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Highly Functionalized Cyclohexenyl Systems: Enzymatic Resolution and Selective Oxirane Opening Reactions of *p*-Benzoquinone Derivatives

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Supporting Information

***rel*-(1*R*,2*S*,5*S*,6*S*)-5-(*tert*-butyldimethylsilyl)oxy-2-(4-methoxy-benzyl)-3-cyclohexen-1-ol (6b).** Clear oil; IR (neat): 3452, 3036, 2953, 2929, 2856, 1612, 1586, 1513, 1463, 1389, 1250, 1174, 1056, 837, 777 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.09 (s, 3H), 0.12 (s, 3H), 0.88 (s, 9H), 3.80 (s, 3H), 4.05 - 4.02 (m, 1H), 4.09 (dd, 1H, *J* =2.5, 5.7 Hz), 4.30 (dd, 1H, *J* = 2.4, 4 Hz), 4.47 (dd, 1H, *J* = 8,8 Hz), 4.56 (d, 1H, *J* = 11.1 Hz), 4.61 (d, 1H, *J* = 11.2 Hz), 5.70 (dd, 1H, *J* = 3,10 Hz), 5.8 (dd, 1H, *J* = 2.4, 10Hz), 6.89 (d, 2H, *J* = 9 Hz), 7.28 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.75, -4.57, 18.0, 25.7, 55.3, 58.6, 70.5, 71.1, 71.6, 76.8, 113.9, 126.6, 129.4, 129.5, 130.0, 159.4; Characterized as the unprotected diol **7** (see below).

***rel*-(1*R*,2*S*,5*S*,6*S*)-2-Benzylamino-6-bromo-5-(*tert*-butyldimethyl-silyl)oxy-3-cyclohexen-1-ol (6c).** Clear oil. IR (neat): 3418, 3028, 2953, 2927, 2885, 2855, 1461, 1388, 1360, 1252, 1098, 1051, 863, 836, 776, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.10 (s, 3H), 0.12 (s, 3H), 0.87 (s, 9H), 3.33 (d, 1H, *J* = 7.2 Hz), 3.81 (dd, 1H, *J* = 7.5, 2.6 Hz), 3.82 (d, 1H, *J* = 12.6 Hz), 3.93 (d, 1H, *J* = 13 Hz), 4.34 (dd, 1H, *J* = 2.6, 2.6 Hz), 4.47 (dd, 1H, *J* = 3.6, 3.6 Hz), 5.68 - 5.63 (m, 1H), 5.84 (dd, 1H, *J* = 10, 2.4 Hz), 7.34 - 7.25 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.7, -4.6, 18.0, 25.7, 51.1, 58.4, 58.5, 69.5, 71.3, 127.2, 127.4, 128.1, 128.5, 128.8, 140.0; MS (EI) m/e: 355 $(M - C_4H_9)^+$, 332 $(M - Br)^+$, 200, 91; HRMS (EI) calcd. for $C_{15}H_{21}NO_2Si$ $(M - C_4H_9)^+$: 354.0525. Found: 354.0516.

***rel*-(1*R*,2*S*,5*S*,6*S*)-6-Bromo-5-(*tert*-butyldimethylsilyl)oxy-2-(*p*-toluenesulfonylamino)-3-cyclohexen-1-ol (6d).** Prepared by the general procedure, except that a 4 h toluene reflux was required. Clear oil; IR (neat): 3495, 3275, 2927, 2855, 1597, 1470, 1388, 1330, 1254, 1159, 1095, 1054, 862, 837, 778, 663 cm^{-1}; ^1H NMR (300 MHz,

$CDCl_3$) δ: 0.06 (s, 3H), 0.09 (s, 3H), 0.86 (s, 9H)., 2.43 (s, 3H), 2.74 (broad s, 1H), 3.89 - 3.86 (m, 2H), 4.2 - 4.18 (m, 1H), 4.40 (dd, 1H, J = 4.0, 4.0 Hz), 4.79 (d, 1H, J = 8.1 Hz), 5.32 (dd, 1H, J = 2.0, 9.9 Hz), 5.63 (dd, 1H,J = 4.2, 10 Hz), 7.32 (d, 2H, J = 7.8 Hz), 7.79 (d, 2H, J = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.8, -4.7, 17.9, 21.5, 25.7, 55.2, 57.3, 70.1, 70.7, 126.8, 127.1, 129.6, 129.9, 137.1, 143.9; MS (EI) m/e: 420 (M - C_4H_9)$^+$, 378, 264, 228, 155 (Tos)$^+$, 108, 91, 75; HRMS (EI) calcd. for $C_{15}H_{21}BrNO_4SSi$ (M - C_4H_9)$^+$: 418.0143. Found: 418.0149.

***rel*-(1*R*,2*S*,5*S*,6*S*)-6-Bromo-2-(4-methoxybenzyl)amino-5-(*tert*-butyldimethylsilyl)oxy-3-cyclohexen-1-ol (6e).** White crystals, mp 115 - 116 °C (pet. ether/THF); IR (thin film): 3316, 2953, 2928, 2886, 2855, 1604, 1513, 1463, 1249, 1100, 1040, 837, 773 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.09 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 3.31 (d, 1H, J = 7.3 Hz), 3.74 (d, 1H, J = 12.6 Hz), 3.79 (s, 3H), 3.81 - 3.78 (m, 1H), 3.88 (d, 1H, J = 12.9 Hz), 4.30 (m, 1H), 4.46 (dd, 1H, J = 3.6, 3.6 Hz), 5.67 - 5.62 (m, 1H), 5.83 (dd, 1H, J = 2.4, 10 Hz), 6.86 (d, 2H, J = 8.4 Hz), 7.25 (d, 2H, J = 9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.7, -4.6, 18.0, 25.7, 50.5, 55.3, 58.2, 58.4, 69.3, 71.3, 113.9, 127.3, 128.7, 129.4, 131.8, 158.8; MS (EI) m/e: 362 (M - Br)$^+$, 230, 121, 75; HRMS (EI) calcd. for $C_{20}H_{32}NO_3Si$ (M - Br)$^+$: 362.2151. Found: 362.2140.

***rel*-(1*R*,2*S*,5*R*,6*S*)-2-Azido-6-bromo-5-(*tert*-butyldimethylsilyl)oxy-3-cyclohexen-1-ol (6f):** To a solution of epoxide **5** (207 mmg, 0.68 mmol) in methanol (6 mL) was added NaN_3 (110 mg, 1.70 mmol) and $ZnSO_4$ (489 mmg, 1.70 mmol). The mixture was stirred for 14 h before being filtered through a Celite™ pad. The resulting solution was concentrated onto Na_2SO_4 and purified by flash chromatography (20:1 pet. ether/EtOAc) to give azido-alcohol **6f** (200 mg, 84 %) as a clear oil: IR (3418, 3039, 2928, 2856, 2107, 1471, 1389, 1254, 1058, 860, 838, 777 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.09 (s, 3H), 0.12 (s, 3H), 0.88 (s, 9H), 2.44 (d, 1H, J = 6.6 Hz), 3.96 (ddd, 1H, J = 6.6, 6.6, 2.6 Hz), 4.05 (app d, 1H, J = 7.3 Hz), 4.21 - 4.23 (m, 1H), 4.48 (dd, 1H, J = 4.0, 4.0 Hz), 5.70 (dd, 1H, J = 2.3, 10.3 Hz), 5.77 - 5.82 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.8, -4.6, 17.9, 25.6, 57.8, 61.9, 70.0, 70.8, 125.3, 129.7; MS (EI) m/e: 291 (M - C_4H_9)$^+$, 249 (M - C_4H_9 - N_3), 221, 182, 167, 139, 75; HRMS (EI) calcd. for $C_8H_{13}N_3BrO_2Si$ (M - C_4H_9)$^+$: 289.9960. Found: 289.9951.

***rel*-(1*R*,2*S*,5*S*,6*S*)-6-Bromo-5-(*tert*-butyldimethylsilyl)oxy-2-phenylthiolcyclohex-3-en-1-ol (6g).** Clear oil; IR (neat): 3452, 3037, 2954, 2885, 1583, 1480, 1438, 1386, 1360, 1255, 1183, 1106, 1048, 926, 838, 773, 744, 691 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.05 (s, 3H), 0.09 (s, 3H), 0.84 (s, 9H), 2.61 (d, 1H, J = 4.2 Hz), 3.79 (dd, 1H, J = 3.0, 3.0 Hz), 4.02 (ddd, 1H, J = 2.4, 3.5, 6.0 Hz), 4.39 (dd, 1H, J = 2.4, 5.4 Hz), 4.42

(dd, 1H, J = 3.0, 5.4 Hz), 5.68 (m, 1H), 5.84 (dd, 1H, J = 3.0, 11 Hz), 7.26 - 7.34 (m, 3H), 7.44 - 7.47 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.7, -4.5, 17.9, 25.7, 50.2, 58.4, 70.2, 70.8, 127.3, 127.8, 129.1, 132.5, 132.9; MS (EI) m/e: 358 $(M - C_4H_9)^+$, 249 $(M - C_4H_9 - SPh)^+$, 203, 175, 139, 110, 75; HRMS (EI) calcd. for $C_{14}H_{18}BrO_2SSi$ $(M - C_4H_9)^+$: 356.9980. Found: 356.9971.

***rel*-(3*R*,4*S*,5*R*,6*S*)-5-Acetoxy-4,6-dibromo-3-(*tert*-butyldimethyl-silyl)oxy-1-cyclohexene (6h).** Waxy, white solid, mp 35 - 36 °C; IR (film): 2955, 2929, 2857, 1751, 1472, 1373, 1257, 1223, 1113, 1036, 838, 778 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.12 (s, 3H), 0.15 (s, 3H), 0.91 (s, 9H), 2.14 (s, 3H), 4.42 (dd, 1H, J = 5.6, 2.3 Hz), 4.52 - 4.56 (m, 1H), 4.60- 4.42 (dd, 1H, J = 5.6, 2.3 Hz), 4.60 - 4.63 (m, 1H), 5.45 (dd, 1H, J = 2.3, 5.3 Hz), 5.68 (dd, 1H, J = 3.0, 10.6 Hz), 5.88 (dd, 1H, J = 3.0, 10.3 Hz); ^{13}C NMR (75 Mz, $CDCl_3$) δ: -4.7, -4.5, 18.0, 20.7, 25.6, 44.4, 51.8, 70.6, 74.4, 127.2, 130.1, 169.7; MS (EI) m/e: 371 $(M - C_4H_9)^+$, 311, 231, 175, 75, 43; HRMS (EI) calcd. for $C_{10}H_{15}BrO_3Si$ $(M - C_4H_9)^+$: 368.9157. Found: 368.9159.

***rel*-(3*R*,4*S*,5*R*,6*S*)-3,5-Diacetoxy-4,6-dibromo-cyclohexene (Diacetate of 6k).** White crystals, mp 98 - 100 °C (pet. ether/THF); IR (neat): 2941, 1742, 1430, 1372, 1221, 1044, 775 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.18 (s, 3H), 4.59 (dd, 1H, J = 12, 4.0 Hz), 4.63 (dd, 1H, J = 8.0, 8.0 Hz), 5.43 (dd, 1H, J = 8.5, 4.0 Hz), 5.69 - 5.73 (m, 2H), 6.03 - 5.98 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.7, 20.8, 43.2, 46.4, 71.2, 74,3, 126.4, 129.3, 169.7, 169.9; MS (EI) m/e: 294 $(M - OAc)^+$, 275 $(M - Br)^+$, 215 $(M - Br - OAc)^+$, 190, 173, 153, 111, 94; HRMS (EI) calcd. for $C_8H_9BrO_2$ $(M - OAc)^+$: 294.8969. Found: 294.8975.

***rel*-(3*R*,4*S*,5*S*,6*S*)-3,5-Diacetoxy-4-bromo-6-iodo-1-cyclohexene (Diacetate of 6l).** Clear plates, mp 112 °C (pet. ether/THF); IR (film): 2978, 2936, 1743, 1371, 1220, 1031, 422 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.15 (s, 3H), 2.16 (s, 3H), 4.71 (d, 1H, J = 7.5 Hz), 4.81 (dd, 1H, J = 4.0, 4.0 Hz), 5.46 (m, 1H), 5.56 (dd, 1H, J = 3.0, 10 Hz), 5.88 (broad d, 1H, J = 7.0 Hz), 6.07 (dd, 1H, J = 3.5, 10 Hz), ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.3, 20.7, 20.9, 46.2, 71.4, 76.0, 125.0, 131.2, 169.8, 170.1; MS (CI) m/e: 403 $(M)^+$, 343 $(M + H - OAc)^+$, 275 $(M - I)^+$, 173; HRMS (EI) calcd. for $C_8H_{10}BrO_2I$ $(M + H - OAc)^+$: 343.8909. Found: 343.8913.

***rel*-(1*R*,2*S*,5*R*,6*S*)-2,5-Diacetoxy-6-bromo-3-cyclohexen-1-ol (6m):** White crystals, mp 100 °C (diethyl ether/pentane); IR (film): 3457, 2936, 1740, 1372, 1225, 1013, 956 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 2.10 (s, 3H), 2.12 (s, 3H), 2.62 (broad s, 1H), 4.02 (dd, 1H, 2.6, 6.0 Hz), 4.36 (dd, 1H, *J* = 2.6, 4.9 Hz), 5.41 (dd, 1H, *J* = 1.8, 6.3 Hz), 5.62 (dd, 1H, *J* = 2.0, 4.6 MHz), 5.81 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 20.8, 21.0, 53.0, 70.1, 71.2, 71.8, 126.6, 128.3, 169.7, 170.8 cm^{-1}; MS (EI) m/e: 295 $(M)^+$, 77 $(M - H_2O)^+$, 233, 153, 111, 43; HRMS (EI) calcd for $C_{10}H_{12}BrO_4$ (M - OH): 274.9919. Found: 274.9925.

***rel*-(1*R*,4*S*,5*R*,6*S*)-5-Bromo-4-(*tert*-Butyldimethylsilyl)oxy-2-cyclohexene-1,6-diol (7):** Into a solution of alcohol **6b** (72 mg, 0.102 mmol) in CH_2Cl_2 (9 mL) at 0 °C was added dropwise TFA (1 mL). After 15 min, the reaction was poured into sat. aq. $NaHCO_3$ (25 mL) followed by the addition of EtOAc (10 mL). The layers were separated and the aqueous layer extracted with EtOAc (4x5 mL). The combined organics were washed with brine and dried over $MgSO_4$. Concentration of the organic solution and purification of the resulting oil by flash chromatograpy (1:1 pet. ether/EtoAc) gave diol **7** (44 mg, 85%) as an oil. IR (neat): 3379, 2954, 2921, 2886, 2851, 1245, 1053, 863, 837, 773 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.09 (s, 3H), 0.11 (s, 3H), 0.88 (s, 9H), 2.79 (broad s, 2H), 3.89 (dd, 1H, *J* = 2.6, 7.0 Hz), 4.23 - 4.26 (m , 1H), 4.49 (dd, 1H, *J* = 3.6, 3.6 Hz), 5.66 (dddd, 1H, *J* = 10, 3.6, 1.6, 1.6 Hz), 5.77 (dd, 1H *J* = 2.0, 10 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.8, -4.7, 18.0, 25.7, 57.9, 70.8, 71.4, 127.7, 129.6; MS (EI) m/e: 265 $(M - C_4H_9)^+$, 247 $(M - C_4H_9 - OH)^+$, 219, 139, 111, 75; HRMS (EI) calcd. for $C_8H_{14}BrO_3Si$ $(M - C_4H_9)^+$: 264.9896. Found; 264.9900.

***rel*-(1*R*,4*R*,5*R*,6*R*)-2-bromo-3(*tert*-butyldimethylsilyl)oxy-4-bis(phenylsulfonyl)methyl-2-cyclohexen-1-ol (11b):** Bis(phenylsulfonyl)-methane (178 mg, 0.6 mmol) was used directly in THF with 15 mol% $Pd(PPh_3)_4$: Yield: 83 % (pale yellow oil); IR (film) 3528, 2929, 2857, 1448, 1335, 1257, 839 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.01 (s, 3H), 0.3 (s, 3H), 0.83 (s, 9H), 2.65 (d, 1H, *J* = 7.5 Hz), 3.42 - 3.45 (m, 1H), 4.09 - 4.13 (dd, 1H, *J* = 3.0, 10.2 Hz), 4.27 - 4.32 (m, 1H), 4.76 - 4.82 (dd, 1H, *J* = 7.8, 10.5 Hz), 4.95 (d, 1H, *J* = 1.5 Hz), 5.81 - 5.90 (m, 2H), 7.51 - 7.59 (m, 4H), 7.66-7.72 (m, 2H), 7.89 - 8.00 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ -3.09, -2.37, 18.52, 26.30, 46.95, 61.58, 68.74, 70.45, 82.80, 127.19, 128.05, 128.82, 129.35, 129.73, 130.29, 134.73, 134.89, 137.94, 139.16.

***rel*-(1*R*,4*S*,5*R*,6*R*)-2-Bromo-3-(*tert*-butyldimethylsilyl)oxy-4-[*p*-toluenesulfonylamino]-2-cyclohexen-1-ol (11c):** The reaction was performed using NaNHTs (115 mg, 0.6 mmol) and $TsNH_2$ (103 mg, 0.6 mmol) in CH_3CN with 5 mol% of $Pd(PPh_3)_4$. Yield: 67 % (colorless oil); IR (film) 3482, 3287, 2928, 2856, 1613, 1472, 1330, 1160, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.05 (s, 3H), 0.054 (s, 3H), 0.83 (s, 9H), 2.19 (d, 1H, J = 4.2 Hz), 2.43 (s, 3H), 3.60 - 3.65 (m, 1H), 4.26 - 4.39 (m, 3H), 5.06 (d, 1H, J = 10.2 Hz), 5.26 - 5.32 (m, 1H), 5.60 - 5.64 (m, 1H), 7.32 (d, 2H, J = 7.8 Hz), 7.77 (d, 2H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$)δ: -5.06, -4.85, 17.78, 21.49, 25.56, 53.73, 56.20, 64.09, 72.83, 124.80, 127.13, 129.82, 130.67, 137.82, 143.67.

