

Supporting Information Available.

1) Data of key intermediates.

9 (faster eluting isomer): m.p. 101-104°C (heptane/ethyl acetate). IR (film): 2958, 1770, 1694, 1660, 1613, 1586, 1514, 1462, 1390, 1326, 1248, 1204, 1104, 1076, 969, 941, 895, 878, 816, 752, 662 cm⁻¹. ¹H NMR (CDCl₃): 1.73 (1H, ddd, *J* = 2.4, 8.8, 12.8); 1.83 (1H, td, *J* = 10.6, 13.3); 1.84 (3H, s); 2.39-2.62 (4H, m); 2.72-2.81 (2H, m); 3.80 (3H, s); 4.02 (3H, s); 4.14 (1H, d, *J* = 15.8); 4.84 (1H, d, *J* = 15.8); 6.85 (2H, d, *J* = 8.7); 7.11 (2H, d, *J* = 8.7) ppm. ¹³C NMR (CDCl₃): 8.6, 29.1, 29.2, 31.7, 33.4, 43.1, 55.1, 59.5, 70.9, 89.5, 113.7 (2C), 127.6 (2C); 129.7, 158.5, 167.7, 172.2, 176.3, 206.3 ppm. APCI(+): 386 ([MH]⁺, 100), 278 (15), 121 (35). HRMS (DCI/NH₃). Calcd for C₂₁H₂₄NO₆ m/z 386.1604; found 386.1601.

10 (slower eluting isomer): m.p. 183-185°C (pentane/ethyl ether/CH₂Cl₂). IR (film): 2926, 1770, 1694, 1661, 1612, 1513, 1443, 1392, 1323, 1248, 1177, 1152, 1055, 1008, 948, 896, 810, 734 cm⁻¹. ¹H NMR (CDCl₃): 1.92-1.98 (2H, m); 2.06 (3H, s); 2.32-2.54 (6H, m); 3.79 (3H, s); 3.91 (1H, d, *J* = 16.3); 4.13 (3H, s); 5.16 (1H, d, *J* = 16.3); 6.83 (2H, d, *J* = 8.6); 7.15 (2H, d, *J* = 8.6). ¹³C NMR (CDCl₃): 8.8, 28.8, 29.1, 30.3, 31.2, 33.7, 43.9, 55.0, 59.7, 70.0, 88.3, 99.5, 113.7 (2C), 127.8 (2C), 158.6, 168.7, 172.0, 175.2, 207.9 ppm. APCI(+): 386 ([MH]⁺, 100), 278 (20), 121 (50). HRMS (DCI/NH₃). Calcd for C₂₁H₂₄NO₆ m/z 386.1604; found 386.1598.

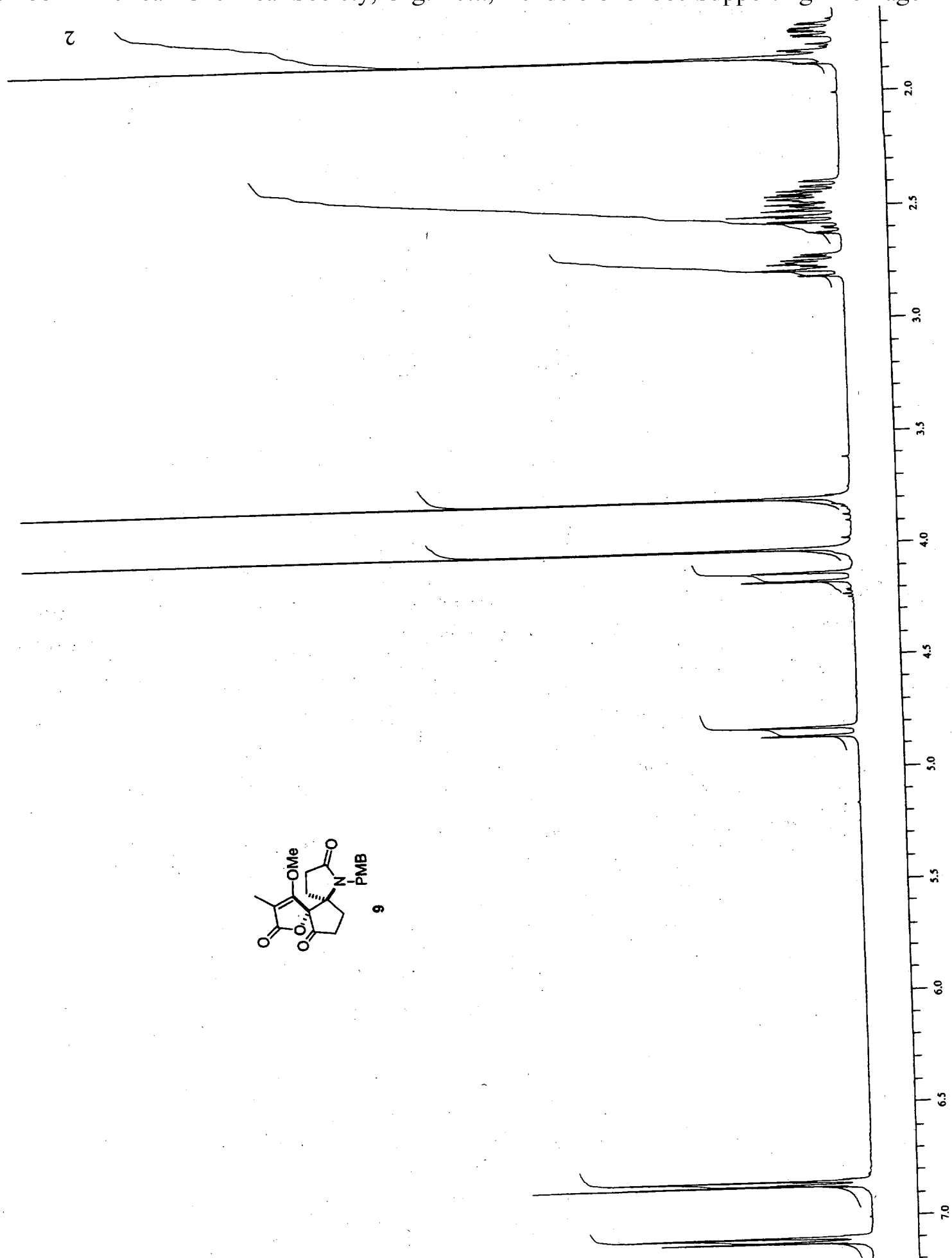
11: m.p. 142-143°C (heptane/ethyl acetate). IR (film): 2940, 1769, 1732, 1704, 1662, 1514, 1386, 1343, 1248, 1144, 1070 cm⁻¹. ¹H NMR (CDCl₃): 1.95 (3H, s); 2.03 (1H, ddd, *J* = 8.9, 12.1, 13.0); 2.35 (1H, dd, *J* = 8.9, 16.8); 2.44 (1H, dd, *J* = 7.9, 13.0); 2.64 (1H, ddd, *J* = 7.9, 12.1, 16.8); 3.78 (3H, s); 3.87 (3H, s); 4.10 (1H, d, *J* = 15.6); 4.88 (1H, d, *J* = 15.6); 6.33 (1H, d, *J* = 6.3); 6.84 (2H, d, *J* = 8.6); 7.07 (2H, d, *J* = 8.6); 7.21 (1H, d, *J* = 6.3) ppm. ¹³C NMR (CDCl₃): 8.9, 29.4, 32.8, 44.4, 55.2, 59.3, 73.4, 89.5, 99.7, 114.0 (2C), 128.4 (2C), 129.8, 132.5, 158.9, 162.5, 168.1, 172.6, 176.0, 195.4 ppm. APCI (+): 384 ([MH]⁺, 100), 276 (25), 121 (55). HRMS (DCI/NH₃). Calcd for C₂₁H₂₂NO₆ m/z 384.1447; found 384.1434. Elemental analysis. Calcd C, 65.79; H, 5.52. Found C, 65.97; H, 5.69.

12: m.p. 153-154°C (heptane/ethyl acetate/CH₂Cl₂). IR (film): 2925, 1770, 1732, 1698, 1662, 1514, 1389, 1321, 1247, 1176, 1063 cm⁻¹. ¹H NMR (CDCl₃): 2.08 (3H, s); 2.11-2.19 (1H, m); 2.31-2.54 (3H, m); 3.64 (1H, d, *J* = 15.9); 3.79 (3H, s); 4.09 (3H, s); 5.13 (1H, d, *J* = 15.9); 6.26 (1H, d, *J* = 6.1); 6.79 (2H, d, *J* = 8.6); 7.02 (1H, d, *J* = 6.1); 7.05 (2H, d, *J* = 8.6) ppm. ¹³C NMR (CDCl₃): 8.8, 27.7, 29.2, 44.1, 55.1, 59.5, 72.0, 85.9, 98.9, 113.8 (2C), 129.0 (2C), 129.7, 133.7, 158.7, 163.6, 169.2, 172.4, 174.5, 197.9 ppm. APCI (+): 384 ([MH]⁺, 100), 276 (52), 121 (45). HRMS (DCI/NH₃). Calcd for C₂₁H₂₂NO₆ m/z 384.1447; found 384.1449. Elemental analysis. Calcd C, 65.79; H, 5.52. Found C, 64.12; H, 5.49.

