Supporting Information for:

Total synthesis of (±)-Maistemonine and (±)-Stemonamide

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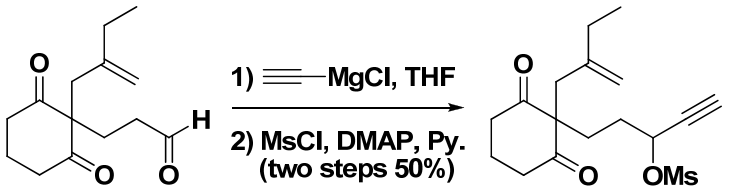
Supporting Information

Experimental Details

General information

For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90 ^{o}C) and ethyl acetate are used. All solvents were purified and dried by standard techniques, and distilled prior to use. All organic extracts were dried over $MgSO_4$, unless otherwise noted. IR spectra were recorded on a fourier transform infrared spectrometer. ^{1}H and ^{13}C NMR spectra were taken on a *Bruker*, AM-400 or AM-600 spectrometer with TMS as an internal standard and $CDCl_3$ as solvent. The MS data were obtained with EI (70 eV). HRMS data were determined on a *Bruker Daltonics* APEXII 47e FT-ICR spectrometer. Melting points were measured on a melting point apparatus and are uncorrected. Starting material **6** is known compound.

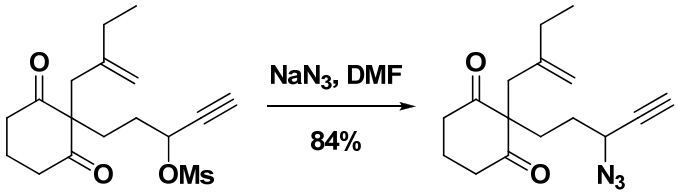


6 **7**

Compound 7. To a solution of 5.0261 g (21.30 mmol) of dione **6** in THF (140 mL) at -78 ^{o}C under argon was added ethynylmagnesium chloride (0.6 M, 35.5 mL, 21.30 mmol). The mixture was stirred for 7.5 h at -78 ^{o}C and then quenched with water (5 mL). After warming up to room temperature, the reaction mixture was diluted with Et_2O (100 mL) and saturated aqueous NH_4Cl (50 mL). The aqueous phase was extracted with Et_2O (3 x 50 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Chromatography (15% EtOAc/petroleum ether) afforded the crude product as a yellow oil (3.5014 g).

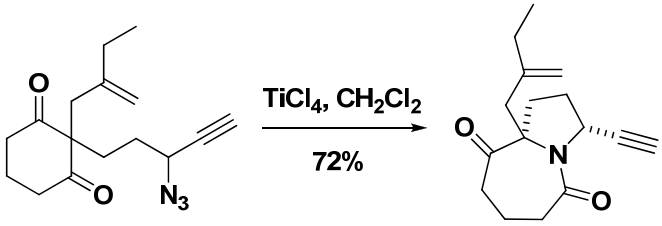
The above crude product was dissolved in pyridine (35 mL) at 40 ^{o}C under argon, DMAP (350 mg, 2.87 mmol) and methanesulfonyl chloride (7.0 mL, 90.44 mmol) was added. After stirring for 30min, the solution allowed to cool on ice-water bath. The reaction was diluted with Et_2O (30 mL) and quenched with water (10 mL). The biphasic mixture was vigorously stirred for 30 min prior to separation of the layers. The organic phase was washed with water (2 x 20 mL) followed by back-extraction of the combined aqueous extracts with Et_2O (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated to yield a yellow oil which was then purified via column chromatography (15% EtOAc/petroleum ether to 25% EtOAc/petroleum ether) to afford compound **7** (3.6205 g, 50% yield, two steps) as a light yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.93-0.97 (t, J = 6.4 Hz, 3H), 1.63-1.69 (m, 2H), 1.84-1.88 (m, 3H), 1.89-2.04 (m, 3H), 2.51 (s, 2H), 2.59-2.62 (m, 4H), 2.71-2.72 (d, J = 2.4 Hz, 1H), 3.09 (s, 3H), 4.54 (s, 1H), 4.81-4.82 (d, J = 1.2 Hz,

1H), 5.05-5.08 (dt, *J* = 6.4, 2 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 12.2, 16.7, 30.0, 30.9, 31.0, 39.1, 39.6, 43.6, 67.7, 70.5, 77.3, 78.6, 113.0, 146.2, 210.2, 210.3; IR (neat) 903, 1360, 1691, 3269 cm^{-1}; MS (EI) *m/z* 340, 311, 261, 245, 201, 173, 131; HRMS (ESI) Calcd. for $C_{17}H_{28}NO_5S$ $(M+NH_4)^+$: 358.1683, Found 358.1676, Error: 2.0 ppm.



7 **5**

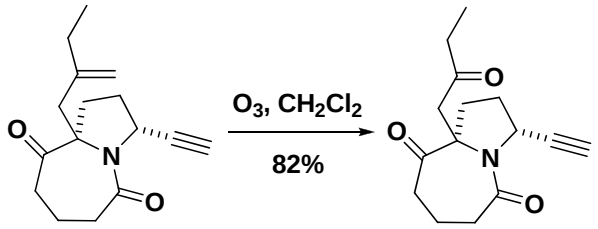
Compound 5. The mesylate **7** (406.6 mg, 1.20 mmol) was treated with NaN_3 (233.2 mg, 3.59 mmol) in 4 mL of DMF at 40 °C under argon. After 1.5 h, the mixture was diluted with Et_2O (10 mL) at 0 °C, and washed with water (2 x 10 mL). The organic phase was dried over $MgSO_4$, filtered and concentrated to yield a yellow oil which was purified via column chromatography (15% EtOAc/ petroleum ether) to give the desired azide **5** (288.3 mg, 84% yield) as a light yellow oil; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.93-0.97 (t, *J* = 6.4 Hz, 3H), 1.42-1.49 (m, 2H), 1.82-1.93 (m, 5H), 1.95-2.03 (m, 1H), 2.50 (s, 2H), 2.57-2.61 (m, 5H), 3.98-4.02 (dt, *J* = 6.8, 2.4 Hz, 1H), 4.53-4.54 (d, *J* = 0.8 Hz, 1H), 4.81-4.82 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 12.2, 16.7, 30.0, 30.5, 32.3, 39.6, 39.7, 43.7, 52.5, 67.8, 75.4, 78.5, 112.9, 146.3, 210.4; IR (neat) 906, 1693, 2104, 3268 cm^{-1}; MS (EI) *m/z* 287, 258, 244, 216, 188, 136; HRMS (ESI) Calcd. for $C_{16}H_{25}N_4O_2$ $(M+NH_4)^+$: 305.1972, Found 305.1969, Error: 1.0 ppm.



5 **4**

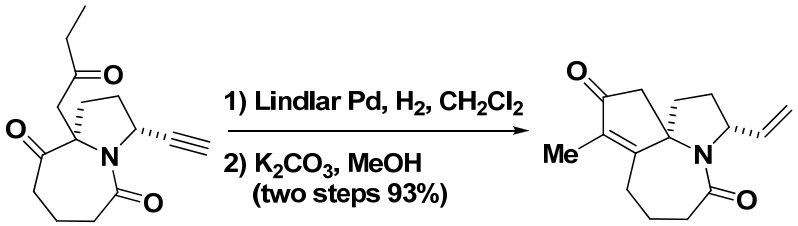
Compound 4. To a solution of the azide **5** (2.5755 g, 8.97 mmol) in CH_2Cl_2 (90 mL) at -15 °C under argon was added $TiCl_4$ (10.83 mL, 1M in CH_2Cl_2). The resulting mixture was stirred at-15 °C for 20 min, then it was quenched with 15 mL water. The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated to give a solid. Chromatography (20% EtOAc/petroleum ether to 35% EtOAc/petroleum ether) afforded **4** (1.6647 g , 72% yield) as an amorphous yellow solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.98-1.01 (t, *J* = 3.2 Hz, 3H), 1.92-2.08 (m, 5H), 2.16-2.34 (m, 5H), 2.41-2.56 (m, 1H), 2.53-2.72 (m, 3H), 3.25-3.33 (m, 1H), 4.80-4.81 (d, *J* = 6.4 Hz, 1H), 4.86 (s, 1H), 4.91-4.92 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 12.2, 22.6, 29.1, 29.6, 33.0, 34.8, 35.9, 40.5, 50.0, 71.0, 74.5, 82.7, 114.6, 146.2, 171.1,

211.9; IR (neat) 907, 1661, 1713, 3254 cm^{-1}; MS (EI) *m/z* 259, 230, 217, 202, 190, 162, 136; HRMS (ESI) Calcd. for $C_{16}H_{22}NO_2$ $(M+H)^+$: 260.1645, Found 260.1649, Error: 1.5 ppm.



4 **8**

Compound 8. Alkene **4** (201 mg, 0.77 mmol) was dissolved in CH_2Cl_2 (12 mL) at room temperature. The reaction mixture was cooled to -78 ^oC, after a brief oxygen purge (ca., 5 min), ozone was bubbled through the reaction mixture very slowly until the reaction was completed by tlc (approximately 11 h). After dimethylsulfide (5 mL) addition, the reaction was stirred at room temperature for 3 days. Concentration of the reaction mixture to give a yellow oil. Chromatography afforded **8** (165.4 mg, 82% yield) as a sticky oil; ^1H NMR (400MHz, $CDCl_3$) δ 1.05-1.08 (t, *J* = 6.4 Hz, 3H), 2.00-2.14 (m, 2H), 2.17-2.36 (m, 5H), 2.38-2.54 (m, 4H), 2.62-2.72 (m, 1H), 2.77-2.92 (m, 2H), 3.19-3.27 (m, 1H), 4.79-4.81 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 7.6, 22.9, 29.4, 33.4, 33.5, 34.4, 38.8, 44.4, 49.7, 71.2, 74.6, 82.5, 170.3, 207.4, 211.4; IR (neat) 1661, 1712, 3302 cm^{-1}; MS (EI) *m/z* 261, 232, 204, 190, 176, 148, 108; HRMS (ESI) Calcd. for $C_{15}H_{20}NO_3$ $(M+H)^+$: 262.1438, Found 262.1431, Error: 1.5 ppm.

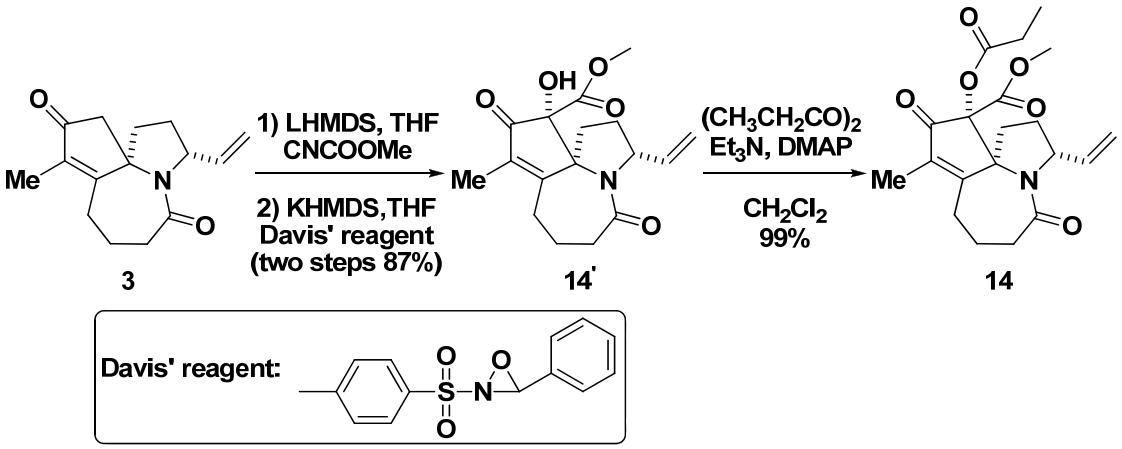


8 **3**

Compound 3. To a solution of **8** (421 mg, 1.61 mmol) in 10 mL of CH_2Cl_2 was added Lindlar catalyst (299.1 mg) and quinoline (38.4 μL, 0.32 mmol). The mixture was exposed to an atmosphere of H_2 at room temperature. After 1.5 h, the resulting mixture was filtered and concentrated to give the crude product as a yellow oil.

The above crude product was dissolved in MeOH (10 mL), followed by addition of K_2CO_3 (262.4 mg, 1.90mmol). After stirring at room temperature for 1 h, the solution was diluted with $CHCl_3$ (20 mL) and water (10 mL). The aqueous phase was extracted with $CHCl_3$ (3 x 10 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (50% EtOAc/petroleum ether to 75% EtOAc/ petroleum ether) to give cyclic enone **3** (367.5 mg, 93% yield, two steps) as a white crystalline solid:

mp 152-154 °C; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.42-1.50 (m, 1H), 1.76 (s, 3H), 1.83-1.93 (m, 2H), 2.10-2.32 (m, 5H), 2.41-2.48 (m, 1H), 2.58-2.67 (m, 2H), 2.81-2.86 (dd, *J* = 4.8, 8.0 Hz, 1H), 4.59-4.63 (t, *J* = 6.8 Hz, 1H), 5.15-5.23 (m, 2H), 5.80-5.89 (ddd, *J* = 6.4, 10.4, 16.8 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.1, 22.3, 23.9, 29.1, 33.1, 38.6, 50.7, 60.0, 70.7, 115.4, 135.9, 137.4, 170.7, 172.3, 203.0; IR (neat) 1000, 1654, 1700 cm^{-1}; MS (EI) *m/z* 245, 230, 202, 178, 135, 91; HRMS (ESI) Calcd. for $C_{15}H_{20}NO_2$ $(M+H)^+$: 246.1489, Found 246.1482, Error: 2.8 ppm.

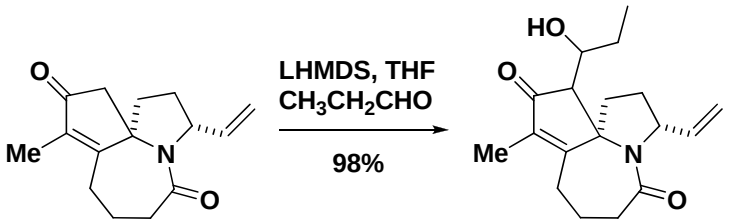


Compound 14'. To a solution of 123.6 mg (0.50 mmol) of ketone **3** in THF (5 mL) at -78 °C under argon was added LHMDS (1.0 M, 757 μL, 0.76 mmol). After stirring at -78 °C for 30 min, $CNCO_2Me$ (68 μL, 0.86 mmol) was added and followed HMPA (132 μL, 0.76 mmol). The resulting mixture was stirred for 30 min and then quenched with water (1 mL). After warming up to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated to give the crude product as a yellow oil.

The above yellow oil was dissolved in dry THF (7 mL) at -15 °C under argon followed by addition of KHMDS (0.91 M, 666 μL, 0.61 mmol). After stirring for 30 min, Davis' reagent (167 mg, 0.86 mmol) was added. The resulting mixture was stirred for 1.5 h and then quenched with water (1 mL). After warming up to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. The residue was purified via silica gel chromatography (20% EtOAc/petroleum ether to 50% EtOAc/petroleum ether) to give compound **14'** (140mg, 87% yield, two steps) as a white amorphous solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.72-1.77 (dd, *J* = 6.4, 6.4 Hz, 1H), 1.89 (s, 3H), 1.94-2.00 (m, 2H), 2.09-2.22 (m, 3H), 2.44-2.58 (m, 2H), 2.73-2.81 (ddd, *J* = 6.4, 14, 14 Hz, 1H), 2.88-2.93 (dd, *J* = 10.4, 12.4 Hz, 1H), 3.72 (s, 3H), 3.84 (brs, 1H), 4.46-4.50 (t, *J* = 8 Hz, 1H), 5.12-5.21 (m, 2H), 5.74-5.83 (ddd, *J* = 7.2, 10, 17.2 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.7, 22.5, 22.9, 29.3, 33.1, 34.1, 53.4, 60.8, 77.4, 84.4 115.1, 136.9, 138.7, 170.3, 170.8,172.4, 199.6; MS (EI) *m/z* 319, 301, 260, 231, 203, 175, 91; HRMS (ESI) Calcd. for

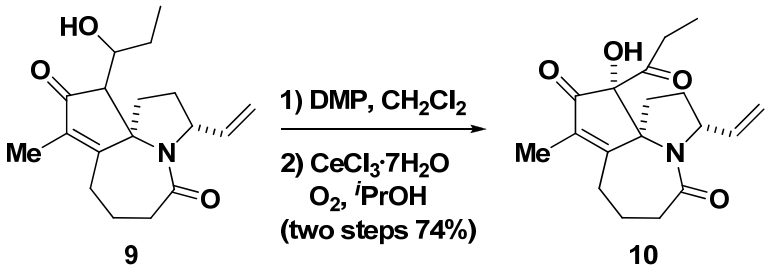
$C_{17}H_{22}NO_5$ $(M+H)^+$: 320.1492, Found 320.1486, Error: 1.9 ppm.

Compound 14. A solution of **14'** (140 mg, 0.44 mmol) in anhydrous CH_2Cl_2 (8 mL) under argon was treated with Et_3N (366 μL, 2.63 mmol), DMAP (33.1 mg, 0.27 mmol), and propionic anhydride (281 μL, 2.19 mmol) at room temperature. The reaction mixture was stirred for 48 h and then concentrated. The residue was purified via silica gel chromatography (15% EtOAc/petroleum ether to 35% EtOAc/petroleum ether) to give **14** (164mg, 99% yield) as a white amorphous solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.15-1.19 (t, *J* = 7.6 Hz, 3H), 1.72-1.77 (dd, *J* = 6.4, 6.4 Hz, 1H), 1.86 (s, 3H), 1.94-2.01 (m, 2H), 2.03-2.15 (m, 3H), 2.35-2.48 (m, 3H), 2.50-2.65 (m, 2H), 2.79-2.85 (dd, *J* = 9.2, 12.4 Hz, 1H), 3.63 (s, 3H), 4.52-4.56 (t, *J* = 8 Hz, 1H), 5.10-5.20 (m, 2H), 5.75-5.84 (ddd, *J* = 7.2, 10.4, 17.6 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.5, 8.8, 22.1, 23.3, 27.5, 28.9, 32.6, 35.2, 52.9, 60.8, 75.9, 88.1, 115.0, 136.7, 138.6, 166.2, 167.3, 171.9, 172.1, 194.7; MS (EI) *m/z* 375, 319, 301, 260, 231, 203, 175; HRMS (ESI) Calcd. for $C_{20}H_{26}NO_6$ $(M+H)^+$: 376.1755, Found 376.1750, Error: 1.3 ppm.



3 **9**

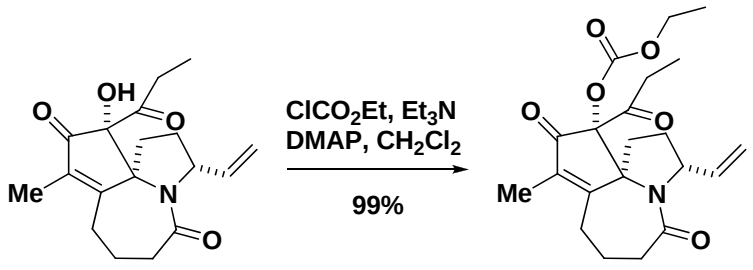
Compound 9. To a solution of 172 mg (0.70 mmol) of ketone **3** in THF (10 mL) at -78 ^{o}C under argon was added LHMDS (1.0 M, 1.06 mL, 1.06 mmol). After stirring at -78 ^{o}C for 1 h, propanal (103 μL, 1.41 mmol) was added. The resulting mixture was stirred for 1 h and then quenched with water (1 mL). After warming up to room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL) and water (5 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Chromatography (40% EtOAc/ petroleum ether to 75% EtOAc/petroleum ether) afforded **9** (208.2 mg, 98% yield) as a white crystalline solid: mp 161-163 ^{o}C; ^{1}H NMR (400MHz, $CDCl_3$) δ 0.94-0.97 (t, *J* = 6.4 Hz, 3H), 1.38-1.42 (dd, *J* = 11.6, 4.8 Hz, 1H), 1.75 (s, 3H), 1.79-1.91 (m, 4H), 1.99-2.13 (m, 3H), 2.15-2.30 (m, 3H), 2.41-2.49 (m, 1H), 2.82-2.88 (dd, *J* = 9.6, 12.4 Hz, 1H), 3.00-3.09 (m, 1H), 3.55-3.59 (ddd, *J* = 2.4, 5.6, 8.0 Hz, 1H), 4.54-4.58 (t, *J* = 7.2 Hz, 1H), 5.13-5.21 (m, 2H), 5.79-5.88 (ddd, *J* = 6.8, 10.4, 17.2 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 7.9, 10.5, 22.4, 22.6, 29.2, 29.4, 33.5, 40.0, 60.6, 61.2, 73.0, 73.4, 115.0, 137.3, 138.2, 170.6, 173.3, 205.3; IR (neat) 1000, 1629, 1702, 3333 cm^{-1}; MS (EI) *m/z* 303, 274, 246, 204, 175, 148, 91; HRMS (ESI) Calcd. for $C_{18}H_{26}NO_3$ $(M+H)^+$: 304.1907, Found 304.1904, Error: 1.0 ppm.



9 **10**

Compound 10. To a CH_2Cl_2 (10 mL) solution of alcohol **9** (278.5 mg, 0.92 mmol) under argon at 0 ^oC was added Dess-Martin periodinane (549.4 mg, 1.30 mmol) followed by slow warming of the reaction mixture to room temperature. After stirring for 1.5 h, the reaction was quenched via addition of saturated aqueous $NaHCO_3$ (10 mL) and $Na_2S_2O_3$ (10 mL), and diluted with CH_2Cl_2 (20 mL). The biphasic mixture was vigorously stirred at room temperature for 30 min and then the aqueous phase was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic extracts were dried over $MgSO_4$, filtered and concentrated to yield the crude product as a yellow oil.

