Synthesis of 3-hydroxy-1-alkenylboronates via phosphine stabilized borylzirconacyclopropenes

Abed Al Aziz Al Quntar,[a] Alina Botvinik,[a] Abraham Rubinstein[b] and Morris Srebnik[a*]

[a]Department of Medicinal Chemistry and Natural Product, [b]Department of Pharmaceutics, School of Pharmacy, Hebrew University, Jerusalem 91120 Israel

morris.srebnik@ekmd.huji.ac.il

Supplementary information

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Typical Procedure for the Synthesis of 4a. To 0.306 g (1.05 mmol) of zirconocene dichloride dissolved in 7 mL of dry THF at -78 ^{o}C was added 1.05 mL of 2 M *n*-BuLi (2.1 mmol) dropwise in a 25 mL round-bottom flask. After stirring at -78 ^{o}C for 2 h, 0.212 g (1.05 mmol) of tributylphosphine was added to the reaction, then, and it was allowed warm to room temperature. After stirring at room temperature for 2 h, it was again cooled to -78 ^{o}C and 0.208 g (1 mmol) of 2-(hex-1-ynyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added and the reaction was warmed gradually to room temperature and stirred overnight. Again, the reaction was cooled to -78 ^{o}C and 2 mmol of acetone was added after which the mixture was stirred for 12 h at room temperature. The reaction was worked up with HCl/ether and the product was separated on silica gel column (80% petroleum ether/20% diethylether), and analyzed by GCMS, elemental analysis, and NMR spectroscopy.

4a: (E)-2-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)heptan-2-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.90 (t, 3 H, J_{HH} = 6.9 Hz,), 1.26 (s, 12 H), 1.33 (s, 6H), 1.20-1.45 (overlap, 4 H), 2.38 (broad t, 2 H, J_{HH} = 7.5 Hz), 5.45 (s, 1 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 13.8, 23.6, 24.7, 28.8, 29.1, 35.3, 74.7, 82.6, 109.8 (broad), 130.0, 172.2; ^{11}B NMR (96.24 MHz): δ = 28.05; MS (EI): *m/z* (%) 268 (0.7), 253 (3.7), 235 (0.4), 211 (8.2), 185 (7.8), 153 (17.4), 129 (5.2), 11 (100), 101 (21.8), 84 (40.6), 82 (41.5), 59 (25.3); Anal. Calcd. for $C_{15}H_{29}BO_3$: C, 67.17; H, 10.90; B, 4.03. Found: C, 67.05; H, 10.81; B, 3.83.

4b: (E)-1-cyclopropyl-1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)hexan-1-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.25-0.45 (overlap, 4 H), 0.70 (t, 3 H, J_{HH} = 6.6 Hz), 0.84 (m, 1 H), 1.20 (s, 12 H), 1.17-1.42 (overlap, 4 H), 2.10 (m, 2 H), 5.74 (s, 1 H), 7.07-7.41 (overlap, 5 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 2.1, 3.1, 14.0, 19.7, 23.7, 24.8, 32.1, 35.2, 79.3, 82.8, 113.5 (broad), 126.6, 126.8, 127.8, 144.5, 169.4; ^{11}B NMR (96.24 MHz): δ = 27.46; MS (EI): *m/z* (%) 356 (0.1), 341 (0.4), 299 (2.7), 281 (0.13), 269 (1.7), 228 (1.1), 210 (2.4), 199 (4.6), 169 (2.6), 147 (100), 129 (5.4), 105 (38.7), 91 (6.9), 84 (6.8), 77 (9.0), 69 (8.0), 55 (6.5); Anal. Calcd. for $C_{22}H_{33}BO_3$: C, 74.16; H, 9.34; B, 3.03. Found: C, 74.04; H, 9.39; B, 3.10.

4c: (E)-1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-1-en-2-yl)-1,2,3,4-tetrahydronaphthalen-1-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.85 (t, 3 H, J_{HH} = 7.2 Hz), 1.28 (s, 12 H), 1.22-1.67 (overlap, 8 H), 1.85-2.10 (overlap, 4H), 2.82 (m, 2H), 5.55 (s, 1 H), 7.06-7.24 (overlap, 4 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 13.8, 19.3, 23.5, 24.9, 30.0, 32.2, 35.3, 36.3, 77.8, 82.7, 112.4 (broad), 126.4, 127.3, 128.6, 128.9, 137.6, 140.5, 170.6; ^{11}B NMR (96.24 MHz): δ = 27.71; MS (EI): *m/z* (%) 356 (1.7), 338 (18.9), 323 (1.8), 295 (13.8), 282 (14.6), 268 (14.0), 210 (16.0), 181 (100), 167 (33.4), 153 (42.0), 141 (5.9), 129 (28.6), 127 (34.9), 115 (3.8), 101 (51.6), 84 (67.3), 55 (23.6); Anal. Calcd. for $C_{22}H_{33}BO_3$: C, 74.16; H, 9.34; B, 3.03. Found: C, 73.98; H, 9.39; B, 3.16.

4d: (E)-2-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)octan-2-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.89 (t, 3 H, J_{HH} = 6.9 Hz,), 1.27 (s, 12 H), 1.34 (s, 6 H), 1.18-1.38 (overlap, 6 H), 2.37 (broad t, 2 H, J_{HH} = 7.4 Hz), 5.46 (s, 1 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 14.0, 22.5, 24.8, 29.5, 30.0, 32.9, 68.0, 82.8, 109.7 (broad), 172.2; ^{11}B NMR (96.24 MHz): δ = 28.00; MS (EI): *m/z* (%) 282 (1.5), 267 (3.2), 264 (12.1), 252 (4.3), 208 (30.4), 135 (67.5), 108 (83.1), 84 (100), 67 (70.0), 55 (75.5); Anal. Calcd. for $C_{16}H_{31}BO_3$: C, 68.09; H, 11.07; B, 3.83. Found: C, 68.22; H, 11.01; B, 3.74.

4e: (E)-1-cyclopropyl-1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)heptan-1-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.35-0.52 (overlap, 4 H), 0.79 (t, 3 H, J_{HH} = 6.9 Hz), 0.86 (m, 1 H), 1.28 (s, 12 H), 1.20-1.47 (overlap, 6 H), 2.17 (m, 2 H), 5.81 (s, 1 H), 7.22-7.48 (overlap, 5 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 1.3, 2.1, 14.0, 19.5, 22.3, 24.8, 32.4, 32.6, 32.7, 79.3, 82.8, 112.8 (broad), 126.6, 126.9, 127.6, 144.5, 169.4; ^{11}B NMR (96.24 MHz): δ = 28.07; MS (EI): *m/z* (%) 370 (0.7), 355 (0.4), 329 (0.8), 299 (3.1), 283 (1.5), 243 (0.9), 199 (5.1), 147 (100), 129 (4.7), 127 (1.8), 105 (34.8), 84 (8.8), 69 (9.6), 55 (9.0); Anal. Calcd. for $C_{23}H_{35}BO_3$: C, 74.59; H, 9.53; B, 2.92. Found: C, 74.73; H, 9.45; B, 3.02.

4f: (E)-1-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-1-en-2-yl)cycloheptanol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.89 (t, 3 H, J_{HH} = 6.9 Hz,), 1.27 (s, 12 H), 1.30-1.90 (overlap, 18 H), 2.38 (broad t, 2 H, J_{HH} = 7.4 Hz), 5.41 (s, 1 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 14.2, 22.6, 24.8, 29.1, 31.6, 32.7, 33.3, 40.4, 79.3, 82.7, 109.8 (broad(, 173.5; ^{11}B NMR (96.24 MHz): δ = 28.09; MS (EI): *m/z* (%) 336 (7.0), 321 (3.6), 277 (42.2), 253 (16.4), 236 (25.4), 207 (75.4),

174 (48.8), 165 (96.7), 135 (27.8), 123 (59.3), 101 (78.0), 84 (100), 83 (8.0), 55 (95.0); Anal. Calcd. for $C_{20}H_{37}BO_3$: C, 71.42; H, 11.09; B, 3.21. Found: C, 71.28; H, 11.13; B, 3.30.

4g: (E)-1-phenyl-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)heptan-1-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.84 (t, 3 H, J_{HH} = 6.9 Hz), 1.27 (s, 12 H), 1.20-1.37 (overlap, 6 H), 1.98 (broad s, 1H), 2.0 (m, 1H), 2.49 (m, 1 H), 5.16 (s, 1 H), 5.67 (s, 1H), 7.25-7.42 (overlap, 5 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 14.0, 22.3, 24.8, 30.3, 31.9, 32.0, 78.1, 82.8, 112.0 (broad), 127.1, 127.7, 128.4, 141.8, 166.6; ^{11}B NMR (96.24 MHz): δ = 28.99; MS (EI): *m/z* (%) 330 (1.6), 315 (3.5), 259 (8.7), 247 (36.4), 203 (26.7), 159 (100), 129 (43.8), 115 (8.6), 105 (16.4), 101 (37.3), 84 (96.2), 83 (32.0), 77 (20.0), 55 (23.7); Anal. Calcd. for $C_{20}H_{31}BO_3$: C, 72.73; H, 9.46; B, 3.27. Found: C, 72.80; H, 9.51; B, 3.13.

4h: (E)-1-(4-methoxyphenyl)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)heptan-1-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.84 (t, 3 H, J_{HH} = 6.9 Hz), 1.27 (s, 12 H), 1.18-1.39 (overlap, 6 H), 1.93 (broad s, 1H), 1.96 (m, 1H), 2.47 (m, 1 H), 3.79 (s, 3H), 5.11 (s, 1 H), 5.67 (s, 1H), 6.85 (d, J_{HH} = 8.7 Hz), 7.25 (d, J_{HH} = 8.7 Hz); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 14.0, 22.3, 24.8, 30.3, 31.9, 32.0, 55.1, 77.4, 82.8, 11.2 (broad), 113.7, 128.4, 134.1, 166.9; ^{11}B NMR (96.24 MHz): δ = 28.05; MS (EI): *m/z* (%) 360 (3.1), 342 (23.6), 285 (13.0), 207 (86.6), 199 (51.8), 141 (50.1), 127 (16.3), 105 (8.4), 101 (81.8), 84 (33.4), 83 (100), 77 (19.3), 55 (34.4); Anal. Calcd. for $C_{21}H_{33}BO_4$: C, 70.00; H, 9.23; B, 3.00. Found: C, 69.87; H, 9.19; B, 3.17.

