Preparation of Covalent Long-Chain Trialkylstannyl and Trialkylsilyl Salts and Examination of their Adsorption on Gold

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Dimethyloctadecylphenylsilane (8). Mg turnings (0.15 g, 6.2×10^{-3} mol) and a catalytic amount of I_2 were placed in a three neck round bottom flask fitted with reflux condensor and heated with an air gun (250 °C) until purple vapors of I_2 appeared. THF (15 mL) was added, followed by 1-bromooctadecane (2.0 g, 6.0×10^{-3} mol), and the mixture was heated to reflux under argon atmosphere for 3 h until only a small amount of Mg remained. It was allowed to cool to room temperature and chlorodimethylphenylsilane (1.0 g, 6.0×10^{-3} mol) was added. This was stirred at reflux for 2.5 h, then at room temperature for 10 h. Hexane (20 mL) was added to the reaction mixture, washed with saturated NH_4Cl solution (15 mL), water (3 × 15 mL) and saturated NaCl solution (15 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered. Hexane was removed by rotary evaporation. The residue was passed through a flash column (100 mL silica gel, hexane). The product containing fraction was distilled under vacuum (1 mbar) using a Kugelrohr distillation apparatus. Octadecane (125° C) was removed followed by the product (175 °C). 1.3 g, 55% yield. Mp 32.0 - 32.5°C. IR (KBr, cm^{-1}): 3069, 2955, 2923, 2853, 1467, 1427, 1113, 837, 699. ^1H NMR (400 MHz, $CDCl_3$): δ 0.26 (s, 6H), 0.74 (t, J = 8 Hz, 2H), 0.89 (t, J = 7 Hz, 3H), 1.26 - 1.30 (m, 32H), 7.34 (m, 3H), 7.51 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −3.03, 14.11, 15.68, 22.68, 23.84, 29.30, 29.36, 29.57, 29.65, 29.69, 31.92, 33.60, 127.66, 128.69, 133.53, 139.79. MS - FAB: 387 (M − H), 373 (M − CH_3), 311 (M − C_6H_5), 135 (M − $C_{18}H_{37}$). Anal. Calcd for $C_{26}H_{48}Si$: C, 80.33; H, 12.45. Found: C, 80.52; H 12.82.

Methyldioctadecylphenylsilane (9). Mg turnings (380 mg, 15.6 mmol) and iodine (< 1 mg) were added to a 50 mL two neck round bottom flask fitted with a condenser and stirred while heating with a heat gun to 250 °C until purple vapors were observed. Diethyl ether (10 mL) was added via syringe followed by 1-bromooctadecane (5.0 g, 15 mmol). The solution was heated to reflux for two hours. Toluene (10 mL) and dichloromethylphenylsilane (960 mg, 5 mmol) were added and the reaction vessel was fitted with a short path distillation head. The diethyl ether was removed, and then the reaction was heated to 100 °C overnight. The solution was cooled to room temperature and hexanes (100 mL) were added. The reaction mixture was washed with saturated NH_4Cl solution (15 mL) followed by water (3 × 15 mL), and saturated NaCl (15 mL). The organic layer was then dried over Na_2SO_4 and filtered. The solvent was removed by rotary evaporation. The residue was passed through a flash column (100 mL silica gel, hexanes). This compound was not isolated pure and the raw material was directly used for reactions with acids. Attempts to purify the product using a Kugelrohr distillation apparatus failed, because it co-distilled with hexatriacontane.

Trioctadecylphenylsilane (10). Mg turnings (0.38 g, 15.6×10^{-3} mol) and a catalytic amount of I_2 were placed in a three neck round bottom flask fitted with reflux condensor and heated with an air gun (250 °C) until purple vapors of I_2 appeared. Diethyl ether (10 mL) was added, followed by 1-bromooctadecane (5.0 g, 15.0×10^{-3} mol) and heated to reflux under argon atmosphere for 2 h. Toluene (10 mL) and trichlorophenylsilane (0.53 g, 2.5×10^{-3} mol) were added and the reaction vessel was fitted with a short path distillation head. Diethyl ether was removed and the reaction was heated to 100 °C overnight. The reaction mixture was allowed to cool to room temperature and hexane (100 mL) added to it, washed with saturated NH_4Cl solution (15 ml), water (3 × 15 mL), and saturated NaCl solution (15 mL). The organic layer was dried over anhydrous Na_2SO_4 and filtered.and concentrated under reduced pressure. The product was purified by first removal of octadecane and hexatriacontane (255° C, 1 mbar) using Kugelrohr distillation apparatus. The product was further purified by passing through a flash column (100 mL silica gel, hexane). 35% yield. Mp 37.0 - 38.8° C. IR (KBr, cm^{-1}): 3069, 3049, 2954, 2922, 2852, 1467, 1110, 721,

699, 477. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.77 (t, *J* = 8 Hz, 6H), 0.89 (t, *J* = 7 Hz, 9H), 1.24 - 1.32 (m, 96H), 7.33 (m, 3H), 7.48 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.42, 14.11, 22.69, 23.76, 29.24, 29.37, 29.60, 29.66, 29.70, 31.93, 33.79, 127.57, 128.54, 134.08, 138.27. Anal. Calcd for $C_{60}H_{116}Si$: C, 83.25; H, 13.51. Found: C, 83.46; H, 12.78.

Methyloctadecyldiphenylsilane (11). The product was purified by using Kugelrohr distillation apparatus, first octadecane was removed (125 °C, 1 mbar) and the product was distilled off at (215° C, 1 mbar). 44% yield. Mp 31.5 - 32.5° C. IR (KBr, cm^{-1}): 3069, 3022, 3011, 2852, 1590, 1568, 1487, 1466, 1428, 1411, 1301, 1251, 1190, 1157, 1112, 1067, 1029, 998, 969, 913, 787, 731, 699, 619, 488. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.61 (s, 3H), 0.96 (t, *J* = 7 Hz, 3H), 1.14 (t, *J* = 9 Hz, 2H), 1.28 - 1.47 (m, 32H), 7.41 (m, 6H), 7.58 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −4.47, 14.12, 14.13, 22.71, 23.80, 29.24, 29.39, 29.59, 29.67, 29.72, 31.95, 33.66, 127.74, 128.99, 134.43, 137.52. Anal. Calcd for $C_{31}H_{50}Si$: C, 82.59; H, 11.18. Found: C, 82.61; H 11.42.

