Rhodium-catalysed Tandem Dehydrogenative Coupling–Michael addition: Direct Synthesis of Phthalides from Benzoic Acids and Alkenes

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Supplementary Information

Contents

1. General remarks

Reagents were purchased from commercial suppliers and used as received. Solid reagents were weighed on a semi-micro balance featuring one hundredth of a milligram precision. Solvents were dried by standard techniques. Melting points were measured on a hot-stage Reichert Thermovar apparatus and are uncorrected. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Varian instrument at 300, 400, or 500 MHz and 75, 100, or 125 MHz, respectively. IR spectra were measured on KBr pastille. High resolution mass spectra (HRMS) were obtained on a sector-field mass spectrometer. Elemental analyses were performed on a FISONS Instrument EA 108 or a Perkin Elmer 240C elemental analyser.

2. General procedure

A mixture of $[(COD)RhCl]_2$ (11.82 mg, 0.024 mmol, 8 mol%) and AgOTf (18.54 mg, 0.072 mmol, 24 mol%) in chlorobenzene (600 μL) was stirred in a glass tube at room temperature for 30 minutes. Dicyclopentadiene (13.0 μL, 0.096 mmol, 32 mol%) was added. Mixture turned instantaneously from light yellow to dark orange. Then, substituted benzoic acid (0.3 mmol, 1.0 equiv), alkene (0.6 mmol, 2.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (239.7 mg, 1.2 mmol, 4.0 equiv), and chlorobenzene (900 μL) were added. The tube was sealed and heated at 120 °C for 48 hours. After this time the reaction mixture was filtered through a short pad of silica gel and eluted with ethyl acetate. The filtrate was concentrated under reduced pressure. Purification of the crude mixture by flash chromatography, preparative thin-layer chromatography (PTLC), or recrystallisation afforded the pure product.

3. Characterisation data of products

4,5,6-Trimethoxy-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1a)

White solid (82 mg, 93% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by recrystallisation (hexane/diethyl ether = 1:1); mp = 124–125 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.10 (t, 3H, *J* = 7.5 Hz), 2.53 (q, 2H, *J* = 7.5 Hz), 2.74 (dd, 1H, *J* = 16.5 Hz, *J* = 9.0 Hz), 3.16 (dd, 1H, *J* = 16.5 Hz, *J* = 3.0 Hz), 3.91 (s, 3H), 3.93 (s, 3H), 3.96 (s, 3H), 5.91 (dd, 1H, *J* = 9.0 Hz, *J* = 3.0 Hz), 7.12 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.6, 37.0, 45.6, 56.4, 61.1, 61.4, 75.7, 102.8, 121.3, 134.6, 147.0, 147.5, 156.0, 170.1, 207.0. IR (KBr): ν 2940, 1765, 1717, 1479, 1420, 1342, 1110. HRMS (ESI): *m/z* calcd for $C_{15}H_{19}O_6$ $[M + H]^+$ 295.1176, found 295.1178.

5,6,7-Trimethoxy-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1b)

White solid (35 mg, 40% yield); prepared following the general procedure from 2,3,4-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 122–123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, 3H, *J* = 7.2 Hz), 2.49 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.57 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.82 (dd, 1H, *J* = 17.2 Hz, *J* = 6.8 Hz), 3.10 (dd, 1H, *J* = 17.2 Hz, *J* = 6.8 Hz), 3.86 (s, 3H), 3.92 (s, 3H), 4.13 (s, 3H), 5.76 (t, 1H, *J* = 6.8 Hz), 6.66 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 36.9, 47.3, 56.5, 61.4, 62.4, 75.5, 99.8, 110.3, 142.0, 147.4, 152.3, 159.7, 167.6, 207.8. IR (KBr): ν 2975, 1737, 1599, 1474, 1418, 1346, 1249, 1196. HRMS (ESI): *m/z* calcd for $C_{15}H_{19}O_6$ $[M + H]^+$ 295.11761, found 295.11778.

5,6,7-*tris*(Benzyloxy)-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1c)

Incolor liquid (118 mg, 75%); prepared following the general procedure from 3,4,5-*tris*(benzyloxy)benzoic acid (133.5 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol) using 3.0 mL of solvent; purified by flash chromatography (hexane/diethyl ether = 1:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.03 (t, 3H, *J* = 7.2 Hz), 2.40 (q, 2H, *J* = 7.2 Hz), 2.58 (dd, 1H, *J* = 16.8 Hz, *J* = 9.2 Hz), 3.05 (dd, 1H, *J* = 16.8 Hz, *J* = 2.8 Hz), 5.15 (m, 6H), 5.51 (dd, 1H, *J* = 9.2 Hz, *J* = 2.8 Hz), 7.23-7.47 (m, 16H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.4, 36.8, 45.1, 71.3, 75.5, 75.6, 75.7, 104.6, 118,2, 121.3, 127.7, 128.4, 128.4, 128.5, 128.6, 128.7, 128.7, 135.5, 135.8, 136.4, 136.6, 146.6, 155.0, 169.8, 206.6. IR (KBr): ν 3065, 2976, 1762, 1717, 1471, 1451, 1339, 1103. HRMS (ESI): *m/z* calcd for $C_{33}H_{30}NaO_6$ $[M + Na]^+$ 545.1935, found 545.1937.

5-Methoxy-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1d)

White solid (22 mg, 31% yield); prepared following the general procedure from 4-methoxybenzoic acid (46.2 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 70–71 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, 3H, *J* = 7.2 Hz), 2.49 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.58 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.85 (dd, 1H, *J* = 17.2 Hz, *J* = 6.4 Hz), 3.11 (dd, 1H, *J* = 17.2 Hz, *J* = 6.4 Hz), 3.88 (s, 3H), 5.86 (t, 1H, *J* = 6.4 Hz), 6.89 (d, 1H, *J* = 2.0 Hz), 7.04 (dd, 1H, *J* = 8.4 Hz, *J* = 2.0 Hz), 7.79 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 36.8, 47.0, 55.9, 76.2, 106.3, 116.8, 118.0, 127.2, 152.3, 164.8, 169.8, 207.5. IR (KBr): ν 2977, 1758, 1715, 1607, 1492, 1289, 1053. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784, found 257.0784.

5-Methyl-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1e)

White solid (28 mg, 43% yield); prepared following the general procedure from *p*-toluic acid (41.7 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 76–77 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.11 (t, 3H, *J* = 7.2 Hz), 2.47 (s, 1H), 2.49 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.57 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.86 (dd, 1H, *J* = 17.2 Hz, *J* = 6.4 Hz), 3.08 (dd, 1H, *J* = 17.2 Hz, *J* = 6.8 Hz), 5.89 (t, 1H, *J* = 6.8 Hz), 7.24 (dd, 1H, *J* = 1.2 Hz, *J* = 0.8 Hz), 7.33 (ddd, 1H, *J* = 7.6 Hz, *J* = 1.2 Hz, *J* = 0.8 Hz), 7.77 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 22.1, 36.8, 47.0, 76.6, 122.6, 123.2, 125.5, 130.6, 145.6, 150.0, 170.1, 207.4. IR (KBr): ν 2980, 1761, 1716, 1616, 1340, 1280, 1052. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_3$ $[M + Na]^+$ 241.0835, found 241.0834.

3-(2-Oxobutyl)naphtho[1,2-*c*]furan-1(3*H*)-one (1f)

White solid (40 mg, 52% yield); prepared following the general procedure from α-naphthoic acid (52.8 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 144–145 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.13 (t, 3H, *J* = 7.6 Hz), 2.52 (dq, 1H, *J* = 18.0 Hz, *J* = 7.6 Hz), 2.60 (dq, 1H, *J* = 18.0 Hz, *J* = 7.6 Hz), 2.94 (dd, 1H, *J* = 16.8 Hz, *J* = 6.0 Hz), 3.12 (dd, 1H, *J* = 16.8 Hz, *J* = 6.8 Hz), 6.03 (t, 1H, *J* = 6.8 Hz), 7.50 (d, 1H, *J* = 8.8 Hz), 7.64 (dd, 1H, *J* = 8.0 Hz, *J* = 1.2 Hz), 7.72 (dd, 1H, *J* = 8.0 Hz, *J* = 1.2 Hz), 7.97 (d, 1H, *J* = 8.4 Hz), 8.13 (d, 1H, *J* = 8.8 Hz), 9.00 (d, 1H, *J* = 8.4 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 7.5, 37.0, 46.8, 76.2, 118.7, 120.0, 123.6, 127.5, 128.4, 129.1, 129.2, 133.5, 135.7, 151.2, 170.3, 207.3. IR (KBr): ν 3058, 2977, 1748, 1716, 1519, 1331. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NaO_3$ $[M + Na]^+$ 277.0835, found 277.0842.

3-(2-Oxobutyl)isobenzofuran-1(3*H*)-one (1g)[1]

White solid (30 mg, 49% yield); prepared following the general procedure from benzoic acid (36.9 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 (t, 3H, *J* = 7.2 Hz), 2.48 (dq, 1H, *J* = 18.0, *J* = 7.2), 2.56 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.88 (dd, 1H, *J* = 17.2 Hz, *J* = 6.0 Hz), 3.08 (dd, 1H, *J* = 17.2 Hz, *J* = 6.8 Hz), 5.94 (t, 1H, *J* = 6.8 Hz), 7.46 (dd, 1H, *J* = 7.6 Hz, *J* = 0.8 Hz), 7.52 (t, 1H, *J* = 7.6 Hz), 7.65 (t, 1H, *J* = 7.6 Hz, *J* = 1.2 Hz), 7.88 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 7.4, 36.8, 46.8, 76.9, 122.3, 125.7, 129.4, 134.2, 149.4, 170.0, 207.3. HRMS (ESI): *m/z* calcd for $C_{12}H_{12}NaO_3$ $[M + Na]^+$ 227.0679, found 227.0684.

3-(2-Oxobutyl)-5-vinylisobenzofuran-1(3*H*)-one (1h)

Pale yellow liquid (28 mg, 40% yield); prepared following the general procedure from 4-vinylbenzoic acid (45.9 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, 3H, *J* = 7.2 Hz), 2.50 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.58 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.88 (dd, 1H, *J* = 17.2 Hz, *J* = 6.8 Hz), 3.12 (dd, 1H, *J* = 17.2 Hz, *J* = 6.8 Hz), 5.46 (d, 1H, *J* = 11.2 Hz), 5.91 (d, 1H, *J* = 17.6 Hz), 5.94 (t, 1H, *J* = 6.8 Hz), 6.79 (dd, 1H, *J* = 17.6 Hz, *J* = 11.2 Hz), 7.45 (s, 1H), 7.57 (d, 1H, *J* = 8.0 Hz), 7.84 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 36.8, 47.0, 76.6, 118.0, 119.8, 124.9, 125.9, 127.5, 135.6, 143.8, 150.2, 169.8, 207.4. IR (KBr): ν 1717, 1684, 1653, 1632, 1559, 1507. HRMS (ESI): *m/z* calcd for $C_{14}H_{14}NaO_3$ $[M + Na]^+$ 253.0835, found 253.0835.

3-(2-Oxobutyl)-5-phenylisobenzofuran-1(3*H*)-one (1i)

White solid (28 mg, 33% yield); prepared following the general procedure from [1,1'-biphenyl]-4-carboxylic acid (60.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 90–91 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, 3H, *J* = 7.2 Hz), 2.50 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.59 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.93 (dd, 1H, *J* = 17.6 Hz, *J* = 6.8 Hz), 3.16 (dd, 1H, *J* = 17.6 Hz, *J* = 6.8 Hz), 6.00 (t, 1H, *J* = 6.8 Hz), 7.48 (m, 3H), 7.60 (d, 2H, *J* = 8.8 Hz), 7.65 (s, 1H), 7.75 (d, 1H, *J* = 8.0 Hz), 7.95 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 6.52, 35.8, 46.0, 75.8, 119.8, 123.5, 125.1, 126.5, 127.7, 127.8, 128.1, 138.6, 146.7, 149.3, 169.0, 206.3. IR (KBr): ν 2980, 1761, 1717, 1615, 1338. HRMS (ESI): *m/z* calcd for $C_{18}H_{16}KO_3$ $[M + K]^+$ 319.0731, found 319.0729.

5-Fluoro-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1j)

White solid (14 mg, 21% yield); prepared following the general procedure from 4-fluorobenzoic acid (42.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1:1); mp = 91–92 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.12 (t, 3H, *J* = 7.5 Hz), 2.49 (dq, 1H, *J* = 22.0 Hz, *J* = 7.5 Hz), 2.57 (dq, 1H, *J* = 22.0 Hz, *J* = 7.5 Hz), 2.86 (dd, 1H, *J* = 17.5 Hz, *J* = 7.0 Hz), 3.18 (dd, 1H, *J* = 17.5 Hz, *J* = 6.0 Hz), 5.91 (t, 1H, *J* = 7.0 Hz), 7.18 (ddt, 1H, *J* = 8.0 Hz, *J* = 2.5 Hz, *J* = 0.5 Hz), 7.23 (tdd, 1H, *J* = 9.0 Hz, *J* = 2.5 Hz, *J* = 0.5 Hz), 7.89 (dd, 1H, *J* = 8.5 Hz, *J* = 5.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 7.5, 36.7, 46.7, 76.2 (d, *J* = 2.9 Hz), 110.0 (d, *J* = 25.4 Hz), 117.7 (d, *J* = 23.3 Hz), 121.9 (d, *J* = 2.0 Hz), 128.2 (d, *J* = 9.7 Hz), 152.3 (d, *J* = 9.8 Hz), 166.6 (d, *J* = 254.9 Hz), 168.9, 207.2. IR (KBr): ν 2979, 2944, 1764, 1603, 1481, 1349. HRMS (ESI): *m/z* calcd for $C_{12}H_{11}FNaO_3$ $[M + Na]^+$ 245.0584, found 245.0574.

5-Iodo-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1k)

White solid (15 mg, 15% yield); prepared following the general procedure from 4-iodobenzoic acid (75.9 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (dichloromethane/ethyl acetate = 58:2); mp = 132–133 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.12 (t, 3H, *J* = 9.5 Hz), 2.49 (dq, 1H, *J* = 22.5 Hz, *J* = 9.5 Hz), 2.57 (dq, 1H, *J* = 22.5 Hz, *J* = 9.5 Hz), 2.86 (dd, 1H, *J* = 17.5 Hz, *J* = 7.0 Hz), 3.14 (dd, 1H, *J* = 17.5 Hz, *J* = 6.5 Hz), 5.90 (t, 1H, *J* = 6.5 Hz), 7.61 (d, 1H, *J* = 1.0 Hz), 7.90 (m, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 6.5, 35.7, 45.6, 75.2, 101.2, 124.4, 125.9, 130.9, 137.9, 150.1, 168.3, 206.5. IR (KBr): ν 2980, 2940, 1762, 1716, 1559, 1541, 1457. HRMS (ESI): *m/z* calcd for $C_{12}H_{11}INaO_3$ $[M + Na]^+$ 352.9645, found 352.9641.

3-(2-Oxobutyl)naphtho[2,3-*c*]furan-1(3*H*)-one (1l)

White solid (**1l** + **1l'** combined yield 53 mg, 69%); prepared following the general procedure from β-naphthoic acid (51.7 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); isolated as a mixture with **1l'**. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.13 (t, 3H, *J* = 6.4 Hz), 2.57 (m, 2H), 2.98 (dd, 1H, *J* = 17.6 Hz, *J* = 6.4 Hz), 3.21 (dd, 1H, *J* = 17.6 Hz, *J* = 6.4 Hz), 6.11 (t, 1H, *J* = 6.4 Hz), 7.61 (m, 2H), 7.85 (m, 2H), 7.92 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 7.5, 36.9, 47.6, 77.0, 121.4, 123.5, 126.8, 127.1, 128.4, 129.1, 129.9, 132.1, 135.9, 143.1, 170.0, 207.5. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NaO_3$ $[M + Na]^+$ 277.0835, found 277.0834.

3-(2-Oxobutyl)naphtho[1,2-*c*]furan-1(3*H*)-one (1l')

White solid (**1l** + **1l'** combined yield 53 mg, 69%); prepared following the general procedure from β-naphthoic acid (51.7 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/diethyl ether = 1.5:2); mp = 109–111 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.14 (t, 3H, *J* = 7.2 Hz), 2.54 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.62 (dq, 1H, *J* = 18.0 Hz, *J* = 7.2 Hz), 2.89 (dd, 1H, *J* = 16.8 Hz, *J* = 9.2 Hz), 3.28 (dd, 1H, *J* = 16.8 Hz, *J* = 2.4 Hz), 6.39 (dd, 1H, *J* = 9.2 Hz, *J* = 2.4 Hz), 7.65-7.72 (m, 2H), 7.83-7.86 (m, 2H), 7.98 (d, 1H, *J* = 8.4 Hz), 8.04 (d, 1H, *J* = 7.6 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 37.2, 47.2, 76.7, 120.6, 123.5, 123.6, 126.4, 128.0, 129.2, 129.7, 130.7, 136.3, 148.8, 170.5, 206.8. IR (KBr): ν 3060, 2977, 1757, 1717, 1459, 1328, 1052. HRMS (ESI): *m/z* calcd for $C_{16}H_{14}NaO_3$ $[M + Na]^+$ 277.0835, found 277.0828.

5-Acetyl-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1m)

White solid (12 mg, 16% yield); prepared following the general procedure from 4-acetylbenzoic acid (54.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (dichloromethane/ethyl acetate = 58:2); mp = 154–155 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.12 (t, 3H, *J* = 7.2 Hz), 2.50 (dq, 1H, *J* = 18.4 Hz, *J* = 7.2 Hz), 2.58 (dq, 1H, *J* = 18.4 Hz, *J* = 7.2 Hz), 2.68 (s, 3H), 2.95 (dd, 1H, *J* = 17.6 Hz, *J* = 6.0 Hz), 3.15 (dd, 1H, *J* = 17.6 Hz, *J* = 6.8 Hz), 6.01 (t, 1H, *J* = 6.4 Hz), 7.99 (d, 1H, *J* = 10.0 Hz), 8.04 (s, 1H), 8.11 (d, 1H, *J* = 10.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 27.2, 36.8, 46.5, 77.2, 122,2, 126.2, 129.4, 129.5, 141.8, 149.7, 169.0, 197.0, 206.9. IR (KBr): ν 2976, 1766, 1715, 1690, 1422, 1362, 1277, 1207, 1056. HRMS (ESI): *m/z* calcd for $C_{14}H_{14}NaO_4$ $[M + Na]^+$ 269.0784, found 269.0782.

6-Methoxy-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1n)

White solid (24 mg, 34% yield); prepared following the general procedure from 3-methoxybenzoic acid (46.2 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/ethyl acetate = 85:15); mp = 63–64 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.10 (t, 3H, *J* = 7.5 Hz), 2.48 (dq, 1H, *J* = 18.0 Hz, *J* = 7.5 Hz), 2.56 (dq, 1H, *J* = 18.0 Hz, *J* = 7.5 Hz), 2.83 (dd, 1H, *J* = 17.0 Hz, *J* = 6.5 Hz), 3.09 (dd, 1H, *J* = 17.0 Hz, *J* = 6.5 Hz), 3.86 (s, 3H), 5.89 (t, 1H, *J* = 6.5 Hz), 7.21 (dd, 1H, *J* = 8.5 Hz, *J* = 2.5 Hz), 7.32 (d, 1H, *J* = 2.5 Hz), 7.35 (dd, 1H, *J* = 8.5 Hz, *J* = 0.5 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.5, 36.9, 47.1, 55.8, 76.9, 107.5, 123.2, 123.3, 127.2, 141.9, 160.8, 170.2, 207.5. IR (KBr): ν 2944, 2856, 1765, 1483, 1423, 1344, 1302, 1145. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784, found 257.0780.

4-Methoxy-3-(2-oxobutyl)isobenzofuran-1(3*H*)-one (1n')

White solid (28 mg, 40% yield); prepared following the general procedure from 3-methoxybenzoic acid (46.2 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol); purified by PTLC (hexane/ethyl acetate = 58:2); mp = 94–95 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 1.09 (t, 3H, *J* = 7.0 Hz), 2.52 (q, 2H, *J* = 7.0 Hz), 2.71 (dd, 1H, *J* = 16.5 Hz, *J* = 9.5 Hz), 3.28 (dd, 1H, *J* = 16.5 Hz, *J* = 3.0 Hz), 3.89 (s, 3H), 5.96 (dd, 1H, *J* = 9.5 Hz, *J* = 3.0 Hz), 7.10 (dd, 1H, *J* = 7.0 Hz, *J* = 1.5 Hz), 7.46-7.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.4, 36.9, 44.8, 55.6, 76.0, 115.0, 117.4, 127.8, 131.2, 136.8, 154.1, 170.0, 206.8. IR (KBr): ν 2980, 1771, 1717, 1611, 1493, 1316, 1275. HRMS (ESI): *m/z* calcd for $C_{13}H_{14}NaO_4$ $[M + Na]^+$ 257.0784, found 257.0777.

4,5,6-Trimethoxy-3-(2-oxobutyl)-7-(3-oxopentyl)isobenzofuran-1(3*H*)-one (2)

White solid (27 mg, 8% yield); prepared from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl ketone (61.6 μL, 0.6 mmol) following the general procedure but using $[Cp^*RhCl_2]_2$ (14.82 mg, 0.024 mmol, 0.08 equiv), AgOTf (30.9 mg, 0.12 mmol, 0.40 equiv), and Ag_2CO_3 (111.0 mg, 0.6 mmol, 2.0 equiv), in dioxane under argon, in the absence of DCPD; purified by PTLC (dichloromethane/ethyl acetate = 58:2); mp = 108–109 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.06 (t, 3H, *J* = 6.0 Hz), 1.10 (t, 3H, *J* = 6.0 Hz), 2.47 (q, 2H, *J* = 7.2 Hz), 2.53 (q, 2H, *J* = 7.2 Hz), 2.67 (dd, 1H, *J* = 9.6 Hz, *J* = 6.9 Hz), 2.74 (dd, 1H, *J* = 16.5 Hz, *J* = 9.0 Hz), 3.16 (dd, 1H, *J* = 16.5 Hz, *J* = 3.0 Hz), 3.25 (dd, 1H, *J* = 9.0 Hz, *J* = 6.9 Hz), 3.85 (s, 3H), 3.91 (s, 3H), 3.95 (s, 1H), 5.86 (dd, 1H, *J* = 9.0 Hz, *J* = 3.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 7.4, 7.8, 19.1, 35.6, 37.0, 42.6, 45.4, 60.9, 61.3, 74.5, 77.2, 118.6, 131.5, 137.4, 145.7, 151.0, 153.6, 169.2, 206.8, 210.5. IR (KBr): ν 2976, 1758, 1716, 1482, 1348, 1115, 1017. HRMS (ESI): *m/z* calcd for $C_{20}H_{27}O_7$ $[M + H]^+$ 379.17513, found 379.17483.

***N*,*N*-Dimethyl-2-(5,6,7-trimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetamide (3)**

White solid (32 mg, 34% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and *N*,*N*-dimethylacrylamide (62.1 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 122–123 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.65 (dd, 1H, *J* = 16.0 Hz, *J* = 9.2 Hz), 3.00 (s, 6H), 3.12 (dd, 1H, *J* = 16.0 Hz, *J* = 1.6 Hz), 3.90 (s, 3H), 3.93 (s, 3H), 3.98 (s, 3H), 6.02 (dd, 1H, *J* = 9.2 Hz, *J* = 1.6 Hz), 7.11 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 35.7, 37.1, 37.4, 56.4, 60.9, 61.2, 76.7, 102.6, 121.3, 134.5, 146.8, 147.5, 155.8, 168.6, 169.9. IR (KBr): ν 2948, 2835, 1762, 1480, 1420, 1344. HRMS (ESI): *m/z* calcd for $C_{15}H_{19}KNO_6$ $[M + K]^+$ 348.0844, found 348.0841.

Methyl 2-(5,6,7-trimethoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (4a)

White solid (59 mg, 66% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and methyl acrylate (54.0 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 76–77 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 2.64 (dd, 1H, *J* = 16.5 Hz, *J* = 9.0 Hz), 3.20 (dd, 1H, *J* = 16.5 Hz, *J* = 3.5 Hz), 3.73 (s, 3H), 3.91 (s, 3H), 3.93 (s, 3H), 3.99 (s, 1H), 5.83 (dd, 1H, *J* = 9.0 Hz, *J* = 3.5 Hz), 7.12 (s, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 38.3, 52.2, 56.4, 60.9, 61.2, 75.7, 102.6, 121.2, 133.6, 146.7, 147.4, 156.0, 169.7, 169.8. IR (KBr): ν 2950, 2839, 1770, 1742, 1616, 1480, 1420, 1344. HRMS (ESI): *m/z* calcd for $C_{14}H_{17}O_7$ $[M + H]^+$ 297.09688, found 297.09678.

(*E*)-Methyl 3-(5,6,7-trimethoxy-1-(2-methoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (4b)

White solid (23 mg, 20% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and vinyl acrylate (54.0 μL, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 161–162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.63 (dd, 1H, *J* = 16.4 Hz, *J* = 8.8 Hz), 3.21 (dd, 1H, *J* = 16.4 Hz, *J* = 3.6 Hz), 3.74 (s, 3H), 3.82 (s, 3H), 3.88 (s, 3H), 3.97 (s, 3H), 4.03 (s, 3H), 5.78 (dd, 1H, *J* = 8.8 Hz, *J* = 3.6 Hz), 7.02 (d, 1H, *J* = 16.4 Hz), 8.51 (d, 1H, *J* = 16.4 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 38.1, 51.8, 52.2, 60.5, 61.0, 61.2, 74.5, 119.4, 123.4, 124.5, 133.9, 137.0, 148.1, 150.5, 156.0, 167.8, 168.4, 169.7. IR (KBr): ν 2952, 2843, 1761, 1718, 1457, 1436. HRMS (ESI): *m/z* calcd for $C_{18}H_{20}NaO_9$ $[M + Na]^+$ 403.1000, found 403.0995.

4,5,6-Trimethoxy-3-((phenylsulfonyl)methyl)isobenzofuran-1(3*H*)-one (5a)

White solid (27 mg, 24% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and phenyl vinyl sulfone (102 mg, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 161–162 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.37 (dd, 1H, *J* = 15.2 Hz, *J* = 9.2 Hz), 3.89 (s, 3H), 3.91 (s, 3H), 4.01 (s, 3H), 4.03 (dd, 1H, *J* = 15.2 Hz, *J* = 2.0 Hz), 5.84 (dd, 1H, *J* = 9.2 Hz, *J* = 2.0 Hz), 7.05 (s, 1H), 7.59 (m, 2H), 7.69 (m, 1H), 7.97 (d, 1H, *J* = 8.0 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 56.5, 59.0, 61.0, 61.3, 73.6, 102.5, 120.8, 128.4, 129.3, 131.6, 134.2, 139.4, 146.6, 147.3, 156.6, 168.8. IR (KBr): ν 2992, 2847, 1772, 1615, 1480, 1422, 1343, 1143, 1107, 1060. HRMS (ESI): *m/z* calcd for $C_{18}H_{18}NaO_7S$ $[M + Na]^+$ 401.0665, found 401.0662.

(*E*)-4,5,6-Trimethoxy-3-((phenylsulfonyl)methyl)-7-(2-(phenylsulfonyl)vinyl)isobenzofuran-1(3*H*)-one (5b)

White solid (80 mg, 49% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and phenyl vinyl sulfone (102 mg, 0.6 mmol); purified by flash chromatography (hexane/diethyl ether = 1:1); mp = 80–81 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.39 (dd, 1H, *J* = 14.8 Hz, *J* = 9.2 Hz), 3.85 (s, 3H), 3.91 (s, 3H), 4.00 (dd, 1H, *J* = 14.8 Hz, *J* = 2.0 Hz), 4.07 (s, 3H), 5.78 (dd, 1H, *J* = 9.2 Hz, *J* = 2.0 Hz), 7.55 (m, 7H), 7.68 (m, 1H), 7.92 (m, 4H), 8.34 (d, 1H, *J* = 16.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 58.4, 60.8, 61.2, 61.4, 72.7, 119.3, 120.9, 127.8, 128.3, 129.3, 129.3, 131.2, 133.3, 133.8, 134.3, 135.0, 139.3, 140.5, 148.9, 150.0, 156.7, 167.2. IR (KBr): ν 3065, 2944, 2851, 1764, 1483, 1447, 1344, 1307, 1145, 1085. HRMS (ESI): *m/z* calcd for $C_{26}H_{24}KO_9S_2$ $[M + K]^+$ 583.0493, found 583.0490.

(*E*)-3-((Ethylsulfonyl)methyl)-7-(2-(ethylsulfonyl)vinyl)-4,5,6-trimethoxyisobenzofuran-1(3*H*)-one (6)

White solid (113 mg, 84% yield); prepared following the general procedure from 3,4,5-trimethoxybenzoic acid (63.6 mg, 0.3 mmol) and ethyl vinyl sulfone (20.9 μL, 0.6 mmol); purified by recrystallisation (hexane/diethyl ether = 2:1); mp = 147–148 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.40 (t, 3H, *J* = 7.6 Hz), 1.44 (t, 3H, *J* = 7.6 Hz), 3.10 (q, 2H, *J* = 7.6 Hz), 3.21 (dd, 1H, *J* = 15.6 Hz, *J* = 10.0 Hz), 3.28 (q, 2H, *J* = 7.6 Hz), 3.77 (dd, 1H, *J* = 15.6 Hz, *J* = 1.6 Hz), 3.93 (s, 3H), 3.97 (s, 3H), 4.12 (s, 3H), 5.84 (d, 1H, *J* = 10.0 Hz, *J* = 1.6 Hz), 7.53 (d, 1H, *J* = 16.0 Hz), 8.27 (d, 1H, *J* = 16.0 Hz). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 6.4, 7.2, 49.2, 49.3, 54.7, 61.0, 61.3, 61.4, 73.2, 118.8, 121.1, 131.0, 133.2, 135.2, 149.0, 150.3, 156.8, 167.4. IR (KBr): ν 2984, 1764, 1603, 1483, 1458, 1344, 1305. HRMS (ESI): *m/z* calcd for $C_{18}H_{24}NaO_9S_2$ $[M + Na]^+$ 471.0754, found 471.0746.

4. Preparation of 7

A solution of $NaNO_2$ (266 mg, 2.16 mmol, 1.01 equiv) in water (3 mL) was added dropwise to an ice-cold suspension of 2-amino-3,4,5-trimethoxybenzoic acid (500 mg, 2.13 mmol, 1.00 equiv) in 48% aqueous HBF_4 (864 μL, 5.40 mmol) under stirring. Stirring was continued at 0 °C for 1 h. After this time, methanol (4 mL), methyl acrylate (262 mL, 2.92 mmol, 1.37 equiv), and $Pd(OAc)_2$ (9.6 mg, 42.8 μmol, 0.02 equiv) were added to the mixture at 0 °C. Mixture was let warm up to room temperature, then heated under reflux (70 °C) for 2 h. After this time, the mixture was cooled down to room temperature, and the solvent removed under vacuum. Et_2O (10 mL) was added to the residue, and the resulting solution was extracted with H_2O (3 x 2 mL). The organic layer was dried over $MgSO_4$ and concentrated at reduced pressure. Purification of the crude mixture by column chromatography on silica gel (eluent: hexane/ethyl acetate = 75/15) afforded methyl 2-carboxy-3,4,5-trimethoxyphenylcynnamate **7** as a white solid (181 mg, 0.61 mmol, 29% yield). Compounds **4a** (261

mg, 0.88 mmol, 41% yield) and **4b** (14 mg, 36.8 μmol, 2% yield) were also recovered. mp = 147–149 °C. ^{1}H NMR [$(CD_3)_2CO$, 400 MHz]: δ 3.73 (s, 3H), 3.84 (s, 3H), 3.90 (s, 3H), 3.95 (s, 3H), 6.55 (d, 1H, J = 6.0 Hz), 7.34 (s, 1H), 8.13 (d, 1H, J = 16.0 Hz). ^{13}C NMR [$(CD_3)_2CO$, 100 MHz]: δ 51.2, 56.0, 60.5, 60.6, 110.3, 121.9, 122.6, 128.3, 139.5, 145.9, 153.8, 154.4, 167.8, 168.0. IR (KBr): ν 2952, 1698, 1682, 1583, 1490, 1325, 1125. Anal. calcd. for $C_{14}H_{16}O_7$: C 56.60; H 5.44; found: C 56.76; H 5.44.

5. Conversion of 7 into 4a

A mixture of $[(COD)RhCl]_2$ (3.94 mg, 0.008 mmol, 8 mol%) and AgOTf (6.18 mg, 0.024 mmol, 24 mol%) in chlorobenzene (200 μL) was stirred in a glass tube at room temperature for 30 minutes. Dicyclopentadiene (4.3 μL, 0.032 mmol, 32 mol%) was added. Mixture turned instantaneously from light yellow to dark orange. Then, **7** (30 mg, 0.10 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (79.7 mg, 0.40 mmol, 4.0 equiv), and chlorobenzene (300 μL) were added. The tube was sealed and heated at 120 °C for 48 hours. After this time the reaction mixture was quenched with 28% NH_4OH (2 mL) and extracted with ethyl acetate (3 x 2 mL). The organic layers were combined and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure to afford **4a** as a white solid (27 mg, 0.091 mmol, 91% yield).

6. Conversion of 7 into 4a and 4b

A mixture of $[(COD)RhCl]_2$ (4.73 mg, 9.6 μmol, 8 mol%) and AgOTf (7.42 mg, 28.8 μmol, 24 mol%) in chlorobenzene (240 μL) was stirred in a glass tube at room temperature for 30 minutes. Dicyclopentadiene (5.2 μL, 38.4 μmol, 32 mol%) was added. Mixture turned instantaneously from light yellow to dark orange. Then, **7** (35 mg, 0.12 mmol, 1.0 equiv), $Cu(OAc)_2 \cdot H_2O$ (93.9 mg, 0.47

mmol, 4.0 equiv), methyl acrylate (10.8 μL, 0.12 mmol, 1.0 equiv) and chlorobenzene (360 μL) were added. The tube was sealed and heated at 120 °C for 48 hours. After this time the reaction mixture was quenched with 28% NH_4OH (2 mL) and extracted with ethyl acetate (3 x 2 mL). The organic layers were combined and filtered through a short pad of silica gel. The filtrate was concentrated under reduced pressure. Purification of the crude mixture by column chromatography on silica gel (eluent: hexane/diethyl ether = 7/3) afforded **4a** (14 mg, 0.048 mmol, 35% yield) and **4b** (30 mg, 0.080 mmol, 65% yield) as white solids.

7. X-ray crystal structure determination of $(COD)_2RhOTf$

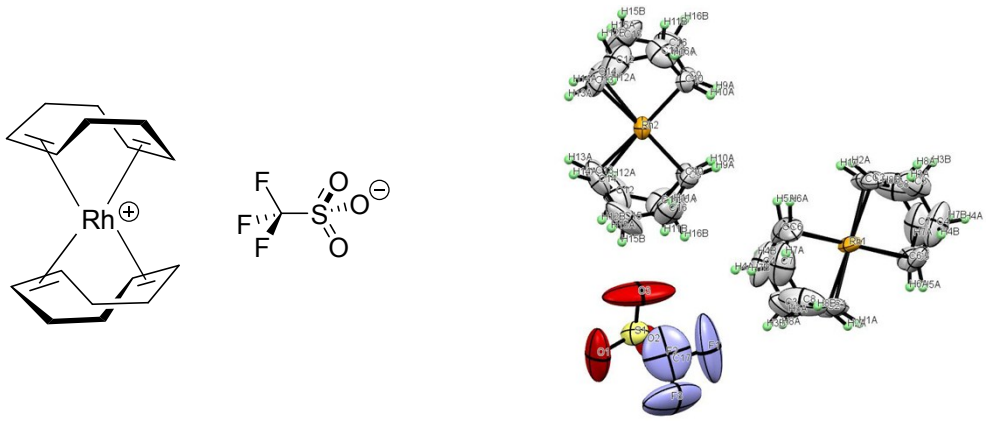


Figure S1 Molecular structure of $(COD)_2RhOTf$ with displacement ellipsoids drawn at 50% probability for non-H atoms.

$[(COD)RhCl]_2$ (200 mg, 0.40 mmol, 1.0 equiv) was dissolved in acetone (15 mL) under nitrogen. Solution was orange. AgOTf (208 mg, 0.81 mmol, 2.0 equiv) was added to this solution. The addition resulted in the immediate formation of a white precipitate and in a color change of solution from orange to pale yellow. After 5 min stirring, *(endo)*-dicyclopentadiene (114.5 μL, 0.81 mmol, 2.0 equiv) was added. Solution color instantaneously turned dark red. After 30 min of additional stirring at room temperature, the mixture was filtered by cannula under nitrogen. Filtrate was dried under vacuum leaving a red solid residue. Single crystals were grown from Me_2CO/Et_2O (15 mL, 1/20 [v/v]) at −18 °C. The single crystal was mounted in a glass capillary. Data for $(COD)_2RhOTf$ were collected at −70 ºC on a Rigaku/MSC Mercury CCD area-detector diffractometer equipped with monochromated MoKα radiation. Calculations for $(COD)_2RhOTf$ were performed with the teXane crystallographic software package of Molecular Structure Corporation. X-ray analysis of $(COD)_2RhOTf$ was consistent with that reported in the literature.[2]

Table S1 Crystal data and structure refinement for **$(COD)_2RhOTf$**.

Empirical formula	C17 H24 F3 O3 Rh S	
Formula weight	468.33	
Temperature	230(2) K	
Wavelength	0.71075 Å	
Crystal system	monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 14.084(4) Å	α= 90°.
	b = 17.652(5) Å	β= 95.320(3)°.
	c = 14.840(4) Å	γ = 90°.
Volume	3673.3(18) $Å^3$	
Z	8	
Density (calculated)	1.694 Mg/m^3	
Absorption coefficient	1.086 mm^{-1}	
F(000)	1904	
Crystal size	0.14 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.31 to 27.44°.	
Index ranges	-18<=h<=10, -15<=k<=22, -19<=l<=19	
Reflections collected	14349	
Independent reflections	4133 [R(int) = 0.0437]	
Completeness to theta = 27.44°	98.4 %	
Max. and min. transmission	0.9477 and 0.8629	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4133 / 7 / 228	
Goodness-of-fit on F^2	1.083	
Final R indices [I>2sigma(I)]	R1 = 0.0618, wR2 = 0.1423	
R indices (all data)	R1 = 0.0867, wR2 = 0.1580	
Largest diff. peak and hole	0.748 and -0.722 e.Å-3	

Table S2 Selected bond lengths [Å] and angles [°] for **$(COD)_2RhOTf$**.