The above yellow oil was dissolved in *i*PrOH (10 mL) at room temperature, followed by addition of $CeCl_3•7H_2O$ (34.2 mg, 0.09 mmol). The flask was then evacuated to 300 mbar, flushed with O_2, and the reaction mixture was stirred at room temperature for 20 h, while a slow stream of oxygen (ca., 50 cm^3h^{-1}) was passed through. After removal of the solvent, the residue was purified by column chromatography (25% EtOAc/petroleum ether to 50% EtOAc/petroleum ether) to give **10** (214.7 mg, 74% yield, two steps) and epimer **10** (27.1 mg, 9.3% yield, ca. 8:1 diastereoselectivity) as white amorphous solids. **Compound 10**: ^1H NMR (400MHz, $CDCl_3$) δ 0.89-0.92 (t, *J* = 7.2 Hz, 3H), 1.72-1.77 (dd, *J* = 5.6, 12.4 Hz, 1H), 1.82 (s, 3H), 1.89-1.98 (m, 3H), 1.99-2.06 (m, 2H), 2.32-2.51 (m, 2H), 2.52-2.63 (m, 1H), 2.64-2.84 (m, 3H), 4.42 (brs, 1H), 4.53-4.57 (t, *J* = 8.0 Hz, 1H), 5.09-5.20 (m, 2H), 5.73-5.82 (ddd, *J* = 7.2, 10.4,17.6 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 7.3, 8.2, 22.5, 23.5, 29.1, 31.5, 32.9, 34.9, 61.3, 76.6, 89.8, 115.5, 135.7, 138.3, 170.6, 172.7, 203.4, 212.4; IR (neat) 984, 1625, 1700, 1723, 3284 cm^{-1}; MS (EI) *m/z* 317, 260, 232, 204, 178, 132, 105; HRMS (ESI) Calcd. for $C_{18}H_{24}NO_4$ $(M+H)^+$: 318.1700, Found 318.1708, Error: 2.5 ppm.



10 **11**

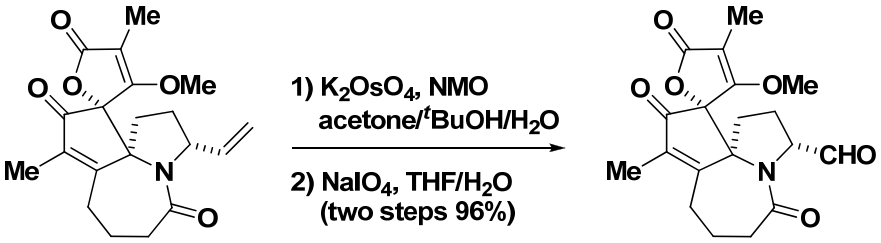
Compound 11. A solution of **10** (285.2 mg, 0.9 mmol) in anhydrous CH_2Cl_2 (10 mL) under argon was treated with Et_3N (1.5 mL, 10.8 mmol), DMAP (439.1 mg, 3.6 mmol), and ethyl chloroformate (0.86 mL, 9.0 mmol) at room temperature. The reaction mixture was stirred for 24 h

and then concentrated. The residue was purified via silica gel chromatography (15% EtOAc/petroleum ether to 35% EtOAc/petroleum ether) to give carbonate **11** (350mg, 99% yield) as a white amorphous solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.01-1.05 (t, *J* = 7.2 Hz, 3H), 1.33-1.37 (t, *J* = 6.8 Hz, 3H), 1.82-1.86 (m, 1H), 1.88 (s. 3H), 1.92-2.01 (m, 1H), 2.02-2.13 (m, 4H), 2.31-2.40 (m, 2H), 2.51-2.67 (m, 3H), 2.80-2.86 (dd, *J* = 8.8, 12.4 Hz, 1H), 4.22-4.33 (m, 2H), 4.56-4.60 (t, *J* = 8.0 Hz, 1H), 5.16-5.26 (m, 2H), 5.76-5.84 (ddd, *J* = 7.2, 10.4, 17.6 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 7.5, 8.4, 14.0, 22.1, 23.3, 29.2, 32.2, 33.0, 35.1, 61.4, 65.3, 75.8, 93.4, 115.8, 137.0, 138.1, 153.5, 166.1, 172.7, 196.7, 206.5; IR (neat) 954, 1655, 1710, 1729, 1760 cm^{-1}; MS (EI) *m/z* 389, 332, 299, 260, 214, 175, 120; HRMS (ESI) Calcd. for $C_{21}H_{28}NO_6$ $(M+H)^+$: 390.1911, Found 390.1918, Error: 1.8 ppm.

11 **2**

Compound 2. To a solution of the carbonate **11** (77 mg, 0.20 mmol) in THF (14.2 mL) at -78 ^{o}C under argon was added KHMDS (0.91 M, 436 μL, 0.40 mmol). The reaction mixture was warmed slowly to 10 ^{o}C over 5 h, and then it was quenched with 3 mL water at 0 ^{o}C. The resulting mixture was diluted with CH_2Cl_2 (10 mL) and treated with 2N HCl to PH = 2. The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL), then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated to give a yellow amorphous solid.

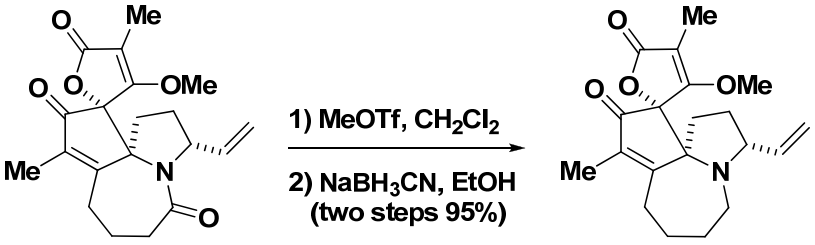
The above crude product was dissolved in CH_2Cl_2 (15.7 mL) under argon, followed by addition of CH_2N_2 (1 M, 1 mL, 1 mmol). After stirring at 0 ^{o}C for 1 h, the solution was quenched with acetic acid (1 mL). Removal of solvent in *vacuo* resulted in a yellow solid which was purified by chromatography (50% EtOAc/petroleum ether to 70% EtOAc/petroleum ether) to give tetracyclic product **2** (53.9 mg, 76% yield, two steps) as a white crystalline solid: mp 178-180 ^{o}C; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.74-1.77 (m, 1H), 1.87 (s, 3H), 1.90-1.97 (m, 1H), 2.03 (s, 3H), 2.07-2.16 (m, 4H), 2.25-2.30 (ddd, *J* = 2.8, 4.4, 14.4 Hz, 1H), 2.49-2.57 (m, 1H), 2.77-2.86 (dt, *J* = 6.4, 14.4 Hz, 1H), 2.92-2.98 (m, 1H), 3.98 (s, 3H), 4.40-4.44 (t, *J* = 7.6, 1H), 5.12-5.20 (m, 2H), 5.71-5.80 (ddd, *J* = 7.2, 10.0, 17.2 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.8, 8.9, 21.8, 22.5, 29.2, 33.8, 35.6, 59.1, 60.9, 75.9, 88.1, 98.6, 115.3, 137.4, 138.6, 169.7, 170.7, 173.1, 173.6, 195.7; IR(neat) 1000, 1647, 1719, 1761 cm^{-1}; MS (EI) *m/z* 357, 302, 242, 202, 175, 149, 83; HRMS (ESI) Calcd. for $C_{20}H_{24}NO_5$ $(M+H)^+$: 358.1649, Found 358.1646, Error: 0.8 ppm.



2 **15**

Compound 15. Potassium osmate dehydrate (1 mg) was added to a stirred solution of **2** (22 mg, 0.062 mmol) and *N*-methylmorpholine *N*-oxide (41.7 mg, 0.31 mmol) in acetone (1 mL), *t*BuOH (0.5 mL) and water (0.5 mL). After stirring for 5.5 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL). The resulting mixture was dried over $MgSO_4$, filtered and evaporated under reduced pressure to give the crude product as a sticky oil.

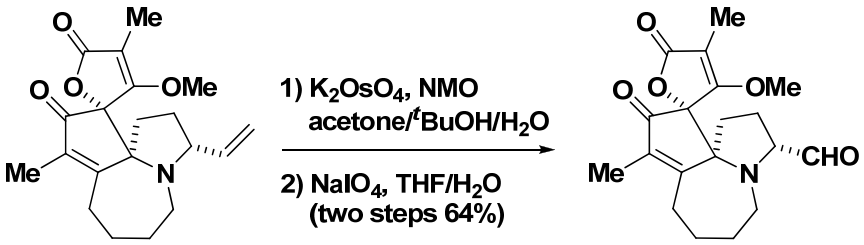
The above crude product was dissolved in THF (4 mL) and water (2 mL) under argon, followed by addition of $NaIO_4$ (26.2 mg, 0.122 mmol). After stirring at room temperature for 2 h, the solution was diluted with CH_2Cl_2 (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), and then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Chromatography (50% EtOAc/petroleum ether to 75% EtOAc/petroleum ether)) afforded the aldehyde **15** (21.2 mg, 96% yield, two steps) as a white amorphous solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.86-1.87 (d, J = 6.4 Hz, 1H), 1.89 (s, 3H), 1.94-2.01 (m, 1H), 2.04 (s, 3H), 2.07-2.23 (m, 4H), 2.29-2.34 (m, 1H), 2.84-2.94 (m, 3H), 3.99 (s, 3H), 4.53-4.56 (d, J = 9.2 Hz, 1H), 9.64-9.65 (d, J = 0.8 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.7, 8.9, 22.2, 22.4, 23.0, 32.2, 35.6, 59.2, 65.0, 75.3, 88.2, 98.8, 137.8, 169.6, 170.0, 173.4, 195.4, 197.5; MS (EI) *m/z* 359, 330, 290, 256, 202, 149, 83; HRMS (ESI) Calcd. for $C_{19}H_{22}NO_6$ $(M+H)^+$: 360.1442, Found 360.1440, Error: 0.6 ppm.



2 **12**

Compound 12. Methyl trifluoromethanesulfonate (0.748 mL, 6.82 mmol) was added in one portion to a solution of **2** (64 mg, 0.18 mmol) in CH_2Cl_2 (10.3 mL) under argon. The reaction mixture was stirred at room temperature for 12 h, and concentrated. The residue was dissolved in EtOH (2.8 mL), and treated with $NaCNBH_3$ (53.5 mg, 0.85 mmol). The reaction mixture was stirred at room temperature for 10 min, treated with the mixture of acetic acid and water (2.8 mL, ca. 1:1), and sequentially stirred at room temperature for 30 min. The resulting mixture was diluted with CH_2Cl_2 (10 mL) and treated with saturated aqueous $NaHCO_3$ (5 mL). The aqueous phase was extracted with

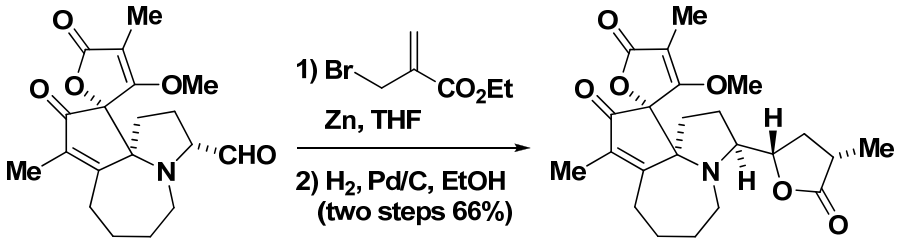
CH_2Cl_2 (3 x 5 mL), and then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Chromatography (15% EtOAc/petroleum ether to 65% EtOAc/petroleum ether) afforded the desired tertiary amine **12** (30.9 mg , 95% yield based on recovery material, two steps) as a white amorphous solid and recovered starting material (30 mg); ^{1}H NMR (400MHz, $CDCl_3$) δ 1.20-1.29 (m, 1H), 1.34-1.39 (dd, *J* = 3.6, 14.0 Hz, 1H), 1.53-1.68 (m, 2H), 1.74-1.82 (m, 4H), 1.90-2.01 (m, 2H), 2.03 (s, 3H), 2.09-2.18 (m, 2H), 2.81-2.92 (m, 2H), 3.05-3.09 (d, *J* = 15.6 Hz, 1H), 3.61-3.66 (dd, *J* = 8.8, 15.2 Hz, 1H), 3.96 (s, 3H), 5.01-5.11 (m, 2H), 5.28-5.37 (ddd, *J* = 8.0, 10.0, 18.0 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.3, 8.8, 24.8, 26.6, 28.3, 31.8, 36.3, 45.7, 58.5, 63.9, 77.7, 91.3, 97.0, 115.9, 135.7, 141.5, 172.4, 174.2, 175.0, 198.7; IR(neat) 992, 1663, 1710, 1758 cm^{-1}; MS (EI) *m/z* 343, 300, 284, 256, 216, 174, 132; HRMS (ESI) Calcd. for $C_{20}H_{26}NO_4$ $(M+H)^+$: 344.1856, Found 344.1859, Error: 0.9 ppm.



12 **13**

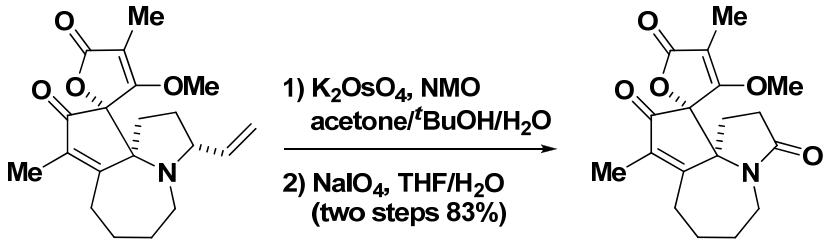
Compound 13. Potassium osmate dehydrate (1 mg) was added to a stirred solution of **12** (15.7 mg, 0.046 mmol) and *N*-methylmorpholine *N*-oxide (31 mg, 0.26 mmol) in acetone (0.8 mL), *t*BuOH (0.4 mL) and water (0.4 mL). After stirring for 3.5 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL). The resulting mixture was dried over $MgSO_4$, filtered and evaporated under reduced pressure to give the crude product as a sticky oil.

The above crude product was dissolved in THF (3 mL) and water (1.5 mL) under argon, followed by addition of $NaIO_4$ (13.8 mg, 0.065 mmol). After stirring at 0 ^{o}C for 3 h, the solution was diluted with CH_2Cl_2 (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), and then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Chromatography (20% EtOAc/petroleum ether) afforded the aldehyde **13** (10 mg, 64% yield, two steps) as a white amorphous solid; ^{1}H NMR (600MHz, $CDCl_3$) δ 1.24-1.33 (m, 1H), 1.46-1.49 (m, 1H), 1.64-1.71 (m, 1H), 1.81 (s, 3H), 1.84-1.93 (m, 2H), 2.01-2.03 (m, 5H), 2.14-2.18 (m, 1H), 2.25-2.27 (dd, *J* = 5.4, 12 Hz, 1H), 2.93-2.95 (d, *J* = 13.2 Hz, 2H), 3.04-3.08 (m, 1H), 3.65-3.68 (m, 1H), 4.02 (s, 3H), 8.98-8.99 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR (150M, $CDCl_3$) δ 8.5, 8.8, 25.4, 25.5, 26.5, 28.2, 36.6, 47.9, 58.8, 68.3, 78.1, 90.8, 97.4, 137.0, 172.0, 172.2, 174.5, 198.0, 201.9; IR (neat) 1662, 1713, 1759, 2779 cm^{-1}; MS (EI) *m/z* 345, 316, 283, 266, 188, 162, 83; HRMS (ESI) Calcd. for $C_{20}H_{24}NO_5$ $(M+H)^+$: 346.1649, Found 346.1643, Error: 1.7 ppm.



13 1e

Compound 1e. Zn (16.5 mg, 0.25 mmol) was added to a solution of aldehyde **13** (17.9 mg, 0.052 mmol) in dry THF (6 mL) under argon**.** The solution was heated up and, when reflux started, a solution of ethyl 2-(bromomethyl)acrylate (16.9 mg, 0.088 mmol) in dry THF (5 mL) was added. After stirring for 10 min, the resulting mixture was cooled to room temperature, quenched with water (10 μL), and concentrated. The residue was dissolved in EtOH (7 mL), and treated with 10% Pd/C (8 mg). The reaction mixture was stirred in an atmosphere of H_2 for 15 h, filtered and concentrated. Chromatography (75% chloroform/petroleum ether) afforded **1e** (14.2 mg, 66% yield, two steps) as a white crystalline solid: mp 189-190 ^{o}C; ^{1}H NMR (600MHz, $CDCl_3$) δ 1.25-1.26 (d, *J* = 7.2 Hz, 3H), 1.33-1.39 (m, 1H), 1.46-1.54 (m, 3H), 1.75-1.82 (m, 4H), 1.85-1.89 (m, 2H), 1.97-1.98 (m, 1H), 2.02 (s, 3H), 2.10-2.13 (m, 1H), 2.24-2.28 (m, 1H), 2.32-2.36 (ddd, *J* = 5.4, 8.8, 14.2 Hz, 1H), 2.55-2.60 (m, 1H), 2.88-2.95 (m, 2H), 3.36-3.40 (m, 1H), 3.58-3.60 (d, *J* = 15.6 Hz, 1H), 3.83-3.87 (ddd, *J* = 6, 7.8, 11.4 Hz, 1H), 4.00 (s, 3H); ^{13}C NMR (150M, $CDCl_3$) δ 8.4, 8.9, 14.9, 24.9, 25.5, 26.6, 28.4, 34.5, 34.8, 35.8, 47.2, 58.8, 63.6, 79.3, 85.1, 91.6, 96.9, 136.4, 172.5, 173.2, 175.0, 179.7, 197.9; IR (neat) 1662, 1709, 1760 cm^{-1}; MS (EI) *m/z* 415, 372, 316, 272, 188, 162, 83; HRMS (ESI) Calcd. for $C_{23}H_{30}NO_6$ $(M+H)^+$: 416.2068, Found 416.2058, Error: 2.4 ppm.

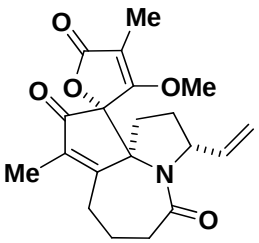


12 1c

Compound 1c. Potassium osmate dehydrate (1 mg) was added to a stirred solution of **12** (8.7 mg, 0.025 mmol) and *N*-methylmorpholine *N*-oxide (17.4 mg, 0.13 mmol) in acetone (0.48 mL), *t*BuOH (0.24 mL) and water (0.24 mL). After stirring for 3.5 h at room temperature, the reaction mixture was diluted with CH_2Cl_2 (10 mL). The resulting mixture was dried over $MgSO_4$, filtered and evaporated under reduced pressure to give the crude product as a sticky oil.

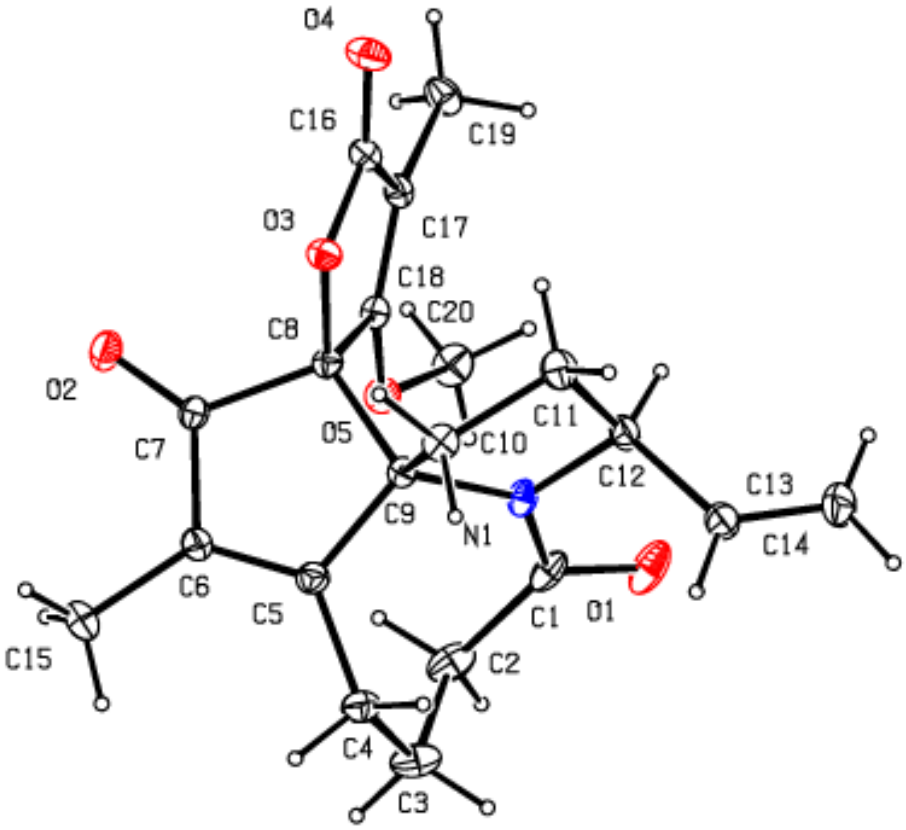
The above crude product was dissolved in THF (2 mL) and water (1 mL) under argon, followed by addition of $NaIO_4$ (54.3 mg, 0.25 mmol). After stirring at 40 ^{o}C for 10 h, the solution was diluted

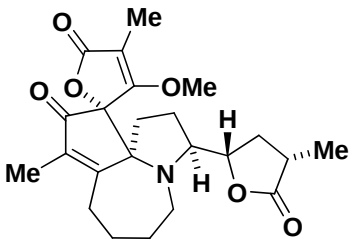
with CH_2Cl_2 (10 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL), and then the combined organic extracts were dried over $MgSO_4$, filtered and concentrated. Chromatography (70% EtOAc/petroleum ether) afforded the **1c** (7 mg, 83% yield, two steps) as a white amorphous solid; ^{1}H NMR (400MHz, $CDCl_3$) δ 1.30-1.47 (m, 2H), 1.81-1.84 (d, *J* = 11.2 Hz, 1H), 1.87 (s, 3H), 1.91-2.00 (m, 1H), 2.02 (s, 3H), 2.11-2.18 (m, 2H), 2.27-2.41 (m, 2H), 2.56-2.66 (m, 1H), 2.82-2.88 (t, *J* = 12.8 Hz, 1H), 2.97-3.02 (dd, *J* = 5.6, 10 Hz, 1H), 4.00 (s, 3H), 4.17-4.21 (d, *J* = 14.8 Hz, 1H); ^{13}C NMR (100M, $CDCl_3$) δ 8.4, 9.1, 27.4, 27.5, 29.9, 30.2, 31.9, 41.3, 59.2, 74.5, 90.0, 99.7, 137.0, 168.7, 170.9, 172.9, 175.8, 196.6; IR (neat) 1662, 1699, 1766, 2925 cm^{-1}; MS (EI) *m/z* 331, 286, 221, 181, 164, 131, 83; HRMS (ESI) Calcd. for $C_{18}H_{21}NO_5$ $(M+H)^+$: 332.1492, Found 332.1495, Error: 0.9 ppm.