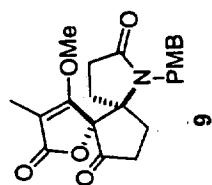
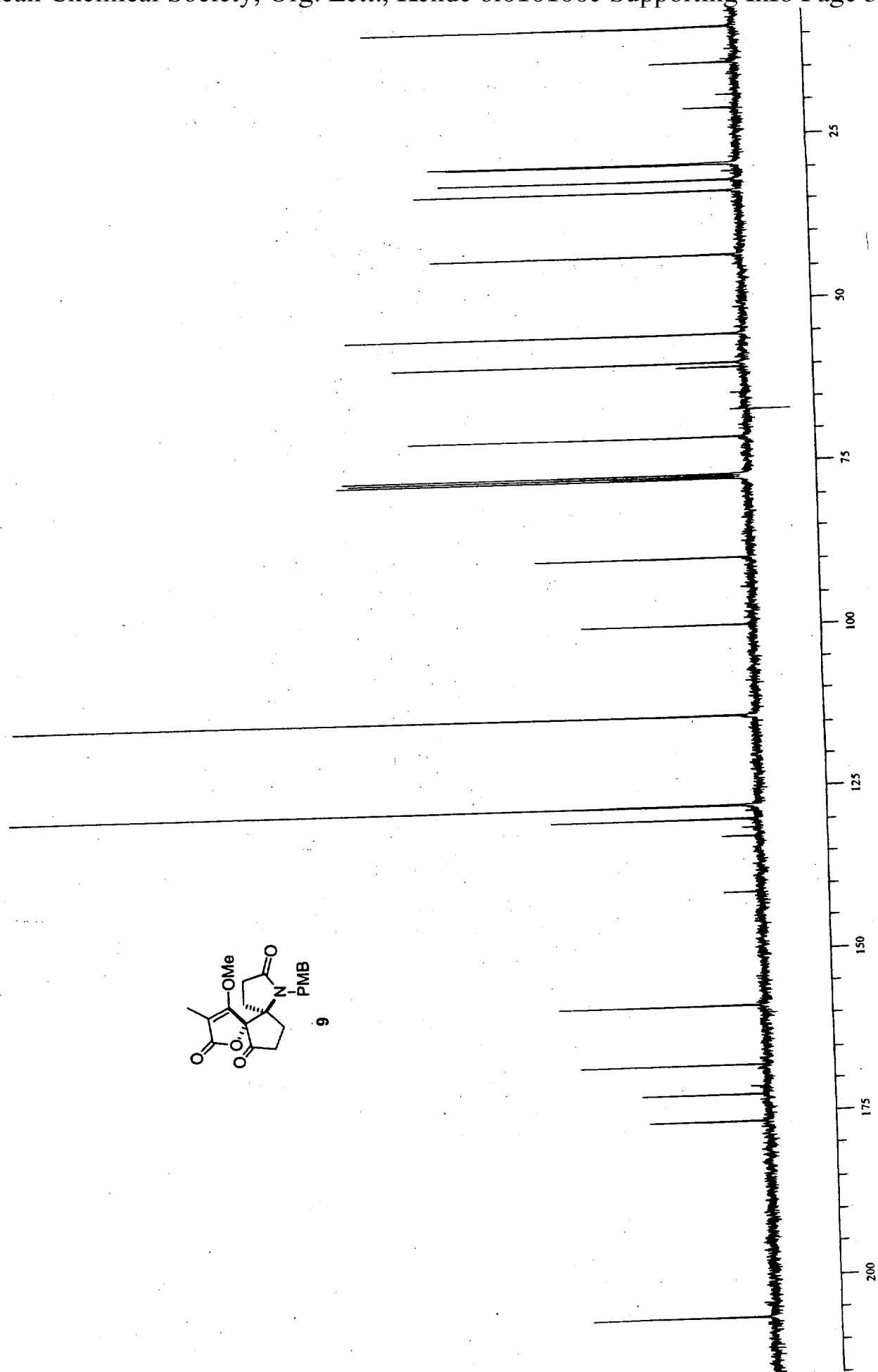
21: IR (film): 3206, 2937, 1766, 1699, 1662, 1456, 1390, 1350, 1329, 1255, 1174, 1150, 1075, 980, 930, 850, 802, 731 cm⁻¹. ¹H NMR (CDCl₃): 1.64-1.74 (2H, m); 1.76-1.86 (2H, m); 1.81 (3H, s); 1.98-2.07 (1H, m); 2.00 (3H, s); 2.27 (1H, dd, *J* = 9.6, 16.8); 2.35-2.40 (2H, m); 2.45-2.61 (2H, m); 3.03 (3H, s); 4.01 (3H, s); 4.22-4.30 (2H, m); 7.53 (1H, bs) ppm. ¹³C NMR (CDCl₃): 8.7, 8.8, 24.2, 25.6, 29.0, 29.5, 30.7, 37.4, 59.7, 69.2, 69.6, 90.3, 97.9, 137.2, 168.0, 171.0, 173.5, 179.1, 194.9 ppm. APCI(+): 428 ([MH]⁺, 100), 332 (15), 122 (12).

22: IR (film): 3341, 2935, 1765, 1704, 1662, 1451, 1390, 1347, 1173, 1109, 1073, 1003, 934, 860, 801, 731 cm⁻¹. ¹H NMR (CDCl₃): 1.65-1.75 (3H, m); 1.84 (3H, s); 1.84-1.90 (1H, m); 2.08 (3H, s); 2.15 (1H, td, *J* = 9.3, 13.4); 2.29 (1H, td, *J* = 9.0, 17.1); 2.37-2.46 (2H, m); 2.48-2.58 (2H, m); 3.05 (3H, s); 4.14 (3H, s); 4.28 (2H, t, *J* = 6.1); 6.41 (1H, bs) ppm. ¹³C NMR (CDCl₃): 8.8, 9.2, 24.7, 26.0, 27.7, 29.2, 37.4, 59.7, 68.8, 69.7, 77.2, 85.3, 101.9, 137.6, 168.5, 171.6, 172.3, 177.3, 196.1 ppm. APCI(+): 428 ([MH]⁺, 100), 332 (15).

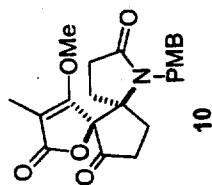
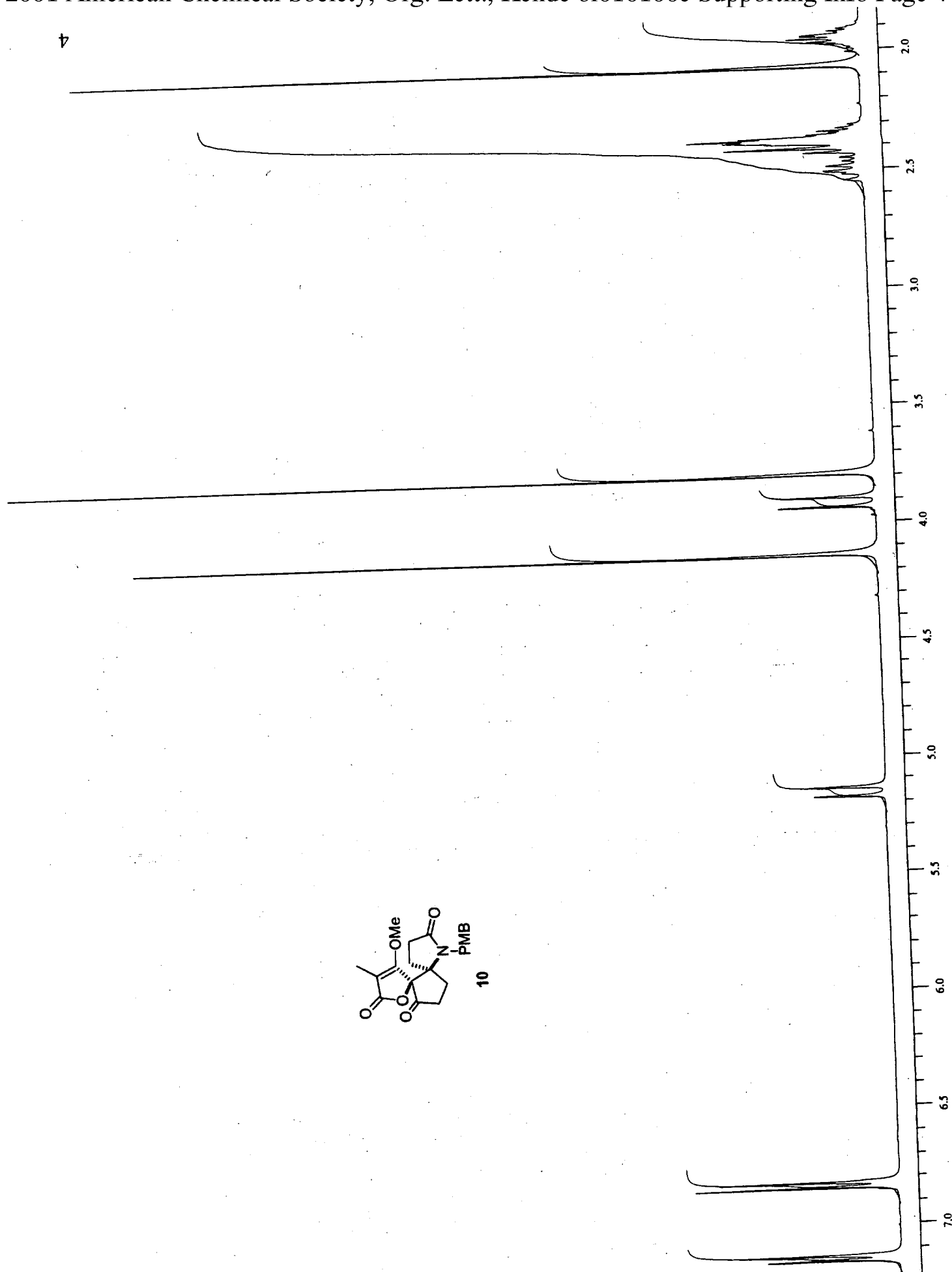
2) NMR spectra of **9**, **10**, **11**, **12**, **21** and **22**.3) NMR spectra of synthetic **1** and **2**.4) ORTEP plots of **1** and **2**.