Dioctadecyldiphenylsilane (12). The product was purified first by removal of octadecane and hexatriacontane (255° C, 1 mbar) using Kugelrohr distillation apparatus and then by passing the remaining residue through silica gel (50 mL, hexane). 75% yield. Mp 35.6 - 36.9° C. IR (KBr, cm^{-1}): 3069, 3050, 2921, 2852, 1465, 1428, 1110, 734, 719, 700, 493, 477. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.89 (t, *J* = 7 Hz, 6H), 1.08 (t, *J* = 9 Hz, 4H), 1.24 - 1.36 (m, 64H), 7.36 (m, 6H), 7.50 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.46, 14.11, 22.68, 23.65, 29.18, 29.36, 29.57, 29.65, 29.69, 31.92, 33.70, 127.65, 128.92, 134.83, 136.75. Anal. Calcd for $C_{48}H_{84}Si$: C, 83.64; H, 12.28. Found: C, 83.94; H, 12.38.

Octadecyltriphenylsilane (13). Octadecyltriphenylsilane was synthesized according to the procedure used for synthesis of **8**. The product was purified first by removal of octadecane and hexatriacontane (255 °C, 1 mbar) using Kugelrohr distillation apparatus and then by passing the remaining residue through silica gel (50 mL, hexane). 60% yield. Mp 73.5 - 75° C. IR (KBr, cm^{-1}): 3066, 2955, 2869, 2850, 1587, 1567, 1466, 1427, 1111, 731, 711, 700, 519, 507, 484. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88 (t, *J* = 8 Hz, 3H), 1.22 - 1.47 (m, 34H), 7.37 (m, 9H), 7.52 (dd, *J* = 7 and 2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.22, 14.10, 22.68, 23.89, 29.14, 29.34, 29.56, 29.65, 29.70, 31.92, 33.78, 127.77, 129.27, 135.41, 135.61. Anal. Calcd for $C_{36}H_{52}Si$: C, 84.31; H, 10.22. Found: C, 84.45; H, 10.50.

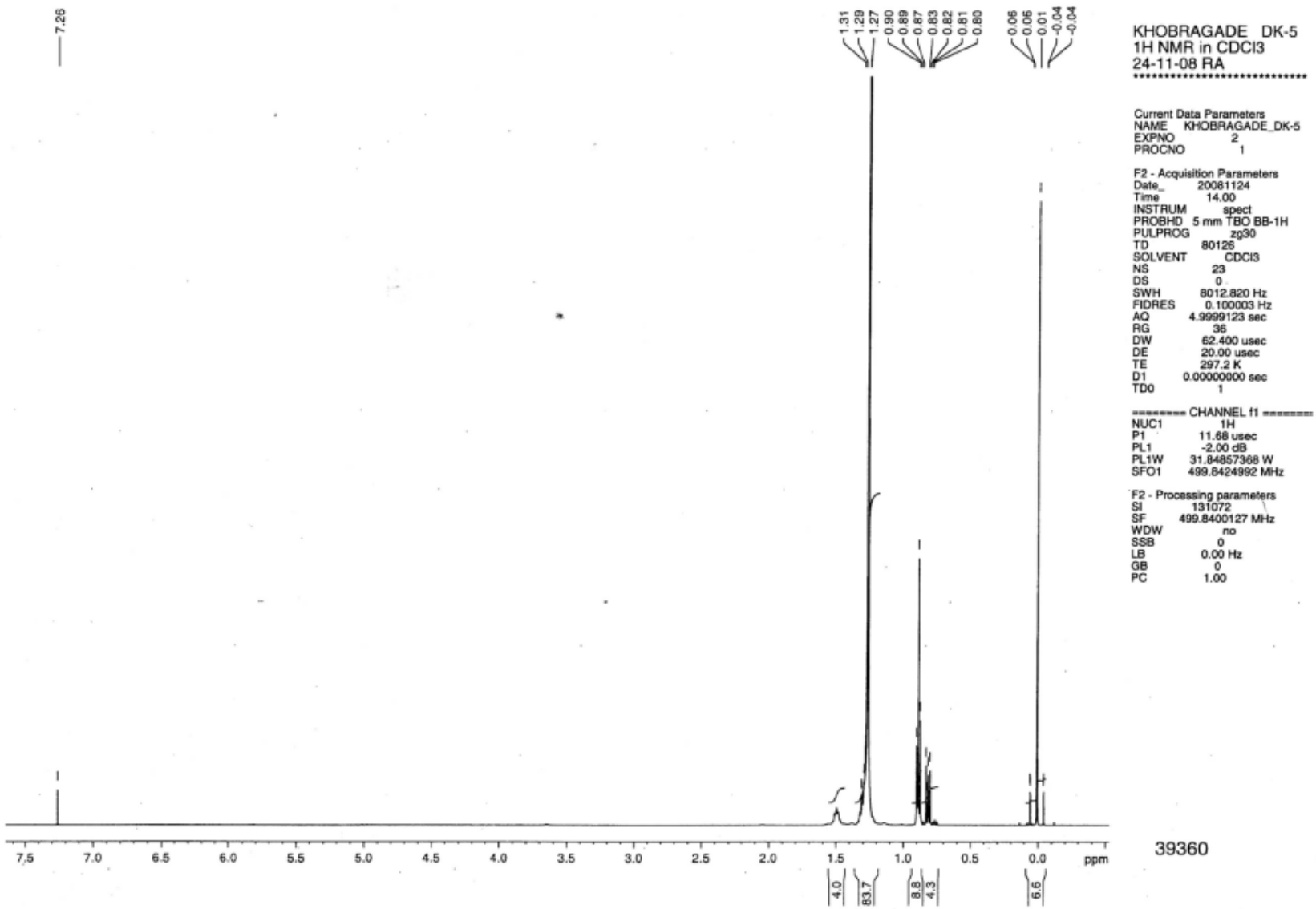
***p*-Anisyltrioctadecylsilane (14)**. 46% yield. Mp 29.5 - 31.0° C. IR (KBr, cm^{-1}): 3082, 2954, 2923, 2853, 1595, 1566, 1503, 1441, 1378, 1277, 1247, 1181, 1110, 1037, 823, 721, 701, 633, 491. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.74 (t, *J* = 7 Hz, 6H), 0.89 (t, *J* = 6 Hz, 9H), 1.24 - 1.32 (m, 96H), 3.81 (s, 3H), 6.90 (d, *J* = 8 Hz, 2H), 7.40 (d, *J* = 8 Hz, 2H)). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.60, 14.11, 22.68, 23.79, 29.26, 29.37, 29.62, 29.66, 29.70, 31.92, 33.82, 54.89, 113.36, 128.95, 135.44, 160.02. Anal. Calcd for $C_{61}H_{118}Si$: C, 81.80; H, 13.28. Found: C, 82.00; H, 13.21.

Solutions of Covalent Silyl Salts were generated in solution and were used in unsuccessful attempts to observe adsorption to a gold surface. They were produced by treatment of an arylsiilane with trifluoromethanesulfonic or trifluoroacetic acid. For instance, **14** (23 mg, 0.025 mmol) was dissolved in CH_2Cl_2 (25 mL) and trifluoroacetic acid (28 mg, 0.025 mmol) was added. After 15 min the ^{1}H NMR of trioctadecylsilyl trifluoroacetate was observed.

