Rhodium(I)-Catalyzed Silylation of Aryl Halides with Triethoxysilane: Practical Synthetic Route to Aryltriethoxysilanes

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[Supporting Information]

General Information. All experiments were carried out under an argon atmosphere. *N,N*-Dimethylformamide (DMF) was distilled from CaH_2 before use. The rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$, was prepared as described in the literature.[1] Triethoxysilane (**1**) and all aryl halides (**2**) were purchased from Tokyo Kasei Kogyo Co., Ltd., and were used without purification. **CAUTION!** A hood should be worn while handling triethoxysilane (**1**), and all contact with the eyes avoided.[2]

Synthesis of Aryltriethoxysilane. Typical Procedure. The general procedure for the synthesis of aryltriethoxysilane (**3**) is illustrated by the synthesis of 4-(triethoxysilyl)acetophenone (Table 2, entry 4). To a solution of $[Rh(cod)(MeCN)_2]BF_4$ (2.7 mg, 0.0071 mmol) in DMF (1 ml) was added 1-iodoacetophenone (60.7 mg, 0.247 mmol), Et_3N (104 μl, 0.75 mmol), and triethoxysilane (91 μl, 0.50 mmol). After being stirred for 2 h at 80 °C, the mixture was concentrated *in vacuo*. The residue was purified by Kugelrohr distillation to give 52.5 mg (75% yield) of the corresponding aryltriethoxysilane: IR (neat) 2977, 2928, 2890, 1689, 1390, 1359, 1265, 1078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, *J*= 7.0 Hz, 9H), 2.62 (s, 3H), 3.88 (q, *J*= 7.0 Hz, 6H), 7.78 (d, *J*= 8.3 Hz, 1H), 7.94 (d, *J*= 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.19, 26.69, 58.88, 127.28, 135.02, 137.29, 138.31, 198.41; MS (EI) *m/e* 282 (9, M^+), 267 (100), 238 (69), 223 (18), 209 (14); exact mass calcd for $C_{14}H_{22}O_4Si$ *m/e* 282.1287, found *m/e* 282.1284. The spectroscopic data matched those from the literature.[3]

Characterization data for the other products follow.

Ethyl 4-(Triethoxysilyl)benzoate (Table 2, entry 2)**:** The title compound was prepared starting from **2b** (229.1 mg, 1.00 mmol). The product was purified by distillation to afford 243.1 mg (78% yield). IR (neat) 2977, 2928, 2361, 1720, 1558, 1445, 1391, 1367, 1279, 1101 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, *J*=7.0 Hz, 9 H), 1.47 (t, *J*=7.0 Hz, 3 H), 3.88 (q, *J*=7.0 Hz, 6 H), 4.39 (q, *J*= 7.0 Hz, 2 H), 7.74 (d, *J*= 8.2 Hz, 2 H), 8.04 (d, *J*= 8.2 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 10.29, 14.16, 54.84, 56.96, 124.55, 128.05, 130.70, 132.94, 162.63; MS (EI) *m/e* 312 (5, M^+), 267 (100), 253 (15), 239 (61), 223 (16), 195 (22), 183 (17), 163 (25), 147 (20); exact mass calcd for $C_{15}H_{24}O_5Si$ *m/e* 312.1393, found *m/e* 312.1392. The spectroscopic data matched those from the literature.[4]

Phenyltriethoxysilane (Table 2, entry 5)**:** The title compound was prepared starting from **2e** (203.8 mg, 1.00 mmol). The product was purified by distillation to afford 206.8 mg (86% yield). IR (neat) 2976, 2928, 2886, 1594, 1483, 1431, 1391, 1295, 1168, 1129, 1103, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, *J*= 7.0 Hz, 9 H), 3.88 (q, *J*= 7.0 Hz, 6 H), 7.3-7.5 (m, 3 H), 7.6-7.8 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.12, 58.68, 127.78, 130.22, 131.08, 134.74; MS (EI) *m/e* 240 (16, M^+), 195 (38), 181 (13), 162 (28), 147 (100), 139 (33), 135 (33); exact mass calcd for $C_{12}H_{20}O_3Si$ *m/e* 240.1182, found *m/e* 240.1141. The spectroscopic data matched those from the literature.[4]

4-(Triethoxysilyl)anisole (Table 2, entry 6)**:** The title compound was prepared starting from **2f** (57.7 mg, 0.247 mmol). The product was purified by distillation to afford 59.9 mg (90% yield). IR (neat) 2975, 2360, 1598, 1567, 1506, 1459, 1390, 1282, 1250 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.24 (t, *J*= 7.0 Hz, 9 H), 3.82 (s, 3H), 3.85 (q, *J*= 7.0 Hz, 6 H), 6.92 (d, *J*= 8.5 Hz, 2 H), 7.61 (d, *J*= 8.5 Hz, 2 H); ^{13}C NMR ($CDCl_3$) δ 18.12, 54.89, 58.55, 113.57, 122.00, 136.37, 161.37; MS (EI) *m/e* 270 (52, M^+), 255 (53), 225 (38), 211 (25), 181 (28), 169 (27), 149 (22), 147 (100), 135 (32); exact mass calcd for $C_{13}H_{22}O_4Si$ *m/e* 270.1287, found *m/e* 270.1261. The spectroscopic data matched those from the literature.[4]

2-Tolyltriethoxysilane (Table 2, entry 7)**:** The title compound was prepared starting from **2g** (54.1 mg, 0.248 mmol). The product was purified by distillation to afford 51.1 mg (81% yield). IR (neat) 2975, 2928, 2886, 1594, 1442, 1391, 1285, 1167, 1138, 1103, 1079 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, *J*= 7.0 Hz, 9H), 2.51 (s, 3H), 3.86 (q, *J*= 7.0 Hz, 6H), 7.1-7.2 (m, 2H), 7.32 (t, *J*= 7.3 Hz, 1H), 7.72 (d, *J*= 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.17, 22.39, 58.48, 124.64, 129.69, 129.82, 130.46, 136.46, 144.51; MS (EI) *m/e* 254 (68, M^+), 209 (65), 195 (25), 181 (22), 162 (74), 147 (100), 135 (50), 119 (67); exact mass calcd for $C_{13}H_{22}O_3Si$ *m/e* 254.1338, found *m/e* 254.1323.

2-(Triethoxysilyl)anisole (Table 2, entry 8)**:** The title compound was prepared starting from **2h** (231.0 mg, 0.987 mmol). The product was purified by distillation to afford 231.6 mg (87% yield). IR (neat) 2975, 2928, 2891, 1592, 1573, 1476, 1429, 1391, 1244, 1168, 1104, 1081 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (t, *J*= 7.0 Hz, 9 H), 3.83 (s, 3H), 3.88 (q, *J*= 7.0 Hz, 6 H), 6.85 (d, *J*= 8.2 Hz, 1 H), 6.96 (dd, *J*= 7.0 and 7.0 Hz, 1 H), 7.40 (dd, *J*= 8.2 and 7.0 Hz, 1 H), 7.65 (d, *J*= 7.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.20, 55.09, 58.65, 109.62, 119.30, 120.48, 132.14, 137.54, 164.37; MS (EI) *m/e* 270 (42, M^+), 255 (33), 181 (42), 151 (33), 147 (100), 139 (40); exact mass calcd for $C_{13}H_{22}O_4Si$ *m/e* 270.1287, found *m/e* 270.1274.

