

**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,  $6.2 \times 10^{-3}$  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,  $6.0 \times 10^{-3}$  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,  $6.0 \times 10^{-3}$  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 ( $3 \times 15$  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,  $CDCl_3$ ):  $\delta$  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,  $CDCl_3$ ):  $\delta$  -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 ( $3 \times 15$  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,  $15.6 \times 10^{-3}$  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,  $15.0 \times 10^{-3}$  mol) and heated to reflux under argon atmosphere for 2 h. Toluene (10 mL) and trichlorophenylsilane (0.53 g,  $2.5 \times 10^{-3}$  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 ( $3 \times 15$  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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  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  $\text{C}_{60}\text{H}_{116}\text{Si}$ : 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,  $\text{cm}^{-1}$ ): 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.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -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  $\text{C}_{31}\text{H}_{50}\text{Si}$ : C, 82.59; H, 11.18. Found: C, 82.61; H 11.42.

**Diocadecyldiphenylsilane (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,  $\text{cm}^{-1}$ ): 3069, 3050, 2921, 2852, 1465, 1428, 1110, 734, 719, 700, 493, 477.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  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  $\text{C}_{48}\text{H}_{84}\text{Si}$ : 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,  $\text{cm}^{-1}$ ): 3066, 2955, 2869, 2850, 1587, 1567, 1466, 1427, 1111, 731, 711, 700, 519, 507, 484.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  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  $\text{C}_{36}\text{H}_{52}\text{Si}$ : 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,  $\text{cm}^{-1}$ ): 3082, 2954, 2923, 2853, 1595, 1566, 1503, 1441, 1378, 1277, 1247, 1181, 1110, 1037, 823, 721, 701, 633, 491.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  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).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  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  $\text{C}_{61}\text{H}_{118}\text{Si}$ : 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 arylsilane with trifluoromethanesulfonic or trifluoroacetic acid. For instance, **14** (23 mg, 0.025 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (25 mL) and trifluoroacetic acid (28 mg, 0.025 mmol) was added. After 15 min the  $^1\text{H}$  NMR of trioctadecylsilyl trifluoroacetate was observed.

**Dimethyloctadecylsilyl Trifluoromethanesulfonate.** Dimethyloctadecylphenylsilane (**8**, 0.018 g,  $0.047 \times 10^{-3}$  mol) was dissolved in  $\text{CDCl}_3$  (1 mL, distilled from  $\text{P}_4\text{O}_{10}$ ). Trifluoromethanesulfonic acid (0.47 mL of a 0.1 M solution in  $\text{CDCl}_3$ ) was added. After 15 min  $^1\text{H}$  NMR was observed revealing the product and benzene. There was no detectable starting material

nor byproducts.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.48 (s, 6H), 0.88 (t,  $J = 7$  Hz, 3H), 0.89 (t,  $J = 7$  Hz, 2H), 1.20 - 1.42 (m, 32H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  -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**).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.88, (t,  $J = 7$  Hz, 9H), 0.89 (t,  $J = 7$  Hz, 6H), 1.20 - 1.42 (m, 96H).

7.26

1.31  
1.29  
1.27  
0.90  
0.89  
0.87  
0.83  
0.82  
0.81  
0.06  
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0.04

KHOBRAGADE DK-5  
1H NMR in CDCl3  
24-11-08 RA

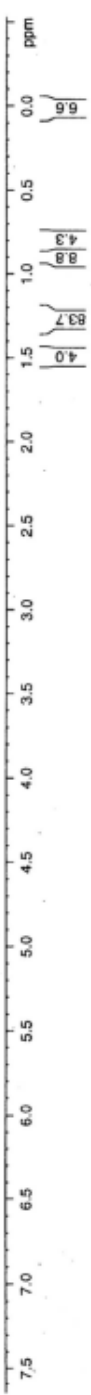
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39360