***rel*-(1*R*,4*S*,5*R*,6*R*)-2-Bromo-3-(*tert*-butyldimethylsilyl)oxy-4-phenylsulfonyl-2-cyclohexen-1-ol (11d):** The reaction was conducted using sodium benzenesulfinate (98.4 mg, 0.6 mmol) in THF-H_2O (2:1) with 5 mol% of $Pd(PPh_3)_4$ at 0 °C. Yield: 48 %; white solid, mp 143-145 °C; IR (KBr) 3250, 2930, 2857, 1650, 1470, 1305, 1255, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.23 (s, 3H), 0.25 (s, 3H), 0.89 (s, 9H), 2.60 (d, 1H,J = 10.5 Hz), 3.84 - 3.87 (m, 1H), 4.09 - 4.12 (dd, 1H, J = 3.0, 6.0 Hz), 4.24 -4.30 (m, 1H), 4.88 - 4.91 (dd, 1H, J = 2.1, 6.3 Hz), 5.63 - 5.68 (dd, 1H, J = 3.9, 9.9 Hz), 6.12 - 6.18 (ddd, 1H, J = 2.4, 4.8, 10.5 Hz), 7.56 - 7.61 (m, 2H), 7.66 - 7.71 (m, 1H), 7.86 - 7.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.62, 18.05, 25.87, 58.00, 65.45, 68.56, 71.06, 120.30, 129.20, 129.33, 134.28, 134.89, 137.47.

***rel*-(1*R*,4*S*,5*R*,6*R*)-4-Azido-2-bromo-4-[(*tert*-butyldimethyl)-silyl]oxy-2-cyclohexen-1-ol (11e):** The reaction was performed using NaN_3 (39 mg, 0.6 mmol) in THF-H_2O (1:1) with 5 mol% $Pd(PPh_3)_4$ at 0 °C. Yield: 65 % (colorless oil); IR (film) 3440, 2930, 2857, 2102, 1463, 1256, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.18 (s, 3H), 0.19 (s, 3H), 0.93 (s, 9H), 2.52 (d, 1H, J = 4.8 Hz), 3.75 - 3.77 (m, 1H), 4.02 - 4.07 (dd, 1H, J = 6.6, 9.6 Hz), 4.14 - 4.19 (dd, 1H ,J = 3.6, 9.6 Hz), 4.39 (m, 1H), 5.78 (dd, 1H, J = 2.4, 9.9 Hz), 5.96 - 6.02 (ddd, 1H, J = 2.4, 4.8, 10.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.46, -4.18, 18.27, 25.92, 58.90, 64.78, 67.18, 71.39, 127.41, 129.69.

***rel*-(1*R*,4*S*,5*R*,6*R*)-6-Bromo-5-(*tert*-butyldimethylsilyl)oxy-4-bis(phenylsulfonyl)methyl-2-cyclohexenyl methyl carbonate (12b):** White solid: mp 144 - 145 °C; IR (KBr) 2929, 2857, 1750, 1584, 1463, 1447, 1336, 1269, 1156, 838 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.06 (s, 3H), 0.30 (s, 3H), 0.86 (s, 9H), 3.52 - 3.56 (m, 1H), 3.86 (s, 3H), 4.10 - 4.15 (dd, 1H, J = 3.6, 11.1 Hz), 4.70 - 4.76 (dd, 1H, J = 9.0, 10.2 Hz), 4.98 (d, 1H, J = 2.4 Hz), 5.29 - 5.32 (m, 1H), 5.61 - 5.67 (m, 1H), 5.88 - 5.92 (dd, 1H, J = 2.4, 9.6

Hz), 7.48 - 7.60 (m, 4H), 7.65 - 7.73 (m, 2H), 7.92 - 7.95 (m, 2H), 8.04 - 8.07 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -3.31, -2.43, 18.60, 26.43, 46.24, 55.15, 55.68, 69.67, 73.28, 82.25, 123.67, 128.67, 129.26, 129.39, 130.10, 131.04, 134.74, 134.90, 138.67, 155.04; HRMS (EI) calcd. for $C_{27}H_{35}BrO_8S_2Si$ $(M)^+$: 658.0726, $(M - C_4H_9)^+$: 601.0022. Found: 601.0011.

***rel*-(1*R*,4*S*,5*R*,6*R*)-6-Bromo-5-(*tert*-butyldimethylsilyl)oxy-4-[*p*-toluenesulfonyl]amino-2-cyclohexenyl methyl carbonate (12c):** White solid: mp 149 - 150 °C; IR (KBr) 3284, 2954, 2857, 1748, 1596, 1462, 1444, 1267, 839 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$)δ : 0.04 (s, 3H), 0.08 (s, 3H), 0.84 (s, 9H), 2.43 (s, 3H), 3.64 - 3.69 (m, 1H), 3.80 (s, 3H), 4.24 - 4.25 (m, 1H), 4.42 - 4.45 (m, 1H), 5.14 (d, 1H, J = 11.1 Hz), 5.33 - 5.35 (m, 1H), 5.40 - 5.46 (m, 1H), 5.61 - 5.65 (m, 1H), 7.32 (d, 2H, J = 8.4 Hz), 7.78 (d, 2H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -5.15, -5.00, 17.78, 21.49, 25.52, 48.06, 53.52, 55.11, 70.23, 72.89, 126.04, 126.23, 127.14, 129.83, 137.76, 143.70, 154.72; HRMS (EI) calcd. for $C_{21}H_{32}BrNO_6SSi$ $(M)^+$: 533.0903, $(M - C_4H_9)^+$: 476.0199. Found: 476.0204.

***rel*-(1*R*,4*S*,5*R*,6*R*)-6-Bromo-5-(*tert*-butyldimethylsilyl)oxy-4-phenylsulfonyl-2-cyclohexenyl methyl carbonate (12d):** White solid: mp 72 - 74 °C; IR (KBr) 2956, 2857, 1751, 1572, 1471, 1446, 1270, 840 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.23 (s, 3H), 0.24 (s, 3H), 0.90 (s, 9H), 3.76 (s, 3H), 3.86 (m, 1H), 4.23 - 4.26 (dd, 1H, J = 3.9, 5.1 Hz), 4.75 - 4.77 (dd, 1H, J = 1.8, 4.8 Hz), 5.19 - 5.20 (m, 1H), 5.97 (m, 2H), 7.52 - 7.57 (m, 2H), 7.62 - 7.67 (m, 1H), 7.86 - 7.89 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.59, 18.03, 25.84, 49.80, 55.02, 68.79, 70.60, 71.06, 121.73, 129.14, 129.41, 129.55, 134.07, 137.44, 154.64; HRMS (EI) calcd. for $C_{20}H_{29}BrO_6SSi$ $(M)^+$: 504.0638, $(M - C_4H_9)^+$ 446.9933. Found: 446.9921.

***rel*-(1*R*,4*S*,5*R*,6*R*)-4-Azido-6-bromo-5-(*tert*-butyldimethylsilyl)oxy-2-cyclohexenyl methyl carbonate (12e):** Colorless oil: IR (film) 2956, 2104, 1752, 1443, 1268 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.02 (s, 3H), 0.021 (s, 3H), 0.93 (s, 9H), 3.78 - 3.80 (m, 1H), 3.83 (s, 3H), 3.99 - 4.04 (dd, 1H, J = 6.0, 9.9 Hz), 4.16 - 4.20 (dd, 1H, J = 3.9, 9.9 Hz), 5.37 (m, 1H), 5.88 - 5.92 (dd, 1H,J = 2.7, 9.9 Hz), 5.98 - 6.04 (ddd, 1H, J = 2.7, 5.1, 10.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.51, -4.18, 18.24, 25.87, 51.48, 55.17, 64.57, 71.90, 72.23, 126.60, 129.45, 154.95; HRMS (EI) calcd. for $C_{14}H_{24}BrN_3O_4Si$ $(M)^+$: 405.0719, $(M - C_4H_9)^+$ 348.0015. Found: 348.0013.

***rel*-(5*R*,6*S*)-5-(*tert*-Butyldimethylsilyl)oxy-6-Bis(phenylsulfonyl)-methyl-1,3- cyclohexadiene (13b):** Colorless oil. Yield: 88 % (71 % by procedure B); IR (film) 2930, 2857, 1584, 1463, 1448, 1259, 893 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.09 (s, 3H), 0.11 (s, 3H), 0.79 (s, 9H), 3.55 - 3.61 (m, 1H), 4.85 (d, 1H, J = 1.2 Hz), 5.21 - 5.27 (m, 1H), 5.70 - 5.74 (m, 1H), 5.79 - 5.85 (m, 2H), 6.01 - 6.05 (m, 1H), 7.49 - 7.63 (m, 4H), 7.64 - 7.72 (m, 2H), 7.83 - 7.86 (m, 2H), 8.03 - 8.06 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.41, -3.36, 17.81, 25.74, 44.87, 70.58, 82.02, 123.86, 124.11, 124.19, 128.79, 129.22, 129.60, 129.64, 131.75, 134.33, 134.51, 137.73, 140.60; HRMS (EI) calcd. for $C_{25}H_{32}O_5S_2Si$: $(M)^+$ 504.1460, $(M - C_4H_9)^+$ 447.0756. Found: 447.0763.

***rel*-(5*R*,6*S*)-5-(*tert*-Butyldimethylsilyl)oxy-6-[(*p*-toluenesulfonyl)-amino]-1,3-cyclohexadiene (13c):** Colorless oil. Yield: 88 % (68 % by procedure B); IR (film): 3275, 2929, 2856, 1599, 1472, 1462, 1332, 1254, 837 cm^{-1} ; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.05 (s, 3H), 0.06 (s, 3H), 0.84 (s, 9H), 2.43 (s, 3H), 3.81 - 3.87 (m, 1H), 4.26 - 4.30 (dd, 1H, J = 3.6, 8.4 Hz), 4.40 - 4.42 (d, 1H, J = 6.6 Hz), 5.67 - 5.72 (m, 1H), 5.74 - 5.79 (m, 1H), 5.87 - 5.91 (m, 2H), 7.30 (d, 2H, J = 7.8 Hz), 7.75 (d, 2H, J = 7.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.63, -4.44, 17.99, 21.49, 25.72, 55.56, 70.05, 124.23, 124.80, 126.61, 127.16, 129.36, 129.73, 137.45, 143.50; HRMS (EI) calcd. for $C_{19}H_{29}NO_3SSi$: $(M)^+$ 379.1637. Found: 379.1642.

***rel*-(5*R*,6*S*)-5-(*tert*-Butyldimethylsilyl)oxy-6-phenylsulfonyl-1,3-cyclohexadiene (13d):** Colorless oil. Yield: 46 % (by procedure B); IR (film): 2929, 2857, 1653, 1472, 1447, 1307, 1050, 837 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ: 0.1 (s, 3H), 0.11 (s, 3H), 0.85 (s, 9H), 3.94 - 3.97 (m, 1H), 4.83 - 4.85 (m, 1 H), 5.60 - 5.66 (dd, 1H, J = 8.4, 9.6 Hz,), 5.70-5.75 (ddd, 1H, J = 1.2, 5.7, 9.9 Hz), 5.78-5.84 (dd, 1H, J = 5.4, 10.2 Hz), 6.13 - 6.18 (ddd, 1H, J = 1.2, 5.4, 10.5 Hz), 7.45 - 7.50 (m, 2H), 7.58 - 7.64 (m, 1H), 7.78 - 7.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: -4.54, -4.34, 18.02, 25.71, 61.89, 69.06, 116.95, 123.08, 126.48, 128.07, 128.42, 129.39, 133.75, 137.07; HRMS (EI) calcd. for $C_{18}H_{26}O_3SSi$: $(M)^+$ 350.1372, $(M - C_4H_9)^+$ 293.0668. Found: 293.0676.

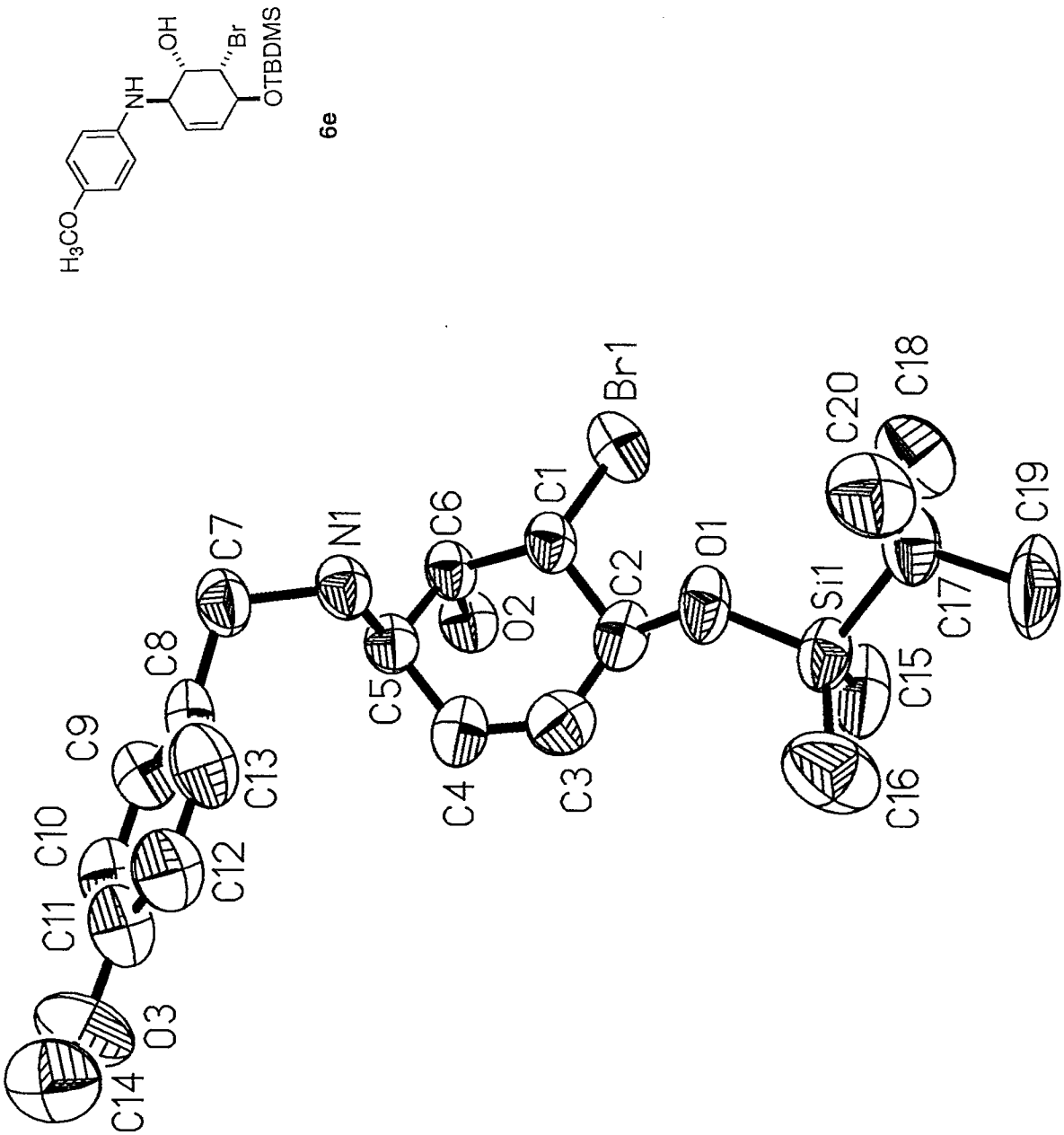

H3CO
NH
OH
Br
OTBDMS
6e
C14
O3
C11
C10
C9
C8
C7
N1
C6
C1
Br1
C13
C12
C5
O2
C2
O1
Si1
C20
C18
C4
C3
C15
C17
C19
C16

Table 1. Crystal data and structure refinement for 6e

Identification code	kort
Empirical formula	C20 H32 Br N O3 Si
Formula weight	442.47
Temperature	295(2) K
Wavelength	1.54178 A
Crystal system	P2(1)
Space group	monoclinic
Unit cell dimensions	a = 12.0209(13) A alpha = 90 deg. b = 7.9943(7) A beta = 113.766(8) deg. c = 12.8223(14) A gamma = 90 deg.
Volume	1127.7(2) A^3
Z	2
Density (calculated)	1.303 Mg/m^3
Absorption coefficient	3.134 mm^-1
F(000)	464
Crystal size	0.25 x 0.20 x 0.15 mm
Theta range for data collection	3.77 to 54.91 deg.
Index ranges	-12<=h<=12, -8<=k<=8, -13<=l<=13
Reflections collected	3183
Independent reflections	2755 [R(int) = 0.0166]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2753 / 1 / 278
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.1035
R indices (all data)	R1 = 0.0409, wR2 = 0.1093
Absolute structure parameter	-0.03(3)
Largest diff. peak and hole	0.551 and -0.360 e.A^-3

