Supplementary Material (ESI) for Green Chemistry

Supporting Information

Eco-friendly and versatile brominating reagent prepared from liquid bromine precursor

Subbarayappa Adimurthy,[1] Gadde Ramachandraiah,[1,*], Ashutosh V. Bedekar,[1] Sudip Ghosh,[2] Brindaban C. Ranu[2,*] and Pushpito K. Ghosh[1,*]

[1]Central Salt and Marine Chemicals Research Institute, Gijubhai Badheka Marg, Bhavnagar 364 002, Gujarat, India.
[2]Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India
Email Address: pkghosh@csmcri.org/ grama@csmcri.org/ ocbcr@iacs.res.in

Generation of BrOH from 2:1 mole ratio of Br^-/BrO_3^-. Absorption spectra of BrOH were recorded on UV-Vis-NIR CARY-500 spectrophotometer. The absorption spectra vs. time of the 2:1 NaBr:$NaBrO_3$ (total Br = 0.012 M) reagent in aqueous solution containing 0.011 N HCl is shown in Figure 1 below. The spectra were recorded at 25 °C in 1 cm quartz cell at 5 min intervals immediately after sample preparation with absorbance at 260 nm increasing with time.[1]

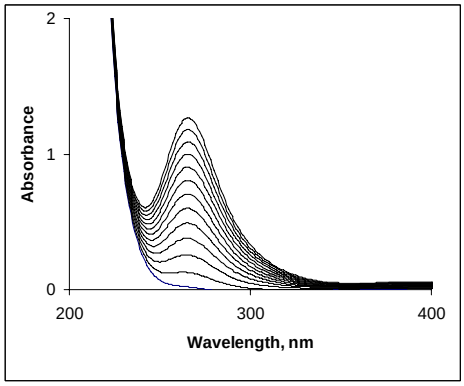


Figure 1

Reaction Calorimetric study of the BPA to TBBP-A process. **This** was carried out in the reaction calorimeter described in the Experimental Section. 15 g (65.8 mmol) of bisphenol A, 75 mL of dichloromethane and 150 mL of an aqueous solution containing

stoichiometric amount of the brominating reagent were taken in the vessel. Stoichiometric amount of 12 N HCl was added slowly through a dropping funnel maintaining the temperature of the reaction mixture between 25-30^{o}C. After addition of HCl, stirring was continued for 30 min and the reaction mixture was drained off. The overall heat evolved 71.9 kJ/kg of reaction mass, which yields an adiabatic temperature rise of 18^{o}C. The total heat evolved was nearly the same as the heat evolved till the completion of addition of HCl indicating that the reaction is fast and goes to completion as HCl addition is over.

Analytical data (Table 1)

Monobromophenol (entry 1, table 1). Crude mixture analyzed by GC on SC-30 column with temperature ramp from 120^{o}C to 200^{o}C @ 2^{o}C/min (please see GC below). Peaks at 6.617 min and 14.762 correspond to 2-bromophenol and 4-bromophenol, respectively, in the ratio of 19:81.

2,4,6-Tribromophenol (entry 2, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz): (δ) 7.7 (2H, s); 5.89 (1H, broad s). IR: ν_{max} (KBr): 3407, 3070, 2358, 1552, 1454, 1379, 1317, 1263, 1228, 1158, 856, 736, 667, 552 cm^{-1}. CHN: Found C, 22.04%; H, 0.84%; Calcd. C, 21.75%; H, 0.90%. Melting point: Observed 91-93° C; Reported 92-94° C.

2,4,4,6-tetrabromo-2,5-cyclohexadienone (entry 3, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.78 (2H, s). IR: ν_{max} (KBr) 3051, 1680, 1582, 1454, 1310, 900, 702, 663, 634 cm^{-1}. CHN: Found C, 17.16%; H, 0.24%; Calcd. C,17.56%; H, 0.49%. Melting point: Observed 123-125° C. (Reported 125-130°C)

4,6-Dibromo-2-chlorophenol (entry 4, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.56 (1H, s); 7.46 (1H, s); 5.91 (1H, broad s). IR: ν_{max} (KBr) 3501, 3081, 1707, 1580, 1477, 1399, 1324, 1277, 1184, 1084, 814, 765, 710, 626, 553 cm^{-1}. CHN : Found C, 25.01%; H, 0.74%; Calcd. C, 25.17%; H, 1.04%.

2,6-Dibromo-4-chlorophenol (entry 5, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.45 (2H, s); 5.86 (1H, broad s). IR: ν_{max} (KBr) 3410, 3078, 1555, 1458, 1385, 1319, 1265, 1216, 1158, 855, 740, 701 cm^{-1}. CHN : Found C, 26.70%; H, 1.11%; Calcd. C, 25.17%; H, 1.04%.

4, 6-Dibromo-2-nitrophenol (entry 6, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 8.41 (1H, s); 8.24 (1H, s); 11.05 (1H, s). IR: ν_{max} (KBr) 3551, 3473, 3414, 3163, 3074, 1599, 1531, 1450, 1393, 1327, 1242, 1151, 1111, 885, 761, 736, 674, 607, 554 cm^{-1}. CHN: Found C, 24.85%; H, 0.86 %; N, 4.54 %; Calcd. C, 24.24%; H, 1.01%; N, 4.71 %. Melting point: Observed 115-117° C (Reported 118° C).

2,6-Dibromo-4-nitrophenol (entry 7, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.431 (1H, s); 7.21 (1H, s); 5.54 (1H, broad s); 2.27 (3H, s). IR: ν_{max} (KBr) 3499, 3404, 3079, 1588, 1565, 1465, 1396, 1316, 1222, 1136, 997, 855, 677, 555 cm^{-1}. CHN: Found C, 24.93%; H, 0.76 %; N, 4.63%; Calcd. C, 24.24%; H, 1.01%; N, 4.71 %. Melting point: Observed 143-145° C (decomposed) (Reported 145° C).

2,6-Dibromo-4-methyl phenol (entry 8, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.33 (2H, s); 5.84 (1H, broad s); 2.25 (3H, s). IR: ν_{max} (KBr) 3632, 3497, 2923, 1681, 1560, 1476, 1319, 1274, 1234, 1161, 852, 776, 737, 704, 559 cm^{-1}. CHN: Found C,

32.34%; H, 3.12 %; Calcd. C, 31.57; H, 2.25%. Melting point: Observed 49-51°C, (Reported 50° C).

4,6-Dibromo-2-methyl phenol (entry 9, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.431 (1H, s); 7.21 (1H, s); 5.54 (1H, broad s); 2.27 (3H, s). IR: ν_{max} (KBr) 3499, 3404, 3079, 1588, 1565, 1465, 1396, 1316, 1222, 1136, 997, 855, 677, 555 cm^{-1}. CHN: Found C, 32.08%; H, 2.10%; Calcd. C, 31.57; H, 2.25%. Melting point: Observed 55-60° C.

4-Bromo-2,6-dimethyl phenol (entry 10, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.25 (2H, s); 4.61 (1H, broad s); 2.21 (6H, s). IR: ν_{max} (KBr) 3372, 2977, 2946, 2916, 1609, 1474, 1329, 1188, 1029, 939, 853, 716 cm^{-1}. CHN : Found C, 48.23%; H, 3.98%; Calcd. C, 47.76%; H, 4.47%. Melting point: Observed 76-81° C (Reported. 76° C).

2, 6 Dibromo-4-Bu^t phenol (entry 11, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.42 (2H, s); 5.95 (1H,broad s) 1.24 (9H, s). IR: ν_{max} (KBr) 3634, 3506, 2963, 2908, 2869, 1725, 1558, 1478, 1393, 1364, 1321, 1243, 1205, 1162, 1044, 870, 821, 737, 710 cm^{-1}. CHN: Found C, 40.09%; H, 4.45%; Calcd. C, 38.96%; H, 3.89%.

1-Bromo-2-naphthol (entry 12, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 8.01-8.05 (1H,d J= 8.0); 7.79 (2H, d J=8.0); 7.59 (1H, t J= 6.0); 7.42 (1H, t J= 8.0); 7.27 (1H, t J=6.0); 5.21 (1H, broad s). IR: ν_{max} (KBr) 3275, 3056, 1629, 1601, 1500, 1432, 1347, 1301, 1234, 984, 928, 810, 744, 517 cm^{-1}. CHN: Found C, 54.09%; H, 2.65%; Calcd. C, 53.80%; H, 3.13%. Melting point: Observed 78-82° C (Reported 80 ° C).

Tetrabromobisphenol-A (entry 13, table 1). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.25 (4H, s); 5.79 (2H, s); 1.58 (6H, s). IR: ν_{max} (KBr) 3514, 3479, 2987, 1554, 1472, 1396, 1363, 1321, 1273, 1239, 1160, 1129, 868, 778, 731, 707, 615 cm^{-1}. CHN: Found C:

32.80%; H, 2.25; Calcd. C, 33.08%; H, 2.20%. Melting point: Observed 178-180° C (Reported 179-182 °C).

Analytical data (Table 2)

2,4,6-Tribromoaniline (entry 1, table 2). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.5 (2H, s); 4.55 (2H, broad s) . IR: ν_{max} (KBr) 3414, 3290, 1615, 1562, 1541,1454, 1382, 1066, 859, 732, 706,547 cm^{-1}. CHN: Found C, 22.10%; H, 1.04%; N, 4.14%; Calcd. C, 21.81%; H, 1.21%; N, 4.24%. Melting point: Observed 120-123° C (Reported 120-122° C).

2, 6-Dibromo-4-nitroaniline (entry 2, table 2). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 8.34 (2H, s); 6.64 (2H, broad s). IR: ν_{max} (KBr) 3480, 3372, 1604, 1501, 1472, 1319, 1299, 1269, 1126, 899, 731, 693 cm^{-1}. CHN: Found C, 24.82%; H, 0.59%; N, 9.39%; Calcd.. C, 24.32%; H, 1.35%; N, 9.45%. Melting point: Observed 205-207° C (Reported 206-208° C).

4, 6-Dibromo-2-nitroaniline (entry 3, table 2). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 8.29 (1H, s); 7.81 (1H, s); 6.64 (2H, broad s). IR: ν_{max} (KBr) 3465, 3352, 1623, 1542, 1495, 1444, 1344, 1317, 1254, 1118, 1095, 873, 760, 689 cm^{-1}. CHN: Found C, 24.70 %; H, 0.60%; N, 9.01 %; Calcd. C, 24.32 %; H, 1.35 %; N, 9.46 %; Melting point: Observed. 115-117° C (Reported 128° C).

2,6-Dibromo-4-methylaniline (entry 4, table 2). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.2 (2H, s); 4.38 (2H, broad s); 2.07 (3H, s). IR: ν_{max} (KBr) 3422, 3306, 2914, 1618, 1581, 1477, 1285, 1212, 1058, 853, 733, 706, 637, 557 cm^{-1}. CHN: Found C, 32.19%; H,

2.18%; N, 5.18%; Calcd. C, 31.69%, H, 2.64%; N, 5.28%. Melting point: Observer 73-76° C (Reported 75° C).

4-Bromo N, N-dimethylaniline (entry 5, table 2). ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.31 (2H, d J= 8.0); 6.6 (2H, d J= 8.0); 2.91 (6H, s). IR: ν_{max} (KBr) 3550, 3474, 3415, 2880, 2805, 1592, 1501, 1445, 1354, 1223, 1190, 1165, 1062, 944, 805, 750, 579, 505 cm^{-1}. CHN: Found C, 47.22%; H, 4.33%; N, 6.74%; Calcd. C, 48.00%; H, 5.00%; N, 7.00%. Melting point: Observed 53-55° C (Reported 55° C).

Analytical data (Table 3)

4-Bromoanisole (entry 1, table 3). ^{1}H-NMR-($CDCl_3$- 200 MHz) (δ) 7.38-7.34 (2H, d J= 8.0); 6.79-6.75 (2H, d J=8.0); 3.83 (3H, s). IR: ν_{max} (Nujal Mull) 3071, 3005, 2959, 2937, 2837, 2538, 2279, 2036, 1871, 1580, 1487, 1380, 1288, 1247, 1179, 1032, 871, 822, 750, 680, 621, 600, 507 cm^{-1} . CHN: Found C, 44.29%; H, 3.17%; Calcd. C, 44.92%; H, 3.74.

2,5-Dibromo-1,4-dimethoxy benzene (entry 2, table 3). ^{1}H-NMR ($CDCl_3$-TMS) (δ) 7.10 (2H, s); 3.85 (6H, s). IR: ν_{max} (KBr) 3494, 3099, 2969, 2944, 1699, 1667, 1494, 1436, 1358, 1275, 1212, 1185, 1065, 1021, 859, 759 cm^{-1}. [Fig 5.17(B)]. CHN: Found C, 33.16%; H, 2.00%; Calcd. C,32.43%, H, 2.70%. Melting point: Observed 140-143° C (Reported 147° C).

4-Bromoacetanilide (entry 3, table 3) ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.44 (4H, m); 2.04 (3H, s), 1.66 (1H, s); IR: ν_{max} (KBr) 3557, 3477, 3294, 3259, 3185, 3113, 1671, 1604, 1535, 1487, 1392, 1369, 1312, 1257, 1170, 1005, 822, 743, 690, 504 cm^{-1}. CHN:

Found C, 44.89%, H, 3.36%; N, 6.5%; Calcd. C, 44.85%; H, 3.77%; N, 6.54%. Melting point: 166-168° C (Reported 167-169° C).

Bromobenzene (entry 4, table 3) ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 7.46 (2H, d J= 8.0); 7.19 (3H, d J= 8.0). IR: ν_{max} (Neat) 3065, 1577, 1474, 1442, 1068, 1019, 999, 735, 682, 673 cm^{-1}. CHN: Found C, 45.66%; H, 3.22%; Calcd. C, 45.86%, H, 3.18%. Boiling point: Observed 154-156°C (Reported 156°C).

1-Bromonaphthalene (entry 5, table 3) ^{1}H-NMR ($CDCl_3$-200 MHz) (δ) 8.21 (1H, d J= 8.0); 7.71-7.68 (3H, d J= 6.0); 7.54-7.39 (2H, m) 7.23-7.16 (1H, t J= 8.0). IR: ν_{max} (Neat) 3054, 1591, 1561, 1501, 1378, 1253, 1199, 1161, 1135, 1021, 955, 790, 764, 650 cm^{-1}. CHN: Found C,55.01%; H, 3.33%; Calcd. C, 57.97%; H: 3.38%.

Analytical Data (Table 4)

2-Bromo-malonic acid diethyl ester (entry 1, Table 4). Yellowish oil; IR (neat): 1715cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.32 (t, *J* = 7.2Hz, 3H), 4.30 (q, *J* = 7.2Hz, 2H), 4.85 (s, 1H); ^{13}CNMR ($CDCl_3$, 75 MHz) δ13.8 (2C), 55.4, 63.1 (2C), 164.4 (2C)

2-Bromo-malonic acid dimethyl ester (entry 2, Table 4). Yellow oil; IR (neat):1722cm^{-}1; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 3.85 (s, 6H), 4.87 (s,1H); ^{13}CNMR ($CDCl_3$, 75 MHz): δ 41.5, 53.9 (2C), 164.9 (2C)

2-Bromo-3-oxo-butyric acid ethyl ester (entry 3, Table 4). Yellow oil; IR (neat) 1728cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 1.34 (t, *J* = 7.2 Hz, 3H), 2.44 (s, 3H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.77 (s, 1H); ^{13}CNMR ($CDCl_3$, 75 MHz): δ 13.8, 26.3, 49.0, 63.1, 165.0, 196.3

2-Bromo-1,3-diphenyl-propane-1,3-dione(entry 4, Table 4). White solid; mp 97-99 ^{0} C ; IR (KBr):1672, 1693 cm-^{1}; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.61 (s,1H), 7.42-7.47 (m, 4H), 7.56-7.60 (m, 2H), 7.97-7.99 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 52.4,128.8 (4C), 129.0 (4C), 133.5 (2C), 134.1 (2C),188.8 (2C)

2-Bromo-1-phenyl-butane-1,3-dione(entry 5, Table 4). Red oil; IR (neat): 1679, 1716, 1739cm^{-1}; ^{1}HNMR ($CDCl_3$, 300 MHz): δ 2.44 (s, 3H), 5.66 (s, 1H), 7.47-7.51 (m, 2H), 7.60-7.64 (m, 1H), 7.96-7.98 (m, 2H); ^{13}CNMR ($CDCl_3$, 75 MHz): δ 27.1, 52.9, 126.9 (2C), 128.5 (2C), 133.6, 134.4, 189.9,198.0

1-Bromo-2-oxo-cyclopentanecarboxylic acid ethyl ester (entry 7, Table 4). Brownish oil; ν_{max}(neat)/cm^{-1} 1722, 1759; $\delta_H/CDCl_3$ 1.31 (t, *J* = 7.2 Hz, 3H), 2.10-2.18 (m, 2H), 2.25-2.52 (m, 3H), 2.70-2.81 (m, 1H), 4.29 (q, *J* = 7.2 Hz, 2H); $\delta_C/CDCl_3$ 13.8, 19.3, 35.2, 38.6, 54.6, 63.0, 166.7, 205.8. (Found: C, 40.57, H, 4.52. $C_8H_{11}O_3Br$ requires C, 40.87; 4.72 %).

1-Bromo-3-methyl-2-oxo-cyclohexanecarboxylic acid methyl ester (entry 8, Table 4). Yellow oil; ν_{max}(neat)/cm^{-1} 1725, 1755; $\delta_H/CDCl_3$ 1.06 (d, *J* = 6.3 Hz, 3H), 1.36-1.38 (m,2H), 1.70-1.77 (m, 1H), 1.97-2.13 (m, 2H) 2.48-2.54 (m, 1H) 2.98-3.04 (m, 1H), 3.78 (s, 3H); $\delta_C/CDCl_3$ 15.2, 24.2, 35.7, 42.1, 44.2, 53.5, 68.2, 168.2, 199.2. (Found: C, 43.19; H, 5.11.$C_9H_{13}O_3Br$ requires C, 43.39; H, 5.26%).

Analytical data (Table 5)

1-Bromo-2-hexanol (entry 1, table 5) ^{1}H-NMR - ($CDCl_3$-200 MHz)- (δ) 0.875-0.91 (3H, t J=6); 1.36-1.57 (6H, m); 2.16 (1H, br s); 3.34-3.53 (2H, m); 3.77 (1H, m). IR:

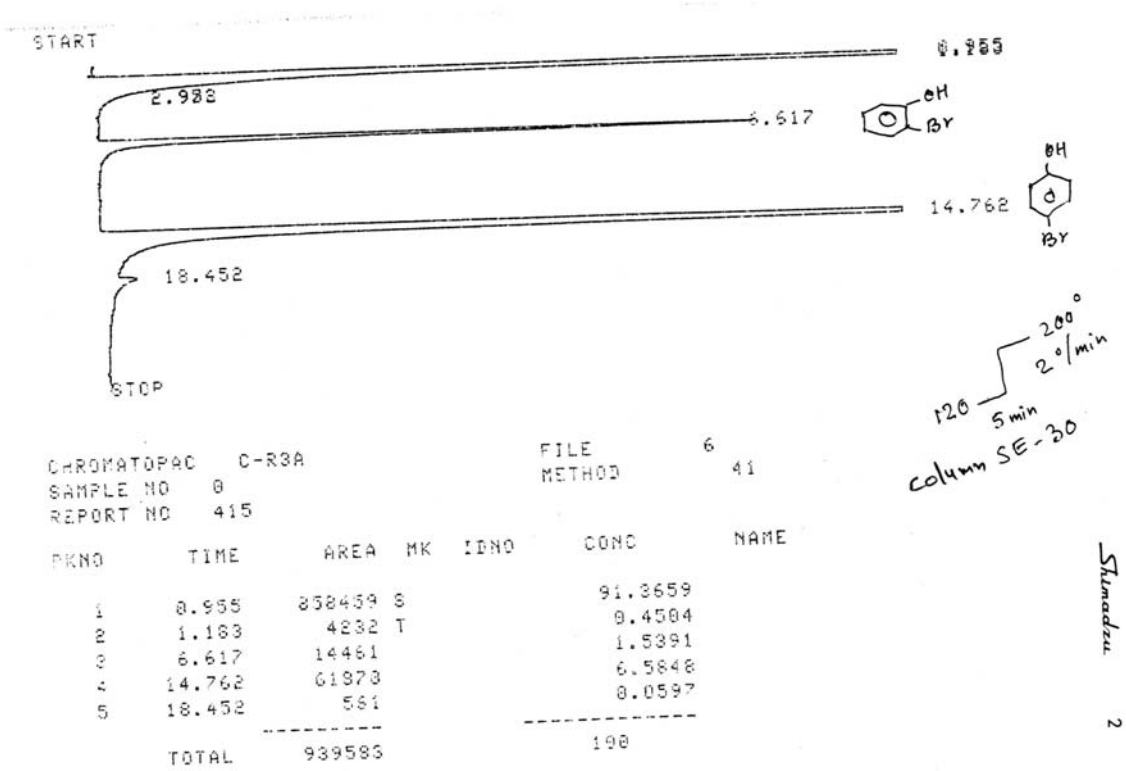
ν_{max} (Neat) 3393, 2958, 2932, 2862, 1463, 1423, 1379,1254, 1221, 1125, 1032, 903, 833, 789, 730, 663 cm^{-1}. CHN: Found C, 38.39%; H, 7.34%; Calcd. C, 39.78%; H, 7.18 %.