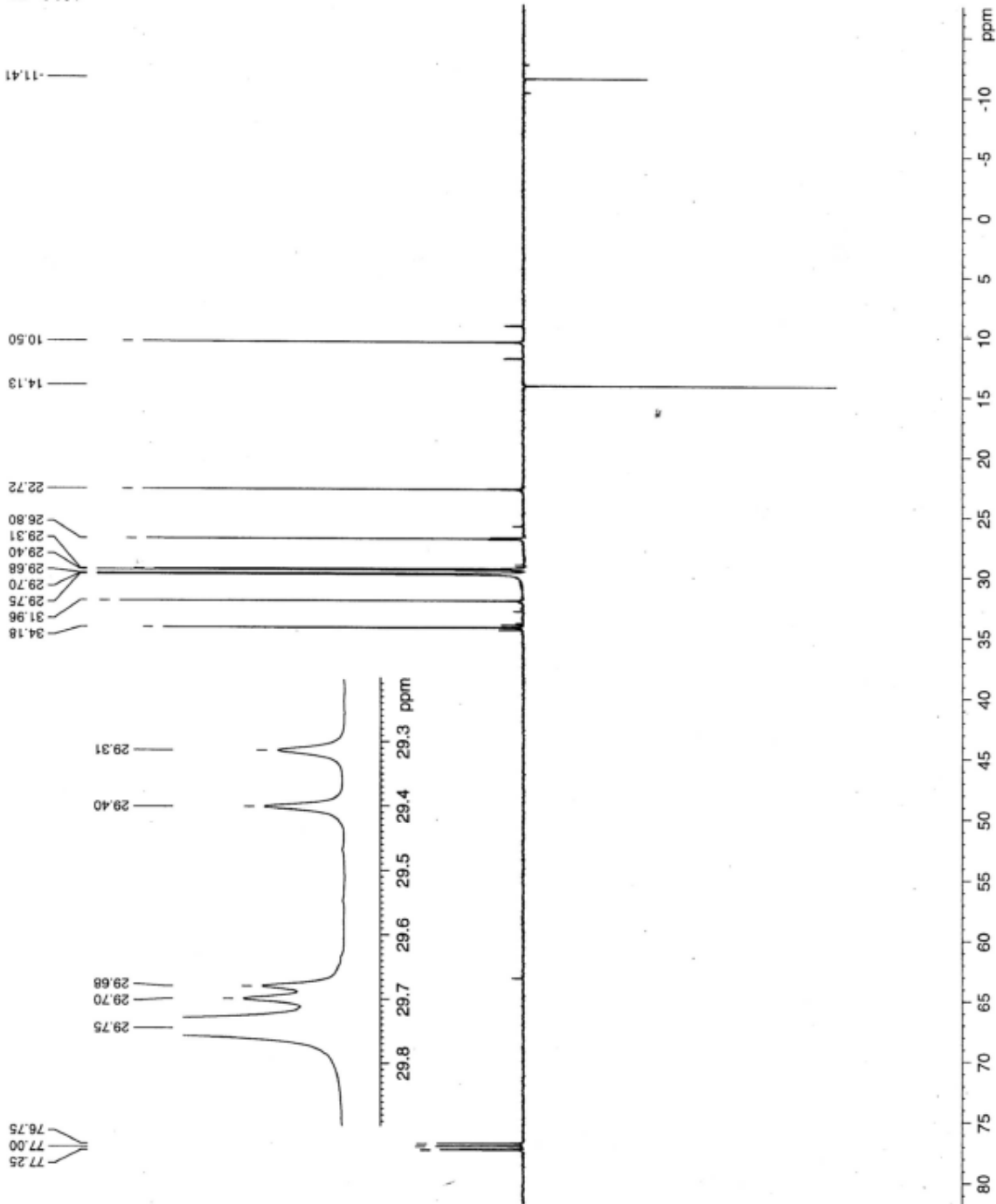
<sup>1</sup>H NMR spectrum of compound 3







