Supporting Information

An Unexpected Diethyl Azodicarboxylate-promoted Dehydrogenation of Tertiaryamine and Tandem Reaction with Sulfonyl Azide

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Experimental Section

All reactions were carried out using standard Schlenk techniques. DMSO, DMF, $ClCH_2CH_2Cl$, CH_2Cl_2 and CH_3CN were distilled from CaH_2. Et_3N, THF, hexane, 1,4-dioxane, and toluene was distilled from sodium/benzophenone. Substituted sulfonyl azides were prepared according to literature.[1] Diphenylphosphoryl azide was prepared from diphenylphosphorochloridate and NaN_3.[2] *N*,*N*-diethyl-3-methylaniline was prepared from 3-methylaniline and ethyl phosphate.[3] Benzyloxycarbonyl azide was prepared from benzyl chloroformate and NaN_3.[4] *N*,*N*-dimethylethylamine, tri-*n*-butylamine, tri-*n*-hexylamine, *N*-ethylmorpholine, *N*-ethyl-*N*-benzylaniline, and *N*,*N*-diethylaniline were purchased from Sigma-Aldrich company. ^1H and ^{13}C NMR spectra were recorded at room temperature in $CDCl_3$ on Bruker AMX-500 MHz instrument with TMS as internal standard. Coupling constants are reported in Hertz (Hz). IR spectra were taken as neat. Low-resolution MS was obtained using EI or ESI ionization. HRMS was obtained using ESI ionization. Elemental analyses were performed on a EA-1110 instrument. Melting points were measured with micro melting point apparatus and are uncorrected.

Caution: Azides and diazoalkanes may be hazardous and/or explosive.

Procedure for the synthesis of **3a**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 hour at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3a**. 0.193 g, 76% yield.
m.p. 77-78 °C (lit.[5] 55-60°C); ^1H NMR (500 MHz, $CDCl_3$) δ= 1.12-1.15 (t, J = 7.3 Hz, 3H), 1.24-1.27 (t, J = 7.3 Hz, 3H), 2.40 (s, 3H), 3.35-3.40 (q, J = 7.2 Hz, 2H), 3.45-3.49 (q, J = 7.2 Hz, 2H), 7.25-7.26 (d, J = 8.0, 2H), 7.75-7.78 (m, 2H), 8.14 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 21.45, 40.9, 47.0, 126.4, 129.3, 139.8, 142.3, 158.1; IR (neat): v=2984, 1606, 1450, 1381, 1293, 1142, 1079, 872, 671 cm^{-1}; MS (EI, 70 eV): m/z (%): 254 (11) [M^+], 161 (43), 155 (14), 99 (97), 72 (100).

Procedure for the synthesis of **3b**: To a 10 mL two-necked round-bottom flask with a mixture of 2, 4, 6-trimethylbenzenesulfonyl azide (0.225 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel

(200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with petroleum ether/acetone (5:1-3:1) as eluent to give the pure product **3b**. 0.20 g, 71% yield.
m.p. 81-82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.12-1.15 (t, *J* = 7.3 Hz, 3H), 1.22-1.25 (t, *J* = 7.3 Hz, 3H), 2.27 (s, 3H), 2.68 (s, 6H), 3.33-3.37 (q, *J* = 7.2 Hz, 2H), 3.42-3.47 (q, *J* = 7.2 Hz, 2H), 6.90 (s,2H), 8.12 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.0, 14.5, 20.9, 22.9, 40.8, 46.8, 131.4, 136.6, 138.3, 141.1, 157.4; IR (neat):*v*=2972, 1609, 1445, 1345, 1291, 1134, 863, 668 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 282 (79) [M^+], 210 (21), 146 (47), 119 (63), 72 (93), 58 (100); Anal. $C_{12}H_{18}N_2O_2S$ Calcd. C, 59.54; H, 7.85; N, 9.92. found C, 59,58; H, 7.73; N, 9.88%.

Procedure for the synthesis of **3c**: To a 10 mL two-necked round-bottom flask with a mixture of benzenesulfonyl azide (0.183 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3c**. 0.154 g, 64% yield.
m.p. 73-75°C (lit.[6] 79-80°C); ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.13-1.16 (t, *J* = 7.3 Hz, 3H), 1.24-1.27 (t, *J* = 7.25 Hz, 3H), 3.36-3.41 (q, *J* = 7.2 Hz, 2H), 3.46-3.50 (q, *J* = 7.2 Hz, 2H), 7.44-7.52 (m, 3H), 7.88-7.89 (m, 2H), 8.16 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 41.0, 47.1, 126.3, 128.7, 131.7, 142.7, 158.2; IR (neat): *v*=2974, 1605, 1448, 1383, 1341, 1145, 1079, 873, 793, 670 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 240 (11) [M^+], 147 (36), 141 (18), 99 (100), 93 (6), 77 (92), 72 (88).

Procedure for the synthesis of **3d**: To a 10 mL two-necked round-bottom flask with a mixture of 2-phthanylsulfonyl azide (0.233 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3d**. 0.211 g, 73% yield.
m.p. 103-104 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.11-1.13 (t, *J* = 7.3 Hz, 3H), 1.22-1.25 (t, *J* = 7.3 Hz, 3H), 3.35-3.39 (q, *J* = 7.2 Hz, 2H), 3.45-3.49 (q, *J* = 7.2 Hz, 2H), 7.55-7.60 (m, 2H), 7.85-7.87 (m, 2H),

7.90-7.94 (m, 2H), 8.21 (s, 1H), 8.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 41.0, 47.1, 122.5, 126.9, 127.2, 127.8, 128.2, 128.9, 129.2, 132.2, 134.5, 139.6, 158.2; IR (neat):*v*=2978, 1600, 1447, 1296, 1145, 874, 665 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 290 (26) [M^+], 197 (35), 127 (100), 99 (77), 72 (56); Anal. $C_{15}H_{18}N_2O_2S$ Calcd. C, 62.04; H, 6.25; N, 9.65. found C, 62.11; H, 6.21; N, 9.58%.

Procedure for the synthesis of **3e**: To a 10 mL two-necked round-bottom flask with a mixture of 2-methoxylcarbonylbenzenesulfonyl azide (0.241 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3e**. 0.215 g, 72% yield.

m.p. 106-107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.13-1.16 (t, *J* = 7.3 Hz, 3H), 1.28-1.31 (t, *J* = 7.3 Hz, 3H), 3.40-3.44 (q, *J* = 7.2 Hz, 2H), 3.45-3.49 (q, *J* = 7.2 Hz, 2H), 3.93 (s, 3H), 7.51-7.58(m, 3H), 8.11 (s,1H), 8.13-8.15 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.0, 14.4, 41.0, 47.1, 52.8, 128.6, 129.0, 130.5, 131.51, 131.54, 140.4, 159.8, 168.3; IR (neat):*v*=2986, 1732, 1605, 1450, 1288, 1155, 1118, 880, 653 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 298 (5) [M^+], 267 (16), 199 (27), 147 (34), 99 (100), 72 (89); Anal. $C_{13}H_{18}N_2O_4S$ Calcd. C, 52.33; H, 6.08; N, 9.39. found C, 52.41; H, 6.23; N, 9.18%.

Procedure for the synthesis of **3f**: To a 10 mL two-necked round-bottom flask with a mixture of 4-isopropylbenzenesulfonyl azide (0.225 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3f**. 0.205 g, 73% yield.

m.p. 60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.14-1.16 (t, *J* = 7.3 Hz, 3H), 1.24-1.27 (m, 9H), 2.92-2.98 (m, 1H), 3.36-3.40 (q, *J* = 7.2 Hz, 2H), 3.46-3.50 (q, *J* = 7.2 Hz, 2H), 7.28-7.31 (m, 2H), 7.78-7.81 (m, 2H), 8.16 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 23.7, 34.1, 40.9, 47.0, 126.4, 126.7, 140.1, 153.0, 158.1; IR (neat):*v*=2963, 1611, 1447, 1346, 1270, 1137, 1083, 876, 659 cm^{-1}; MS (EI, 70 eV): *m*/*z*

(%): 282 (6) [M^+], 189 (15), 149 (14), 99 (43), 69 (100); Anal. $C_{14}H_{22}N_2O_2S$ Calcd. C, 59.54; H, 7.85; N, 9.92. found C, 59.42; H, 7.93; N, 9.96%.

Procedure for the synthesis of **3g**: To a 10 mL two-necked round-bottom flask with a mixture of 4-chlorobenzenesulfonyl azide (0.218 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C) for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3g**. 0.195 g, 71% yield.

m.p. 90-91 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.13-1.16 (t, J = 7.3 Hz, 3H), 1.25-1.28 (t, J = 7.3 Hz, 3H), 3.37-3.42 (q, J = 7.2 Hz, 2H), 3.46-3.50 (q, J = 7.3 Hz, 2H), 7.42-7.44 (m, 2H), 7.80-7.84 (m, 2H), 8.14 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 41.1, 47.2, 127.9, 128.9, 138.0, 141.2, 158.1; IR (neat):v=2977, 1614, 1447, 1343, 1299, 1151, 1083, 954, 879, 633 cm^{-1}; MS (EI, 70 eV): m/z (%): 274 (10) [M^+], 276 (4), 181 (23), 111 (57), 99 (100), 72 (95); Anal. $C_{11}H_{15}ClN_2O_2S$ Calcd. C, 48.08; H, 5.50; N, 10.20. found C, 48.09; H, 5.40; N, 10.31%.

Procedure for the synthesis of **3h**: To a 10 mL two-necked round-bottom flask with a mixture of 4-methoxylbenzenesulfonyl azide (0.213 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C) for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:2) as eluent to give the purified product **3h**. 0.178 g, 66% yield.

m.p. 72-73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.12-1.15 (t, J = 7.3 Hz, 3H), 1.24-1.27 (t, J = 7.3 Hz, 3H), 3.35-3.40 (q, J = 7.2 Hz, 2H), 3.44-3.49 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 6.92-6.95 (m, 2H), 7.80-7.82 (m, 2H), 8.14 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 40.9, 47.0, 55.5, 113.8, 128.3, 134.6, 157.9, 162.2; IR (neat):v=2945, 1606, 1455, 1377, 1291, 1255, 1136, 876, 671 cm^{-1}; MS (EI, 70 eV): m/z (%): 270 (26) [M^+], 177 (29), 171 (26), 99 (100), 73 (57); Anal. $C_{12}H_{18}N_2O_3S$ Calcd. C, 53.31; H, 6.71; N, 10.36. found C, 53.48; H, 6.51; N, 10.35%.

Procedure for the synthesis of **3i**: To a 10 mL two-necked round-bottom flask with a mixture of 3-nitrobenzenesulfonyl azide (0.228 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane

(3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3i**. 0.185 g, 65% yield.
m.p. 53 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.16-1.19 (t, *J* = 7.3 Hz, 3H), 1.29-1.32 (t, *J* = 7.3 Hz, 3H), 3.43-3.47 (q, *J* = 7.2 Hz, 2H), 3.49-3.53 (q, *J* = 7.2 Hz, 2H), 7.68-7.71 (t, *J* = 8.0 Hz, 1H), 8.19 (s, 1H), 8.23-8.25 (d, *J* = 7.5 Hz, 1H), 8.35-8.37 (m, 1H), 8.71 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.4, 41.3, 47.4, 121.7, 126.3, 130.1, 132.2, 144.8, 148.0, 158.4; IR (neat):*v*=2979, 1603, 1525, 1385, 1155, 1115, 885, 869, 664 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 285 (9) [M^+], 192 (27), 122 (21), 99 (100), 72 (88); Anal. $C_{11}H_{15}N_3O_4S$ Calcd. C, 46.31; H, 5.30; N, 14.73. found C, 46.48; H, 5.10; N, 14.76%.

Procedure for the synthesis of **3j**: To a 10 mL two-necked round-bottom flask with a mixture of 2-thienylsulfonyl azide (0.189 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C) for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3j**. 0.153 g, 62% yield.
m.p. 59-60 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.16-1.19 (t, *J* = 7.3 Hz, 3H), 1.26-1.29 (t, *J* = 7.3 Hz, 3H), 3.38-3.42 (q, *J* = 7.2 Hz, 2H), 3.48-3.52 (q, *J* = 7.2 Hz, 2H), 7.02-7.03 (q, *J* = 2.8 Hz, 1H), 7.49-7.50 (q, *J* = 2.0 Hz, 1H), 7.58-7.59 (q, *J* = 1.7 Hz, 1H), 8.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.1, 14.5, 41.2, 47.3, 126.9, 130.3, 130.5, 144.3, 158.3; IR (neat):*v*=2969, 1616, 1449, 1337, 1290, 1135, 885, 742, 671 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 246 (15) [M^+], 147 (33), 99 (100), 72 (86); Anal. $C_9H_{14}N_2O_2S_2$ Calcd. C, 43.88; H, 5.73; N, 11.37. found C, 43.98; H, 5.47; N, 11.34%.

Procedure for the synthesis of **3k**: To a 10 mL two-necked round-bottom flask with a mixture of 4-methylbenzylsulfonyl azide (0.211 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh)

with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3k**. 0.209 g, 78% yield.
m.p. 84-85 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.04-1.07 (t, *J* = 7.3 Hz, 3H), 1.15-1.18 (t, *J* = 7.3 Hz, 3H), 2.33 (s, 3H), 3.13-3.15 (q, *J* = 7.2 Hz, 2H), 3.41-3.44 (q, *J* = 7.2 Hz, 2H), 4.23 (s, 2H), 7.12-7.14 (d, *J* = 8.0 Hz, 2H), 7.22-7.23 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.0, 14.4, 21.2, 40.8, 46.8, 59.3, 127.3, 129.1, 130.8, 138.1, 159.5; IR (neat):*v*=2969, 1606, 1451, 1340, 1295, 1114, 952, 900, 705 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 268 (21) [M^+], 204 (93), 175 (41), 105 (100), 99 (77), 77 (64), 72 (82); Anal. $C_{13}H_{20}N_2O_2S$ Calcd. C, 58.18; H, 7.51; N, 10.44. found C, 58.29; H, 7.53; N, 10.35%.

Procedure for the synthesis of **3l**: To a 10 mL two-necked round-bottom flask with a mixture of *n*-butylsulfonyl azide (0.163 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added triethylamine (0.14 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3l**. 0.2 g, 91% yield.
light yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 0.92-0.95 (t, *J* = 7.5 Hz, 3H), 1.19-1.22 (t, *J* = 7.3 Hz, 3H), 1.26-1.29 (t, *J* = 7.3 Hz, 3H), 1.42-1.48 (m, 2H), 1.73-1.79 (m, 2H), 3.00-3.03 (m, 2H), 3.37-3.42 (q, *J* = 7.2 Hz, 2H), 3.48-3.52 (q, *J* = 7.2 Hz, 2H), 8.04 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 11.9, 13.6, 14.5, 21.5, 25.7, 40.8, 47.0, 53.6, 158.3; IR (neat):*v*=2962, 2874, 1606, 1452, 1346, 1267, 1121, 872, 613 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 220 (19) [M^+], 163 (17), 99 (91), 72 (100); HRMS (ESI) calcd for $C_9H_{20}N_2O_2S$ ([M+Na]$^+$) 243.1138, found 243.1130.

Procedure for the synthesis of **3m**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.236 mL, 1.5 mmol) in anhydrous 1,4-dioxane (3 mL), was added dimethylethylamine (0..237 mL, 2.2 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3m**. 0.104 g, 46% yield.

m.p. 132-133 °C (lit.[7] 136-137 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ= 2.40 (s, 3H), 3.01 (s, 3H), 3.12 (s, 3H), 7.25-7.27 (d, *J* = 8.5 Hz, 2H), 7.76-7.78 (d, *J* = 8.0 Hz, 2H), 8.13 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 21.5, 35.5, 41.4, 126.5, 129.3, 139.6, 142.4, 159.1; IR (neat):*v*=1626, 1436, 1334, 1280, 1147, 1084, 912, 850, 672 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 226 (24) [M^+], 91 (73), 71 (100).

Procedure for the synthesis of **3n**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added tri-*n*-butylamine (0.238 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with petroleum ether/acetone (5:1-2:1) as eluent to give the pure product **3n**. 0.229 g, 74% yield.
viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 0.84-0.87 (t, *J* = 7.3 Hz, 3H), 0.91-0.94 (t, *J* = 7.3 Hz, 3H), 1.24-1.31 (m, 4H), 1.49-1.52 (m, 2H), 1.55-1.58 (m, 2H), 2.38 (s, 3H), 3.28-3.31 (t, *J* = 7.3 Hz, 2H), 3.37-3.40 (t, *J* = 7.5 Hz, 2H), 7.24-7.25 (d, *J* = 8.0 Hz, 2H), 7.73-7.76 (m, 2H), 8.14 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 13.4, 13.5, 19.4, 19.7, 21.3, 28.5, 30.5, 45.7, 52.1, 126.1, 129.0, 139.7, 142.0, 158.7; IR (neat):*v*=2958, 2872, 1603, 1455, 1345, 1281, 1144, 1086, 671 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 310 (4) [M^+], 267 (41), 155 (93), 113 (78), 91 (100); HRMS (ESI) calcd for $C_{16}H_{26}N_2O_2S$ ([M+Na]$^+$) 333.1607, found 333.1603.

Procedure for the synthesis of **3o**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added tri-*n*-hexylamine (0.339 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with petroleum ether/acetone (5:1-2:1) as eluent to give the pure product **3o**. 0.231 g, 63% yield.
viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 0.82-0.84 (t, *J* = 6.8 Hz, 3H), 0.87-0.90 (t, *J* = 7.5 Hz, 3H), 1.19-1.30 (m, 12H), 1.50-1.59 (m, 4H), 2.39 (s, 3H), 3.27-3.29 (t, *J* = 8.5 Hz, 2H), 3.37-3.40 (t, *J* = 8.5 Hz, 2H), 7.23-7.25 (d, *J* = 8.0 Hz, 2H), 7.73-7.76 (m, 3H), 8.13 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 13.9, 21.4, 22.4, 22.4, 26.0, 26.3, 26.5, 28.6, 31.2, 31.3, 46.2, 52.5, 126.3, 129.2, 139.9, 142.1, 158.8; IR (neat):*v*=2928, 2857, 1604, 1453, 1346, 1297, 1282, 1145, 1087, 672 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 366

(3) [M^+], 295 (65), 211 (88), 155 (41), 141 (85), 91 (100); HRMS (ESI) calcd for $C_{20}H_{34}N_2O_2S$ ([M+Na]$^+$) 389.2233, found 389.2251.

Procedure for the synthesis of **3p**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added *N*,*N*-diethylcyclohexylamine (0.183 mL, 1 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of remained 2H-DEAD with petroleum ether/acetone (6:1-4:1) as eluent to give the pure product **3p**. 0.175 g, 57% yield.

m.p. 94-96 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.12-1.32 (m, 8H), 1.48-1.51 (m, 2.4H), 1.68-1.71 (m, 2.4H), 1.85-1.88 (m, 4H), 2.39 (s, 3.6H), 3.18-3.24 (m, 1H), 3.30-3.35 (q, *J* = 7.0 Hz, 0.4H), 3.41-3.45 (q, *J* = 7.0 Hz, 2H), 4.14-4.20 (m, 0.2H), 7.24-7.27 (m, 2.4H), 7.45-7.77 (m, 2.4H), 8.16 (s, 0.2H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 13.3, 17.0, 21.4, 25.0, 25.3, 25.4, 25.6, 30.0, 32.6, 40.6, 43.2, 56.2, 63.0, 126.29, 126.3, 129.2, 139.9, 140.0, 142.11, 142.14, 157.3, 158.6; MS (ESI): ([M+Na]$^+$) 331.3; HRMS (ESI) calcd for $C_{16}H_{24}N_2O_2S$ ([M]$^+$) 308.1558, found 308.1562.

Procedure for the synthesis of **3q**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesullfonyl azide (0.197 g, 1 mmol) and DEAD (0.471 mL, 3 mmol) was added *N,N*-diethylaniline (0.159 mL, 1 mmol). The resulting mixture was stirred for 6 h at 75°C. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3q**. 0.154 g, 51% yield.

m.p. 100-101 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.16-1.19 (t, *J* = 7.0 Hz, 3H), 2.41 (s, 3H), 3.95-3.99 (q, *J* = 6.7 Hz, 2H), 7.18-7.20 (d, *J* = 7.0 Hz, 2H), 7.28-7.29 (d, *J* = 7.5 Hz, 2H), 7.33-7.36 (t, *J* = 7.0 Hz, 1H), 7.42-7.45 (t, *J* = 7.0 Hz, 2H), 7.81-7.82 (d, *J* = 7.5 Hz, 2H), 8.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.4, 21.5, 44.1, 123.6, 126.6, 127.7, 129.4, 129.9, 139.2, 141.9, 142.7, 158.1; IR (neat):*v*=3084, 1609, 1534, 1436, 1349, 1292, 1106, 856, 664 cm^{-1}; MS (EI, 70 ev): *m*/*z* (%): 302 (15) [M^+], 209 (18), 147 (100), 119 (41), 91 (73); Anal. $C_{16}H_{18}N_2O_2S$ Calcd. C, 63.55; H, 6.00; N, 9.26. found C, 63.53; H, 6.03; N, 9.22%.

Procedure for the synthesis of **3r**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesullfonyl azide (0.197 g, 1 mmol) and DEAD (0.471 mL, 3 mmol) was added *N*,*N*-diethyl-3-methylaniline (0.163 g, 1 mmol). The resulting mixture was stirred for 6 h at 75°C. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3r**. 0.066 g, 21% yield.

m.p. 53-54 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.15-1.18 (t, *J* = 7.0 Hz, 3H), 2.39 (s, 3H), 2.41 (s, 3H), 3.93-3.97 (q, *J* = 7.0 Hz, 2H), 6.98-6.99 (d, *J* = 6.0 Hz, 2H), 7.14-7.16 (d, *J* = 8.0 Hz, 1H), 7.26-7.31 (m, 3H), 7.80-7.82 (d, *J* = 8.5 Hz, 2H), 8.44 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.4, 21.3, 21.5, 44.0, 120.5, 124.2, 126.6, 128.4, 129.4, 129.6, 139.2, 140.1, 141.9, 142.6, 158.1; MS (ESI): ($[M+Na]^+$) 339.1; HRMS (ESI) calcd for $C_{17}H_{20}N_2O_2S$ ($[M]^+$) 316.1245, found 316.1244.