2

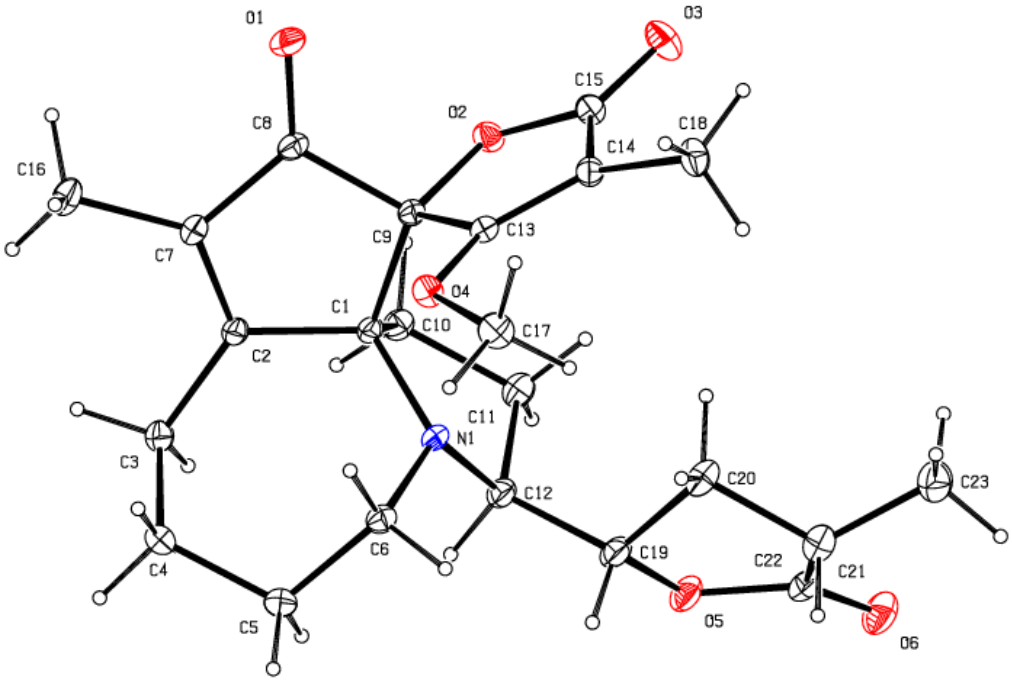
The structure of our synthetic tetracyclic compound **2** was corroborated by single-crystal. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 782619.

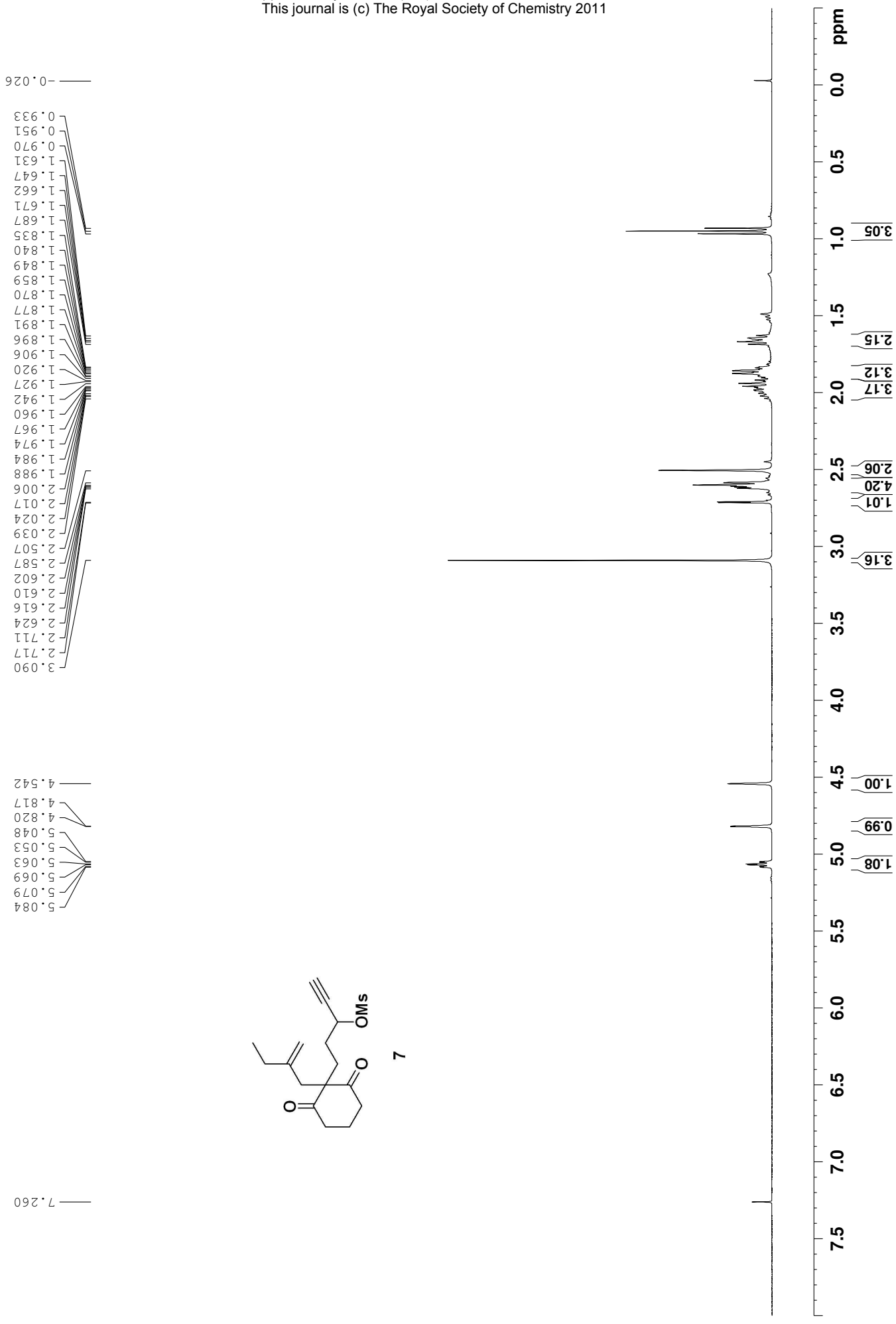




Maistemonine (1e)

The structure of our synthetic Maistemonine (**1e)** was corroborated by single-crystal. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 782618.

