

Electronic Supplementary Information

One-Pot Synthesis of 3,5-Alkylated Acetophenone and Methyl Benzoate Derivatives via Anionic Domino Process

Roberto Ballini,* Luciano Barboni,* Dennis Fiorini, Guido Giarlo, and Alessandro Palmieri

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Method of preparation of compounds **6**: To a stirred solution of dinitrocompound **1** (1 mmol) in acetonitrile (4 mL) were added, at room temperature, the appropriate enone **2** (1 mmol) and DBU (3 mmol). The resulted mixture was stirred for 1 h, then was added 4N HCl (8 mL). After stirring for further 0.5 h the aqueous layer was extracted with CH₂Cl₂ (3 x 30 mL). Finally organic layer was dried over anhydrous Na₂SO₄, filtered, concentrated under vacuum to afford the crude product **6**, that was purified by flash chromatography (silica gel, hexane-ethyl acetate as eluant).

Analytical data of compounds **6a-o**

1-(3-Methyl-5-pentyl-phenyl)-ethanone (entry 6a):

Oil (yield 55%); ¹H NMR (CDCl₃, 300 MHz) δ = 0.90 (t, *J* = 6.6 Hz, 3H), 1.27-1.43 (m, 4H), 1.52-1.70 (m, 2H), 2.39 (s, 3H), 2.57-2.66 (m, 5H), 7.20 (s, 1H), 7.59 (s, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ = 14.2, 21.4, 22.7, 26.9, 31.3, 31.6, 35.9, 125.6, 126.6, 134.3, 137.4, 138.3, 143.5, 198.8. GC-MS (70 eV): *m/z* (%) = 204 (33) [M]⁺, 189 (100), 147 (17), 105 (21), 43 (11). IR (neat) = 2920, 1710, 1603 cm⁻¹.

1-(5-Pentyl-biphenyl-3-yl)-ethanone (entry 6b):

Oil (yield 62%); ¹H NMR (CDCl₃, 300 MHz) δ = 0.93 (t, *J* = 6.6 Hz, 3H), 1.32-1.48 (m, 4H), 1.63-1.81 (m, 2H), 2.67 (s, 3H), 2.75 (t, *J* = 7.3 Hz, 2H), 7.38-7.56 (m, 3H), 7.60-7.68 (m, 3H), 7.79 (t, *J* = 1.5 Hz, 1H), 8.02 (t, *J* = 1.5 Hz, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ = 14.2, 22.7, 27.0, 31.4, 31.7, 36.1, 124.9, 127.3, 127.4, 127.9, 129.0, 132.2, 137.9, 140.6, 141.8, 144.2, 198.6. GC-MS (70 eV): *m/z* (%) = 266 (71) [M]⁺, 251 (100), 210 (29), 178 (18) 165 (73), 152 (29), 115 (12), 43 (75), 29 (13). IR (neat) = 2929, 1684, 1598, 879, 762, 699 cm⁻¹.

1-(3-Methyl-5-octyl-phenyl)-ethanone (entry 6c):

Oil (yield 58%); ^1H NMR (CDCl_3 , 300 MHz) δ = 0.89 (t, J = 6.6 Hz, 3H), 1.21-1.40 (m, 10H), 1.53-1.72 (m, 2H), 2.39 (s, 3H), 2.55-2.69 (m, 5H), 7.21 (s, 1H), 7.60 (s, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 14.3, 21.5, 22.9, 26.9, 29.4, 29.5, 29.6, 31.7, 32.1, 36.0, 125.7, 126.6, 134.3, 137.5, 138.3, 143.6, 198.8. GC-MS (70 eV): m/z (%) = 246 (38) $[\text{M}]^+$, 231 (100), 148 (33), 105 (48), 91 (12), 77 (10), 43 (42), 29 (9). IR (neat) = 2924, 1682, 1603, 1455, 863, 697 cm^{-1} .

1-(3-Methyl-5-phenethylphenyl)-ethanone (entry 6d):

Oil (yield 57%); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.38 (s, 3H), 2.56 (s, 3H), 2.95 (s, 4H), 7.16-7.24 (m, 4H), 7.27-7.33 (m, 2H) 7.56 (s, 1H), 7.61 (s, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.5, 27.0, 38.0, 38.1, 125.9, 126.3, 127.0, 128.6, 128.7, 134.4, 137.5, 138.5, 141.6, 142.3, 198.9. GC-MS (70 eV): m/z (%) = 238 (81) $[\text{M}]^+$, 223 (34), 147 (100), 91 (86), 43 (8). IR (neat) = 3026, 1678, 1602, 861, 749 cm^{-1} .

1-(5-Octyl-biphenyl-3-yl)-ethanone (entry 6e):

Oil (yield 61%); ^1H NMR (CDCl_3 , 300 MHz) δ = 0.90 (t, J = 6.6 Hz, 3H), 1.20-1.47 (m, 10H), 1.58-1.80 (m, 2H), 2.67 (s, 3H), 2.74 (t, J = 7.3 Hz, 2H), 7.38-7.54 (m, 3H), 7.60-7.68 (m, 3H), 7.78 (t, J = 1.6 Hz, 1H), 8.01 (t, J = 1.6 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 14.3, 22.9, 27.0, 29.5, 29.6, 29.7, 31.7, 32.1, 36.2, 124.9, 127.3, 127.4, 127.9, 129.1, 132.2, 138.0, 140.7, 141.9, 144.2, 198.5. GC-MS (70 eV): m/z (%) = 308 (100) $[\text{M}]^+$, 293 (88), 210 (51), 178 (28), 165 (91), 152 (33), 115 (13) 43 (92), 29 (19). IR (neat) = 3003, 2926, 1686, 1598, 880, 761, 700 cm^{-1} .

3-Methyl-5-pentyl-benzoic acid methyl ester (entry 6f):

Oil (yield 60%); ^1H NMR (CDCl_3 , 300 MHz) δ = 0.90 (t, J = 6.6 Hz, 3H), 1.23-1.44 (m, 4H), 1.56-1.73 (m, 2H), 2.37 (s, 3H), 2.61 (t, J = 7.3 Hz, 2H), 3.90 (s, 3H), 7.19 (s, 1H), 7.68 (s, 2H). ^{13}C NMR

(CDCl₃, 75 MHz) δ = 14.2, 21.4, 22.7, 31.3, 31.7, 35.9, 52.1, 126.9, 127.7, 130.2, 134.1, 138.2, 143.3, 167.7. GC-MS (70 eV): m/z (%) = 220 (61) [M]⁺, 189 (24), 177 (9), 164 (100), 133 (12), 105 (51). IR (neat) = 2929, 1722, 16027, 1118, 882, 758, 701 cm⁻¹.

3-Methyl-5-phenethyl-benzoic acid methyl ester (entry 6g):

Oil (yield 59%); ¹H NMR (CDCl₃, 300 MHz) δ = 2.39 (s, 3H), 2.95 (s, 4H), 3.93 (s, 3H), 7.18-7.39 (m, 6H), 7.72-7.75 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ = 21.4, 37.9, 38.0, 52.2, 126.2, 126.9, 128.0, 128.5, 128.6, 130.3, 134.2, 138.3, 141.6, 142.2, 167.6. GC-MS (70 eV): m/z (%) = 254 (57) [M]⁺, 223 (12), 163 (100), 104 (7), 91 (52). IR (neat) = 3026, 2948, 1720, 1218, 770, 699 cm⁻¹.

1-(5-Methyl-4'-trifluoromethyl-biphenyl-3-yl)-ethanone (entry 6h):

White solid, m.p. 96-98°C (yield 58%); ¹H NMR (CDCl₃, 300 MHz) δ = 2.50 (m, 3H), 2.65 (s, 3H), 7.60 (s, 1H), 7.71 (s, 4H), 7.80 (s, 1H), 7.98 (s, 1H). ¹³C NMR (CDCl₃, 75 MHz) δ = 21.6, 26.7, 121.7, 124.6, 125.8, 125.9, 126.0, 126.1, 127.1, 127.7, 128.9, 129.6, 130.3, 132.7, 138.1, 139.4, 140.4, 144.1, 198.2. GC-MS (70 eV): m/z (%) = 278 (47) [M]⁺, 263 (100), 235 (18), 215 (13), 165 (29), 43 (3). IR (nujol) = 2954, 1684, 1619, 1190, 842, 773 cm⁻¹.

1-(4''-Methoxy-[1,1';3',1'']terphenyl-5'-yl)-ethanone (entry 6i):

Oil (yield 61%); ¹H NMR (CDCl₃, 300 MHz) δ = 2.71 (s, 3H), 3.89 (s, 3H), 7.00-7.09 (m, 2H), 7.39-7.54 (m, 3H), 7.57-7.78 (m, 4H), 7.96 (t, *J* = 1.5 Hz, 1H), 8.10-8.13 (m, 2H). ¹³C NMR (CDCl₃, 75 MHz) δ = 27.1, 55.6, 114.6, 125.5, 125.6, 127.5, 128.1, 128.6, 129.1, 130.3, 132.8, 138.3, 140.5, 142.1, 142.4, 159.8, 198.3. GC-MS (70 eV): m/z (%) = 302 (99) [M]⁺, 287 (53), 259 (32), 244 (15), 228 (22), 215 (100), 189 (22), 43 (30). IR (neat) = 3001, 2932, 1681, 1608, 1180, 1032, 964, 883, 761 cm⁻¹.