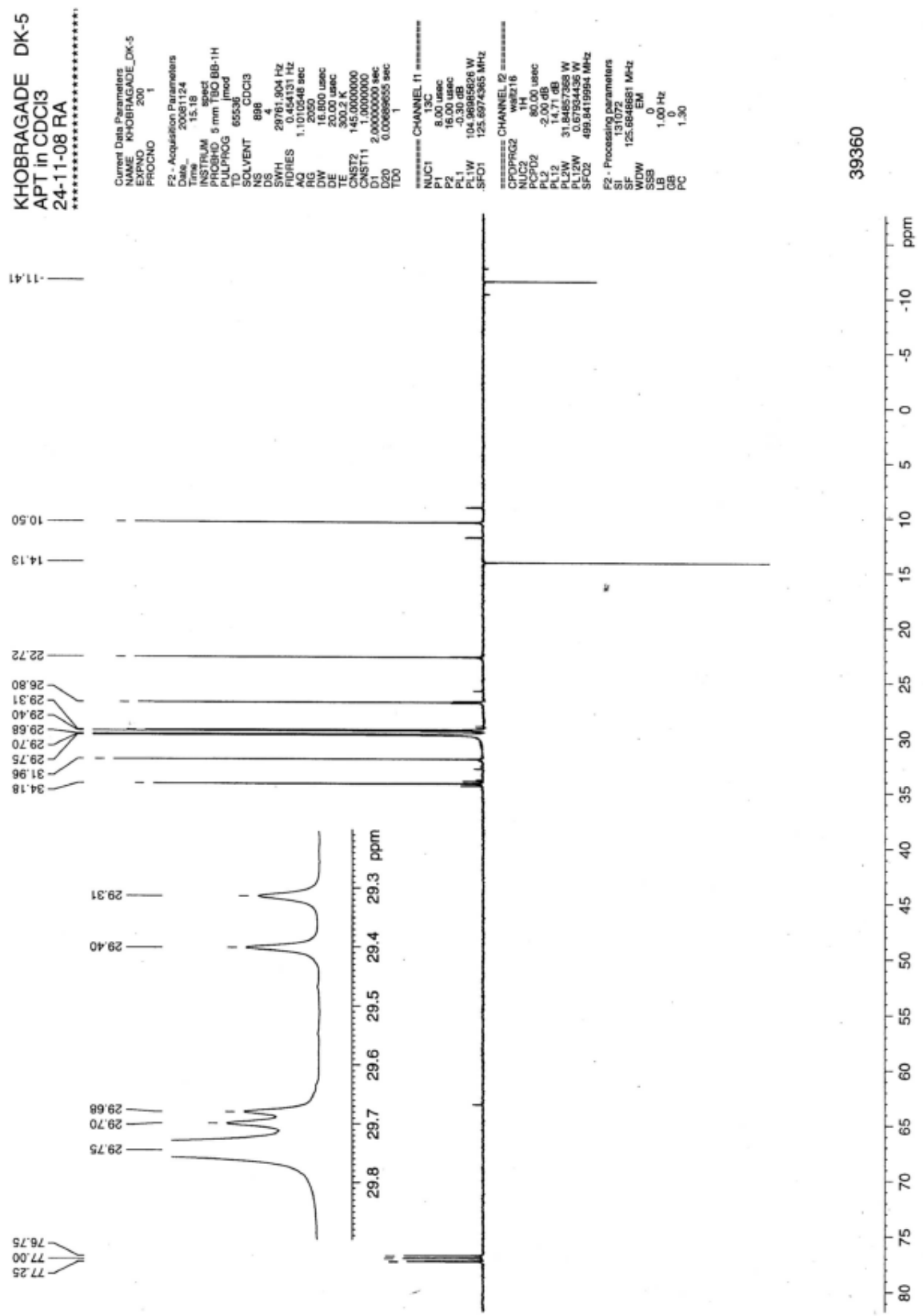
Dimethyloctadecylsilyl Trifluoromethanesulfonate.. Dimethyloctadecylphenylsilane (**8**, 0.018 g, 0.047 × 10^{-3} mol) was dissolved in $CDCl_3$ (1 mL, distilled from P_4O_{10}). Trifluoromethanesulfonic acid (0.47 mL of a 0.1 M solution in $CDCl_3$) was added. After 15 min ^{1}H NMR was observed revealing the product and benzene. There was no detectable starting material

nor byproducts. ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.48 (s, 6H), 0.88 (t, J = 7 Hz, 3H), 0.89 (t, J = 7 Hz, 2H), 1.20 - 1.42 (m, 32H). ^{13}C NMR (100 MHz, $CDCl_3$): δ −1.25, 14.07, 16.21, 22.02, 22.68, 29.10, 29.36, 29.42, 29.60, 29.69, 31.92, 32.82.