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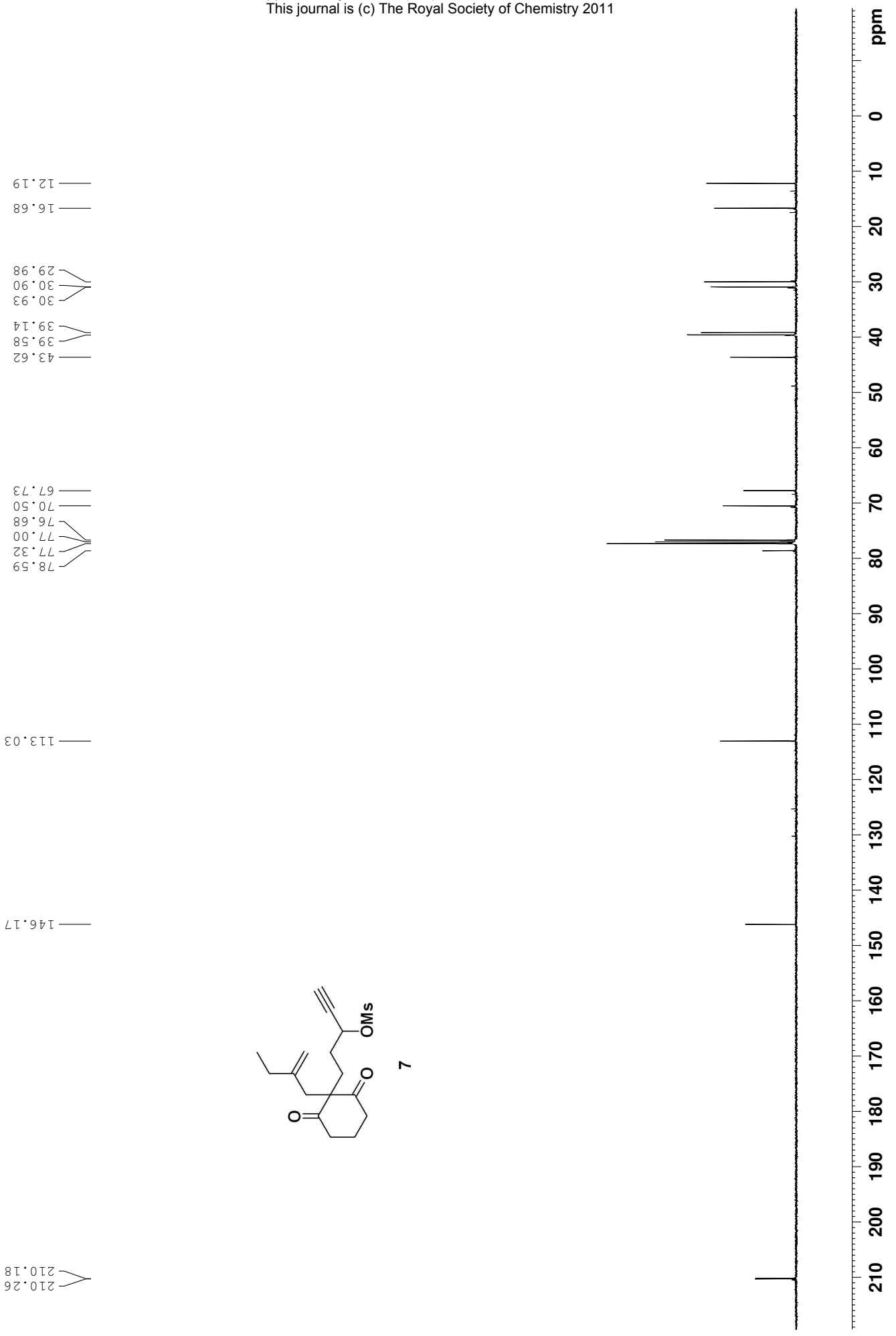
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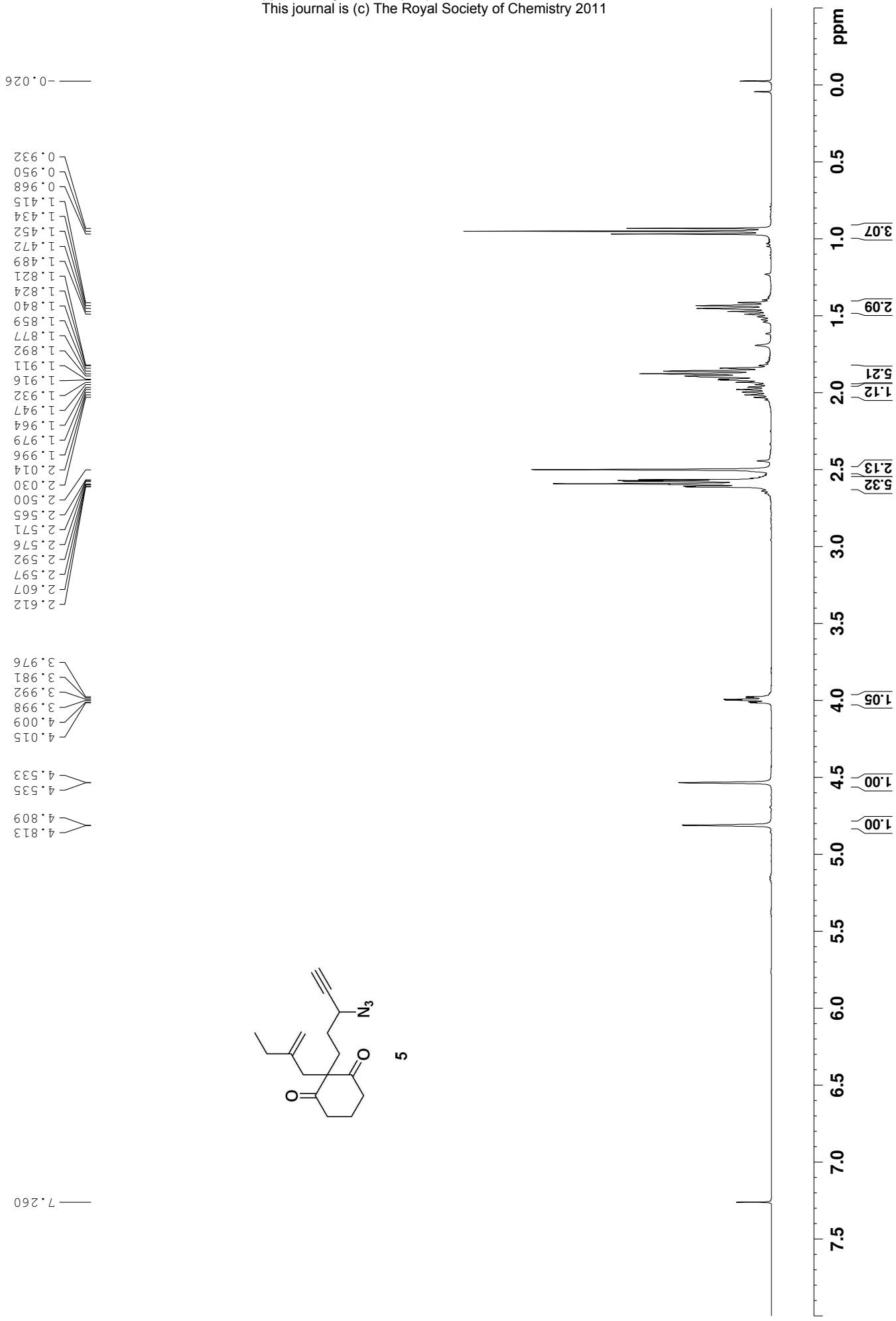
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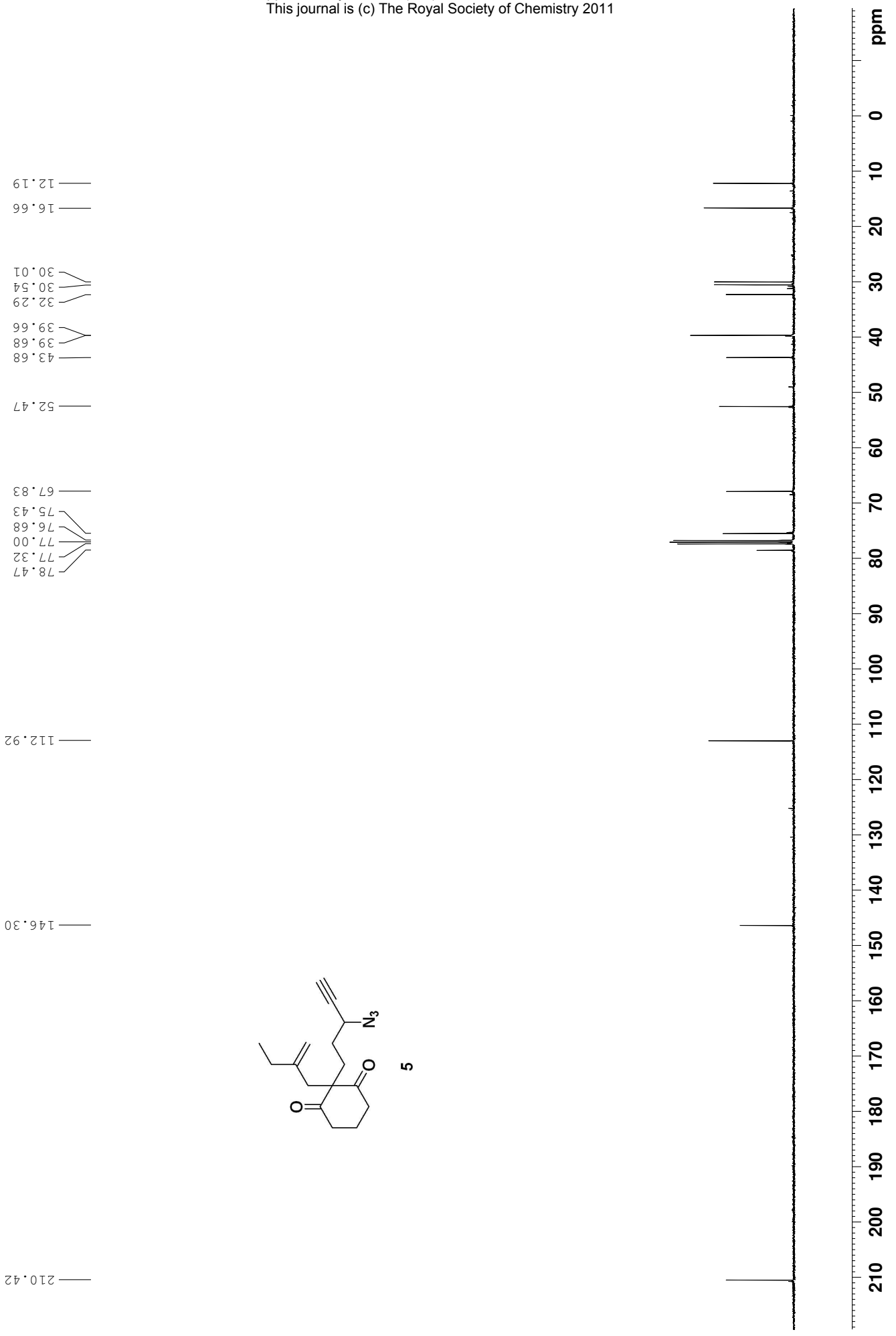
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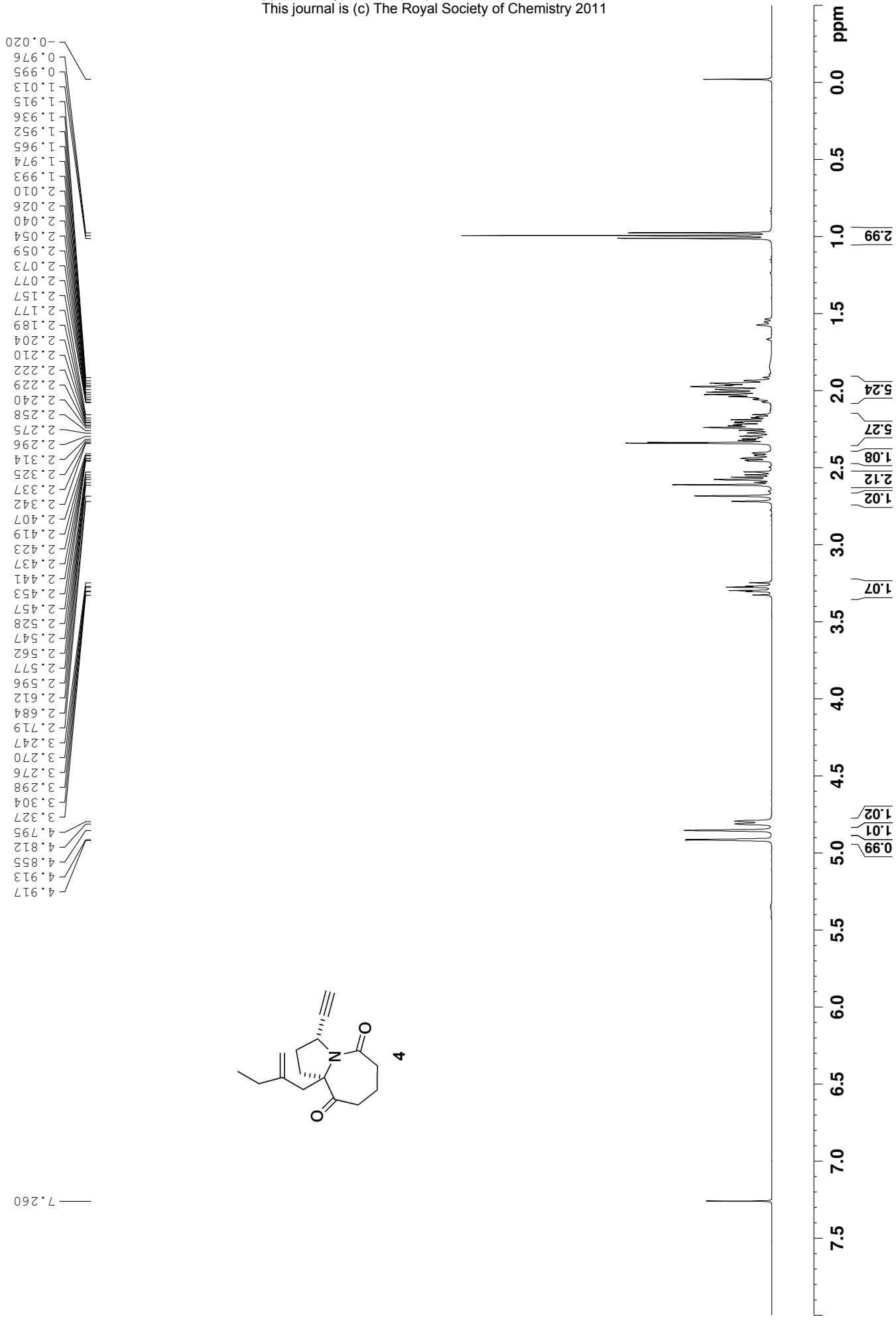
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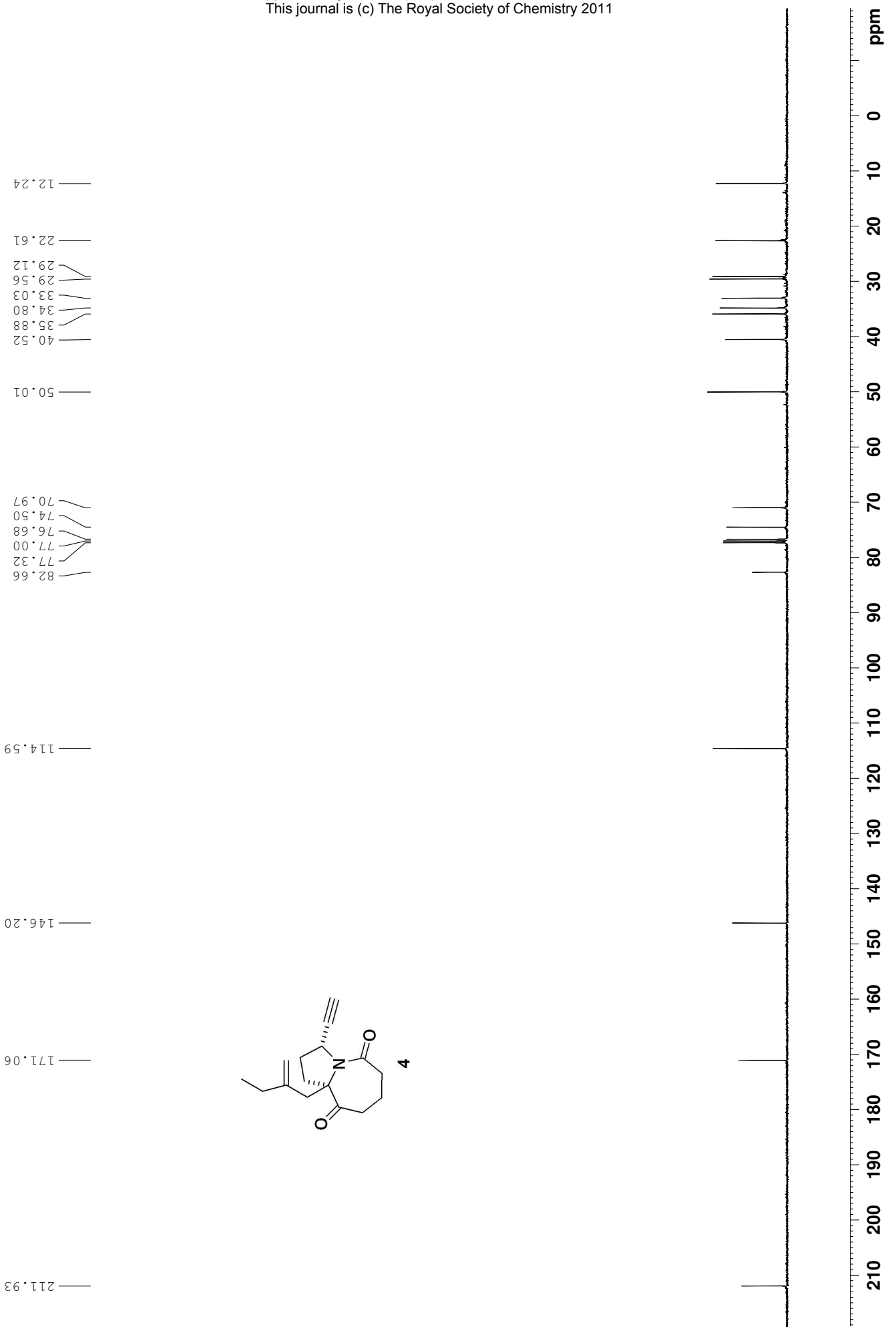
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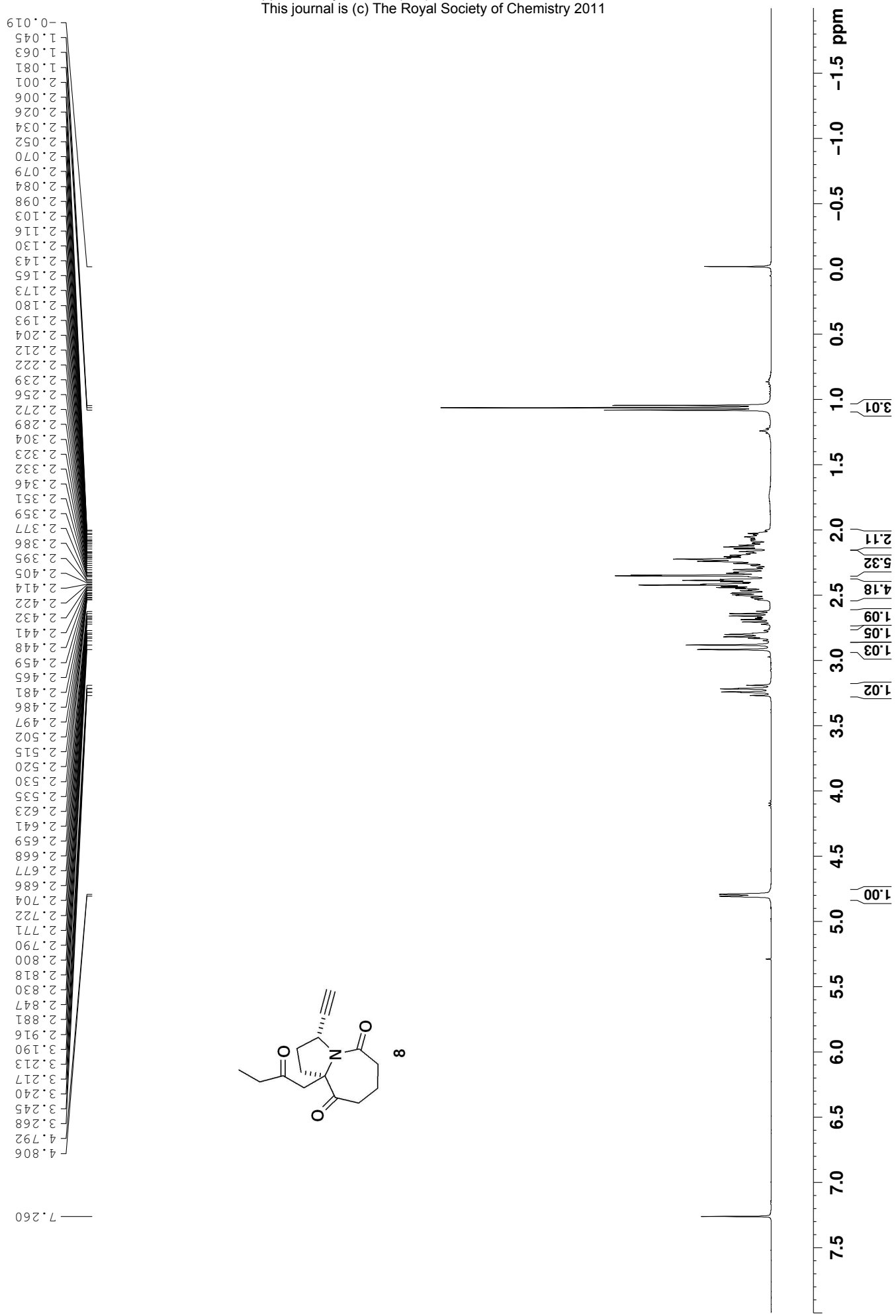
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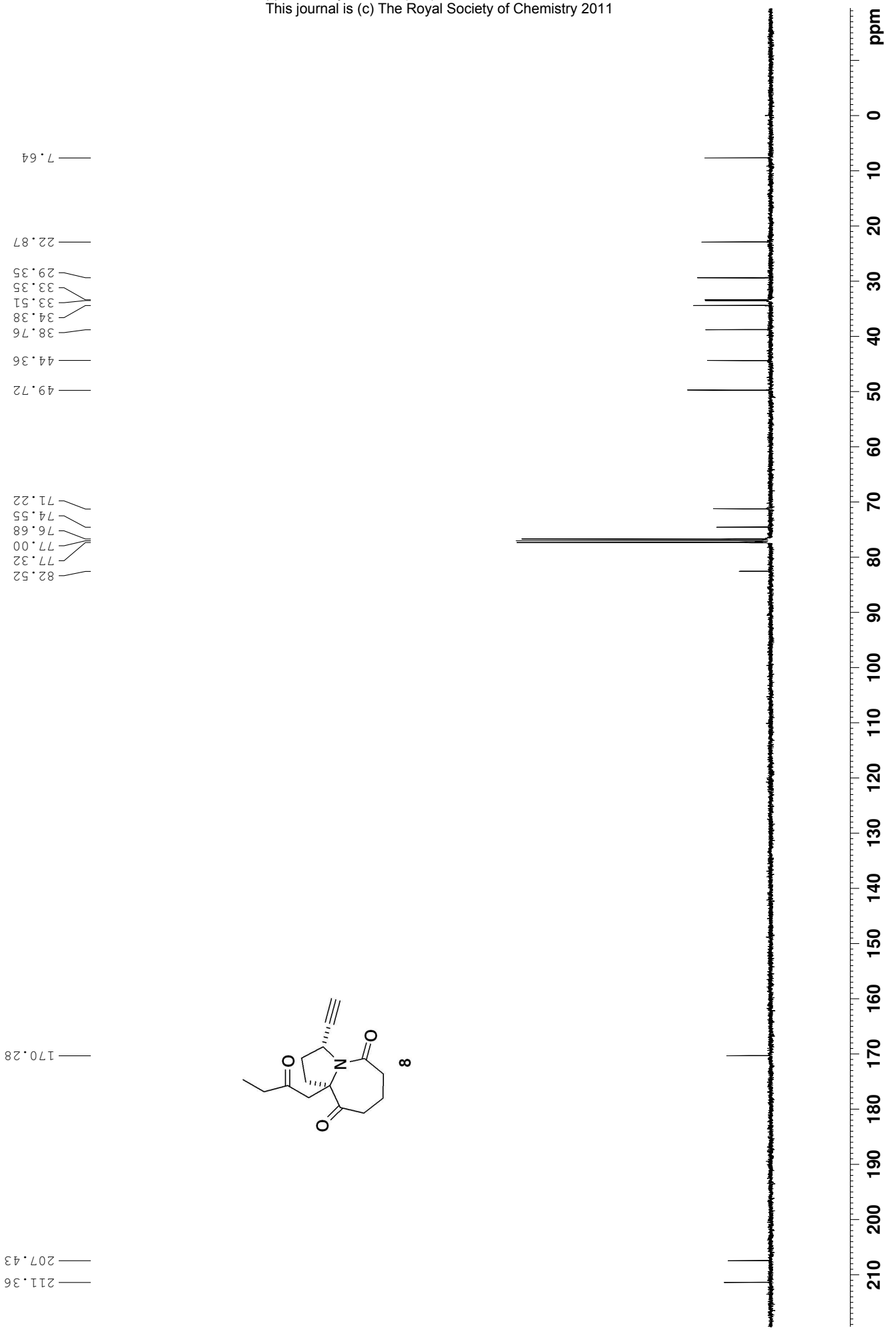
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O
O
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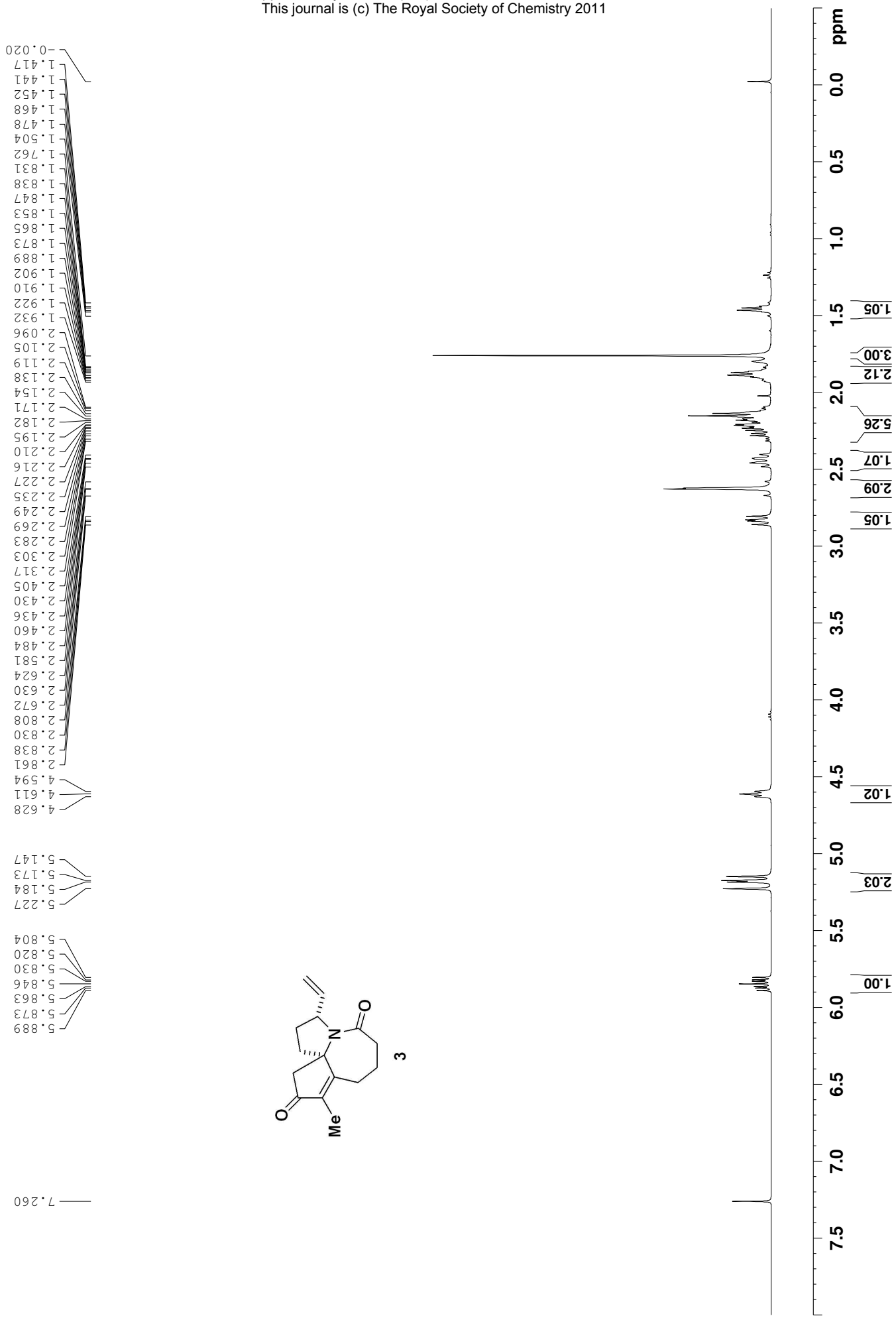
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O
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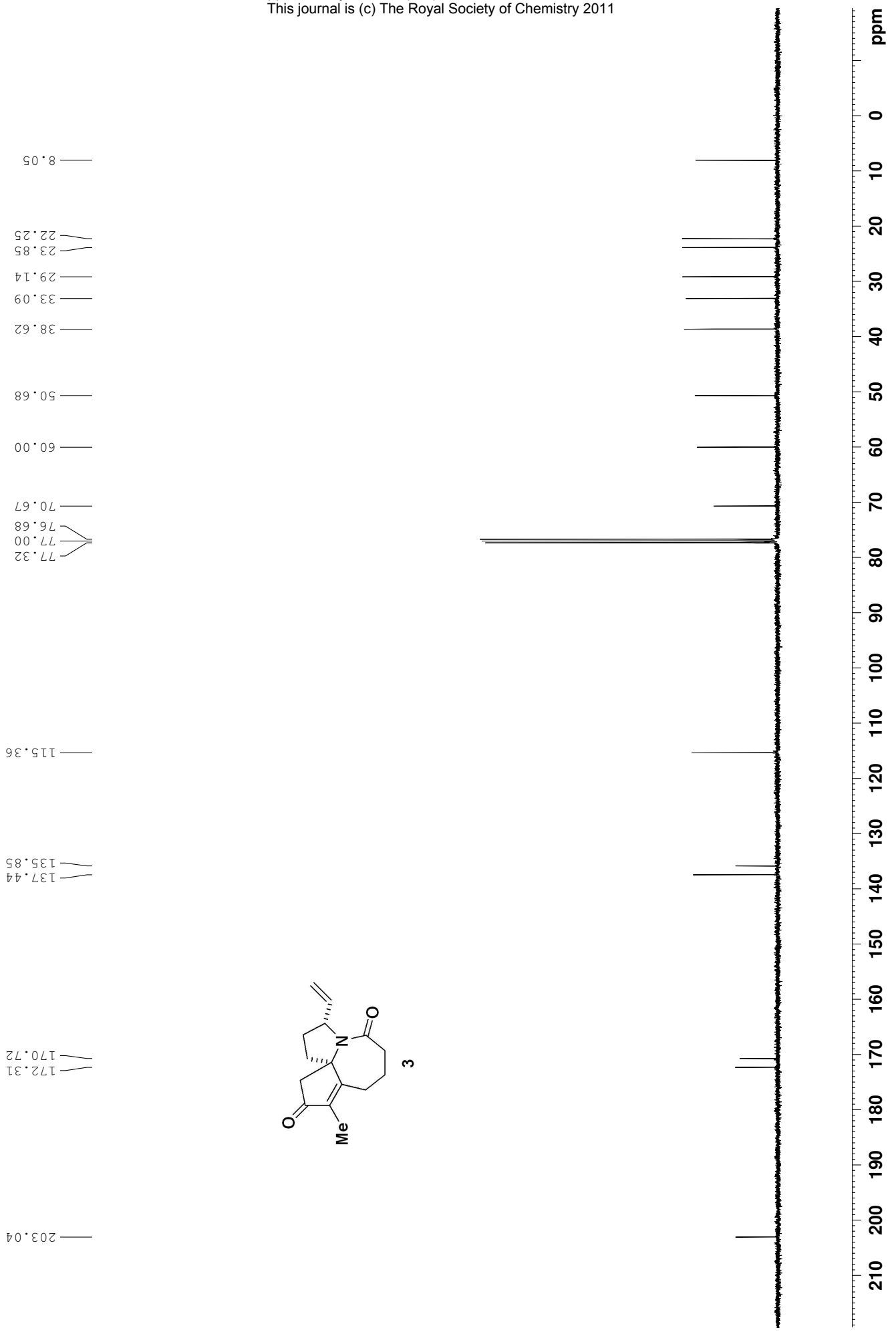
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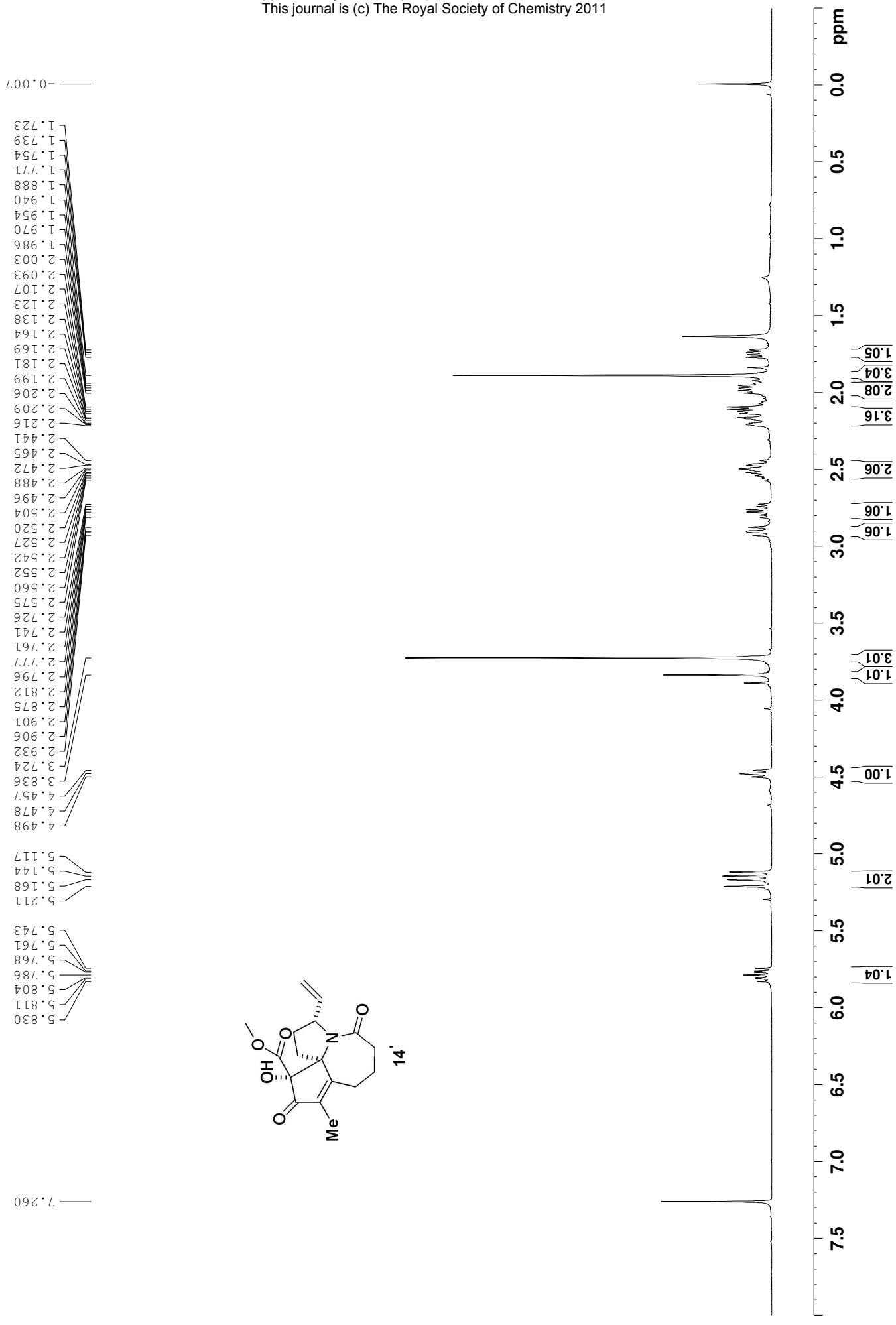
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2.552
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2.741
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2.875
2.901
2.906
2.932
3.724
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2.08
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2.06
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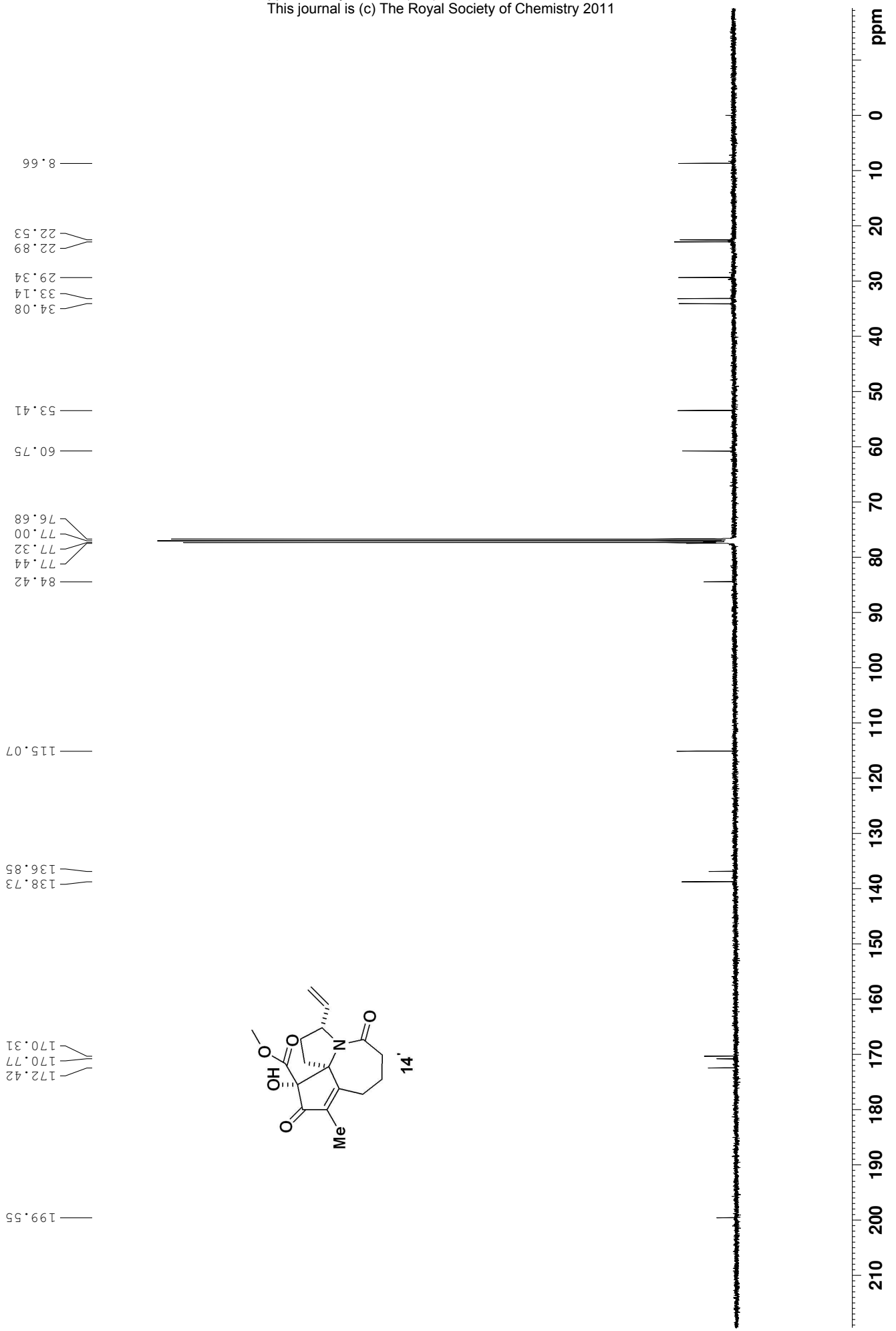
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115.07
136.85
138.73
170.31
170.77
172.42
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70
80
90
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160
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180
190
200
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OH
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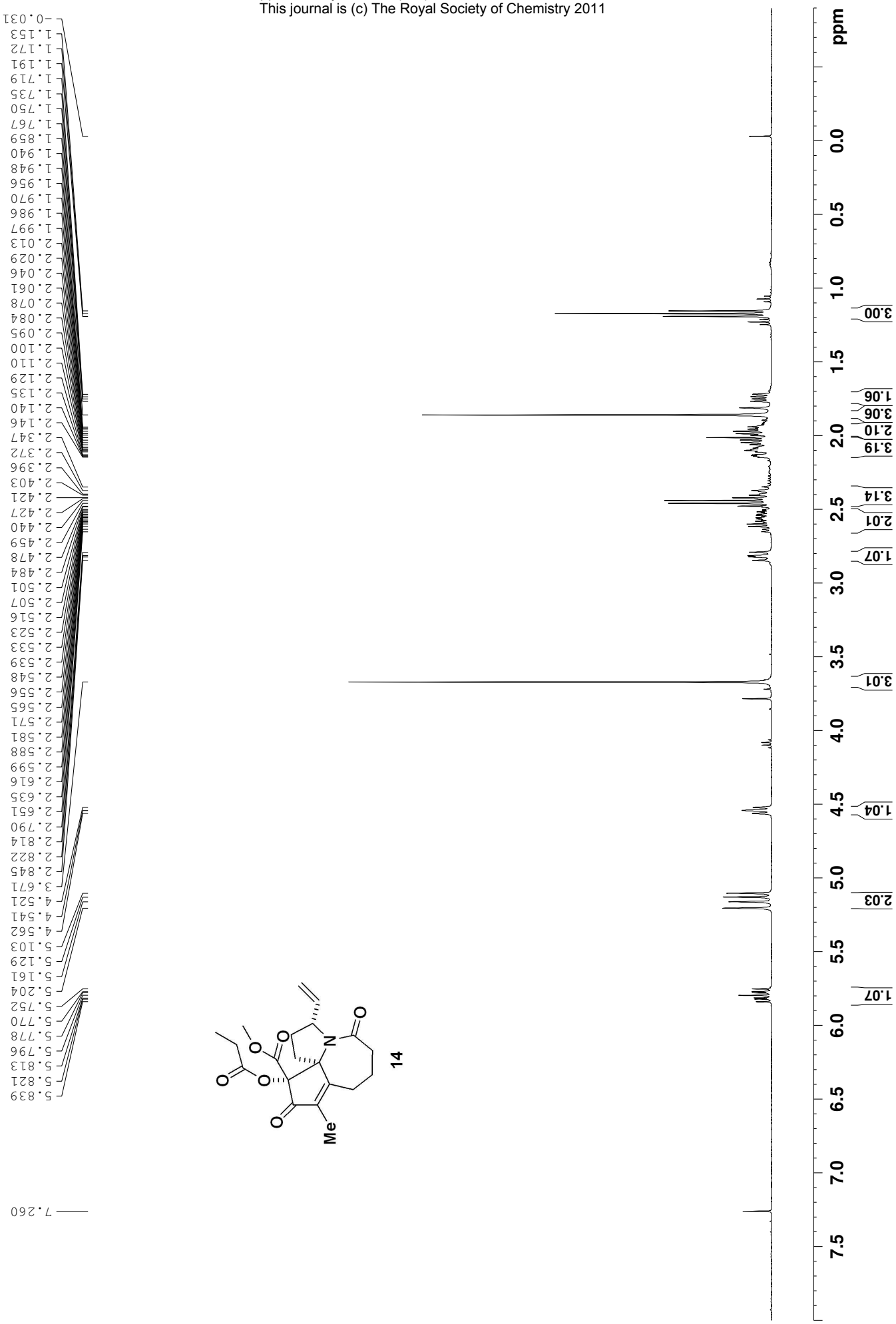
N
O
O
Me
14'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1.970
1.986
1.997
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2.046
2.061
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2.084
2.095
2.100
2.110