Procedure for the synthesis of **3s**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesullfonyl azide (0.197 g, 1 mmol) and DEAD (0.471 mL, 3 mmol) was added *N*-ethyl-*N*-benzylaniline (0.211 g, 1 mmol). The resulting mixture was stirred for 6 h at 75°C. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with petroleum ether/acetone (4:1-6:1) as eluent to give the pure product **3s**. 0.124 g, 34% yield.

m.p. 104-105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 2.42 (s, 3H), 5.11 (s, 2H), 7.10-7.14 (m, 4H), 7.14-7.21 (m, 3H), 7.25-7.30 (m, 3H), 7.33-7.37 (m, 2H), 7.75-7.77 (d, *J* = 8.5 Hz, 2H), 8.63 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 21.5, 52.6, 123.5, 126.5, 127.7, 127.8, 127.9, 128.6, 129.3, 129.8, 135.1, 139.0, 142.1, 142.7, 158.7; MS (ESI): ($[M+Na]^+$) 387.2; HRMS (ESI) calcd for $C_{21}H_{20}N_2O_2S$ ($[M]^+$) 364.1245, found 364.1248.

Procedure for the synthesis of **3t**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesulfonyl azide (0.197 g, 1 mmol) and DEAD (0.314 mL, 2 mmol) in anhydrous 1,4-dioxane (3 mL), was added *N*-ethylmorpholine (0.254 mL, 2 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of remained 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3t**. 0.219 g, 82% yield.

m.p. 176-177 °C (lit.[8] 169-170 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ= 2.40 (s, 3H), 3.49-3.51 (t, *J* = 4.5 Hz, 2H), 3.67 (s, 4H), 3.73-3.75 (t, *J* = 4.5 Hz, 2H), 7.26-7.28 (d, *J* = 7.5 Hz, 2H),7.76-7.77 (t, *J* = 8.0 Hz, 2H), 8.21 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 21.5, 44.2, 50.3, 65.9, 66.8, 126.6, 129.4, 139.2, 142.7, 157.7; IR (neat):*v*=2870, 1607, 1438, 1338, 1290, 1137, 1085, 852, 669 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 268 (14) [M^+], 155 (11), 113 (100), 91 (70).

Procedure for the synthesis of **3u**: To a 10 mL two-necked round-bottom flask with a mixture of 2-phthanylsullfonyl azide (0.233 g, 1 mmol) and DEAD (0.314 mL, 2 mmol) in anhydrous 1,4-dioxane (3 mL), was added *N*-ethylmorpholine (0.254 mL, 2 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3u**. 0.240 g, 79% yield.
m.p. 202-203 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 3.51 (s, 2H), 3.67 (s, 4H), 3.74 (s, 2H), 7.56-7.62 (m, 2H), 7.86-7.89 (m, 2H), 7.92-7.96 (m, 2H), 8.27 (s, 1H), 8.47 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 44.3, 50.4, 65.9, 66.8, 122.5, 127.3, 127.3, 127.8, 128.4, 129.0, 129.2, 132.2, 134.6, 138.9, 157.8; IR (neat):*v*=2913, 1609, 1438, 1340, 1293, 1144, 1109, 949, 858, 666 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 304 (37) [M^+], 191 (5), 127 (100), 113 (79), 86 (43); Anal. $C_{15}H_{16}N_2O_3S$ Calcd. C, 59.19; H, 5.30; N, 9.20. found C, 59.24; H, 5.25; N, 9.13%.

Procedure for the synthesis of **3v**: To a 10 mL two-necked round-bottom flask with a mixture of 3-nitrobenzenesullfonyl azide (0.228 g, 1 mmol) and DEAD (0.314 mL, 2 mmol) in anhydrous 1,4-dioxane (3 mL), was added *N*-ethylmorpholine (0.254 mL, 2 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C） for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product **3v**. 0.224 g, 75% yield.
m.p. 154-155 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 3.57-3.59 (t, *J* = 4.8 Hz, 2H), 3.72 (s, 4H), 3.79-3.81 (t, *J* = 4.8 Hz, 2H), 7.69-7.72 (t, *J* = 8.0 Hz, 1H), 8.23-8.26 (m, 2H), 8.37-8.39 (d, *J* = 8.0 Hz, 1H), 8.69 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 44.5, 50.6, 65.8, 66.8, 121.9, 126.5, 130.2, 132.3, 144.2, 148.1, 158.0; IR (neat):*v*=2974, 1608, 1432, 1364, 1293, 1237, 1143, 1109, 860, 668 cm^{-1}; MS (EI, 70 eV): *m*/*z*

(%): 299 (7) [M^+], 186 (9), 113 (100), 86 (54); Anal. $C_{11}H_{13}N_3O_5S$ Calcd. C, 44.14; H, 4.38; N, 14.04. found C, 44.21; H, 4.35; N, 14.10%.

Procedure for the synthesis of **3w**: To a 10 mL two-necked round-bottom flask with a mixture of diphenylphosphoryl azide (0.275 g, 1 mmol) and DEAD (0.471 mL, 3 mmol) was added triethylamine (0.42 mL, 3 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C) for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-3:1) as eluent to give the pure product **3w**. 0.140 g, 42% yield.
Viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.03-1.06 (t, J = 7.5 Hz, 3H), 1.15-1.17 (t, J = 8.0 Hz, 3H), 3.24-3.29 (q, J = 7.0 Hz, 2H), 3.40-3.44 (q, J = 7.0 Hz, 2H), 7.10-7.12 (m, 2H), 7.24-7.30 (m, 8H), 8.03, 8.07 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 11.9, 14.5, 39.7, 46.1, 120.66, 120.69, 124.4, 129.4, 151.4, 151.5, 159.95, 160.03; MS (ESI): ($[M+H]^+$) 333.2; HRMS (ESI) calcd for $C_{17}H_{21}N_2O_3P$ ($[M]^+$) 332.1290, found 332.1294.

Procedure for the synthesis of **3x**: To a 10 mL two-necked round-bottom flask with a mixture of benzyloxycarbonyl azide (0.177 g, 1 mmol) and DEAD (0.471 mL, 3 mmol) was added triethylamine (0.42 mL, 3 mmol). The resulting mixture was stirred for 1 h at 10-15°C, then at ambient temperature (about 25-30°C) for 4 h. Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (1:1-3:1) as eluent to give the pure product **3x**. 0.035 g, 15% yield.
Viscous oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.16-1.19 (t, J = 7.0 Hz, 3H), 1.23-1.25 (t, J = 8.0 Hz, 3H), 3.33-3.74 (q, J = 8.0 Hz, 2H), 3.53-3.57 (q, J = 7.0 Hz, 2H), 5.18 (s, 2H), 7.27-7.34 (m, 3H), 7.41-7.42 (d, J = 7.0 Hz, 2H), 8.48 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 12.2, 14.5, 40.4, 46.8, 67.4, 127.8, 128.3, 128.4, 136.9, 162.2, 164.7; MS (ESI): ($[M+H]^+$) 235.1; HRMS (ESI) calcd for $C_{13}H_{18}N_2O_2$ ($[M]^+$) 234.1368, found 234.1360.

Procedure for the synthesis of **3y** and **3z**: To a 10 mL two-necked round-bottom flask with a mixture of *p*-toluenesullfonyl azide (0.197 g, 1 mmol) and DEAD (0.157 mL, 1 mmol) in anhydrous 1,4-dioxane (3 mL), was added *N*-ethylpiperidine (0.137 mL, 1 mmol). The resulting mixture was stirred for 6 h at

ambient temperature (about 25-30°C). Then the mixture was evaporated to almost dryness under reduced pressure. Purification was done by column chromatography on silica gel (200-300 mesh) with petroleum ether/ethyl acetate (3:1-1:1) as eluent to give the crude product. Then the second column chromatography on silica gel (200-300 mesh) was used to remove a little amount of 2H-DEAD with diethyl ether/petroleum ether (2:1-5:1) as eluent to give the pure product. **3y**: 0.135 g, 51%; **3z**: 0.04 g, 14% yield. **3y**: m.p. 147-149 °C (lit.[8] 150 °C); ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.57-1.60 (m, 2H), 1.64-1.69 (m, 4H), 2.39 (s, 3H), 3.40-3.42 (t, *J* = 5.1 Hz, 2H), 3.58-3.60 (t, *J* = 5.8 Hz, 2H), 7.25-7.28 (t, *J* = 8.5 Hz, 2H), 7.75-7.78 (m, 2H), 8.12(s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 21.5, 23.9, 24.8, 26.4, 44.6, 51.9, 126.5, 129.3, 139.7, 142.3, 157.3; IR (neat):*v*=2944, 1604, 1444, 1357, 1293, 1145, 1085, 924, 873, 671 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 266 (7) [M^+], 155 (3), 111 (96), 91 (42), 84 (100).

3z: m.p. 109-110 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ= 1.12-1.15 (t, *J* = 7.0 Hz, 3H), 1.72-1.82 (m, 4H), 2.39 (s, 3H), 3.02-3.05 (t, *J* = 6.5 Hz, 2H), 3.32-3.34 (t, *J* = 6.0 Hz, 2H), 3.47-3.52 (q, *J* = 7.3 Hz, 2H), 7.24-7.25 (d, *J* = 8.0 Hz, 2H), 7.80-7.82 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ= 11.3, 19.6, 21.4, 22.3, 28.6, 45.5, 48.2, 126.2, 129.0, 141.5, 141.6, 165.2; IR (neat): *v*=2872, 1562, 1470, 1444, 1269, 1135, 823, 697, 657 cm^{-1}; MS (EI, 70 eV): *m*/*z* (%): 281 (6) [M^++1], 187 (9), 125 (82), 72 (57), 59 (100); Anal. $C_{14}H_{20}N_2O_2S$ Calcd. C, 59.97; H, 7.19; N, 9.99. found C, 60.01; H, 7.20; N, 9.97%.

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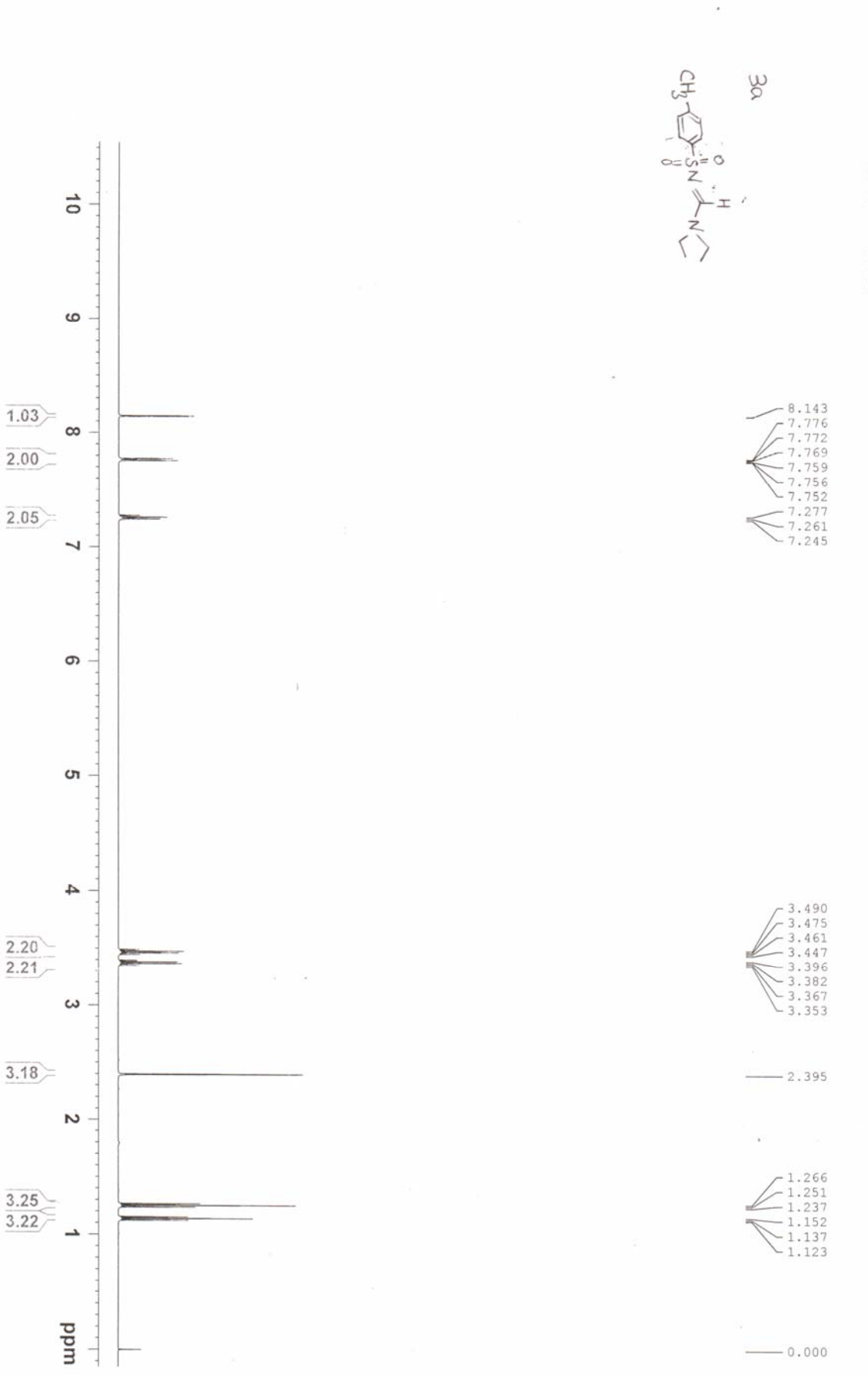
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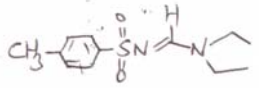
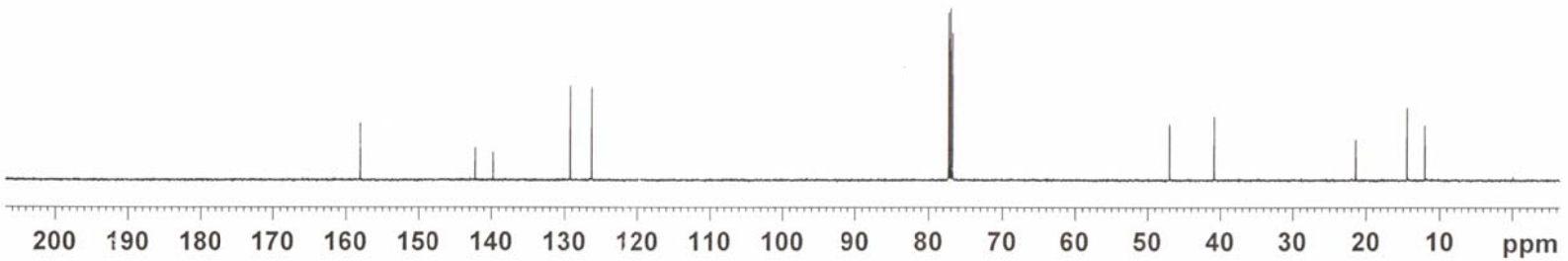
1.152
1.137
1.123
0.000
1.03
2.00
2.05
2.20
2.21
3.18
3.25
3.22
ppm

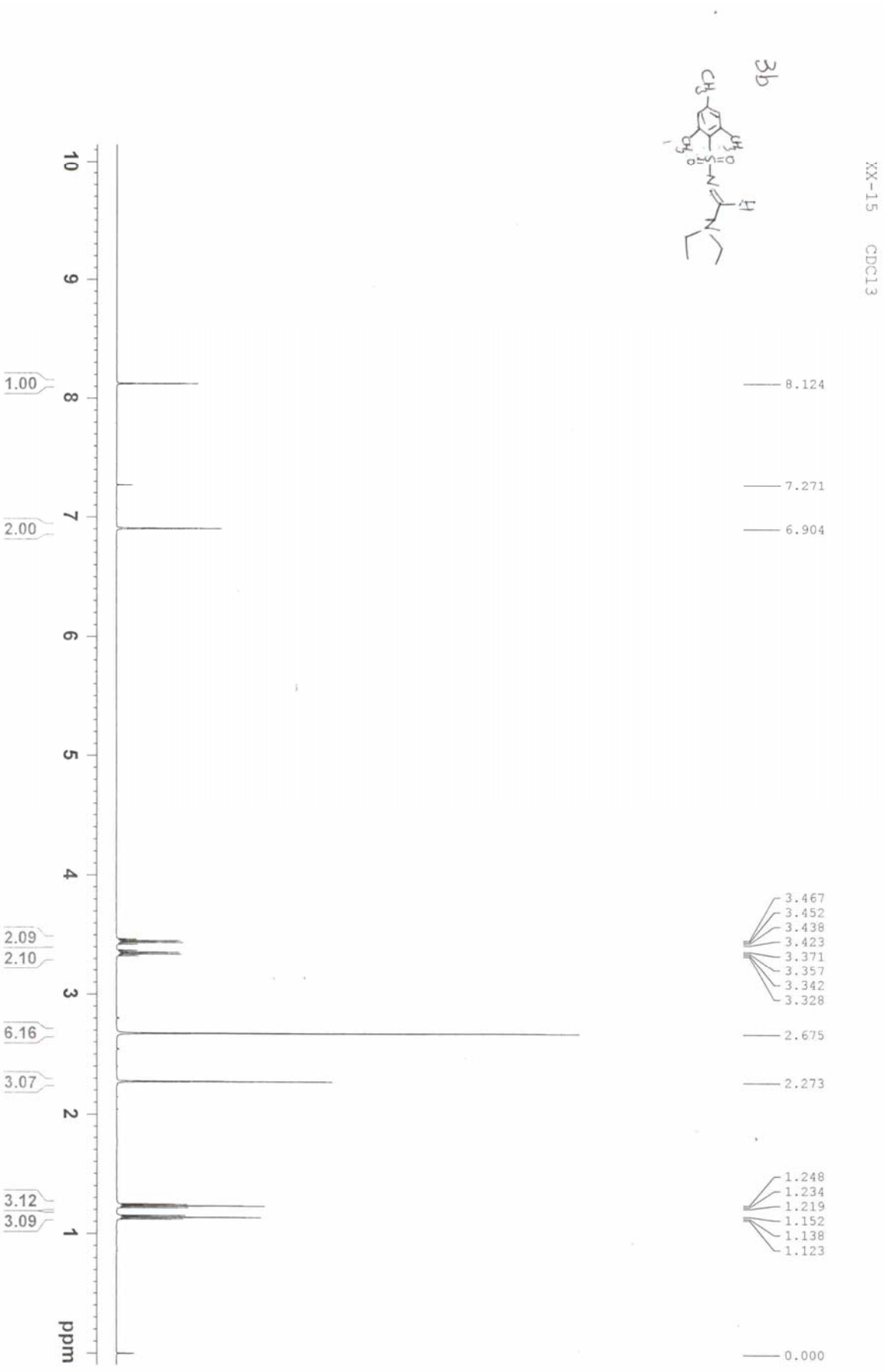
xxl-1 CDCl3

158.06
142.25
139.80
129.27
126.35
77.32
77.06
76.81
47.04
40.90
21.45
14.50
12.08

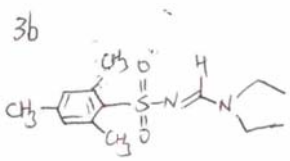
3a



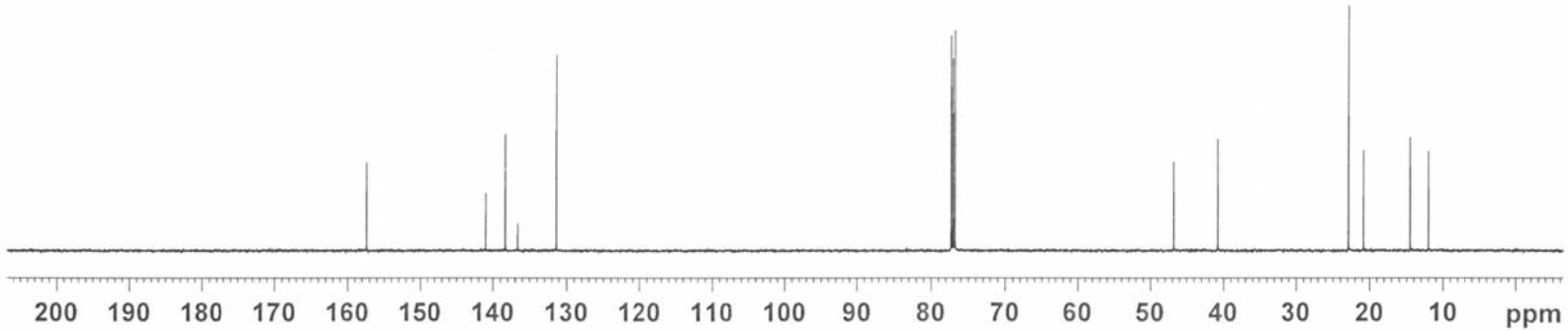


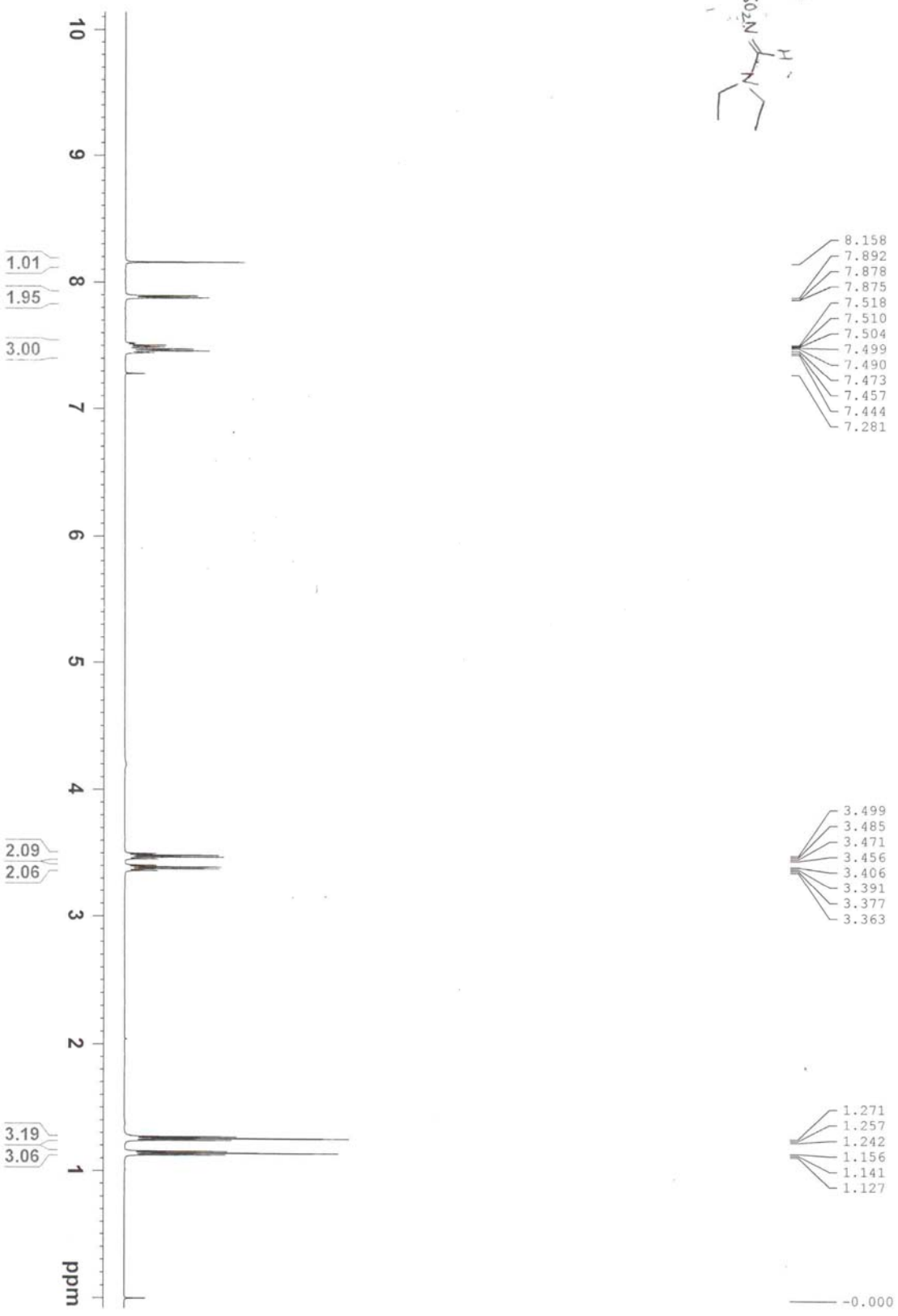

3b
XX-15 CDCl3
8.124
7.271
6.904
3.467
3.452
3.438
3.423
3.371
3.357
3.342
3.328
2.675
2.273
1.248
1.234
1.219
1.152
1.138
1.123
0.000
1.00
2.00
2.09
2.10
6.16
3.07
3.12
3.09
ppm