1-Bromo-2-octanol (entry 2, table 5) ^{1}H-NMR- ($CDCl_3$-200 MHz)- (δ) 0.84-0.88 (3H, t J= 4); 1.28-1.53 (10H, m); 1.99 (1H, s); 3.33-3.56 (2H, m); 3.78-3.82 (1H, m). IR: ν_{max} (Neat) 3393, 2928, 2857, 1463, 1423, 1378, 1223, 1127, 1036, 663 cm^{-1}.CHN: Found C, 43.89%; H, 6.48%; Calcd. C, 45.93%; H, 8.13%.

2-Bromocyclohexanol (entry 3, table 5) ^{1}H-NMR- ($CDCl_3$-200 MHz)- (δ) 1.22-1.42 (3H, m); 1.65-1.88 (3H, m); 2.09-2.16 (1H, m); 2.24-2.37 (1H, m); 2.57 (1H, s); 3.55-3.67 (1H, m); 3.84-3.96 (1H, m). IR: ν_{max} (Neat) 3400, 2938, 2861, 1726, 1449, 1360, 1253, 1186, 1073, 956862, 690 cm^{-1}. CHN: Found C, 40.06%; H, 6.19%; Calcd. C, 40.22%; H, 6.15%.

2-Bromo-1-phenylethanol (entry 4, table 5) ^{1}H-NMR ($CDCl_3$-200 MHz)- (δ) 2.53 (1H, s); 3.53-3.61 (2H, m); 4.88-4.94 (1H, dd J= 4 & 4); 7.18-7.30 (5H, m). IR: ν_{max} (Neat) 3403, 3063, 3031, 2962, 2893, 1956, 1887, 1813, 1680, 1493, 1452, 1420, 1256, 1217, 1198, 1118, 1061, 1028, 990, 917, 870, 813,762, 701, 666, 592 cm^{-1}. CHN: Found C, 48.05%; H, 4.75%; Calcd. C, 47.76%; H, 4.47%.

2-Bromo-1-[4-methylphenyl] ethanol (entry 5, Table 5):^{1}H-NMR- ($CDCl_3$-200 MHz)- (δ) 2.63 (3H, s); 3.54-3.61 (2H, m); 4.88-4.94 (1H, dd J= 4 & 4); 7.25-7.36 (5H, m). IR: ν_{max} (Neat) 3400, 3024, 2960, 2922, 1613, 1514, 1421, 1379,1312, 1217, 1198, 1067, 1021, 993, 818, 765, 722, 643 cm^{-1}. CHN: Found C, 47.68%; H, 4.47%; Calcd. C, 50.23%; H, 5.11%.

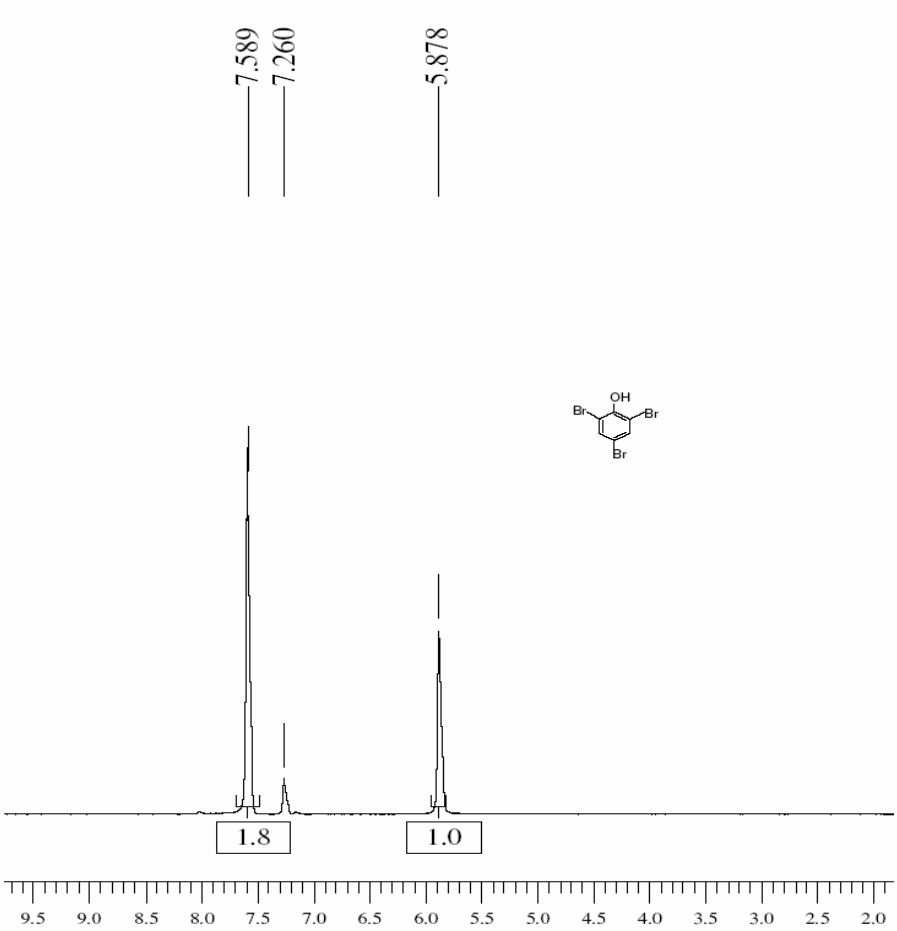


CHROMATOPAC C-R3A
SAMPLE NO 0
REPORT NO 415

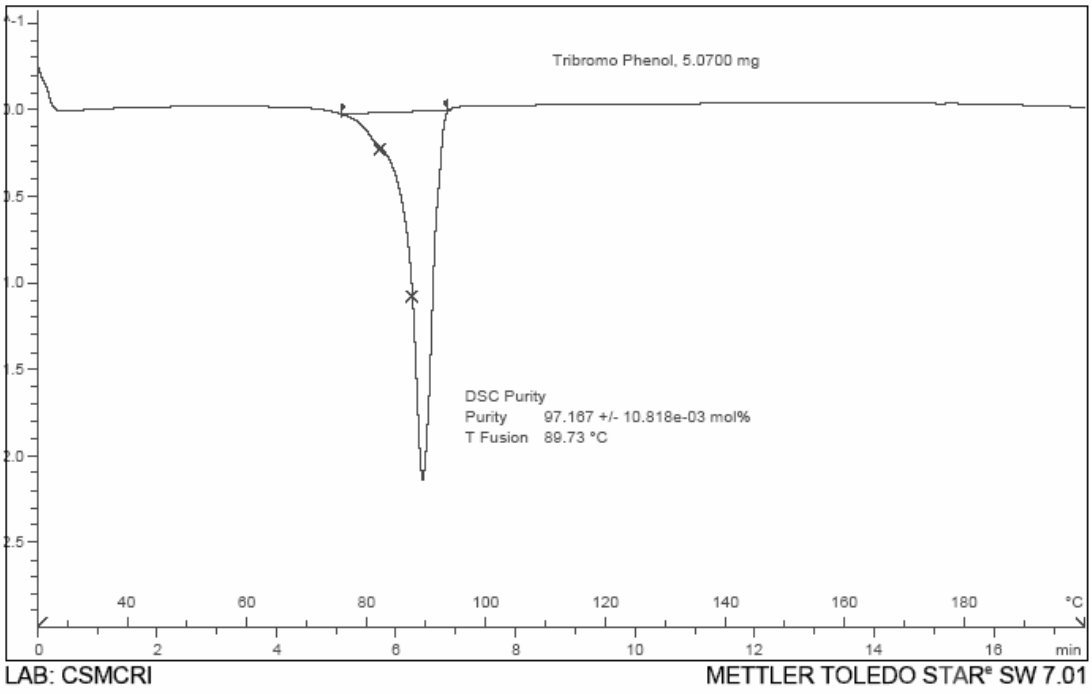
FILE 6
METHOD 41

PKNO	TIME	AREA	MK	IDNO	CONC	NAME
1	0.955	858459	S		91.3659	
2	1.183	4232	T		0.4504	
3	6.617	14461			1.5391	
4	14.762	61873			6.5848	
5	18.452	561			0.0597	
	TOTAL	939583			100	

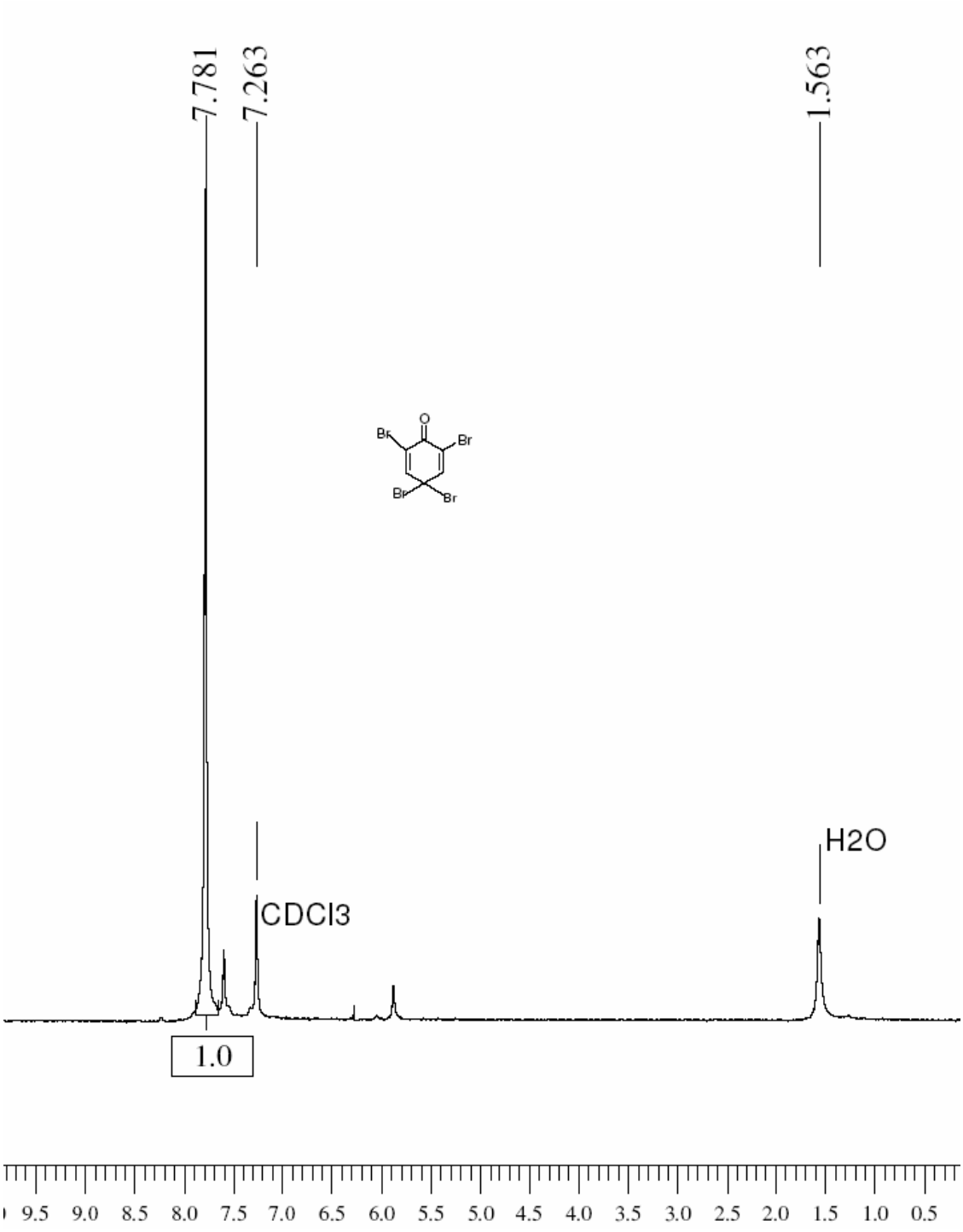
Gas chromatogram (entry 1, Table 1)
p/o –bromophenol (81:19)



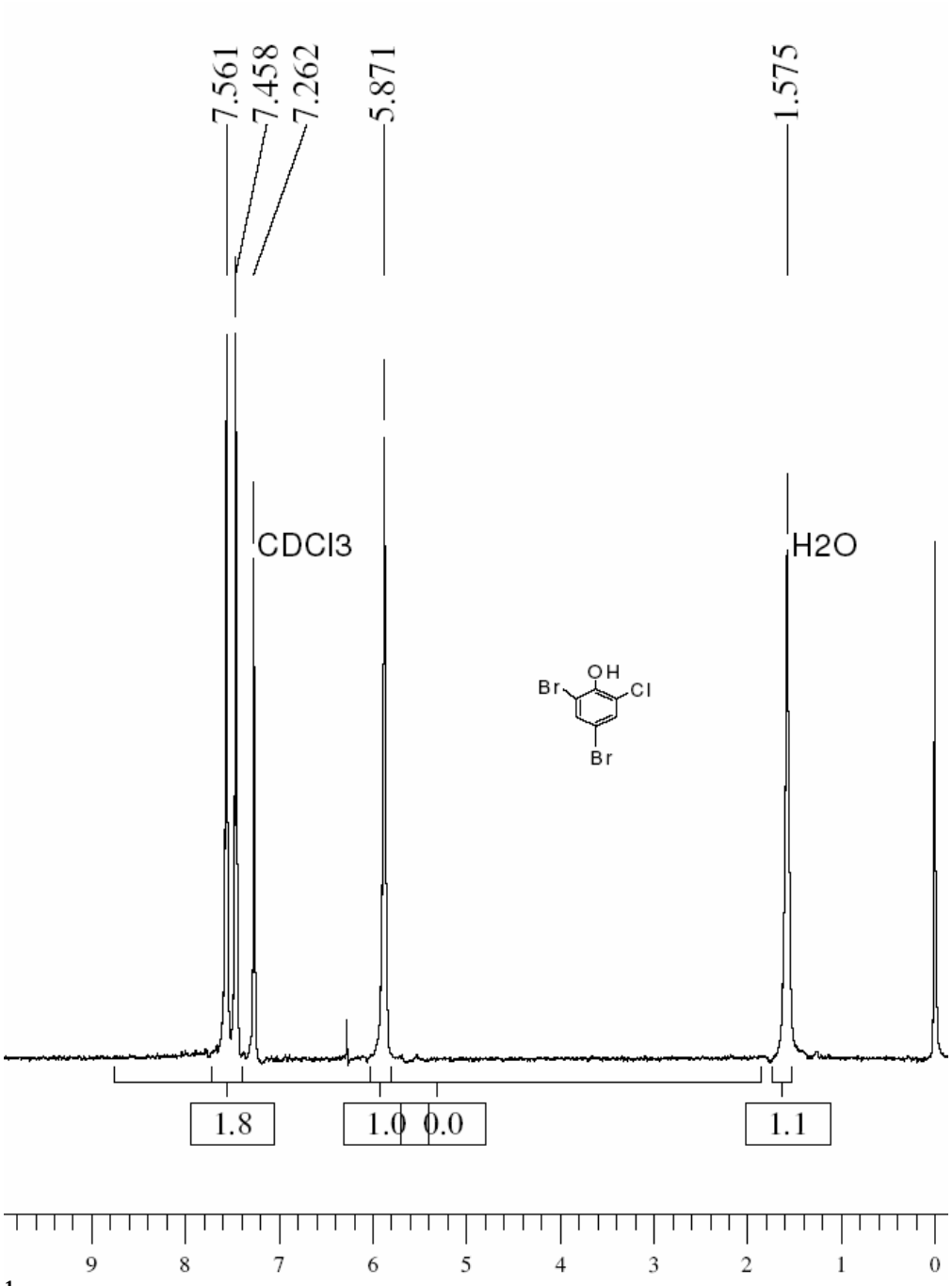
^{1}H-NMR (entry 2, Table 1) Ref 2.