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2.484
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2.507
2.516
2.523
2.533
2.539
2.548
2.556
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2.571
2.581
2.588
2.599
2.616
2.635
2.651
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6.0
6.5
7.0
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3.06
2.10
3.19
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1.04
2.03
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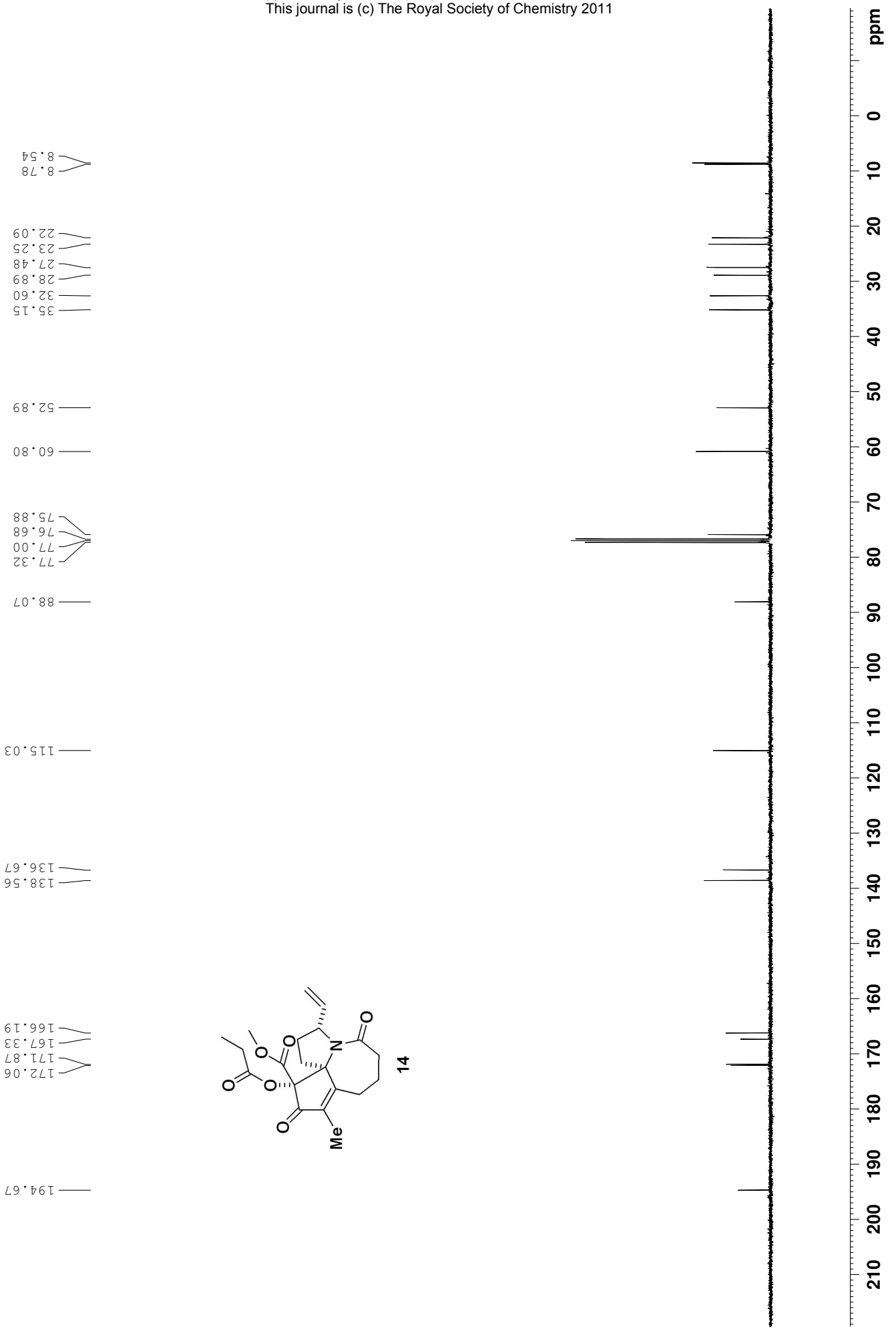
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167.33
171.87
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O
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O
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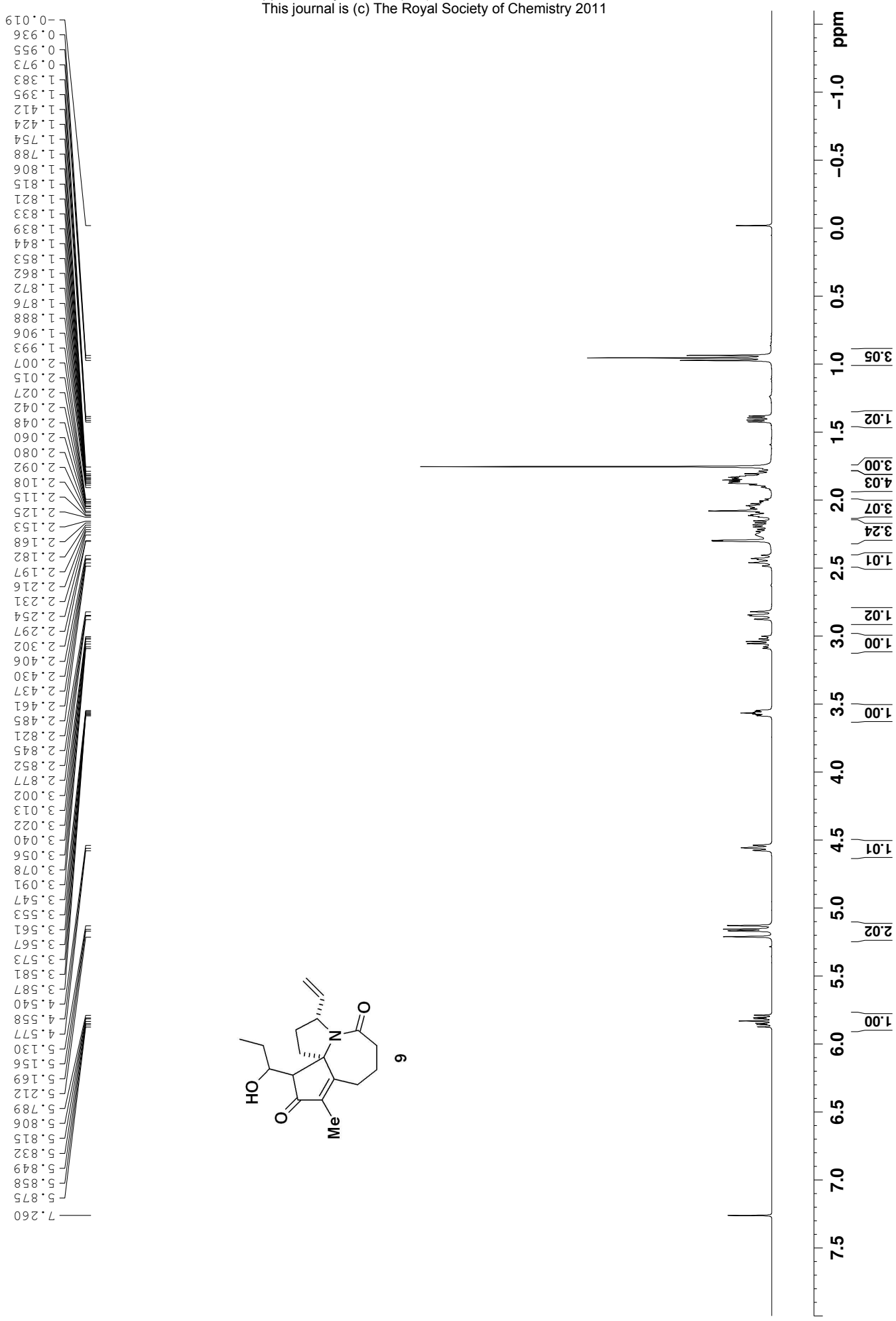
Me
14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−1.0
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1.02
3.00
4.03
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1.00
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1.00
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Me
N
O
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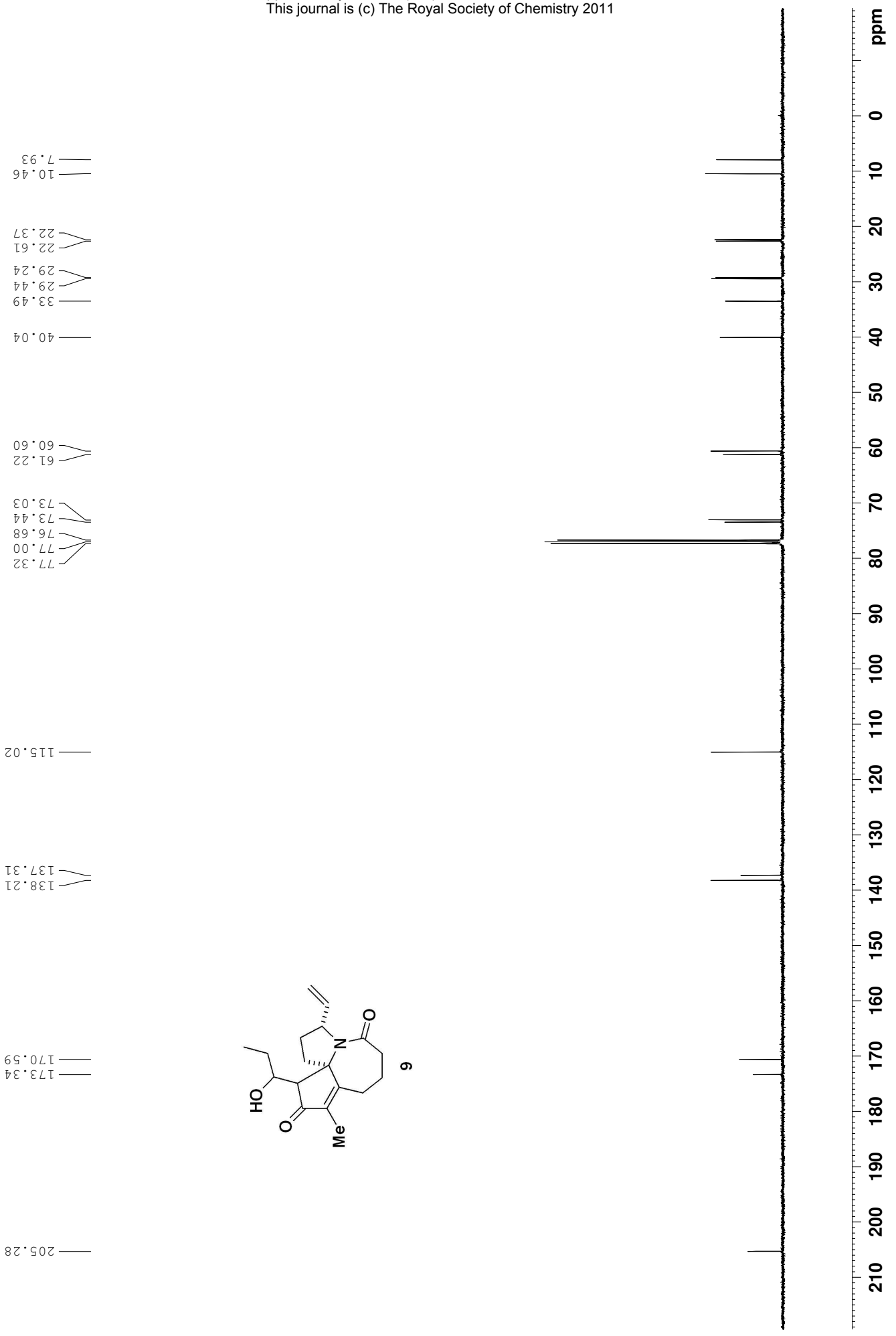
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77.32
115.02
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138.21
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173.34
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20
30
40
50
60
70
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210
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O
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O
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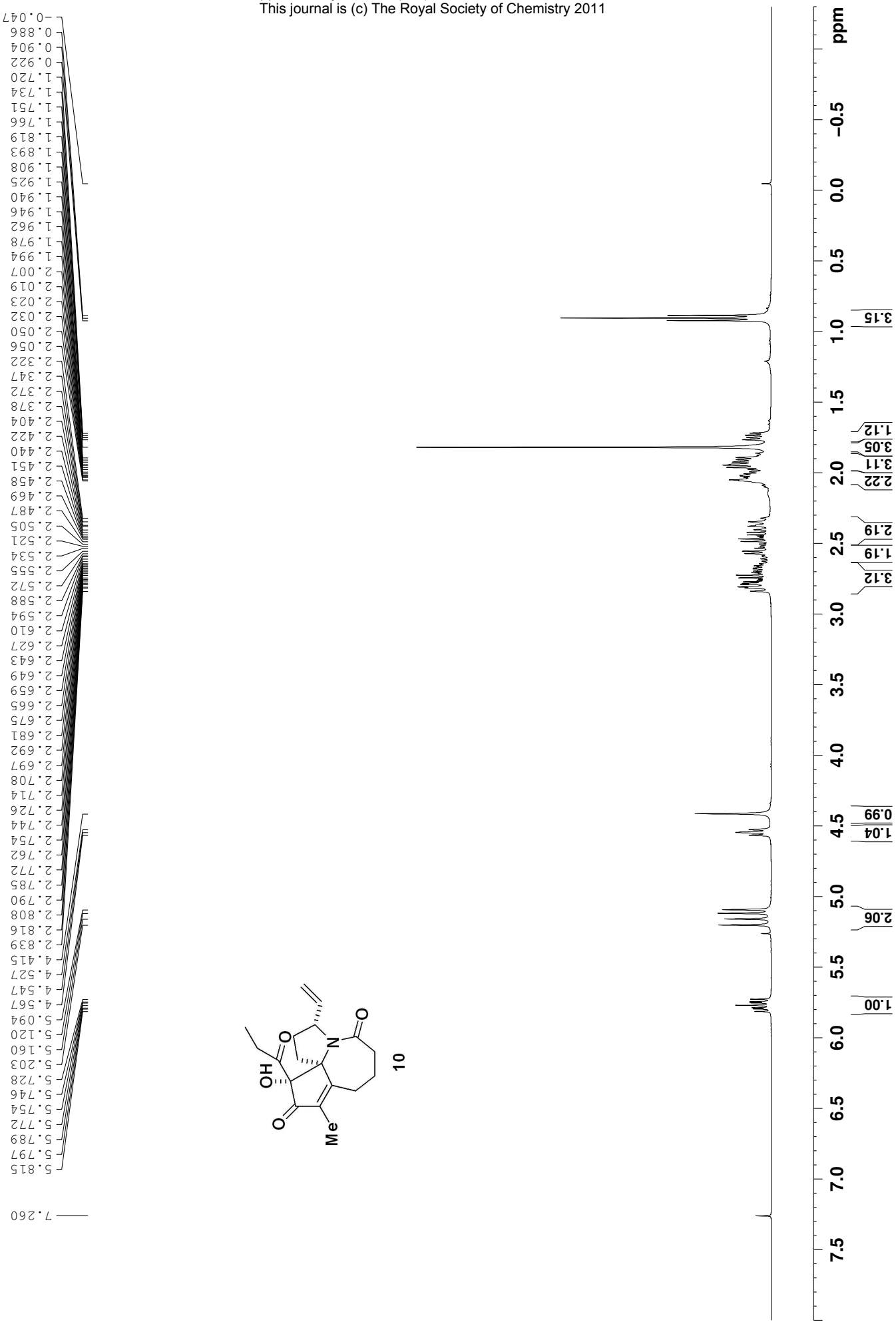
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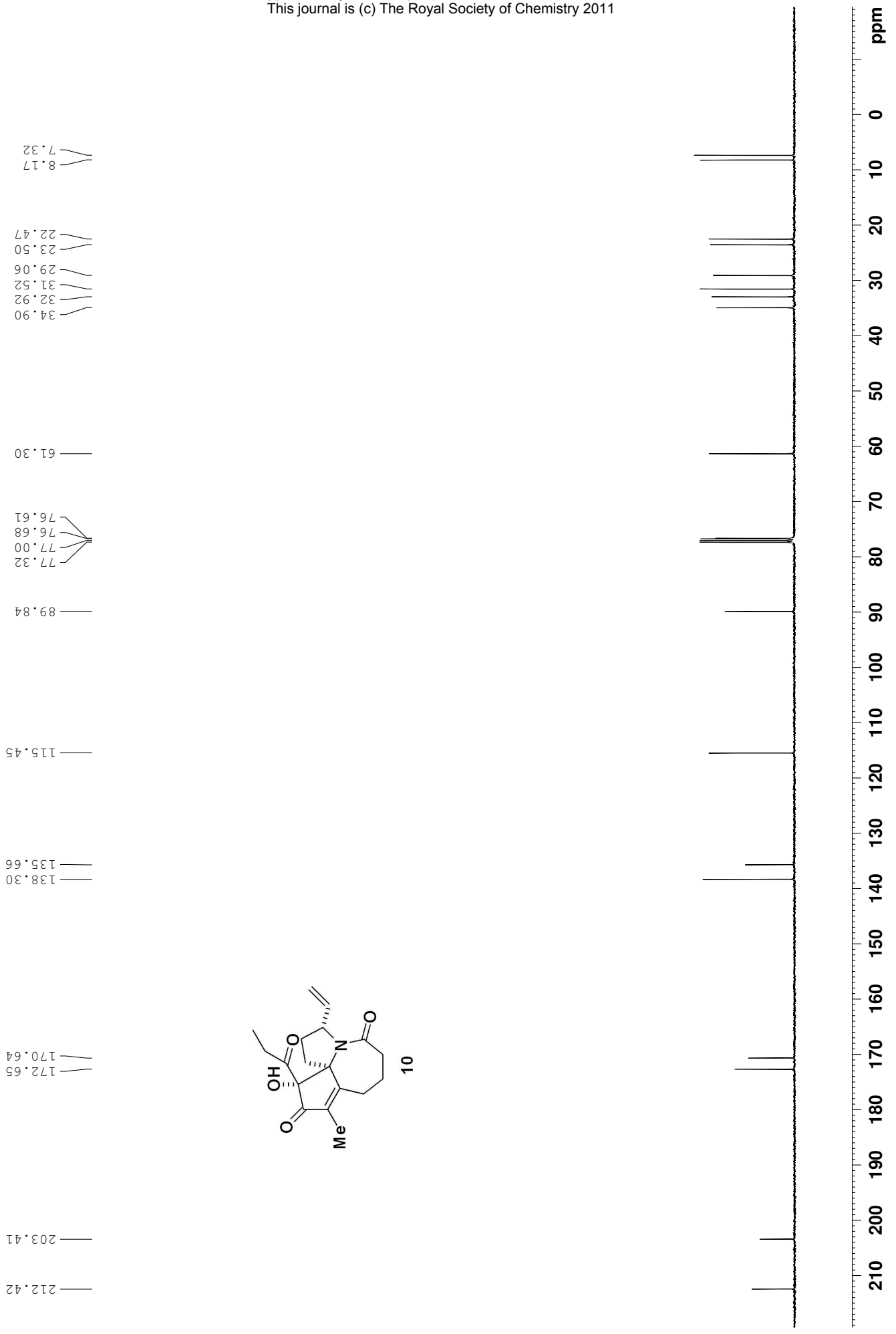
O
O
Me
10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172.65
203.41
212.42
OH
O
O
N
O
Me
10
ppm
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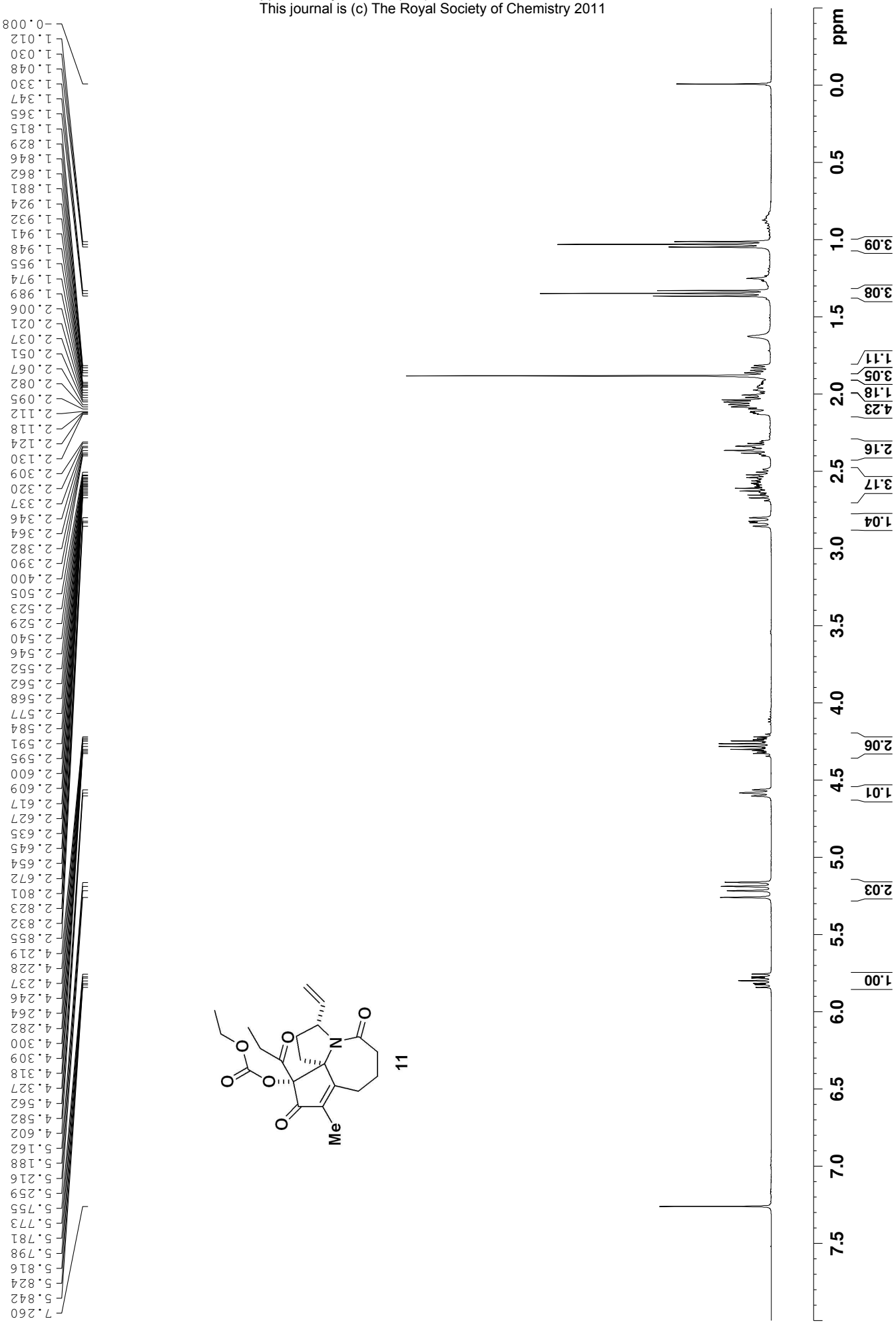
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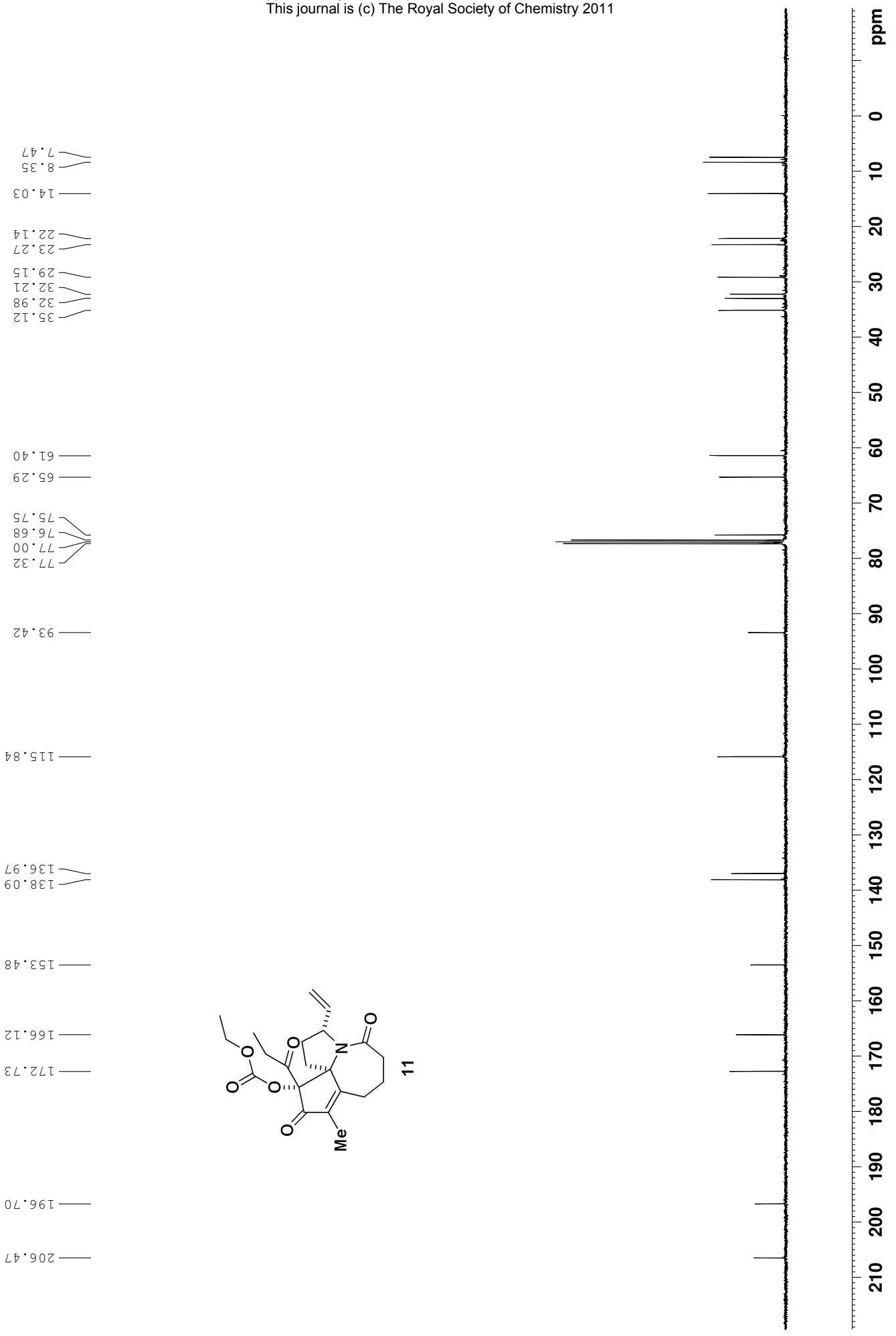