3,4-Difluorophenyltriethoxysilane (Table 2, entry 9)**:** The title compound was prepared starting from **2i** (47.5 mg, 0.246 mmol). The product was purified by distillation to afford 51.4 mg (76% yield). IR (neat) 2978, 2929, 2891, 1607, 1511, 1392, 1275, 1168, 1089 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, *J*= 7.0 Hz, 9H), 3.86 (q, *J*= 7.0 Hz, 6H), 7.18 (dt, *J*= 10.3 and 7.9 Hz, 1H), 7.39 (br s, 1H), 7.46 (t, *J*= 10.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 18.29, 59.05, 117.42 (d, *J*= 15.5 Hz), 123.60 (dd, *J*= 18.5 and 2.1 Hz), 131.4 (d, *J*= 4.1 Hz), 131.5 (d, *J*= 4.1 Hz), 150.47 (dd, *J*= 250.3 and 12.4 Hz), 152.18 (dd, *J*= 251.4 and 12.4 Hz); MS (EI) *m/e* 276 (15, M^+), 261 (17), 231 (100), 217 (31), 203 (16), 187 (27), 175 (53), 162 (55), 147 (71); exact mass calcd for $C_{12}H_{18}F_2O_3Si$ *m/e* 276.0994, found *m/e* 276.0980.

3-(Triethoxysilyl)benzotrifluoride (Table 2, entry 10)**:** The title compound was prepared starting from **2b** (227.1 mg, 1.01 mmol). The product was purified by distillation to afford 218.8 mg (70% yield). IR (neat) 2978, 2930, 2892, 1607, 1511, 1393, 1329, 1275, 1169, 1131, 1078 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, *J*= 7.0 Hz, 9H), 3.89 (q, *J*= 7.0 Hz, 6H), 7.50 (t, *J*= 7.6 Hz, 1H), 7.68 (d, *J*= 7.6 Hz, 1H), 7.85 (d, *J*= 7.6 Hz, 1H), 7.92 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.86, 58.71, 124.17 (q, *J*= 272.4 Hz), 126.71 (q, *J*= 4.1 Hz), 127.97, 129.94 (q, *J*= 32.1 Hz), 131.08 (q, *J*= 2.1 Hz), 132.68, 137.89; MS (EI) *m/e* 308 (2, M^+), 293 (15), 263 (100), 249 (38), 235 (15), 219 (26), 207 (49), 191 (24), 181 (56), 163 (18), 154 (24), 147 (26); exact mass calcd for $C_{13}H_{19}F_3O_3Si$ *m/e* 308.1056, found *m/e* 308.1083.

3-Pyridyltriethoxysilane (Table 2, entry 11)**:** The title compound was prepared starting from **2k** (39.5 mg, 0.250 mmol). The product was purified by distillation to afford 46.9 mg (80% yield). IR (neat) 2977, 2929, 2890, 1578, 1561, 1395, 1167, 1138, 1080 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.26 (t, *J* = 7.0 Hz, 9 H), 3.89 (q, *J* = 7.0 Hz, 6 H), 7.29 (dd, *J*= 7.4 and 4.9 Hz, 1 H), 7.95 (d, *J*= 7.4 Hz, 1 H), 8.65 (d, *J*= 4.9 Hz, 1 H), 8.83 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 18.04, 58.80, 123.07, 126.55, 142.36, 151.05, 154.99; MS (EI) *m/e* 241 (54, M^+), 240 (100), 226 (18), 212 (27), 196 (88), 147 (29), 182 (25); exact mass calcd for $C_{11}H_{19}O_3NSi$ *m/e* 241.1134, found *m/e* 241.1112. The spectroschopic data matched those from the literature.[4]

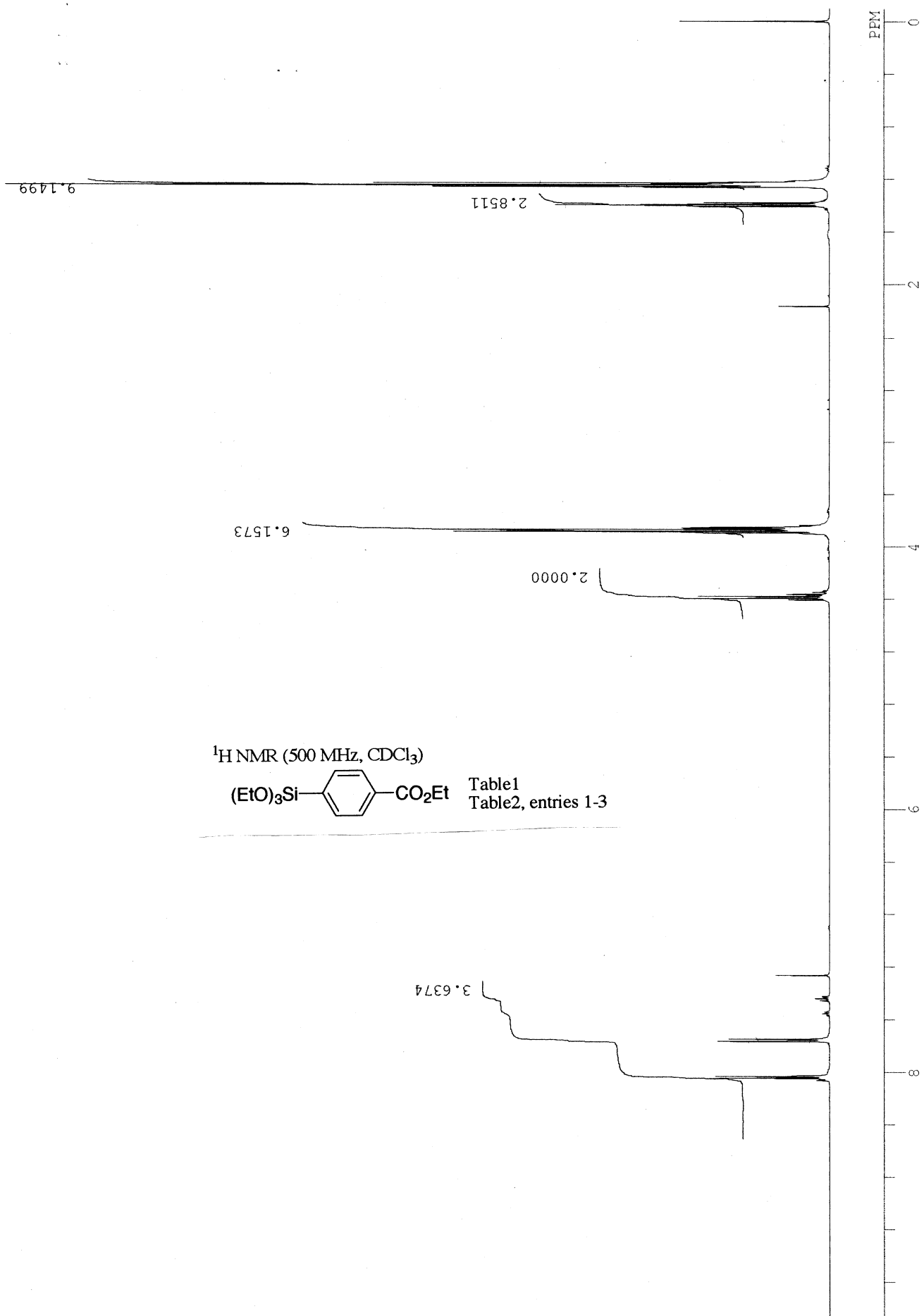
Reference

(1) Green, M.; Kuc, T. A. Taylor, S. H. *J. Chem. Soc. (A)* **1971**, 2334.

