Supplementary Material (ESI) for Chemical Communications

Stereoselective Synthesis of Spirocyclopentanones *via* N-Heterocyclic Carbene Catalyzed Reaction of Enals and Dienones

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Contents

(1) General remarks: All reactions were carried out in oven-dried glassware. Progress of reactions was monitored by Thin Layer Chromatography while purification was effected by column chromatography, using silica gel (60-120 mesh). Melting points were recorded on a Buchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 (^{1}H) and 75 (^{13}C) MHz respectively on a Brucker Advance DPX-300 MHz. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H) or $CDCl_3$ (^{13}C) as internal standards. IR spectra were recorded on Bomem MB series FT-IR spectrometer, absorbencies are reported in cm^{-1}

(2) General experimental procedures:

(a) *Synthesis of 1,3,4-trisubstituted cyclopentene **4a** and 2,3,4-trisubstituted cyclopentanone **5a***:- DBU (18 mg, 12 mol %) was added to a suspension of the 1,3-dimesityl imidazolium chloride[1] **3** (21 mg, 6 mol %) in 3 ml dry CH_2Cl_2 under argon atmosphere. This was followed by the addition of 4-methoxycinnamaldehyde **1** (162 mg, 1 mmol) and dienone **2** (259 mg, 0.7 mmol) and the resulting solution was stirred for 8h at room temperature (30°C). Initial green colour of the reaction mixture gradually changed into wine red on completion of the reaction. The reaction mixture was then passed through a short pad of Celite®. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60-120 mesh) column using 95:5 hexane-ethyl acetate solvent mixture

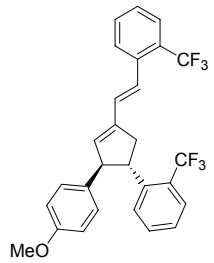
[1] Arduengo, A. J. III.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, 55, 14523.

as eluent to afford **4a** (119 mg, 32% yield, 10:1 dr[2]) & **5a** (109 mg, 32%)**. CCDC** file number for **5a**: 638979.

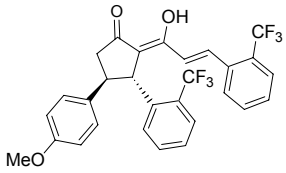
(b) *Synthesis of spirocyclopentanone **8a***:- DBU (18 mg, 12 mol %) was added to a suspension of the 1,3-dimesityl imidazolium chloride **3** (21 mg, 6 mol %) in 3 ml dry CH_2Cl_2 under argon atmosphere. This was followed by the addition of cinnamaldehyde **6** (132 mg, 1 mmol) and dienone **7** (224 mg, 0.7 mmol) and the resulting solution was stirred for 8h at room temperature (30°C). Initial green colour of the reaction mixture gradually changed into wine red on completion of the reaction. The reaction mixture was then passed through a short pad of Celite®. After the removal of the solvent, the residue was subjected to chromatography on a silica gel (60-120 mesh) column using 80:20 hexane-ethyl acetate solvent mixture as eluent to afford **8a** (189 mg, 60%)**. CCDC** file number for **8a**: 653444.

(3) Characterization data for selected compounds

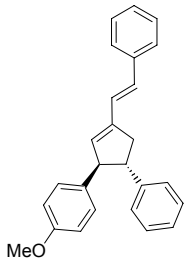
Compound 4a

	Colourless viscous liquid **IR** (Film) ν_{max}: 3031, 2911, 2821, 1618, 1530, 1472, 1275, 1190, 1062 cm^{-1}. **^{1}H NMR**: δ 7.28-7.16 (m, 4H), 6.98-6.95 (m, 3H), 6.85 (d, 1H, J = 17.1 Hz), 6.77-6.67 (m, 4H), 6.56 (d, 2H), 5.99 (s, 1H), 4.12 (s, 1H), 3.73 (s, 3H), 3.34-3.26 (m, 1H), 3.06-2.94 (m, 1H), 2.72-2.69 (m, 1H) **^{13}C NMR**: δ 158.5, 149.0, 142.1, 140.6, 135.9, 134.2, 133.4, 131.6, 129.6, 128.5, 128.4, 127.6, 127.3, 126.9, 125.5, 125.4, 124.5, 122.5, 114.0, 60.1, 55.9, 55.0, 54.9, 54.6, 49.9, 41.5 **HRMS (EI)** for $C_{28}H_{22}F_6O$: Calcd.: 488.1575, found :488.1577

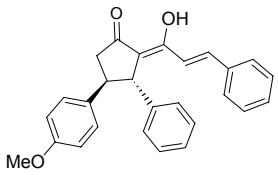
Compound 5a

	Yellow solid. Mp :142-144 °C **IR** (KBr) ν_{max}: 3658, 3032, 2931, 1741, 1640, 1629, 1578, 1510, 1457, 1308, 1245, 1117 cm^{-1}. **^{1}H NMR**: δ 13.81 (s, 1H), 7.81 (d, 1H, *J* = 12.8 Hz), 7.69-7.53 (m, 3H),7.42-7.35 (m, 4H), 7.16 (d, 1H, *J* = 7.3 Hz), 7.01 (d, 2H, *J* = 8.6 Hz), 6.79 (d, 2H, *J* = 8.6 Hz), 6.09 (d, 1H, *J* = 15.5 Hz), 4.60 (d, 1H, *J* = 3.5 Hz), 3.77 (s, 3H), 3.33-3.27 (m, 1H), 3.13 (dd, 1H, J_1 = 18.4 Hz, J_2 = 8.7 Hz), 2.68 (dd, 1H, J_1 = 18.4 Hz, J_2 = 5.3 Hz). **^{13}C NMR**: δ 207.6, 164.6, 158.6, 139.5, 137.5, 131.4, 130.6, 130.0, 129.1, 127.9, 118.1, 117.2, 116.9, 116.7, 115.1, 114.8, 114.7, 113.5, 11.4, 113.1, 113.0, 56.1, 54.2, 52.8, 52.7, 52.3, 51.8, 44.7 **HRMS (EI)** for $C_{29}H_{22}F_6O_3$: Calcd. 532.1473, found : 532.1477

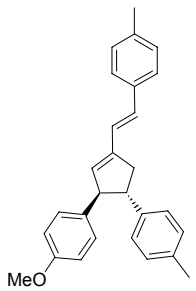
Compound 4b

	Colourless viscous liquid **IR** (Film) ν_{max}: 3026, 2917, 2824, 1620, 1537, 1466, 1271, 1188, 1055 cm^{-1}. **^{1}H NMR**: δ 7.43 (d, 2H, *J* = 10.5 Hz), 7.31-7.17 (m, 8H), 7.03-6.97 (m, 3H), 6.76 (d, 2H, *J* = 8.7 Hz), 6.49 (d, 1H, *J* = 16.2 Hz), 5.87 (s, 1H), 3.99 (d, 1H, *J* = 6.0 Hz), 3.73(s, 3H), 3.35-3.27 (m, 1H), 3.21-3.13 (m, 1H), 2.83-2.75 (m, 1H) **^{13}C NMR**: δ 158.2, 145.3, 142.1, 137.4, 136.8, 133.9, 130.8, 130.0, 129.6, 128.9, 128.6, 128.4, 128.3, 128.2, 127.5, 127.3, 126.4, 126.2, 125.2, 114.1, 113.8, 113.1, 59.9, 55.1, 54.8, 40.1 **HRMS (EI)** for $C_{26}H_{24}O$: Calcd.: 352.1827, found : 352.1821

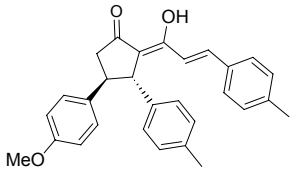
Compound 5b

	Yellow viscous liquid **IR** (Film) ν_{max} : 3674, 3026, 2954, 2828, 1737, 1645, 1581, 1514, 1454, 1361, 1246, 1178 cm^{-1}. **^{1}H NMR**: δ 13.9 (s, 1H), 7.45 (d, 1H, *J* = 15.7 Hz), 7.31-7.14 (m, 8H), 7.08-7.02 (m, 4H), 6.80 (d, 2H, *J* = 8.5 Hz), 5.99 (d, 1H, *J* = 15.8 Hz), 4.11 (d, 1H, *J* = 6.89 Hz), 3.78 (s, 3H), 3.35-3.27 (m, 1H), 2.97 (dd, 1H, J_1 = 18.2 Hz, J_2 = 8.5 Hz), 2.73 (dd, 1H, J_1 = 18.1 Hz, J_2 = 8.7 Hz) **^{13}C NMR**: δ 207.8, 167.2, 157.9, 144.5, 139.6, 133.9, 129.9, 129.6, 128.9, 128.7, 128.6, 128.4, 128.3, 128.0, 127.7, 127.6, 127.5, 127.3, 126.8, 119.8, 113.9, 113.8, 55.8, 50.7, 44.4, 40.1. **HRMS (EI)** for $C_{27}H_{24}O_3$: Calcd. : 396.1725, found : 396.1729

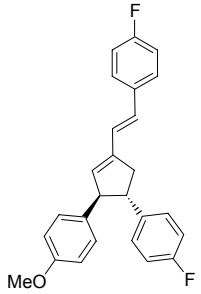
Compound 4c

	Colourless viscous liquid **IR** (Film) ν_{max}: 3033, 2911, 1607, 1518, 1457, 1301, 1224, 1171, 1101 cm^{-1}. **^{1}H NMR**: δ 7.30 (d, 2H, *J* = 8.0 Hz), 7.12-6.97 (m, 9H), 6.79 (d, 2H, *J* = 9.7 Hz), 6.46 (d, 1H, *J* = 16.1 Hz), 5.89 (s, 1H), 3.96 (d, 1H, *J* = 6.1 Hz), 3.74 (s, 3H), 3.31-3.23 (m, 1H), 3.18 – 3.10 (m, 1H), 2.79-2.72 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H) **^{13}C NMR**: δ 158.4, 142.5, 142.4, 137.4, 137.3, 135.7, 134.9, 13.6, 130.1, 129.9, 129.6, 129.3, 128.5, 127.5, 126.6, 124.7, 124.5, 113.9, 110.9, 60.1, 55.5, 54.7, 40.4, 21.5, 21.3 **HRMS (EI)** for $C_{28}H_{28}O$: Calcd.: 380.2140, found : 380.2135

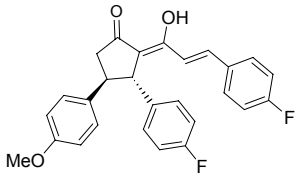
Compound 5c

	Yellow viscous liquid **IR** (Film) ν_{max}: 3668, 3022, 1685, 1641, 1612, 1582, 1513, 1461, 1372, 1247, 1181, 1036 cm^{-1}. **^{1}H NMR**: δ 13.9 (s, 1H), 7.42 (d, 2H, *J* = 15.5 Hz), 7.11-6.98 (m, 9H), 6.79 (d, 2H, *J* = 8.6 Hz), 5.96 (d, 1H, *J* = 15.8 Hz), 4.08 (d, 1H, *J* = 6.7 Hz), 3.78 (s, 3H), 3.32-3.25 (m, 1H), 2.96 (dd, 1H, J_1 = 18.2 Hz, J_2 = 8.6 Hz), 2.70 (dd, 1H, J_1 = 18.1 Hz, J_2 = 8.4 Hz), 2.33 (s, 3H), 2.30 (s, 3H) **^{13}C NMR**: δ 208.1, 167.9, 158.7, 141.9, 140.3, 139.9, 136.6, 135.7, 132.9, 132.0, 130.0, 129.8, 129.7, 129.5, 129.3, 128.9, 128.6, 128.3, 128.1, 127.8, 119.2, 114.3, 113.9, 55.4, 54.2, 50.9, 44.7, 21.8, 21.4 **HRMS (EI)** for $C_{29}H_{28}O_3$: Calcd. : 424.2038, found : 424.2045

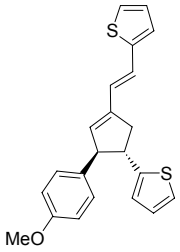
Compound 4d

	Colourless viscous liquid **IR** (Film) ν_{max}: 3034, 2908, 1604, 1508, 1462, 1300, 1228, 1190, 1047 cm^{-1}. **^{1}H NMR**: δ 7.40-7.36 (m, 2H), 7.16-7.11 (m, 2H), 7.03-6.94 (m, 7H), 6.78 (d, 2H, *J* = 8.5 Hz), 6.46 (d, 1H, *J* = 16.1 Hz), 5.86 (s, 1H), 3.92 (d, 1H, *J* = 5.9 Hz), 3.76 (s, 3H), 3.33-3.25 (m, 1H), 3.19-3.11 (m, 1H), 2.78-2.70 (m, 1H) **^{13}C NMR**: δ 164.2, 163.3, 160.9, 160.1, 158.6, 142.1, 141.1, 141.0, 136.7, 134.1, 133.8, 133.7, 129.8, 1291, 128.9, 128.8, 128.1, 128.0, 125.1, 116.0, 115.7, 115.6, 115.3, 114.1, 60.3, 55.4, 40.3 **HRMS (EI)** for $C_{26}H_{22}F_2O$: Calcd. : 388.1639, found : 388.1620

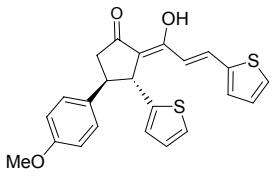
Compound 5d

	Yellow viscous liquid **IR** (Film) ν_{max}: 3674, 3041, 2964, 1671, 1645, 1598, 1511, 1464, 1373, 1306, 1239, 1179, 1157, 1032 cm^{-1}. **^{1}H NMR**: δ 13.94 (s, 1H), 7.43(d, 1H, *J* = 15.7 Hz), 7.13-6.91 (m, 10 H), 6.81 (d, 2H, *J* = 8.5 Hz), 5.88 (d, 1H, *J* = 15.8 Hz), 4.1 (d, 1H, *J* = 7.0 Hz), 3.78 (s, 3H), 3.27-3.18 (m, 1H), 2.94 (dd, 1H, J_1 = 18.0 Hz, J_2 = 8.4 Hz), 2.73 (dd, 1H, J_1 = 18.2 Hz, J_2 = 9.1 Hz) **^{13}C NMR**: δ 207.6, 167.2, 158.6, 140.2, 138.6, 134.5, 131.4, 129.6, 129.5, 129.0, 128.9, 128.1, 119.3, 116.1, 115.9, 115.8, 115.6, 114.6, 114.1, 113.4, 55.2,53.6, 51.0, 44.4 **HRMS (EI)** for $C_{27}H_{22}F_2O_3$: Calcd. : 432.1537, found : 432.1555

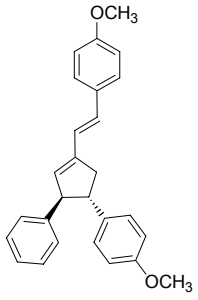
Compound 4e

	Colourless viscous liquid **IR** (Film) ν_{max}: 3037, 2910, 1606, 1510, 1465, 1302, 1230, 1190, 1060 cm^{-1}. **^{1}H NMR**: δ 7.15-7.05 (m, 4H), 6.97-6.94 (m, 2H), 6.89-6.87 (m, 1H), 6.82-6.79 (m, 3H), 6.73-6.62 (m, 2H), 5.84 (s, 1H), 3.99 (d, 1H, *J* = 7.3 Hz), 3.77 (s, 3H), 3.59 (m, 1H), 3.23-3.15 (m, 1H), 2.83-2.75 (m, 1H) **^{13}C NMR**: δ 158.4, 148.2, 142.9, 141.4, 135.9, 133.7, 129.5, 128.5, 127.6, 126.6, 125.9, 124.5, 124.3, 123.6, 123.2, 122.9, 113.8, 113.2, 60.1, 55.1, 50.2, 4.07 **HRMS (EI)** for $C_{22}H_{20}O_3S_2$: Calcd.: 364.0956, found : 364.0952

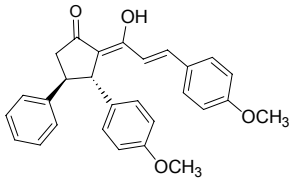
Compound 5e

	Yellow viscous liquid **IR** (Film) ν_{max}: 3674, 3070,2963, 1670, 1633, 1609, 1583, 1513, 1424, 1366, 1301, 1247, 1180, 1033 cm^{-1}. **^{1}H NMR**: δ 13.8 (s, 1H), 7.62 (d, 1H, J = 15.4 Hz), 7.26 (d, 1H, 3.5 Hz), 7.18 (d, 1H, J = 4.9 Hz), 7.09-7.06 (m, 3H), 6.97-6.90 (m, 2H), 6.83-6.80 (m, 3H), 6.02 (d, 1H, J = 15.4 Hz0, 4.35 (d, 1H, J = 5.8 Hz), 3.78 (s, 3H), 3.44-3.37 (m, 1H), 3.01 (dd, 1H, J1 = 18.2 Hz, J2 = 7.6 Hz), 2.69 (dd, 1H, J1 = 18.2 Hz, J2 = 7.6 Hz) **^{13}C NMR**: δ 206.7, 167.5, 158.5, 148.7, 141.0, 134.9, 132.6, 130.3, 130.1, 128.3, 128.1, 127.9, 126.8, 124.5, 124.3, 118.4, 114.5, 114.1, 113.6, 55.1, 50.9, 49.3, 43.9 **HRMS (EI)** for $C_{23}H_{20}O_3S_2$: Calcd. : 408.0854, found : 408.0870

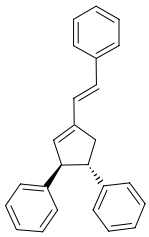
Compound 4f

	Colourless viscous liquid **IR** (Film) ν_{max}: 3019, 2914, 2831, 1617, 1542, 1474, 1269, 1168, 1061 cm^{-1}. **^{1}H NMR**: δ 7.35 (d, 2H, *J* = 8.7 Hz), 7.23-7.19 (m, 3H), 7.12-7.06 (m, 4H), 6.93 (d, 1H, *J* = 16.1 Hz), 6.86-6.78 (m, 4H), 6.46 (d, 1H, *J* = 16.1 Hz), 5.84 (s, 1H), 3.98 (d, 1H, *J* = 5.9 Hz), 3.80 (s, 3H), 3.77 (s, 3H), 3.31-3.26 (m, 1H), 3.19-3.11 (m, 1H), 2.80-2.75 (m, 1H) **^{13}C NMR**: δ 159.1, 158.0, 144.9, 142.6, 137.4, 132.4, 130.2, 129.6, 129.3, 128.8, 128.4, 128.2, 127.6, 127.4, 126.3, 123.2, 114.1, 113.8, 112.9, 60.7, 55.2, 53.9, 40.3 **HRMS (EI)** for $C_{27}H_{26}O_2$: Calcd.: 382.1933, found : 382.1940

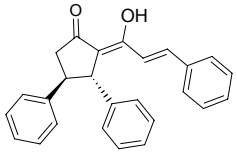
Compound 5f

	Yellow viscous liquid **IR** (Film) ν_{max}: 3662, 3026, 2954, 2828, 1737, 1645, 1581, 1514, 1454, 1361, 1246, 1178 cm^{-1}. **^{1}H NMR**: δ 14.03 (s, 1H), 7.43 (d, 1H, *J* = 15.7Hz), 7.27-7.22 (m, 3H), 7.14-7.05 (m, 6H), 6.82 (d, 2H, *J* = 8.6 Hz), 6.75 (d, 2H, *J* = 8.7 Hz), 5.90 (d, 1H, *J* = 15.7 Hz), 4.11 (d, 1H, *J* = 6.4 Hz), 3.77 (s, 6H), 3.33-3.25 (m, 1H), 2.97 (dd, 1H, J_1 = 14.8 Hz, J_2 = 8.3 Hz), 2.72 (dd, 1H, J_1 = 18.1 Hz, J_2 = 8.2 Hz) **^{13}C NMR**: δ 207.2, 168.2, 161.0, 158.5, 143.5, 139.5, 136.7, 129.5, 128.7, 128.5, 128.1, 127.1, 126.8, 117.4, 114.2, 113.3, 113.1, 55.2, 53.4, 51.4, 44.2 **HRMS (EI)** for $C_{28}H_{26}O_4$: Calcd. : 426.1831, found : 426.1825

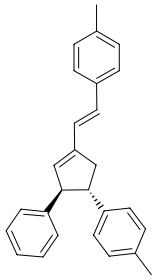
Compound 4g

	Colourless viscous liquid **IR** (Film) ν_{max}: 3021, 2917, 1611, 1521, 1443, 1308, 1227, 1173, 1109 cm^{-1}. **^{1}H NMR**: δ 7.41 (d, 2H, *J* = 7.7 Hz), 7.32-7.19 (m, 10H), 7.09-6.97 (m, 4H), 6.50 (d, 1H, *J* = 16.1Hz), 5.9 (s, 1H), 4.04 (d,1H, *J* = 5.8 Hz), 3.37-3.32 (m, 1H), 3.24-3.15 (m, 1H), 2.85-2.78 (m, 1H) **^{13}C NMR**: δ 145.3, 144.7, 142.4, 141.5, 137.4, 133.5, 130.1, 128.7, 128.6, 128.5, 128.4, 127.7, 127.5, 127.4, 127.3, 126.4, 126.3, 125.8, 125.1, 60.7, 54.6, 40.2 **HRMS (EI)** for $C_{25}H_{22}$: Calcd.: 322.1721, found : 322.1718

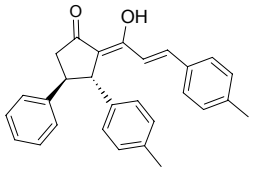
Compound 5g

	Yellow viscous liquid **IR** (Film) ν_{max}: 3654, 3060, 3031, 1925, 1679, 1610, 1581, 1494, 1455, 1367, 1236, 1118 cm^{-1}. **^{1}H NMR**: δ 13.88 (s, 1H), 7.29-7.07 (m, 16H), 5.99 (d, 1H, *J* = 15.8Hz), 4.17 (d, 1H, *J* = 6.6 Hz), 3.39-3.31 (m, 1H), 3.04-2.95 (m, 1H), 2.81-2.72 (m, 1H) **^{13}C NMR**: δ 207.8, 167.4, 144.5, 143.1, 139.8, 135.2, 129.7, 129.1, 128.9, 128.7, 128.5, 128.3, 127.8, 127.5, 127.1, 126.9, 126.8, 126.4, 119.8, 113.6, 54.1, 51.3, 44.3 **HRMS (EI)** for $C_{26}H_{22}O_2$: Calcd. : 366.1620, found : 366.1618

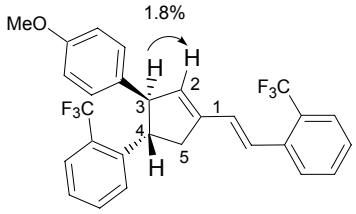
Compound 4h

	Colourless viscous liquid **IR** (Film) ν_{max}: 3022, 2911, 2832, 1614, 1547, 1472, 1269, 1179, 1062 cm^{-1}. **^{1}H NMR**: δ 7.35-6.99 (m, 14H), 6.47 (d, 1H, *J* = 16.1 Hz), 5.86 (s, 1H), 4.01 (d, 1H, *J* = 6.0 Hz), 3.35-3.28 (m, 1H), 3.20-3.12 (m, 1H), 2.81-2.74 (m, 1H), 2.33 (s, 3H), 2.31 (s, 3H) **^{13}C NMR**: δ 144.9, 142.6, 142.3, 137.2, 135.6, 134.7, 133.0, 130.0, 129.4, 129.1, 128.8, 128.3, 128.2, 127.7, 127.4, 127.2, 126.3, 124.3, 60.6, 54.3, 40.3, 21.3, 21.1 **HRMS (EI)** for $C_{27}H_{26}$: Calcd.: 350.2034, found : 350.2032

Compound 5h

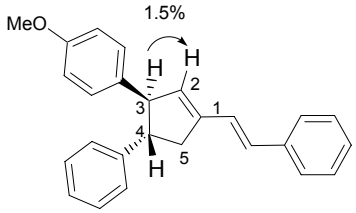
	Yellow viscous liquid **IR** (Film) ν_{max}: 3654, 3060, 3031, 1925, 1679, 1610, 1581, 1494, 1455, 1367, 1236, 1118 cm^{-1}. **^{1}H NMR**: δ 13.93 (s, 1H), 7.41 (d, 1H, *J* = 15.7 Hz, 7.26-7.21 (m, 3H), 7.13-6.99 (m, 10 H), 5.95 (d, 1H, *J* = 15.8 Hz), 4.12 (d, 1H, *J* = 6.3 Hz), 3.35-3.28 (m, 1H), 2.97 (dd, 1H, J_1 = 18.1 Hz, J_2 = 8.1 Hz), 2.72 (dd, 1H, J_1 = 18.2 Hz, J_2 = 8.1 Hz), 2.31 (s, 3H), 2.28 (s, 3H) **^{13}C NMR**: δ 207.8, 167.9, 143.7, 141.8, 140.2, 139.9, 136.5, 132.9, 129.8, 129.7, 129.3, 128.9, 128.7, 128.1, 127.7, 127.2, 119.1, 113.7, 53.9, 51.5, 44.5, 21.7, 21.3 **HRMS (EI)** for $C_{28}H_{26}O_2$: Calcd. : 394.1933, found : 394.1927

^{1}H nOe Studies of compound 4a



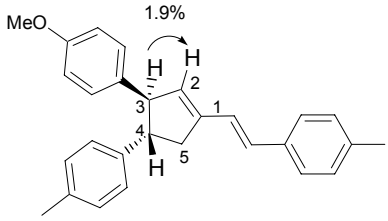
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 4.12) causes an nOe enhancement of 1.8% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4b



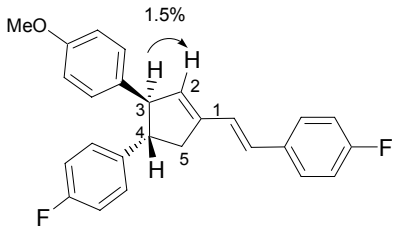
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 3.99) causes an nOe enhancement of 1.5% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4c



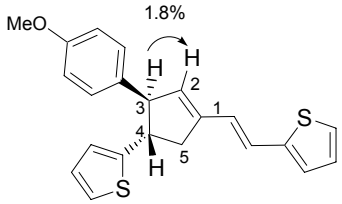
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 3.96) causes an nOe enhancement of 1.9% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4d



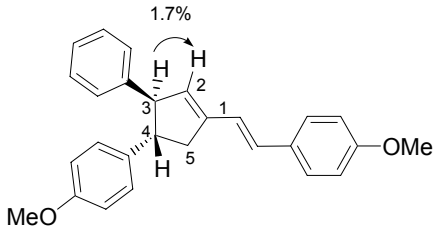
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 3.92) causes an nOe enhancement of 1.5% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4e



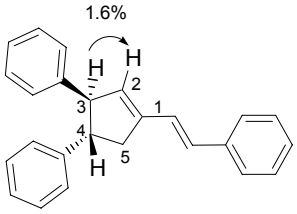
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 3.99) causes an nOe enhancement of 1.8% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4f



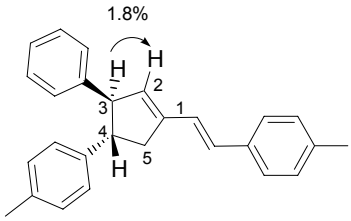
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 3.98) causes an nOe enhancement of 1.7% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4g



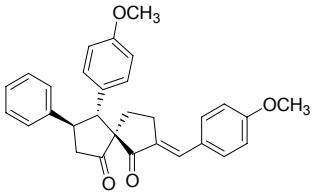
The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 4.04) causes an nOe enhancement of 1.6% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

^{1}H nOe Studies of compound 4h

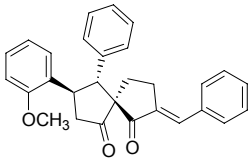


The relative stereochemistry of C3-H and C4-H is established from ^{1}H nOe studies. Irradiation of C3-H (δ 4.01) causes an nOe enhancement of 1.8% to C2-H signal while did not show any nOe at C4-H, which implies their trans relationship.