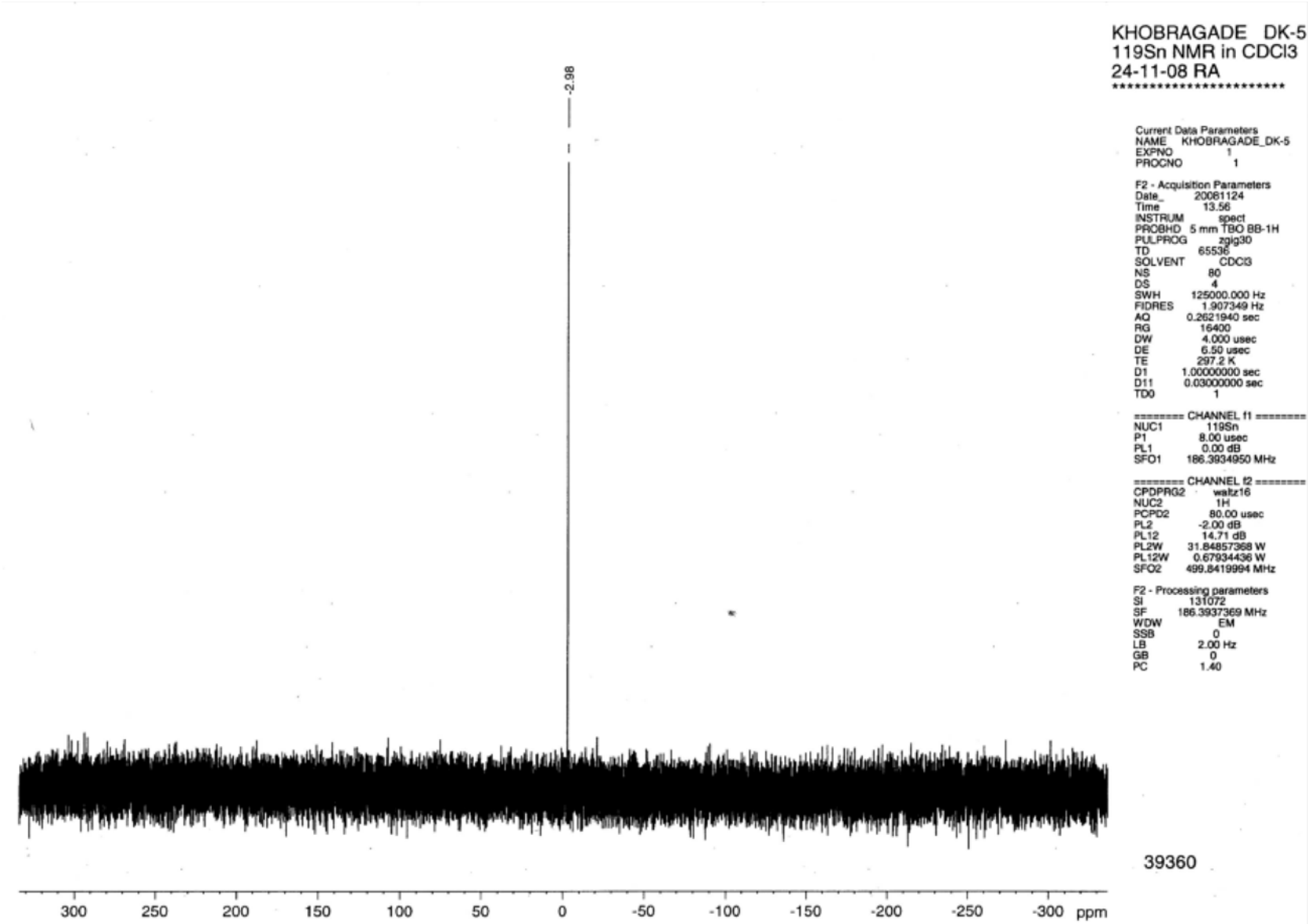
Trioctadecylsilyl Trifluoromethanesulfonate. This was prepared similarly from trioctadecylphenylsilane (**10**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.88, (t, J = 7 Hz, 9H), 0.89 (t, J = 7 Hz, 6H), 1.20 - 1.42 (m, 96H).