Table 3. Bond lengths [A] and angles [deg] for **6e**

Br(1)-C(1)	1.953(4)
Si(1)-O(1)	1.643(4)
Si(1)-C(15)	1.827(7)
Si(1)-C(16)	1.846(7)
Si(1)-C(17)	1.865(6)
C(1)-C(6)	1.521(6)
C(1)-C(2)	1.532(6)
C(2)-O(1)	1.437(6)
C(2)-C(3)	1.472(7)
C(3)-C(4)	1.318(8)
C(4)-C(5)	1.501(7)
C(5)-N(1)	1.488(5)
C(5)-C(6)	1.529(7)
C(6)-O(2)	1.417(5)
N(1)-C(7)	1.472(7)
C(7)-C(8)	1.486(8)
C(8)-C(13)	1.363(8)
C(8)-C(9)	1.381(8)
C(9)-C(10)	1.374(8)
C(10)-C(11)	1.383(8)
C(11)-O(3)	1.337(7)
C(11)-C(12)	1.387(8)
C(12)-C(13)	1.368(9)
O(3)-C(14)	1.407(8)
C(17)-C(20)	1.515(9)
C(17)-C(18)	1.548(9)
C(17)-C(19)	1.568(8)
O(1)-Si(1)-C(15)	110.0(2)
O(1)-Si(1)-C(16)	110.2(3)
C(15)-Si(1)-C(16)	109.9(4)
O(1)-Si(1)-C(17)	103.9(2)
C(15)-Si(1)-C(17)	112.3(3)
C(16)-Si(1)-C(17)	110.5(3)
C(6)-C(1)-C(2)	112.3(4)
C(6)-C(1)-Br(1)	110.3(3)
C(2)-C(1)-Br(1)	109.8(3)
O(1)-C(2)-C(3)	111.8(5)
O(1)-C(2)-C(1)	106.9(4)
C(3)-C(2)-C(1)	109.7(4)
C(4)-C(3)-C(2)	126.3(5)
C(3)-C(4)-C(5)	122.1(6)
N(1)-C(5)-C(4)	109.9(4)
N(1)-C(5)-C(6)	110.9(4)
C(4)-C(5)-C(6)	111.5(4)
O(2)-C(6)-C(1)	111.8(4)
O(2)-C(6)-C(5)	108.1(4)
C(1)-C(6)-C(5)	108.7(4)
C(2)-O(1)-Si(1)	128.4(3)
C(7)-N(1)-C(5)	113.5(4)
N(1)-C(7)-C(8)	116.0(5)
C(13)-C(8)-C(9)	116.3(5)
C(13)-C(8)-C(7)	121.6(6)
C(9)-C(8)-C(7)	122.0(5)
C(10)-C(9)-C(8)	122.5(5)
C(9)-C(10)-C(11)	119.9(5)
O(3)-C(11)-C(10)	116.8(5)
O(3)-C(11)-C(12)	125.1(5)
C(10)-C(11)-C(12)	118.1(6)
C(13)-C(12)-C(11)	120.0(5)
C(8)-C(13)-C(12)	123.1(5)
C(11)-O(3)-C(14)	118.6(5)
C(20)-C(17)-C(18)	109.3(6)
C(20)-C(17)-C(19)	108.2(6)
C(18)-C(17)-C(19)	108.2(6)
C(20)-C(17)-Si(1)	111.0(4)
C(18)-C(17)-Si(1)	110.4(4)
C(19)-C(17)-Si(1)	109.6(5)

Symmetry transformations used to generate equivalent atoms:

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **6e** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	9372(1)	7(1)	1934(1)	80(1)
Si(1)	12779(1)	-1956(2)	4618(1)	71(1)
C(1)	10770(4)	-224(6)	1535(3)	54(1)
C(2)	11949(5)	-115(7)	2614(4)	64(1)
C(3)	12990(5)	87(9)	2297(4)	71(1)
C(4)	12938(6)	497(6)	1283(4)	62(1)
C(5)	11753(4)	757(6)	278(4)	54(1)
C(6)	10715(5)	1081(5)	653(4)	53(1)
O(1)	12035(4)	-1631(4)	3244(3)	69(1)
O(2)	10849(3)	2726(4)	1101(3)	63(1)
N(1)	11481(4)	-713(5)	-498(3)	59(1)
C(7)	11580(6)	-352(8)	-1583(5)	67(2)
C(8)	12811(4)	108(8)	-1500(3)	58(1)
C(9)	13088(5)	1709(7)	-1722(4)	67(1)
C(10)	14218(6)	2143(7)	-1662(5)	76(2)
C(11)	15129(6)	952(7)	-1372(5)	73(2)
C(12)	14864(6)	-660(7)	-1143(6)	79(2)
C(13)	13727(6)	-1036(7)	-1210(5)	79(2)
O(3)	16202(4)	1455(5)	-1343(5)	103(1)
C(14)	16994(6)	249(11)	-1465(6)	101(2)
C(15)	12713(7)	-89(10)	5414(4)	99(2)
C(16)	14378(6)	-2493(11)	4940(8)	122(3)
C(17)	11978(6)	-3772(7)	4916(5)	83(2)
C(18)	10688(7)	-3256(11)	4786(7)	112(2)
C(19)	12704(8)	-4388(11)	6170(5)	134(3)
C(20)	11882(7)	-5215(9)	4118(6)	105(2)

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for 6e
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

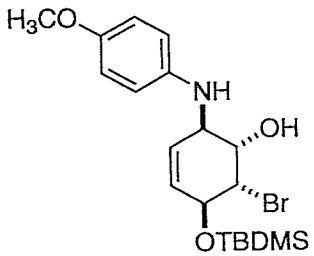
	U11	U22	U33	U23	U13	U12
Br(1)	105(1)	68(1)	89(1)	6(1)	61(1)	-3(1)
Si(1)	100(1)	55(1)	50(1)	9(1)	22(1)	5(1)
C(1)	79(3)	32(2)	52(2)	8(2)	26(2)	0(2)
C(2)	104(3)	35(2)	45(2)	-2(2)	22(2)	-6(3)
C(3)	76(3)	58(3)	67(3)	1(3)	15(2)	-6(3)
C(4)	80(4)	47(3)	59(3)	0(2)	27(3)	-4(2)
C(5)	74(3)	39(2)	51(3)	1(2)	29(2)	-5(2)
C(6)	75(3)	36(2)	47(3)	5(2)	24(2)	-1(2)
O(1)	114(3)	40(2)	50(2)	8(1)	29(2)	1(2)
O(2)	94(2)	37(2)	62(2)	-1(1)	35(2)	-1(2)
N(1)	91(3)	42(2)	53(2)	-3(2)	37(2)	-13(2)
C(7)	91(4)	63(4)	49(3)	-1(3)	29(3)	-3(4)
C(8)	89(3)	49(2)	42(2)	3(2)	33(2)	0(3)
C(9)	83(4)	52(3)	74(3)	0(3)	40(3)	7(3)
C(10)	108(5)	44(3)	81(4)	2(3)	46(3)	3(3)
C(11)	96(4)	54(3)	81(4)	13(3)	47(3)	10(3)
C(12)	91(4)	56(3)	98(4)	21(3)	46(3)	22(3)
C(13)	122(5)	45(3)	85(4)	16(3)	60(3)	10(3)
O(3)	97(3)	66(3)	169(4)	6(3)	79(3)	3(2)
C(14)	92(4)	97(5)	120(5)	-16(5)	48(3)	6(4)
C(15)	162(5)	69(3)	63(3)	-2(4)	44(3)	-6(5)
C(16)	96(5)	116(6)	151(7)	42(5)	46(5)	13(4)
C(17)	116(5)	63(3)	68(3)	22(3)	36(3)	8(3)
C(18)	125(6)	97(5)	133(6)	24(5)	71(5)	5(4)
C(19)	192(8)	116(7)	76(4)	51(4)	35(5)	4(5)
C(20)	135(5)	59(4)	117(5)	2(4)	46(4)	-8(4)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6e**

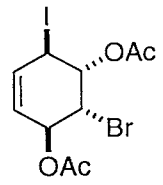
	x	y	z	U(eq)
H(02)	11104(45)	2682(4)	1798(4)	76
H(N1)	11285(4)	-1678(5)	-329(3)	71
H(1)	10733(4)	-1333(6)	1197(3)	65
H(2)	11891(45)	925(75)	3005(46)	74(15)
H(3)	13722(52)	-86(118)	2894(53)	107(20)
H(4)	13573(45)	551(63)	1203(42)	58(16)
H(5)	11918(28)	1695(50)	-150(28)	24(8)
H(6)	9988(41)	992(52)	-13(40)	43(10)
H(7A)	11139(46)	-1238(70)	-2125(45)	68(14)
H(7B)	11153(37)	288(59)	-1895(35)	26(13)
H(9)	12486(5)	2525(7)	-1920(4)	80
H(10)	14397(39)	3338(68)	-1540(38)	55(12)
H(12)	15459(6)	-1485(7)	-945(6)	95
H(13)	13539(46)	-2212(81)	-1066(46)	77(15)
H(14A)	17337(32)	-406(38)	-782(16)	121
H(14B)	17633(24)	799(11)	-1600(38)	121
H(14C)	16550(10)	-468(37)	-2098(25)	121
H(15A)	13225(30)	764(21)	5316(29)	118
H(15B)	12989(38)	-361(16)	6208(7)	118
H(15C)	11891(9)	309(32)	5135(25)	118
H(16A)	14821(14)	-2583(75)	5750(8)	146
H(16B)	14734(17)	-1634(40)	4650(48)	146
H(16C)	14410(7)	-3541(40)	4588(43)	146
H(18A)	10748(7)	-2384(45)	5321(31)	135
H(18B)	10282(18)	-4205(18)	4932(44)	135
H(18C)	10233(17)	-2858(62)	4026(15)	135
H(19A)	12736(51)	-3509(31)	6691(6)	161
H(19B)	13515(21)	-4688(78)	6272(17)	161
H(19C)	12305(35)	-5346(52)	6314(19)	161
H(20A)	11364(34)	-4901(22)	3353(8)	126
H(20B)	11546(38)	-6172(19)	4340(24)	126
H(20C)	12676(9)	-5485(38)	4157(30)	126

Selected torsion angles

-165.88	(0.39)	C6 - C1 - C2 - O1
71.09	(0.43)	Br1 - C1 - C2 - O1
-44.48	(0.61)	C6 - C1 - C2 - C3
-167.51	(0.41)	Br1 - C1 - C2 - C3
132.86	(0.60)	O1 - C2 - C3 - C4
14.47	(0.86)	C1 - C2 - C3 - C4
-2.32	(0.92)	C2 - C3 - C4 - C5
-103.98	(0.56)	C3 - C4 - C5 - N1
19.46	(0.65)	C3 - C4 - C5 - C6
-56.72	(0.55)	C2 - C1 - C6 - O2
66.05	(0.44)	Br1 - C1 - C6 - O2
62.60	(0.51)	C2 - C1 - C6 - C5
-174.63	(0.29)	Br1 - C1 - C6 - C5
-163.31	(0.33)	N1 - C5 - C6 - O2
73.83	(0.45)	C4 - C5 - C6 - O2
75.11	(0.44)	N1 - C5 - C6 - C1
-47.76	(0.49)	C4 - C5 - C6 - C1
84.18	(0.53)	C3 - C2 - O1 - Si1
-155.78	(0.35)	C1 - C2 - O1 - Si1
35.98	(0.52)	C15 - Si1 - O1 - C2
-85.35	(0.51)	C16 - Si1 - O1 - C2
156.31	(0.45)	C17 - Si1 - O1 - C2
-109.78	(0.52)	C4 - C5 - N1 - C7
126.46	(0.48)	C6 - C5 - N1 - C7
63.98	(0.70)	C5 - N1 - C7 - C8
70.57	(0.70)	N1 - C7 - C8 - C13
-110.12	(0.59)	N1 - C7 - C8 - C9
0.20	(0.77)	C13 - C8 - C9 - C10
-179.15	(0.48)	C7 - C8 - C9 - C10
0.17	(0.88)	C8 - C9 - C10 - C11
179.19	(0.55)	C9 - C10 - C11 - O3
-0.32	(0.96)	C9 - C10 - C11 - C12
-179.35	(0.60)	O3 - C11 - C12 - C13
0.12	(1.05)	C10 - C11 - C12 - C13
-0.42	(0.86)	C9 - C8 - C13 - C12
178.93	(0.56)	C7 - C8 - C13 - C12
0.27	(1.06)	C11 - C12 - C13 - C8
-157.30	(0.63)	C10 - C11 - O3 - C14
22.18	(1.01)	C12 - C11 - O3 - C14
52.63	(0.49)	O1 - Si1 - C17 - C20
171.43	(0.45)	C15 - Si1 - C17 - C20
-65.51	(0.56)	C16 - Si1 - C17 - C20
-68.72	(0.50)	O1 - Si1 - C17 - C18
50.08	(0.55)	C15 - Si1 - C17 - C18
173.14	(0.54)	C16 - Si1 - C17 - C18
172.14	(0.49)	O1 - Si1 - C17 - C19
-69.06	(0.59)	C15 - Si1 - C17 - C19
54.00	(0.64)	C16 - Si1 - C17 - C19



6e



6l diacetate

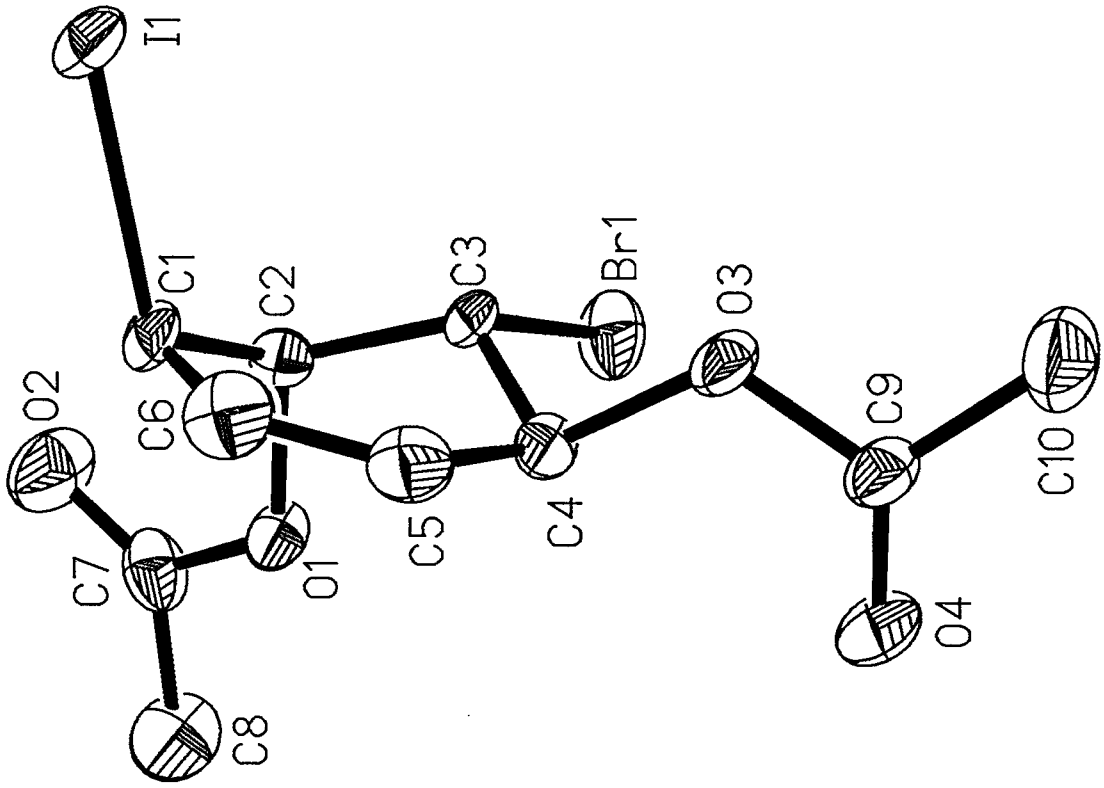


Table 1. Crystal data and structure refinement for **61 diacetate**

Identification code	brio
Empirical formula	C10 H12 Br I O4
Formula weight	403.01
Temperature	295(2) K
Wavelength	1.54178 A
Crystal system	monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 8.5086(11) A alpha = 90 deg. b = 11.9791(13) A beta = 96.630(13) deg. c = 13.203(3) A gamma = 90 deg.
Volume	1336.7(3) A^3
Z	4
Density (calculated)	2.003 Mg/m^3
Absorption coefficient	22.330 mm^-1
F(000)	768
Crystal size	0.40 x 0.40 x 0.20 mm
Theta range for data collection	5.00 to 54.96 deg.
Index ranges	0<=h<=9, 0<=k<=12, -14<=l<=13
Reflections collected	1612
Independent reflections	1497 [R(int) = 0.0518]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1487 / 0 / 147
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0468, wR2 = 0.1234
R indices (all data)	R1 = 0.0505, wR2 = 0.1318
Extinction coefficient	0.0036(3)
Largest diff. peak and hole	1.621 and -1.379 e.A^-3

61 diacetate

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
I(1)	1802(1)	554(1)	3978(1)	39(1)
Br(1)	1526(1)	-3593(1)	5052(1)	39(1)
C(1)	1404(9)	-890(7)	2980(6)	28(2)
C(2)	1985(9)	-1929(7)	3563(6)	26(2)
C(3)	767(9)	-2307(6)	4241(5)	23(2)
C(4)	-815(9)	-2574(6)	3622(6)	25(2)
C(5)	-1291(10)	-1672(7)	2874(6)	34(2)
C(6)	-330(10)	-932(7)	2582(6)	35(2)
O(1)	2150(6)	-2818(4)	2838(4)	29(1)
C(7)	3556(10)	-2875(8)	2456(6)	35(2)
O(2)	4576(7)	-2190(6)	2664(5)	52(2)
C(8)	3638(11)	-3868(9)	1802(8)	52(3)
O(3)	-1962(6)	-2641(4)	4361(4)	32(1)
C(9)	-2899(9)	-3546(7)	4341(6)	29(2)
O(4)	-2861(9)	-4282(5)	3749(5)	47(2)
C(10)	-3919(11)	-3493(8)	5178(8)	50(2)

Table 3. Bond lengths [A] and angles [deg]

I(1)-C(1)	2.176(8)
Br(1)-C(3)	1.943(7)
C(1)-C(6)	1.509(12)
C(1)-C(2)	1.515(11)
C(2)-O(1)	1.449(9)
C(2)-C(3)	1.515(11)
C(3)-C(4)	1.526(11)
C(4)-O(3)	1.460(9)
C(4)-C(5)	1.487(12)
C(5)-C(6)	1.295(12)
O(1)-C(7)	1.353(10)
C(7)-O(2)	1.202(11)
C(7)-C(8)	1.477(14)
O(3)-C(9)	1.344(10)
C(9)-O(4)	1.181(10)
C(9)-C(10)	1.483(12)
C(6)-C(1)-C(2)	113.4(7)
C(6)-C(1)-I(1)	108.4(5)
C(2)-C(1)-I(1)	109.0(5)
O(1)-C(2)-C(3)	107.1(6)
O(1)-C(2)-C(1)	108.6(6)
C(3)-C(2)-C(1)	109.9(6)
C(2)-C(3)-C(4)	111.5(6)
C(2)-C(3)-Br(1)	110.9(5)
C(4)-C(3)-Br(1)	110.2(5)
O(3)-C(4)-C(5)	109.4(6)
O(3)-C(4)-C(3)	105.7(6)
C(5)-C(4)-C(3)	111.1(6)
C(6)-C(5)-C(4)	124.2(7)
C(5)-C(6)-C(1)	123.0(7)
C(7)-O(1)-C(2)	116.1(6)
O(2)-C(7)-O(1)	121.8(8)
O(2)-C(7)-C(8)	127.0(8)
O(1)-C(7)-C(8)	111.3(8)
C(9)-O(3)-C(4)	118.2(6)
O(4)-C(9)-O(3)	123.6(8)
O(4)-C(9)-C(10)	126.0(8)
O(3)-C(9)-C(10)	110.4(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **61 diacetate**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