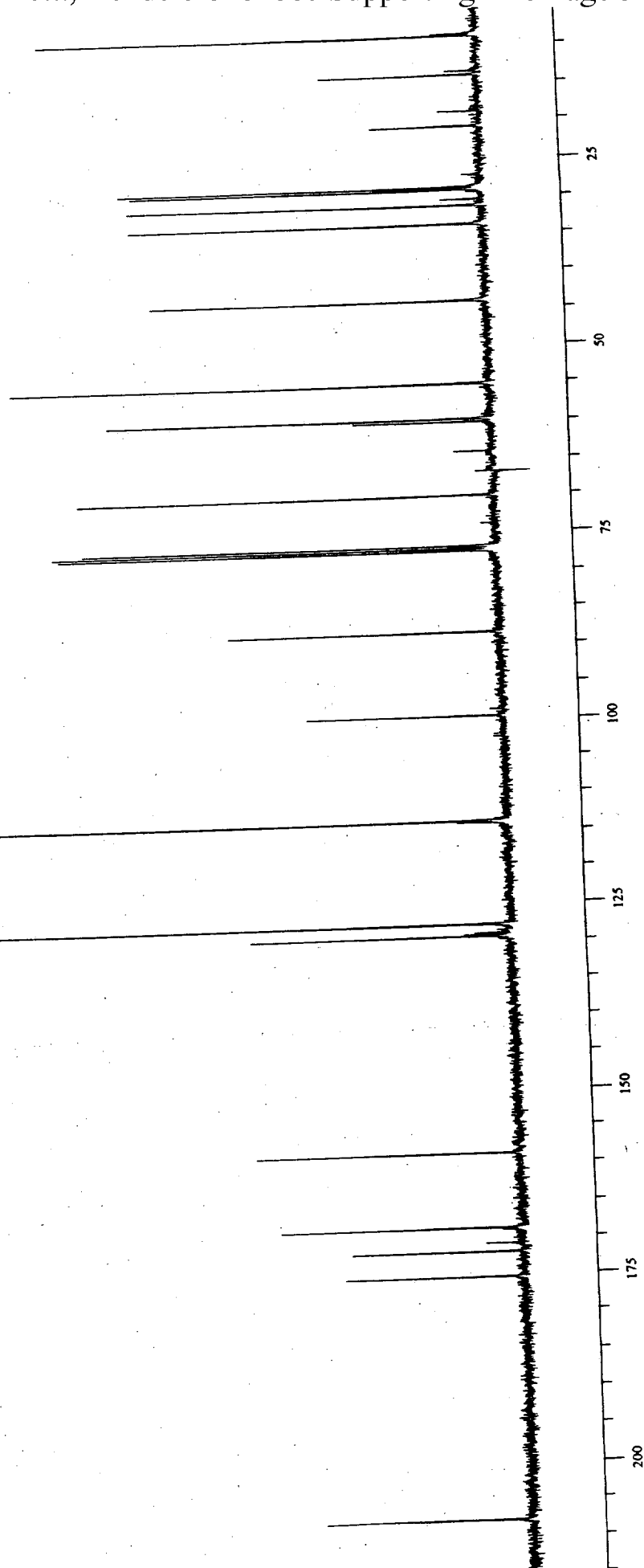
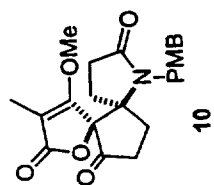
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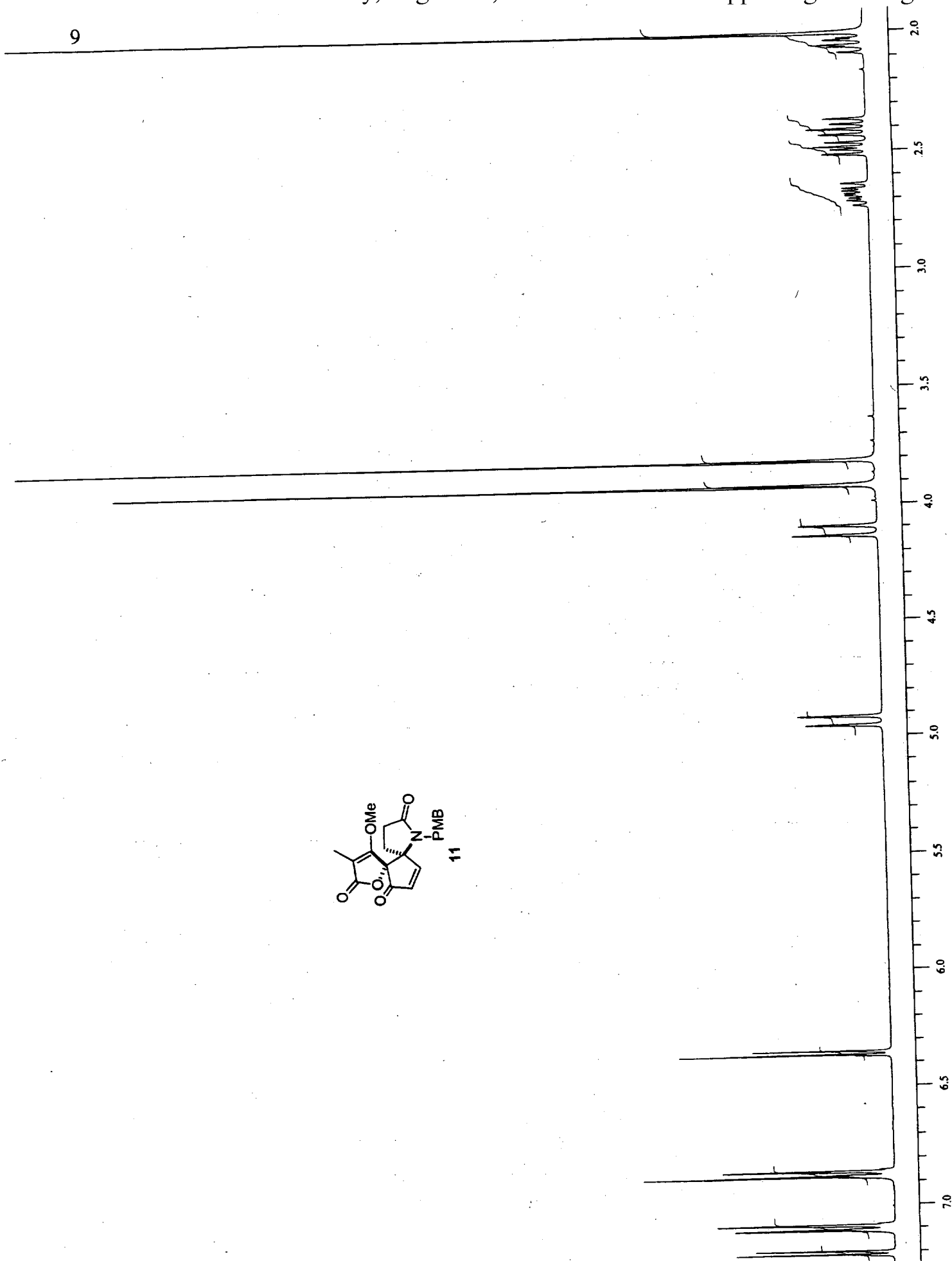
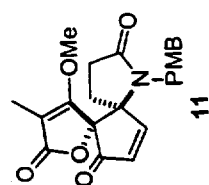
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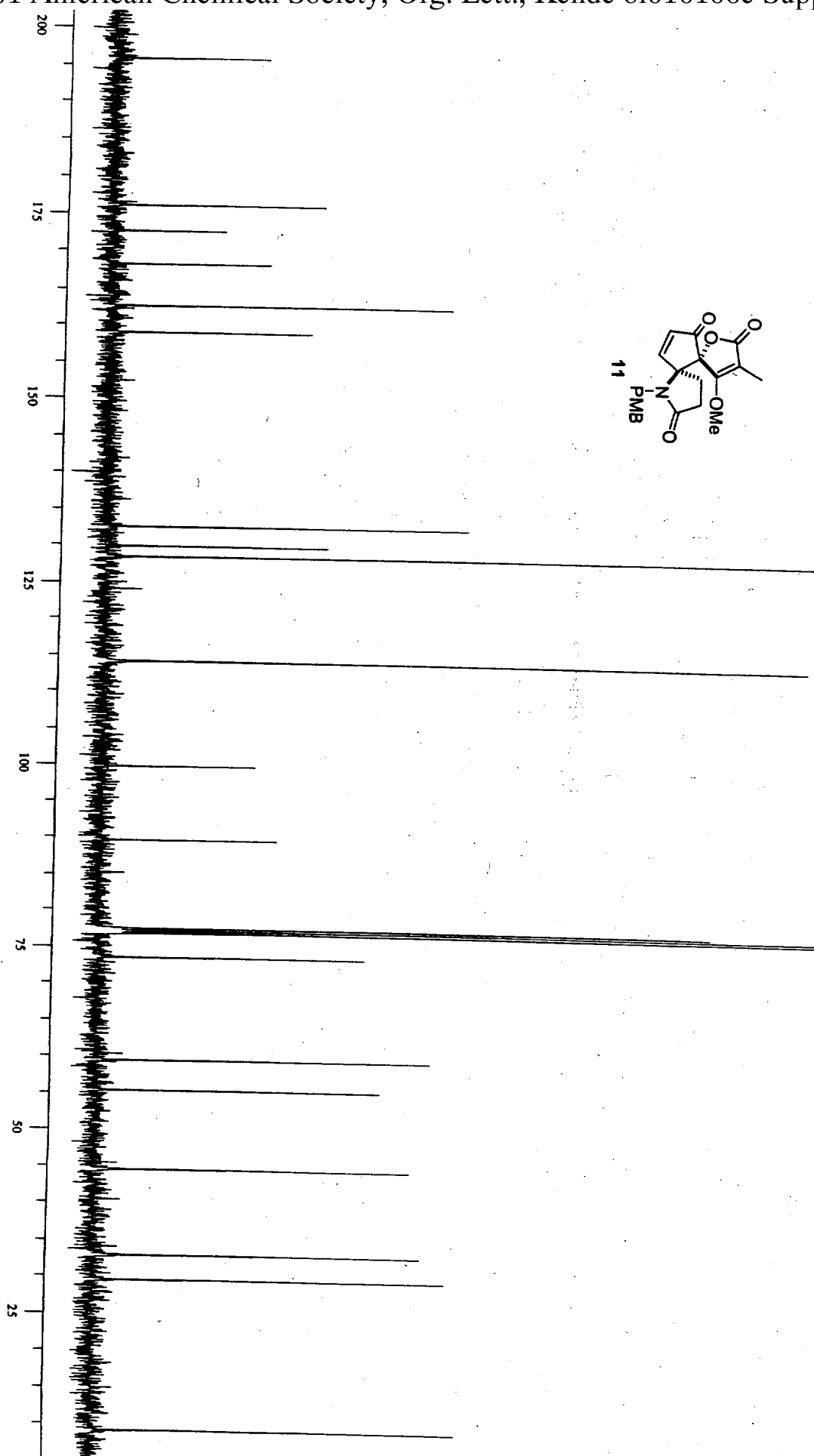