Rh(1)-C(5)	2.214(7)
Rh(1)-C(2)	2.220(6)
Rh(1)-C(1)	2.231(7)
Rh(1)-C(6)	2.232(7)
C(1)-C(2)	1.343(10)
C(1)-C(8)	1.472(13)
C(1)-H(1A)	0.9900
C(2)-C(3)	1.491(10)
C(3)-C(4)	1.479(13)
C(3)-H(3A)	0.9800
C(4)-C(5)	1.492(14)
C(5)-C(6)	1.350(12)
C(6)-C(7)	1.480(13)
C(7)-C(8)	1.384(14)
S(1)-O(3)	1.315(8)
S(1)-O(2)	1.394(5)
S(1)-O(1)	1.405(7)
S(1)-C(17)	1.813(10)
C(17)-F(3)	1.218(12)
C(17)-F(1)	1.241(10)
C(17)-F(2)	1.292(11)
C(5)-Rh(1)-C(2)	81.7(3)
C(5)-Rh(1)-C(1)	90.8(3)
C(2)-Rh(1)-C(1)	35.1(3)
C(5)-Rh(1)-C(6)	35.4(3)
C(2)-Rh(1)-C(6)	90.9(3)
C(1)-Rh(1)-C(6)	79.0(3)
C(2)-C(1)-C(8)	127.9(9)
C(2)-C(1)-Rh(1)	72.0(4)
C(8)-C(1)-Rh(1)	109.2(6)
C(2)-C(1)-H(1A)	113.2
C(1)-C(2)-C(3)	124.8(8)
C(1)-C(2)-Rh(1)	72.9(4)

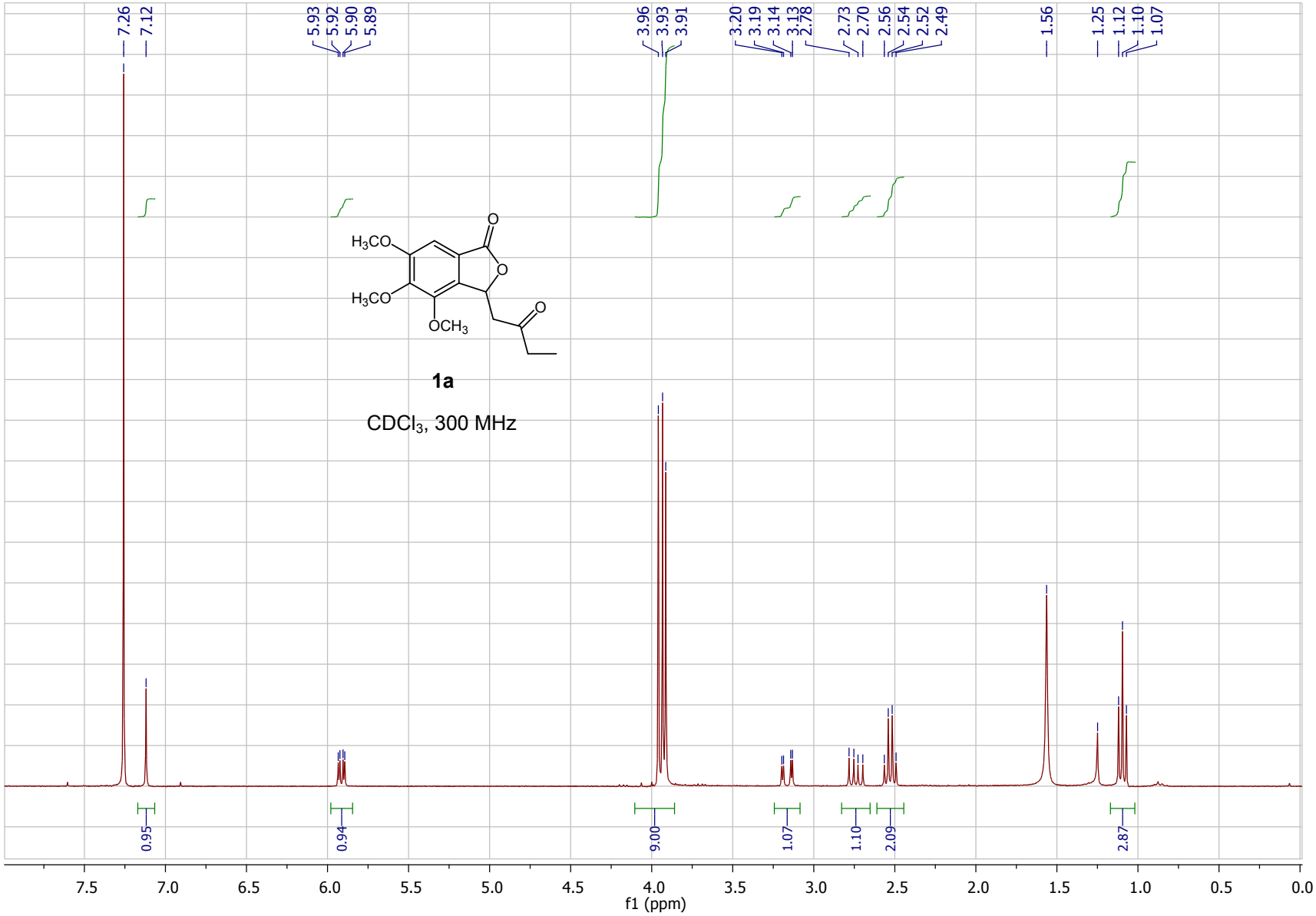
C(3)-C(2)-Rh(1)	108.0(5)
C(1)-C(2)-H(2A)	114.4
C(4)-C(3)-C(2)	118.7(8)
O(3)-S(1)-O(2)	113.2(6)
O(3)-S(1)-O(1)	119.5(8)
O(2)-S(1)-O(1)	110.1(5)
O(3)-S(1)-C(17)	105.2(6)
O(2)-S(1)-C(17)	105.0(4)
O(1)-S(1)-C(17)	102.0(5)
F(3)-C(17)-F(1)	109.1(14)
F(3)-C(17)-F(2)	108.3(11)
F(1)-C(17)-F(2)	105.8(9)
F(3)-C(17)-S(1)	112.9(7)
F(1)-C(17)-S(1)	109.7(9)
F(2)-C(17)-S(1)	110.7(9)

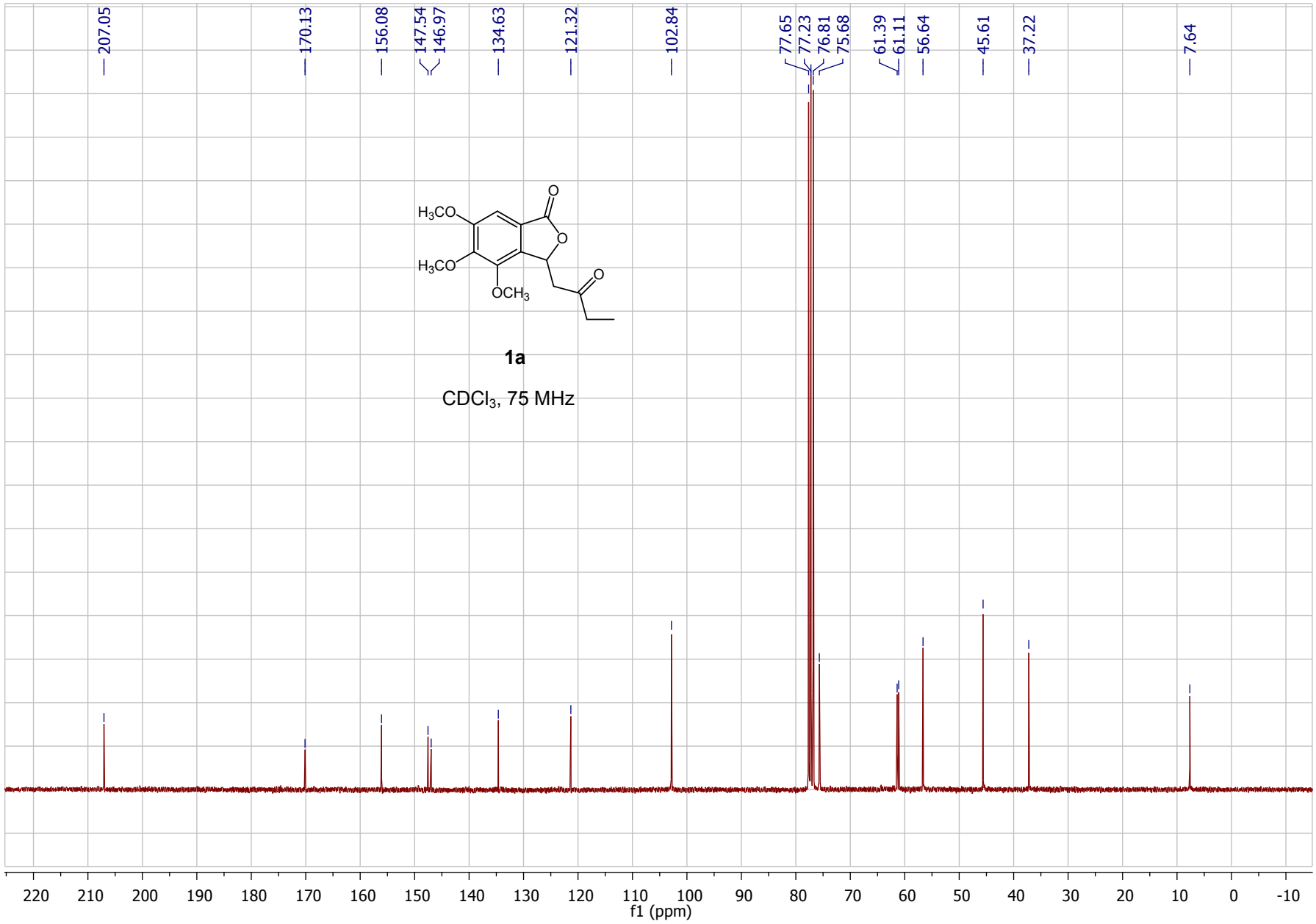
8. References

(1) H. Zhang, S. Zhang, L. Liu, G. Luo, W. Duan, W. Wang, *J. Org. Chem.* **2010**, *75*, 368−374.

(2) L. Dahlenburg, N. Osthoff, F. W. Heinemann *Acta Cryst.* **2001**, *E57*, m117−m118.

9. NMR spectra of products

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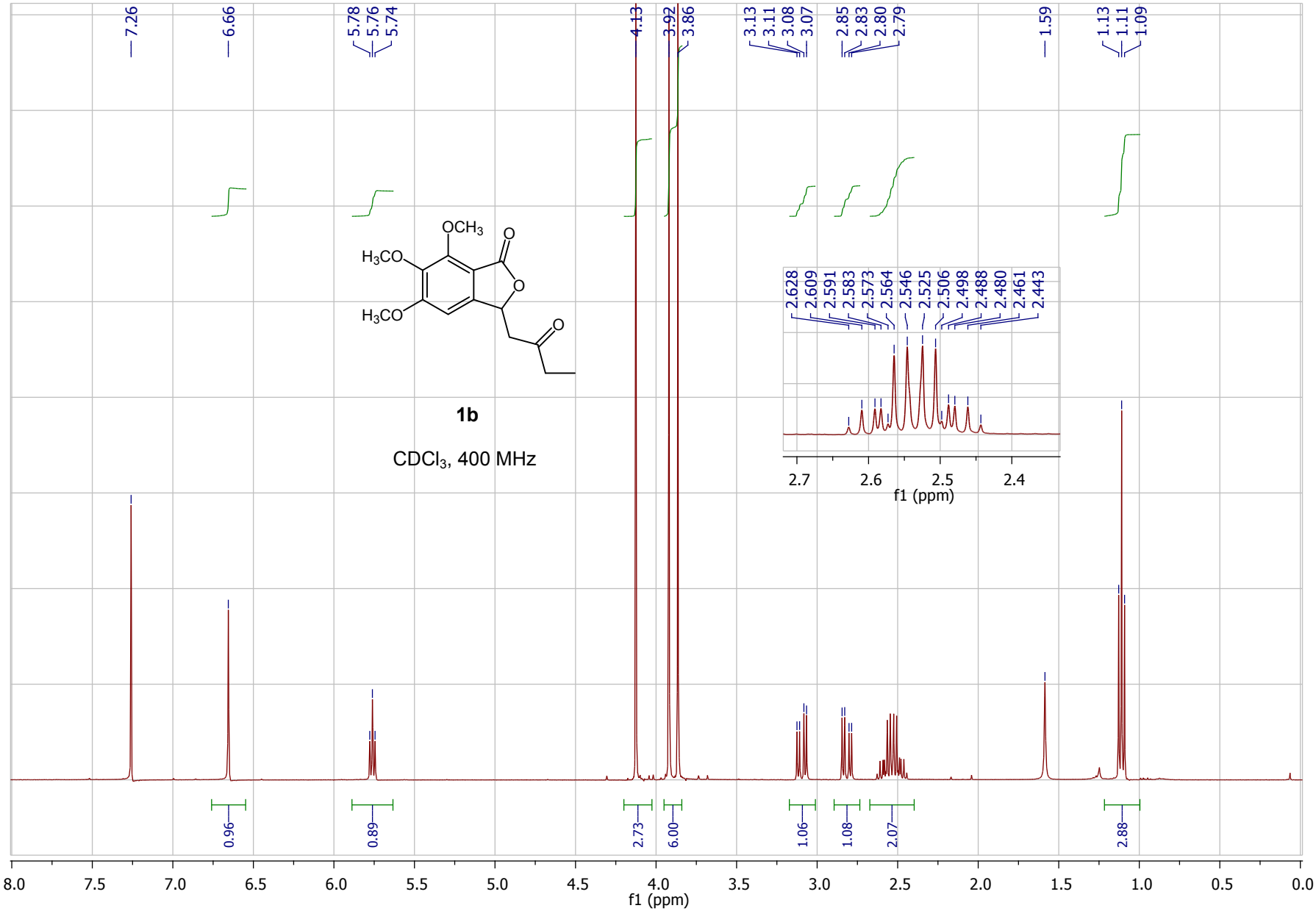
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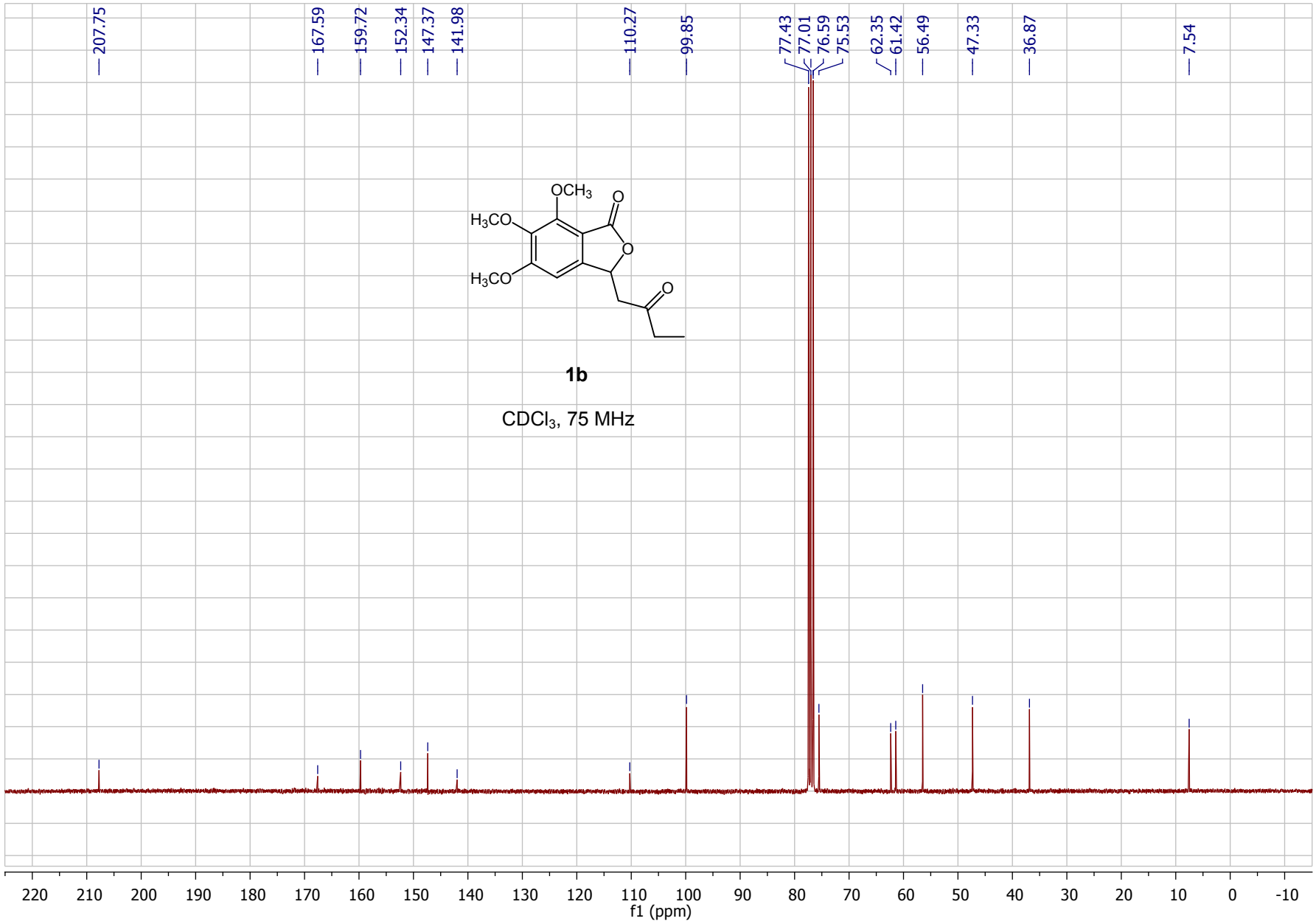
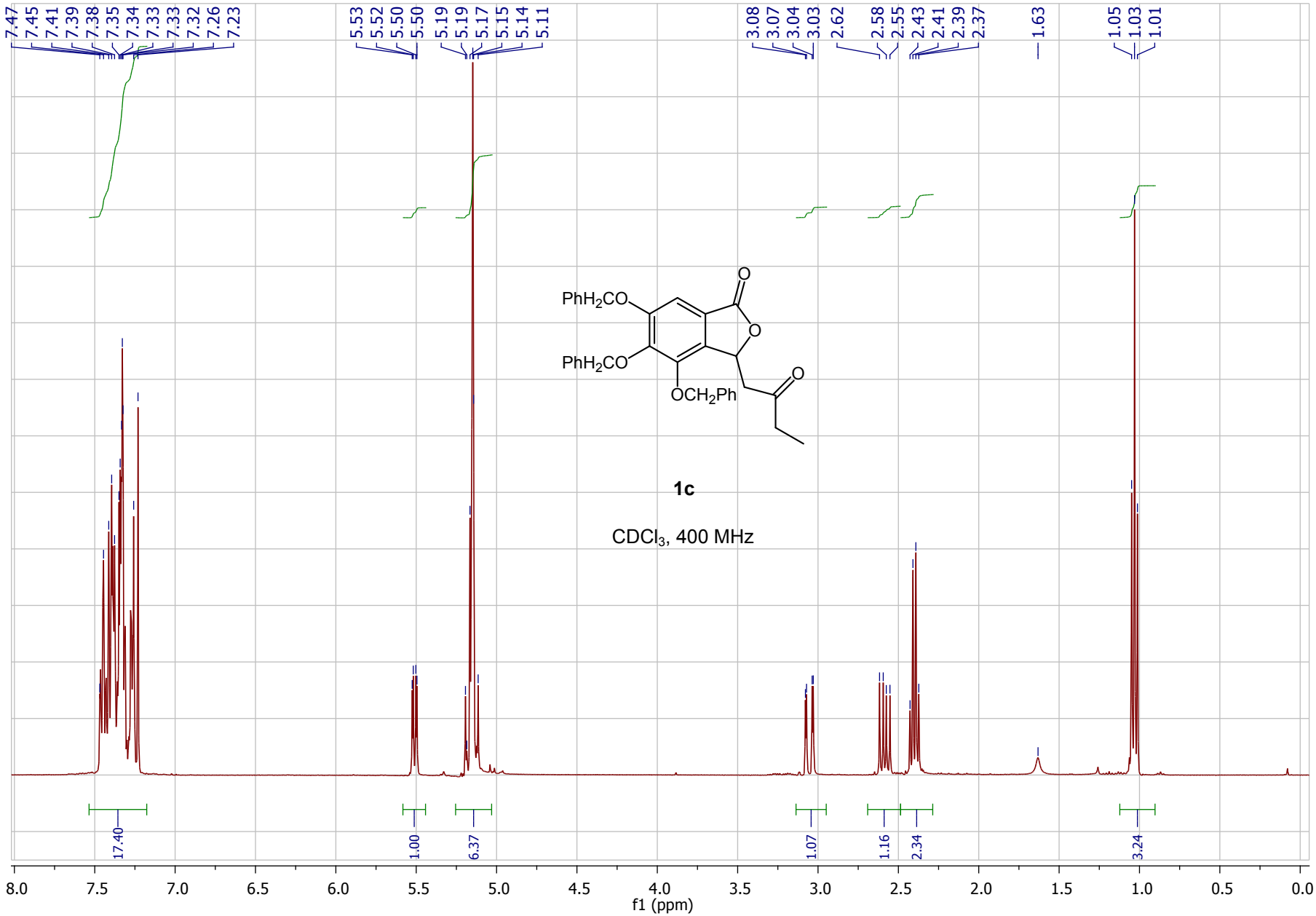
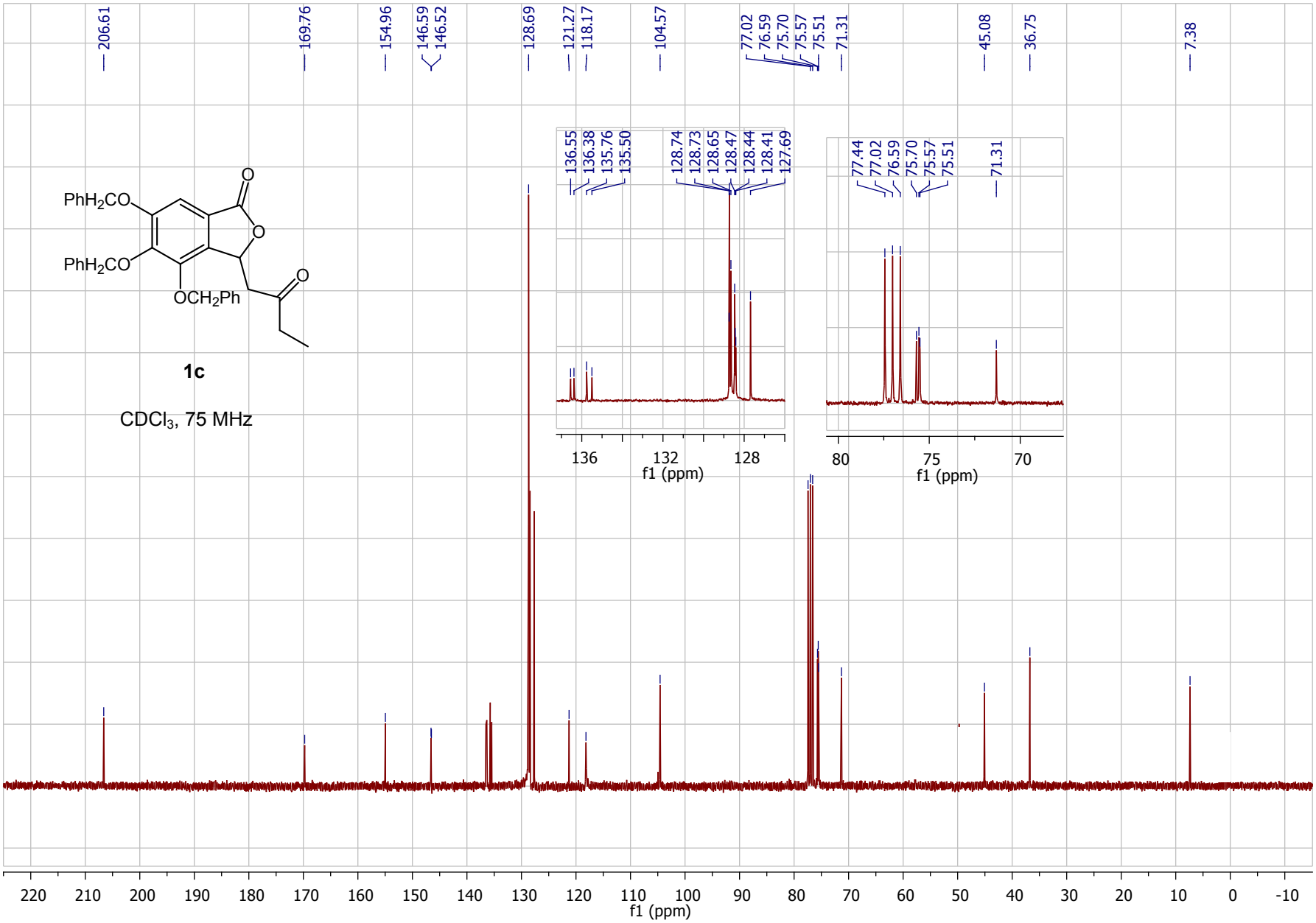
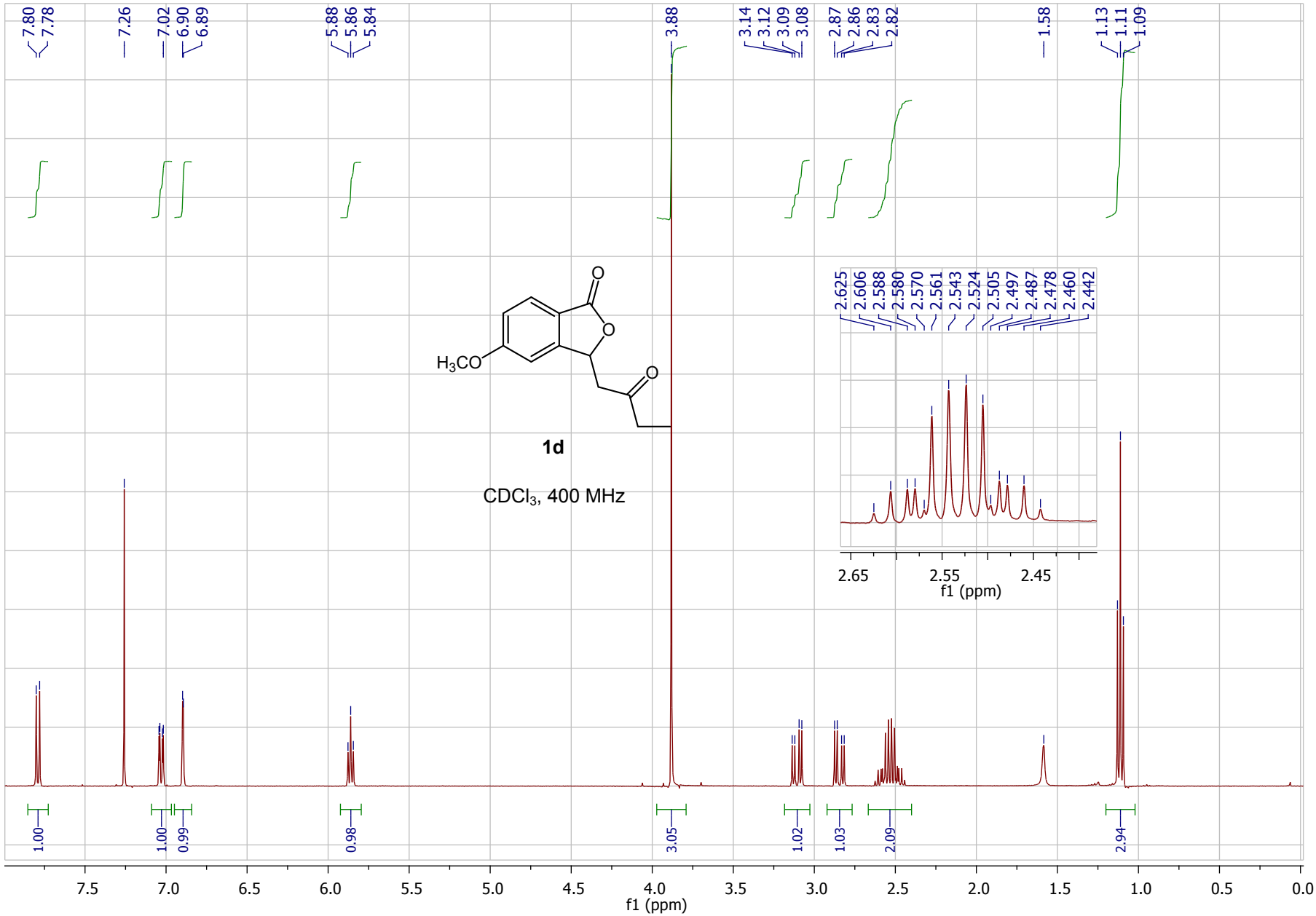
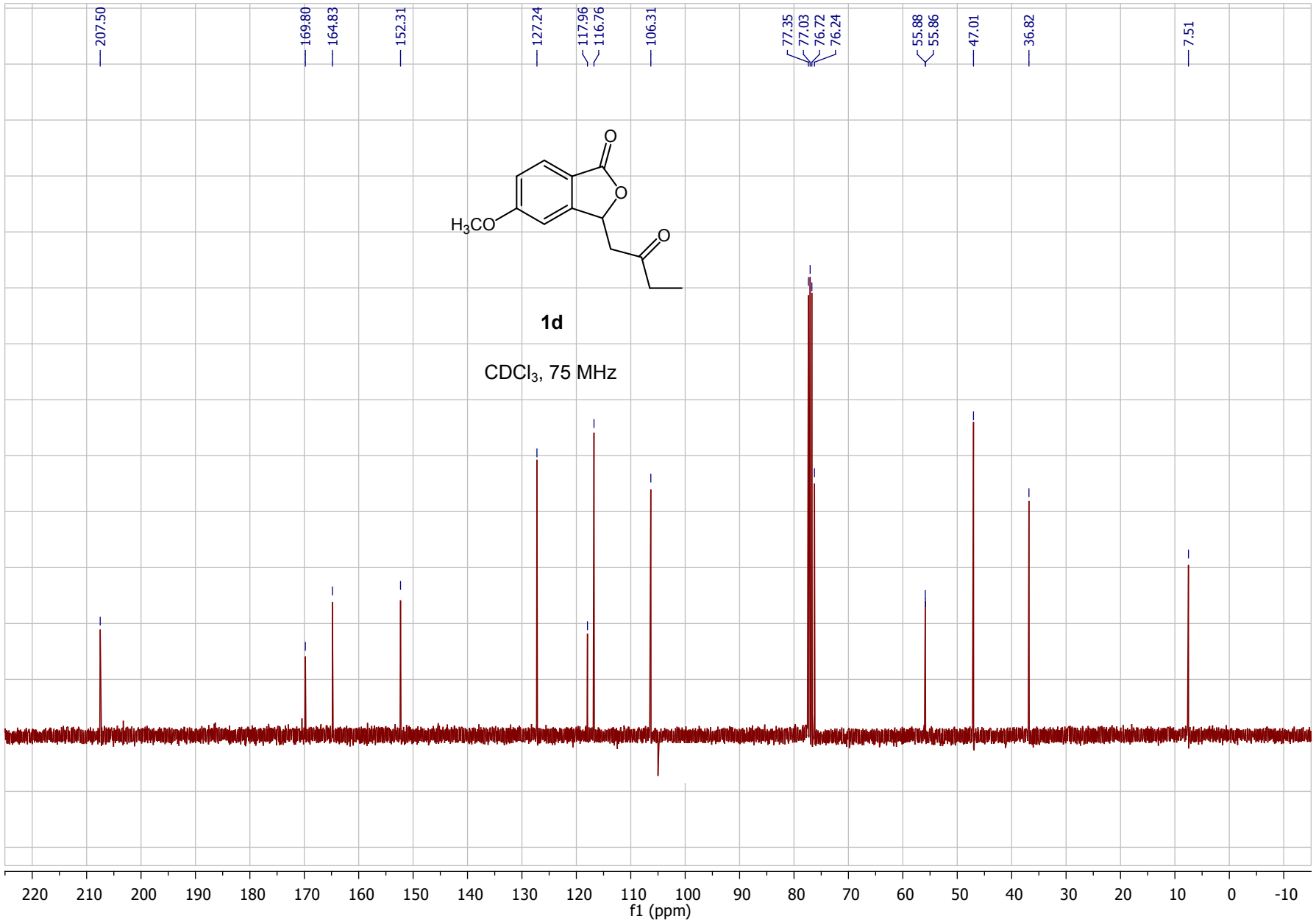
2.85
2.83
2.80
2.79
1.59
1.13
1.11
1.09
OCH3
H3CO
H3CO
O
O
O
1b
CDCl3, 400 MHz
2.628
2.609
2.591
2.583
2.573
2.564
2.546
2.525
2.506
2.498
2.488
2.480
2.461
2.443
2.7
2.6
2.5
2.4
f1 (ppm)
0.96
0.89
2.73
6.00
1.06
1.08
2.07
2.88
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

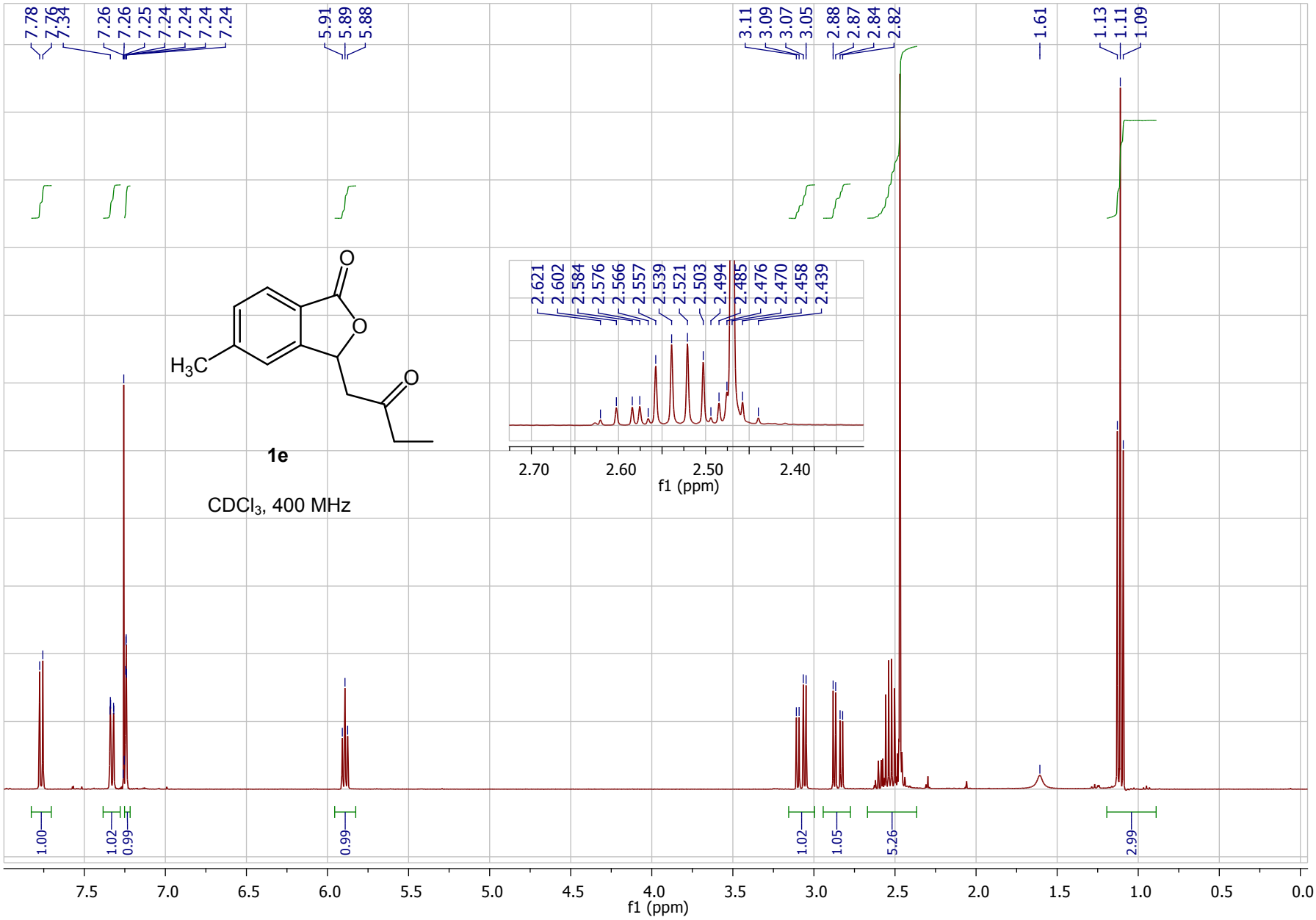

207.75
167.59
159.72
152.34
147.37
141.98
110.27
99.85
77.43
77.01
76.59
75.53
62.35
61.42
56.49
47.33
36.87
7.54
OCH3
H3CO
H3CO
O
O
O
1b
CDCl3, 75 MHz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