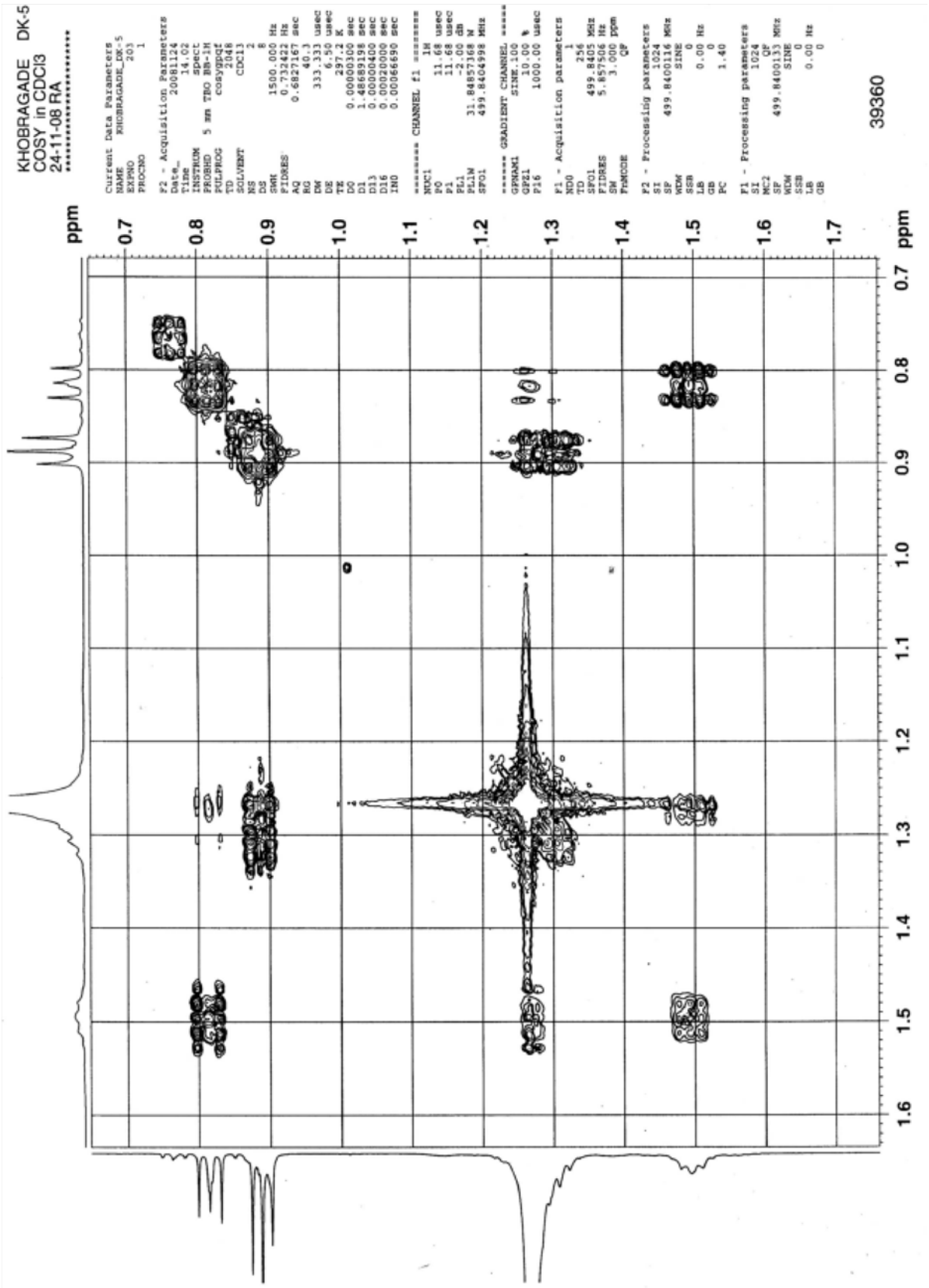
^{1}H NMR spectrum of compound **3**



^{13}C NMR spectrum of compound **3**



^{119}Sn NMR spectrum of compound **3**