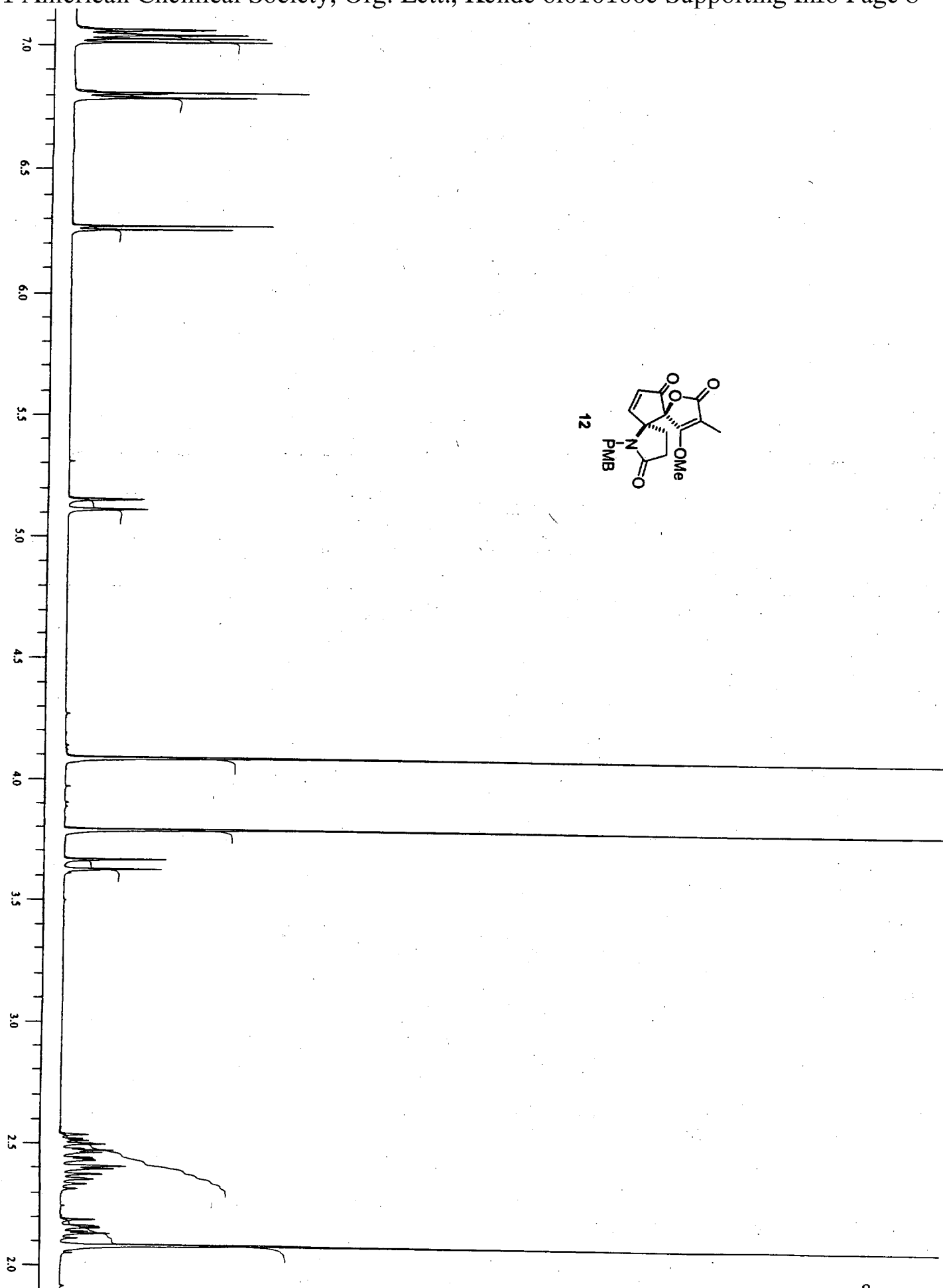
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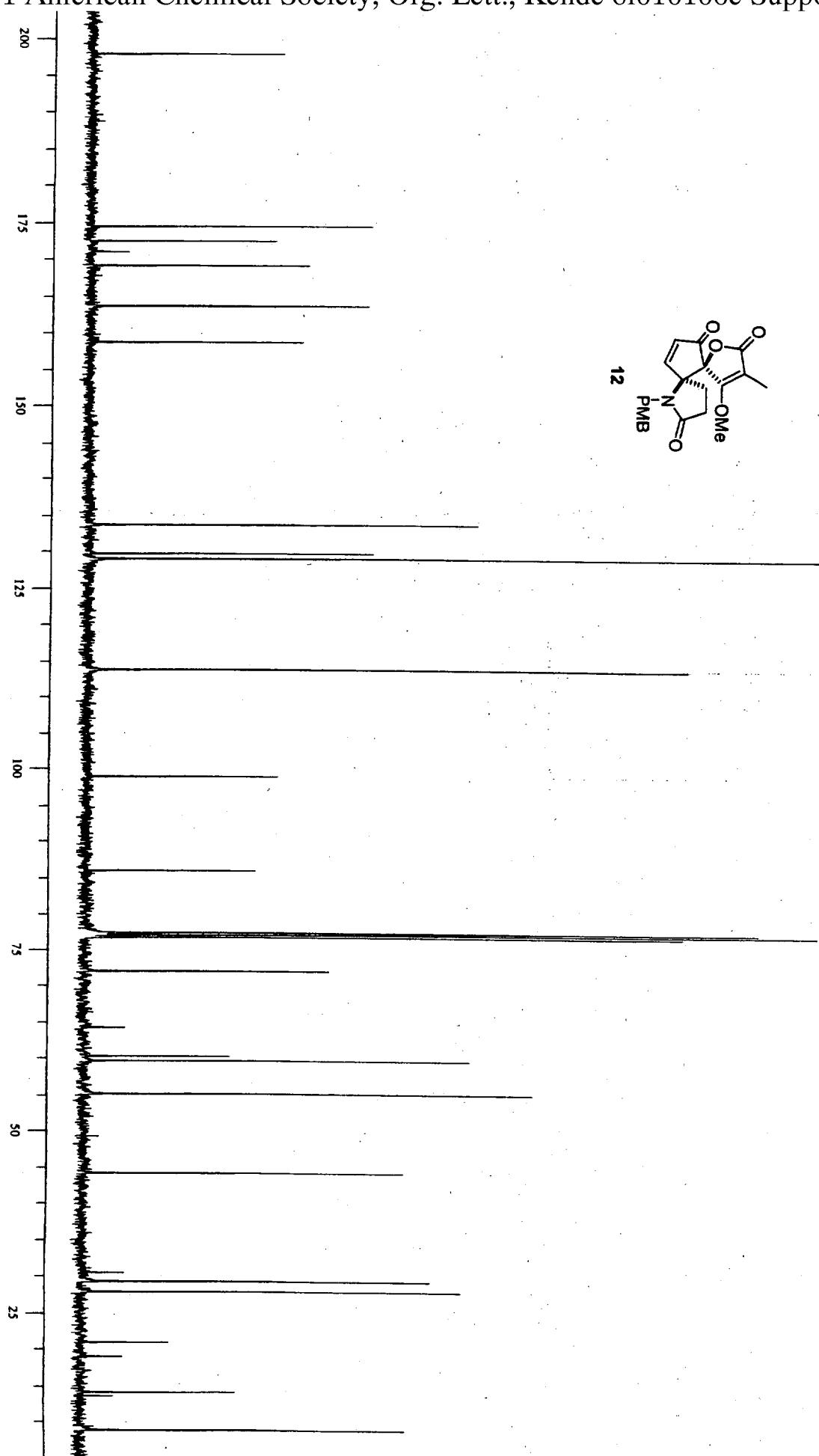