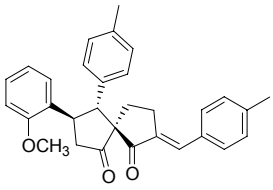
Compound 8a

	Yellow solid. Mp : 169-171 °C **IR** (KBr) ν_{max}: 3024, 2914, 1741, 1689, 1614, 1587, 1512, 1457, 1303, 1257, 1170, 1078 cm^{-1}. **^{1}H NMR**: δ 7.47–7.42 (m, 3H), 7.32-7.22 (m, 5H), 7.16 (d, 1H, *J* = 7.2 Hz) , 7.03 (d, 2H, *J* = 8.6 Hz), 6.94-6.88 (m, 2H), 6.71 (d, 2H, *J* = 8.6 Hz), 4.42 (d, 1H, *J* = 12.2 Hz), 3.83 (s, 3H), 3.70-3.67 (m, 4H), 3.09-2.86 (m, 2H), 2.77-2.71 (m, 1H), 2.67-2.56 (m, 1H), 2.19-2.16 (m, 1H), 1.66-1.62 (m, 1H) **^{13}C NMR**: 213.5, 204.4, 160.9, 158.5, 140.7, 135.2, 134.6, 133.3, 133.1, 132.7, 132.5, 129.9, 129.1, 128.8, 128.7, 128.1, 127.5, 126.9, 114.3, 114.2, 113.8, 70.1, 55.3, 54.9, 54.3, 47.9, 43.5, 27.1. **HRMS (EI)** for $C_{30}H_{28}O_4$ Calcd: 452.1988, found: 452.1976

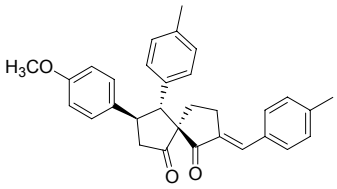
Compound 8b

	White solid. Mp : 172-174 °C **IR** (KBr) ν_{max}: 3027, 2925, 1740, 1684, 1618, 1588, 1490, 1301, 1248, 1181, 1095 cm^{-1}. **^{1}H NMR**: δ 7.48-7.46 (m, 3H), 7.37-7.26 (m, 4H), 7.16-7.09 (m, 6H), 6.85-6.79 (m, 2H), 4.64 (d, 1H, *J* = 12.7 Hz), 4.19-4.17 (m, 1H), 3.86 (s, 3H), 3.06-2.96 (m, 2H), 2.59-2.48 (m, 2H), 2.18-2.17 (m, 1H), 1.65-1.60 (m, 1H). **^{13}CNMR:** 214.1, 204.9, 157.5, 137.2, 135.8, 135.3, 134.3, 130.8, 129.6, 128.7, 128.6, 128.4, 127.7, 127.1, 126.9, 120.9, 110.4, 69.9, 55.3, 52.7, 46.5, 35.6, 27.0. **HRMS (EI)** for $C_{29}H_{26}O_3$: Calcd: 422.1882, found: 422.1888

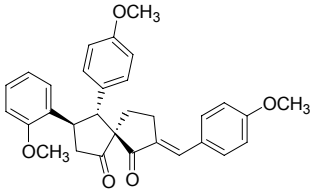
Compound 8c

	White solid. Mp : 202-204 °C **IR** (KBr) ν_{max}: 3026, 2914 1732, 1695, 1624, 1602, 1494, 1301, 1244, 1176, 1099 cm^{-1}. **^{1}H NMR**: δ 7.43-7.37 (m, 3H), 7.29-7.25 (m, 3H), 7.18-7.12 (m, 3H), 7.03-6.94 (m, 3H), 6.83-6.80(m, 2H), 4.59 (d, 1H, *J* = 12.8 Hz), 4.15-4.13 (m, 1H), 3.88 (s, 3H), 3.03-2.95 (m, 2H), 2.57-2.47 (m, 2H), 2.37 (s, 3H), 2.21 (s, 3H), 2.17-2.16 (m, 1H), 1.66-1.62 (m, 1H) . **^{13}CNMR:** 214.4, 205.1, 157.5, 139.9, 136.3, 134.8, 134.3, 134.1, 132.6, 130.9, 129.4, 129.1, 128.8, 128.6, 127.6, 127.1, 120.9, 110.3, 69.9, 55.3, 52.4, 46.6, 35.6, 26.9, 26.8, 21.5. **HRMS (EI)** for $C_{31}H_{30}O_3$: Calcd: 450.2195, found: 450.2194

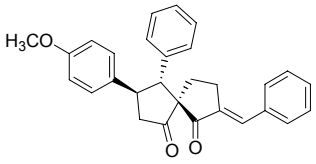
Compound 8d

	White solid. Mp : 156-158 °C **IR** (KBr) ν_{max}: 3022, 2916, 1738, 1691, 1614, 1581, 1511, 1459, 1255, 1165, 1060 cm^{-1}. **^{1}H NMR**: δ 7.42-7.37 (m, 3H), 7.25-7.16 (m, 6H), 6.98 (s, 3H), 6.77 (d, 2H, J = 8.6 Hz), 4.38 (d, 1H, J = 12.3 Hz) 3.73 (s, 3H), 3.70-3.66 (m, 1H) 3.09-2.98 (m, 1H), 2.87 (dd, 1H, J_1 = 17.8 Hz, J_2 = 7.3 Hz), 2.68 (dd, 1H, J_1 = 17.8 Hz, J_2 = 12.6 Hz) 2.59-2.51 (m, 1H),2.37 (s, 3H), 2.23 (s, 3H), 2.15-2.13 (m, 1H), 1.63-1.58 (m,1H) **^{13}CNMR:** 213.8, 203.3, 157.3, 132.8, 132.1, 130.4, 130.0, 128.6, 128.3, 115.2, 113.3, 70.3, 58.1, 56.1, 55.7, 27.2 **HRMS (EI)** for $C_{31}H_{30}O_3$: Calcd: 450.2195, found: 450.2186

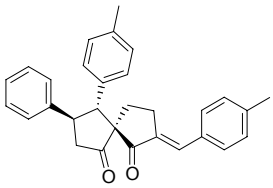
Compound 8e

	White solid. Mp : 143-145 °C **IR** (KBr) ν_{max}: 3030, 2920, 1739, 1691, 1620, 1598, 1478, 1310, 1239, 1175, 1080 cm^{-1}. **^{1}H NMR**: δ 7.47-7.42 (m, 3H), 7.30-7.25 (m, 1H), 7.15-7.03 (m, 3H), 6.90-6.80 (m, 4H), 6.69 (d, 2H, J = 8.7 Hz), 4.57 (d, 1H, J = 12.8 Hz), 4.13-4.10 (m, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.69 (s, 3H), 3.02-2.94 (m, 2H), 2.56-2.46 (m, 2H), 2.18-2.16 (m, 1H), 1.68-1.64 (m, 1H). **^{13}CNMR**:δ 214.8, 205.2, 161.0, 158.6, 157.7, 134.4, 133.6, 132.8, 129.9, 129.4,128.9, 128.3, 127.8, 127.3, 121.2, 117.3, 114.4, 113.9, 113.5, 110.6, 109.8, 70.2, 55.5, 55.4, 55.1, 52.3, 46.9, 35.9, 27.1. **HRMS (EI)** for $C_{31}H_{30}O_5$: Calcd : 482.2093, found: 482.2097

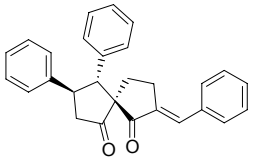
Compound 8f

	White solid. Mp : 134-136 °C **IR** (KBr) ν_{max}: 3025, 2918, 1741, 1696, 1617, 1592, 1492, 1306, 1241, 1176, 1093 cm^{-1}. **^{1}H NMR**: δ 7.49-7.46 (m, 3H), 7.37-7.35 (m, 3H), 7.24-7.17 (m, 5H), 7.14-7.09 (m, 3H), 6.78(d, 2H, J = 8.6 Hz), 4.42 (d, 1H, J = 12.3 Hz), 3.73 (s, 3H), 3.72-3.65 (m, 1H), 3.12-3.01 (m, 1H), 2.89 (dd, 1H, J_1 = 17.9 Hz, J_2 = 7.3 Hz), 2.71 (dd, 1H, J_1 = 17.8 Hz, J_2 = 12.6 Hz), 2.60-2.52 (m, 1H), 2.21-2.14 (m, 1H), 1.62-1.55 (m,1H) **^{13}CNMR:** 213.1, 204.4, 158.4, 137.2, 135.4, 135.3, 134.7, 134.5, 132.4, 130.8, 129.6, 128.9, 128.5, 128.4, 127.1, 114.1, 70.1, 55.1, 54.9, 47.9, 42.5, 27.2. **HRMS (EI)** for $C_{29}H_{26}O_3$: Calcd: 422.1882, found: 422.1869

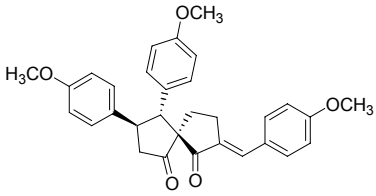
Compound 8g

	White solid. Mp : 157-159 °C **IR** (KBr) ν_{max}: 3031, 2917, 1736, 1688, 1620, 1580, 1501, 1459, 1302, 1261, 1210, 1080 cm^{-1}. **^{1}H NMR**: δ 7.43-7.24 (m, 6H), 7.18-7.12 (m, 4H), 6.99 (s, 4H), 4.44 (d, 1H, J = 12.3 Hz), 3.75-3.71 (m, 1H), 3.08-2.99 (m, 1H), 2.90 (dd, 1H, J_1 = 17.8 Hz, J_2 = 7.3 Hz), 2.73 (dd, 1H, J_1 = 17.8 Hz, J_2 = 12.5 Hz), 2.60-2.57 (m, 1H), 2.36 (s, 3H), 2.22 (s, 3H), 2.17-2.13 (m, 1H), 1.64-1.59 (m, 1H) **^{13}C NMR**: 213.3, 204.5, 140.7, 140.0, 136.6, 134.7, 134.5, 134.0, 132.6, 130.9, 129.4, 129.2, 128.8, 128.7, 127.5, 126.9, 70.1, 54.6, 47.9, 43.3, 27.2, 26.9, 21.6. **HRMS (EI)** for $C_{30}H_{28}O_2$ Calcd: 420.2089, Found: 420.2076

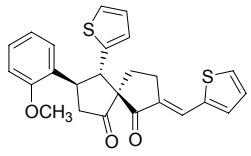
Compound 8h

	White solid. Mp : 166-168 °C **IR** (KBr) ν_{max}: 3028, 2911, 1737, 1693, 1602, 1488, 1301, 1247, 1168, 1079 cm^{-1}. **^{1}H NMR**: δ 7.49-7.47 (m, 3H), 7.38-7.27 (m, 5H), 7.22-7.10 (m, 9H), 4.48 (d, 1H, J = 12.3 Hz), 3.77-3.74 (m, 1H), 3.13-3.02 (m, 1H), 2.93 (dd, 1H, J_1 = 17.9 Hz, J_2 = 7.3 Hz), 2.75 (dd, 1H, J_1 = 17.9 Hz, J_2 = 12.5 Hz), 2.62-2.58 (m, 1H), 2.22-2.16 (m, 1H), 1.63-1.59 (m,1H) **^{13}CNMR:** 213.0, 204.4, 140.5, 137.1, 135.4, 134.8, 134.6, 130.7, 129.7, 128.9, 128.7, 128.5, 127.5, 127.2, 126.9, 70.0, 55.0, 47.9, 27.2. **HRMS (EI)** for $C_{28}H_{24}O_2$: Calcd: 392.1776, found: 392.1786

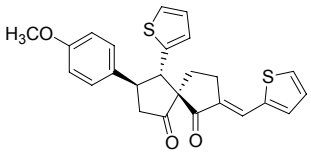
Compound 8i

	White solid. Mp : 152-154 °C **IR** (KBr) ν_{max}: 3029, 2914, 1740, 1696, 1621, 1600, 1495, 1303, 1247, 1228, 1180, 1091 cm^{-1}. **^{1}H NMR**: δ 7.43 (d, 3H, J = 8.8 Hz), 7.25-7.20 (m, 2H), 7.02 (d, 2H, J = 8.5 Hz), 6.87 (d, 2H, J = 8.6 Hz), 6.79-6.69 (m, 4H), 4.35 (d, 1H, J = 12.3 z), 3.80 (s, 3H), 3.71 (s, 3H), 3.68 (s, 3H), 3.65-3.63 (m, 1H), 3.06-2.95 (m, 1H), 2.86 (dd, 1H, J_1 = 17.8 Hz, J_2 = 7.2 Hz), 2.67 (dd, 1H, J_1 = 17.8 Hz, J_2 = 12.4 Hz), 2.56-5.48 (m, 1H), 2.19-2.15 (m, 1H), 1.65-1.61 (m, 1H) **^{13}CNMR:** 213.6, 204.5, 160.8, 158.4, 158.3, 134.5, 133.0, 132.6, 132.5, 129.8, 129.1, 128.3, 128.0, 114.2, 114.0, 113.8, 70.1, 55.2, 54.9, 54.5, 48.0, 47.7, 27.1, 26.8 **HRMS (EI)** for $C_{31}H_{30}O_5$: Calcd: 482.2093, found: 482.2094

Compound 8j

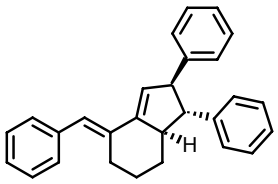
	White solid. Mp : 162 -164 °C **IR** (KBr) ν_{max}: 3031, 2901, 1738, 1691, 1625, 1588, 1497, 1309, 1236, 1221, 1158, 1084 cm^{-1}. **^{1}H NMR**: δ 7.70 (s, 1H), 7.53 (d, 1H, *J* = 5.0 Hz), 7.38 (d, 1H, *J* = 3.6 Hz), 7.34-7.31 (m, 1H), 7.19-7.11 (m, 2H), 7.05-7.03 (m, 1H), 6.91-6.80 (m, 3H), 6.76-6.75 (m, 1H), 4.88 (d, 1H, *J* = 12.4 Hz), 4.08-3.97 (m, 1H), 3.90 (s, 3H), 3.01-2.93 (m, 2H), 2.70-2.50 (m, 2H), 2.25-2.18 (m, 1H), 1.86-1.75 (m, 1H) **^{13}CNMR:** 213.8, 203.9, 157.7, 141.0, 140.0, 133.6, 130.9, 128.6, 128.2, 127.5, 127.3, 127.0, 126.1, 124.5, 121.1, 110.7, 70.8, 55.5, 48.2, 46.4, 38.5, 26.8 **HRMS (EI)** for $C_{25}H_{22}O_3S_2$: Calcd: 434.1010, found: 434.1008

Compound 8k

	White solid. Mp : 157 -159°C **IR** (KBr) ν_{max}: 3025, 2911, 1737, 1688, 1617, 1605, 1493, 1310, 1245, 1220, 1177, 1088 cm^{-1}. **^{1}H NMR**: δ 7.69 (s, 1H), 7.53 (d, 1H, *J* = 4.9 Hz), 7.38 (d, 1H, *J* = 3.6 Hz), 7.29 (s, 1H), 7.14-7.11 (m, 1H), 7.08 (d, 1H, *J* = 4.9 Hz), 6.84-6.80 (m, 3H), 6.72 (d, 1H, *J* = 3.4 Hz), 4.65 (d, 1H, *J* = 12.3 hz), 3.76 (s, 3H), 3.62-3.51 (m, 1H), 2.99-2.83 (m, 2H, 2.70-2.60 (m, 2H), 2.24-2.17 (m, 1H), 1.85-1.75 (m, 1H) **^{13}CNMR:** 212.5, 203.3, 158.6, 140.6, 139.8, 133.4, 132.8, 132.2, 130.8, 128.4, 127.4, 126.9, 126.2, 124.4, 114.1, 70.7, 55.0, 50.6, 47.9, 44.8, 26.8, 26.7 **HRMS (EI)** for $C_{25}H_{22}O_3S_2$: Calcd: 434.1010, found: 434.1014

Compound 10

DBU (18 mg, 12 mol %) was added to a suspension of the carbene precursor 1,3-dimesityl imidazolium chloride **3** (21 mg, 6 mol %) in dry CH_2Cl_2 under argon atmosphere. This was followed by the addition of enal **6** (132 mg, 1 mmol) and dienone **9** (192 mg, 0.7 mmol) and the resulting solution was stirred for 8 h at room temparature. Removal of solvent followed by column chromatography as described in the general procedure afforded the bicyclic cyclopentene derivative **10** as a colorless viscous liquid (202 mg, 80%).



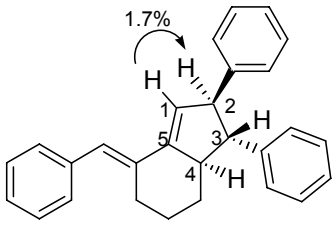
IR (film) ν_{max}: 3026, 2926, 1600, 1494, 1450 cm^{-1}.

^{1}H NMR: δ 7.31–7.06 (m, 15H), 6.78 (s, 1H), 5.87 (s, 1H), 4.06–4.03 (m, 1H), 2.99–2.85 (m, 3H), 2.29–2.25 (m, 1H), 1.97–1.81 (m, 2H), 1.42–1.27 (m, 2H).

^{13}C NMR: δ 146.6, 144.6, 142.5, 137.4, 136.7, 129.4, 128.5, 127.7, 126.5, 125.2, 124.0, 65.3, 58.4, 53.8, 32.3, 29.7, 25.7.

HRMS (EI) for $C_{28}H_{26}$: calcd.: 362.2034, found: 362.2033.

^{1}H nOe Studies of compound 10



The relative stereochemistry of compound **10** is obtained from ^{1}H nOe studies. The irradiation of C4-H signal (δ 2.29-2.25) causes an nOe enhancement of 1.5% to C2-H signal (δ 4.06-4.03), thus confirming their *cis* relationship. In addition, irradiation of the C2-H (δ 4.06-4.03) enhanced the C1-H signal (δ 5.87), but did not show any enhancement of the signal due to C3-H thus indicating the *trans* relationship of C3-H with these protons.

Molecular packing diagram of compound 5a

In an attempt to understand the stabilization of the enolic form of the cyclopentanone in the solid state, we have examined the molecular packing and interactions present in this compound. A view of the H-bonding interactions is given in Figure 1. There is a strong intramolecular O-H…..O interaction between the enolic hydrogen and ketonic oxygen. The exocyclic ketonic oxygen further acts as an acceptor via intermolecular C-H…..O interaction with a phenyl hydrogen which link the molecules in an infinite chain with base vector [1,-1,0]. Thus the stabilization of the enolic form cyclopentanone in the solid state is chiefly attributed to the strong intramolecular O-H...O hydrogen bonding and weak intermolecular C-H...O interactions.

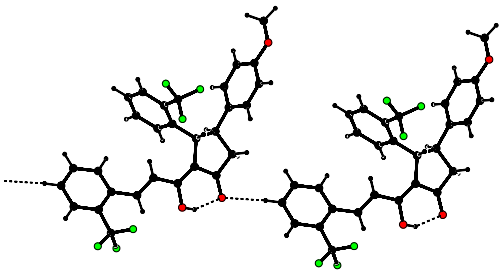
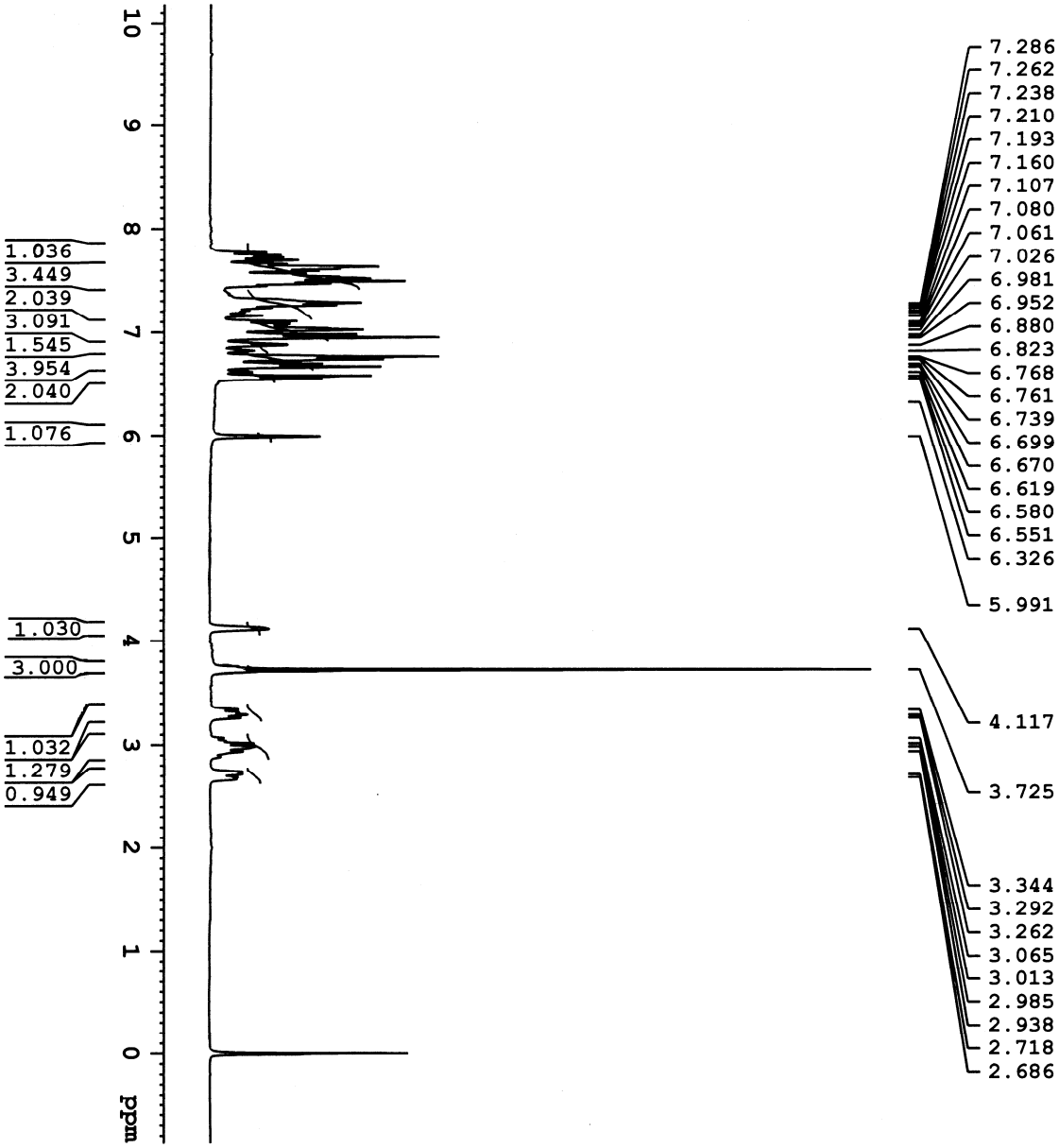
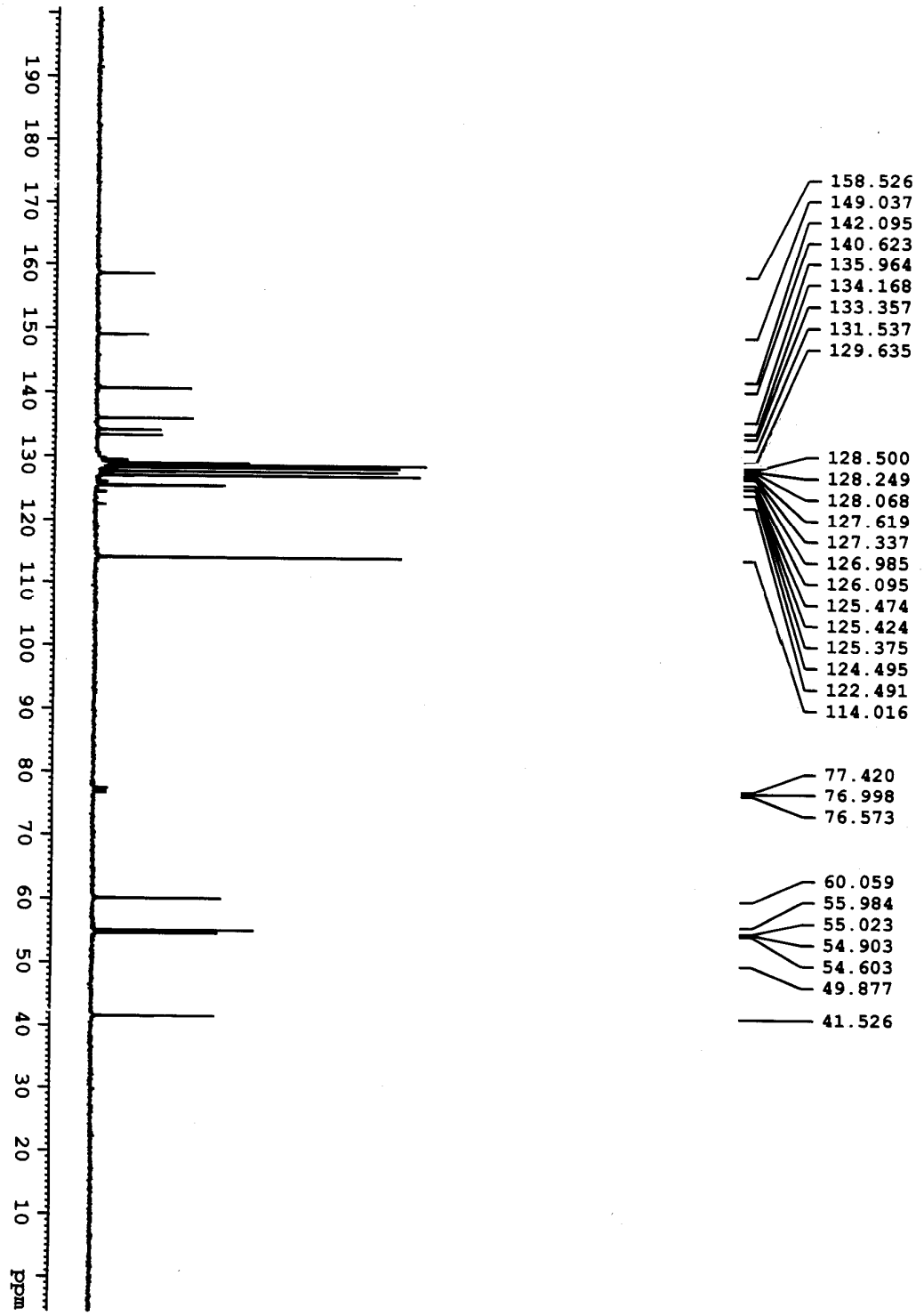


Figure 1. Close up view of the O-H….O and C-H…O hydrogen bonding interactions present in the compound **5a**.

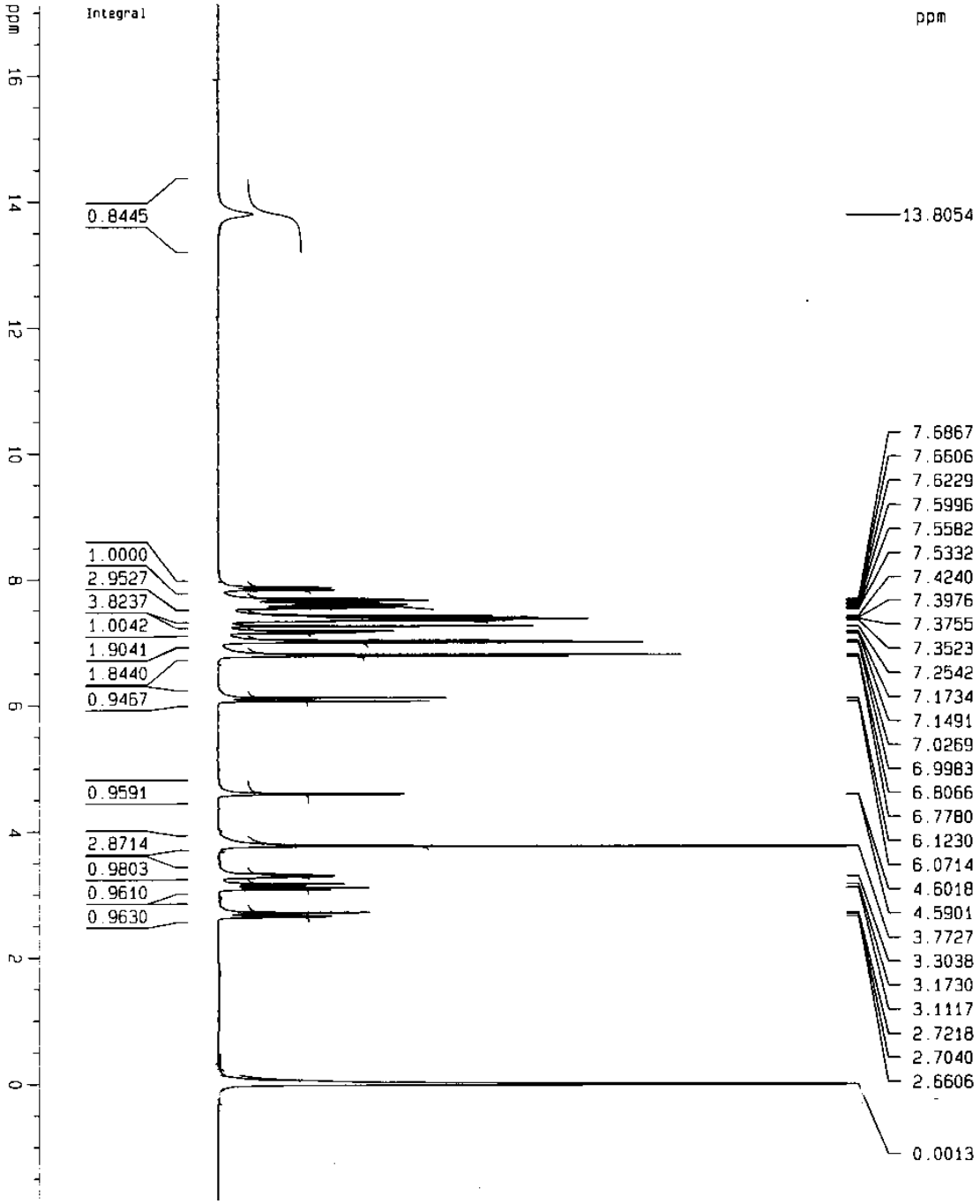
Compound 4a.



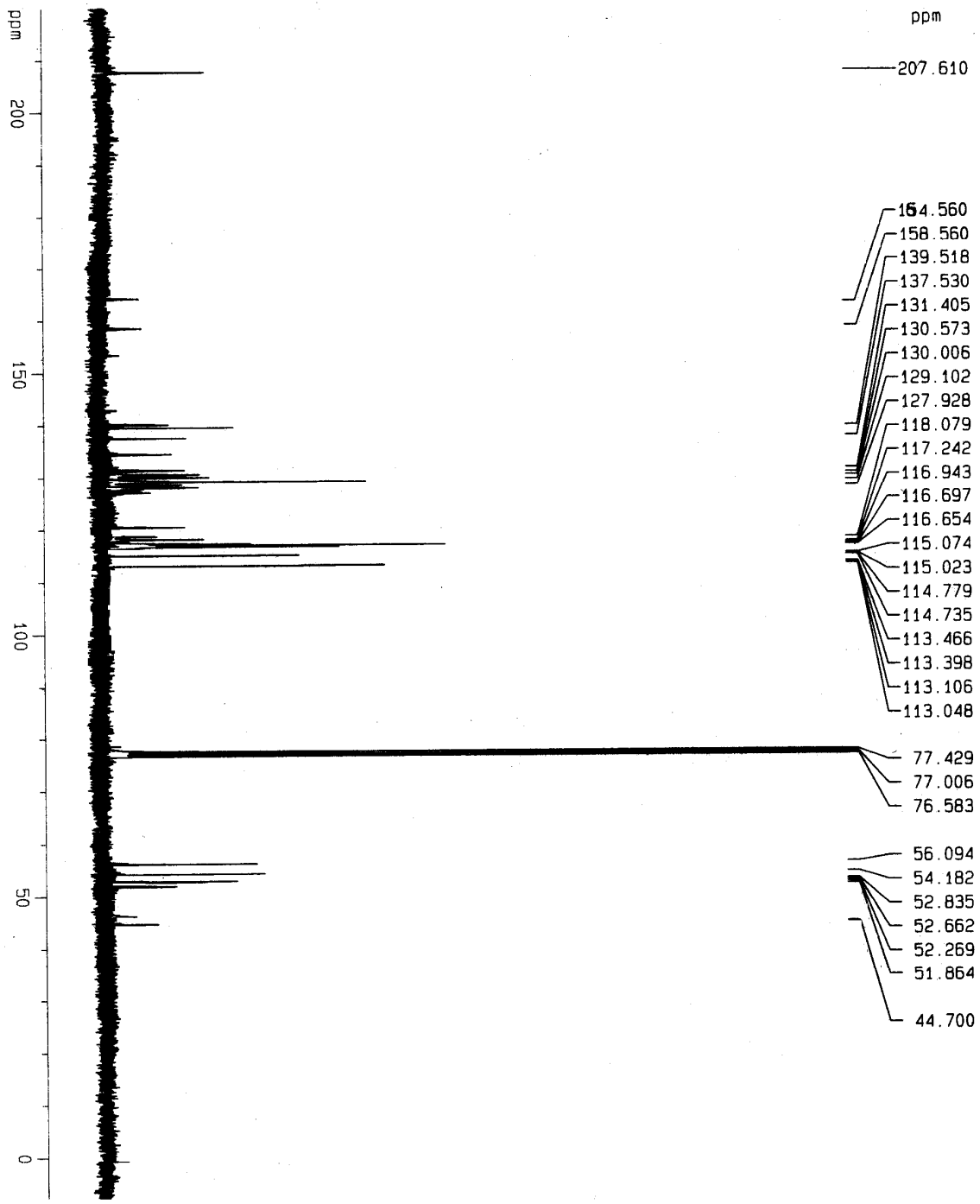
Compound 4a.