KHOBRAGADE DK-5  
APT in CDCl3  
24-11-08 RA



<sup>13</sup>C NMR spectrum of compound 3

KHOBRADE DK-5  
 119Sn NMR in CDCl3  
 24-11-08 RA  
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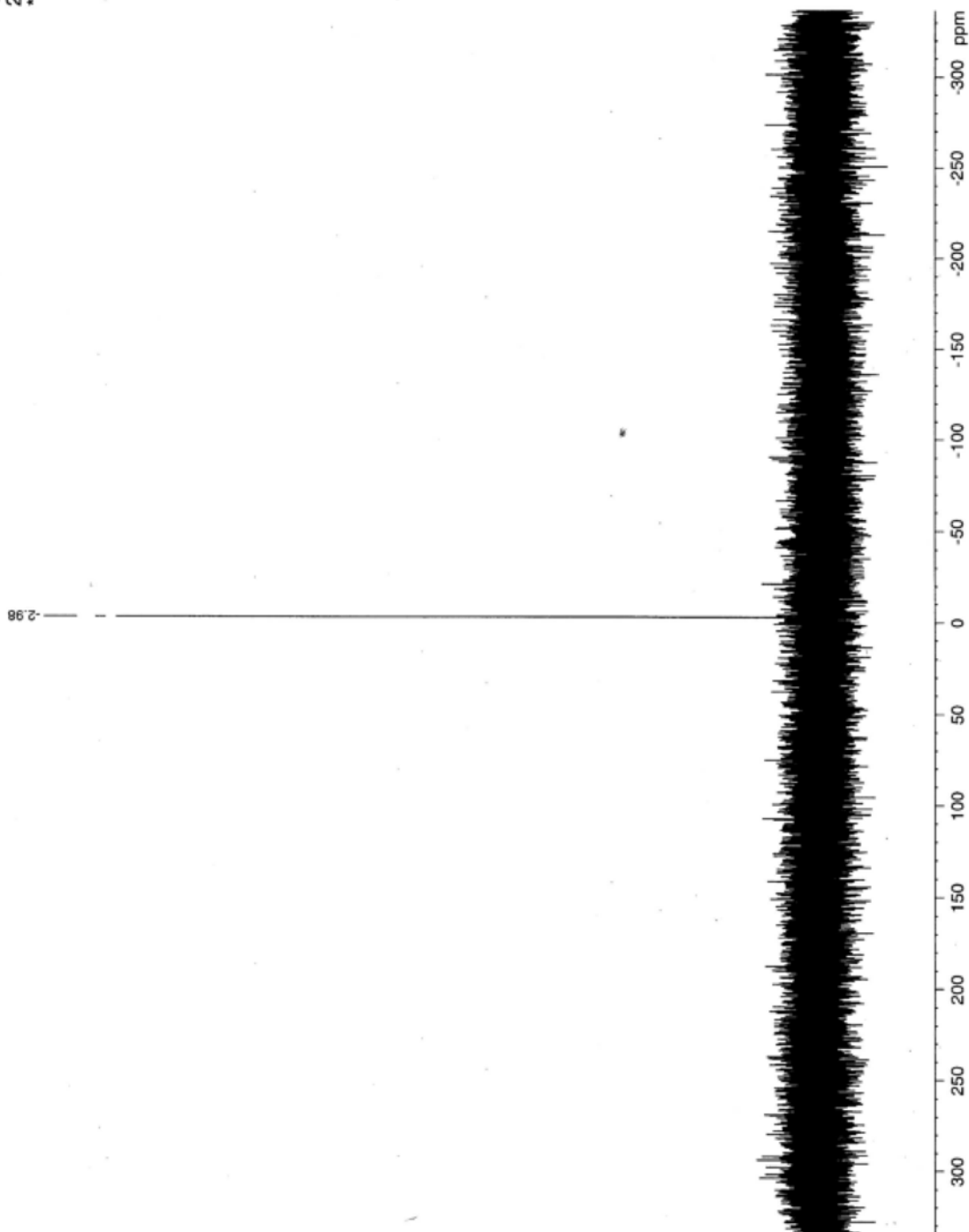
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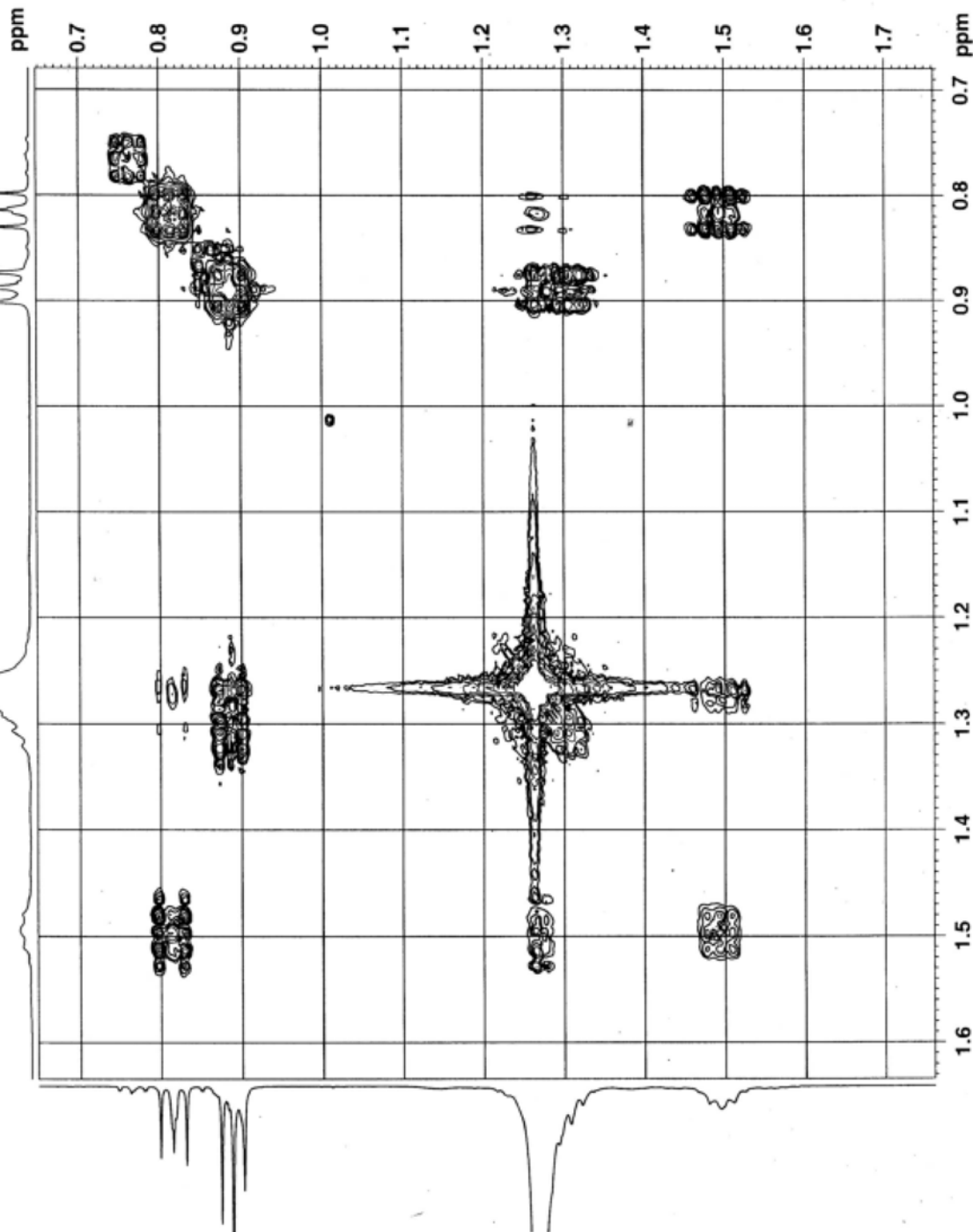
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<sup>119</sup>Sn NMR spectrum of compound **3**