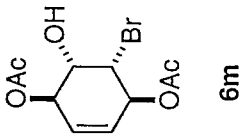
	U11	U22	U33	U23	U13	U12
I(1)	54(1)	18(1)	49(1)	-7(1)	21(1)	-12(1)
Br(1)	44(1)	29(1)	46(1)	14(1)	11(1)	3(1)
C(1)	41(5)	11(4)	35(4)	1(3)	14(4)	-5(3)
C(2)	30(4)	24(4)	26(4)	-5(4)	8(3)	-2(4)
C(3)	32(4)	12(4)	27(4)	-2(3)	9(3)	-6(3)
C(4)	23(4)	21(4)	34(4)	-7(3)	15(3)	0(3)
C(5)	34(4)	36(5)	31(4)	-3(4)	0(4)	-1(4)
C(6)	40(5)	27(5)	36(5)	7(4)	-4(4)	8(4)
O(1)	26(3)	19(3)	46(3)	-8(2)	19(2)	-1(2)
C(7)	35(5)	33(5)	40(5)	7(4)	17(4)	8(4)
O(2)	36(3)	51(4)	74(4)	-18(4)	23(3)	-13(3)
C(8)	43(5)	44(6)	73(7)	-16(5)	27(5)	4(5)
O(3)	31(3)	21(3)	48(3)	-16(2)	20(3)	-9(2)
C(9)	27(4)	21(5)	39(5)	-5(4)	5(3)	-3(3)
O(4)	70(4)	19(3)	56(4)	-15(3)	22(3)	-17(3)
C(10)	40(5)	46(6)	69(6)	-4(5)	25(5)	-10(5)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **61 diacetate**

	x	y	z	U(eq)
H(10A)	-4171(59)	-2728(9)	5305(32)	60
H(10B)	-3370(31)	-3814(46)	5784(16)	60
H(10C)	-4878(34)	-3901(44)	4985(21)	60
H(1)	2000	-767	2407	60
H(2)	3000	-1732	4003	60
H(3)	600	-1627	4805	60
H(4)	-1000	-3430	3337	60
H(5)	-2400	-1690	2527	60
H(6)	-600	-449	2046	50
H(8A)	2600	-4257	1544	60
H(8B)	4200	-3637	1042	60
H(8C)	4800	-4255	1797	50

Selected torsion angles

75.58 (0.79)	C6 - C1 - C2 - O1
-163.55 (0.43)	I1 - C1 - C2 - O1
-41.37 (0.86)	C6 - C1 - C2 - C3
79.50 (0.61)	I1 - C1 - C2 - C3
-58.17 (0.76)	O1 - C2 - C3 - C4
59.71 (0.79)	C1 - C2 - C3 - C4
65.12 (0.61)	O1 - C2 - C3 - Br1
-177.00 (0.48)	C1 - C2 - C3 - Br1
-165.75 (0.59)	C2 - C3 - C4 - O3
70.58 (0.60)	Br1 - C3 - C4 - O3
-47.21 (0.83)	C2 - C3 - C4 - C5
-170.88 (0.51)	Br1 - C3 - C4 - C5
134.25 (0.84)	O3 - C4 - C5 - C6
17.99 (1.10)	C3 - C4 - C5 - C6
-0.72 (1.34)	C4 - C5 - C6 - C1
12.85 (1.17)	C2 - C1 - C6 - C5
-108.40 (0.85)	I1 - C1 - C6 - C5
-153.85 (0.63)	C3 - C2 - O1 - C7
87.44 (0.75)	C1 - C2 - O1 - C7
-3.92 (1.11)	C2 - O1 - C7 - O2
174.88 (0.73)	C2 - O1 - C7 - C8
111.19 (0.73)	C5 - C4 - O3 - C9
-129.17 (0.66)	C3 - C4 - O3 - C9
-1.16 (1.15)	C4 - O3 - C9 - O4
177.02 (0.69)	C4 - O3 - C9 - C10



6m

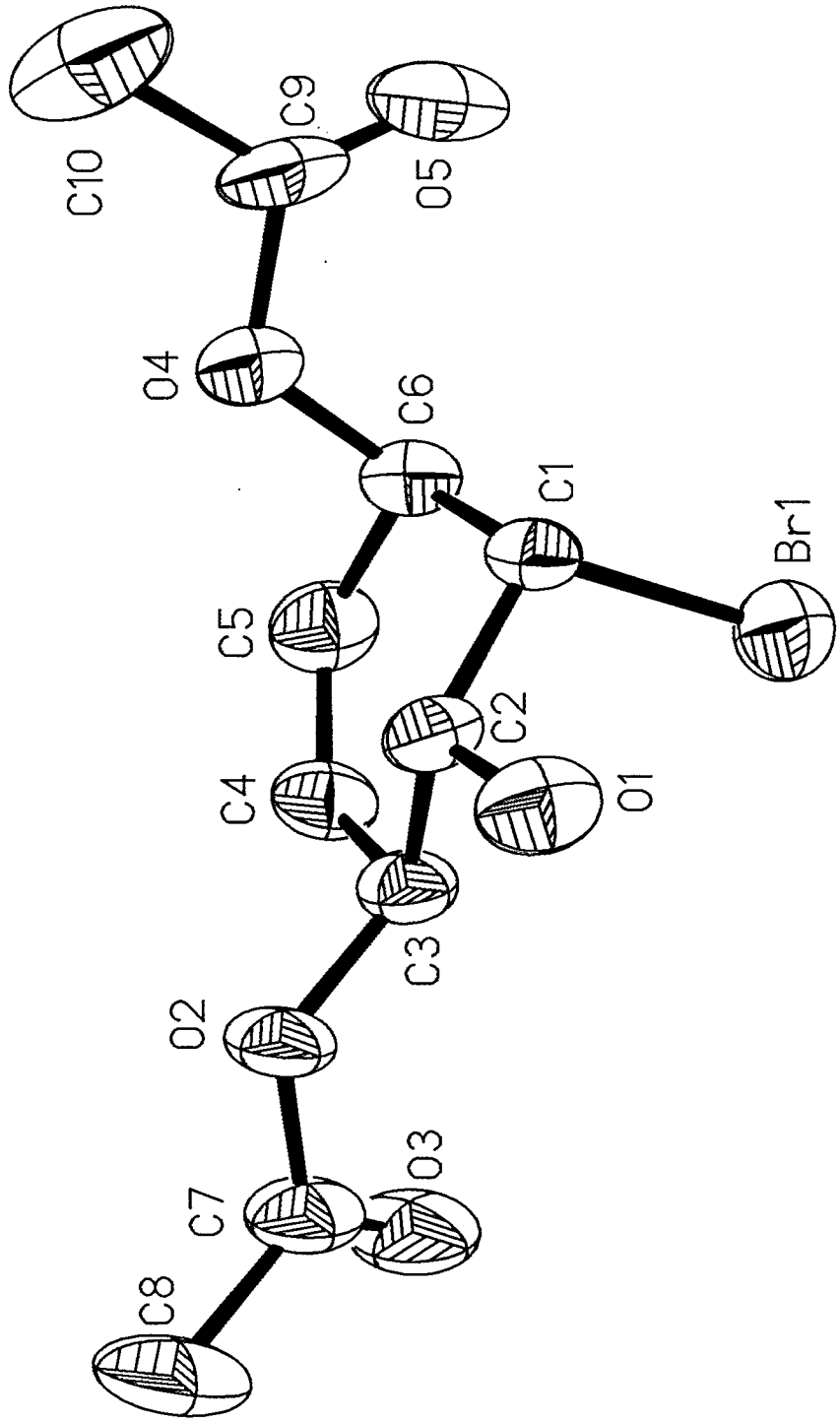


Table 1. Crystal data and structure refinement for 6m

Identification code	core
Empirical formula	C10 H13 Br O5
Formula weight	293.11
Temperature	295(2) K
Wavelength	0.71073 A
Crystal system	orthorhombic
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 7.13180(10) A alpha = 90 deg. b = 11.8336(2) A beta = 90 deg. c = 14.2132(2) A gamma = 90 deg.
Volume	1199.52(3) A^3
Z	4
Density (calculated)	1.623 Mg/m^3
Absorption coefficient	3.430 mm^-1
F(000)	592
Crystal size	0.50 x 0.40 x 0.35 mm
Theta range for data collection	2.24 to 28.32 deg.
Index ranges	-9<=h<=8, 0<=k<=15, 0<=l<=18
Reflections collected	2607
Independent reflections	2607 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2605 / 0 / 149
Goodness-of-fit on F^2	0.940
Final R indices [I>2sigma(I)]	R1 = 0.0571, wR2 = 0.1309
R indices (all data)	R1 = 0.0813, wR2 = 0.1418
Absolute structure parameter	0.04(2)
Extinction coefficient	0.000(2)
Largest diff. peak and hole	1.553 and -0.688 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **6m** U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Br(1)	1617(1)	3991(1)	2573(1)	60(1)
C(1)	1333(8)	2435(4)	3009(3)	41(1)
C(2)	1697(7)	1614(4)	2200(3)	38(1)
O(1)	3562(5)	1620(3)	1912(2)	50(1)
C(3)	325(7)	1837(5)	1417(3)	41(1)
C(4)	-1621(9)	1906(5)	1787(3)	47(1)
C(5)	-2069(8)	2097(5)	2669(4)	54(1)
C(6)	-596(8)	2292(5)	3408(3)	43(1)
O(2)	519(6)	912(3)	755(2)	48(1)
C(7)	61(8)	1138(6)	-143(3)	54(2)
O(3)	-564(8)	2031(4)	-380(3)	71(1)
C(8)	430(12)	160(7)	-763(4)	82(2)
O(4)	-642(6)	1280(3)	3984(2)	51(1)
C(9)	-93(9)	1399(6)	4891(4)	60(2)
O(5)	409(9)	2269(5)	5212(3)	88(2)
C(10)	-214(13)	290(6)	5397(5)	92(3)

Table 3. Bond lengths [A] and angles [deg] for **6m**

Br(1)-C(1)	1.953(5)	C(6)-C(1)-C(2)	111.7(4)
C(1)-C(6)	1.497(7)	C(6)-C(1)-Br(1)	108.7(4)
C(1)-C(2)	1.527(6)	C(2)-C(1)-Br(1)	110.1(3)
C(2)-O(1)	1.392(6)	O(1)-C(2)-C(3)	113.8(4)
C(2)-C(3)	1.505(6)	O(1)-C(2)-C(1)	112.4(4)
C(3)-O(2)	1.449(6)	C(3)-C(2)-C(1)	109.6(4)
C(3)-C(4)	1.487(8)	O(2)-C(3)-C(4)	111.1(4)
C(4)-C(5)	1.313(7)	O(2)-C(3)-C(2)	106.6(4)
C(5)-C(6)	1.503(7)	C(4)-C(3)-C(2)	110.8(4)
C(6)-O(4)	1.451(6)	C(5)-C(4)-C(3)	125.1(5)
O(2)-C(7)	1.344(6)	C(4)-C(5)-C(6)	121.5(5)
C(7)-O(3)	1.195(8)	O(4)-C(6)-C(5)	104.6(4)
C(7)-C(8)	1.478(9)	O(4)-C(6)-C(1)	109.1(4)
O(4)-C(9)	1.355(7)	C(5)-C(6)-C(1)	113.3(4)
C(9)-O(5)	1.182(8)	C(7)-O(2)-C(3)	116.3(4)
C(9)-C(10)	1.499(9)	O(3)-C(7)-O(2)	122.2(6)
		O(3)-C(7)-C(8)	126.2(5)
		O(2)-C(7)-C(8)	111.6(6)
		C(9)-O(4)-C(6)	116.4(5)
		O(5)-C(9)-O(4)	123.1(6)
		O(5)-C(9)-C(10)	126.5(6)
		O(4)-C(9)-C(10)	110.5(6)

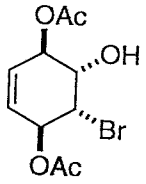
Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for **6m**
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Br(1)	80(1)	48(1)	52(1)	-2(1)	7(1)	-7(1)
C(1)	49(3)	49(3)	25(2)	0(2)	-6(2)	-4(2)
C(2)	38(3)	51(3)	26(2)	5(2)	2(2)	-2(2)
O(1)	44(2)	67(3)	40(2)	3(2)	3(2)	6(2)
C(3)	54(3)	45(3)	25(2)	3(2)	-4(2)	4(3)
C(4)	44(3)	64(3)	34(2)	-3(2)	-12(3)	5(3)
C(5)	44(3)	71(4)	48(3)	2(3)	5(3)	3(3)
C(6)	48(3)	51(3)	30(2)	-1(2)	1(2)	5(3)
O(2)	66(2)	55(2)	22(2)	-2(2)	-8(2)	3(2)
C(7)	56(4)	79(5)	26(2)	-3(3)	-8(2)	-3(4)
O(3)	101(4)	81(3)	30(2)	7(2)	-17(2)	13(3)
C(8)	100(6)	118(6)	28(3)	-22(3)	-8(3)	2(5)
O(4)	64(2)	58(2)	31(2)	1(2)	7(2)	-2(2)
C(9)	60(4)	94(5)	25(3)	15(3)	5(2)	2(4)
O(5)	135(5)	95(4)	33(2)	-5(2)	-19(3)	-8(4)
C(10)	116(8)	105(6)	55(4)	27(4)	22(4)	19(6)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **6m**

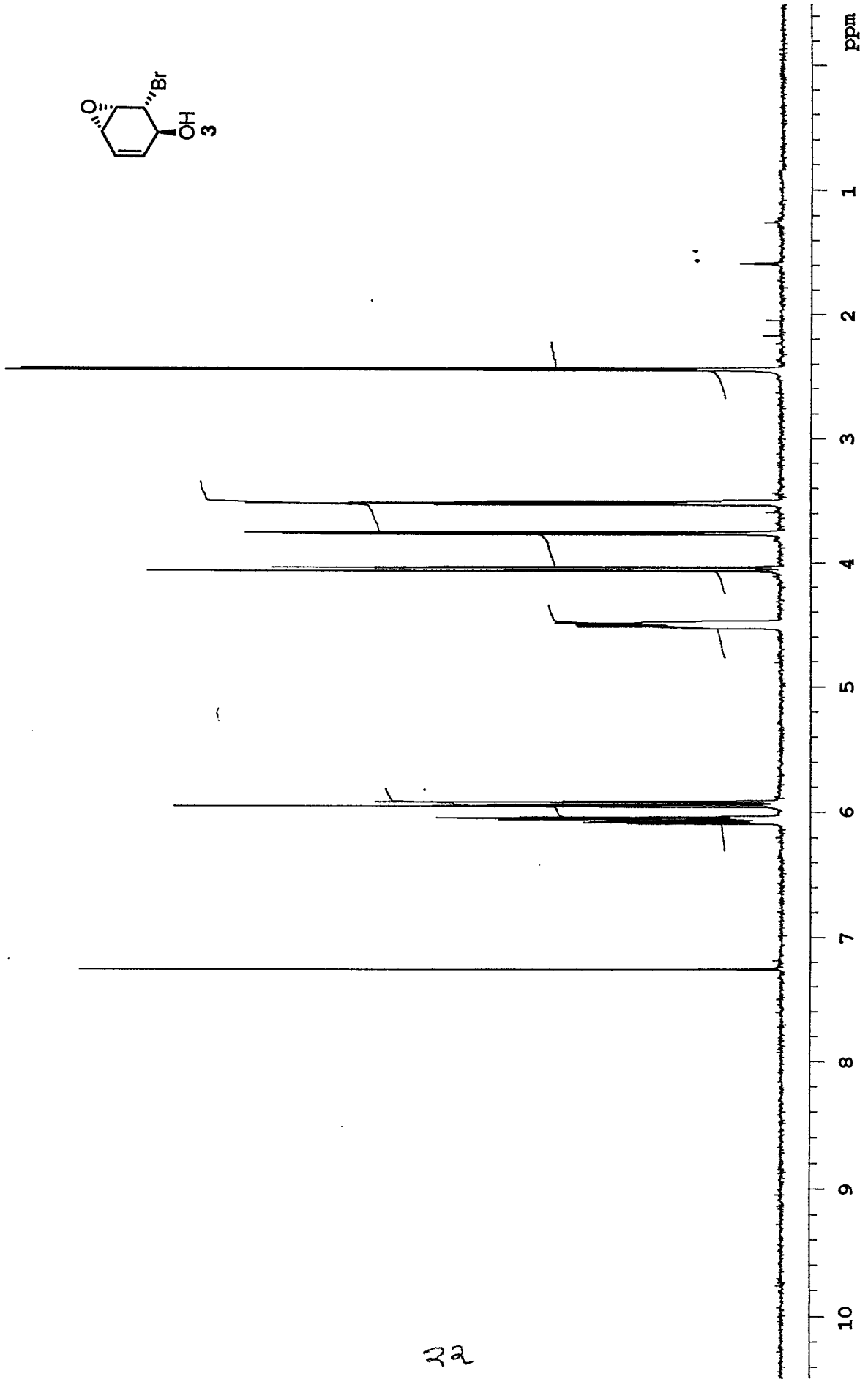
	x	y	z	U(eq)
H(1)	2253(8)	2293(4)	3507(3)	49
H(2)	1431(7)	854(4)	2438(3)	46
H(1A)	3699(19)	2080(38)	1486(30)	60
H(3)	648(7)	2549(5)	1105(3)	49
H(4)	-2597(9)	1806(5)	1362(3)	57
H(5)	-3327(8)	2112(5)	2840(4)	65
H(6)	-926(8)	2953(5)	3789(3)	51
H(8A)	604(73)	-505(11)	-387(4)	99
H(8B)	1541(40)	300(20)	-1126(26)	99
H(8C)	-616(32)	52(27)	-1179(24)	99
H(10A)	-122(71)	-317(6)	4951(6)	110
H(10B)	-1391(33)	242(19)	5723(30)	110
H(10C)	794(44)	234(19)	5843(26)	110