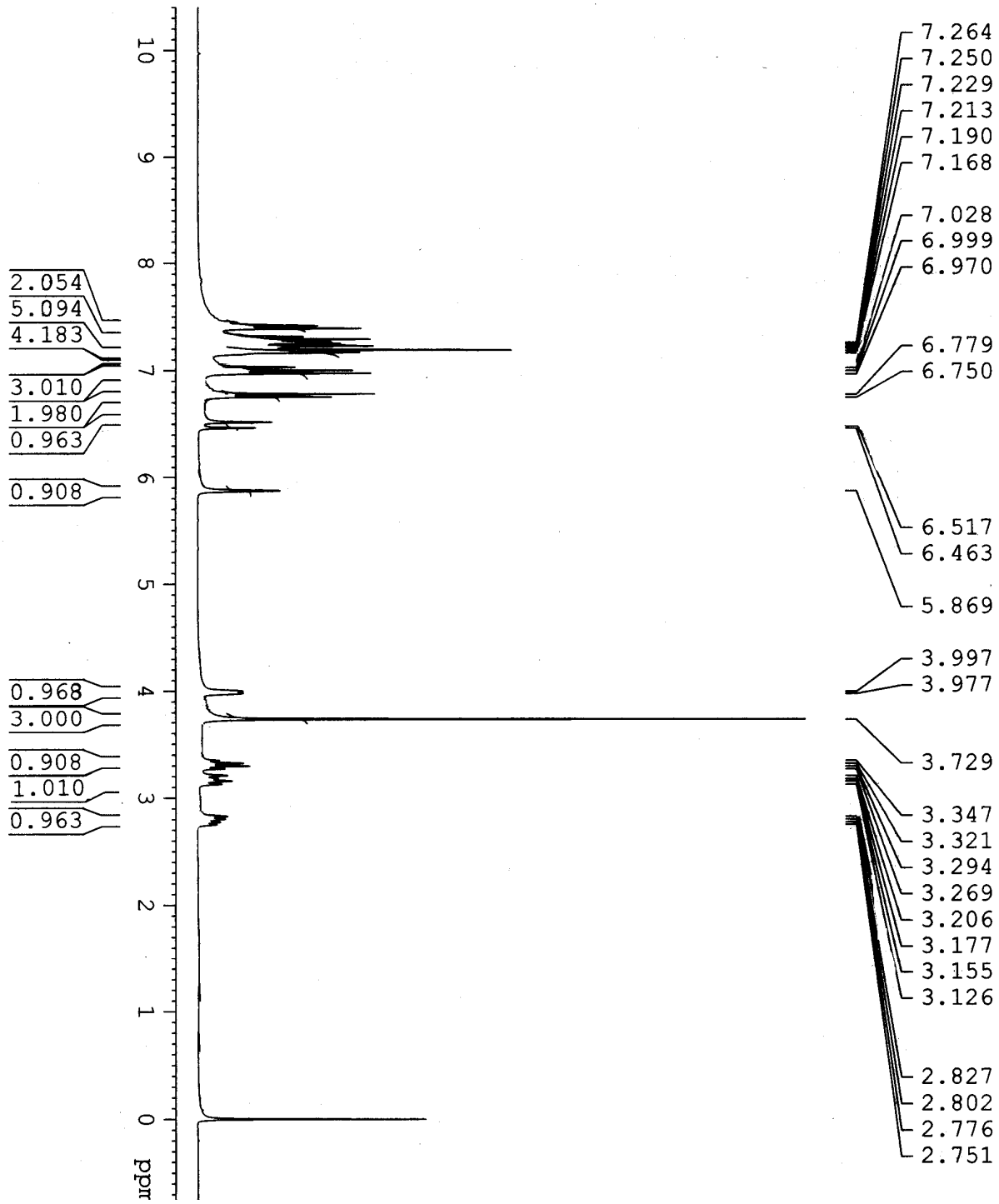
Compound 5a.



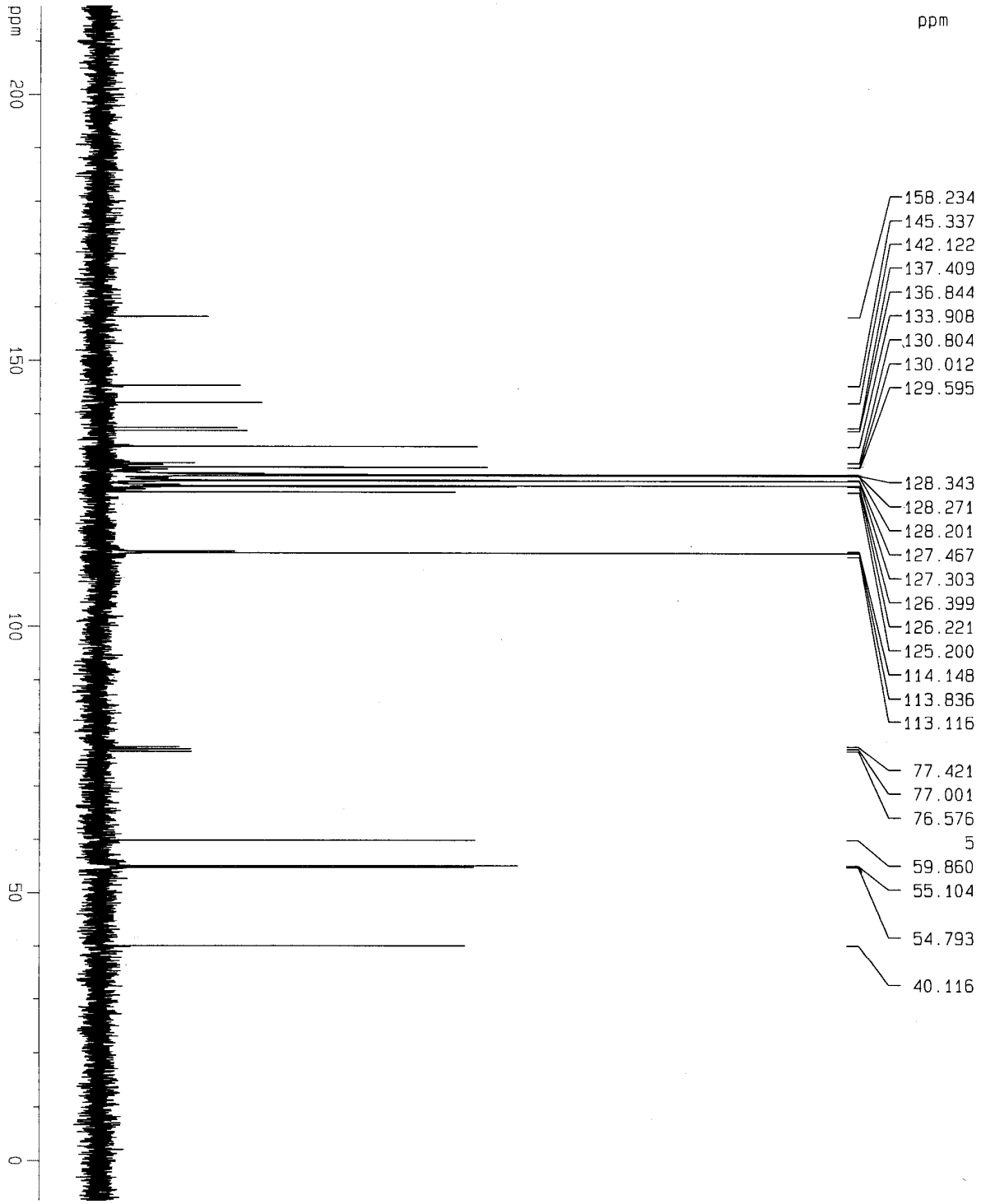
Compound 5a.



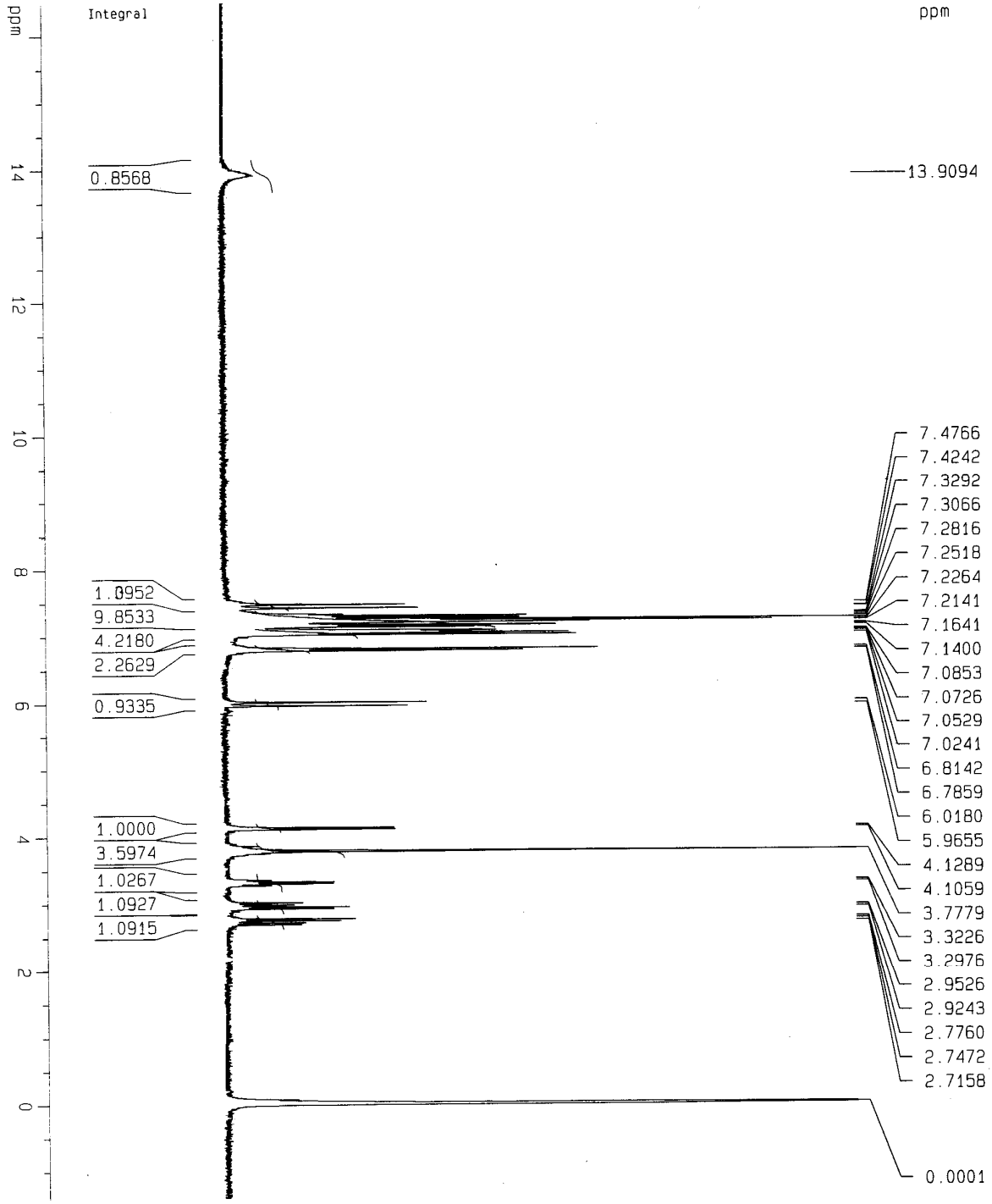
Compound 4b.



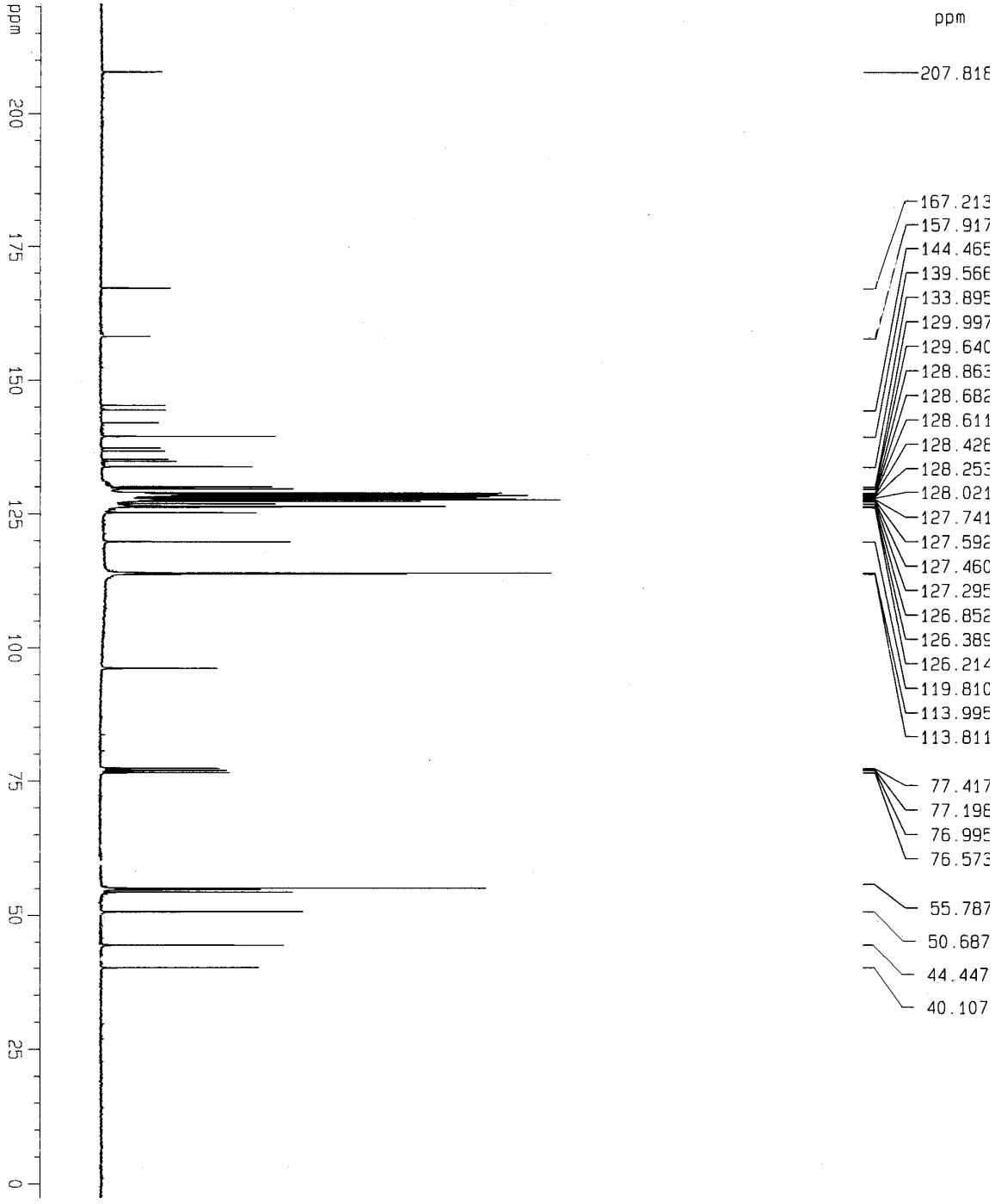
Compound 4b.



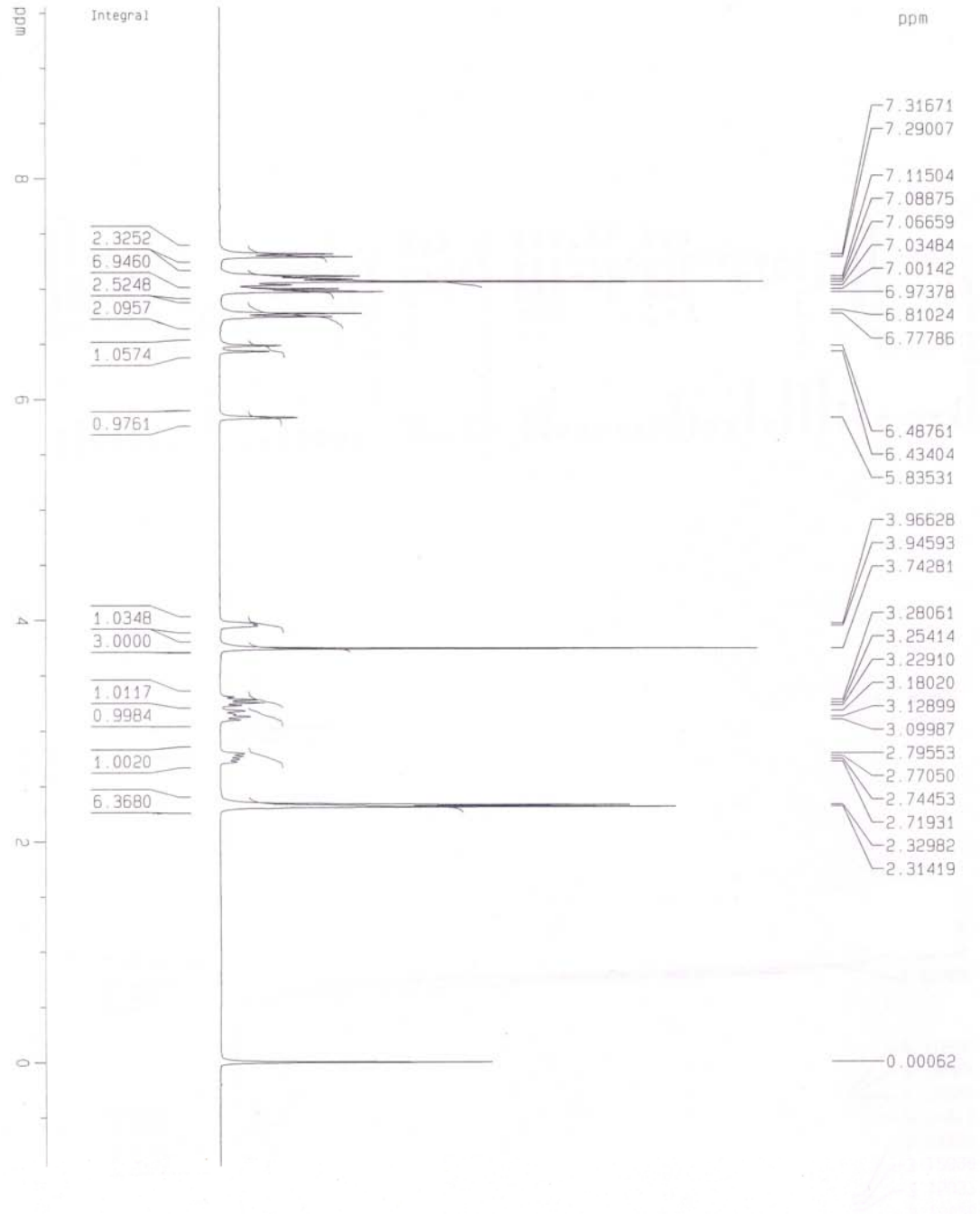
Compound 5b.



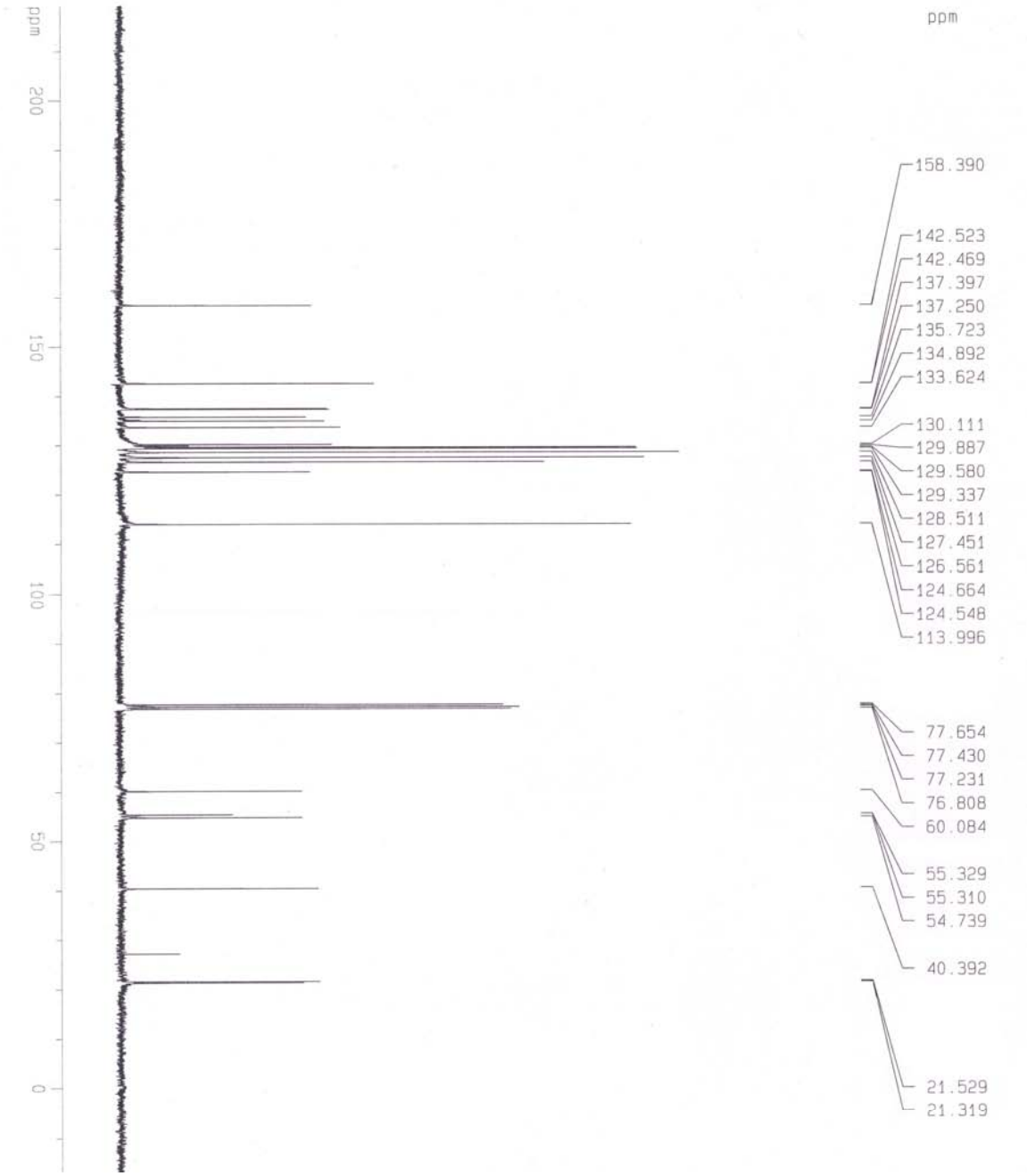
Compound 5b.



Compound 4c.



Compound 4c.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129.580
129.337
128.511
127.451
126.561
124.664
124.548
113.996
77.654
77.430
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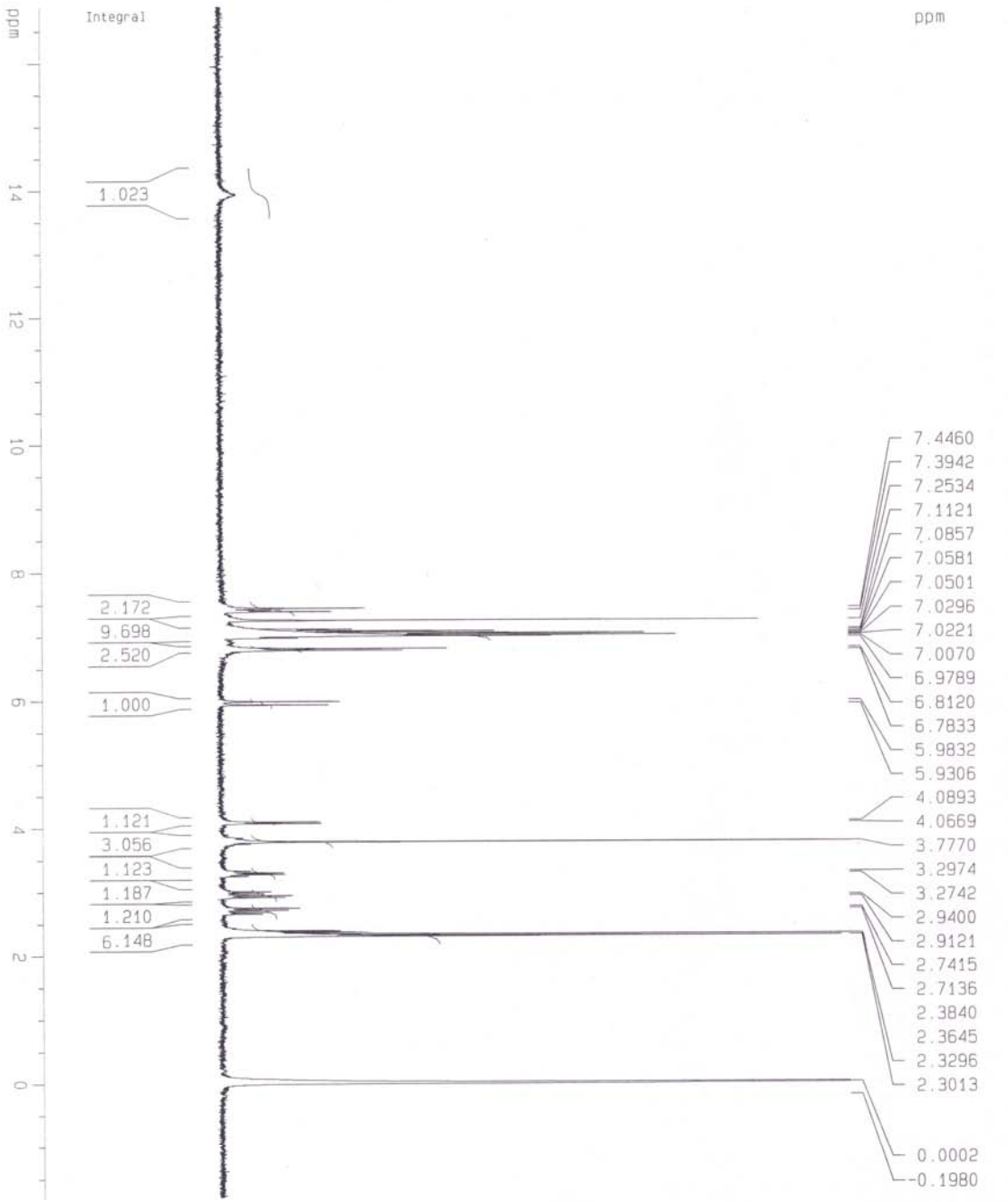
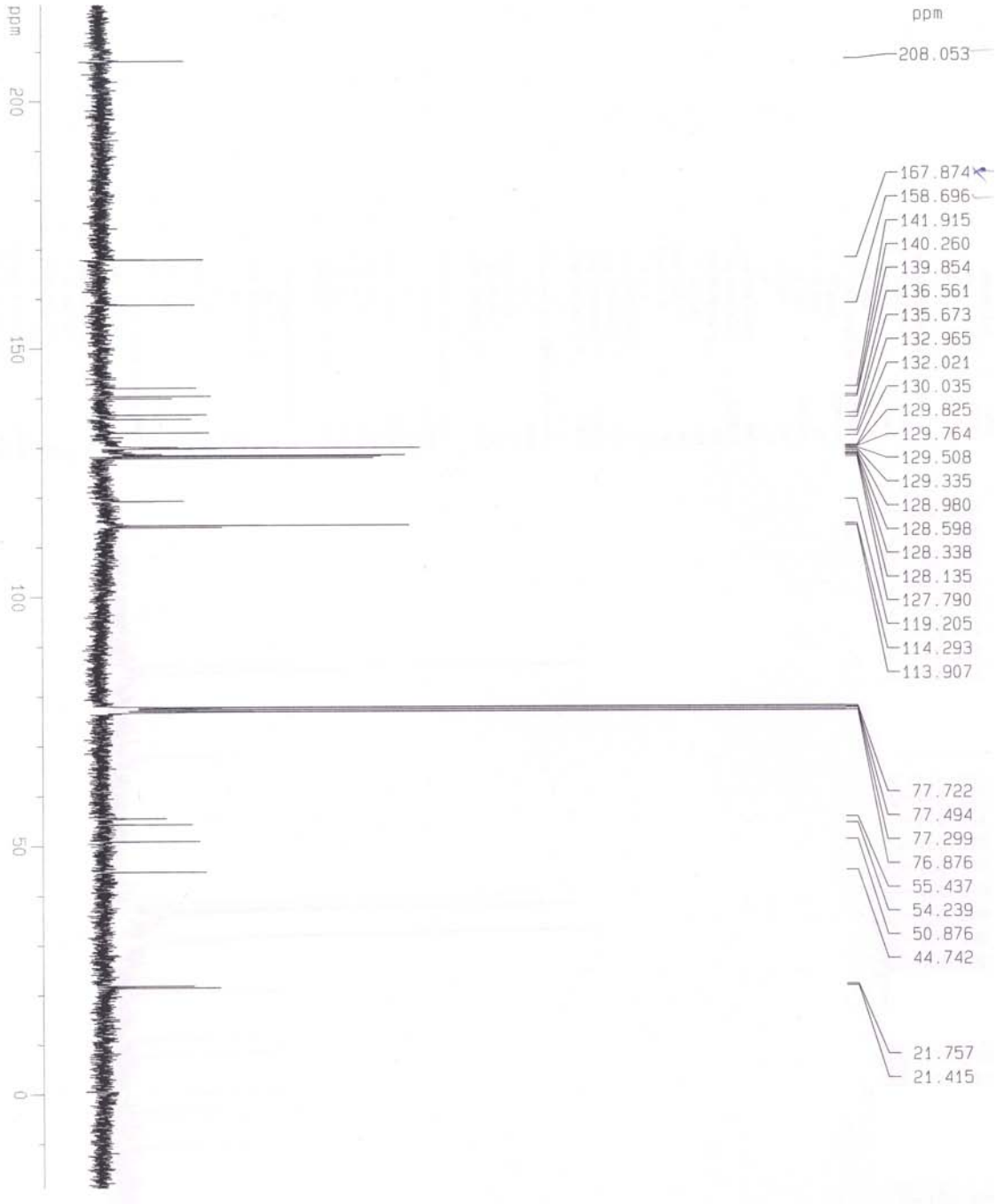
76.808
60.084
55.329
55.310
54.739
40.392
21.529
21.319

Compound 5c.