XX-15 CDCl3



157.42
141.05
138.34
136.64
131.42
77.32
77.06
76.81
46.82
40.82
22.93
20.87
14.54
12.04

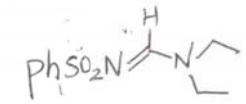


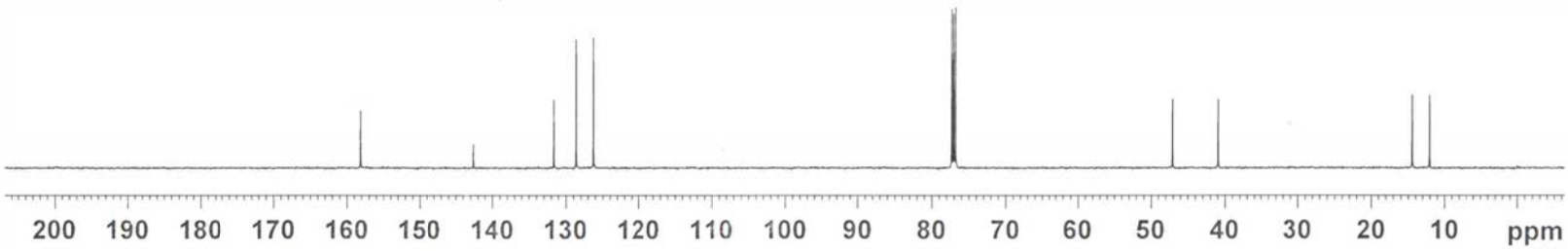

3c
PhSO2N
H
N
xx2 CDC13
8.158
7.892
7.878
7.875
7.518
7.510
7.504
7.499
7.490
7.473
7.457
7.444
7.281
3.499
3.485
3.471
3.456
3.406
3.391
3.377
3.363
1.271
1.257
1.242
1.156
1.141
1.127
-0.000
1.01
1.95
3.00
2.09
2.06
3.19
3.06
10
9
8
7
6
5
4
3
2
1
ppm

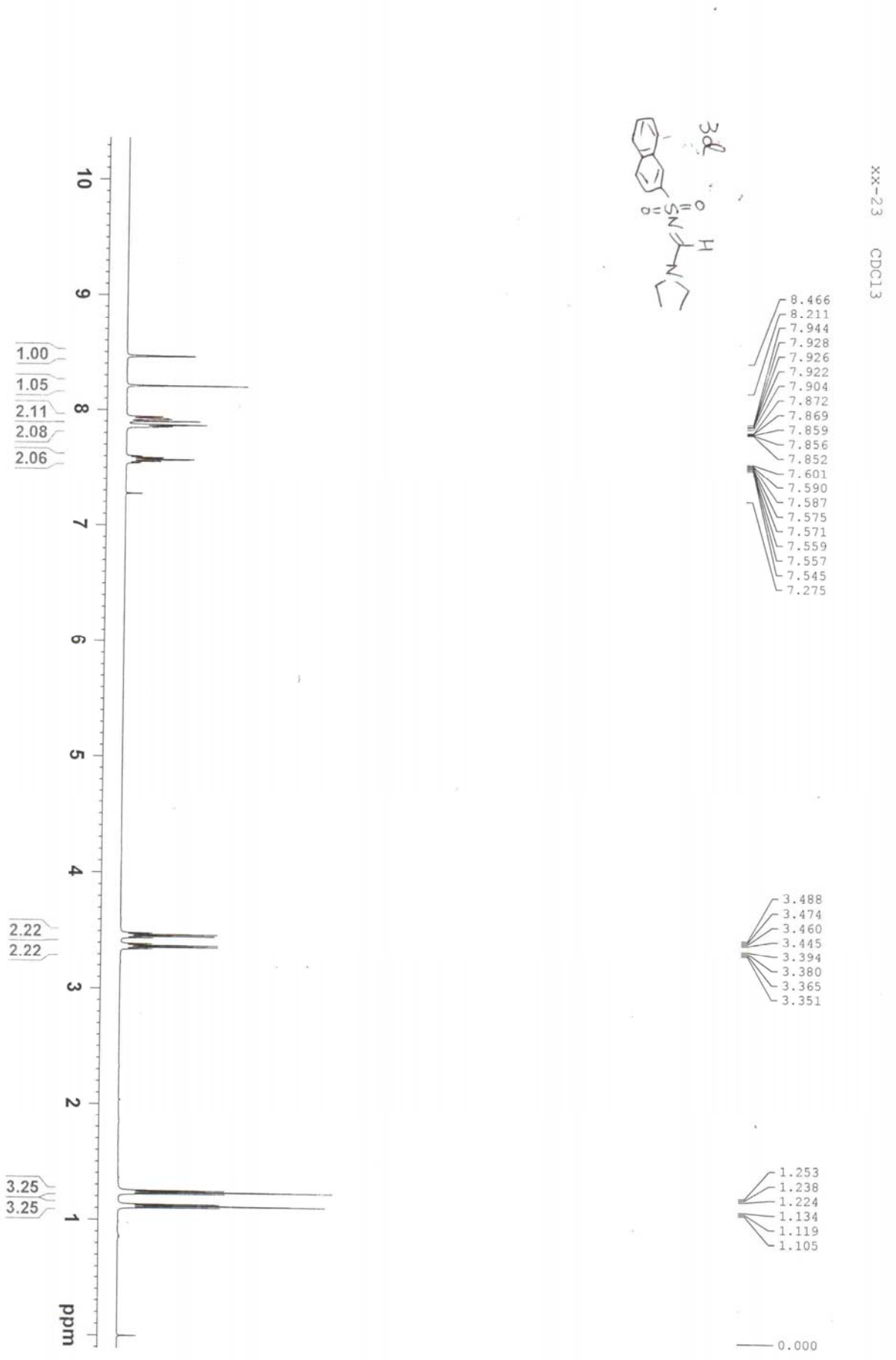
XX2 CDCl3

158.19
142.65
131.70
128.66
126.30
77.33
77.07
76.82
47.10
40.97
14.48
12.07

3c



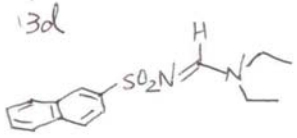


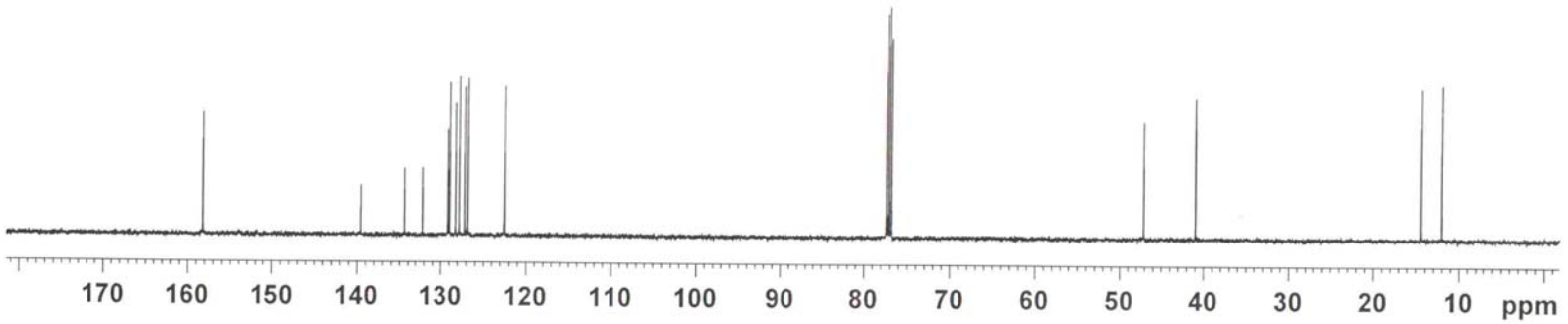

xx-23 CDCl3
3a
8.466
8.211
7.944
7.928
7.926
7.922
7.904
7.872
7.869
7.859
7.856
7.852
7.601
7.590
7.587
7.575
7.571
7.559
7.557
7.545
7.275
3.488
3.474
3.460
3.445
3.394
3.380
3.365
3.351
1.253
1.238
1.224
1.134
1.119
1.105
0.000
1.00
1.05
2.11
2.08
2.06
2.22
2.22
3.25
3.25
ppm

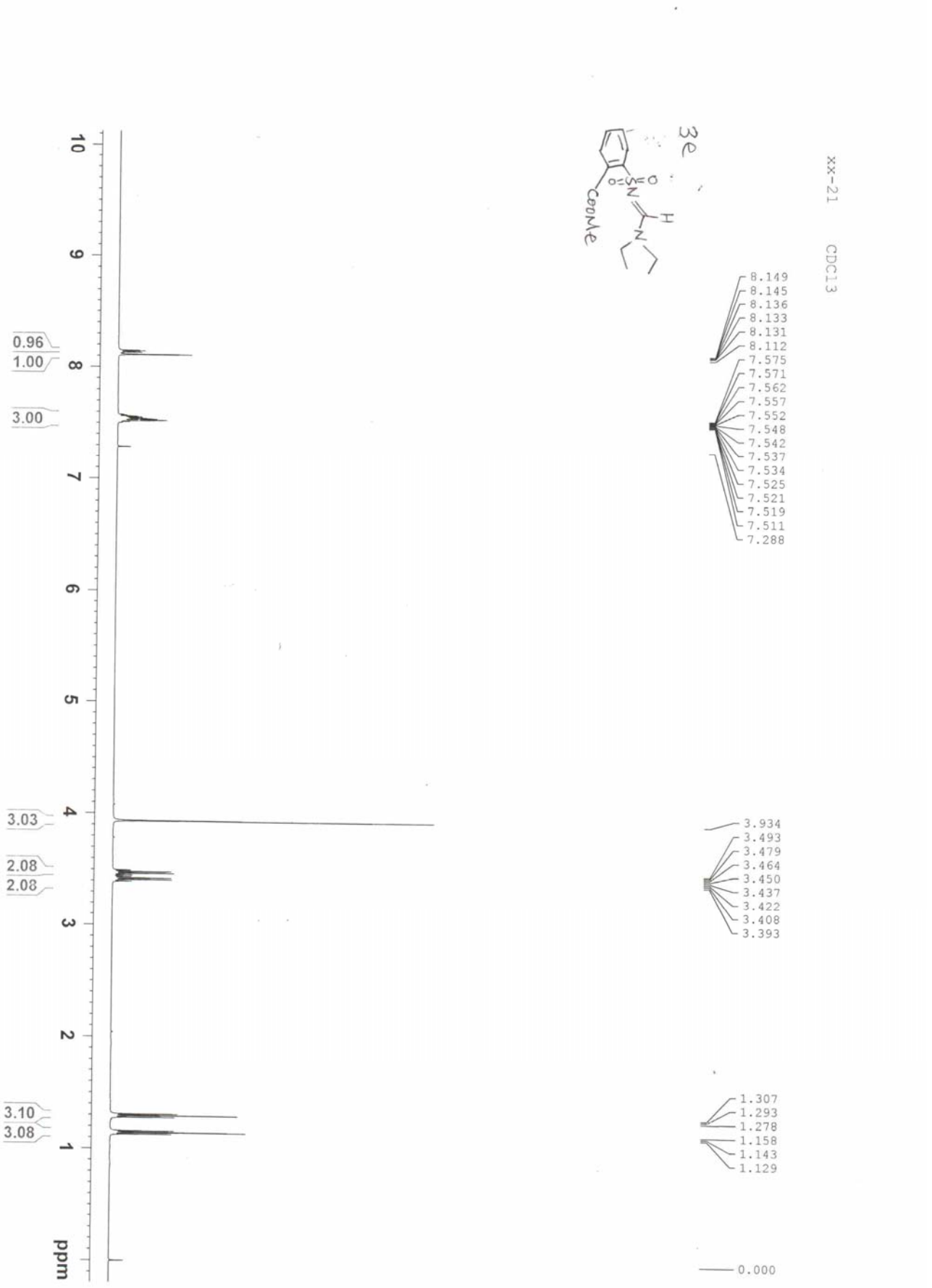
XX-23 CDCl3

158.21
139.57
134.45
132.19
129.16
128.94
128.23
127.81
127.17
126.87
122.51
77.36
77.11
76.85
47.14
40.99
14.48
12.06

3d



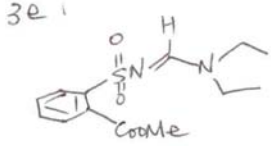


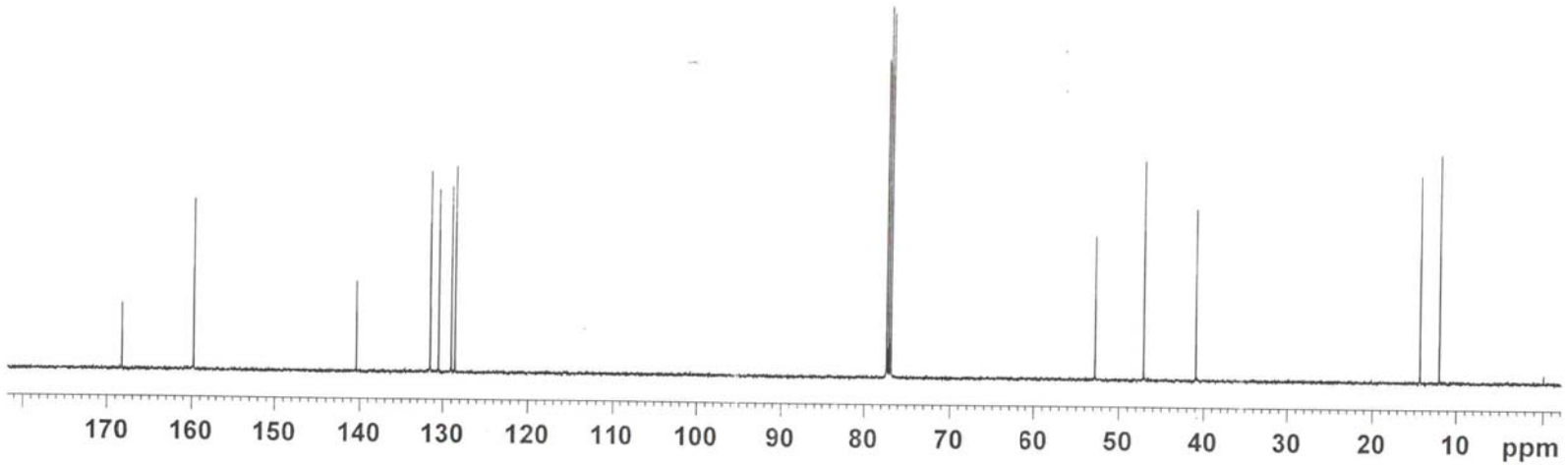

xx-21 CDCl3
3e
COOMe
8.149
8.145
8.136
8.133
8.131
8.112
7.575
7.571
7.562
7.557
7.552
7.548
7.542
7.537
7.534
7.525
7.521
7.519
7.511
7.288
3.934
3.493
3.479
3.464
3.450
3.437
3.422
3.408
3.393
1.307
1.293
1.278
1.158
1.143
1.129
0.000
0.96
1.00
3.00
3.03
2.08
2.08
3.10
3.08
ppm

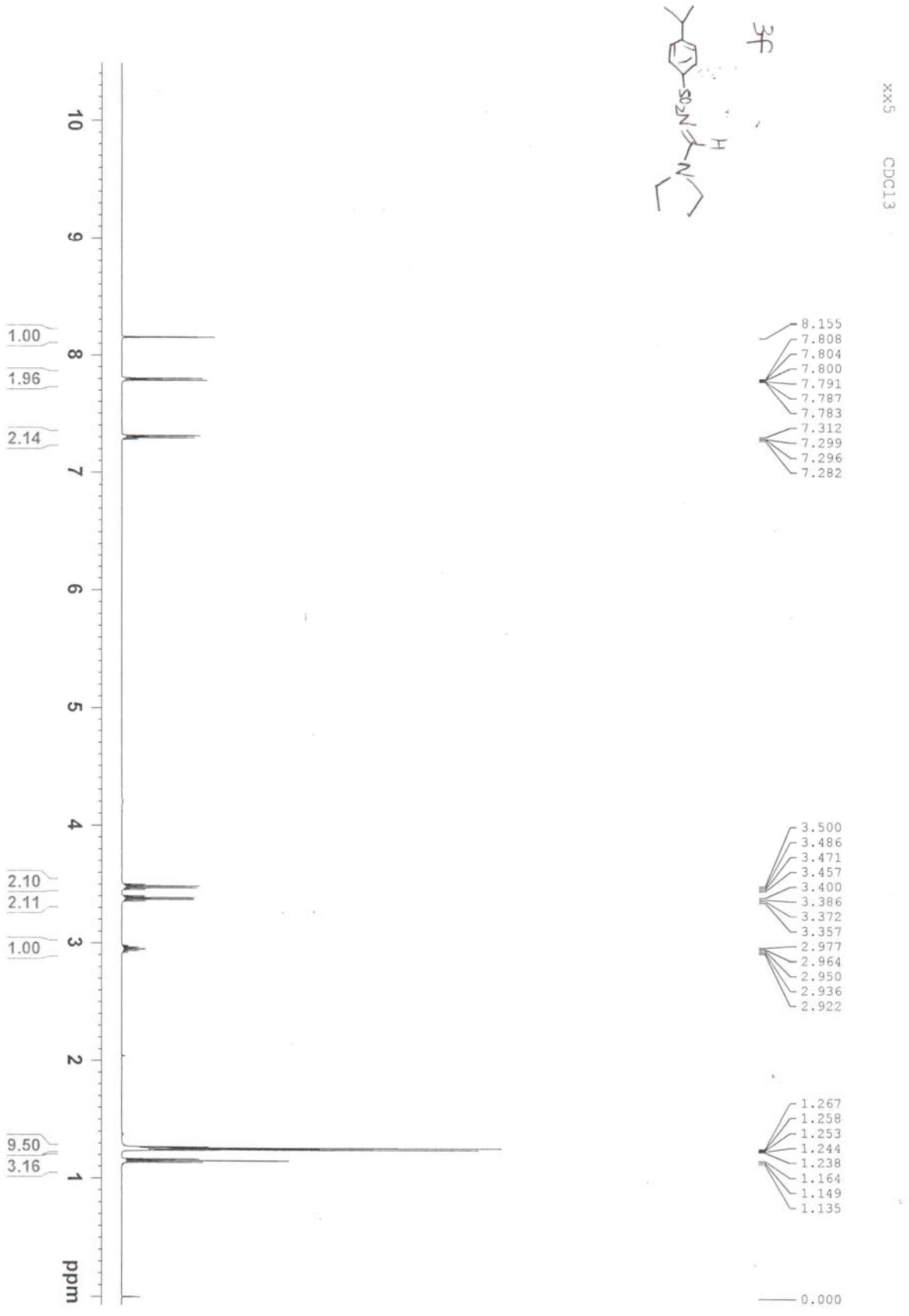
xx-21 CDCl3

168.31
159.76
140.42
131.54
131.51
130.53
129.02
128.58
77.34
77.09
76.83
52.84
47.14
40.96
14.39
12.03

3e



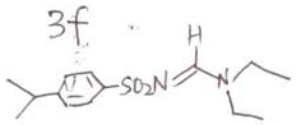


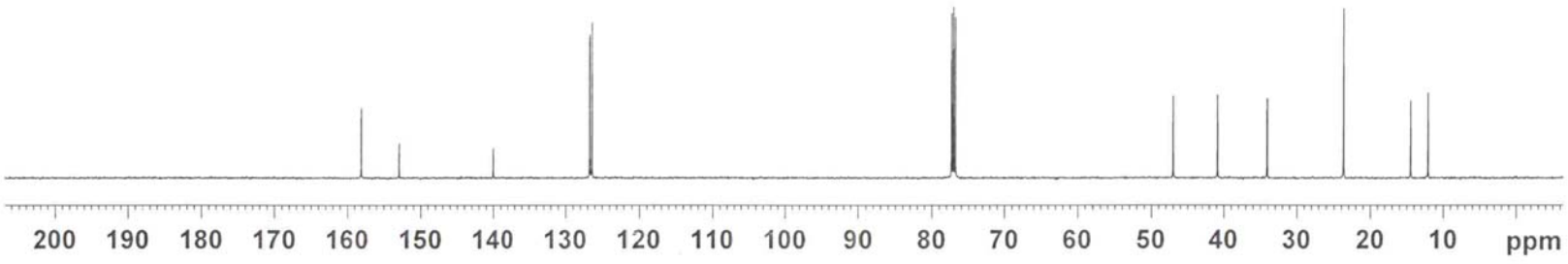

3f
xx5 CDC13
8.155
7.808
7.804
7.800
7.791
7.787
7.783
7.312
7.299
7.296
7.282
3.500
3.486
3.471
3.457
3.400
3.386
3.372
3.357
2.977
2.964
2.950
2.936
2.922
1.267
1.258
1.253
1.244
1.238
1.164
1.149
1.135
0.000
1.00
1.96
2.14
2.10
2.11
1.00
9.50
3.16
ppm