6m

Selected torsion angles

-171.22 (0.39)	C6 - C1 - C2 - O1
67.91 (0.44)	Br1 - C1 - C2 - O1
61.23 (0.52)	C6 - C1 - C2 - C3
-59.65 (0.47)	Br1 - C1 - C2 - C3
63.29 (0.54)	O1 - C2 - C3 - O2
-169.95 (0.39)	C1 - C2 - C3 - O2
-175.65 (0.46)	O1 - C2 - C3 - C4
-48.89 (0.57)	C1 - C2 - C3 - C4
137.84 (0.56)	O2 - C3 - C4 - C5
19.49 (0.82)	C2 - C3 - C4 - C5
1.20 (0.96)	C3 - C4 - C5 - C6
-109.12 (0.59)	C4 - C5 - C6 - O4
9.57 (0.80)	C4 - C5 - C6 - C1
75.69 (0.48)	C2 - C1 - C6 - O4
-162.67 (0.30)	Br1 - C1 - C6 - O4
-40.33 (0.60)	C2 - C1 - C6 - C5
81.30 (0.48)	Br1 - C1 - C6 - C5
85.77 (0.57)	C4 - C3 - O2 - C7
-153.42 (0.46)	C2 - C3 - O2 - C7
-3.72 (0.88)	C3 - O2 - C7 - O3
176.29 (0.53)	C3 - O2 - C7 - C8
-152.74 (0.48)	C5 - C6 - O4 - C9
85.78 (0.55)	C1 - C6 - O4 - C9
-0.30 (0.96)	C6 - O4 - C9 - O5
179.98 (0.54)	C6 - O4 - C9 - C10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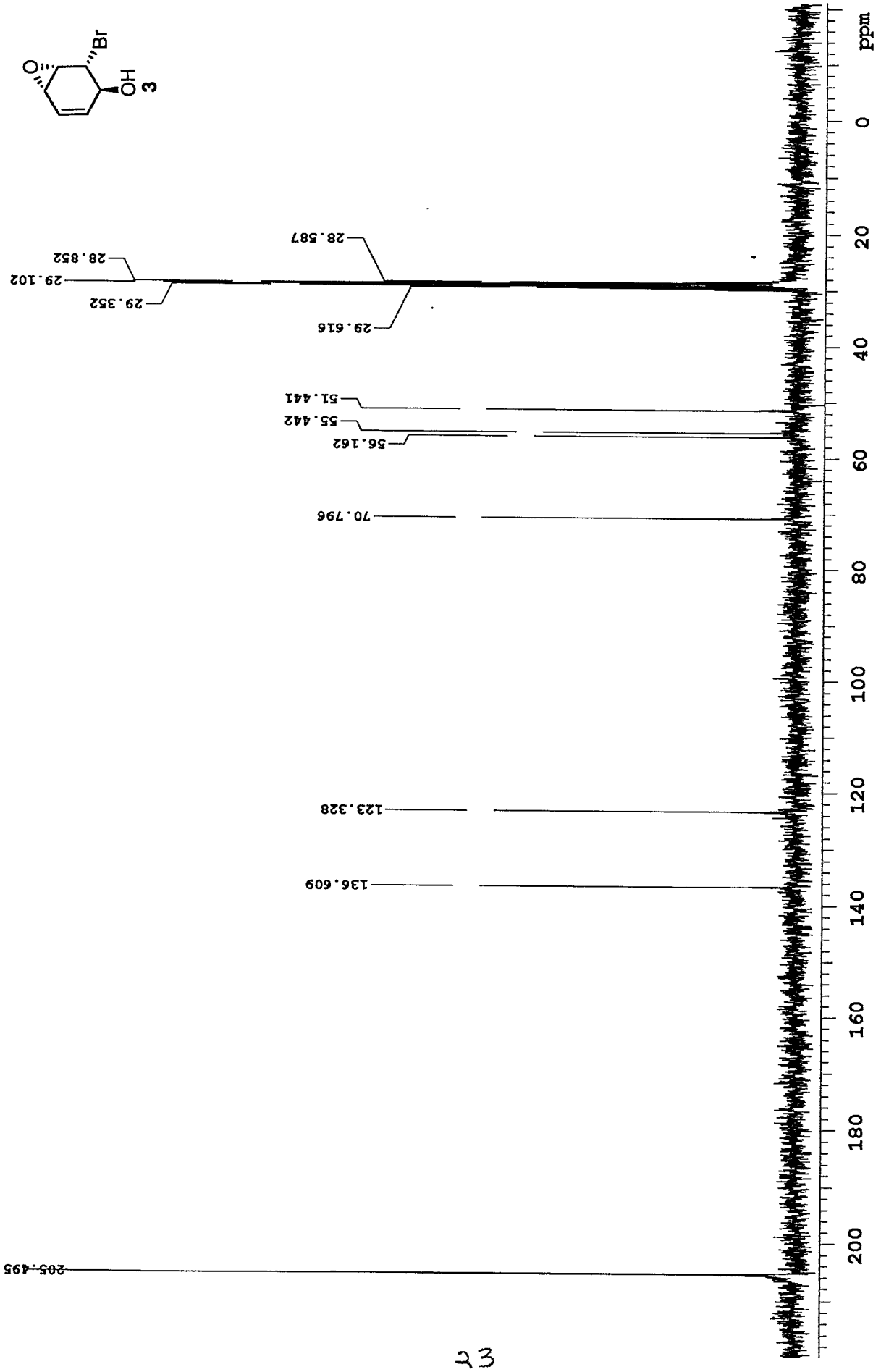
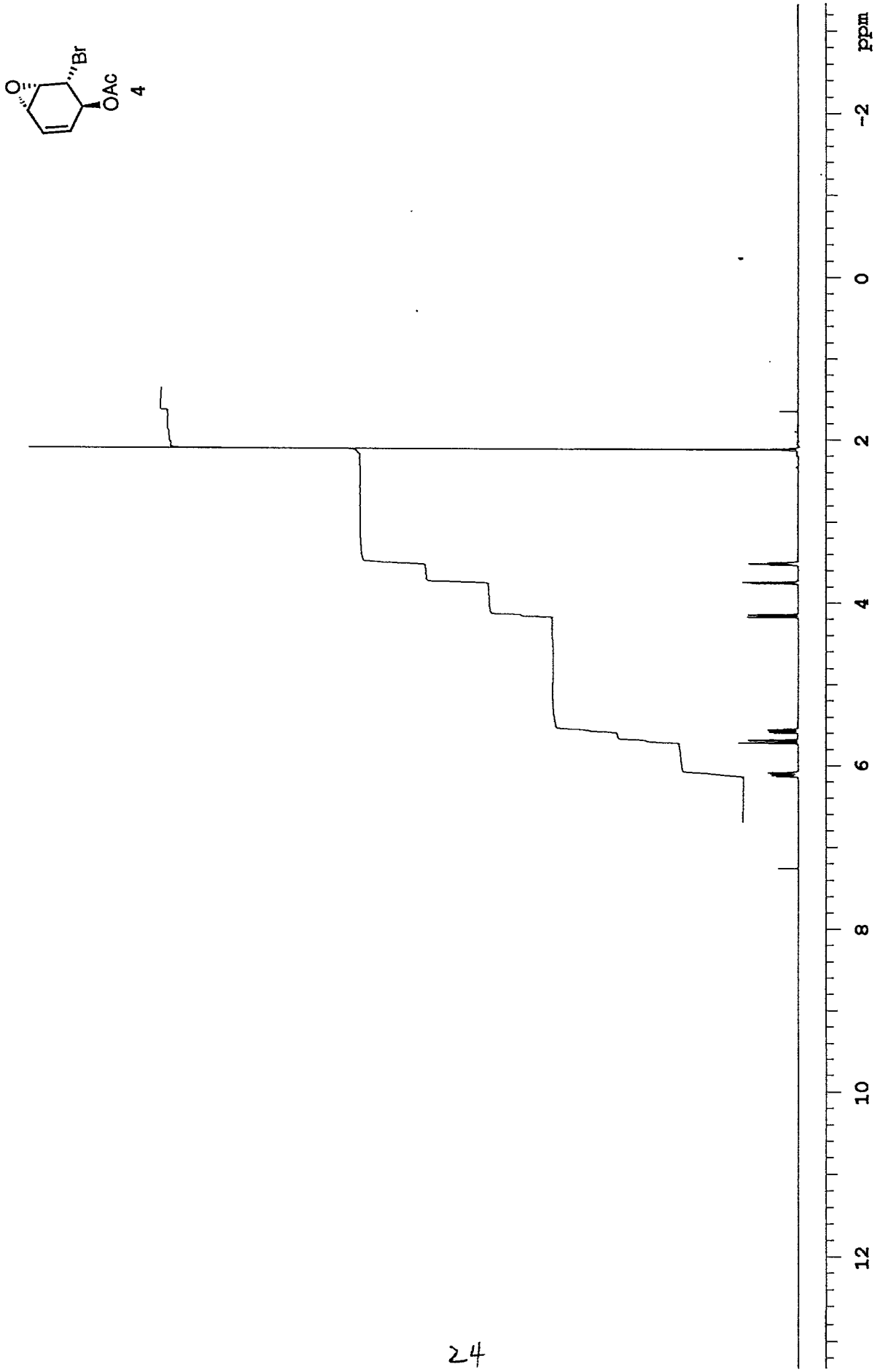
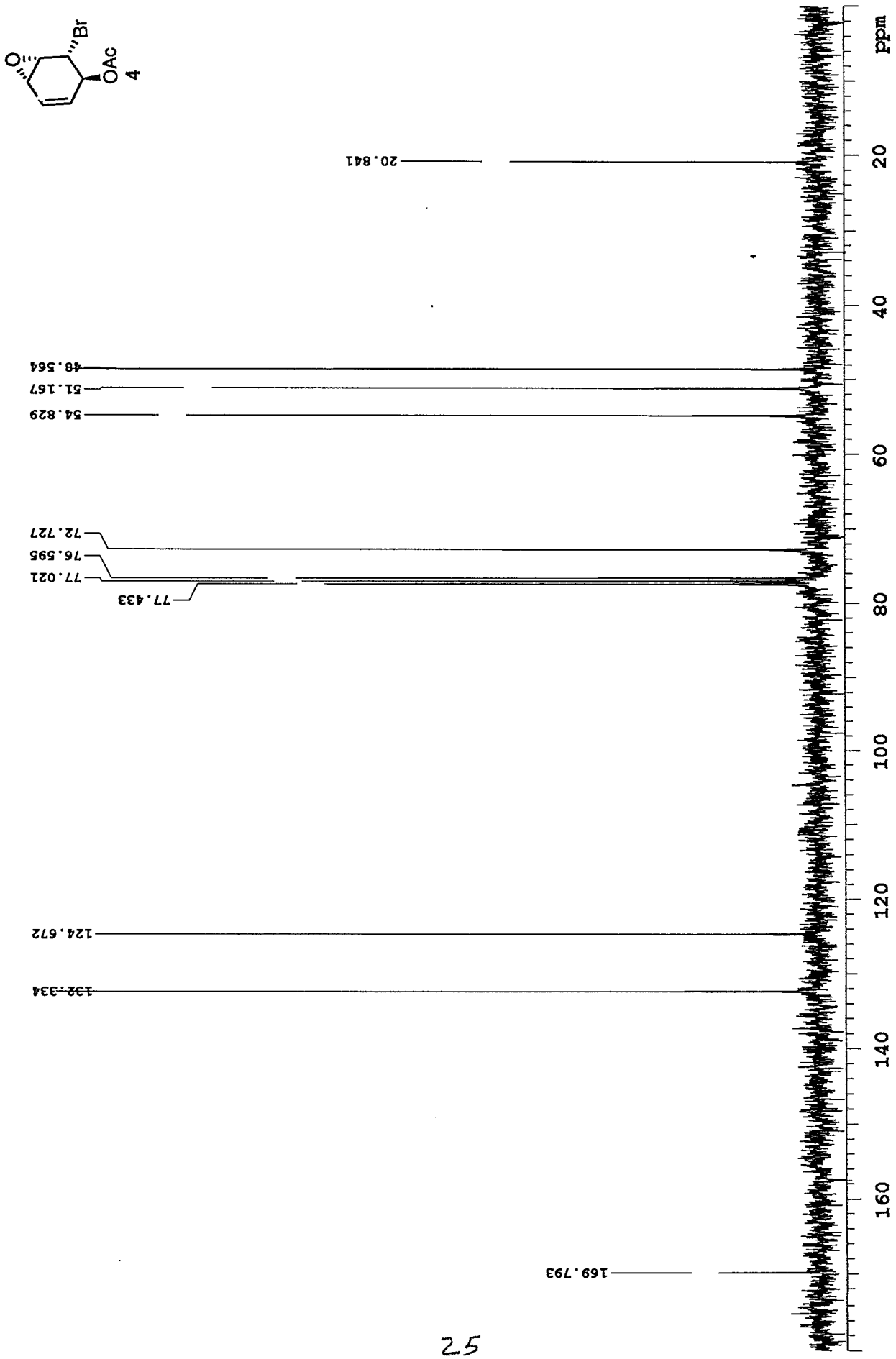
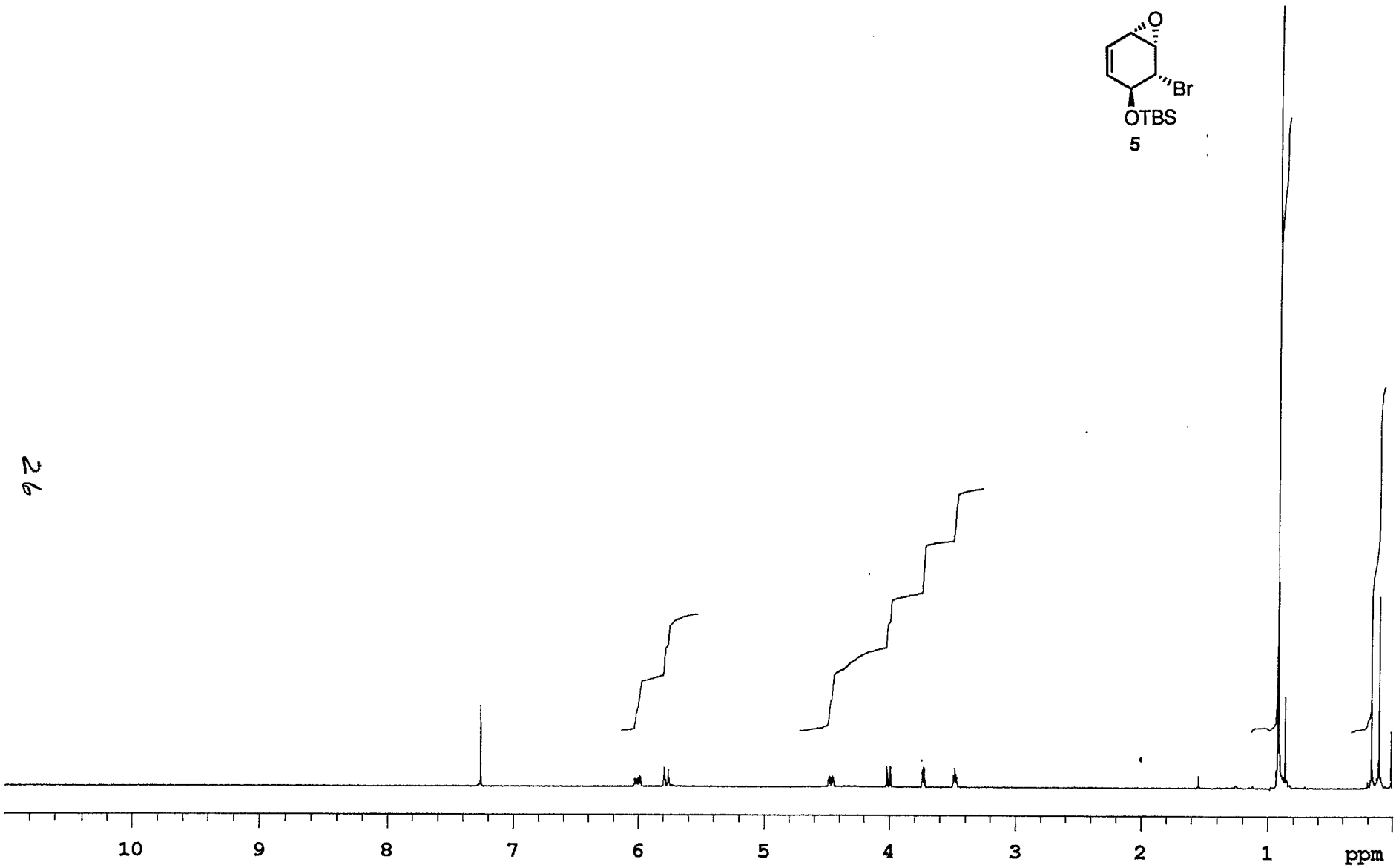
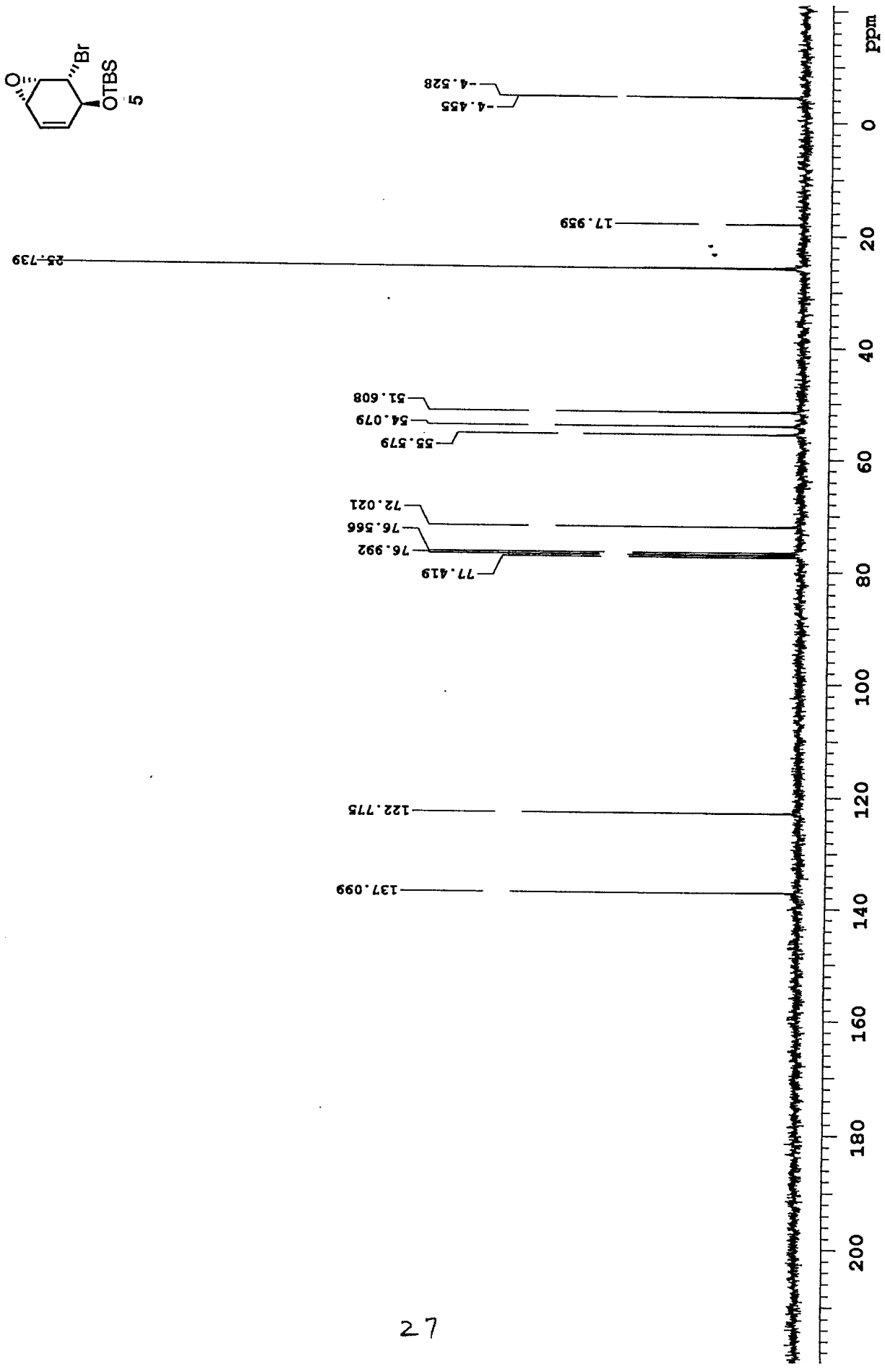
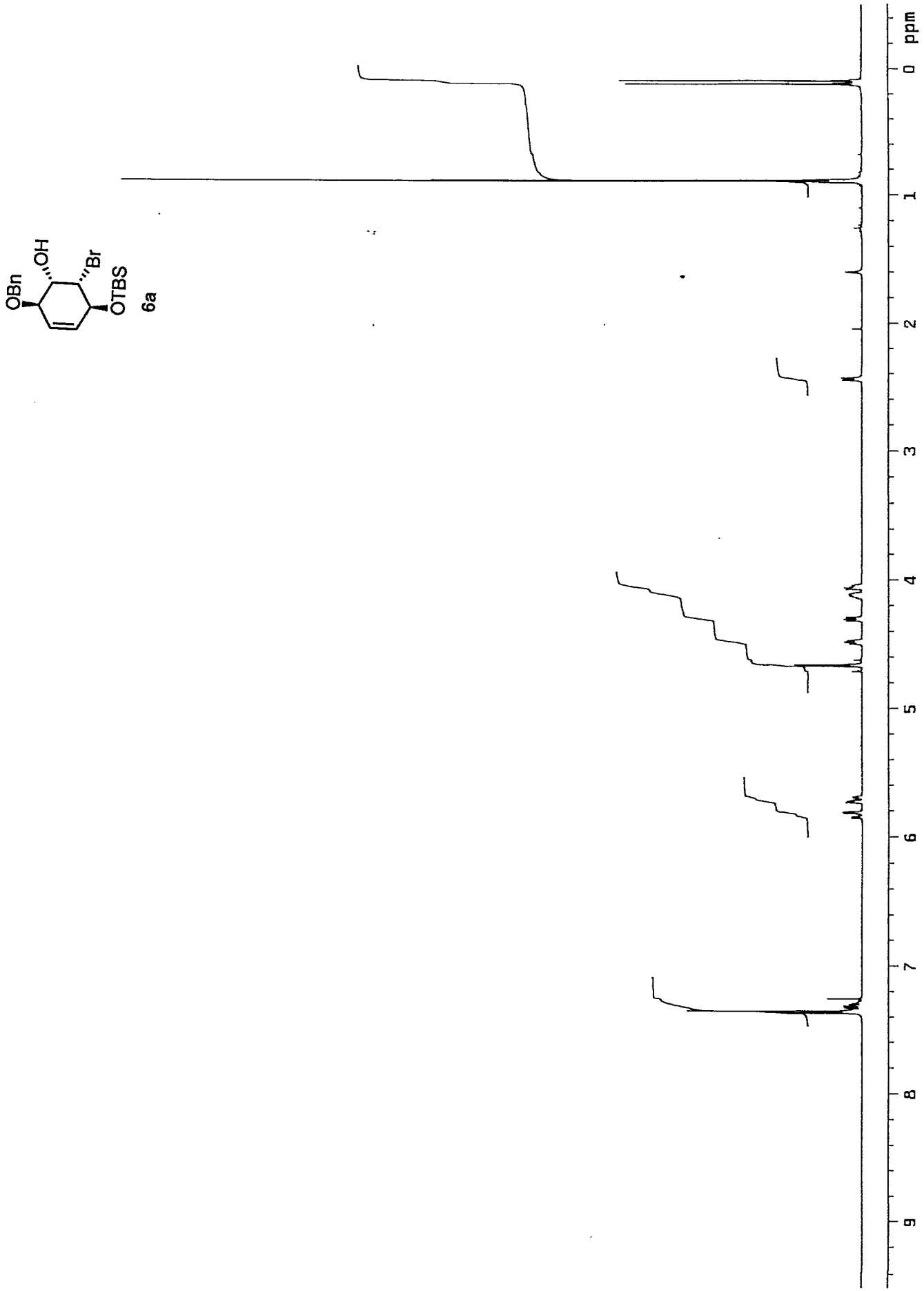