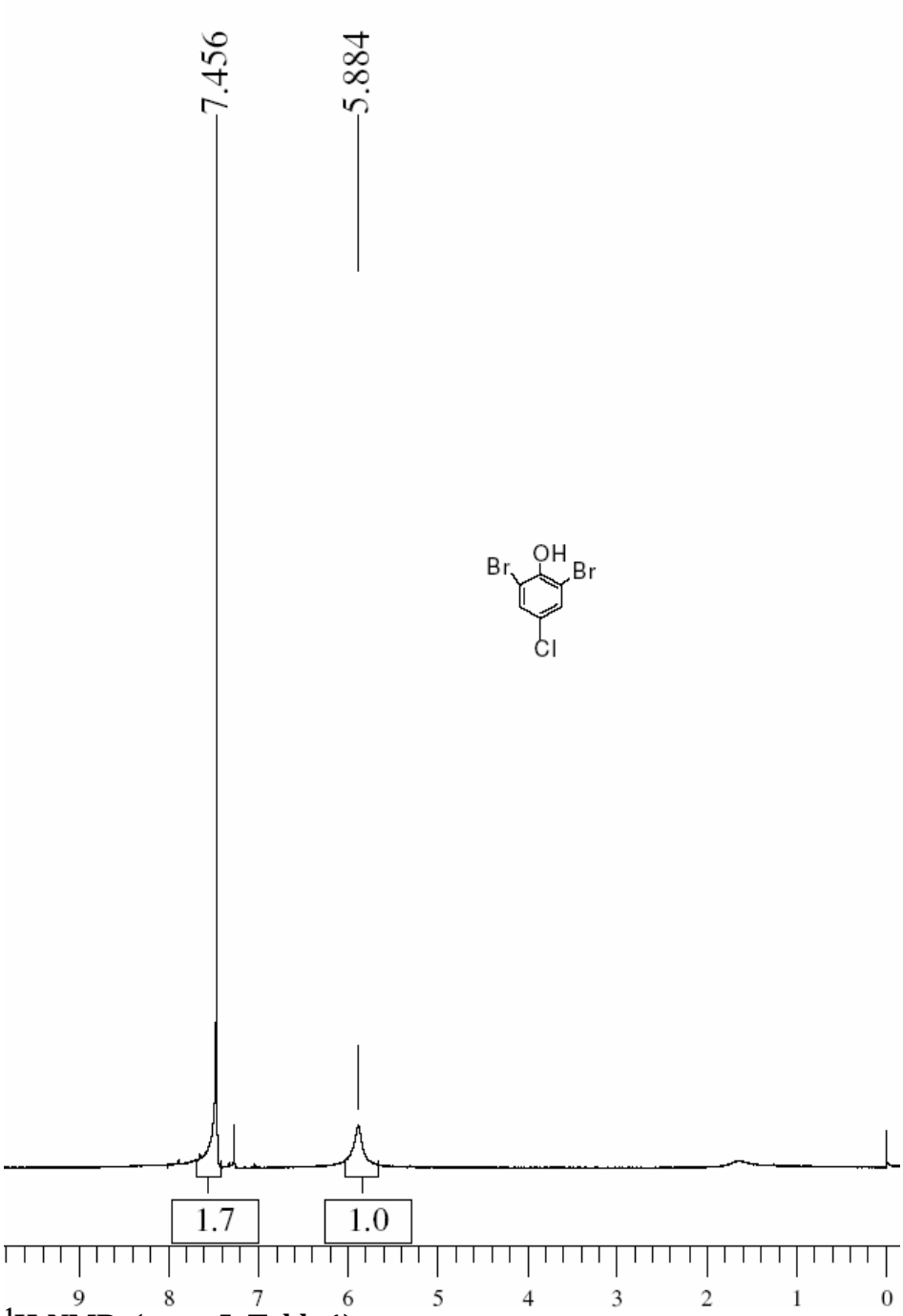
DSC (entry 2, Table 1)



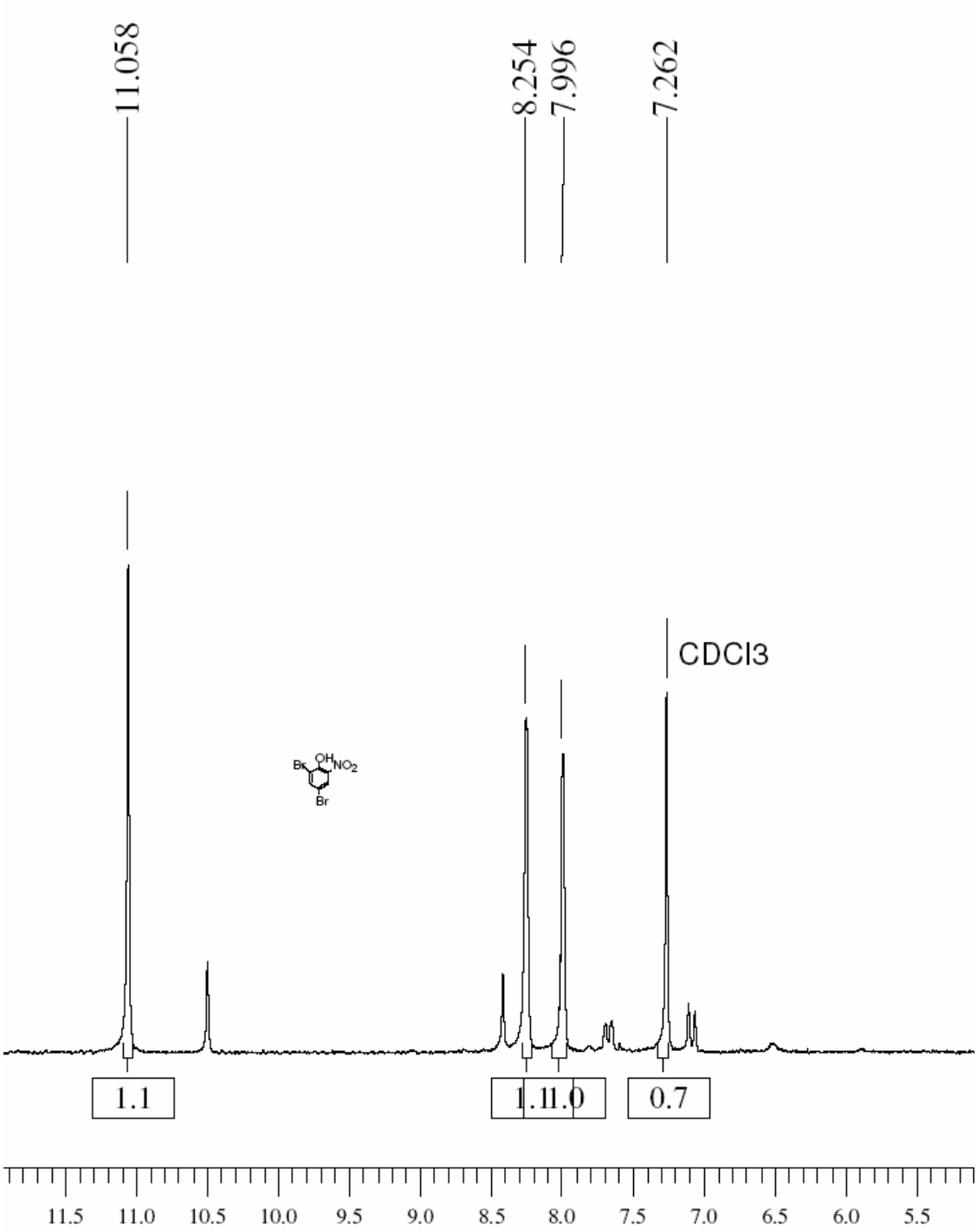
^{1}H-NMR (entry 3, Table 1)



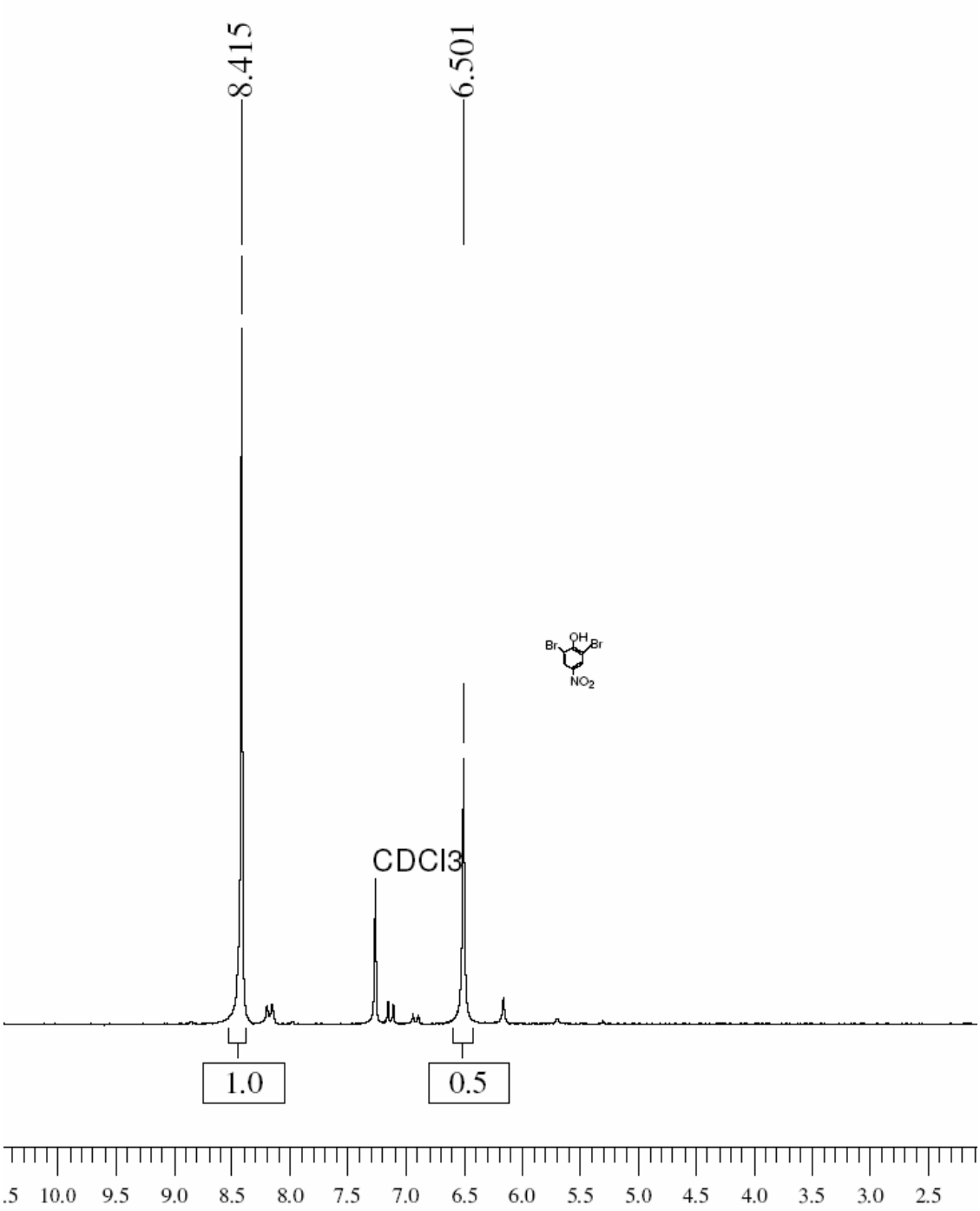
^{1}H-NMR (entry 4, Table 1)



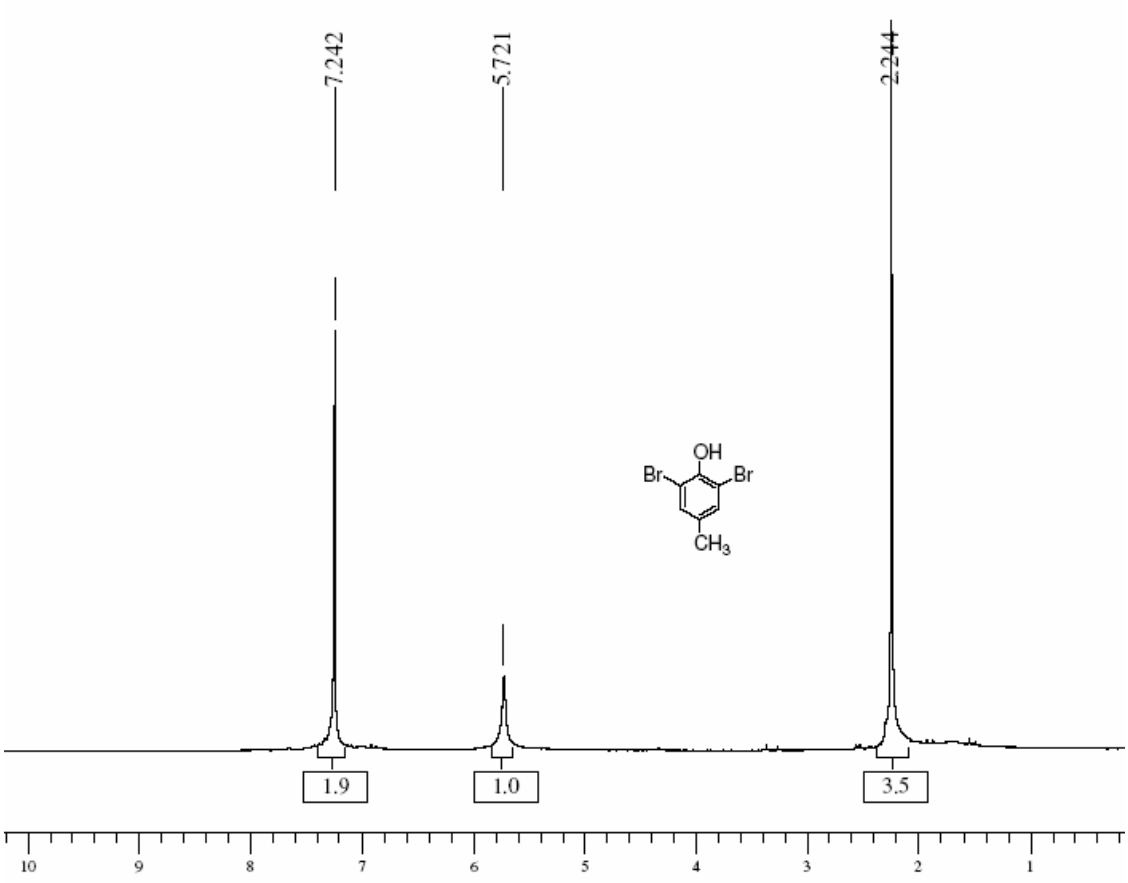
^{1}H-NMR (entry 5, Table 1)



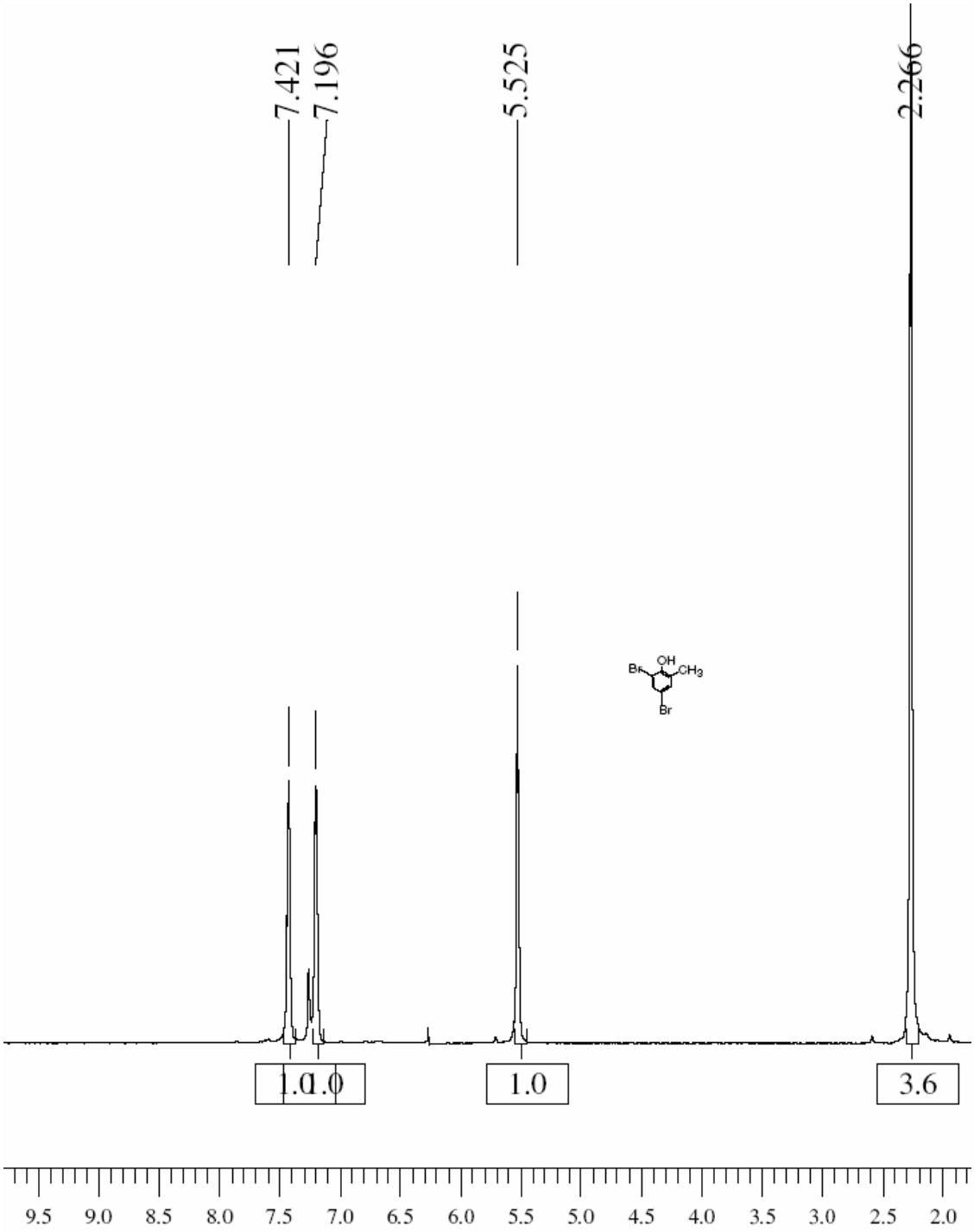
^{1}H-NMR (entry 6, Table 1)



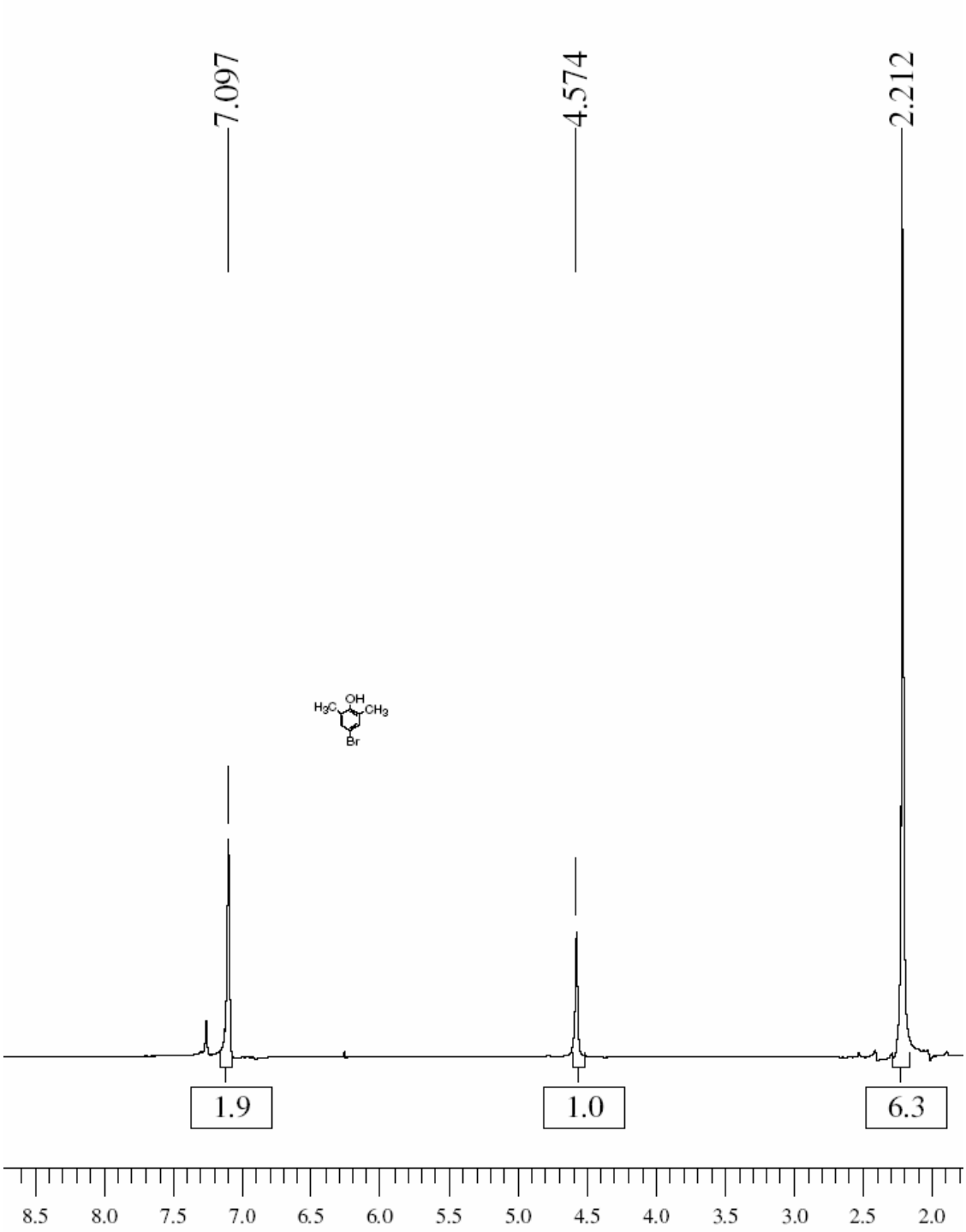
^{1}H-NMR (entry 7, Table 1) Ref 2 p 262.