KHOBAGADE DK-5  
COSY in CDCl3  
24-11-08 RA



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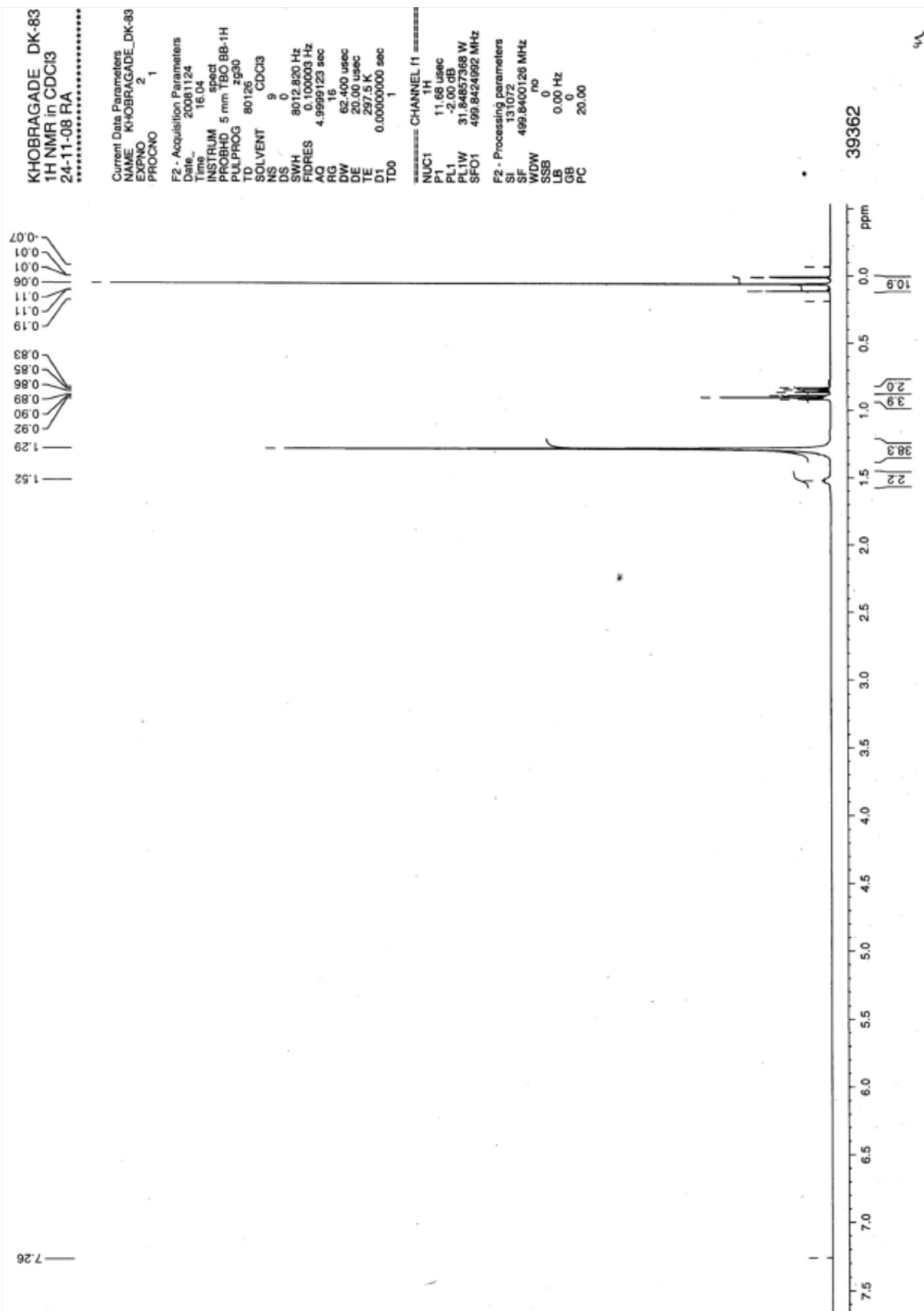
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39360