Br
O
OH
3
28.587
28.852
29.102
29.352
29.616
51.441
55.442
56.162
70.796
123.328
136.609
205.495
ppm
0
20
40
60
80
100
120
140
160
180
200

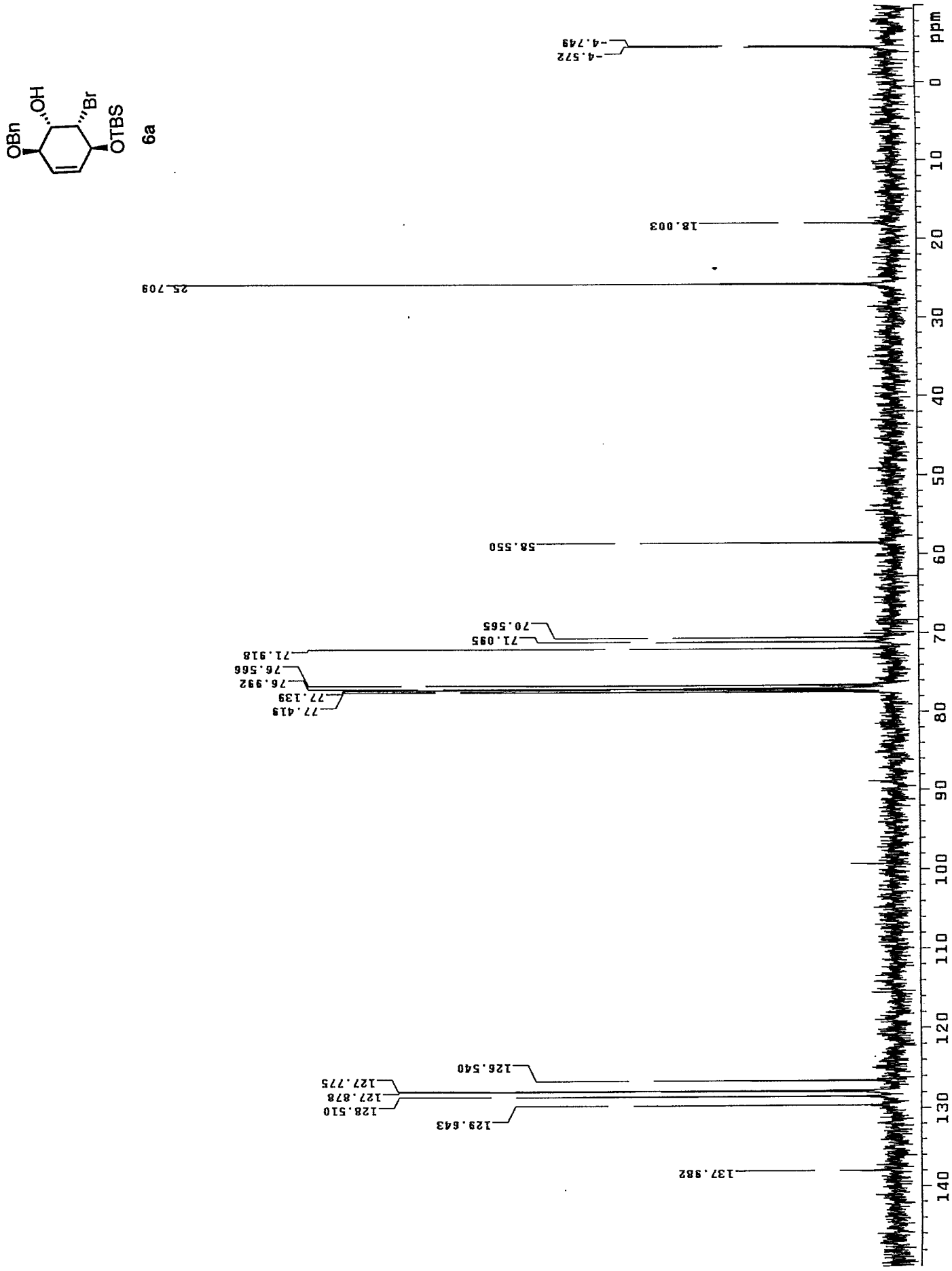

Br
OAc
4
ppm
-2
0
2
4
6
8
10
12

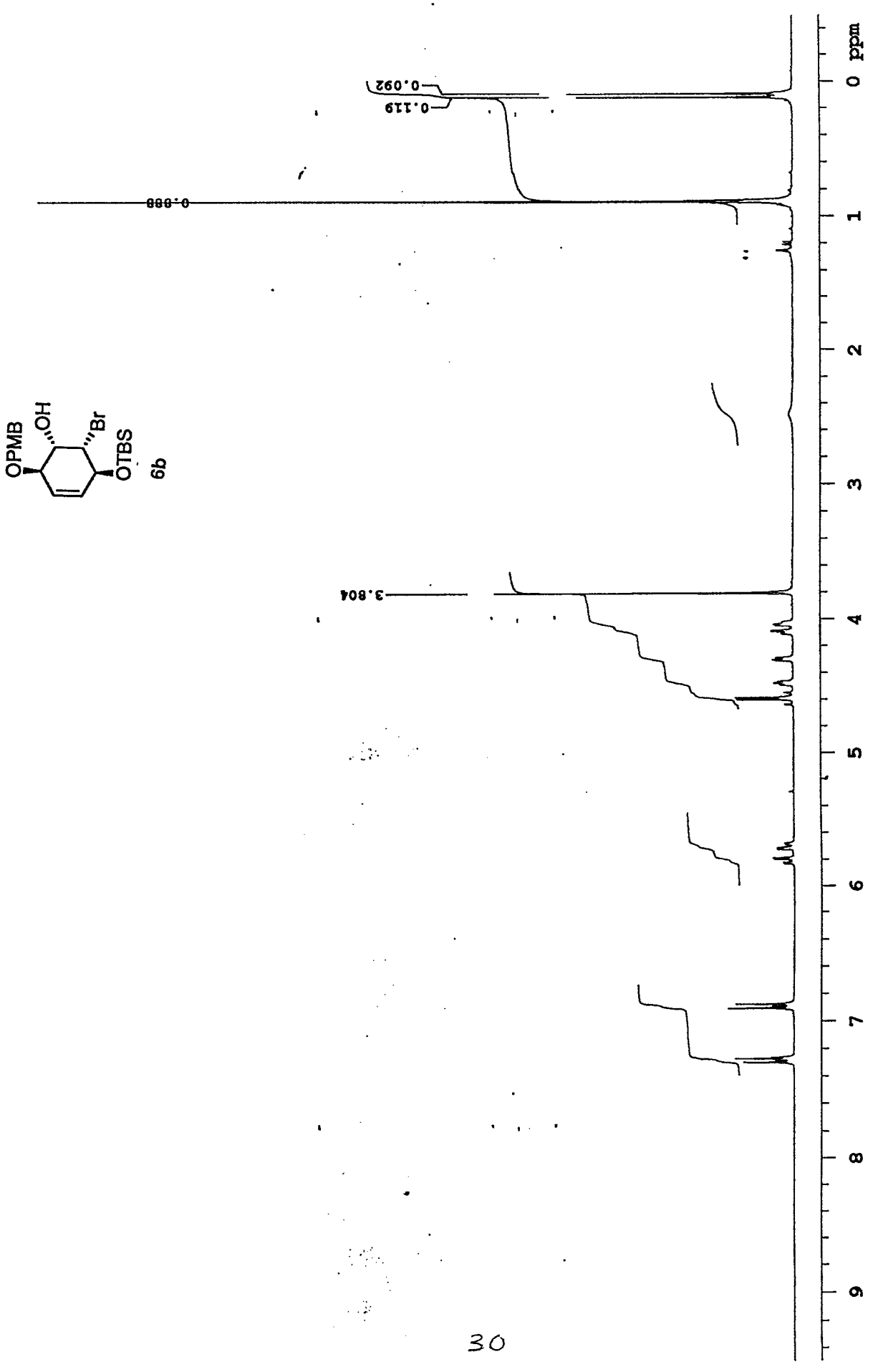

Br
OAc
4
20.841
48.564
51.167
54.829
72.727
76.595
77.021
77.433
124.672
132.334
169.793
ppm
20
40
60
80
100
120
140
160

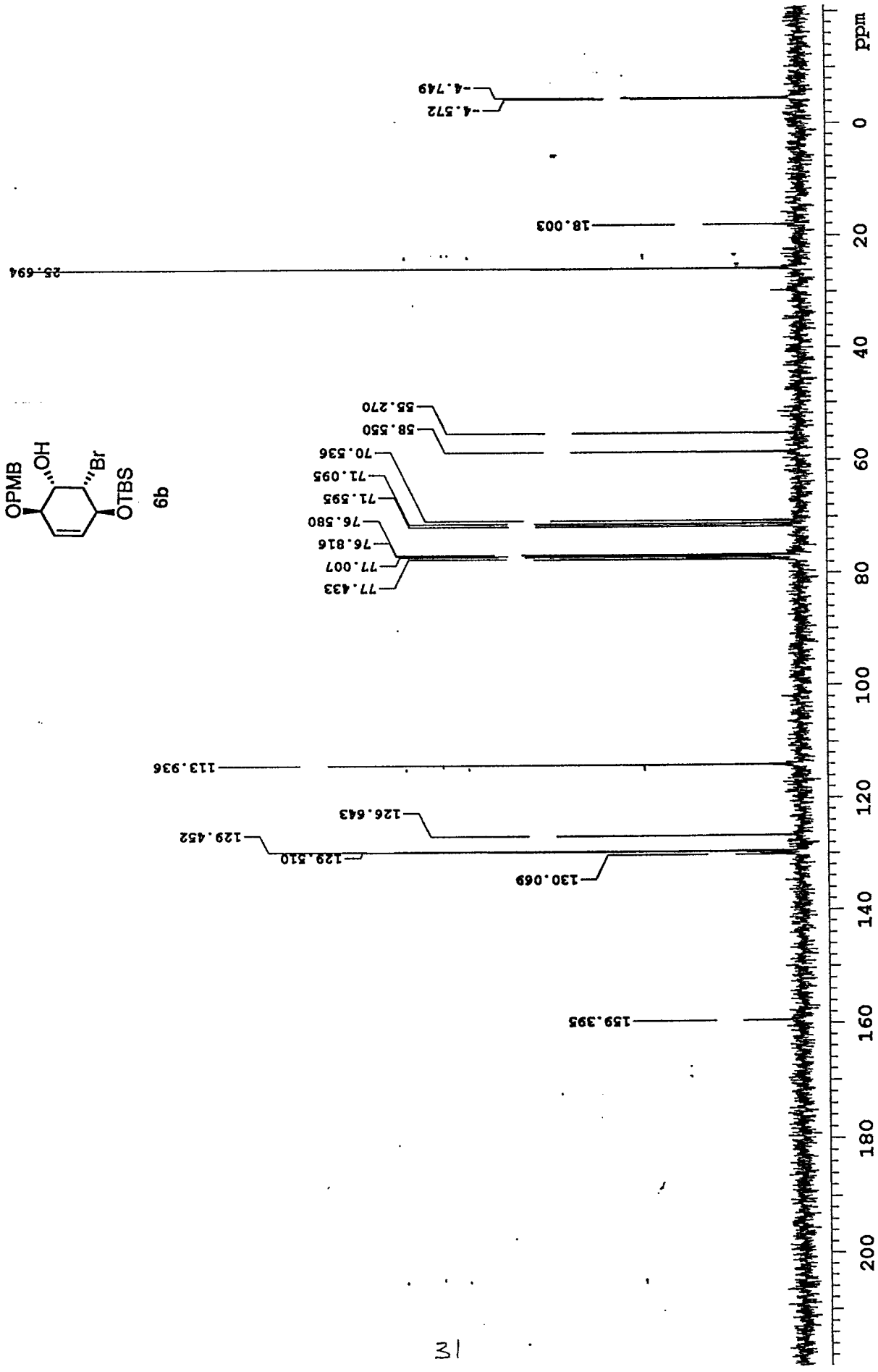



Br
OTBS
5
-4.528
-4.455
17.959
25.739
51.608
54.079
55.579
72.021
76.566
76.992
77.419
122.775
137.099
ppm
0
20
40
60
80
100
120
140
160
180
200


