Supporting information

Oxygenation of saturated C-H bonds with methyl(trifluoromethyl)dioxirane: effect of the substituents and the solvent on the reaction rate

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General. Solvents were purified by standard procedures[1] and distilled before use. Methyl(trifluoromethyl)dioxirane (**1a**) in ketone-free dichloromethane solution[2a] was prepared as described by Adam and co-workers[2b] and the peroxidic content of the solutions was determined by iodometric titration.[3] Solvents were removed under vacuum at 0 ^{o}C in all the cases.

2-Adamantylacetate [19066-22-9] (**2e**) was prepared by reacting of 2-adamantanol with acetic anhydride in pyridine.[4] 2-Adamantylacetamide [52917-72-3] (**2b**) was prepared by reacting 2-adamantylamine with acetic anhydride.[5] 2-Chloroadamantane [7346-41-0] (**2g**) was prepared by reacting 2-adamantanol with concentrated hydrochloric acid and calcium chloride.[6] 2-Fluoroadamantane [16668-83-0] (**2h**) was prepared by reacting of 2-adamantanol with diethylaminosulfur trifluoride (DAST) following a reported procedure.[7] 2-Adamantyl methanesulfonate [31616-68-9] (**2i**) and 2-adamantyl *para*-toluensulfonate [25139-43-9] (**2k**) were prepared from 2-adamantanol by reacting it with methanesulfonyl chloride and triethylamine in dry dichloromethane[8] and with *para*-toluensulfonyl chloride in dry pyridine respectively.[9] 2-Adamantyl nitrate [64662-51-7] (**2m**) was obtained by reacting 2-bromoadamantane with silver nitrate in anhydrous diethyl ether.[10] 2-Adamantylammonium *para*-chlorobencenesulfonate (**2o**) was synthesized by reacting 2-adamantyl amine with *para*-chlorobencenesulfonic acid in diethyl ether and purified by recrystallization from dichloromethane/hexane.[11] 2-Adamantanecarbonitrile [35856-00-9] (**2j**) was obtained by reacting 2-adamantanone with *para*-tolylsulfonylmethyl isocyanide and potassium *tert*-butoxide following a reported procedure.[12] Reaction of 2-adamantanecarbonitrile (**2j**) with concentrated hydrochloric acid in glacial acetic acid[13] yielded 2-adamantanecarboxylic acid [15897-81-1]. Methyl 2-adamantanecarboxylate [22635-52-5] (**2d**) was prepared by esterification of 2-adamantanecarboxylic acid with methanol

and sulfuric acid.[14] 2-Adamantylmethylketone [22635-58-1] (**2c**) was obtained by reacting 2-adamantanecarboxylic acid with methyllithium.[15] 2-Adamantylmethyl acetate [56419-22-8] (**2a**) was synthesized by reacting lithium aluminium hydride with methyl 2-adamantane carboxylate [22635-52-5],[16] followed by esterification of 2-adamantanemethanol with acetic anhydride in pyridine.[4] 2-Trifluoromethyladamantane [70422-19-4] (**2f**) was prepared by reacting *O*-2-trifluoromethyl-2-adamantyl-S-methyl dithiocarbonate [335379-32-3] with tributyltin hydride in toluene under reflux[17] followed by acid hydrolysis, extraction with dichloromethane and evaporation of the solvents at 0 ^{o}C. *O*-2-trifluoromethyl-2-adamantyl-S-methyl dithiocarbonate was prepared by reacting 2-trifluoromethyl-2-adamantanol [118143-23-0] with potassium hydride, carbon disulfide and methyl iodide.[17] 2-Trifluoromethyl-2-adamantanol was obtained by reacting 2-adamantanone with trifluoromethyltrimethylsilane following a reported procedure.[18] 2-Adamantylmethyl sulfone [23695-67-2] (**2l**) was synthesized[19] by reduction of 2-adamantanethione [23695-65-0] with sodium borohydride, reaction of 2-adamantanethiol [23695-66-1] with sodium ethoxide and methyl iodide and oxidation of the resulting 2-adamantyl methyl sulfide [30979-72-7] with *meta*-chloroperbenzoic acid.[20] 2-Nitroadamantane [54564-31-7] (**2n**) was prepared by oxidation of 2-adamantylamine with *meta*-chloroperbenzoic acid.[20] All products were purified by column chromatography and fully characterized by spectroscopic techniques.

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Spectral characterization of compounds 3.

(*Z*)-5-Hydroxy-2-adamantylmethyl acetate (*Z*-3a). ^{13}C NMR ($CDCl_3$, 75MHz): δ ppm 67.9, 45.6, 41.7, 39.7, 37.0, 31.9, 30.5; MS (EI^+, 70 eV) (*m/z, %*): 224 (5, $[M^+]$), 206 (35), 164 (100), 149 (7), 135 (5), 121 (32), 107 (80), 95 (90); HRMS (EI^+) calcd for $C_{13}H_{20}O_3$ 224.1412, found 224.1404.

(*E*)-5-Hydroxy-2-adamantylmethyl acetate (*E*-3a). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 68.1, 45.9, 45.6, 42.0, 31.4, 30.3, 30.1; MS (EI^+, 70 eV) (*m/z, %*): 224 (0.5, $[M^+]$), 164 (100), 149 (6), 135 (2), 121 (28), 107 (40), 95 (60); HRMS (CI^+) calcd for $C_{13}H_{20}O_3$ (MH^+-H_2) 223.1334, found 223.1329.

(*Z*)-*N*-(5-Hydroxy-2-adamantyl)acetamide (*Z*-3b). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 67.8, 54.1, 46.1, 40.0, 35.9, 35.0, 31.1; MS (EI^+, 70 eV) (*m/z, %*): 209 (100, $[M^+]$), 191 (32), 166 (28), 150 (40), 132 (23), 107 (37), 92 (44), 60 (55); HRMS (EI^+) calcd for $C_{12}H_{19}NO_2$ 209.1416, found 209.1417.

***(E)*-N-(5-Hydroxy-2-adamantyl)acetamide (Z-3b).** ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 67.8, 54.6, 46.1, 45.2, 35.0, 31.1, 31.1; MS (EI^+, 70 eV) (m/z, %): 209 (100, $[M^+]$), 191 (27), 166 (36), 150 (43), 132 (26), 107 (30), 92 (42), 60 (50); HRMS (EI^+) calcd for $C_{12}H_{19}NO_2$ 209.1416, found 209.1417.

(*Z*)-2-(5-Hydroxyadamantyl)methylketone (*Z*-3c). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 210.2, 67.5, 56.0, 44.6, 41.2, 36.6, 31.7, 29.9, 27.4; MS (EI^+, 70 eV) (*m/z, %*): 194 (7, $[M^+]$), 150 (10), 77 (20), 73 (49), 43 (100), 39 (24); HRMS (EI^+) calcd for $C_{12}H_{18}O_2$ 194.1306, found 194.1304.

(*E*)-2-(5-Hydroxyadamantyl)methylketone (*E*-3c). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 210.0, 67.9, 56.4, 45.5, 45.0, 31.8, 31.5, 29.9, 27.9; MS (EI^+, 70 eV) (*m/z, %*): 194 (9, [M^+]), 150 (18), 95 (20), 91 (27), 77 (32), 73 (27), 43 (100), 39(30); HRMS (EI^+) calcd for $C_{12}H_{18}O_2$ 194.1306, found 194.1304.

(*Z*)-Methyl 5-hydroxy-2-adamantanecarboxylate (*Z*-3d). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.2, 67.4, 51.4, 47.9, 44.7, 41.4, 36.3, 32.0, 29.8; MS (EI^+, 70 eV) (*m/z, %*): 210 (63, [M^+]), 195 (10), 178 (22), 151 (23), 109 (23), 101 (26), 95 (100), 91 (30), 79 (38), 77 (30), 74 (25), 41 (29), 39 (21); HRMS (EI^+) calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1252.

(*E*)-Methyl 5-hydroxy-2-adamantanecarboxylate (*E*-3d). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.3, 67.5, 51.4, 48.2, 45.1, 44.9, 32.0, 31.7, 29.6; MS (EI^+, 70 eV) (*m/z, %*): 210 (41, [M^+]), 195 (7), 178 (38), 147 (18), 116 (20), 101 (32), 95 (100), 91 (48), 79 (41), 77 (49), 73 (67), 59 (44), 41 (49), 39 (45), 29 (27), 15 (34); HRMS (EI^+): calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1253.

(*Z*)-5-Hydroxy-2-adamantyl acetate (*Z*-3e). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 74.7, 67.1, 44.9, 39.3, 34.3, 34.6, 29.2; MS (mixture of isomers) (EI^+, 70 eV) (*m/z, %*): 210 (3, [M^+]), 184 (3), 164 (2), 150 (83), 132 (24), 108 (43), 107 (55), 95 (84), 93 (74), 92 (100), 79 (27); HRMS (EI^+) calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1253.

(*E*)- 5-Hydroxy-2-adamantyl acetate (*E*-3e). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 75.5, 67.1, 44.6, 43.1, 33.2, 33.2, 29.4; MS (mixture of isomers) (EI^+, 70 eV) (*m/z, %*): 210 (3, [M^+]), 184 (3), 164 (2), 150 (83), 132 (24), 108 (43), 107 (55), 95 (84), 93 (74), 92 (100), 79 (27); HRMS (EI^+) calcd for $C_{12}H_{18}O_3$ 210.1256, found 210.1253.

(*Z*)-4-Trifluoromethyl-1-adamantanol (*Z*-3f). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 127.5 (q, *J* = 280 Hz), 67.2, 46.4 (q, *J* = 25 Hz), 45.1, 40.1 (d, *J* = 1 Hz), 37.3, 30.1, 30.0 (q, *J* = 2 Hz); MS (EI^+, 70 eV) (*m/z, %*): 220 (32, [M^+]), 163 (50), 143 (10), 95 (100), 77 (12); HRMS (EI^+) calcd for $C_{11}H_{15}F_3O$ 220.1075, found 220.1074.

(*E*)-4-Trifluoromethyl-1-adamantanol (*E*-3f). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 127.8 (q, *J* = 281 Hz), 67.7, 46.7 (q, *J* = 26 Hz), 46.0, 45.3, 30.5 (q, *J* = 1 Hz), 29.3 (q, *J* = 2 Hz), 29.2; MS (EI^+, 70 eV) (*m/z, %*): 220 (22, [M^+]), 163 (9), 95 (100), 77 (6); HRMS (EI^+) calcd for $C_{11}H_{15}F_3O$ 220.1075, found 220.1076.

(*Z*)-4-Chloro-1-adamantanol (*Z*-3g). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 67.4, 65.4, 44.9, 38.8, 38.5, 36.5, 29.0; MS (EI^+, 70 eV) (*m/z, %*): 186 (20, [M^+]), 96 (21), 95 (100); HRMS (EI^+) calcd for $C_{10}H_{15}ClO$ 186.0811, found 210.1253.

(*E*)-4-Chloro-1-adamantanol (*E*-3g). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 67.0, 65.8, 45.5, 44.9, 37.4, 29.7, 29.5; MS (EI^+, 70 eV) (*m/z, %*): 186 (25, [M^+]), 96 (16), 95 (100); HRMS (EI^+) calcd for $C_{10}H_{15}ClO$ 186.0811, found 186.0814.

(*Z*)-4-Fluor-1-adamantanol (*Z*-3h). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 93.2, 67.2, 44.6, 39.2, 35.3, 34.1, 29.1; MS (EI^+, 70 eV) (*m/z, %*): 170 (100, [M^+]), 150 (7), 113 (14), 95 (75), 71 (7), 57 (10); HRMS (EI^+) calcd for $C_{10}H_{14}FO$ 170.1107, found 170.1100.

(*E*)-4-Fluor-1-adamantanol (*E*-3h). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 94.2, 67.5, 45.1, 42.5, 34.3, 30.0, 29.5; MS (EI^+, 70 eV) (*m/z, %*): 170 (35, [M^+]), 155 (6), 139 (8), 125 (11), 11 (18), 95 (100), 85 (29), 71 (46), 57 (93); HRMS (EI^+) calcd for $C_{10}H_{14}FO$ 170.1107, found 170.1101.

(*Z*)-5-Hydroxy-2-adamantyl methanesulfonate (*Z*-3i). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 83.1, 66.9, 44.5, 38.9, 38.7, 35.7, 34.7, 28.8; MS (EI^+, 70 eV) (*m/z, %*): 246 (0.5, [M^+]), 167 (2), 150 (100), 132 (10), 121 (3), 107 (80), 95 (90), 92 (85); HRMS (EI^+) calcd for $C_{11}H_{18}O_4S$ 246.0925, found 246.0920.

(*E*)-5-Hydroxy-2-adamantyl methanesulfonate (*E*-3i). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 83.9, 66.9, 44.9, 43.1, 38.7, 34.6, 29.8, 29.2; MS (EI^+, 70 eV) (*m/z, %*): 246 (0.1, [M^+]), 167 (2), 150 (80), 132 (10), 121 (3), 107 (15), 95 (72), 92 (100); HRMS (EI^+) calcd for $C_{11}H_{18}O_4S$ 246.0926, found 246,0930.

(*Z*)-5-Hydroxy-2-adamantanecarbonitrile (*Z*-3j). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 121.4, 66.9, 44.2, 41.0, 35.5, 35.1, 33.1, 29.1; MS (EI^+, 70 eV) (*m/z, %*): 177 (19, [M^+]), 95 (100); HRMS (CI^+) calcd for $C_{11}H_{16}NO$ 178.1232, found 178.1231.

(*E*)-5-Hydroxy-2-adamantanecarbonitrile (*E*-3j). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 121.6, 66.7, 44.6, 44.0, 35.8, 32.9, 31.7, 29.4; MS (EI^+, 70 eV) (*m/z, %*): 177 (19, [M^+]), 120 (20), 95 (100); HRMS (CI^+): calcd for $C_{11}H_{16}NO$ 178.1232, found 178.1234.

(*Z*)-5-Hydroxy-2-adamantyl *para*-toluensulfonate (*Z*-3k). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 146.0, 136.2, 131.3, 129.0, 85.1, 68.5, 46.0, 40.5, 37.0, 36.4, 30.4, 23.15; MS (EI^+, 70 eV) (*m/z, %*): 322 (17, [M^+]), 173 (7), 150 (56), 132 (22), 117 (14), 109 (10), 108 (32), 107 (67), 95 (100), 93 (58), 91 (81); HRMS (EI^+)calcd for $C_{17}H_{22}O_4S$ 322.1239, found 322.1238.

(*E*)-5-Hydroxy-2-adamantyl *para*-toluensulfonate (*E*-3k). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 144.5, 134.5, 129.8, 127.5, 84.2, 67.0, 44.9, 43.2, 34.3, 29.7, 29.2, 21.6;

MS (EI^+, 70 eV) (*m/z, %*): 322 (17, [M^+]), 279 (5), 173 (8), 150 (62), 132 (28), 108 (21), 95 (94), 93 (87), 91 (100); HRMS (EI^+) calcd for $C_{17}H_{22}O_4S$ 322.1280, found 322.1240.

(*Z*)-(5-Hydroxy-2-adamantyl)methylsulfone (*Z*-3l). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 67.0, 66.2, 44.1, 39.8, 39.5, 37.4, 30.9, 29.7; MS (EI^+, 70 eV) (*m/z, %*): 230 (1, [M^+]), 151 (100), 107 (25), 95 (20), 91 (20), HRMS (EI^+) calcd for $C_{11}H_{18}SO_3$ 230.0977, found 230.0976.

(*E*)-(5-Hydroxy-2-adamantyl)methylsulfone (*E*-3l). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 67.4, 66.5, 45.8, 44.9, 40.3, 30.3, 29.9, 29.3; MS (EI^+, 70 eV) (*m/z, %*): 230 (1, [M^+]), 151 (100), 107 (20), 91 (22); HRMS (EI^+) calcd for $C_{11}H_{18}SO_3$ 230.0977, found 230.0976.

(*Z*)-5-Hydroxy-2-adamantyl nitrate (*Z*-3m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm 84.0, 67.0, 44.4, 39.5, 34.8, 33.5, 29.1; MS (EI^+, 70 eV) (*m/z, %*): 213 (27, [M^+]), 167 (16), 151 (35), 149 (100), 131 (25), 121 (72), 107 (34), 95 (52), 79 (55), 67 (32); HRMS (EI^+) calcd for $C_{10}H_{15}NO_4$ 213.1001, found 213.1001.

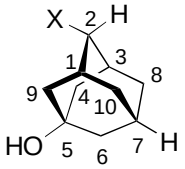
(*E*)-5-Hydroxy-2-adamantyl nitrate (*E*-3m). ^{13}C NMR ($CDCl_3$, 75 MHz): δ ppm. 84.67, 67.2, 44.8, 43.2, 32.4, 30.2, 29.2; MS (EI^+, 70 eV) (*m/z, %*): 213 (7, [M^+]), 167 (20), 149 (100), 131 (20), 121 (58), 107 (35), 95 (48), 79 (55), 67 (32); HRMS (EI^+) calcd for $C_{10}H_{15}NO_4$ 213.1001, found 213.0997.

(*Z*)-4-Nitro-1-adamantanol (*Z*-3n). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 86.5, 66.7, 44.3, 39.8, 35.3, 33.7, 29.0; MS (EI^+, 70 eV) (*m/z, %*): 197 (1, [M^+]), 151 (100), 107 (52), 95 (34), 93 (37), 91 (31); HRMS (CI^-) calcd for $C_{10}H_{14}NO_3$ 196.0974, found 196.0968.

(*E*)-4-Nitro-1-adamantanol (*E*-3n). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 87.1, 67.1, 44.8, 43.7, 33.0, 30.7, 28.9; MS (EI^+, 70 eV) (*m/z, %*): 197 (8, [M^+]), 151 (100), 133 (14), 107 (32), 95 (45), 93 (37), 91 (33), 81 (20), 79 (24); HRMS (CI^-) calcd for $C_{10}H_{14}NO_3$ 196.0974, found 196.0974.