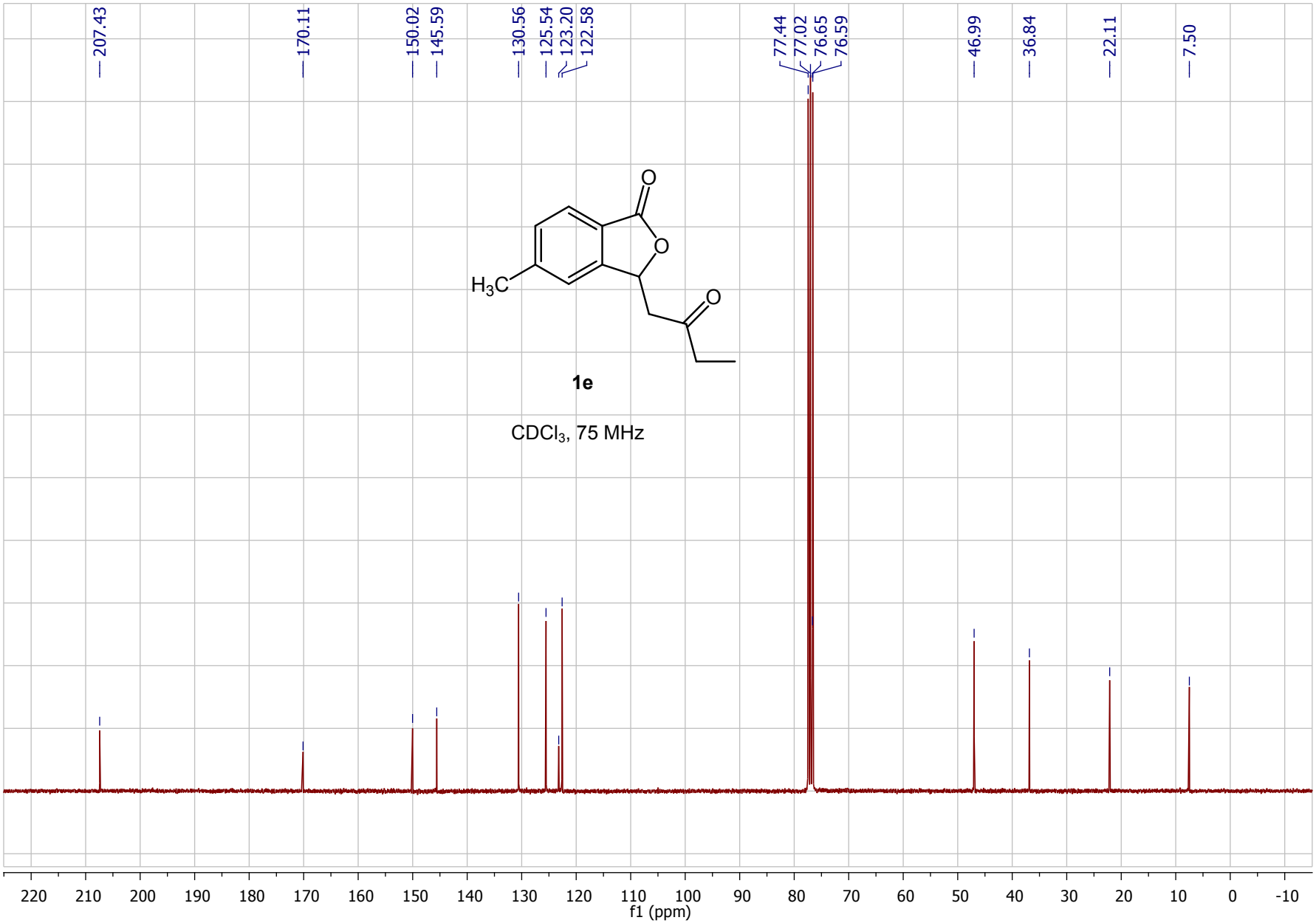

7.47
7.45
7.41
7.39
7.38
7.35
7.34
7.33
7.33
7.32
7.26
7.23
5.53
5.52
5.50
5.50
5.19
5.19
5.17
5.15
5.14
5.11
3.08
3.07
3.04
3.03
2.62
2.58
2.55
2.43
2.41
2.39
2.37
1.63
1.05
1.03
1.01
PhH2CO
PhH2CO
OCH2Ph
O
O
O
1c
CDCl3, 400 MHz
17.40
1.00
6.37
1.07
1.16
2.34
3.24
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

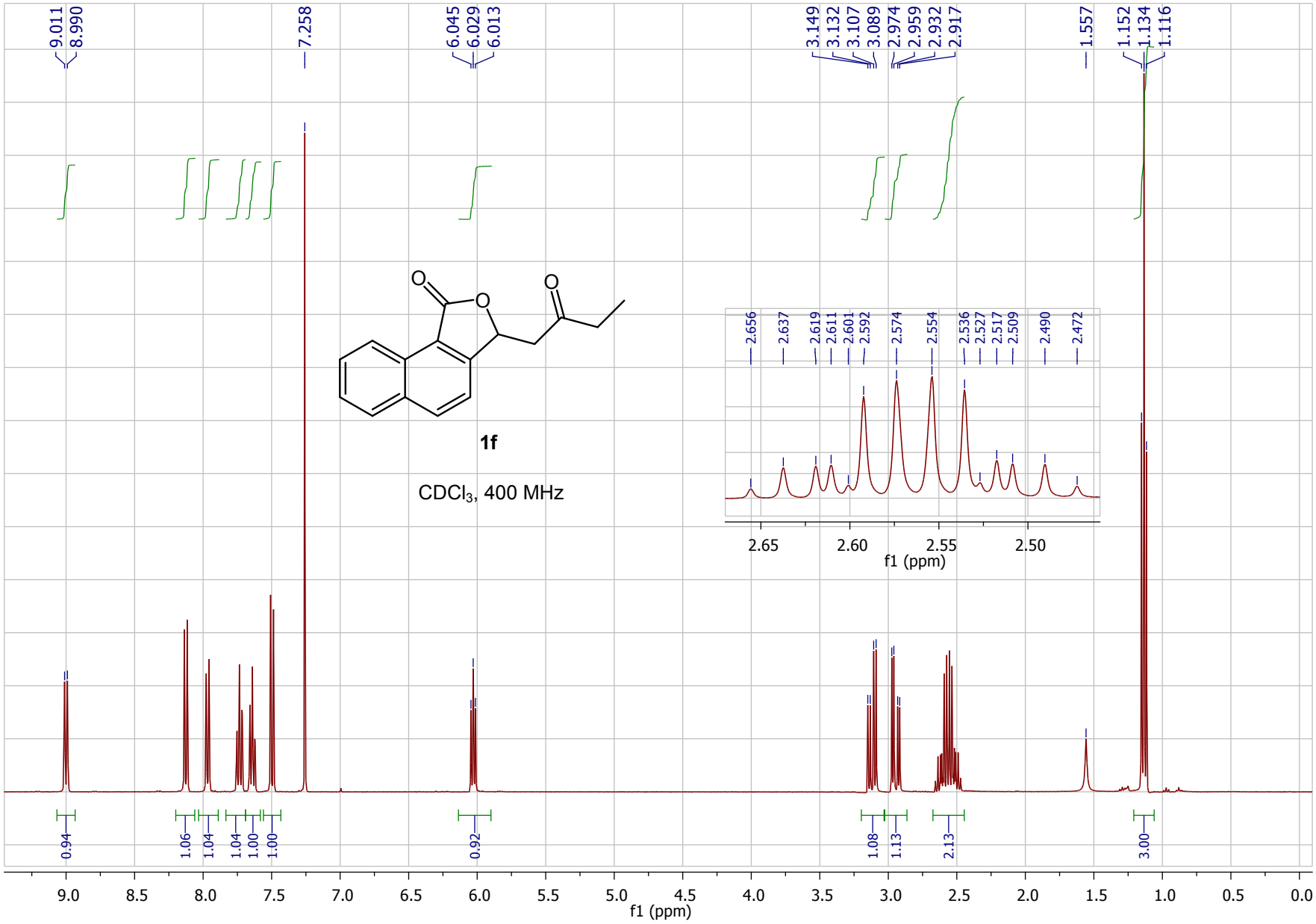

206.61
169.76
154.96
146.59
146.52
128.69
121.27
118.17
104.57
77.02
76.59
75.70
75.57
75.51
71.31
45.08
36.75
7.38
136.55
136.38
135.76
135.50
128.74
128.73
128.65
128.47
128.44
128.41
127.69
77.44
77.02
76.59
75.70
75.57
75.51
71.31
PhH2CO
PhH2CO
OCH2Ph
O
O
O
1c
CDCl3, 75 MHz
136
132
128
f1 (ppm)
80
75
70
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

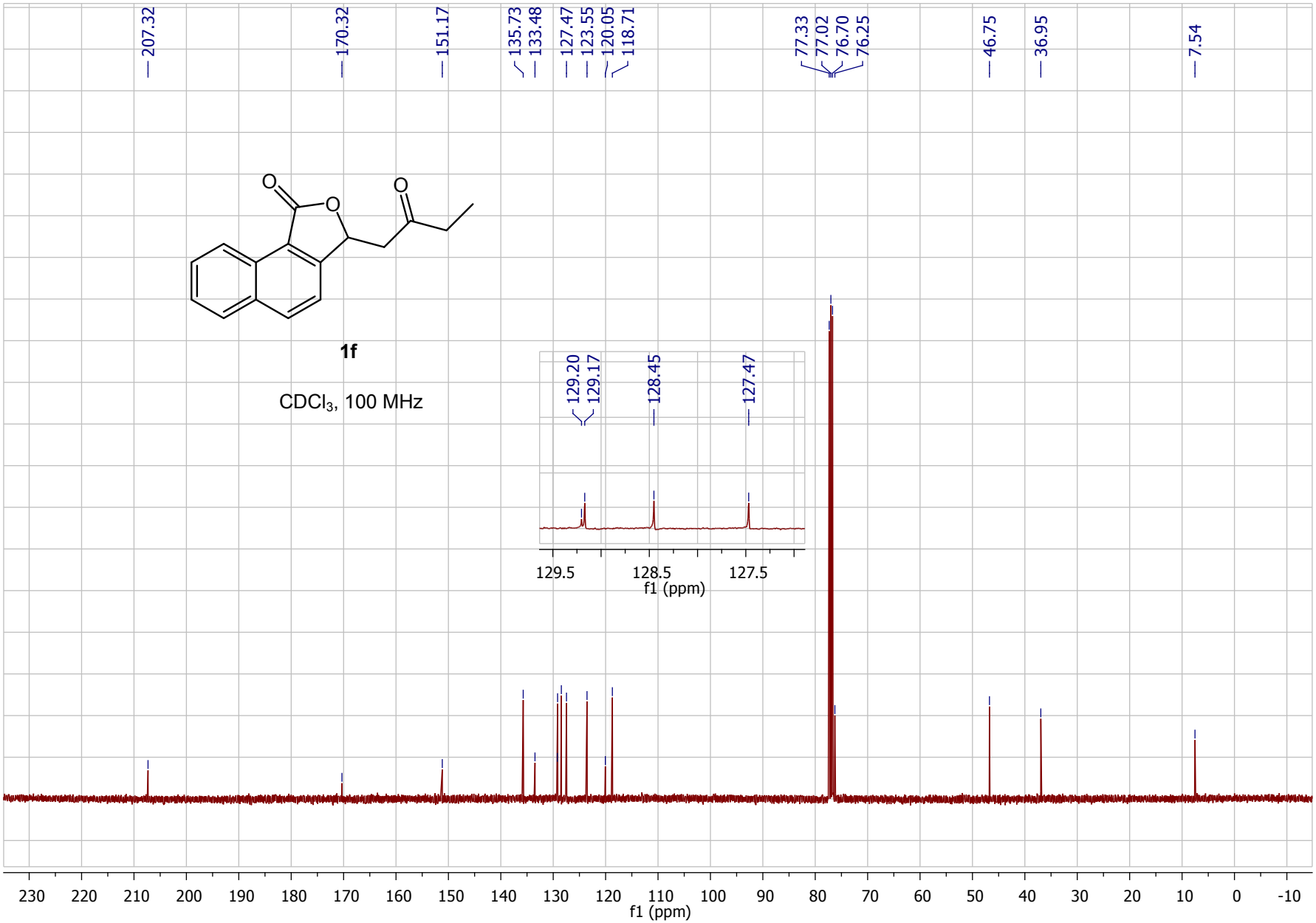

7.80
7.78
7.26
7.02
6.90
6.89
5.88
5.86
5.84
3.88
3.14
3.12
3.09
3.08
2.87
2.86
2.83
2.82
1.58
1.13
1.11
1.09
2.625
2.606
2.588
2.580
2.570
2.561
2.543
2.524
2.505
2.497
2.487
2.478
2.460
2.442
H3CO
O
O
O
1d
CDCl3, 400 MHz
2.65
2.55
2.45
f1 (ppm)
1.00
1.00
0.99
0.98
3.05
1.02
1.03
2.09
2.94
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

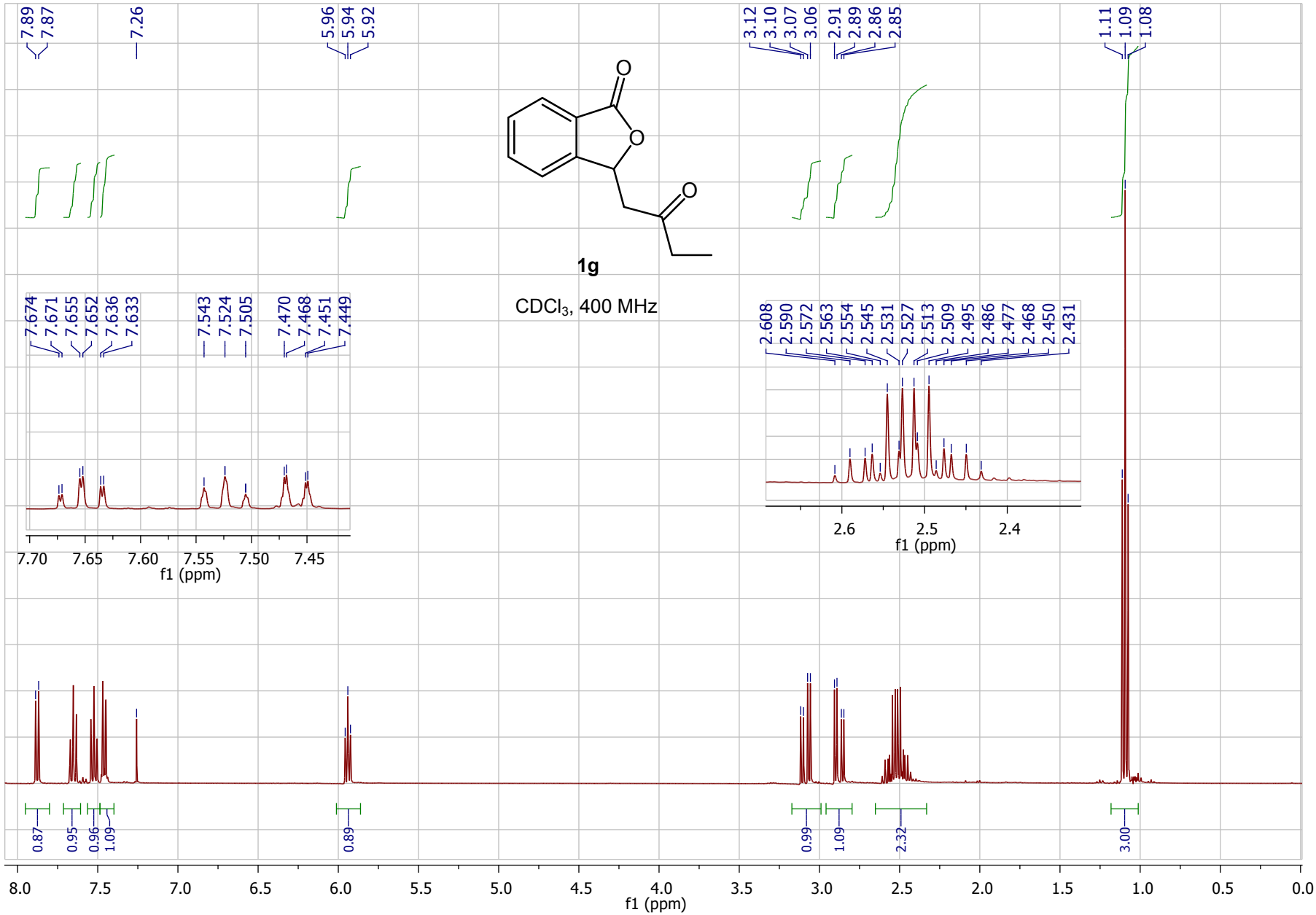

207.50
169.80
164.83
152.31
127.24
117.96
116.76
106.31
77.35
77.03
76.72
76.24
55.88
55.86
47.01
36.82
7.51
O
O
O
H3CO
1d
CDCl3, 75 MHz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

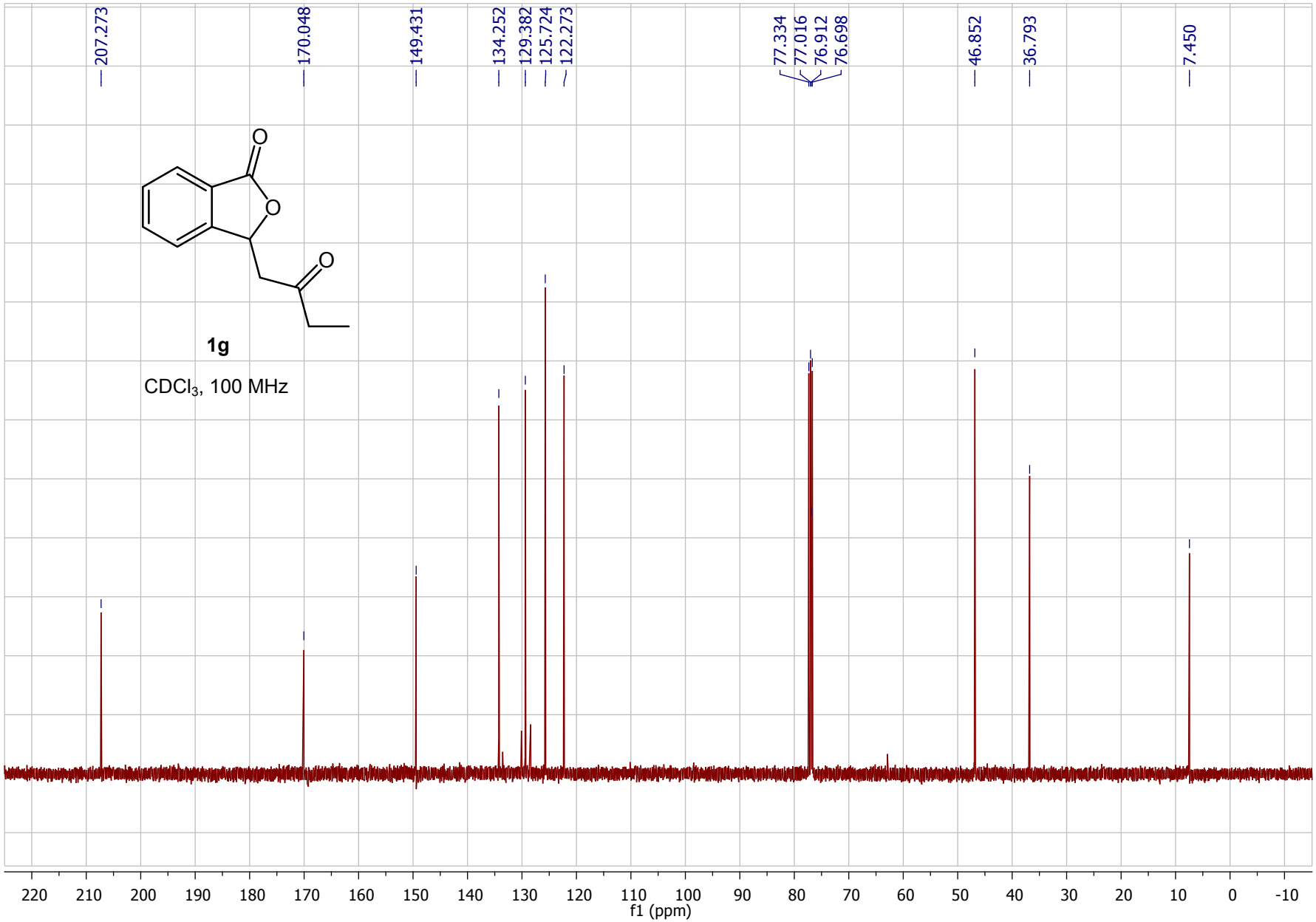

7.78
7.76
7.34
7.26
7.26
7.25
7.24
7.24
7.24
7.24
5.91
5.89
5.88
3.11
3.09
3.07
3.05
2.88
2.87
2.84
2.82
1.61
1.13
1.11
1.09
2.621
2.602
2.584
2.576
2.566
2.557
2.539
2.521
2.503
2.494
2.485
2.476
2.470
2.458
2.439
O
O
O
H3C
1e
CDCl3, 400 MHz
2.70
2.60
2.50
2.40
f1 (ppm)
1.00
1.02
0.99
0.99
1.02
1.05
5.26
2.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

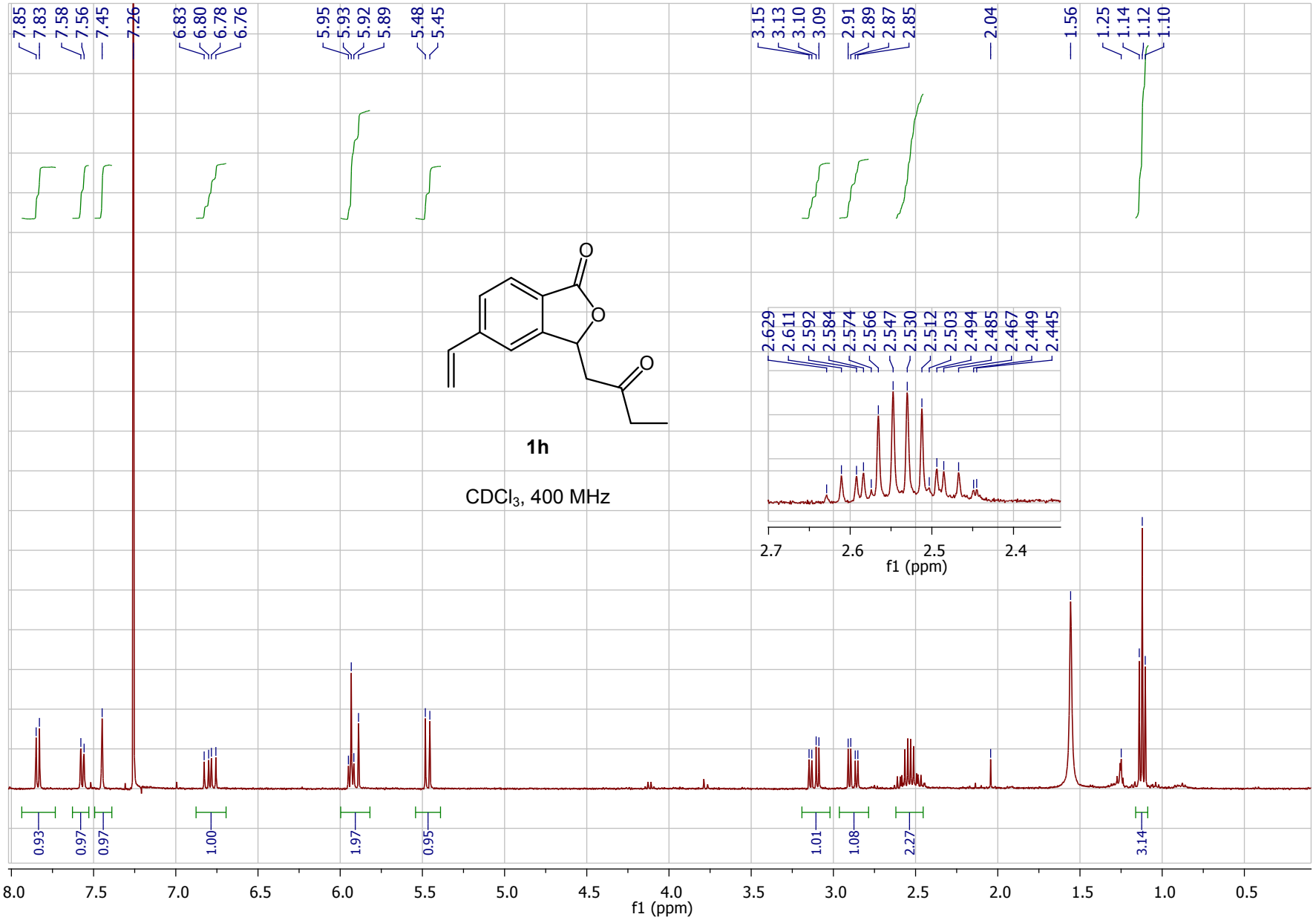

207.43
170.11
150.02
145.59
130.56
125.54
123.20
122.58
77.44
77.02
76.65
76.59
46.99
36.84
22.11
7.50
O
O
O
H3C
1e
CDCl3, 75 MHz
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

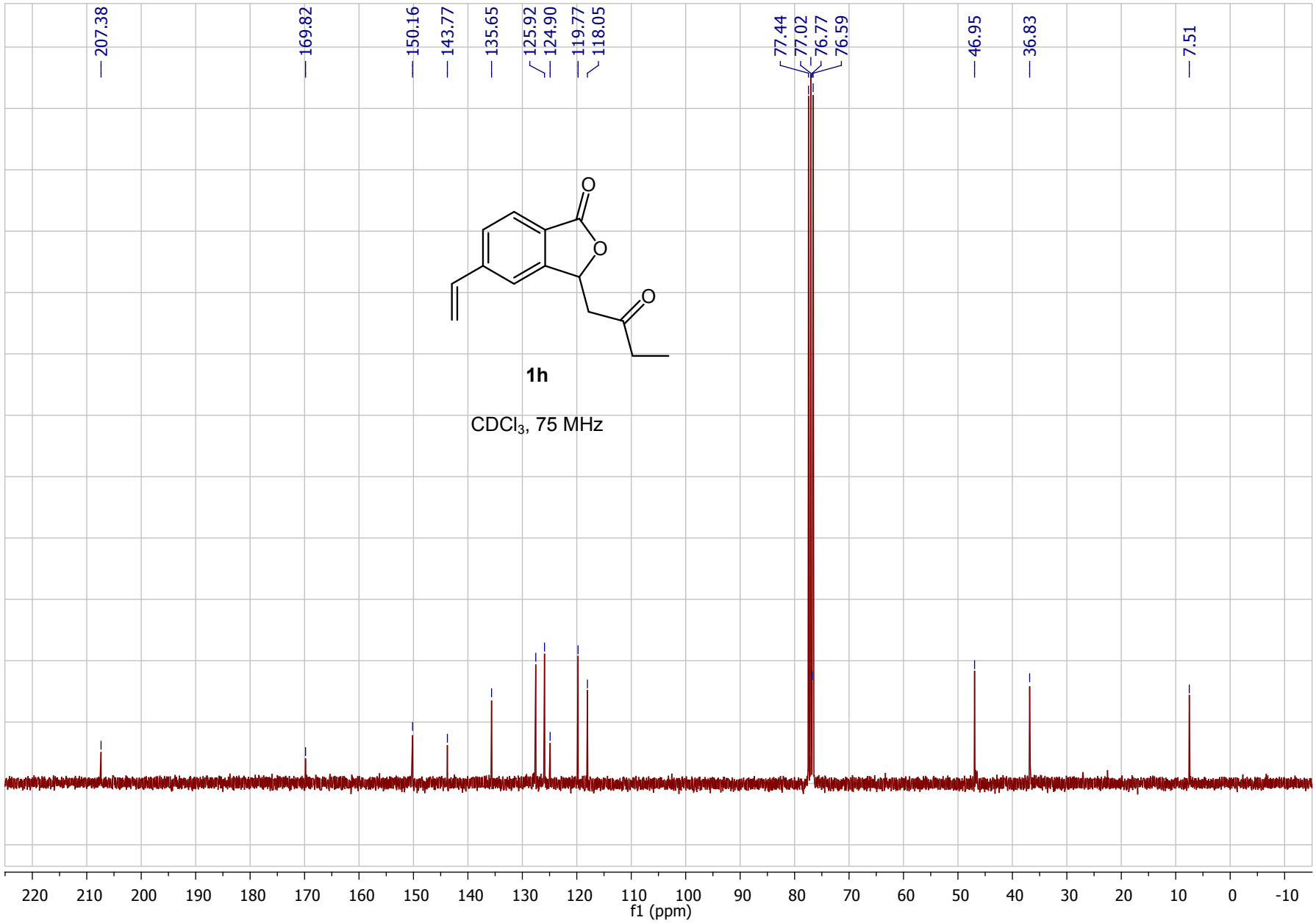

9.011
8.990
7.258
6.045
6.029
6.013
3.149
3.132
3.107
3.089
2.974
2.959
2.932
2.917
1.557
1.152
1.134
1.116
O
O
O
1f
CDCl3, 400 MHz
2.656
2.637
2.619
2.611
2.601
2.592
2.574
2.554
2.536
2.527
2.517
2.509
2.490
2.472
2.65
2.60
2.55
2.50
f1 (ppm)
0.94
1.06
1.04
1.04
1.00
1.00
0.92
1.08
1.13
2.13
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

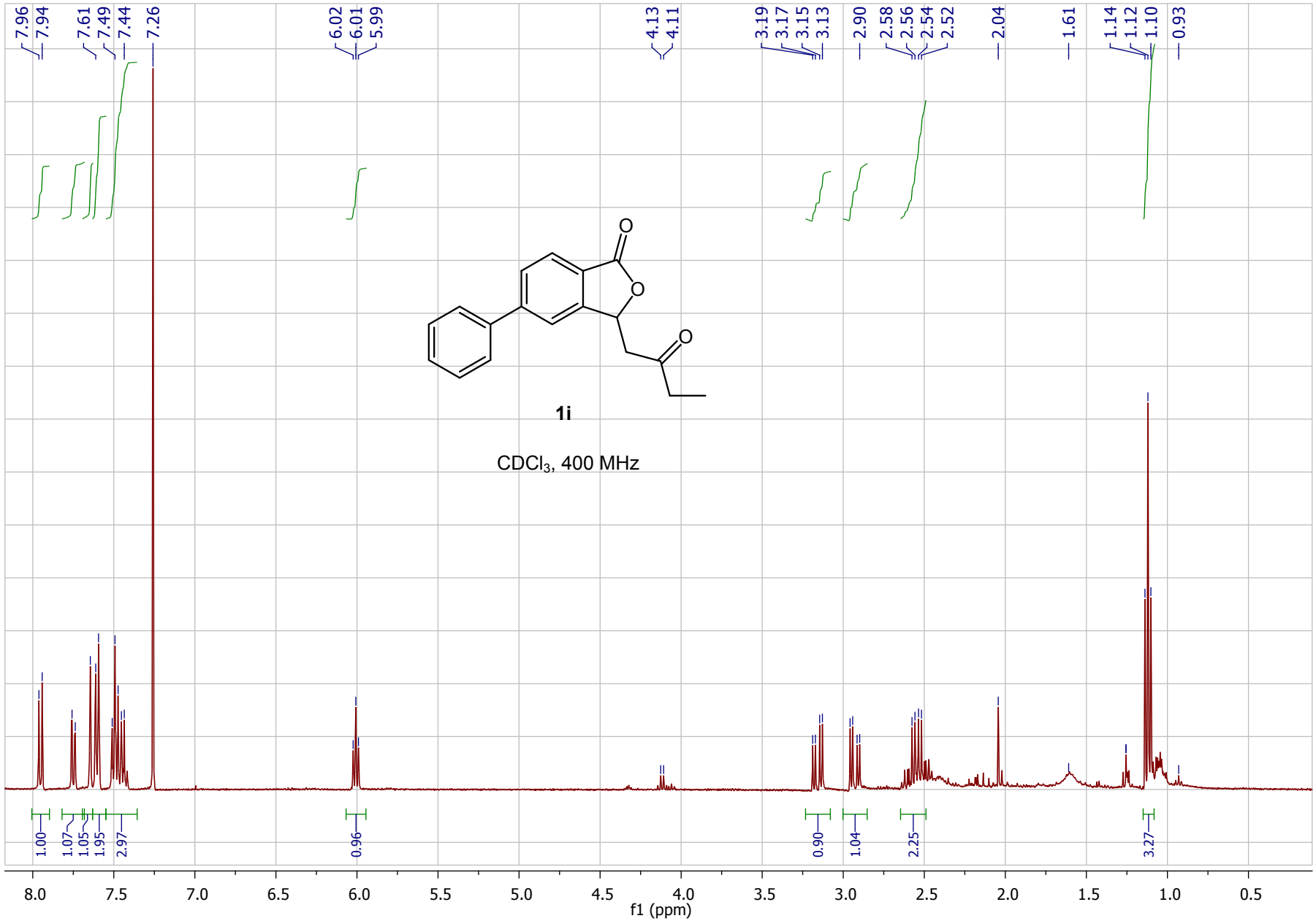

207.32
170.32
151.17
135.73
133.48
127.47
123.55
120.05
118.71
77.33
77.02
76.70
76.25
46.75
36.95
7.54
O
O
O
1f
CDCl3, 100 MHz
129.20
129.17
128.45
127.47
129.5
128.5
127.5
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

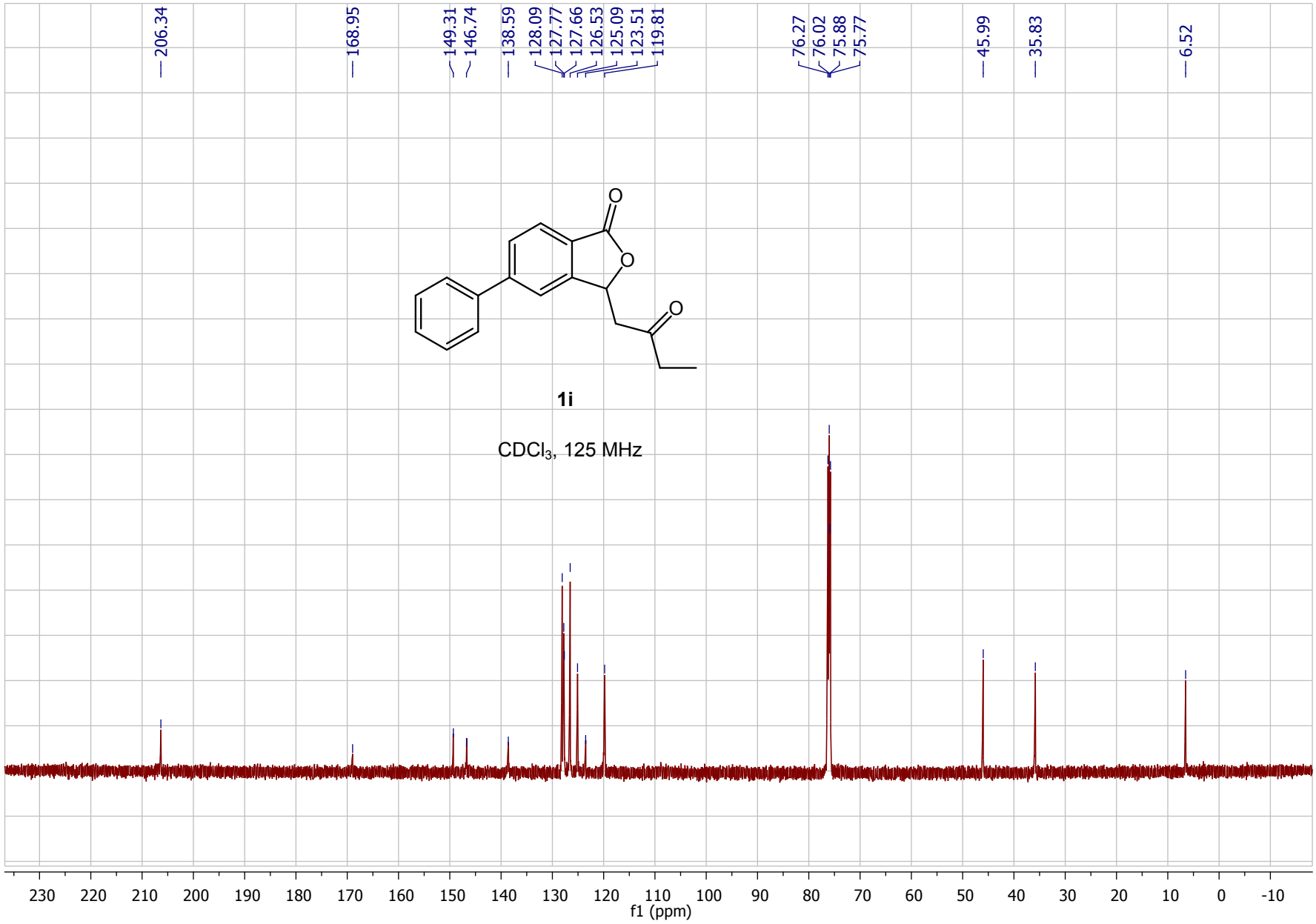

7.89
7.87
7.26
5.96
5.94
5.92
3.12
3.10
3.07
3.06
2.91
2.89
2.86
2.85
1.11
1.09
1.08
O
O
O
1g
CDCl3, 400 MHz
7.674
7.671
7.655
7.652
7.636
7.633
7.543
7.524
7.505
7.470
7.468
7.451
7.449
7.70 7.65 7.60 7.55 7.50 7.45
f1 (ppm)
2.608
2.590
2.572
2.563
2.554
2.545
2.531
2.527
2.513
2.509
2.495
2.486
2.477
2.468
2.450
2.431
2.6 2.5 2.4
f1 (ppm)
0.87
0.95
0.96
1.09
0.89
0.99
1.09
2.32
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