5-Methyl-4'-trifluoromethyl-biphenyl-3-carboxylic acid methyl ester (entry 6j):

Oil (yield 60%); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.47 (s, 3H), 3.94 (s, 3H), 7.57-7.60 (m, 1H), 7.71 (s, 4H), 7.88-7.91 (m, 1H), 8.08 (t, J = 1.6 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.5, 52.4, 121.7, 125.8, 125.9, 126.0, 126.1, 127.1, 127.7, 129.6, 130.1, 131.1, 132.6, 139.2, 140.2, 144.0, 167.2. GC-MS (70 eV): m/z (%) = 294 (75) $[\text{M}]^+$, 275 (8), 263 (100), 235 (17), 215 (12), 165 (28). IR (neat) = 2954, 1727, 1619, 1194, 840, 770 cm^{-1} .

4'-Methoxy-5-methyl-biphenyl-3-carboxylic acid methyl ester (entry 6k):

Pale yellow solid, m.p. 68-70°C (yield 77%); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.43 (s, 3H), 3.83 (s, 3H), 3.91 (s, 3H), 6.92-7.01 (m, 2H), 7.48-7.58 (m, 3H), 7.76-7.82 (m, 1H), 8.01-8.06 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.6, 52.3, 55.5, 114.4, 125.2, 128.3, 128.6, 130.7, 132.1, 132.9, 138.8, 141.2, 159.6, 167.5. GC-MS (70 eV): m/z (%) = 256 (100) $[\text{M}]^+$, 241 (27), 225 (32), 213 (19), 197 (16), 182 (16), 165 (17), 153 (31), 139 (18), 115 (8). IR (nujol) = 3020, 2951, 1720, 1609, 1180, 831, 770 cm^{-1} .

1-(4'-Methoxy-5-methyl-biphenyl-3-yl)-ethanone (entry 6l):

Oil (yield 66%); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.47 (s, 3H), 2.64 (s, 3H), 3.86 (s, 3H), 6.95-7.05 (m, 2H), 7.51-7.60 (m, 3H), 7.71 (s, 1H), 7.92-7.97 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.7, 27.0, 55.6, 114.5, 124.1, 127.4, 128.4, 132.3, 133.0, 137.9, 139.0, 141.4, 159.7, 198.7. GC-MS (70 eV): m/z (%) = 240 (100) $[\text{M}]^+$, 225 (98), 197 (49), 182 (35), 165 (35), 153 (46), 139 (30), 115 (11), 89 (8), 77 (7), 63 (12), 43 (22). IR (neat) = 3002, 2933, 1682, 1609, 1181, 1033, 829 cm^{-1} .

5-Methyl-3'-nitro-biphenyl-3-carboxylic acid methyl ester (entry 6m):

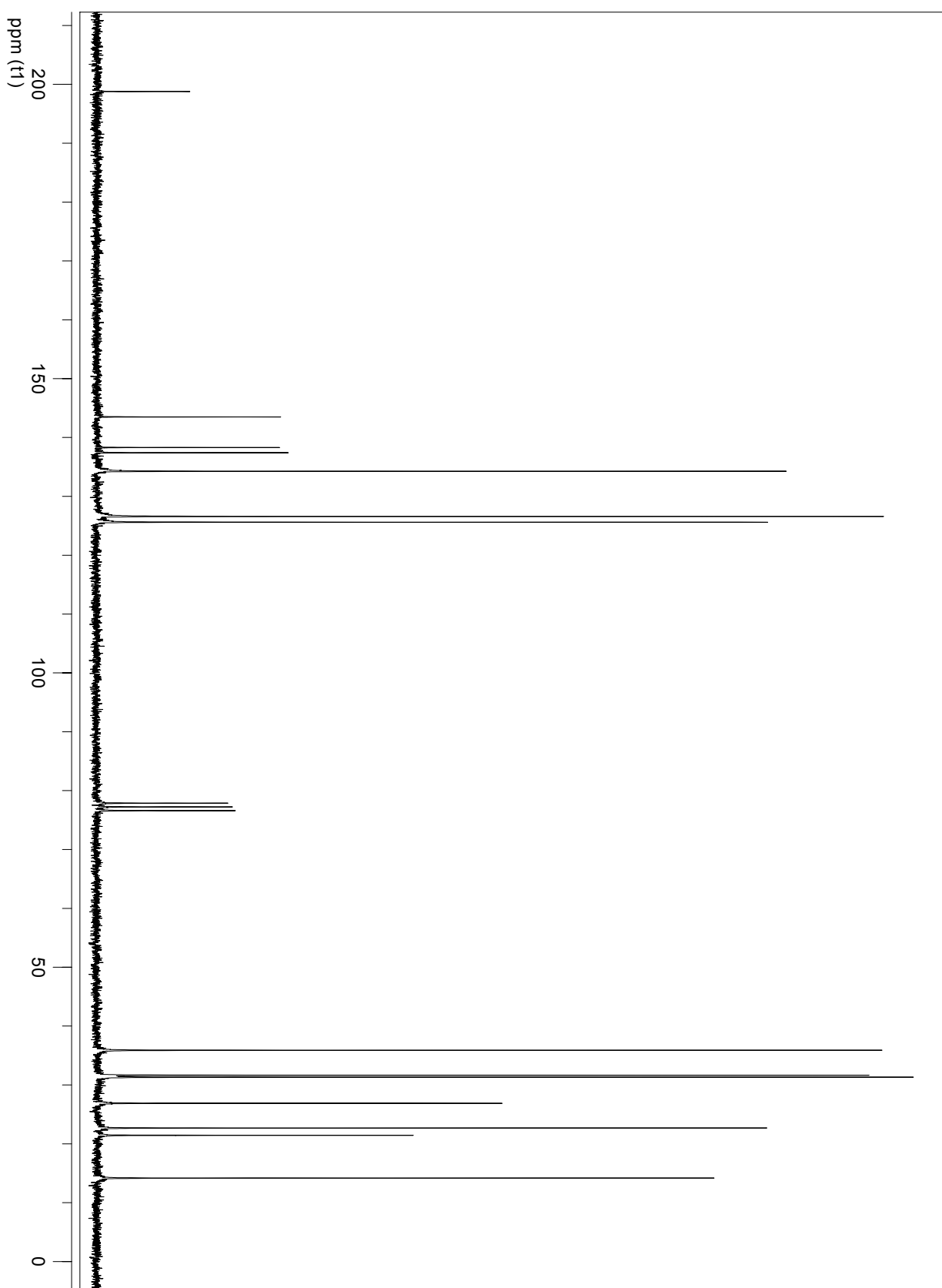
Pale yellow solid, m.p. 106-108°C (yield 42 %); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.49 (s, 3H), 3.95 (s, 3H), 7.58-7.68 (m, 2H), 7.90-7.98 (m, 2H), 8.07-8.12 (m, 1H), 8.22 (dd, J = 8.0 Hz, J = 2.2 Hz, 1H), 8.46 (t, J = 1.9 Hz, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.5, 52.5, 122.1, 122.6, 125.7, 130.0, 130.4, 131.2, 132.4, 133.3, 139.0, 139.5, 142.1, 148.9, 167.0. GC-MS (70 eV): m/z (%) = 271 (68) $[\text{M}]^+$, 240 (92), 212 (8), 165 (100), 152 (13), 139 (24), 115 (13), 89 (8), 75 (7). IR (nujol) = 1725, 1606, 1516, 1353, 804, 763, 737 cm^{-1} .

5-Methyl-biphenyl-3-carboxylic acid methyl ester (entry 6n):