Compound 5c.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ppm
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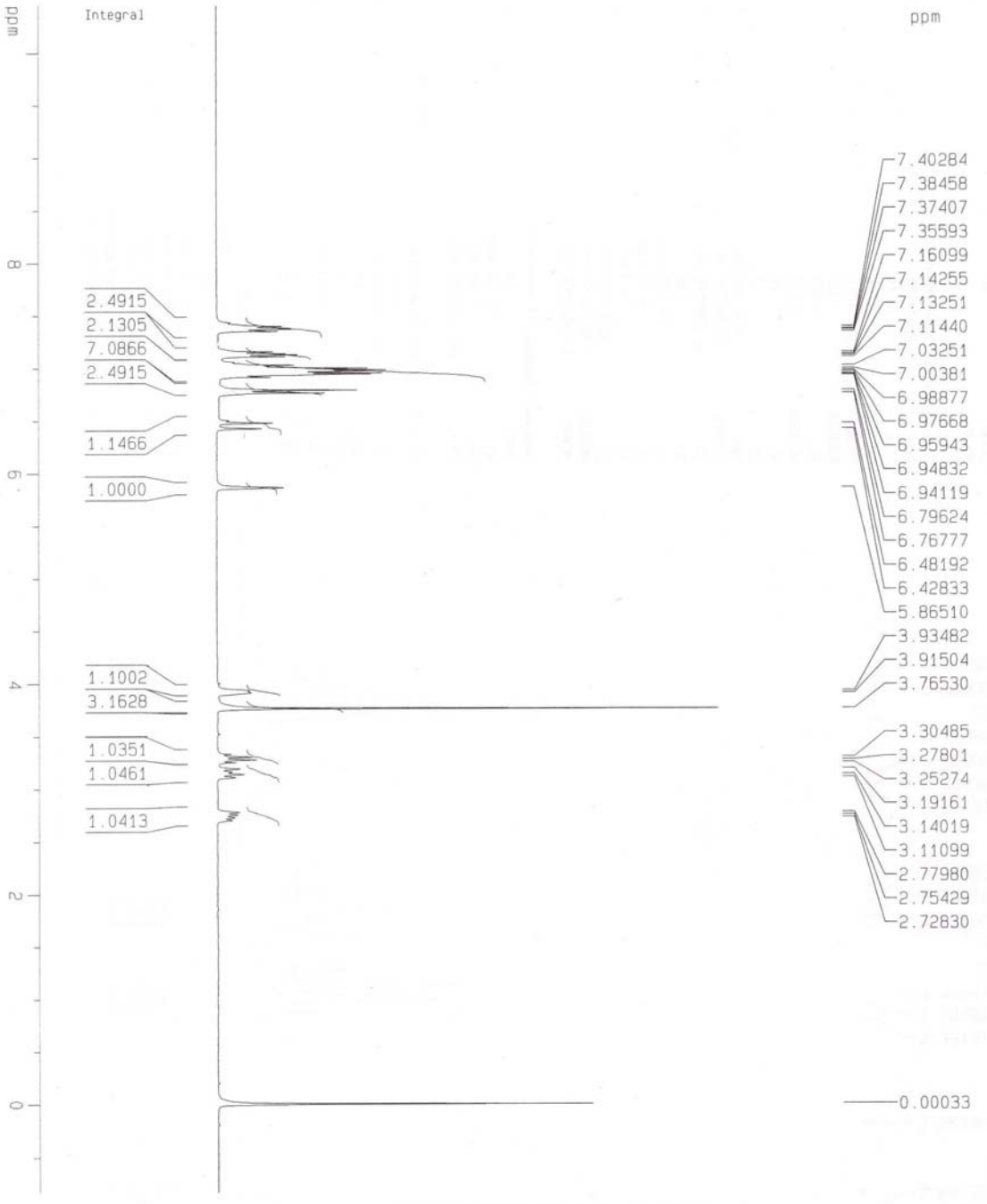
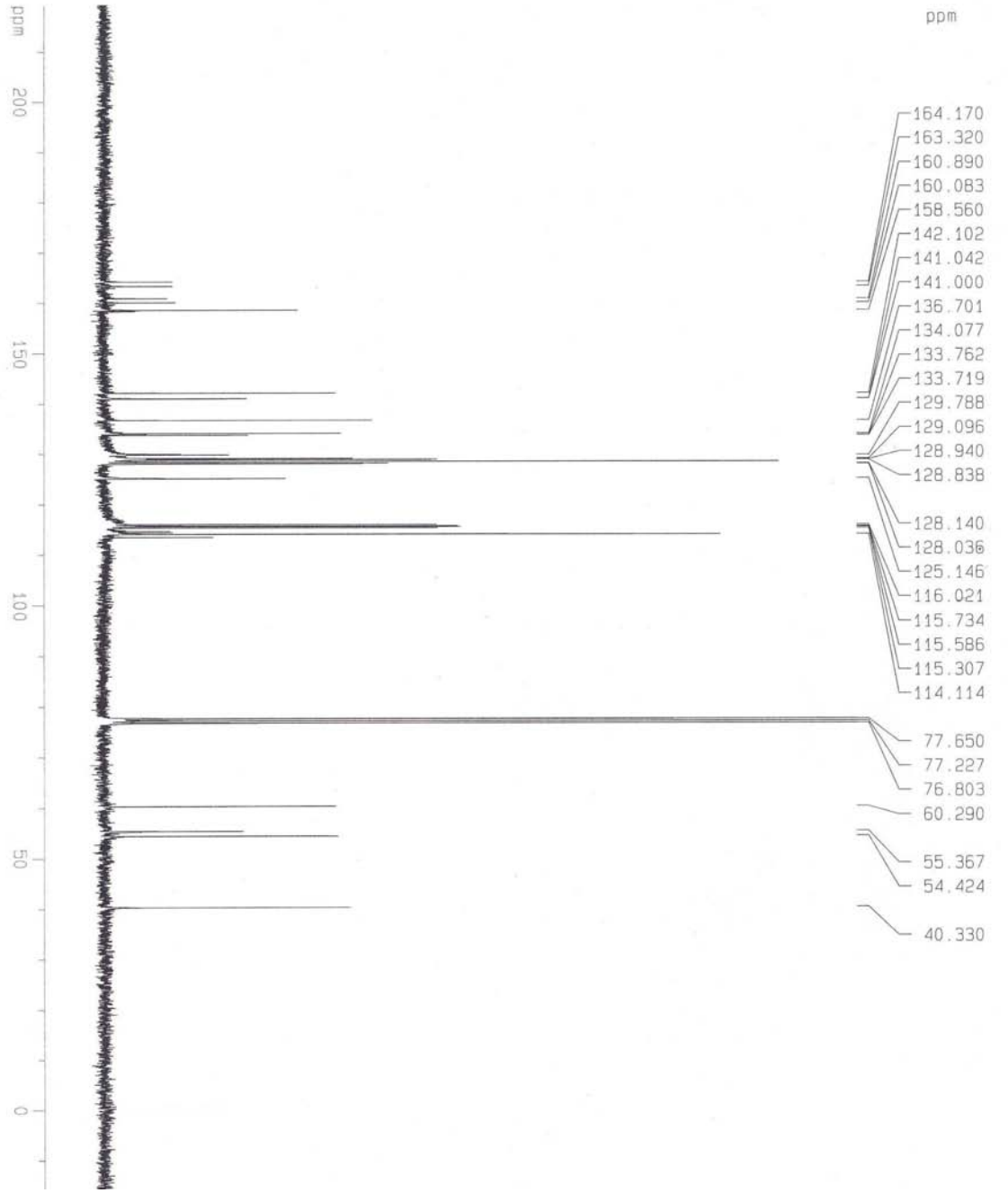
100
50
0

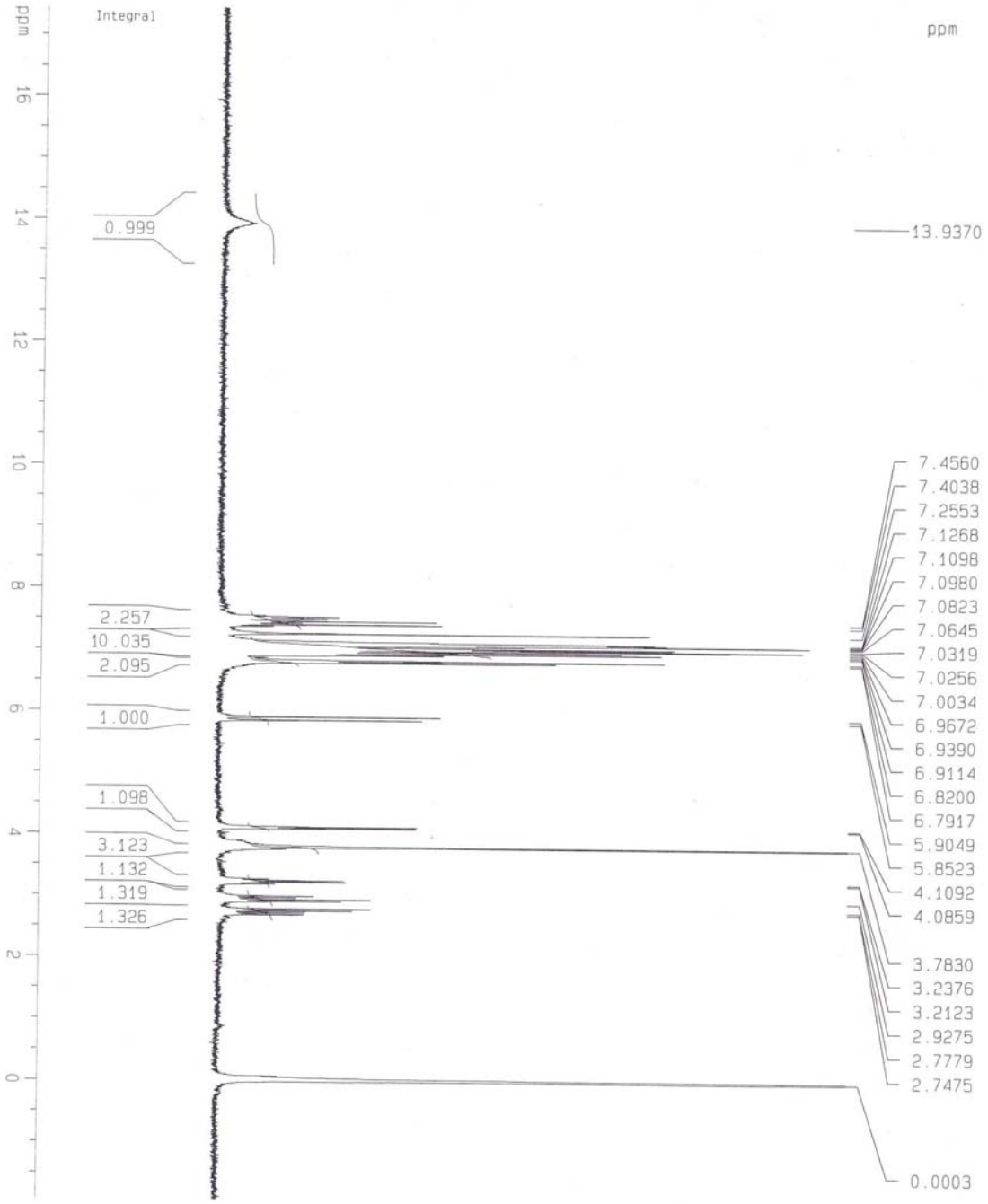
Compound 4d.



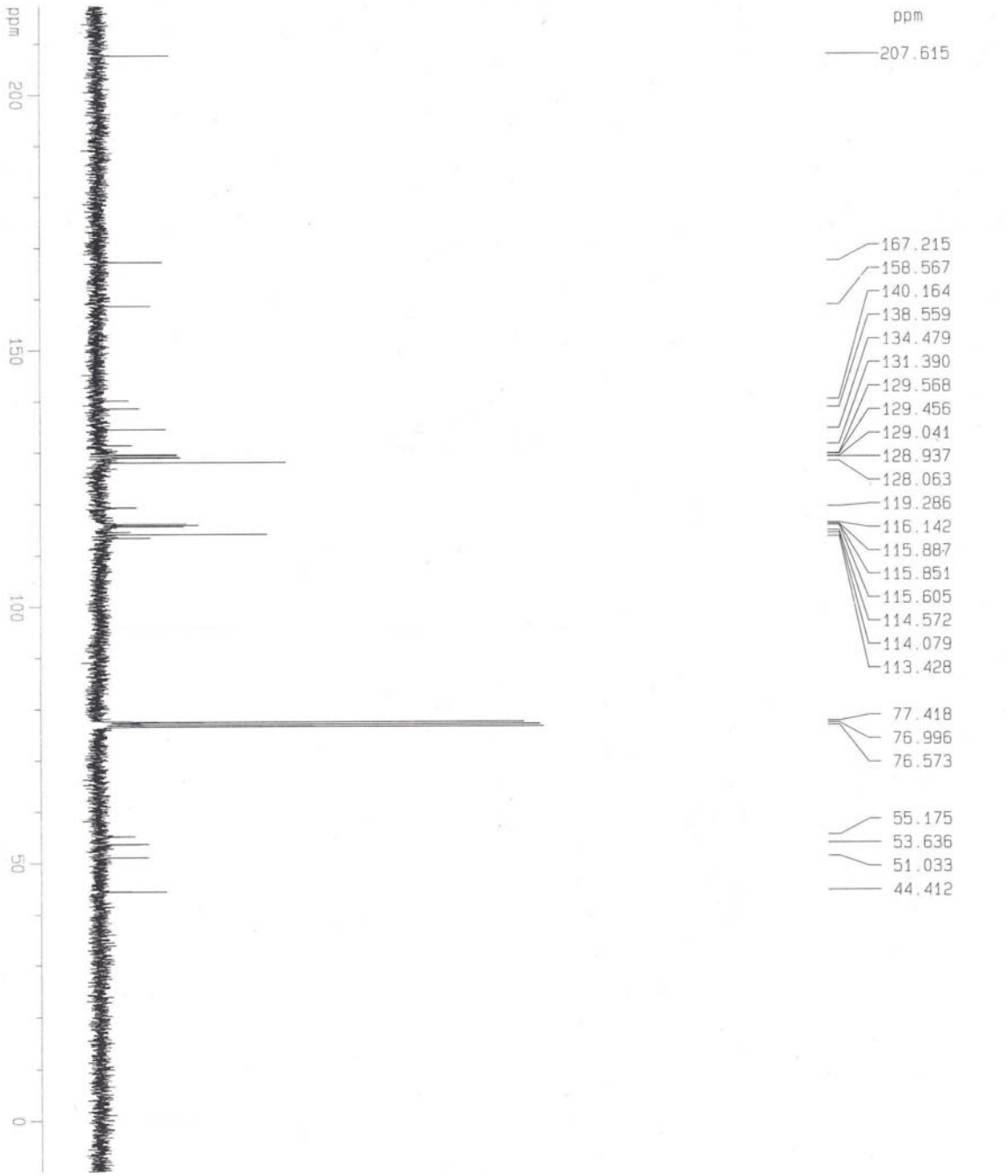
Compound 4d.



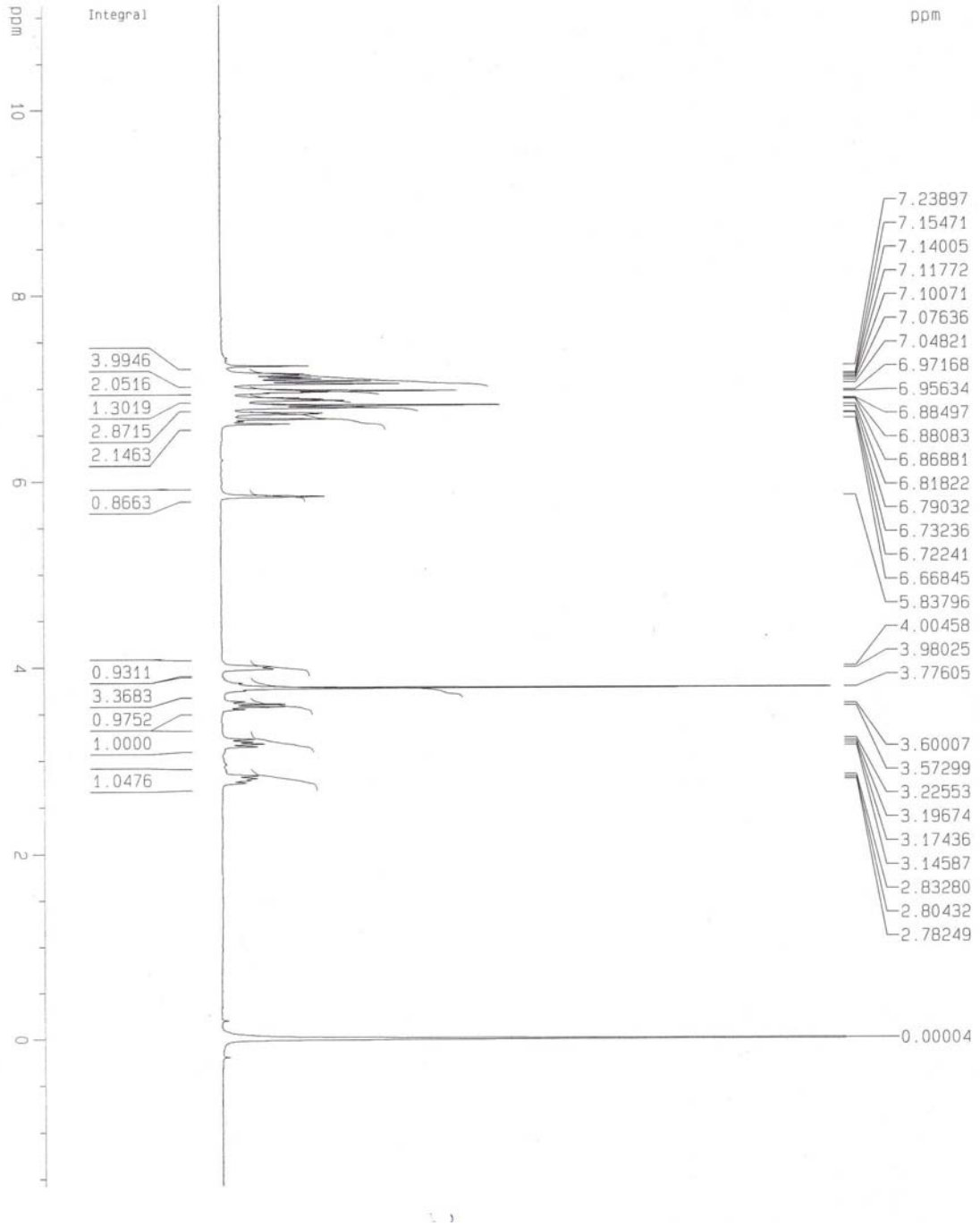
Compound 5d.



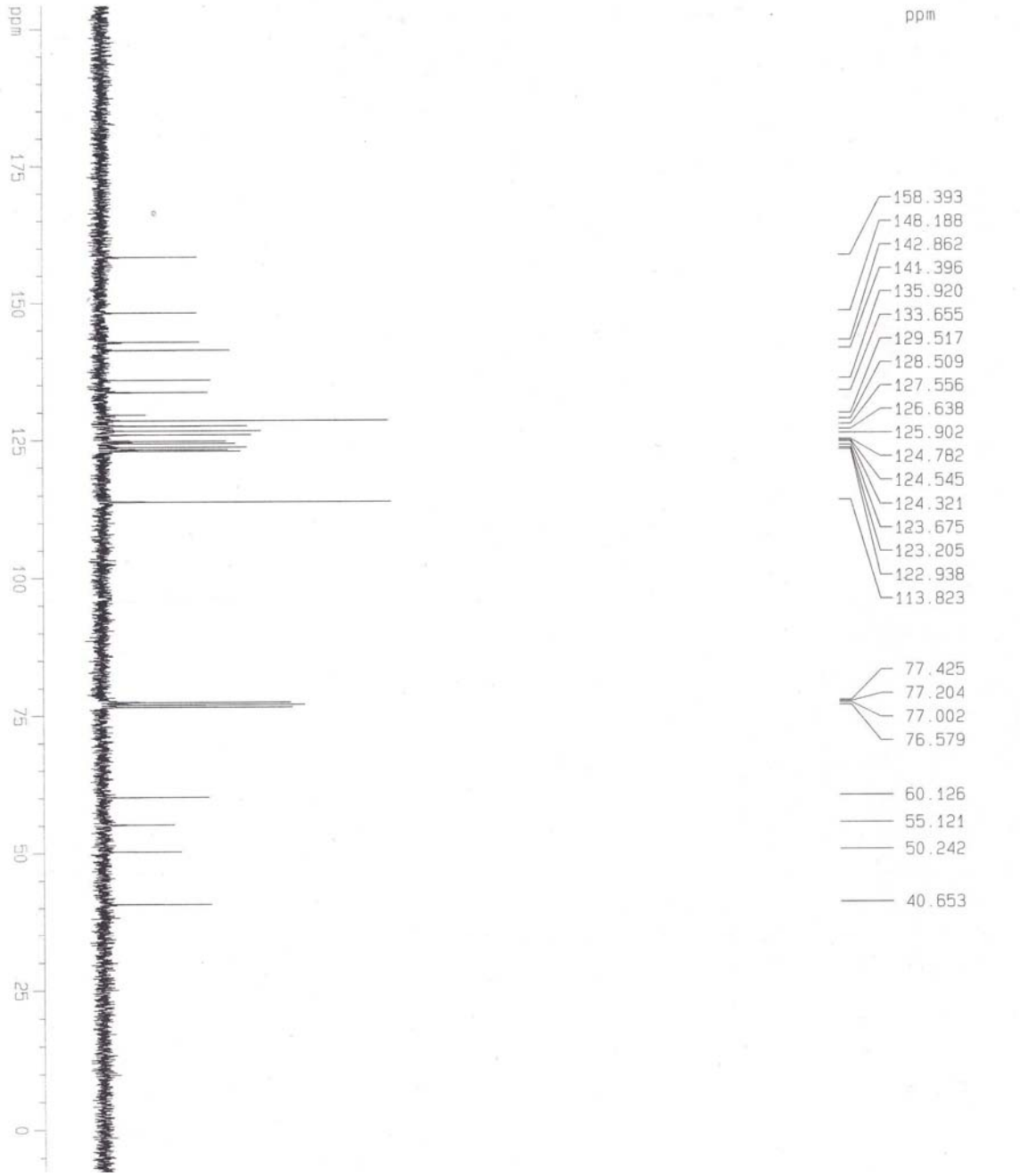
Compound 5d



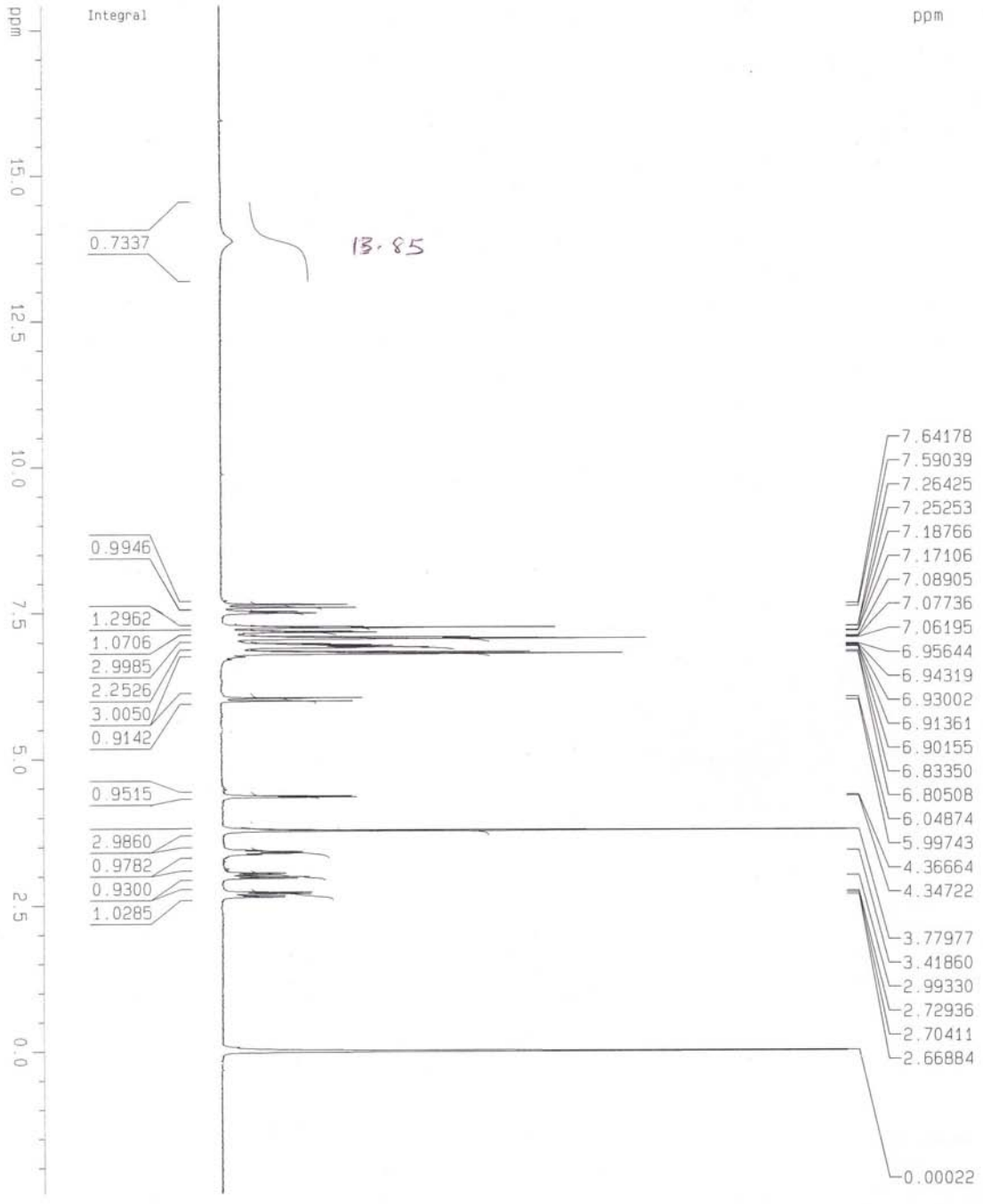
Compound 4e.



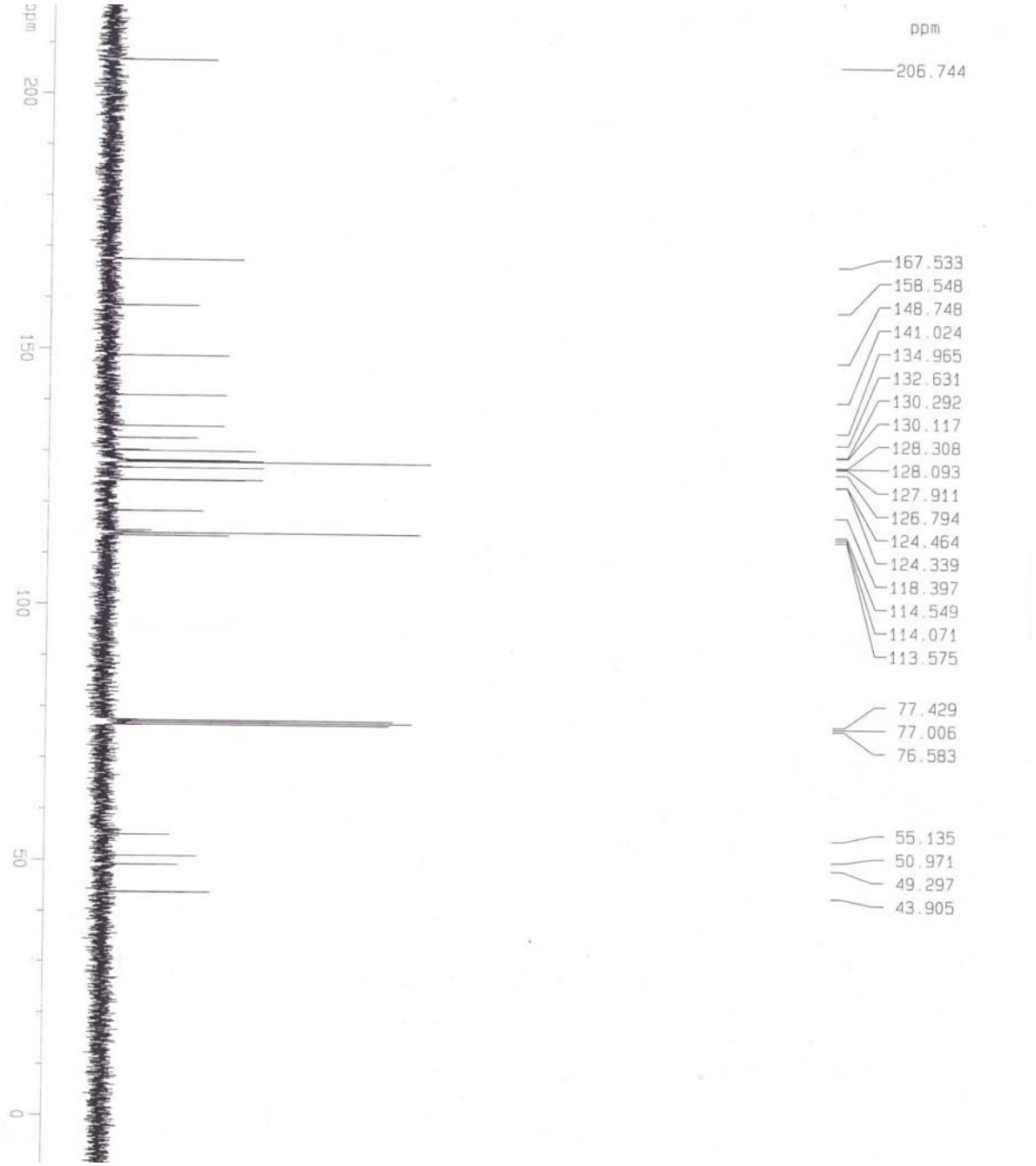
Compound 4e.



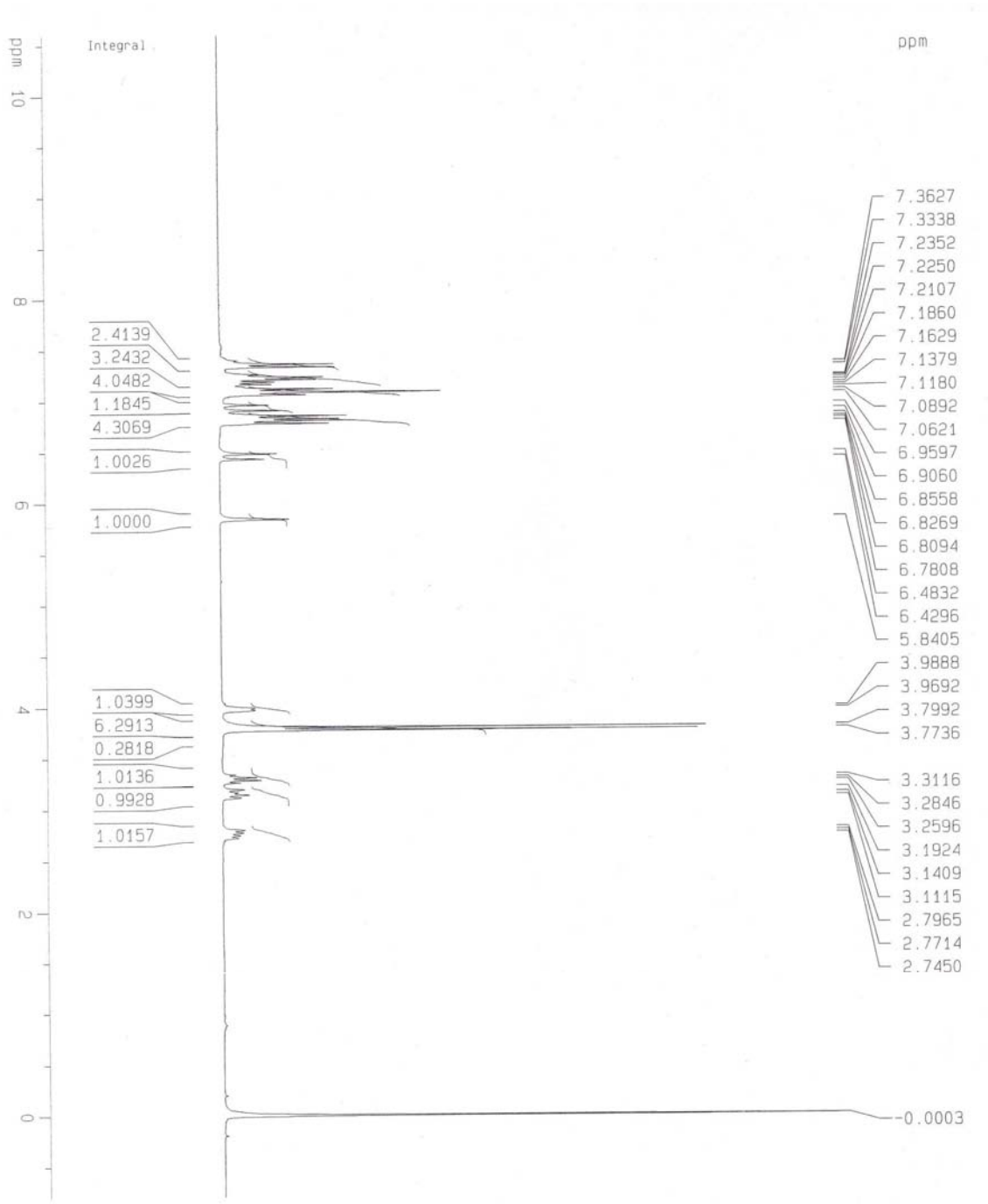
Compound 5e.