(2) *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; Wiley: New York, 1995; Vol. 7, pp 5083.

(3) Manoso, A. S.; DeShong, P. *J. Org. Chem.* **2001**, *66*, 7449.

(4) Murata, M.; Suzuki, K.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **1997**, *62*, 8569.



^{1}H NMR (500 MHz, $CDCl_3$)

$(EtO)_3Si$—C$_6$H$_4$—CO_2Et

Table1
Table2, entries 1-3

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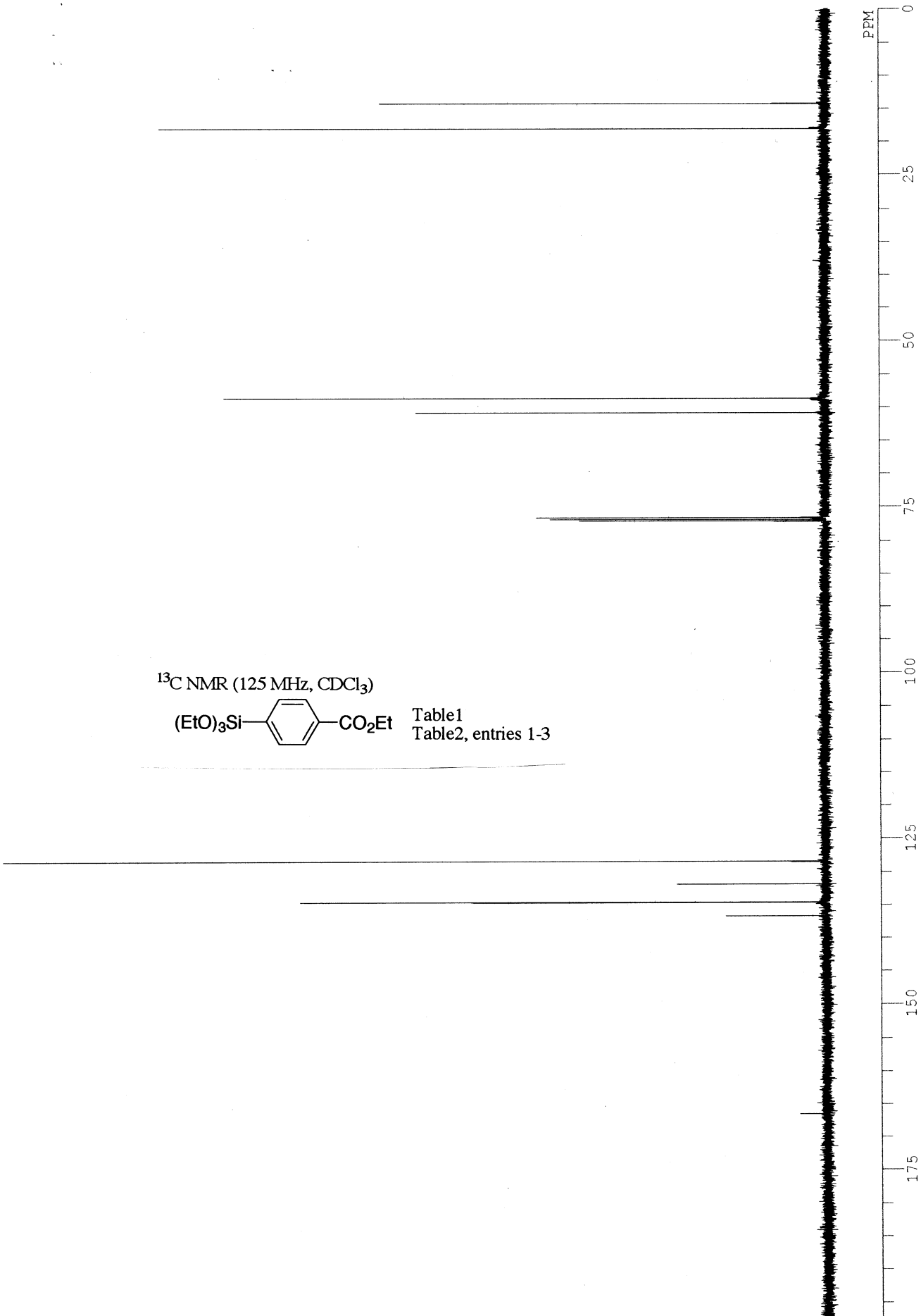

^{13}C NMR (125 MHz, $CDCl_3$)

$(EtO)_3Si$—C$_6$H$_4$—CO_2Et

Table1
Table2, entries 1-3

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^{1}H NMR (500 MHz, $CDCl_3$)

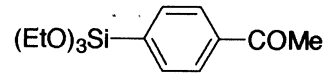
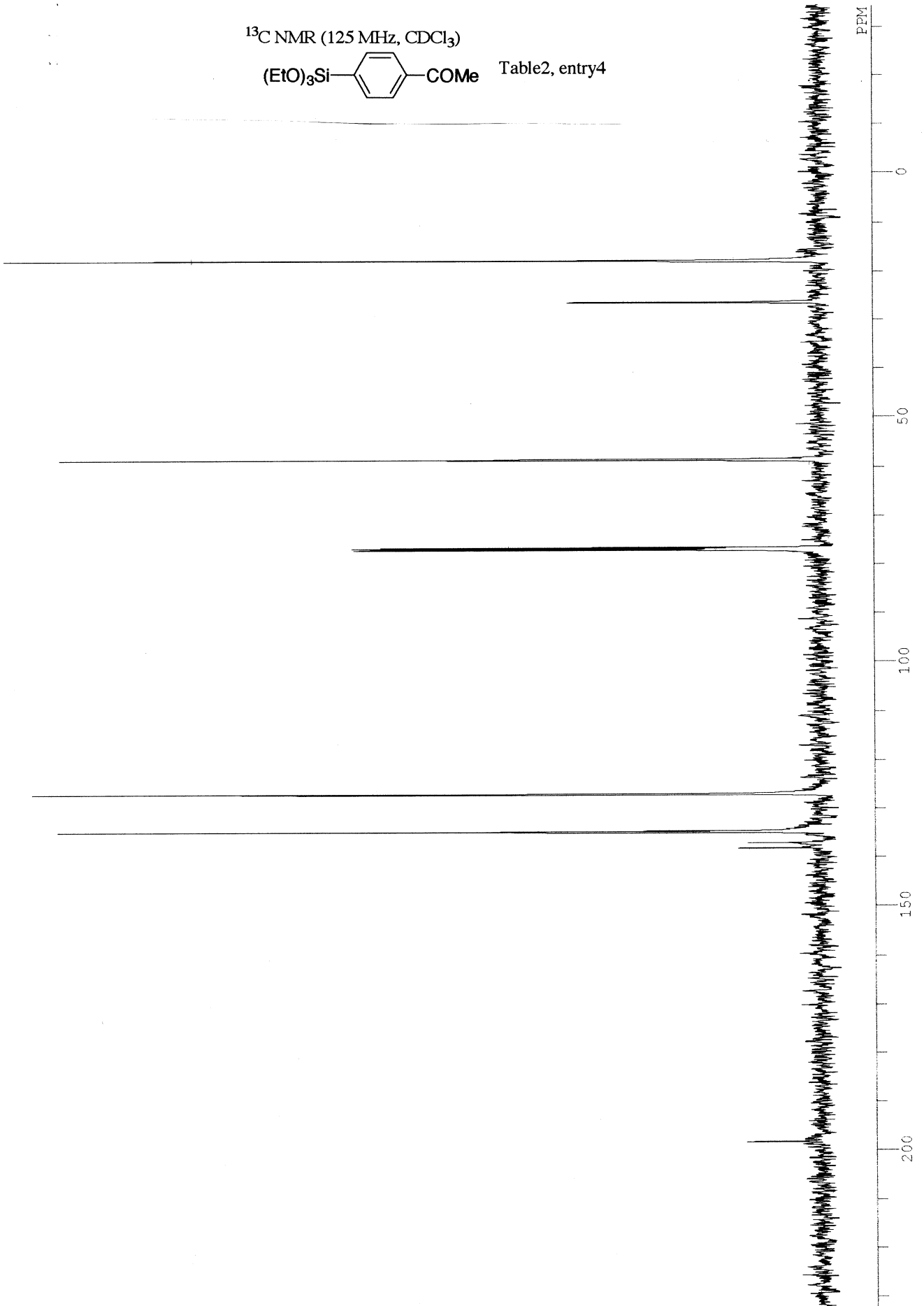