COSY  $^1\text{H}$  -  $^1\text{H}$  NMR spectrum of compound 3





<sup>1</sup>H NMR spectrum of compound **4**

KHOBRAGADE  
APT in CDCl3  
24-11-08 RA

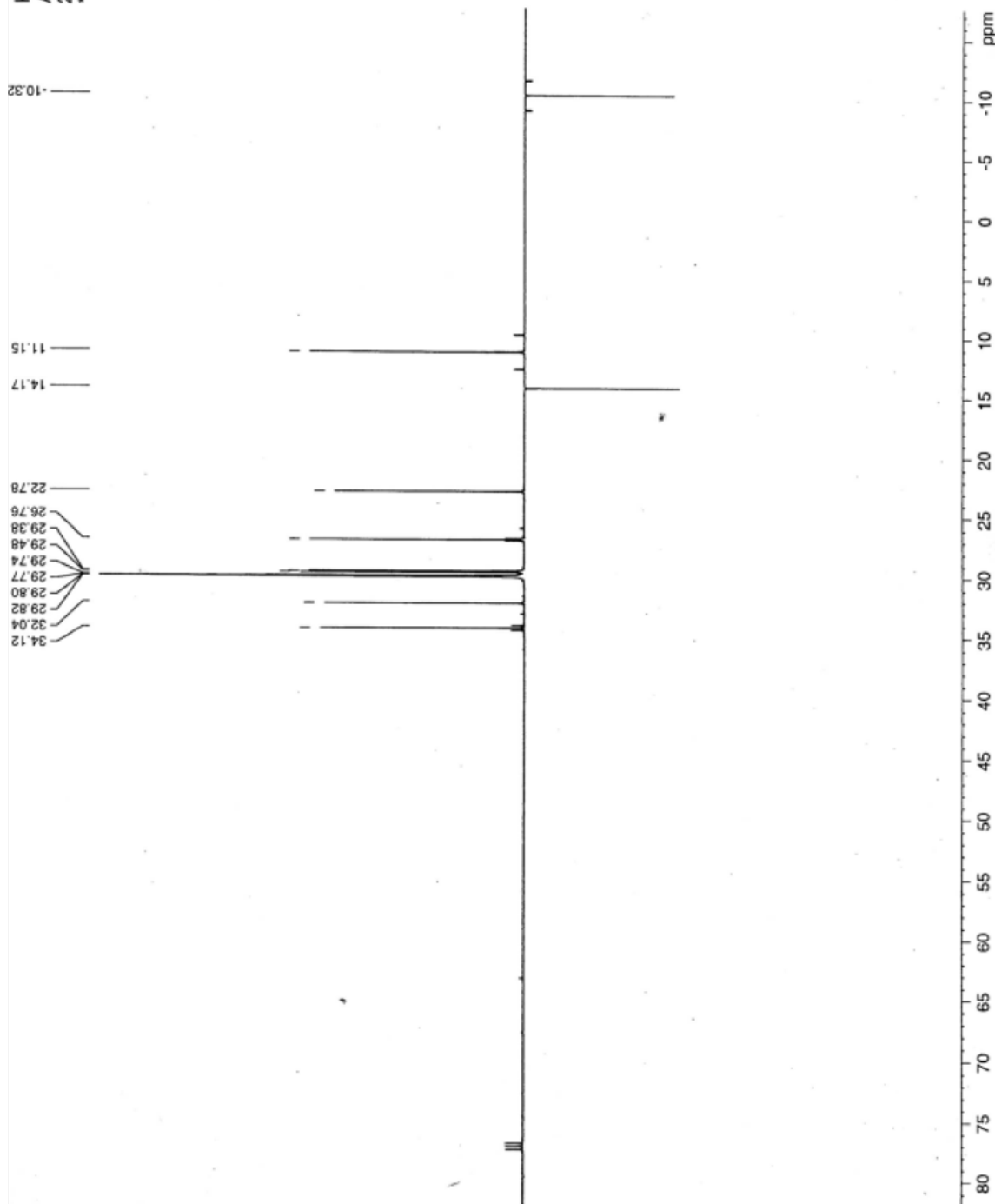