(*Z*)-4-Amino-1-adamantanol (*Z*-3o). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 67.4, 55.3, 45.8, 38.7, 36.5, 35.1, 30.7 ; MS (EI^+, 70 eV) (*m/z, %*): 167 (31, [M^+]), 166 (50), 150 (24), 107 (52), 95 (55), 79 (40), 70 (40), 56 (100); HRMS (CI^-) calcd for $C_{10}H_{17}NO$167.1310, found 167.1308.

(*E*)-4-Amino-1-adamantanol (*E*-3o). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 67.2, 55.9, 45.7, 44.6, 34.2, 30.8, 29.9; MS (EI^+, 70 eV) (*m/z, %*): 167 (25, [M^+]), 150 (22), 108 (25), 107 (42), 95 (48), 79 (34), 70 (40), 56 (100), 79 (24); HRMS (CI^-) calcd for $C_{10}H_{14}NO_3$ 167.1310, found 167.1311.

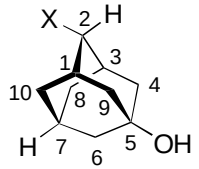


(Z)-**3**

Table 1: ^{13}C-NMR and HRMS data for isomers *Z* of compounds **3**.[a]

X	***C*$_{1,3}$**	***C*$_2$**	***C*$_{4,9}$**	***C*$_5$**	***C*$_6$**	***C*$_7$**	***C*$_{8,10}$**	**HRMS**[b]
CH_2OCOCH_3	36.97	41.77	39.73	67.91	45.60	30.46	31.90	CI^+ (223.1334) 223.1330[c]
$NHCOCH_3$	35.90	54.17	39.97	67.83	46.10	31.12	36.88	EI^+ (209.1416) 209.1417[c]
$COCH_3$	31.69	56.02	41.18	67.54	44.56	29.94	36.62	EI^+ (194.130680) 194.130395
$COOCH_3$	32.03	47.93	41.35	67.37	44.71	29.76	36.31	EI^+ (210.125595) 210.125247[c]
$OCOCH_3$[c]	34.35	74.73	39.31	67.11	44.78	29.18	34.59	EI^+ (210.1256) 210.1253[c]
CF_3	29.99 (2 Hz)	46.42 (25 Hz)	40.06 (1 Hz)	67.21	45.14	30.13	37.26	EI^+ (220.1075) 2220.1074
Cl	38.52	65.39	38.76	67.43	44.91	29.04	36.47	EI^+ (186.081143) 186.081211
F	35.35 (18 Hz)	93.23 (178 Hz)	39.25	67.21	44.55	29.10	34.07 (9 Hz)	EI^+ (170.1107) 170.1100
OSO_2CH_3	34.72	83.13	38.88	66.83	44.46	28.80	35.66	EI^+ (246.0926) 246.0920
CN	31.11	35.53	40.97	66.86	44.16	29.12	35.06	CI^+ (178.123189) 178.123115
OTs	35.42	83.52	38.97	66.95	44.48	28.89	34.81	EI^+ (322.1239) 322.1238
SO_2CH_3	30.88	66.17	39.48	67.02	44.08	29.74	37.37	EI^+ (230.097666) 230.097565[c]
ONO_2	33.48	84.00	39.46	66.99	44.38	29.13	34.80	EI^+ (213.1001) 213.1001
NO_2	33.70	86.52	38.95	66.67	44.34	28.99	35.29	CI^- (196.0974) 196.0968
NH_3^{+d}	35.14	55.34	38.74	67.36	45.77	30.67	36.52	EI^+(168.1388) 168.1372

[a] ^{13}C NMR at 52.80 MHz, chloroform-d_1, δ (ppm). Only representative signals are reported. [b] (Calculated) Found. [c] Data corresponds to the mixture of isomers. [d] Spectra recorded in methanol-d_4.



(E)-**3**

Table 2: ^{13}C-NMR and HRMS data for isomers *E* of compounds **3**.[a]

X	$C_{1,3}$	C_2	$C_{4,9}$	C_5	C_6	C_7	$C_{8,10}$	**HRMS**[b]
CH_2OCOCH_3	31.39	41.99	45.91	68.12	45.63	36.15	30.28	CI^+ (223.1334) 223.1329
$NHCOCH_3$	35.03	54.60	45.21	67.83	45.93	31.12	31.12	EI^+ (209.1416) 209.1417[c]
$COCH_3$	31.51	56.43	45.55	67.90	45.00	29.93	31.83	EI^+ (194.130680) 194.130394
$COOCH_3$	31.99	48.24	45.15	67.45	44.87	29.63	31.68	EI^+ (210.125595) 210.125247[c]
$OCOCH_3$[c]	33.32	75.51	43.12	67.11	44.88	29.37	30.15	EI^+ (210.1256) 210.1253[c]
CF_3	29.28 (2 Hz)	46.72 (26 Hz)	46.00	67.66	45.33	29.24	30.54 (1 Hz)	EI^+ (220.1075) 2220.1076
Cl	37.41	65.78	44.89	66.99	45.47	29.74	29.50	EI^+ (186.081143) 186.081482
F	34.33 (18 Hz)	94.16 (178Hz)	42.53 (9 Hz)	67.45	45.09	29.60	30.03	EI^+ (170.1107) 170.1101
OSO_2CH_3	34.66	83.89	43.15	66.90	44.90	29.20	29.78	EI^+ (246.0926) 246.0930
CN	32.87	35.83	44.04	66.69	44.59	29.41	31.67	CI^+ (178.123189) 178.123447
OTs	33.34	84.26	42.21	65.99	43.97	28.20	28.76	EI^+ (322.1239) 322.1240
SO_2CH_3	30.27	66.49	45.85	67.44	44.91	29.26	29.93	EI^+(230.097666) 230.097565[c]
ONO_2	32.45	84.67	43.18	67.18	44.81	29.20	30.18	EI^+ (213.1001) 213.0997[c]
NO_2	33.01	87.11	43.68	67.06	44.78	28.91	30.67	CI^- (196.0974) 196.0974
NH_3^+	34.21	55.93	44.64	67.24	45.73	30.78	29.88	EI^+ (168.1388) 168.1342[c]

[a] ^{13}C NMR at 52.80 MHz, chloroform-d_1, δ (ppm). Only representative signals are reported. [b] (Calculated) Found. [c] Data corresponds to the mixture of isomers. [d] Spectra recorded in methanol-d_4.

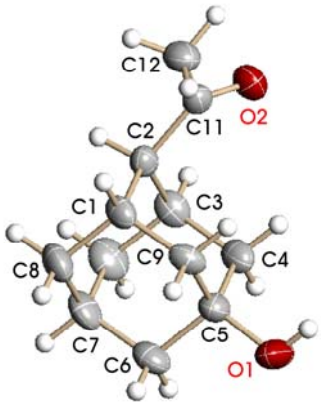


Figure 1. Ellipsoid plot of compound (*Z*)-**3c** in the crystal (40% probability level).

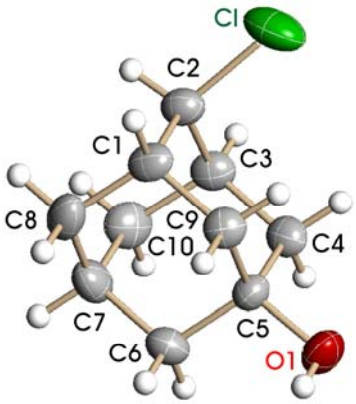


Figure 2. Ellipsoid plot of one of the two molecules of compound (*Z*)-**3g** in the crystal asymmetric unit.

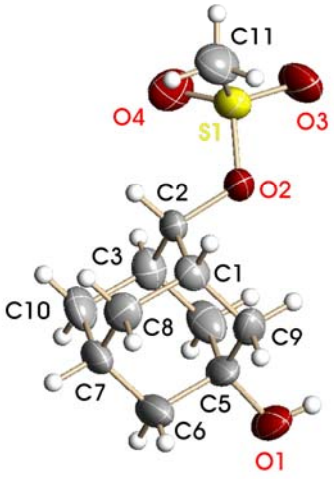


Figure 3. Ellipsoid plot of one of the four molecules of compound (*Z*)-**3i** in the crystal asymmetric unit (40% probability level).

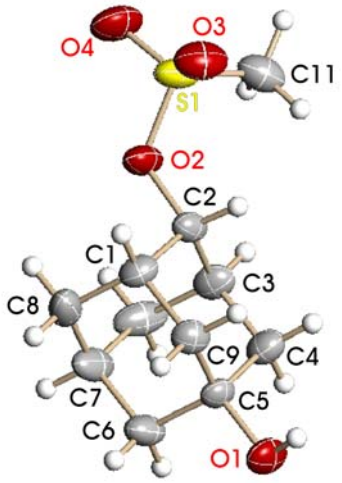


Figure 4. Ellipsoid plot of one of the two molecules of compound (*E*)-**3i** in the crystal asymmetric unit.

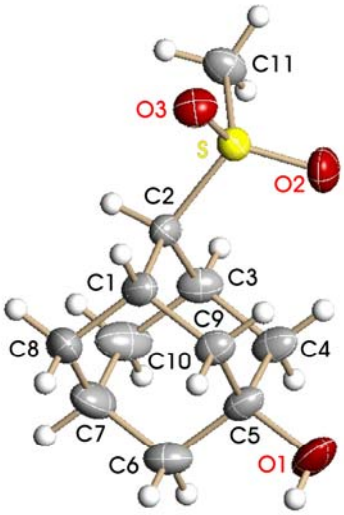


Figure 5. Ellipsoid plot of compound (*Z*)-**3l** in the crystal.

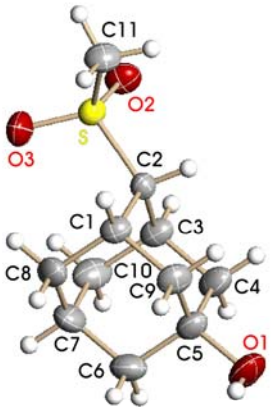


Figure 6. Ellipsoid plot of compound (*E*)-**3l** in the crystal.

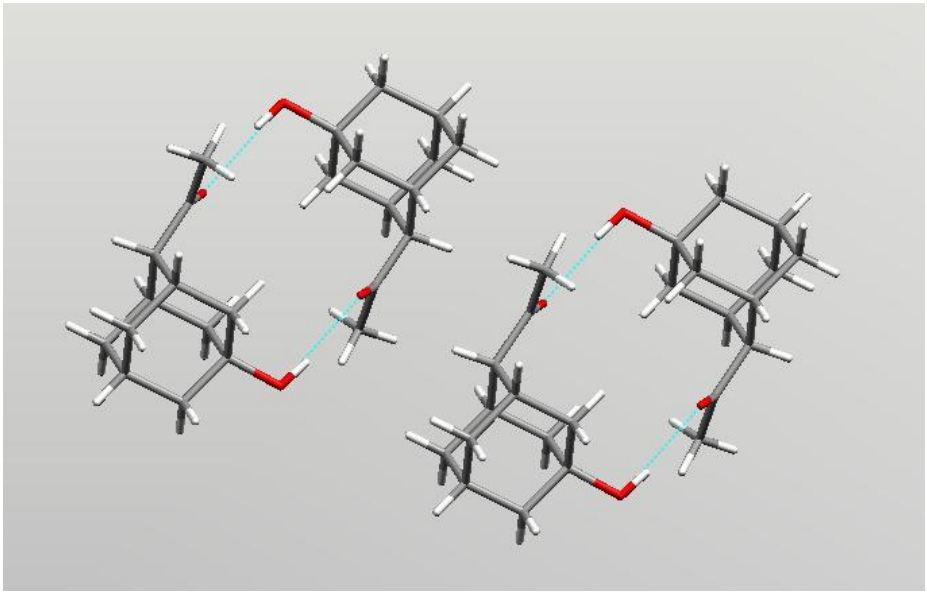


Figure 7. Crystal view of compound (*Z*)-**3c** showing two dimers formed through intermolecular O-H···O=C hydrogen bonds. White hydrogen, grey carbon and red oxygen atoms. O-H···O=C interactions are shown in light blue colour.

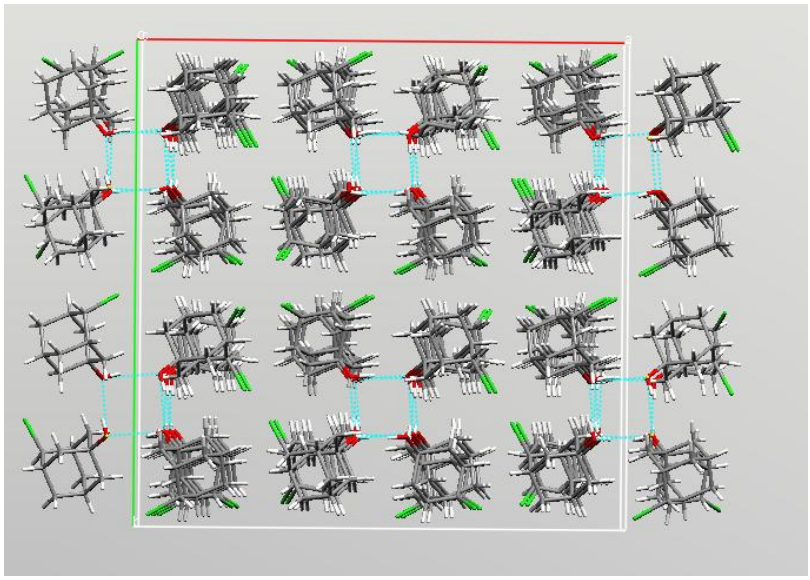


Figure 8. Crystal view of compound (*Z*)-**3g** along the *c* axis showing the stacking of tetramers, which are formed along a 4-fold axis through intermolecular O-H···O hydrogen bonds. White hydrogen, grey carbon, green chlorine and red oxygen atoms. O-H···O interactions are shown in light blue colour.

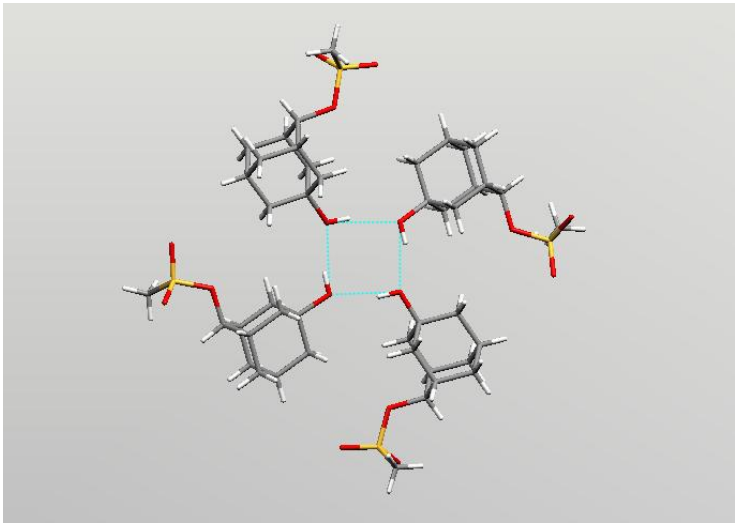


Figure 9. Crystal asymmetric unit of compound (*Z*)-**3i** showing the tetramer formed through intermolecular O-H···O hydrogen bonds. White hydrogen, grey carbon, yellow sulphur and red oxygen atoms. O-H···O interactions are shown in light blue colour.

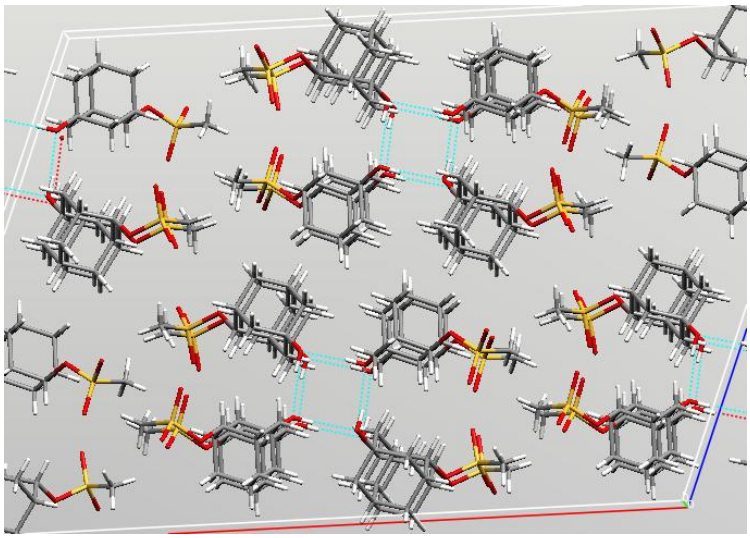


Figure 10. Crystal view of compound (*E*)-**3i** along the *b* axis showing the stacking of tetramers, which are formed through intermolecular O-H···O hydrogen bonds. White hydrogen, grey carbon, yellow sulphur and red oxygen atoms. O-H···O interactions are shown in light blue colour.

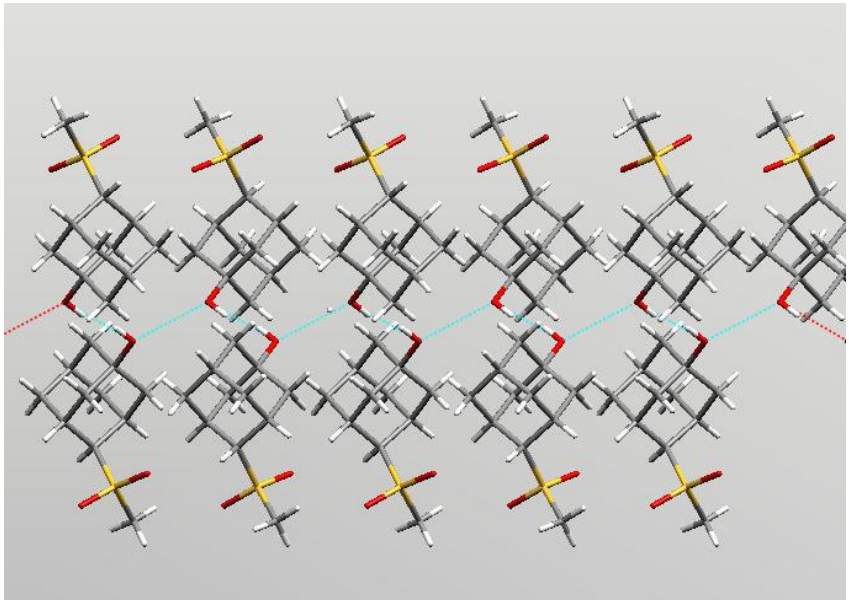


Figure 11. Crystal view of compound (*Z*)-**3l** along the *b* axis showing the infinite zigzag chains, which are formed through intermolecular O-H···O hydrogen bonds. The hydroxyl group is disordered over two sites and the two alternative H atom sites correspond to opposite directions of H bonding along the chain. White hydrogen, grey carbon, yellow sulphur and red oxygen atoms. O-H···O interactions are shown in light blue colour.

