Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information

Ti-mediated Direct and Stereoselective Mannich Reactions between Esters and Oxime Ethers

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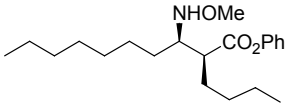
General

All reactions were carried out in oven-dried glassware under an argon atmosphere. Flash column chromatography was performed with silica gel Merck 60 (230-400 mesh ASTM). TLC analysis was performed on 0.25 mm Silicagel Merck 60 F_{254} plates. Melting points were determined on a hot stage microscope apparatus (Yanagimoto) and were uncorrected. NMR spectra were recorded on a JEOL DELTA 300 spectrometer, operating at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR. Chemical shifts (δ ppm) in $CDCl_3$ were reported downfield from TMS (= 0) for ^{1}H NMR. For ^{13}C NMR, chemical shifts were reported in the scale relative to $CDCl_3$ (77.00 ppm) as an internal reference. IR Spectra were recorded on a JASCO FT/IR-5300 spectrophotometer. Mass spectra were measured on a JEOL JMS-T100LC spectrometer.

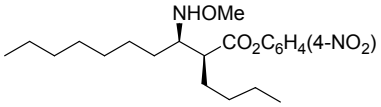
Spectra data of new compounds 1-11 (Table 1)

Phenyl *syn*-2-butyl-3-(methoxyamino)decanoate (1)



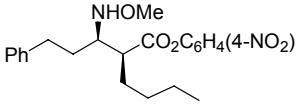
(*syn* / *anti* = 90 / 10). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 6.9 Hz), 0.93 (3H, t, *J* = 6.9 Hz), 1.19-1.68 (17H, m), 1.76-1.92 (1H, m), 2.76-2.85 (*anti*, 0.10H, m), 2.86-2.96 (*syn*, 0.90H, m), 3.12-3.26 (1H, m), 3.53 (*anti*, 0.30H, s), 3.54 (*syn*, 2.70H, s), 7.03-7.11 (2H, m), 7.18-7.26 (1H, m), 7.33-7.42 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 22.5, 22.6, 26.8, 27.7, 29.1, 29.6, 30.2, 31.5, 31.7, 47.4, 61.9, 62.7, 121.5, 125.6, 129.3, 150.8, 173.3; IR (neat) 2928, 2857, 1755, 1493, 1468, 1196 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{35}N_1O_3$ (M + Na^+) 372.2515, found 372.2513.

4-Nitrophenyl *syn*-2-butyl-3-(methoxyamino)decanoate (2)



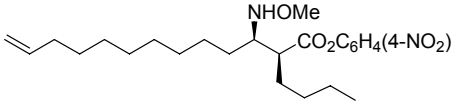
(*syn* / *anti* = 94 / 6). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 6.9 Hz), 0.94 (3H, t, *J* = 6.9 Hz), 1.18-1.67 (18H, m), 1.79-1.94 (1H, m), 2.85-2.96 (1H, m), 3.24-3.37 (1H, m), 3.53 (*anti*, 0.18H, s), 3.56 (*syn*,2.82H, s), 7.23-7.32 (2H, m), 8.23-8.32 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 22.6, 22.6, 26.8, 26.9, 29.1, 29.5, 30.3, 31.7, 47.6, 61.9, 62.7, 122.4, 125.1, 145.2, 155.7, 172.6; IR (neat) 2930, 2859, 1765, 1526, 1346, 1208, 1105 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{34}N_2O_5$ (M + Na^+) 417.2365, found 417.2369.

4-Nitrophenyl *syn*-3-(methoxyamino)-3-phenylpropyl)hexanoate (3)



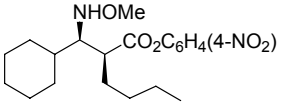
(*syn* / *anti* = 95 / 5). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.91 (3H, t, *J* = 7.2 Hz), 1.21-1.48 (4H, m), 1.50-1.64 (1H, m), 1.75-1.93 (3H, m), 2.59-2.78 (1H, m), 2.81-2.99 (2H, m), 3.19-3.33 (1H, m), 3.53 (*anti*, 0.15H, s), 3.54 (*syn*, 2.95H, s), 7.16-7.34 (7H, m), 8.22-8.29 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.5, 27.2, 30.0, 30.8, 32.9, 47.6, 61.7, 62.0, 122.4, 125.1, 126.0, 128.3, 128.4, 141.3, 145.1, 155.5, 172.3; IR (neat) 2934, 1763, 1525, 1346, 1209, 1111 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{28}N_2O_5$ (M + Na^+) 423.1896, found 423.1891.

4-Nitrophenyl *syn*-2-butyl-3-(methoxyamino)trideca-12-enoate (4)



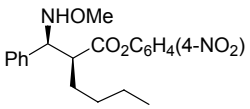
(*syn* / *anti* = 96 / 4). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (*anti*, 0.12H, t, *J* = 7.2 Hz), 0.95 (*syn*, 2.88H, t, *J* = 6.9 Hz), 1.21-1.65 (19H, m), 1.77-1.93 (1H, m), 1.98-2.10 (2H, m), 2.74-2.84 (*anti*, 0.04H, m), 2.85-2.93 (*syn*, 0.96H, m), 3.15-3.23 (*anti*, 0.04H, m), 3.23-3.33 (*syn*, 0.96H, m), 3.50 (*anti*, 0.12H, s), 3.52 (*syn*, 2.88H, s), 7.23-7.31 (2H, m), 8.23-8.30 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.6, 26.8, 28.8, 29.0, 29.3, 29.5, 30.2, 33.7, 47.6, 61.9, 62.6, 114.1, 122.4, 125.1, 139.0, 145.1, 155.7, 172.5; IR (neat) 2928, 2857, 1765, 1526, 1346, 1209, 1101 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{38}N_2O_5$ (M + Na^+) 457.2678, found 457.2670.

4-Nitrophenyl *syn*-2-(cyclohexyl(methoxyamino)methyl)hexanoate (5)



(*syn* / *anti* = 74 / 26). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94 (3H, t, *J* = 7.2 Hz,), 1.02-2.03 (17H, m), 2.74-2.84 (1H, m), 3.06 (*anti*, 0.26H, dd, *J* = 4.5 Hz, 7.9 Hz), 3.27 (*syn*, 0.74H, dd, *J* = 4.1 Hz, 7.9 Hz), 3.44 (*anti*, 0.78H, s), 3.45 (*syn*, 2.22H, s), 7.23-7.31 (2H, m), 8.22-8.31 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 22.8, 25.1, 26.1, 26.2, 26.3, 26.4, 26.5, 26.7, 27.6, 29.3, 29.8, 30.1, 30.4, 30.7, 31.0, 37.7, 38.4, 45.9, 47.1, 61.4, 66.8, 67.2, 122.4, 125.1, 145.1, 155.8, 156.0, 173.0; IR (neat) 2930, 2857, 1765, 1526, 1346, 1209 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{30}N_2O_5$ (M + Na^+) 401.2052, found 401.2046.

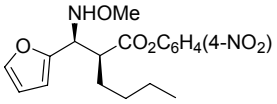
4-Nitorophenyl *syn*-3-(1-methoxyamino-1-phenyl)methylhexanoate (6)



(*syn* / *anti* = >99 / 1). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (3H, t, *J* = 6.5 Hz), 1.29-1.51 (4H, m), 1.79-2.00 (2H, m), 3.06-3.19 (1H, m), 3.50

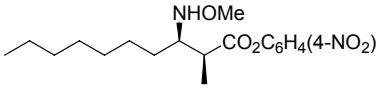
(3H, s), 4.27 (1H, d, *J* = 8.3 Hz), 6.74-6.82 (2H, m), 7.29-7.43 (5H, m), 8.12-8.19 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.4, 28.8, 29.8, 49.6, 62.0, 66.8, 122.3, 124.9, 128.0, 128.4, 139.2, 145.2, 155.1, 171.5; IR (neat) 2957, 2934, 2872, 1763, 1526, 1346, 1208, 1109 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}N_2O_5$ (M + Na^+) 395.1583, found 395.1587.

4-Nitorophenyl *syn*-2-[(methoxyamino)(phenyl)methyl]hexanoate (7)



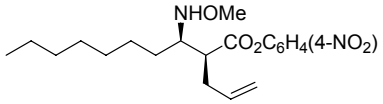
(*syn* / *anti* = >99 / 1). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.92 (3H, t, *J* = 7.2 Hz), 1.31-1.51 (4H, m), 1.80-1.94 (2H, m), 3.19 (1H, q, *J* = 7.2 Hz), 3.53 (3H, s), 4.42 (1H, d, *J* = 7.9 Hz), 5.94-6.03 (1H, brs), 6.30-6.41 (2H, m), 7.05-7.13 (2H, m), 7.39-7.44 (1H, m), 8.20-8.28 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.8, 22.4, 28.3, 29.6, 47.2, 60.1, 62.0, 108.4, 110.3, 122.3, 125.0, 142.0, 145.2, 152.2, 155.3, 171.3; IR (neat) 2959, 29361763, 1528, 1348, 1208 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}N_2O_6$ (M + Na^+) 385.1376, found 385.1384.

4-Nitrophenyl *syn*-2-methyl-3-(methoxyamino)decanoate (8)



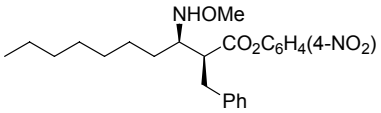
(*syn* / *anti* = 90 / 10). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.6 Hz), 1.17-1.52 (12H, m), 2.82-3.04 (1H, m), 3.47 (*syn*, 2.70H, s), 3.51 (*anti*, 0.30H, s), 5.56-5.70 (1H, brs), 7.22-7.31 (2H, m), 8.21-8.31 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 9.8, 14.0, 22.6, 26.7, 29.1, 29.4, 29.5, 31.7, 41.2, 61.7, 62.0, 122.4, 125.0, 145.1, 155.9, 173.0; IR (neat) 2930, 1765, 1593, 1526, 1348 cm^{-1}; ; HRMS (ESI) calcd for $C_{18}H_{28}N_2O_5$ (M + Na^+) 374.4927, found 374.4922.

4-Nitrophenyl 2 *syn*-(but-3-enyl)-3-(methoxyamino)decanoate (9)



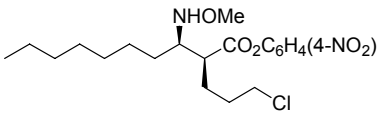
(*syn* / *anti* = 95 / 5). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 7.2 Hz), 1.19-1.69 (12H, m), 2.35-2.67 (2H, m), 2.89-2.97 (*anti*, 0.05H, m), 2.98-3.06 (*syn*, 0.95H, m), 3.19-3.26 (*anti*, 0.05H, m), 3.26-3.36 (*syn*, 0.95H, m), 3.51 (*anti*, 0.15H, s), 3.52 (*syn*, 2.85H, s), 5.07-5.22 (2H, m), 5.90 (1H, ddt, *J* = 6.9, 10.3, 16.9 Hz), 7.21-7.29 (2H, m), 8.23-8.30 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.5, 26.7, 29.1, 29.5, 31.7, 47.1, 61.9, 62.1, 117.0, 122.4, 125.0, 135.5, 145.2, 155.6, 171.8; IR (neat) 2930, 2857, 1765, 1526, 1348, 1209, 1111 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{30}N_2O_5$ (M + Na^+) 401.2052, found 401.2044.

4-Nitrophenyl *syn*-3-(methoxyamino)-2-phenethyldecanoate (10)



(*syn* / *anti* = 90 / 10). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.9 Hz), 1.17-1.71 (12H, m), 2.90-2.98 (*anti*, 0.20H, m), 3.02-3.14 (*syn*, 1.80H, m), 3.23-3.41 (2H, m), 3.55 (*anti*, 0.30H, s), 3.59 (*syn*, 2.70H, s), 6.87-7.02 (2H, m), 7.15-7.38 (5H, m), 8.13-8.28 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 26.76, 29.1, 29.2, 29.5, 31.7, 33.8, 49.8, 62.0, 62.5, 122.4, 125.0, 126.5, 128.5, 128.9, 139.2, 145.2, 155.4, 171.9; IR (neat) 2930, 2857, 1763, 1526, 1346, 1209, 1111 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{32}N_2O_5$ (M + Na^+) 451.2209, found 451.2205.

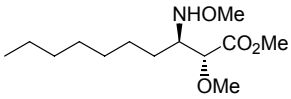
4-Nitrophenyl *syn*-3-(methoxyamino)-4-chloropropyldecanoate (11)



(*syn* / *anti* = 97 / 3). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.9 Hz), 1.19-1.57 (12H, m), 1.72-2.09 (4H, m), 2.80-2.93 (1H, m), 3.34-3.42 (1H, m), 3.48 (*anti*, 0.09H, s), 3.50 (*syn*, 2.91H, s), 7.22-7.31 (2H, m), 8.24-8.30 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.5, 24.0, 26.7, 29.0, 29.1, 29.4, 30.9, 31.6, 44.6, 46.8, 61.8, 62.4, 122.4, 125.1, 145.1, 155.5, 172.0; IR (neat) 2930, 2857, 1765, 1526, 1346 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{31}ClN_2O_5$ (M + Na^+) 436.4850, found 436.4856.

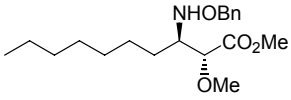
Spectra data of new compounds 12-19 (Table 2)

Methyl *syn*-2-methoxy-3-methoxyaminodecanoate (12)



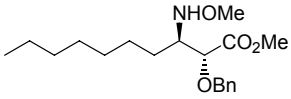
(*syn* / *anti* = 2 / 98). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 6.9 Hz), 1.14-1.50 (12H, m), 3.17-3.28 (1H, m), 3.46 (3H, s), 3.53 (3H, s), 3.77 (3H, s), 4.17 (*anti*, 0.98H, d, *J* = 3.4 Hz), 4.31 (*anti*, 0.02H, d, *J* = 7.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.5, 26.5, 28.9, 29.3, 31.6, 51.5, 59.0, 61.3, 61.8, 79.0, 172.3; IR (neat) 2930, 2857, 1753, 1466, 1437, 1269, 1200, 1142 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{27}N_1O_4$ (M + Na^+) 284.1838, found 284.1835.

Methyl *syn*-2-benzyloxy-3-methoxyaminodecanoate (13)



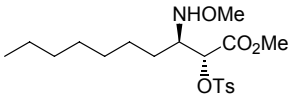
(*syn* / *anti* = 1 / >99). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 7.9 Hz), 1.11-1.45 (12H, m), 3.13-3.27 (1H, m), 3.44 (3H, s), 3.74 (3H, s), 4.23 (1H, d, *J* = 3.4 Hz), 4.68 (1H, d, *J* = 12.4 Hz), 4.71 (1H, d, *J* = 12.4 Hz), 7.26-7.38 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.6, 26.6, 29.0, 29.4, 31.7, 51.7, 59.2, 62.3, 75.9, 79.2, 127.7, 128.2, 128.5, 137.9, 172.5; IR (neat) 2930, 2857, 1753, 1466, 1437, 1269, 1200, 1142 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{31}N_1O_4$ (M + Na^+) 360.2151, found 360.2147.

Methyl 2-benzyloxy-3-methoxyaminodecanoate (14)



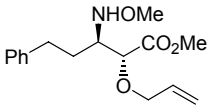
(*syn* / *anti* = 4 / 96). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 7.2 Hz), 1.14-1.48 (12H, m), 3.20-3.32 (1H, m), 3.47 (3H, s), 3.76 (3H, s), 4.39 (1H, d, *J* = 3.8 Hz), 4.43 (*anti*, 0.96H, d, *J* = 11.4 Hz), 4.79 (*anti*, 0.96H, d, *J* = 11.4 Hz), 5.14 (*syn*, 0.04H, d, *J* = 12.4 Hz), 5.27 (*syn*, 0.04H, d, *J* = 12.4 Hz), 7.23-7.40 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 26.6, 26.8, 29.0, 29.4, 31.7, 51.7, 61.3, 62.0, 73.1, 77.1, 127.8, 127.9, 128.3, 137.5, 127.6; IR (neat) 2924, 2859, 1752, 1456, 1138 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{31}N_1O_4$ (M + Na^+) 360.2151, found 360.2153.

Methyl 3-methoxyamino-2-tosyloxydecanoate (15)



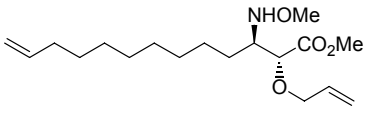
(*syn* / *anti* = 9/ 91). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (3H, t, *J* = 6.9 Hz), 1.15-1.47 (12H, m), 2.45 (3H, s), 3.36 (*anti*, 2.67H, s), 3.38-3.45 (1H, m), 3.42 (*syn*, 0.33H, s), 3.64 (*anti*, 2.72H, s), 3.69 (*syn*, 0.28H, s), 4.95 (*anti*, 0.91H, d, *J* = 3.1 Hz), 5.34 (*syn*, 0.09H, d, *J* = 3.4 Hz), 7.31-7.37 (2H, m), 7.80-7.88 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 21.6, 22.6, 26.2, 27.9, 29.0, 29.3, 31.7, 52.3, 61.4, 61.5, 76.3, 128.1, 129.6, 133.2, 145.1, 168.7; IR (neat) 2928, 2859, 1767, 1375, 1179 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{31}N_1O_6S_1$ (M + Na^+) 424.1770, found 424.1766.

Methyl 2-allyloxy-3-methoxyamino-5-phenylpentanoate (16)



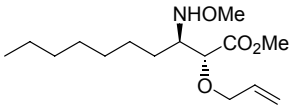
(*syn* / *anti* = 1 / >99). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.54-1.75 (2H, m), 2.54-2.69 (1H, m), 2.75-2.89 (1H, m), 3.21-3.30 (1H, m), 3.53 (3H, s), 3.66 (3H, s), 3.89-4.00 (1H, m), 4.18-4.27 (1H, m), 4.32 (1H, d, *J* = 3.4 Hz), 5.15-5.33 (2H, m), 5.92 (1H, ddt, *J* = 6.2, 10.3, 17.2 Hz), 7.13-7.31 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 28.4, 32.5, 51.7, 60.9, 61.5, 72.2, 76.6, 117.7, 125.8, 128.2, 128.4, 134.0, 141.8, 172.4; IR (neat) 3268, 2949, 1752, 1454, 1435, 1269, 1208, 1138 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}N_1O_4$ (M + Na^+) 316.1525, found 316.1531.

Methyl 2-allyloxy-3-methoxyaminotridec-12-enoate (17)



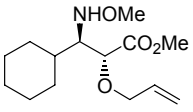
(*syn* / *anti* = 1 / >99). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16-1.50 (14H, m), 1.97-2.09 (2H, m), 3.18-3.31 (1H, m), 3.52 (3H, s), 3.76 (3H, s), 3.91-4.01 (1H, m), 4.19-4.28 (1H, m), 4.33 (1H, d, *J* = 3.4 Hz), 4.88-5.04 (2H, m), 5.16-5.33 (2H, m), 5.81 (1H, ddt, *J* = 6.5, 10.3, 17.2 Hz), 5.93 (1H, ddt, *J* = 6.2, 10.3, 16.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.6, 26.7, 28.8, 29.0, 29.2, 29.3, 29.4, 33.7, 51.7, 61.3, 61.9, 72.2, 76.6, 114.0, 117.7, 134.0, 139.1, 172.6; IR (neat) 2928, 2857, 1753, 1460, 1437, 1265, 1206, 1140 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{33}N_1O_4$ (M + Na^+) 350.2307, found 350.2306.

Methyl 2-allyloxy-3-methoxyaminodecanoate (18)



(*syn* / *anti* = 1 / >99). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (3H, t, *J* = 6.9 Hz), 1.16-1.49 (12H, m), 3.19-3.31 (1H, m), 3.52 (3H, s), 3.75 (3H, s), 3.91-4.01 (1H, m), 4.19-4.28 (1H, m), 4.33 (1H, d, *J* = 3.1 Hz), 5.14-5.34 (2H, m), 5.93 (1H, ddt, *J* = 5.9, 10.3, 17.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.6, 26.6, 26.7, 29.0, 29.4, 31.7, 51.7, 61.3, 61.9, 72.2, 76.6, 117.7, 134.0, 172.6; IR (neat) 2953, 2855, 1753, 1462, 1453, 1267, 1204, 1140 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{29}N_1O_4$ ($M + Na^+$) 310.1994, found 310.1998.

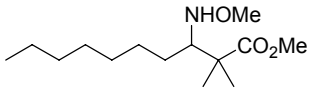
Methyl 3-cyclohexyl-2-allyloxy-3-methoxyamino-propanoate (19)



(*syn* / *anti* = 1 / >99). Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85-1.34 (5H, m), 1.42-1.56 (1H, m), 1.57-1.80 (4H, m), 1.87-2.00 (1H, m), 3.10 (1H, dd, *J* = 4.8, 5.49 Hz), 3.47 (3H, s), 3.75 (3H, s), 3.88-3.98 (1H, m), 4.20-4.29 (1H, m), 4.30 (1H, d, *J* = 4.1 Hz), 5.14-5.33 (2H, m), 5.92 (1H, ddt, *J* = 5.9, 10.3, 16.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 26.5, 28.9, 30.6, 37.3, 51.6, 61.0, 66.5, 72.2, 76.6, 117.5, 134.1, 173.0; IR (neat) 2928, 2855, 1752, 1451, 1263, 1209, 1150, 1105, 1022 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{25}N_1O_4$ ($M + Na^+$) 294.1681, found 294.1685.

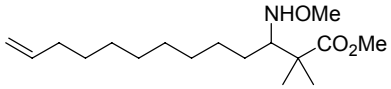
Spectra data of new compounds 20-37 (Table 3)

Methyl 3-(methoxyamino)-2,2-dimethyldecanoate (20)



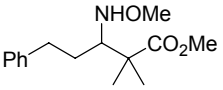
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.5 Hz), 1.06-1.42 (11H, m), 1.15 (6H, s), 1.44-1.55 (1H, m), 3.11 (1H , dd, *J* = 2.4 Hz, *J* = 10.0 Hz), 3.41 (3H, s), 3.65 (3H, s), 5.56 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 20.2, 22.6, 23.2, 27.6, 28.0, 29.2, 29.7, 31.8, 45.5, 51.5, 61.3, 66.2, 178.1; IR (neat) 2928, 2857, 1736, 1466, 1435, 1263, 1192, 1142; HRMS (ESI) calcd for $C_{14}H_{29}N_1O_3$ (M + Na^+) 282.2045, found 282.2040.

Methyl 3-(methoxyamino)-2,2-dimethyltridec-12-enoate (21)



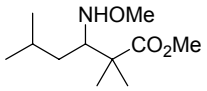
Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08-1.56 (14H, m), 1.15 (6H, s), 1.97-2.09 (2H, m), 3.11 (1H , dd, *J* = 2.1 Hz, *J* = 9.6 Hz), 3.41 (3H, s), 3.65 (3H, s), 4.86-5.04 (2H, m), 5.56 (1H, br s), 5.81 (1H, ddt, *J* = 6.5 Hz, *J* = 10.5 Hz, *J* = 17.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 23.2, 27.6, 28.0, 28.9, 29.1, 29.4, 29.7, 45.5, 51.6, 61.3, 66.2, 114.1, 139.2, 178.2; IR (neat) 2930, 2855, 1736, 1466, 1435, 1262, 1192, 1138; HRMS (ESI) calcd for $C_{17}H_{33}N_1O_3$ (M + Na^+) 322.2358, found 322.2366.