OBn
OH
Br
OTBS
6a
ppm
0
1
2
3
4
5
6
7
8
9


OBn
OH
Br
OTBS
6a
-4.749
-4.572
18.003
25.709
58.550
70.565
71.095
71.918
76.566
76.992
77.139
77.419
126.540
127.775
127.878
128.510
129.643
137.982
ppm
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140




OPMB
OH
Br
OTBS
6b
-4.749
-4.572
18.003
25.694
55.270
58.550
70.536
71.095
71.595
76.580
76.816
77.007
77.433
113.936
126.643
129.452
129.510
130.069
159.395
ppm
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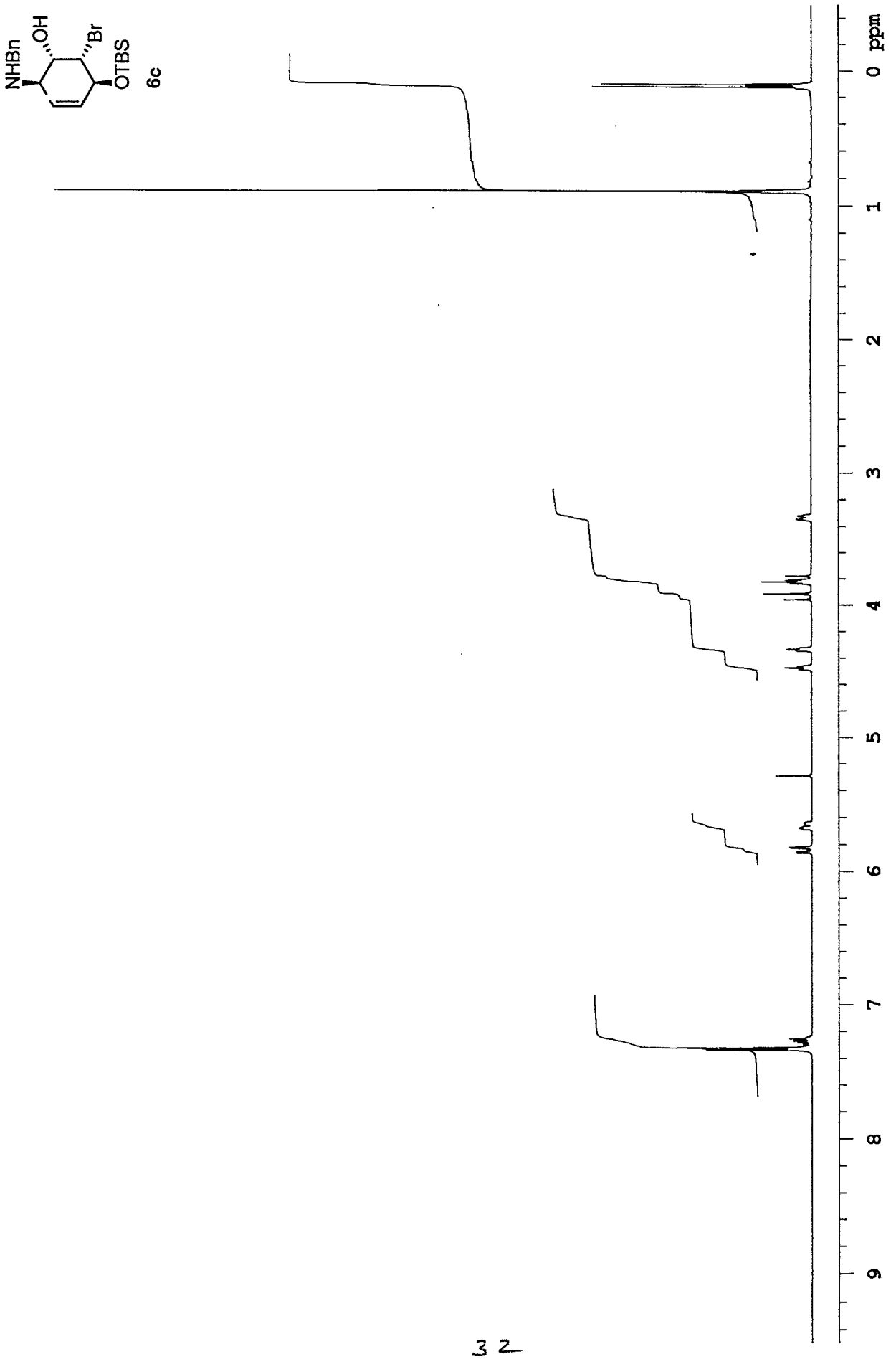
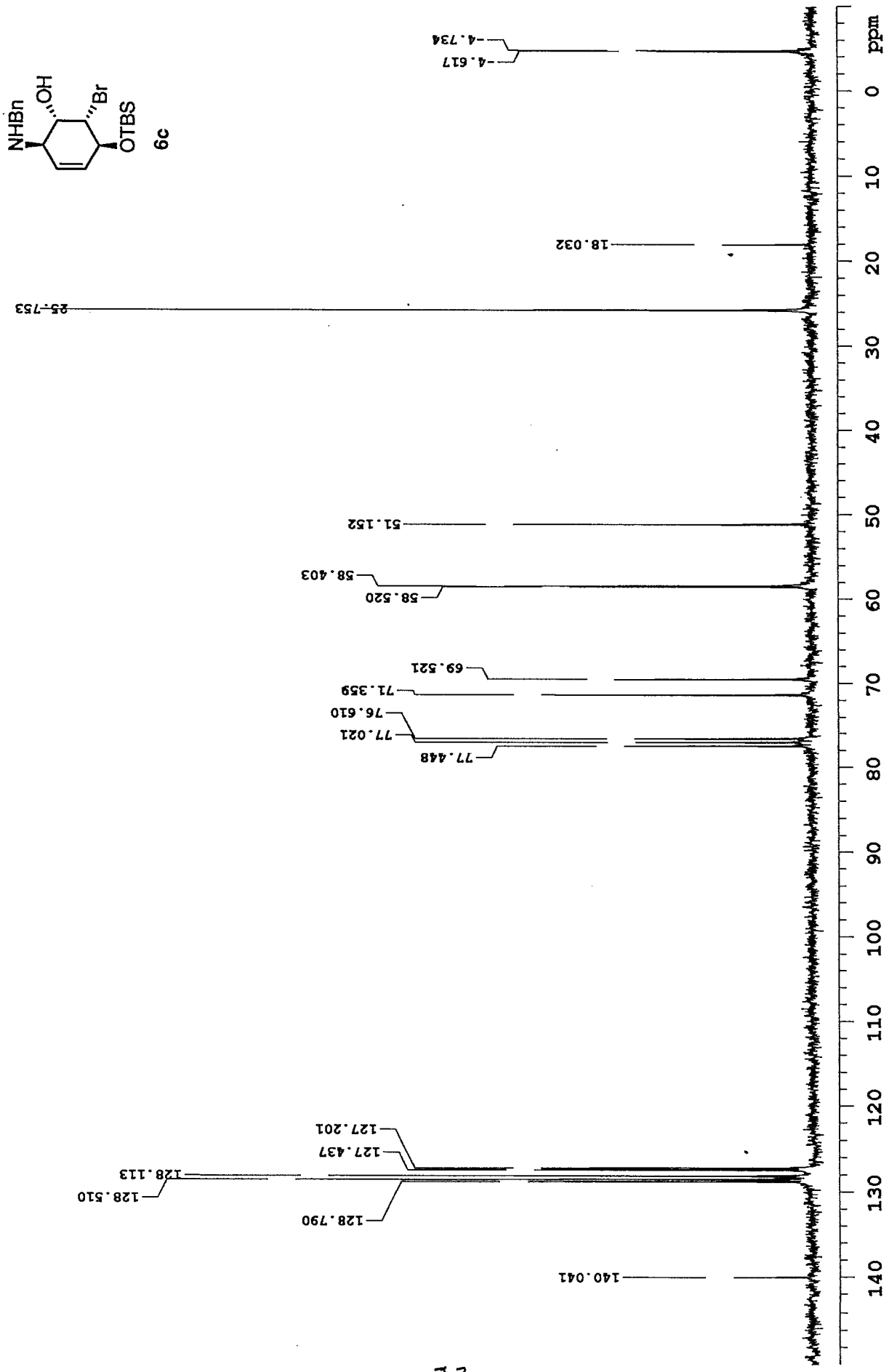
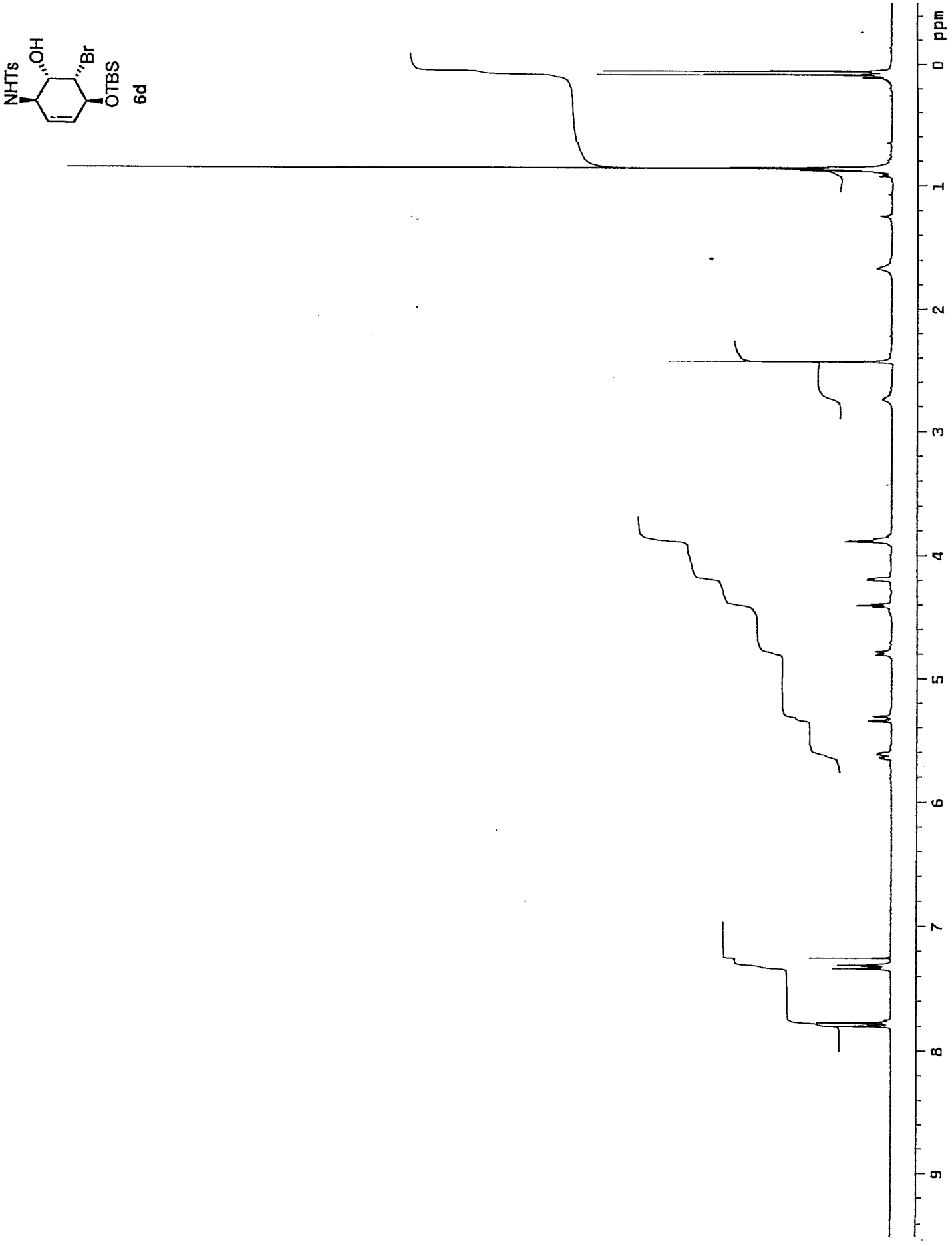
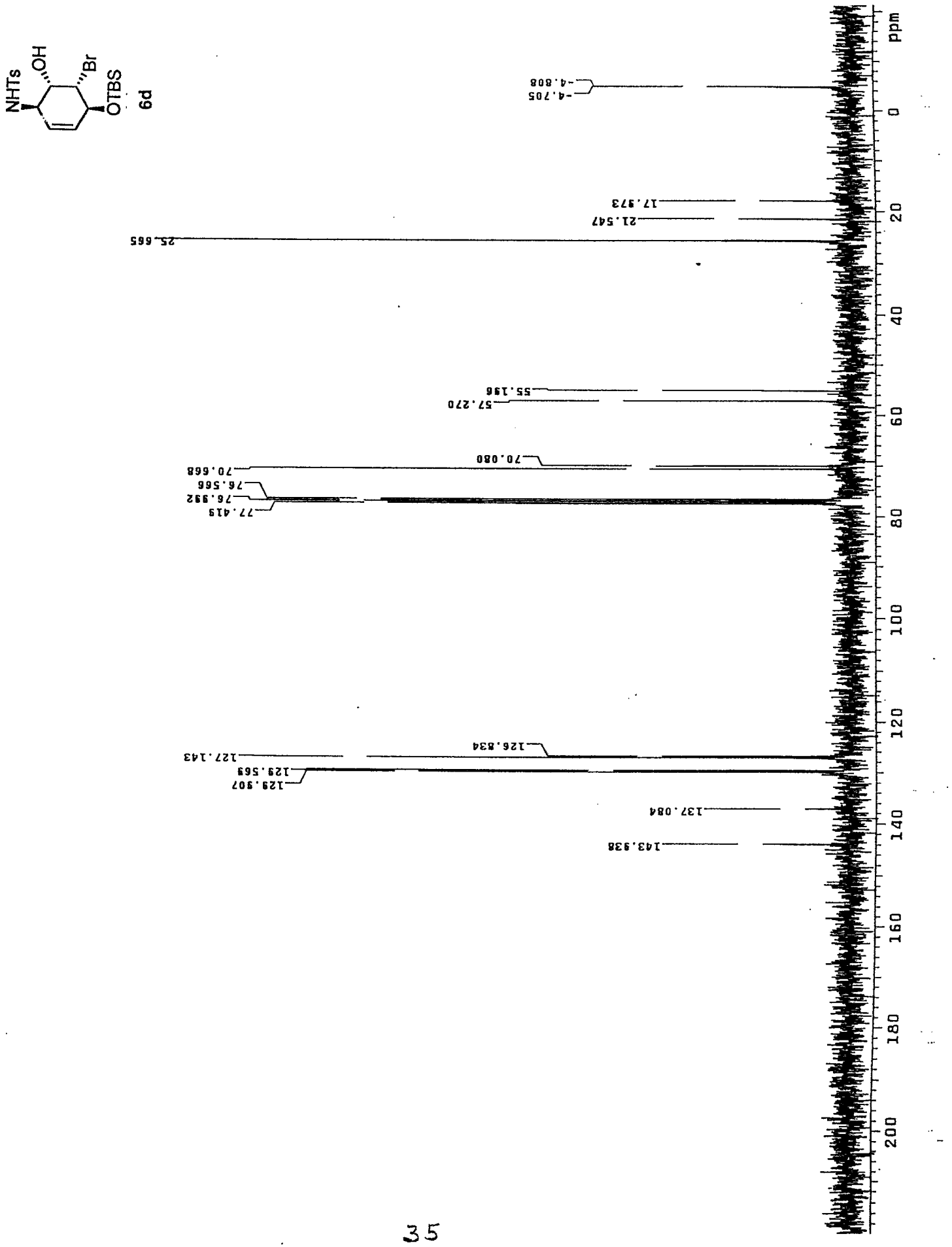
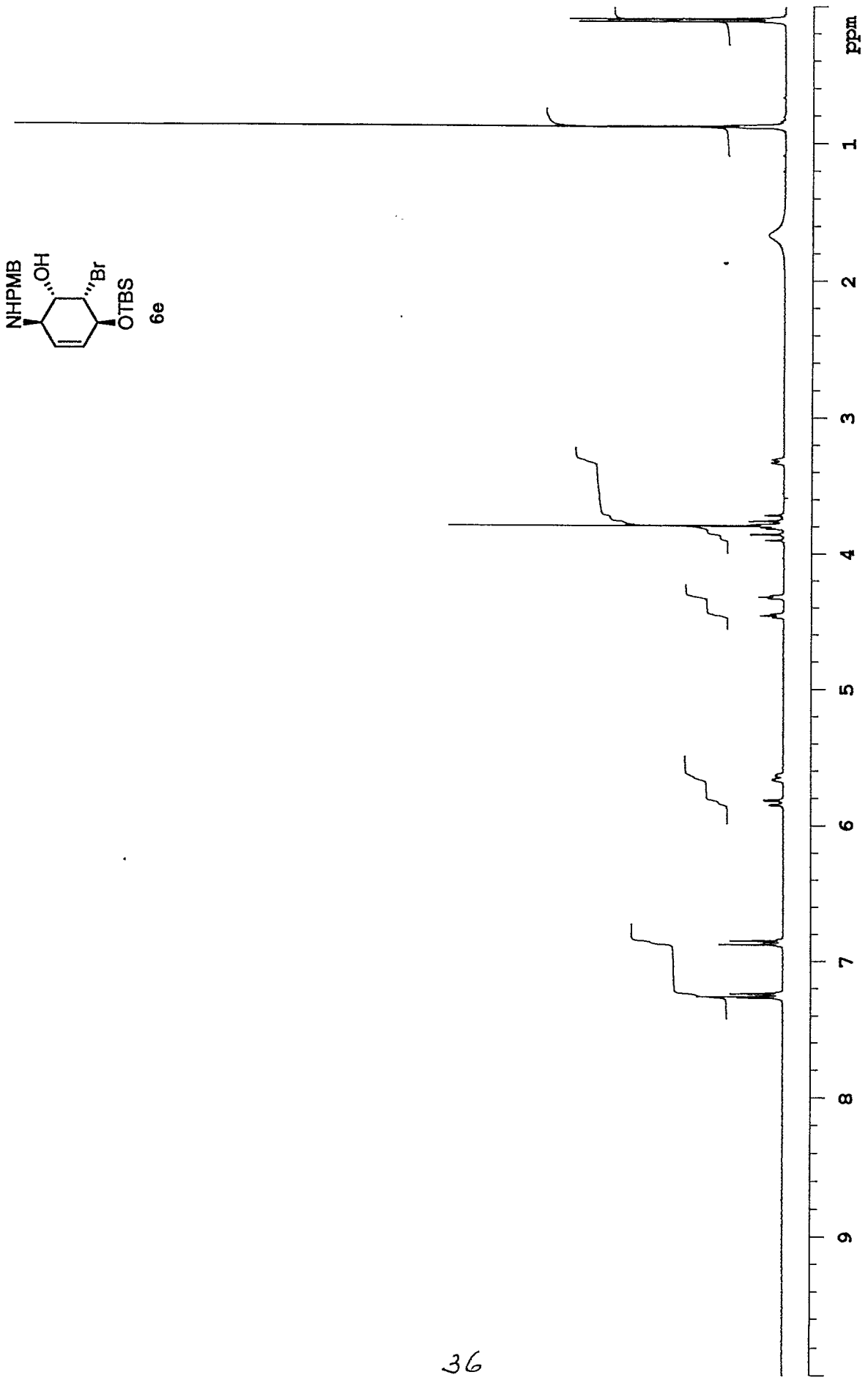
40
60
80
100
120
140
160
180
200