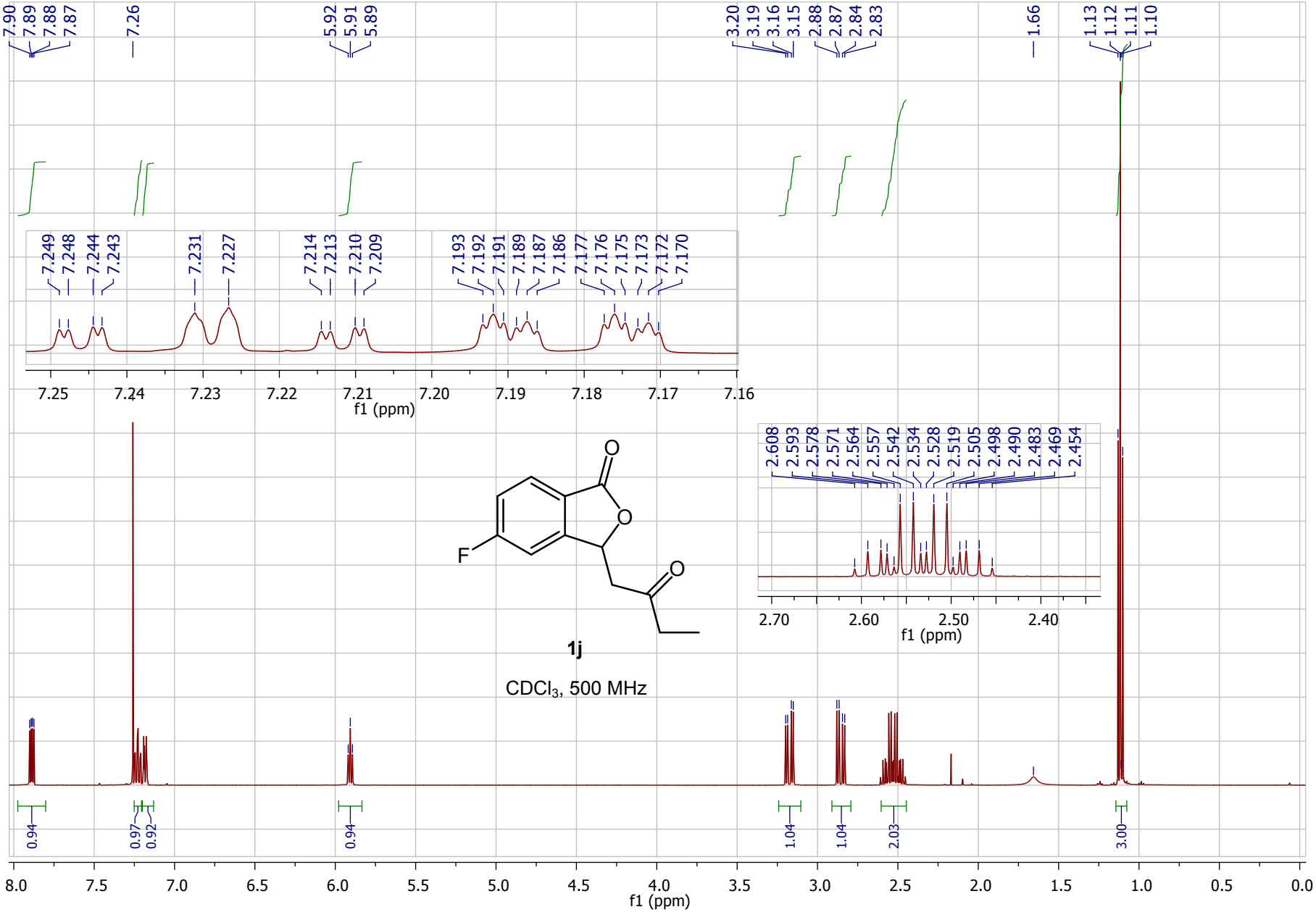

207.273
170.048
149.431
134.252
129.382
125.724
122.273
77.334
77.016
76.912
76.698
46.852
36.793
7.450
O
O
O
1g
CDCl3, 100 MHz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

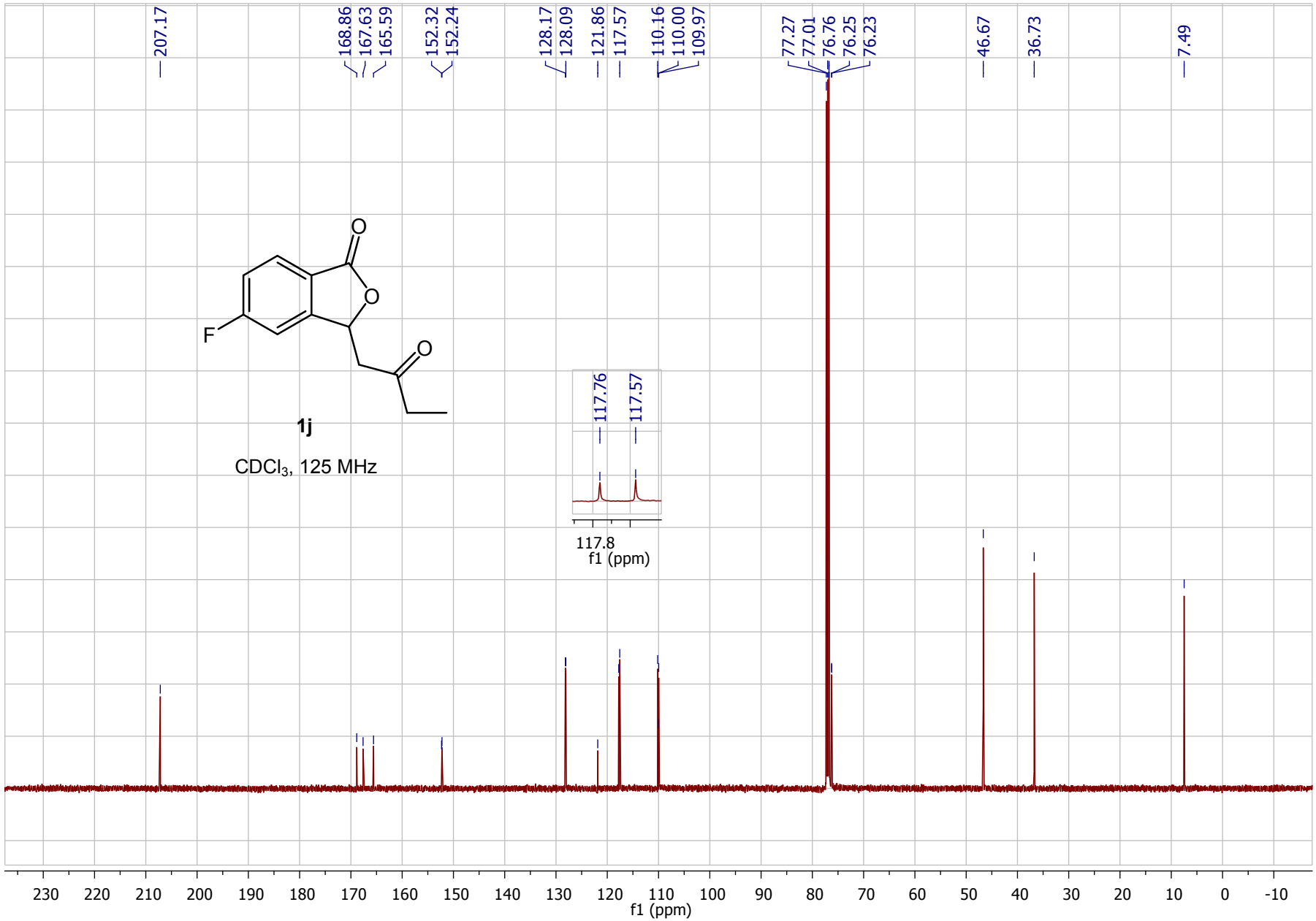

7.85
7.83
7.58
7.56
7.45
7.26
6.83
6.80
6.78
6.76
5.95
5.93
5.92
5.89
5.48
5.45
3.15
3.13
3.10
3.09
2.91
2.89
2.87
2.85
2.04
1.56
1.25
1.14
1.12
1.10
O
O
O
1h
CDCl3, 400 MHz
2.629
2.611
2.592
2.584
2.574
2.566
2.547
2.530
2.512
2.503
2.494
2.485
2.467
2.449
2.445
2.7
2.6
2.5
2.4
f1 (ppm)
0.93
0.97
0.97
1.00
1.97
0.95
1.01
1.08
2.27
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

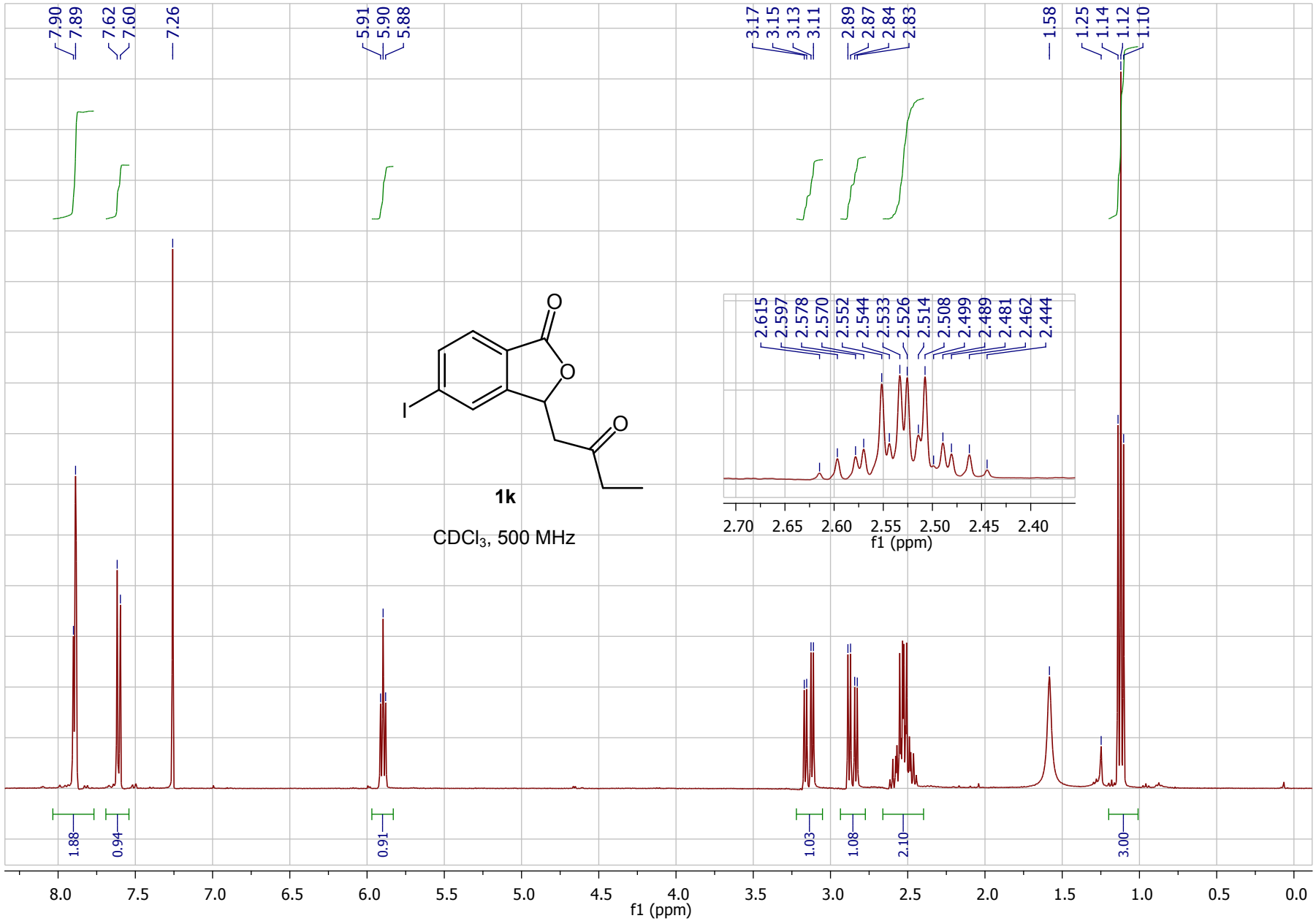

207.38
169.82
150.16
143.77
135.65
125.92
124.90
119.77
118.05
77.44
77.02
76.77
76.59
46.95
36.83
7.51
O
O
O
1h
CDCl3, 75 MHz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

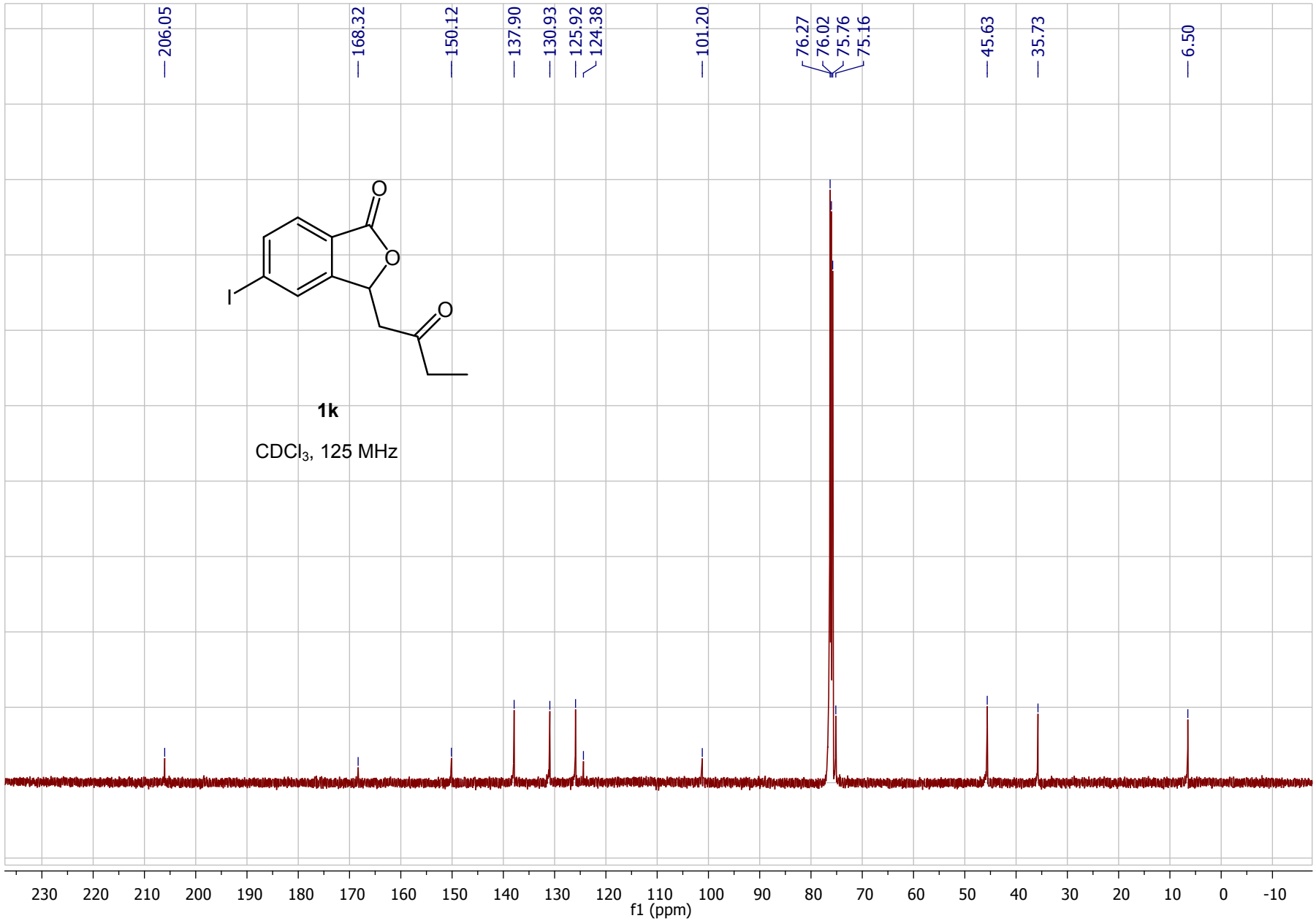

7.96
7.94
7.61
7.49
7.44
7.26
6.02
6.01
5.99
4.13
4.11
3.19
3.17
3.15
3.13
2.90
2.58
2.56
2.54
2.52
2.04
1.61
1.14
1.12
1.10
0.93
O
O
O
1i
CDCl3, 400 MHz
1.00
1.07
1.05
1.95
2.97
0.96
0.90
1.04
2.25
3.27
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

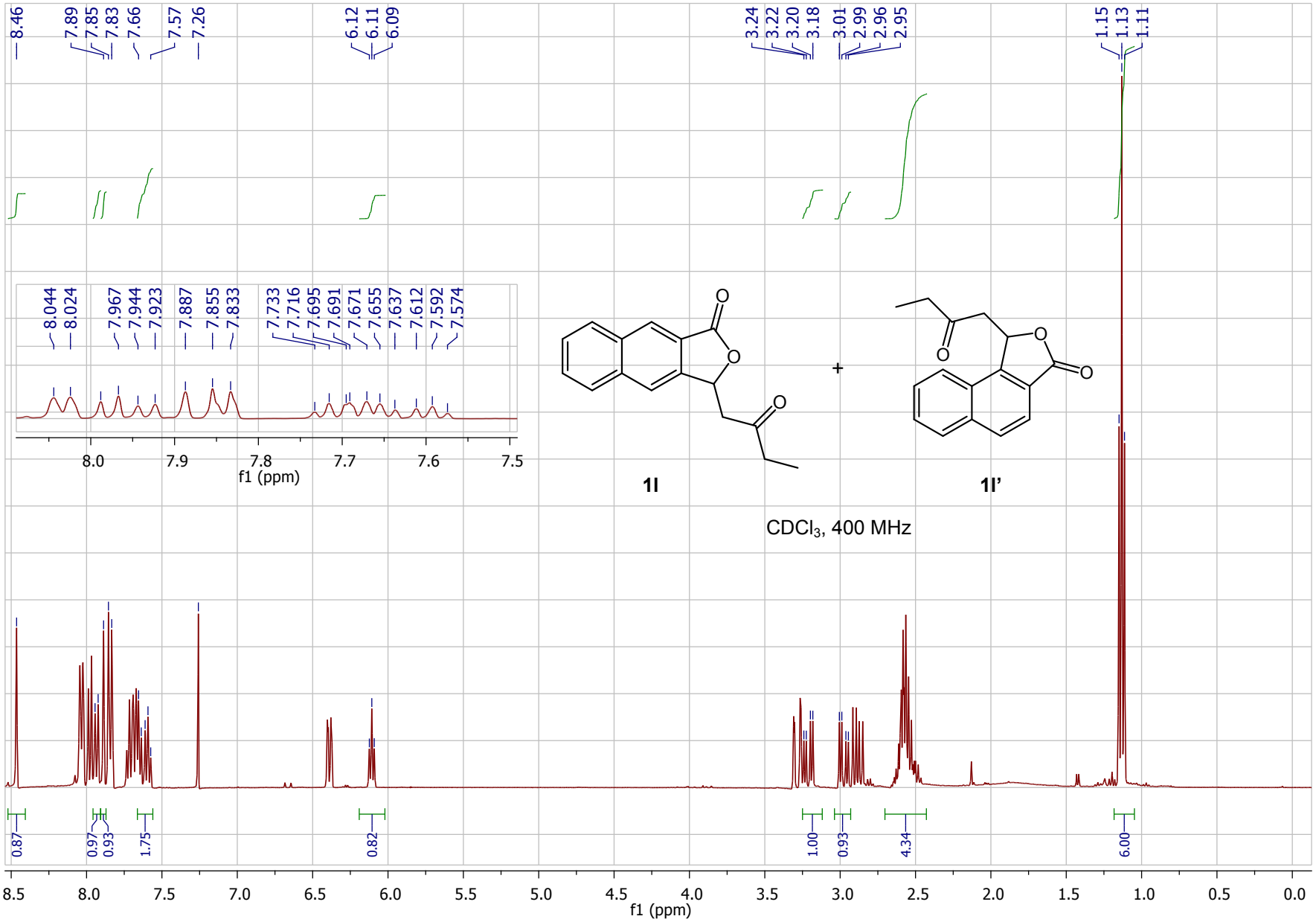

206.34
168.95
149.31
146.74
138.59
128.09
127.77
127.66
126.53
125.09
123.51
119.81
76.27
76.02
75.88
75.77
45.99
35.83
6.52
O
O
O
1i
CDCl3, 125 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

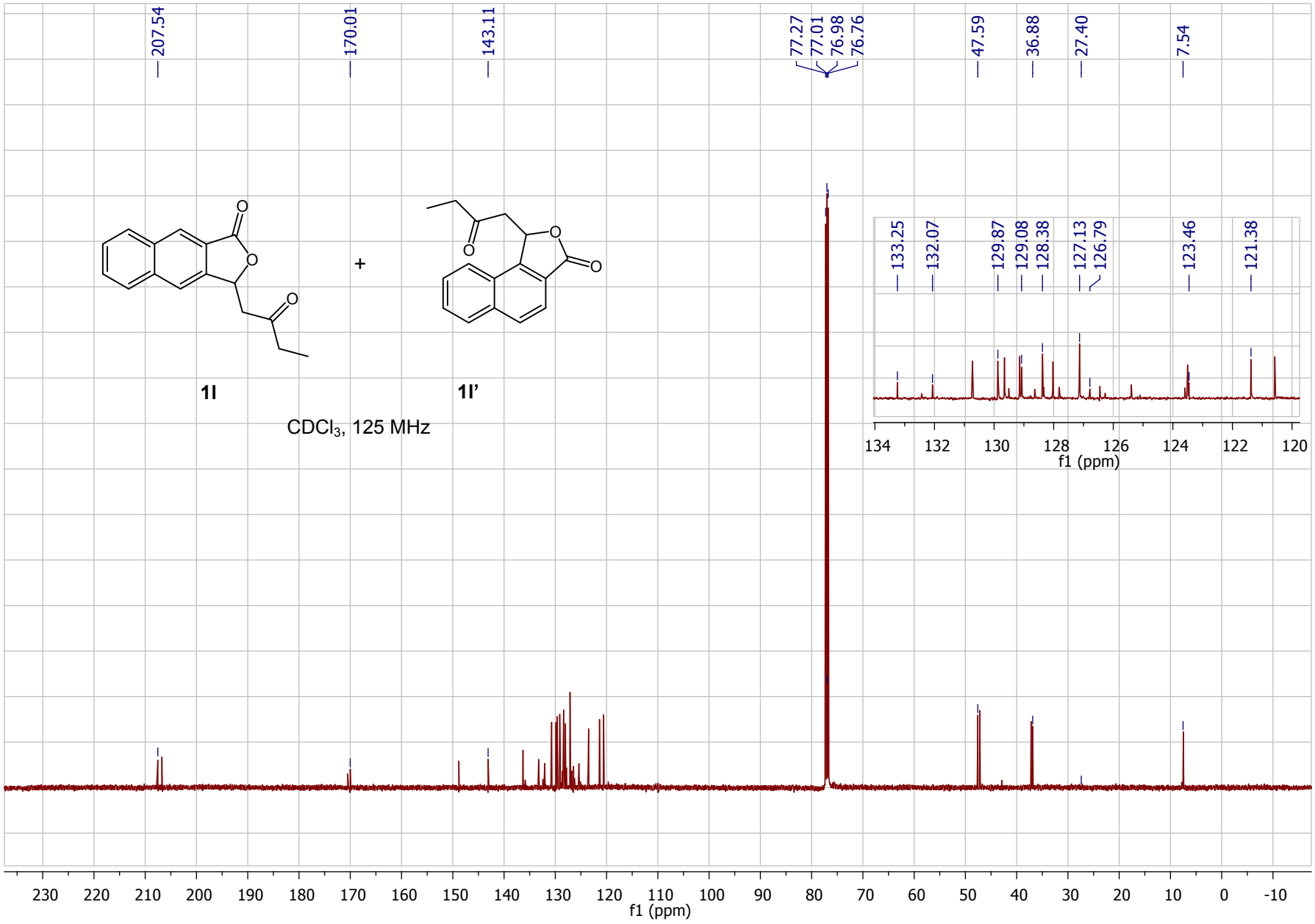

7.90
7.89
7.88
7.87
7.26
5.92
5.91
5.89
3.20
3.19
3.16
3.15
2.88
2.87
2.84
2.83
1.66
1.13
1.12
1.11
1.10
7.249
7.248
7.244
7.243
7.231
7.227
7.214
7.213
7.210
7.209
7.193
7.192
7.191
7.189
7.187
7.186
7.177
7.176
7.175
7.173
7.172
7.170
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.17
7.16
f1 (ppm)
2.608
2.593
2.578
2.571
2.564
2.557
2.542
2.534
2.528
2.519
2.505
2.498
2.490
2.483
2.469
2.454
2.70
2.60
2.50
2.40
f1 (ppm)
O
O
O
F
1j
CDCl3, 500 MHz
0.94
0.97
0.92
0.94
1.04
1.04
2.03
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

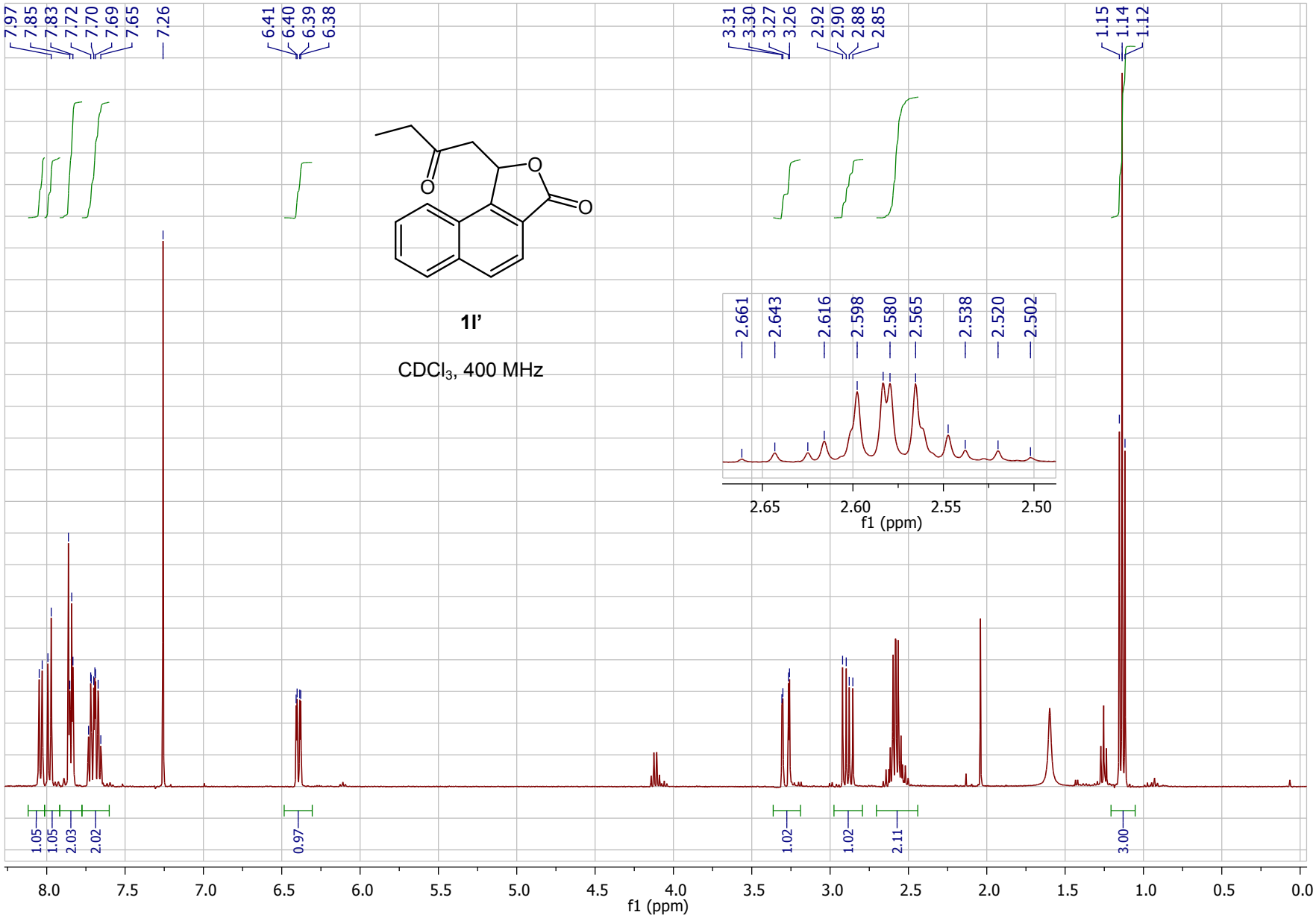

207.17
168.86
167.63
165.59
152.32
152.24
128.17
128.09
121.86
117.57
110.16
110.00
109.97
77.27
77.01
76.76
76.25
76.23
46.67
36.73
7.49
O
O
O
F
1j
CDCl3, 125 MHz
117.76
117.57
117.8
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

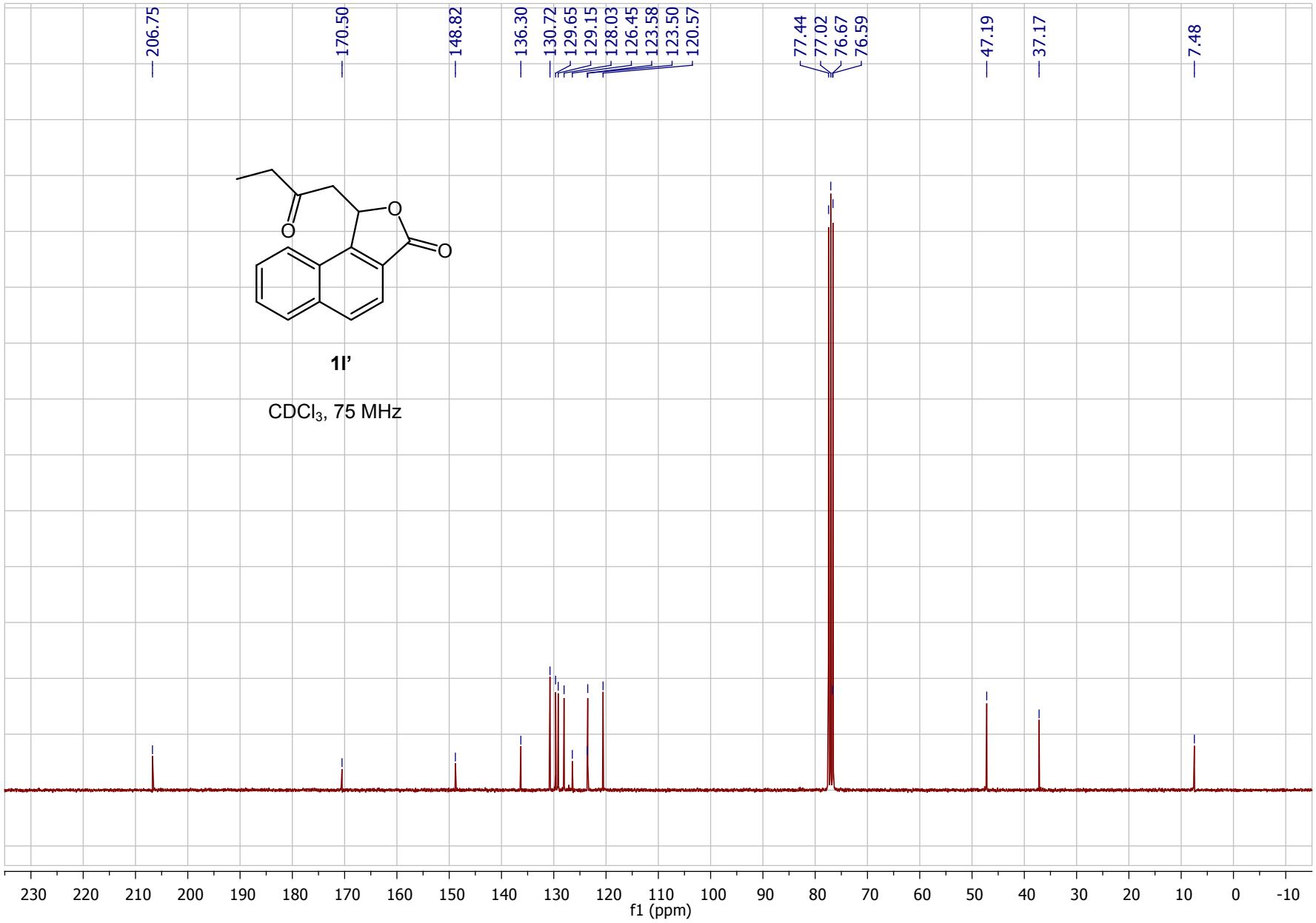

7.90
7.89
7.62
7.60
7.26
5.91
5.90
5.88
3.17
3.15
3.13
3.11
2.89
2.87
2.84
2.83
1.58
1.25
1.14
1.12
1.10
2.615
2.597
2.578
2.570
2.552
2.544
2.533
2.526
2.514
2.508
2.499
2.489
2.481
2.462
2.444
I
O
O
O
1k
CDCl3, 500 MHz
1.88
0.94
0.91
1.03
1.08
2.10
3.00
f1 (ppm)
f1 (ppm)

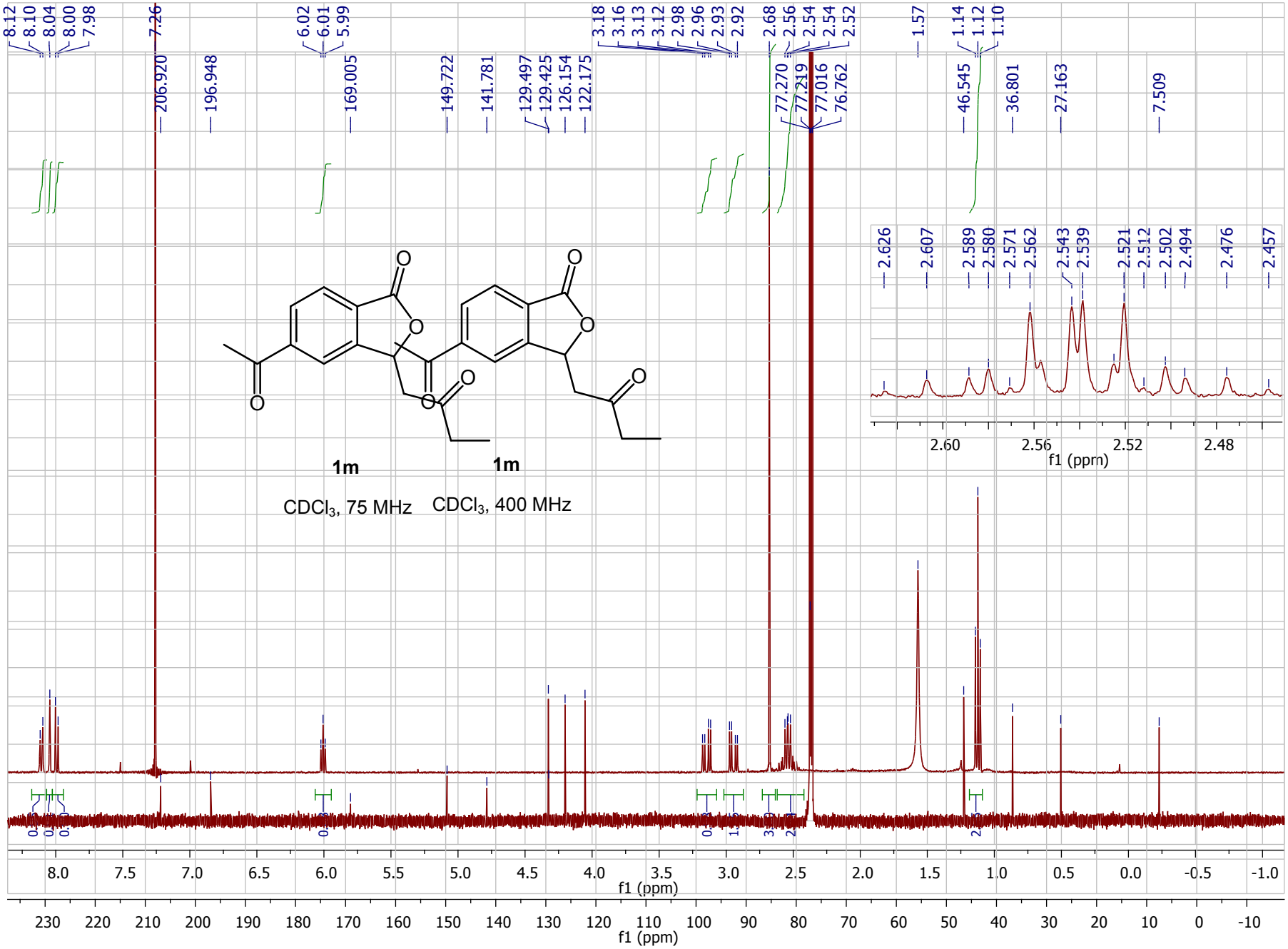

206.05
168.32
150.12
137.90
130.93
125.92
124.38
101.20
76.27
76.02
75.76
75.16
45.63
35.73
6.50
O
O
O
I
1k
CDCl3, 125 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

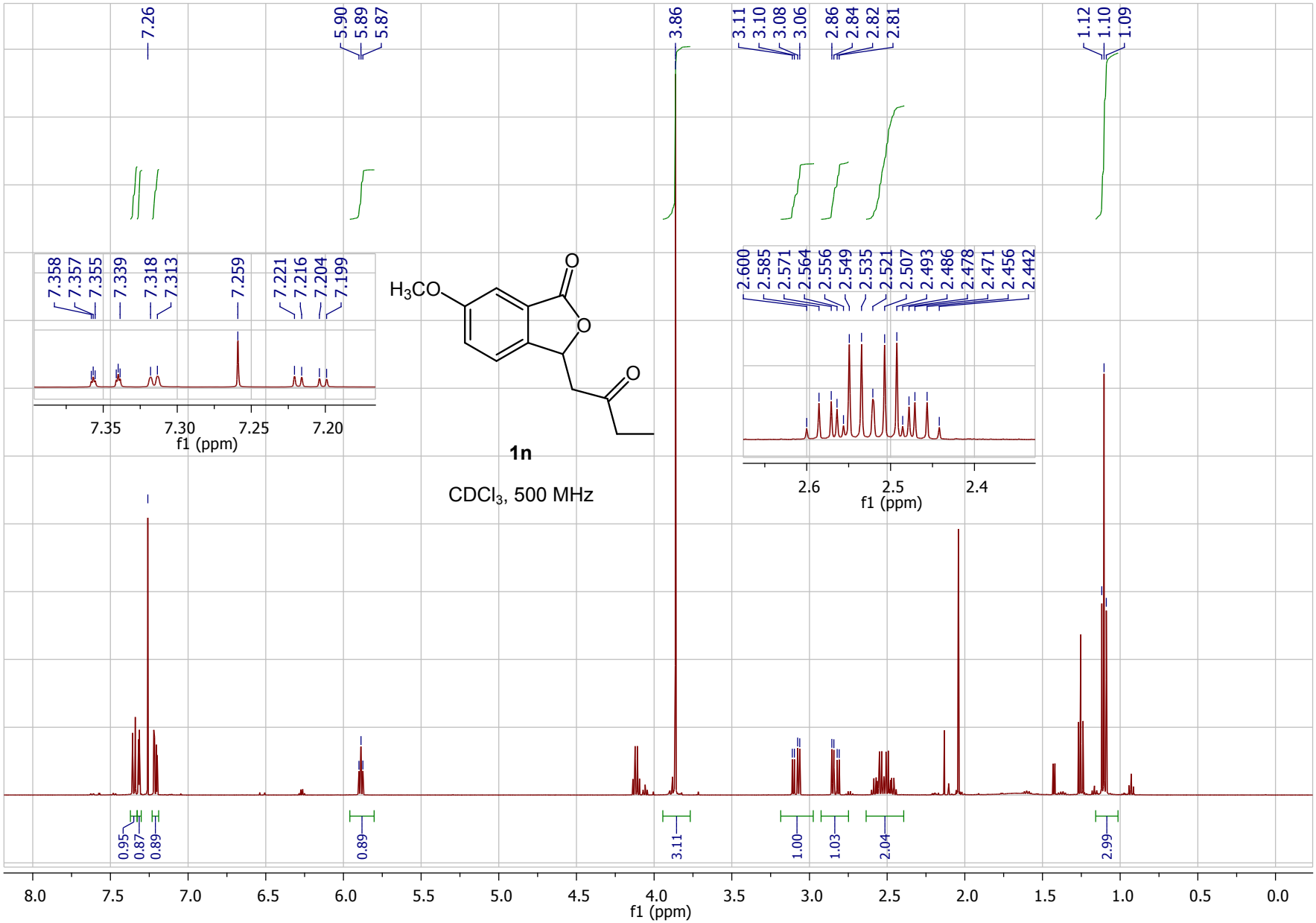

8.46
7.89
7.85
7.83
7.66
7.57
7.26
6.12
6.11
6.09
3.24
3.22
3.20
3.18
3.01
2.99
2.96
2.95
1.15
1.13
1.11
8.044
8.024
7.967
7.944
7.923
7.887
7.855
7.833
7.733
7.716
7.695
7.691
7.671
7.655
7.637
7.612
7.592
7.574
8.0
7.9
7.8
7.7
7.6
7.5
f1 (ppm)
O
O
O
+
O
O
O
1l
1l'
CDCl3, 400 MHz
0.87
0.97
0.93
1.75
0.82
1.00
0.93
4.34
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