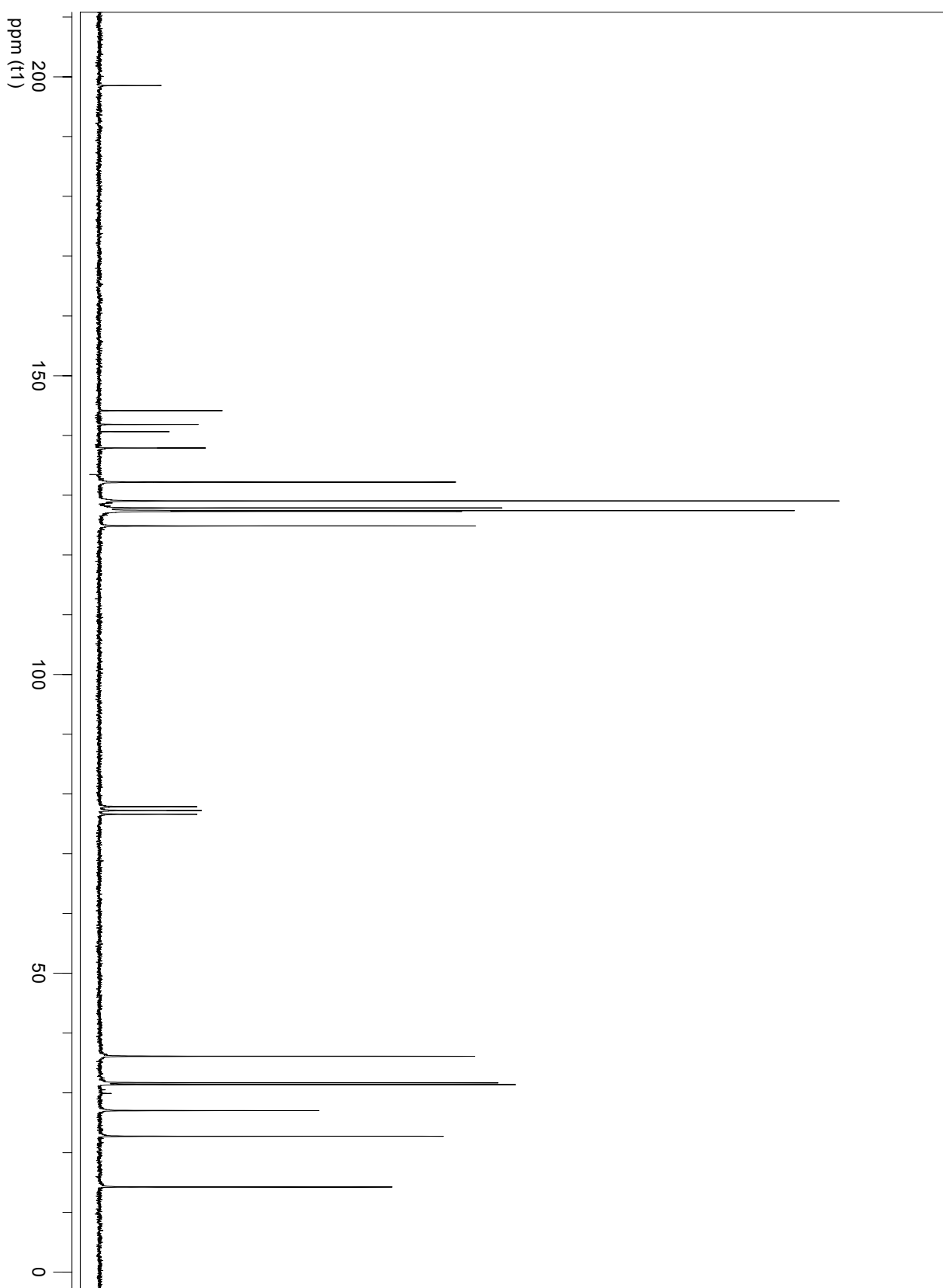
Oil (yield 76 %); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.48 (s, 3H), 3.96 (s, 3H), 7.37-7.53 (m, 3H), 7.60-7.68 (m, 3H), 7.86-7.89 (m, 1H), 8.10-8.14 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.6, 52.3, 125.8, 127.4, 127.9, 129.0, 129.2, 130.9, 132.6, 138.9, 140.5, 141.7, 167.4. GC-MS (70 eV): m/z (%) = 226 (100) $[\text{M}]^+$, 195 (93), 165 (41), 152 (35), 98 (6), 82 (6). IR (neat) = 3034, 2950, 1714, 1600, 1436, 1195, 878, 758, 697 cm^{-1} .

3-Methyl-5-pyridin-2-yl-benzoic acid methyl ester (entry 6o):

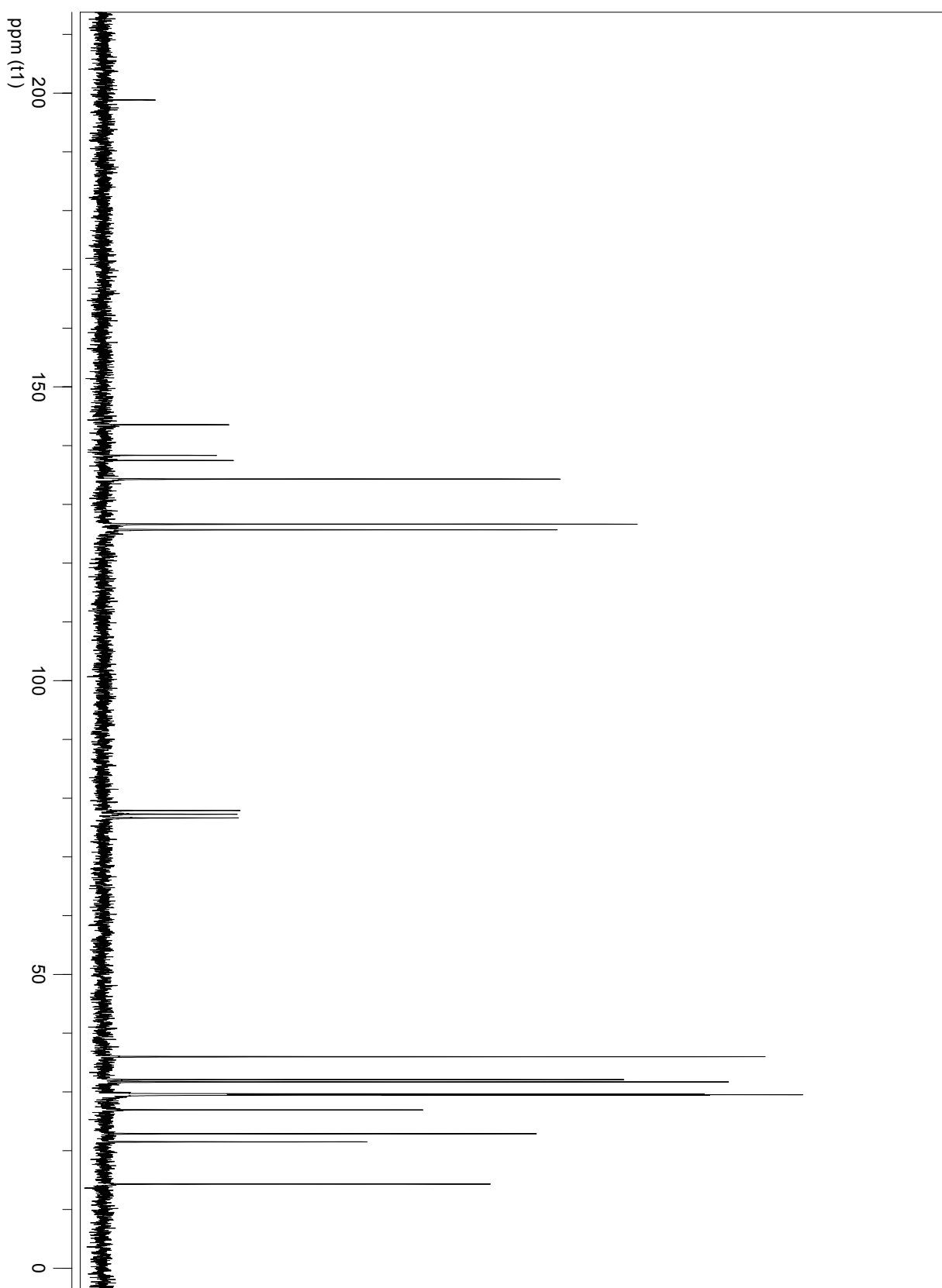
Pale yellow solid, m.p. 38-40°C (yield 43%); ^1H NMR (CDCl_3 , 300 MHz) δ = 2.47 (s, 3H), 3.93 (s, 3H), 7.22-7.27 (m, 1H), 7.74-7.79 (m, 2H), 7.90 (s, 1H), 8.06 (s, 1H), 8.39 (s, 1H), 8.66-8.71 (m, 1H). ^{13}C NMR (CDCl_3 , 75 MHz) δ = 21.5, 52.3, 120.9, 122.7, 125.4, 130.7, 130.8, 132.3, 137.0, 139.0, 139.8, 149.9, 156.7, 167.3. GC-MS (70 eV): m/z (%) = 227 (20) $[\text{M}]^+$, 196 (13), 169 (100), 139 (9), 115 (7), 89 (5), 78 (5). IR (nujol) = 1731, 1587, 1197, 887, 764 cm^{-1} .