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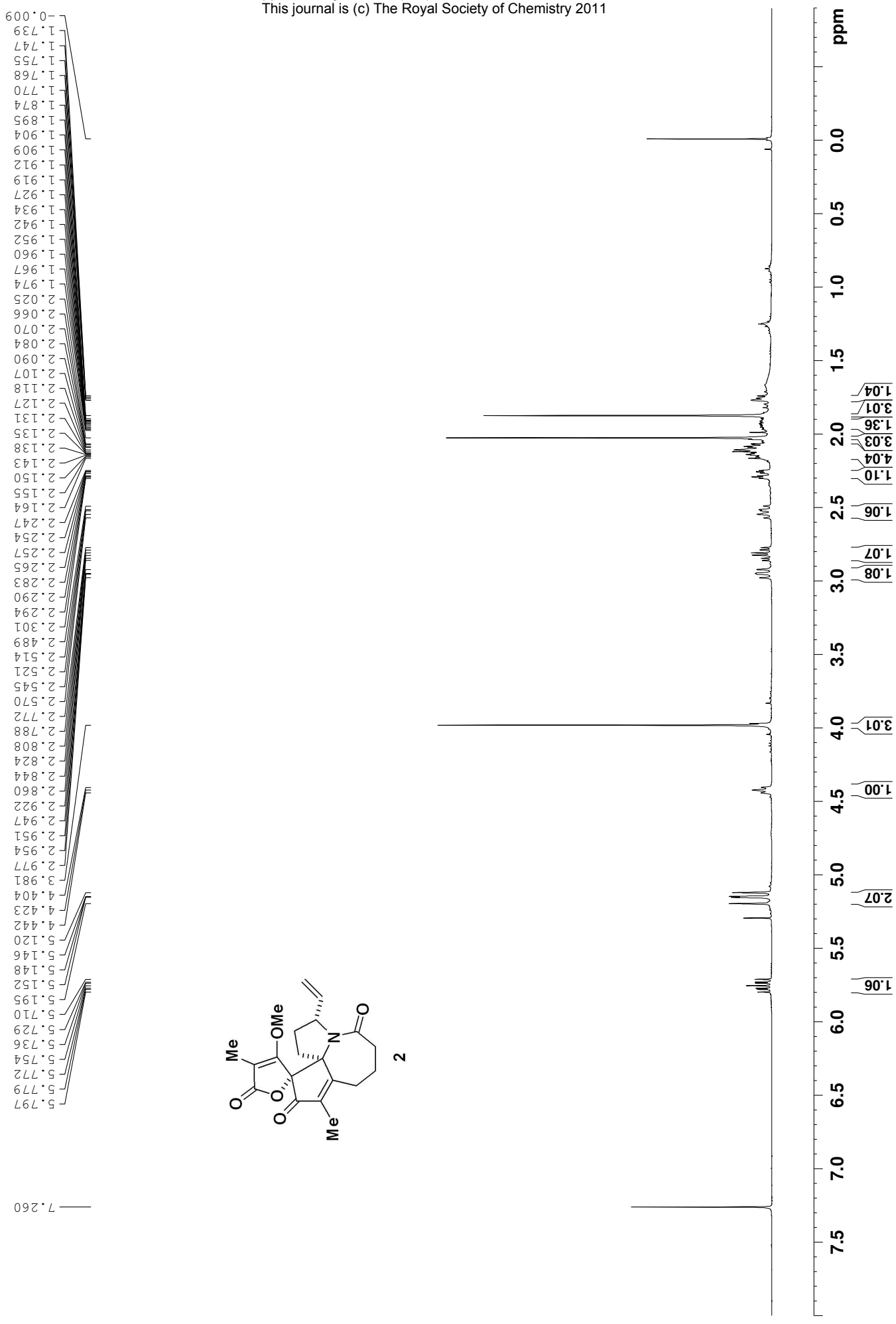
Me
11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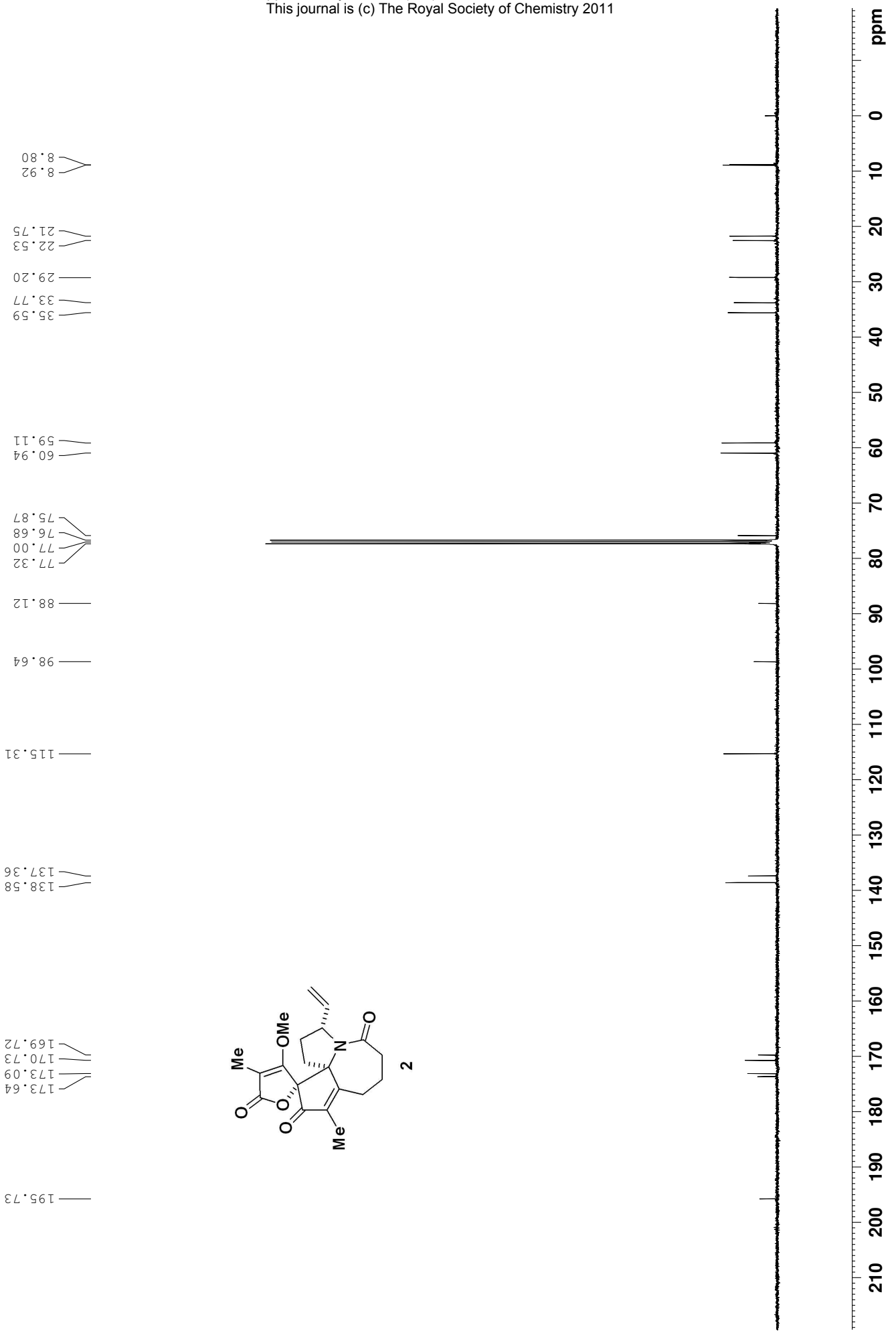
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137.36
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170.73
173.09
173.64
195.73
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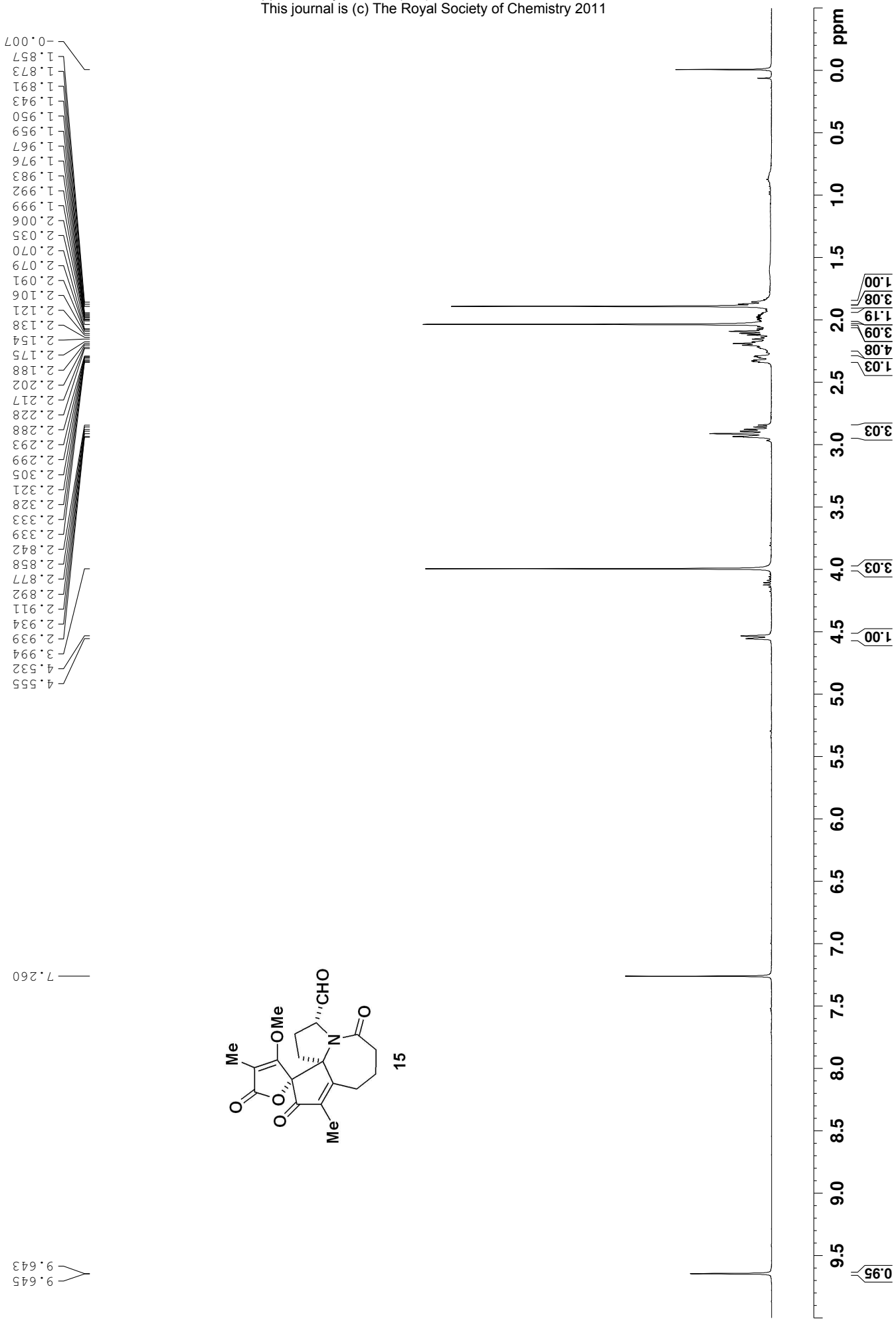
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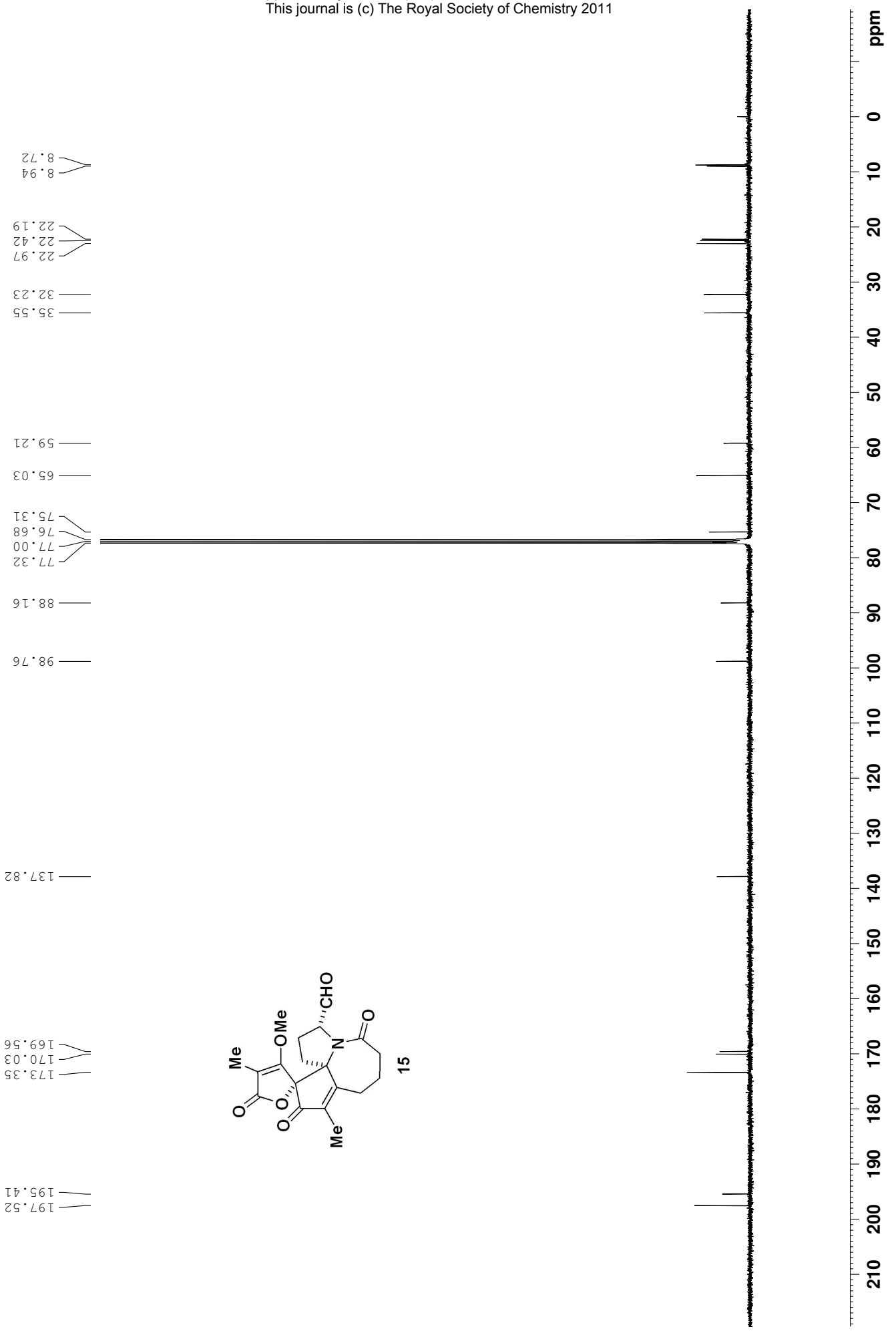
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173.35
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197.52
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Me
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O
O
O
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ppm
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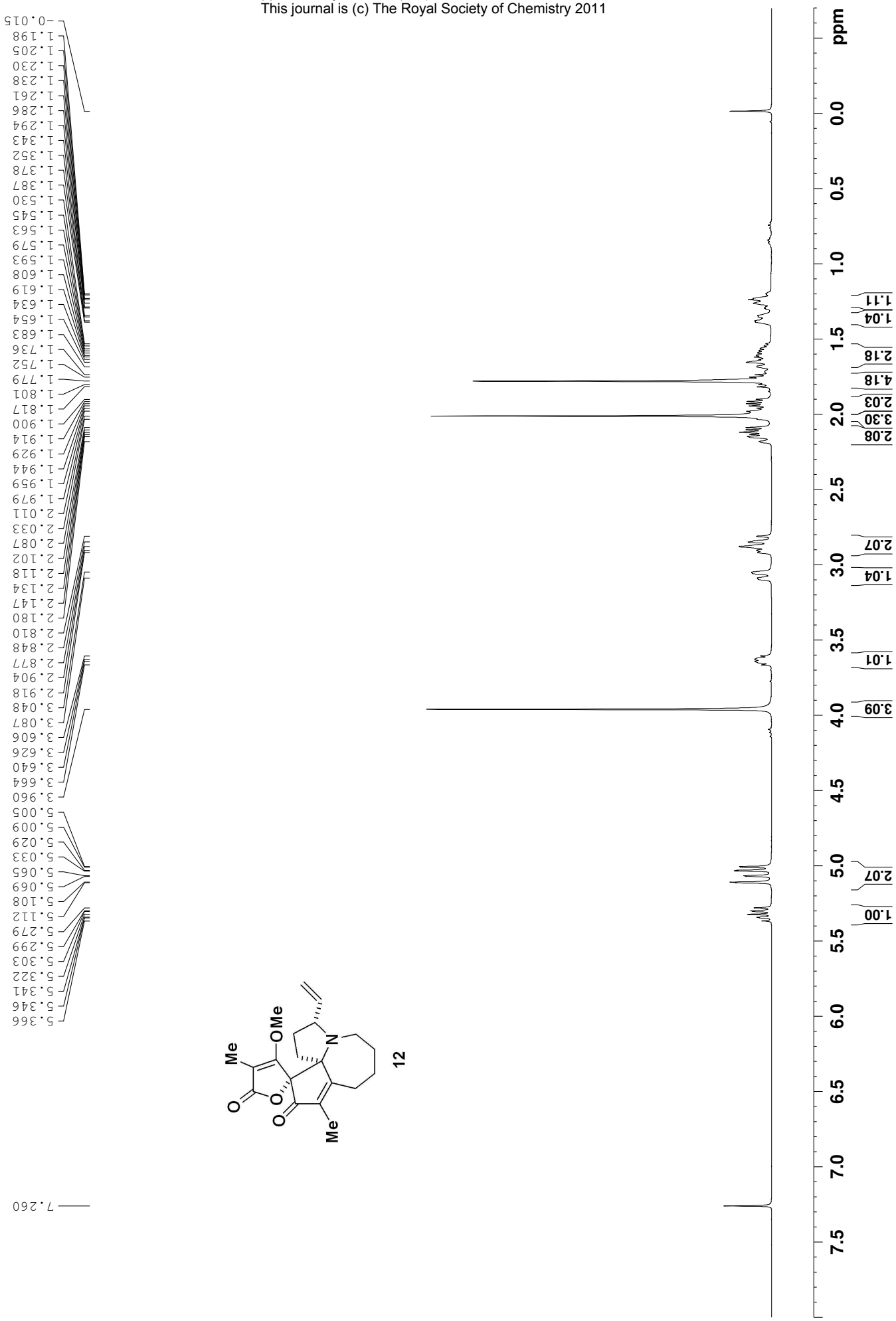
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2.848
2.877
2.904
2.918
3.048
3.087
3.606
3.626
3.640
3.664
3.960
5.005
5.009
5.029
5.033
5.065
5.069
5.108
5.112
5.279
5.299
5.303
5.322
5.341
5.346
7.260
Me
OMe
O
O
O
N
Me
12
ppm
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
1.11
1.04
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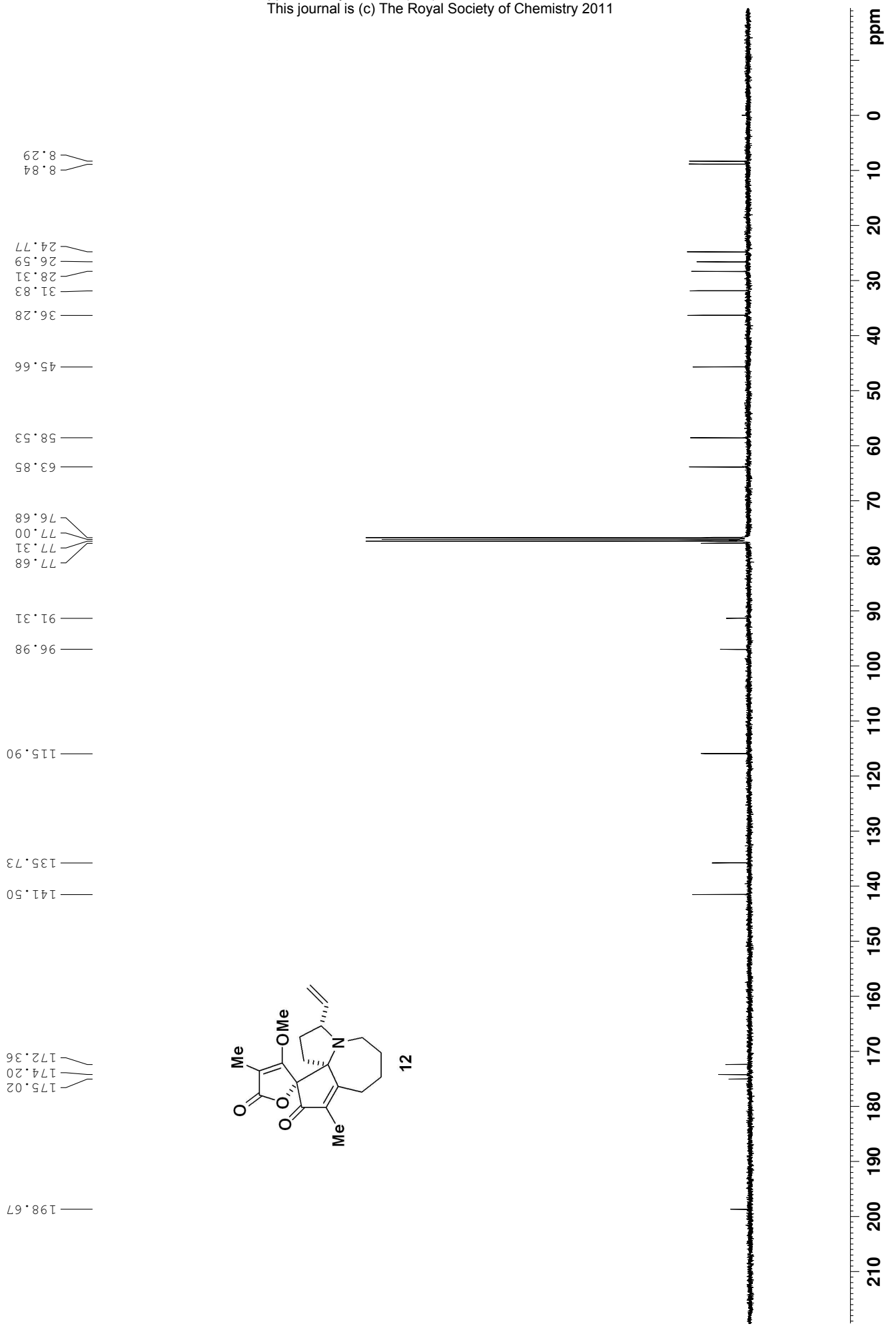
4.18
2.03
3.30
2.08
2.07
1.04
1.01
3.09
2.07
1.00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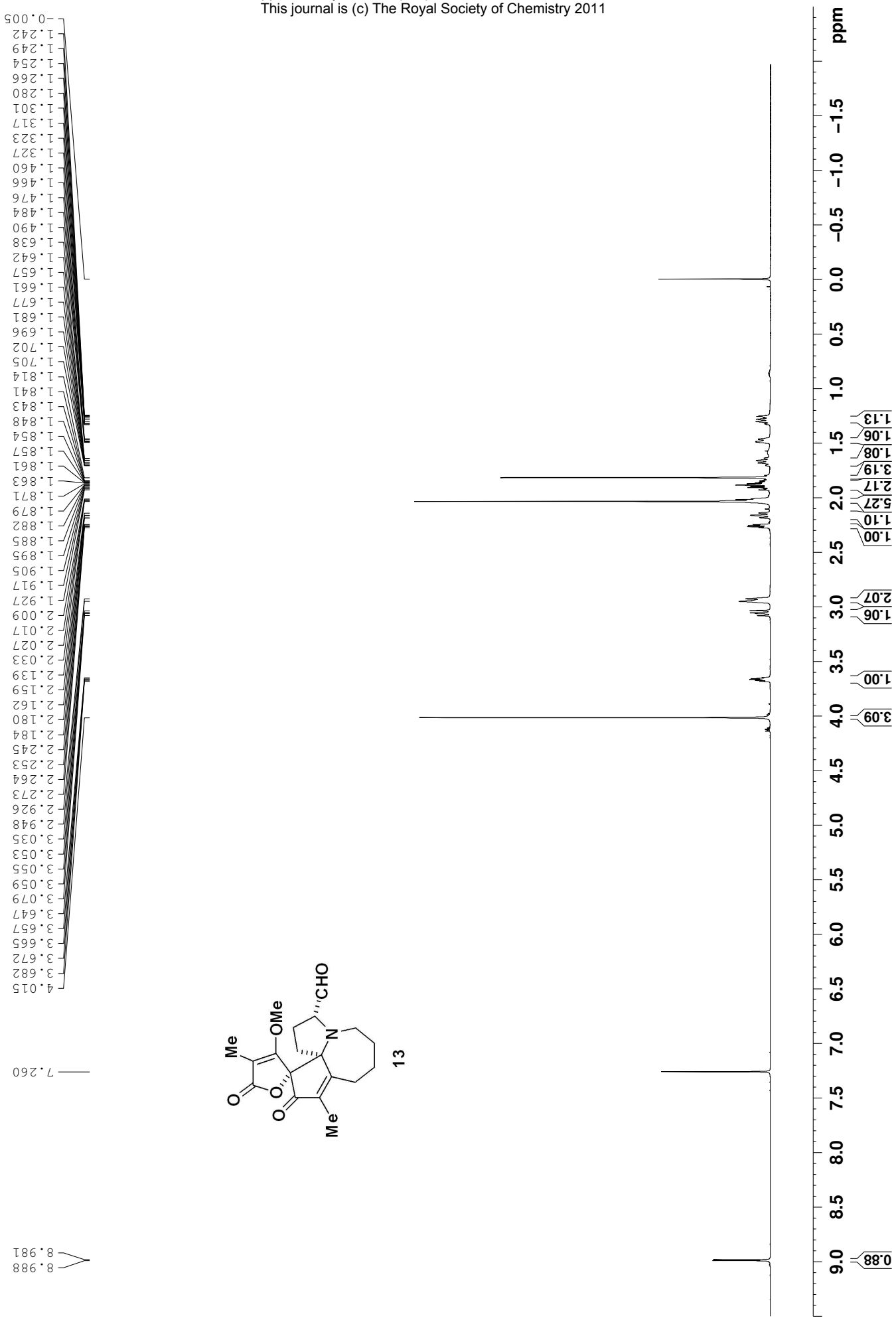
8.84
24.77
26.59
28.31
31.83
36.28
45.66
58.53
63.85
76.68
77.00
77.31
77.68
91.31
96.98
115.90
135.73
141.50
172.36
174.20
175.02
198.67
Me
OMe
N
O
O
O
Me
12
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210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8.0
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7.0
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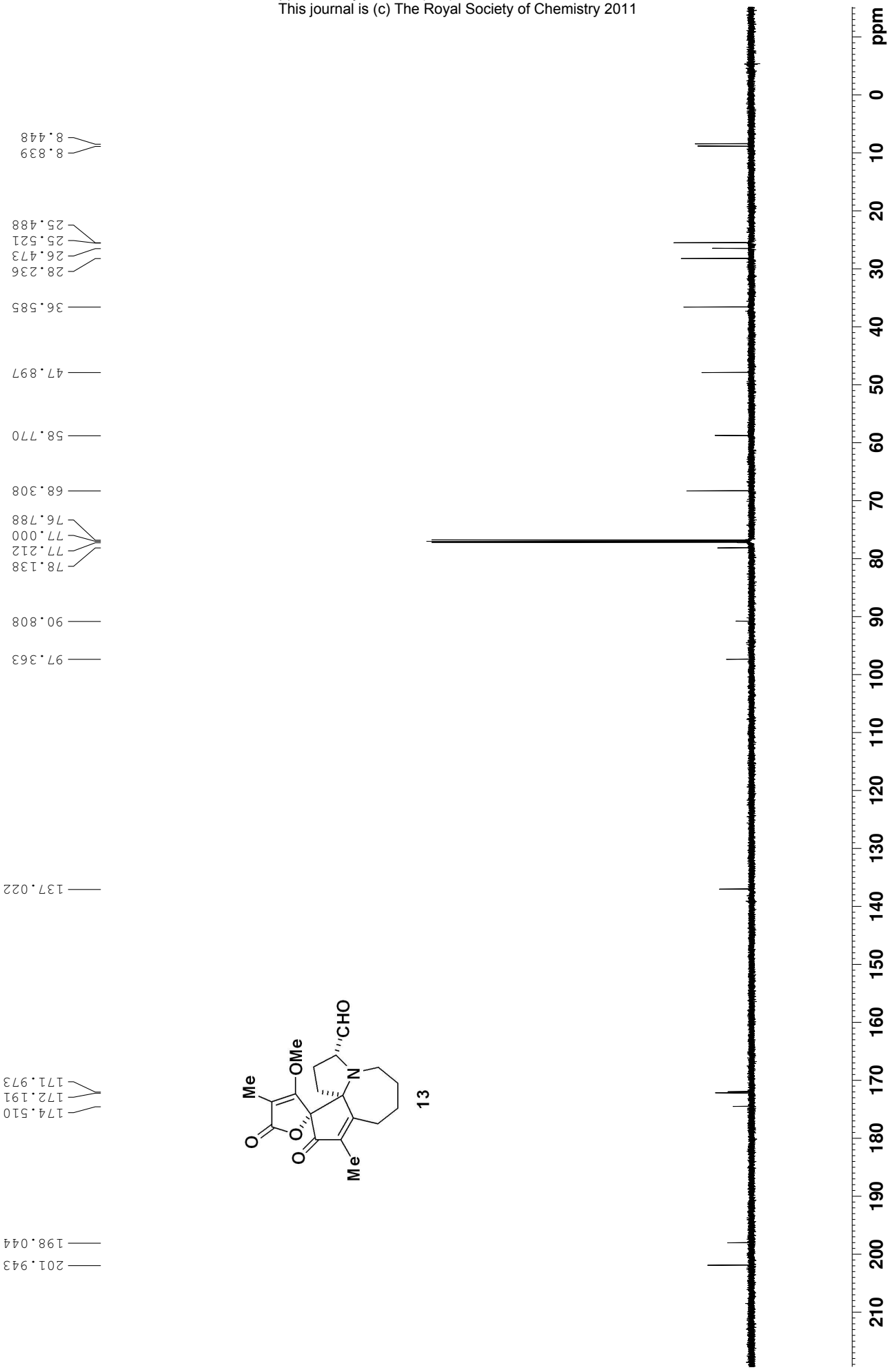
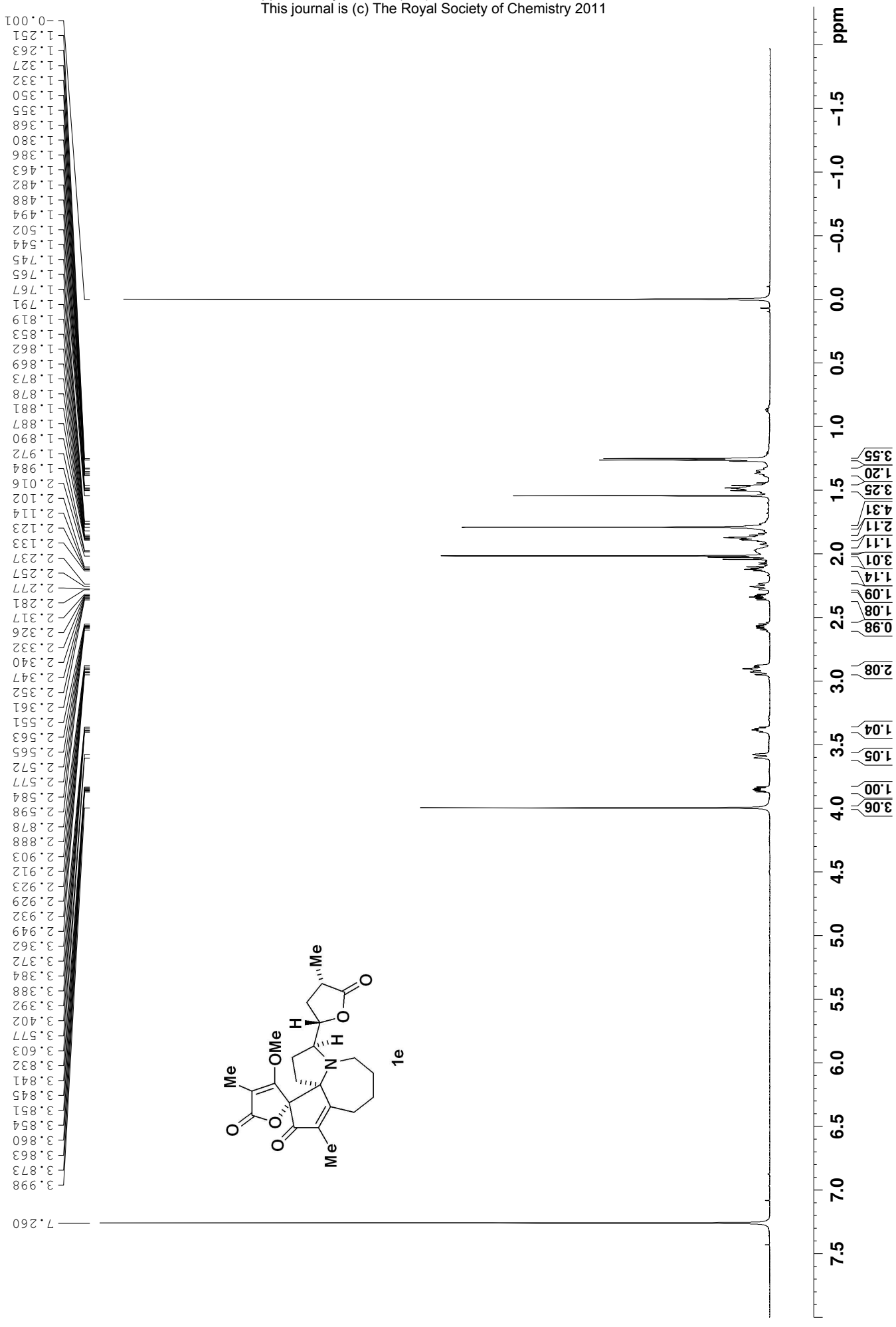
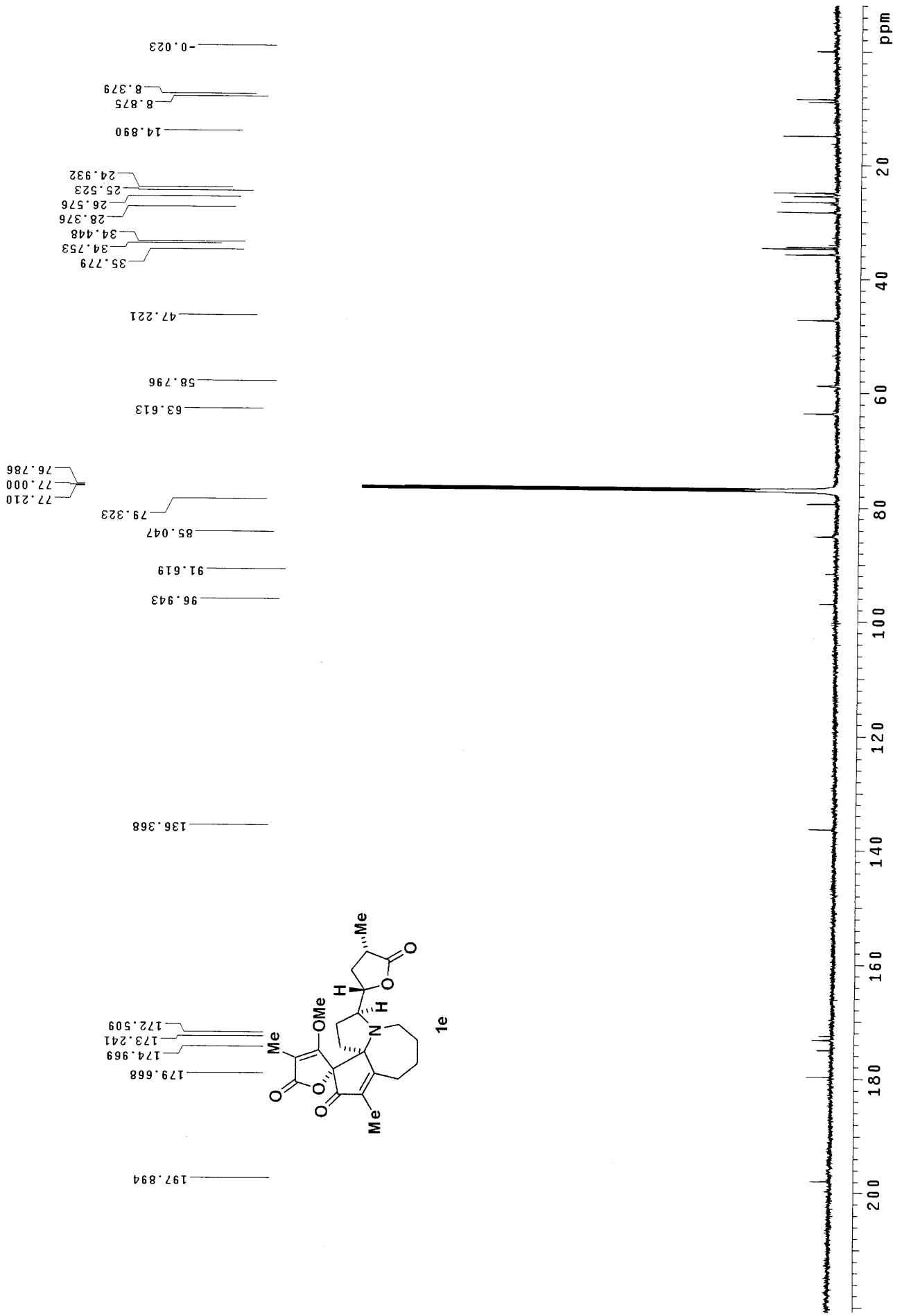
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
0.88
3.09
1.00
1.06
2.07
1.00
1.10
5.27
2.17
3.19
1.08
1.06
1.13
7.260
8.981
8.988
CHO
N
OMe
Me
O
O
O
Me
13