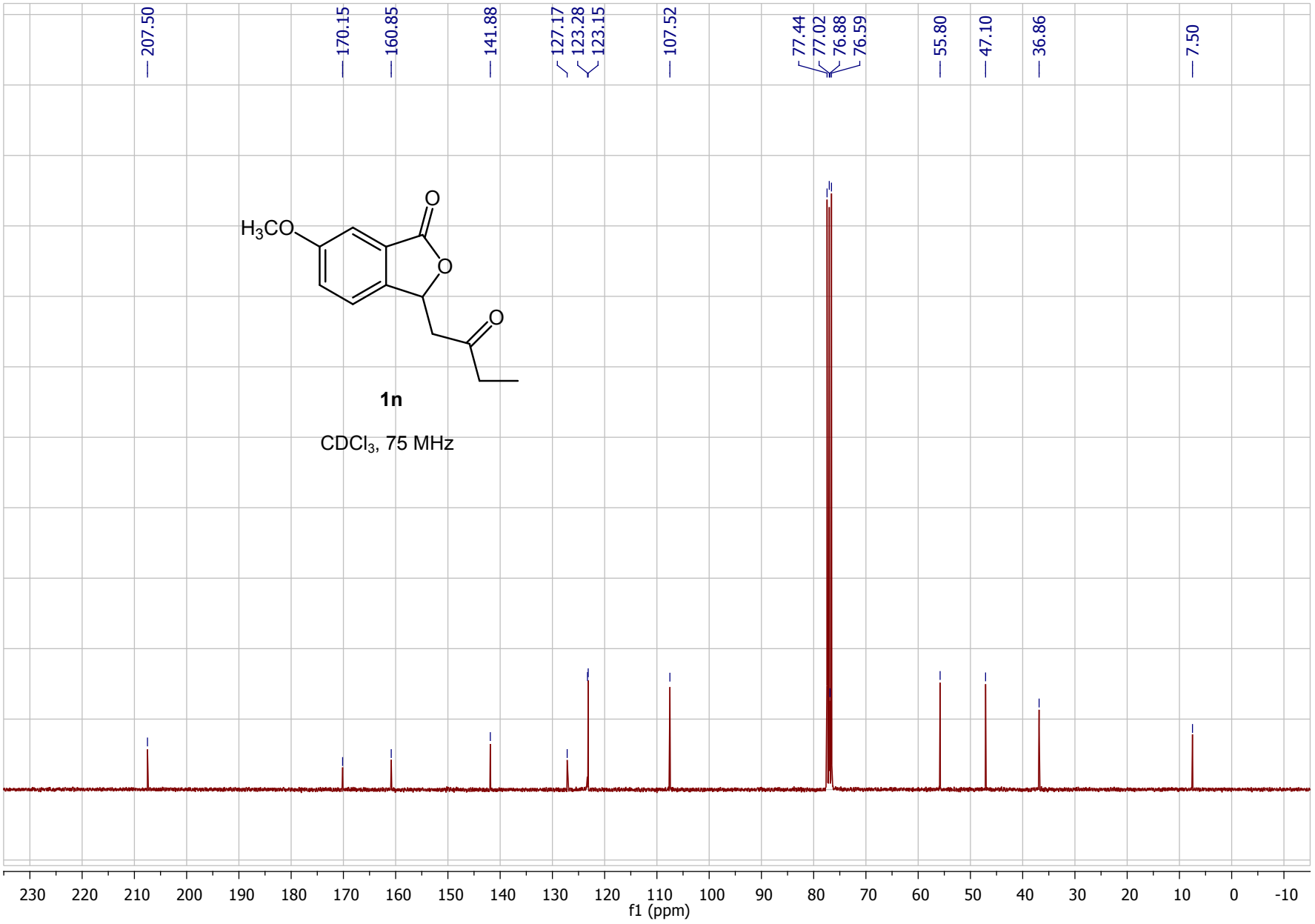

207.54
170.01
143.11
77.27
77.01
76.98
76.76
47.59
36.88
27.40
7.54
133.25
132.07
129.87
129.08
128.38
127.13
126.79
123.46
121.38
1l
1l'
+
CDCl3, 125 MHz
f1 (ppm)
f1 (ppm)

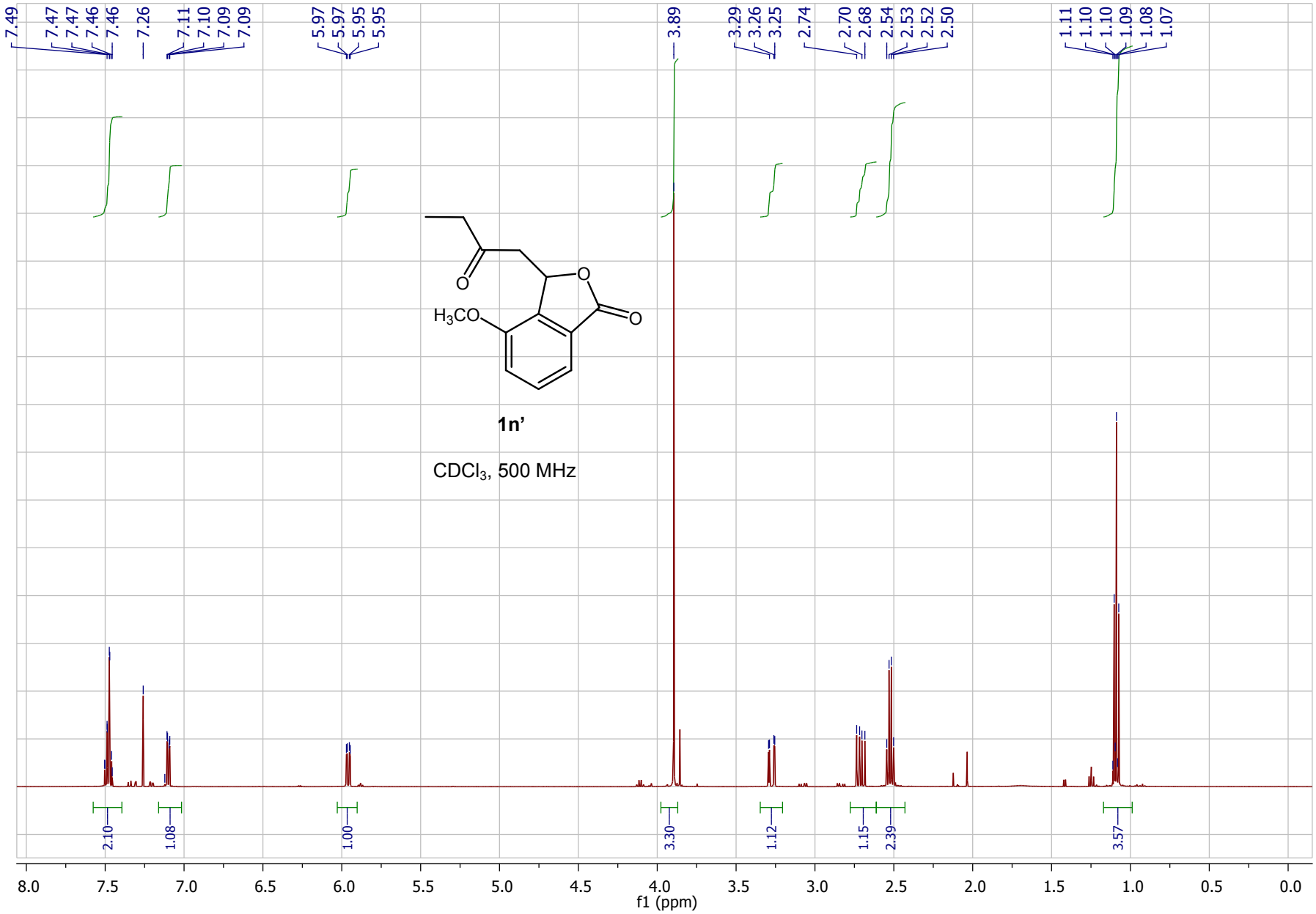

7.97
7.85
7.83
7.72
7.70
7.69
7.65
7.26
6.41
6.40
6.39
6.38
3.31
3.30
3.27
3.26
2.92
2.90
2.88
2.85
1.15
1.14
1.12
1l'
CDCl3, 400 MHz
2.661
2.643
2.616
2.598
2.580
2.565
2.538
2.520
2.502
2.65
2.60
2.55
2.50
f1 (ppm)
1.05
1.05
2.03
2.02
0.97
1.02
1.02
2.11
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

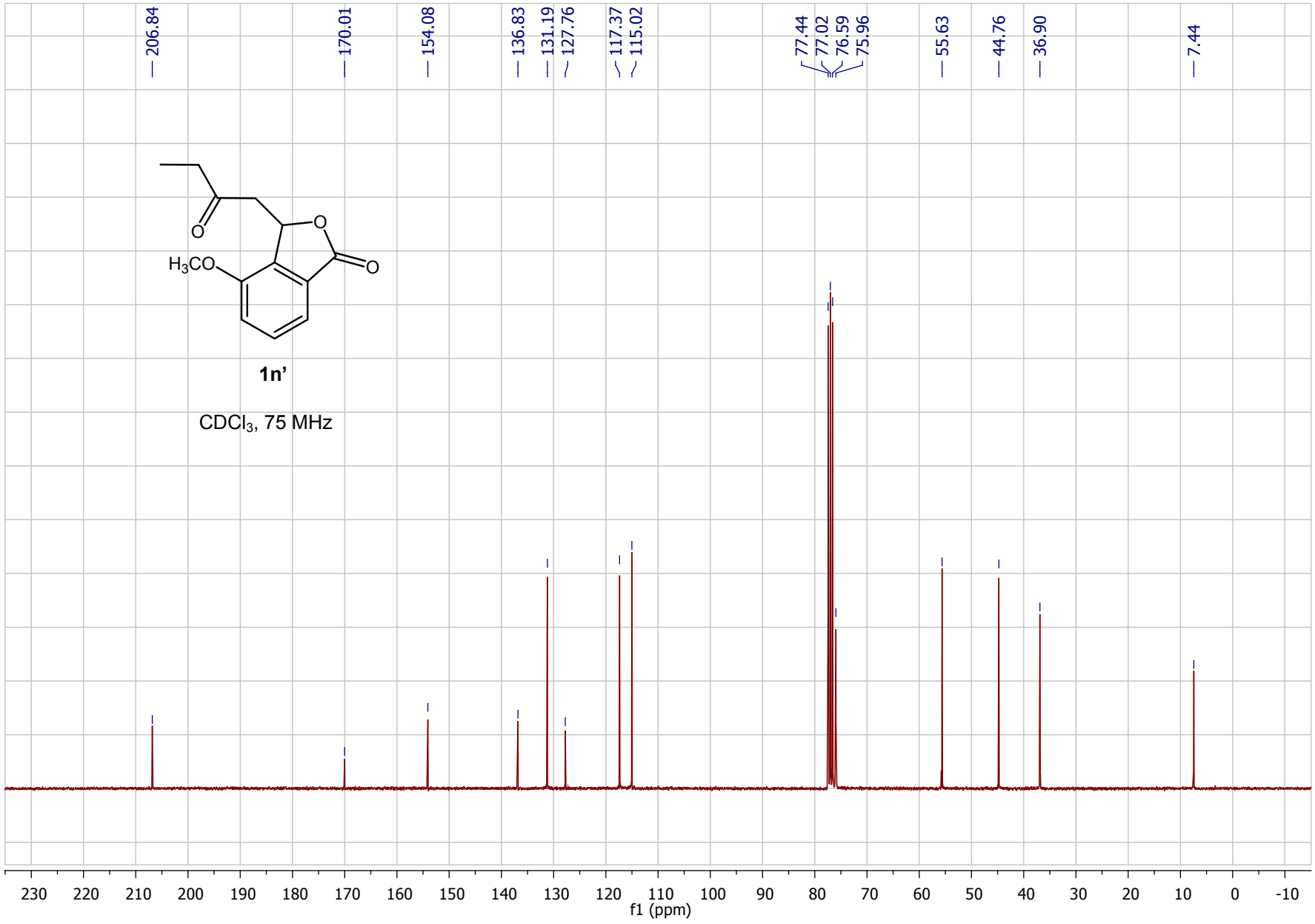

206.75
170.50
148.82
136.30
130.72
129.65
129.15
128.03
126.45
123.58
123.50
120.57
77.44
77.02
76.67
76.59
47.19
37.17
7.48
O
O
O
1l’
CDCl3, 75 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

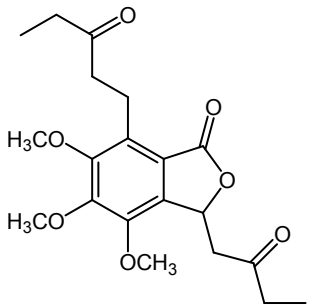

8.12
8.10
8.04
8.00
7.98
7.26
6.02
6.01
5.99
3.18
3.16
3.13
3.12
2.98
2.96
2.93
2.92
2.68
2.56
2.54
2.54
2.52
1.57
1.14
1.12
1.10
206.920
196.948
169.005
149.722
141.781
129.497
129.425
126.154
122.175
77.270
77.219
77.016
76.762
46.545
36.801
27.163
7.509
2.626
2.607
2.589
2.580
2.571
2.562
2.543
2.539
2.521
2.512
2.502
2.494
2.476
2.457
2.60
2.56
2.52
2.48
f1 (ppm)
1m
1m
CDCl3, 75 MHz
CDCl3, 400 MHz
f1 (ppm)
f1 (ppm)


7.26
5.90
5.89
5.87
3.86
3.11
3.10
3.08
3.06
2.86
2.84
2.82
2.81
1.12
1.10
1.09
7.358
7.357
7.355
7.339
7.318
7.313
7.259
7.221
7.216
7.204
7.199
7.35
7.30
7.25
7.20
f1 (ppm)
2.600
2.585
2.571
2.564
2.556
2.549
2.535
2.521
2.507
2.493
2.486
2.478
2.471
2.456
2.442
2.6
2.5
2.4
f1 (ppm)
H3CO
O
O
O
1n
CDCl3, 500 MHz
0.95
0.87
0.89
0.89
3.11
1.00
1.03
2.04
2.99
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.50
170.15
160.85
141.88
127.17
123.28
123.15
107.52
77.44
77.02
76.88
76.59
55.80
47.10
36.86
7.50
H3CO
O
O
O
1n
CDCl3, 75 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

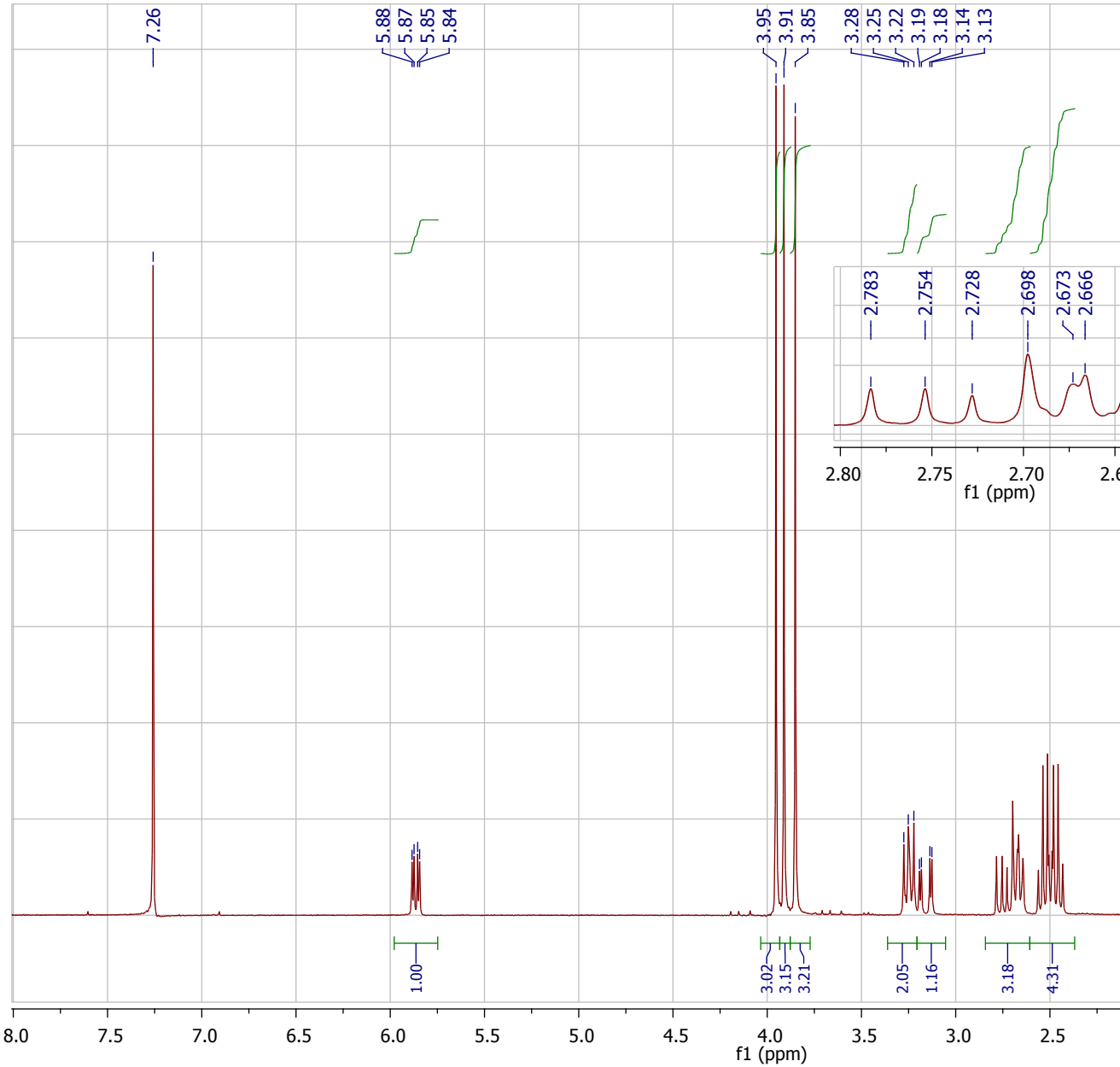

7.49
7.47
7.47
7.46
7.46
7.26
7.11
7.10
7.09
7.09
5.97
5.97
5.95
5.95
3.89
3.29
3.26
3.25
2.74
2.70
2.68
2.54
2.53
2.52
2.50
1.11
1.10
1.10
1.09
1.08
1.07
O
O
O
H3CO
1n'
CDCl3, 500 MHz
2.10
1.08
1.00
3.30
1.12
1.15
2.39
3.57
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

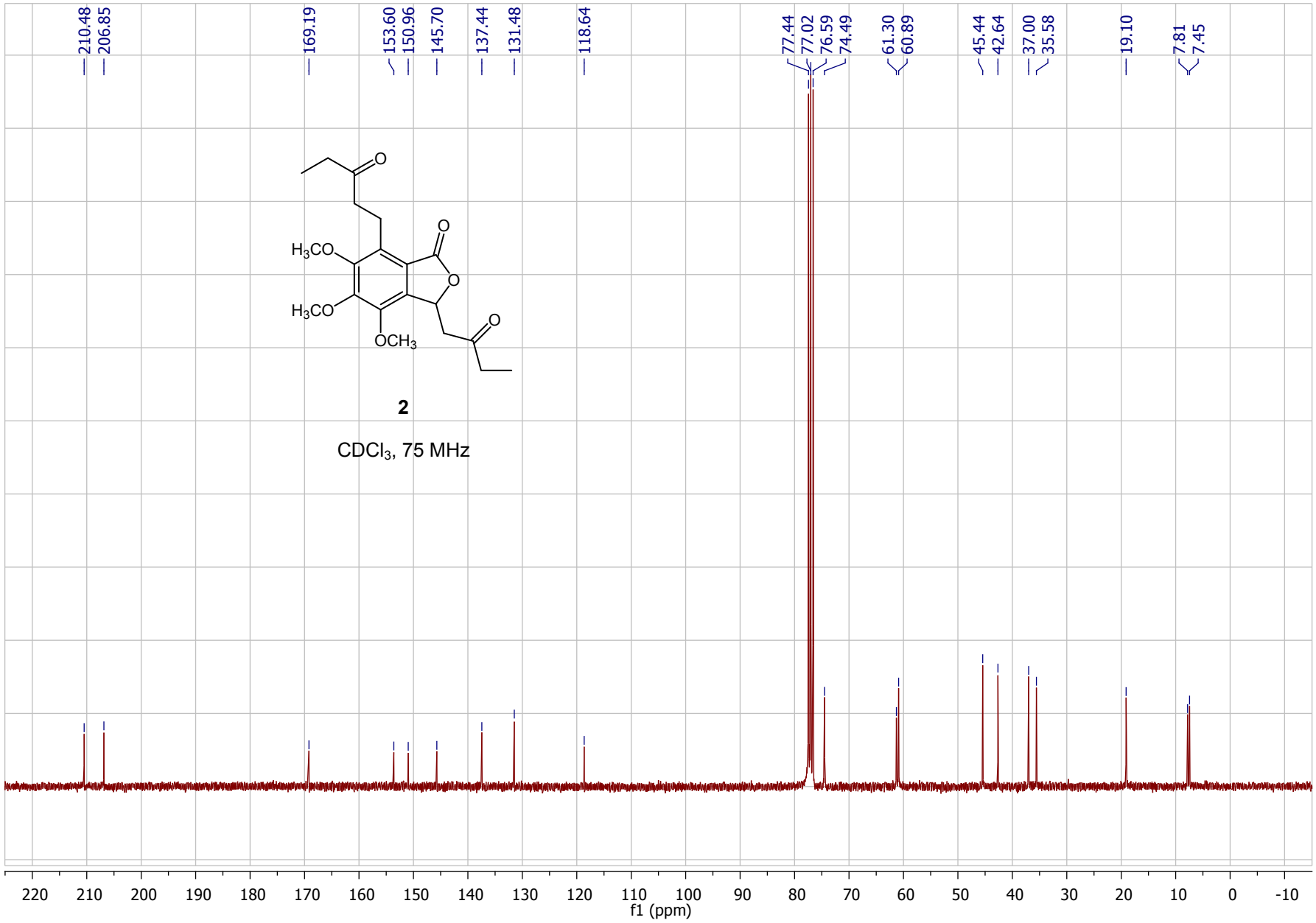

206.84
170.01
154.08
136.83
131.19
127.76
117.37
115.02
77.44
77.02
76.59
75.96
55.63
44.76
36.90
7.44
O
O
H3CO
O
1n'
CDCl3, 75 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

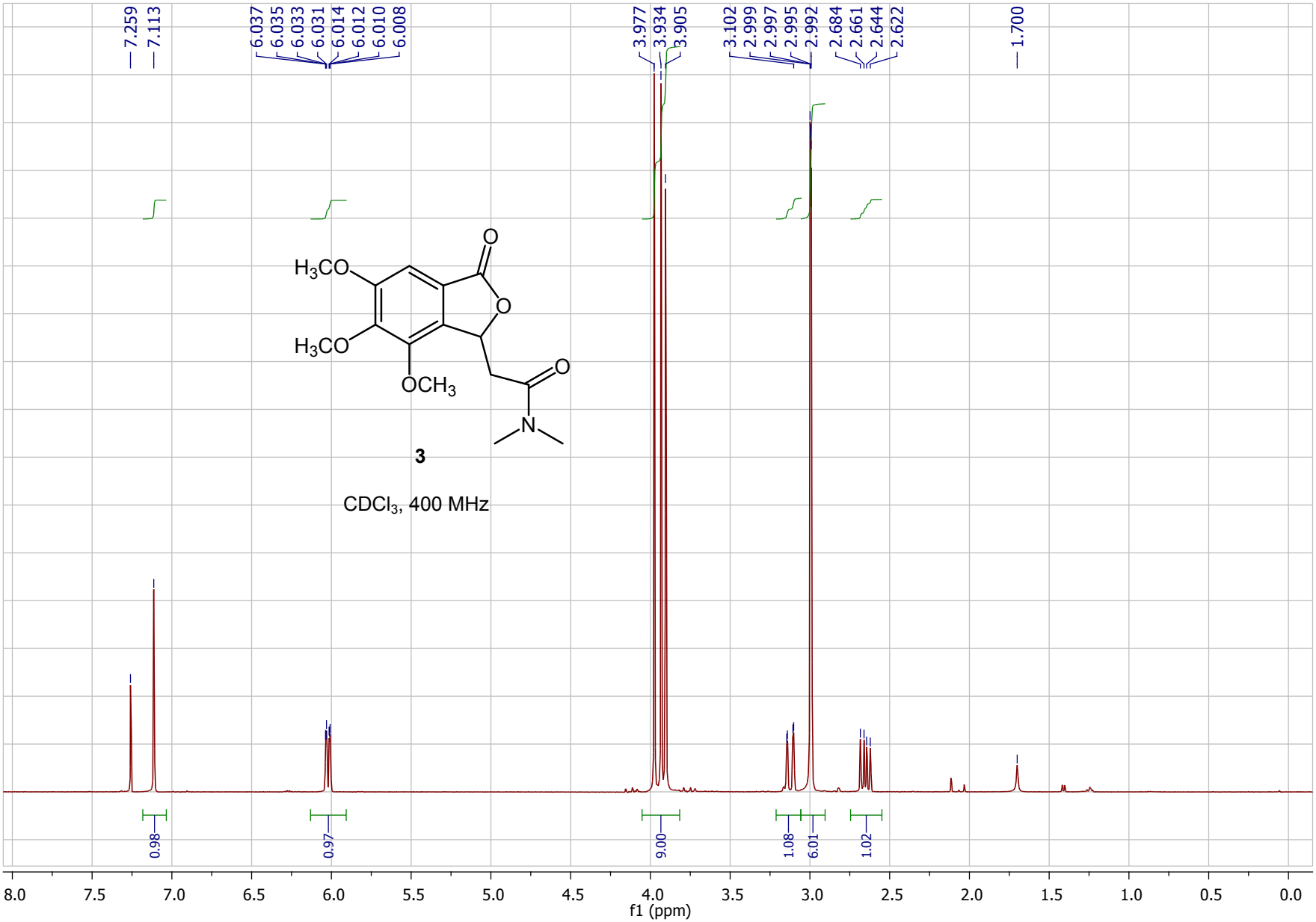


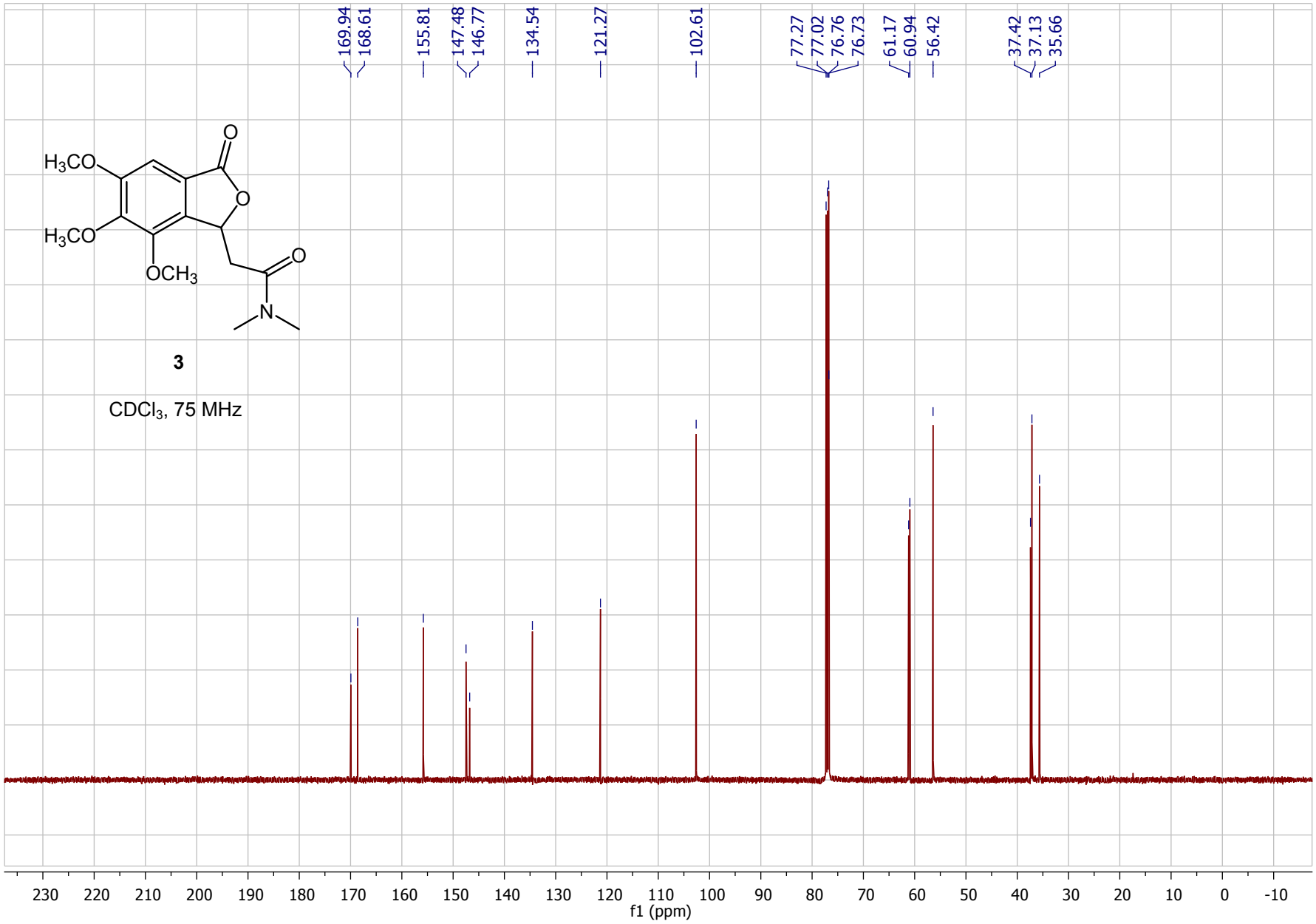
2

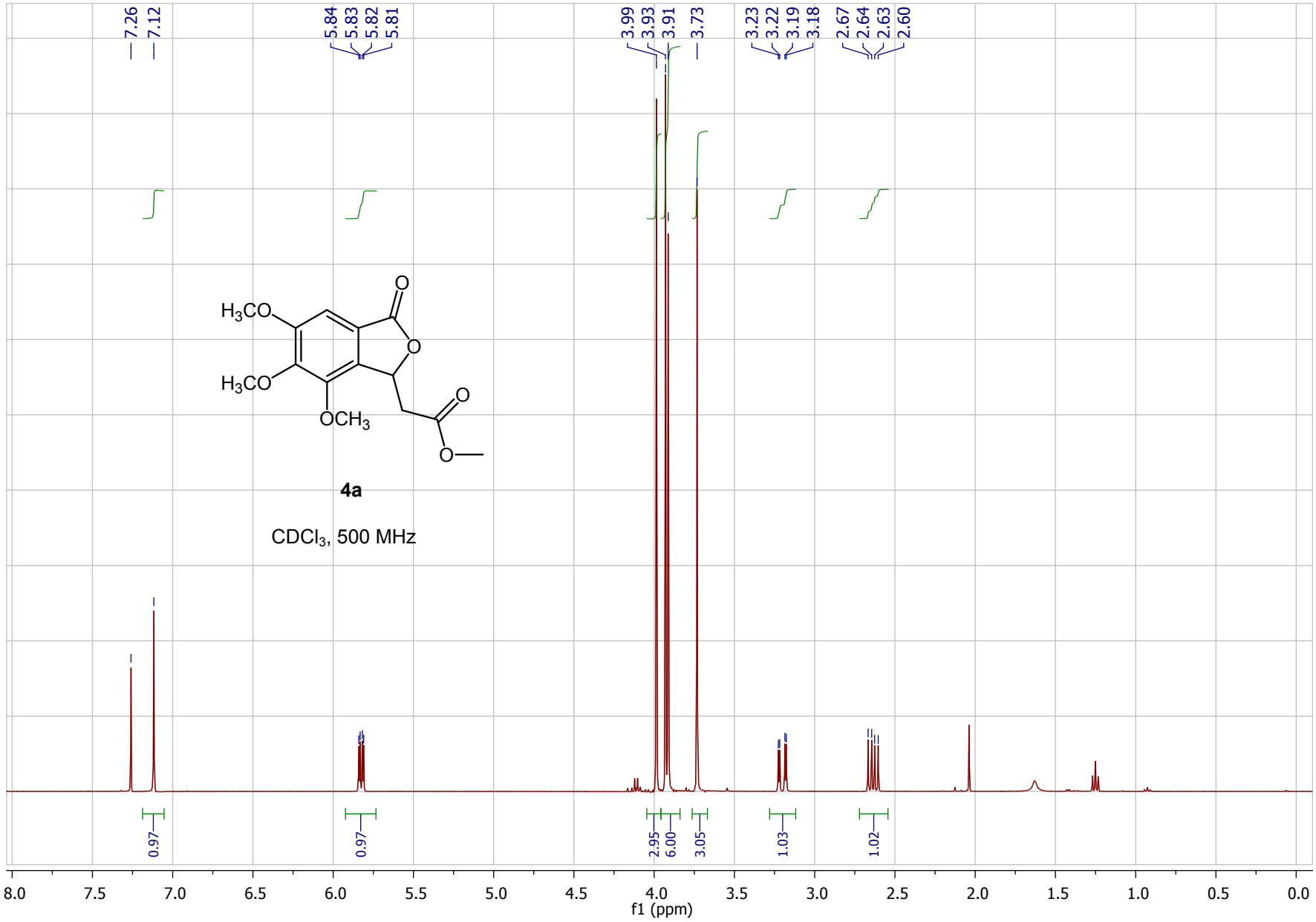
$CDCl_3$, 300 MHz

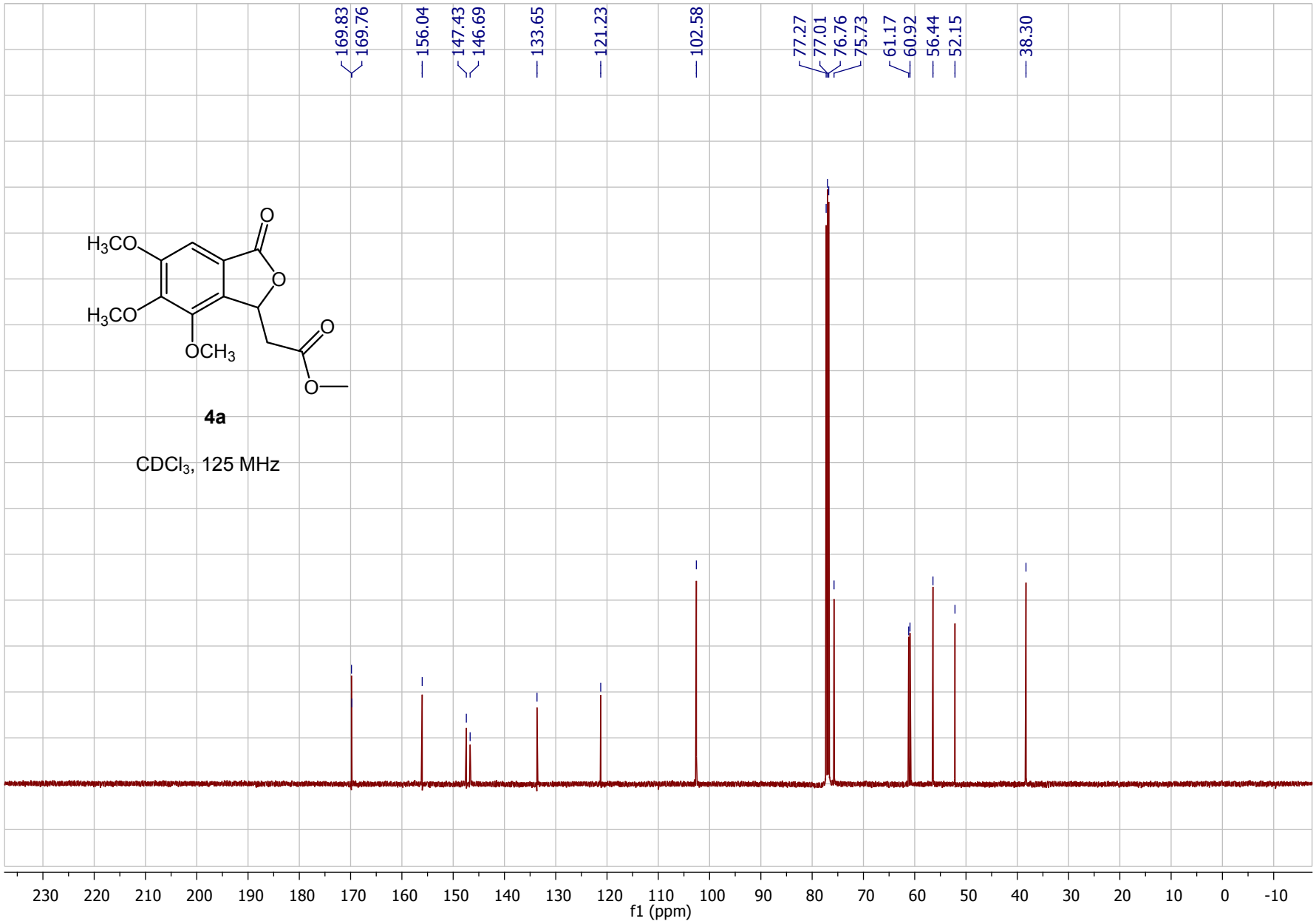


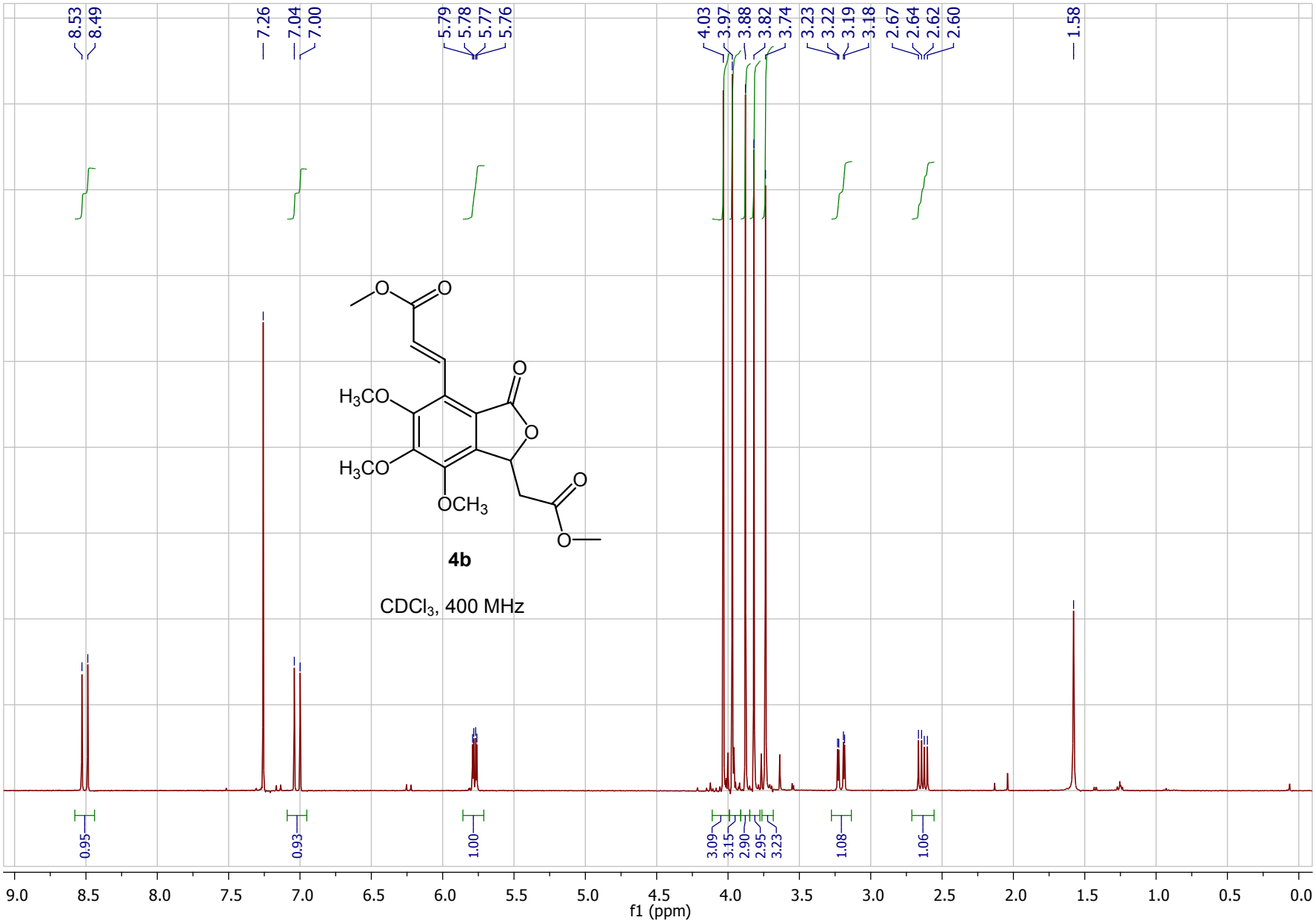

210.48
206.85
169.19
153.60
150.96
145.70
137.44
131.48
118.64
77.44
77.02
76.59
74.49
61.30
60.89
45.44
42.64
37.00
35.58
19.10
7.81
7.45
O
O
O
O
H3CO
H3CO
OCH3
2
CDCl3, 75 MHz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