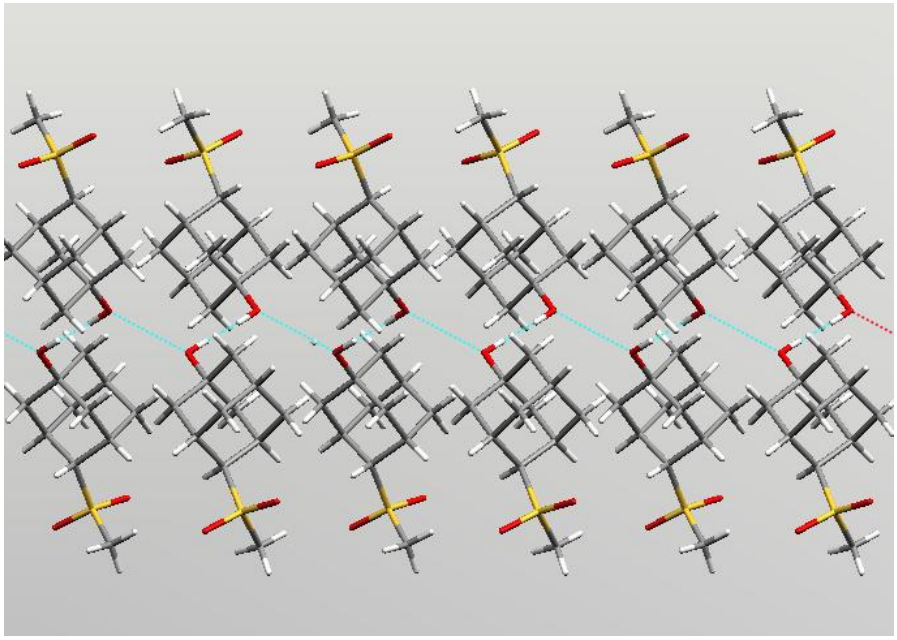
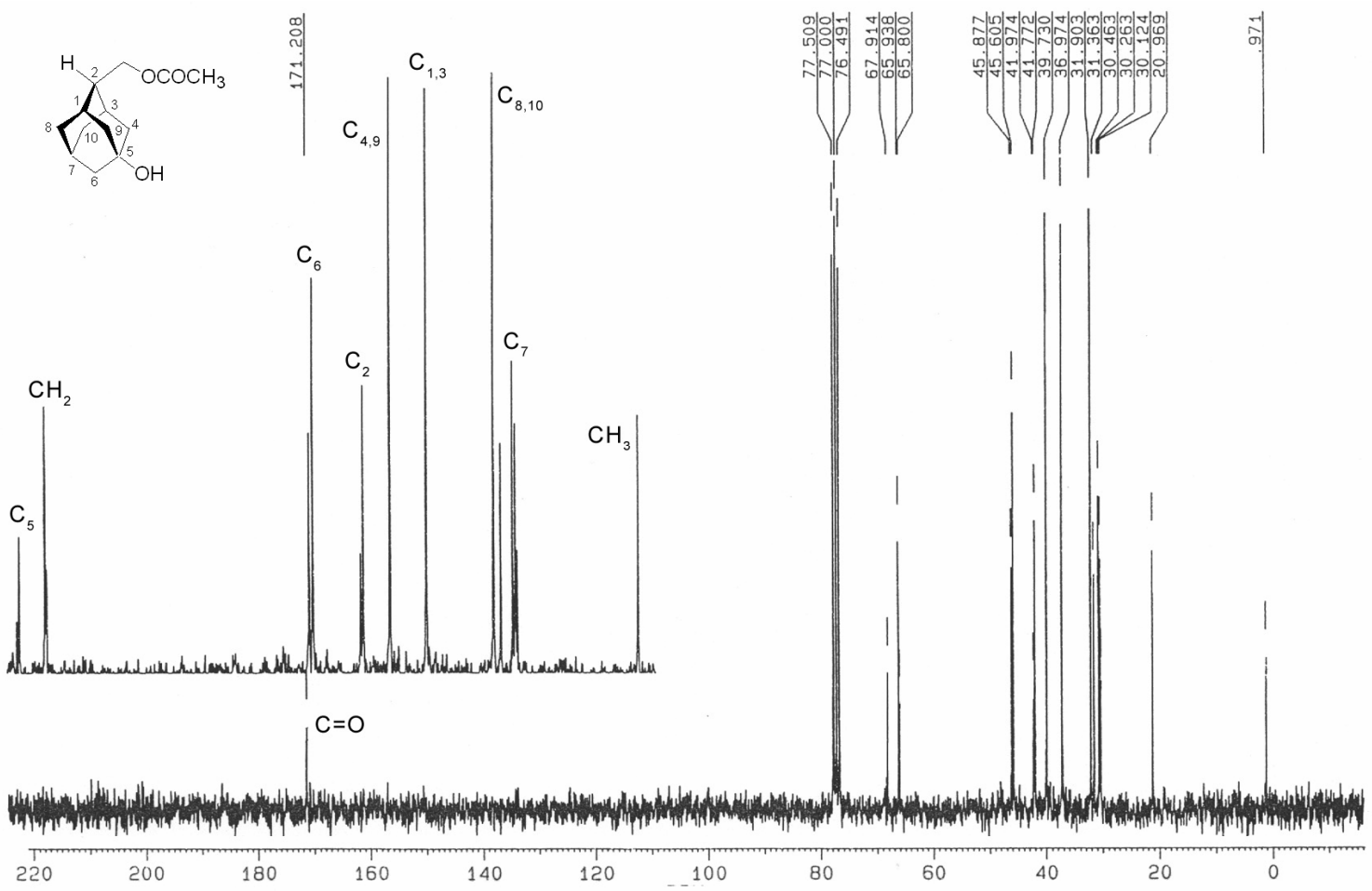
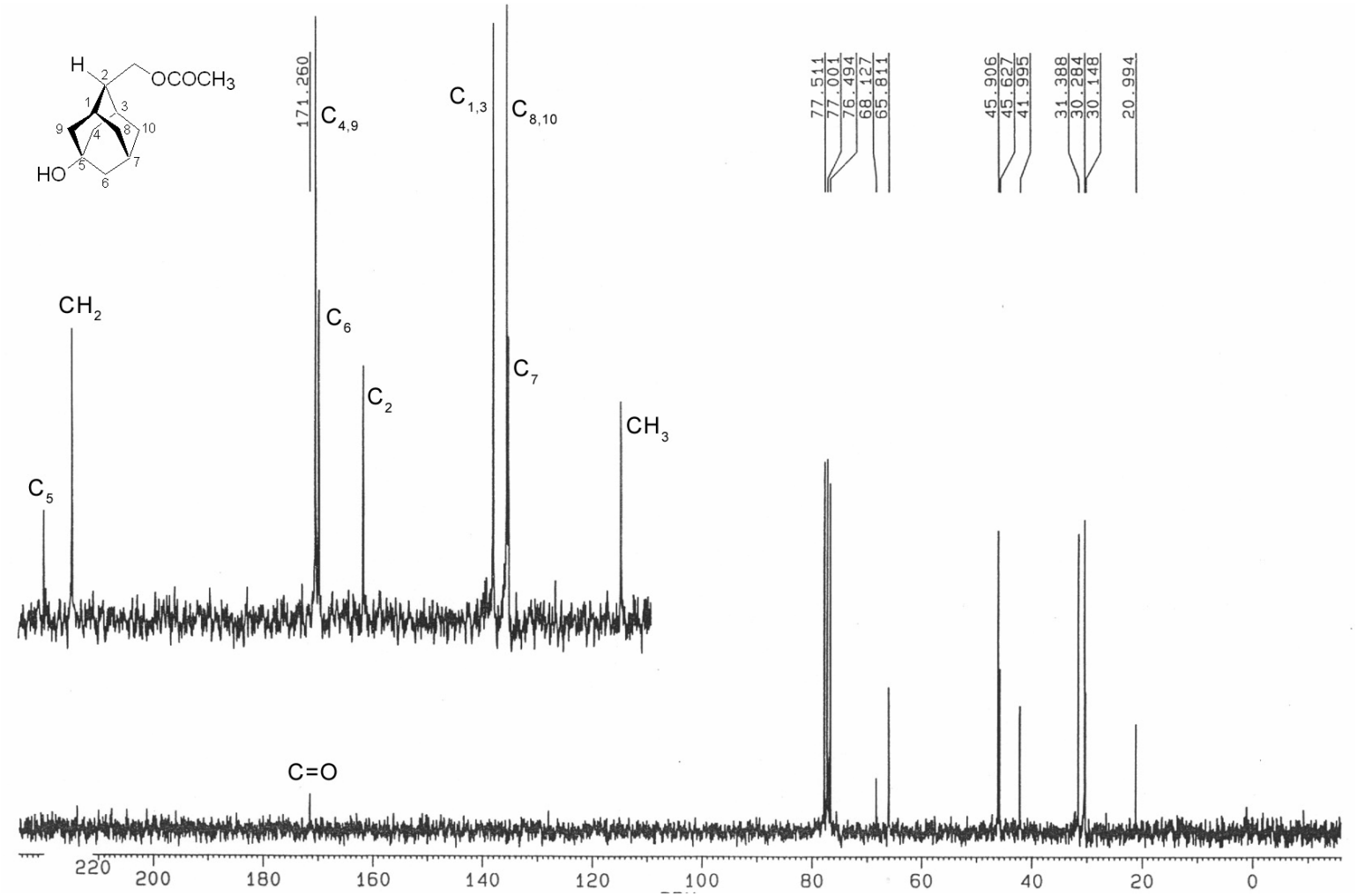


Figure 12. Crystal view of compound (*E*)-**3l** along the *b* axis showing the infinite zigzag chains, which are formed through intermolecular O-H···O hydrogen bonds. The hydroxyl group is disordered over two sites and the two alternative H atom sites correspond to opposite directions of H bonding along the chain. White hydrogen, grey carbon, yellow sulphur and red oxygen atoms. O-H···O interactions are shown in light blue colour.

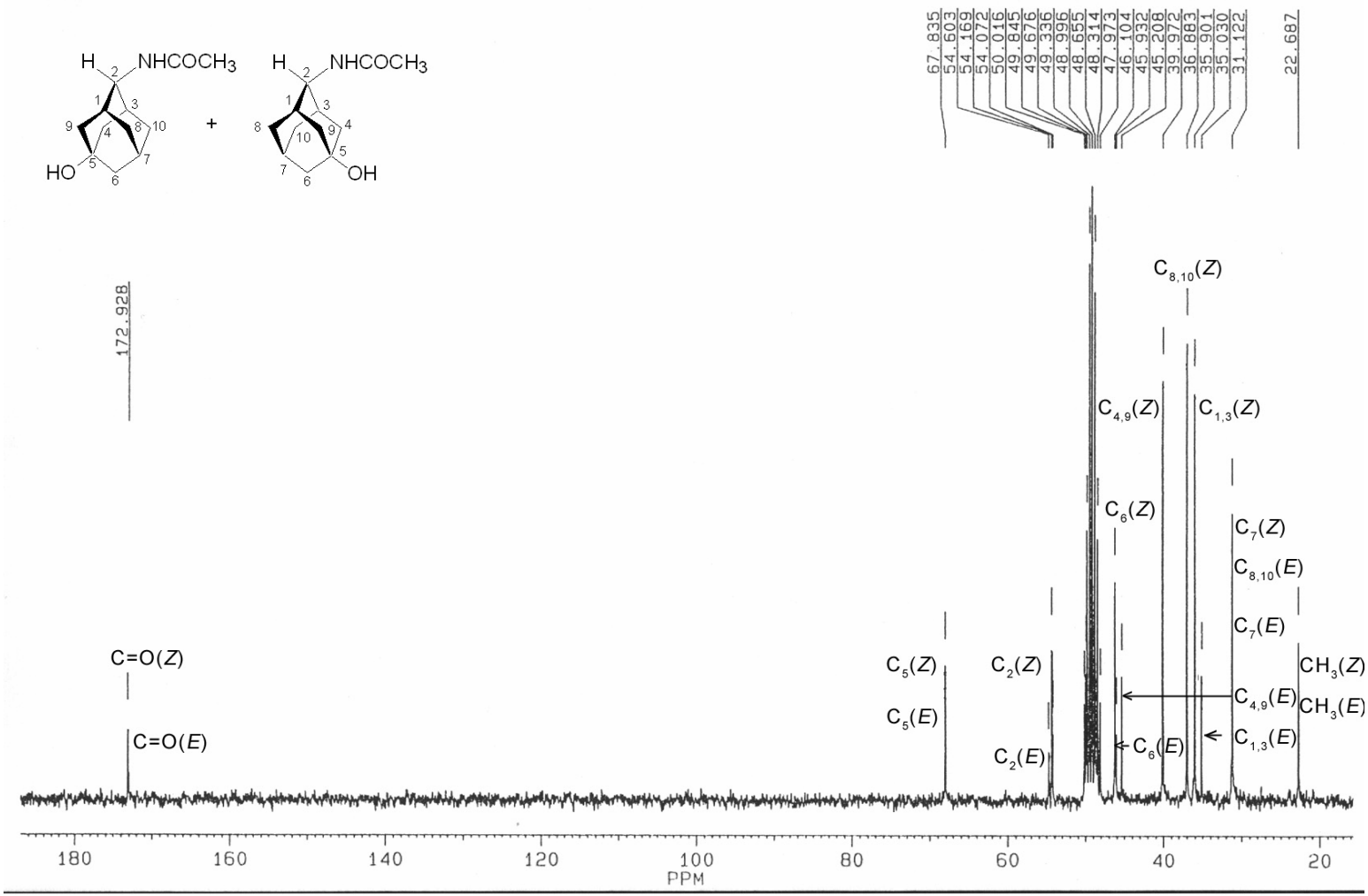
(*Z*)-5-Hydroxy-2-adamantylmethyl acetate (*Z*-3a)



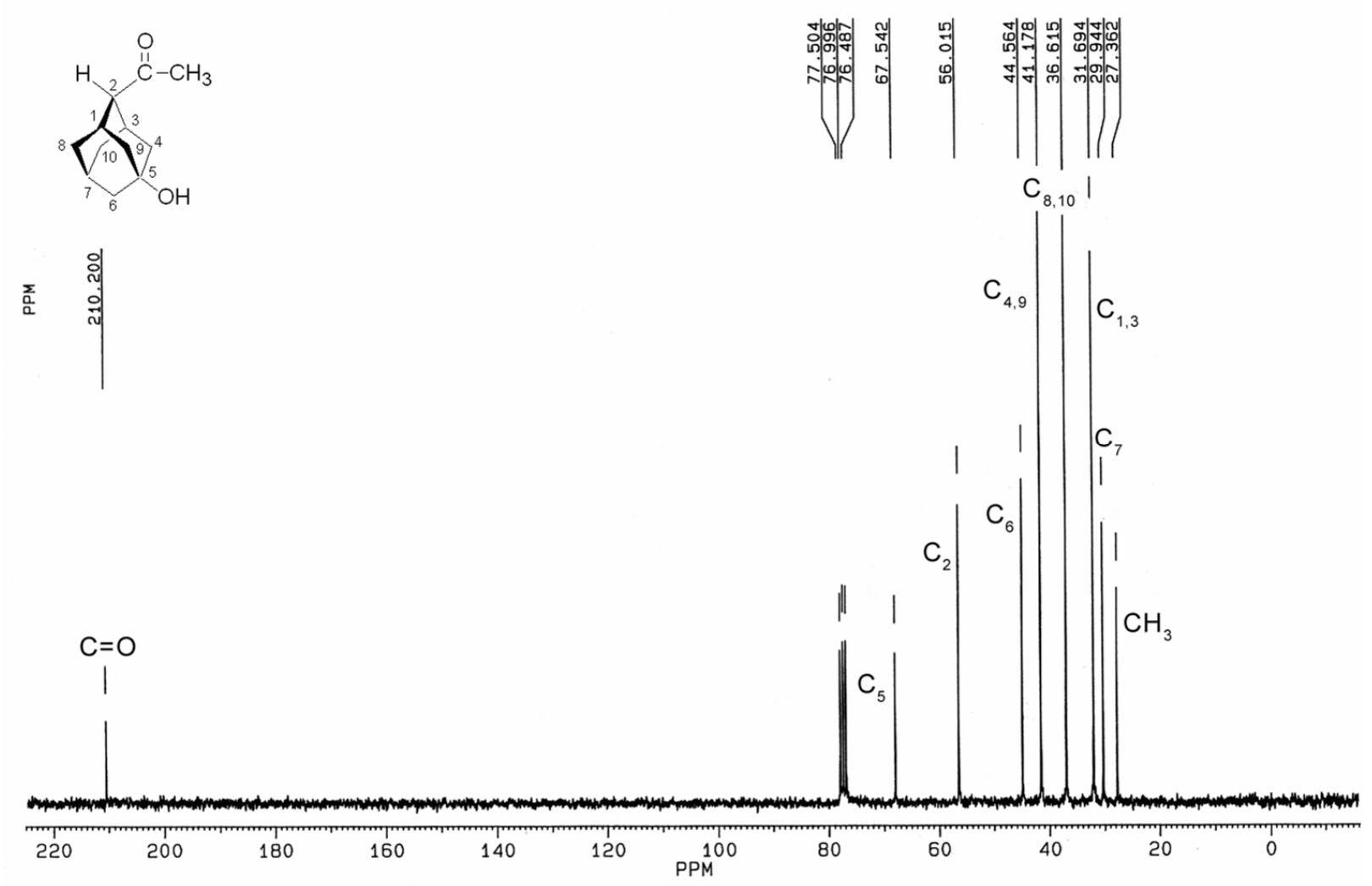
(*E*)-5-Hydroxy-2-adamantylmethyl acetate (*E*-3a)