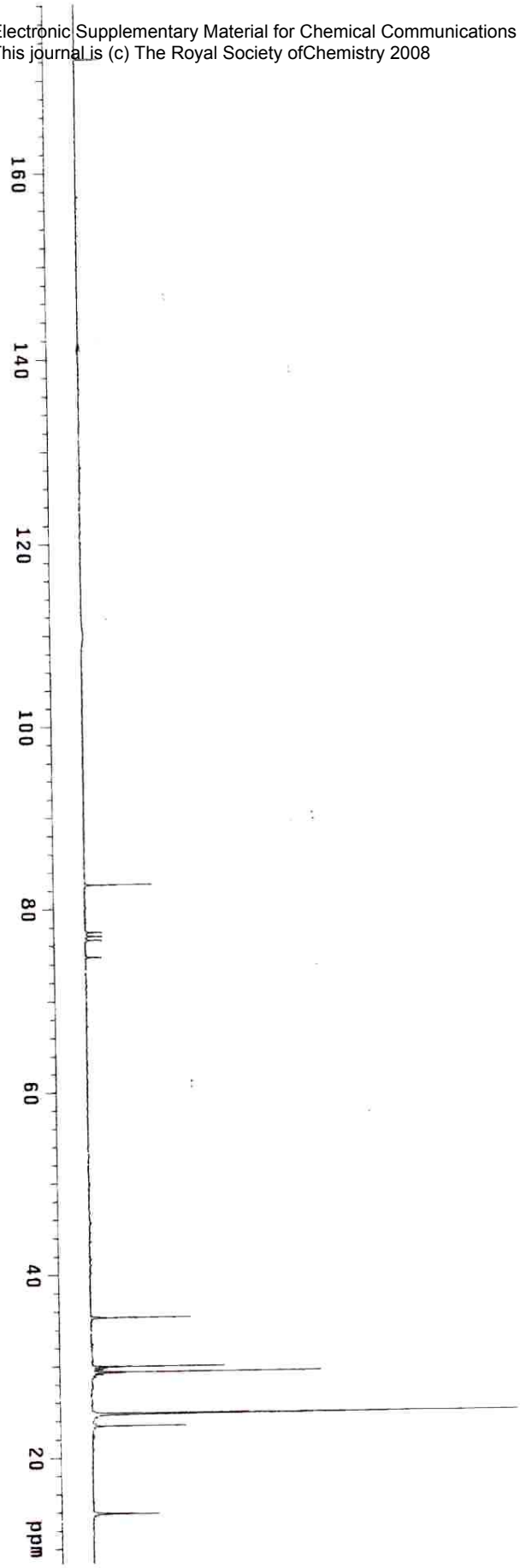
4i: (E)-2-methyl-3-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol

^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 1.25 (s, 12 H), 1.47 (s, 6H), 7.02 (s, 1H), 7.18-7.35 (overlap, 5H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 24.8, 30.2, 74.1, 83.6, 127.2, 128.0, 128.1, 135.4, 139.0; ^{11}B NMR (96.24 MHz): δ = 27.97; MS (EI): *m/z* (%) 288 (3.1), 270 (4.5), 255 (13.0), 213 (5.8),

169 (14.6), 155 (16.6), 142 (67.1), 128 (26.8), 127 (7.3), 101 (32.0), 84 (100), 69 (25.2), 55 (9.3); Anal. Calcd. for $C_{17}H_{25}BO_3$: C, 70.85; H, 8.74; B, 3.75. Found: C, 71.01; H, 8.68; B, 3.66.

6: ^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.94 (t, 3 H, J_{HH} = 6.8 Hz,), 1.26 (s, 12 H), 1.20-1.45 (overlap, 6 H), 2.37 (broad t, 2 H, J_{HH} = 7.5 Hz), 5.45; ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 14.1, 22.5, 24.8, 30.1, 31.9, 82.7, 113.1 (broad), 164.5; ^{11}B NMR (96.24 MHz): δ = 28.03; MS (EI): *m/z* (%) 226 (6.0), 211 (22.3), 182 (12.3), 169 (18.7), 155 (30.2), 140 (36.0), 127 (25.8), 126 (57.6), 101 (99.2), 84 (93.7), 83 (100), 69 (67.3), 55 (50.2); Anal. Calcd. for $C_{13}H_{23}D_2BO_2$: C, 69.04; H, 12.03; B, 4.78. Found: C, 68.93; H, 11.93; B, 4.94.

7: ^{1}H NMR: ($CDCl_3$, 300 MHz) δ = 0.19-0.53 (overlap, 4 H), 0.78 (t, 3 H, J_{HH} = 6.6 Hz), 0.84 (m, 1 H), 1.20 (s, 12 H), 1.15-1.53 (overlap, 4 H), 2.18 (m, 2 H), 7.20-7.48 (overlap, 5 H); ^{13}C NMR: (CDCl3, 75.5 MHz) δ = 1.4, 2.1, 13.8, 19.6, 23.5, 24.9, 32.1, 35.3, 78.7, 82.8, 112.5 (broad), 126.6, 127.0, 127.8, 144.6, 169.5; ^{11}B NMR (96.24 MHz): δ = 28.00; MS (EI): *m/z* (%) 357 (0.5), 342 (0.3), 300 (1.7), 299 (1.6), 270 (1.1), 229 (1.1), 211 (2.1), 200 (3.1), 170 (2.5), 147 (100), 129 (5.7), 105 (39.3), 84 (9.4), 77 (8.9), 69 (11.6), 55 (9.3); Anal. Calcd. for $C_{22}H_{32}DBO_3$: C, 73.95; H, 9.59; B, 3.03. Found: C, 74.09; H, 9.65; B, 2.95.



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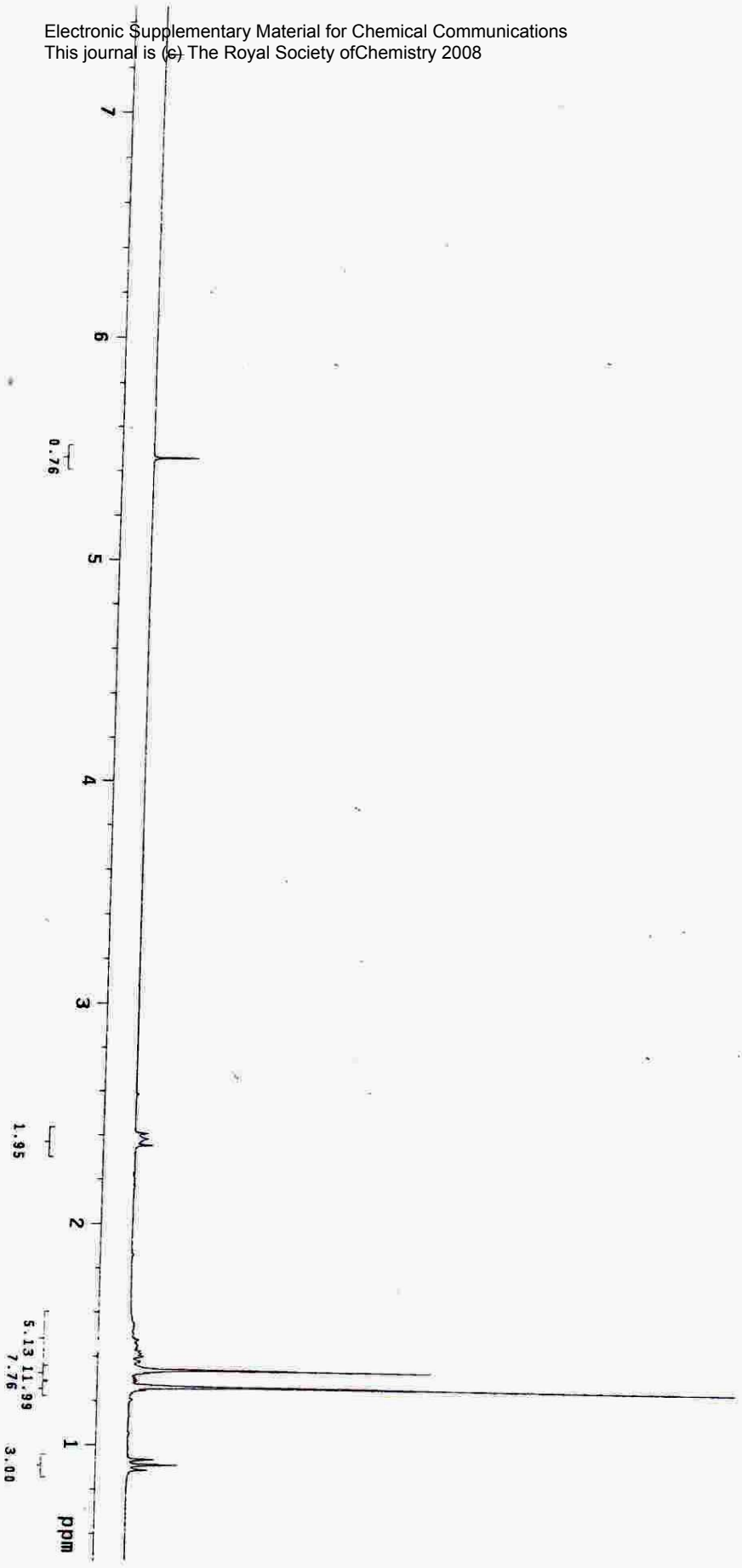