8.448
8.839
25.488
25.521
26.473
28.236
36.585
47.897
58.770
68.308
76.788
77.000
77.212
78.138
90.808
97.363
137.022
171.973
172.191
174.510
198.044
201.943
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
Me
OMe
CHO
N
O
O
O
Me
13


ppm
7.260
3.998
3.873
3.863
3.860
3.854
3.851
3.845
3.841
3.832
3.603
3.577
3.402
3.392
3.388
3.384
3.372
3.362
2.949
2.932
2.929
2.923
2.912
2.903
2.888
2.878
2.598
2.584
2.577
2.572
2.565
2.563
2.551
2.361
2.352
2.347
2.340
2.332
2.326
2.317
2.281
2.277
2.257
2.237
2.133
2.123
2.114
2.102
2.016
1.984
1.972
1.890
1.887
1.881
1.878
1.873
1.869
1.862
1.853
1.819
1.791
1.767
1.765
1.745
1.544
1.502
1.494
1.488
1.482
1.463
1.386
1.380
1.368
1.355
1.350
1.332
1.327
1.263
1.251
-0.001
3.55
1.20
3.25
4.31
2.11
1.11
3.01
1.14
1.09
1.08
0.98
2.08
1.04
1.05
1.00
3.06
Me
OMe
H
H
N
O
O
O
O
O
Me
Me
1e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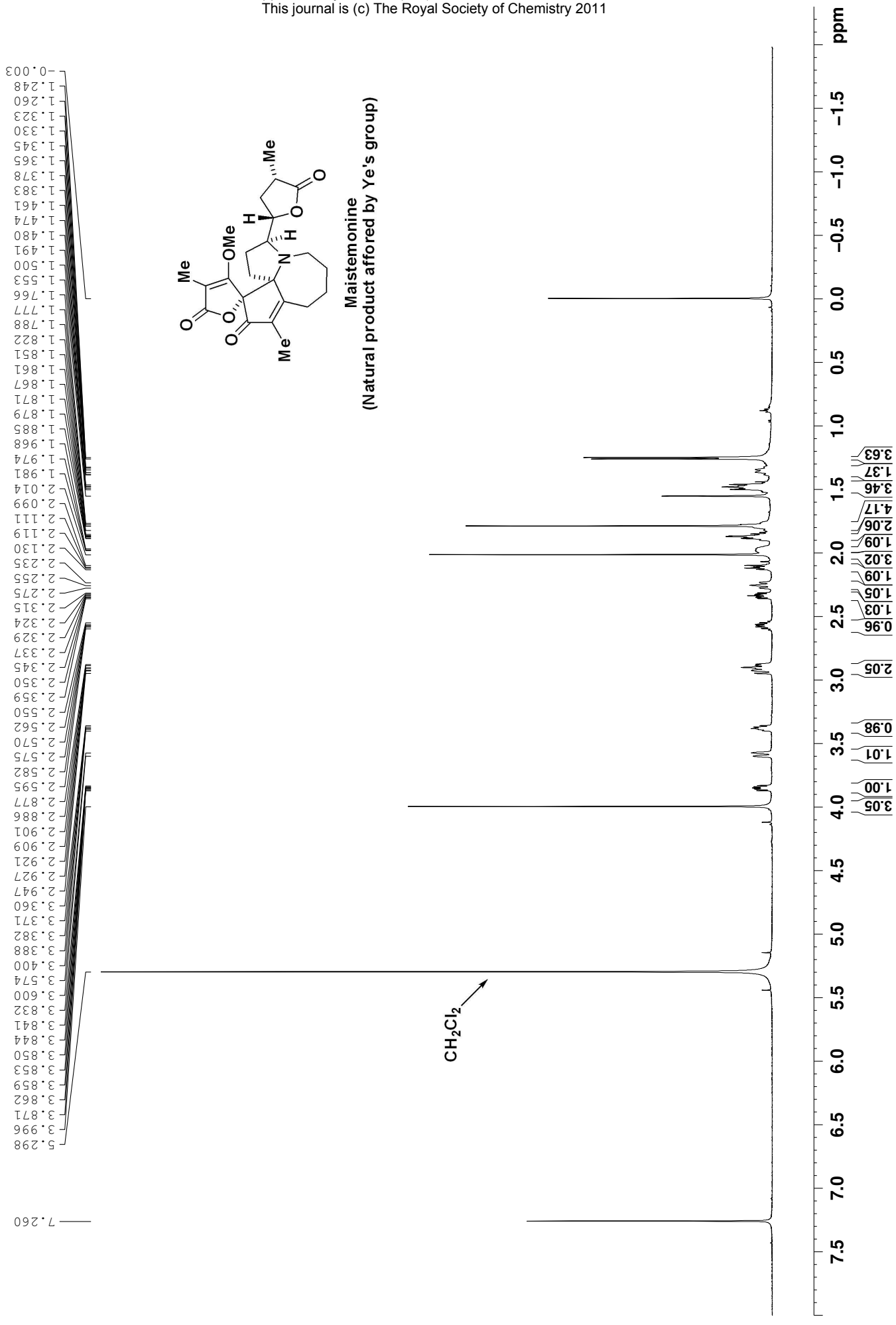
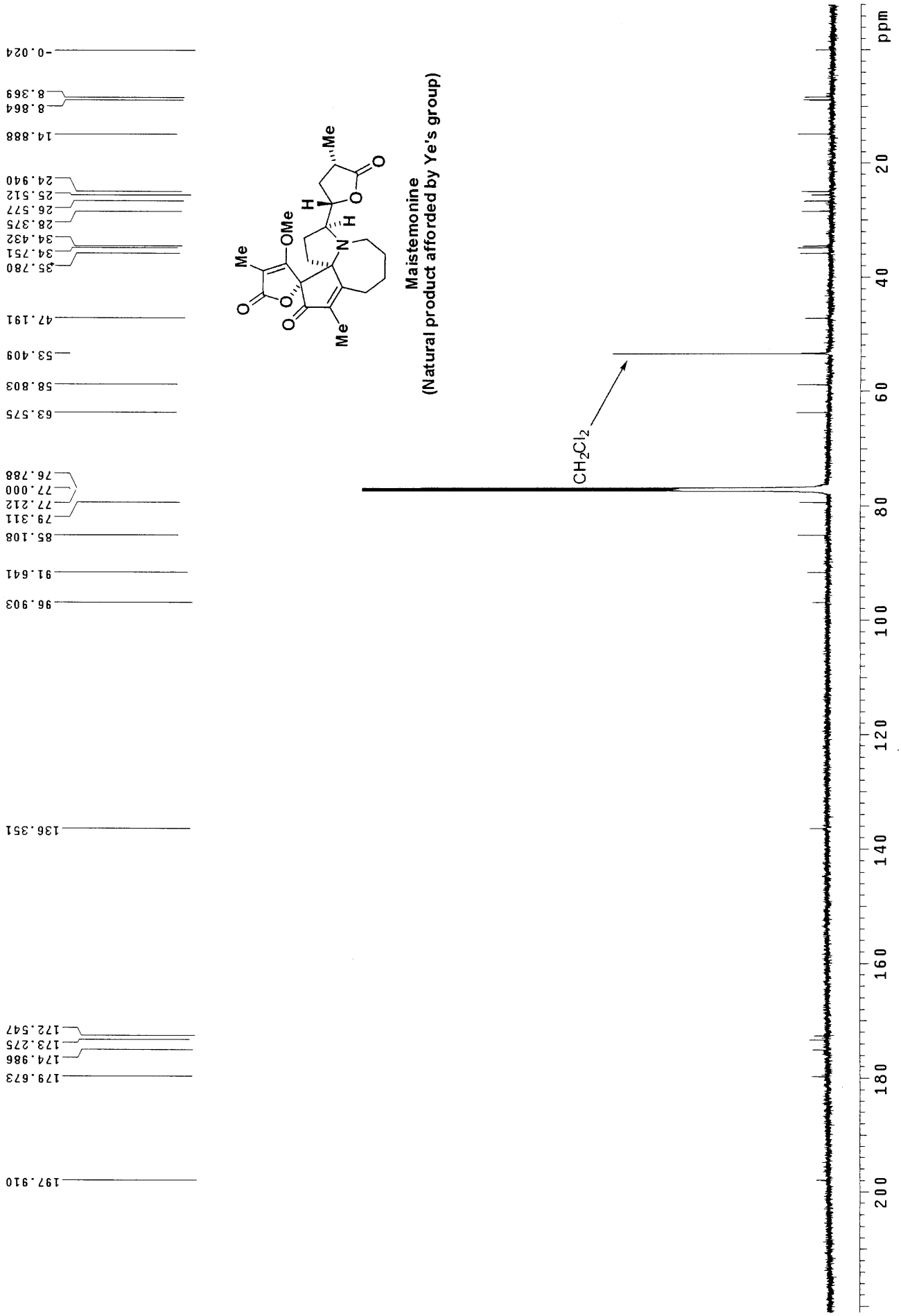
14.890
24.932
25.523
26.576
28.376
34.448
34.753
35.779
47.221
58.796
63.613
76.786
77.000
77.210
79.323
85.047
91.619
96.943
136.368
172.509
173.241
174.969
179.668
197.894
OMe
Me
Me
Me
H
H
N
O
O
O
O
O
1e
ppm
20
40
60
80
100
120
140
160
180
200