XX5 CDCl3

158.13
152.99
140.06
126.74
126.42
77.33
77.08
76.82
47.02
40.89
34.09
23.70
14.48
12.08

3f



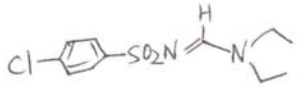


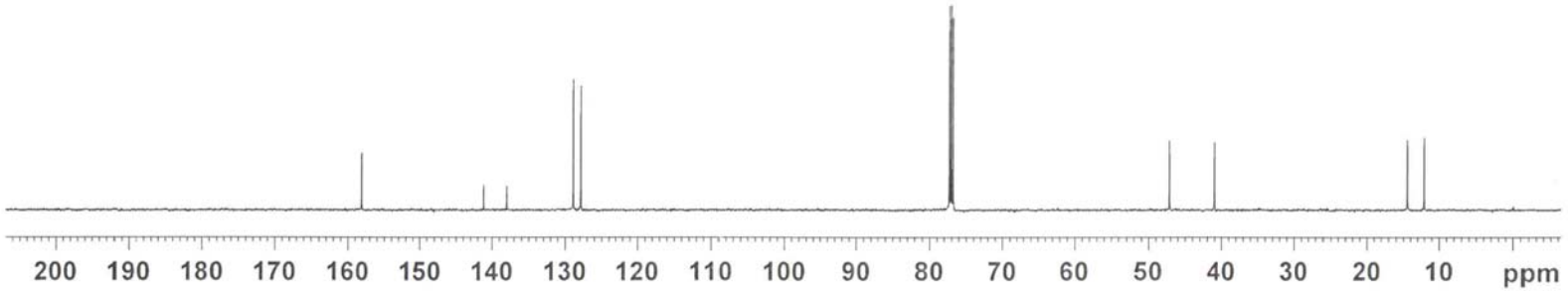
xx4 CDC13
3g
8.139
7.835
7.830
7.826
7.816
7.813
7.808
7.443
7.438
7.434
7.424
7.421
7.416
7.278
3.498
3.484
3.470
3.455
3.417
3.402
3.388
3.374
1.283
1.268
1.254
1.159
1.145
1.130
-0.000
1.00
1.96
1.96
2.12
2.13
3.35
3.02
ppm

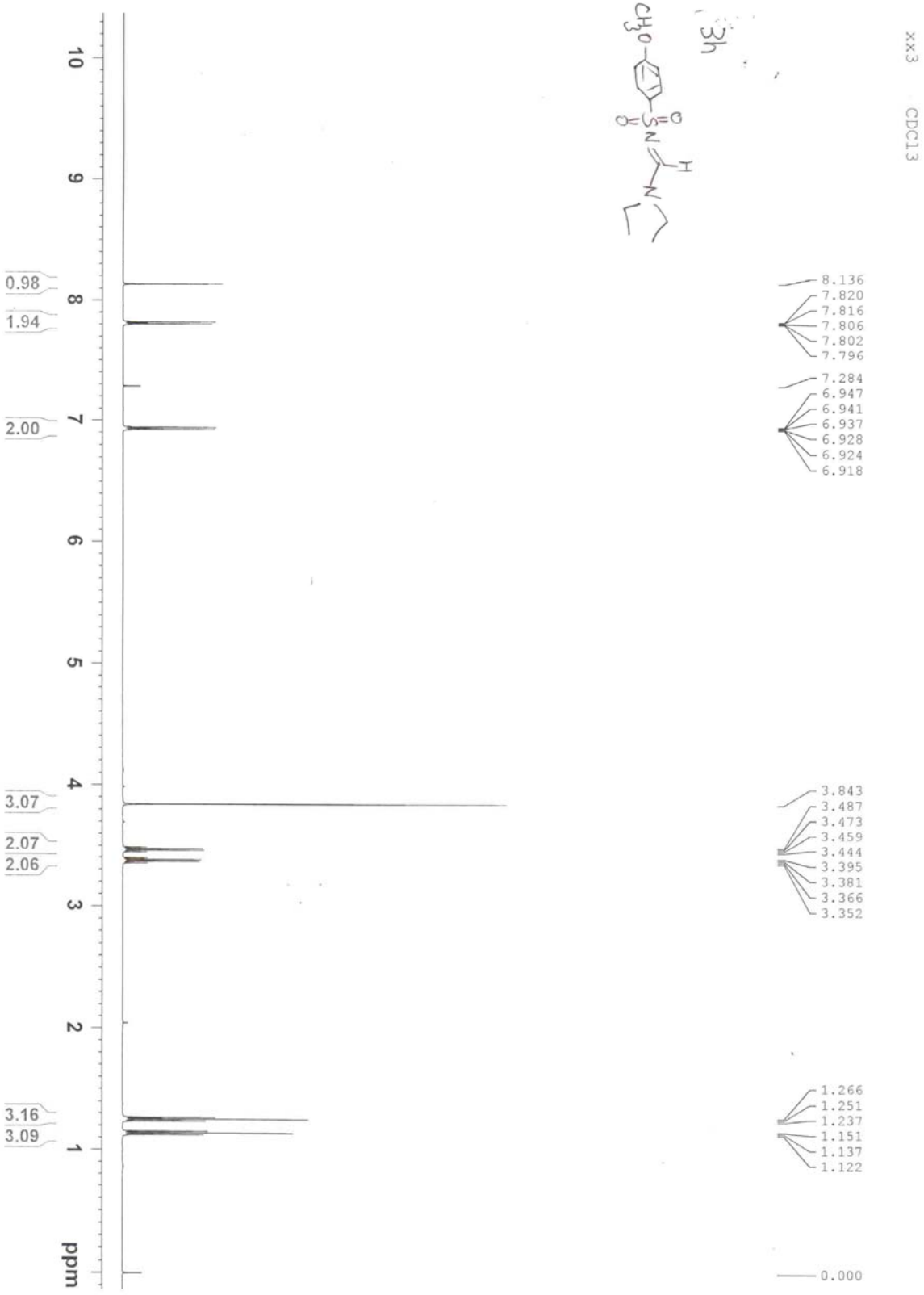
XX4 CDCl3

158.13
141.23
138.00
128.91
127.87
77.31
77.05
76.80
47.19
41.05
14.47
12.06

3g



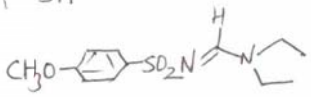


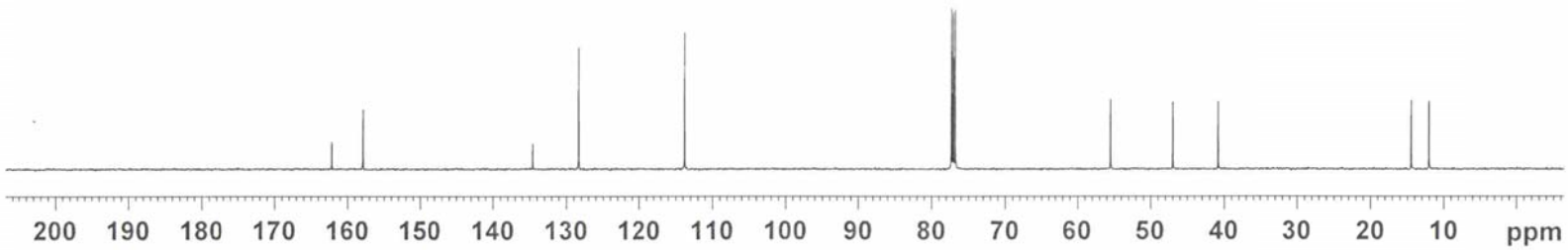

xx3
CDC13
3h
8.136
7.820
7.816
7.806
7.802
7.796
7.284
6.947
6.941
6.937
6.928
6.924
6.918
3.843
3.487
3.473
3.459
3.444
3.395
3.381
3.366
3.352
1.266
1.251
1.237
1.151
1.137
1.122
0.000
0.98
1.94
2.00
3.07
2.07
2.06
3.16
3.09
ppm

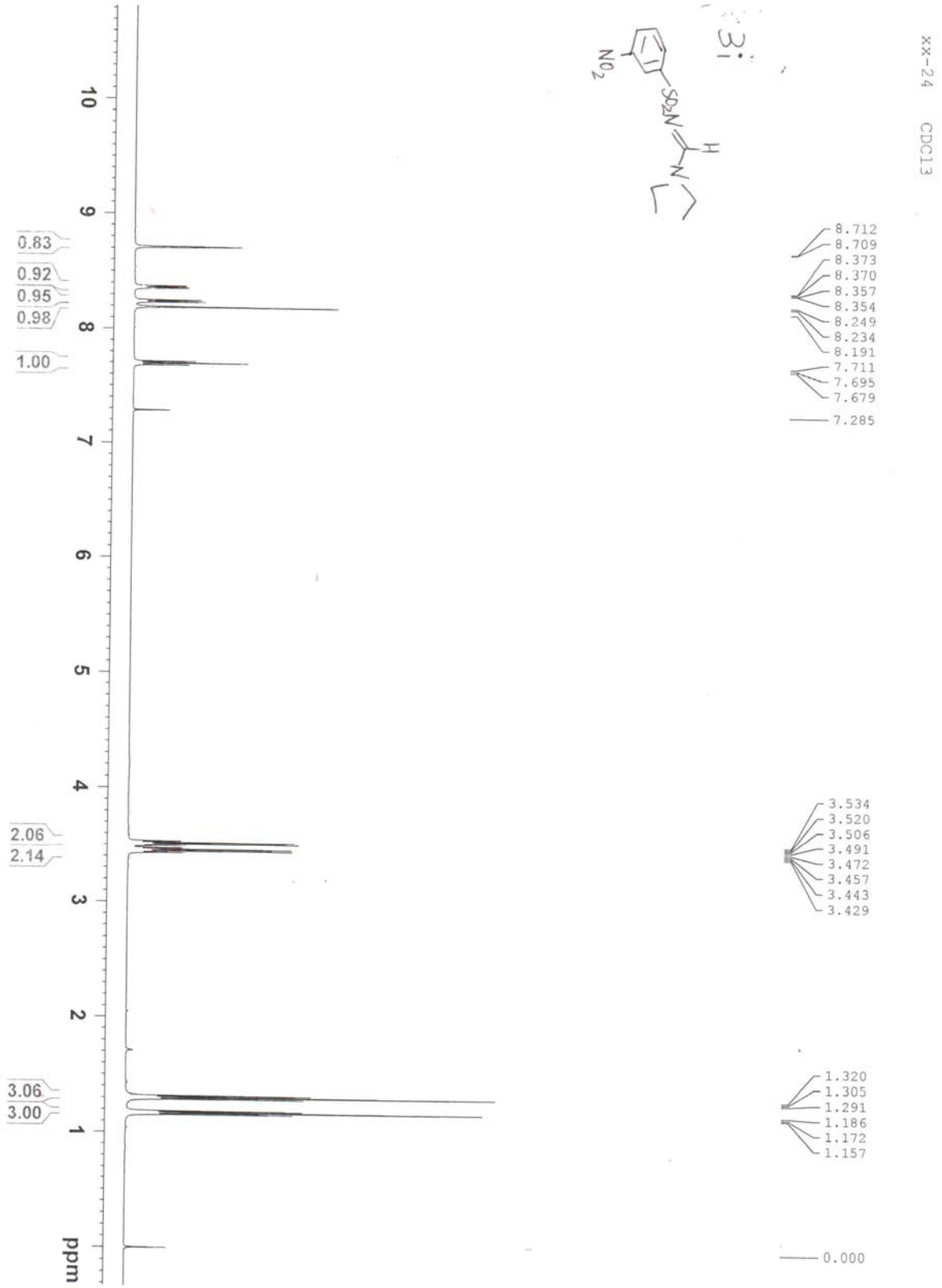
XX3 CDCl3

162.15
157.89
134.62
128.34
113.82
77.33
77.07
76.82
55.51
47.01
40.86
14.50
12.07

3h



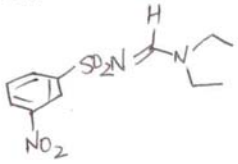


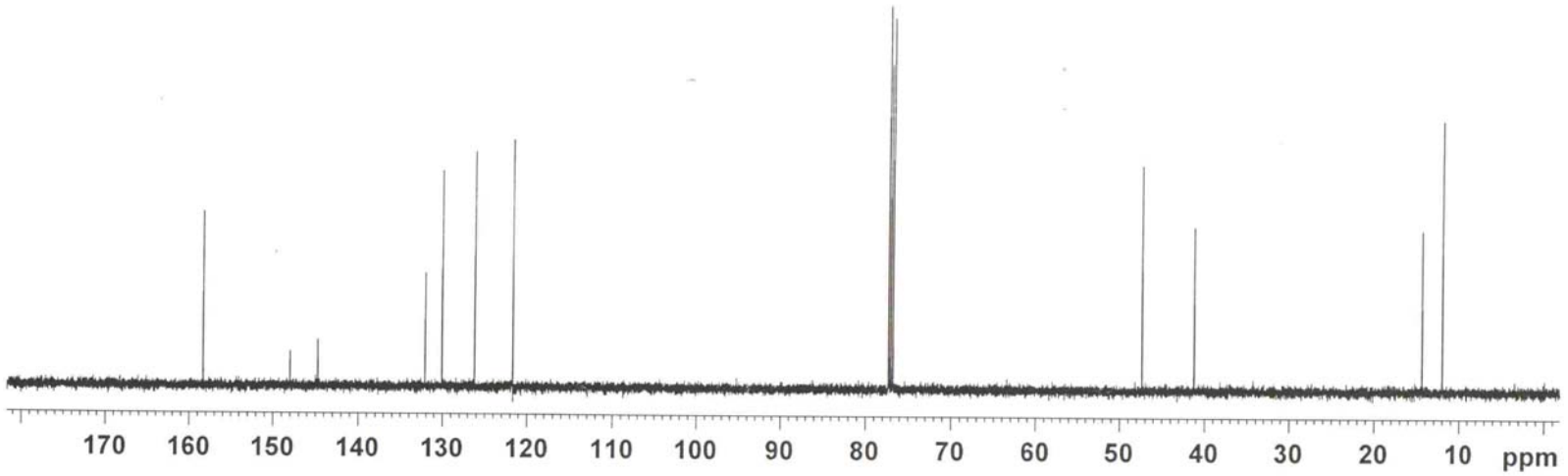

xx-24 CDC13
3i
NO2
SO2N
H
N
8.712
8.709
8.373
8.370
8.357
8.354
8.249
8.234
8.191
7.711
7.695
7.679
7.285
3.534
3.520
3.506
3.491
3.472
3.457
3.443
3.429
1.320
1.305
1.291
1.186
1.172
1.157
0.000
0.83
0.92
0.95
0.98
1.00
2.06
2.14
3.06
3.00
10
9
8
7
6
5
4
3
2
1
ppm

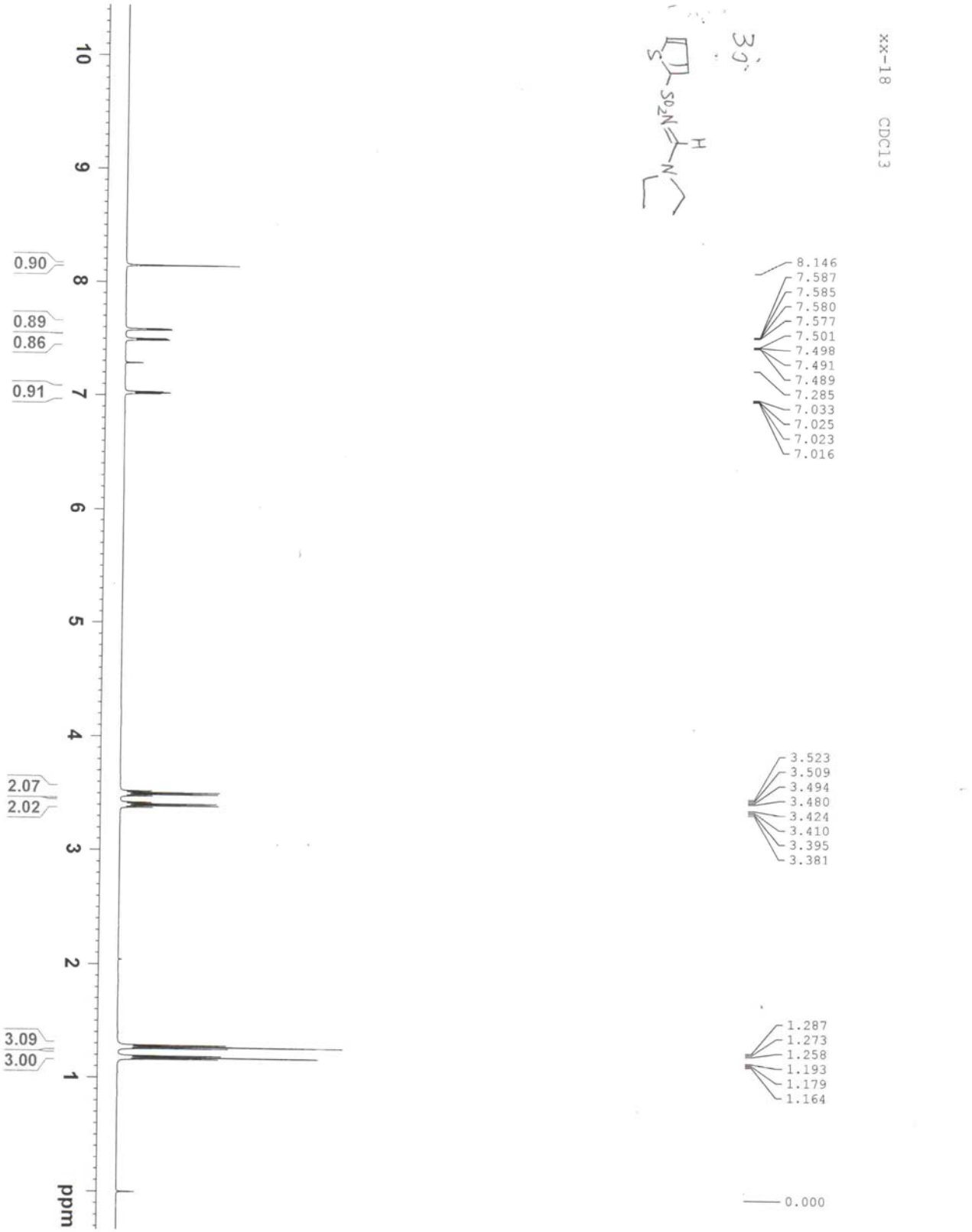
XX-24 CDCl3

158.37
148.04
144.78
132.15
130.08
126.25
121.72
77.32
77.06
76.81
47.42
41.27
14.43
12.05

3i



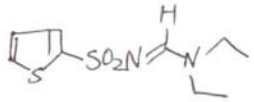


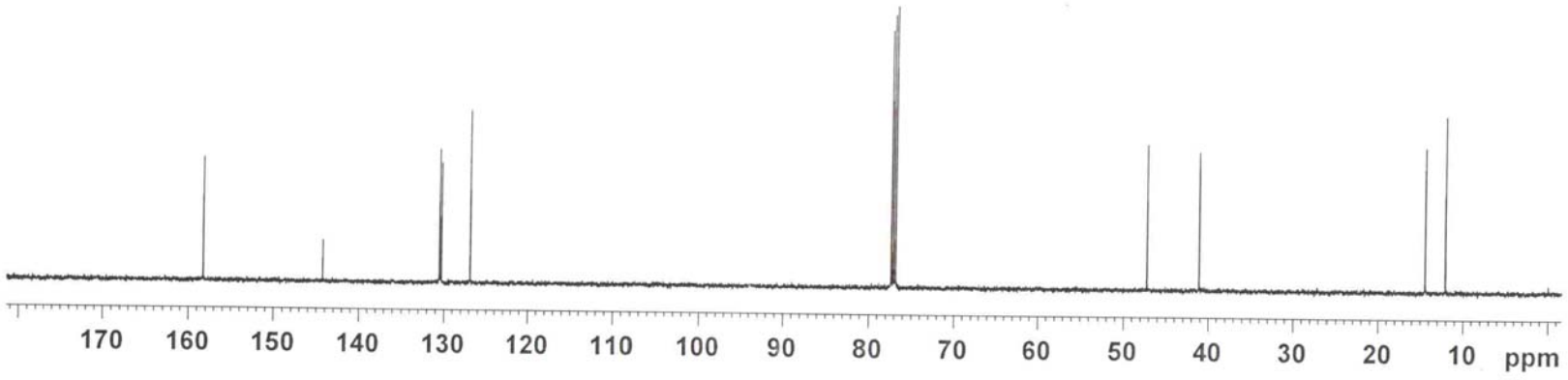

xx-18 CDCl3
3g
8.146
7.587
7.585
7.580
7.577
7.501
7.498
7.491
7.489
7.285
7.033
7.025
7.023
7.016
3.523
3.509
3.494
3.480
3.424
3.410
3.395
3.381
1.287
1.273
1.258
1.193
1.179
1.164
0.000
0.90
0.89
0.86
0.91
2.07
2.02
3.09
3.00
ppm