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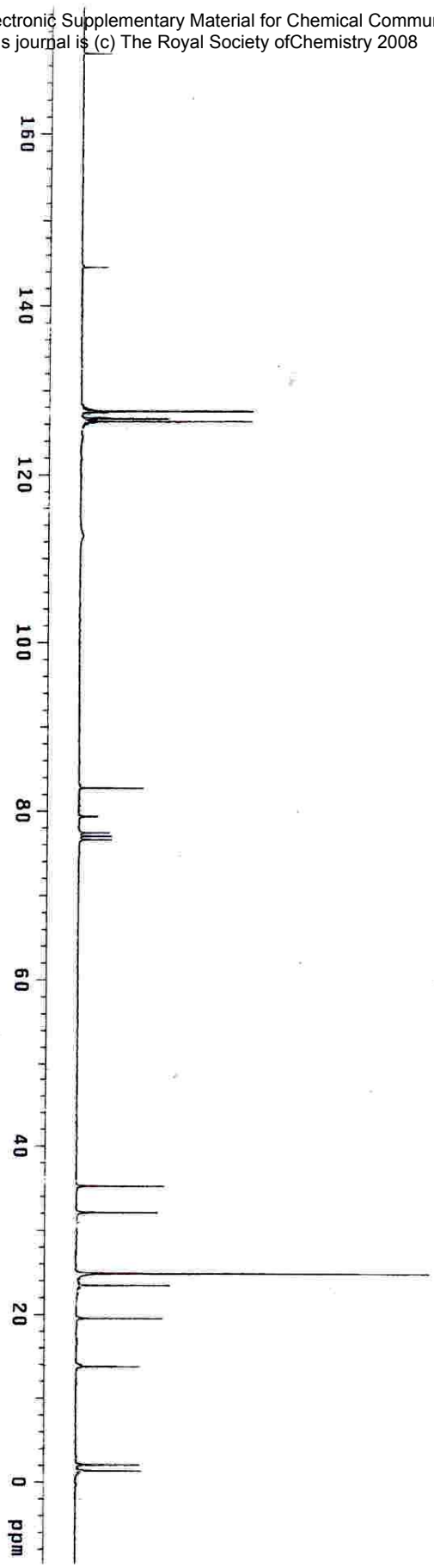

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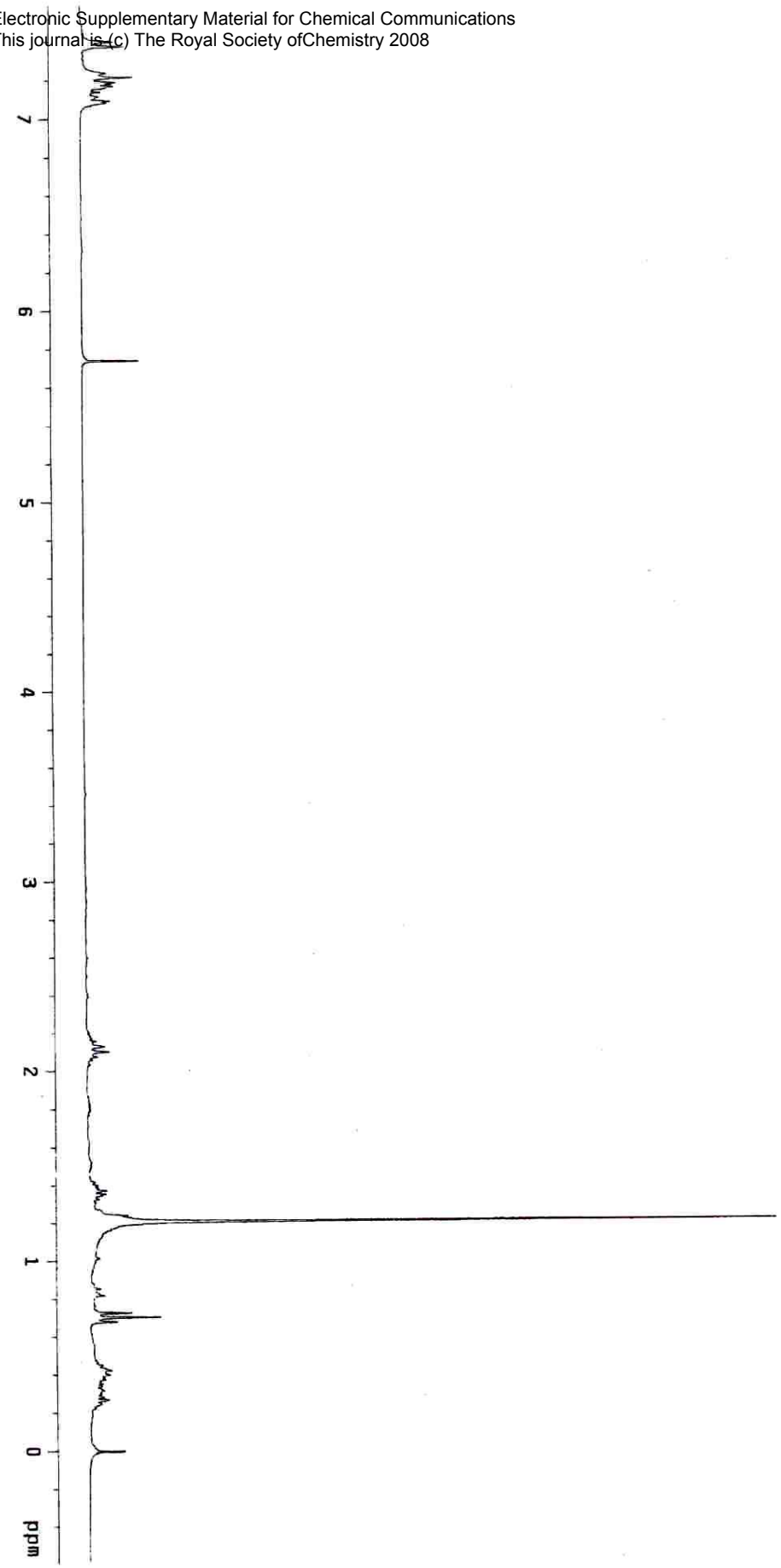

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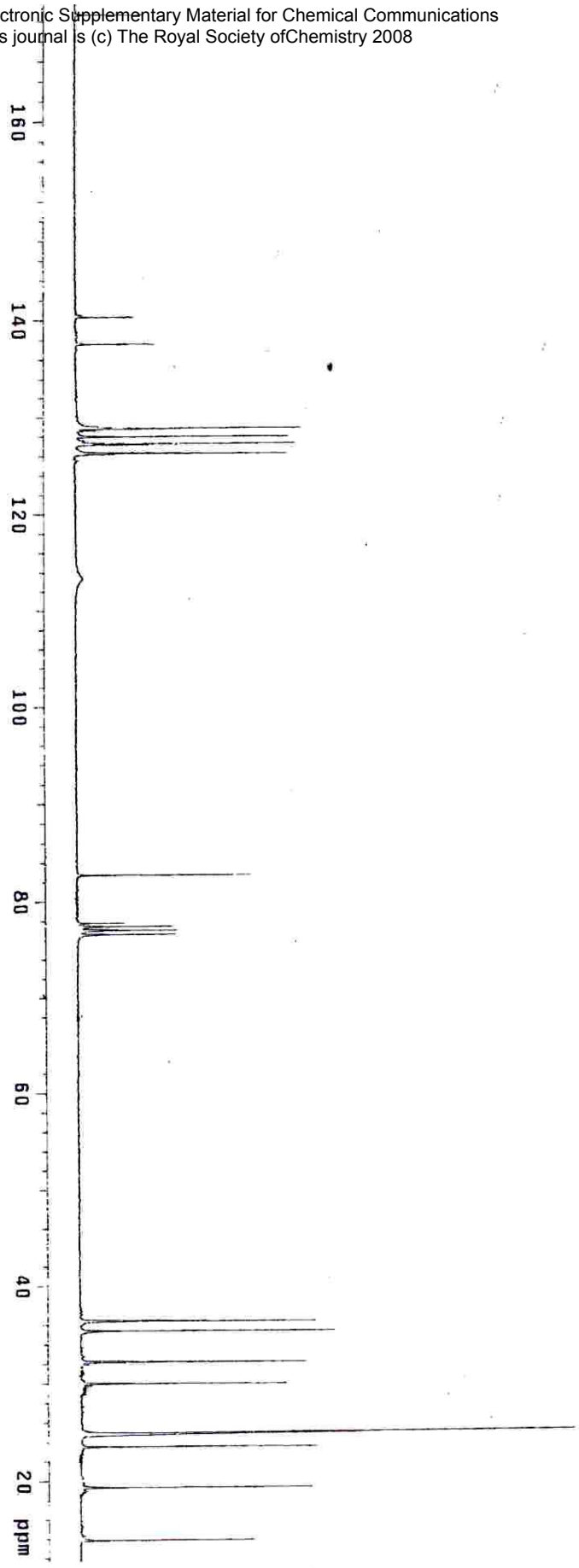

