(9)	C2A-C3A-C4A-C5A	-1.59(17)
O4A-C4A-C5A-C6A	-19.82(15)	C3A-C4A-C5A-C6A	162.07(9)
C4A-C5A-C6A-O6A	-71.96(11)	C4A-C5A-C6A-C7A	167.48(9)
C5A-C6A-O6A-C10A	177.01(8)	C7A-C6A-O6A-C10A	-62.44(10)
O6A-C6A-C7A-C8A	50.48(12)	C5A-C6A-C7A-C8A	168.39(9)
C6A-C7A-C8A-O8A	139.04(11)	C6A-C7A-C8A-C9A	-42.81(13)
O8A-C8A-C9A-C10A	-137.66(11)	C7A-C8A-C9A-C10A	44.21(12)
C6A-O6A-C10A-C11A	-65.45(11)	C6A-O6A-C10A-C9A	62.98(10)
C8A-C9A-C10A-O6A	-52.47(12)	C8A-C9A-C10A-C11A	73.63(11)
O6A-C10A-C11A-C12A	130.79(10)	C9A-C10A-C11A-C12A	5.55(14)
O6A-C10A-C11A-C16A	-50.84(13)	C9A-C10A-C11A-C16A	-176.09(9)
C16A-C11A-C12A-C13A	-0.69(16)	C10A-C11A-C12A-C13A	177.67(10)
C11A-C12A-C13A-C14A	0.86(17)	C12A-C13A-C14A-C15A	-0.38(18)
C13A-C14A-C15A-C16A	-0.25(18)	C14A-C15A-C16A-C11A	0.42(18)
C12A-C11A-C16A-C15A	0.06(16)	C10A-C11A-C16A-C15A	-178.39(10)
C1B-O1B-C2B-O2B	1.79(18)	C1B-O1B-C2B-C3B	-178.84(11)
O2B-C2B-C3B-N1B	-178.43(11)	O1B-C2B-C3B-N1B	2.21(14)

O2B-C2B-C3B-C4B	-1.0(2)	O1B-C2B-C3B-C4B	179.61(11)
C2B-C3B-N1B-N2B	164.(3)	C4B-C3B-N1B-N2B	-14.(3)
N1B-C3B-C4B-O4B	-7.14(15)	C2B-C3B-C4B-O4B	175.41(11)
N1B-C3B-C4B-C5B	170.20(10)	C2B-C3B-C4B-C5B	-7.25(18)
O4B-C4B-C5B-C6B	-14.82(16)	C3B-C4B-C5B-C6B	167.93(9)
C4B-C5B-C6B-O6B	-73.25(11)	C4B-C5B-C6B-C7B	166.24(9)
C5B-C6B-O6B-C10B	177.78(8)	C7B-C6B-O6B-C10B	-61.66(11)
O6B-C6B-C7B-C8B	48.66(12)	C5B-C6B-C7B-C8B	166.10(9)
C6B-C7B-C8B-O8B	140.45(11)	C6B-C7B-C8B-C9B	-41.71(13)
O8B-C8B-C9B-C10B	-137.81(11)	C7B-C8B-C9B-C10B	44.36(13)
C6B-O6B-C10B-C11B	-66.21(11)	C6B-O6B-C10B-C9B	63.51(11)
C8B-C9B-C10B-O6B	-53.24(12)	C8B-C9B-C10B-C11B	74.05(12)
O6B-C10B-C11B-C12B	136.90(11)	C9B-C10B-C11B-C12B	10.96(15)
O6B-C10B-C11B-C16B	-47.08(13)	C9B-C10B-C11B-C16B	-173.03(10)
C16B-C11B-C12B-C13B	-1.20(17)	C10B-C11B-C12B-C13B	174.80(10)
C11B-C12B-C13B-C14B	0.63(18)	C12B-C13B-C14B-C15B	0.37(18)
C13B-C14B-C15B-C16B	-0.78(19)	C14B-C15B-C16B-C11B	0.19(19)
C12B-C11B-C16B-C15B	0.79(18)	C10B-C11B-C16B-C15B	-175.43(11)