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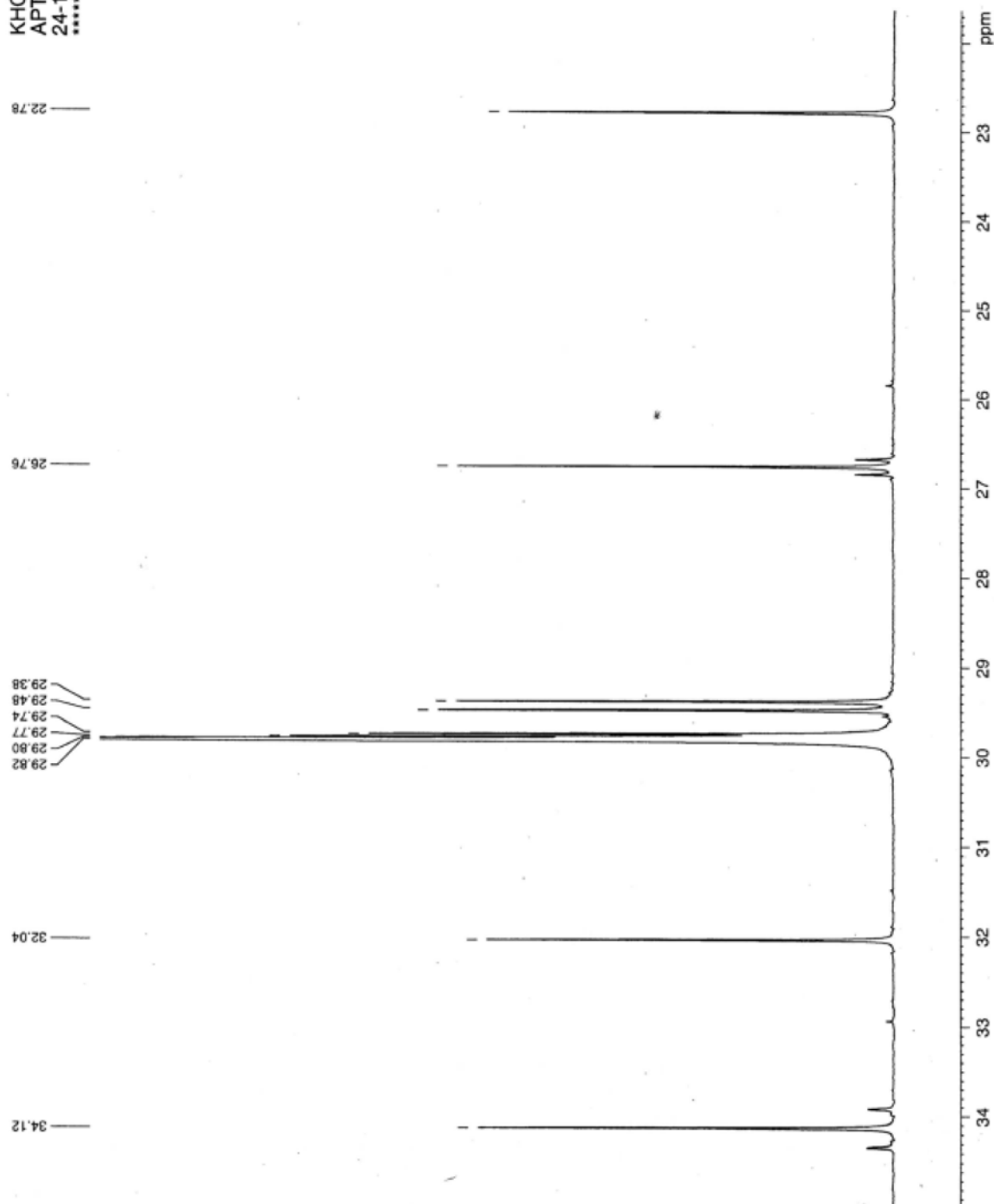
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<sup>13</sup>C NMR spectrum of compound 4