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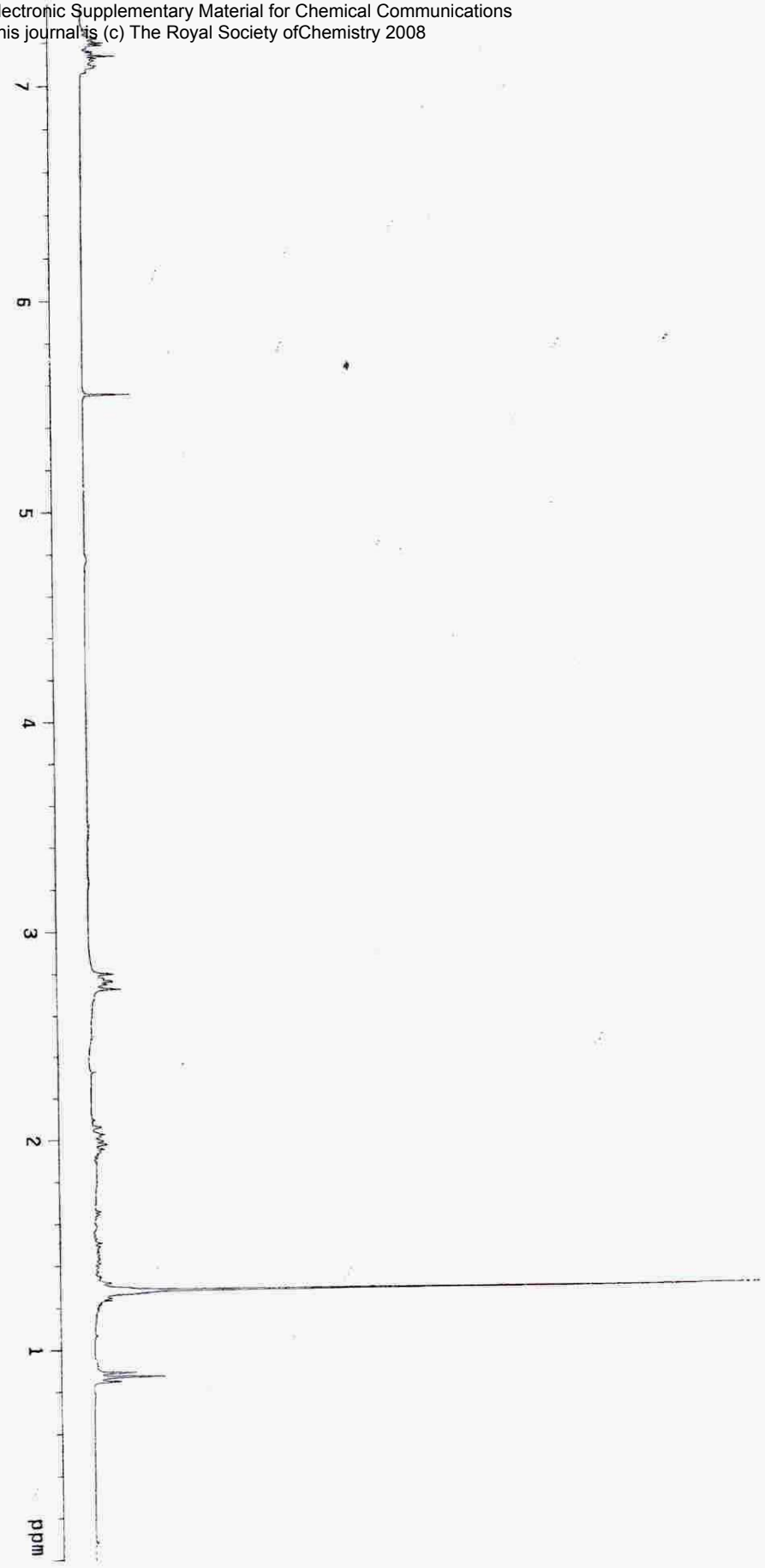

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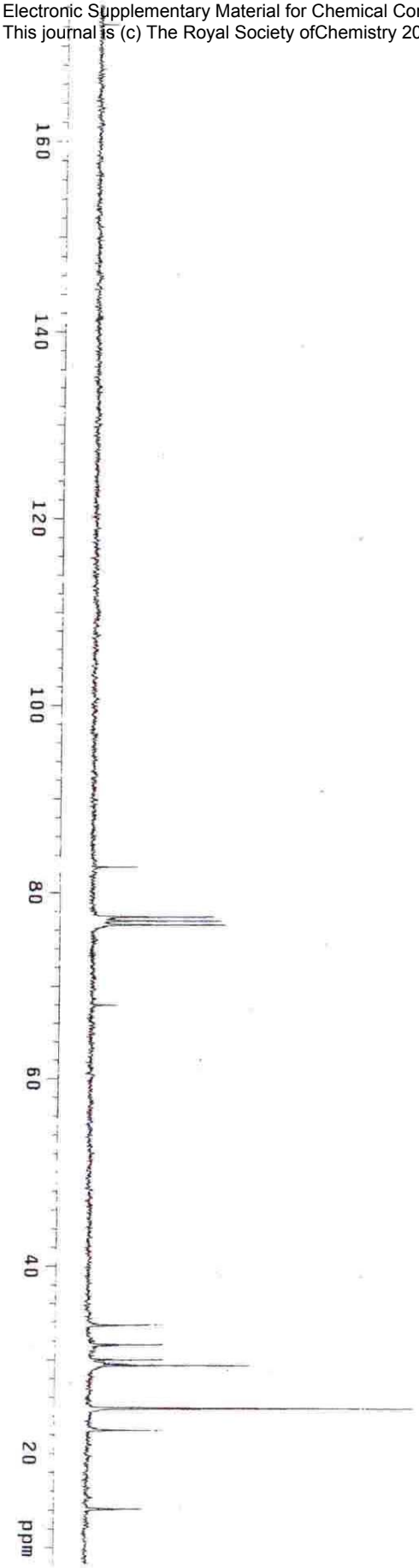

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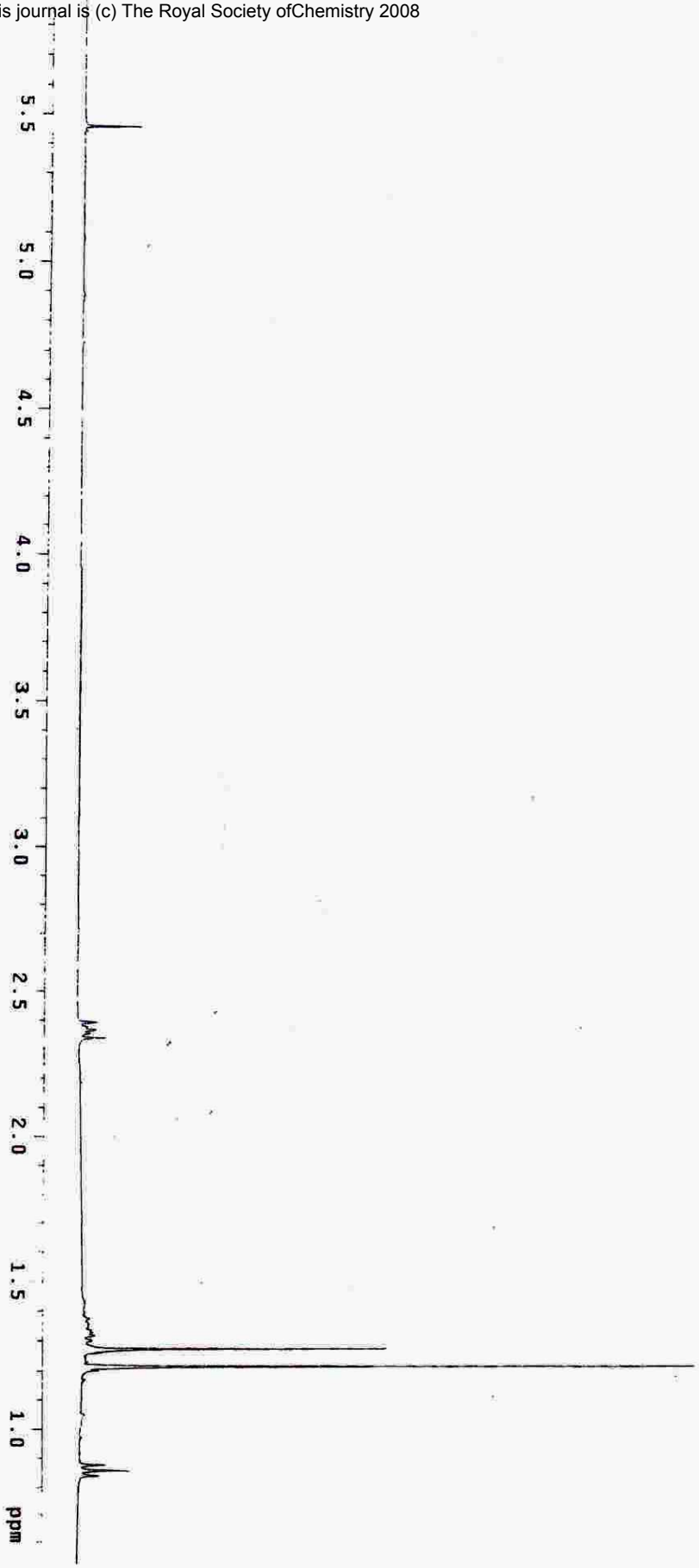

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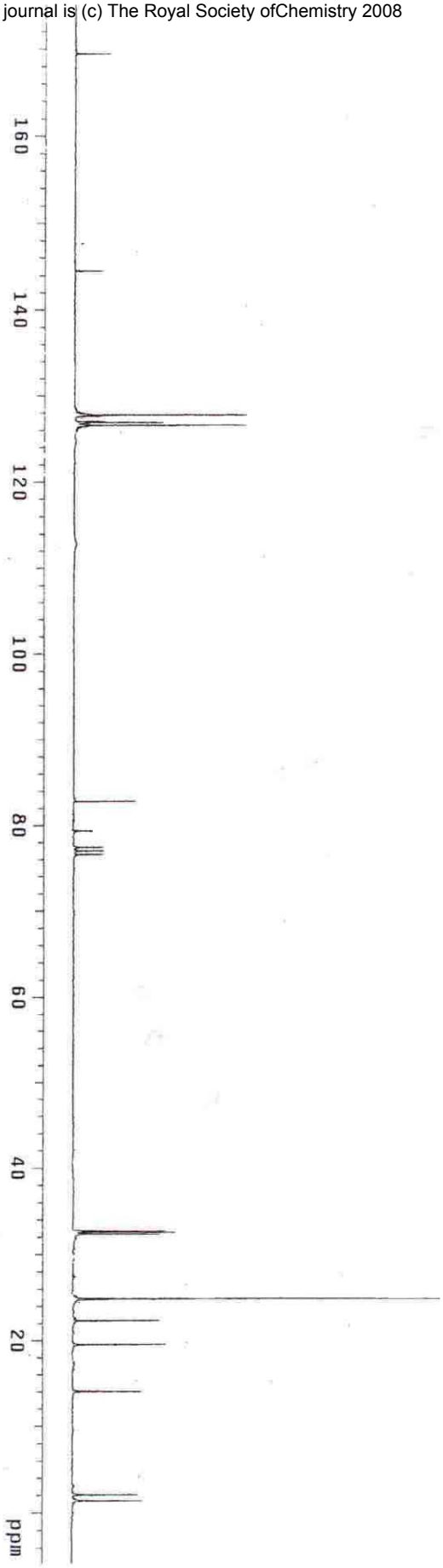