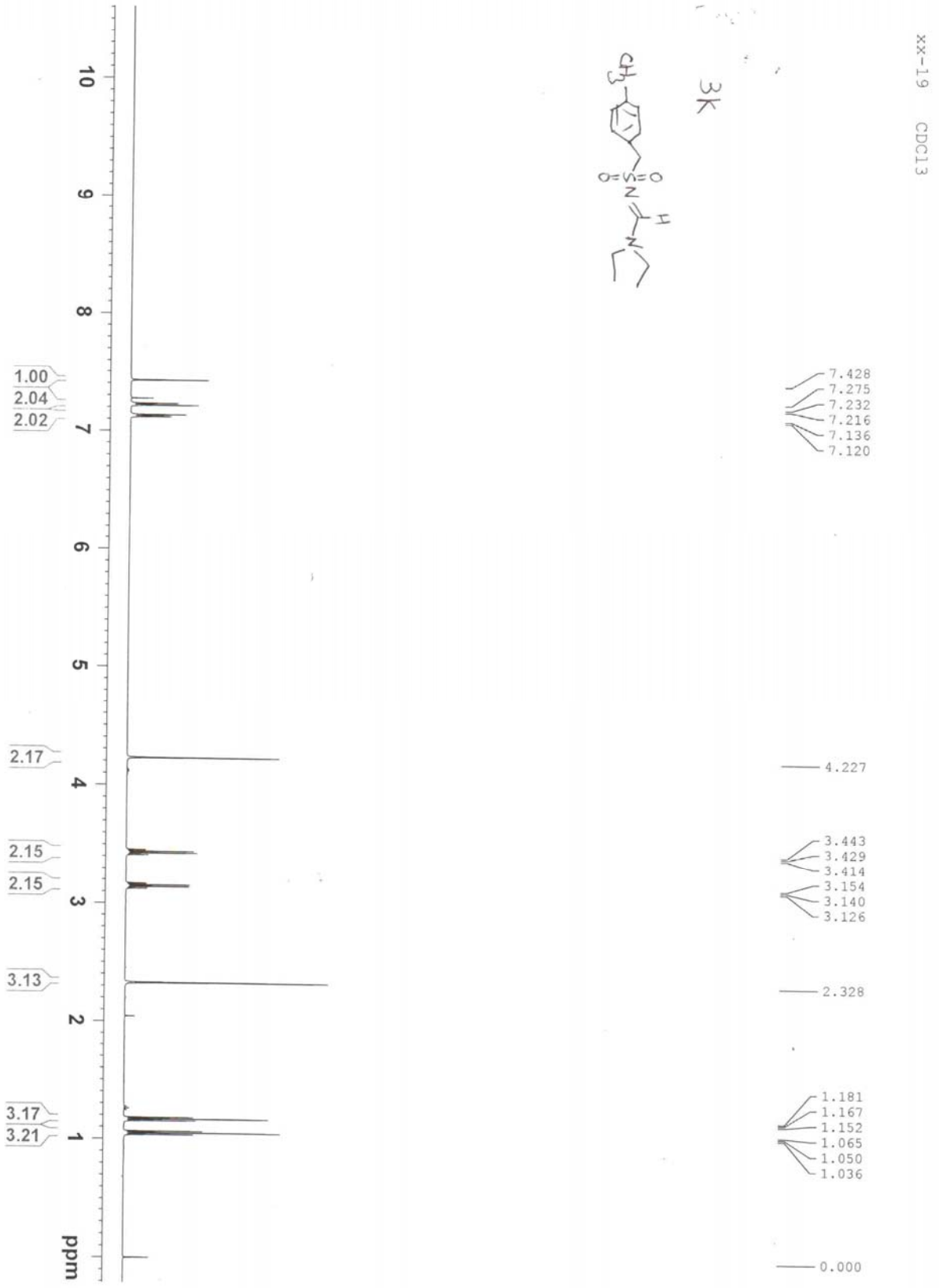
XX-18 CDCl3

158.27
144.25
130.51
130.29
126.90
77.34
77.09
76.83
47.28
41.16
14.48
12.13

3j



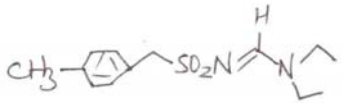


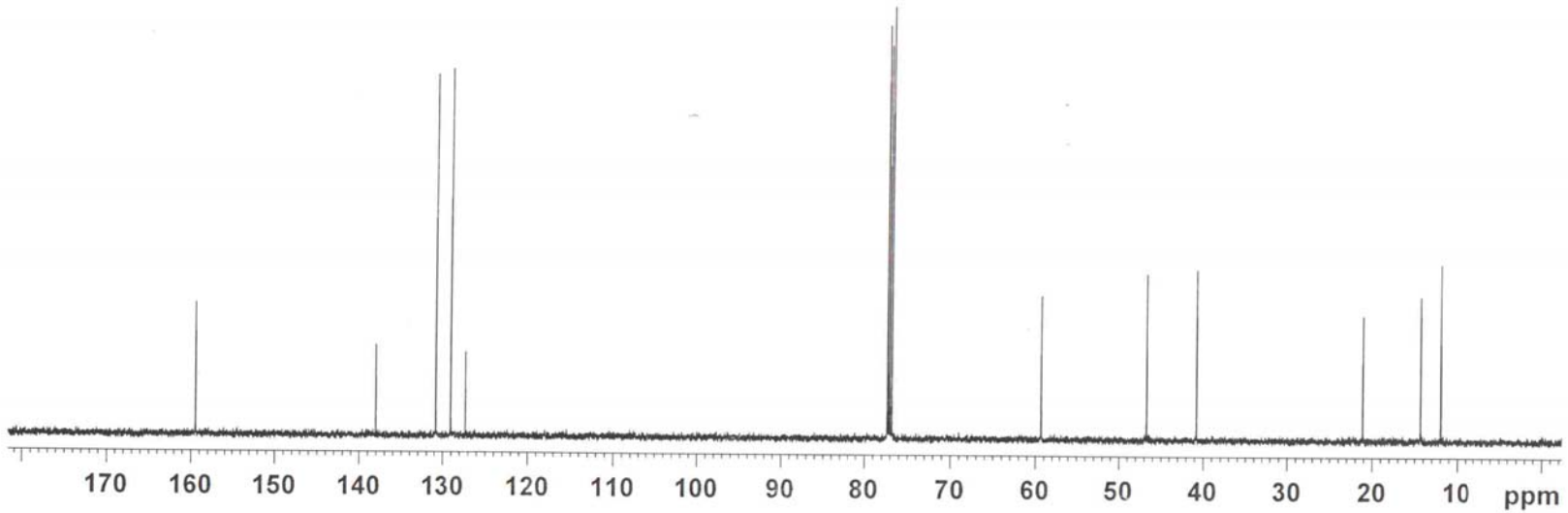

xx-19 CDC13
3k
7.428
7.275
7.232
7.216
7.136
7.120
4.227
3.443
3.429
3.414
3.154
3.140
3.126
2.328
1.181
1.167
1.152
1.065
1.050
1.036
0.000
1.00
2.04
2.02
2.17
2.15
2.15
3.13
3.17
3.21
ppm

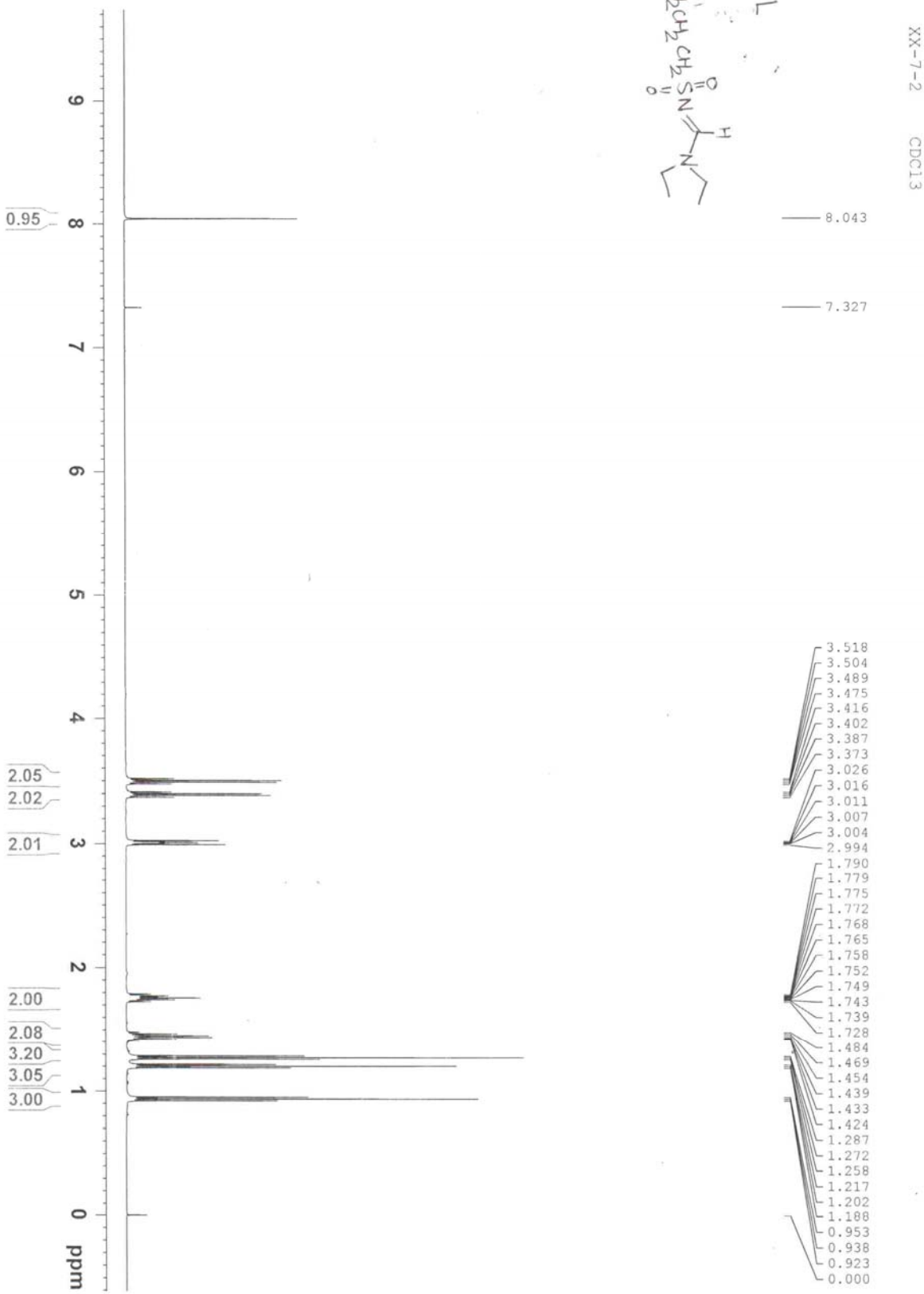
XX-19 CDCl3

159.47
138.05
130.81
129.07
127.33
77.32
77.07
76.81
59.33
46.75
40.82
21.15
14.38
12.00

3K






XX-7-2 CDC13
3L
8.043
7.327
3.518
3.504
3.489
3.475
3.416
3.402
3.387
3.373
3.026
3.016
3.011
3.007
3.004
2.994
1.790
1.779
1.775
1.772
1.768
1.765
1.758
1.752
1.749
1.743
1.739
1.728
1.484
1.469
1.454
1.439
1.433
1.424
1.287
1.272
1.258
1.217
1.202
1.188
0.953
0.938
0.923
0.000
0.95
2.05
2.02
2.01
2.00
2.08
3.20
3.05
3.00
9
8
7
6
5
4
3
2
1
0
ppm

XX-7-2 CDCl3

158.33

77.39
77.14
76.88

53.60

46.94

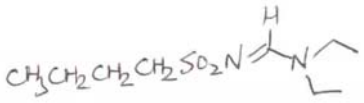
40.78

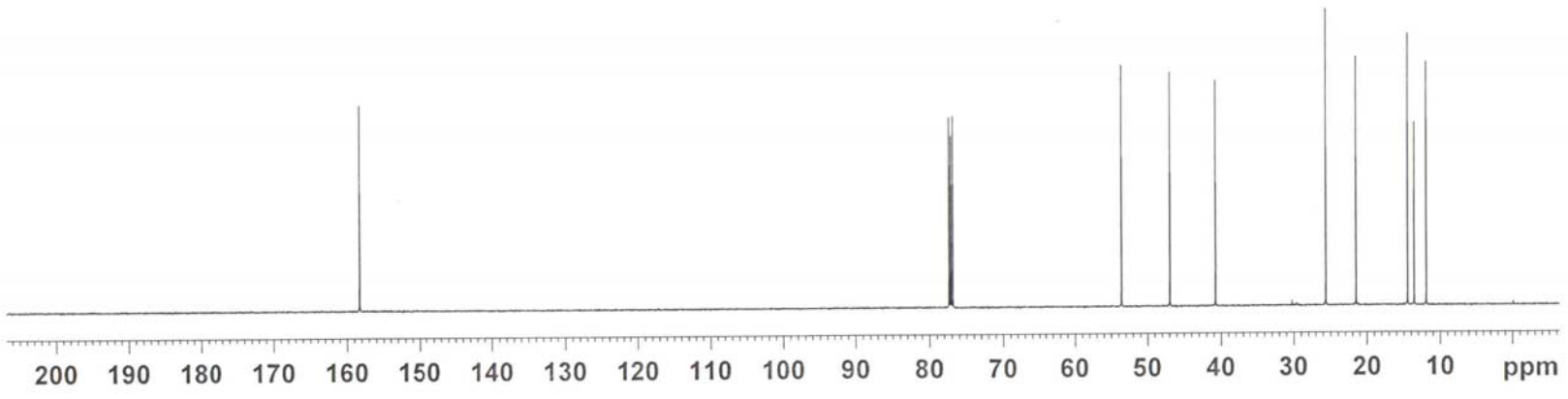
25.66

21.51

14.47
13.58
11.92

3L

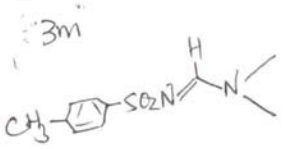


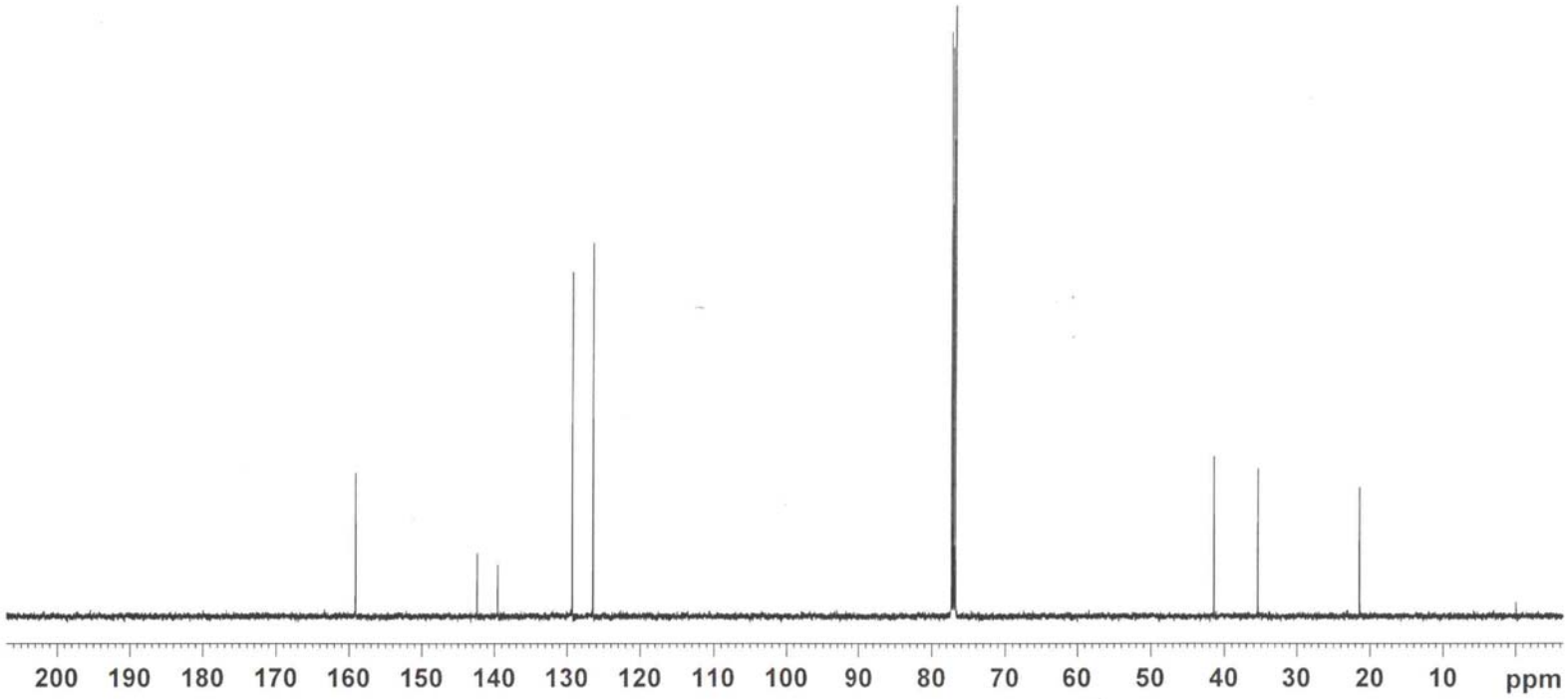


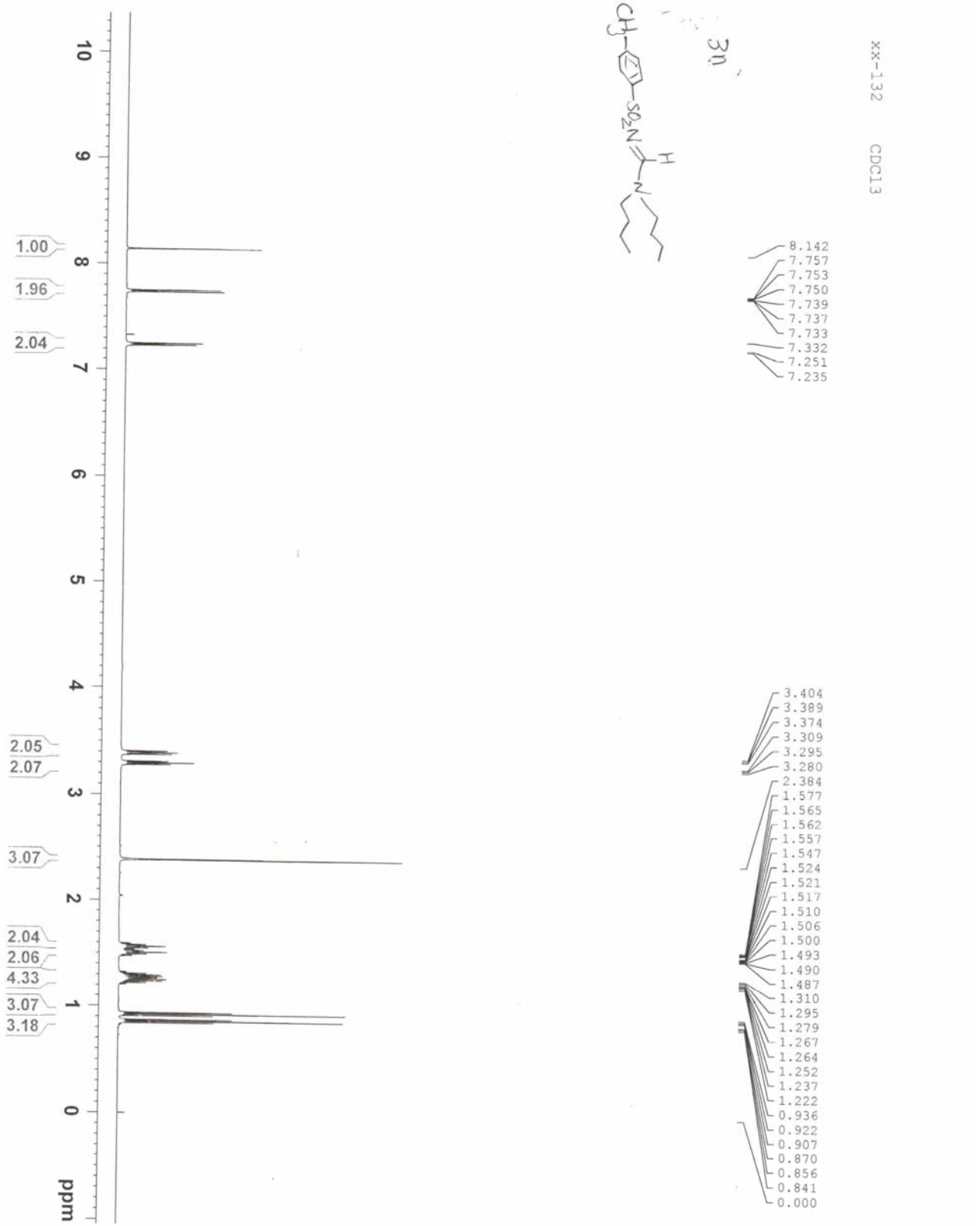
XX-34 CDC13
3m
8.131
7.780
7.764
7.272
7.265
7.248
3.119
3.009
2.397
0.000
1.03
2.03
2.20
3.32
3.20
3.22
ppm

XX-34 CDCl3

159.09
142.43
139.59
129.31
126.50
77.30
77.05
76.79
41.43
35.48
21.46



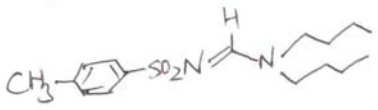


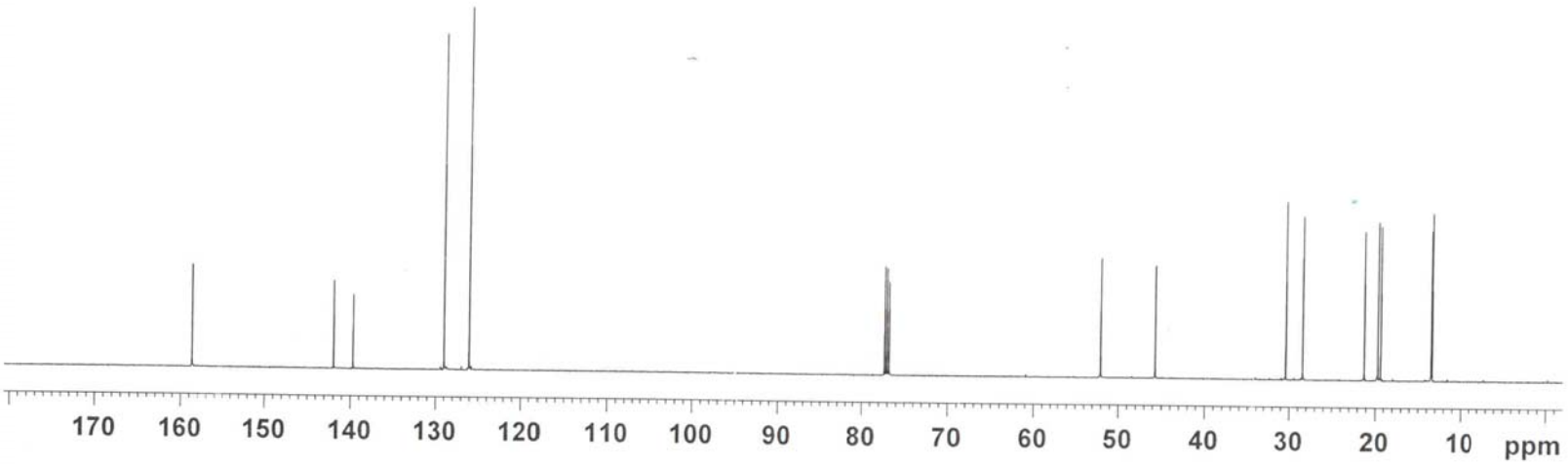

xx-132 CDCl3
3n
8.142
7.757
7.753
7.750
7.739
7.737
7.733
7.332
7.251
7.235
3.404
3.389
3.374
3.309
3.295
3.280
2.384
1.577
1.565
1.562
1.557
1.547
1.524
1.521
1.517
1.510
1.506
1.500
1.493
1.490
1.487
1.310
1.295
1.279
1.267
1.264
1.252
1.237
1.222
0.936
0.922
0.907
0.870
0.856
0.841
0.000
1.00
1.96
2.04
2.05
2.07
3.07
2.04
2.06
4.33
3.07
3.18
ppm