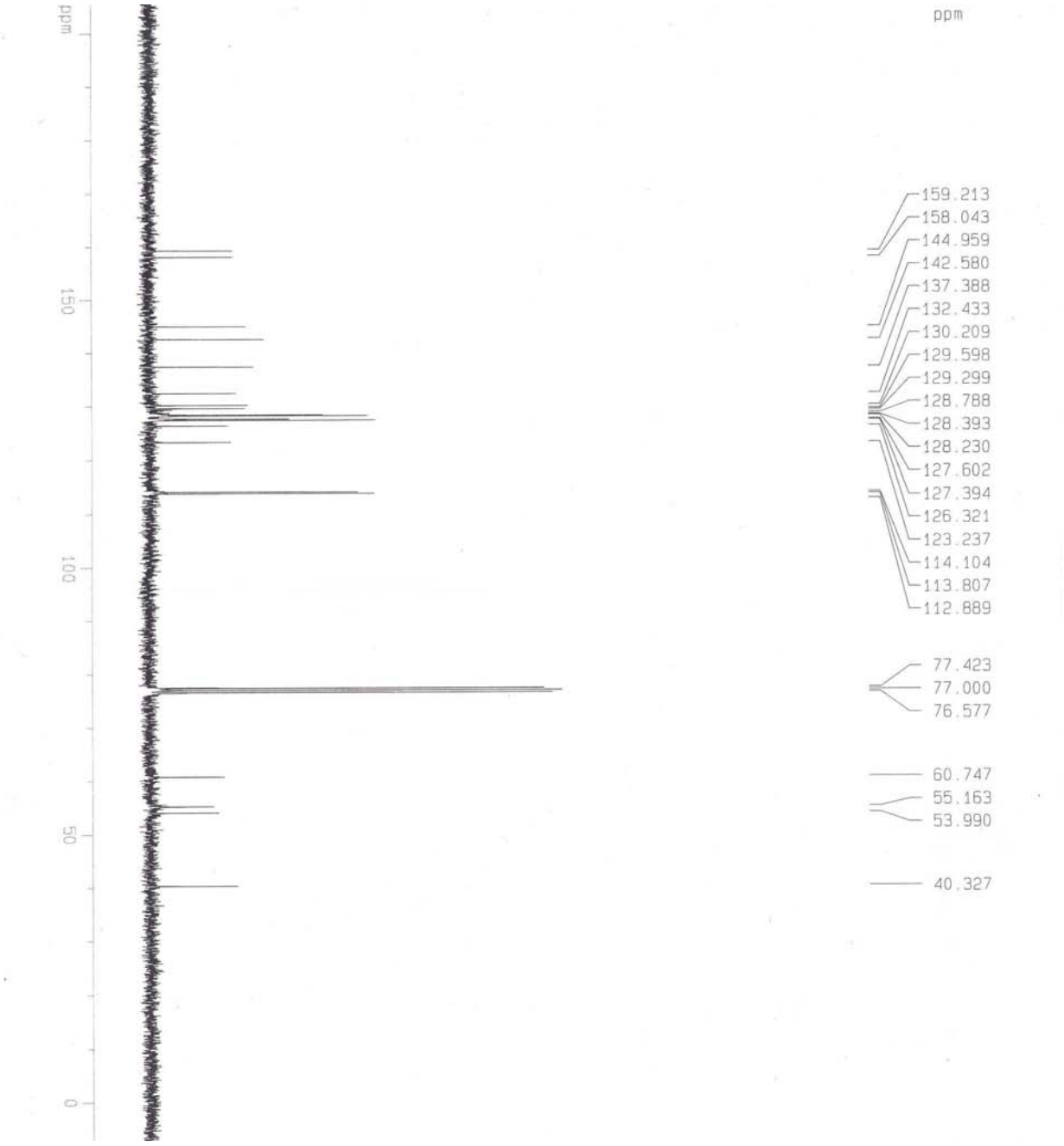
Compound 5e.



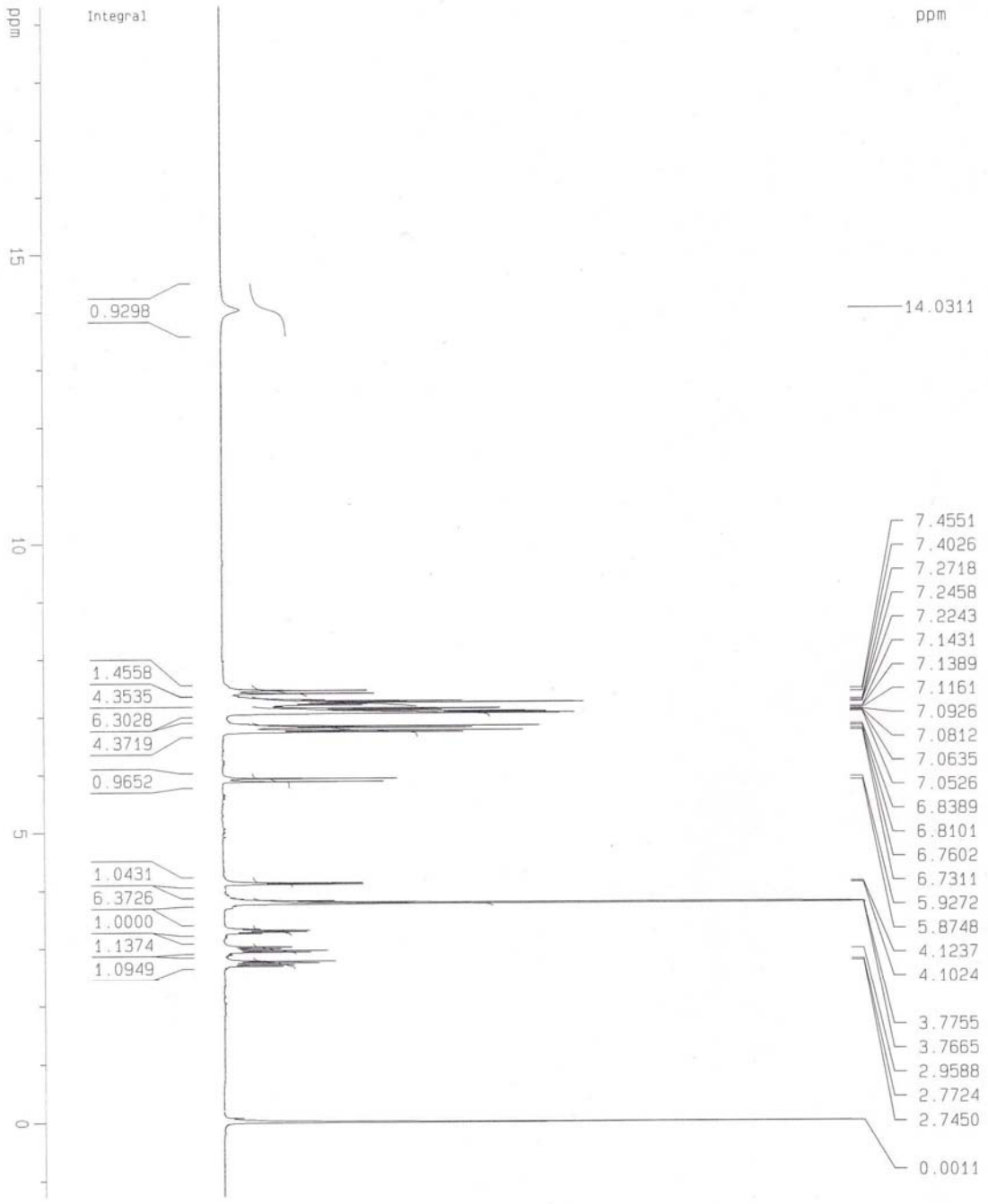
Compound 4f.



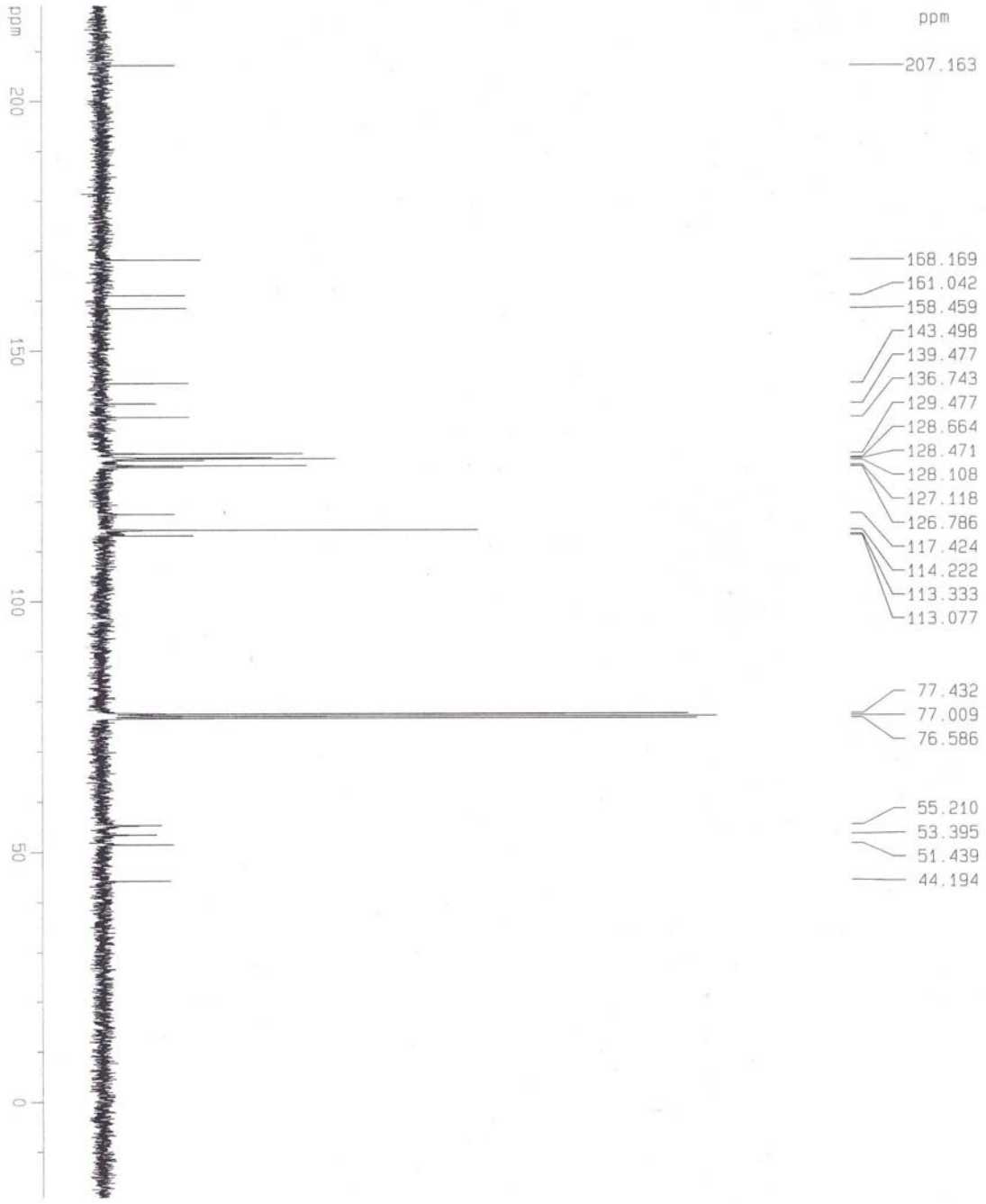
Compound 4f.



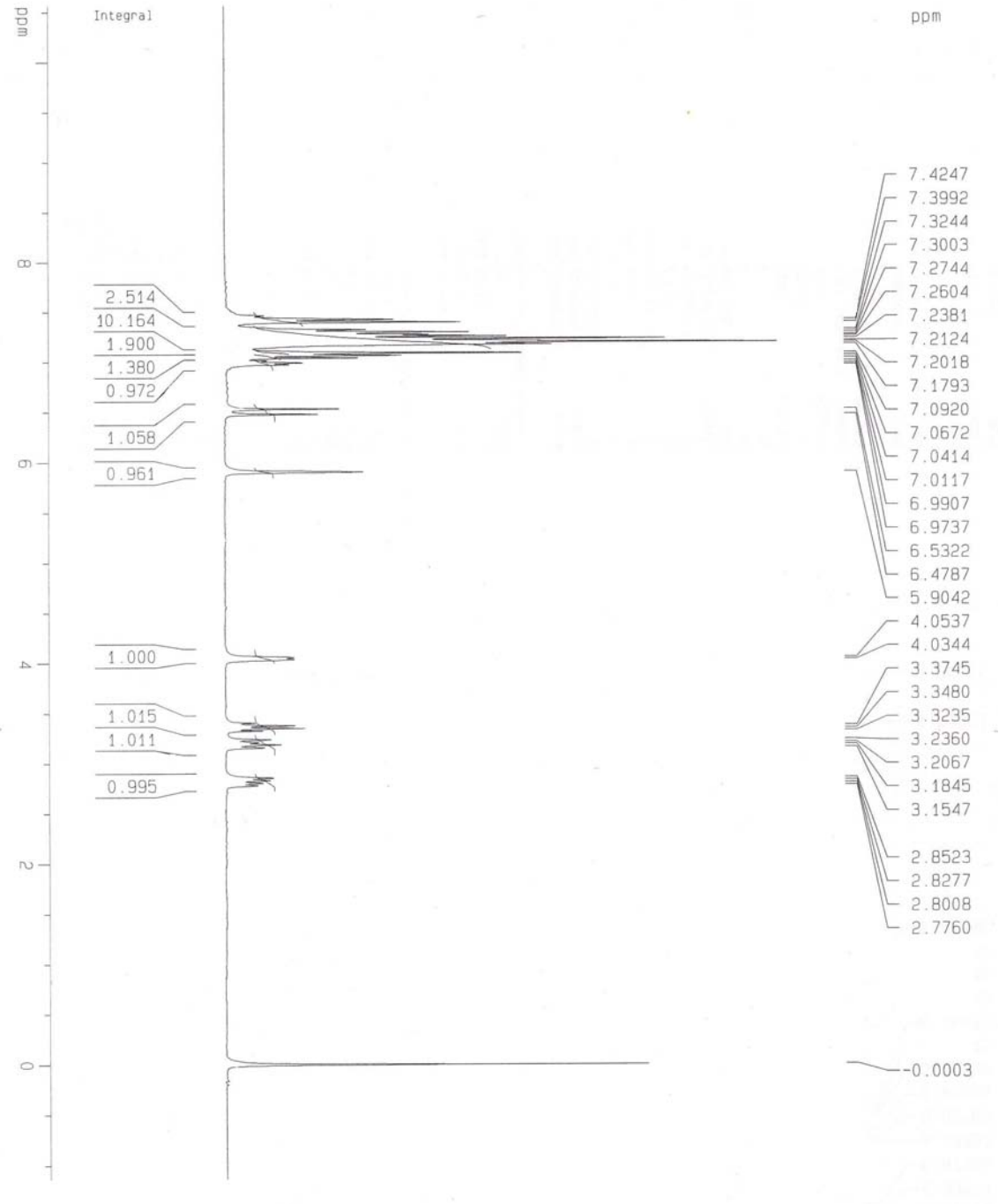
Compound 5f.



Compound 5f.



Compound 4g.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0.961
1.000
1.015
1.011
0.995
7.4247
7.3992
7.3244
7.3003
7.2744
7.2604
7.2381
7.2124
7.2018
7.1793
7.0920
7.0672
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7.0117
6.9907
6.9737
6.5322
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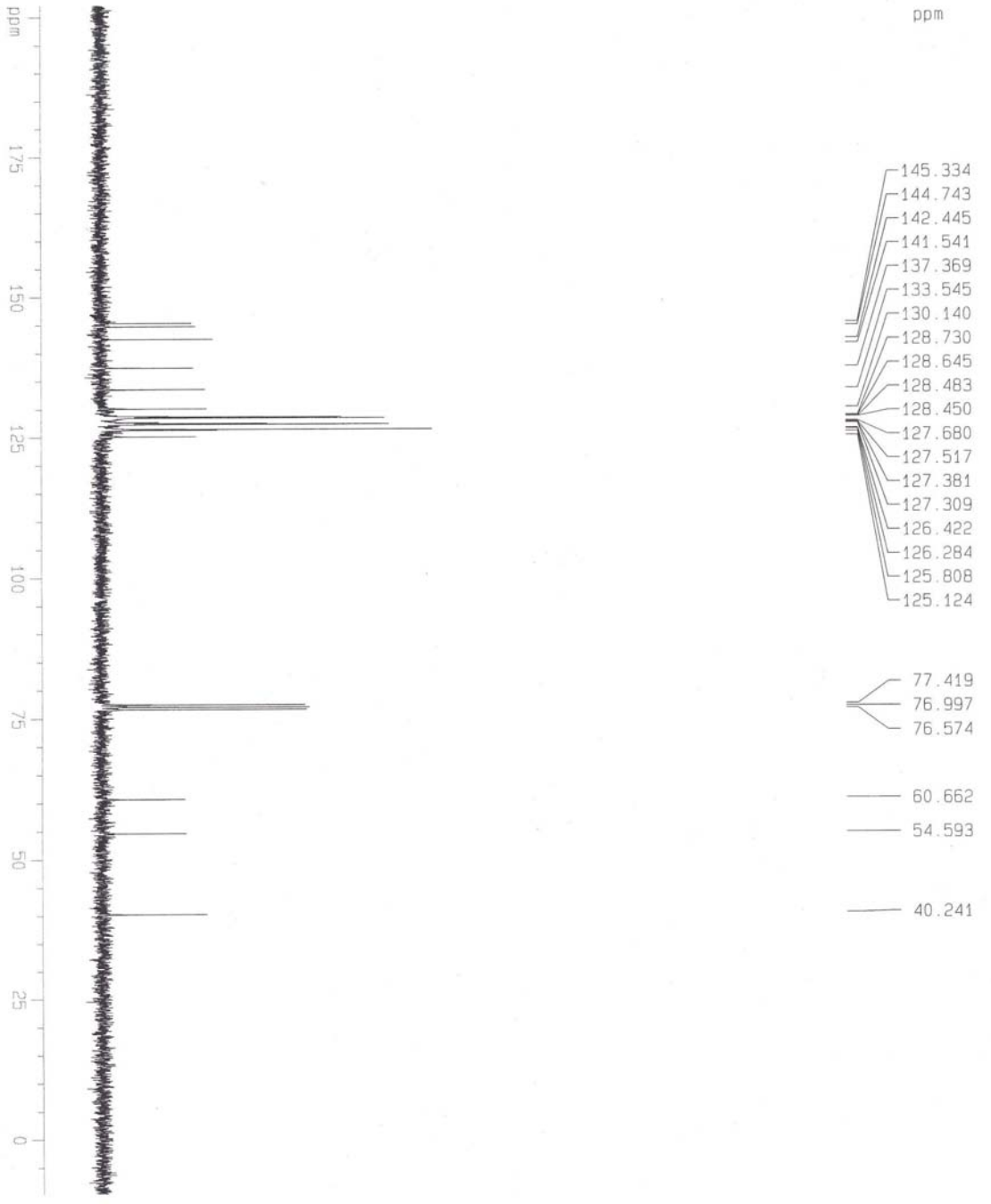
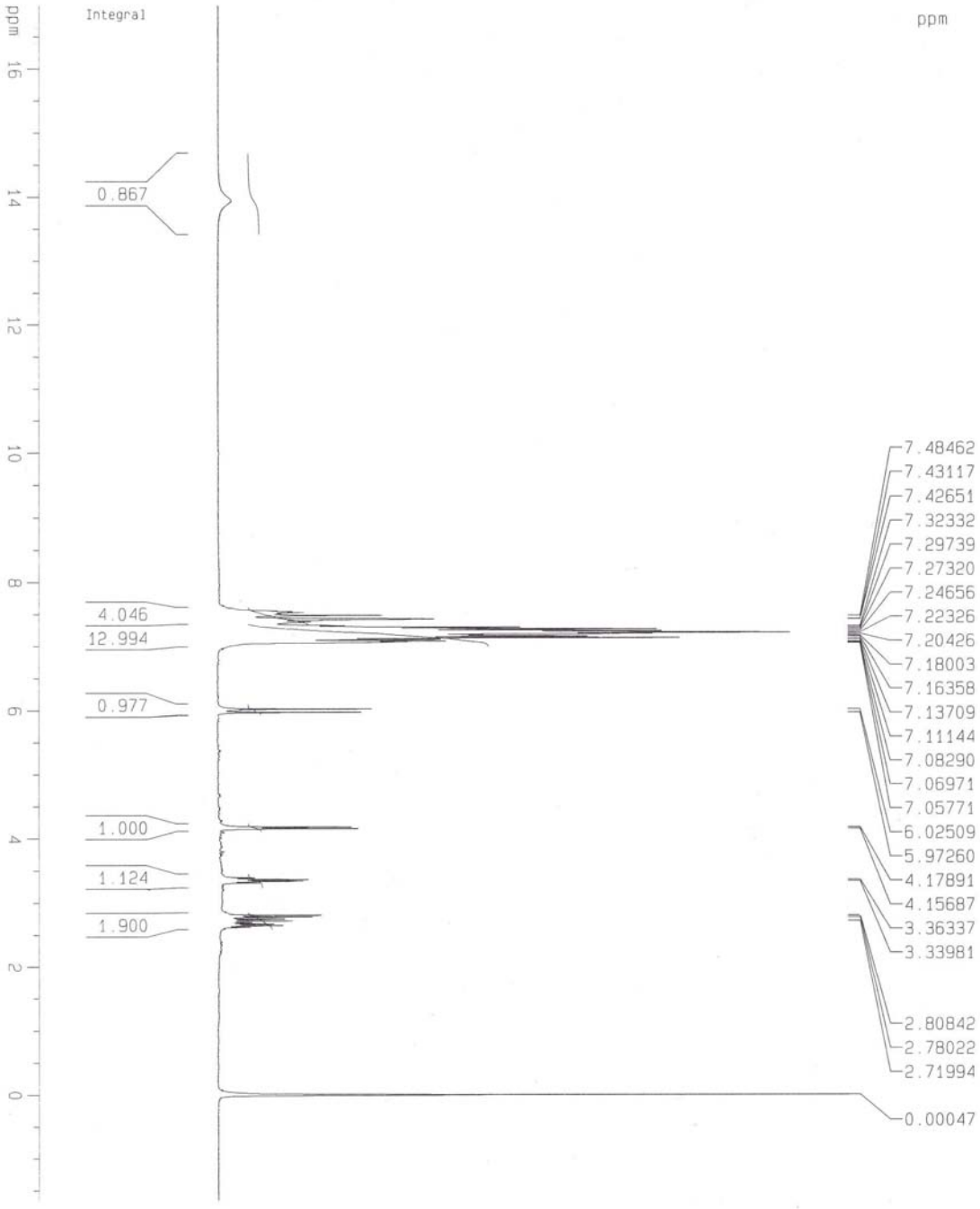
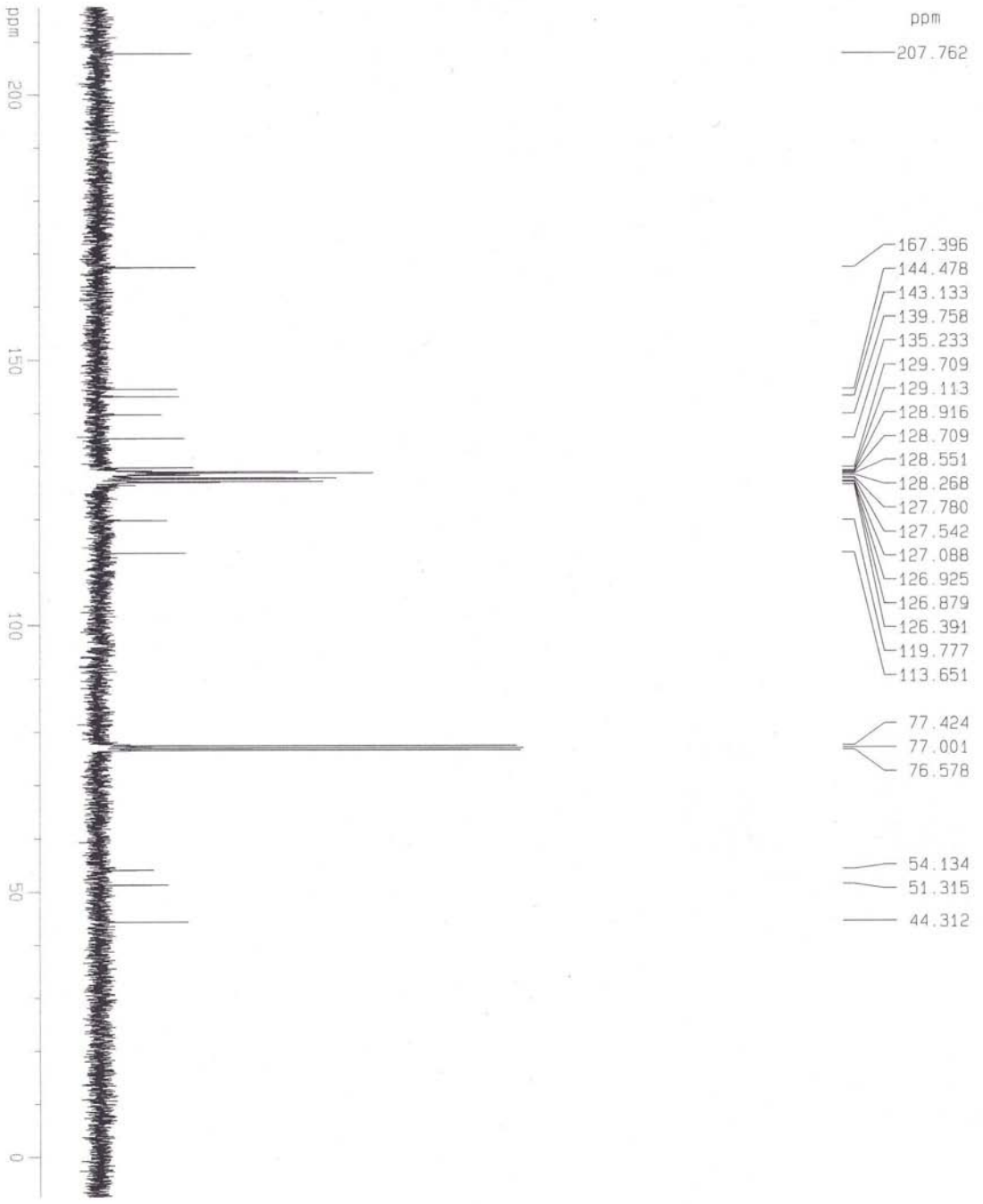
Compound 4g.



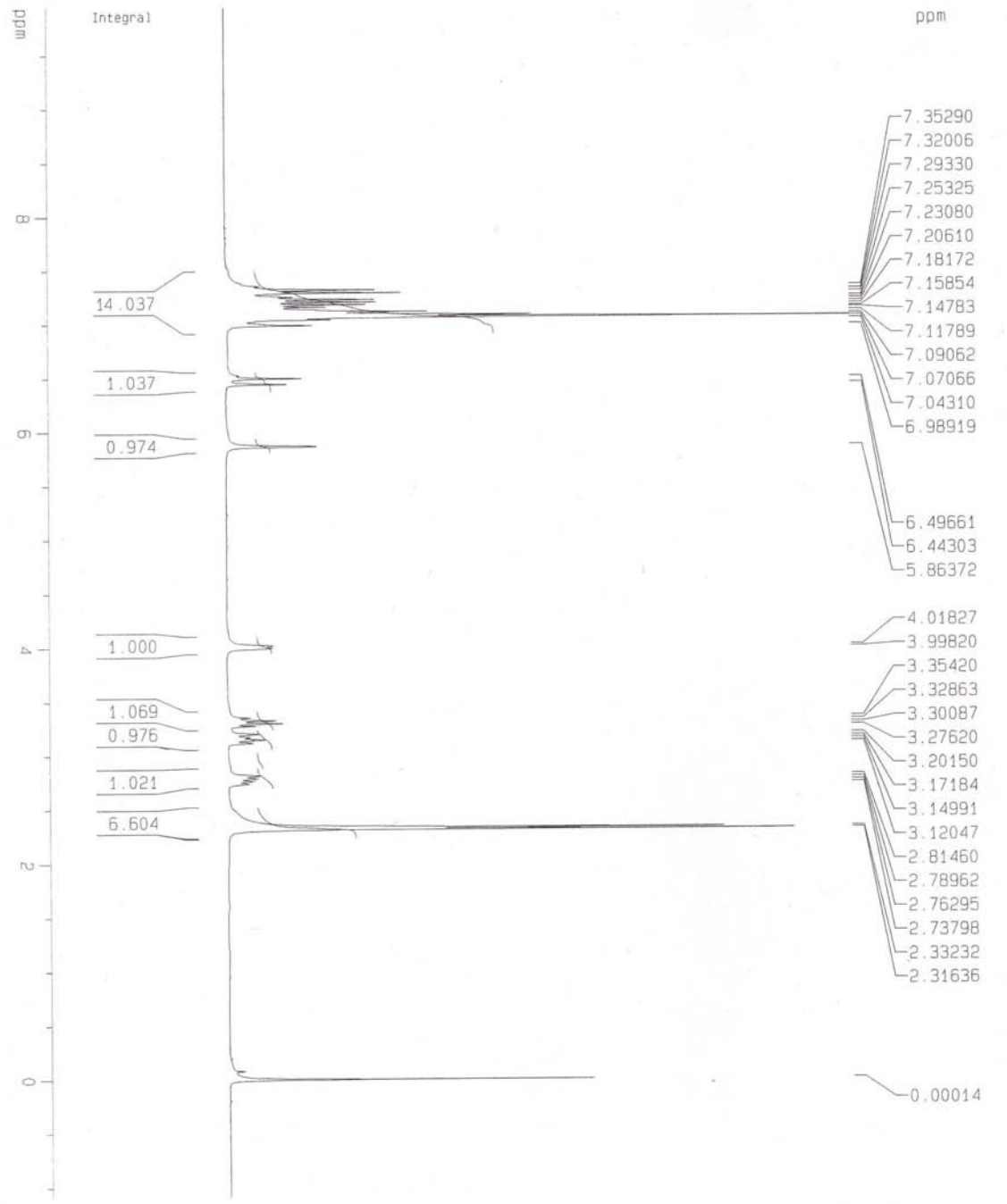
Compound 5g.