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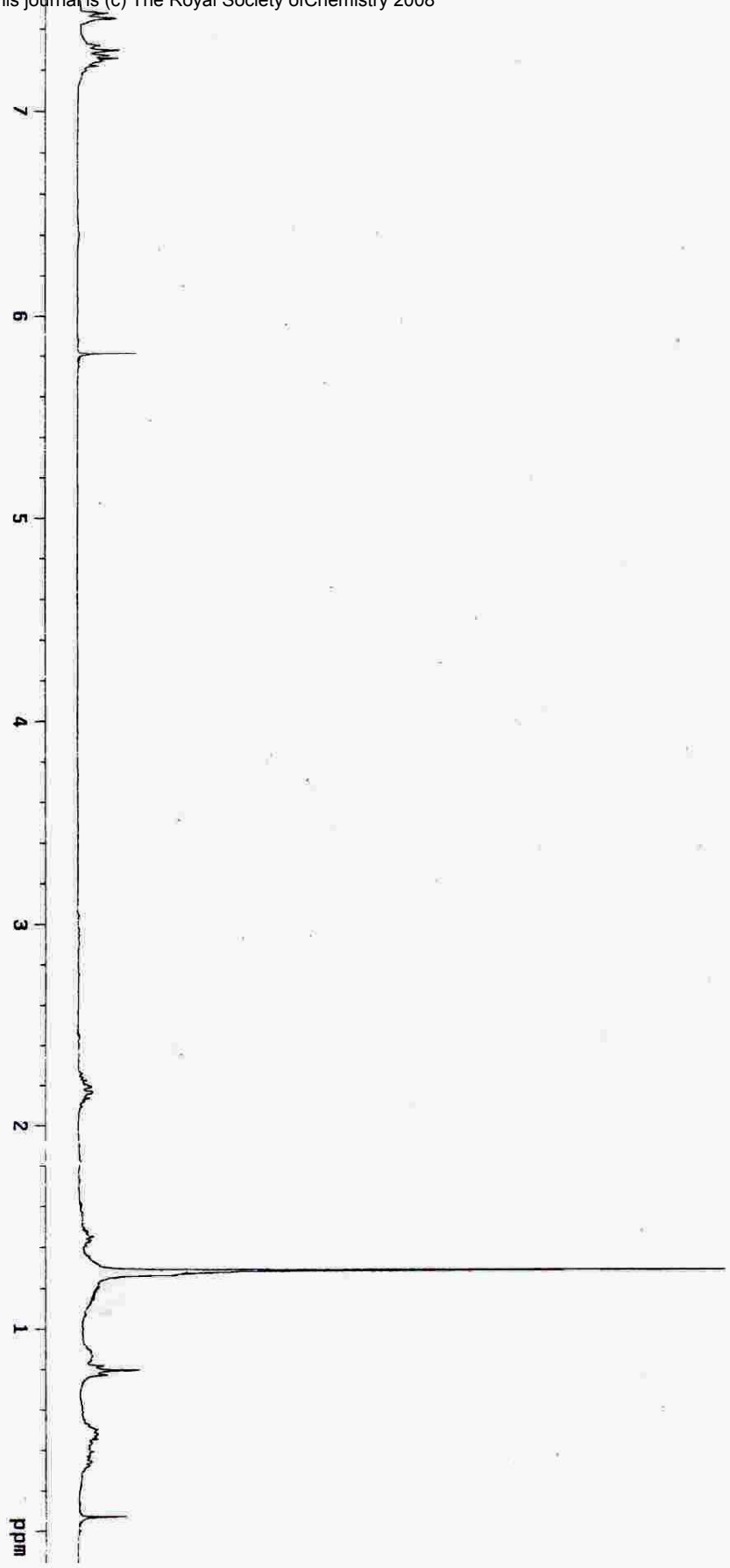

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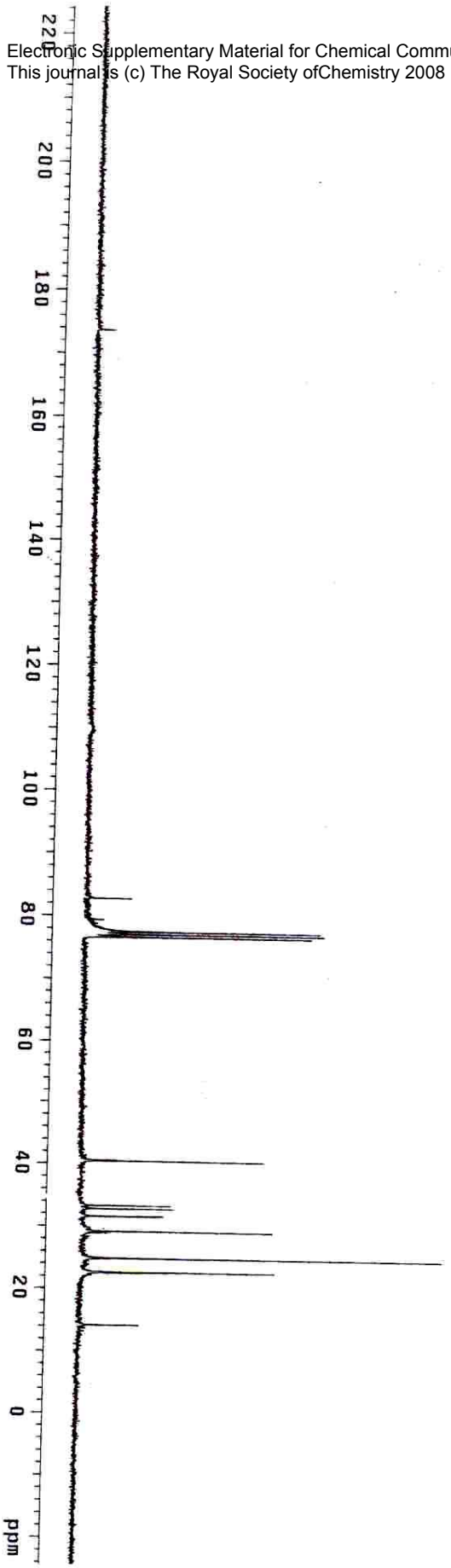

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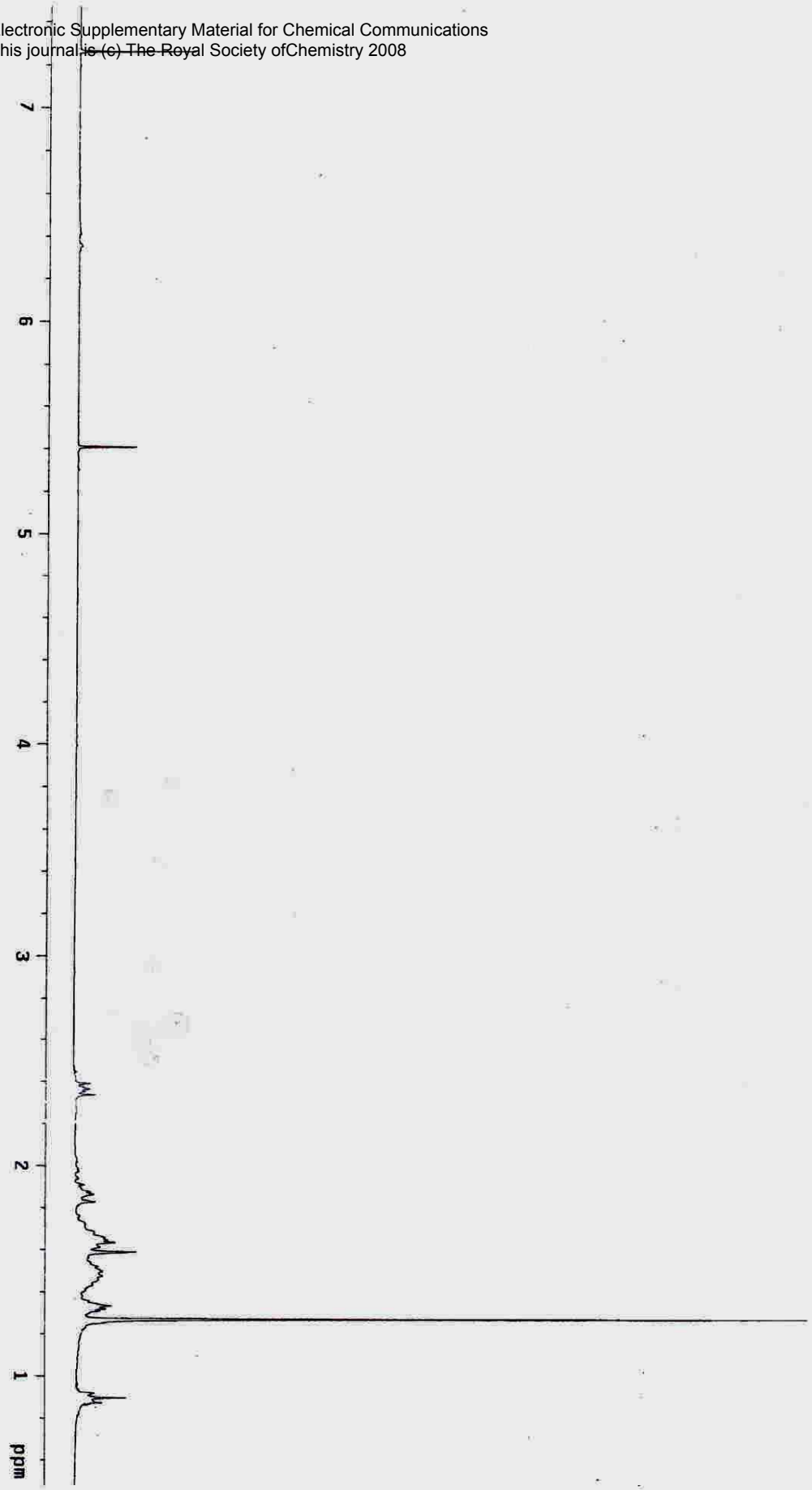