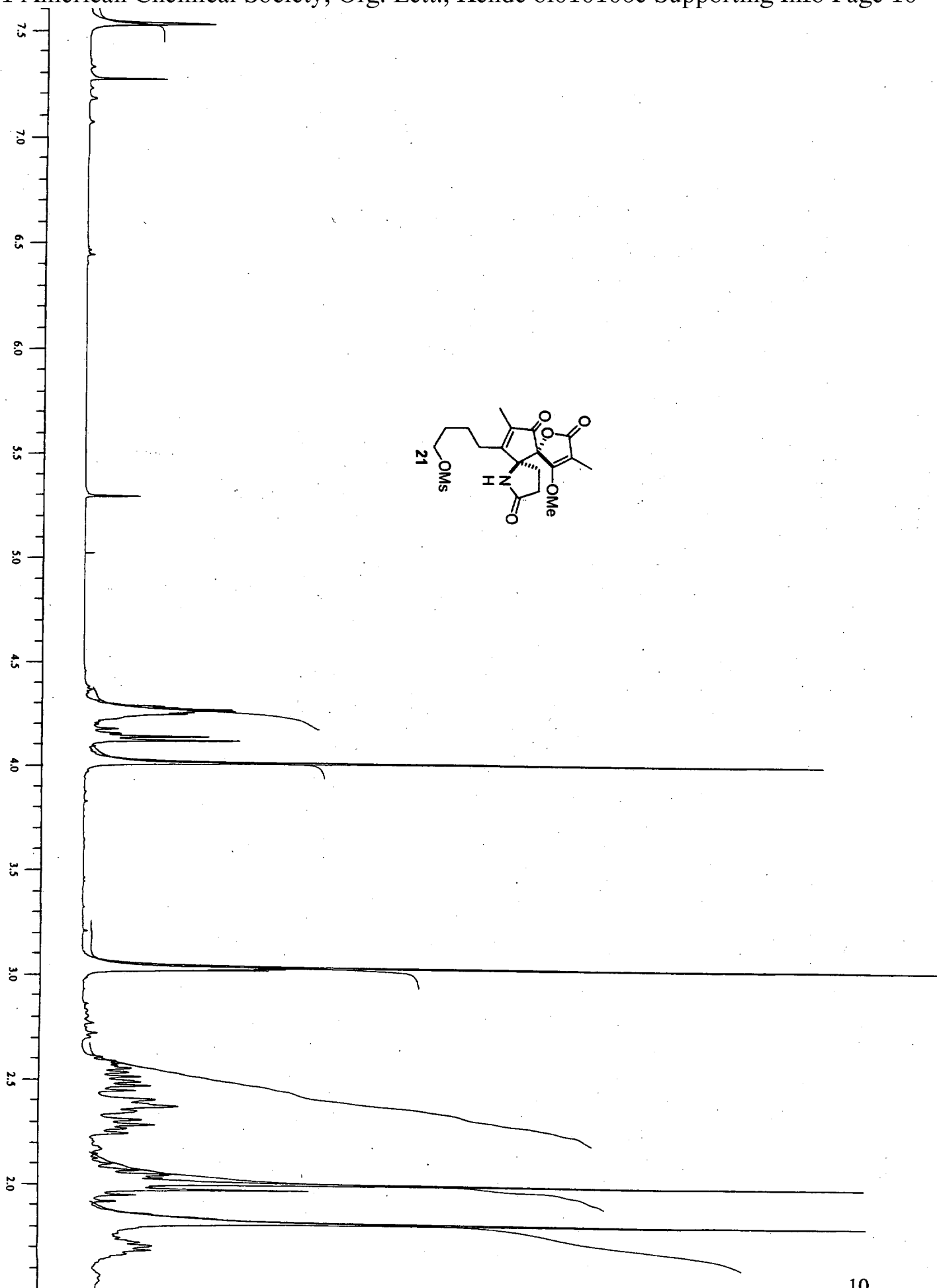
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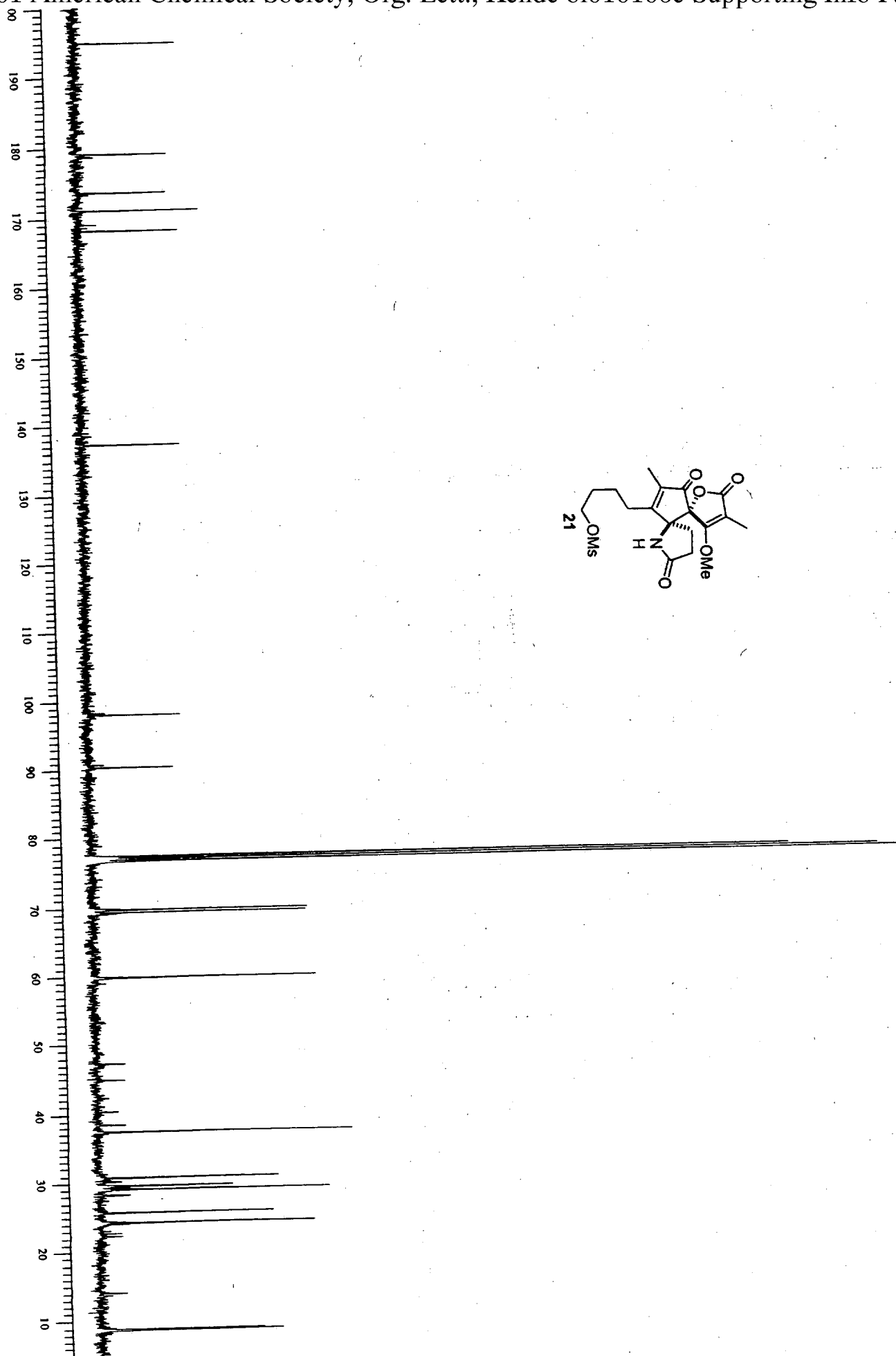