Methyl 3-(methoxyamino)-2,2-dimethyl-5-phenylpentanoate (22)



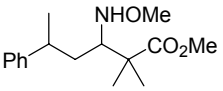
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.148 (3H, s), 1.150 (3H, s), 1.47-1.62 (1H, m), 1.65-1.78 (1H, m), 2.65 (1H, ddd, *J* = 6.5 Hz, *J* = 9.6 Hz, *Jgem* = 13.8 Hz), 2.89 (1H, ddd, *J* = 5.2 Hz, *J* = 10.0 Hz, *Jgem* = 13.8 Hz), 3.16 (1H , dd, *J* = 2.1 Hz, *J* = 10.0 Hz), 3.44 (3H, s), 3.63 (3H, s), 5.66 (1H, br s), 7.15-7.34 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5, 23.2, 30.4, 33.9, 45.7, 51.6, 61.4, 65.6, 125.9, 128.4, 140.0, 177.9; IR (neat) 2978, 2948, 1732, 1456, 1435, 1269, 1192, 1134; HRMS (ESI) calcd for $C_{15}H_{23}N_1O_3$ (M + Na^+) 288.1576, found 288.1576

Methyl 3-(methoxyamino)-2,2,5-trimethylhexanoate (23)



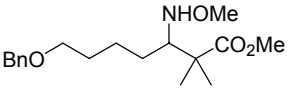
Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.925 (3H, d, *J* = 6.5 Hz), 0.927 (3H, d, *J* = 6.5 Hz), 1.02-1.19 (2H, m), 1.14 (3H, s), 1.15 (3H, s), 1.65-1.82 (1H, m), 3.23 (1H, dd, *J* = 3.4 Hz, *J* = 8.9 Hz), 3.41 (3H, s), 3.66 (3H, s), 5.53 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.0, 21.6, 23.0, 23.9, 25.6, 37.3, 45.4, 51.5, 61.2, 63.9, 178.2; IR (neat) 2955, 2872, 1734, 1468, 1435, 1262, 1192, 1140; HRMS (ESI) calcd for $C_{11}H_{23}N_1O_3$ (M + Na^+) 240.1576, found 240.1574.

Methyl 3-(methoxyamino)-2,2-dimethyl-5-phenylhexanoate (24)



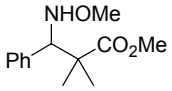
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ1.04 (2.13H, s), 1.09 (2.13H, s), 1.15 (0.87H, s), 1.17 (0.87H, s), 1.26 (2.13H, d, *J* = 6.9 Hz), 1.29 (0.87H, d, *J* = 6.9 Hz) 1.42-1.59 (0.71H and 0.58H , m), 1.65 (0.71H, ddd, *J* = 2.1 Hz, *J* = 10.7 Hz, *Jgem* = 14.5 Hz), 2.81 (0.71H, dd, *J* = 2.1 Hz, *J* = 10.7 Hz), 2.90-3.06 (1H, m) 3.29 (0.29H, dd, *J* = 3.1 Hz, *J* = 9.3 Hz), 3.34 (0.87H, s), 3.40 (2.13H, s), 3.54 (2.13H, s), 3.66 (0.87H, s), 7.15-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.3, 20.7, 21.1, 22.9, 23.1, 23.7, 36.7, 37.2, 37.4, 37.5, 45.5, 45.6, 51.5, 51.6, 61.2, 61.3, 63.6, 64.2, 126.1, 126.8, 127.2, 128.4, 128.5, 146.3, 147.7, 177.8, 178.0; IR (neat) 2951, 1732, 1454, 1435, 1260, 1192, 1138; HRMS (ESI) calcd for $C_{16}H_{25}N_1O_3$ (M + Na^+) 302.1732, found 302.1729.

Methyl 7-benzyloxy-3-(methoxyamino)-2,2-dimethylheptanoate (25)



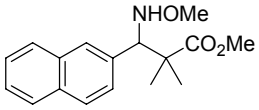
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.14 (6H, s), 1.15-1.29 (1H, m), 1.33-1.50 (2H, m), 1.53-1.74 (3H, m), 3.11 (1H, dd, *J* = 2.1 Hz, *J* = 10.0 Hz), 3.40 (3H, s), 3.48 (2H, t, *J* = 6.1 Hz), 3.65 (3H, s), 4.50 (2H, s), 5.57 (1H, br s), 7.22-7.36 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.2, 23.2, 24.3, 27.9, 29.8, 45.5, 51.5, 61.2, 66.1, 70.1, 72.8, 127.5, 127.6, 128.3, 178.0; IR (neat) 2945, 2863, 1732, 1454, 1435, 1262, 1192, 1105; HRMS (ESI) calcd for $C_{18}H_{29}N_1O_4$ (M + Na^+) 346.1994, found 346.1992.

Methyl 3-(methoxyamino)-2,2-dimethyl-3-phenylpropanoate (26)



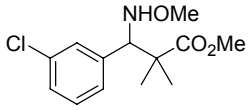
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.03 (3H, s), 1.16 (3H, s), 3.43 (3H, s), 3.70 (3H, s), 4.38 (1H, s), 5.99 (1H, br s), 7.25-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.0, 24.7, 45.4, 51.8, 61.8, 70.3, 127.7, 127.9, 128.7, 137.9, 177.4; IR (neat) 2980, 2949, 1734, 1468, 1252, 1192, 1136, 1057; HRMS (ESI) calcd for $C_{13}H_{19}N_1O_3$ (M + Na^+) 260.1263, found 260.1260.

Methyl 3-(methoxyamino)-2,2-dimethyl-3-(2-naphthyl)propanoate (27)



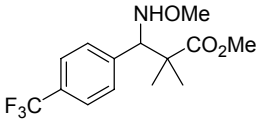
Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.21 (3H, s), 3.45 (3H, s), 3.72 (3H, s), 4.55 (1H, s), 6.12 (1H, br s), 7.42-7.51 (3H, m) 7.73-7.86 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.3, 24.8, 45.7, 51.9, 61.9, 70.4, 125.9, 126.0, 126.7, 127.4, 127.6, 128.0, 132.9, 133.0, 135.5, 177.4; IR (neat) 2980, 2948, 1734, 1468, 1258, 1192, 1134, 1053; HRMS (ESI) calcd for $C_{17}H_{21}N_1O_3$ (M + Na^+) 310.1419, found 310.1422

Methyl 3-(3-chlorophenyl)-3-(methoxyamino)-2,2-dimethylpropanoate (28)



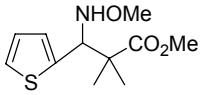
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (3H, s), 1.15 (3H, s), 3.43 (3H, s), 3.71 (3H, s), 4.33 (1H, s), 6.02 (1H, brs), 7.16-7.34 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 24.5, 45.4, 52.0, 61.9, 69.9, 127.0, 127.9, 128.8, 129.1, 133.9, 140.3, 177.0; IR (neat) 2982, 2949, 1734, 1470, 1433, 1269, 1250, 1192, 1138; HRMS (ESI) calcd for $C_{13}H_{18}Cl_1N_1O_3$ (M + Na^+) 294.0873, found 294.0871.

Methyl 3-(4-trifluorophenyl)-3-(methoxyamino)-2,2-dimethylpropanoate (29)



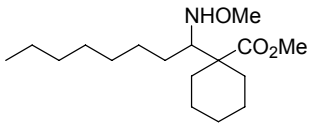
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.05 (3H, s), 1.15 (3H, s), 3.42 (3H, s), 3.71 (3H, s), 4.41 (1H, s), 6.09 (1H, br s), 7.45 (2H, d, J = 8.3 Hz), 7.59 (2H, d, J = 8.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 24.5, 45.4, 52.0, 61.9, 69.9, 124.1 [d, ^1J (^{13}C, ^{19}F) = 271 Hz], 124.8 [q, ^3J (^{13}C, ^{19}F) = 3 Hz], 129.1, 129.9 [q, ^3J (^{13}C, ^{19}F) = 32 Hz]; IR (neat) 2984, 2951, 1732, 1468, 1327, 1258, 1165, 1127, 1069, 1019; HRMS (ESI) calcd for $C_{14}H_{18}F_3N_1O_3$ (M + Na^+) 328.1136, found 328.1132.

Methyl 3-(methoxyamino)-2,2-dimethyl-3-(2-thiophenyl)propanoate (30)



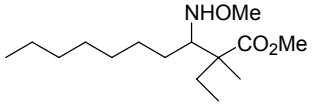
Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.11 (3H, s), 1.26 (3H, s), 3.46 (3H, s), 3.71 (3H, s), 4.68 (1H, d, J = 6.5 Hz), 5.85 (1H, br d, J = 6.5 Hz), 6.95-7.01 (2H, m) 7.21-7.27 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 19.4, 24.6, 45.5, 51.9, 61.8, 66.5, 124.7, 126.3, 126.9, 140.7, 177.2; IR (neat) 2982, 2948, 1730, 1466, 1435, 1262, 1217, 1192, 1136; HRMS (ESI) calcd for $C_{11}H_{17}N_1O_3S$ (M + Na^+) 266.0827, found 266.0828.

Methyl 2-(1-(methoxyamino)octyl)carboxylate (31)



Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, J = 6.9 Hz), 1.04-1.71 (20H, m), 2.03-2.15 (2H, m), 2.79 (1H, dd J = 2.1 Hz, J = 10.0 Hz), 3.43 (3H, s), 3.67 (3H, s), 5.68 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.6, 23.2, 23.4, 25.9, 27.7, 28.2, 29.2, 29.6, 30.5, 31.7, 31.8, 51.1, 51.4, 61.2, 67.8, 176.2; IR (neat) 2930, 2857, 1734, 1453, 1215, 1154, 1132, 1057; HRMS (ESI) calcd for $C_{17}H_{33}N_1O_3$ (M + Na^+) 322.2358, found 322.2361

Methyl 2-ethyl-3-(methoxyamino)-2-methyldecanoate (32)

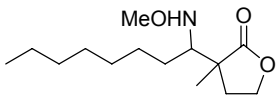


(54 : 46 of stereoisomers). Major product; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.83 (3H, t, J = 7.6 Hz), 0.88 (3H, t, J = 6.5 Hz), 1.11 (3H, s), 1.18-1.38 (10H, m), 1.45-1.59 (2H, m), 1.57 (1H, dq, J = 7.6 Hz, *Jgem* = 13.8 Hz), 1.84 (1H, dq, J = 7.6 Hz, *Jgem* = 13.8 Hz), 3.02 (1H, dd, J = 3.1 Hz, J = 8.6 Hz), 3.45 (3H, s), 3.66 (3H, s), 5.55 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.1, 14.1, 16.8, 22.6, 27.6, 29.2, 29.4, 29.5, 29.6, 31.8, 50.7, 51.4, 61.3, 66.5, 176.9; IR (neat) 2928, 2857, 1732, 1460, 1235, 1190, 1146, 1055; HRMS (ESI) calcd for $C_{15}H_{31}N_1O_3$ (M + Na^+) 296.2202, found 296.2200.

Minor product; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (3H, t, J = 7.6 Hz), 0.88 (3H, t, J

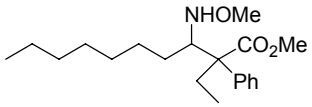
= 6.5 Hz), 1.07 (3H, s), 1.19-1.58 (13H, m), 1.67 (1H, dq, *J* = 7.6 Hz, *Jgem* = 14.8 Hz), 3.16 (1H, dd, *J* = 1.7 Hz, *J* = 10.0 Hz), 3.39 (3H, s), 3.65 (3H, s), 5.58 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 8.9, 14.1, 14.9, 22.6, 27.7, 29.2, 29.8, 30.1, 31.8, 49.8, 51.3, 61.3, 66.3, 177.2; IR (neat) 2928, 2857, 1736, 1460, 1236, 1192, 1148, 1053; HRMS (ESI) calcd for $C_{15}H_{31}N_1O_3$ (M + Na^+) 296.2202, found 296.2204.

Dihydro-3-(1-(methoxyamino)octyl)-3-methylfurane-2(3*H*)-one (34)



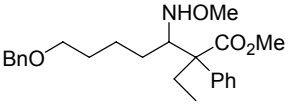
(Major stereoisomers). Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (3H, t, *J* = 6.9 Hz), 1.18-1.40 (10H, m), 1.23 (3H, s), 1.42-1.60 (2H, m), 1.83 (1H, ddd, *J* = 4.8 Hz, *J* = 7.9 Hz, *Jgem* = 13.1 Hz), 2.58 (1H, ddd, *J* = 7.6 Hz, *J* = 8.9 Hz, *Jgem* = 13.1 Hz), 3.13 (1H, dd, *J* = 2.1 Hz, *J* = 9.3 Hz), 3.44 (3H, s), 4.19-4.31 (1H, m), 4.32 (1H, dt, *J* = 5.2 Hz, *J* = 8.9 Hz) 5.59 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 22.2, 22.6, 26.9, 27.6, 29.1, 29.7, 30.3, 31.8, 45.7, 61.4, 63.7, 65.2, 181.9; IR (neat) 2928, 2857, 1765, 1460, 1196, 1088, 1033; HRMS (ESI) calcd for $C_{14}H_{27}N_1O_3$ (M + Na^+) 280.1889, found 280.1891.

Methyl 2-ethyl-3-(methoxyamino)-2-phenyldecanoate (35)



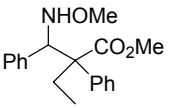
Major stereoisomers; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 7.2 Hz), 0.87 (3H, t, *J* = 6.9 Hz), 1.17-1.59 (12H, m), 2.16 (1H, dq, *J* = 7.2 Hz, *Jgem* = 14.3 Hz), 2.31 (1H, dq, *J* = 7.2 Hz, *Jgem* = 14.3 Hz), 3.45 (3H, s), 3.51 (1H, dd, *J* = 1.7 Hz, *J* = 10.2 Hz), 3.73 (3H, s), 5.43 (1H, br s), 7.20-7.35 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.4, 14.1, 22.6, 27.8, 28.8, 29.2, 29.7, 31.8, 32.0, 51.7, 60.0, 61.1, 63.9, 126.7, 127.6, 128.4, 139.2, 175.4; IR (neat) 2930, 2857, 1732, 1464, 1225, 1134, 1080, 1038, 1007; HRMS (ESI) calcd for $C_{20}H_{33}N_1O_3$ (M + Na^+) 358.2358, found 358.2362.

Methyl 7-benzyloxy-2-ethyl-3-(methoxyamino)-2-phenylheptanoate (36)



Major stereoisomers; Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (3H, t, *J* = 7.2 Hz), 1.41-1.71 (6H, m), 2.15 (1H, dq, *J* = 7.2 Hz, *Jgem* = 14.5 Hz), 2.31 (1H, dq, *J* = 7.2 Hz, *Jgem* = 14.5 Hz), 3.37-3.47 (2H, m), 3.44 (3H, s), 3.48-3.55 (1H, m), 3.72 (3H, s), 4.48 (2H, s), 5.44 (1H, br s), 7.19-7.37 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.4, 24.3, 28.7, 29.7, 31.8, 51.7, 60.0, 61.1, 63.7, 70.3, 72.8, 126.7, 127.4, 127.6, 127.7, 128.3, 128.4, 138.7, 139.2, 175.3; IR (neat) 2942, 2865, 1728, 1454, 1225, 1105; HRMS (ESI) calcd for $C_{24}H_{33}N_1O_4$ (M + Na^+) 422.2307, found 422.2303.

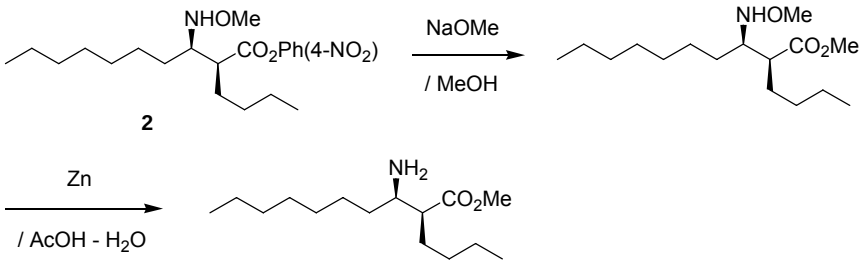
Methyl 2-((methoxyamino)(phenyl)methyl)-2-phenylbutanoate (37)



Major stereoisomers; Colorless crystals; mp 55-57 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81 (3H x 6/7, t, *J* = 7.2 Hz), 0.86 (3H x 1/7, t, *J* = 7.2 Hz), 1.85 (1H, dq *J* = 7.2 Hz, *Jgem* = 14.5 Hz), 2.06 (1H, dq *J* = 7.2 Hz, *Jgem* = 14.5 Hz), 3.37 (3H x 6/7, s), 3.43 (3H, x 1/7, s), 3.73 (3H x 6/7, s), 3.79 (3H, x 1/7, s), 4.69 (1H x 6/7, d, *J* = 6.2 Hz), 4.83 (1H, x 6/7, d *J* = 9.3 Hz), 6.45 (1H x 6/7, br d, *J* = 6.2 Hz), 6.59 (1H x 1/7, br d, *J* = 9.3 Hz), 7.04-7.11 (4H, m), 7.17-7.32 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.7, 28.3, 51.8, 59.4, 61.9, 69.9, 126.9, 127.4, 127.5, 127.7, 128.0, 138.9, 139.6, 174.5; IR (neat) 2930, 2859, 1780, 1466, 1437, 1219, 1192, 1165; HRMS (ESI) calcd for $C_{19}H_{23}N_1O_3$ (M + Na^+) 336.1576, found 336.1579.

Derivitazation of *syn*-3-(methoxyamino)-2-substituted esters 2 and 18 to the corresponding *syn*-3-amino-2-substituted esters and the determination of *syn*- or *anti*-seleochemistry

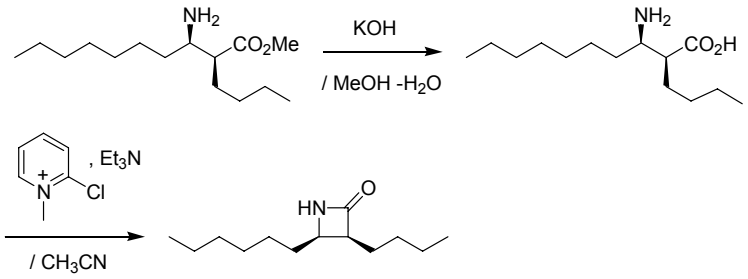
Methyl *syn*-3-amino-2-butyldecanoate



4-Nitrophenyl *syn*-2-butyl-3-(methoxyamino)decanoate **2** (784 mg, 2.0 mmol) and NaOMe (108 mg, 2.0 mmol) in MeOH (2.0 mL) was stirred at room temperature for 5 h. Water was added to the mixture, which was extracted twice with Et_2O. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated The obtained crude oil was purified by SiO_2-column chromatography to give the desired methyl ester. A suspension of the ester (288 mg, 1.0 mmol) and Zn powder (654 mg, 10.0 mmol) in AcOH (2.0 mL) and H_2O (2.0 mL) was heated at 100 ^oC for 3 h under an Ar atmosphere. Water was added to the mixture, which was extracted five times with $CHCl_3$. The combined organic phase was washed with water, brine, dried (Na_2SO_4) and concentrated. The obtained crude oil was purified by SiO_2-column chromatography to give the desired product (220 mg, 85%).

Pale yellow oil; ^1H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.9 Hz), 0.89 (3H, t, *J* = 6.9 Hz), 1.15-1.74 (18H, m), 2.33 (1H, ddd, *J* = 4.1 Hz, *J* = 5.5 Hz, *J* = 10.7 Hz), 2.86-2.96 (1H, m), 3.69 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.9, 14.0, 22.6, 22.7, 26.4, 27.2, 29.2, 29.5, 30.0, 31.7, 35.4, 51.3, 52.2, 53.1, 175.8; IR (neat) 2928, 2857, 1734, 1460, 1437, 1217, 1192, 1165; HRMS (ESI) calcd for $C_{15}H_{31}N_1O_2$ ($M + Na^+$) 258.2433, found 258.2430.

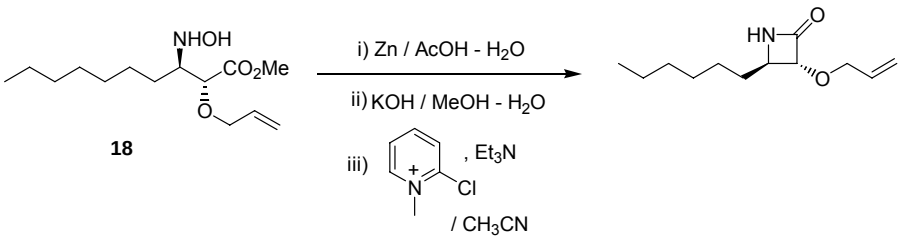
Syn-3-butyl-4-hexylazetidinone



A mixture of methyl *syn*-3-amino-2-butyldecanoate (200 mg, 0.78 mmol) and KOH (218 mg, 39 mmol) - H_2O (5:1; 1.0 mL) was stirred for 10 h at room temperature. 1M HCl aqueous solution was added to the mixture to adjust pH 7. The mixture was extracted three times with $CHCl_3$, which was washed with brine, dried (Na_2SO_4) and concentrated to give crude β-aminoacid (170 mg). Et_3N (236 mg, 2.33 mmol) was added to a stirred solution of the β-aminoacid and 2-chloro-1-methylpyridinium iodide (238 mg, 0.93 mmol) in CH_3CN (2.0 mL) at 45-55 ˚C under an Ar atmosphere. After stirring at the same temperature for 19 h, water was added to the mixture, which was extracted five times with $CHCl_3$. The combined organic phase was washed with water, brine, and dried (Na_2SO_4) and concentrated to give the desired product β-lactam (90 mg, 54%).

(*syn* / *anti* = 90 / 10). colorless oil; ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.9 Hz), 0.91 (3H, t, *J* = 6.9 Hz), 2.68-2.76 (*anti*, 0.10H, m), 3.09-3.20 (*syn*, 0.90H, m), 3.27 (*syn,* 0.10H, ddd, *J* = 6.9, 6.9, 2.1 Hz), 3.63 (*anti,* 0.90H, ddd, *J* = 9.3, 5.2, 4.5 Hz), 5.87-6.00 (1H, brs); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 14.0, 22.5, 22.7, 24.4, 26.3, 26.7, 28.2, 29.1, 29.4, 30.2, 30.7, 31.7, 35.1, 52.3, 52.9, 55.3, 56.8, 171.7, 172.4; IR (neat) 3248, 2928, 2857, 1752, 1464, 1379 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{27}N_1O_1$ ($M + Na^+$) 248.1990, found 248.1991.

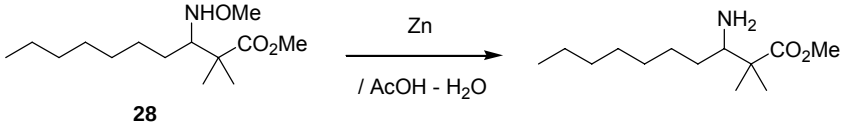
***Anti*-3-butyl-2-allyloxy-4-hexylazetidinone**



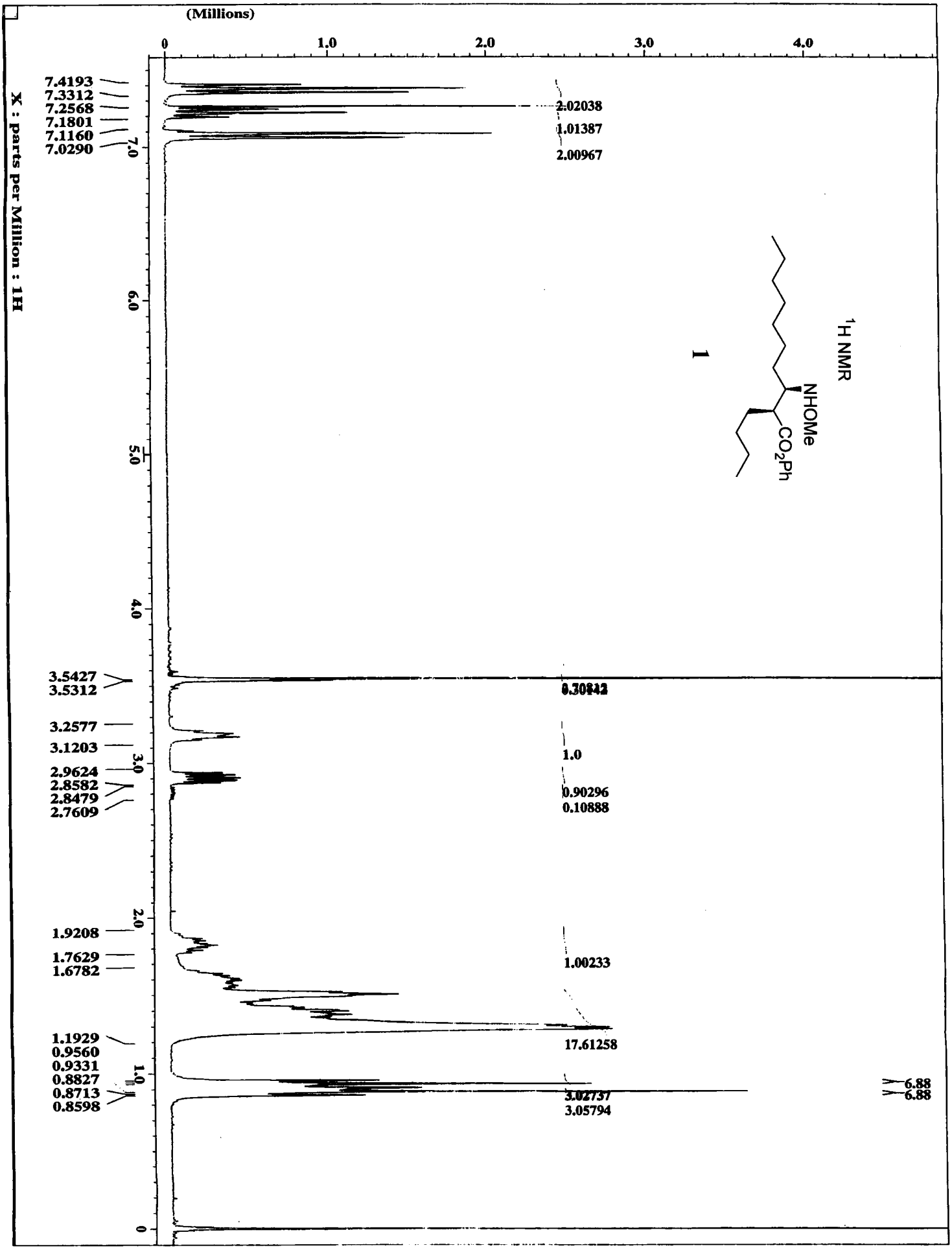
A similar procedure using methyl 2-allyloxy-3-methoxya minodecanoate **18** (137 mg, 0.50 mmol) gave the desired product (58 mg, 55%).