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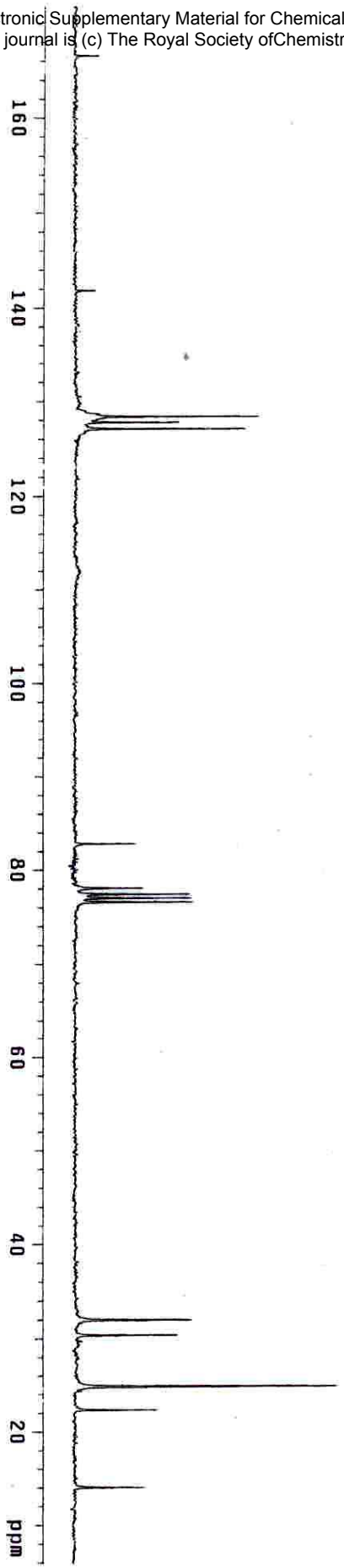

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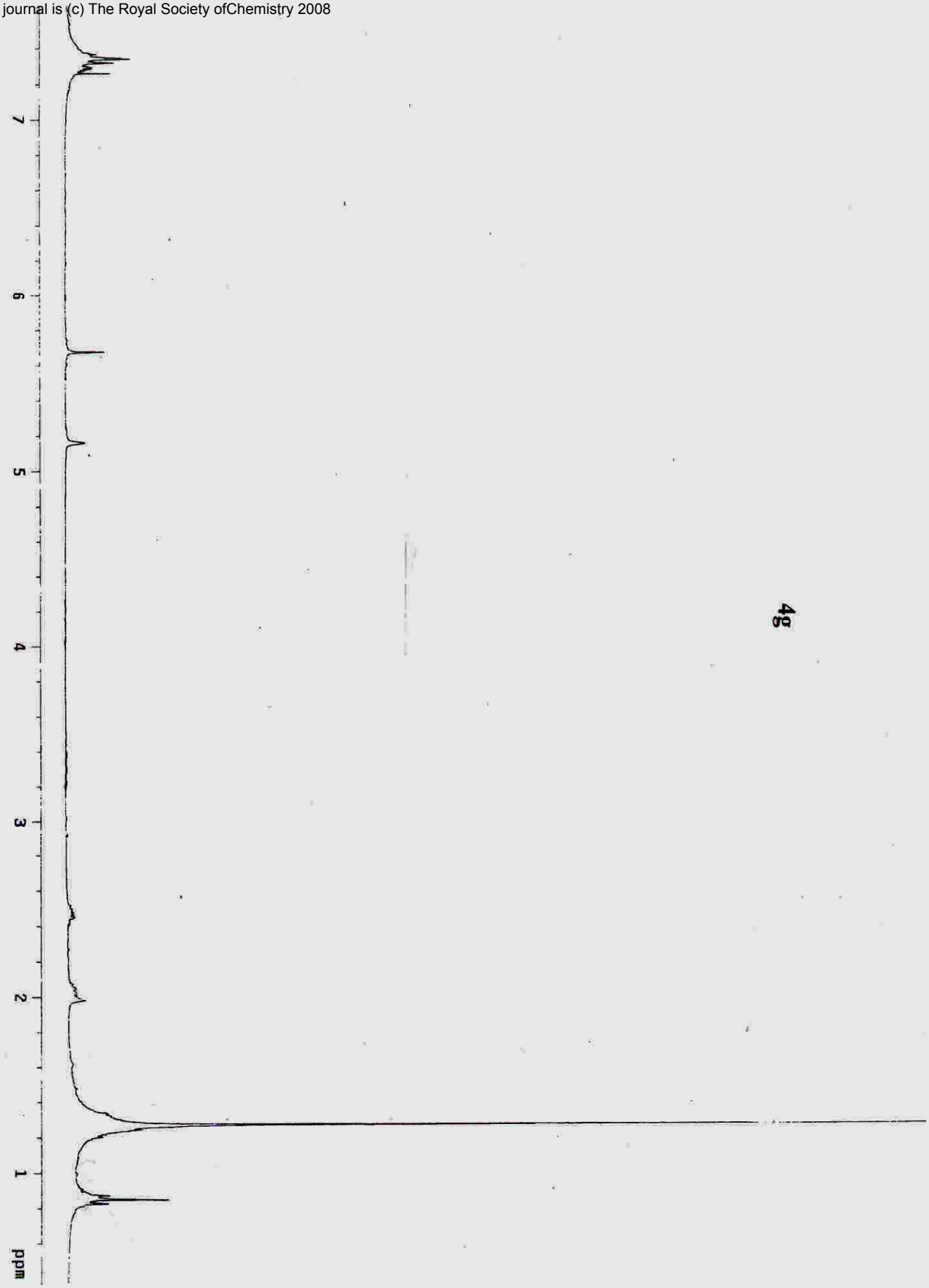
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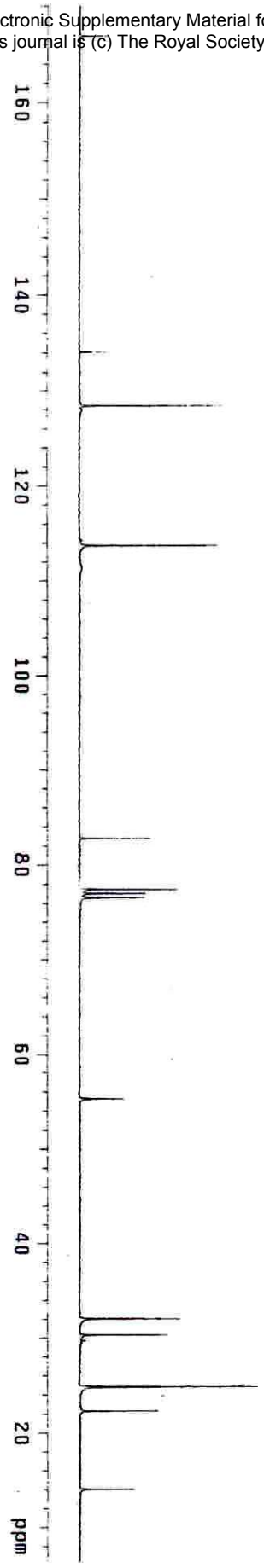