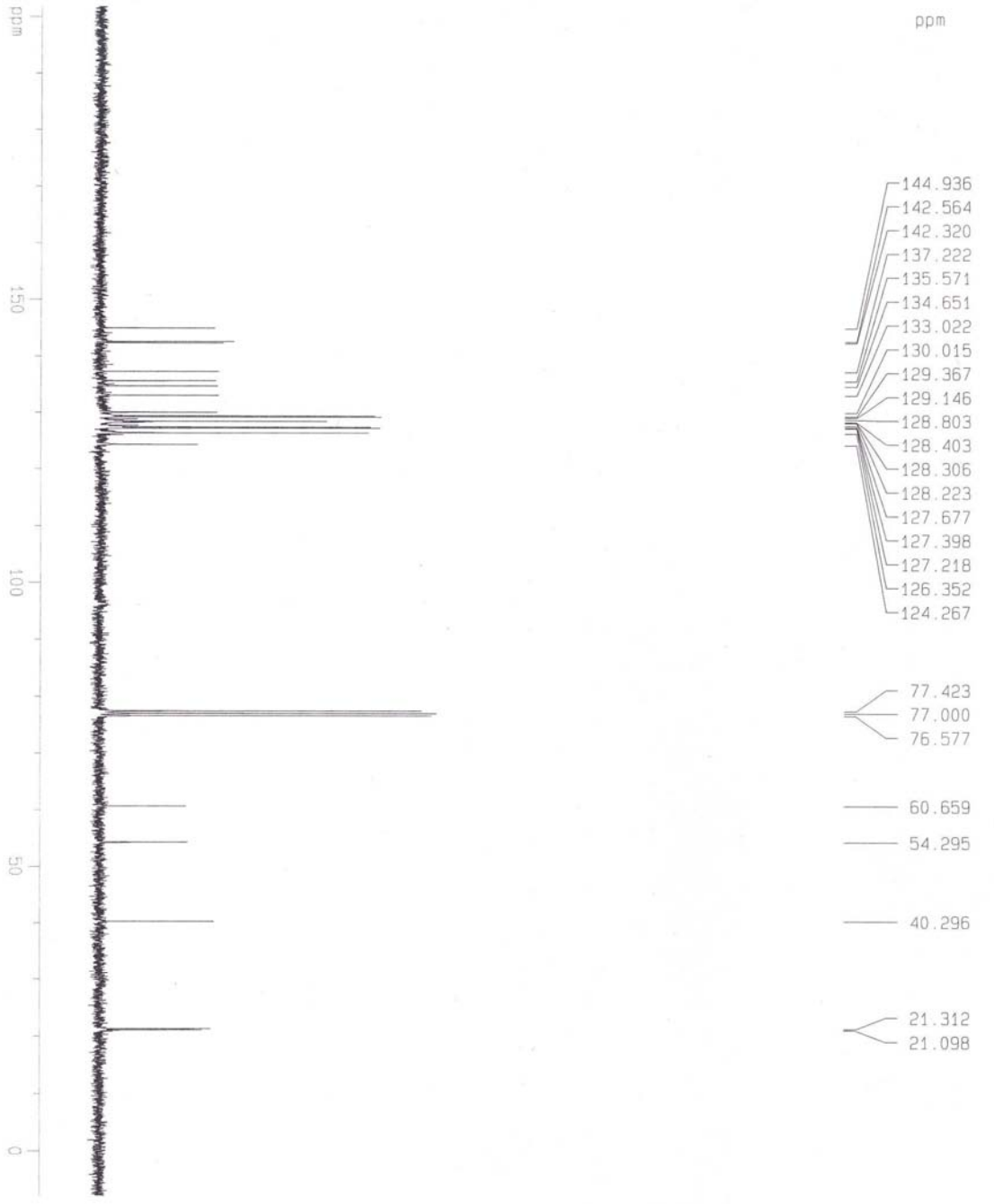
Compound 5g.



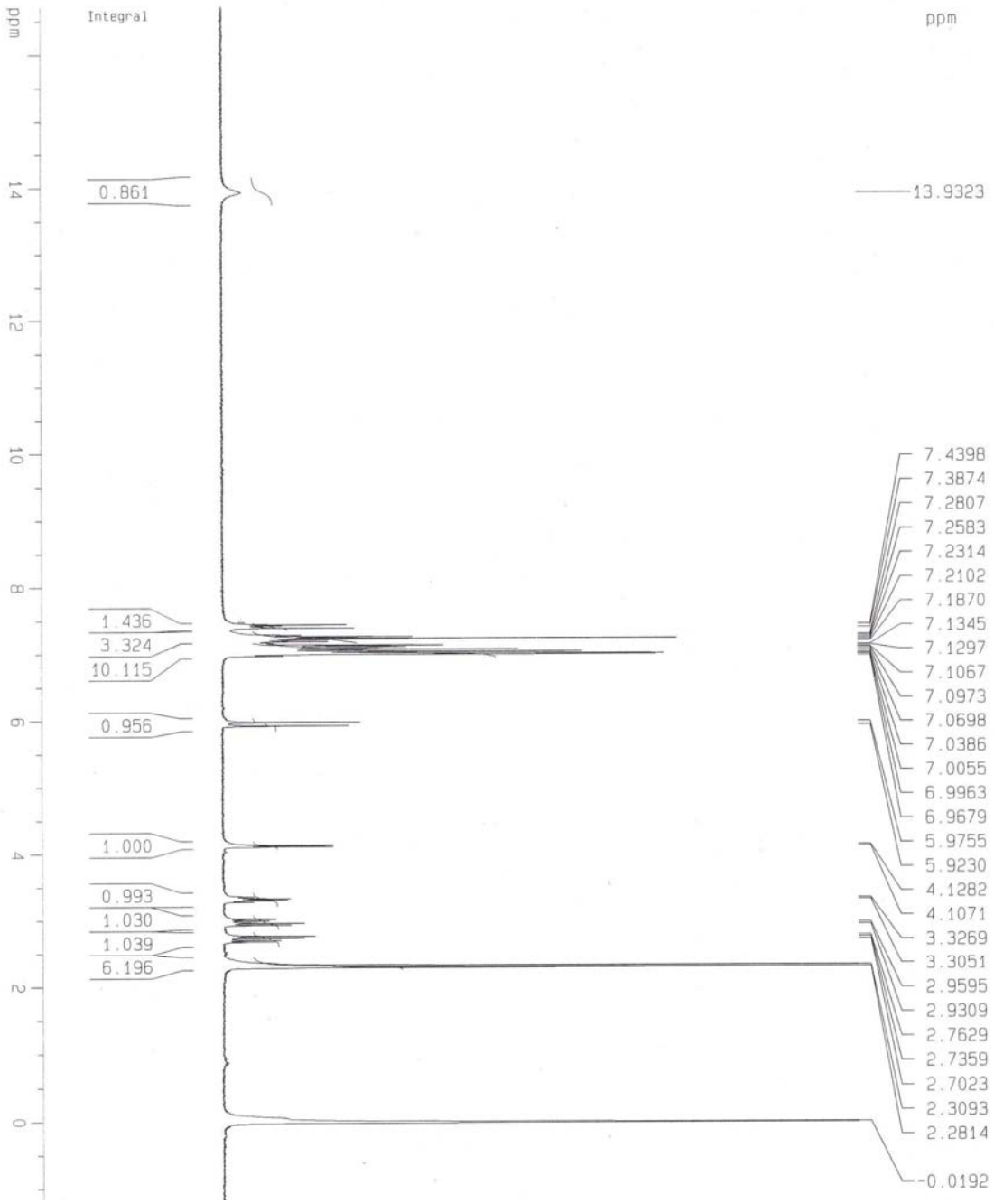
Compound 4h.



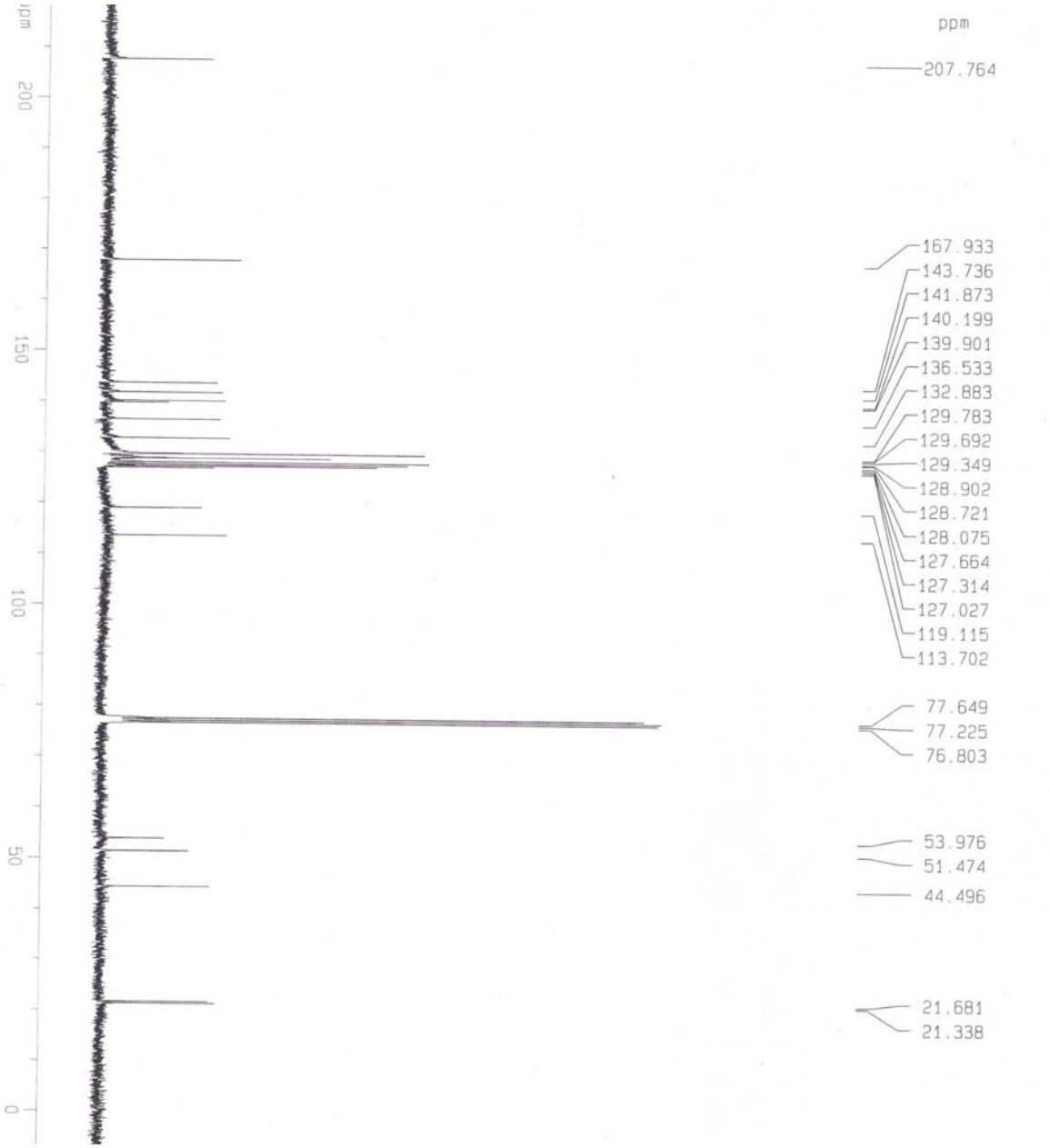
Compound 4h.



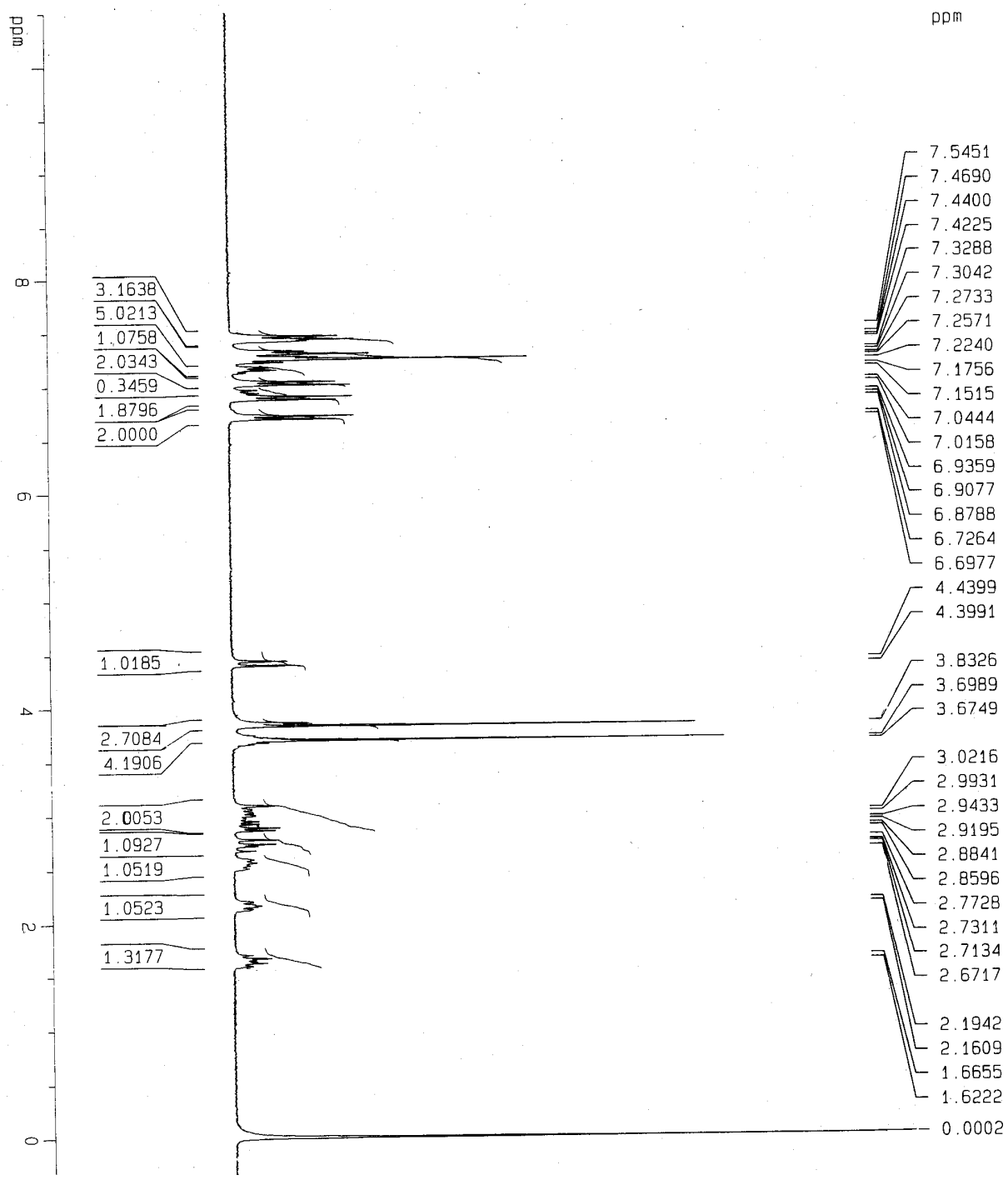
Compound 5h.



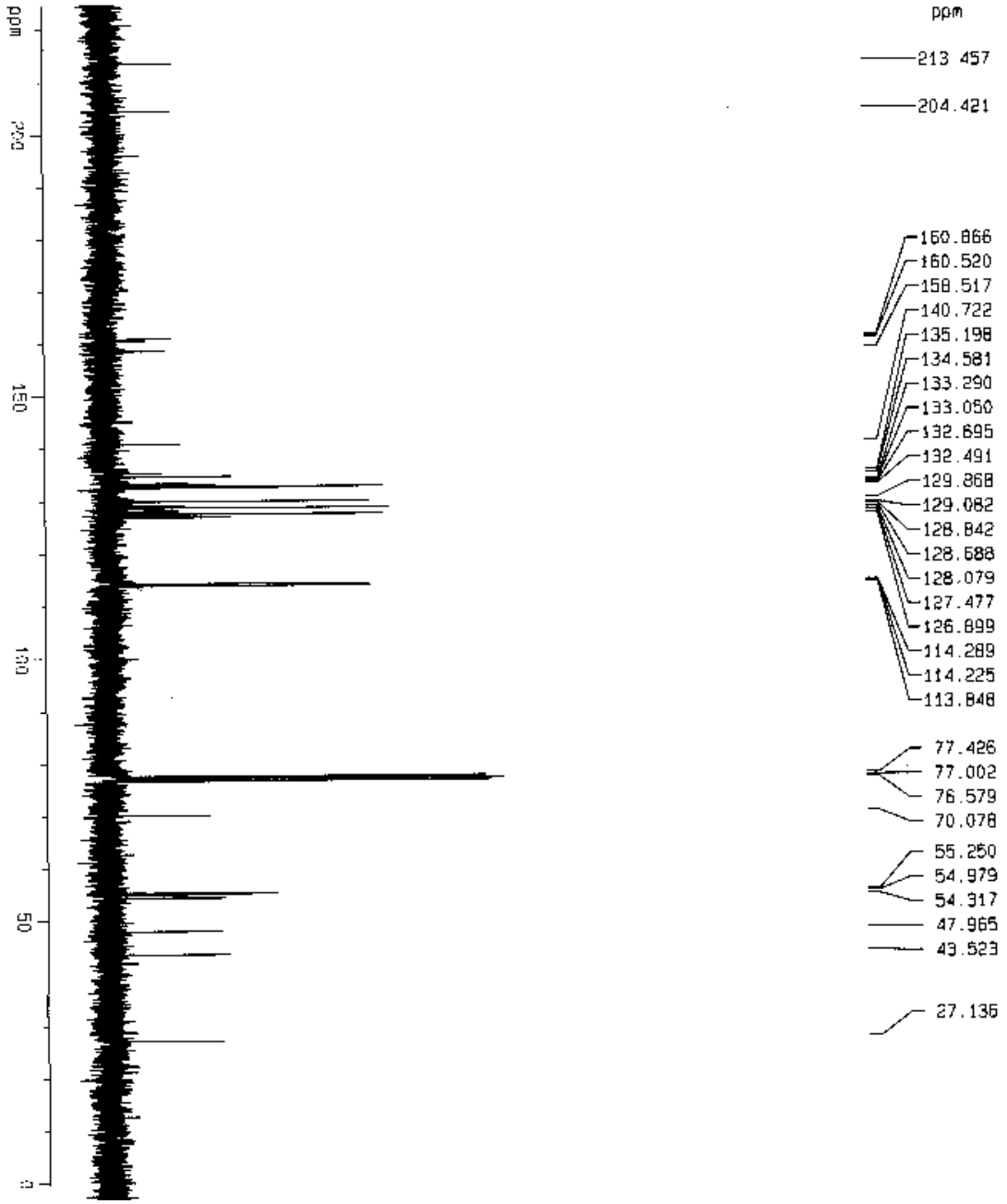
Compound 5h.



Compound 8a.



Compound 8a.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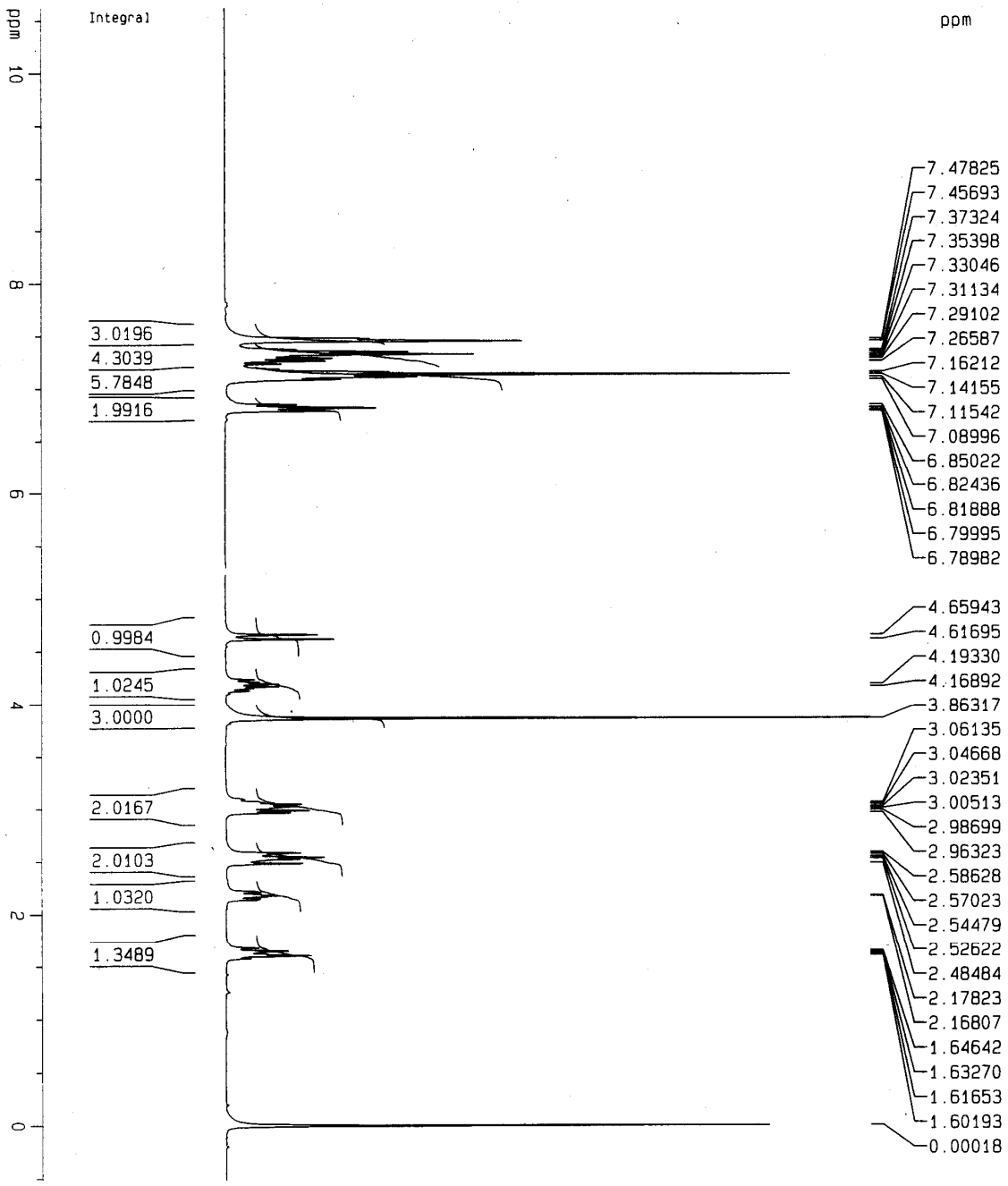
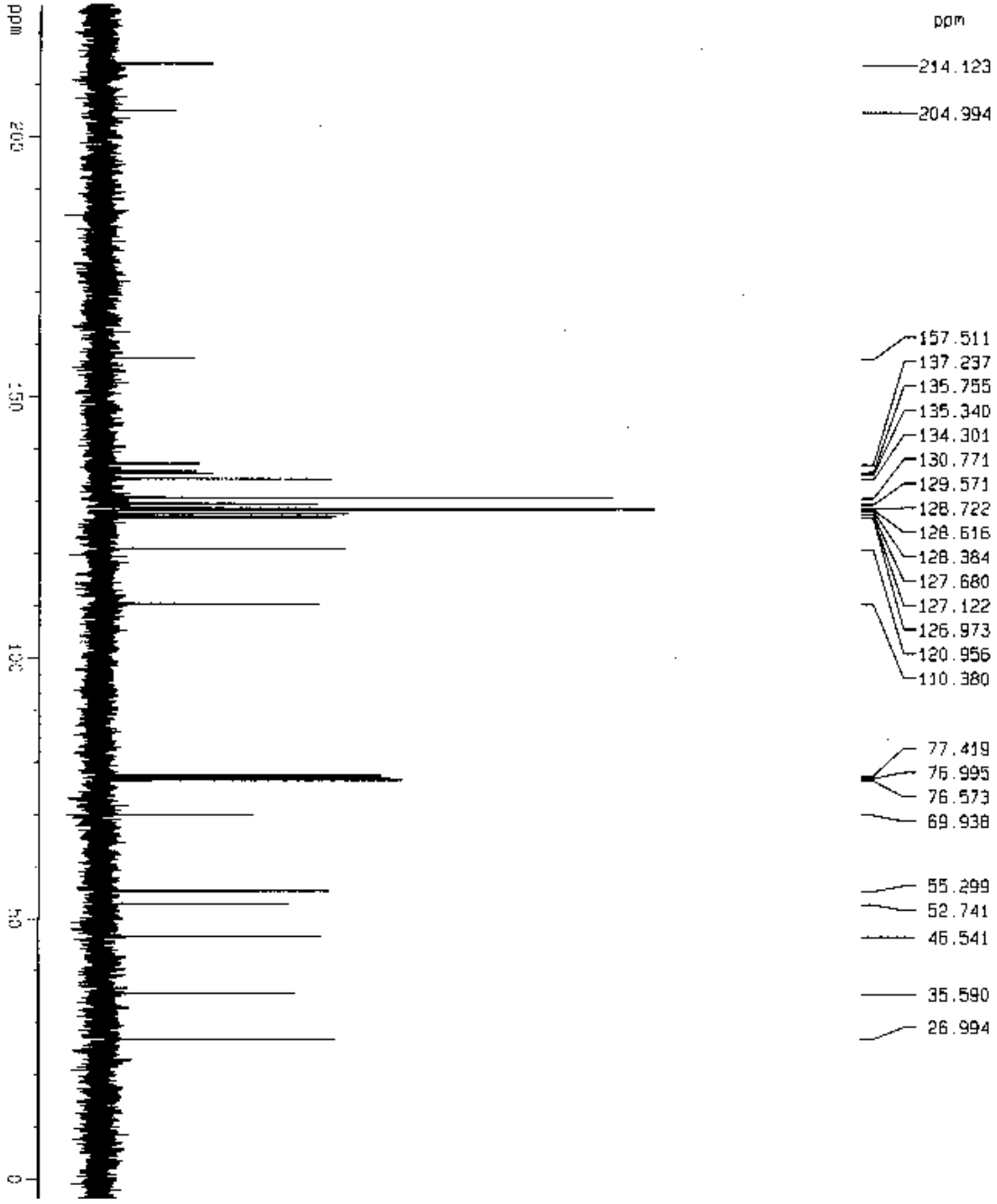
129.082
128.842
128.688
128.079
127.477
126.899
114.289
114.225
113.848
77.426
77.002
76.579
70.078
55.250
54.979
54.317
47.965
43.523
27.136
200
150
100
50
0

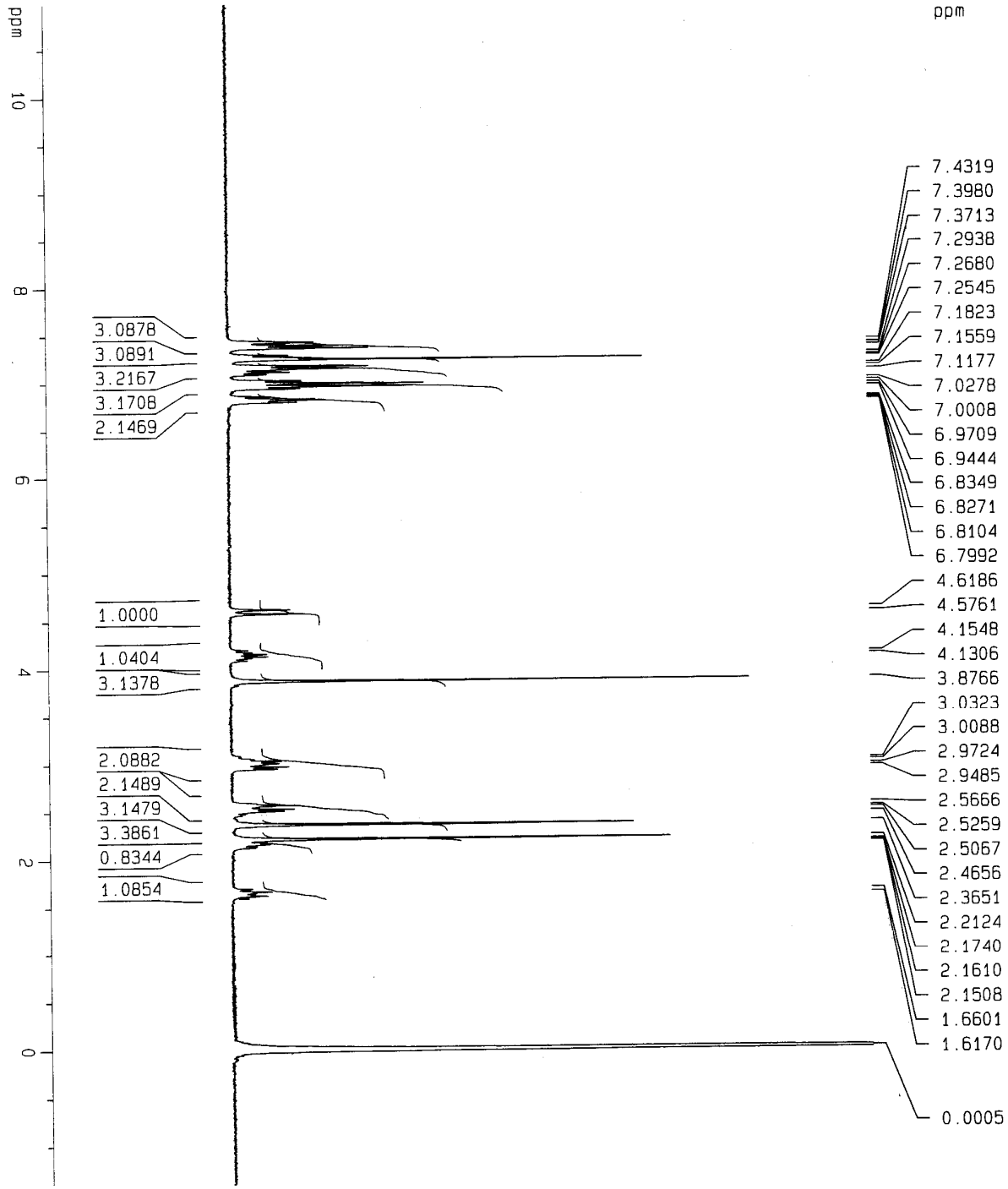
Compound 8b.