(*syn* / *anti* = 1 / >99).
Yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.89 (3H, t, *J* = 6.9 Hz), 1.19-1.49 (10H, m), 1.55-1.70 (2H, m), 3.57 (*anti,* 1H, ddd, *J* = 6.9, 6.9, 1.7 Hz), 4.08-4.18 (1H, m), 4.21-4.31 (2H, m), 5.19-5.38 (2H, m), 5.84-6.01 (1H, m), 6.02-6.17 (1H, brs); ^{13}C NMR (75 MHz, $CDCl_3$): δ 13.9, 22.4, 26.1, 28.9, 29.1, 31.5, 33.2, 57.3, 86.1, 117.8, 133.7, 166.8, 167.9; IR (neat) 3274, 2926, 2857, 1763, 1182, 1144 cm^{-1}. HRMS (ESI) calcd for $C_{13}H_{23}N_1O_2$ (M + Na^+) 248.1626, found 248.1631.

Methyl 3-amino-2,2-dimethyldecanoate



A similar procedure using methyl 3-(methoxyamino)-2,2-dim ethyldecanoate **28** (144 mg, 0.50 mmol) and Zn powder (327 mg, 5.0 mmol) gave the desired product (100 mg, 87%).
Pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.9 Hz), 1.13 (3H, s), 1.14 (3H, s), 1.21-1.60 (12H, m), 2.83 (1H , dd, *J* = 2.1 Hz, *J* = 10.7 Hz), 3.68 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 20.9, 21.3, 22.6, 27.3, 29.3, 29.8, 31.8, 32.5, 47.6, 51.6, 57.7, 178.1; IR (neat) 2928, 2857, 1732, 1466, 1389, 1265, 1192, 1134; HRMS (ESI) calcd for $C_{13}H_{27}N_1O_2$ (M + Na^+) 230.2120, found 230.2119.


(Millions)
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1.0
2.0
3.0
4.0
X : parts per Million : 1H
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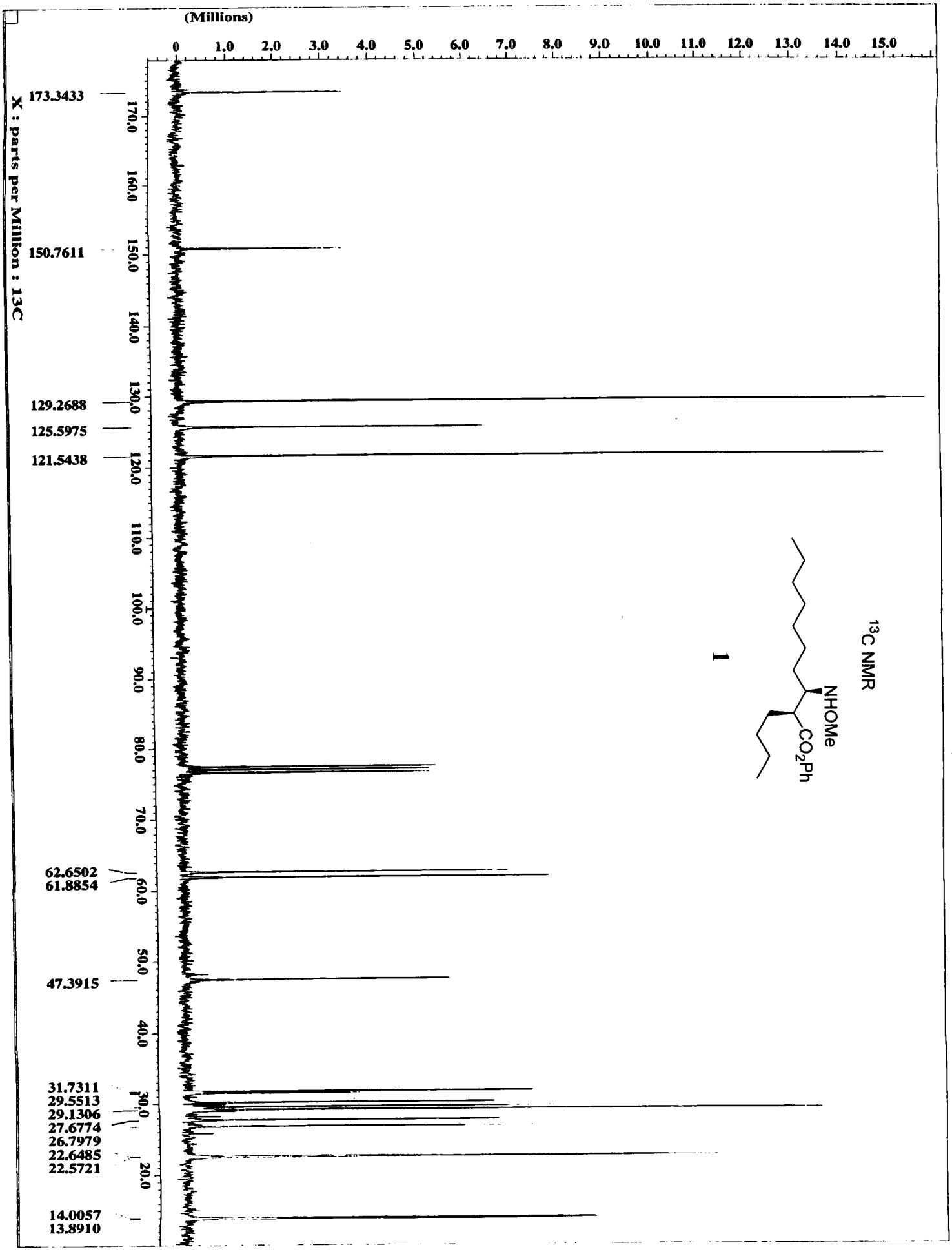
7.3312
7.2568
7.1801
7.1160
7.0290
2.02038
1.01387
2.00967
7.0
6.0
5.0
4.0
3.5427
3.5312
3.2577
3.1203
2.9624
2.8582
2.8479
2.7609
1.0
0.90296
0.10888
3.0
2.0
1.9208
1.7629
1.6782
1.00233
17.61258
1.1929
0.9560
0.9331
0.8827
0.8713
0.8598
3.02737
3.05794
6.88
6.88
1.0
0
1
NHOMe
CO2Ph
1H NMR


(Millions)
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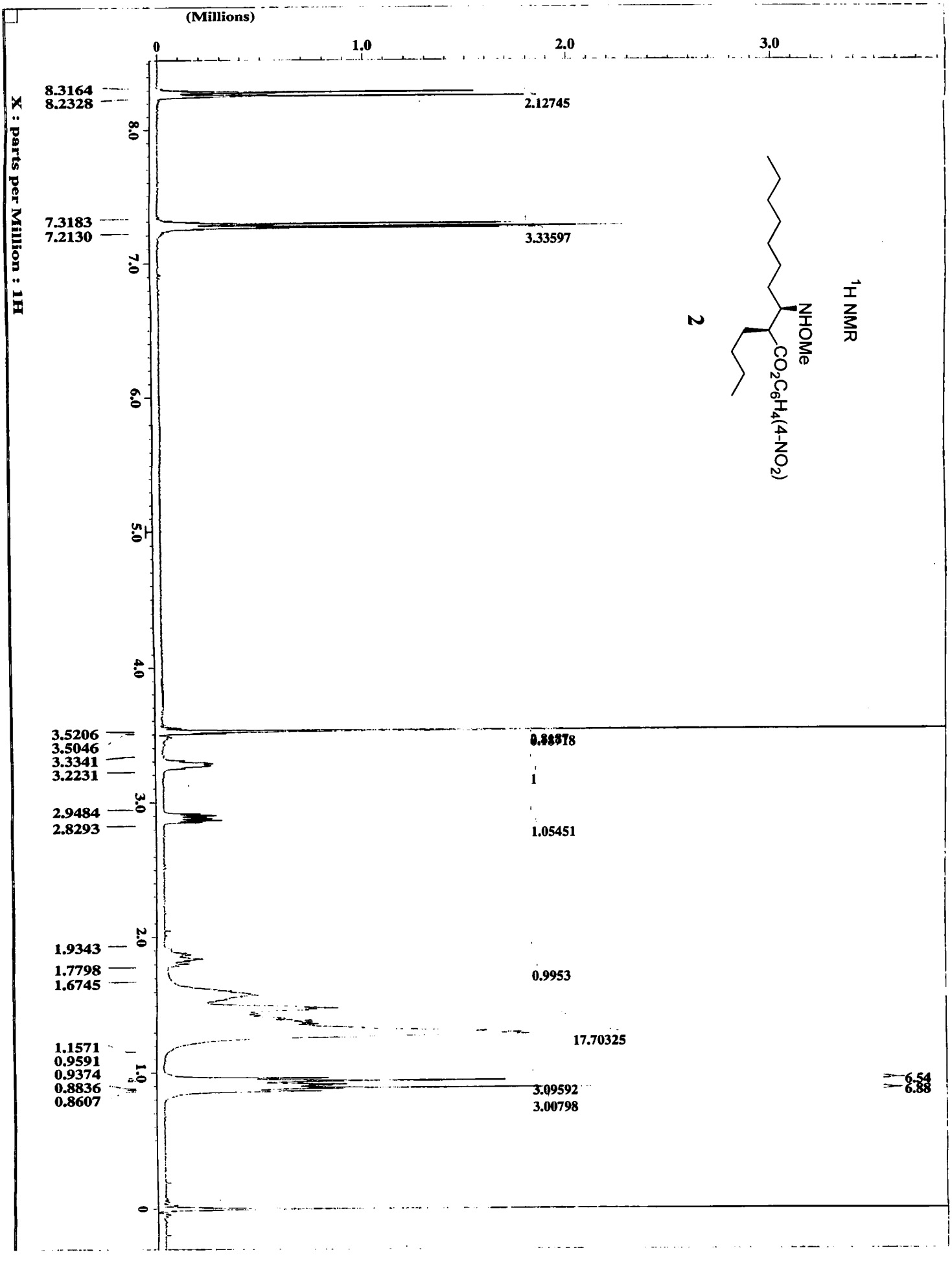
X : parts per Million : 13C
173.3433
150.7611
129.2688
125.5975
121.5438
62.6502
61.8854
47.3915
31.7311
29.5513
29.1306
27.6774
26.7979
22.6485
22.5721
14.0057
13.8910
170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0
1
NHOMe
CO2Ph
13C NMR


(Millions)
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2.0
3.0
X : parts per Million : 1H
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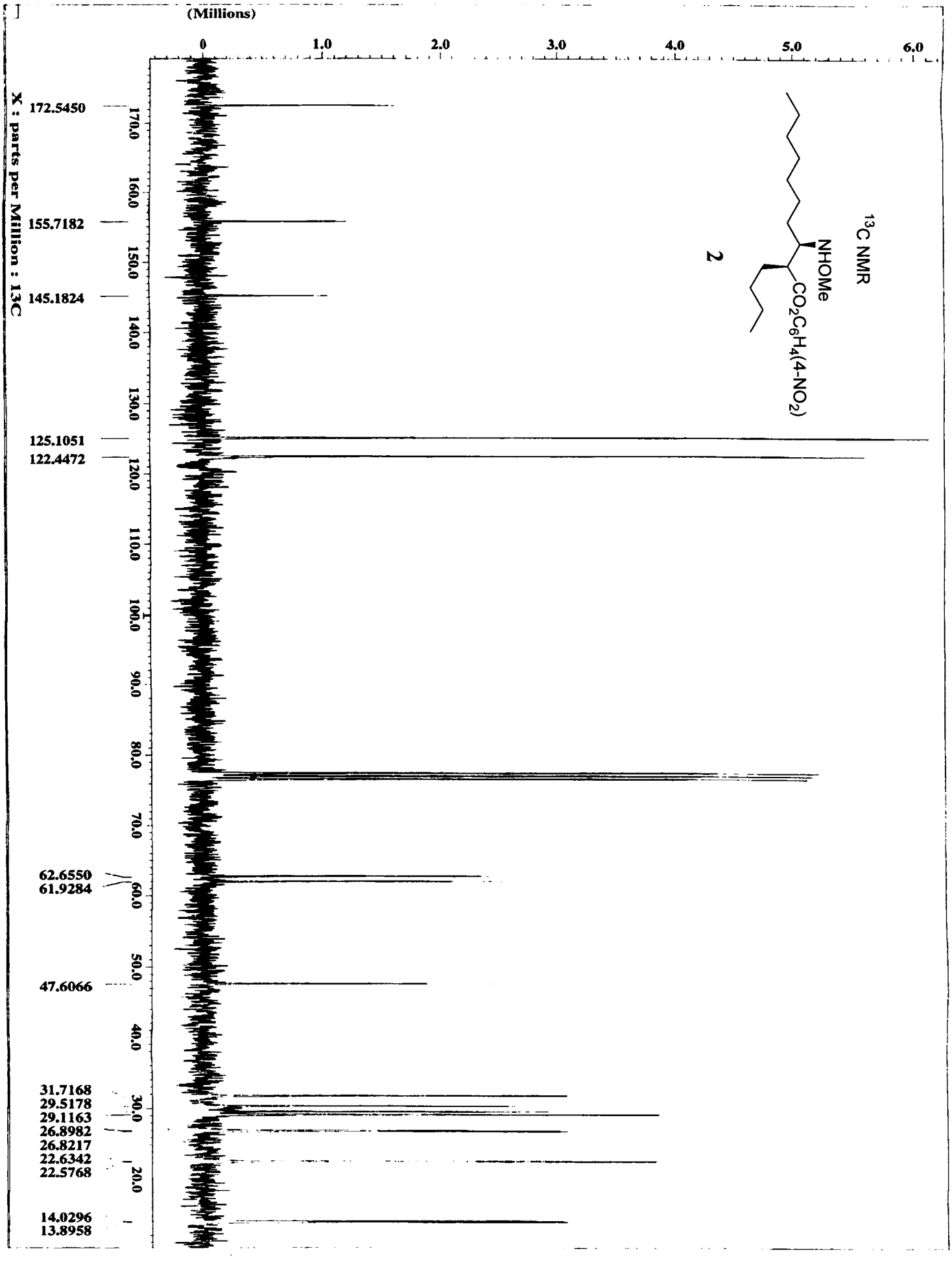
8.2328
7.3183
7.2130
3.5206
3.5046
3.3341
3.2231
2.9484
2.8293
1.9343
1.7798
1.6745
1.1571
0.9591
0.9374
0.8836
0.8607
2.12745
3.33597
1
1.05451
0.9953
17.70325
3.09592
3.00798
6.54
6.88
2
NHOMe
$CO_2C_6H_4(4\text{-}NO_2)$
^{1}H NMR


(Millions)
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2.0
3.0
4.0
5.0
6.0
X : parts per Million : 13C
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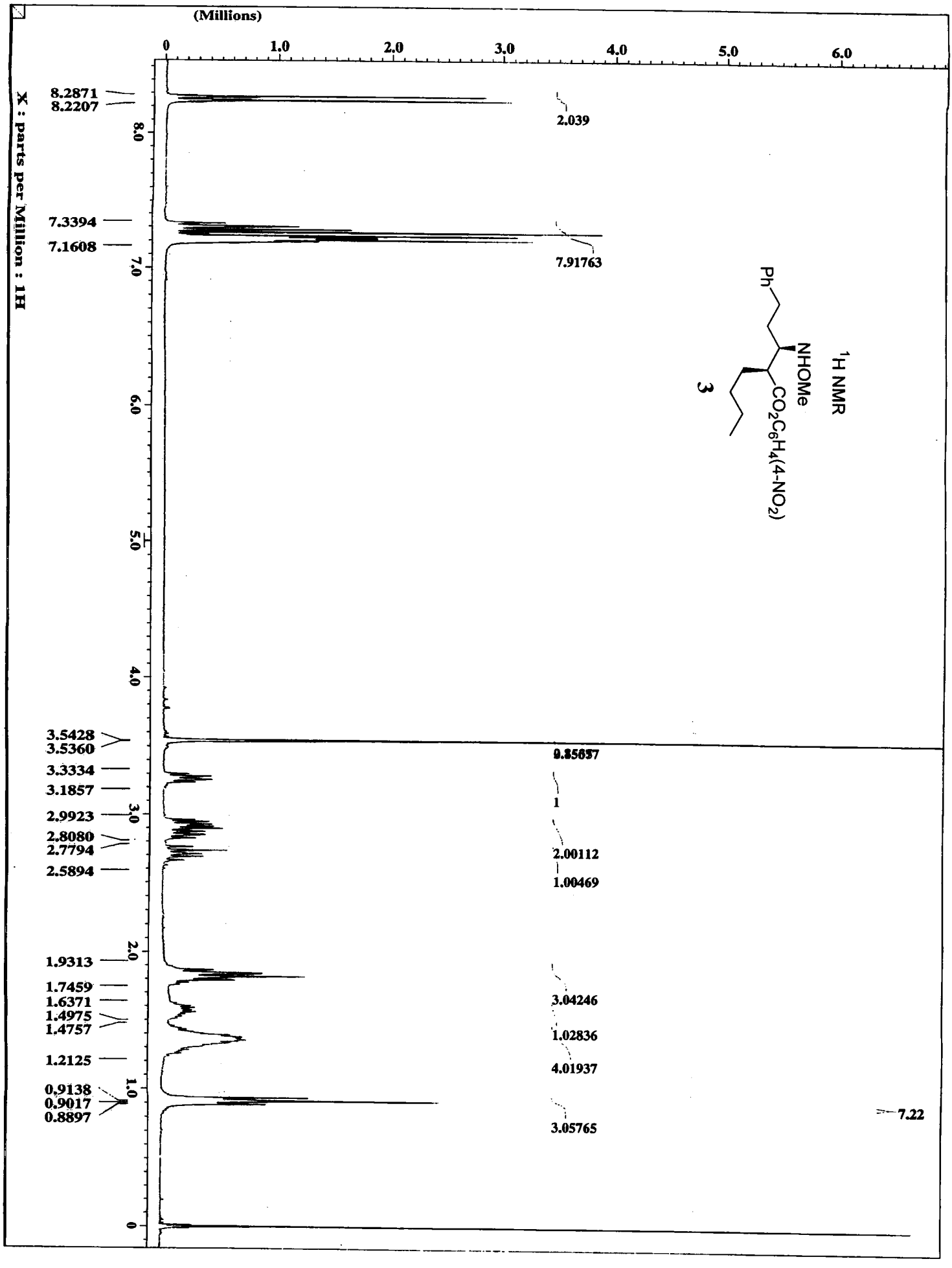
155.7182
145.1824
125.1051
122.4472
62.6550
61.9284
47.6066
31.7168
29.5178
29.1163
26.8982
26.8217
22.6342
22.5768
14.0296
13.8958
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
^{13}C NMR
2
NHOMe
$CO_2C_6H_4(4\text{-}NO_2)$


(Millions)
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3.0
4.0
5.0
6.0
X : parts per Million : 1H
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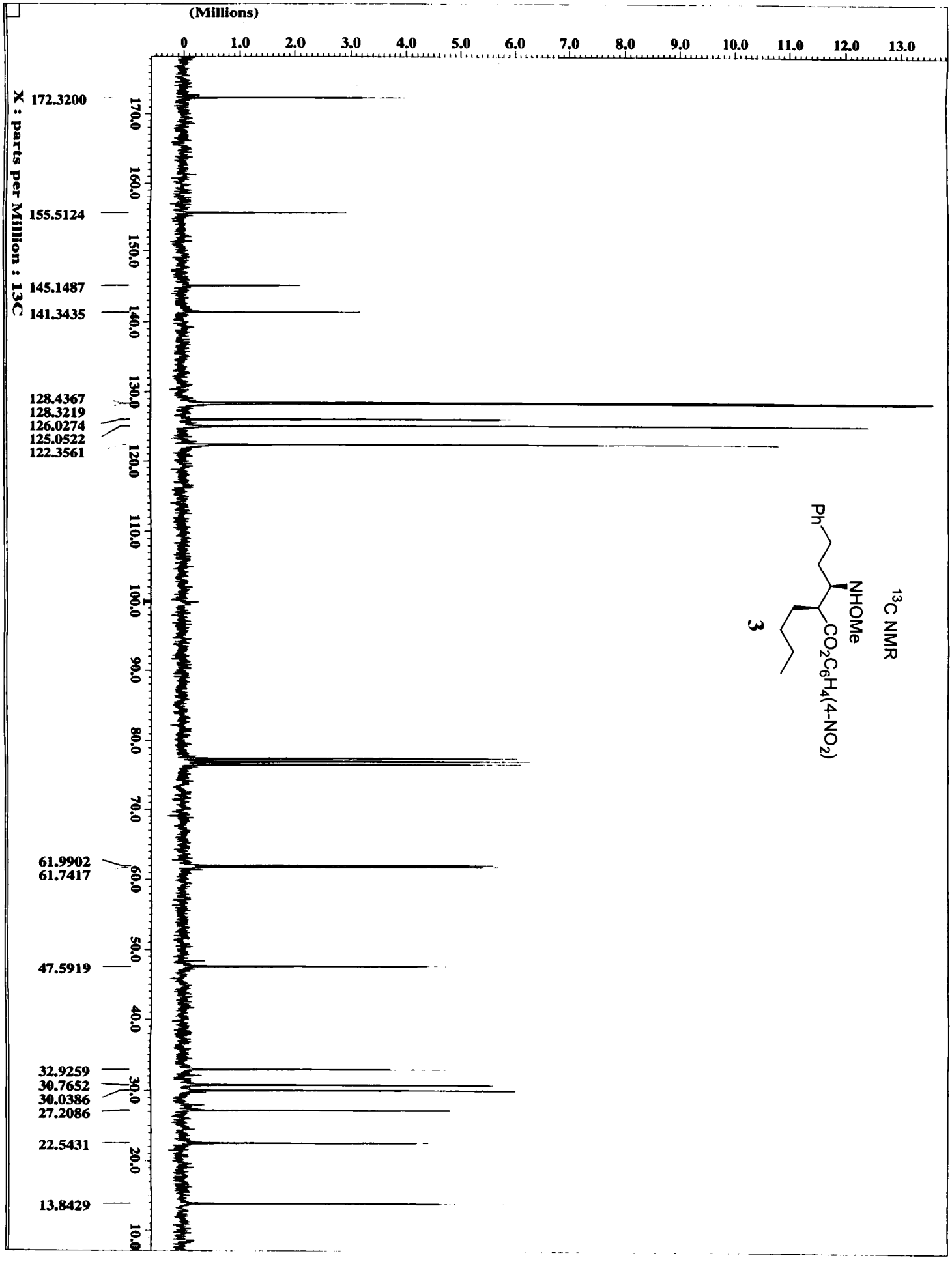
7.1608
3.5428
3.5360
3.3334
3.1857
2.9923
2.8080
2.7794
2.5894
1.9313
1.7459
1.6371
1.4975
1.4757
1.2125
0.9138
0.9017
0.8897
2.039
7.91763
1
2.00112
1.00469
3.04246
1.02836
4.01937
3.05765
7.22
Ph
NHOMe
CO2C6H4(4-NO2)
3
1H NMR