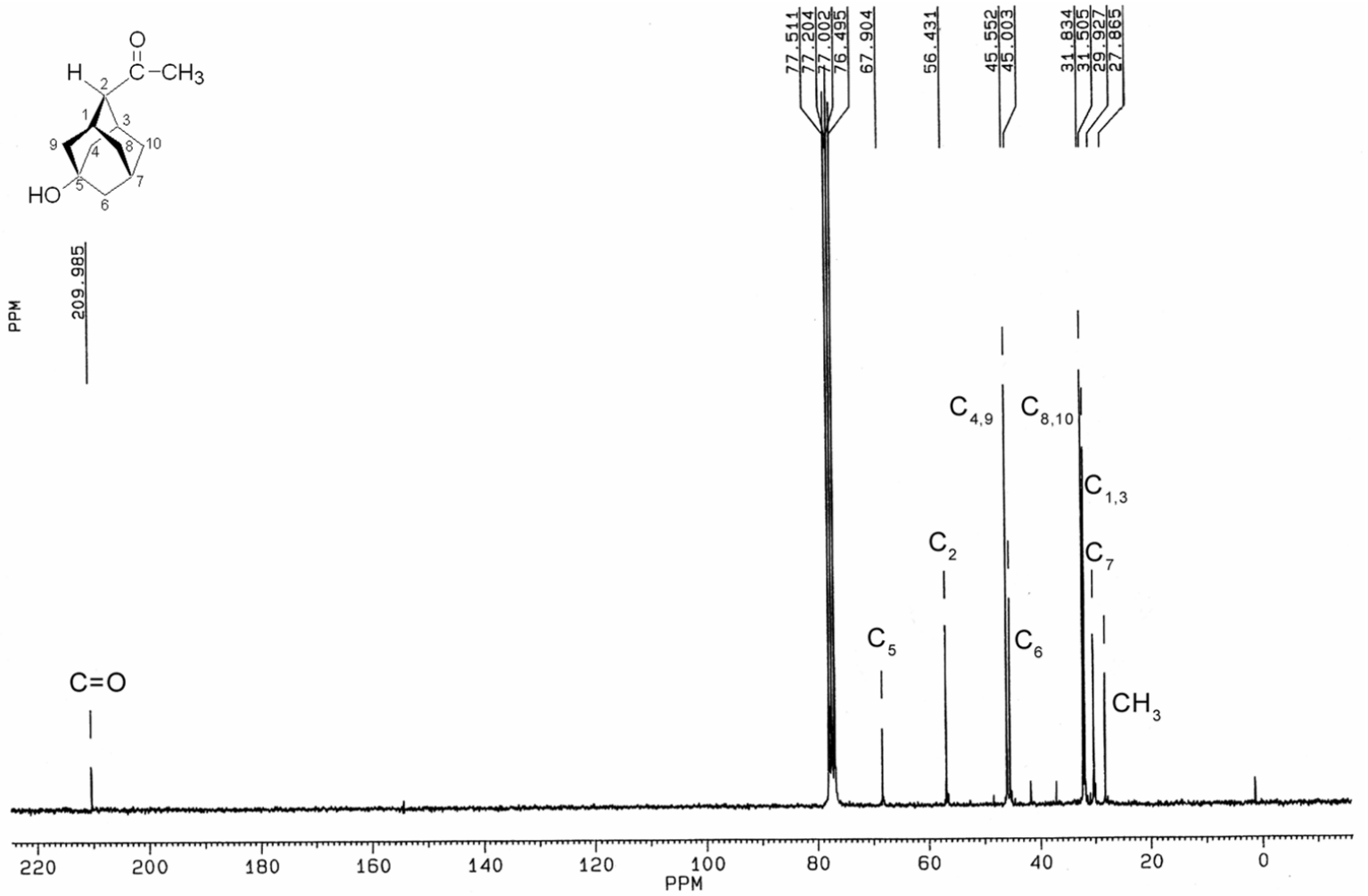
***N*-(5-Hydroxy-2-adamantyl)acetamide (3b)**



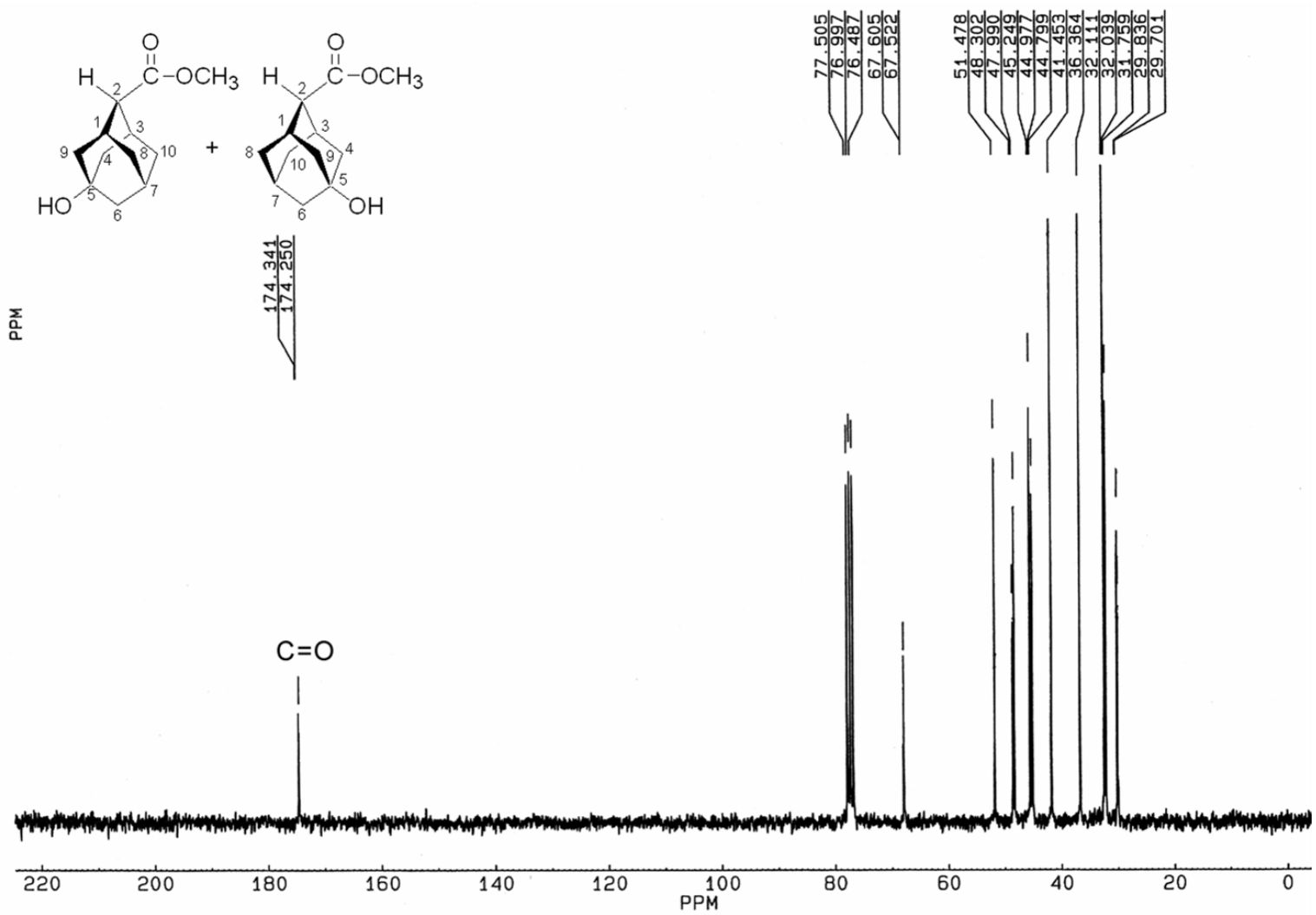
(*Z*)-2-(5-Hydroxyadamantyl)methylketone (*Z*-3c)



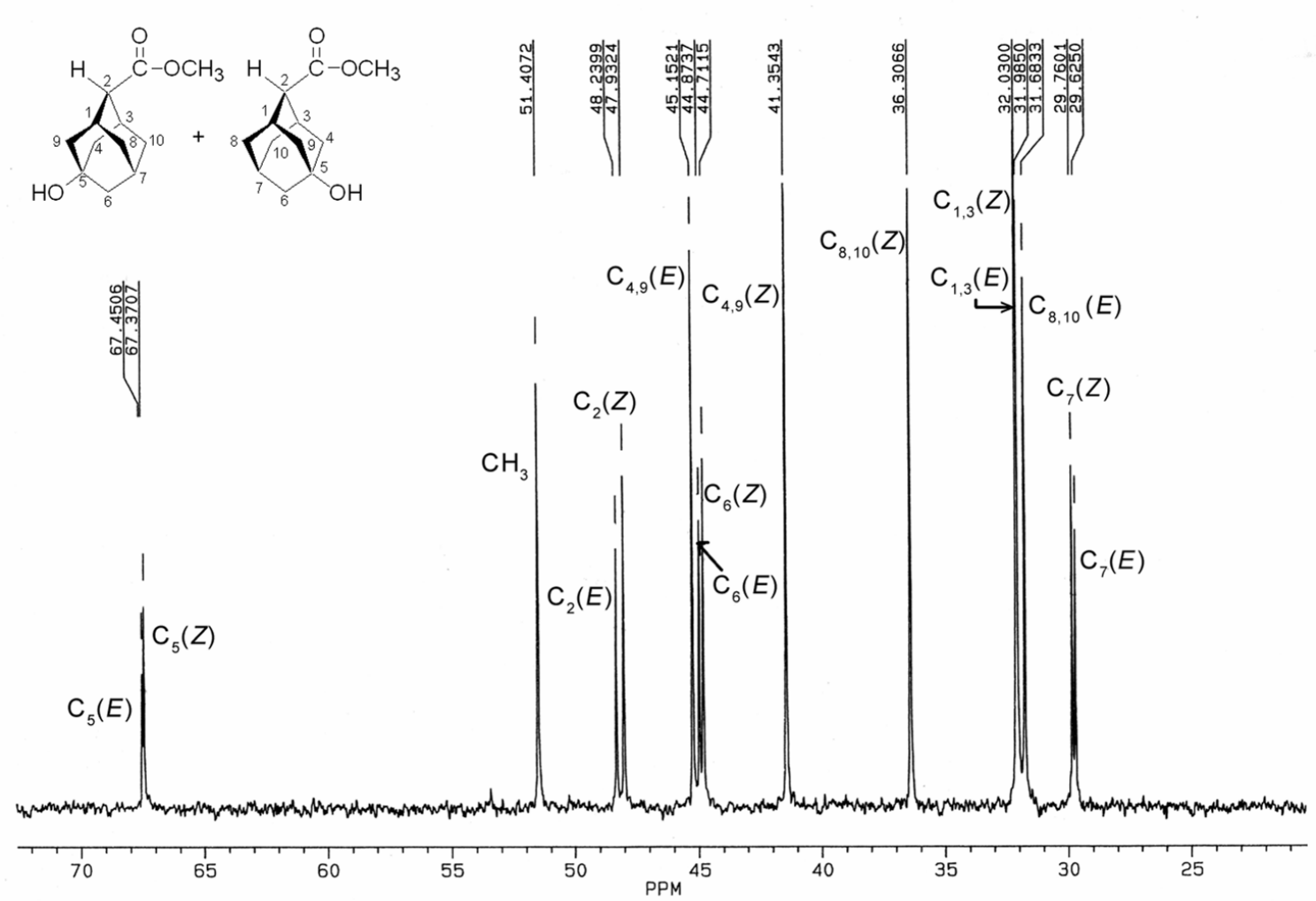
(*E*)-2-(5-Hydroxyadamantyl)methylketone (*E*-3c)



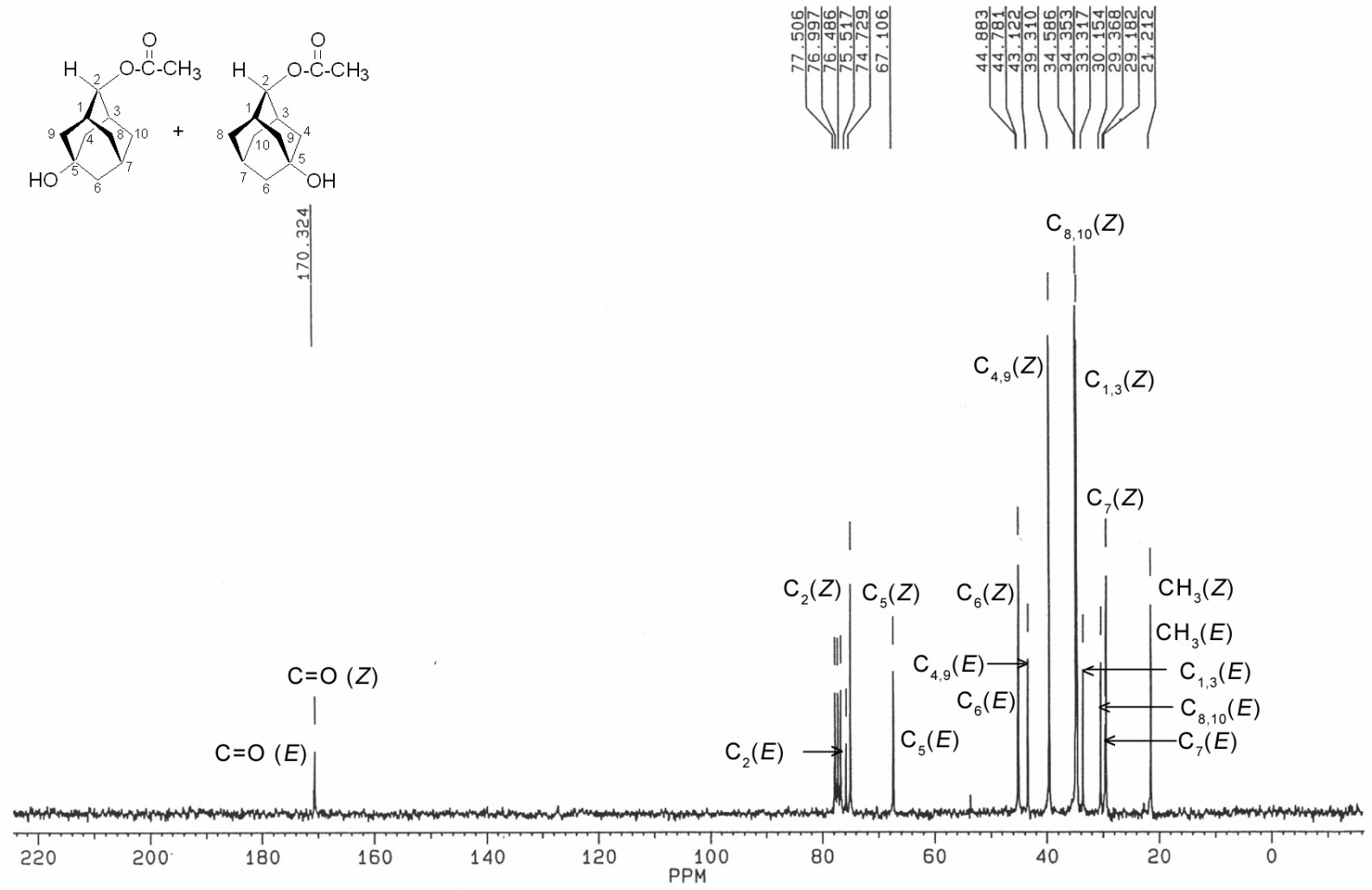
Methyl 5-hydroxy-2-adamantanecarboxylate (3d)