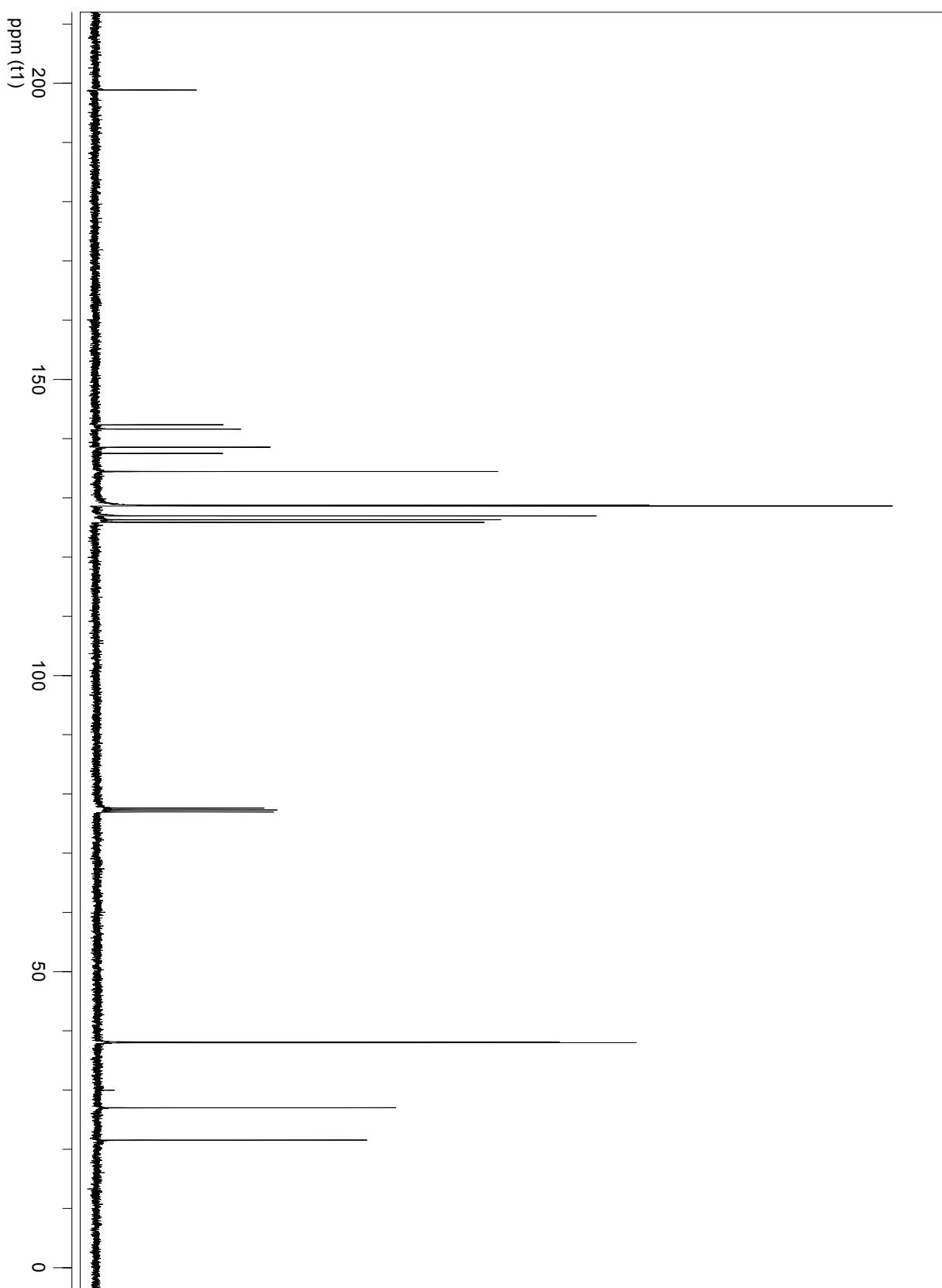
^{13}C -NMR spectrum of compound **6a**



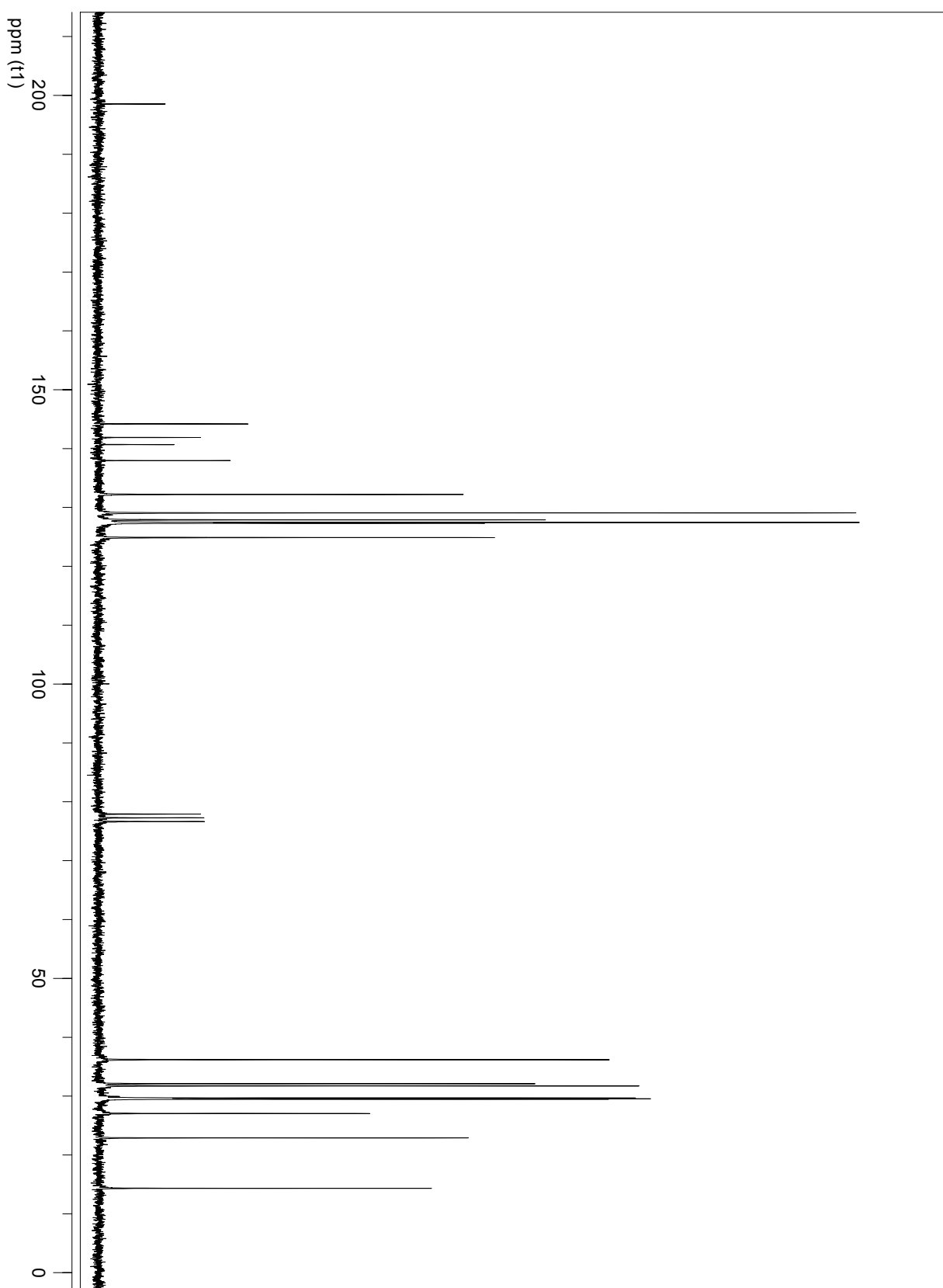
^{13}C -NMR spectrum of compound **6b**



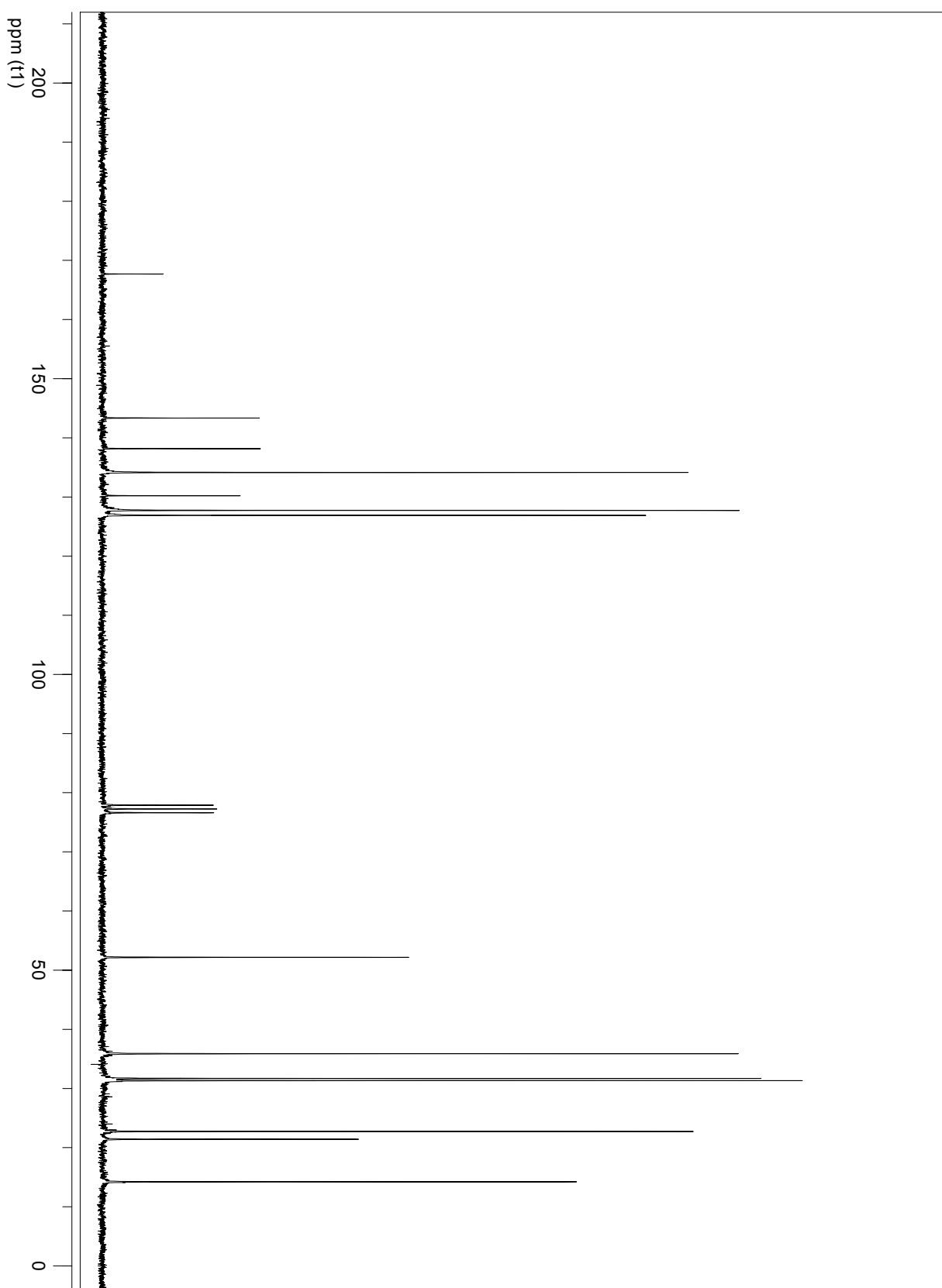