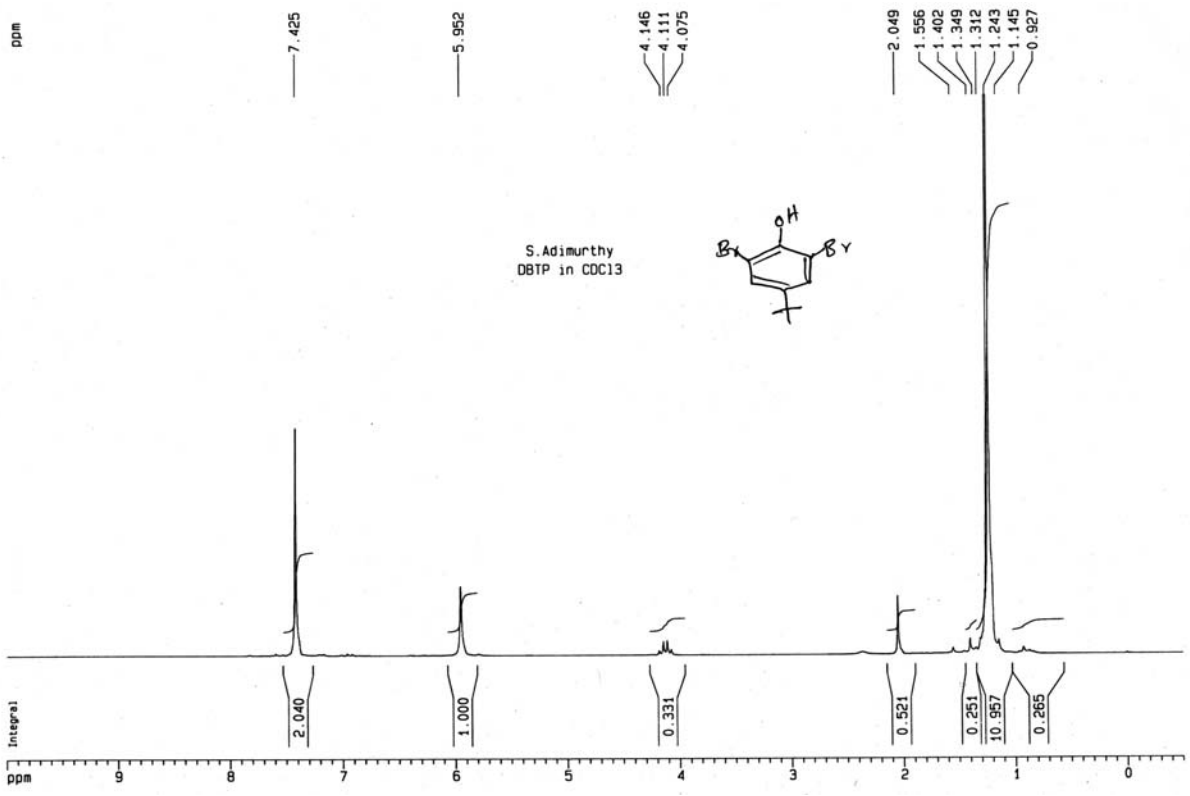
^{1}H-NMR (entry 8, Table 1) Ref 2 p 290.



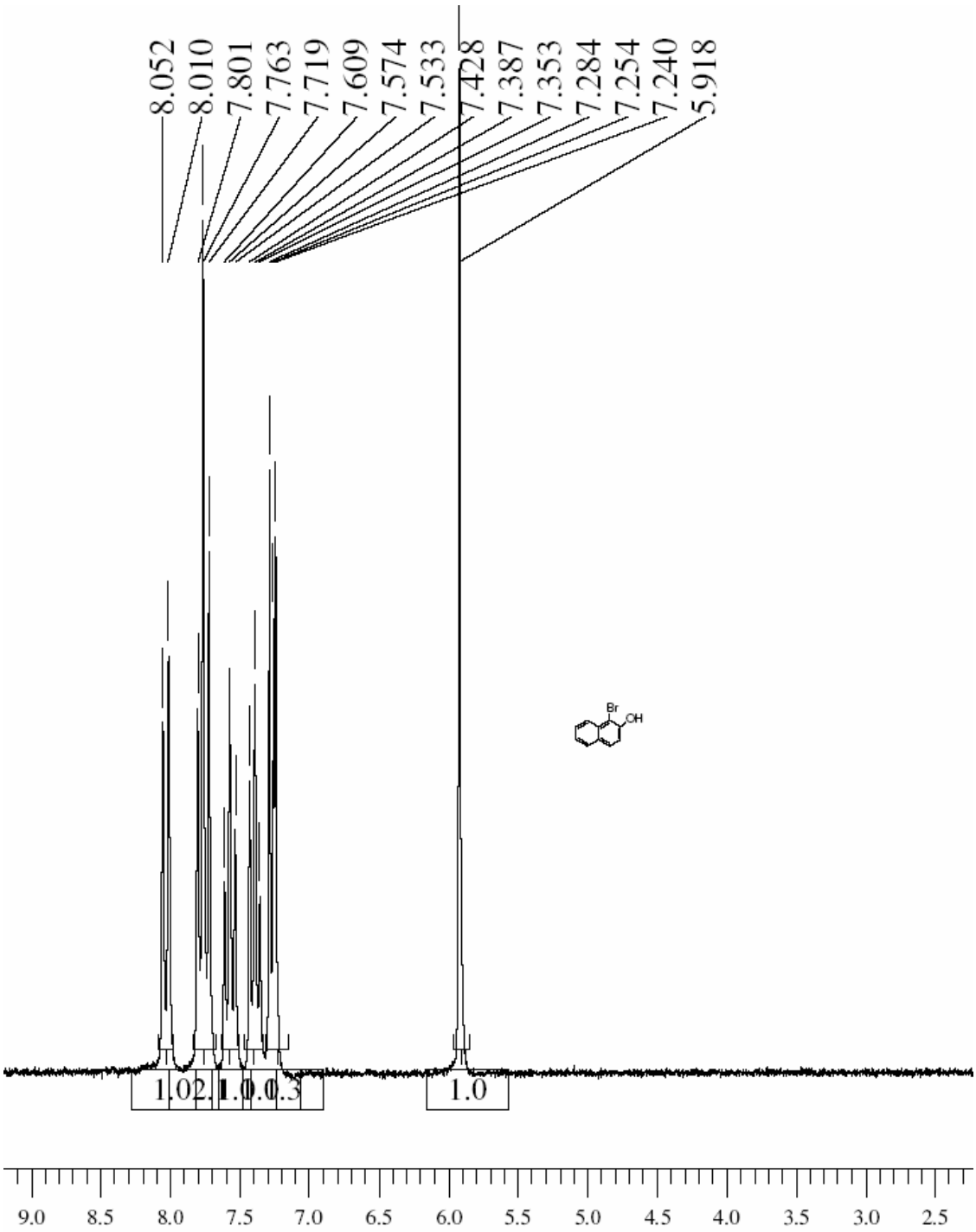
^{1}H-NMR (entry 9, Table 1)



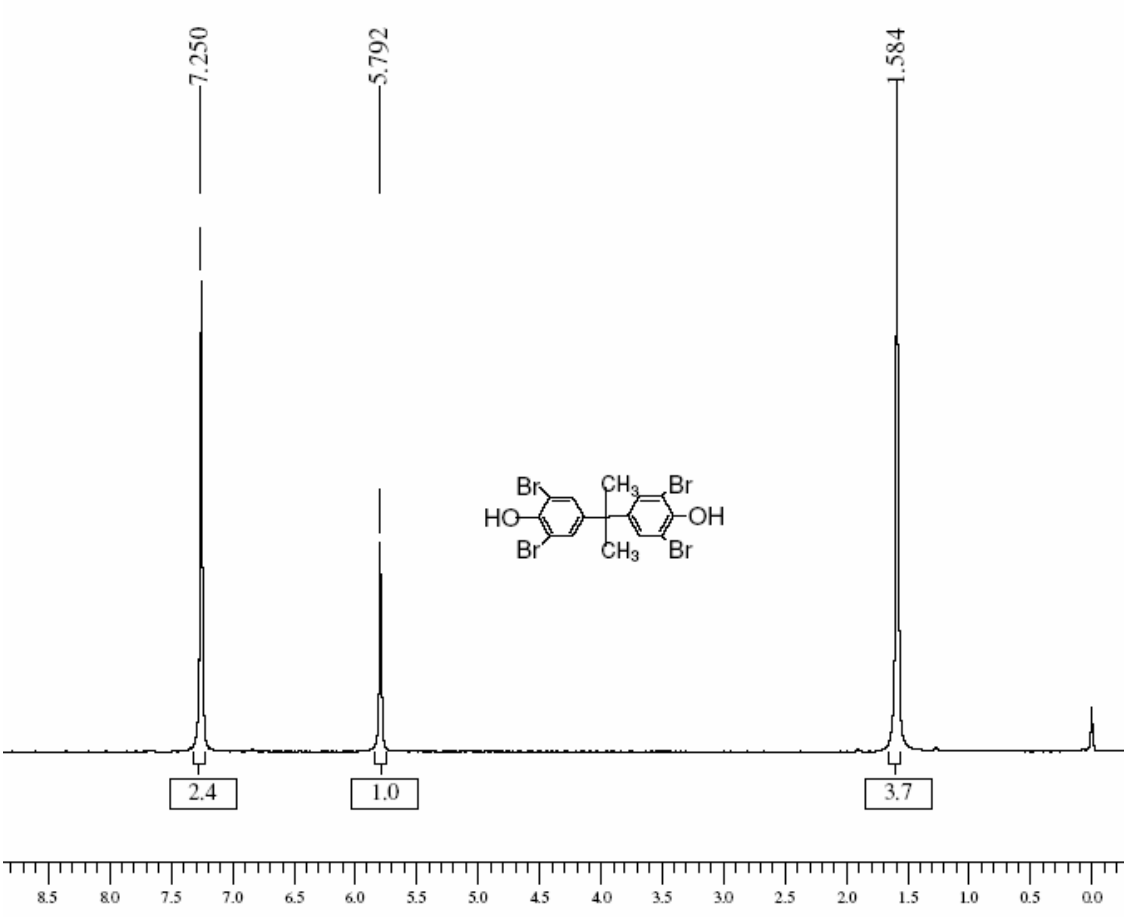
^{1}H-NMR (entry 10, Table 1) Ref 2 p 289.



^{1}H-NMR (entry 11, Table 1)



^{1}H-NMR (entry 12, Table 1) Ref 2 p 309.

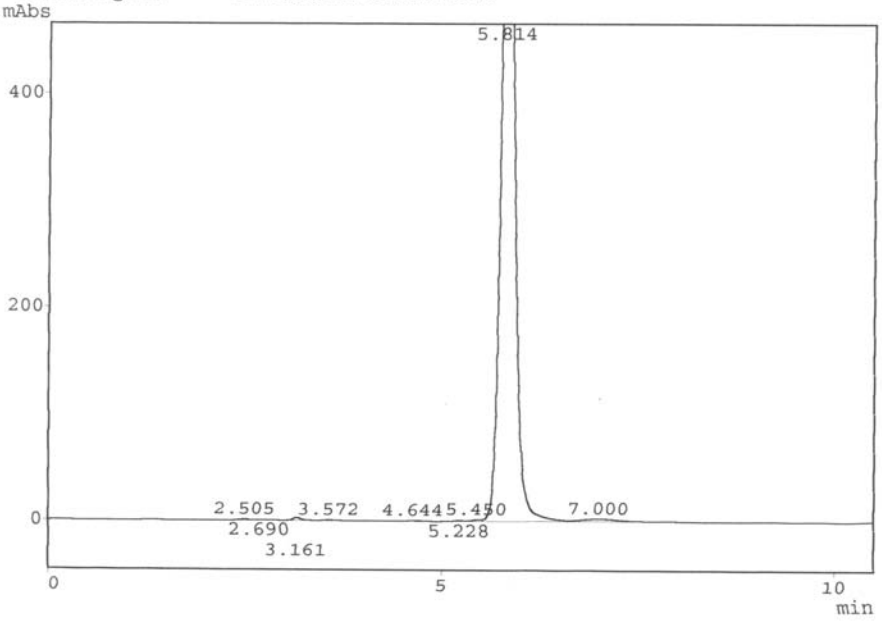


^{1}H-NMR (entry 13, Table 1) Ref 2 p 323.

CLASS-LC10 Ver.=1.63 SYS=1 Ch=1 REPORT.NO=5 DATA=08010602.D01 06/01/08 12:54
Sample : TBBPA_32
ID : TBBPA_32
Type : Unknown
Detector : SPD-10A Single
Operator : Harshad
Method Name : 08010602.M01

Batch No:- 32.

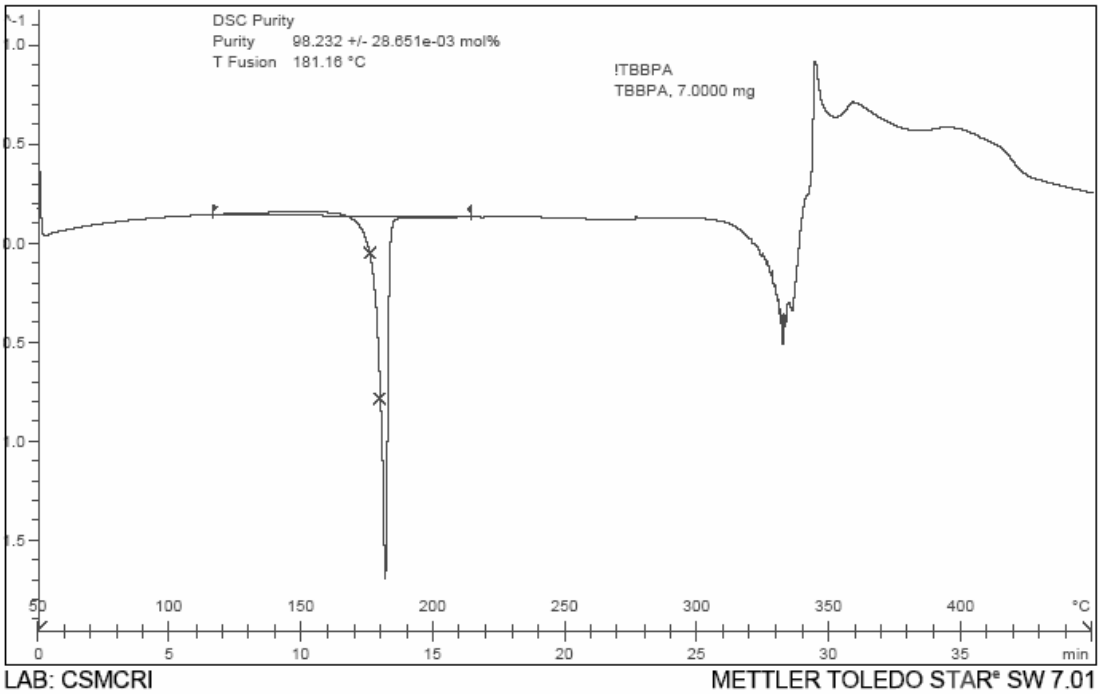
*** Chromatogram *** Filename:08010602.C01



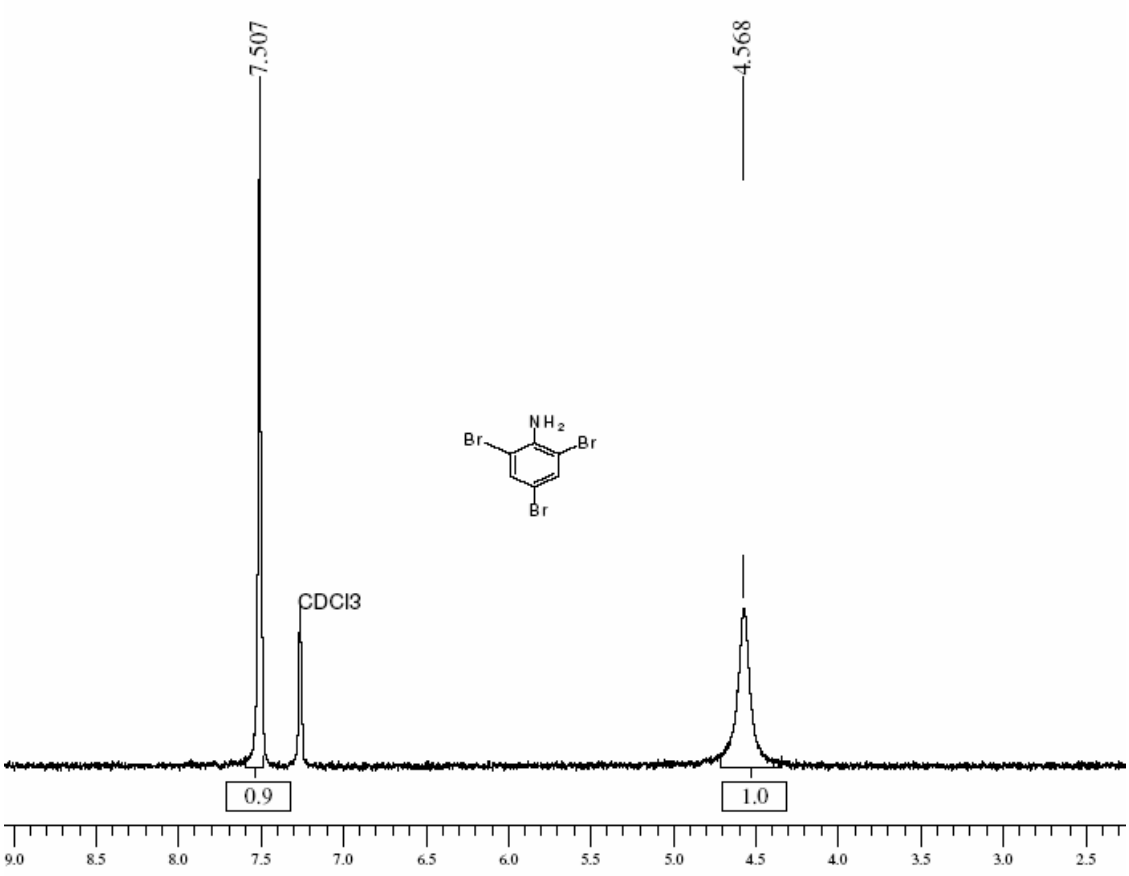
*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2.505	8607	1160			0.0995	
2	2.690	2795	366	V		0.0323	
3	3.161	17860	2571			0.2064	
4	3.572	5386	577			0.0622	
5	4.644	9185	660			0.1061	
6	5.228	5956	686			0.0688	
7	5.450	14289	1555	V		0.1651	
8	5.814	8516406	751087	V		98.4107	
9	7.000	73462	2286	V		0.8489	
		8653946	760948			100.0000	

HPLC (entry 13, Table 1)

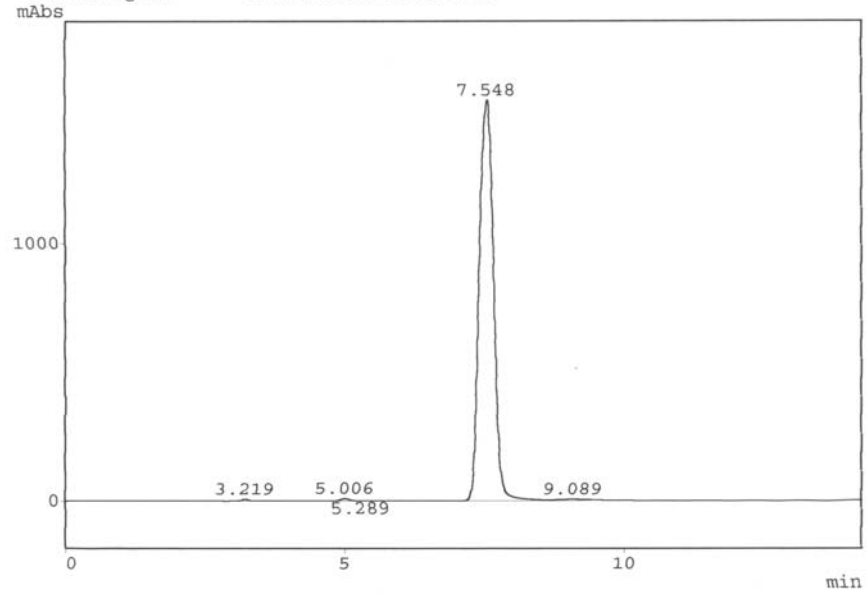


DSC (entry 13, Table 1) (Tetrabromobisphenol-A)