Maistemonine
(Natural product afford by Ye's group)
Me
OMe
O
O
O
Me
H
N
H
O
O
Me
CH_2Cl_2
ppm
7.260
5.298
3.996
3.871
3.862
3.859
3.853
3.850
3.844
3.841
3.832
3.600
3.574
3.400
3.388
3.382
3.371
3.360
2.947
2.927
2.921
2.909
2.901
2.886
2.877
2.595
2.582
2.575
2.570
2.562
2.550
2.359
2.350
2.345
2.337
2.329
2.324
2.315
2.275
2.255
2.235
2.130
2.119
2.111
2.099
2.014
1.981
1.974
1.885
1.879
1.871
1.867
1.861
1.851
1.822
1.788
1.777
1.766
1.553
1.500
1.491
1.480
1.474
1.461
1.383
1.378
1.365
1.345
1.330
1.323
1.260
1.248
−0.003
3.63
1.37
3.46
4.17
2.06
1.09
3.02
1.09
1.05
1.03
0.96
2.05
0.98
1.01
1.00
3.05


Maistemonine
(Natural product afforded by Ye's group)
CH2Cl2
ppm
-0.024
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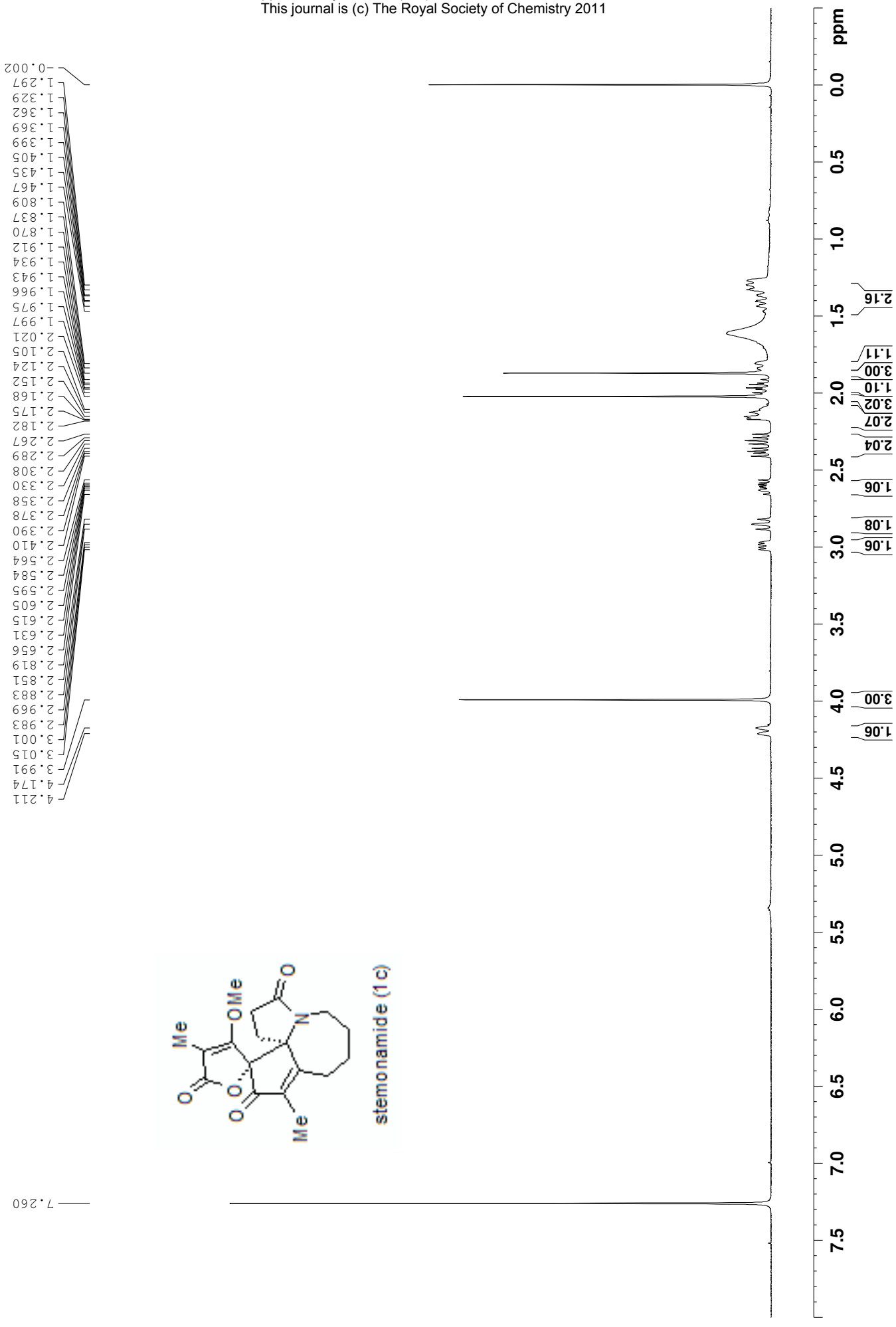
8.864
14.888
24.940
25.512
26.577
28.375
34.432
34.751
35.780
47.191
53.409
58.803
63.575
76.788
77.000
77.212
79.311
85.108
91.641
96.903
136.351
172.547
173.275
174.986
179.673
197.910


ppm
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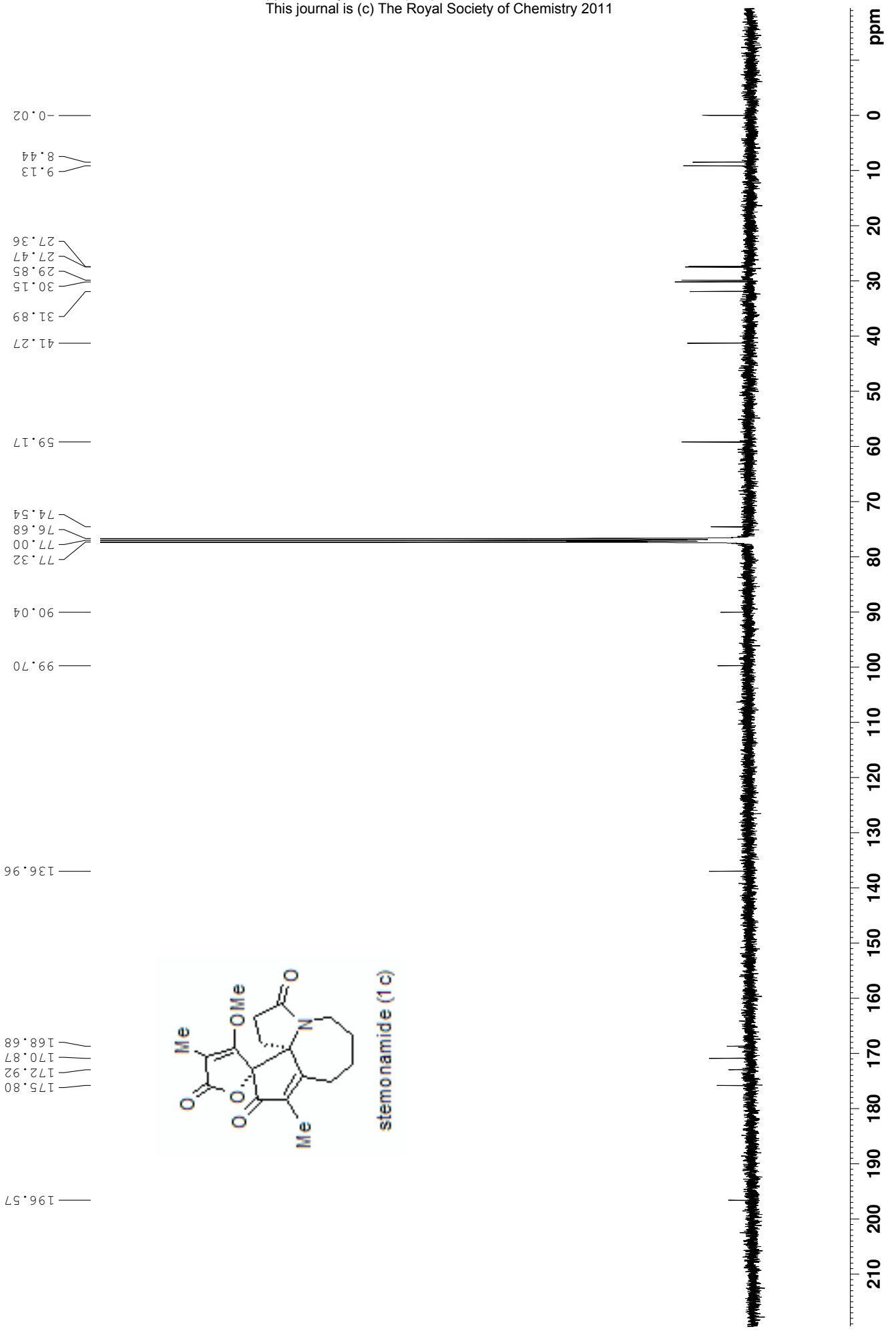
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
2.16
1.11
3.00
1.10
3.02
2.07
2.04
1.06
1.08
1.06
3.00
1.06
-0.002
1.297
1.329
1.362
1.369
1.399
1.405
1.435
1.467
1.809
1.837
1.870
1.912
1.934
1.943
1.966
1.975
1.997
2.021
2.105
2.124
2.152
2.168
2.175
2.182
2.267
2.289
2.308
2.330
2.358
2.378
2.390
2.410
2.564
2.584
2.595
2.605
2.615
2.631
2.656
2.819
2.851
2.883
2.969
2.983
3.001
3.015
3.991
4.174
4.211
7.260
Me
OMe
O
N
O
O
O
Me
stemonamide (1c)


-0.02
8.44
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29.85
30.15
31.89
41.27
59.17
74.54
76.68
77.00
77.32
90.04
99.70
136.96
168.68
170.87
172.92
175.80
196.57
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
Me
OMe
O
N
O
O
O
Me
stemonamide (1c)