^{13}C -NMR spectrum of compound **6c**



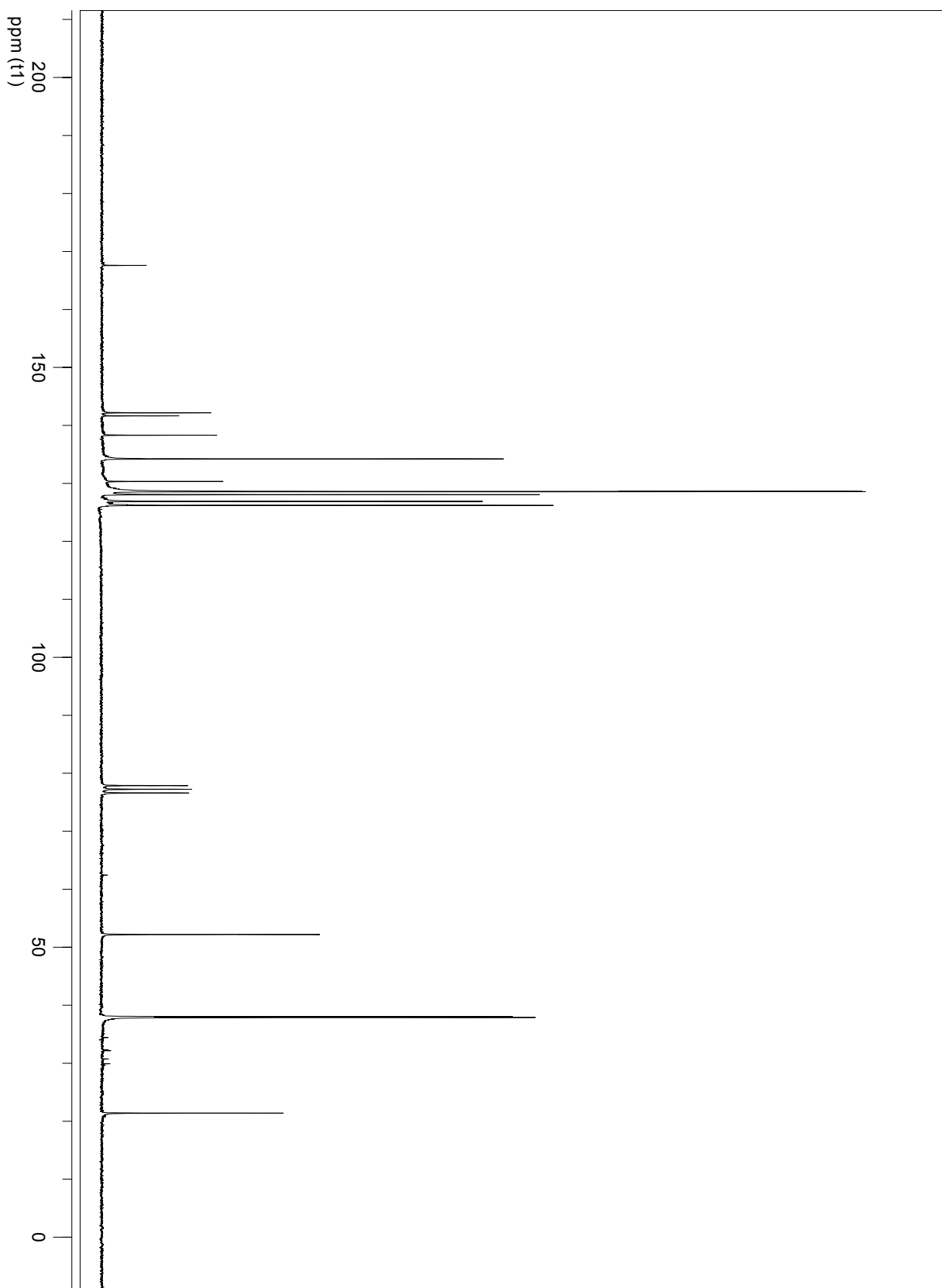
^{13}C -NMR spectrum of compound **6d**



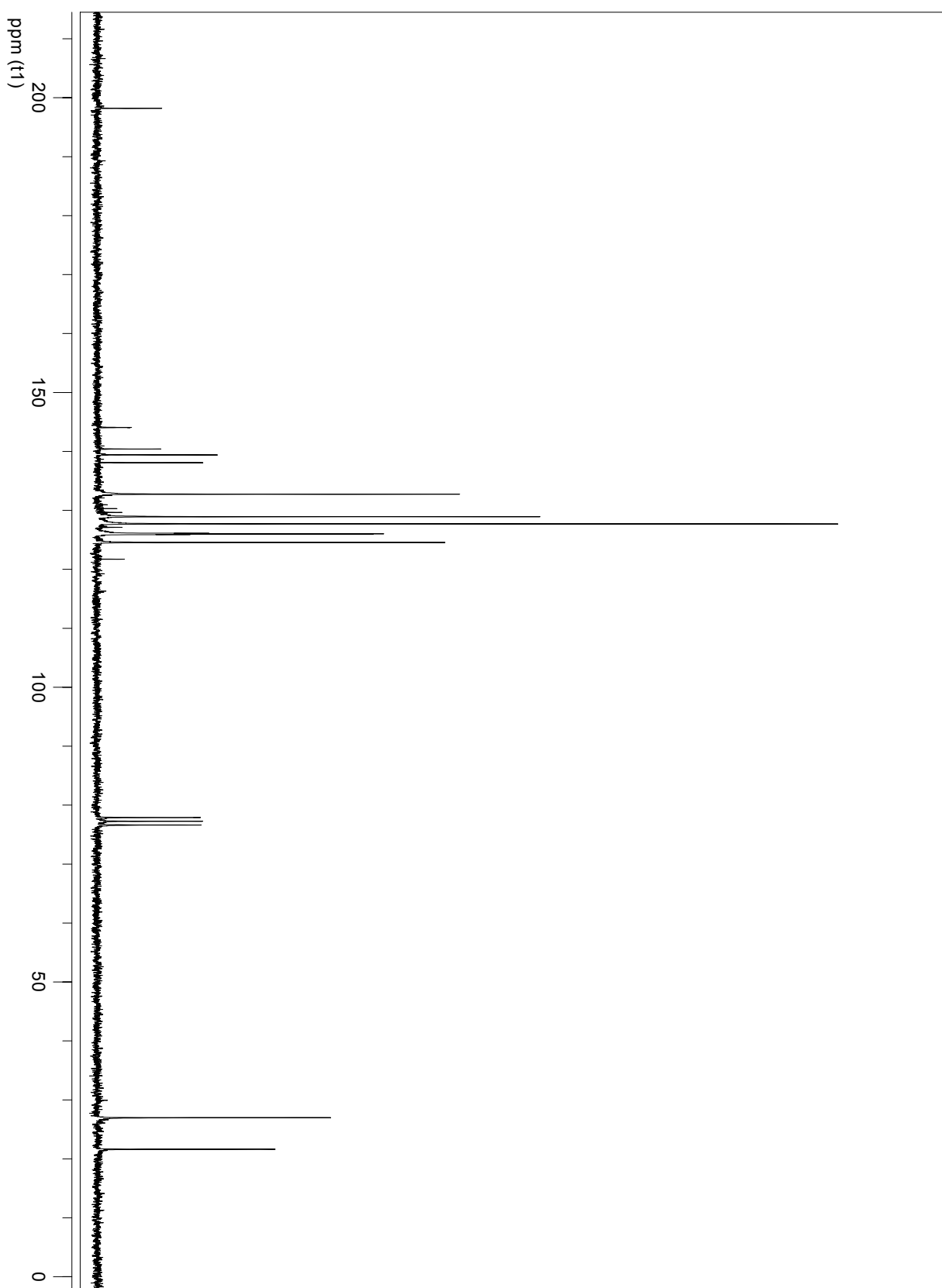
^{13}C -NMR spectrum of compound **6e**



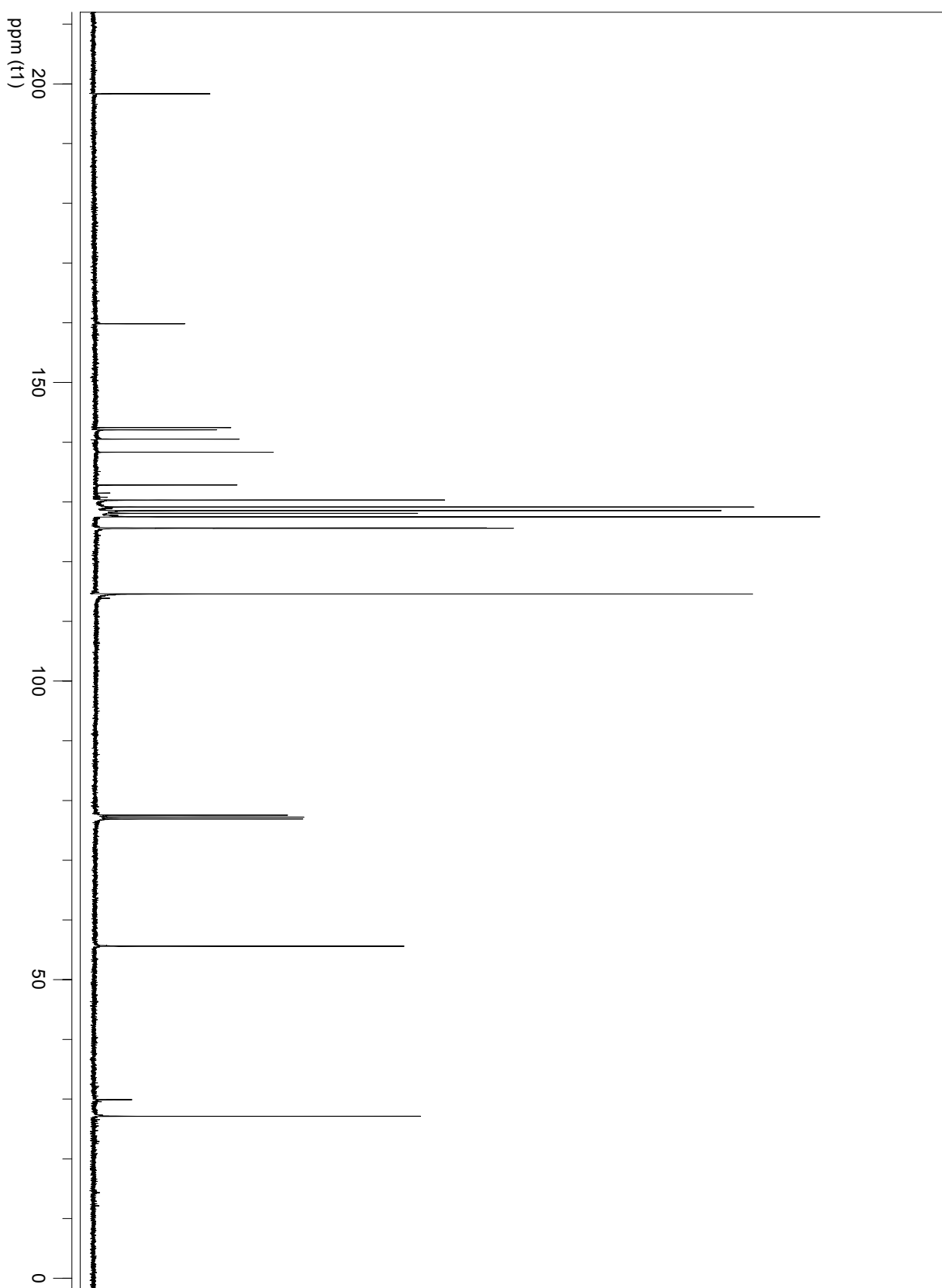