^{1}H-NMR (entry 1, Table 2)

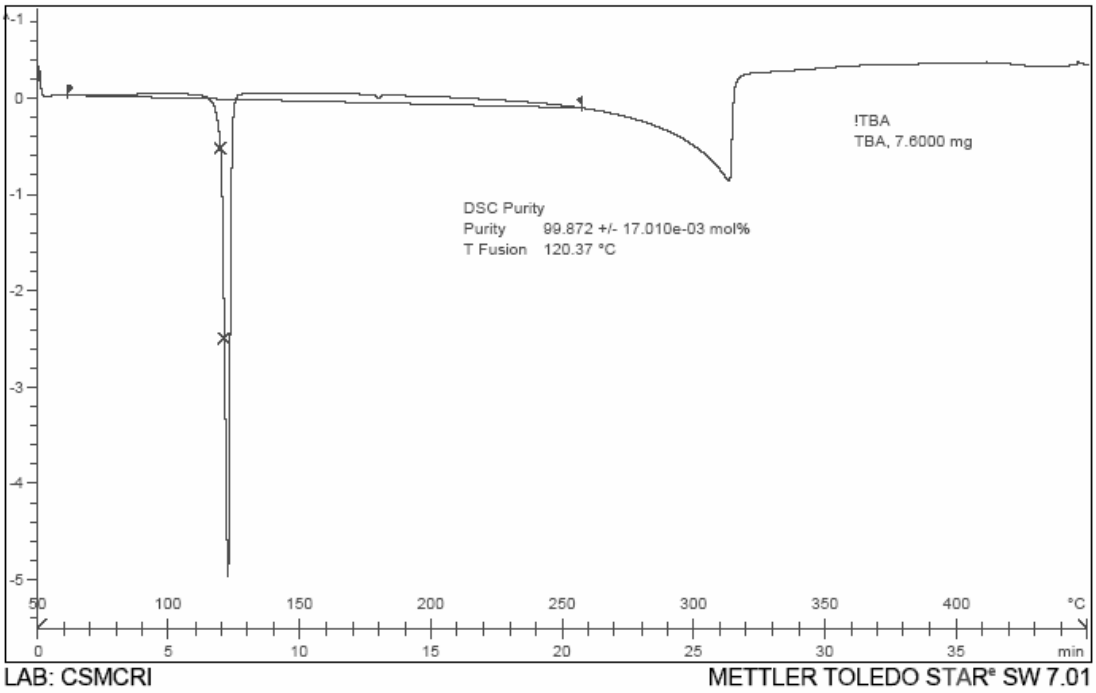
```
CLASS-LC10 Ver.=1.63  SYS=1 Ch=1 REPORT.NO=7  DATA=23120507.D01 05/12/23 17:16
Sample          : tba     Beta : 17
ID              : tba
Type            : Unknown
Detector        : SPD-10A Single
Operator        : Harshad
Method Name     : 23120507.M01

*** Chromatogram ***  Filename:23120507.C01
```



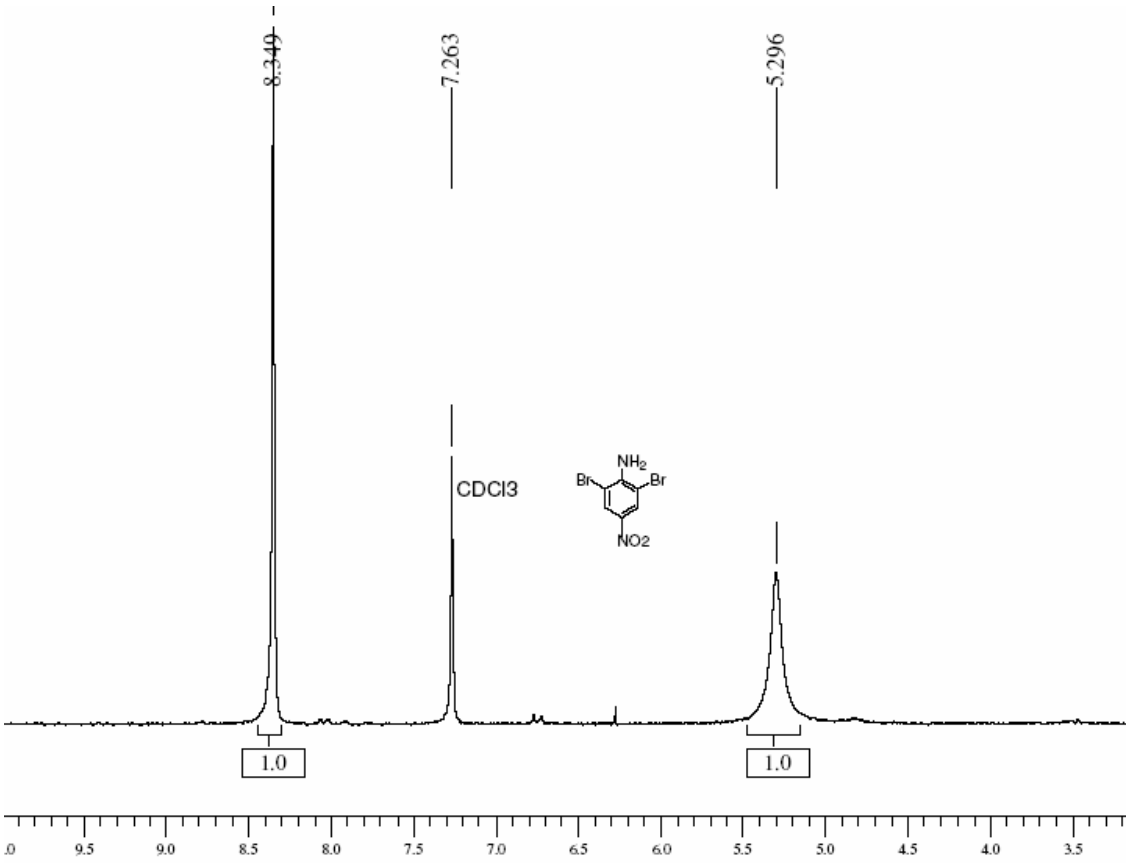
*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3.219	52621	7102			0.1874	
2	5.006	102132	9162			0.3636	
3	5.289	10113	1048	V		0.0360	
4	7.548	27700373	1555006			98.6283	
5	9.089	220369	4835	V		0.7846	
		28085609	1577152			100.0000	

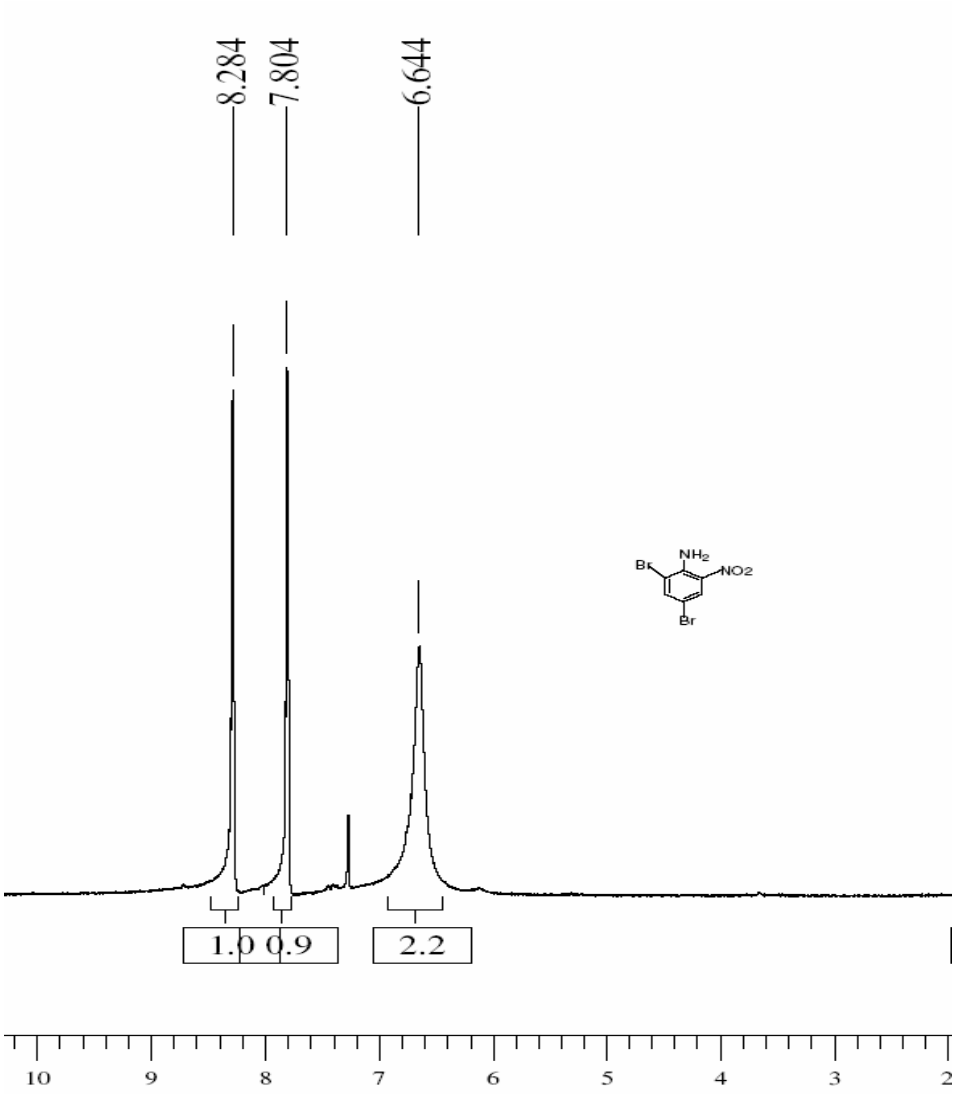
HPLC (entry 1, Table 2)



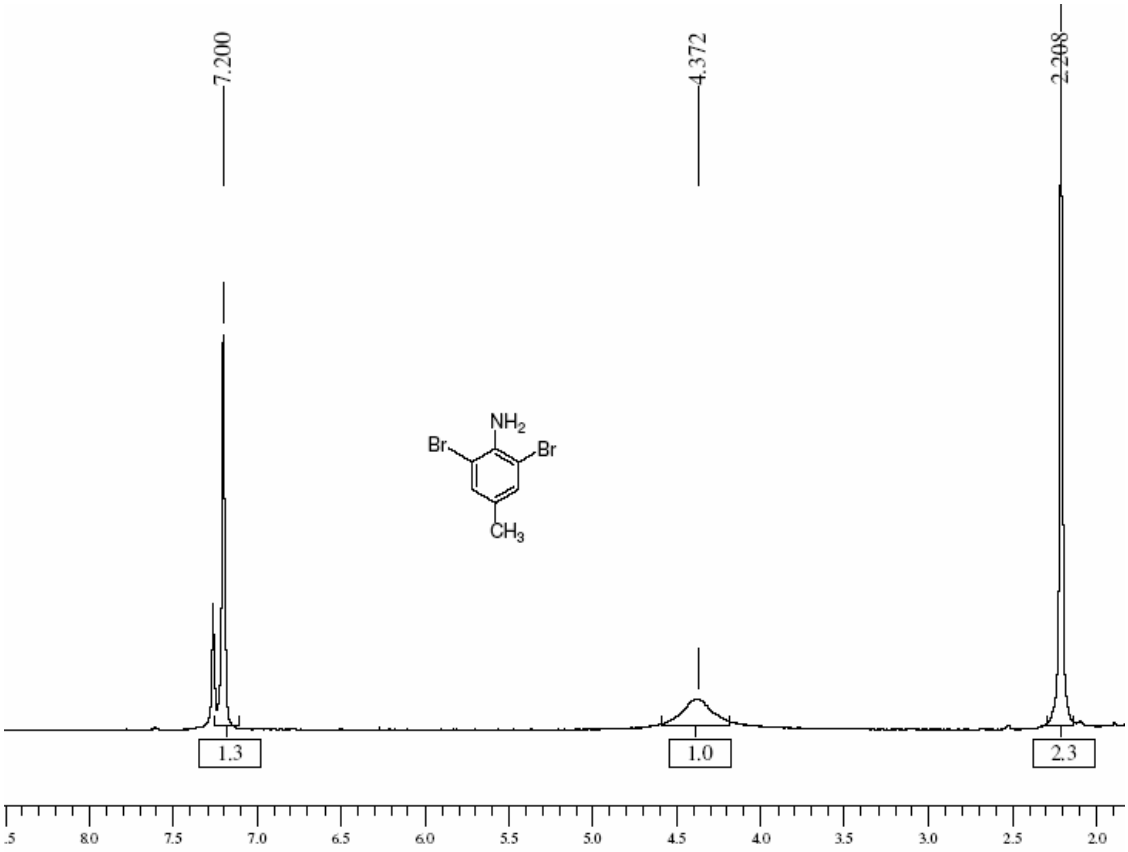
DSC (entry 1, Table 2) (Tribromoaniline)



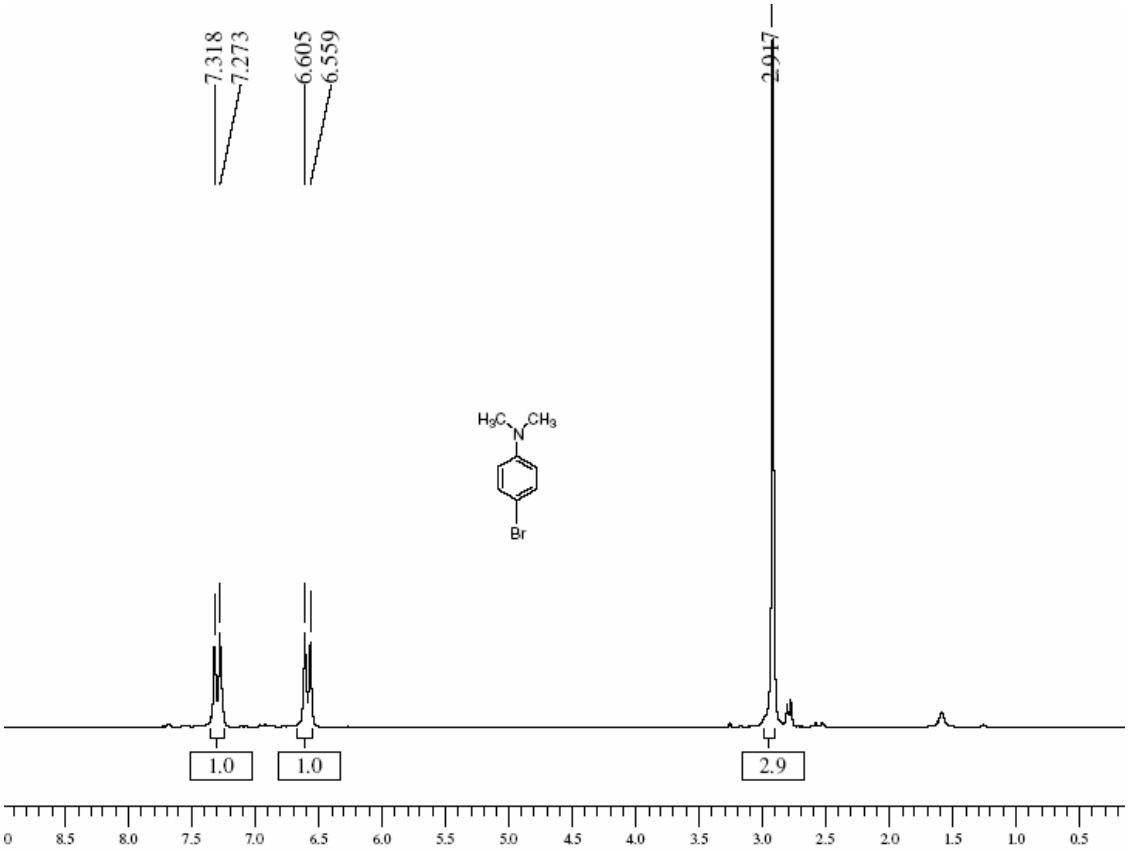
^{1}H-NMR (entry 2, Table 2) Ref 2 p 765.



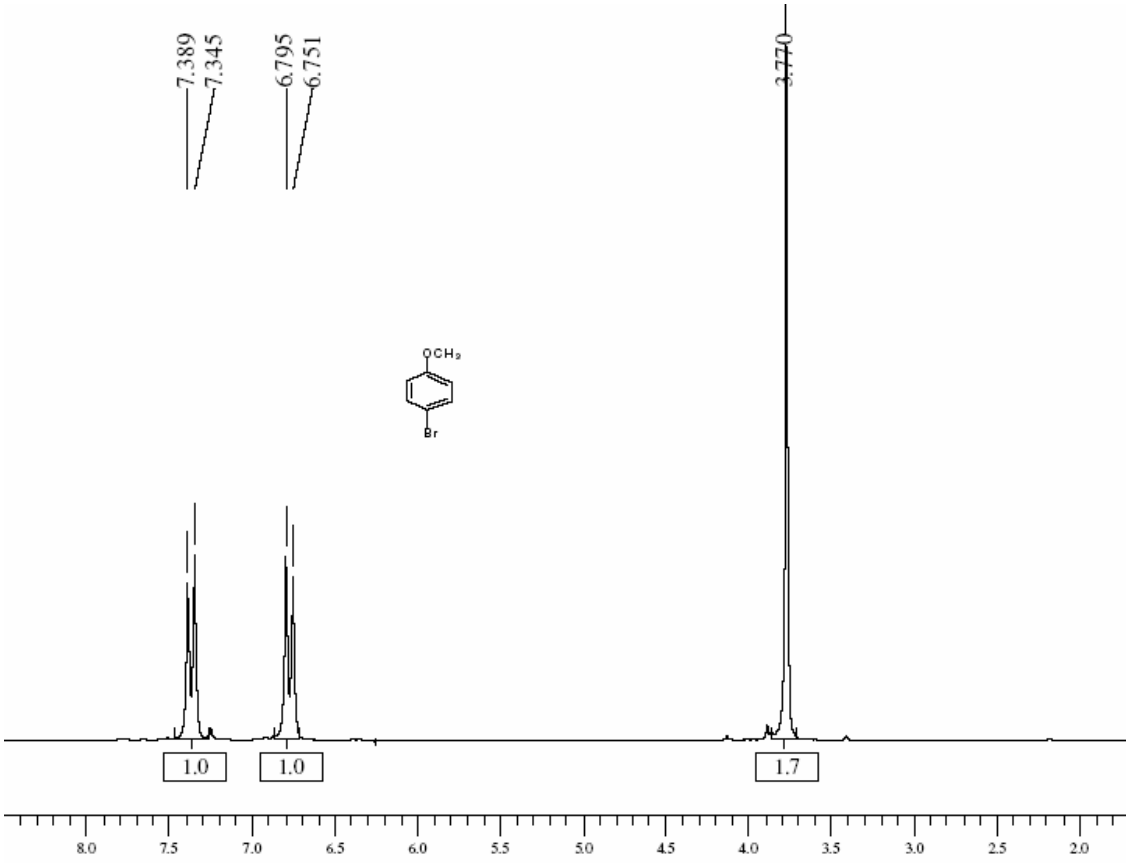
^{1}H-NMR (entry 3, Table 2) Ref 2 p 765.