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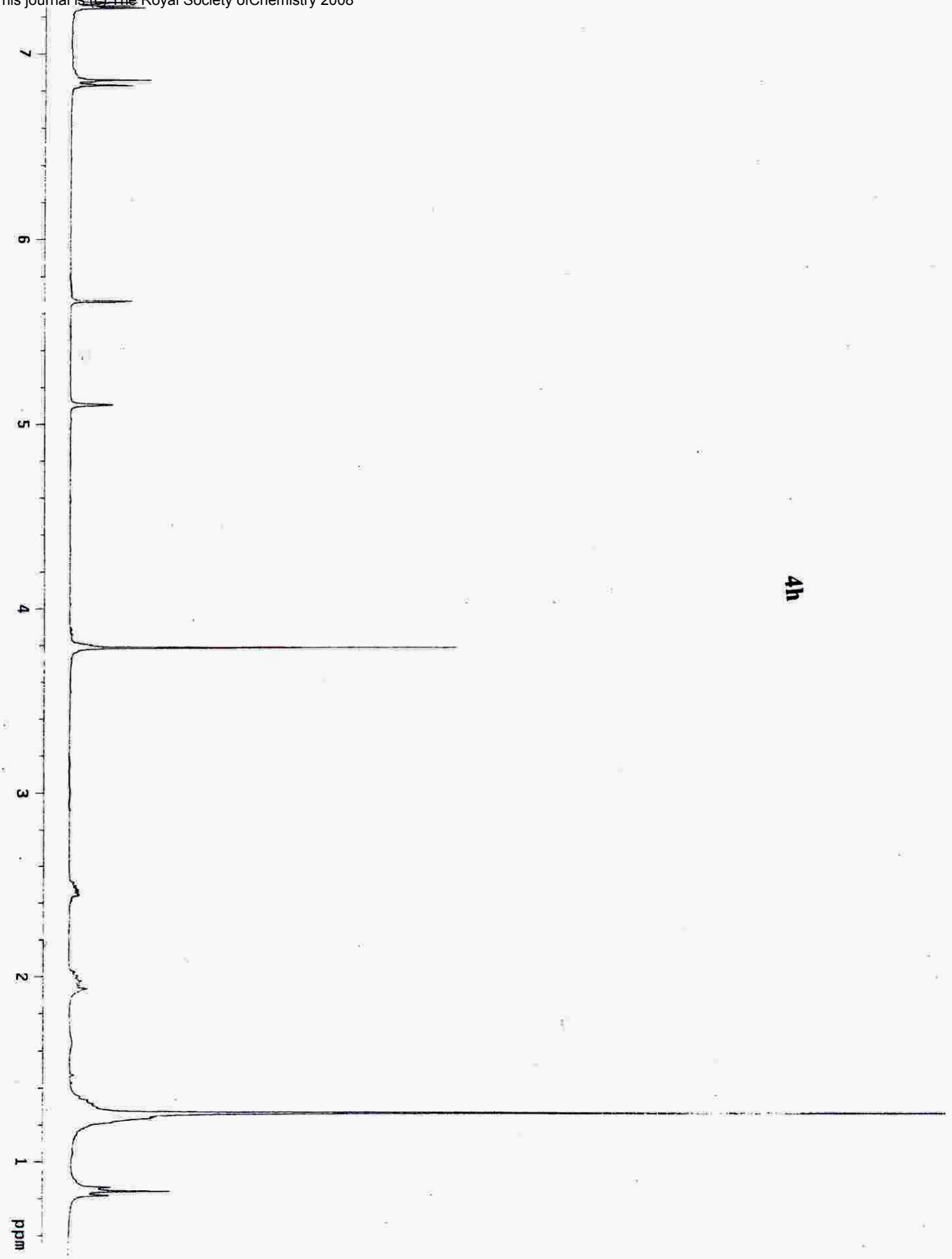

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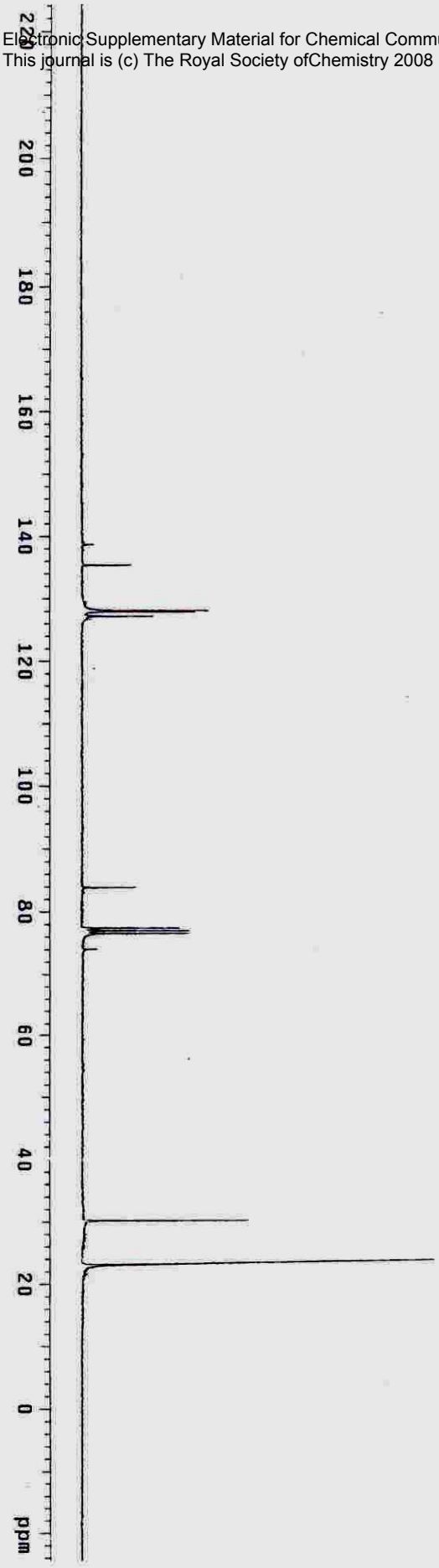

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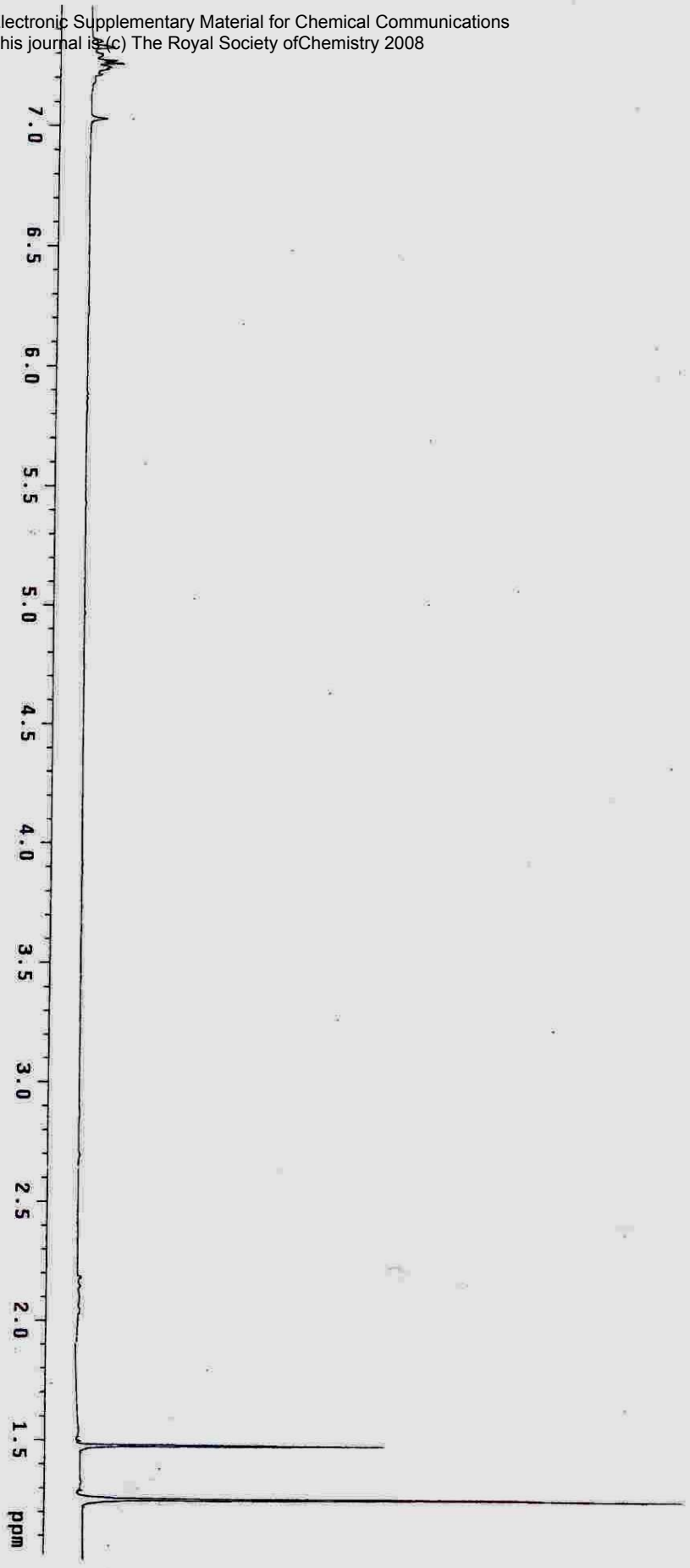

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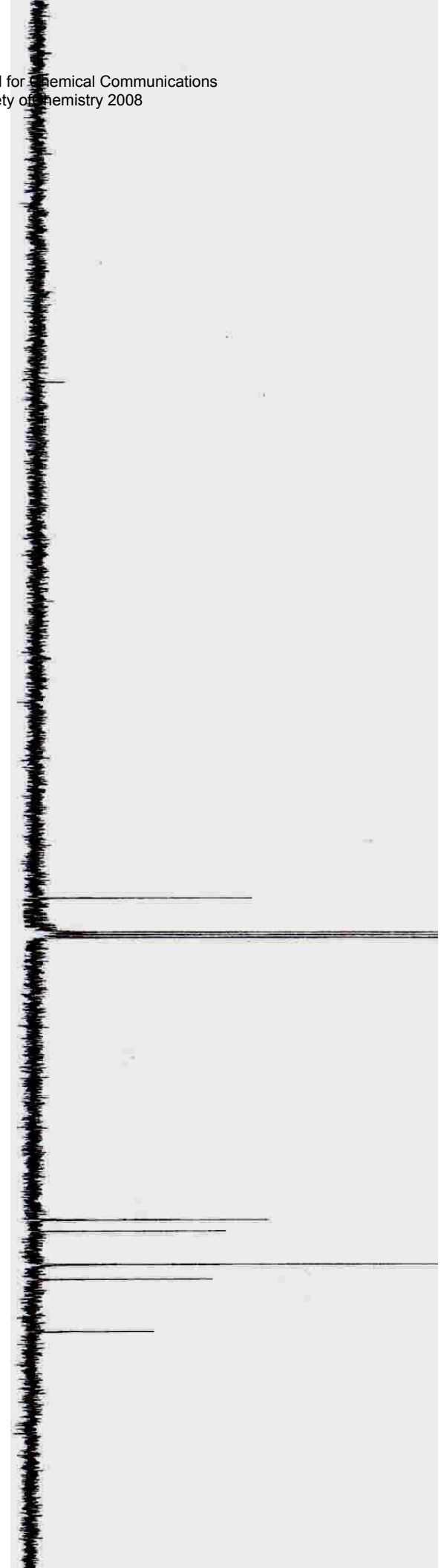