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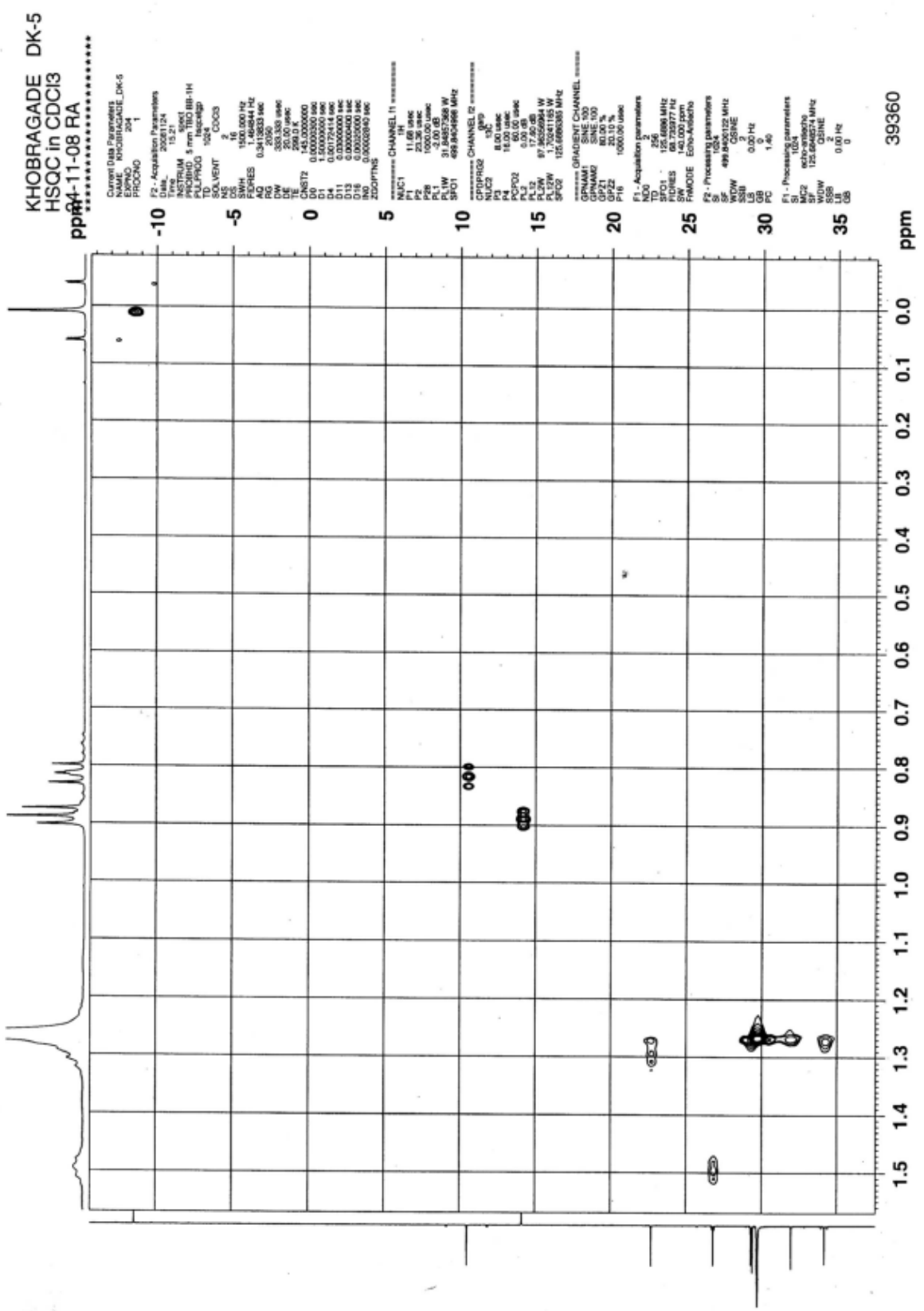

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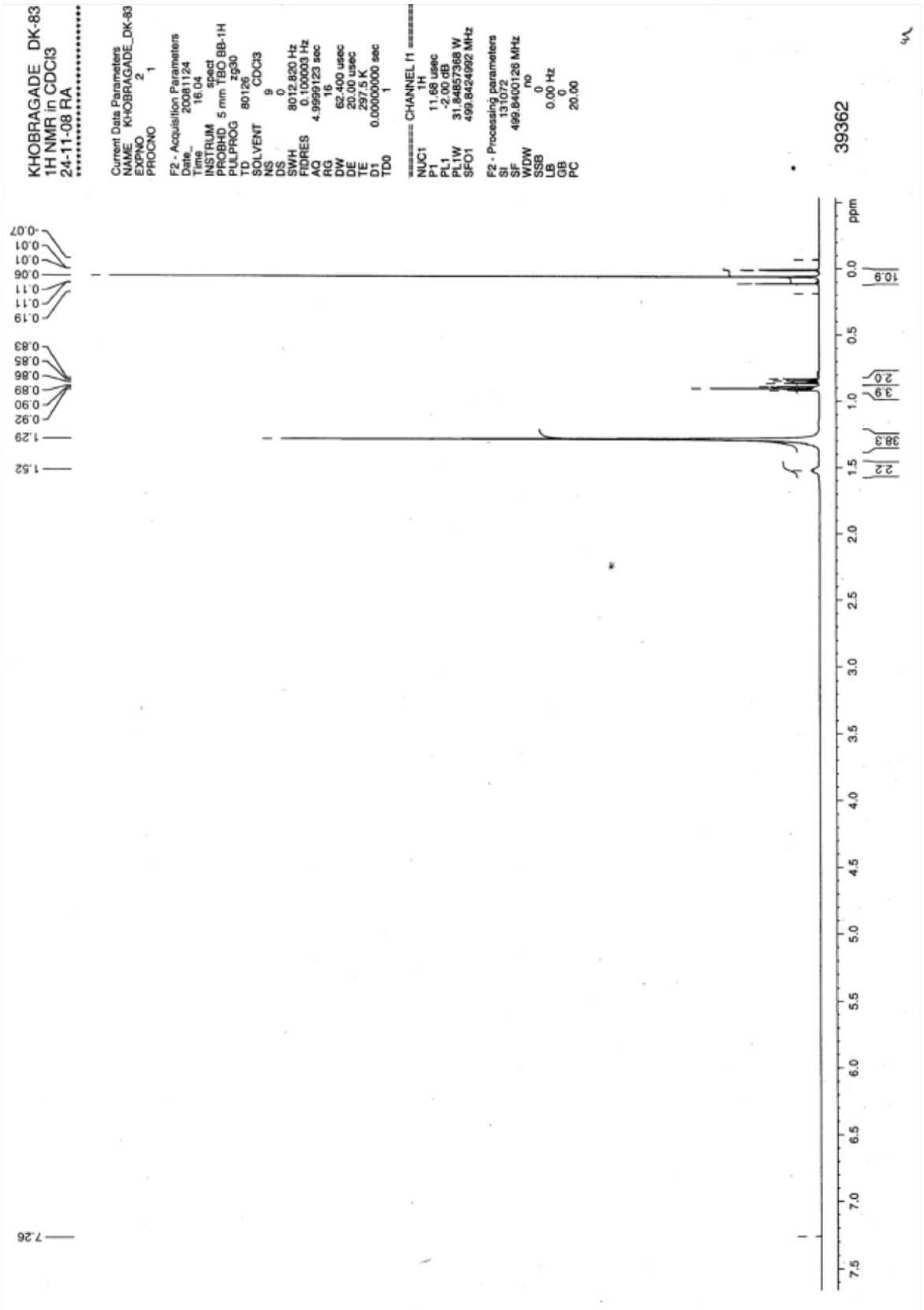