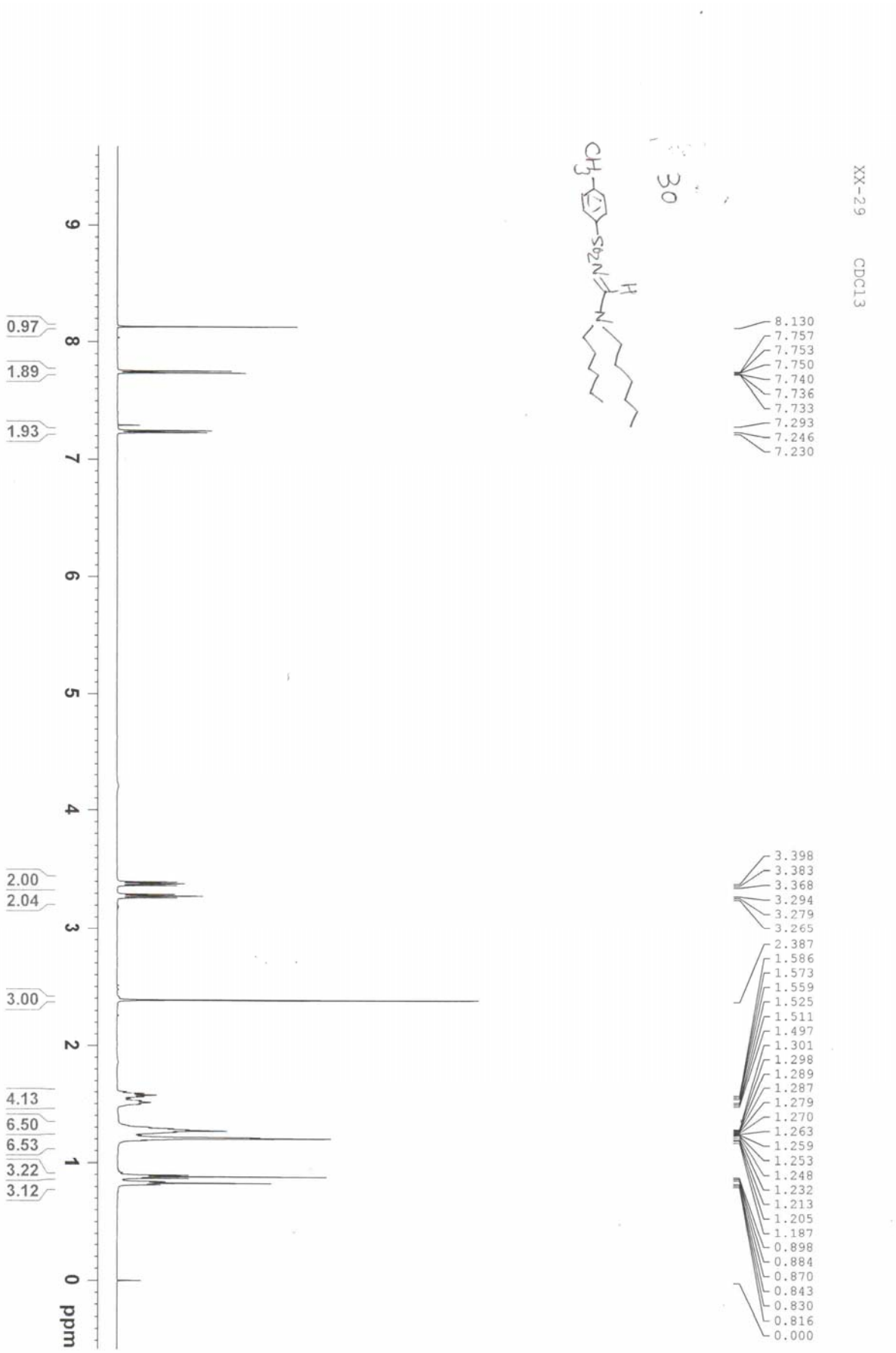
xx-132 CDCl3

158.66
141.99
139.73
129.04
126.08
77.36
77.10
76.85
52.10
45.74
30.45
28.48
21.25
19.72
19.40
13.50
13.40

3n



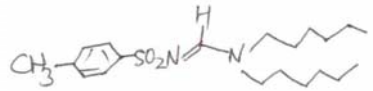


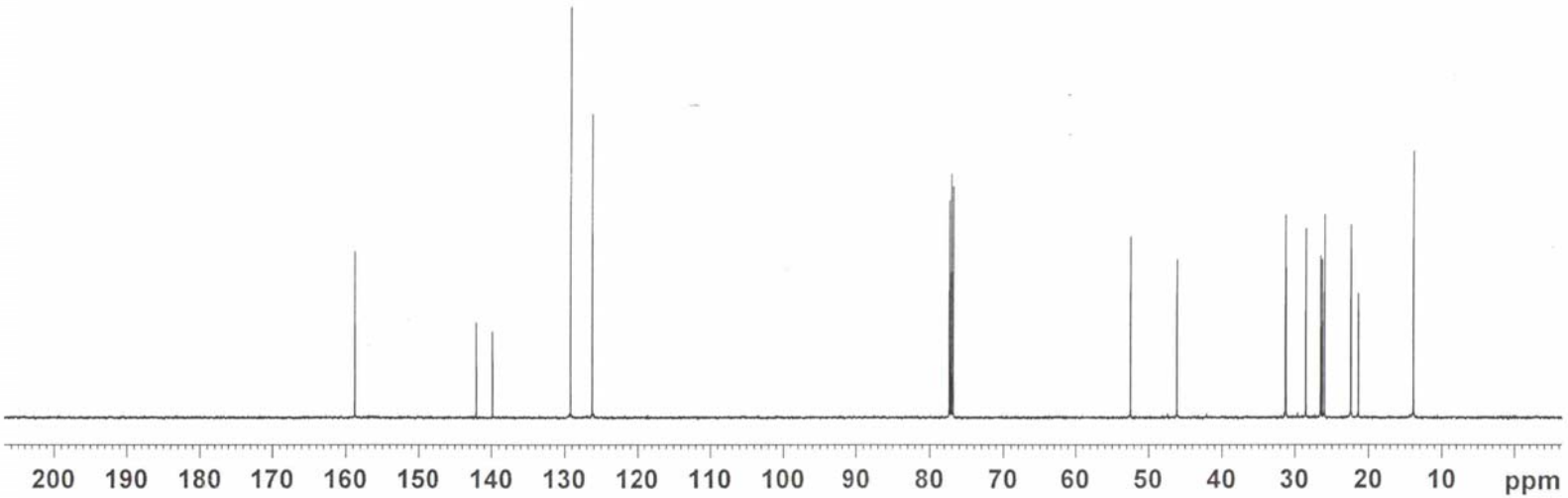

XX-29 CDCl3
30
8.130
7.757
7.753
7.750
7.740
7.736
7.733
7.293
7.246
7.230
3.398
3.383
3.368
3.294
3.279
3.265
2.387
1.586
1.573
1.559
1.525
1.511
1.497
1.301
1.298
1.289
1.287
1.279
1.270
1.263
1.259
1.253
1.248
1.232
1.213
1.205
1.187
0.898
0.884
0.870
0.843
0.830
0.816
0.000
0.97
1.89
1.93
2.00
2.04
3.00
4.13
6.50
6.53
3.22
3.12
ppm

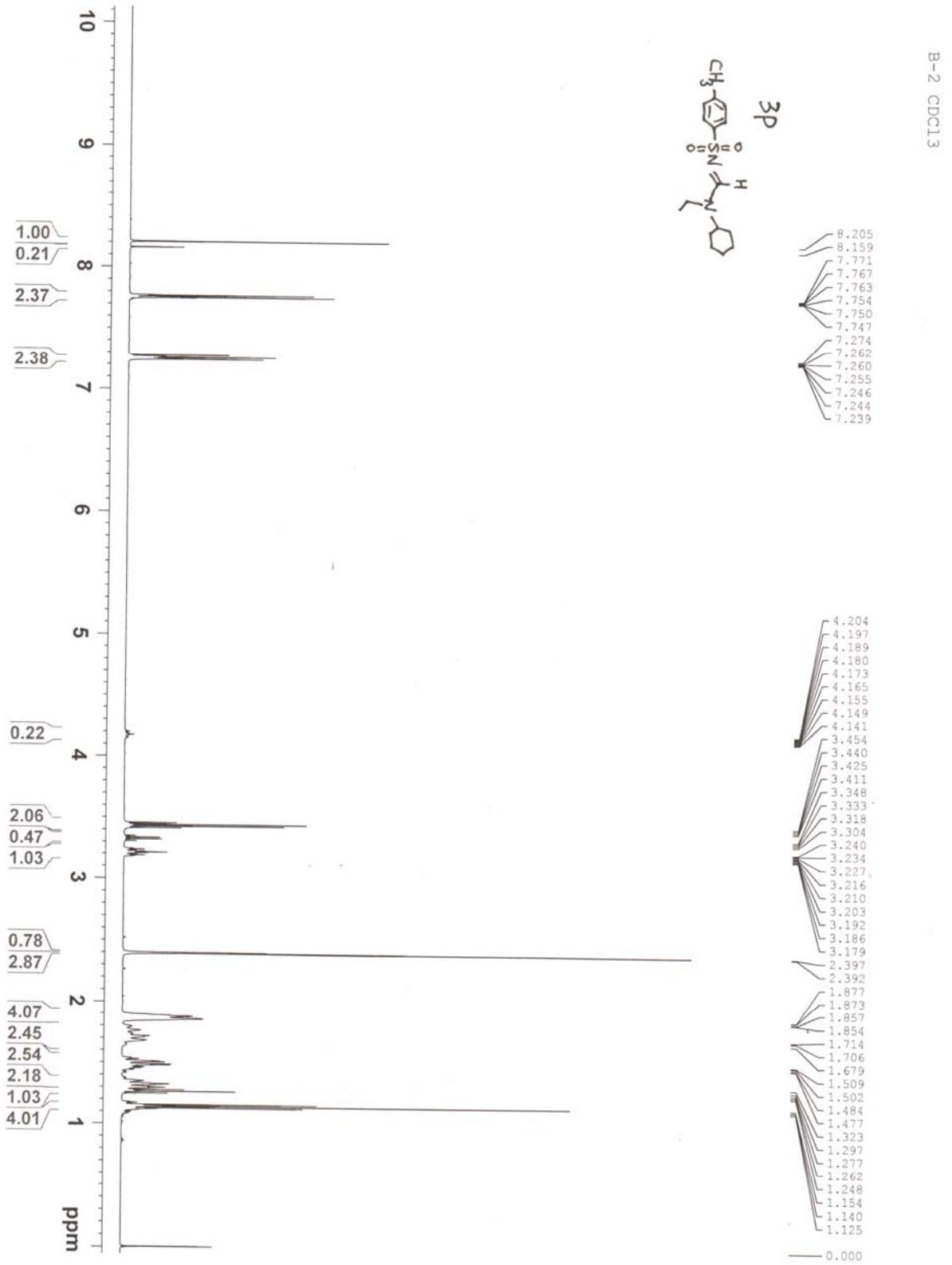
XX-29 CDCl3

158.77
142.13
139.91
129.20
126.27
77.37
77.11
76.86
52.53
46.15
31.31
31.23
28.55
26.54
26.31
26.01
22.43
22.40
21.40
13.91

30



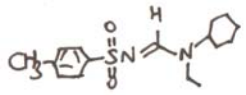



B-2 CDC13
3p
8.205
8.159
7.771
7.767
7.763
7.754
7.750
7.747
7.274
7.262
7.260
7.255
7.246
7.244
7.239
4.204
4.197
4.189
4.180
4.173
4.165
4.155
4.149
4.141
3.454
3.440
3.425
3.411
3.348
3.333
3.318
3.304
3.240
3.234
3.227
3.216
3.210
3.203
3.192
3.186
3.179
2.397
2.392
1.877
1.873
1.857
1.854
1.714
1.706
1.679
1.509
1.502
1.484
1.477
1.323
1.297
1.277
1.262
1.248
1.154
1.140
1.125
0.000
1.00
0.21
2.37
2.38
0.22
2.06
0.47
1.03
0.78
2.87
4.07
2.45
2.54
2.18
1.03
4.01
ppm

B-2 CDCl3

158.55
157.25
142.14
142.11
139.98
139.92
129.23
126.34
126.29
77.30
77.05
76.79
63.00
56.15
43.22
40.57
32.55
30.01
25.59
25.40
25.28
24.99
21.44
16.98
13.31

3P

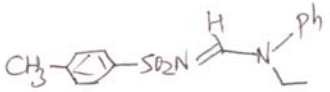


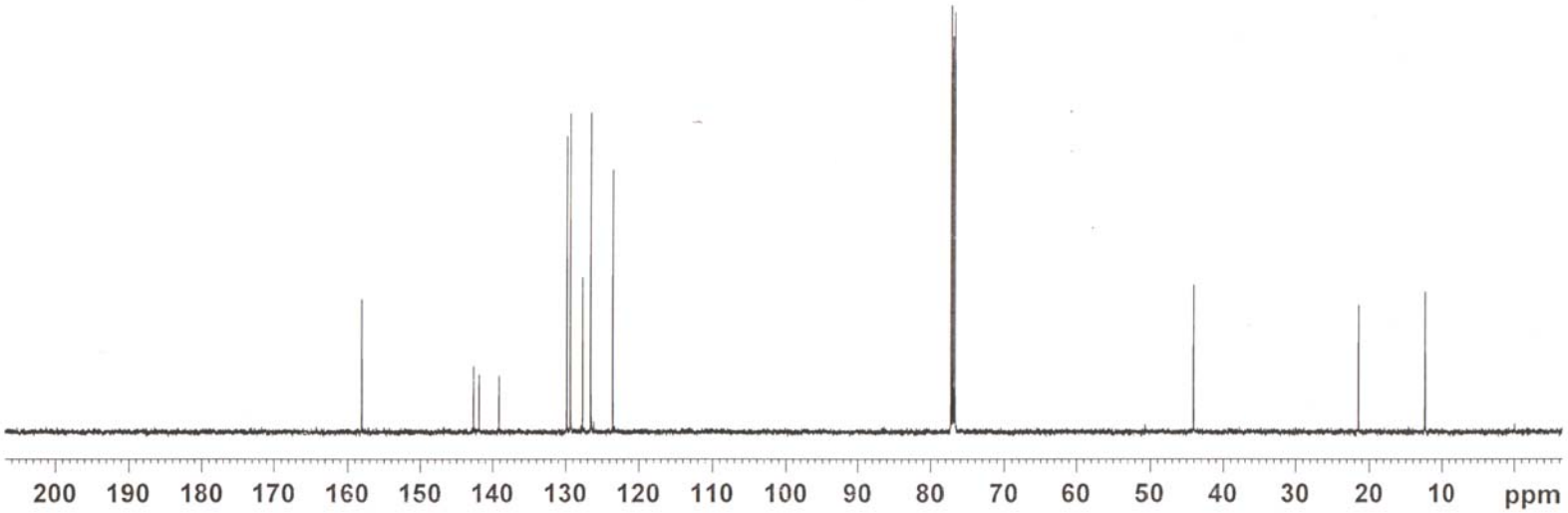
xx-9 CDC13
3g
8.452
7.820
7.805
7.445
7.431
7.417
7.357
7.343
7.329
7.291
7.276
7.196
7.181
3.986
3.973
3.959
3.946
2.412
1.188
1.174
1.160
0.000
1.00
1.97
2.05
1.08
2.27
2.23
2.18
3.10
ppm

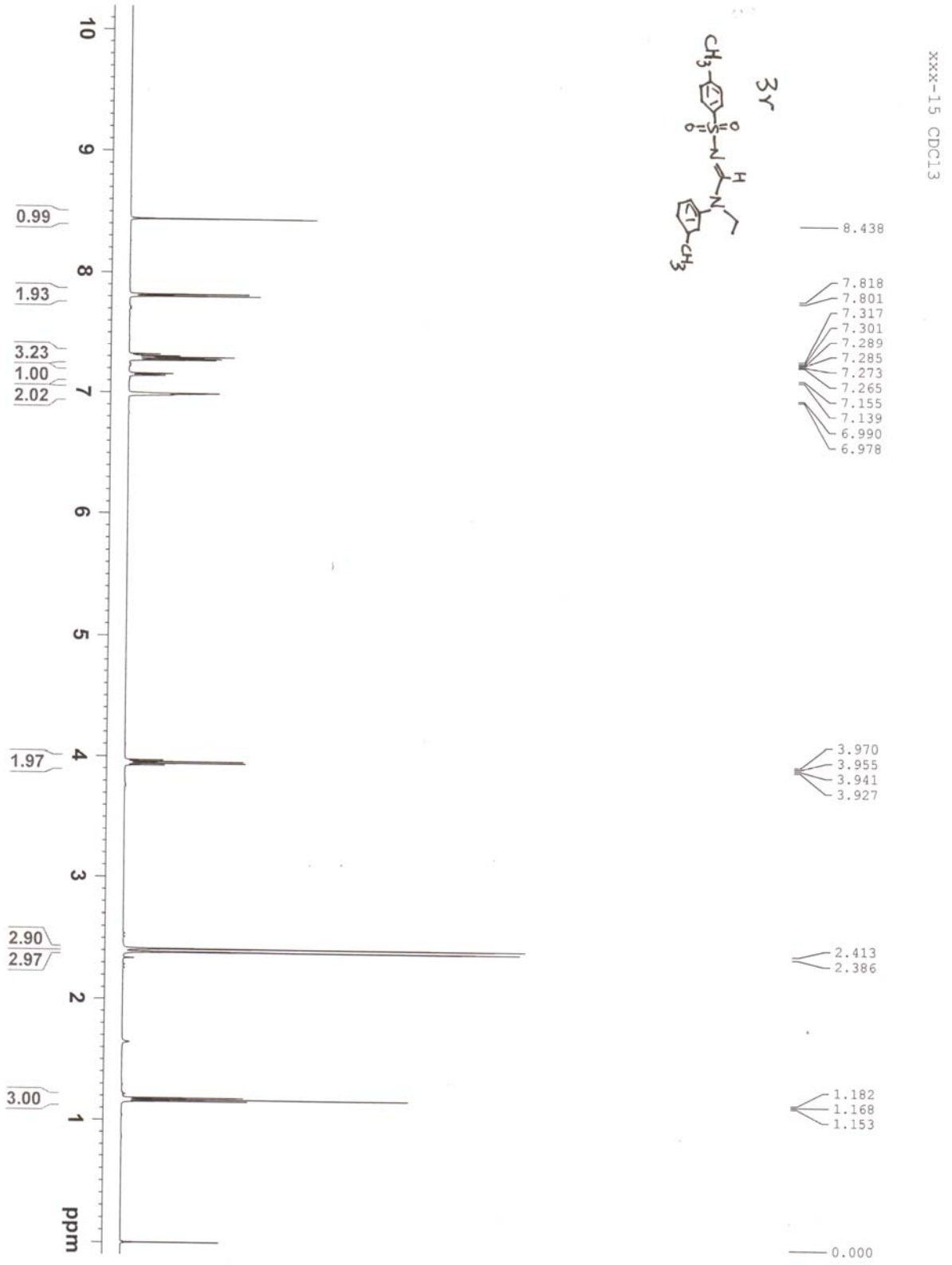
XX-9 CDCl3

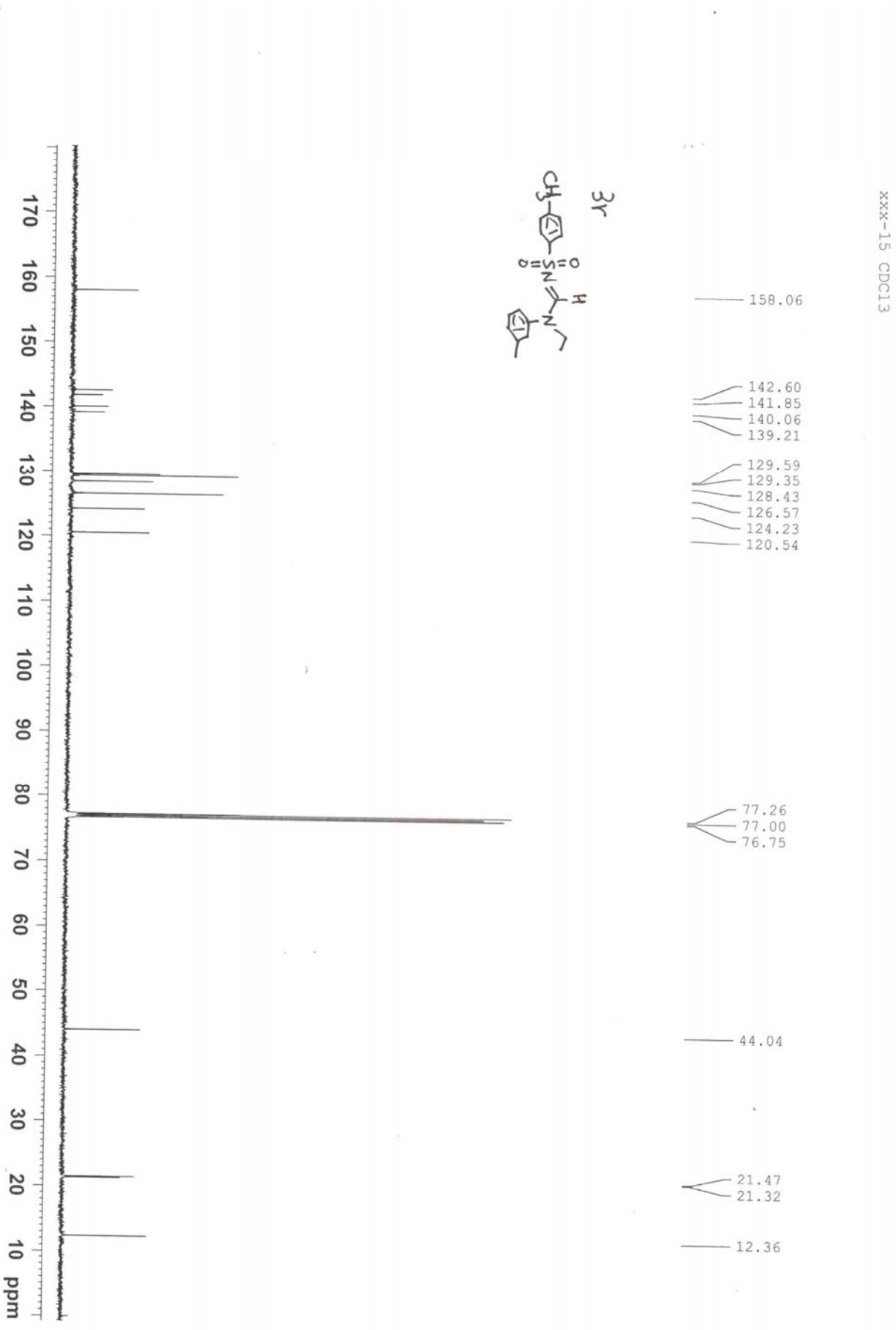
158.11
142.69
141.93
139.16
129.89
129.40
127.71
126.61
123.59
77.31
77.05
76.80
44.11
21.50
12.38