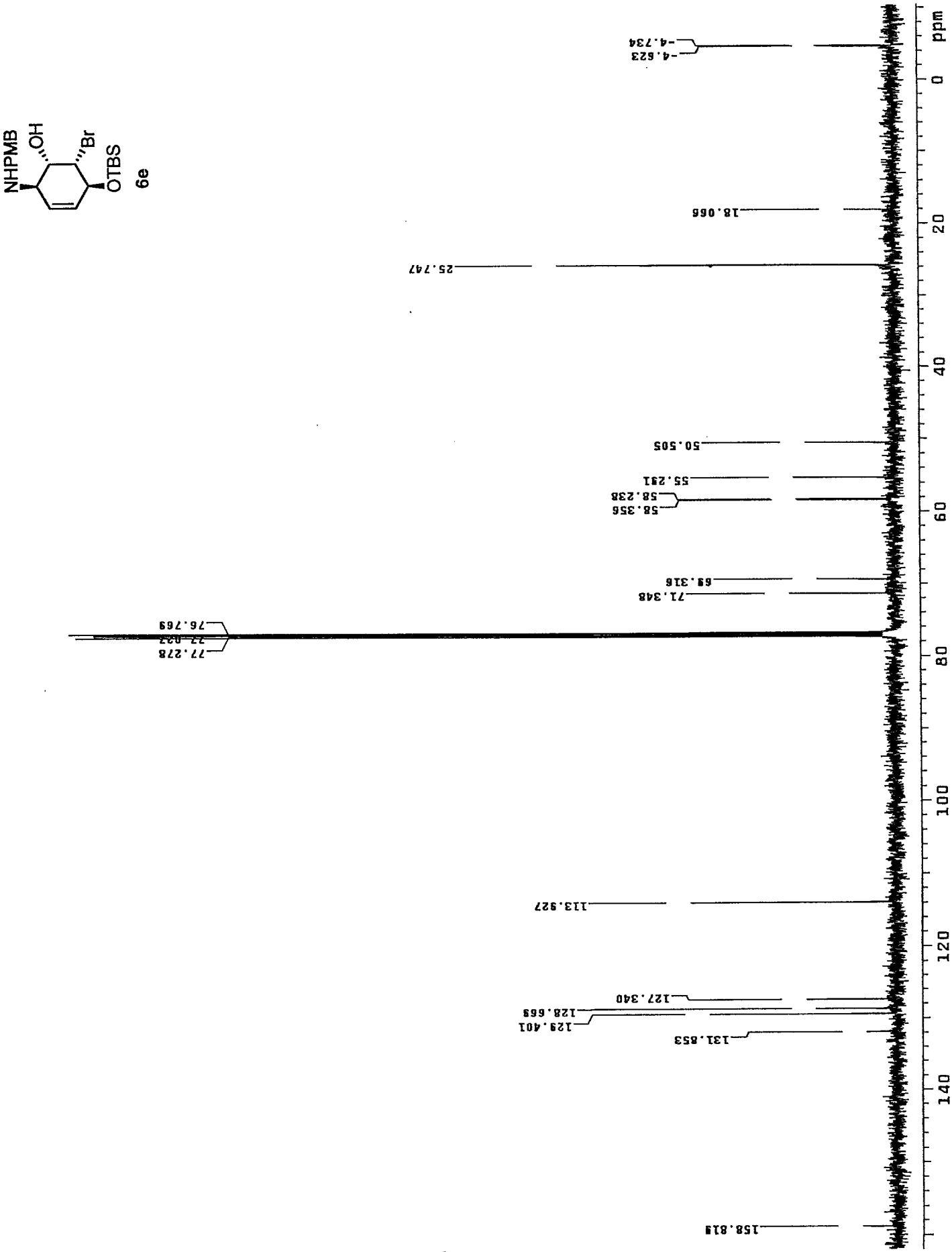

NHBn
OH
Br
OTBS
6c
0 ppm
1
2
3
4
5
6
7
8
9

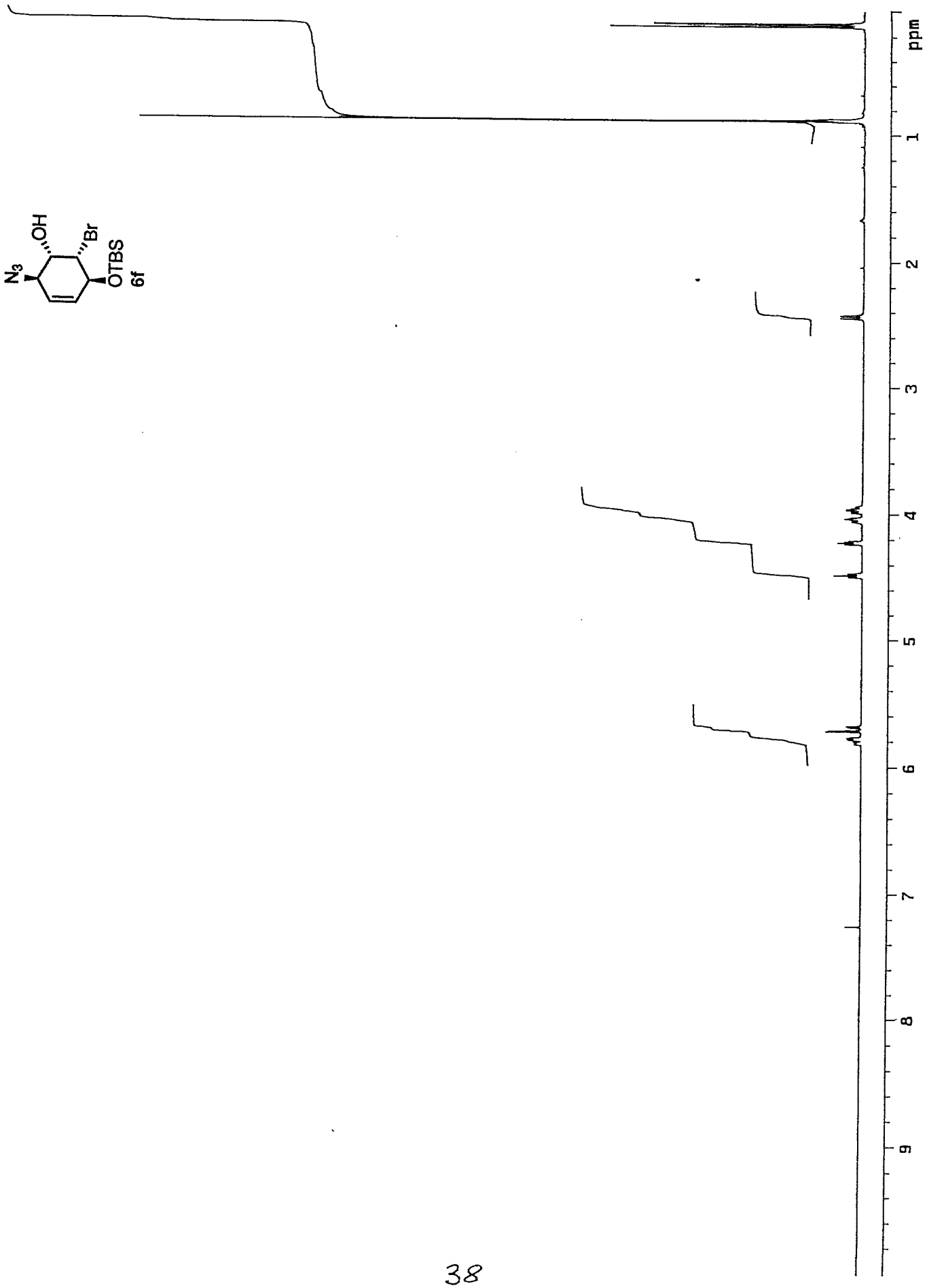

NHBn
OH
Br
OTBS
6c
-4.734
-4.617
18.032
25.753
51.152
58.403
58.520
69.521
71.359
76.610
77.021
77.448
127.201
127.437
128.113
128.510
128.790
140.041
ppm

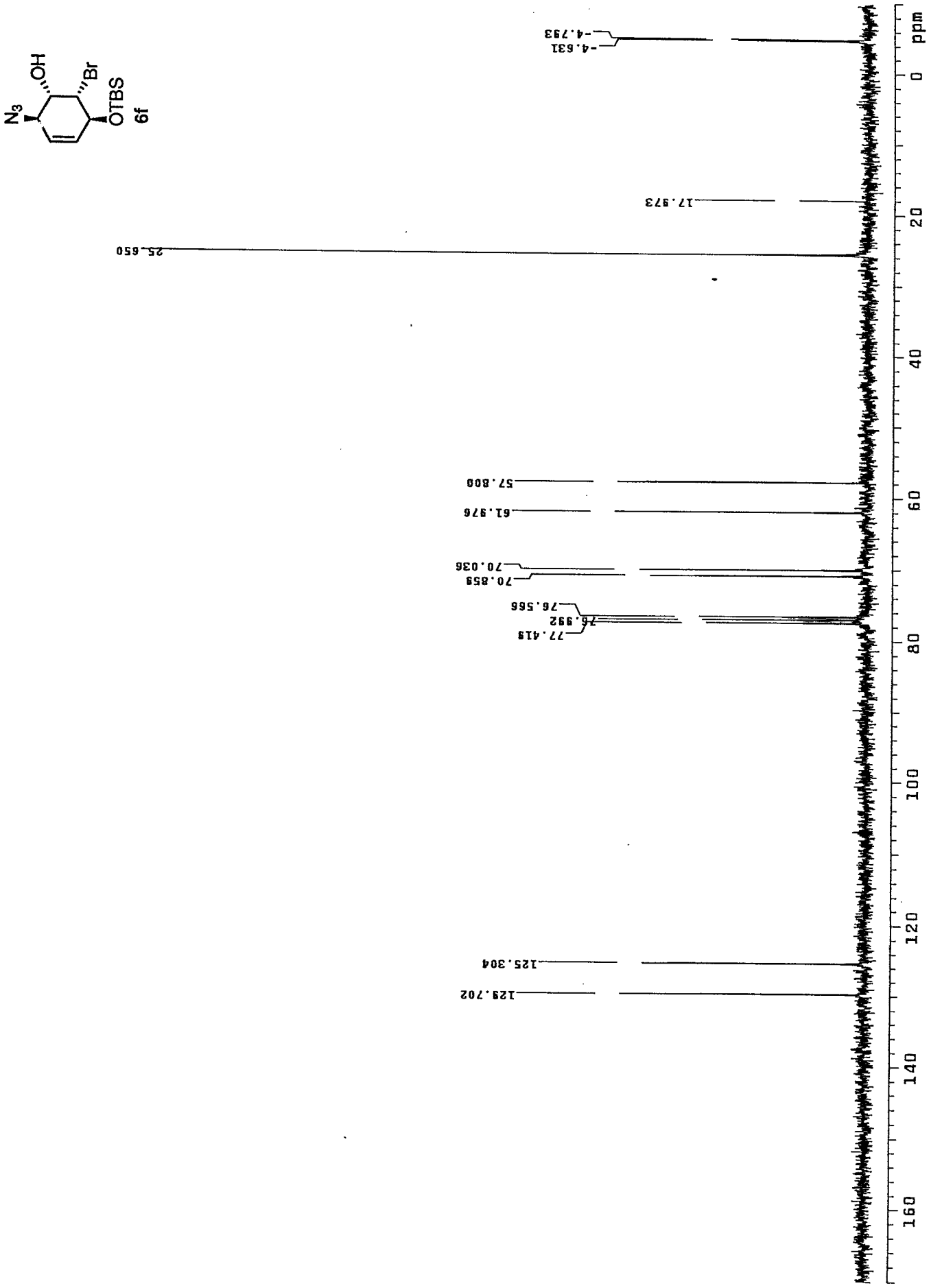

NHTs
OH
Br
OTBS
6d
ppm
0
1
2
3
4
5
6
7
8
9

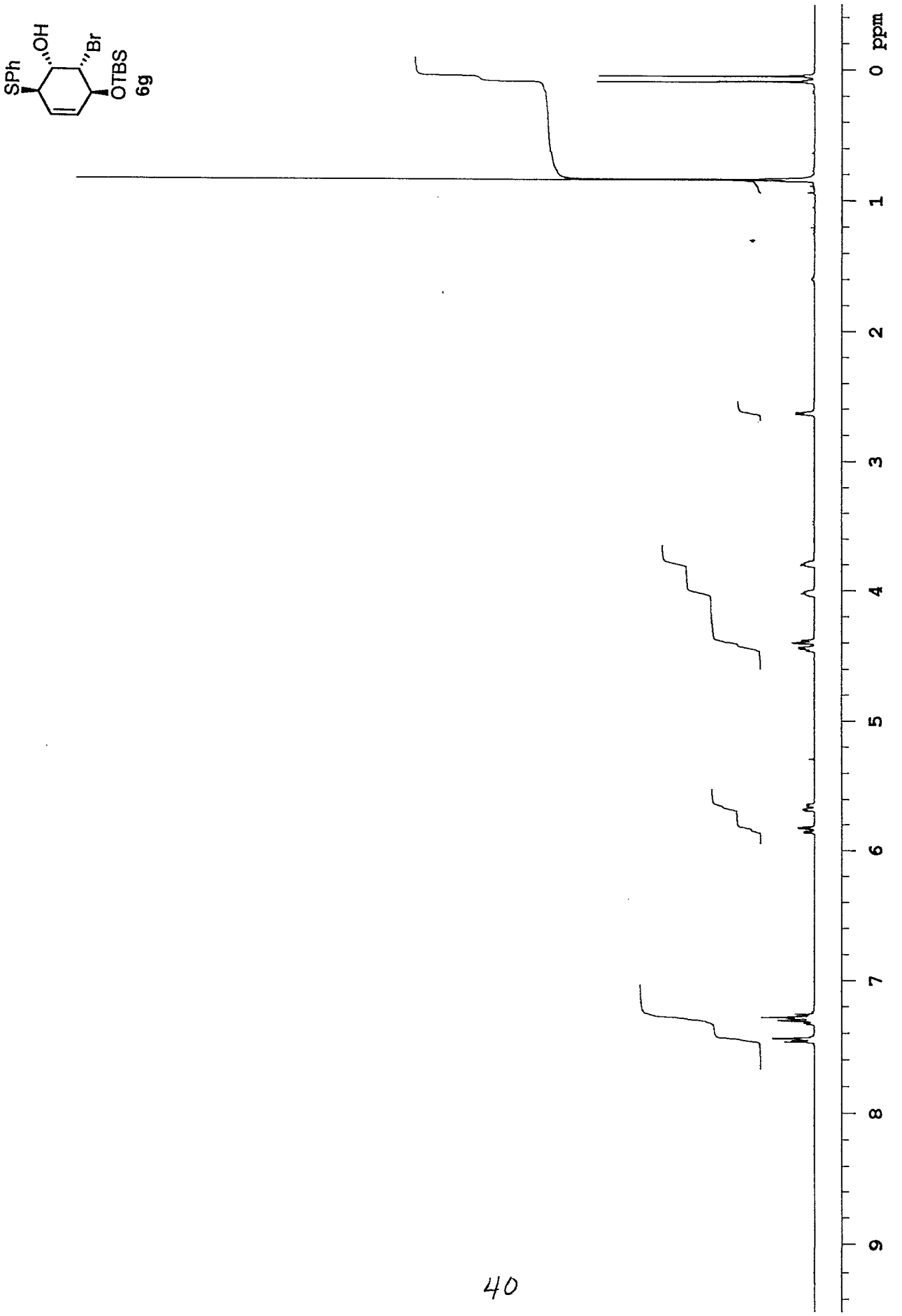



NHPMB
OH
Br
OTBS
6e
ppm
1
2
3
4
5
6
7
8
9


NHPMB
OH
Br
OTBS
6e
-4.734
-4.623
18.066
25.747
50.505
55.291
58.356
58.238
69.316
71.348
76.769
77.278
113.927
127.340
128.668
129.401
131.853
158.819
ppm
0
20
40
60
80
100
120
140


OH
Br
N3
OTBS
6f
ppm
1
2
3
4
5
6
7
8
9




SPh
OH
Br
OTBS
6g
0 ppm
1
2
3
4
5
6
7
8
9