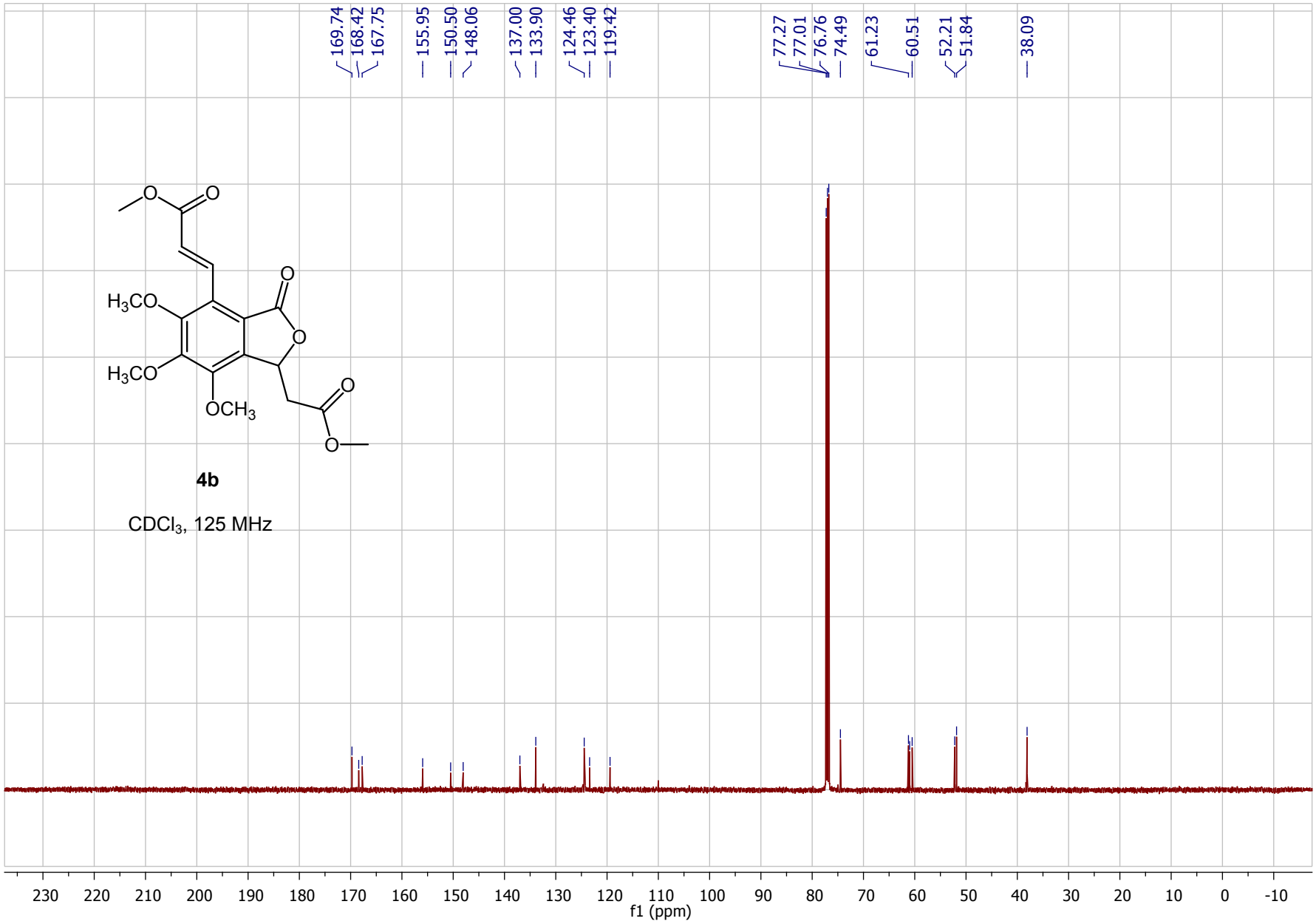

7.259
7.113
6.037
6.035
6.033
6.031
6.014
6.012
6.010
6.008
3.977
3.934
3.905
3.102
2.999
2.997
2.995
2.992
2.684
2.661
2.644
2.622
1.700
H3CO
H3CO
OCH3
O
O
O
N
3
CDCl3, 400 MHz
0.98
0.97
9.00
1.08
6.01
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

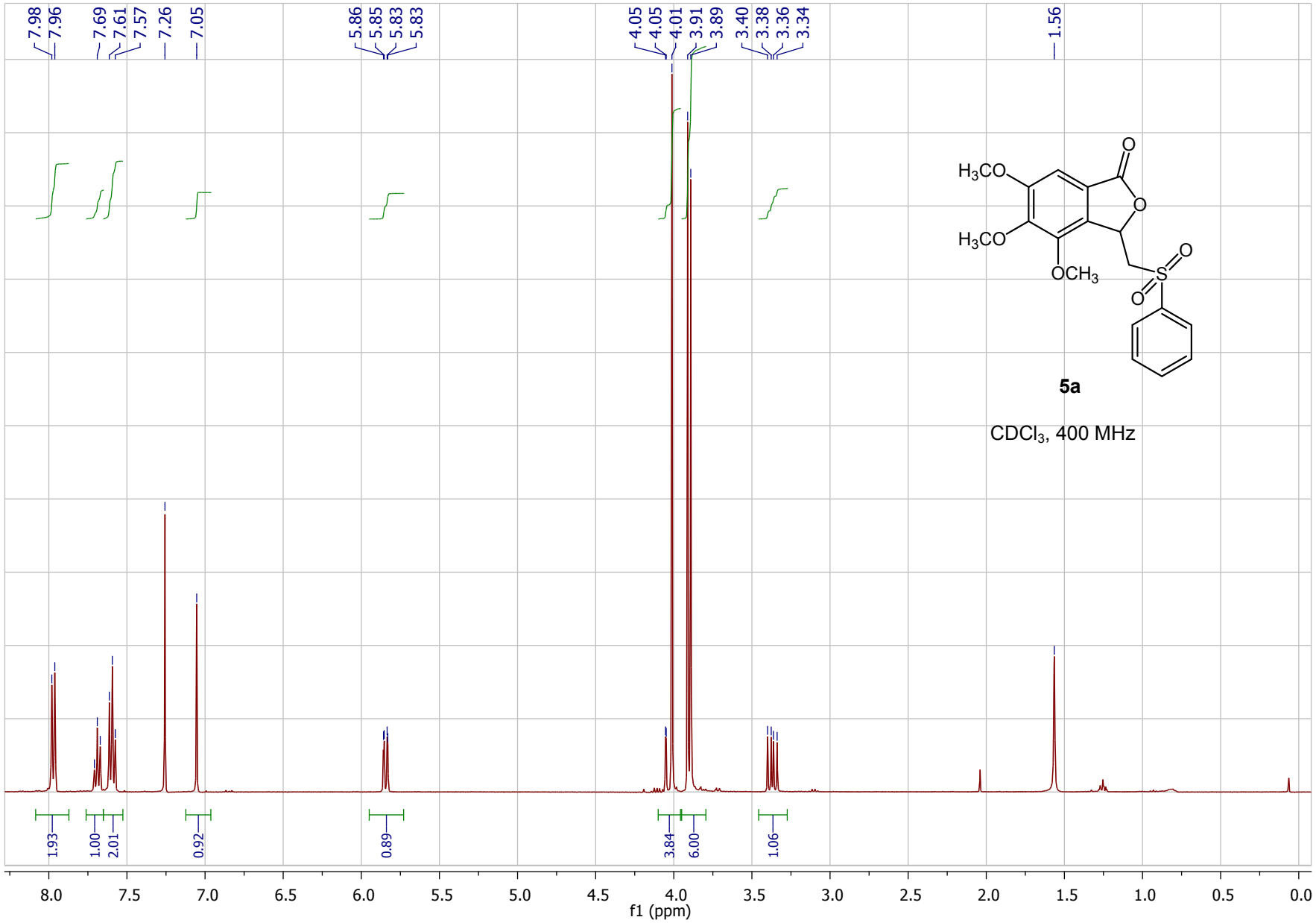

169.94
168.61
155.81
147.48
146.77
134.54
121.27
102.61
77.27
77.02
76.76
76.73
61.17
60.94
56.42
37.42
37.13
35.66
H3CO
H3CO
OCH3
O
O
O
N
3
CDCl3, 75 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

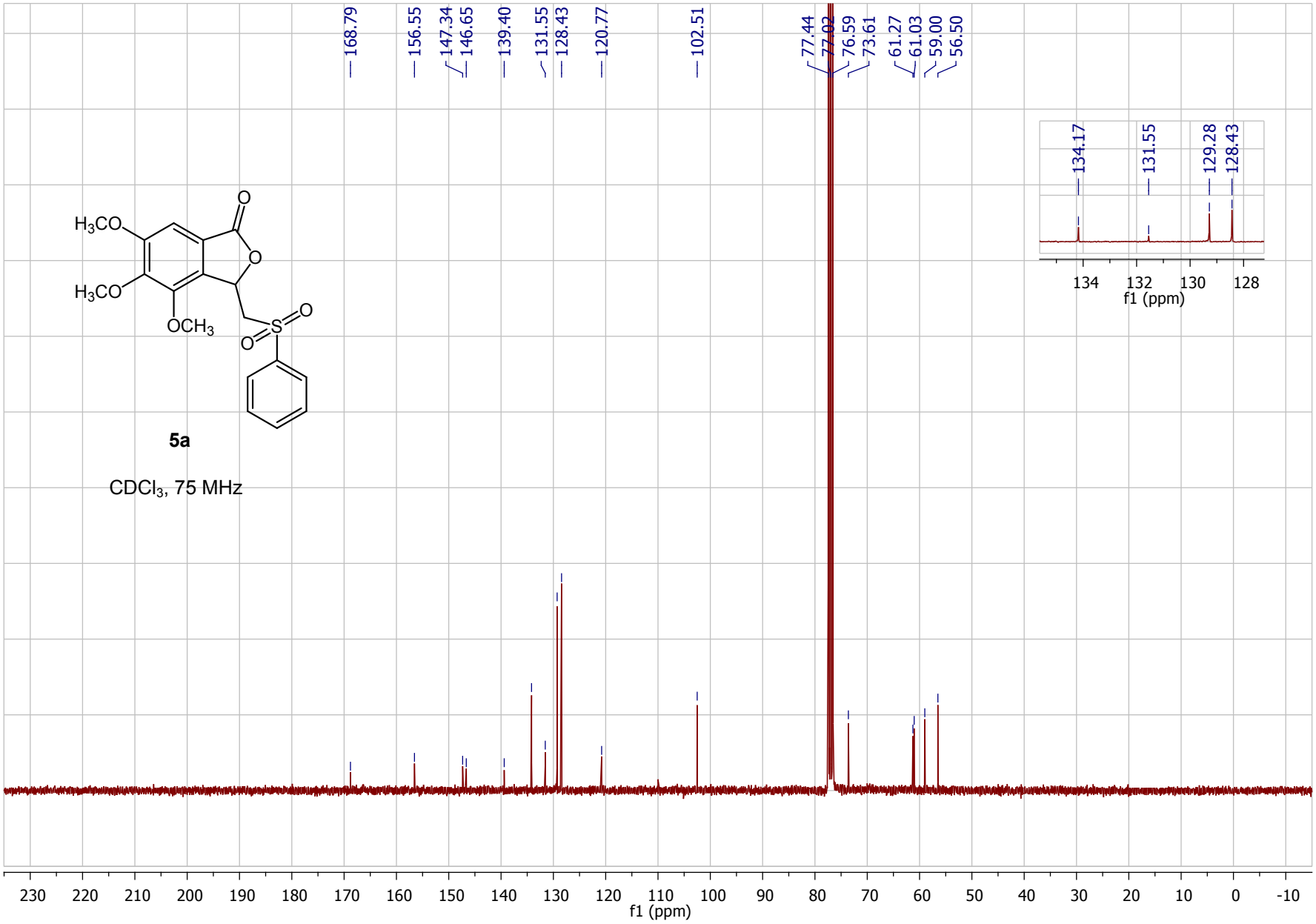

7.26
7.12
5.84
5.83
5.82
5.81
3.99
3.93
3.91
3.73
3.23
3.22
3.19
3.18
2.67
2.64
2.63
2.60
H3CO
H3CO
OCH3
O
O
O
O
4a
CDCl3, 500 MHz
0.97
0.97
2.95
6.00
3.05
1.03
1.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

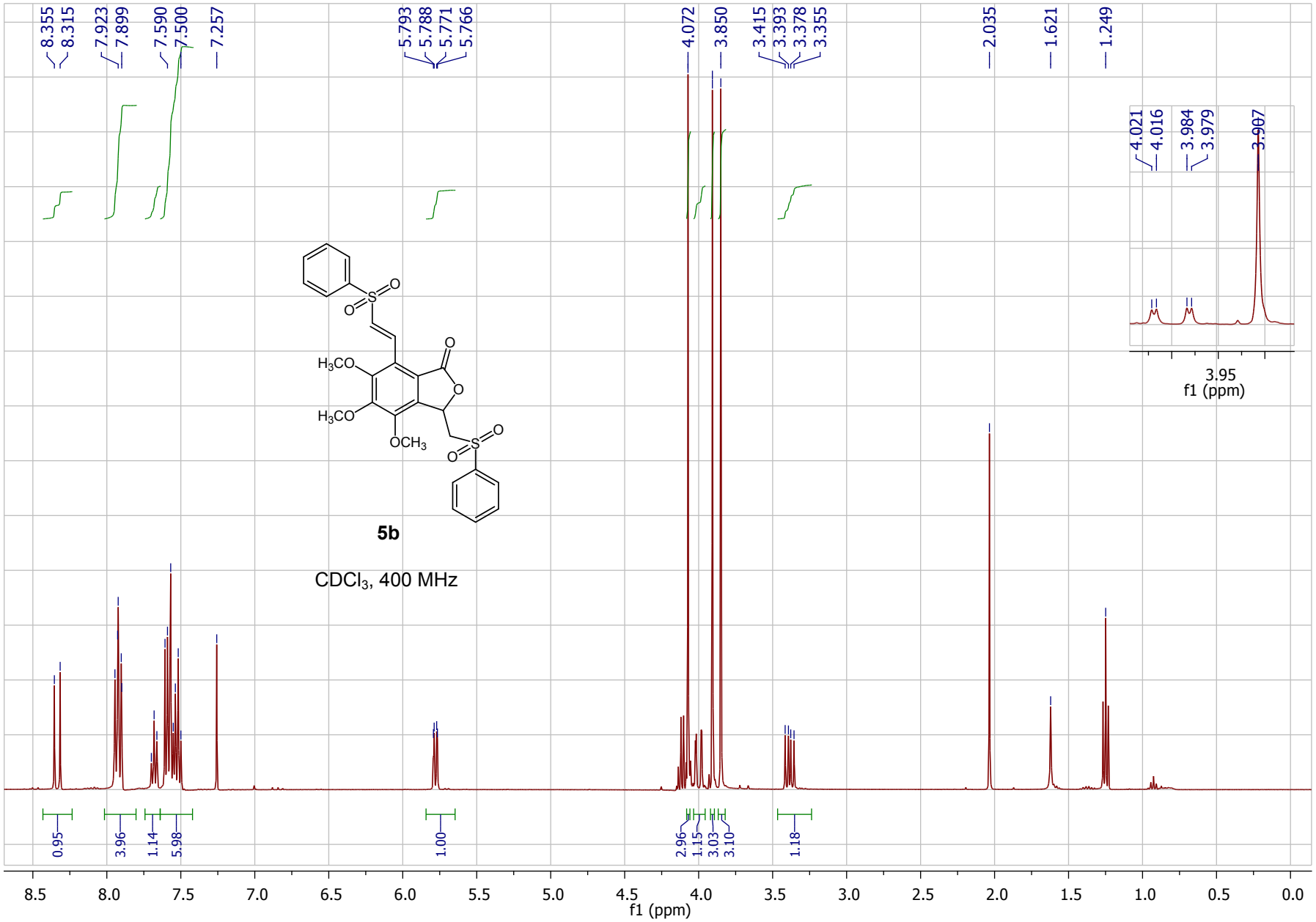

169.83
169.76
156.04
147.43
146.69
133.65
121.23
102.58
77.27
77.01
76.76
75.73
61.17
60.92
56.44
52.15
38.30
H3CO
H3CO
OCH3
O
O
O
O
4a
CDCl3, 125 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

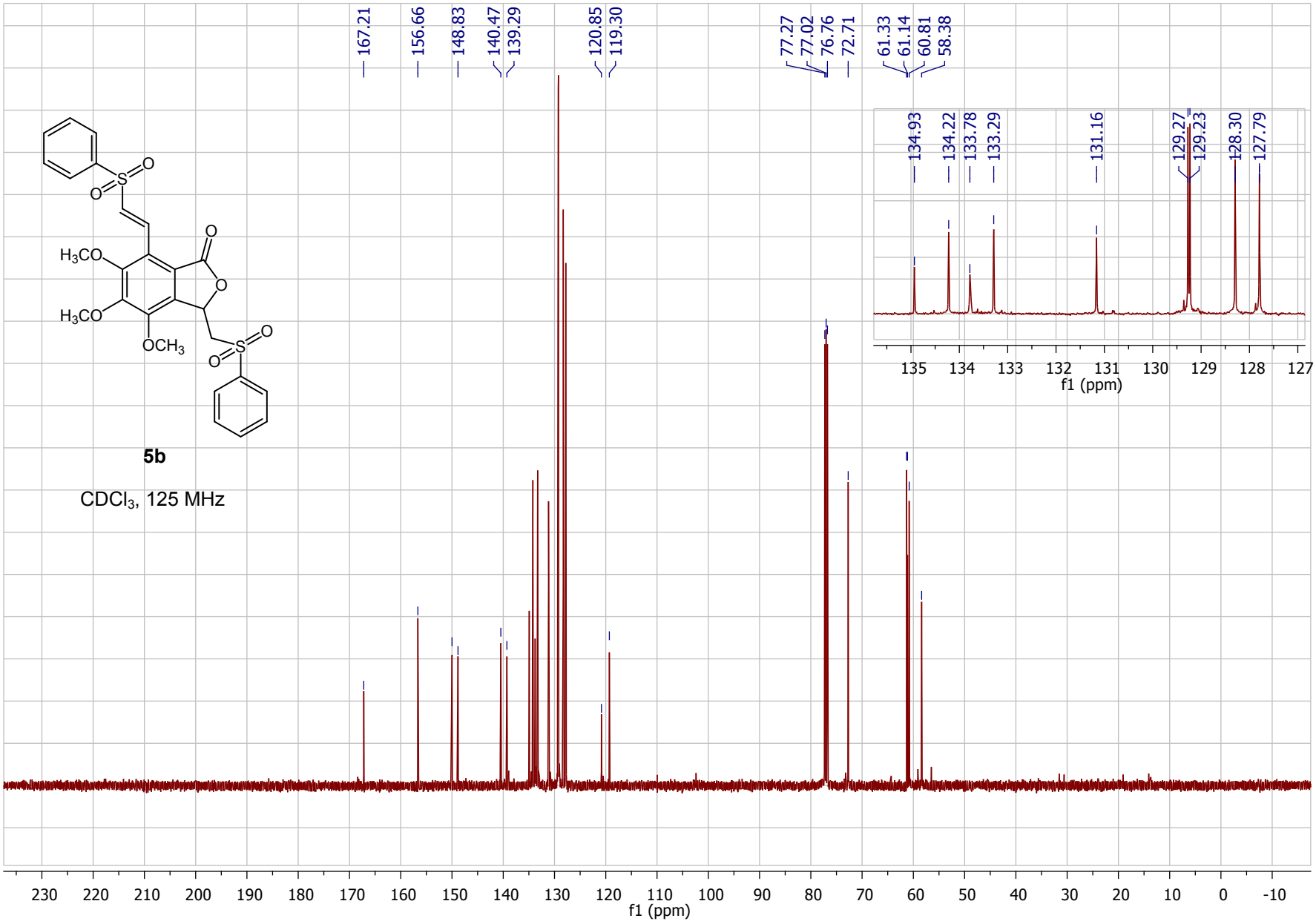

8.53
8.49
7.26
7.04
7.00
5.79
5.78
5.77
5.76
4.03
3.97
3.88
3.82
3.74
3.23
3.22
3.19
3.18
2.67
2.64
2.62
2.60
1.58
H3CO
H3CO
OCH3
O
O
O
O
O
O
4b
CDCl3, 400 MHz
0.95
0.93
1.00
3.09
3.15
2.90
2.95
3.23
1.08
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

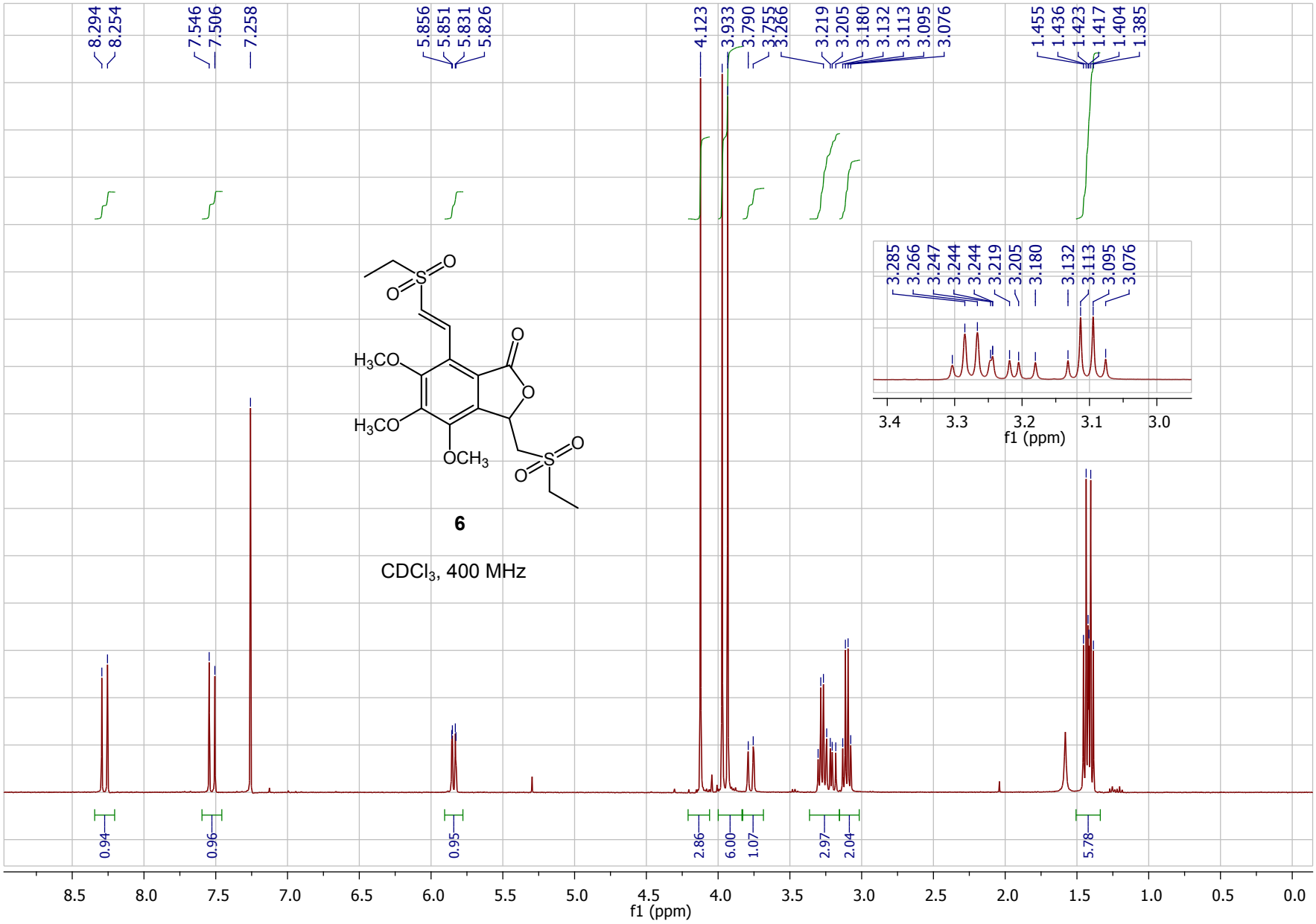

169.74
168.42
167.75
155.95
150.50
148.06
137.00
133.90
124.46
123.40
119.42
77.27
77.01
76.76
74.49
61.23
60.51
52.21
51.84
38.09
H3CO
H3CO
OCH3
4b
CDCl3, 125 MHz
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

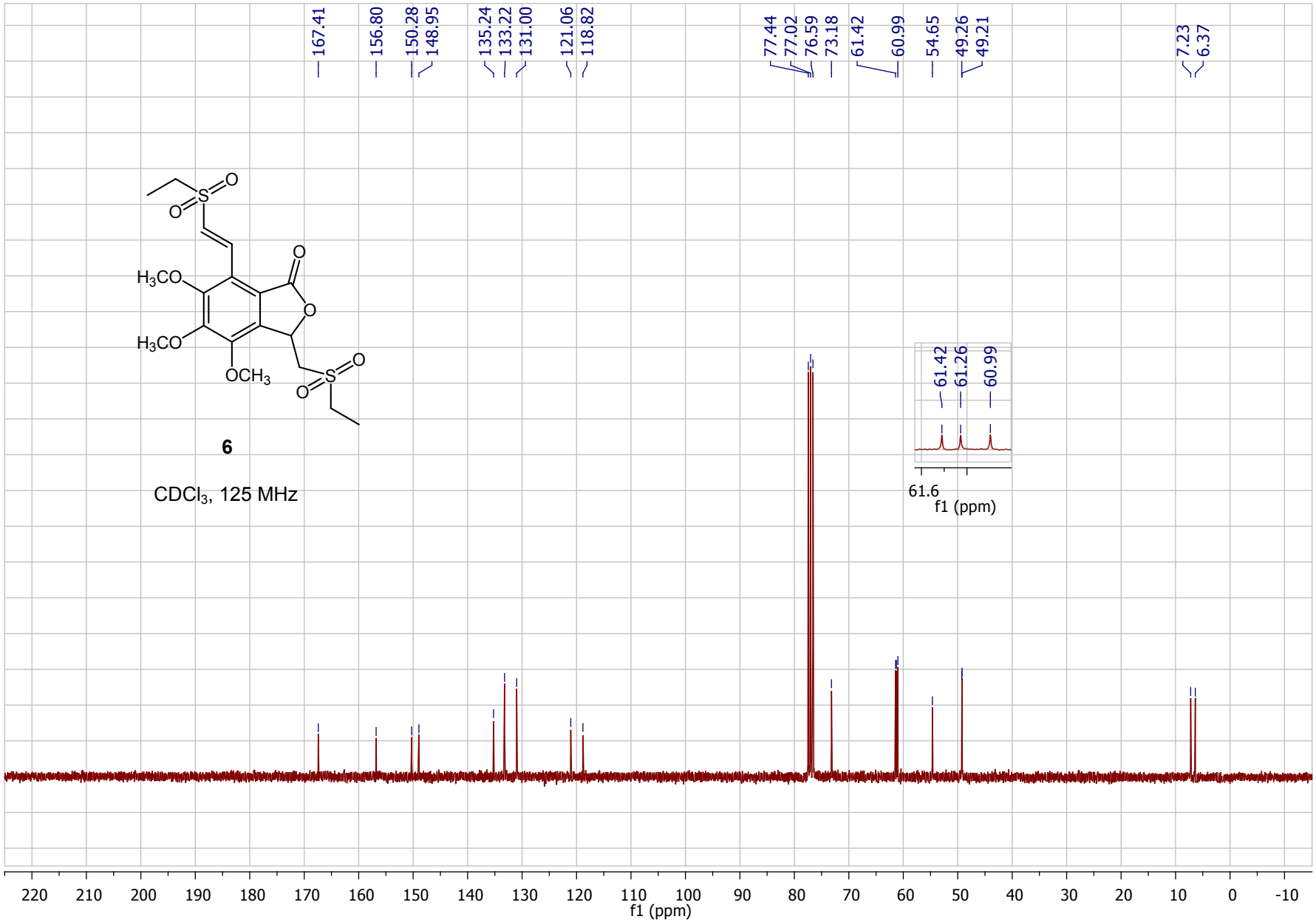

7.98
7.96
7.69
7.61
7.57
7.26
7.05
5.86
5.85
5.83
5.83
4.05
4.05
4.01
3.91
3.89
3.40
3.38
3.36
3.34
1.56
H3CO
H3CO
OCH3
O
O
S
O
O
5a
CDCl3, 400 MHz
1.93
1.00
2.01
0.92
0.89
3.84
6.00
1.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

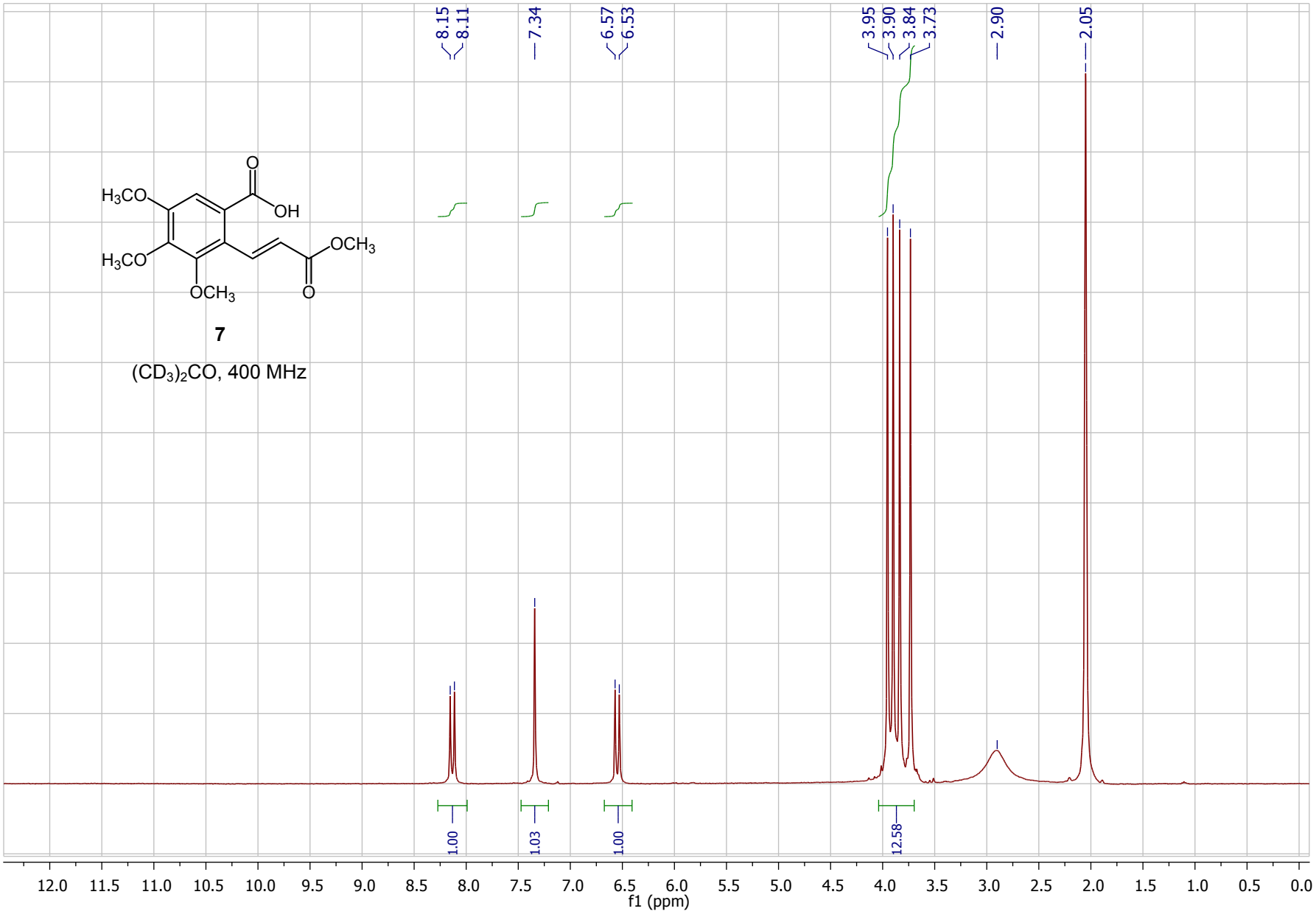

168.79
156.55
147.34
146.65
139.40
131.55
128.43
120.77
102.51
77.44
77.02
76.59
73.61
61.27
61.03
59.00
56.50
134.17
131.55
129.28
128.43
134
132
130
128
f1 (ppm)
H3CO
H3CO
OCH3
O
O
S
O
O
5a
CDCl3, 75 MHz
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