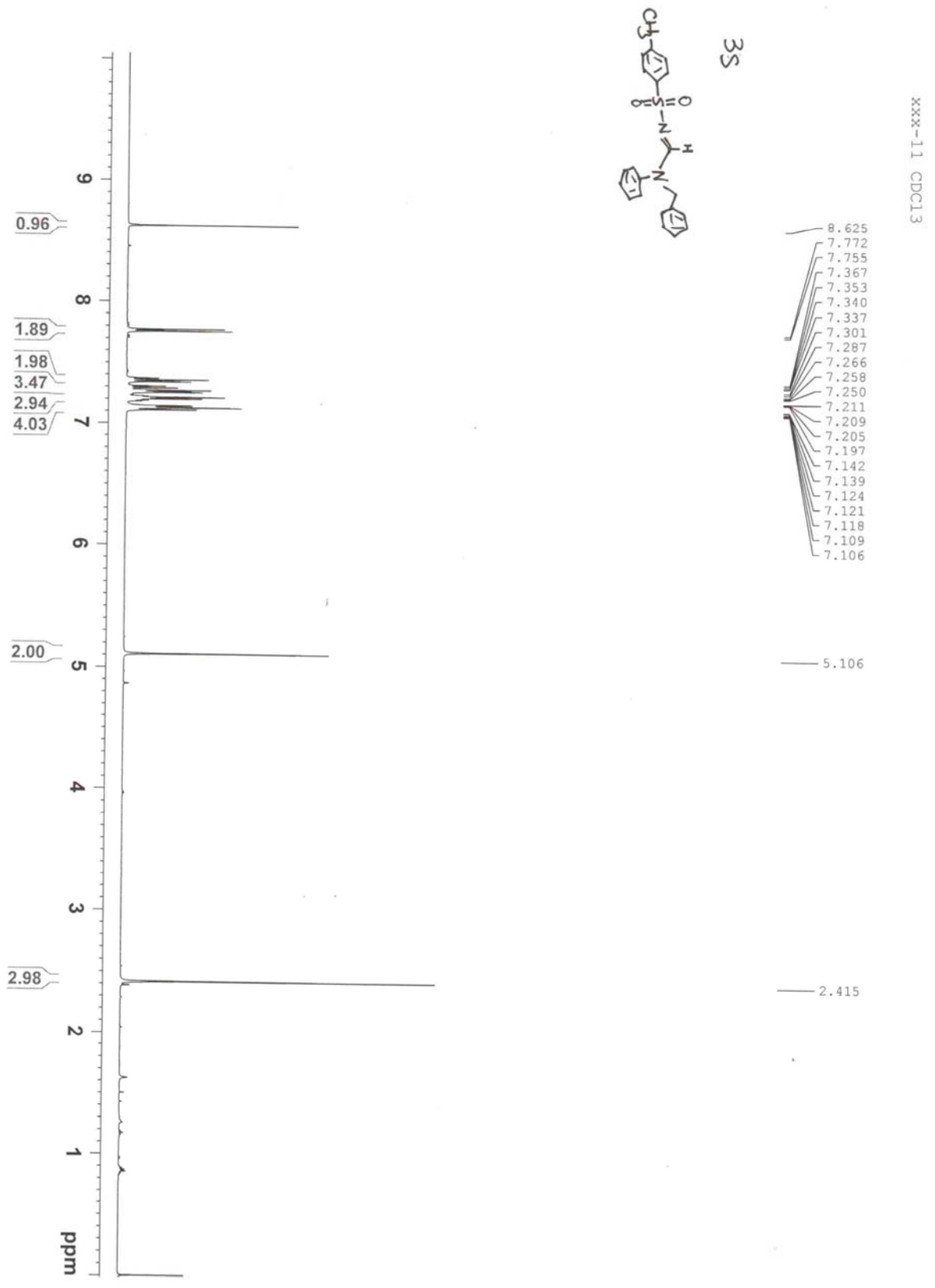
3q






xxx-15 CDC13
3r
8.438
7.818
7.801
7.317
7.301
7.289
7.285
7.273
7.265
7.155
7.139
6.990
6.978
3.970
3.955
3.941
3.927
2.413
2.386
1.182
1.168
1.153
0.000
0.99
1.93
3.23
1.00
2.02
1.97
2.90
2.97
3.00
ppm

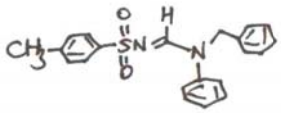

xxx-15 CDCl3
3r
158.06
142.60
141.85
140.06
139.21
129.59
129.35
128.43
126.57
124.23
120.54
77.26
77.00
76.75
44.04
21.47
21.32
12.36
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

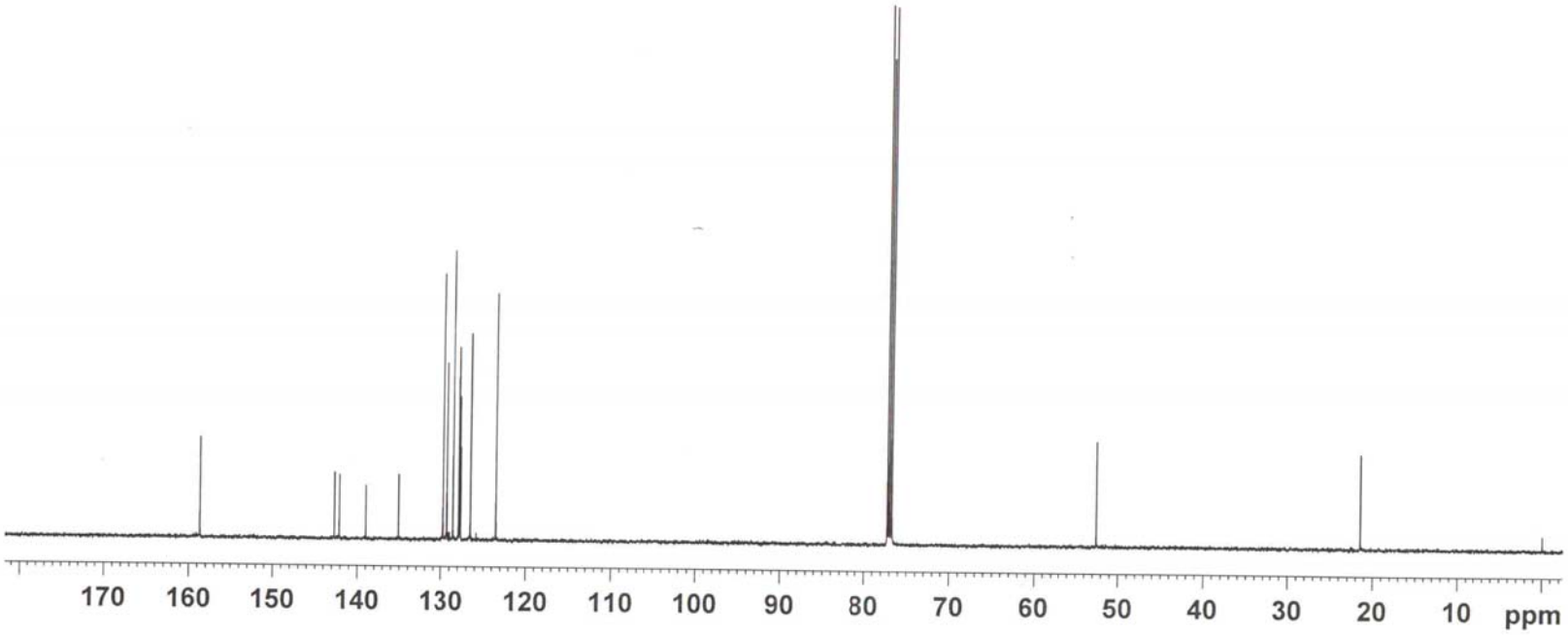

3s
xxx-11 CDC13
8.625
7.772
7.755
7.367
7.353
7.340
7.337
7.301
7.287
7.266
7.258
7.250
7.211
7.209
7.205
7.197
7.142
7.139
7.124
7.121
7.118
7.109
7.106
5.106
2.415
0.96
1.89
1.98
3.47
2.94
4.03
2.00
2.98
ppm

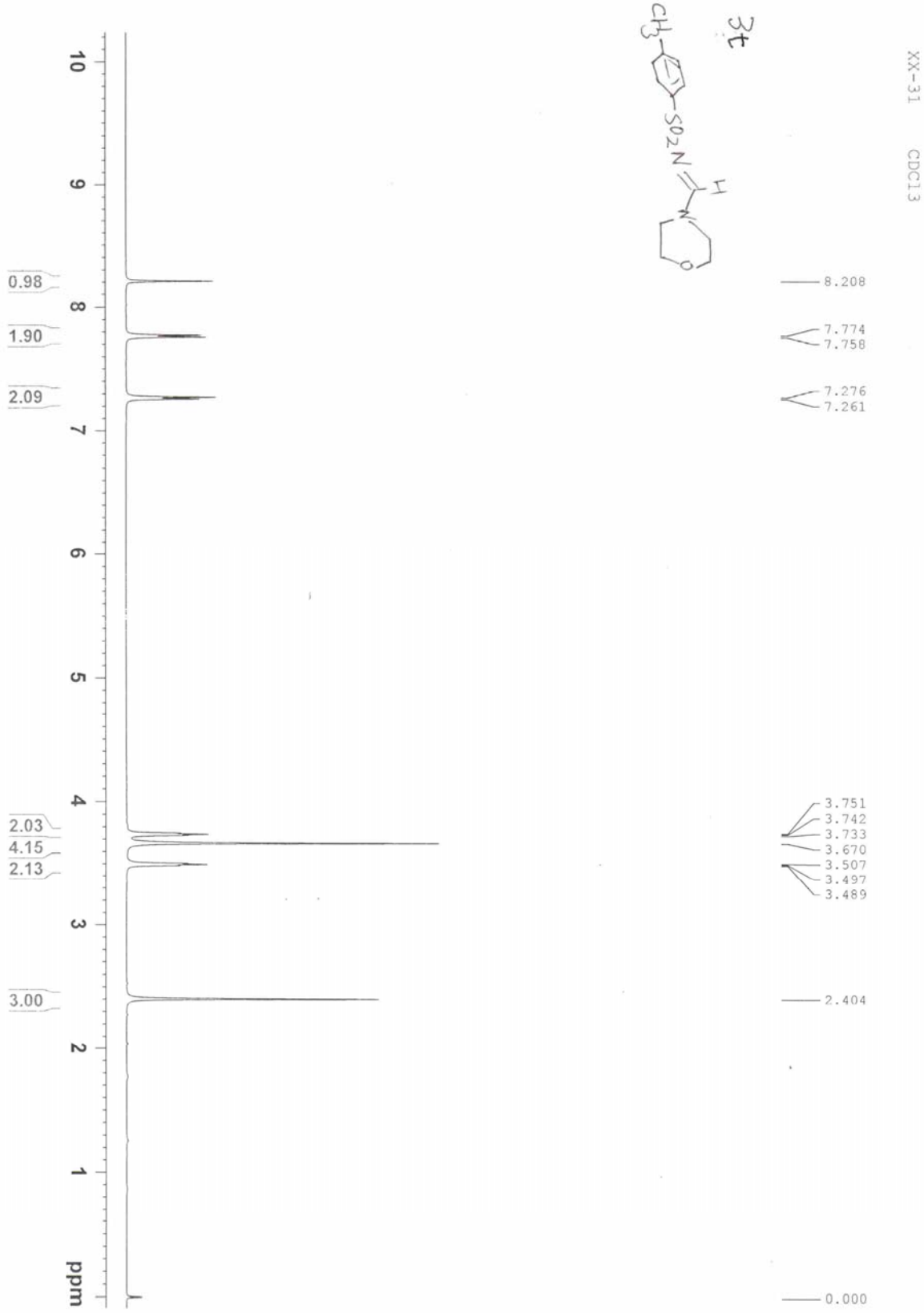
xxx-11 CDCl3

158.68
142.69
142.12
138.99
135.10
129.77
129.32
128.60
127.91
127.78
127.69
126.54
123.54
77.26
77.00
76.75
52.58
21.48

3s



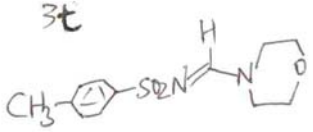


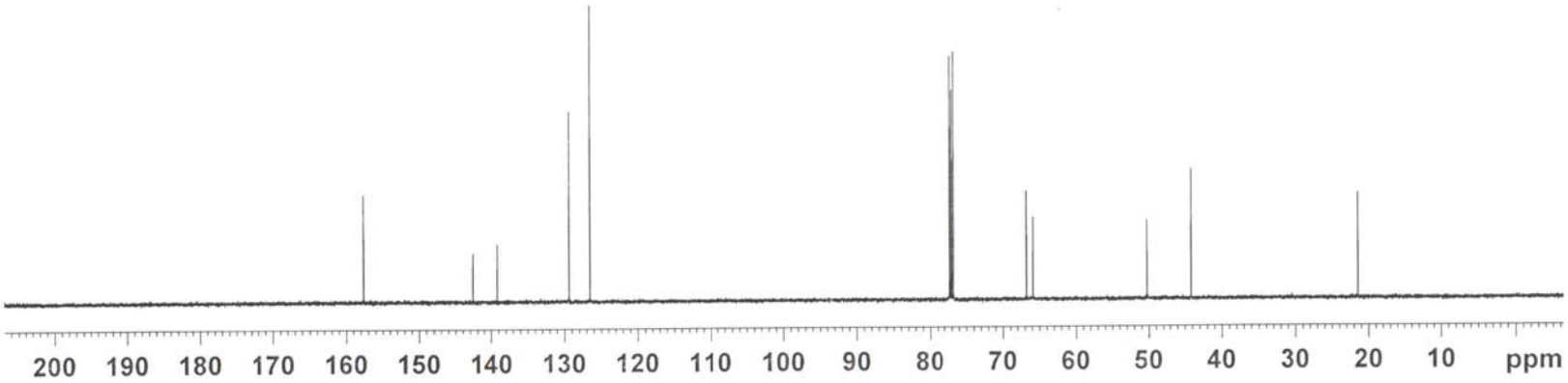

XX-31 CDCl3
3t
CH3
SO2N
H
O
8.208
7.774
7.758
7.276
7.261
3.751
3.742
3.733
3.670
3.507
3.497
3.489
2.404
0.000
0.98
1.90
2.09
2.03
4.15
2.13
3.00
ppm

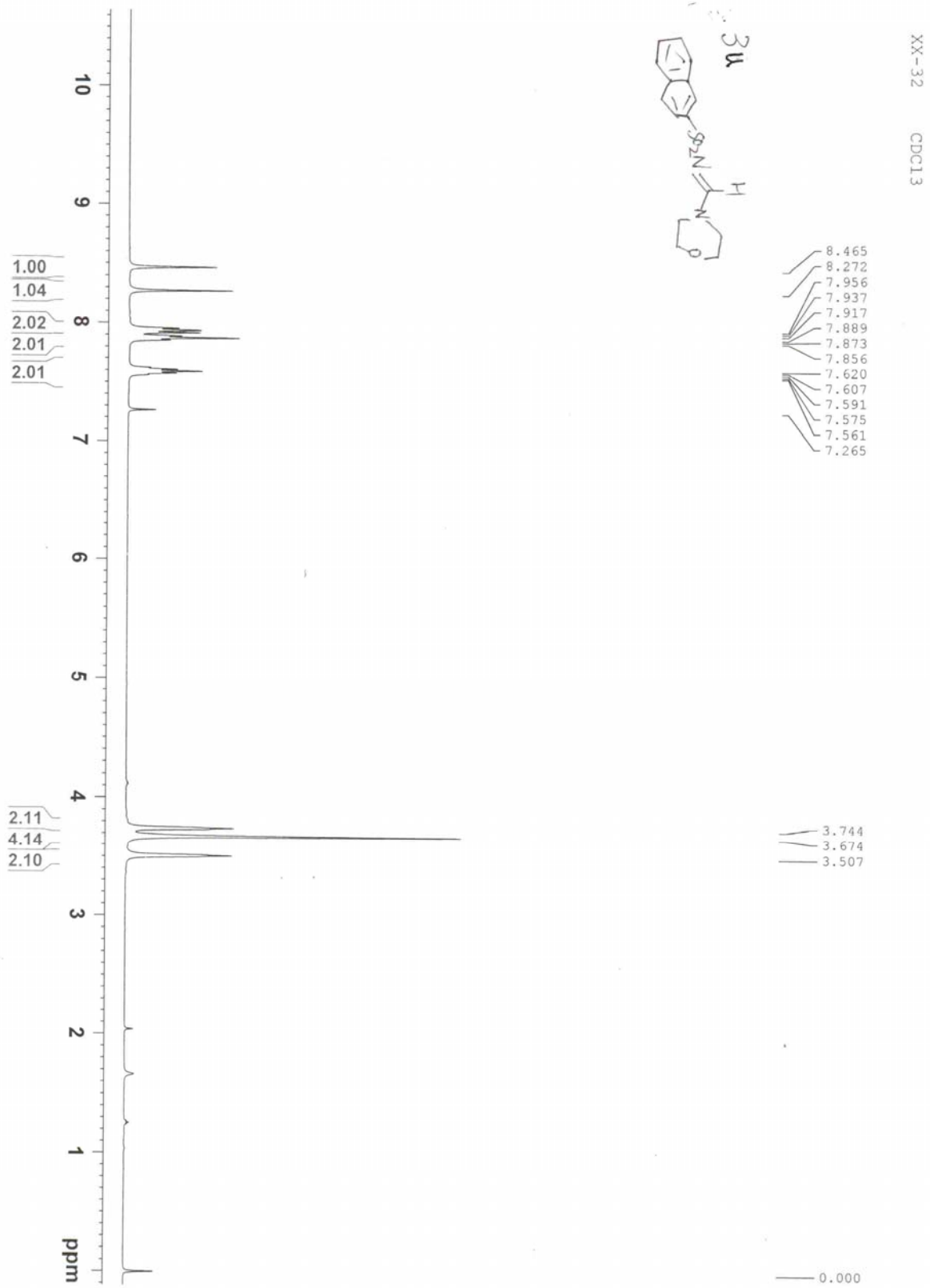
XX-31 CDCl3

157.65
142.66
139.20
129.38
126.56
77.32
77.07
76.81
66.81
65.91
50.29
44.19
21.49

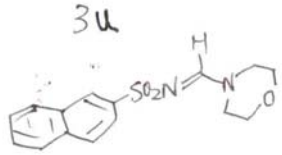
3t





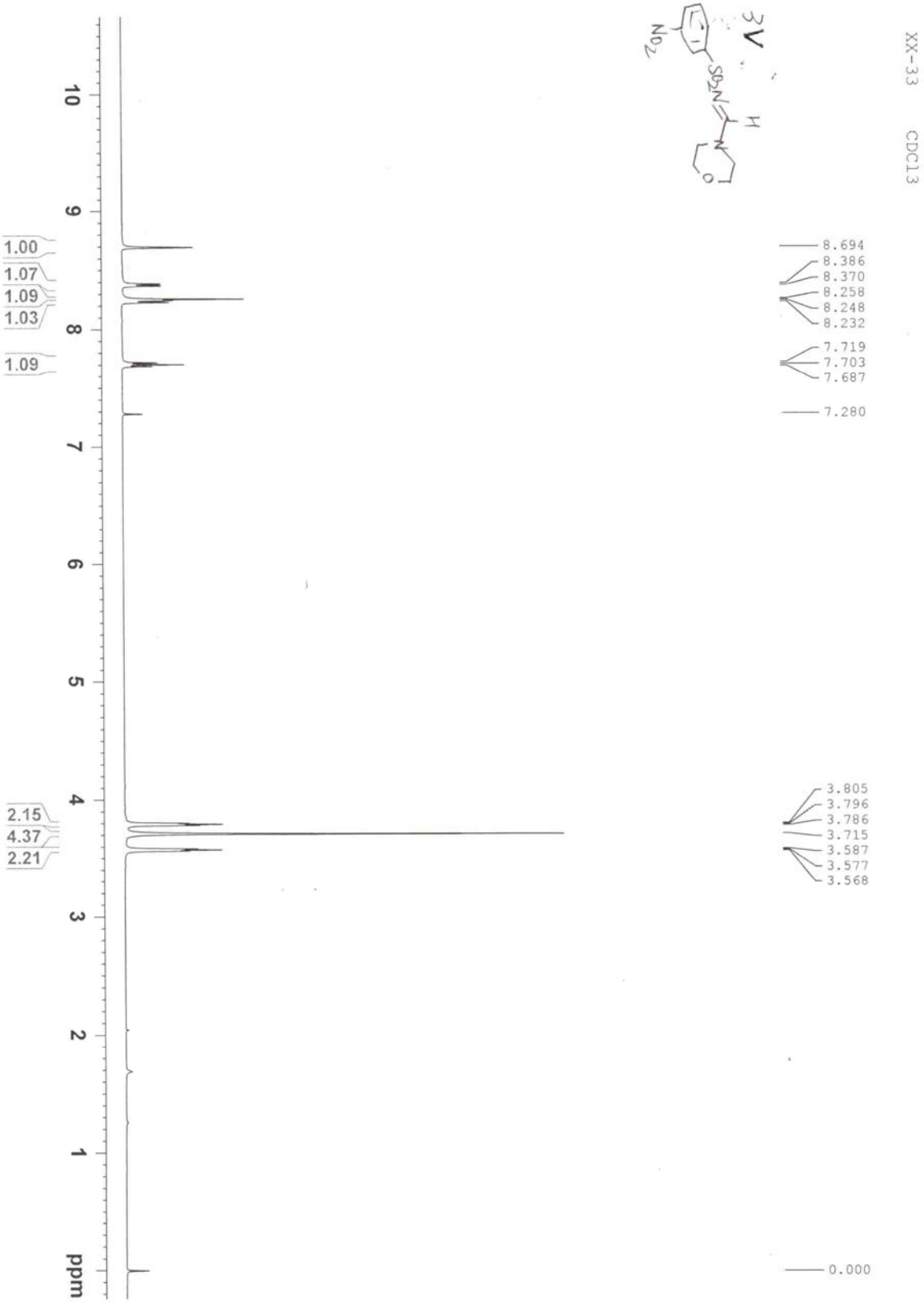

XX-32 CDCl3
3u
8.465
8.272
7.956
7.937
7.917
7.889
7.873
7.856
7.620
7.607
7.591
7.575
7.561
7.265
3.744
3.674
3.507
0.000
1.00
1.04
2.02
2.01
2.01
2.11
4.14
2.10
ppm