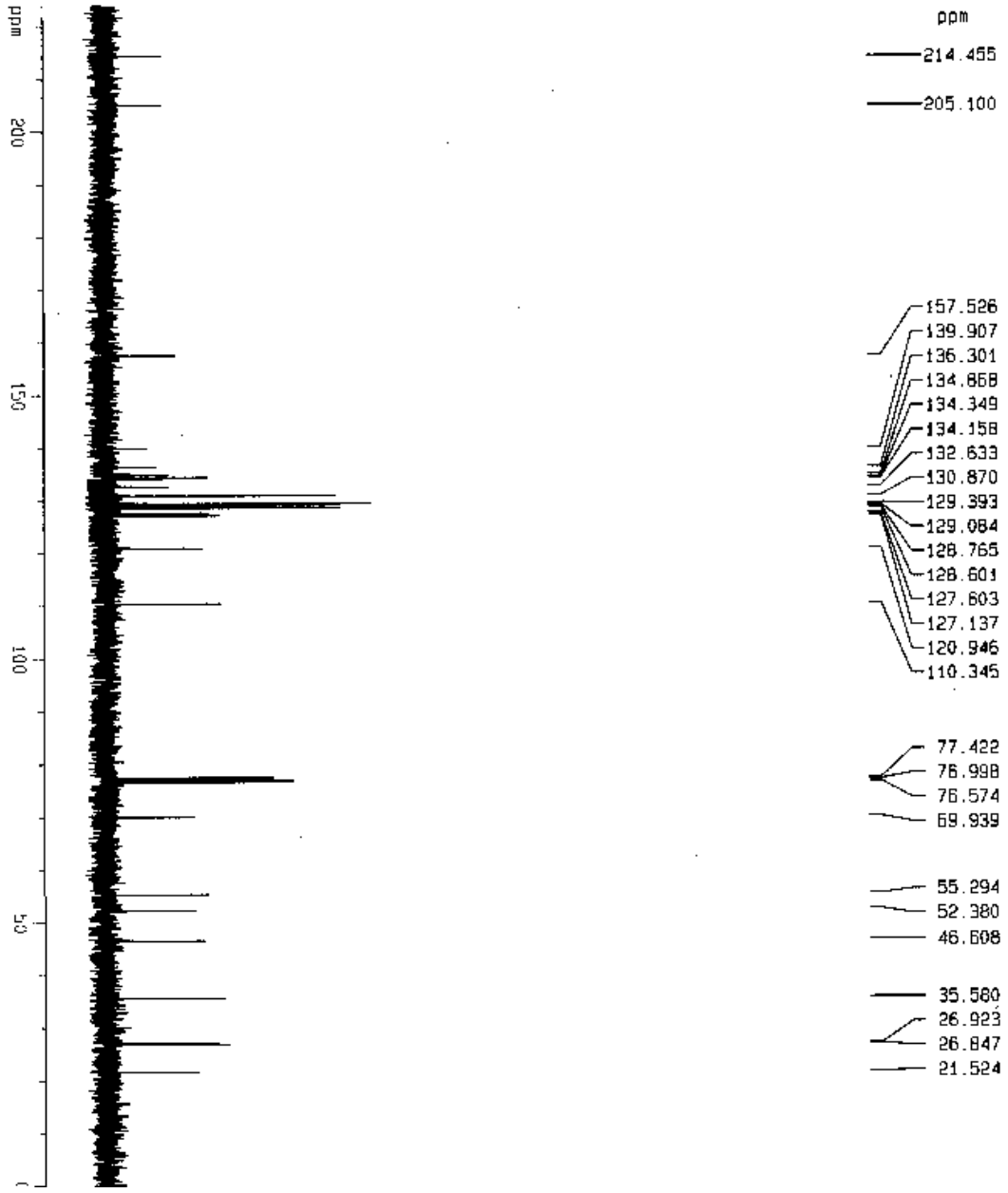
Compound 8b.


ppm
214.123
204.994
157.511
137.237
135.755
135.340
134.301
130.771
129.571
128.722
128.616
128.384
127.680
127.122
126.973
120.956
110.380
77.419
76.995
76.573
69.938
55.299
52.741
46.541
35.590
26.994
200
150
100
50
0

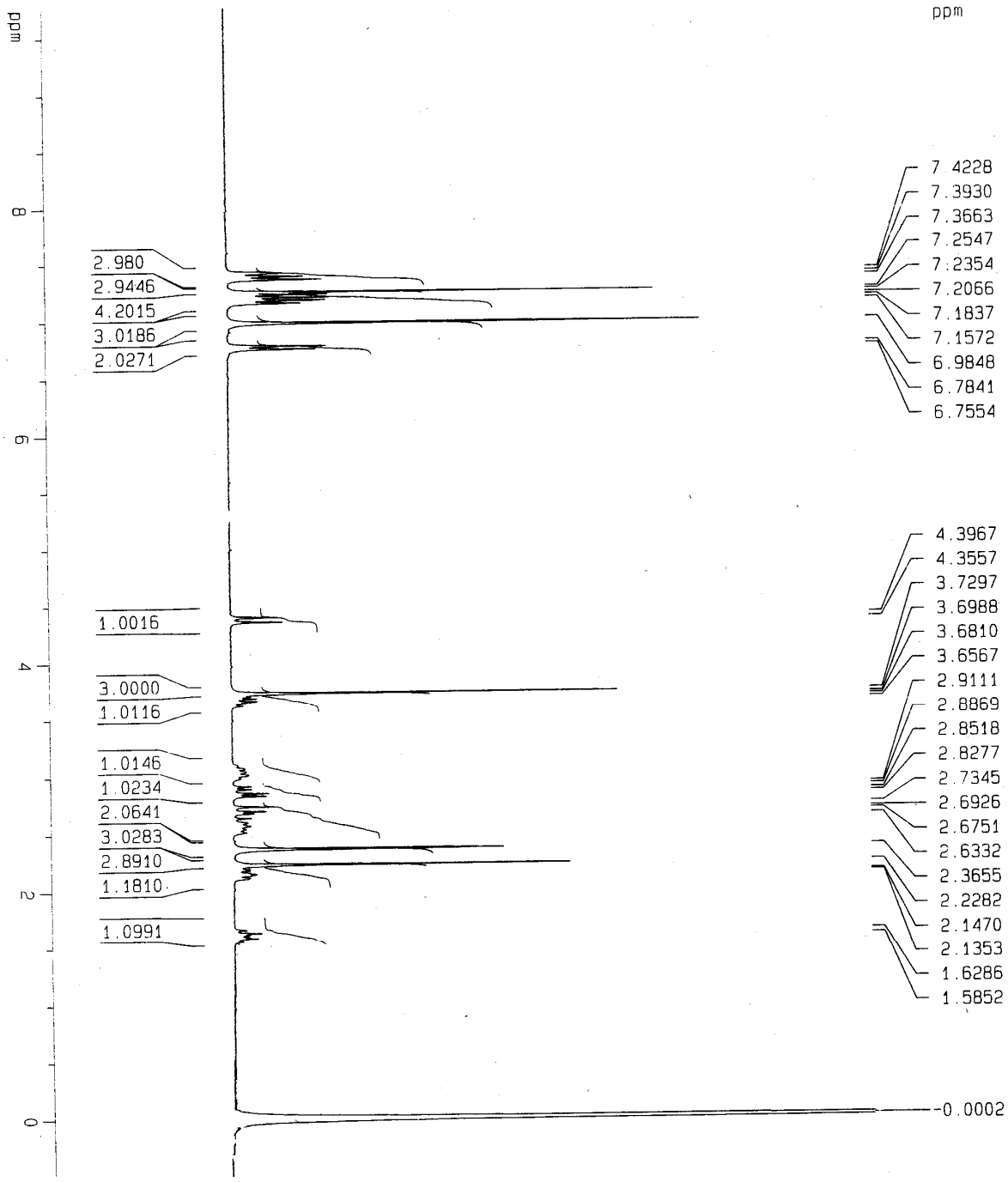
Compound 8c.



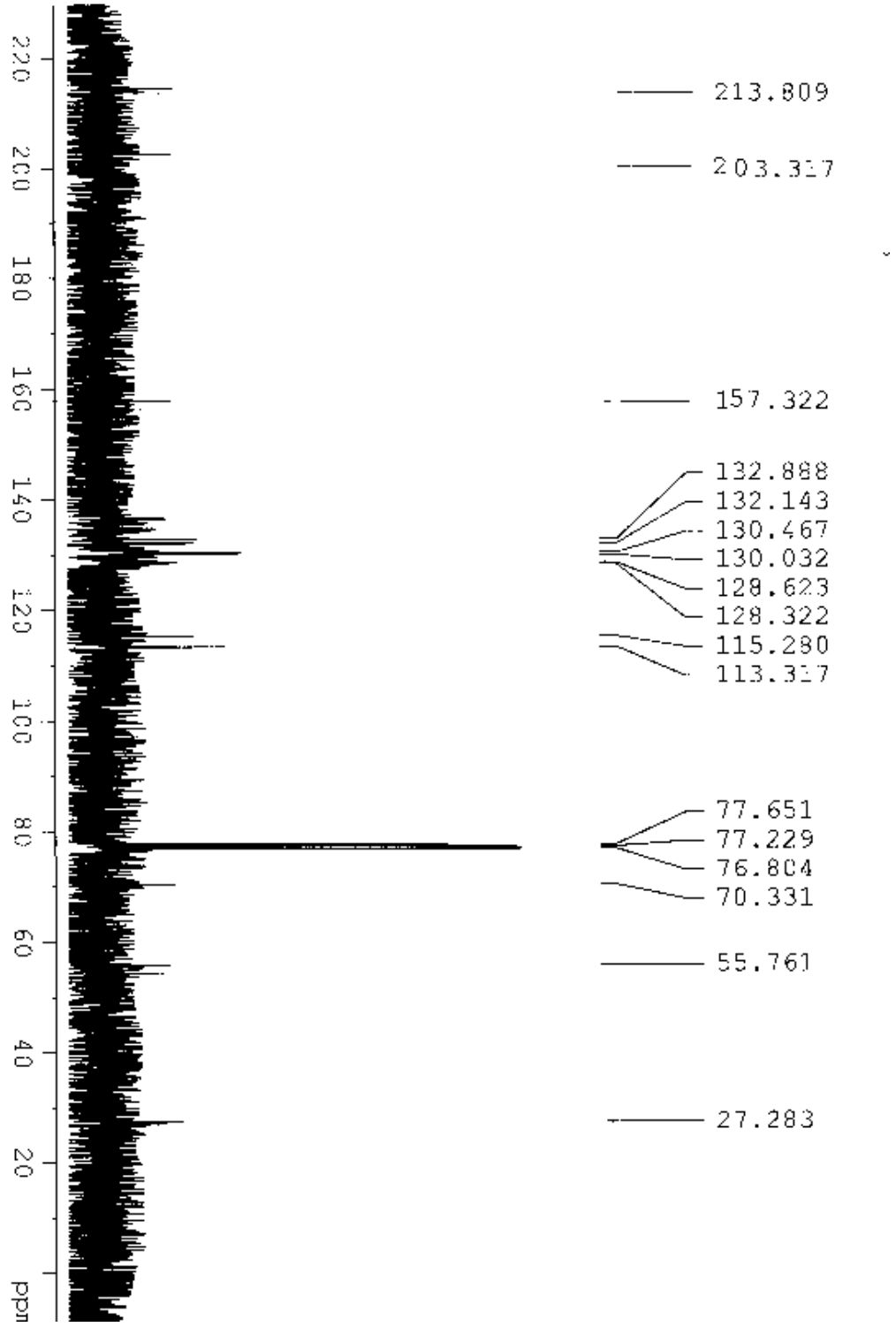
Compound 8c.



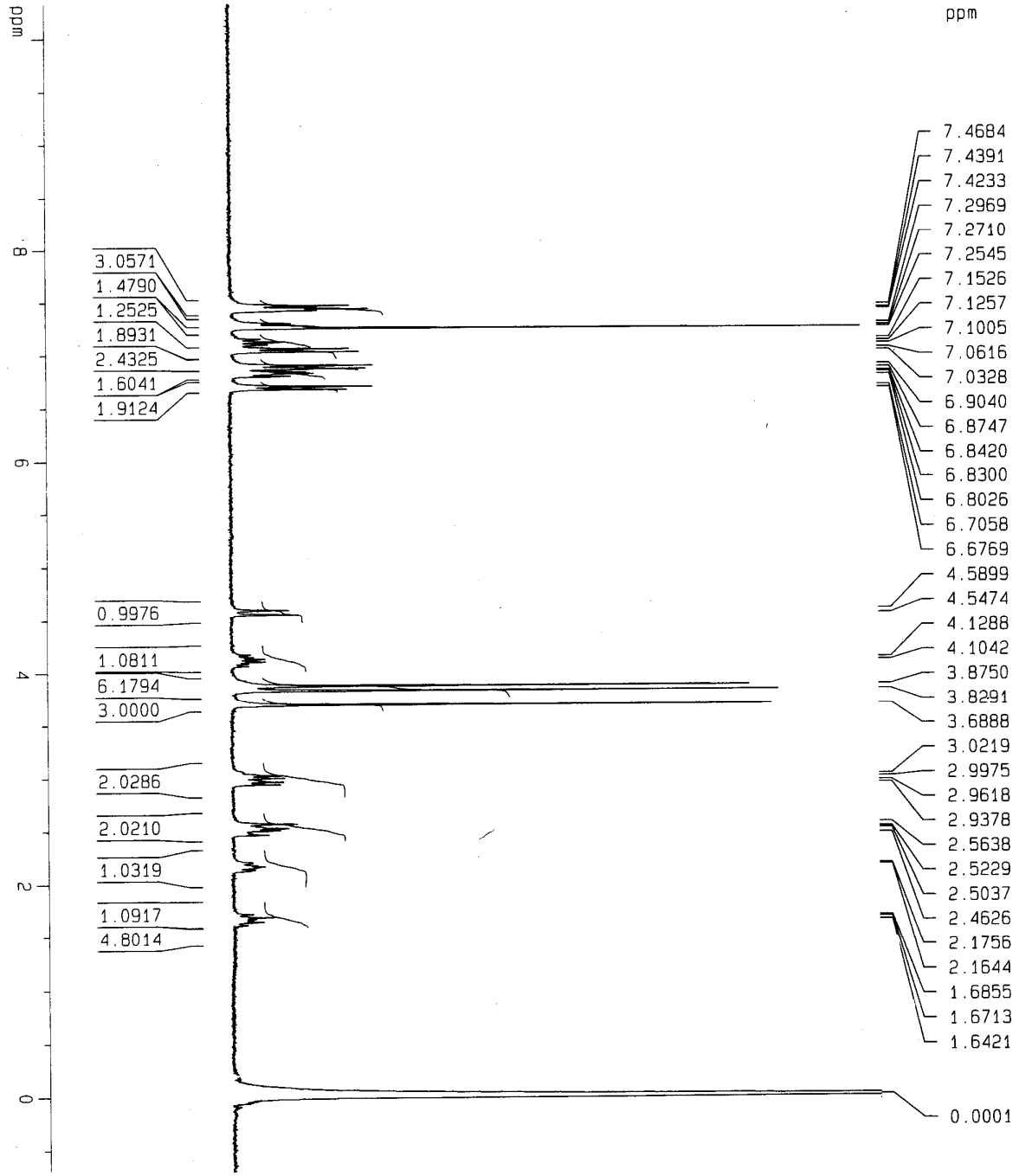
Compound 8d.



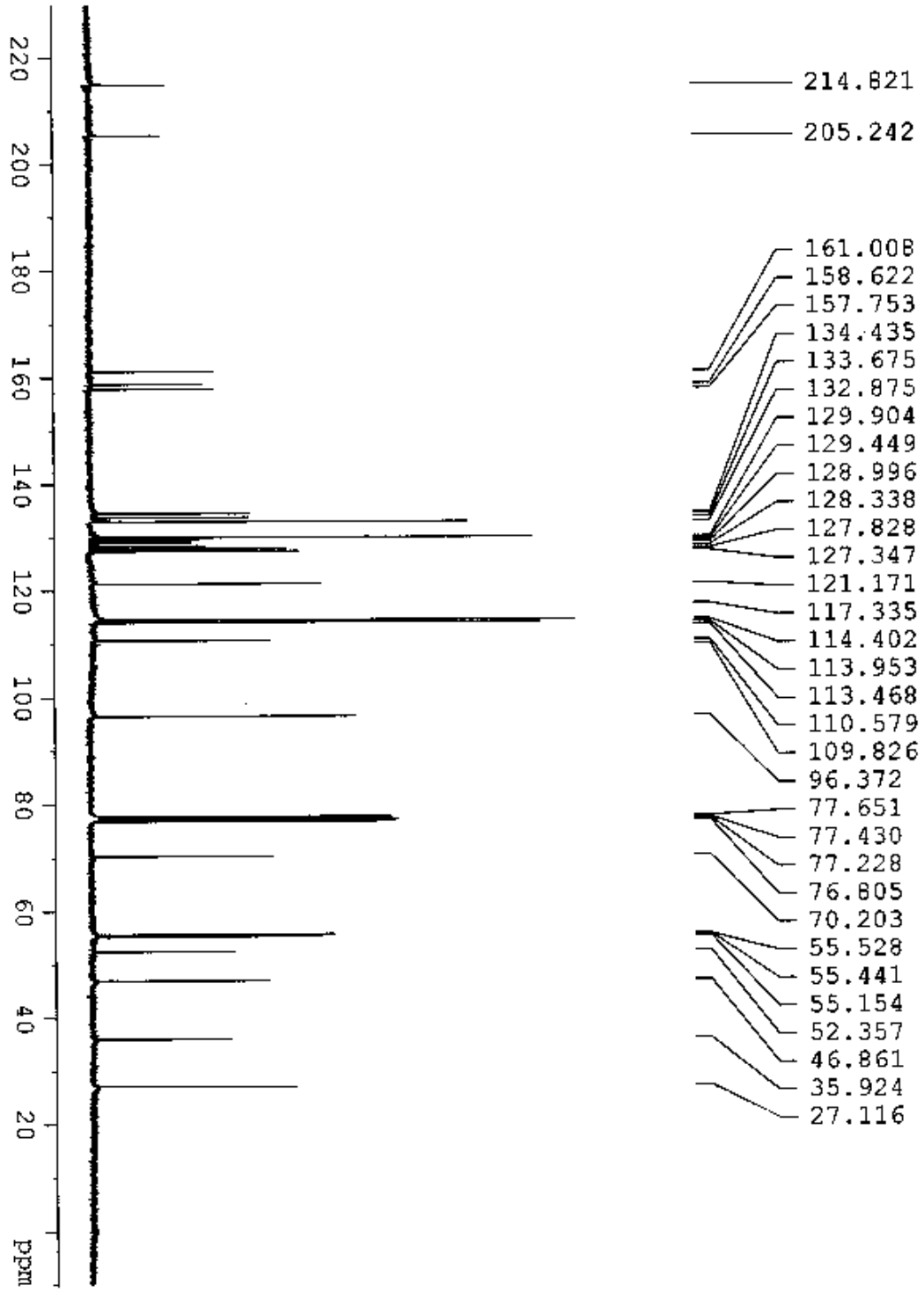
Compound 8d.



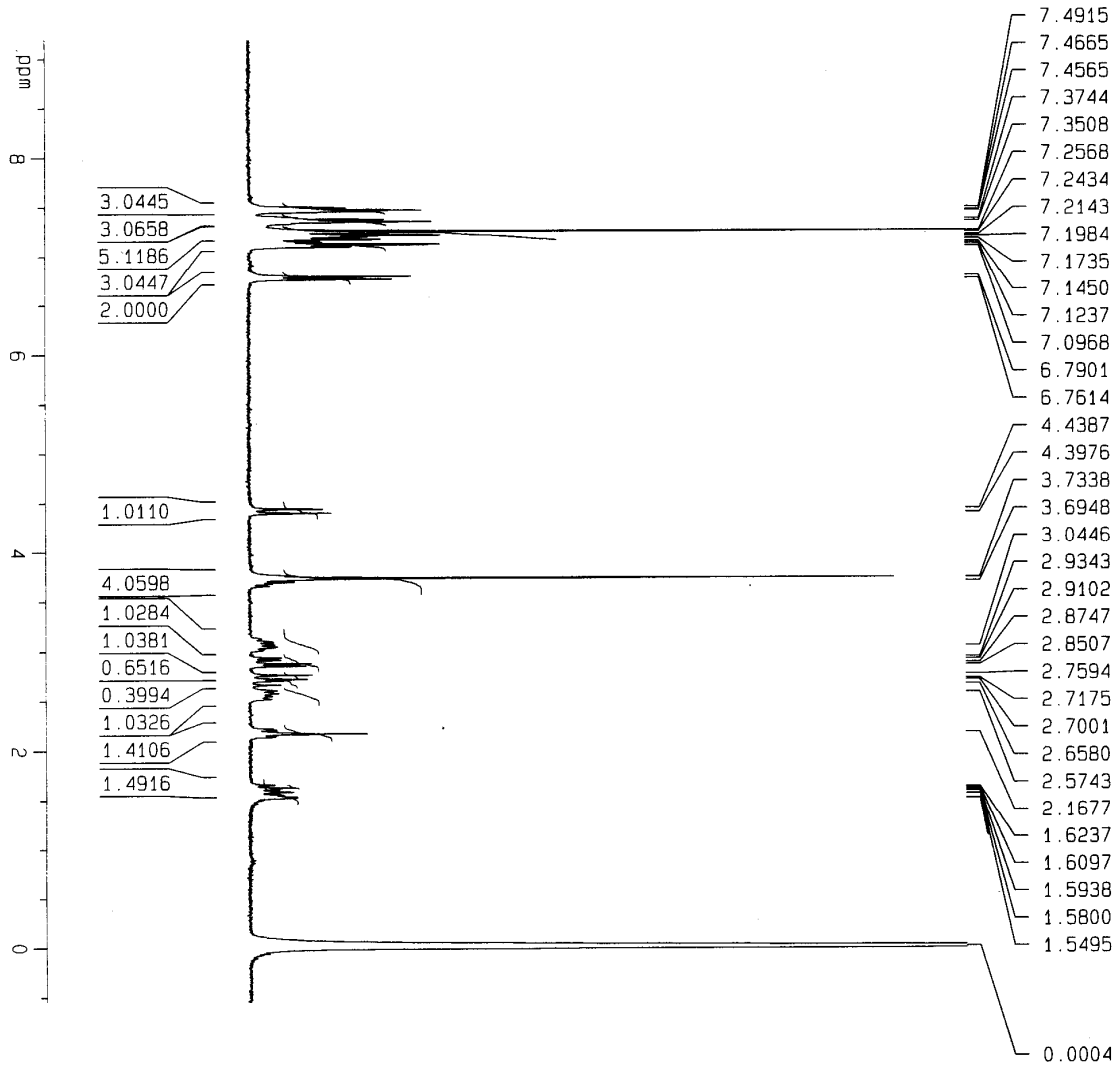
Compound 8e.



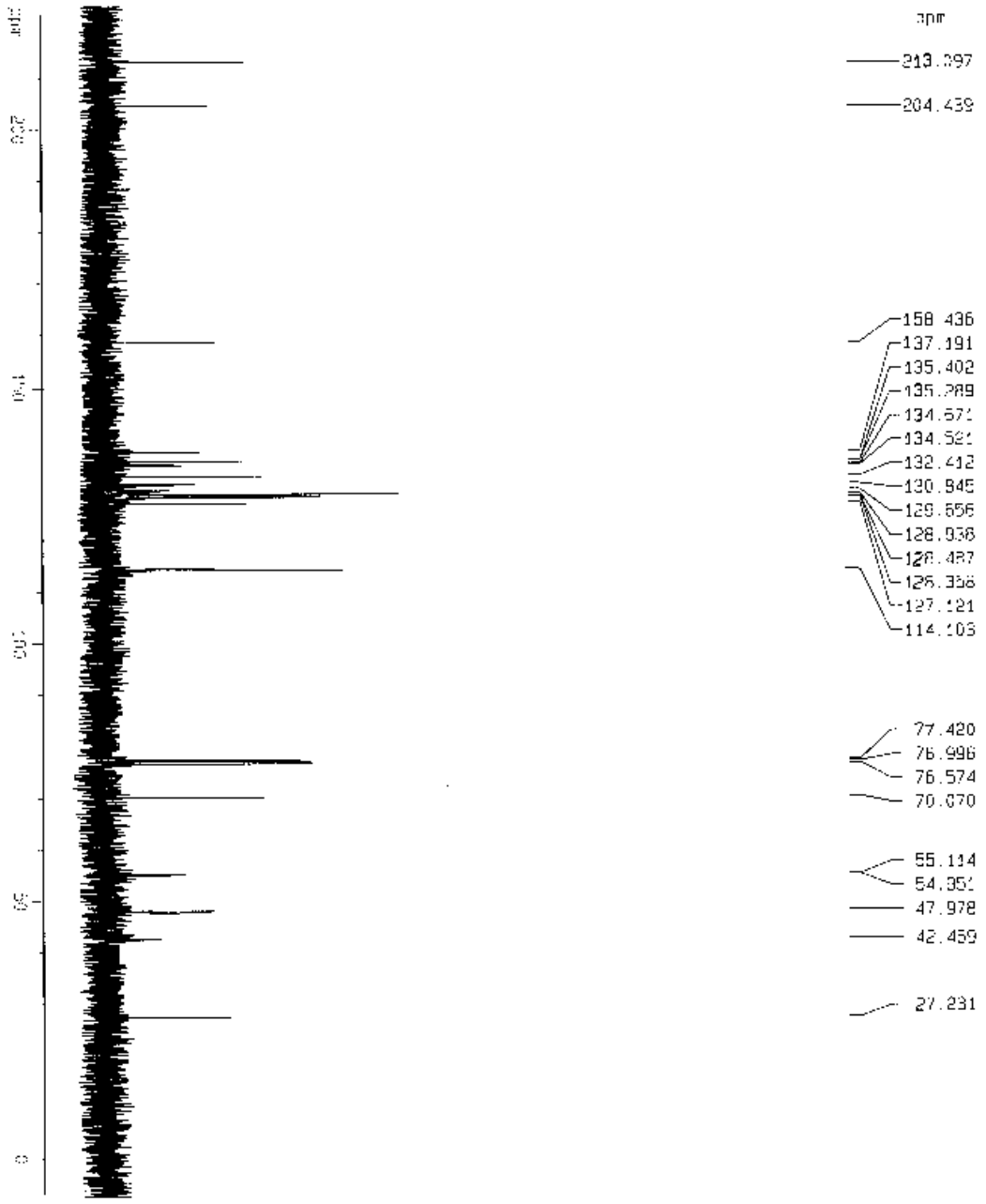
Compound 8e.



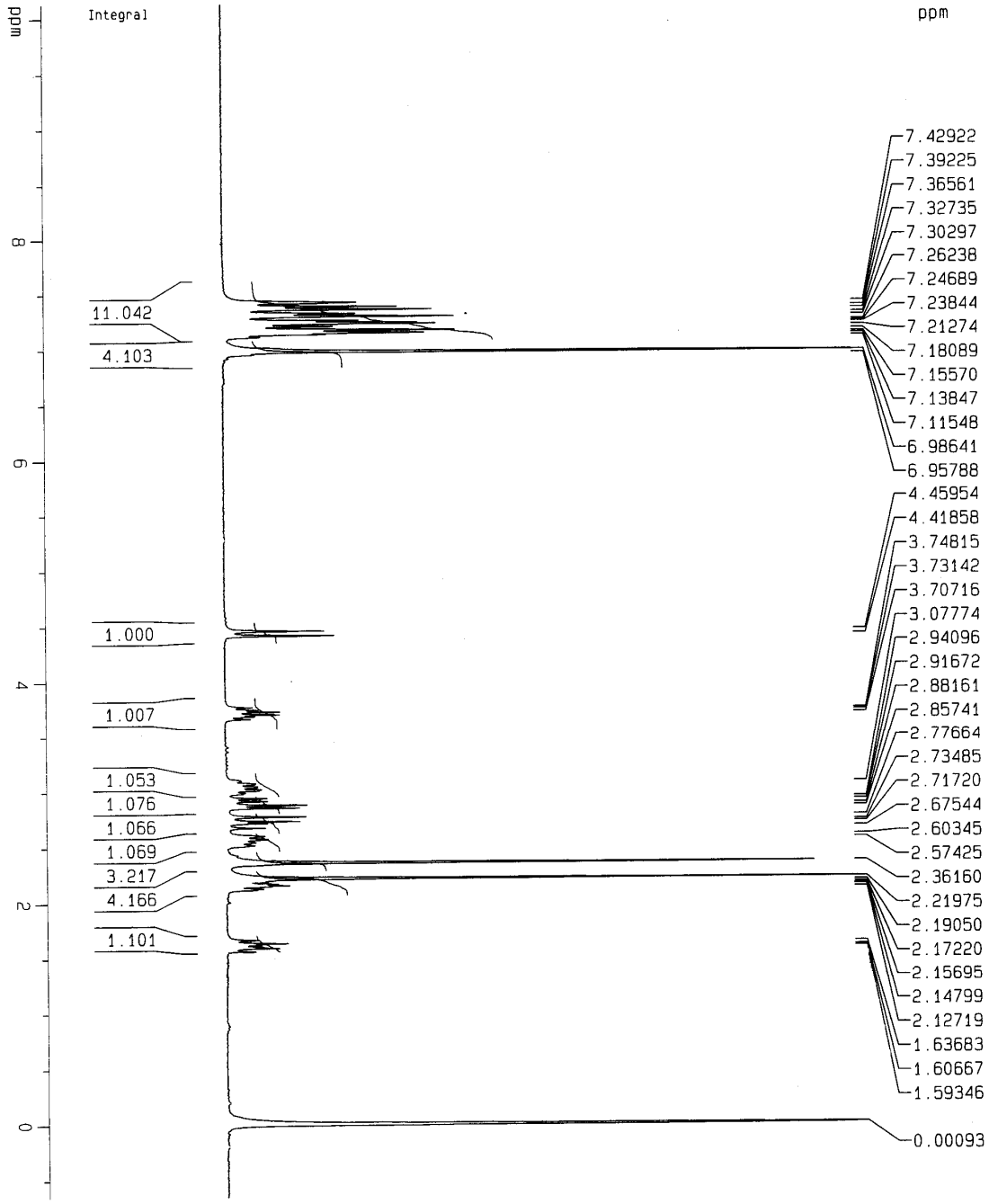
Compound 8f.