Table2, entry 4

^{13}C NMR (125 MHz, $CDCl_3$)

$(EtO)_3Si$—C$_6$H$_4$—COMe Table2, entry4



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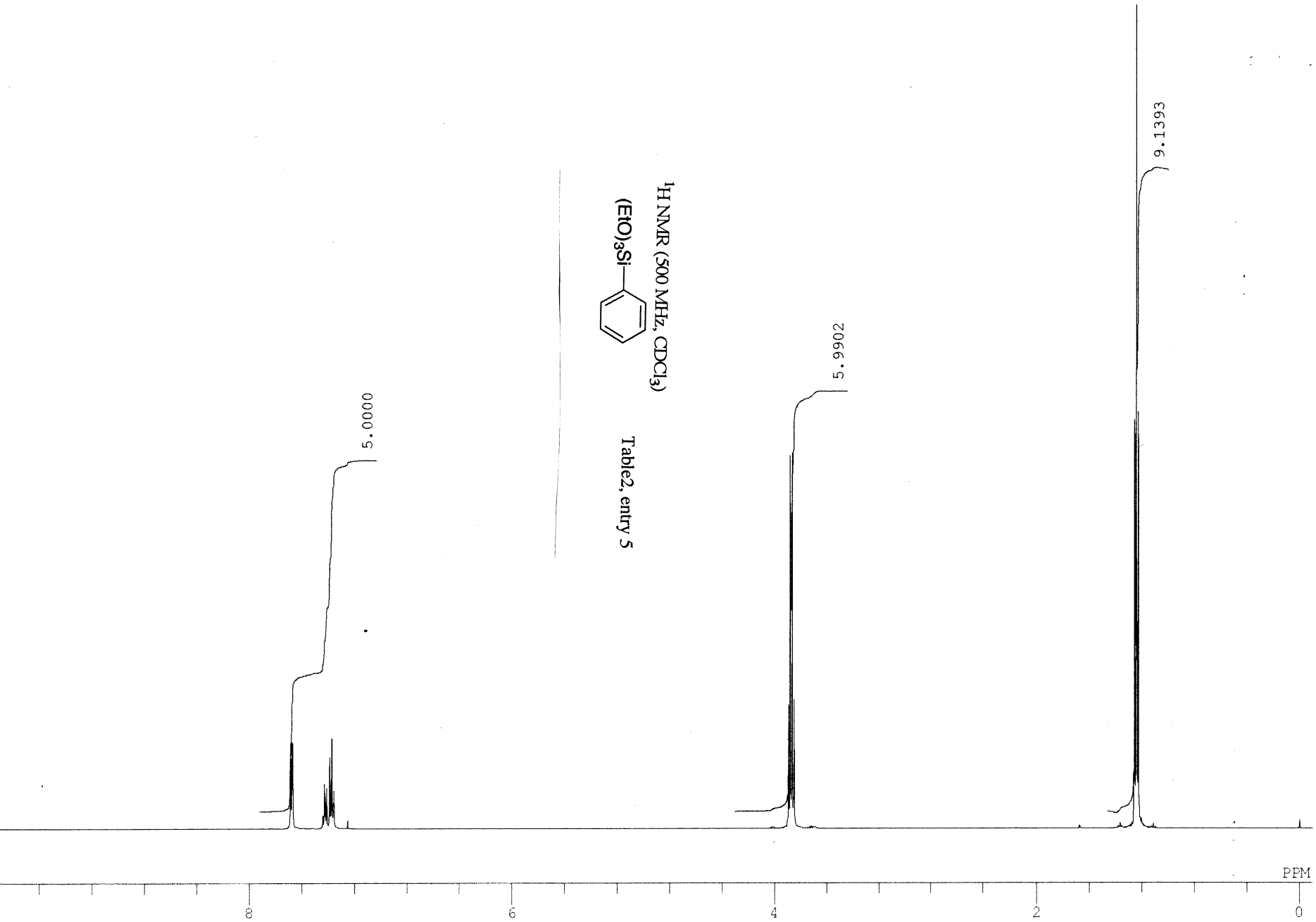

^{1}H NMR (500 MHz, $CDCl_3$)