(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
X : parts per Million : 13C
172.3200
155.5124
145.1487
141.3435
128.4367
128.3219
126.0274
125.0522
122.3561
61.9902
61.7417
47.5919
32.9259
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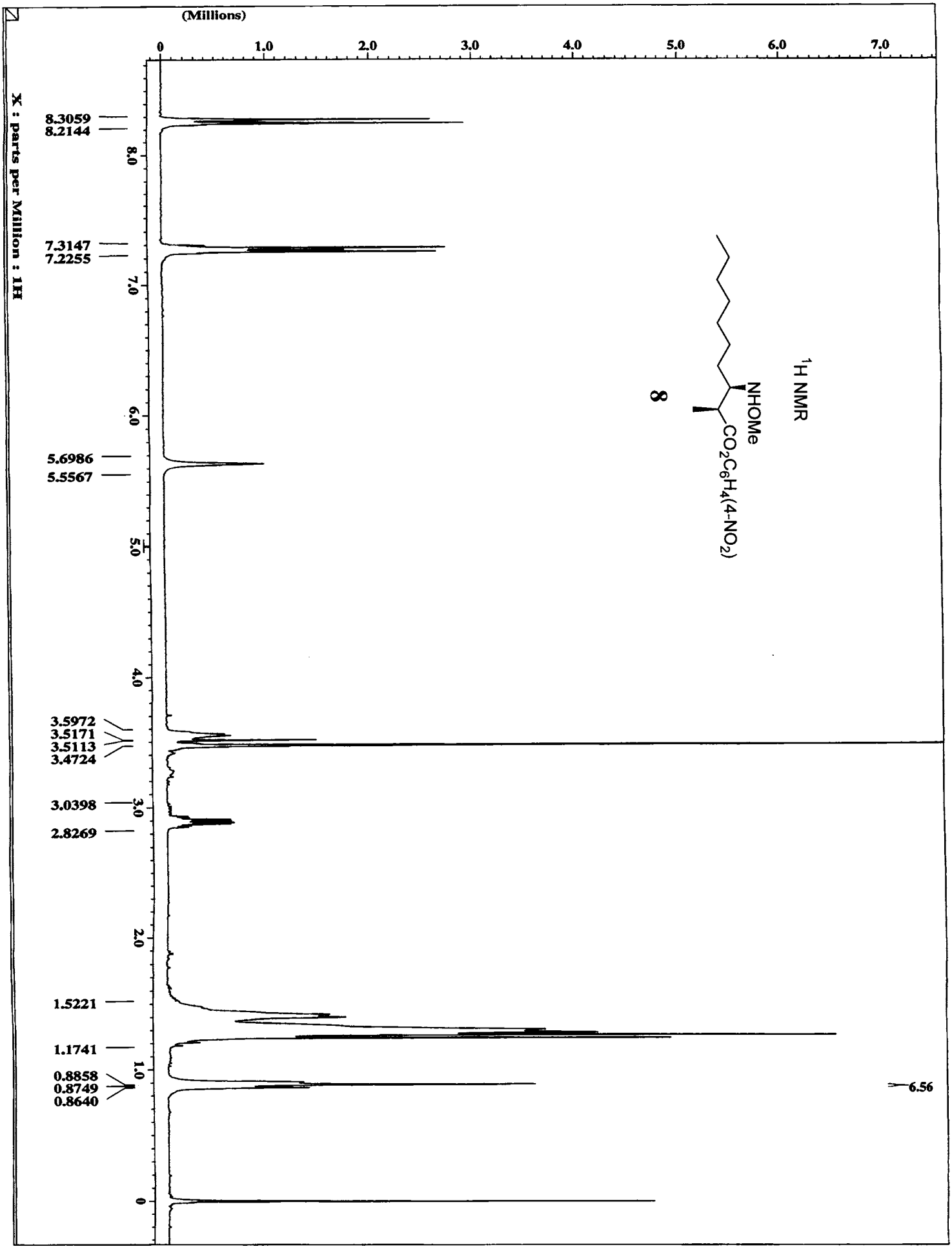
Ph
NHOMe
CO2C6H4(4-NO2)
3
13C NMR


(Millions)
X : parts per Million : 1H
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7.3147
7.2255
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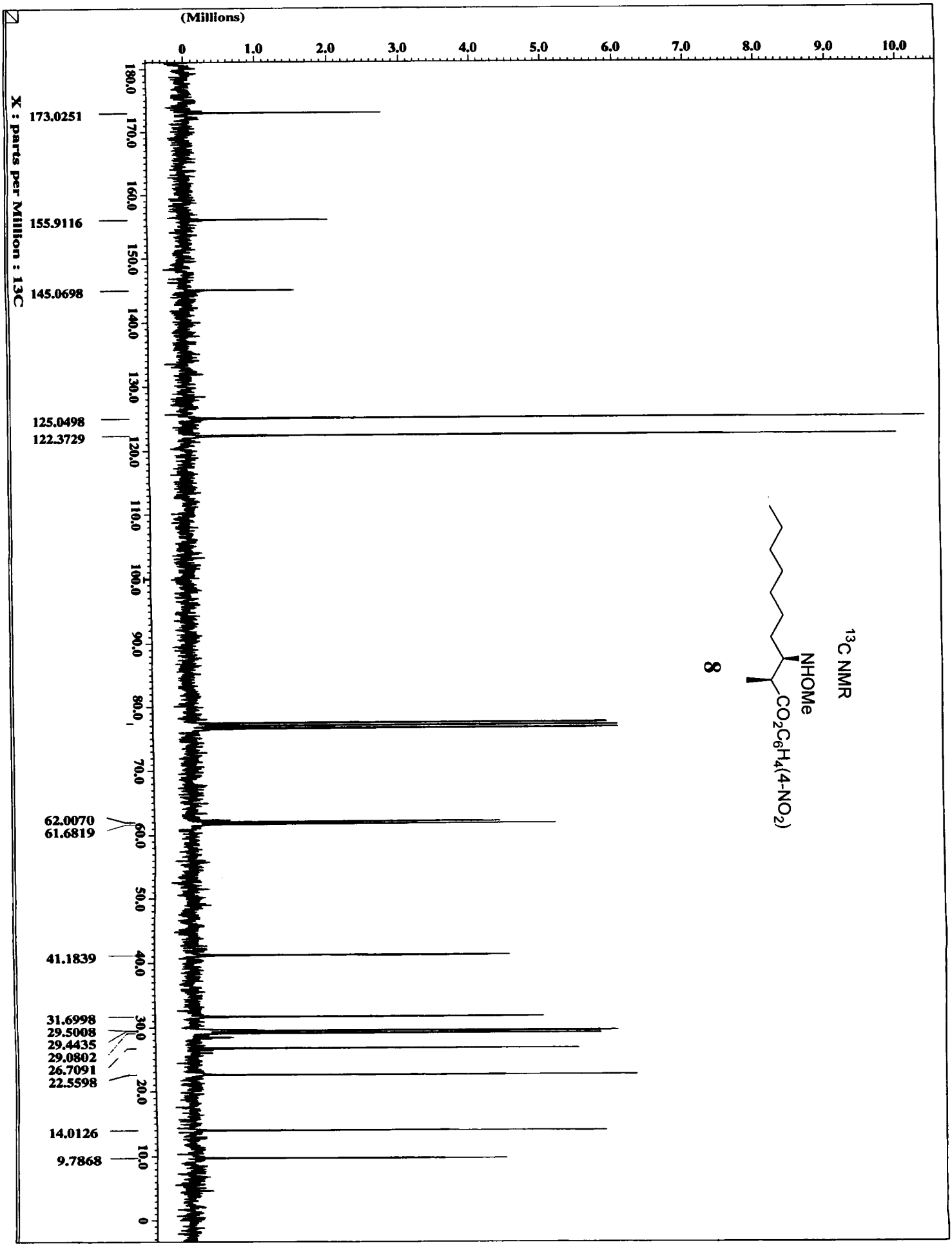
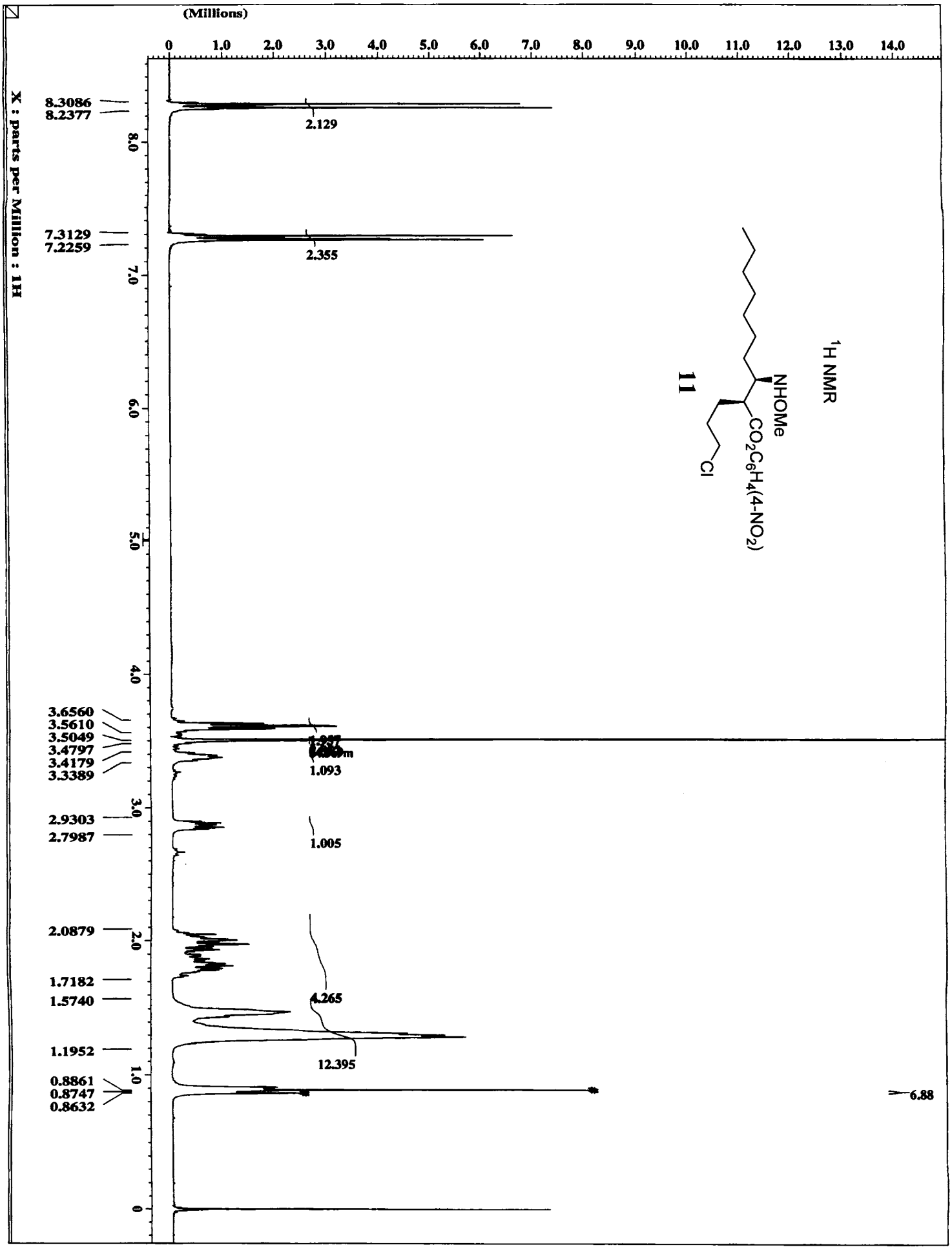
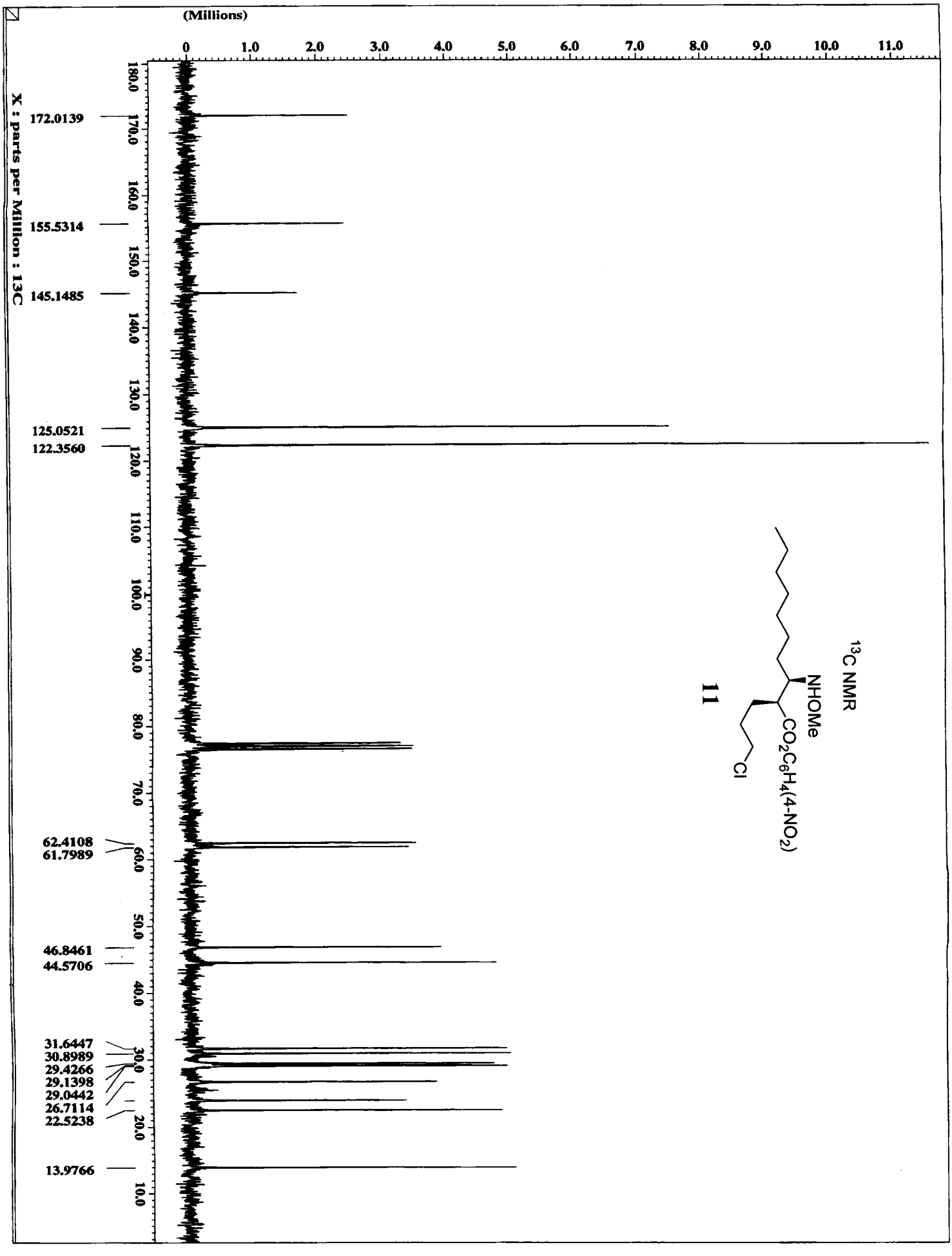
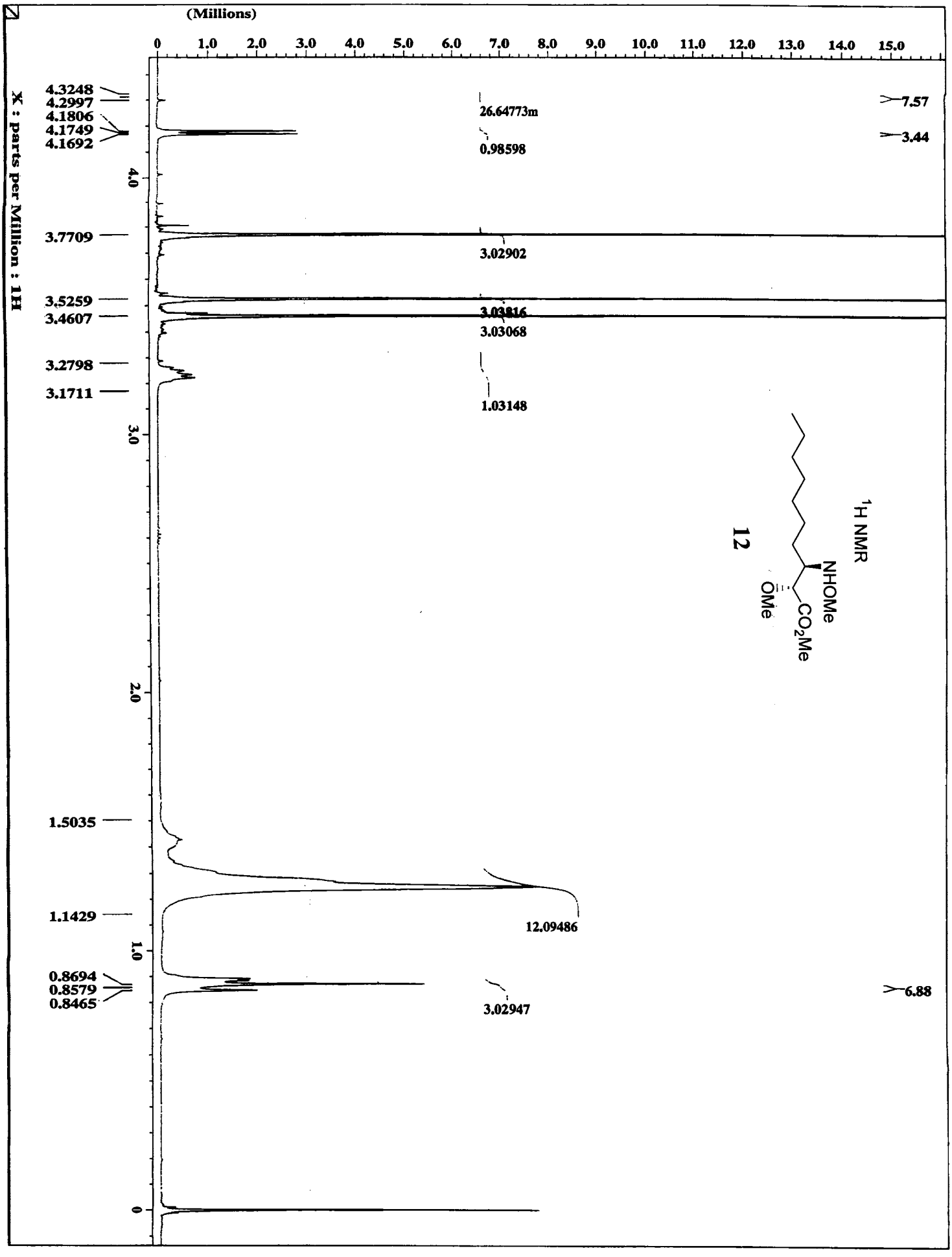
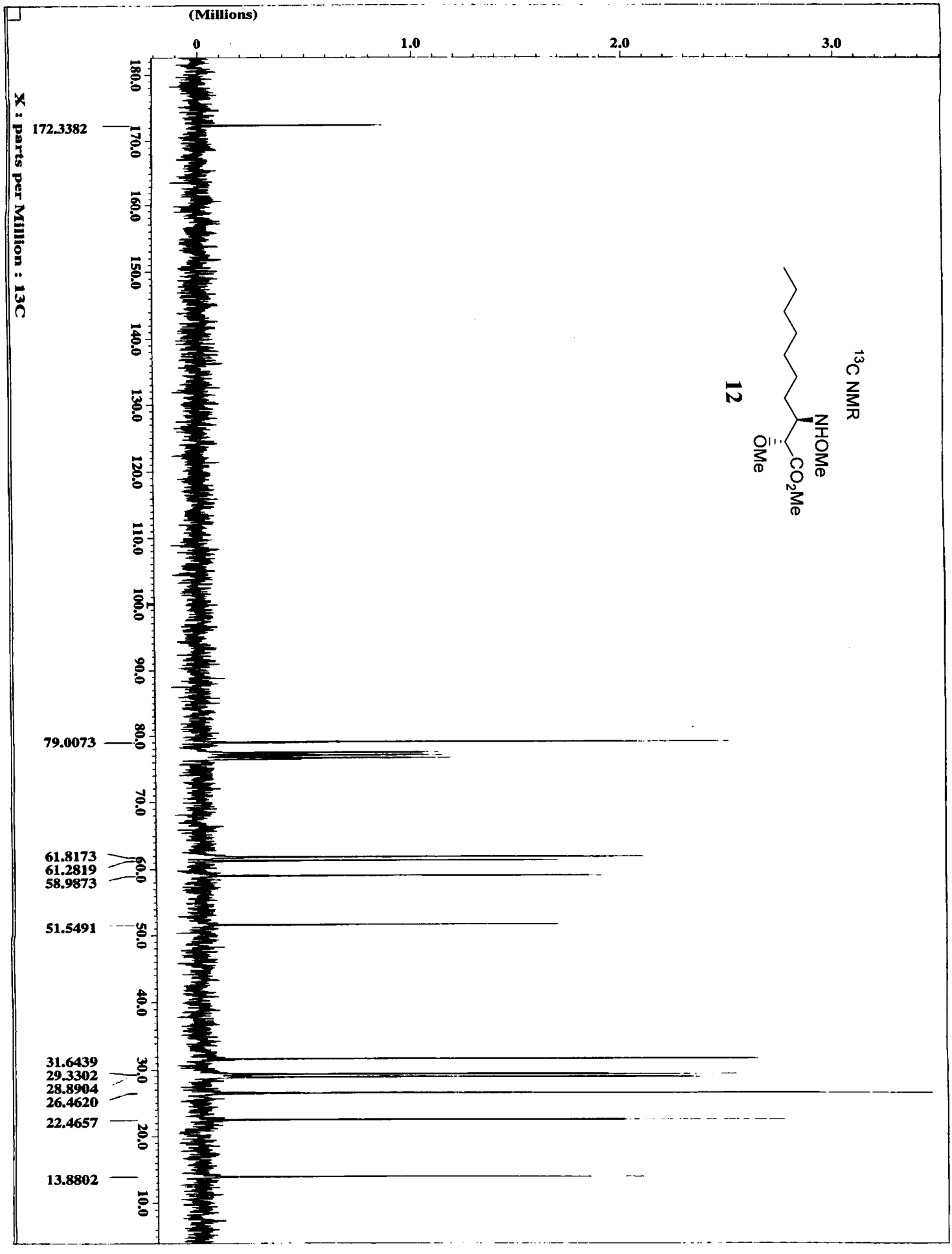
5.5567
3.5972
3.5171
3.5113
3.4724
3.0398
2.8269
1.5221
1.1741
0.8858
0.8749
0.8640
6.56
8
NHOMe
CO2C6H4(4-NO2)
1H NMR