Table 7. Anisotropic atomic displacement parameters (Å^2) for UM2037.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1A	0.0269(6)	0.0205(5)	0.0303(6)	0.0055(5)	0.0025(5)	-0.0024(5)
O1A	0.0233(4)	0.0217(4)	0.0230(4)	0.0042(3)	0.0019(3)	-0.0010(3)
C2A	0.0183(5)	0.0211(5)	0.0211(5)	0.0010(4)	0.0060(4)	0.0042(4)
O2A	0.0294(4)	0.0260(4)	0.0205(4)	0.0057(3)	0.0036(3)	-0.0017(3)
C3A	0.0183(5)	0.0236(5)	0.0156(5)	0.0033(4)	0.0048(4)	0.0050(4)
N1A	0.0169(4)	0.0214(4)	0.0230(5)	0.0033(4)	0.0063(4)	0.0037(4)
N2A	0.0273(5)	0.0344(6)	0.0235(5)	0.0068(4)	0.0026(4)	0.0057(4)
C4A	0.0162(5)	0.0213(5)	0.0205(5)	0.0021(4)	0.0079(4)	0.0059(4)
O4A	0.0217(4)	0.0214(4)	0.0229(4)	0.0055(3)	0.0086(3)	0.0047(3)
C5A	0.0191(5)	0.0251(5)	0.0189(5)	0.0030(4)	0.0068(4)	0.0003(4)
C6A	0.0179(5)	0.0188(5)	0.0186(5)	0.0027(4)	0.0074(4)	0.0036(4)
O6A	0.0177(4)	0.0160(3)	0.0217(4)	0.0011(3)	0.0082(3)	0.0016(3)
C7A	0.0198(5)	0.0235(5)	0.0191(5)	0.0024(4)	0.0073(4)	0.0031(4)
C8A	0.0230(5)	0.0220(5)	0.0184(5)	0.0049(4)	0.0055(4)	0.0032(4)
O8A	0.0301(5)	0.0330(5)	0.0264(4)	-0.0065(4)	0.0086(4)	-0.0019(4)
C9A	0.0182(5)	0.0225(5)	0.0227(5)	0.0038(4)	0.0055(4)	0.0027(4)
C10A	0.0163(5)	0.0181(5)	0.0223(5)	0.0027(4)	0.0077(4)	0.0025(4)
C11A	0.0153(5)	0.0193(5)	0.0261(6)	0.0046(4)	0.0104(4)	0.0032(4)
C12A	0.0208(5)	0.0217(5)	0.0302(6)	0.0014(5)	0.0119(5)	0.0026(4)
C13A	0.0253(6)	0.0182(5)	0.0487(8)	0.0035(5)	0.0195(6)	0.0033(4)
C14A	0.0245(6)	0.0255(6)	0.0502(8)	0.0188(6)	0.0196(6)	0.0089(5)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15A	0.0237(6)	0.0354(7)	0.0324(7)	0.0149(5)	0.0095(5)	0.0053(5)
C16A	0.0219(5)	0.0241(6)	0.0272(6)	0.0052(5)	0.0084(5)	0.0010(4)
C1B	0.0286(7)	0.0457(8)	0.0394(8)	0.0176(6)	0.0002(6)	-0.0136(6)
O1B	0.0231(4)	0.0322(5)	0.0277(4)	0.0099(4)	0.0005(3)	-0.0052(3)
C2B	0.0220(5)	0.0203(5)	0.0226(6)	0.0011(4)	0.0045(4)	0.0018(4)
O2B	0.0246(4)	0.0273(4)	0.0262(4)	0.0101(3)	0.0036(3)	0.0016(3)
C3B	0.0214(5)	0.0228(5)	0.0169(5)	0.0036(4)	0.0036(4)	0.0057(4)
N1B	0.0202(5)	0.0277(5)	0.0221(5)	0.0036(4)	0.0077(4)	0.0033(4)
N2B	0.0253(5)	0.0512(7)	0.0253(6)	0.0125(5)	0.0064(4)	0.0075(5)
C4B	0.0221(5)	0.0208(5)	0.0186(5)	0.0002(4)	0.0073(4)	0.0049(4)
O4B	0.0253(4)	0.0290(4)	0.0223(4)	0.0075(3)	0.0083(3)	0.0033(3)
C5B	0.0219(5)	0.0217(5)	0.0228(6)	0.0047(4)	0.0043(4)	0.0027(4)
C6B	0.0200(5)	0.0197(5)	0.0184(5)	0.0021(4)	0.0061(4)	0.0039(4)
O6B	0.0196(4)	0.0206(4)	0.0230(4)	0.0009(3)	0.0095(3)	0.0035(3)
C7B	0.0225(5)	0.0205(5)	0.0203(5)	0.0029(4)	0.0057(4)	0.0046(4)
C8B	0.0236(5)	0.0243(5)	0.0170(5)	0.0066(4)	0.0063(4)	0.0047(4)
O8B	0.0219(4)	0.0305(4)	0.0323(5)	0.0070(4)	0.0067(4)	0.0065(3)
C9B	0.0255(6)	0.0240(5)	0.0187(5)	0.0010(4)	0.0052(4)	0.0023(4)
C10B	0.0221(5)	0.0199(5)	0.0213(5)	0.0003(4)	0.0083(4)	0.0034(4)
C11B	0.0248(5)	0.0163(5)	0.0216(5)	-0.0002(4)	0.0082(4)	0.0026(4)
C12B	0.0237(6)	0.0230(5)	0.0253(6)	-0.0015(4)	0.0073(5)	0.0008(4)
C13B	0.0300(6)	0.0255(6)	0.0318(6)	-0.0046(5)	0.0154(5)	-0.0057(5)
C14B	0.0456(7)	0.0215(6)	0.0255(6)	0.0005(5)	0.0158(6)	-0.0043(5)
C15B	0.0390(7)	0.0284(6)	0.0275(6)	0.0076(5)	0.0063(5)	0.0045(5)
C16B	0.0266(6)	0.0277(6)	0.0313(6)	0.0069(5)	0.0092(5)	0.0054(5)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters ($Å^2$) for UM2037.