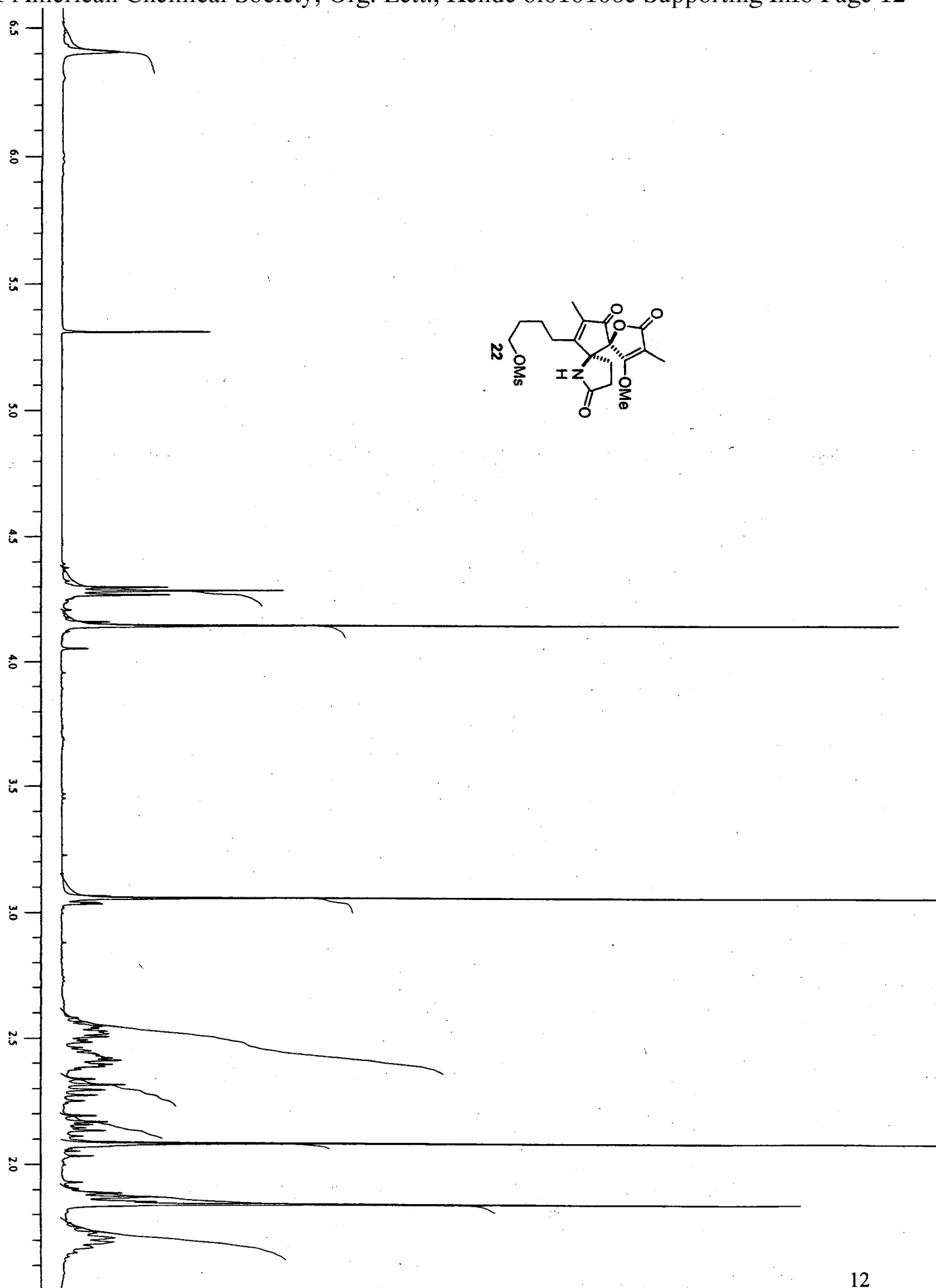


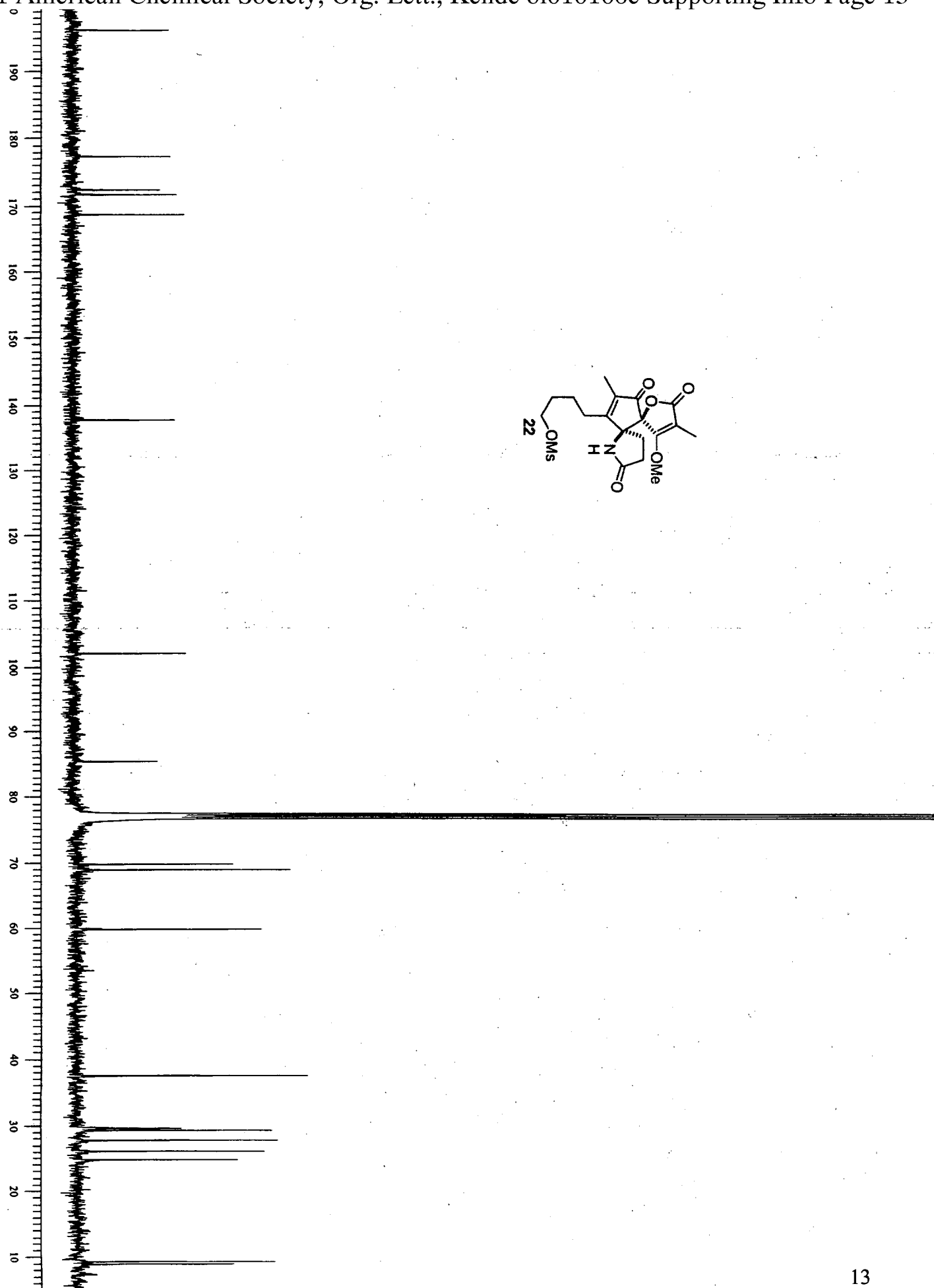


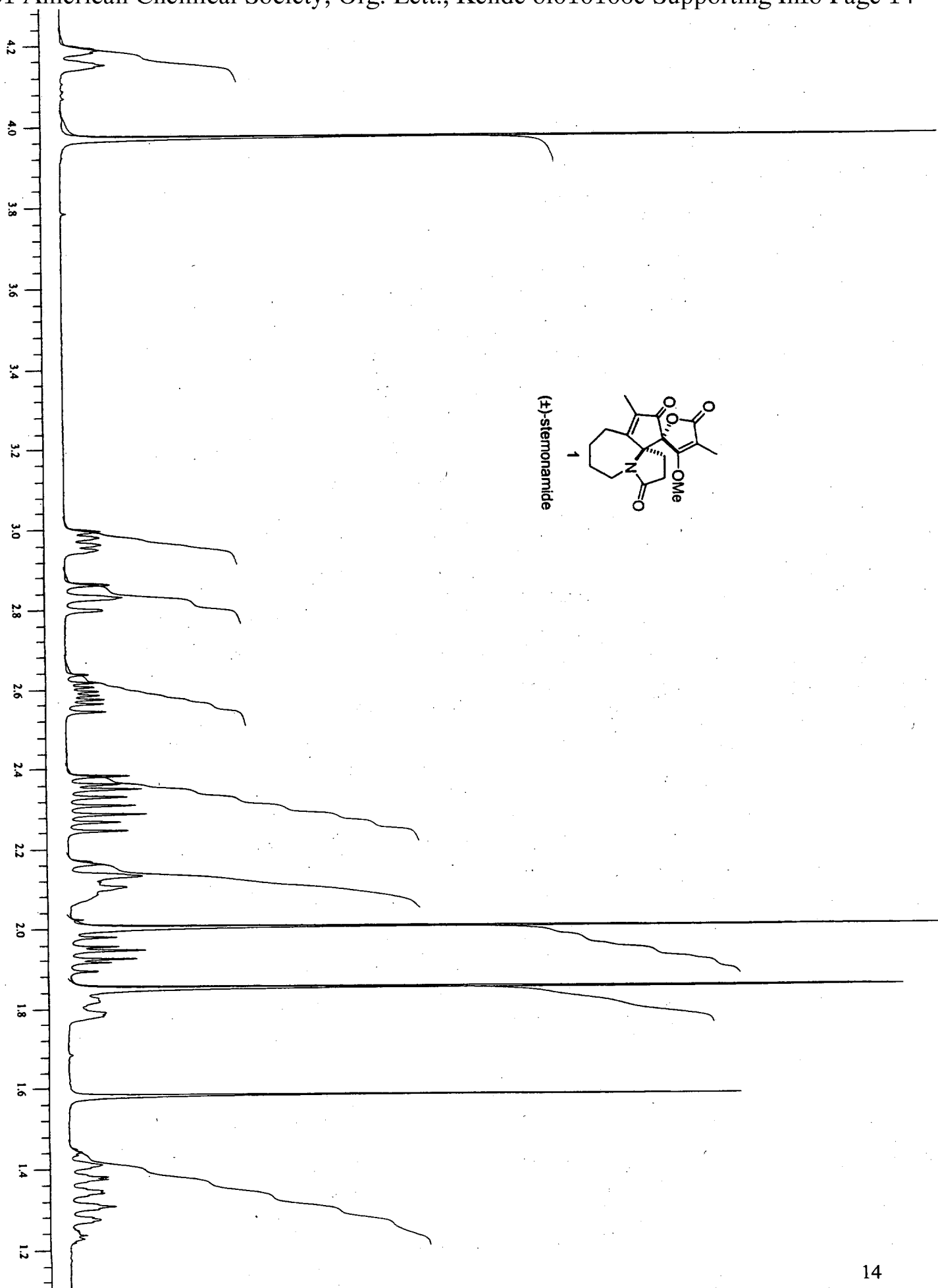