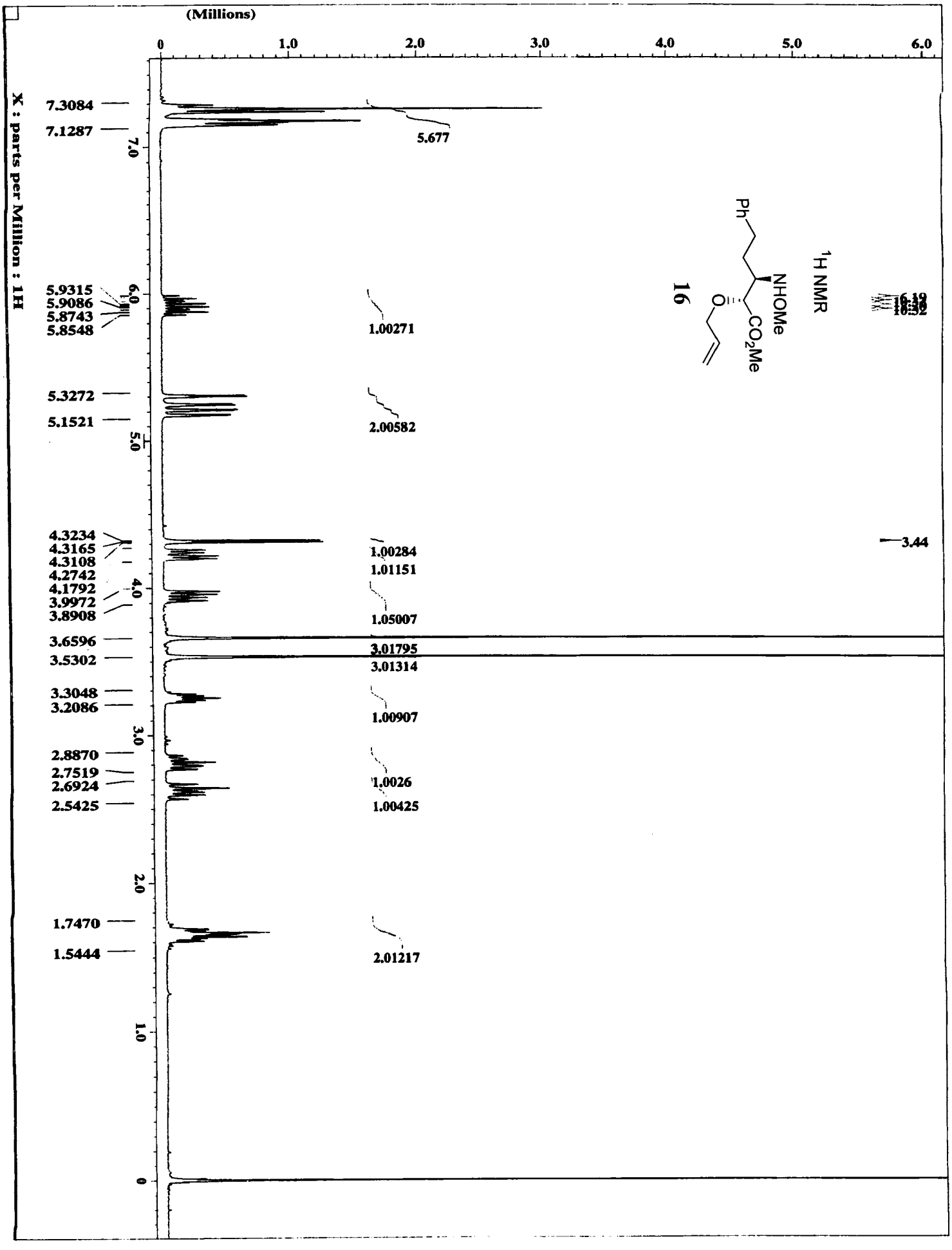

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
X : parts per Million : 13C
173.0251
155.9116
145.0698
125.0498
122.3729
62.0070
61.6819
41.1839
31.6998
29.5008
29.4435
29.0802
26.7091
22.5598
14.0126
9.7868
^{13}C NMR
8
NHOMe
$CO_2C_6H_4(4\text{-}NO_2)$

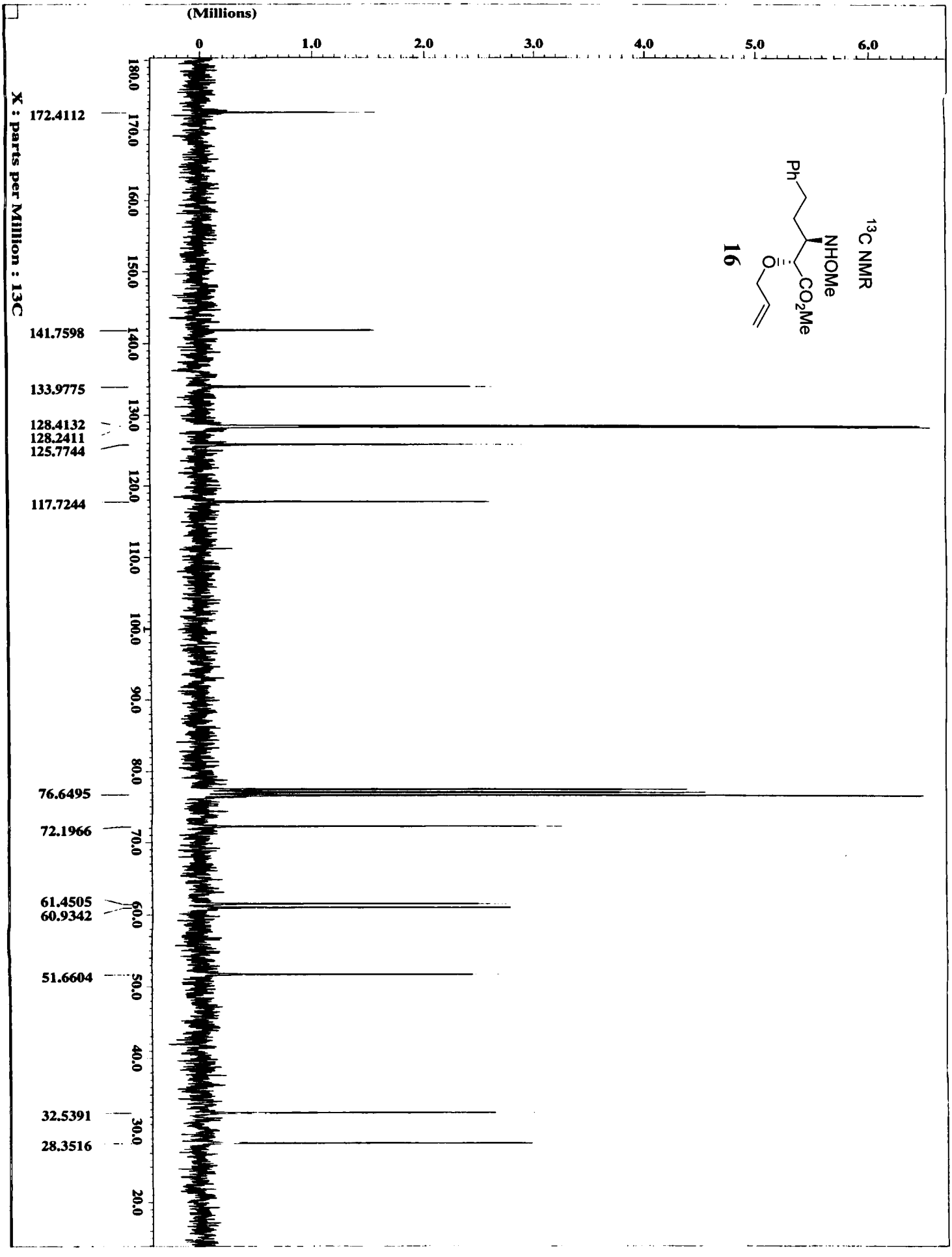

(Millions)
X : parts per Million : 1H
8.3086
8.2377
7.3129
7.2259
3.6560
3.5610
3.5049
3.4797
3.4179
3.3389
2.9303
2.7987
2.0879
1.7182
1.5740
1.1952
0.8861
0.8747
0.8632
2.129
2.355
1.093
1.005
4.265
12.395
6.88
11
NHOMe
CO2C6H4(4-NO2)
Cl
1H NMR

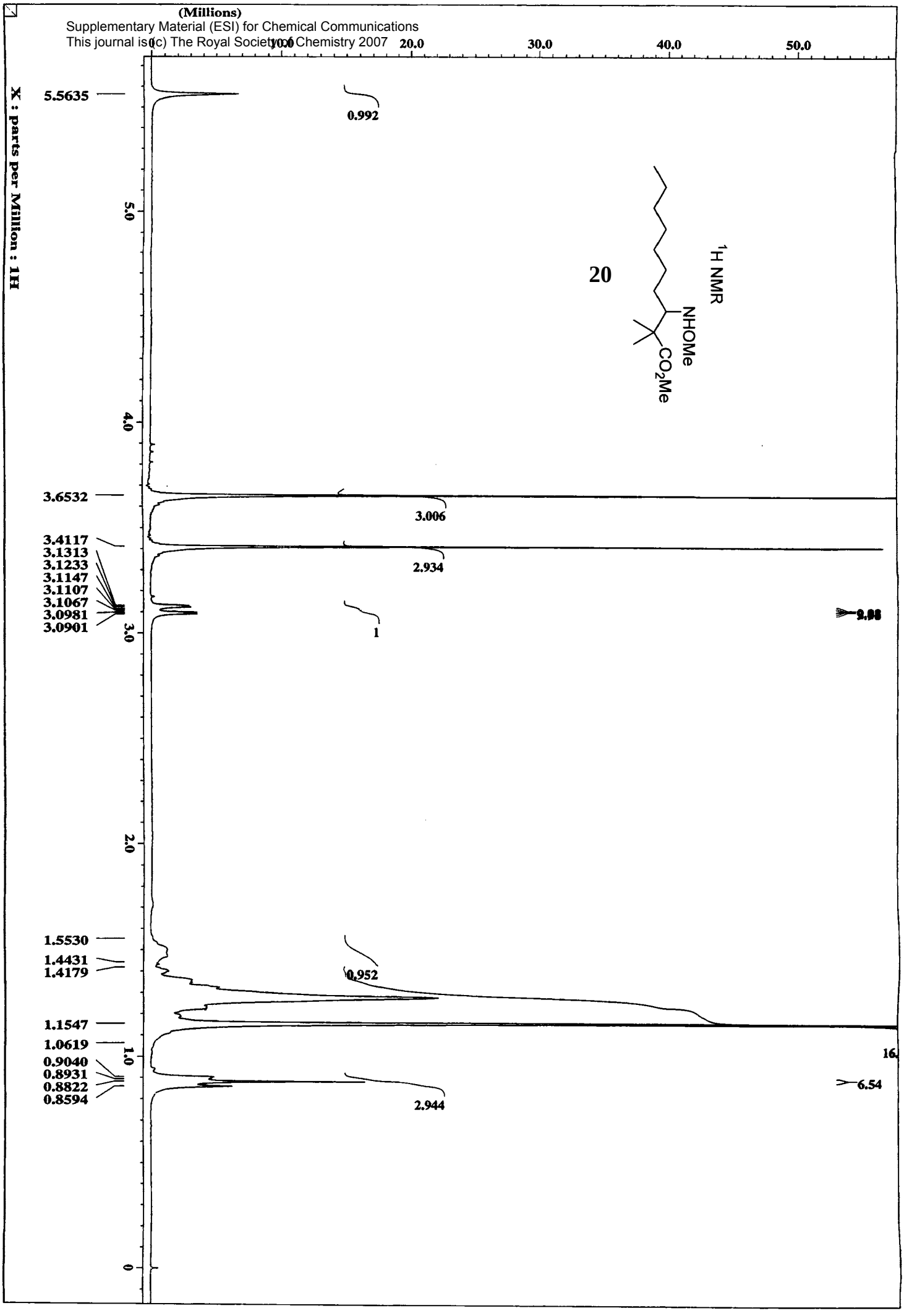

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
X : parts per Million : 13C
172.0139
155.5314
145.1485
125.0521
122.3560
62.4108
61.7989
46.8461
44.5706
31.6447
30.8989
29.4266
29.1398
29.0442
26.7114
22.5238
13.9766
^{13}C NMR
11
NHOMe
$CO_2C_6H_4(4\text{-}NO_2)$
Cl

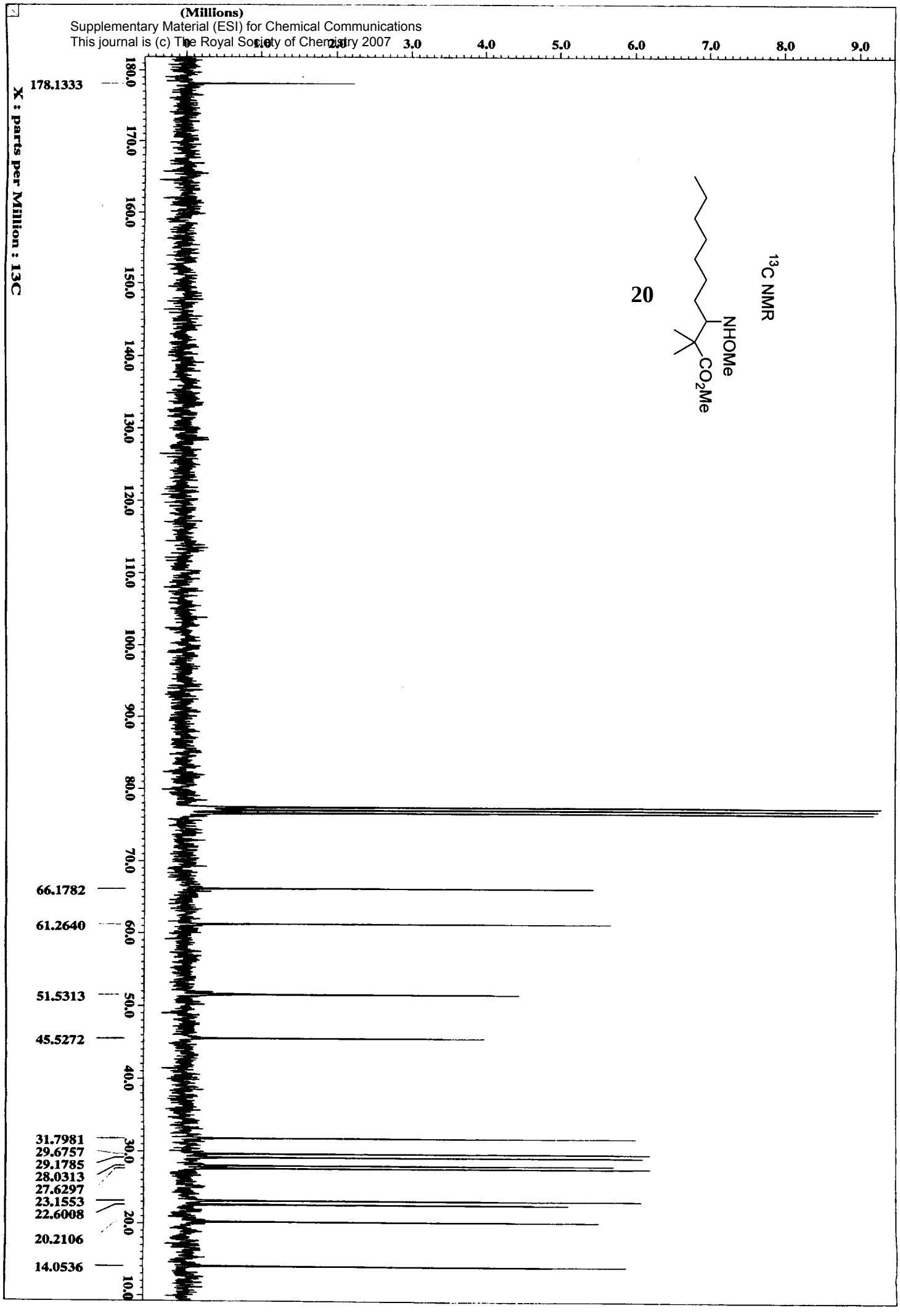

(Millions)
0 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 14.0 15.0
X : parts per Million : 1H
4.3248
4.2997
4.1806
4.1749
4.1692
3.7709
3.5259
3.4607
3.2798
3.1711
1.5035
1.1429
0.8694
0.8579
0.8465
26.64773m
0.98598
3.02902
3.03816
3.03068
1.03148
12.09486
3.02947
7.57
3.44
6.88
12
NHOMe
OMe
CO2Me
1H NMR

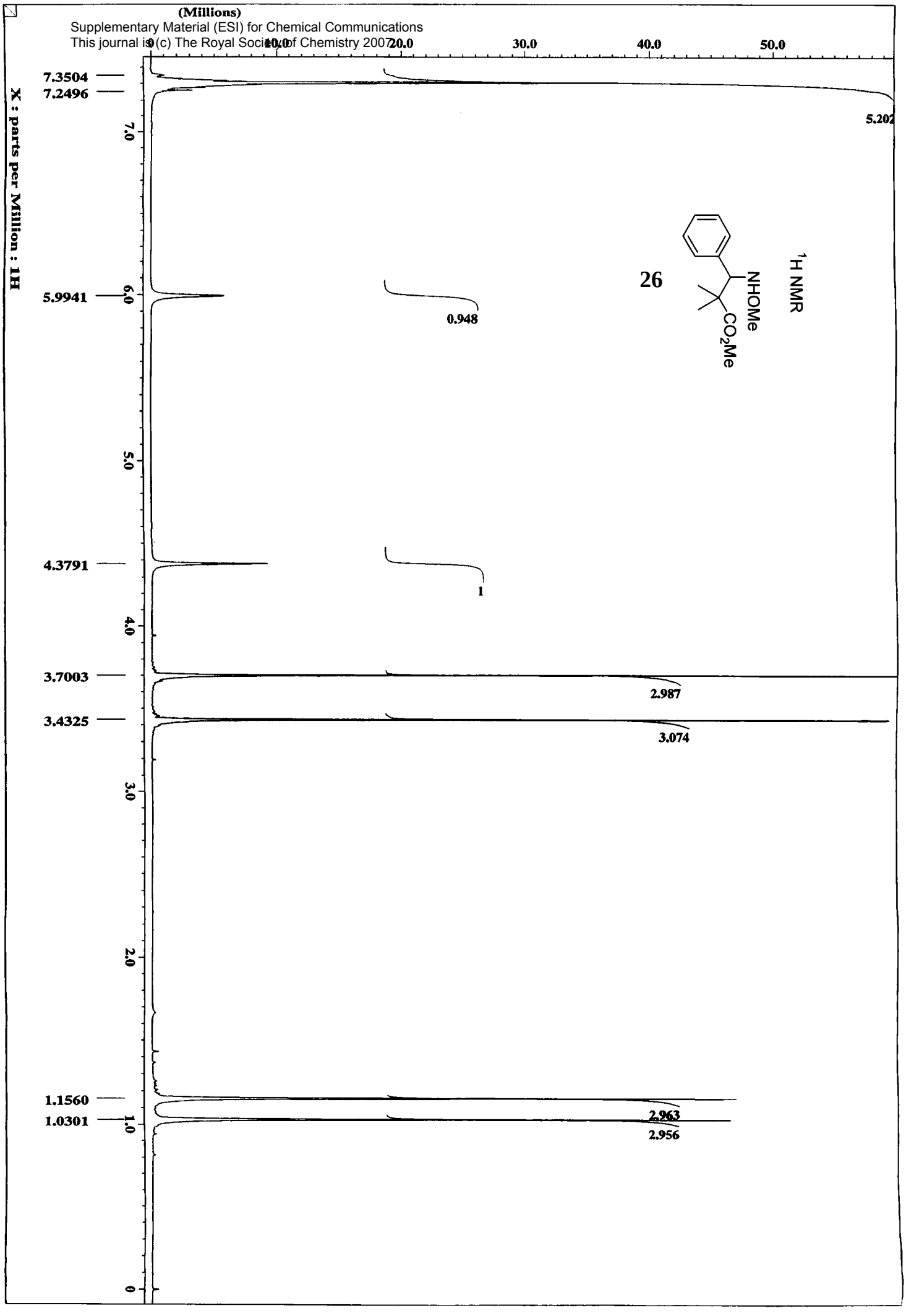

(Millions)
0
1.0
2.0
3.0
X : parts per Million : 13C
172.3382
79.0073
61.8173
61.2819
58.9873
51.5491
31.6439
29.3302
28.8904
26.4620
22.4657
13.8802
^{13}C NMR
12
NHOMe
CO2Me
OMe

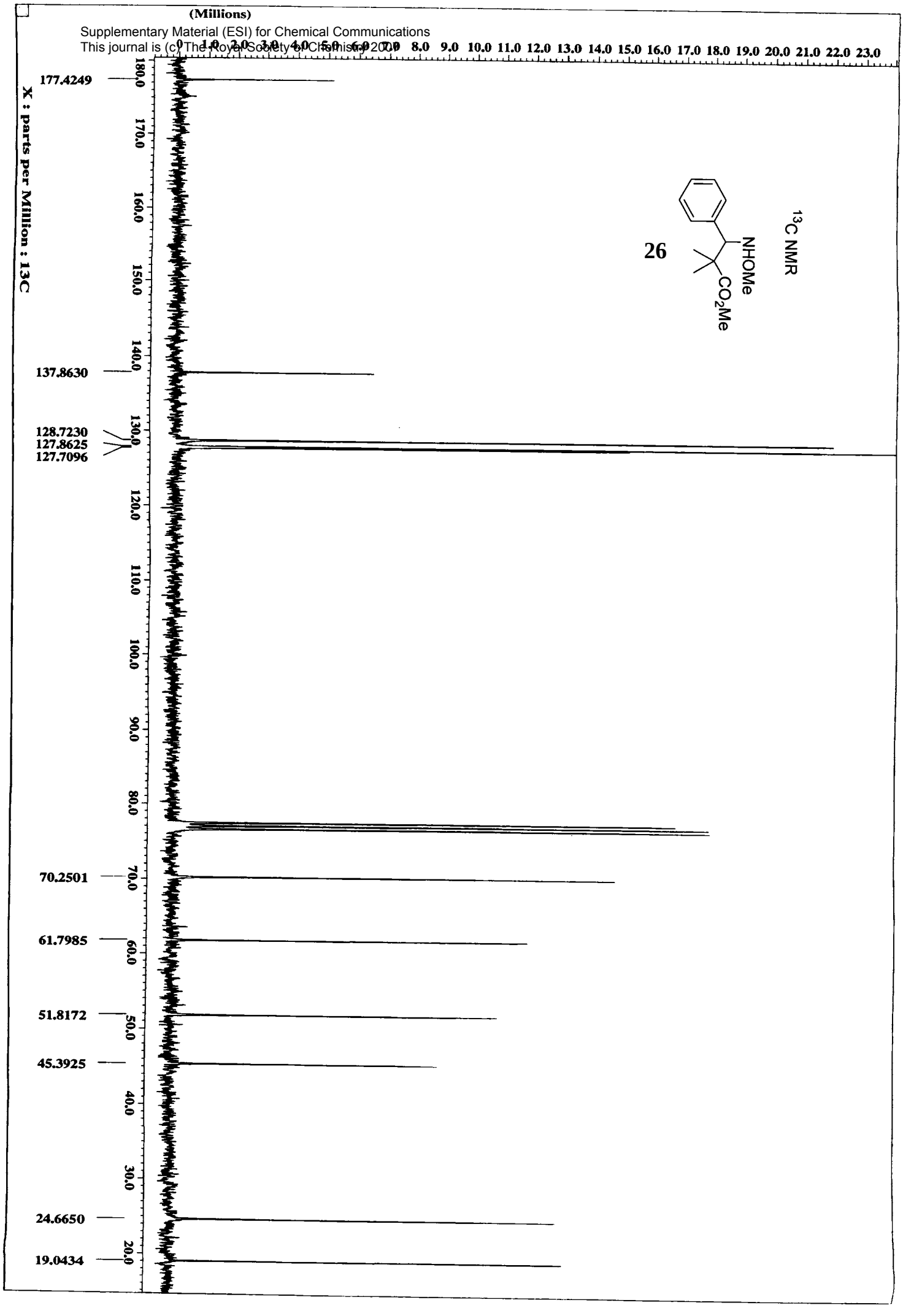

(Millions)
X : parts per Million : 1H
7.3084
7.1287
5.9315
5.9086
5.8743
5.8548
5.3272
5.1521
4.3234
4.3165
4.3108
4.2742
4.1792
3.9972
3.8908
3.6596
3.5302
3.3048
3.2086
2.8870
2.7519
2.6924
2.5425
1.7470
1.5444
5.677
1.00271
2.00582
1.00284
1.01151
1.05007
3.01795
3.01314
1.00907
1.0026
1.00425
2.01217
3.44
16
Ph
NHOMe
CO2Me
1H NMR