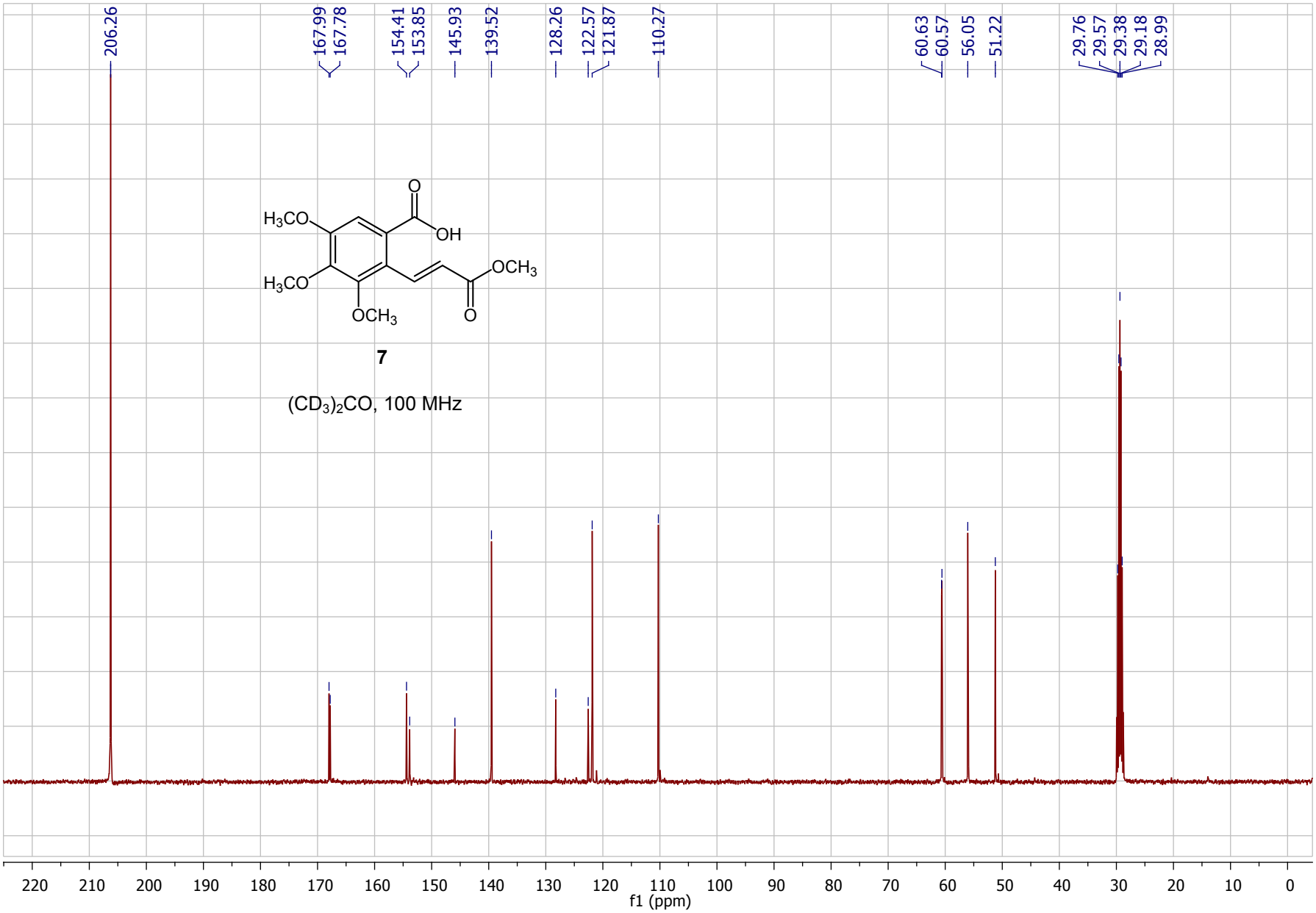

8.355
8.315
7.923
7.899
7.590
7.500
7.257
5.793
5.788
5.771
5.766
4.072
3.850
3.415
3.393
3.378
3.355
2.035
1.621
1.249
4.021
4.016
3.984
3.979
3.907
3.95
f1 (ppm)
H3CO
H3CO
OCH3
5b
CDCl3, 400 MHz
0.95
3.96
1.14
5.98
1.00
2.96
1.15
3.03
3.10
1.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.21
156.66
148.83
140.47
139.29
120.85
119.30
77.27
77.02
76.76
72.71
61.33
61.14
60.81
58.38
134.93
134.22
133.78
133.29
131.16
129.27
129.23
128.30
127.79
f1 (ppm)
f1 (ppm)
H3CO
H3CO
OCH3
5b
CDCl3, 125 MHz


8.294
8.254
7.546
7.506
7.258
5.856
5.851
5.831
5.826
4.123
3.933
3.790
3.755
3.266
3.219
3.205
3.180
3.132
3.113
3.095
3.076
1.455
1.436
1.423
1.417
1.404
1.385
3.285
3.266
3.247
3.244
3.244
3.219
3.205
3.180
3.132
3.113
3.095
3.076
3.4
3.3
3.2
3.1
3.0
f1 (ppm)
H3CO
H3CO
OCH3
O
S
O
O
O
O
S
O
O
6
CDCl3, 400 MHz
0.94
0.96
0.95
2.86
6.00
1.07
2.97
2.04
5.78
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

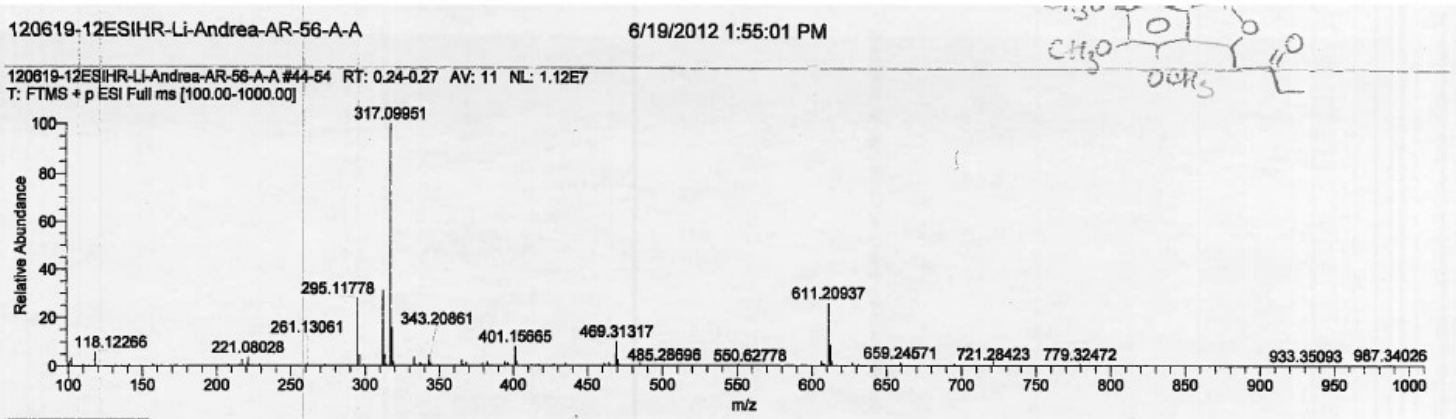

167.41
156.80
150.28
148.95
135.24
133.22
131.00
121.06
118.82
77.44
77.02
76.59
73.18
61.42
60.99
54.65
49.26
49.21
7.23
6.37
H3CO
H3CO
OCH3
6
CDCl3, 125 MHz
61.42
61.26
60.99
61.6
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

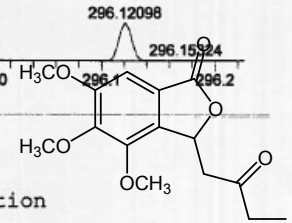

8.15
8.11
7.34
6.57
6.53
3.95
3.90
3.84
3.73
2.90
2.05
H3CO
OH
H3CO
OCH3
OCH3
O
O
7
(CD3)2CO, 400 MHz
1.00
1.03
1.00
12.58
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


206.26
167.99
167.78
154.41
153.85
145.93
139.52
128.26
122.57
121.87
110.27
60.63
60.57
56.05
51.22
29.76
29.57
29.38
29.18
28.99
H3CO
H3CO
OCH3
OH
OCH3
O
O
7
(CD3)2CO, 100 MHz
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

10. HRMS spectra of products

120619-12ESIHR-Li-Andrea-AR-56-A-A 6/19/2012 1:55:01 PM





1a

120619-12ESIHR-Li-Andrea-AR-56-A-A#44-54 RT: 0.24-0.27 AV: 11
T: FTMS + p ESI Full ms [100.00-1000.00]
m/z= 295.10125-295.13046

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
295.11778	3133532.3	100.00	23623.09	1.00	295.11761	0.17	6.5	$C_{15}H_{19}O_6$
					295.11895	-1.17	11.5	$C_{16}H_{15}O_2N_4$
					295.11627	1.51	7.0	$C_{13}H_{17}O_5N_3$
					295.12029	-2.51	11.0	$C_{18}H_{17}O_3N$
					295.11359	4.19	2.5	$C_{10}H_{19}O_8N_2$

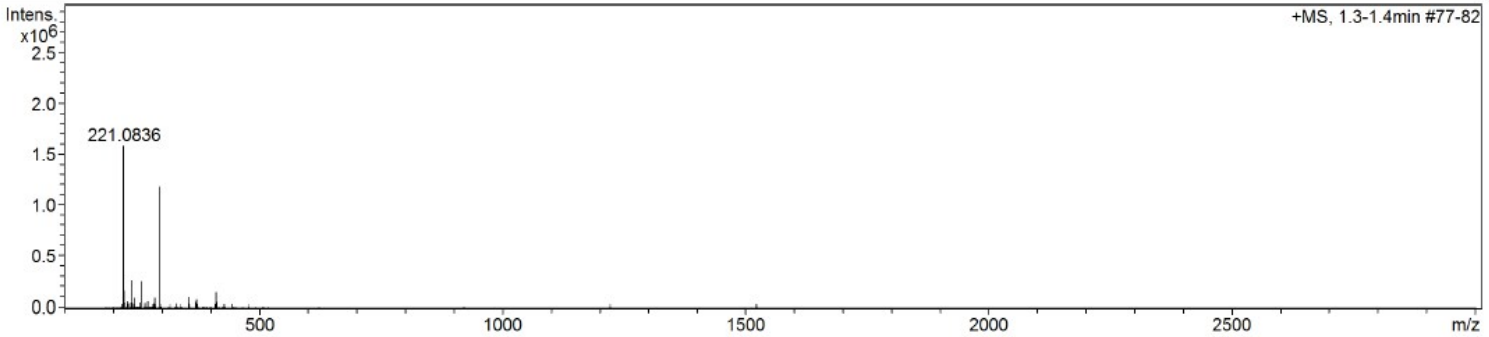
Mass Spectrum SmartFormula Report

Analysis Info

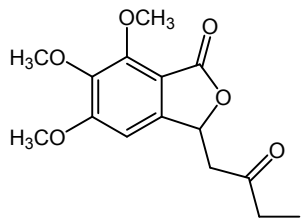
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-276-A +ve DIP.d	Acquisition Date	12/18/2012 2:25:21 PM
Method	APCI_Tune_pos_Mid_AW2.m	Operator	ADM
Sample Name	Testing DIP test 22012-12-17-Li-Renzetti AR-276-A +ve D	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	APCI	Ion Polarity	Positive	Set Nebulizer	5.0 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	150 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	1.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	1000.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
295.1185	1	C15H19O6	295.1176	-3.0	20.4	1	100.00	6.5	even	ok



1b

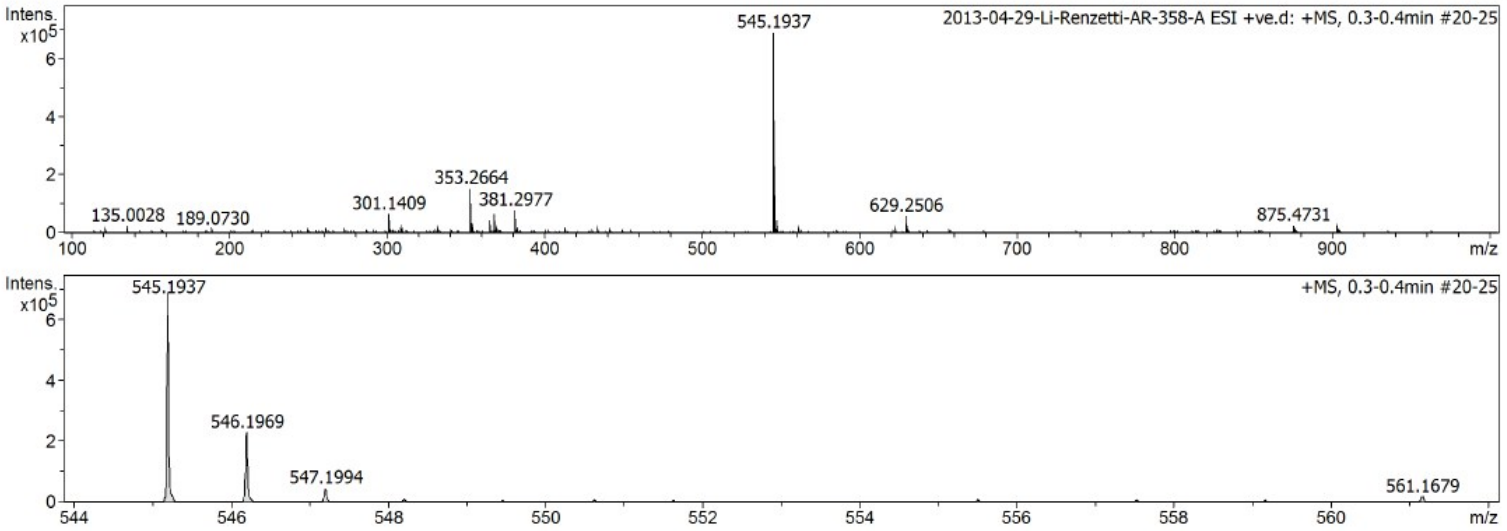
Mass Spectrum SmartFormula Report

Analysis Info

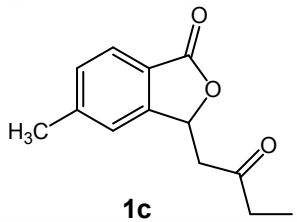
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-358-A ESI +ve.d	Acquisition Date	4/29/2013 3:14:02 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-358-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
545.1937	1	C33H30NaO6	545.1935	0.5	17.0	1	100.00	18.5	even	ok
	2	C34H26N4NaO2	545.1948	1.9	28.3	2	52.62	23.5	even	ok



1c

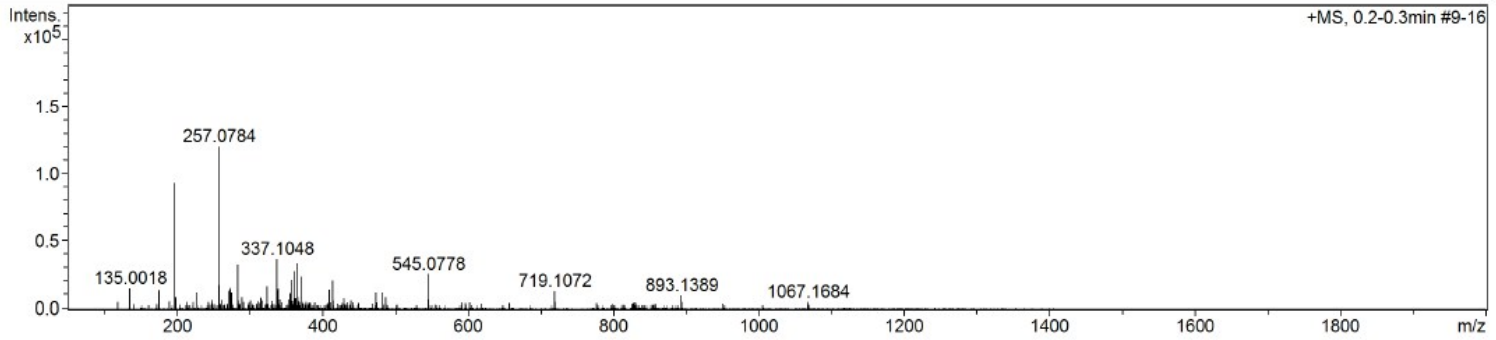
Mass Spectrum SmartFormula Report

Analysis Info

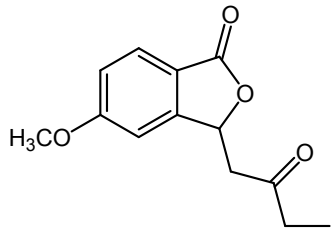
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-320-A 2 +ve.d	Acquisition Date	12/19/2012 3:26:47 PM
Method	Tune_pos_low_AW_NaFormate_cal_100-2000.m	Operator	ADM
Sample Name	2012-12-17-Li-Renzetti AR-320-A +ve 2	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
257.0784	1	C13H14NaO4	257.0784	0.2	3.7	1	100.00	6.5	even	ok



1d

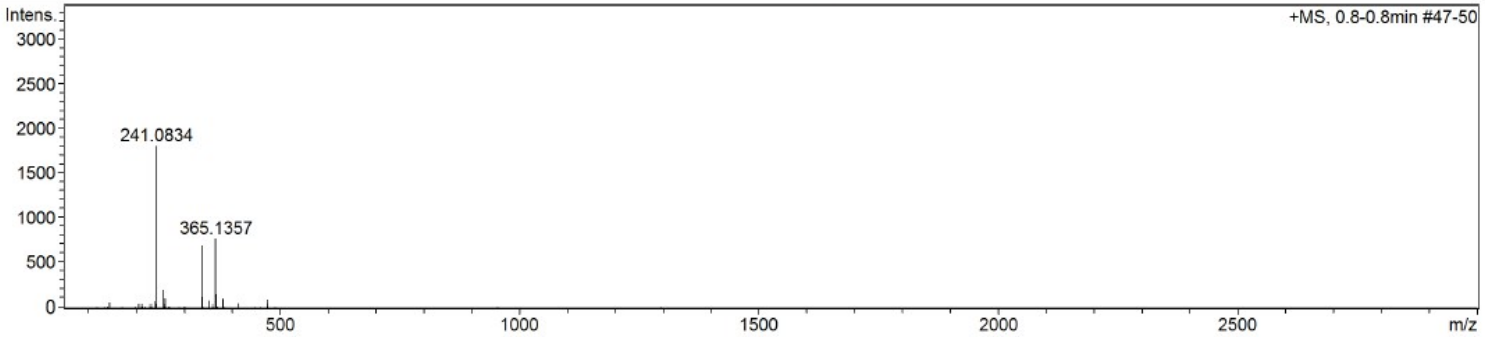
Mass Spectrum SmartFormula Report

Analysis Info

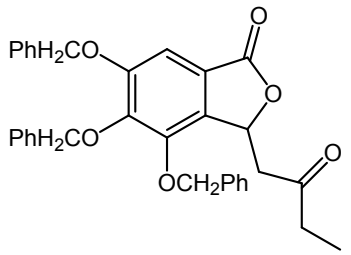
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-327 +ve.d	Acquisition Date	12/18/2012 10:57:41 AM
Method	Tune_pos_low_AW_NaFormate_cal.m	Operator	ADM
Sample Name	2012-12-17-Li-Renzetti AR-327 +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
241.0834	1	C13H14NaO3	241.0835	0.5	10.3	1	100.00	6.5	even	ok



1e

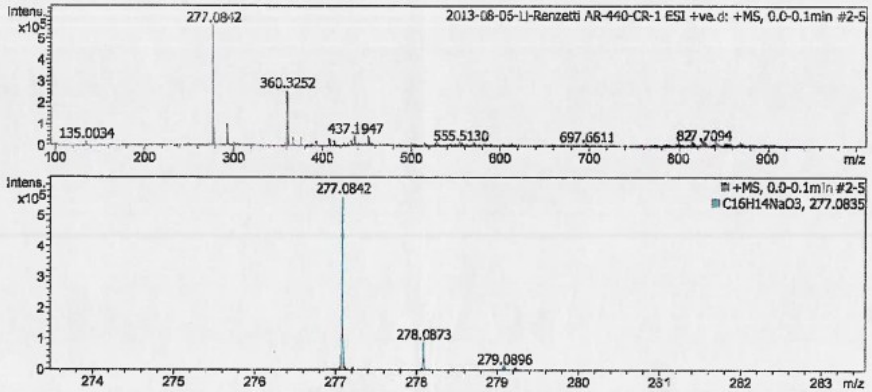
Mass Spectrum SmartFormula Report

Analysis Info

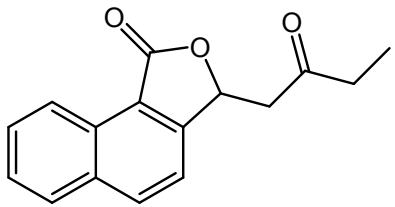
Analysis Name	D:\Data\Li\2013-08-06-Li-Renzetti AR-440-CR-1 ESI +ve.d	Acquisition Date	8/6/2013 4:29:51 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-08-06-Li-Renzetti AR-440-CR-1 ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.6 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
277.0842	1	C16H14NaO3	277.0835	2.6	9.7	1	100.00	9.5	even	ok



1f

Bruker Compass DataAnalysis 4.1 printed 8/6/2013 4:30:28 PM by: ADM Page 1 of 1

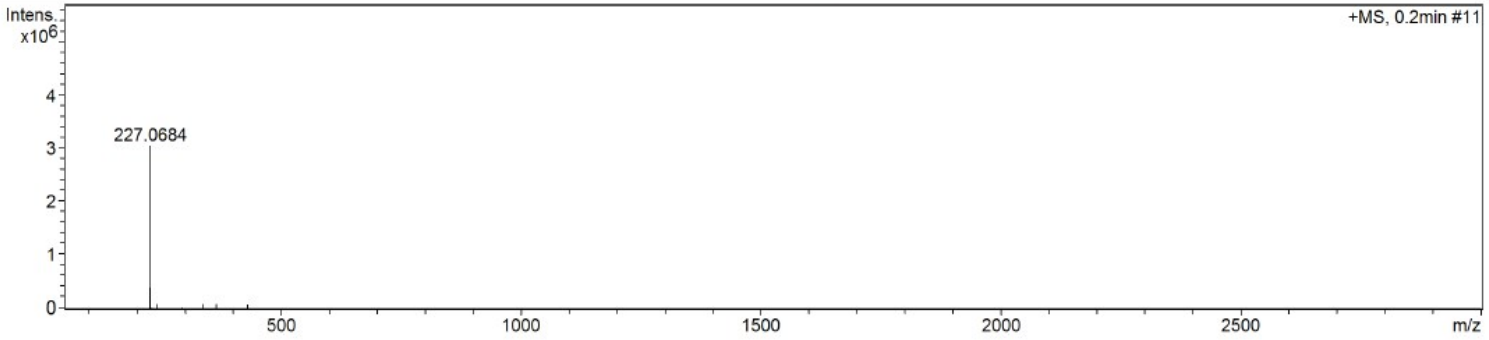
Mass Spectrum SmartFormula Report

Analysis Info

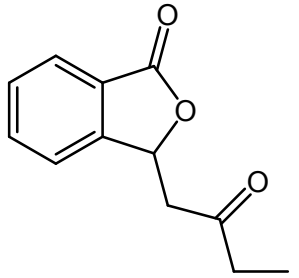
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-325-A +ve.d	Acquisition Date	12/18/2012 4:44:33 PM
Method	Tune_pos_low_AW_NaFormate_cal.m	Operator	ADM
Sample Name	2012-12-17-Li-Renzetti AR-325-A +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
227.0684	1	C12H12NaO3	227.0679	-2.2	7.6	1	100.00	6.5	even	ok



1g

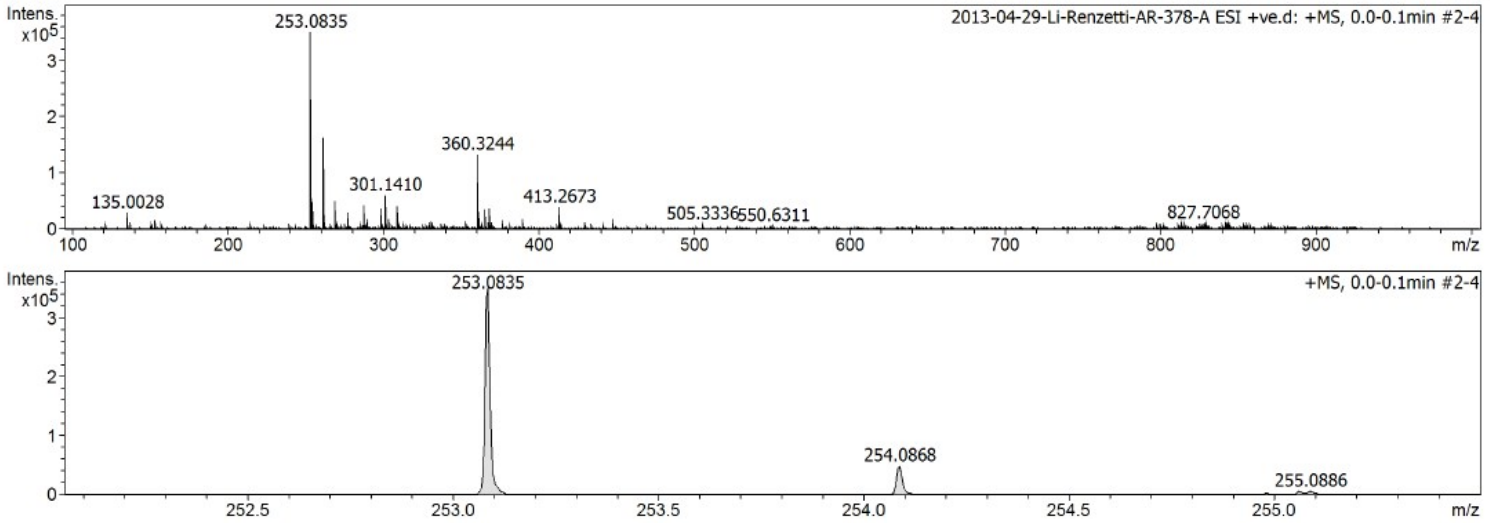
Mass Spectrum SmartFormula Report

Analysis Info

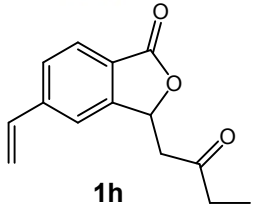
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-378-A ESI +ve.d	Acquisition Date	4/29/2013 3:35:54 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-378-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
253.0835	1	C14H14NaO3	253.0835	0.1	9.5	1	100.00	7.5	even	ok



1h

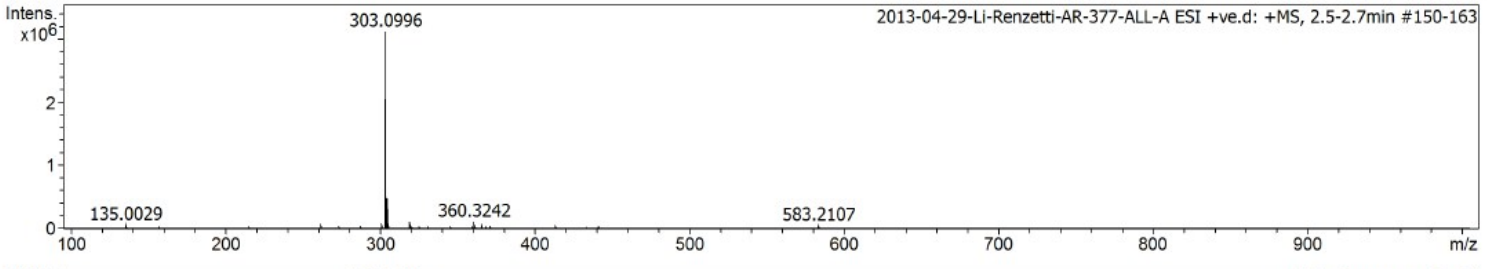
Mass Spectrum SmartFormula Report

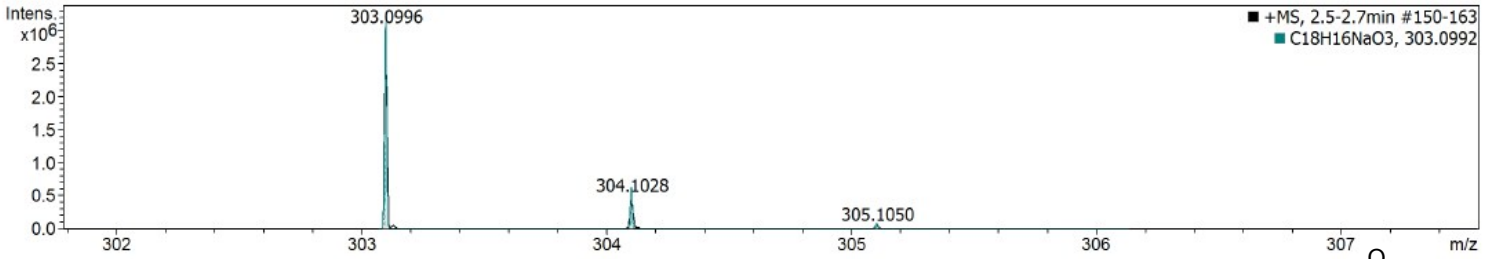
Analysis Info

Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-377-ALL-A ESI +ve.d	Acquisition Date	4/29/2013 4:05:49 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-377-ALL-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

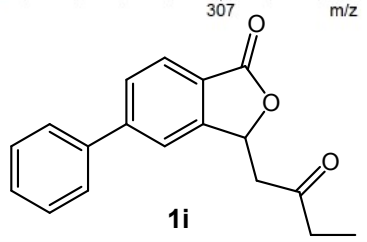
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
303.0996	1	C18H16NaO3	303.0992	1.4	25.2	1	100.00	10.5	even	ok
319.0729	1	C18H16KO3	319.0731	-0.5	11.2	1	100.00	10.5	even	ok



1i

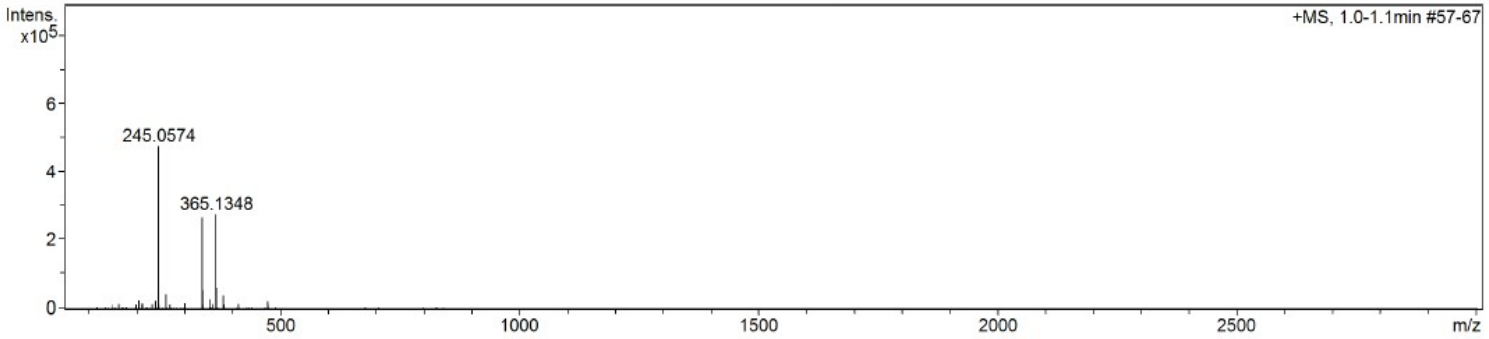
Mass Spectrum SmartFormula Report

Analysis Info

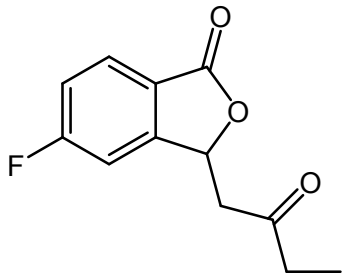
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-323-A +ve.d	Acquisition Date	12/18/2012 11:05:42 AM
Method	Tune_pos_low_AW_NaFormate_cal.m	Operator	ADM
Sample Name	2012-12-17-Li-Renzetti AR-323-A +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
245.0574	1	C2H9F3N6NaO3	245.0580	2.7	39.4	3	61.89	-0.5	even	ok
	2	C7H10F2N3NaO3	245.0582	3.5	14.4	2	100.00	3.0	odd	ok
	3	C12H11FNaO3	245.0584	4.3	10.7	1	95.92	6.5	even	ok



1j

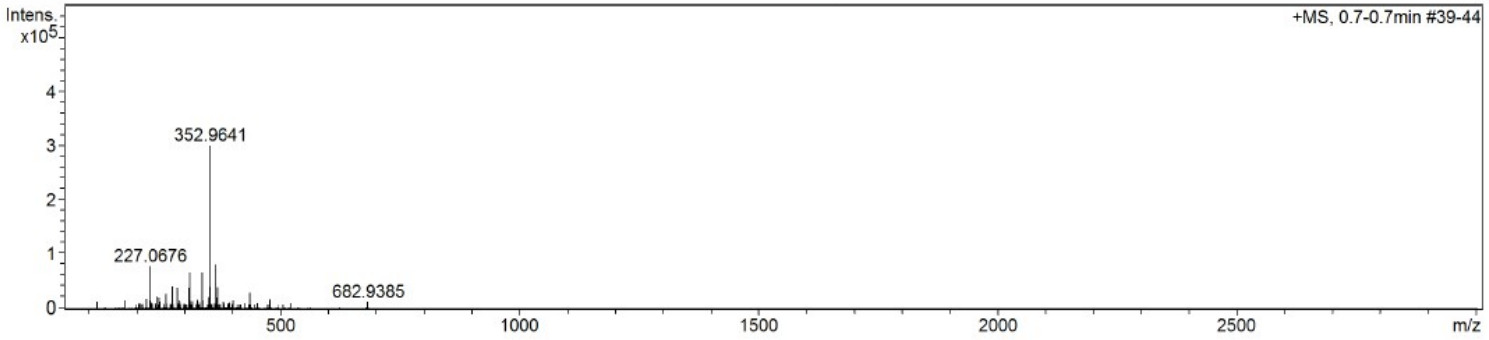
Mass Spectrum SmartFormula Report

Analysis Info

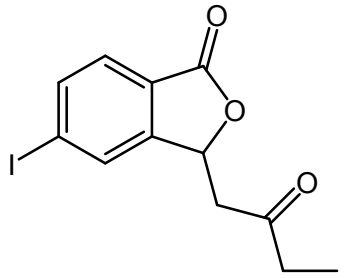
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-324-A +ve.d	Acquisition Date	12/18/2012 11:11:38 AM
Method	Tune_pos_low_AW_NaFormate_cal.m	Operator	ADM
Sample Name	2012-12-17-Li-Renzetti AR-324A +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
352.9641	1	C12H11INaO3	352.9645	1.3	4.3	1	100.00	6.5	even	ok



1k

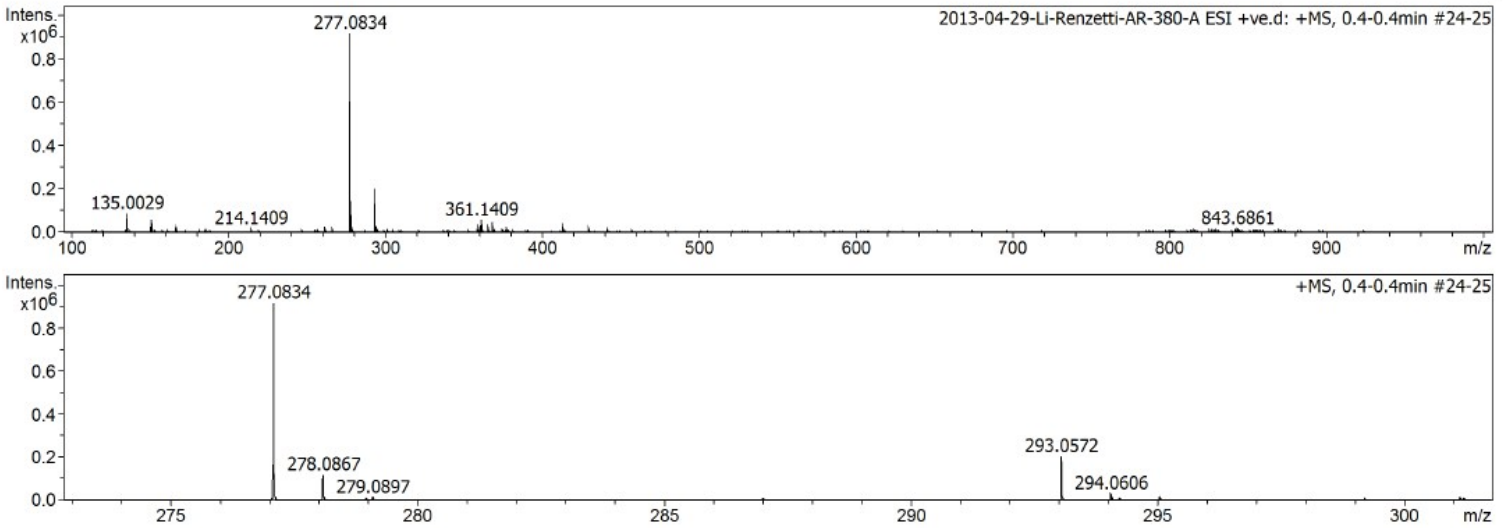
Mass Spectrum SmartFormula Report

Analysis Info

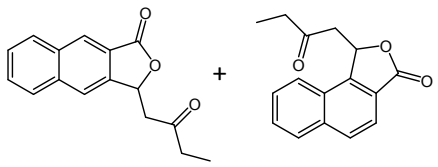
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-380-A ESI +ve.d	Acquisition Date	4/29/2013 4:57:59 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-380-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
277.0834	1	C14H9N6O	277.0832	-0.6	27.6	1	100.00	13.5	even	ok
	1	C16H14NaO3	277.0835	0.4	28.5	1	100.00	9.5	even	ok
	1	C13H18KO4	277.0837	-1.0	40.3	1	100.00	4.5	even	ok
293.0572	1	C17H5N6	293.0570	-0.7	47.4	1	100.00	18.5	even	ok
	1	C19H10NaO2	293.0573	-0.3	46.7	1	100.00	14.5	even	ok
	1	C16H14KO3	293.0575	0.8	25.1	1	100.00	9.5	even	ok