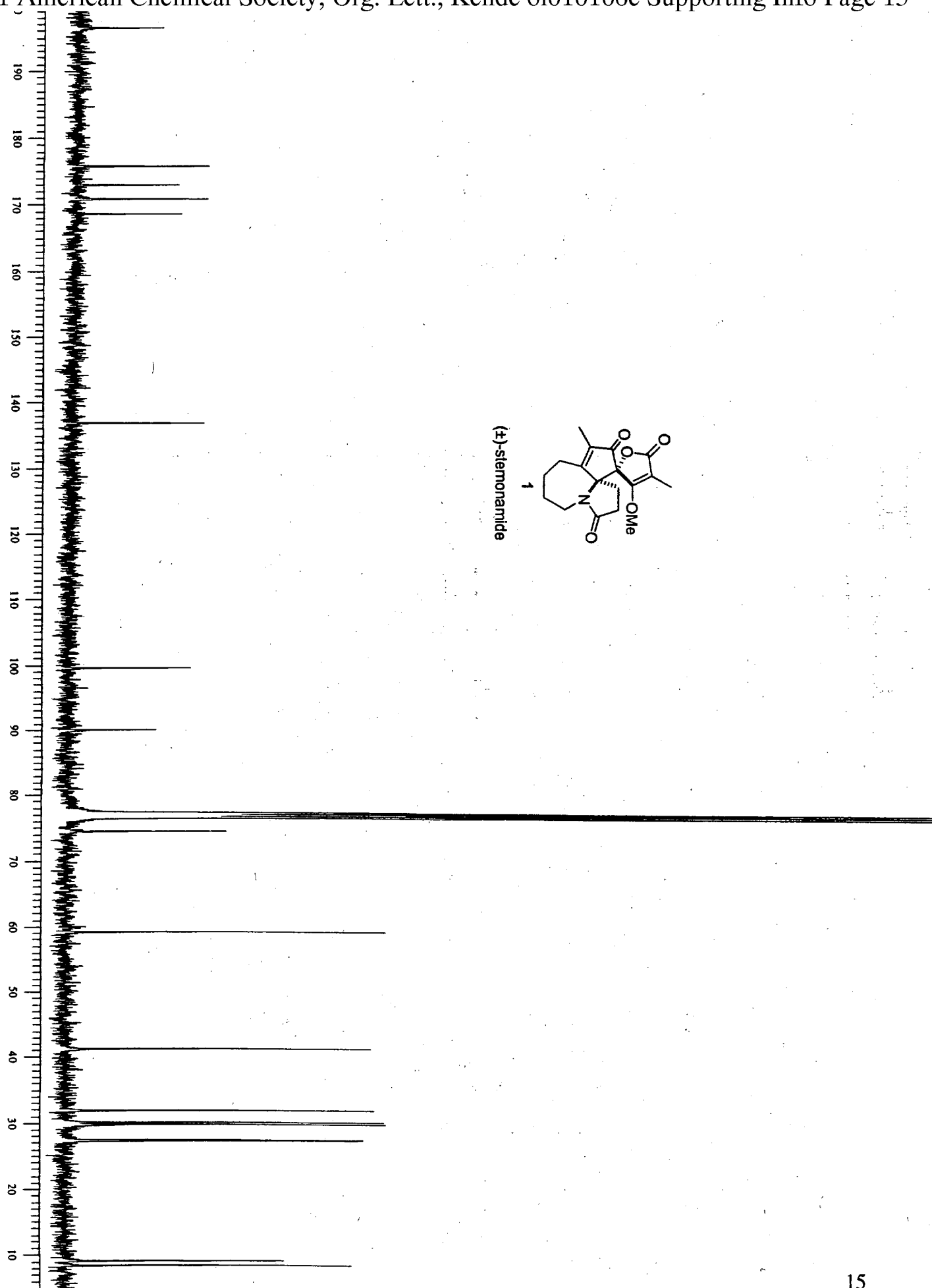


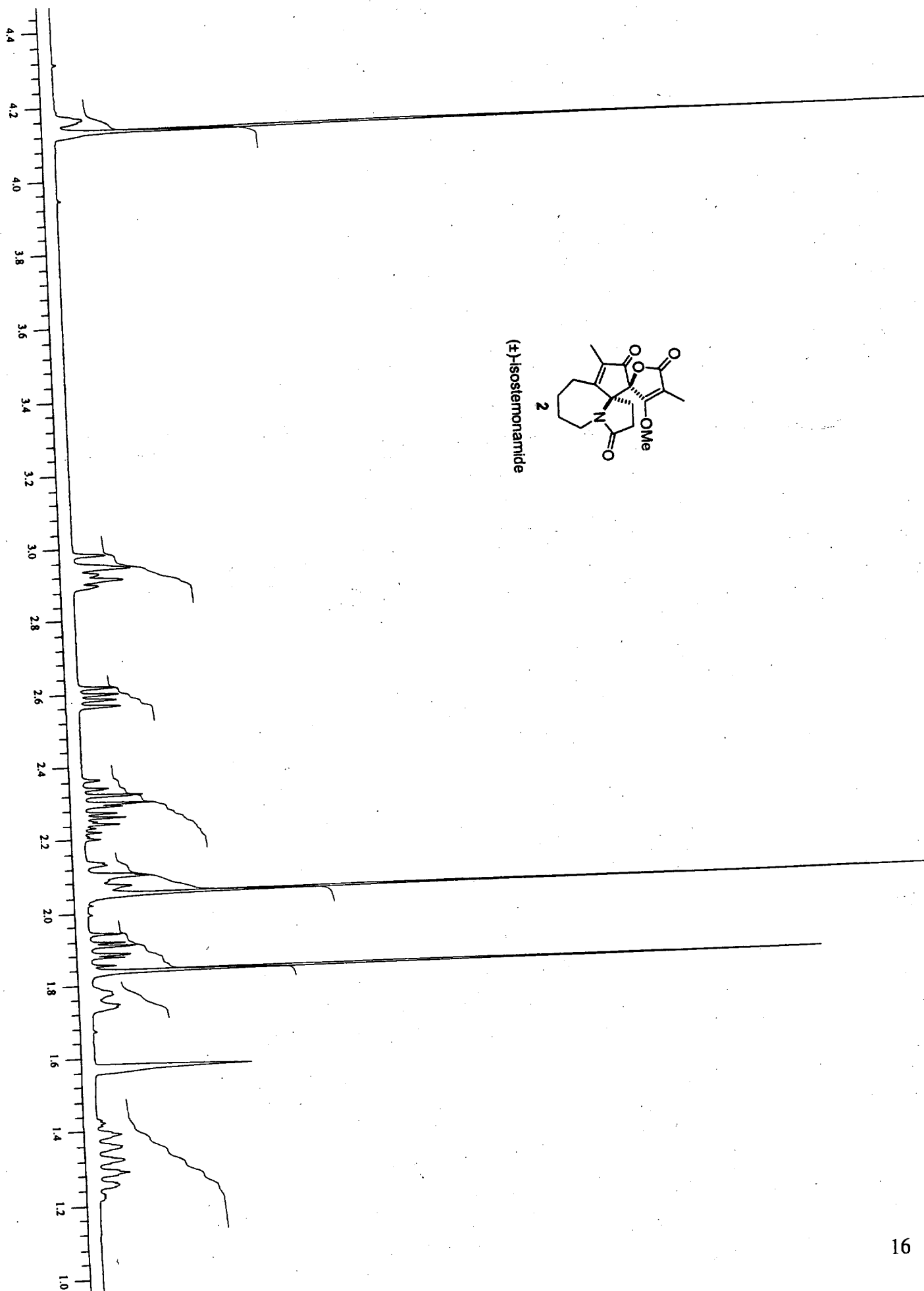


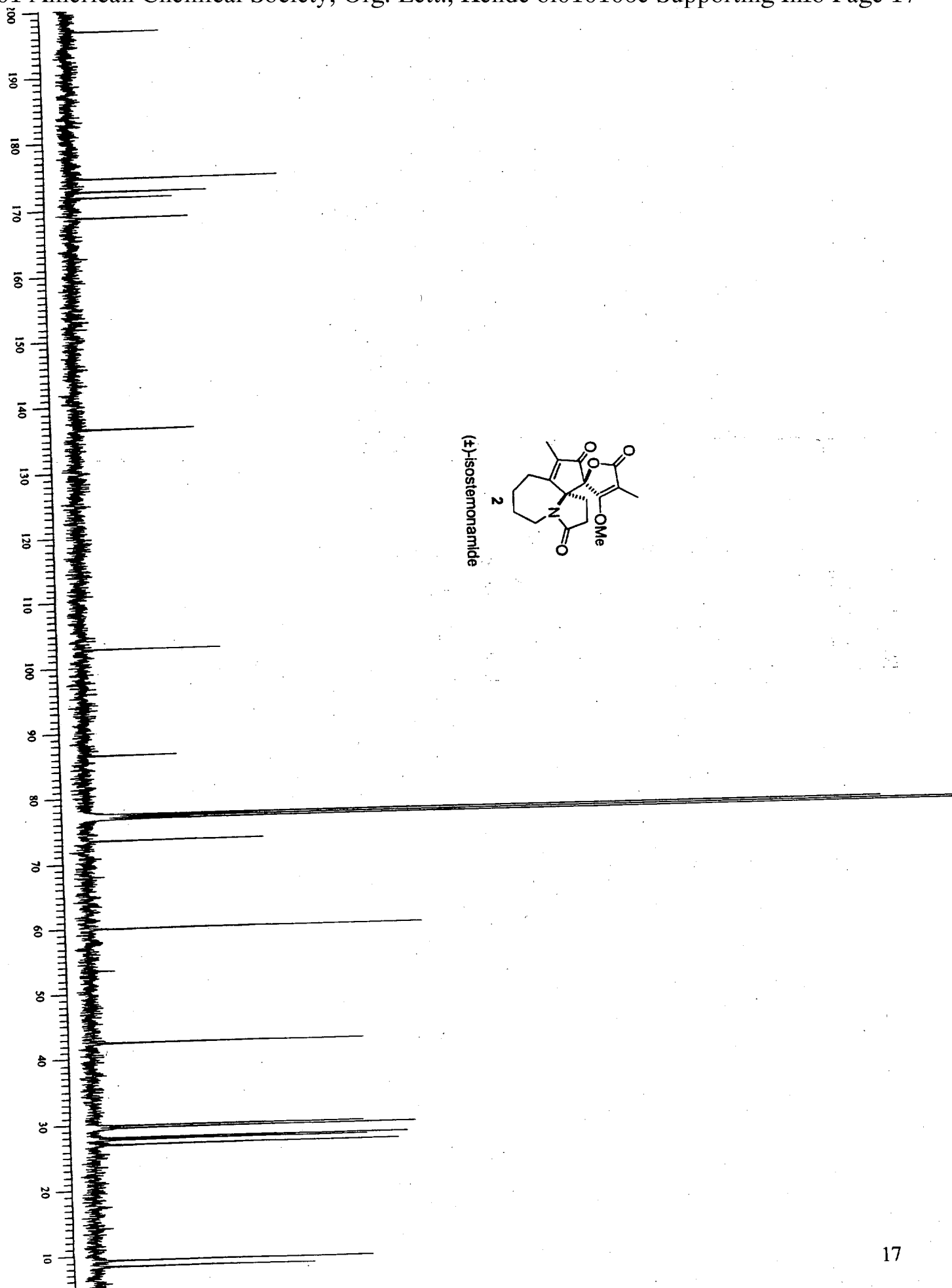


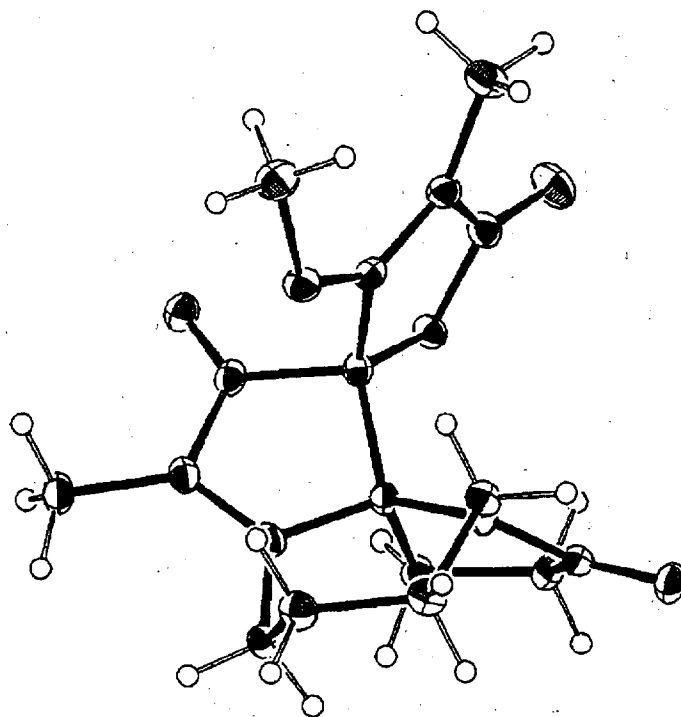