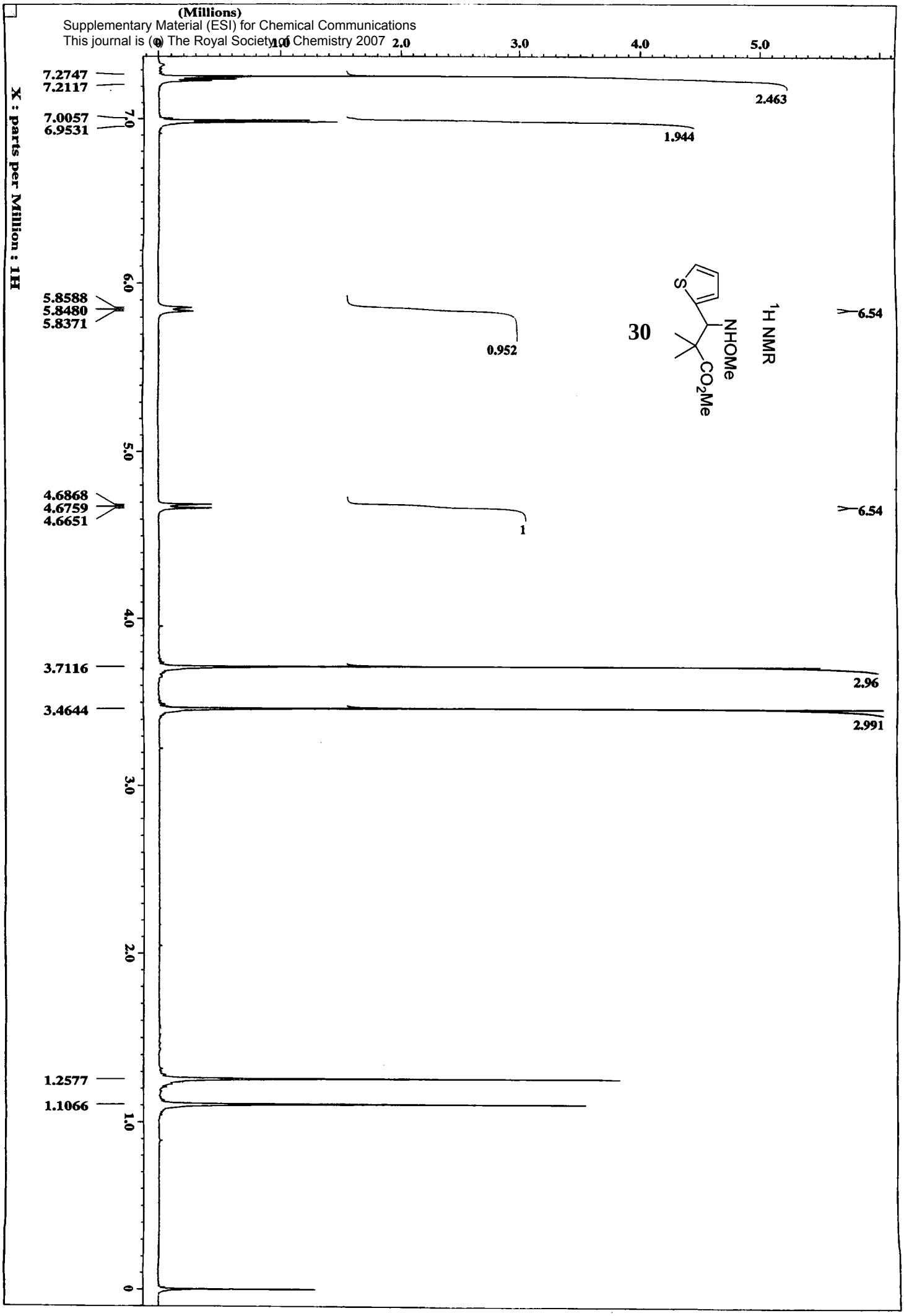

(Millions)
0
1.0
2.0
3.0
4.0
5.0
6.0
X : parts per Million : 13C
172.4112
141.7598
133.9775
128.4132
128.2411
125.7744
117.7244
76.6495
72.1966
61.4505
60.9342
51.6604
32.5391
28.3516
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
Ph
NHOMe
CO2Me
O
16
13C NMR

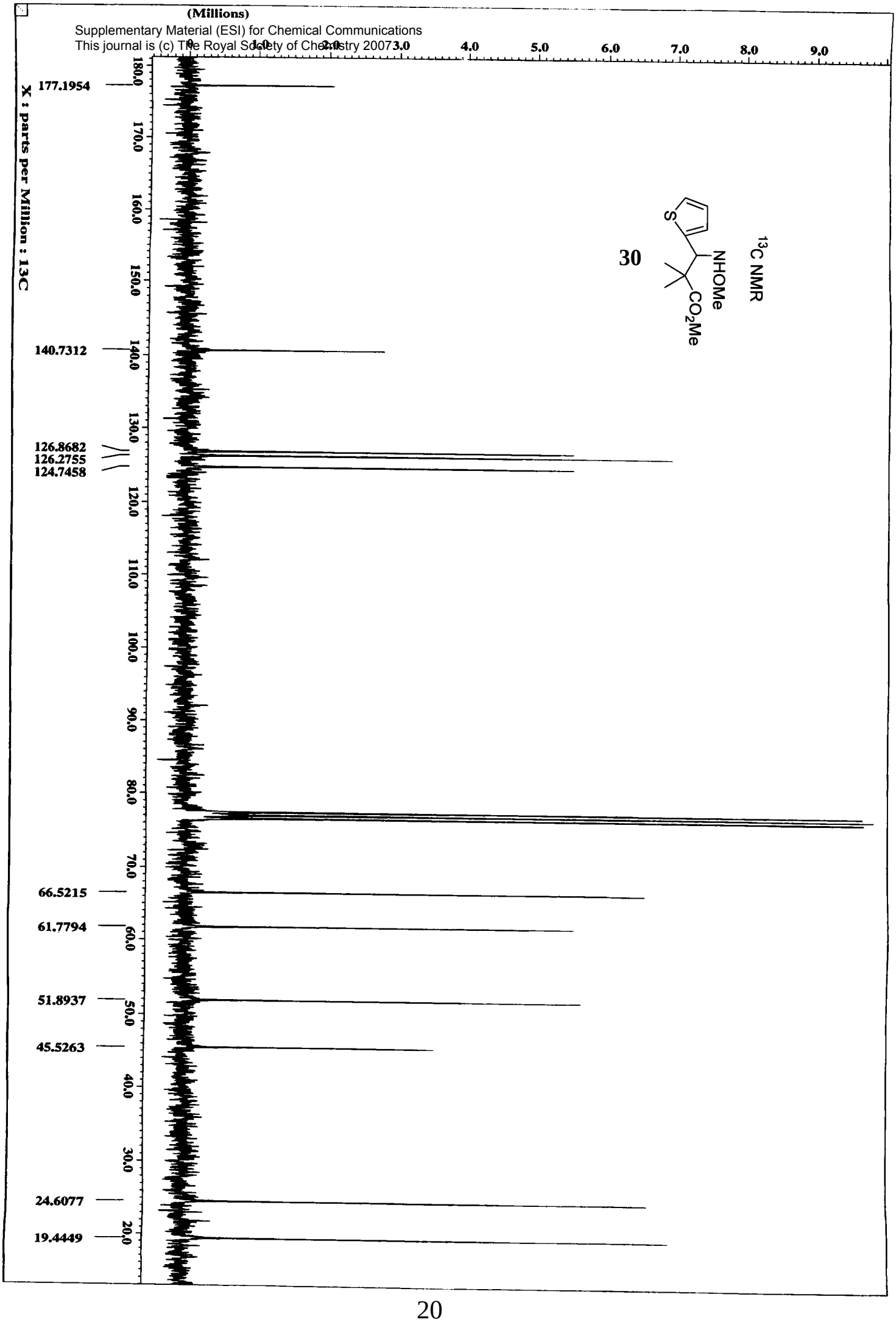

(Millions)
X : parts per Million : 1H
5.5635
3.6532
3.4117
3.1313
3.1233
3.1147
3.1107
3.1067
3.0981
3.0901
1.5530
1.4431
1.4179
1.1547
1.0619
0.9040
0.8931
0.8822
0.8594
0.992
3.006
2.934
1
0.952
2.944
16.
6.54
20
^{1}H NMR
NHOMe
CO_2Me

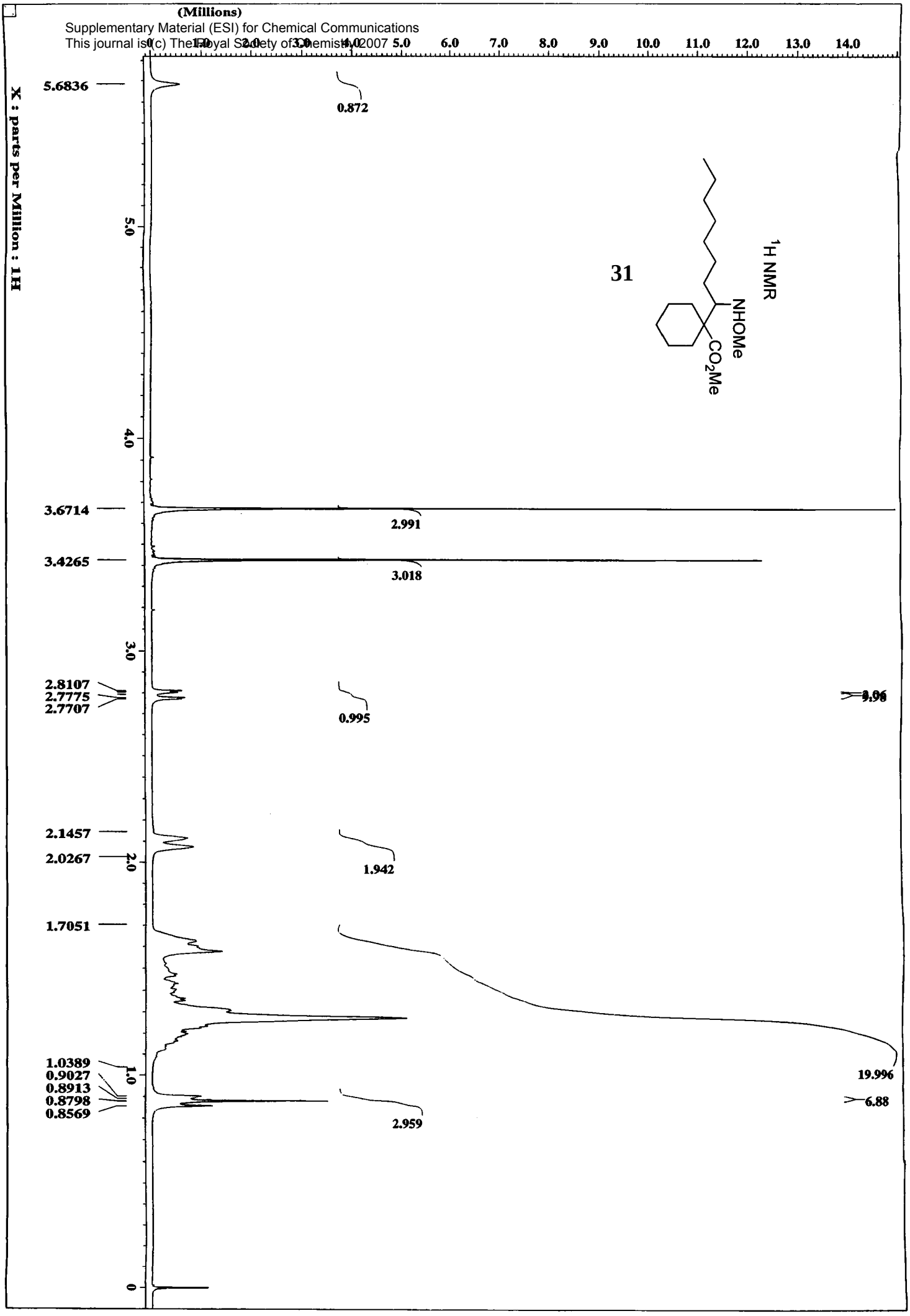


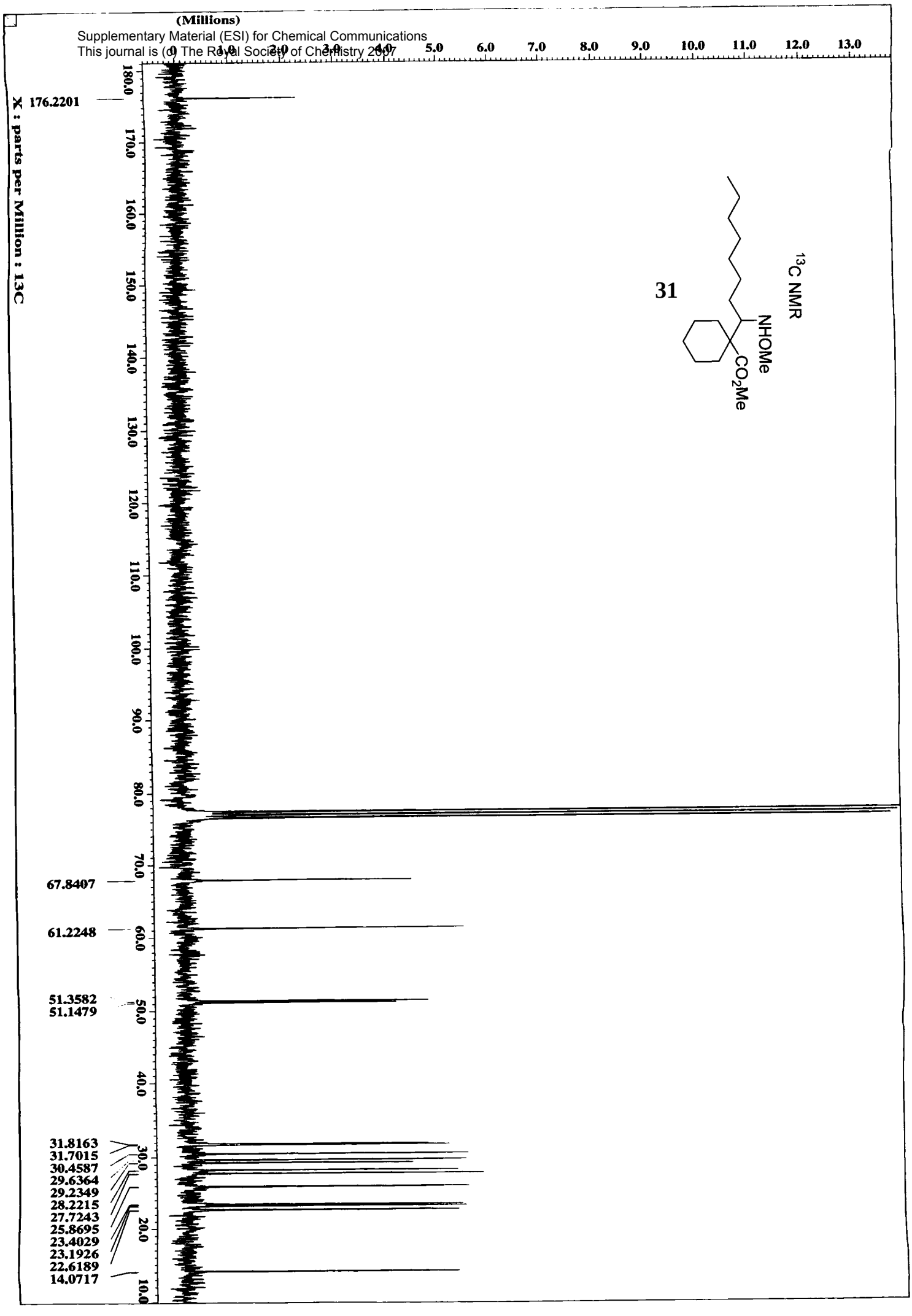

(Millions)
X : parts per Million : 1H
7.3504
7.2496
5.9941
4.3791
3.7003
3.4325
1.1560
1.0301
5.202
0.948
1
2.987
3.074
2.963
2.956
26
NHOMe
CO2Me
1H NMR

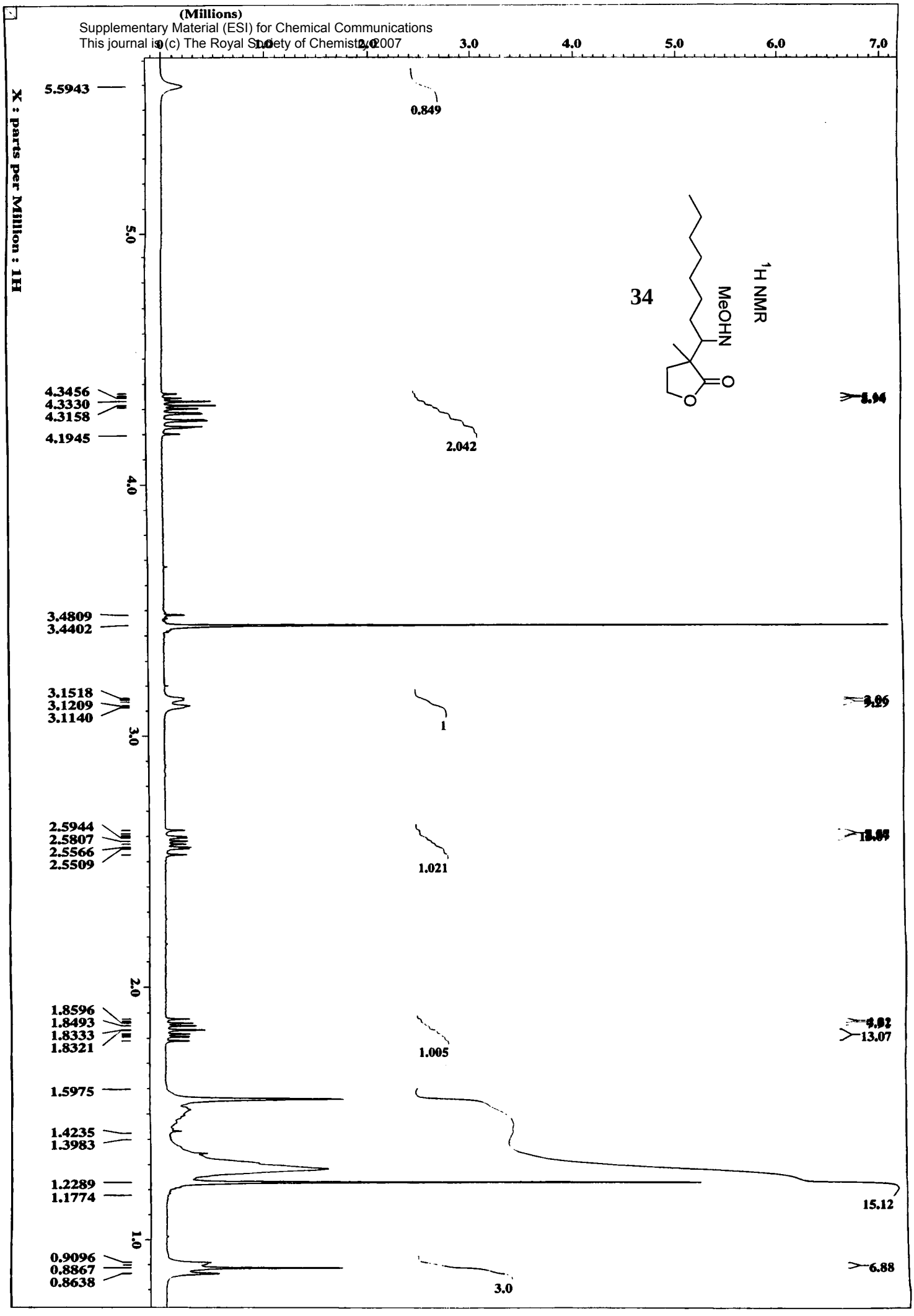

(Millions)
X : parts per Million : 13C
177.4249
137.8630
128.7230
127.8625
127.7096
70.2501
61.7985
51.8172
45.3925
24.6650
19.0434
26
NHOMe
CO2Me
13C NMR

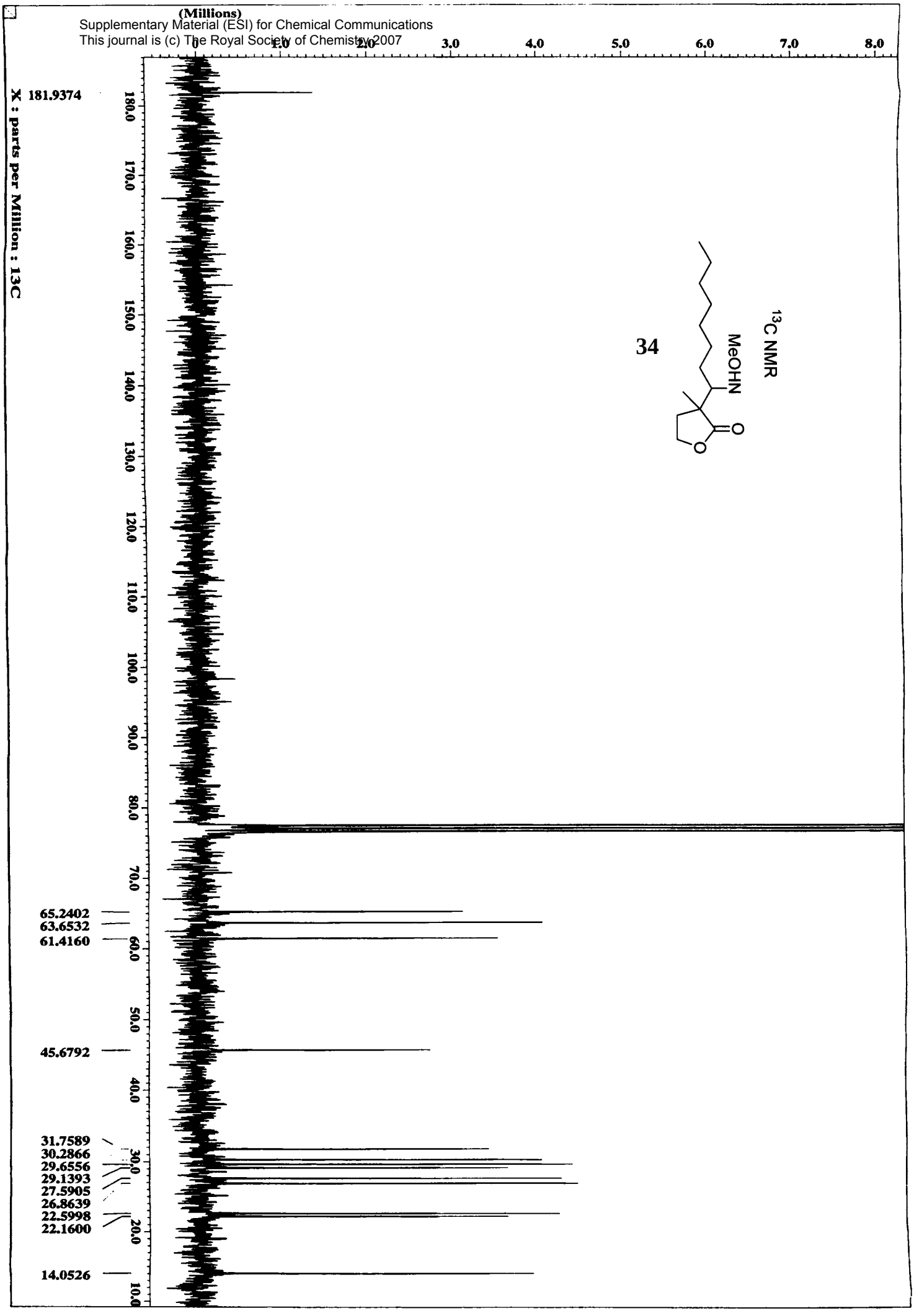

(Millions)
X : parts per Million : 1H
7.2747
7.2117
7.0057
6.9531
5.8588
5.8480
5.8371
4.6868
4.6759
4.6651
3.7116
3.4644
1.2577
1.1066
2.463
1.944
0.952
1
2.96
2.991
6.54
6.54
30
S
NHOMe
CO2Me
1H NMR