^{13}C -NMR spectrum of compound **6f**



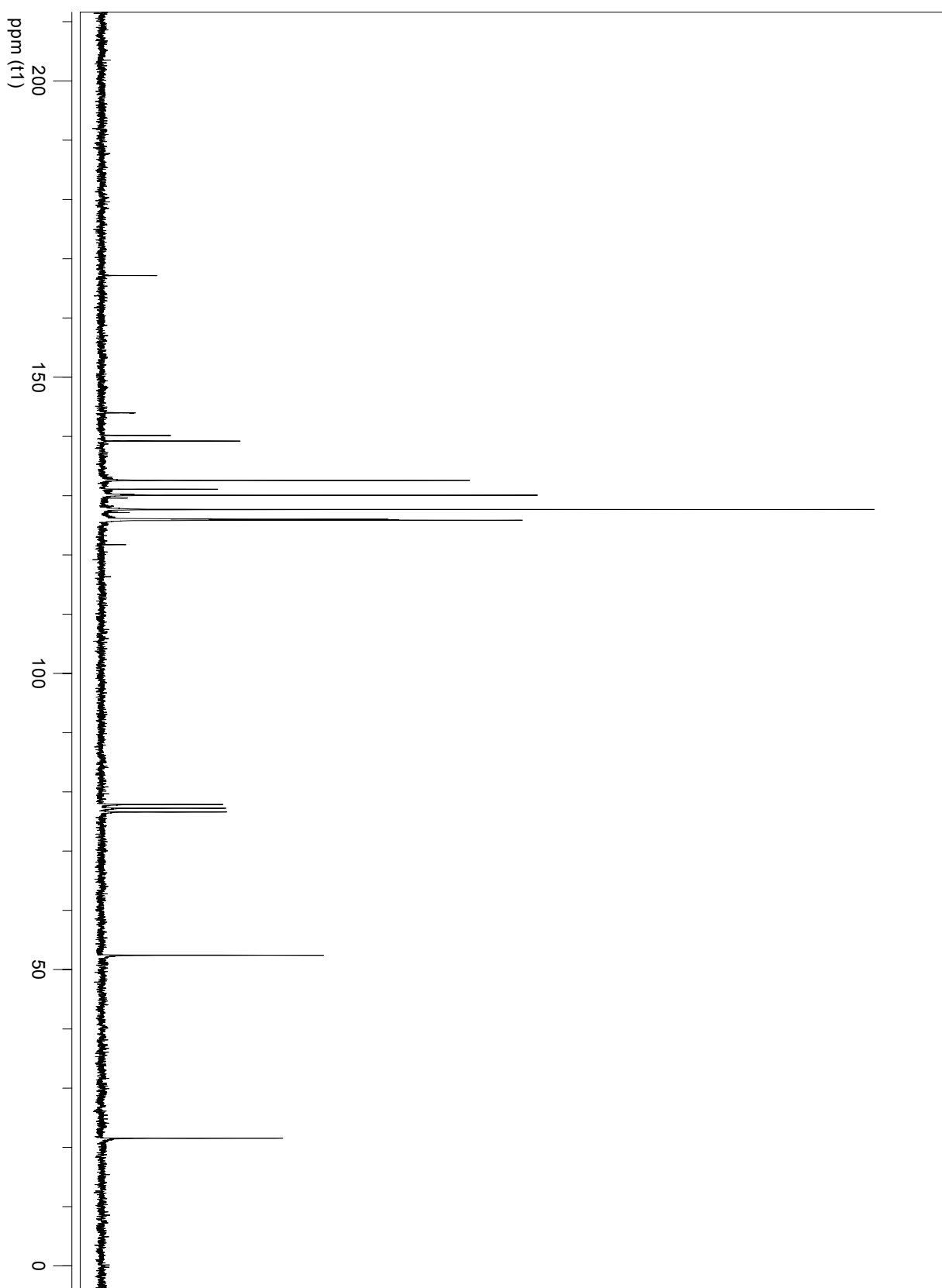
^{13}C -NMR spectrum of compound **6g**



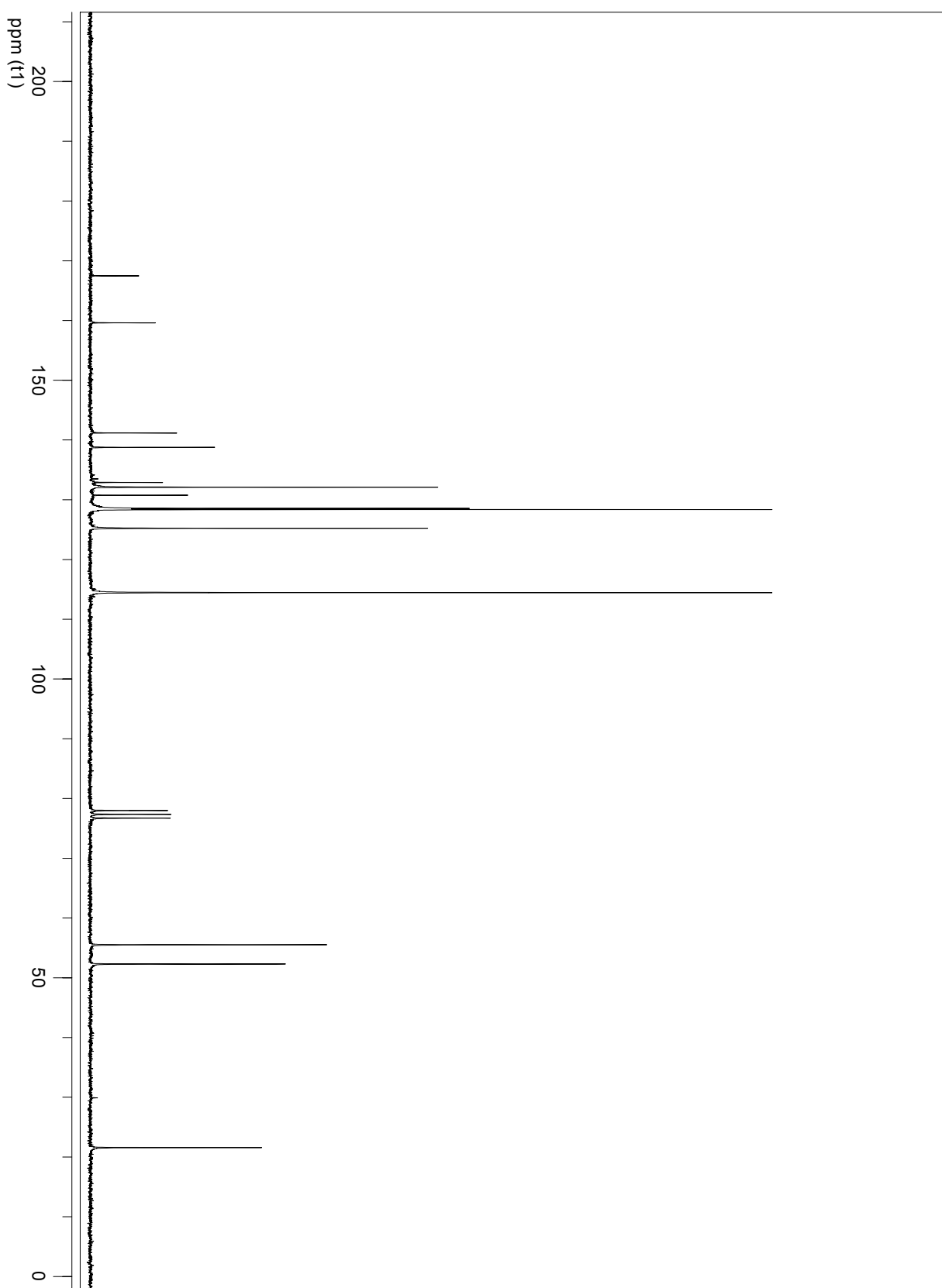
^{13}C -NMR spectrum of compound **6h**