$(EtO)_3Si$—

Table2, entry 5

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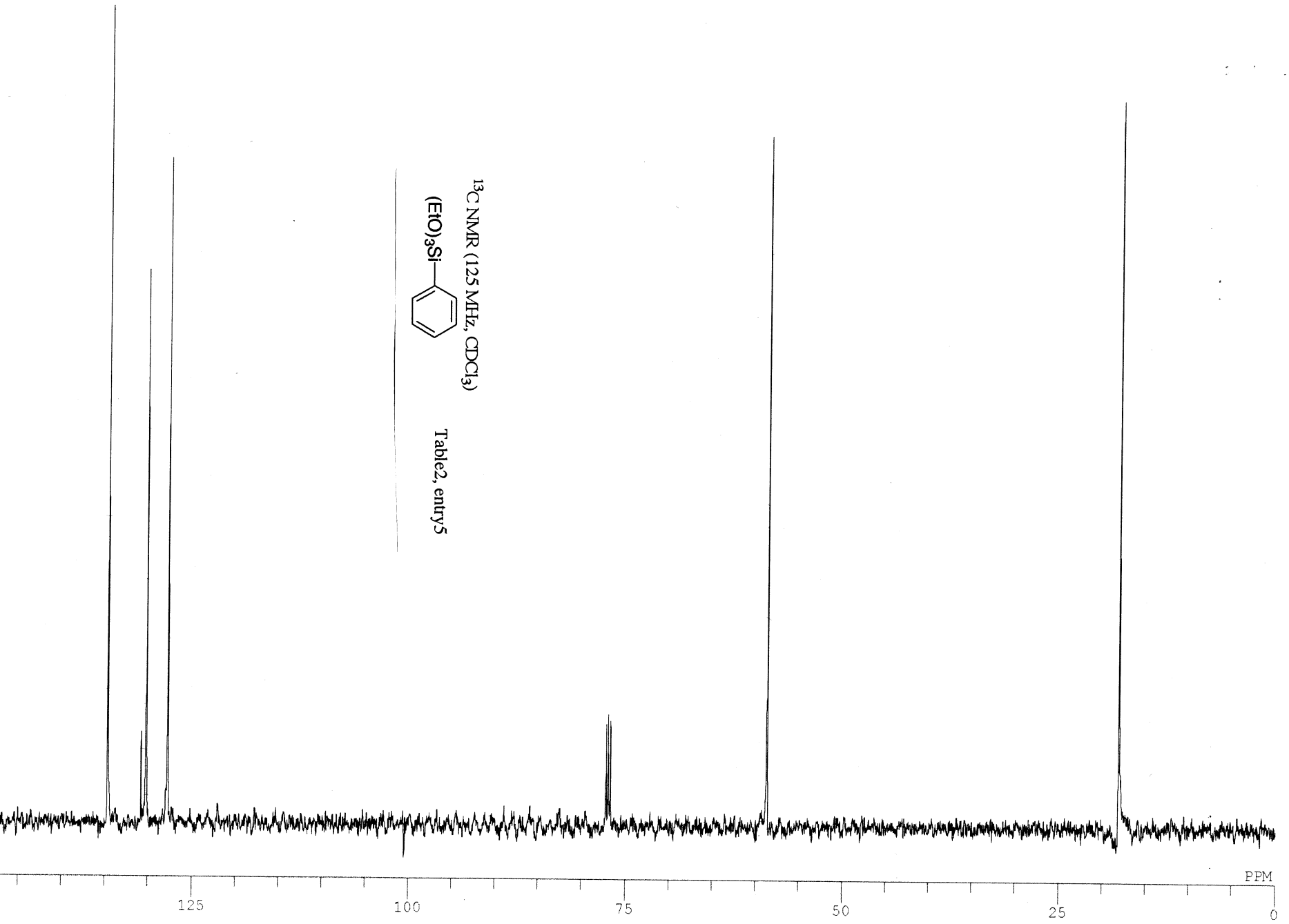
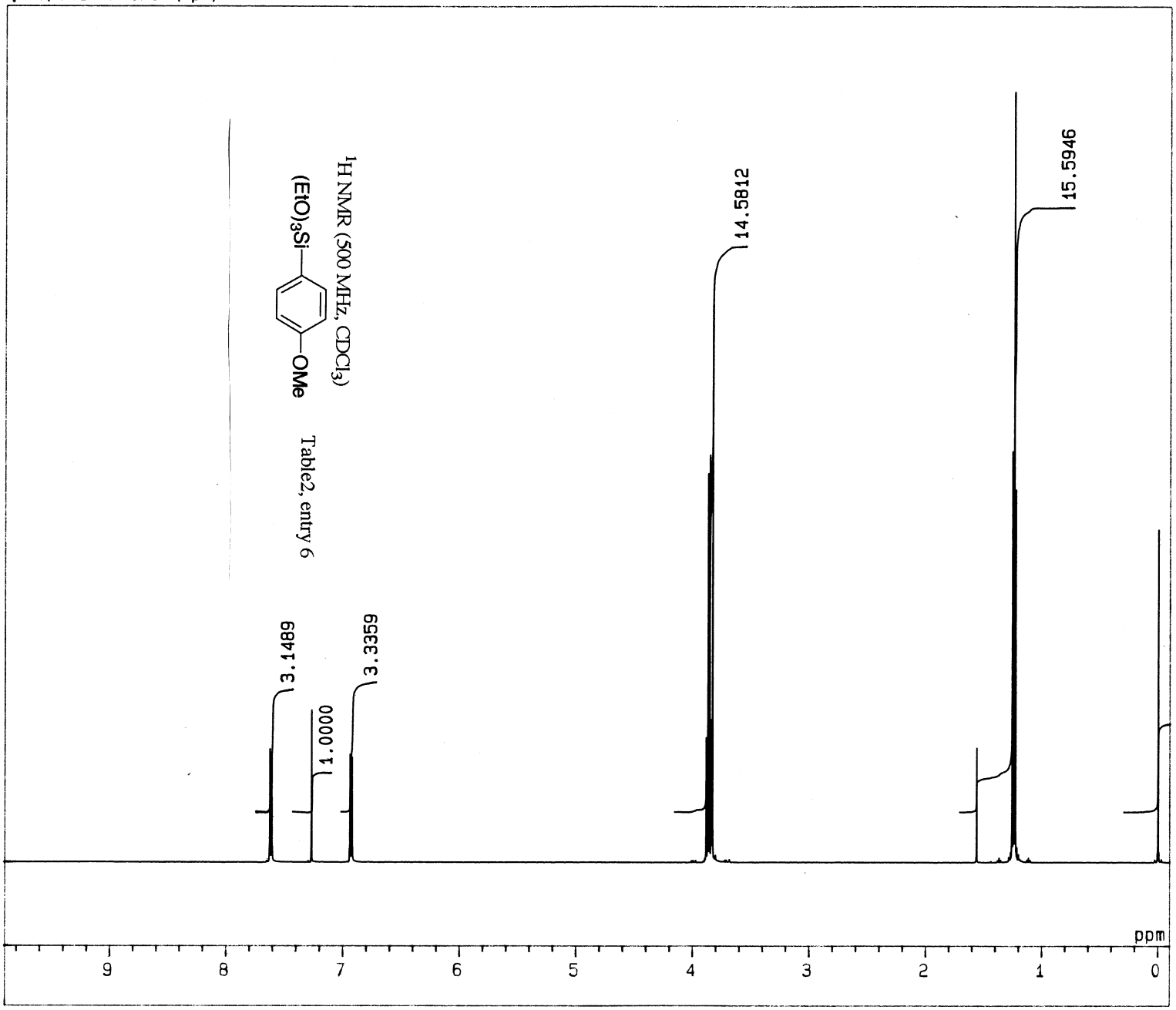


(EtO) 3Si-Ph-OMe (-p-)