XX-32 CDCl3

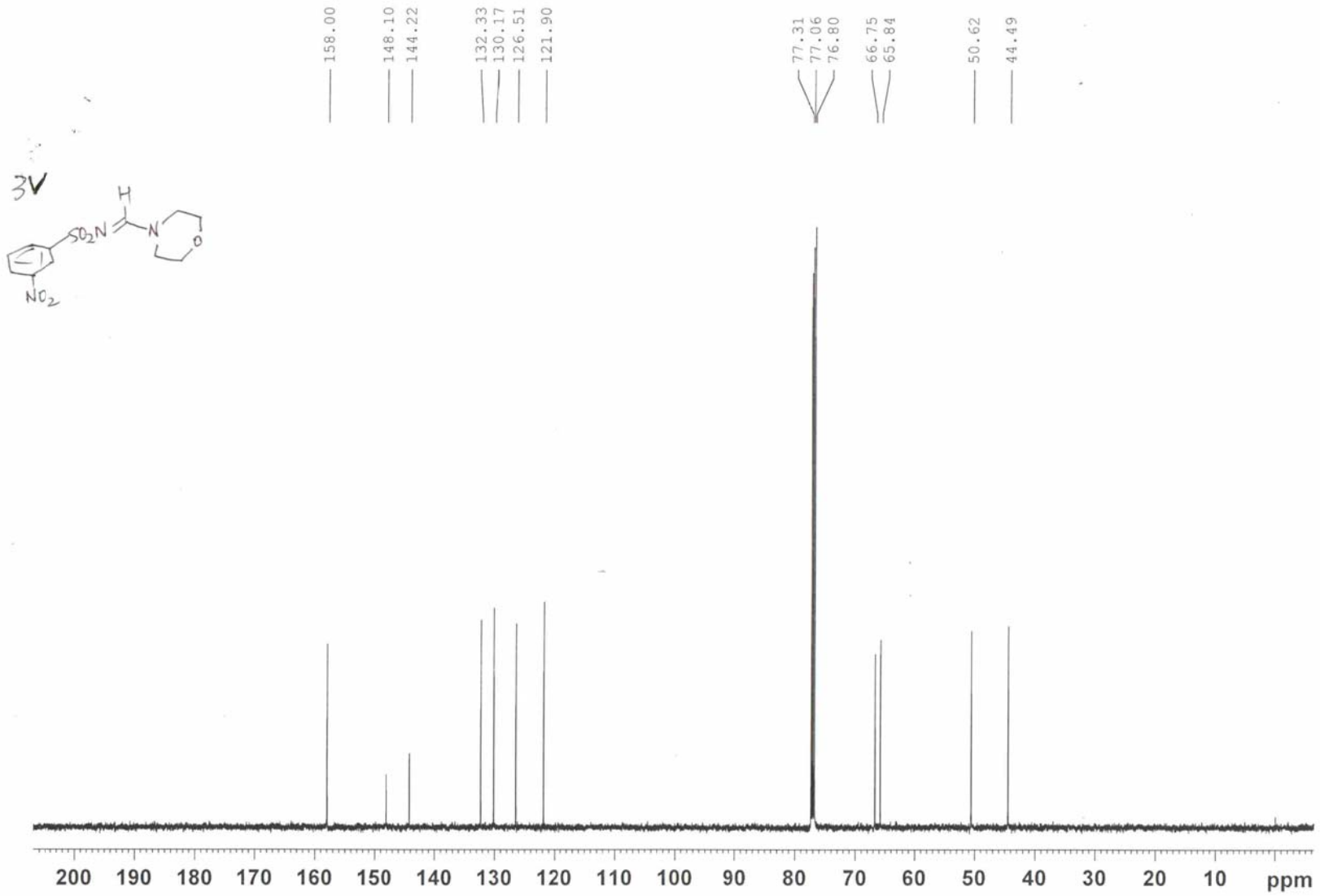


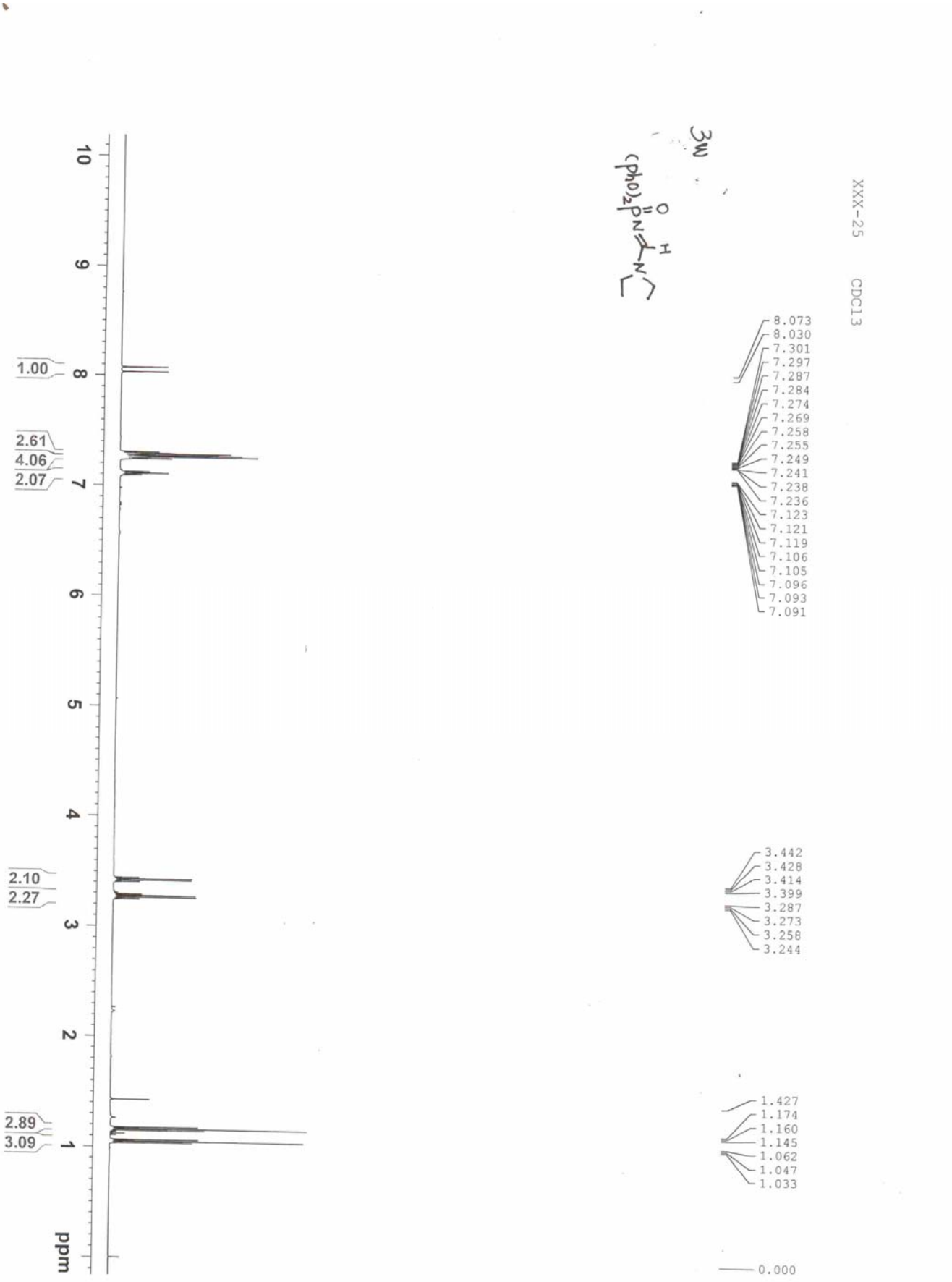
157.76
138.94
134.59
132.20
129.20
129.04
128.41
127.84
127.28
127.25
122.53
77.30
77.05
76.79
66.80
65.90
50.37
44.26

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


XX-33 CDC13
3V
8.694
8.386
8.370
8.258
8.248
8.232
7.719
7.703
7.687
7.280
3.805
3.796
3.786
3.715
3.587
3.577
3.568
0.000
1.00
1.07
1.09
1.03
1.09
2.15
4.37
2.21
ppm

XX-33 CDCl3


158.00
148.10
144.22
132.33
130.17
126.51
121.90
77.31
77.06
76.80
66.75
65.84
50.62
44.49
3V
H
SO2N
N
O
NO2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


3w
XXX-25 CDCl3
8.073
8.030
7.301
7.297
7.287
7.284
7.274
7.269
7.258
7.255
7.249
7.241
7.238
7.236
7.123
7.121
7.119
7.106
7.105
7.096
7.093
7.091
3.442
3.428
3.414
3.399
3.287
3.273
3.258
3.244
1.427
1.174
1.160
1.145
1.062
1.047
1.033
0.000
1.00
2.61
4.06
2.07
2.10
2.27
2.89
3.09
ppm

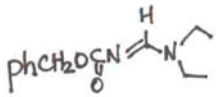
XXX-25 CDCl3
3w
160.03
159.95
151.50
151.44
129.38
124.39
120.69
120.66
77.42
77.16
76.91
46.10
39.67
14.53
11.94
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

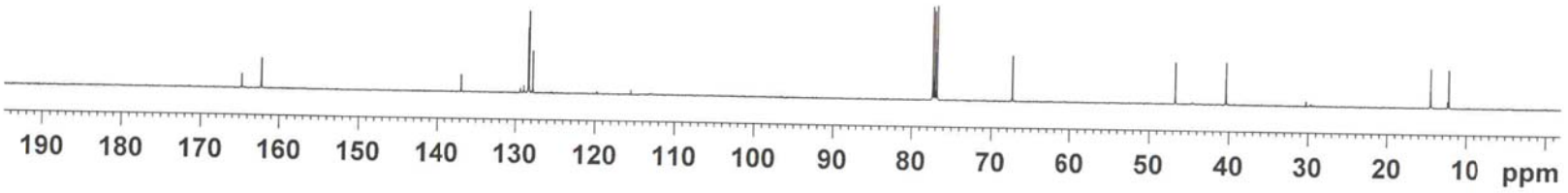
xxx-24-1 CDC13
3X
PhCH2OCNEt2
O
8.480
7.423
7.409
7.344
7.342
7.328
7.325
7.313
7.290
7.276
7.271
5.182
3.570
3.556
3.542
3.527
3.374
3.360
3.346
3.331
3.319
3.305
1.430
1.254
1.240
1.226
1.192
1.178
1.164
1.149
1.135
1.121
0.000
0.94
1.76
1.82
0.99
1.95
1.97
2.06
3.32
3.00
ppm

xxx-24-1 CDCl3

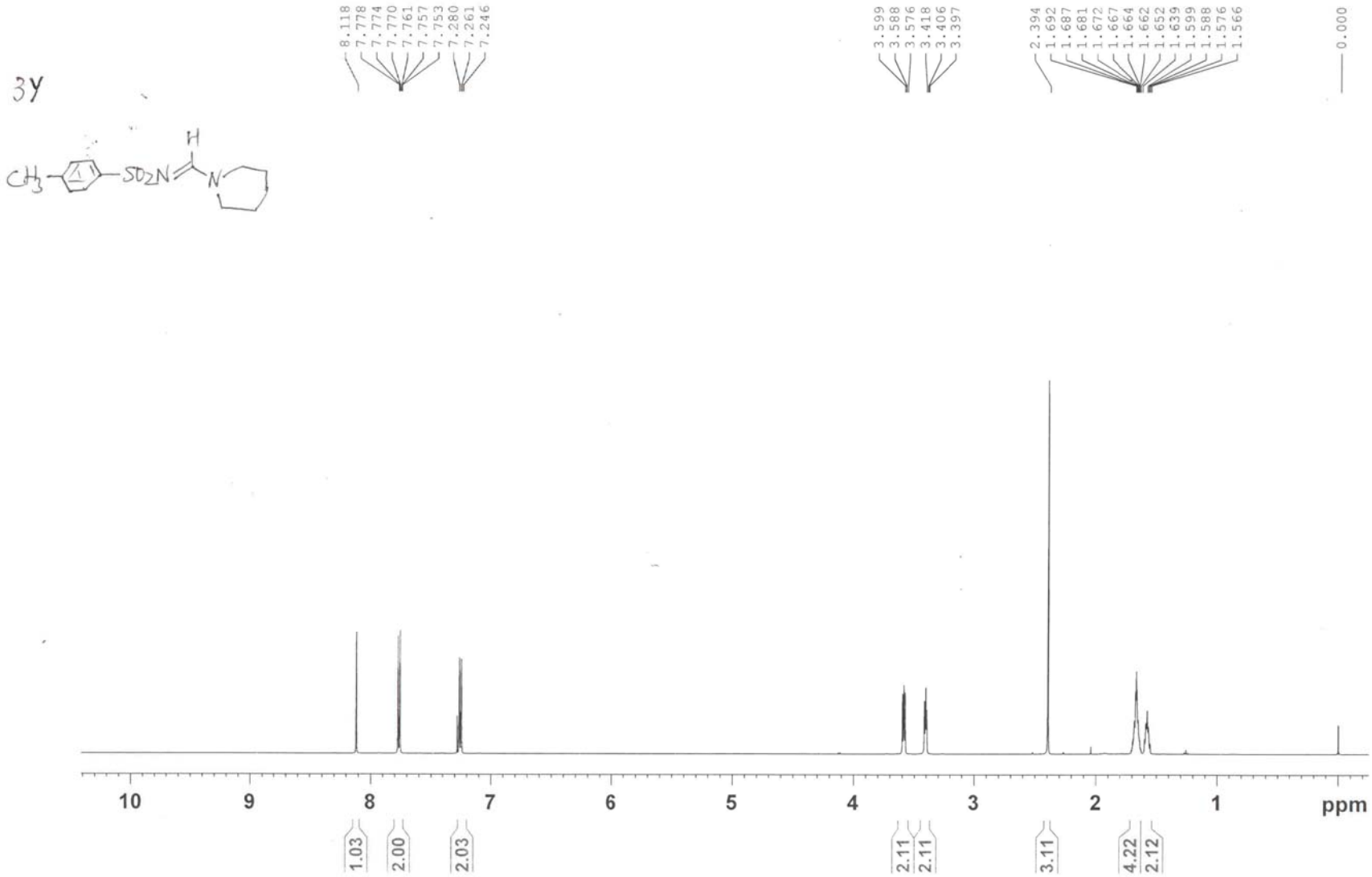
164.69
162.22
136.92
128.41
128.32
127.84
77.34
77.08
76.83
67.36
46.75
40.42
14.54
12.24

3X





XX-121 CDCl3

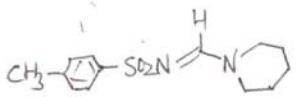


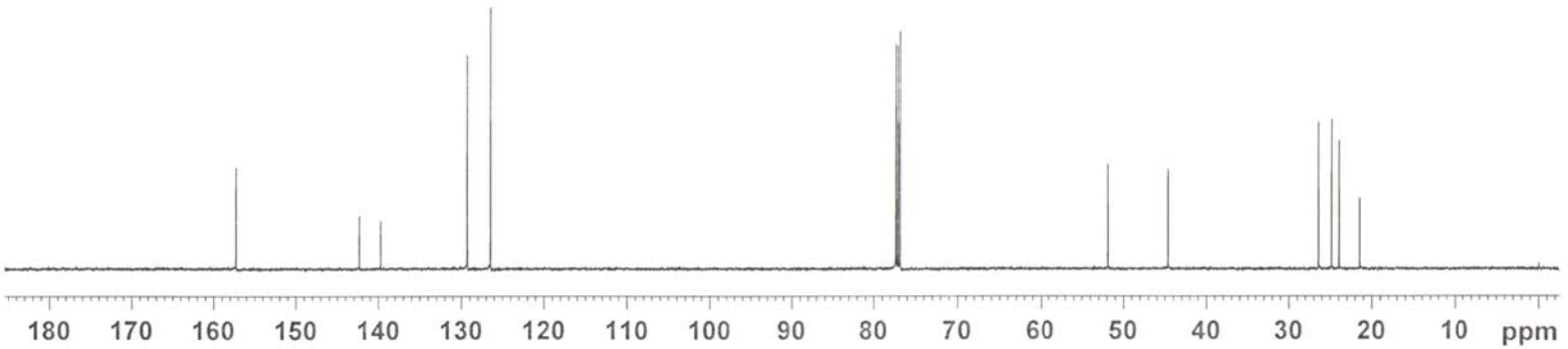
3y

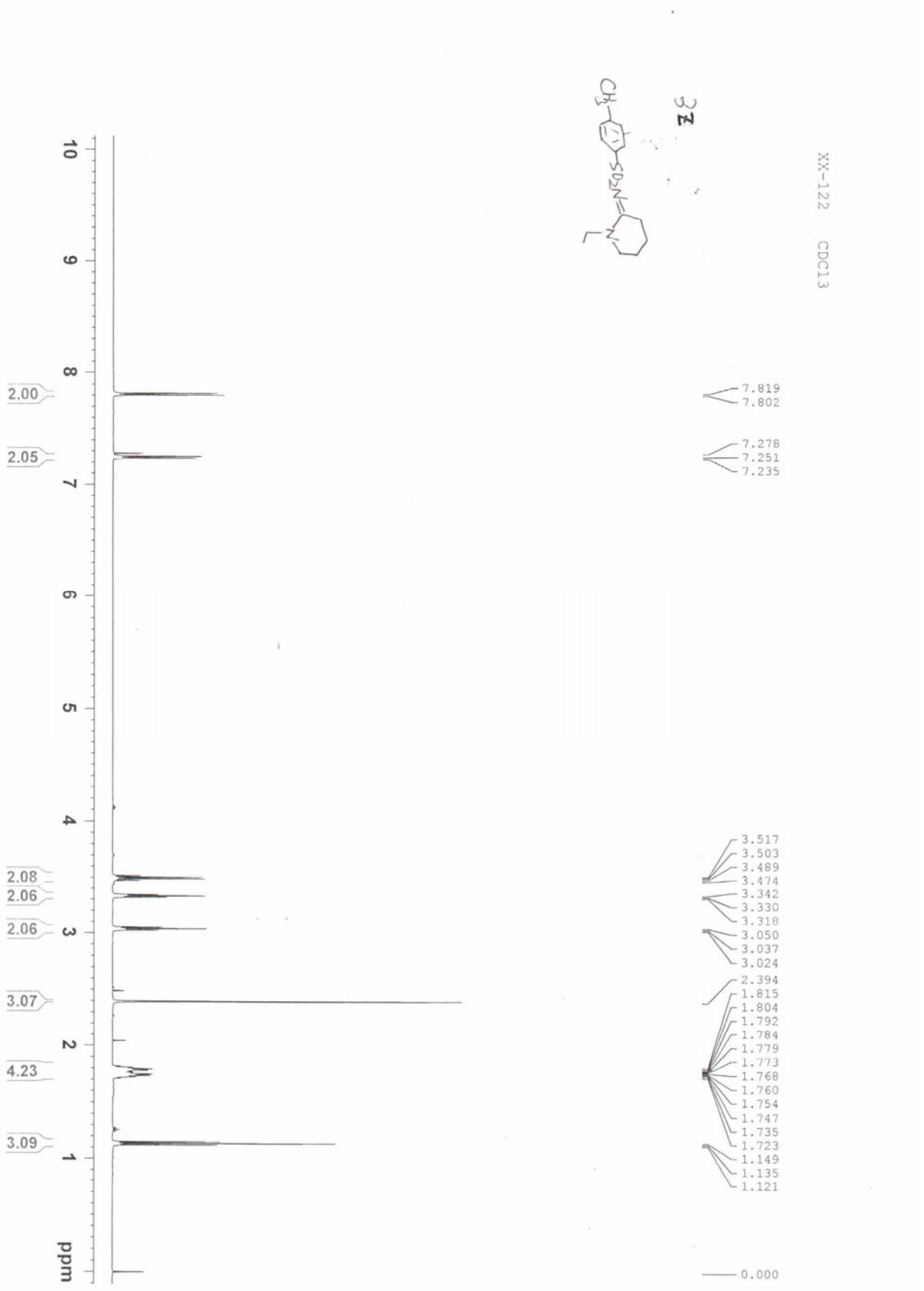
XX-121 CDCl3

157.26
142.31
139.73
129.28
126.45
77.34
77.09
76.83
51.88
44.62
26.41
24.84
23.94
21.46

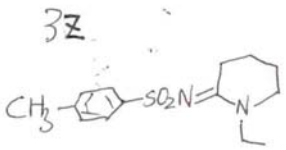
3y






XX-122 CDC13
3z
7.819
7.802
7.278
7.251
7.235
3.517
3.503
3.489
3.474
3.342
3.330
3.318
3.050
3.037
3.024
2.394
1.815
1.804
1.792
1.784
1.779
1.773
1.768
1.760
1.754
1.747
1.735
1.723
1.149
1.135
1.121
0.000
2.00
2.05
2.08
2.06
2.06
3.07
4.23
3.09
ppm

XX-122 CDCl3



165.18
141.58
141.53
129.04
126.15
77.32
77.06
76.81
48.20
45.52
28.55
22.26
21.42
19.58
11.34