	x/a	y/b	z/c	U(eq)
H1A1	-0.3054	-0.1403	-0.0963	0.035(2)
H1A2	-0.4407	-0.1174	-0.1709	0.035(2)
H1A3	-0.3877	-0.0600	-0.0536	0.035(2)
H5A1	0.0319	0.2174	0.0661	0.030(3)
H5A2	-0.0417	0.3207	0.0873	0.030(3)
H6A	0.1352	0.4679	0.0584	0.014(3)
H7A1	0.1341	0.4480	0.2313	0.026(2)
H7A2	0.1826	0.3216	0.2365	0.026(2)
H9A1	0.4398	0.3501	0.2213	0.030(4)
H9A2	0.4997	0.4886	0.2131	0.027(3)
H10A	0.4163	0.3714	0.0486	0.017(3)
H12A	0.4465	0.6519	0.1460	0.026(3)
H13A	0.4390	0.8275	0.0533	0.036(4)

	x/a	y/b	z/c	U(eq)
H14A	0.3379	0.8147	-0.1262	0.037(4)
H15A	0.2463	0.6253	-0.2139	0.037(4)
H16A	0.2570	0.4500	-0.1222	0.030(4)
H1B1	0.6130	1.2649	0.3767	0.055(3)
H1B2	0.6974	1.3186	0.4914	0.055(3)
H1B3	0.5688	1.3677	0.4331	0.055(3)
H5B1	0.1522	1.0732	0.3117	0.033(3)
H5B2	0.1026	1.1447	0.3905	0.033(3)
H6B	-0.0424	0.9538	0.3974	0.018(3)
H7B1	-0.1397	1.1024	0.3024	0.026(2)
H7B2	-0.0793	1.0843	0.2099	0.026(2)
H9B1	-0.1844	0.8504	0.1023	0.036(4)
H9B2	-0.2929	0.7757	0.1464	0.027(3)
H10B	-0.0842	0.7196	0.2106	0.018(3)
H12B	-0.3405	0.7272	0.2861	0.028(3)
H13B	-0.3943	0.6235	0.4223	0.035(4)
H14B	-0.2341	0.5631	0.5578	0.039(4)
H15B	-0.0189	0.6084	0.5577	0.042(4)
H16B	0.0346	0.7096	0.4210	0.034(4)

Table 9: Data collection details for UM2037.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s	Wavelength/Å
Omega	50.039	-31.50	-31.50	0.00	54.71	0.50	366	24.00	0.71073
Omega	50.039	-31.50	-31.50	120.00	54.71	0.50	366	24.00	0.71073
Omega	50.039	-31.50	-31.50	240.00	54.71	0.50	366	24.00	0.71073
Phi	50.039	-31.50	-211.50	0.00	54.71	0.50	720	24.00	0.71073

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