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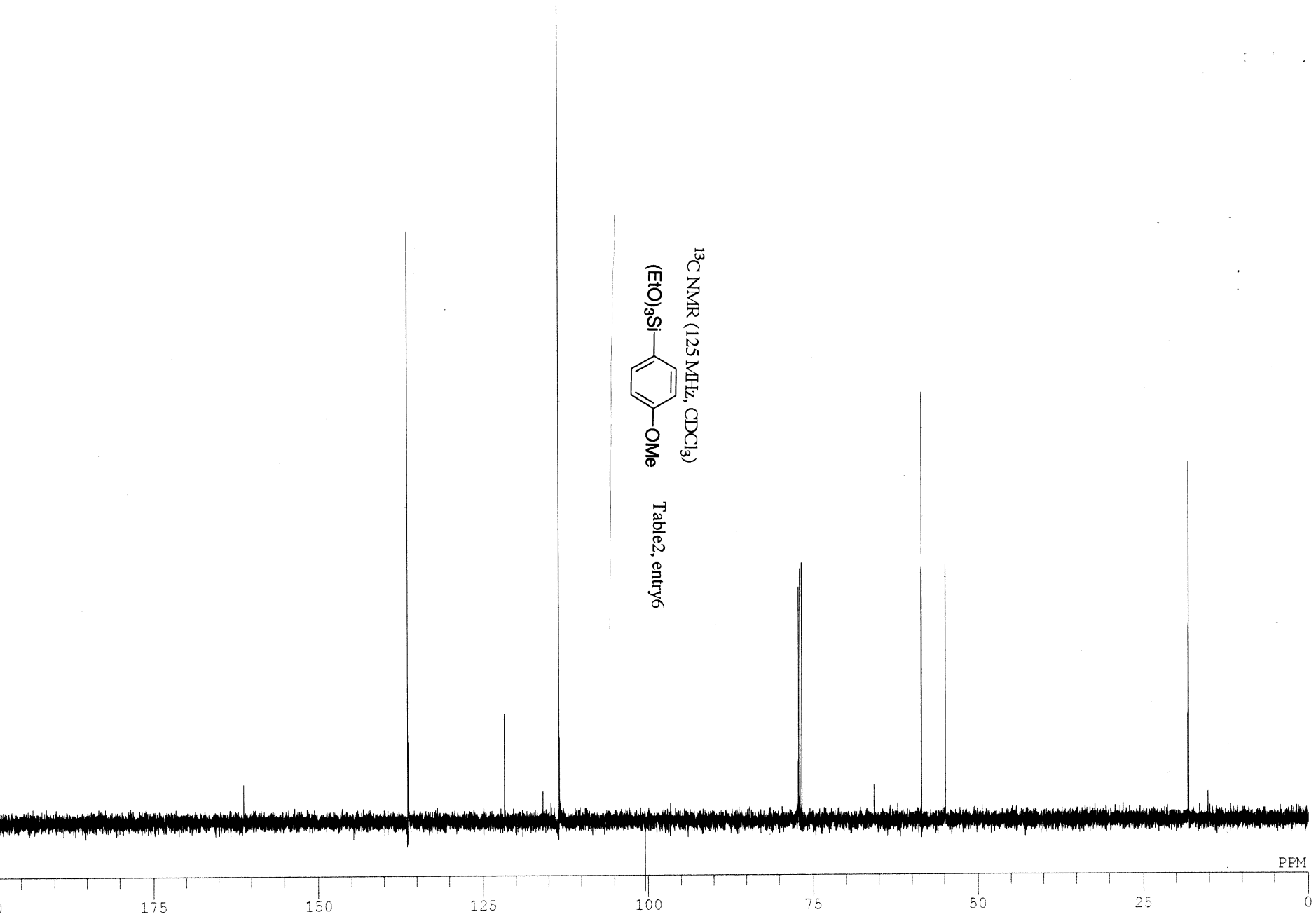
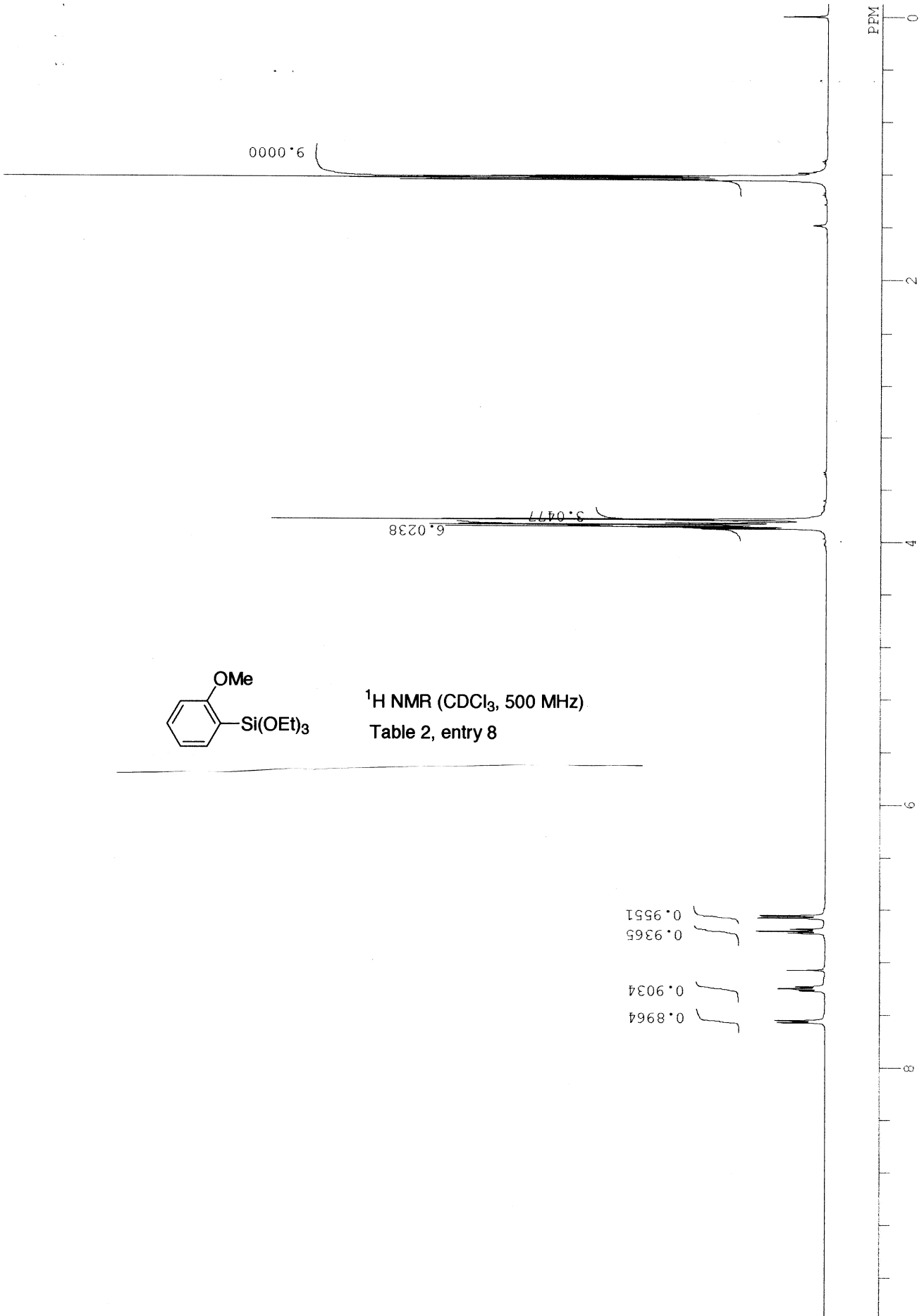


^{1}H NMR (500 MHz, $CDCl_3$)

Table 2, entry 7

^{13}C NMR (125 MHz, $CDCl_3$)

Table 2, entry 7



^{1}H NMR ($CDCl_3$, 500 MHz)