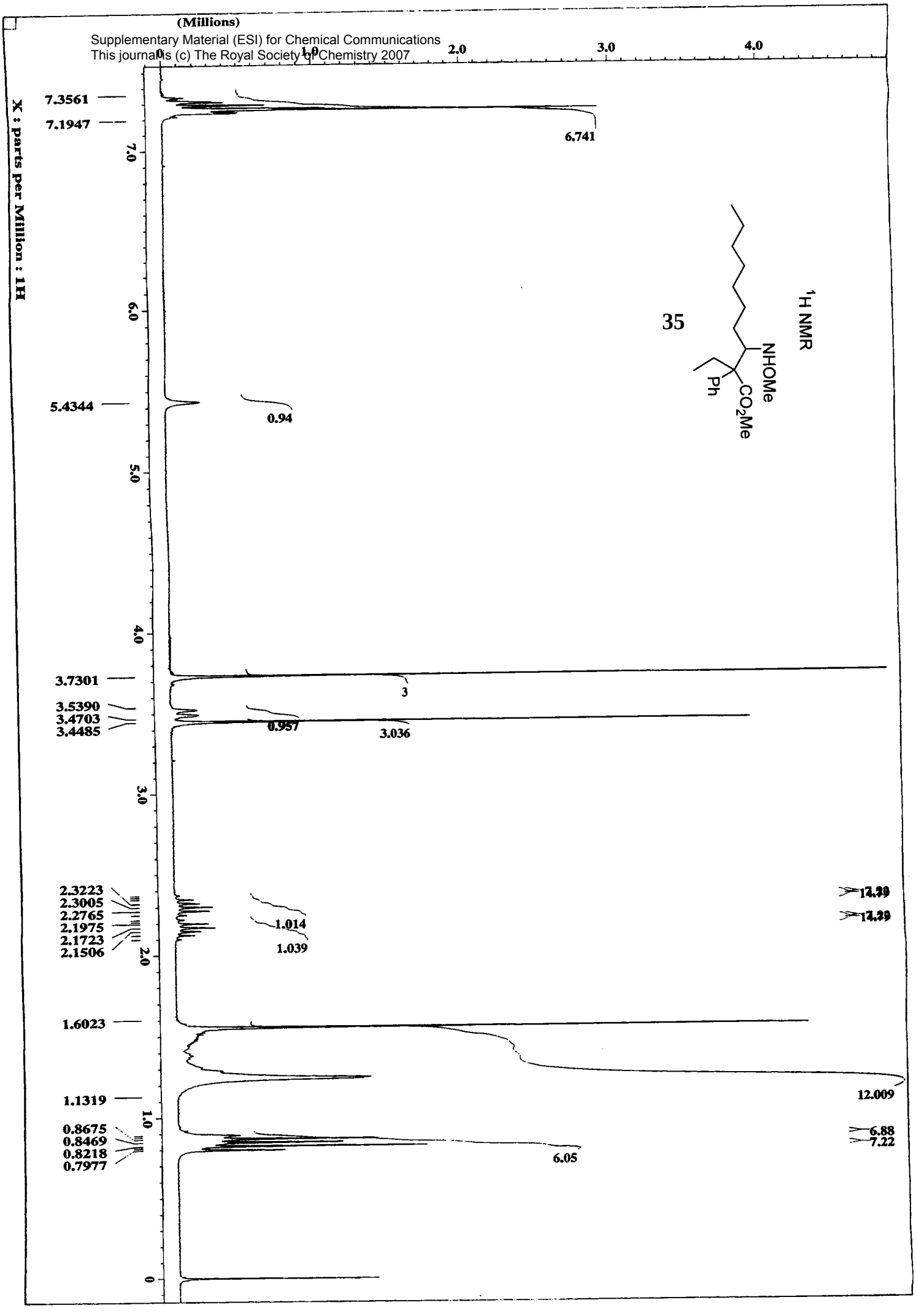

(Millions)
X : parts per Million : 13C
177.1954
140.7312
126.8682
126.2755
124.7458
66.5215
61.7794
51.8937
45.5263
24.6077
19.4449
30
NHOMe
CO2Me
13C NMR

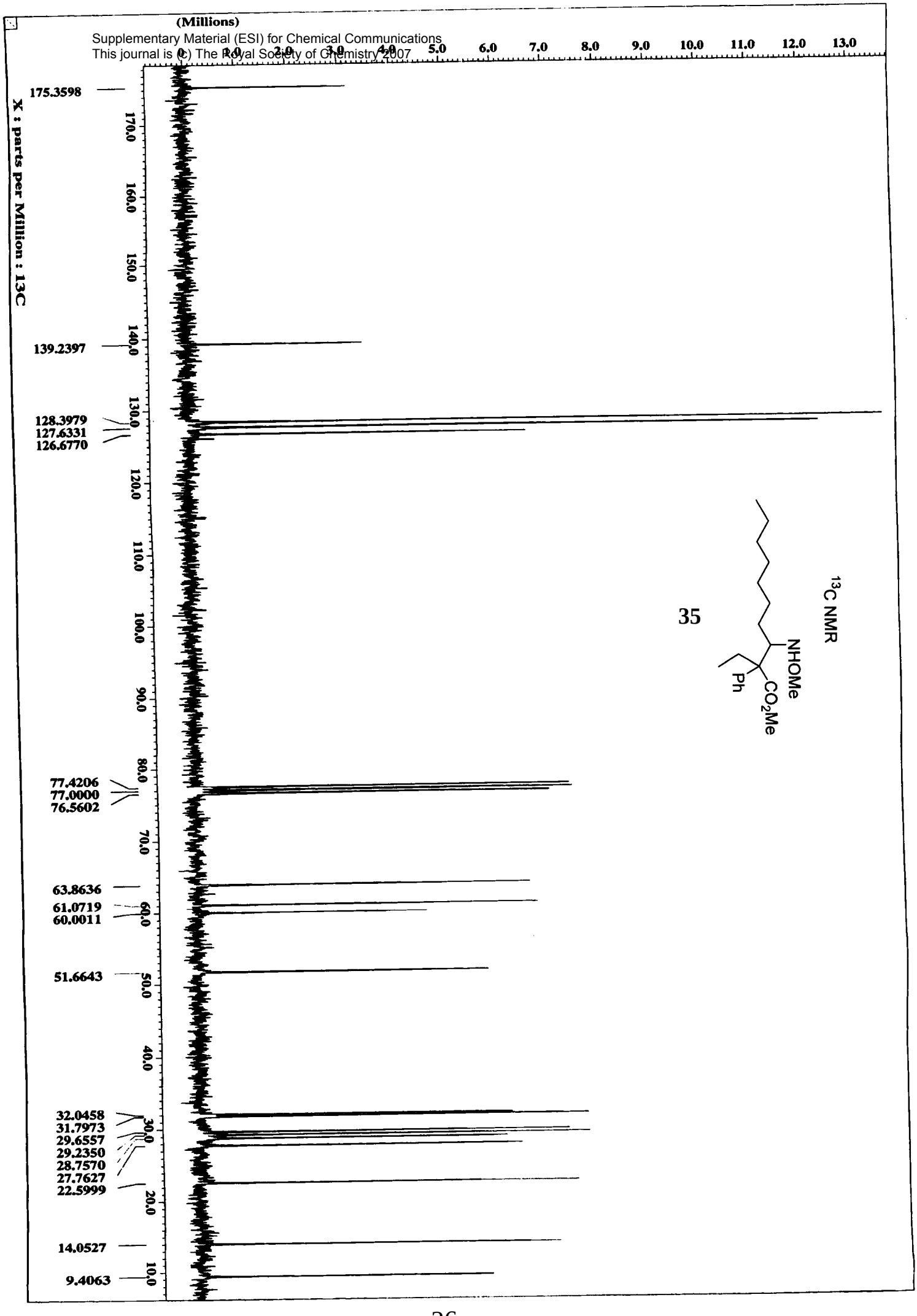

(Millions)
X : parts per Million : 1H
31
^{1}H NMR
NHOMe
CO_2Me
5.6836
3.6714
3.4265
2.8107
2.7775
2.7707
2.1457
2.0267
1.7051
1.0389
0.9027
0.8913
0.8798
0.8569
0.872
2.991
3.018
0.995
1.942
2.959
19.996
6.88

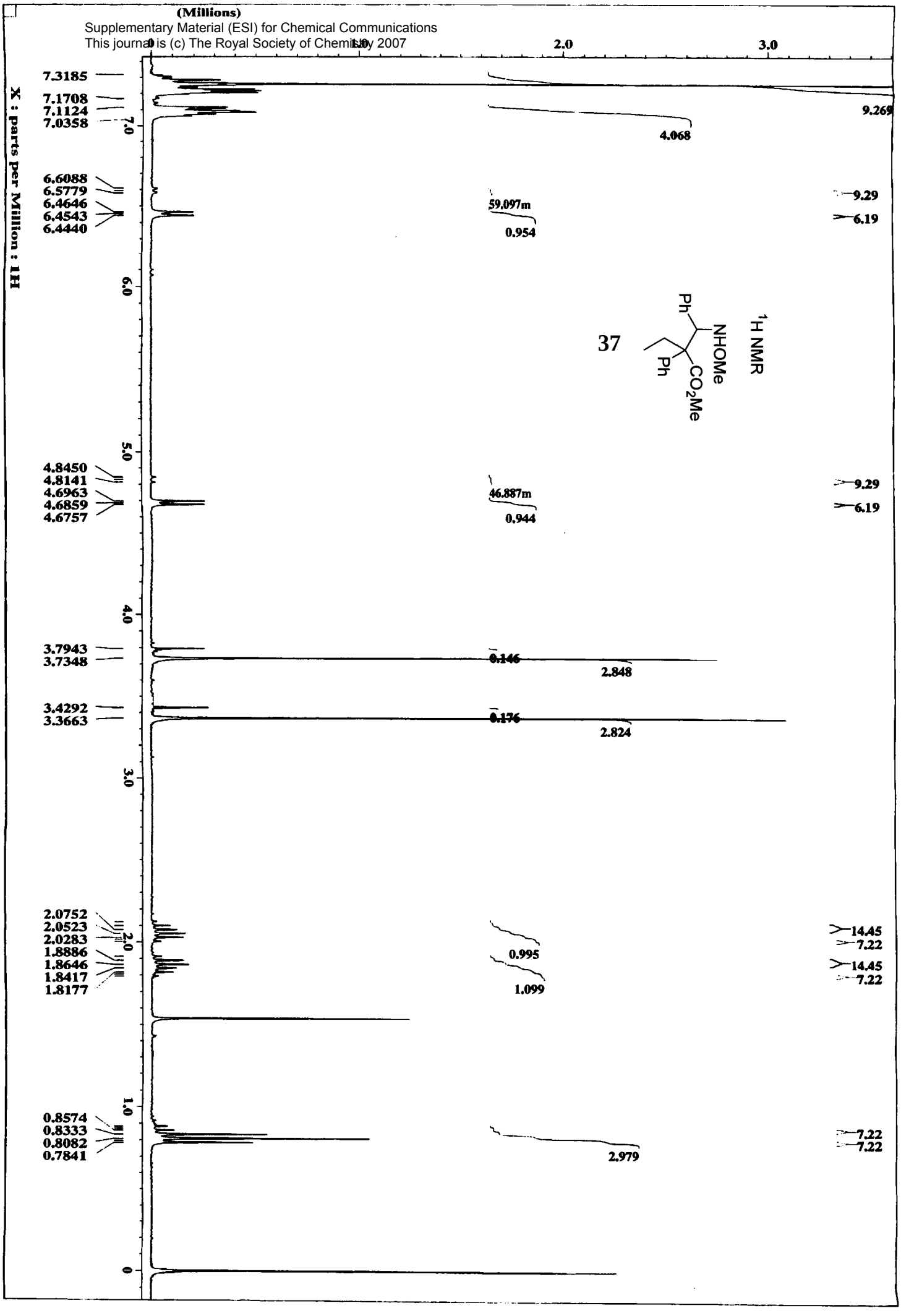

(Millions)
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
X : parts per Million : 13C
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
176.2201
67.8407
61.2248
51.3582
51.1479
31.8163
31.7015
30.4587
29.6364
29.2349
28.2215
27.7243
25.8695
23.4029
23.1926
22.6189
14.0717
31
NHOMe
CO2Me
13C NMR

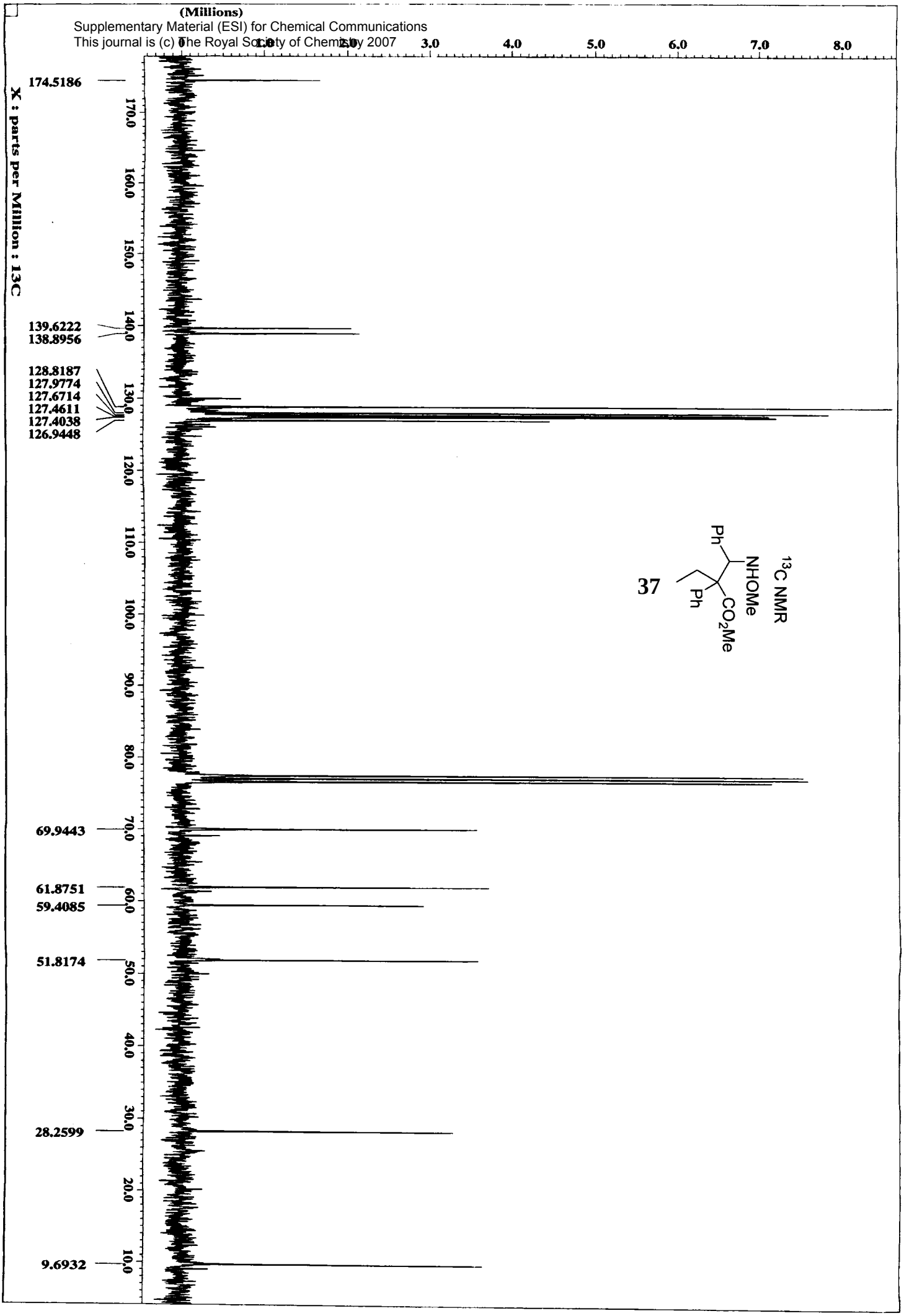

(Millions)
X : parts per Million : 1H
5.5943
4.3456
4.3330
4.3158
4.1945
3.4809
3.4402
3.1518
3.1209
3.1140
2.5944
2.5807
2.5566
2.5509
1.8596
1.8493
1.8333
1.8321
1.5975
1.4235
1.3983
1.2289
1.1774
0.9096
0.8867
0.8638
0.849
2.042
1
1.021
1.005
3.0
15.12
6.88
13.07
34
MeOHN
1H NMR

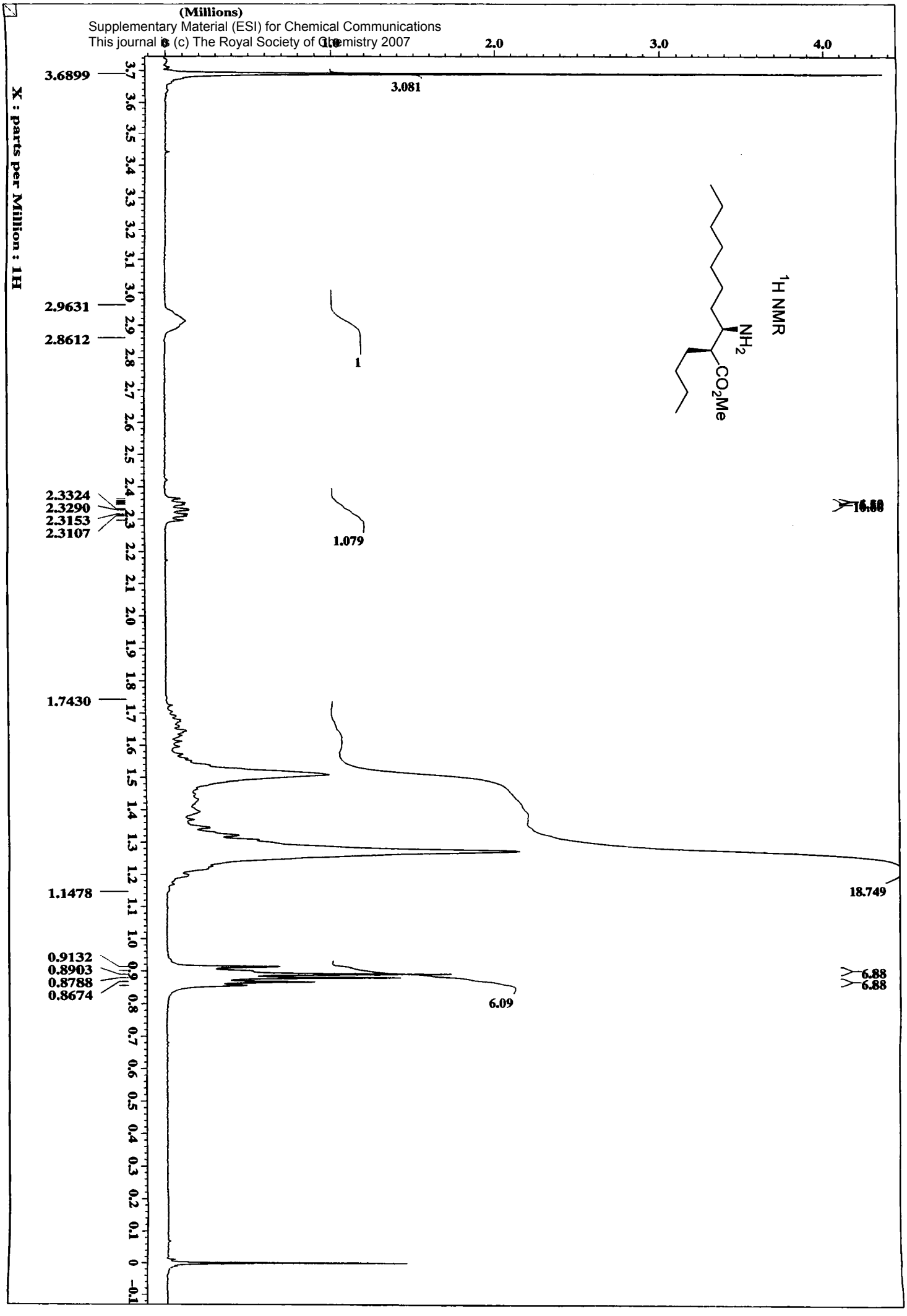

(Millions)
X : parts per Million : 13C
181.9374
65.2402
63.6532
61.4160
45.6792
31.7589
30.2866
29.6556
29.1393
27.5905
26.8639
22.5998
22.1600
14.0526
34
MeOHN
O
O
13C NMR


(Millions)
X : parts per Million : 1H
7.3561
7.1947
6.741
5.4344
0.94
3.7301
3.5390
3.4703
3.4485
3
0.957
3.036
2.3223
2.3005
2.2765
2.1975
2.1723
2.1506
1.014
1.039
1.6023
1.1319
12.009
0.8675
0.8469
0.8218
0.7977
6.05
6.88
7.22
35
NHOMe
Ph
CO2Me
1H NMR


(Millions)
X : parts per Million : 13C
175.3598
139.2397
128.3979
127.6331
126.6770
77.4206
77.0000
76.5602
63.8636
61.0719
60.0011
51.6643
32.0458
31.7973
29.6557
29.2350
28.7570
27.7627
22.5999
14.0527
9.4063
35
NHOMe
Ph
CO2Me
13C NMR


(Millions)
X : parts per Million : 1H
7.3185
7.1708
7.1124
7.0358
6.6088
6.5779
6.4646
6.4543
6.4440
4.8450
4.8141
4.6963
4.6859
4.6757
3.7943
3.7348
3.4292
3.3663
2.0752
2.0523
2.0283
1.8886
1.8646
1.8417
1.8177
0.8574
0.8333
0.8082
0.7841
4.068
59.097m
0.954
46.887m
0.944
0.146
2.848
0.176
2.824
0.995
1.099
2.979
9.269
9.29
6.19
9.29
6.19
14.45
7.22
14.45
7.22
7.22
7.22
37
Ph
NHOMe
Ph
CO2Me
1H NMR