KHOBAGADE DK-83  
APT in CDCl3  
24-11-08 RA  
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<sup>13</sup>C NMR spectrum of compound **4** expanded

KHOBRADE DK-  
<sup>119</sup>Sn NMR in CDCl<sub>3</sub>  
 24-11-08 RA  
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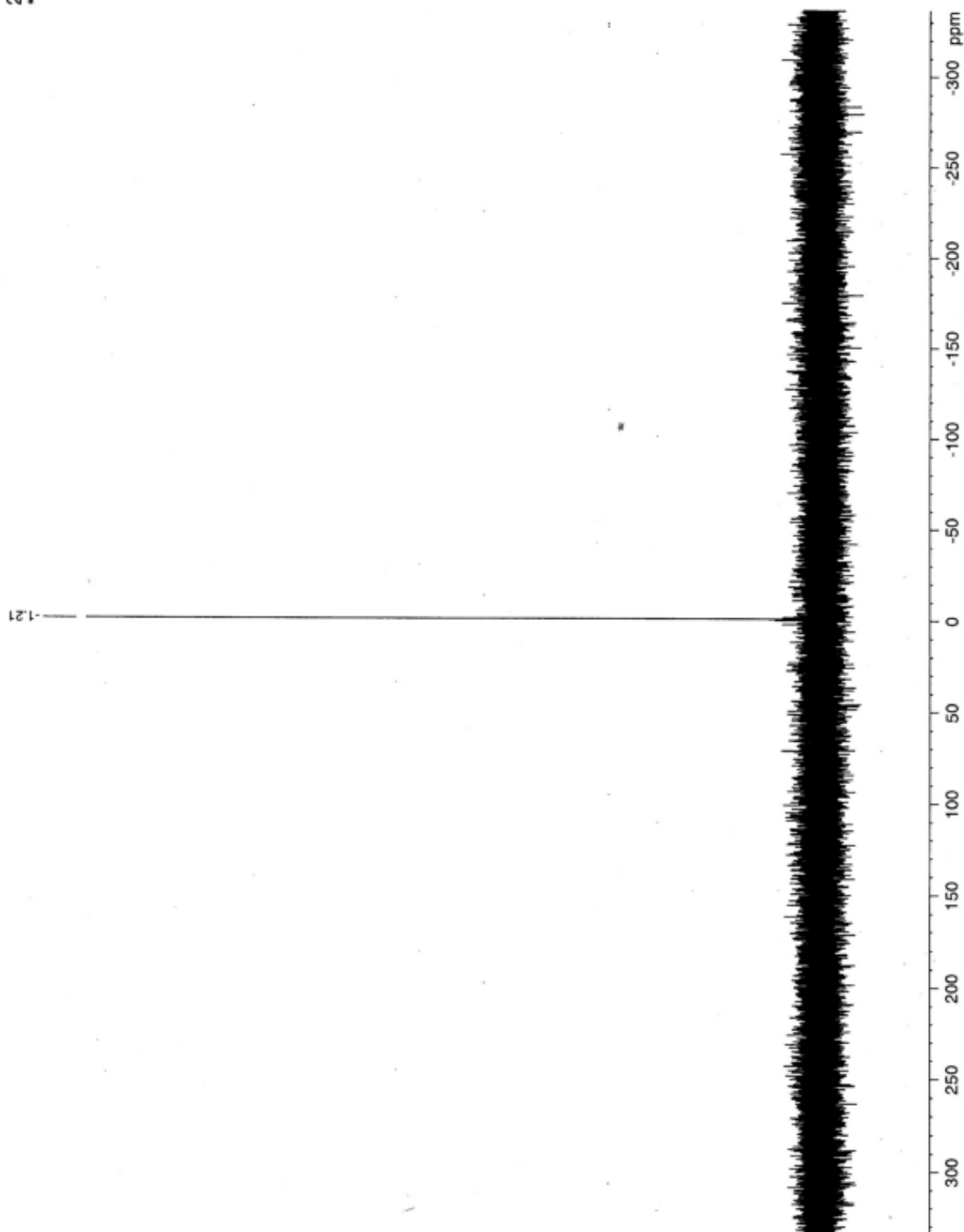
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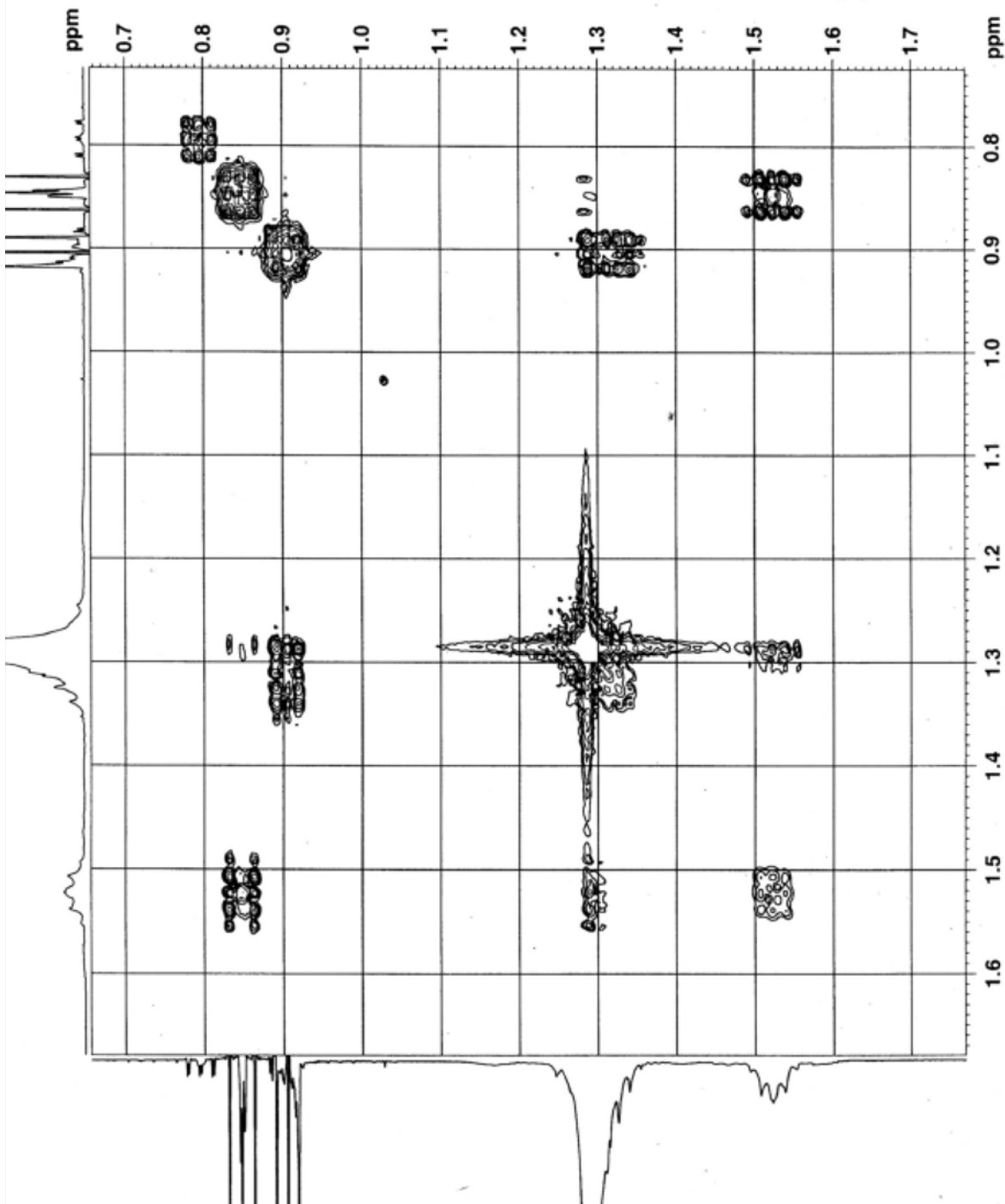