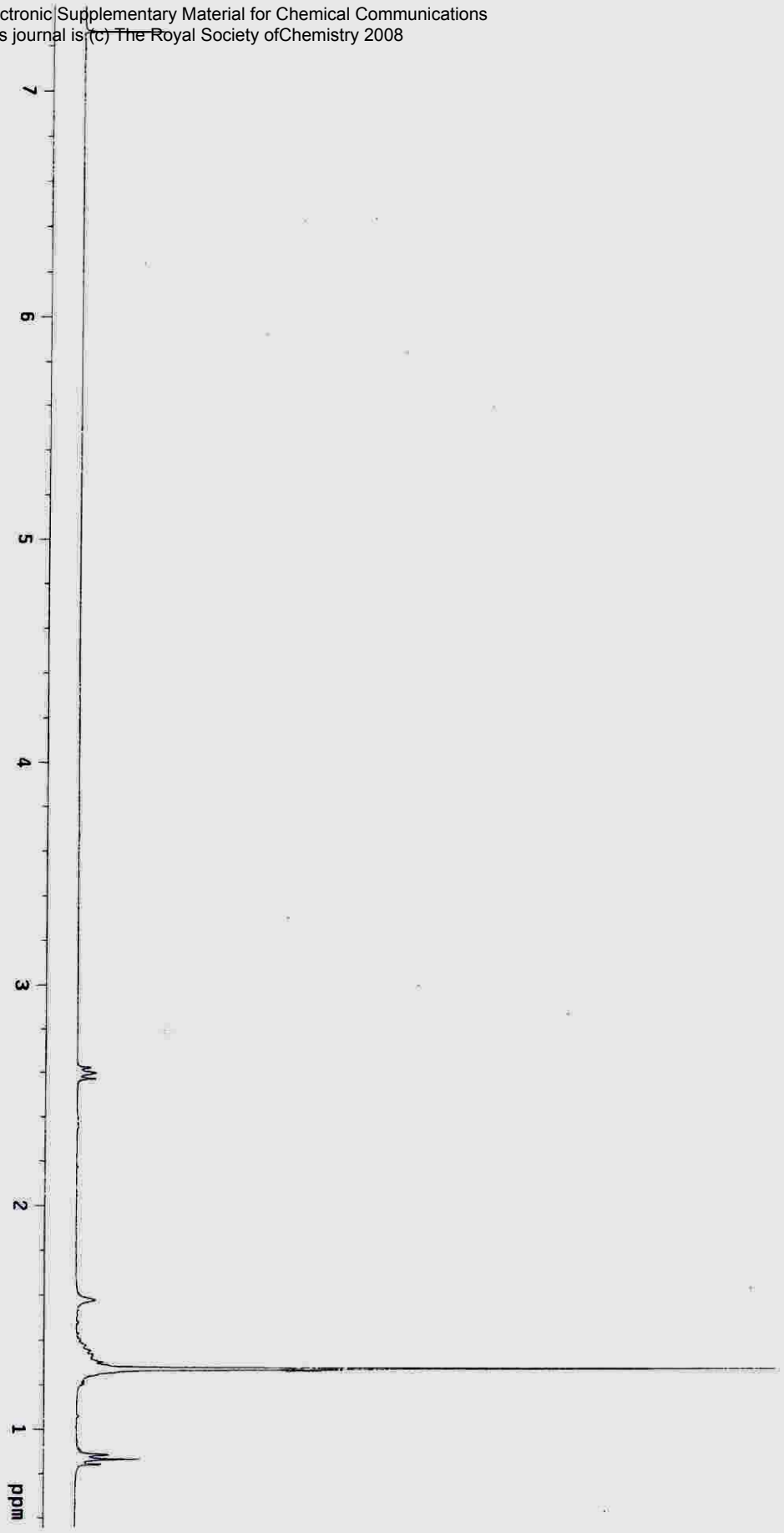

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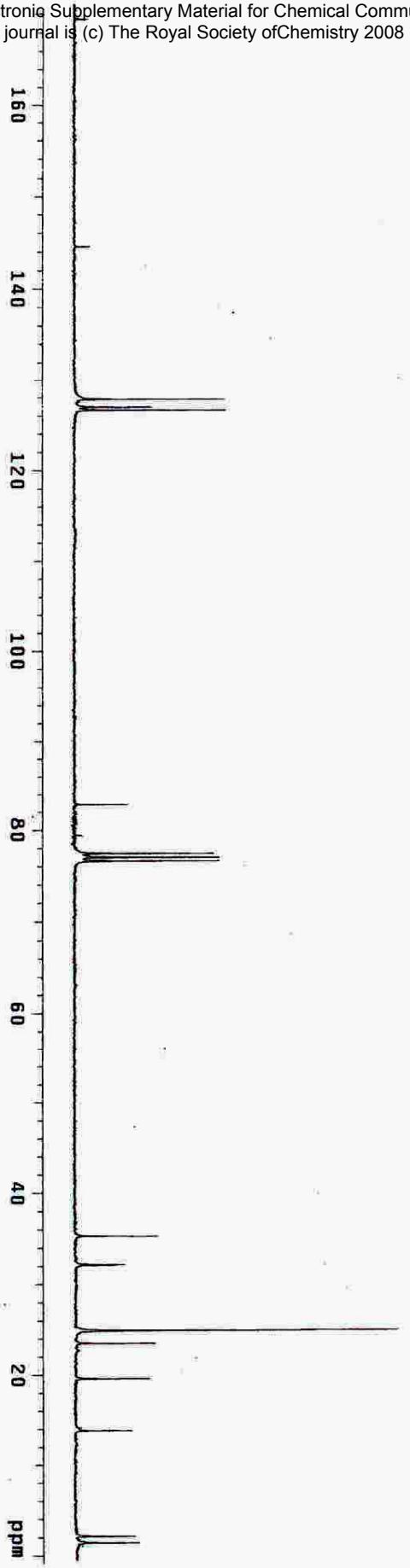
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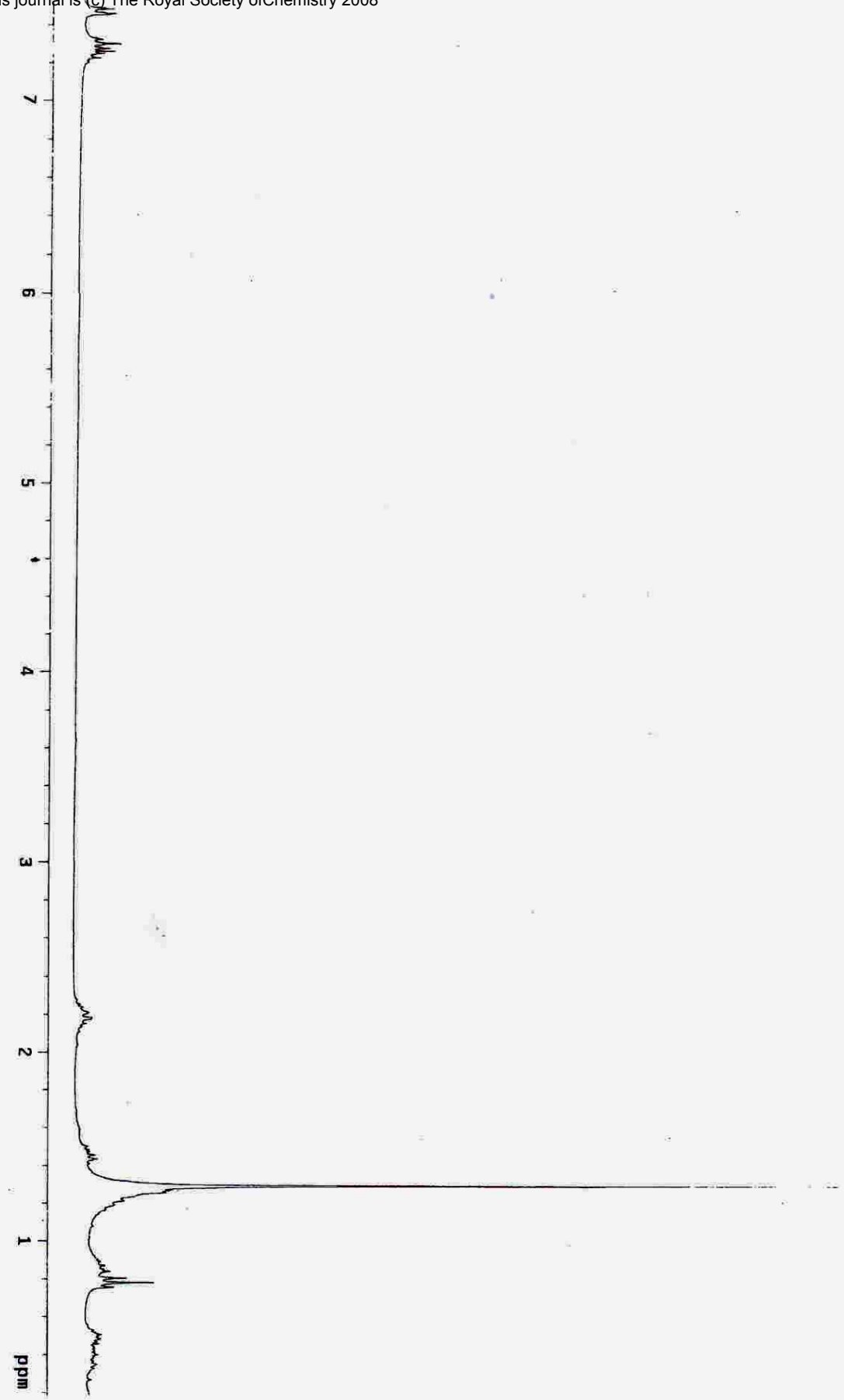

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