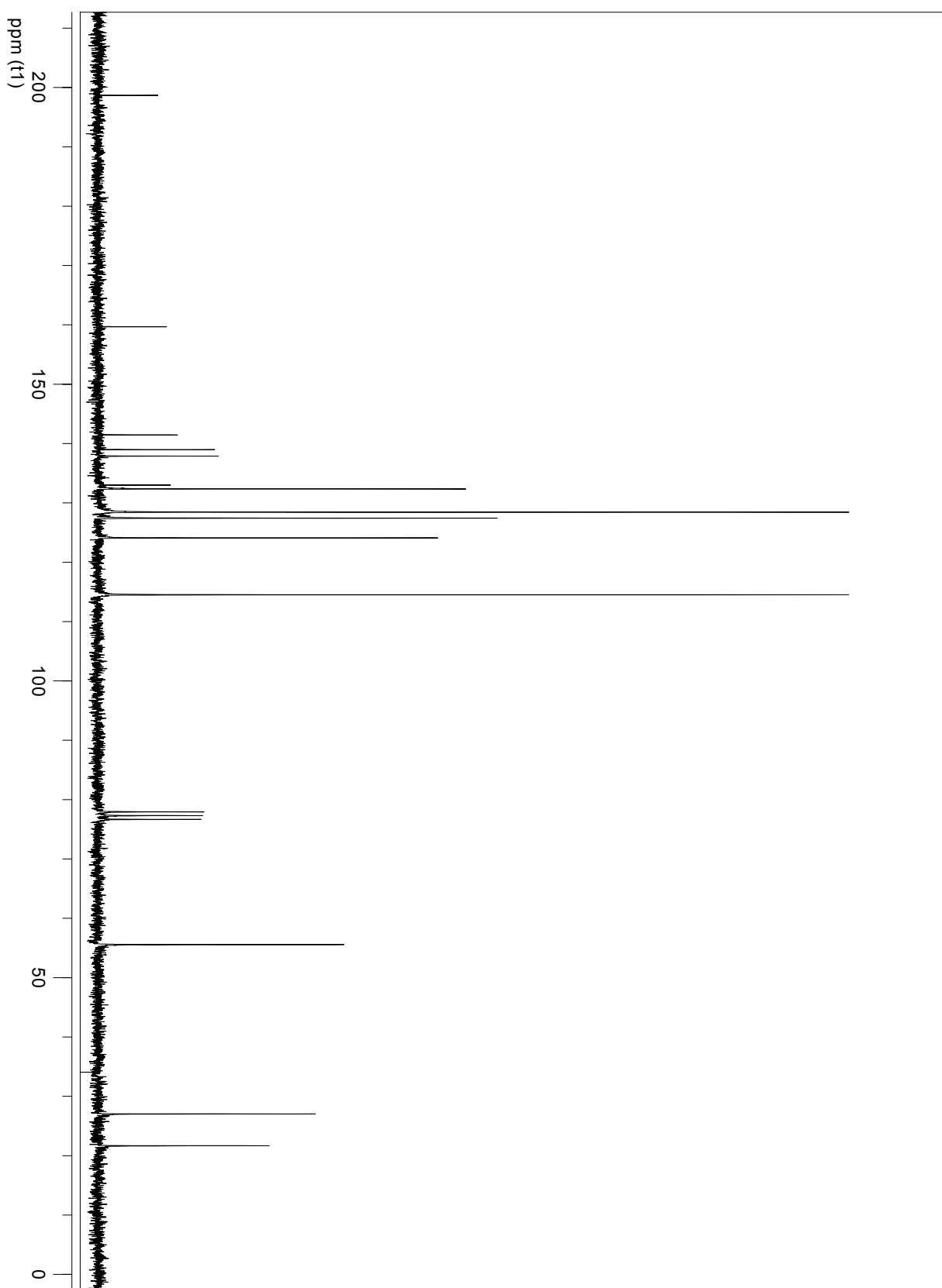
^{13}C -NMR spectrum of compound **6i**



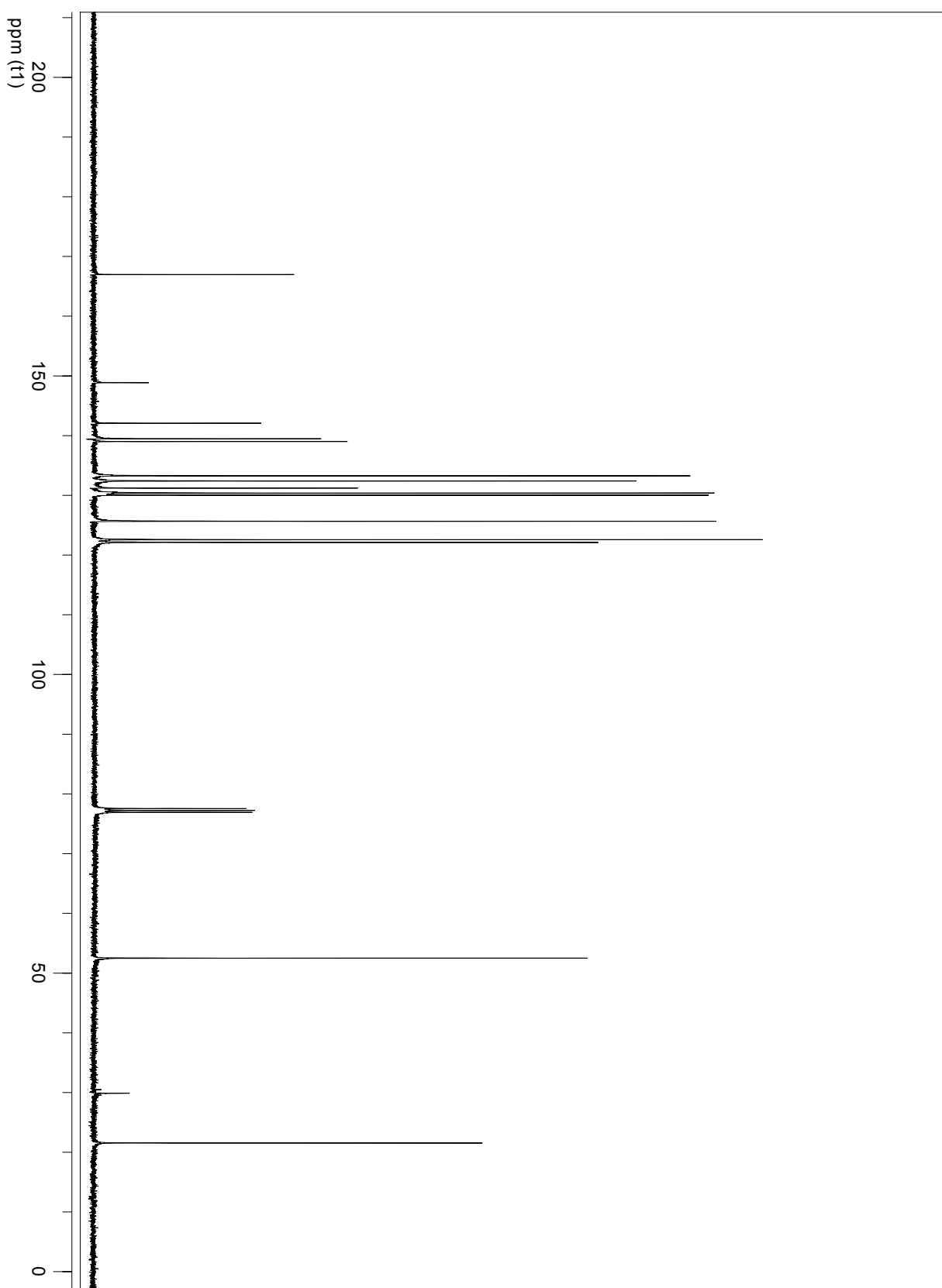
^{13}C -NMR spectrum of compound **6j**



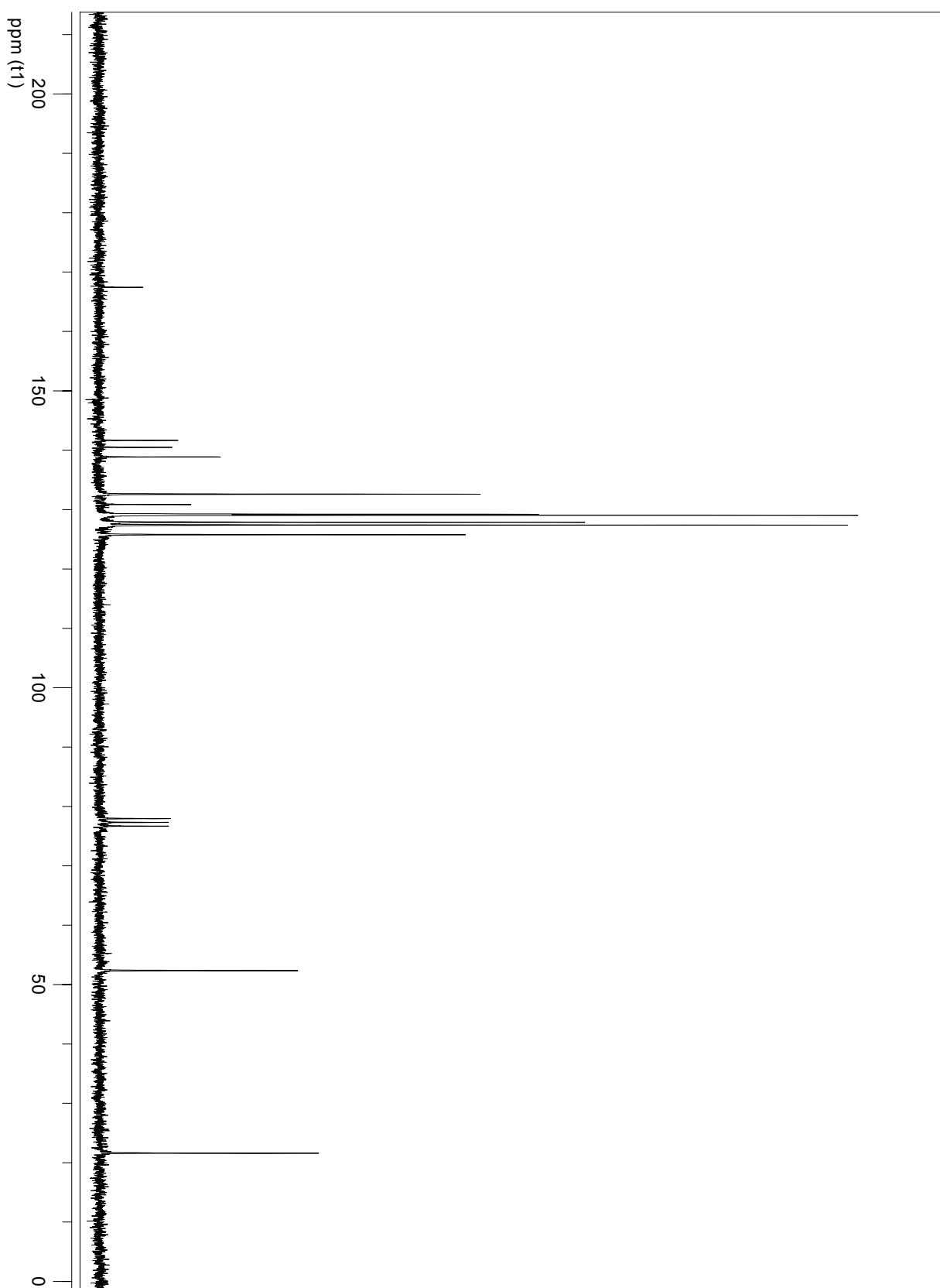
^{13}C -NMR spectrum of compound **6k**