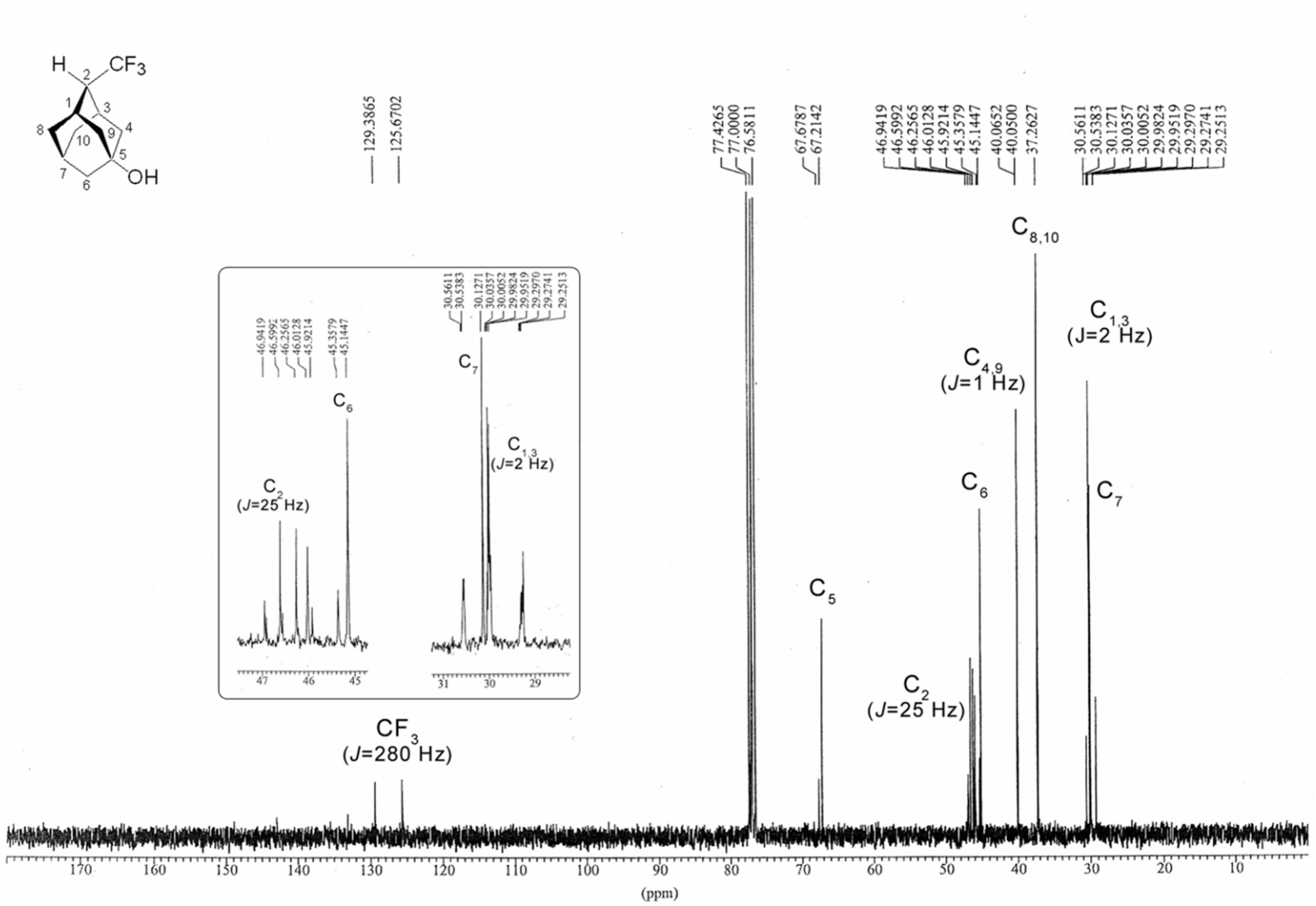
Methyl 5-hydroxy-2-adamantanecarboxylate (3d)



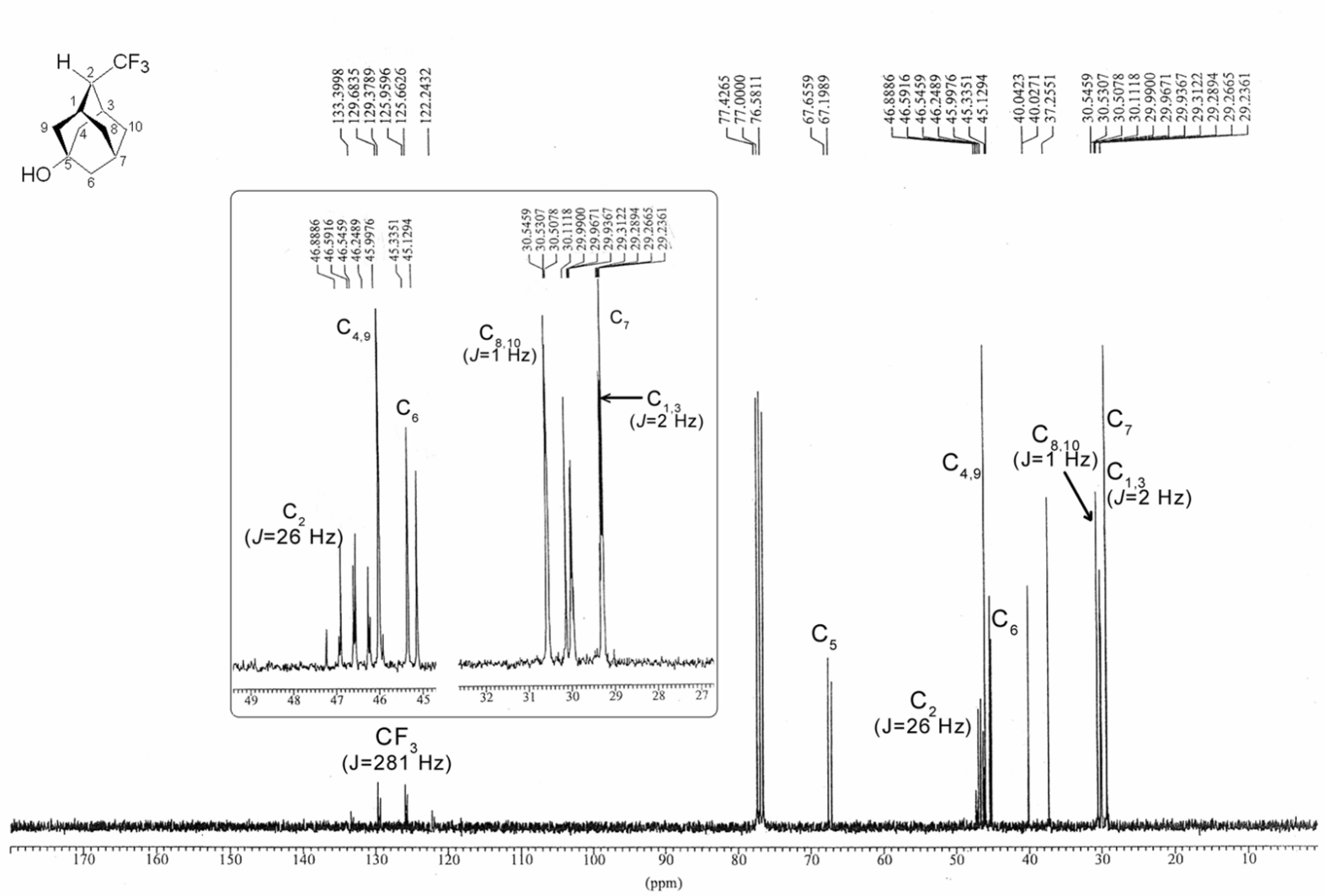
5-Hydroxy-2-adamantyl acetate (3e)



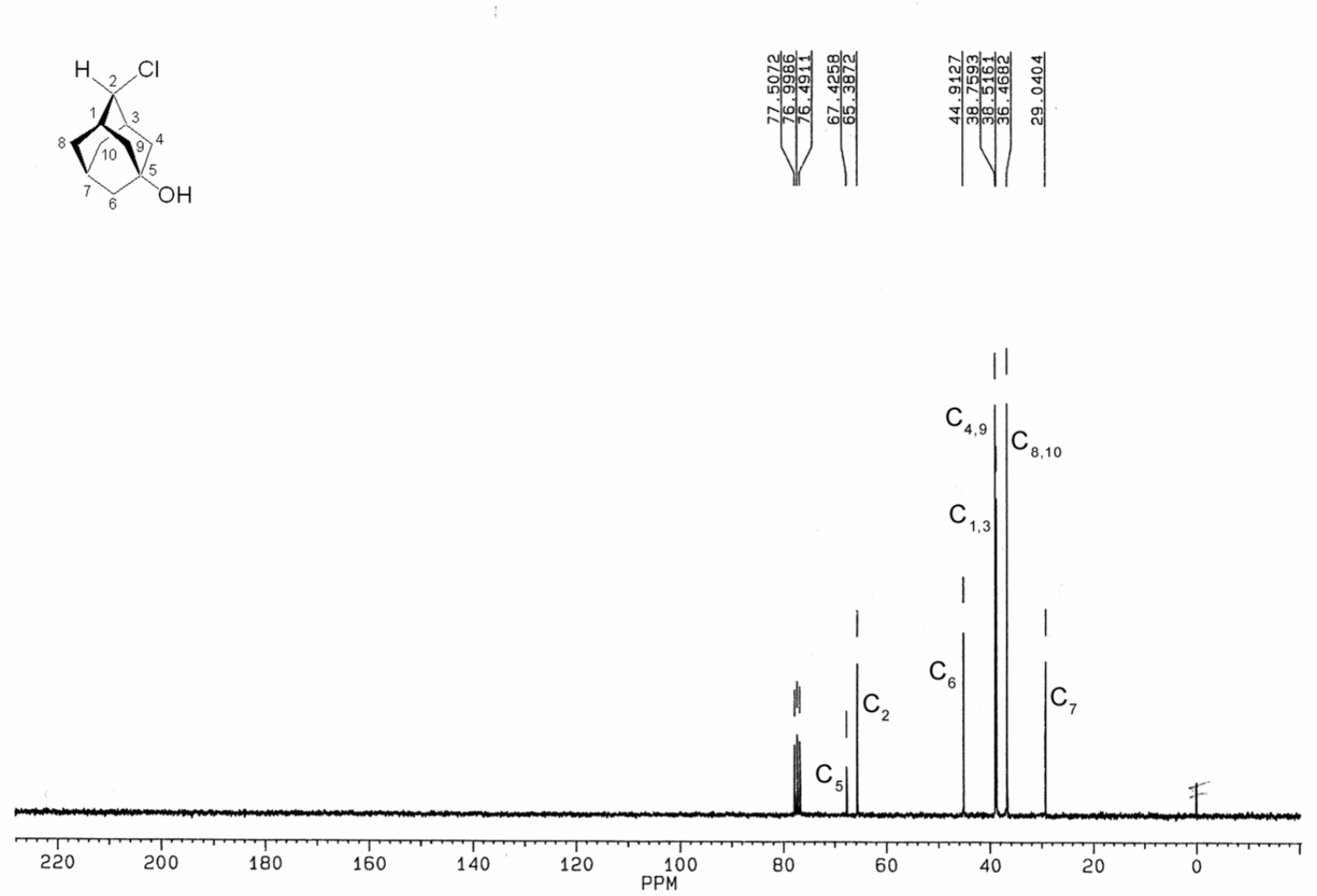
(*Z*)-4-Trifluoromethyl-1-adamantanol (*Z*-3f)



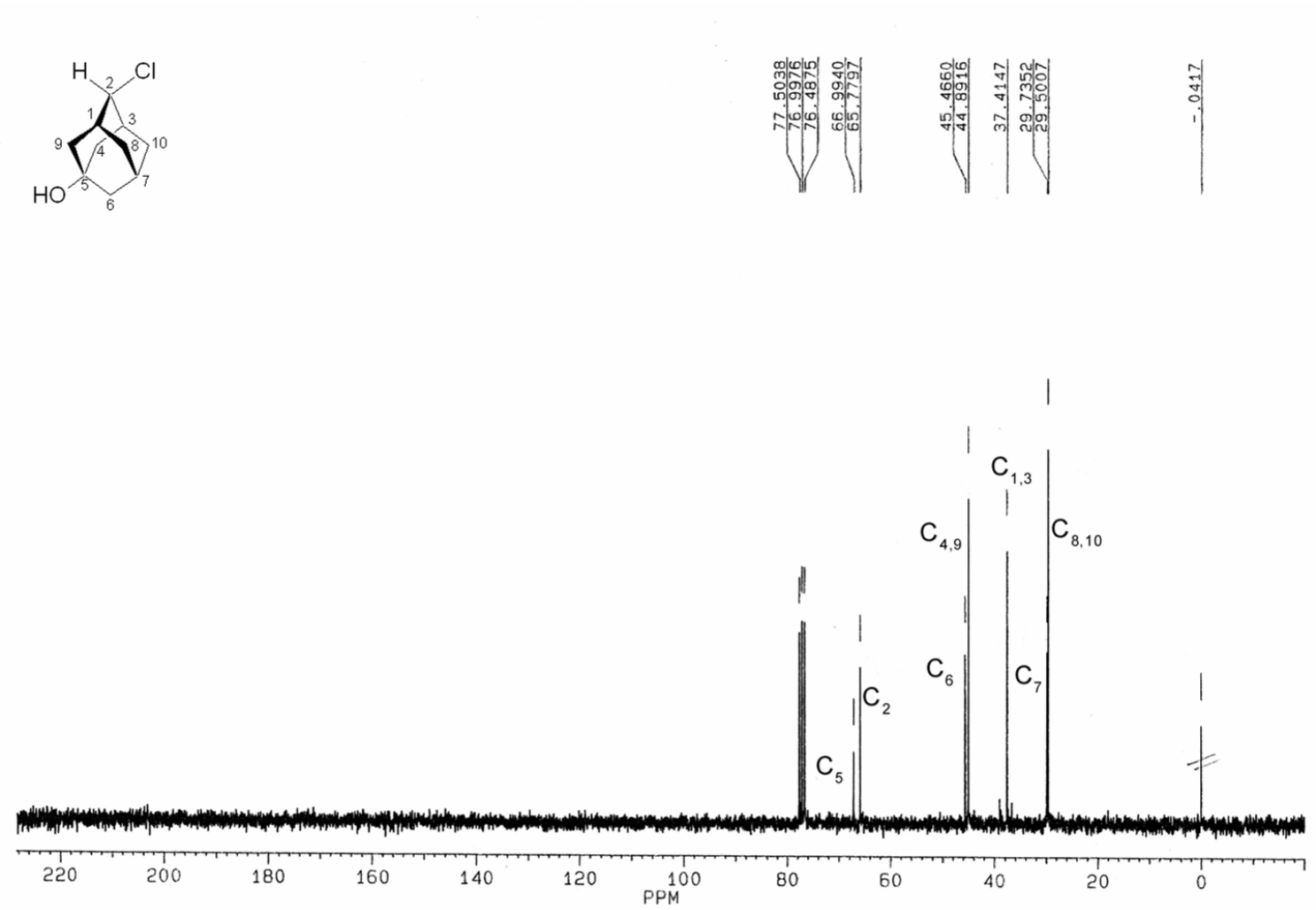
(*E*)-4-Trifluoromethyl-1-adamantanol (*E*-3f)



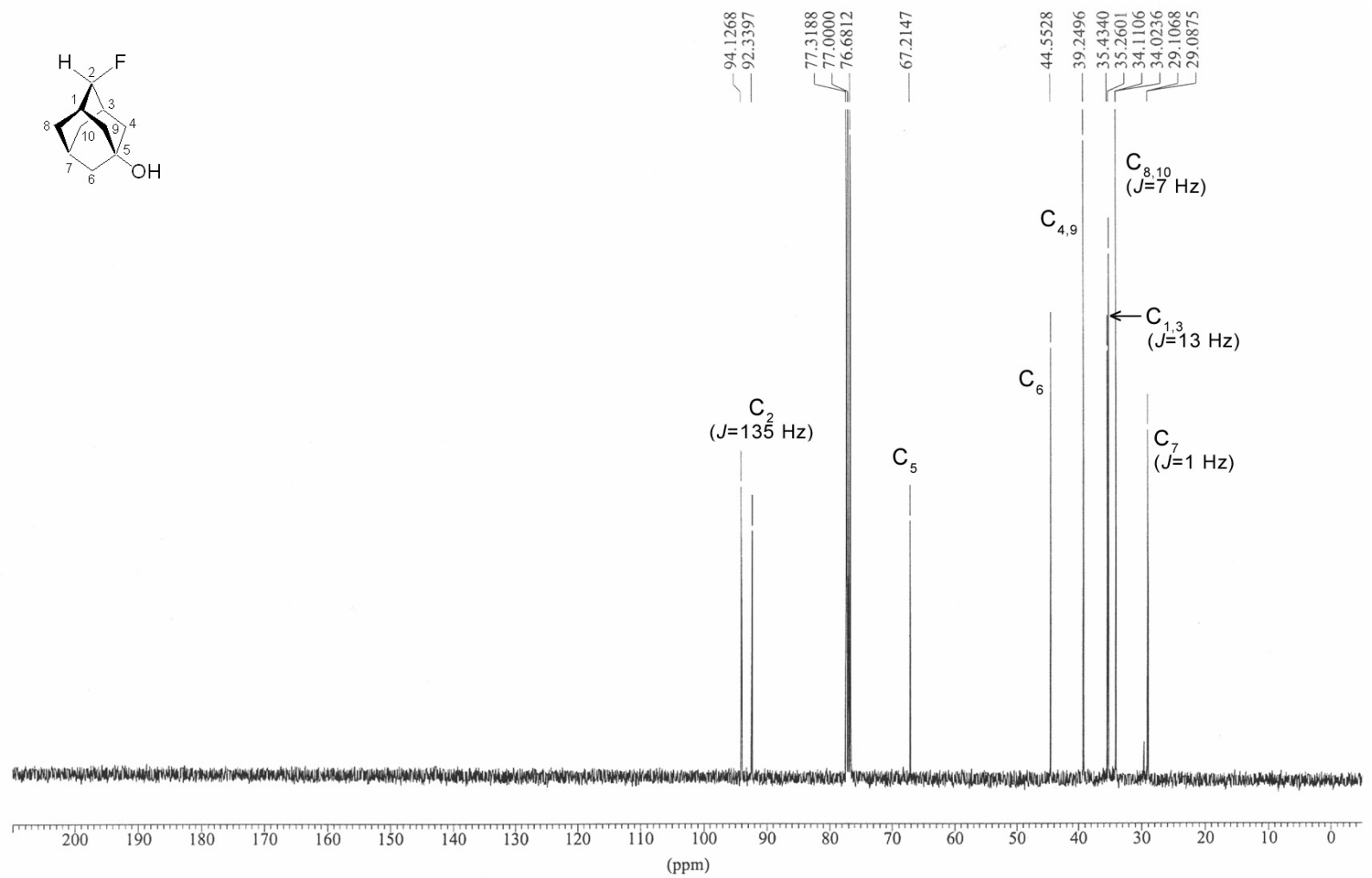
(Z)-4-Chloro-1-adamantanol (Z-3g)