Table 2, entry 8

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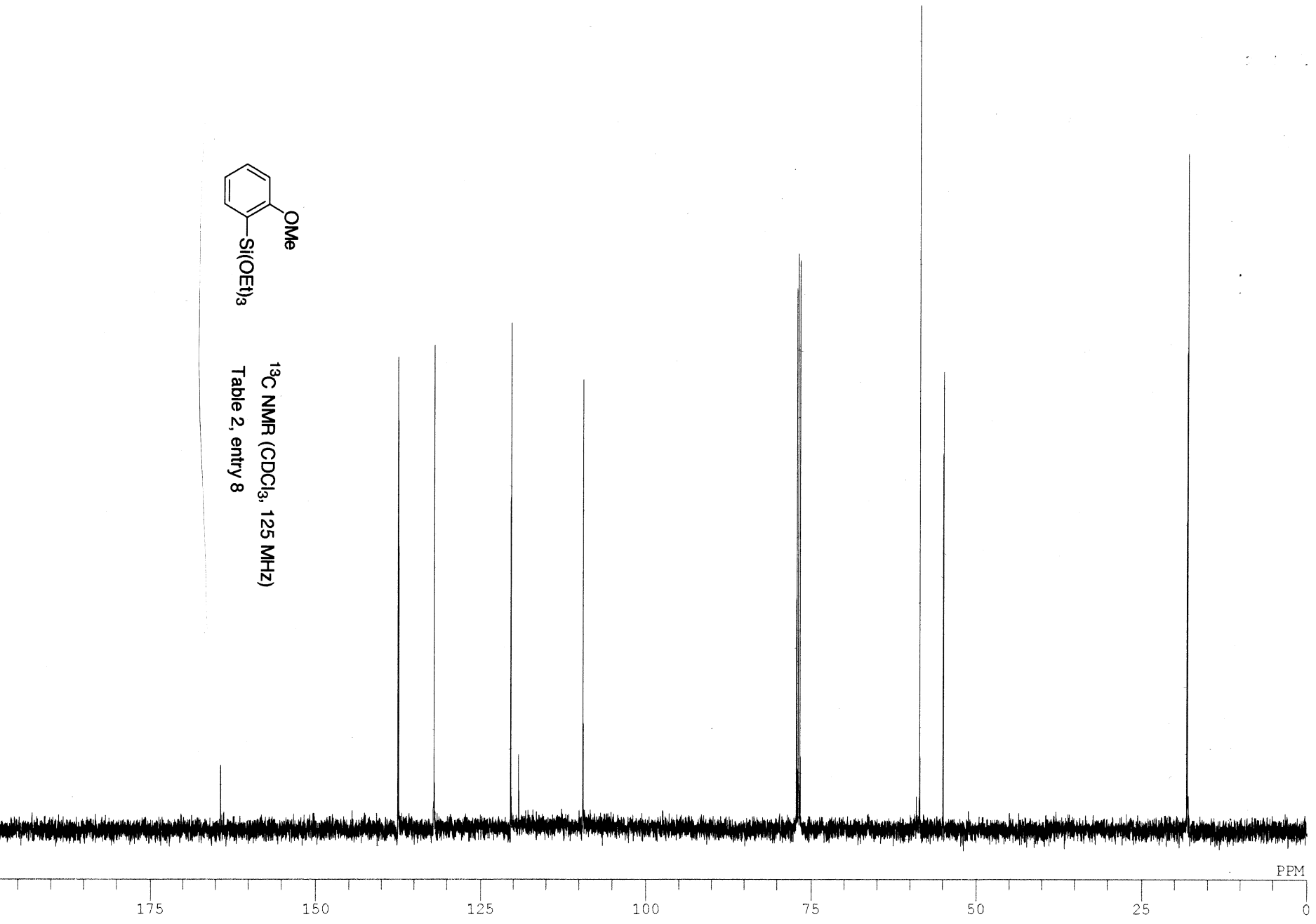
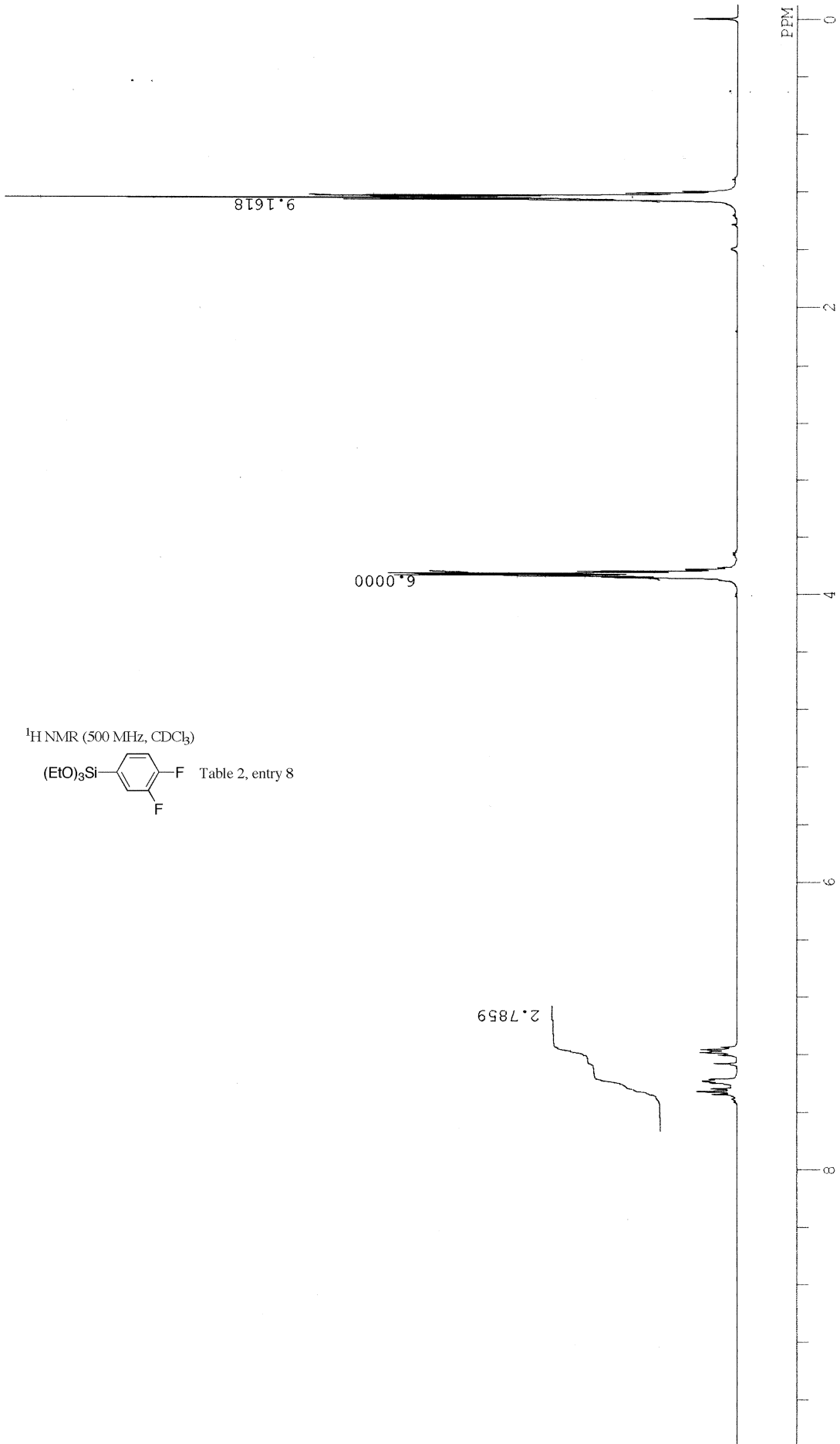
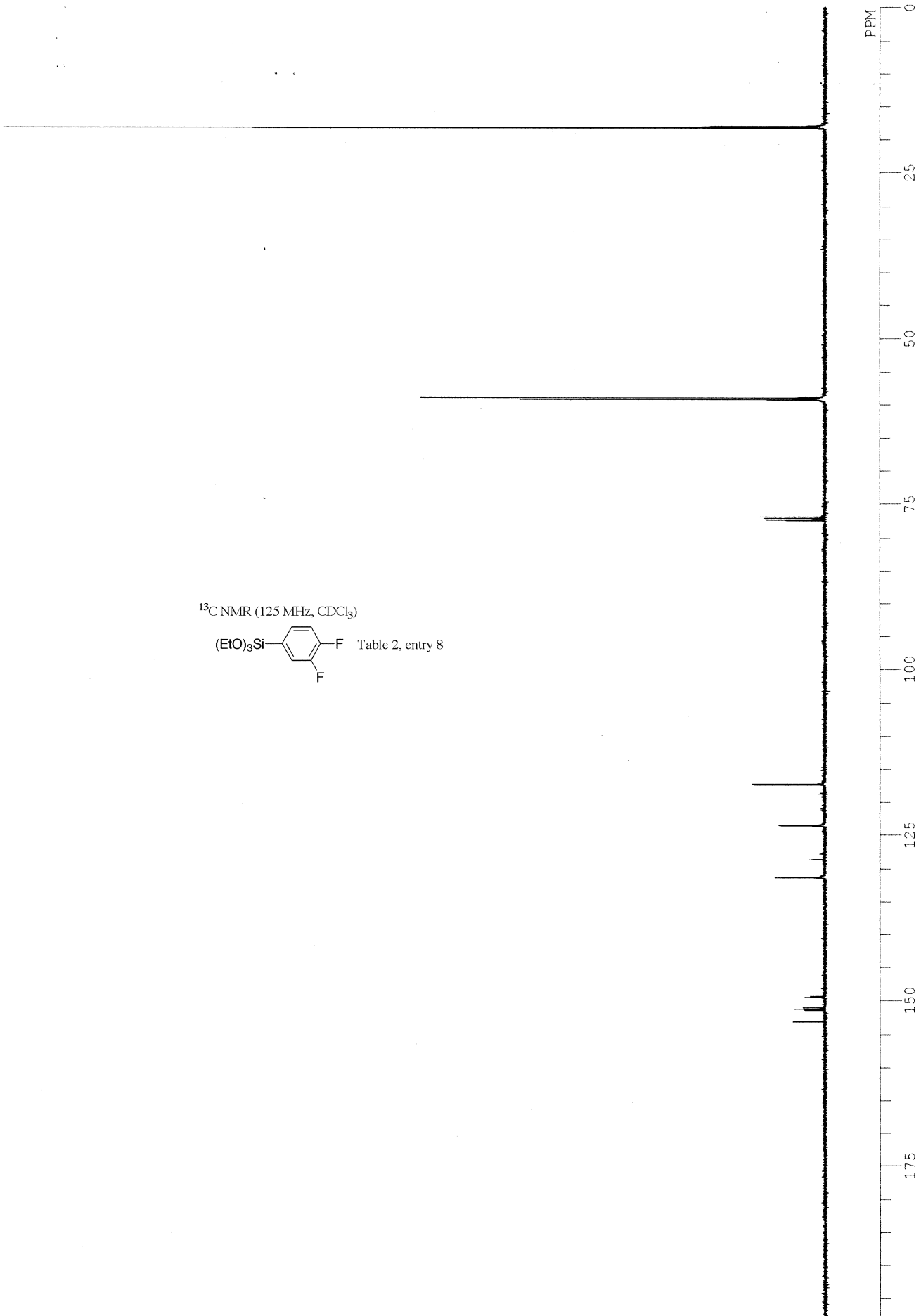