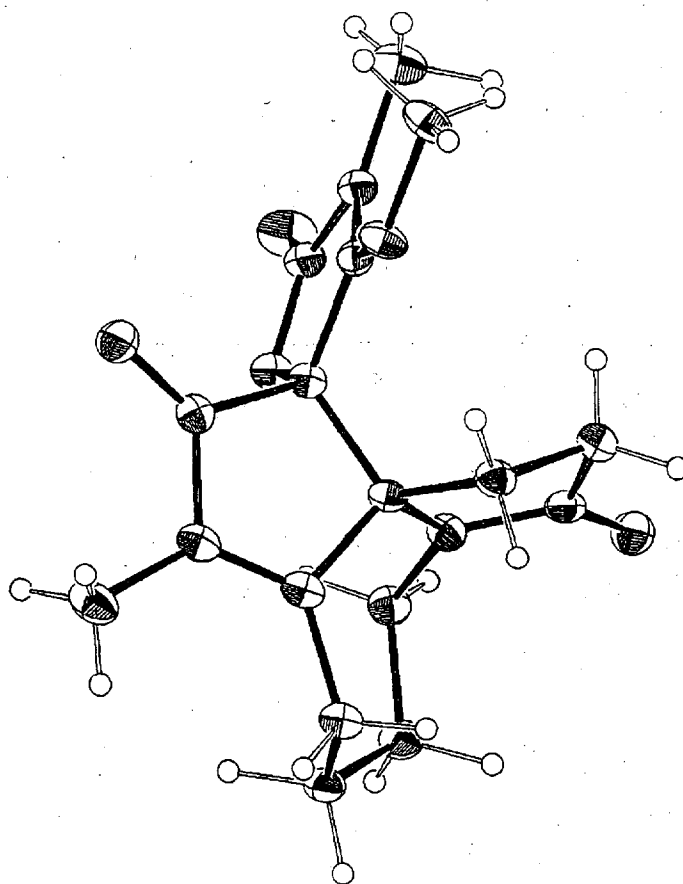








ORTEP plot of (±)-stemonamide (1)



ORTEP plot of (±)-isostemonamide (2)