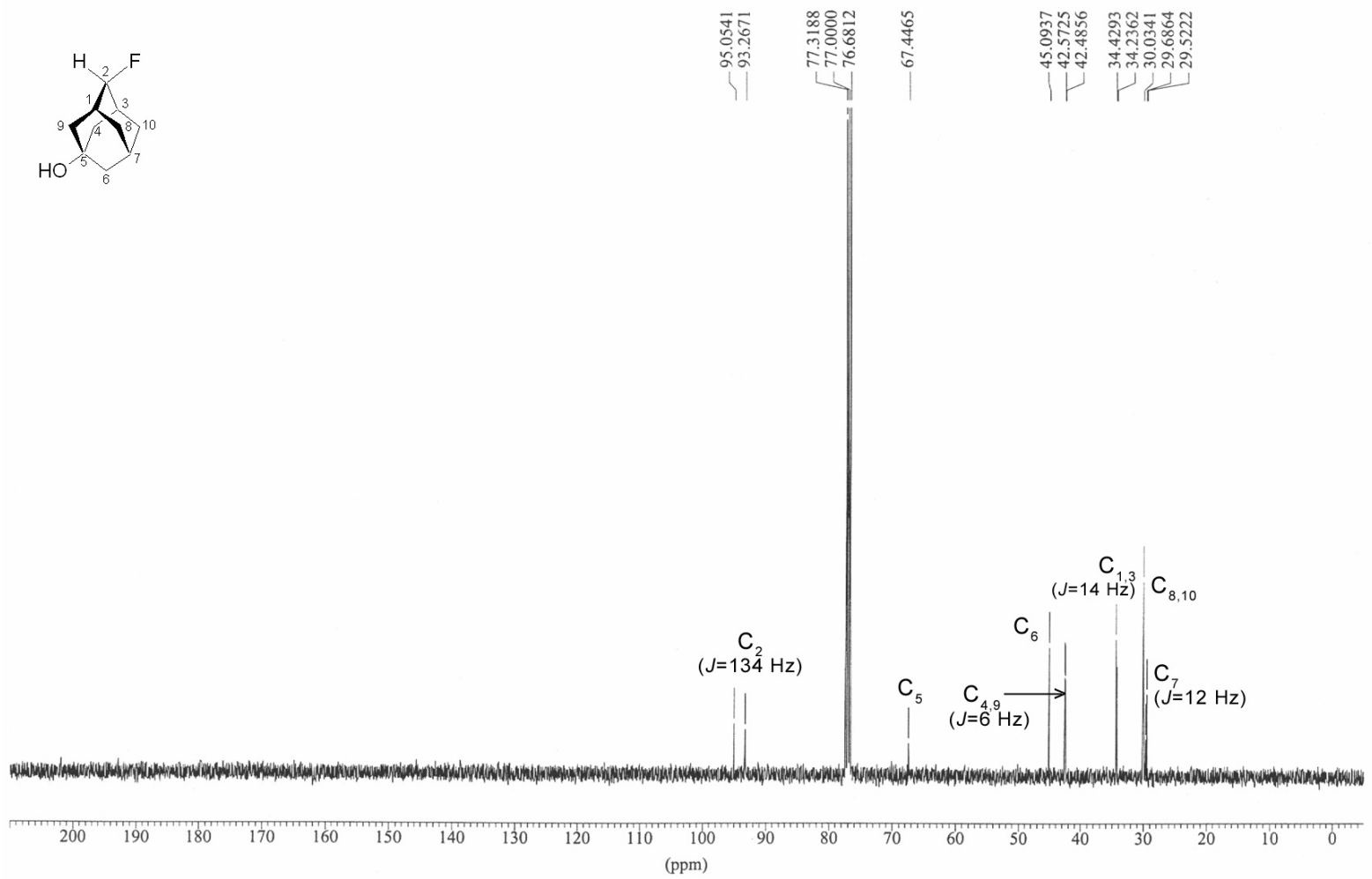
(*E*)-4-Chloro-1-adamantanol (*E*-3g)



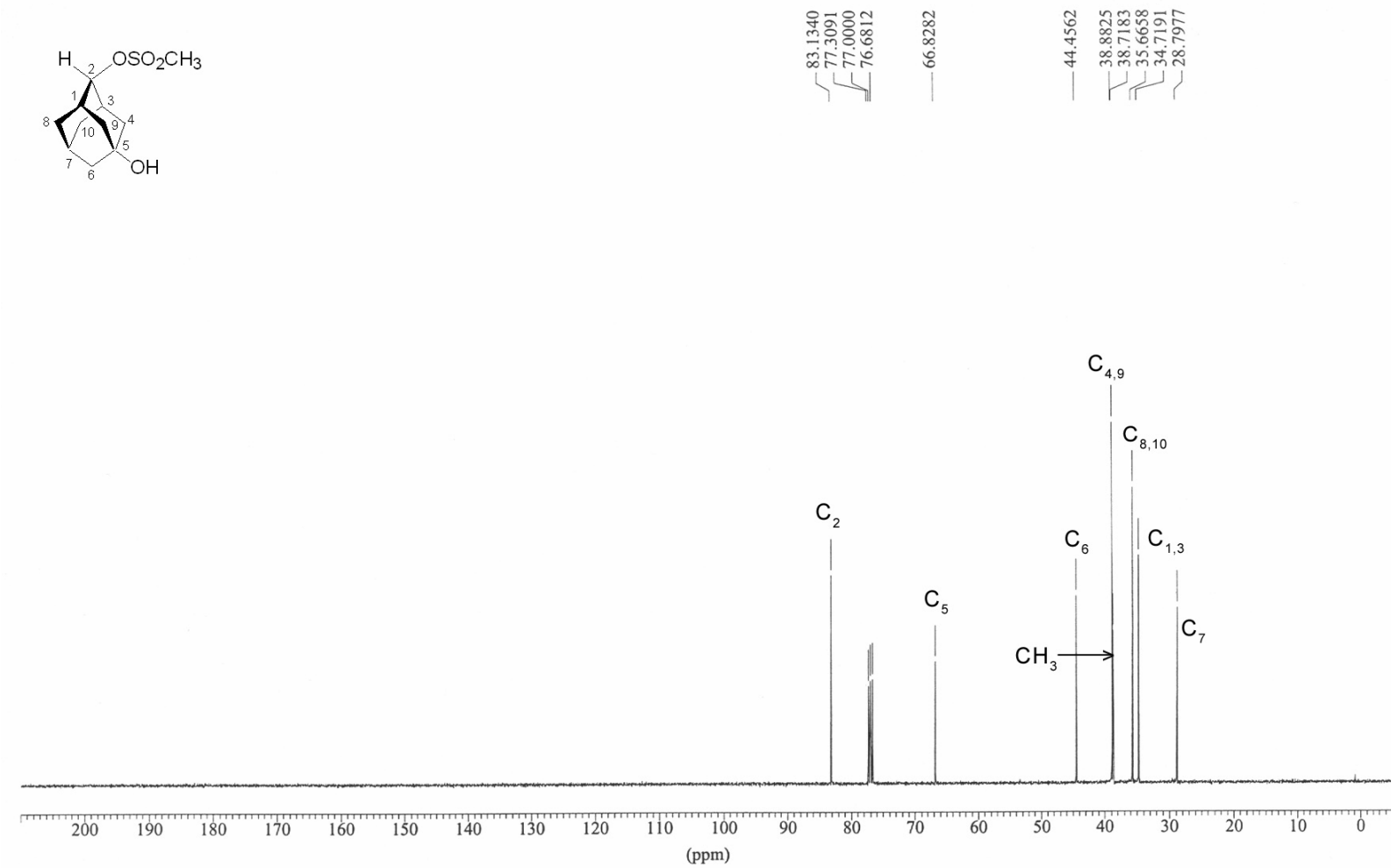
(*Z*)-4-Fluor-1-adamantanol (*Z*-3h)



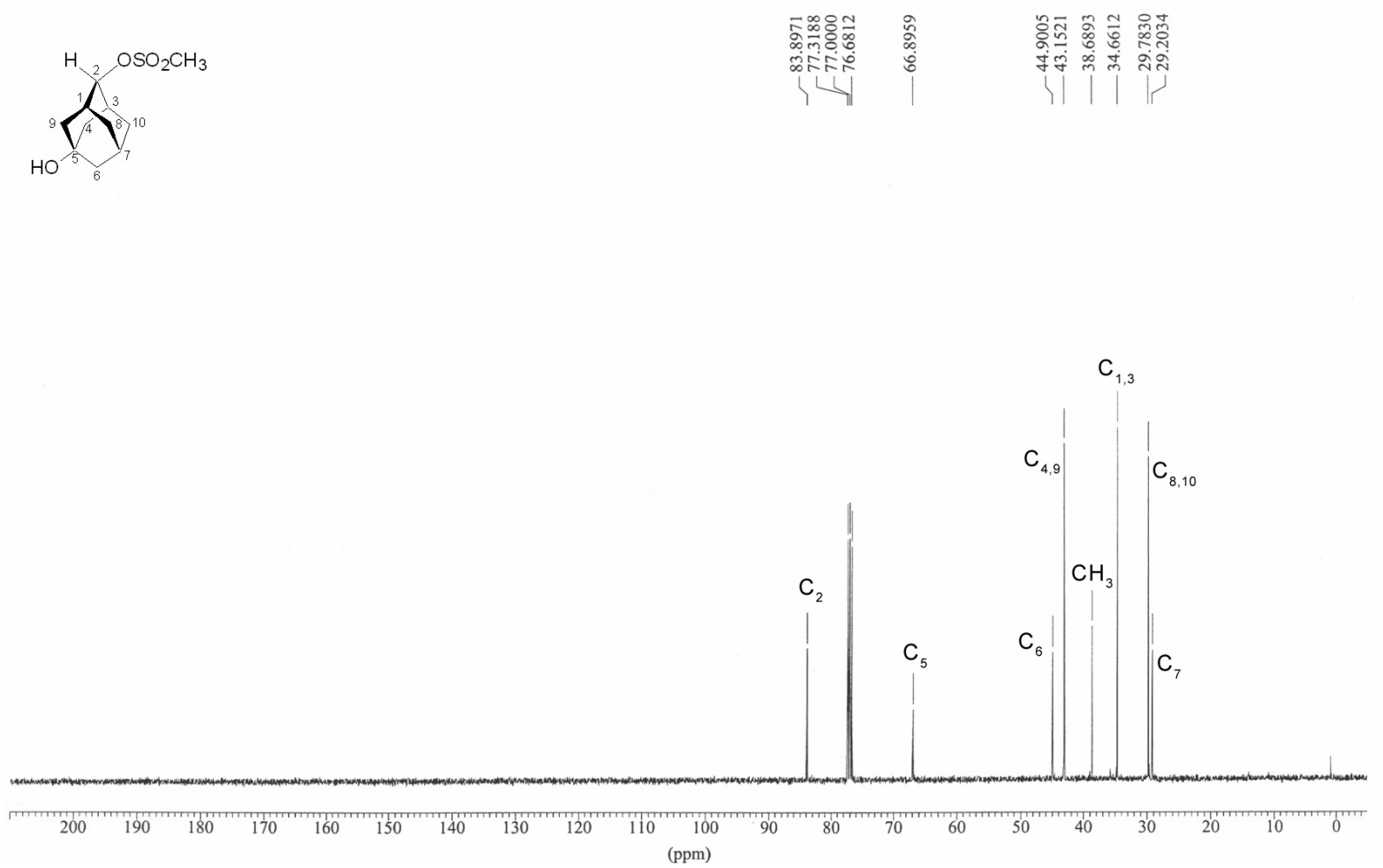
(*E*)-4-Fluor-1-adamantanol (*E*-3h)



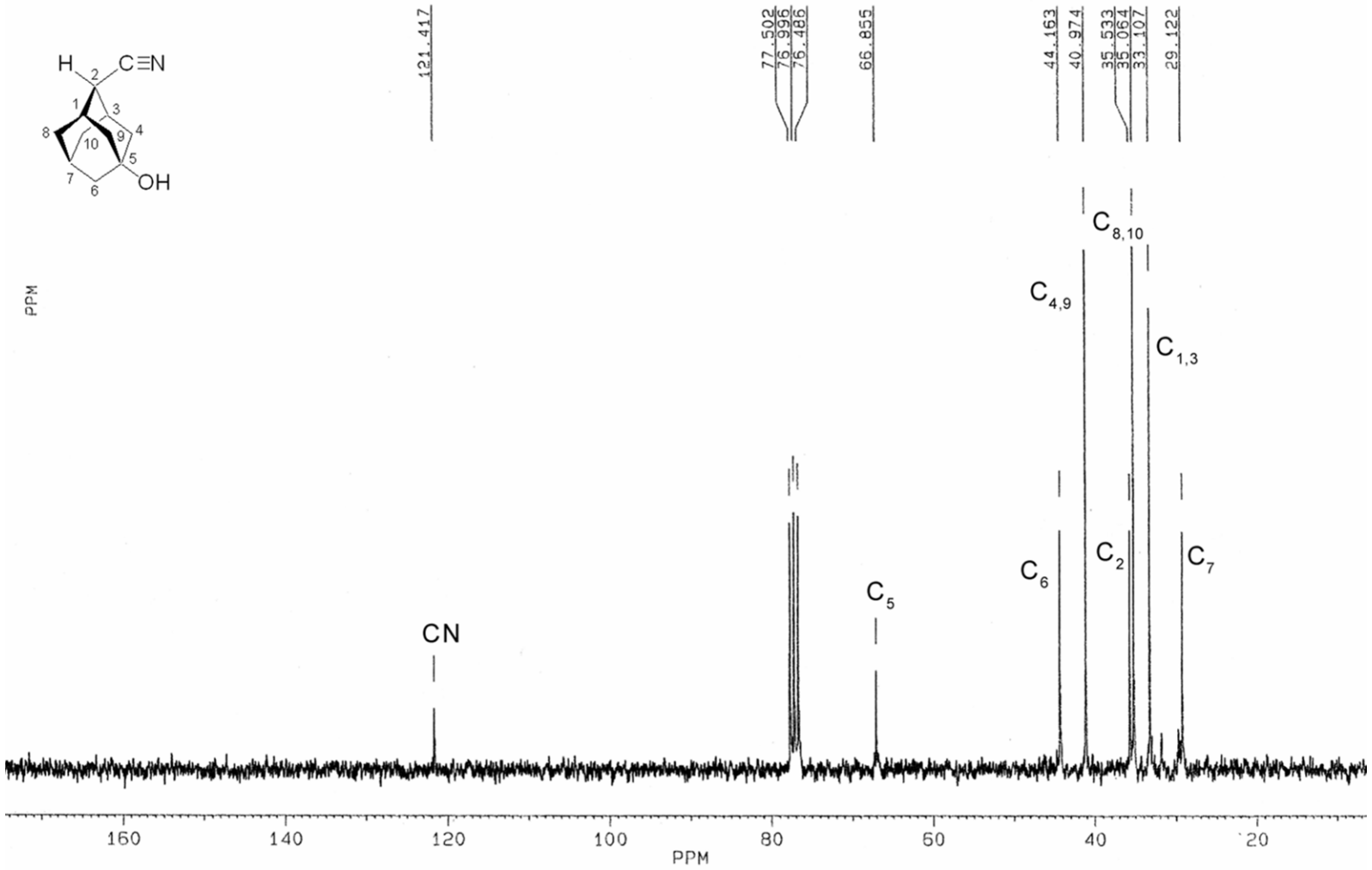
(*Z*)-5-Hydroxy-2-adamantyl methanesulfonate (*Z*-3i)



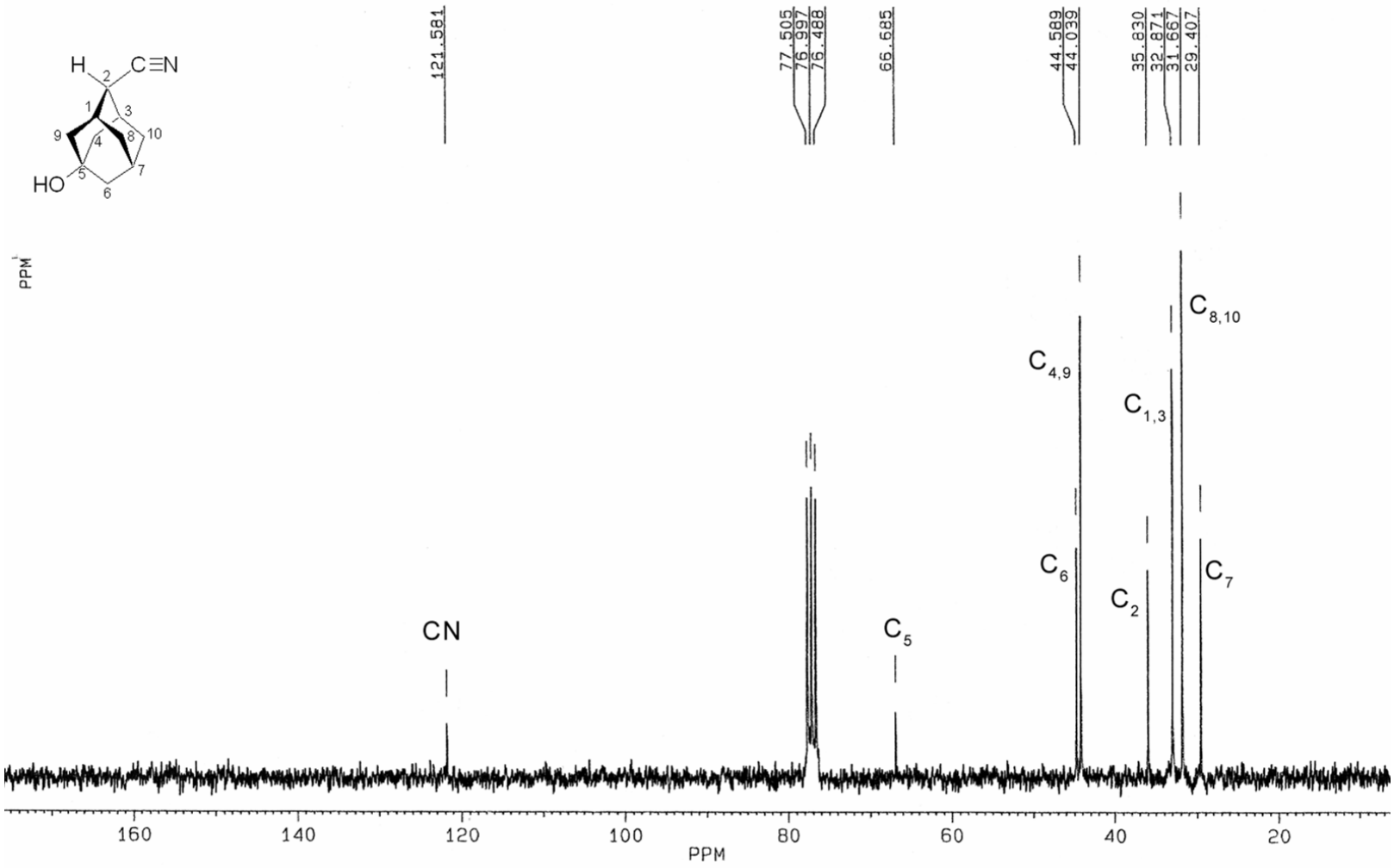
(*E*)-5-Hydroxy-2-adamantyl methanesulfonate (*E*-3i)