^{1}H NMR (500 MHz, $CDCl_3$)

$(EtO)_3Si$—C$_6$H$_3$F$_2$ Table 2, entry 8



^{13}C NMR (125 MHz, $CDCl_3$)

Table 2, entry 8

^{1}H NMR (500 MHz, $CDCl_3$)

Table 2, entry 9

^{13}C NMR (125 MHz, $CDCl_3$)

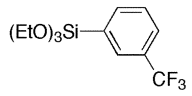
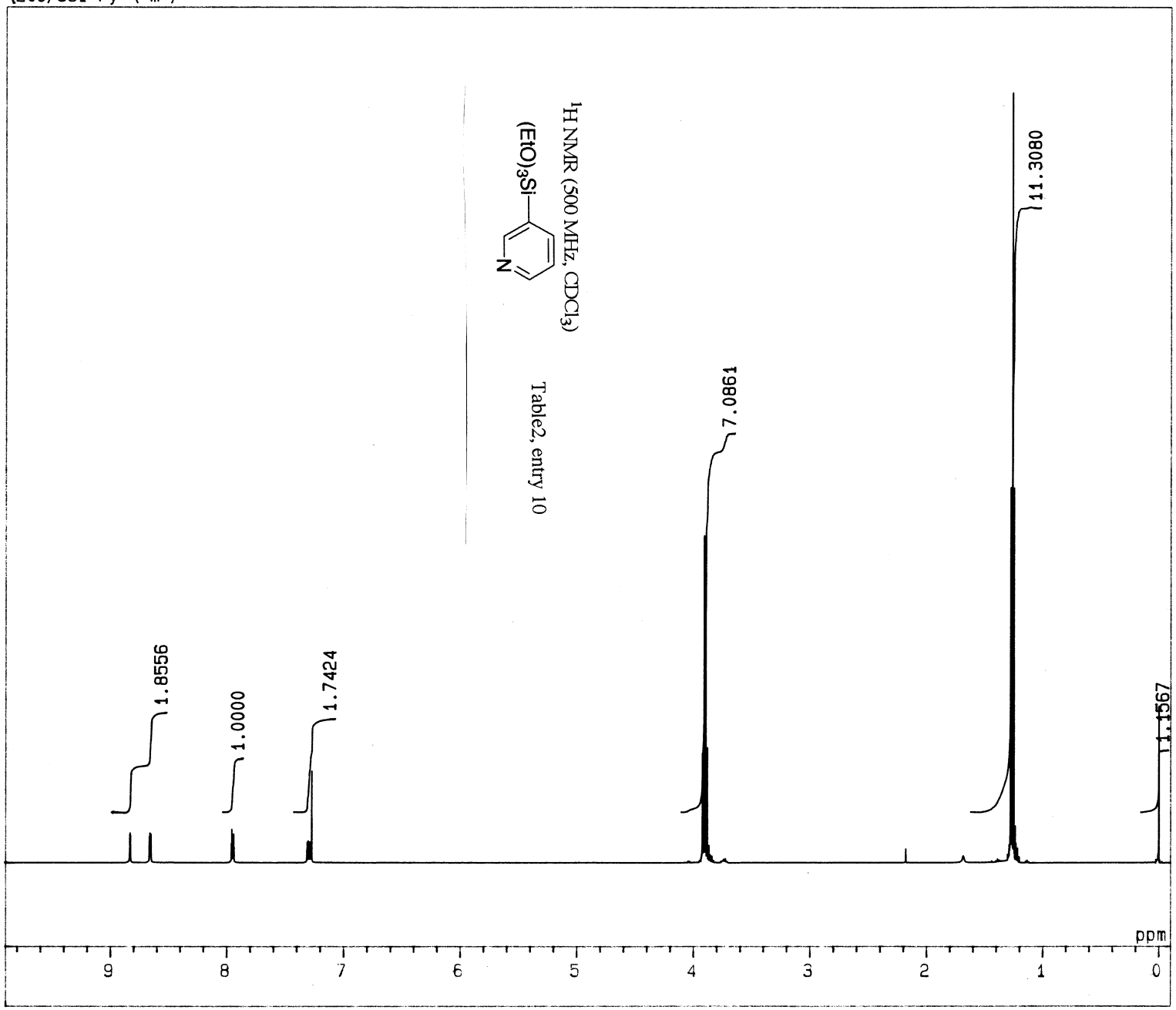


Table 2, entry 9

(EtO) 3Si-Py (-m-)



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OBSET : 162410.00 Hz

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