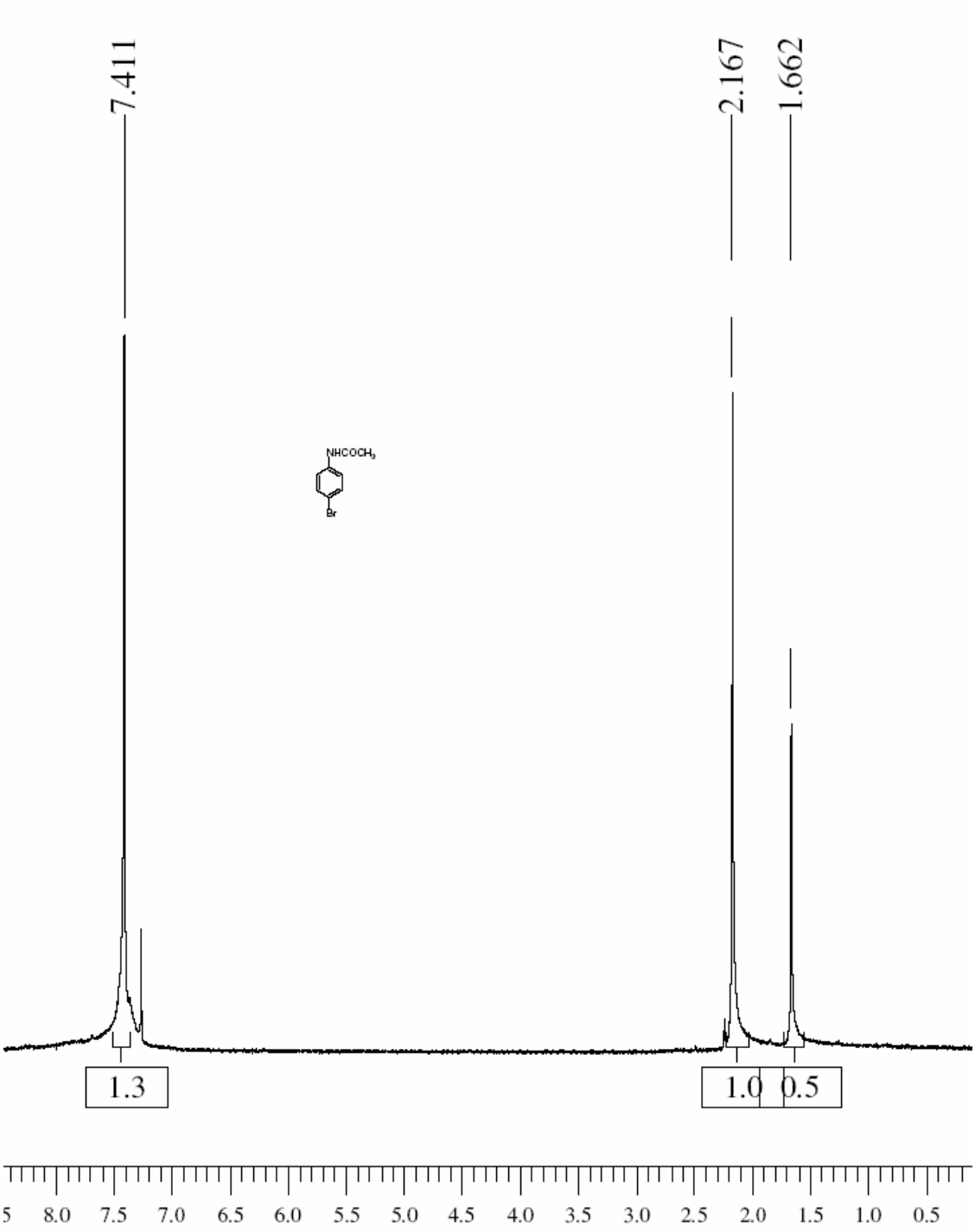
^{1}H-NMR (entry 4, Table 2) Ref 2 p 525.



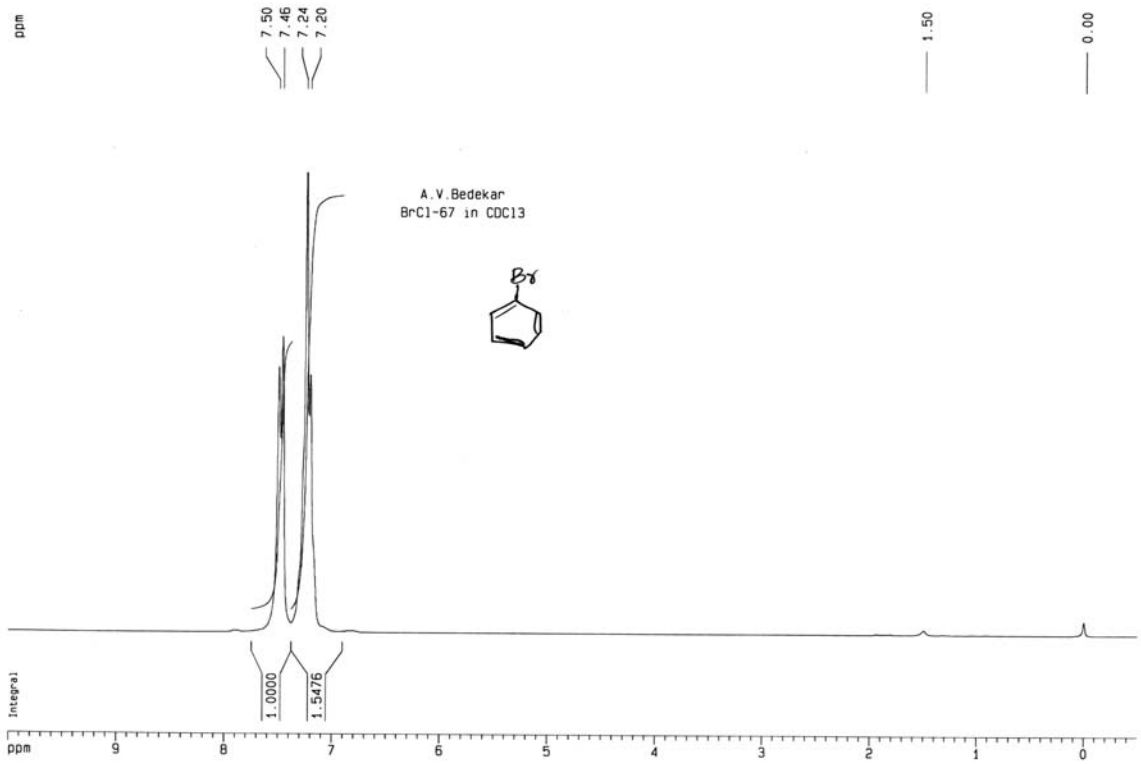
^{1}H-NMR (entry 5, Table 2) Ref 2 p 482.



^{1}H-NMR (entry 1, Table 3) Ref 2 p 187.



^{1}H-NMR (entry 3, Table 3)

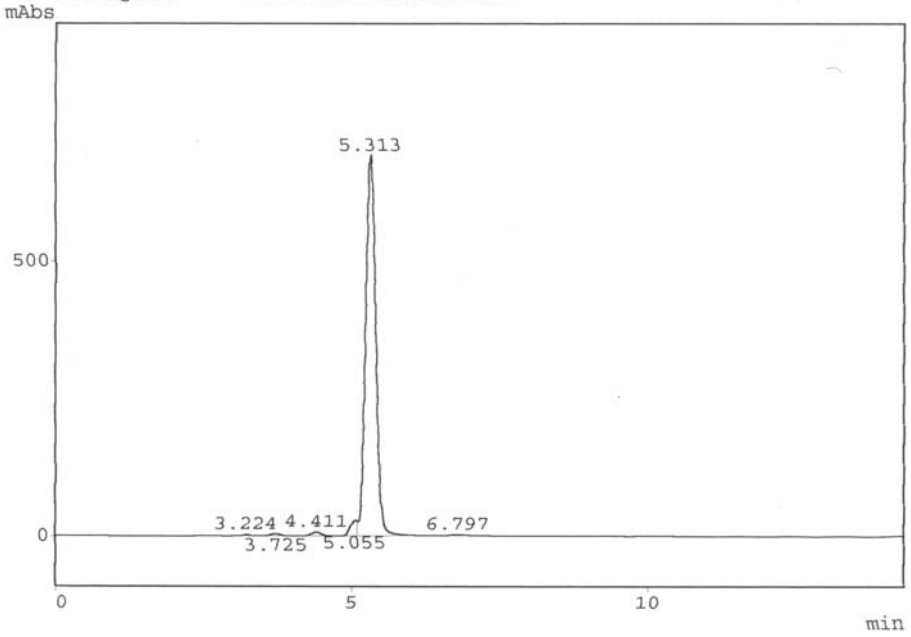


^{1}H-NMR (entry 4, Table 3) Ref 2 p 61.

CLASS-LC10 Ver.=1.63 SYS=1 Ch=1 REPORT.NO=6 DATA=23120506.D01 05/12/23 17:01
Sample : bromo benzene 3
ID : bromo benzene 3
Type : Unknown
Detector : SPD-10A Single
Operator : Harshad
Method Name : 23120506.M01

Batch :- 3

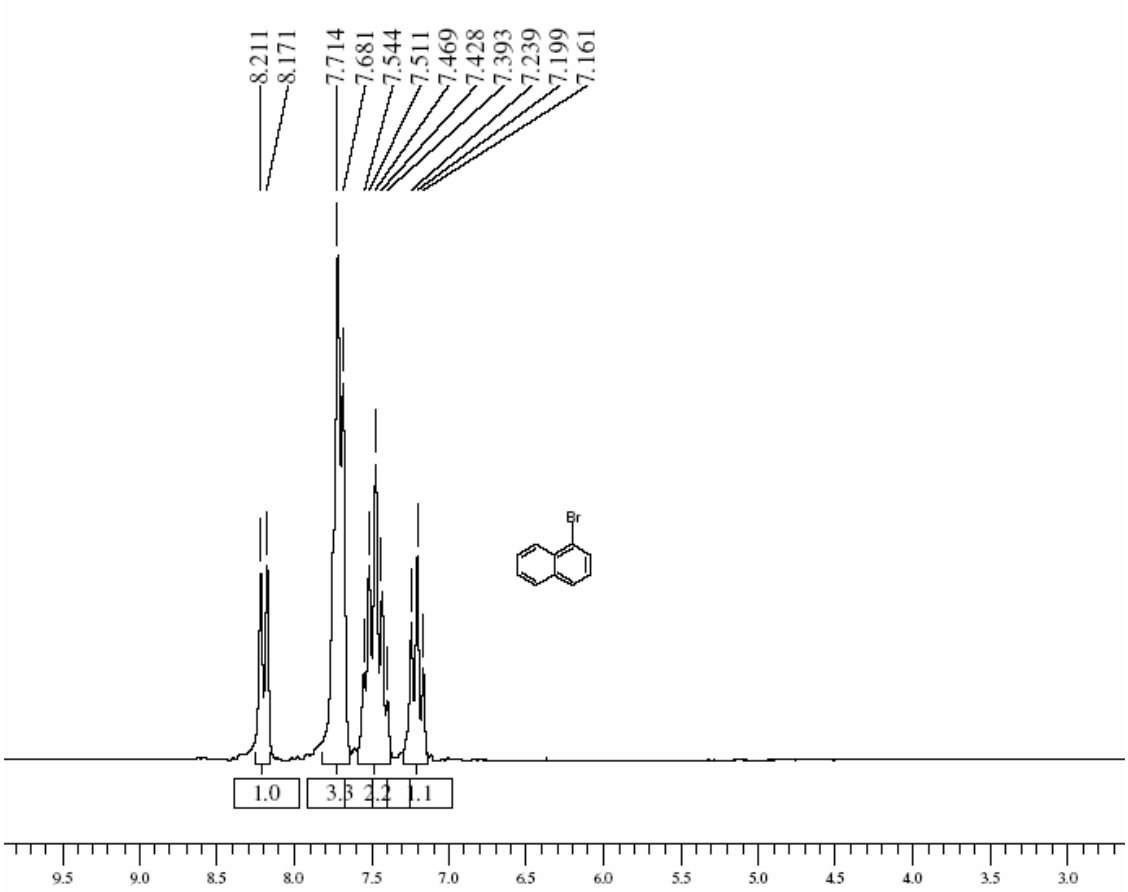
*** Chromatogram *** Filename:23120506.C01



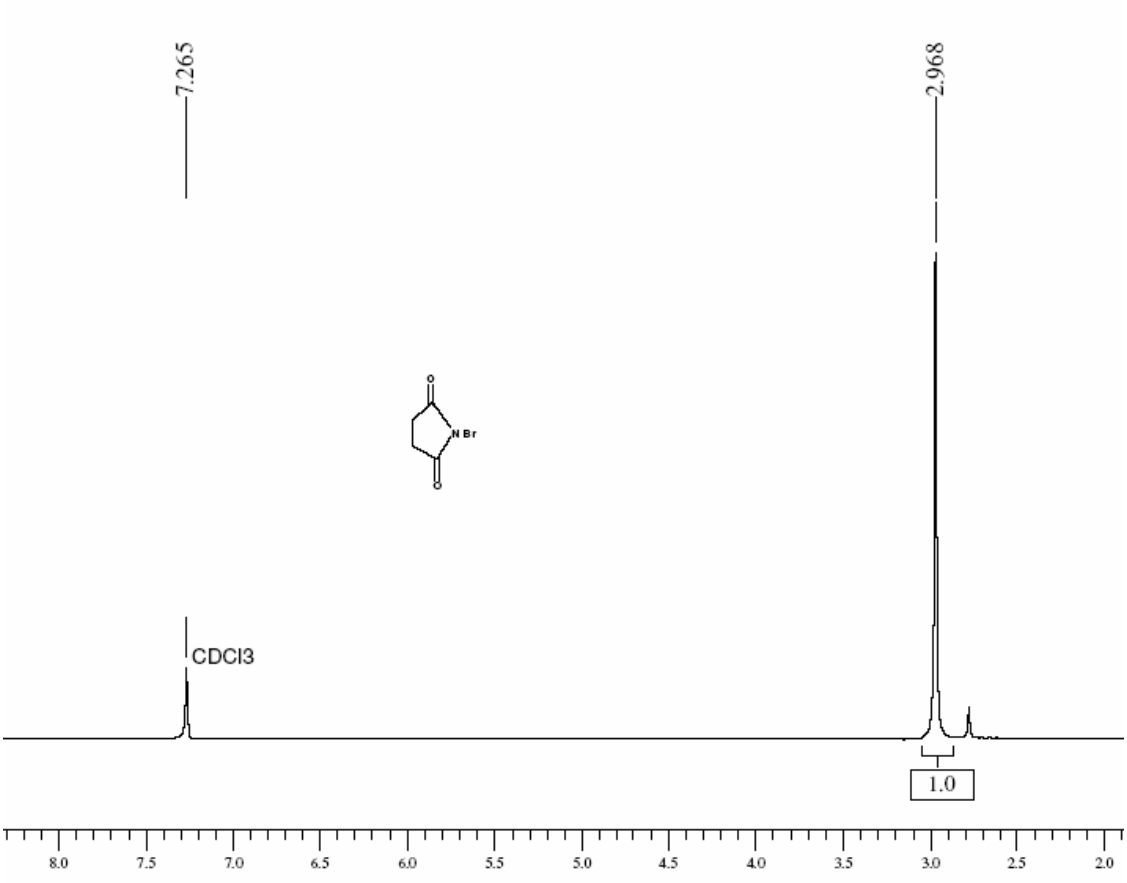
*** Peak Report ***

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3.224	15546	2155			0.1797	
2	3.725	44697	4034			0.5166	
3	4.411	81267	7013			0.9392	
4	5.055	233762	28682			2.7015	
5	5.313	8253723	692401	V		95.3865	
6	6.797	23934	1665			0.2766	
		8652929	735949			100.0000	

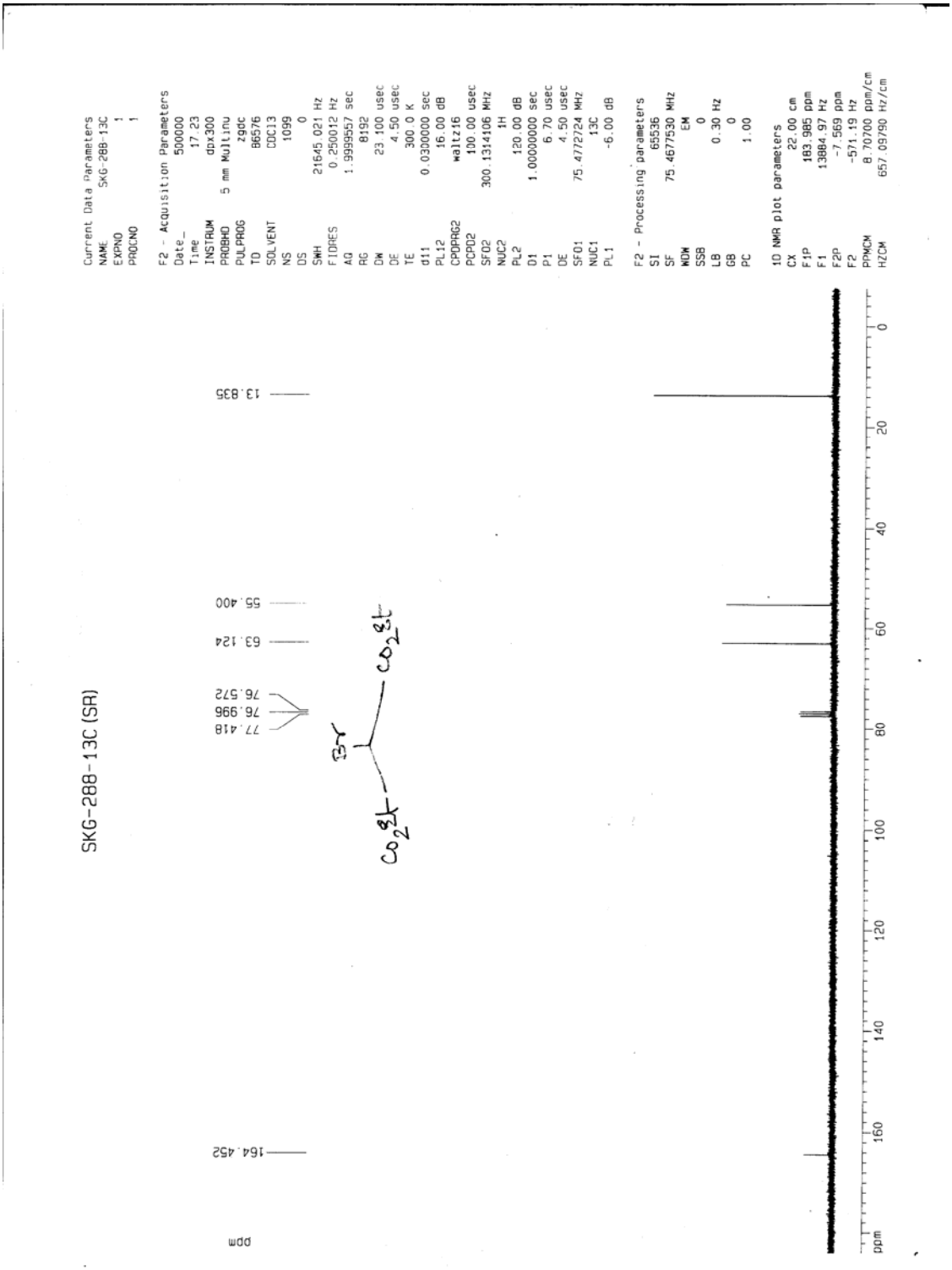
HPLC (entry 4, Table 3)