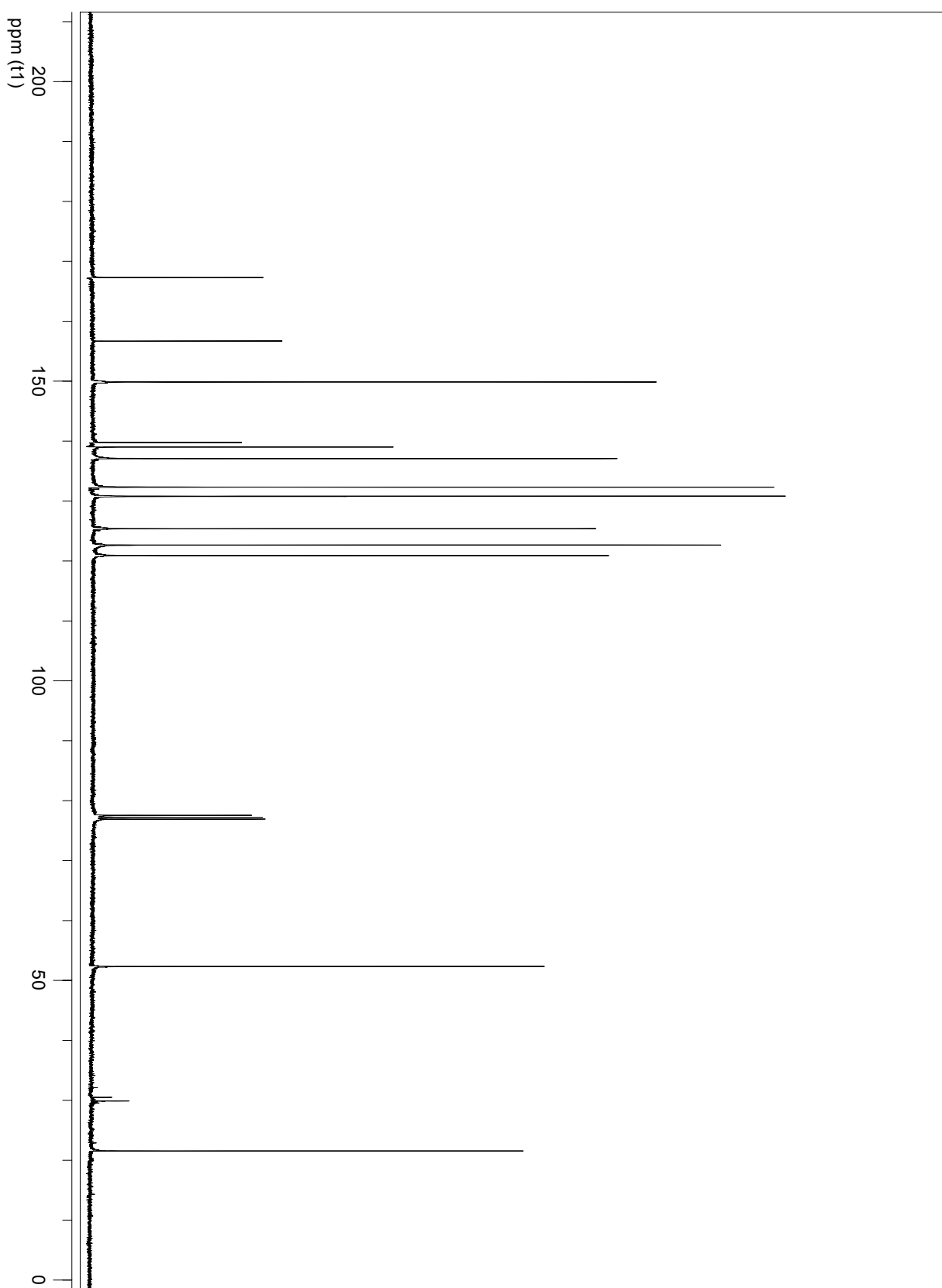
^{13}C -NMR spectrum of compound **6I**



^{13}C -NMR spectrum of compound **6m**



^{13}C -NMR spectrum of compound **6n**



^{13}C -NMR spectrum of compound **60**