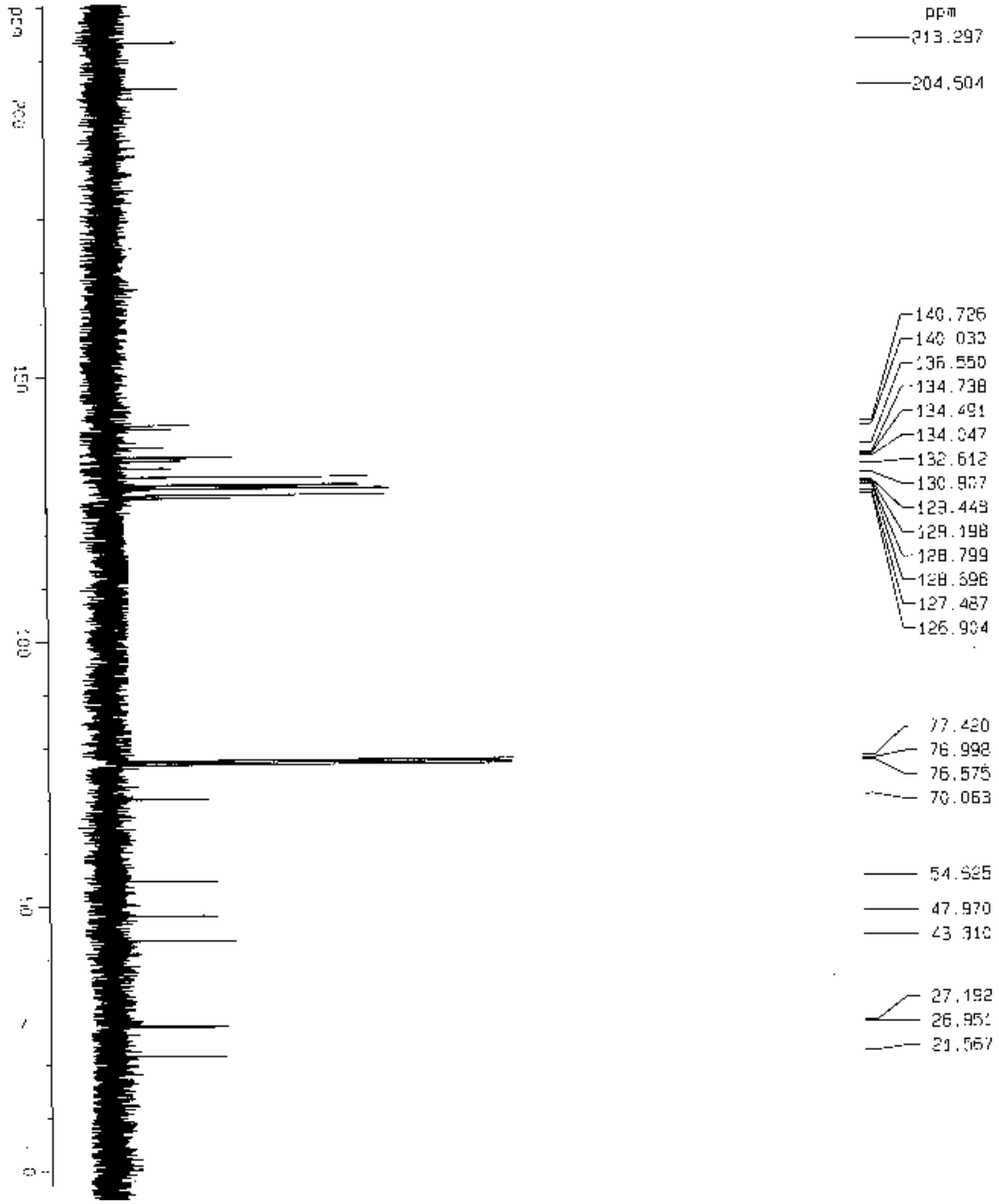
Compound 8f.


ppm
213.397
204.439
158.436
137.191
135.402
135.289
134.672
134.521
132.412
130.845
129.656
128.938
128.487
126.356
127.121
114.103
77.420
76.996
76.574
70.070
55.114
54.351
47.978
42.459
27.231

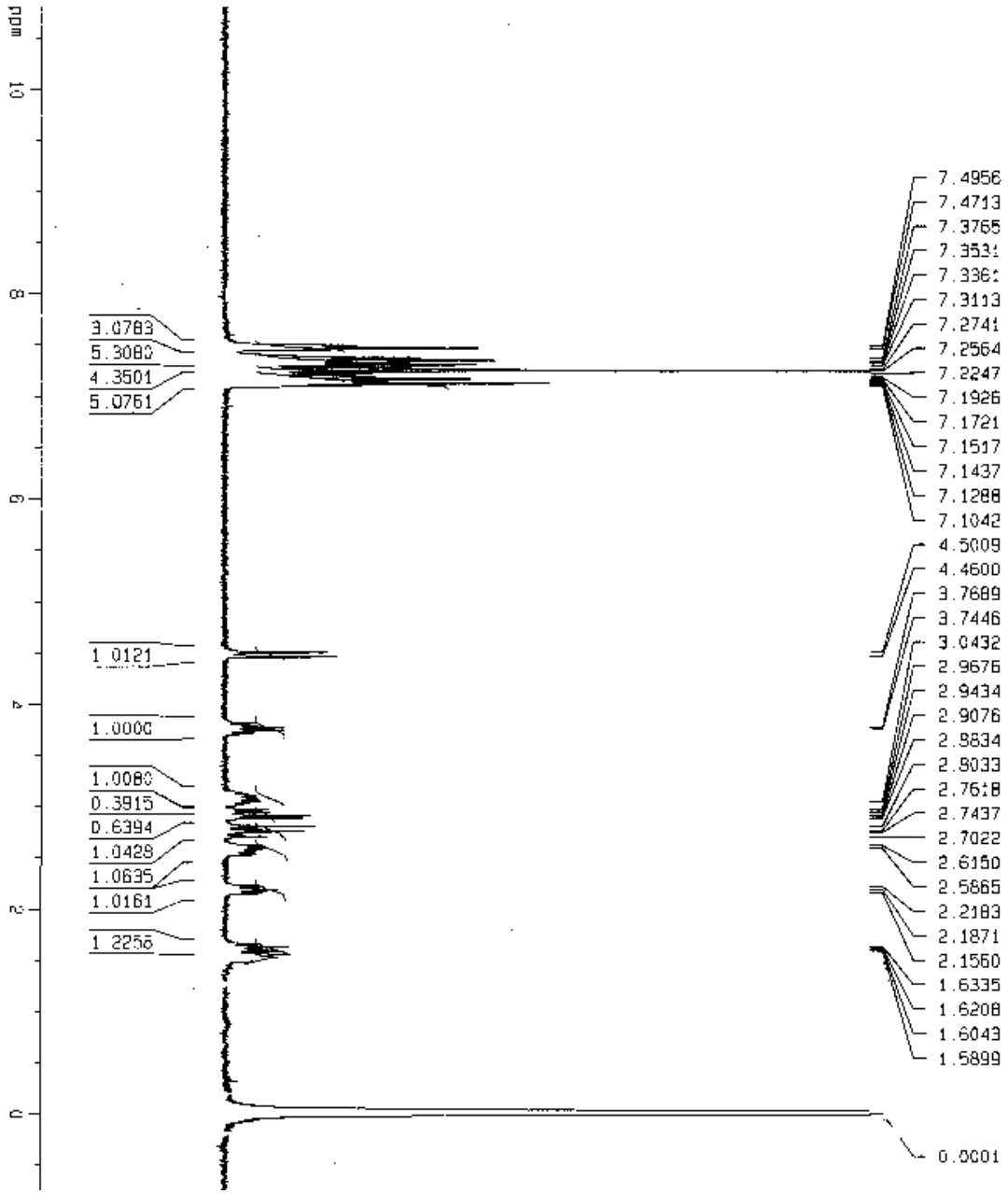
Compound 8g.



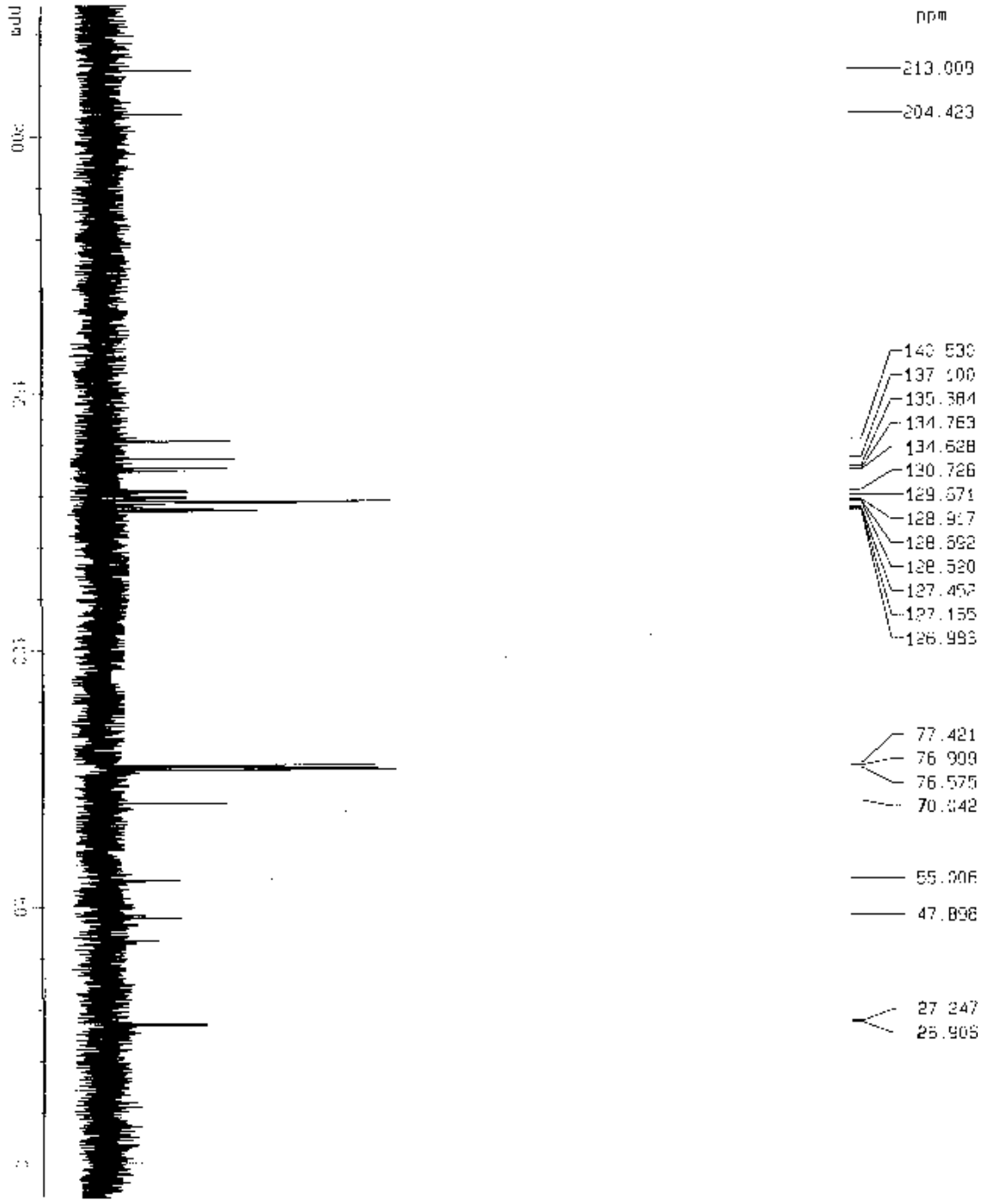
Compound 8g.



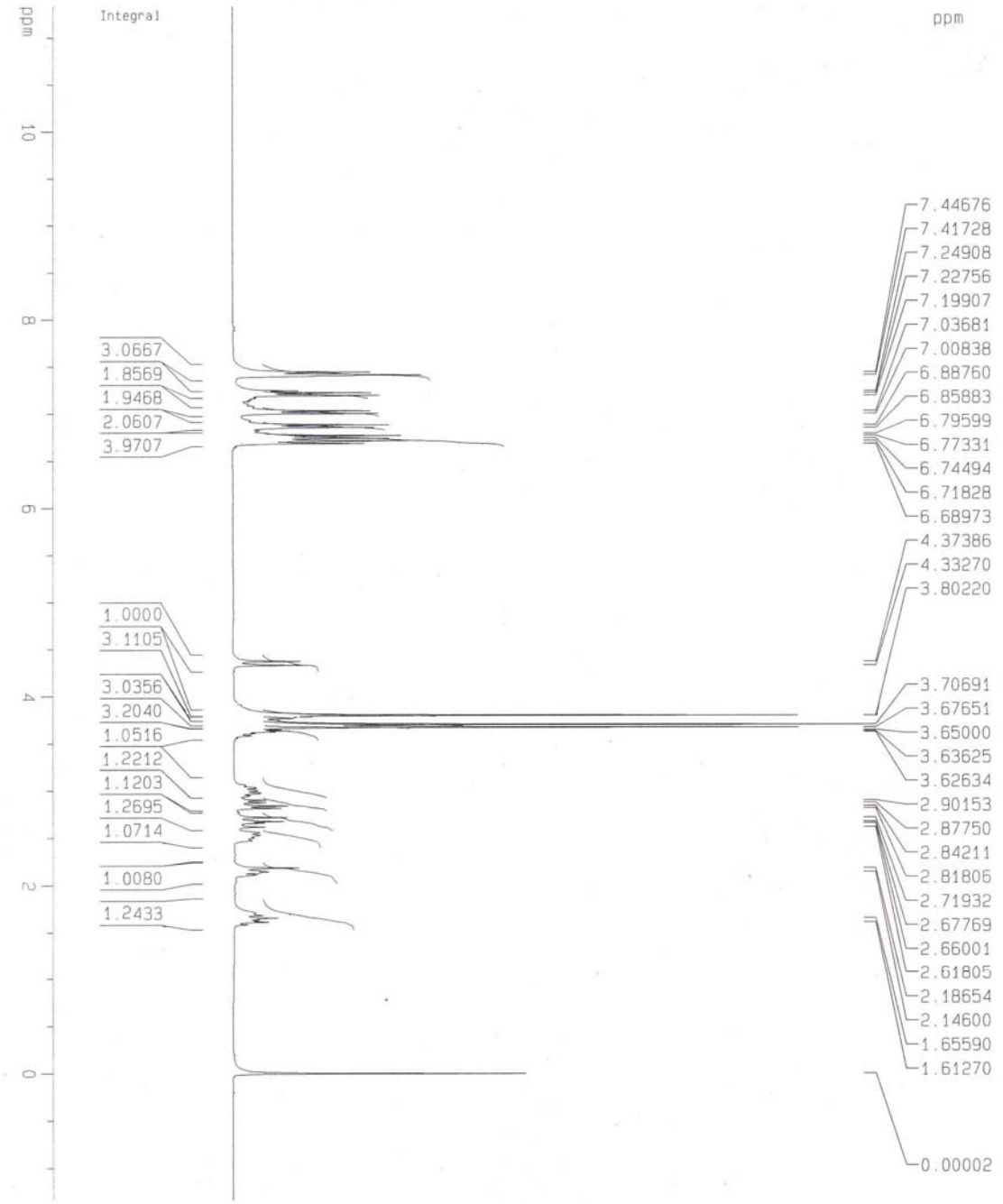
Compound 8h.


ppm
10
8
6
4
2
0
3.0783
5.3080
4.3501
5.0761
1.0121
1.0000
1.0080
0.3915
0.6394
1.0428
1.0635
1.0161
1.2256
7.4956
7.4713
7.3765
7.3531
7.3361
7.3113
7.2741
7.2564
7.2247
7.1926
7.1721
7.1517
7.1437
7.1288
7.1042
4.5009
4.4600
3.7689
3.7446
3.0432
2.9676
2.9434
2.9076
2.8834
2.8033
2.7618
2.7437
2.7022
2.6150
2.5865
2.2183
2.1871
2.1560
1.6335
1.6208
1.6043
1.5899
0.0001

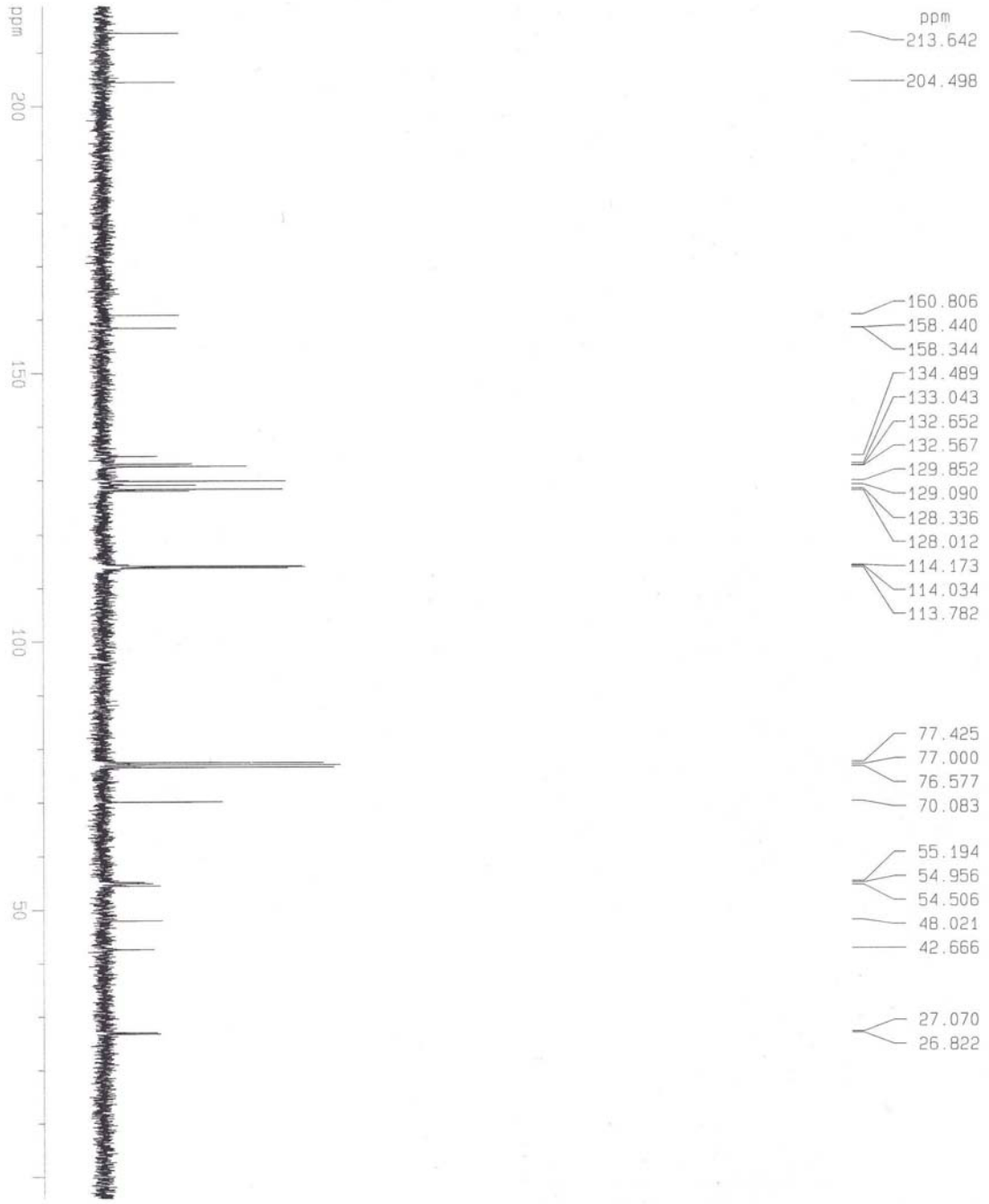
Compound 8h.


ppm
213.009
204.423
140.530
137.100
135.384
134.769
134.628
130.726
129.571
128.917
128.592
128.520
127.452
127.155
126.993
77.421
76.909
76.575
70.342
55.006
47.896
27.247
25.905

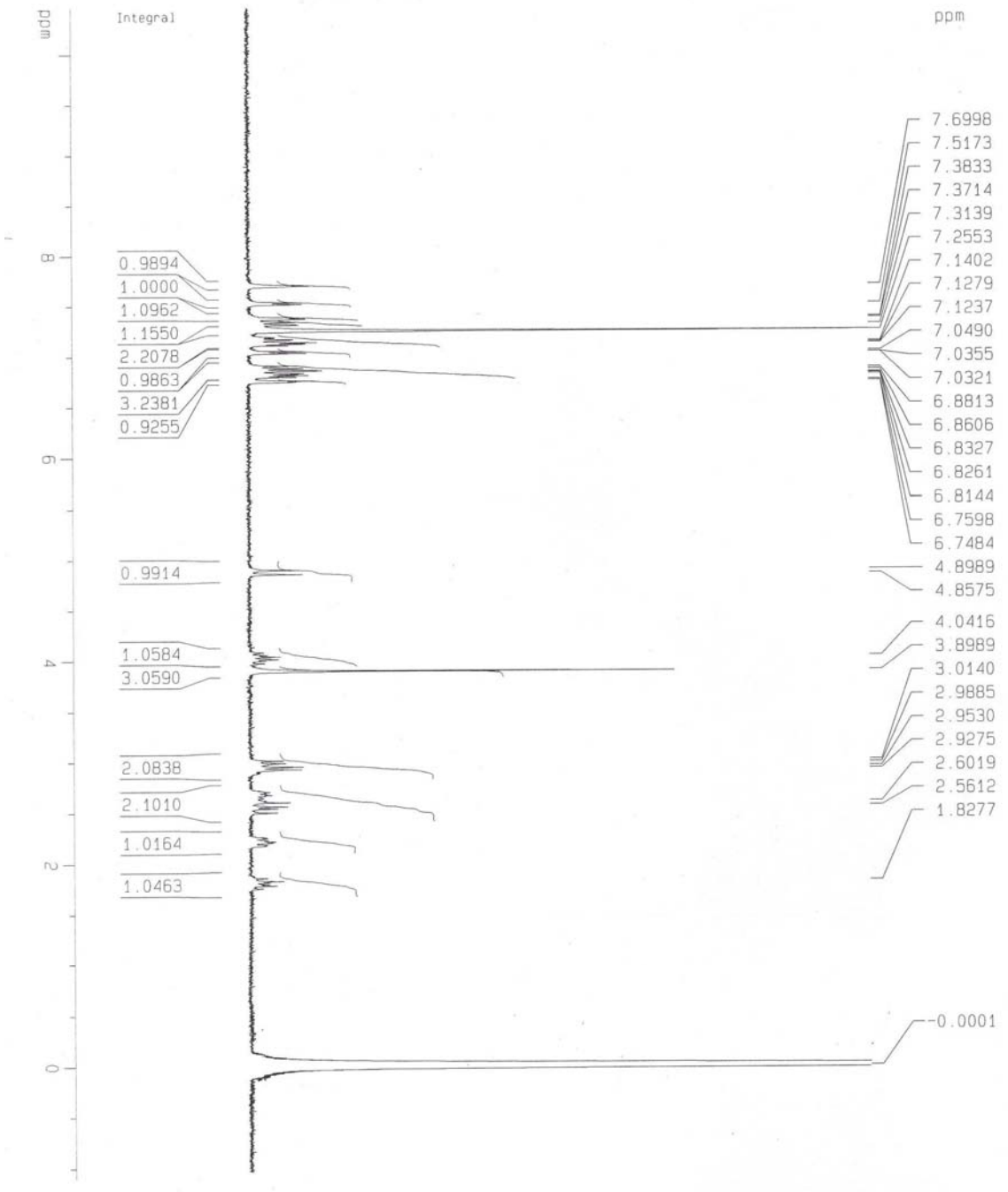
Compound 8i.



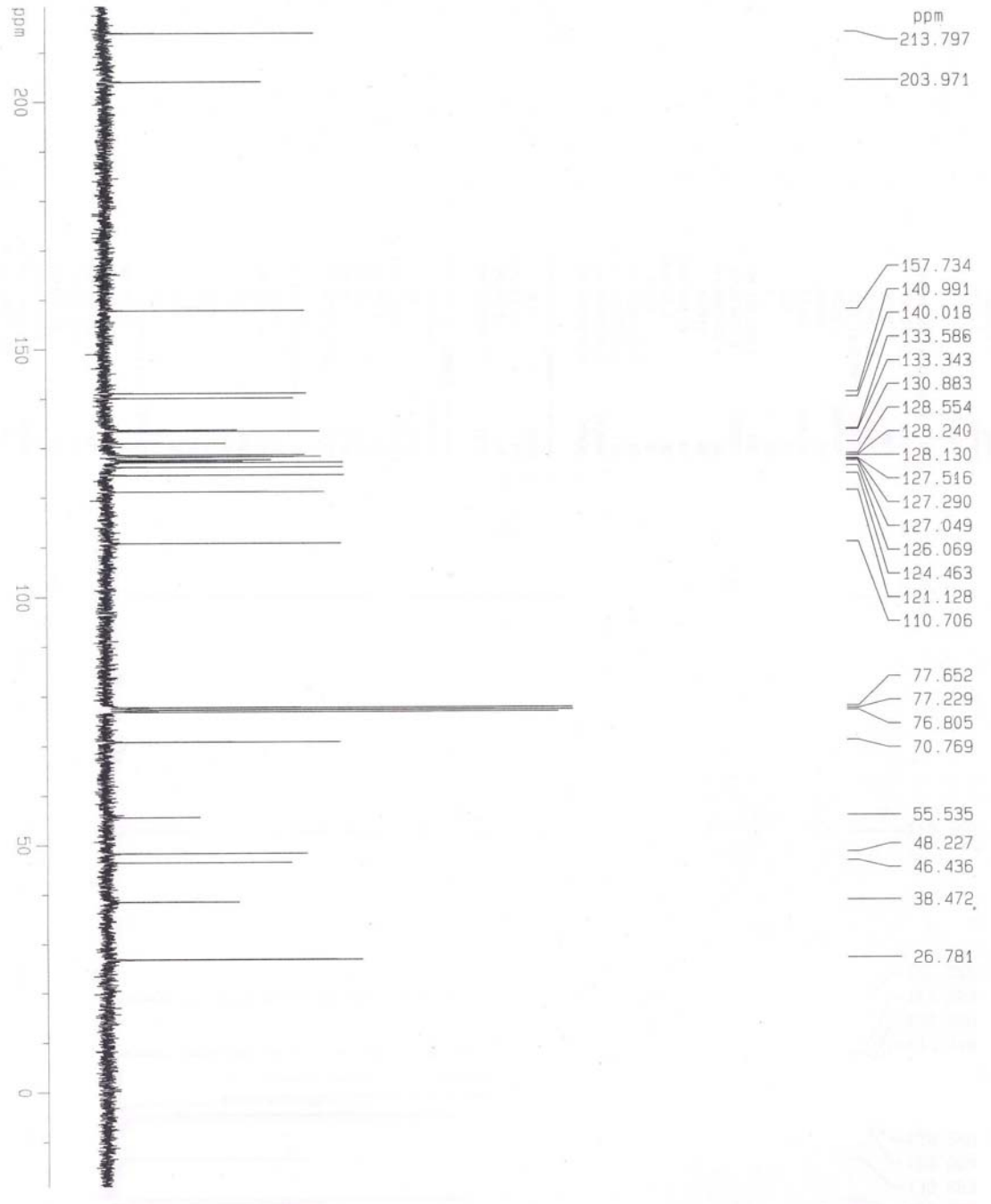
Compound 8i.


ppm
213.642
204.498
160.806
158.440
158.344
134.489
133.043
132.652
132.567
129.852
129.090
128.336
128.012
114.173
114.034
113.782
77.425
77.000
76.577
70.083
55.194
54.956
54.506
48.021
42.666
27.070
26.822
ppm
200
150
100
50

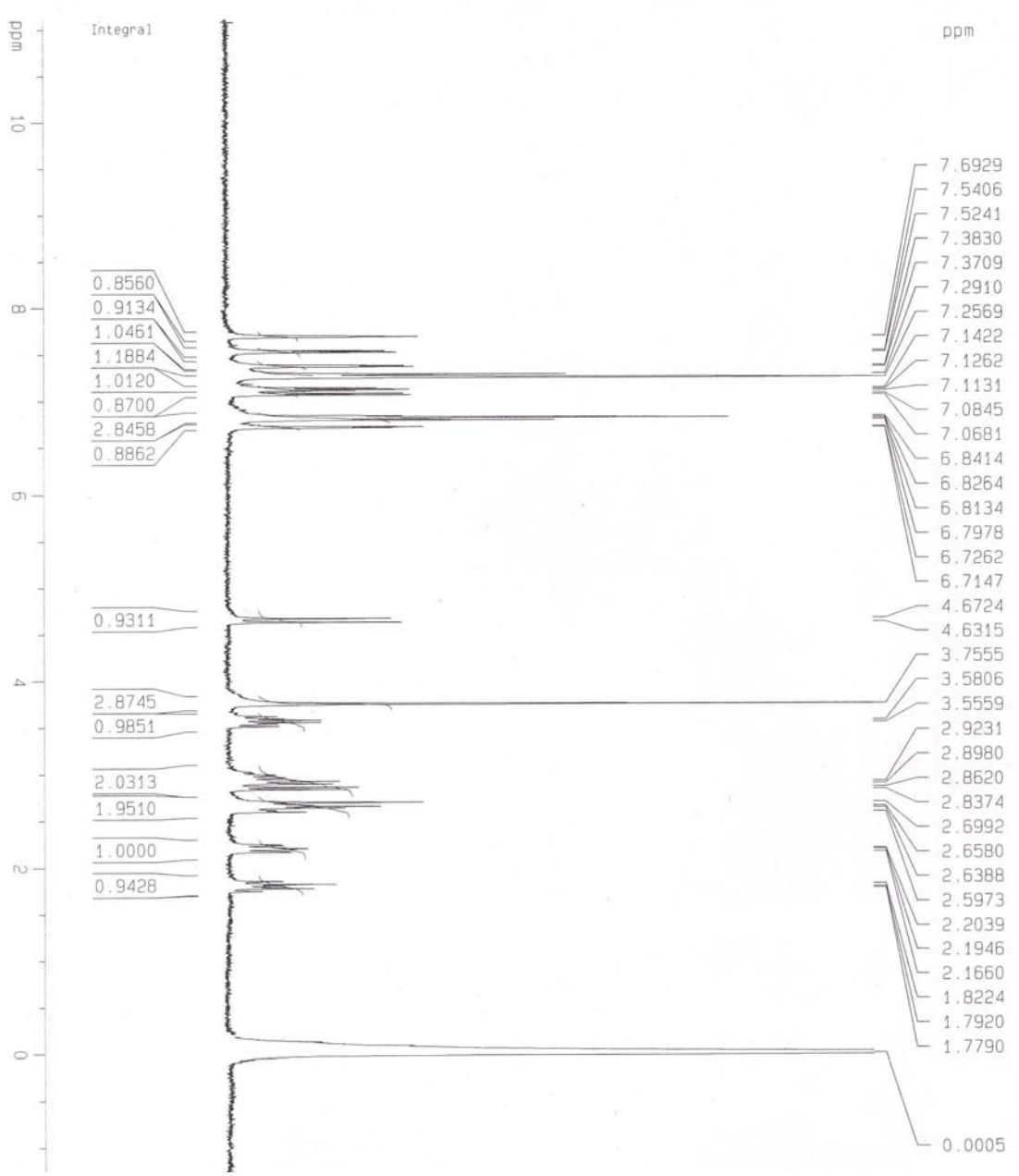
Compound 8j.



Compound 8j.



Compound 8k.



Compound 8k.