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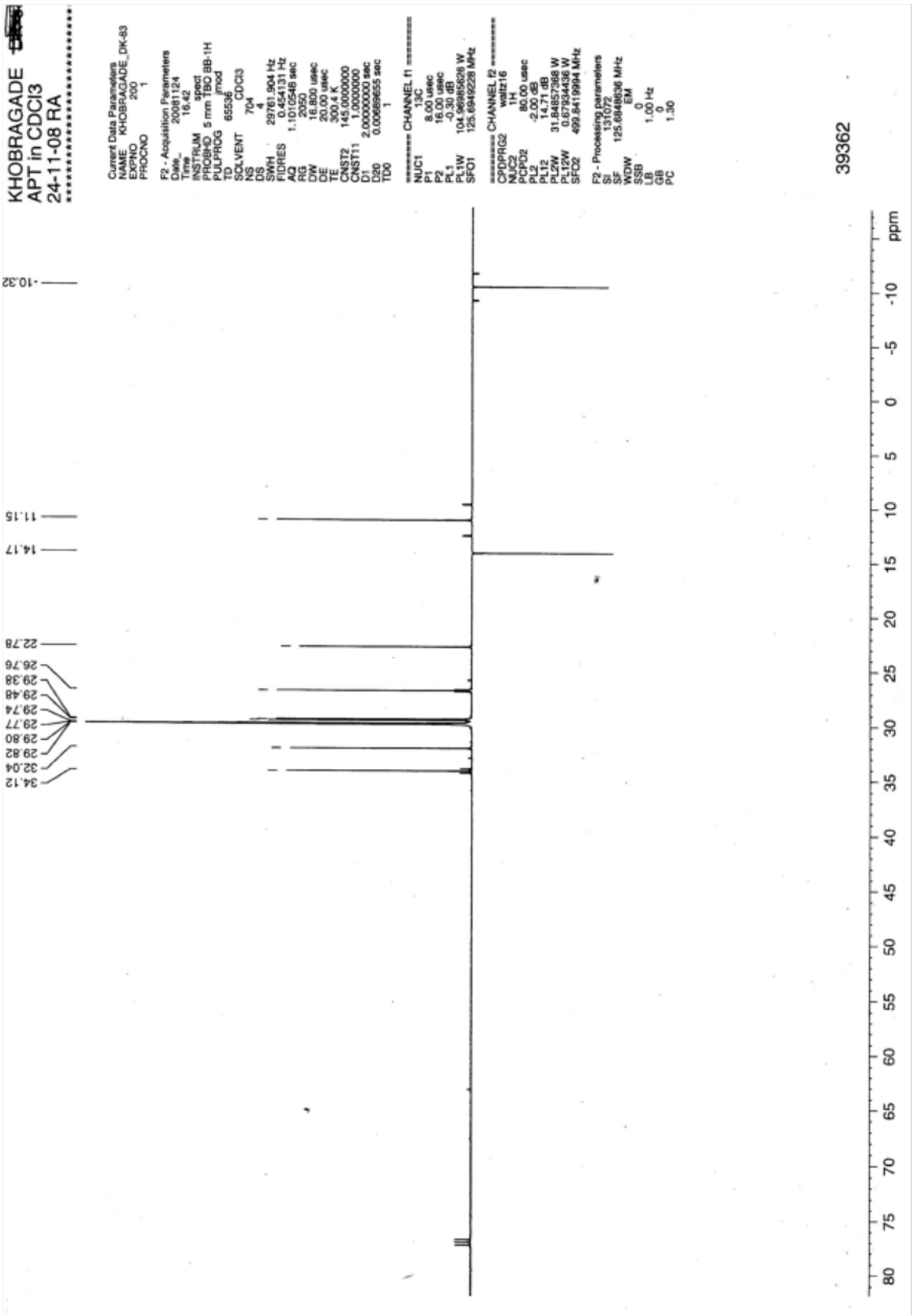
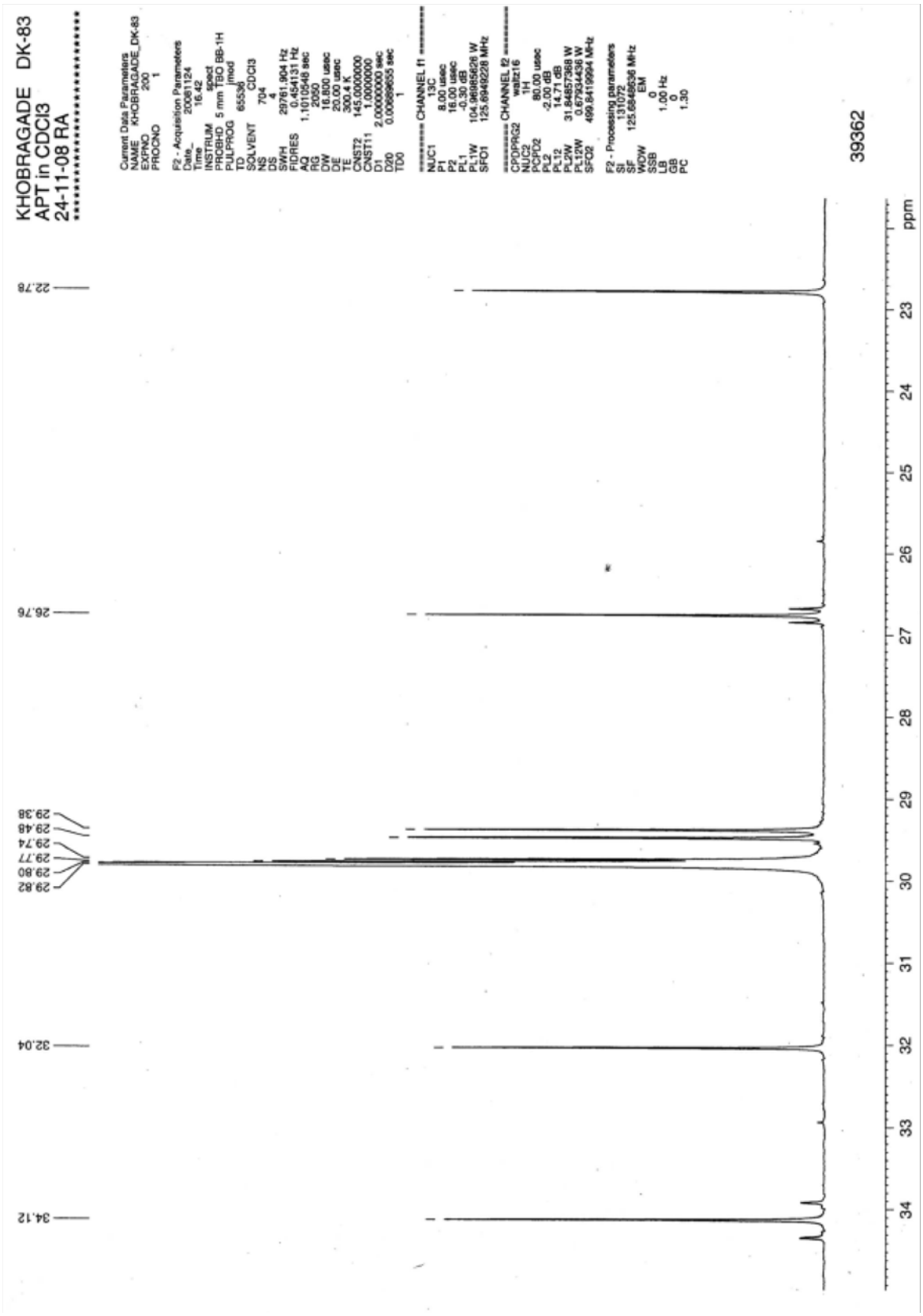
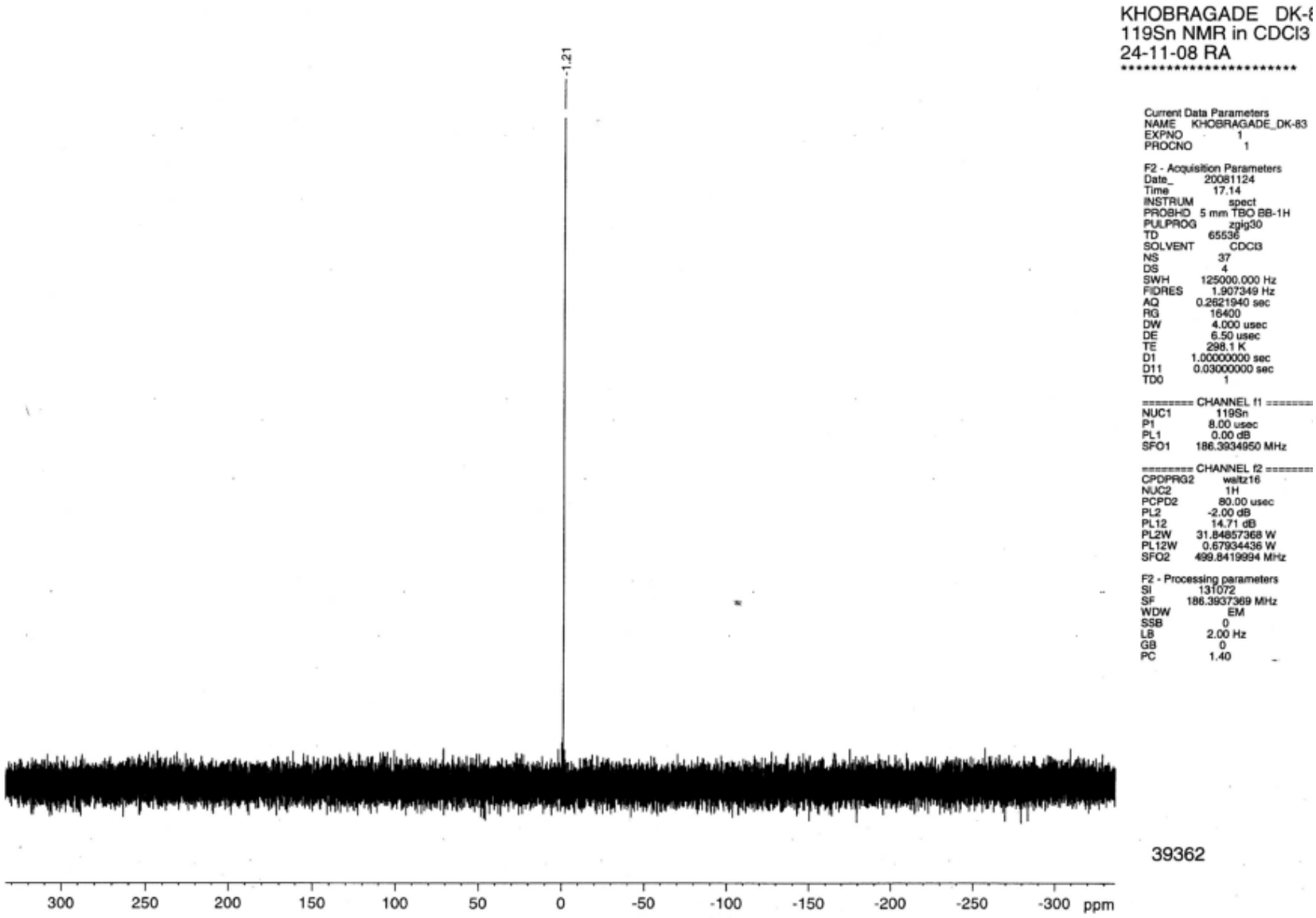