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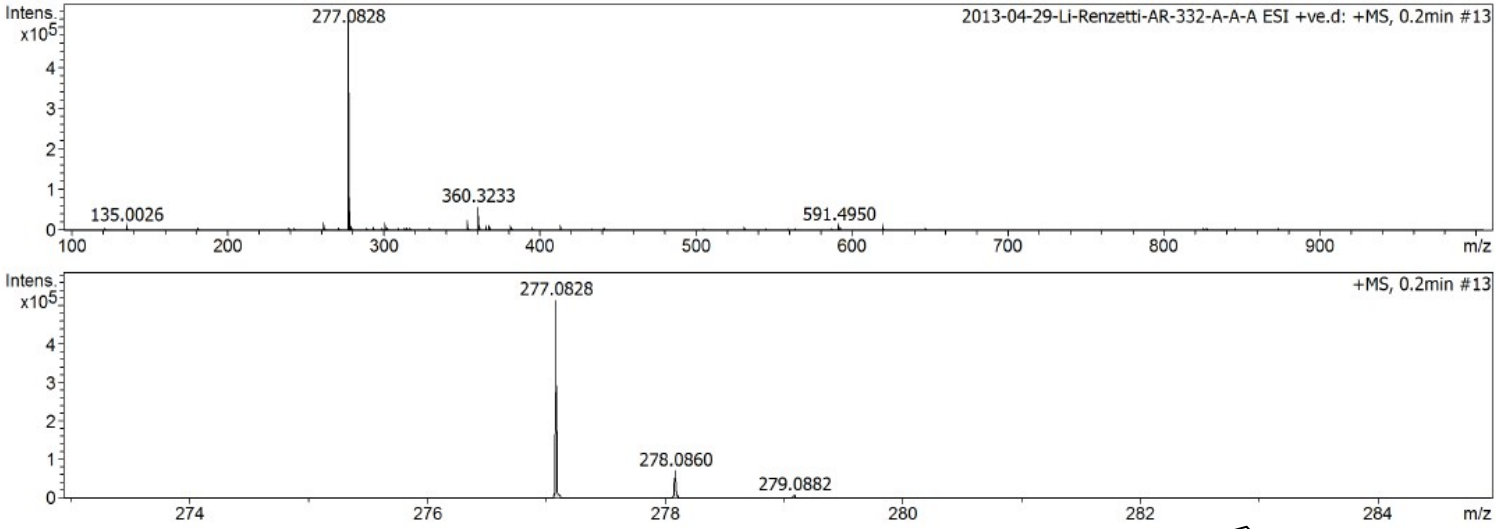
Mass Spectrum SmartFormula Report

Analysis Info

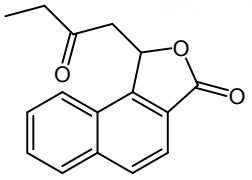
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-332-A-A-A ESI +ve.d	Acquisition Date	4/29/2013 3:26:25 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-332-A-A-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
277.0828	1	C16H14NaO3	277.0835	2.7	23.3	1	100.00	9.5	even	ok
	2	CH10N12NaO4	277.0840	4.5	45.5	2	42.52	2.5	even	ok
	3	H14N8NaO8	277.0827	-0.3	59.0	3	50.18	-2.5	even	ok



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Bruker Compass DataAnalysis 4.1 printed: 4/29/2013 3:30:53 PM by: ADM Page 1 of 1

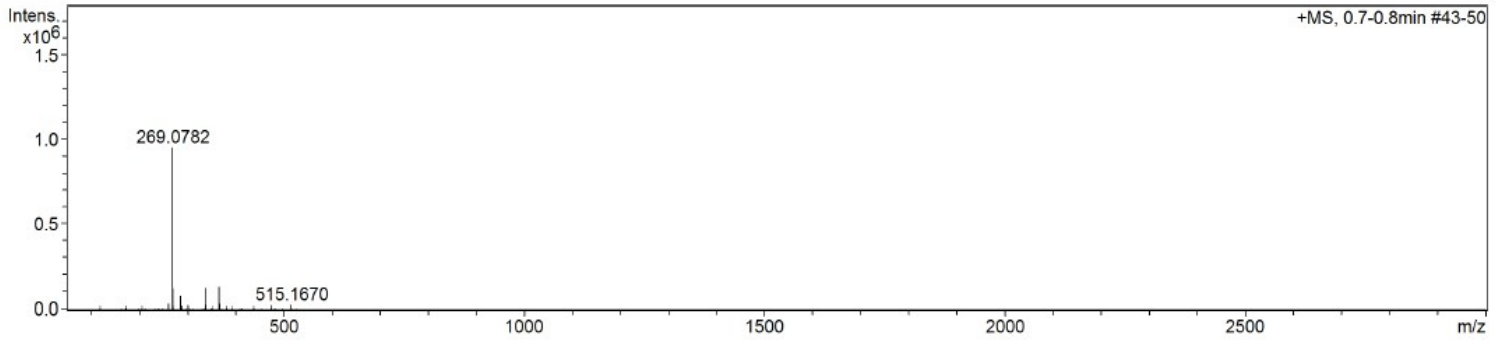
Mass Spectrum SmartFormula Report

Analysis Info

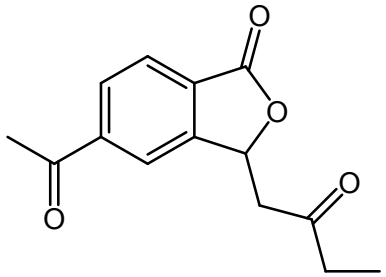
Analysis Name	D:\Data\Li\2012-12-17-Li-Renzetti AR-322-A +ve.d	Acquisition Date	12/18/2012 11:14:59 AM
Method	Tune_pos_low_AW_NaFormate_cal.m	Operator	ADM
Sample Name	2012-12-17-Li-Renzetti AR-322-A +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.0 Bar
Focus	Active	Set Capillary	3000 V	Set Dry Heater	200 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
269.0782	1	C14H14NaO4	269.0784	0.9	18.7	1	100.00	7.5	even	ok



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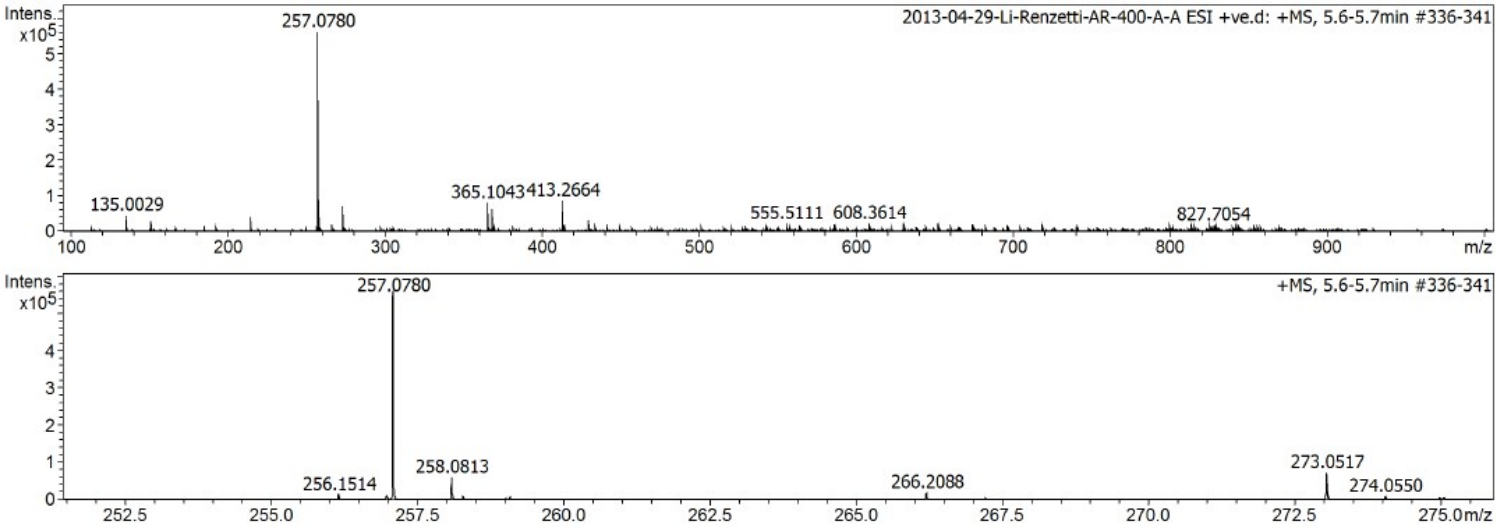
Mass Spectrum SmartFormula Report

Analysis Info

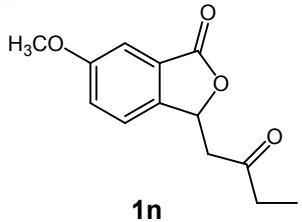
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-400-A-A ESI +ve.d	Acquisition Date	4/29/2013 2:20:36 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-400-A-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
257.0780	1	C13H14NaO4	257.0784	-1.7	22.9	1	100.00	6.5	even	ok
273.0517	1	C11H12KN3O3	273.0510	-2.4	15.5	1	100.00	7.0	odd	ok
	2	C13H14KO4	273.0524	2.5	21.2	2	87.67	6.5	even	ok



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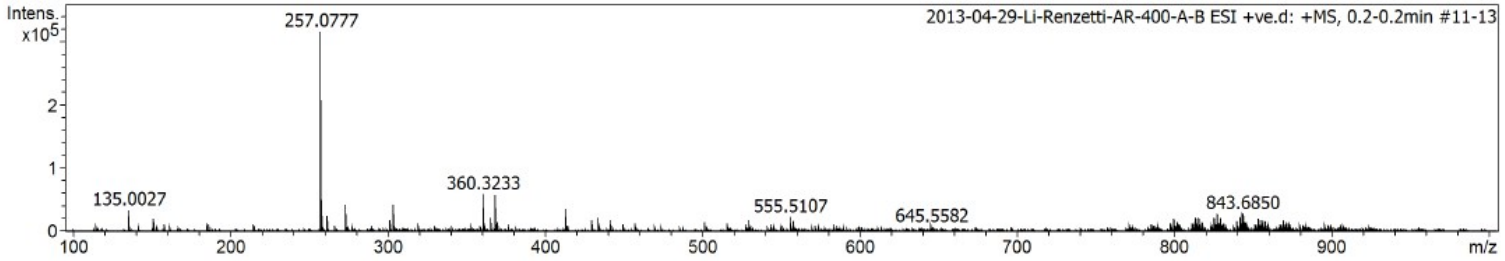
Mass Spectrum SmartFormula Report

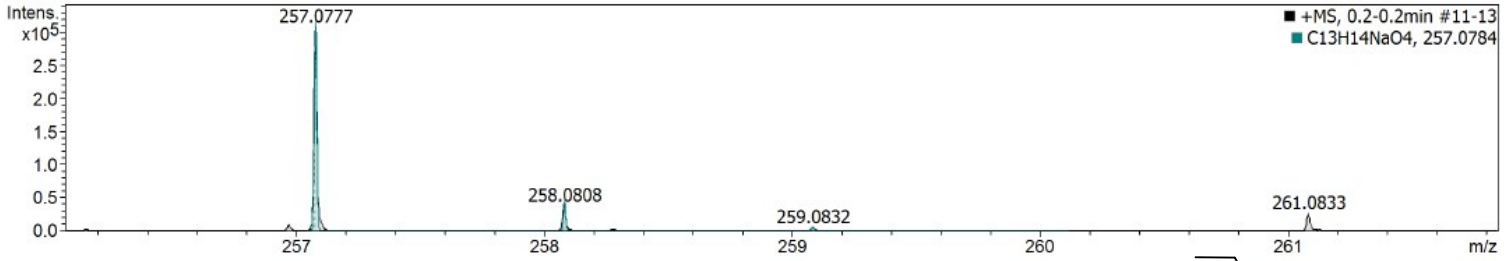
Analysis Info

Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-400-A-B ESI +ve.d	Acquisition Date	4/29/2013 4:43:24 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-400-A-B ESI +ve	Instrument	maXis impact 282001.00044
Comment			

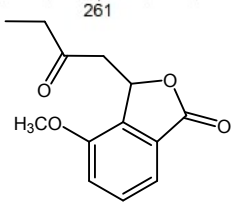
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



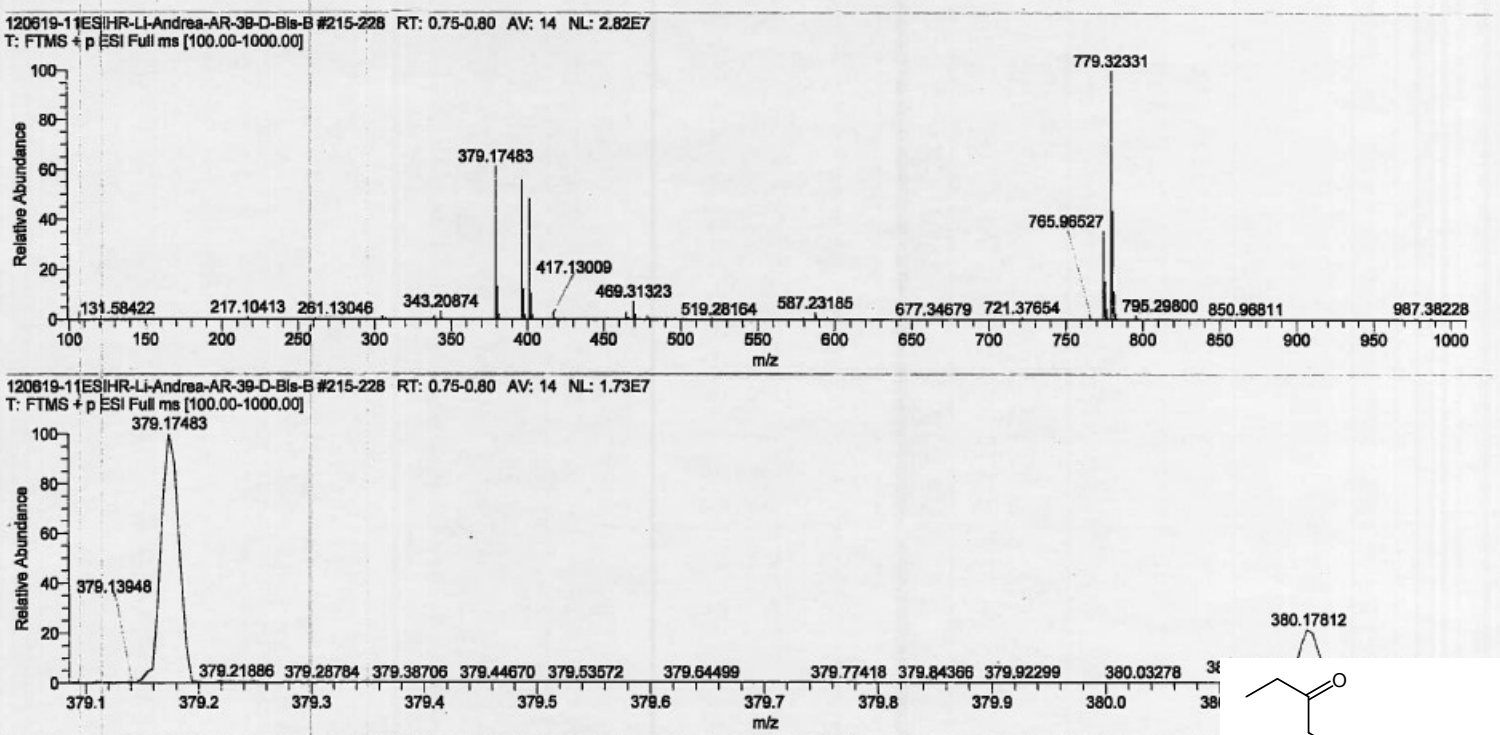


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
257.0777	1	C13H14NaO4	257.0784	3.0	16.4	1	100.00	6.5	even	ok



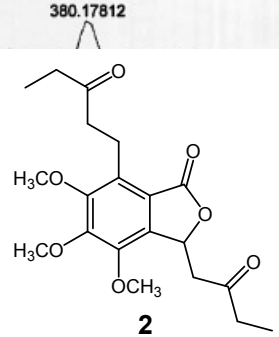
1n'

120619-11ESIHR-Li-Andrea-AR-39-D-Bis-B 6/19/2012 1:40:16 PM



120619-11ESIHR-Li-Andrea-AR-39-D-Bis-B#215-228 RT: 0.75-0.80 AV: 14
T: FTMS + p ESI Full ms [100.00-1000.00]
m/z= 379.15152-379.19472

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	Composit:
379.17483	17365958.0	100.00	21444.06	1.00	379.17513	-0.30	7.5	$C_{20}H_{27}O_7$
					379.17379	1.05	8.0	$C_{18}H_{25}O_6N_3$
					379.17647	-1.63	12.5	$C_{21}H_{23}O_3N_4$
					379.17781	-2.98	12.0	$C_{23}H_{25}O_4N$
					379.17915	-4.31	17.0	$C_{24}H_{21}N_5$



2

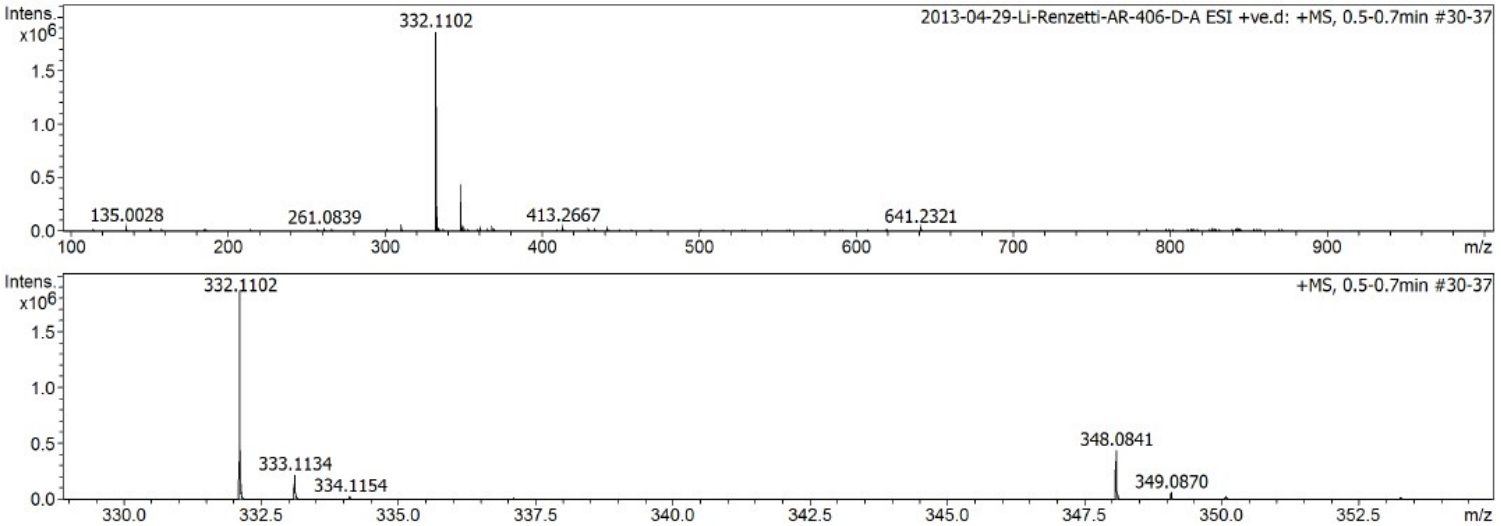
Mass Spectrum SmartFormula Report

Analysis Info

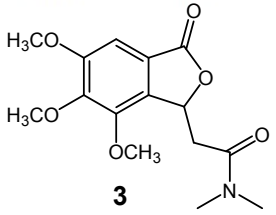
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-406-D-A ESI +ve.d	Acquisition Date	4/29/2013 5:13:32 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-406-D-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

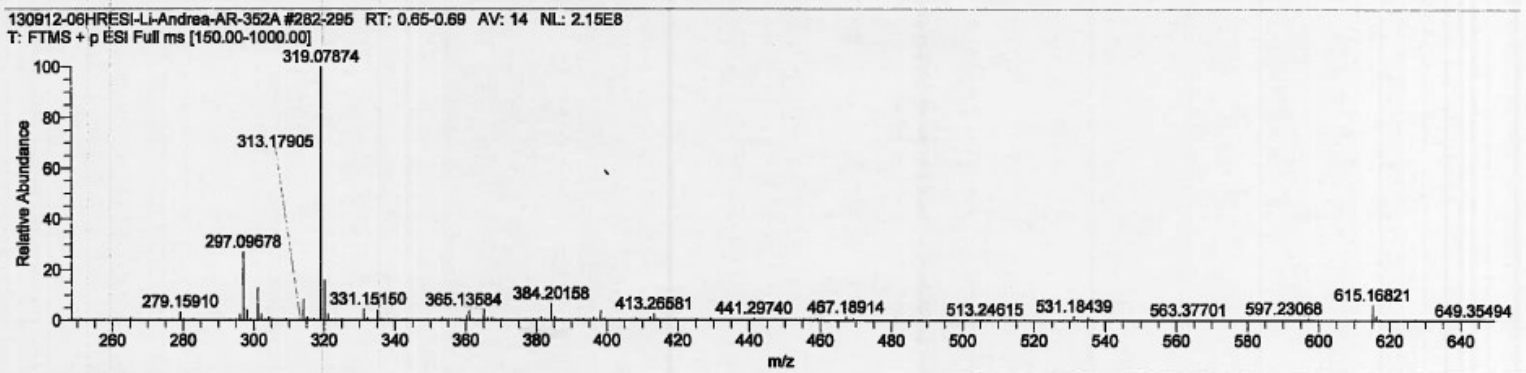


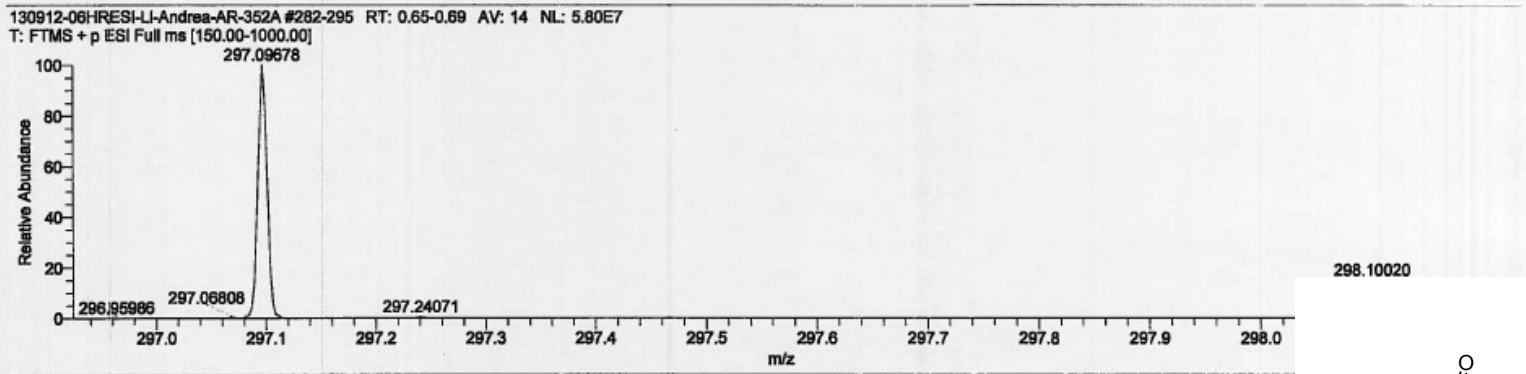
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
332.1102	1	C13H14N7O4	332.1102	-0.0	30.3	1	100.00	10.5	even	ok
	1	C15H19NNaO6	332.1105	0.8	31.3	1	100.00	6.5	even	ok
348.0841	1	C16H10N7O3	348.0840	0.3	47.2	1	100.00	15.5	even	ok
	1	C18H15NNaO5	348.0842	-0.5	46.5	1	100.00	11.5	even	ok
	1	C15H19KNO6	348.0844	0.9	25.7	1	100.00	6.5	even	ok



3

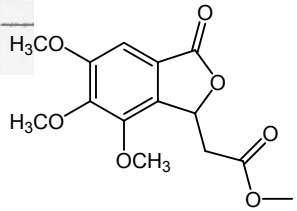
130912-06HRESI-Li-Andrea-AR-352A 9/12/2013 12:23:06 PM



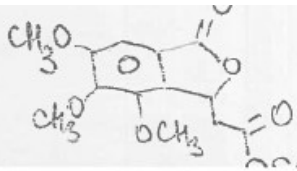


130912-06HRESI-Li-Andrea-AR-352A#282-295 RT: 0.65-0.69 AV: 14
T: FTMS + p ESI Full ms [150.00-1000.00]
m/z= 297.08533-297.10026

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta (ppm)	RDB equiv.	
297.09678	58123612.0	100.00	32277.95	1.00	297.09688	-0.33	6.5	C1
					297.09581	3.26	8.5	C1
					297.09822	-4.83	11.5	C1



4a



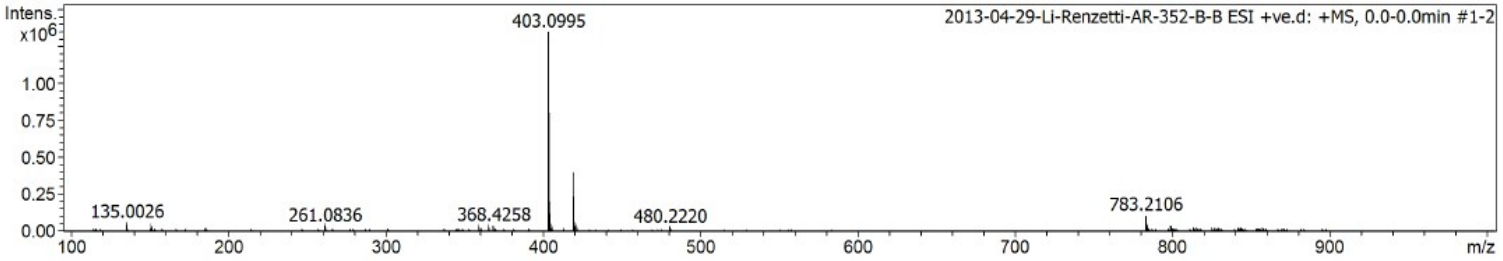
Mass Spectrum SmartFormula Report

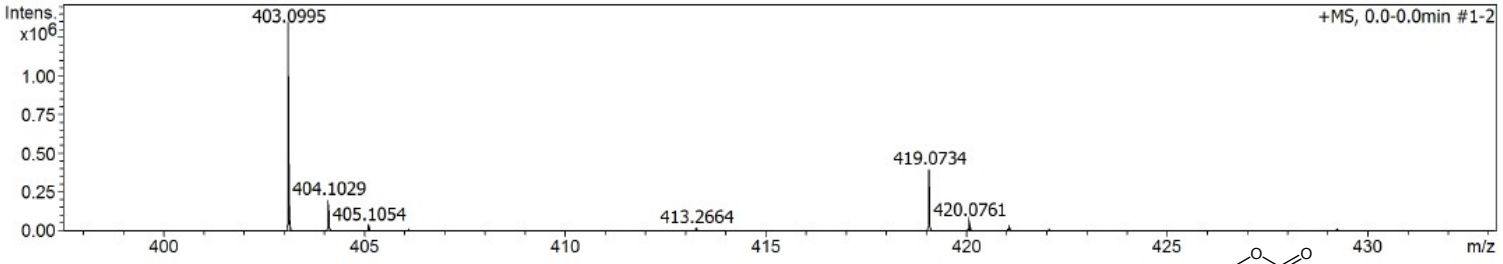
Analysis Info

Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-352-B-B ESI +ve.d	Acquisition Date	4/29/2013 5:56:26 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-352-B-B ESI +ve	Instrument	maXis impact 282001.00044
Comment			

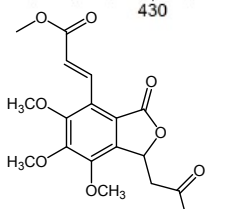
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
403.0995	1	C18H20NaO9	403.1000	1.0	27.4	1	100.00	8.5	even	ok
419.0734	1	C18H20KO9	419.0739	-1.1	26.7	1	100.00	8.5	even	ok



4b

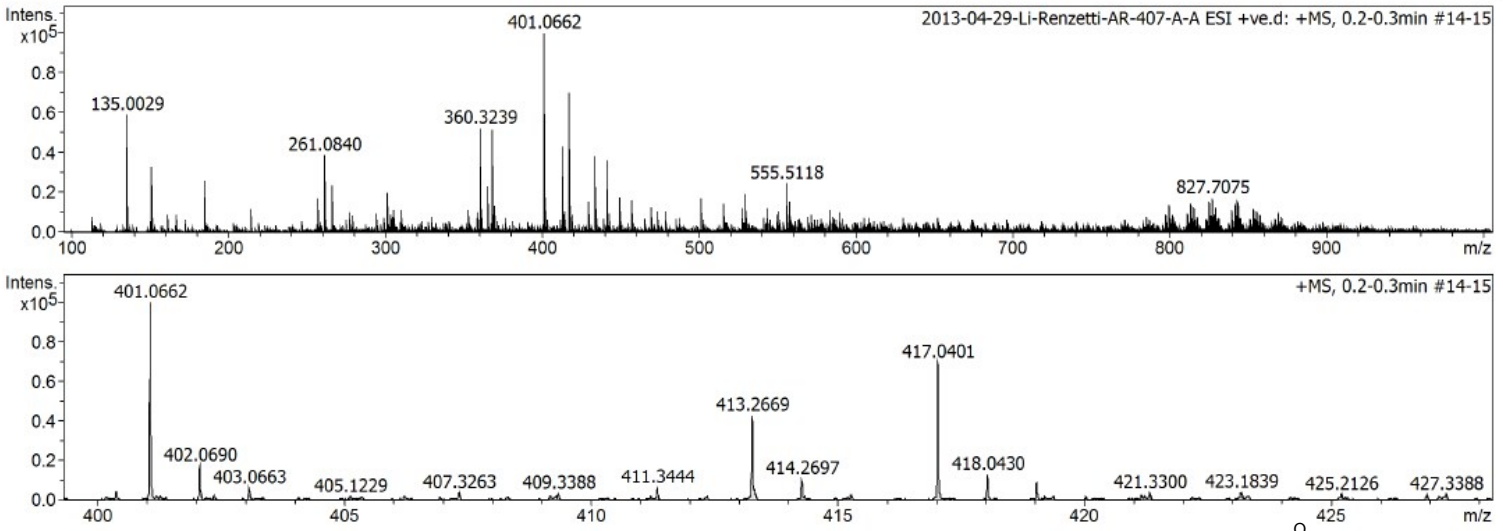
Mass Spectrum SmartFormula Report

Analysis Info

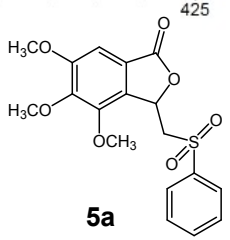
Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-407-A-A ESI +ve.d	Acquisition Date	4/29/2013 5:49:43 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-407-A-A ESI +ve	Instrument	maXis impact 282001.00044
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
401.0662	1	C18H18NaO7S	401.0665	0.9	19.5	1	100.00	9.5	even	ok
417.0401	1	C18H18KO7S	417.0405	1.0	16.2	1	100.00	9.5	even	ok



5a

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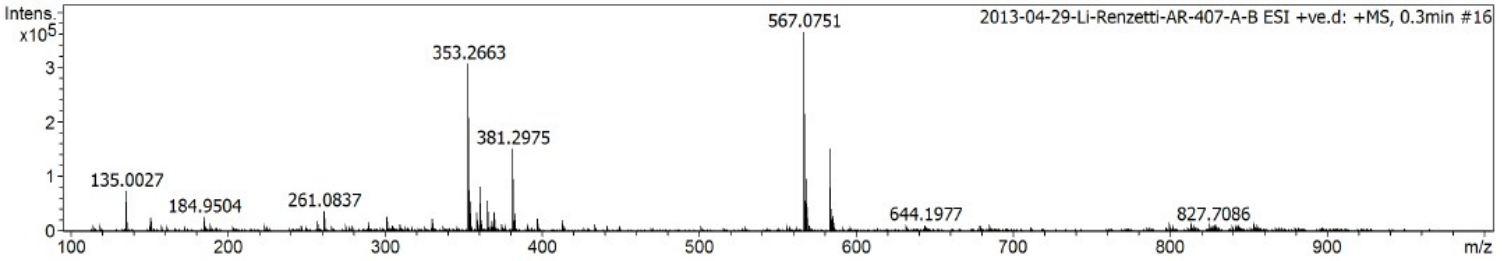
Mass Spectrum SmartFormula Report

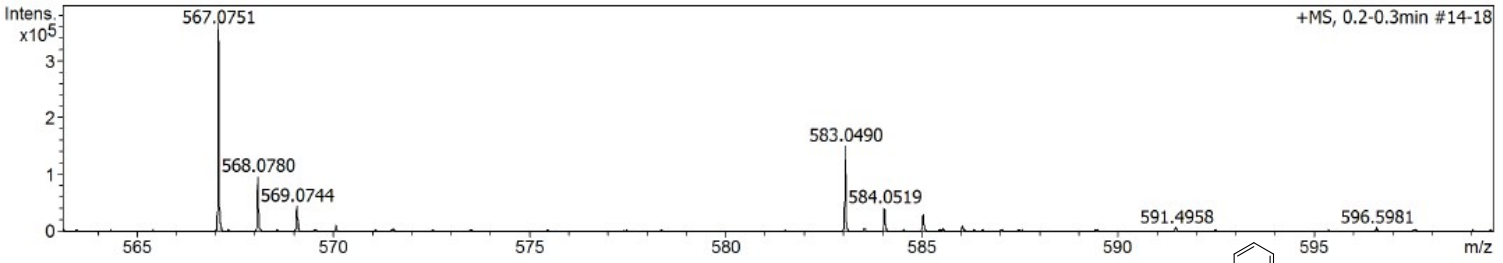
Analysis Info

Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-407-A-B ESI +ve.d	Acquisition Date	4/29/2013 5:41:22 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-407-A-B ESI +ve	Instrument	maXis impact 282001.00044
Comment			

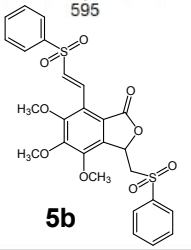
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
567.0751	1	C26H24NaO9S2	567.0754	0.6	24.4	1	100.00	14.5	even	ok
	2	C18H28N2NaO11S3	567.0747	0.6	31.6	2	83.69	5.5	even	ok
	3	C14H28N2NaO16S2	567.0772	3.8	35.6	3	24.32	1.5	even	ok
583.0490	1	C21H24N2NaO10S3	583.0485	-0.7	3.8	1	100.00	10.5	even	ok
	1	C26H24KO9S2	583.0493	0.6	20.4	1	100.00	14.5	even	ok
	2	C18H28KN2O11S3	583.0487	-0.5	31.7	2	80.62	5.5	even	ok



5b

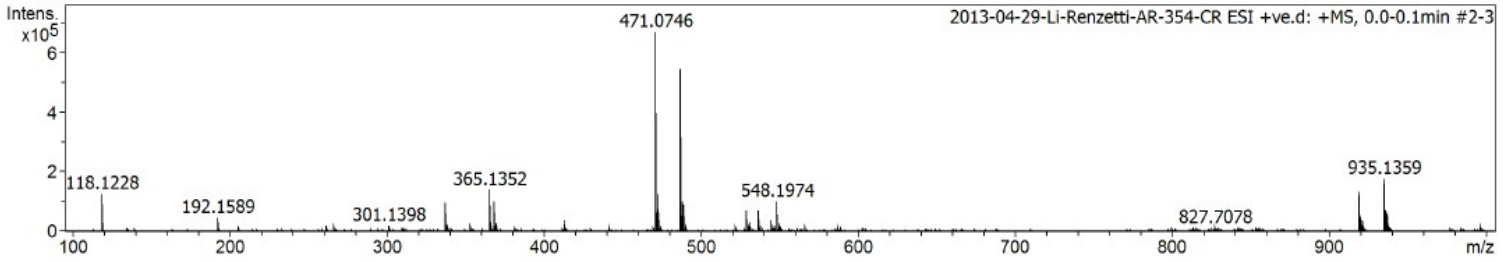
Mass Spectrum SmartFormula Report

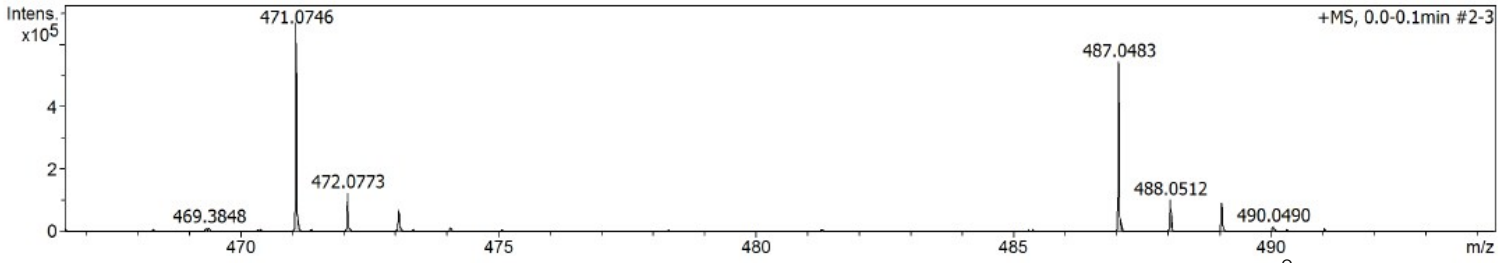
Analysis Info

Analysis Name	D:\Data\Li\2013-04-29-Li-Renzetti-AR-354-CR ESI +ve.d	Acquisition Date	4/29/2013 5:33:22 PM
Method	Tune_pos_Low_Na_Formate_100-1000.m	Operator	ADM
Sample Name	2013-04-29-Li-Renzetti-AR-354-CR ESI +ve	Instrument	maXis impact 282001.00044
Comment			

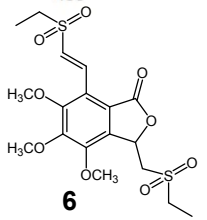
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
471.0746	1	C18H24NaO9S2	471.0754	-1.6	22.7	1	100.00	6.5	even	ok
487.0483	1	C13H24N2NaO10S3	487.0485	-0.5	3.6	1	100.00	2.5	even	ok



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