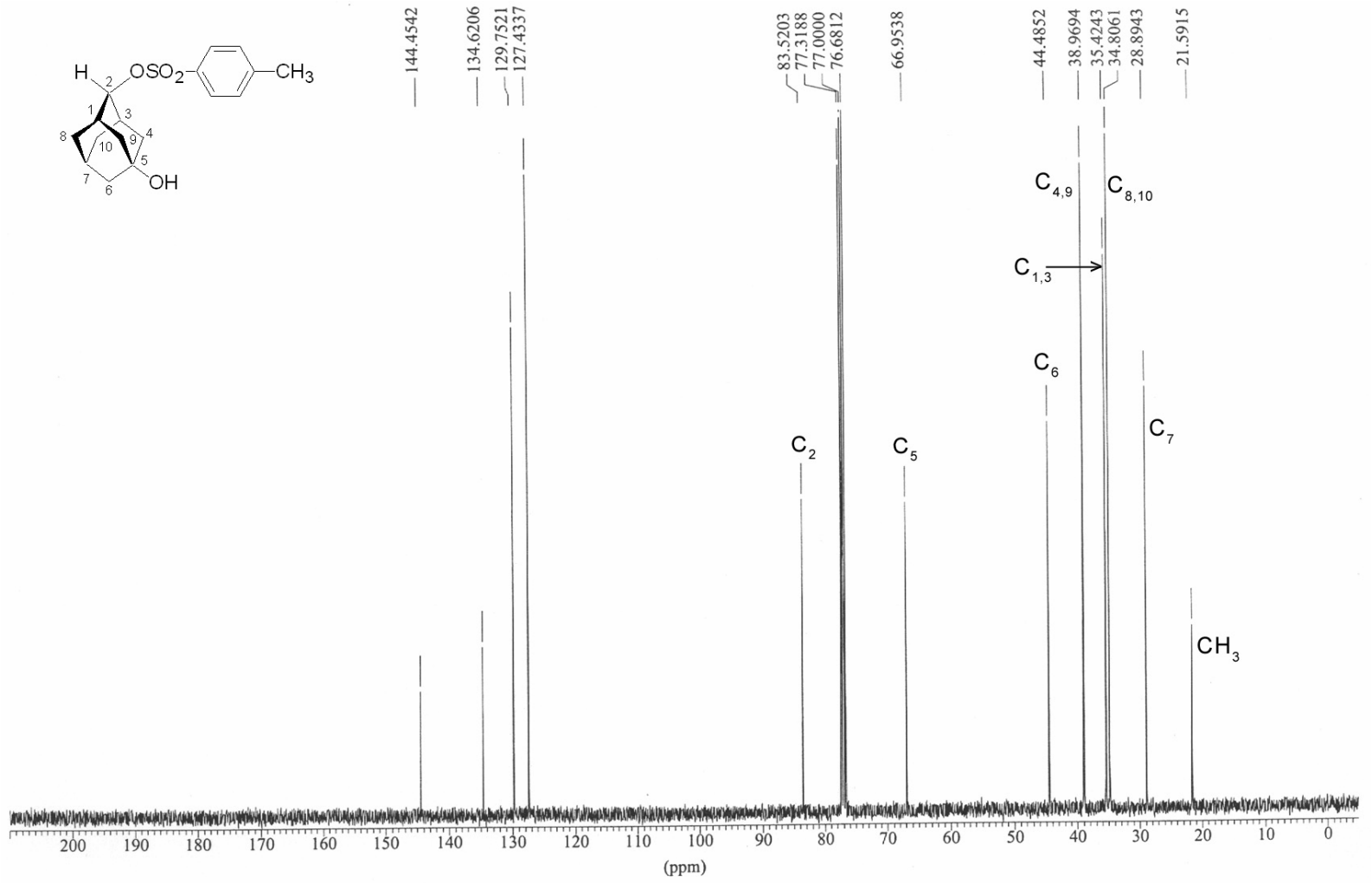
(*Z*)-5-Hydroxy-2-adamantanecarbonitrile (*Z*-3j)



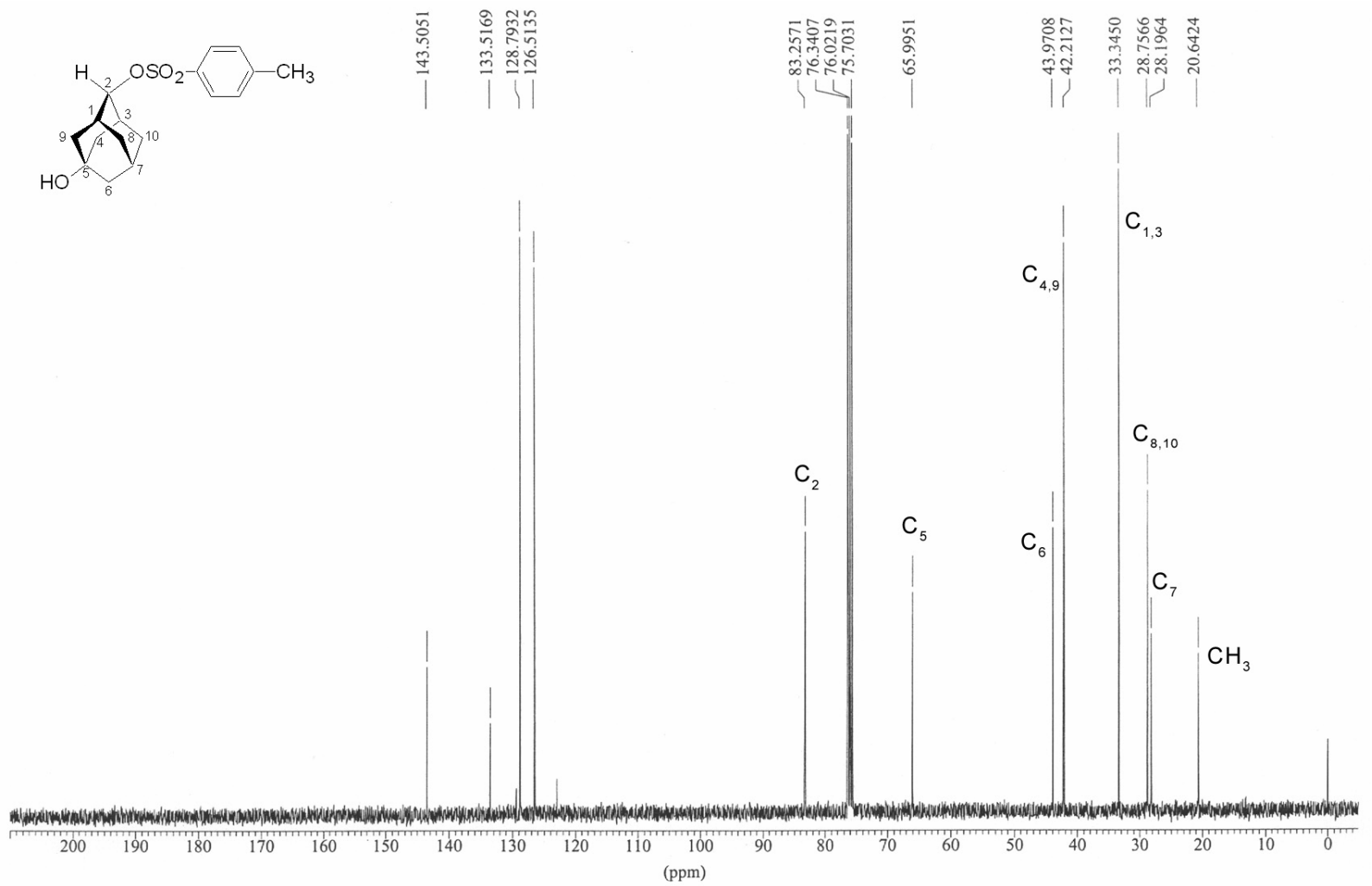
(*E*)-5-Hydroxy-2-adamantanecarbonitrile (*E*-3j)



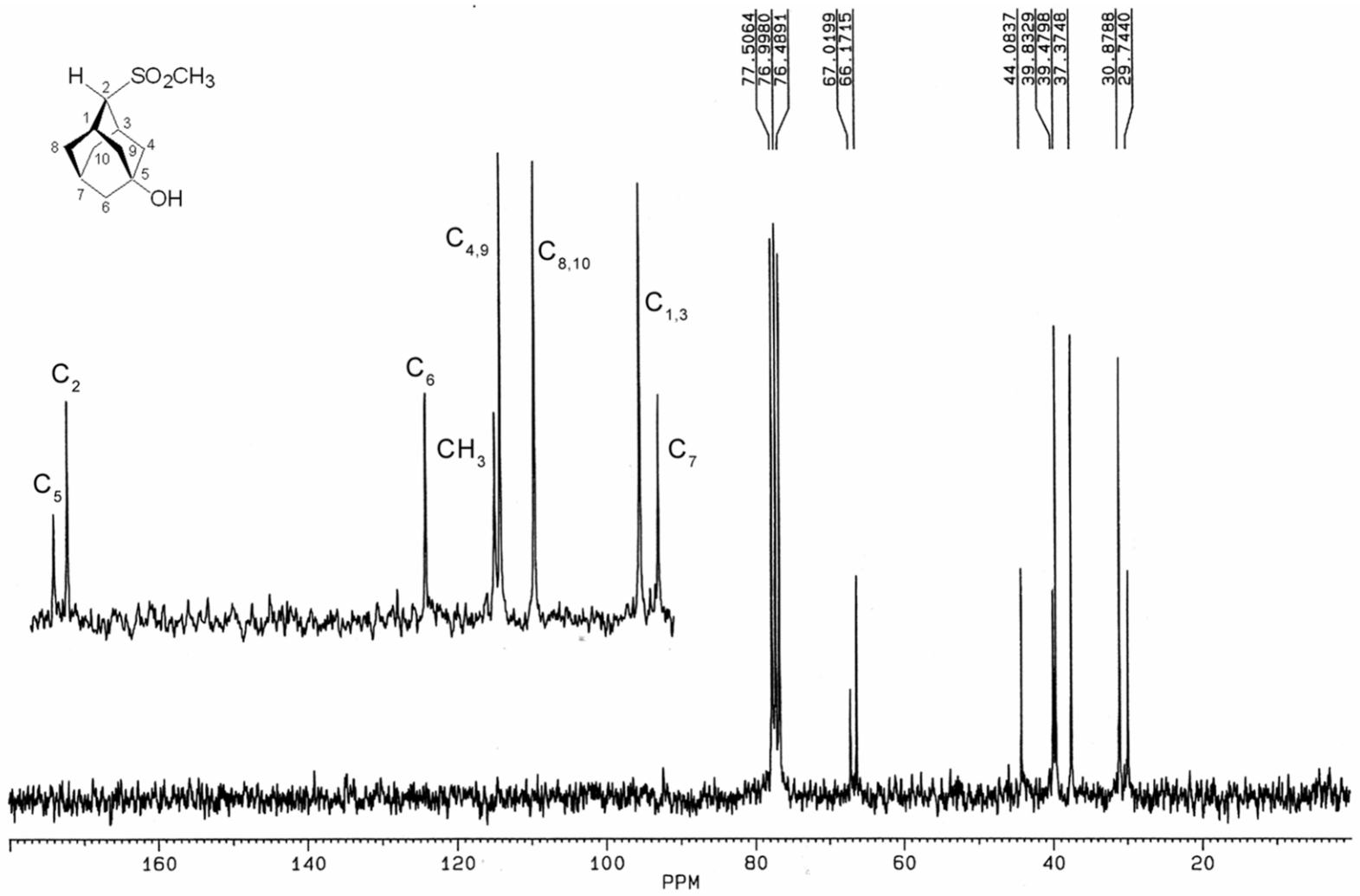
(*Z*)-5-Hydroxy-2-adamantyl *para*-toluensulfonate (*Z*-3k)



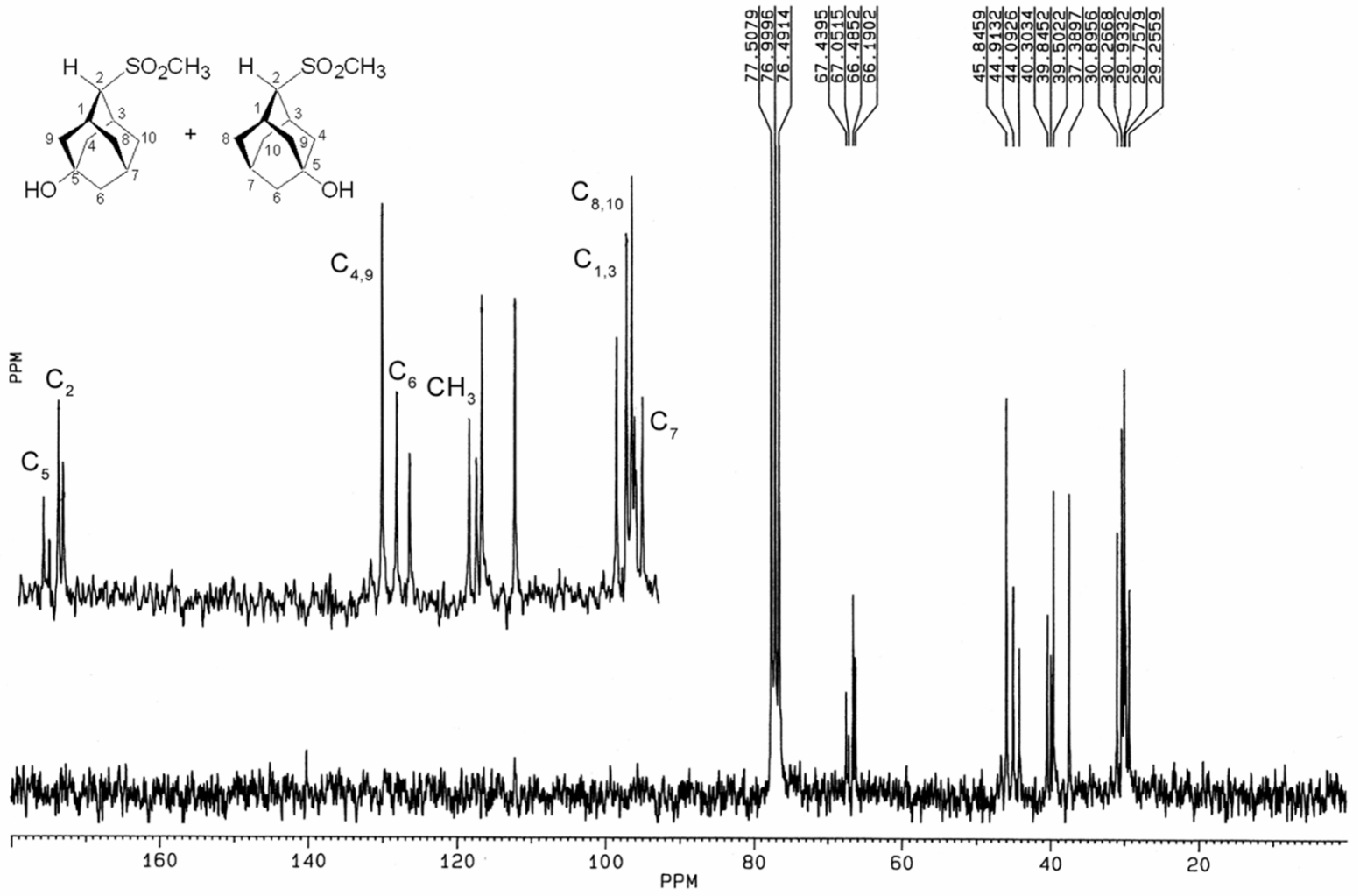
(*E*)-5-Hydroxy-2-adamantyl *para*-toluensulfonate (*E*-3k)