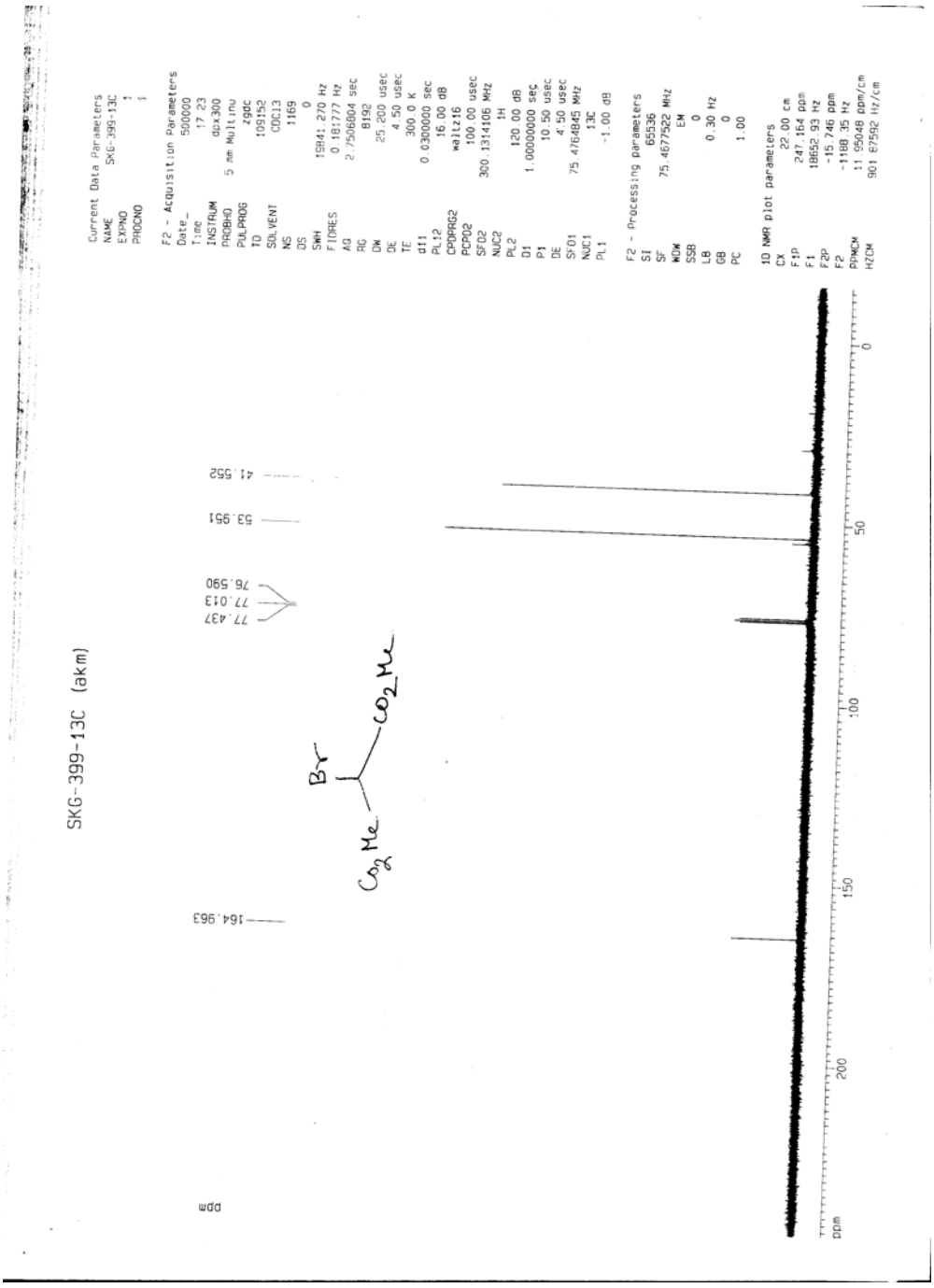
^{1}H-NMR (entry 5, Table 3) Ref 2 p 167.



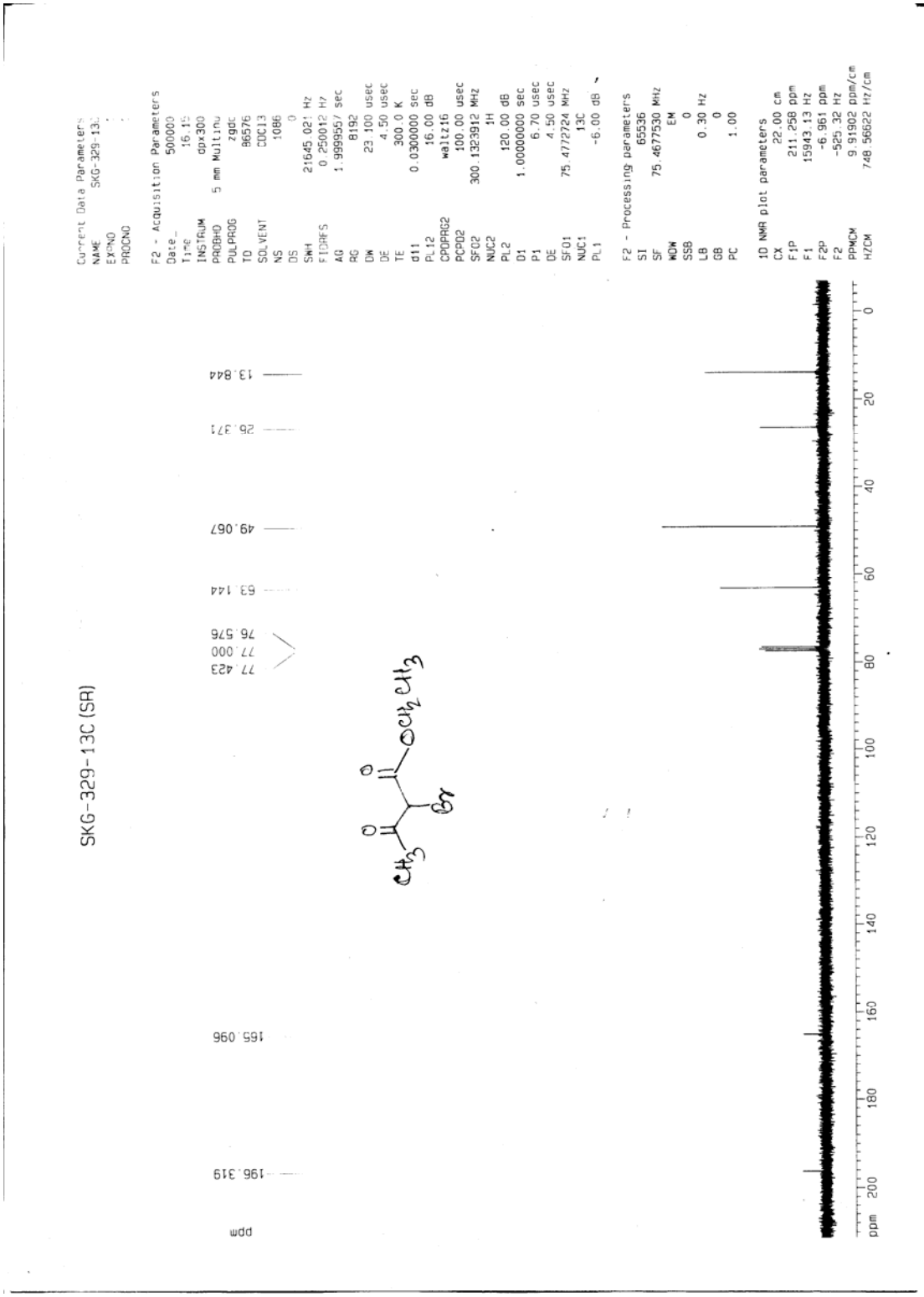
^{1}H-NMR N-Bromosuccinimide (NBS)



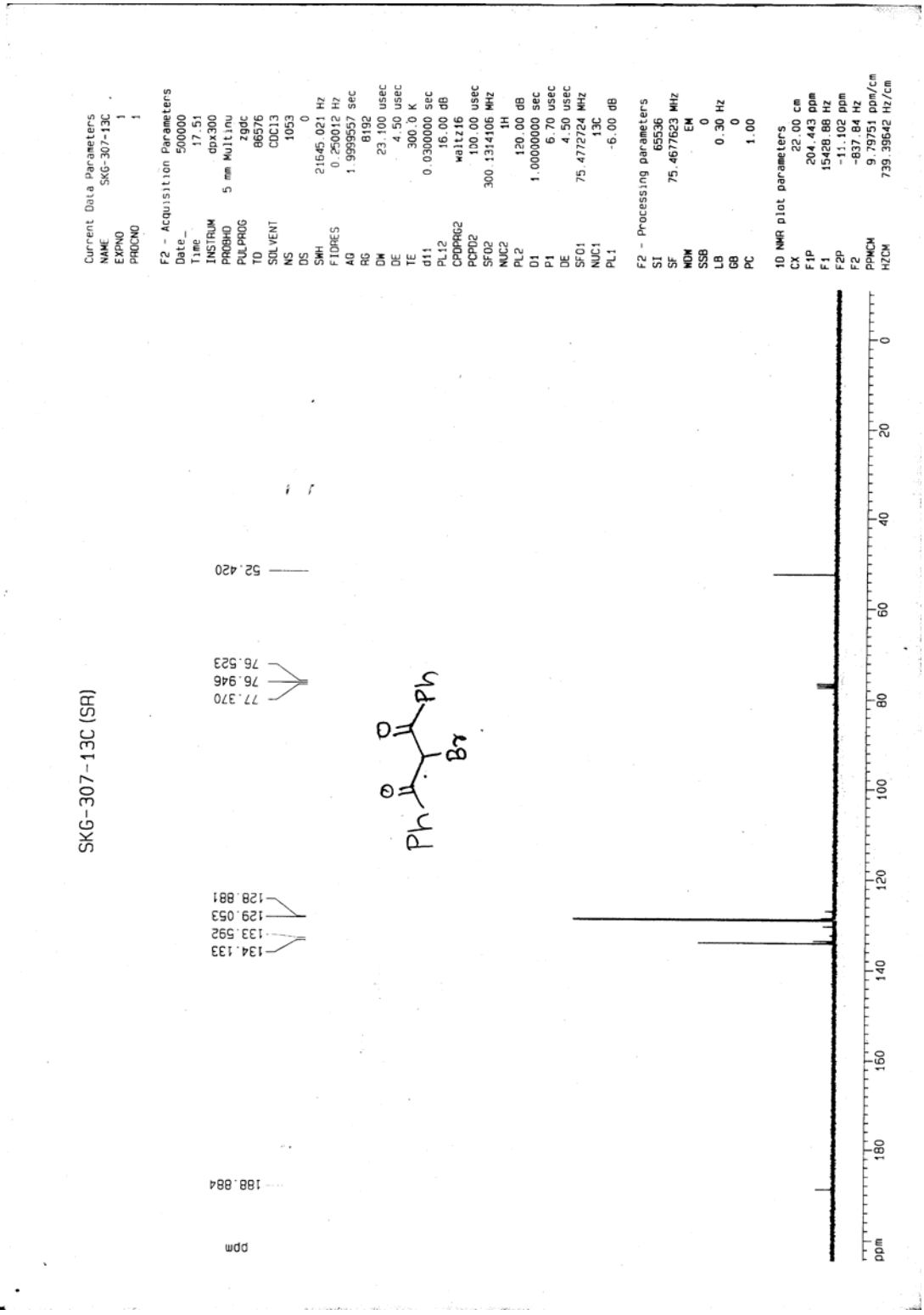
(ENTRY-1, Table 4)



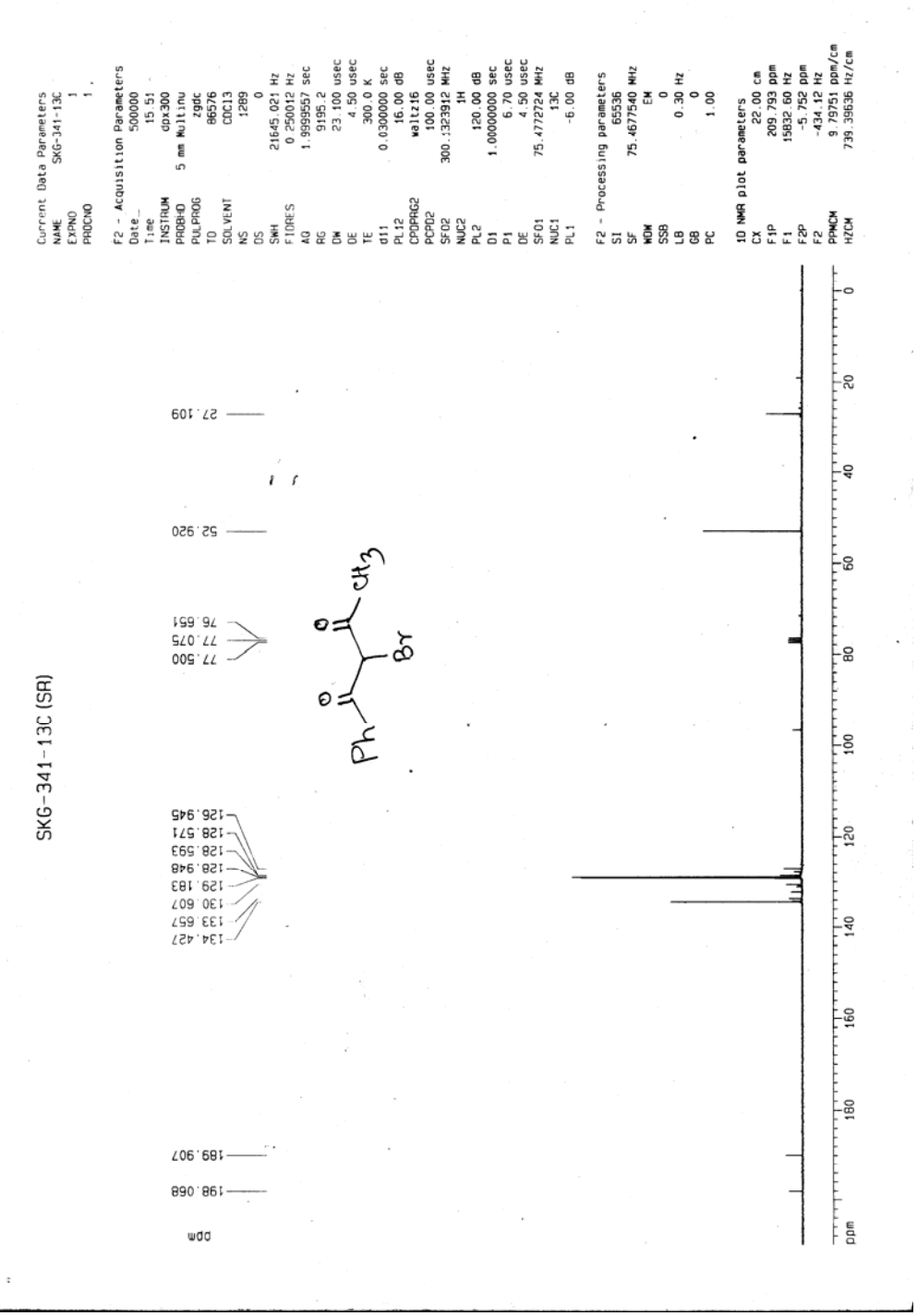
(ENTRY-2, Table 4)



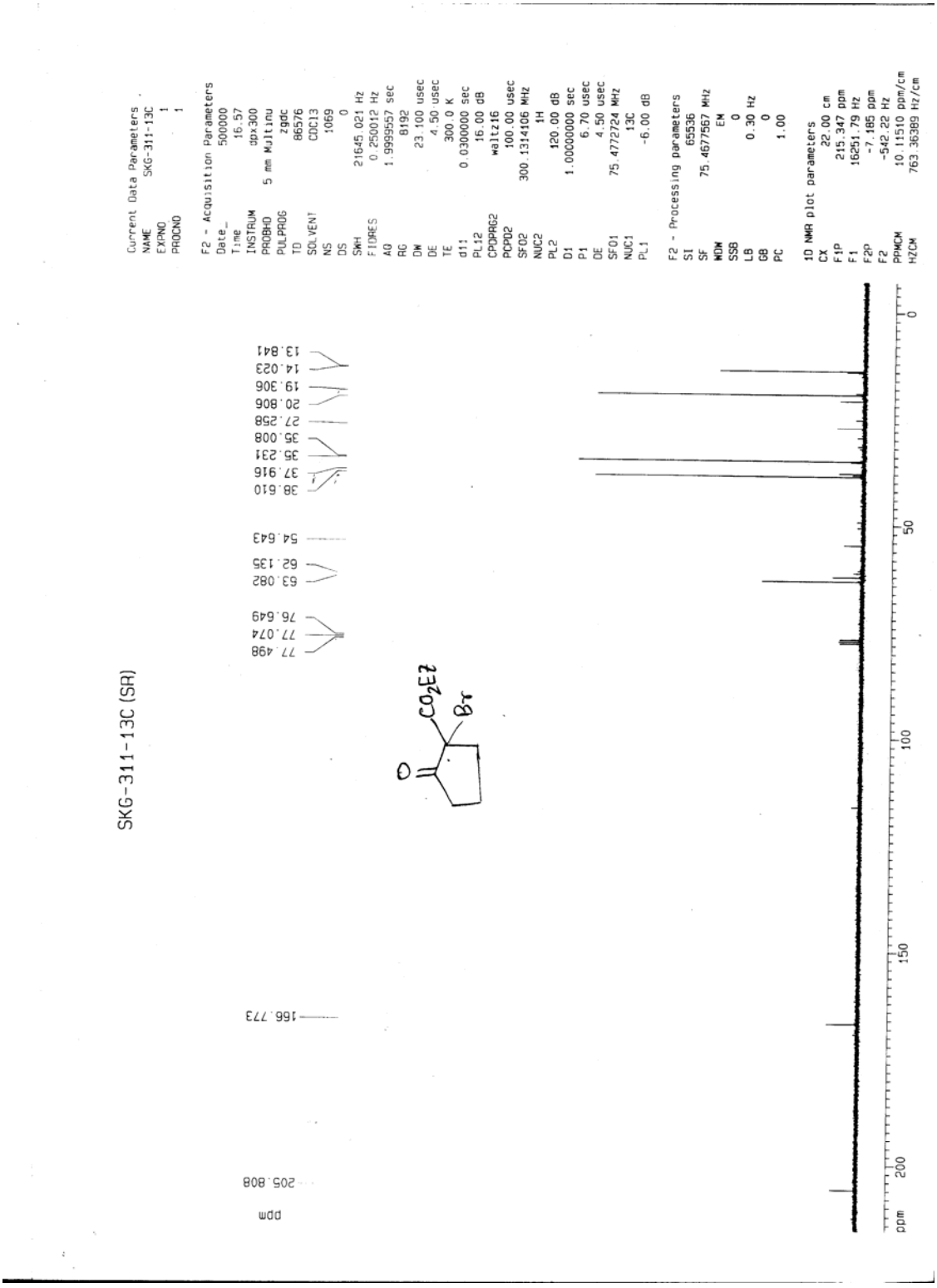
(ENTRY-3, Table 4)