39362

<sup>119</sup>Sn NMR spectrum of compound 4



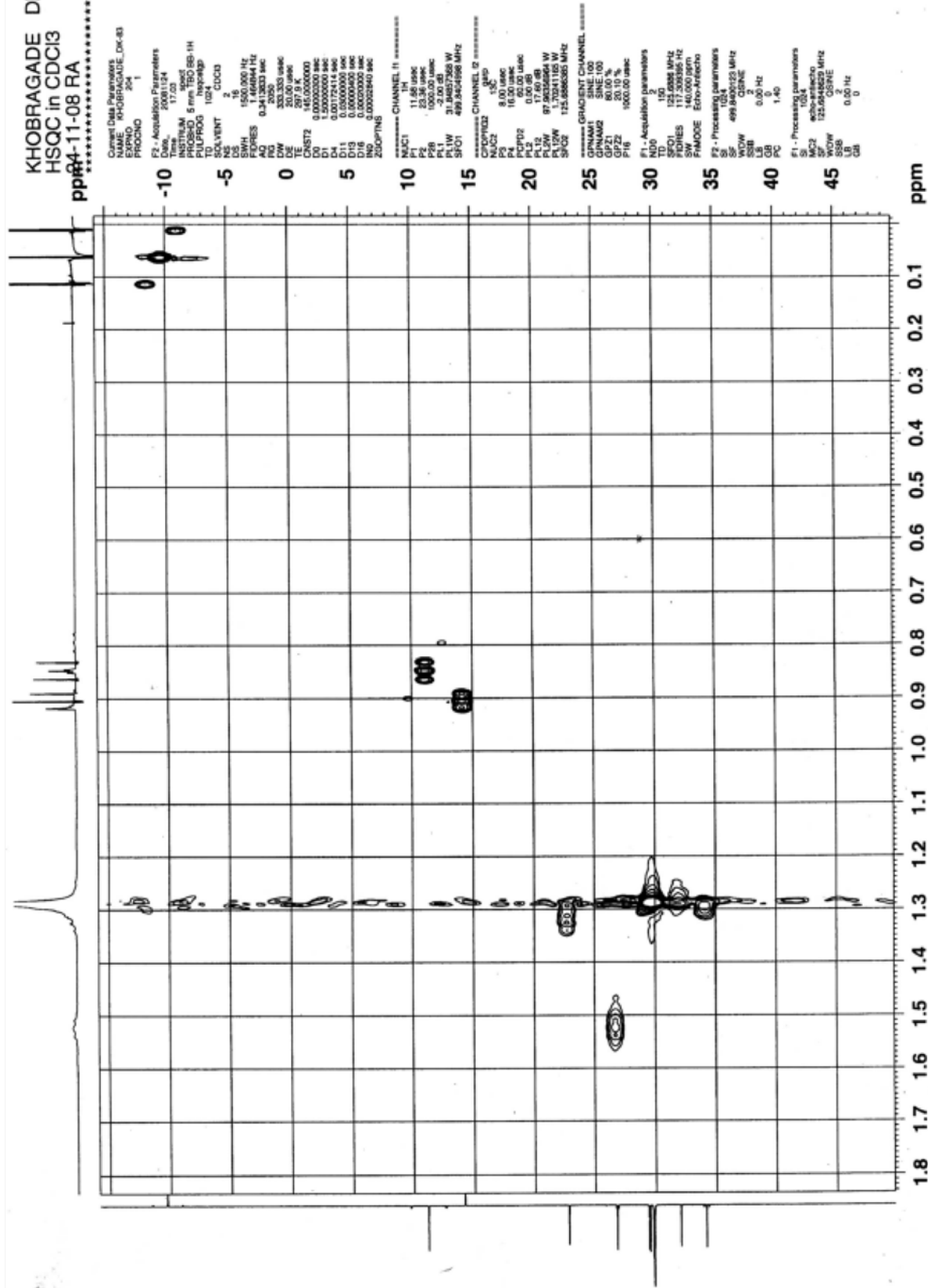
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 24-11-08 RA



39362

COSY <sup>1</sup>H - <sup>1</sup>H NMR of compound 4

KHOBRAGADE DK  
HSQC in CDCI3  
ppm 4-11-08 RA



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