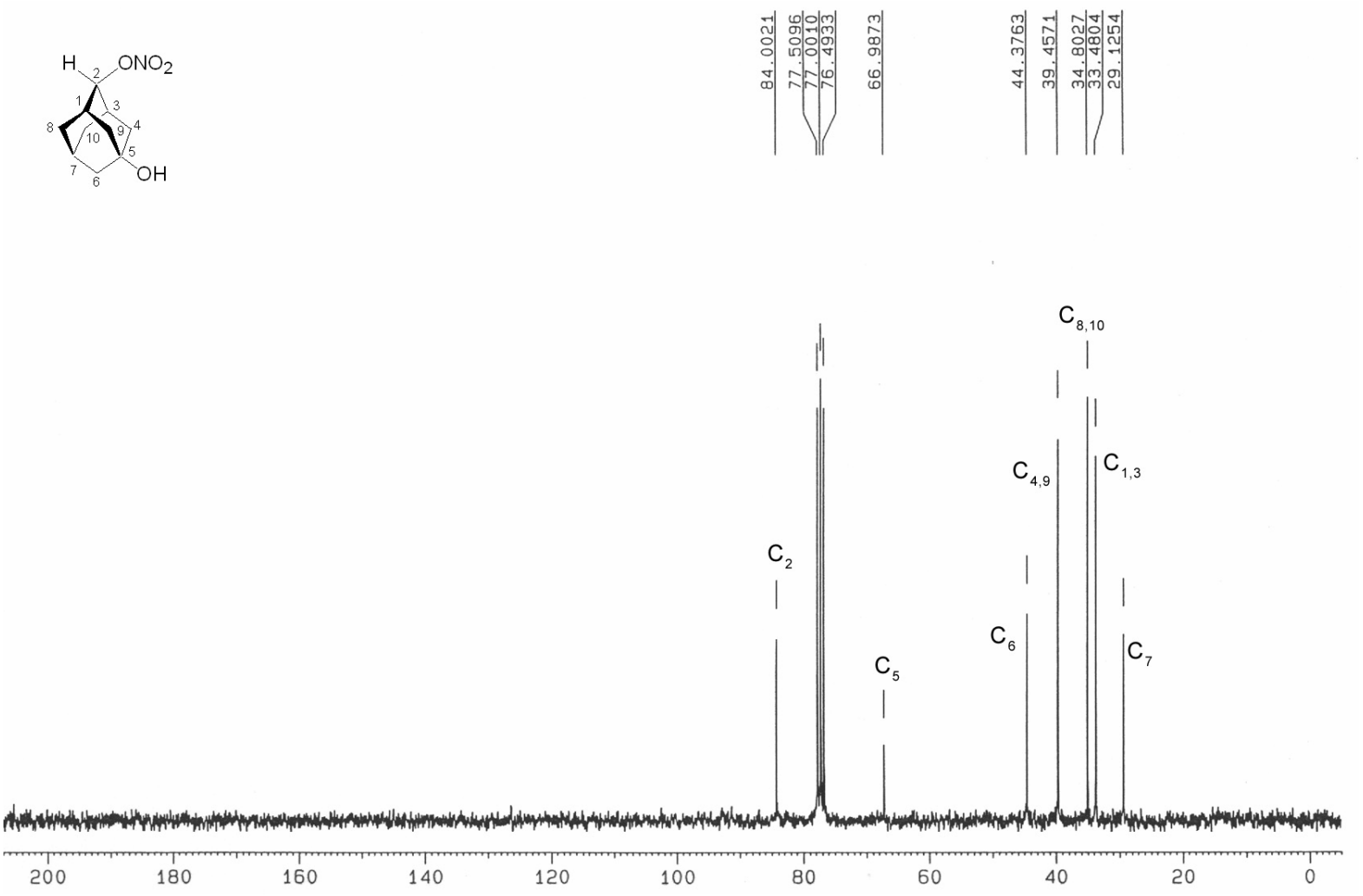
(*Z*)-(5-Hydroxy-2-adamantyl)methylsulfone (*Z*-3l)



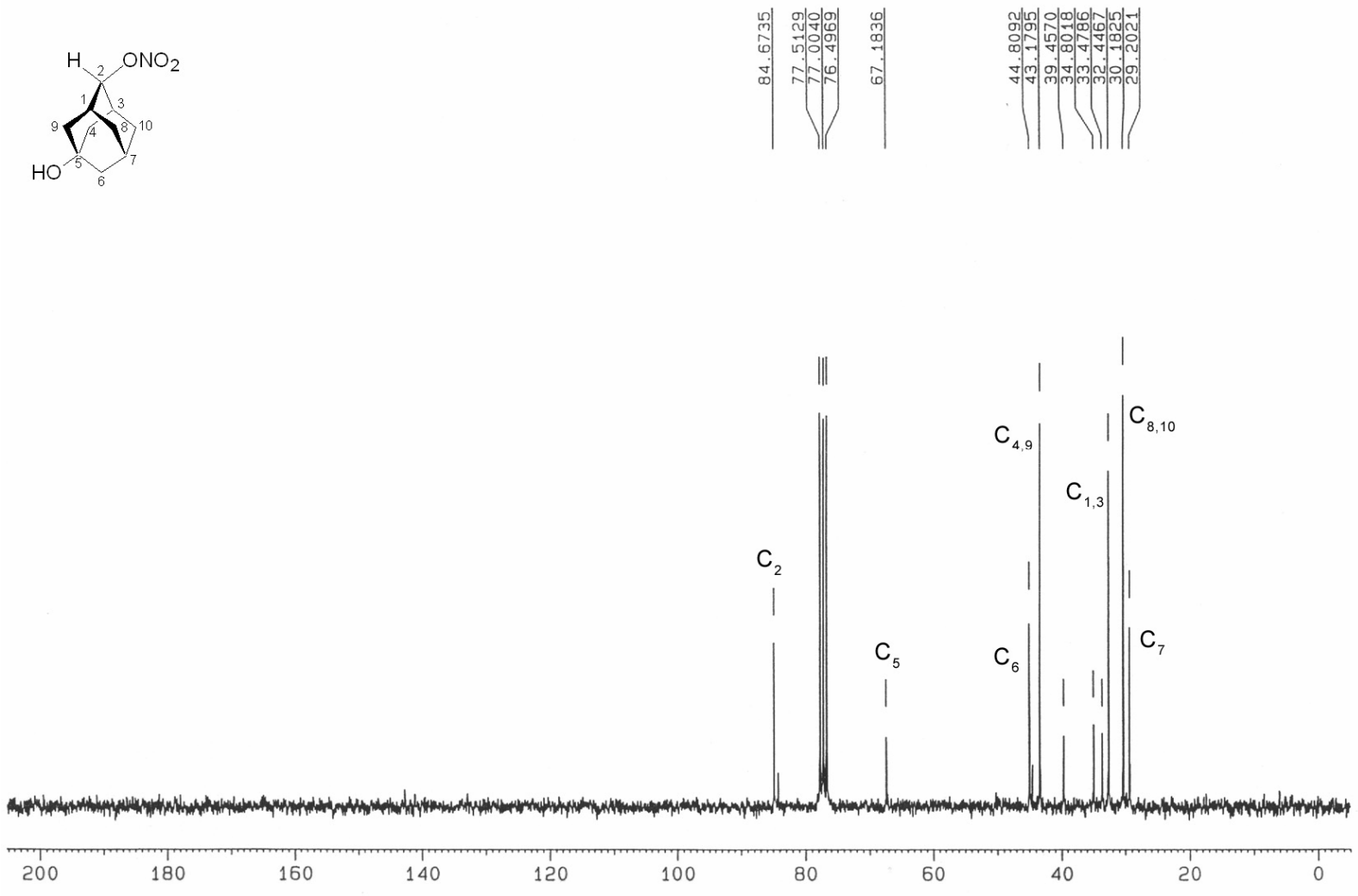
(5-Hydroxy-2-adamantyl)methylsulfone (3l)



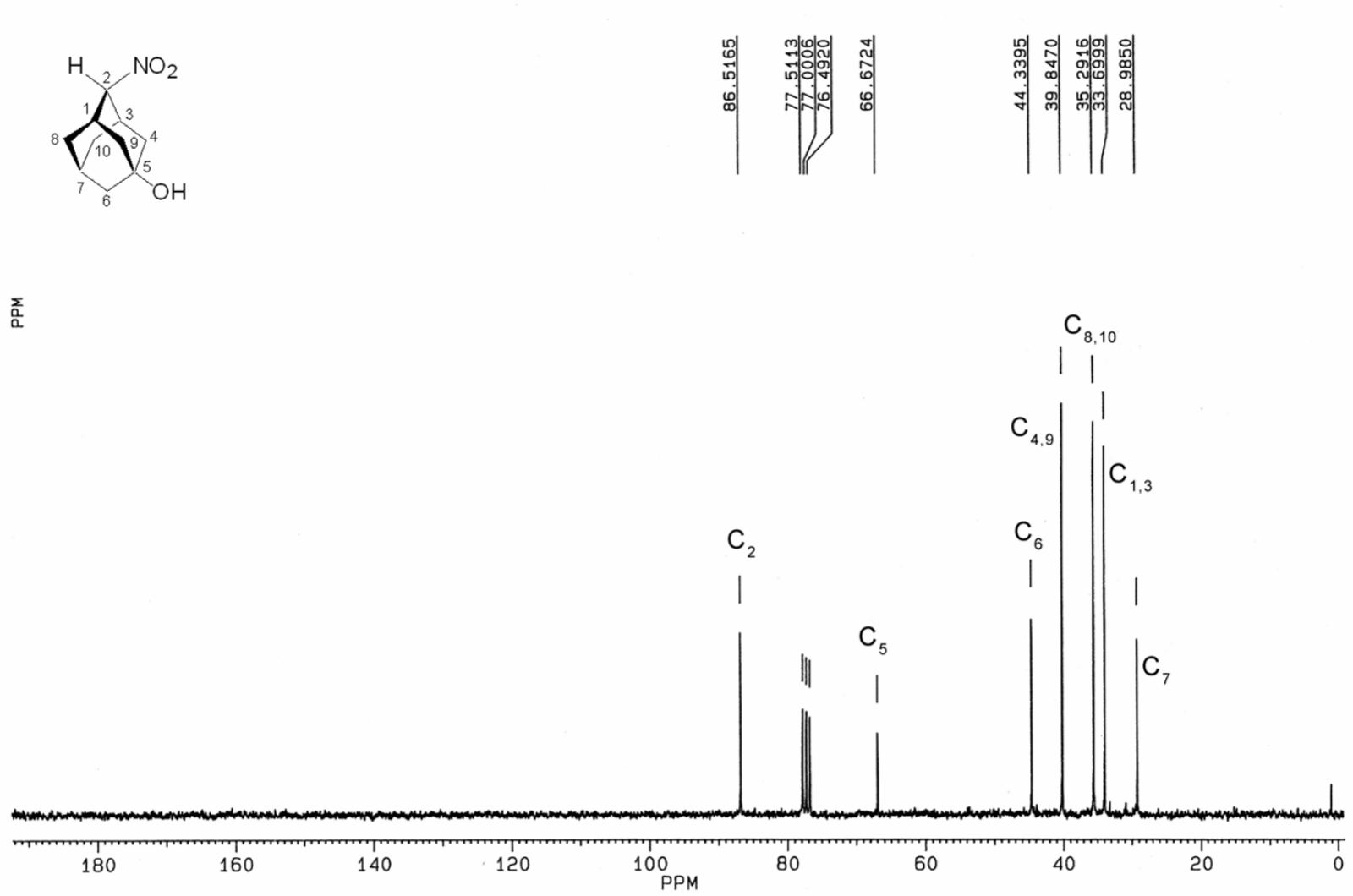
(*Z*)-5-Hydroxy-2-adamantyl nitrate (*Z*-3m)



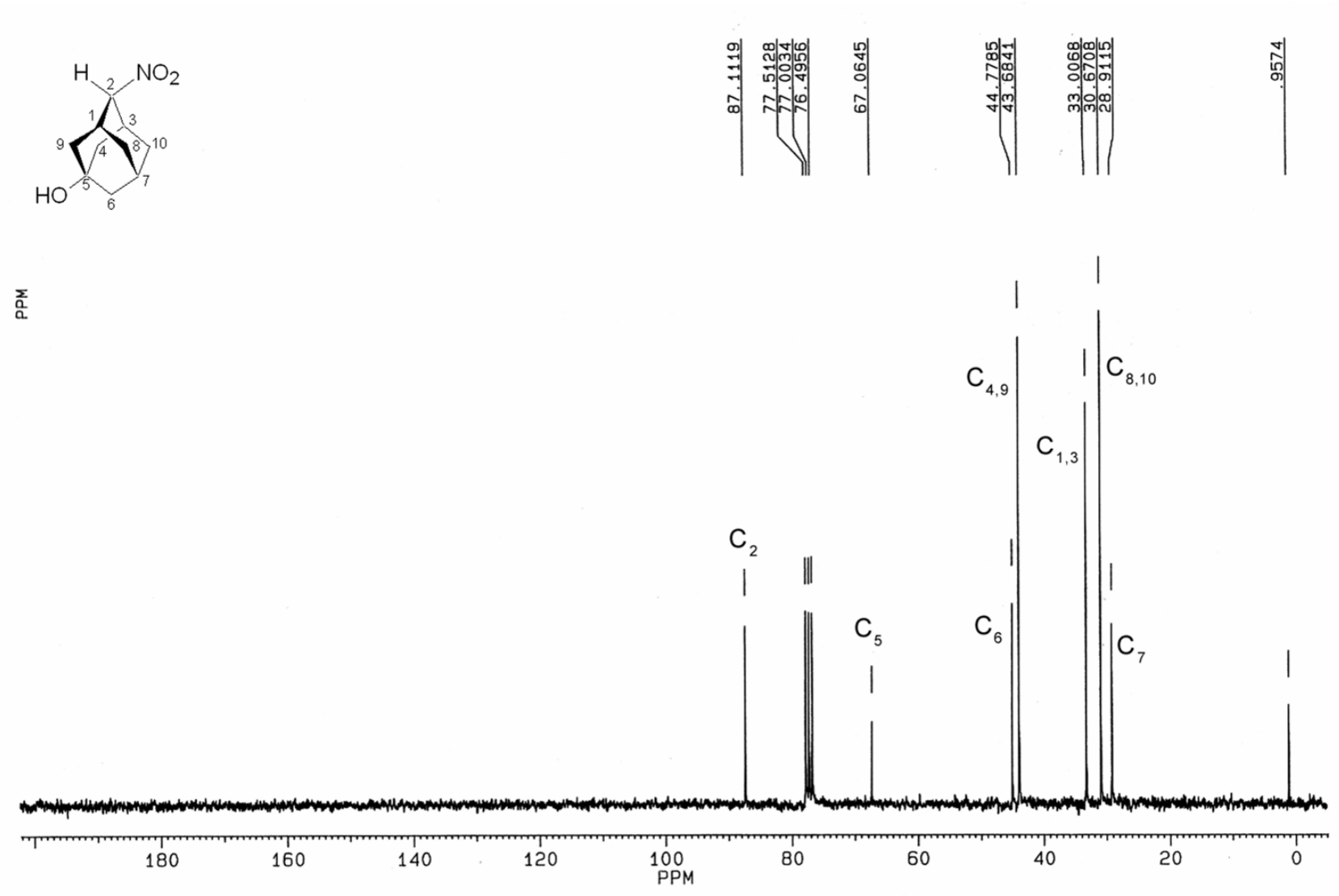
(*E*)-5-Hydroxy-2-adamantyl nitrate (*E*-3m)



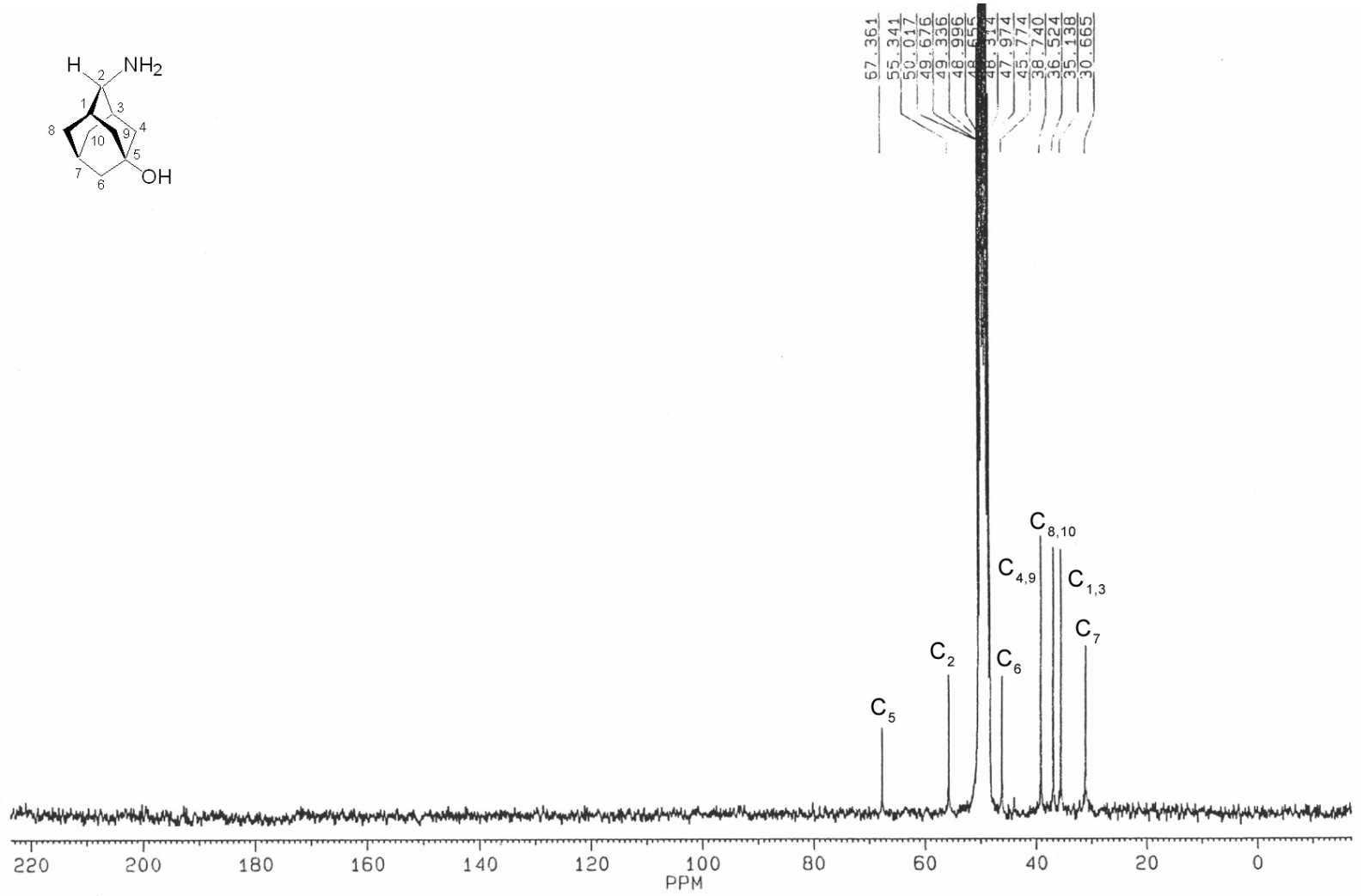
(*Z*)-4-Nitro-1-adamantanol (*Z*-3n)



(*E*)-4-Nitro-1-adamantanol (*E*-3n)



(*Z*)-4-Amino-1-adamantanol (*Z*-3o)



(*E*)-4-Amino-1-adamantanol (*E*-3o)