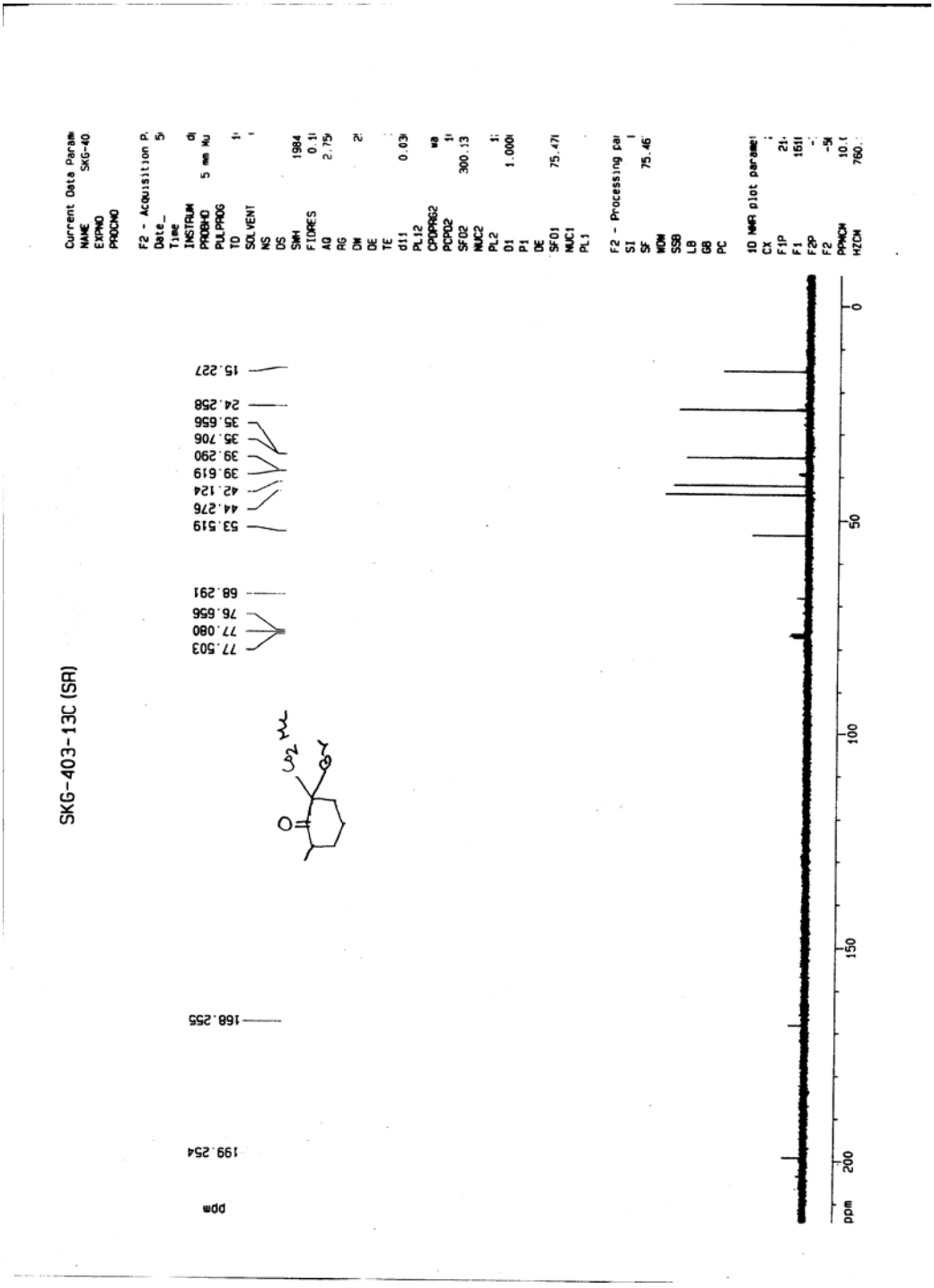
(ENTRY-4, Table 4)



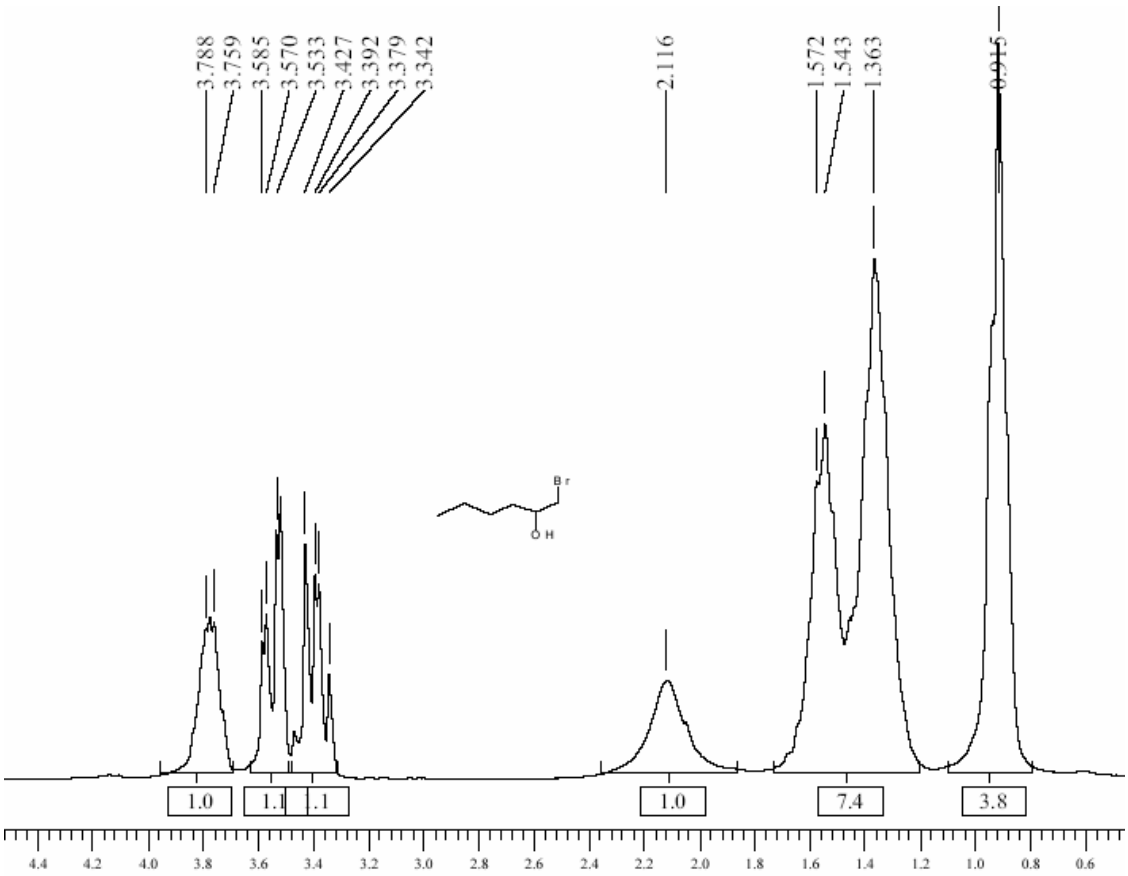
(ENTRY-5, Table 4)



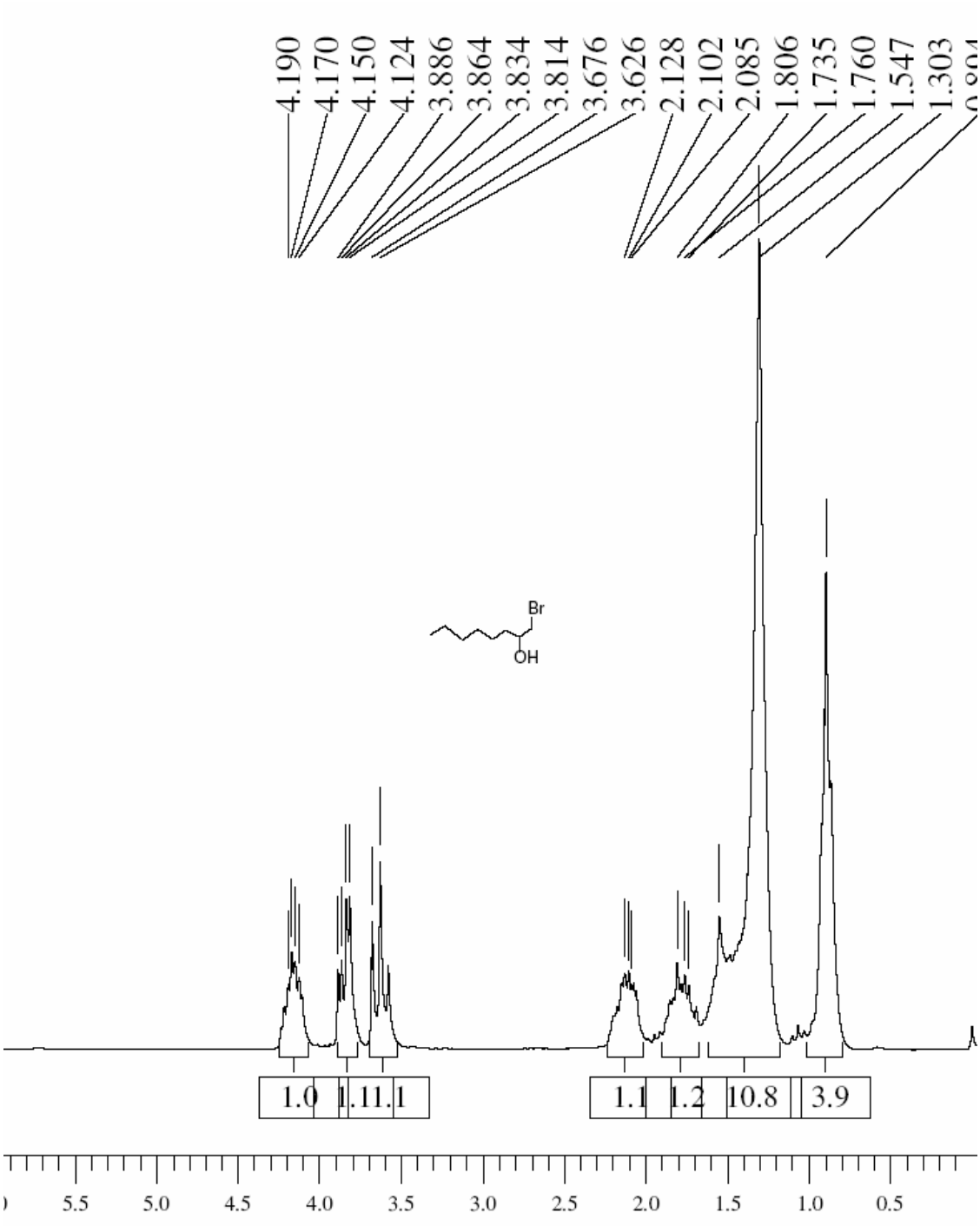
(ENTRY-7, Table 4)



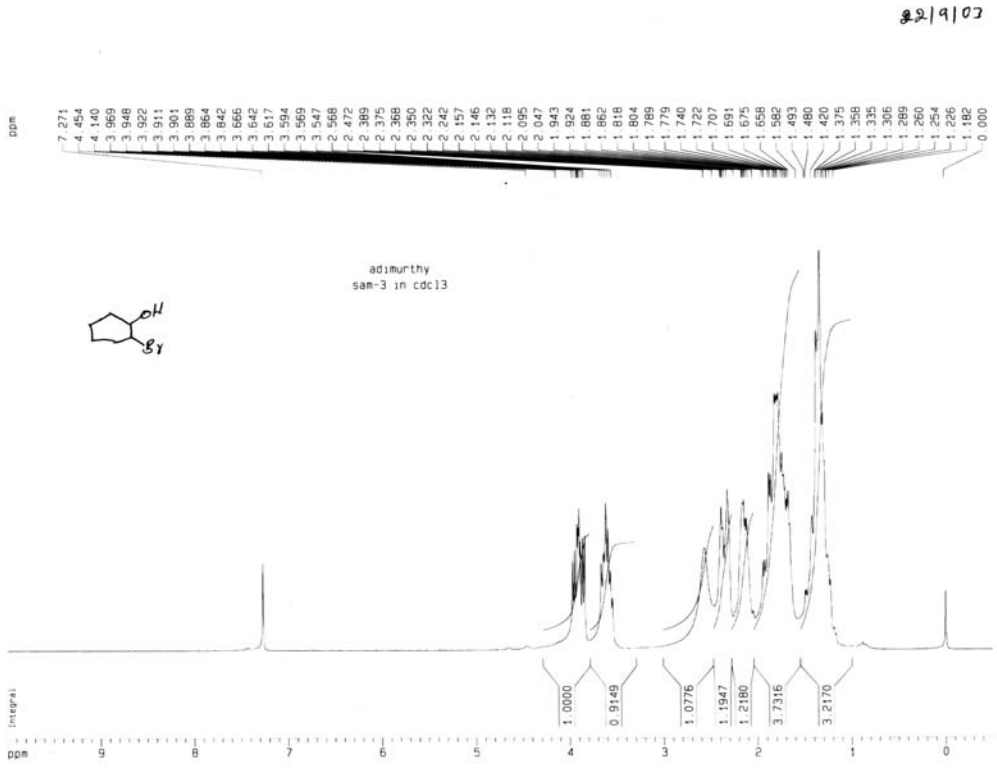
(ENTRY-8, Table 4)



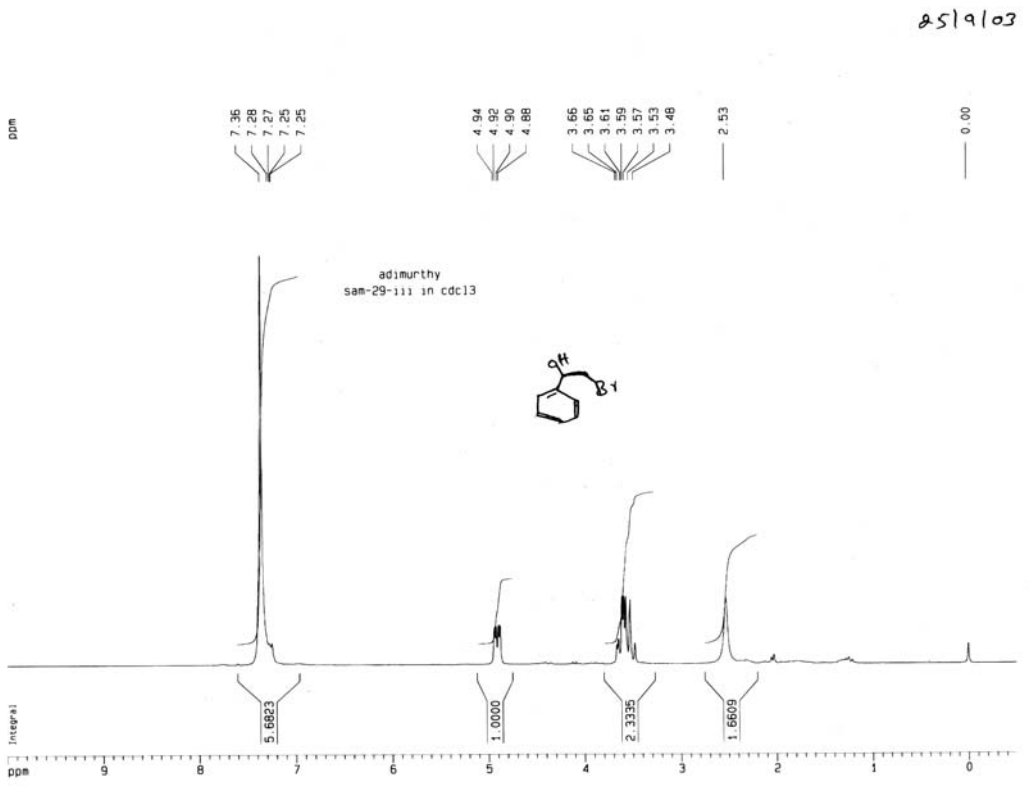
^{1}H-NMR (entry 1, Table 5) Ref 3a



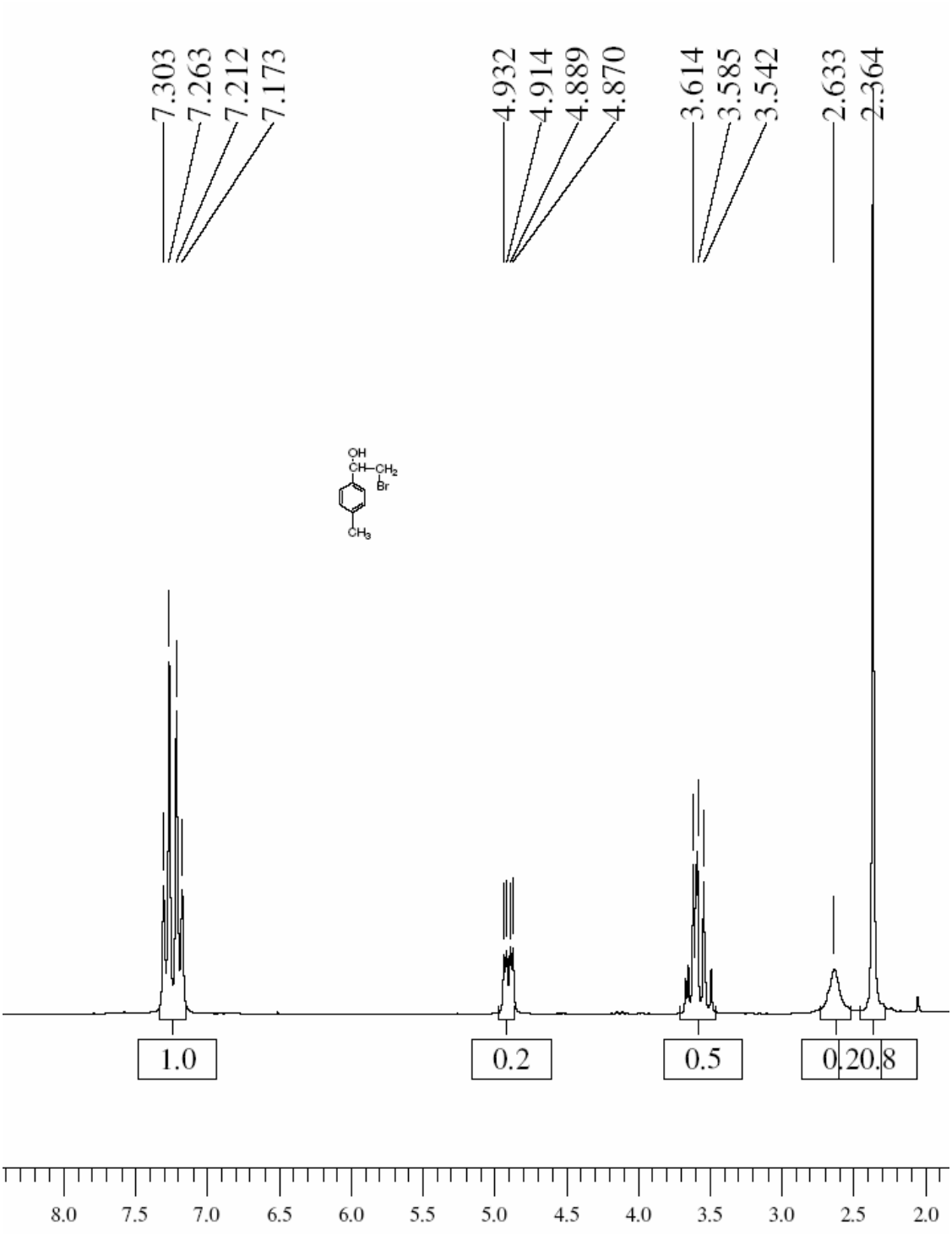
^{1}H-NMR (entry 2, Table 5); Ref 3a



^{1}H-NMR (entry 3, Table 5) Ref 3a



[1]H-NMR (entry 4, Table 5) Ref 3b.



^{1}H-NMR (entry 5, Table 5)

References

1 a) Kumar, K.; Margerum, D. W. *Inorg. Chem*. **1987**, *26*, 2706-2711. b) Beckwith, R.C.; Margerrum, D. W. *Inorg. Chem*. **1997**, *36*, 3754.

2 Pauchert, C. J.; Behnke, J. *The Aldrich Library of* ^{13}C *and* ^{1}H *– FT NMR Spectra* Edition I, vol –II, 1993, p 291.

3 a) Masuda, H. ; Takase, K. ; Nishio, M. ;Hasegawa, A. ; Nishiyama, Y. and Ishii, Y. *J. Org. Chem*. **1994**, *59*, 5550. b) Sharghi, H.; Niknam, K. and Pooyan, M. *Tetrahedron* **2001,** *57*,6057.