(Millions)
X : parts per Million : 1H
3.6899
2.9631
2.8612
2.3324
2.3290
2.3153
2.3107
1.7430
1.1478
0.9132
0.8903
0.8788
0.8674
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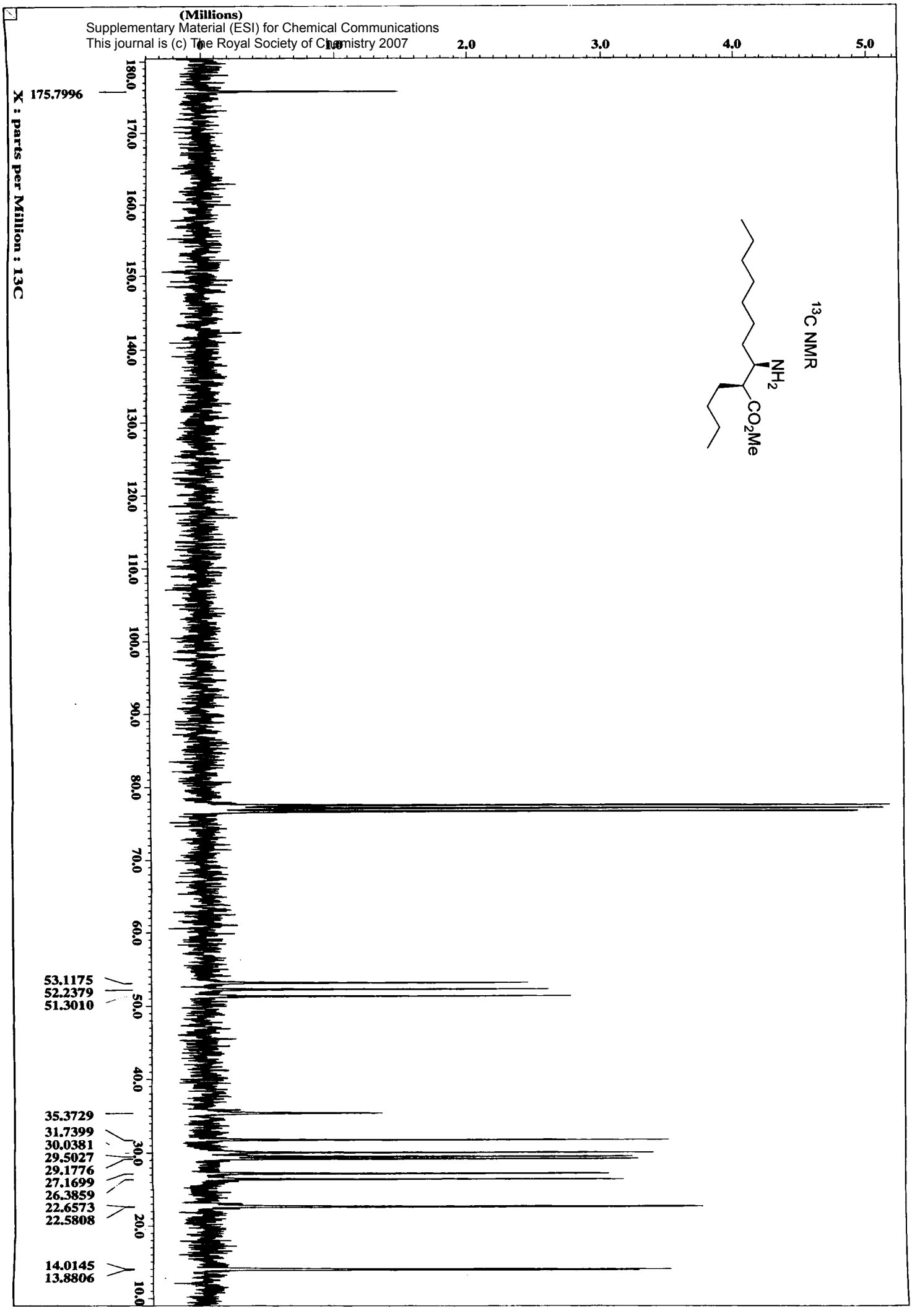
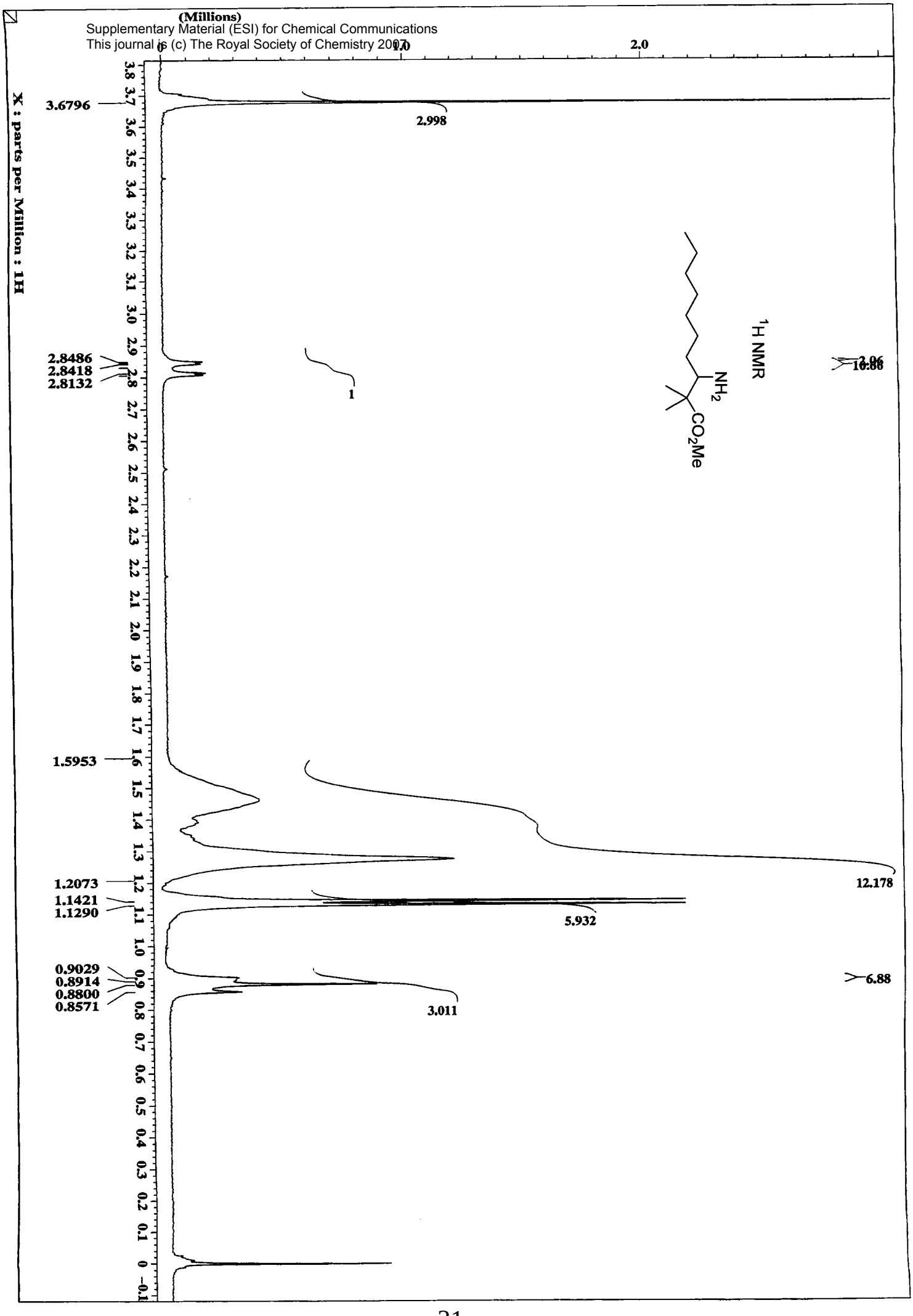
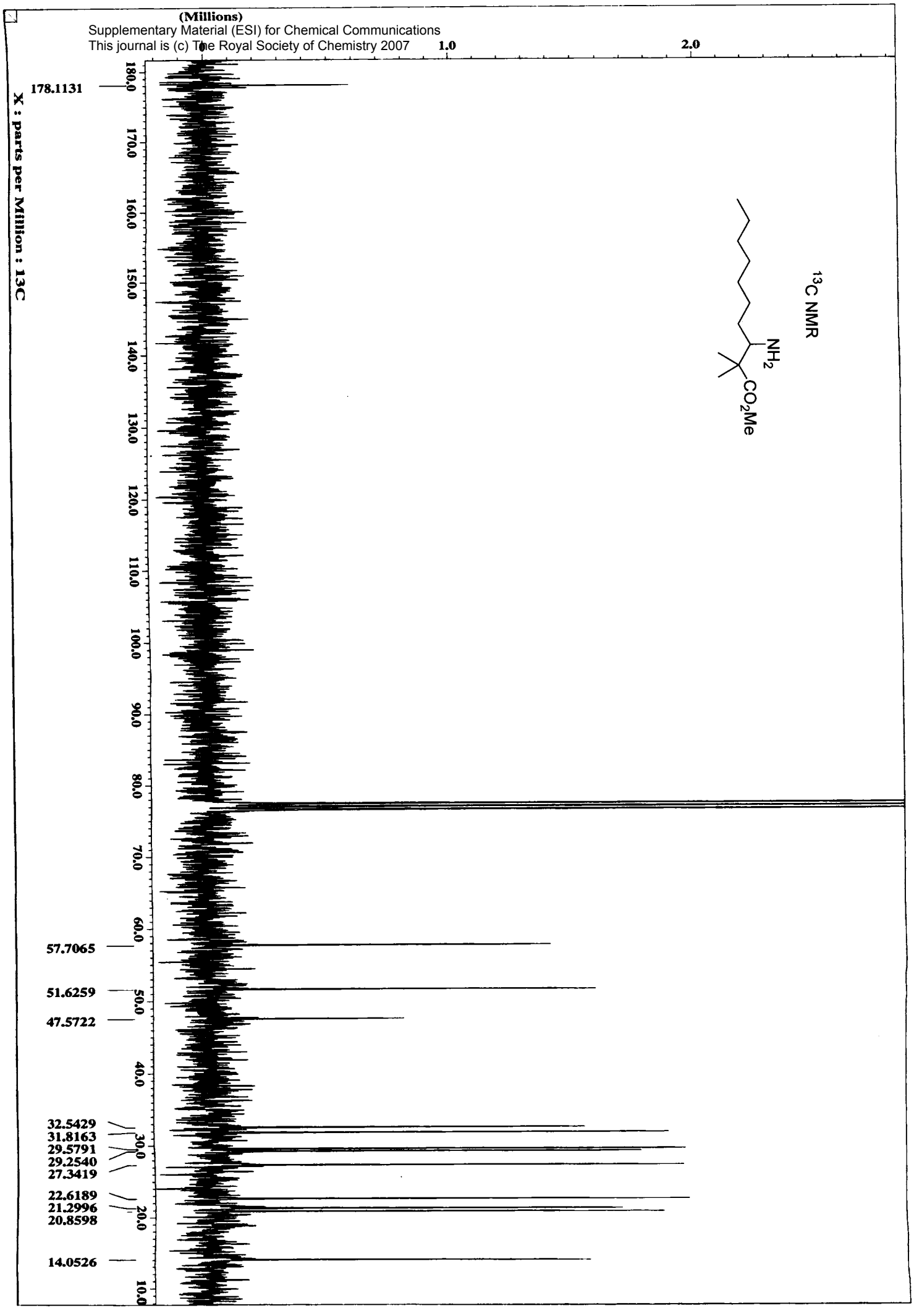
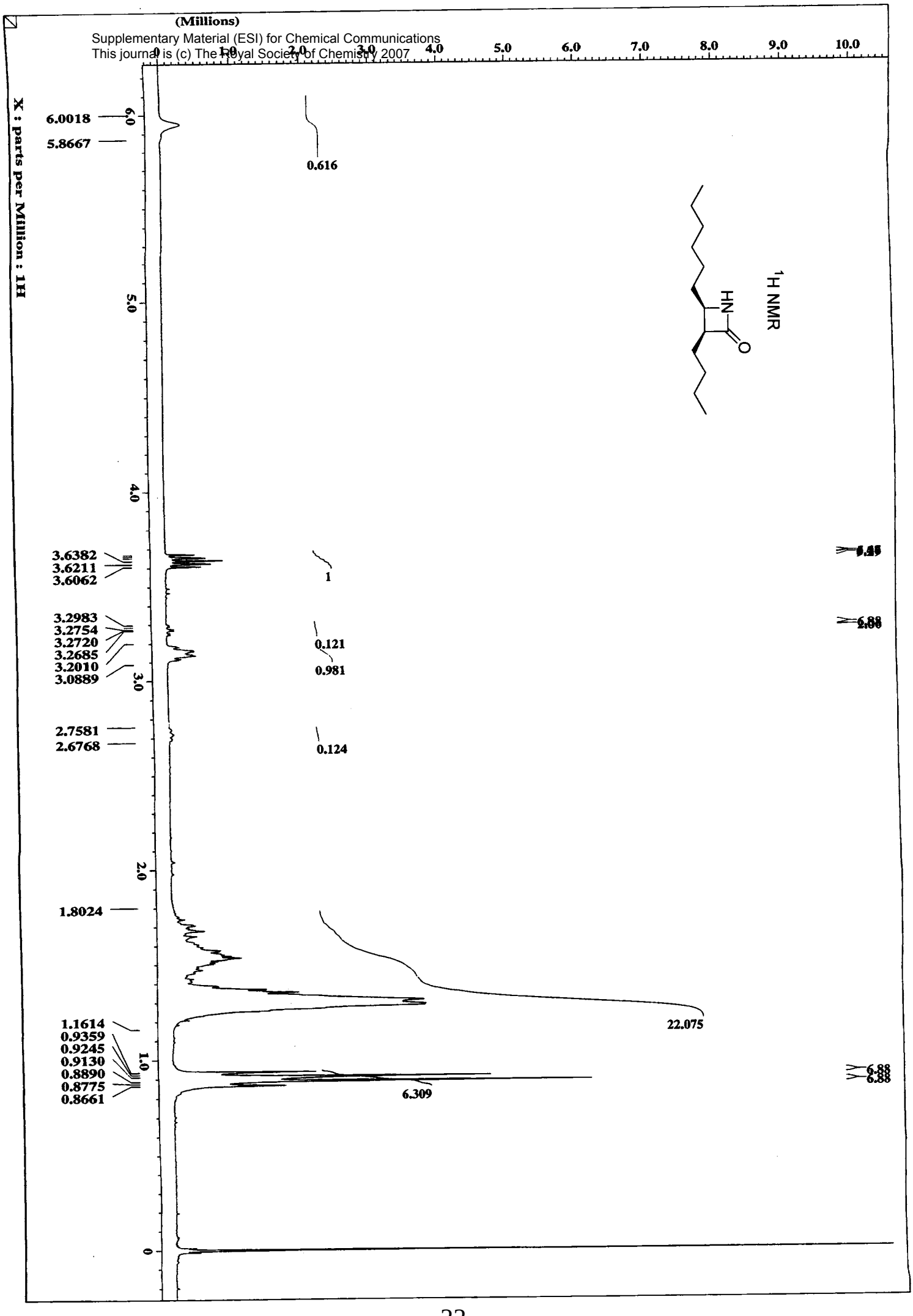
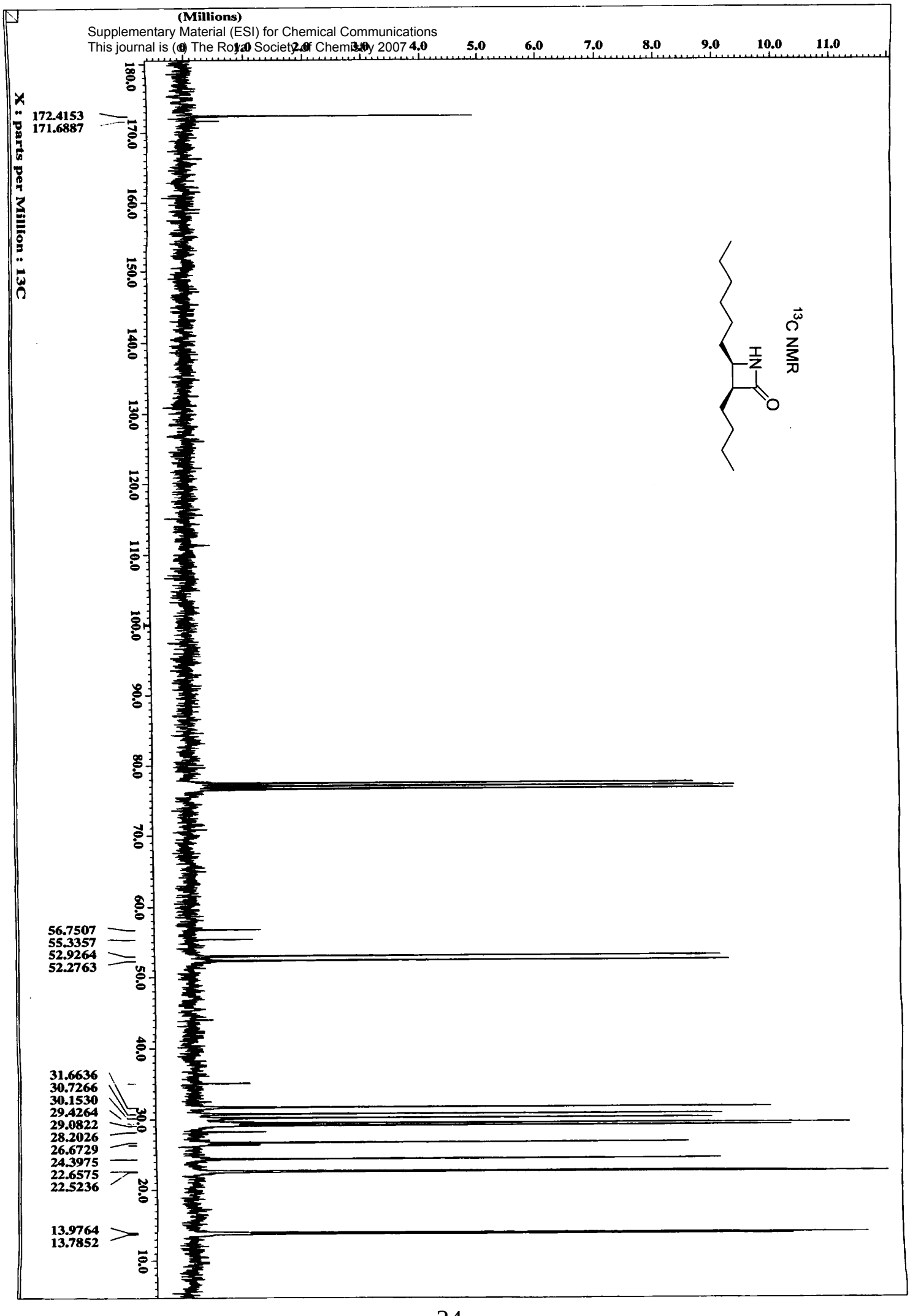
1
1.079
6.09
18.749
6.88
6.88
^{1}H NMR
NH$_2$
CO$_2$Me

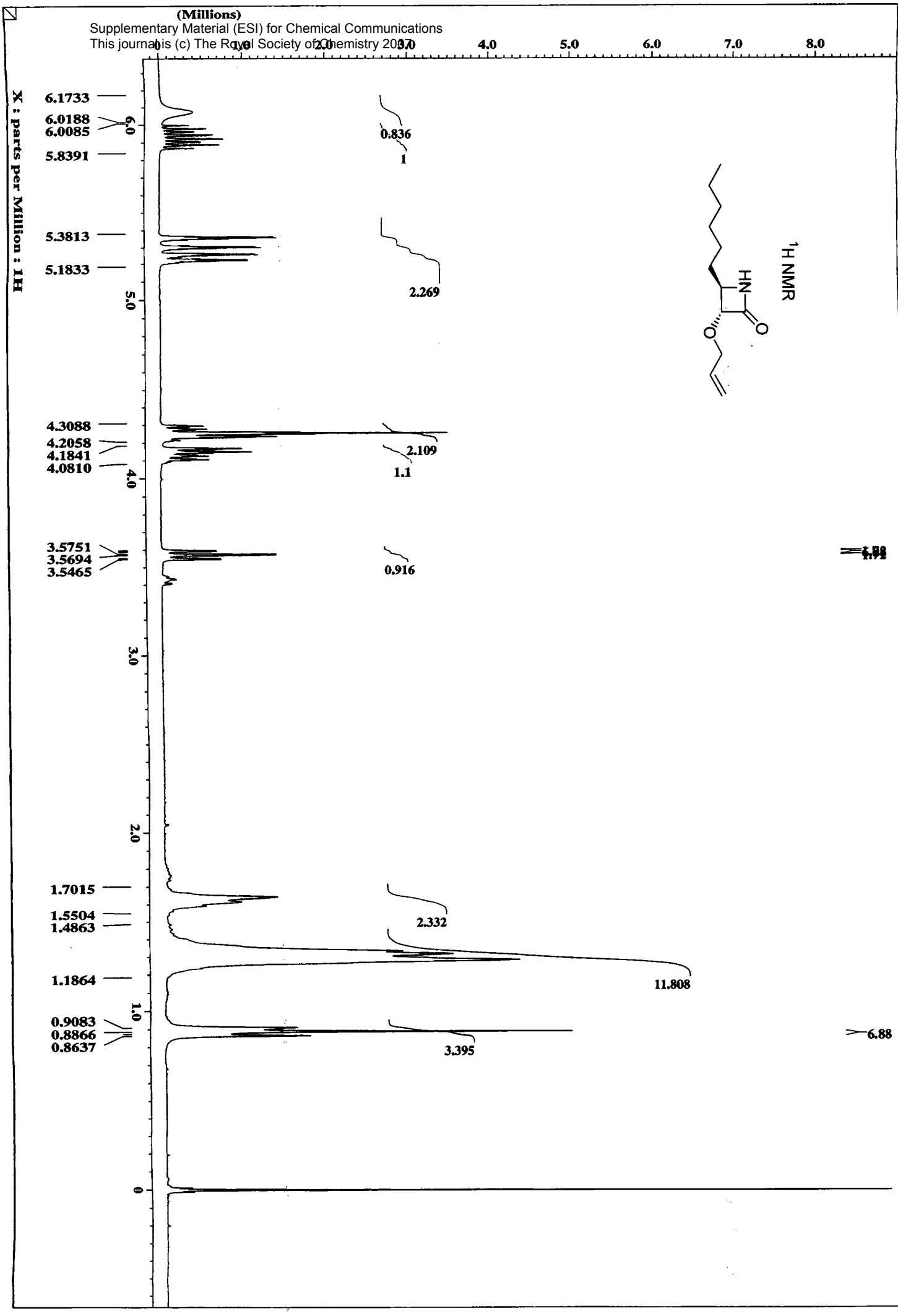

(Millions)
1.0
2.0
3.0
4.0
5.0
X : parts per Million : 13C
175.7996
53.1175
52.2379
51.3010
35.3729
31.7399
30.0381
29.5027
29.1776
27.1699
26.3859
22.6573
22.5808
14.0145
13.8806
^{13}C NMR
NH2
CO2Me

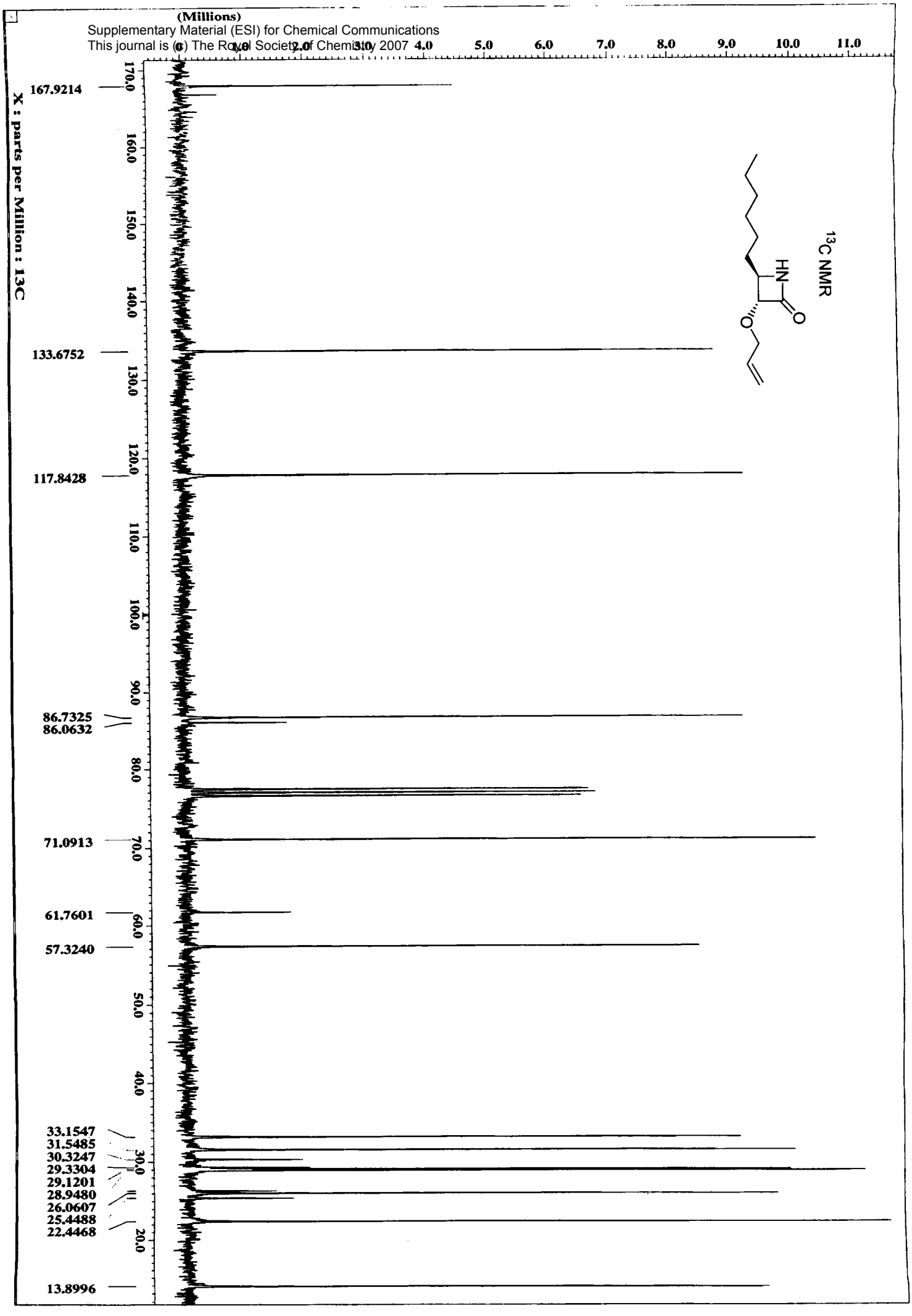

(Millions)
X : parts per Million : 1H
3.6796
2.998
2.8486
2.8418
2.8132
1
1.5953
1.2073
1.1421
1.1290
0.9029
0.8914
0.8800
0.8571
3.011
5.932
12.178
6.88
^{1}H NMR
NH$_2$
CO$_2$Me


(Millions)
1.0
2.0
X : parts per Million : 13C
178.1131
57.7065
51.6259
47.5722
32.5429
31.8163
29.5791
29.2540
27.3419
22.6189
21.2996
20.8598
14.0526
^{13}C NMR
NH2
CO2Me






(Millions)
X : parts per Million : 1H
6.1733
6.0188
6.0085
5.8391
5.3813
5.1833
4.3088
4.2058
4.1841
4.0810
3.5751
3.5694
3.5465
1.7015
1.5504
1.4863
1.1864
0.9083
0.8866
0.8637
0.836
1
2.269
2.109
1.1
0.916
2.332
11.808
3.395
6.88
HN
O
O
1H NMR


(Millions)
X : parts per Million : 13C
167.9214
133.6752
117.8428
86.7325
86.0632
71.0913
61.7601
57.3240
33.1547
31.5485
30.3247
29.3304
29.1201
28.9480
26.0607
25.4488
22.4468
13.8996
^{13}C NMR