^{13}C NMR spectrum of compound **4**



^{13}C NMR spectrum of compound **4** expanded



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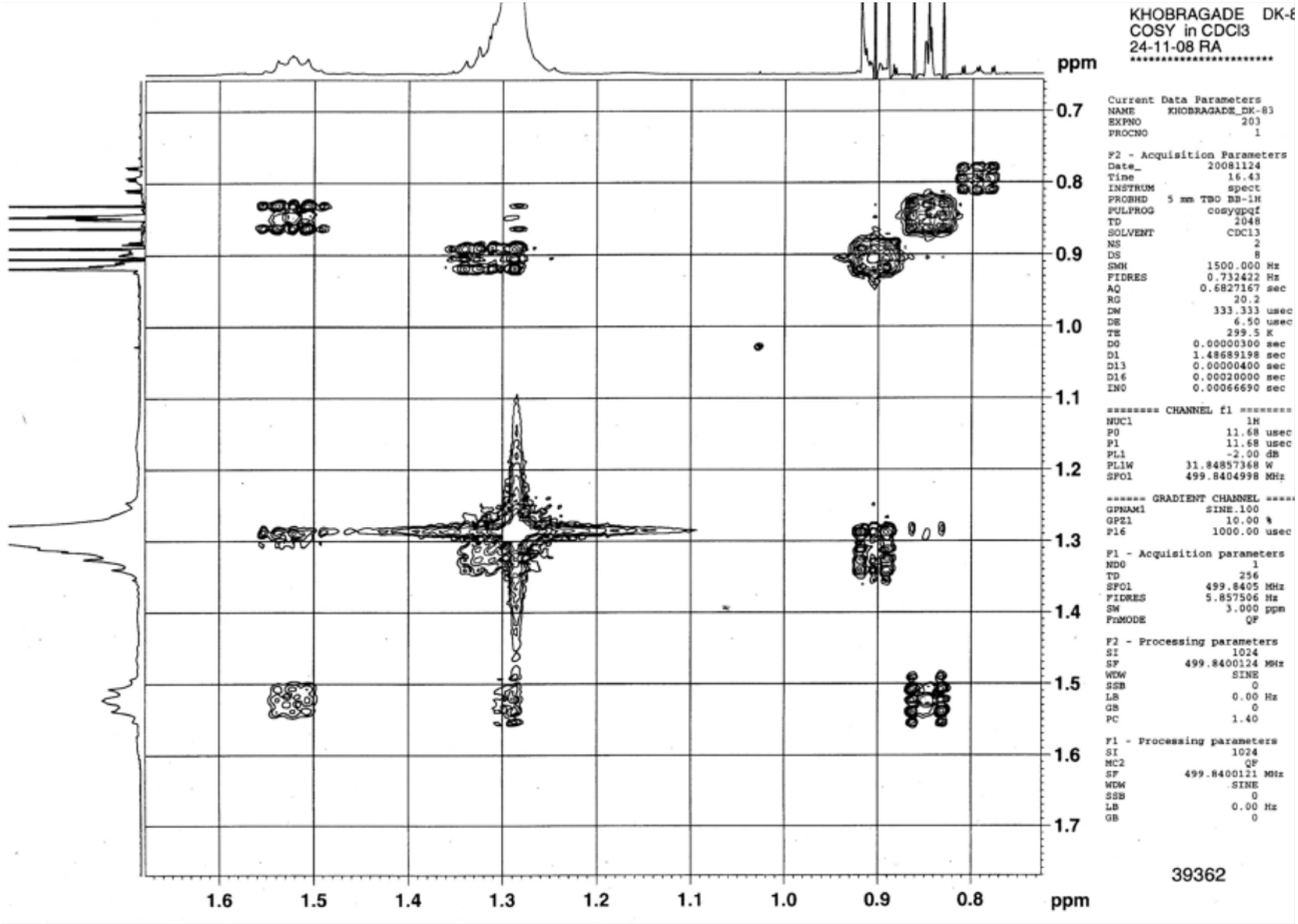
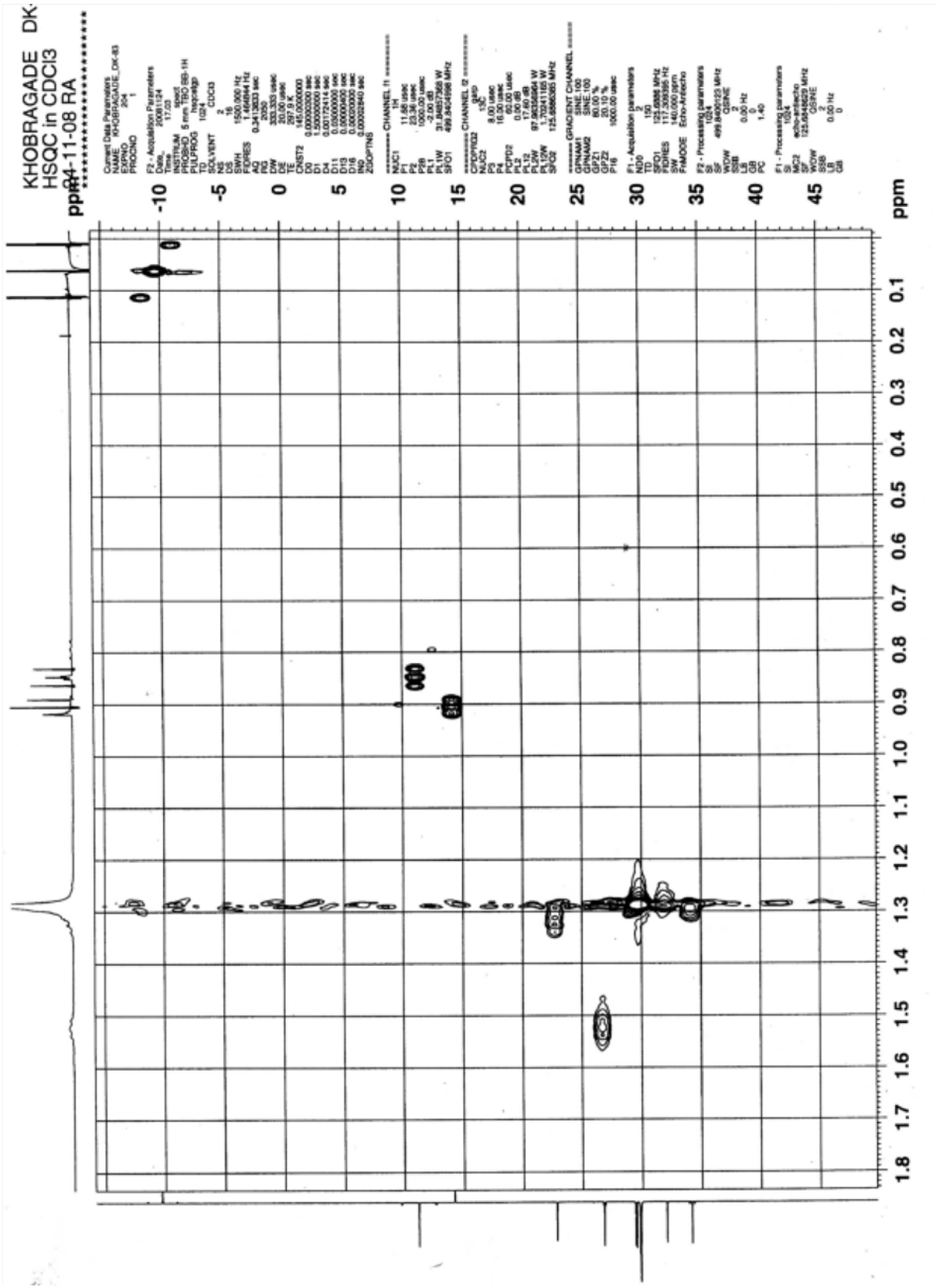


COSY ^{1}H - ^{1}H NMR of compound **4**



HSQC ^{1}H-^{13}C NMR spectrum of compound **4**